Supporting information

# Chemo- and Regioselective Functionalization of Polyols through Catalytic C($sp^3$)–C($sp^3$) Kumada-type Coupling of Cyclic Sulfate Esters

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# General considerations

N-methylmorpholine-N-oxide, $OsO_4$ solution in *tert*-butanol, Grignard reagents, $CD_3COOD$, 9-BBN solution, $Li_2CuCl_4$ solution in THF, $NaIO_4$, and organic starting materials were purchased from Sigma Aldrich. Ruthenium(III) chloride hydrate was purchased from Strem. Cyclic sulfates were prepared using slightly modified literature procedures as explained below.[1]

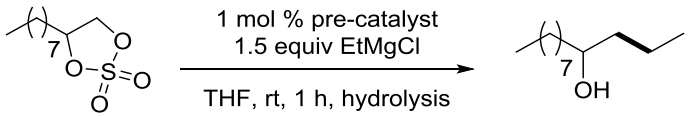
Column chromatography procedures were performed using Silica gel 60 (particle size 40–63 µM, Merck) at elevated pressure, the fractions were analyzed by thin layer chromatography (Macherey-Nagel, TLC plates SIL G-25 $UV_{254}$) and spots observed either under UV light ($\lambda$ = 254 nm), or by staining with solutions of potassium permanganate or ceric ammonium molybdate.

HPLC analyses were provided by the HPLC Department of the Max-Planck Institut für Kohlenforschung. GC chromatographic analyses were performed on an Agilent Technologies 6890N GC system, equipped with an Optima 5 column (30 m × 0.25 mm, film thickness 0.25 µm). Specific rotation was measured on an Autopol IV polarimeter from Rudolph Research Analytical. Infrared spectra were collected on a Perkin Elmer FT-IR Spectrum Two system. Yields of 4-decane and 1-decene were determined by comparison to a tridecane internal standard. Yields of decenes and dodecenes were determined by assuming identical response factors for 1-decene and 1-dodecene with respect to tridecane.

Solution NMR spectra were collected on Bruker Ascend 500 ($^1$H NMR, 500.81 MHz; $^{13}$C NMR, 125.94 MHz), Bruker Avance I 400 ($^1$H NMR, 400.13 MHz; $^{13}$C NMR, 100.63 MHz), and Bruker NanoBay 300 ($^1$H NMR, 300.13 MHz; $^{13}$C NMR, 75.48 MHz) spectrometers, using deuterated solvents as indicated. $^1$H and $^{13}$C NMR spectra were referenced to residual solvent peaks. THF-$d_8$ was dried over CaH.

High-resolution mass spectrometric measurements were provided by the Mass Spectrometry Department of the Max-Planck Insitut für Kohlenforschung. Results were reported in *m/z* units, with detection of either the molecular cation $[M+Na]^+$, or anion $[M]^-$.

# Optimization of reaction conditions




Inside of a dry box a set of dram vials equipped with a PTFE-coated stir bar were charged with decanediol 1,2-cyclic sulfate (0.3 mmol, 1.0 mL of a 302.9 mM stock solution in dry THF), followed by tridecane internal standard (0.3 mmol, 1.0 mL of a 302.4 mM stock solution). The vials were removed from the dry box and 1.5 equivalents of ethylmagnesium chloride (225 μL, 2.0 M solution), were added all-at-once at RT via syringe. Once the addition was completed, the reactions were stirred at RT for additional 60 min and then quenched and hydrolysed with 2 mL of 20% $H_2SO_4$ overnight. The products were extracted with 5 mL of MTBE, the extracts were washed once with a 5 mL portion of $Na_2CO_3$ and dried over $MgSO_4$, transferred to suitable vials and analyzed by gas chromatography. Results are summarized in Table S1.

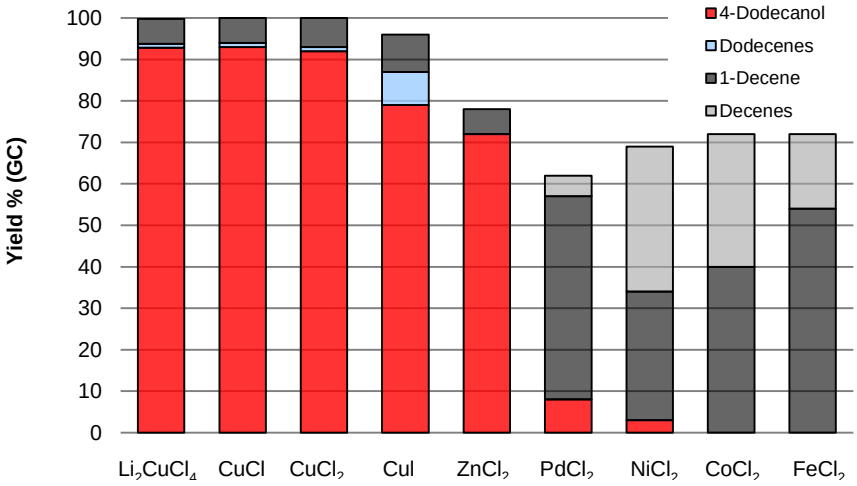
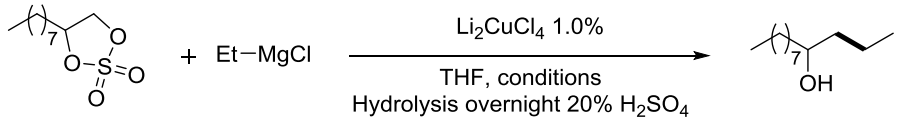



