Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

A General Electron Transfer Reduction of Lactones Using SmI_2–H_2O

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Supplementary Information

Table of Contents 1

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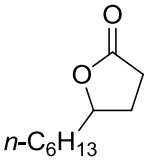
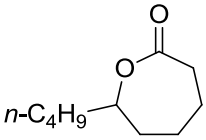
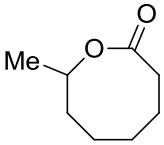
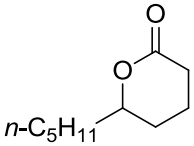
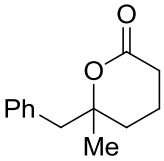
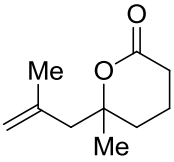
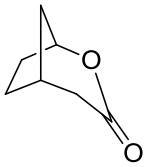
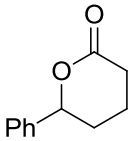
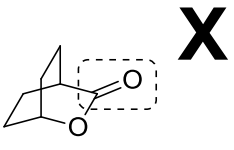
Table ESI-1. Comparison of reactivity of lactones using SmI_2–H_2O and SmI_2–H_2O–Et_3N.

entry	lactone	SmI_2–H_2O	SmI_2–H_2O–Et_3N
1		<5%	98%
2		<5%	87%
3		<5%	85%
4		83%/24 h	99%/30 s
5		63%	87%
6		<10%	97%
7		49%	93%
8		12%	84%

In addition, we determined that the following lactones are unreactive with SmI_2–H_2O reagent: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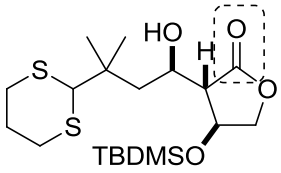
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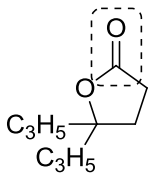

X

List of Known Compounds

Unless stated otherwise, all starting materials and products used in this study have been described in the literature or are commercially available. Lactones were purchased from commercial suppliers at the highest quality and used without further purification. Samarium(II) iodide was prepared by standard methods and titrated prior to use.[1-4] Tetrahydrofuran (THF) was purchased from Fisher Scientific or Sigma Aldrich and used as received or purified by distillation from Na/Ph_2CO under nitrogen. For experiments described in Scheme 1, SmI_2 powder purchased from Aldrich-APL (AAPL, cat. no. 40943-0, 141-31) was used.

Preparation of Starting Materials

Lactone **1c** (Table 1, entry 3) was prepared according to the procedure published by Johnson *et al*.[5] Lactone **1c** has been described in literature.[6]

Lactone **1e** (Table 1, entry 5) was prepared according to the procedure published by Keck *et al*.[7]

Lactone **1f** (Table 1, entry 6) was prepared according to the procedure published by Fürstner *et al*.[8]

Lactone **1i** (Table 1, entry 9) was prepared according to the procedure published by Parmar *et al*.[9]

Lactone **1j** (Table 1, entry 10) was prepared according to the procedure published by Girard *et al*.[1]

Lactone **1k** (Table 1, entry 11) was prepared according to the procedure published by Parmar *et al*.[10]

Lactone **1m** (Table 1, entry 13) was prepared according to the procedure published by Rosen *et al*.[11]

Lactone **1n** (Table 1, entry 14) was prepared according to the procedure published by Rosen *et al*.[11]

Lactone **1o** (Table 1, entry 15) was prepared according to the procedure published by Tani and Stoltz.[12]

Lactone **5** (Scheme 2) was prepared according to the procedure published by Harb *et al*.[13] Full details of the synthesis of lactone **5** will be published separately.

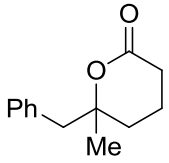
Lactone **8a** (Scheme 3) was prepared according to the procedure published by Parmar *et al*.[10]

Lactone **8b** (Scheme 3) was prepared according to the procedure published by Parmar *et al*.[10]

Lactone **10b** (Scheme 3) was prepared according to the procedure published by Hoefgen *et al*.[14]

Experimental Procedures and Characterization Data: Starting Materials

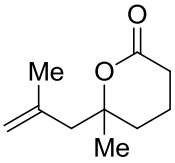
6-Benzyl-6-methyltetrahydro-2*H*-pyran-2-one (Table 1, entry 10)



1j

To a solution of samarium(II) iodide (THF, 7.0 mmol), ethyl 5-oxohexanoate (2.33 mmol) in THF (5 mL) was added at room temperature, followed by benzyl bromide (2.33 mmol) in THF (5 mL). After stirring overnight at rt, the reaction was quenched by bubbling air through the reaction mixture (until decolorization occurred to give green color). The reaction was diluted with 0.1 N HCl (250 mL), extracted with diethyl ether (3 x 250 mL), dried and concentrated. Chromatography (1/10-1/1 EtOAc/hexanes) afforded the title compound as oil. Yield 32%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.40 (s, 3H), 1.58-1.93 (m, 4H), 2.26-2.39 (m, 1H), 2.45-2.56 (m, 1H), 2.92 (d, *J* = 13.5 Hz, 1H), 3.04 (d, *J* = 13.5 Hz, 1H), 7.21-7.35 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.6, 29.8, 19.3, 31.2, 48.0, 84.1, 126.9, 128.3, 130.6, 136.0, 171.2; IR (neat) 3029, 22952, 1726, 1496, 1454, 1381, 1331, 1268, 1234, 1088, 1054, 1012, 989, 927 cm^{-1}; HRMS calcd for $C_{13}H_{16}O_2Na$ (M^+ + Na) 227.1043, found 227.1044.

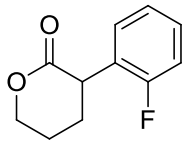
6-Methyl-6-(2-methylallyl)tetrahydro-2*H*-pyran-2-one (Table 1, entry 11)



1k

To a suspension of SmI_2 (THF, 20 mmol) at 0 °C was added NiI_2 (0.13 mmol, 2 mol %), followed by 3-bromo-2-methylprop-1-ene (7.34 mmol) and ethyl 5-oxohexanoate (6.89 mmol). The reaction mixture was stirred for 30 minutes at 0 °C and then quenched by bubbling air through the solution. The reaction mixture was diluted with potassium sodium tartrate, extracted with Et_2O (3 x 200 mL), dried and concentrated. Chromatography (40/60 EtOAc/hexanes) afforded the title compound as oil. Yield 98%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39 (s, 3H), 1.63-1.97 (m, 4H), 1.83 (s, 3H), 2.39 (d, *J* = 2.8 Hz, 2H), 2.42-2.61 (m, 2H), 4.77 (d, *J* = 0.9 Hz, 1H), 4.95 (dd, *J* = 1.5, 2.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.6, 24.4, 26.8, 29.3, 31.9, 49.6, 84.1, 116.2, 141.1, 171.0; IR (neat) 3075, 2950, 1722, 1643, 1451, 1233 cm^{-1}; HRMS calcd for $C_{10}H_{17}O_2$ (M^+ + H) 169.1224, found 169.1223.

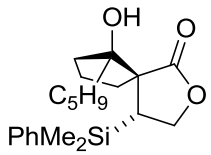
3-(2-Fluorophenyl)tetrahydro-2*H*-pyran-2-one (Table 1, entry 14)



1n

Following the procedure published by Rosen *et al.*,[11] the reaction of 2-(2-fluorophenyl)acetic acid (25 mmol), *n*-hexyllithium (50 mmol) and 1-bromo-3-chloropropane (27.5 mmol) in THF (100 mL) for 18 h at rt afforded after work-up 5-chloro-2-(2-fluorophenyl)pentanoic acid, which was used directly in the cyclization step using DBU (25 mmol) in THF at 60 °C for 18 h. Chromatography (1/10-4/1 EtOAc/hexanes) afforded the title compound as a white solid (mp = 80-82 °C). Yield 74% (2 steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.87-2.01 (m, 3H), 2.09-2.18 (m, 1H), 3.77-3.83 (m, 1H), 4.31-4.43 (m, 2H), 6.94-7.05 (m, 2H), 7.11-2.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.5, 27.5, 42.2 (d, J^3 = 1.9 Hz), 69.7, 115.7 (d, J^2 = 21.2 Hz), 124.4 (d, J^4 = 3.7 Hz), 126.8 (d, J^2 = 13.7 Hz), 129.2 (d, J^3 = 8.3 Hz), 130.3 (d, J^3 = 4.5 Hz), 160.5 (d, J^1 = 246.0 Hz), 171.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.0; IR (neat) 2955, 2905, 1732, 1619, 1588, 1494, 1456, 1401, 1257, 1231, 1156, 1113, 1080, 964, 864, 798, 760 cm^{-1}; HRMS calcd for $C_{11}H_{12}O_2F$ (M^+ + H) 195.0816, found 195.0815.

***rac*-(4*R*, 5*S*, 6*S*)-4-(Dimethyl(phenyl)silyl)-6-hydroxy-6-(pent-4-en-1-yl)-2-oxaspiro[4.4]nonan-1-one** (Figure 4)



5

Lactone **5** was prepared according to the procedure published by Harb *et al.*[13] Full details of the synthesis of lactone **5** will be published separately. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.40 (s, 3H), 0.48 (s, 3H), 1.29-1.47 (m, 5H), 1.65-1.73 (m, 1H), 1.75-1.84 (m, 2H), 1.88-1.98 (m, 1H), 2.02-2.08 (m, 3H), 2.12 (ddd, *J* = 2.3, 5.5, 13.4 Hz, 1H), 3.79 (d, *J* = 1.3 Hz, 1H), 4.15 (t, *J* = 8.6 Hz, 1H), 4.32 (t, *J* = 8.8 Hz, 1H), 4.97-5.06 (m, 2H), 5.79 (m, 1H), 7.35-7.56 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -3.1, -2.9, 20.7, 23.2, 30.6, 31.7, 34.1, 35.5, 36.3, 58.0, 68.1, 85.6, 114.9, 128.2, 129.8, 133.6, 136.5, 138.5, 183.1; IR (neat) 3426, 3065, 2951, 1760, 1739, 1427, 1375, 1250, 1170, 1114, 1031 cm^{-1}; HRMS calcd for $C_{21}H_{34}O_3SiNa$ (M^+ + Na) 381.1857, found 381.1850.

Experimental Procedures and Characterization Data: Reduction of Lactones

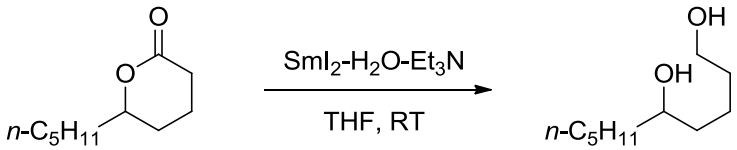
Reduction of Lactones Using SmI_2–H_2O: Standard Procedure. *Method A:* To lactone (neat or in 1.0 mL of THF), samarium(II) iodide (THF solution, typically 6 or 8 equiv) was added, followed by amine (typically 18 or 24 equiv) and water (typically 18 or 24 equiv) under inert atmosphere at room temperature and stirred vigorously. After the specified time (typically 2 h), the excess of SmI_2 was oxidized by bubbling air through the reaction mixture. The reaction mixture was diluted with CH_2Cl_2 (30 mL) and HCl (30 mL, 0.1 *N* or 1 *N*). The aqueous layer was extracted with CH_2Cl_2 (3 x 30 mL), organic layers were combined, 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.

Method B: To a solution of samarium(II) iodide (THF solution, typically 6 or 8 equiv), amine (typically 18 or 24 equiv) was added, followed by water (typically 18 or 24 equiv) and lactone (in 1.0 mL of THF) under inert atmosphere at room temperature and stirred vigorously. Work-up and purification proceed as described in Method A.

Note: in terms of substrate scope or efficiency of the reaction, there are no differences between Methods A and B. Method B was developed for experimental convenience.

Note: we have noticed marginal differences in reactivity between systems employing SmI_2–H_2O–amine in 6-18-18 ratio and SmI_2–H_2O–amine in 8-24-24 ratio. Due to a slightly higher reactivity, the latter system has been typically preferred. 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.

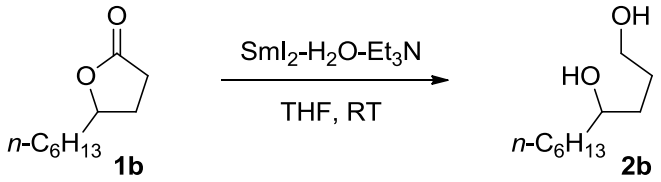
Decane-1,5-diol (Table 1, entry 1)[15]



1a **2a**

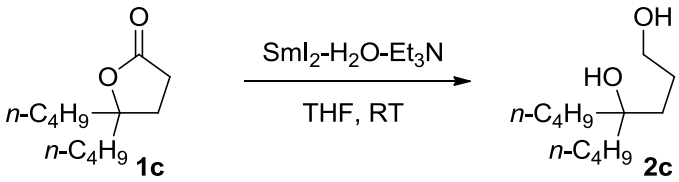
According to the general procedure *Method A*, the reaction of 6-pentyltetrahydro-2*H*-pyran-2-one (0.10 mmol), samarium(II) iodide (0.8 mmol), water (2.4 mmol) and triethylamine (1.6 mmol) for 2 h at rt, afforded after chromatography (EtOAc) the title compound in 97% yield. Oil (R_f = 0.50, EtOAc). ^{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. Note: the synthesis of this compound has been published previously.[16]

Decane-1,4-diol (Table 1, entry 2)[17]



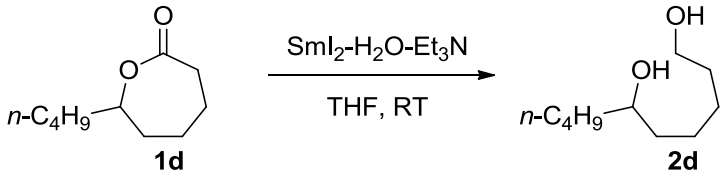
According to the general procedure *Method A*, the reaction of 5-hexyldihydrofuran-2(3*H*)-one (0.10 mmol), samarium(II) iodide (0.8 mmol), water (1.6 mmol) and triethylamine (2.4 mmol) for 2 h at rt, afforded after chromatography (EtOAc) the title compound in 98% yield. Oil (R_f = 0.45, EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.82 (t, *J* = 7.5 Hz, 3H), 1.17-1.28 (m, 7H), 1.31-1.44 (m, 4H), 1.55-1.66 (m, 3H), 2.42 (br, 2H), 3.53-3.65 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 22.6, 25.7, 29.2, 29.3, 31.8, 34.4, 37.6, 63.0, 71.9.

4-Butyloctane-1,4-diol (Table 1, entry 3)[18]



According to the general procedure *Method A*, the reaction of 5,5-dibutyldihydrofuran-2(3*H*)-one (0.25 mmol), samarium(II) iodide (1.5 mmol), water (9.0 mmol) and triethylamine (9.0 mmol) for 2 h at rt, afforded after chromatography (4/1 EtOAc/hexanes) the title compound in 93% yield. Oil (R_f = 0.5, 4/1 EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.92 (t, *J* = 7.3 Hz, 6H), 1.22-1.35 (m, 8H), 1.43-1.48 (m, 4H), 1.51-1.56 (m, 2H), 1.59-1.67 (m, 2H), 1.80 (br, 2H), 3.66 (t, *J* = 6.1 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 23.3, 25.8, 26.7, 36.0, 38.9, 63.5, 74.2.

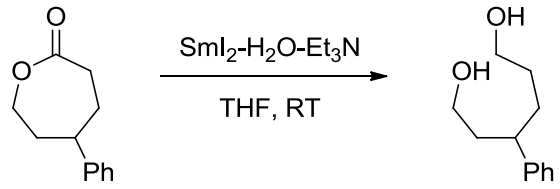
Decane-1,6-diol (Table 1, entry 4)[19]



According to the general procedure *Method A*, the reaction of 7-butyloxepan-2-one (0.10 mmol), samarium(II) iodide (0.8 mmol), water (1.6 mmol) and triethylamine (2.4 mmol) for 2 h at rt, afforded after chromatography (1/10-1/1 EtOAc/hexanes-EtOAc) the title compound in 87% yield. Oil (R_f = 0.56, EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.84 (t, *J* = 7.2 Hz, 3H), 1.15-1.43

(m, 14H), 1.46-1.57 (m, 2H), 3.47-3.55 (m, 1H), 3.58 (t, *J* = 6.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 22.8, 25.4, 25.8, 27.8, 32.7, 37.3, 37.4, 62.9, 71.9.

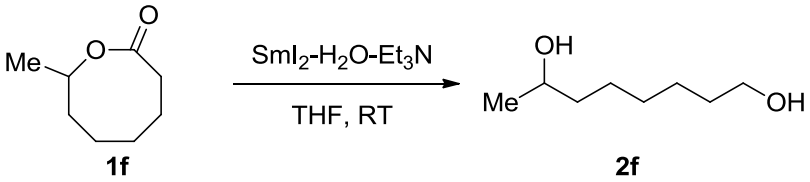
3-Phenylhexane-1,6-diol (Table 1, entry 5)



1e **2e**

According to the general procedure *Method B*, the reaction of 5-phenyloxepan-2-one (0.25 mmol), samarium(II) iodide (2.0 mmol), water (6.0 mmol) and triethylamine (6.0 mmol) for 4 h at rt, afforded after chromatography (40/60-70/30 EtOAc/hexanes) the title compound in 99% yield. Oil (R_f = 0.27, 70/30 EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34-1.51 (m, 4H), 1.59-1.69 (m, 1H), 1.73-1.87 (m, 2H), 1.91-1.99 (m, 1H), 2.73 (tt, *J* = 5.0, 9.9 Hz, 1H), 3.46 (dt, *J* = 7.0, 10.6 Hz, 1H), 3.52-3.55 (m, 1H), 3.58 (t, *J* = 6.5 Hz, 2H), 7.13-7.24 (m, 2H), 7.28-7.34 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.6, 32.8, 39.6, 42.1, 60.9, 62.8, 126.3, 127.6, 128.5, 144.7; IR (neat) 2399, 2856, 2926, 3301 cm^{-1}; HRMS calcd for $C_{12}H_{19}O_2$ (M^+ + H) 195.1380, found 195.1378.

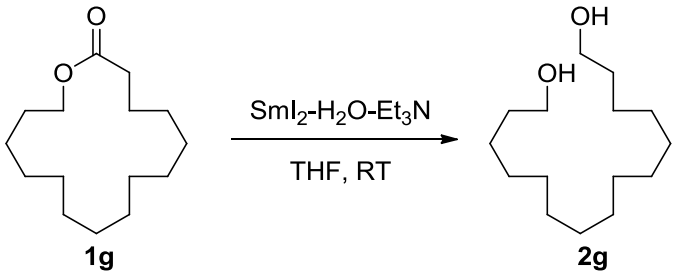
Octane-1,7-diol (Table 1, entry 6)[20]



1f **2f**

According to the general procedure *Method A*, the reaction of 8-methyloxocan-2-one (0.25 mmol), samarium(II) iodide (2.0 mmol), water (6.0) and triethylamine (6.0 mmol) for 2 h at rt, afforded after chromatography (EtOAc) the title compound in 85% yield. Oil (R_f = 0.37, EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.17 (d, *J* = 6.0 Hz, 3H), 1.27-1.49 (m, 8H), 1.55 (m, 2H), 1.95 (br, 2H), 3.61 (t, *J* = 6.6 Hz, 2H), 3.73-3.81 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.4, 25.6, 29.3, 32.6, 39.1, 62.8, 68.0.

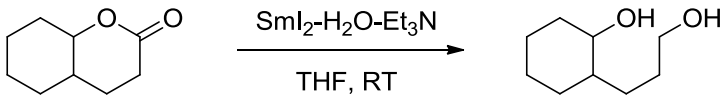
Pentadecane-1,15-diol (Table 1, entry 7)[21]



1g **2g**

According to the general procedure *Method B*, the reaction of oxacyclohexadecan-2-one (0.25 mmol), samarium(II) iodide (2.0 mmol), water (6.0) and triethylamine (6.0 mmol) for 4 h at rt, afforded after chromatography (40/60 EtOAc/hexanes) the title compound in 92% yield. Solid (R_f = 0.23, 40/60 EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.26 (m, 22H), 1.57 (m, 4H), 3.63 (t, *J* = 6.6 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.7, 29.4, 29.5, 29.6, 29.6, 32.8, 63.1.

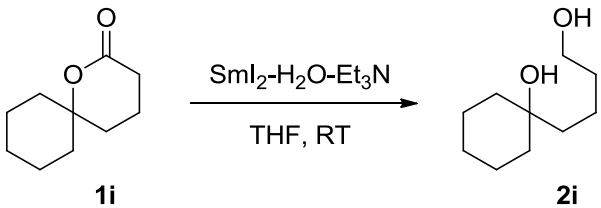
2-(3-Hydroxypropyl)cyclohexanol (Table 1, entry 8)[15]



1h **2h**

According to the general procedure *Method B*, the reaction of octahydro-2*H*-chromen-2-one (0.25 mmol, mixture of *cis* and *trans* isomers), samarium(II) iodide (2.0 mmol), water (6.0 mmol) and triethylamine (6.0 mmol) for 4 h at rt, afforded after chromatography (40/60-70/30 EtOAc/hexanes) the title compound in 90% yield. Oil (R_f = 0.16, 0.21, 60/40 EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.84-1.02 (m, 1H), 1.54 (m, 26H), 3.23 (td, *J* = 4.4, 9.5 Hz, 1H), 3.58-3.71 (m, 4H), 3.87-3.93 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.5, 24.9, 25.0, 25.6, 26.8, 27.7, 28.2, 29.4, 30.0, 30.4, 32.9, 35.7, 41.0, 44.5, 62.9, 63.1, 69.1, 74.6.

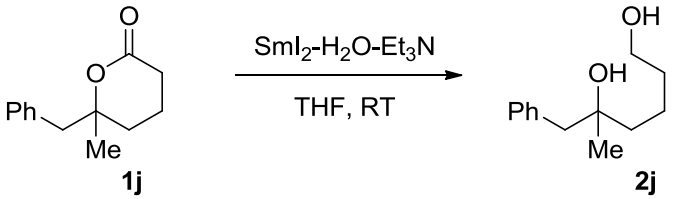
1-(4-Hydroxybutyl)cyclohexanol (Table 1, entry 9)[22]



1i **2i**

According to the general procedure *Method B*, the reaction of 1-oxaspiro[5.5]undecan-2-one (0.25 mmol), samarium(II) iodide (2.0 mmol), water (6.0 mmol) and triethylamine (6.0 mmol) for 4 h at rt, afforded after chromatography (60/40 EtOAc/hexanes) the title compound in 99% yield. Oil (R_f = 0.17, 1/1 EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.36-1.62 (m, 18H), 3.66 (t, *J* = 6.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.0, 22.2, 25.8, 33.1, 37.4, 62.7, 71.4. Note: the starting material (**1i**) was inseparable from 6-(but-3-en-1-yl)tetrahydro-2H-pyran-2-one impurity formed during its synthesis (88% purity of **1i**). Accordingly, the product of the reaction of (**1i**) with SmI_2-Et_3N-H_2O was also inseparable from non-8-ene-1,5-diol formed during the reduction (91% purity of **2i**). The isolated yield of (**2i**) is corrected for the above impurity.

