Electronic Supplementary Material (ESI) for Chemical Communications

Electron Transfer Reduction of Unactivated Esters using SmI_2-H_2O

Michal Szostak, Malcolm Spain and David J. Procter*

School of Chemistry, University of Manchester, Oxford Road, Manchester, M13 9PL, United Kingdom

david.j.procter@manchester.ac.uk

Electronic Supplementary Information

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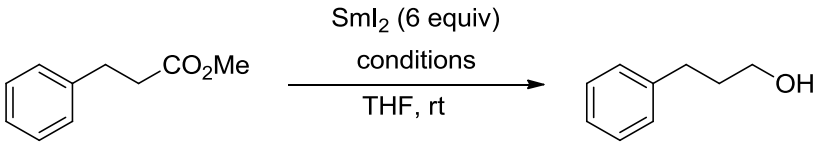
Corresponding Author:

Professor David J. Procter
School of Chemistry
University of Manchester
Oxford Road
Manchester, M13 9PL
United Kingdom

Additional Optimization Data

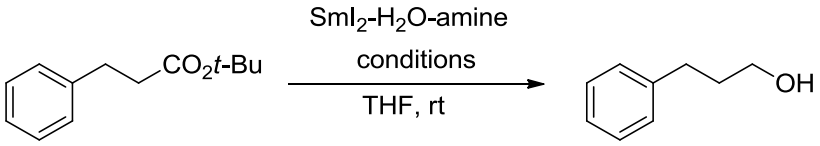
Table ESI-1. Optimization of reduction of hydrocinnamic methyl ester with SmI_2.[a]



entry	amine	proton source	equiv (amine)	equiv (proton source)	time[b]	conversion[c] [%]
1	Et_3N	H_2O	12	18	5 min	96
2	*i*-Pr_2NH	H_2O	12	18	5 min	86
3	*n*-$BuNH_2$	H_2O	12	18	5 min	99
4	pyrrolidine	H_2O	12	18	5 min	99
5	piperidine	H_2O	12	18	5 min	94
6	morpholine	H_2O	12	18	5 min	90
7	*N*-methylmorpholine	H_2O	12	18	24 h	91
8	$Me_2N(CH_2)_2OH$	H_2O	12	18	24 h	74
9	Et_3N	MeOH	12	18	24 h	9
10	Et_3N	*t*-BuOH	12	18	24 h	<2
11	Et_3N	$(HOCH_2)_2$	12	9	24 h	94
12	Et_3N	-	12	-	24 h	5-7
13	pyrrolidine	-	12	-	18 h	<2
14	$Me_2N(CH_2)_2OH$	-	12	-	24 h	<2
15	-	H_2O	-	12	72 h	<2
16	-	H_2O	-	800	24 h	<2

[a]All reactions carried out using standard Schlenk techniques for handling air-sensitive reagents. [b]Quenched by bubbling air through reaction mixtures. [c]Determined by GC or ^1H NMR.

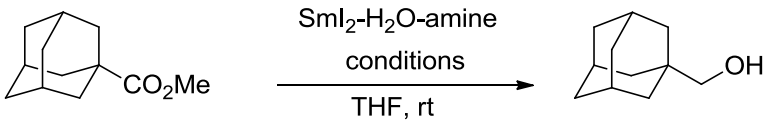
Table ESI-2. Optimization of reduction of hydrocinnamic acid *tert*-butyl ester with SmI_2-H_2O.[a]



entry	amine	SmI_2 (equiv)	H_2O (equiv)	amine (equiv)	time[b]	conversion[c] [%]
1	Et_3N	6	18	18	24 h	56
2	pyrrolidine	6	18	18	24 h	74
3	Et_3N	6	18	36	24 h	60
4	pyrrolidine	6	18	36	24 h	87
5	Et_3N	10	30	30	24 h	81
6	Et_3N	16	48	48	24 h	>98
7	Et_3N	8	24	192	24 h	88
8	Et_3N	8	192	192	24 h	50

[a,b,c]See, Table ESI-1.

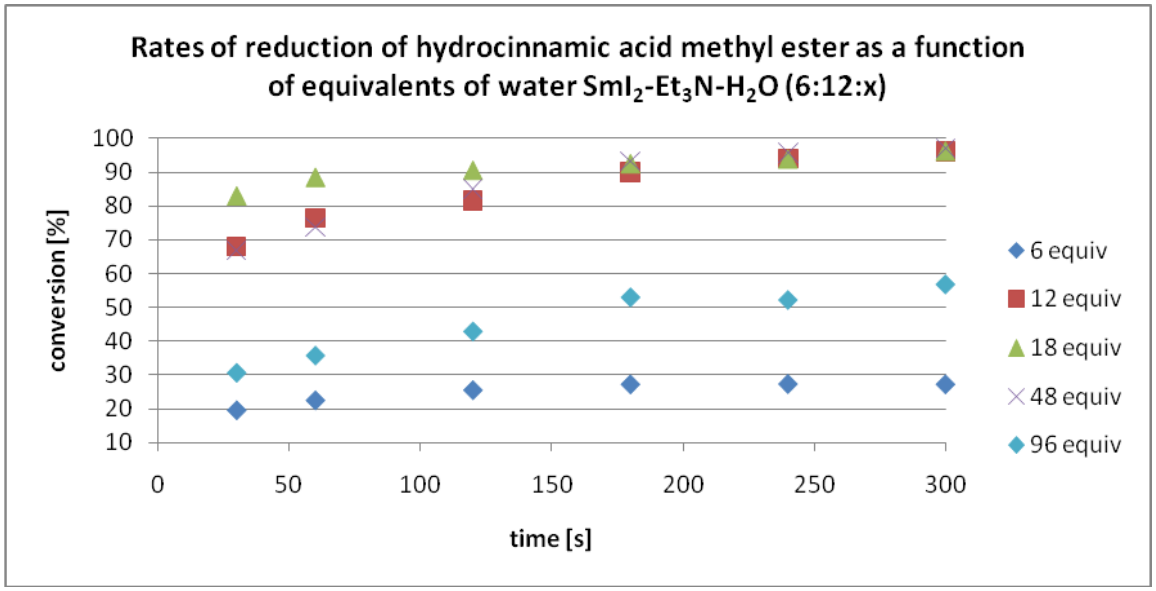
Table ESI-3. Optimization of reduction of methyl adamantane-1-carboxylate with SmI_2-H_2O.[a]



entry	amine	SmI_2 (equiv)	H_2O (equiv)	amine (equiv)	time[b]	conversion[c] [%]
1	Et_3N	6	18	18	24 h	77
2	pyrrolidine	6	18	18	24 h	93
3	Et_3N	6	18	36	24 h	91
4	pyrrolidine	6	18	36	24 h	88
5	Et_3N	10	30	30	24 h	>98
6	Et_3N	8	24	96	24 h	>98
7	Et_3N	8	96	96	24 h	>95
8	Et_3N	8	192	192	24 h	84

[a,b,c]See, Table ESI-1.

Figure ESI-1. Influence of concentration of water on reduction of hydrocinnamic acid methyl ester.



Interestingly, we have determined that the rate of reduction of hydrocinnamic acid methyl ester with SmI_2-H_2O-Et_3N does not exhibit a linear dependance on concentration of water (Figure ESI-1). Detailed studies on the mechanism and kinetic profile of the reduction of unactivated esters with SmI_2 are in progress and will be disclosed in a full account of this work.

List of Known Compounds

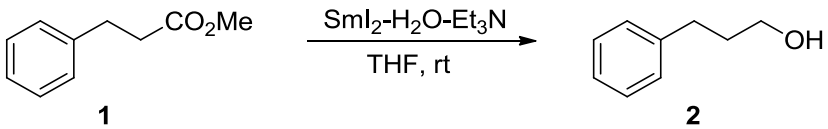
All compounds used in this study have been described in literature or are commercially available. Esters were purchased from commercial suppliers or prepared by standard methods.[1-9] Samarium(II) iodide was prepared by standard methods and titrated prior to use.[10-13] Tetrahydrofuran (THF) was purchased from Fisher Scientific and purified by passing through activated alumina columns.

Experimental Procedures and Characterization Data

General procedure for the reduction of esters with SmI_2-H_2O. To ester (neat or dissolved in 1.0 mL of THF), samarium(II) iodide (THF solution, typically 6 or 8 equiv) was added, followed by amine (typically 18 or 24 equiv) and water (typically 18 or 24 equiv) under inert atmosphere at room temperature and stirred vigorously. After the specified time (typically 2-6 h), the excess of SmI_2 was oxidized by bubbling air through the reaction mixture. The reaction mixture was diluted with EtOAc (20 mL) and HCl (10 mL, 1.0 *M*). The aqueous layer was extracted with EtOAc (3 x 20 mL), organic layers were combined, washed with brine (1 x 10 mL), dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography using a short plug of silica gel. All yields refer to isolated yields unless stated otherwise.

Note: we have noticed very small differences in reactivity between systems employing SmI_2-H_2O-amine in 6-18-12 ratio and SmI_2-H_2O-amine in 6-18-18 ratio. Due to a slightly higher reactivity the latter system has been typically preferred. For the reduction of more sterically-demanding esters systems employing SmI_2-H_2O-amine in 8-24-24 ratio have been typically preferred over the systems employing 6 equivalents of SmI_2, however conversions higher than 95% have been routinely observed even with the limiting number of equivalents of the reductant. As shown in Tables ESI-2 and ESI-3, in the case of very demanding substrates the increase of reactivity could be typically achieved by employing larger number of equivalents of the reducing agent. The amount of samarium(II) iodide used (typically, 6-8 equiv) is consistent with the proposed four-electron mechanism: a 1.5-2-fold excess of the reagent was used to ensure that the reactions were complete.

3-Phenylpropan-1-ol (Table 1, entry 1)

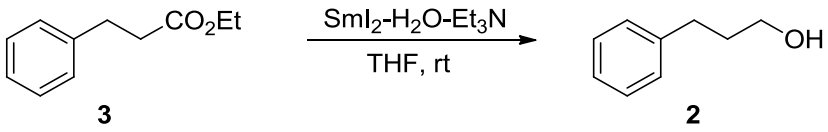


1 **2**

According to the general procedure, the reaction of methyl 3-phenylpropanoate (0.25 mmol), samarium(II) iodide (1.5 mmol), water (4.5 mmol) and triethylamine (4.5 mmol) for 2 h at rt, afforded after chromatography (1/4-1/1 EtOAc/hexanes) the title compound in 97% yield. Oil (R_f

= 0.20, 1/4 EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.27 (br, 1H), 1.80-1.86 (m, 2H), 2.64 (t, *J* = 7.5 Hz, 2H), 3.61 (t, *J* = 6.5 Hz, 2H), 7.10-7.24 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 32.1, 34.3, 62.3, 125.9, 128.4, 128.5, 141.8.

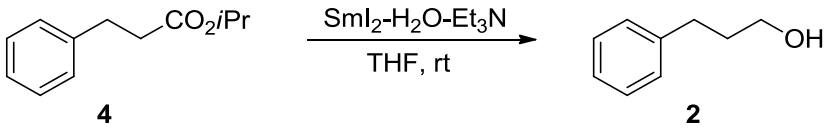
3-Phenylpropan-1-ol (Table 1, entry 2)



3 **2**

According to the general procedure, the reaction of ethyl 3-phenylpropanoate (0.10 mmol), samarium(II) iodide (0.6 mmol), water (1.8 mmol) and triethylamine (1.8 mmol) for 2 h at rt, afforded after chromatography (1/4-1/1 EtOAc/hexanes) the title compound in 99% yield. Oil (R_f = 0.20, 1/4 EtOAc/hexanes). Spectroscopic properties matched those previously described.

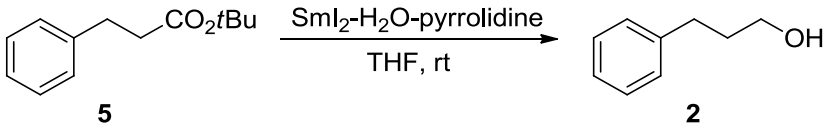
3-Phenylpropan-1-ol (Table 1, entry 3)



4 **2**

According to the general procedure, the reaction of isopropyl 3-phenylpropanoate (0.10 mmol), samarium(II) iodide (0.8 mmol), water (2.4 mmol) and triethylamine (2.4 mmol) for 5 h at rt, afforded after chromatography (1/10-1/1 EtOAc/hexanes) the title compound in 88% yield. Oil (R_f = 0.20, 1/4 EtOAc/hexanes). Spectroscopic properties matched those previously described.

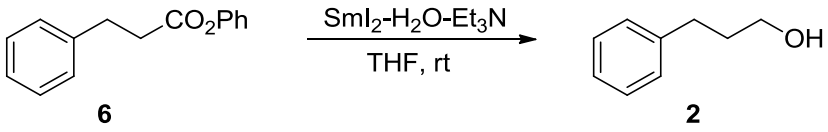
3-Phenylpropan-1-ol (Table 1, entry 4)



5 **2**

According to the general procedure, the reaction of *tert*-butyl 3-phenylpropanoate (0.10 mmol), samarium(II) iodide (1.2 mmol), water (3.6 mmol) and pyrrolidine (3.6 mmol) for 5 h at rt, afforded after chromatography (1/10-1/1 EtOAc/hexanes) the title compound in 83% yield. Oil (R_f = 0.20, 1/4 EtOAc/hexanes). Spectroscopic properties matched those previously described.

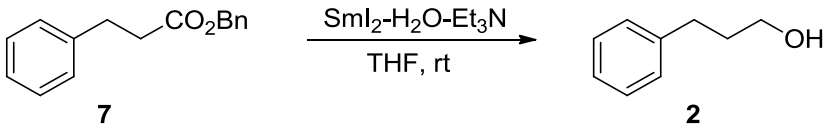
3-Phenylpropan-1-ol (Table 1, entry 5)



6 **2**

According to the general procedure, the reaction of phenyl 3-phenylpropanoate (0.10 mmol), samarium(II) iodide (0.6 mmol), water (1.8 mmol) and triethylamine (1.8 mmol) for 2 h at rt, afforded after chromatography (1/10-1/1 EtOAc/hexanes) the title compound in 94% yield. Oil (R_f = 0.20, 1/4 EtOAc/hexanes). Spectroscopic properties matched those previously described.