**Table S1**. Evaluation of metal pre-catalysts.




Inside of a dry box a set of dram vials equipped with a PTFE-coated stir bar were charged with decanediol 1,2-cyclic sulfate (0.142 mmol, 1.0 mL of a 1.42 mM stock solution in dry THF), followed by tridecane internal standard, $Li_2CuCl_4$ (1.4 μmol, 14 μL of a commercial 0.1 M solution) and 1.0, 1.5 or 2.0 equivalents of ethylmagnesium chloride (107 μL, 2.0 M solution), at either RT, 0°C or –30°C, added either dropwise or all-at-once, according to the table below. For reactions in which Grignard addition was done all-at-once, the reactions were removed from their respective cooling baths right after the addition was completed and were subsequently stirred for 1 h, and quenched with 2 mL of 20% $H_2SO_4$. For reactions where addition was done dropwise, the addition was completed over the span of 30 min with a syringe pump. Once the addition was completed, the reactions were removed from their respective cooling bath and were stirred at RT for additional 30 min and quenched with 2 mL of 20% $H_2SO_4$. The products were extracted with 2 mL of MTBE, the extracts dried over $MgSO_4$, transferred to suitable vials and analyzed by gas chromatography. Results are summarized in Table S2.

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|
| 1.5 eq. All-at-once RT | 1.5 eq. Dropwise RT | 1.5 eq All-at-once 0°C | 1.5 eq. Dropwise 0°C | 1.5 eq. All-at-once –30°C | 1.5 eq. Dropwise –30°C | 1.0 eq. All-at-once RT | 2.0 eq. All-at-once RT |

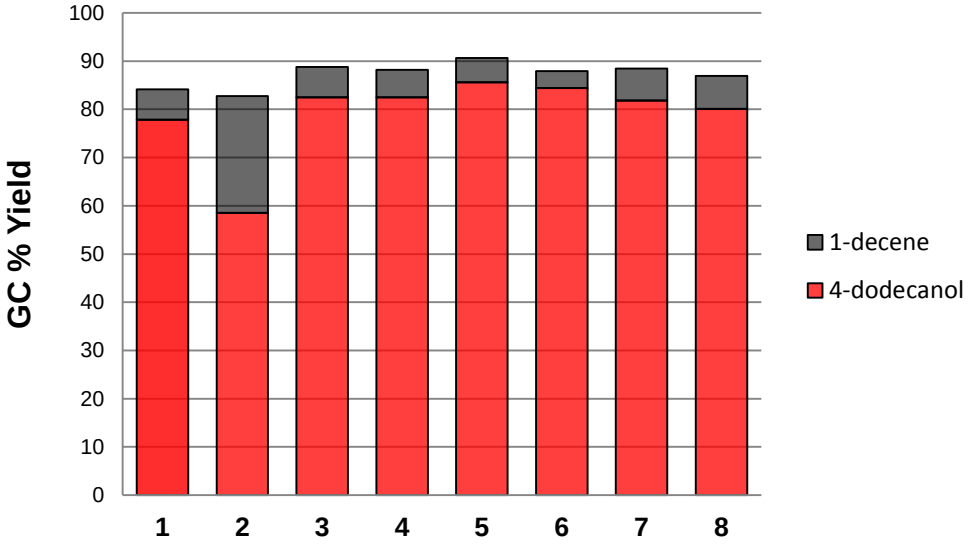
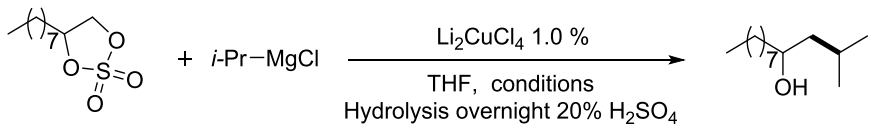



**Table S2.** Optimization of reaction temperature and addition rate of primary alkyl Grignard, using decanediol 1,2-cyclic sulfate as the coupling partner.




Inside of a dry box a set of dram vials equipped with a PTFE-coated stir bar were charged with 1.0 mL of dry THF, decanediol 1,2-cyclic sulfate (0.3 mmol, 1.0 mL of a 3.0 mM stock solution in dry THF), followed by tridecane internal standard, $Li_2CuCl_4$ (3.0 μmol, 30 μL of a commercial 0.1 M solution), $CuCl_2$ (9.0 μmol, 1.2 mg), CuCN (9.0 μmol, 0.8 mg), the corresponding additive phenylpropyne (0.03 mmol, 4.0 μL) or benzonitrile (0.3 mmol, 30 μL) were added and 1.0, or 1.5 equivalents of a commercial 2.0 M solution *i*-propylmagnesium chloride, at either RT or 0°C, added either dropwise or all-at-once, according to the table below. For reactions in which Grignard addition was done all-at-once, the reactions were removed from their respective cooling baths right after the addition was completed and were subsequently stirred for 1 h, and quenched with 2 mL of 20% $H_2SO_4$. For reactions where addition was done dropwise, the addition was completed over the span of 30 min with a syringe pump. Once the addition was completed, the reactions were removed from their respective cooling bath and were stirred at RT for additional 30 min and quenched with 2 mL of 20% $H_2SO_4$. The products were extracted with 2 mL of MTBE, the extracts dried over $MgSO_4$, transferred to suitable vials and analyzed by gas chromatography. Results are summarized in Table S3