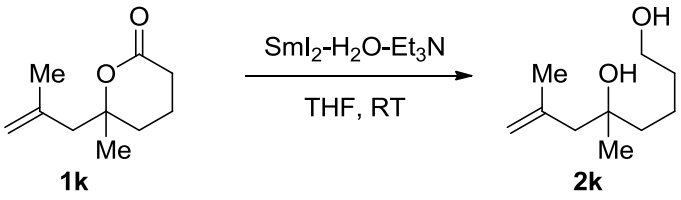
5-Methyl-6-phenylhexane-1,5-diol (Table 1, entry 10)



1j **2j**

According to the general procedure *Method A*, the reaction of 6-benzyl-6-methyltetrahydro-2*H*-pyran-2-one (0.10 mmol), samarium(II) iodide (0.6 mmol), water (3.6 mmol) and triethylamine (3.4 mmol) for 2 h at rt, afforded after chromatography (1/10-1/1 EtOAc/hexanes-EtOAc) the title compound in 87% yield. Oil (R_f = 0.45, EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.08 (s, 3H), 1.41-1.54 (m, 8H), 2.65 (d, *J* = 13.0 Hz, 1H), 2.71 (d, *J* = 13.0 Hz, 1H), 3.59 (t, *J* = 6.5 Hz, 2H), 7.12-7.26 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.1, 25.4, 32.0, 40.3, 47.0, 61.7, 71.5, 125.5, 127.2, 129.5, 136.4; IR (neat) 3347, 2937, 2869, 1453, 1372, 1117, 1075, 1032, 921, 782, 728, 702 cm^{-1}; HRMS calcd for $C_{13}H_{20}O_2Na$ (M^+ + Na) 231.1356, found 231.1363.

5,7-Dimethyloct-7-ene-1,5-diol (Table 1, entry 11)

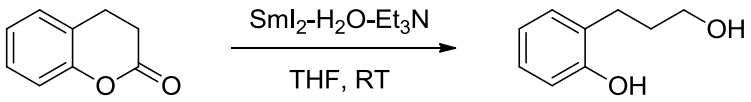


1k **2k**

According to the general procedure *Method A*, the reaction of 6-methyl-6-(2-methylallyl)tetrahydro-2*H*-pyran-2-one (0.10 mmol), samarium(II) iodide (0.8 mmol), water (2.4 mmol) and triethylamine (1.8 mmol) for 2 h at rt, afforded after chromatography (EtOAc) the

title compound in 97% yield. Oil (R_f = 0.41, 80/20 EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.19 (s, 3H), 1.43-1.53 (m, 4H), 1.55-1.62 (m, 2H), 1.64-1.69 (br, 2H) 1.85 (s, 3H), 2.10 (d, *J* = 13.0 Hz, 1H), 2.16 (d, *J* = 13.0 Hz, 1H), 3.67 (t, *J* = 6.5 Hz, 2H), 4.73-4.78 (m, 1H), 4.90-4.96 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.2, 25.1, 27.0, 33.1, 42.1, 49.4, 62.7, 72.3, 114.9, 142.8; IR (neat) 3336, 3072, 2937, 2967, 1641, 1457, 1373 cm^{-1}; HRMS calcd for $C_{10}H_{20}O_2Na$ (M^+ + Na) 195.1356, found 195.1356.

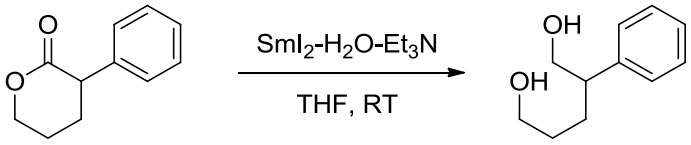
2-(3-Hydroxypropyl)phenol (Table 1, entry 12)[15]



1l **2l**

According to the general procedure *Method A*, 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. Note: the synthesis of this compound has been published previously.[16]

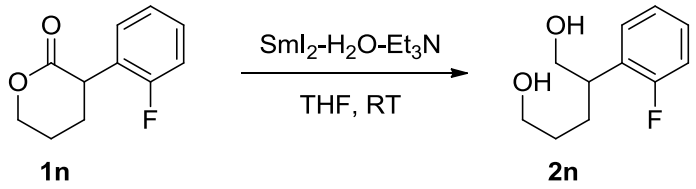
2-Phenylpentane-1,5-diol (Table 1, entry 13)[23]



1m **2m**

According to the general procedure *Method A*, the reaction of 3-phenyltetrahydro-2*H*-pyran-2-one (0.25 mmol), samarium(II) iodide (2.0 mmol), water (6.0) and triethylamine (6.0 mmol) for 2 h at rt, afforded after chromatography (EtOAc) the title compound in 99% yield. Oil (R_f = 0.39, EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.04-1.87 (m, 6H), 2.62-2.82 (m, 1H), 3.61 (t, *J* = 6.4 Hz, 2H), 3.76 (d, *J* = 7.0 Hz, 2H), 7.15-7.41 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.2, 30.5, 48.4, 62.8, 67.5, 126.9, 128.0, 128.7, 142.0.

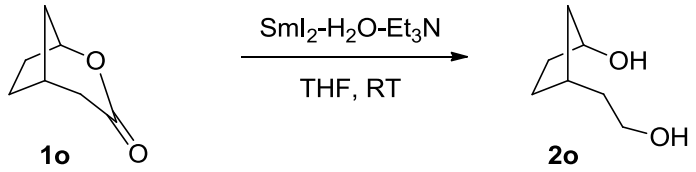
2-(2-Fluorophenyl)pentane-1,5-diol (Table 1, entry 14)



1n **2n**

According to the general procedure *Method A*, the reaction of 3-(2-fluorophenyl)tetrahydro-2*H*-pyran-2-one (0.25 mmol), samarium(II) iodide (2.0 mmol), water (6.0) and triethylamine (6.0 mmol) for 2 h at rt, afforded after chromatography (EtOAc) the title compound in 88% yield. Oil (R_f = 0.42, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (br, 1H), 1.41-1.63 (m, 3H), 1.63-1.76 (m, 1H), 1.83-1.94 (m, 1H), 3.15-3.27 (m, 1H), 3.63 (br, 2H), 3.82 (t, *J* = 5.8 Hz, 2H), 7.01-7.09 (m, 1H), 7.10-7.16 (m, 1H), 7.19-7.29 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.2, 30.3, 41.1, 62.6, 66.2, 115.6 (d, J^2 = 22.9 Hz), 124.3 (d, J^4 = 3.3 Hz), 128.0 (d, J^3 = 8.2 Hz), 128.9 (d, J^2 = 14.2 Hz), 128.9 (d, J^3 = 4.9 Hz), 161.4 (d, J^1 = 244.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.1; IR (neat) 3345, 3054, 2941, 2874, 1583, 1491, 1453, 1422, 1265, 1225, 1176, 1037, 941, 896, 824 cm^{-1}; HRMS calcd for $C_{11}H_{15}O_2FNa$ (M^+ + Na) 221.0949, found 221.0950.

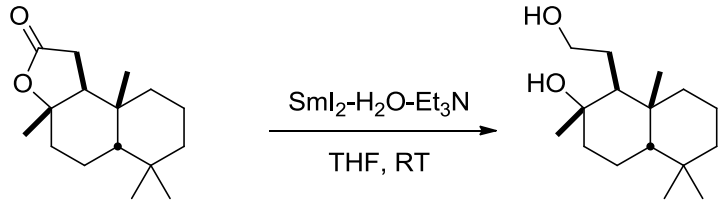
***rac*-(1*S*, 3*S*)-3-(2-Hydroxyethyl)cyclopentanol** (Table 1, entry 15)[12]



1o **2o**

According to the general procedure *Method A*, the reaction of *rac*-(1*S*,5*R*)-2-oxabicyclo[3.2.1]octan-3-one (0.25 mmol), samarium(II) iodide (1.12 mmol), water (9.0 mmol) and triethylamine (9.0 mmol) for 3 h at rt afforded the title compound in 93% yield (GC vs. internal standard). GC (GCTCM-5 30 mm x 0.32 mm; mobile phase: helium; flow rate: 1.0 mL/min; 70 °C, 4 min; 70 °C to 220 °C, 10 °C/min; retention time: **1o**, 11.32 min; **2o**,14.84 min). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.13-1.18 (m, 1H), 1.32-1.38 (m, 1H), 1.57-1.64 (m, 3H), 1.66-1.74 (m, 2H), 1.81-1.90 (m, 1H), 2.05-2.12 (m, 1H), 2.76 (br, 2H), 3.56 (t, *J* = 6.5 Hz, 2H), 4.21-4.25 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.0, 34.7, 35.1, 39.2, 41.9, 61.3, 73.1.

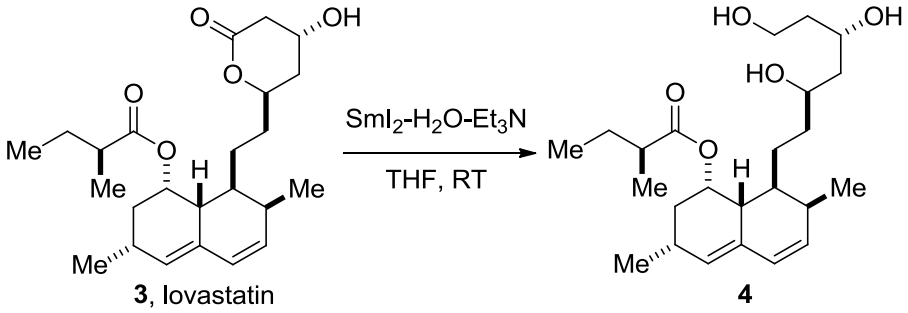
(+)-(1*S*,2*S*,4a*S*,8a*R*)-1-(2-Hydroxyethyl)-2,5,5,8a-tetramethyldecahydronaphthalen-2-ol (Table 1, entry 16)[24]



1p **2p**

According to the general procedure *Method B*, the reaction of (+)-(3a*R*)-sclareolide (0.25 mmol), samarium(II) iodide (2.0 mmol), water (6.0) and triethylamine (6.0 mmol) for 2 h at rt, afforded after chromatography (EtOAc) the title compound in 99% yield. Solid (R_f = 0.15, 40/60 EtOAc/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.78 (s, 6H), 0.87 (s, 3H) 0.90-0.97 (m, 2H), 1.09-1.17 (m, 1H), 1.18 (s, 3H), 1.21-1.32 (m, 2H), 1.33-1.51 (m, 3H), 1.51-1.72 (m, 5H), 1.89 (dt, *J* = 3.2, 12.3 Hz, 1H), 3.43 (ddd, *J* = 6.0, 8.0, 9.9 Hz, 1H), 3.77 (dt, *J* = 4.3, 9.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.2, 18.4, 20.3, 21.4, 24.5, 27.8, 33.2, 33.3, 38.9, 39.2, 41.8, 44.0, 56.0, 59.2, 63.9, 72.9.

(1*S*,3*R*,7*S*,8*S*,8a*R*)-3,7-Dimethyl-8-((3*R*,5*S*)-3,5,7-trihydroxyheptyl)-1,2,3,7,8,8a-hexahydronaphthalen-1-yl 2-methylbutanoate (Scheme 1)

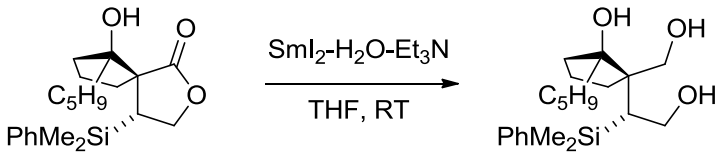


3, Iovastatin **4**

According to the general procedure *Method A*, the reaction of lovastatin (0.10 mmol), samarium(II) iodide (0.5 mmol), water (3.0) and triethylamine (3.0 mmol) for 1 h at rt, afforded after purification by preparative thin layer chromatography (EtOAc) the title compound in 87% yield. Oil (R_f = 0.34, EtOAc). Note: a modified procedure was used. To samarium(II) iodide powder, substrate in 8.0 mL of THF was added, followed by amine and water. Products resulting from non-selective reduction were not detected by analysis of crude reaction mixture by ^{1}H NMR.[25] ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.79-0.83 (m, 6H), 1.01 (d, *J* = 7.5 Hz, 3H), 1.04 (d, *J* = 7.0 Hz, 3H), 1.08-1.22 (m, 2H), 1.32-1.41 (m, 1H), 1.42-1.61 (m, 6H), 1.64 (q, *J* = 5.5 Hz, 2H), 1.85-1.88 (m, 2H), 2.18 (dd, *J* = 2.5, 12.0 Hz, 1H), 2.23-2.32 (m, 2H), 2.34-2.41 (m, 1H), 3.00 (br, 1H), 3.60 (br, 1H), 3.69-3.83 (m, 3H), 4.02-4.07 (m, 1H), 4.28 (br, 1H), 5.35 (q, *J* = 3.0 Hz,

1H), 5.45 (t, *J* = 3.0 Hz, 1H), 5.72 (dd, *J* = 6.5, 9.5 Hz, 1H), 5.92 (d, *J* = 9.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.7, 13.9, 16.3, 22.9, 24.2, 26.8, 27.5, 30.5, 32.9, 35.1, 36.2, 37.5, 38.8, 41.5, 43.0, 61.2, 68.1, 72.8, 73.0, 128.3, 129.6, 131.6, 133.3, 177.2; IR (neat) 3372, 3019, 2935, 2874, 1711, 1462, 1373, 1264, 1195, 1158, 1125, 1081, 1056, 974 cm^{-1}; HRMS calcd for $C_{24}H_{41}O_5$ (M^+ + H) 409.2949, found 409.2932.

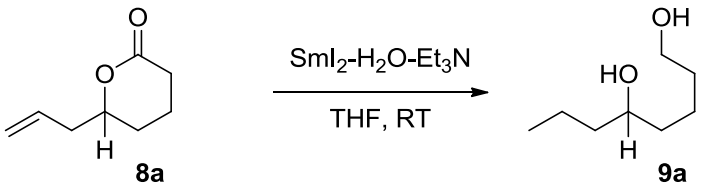
***rac*-(1*S*,2*R*)-2-((*R*)-1-(Dimethyl(phenyl)silyl)-2-hydroxyethyl)-2-(hydroxymethyl)-1-(pent-4-en-1-yl)cyclopentanol** (Scheme 1)



5 **6**

According to the general procedure *Method B*, the reaction of lactone **5** (0.028 mmol), samarium(II) iodide (0.22 mmol), water (0.67) and triethylamine (0.67 mmol) for 30 min at rt, afforded after purification by chromatography (20/80 EtOAc/hexanes) the title compound in 91% yield. Oil (R_f = 0.20, 30/70 EtOAc/hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.46 (s, 3H), 0.48 (s, 3H), 1.12-1.19 (m, 2H), 1.20-1.69 (m, 7H), 1.82 (qd, *J* = 1.5, 11.3 Hz, 1H), 1.99 (ddd, *J* = 2.3, 9.6, 13.3 Hz, 1H), 2.05-2.16 (m, 2 H), 3.62 (d, *J* = 12.6 Hz, 1H), 3.85 (dd, *J* = 5.5, 10.7 Hz, 1H), 3.97 (dd, *J* = 1.5, 12.6 Hz, 1H), 4.47 (dd, *J* = 0.9, 10.7 Hz, 1H), 4.94-5.08 (m, 2 H), 5.73-5.91 (ddt, *J* = 6.7, 10.3, 17.0 Hz, 1H), 7.31-7.43 (m, 3H), 7.59 (dd, *J* = 2.9, 6.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ -0.1, 0.2, 17.9, 22.5, 33.9, 34.3, 34.4, 34.5, 36.2, 51.3, 61.5, 68.3, 87.6, 114.6, 127.8, 128.8, 133.9, 138.7, 140.2; IR (neat) 3289, 2952, 2877, 1426, 1249, 1109 cm^{-1}; HRMS calcd for $C_{21}H_{34}O_3SiNa$ (M^+ + Na) 385.2169, found 385.2170.

Octane-1,5-diol (Scheme 3, entry 1)[26]

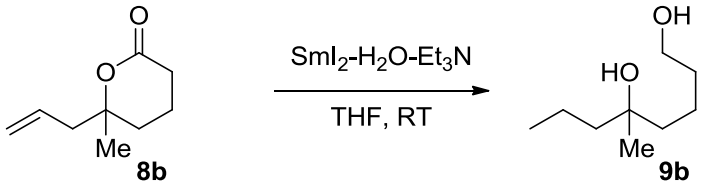


8a **9a**

According to the general procedure *Method A*, the reaction of 6-allyltetrahydro-2*H*-pyran-2-one (0.10 mmol), samarium(II) iodide (1.0 mmol), water (6.0) and triethylamine (6.0 mmol) for 15 h at rt, afforded after chromatography the title compound in 98% yield (^{1}H NMR vs. internal standard). Note: the product is volatile. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86 (t, *J* = 7.2 Hz, 3H),

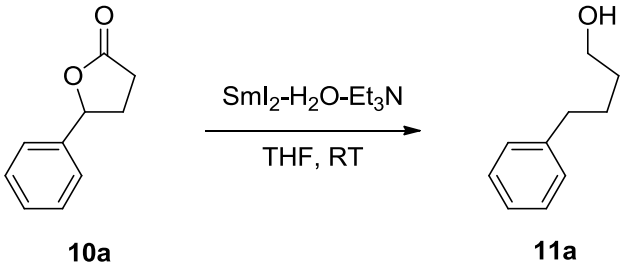
1.18-1.56 (m, 10H), 1.70 (br, 2H), 3.55 (m, 1H), 3.59 (t, *J* = 6.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 18.9, 21.8, 32.6, 37.0, 39.7, 62.7, 71.6.

5-Methyloctane-1,5-diol (Scheme 3, entry 2)



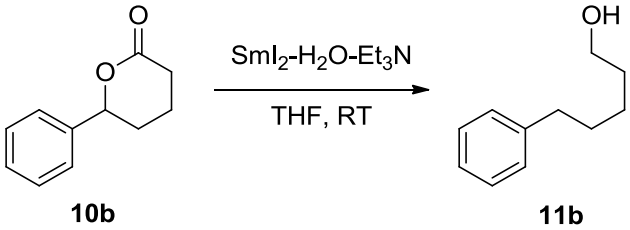
According to the general procedure *Method A*, the reaction of 6-allyl-6-methyltetrahydro-2*H*-pyran-2-one (0.10 mmol), samarium(II) iodide (1.0 mmol), water (3.0) and triethylamine (3.0 mmol) for 5 h at rt, afforded after chromatography the title compound in 84% yield. Oil (R_f = 0.44, EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, *J* = 7.2 Hz, 3H), 1.09 (s, 3H), 1.24-1.43 (m, 8H), 1.46-1.57 (m, 4H), 3.59 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.7, 17.2, 20.0, 26.9, 33.1, 41.4, 44.3, 62.7, 72.8; IR (neat) 3338, 2955, 2934, 2871, 1458, 1372, 1191, 1152, 1070, 1038, 1011, 932, 898, 857 cm^{-1}; HRMS calcd for $C_9H_{20}O_2Na$ (M^+ + Na) 183.1356, found 183.1364.

4-Phenylbutan-1-ol (Scheme 3, entry 1)[27]



According to the general procedure *Method A*, the reaction of 5-phenyldihydrofuran-2(3*H*)-one (0.1 mmol), samarium(II) iodide (1.8 mmol), water (5.4 mmol) and triethylamine (5.4 mmol) for 18 h at rt, afforded the title compound in 92% yield (^{1}H NMR vs. internal standard). Analytical sample of the title product was obtained after purification by chromatography (1/4 EtOAc/hexanes). Oil (R_f = 0.18, 1/4 EtOAc/hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20-1.81 (m, 5H), 2.72 (t, *J* = 7.4 Hz, 2H), 3.50-3.75 (m, 2H), 7.16-7.22 (m, 3H), 7.25-7.32 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.5, 32.3, 35.6, 62.8, 125.7, 128.3, 128.4, 142.3.

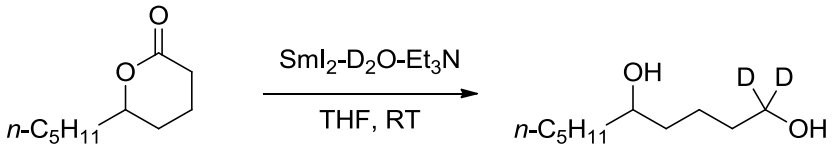
5-Phenylpentan-1-ol (Scheme 3, entry 2)[28]



10b **11b**

According to the general procedure *Method A*, the reaction of 6-phenyltetrahydro-2*H*-pyran-2-one (0.09 mmol), samarium(II) iodide (1.6 mmol), water (4.8 mmol) and triethylamine (4.8 mmol) for 18 h at rt, afforded after chromatography (1/4 EtOAc/hexanes) the title compound in 84% yield. Oil (R_f = 0.32, 30/70 EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.13-1.50 (m, 2H), 1.50-1.76 (m, 5H), 2.63 (t, *J* = 7.5 Hz, 2H), 3.65 (t, *J* = 6.1 Hz, 2H), 7.11-7.23 (m, 3H), 7.24-7.39 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.4, 31.2, 32.6, 35.9, 62.9, 125.6, 128.2, 128.4, 142.5.

1,1-*D*,*D*-**Decane-1,5-diol** (Scheme 4)[15]

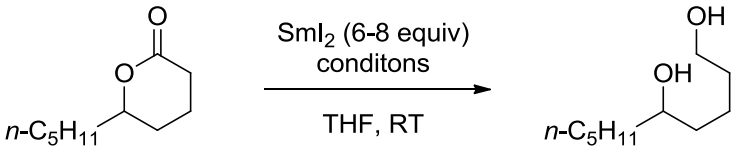


1a **2a**-*D*,*D*

According to the general procedure *Method A*, the reaction of 6-pentyltetrahydro-2*H*-pyran-2-one (0.25 mmol), samarium(II) iodide (1.5 mmol), D_2O (9.0 mmol) and triethylamine (9.0 mmol) for 15 min at rt, afforded after chromatography (4/1 EtOAc/hexanes) the title compound in 99% yield. Oil (R_f = 0.32, 30/70 EtOAc/hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, *J* = 6.6 Hz, 3H), 1.25-1.66 (m, 16H), 3.58-3.66 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 21.7, 22.6, 25.3, 31.9, 32.3, 36.9, 37.5, 61.8 (t, J^1 = 21.2 Hz), 71.8. HRMS calcd for $C_{10}H_{21}{}^2H_2O_2$ (M^+ + H) 177.1819, found 177.1817. Note: integration of the area at 3.58-3.66 in ^{1}H NMR indicates >98% of deuterium incorporation at 1-position of (**2a**). Note: MS and HRMS spectra show that peaks corresponding to [M+] of non-deuterated diols (**2a**) are not present, indicating >99% of deuterium incorporation.