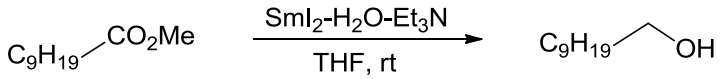
3-Phenylpropan-1-ol (Table 1, entry 6)



7 **2**

According to the general procedure, the reaction of benzyl 3-phenylpropanoate (0.10 mmol), samarium(II) iodide (1.0 mmol), water (3.0 mmol) and triethylamine (3.0 mmol) for 2 h at rt, afforded after chromatography (1/10-1/1 EtOAc/hexanes) the title compound in 97% yield. Oil (R_f = 0.20, 1/4 EtOAc/hexanes). Spectroscopic properties matched those previously described.

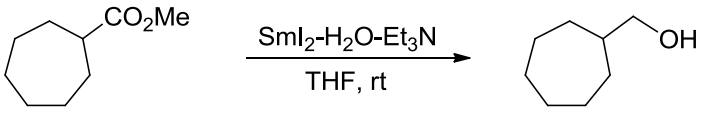
Decan-1-ol (Table 2, entry 1)



8 **8a**

According to the general procedure, the reaction of methyl decanoate (0.10 mmol), samarium(II) iodide (0.8 mmol), water (2.4 mmol) and triethylamine (1.8 mmol) for 15 h at rt, afforded after chromatography (1/1 EtOAc/hexanes-EtOAc) the title compound in 95% yield. Oil (R_f = 0.24, 1/4 EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.81 (t, *J* = 6.9 Hz, 3H), 1.15-1.33 (m, 15H), 1.47-1.52 (m, 2H), 3.57 (t, *J* = 5.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 22.7, 25.7, 29.3, 29.4, 29.6, 29.6, 31.9, 32.8, 63.1.

Cycloheptylmethanol (Table 2, entry 2)

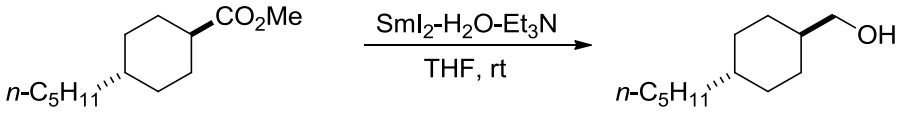


9 **9a**

According to the general procedure, the reaction of methyl cycloheptanecarboxylate (0.10 mmol), samarium(II) iodide (0.8 mmol), water (2.4 mmol) and triethylamine (2.4 mmol) for 3 h at rt, afforded after chromatography (CH_2Cl_2-1/4 Et_2O/CH_2Cl_2) the title compound in 98% yield. Note: work-up with CH_2Cl_2 (3 x 20 mL) and 1.0 *M* HCl (1 x 10 mL). Oil (R_f = 0.39, 1/4 Et_2O/CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.08-1.15 (m, 2H), 1.30 (br, 1H), 1.34-1.46 (m,

5H), 1.48-1.64 (m, 4H), 1.65-1.71 (m, 2H), 3.35 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.5, 28.6, 30.8, 42.1, 68.7.

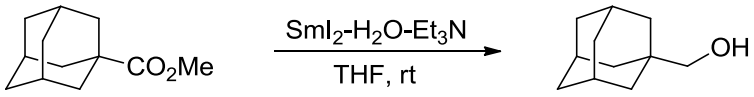
***trans*-4-(Pentylcyclohexyl)methanol** (Table 2, entry 3)



10 **10a**

According to the general procedure, the reaction of methyl *trans*-4-pentylcyclohexanecarboxylate (0.10 mmol), samarium(II) iodide (0.8 mmol), water (2.4 mmol) and triethylamine (2.4 mmol) for 6 h at rt, afforded after chromatography (1/10-1/4 EtOAc/hexanes) the title compound in 87% yield. Oil (R_f = 0.43, 1/4 EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.77-0.92 (m, 7H), 1.06-1.28 (m, 10H), 1.35 (br, 1H), 1.71 (d, *J* = 8.7 Hz, 4H), 3.37 (d, *J* = 6.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 22.7, 26.6, 29.5, 32.2, 32.7, 37.4, 37.8, 40.7, 68.8.

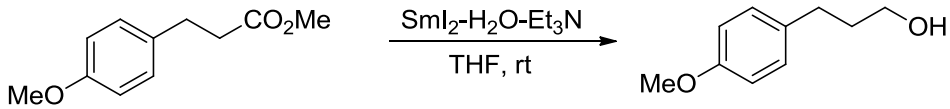
1-Adamantanemethanol (Table 2, entry 4)



11 **11a**

According to the general procedure, the reaction of methyl adamantane-1-carboxylate (0.10 mmol), samarium(II) iodide (1.0 mmol), water (3.0 mmol) and triethylamine (3.0 mmol) for 20 h at rt, afforded after chromatography (1/10-1/1 EtOAc/hexanes) the title compound in 80% yield. Solid (R_f = 0.57, 1/4 EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.23 (br, 1H), 1.44 (m, 6H), 1.57 (m, 1H), 1.59 (m, 2H), 1.65 (m, 2H), 1.68 (m, 1H), 1.92 (m, 3H), 3.13 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.2, 34.5, 37.2, 39.0, 73.9.

3-(4-Methoxyphenyl)propan-1-ol (Table 2, entry 5)

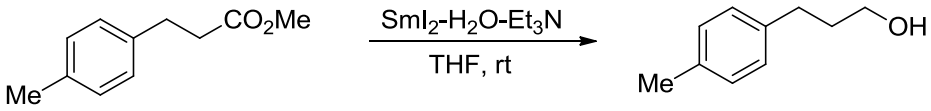


12 **12a**

According to the general procedure, the reaction of methyl 3-(4-methoxyphenyl)propanoate (0.25 mmol), samarium(II) iodide (1.5 mmol), water (4.5 mmol) and triethylamine (4.5 mmol) for 2 h at rt, afforded after chromatography (1/4-1/1 EtOAc/hexanes) the title compound in 99% yield. Oil (R_f = 0.62, 1/1 EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.55 (br, 1H), 1.75-

1.81 (m, 2H), 2.57 (t, *J* = 7.5 Hz, 2H), 3.58 (t, *J* = 6.5 Hz, 2H), 3.71 (s, 3H), 6.75 (d, *J* = 8.5 Hz, 2H), 7.03 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.2, 34.5, 55.3, 62.2, 113.8, 129.3, 133.9, 157.8.

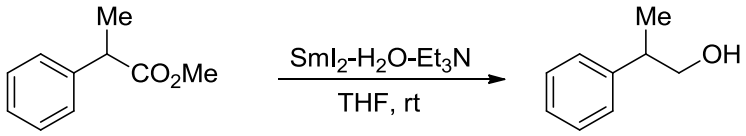
3-(*p*-Tolyl)propan-1-ol (Table 2, entry 6)



13 **13a**

According to the general procedure, the reaction of methyl 3-(*p*-tolyl)propanoate (0.10 mmol), samarium(II) iodide (0.6 mmol), water (1.8 mmol) and triethylamine (1.8 mmol) for 3 h at rt, afforded after chromatography (1/10-1/1 EtOAc/hexanes) the title compound in 97% yield. Oil (R_f = 0.63, 1/1 EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.24 (br, 1H), 1.76-1.85 (m, 2H), 2.25 (s, 3H), 2.60 (t, *J* = 7.5 Hz, 2H), 3.60 (t, *J* = 6.6 Hz, 2H), 7.02 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.0, 31.6, 34.4, 62.4, 128.3, 129.1, 135.3, 138.7.

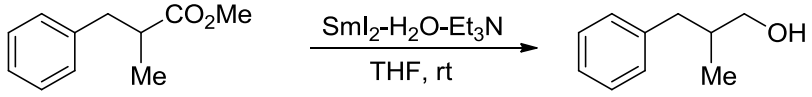
2-Phenylpropan-1-ol (Table 2, entry 7)



14 **14a**

According to the general procedure, the reaction of methyl 2-phenylpropanoate (0.25 mmol), samarium(II) iodide (1.5 mmol), water (4.5 mmol) and triethylamine (4.5 mmol) for 24 h at rt, afforded after chromatography (1/10-1/1 EtOAc/hexanes) the title compound in 95% yield. Oil (R_f = 0.56, 1/1 EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.21 (d, *J* = 7.0 Hz, 3H), 1.33 (br, 1H), 2.84-2.91 (m, 1H), 3.63 (d, *J* = 7.0 Hz, 2H), 7.14-7.18 (m, 3H), 7.24-7.28 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.6, 42.5, 68.7, 126.7, 127.5, 128.7, 143.7.

2-Methyl-3-phenylpropan-1-ol (Table 2, entry 8)

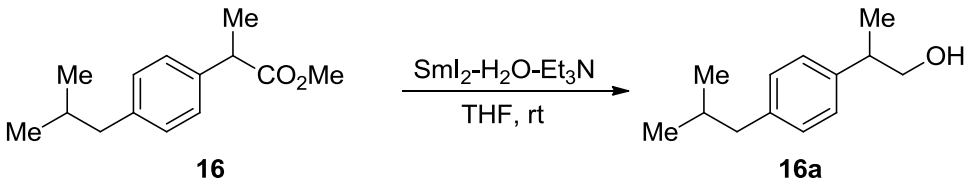


15 **15a**

According to the general procedure, the reaction of methyl 2-methyl-3-phenylpropanoate (0.10 mmol), samarium(II) iodide (0.8 mmol), water (2.4 mmol) and triethylamine (2.4 mmol) for 20 h at rt, afforded after chromatography (1/10-1/1 EtOAc/hexanes) the title compound in 85% yield. Oil (R_f = 0.66, 1/1 EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.85 (d, *J* = 6.5 Hz, 3H), 1.35

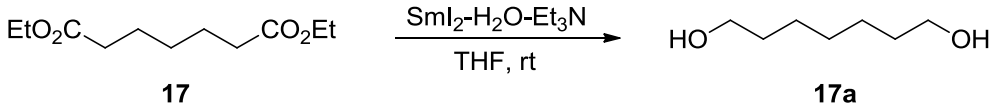
(br, 1H), 1.83-1.92 (m, 1H), 2.36 (dd, *J* = 8.5, 13.5 Hz, 1H), 2.69 (dd, *J* = 6.5, 13.5 Hz, 1H), 3.38-3.49 (m, 2H), 7.09-7.14 (m, 3H), 7.19-7.23 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.5, 37.8, 39.7, 67.7, 125.9, 128.3, 129.2, 140.6.

2-(4-Isobutylphenyl)propan-1-ol (Table 2, entry 9)



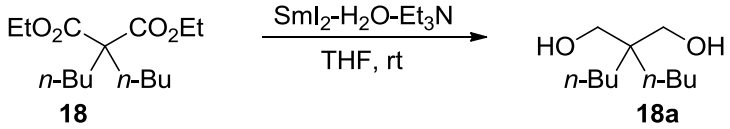
According to the general procedure, the reaction of methyl 2-(4-isobutylphenyl)propanoate (0.10 mmol), samarium(II) iodide (0.8 mmol), water (2.4 mmol) and triethylamine (2.4 mmol) for 20 h at rt, afforded after chromatography (1/10-1/1 EtOAc/hexanes) the title compound in 88% yield. Oil (R_f = 0.79, 1/1 EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.83 (d, *J* = 7.0 Hz, 6H), 1.19 (d, *J* = 7.0 Hz, 3H), 1.54 (br, 1H), 1.73-1.82 (m, 1H), 2.38 (d, *J* = 7.0 Hz, 2H), 2.81-2.89 (m, 1H), 3.61 (d, *J* = 6.5 Hz, 2H), 7.02-7.09 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 17.6, 22.4, 30.3, 42.0, 45.0, 68.8, 127.2, 129.4, 140.1, 140.7.

Heptane-1,7-diol (Table 2, entry 10)



According to the general procedure, the reaction of diethyl heptanedioate (0.10 mmol), samarium(II) iodide (1.2 mmol), water (3.6 mmol) and triethylamine (3.6 mmol) for 20 h at rt, afforded after chromatography (1/10-1/1 EtOAc/hexanes) the title compound in 87% yield. Oil (R_f = 0.35, EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.25 (br, 2H), 1.28-1.33 (m, 6H), 1.47-1.54 (m, 4H), 3.58 (t, *J* = 6.6 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.7, 29.2, 32.7, 63.0.

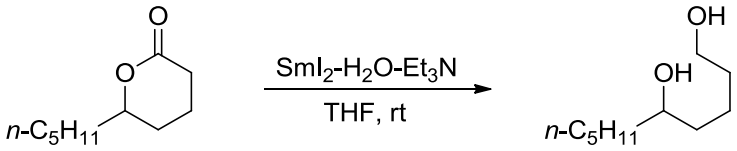
2,2-Dibutylpropane-1,3-diol (Table 2, entry 11)



According to the general procedure, the reaction of diethyl 2,2-dibutylmalonate (0.10 mmol), samarium(II) iodide (1.6 mmol), water (4.8 mmol) and triethylamine (4.8 mmol) for 18 h at rt, afforded after chromatography (1/10-1/1 EtOAc/hexanes-EtOAc) the title compound in 76% yield. Oil (R_f = 0.64, EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.84 (t, *J* = 6.9 Hz, 6H), 1.05-1.31

(m, 12H), 2.36 (br, 2H), 3.50 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 23.6, 25.1, 30.6, 40.9, 69.5.

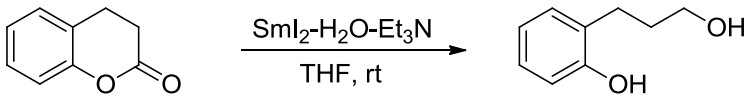
Decane-1,5-diol (Table 2, entry 12)



19 **19a**

According to the general procedure, the reaction of 6-pentyltetrahydro-2*H*-pyran-2-one (0.10 mmol), samarium(II) iodide (0.8 mmol), water (2.4 mmol) and triethylamine (1.6 mmol) for 2 h at rt, afforded after chromatography (EtOAc) the title compound in 97% yield. Oil (R_f = 0.50, EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.82 (t, *J* = 6.9 Hz, 3H), 1.19-1.28 (m, 5H), 1.32-1.58 (m, 7H), 1.48-1.58 (m, 2H), 1.61 (br, 2H), 3.51-3.56 (m, 1H), 3.59 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 21.8, 22.6, 25.3, 31.9, 32.6, 37.0, 37.5, 62.7, 71.9.

