Supplementary information

Electrochemical Reduction of Benzoic Acid Esters using Water as H/D Source

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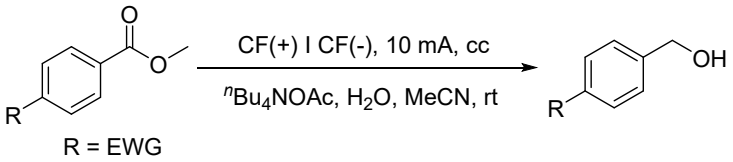
1. General information

All reagents were commercial and were used without further purification. Acetonitrile (MeCN) was purchased from Damao Chemcal Reagent Company and water comes from municipal water. Column chromatography was performed on silica gel (300-400 mesh) and reactions were monitored by thin-layer chromatography (TLC) using 254 nm UV light for visualization, and phosphomolybdic acid heat as developing agents. ^{1}H NMR (400 MHz or 600MHz), ^{13}C NMR (101 MHz or 150 MHz), ^{19}F (376 MHz), ^{31}P (162 MHz) and ^{11}B (128 MHz) were measured on Bruker Avance III 400 or 600 spectrometer. Chemical shifts are expressed in parts per million (ppm) with respect to tetramethylsilane. Coupling constants were reported as Hertz (Hz), signal shapes and splitting patterns were indicated as follows: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet. High-resolution mass spectra (HRMS) were recorded on Agilent mass spectrometer equipped with the ESI or APCI source and a Q-TOF detector.

2. General procedures of electrochemical reduction of methyl benzoates

2.1. General procedure for methyl benzoates with electron-withdrawing group (General procedure A):



R = EWG

To a 10 mL two-necked heart-shaped flask was charged with the substrate (0.3 mmol), $^{n}Bu_4NOAc$ (90.4 mg, 0.3 mmol, 1.0 equiv), H_2O (1 ml), MeCN (6 ml) and a magnetic stir bar. The bottle was equipped with a rubber stopper, through which carbon felts (CF, 1.5 cm x 1 cm x 0.5 cm) as anode and cathode were installed. Two electrodes were attached to a titanium wire and separated with a Teflon film. A Teflon wire tied around two electrodes. The whole cell was an undivided cell. The mixture was stirred under room temperature and 10 mA constant current electrolysis, and reacted until the substrates disappear. The reaction mixture was concentrated under the reduced pressure. The yield was measured by ^{1}H NMR analysis of crude reaction mixture with mesitylene as an internal standard. The residue was purified by flash chromatography to afford the desired product. Followings are the photographic guide for the reaction.

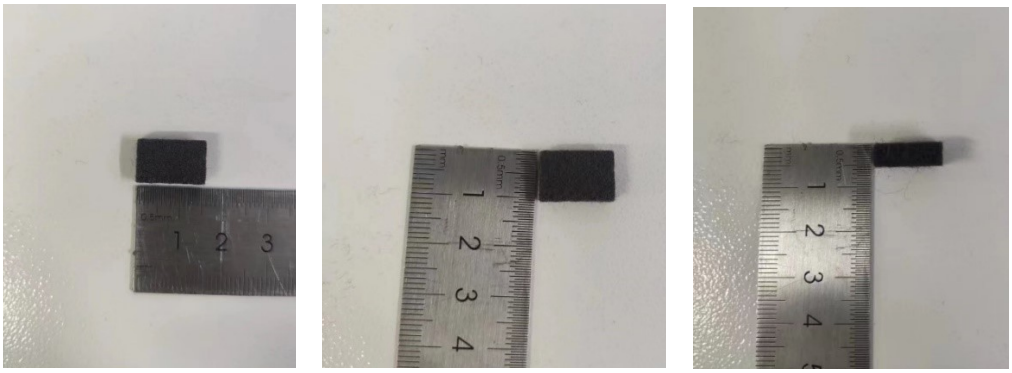


Figure S1. Size of graphite felt anode

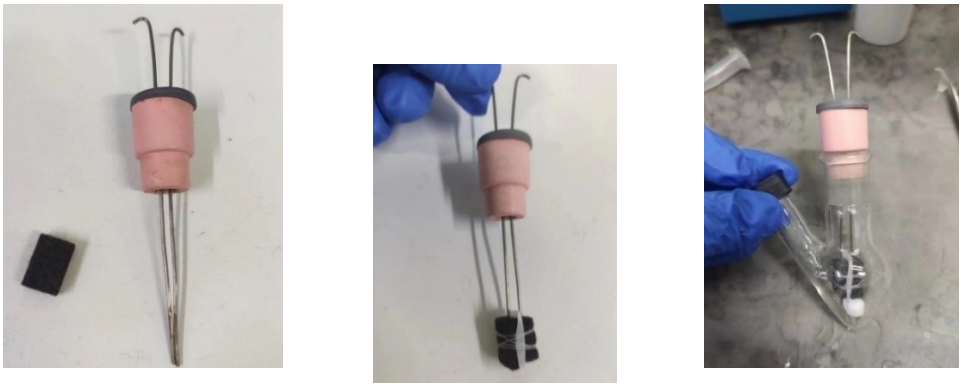


Figure S2. Electrodes and electrochemical cell

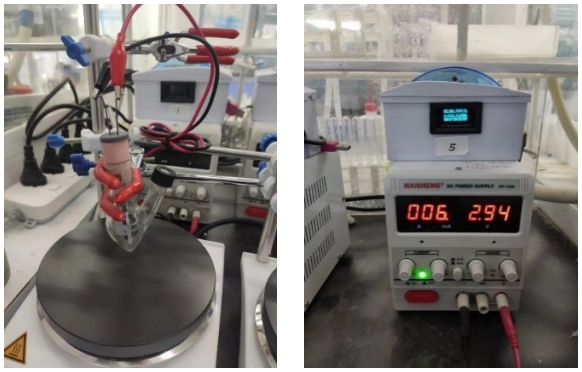
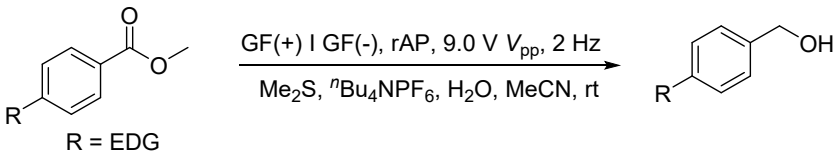


Figure S3. Details and equipment of the electrochemical reaction

2.2. General procedure for methyl benzoates with electron-donating group (General procedure B):



To a 10 mL two-necked heart-shaped flask was charged with the substrate (0.3 mmol), Me_2S (55.8 mg, 0.9 mmol, 3.0 equiv), $^nBu_4NPF_6$ (116.2 mg, 0.3 mmol, 1.0 equiv), H_2O (1 ml), MeCN (6 ml) and a magnetic stir bar. The bottle was equipped with a rubber stopper, through which graphite felts (GF, 1.5 cm x 1 cm x 0.5 cm) as anode and cathode were installed. Two electrodes were attached to a titanium wire and separated with a Teflon film. A Teflon wire tied around two electrodes. The whole cell was an undivided cell. The rAP power supply constituted with a combination of a signal generator and an amplifier. The rAP waveform was generated from a signal generator (FeelElec, FY6900-20M) and the output was adjusted by an amplifier (FPA2000-30W). The mixture was stirred under room temperature and 9.0 V V_{pp} of rAP (detected by oscilloscope, set 0.9 V on signal generator, peak to peak, 0.45 V from the offset, alternating frequency: 2 Hz, the current was around 60 mA) were applied to the reaction until the substrates disappear. The reaction mixture was concentrated under the reduced pressure. The yield was measured by ^{1}H NMR analysis of the crude reaction mixture with mesitylene as an internal standard. The residue was purified by flash chromatography to afford the desired product. Followings are the photographic guide for the reaction.

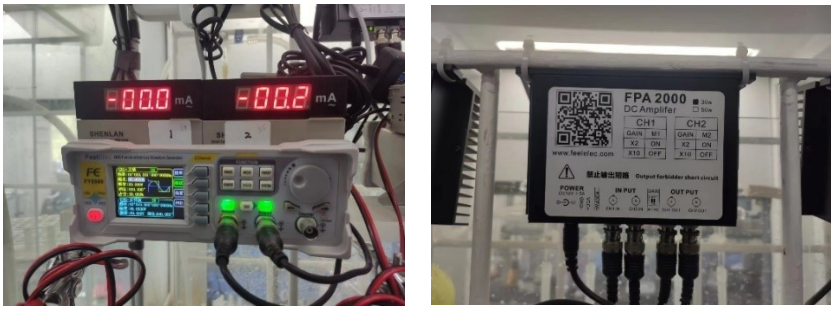
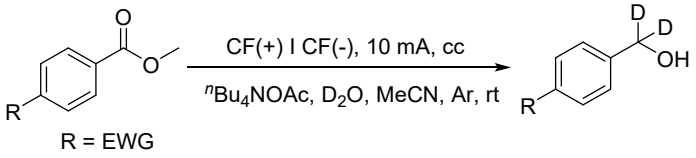


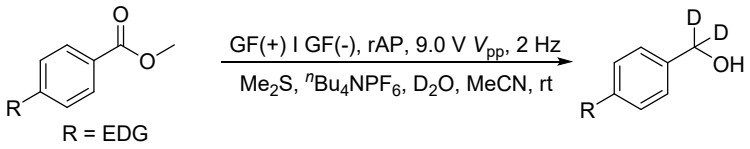
Figure S4. Left: signal generator. Right: amplifier

2.3. General procedure for methyl benzoates with electron-withdrawing group using D_2O as hydrogen source (General procedure C):



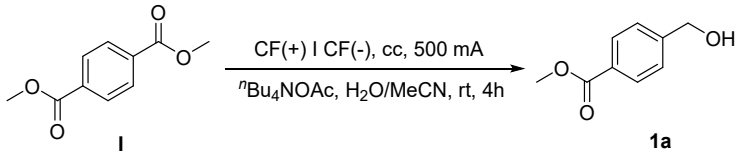
To a 10 mL two-necked heart-shaped flask under Ar atmosphere was charged with the substrate (0.3 mmol), ^{n}Bu$_4$NOAc (90.4 mg, 0.3 mmol, 1.0 equiv), D$_2$O (300 mg, 1.5 mmol, 50 equiv), MeCN (6.5 ml, extra dry with molecular sieves, water < 30 ppm) and a magnetic stir bar. The equipment was same as in **General procedure A**. The mixture was stirred under room temperature and 10 mA constant current electrolysis, and reacted until the substrates disappear. The reaction mixture was concentrated under the reduced pressure. The residue was purified by flash chromatography to afford the desired product.

2.4. General procedure for methyl benzoates with electron-donating group using D$_2$O as hydrogen source (General procedure D):



To a 10 mL two-necked heart-shaped flask under Ar atmosphere was charged with the substrate (0.3 mmol), Me$_2$S (55.8 mg, 0.9 mmol, 3.0 equiv), ^{n}Bu$_4$NPF$_6$ (116.2 mg, 0.3 mmol, 1.0 equiv), D$_2$O (300 mg, 1.5 mmol, 50 equiv), MeCN (6.5 ml, extra dry with molecular sieves, water < 30 ppm) and a magnetic stir bar. The equipment was same as in **General procedure B**. The mixture was stirred under room temperature and 9.0 V V_{pp} of rAP (detected by oscilloscope, set 0.9 V on signal generator, peak to peak, 0.45 V from the offset, alternating frequency: 2 Hz, the current was around 60 mA), and reacted until substrates disappear. The reaction mixture was concentrated under the reduced pressure. The residue was purified by flash chromatography to afford the desired product.

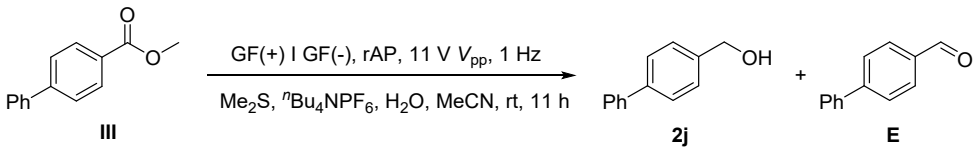
2.5 Gram scale reaction of electrochemical reduction of dimethyl terephthalate:



To a 250 mL glass beaker was charged with dimethyl terephthalate (5.82 g, 30 mmol), ^{n}Bu$_4$NOAc (2.26 g, 7.5 mmol, 0.25 equiv), H$_2$O (25 ml), MeCN (150 ml) and a magnetic stir bar. The bottle was equipped with a paper case cover, through which carbon felts (4 cm x 18 cm x 0.5 cm) as anode and cathode were installed. Two electrodes were attached to a titanium wire and separated with polypropene foam (pore diameter: 200 μm aperture). A Teflon wire tied around two electrodes. The whole cell was an undivided cell. The mixture was stirred under room temperature and 500 mA constant current electrolysis, and reacted for 4 h. The reaction mixture was concentrated under the reduced pressure, and the residue was purified by flash chromatography (PE/EtOAc = 2/1) to afford the desired product as a white solid with 62.7% yield (3.12 g). Followings are the photographic guide for the reaction.

Figure S5. Details and the equipment for the gram scale reaction of dimethyl terephthalate

2.6 Gram scale reaction of electrochemical reduction of methyl 4-phenylbenzoate:



To a 250 mL eggplant shaped bottle was charged with the methyl 4-phenylbenzoate (1.27 g, 6 mmol), Me_2S (744 mg, 12 mmol, 2.0 equiv), $^nBu_4NPF_6$ (2.32 g, 6 mmol, 1.0 equiv), H_2O (20 ml), MeCN (120 ml) and a magnetic stir bar. The bottle was equipped with a rubber stopper, through which graphite felts (1.5 cm x 2 cm x 0.5 cm) as anode and cathode were installed. Two electrodes were attached to a titanium wire and separated with a Teflon film. A Teflon wire tied around two electrodes. The whole cell was an undivided cell. The rAP power supply constituted with a combination of a signal generator and an amplifier. The rAP waveform was generated from a signal generator (FeelElec, FY6900-20M) and the output was adjusted by an amplifier (FPA2000-30W). The mixture was stirred under room temperature and 11 V V_{pp} of rAP (detected by oscilloscope, set 1.1 V on signal generator, peak to peak, 0.55 V from the offset, alternating frequency: 1 Hz, the current was around 150 mA), and reacted for 11 h. The reaction mixture was concentrated under the reduced pressure, and residue was purified by flash chromatography (PE/EtOAc = 4/1) to afford the desired product as a white solid with 71% yield (780 mg). 4-Biphenylcarboxaldehyde (41 mg) was obtained as a white solid (PE/EtOAc = 50/1). ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.04 (s, 1H), 7.99 – 7.89 (m, 2H), 7.77 – 7.70 (m, 2H), 7.68 – 7.59 (m, 2H), 7.51 – 7.45 (m, 2H), 7.43 – 7.38 (m, 1H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 192.2, 147.2, 139.7, 135.2, 130.4, 129.1, 128.6, 127.8, 127.5. Followings are the photographic guide for the reaction.

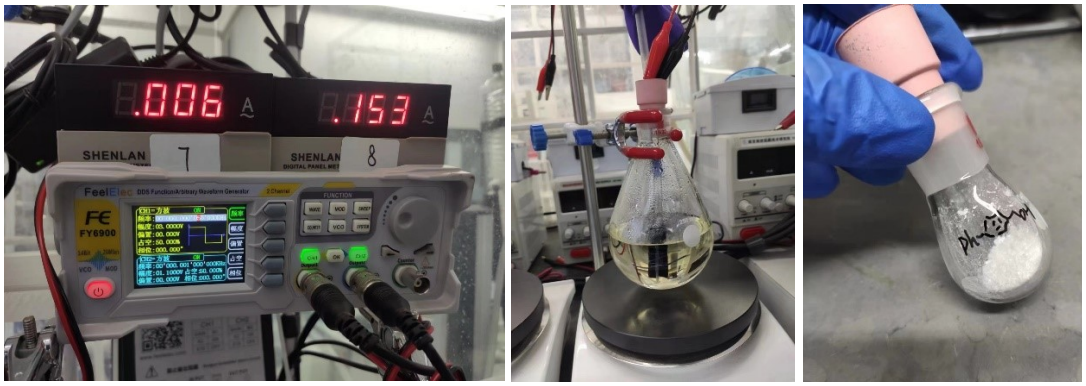
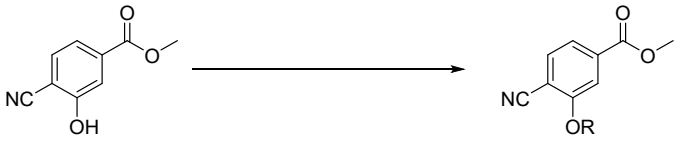


Figure S6. Details and the equipment for the gram scale reaction of methyl 4-phenylbenzoate

3. Synthesis of substrates (new compounds)

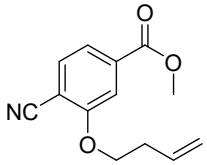
3.1. General procedure for the synthesis of methyl 3-alkoxyl-4-cyanobenzoates:



Method A: To a solution of methyl 4-cyano-3-hydroxybenzoate (442.5 mg, 2.5 mmol) in DMF (10 ml) was added NaH (60%, 150 mg, 3.75 mmol, 1.5 equiv), and the mixture was stirred for 10 min. Alkyl halide (3.75 mmol, 1.5 equiv) was added to the solution and the mixture was stirred for 10 h. After the reaction was completed (monitored by TLC), the reaction solution was quenched by adding aq. NH_4Cl (50 ml), extracted by EtOAc (50 ml x 2). The organic layers were combined, washed by H_2O (50 ml x 3) and aq. NaCl (50 ml x 1), dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography to afford the desired product.

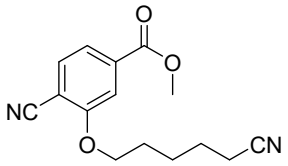
Method B: To a solution of methyl 4-cyano-3-hydroxybenzoate (442.5 mg, 2.5 mmol) in acetone (10 ml) was added K_2CO_3 (659 mg, 5 mmol, 2 equiv) and alkyl halide (3.25 mmol, 1.3 equiv). The solution was stirred at reflux for 6 h. After the reaction was completed (monitored by TLC), the reaction solution was cooled to room temperature, filtered and concentrated. The residue was diluted with EtOAc (50 ml), washed by aq. NaCl (50 ml x 1), dried over Na_2SO_4, filtered and concentrated. The solid residue was washed by PE/EtOAc (10:1) to afford the desired product.

Methyl 3-(but-3-en-1-yloxy)-4-cyanobenzoate



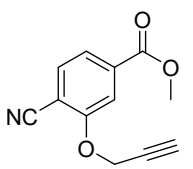
Following the **method A** with 4-bromobut-1-ene, the desired product was obtained as a white solid in 57% yield (330 mg). Melting point: 64 – 66 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.79 – 7.50 (m, 3H), 5.98 – 5.88 (m, 1H), 5.40 – 5.07 (m, 2H), 4.19 (t, *J* = 6.7 Hz, 2H), 3.95 (s, 3H), 2.64 (q, *J* = 6.7 Hz, 2H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 165.6, 160.5, 135.4, 133.8, 133.4, 121.6, 118.0, 115.6, 112.9, 106.2, 68.6, 52.8, 33.2. HRMS m/z (ESI) called for $C_{13}H_{13}NO_3Na^+$ $(M + Na)^+$ 254.0793, found 354.0789.

Methyl 4-cyano-3-((5-cyanopentyl)oxy)benzoate



Following the **method A** with 6-bromohexanenitrile, the desired product was obtained as a yellow solid in 60% yield (485 mg). Melting point: 62 – 64 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.76 – 7.54 (m, 3H), 4.19 (t, *J* = 6.1 Hz, 2H), 3.97 (s, 3H), 2.44 (t, *J* = 6.9 Hz, 2H), 2.00 – 1.91 (m, 2H), 1.86 – 1.78 (m, 2H), 1.78 – 1.69 (m, 2H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 165.5, 160.5, 135.5, 133.8, 121.7, 119.6, 115.6, 112.8, 106.1, 68.9, 52.8, 28.1, 25.3, 25.1, 17.2. HRMS m/z (ESI) called for $C_{15}H_{16}N_2O_3Na^+$ $(M + Na)^+$ 295.1059, found 295.1058.

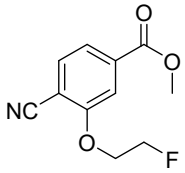
Methyl 4-cyano-3-(prop-2-yn-1-yloxy)benzoate



Following the **method B** with 3-bromoprop-1-yne, the desired product was obtained as a yellow solid in 93% yield (500 mg). Melting point: 137 – 139 °C.^{1}H NMR (400 MHz, chloroform-*d*) δ 7.79 (d, *J* = 1.3 Hz, 1H), 7.73 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 4.90 (d, *J* = 2.4 Hz, 2H), 3.97 (s, 3H), 2.61 (d, *J* = 2.4 Hz, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 165.4, 159.0, 135.4, 133.9, 115.3, 113.7, 106.6, 77.4, 77.3 (d, *J* =

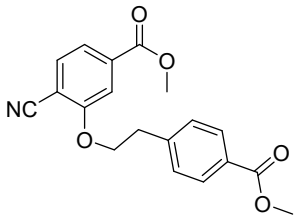
12.3 Hz), 76.6 (d, J = 2.5 Hz), 56.8, 52.9. HRMS m/z (ESI) called for $C_{12}H_9NO_3Na^+$ $(M + Na)^+$ 238.0480, found 238.0478.

Methyl 4-cyano-3-(2-fluoroethoxy)benzoate



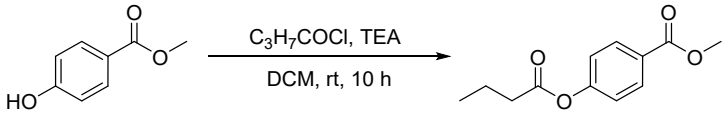
Following the **method A** with 1-fluoro-2-iodoethane, the desired product was obtained as a white solid in 61% yield (340 mg). Melting point: 142 – 144 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.76 – 7.60 (m, 3H), 4.95 – 4.86 (m, 1H), 4.83 – 4.74 (m, 1H), 4.51 – 4.43 (m, 1H), 4.42 – 4.36 (m, 1H), 3.96 (s, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 165.4, 160.0, 135.5, 134.0, 122.3, 115.3, 113.1, 106.5, 81.3 (d, J = 172.5 Hz), 68.5 (d, J = 21.2 Hz), 52.8. ^{19}F NMR (376 MHz, chloroform-*d*) δ –223.59. HRMS m/z (ESI) called for $C_{11}H_{10}FNO_3Na^+$ $(M + Na)^+$ 246.0542, found 246.0540.

Methyl 4-cyano-3-(4-(methoxycarbonyl)phenethoxy)benzoate



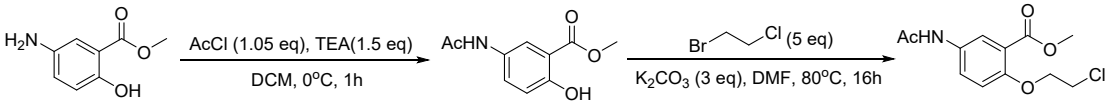
Following the **method B** with methyl 4-(2-bromoethyl)benzoate, the desired product was obtained as a yellow solid in 9.4 % yield (80 mg). Melting point: 169 – 171 °C. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.01 (d, J = 8.2 Hz, 2H), 7.68 – 7.59 (m, 2H), 7.56 (d, J = 1.3 Hz, 1H), 7.43 (d, J = 8.2 Hz, 2H), 4.34 (t, J = 6.5 Hz, 2H), 3.93 (s, 3H), 3.91 (s, 3H), 3.24 (t, J = 6.5 Hz, 2H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 167.0, 165.5, 160.3, 142.9, 135.4, 133.8, 129.9, 129.4, 128.8, 121.8, 115.5, 112.7, 106.2, 69.5, 52.8, 52.1, 35.5. HRMS m/z (ESI) called for $C_{19}H_{17}NO_5Na^+$ $(M + Na)^+$ 362.1004, found 362.1004.

3.2. Synthesis of methyl 4-(butyryloxy)benzoate



To a solution of methyl 4-hydroxybenzoate (761 mg, 5 mmol) and Et_3N (758 mg, 7.5 mmol, 1.5 equiv) in DCM (10 ml) was added butyryl chloride (586 mg, 5.5 mmol, 1.1 equiv) dropwise. The mixture was stirred at room temperature for 10 h. After the reaction was completed (monitored by TLC), the reaction solution was diluted with DCM (50 ml), washed by aq. $NaHCO_3$ (50 ml x 1) and aq. NaCl (50 ml x 1), dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (PE/EtOAc = 10/1) to give pure product as a colorless oil in 95% yield (1.05 g). ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.07 (d, J = 8.7 Hz, 2H), 7.16 (d, J = 8.7 Hz, 2H), 3.91 (s, 3H), 2.56 (t, J = 7.4 Hz, 2H), 1.79 (q, J = 7.4 Hz, 2H), 1.05 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 171.5, 166.3, 154.4, 131.1, 127.6, 121.6, 52.2, 36.1, 18.4, 13.6. HRMS m/z (ESI) called for $C_{12}H_{14}O_4Na^+$ $(M + Na)^+$ 245.0790, found 245.0788.

3.3. Synthesis of methyl 5-acetamido-2-(2-chloroethoxy)benzoate.



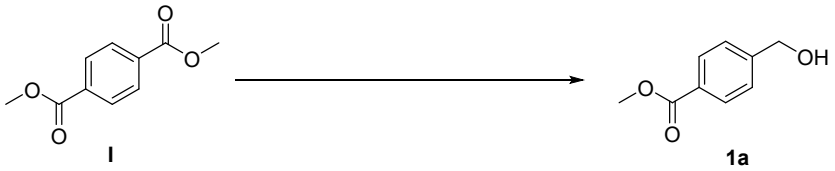
To a solution of methyl 5-amino-2-hydroxybenzoate (836 mg, 5 mmol) and Et3N (755 mg, 7.5 mmol, 1.05 equiv) in DCM (25 ml) was added acetyl chloride (412 mg, 5.25 mmol, 1.01 equiv) dropwise at 0 oC. The mixture was stirred at 0 oC for 1 h. After the reaction was completed (monitored by TLC), the reaction solution was diluted with DCM (50 ml), washed by aq. $NaHCO_3$ (50 ml x 1) and aq. NaCl (50

ml x 1), dried over Na_2SO_4, filtered and concentrated. The residue was washed by PE/EtOAc = 10/1 to give methyl 5-acetamido-2-hydroxybenzoate as a brown solid in 92% yield (0.97 g). ^{1}H NMR (400 MHz, chloroform-d) δ10.62 (s, 1H), 8.02 (d, J = 2.6 Hz, 1H), 7.49 (dd, J = 9.0, 2.7 Hz, 1H), 7.33 (s, 1H), 6.94 (d, J = 8.9 Hz, 1H), 3.93 (s, 3H), 2.16 (s, 3H).

A solution of methyl 5-acetamido-2-hydroxybenzoate (530 mg, 2.54 mmol), K_2CO_3 (1.05 g, 7.62 mmol, 3 equiv) and 1-bromo-2-chloroethane (1.82 g, 12.7 mmol, 5 equiv) in DMF (10 ml) was stirred at 80 ^{o}C for 16 h. After the reaction was completed (monitored by TLC), the reaction solution was diluted with EA (50 ml), washed by aq. NaCl (30 ml x 3), dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (PE/EtOAc = 10/1) to give pure product as a white solid in 55% yield (375 mg).^{1}H NMR (400 MHz, chloroform-d) δ7.81 – 7.74 (m, 2H), 7.38 (d, *J* = 13.7 Hz, 1H), 6.95 (d, *J* = 8.7 Hz, 1H), 4.27 (t, *J* = 6.0 Hz, 2H), 3.88 (s, 3H), 3.83 (t, *J* = 6.1 Hz, 2H), 2.17 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.4, 166.1, 154.5, 131.7, 125.7, 123.4, 121.4, 115.6, 70.1, 52.2, 41.7, 24.4.

4. Optimization of reaction conditions

4.1 Optimization of the electrochemical reduction of methyl benzoate with electron withdrawing group



4.1.1 Screen of the cathode

cathode	yield	cathode	yield	cathode	yield	cathode	yield
CF	65%	RVC	15%	Ag	46%	Zn	15%
carbon rod	36%	Fe	61%	Al	19%	Pb	11%
		Cu	30%	Ni	0%	Pt	32%

Condition: **I** (0.3 mmol), Et_3N (2.4 mmol), $Zn(OTf)_2$ (0.06 mmol), H_2O (15 mmol), $^nBu_4NI$ (0.3 mmol), MeCN (7 mL), carbon felt (1 cm × 1.5 cm × 0.5 cm) as anode, 13.3 mA/cm^3, rt, 8 h. Yields were determined by HNMR with mesitylene as an internal standard.

4.1.2 Screen of the anode

anode	yield	anode	yield	anode	yield	anode	yield
carbon felt	65%	RVC	50%	carbon rod	0%	Pt	30%

Condition: **I** (0.3 mmol), Et_3N (2.4 mmol), $Zn(OTf)_2$ (0.06 mmol), H_2O (15 mmol), $^nBu_4NI$ (0.3 mmol), MeCN (7 mL), carbon felt (1 cm × 1.5 cm × 0.5 cm) as cathode, 13.3 mA/cm^3, rt, 8 h. Yields were determined by HNMR with mesitylene as an internal standard.

4.1.3 Screen of the electrolyte

electrolyte	yield	electrolyte	yield	electrolyte	yield
$^nBu_4NOAc$	71%	$^nBu_4NI$	13%	$^nBu_4ClO_4$	50%
LiOAc	0	$LiOCl_4$	0		

Condition: **I** (0.3 mmol), H_2O (6 mmol), electrolyte (0.3 mmol), MeCN (7 mL), carbon felt (1 cm × 1.5 cm × 0.5 cm) as anode and cathode, C.V. = 3.8 V, rt, 10 h. Yields were determined by HNMR with mesitylene as an internal standard.

4.1.4 Screen of the constant voltage (C. V.) and constant current(C. C.)

C. V.	yield	C. C.	yield
4.0 V	53%	5 mA	0% (100%) [a]
3.8 V	71%	10 mA	53% (24%) [b]
3.7 V	73%	15 mA	19% (40%) [b]
3.0 V	0% (100%) [a]	20 mA	0% (71%) [b]

Condition: **I** (0.3 mmol), H_2O (6 mmol), $^nBu_4NOAc$ (0.15 mmol), MeCN (7 mL), carbon felt (1 cm × 1.5 cm × 0.5 cm) as anode and cathode, C.V. or C. C., rt, 6 h. Yields were determined by HNMR with mesitylene as an internal standard. [a] SM recovered. [b] yields of methyl 4-methylbenzoate.

4.1.5 Screen of the solvent

solvent	yield	solvent	yield	solvent	yield

MeCN	63%	MeOH	32%	THF	43% (20%) [a]
DMF	33% (27%)[a]	*i*PrOH	35% (40%)[a]	HFIP	0%
DMSO	28%	DCE	37%	acetone	31%
MeCN/H_2O=6/1	83%				

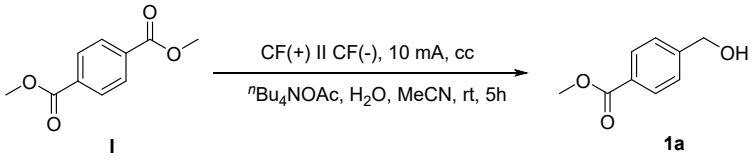
Condition: **I** (0.3 mmol), H_2O (6 mmol), $^nBu_4NOAc$ (0.15 mmol), solvent (7 mL), carbon felt (1 cm × 1.5 cm × 0.5 cm) as anode and cathode, 13.3 mA/cm^3, rt, 5.5 h. Yields were determined by HNMR with mesitylene as an internal standard. [a] yields of methyl 4-methylbenzoate.

4.1.6 Screen of equiv of H_2O

H_2O (equiv)	yield	H_2O (equiv)	yield	H_2O (equiv)	yield
2	52%	20	80%	200	83%
5	57%	50	77%		
10	72%	100	80%		

Condition: **I** (0.3 mmol), $^nBu_4NOAc$ (0.3 mmol), MeCN (7 mL), carbon felt (1 cm × 1.5 cm × 0.5 cm) as anode and cathode, 13.3 mA/cm^3, rt, 10 h. Yields were determined by HNMR with mesitylene as an internal standard.

4.1.7 Optimization of the reaction of I with H_2O as the hydrogen source in undivided cells.

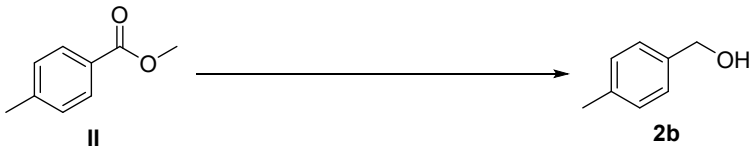


I **1a**

Entry	Deviation from optimized conditions[a]	Conv. [b]	Yield[c]
1	**None**	**100%**	**83%(78%[d])**
2	No electric current	0	0
3	No H_2O	99%	15%
4	DMF instead of MeCN	96%	50%
5	iPrOH instead of MeCN	97%	41%
6	THF instead of MeCN	100%	65%
7	iPrOH instead of H_2O	98%	34%
8	Et_3N instead of H_2O	98%	11%
9	$^nBu_4PF_6$ supporting electrolyte	94%	73%
10	$LiPF_6$ supporting electrolyte	44%	0
11	Graphite felt instead of carbon felt	86%	22%

[a] Optimized condition: **I** (0.3 mmol), $^nBu_4NOAc$ (0.3 mmol), H_2O/MeCN (1/6, 7 mL), carbon felt (1 cm × 1.5 cm × 0.5 cm) as anode and cathode, 13.3 mA/cm^3, rt, 5 h. [b] Conversions were determined by HNMR with mesitylene as an internal standard. [c] Yields were determined HNMR with mesitylene as an internal standard. [d] Isolated yield.

4.2 Optimization of the electrochemical reduction of methyl benzoate with electron donating group.



II **2b**

4.2.1 Screen of the electrolyte

electrolyte	yield	electrolyte	yield	electrolyte	yield	electrolyte	yield
$^{n}Bu_4NPF_6$	90%	$^{n}Bu_4OAc$	88%	$^{n}Bu_4BF_4$	88%	$^{n}Bu_4ClO_4$	87%
$^{n}Bu_4Cl$	77%	$LiClO_4$	90%	$Mg(ClO_4)_2$	82%		

Condition: **II** (0.3 mmol), electrolyte (0.3 mmol), H_2O/MeCN = 1/6 (7 mL), Me_2S (0.9 mmol), graphite felt (1 cm × 1.5 cm × 0.5 cm) as anode and cathode, 9.0 V V_{pp} of rAP, 2 Hz, rt, 10 h. Yields were determined by HNMR with mesitylene as an internal standard.

4.2.2 Screen of the equiv of electrolyte

equiv	yield
2.0	90%
1.0	90%
0.5	71%

Condition: **II** (0.3 mmol), $^{n}Bu_4NPF_6$, H_2O/MeCN = 1/6 (7 mL), Me_2S (0.9 mmol), graphite felt (1 cm × 1.5 cm × 0.5 cm) as anode and cathode, 9.0 V V_{pp} of rAP, 2 Hz, rt, 10 h. Yields were determined by HNMR with mesitylene as an internal standard.

4.2.3 Screen of the solvent

electrolyte	yield	electrolyte	yield	electrolyte	yield	electrolyte	yield
MeCN	90%	THF	28%	DMF	40%	DMSO	55%
EtOH	26%	Acetone	46%	MeOH	49%	THF/EtOH=1/1	43%

Condition: **II** (0.3 mmol), $^{n}Bu_4NPF_6$ (0.3 mmol), H_2O/solvent = 1/6 (7 mL), Me_2S (0.9 mmol), graphite felt (1 cm × 1.5 cm × 0.5 cm) as anode and cathode, 9.0 V V_{pp} of rAP, 2 Hz, rt, 10 h. Yields were determined by HNMR with mesitylene as an internal standard.

4.2.4 Screen of the additives

additive	yield	additive	yield	additive	yield	additive	yield
Me_2S	90%	Ph_2S	75%	3, 5-diMePhSH	0%	Et_3N	3%
Et_2S	82%	Ph_3P	84%	1,3-Dithiane	70%	DIEA	3%

Condition: **II** (0.3 mmol), $^{n}Bu_4NPF_6$ (0.3 mmol), H_2O/MeCN = 1/6 (7 mL), additive (0.9 mmol), graphite felt (1 cm × 1.5 cm × 0.5 cm) as anode and cathode, 9.0 V V_{pp} of rAP, 2 Hz, rt, 10 h. Yields were determined by HNMR with mesitylene as an internal standard.

4.2.5 Screen of the equiv of Me_2S.

equiv	yield
1.0	44% (46%)[a]

2.0	90%
3.0	90%

Condition: **II** (0.3 mmol), $^{n}Bu_4NPF_6$ (0.3 mmol), H_2O/MeCN = 1/6 (7 mL), Me_2S, graphite felt (1 cm × 1.5 cm × 0.5 cm) as anode and cathode, 9.0 V V_{pp} of rAP, 2 Hz, rt, 10 h. Yields were determined by HNMR with mesitylene as an internal standard. [a] SM recovered.

4.2.6 Screen of the equiv of H_2O.

equiv	yield	equiv	yield	equiv	yield
2	1% (88%)[a]	20	86%	200	90%
5	1.5% (95%)[a]	50	88%		
10	86%	100	87%		

Condition: **II** (0.3 mmol), $^{n}Bu_4NPF_6$ (0.3 mmol), MeCN (6 mL), Me_2S (0.9 mmol), graphite felt (1 cm × 1.5 cm × 0.5 cm) as anode and cathode, 9.0 V V_{pp} of rAP, 2 Hz, rt, 10 h. Yields were determined by HNMR with mesitylene as an internal standard. [a] SM recovered.

4.2.7 Screen of the voltage.

Voltage (V V_{pp})	yield
7.0	37% (21%)[a]
8.0	87%
9.0	90%
10.0 V	70%

Condition: **II** (0.3 mmol), $^{n}Bu_4NPF_6$ (0.3 mmol), H_2O/MeCN = 6/1 (7 mL), Me_2S (0.9 mmol), graphite felt (1 cm × 1.5 cm × 0.5 cm) as anode and cathode, rAP, 2 Hz, rt, 10 h. Yields were determined by HNMR with mesitylene as an internal standard. [a] SM recovered.

4.2.8 Screen of the frequency.

frequency	yield	frequency	yield	frequency	yield
0.5 Hz	67%	1 Hz	85%	2 Hz	90%
3 Hz	90%	5 Hz	88%	10 Hz	81%
20 Hz	53% (15%) [a]				

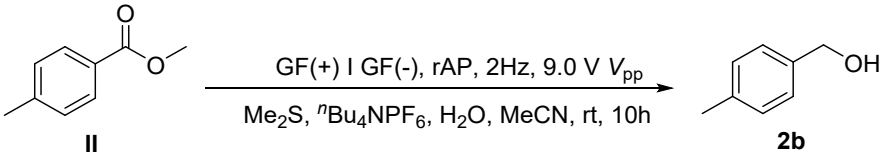
Condition: **II** (0.3 mmol), $^{n}Bu_4NPF_6$ (0.3 mmol), H_2O/MeCN = 6/1 (7 mL), Me_2S (0.9 mmol), graphite felt (1 cm × 1.5 cm × 0.5 cm) as anode and cathode, 9.0 V V_{pp} of rAP, rt, 10 h. Yields were determined by HNMR with mesitylene as an internal standard. [a] SM recovered.

4.2.9 Control reaction.

Entry	yield
No Me_2S	8% (53%) [a]
No H_2O	2.5% (75%) [a]
No H_2O/Me_2S	0% (80%) [a]

Condition: **II** (0.3 mmol), $^{n}Bu_4NPF_6$ (0.3 mmol), H_2O/MeCN = 6/1 (7 mL), Me_2S (0.9 mmol), graphite felt (1 cm × 1.5 cm × 0.5 cm) as anode and cathode, 9.0 V V_{pp} of rAP, rt, 10 h. Yields were determined by HNMR with mesitylene as an internal standard. [a] SM recovered.

4.2.10 Optimization of the reduction of II with H_2O as the hydrogen source in undivided cells.

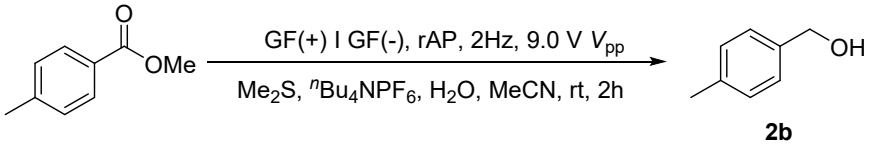


II **2b**

Entry	Deviation from optimized conditions[a]	Conv. [b]	Yield[c]
1	**None**	**100%**	**90%(86%[d])**
2	No Me_2S	47%	8%
3	No H_2O	25%	2.5%
4	DMF instead of MeCN	97%	40%
5	EtOH instead of MeCN	72%	26%
6	THF instead of MeCN	82%	28%
7	Ph_3P instead of Me_2S	100%	84%
8	Et_3N instead of Me_2S	100%	3%
9	$^nBu_4NOAc$ supporting electrolyte	100%	88%
10	$LiClO_4$ supporting electrolyte	100%	90%
11	0.5 Hz	100%	67%
12	10 Hz	99%	81%
13	8.0 V V_{pp}	100	74%
14	Carbon felt instead of graphite felt	86%	22%
15	Pb as cathode, 20 mA, cc	94%	8
16	DC, 4.5 V (C.V.)	100%	0%

[a] Optimized condition: **II** (0.3 mmol), Me_2S (0.9 mmol), $^nBu_4NPF_6$ (0.3 mmol), H_2O/MeCN (1/6, 7 mL), graphite felt (1 cm × 1.5 cm × 0.5 cm) as anode and cathode, 9.0 V V_{pp} of rAP, 2 Hz, rt, 10 h. [b] Conversions were determined by HNMR with mesitylene as an internal standard. [c] Yields were determined HNMR with mesitylene as an internal standard. [d] Isolated yield.

4.2.11 Measuring the consumption of electricity



2b

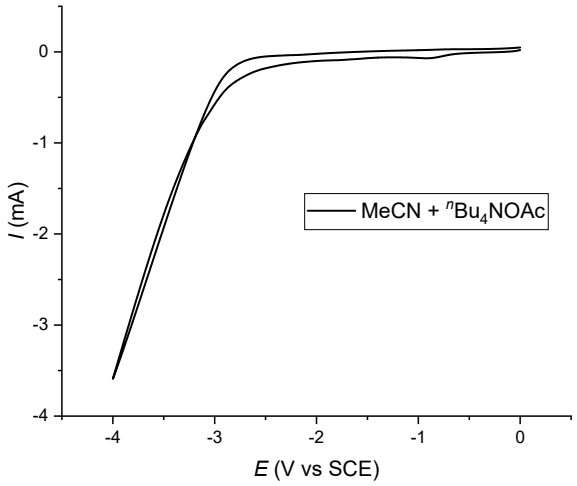
IKA Electrasyn 2.0 22 F/mol 69% NMR yield

This reaction was conducted with IKA Electrasyn 2.0 with the function measuring the consumption of electricity of rAP.

5. Mechanism Study

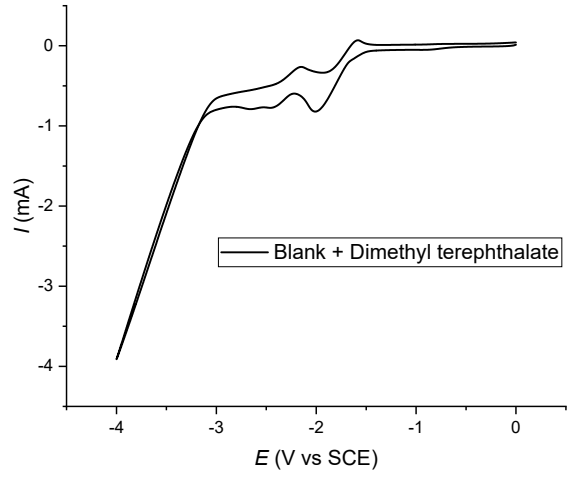
5.1 Cyclic voltammetry experiments of reactants

5.1.1. Cathodic reduction: MeCN + $^{n}Bu_4NOAc$ (Blank-1)



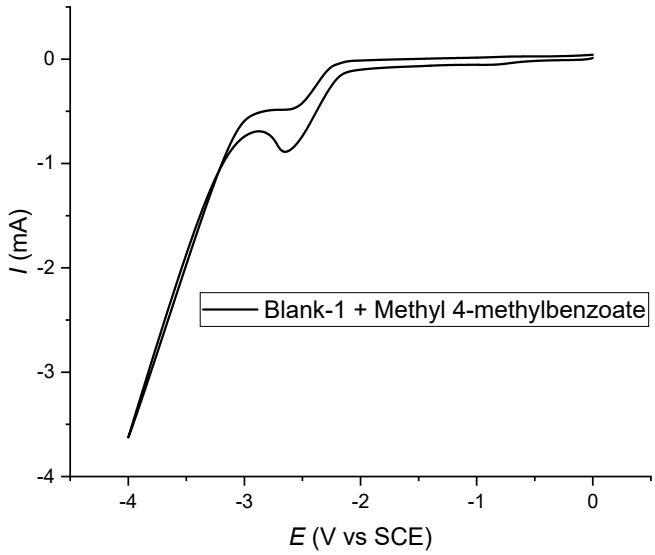
CV condition: glassy carbon working electrode, Pt wire counter electrode, SCE reference electrode, 0.1 V/S, $^{n}Bu_4NOAc$ (0.3 mmol), MeCN (6 mL).

5.1.2. Cathodic reduction: Blank-1 + Dimethyl terephthalate (I)



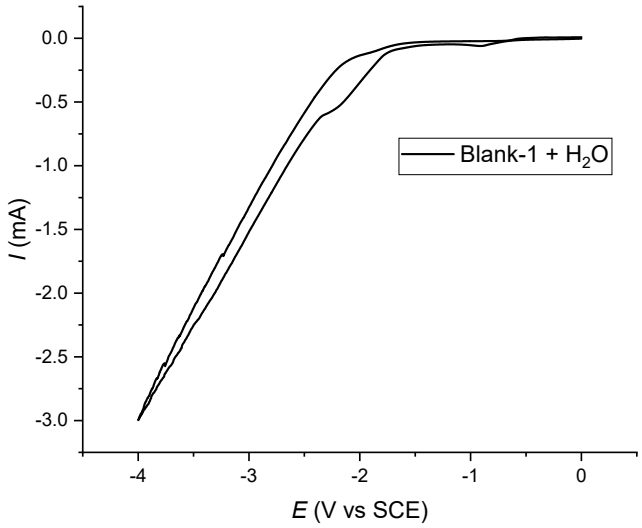
CV condition: glassy carbon working electrode, Pt wire counter electrode, SCE reference electrode, 0.1 V/S, **I** (0.3 mmol), *n*-Bu_4NOAc (0.3 mmol), MeCN (6 mL).

5.1.3. Cathodic reduction: Blank-1 + Methyl 4-methylbenzoate (II)



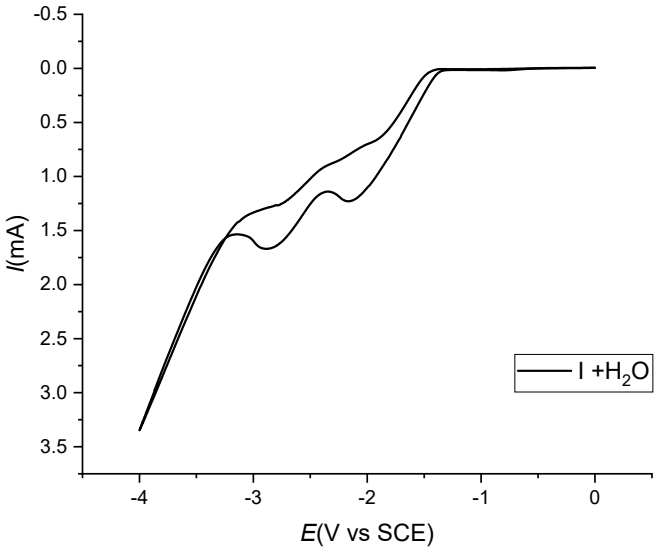
CV condition: glassy carbon working electrode, Pt wire counter electrode, SCE reference electrode, 0.1 V/S, **II** (0.3 mmol), $^{n}Bu_4NOAc$ (0.3 mmol), MeCN (6 mL).

5.1.4. Cathodic reduction: Blank-1 + H_2O



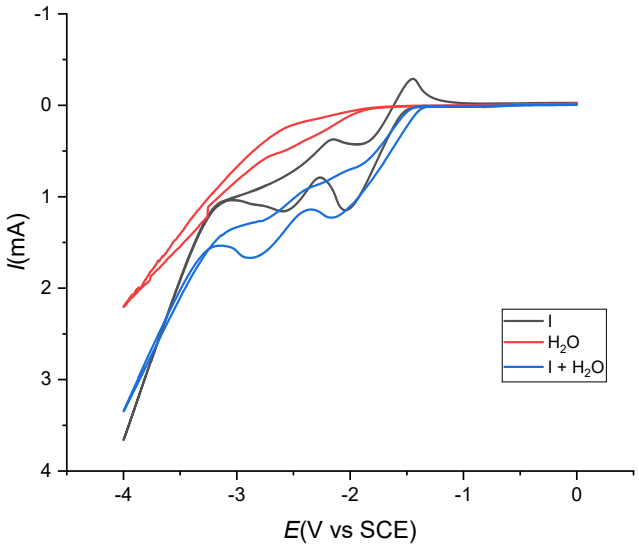
CV condition: glassy carbon working electrode, Pt wire counter electrode, SCE reference electrode, 0.1 V/S, H_2O(0.1 ml), $^{n}Bu_4NOAc$ (0.3 mmol), MeCN (6 mL).

5.1.5. Cathodic reduction of I and H_2O

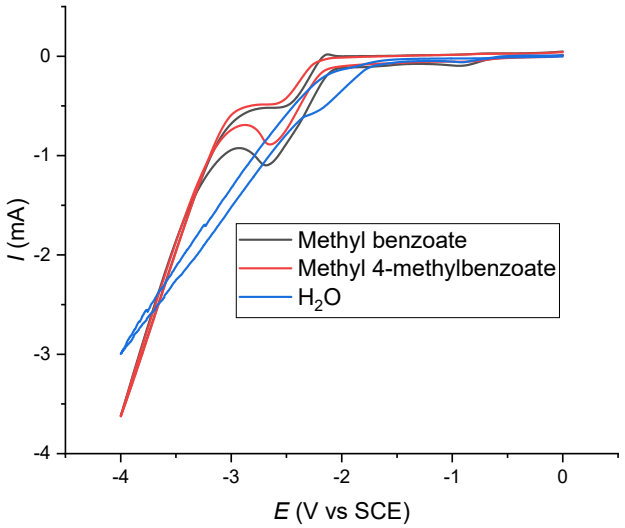


CV condition: glassy carbon working electrode, Pt wire counter electrode, SCE reference electrode, 0.1 V/S, **I** (0.3 mmol), H_2O(0.1 ml), $^{n}Bu_4NOAc$ (0.3 mmol), MeCN (6 mL).

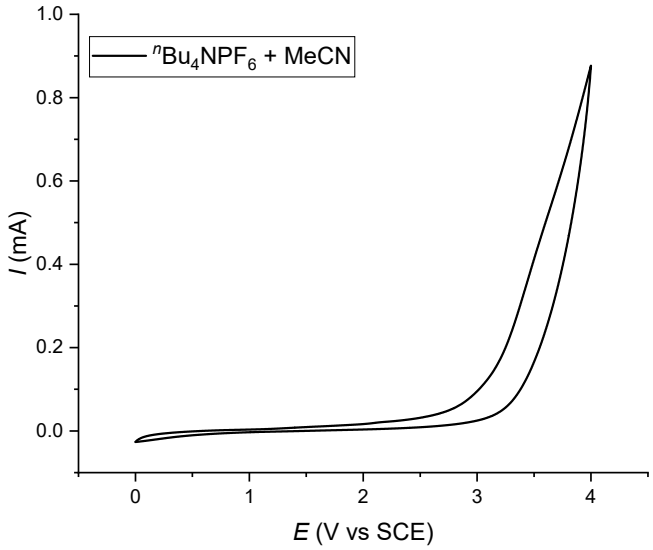
5.1.6. Cathodic reduction of I/H_2O/I and H_2O



5.1.7. Cathodic reduction of I/H_2O.

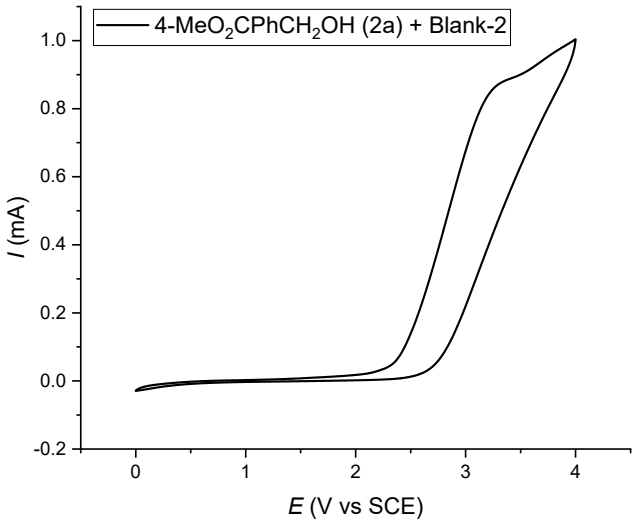


5.1.8. Anodic oxidation: MeCN + $^{n}Bu_4NPF_6$ (Blank-2)



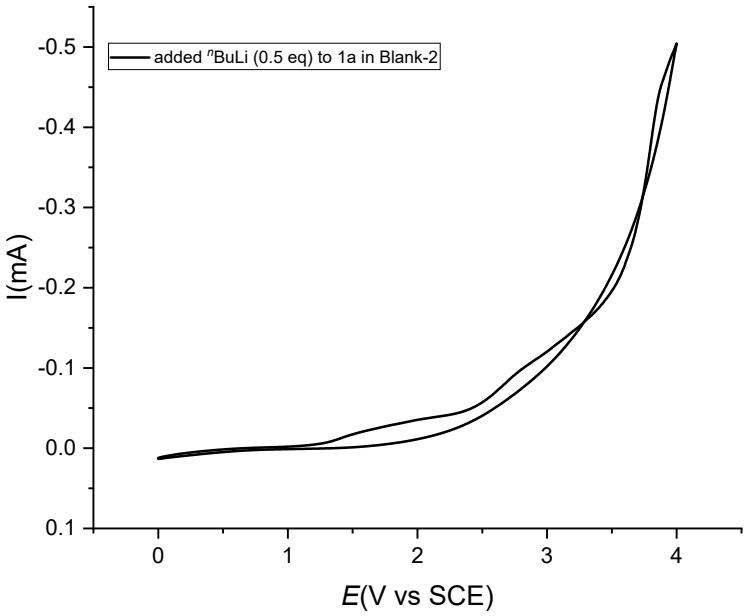
CV condition: glassy carbon working electrode, Pt wire counter electrode, SCE reference electrode, 0.1 V/S, $^{n}Bu_4NPF_6$ (0.3 mmol), MeCN (6 mL).

5.1.9. Anodic oxidation: 4-MeO_2CPhCH_2OH (1a) + Blank-2



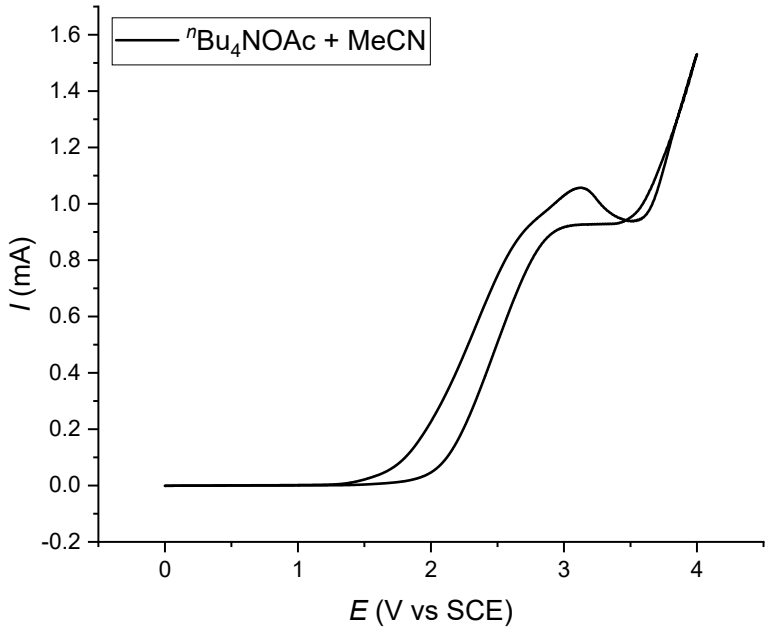
CV condition: glassy carbon working electrode, Pt wire counter electrode, SCE reference electrode, 0.1 V/S, **1** (0.3 mmol), $^{n}Bu_4NPF_6$ (0.3 mmol), MeCN (6 mL).

5.1.10. Anodic oxidation: 4-MeO_2CPhCH_2OH (1a) + ^{n}BuLi (0.5 eq) + Blank-2



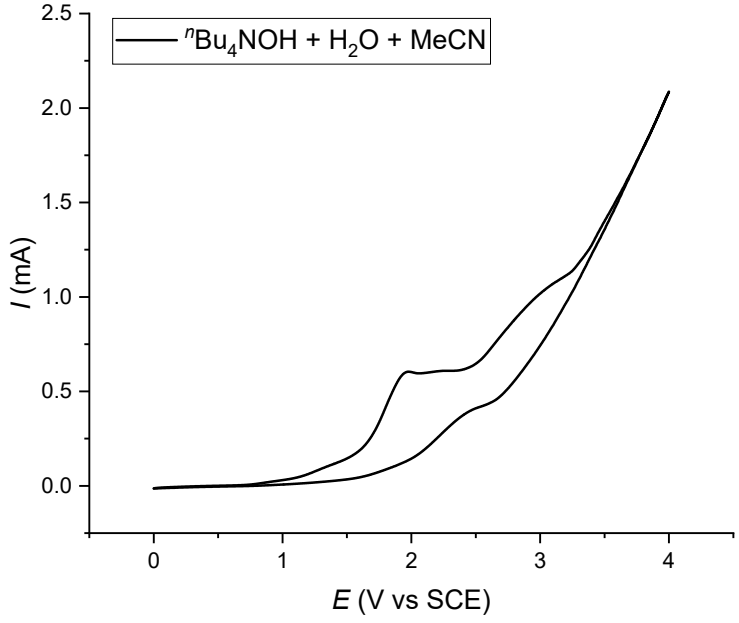
CV condition: glassy carbon working electrode, Pt wire counter electrode, SCE reference electrode, 0.1 V/S, **1** (0.3 mmol), ^{n}BuLi (0.15 mmol), $^{n}Bu_4NPF_6$ (0.3 mmol), MeCN (6 mL).

5.1.11. Anodic oxidation: $^{n}Bu_4NOAc$ + MeCN



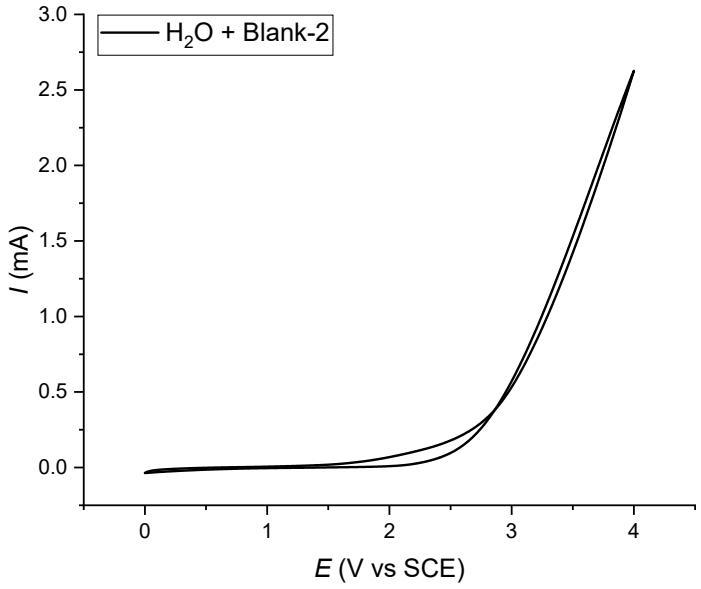
CV condition: glassy carbon working electrode, Pt wire counter electrode, SCE reference electrode, 0.1 V/S, $^{n}Bu_4NOAc$ (0.3 mmol), MeCN (6 mL).

5.1.12. Anodic oxidation: $^{n}Bu_4NOH$ + H_2O + MeCN



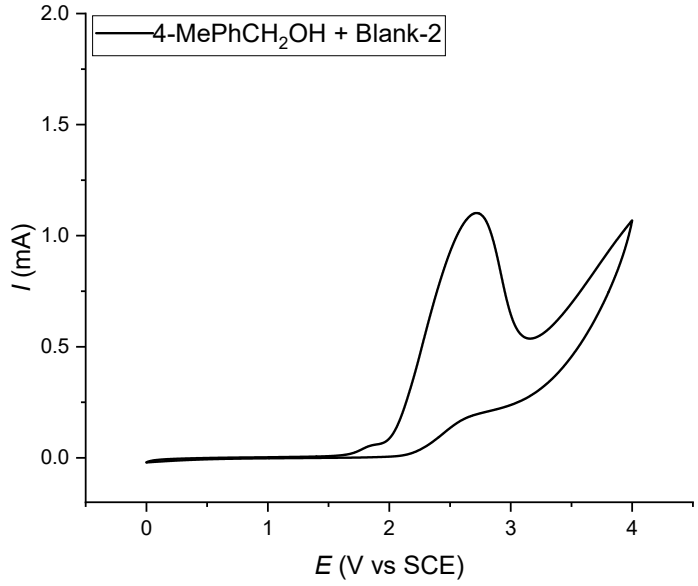
CV condition: glassy carbon working electrode, Pt wire counter electrode, SCE reference electrode, 0.1 V/S, $^{n}Bu_4NOH$ (40% in H_2O, 0.3 mmol), MeCN (6 mL).

5.1.13. Anodic oxidation: H_2O + Blank-2



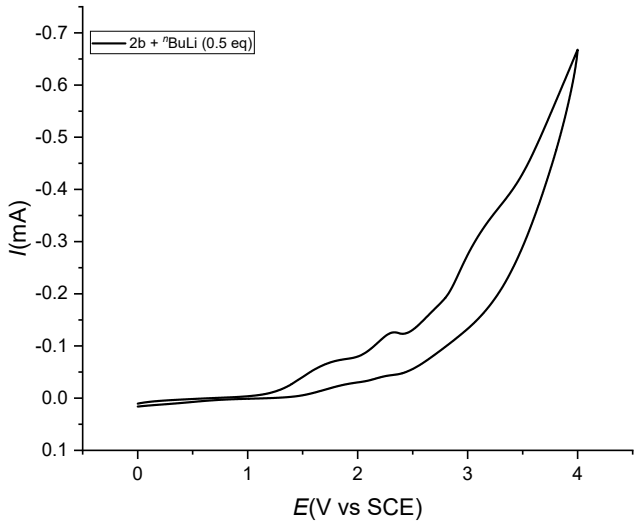
CV condition: glassy carbon working electrode, Pt wire counter electrode, SCE reference electrode, 0.1 V/S, H_2O (1 mL), $^{n}Bu_4NPF_6$ (0.3 mmol), MeCN (6 mL).

5.1.14. Anodic oxidation: 4-MePhCH_2OH (2b) + Blank-2



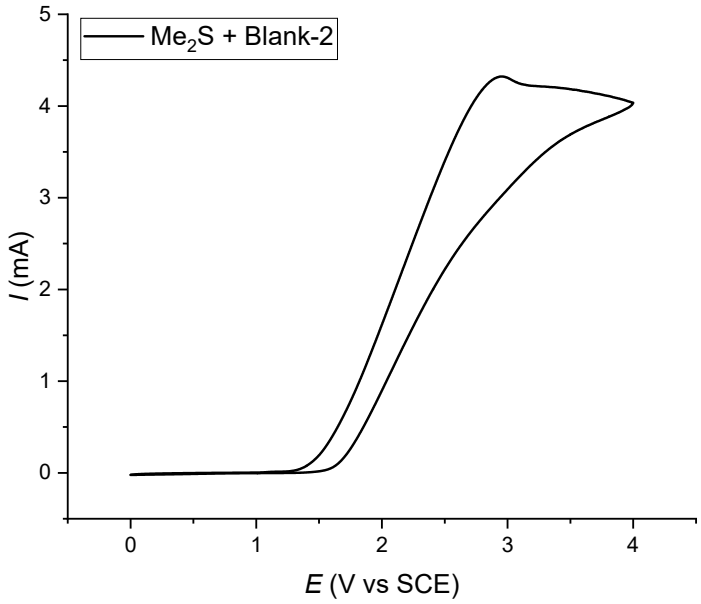
CV condition: glassy carbon working electrode, Pt wire counter electrode, SCE reference electrode, 0.1 V/S, **2b** (0.3 mmol), $^{n}Bu_4NPF_6$ (0.3 mmol), MeCN (6 mL).

5.1.15. Anodic oxidation: 4-MePhCH$_2$OH (2b) + ^{n}BuLi (0.5 eq) + Blank-2



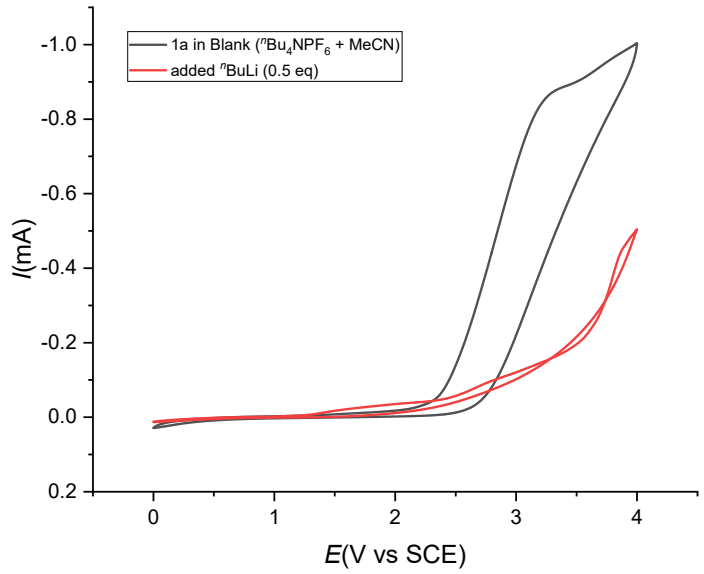
CV condition: glassy carbon working electrode, Pt wire counter electrode, SCE reference electrode, 0.1 V/S, **2b** (0.3 mmol), ^{n}BuLi (0.15 mmol), ^{n}Bu$_4$NPF$_6$ (0.3 mmol), MeCN (6 mL).

5.1.16. Anodic oxidation: Me$_2$S + Blank-2

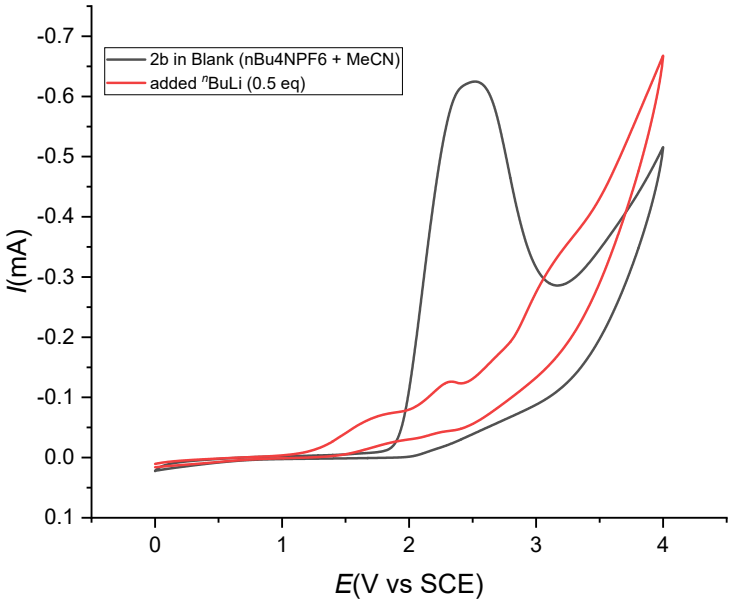


CV condition: glassy carbon working electrode, Pt wire counter electrode, SCE reference electrode, 0.1 V/S, Me$_2$S (0.6 mmol), ^{n}Bu$_4$NPF$_6$ (0.3 mmol), MeCN (6 mL).