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|
| 1.5 eq.<br>Dropwise<br>RT<br>$Li_2CuCl_4$ 1% | 1.1 eq.<br>All-at-once<br>0°C<br>$Li_2CuCl_4$ 1% | 1.1 eq<br>All-at-once<br>RT<br>$Li_2CuCl_4$ 1% | 1.5 eq<br>All-at-once<br>RT<br>$CuCl_2$ 3%<br>Phenylpropyne 10 % | 1.5 eq<br>All-at-once<br>RT<br>CuCN 3% | 1.5 eq<br>All-at-once<br>RT<br>$CuCl_2$ 3%<br>1 eq benzonitrile | 1.5 eq.<br>All-at-once<br>0°C<br>$Li_2CuCl_4$ 1% | 1.5 eq.<br>All-at-once<br>RT<br>$Li_2CuCl_4$ 1% |

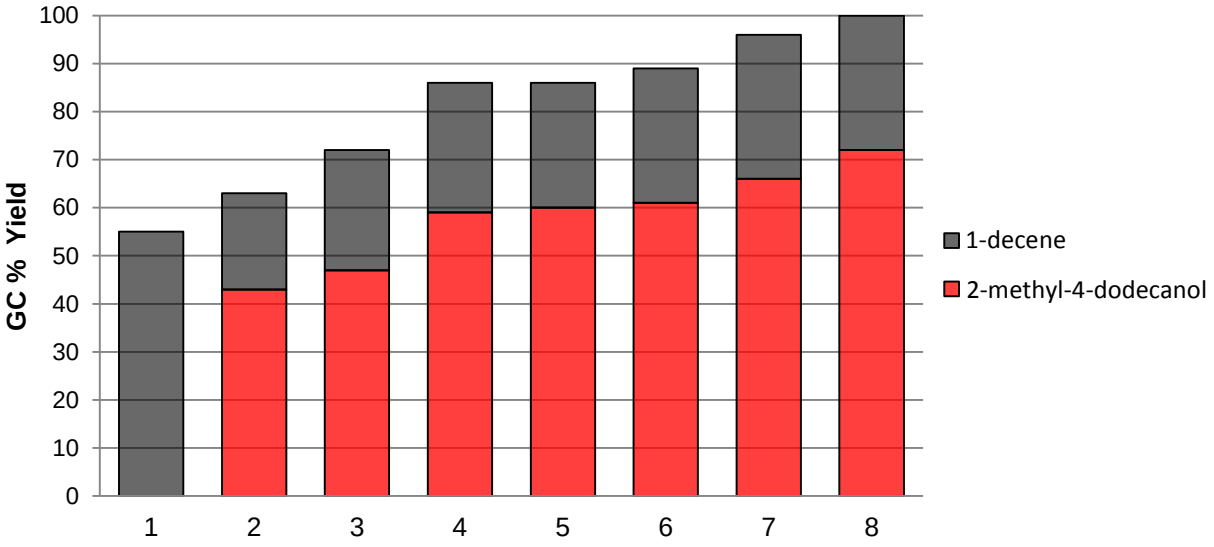



**Table S3.** Optimization of reaction temperature, addition rate of secondary alkyl Grignard, and copper catalyst system using decanediol 1,2-cyclic sulfate as the coupling partner.

# Substrate syntheses

## Procedure 1. Olefin dihydroxylation.

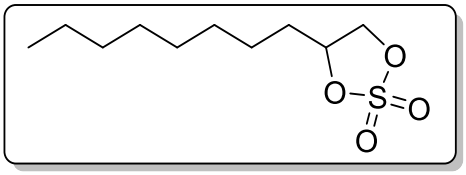
The requisite olefin was suspended in a mixture of *tert*-butanol/acetone/water 1:3:7, and placed in an ice cooling bath. 1.1 equivalents of N-methylmorpholine N-oxide and 1% mol of $OsO_4$, commercially available as a 4% solution in water, were then added. The mixture was allowed to warm up to room temperature slowly by allowing the ice to melt over the course of a night. The next morning the mixture was extracted with 3 portion of MTBE, the organic extracts were washed once with saturated $Na_2S_2O_3$, once with brine, and collected and washed over $MgSO_4$. The organic solution was concentrated *in vacuo* and the products were purified by column chromatography using a solution of 10% methanol in DCM as the eluent.

## Procedure 2. Synthesis of cyclic sulfates from diols.

**Step 1.** A two-neck round bottom flask equipped with a PTFE-coated stir bar was evacuated and refilled with argon three times. After the final argon refilling, the respective diol (1 equivalent), and dry $CH_2Cl_2$ were charged via cannula (enough to obtain a ≈ 0.5 M solution), followed by $NEt_3$ (3 equivalents). The resulting mixture was cooled used an ice bath. $SOCl_2$ (1.2 equivalents) was added dropwise over 10 min via syringe while the solution was kept under constant stirring. Once the addition was completed, the reaction mixture was stirred for additional 10 minutes, after which the ice bath was removed and stirring was continued for an additional hour. The reaction mixture was quenched by adding 10 mL of a saturated aqueous solution of $NH_4Cl$. The mixture was extracted with 3 portions of MTBE, the organic extracts were collected and washed with 20 mL of brine, and dried over $MgSO_4$. The brown organic solution was filtered through a short path of Celite and the solvents evaporated to obtain a dark brown oil that was used in the following step without any further purification.

**Step 2.** 50 mL of a solution of acetonitrile and water (1:1.2) was charged in the flask containing the brown oil obtained in Step 1, followed by addition of $NaIO_4$ (1.5 equivalents), and this mixture was cooled with an ice bath. $RuCl_3 \bullet (H_2O)_3$ (1.0% mol ) was added in a single portion, the resulting mixture was removed from the cooling bath and stirred for 1 h. 20 mL of MTBE were added to the mixture, the mixture was filtered through a short path of Celite to remove all the solids formed during the reaction, and the filtrate was extracted with 3 portions of MTBE. The organic extracts were washed with one portion of brine, and dried over $MgSO_4$. Volatiles were removed *in vacuo* and the crude product was purified by column chromatography using the conditions noted in each particular entry.