Mechanistic Studies

Table ESI-2. Evaluation of the role of additives on the reaction of lactones with SmI_2.[a]

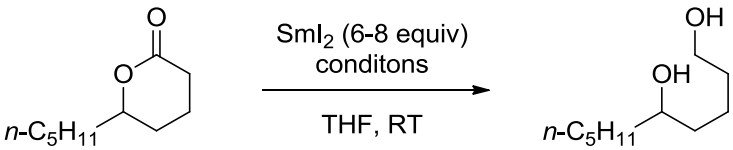


1a **2a**

entry	proton source	amine	proton source (equiv)	amine (equiv)	time (h)	conversion[b] (%)	yield[b] (%)
1	H_2O	-	25	-	2	7	6
2	H_2O	-	800	-	2	33	31
3	MeOH	-	50	-	2	<5	-
4	MeOH	-	800	-	2	<5	-
5	$(CH_2OH)_2$	-	32	-	2	5	5
6	-	Et_3N	-	18	18	<5	<5

[a]All reactions carried out using standard Schlenk techniques for handling air-sensitive reagents. [b]Determined by ^1H NMR.

Table ESI-3. Evaluation of the role of amines on the reduction of lactones with SmI_2.[a]

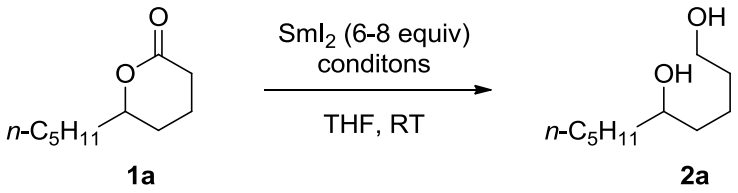


1a **2a**

entry	proton source	amine	proton source (equiv)	amine (equiv)	time (h)	conversion[b] (%)	yield[b] (%)
1	H_2O	Et_3N	16	24	2	>95	99
2	H_2O	*n*-$BuNH_2$	18	18	2	>95	99
3	H_2O	*i*-Pr_2NH	18	18	2	>95	99
4	H_2O	pyrrolidine	18	18	2	>95	99

[a,b]See, Table ESI-2.

Table ESI-4. Evaluation of the role of proton sources on the reduction of lactones with SmI_2.[a]

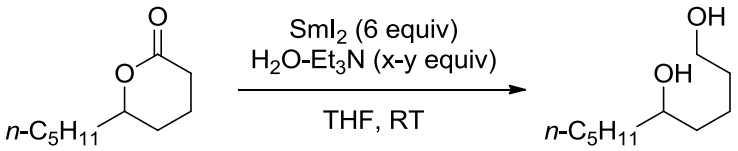


1a **2a**

entry	proton source	amine	proton source (equiv)	amine (equiv)	time (h)	conversion[b] (%)	yield[b] (%)
1	H_2O	Et_3N	16	24	2	>95	99
2	H_2O	Et_3N	18	18	30 s	>95	99
3	MeOH	Et_3N	18	18	18	58	58
4	*t*-BuOH	Et_3N	18	18	18	<5	<5
5	$(CH_2OH)_2$	Et_3N	9	18	18	>95	99
6	$(CH_2OH)_2$	Et_3N	12	24	30 s	>95	88

[a,b]See, Table ESI-2.

Table ESI-5. Determination of the ratio of SmI_2–H_2O–Et_3N required to form the active complex.[a]

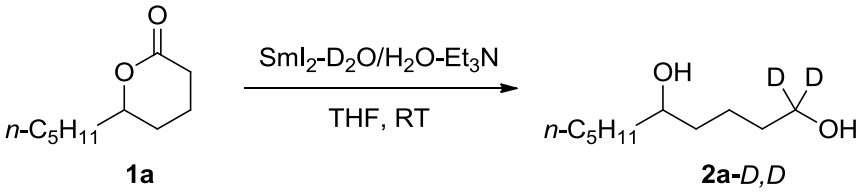


1a **2a**

entry	H_2O (equiv)	Et_3N (equiv)	time (h)	conversion[b] (%)	yield[b] (%)
1	12	18	24	>95	83
2	6	12	24	55	31
3	12	6	24	>95	75
4	18	1	24	15	11
5	18	3	24	50	45
6	18	6	24	>95	99

[a,b]See, Table ESI-2.

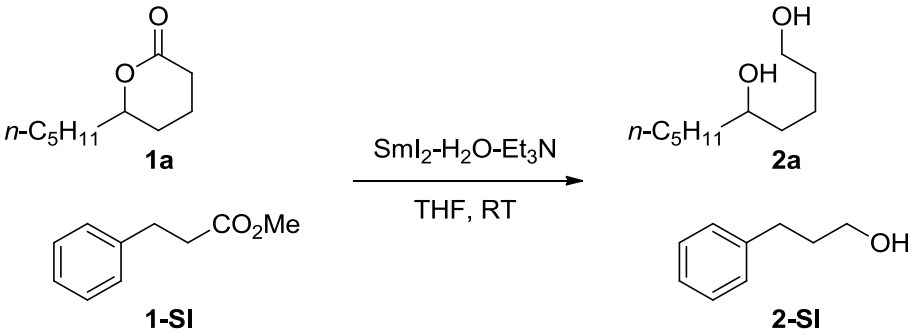
A) Determination of primary kinetic isotope effect[9,15-16,29-30]



1a **2a-*D,D***

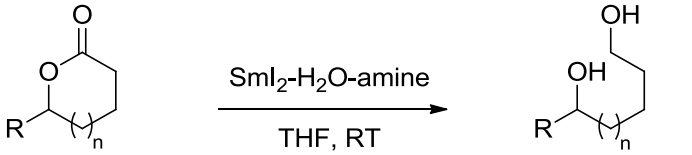
According to the general procedure, the reaction of 6-pentyltetrahydro-2*H*-pyran-2-one (0.10 mmol), samarium(II) iodide (0.6 mmol), deuterium oxide/water (1:1, 1.8 mmol) and triethylamine (1.2 mmol) for 2 h at rt, afforded 1,1-*D*,*D*-decane-1,5-diol and decane-1,5-diol. The amount of each species was determined by ^{1}H NMR (500 MHz, $CDCl_3$,). Kinetic isotope effect, k_H/k_D = 1.2.

B) Competition between 6-membered lactones and aliphatic esters



According to the general procedure, the reaction of **1a** (0.10 mmol) and methyl 3-phenylpropanoate **1-SI** (0.10 mmol), samarium(II) iodide (0.3 mmol), water (2.4 mmol) and triethylamine (2.4 mmol) for 5 min at rt, afforded decane-1,5-diol (**2a**) and 3-phenylpropan-1-ol (**2-SI**) in >95:5 ratio (determined by ^{1}H NMR (500 MHz, $CDCl_3$).

C) Determination of the relative order of reactivity of 5-, 6- and 7-membered lactones



1a, 1b or **1d** **2a, 2b** or **2d**

entry	**1**	R_1	n	conversion (%)	yield (%)
1	**1a**	*n*-C_5H_{11}	1	>95	99
2	**1b**	*n*-C_6H_{13}	0	72	72
3	**1d**	*n*-C_4H_9	2	>95	98

According to the general procedure, lactone **1a**, **1b** or **1d** (0.10 mmol) was reacted with samarium(II) iodide (0.6 mmol), water (1.8 mmol) and *N*-methylmorpholine (1.2 mmol) at room temperature. The reaction was quenched after 5 min by bubbling air through the reaction mixture until decolorization to give white color (~15-30 s). The amount of each species present was determined by ^{1}H NMR (500 MHz, $CDCl_3$). Although the reaction of lactones with SmI_2–H_2O–Et_3N under all tested reaction conditions was too fast to accurately determine relative rates of reduction of 6- and 7-membered lactones, based on the literature precedent for the related reaction of lactones with SmI_2-H_2O system[15] we tentatively assign the relative rates of reduction of lactones with SmI_2–H_2O–amine as 6- > 7- > 5-membered lactones.