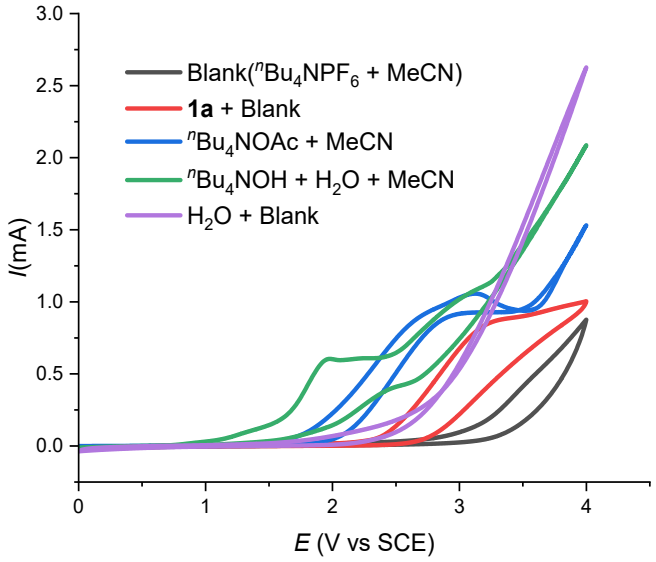
5.1.17. Anodic oxidation of 4-MeO_2CPhCH_2OH (1a) and it's Li^+ salt.



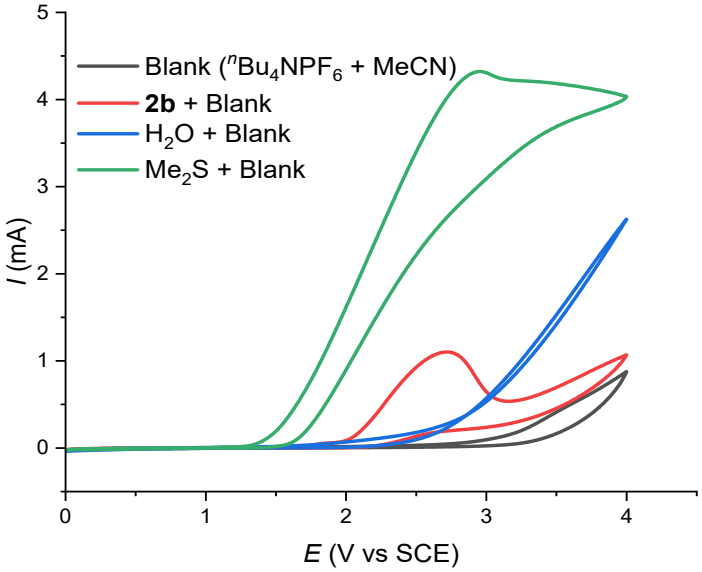
5.1.18. Anodic oxidation of 4-$MePhCH_2OH$ (2b) and it's Li^+ salt.



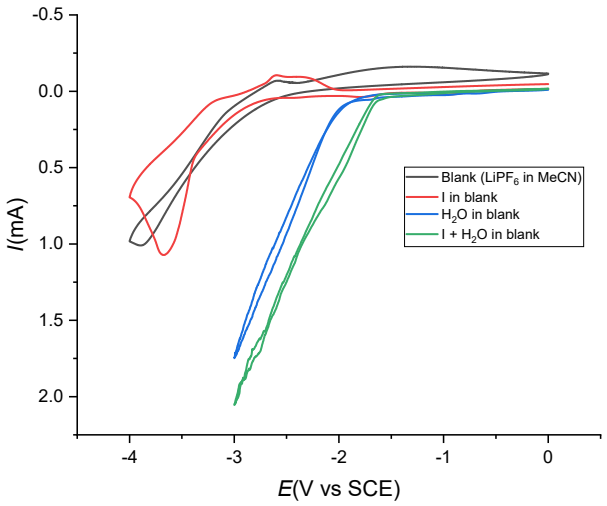
5.1.19. Anodic oxidation of 4-MeO_2CPhCH_2OH (1a) and reagents



5.1.20 Anodic oxidation of 4-$MePhCH_2OH$ (2b) and Me_2S.

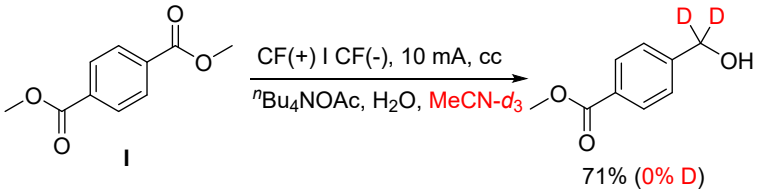


5.1.21 Cathodic reduction of Dimethyl terephthalate (I) and H_2O in $LiPF_6$ + MeCN.



CV condition: glassy carbon working electrode, Pt wire counter electrode, SCE reference electrode, 0.1 V/S, I (0.3 mmol), $LiPF_6$ (0.3 mmol), H_2O (1 ml), MeCN (6 mL).

5.2. Deuteration reaction with MeCN-d_3 as solvent.



To a 10 mL two-necked heart-shaped flask was charged with the dimethyl terephthalate (**I**, 0.3 mmol), *n*-Bu_4NOAc (90.4 mg, 0.3 mmol, 1.0 equiv), H_2O (1 ml), MeCN-d_3 (6 ml) and a magnetic stir bar. The equipment was same as in **General procedure A**. The mixture was stirred under room temperature and 10 mA constant current electrolysis, and reacted until the substrate disappears. The reaction mixture was concentrated under the reduced pressure. The residue was purified by flash chromatography (PE/EtOAc = 4/1) to yield product with 0% deuteration in 71% yield (35.1 mg). ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.00 (d, *J* = 7.9 Hz, 2H), 7.41 (d, *J* = 7.9 Hz, 2H), 4.74 (s, 2H), 3.90 (s, 3H), 2.46 (s, 1H).

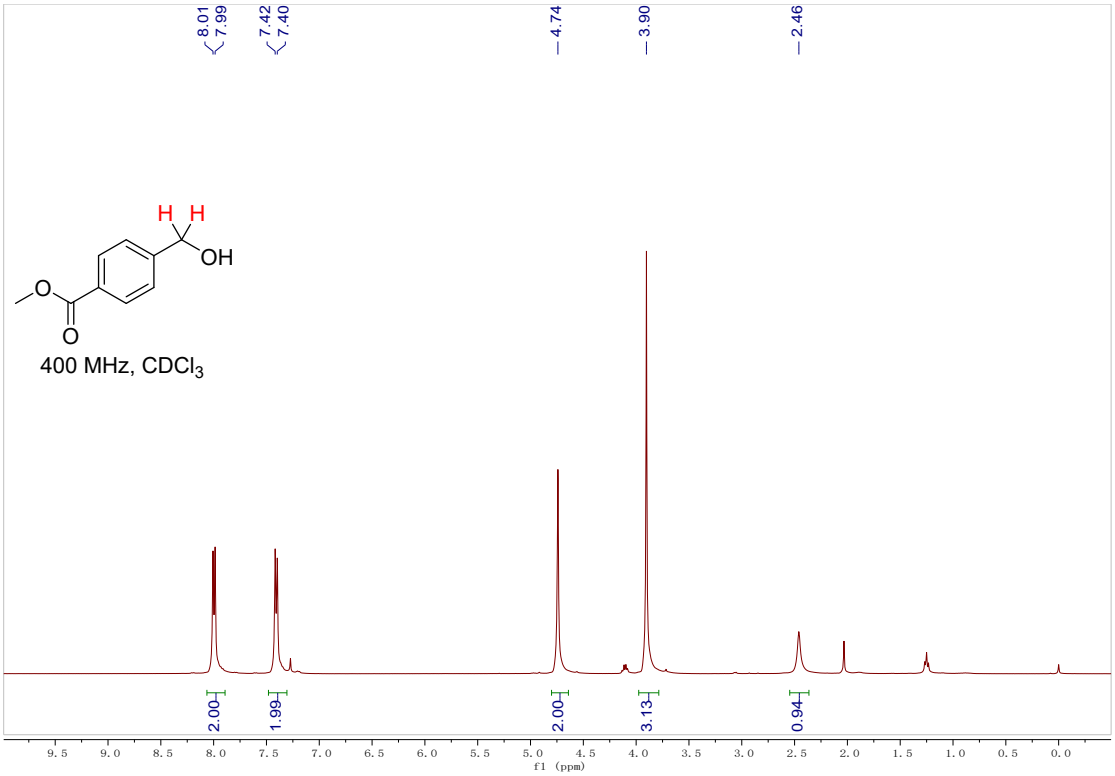
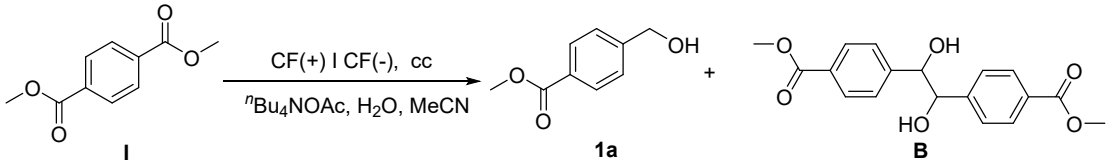


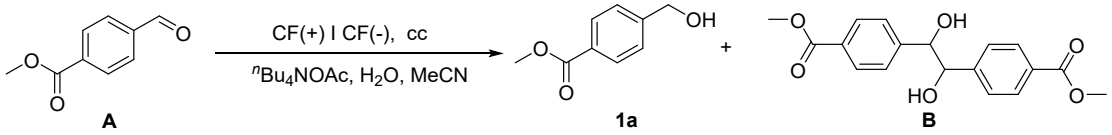
Figure S7. H NMR of the product in the deuteration reaction with ACN-d_3 as solvent

5.3. Confirmation of byproduct structures



To a 100 mL glass beaker was charged with the dimethyl terephthalate (**I**, 1.94 g, 10 mmol), $^{n}Bu_4NOAc$ (1.21 g, 4 mmol, 0.4 equiv), H_2O (1.8 ml, 100 mmol, 10 equiv), MeCN (80 ml) and a magnetic stir bar. The bottle was equipped with a plastic cap, through which carbon felts (4 cm x 4 cm x 0.5 cm) as anode and cathode were installed. Two electrodes were attached to a titanium wire and separated with a Teflon film. A Teflon wire tied around two electrodes. The whole cell was an undivided cell. The mixture was stirred under room temperature and 100 mA constant current electrolysis, and reacted for 16 h. The reaction mixture was concentrated under the reduced pressure, and purified by flash chromatography (PE/EtOAc = 1/1) to afford the desired byproduct **B** as a white solid with 13% yield (210 mg, two isomers, ratio 5/8). Byproduct **B** has two steric isomers. **Isomer B-1**: ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.85 (d, J = 8.0 Hz, 4H), 7.37 (d, J = 8.0 Hz, 4H), 5.53 (s, 2H), 4.73 – 4.65 (m, 2H), 3.84 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.7, 148.9, 128.8, 128.6, 128.1, 76.9, 52.4. **Isomer B-2**: ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.78 (d, J = 8.0 Hz, 4H), 7.25 (d, J = 8.1 Hz, 4H), 5.63 (s, 2H), 4.77 (d, J = 3.2 Hz, 2H), 3.82 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.7, 148.1, 128.6, 128.5, 127.8, 77.1, 52.4. HRMS m/z (ESI) called for $C_{18}H_{18}O_6Na^+$ (M + Na) $^+$ 353.1001, found 353.0997.

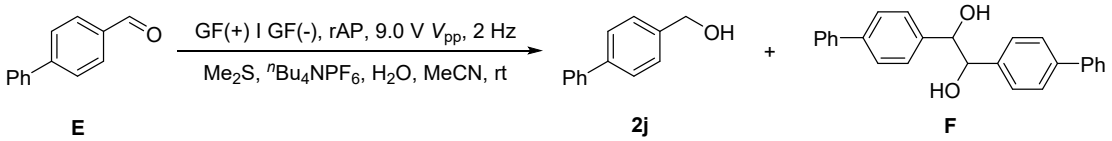
5.4. Benzaldehyde as substrate in standard condition.



A added in one batch, 2.5 h, 25% **1a**, 42% **B**
A added via pump in 3 h, 31% **1a**, 48% **B**

Method A: To a 10 mL two-necked heart-shaped flask was charged with methyl 4-formylbenzoate (**A**, 39.3 mg, 0.3 mmol), $^{n}Bu_4NOAc$ (90.4 mg, 0.3 mmol, 1.0 equiv), H_2O (1 ml), MeCN (6 ml) and a magnetic stir bar. The equipment was same as **General procedure A**. The mixture stirred under room temperature and 10 mA constant current electrolysis, and reacted until the substrate disappears (2.5 h). The reaction mixture was concentrated under the reduced pressure. ^{1}H NMR analysis of the crude reaction mixture showed 25% desired product **1a** and 42% byproduct **B**.

Method B: To a 10 mL two-necked heart-shaped flask was charged with $^{n}Bu_4NOAc$ (90.4 mg, 0.3 mmol), H_2O (1 ml), MeCN (5 ml) and a magnetic stir bar. The equipment was same as in **General procedure A**. The mixture was stirred under room temperature and 10 mA constant current electrolysis. Methyl 4-formylbenzoate (**A**, 39.3 mg, 0.3 mmol) in MeCN (1 mL) was injected into the mixture by a pump in 3 h. The reaction mixture was concentrated under the reduced pressure. ^{1}H NMR spectroscopic analysis of the crude reaction mixture showed 31% desired product **1a** and 48% byproduct **B**.

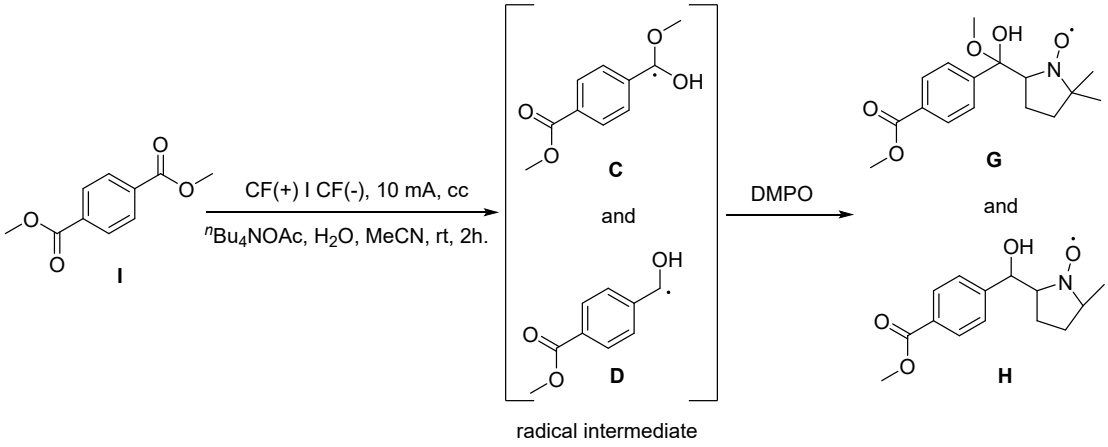


E added in one batch, 1 h, 38% **2j**, 40% **F**
E added via pump in 3 h, 93% **2j**, 7% **F**

Method A: To a 10 mL two-necked heart-shaped flask was charged with [1,1'-biphenyl]-4-carbaldehyde (**E**, 0.3 mmol), Me_2S (55.8 mg, 0.9 mmol, 3.0 equiv), $^{n}Bu_4NPF_6$ (116.2 mg, 0.3 mmol, 1.0 equiv), H_2O (1 mL), MeCN (6 ml) and a magnetic stir bar. The equipment was same as is **General procedure B**. The mixture was stirred under room temperature and 9.0 V V_{pp} of rAP (detected by oscilloscope, set 0.9 V on signal generator, peak to peak, 0.45 V from the offset, alternating frequency: 2 Hz, the current was around 60 mA) and reacted until the substrate disappears (1h). The reaction mixture was concentrated under the reduced pressure. ^{1}H NMR spectroscopic analysis of the crude reaction mixture with mesitylene as an internal standard found 38% desired product **2j** and 40% byproduct **F**.

Method B: To a 10 mL two-necked heart-shaped flask was charged with Me_2S (55.8 mg, 0.9 mmol, 3.0 equiv), $^{n}Bu_4NPF_6$ (116.2 mg, 0.3 mmol, 1.0 equiv), H_2O (1 mL), MeCN (5 ml) and a magnetic stir bar. The equipment was same as in **General procedure B**. The mixture was stirred under room temperature and 9.0 V V_{pp} of rAP (detected by oscilloscope, set 0.9 V on signal generator, peak to peak, 0.45 V from the offset, alternating frequency: 2 Hz, the current was around 60 mA). The [1,1'-biphenyl]-4-carbaldehyde (**E**, 0.3 mmol) in MeCN (2 mL) was injected into the mixture by a pump in 3 h. The reaction mixture was concentrated under the reduced pressure. ^{1}H NMR spectroscopic analysis of the crude reaction mixture with mesitylene as an internal standard found 93% desired product **2j** and 7% byproduct **F**.

5.5. Electron paramagnetic resonance (EPR) experiments.



To a 10 mL two-necked heart-shaped flask was charged with the dimethyl terephthalate (**I**, 0.3 mmol), $^{n}Bu_4NOAc$ (90.4 mg, 0.3 mmol, 1.0 equiv), H_2O (1 ml), MeCN (6 ml). The equipment was same as in **General procedure A**. The mixture was stirred under room temperature and 10 mA constant current electrolysis and reacted for 2 hours. The 100 μL of the reaction mixture was sampled quickly and injected to 17 mg 5, 5-dimethyl-1-pyrroline N-Oxide (DMPO) in a small tube and analyzed by EPR. (Control experiment without dimethyl terephthalate (**I**)).

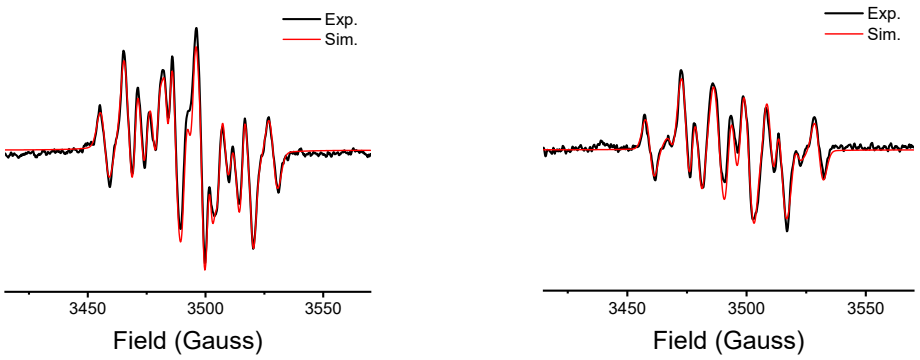


Figure S8. EPR spectra.

Left: with dimethyl terephthalate (**I**); Right: without dimethyl terephthalate (**I**)

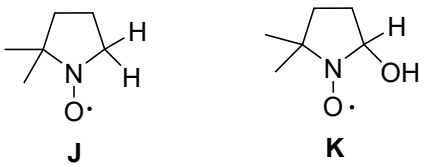
Component 1: g = 2.003, A_N = 15.03G, $A_{H\beta}$ = 23.21G

Component 2: g = 2.003, A_N = 15.20G, $A_{H\beta}$ = 19.16G

Component 3: g = 2.003, A_N = 15.32G, $A_{H\beta}$ = 20.34G

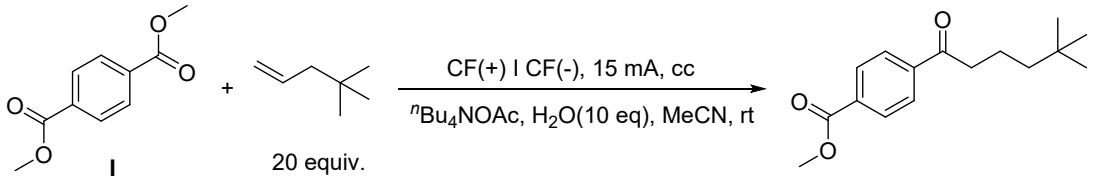
Component 4: g = 2.003, A_N = 13.39G, $A_{H\beta}$ = 13.39G

Components 3 and 4 both exist in two spectrums, we proposed that these radical signals belong to species J (Component 3) and K (Component 4) which formed from H• and OH• trapped by DMPO.



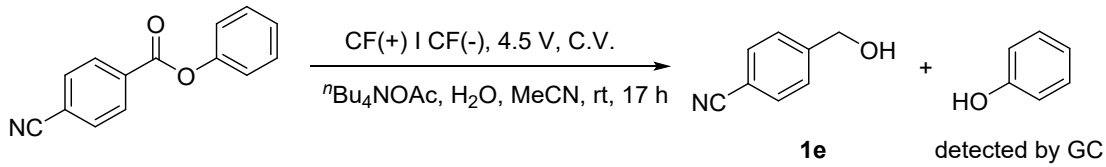
Component 1 and 2, we proposed that these radical signals belong to species C and D, but can't assign exactly.

5.6. Free radical trapping experiments.



To a 10 mL two-necked heart-shaped flask was charged with the dimethyl terephthalate (**I**, 0.3 mmol), ^{n}Bu$_4$NOAc (90.4 mg, 0.3 mmol, 1.0 equiv), H_2O (54 mg, 3 mmol, 10 equiv), 4,4-dimethylpent-1-ene (589 mg, 6 mmol, 20 equiv), MeCN (6 ml). The equipment was same as in **General procedure A**. The mixture was stirred under room temperature and 15 mA constant current electrolysis and reacted for 5 hours. The reaction mixture was concentrated under the reduced pressure. The residue was purified by flash chromatography (PE/EtOAc = 10/1) to afford methyl 4-(5,5-dimethylhexanoyl)benzoate as a colorless oil in 4% yield (3.1 mg). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 3.91 (s, 3H), 2.71 – 2.58 (m, 2H), 2.50 (t, *J* = 7.1 Hz, 2H), 1.97 – 1.84 (m, 2H), 1.12 (s, 9H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 215.7, 167.2, 147.4, 129.7, 128.5, 127.8, 52.1, 35.4, 35.1, 29.7, 26.4, 24.9. HRMS m/z (ESI) called for $C_{16}H_{23}O_3^+$ $(M + H)^+$ 263.1647, found 263.1645.

5.7. Electrochemical reduction of phenyl 4-cyanobenzoate to detect reductive products.



To a 10 mL two-necked heart-shaped flask was charged with phenyl 4-cyanobenzoate (66.9 mg, 0.3 mmol), ^{n}Bu$_4$NOAc (90.4 mg, 0.3 mmol, 1.0 equiv), H_2O (1 ml), MeCN (6 ml) and a magnetic stir bar. The equipment was same as in **General procedure A**. The mixture was stirred under room temperature and 4.5 V constant voltage electrolysis and reacted until the substrates disappear (17 h). The reaction mixture was concentrated under the reduced pressure. ^{1}H NMR spectroscopic analysis of the crude reaction mixture with mesitylene as an internal standard found 54% desired product **1e**. GC analysis of the crude reaction mixture found that phenol is another product.

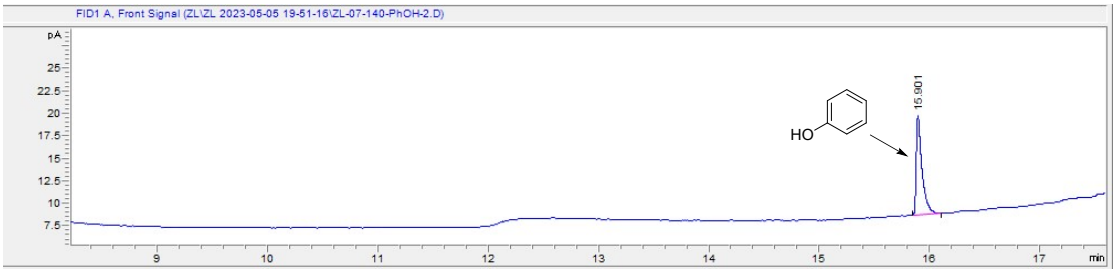


Figure S9. Standard sample of phenol

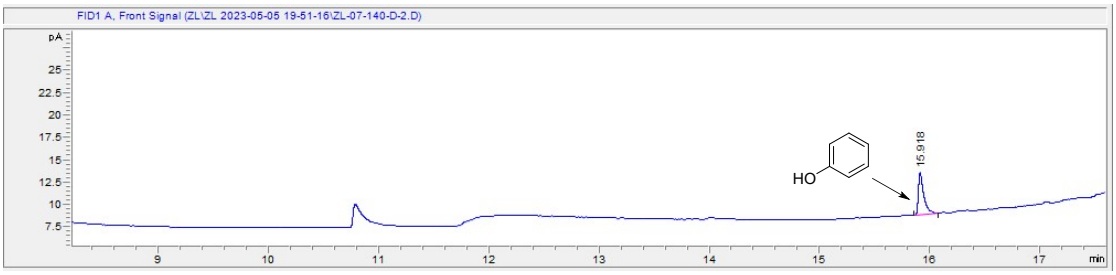
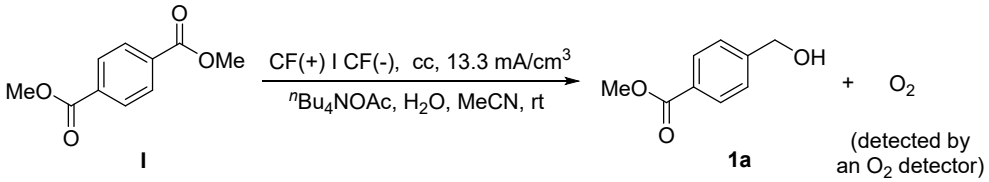


Figure S10. Sample of reaction mixture with **104** as substrate

5.8. Oxygen detection.



The experimental facility was set up as following picture (Fig. S11). To a 15 mL Schlenk bottle was charged with dimethyl terephthalate (116 mg, 0.6 mmol), $^{n}Bu_4NOAc$ (90.4 mg, 0.3 mmol, 0.5 equiv), H_2O (1.5 ml), MeCN (9 ml) and a magnetic stir bar. The bottle was equipped with a rubber stopper, through which carbon felts (1.5 cm x 2 cm x 0.5 cm) as anode and cathode were installed. Two electrodes were attached to a titanium wire and separated with a Teflon film. A Teflon wire tied around two electrodes. The whole cell was an undivided cell. Ar flow was introduced to the anode carbon felt through a long needle. The Schlenk bottle was connected with an O_2 detector (AS8901) by rubber hose. The system was flushed by Ar flow for 30 mins (make sure the Ar flow is constant) until the oxygen detector showed a steady value at about 2.5. The mixture was stirred under room temperature and 20 mA constant current electrolysis and reacted for 4.5 h. During the reaction, the electricity turned on for 1 h then turned off for 10 min, circularly. The oxygen content was detected every 10 minutes (electricity on) / 2 min (electricity off). After the reaction was complete, the mixture was concentrated under the reduced pressure. ^{1}H NMR spectroscopic analysis of the crude reaction mixture with mesitylene as an internal standard found the NMR yield was 83%.

Figure S11. The experimental facility. Left: electricity off; Right: electricity on

The oxygen content / time:

electricity	Time (min)	O_2 cont. (vol%)	electricity	Time (min)	O_2 cont. (vol%)
off	10	2.5	off	168	2.4
	20	2.5		170	2.3
	30	2.5	on	180	9.9
on	40	10.0		190	9.6
	50	11.4		200	10.1
	60	11.3		210	11.1
	70	11.2		220	10.8
	80	10.9		230	11.5
	90	10.3	off	232	6.8
off	92	2.7		234	3.6
	94	2.5		236	3.7
	96	2.5		238	3.6
	98	2.4		240	3.6
	100	2.3	on	250	9.3
on	110	10.6		260	10.7
	120	10.2		270	11.5
	130	11.0		280	11.5
	140	11.0		290	12.6
	150	11.5		300	12.5
	160	12.4	off	302	7.7
off	162	4.3		304	5.7
	164	2.8		306	4.8
	166	2.5		308	5.1

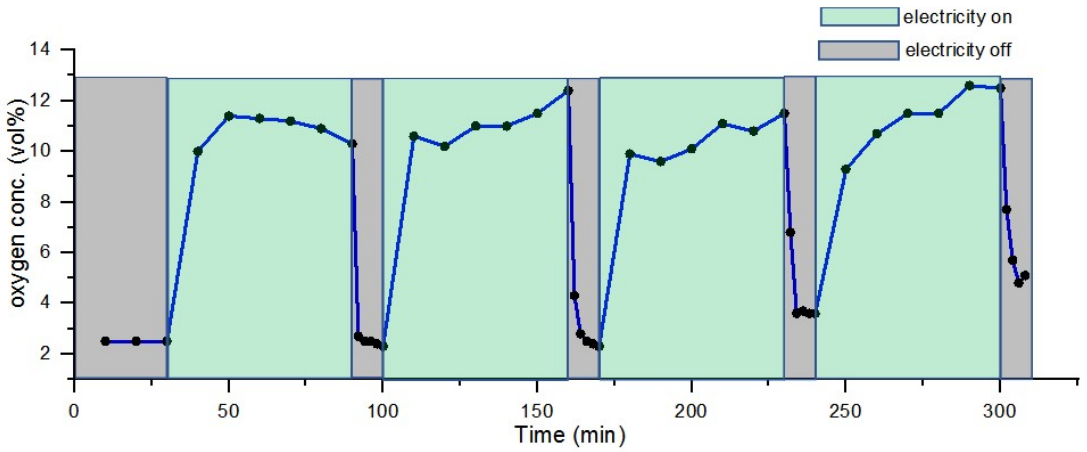


Figure S12. Oxygen detection

5.9. Observation of DMSO during the rAP reaction.

During entry 1 (Table 2), we observed the formation of DMSO.

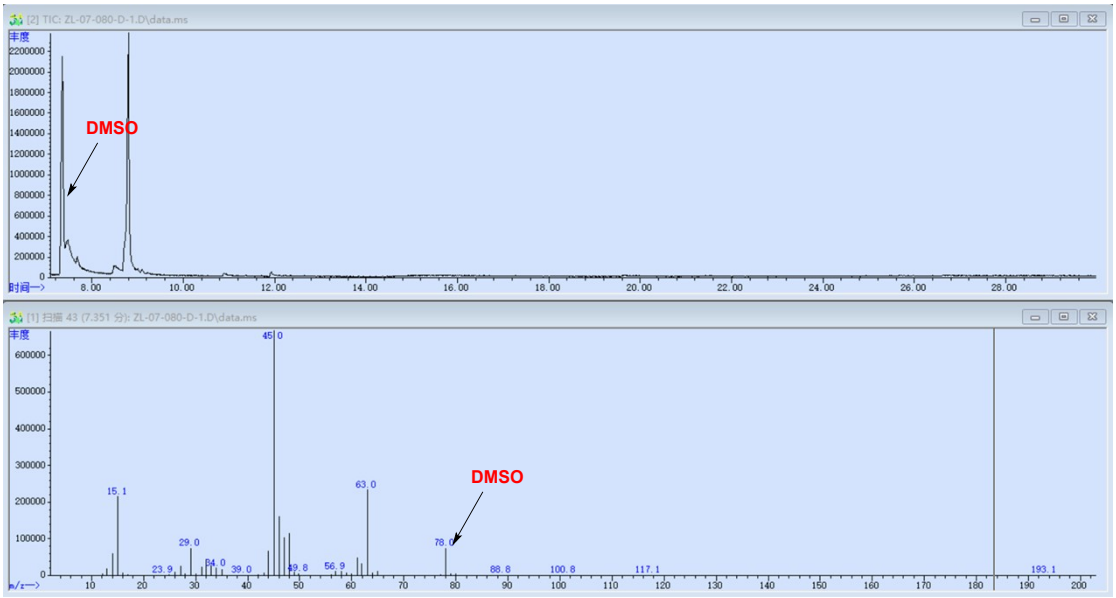
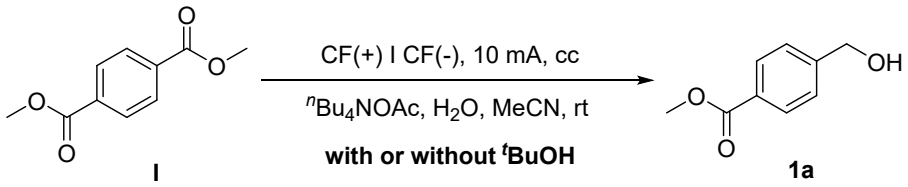


Figure S13. The GCMS spectra of entry 1 (Table 2)

5.10. Experiments for kinetic study without / with tertiary butanol (ᵗBuOH).



To two same 10 mL two-necked heart-shaped flask was charged with the dimethyl terephthalate (**I**, 0.3 mmol), $^{n}Bu_4NOAc$ (90.4 mg, 0.3 mmol, 1.0 equiv), H_2O (1 ml), MeCN (6 ml), adiponitrile (34.1 μL, 0.3 mmol, as an internal standard) and without or with 200 μL $^{t}BuOH$ (7 equiv), respectively. The equipment was same as in **General procedure A**. The mixture was stirred under room temperature and 10 mA constant current electrolysis. A 50 μL of reaction mixture was taken and analyzed by GC every 30 minutes.

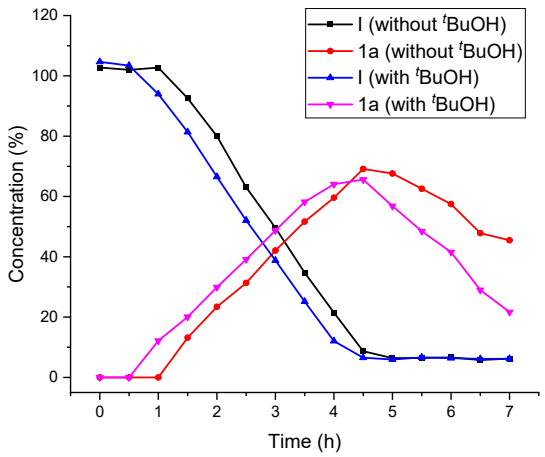
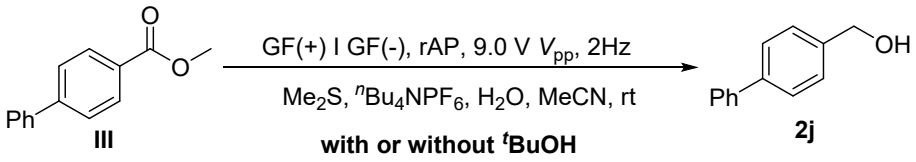


Figure S14. Experiments for kinetic study of **I** without / with tertiary butanol.



To two same 10 mL two-necked heart-shaped flask was charged with methyl 4-phenylbenzoate (**III**, 0.3 mmol), Me_2S (55.8 mg, 0.9 mmol, 3.0 equiv), $^nBu_4NPF_6$ (116.2 mg, 0.3 mmol, 1.0 equiv), H_2O (1 ml), MeCN (6 ml), adiponitrile (34.1 μL, 0.3 mmol, as an internal standard) and without / with 200 μL ^{t}BuOH (7 equiv), respectively. The equipment was same as in **General procedure B**. The mixture was stirred under room temperature and 9.0 V V_{pp} of rAP (detected by oscilloscope, set 0.9 V on signal generator, peak to peak, 0.45 V from the offset, alternating frequency: 2 Hz). A 50 μL of reaction mixture was taken and analyzed by GC every 10 minutes.

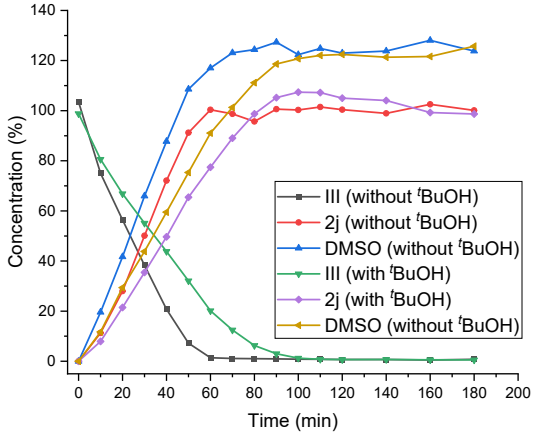
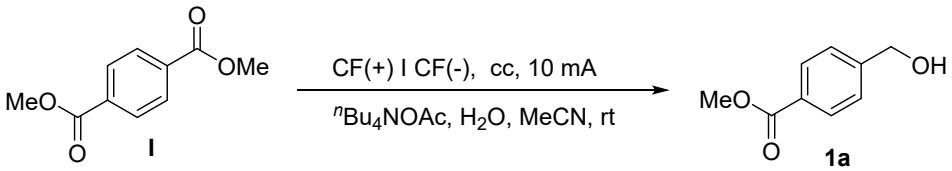


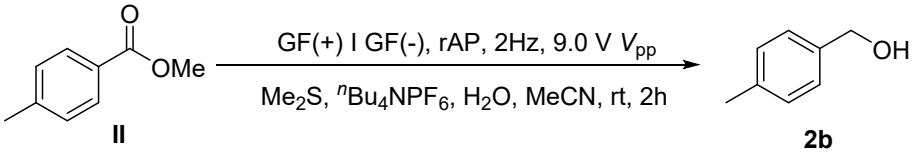
Figure S15. Experiments for kinetic study of **III** without / with tertiary butanol

5.11. Experiments with Et_3N.



		conv.	yield
Et_3N (6 eq) instead of H_2O	5 h	98%	11%
Et_3N (6 eq) + **Pivalic acid (6 eq)** instead of H_2O	8 h	100%	70%

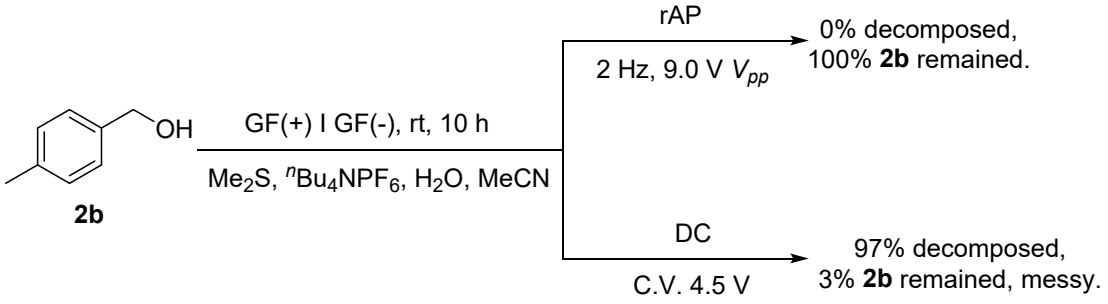
To a 10 mL two-necked heart-shaped flask was charged with the dimethyl terephthalate (**I**, 0.3 mmol), $^nBu_4NOAc$ (90.4 mg, 0.3 mmol, 1.0 equiv), Et_3N (181.8 mg, 1.8 mmol, 6.0 equiv), pivalic acid (183.8 mg, 1.8 mmol, 6.0 equiv) or not, MeCN (6 ml). The equipment was same as in **General procedure A**. The mixture was stirred under room temperature and 10 mA constant current electrolysis until the reaction were complete. The yield was measured by ^{1}H NMR analysis of crude reaction mixture with mesitylene as an internal standard.



	conv.	yield
Et_3N (6 eq) instead of Me_2S	100%	3%
Et_3N (6 eq) + **Pivalic acid (6 eq)** instead of Me_2S	100%	81%

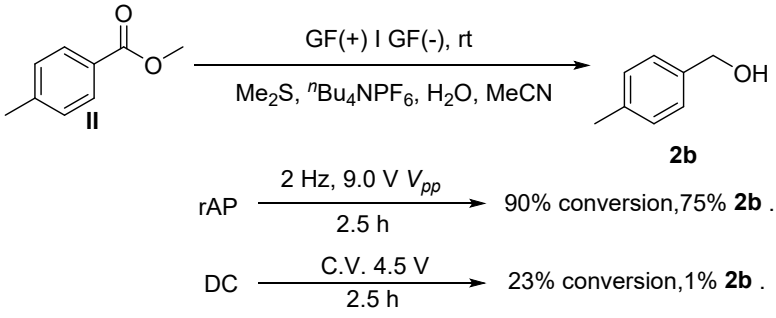
To a 10 mL two-necked heart-shaped flask was charged with methyl 4-methylbenzoate (II, 0.3 mmol), Et_3N (181.8 mg, 1.8 mmol, 6.0 equiv), pivalic acid (183.8 mg, 1.8 mmol, 6.0 equiv) or not, $^nBu_4NPF_6$ (116.2 mg, 0.3 mmol, 1.0 equiv), H_2O (1 ml), MeCN (6 ml) and a magnetic stir bar. The equipment was same as in **General procedure B**. The mixture was stirred under room temperature and 9.0 V V_{pp} of rAP (detected by oscilloscope, set 0.9 V on signal generator, peak to peak, 0.45 V from the offset, alternating frequency: 2 Hz, the current was around 60 mA), and reacted until substrates disappear (about 2 hours). The reaction mixture was concentrated under the reduced pressure. The yield was measured by ^1H NMR analysis of crude reaction mixture with mesitylene as an internal standard.

5.12. Stability experiment of 4-methylbenzyl alcohol (2b).



To a 10 mL two-necked heart-shaped flask was charged with 4-methylbenzyl alcohol (2b, 0.3 mmol), Me_2S (55.8 mg, 0.9 mmol, 3.0 equiv), $^nBu_4NPF_6$ (116.2 mg, 0.3 mmol, 1.0 equiv), H_2O (1 ml), MeCN (6 ml) and a magnetic stir bar. The equipment was same as in **General procedure B**. For DC condition, the mixture was stirred under room temperature and 4.5 V constant voltage electrolysis for 10 hours. For rAP condition, the mixture was stirred under room temperature and 9.0 V V_{pp} of rAP (detected by oscilloscope, set 0.9 V on signal generator, peak to peak, 0.45 V from the offset, alternating frequency: 2 Hz) for 10 hours. The yield was measured by ^1H NMR analysis of crude reaction mixture with mesitylene as an internal standard.

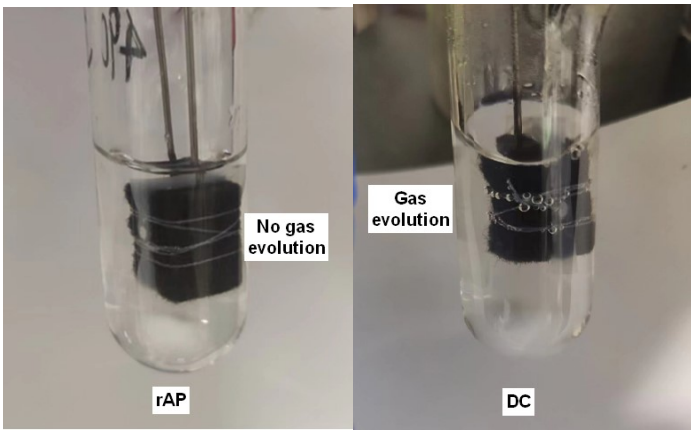
5.13. Measured the conversion of methyl 4-methylbenzoate (II) in a short time.



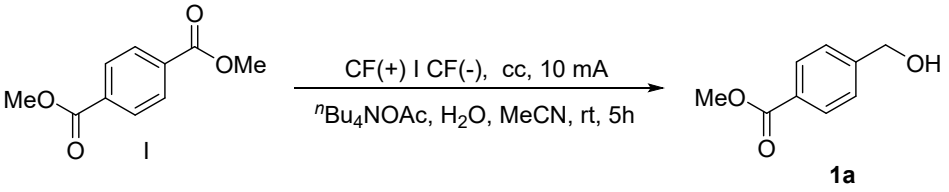
To a 10 mL two-necked heart-shaped flask was charged with methyl 4-methylbenzoate (II, 0.3 mmol), Me_2S (55.8 mg, 0.9 mmol, 3.0 equiv), $^nBu_4NPF_6$ (116.2 mg, 0.3 mmol, 1.0 equiv), H_2O (1 ml), MeCN (6 ml) and a magnetic stir bar. The equipment was same as in **General procedure B**. For DC condition, the mixture was stirred under room temperature and 4.5 V constant voltage electrolysis for 2.5 hours. For rAP condition, the mixture was stirred under room temperature and 9.0 V V_{pp} of rAP (detected by oscilloscope, set 0.9 V on signal generator, peak to peak, 0.45 V from the offset, alternating frequency: 2 Hz) for 2.5 hours. The result was measured by ^{1}H NMR analysis of crude reaction mixture with mesitylene as an internal standard.

5.14. The H_2 gas evolution reaction.

During the reactions on section 5.13, we observed a lot of H_2 gas evolution from the cathode under DC condition, while no H_2 gas evolution under rAP condition



5.15. Other Li+ salt as electrolyte with dimethyl terephthalate (I).



A. $LiClO_4$ as electrolyte, 87% SM remained, 13% **1a**.

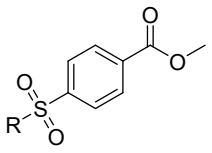
B. LiPF6(1 eq) + ^{n}Bu$_4$NOAc as electrolyte, 29% SM remained, 35% **1a**.

To a 10 mL two-necked heart-shaped flask was charged with the dimethyl terephthalate (**I**, 0.3 mmol), electrolyte (0.3 mmol, 1.0 equiv), H_2O (1 ml), MeCN (6 ml). The equipment was same as in **General procedure A**. The mixture was stirred under room temperature and 10 mA constant current electrolysis for 5 h. The yield was measured by ^{1}H NMR analysis of crude reaction mixture with mesitylene as an internal standard.

6. Unsuccessful substrates

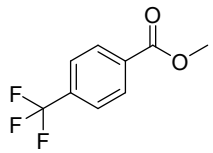
The following substrates were unsuccessful under standard reaction conditions. Yields were determined by HNMR analysis with mesitylene as an internal standard.

For DC:

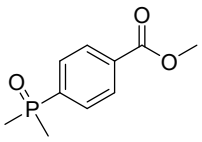


R = OPh or OMe or OEt or NHC_3H_7 or NHPh

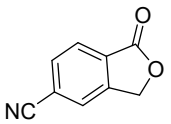
ND, major de-SO_2R



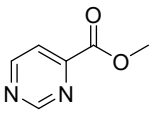
ND, major de-F



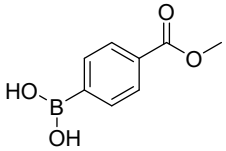
22%



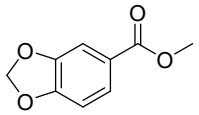
ND, major de-CN



ND, messy

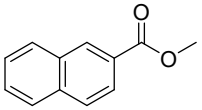


ND, messy

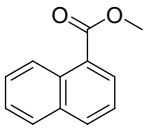


ND, messy

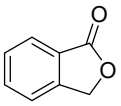
For rAP:



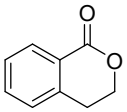
28%



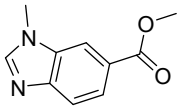
ND, messy



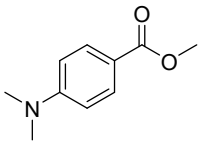
23%



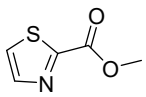
21%



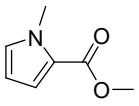
17%



ND, messy



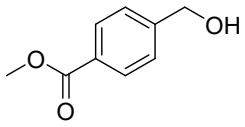
ND, messy



ND, messy

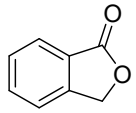
7. Analytic data of products

Methyl 4-(hydroxymethyl)benzoate (1a)[1]



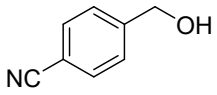
General procedure A, reacted for 5 h (6.25 F/mol), white solid. ^{1}H NMR yield 83%, isolated yield 78%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 4.76 (s, 2H), 3.91 (s, 3H), 1.93 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 167.0, 146.0, 129.9, 129.4, 126.5, 64.7, 52.1.

Isobenzofuran-1(3H)-one (1b)[2]



General procedure A, reacted for 13 h (16.25 F/mol), white solid. ^{1}H NMR yield 87%, isolated yield 75%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.93 (d, *J* = 7.6 Hz, 1H), 7.69 (td, *J* = 7.5, 1.0 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.50 (dt, *J* = 7.6, 1.0 Hz, 1H), 5.33 (s, 2H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 171.1, 146.5, 134.0, 129.0, 125.8, 122.1, 69.6.

4-(Hydroxymethyl)benzonitrile (1c/1d/1e)[1]

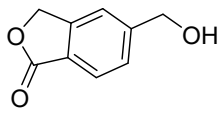


General procedure A, with methyl 4-cyanobenzoate, 3.5 V constant voltage, reacted for 8.5 h (7 F/mol), white solid. ^{1}H NMR yield 87%, isolated yield 72%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 4.77 (s, 2H), 2.05 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 146.2, 132.3, 127.0, 118.8, 111.2, 64.2.

General procedure A, with butyl 4-cyanobenzoate, reacted for 5 h (6.25 F/mol). ^{1}H NMR yield 66%.

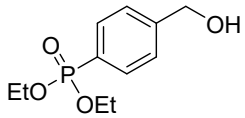
General procedure A, with phenyl 4-cyanobenzoatewith and 4.5 V constant voltage, reacted for 17 h (17.75 F/mol). ^{1}H NMR yield 54%.

5-(Hydroxymethyl)isobenzofuran-1(3H)-one (1f)[3]



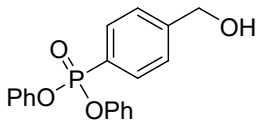
General procedure A, with 3.5 V constant voltage, reacted for 7 h (5.63 F/mol), white solid. ^{1}H NMR 72%, isolated yield 65%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.88 (d, *J* = 7.9 Hz, 1H), 7.54 (s, 1H), 7.50 (d, *J* = 7.9 Hz, 1H), 5.30 (s, 2H), 4.86 (s, 2H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 170.9, 147.9, 147.2, 127.4, 125.8, 124.9, 119.8, 69.6, 64.5.

Diethyl (4-(hydroxymethyl)phenyl)phosphonate (1g)[4]



General procedure A, with ethyl 4-(diethoxyphosphoryl)benzoate and Tol_3N (0.2 equiv), 15 mA constant current, reacted for 14 h (26.25 F/mol), colourless oil. ^{1}H NMR yield 73%, isolated yield 65%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.68 (dd, *J* = 13.2, 8.1 Hz, 2H), 7.41 (dd, *J* = 8.1, 4.0 Hz, 2H), 4.70 (s, 2H), 4.17 – 3.91 (m, 4H), 3.63 (s, 1H), 1.27 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 146.4 (d, *J* = 3.2 Hz), 131.8 (d, *J* = 10.3 Hz), 126.6 (d, *J* = 189.8 Hz), 126.5 (d, *J* = 15.4 Hz), 64.2 (d, *J* = 1.3 Hz), 62.2 (d, *J* = 5.5 Hz), 16.3 (d, *J* = 6.5 Hz). ^{31}P NMR (162 MHz, chloroform-*d*) δ 19.14.

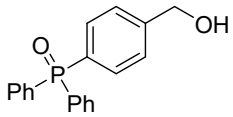
Diphenyl (4-(hydroxymethyl)phenyl)phosphonate (1h)



General procedure A, reacted for 7 h (8.75 F/mol), colourless oil. ^{1}H NMR yield 88%, isolated yield 66%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.88 (ddd, *J* = 13.8, 8.0, 1.7 Hz, 2H), 7.45 (dd, *J* = 8.0, 4.5 Hz, 2H), 7.33 – 7.25 (m, 4H), 7.24 – 7.11 (m, 6H), 4.70 (s, 2H), 3.07 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 150.3 (d,

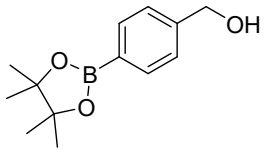
J = 7.7 Hz), 147.1 (d, *J* = 3.4 Hz), 132.4 (d, *J* = 10.9 Hz), 129.8, 126.6 (d, *J* = 16.2 Hz), 125.2 (d, *J* = 1.3 Hz), 125.2 (d, *J* = 194.7 Hz), 120.6 (d, *J* = 4.5 Hz), 64.2. ^{31}P NMR (162 MHz, chloroform-*d*) δ 11.94. HRMS m/z (ESI) called for $C_{19}H_{17}O_4PNa^+$ (M + Na) $^+$ 363.0762, found 363.0760.

(4-(hydroxymethyl)phenyl)diphenylphosphine oxide (1i)[5]



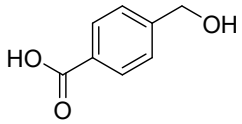
General procedure A, with Tol_3N (0.2 equiv), reacted for 6 h (7.5 F/mol), white solid. ^{1}H NMR yield 30%, isolated yield 25%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.57 (m, 4H), 7.56 – 7.47 (m, 4H), 7.48 – 7.40 (m, 4H), 7.38 (dd, *J* = 8.2, 2.7 Hz, 2H), 4.72 (s, 2H), 3.66 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.4 (d, *J* = 2.9 Hz), 132.3(d, *J* = 104.7 Hz), 132.1, 132.1 (d, *J* = 7.1 Hz), 132.0, 130.4 (d, *J* = 106.0 Hz), 128.5 (d, *J* = 11.9 Hz), 126.6 (d, *J* = 12.5 Hz), 64.12. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 29.88.

(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanol (1j)[6]



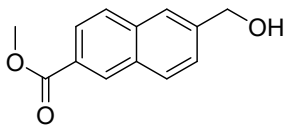
General procedure A, with Tol_3N (0.2 equiv), reacted for 16 h (20 F/mol), yellow solid. ^{1}H NMR yield 38%, isolated yield 35%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 4.73 (s, 2H), 2.07 (s, 1H), 1.37 (s, 12H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 144.0, 135.1, 126.1, 83.8, 65.2, 24.9. ^{11}B NMR (128 MHz, chloroform-*d*) δ 30.05.

4-(hydroxymethyl)benzoic acid (1k)[7]



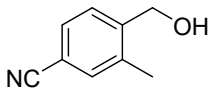
General procedure A, reacted for 9 h (11.25 F/mol), white solid. 1H NMR yield 36%, isolated yield 32%. 1H NMR (400 MHz, DMSO-d6) δ 12.83 (s, 1H), 7.91 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 5.35 (s, 1H), 4.58 (s, 2H). 13C NMR (101 MHz, DMSO-d6) δ 167.8, 148.3, 129.7, 129.6, 126.6, 62.90.

Methyl 6-(hydroxymethyl)-2-naphthoate (1l)[8]



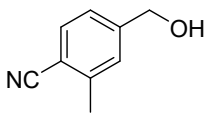
General procedure A, with Tol_3N (0.2 equiv), reacted for 8 h (10 F/mol), white solid. ^{1}H NMR yield 68%, isolated yield 54%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.57 (s, 1H), 8.04 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.92 (d, *J* = 8.6 Hz, 1H), 7.88 – 7.81 (m, 2H), 7.52 (dd, *J* = 8.4, 1.7 Hz, 1H), 4.88 (s, 2H), 3.98 (s, 3H), 2.08 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 167.3, 141.0, 135.5, 131.9, 130.9, 129.7, 128.1, 127.3, 125.8, 125.6, 125.0, 65.2, 52.3.

4-(hydroxymethyl)-3-methylbenzonitrile (1m)[9]



General procedure A, with 7.5 mA constant current, reacted for 11 h (10.3 F/mol), white solid. ^{1}H NMR yield 70%, isolated yield 57%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.57 – 7.48 (m, 2H), 7.42 (d, *J* = 1.6 Hz, 1H), 4.74 (s, 2H), 2.32 (s, 3H), 2.03 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 144.2, 136.7, 133.3, 130.0, 127.1, 119.1, 110.9, 62.5, 18.4.

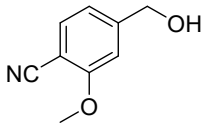
4-(hydroxymethyl)-2-methylbenzonitrile (1n)[9]



General procedure A, with 3.5 V constant voltage, reacted for 12 h (8 F/mol), colourless oil. ^{1}H NMR yield 70%, isolated yield 54%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.57 (d, *J* = 8.0 Hz, 1H), 7.33 (s, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 4.73 (s, 2H), 2.54 (s, 3H), 2.16 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 146.0, 142.2, 132.7, 128.2,

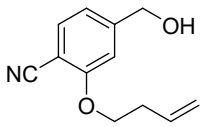
124.3, 118.2, 111.5, 64.3, 20.5.

4-(Hydroxymethyl)-2-methoxybenzonitrile (1o)[10]



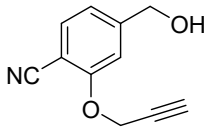
General procedure A, reacted for 5 h (6.25 F/mol), white solid. ^{1}H NMR yield 65%, isolated yield 60%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.47 (d, *J* = 7.9 Hz, 1H), 7.02 (s, 1H), 6.94 (d, *J* = 7.9 Hz, 1H), 4.73 (s, 2H), 3.91 (s, 3H), 2.52 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 161.6, 148.7, 133.7, 118.5, 116.7, 109.1, 100.2, 64.2, 56.1.

2-(But-3-en-1-yloxy)-4-(hydroxymethyl)benzonitrile (1p)



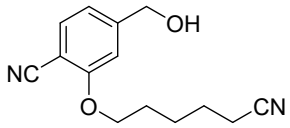
General procedure A, reacted for 5 h (6.25 F/mol), colourless oil. ^{1}H NMR yield 68%, isolated yield 56%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.48 (d, *J* = 7.8 Hz, 1H), 7.01 (d, *J* = 1.3 Hz, 1H), 6.94 (dd, *J* = 7.8, 1.3 Hz, 1H), 5.91 (ddt, *J* = 17.1, 10.2, 6.8 Hz, 1H), 5.30 – 5.02 (m, 2H), 4.73 (s, 2H), 4.11 (t, *J* = 6.7 Hz, 2H), 2.66 – 2.55 (m, 2H), 2.29 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 160.9, 148.4, 133.7, 133.6, 118.5, 117.8, 116.5, 110.0, 100.7, 68.3, 64.3, 33.3. HRMS m/z (ESI) called for $C_{12}H_{13}NO_2Na^+$ (M + Na) $^+$ 226.0844, found 226.0843.

4-(Hydroxymethyl)-2-(prop-2-yn-1-yloxy)benzonitrile (1q)



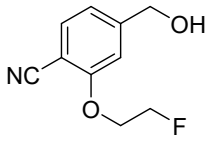
General procedure A, reacted for 5 h (6.25 F/mol), white solid. Melting point: 79 – 81 °C. ^{1}H NMR yield 53%, isolated yield 48%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.53 (d, *J* = 7.9 Hz, 1H), 7.18 (s, 1H), 7.02 (d, *J* = 7.9 Hz, 1H), 4.83 (d, *J* = 2.3 Hz, 2H), 4.76 (s, 2H), 2.57 (s, 1H), 2.19 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 159.4, 148.4, 133.9, 119.4, 116.3, 110.6, 101.1, 77.2, 76.9, 64.3, 56.5. HRMS m/z (ESI) called for $C_{11}H_9NO_2Na^+$ $(M + Na)^+$ 210.0531, found 210.0528.

2-((5-Cyanopentyl)oxy)-4-(hydroxymethyl)benzonitrile (1r)



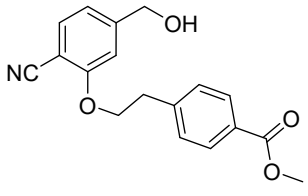
General procedure A, reacted for 5 h (6.25 F/mol), colourless oil. ^{1}H NMR yield 50%, isolated yield 45%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.48 (d, *J* = 7.8 Hz, 1H), 7.00 (s, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 4.71 (s, 2H), 4.09 (t, *J* = 6.1 Hz, 2H), 2.39 (t, *J* = 6.9 Hz, 2H), 1.93 – 1.83 (m, 2H), 1.81 – 1.72 (m, 2H), 1.73 – 1.61 (m, 2H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 160.9, 148.6, 133.7, 119.7, 118.6, 116.6, 110.0, 100.5, 68.6, 64.2, 28.1, 25.3, 25.0, 17.1. HRMS m/z (ESI) called for $C_{14}H_{16}N_2O_2Na^+$ $(M + Na)^+$ 227.1109, found 227.1108.

2-(2-Fluoroethoxy)-4-(hydroxymethyl)benzonitrile (1s)



General procedure A, reacted for 5 h (6.25 F/mol), white solid. Melting point: 87 – 89 °C. ^{1}H NMR yield 67%, isolated yield 60%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.54 (d, *J* = 7.9 Hz, 1H), 7.06 (s, 1H), 7.00 (d, *J* = 7.9 Hz, 1H), 4.95 – 4.85 (m, 1H), 4.78 – 4.74 (m, 1H), 4.76 (s, 2H), 4.45 – 4.37 (m, 1H), 4.37 – 4.29 (m, 1H), 2.03 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 160.4, 148.4, 133.9, 119.1, 116.2, 110.3, 101.1, 81.5 (d, *J* = 172.0 Hz), 68.2 (d, *J* = 21.2 Hz), 64.3. ^{19}F NMR (376 MHz, chloroform-*d*) δ –223.5. HRMS m/z (ESI) called for $C_{10}H_{10}FNO_2Na^+$ $(M + Na)^+$ 218.0593, found 218.0590.

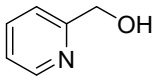
Methyl 4-(2-(2-cyano-5-(hydroxymethyl)phenoxy)ethyl)benzoate (1t)



General procedure A, reacted for 5 h (6.25 F/mol), white solid. Melting point: 117 – 119 °C. ^{1}H NMR yield 44%, isolated yield 39%. ^{1}H

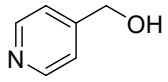
NMR (600 MHz, chloroform-*d*) δ 7.97 (d, *J* = 7.9 Hz, 2H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 7.9 Hz, 2H), 6.98(s, 1H), 6.92 (d, *J* = 7.9 Hz, 1H), 4.71(s, 2H), 4.26 (t, *J* = 6.5 Hz, 2H), 3.89(s, 3H), 3.18 (t, *J* = 6.5 Hz, 2H), 2.49(s, 1H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 167.1, 160.7, 148.6, 143.2, 133.7, 129.9, 129.4, 128.6, 118.7 116.5, 109.8, 100.5, 69.1, 64.2, 52.1, 35.6. HRMS m/z (ESI) called for $C_{18}H_{17}NO_4Na^+$ $(M + Na)^+$ 334.1055, found 334.1052.

Pyridin-2-ylmethanol (1u)[1]



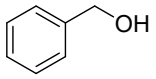
General procedure A, with 3.3 V constant voltage, reacted for 14 h (6.5 F/mol), colourless oil. ^{1}H NMR yield 47%, isolated yield 40%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.51 (d, *J* = 5.0 Hz, 1H), 7.67 (td, *J* = 7.8, 1.7 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.22 – 7.13 (m, 1H), 4.74 (s, 2H), 4.61 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 159.4, 148.4, 136.9, 122.4, 120.8, 64.3.

Pyridin-4-ylmethanol (1v)[1]



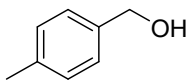
General procedure A, with 7.5 mA constant current, reacted for 16 h (15 F/mol), white solid. ^{1}H NMR yield 65%, isolated yield 51%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.44 (d, *J* = 5.1 Hz, 2H), 7.30 (d, *J* = 5.1 Hz, 2H), 4.80 (s, 1H), 4.73 (s, 2H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 151.4, 149.1, 121.3, 62.9.

Phenylmethanol (2a)[1]



General procedure B, reacted for 3.5 h, colourless oil. ^{1}H NMR yield 65%, isolated yield 63%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.44 – 7.19 (m, 5H), 4.69 (s, 2H), 1.88 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 140.9, 128.6, 127.7, 127.0, 65.4.

***p*-Tolylmethanol (2b/2c/2d)[1]**

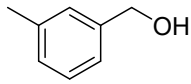


General procedure B, with methyl 4-methylbenzoat, reacted for 10 h, white solid. ^{1}H NMR yield 90%, isolated yield 86%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.26 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 4.65 (s, 2H), 2.36 (s, 3H), 1.64 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 137.9, 137.4, 129.3, 127.1, 65.3, 21.2.

General procedure B, with butyl 4-methylbenzoate, reacted for 3 h. ^{1}H NMR yield 74%.

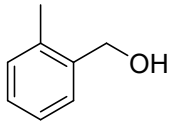
General procedure B, with phenyl 4-methylbenzoate, reacted for 22 h. ^{1}H NMR yield 66%.

***m*-Tolylmethanol (2e)[11]**



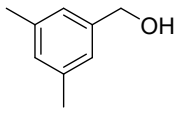
General procedure B, reacted for 3.5 h, colourless oil. ^{1}H NMR yield 79%, isolated yield 65%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.23 (d, *J* = 7.4 Hz, 1H), 7.19 – 7.05 (m, 3H), 4.63 (s, 2H), 2.35 (s, 3H), 1.86 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 140.8, 138.3, 128.5, 128.4, 127.8, 124.1, 65.4, 21.4.

***o*-Tolylmethanol (2f)[1]**



General procedure B, reacted for 3.5 h, colourless oil. ^{1}H NMR yield 78%, isolated yield 68%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.37 – 7.34 (m, 1H), 7.25 – 7.16 (m, 3H), 4.70 (s, 2H), 2.36 (s, 3H), 1.64 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 138.7, 136.1, 130.4, 127.8, 127.6, 126.1, 63.6, 18.7.

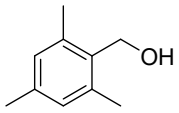
(3,5-Dimethylphenyl)methanol (2g)[12]



General procedure B, reacted for 3.5 h, colourless oil. ^{1}H NMR yield 84%, isolated yield 82%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 6.99 (s, 2H), 6.95 (s, 1H), 4.62 (s, 2H), 2.33 (s, 6H), 1.78 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 140.8, 138.2,

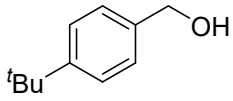
129.3, 124.9, 65.4, 21.3.

Mesitylmethanol (2h)[13]



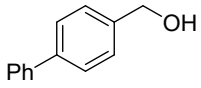
General procedure B, with trimethyl borate (0.2 equiv), reacted for 17 h, white solid. ^{1}H NMR yield 68%, isolated yield 61%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 6.88 (s, 2H), 4.71 (s, 2H), 2.40 (s, 6H), 2.28 (s, 3H), 1.29 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 137.7, 137.3, 133.7, 129.2, 59.2, 21.0, 19.4.

(4-(tert-Butyl)phenyl)methanol (2i)[13]



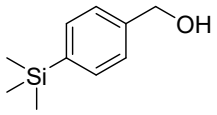
General procedure B, reacted for 9 h, colourless oil. ^{1}H NMR yield 76%, isolated yield 73%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 4.66 (s, 2H), 1.80 (s, 1H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 150.7, 138.0, 126.9, 125.5, 65.2, 34.6, 31.3.

[1, 1'-Biphenyl]-4-ylmethanol (2j)[1]



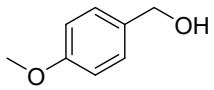
General procedure B, reacted for 9 h, white solid. ^{1}H NMR yield 91%, isolated yield 90%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.61 (d, *J* = 8.0 Hz, 4H), 7.46 (t, *J* = 7.9 Hz, 4H), 7.41 – 7.28 (m, 1H), 4.74 (s, 2H), 1.92 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 140.8, 140.7, 139.9, 128.8, 127.5, 127.4, 127.1, 65.1.

(4-(Trimethylsilyl)phenyl)methanol (2k)[14]



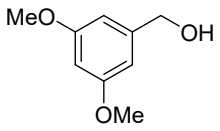
General procedure B, reacted for 3 h, colourless oil. ^{1}H NMR yield 81%, isolated yield 74%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.68 (s, 2H), 2.01 (s, 1H), 0.28 (s, 9H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 142.5, 141.0, 134.7, 127.5, 66.4, 0.0.

(4-Methoxyphenyl)methanol (2l)[1]



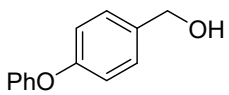
General procedure B, reacted for 10 h, colourless oil. ^{1}H NMR yield 65%, isolated yield 64%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.29 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 4.61 (s, 2H), 3.81 (s, 3H), 1.74 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 159.2, 133.1, 128.7, 114.0, 65.1, 55.3.

(3,5-dimethoxyphenyl)methanol (2m)[15]



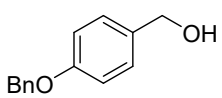
General procedure B, reacted for 3.5 h, white solid. ^{1}H NMR yield 32%, isolated yield 29%.^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.52 (d, *J* = 2.3 Hz, 2H), 6.39 (d, *J* = 2.3 Hz, 1H), 4.63 (s, 2H), 3.79 (s, 6H), 1.89 – 1.80 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 161.0, 143.4, 104.6, 99.7, 65.4, 55.4.

(4-Phenoxyphenyl)methanol (2n)[16]



General procedure B, reacted for 10 h, white solid. ^{1}H NMR yield 91%, isolated yield 84%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.38 – 7.30 (m, 4H), 7.14 – 7.09 (m, 1H), 7.04 – 6.98 (m, 4H), 4.65 (s, 2H), 2.06 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 157.2, 156.8, 135.8, 129.8, 128.7, 123.3, 119.0, 118.9, 64.9.