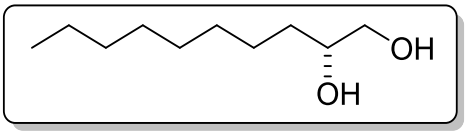
**1,2-Decanediol cyclic sulfate**



Prepared from 1,2-decanediol using procedure 1, and purified by column chromatography using a mixture of MTBE/Pentane 2:5. Clear oil, 3.8 g, 56%.

**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S1) δ 0.86 (t, $J_{H-H}$ = 6.9 Hz, 3H), 1.25 – 1.49 (m, 12H), 1.71 – 1.77 (m, 1H), 1.87 – 1.94 (m, 1H), 4.33 (t, $^3J_{H-H}$ = 8.4 Hz, 1H), 4.71 (dd, $J_{H-H}$ = 8.8, 5.9 Hz, 1H), 4.94 – 5.00 (m, 1H). **$^{13}$C{$^1$H} NMR** (125.93 MHz, $CDCl_3$) (Figure NMR-S2) δ 14.1 (s), 22.6 (s), 24.6 (s), 29.0 (s), 29.1 (s), 29.2 (s), 31.8 (s), 32.2 (s), 73.1 (s), 83.4 (s). **HRMS (EI+)** calculated for $C_{10}H_{20}O_4S_1$ [$M^+$] 259.0974, found: 259.0974.

**(R)-1,2-Decanediol**

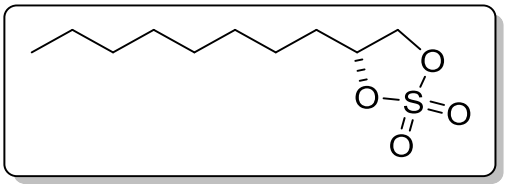


Prepared by hydrolytic kinetic resolution[2] of 2-octyloxirane[3] and purified by crystallization from MTBE. White crystalline solid. 1.09 g, 65% (overall 33% yield of a maximum expected yield of 50%).

Specific rotation $[\alpha]_D^{25}$ –0.31 degcm$^3$g$^{-1}$dm$^{-1}$ (*c* 0.65 gcm$^{-3}$, $CH_2Cl_2$).[2] Enantiomeric excess: 99.7%

**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S3) δ 0.88 (t, $J_{H-H}$ = 6.9 Hz, 3H), 1.28-1.44 (m,14H), 2.29 (bs, 1H), 2.36 (b, 1H), 3.44 (t, $J_{H-H}$ = 9 Hz, 1H), 3.66 (b, 1H), 4.97 (m, 1H). **$^{13}$C{$^1$H} NMR** (125.93 MHz, $CDCl_3$) (Figure NMR-S4) δ 14.3 (s), 22.8 (s), 25.7 (s), 29.4 (s), 29.7 (s), 29.8 (s), 32.0 (s), 33.4 (s), 66.9 (s), 72.4 (s).The enantiopurity of the benzoate derivative was determined by chiral HPLC. (Formed by reaction of 1,2-decanediol with 1 equiv. of benzoyl chloride in the presence of 3 equiv. of triethylamine and 20% mol of DMAP). HPLC analysis (Chiralpak AD-3, n-heptane/isopropanol = 99.0/1.0, 1.0 mL/min) $t_R$ = 7.56 min, $t_R$ = 8.51 min.

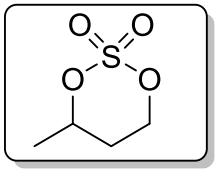
**(R) 1,2-Decanediol cyclic sulfate**



Purified by column chromatography using a mixture of MTBE/Pentane 2:5. Clear oil, 392 mg, 65%.

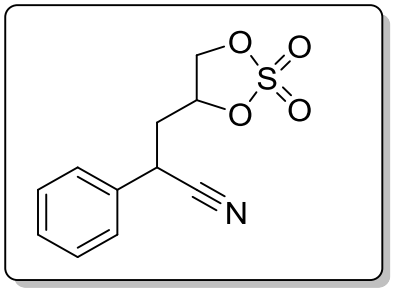
**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S5) δ 0.88 (t, $^3J_{H-H}$ = 6.9 Hz, 3H), 1.27-1.49 (m, 12H), 1.76 (m, 1H), 1.92 (m, 1H), 4.34 (t, $J_{H-H}$ = 8.4 Hz, 1H), 4.71 (dd, $J_{H-H}$ = 8.8, 5.9 Hz, 1H), 4.98 (m, 1H).