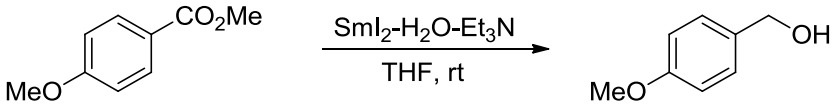
2-(3-Hydroxypropyl)phenol (Table 2, entry 13)



20 **20a**

According to the general procedure, the reaction of chroman-2-one (0.10 mmol), samarium(II) iodide (0.6 mmol), water (1.8 mmol) and triethylamine (1.8 mmol) for 2 h at rt, afforded after chromatography (1/10-1/1 EtOAc/hexanes) the title compound in 92% yield. Oil (R_f = 0.50, EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.78-1.84 (m, 2H), 2.51 (br, 1H), 2.71 (t, *J* = 6.8 Hz, 2H), 3.57 (t, *J* = 5.8 Hz, 2H), 6.76-6.82 (m, 2H), 7.02-7.05 (m, 2H), 7.06 (br, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.1, 32.2, 60.8, 116.1, 120.8, 127.2, 127.6, 130.7, 154.6.

(4-Methoxyphenyl)methanol (Table 2, entry 14)

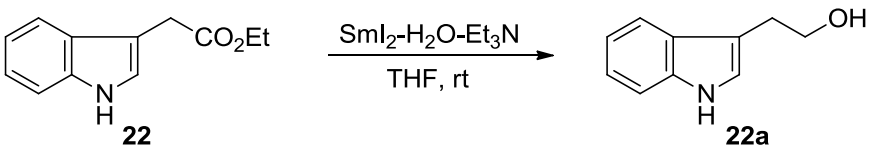


21 **21a**

According to the general procedure, the reaction of methyl 4-methoxybenzoate (0.10 mmol), samarium(II) iodide (0.6 mmol), water (1.8 mmol) and triethylamine (1.8 mmol) for 1 h at rt, afforded after chromatography (4/1 EtOAc/hexanes) the title compound in 90% yield. Oil (R_f = 0.54, 4/1 EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.57 (br, 1H), 3.74 (s, 3H), 4.54 (s,

2H), 6.82 (d, *J* = 8.7 Hz, 2H), 7.22 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.3, 65.1, 114.0, 128.7, 133.2, 159.3.

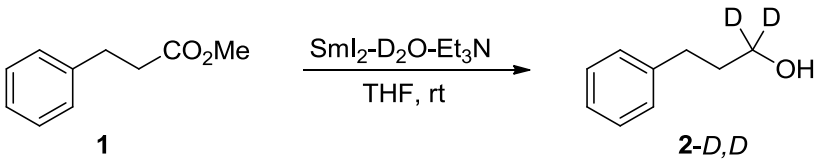
2-(1*H*-Indol-3-yl)ethanol (Table 2, entry 15)



According to the general procedure, the reaction of ethyl 2-(1*H*-indol-3-yl)acetate (0.10 mmol), samarium(II) iodide (0.8 mmol), water (2.4 mmol) and triethylamine (2.4 mmol) for 20 h at rt, afforded after chromatography (1/10-1/1 EtOAc/hexanes) the title compound in 81% yield. Oil (R_f = 0.33, 1/1 EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.47 (br, 1H), 2.97 (t, *J* = 6.3 Hz, 2H), 3.84 (t, *J* = 6.3 Hz, 2H), 7.01 (d, *J* = 1.5 Hz, 1H), 7.06 (t, *J* = 7.0 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.99 (br, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.8, 62.6, 111.3, 112.3, 118.9, 119.5, 122.3, 122.5, 127.4, 136.5.

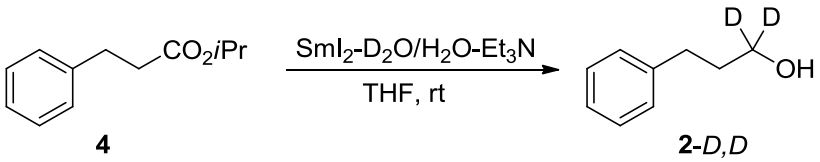
Mechanistic Studies

A) Deuterium incorporation



According to the general procedure, the reaction of methyl 3-phenylpropanoate (0.10 mmol), samarium(II) iodide (0.6 mmol), deuterium oxide (1.8 mmol) and triethylamine (1.2 mmol) for 3 h at rt, afforded 1,1-*D*,*D*-3-phenylpropan-1-ol with >97% deuterium incorporation. Yield 88% (^{1}H NMR vs. internal standard). Purification by chromatography (1/4-1/1 EtOAc/hexanes) afforded the title product (R_f = 0.20, 1/4 EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.50 (br, 1H), 1.82 (t, *J* = 7.7 Hz, 2H), 2.64 (t, *J* = 7.5 Hz, 2H), 7.10-7.24 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 32.0, 34.0, 61.6 (t, J^1 = 21.3 Hz), 125.9, 128.4, 128.4, 141.8.

B) Determination of primary kinetic isotope effect[14-16]



Method 1. According to the general procedure, the reaction of isopropyl 3-phenylpropanoate (0.10 mmol), samarium(II) iodide (0.6 mmol), deuterium oxide/water (1:1, 1.8 mmol) and triethylamine (1.2 mmol) for 5 min at rt, afforded 1,1-*D*,*D*-3-phenylpropan-1-ol and 3-phenylpropan-1-ol (45% conversion). The amount of each species was determined by ^{1}H NMR (500 MHz, $CDCl_3$,). Kinetic isotope effect, k_H/k_D = 1.4.

Method 2. According to the general procedure, the reaction of isopropyl 3-phenylpropanoate (0.10 mmol), samarium(II) iodide (0.6 mmol), water (1.8 mmol) and triethylamine (1.2 mmol) and the reaction of isopropyl 3-phenylpropanoate (0.10 mmol), samarium(II) iodide (0.6 mmol), deuterium oxide (1.8 mmol) and triethylamine (1.2 mmol) were followed by GC with undecane as the internal standard. Initial rates were determined from the slopes at low conversion. Kinetic isotope effect, k_H/k_D = 1.5.

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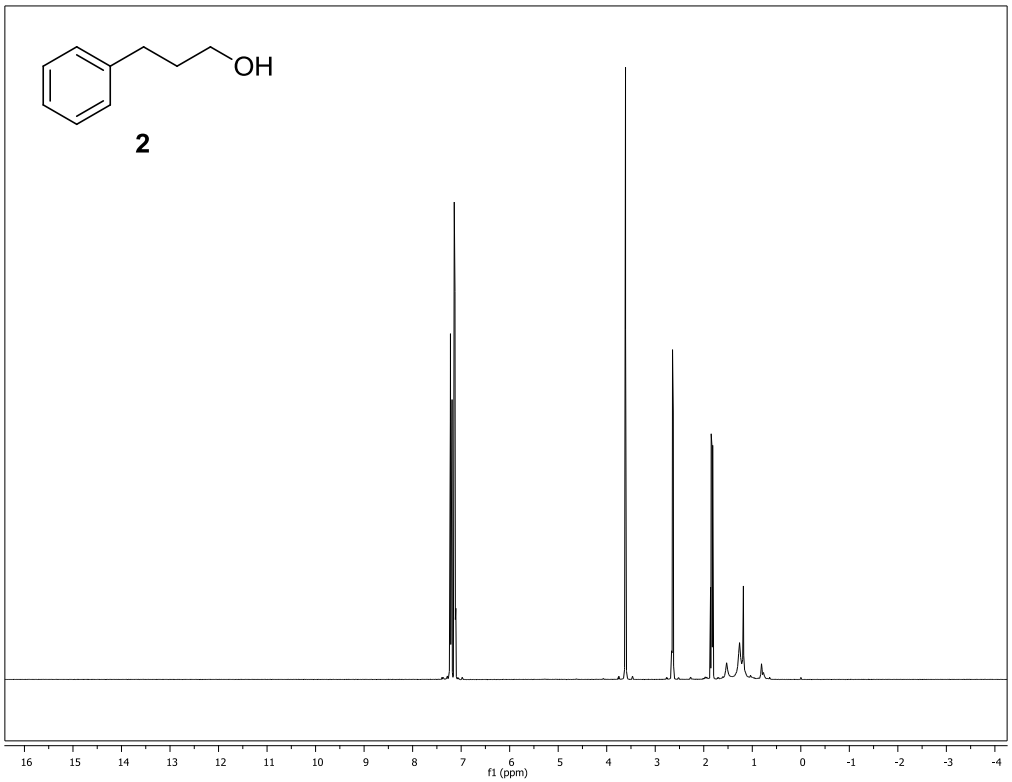
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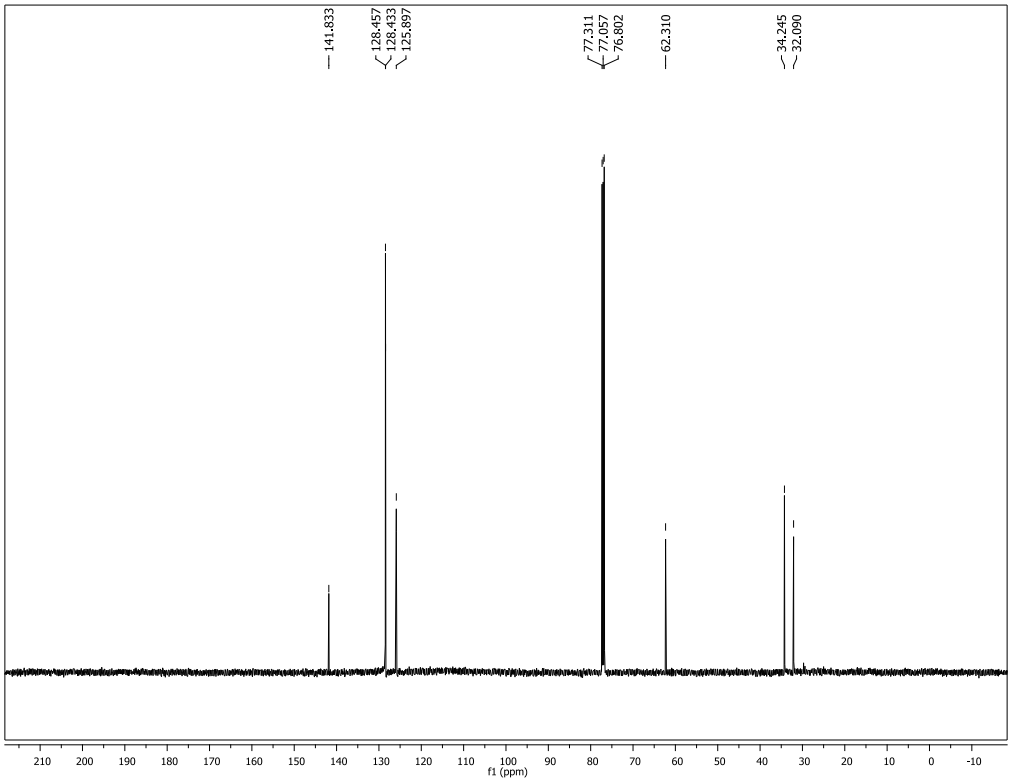
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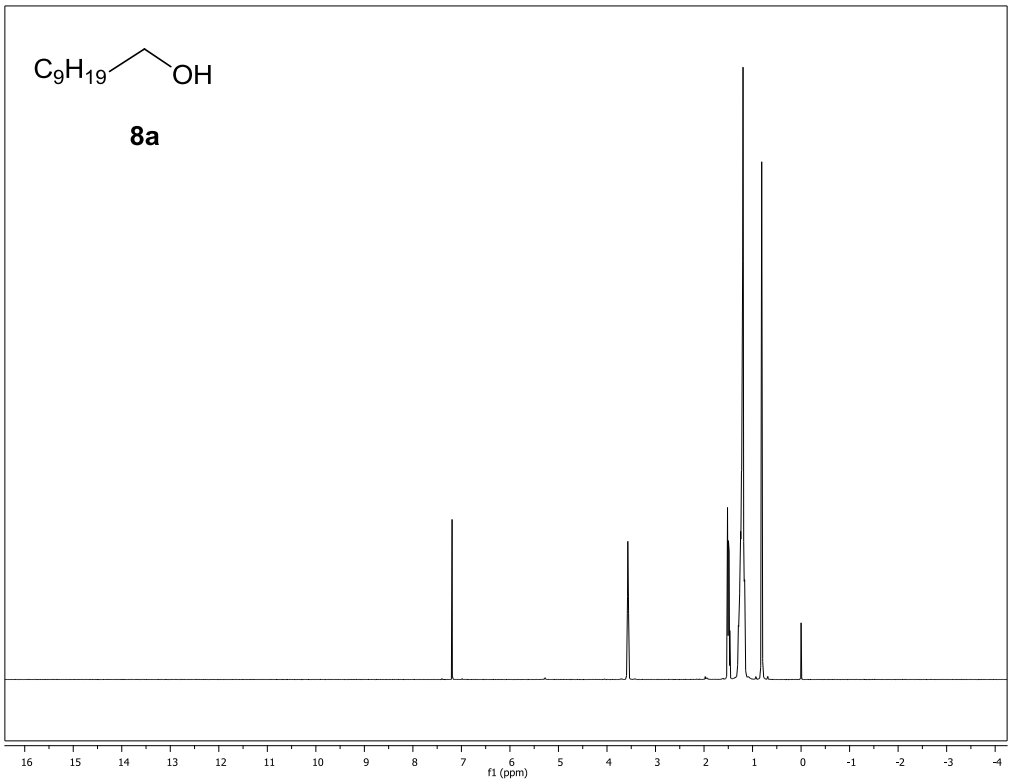