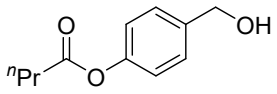
(4-(Benzyloxy)phenyl)methanol (2o)[16]



General procedure B, reacted for17 h, white solid. ^{1}H NMR yield 66%, isolated yield 59%. ^{1}H NMR (600 MHz, chloroform-*d*) δ 7.44 (d, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 2H), 6.98 (d, *J* = 8.2

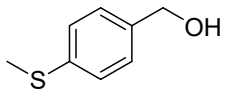
Hz, 2H), 5.08 (s, 2H), 4.61(s, 2H), 1.78(s, 1H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 158.4, 137.0, 133.4, 128.7, 128.6, 128.0, 127.5, 115.0, 70.1, 65.0.

4-(Hydroxymethyl)phenyl butyrate (2p)[17]



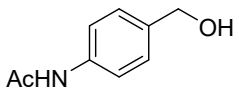
General procedure B, reacted for 3 h, colourless oil. ^{1}H NMR yield 72%, isolated yield 69%. ^{1}H NMR (600 MHz, chloroform-*d*) δ 7.34 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 8.2 Hz, 2H), 4.63(s, 2H), 2.53 (t, *J* = 7.4 Hz, 2H), 2.14(s, 1H), 1.78 (q, *J* = 7.4 Hz, 2H), 1.04 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 172.4, 150.1, 138.5, 128.1, 121.7, 64.7, 36.2, 18.5, 13.7.

(4-(Methylthio)phenyl)methanol (2q)[11]



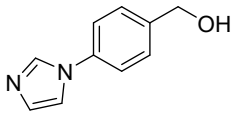
General procedure B, reacted for 3 h, colourless oil. ^{1}H NMR yield 62%, isolated yield 54%. ^{1}H NMR (600 MHz, chloroform-*d*) δ 7.26 (q, *J* = 8.0 Hz, 4H), 4.63(s, 2H), 2.48(s, 3H), 1.86(s, 1H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 137.8, 137.8, 127.7, 126.8, 64.9, 16.0.

N-(4-(Hydroxymethyl)phenyl)acetamide (2r)[18]



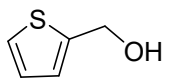
General procedure B, reacted for 10 h, white solid. ^{1}H NMR yield 56%, isolated yield 51%. ^{1}H NMR (600 MHz, methanol-d_4) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 4.57(s, 2H), 2.13(s, 3H). ^{13}C NMR (151 MHz, methanol-d_4) δ 170.2, 137.7, 137.1, 127.2, 119.7, 63.5, 22.4.

(4-(1H-Imidazol-1-yl)phenyl)methanol (2s)[19]



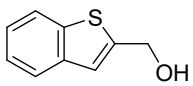
General procedure B, reacted for 10 h, white solid. ^{1}H NMR yield 44%, isolated yield 38%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.76 (t, *J* = 1.2 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.26 (s, 1H), 7.17 (t, *J* = 1.2 Hz, 1H), 4.76 (s, 2H), 3.12 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 140.2, 136.4, 135.6, 130.2, 128.4, 121.5, 118.3, 64.2.

Thiophen-2-ylmethanol (2t)[1]



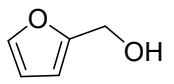
General procedure B, with trimethyl borate (0.2 equiv) and 8.0 V V_{pp} of rAP, reacted for 5 h, yellow oil. ^{1}H NMR yield 42%, isolated yield 36%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.45 – 7.20 (m, 1H), 7.05 – 6.95 (m, 2H), 4.83 (s, 2H), 1.95 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 144.0, 126.9, 125.6, 125.5, 60.0.

Benzo[b]thiophen-2-ylmethanol (2u)[19]



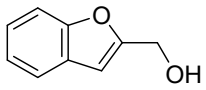
General procedure B, reacted for 3 h, white solid. ^{1}H NMR yield 40%, isolated yield 39%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.82 (d, *J* = 7.2 Hz, 1H), 7.73 (dd, *J* = 7.2, 1.9 Hz, 1H), 7.33 (pd, *J* = 7.2, 1.4 Hz, 2H), 7.21 (s, 1H), 4.92 (s, 2H), 2.10 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 144.8, 134.0, 139.6, 124.4, 124.3, 123.6, 122.5, 121.5, 60.9.

Furan-2-ylmethanol (2v)[1]



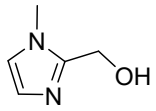
General procedure B, reacted for 3 h, colourless oil. ^{1}H NMR yield 28%, isolated yield 25%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.40 (dd, *J* = 1.8, 0.8 Hz, 1H), 6.34 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.29 (dd, *J* = 3.2, 0.8 Hz, 1H), 4.59 (s, 2H), 2.12 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 154.0, 142.6, 110.4, 107.8, 57.3.

Benzofuran-2-ylmethanol (2w)[20]



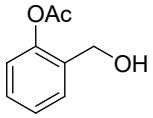
General procedure B, reacted for 3 h, colourless oil. ^{1}H NMR yield 40%, isolated yield 34%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.54 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.30 – 7.16 (m, 2H), 6.64 (s, 1H), 4.76 (s, 2H), 2.14 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 156.4, 155.1, 128.2, 124.4, 122.9, 121.2, 111.3, 104.2, 58.2.

(1-Methyl-1H-imidazol-2-yl)methanol (2x)[21]



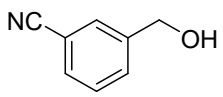
General procedure B, reacted for 3.5 h, white solid. ^{1}H NMR yield 70%, isolated yield 60%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 6.81 (d, *J* = 1.3 Hz, 1H), 6.77 (d, *J* = 1.3 Hz, 1H), 6.44 (s, 1H), 4.59 (s, 2H), 3.70 (s, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 148.2, 126.4, 121.4, 55.4, 32.8.

2-(hydroxymethyl)phenyl acetate (2y)[22]



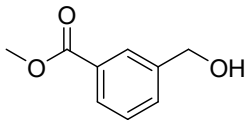
General procedure B, with alternating frequency: 10 Hz, reacted for 10 h, yellow oil. ^{1}H NMR yield 45%, isolated yield 41%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.79 (s, 1H), 7.26 (d, *J* = 7.6 Hz, 2H), 7.01 – 6.84 (m, 2H), 5.12 (s, 2H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 173.7, 155.5, 132.2, 131.2, 121.7, 120.6, 117.8, 63.3, 21.0.

3-(Hydroxymethyl)benzonitrile (2aa)[13]



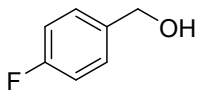
General procedure B, reacted for 17 h, colourless oil. ^{1}H NMR yield 55%, isolated yield 54%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.66 (d, *J* = 1.7 Hz, 1H), 7.63 – 7.54 (m, 2H), 7.46 (t, *J* = 7.7 Hz, 1H), 4.73 (s, 2H), 2.23 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 142.3, 131.2, 131.1, 130.2, 129.3, 118.8, 112.5, 64.0.

Methyl 3-(hydroxymethyl)benzoate (2ab)[23]



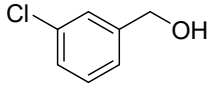
General procedure B, reacted for 10 h, white solid. ^{1}H NMR yield 54%, isolated yield 51%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.03 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 4.75 (s, 2H), 3.91 (s, 3H), 1.98 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 167.0, 141.2, 131.4, 130.4, 128.8, 128.7, 128.0, 64.8, 52.2.

(4-Fluorophenyl)methanol (2ac)[1]



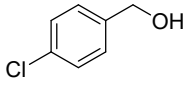
General procedure B, reacted for 9 h, colourless oil. ^{1}H NMR yield 67%, isolated yield 52%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.27 (dd, *J* = 8.7, 5.6 Hz, 2H), 7.01 (t, *J* = 8.7 Hz, 2H), 4.57 (s, 2H), 2.58 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 162.3 (d, *J* = 245.2 Hz), 136.6 (d, *J* = 3.1 Hz), 128.8 (d, *J* = 8.1 Hz), 115.3 (d, *J* = 21.5 Hz), 64.4. ^{19}F NMR (376 MHz, chloroform-*d*) δ –114.9.

(3-Chlorophenyl)methanol (2ad)[24]



General procedure B and 8.0 V V_{pp} of rAP, reacted for 9 h, colourless oil. ^{1}H NMR yield 82%, isolated yield 70%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.33 (s, 1H), 7.28 – 7.22 (m, 2H), 7.22 – 7.15 (m, 1H), 4.63 (s, 2H), 2.14 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 142.8, 134.4, 129.8, 127.7, 127.0, 124.9, 64.5.

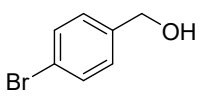
(4-Chlorophenyl)methanol (2ae)[1]



General procedure B, reacted for 6 h, white solid. ^{1}H NMR yield 66%, isolated yield 60%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.26 – 7.17 (m, 4H), 4.58 (s, 2H),

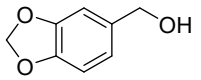
1.74 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 139.3, 133.4, 128.7, 128.3, 64.6.

(4-Bromophenyl)methanol (2af)[1]



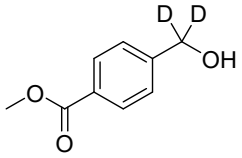
General procedure B, and 8.0 V V_{pp} of rAP, reacted for 7 h, white solid. ^{1}H NMR yield 34%, isolated yield 34%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 4.63 (s, 2H), 1.98 (s, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 139.8, 131.6, 128.6, 121.5, 64.6.

Benzo[d][1,3]dioxol-5-ylmethanoll (2ag)[25]



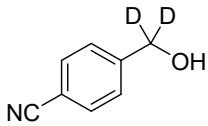
General procedure B, reacted for 7 h, white solid. ^{1}H NMR yield 30%, isolated yield 29%. ^{1}H NMR (400 MHz, chloroform-*d*) δ 6.87 (s, 1H), 6.84 – 6.75 (m, 2H), 5.95 (s, 2H), 4.57 (d, *J* = 5.8 Hz, 2H), 1.72 (t, *J* = 5.8 Hz, 1H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 147.8, 147.1, 134.9, 120.5, 108.3, 107.9, 101.0, 65.3.

Methyl 4-(hydroxymethyl-*d*$_2$)benzoate (3a)



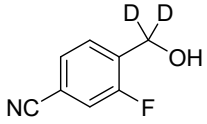
General procedure C, reacted for 4 h (5 F/mol), white solid. Melting point: 51 – 53 °C. Isolated yield 60% (95% D). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 3H), 2.43 (s, 1H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 167.1, 146.0, 129.8, 129.2, 126.5, 64.6 – 63.4 (m), 52.2. HRMS m/z (ESI) called for $C_9H_8D_2O_3Na^+$ $(M + Na)^+$ 191.0653, found 191.0650.

4-(Hydroxymethyl-*d*$_2$)benzonitrile (3b)[26]



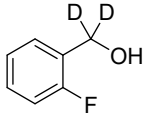
General procedure C, with 3.5 V constant voltage, reacted for 5 h (5.75 F/mol), colourless oil. Isolated yield 58% (96% D). ^{1}H NMR (600 MHz, chloroform-*d*) δ 7.64 (d, *J* = 7.9 Hz, 2H), 7.48 (d, *J* = 7.9 Hz, 2H), 2.30 (s, 1H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 146.2, 132.3, 127.1 (d, *J* = 2.7 Hz), 118.9, 111.1, 64.8 – 62.4 (m).

3-Fluoro-4-(hydroxymethyl- *d*$_2$)benzonitrile (3c)[28]



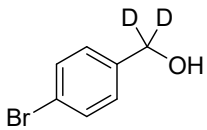
General procedure C, reacted for 4 h (5 F/mol), colourless oil. Isolated yield 70% (97% D). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.64 (t, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 9.4 Hz, 1H), 2.44 (s, 1H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 159.5 (d, *J* = 249.8 Hz), 133.9 (d, *J* = 14.6 Hz), 129.6 (d, *J* = 5.3 Hz), 128.5 (d, *J* = 3.9 Hz), 118.8 (d, *J* = 24.5 Hz), 117.7, 112.4 (d, *J* = 9.5 Hz), 58.5 – 57.1 (m). ^{19}F NMR (376 MHz, chloroform-*d*) δ –116.4.

(2-Fluorophenyl)methan-*d*$_2$-ol (3d)[28]



General procedure D, with 8.0 V V_{pp} of rAP, reacted for 3 h, colourless oil. Isolated yield 70% (97% D). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.42 (td, *J* = 7.5, 1.8 Hz, 1H), 7.34 – 7.23 (m, 1H), 7.15 (td, *J* = 7.5, 1.2 Hz, 1H), 7.05 (ddd, *J* = 10.2, 8.2, 1.2 Hz, 1H), 1.85 (s, 1H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 160.7 (d, *J* = 246.2 Hz), 129.4 (d, *J* = 15.9 Hz), 129.4 (d, *J* =1.5 Hz), 127.7 (d, *J* = 14.7 Hz), 124.3 (d, *J* = 3.8 Hz), 115.3 (d, *J* = 21.2 Hz), 59.9 – 57.7 (m). ^{19}F NMR (376 MHz, chloroform-*d*) δ –119.9.

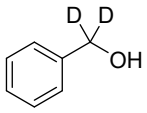
(4-Bromophenyl)methan- *d*$_2$-ol (3e)[29]



General procedure D, reacted for 4.5 h, white solid. Isolated yield 28% (97% D). ^{1}H NMR (600 MHz, chloroform-*d*) δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 1.75 (s, 1H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 139.7, 131.7, 128.7, 121.5,

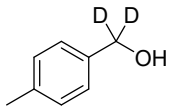
65.0 – 62.8 (m).

Phenylmethan-d_2-ol (3f)[28]



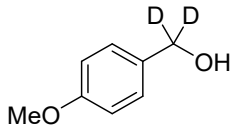
General procedure D, with 8.0 V V_{pp} of rAP, reacted for 3.5 h, colourless oil. Isolated yield 51% (95% D). ^{1}H NMR (600 MHz, chloroform-*d*) δ 7.52 – 7.03 (m, 5H), 2.63(s, 1H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 140.8, 128.6, 127.6, 127.1, 65.1 – 63.9 (m).

***p*-Tolylmethan-d_2-ol (3g)[28]**



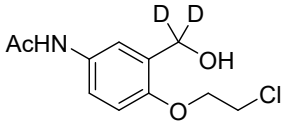
General procedure D, reacted for 10 h, white solid. Isolated yield 65% (95% D). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.26 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 2.36 (s, 3H), 1.62 (s, 1H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 137.8, 137.5, 129.3, 127.2, 65.0 – 64.5 (m), 21.2.

(4-Methoxyphenyl)methan- d_2-ol (3h)[28]



General procedure D, reacted for 4 h, colourless oil. Isolated yield 88% (92% D). ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.27 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H), 1.91 (s, 1H). ^{13}C NMR (151 MHz, chloroform-*d*) δ 159.2, 133.1, 128.7, 114.0, 66.4 – 63.4 (m), 55.3.

N-(4-(2-chloroethoxy)-3-(hydroxymethyl-d_2)phenyl)acetamide (3i)



General procedure D, with $LiClO_4$ as electrolyte, reacted for 8 h, yellow oil. Isolated yield 35% (96% D). ^{1}H NMR (600 MHz, methanol-d_4) δ 7.52 (d, *J* = 2.7 Hz, 1H), 7.45 (dd, *J* = 8.5, 2.7 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 4.24 (t, *J* = 5.4 Hz, 2H), 3.86 (t, *J* = 5.4 Hz, 2H), 2.10 (s, 3H). ^{13}C NMR (151 MHz, methanol-d_4) δ 170.1, 152.2, 132.0, 130.3, 120.4, 120.2, 111.6, 68.65, 58.0 – 58.2 (m), 42.1, 22.2.

8. References

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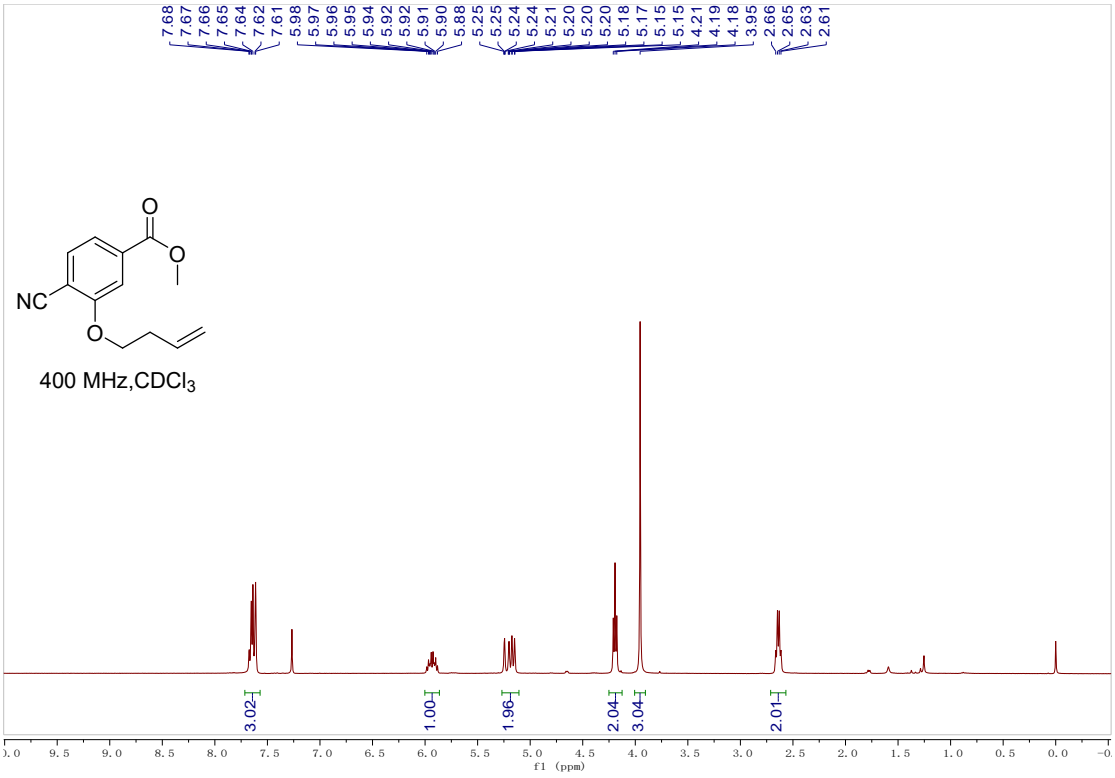
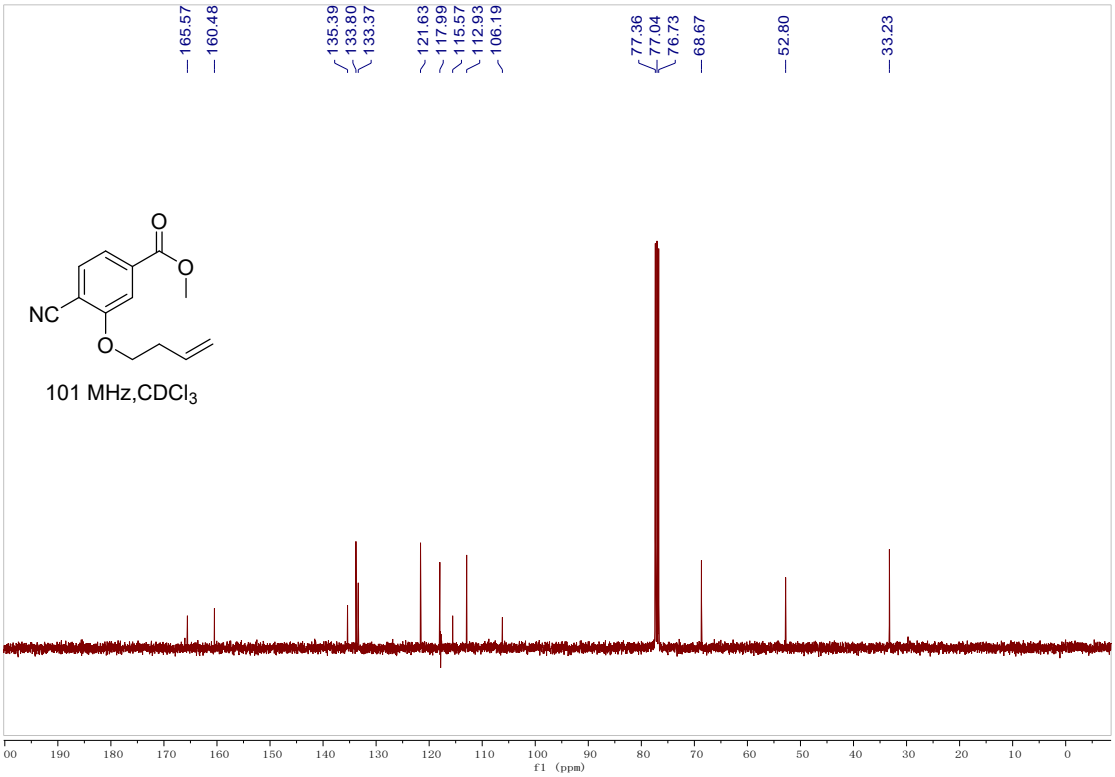
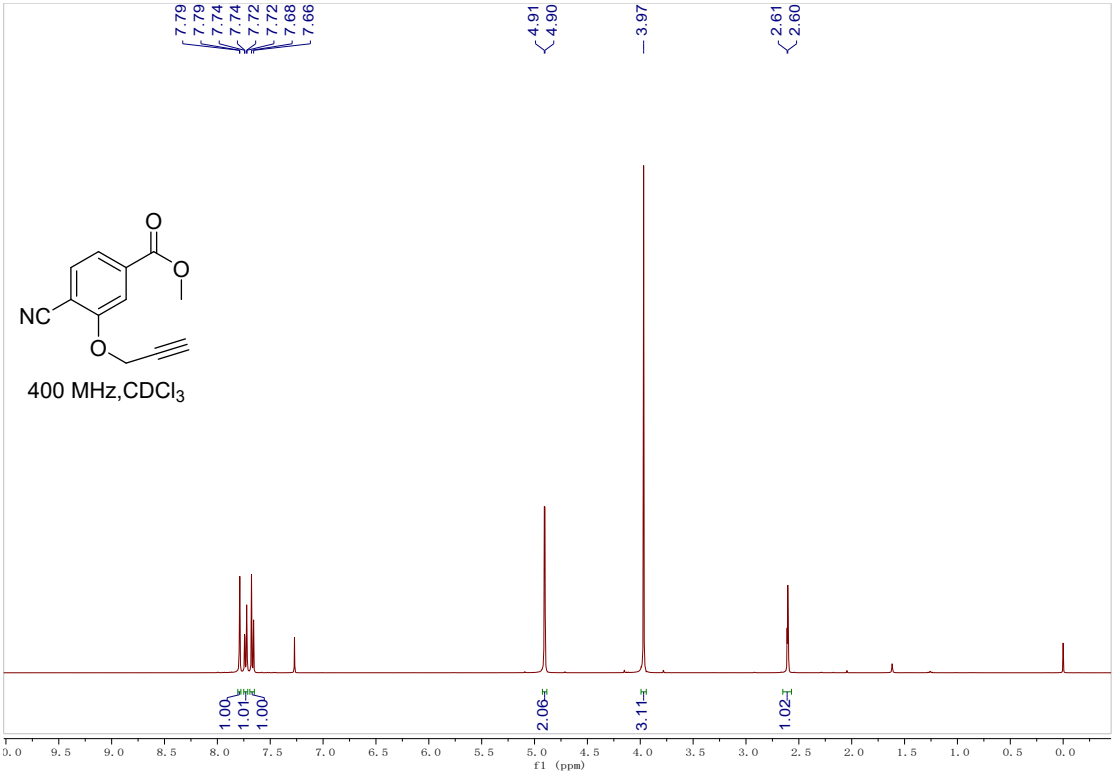
9. NMR spectra for new substrates and intermediates

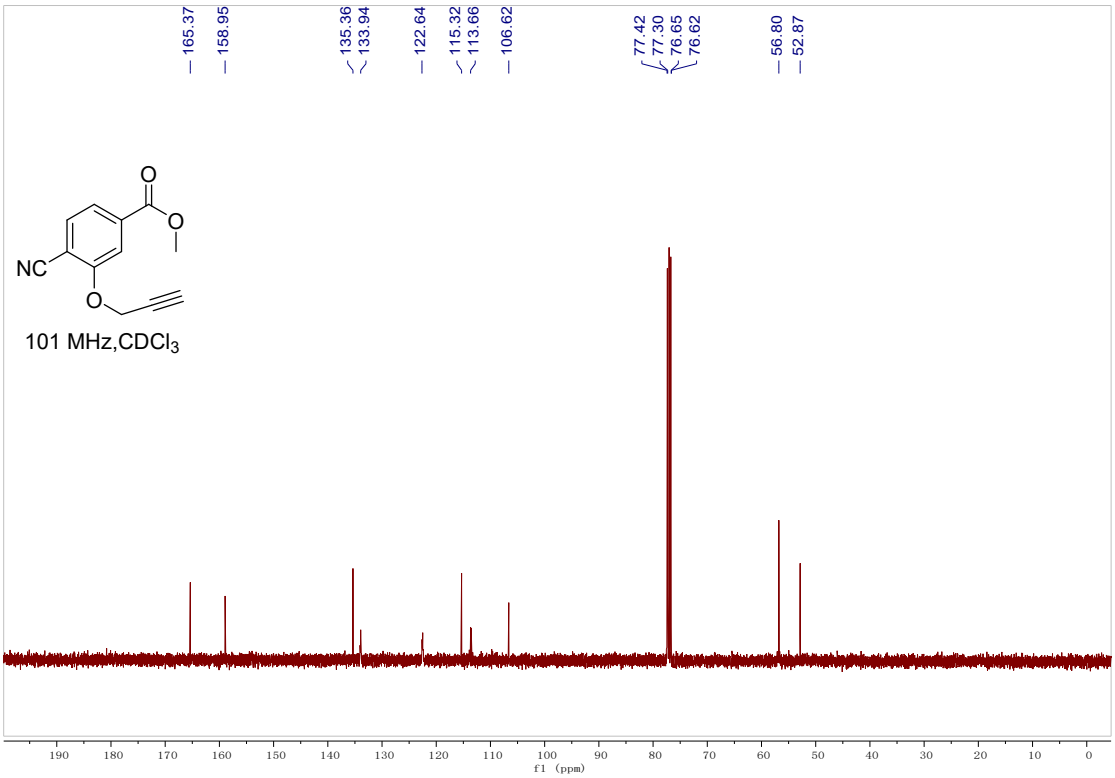
Methyl 3-(but-3-en-1-yloxy)-4-cyanobenzoate





Methyl 4-cyano-3-(prop-2-yn-1-yloxy)benzoate





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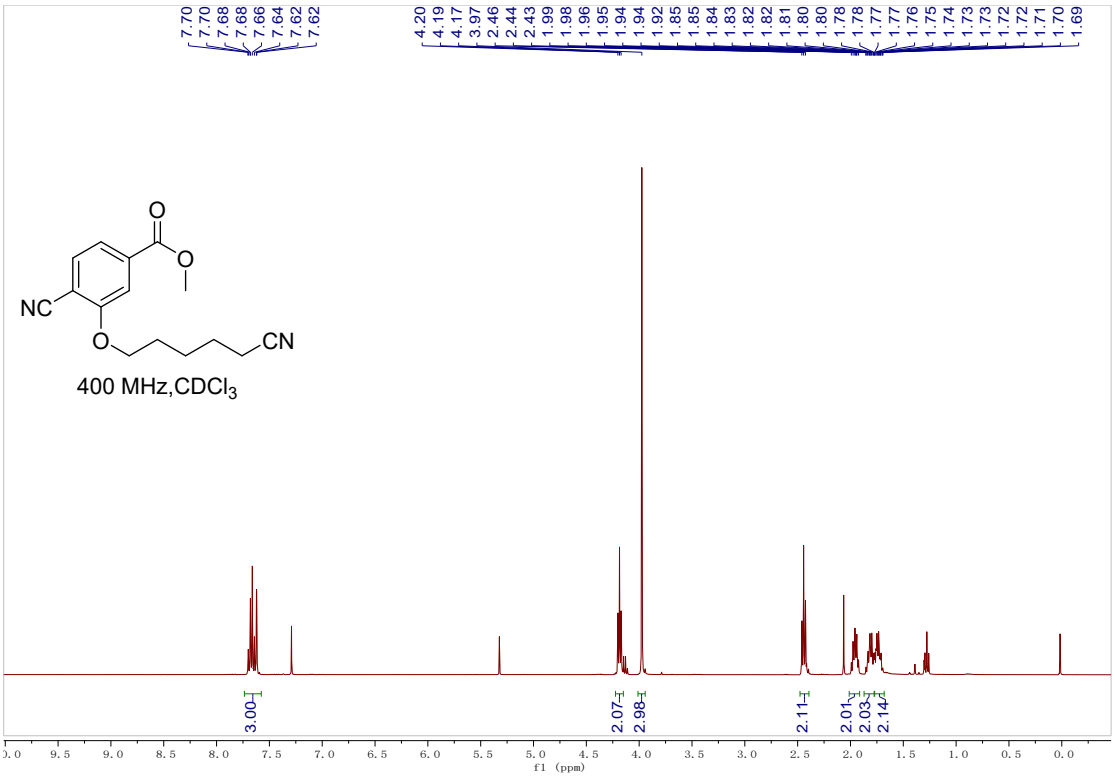

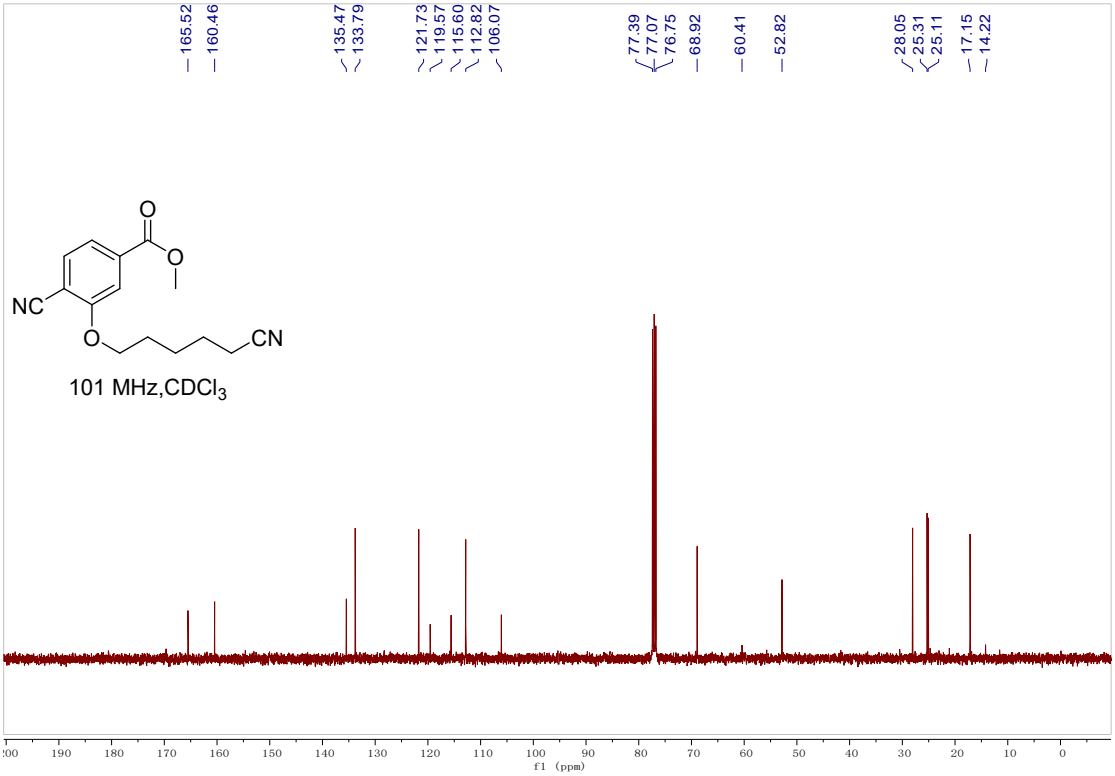

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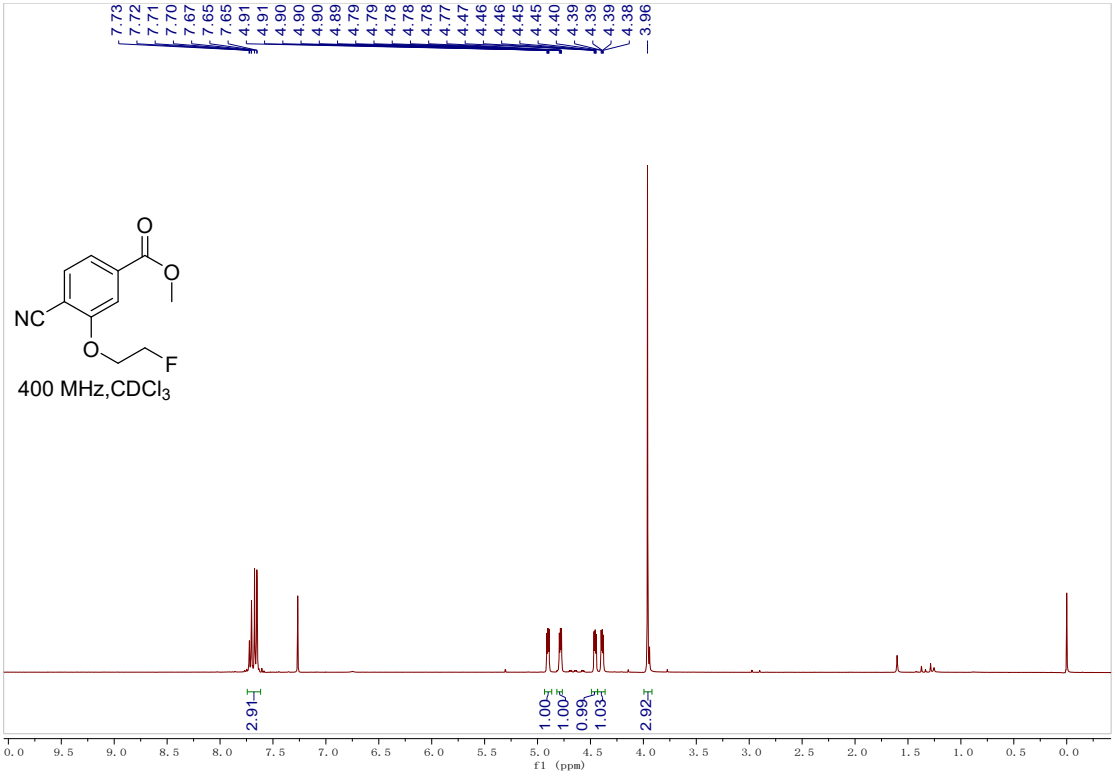
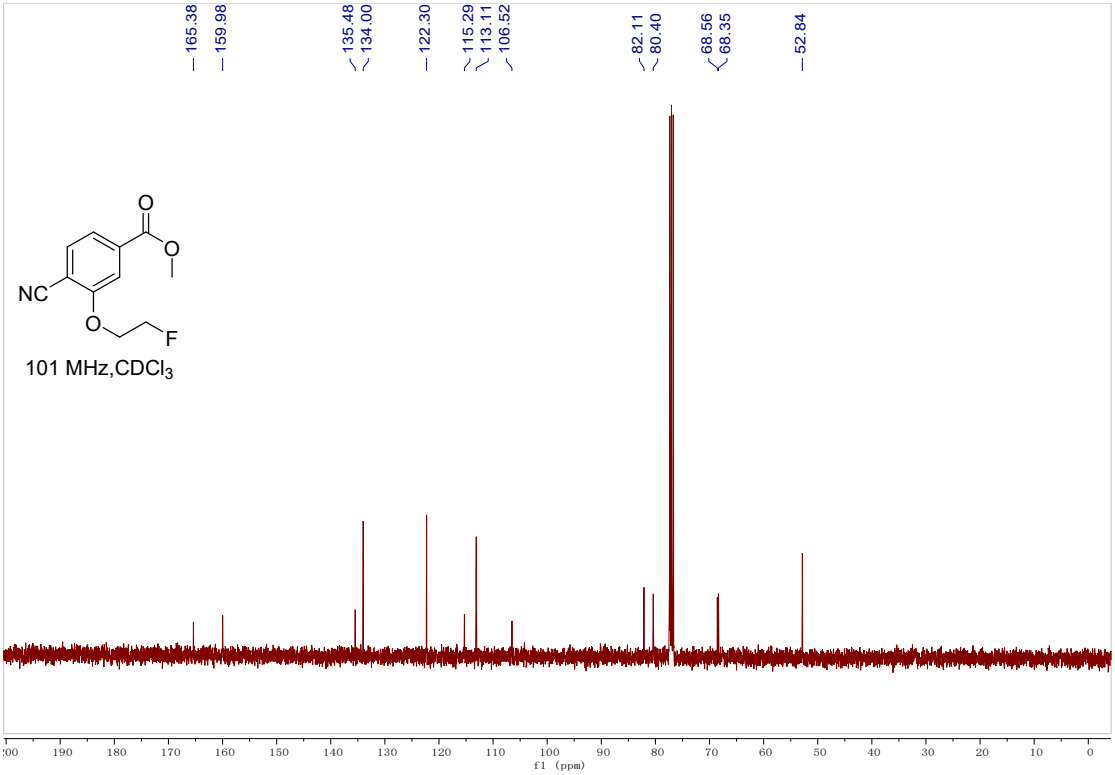
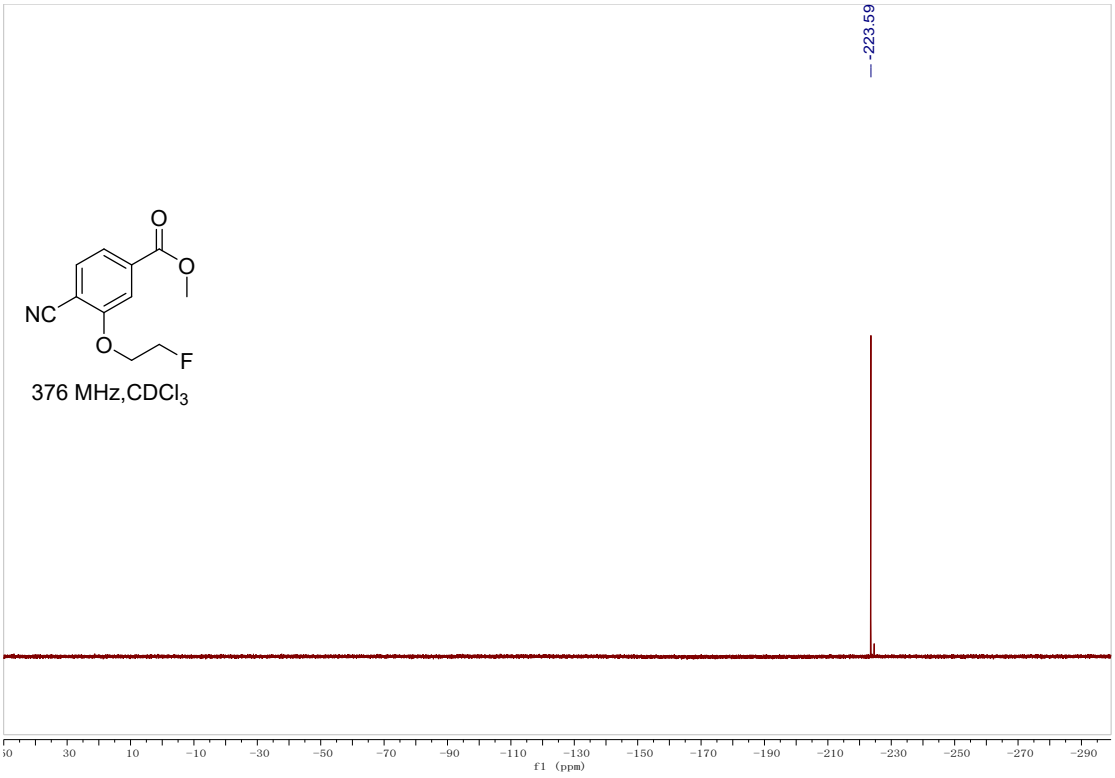
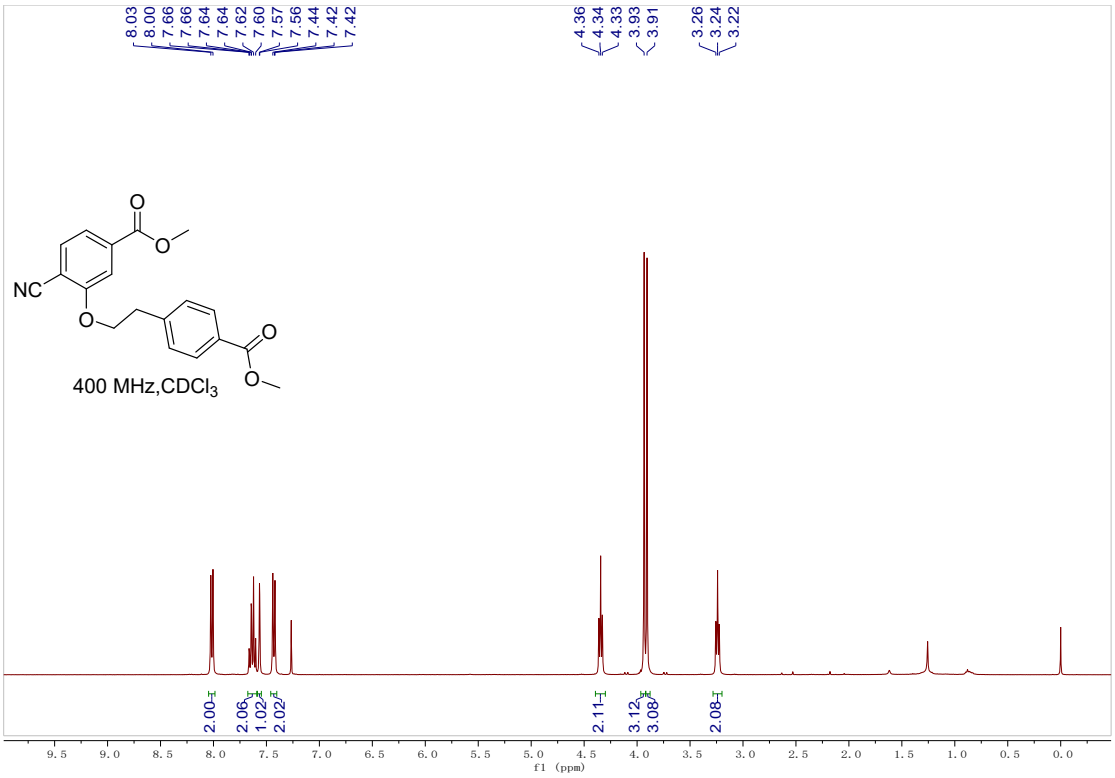
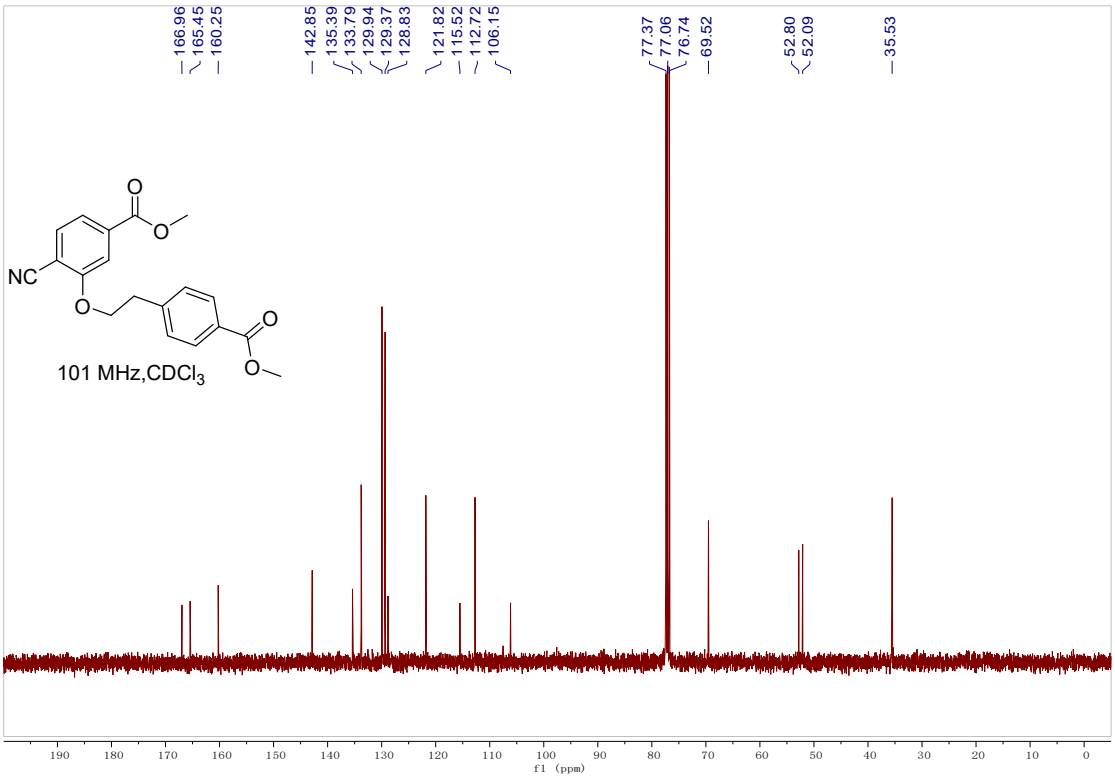




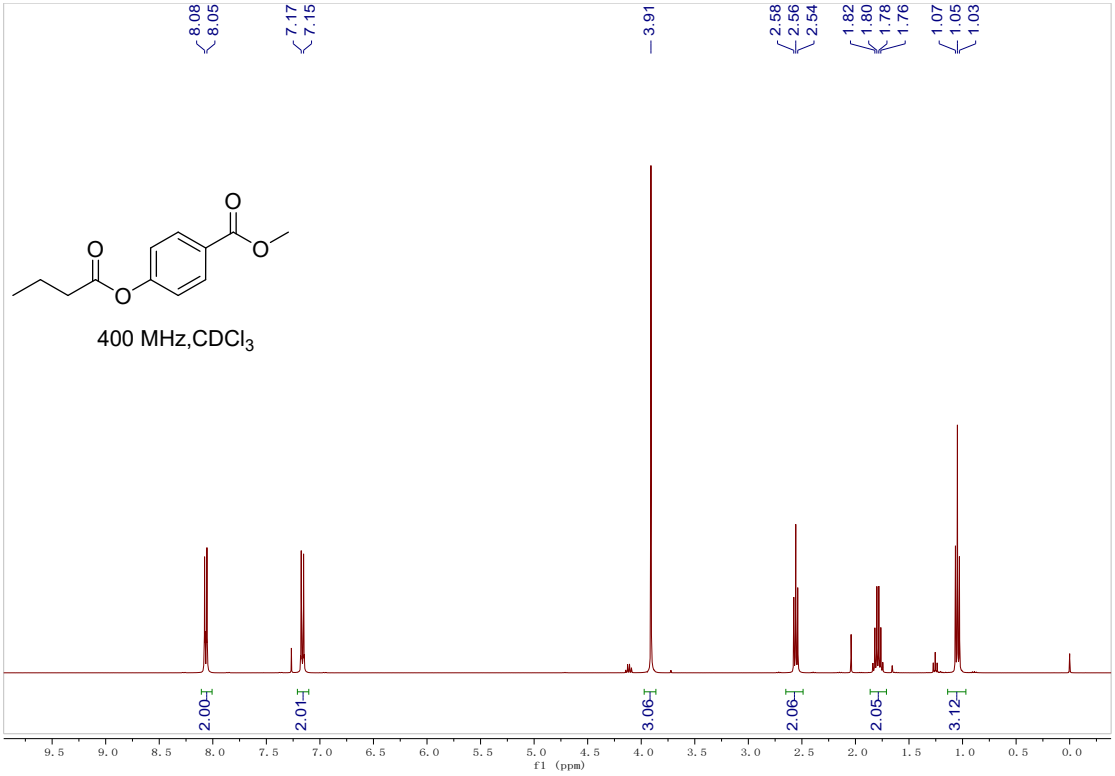

-223.59
O
O
NC
O
F
376 MHz,CDCl3
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

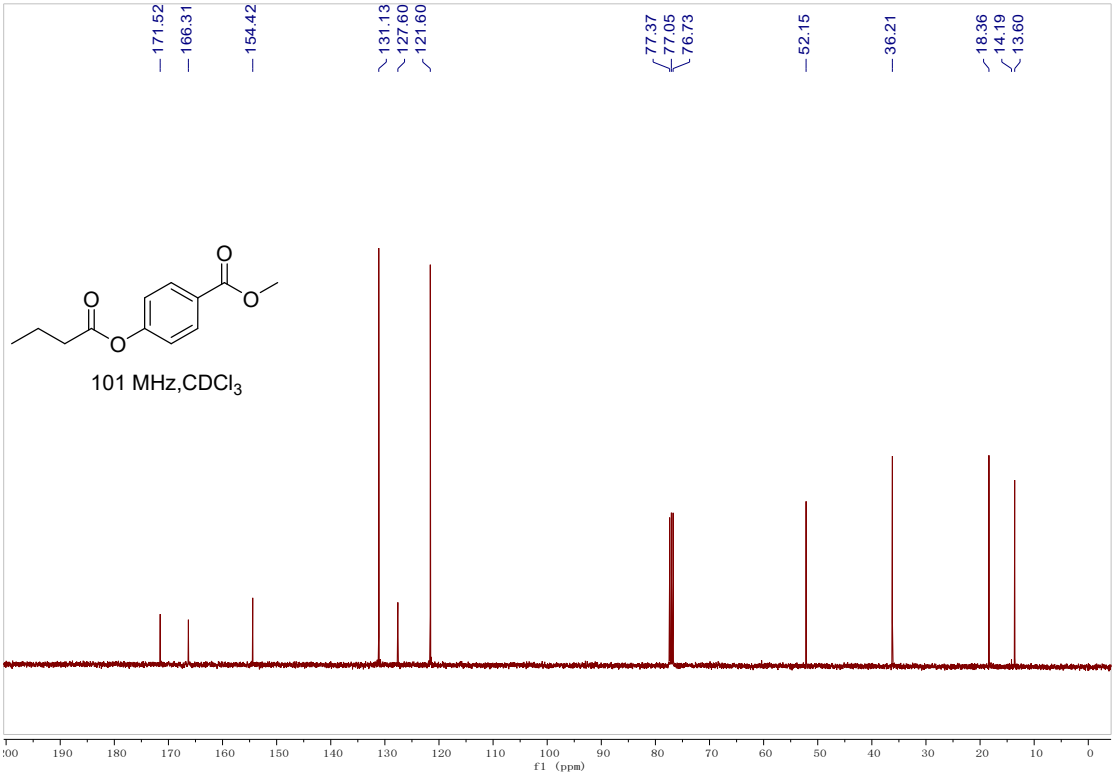
Methyl 4-cyano-3-(4-(methoxycarbonyl)phenethoxy)benzoate





Methyl 4-(butyryloxy)benzoate





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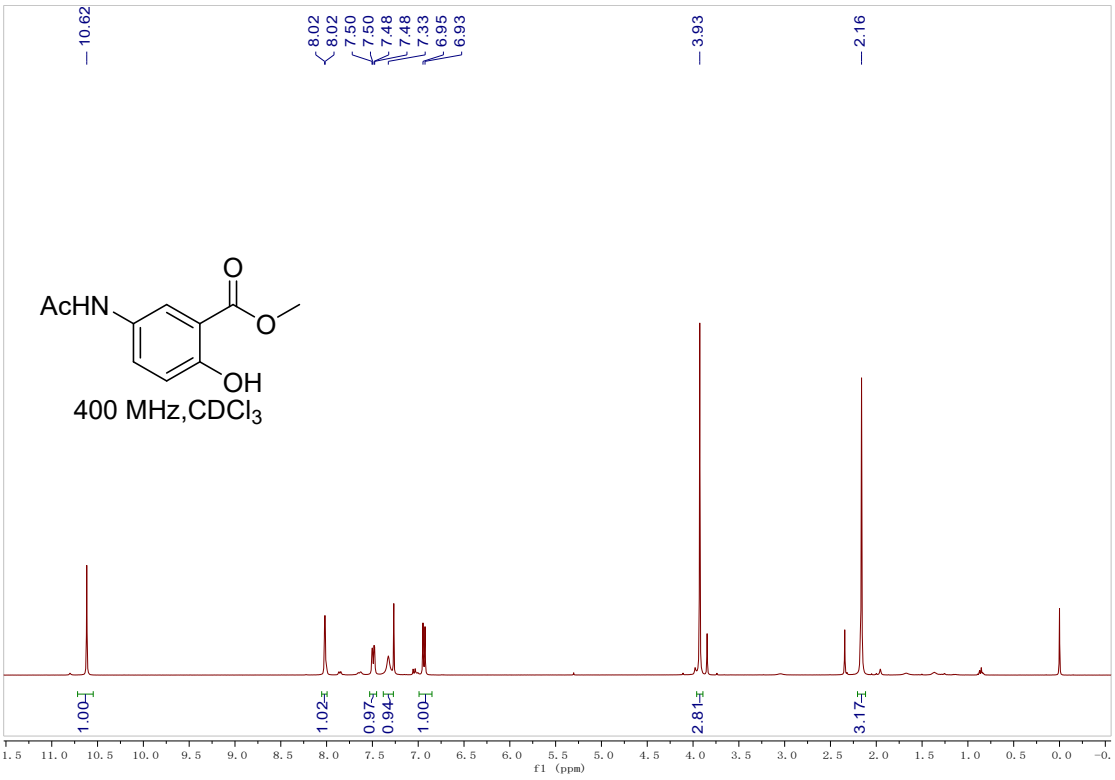

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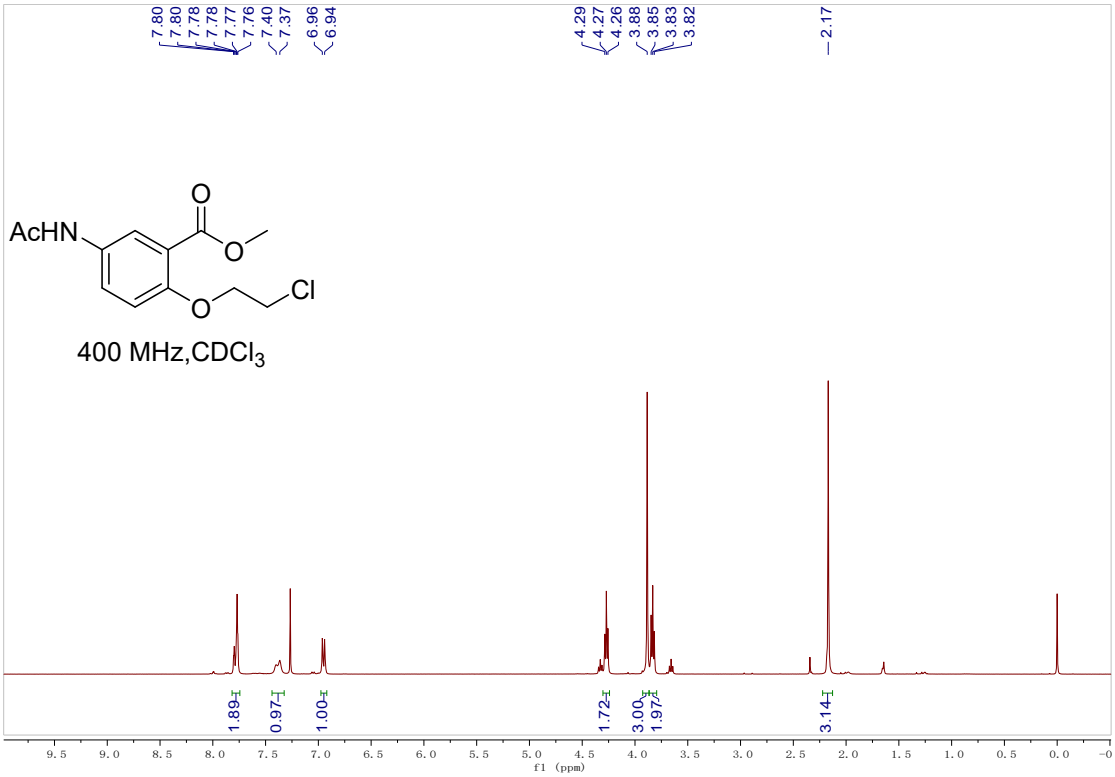
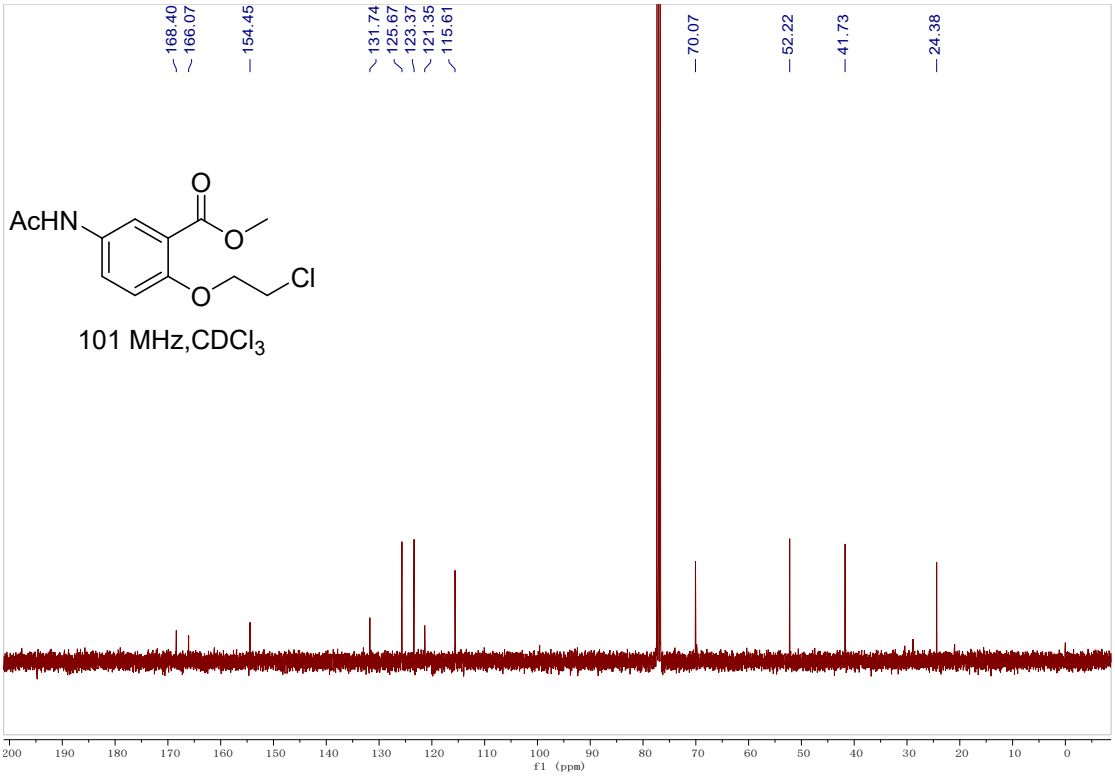
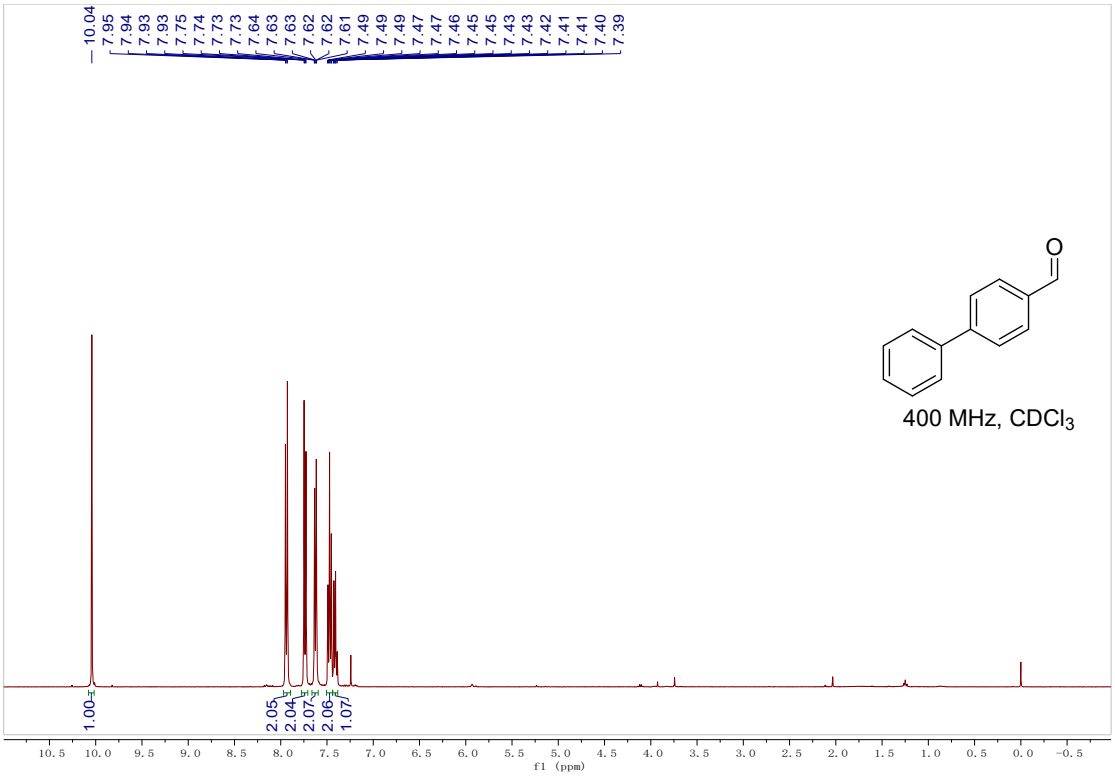
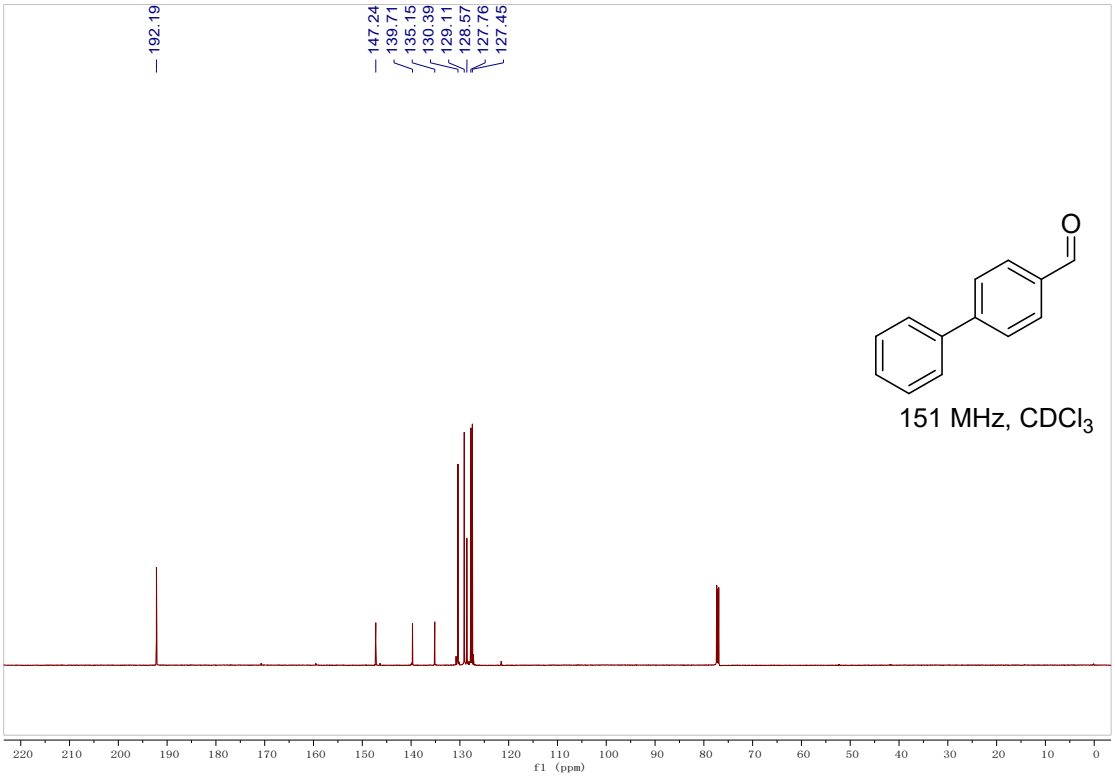


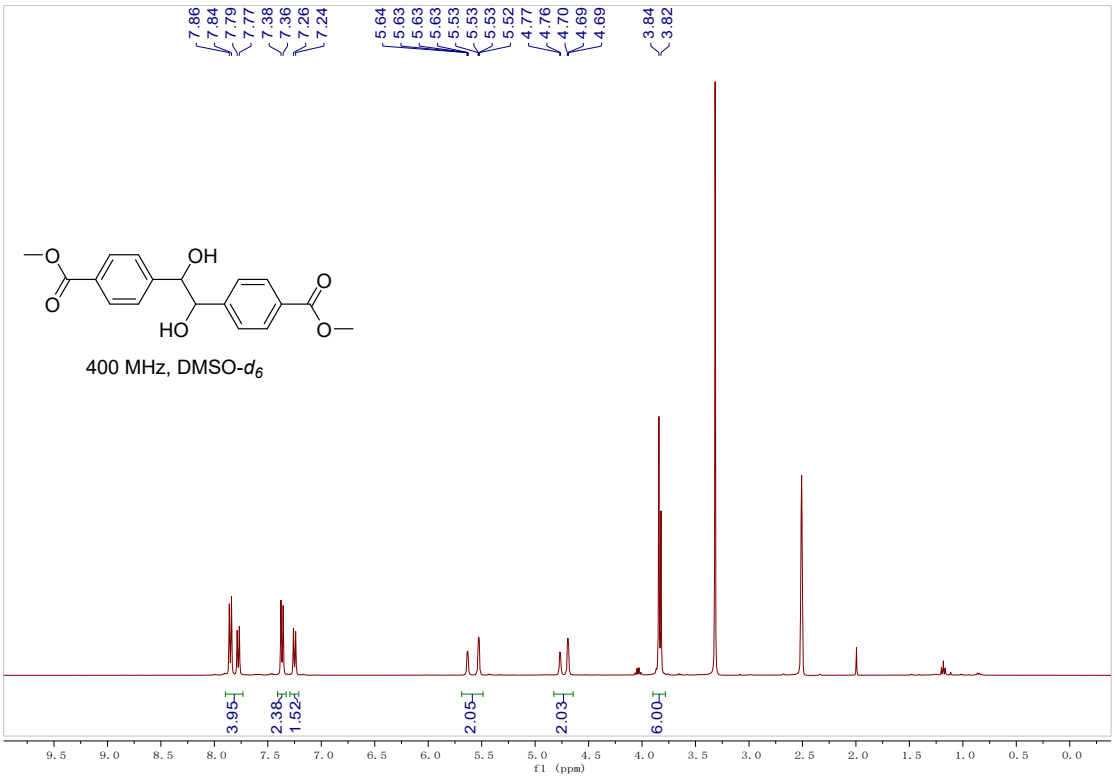


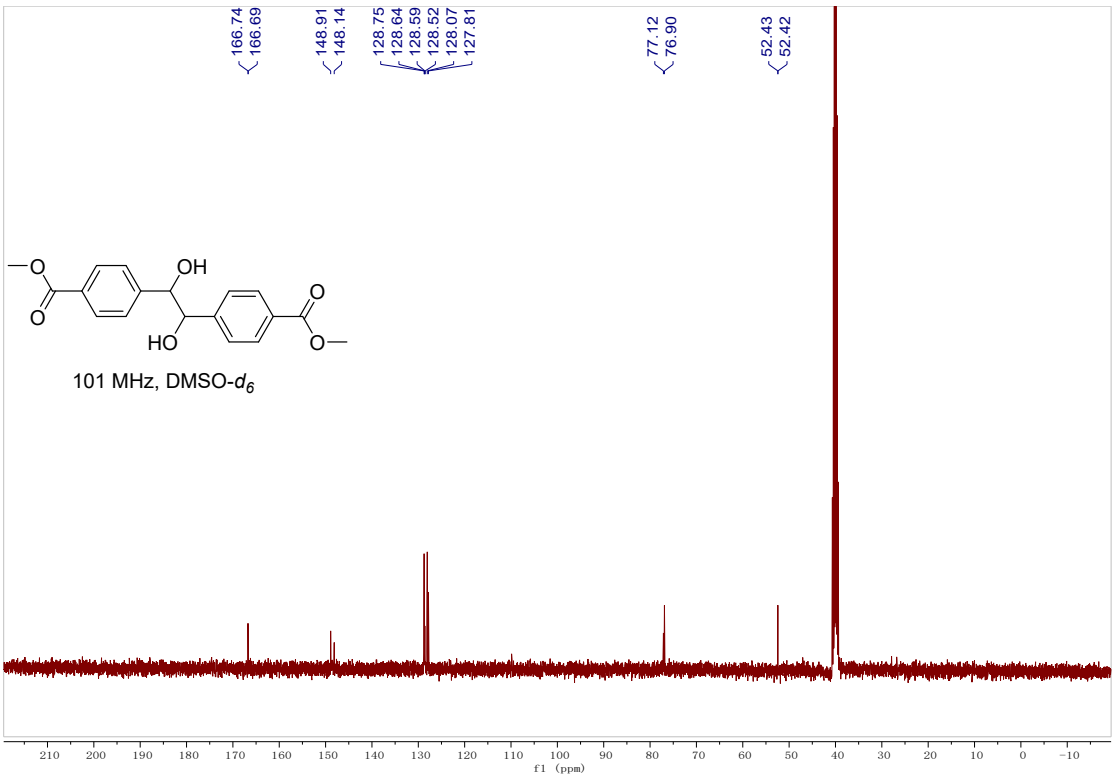
4-Biphenylcarboxaldehyde (E)