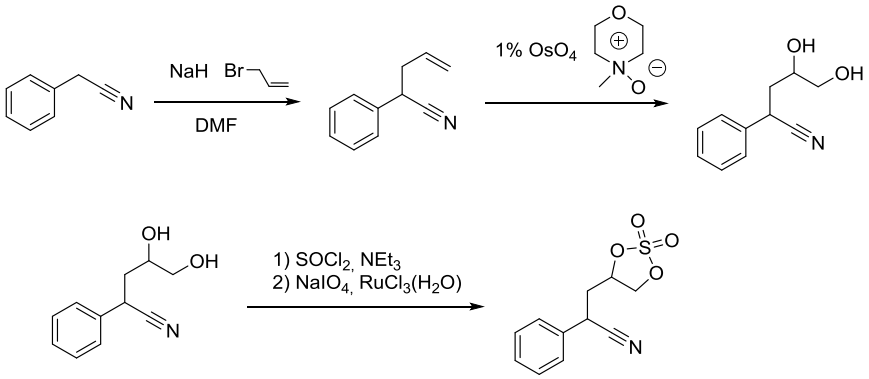
**1,3-Butanediol cyclic sulfate**



Prepared from 1,3-butanediol following procedure 2.
Purified by distillation under reduced pressure. Light yellow solid 4.727 g, 62%.
**$^{1}$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S6) $\delta$ 1.43 (d, $^{3}J_{H\text{-}H}$ = 6.0 Hz, 3H, –$CH_3$), 1.89 (m, 1H), 2.08 (m, 1H), 4.55 (dd, $J_{H\text{-}H}$ = 10.9, 4.2 Hz, 1H), 4.73, (t, $J_{H\text{-}H}$ = 11.9 Hz, 1H), 5.00 (m, 1H). **$^{13}$C{$^{1}$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S7) $\delta$ 20.6 (s), 30.7 (s), 72.3 (s), 83.1 (s).

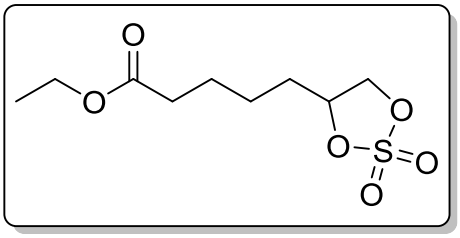
**3-(2,2-Dioxido-1,3,2-dioxathiolan-4-yl)-2-phenylpropanenitrile**





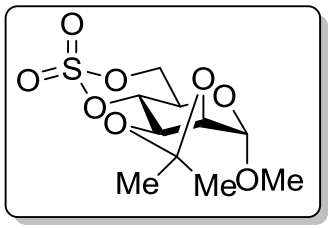

Purified by column chromatography initially with neat $CH_2Cl_2$, followed by a second purification step using a mixture of MTBE/Pentane 1:1. White solid 0.120 g, 30%.
**$^{1}$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S8) $\delta$ 2.30 (ddd, $J_{H\text{-}H}$ = 14.5, 11.3, 3.0 Hz, 1H), 2.51 (ddd, $J_{H\text{-}H}$ = 14.7, 10.4, 4.3 Hz, 1H), 4.12 (dd, $J_{H\text{-}H}$ = 11.3, 4.2 Hz, 1H), 4.36 (dd, $J_{H\text{-}H}$ = 9.0, 6.6 Hz, 1H), 4.83 (dd, $J_{H\text{-}H}$ = 9.0, 6.3 Hz, 1H), 5.30 (dtd, $J_{H\text{-}H}$ 10.5, 6.4, 3.0 Hz, 1H), 7.37 – 7.46 (m, 5H) **$^{13}$C{$^{1}$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S9) $\delta$ 34.0 (s), 39.2 (s), 72.0 (s), 79.5 (s), 119.0 (s), 127.1 (s), 129.1 (s), 129.7 (s), 133.7 (s). **HR-MS (ESI+)** calc. for $C_{11}H_{11}O_4N_1S_1Na_1$ $[M+Na]^+$ 276.0301, found: 276.0300.

**Ethyl 5-(2,2-dioxido-1,3,2-dioxathiolan-4-yl)pentanoate**



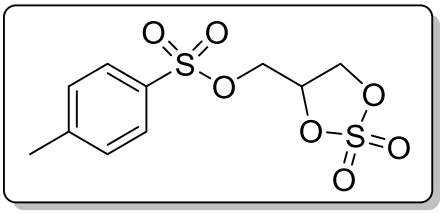
Prepared from 6-ethyl heptenoate following procedures 1 and 2.
Purified by column chromatography using an eluent mixture of 3:1 $CH_2Cl_2$/pentane. Clear oil 1.99 g, 83%.
**$^1$H NMR** (500.81 MHz, $CDCl_3$) (fFigure NMR-S10) $\delta$ 1.19 (t, $J_{H-H}$ = 7.2 Hz, 3H), 1.39 – 1.53 (m, 2H), 1.62 (m, 2H), 1.73 (m, 1H), 1.88 (m, 1H), 2.26 (t, $J_{H-H}$ = 7.3 Hz, 2H), 4.05 (q, $J_{H-H}$ = 7.1 Hz, 2H), 4.30 (dd, $J_{H-H}$ = 8.7, 8.1 Hz, 1H), 4.69 (dd, $J_{H-H}$ = 8.7, 6.0 Hz, 1H), 4.94 (tdd, $J_{H-H}$ = 8.2, 6.0, 4.6 Hz, 1H). **$^{13}$C{$^1$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S11) $\delta$ 14.1 (s), 24.0 (s), 24.1 (s), 31.8 (s), 33.6 (s), 60.3 (s), 72.9 (s), 83.0 (s), 173.1 (s). **HR-MS (ESI+)** calc. for $C_9H_{16}O_6S_1Na_1$ $[M+Na]^+$ 275.0560, found: 275.0558.