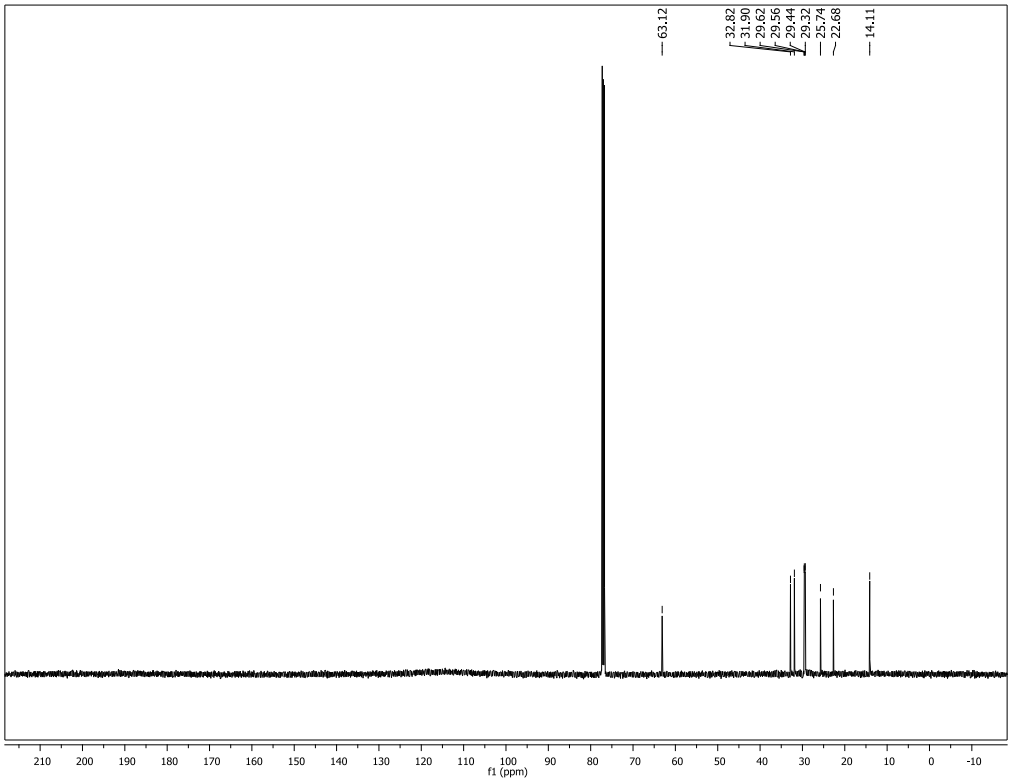

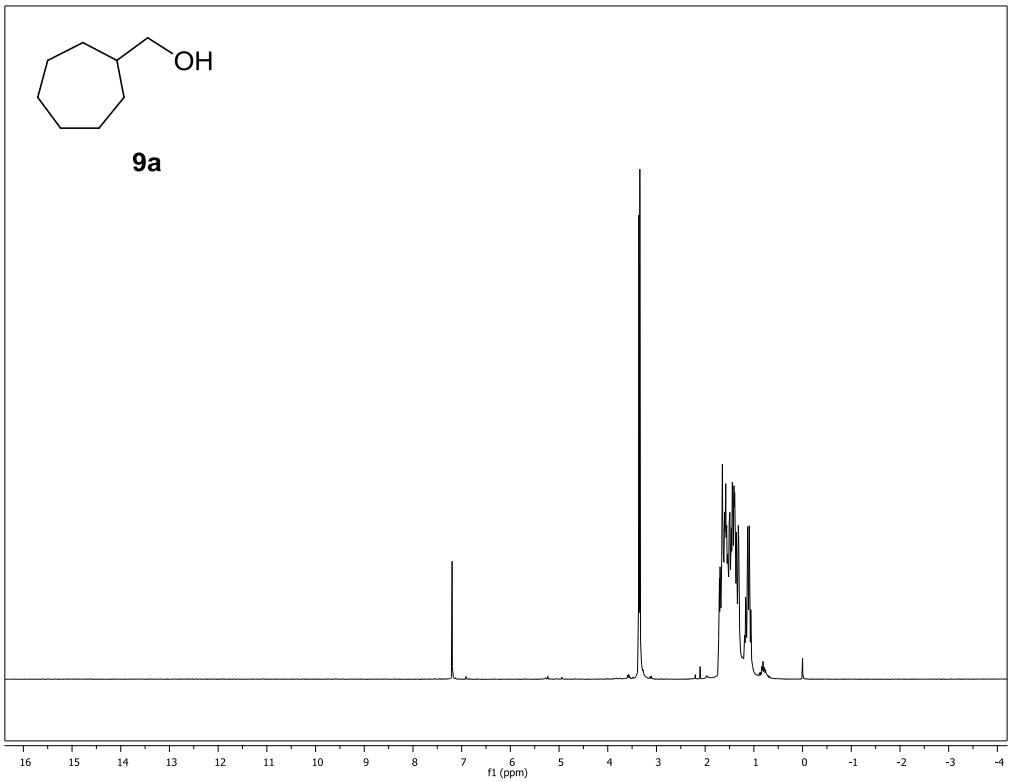

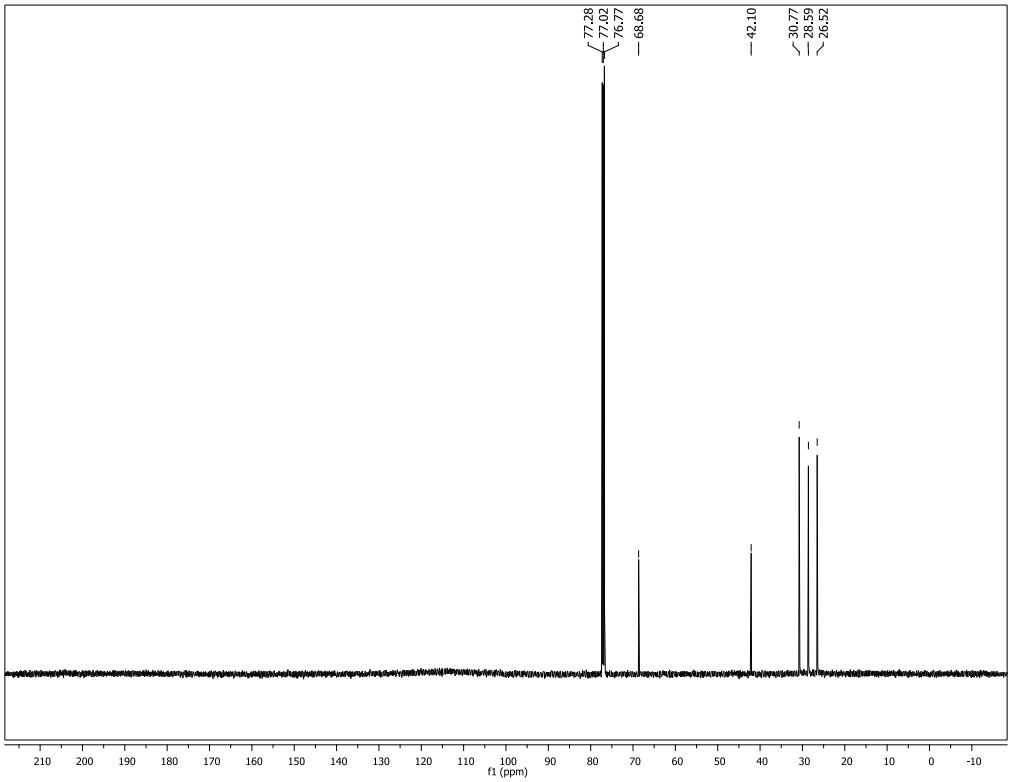

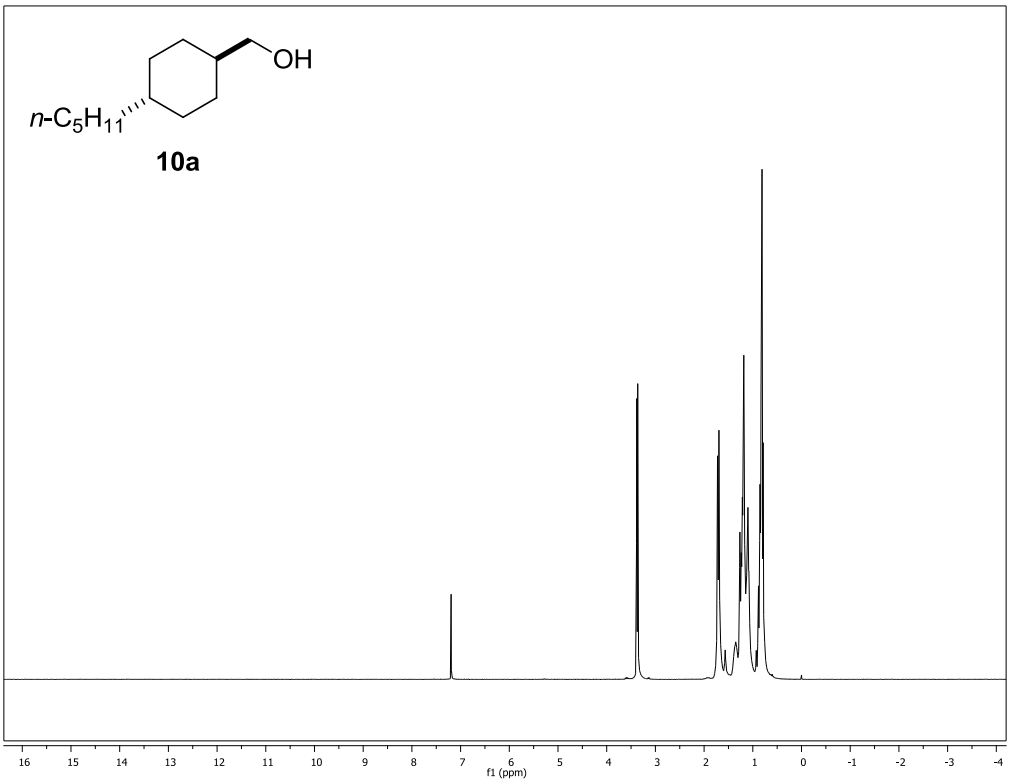

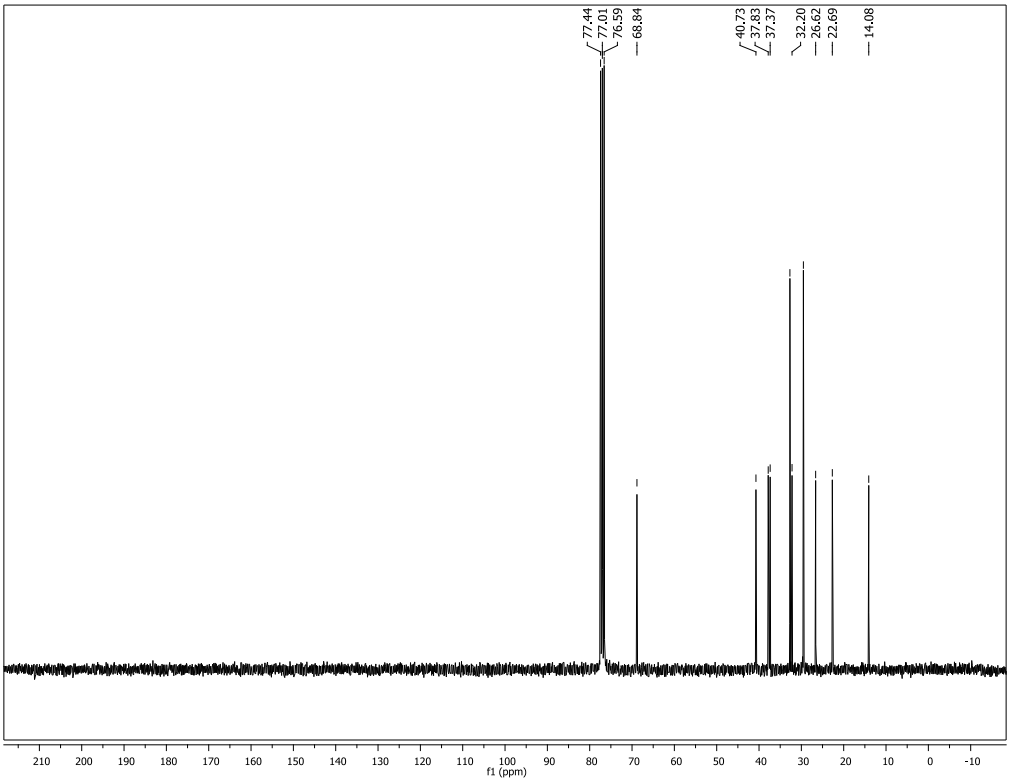

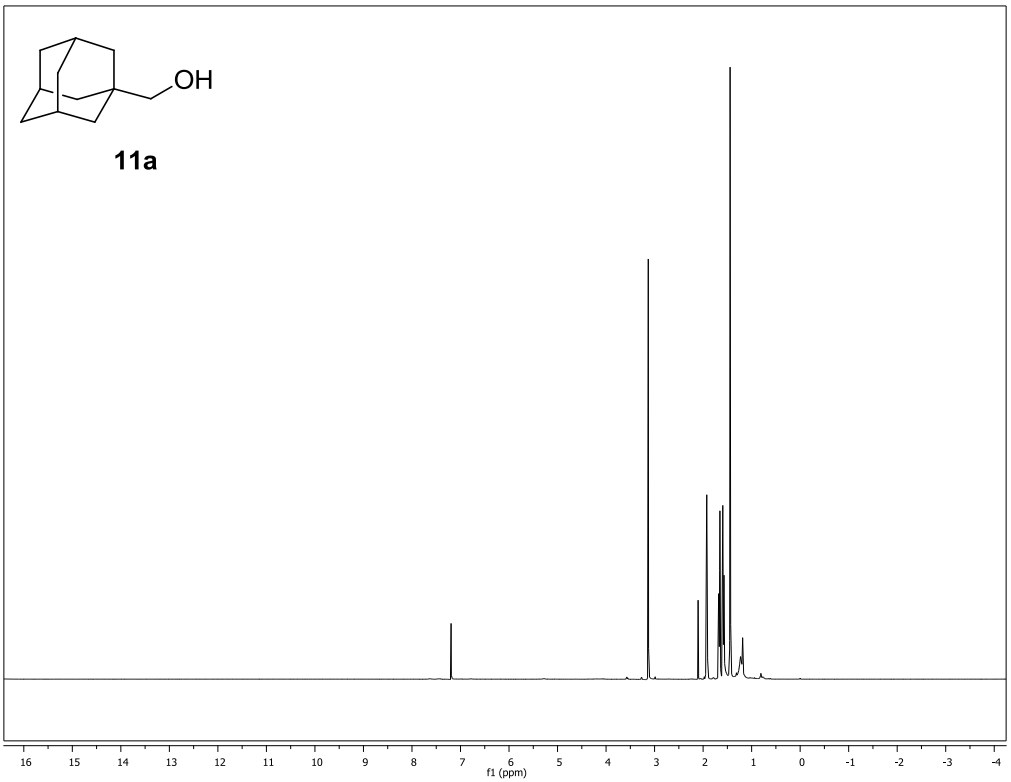

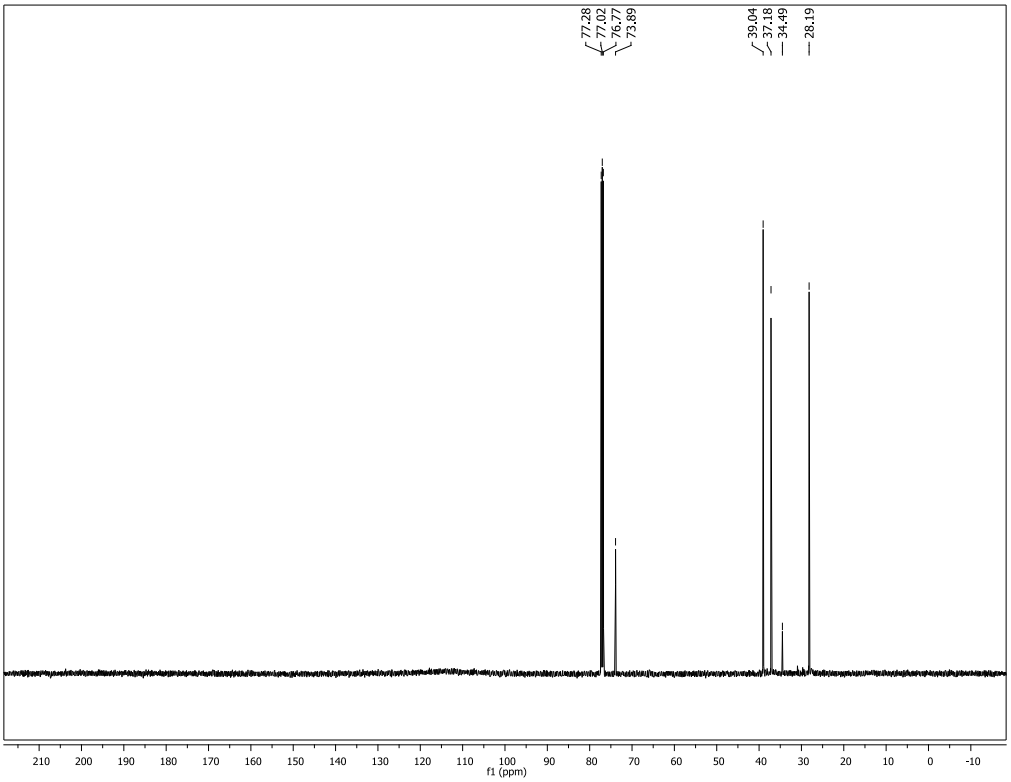

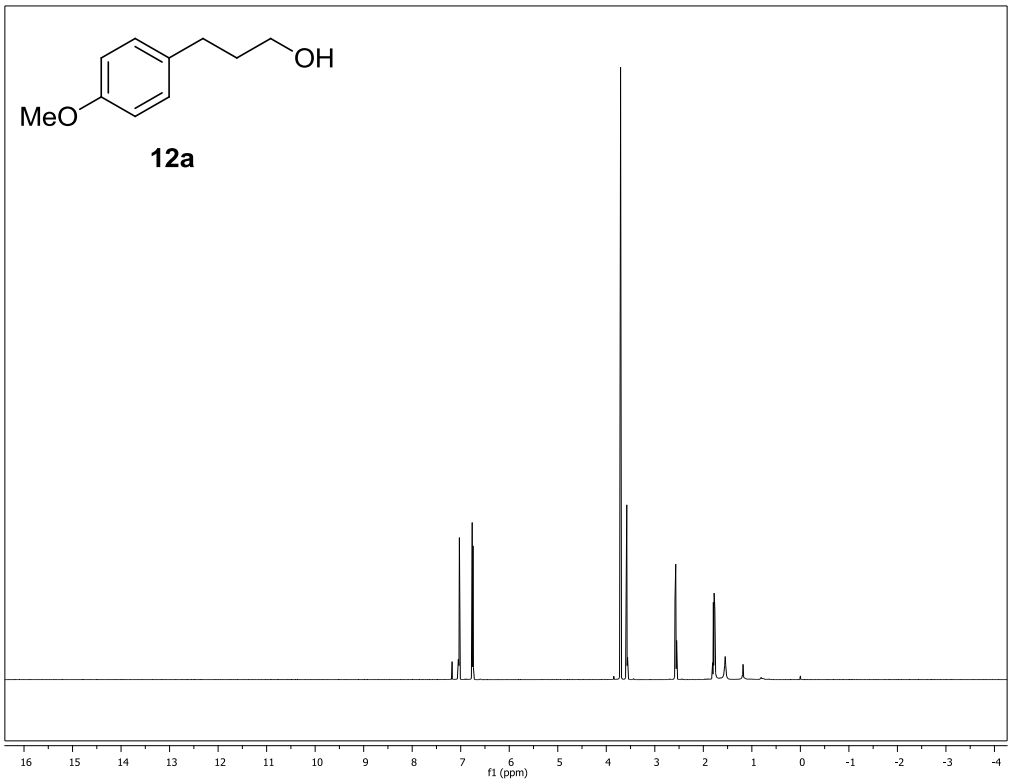
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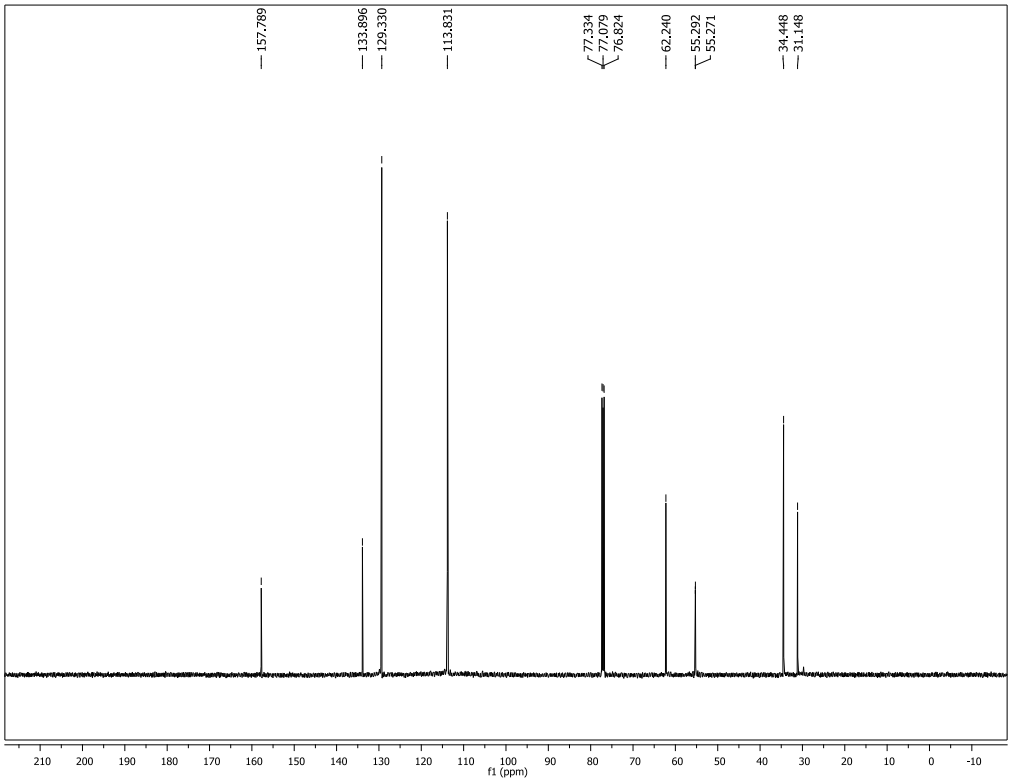
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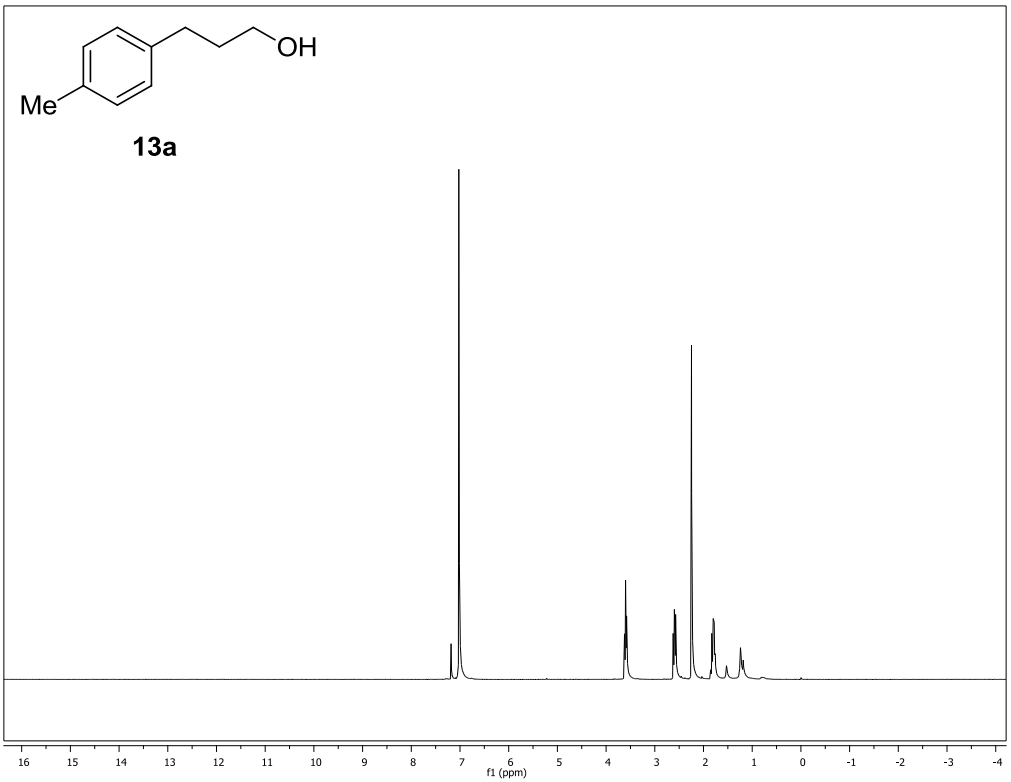
34.448
31.148
f1 (ppm)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Me