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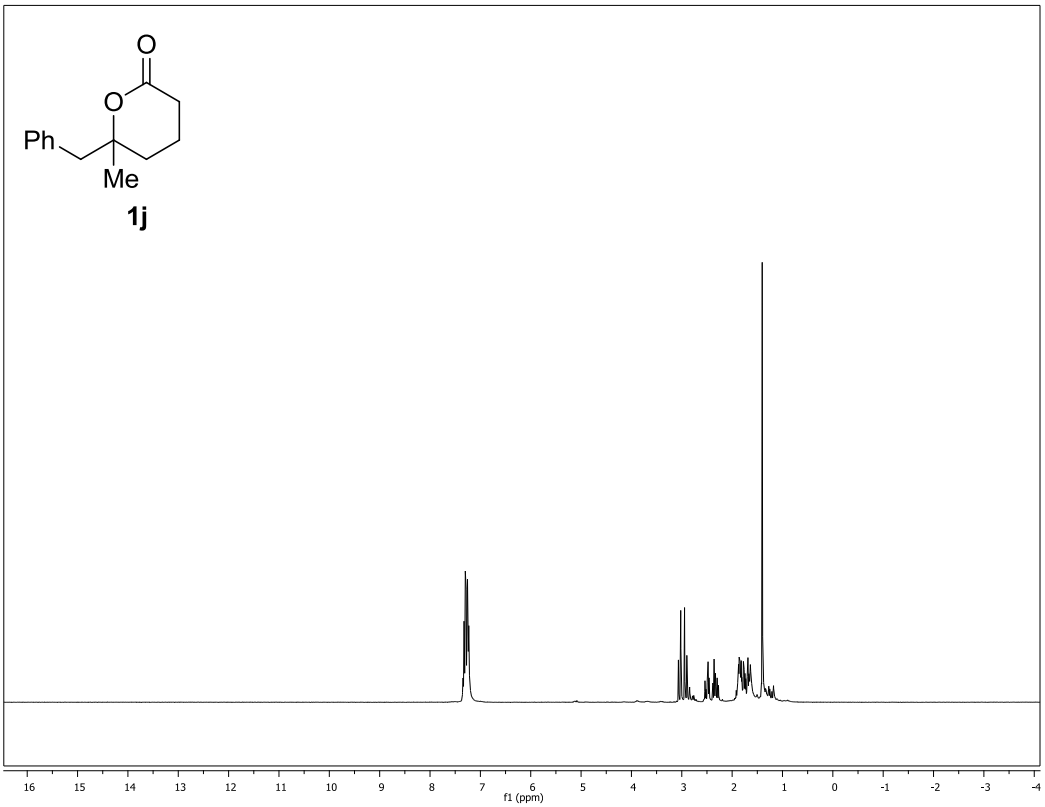
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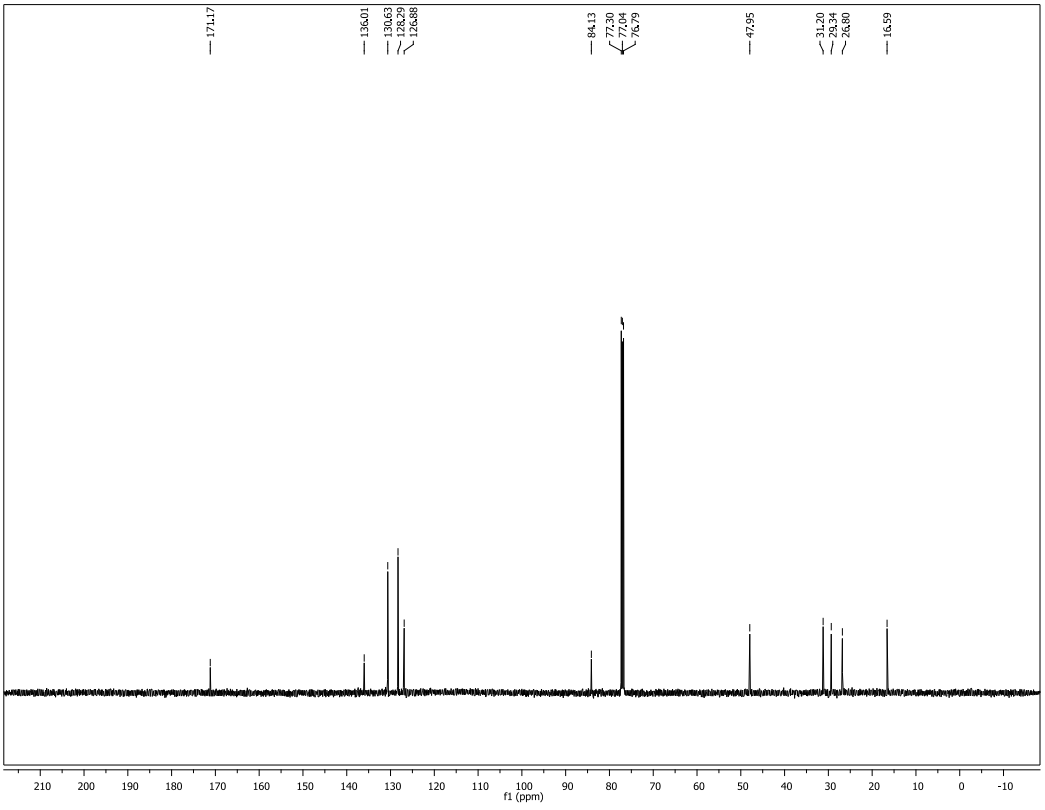
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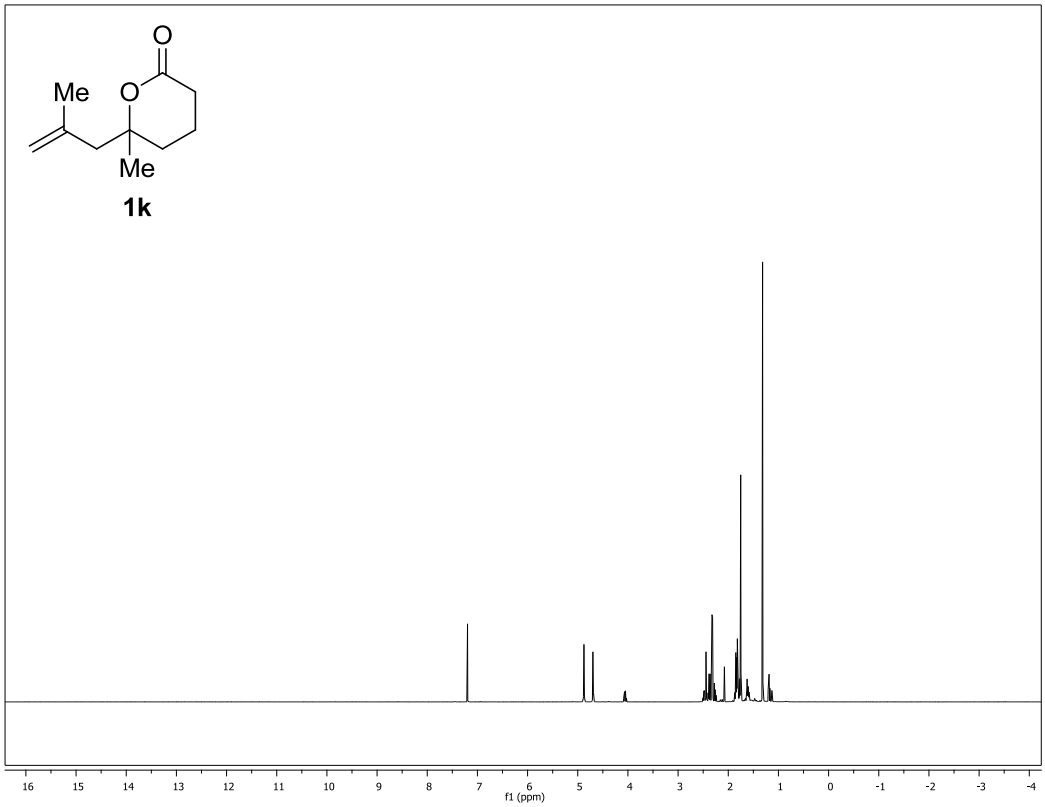
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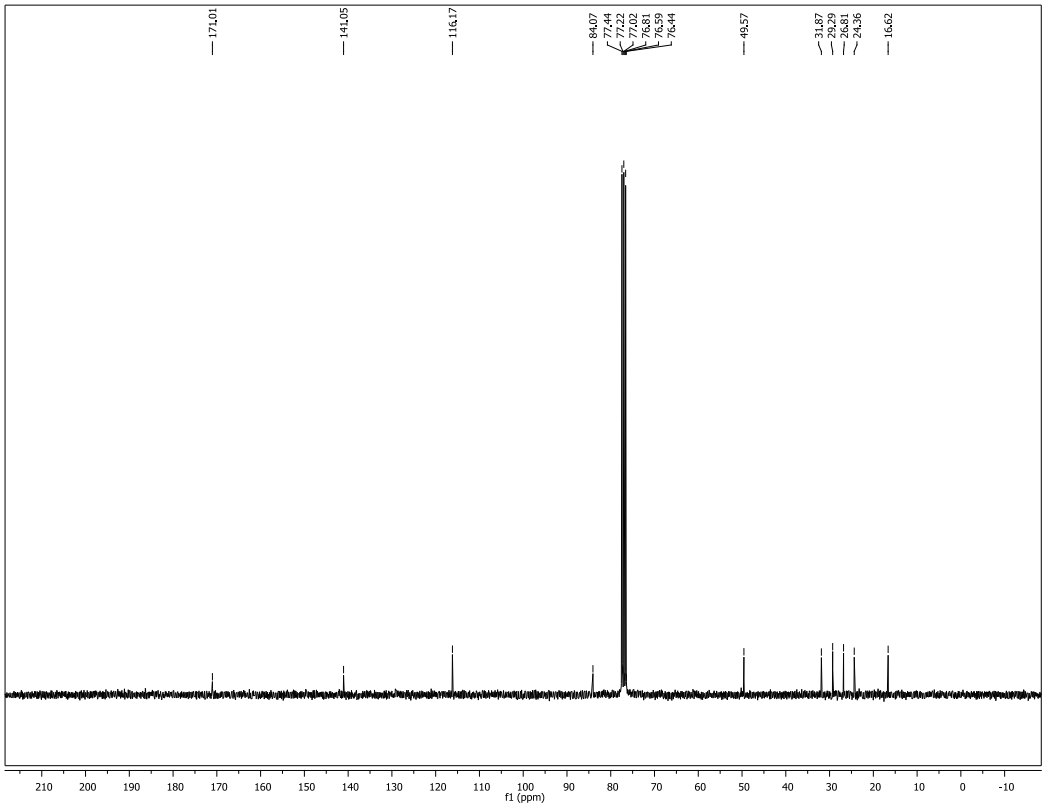
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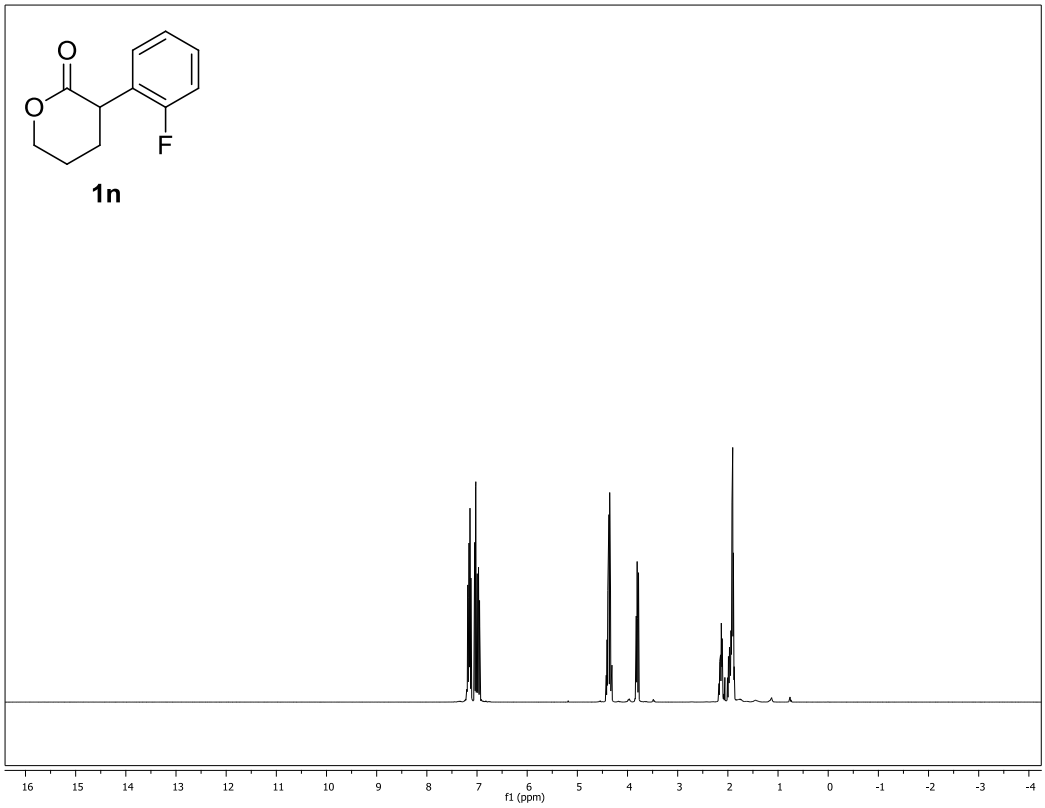
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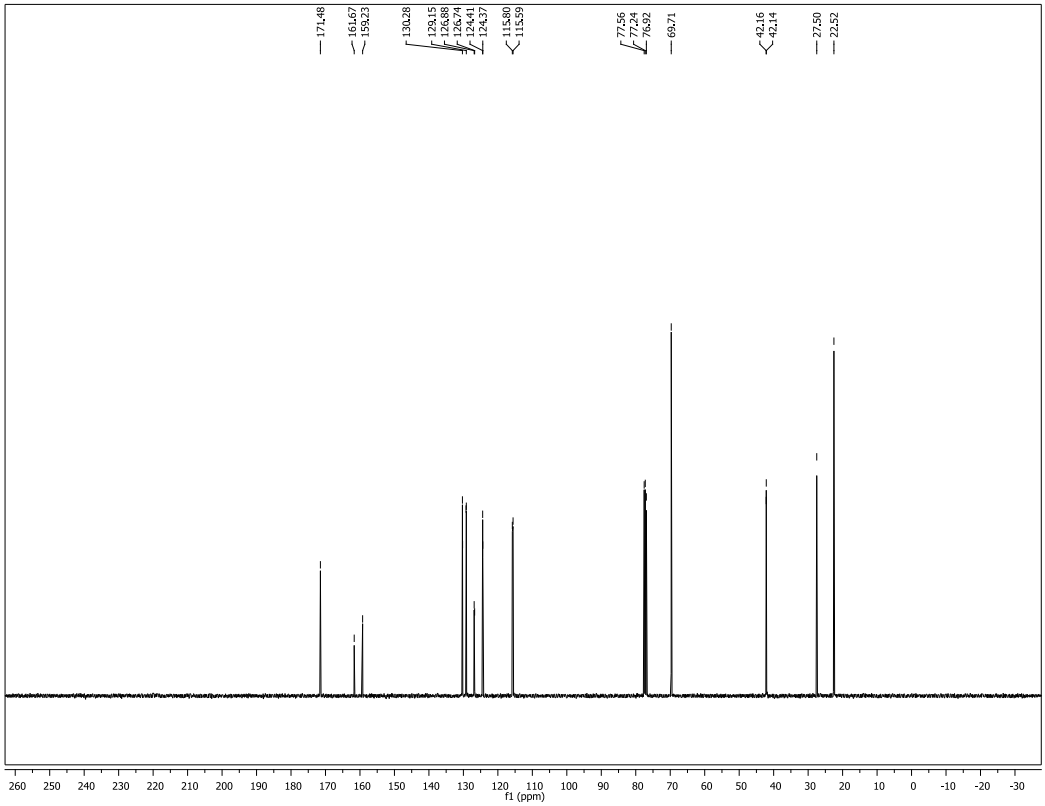
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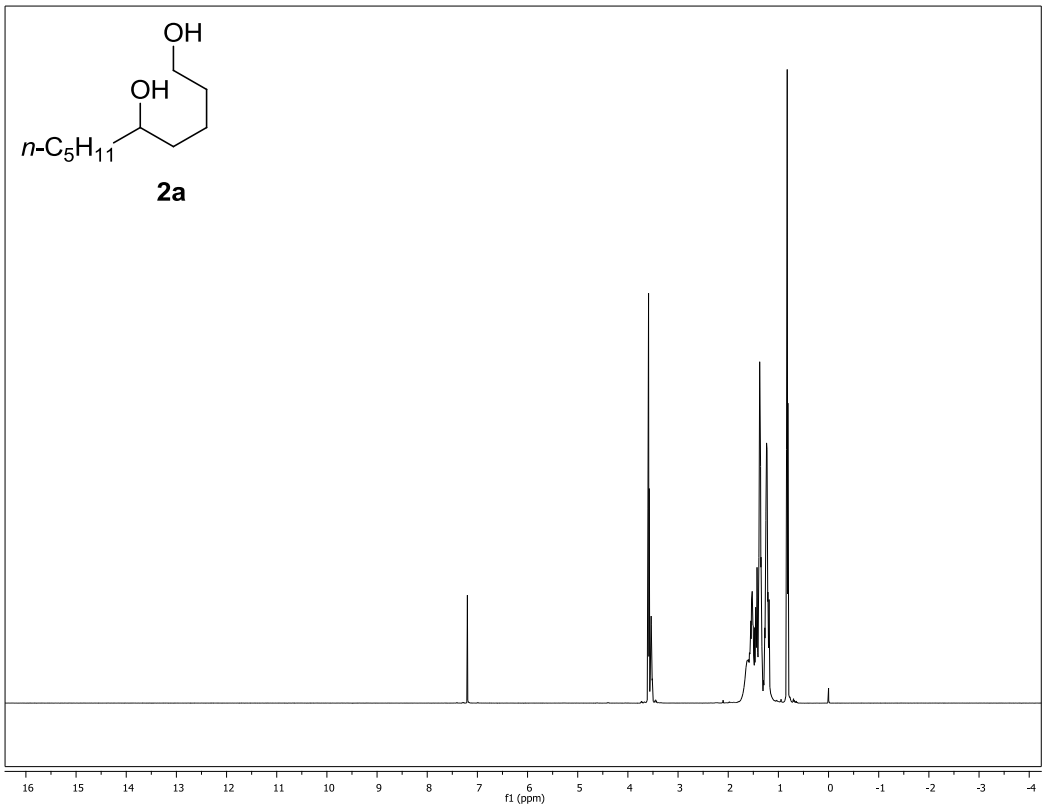
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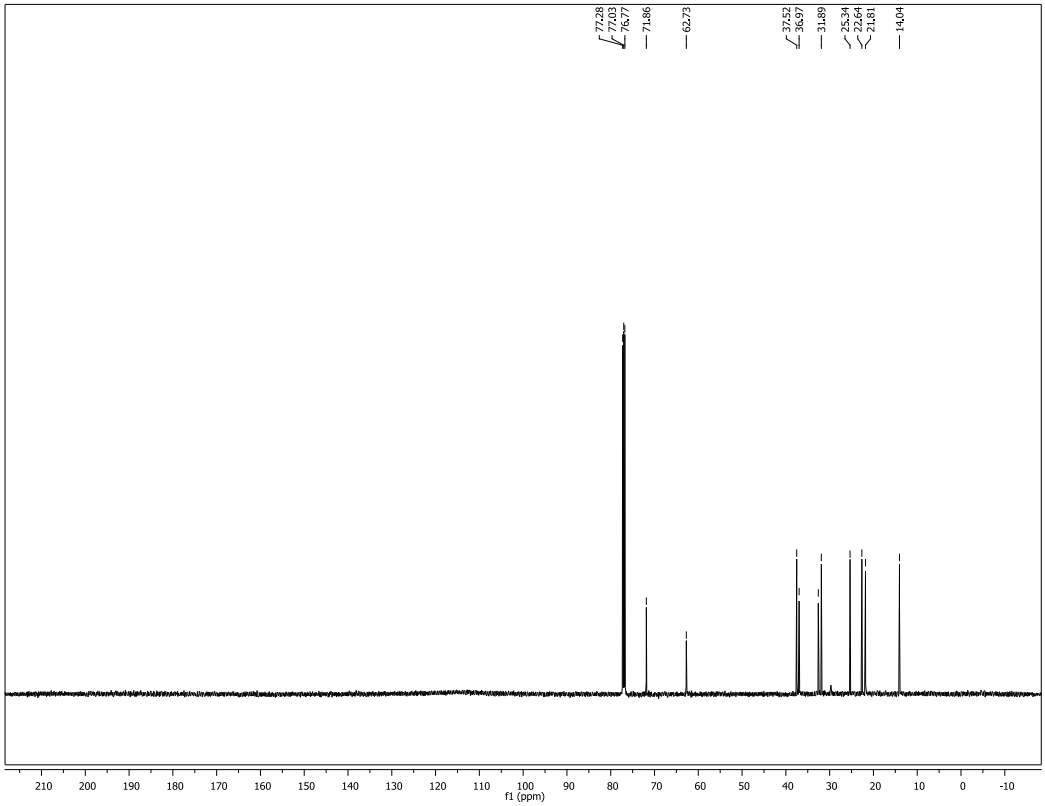
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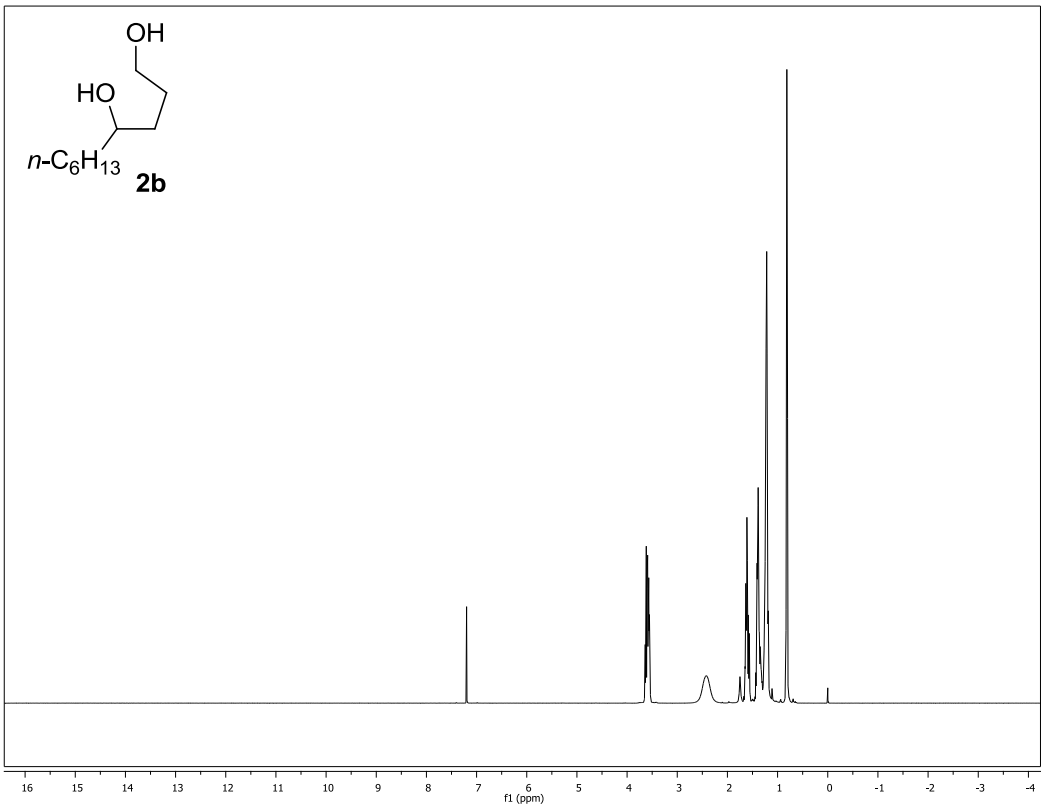
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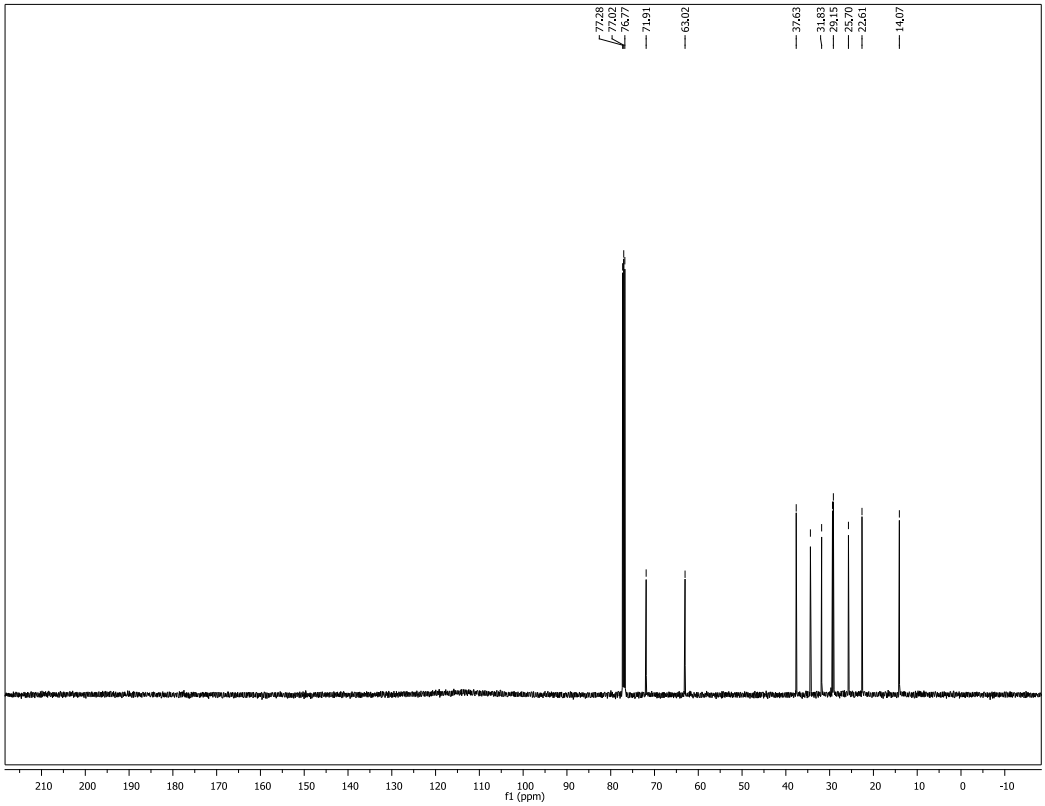
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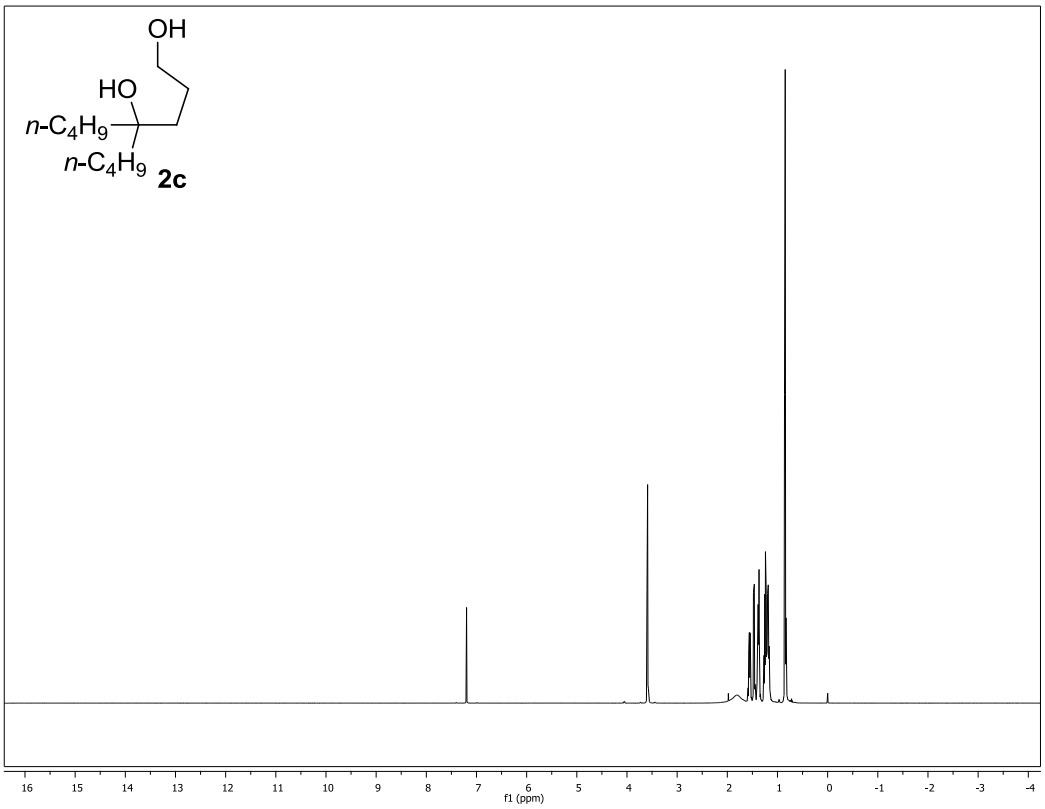
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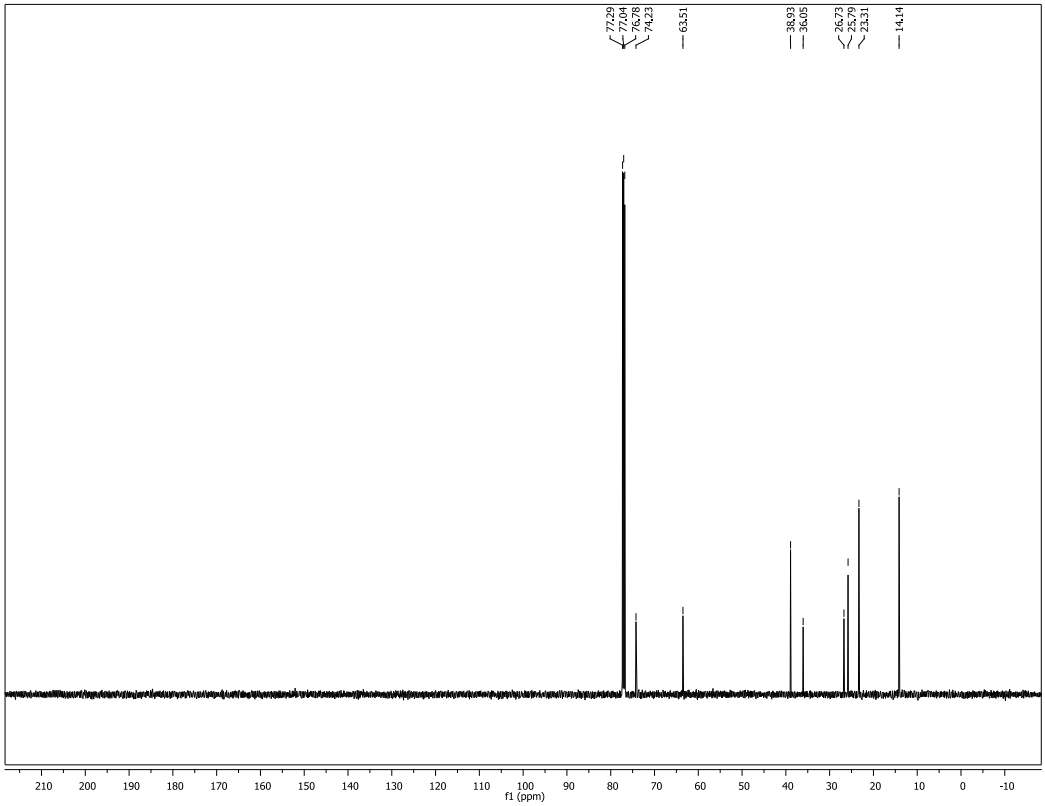
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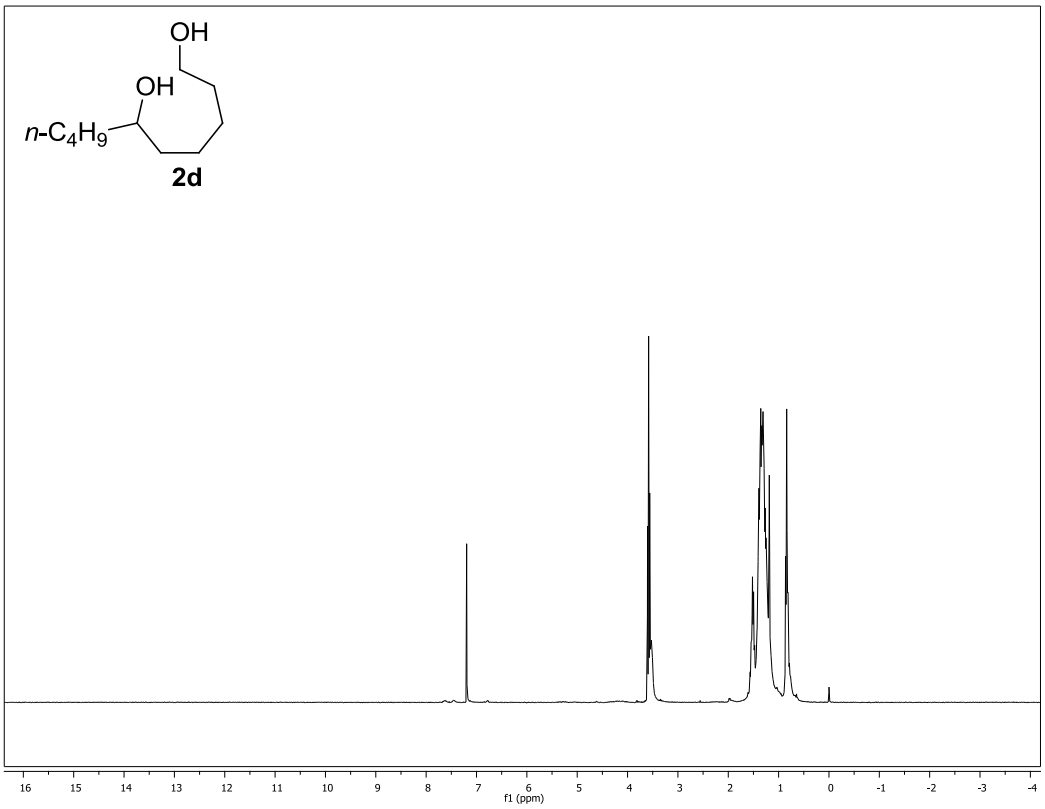
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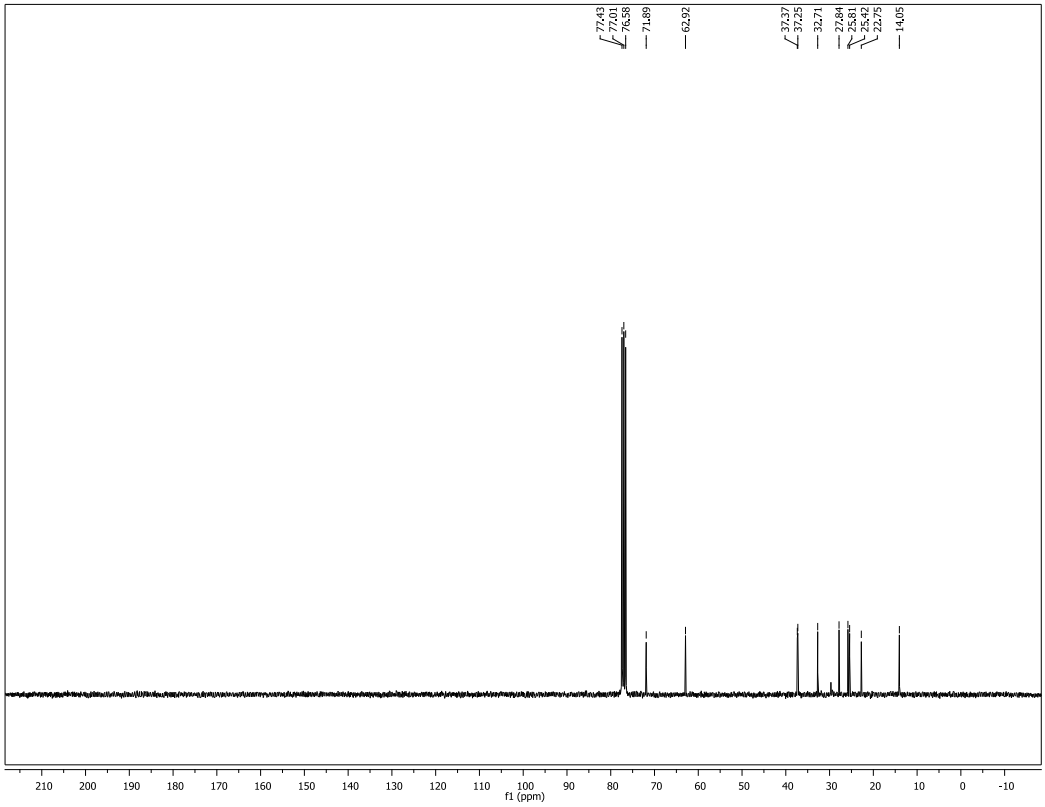
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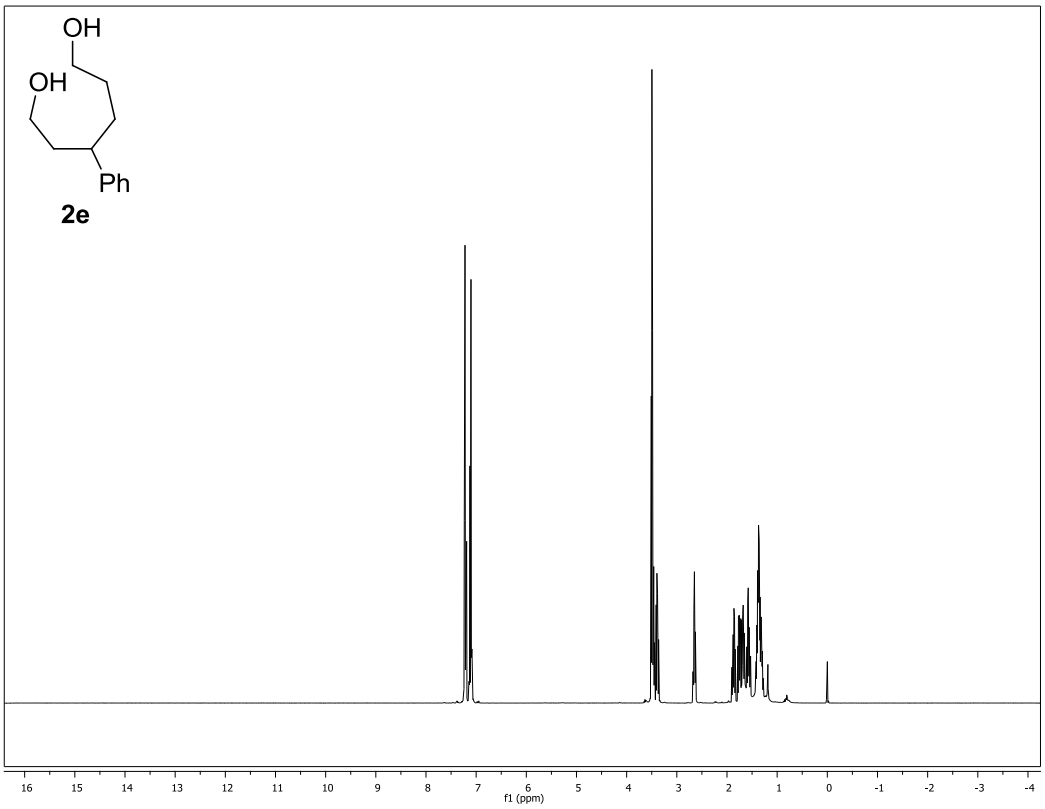
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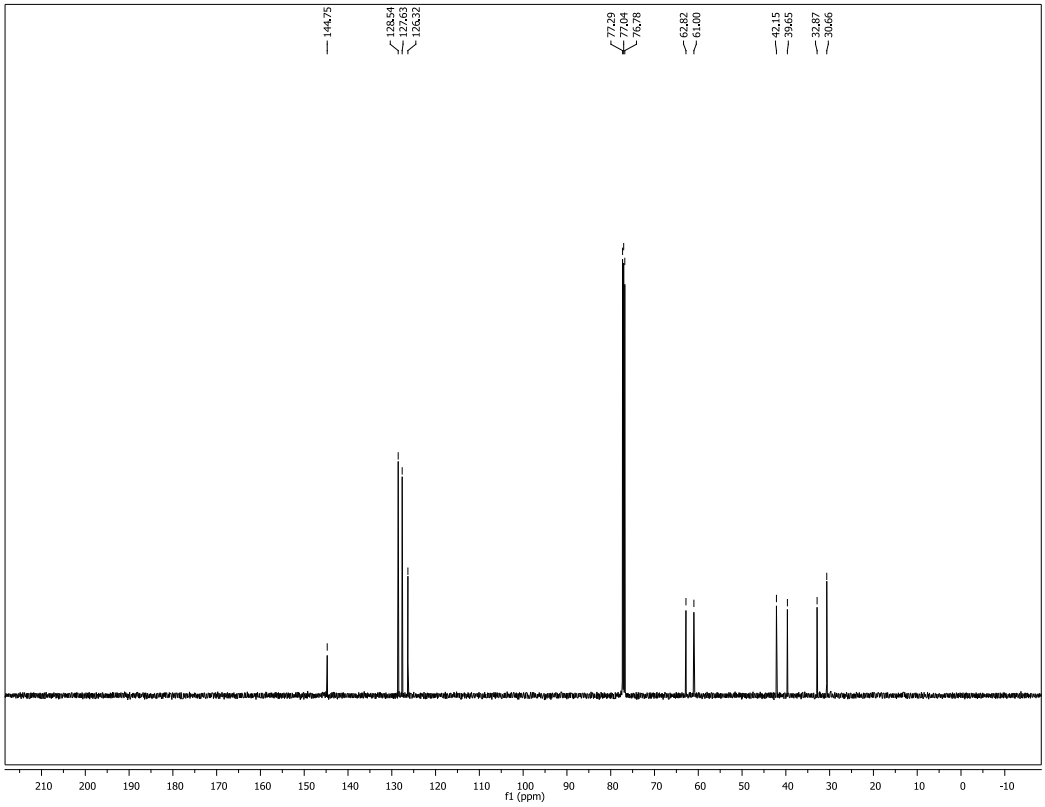
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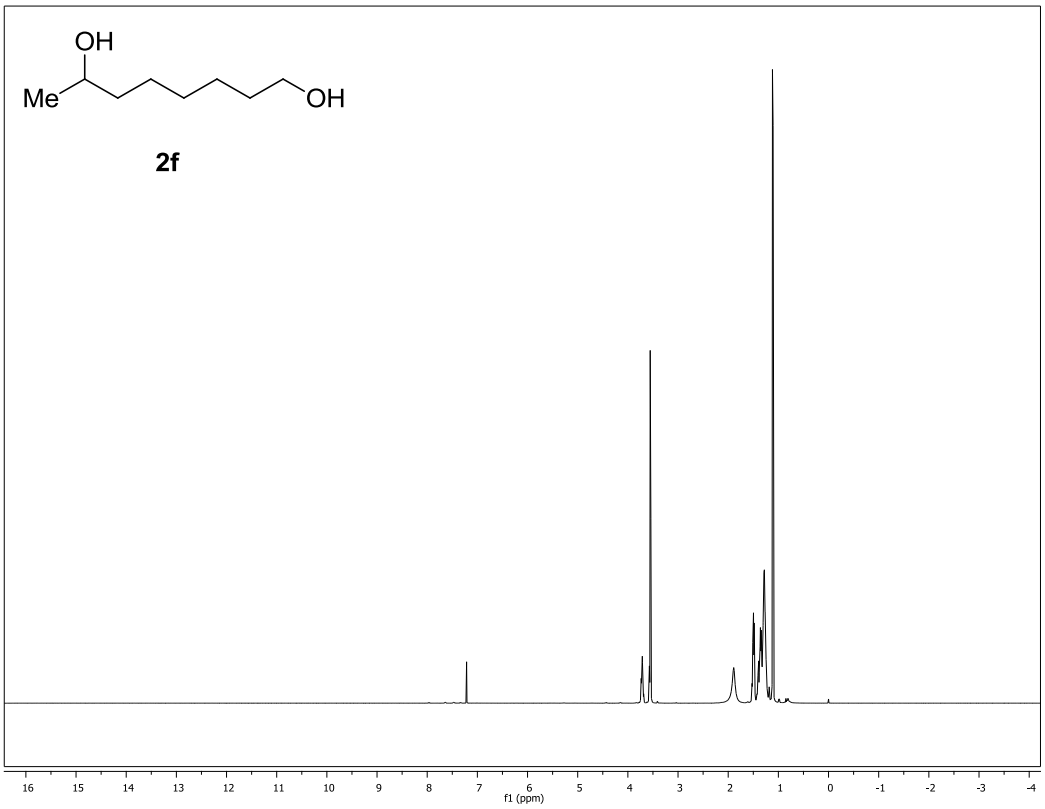
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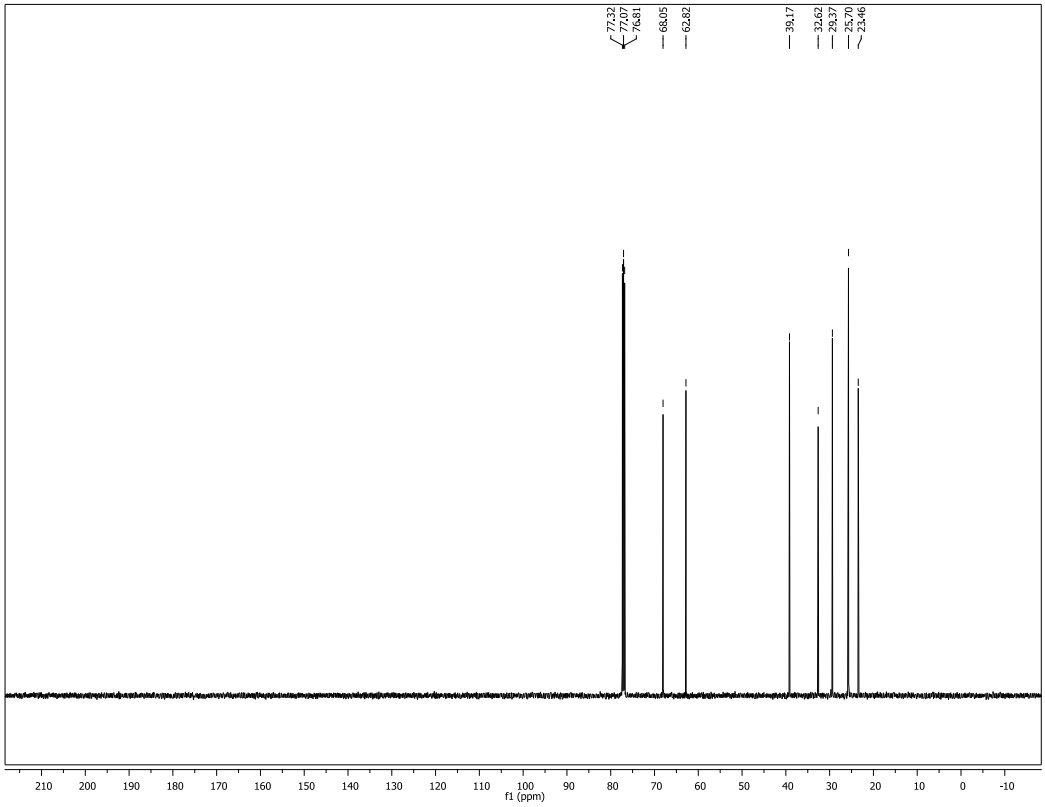
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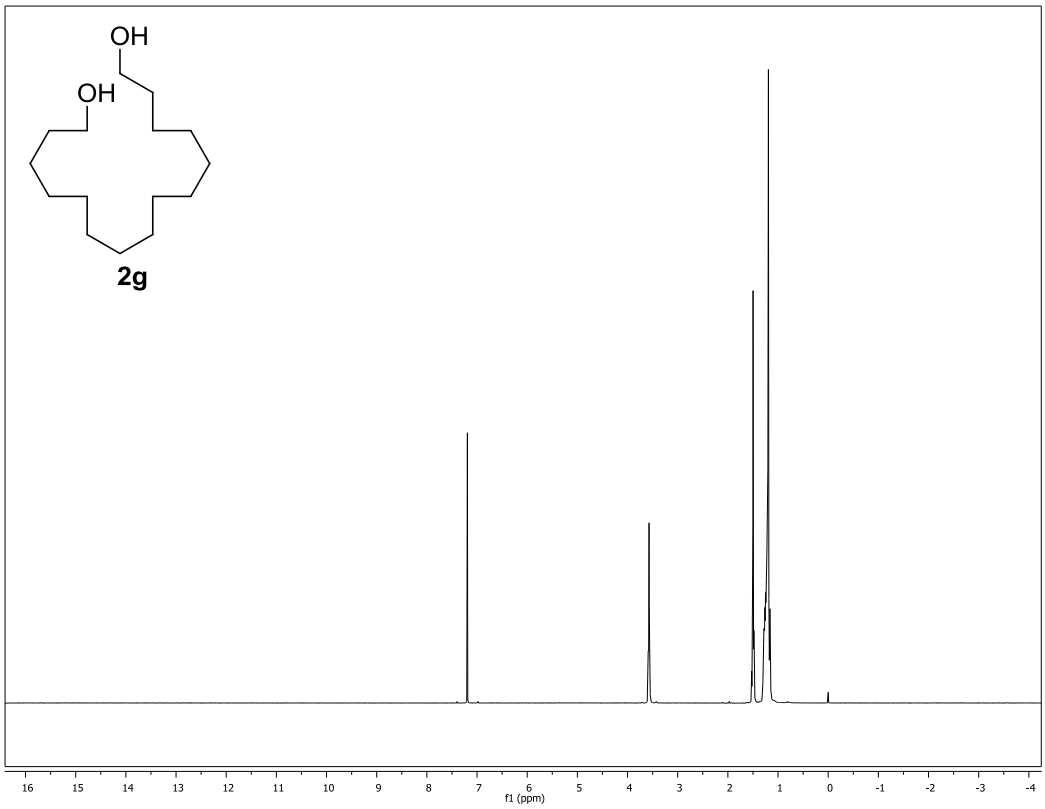
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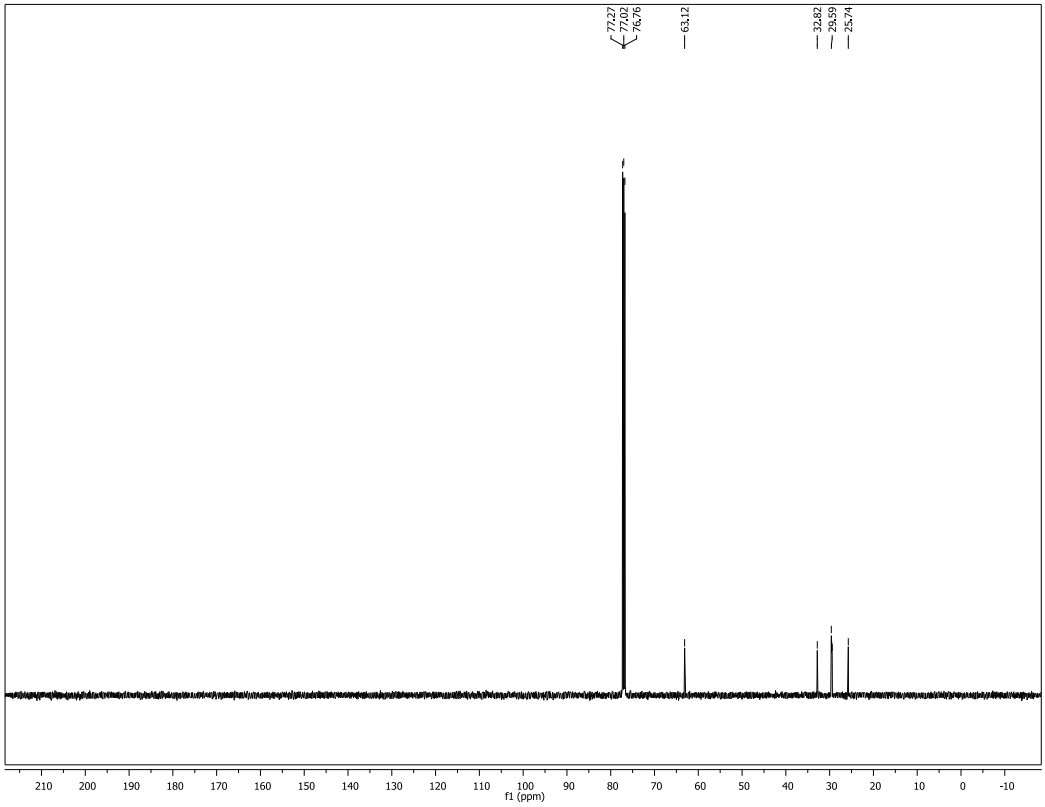
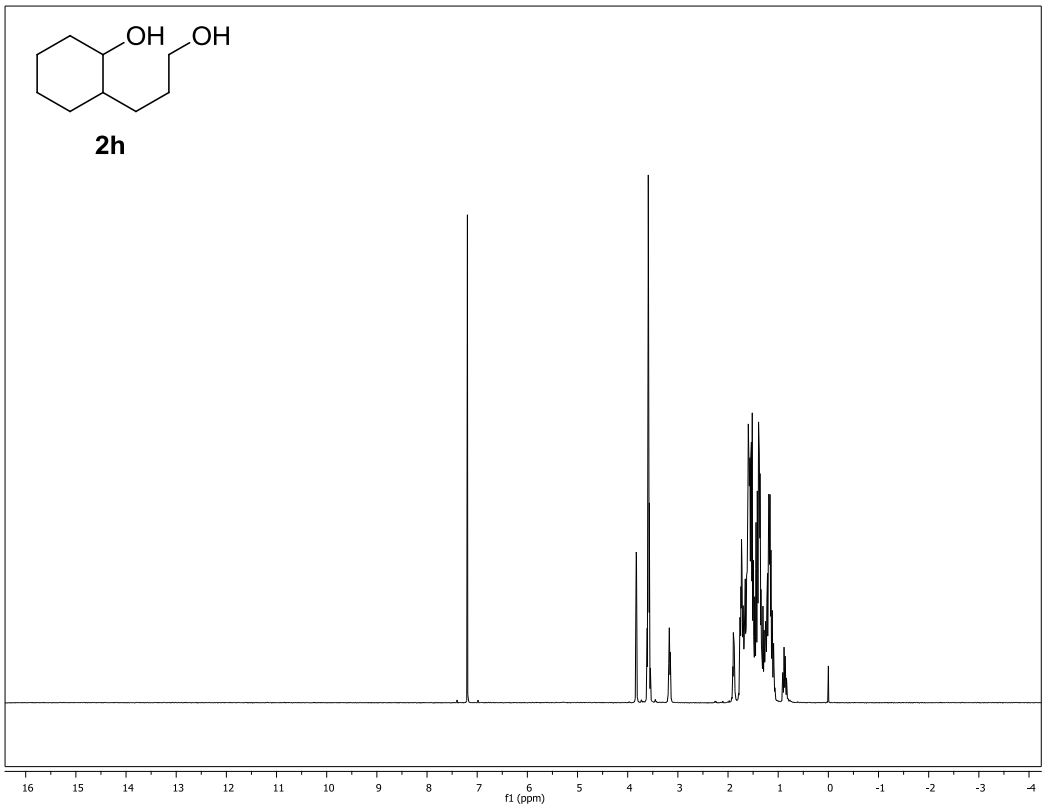
OH
2g
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