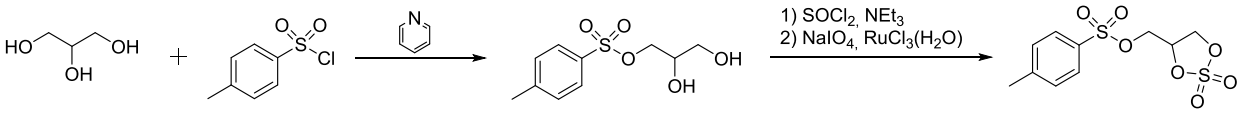
## Methyl-2,3-*O*-isopropylidene-$\alpha$-d-mannopyranoside-1,3-cyclic sulfate



Under an argon atmosphere, methyl-2,3-*O*-isopropylidene-$\alpha$-d-mannopyranoside[4] (257 mg, 1.01 mmol), $NEt_3$ (0.5 mL, 3.29 mmol) and 40 mL of dry $CH_2Cl_2$ were charged in a Schlenk flask. The flask was placed in an ice bath and $SOCl_2$ (0.1 mL,1.37 mmol) was added dropwise. Once addition of $SOCl_2$ was completed, the mixture was stirred for 30 min with the flask still in the ice bath. After 30 minutes the flask was removed from the bath and the mixture was stirred for 2 h at room temperature, at which point the reaction mixture acquired a wine-red color. Volatiles were removed *in vacuo*, the residue was dissolved in $CH_2Cl_2$ and the organic phase was washed with *ca.* 20 mL of a saturated aqueous solution of $NH_4Cl$. The aqueous phase was extracted with two 20 mL portions of $CH_2Cl_2$. The organic phases were collected, dried over $Na_2SO_4$, filtered through Celite and the solvent was removed *in vacuo*. The residue was dissolved in 40 mL of a mixture of acetonitrile/water 1:1.2 and the resulting solution was placed in an ice bath. Once the temperature equilibrated with the ice bath, $NaIO_4$ (700 mg, 3.29 mmol) and $RuCl_3(H_2O)_3$ (2 mg, 007 mmol) were added. The reaction mixture was initially kept over the ice bath and then removed after 10 min. The mixture was stirred at RT for 1 hour. The mixture was filtered through Celite and the filtrate was extracted with 50 mL of $CH_2Cl_2$. The remaining aqueous phase was extracted with two 20 mL portions of $CH_2Cl_2$. The organic extracts were collected, dried over $Na_2SO_4$ and dried *in vacuo* to obtain a yellow solid that was purified by column chromatography using neat $CH_2Cl_2$.
White solid 267 mg, 82%.
**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S12) $\delta$ 1.38 (s, 3H). 1.58 (s, 3H), 3.43 (s, 3H), 4.04 (td, $J_{H-H}$ = 10.7, 5.4 Hz, 1H), 4.24 (d, $J_{H-H}$ = 5.5 Hz, 1H), 4.32 (dd, $J_{H-H}$ = 7.9, 5.6 Hz, 1H), 4.54 (dd, $J_{H-H}$ = 10.7, 5.5 Hz, 1H), 4.61 (dd, $J_{H-H}$ = 10.5, 7.9 Hz, 1H), 4.65 (t, $J_{H-H}$ = 10.6 Hz, 1H), 5.00 (s, 1H). **$^{13}$C{$^1$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S13) 26.2 (s), 28.0 (s), 55.9 (s), 58.6 (s), 72.1 (s), 73.3 (s), 76.0 (s), 84.3 (s), 99.1 (s), 110.8 (s). **HR-MS (ESI+)** calc. for $C_{10}H_{16}O_8S_1Na_1$ $[M+Na]^+$ 319.0458, found: 319.0460.

**Glycerol 3-tosyl-1,2-cyclic sulfate**



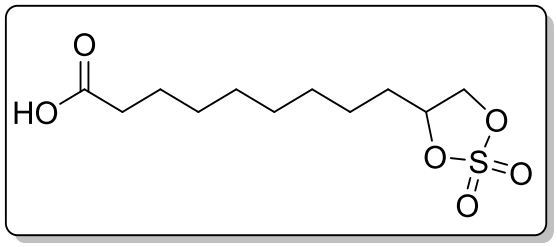



The first step in the synthesis of the target cyclic sulfate was the preparation of 2,3-dihydroxypropyl 4-methylbenzenesulfonate. This intermediate was prepared by slow addition of 4-toluenesulfonyl chloride (10.4 g, 54.3 mmol) to a solution of glycerol (5.0 g, 54.3 mmol) in pyridine (24.5 g, 309.1 mmol) kept at –78°C. Once addition was complete, the reaction mixture was allowed to warm up to room temperature and was stirred for further 48 h. The compound was purified by column chromatography using 10% methanol in DCM. The isolated compound was used to prepare the target cyclic sulfate following procedure 1.

Purified by column chromatography using neat $CH_2Cl_2$.White solid, 1.9 g, 76%.

**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S14) $\delta$ 2.48 (s, 3H), 4.27 – 4.33 (m, 2H), 4.58 (dd, $J_{H-H}$ = 9.2, 6.1 Hz, 1H), 4.78 (dd, $J_{H-H}$ = 9.2, 6.7 Hz, 1H), 5.09 – 5.14 (m, 1H), 7.36 – 7.43 (m, 2H), 7.78 – 7.85 (m, 2H). **$^{13}$C{$^1$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S15) 21.9 (s), 66.0 (s), 68.9 (s), 77.6 (s), 128.2 (s), 130.4 (s), 131.7 (s), 146.2 (s). **HR-MS (ESI+)** calc. for $C_{10}H_{12}O_7S_2Na_1$ $[M+Na]^+$ 330.9917, found 330.9913.

**Undecanoic acid 1,2-cyclic sulfate**

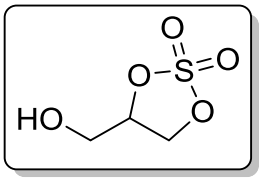


Prepared from 10-undecenoic acid following procedures 1 and 2.

Purified by column chromatography using ethyl acetate/$CH_2Cl_2$.1:4. White solid, 250 mg, 30%.