13a
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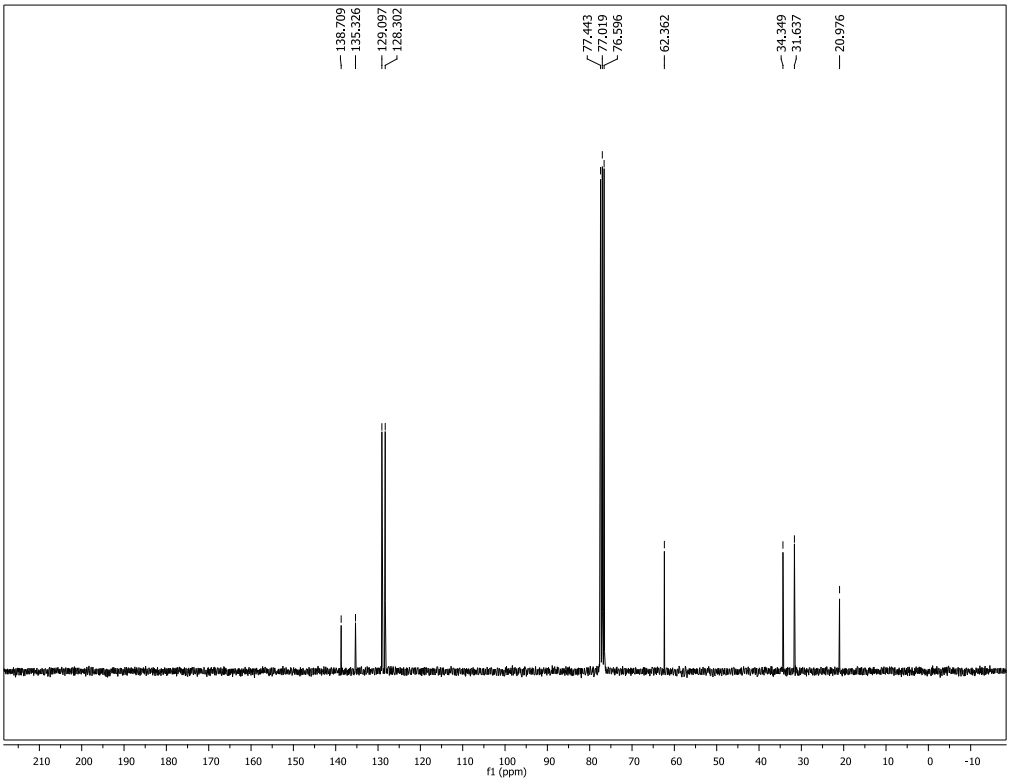
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31.637
20.976
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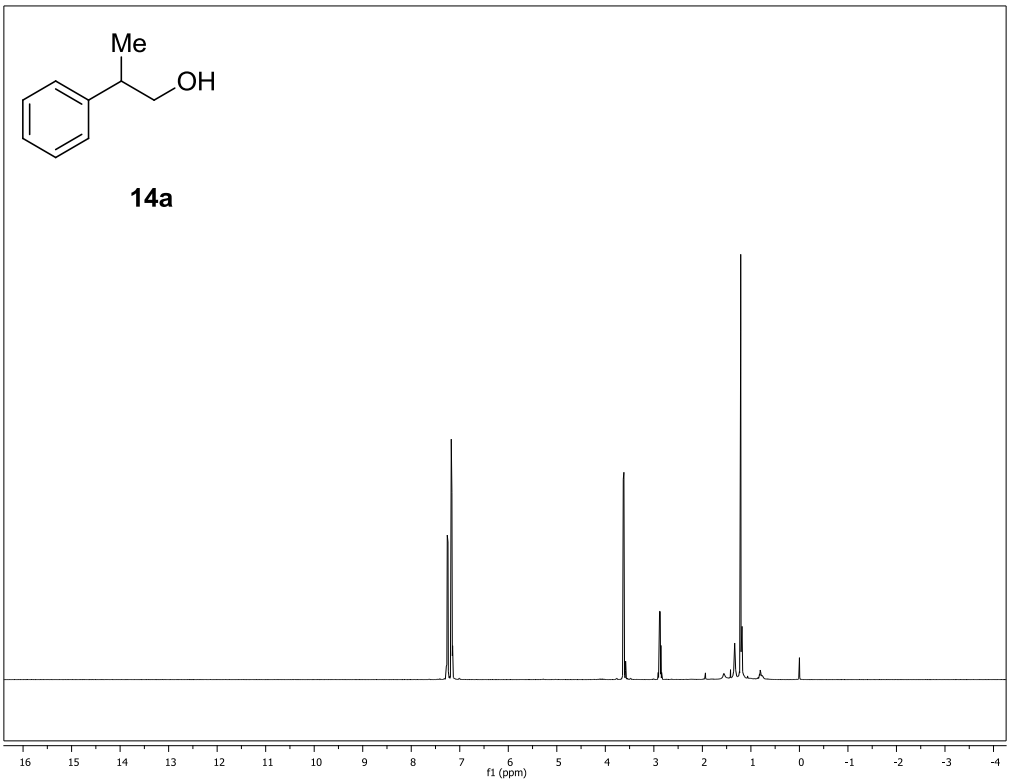
f1 (ppm)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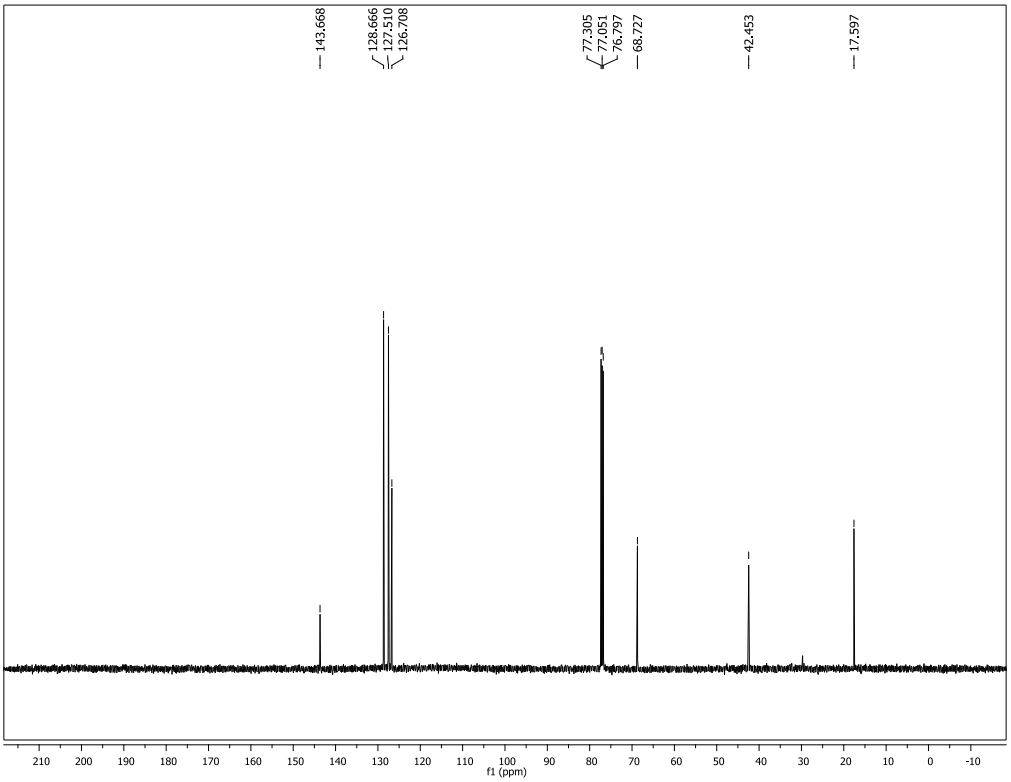
f1 (ppm)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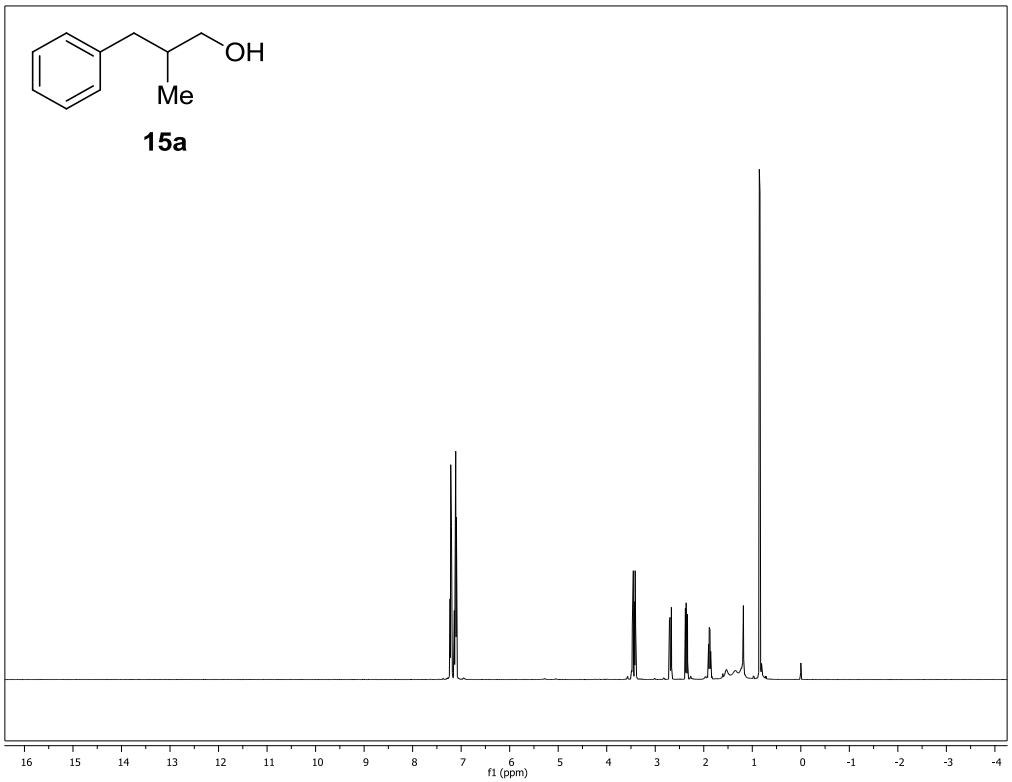
f1 (ppm)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Me