77.27
77.02
76.76
63.12
32.82
29.59
25.74
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
OH
2h
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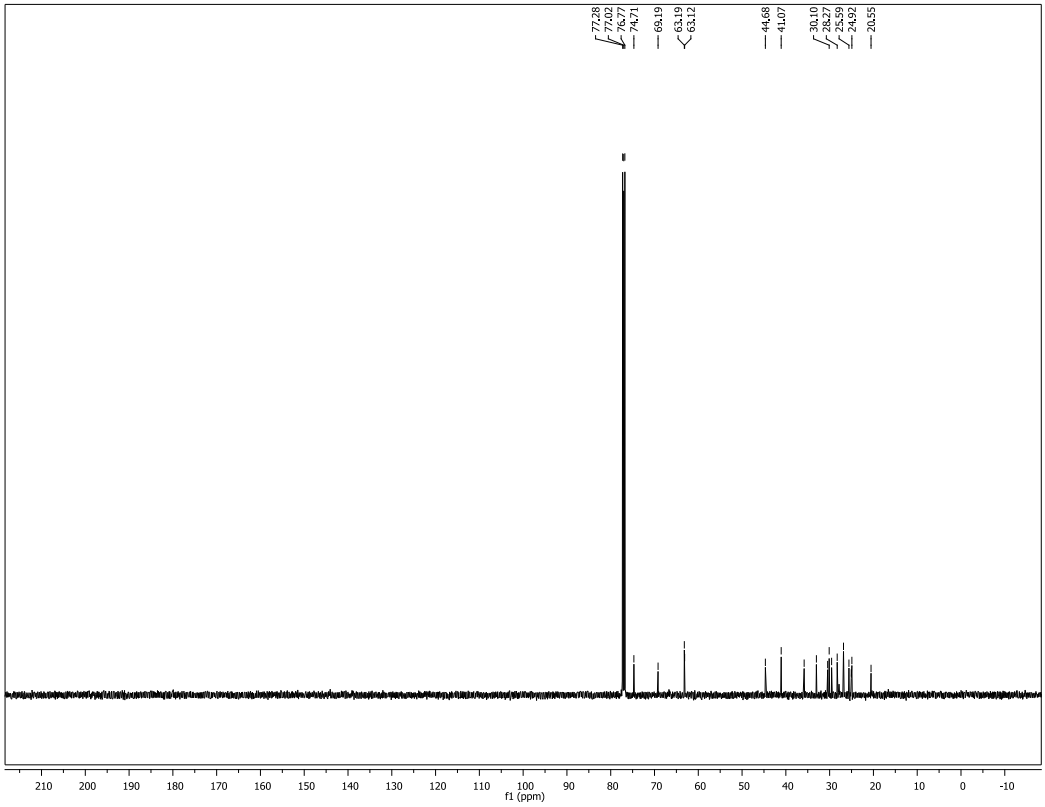
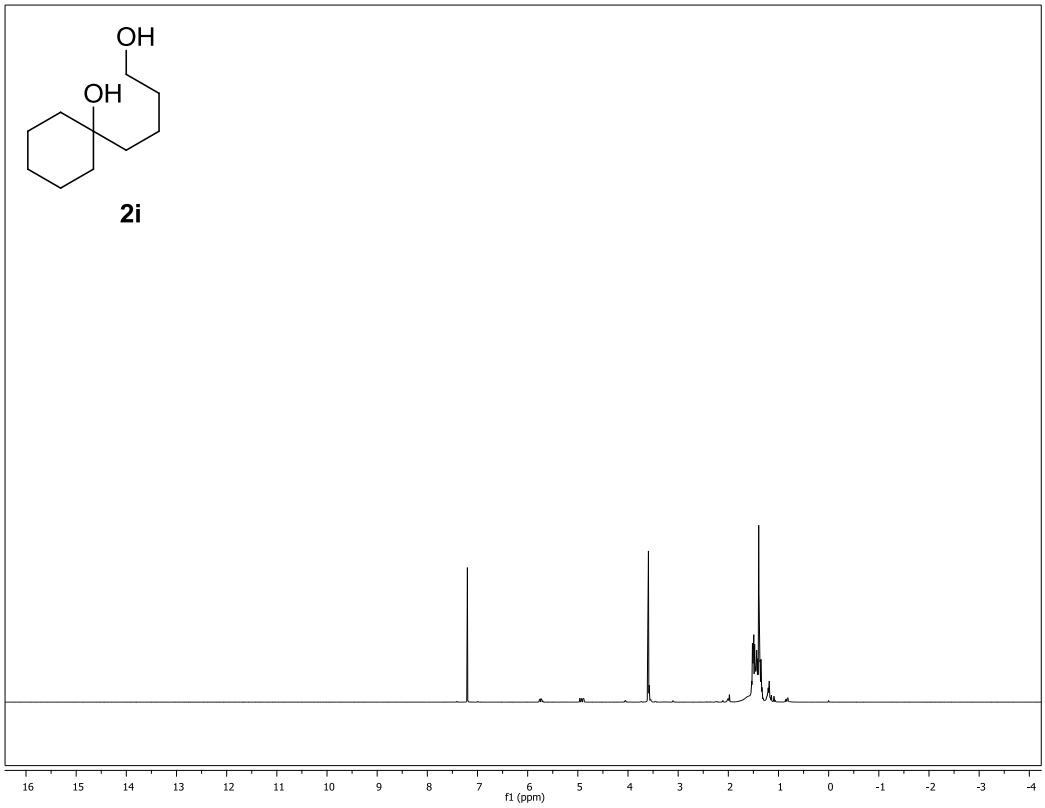
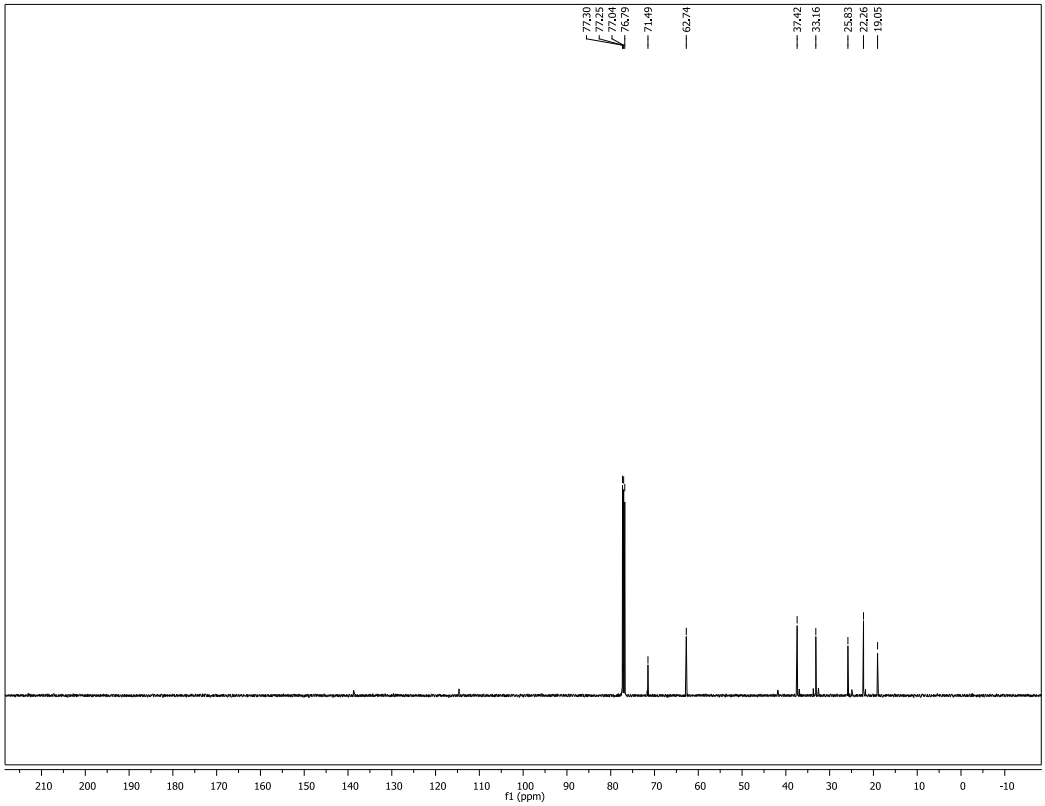
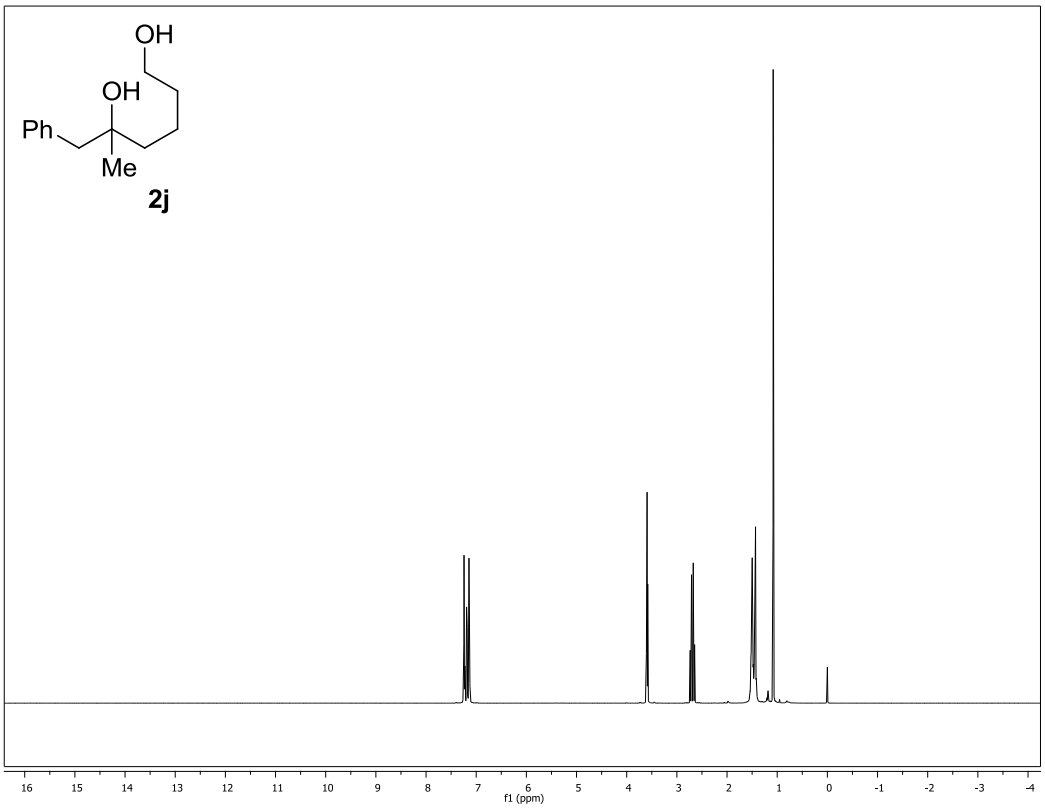
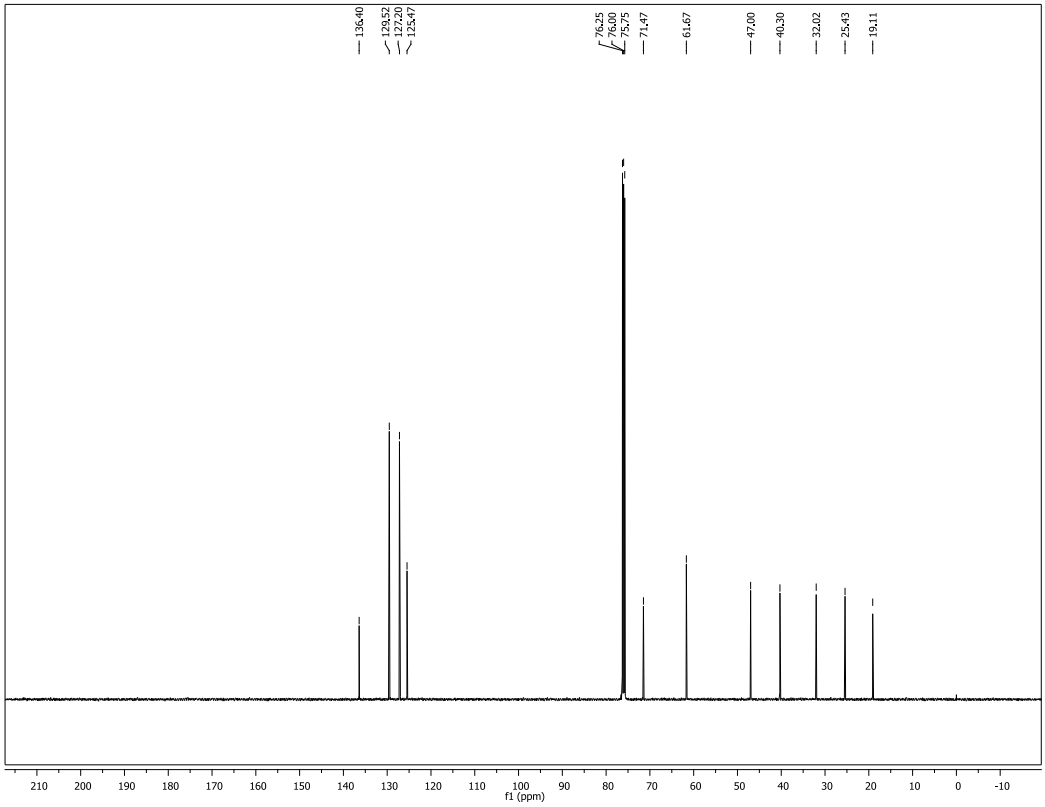
f1 (ppm)