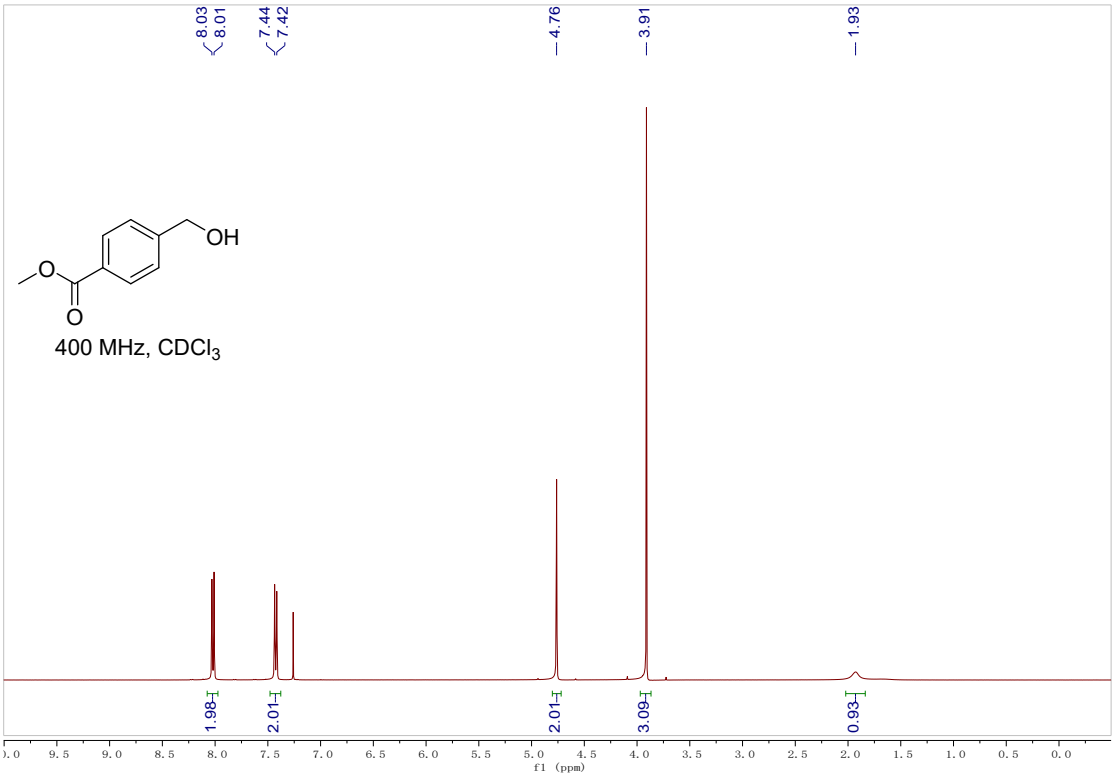
Dimethyl 4,4'-(1,2-dihydroxyethane-1,2-diyl)dibenzoate (B)

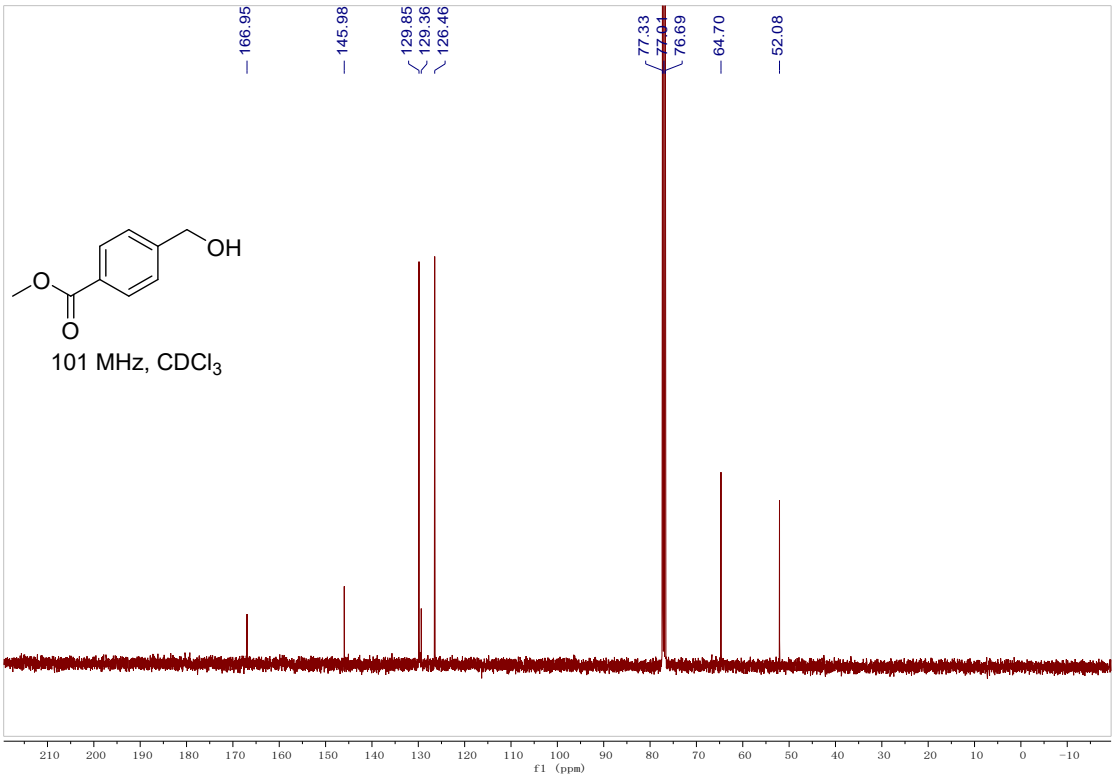




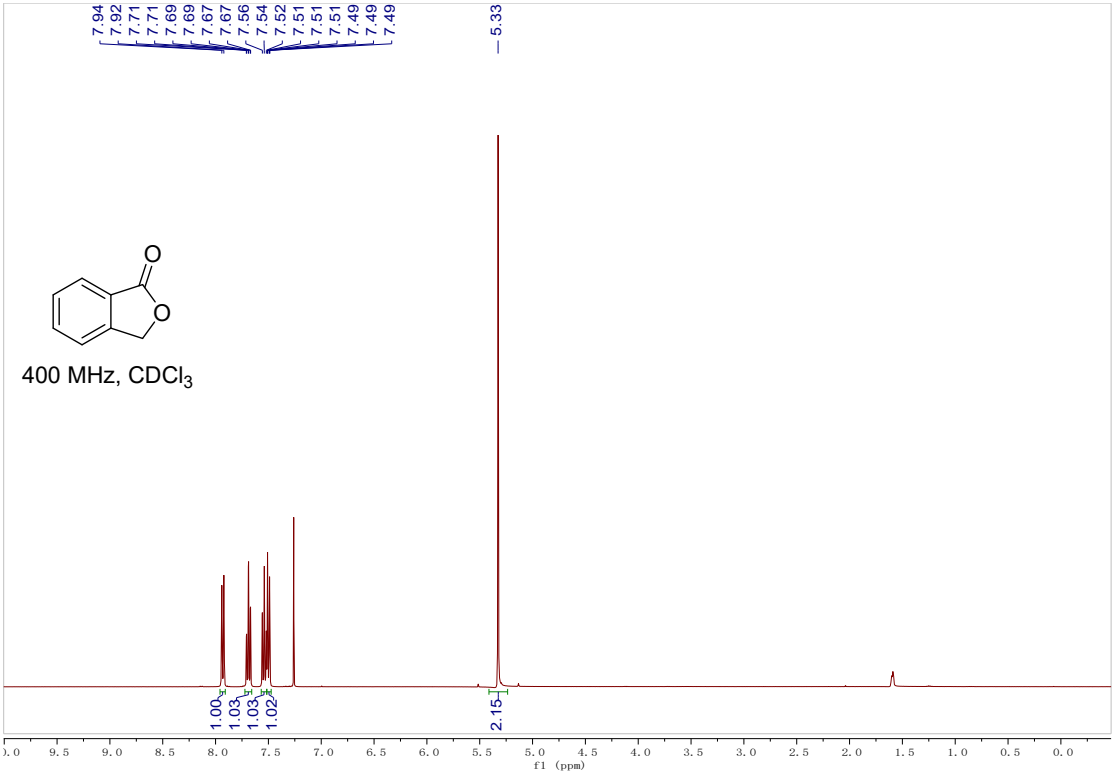
10. NMR spectra for products

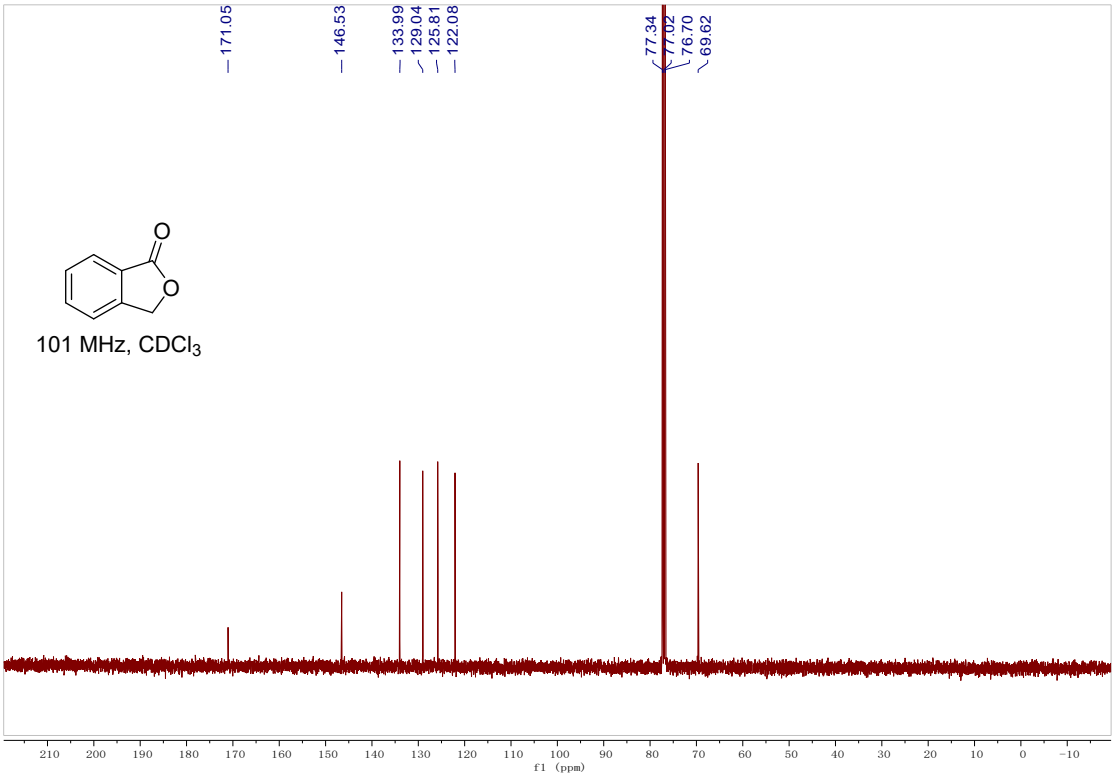
Methyl 4-(hydroxymethyl)benzoate (1a)



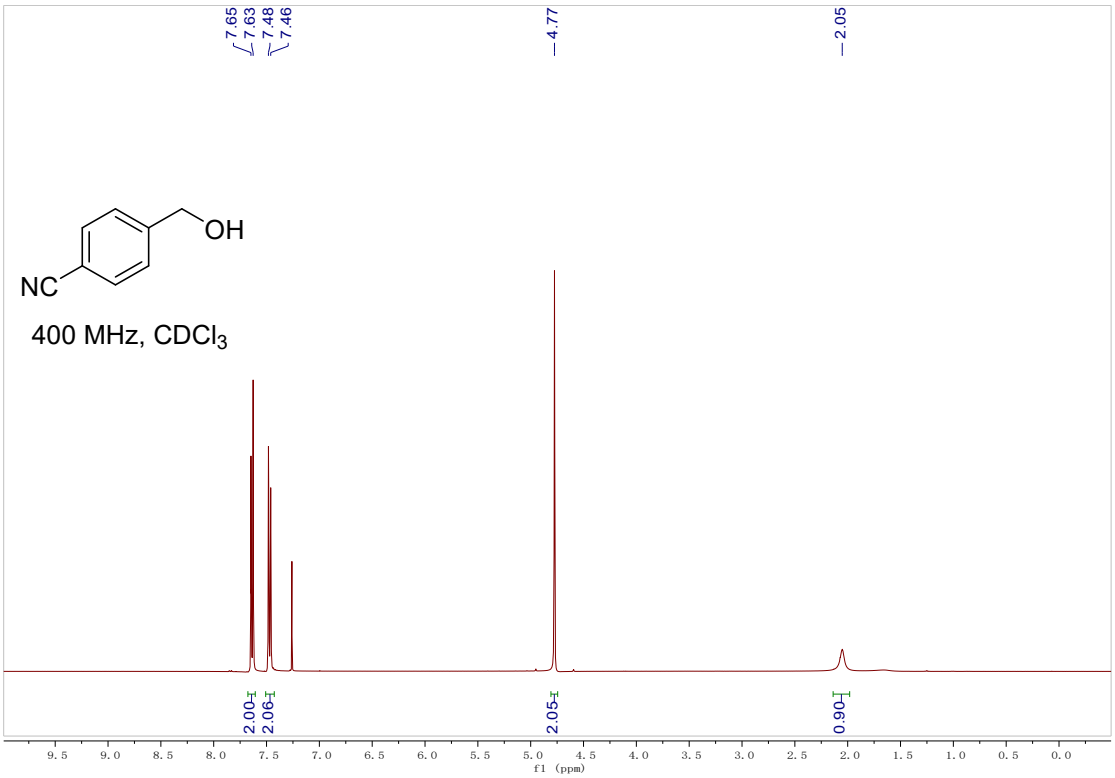


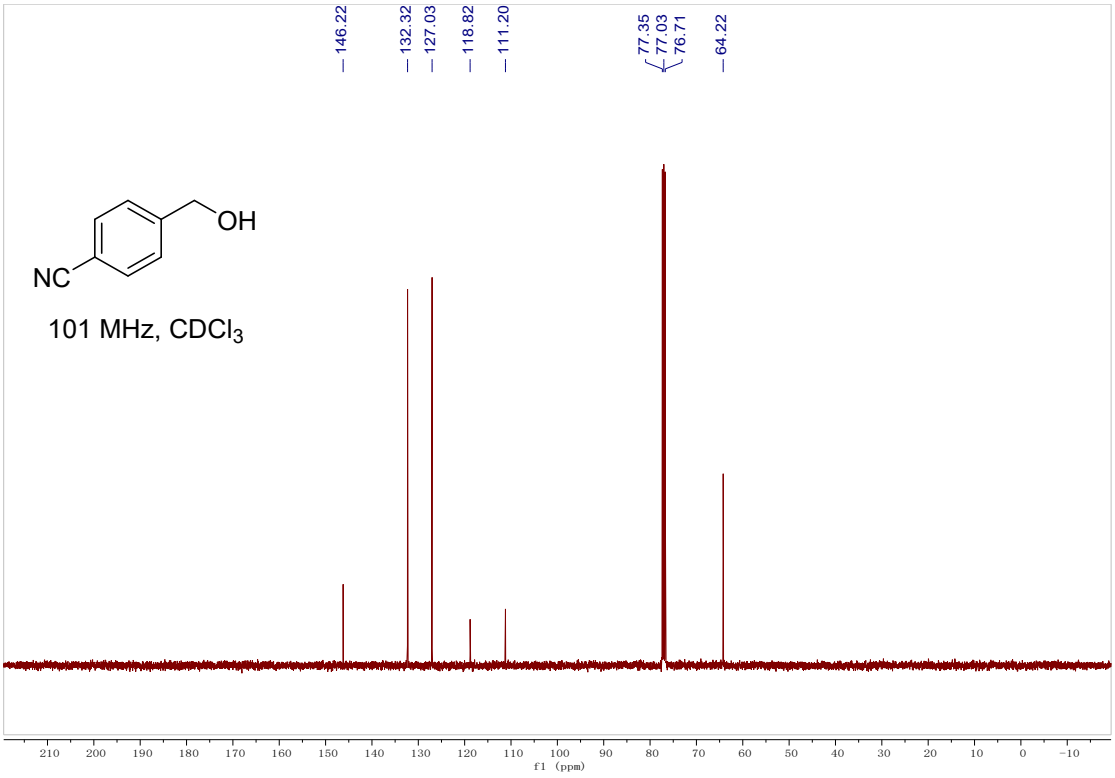
Isobenzofuran-1(3H)-one (1b)



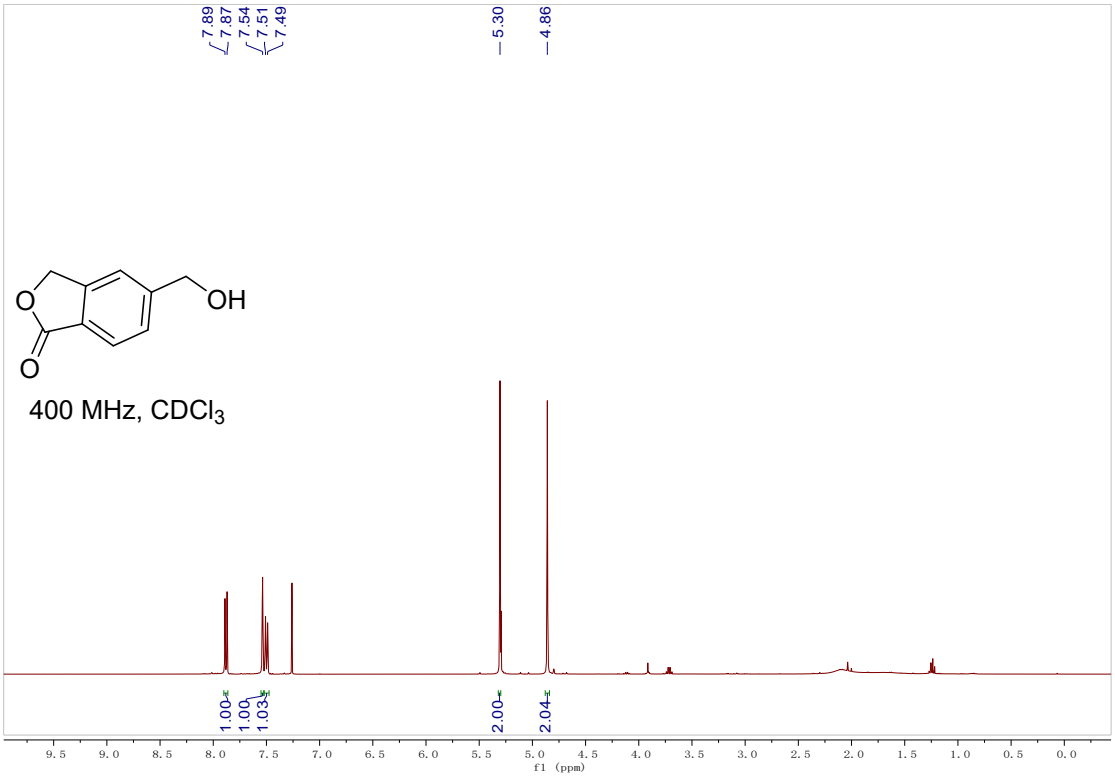


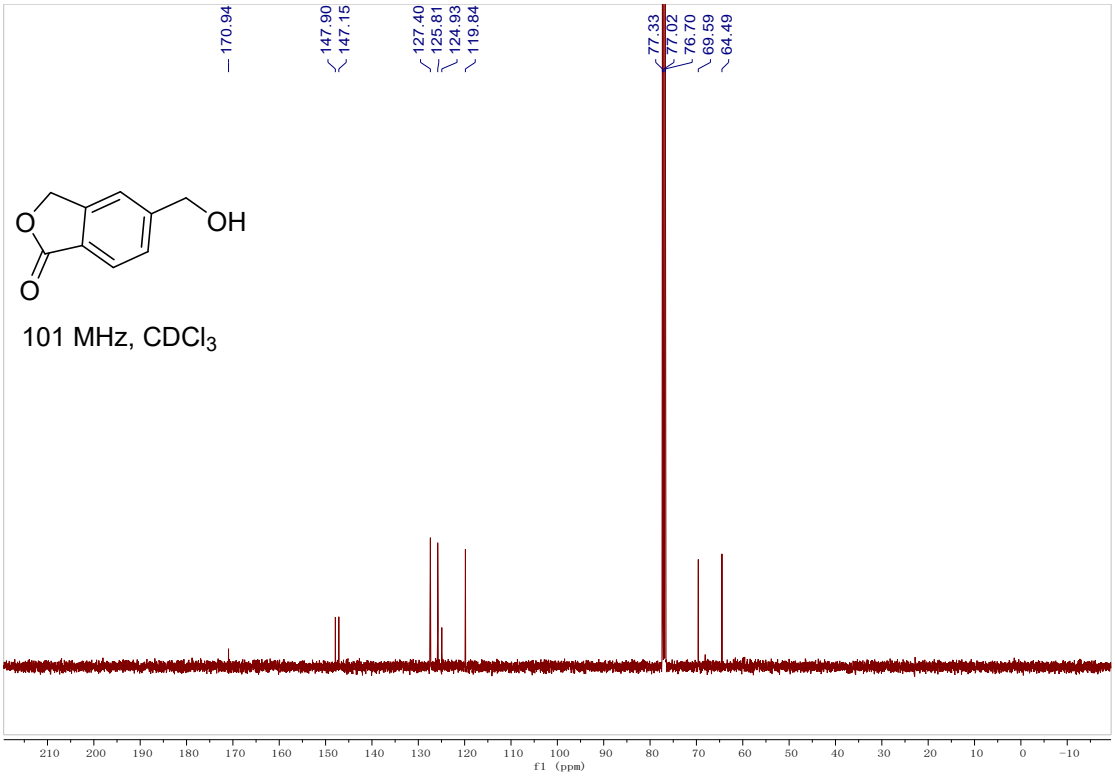
4-(Hydroxymethyl)benzonitrile (1c)





5-(Hydroxymethyl)isobenzofuran-1(3H)-one (1f)





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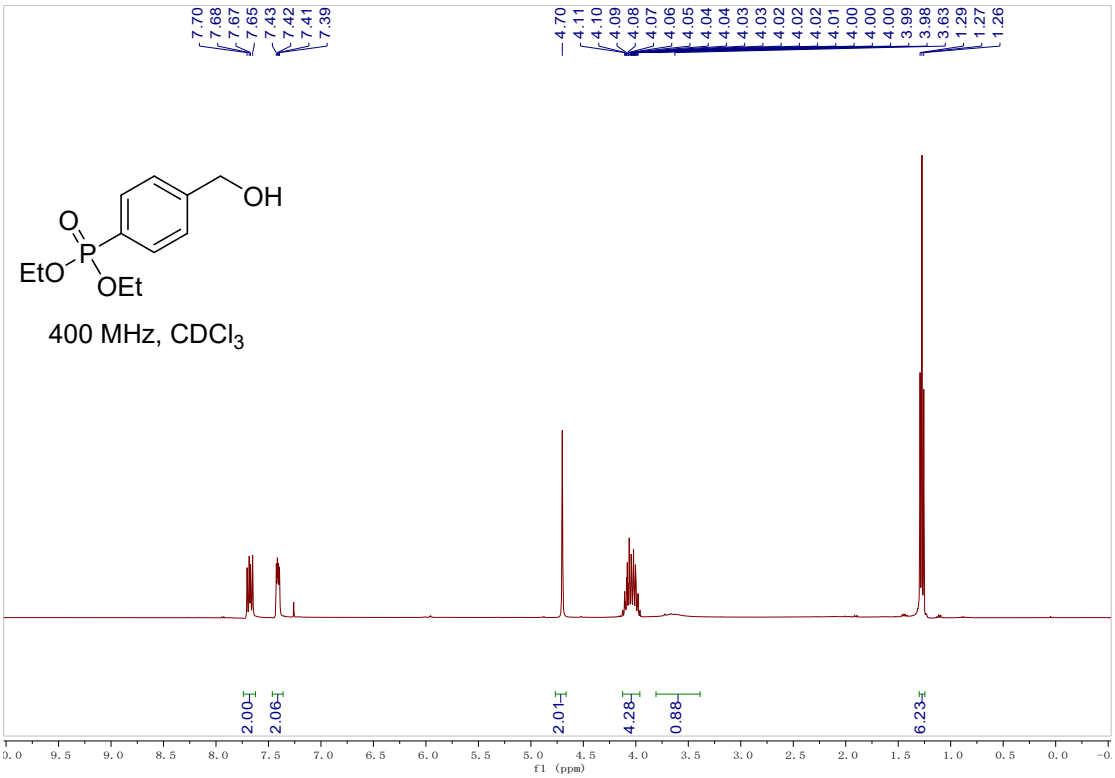
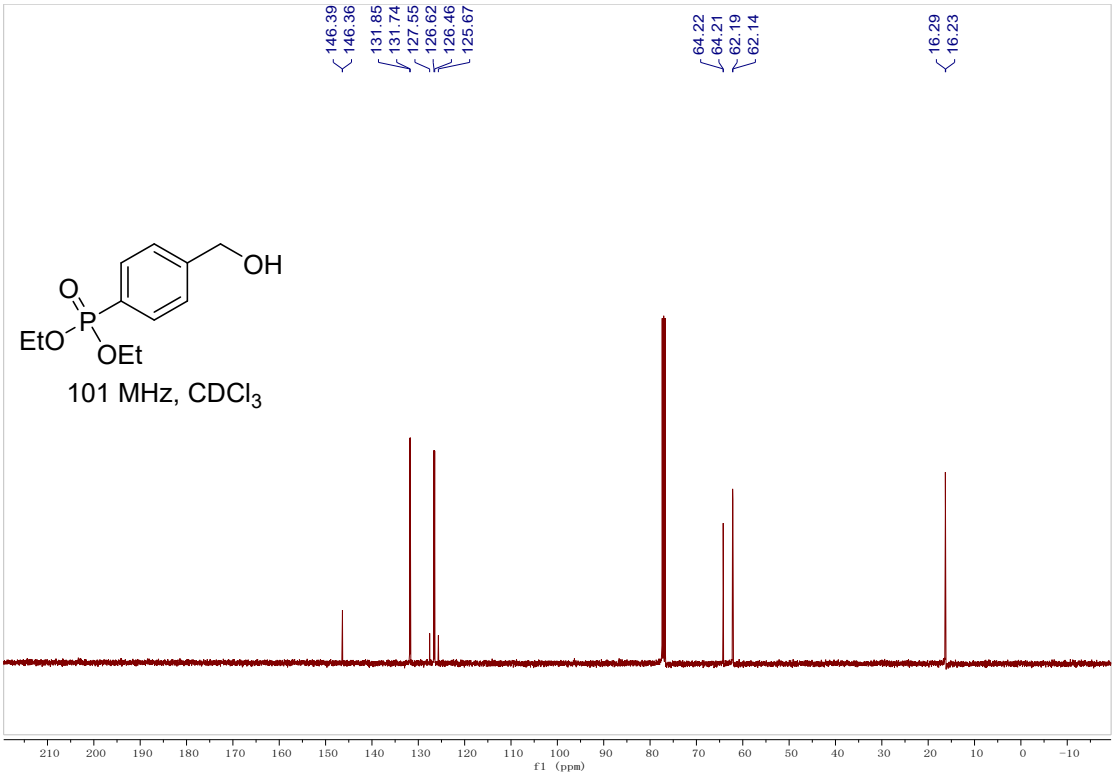
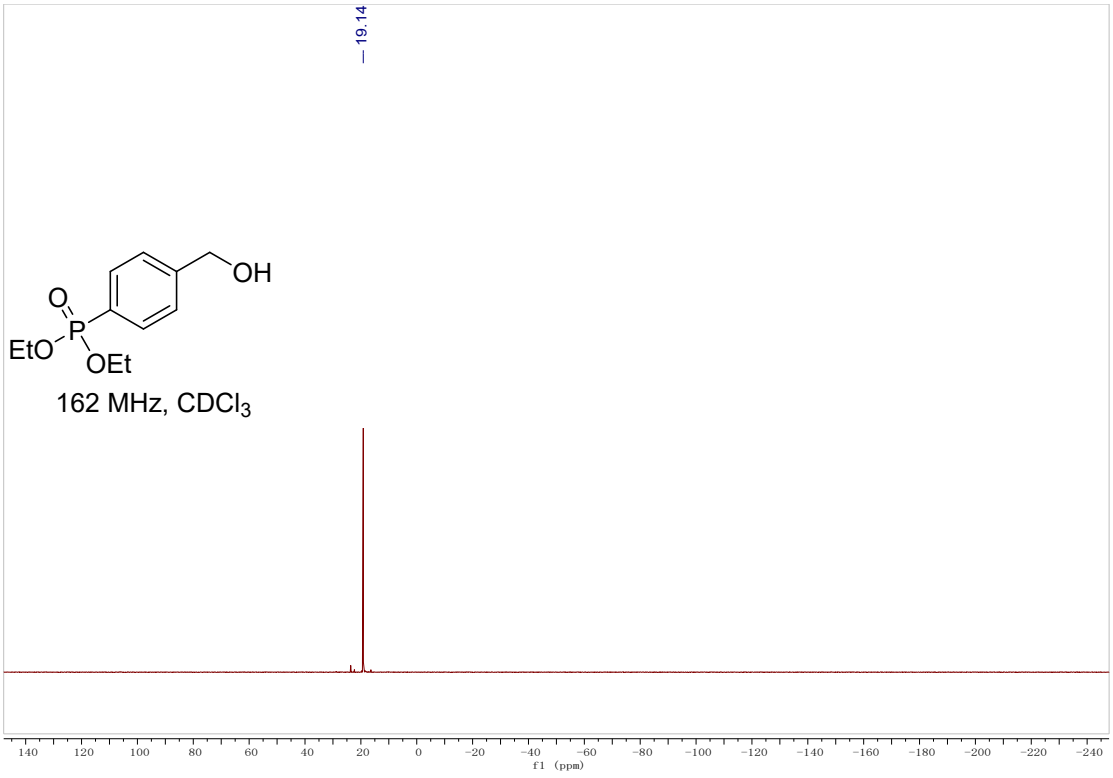
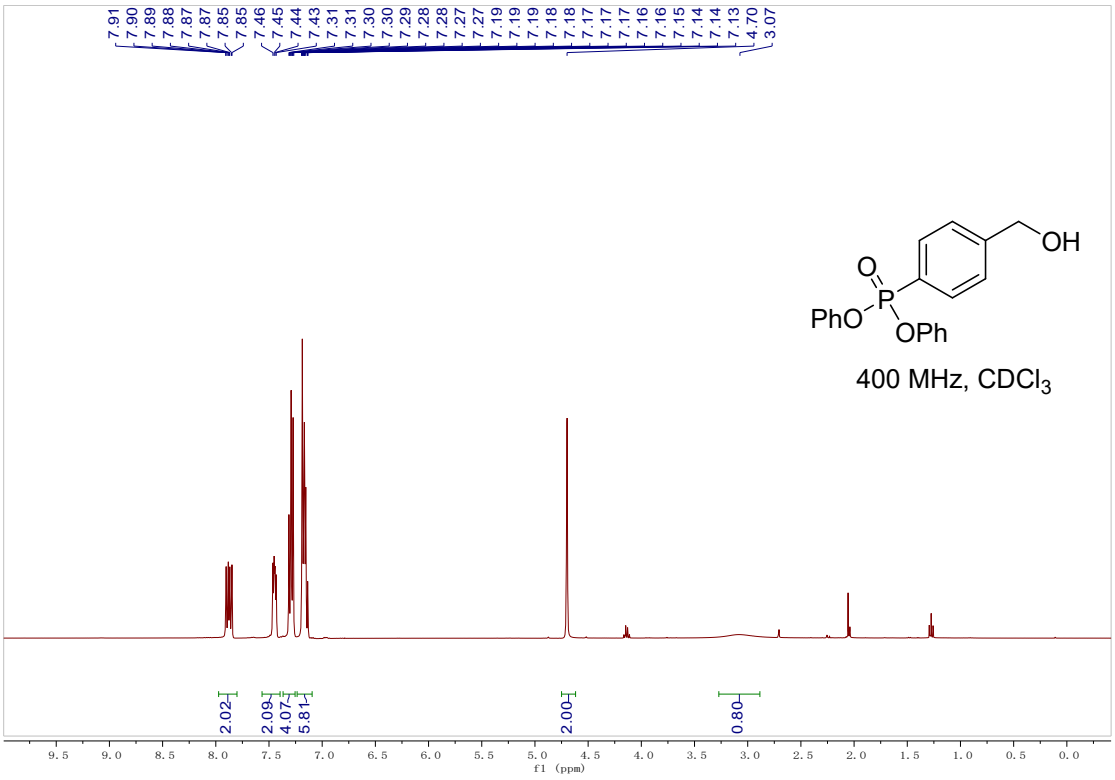
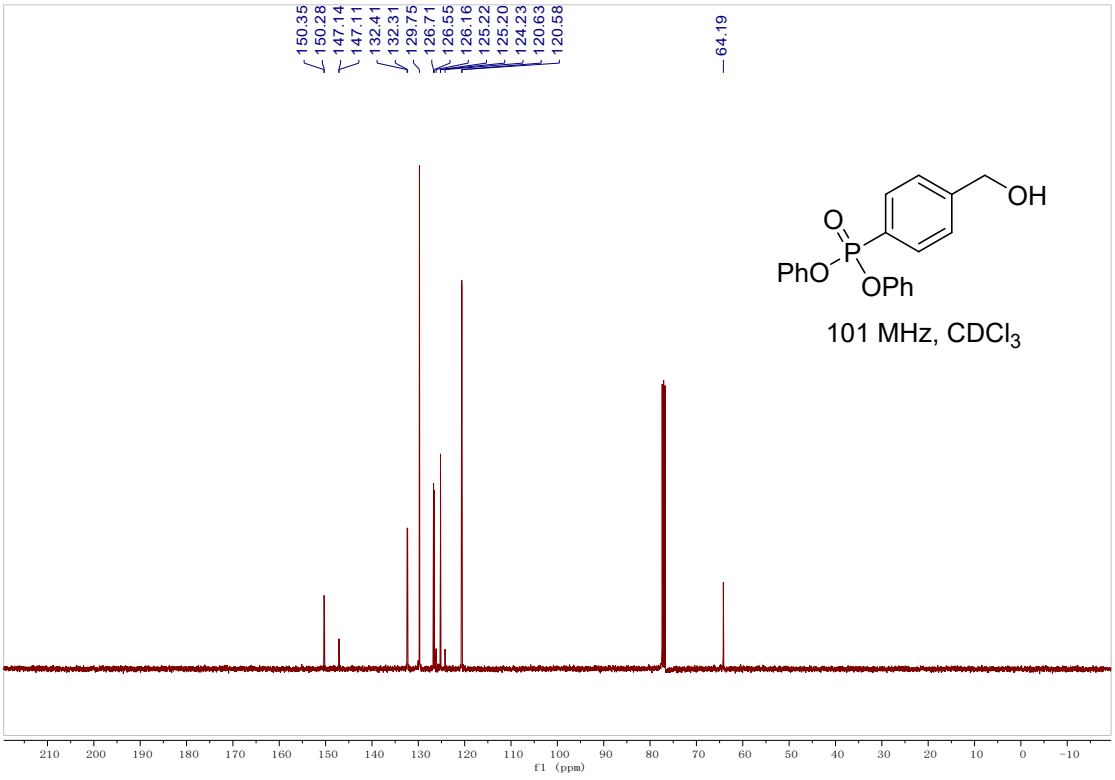


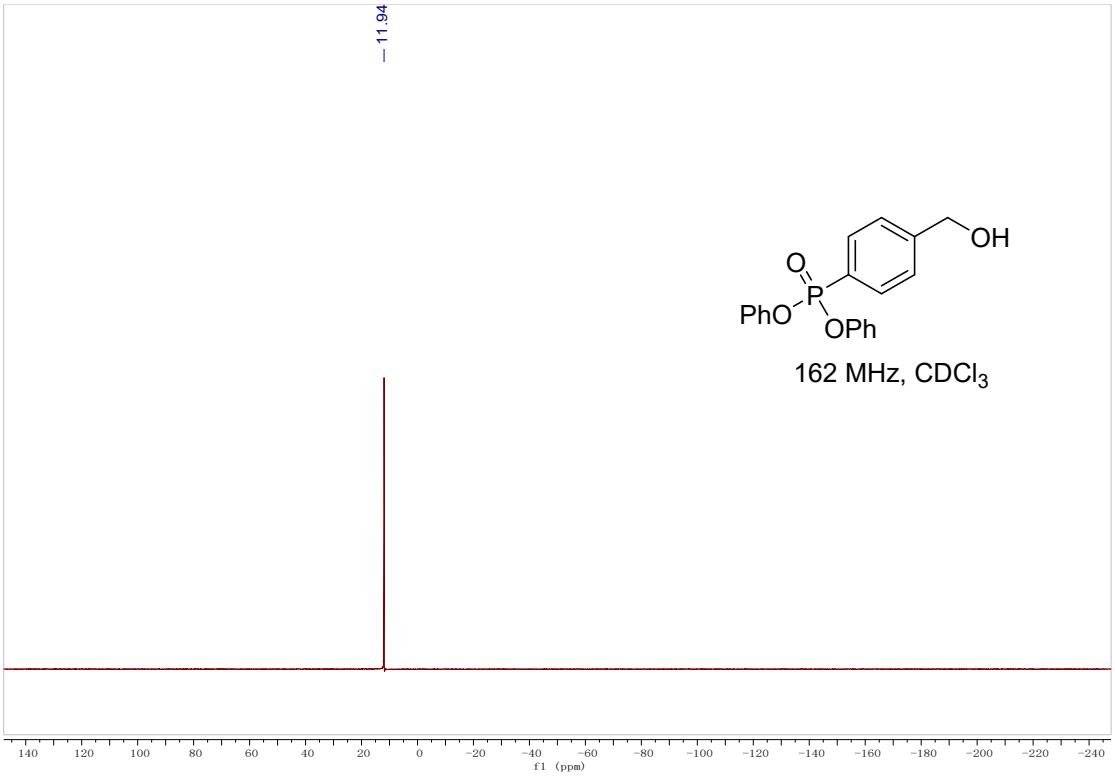



19.14
OH
O
P
EtO
OEt
162 MHz, CDCl3
140
120
100
80
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−200
−220
−240
f1 (ppm)

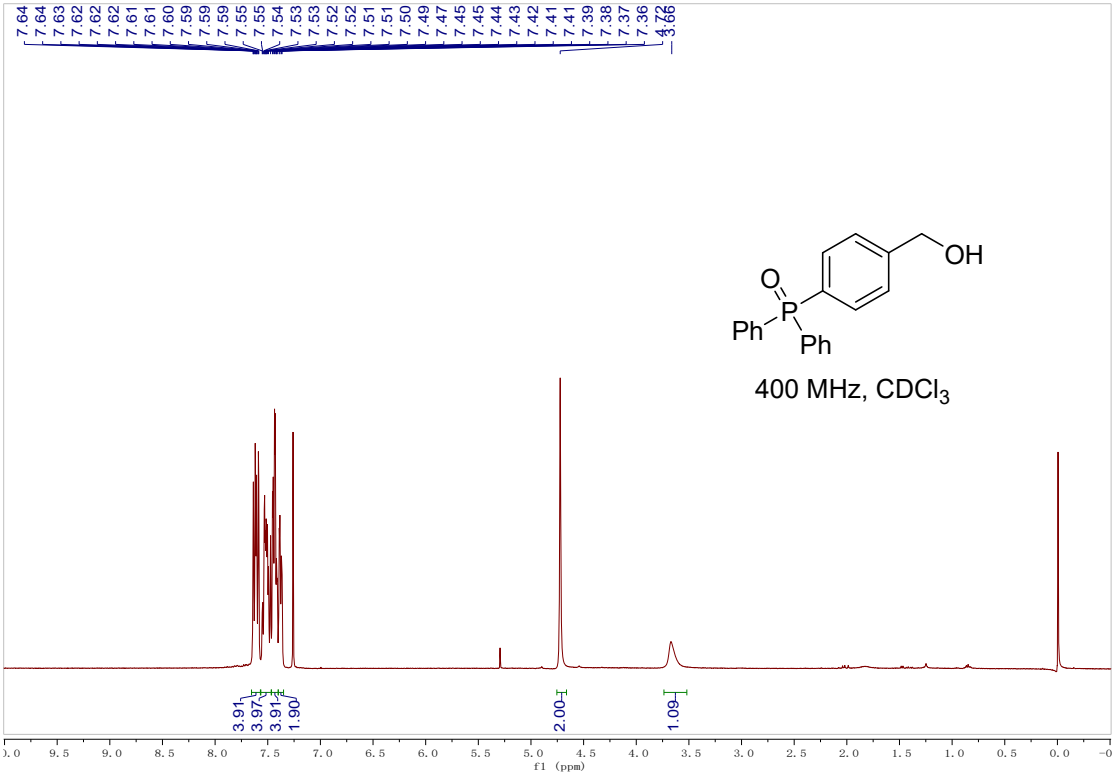
Diphenyl (4-(hydroxymethyl)phenyl)phosphonate (1h)

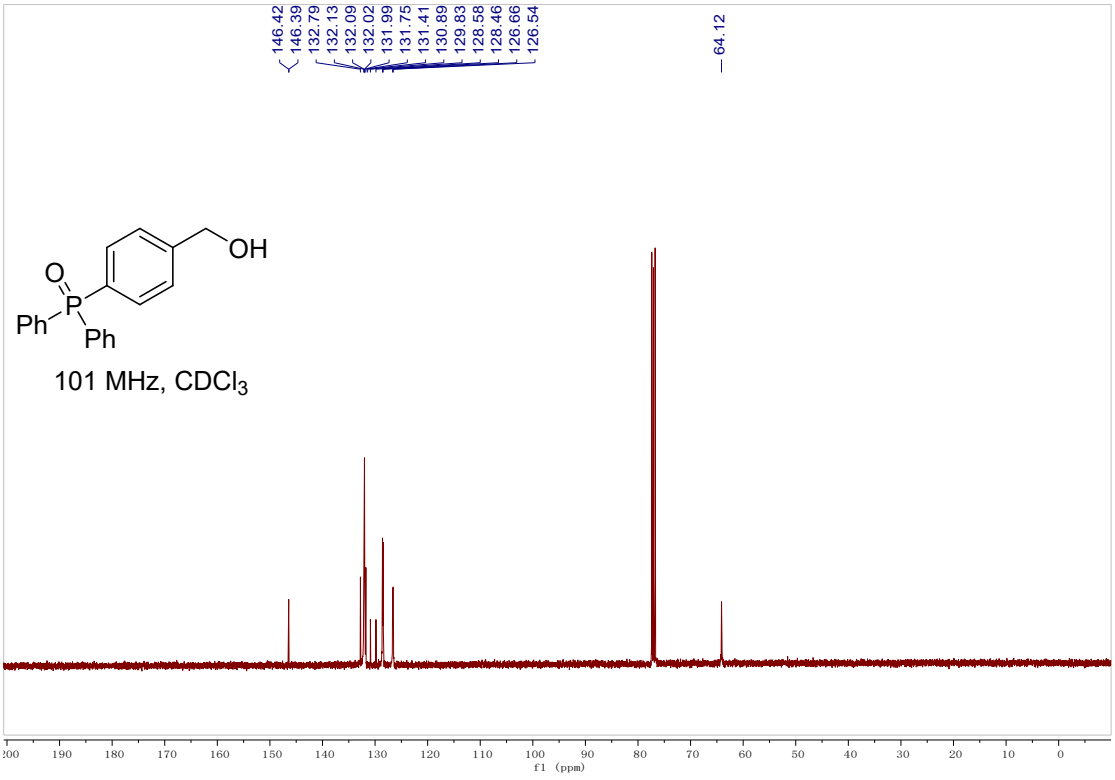


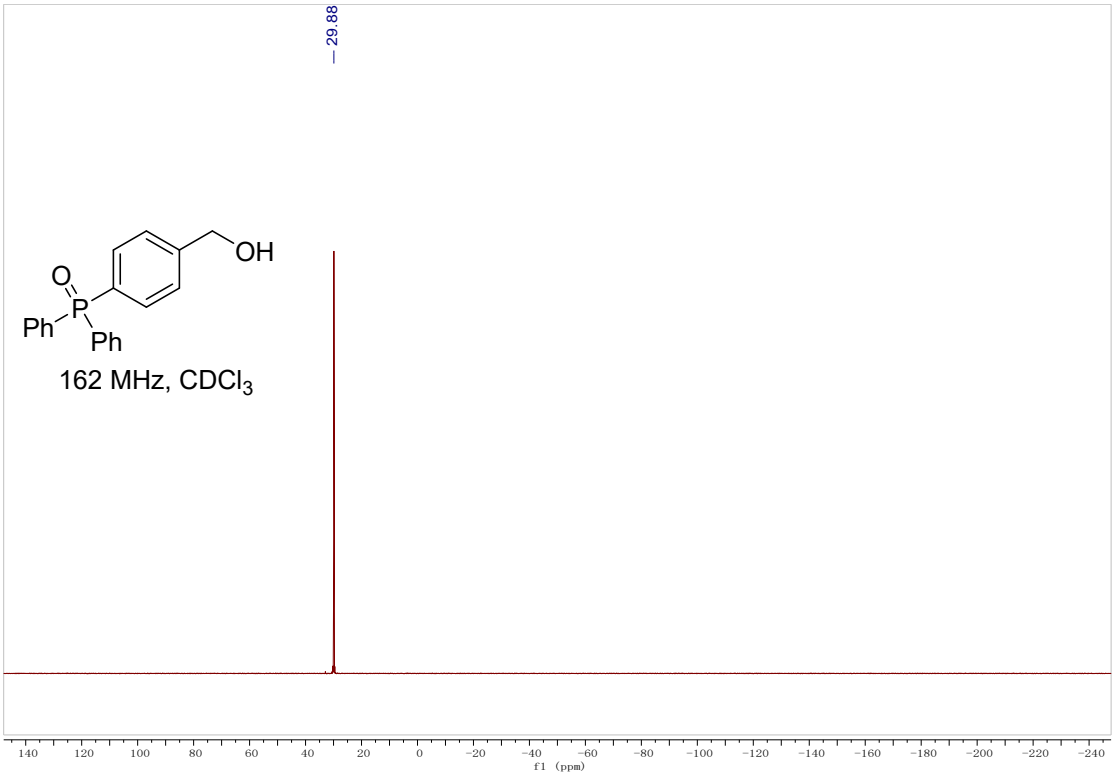



11.94
OH
O
P
PhO
OPh
162 MHz, CDCl3
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

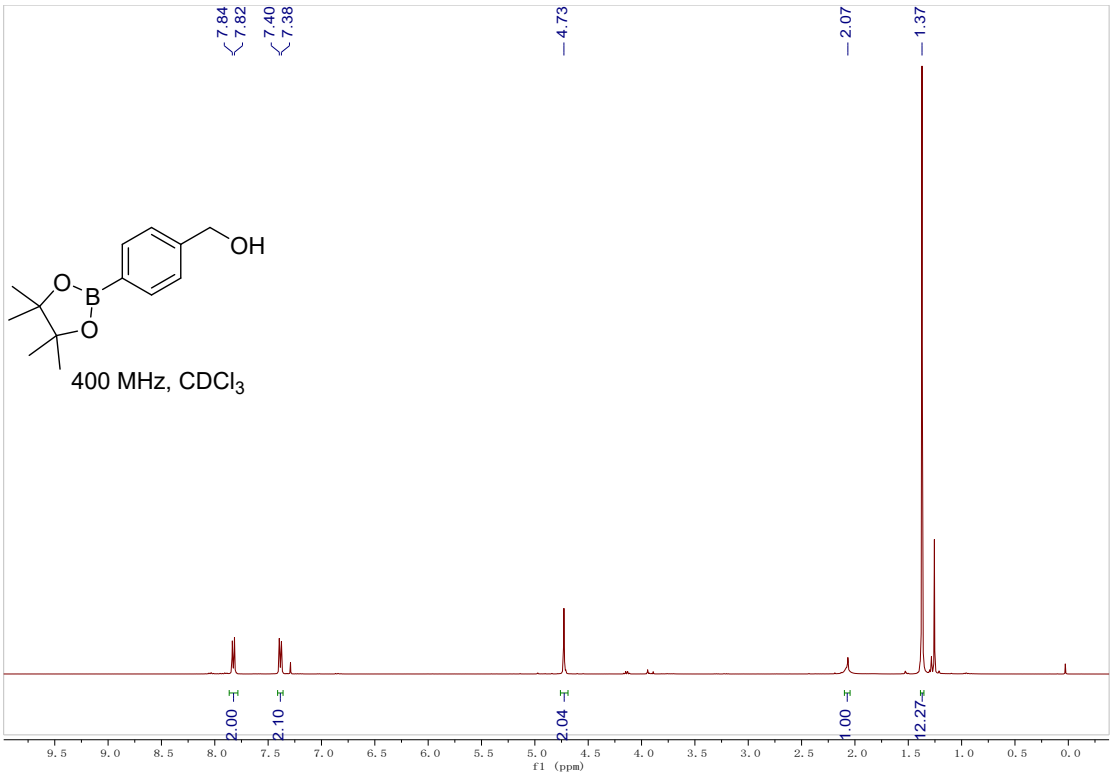
(4-(hydroxymethyl)phenyl)diphenylphosphine oxide (1i)

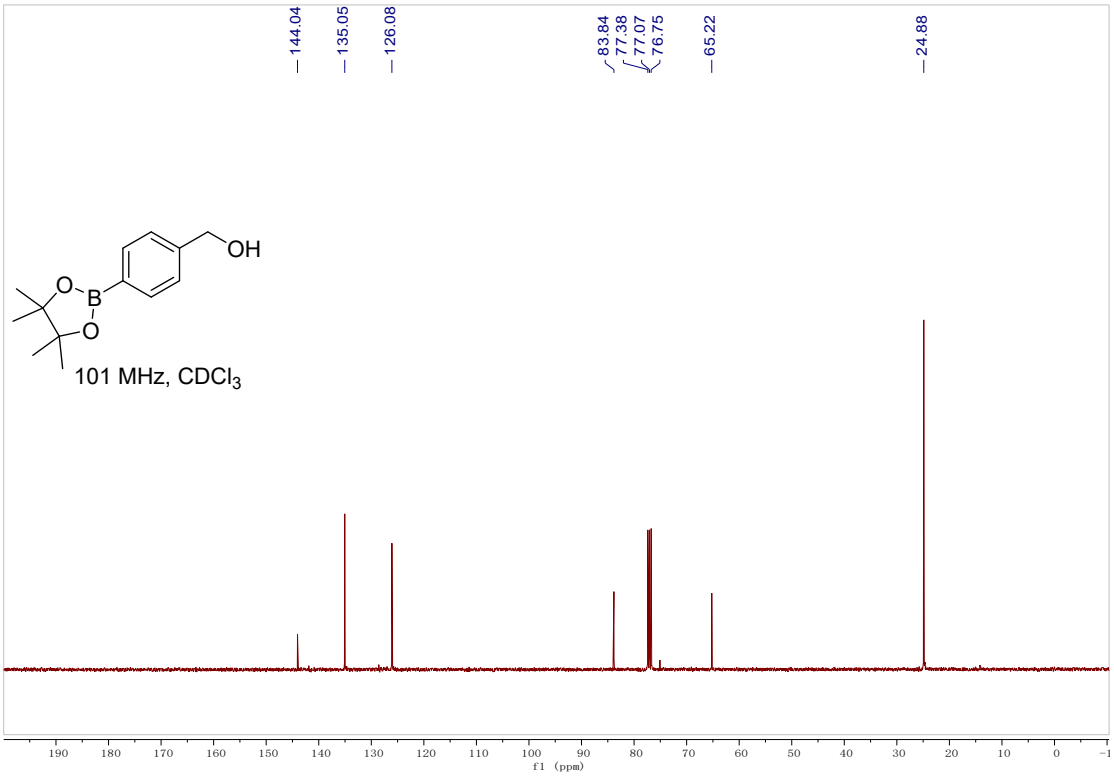


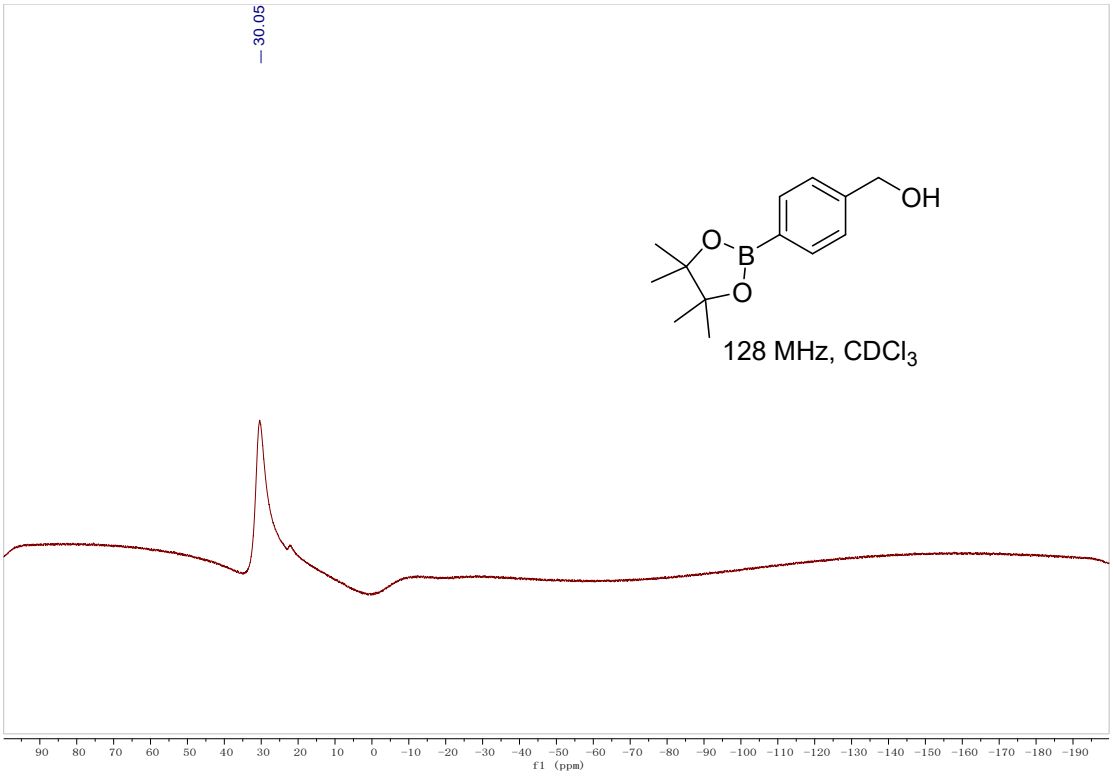



29.88
OH
O
P
Ph
Ph
162 MHz, CDCl3
140
120
100
80
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
−200
−220
−240
f1 (ppm)

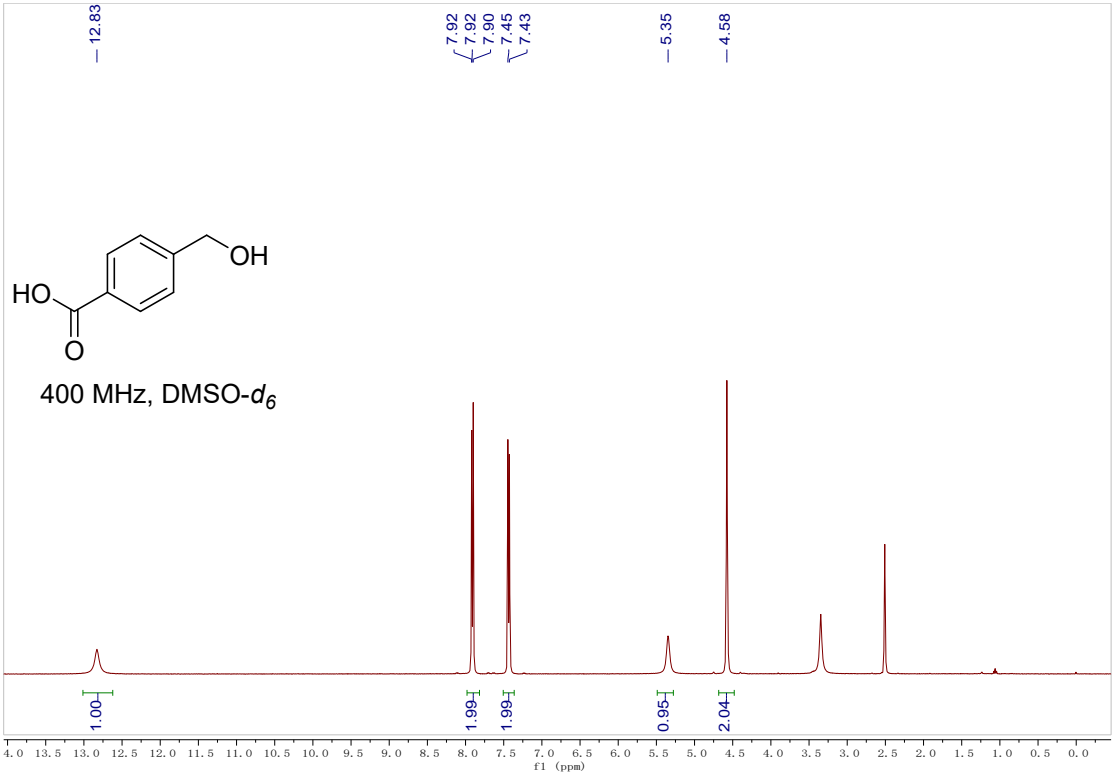
(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanol (1j)

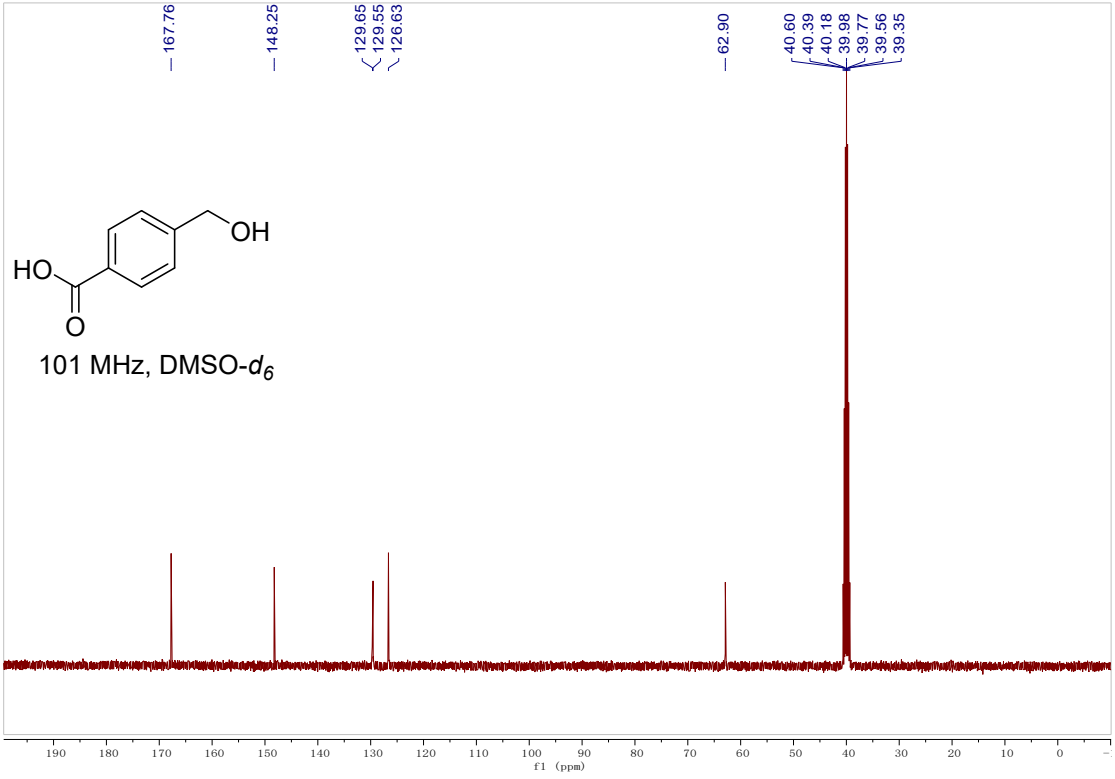




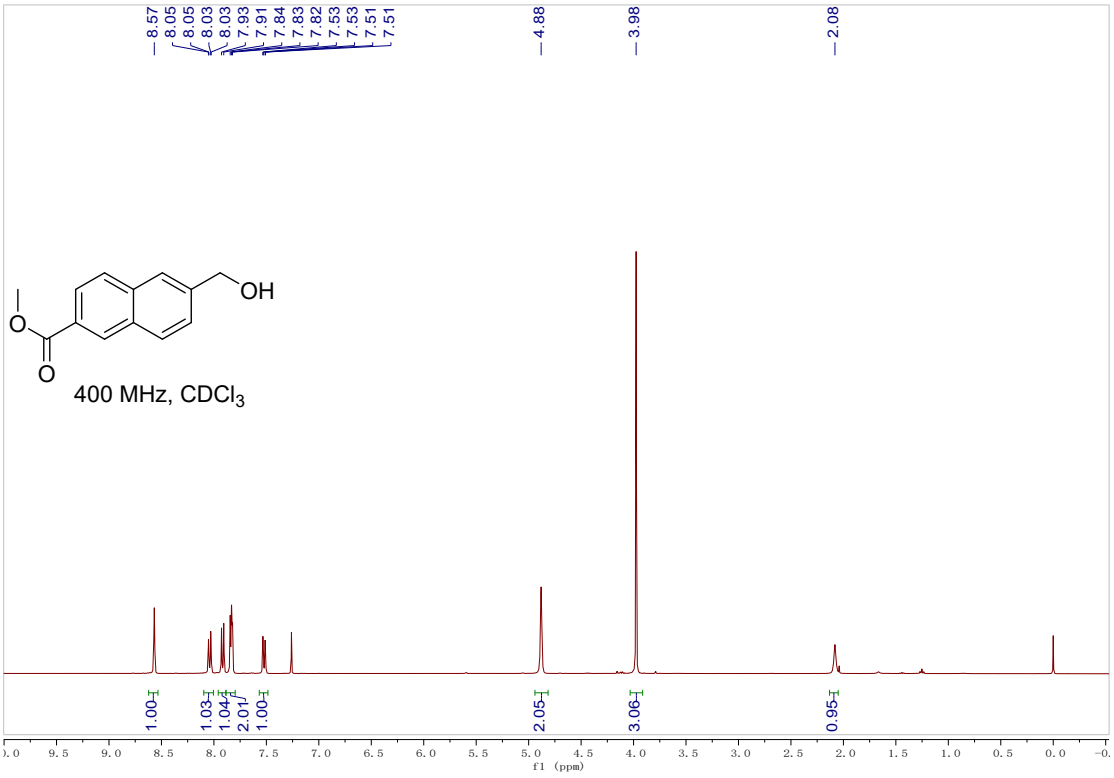

30.05
OH
O
B
O
128 MHz, CDCl3
90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190
f1 (ppm)

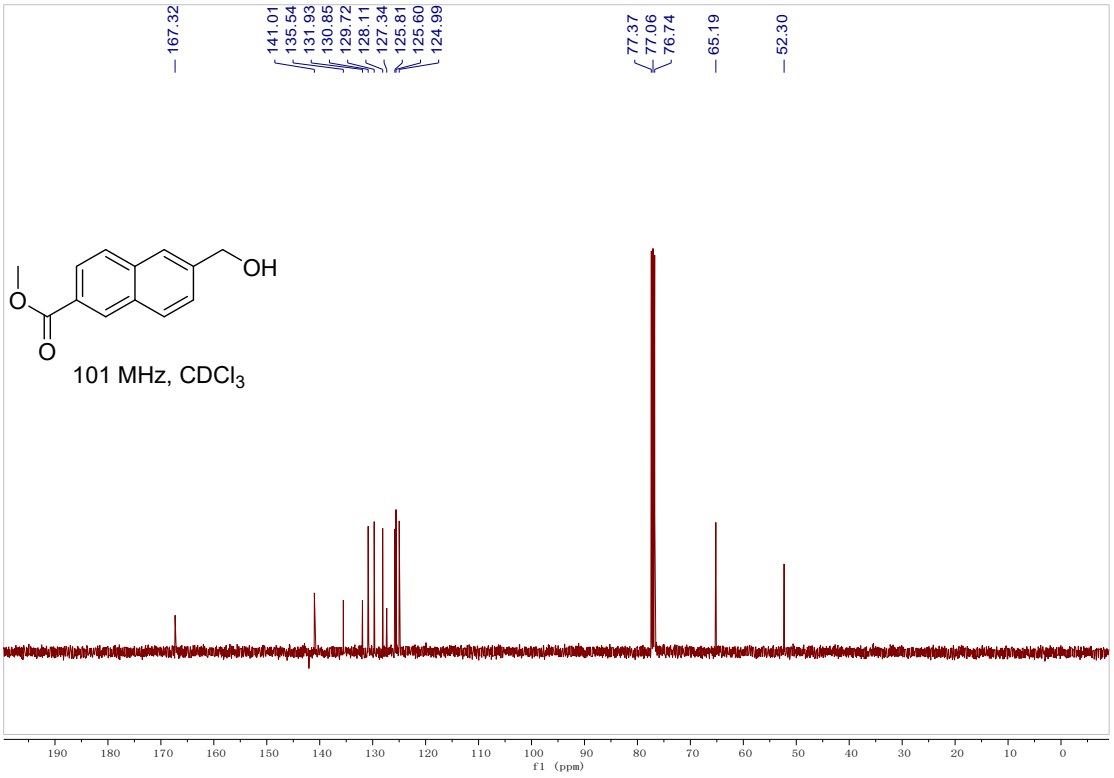
4-(hydroxymethyl)benzoic acid (1k)



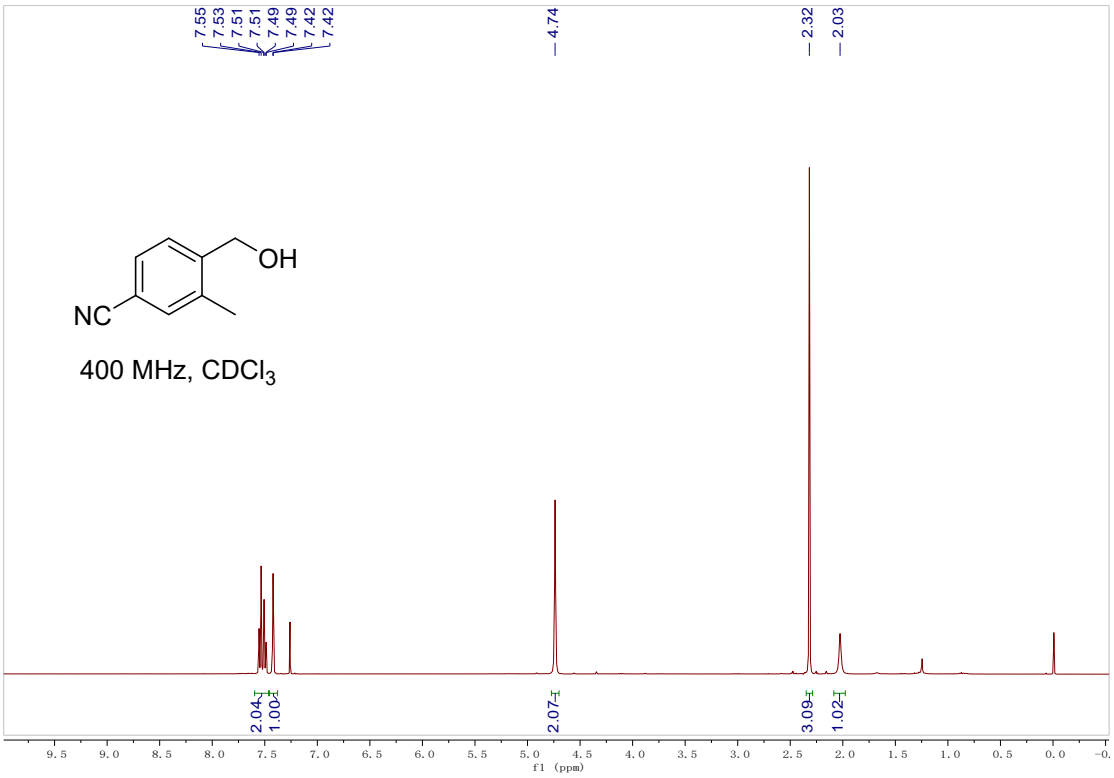


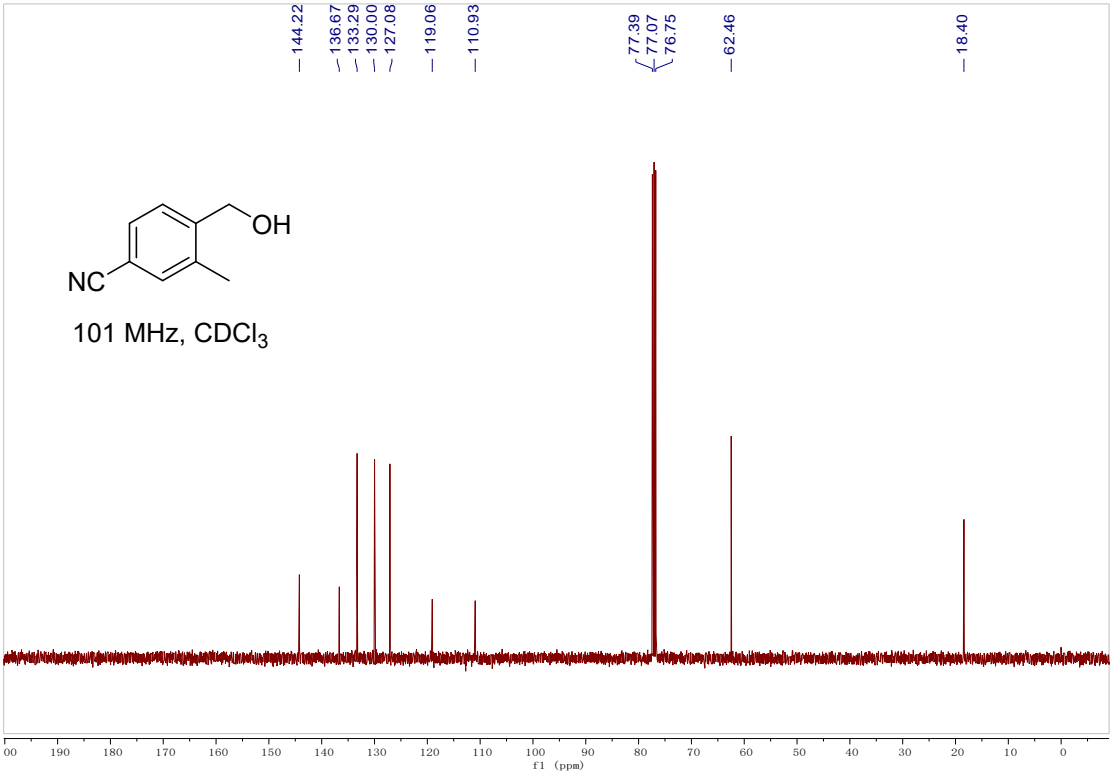
Methyl 6-(hydroxymethyl)-2-naphthoate (1l)