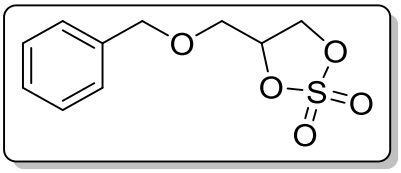
**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S16) $\delta$ 1.33 – 1.37 (m, 8H), 1.40 – 1.44 (m, 1H), 1.47 – 1.54 (m, 1H), 1.61 – 1.67 (m, 2H), 1.72 – 1.79 (m, 1H), 1.91 – 1.99 (m, 1H), 2.36 (t, $J_{H-H}$ = 7.4 Hz, 2H), 4.35 (t, $J_{H-H}$ = 8.4 Hz, 1H), 4.71 (dd, $J_{H-H}$ = 8.7, 6.0 Hz, 1H), 4.98 (ddt, $J_{H-H}$ = 8.1, 6.0, 4.9 Hz, 1H). **$^{13}$C{$^1$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S17) $\delta$ 24.7 (s), 29.0 (s), 29.0 (s), 29.1 (s), 29.1 (s), 32.4 (s), 34.1 (s), 73.0 (s), 83.0 (s), 179.8 (s).

**Glycerol 1,2-cyclic sulfate**



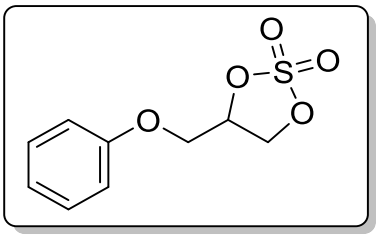
Prepared from glycerol using procedure 2.[5] Purified by column chromatography using a solution of 10% methanol in DCM. White solid, 3.03 g, 36%.
**$^{1}$H NMR** (500.81 MHz, DMSO-$d_1$) (Figure NMR-S18) δ 4.36 – 4.44 (m, 1H), 4.43 – 4.51 (m, 1H), 4.51 – 4.68 (m, 3H).
**$^{13}$C{$^{1}$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S19) δ 71.1 (s), 71.9 (s), 74.7 (s). **HR-MS (ESI+)** calc. for $C_3H_5O_5S$ $[M – H]^-$ 152.9863, found 152.9863.

**Benzylglycerol 2,3-cyclic sulfate**



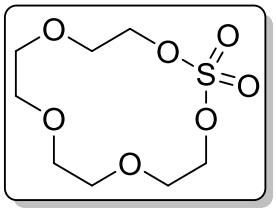
Prepared from benzyl allyl ether using procedures 1 and 2. Spectroscopic data match literature values.[6]
**$^{1}$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S20) δ 3.78 (d, *J* = 4.9 Hz, 2H), 4.55 – 4.66 (m, 3H), 4.71 (dd, *J* = 8.8, 6.5 Hz, 1H), 5.06 (tt, *J* = 6.7, 4.8 Hz, 1H), 7.32 – 7.43 (m, 5H).

**Phenylglycerol 2,3-cyclic sulfate (Scheme 1, 2a)**



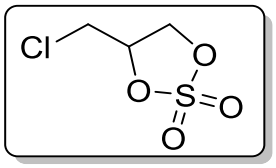
Prepared from allyl phenyl ether following procedure 1, and one-pot synthesis of the cyclic sulfate from the respective diol using literature procedures.[1] Purified by column chromatography using a mixture of pentane/MTBE 1:1. 0.63 g, 23% yield.
**$^{1}$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S21) δ 4.20 – 4.35 (m, 2H), 4.73 (dd, *J* = 9.0, 6.6 Hz, 1H), 4.83 (dd, *J* = 9.0, 6.6 Hz, 1H), 5.24 (tt, *J* = 6.6, 5.0 Hz, 1H), 6.89 – 6.98 (m, 2H), 7.05 (tt, *J* = 7.4, 1.0 Hz, 1H), 7.29 – 7.40 (m, 2H).
**$^{13}$C{$^{1}$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S22) δ 65.7 (s), 69.7 (s), 79.1 (s), 114.7 (s), 122.3 (s), 129.9 (s), 157.5 (s). **HR-MS (ESI+)** calc. for $C_9H_{10}O_5S$ $[M]^+$ 230.0243, found 230.0243.

**Tetraethylene glycol macrocyclic sulfate**



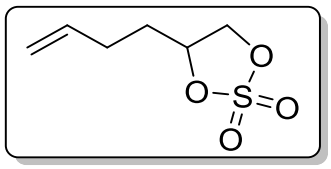
Prepared tetraethylene glycol using procedure 2. Purified by column chromatography using neat MTBE. White solid,1.64g, 25%. Spectroscopic data match literature values.[7]
**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S23) δ 3.63 – 3.68 (m, 4H), 3.68 – 3.72 (m, 4H), 3.83 – 3.87 (m, 4H), 4.41 – 4.53 (m, 4H).

**3-Chloro-1, 2-propanediol cyclic sulfate**



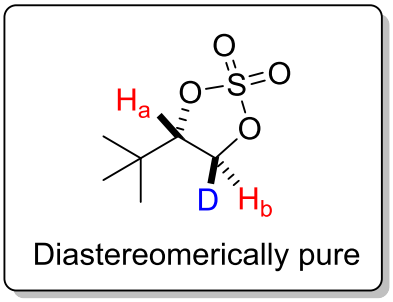
Prepared from 3-chloropropane-1,2-diol using procedure 2. Purified by column chromatography using DCM. Clear oil, 6.4 g, 41%. Spectroscopic data match literature values.[8]
**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S24) δ 3.81 (d, *J* = 5.5 Hz, 2H), 4.62 (dd, *J* = 9.2, 6.2 Hz, 1H), 4.81 (dd, *J* = 9.3, 6.5 Hz, 1H), 5.14 (tt, *J* = 6.3, 5.5 Hz, 1H).