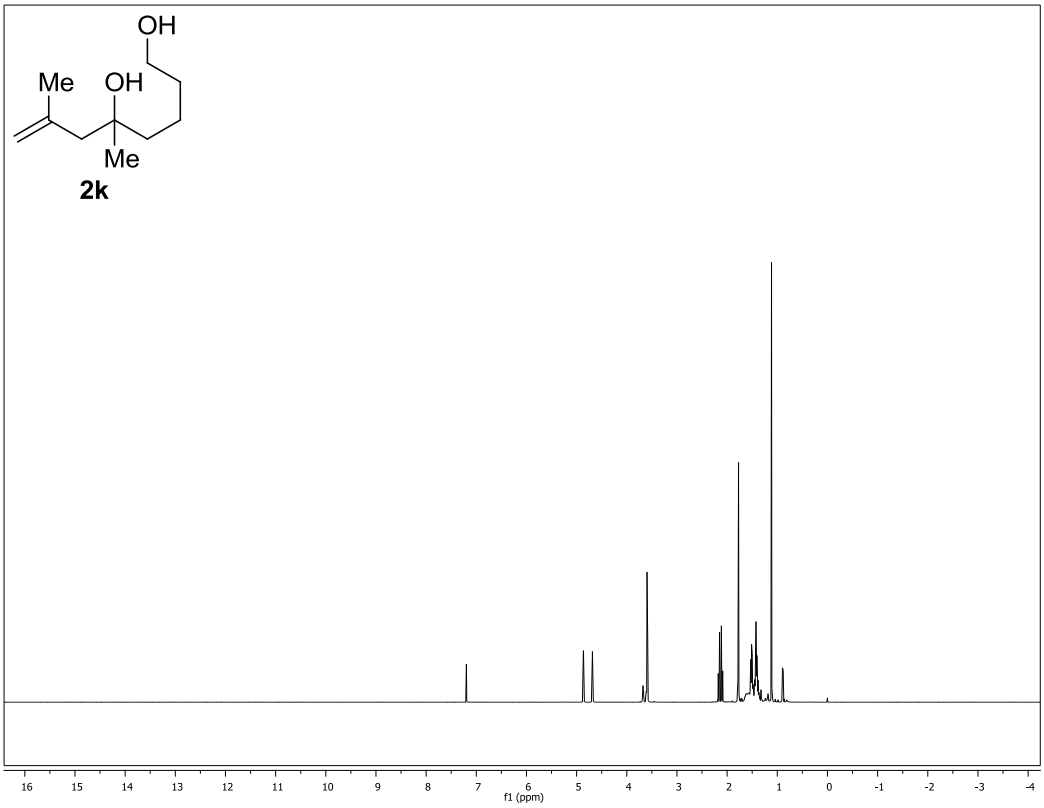

77.28
77.02
76.77
74.71
69.19
63.19
63.12
44.68
41.07
30.10
28.27
25.59
24.92
20.55
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

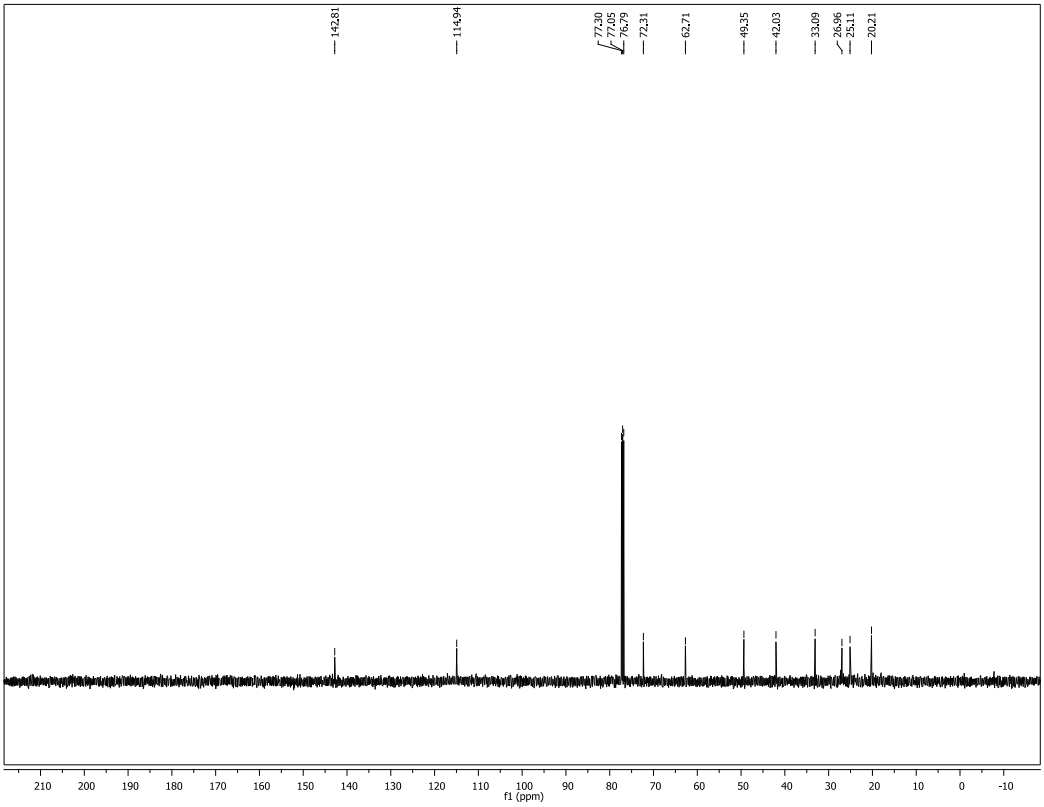

OH
OH
2i
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

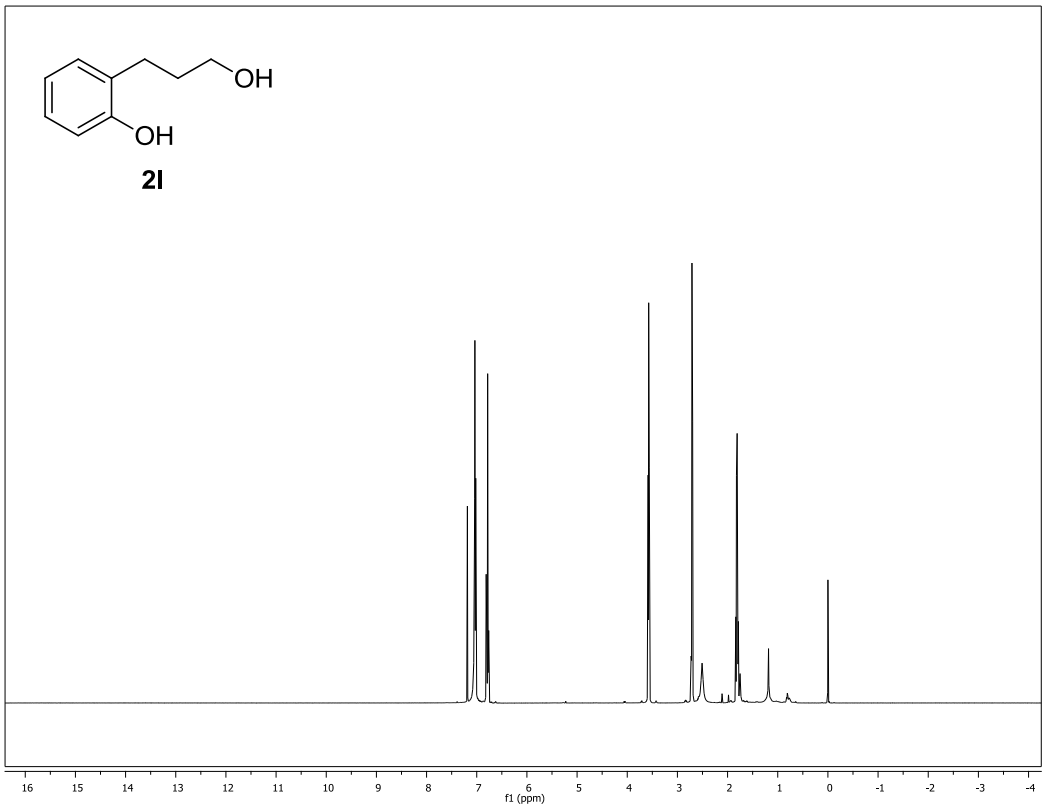

77.30
77.25
77.04
76.79
71.49
62.74
37.42
33.16
25.83
22.26
19.05
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


OH
OH
Ph
Me
2j
f1 (ppm)

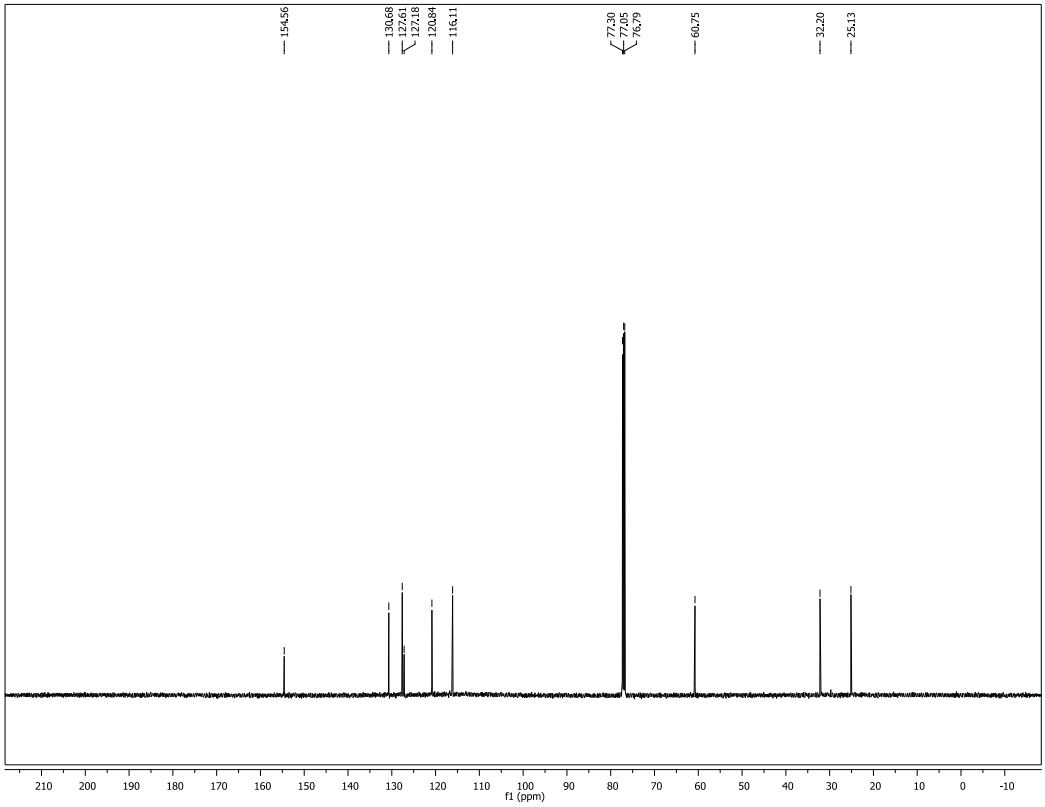

136.40
129.52
127.20
125.47
76.25
76.00
75.75
71.47
61.67
47.00
40.30
32.02
25.43
19.11
f1 (ppm)