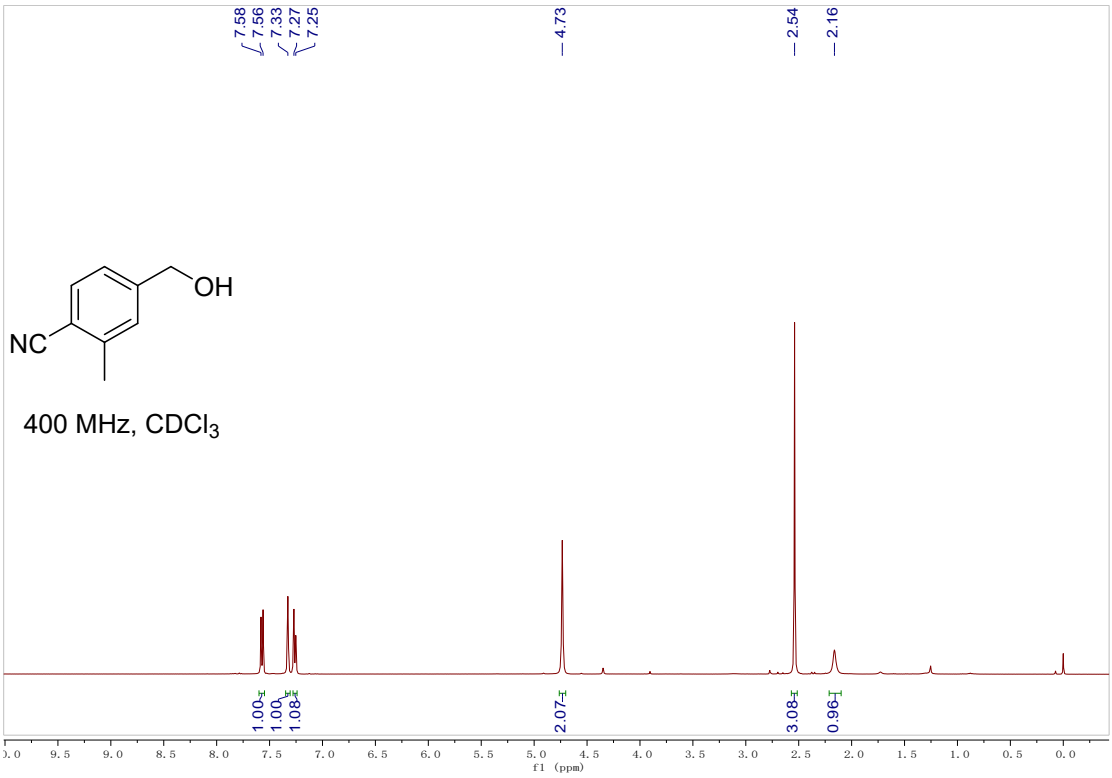


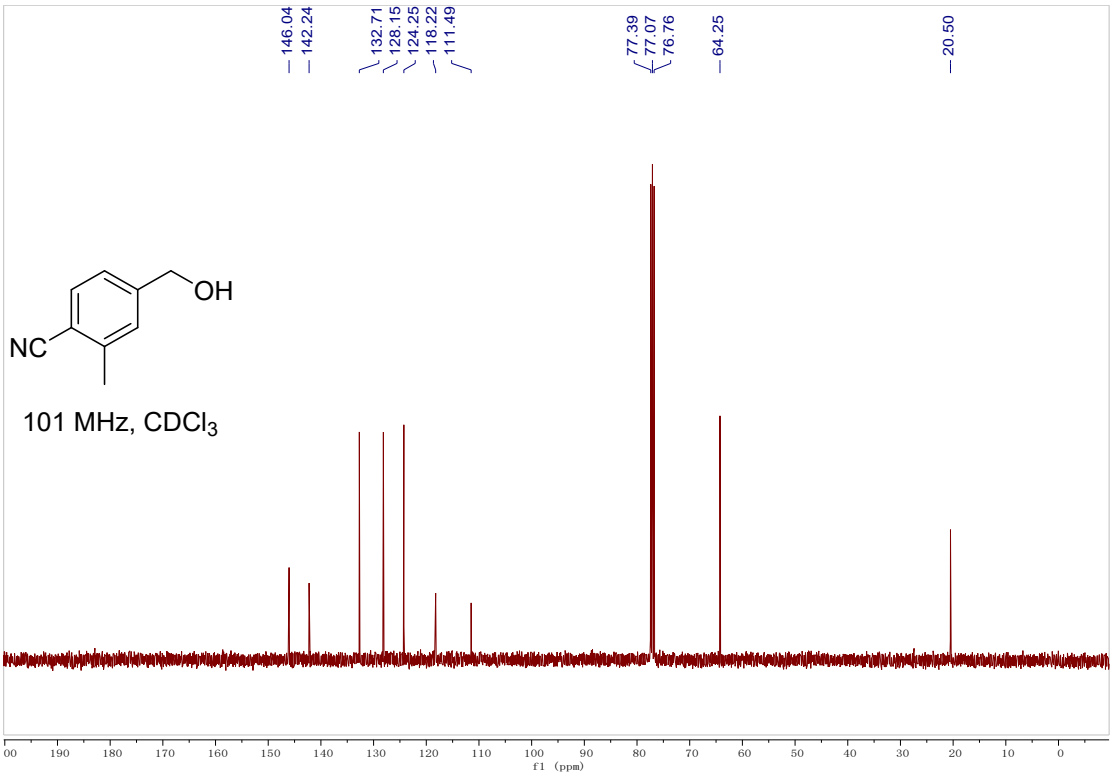
4-(Hydroxymethyl)-3-methylbenzonitrile (1m)



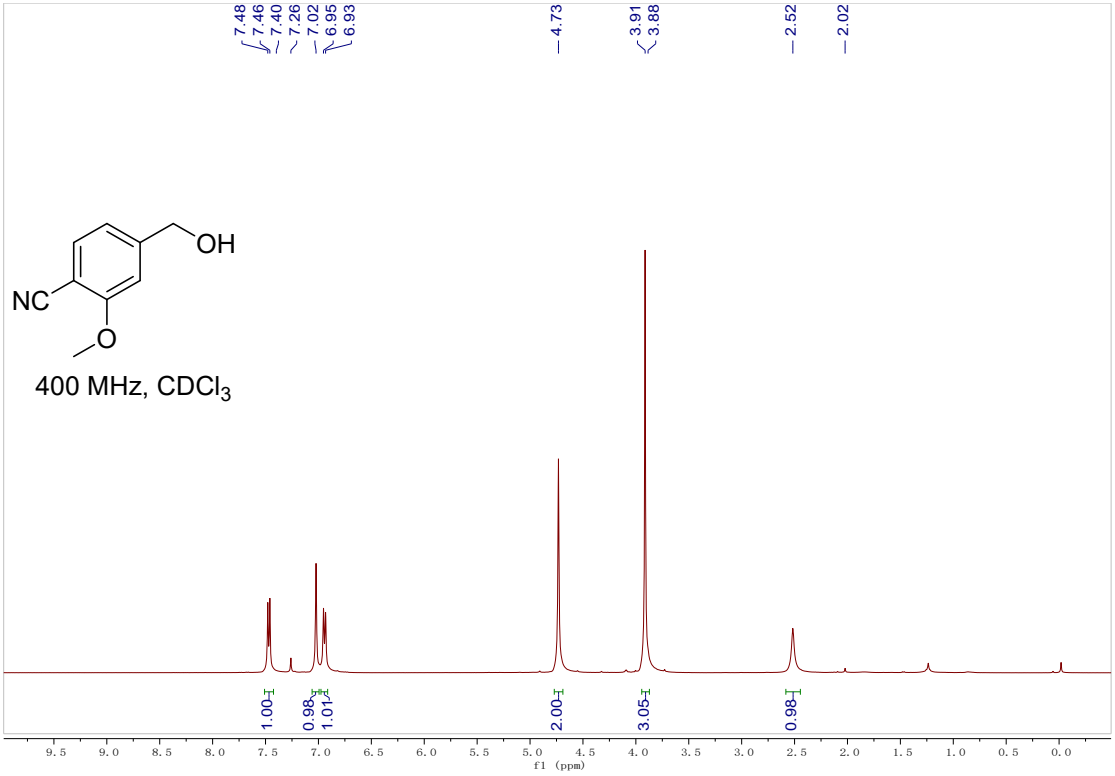


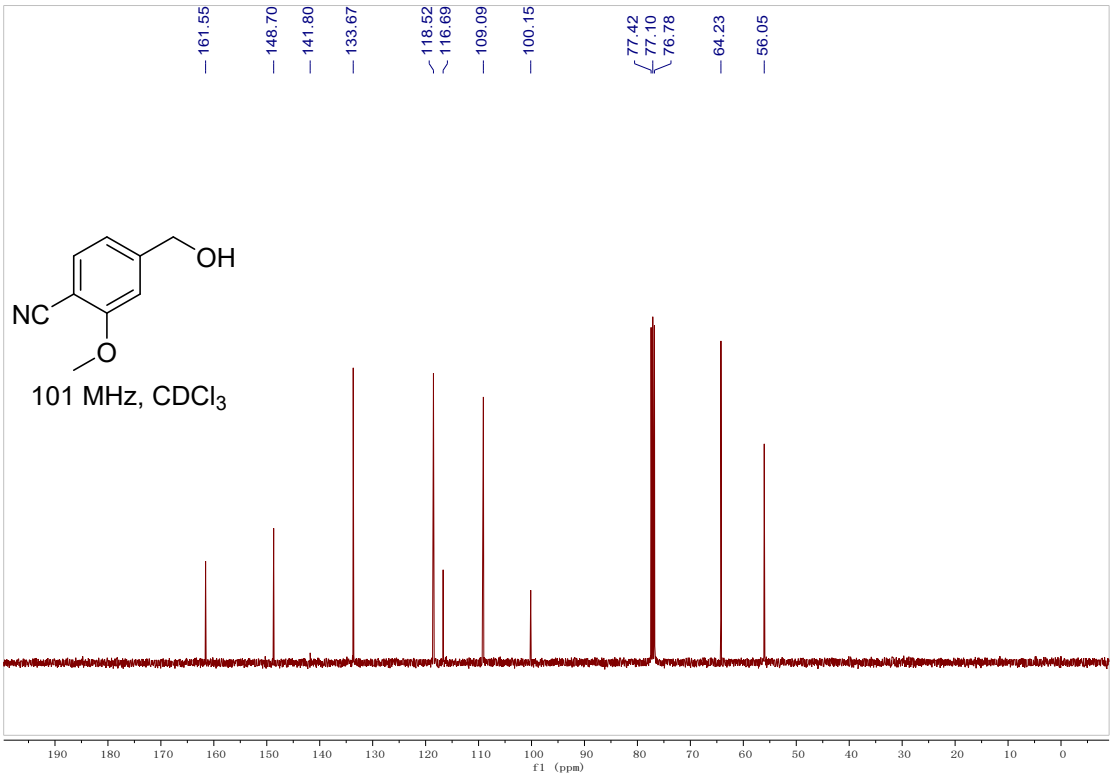
4-(Hydroxymethyl)-2-methylbenzonitrile (1n)



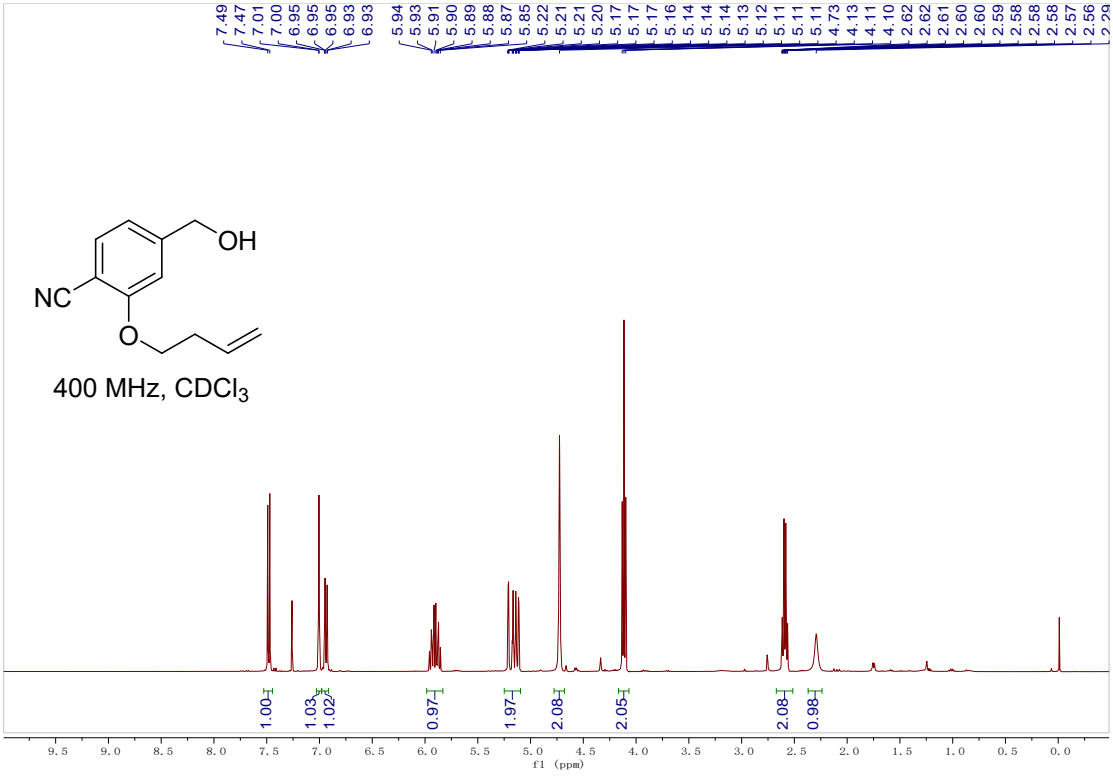


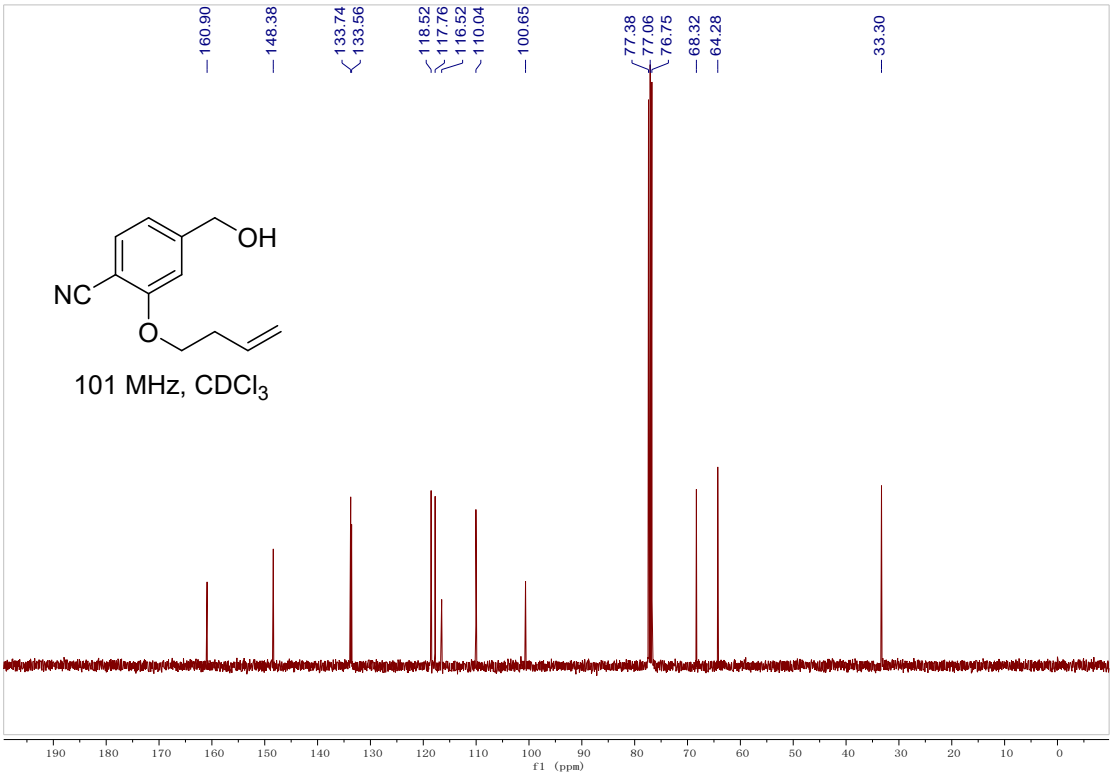
4-(Hydroxymethyl)-2-methoxybenzonitrile (1o)



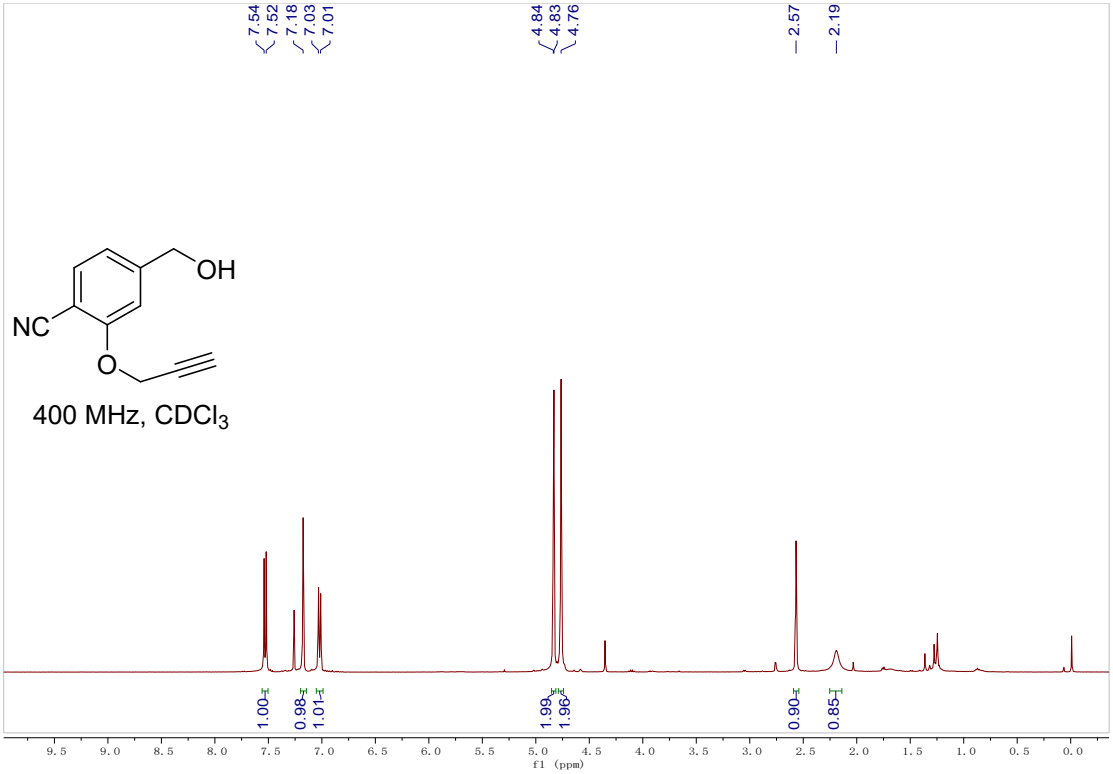


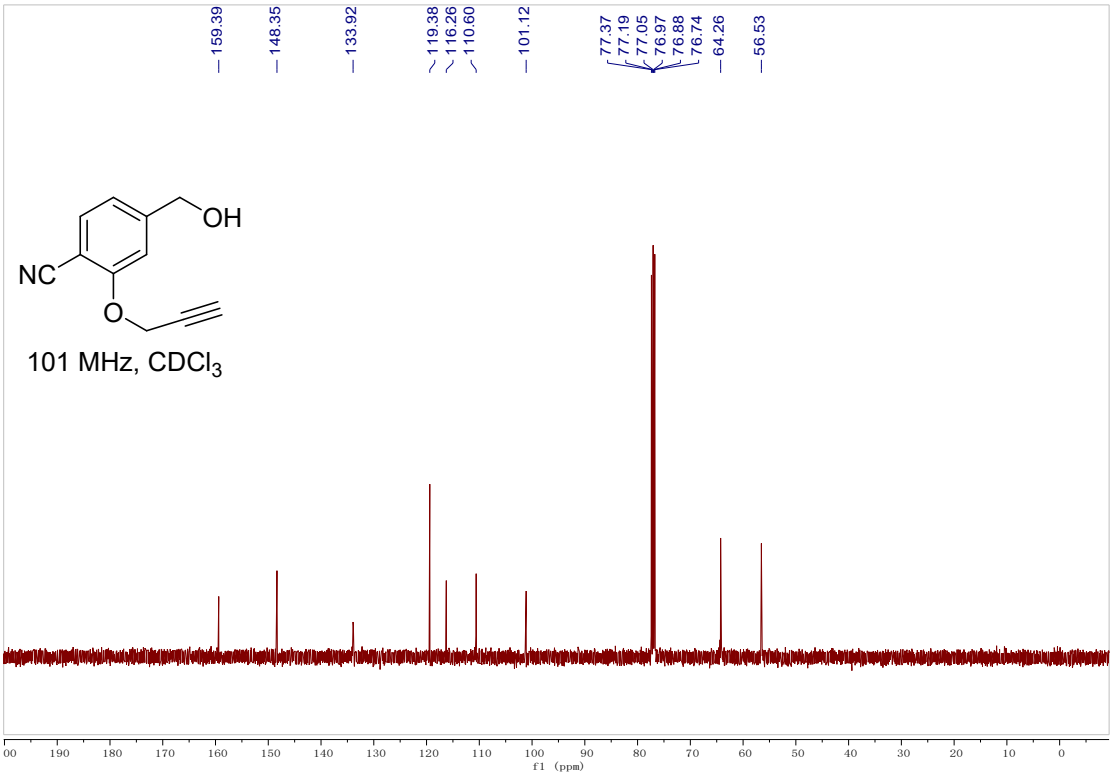
2-(But-3-en-1-yloxy)-4-(hydroxymethyl)benzonitrile (1p)



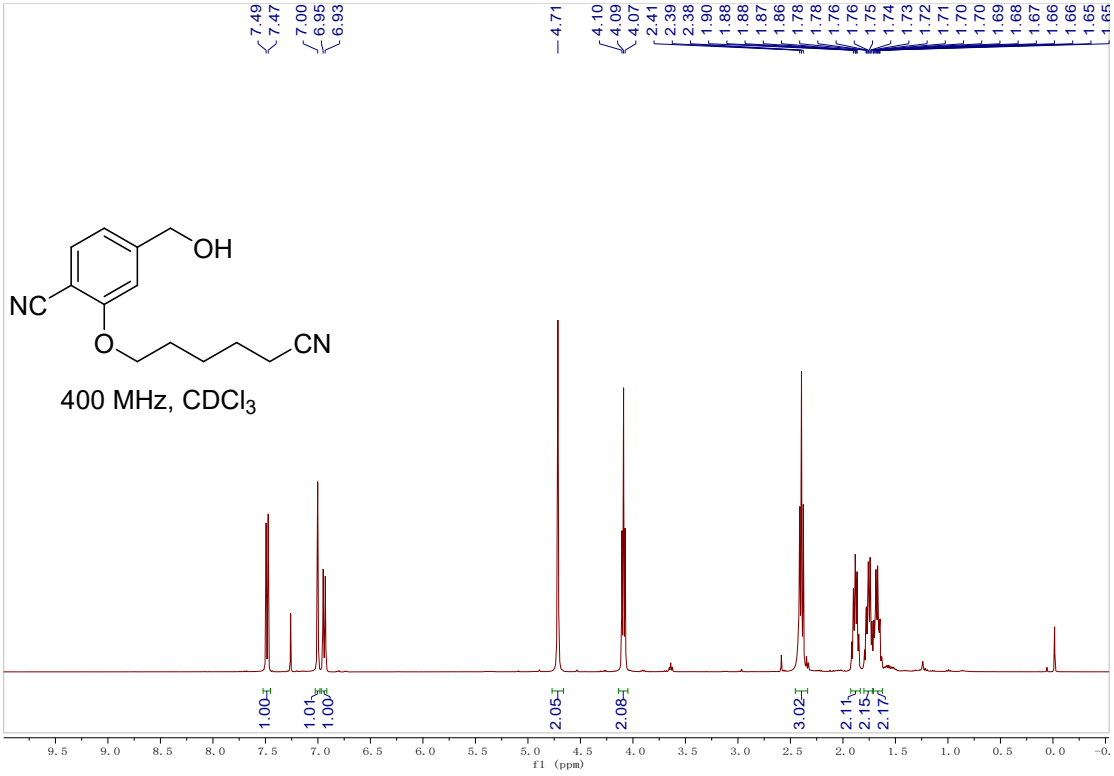


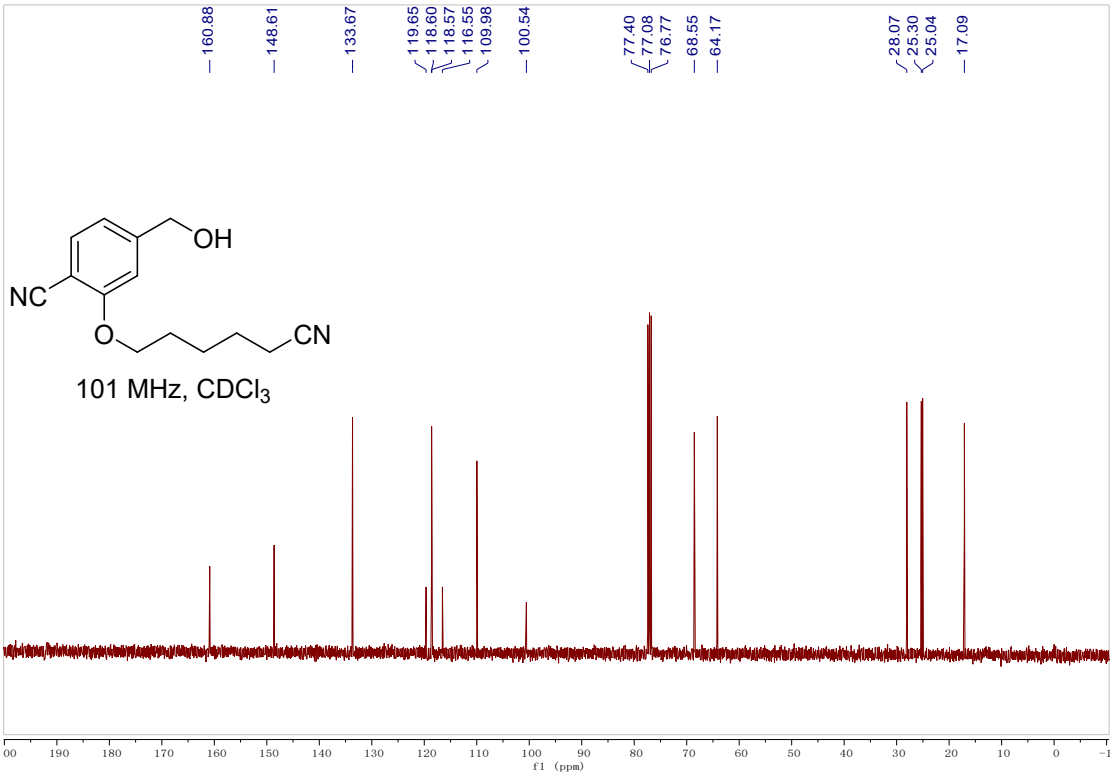
4-(Hydroxymethyl)-2-(prop-2-yn-1-yloxy)benzonitrile (1q)



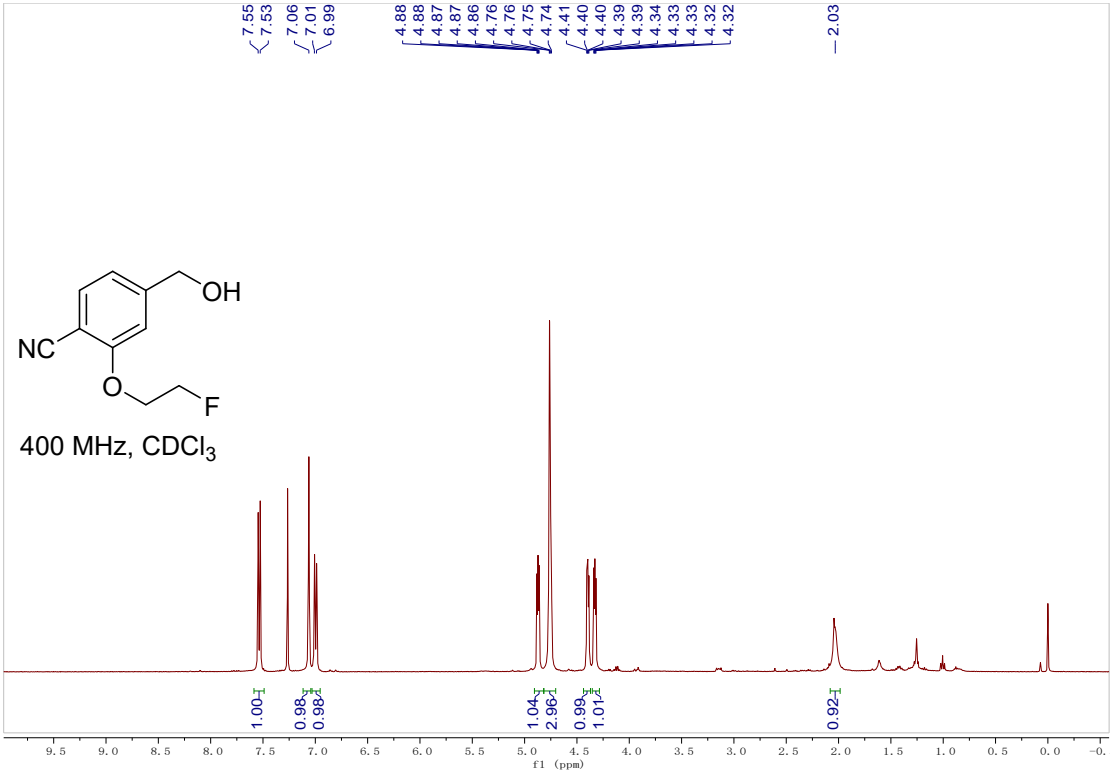


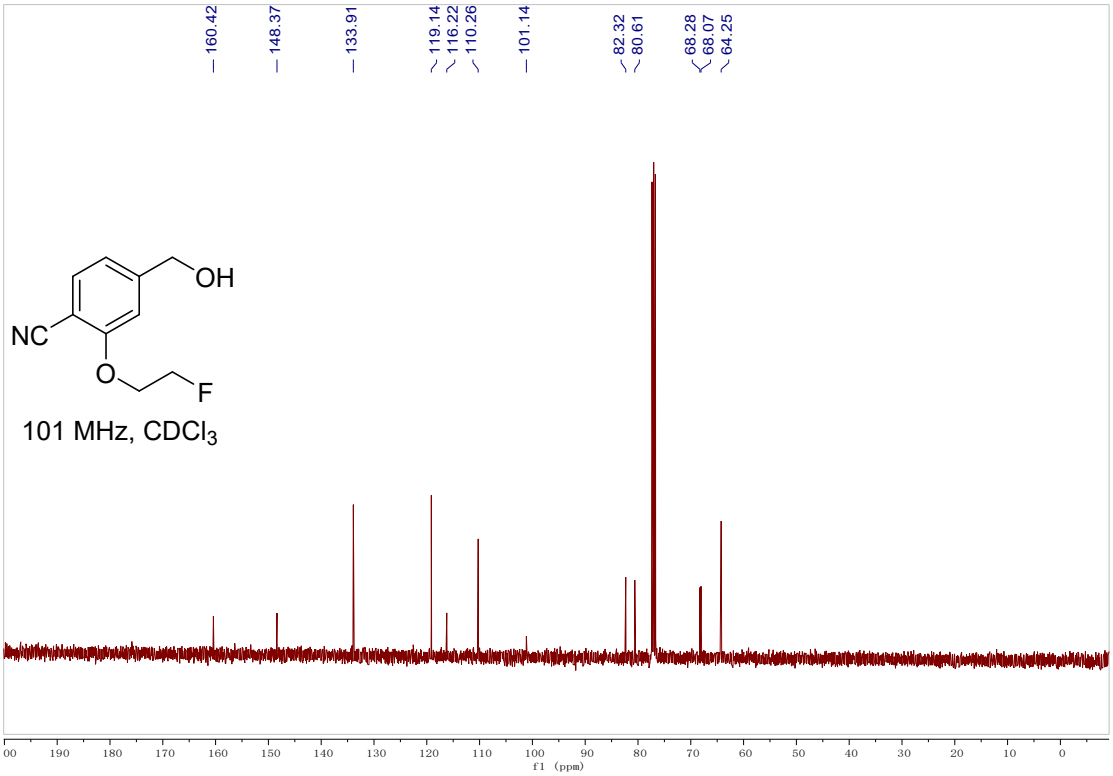
2-((5-Cyanopentyl)oxy)-4-(hydroxymethyl)benzonitrile (1r)

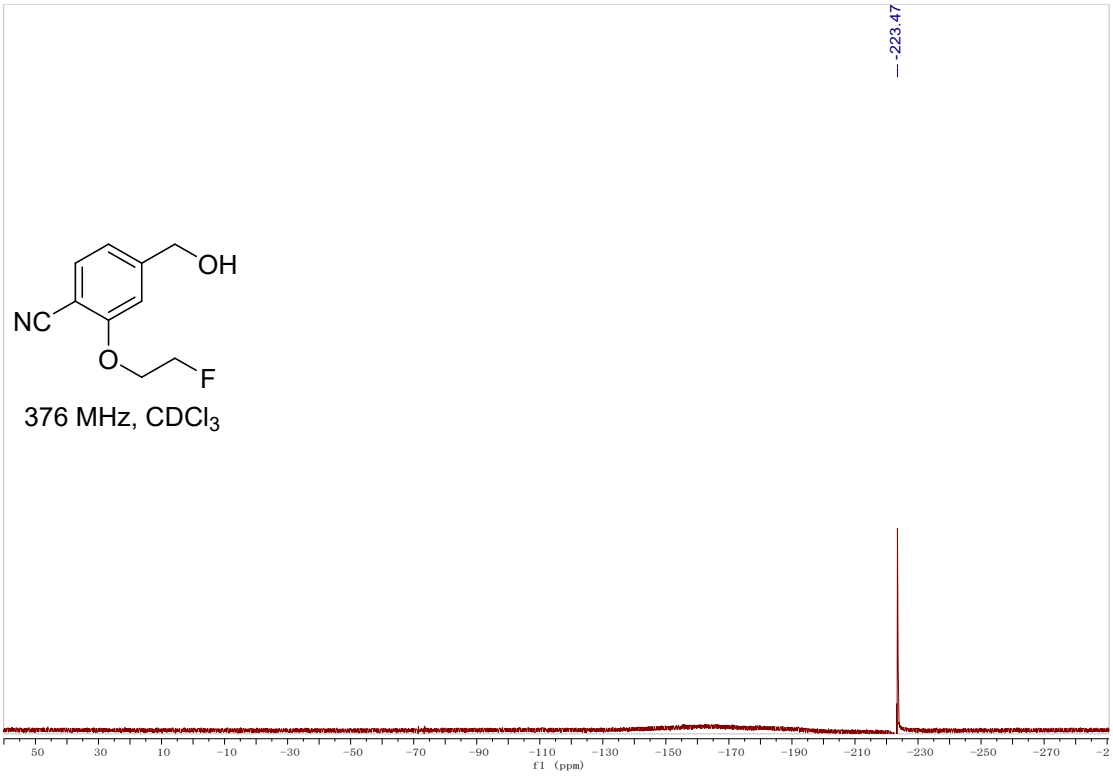




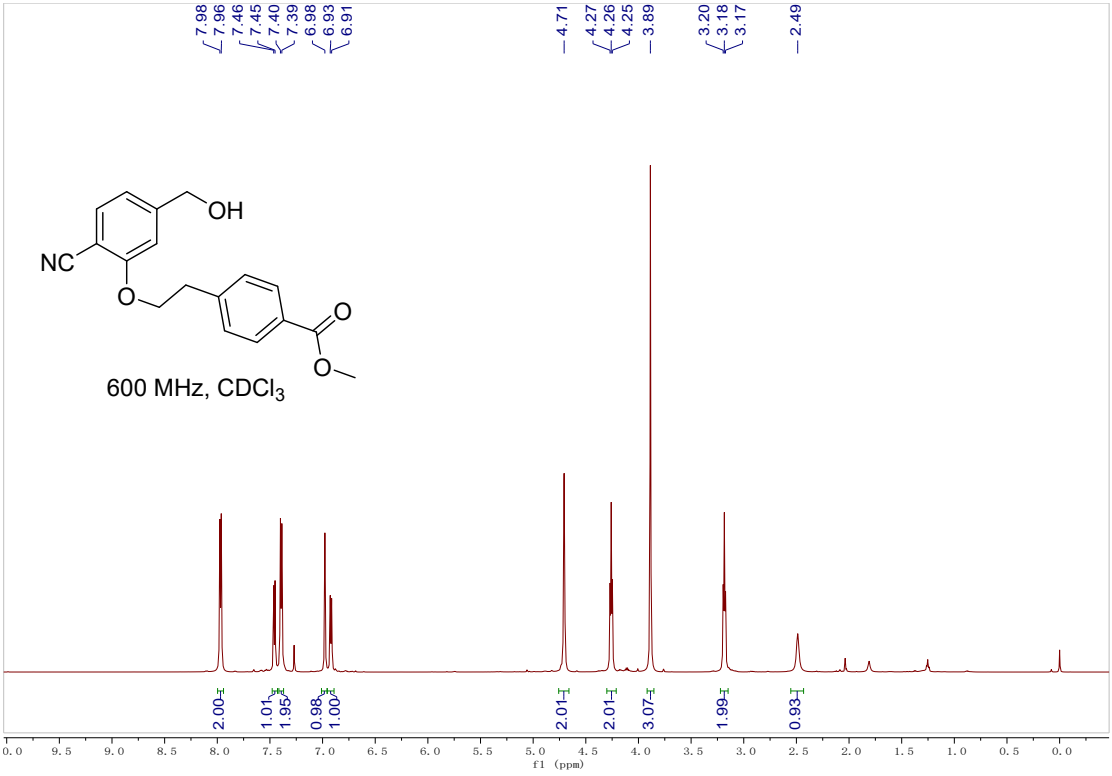
2-(2-Fluoroethoxy)-4-(hydroxymethyl)benzonitrile (1s)

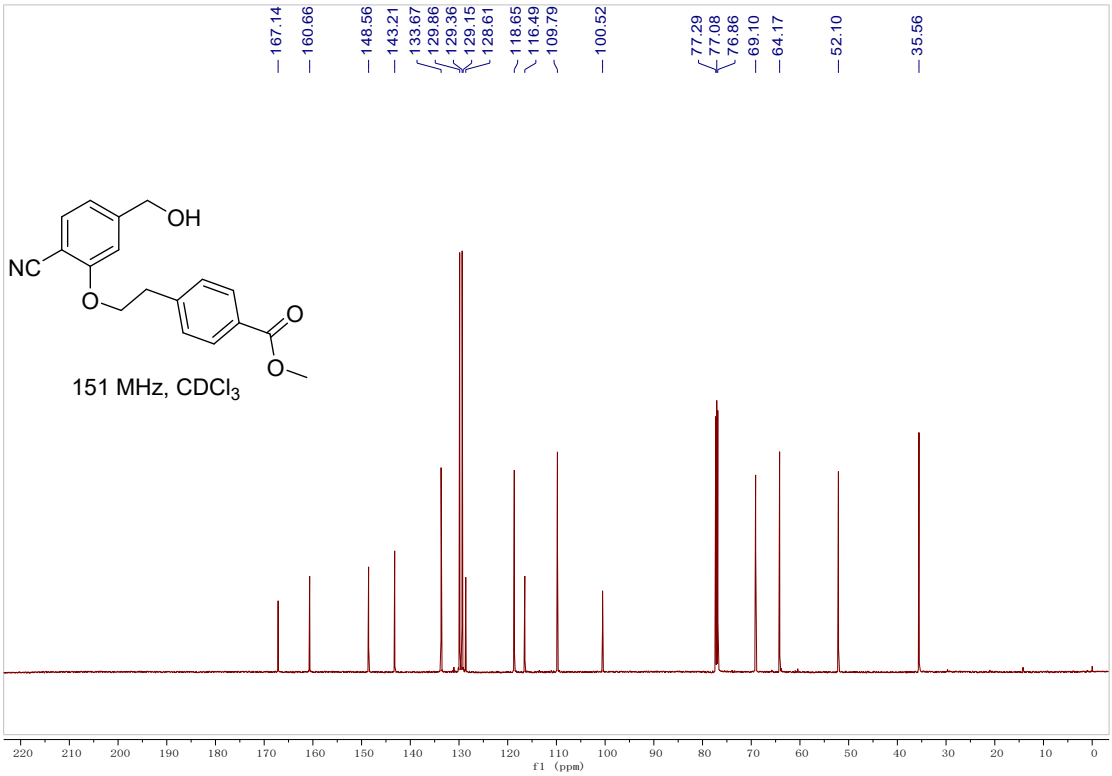




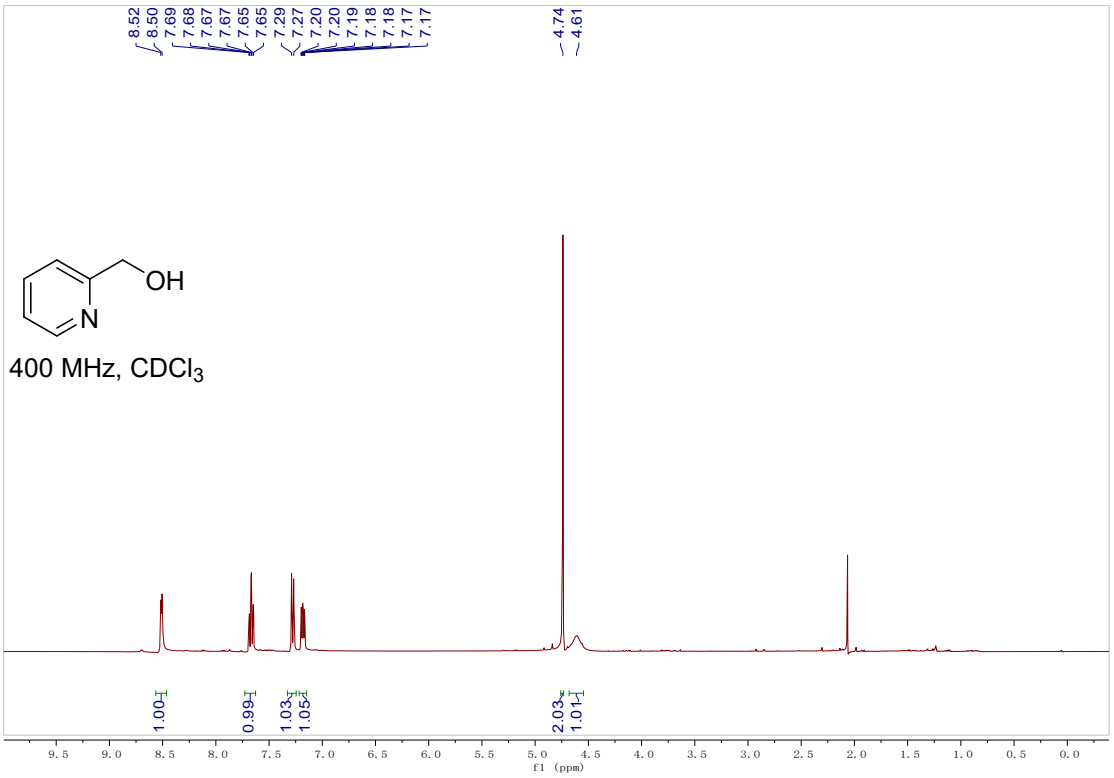

-223.47
OH
NC
O
F
376 MHz, CDCl3
50
30
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
−190
−210
−230
−250
−270
f1 (ppm)

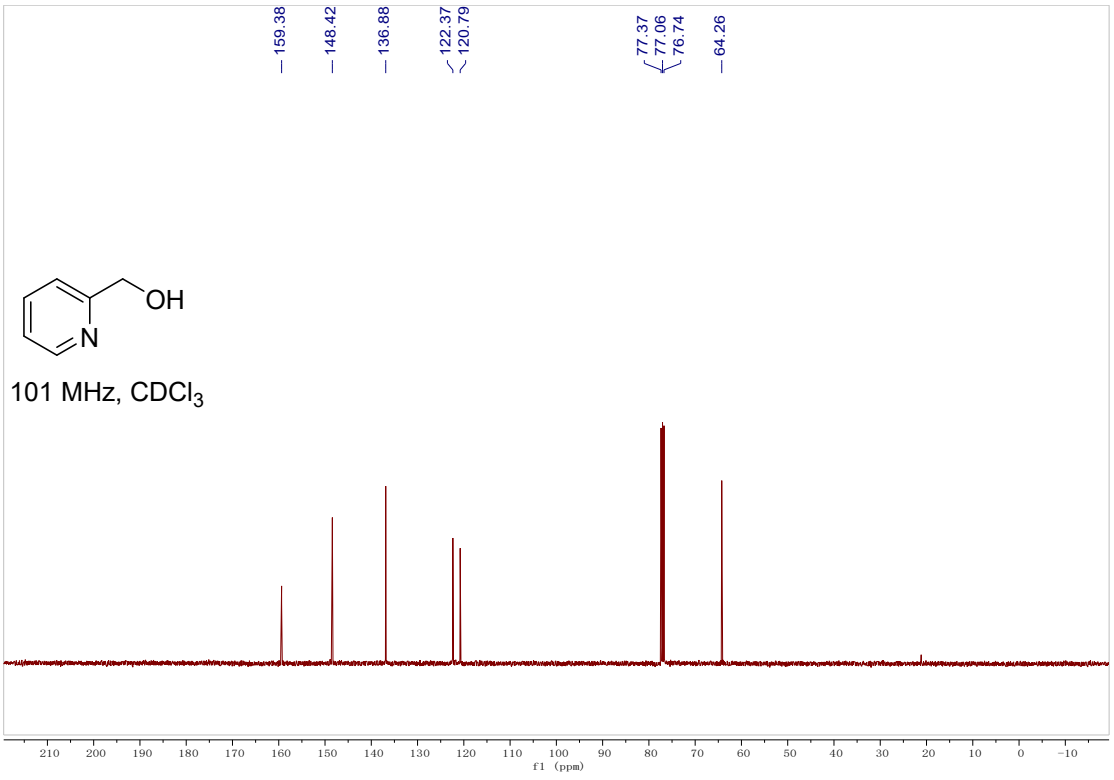
Methyl 4-(2-(2-cyano-5-(hydroxymethyl)phenoxy)ethyl)benzoate (1t)



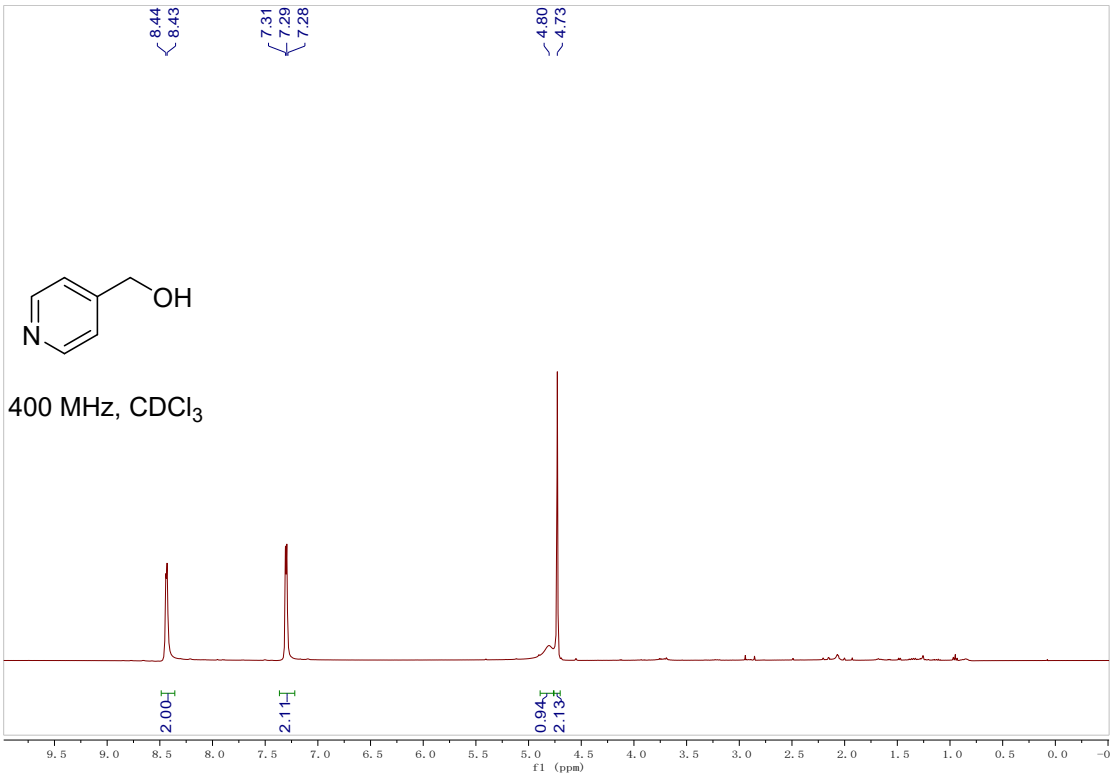


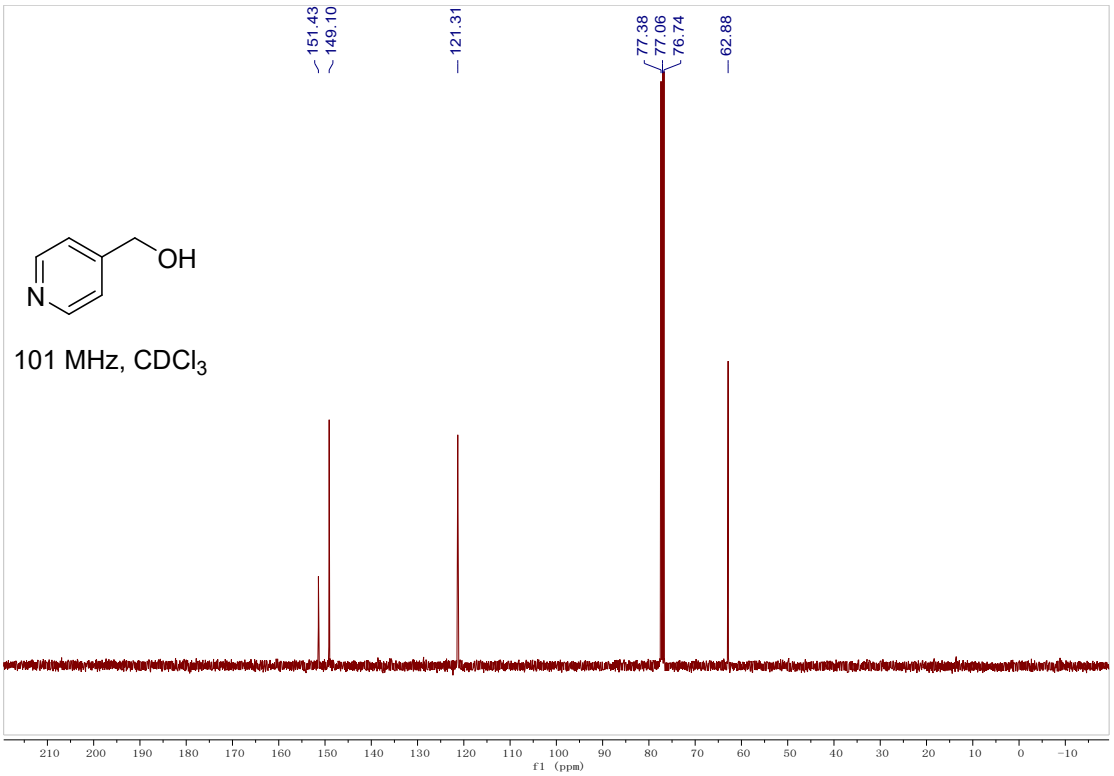
Pyridin-2-ylmethanol (1u)



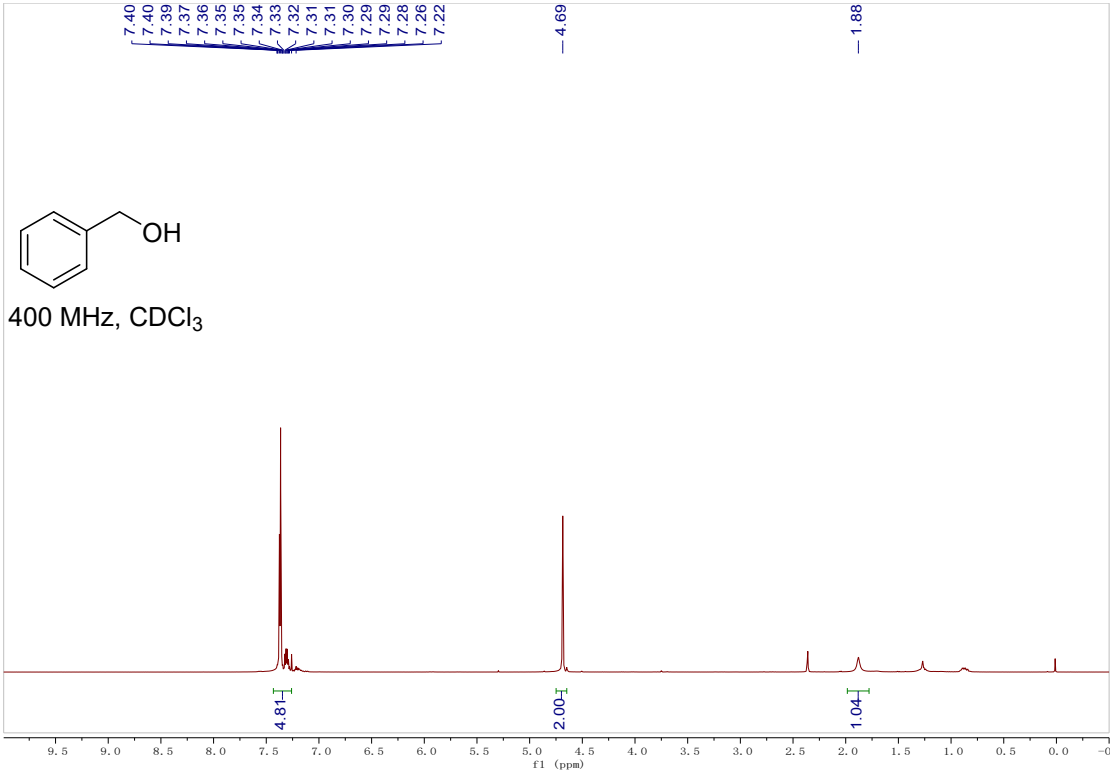


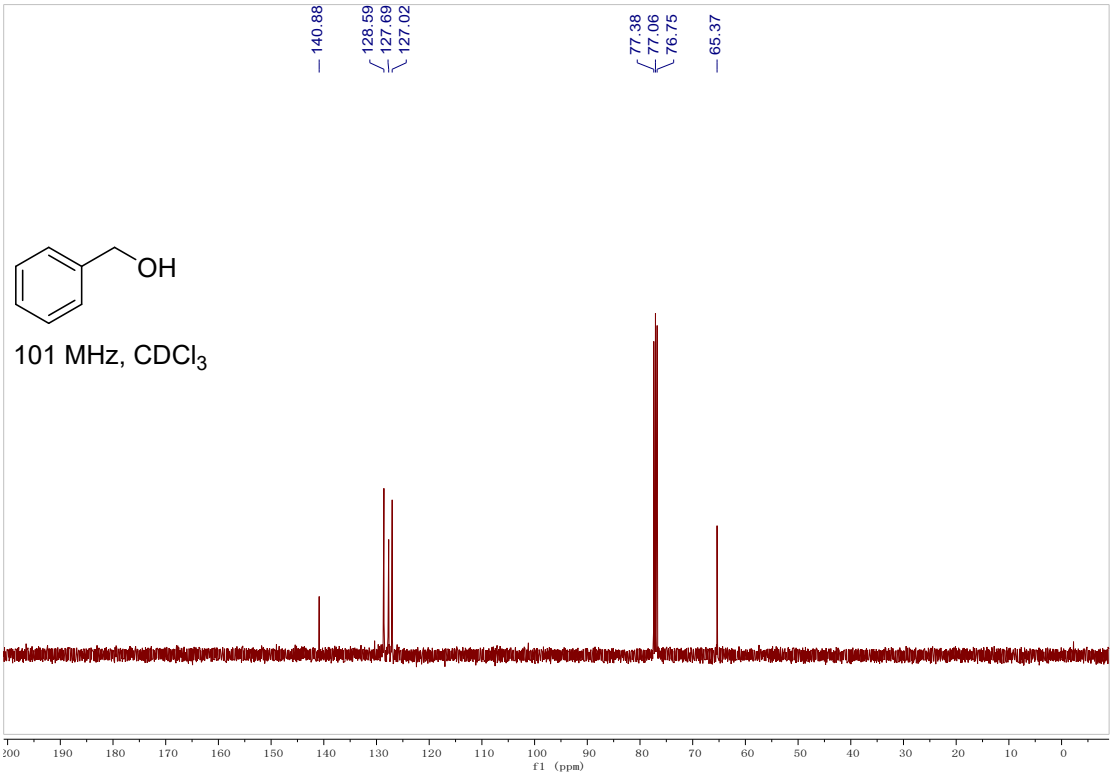
Pyridin-4-ylmethanol (1v)



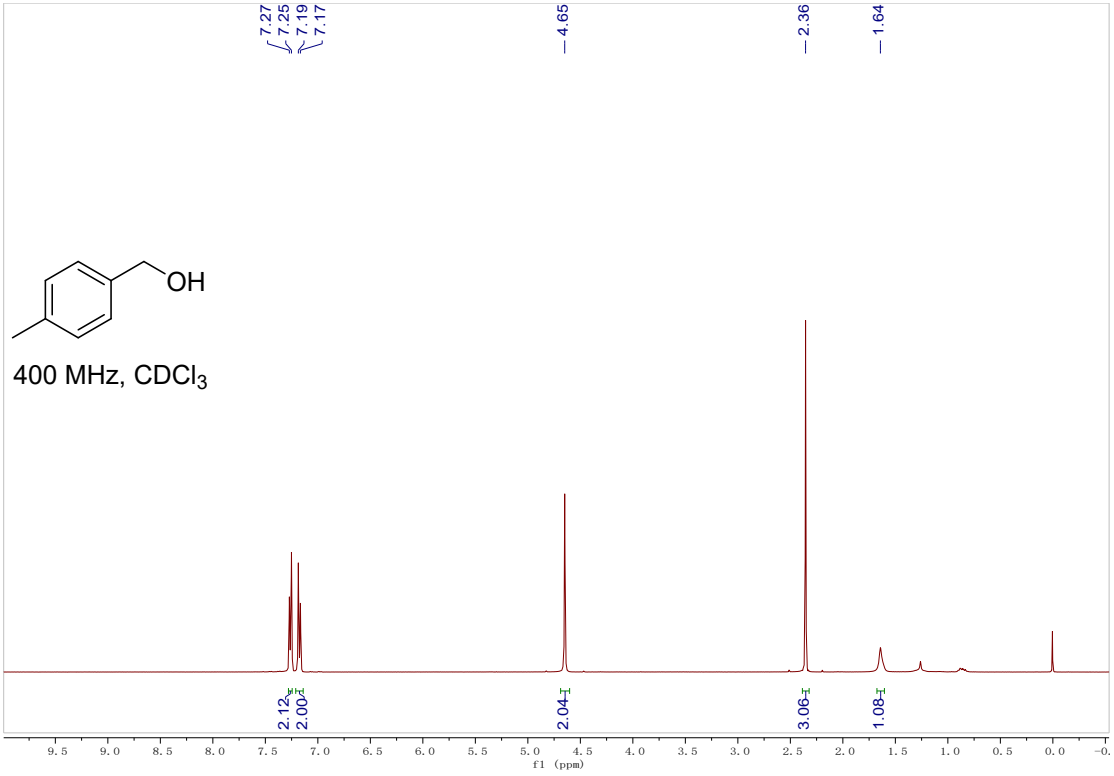


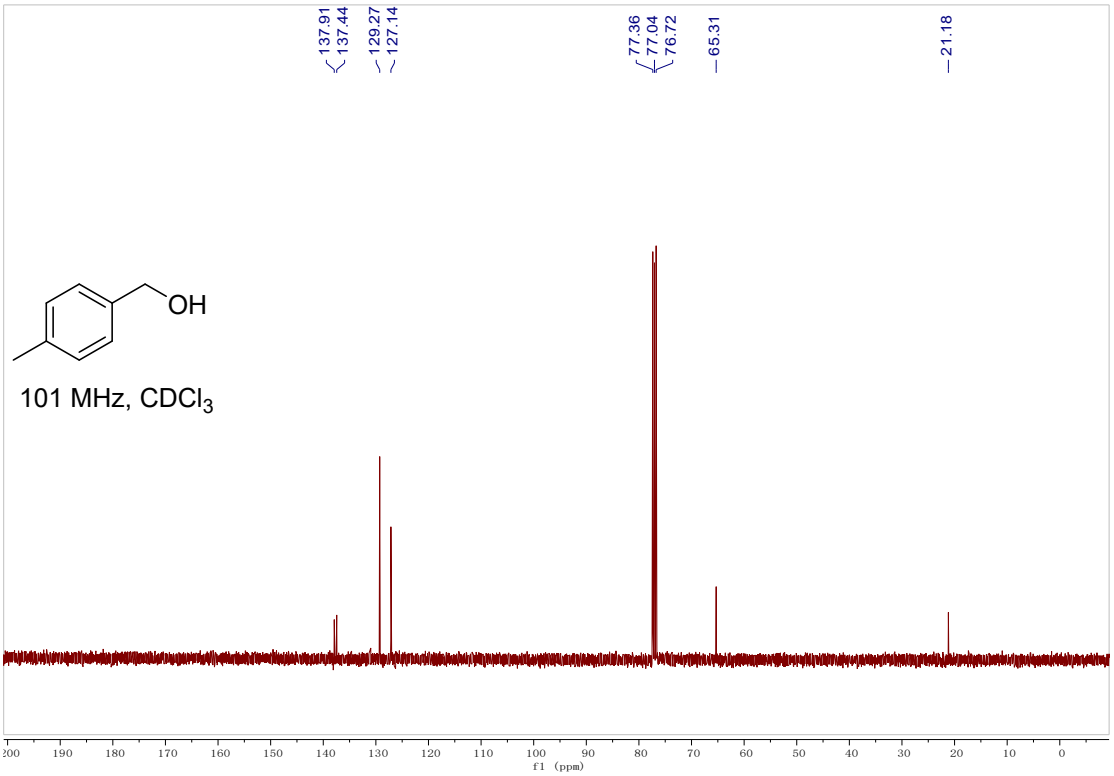
Phenylmethanol (2a)