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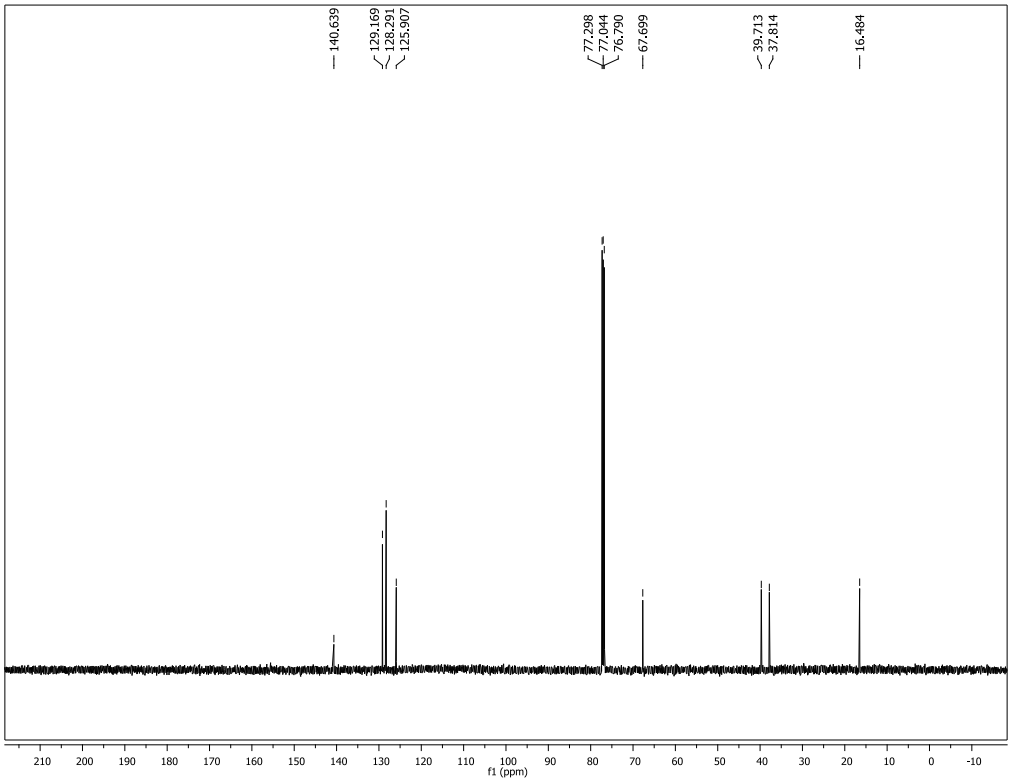
f1 (ppm)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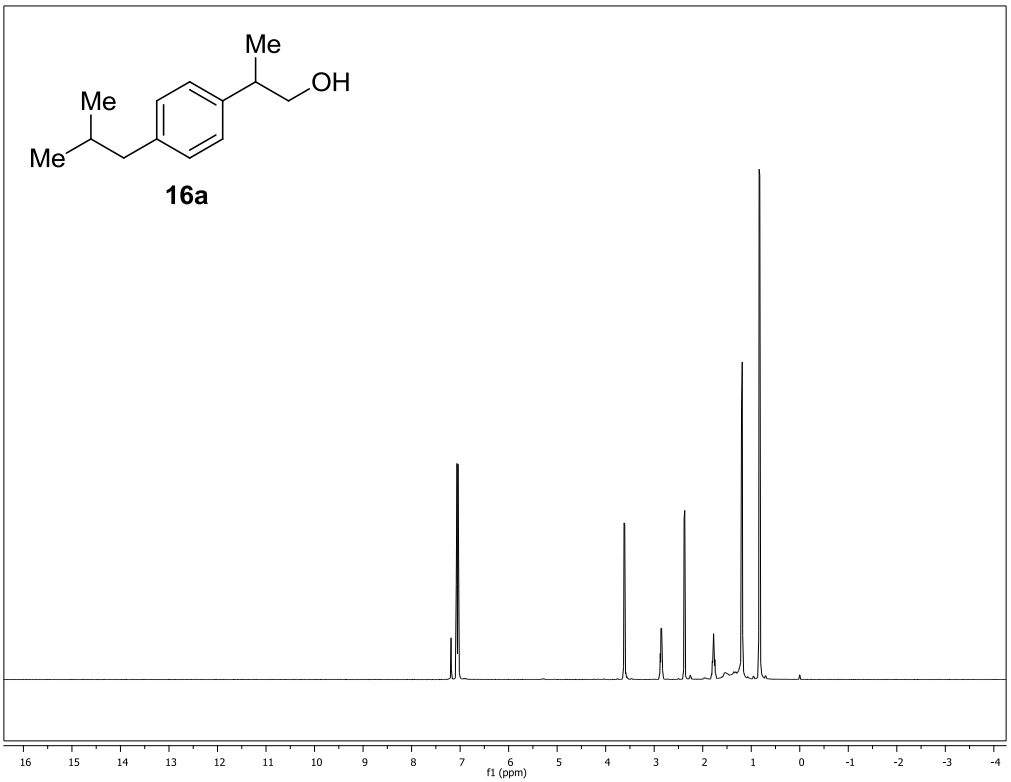
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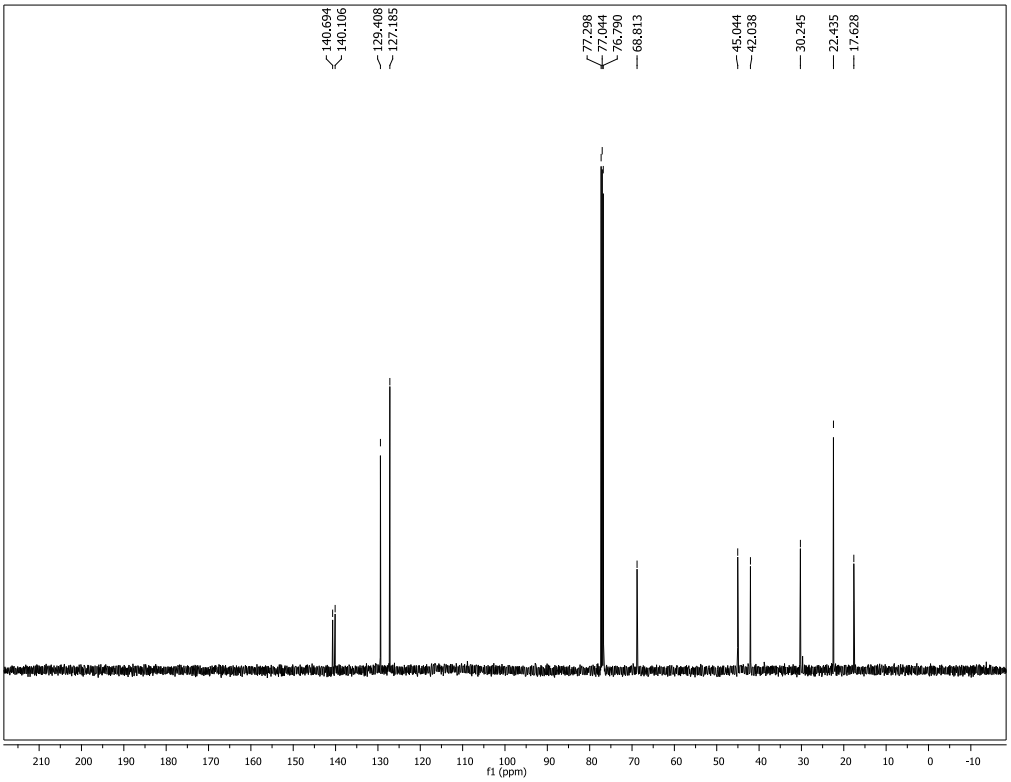
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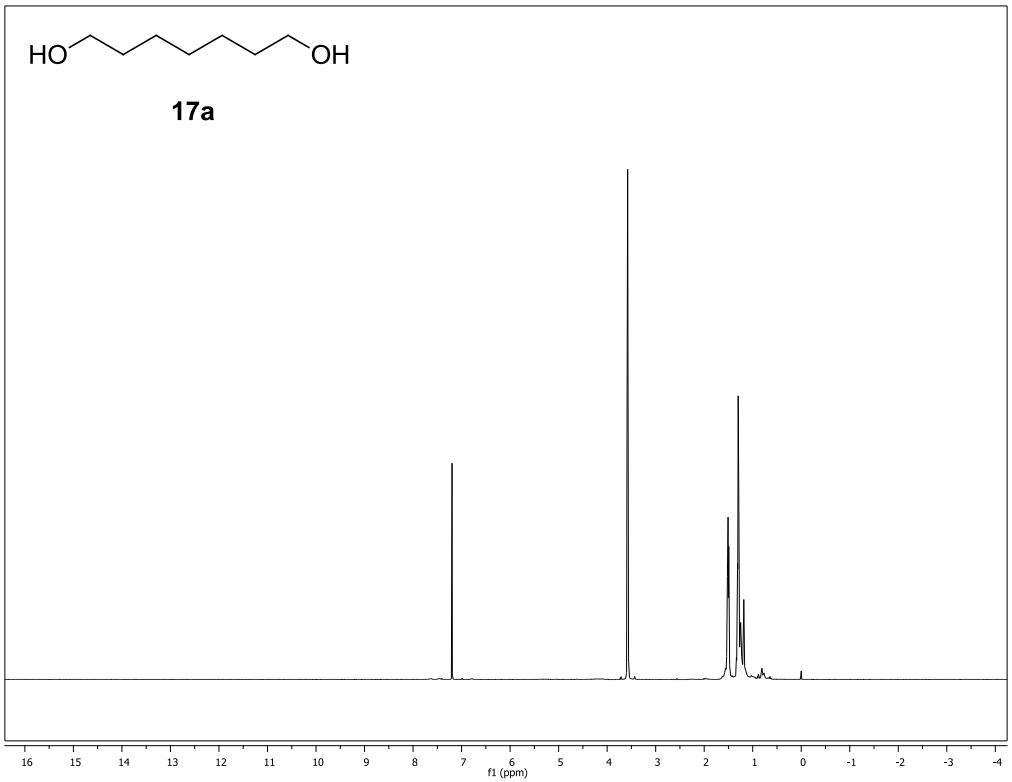
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17a
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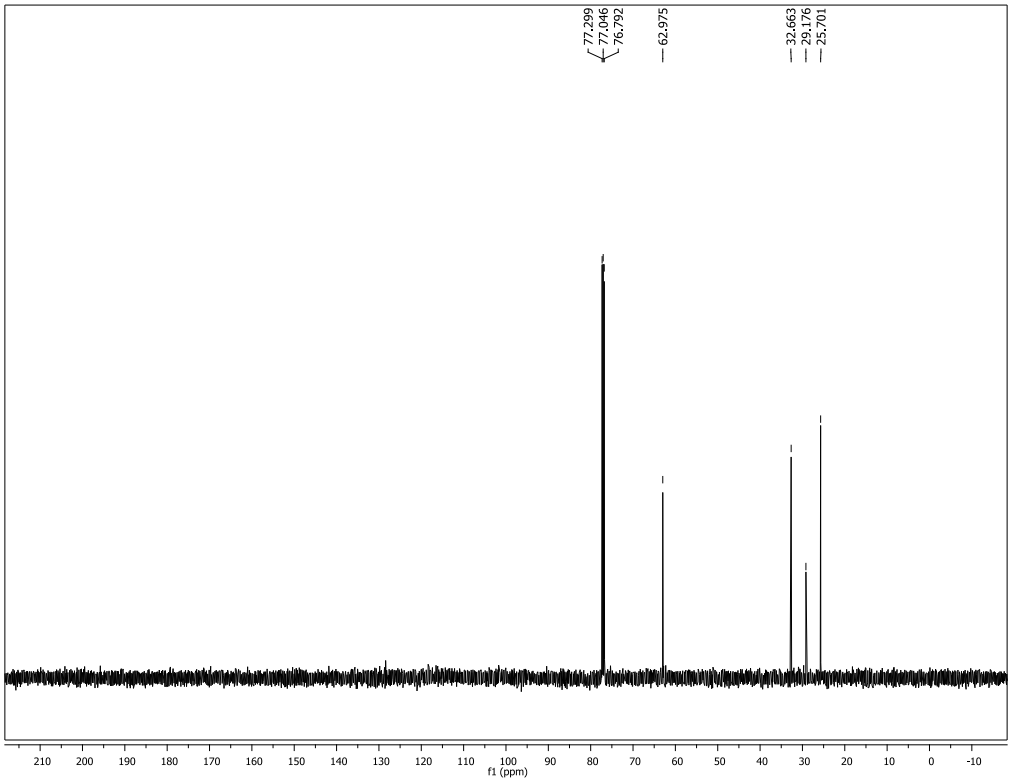