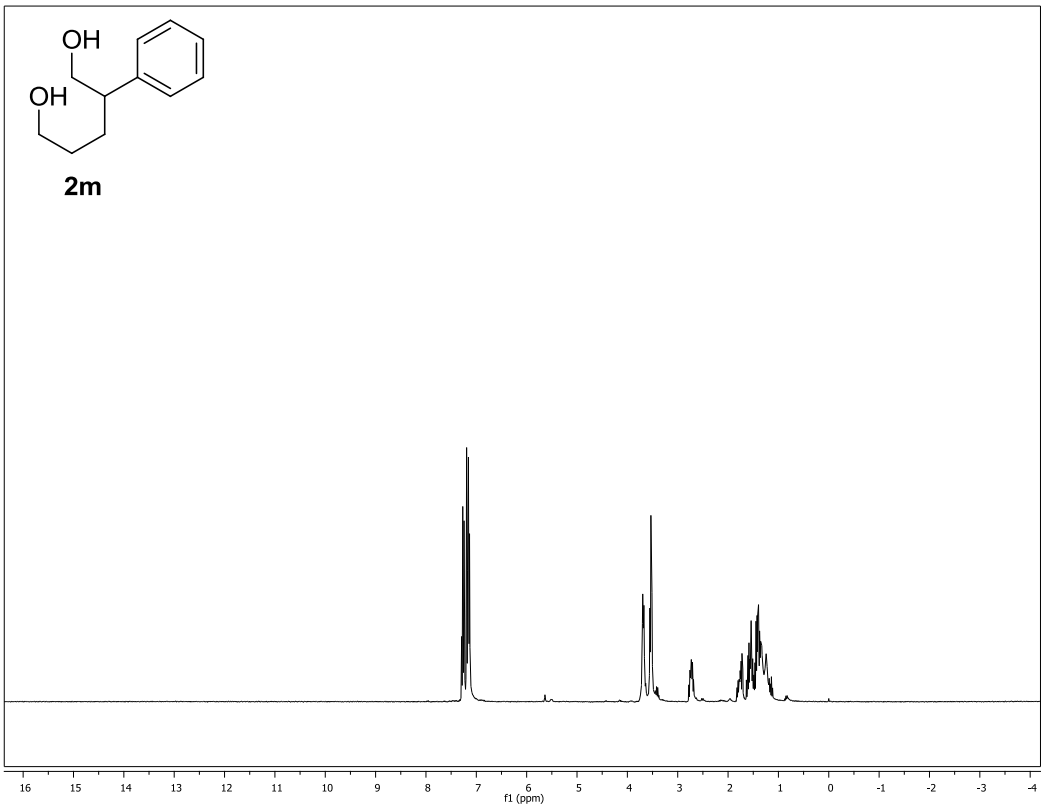


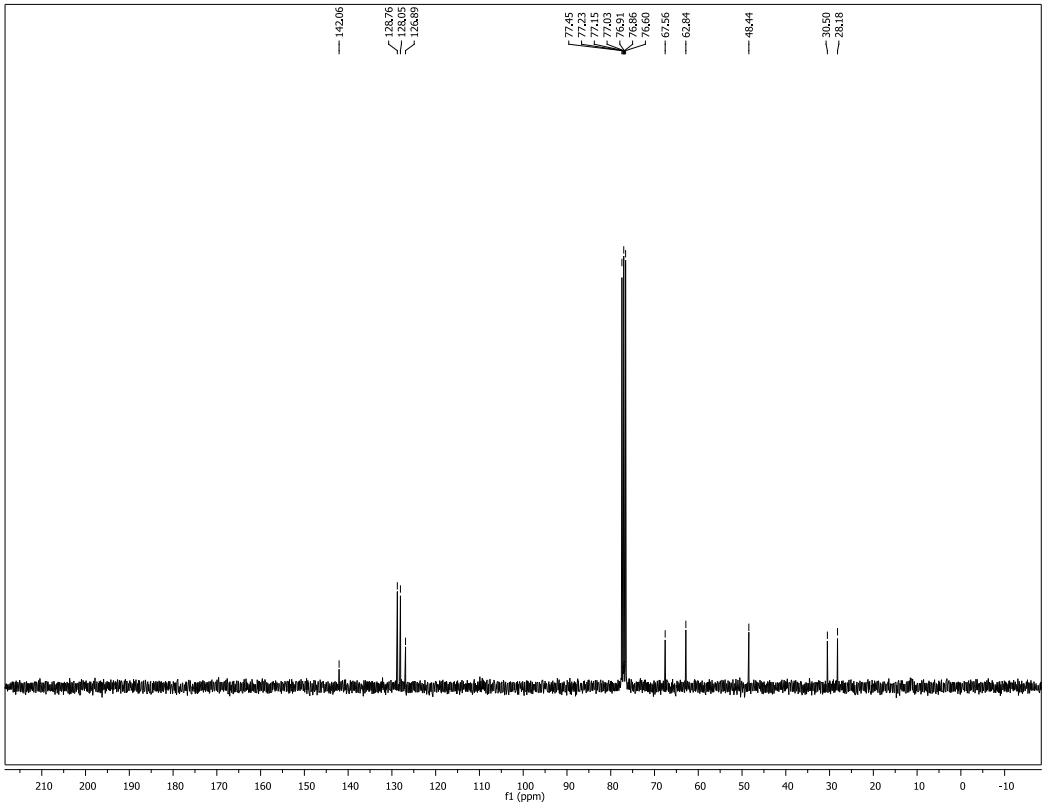


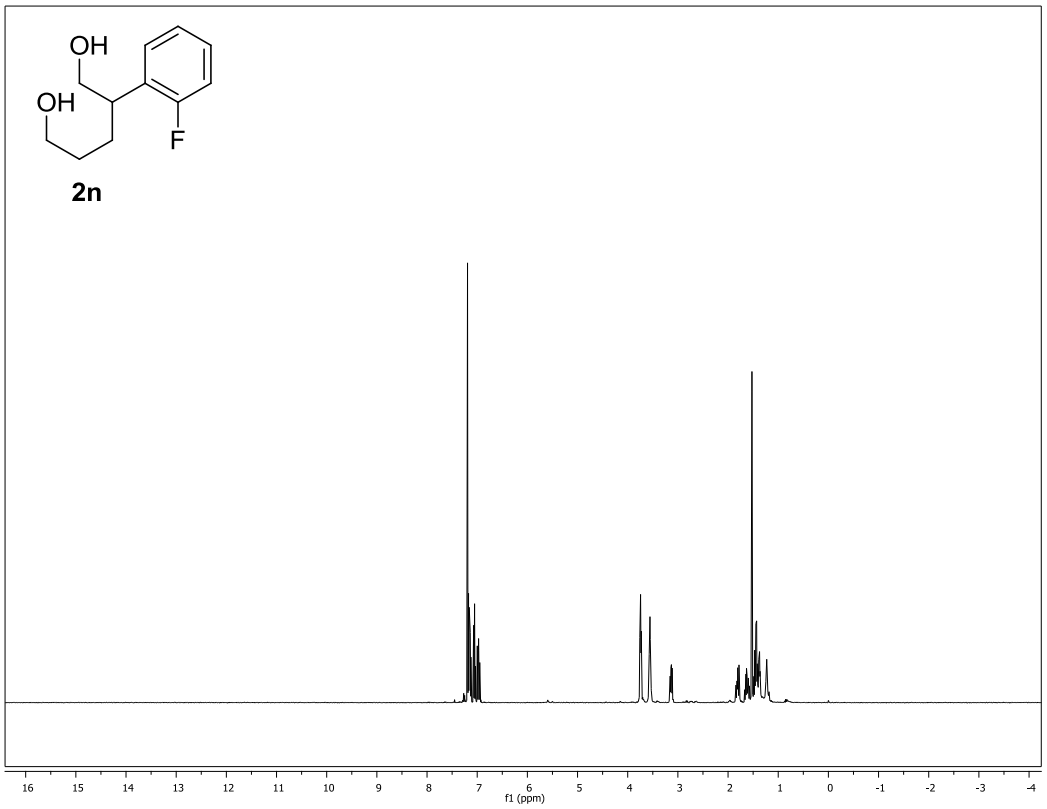

OH
OH
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

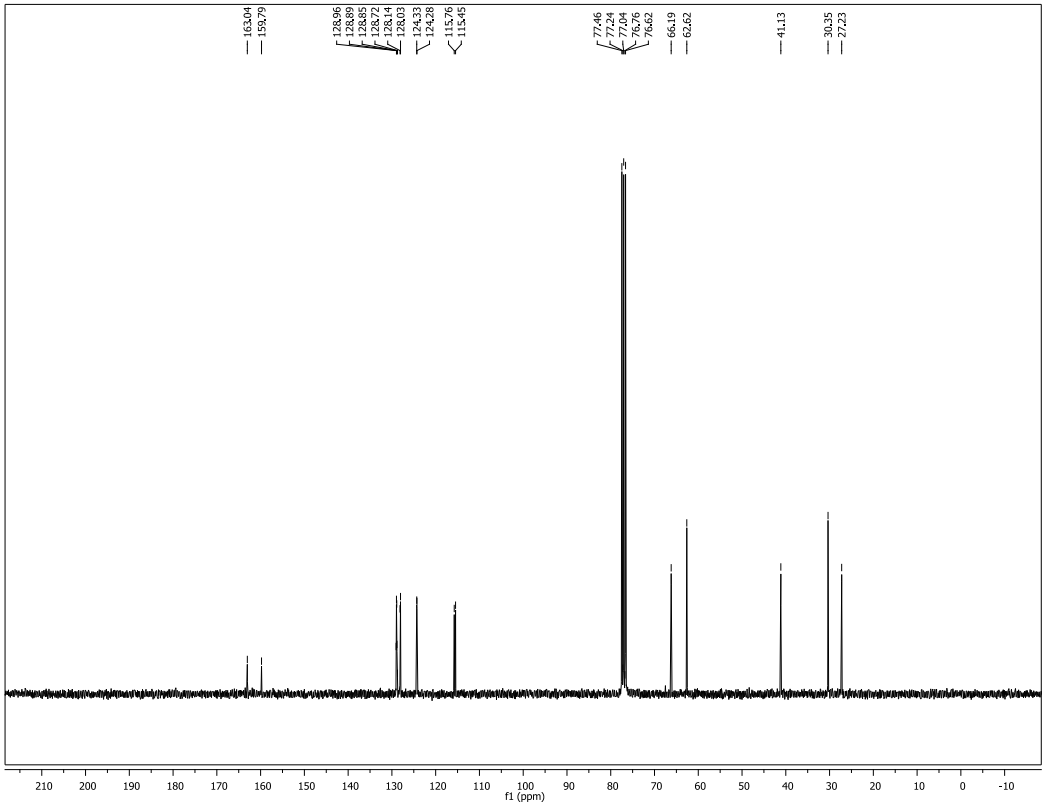
2l

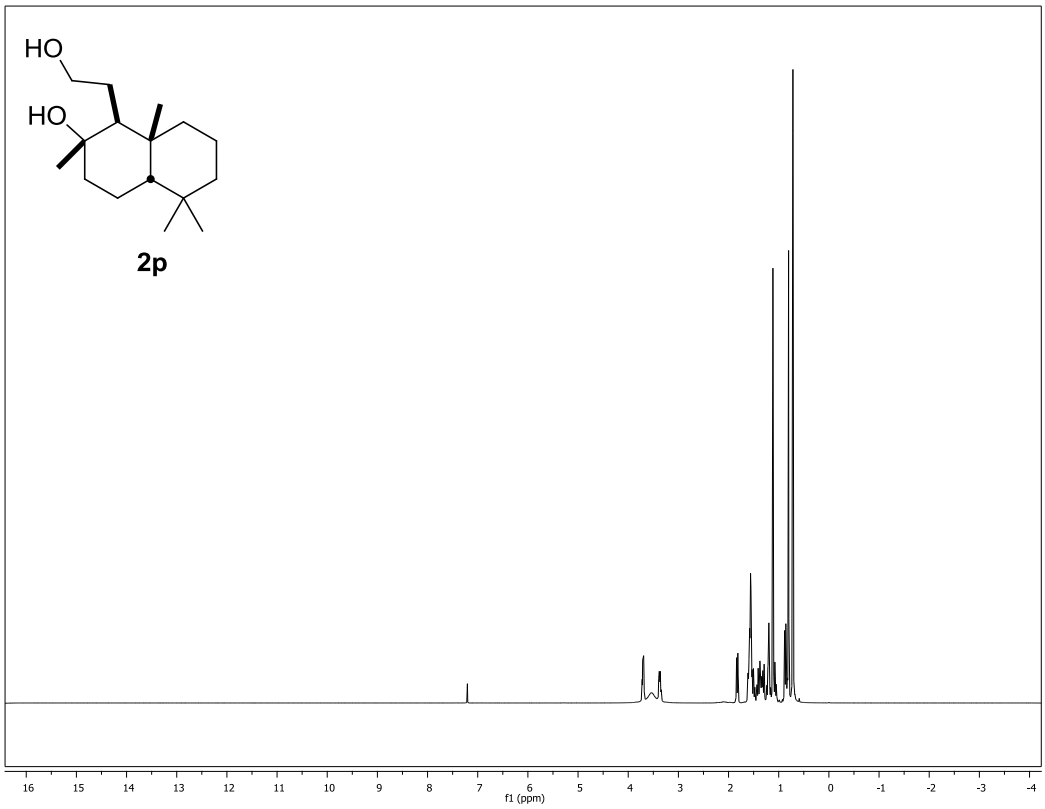

154.56
130.68
127.61
127.18
120.84
116.11
77.30
77.05
76.79
60.75
32.20
25.13
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

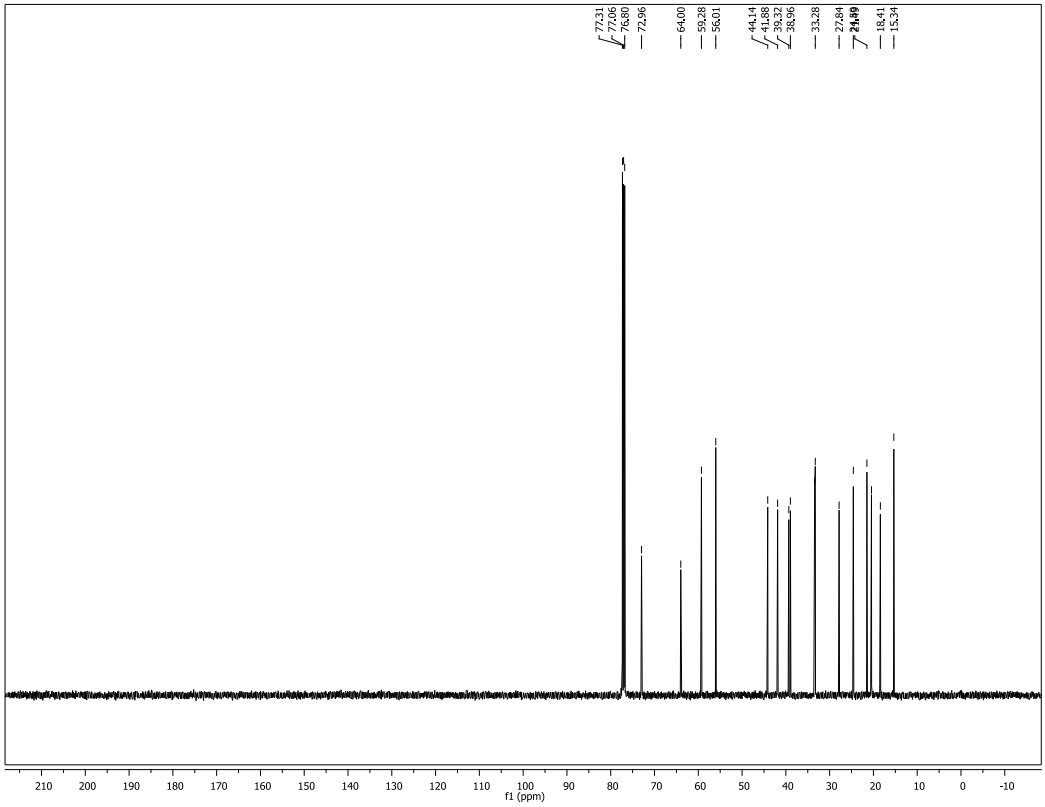

OH
OH
2m
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

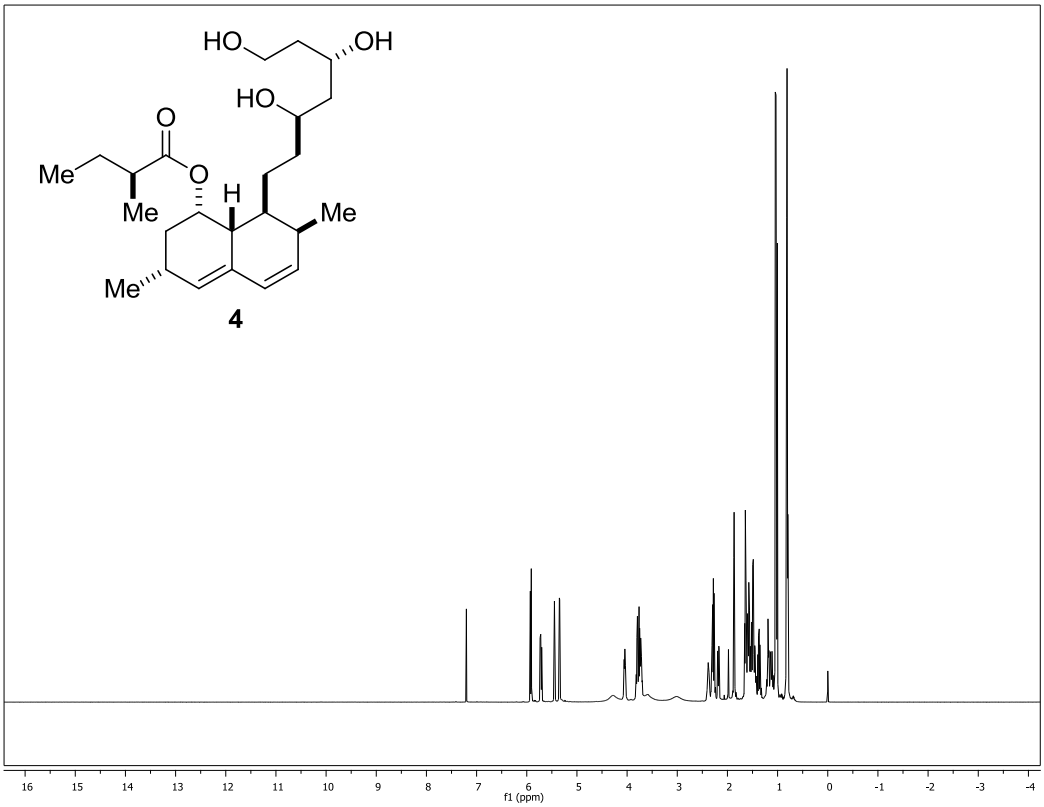

142.06
128.76
128.05
126.89
77.45
77.23
77.15
77.03
76.91
76.86
76.60
67.56
62.84
48.44
30.50
28.18
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

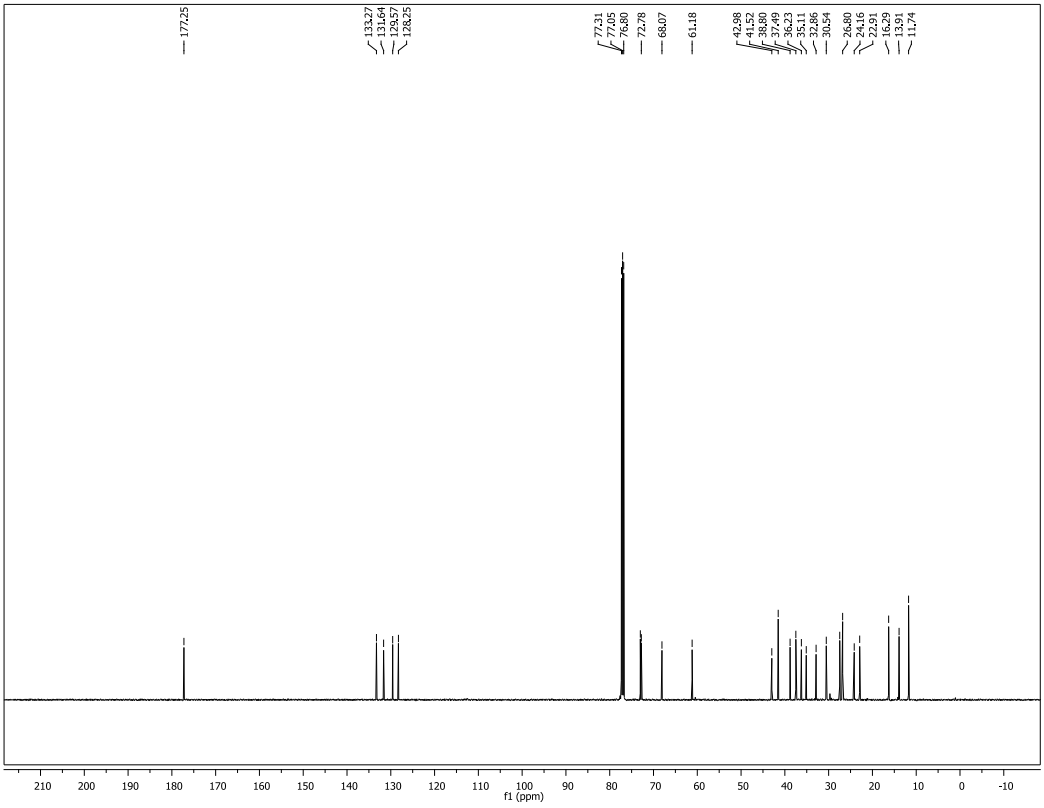

OH
OH
F
2n
f1 (ppm)

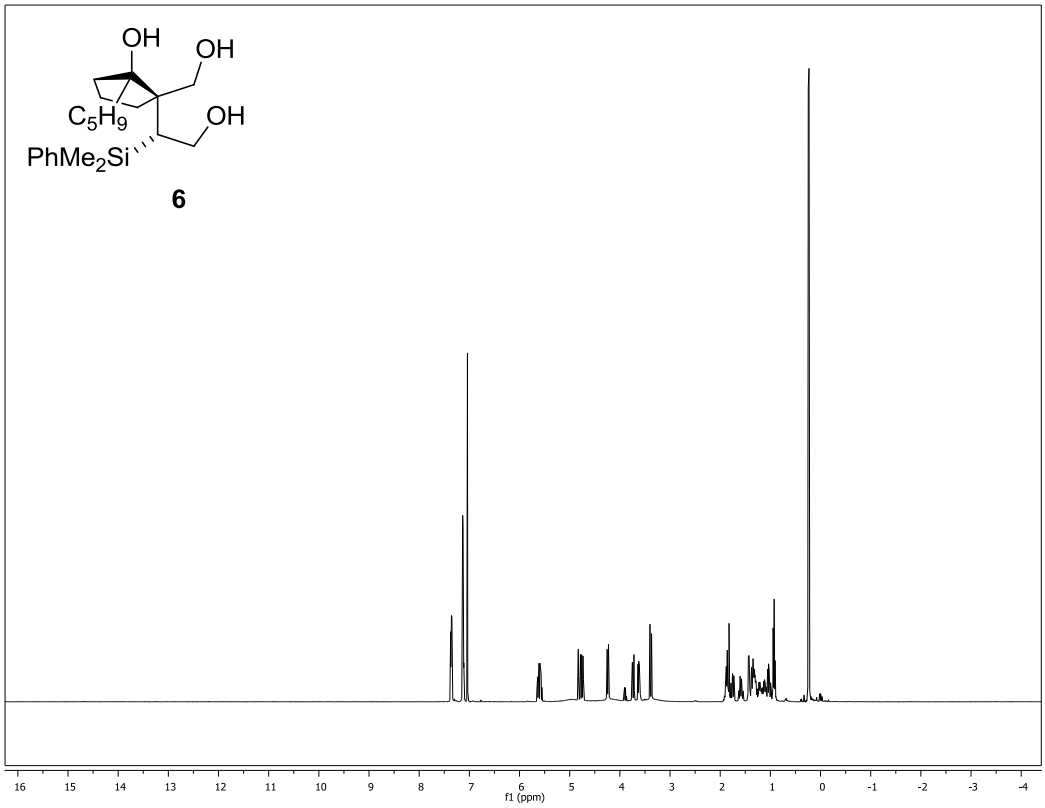

163.04
159.79
128.96
128.89
128.85
128.72
128.14
128.03
124.33
124.28
115.76
115.45
77.46
77.24
77.04
76.76
76.62
66.19
62.62
41.13
30.35
27.23
f1 (ppm)

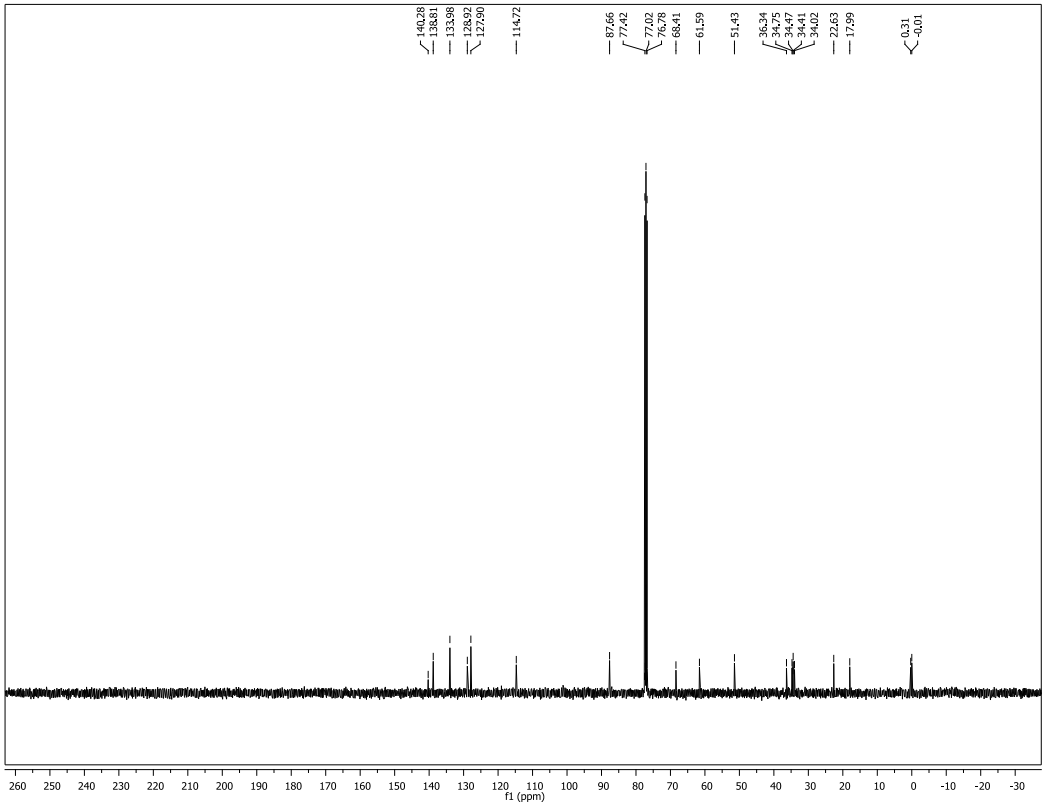

HO
HO
2p
f1 (ppm)