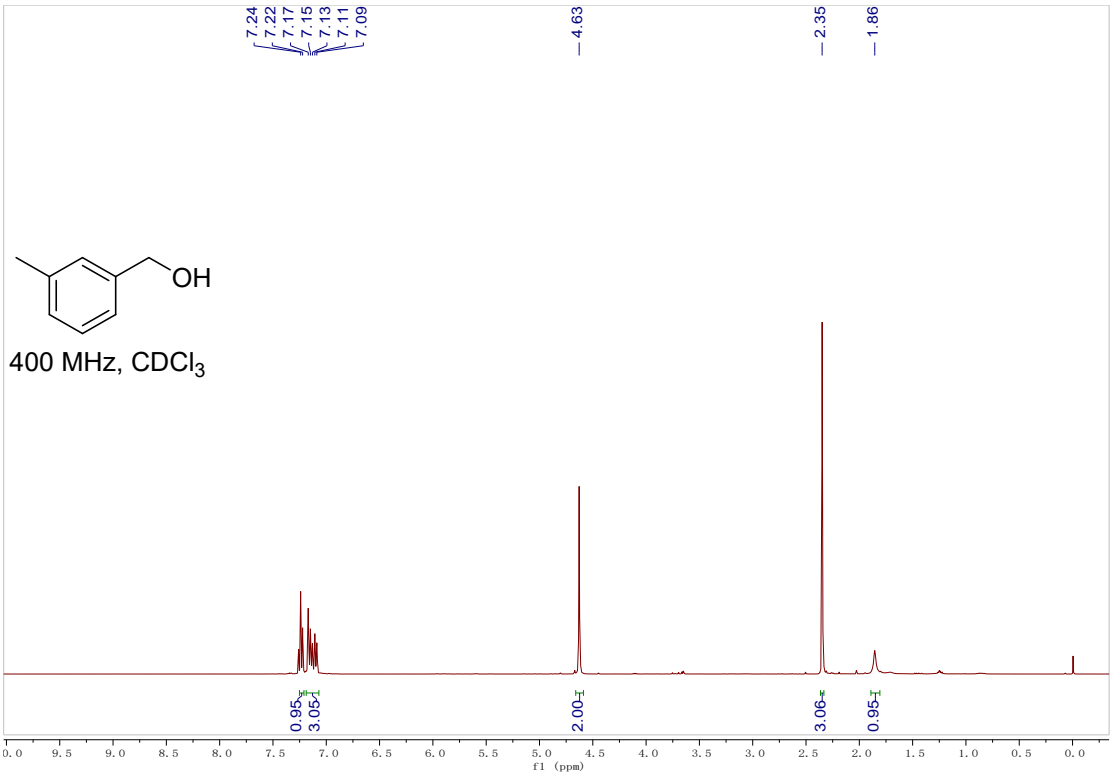


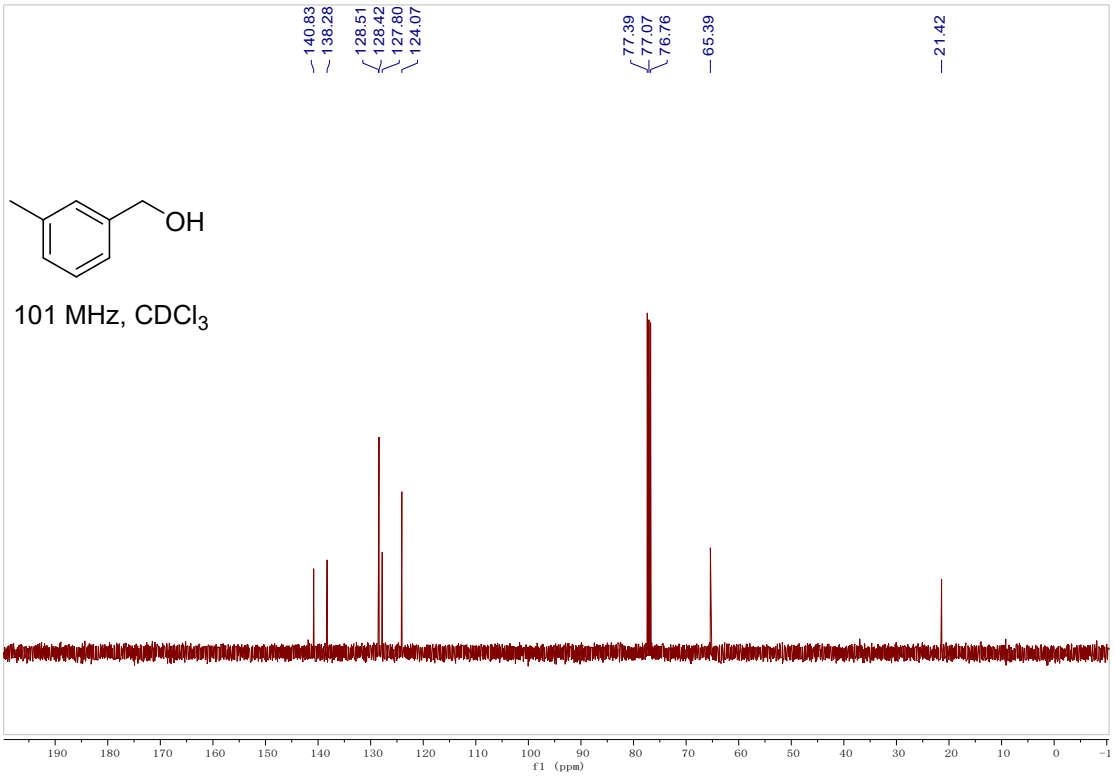
***p*-Tolylmethanol (2b)**



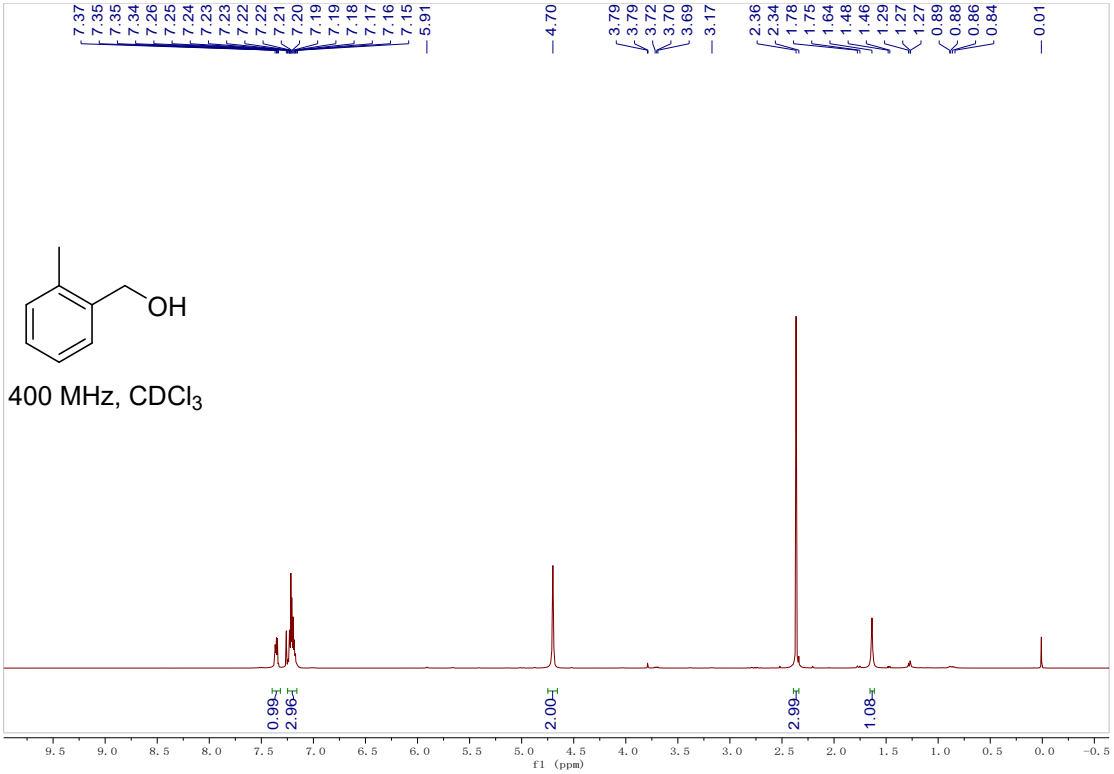


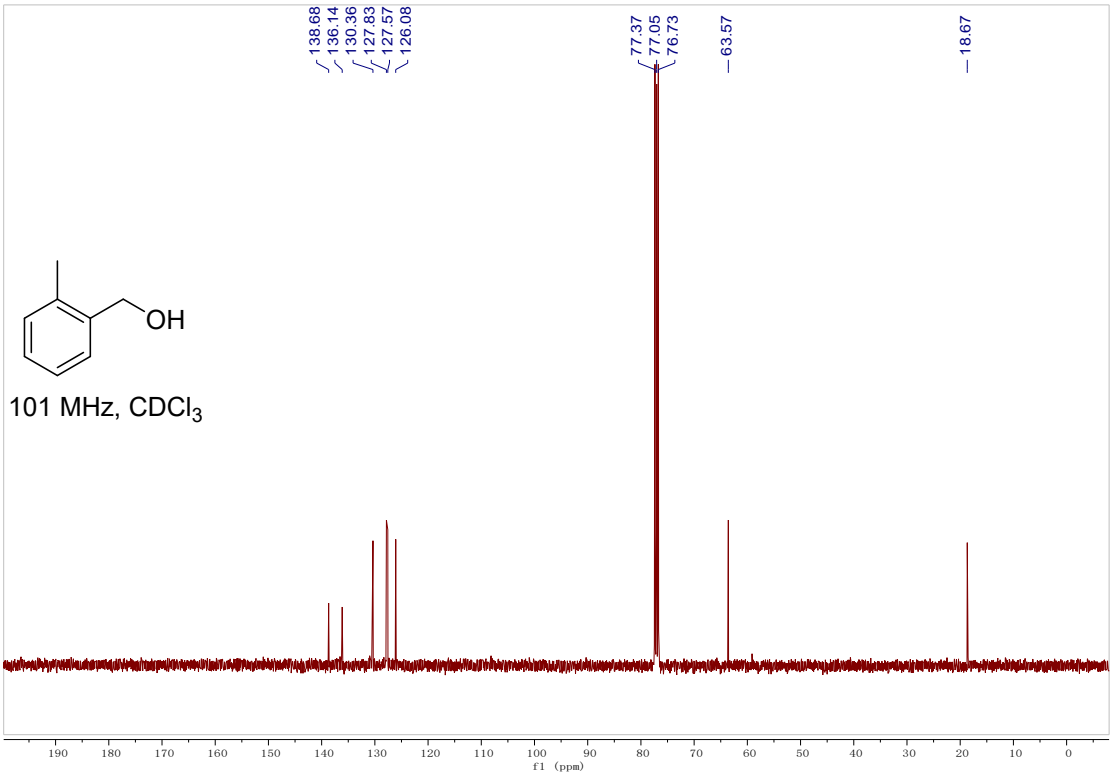
***m*-Tolylmethanol (2e)**



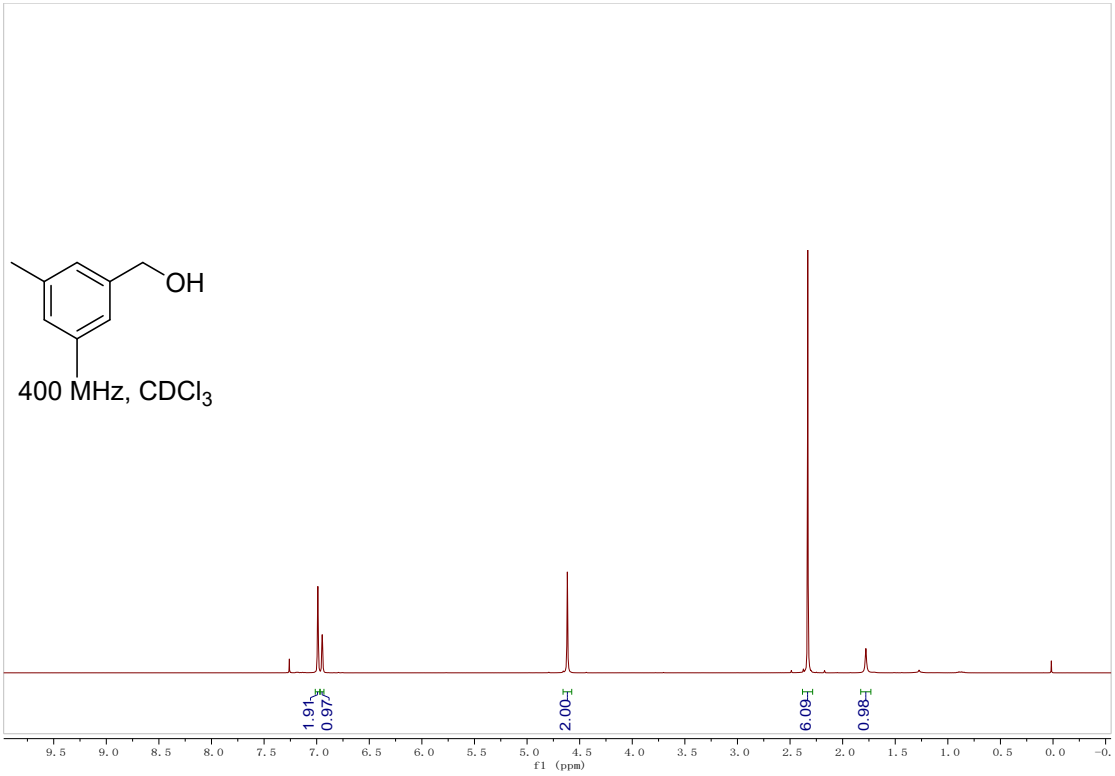


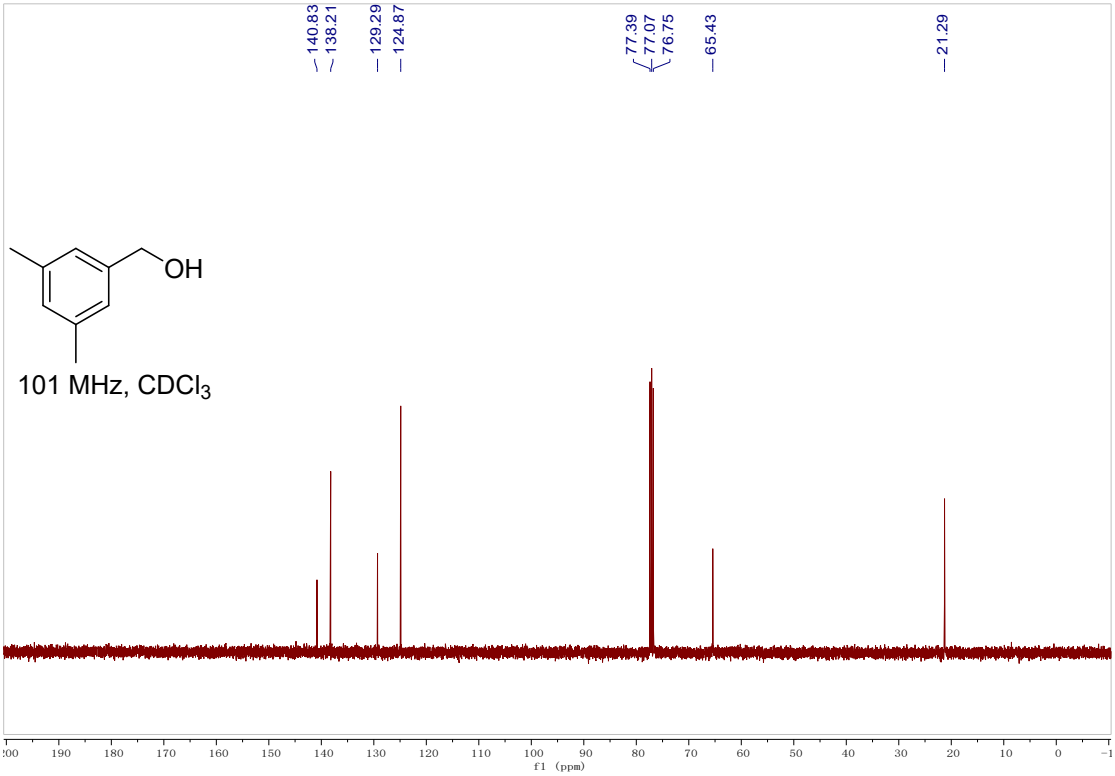
***o*-Tolylmethanol (2f)**



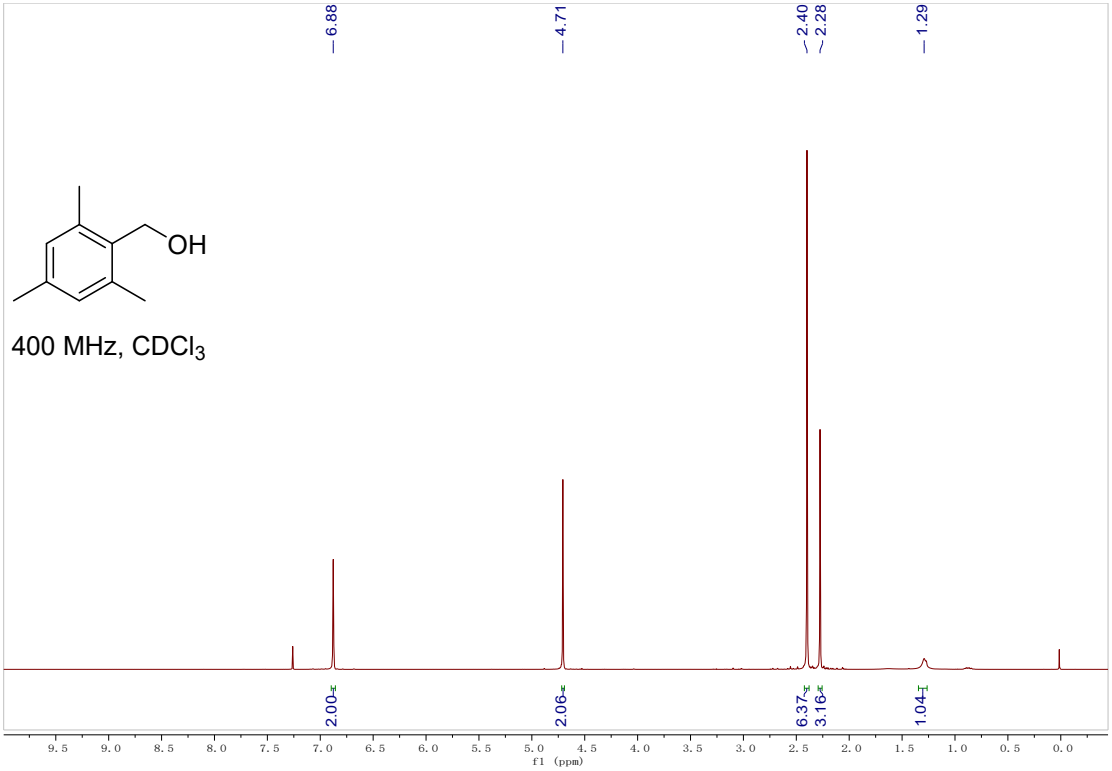


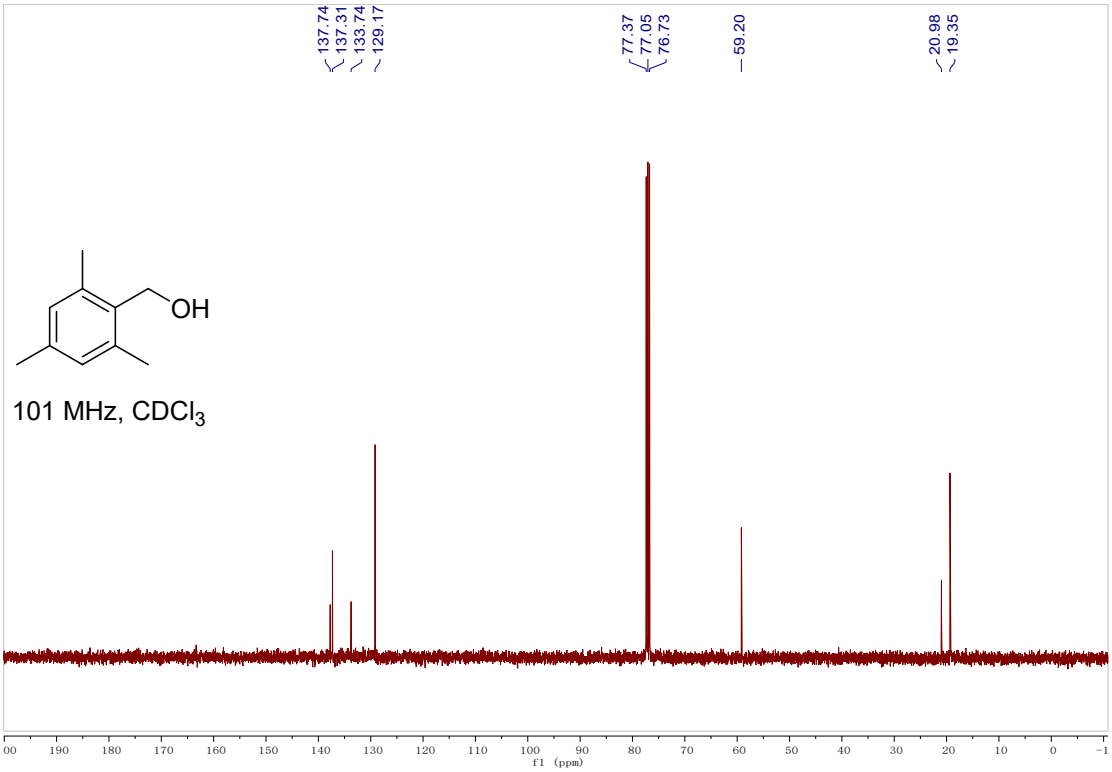
(3,5-Dimethylphenyl)methanol (2g)



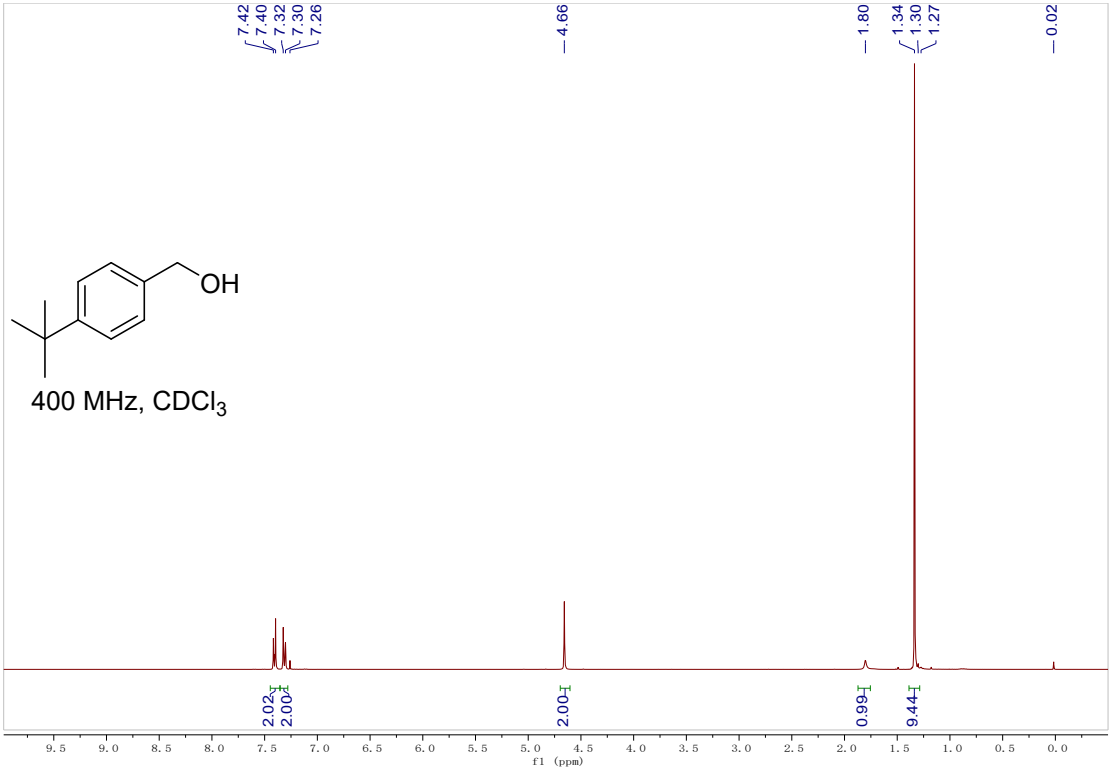


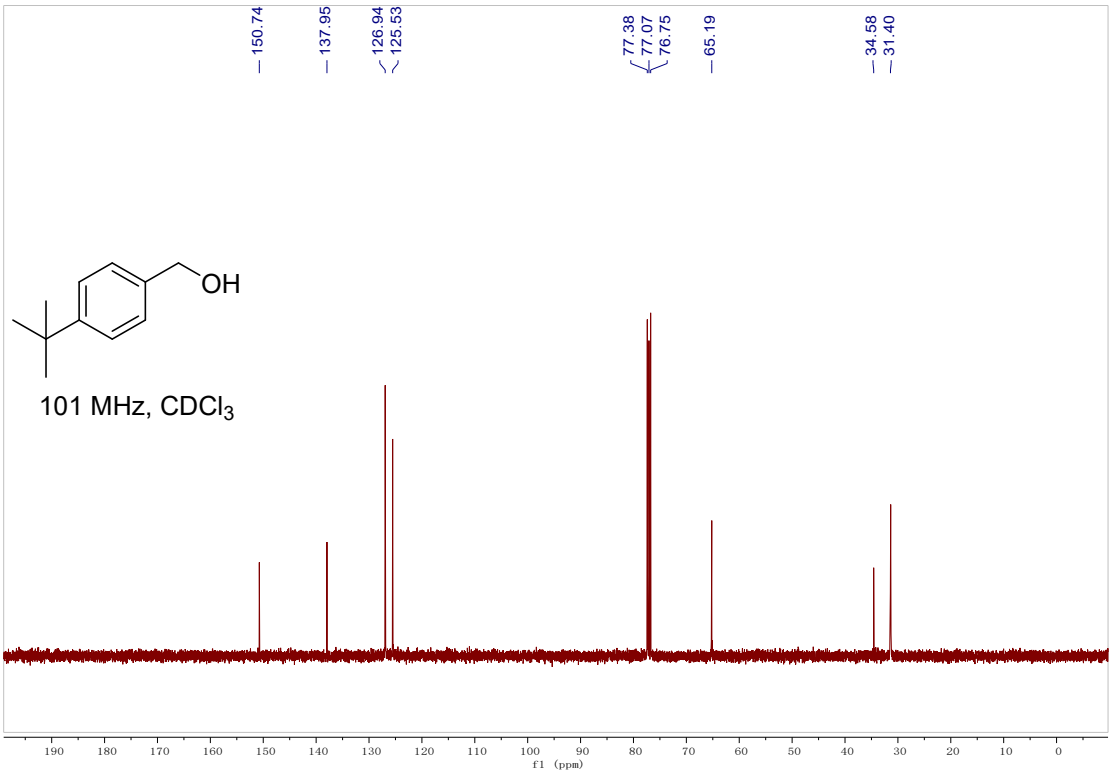
Mesitylmethanol (2h)



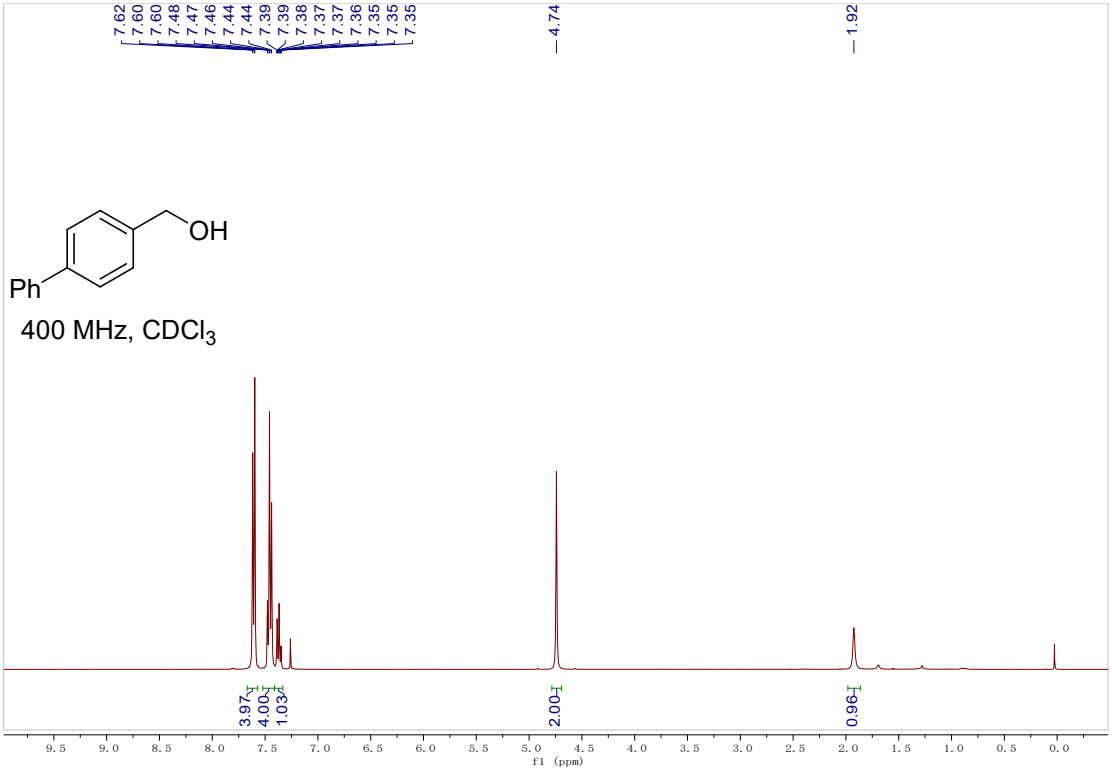


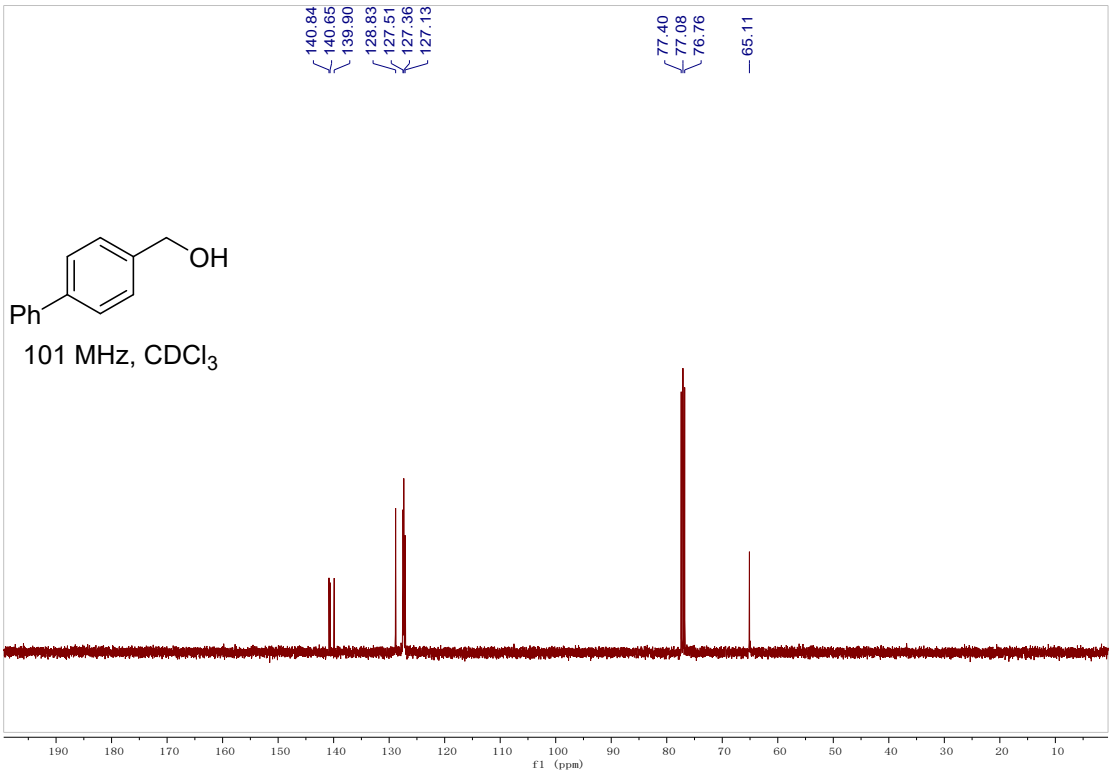
(4-(tert-Butyl)phenyl)methanol (2i)



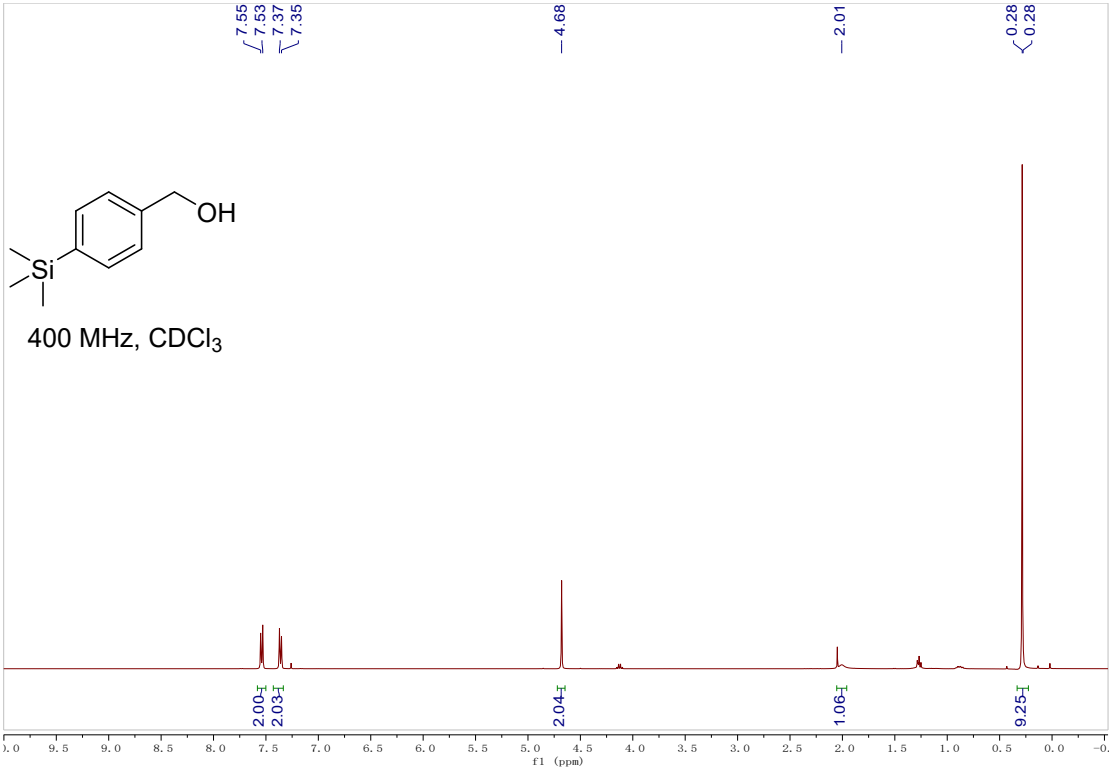


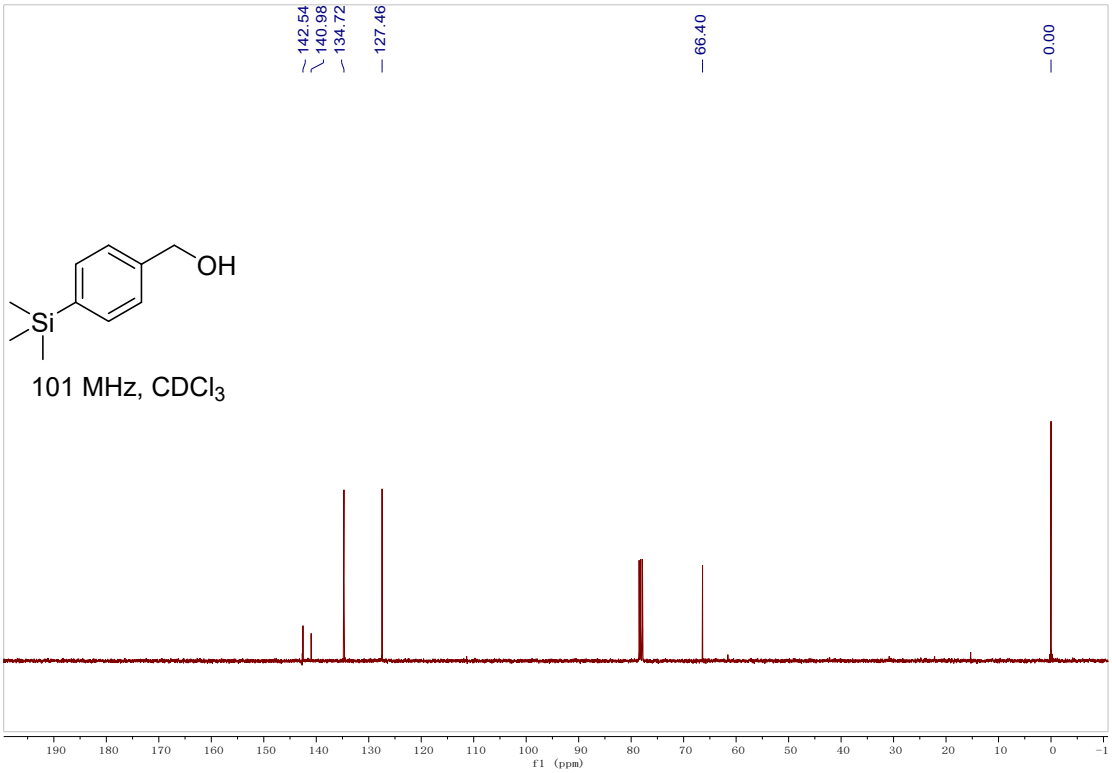
[1, 1'-Biphenyl]-4-ylmethanol (2j)



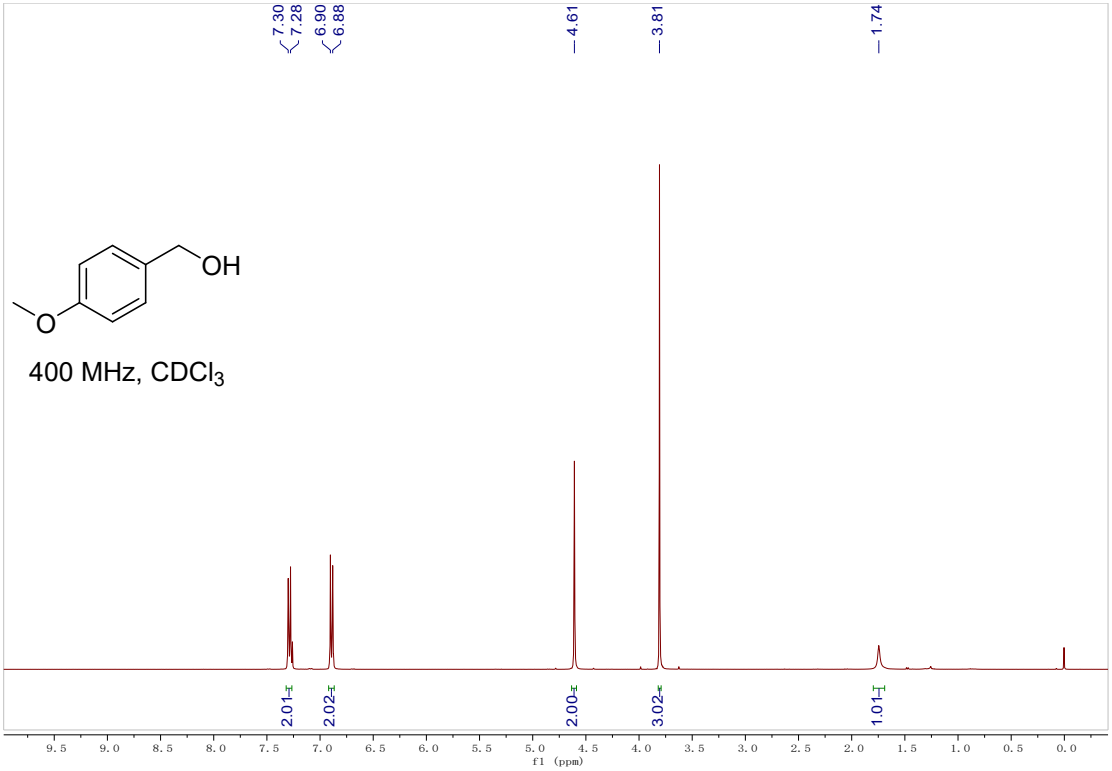


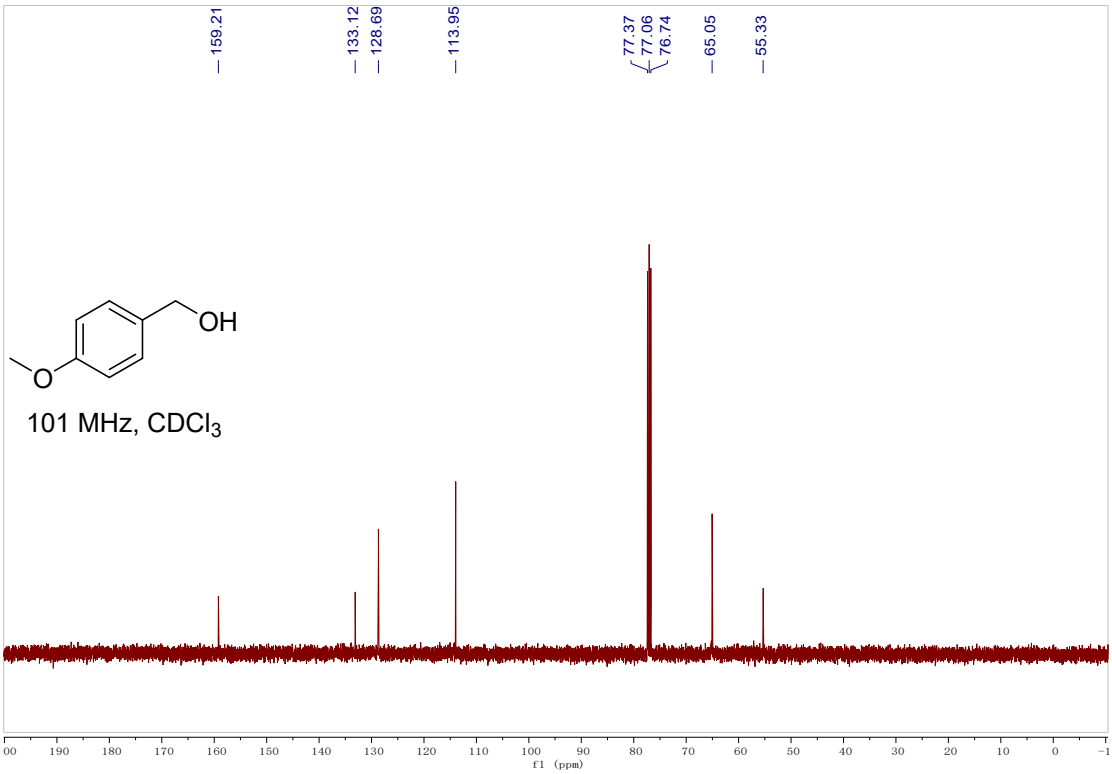
(4-(Trimethylsilyl)phenyl)methanol (2k)



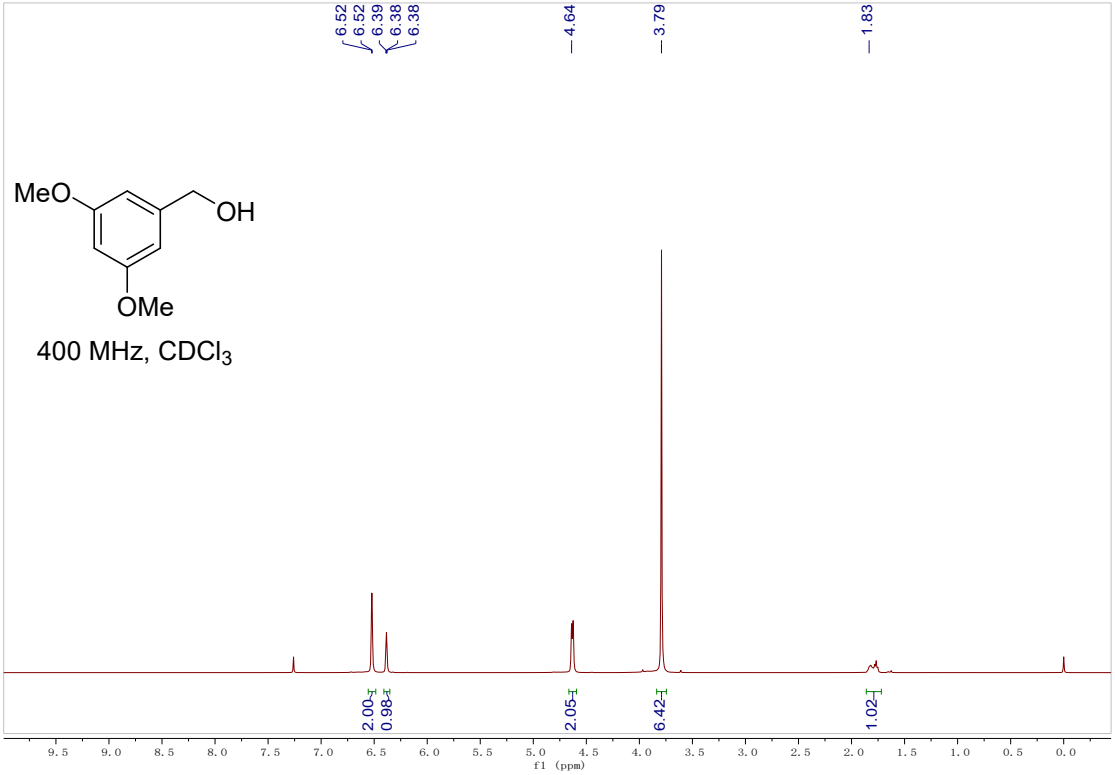


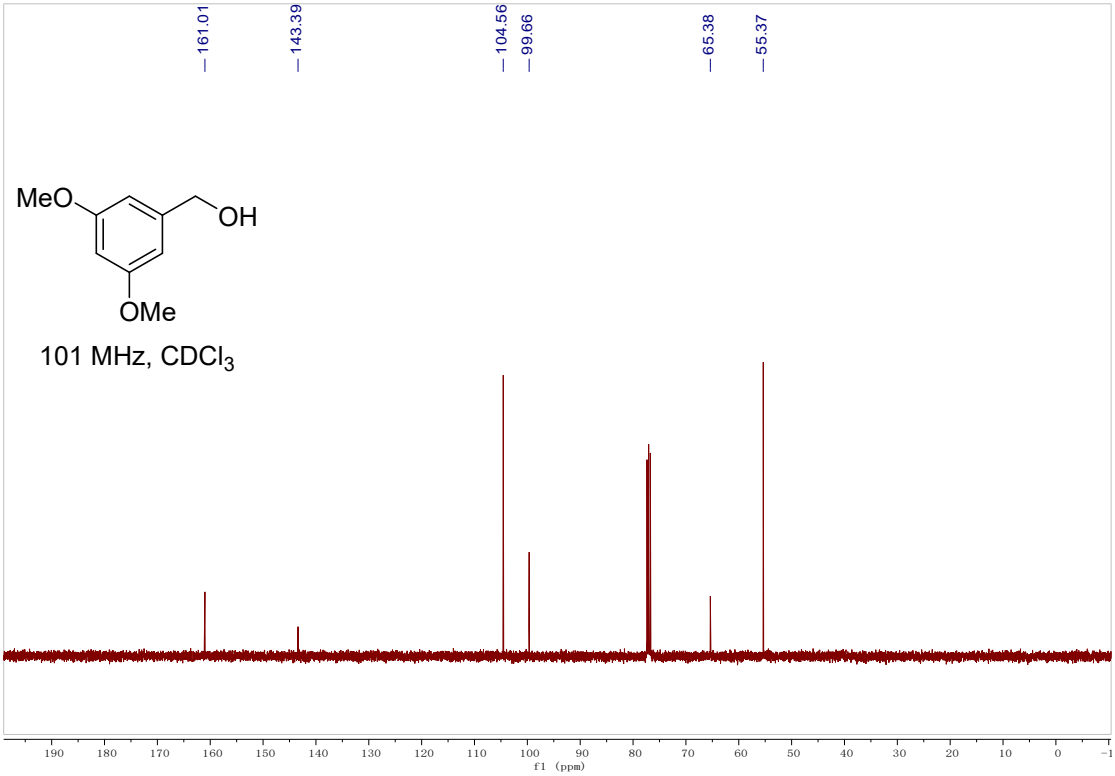
(4-Methoxyphenyl)methanol (2l)



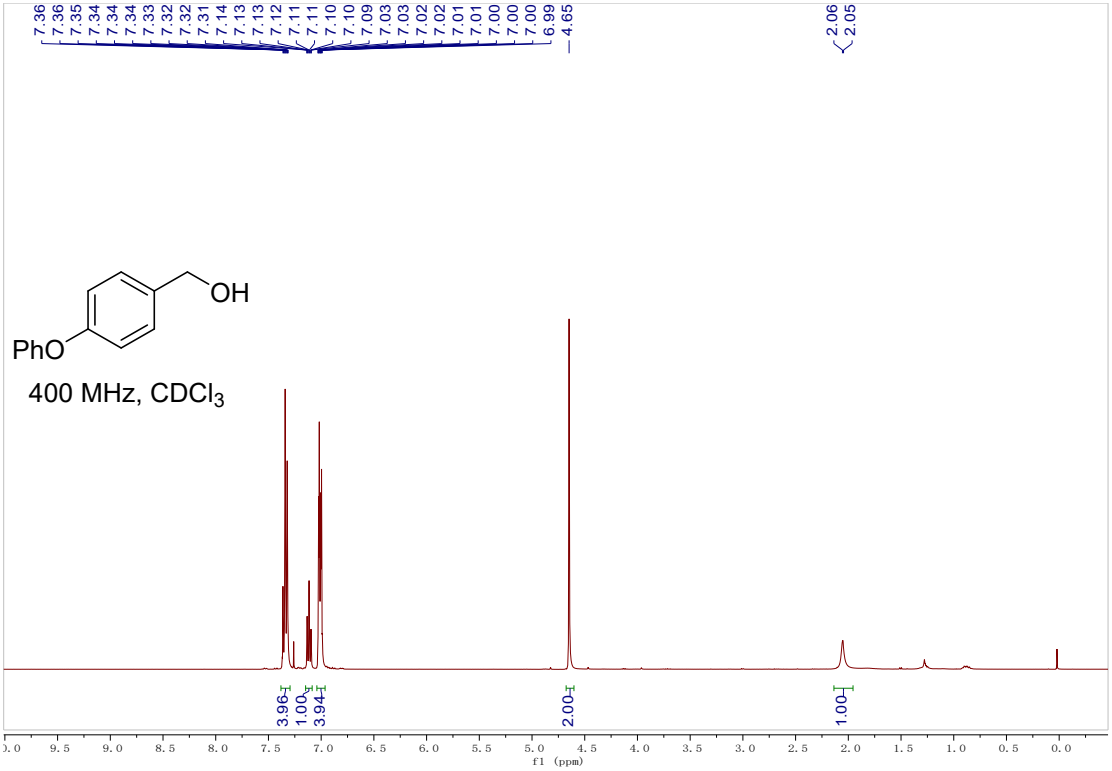


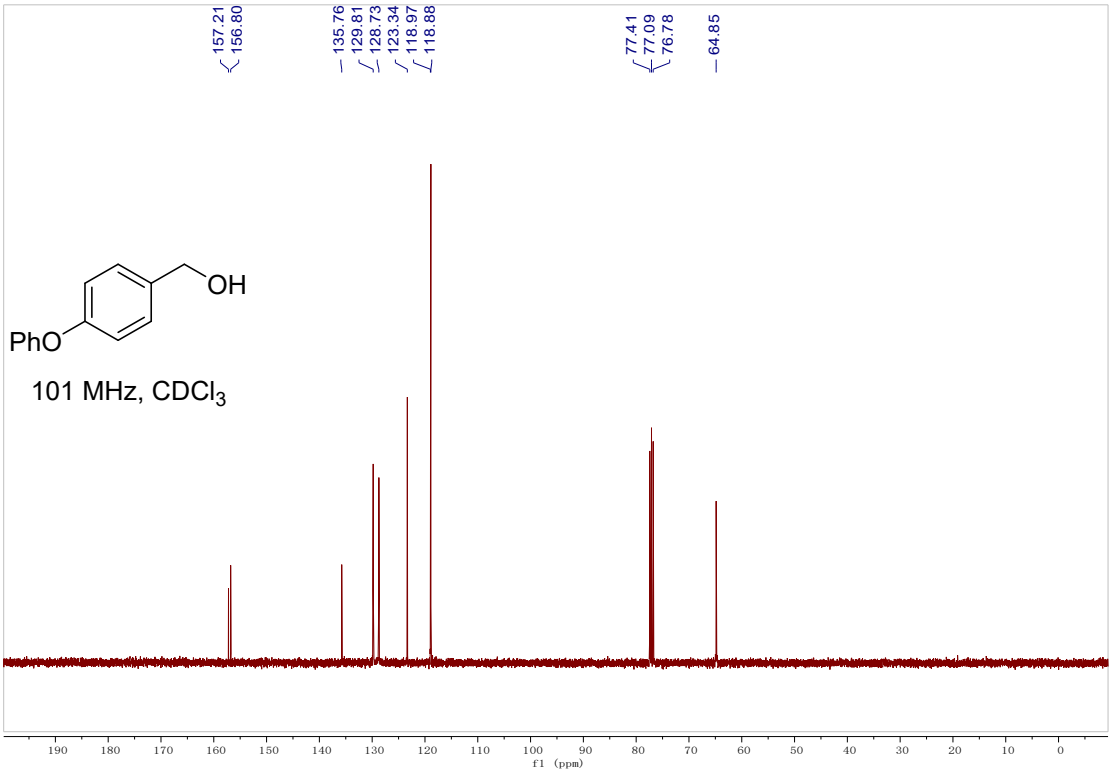
(3,5-dimethoxyphenyl)methanol (2m)



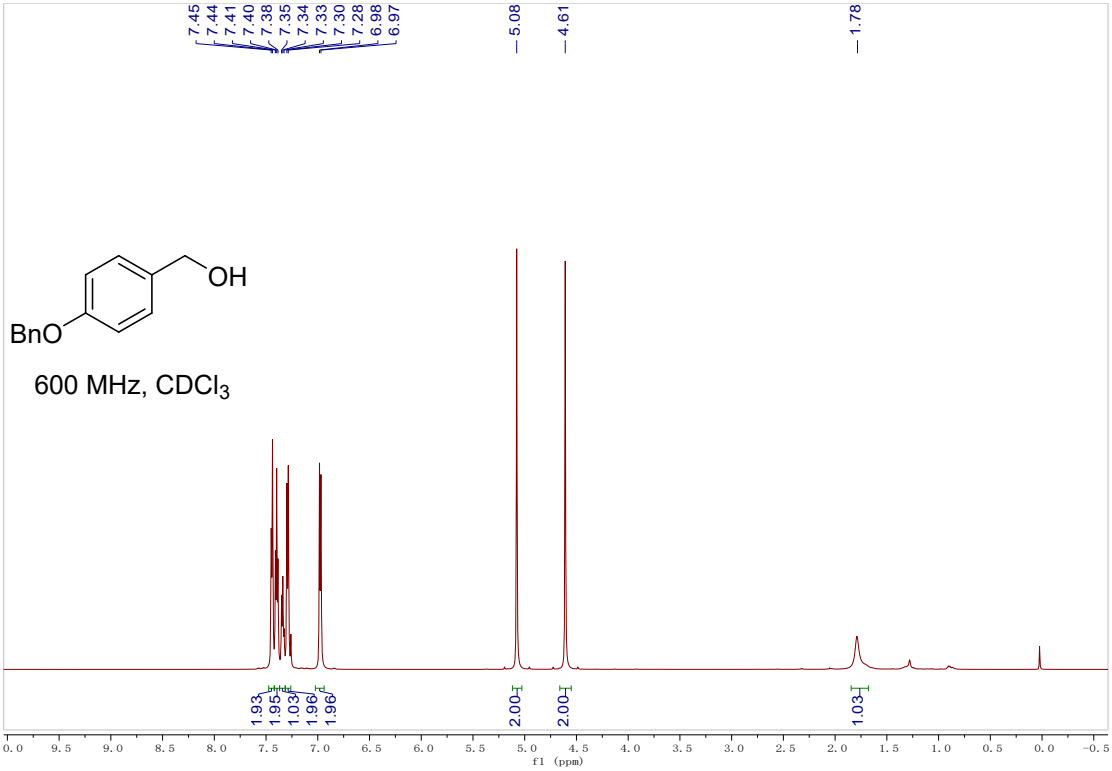


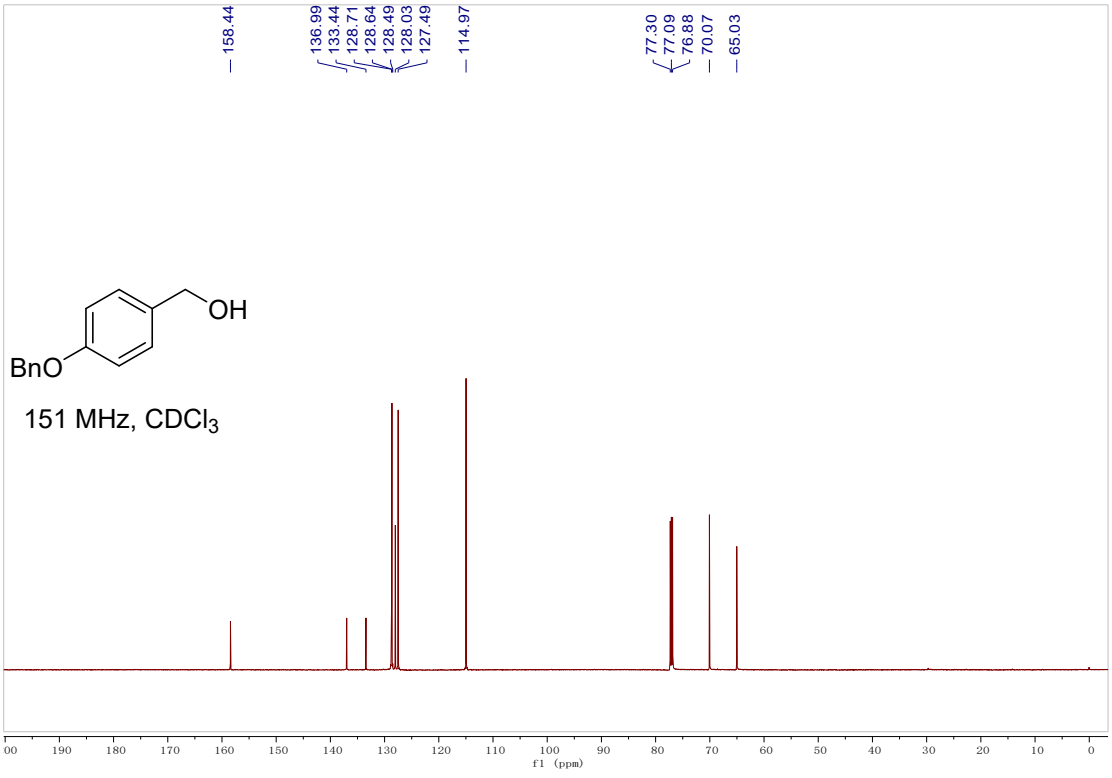
(4-Phenoxyphenyl)methanol (2n)



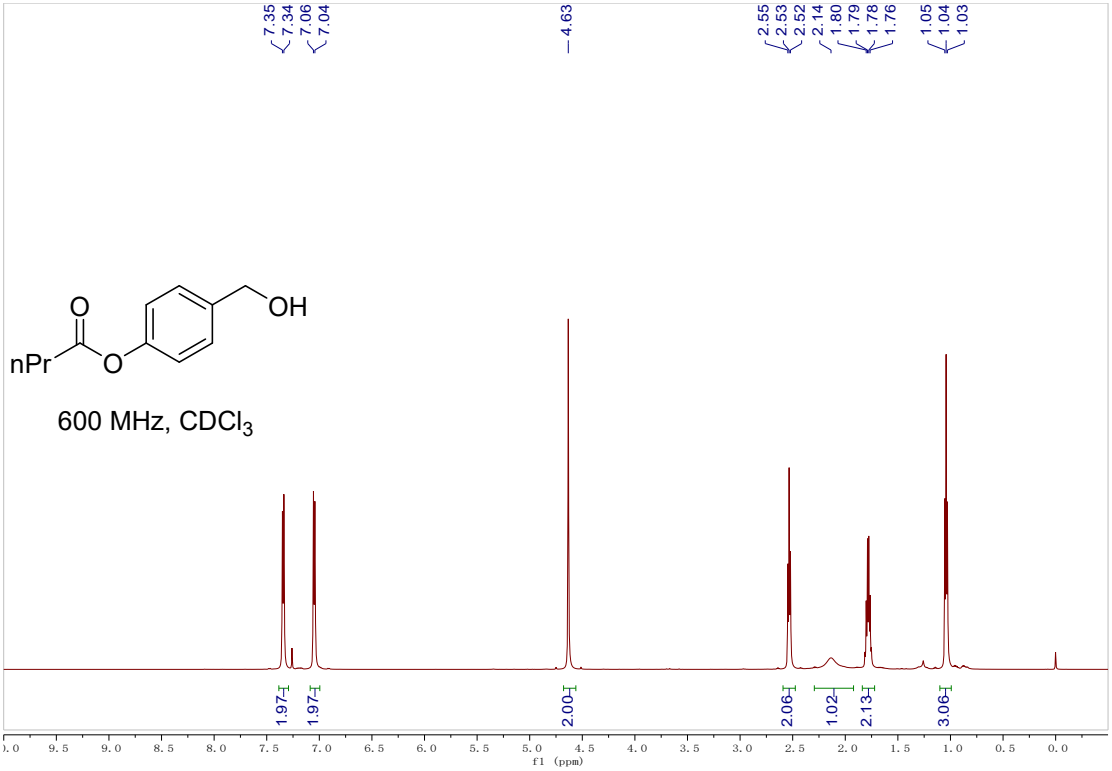


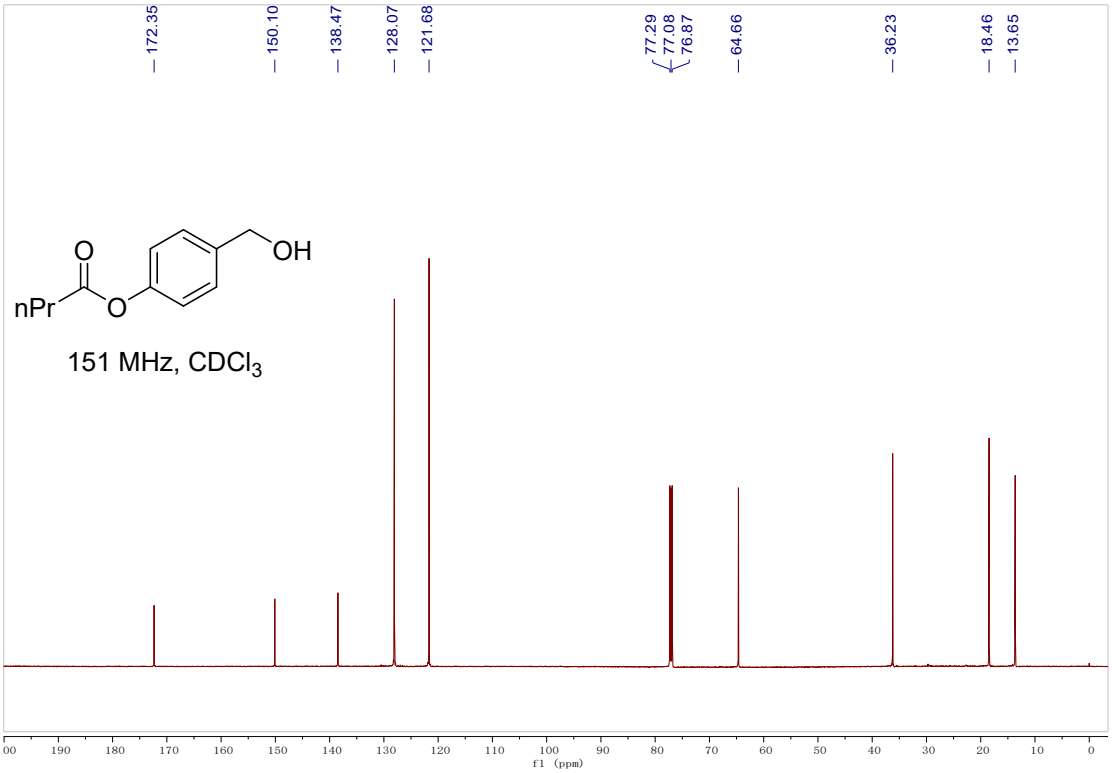
(4-(Benzyloxy)phenyl)methanol (2o)



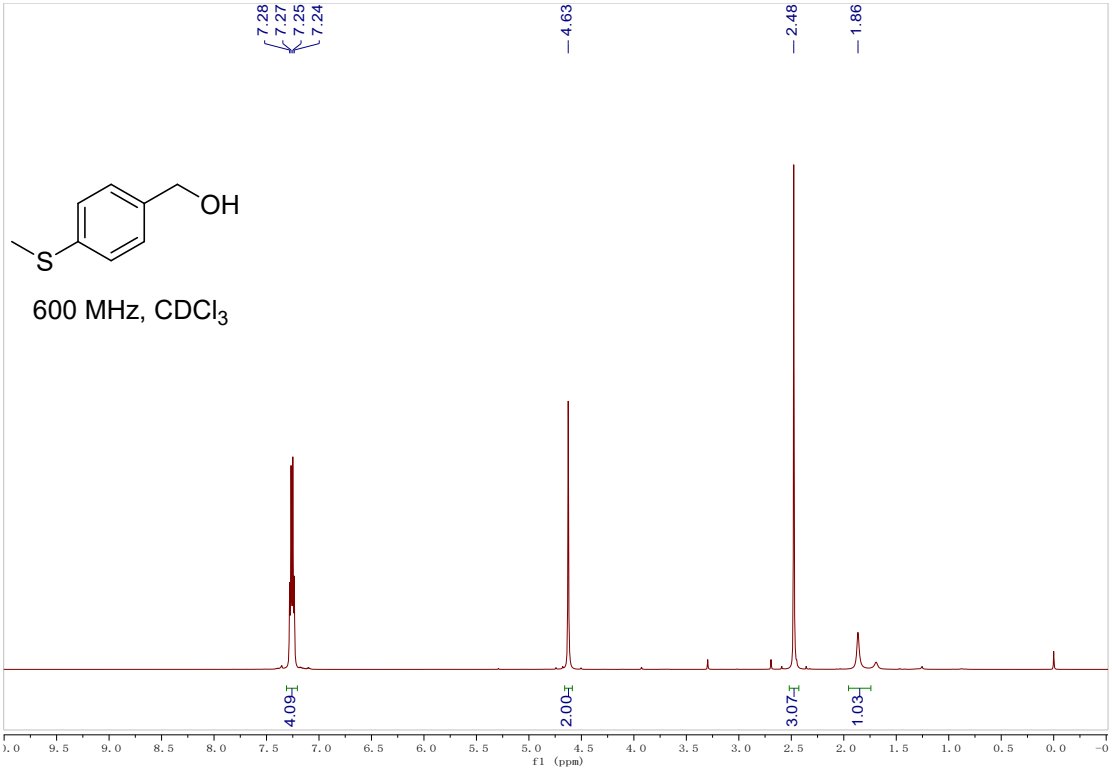


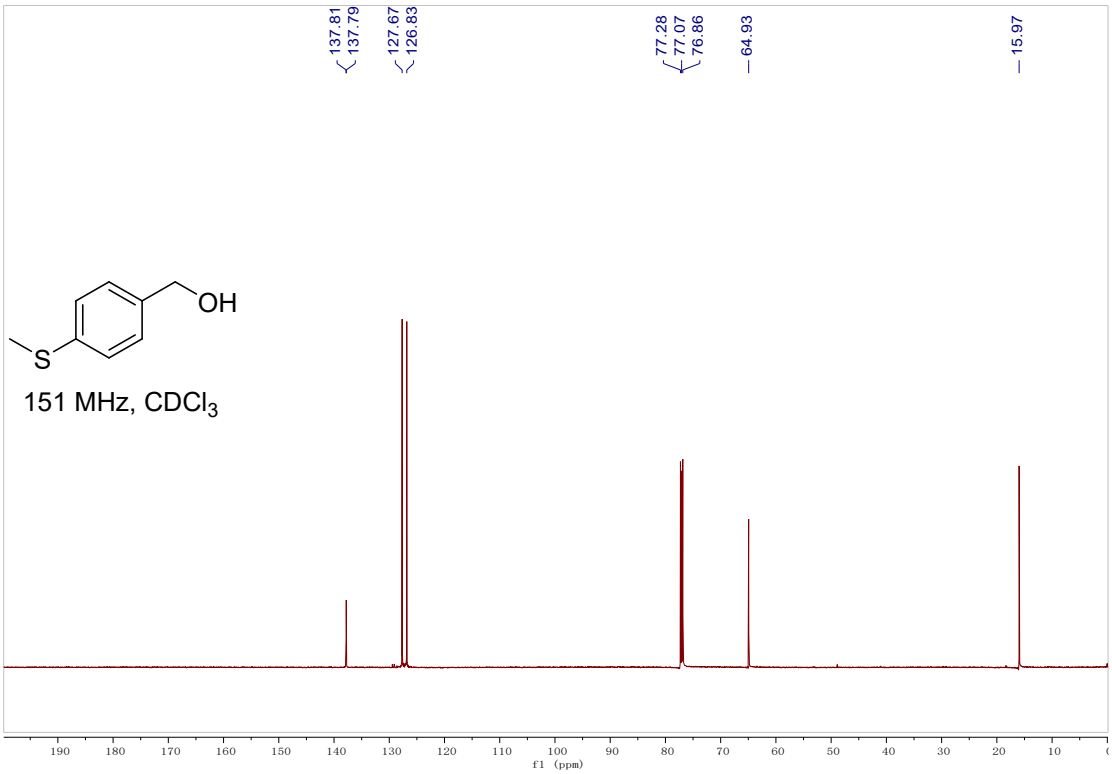
4-(Hydroxymethyl)phenyl butyrate (2p)