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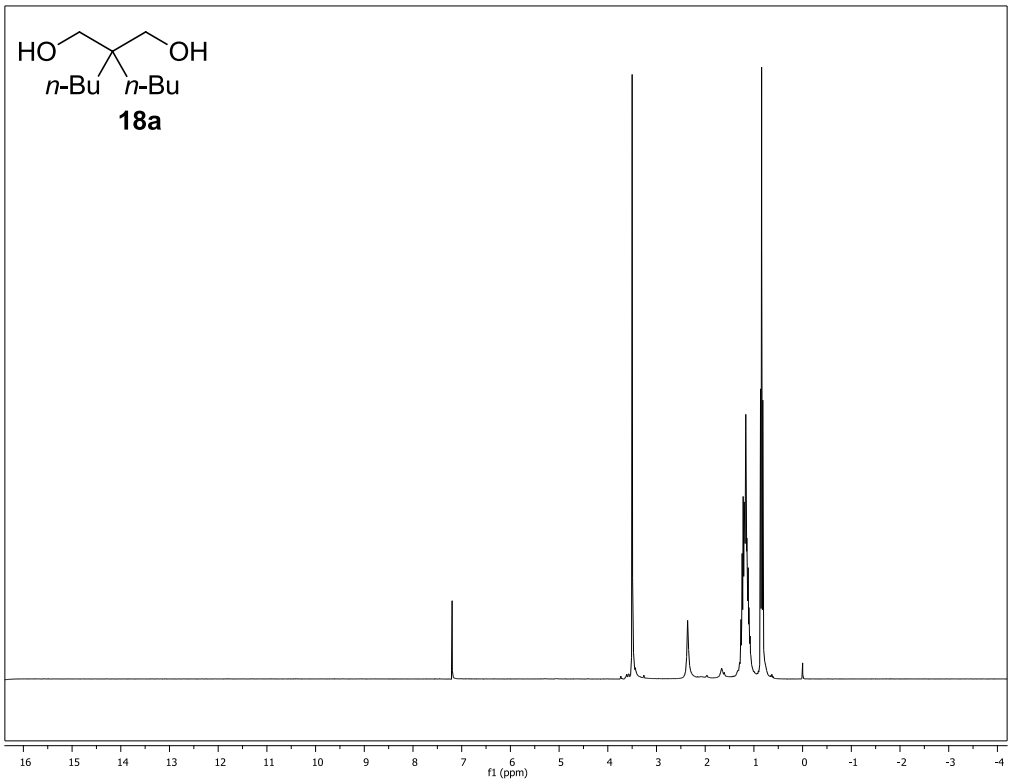
f1 (ppm)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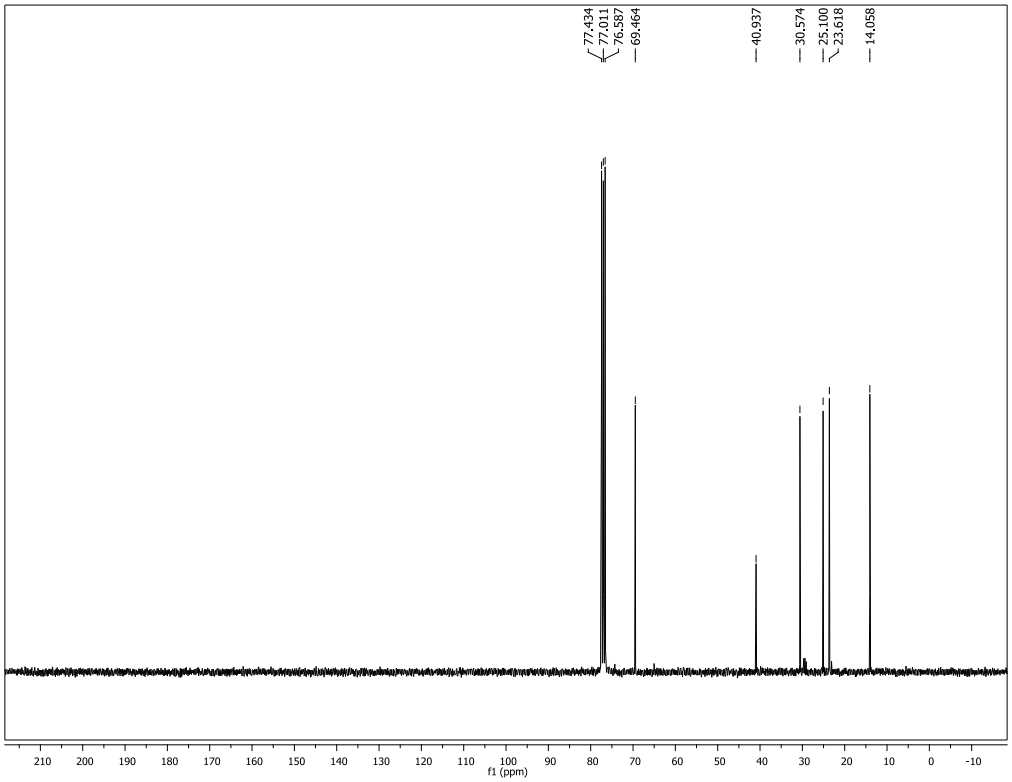
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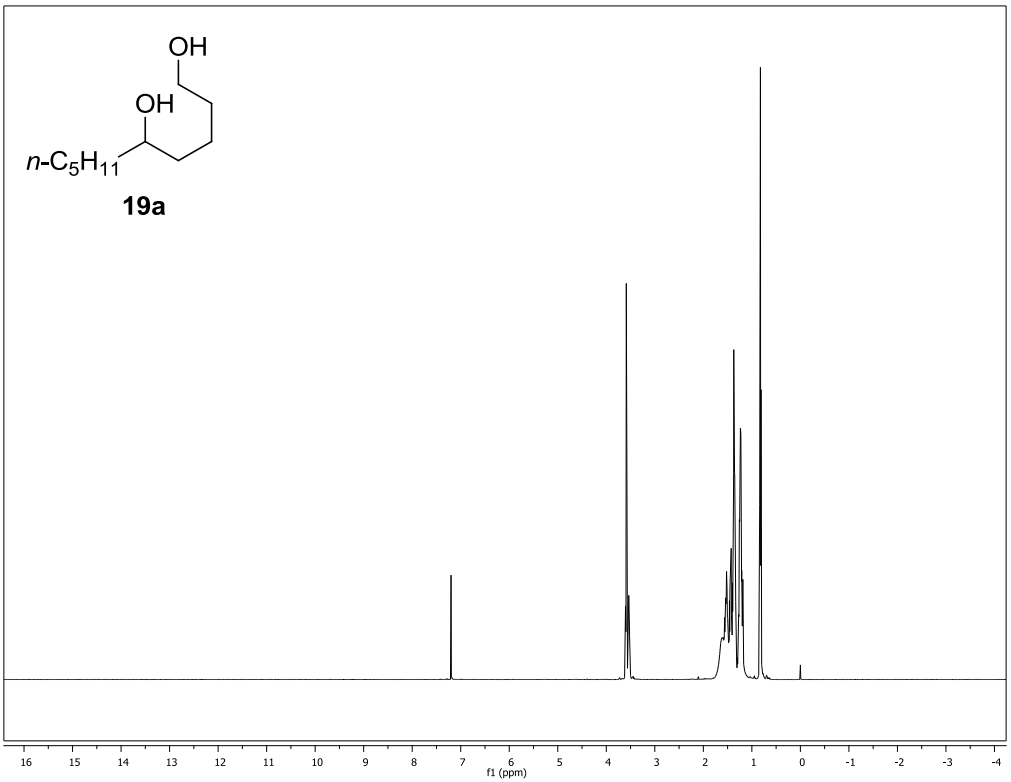
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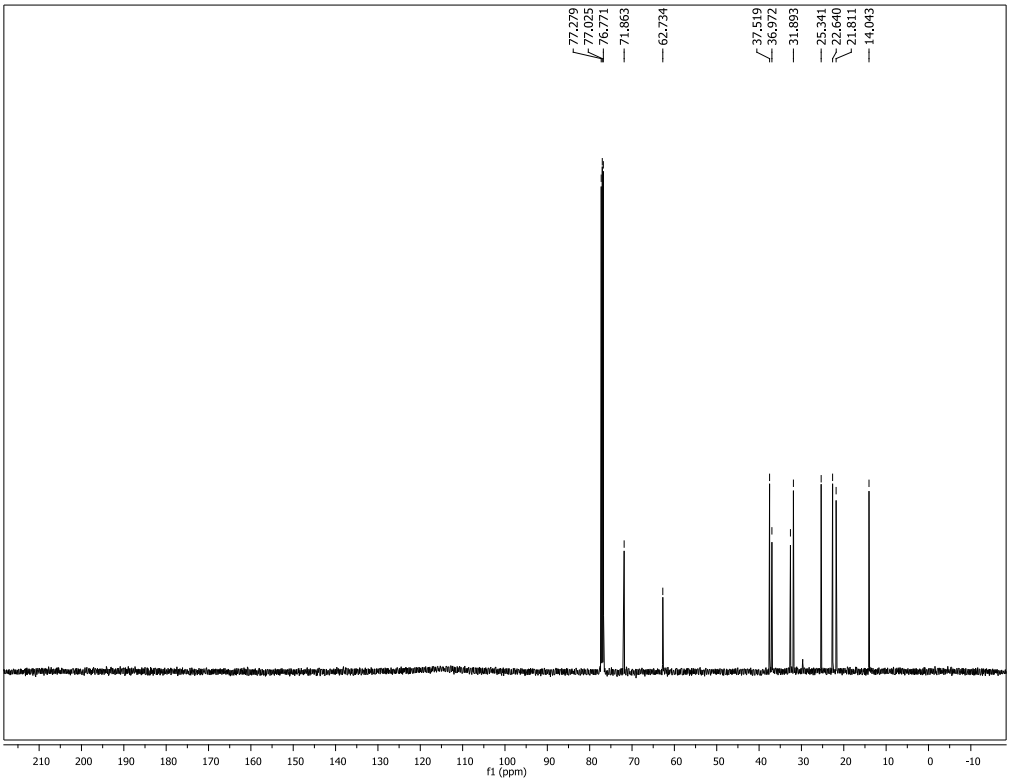
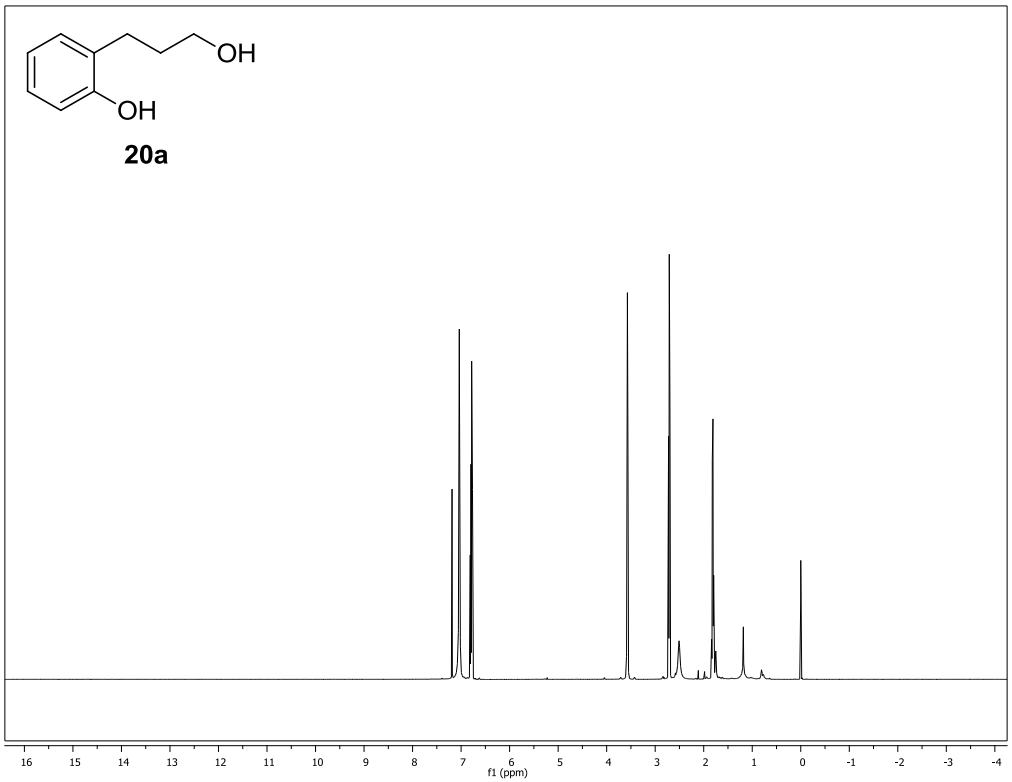
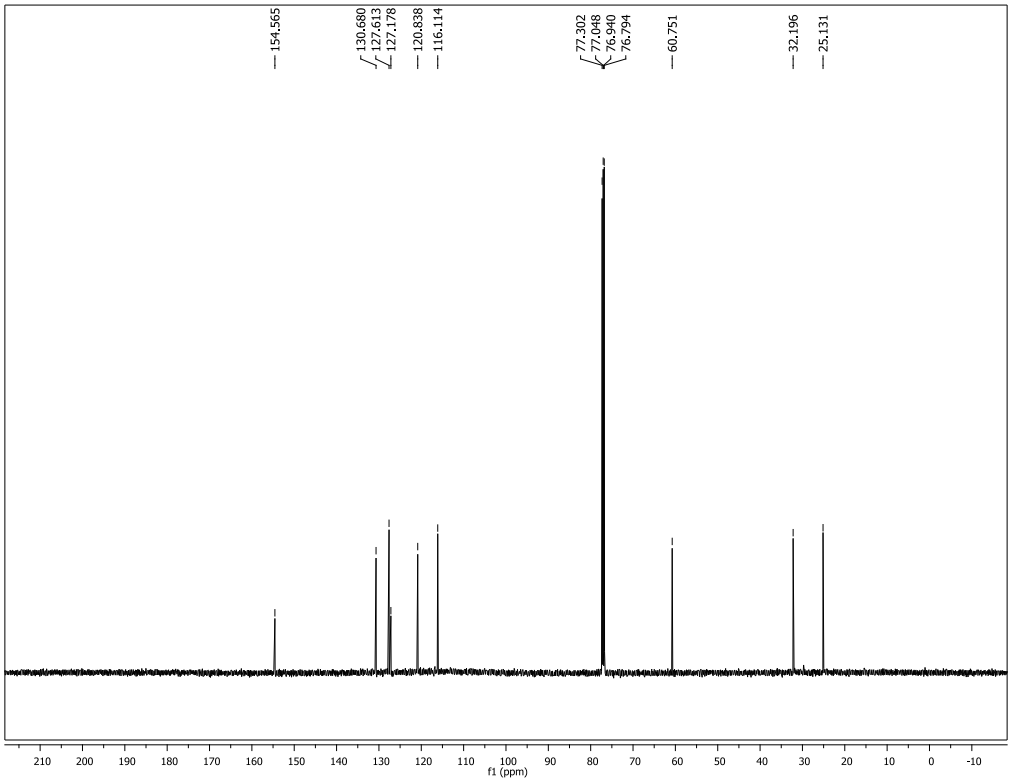
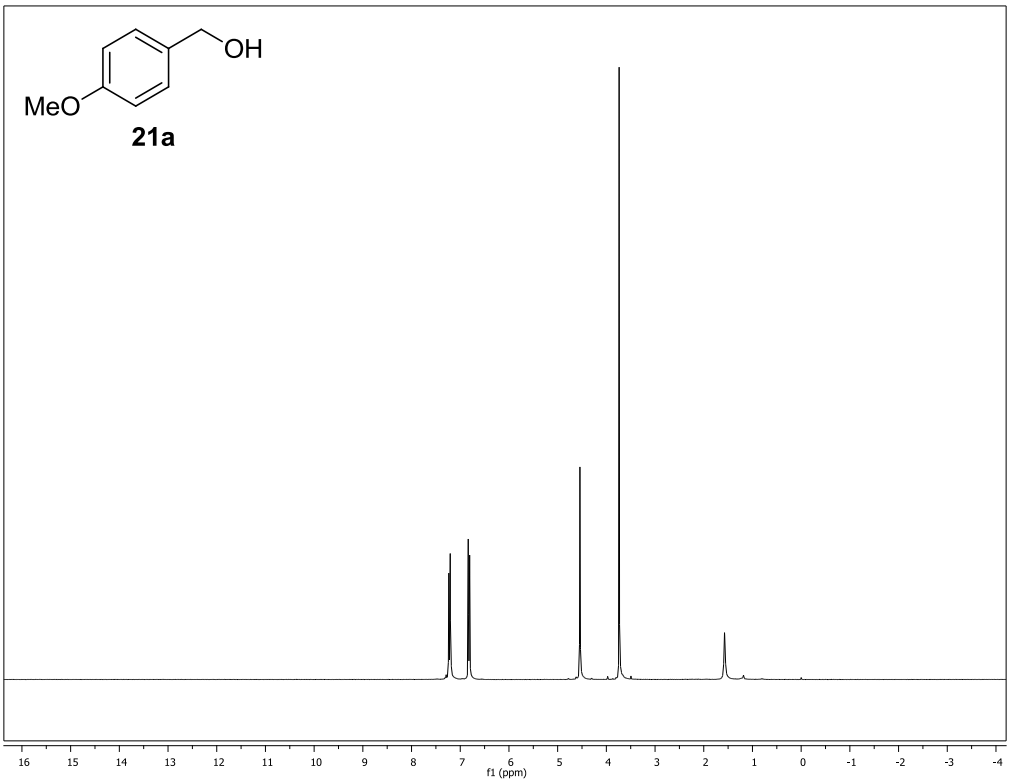
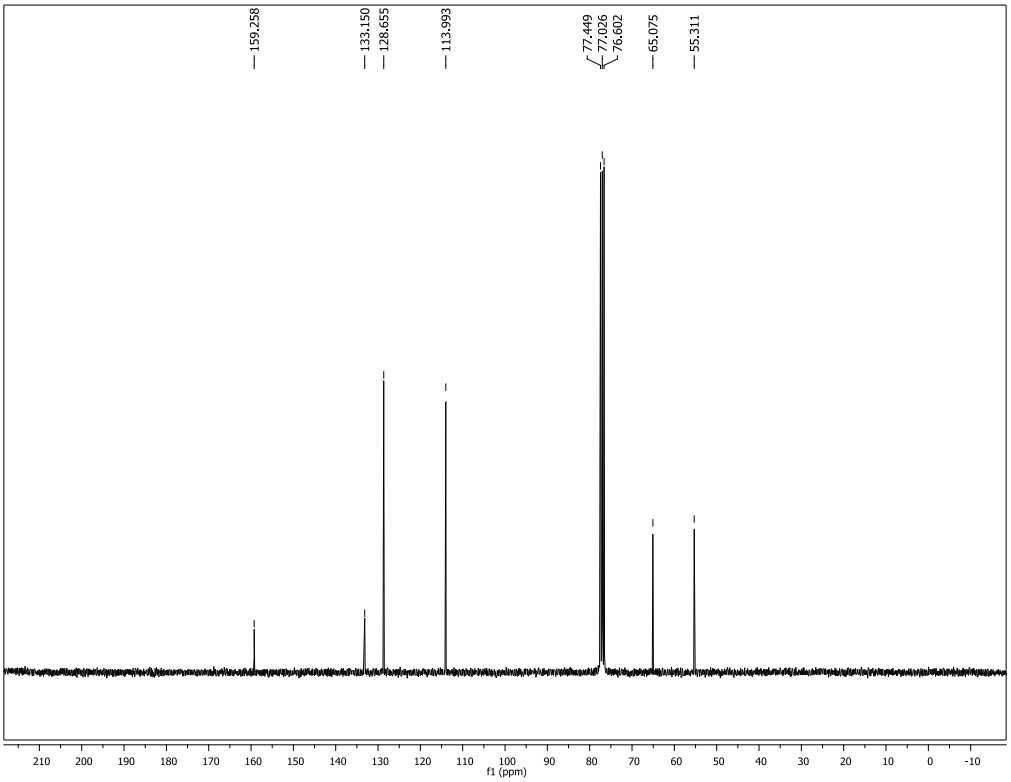
n-C5H11
19a
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