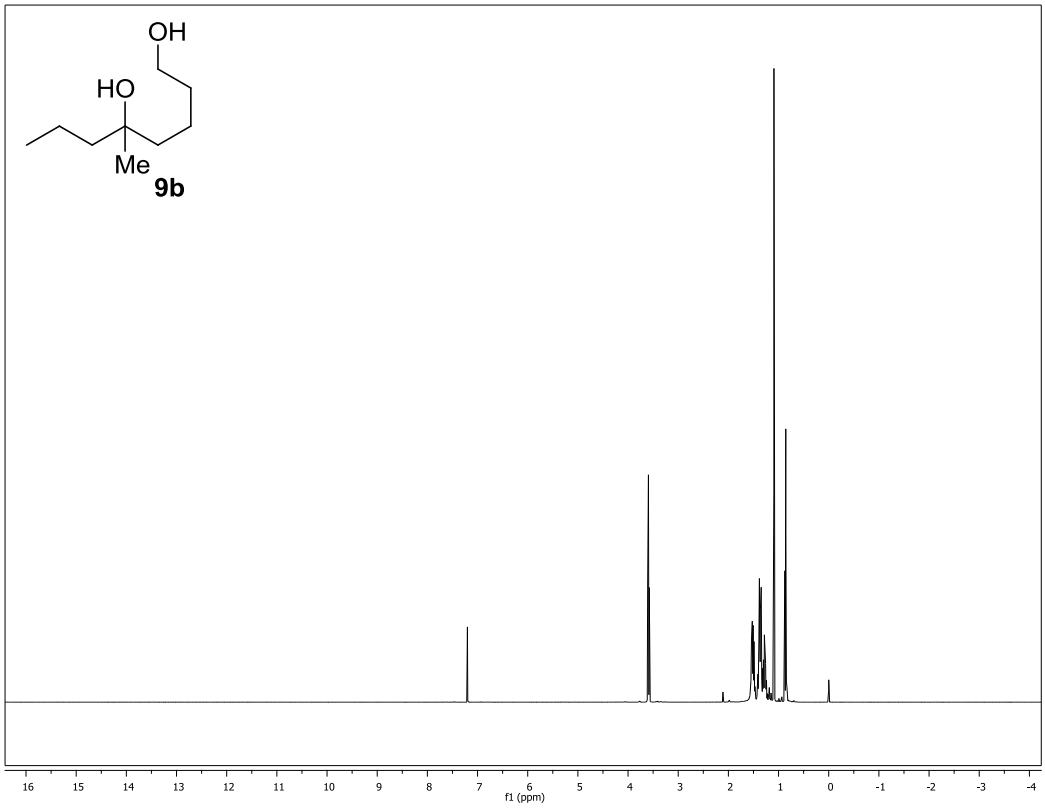

77.31
77.06
76.80
72.96
64.00
59.28
56.01
44.14
41.88
39.32
38.96
33.28
27.84
21.49
18.41
15.34
f1 (ppm)

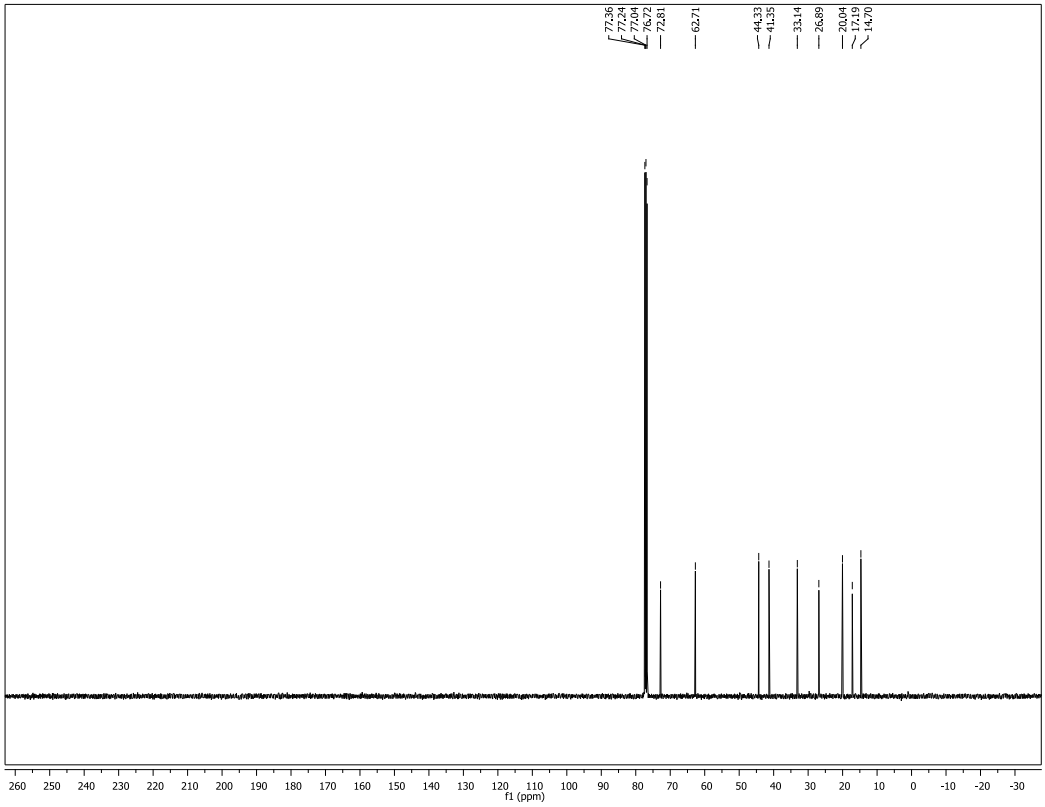

HO
OH
HO
O
Me
O
H
Me
Me
Me
4
f1 (ppm)

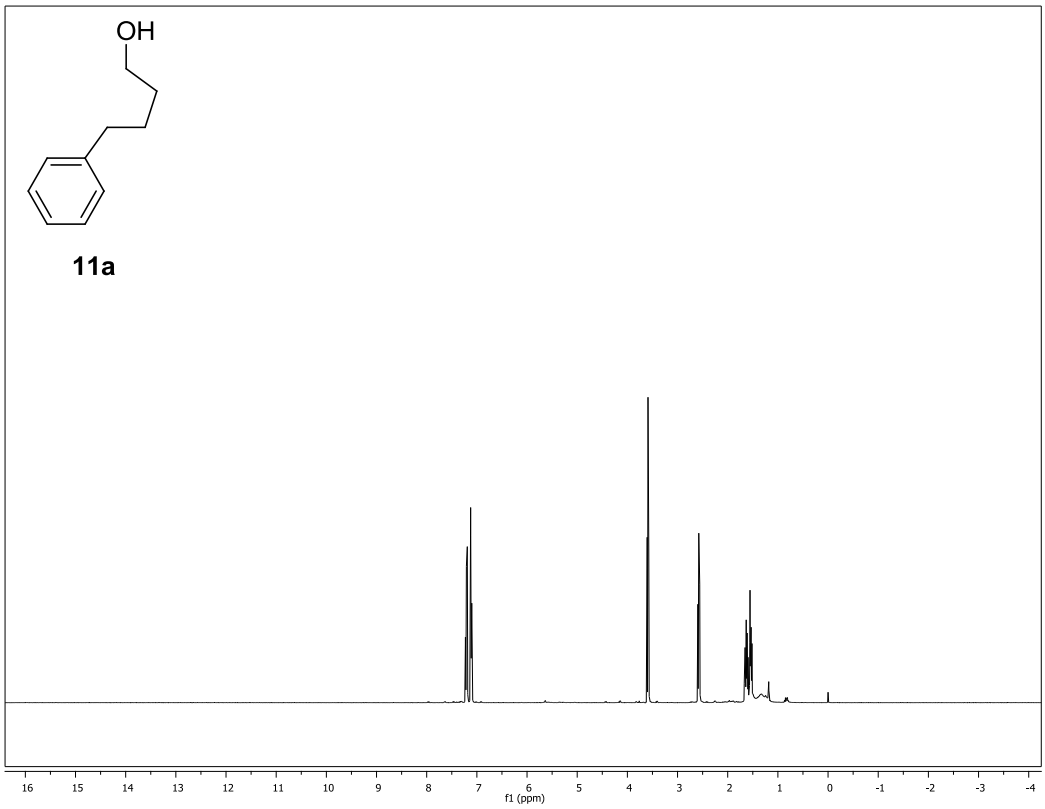

177.25
133.27
131.64
129.57
128.25
77.31
77.05
76.80
72.78
68.07
61.18
42.98
41.52
38.80
37.49
36.23
35.11
32.86
30.54
26.80
24.16
22.91
16.29
13.91
11.74
f1 (ppm)

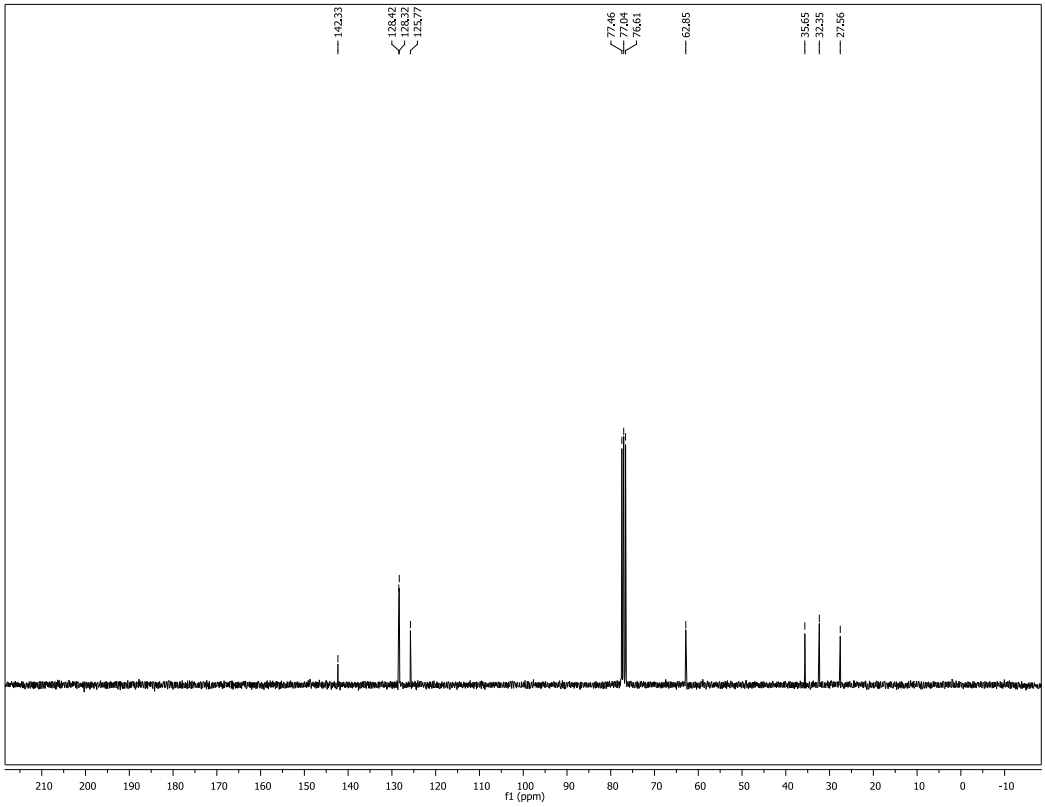

OH
OH
OH
C5H9
PhMe2Si
6
f1 (ppm)

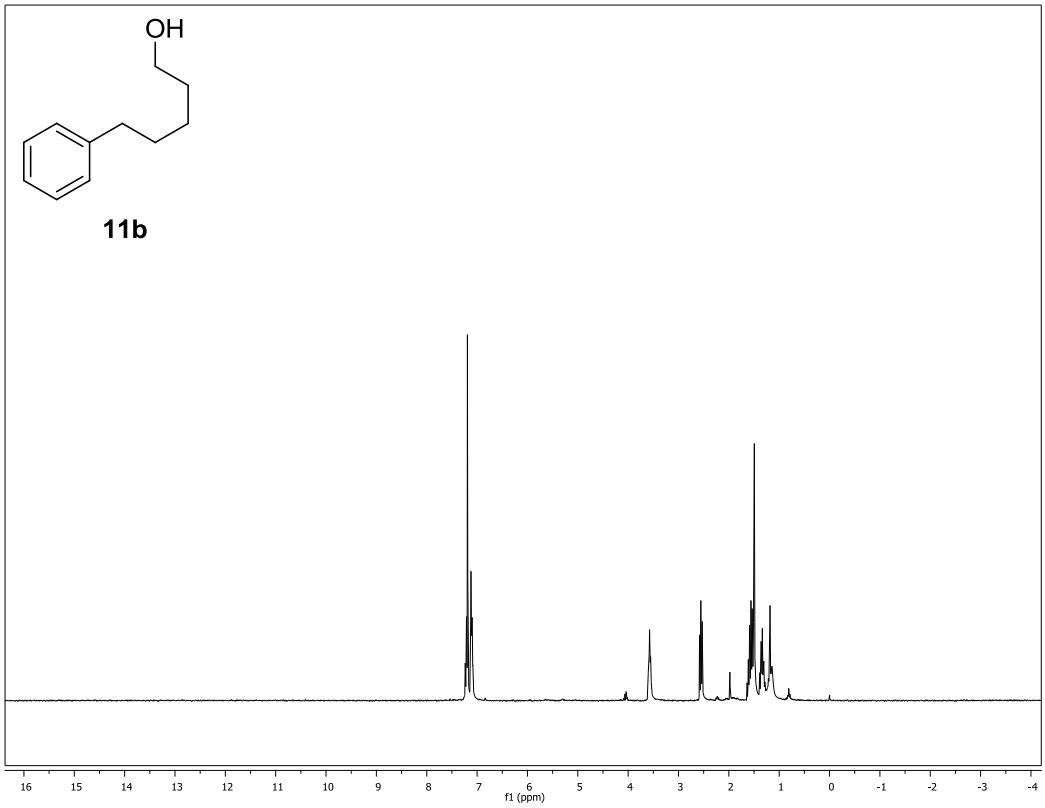

140.28
138.61
133.98
128.92
127.90
114.72
87.66
77.42
77.02
76.78
68.41
61.59
51.43
36.34
34.75
34.47
34.41
34.02
22.63
17.99
0.31
-0.01
f1 (ppm)

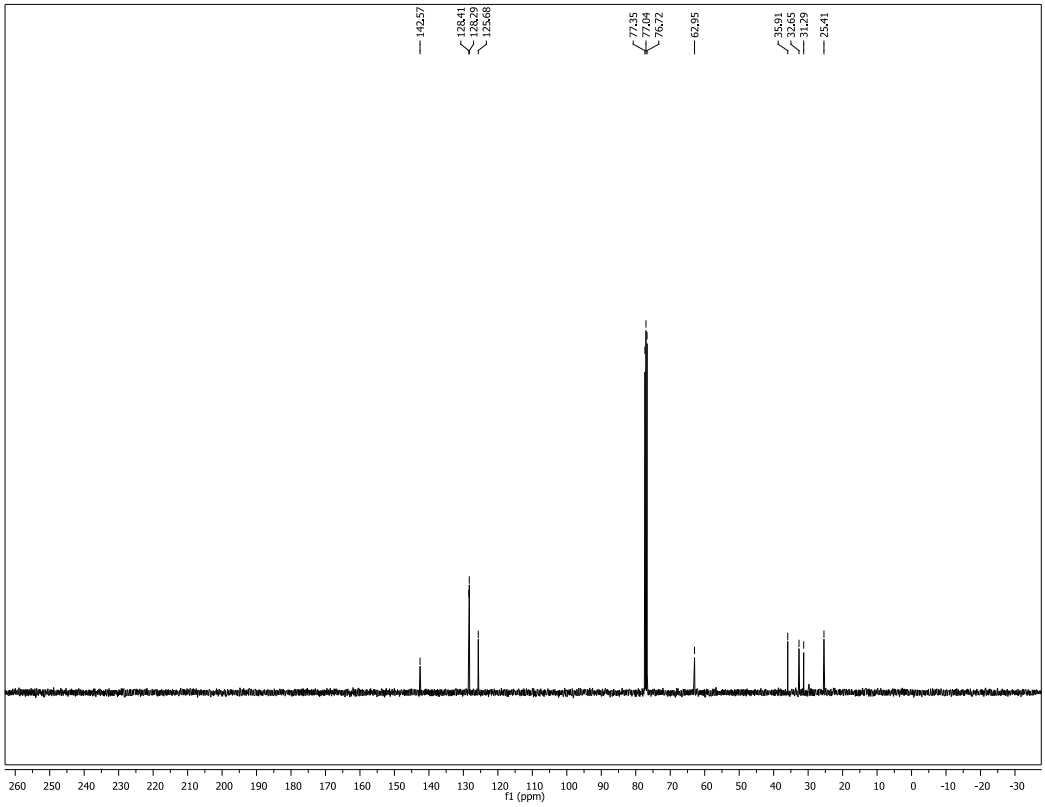

OH
HO
Me
9b
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

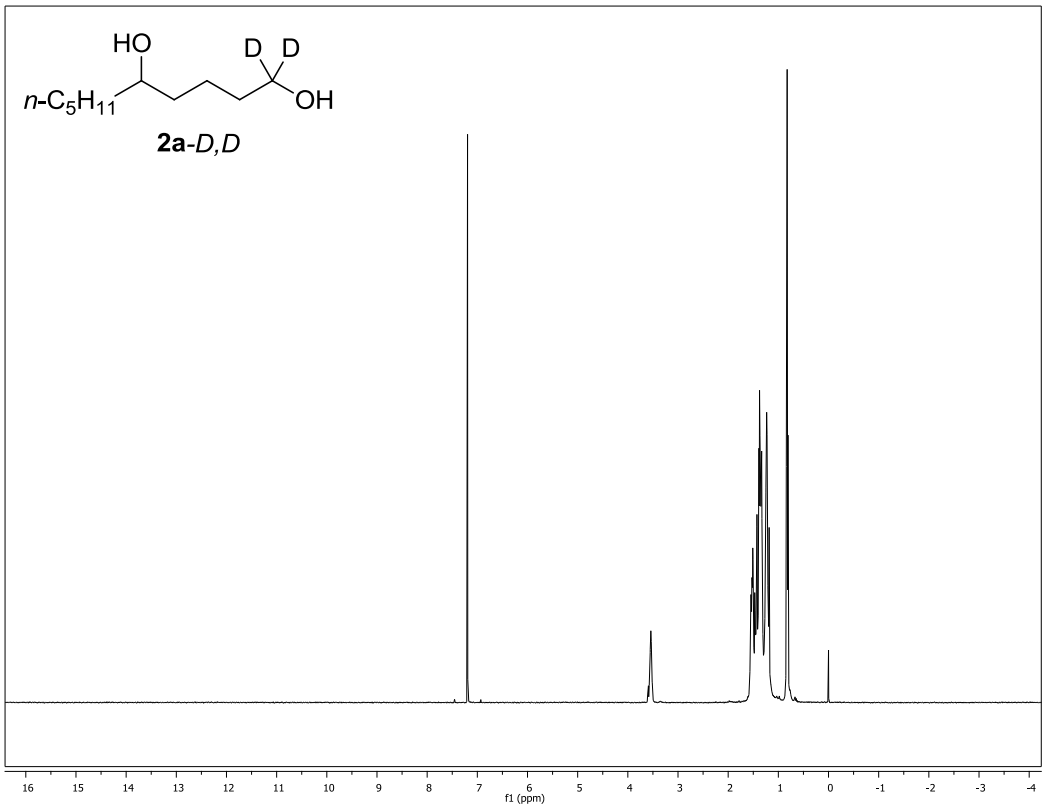

77.36
77.24
77.04
76.72
72.81
62.71
44.33
41.35
33.14
26.89
20.04
17.19
14.70
260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)

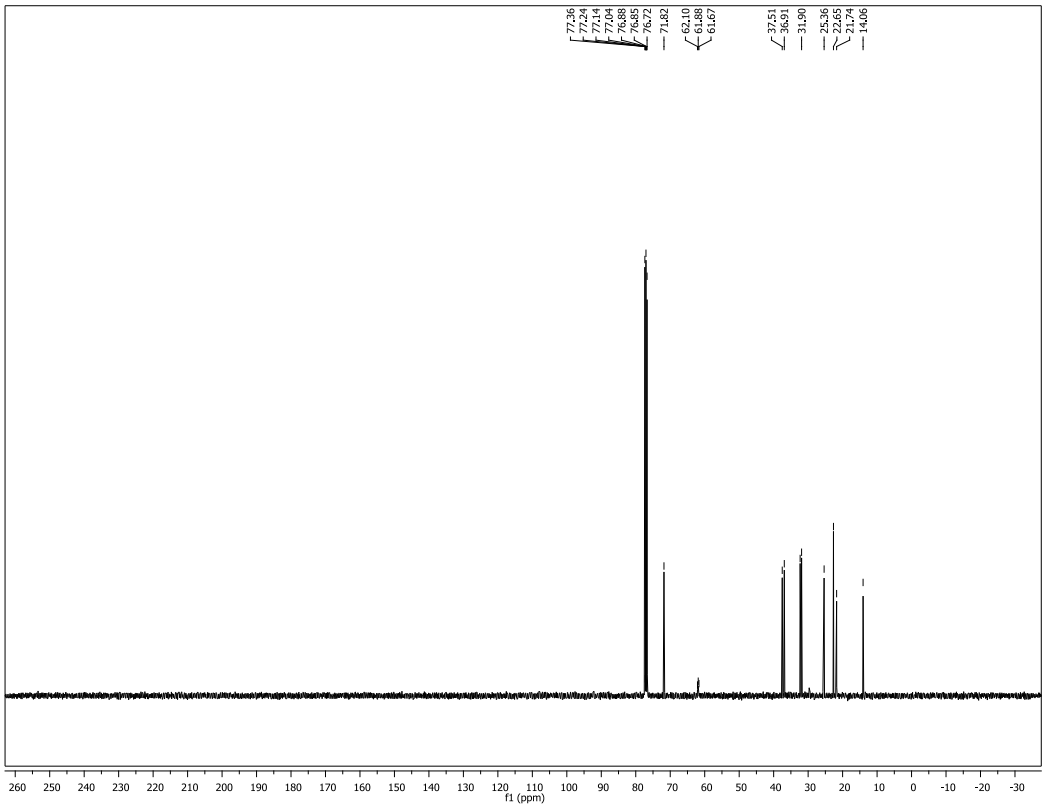

OH
11a
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


142.33
128.42
128.32
125.77
77.46
77.04
76.61
62.85
35.65
32.35
27.56
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
11b
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


142.57
128.41
128.29
125.68
77.35
77.04
76.72
62.95
35.91
32.65
31.29
25.41
260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)


HO
D D
n-C5H11
OH
2a-D,D
f1 (ppm)


77.36
77.24
77.14
77.04
76.88
76.85
76.72
71.82
62.10
61.88
61.67
37.51
36.91
31.90
25.36
22.65
21.74
14.06
f1 (ppm)