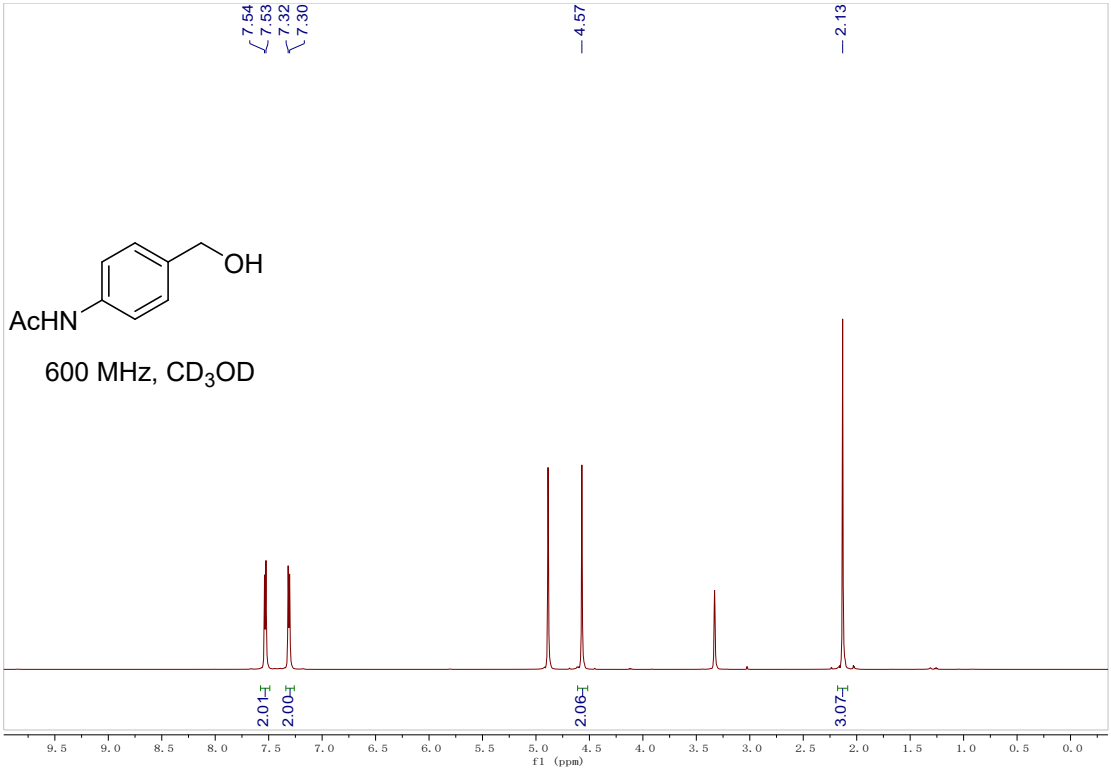


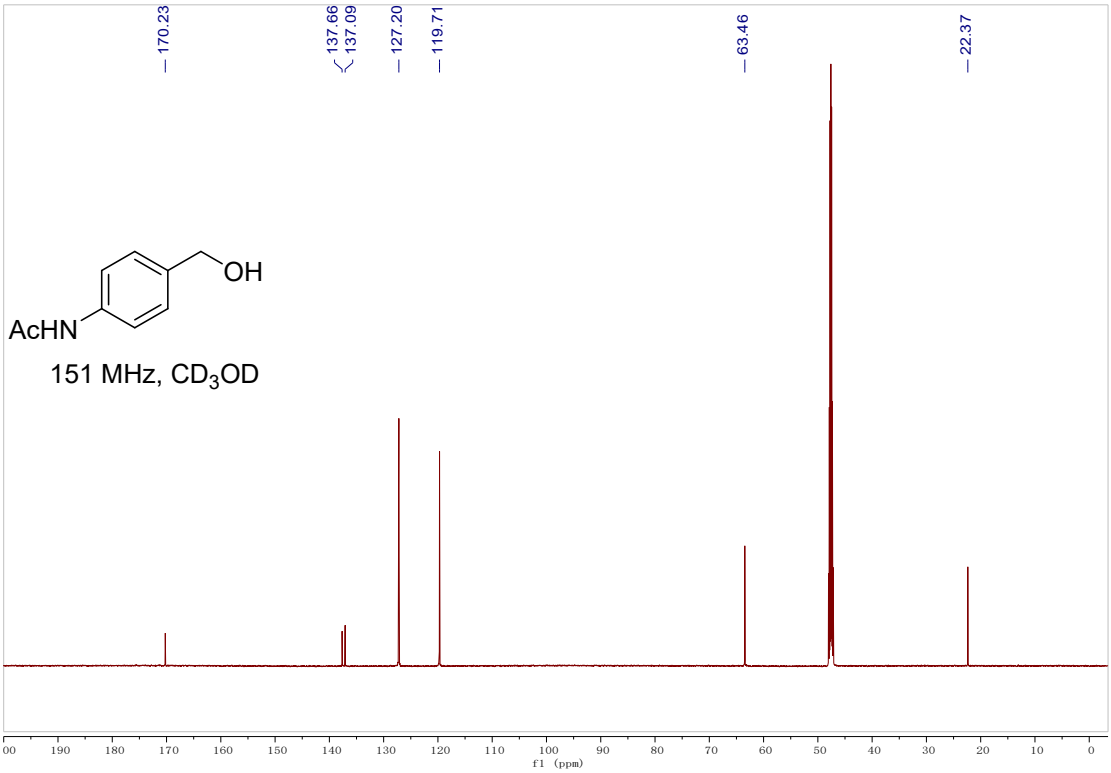
(4-(Methylthio)phenyl)methanol (2q)



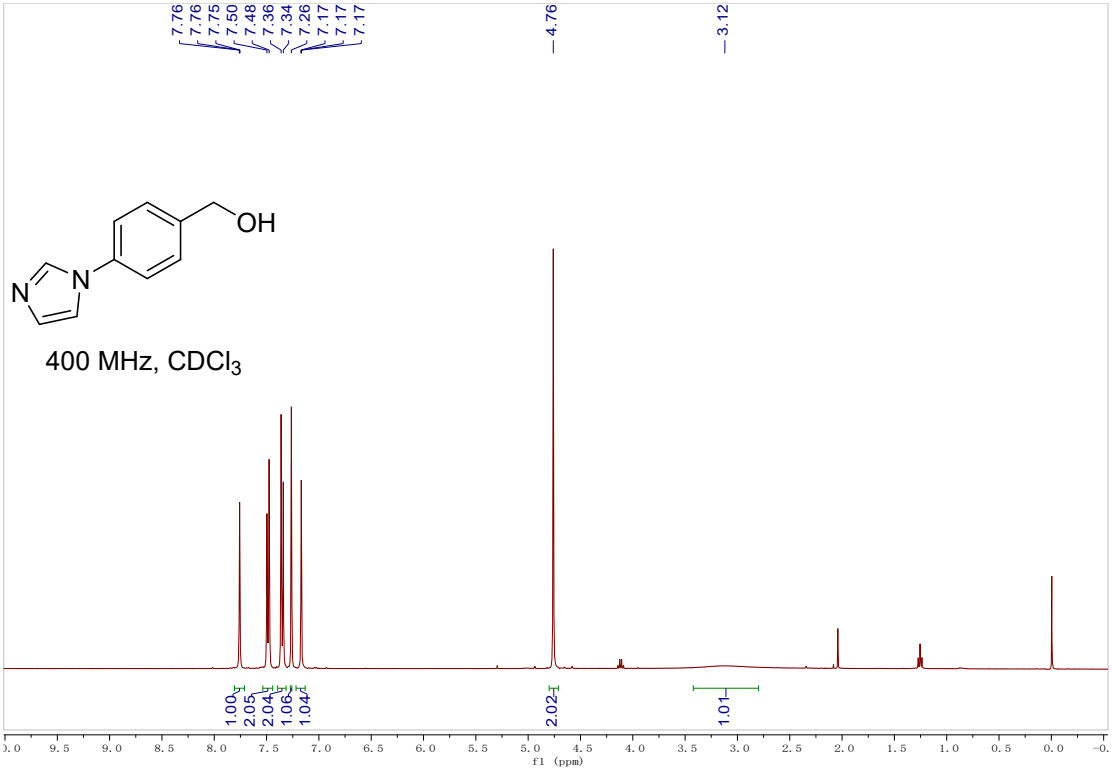


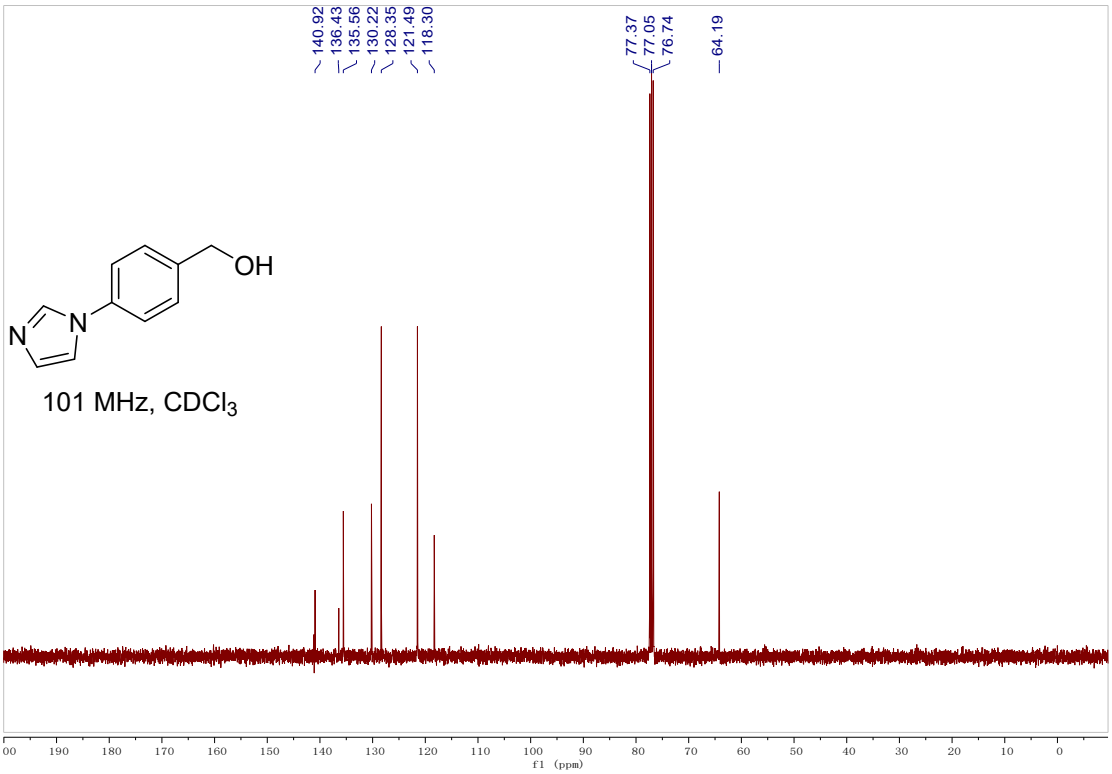
N-(4-(Hydroxymethyl)phenyl)acetamide (2r)



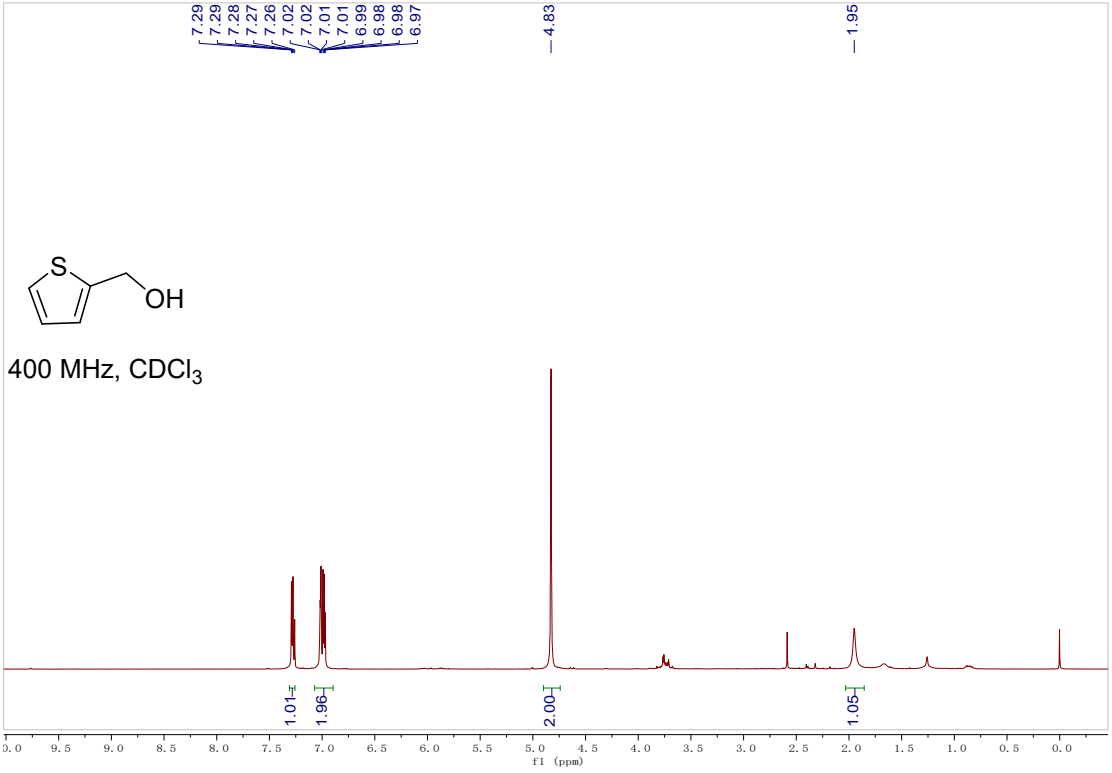


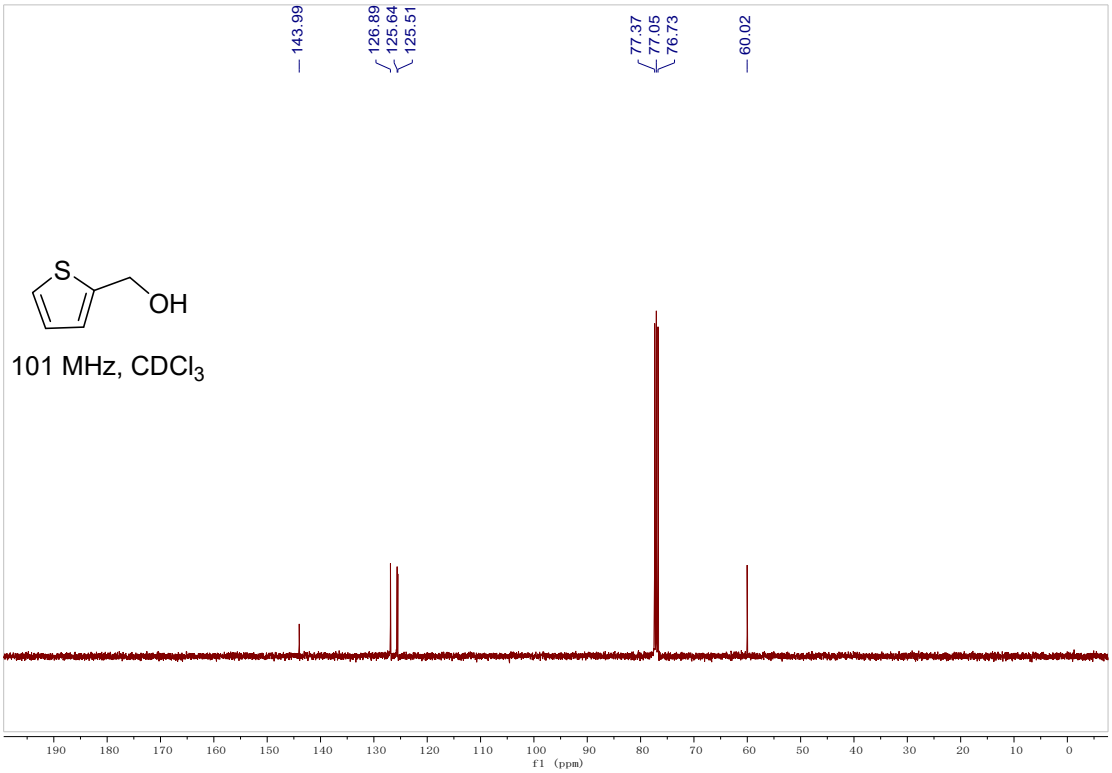
(4-(1H-Imidazol-1-yl)phenyl)methanol (2s)



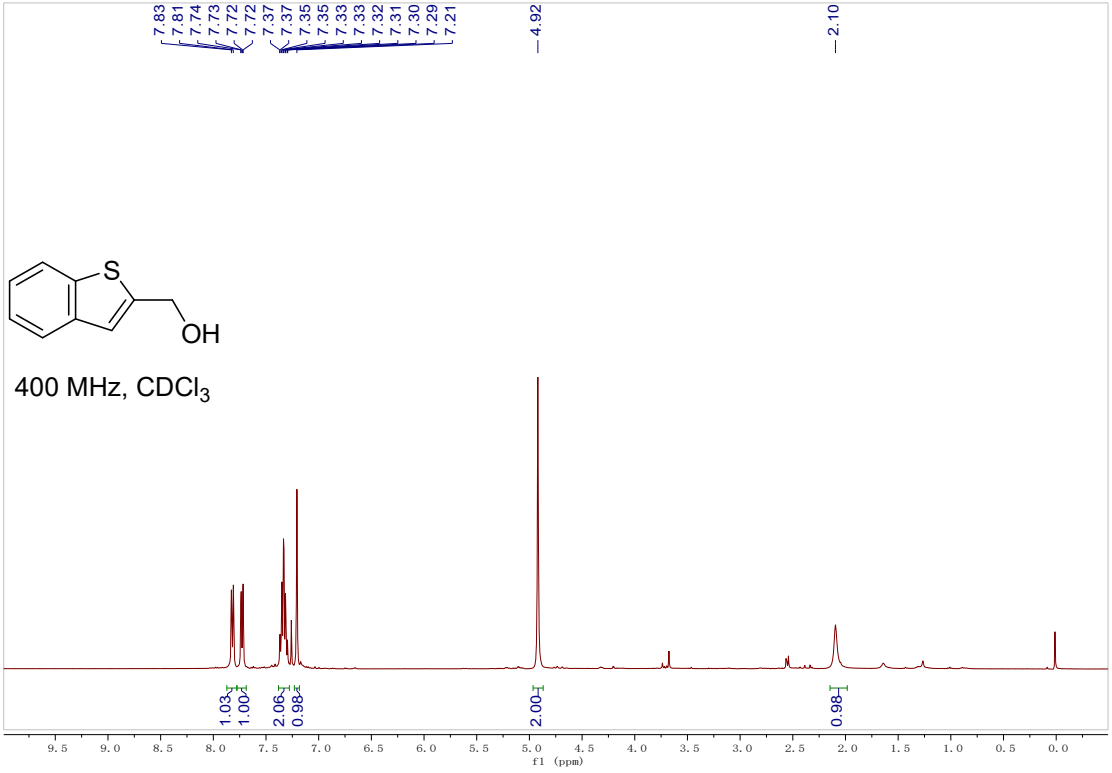


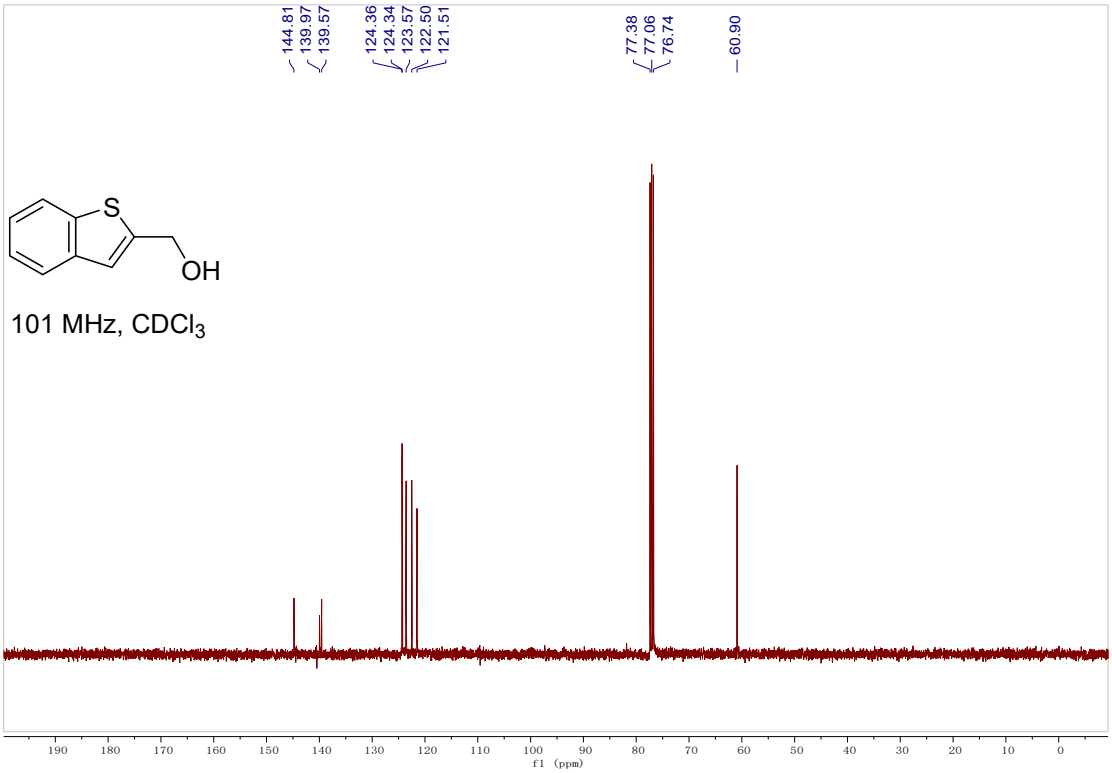
Thiophen-2-ylmethanol (2t)



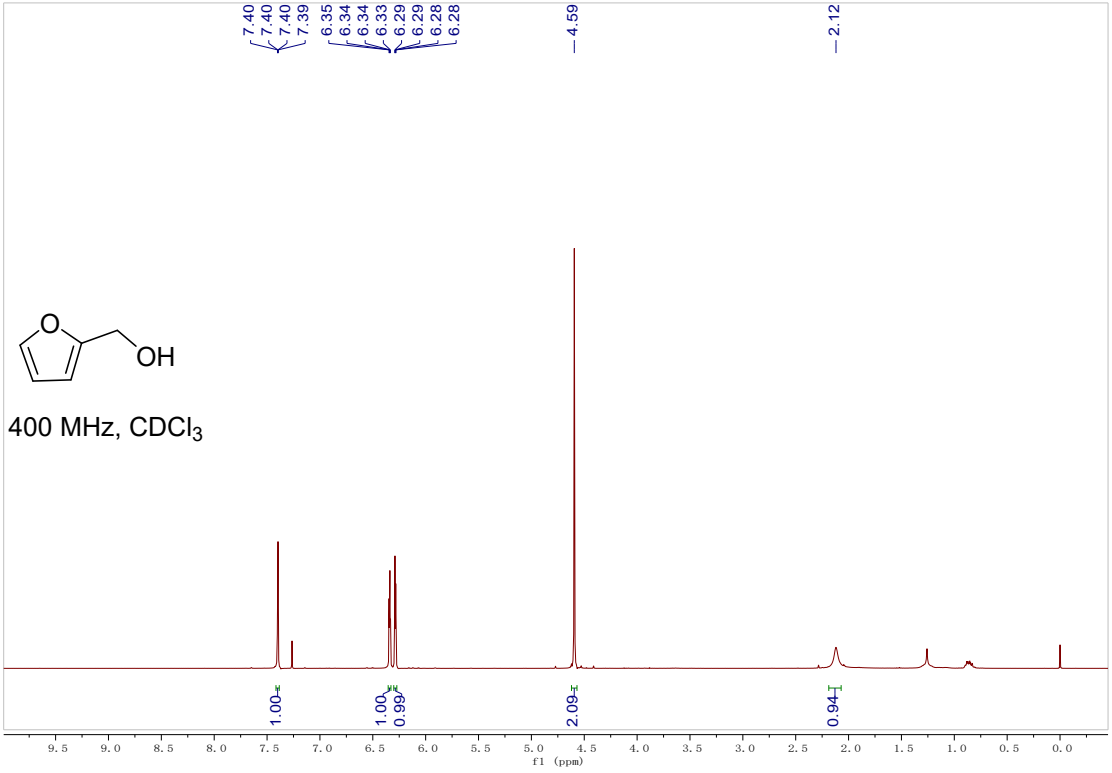


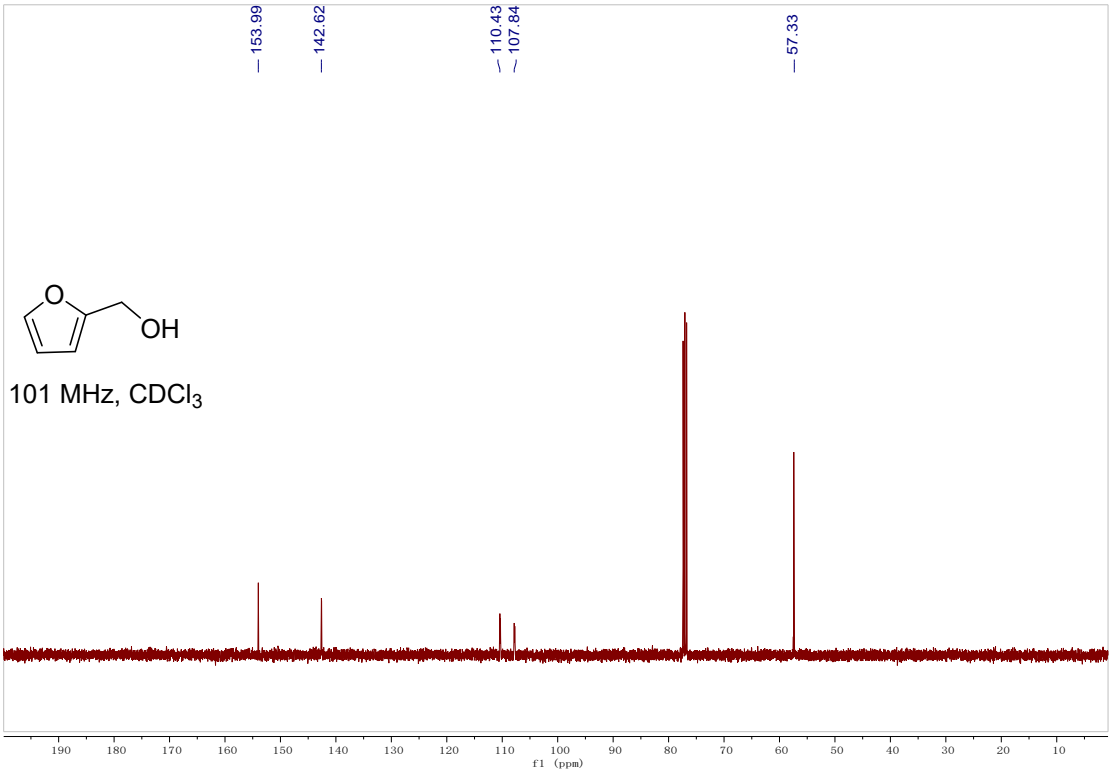
Benzo[b]thiophen-2-ylmethanol (2u)



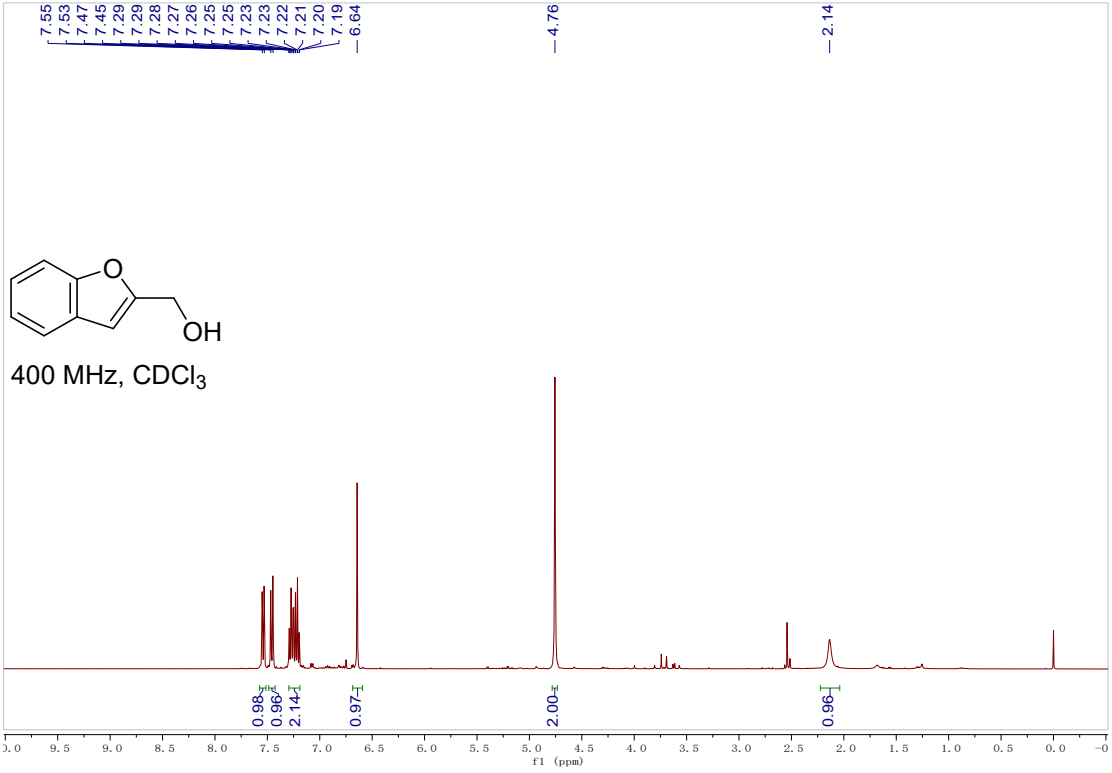


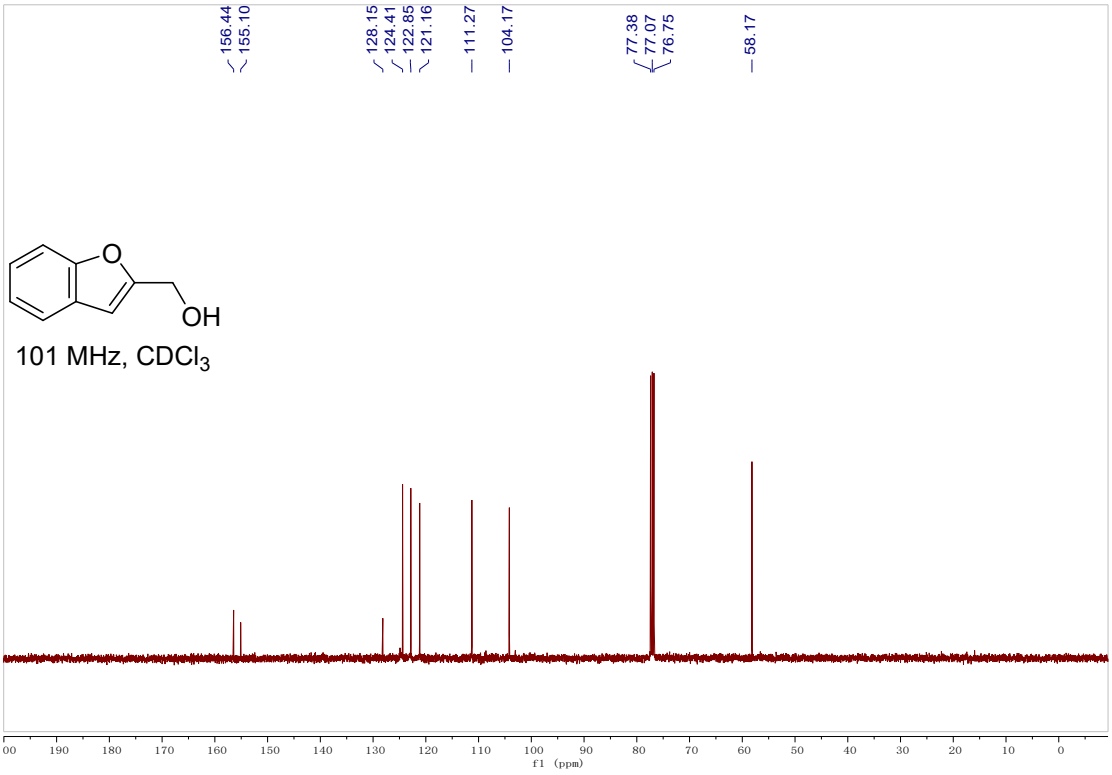
Furan-2-ylmethanol (2v)



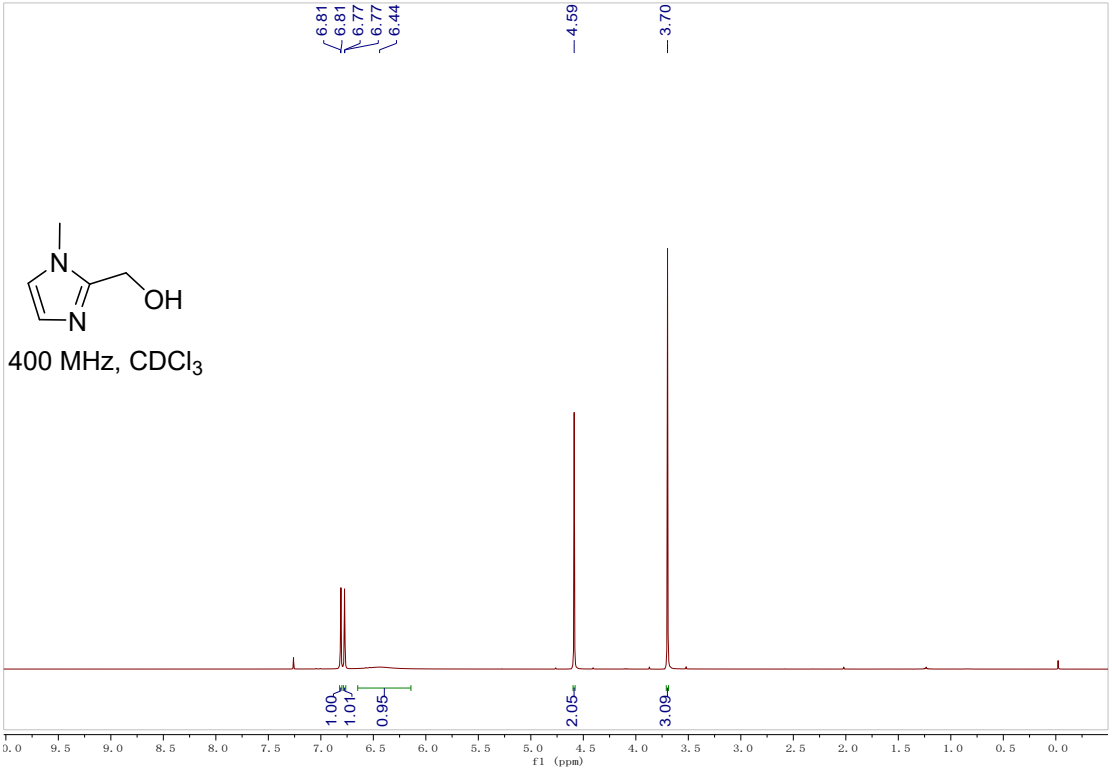


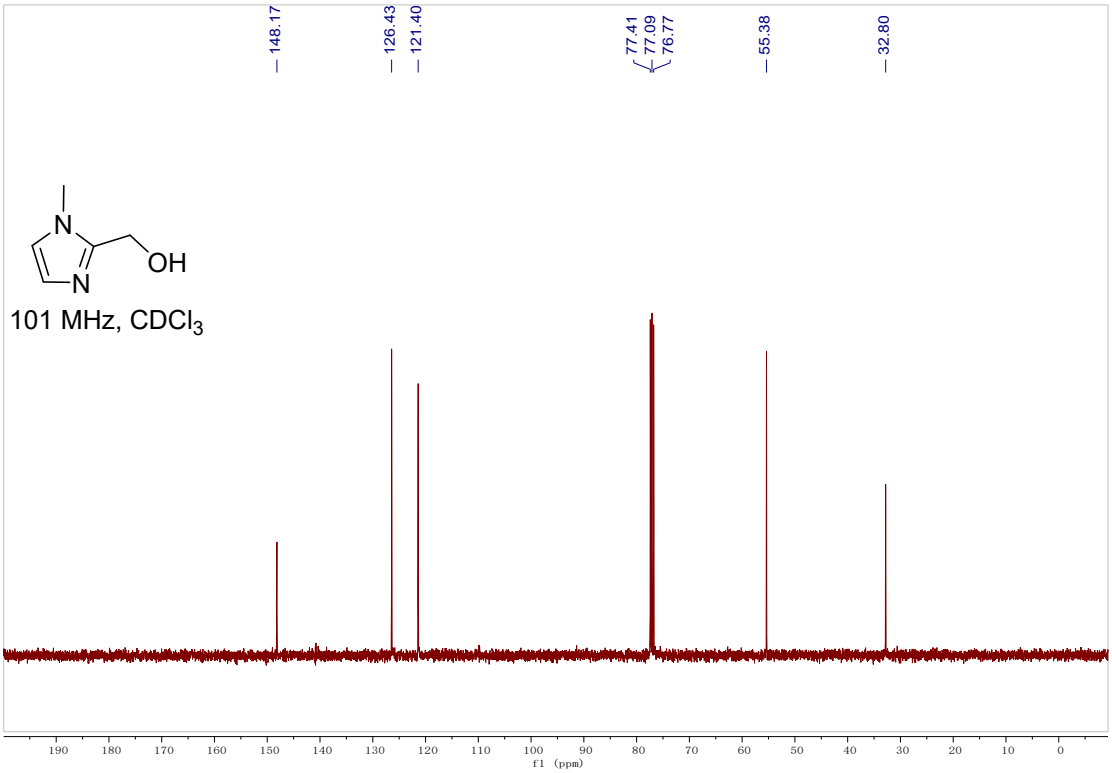
Benzofuran-2-ylmethanol (2w)



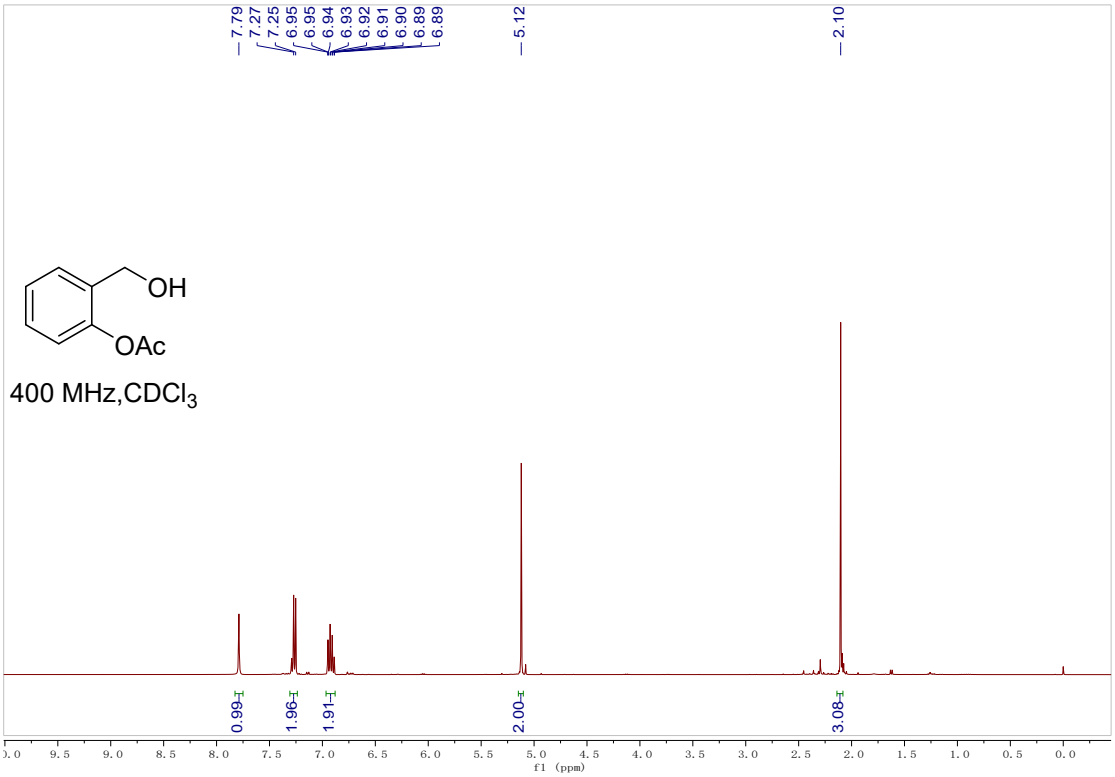


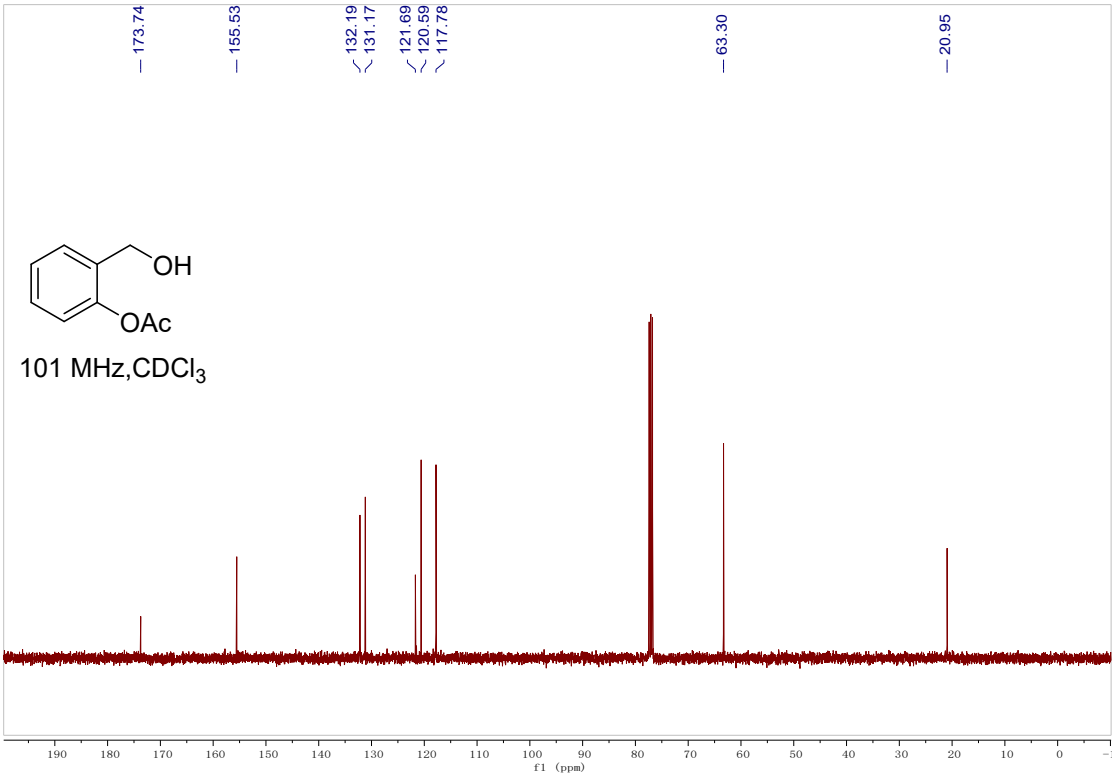
(1-Methyl-1H-imidazol-2-yl)methanol (2x)



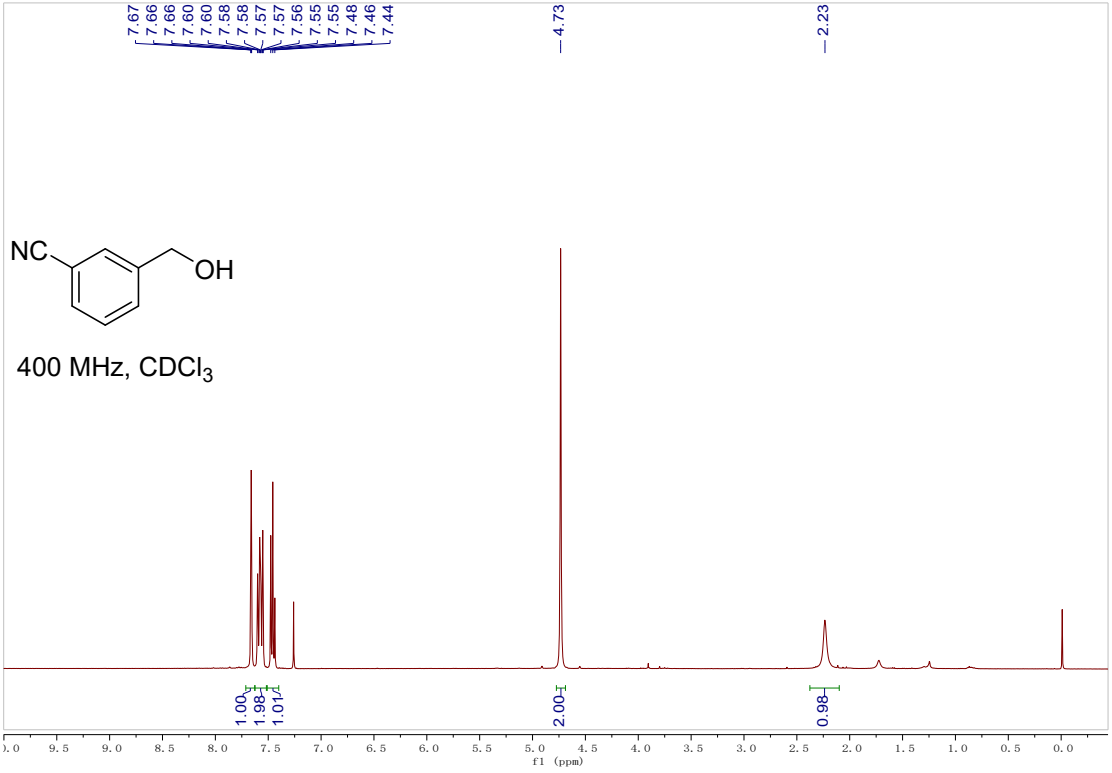


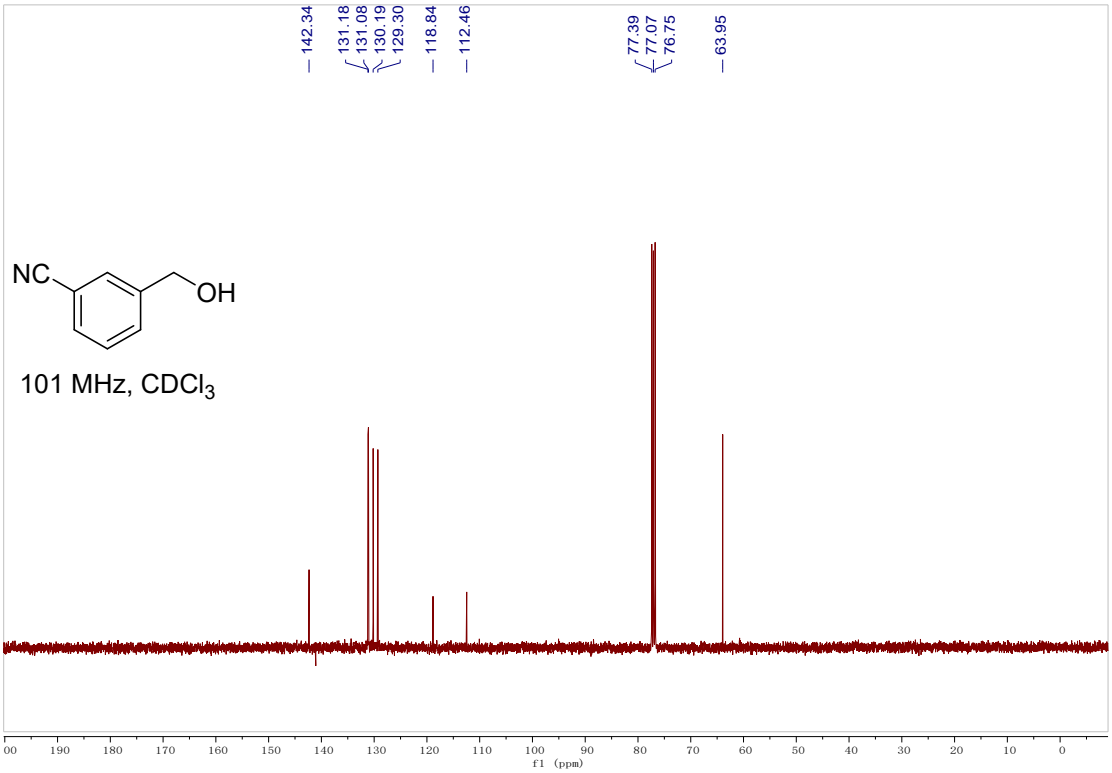
2-(hydroxymethyl)phenyl acetate (2y)



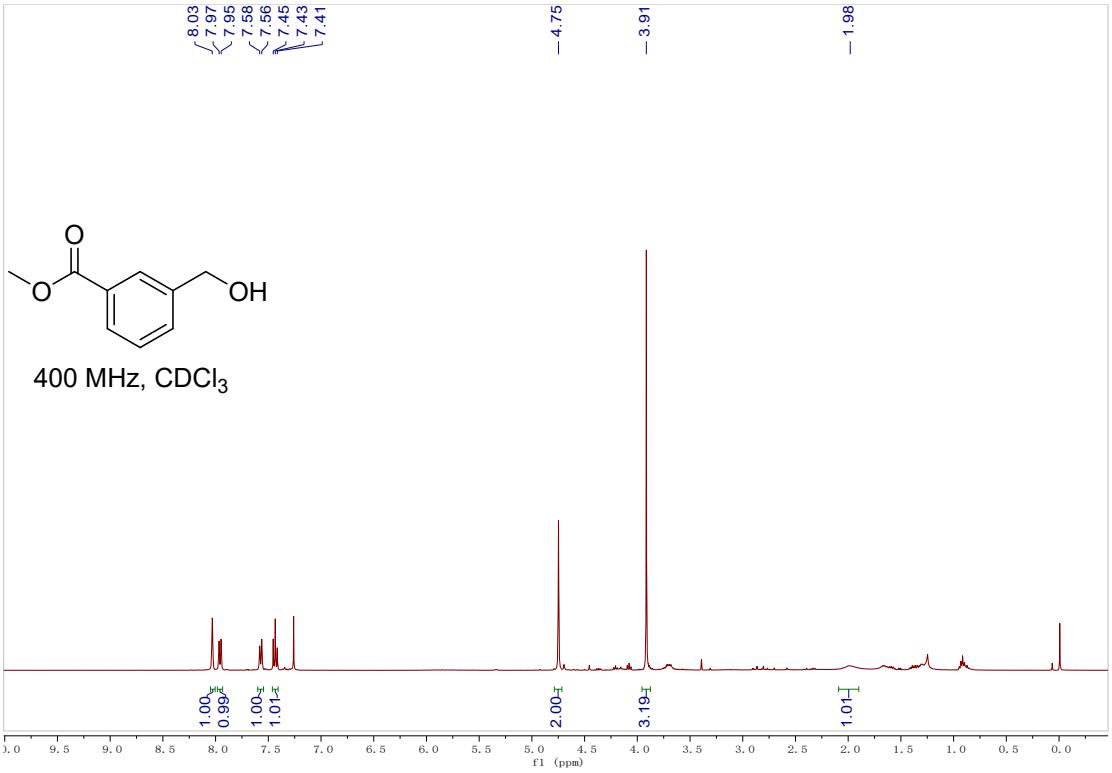


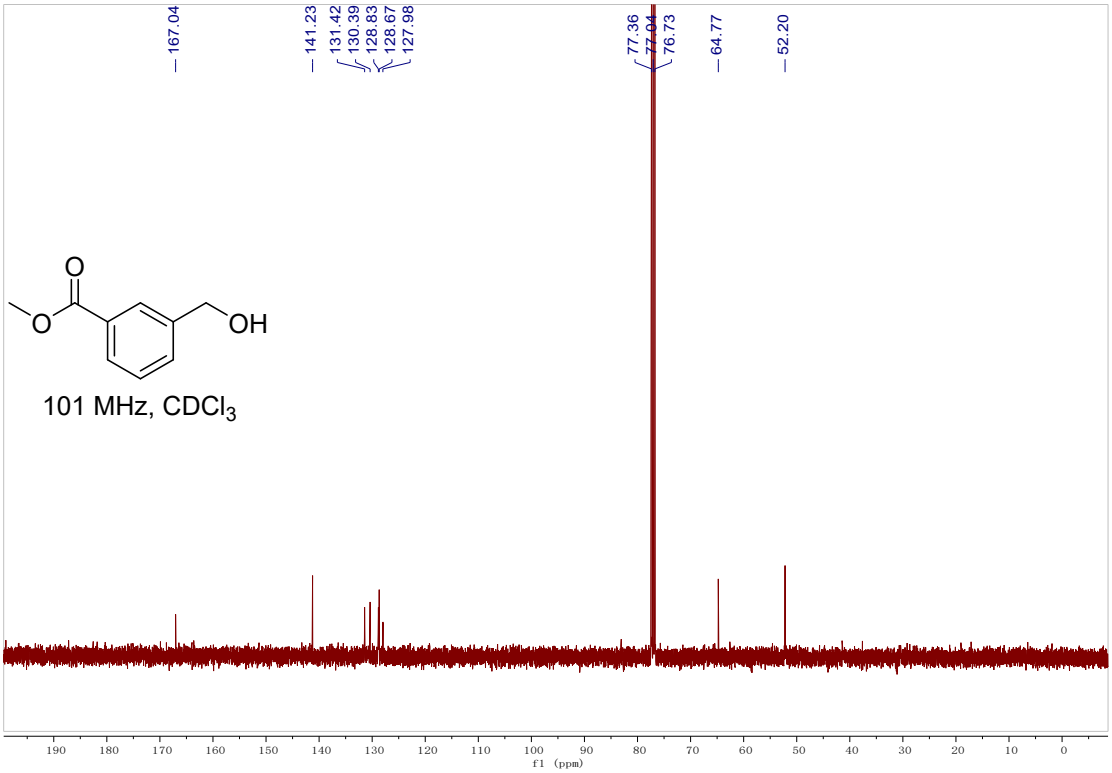
3-(Hydroxymethyl)benzonitrile (2aa)



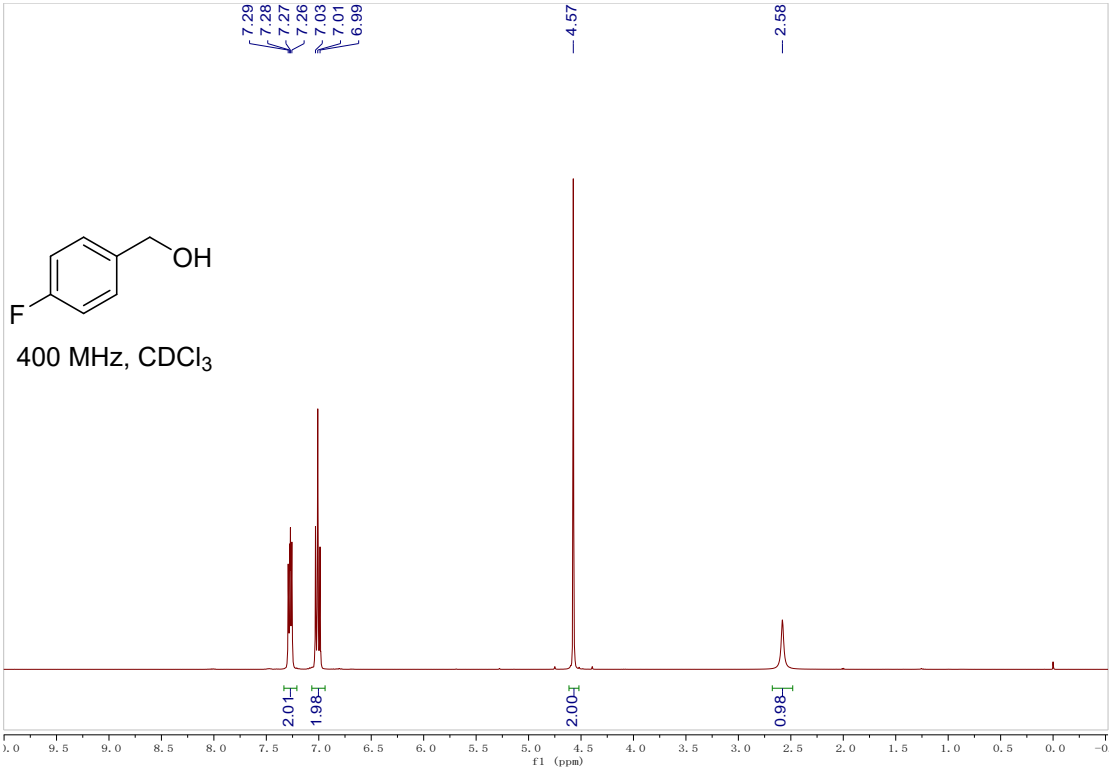


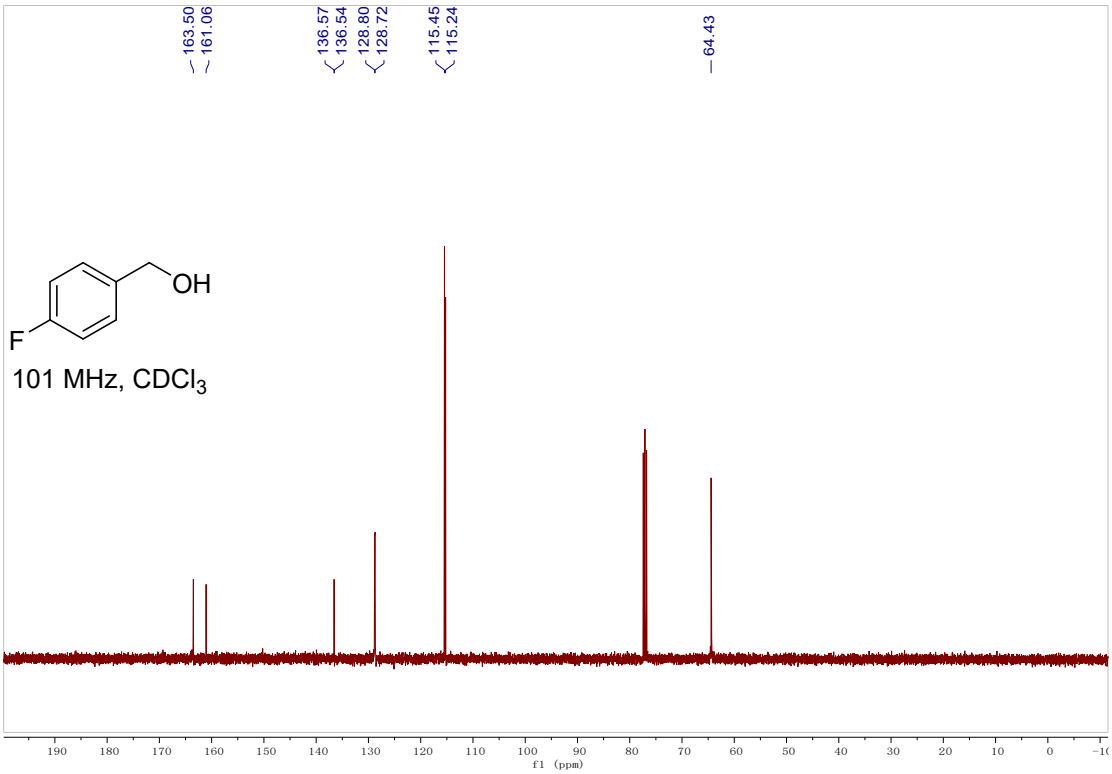
Methyl 3-(hydroxymethyl)benzoate (2ab)

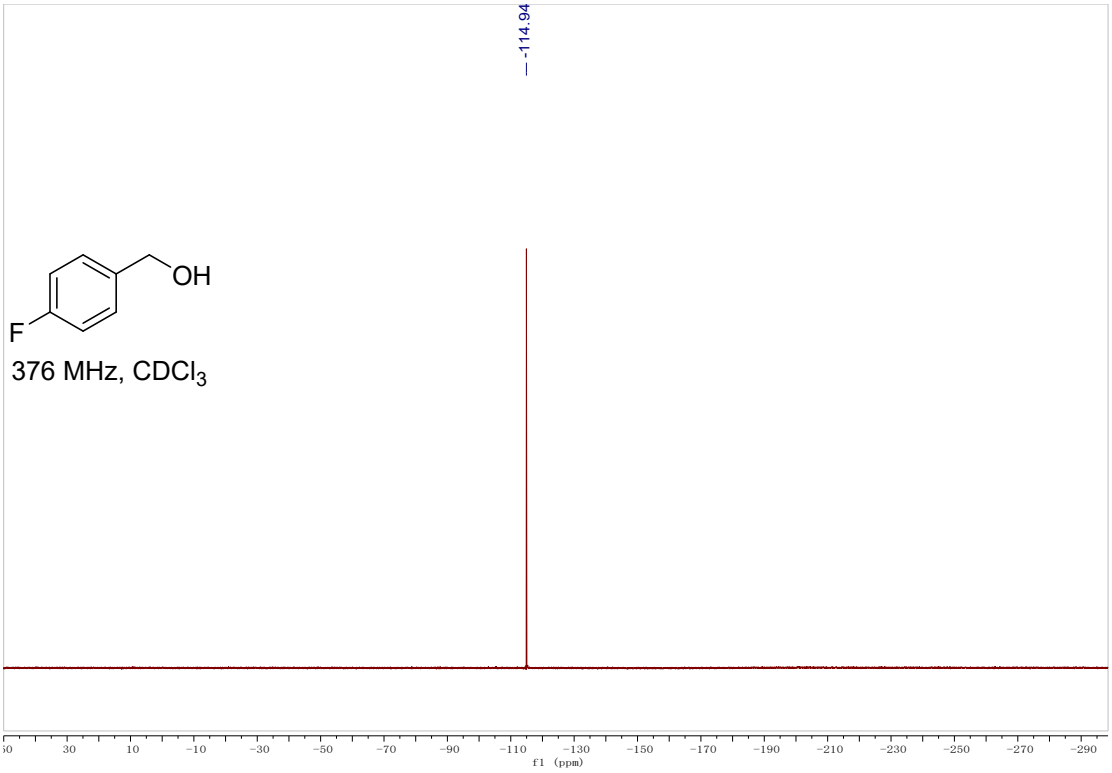

8.03
7.97
7.95
7.58
7.56
7.45
7.43
7.41
4.75
3.91
1.98
O
O
OH
400 MHz, CDCl3
1.00
0.99
1.00
1.01
2.00
3.19
1.01
f1 (ppm)


167.04
141.23
131.42
130.39
128.83
128.67
127.98
77.36
77.04
76.73
64.77
52.20
O
O
OH
101 MHz, CDCl3
f1 (ppm)

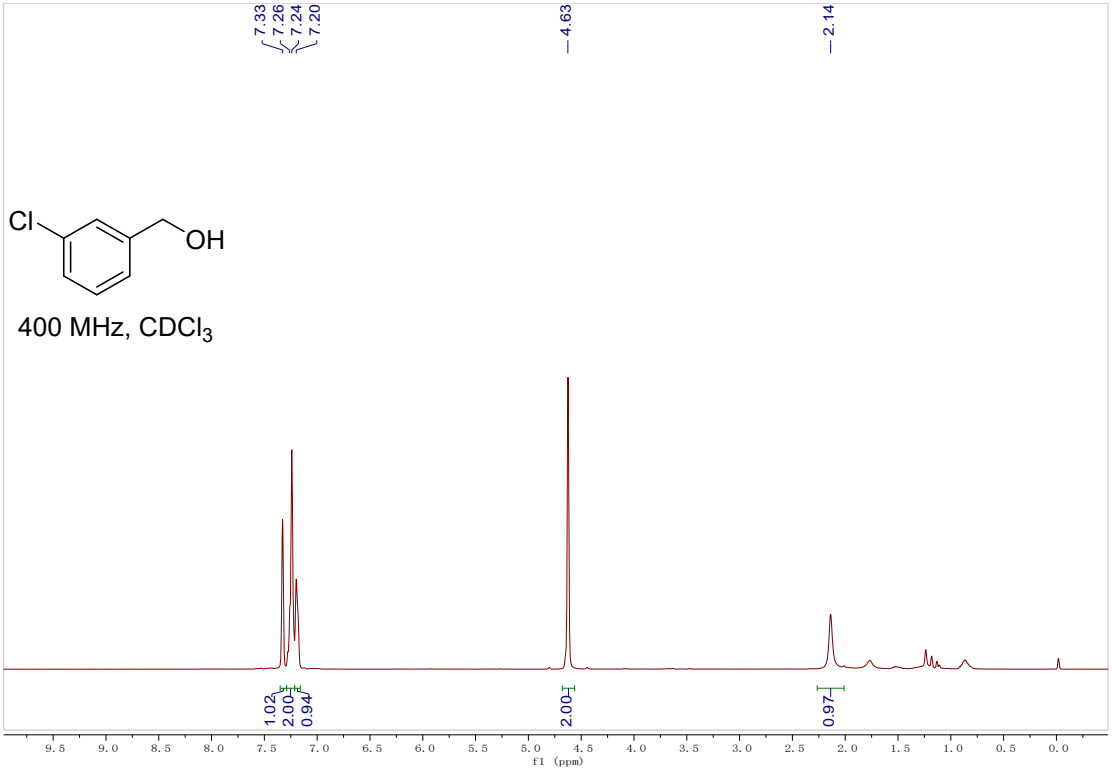
(4-Fluorophenyl)methanol (2ac)

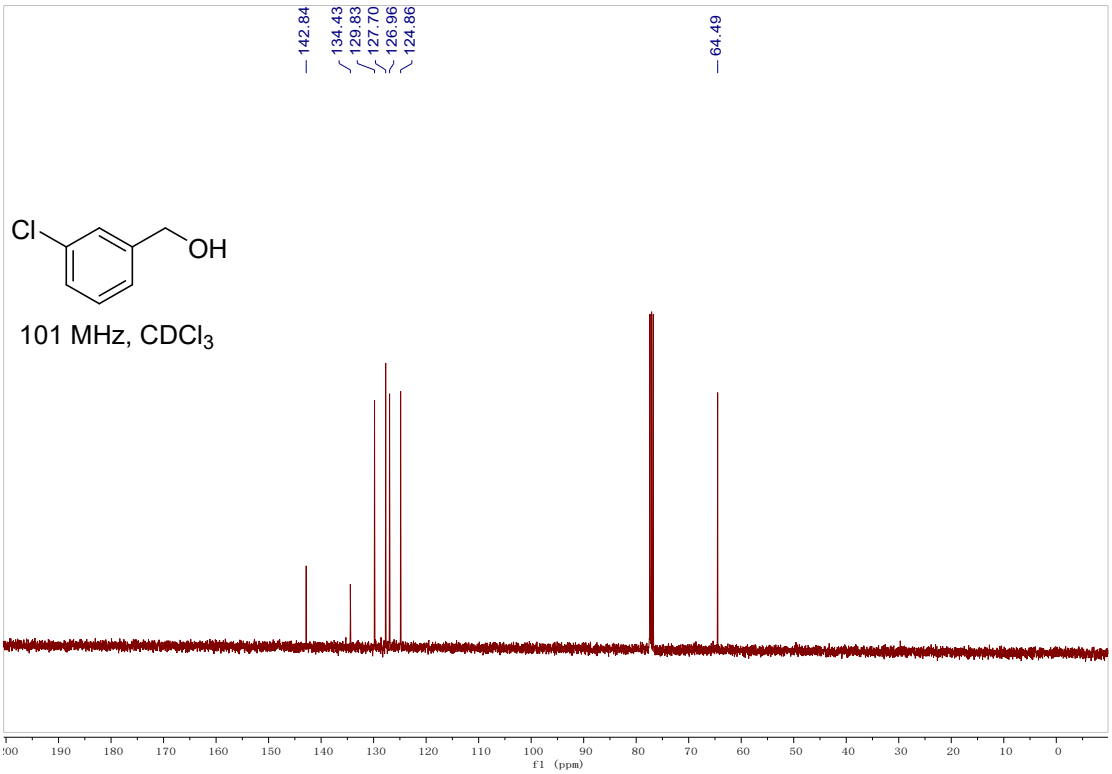




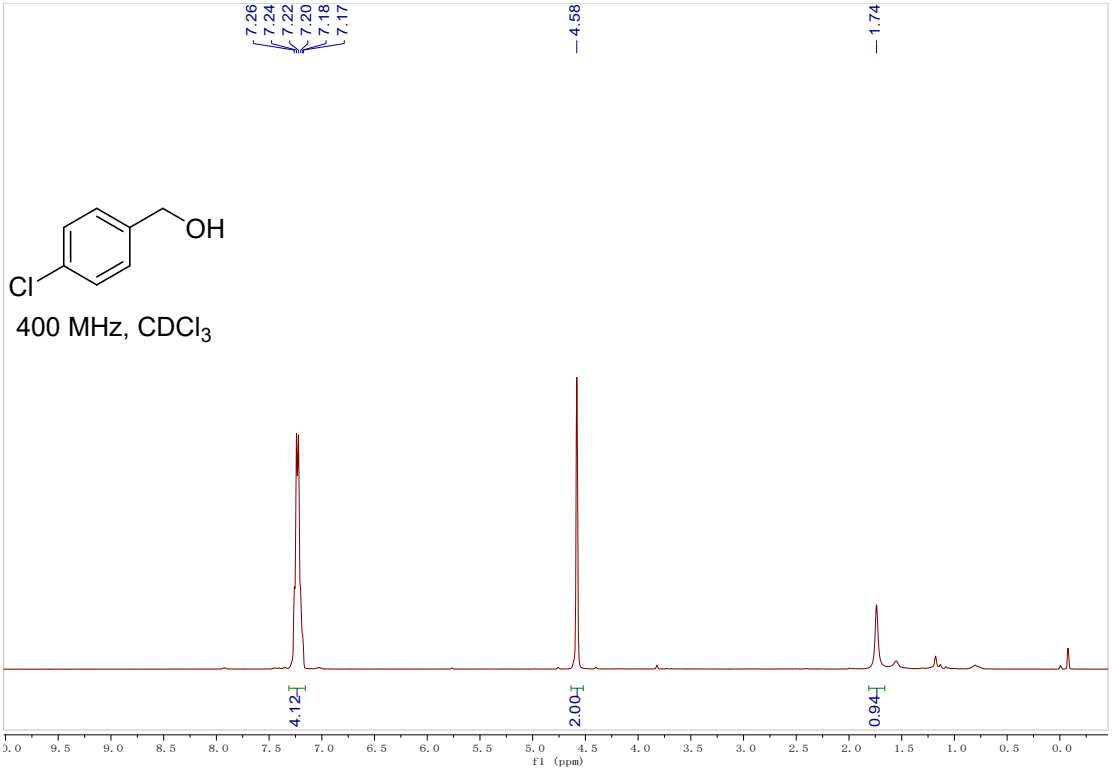

-114.94
OH
F
376 MHz, CDCl3
30
10
−10
−30
−50
−70
−90
−110
−130
−150
−170
−190
−210
−230
−250
−270
−290
f1 (ppm)