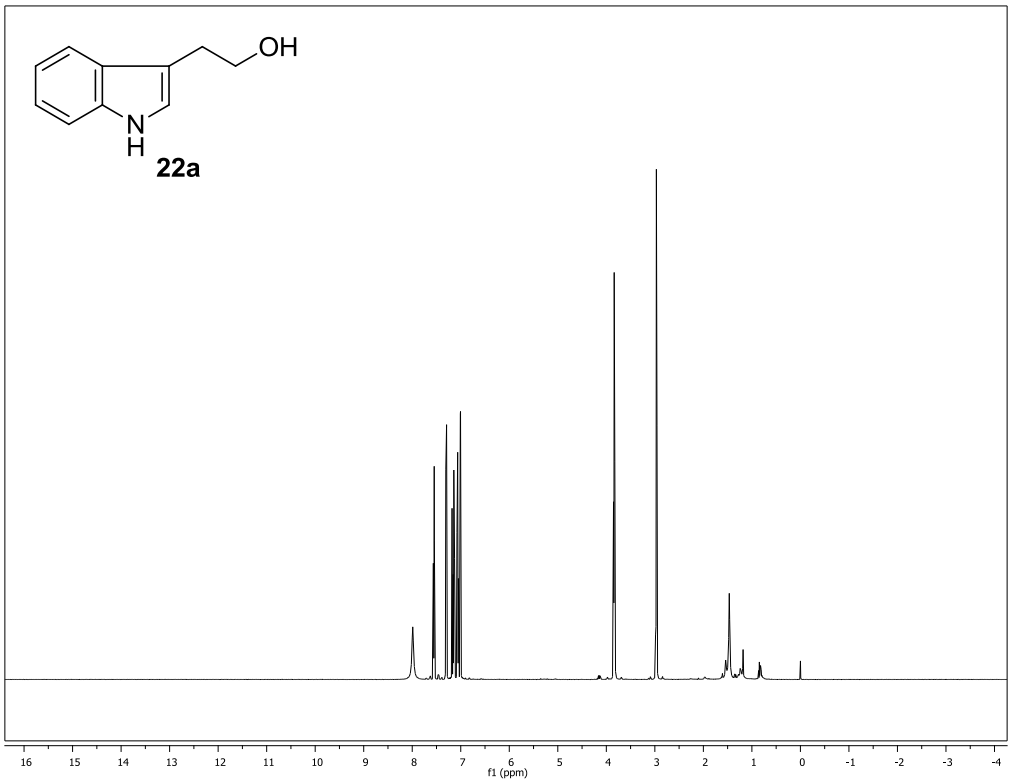

77.279
77.025
76.771
71.863
62.734
37.519
36.972
31.893
25.341
22.640
21.811
14.043
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

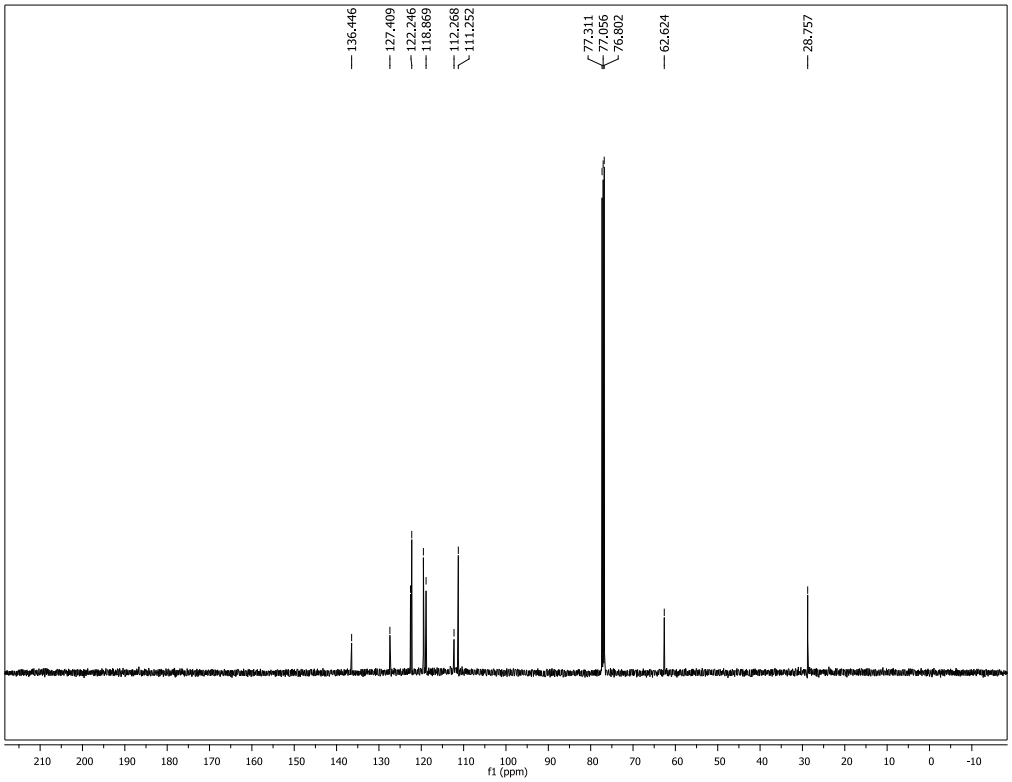





OH
MeO
21a
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


159.258
133.150
128.655
113.993
77.449
77.026
76.602
65.075
55.311
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


OH
N
H
22a
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


136.446
127.409
122.246
118.869
112.268
111.252
77.311
77.056
76.802
62.624
28.757
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)