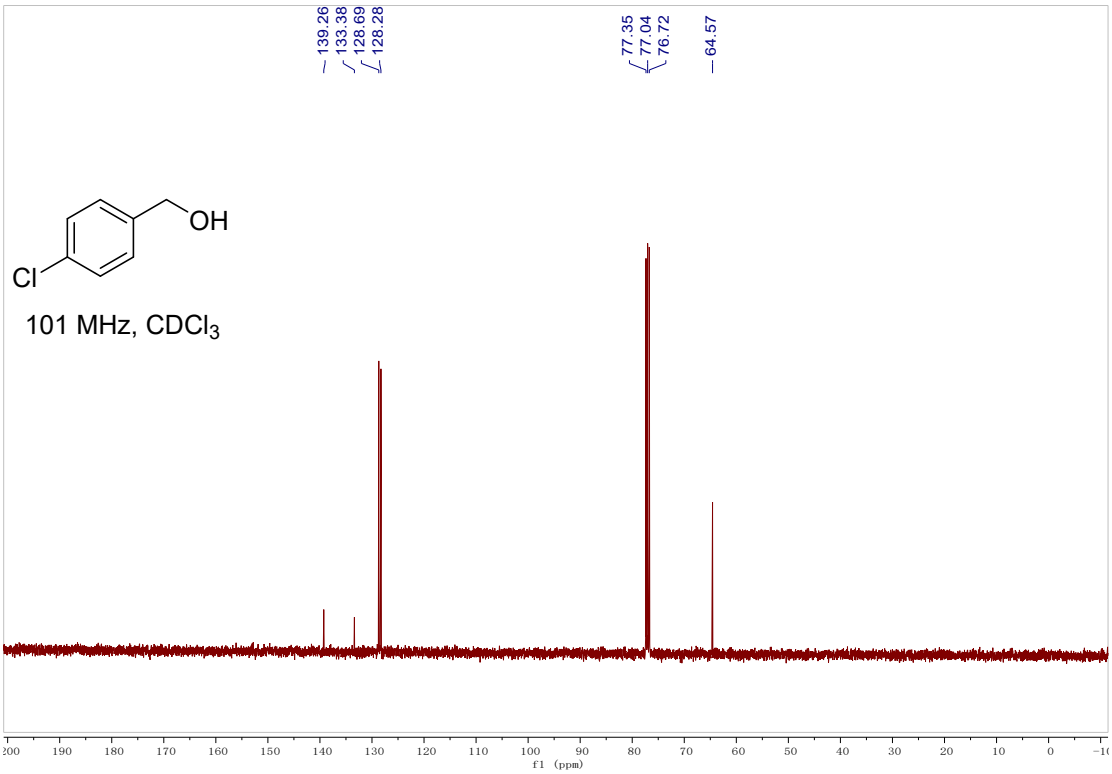
(3-Chlorophenyl)methanol (2ad)



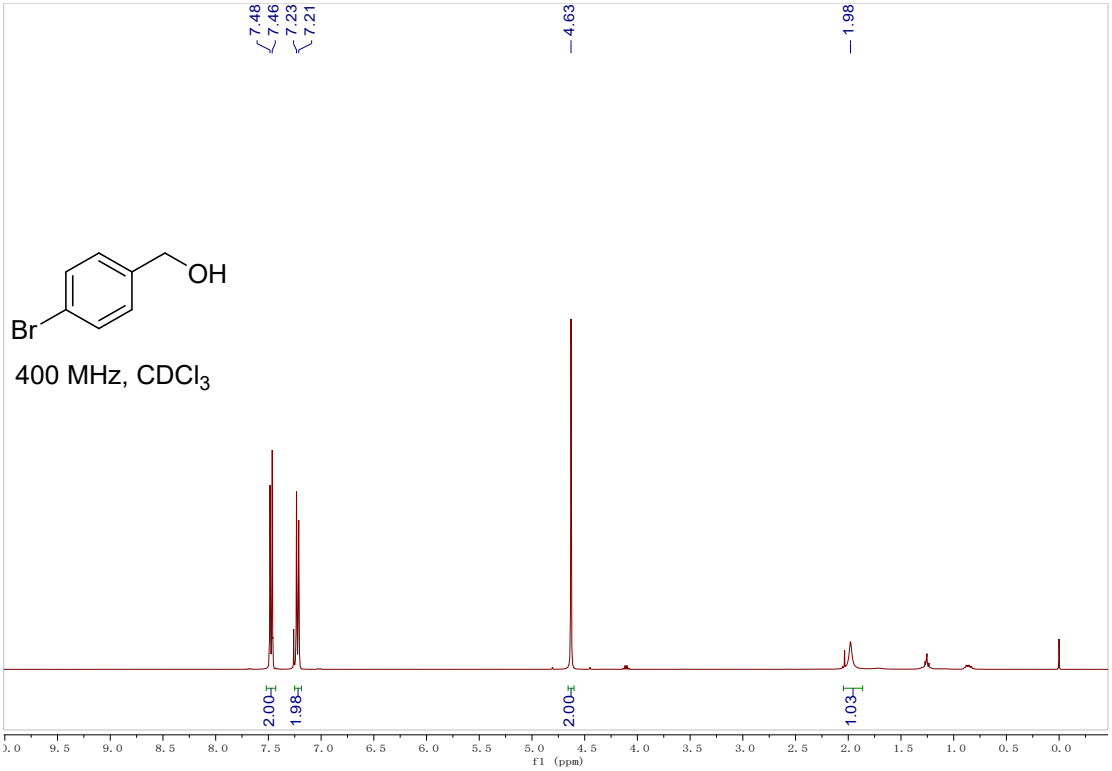


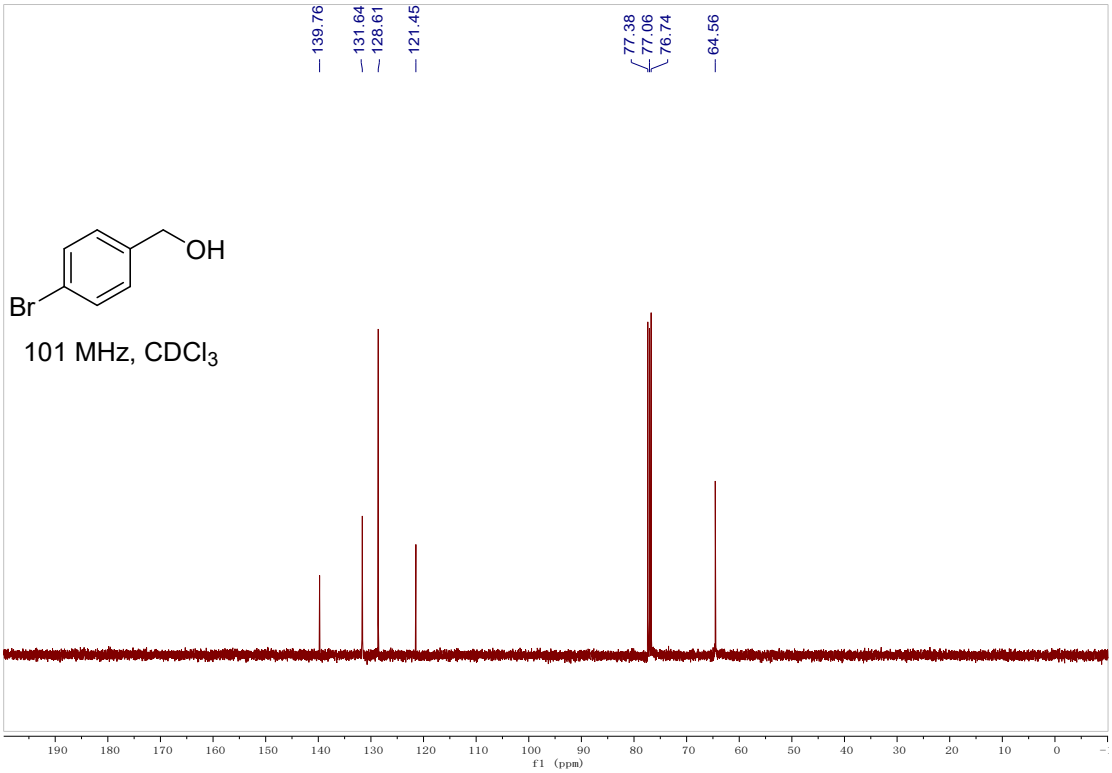
(4-Chlorophenyl)methanol (2ae)



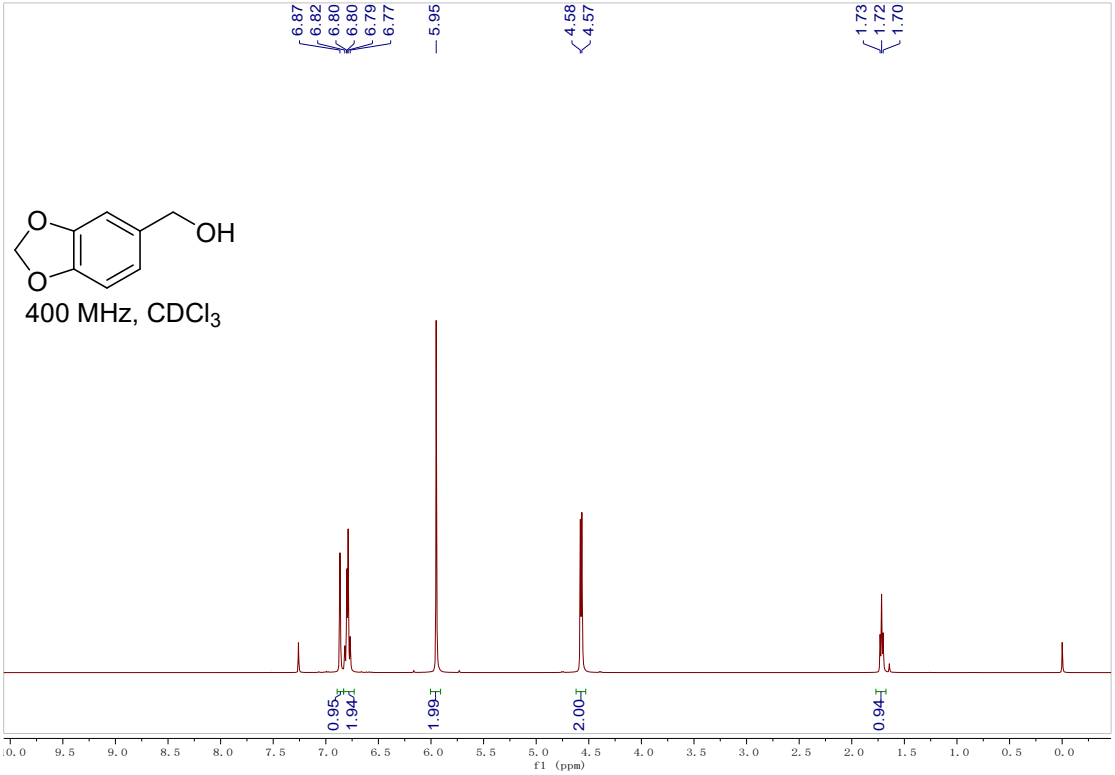


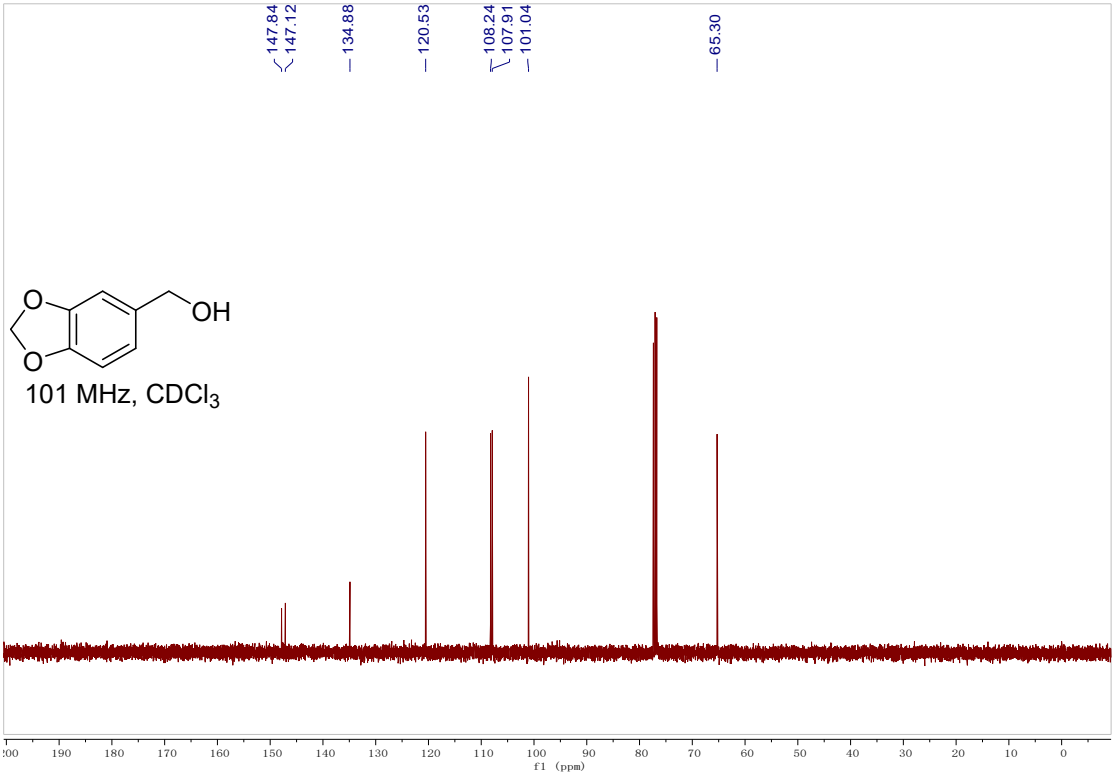
(4-Bromophenyl)methanol (2af)



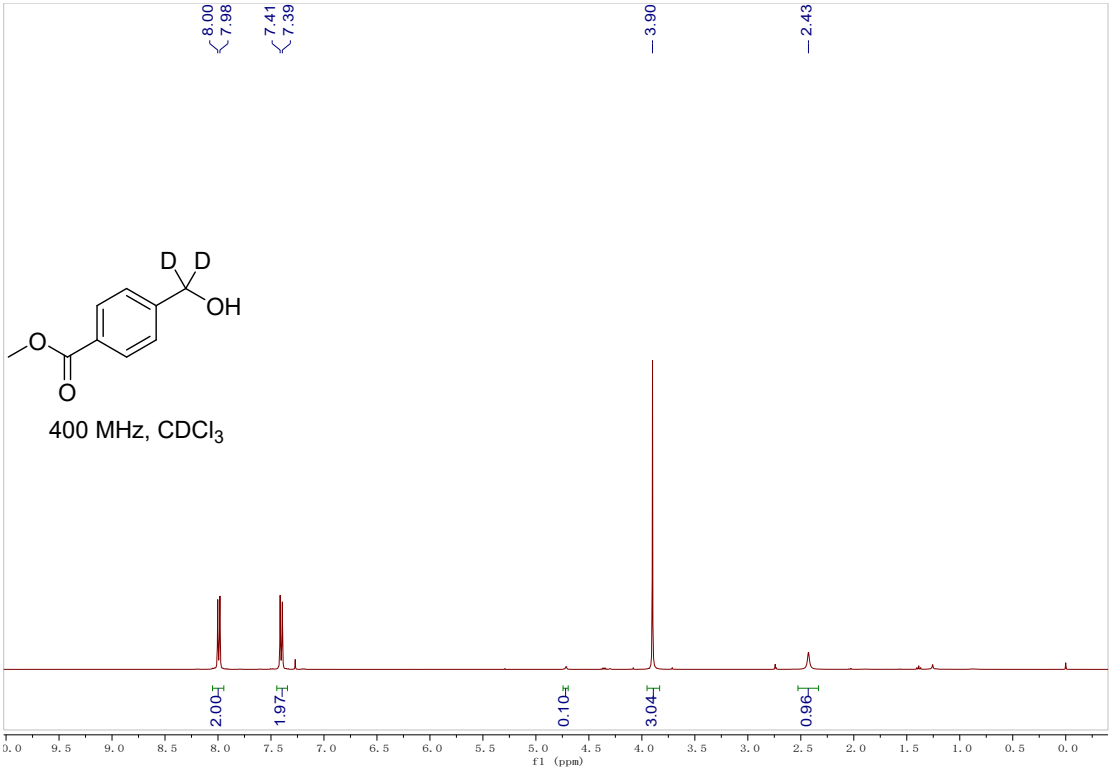


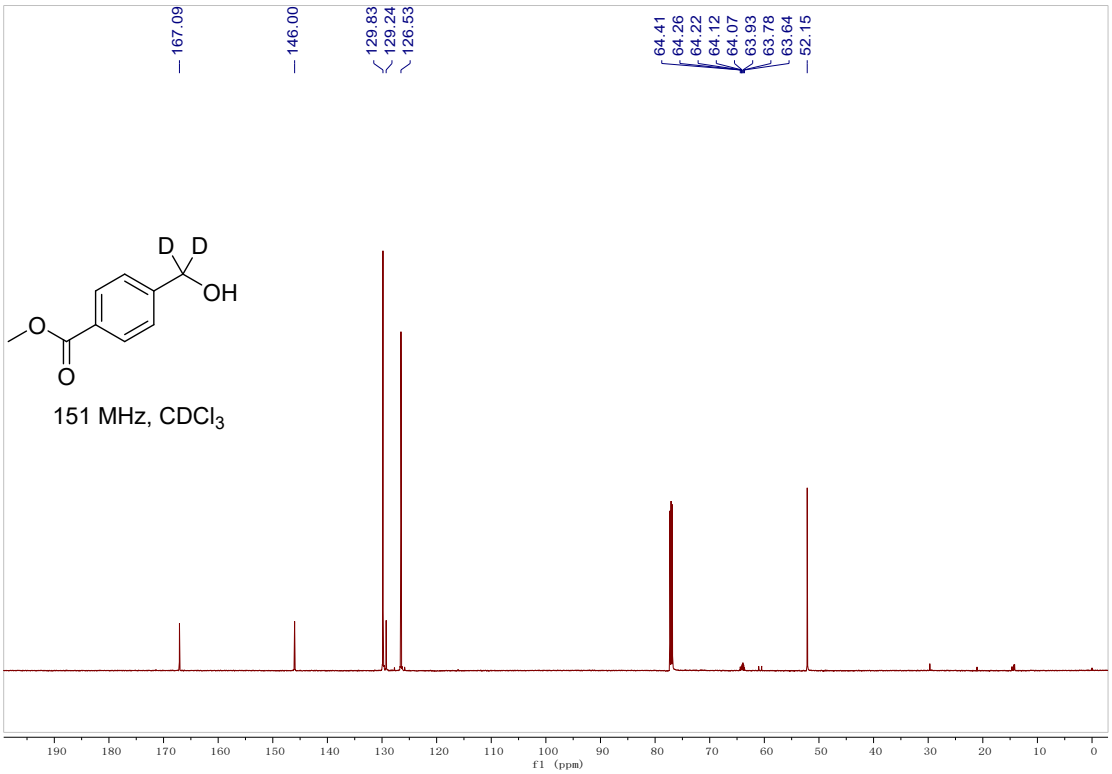
Benzo[d][1,3]dioxol-5-ylmethanol (2ag)



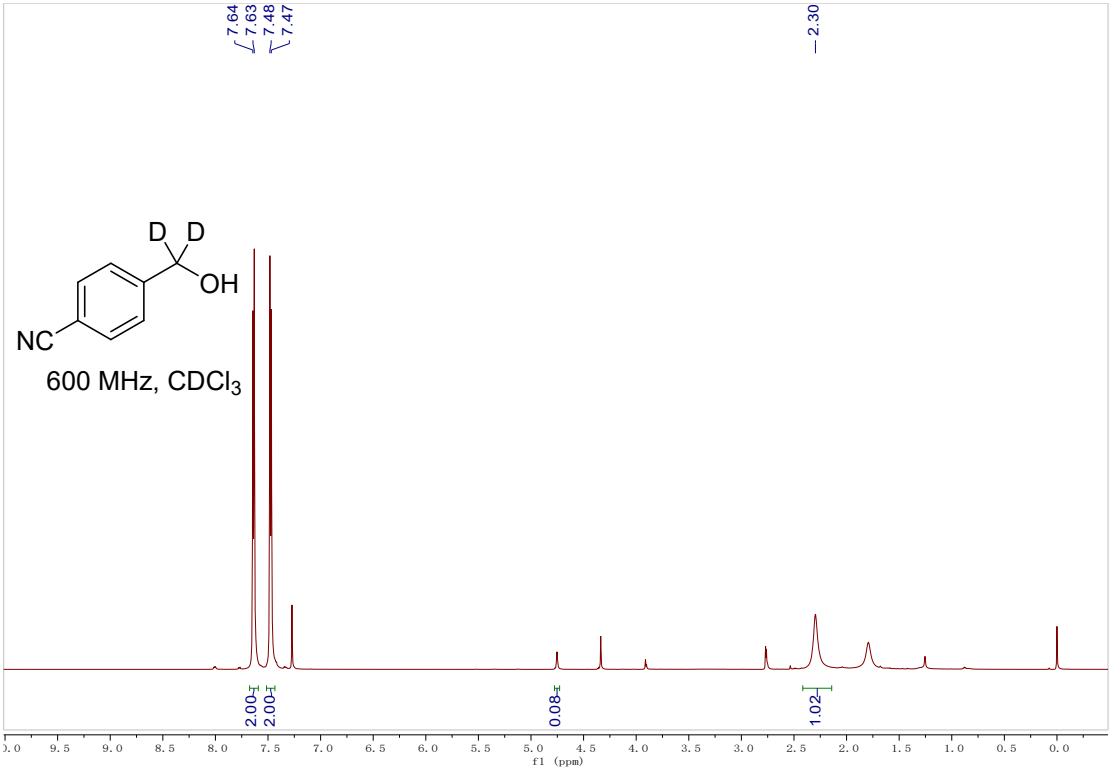


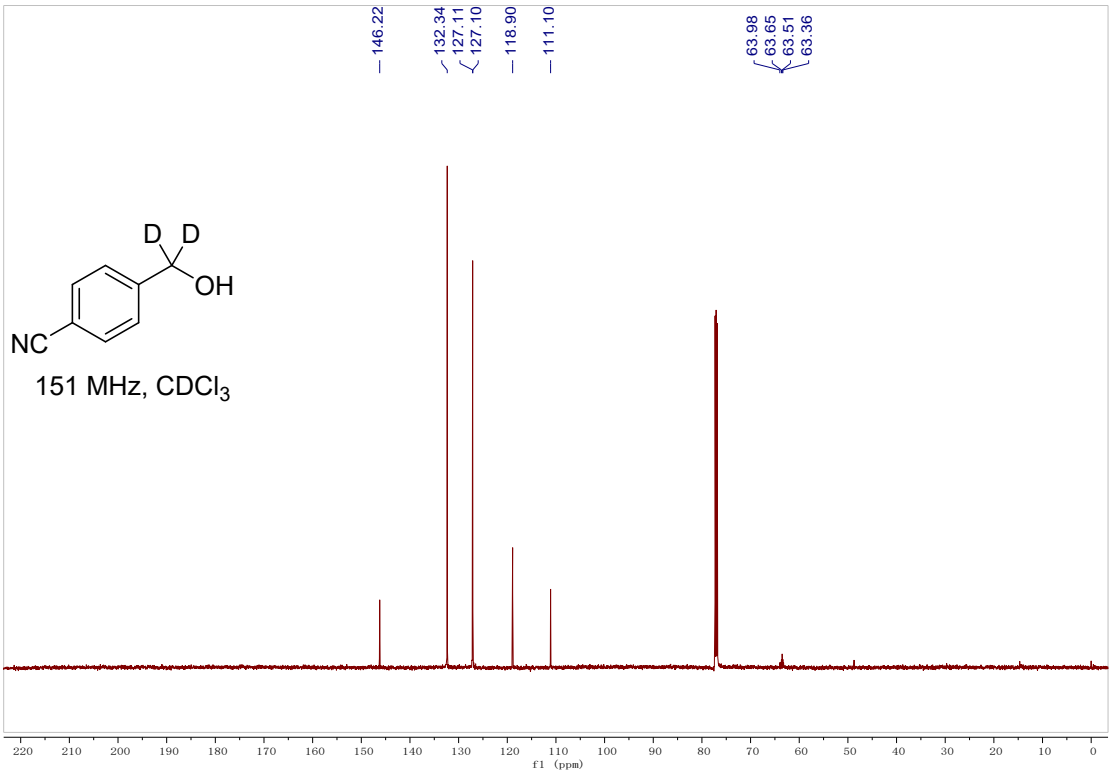
Methyl 4-(hydroxymethyl-d_2)benzoate (3a)



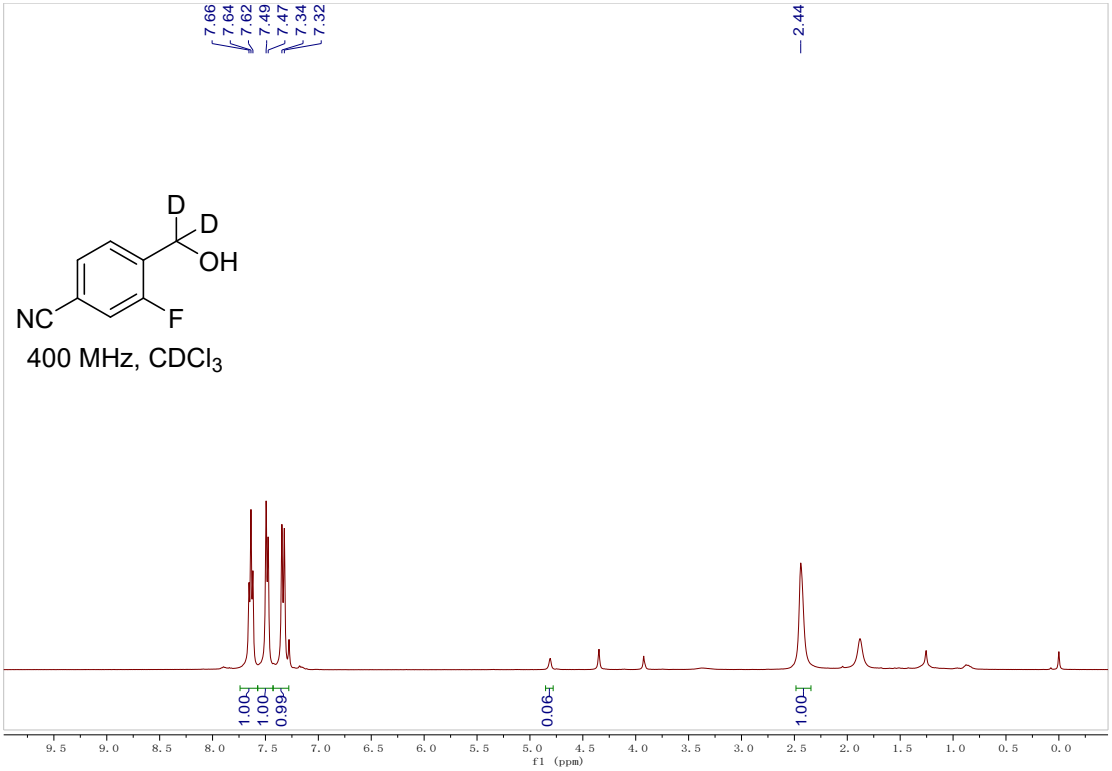


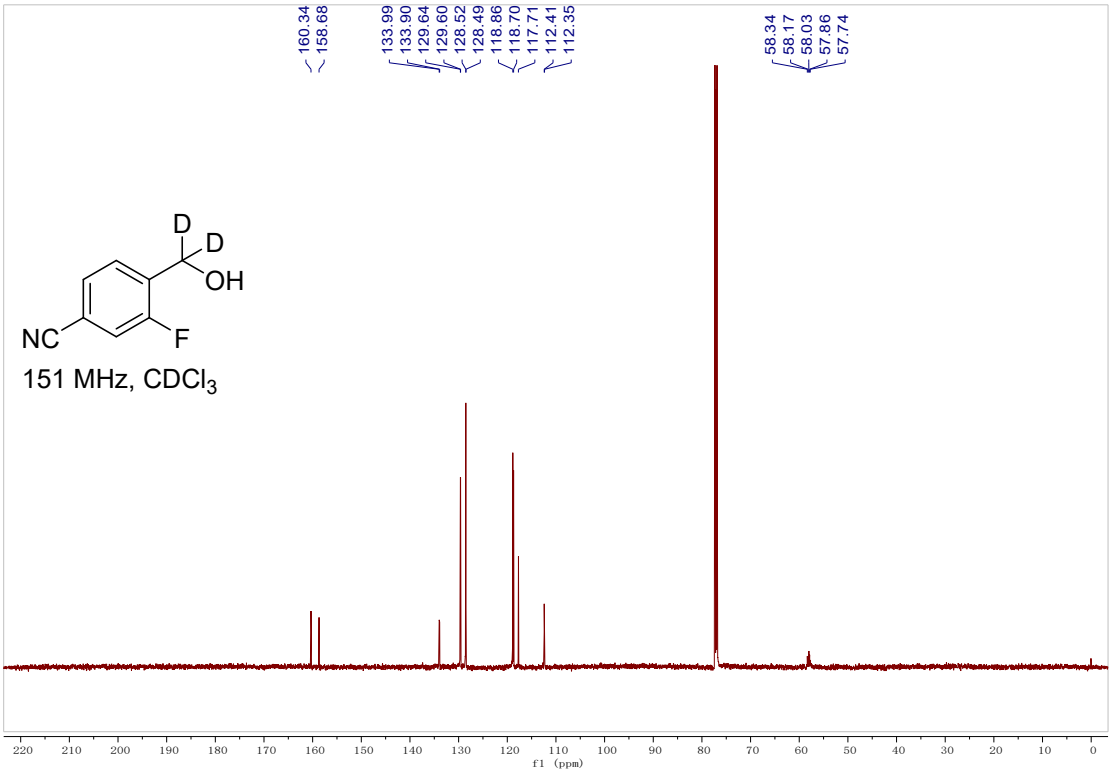
4-(Hydroxymethyl-d_2)benzonitrile (3b)

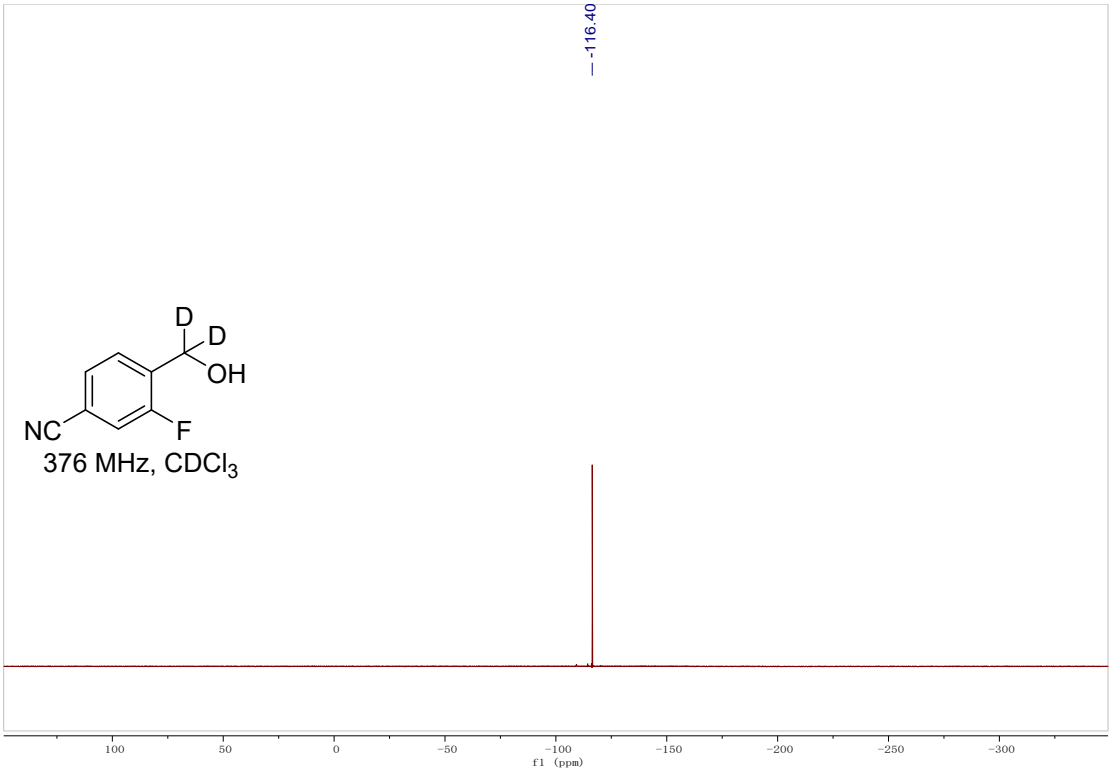




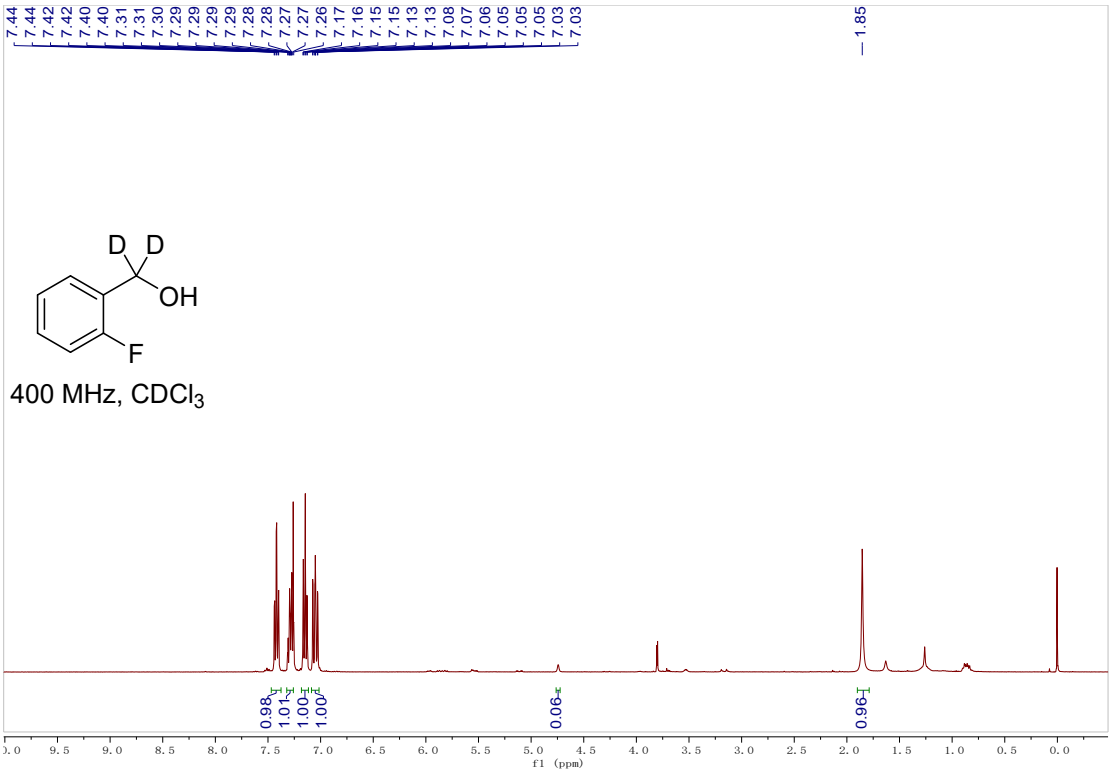
3-Fluoro-4-(hydroxymethyl-d_2)benzonitrile (3c)

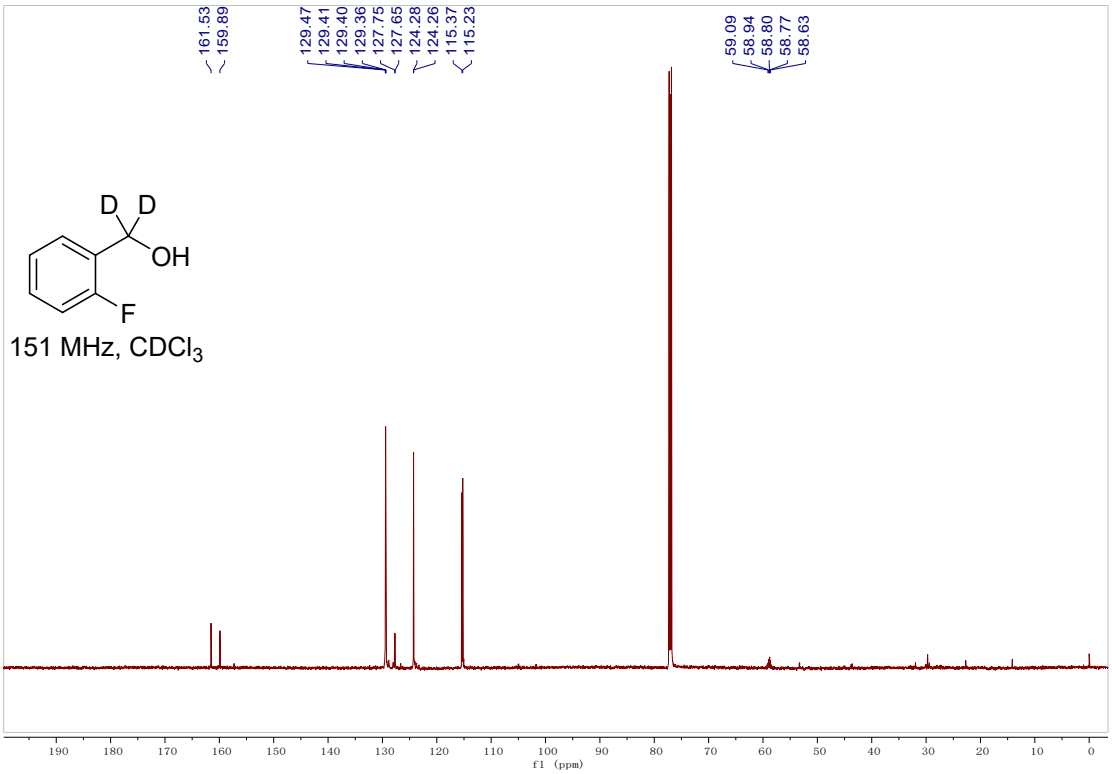


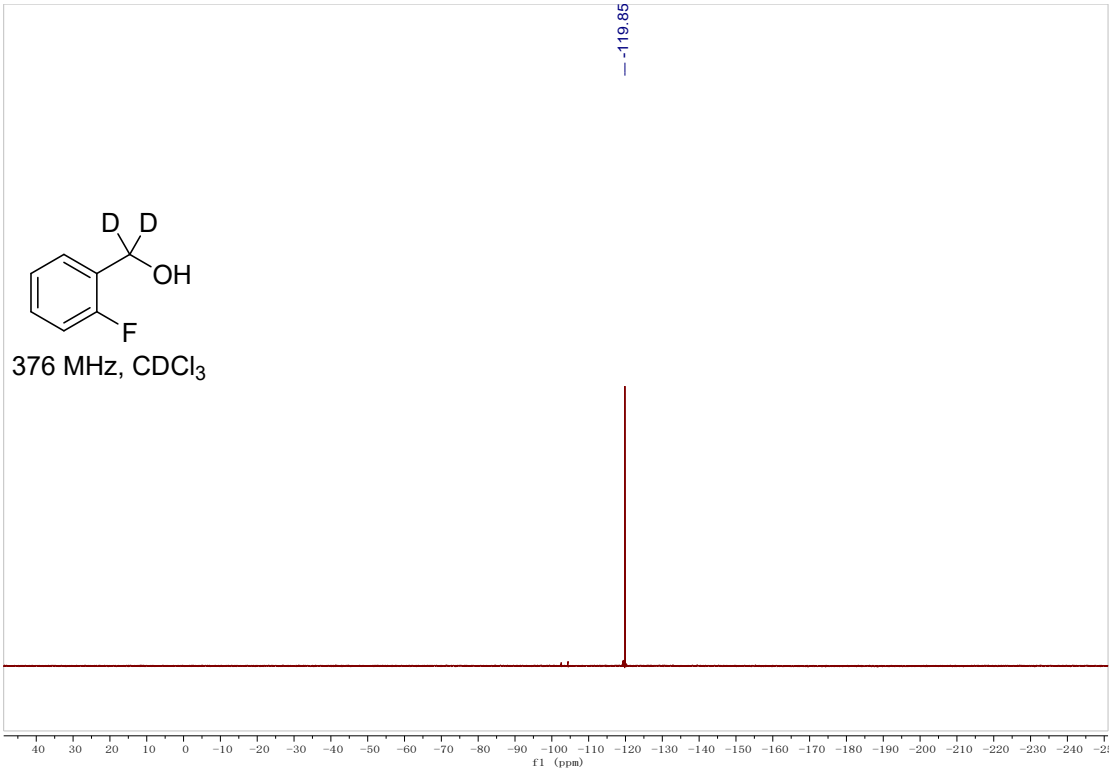



-116.40
D
D
OH
NC
F
376 MHz, CDCl3
100
50
0
−50
−100
−150
−200
−250
−300
f1 (ppm)

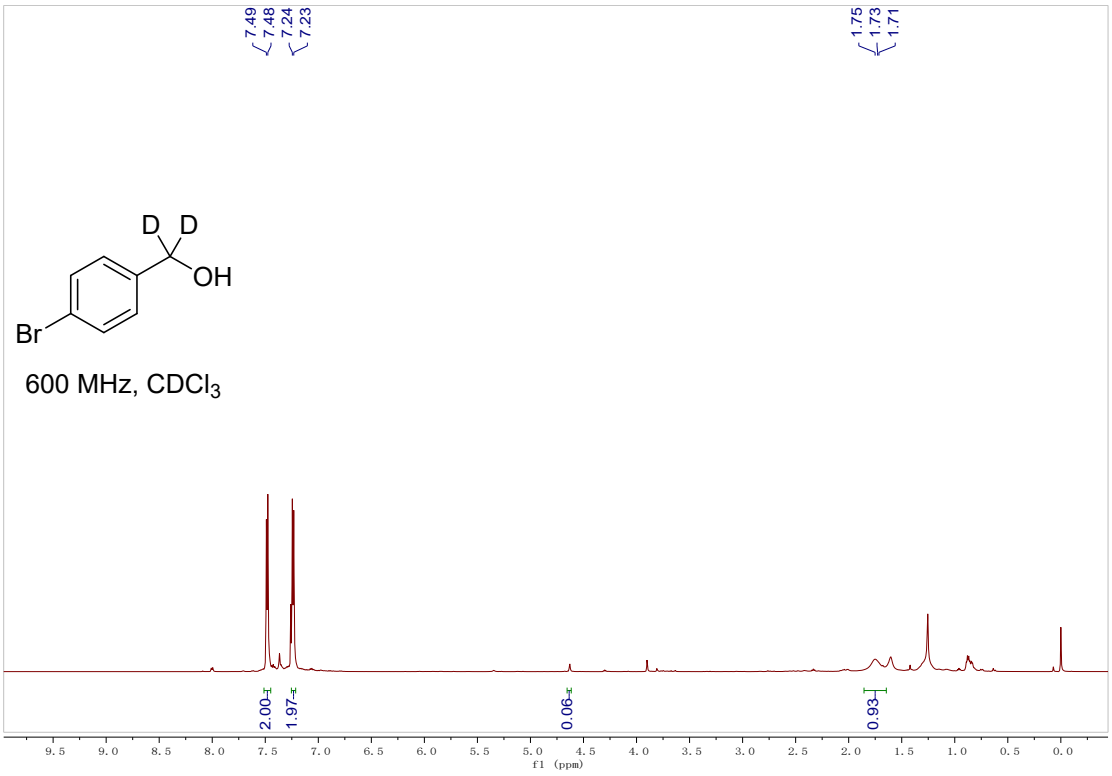
(2-Fluorophenyl)methan-d_2-ol (3d)

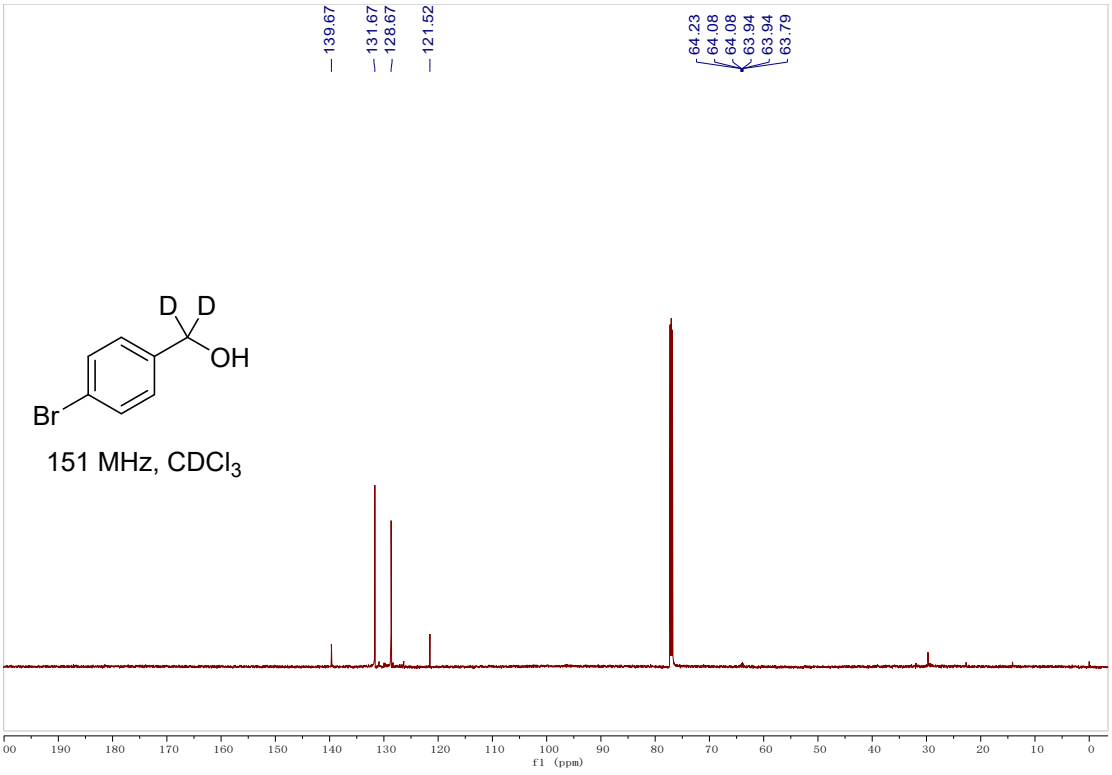




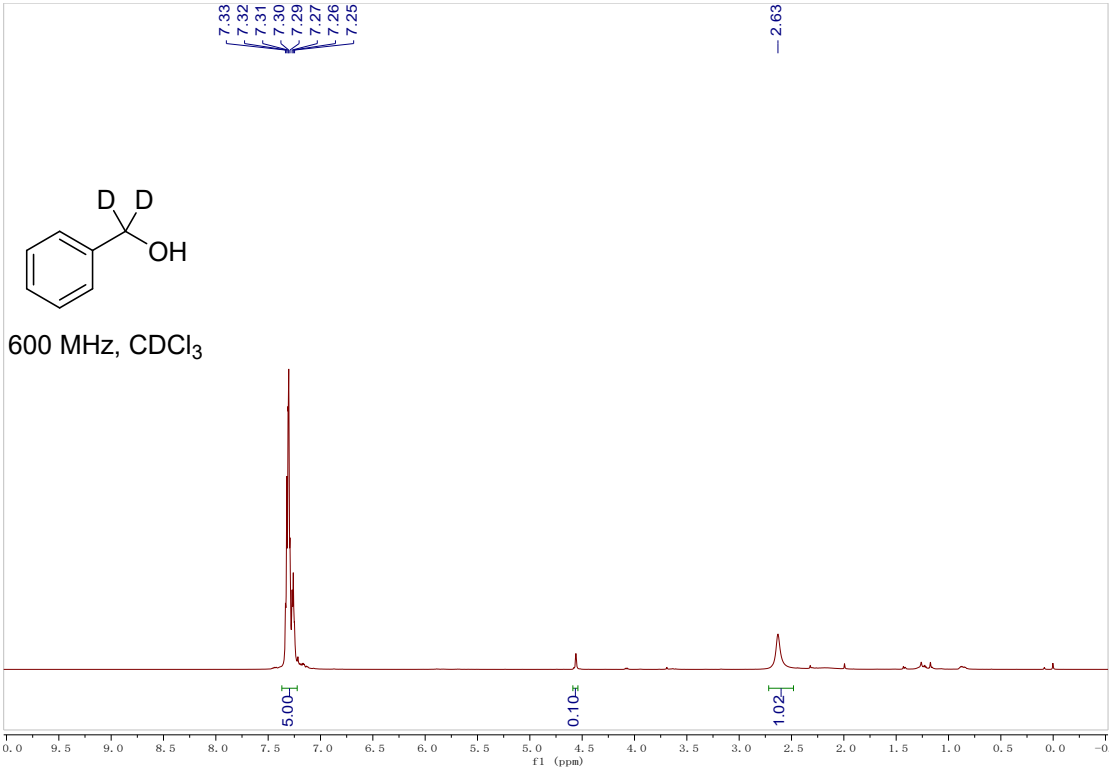

-119.85
D D
OH
F
376 MHz, CDCl3
40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220 −230 −240
f1 (ppm)

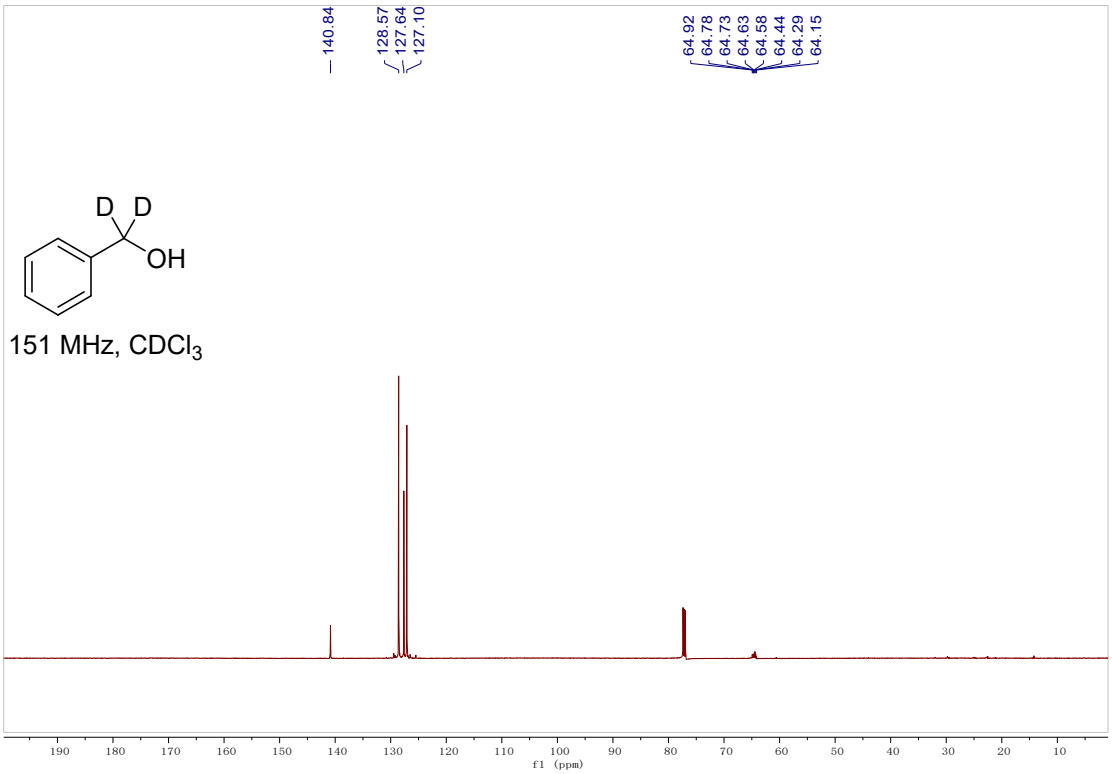
(4-Bromophenyl)methan-d_2-ol (3e)



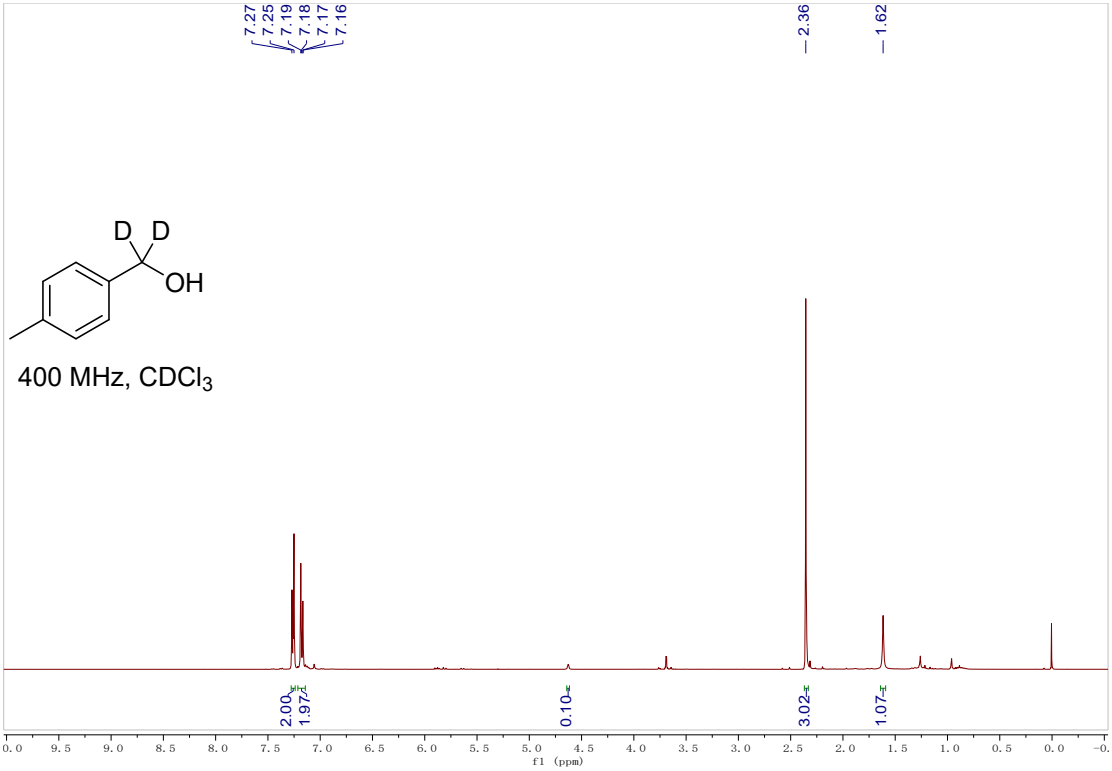


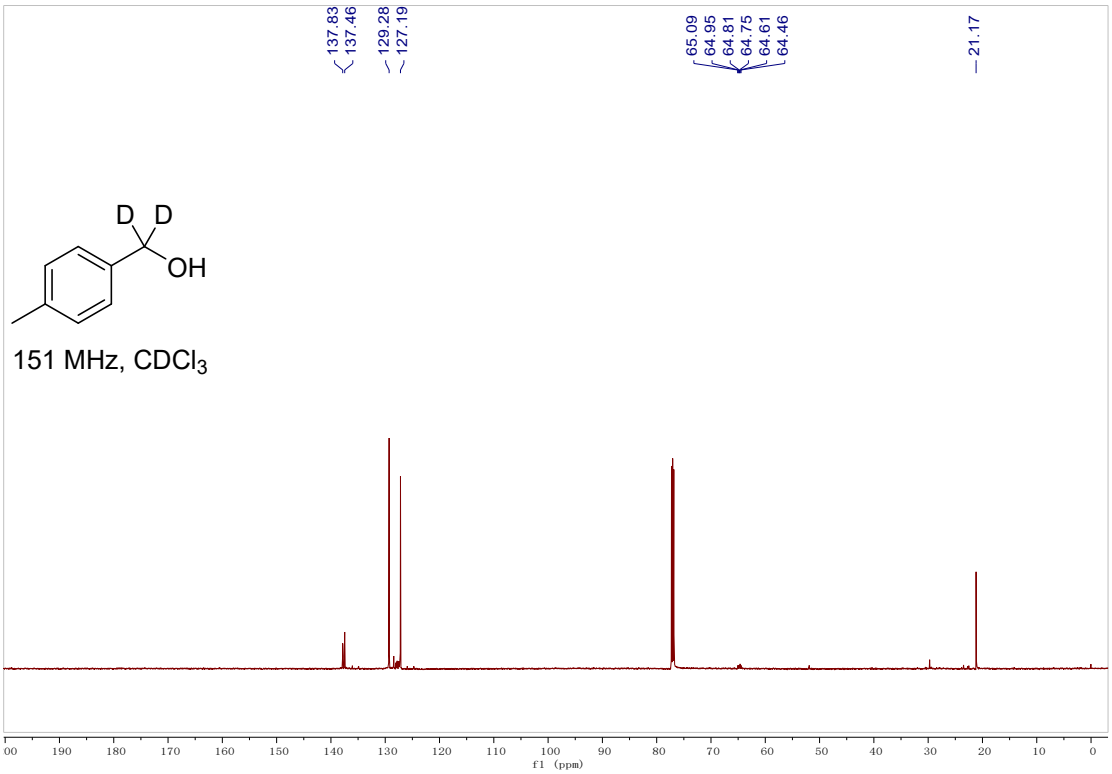
Phenylmethan-d_2-ol (3f)



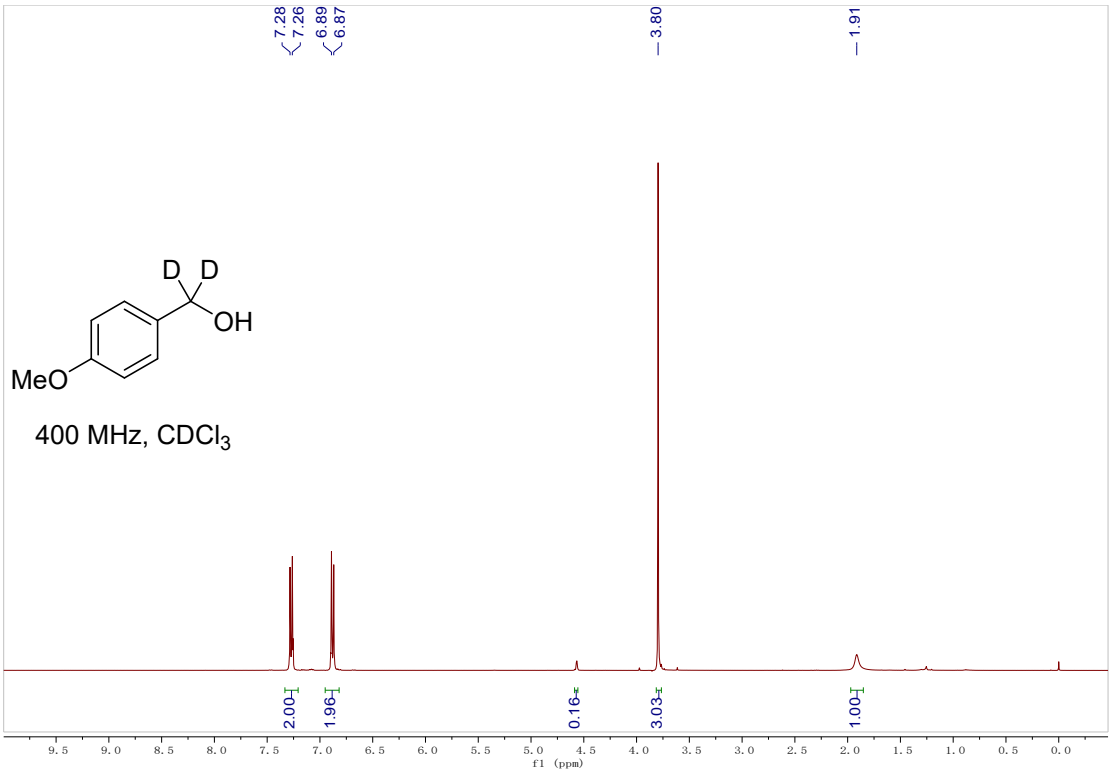


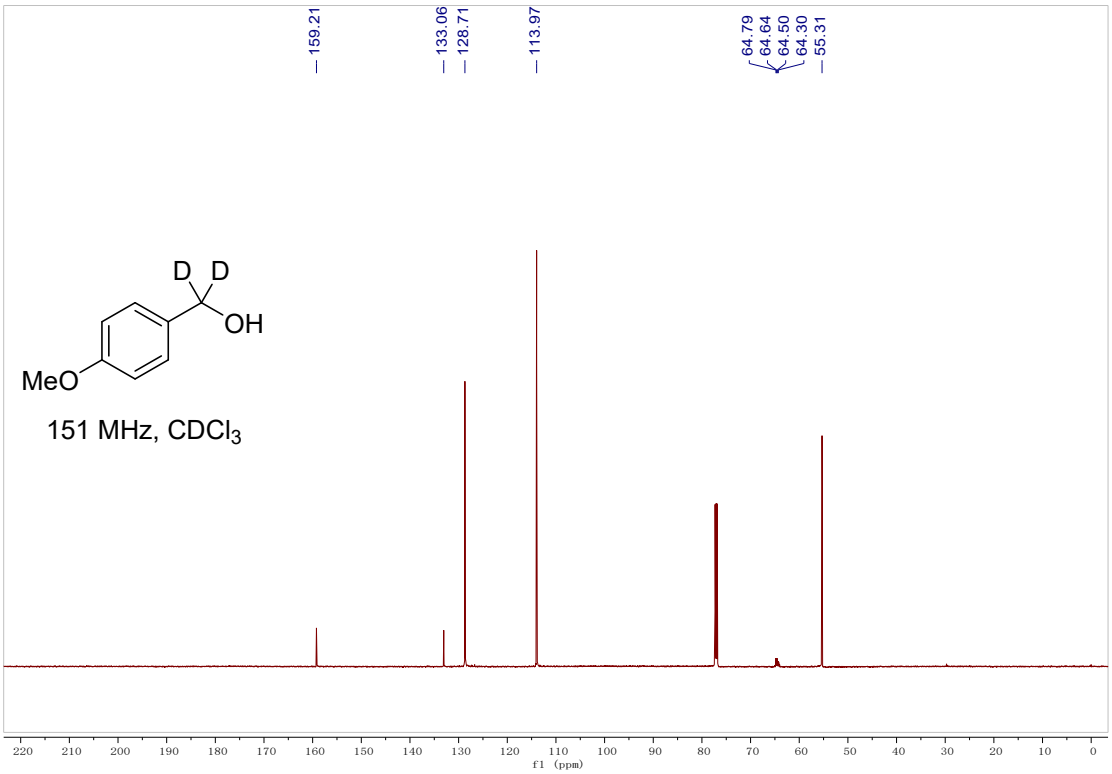
***p*-Tolylmethan-d_2-ol (3g)**



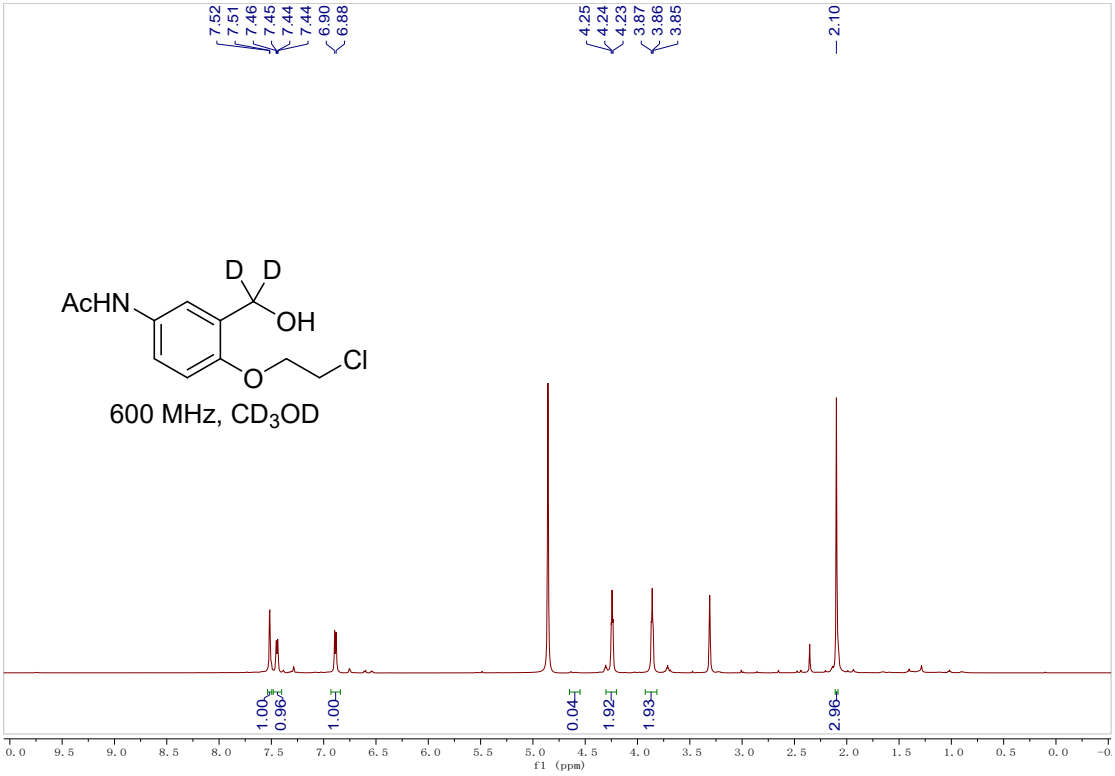


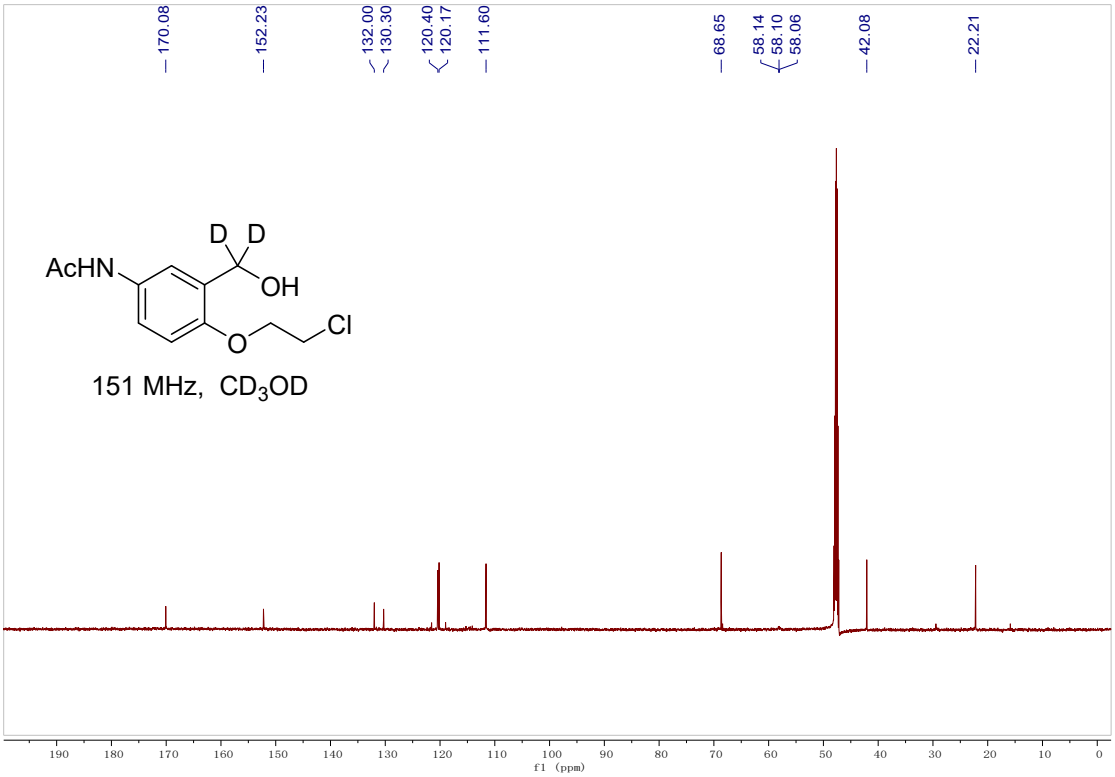
(4-Methoxyphenyl)methan-d_2-ol (3h)





N-(4-(2-chloroethoxy)-3-(hydroxymethyl-d_2)phenyl)acetamide (3i)





l