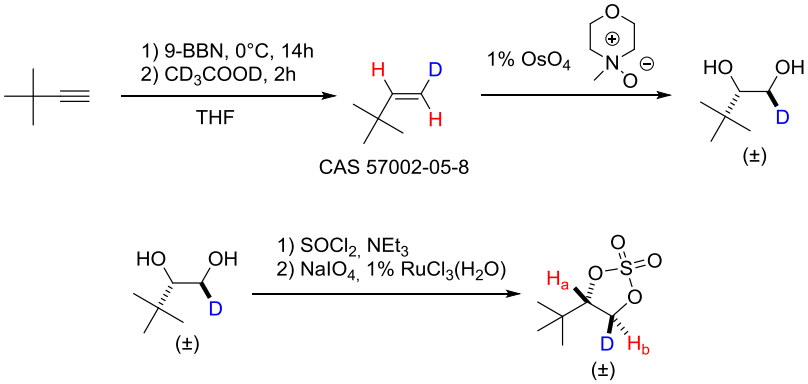
**6-Hexene 1,2-cyclic sulfate (Scheme 1, 2b)**



Prepared from 1,5-hexadiene using procedures 1 and 2. Purified by column chromatography using a MTBE/hexanes 1:6. Clear oil, 200 mg, 11%.
**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S25) δ 1.72 – 1.78 (m, 1H), 1.82 – 1.89 (m, 1H), 2.16 – 2.33 (m, 2H), 3.95 (dd, $J_{H-H}$ = 8.3, 6.9 Hz, 1H), 4.70 (dd, $J_{H-H}$ = 8.2, 6.2 Hz, 1H), 5.00 (m, 1H), 5.05 (dq, *J* = 10.1, 1.4 Hz, 1H), 5.09 (dq, $J_{H-H}$ = 17.1, 1.6 Hz, 1H), 5.80 (ddt, $J_{H-H}$ = 17.0, 10.2, 6.7 Hz, 1H). **$^{13}$C{$^1$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S26) δ 29.6 (s), 31.6 (s), 71.6 (s), 79.7 (s), 116.3 (s), 136.5 (s). **HR-MS (ESI+)** calc. for $C_6 H_{10} O_4 S_1 Na_1$ $[M+Na]^+$ 201.0192, found 201.0194.

**(±) 3,3-Dimethylbutane-1,2-diol cyclic sulfate (4)**




The requisite labeled olefin was prepared by a slightly modified literature procedure.[9] 112 mL of 0.5 M 9-BBN solution (56.0 mmol) was charged in a cooling-jacketed Schlenk flask equipped with a PTFE-coated stir bar along with 50 mL of dry THF. The flask was connected to a cooling system with the refrigerant fluid temperature set at 0 °C, and 3,3-dimethylbutyne (5.00 g, 59.65 mmol) was added dropwise, followed by stirring at that temperature for 14 h. $CD_3COOD$ (3.0 mL) was added and stirred at 0 °C for 2 h, and then at RT for 2 h. The mixture was distilled directly at atmospheric pressure, under argon, to obtain the desired product, which distilled at 42 °C. An NMR spectrum was collected to confirm formation of the desired labeled olefin. The target cyclic sulfate was prepared following procedures 1 and 2.Purified by column chromatography using a MTBE/pentane 1:5.

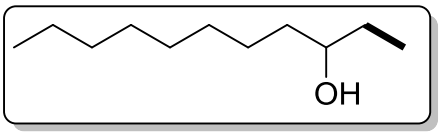
Yield of diol: 6%. The target cyclic sulfate was obtained as a iastomerically pure white solid, 453 mg. Yield of cyclic sulfate from diol: 76%.

**$^1$H NMR** (300.13 MHz, $CDCl_3$) (Figure NMR-S27) $\delta$ 1.04 (s, 9H), 4.48 (dt, $J_{a\text{-}b}$ = 8.8 Hz, $J_{H\text{-}D}$ = 1.3 Hz, 1H), 4.68 (dt, $^3J_{a\text{-}b}$ = 8.7 Hz, $J_{H\text{-}D}$ = 0.9 Hz, 1H). **$^{13}$C{$^1$H} NMR** (100.63 MHz, $CDCl_3$) (Figure NMR-S28) $\delta$ 24.6 (s), 33.4 (s), 69.2 (t, $^1J_{C\text{-}D}$ = 23.9 Hz), 89.2 (s). **HR-MS (CI)** calc. for $C_6H_{12}D_1O_4S_1$ $[M+H]^+$ 182.0597, found 182.0598.

# Catalytic reactions

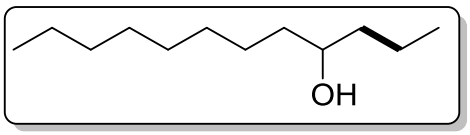
Inside of a dry box, the appropriate cyclic sulfate (1.0 mmol) and 9 mL of dry THF were charged in a 14 mL dram vial equipped with a PTFE-lined stir bar. The vial was closed with a septum screw cap and was then removed from the dry box. $Li_2CuCl_4$ (1% mol, 100 μL of a 0.1 M commercial solution in THF) was charged and the vial was placed on a stir plate. The appropriate alkylmagnesium chloride reagent (1.5 mmol) was added quickly and in a single portion to the reaction mixture under vigorous stirring to allow for fast mixing. After 1 h, the reaction mixture was quenched with 2 mL of a 20% aqueous solution of $H_2SO_4$ and the mixture was stirred overnight to effect complete hydrolysis of the resulting sulfate. This mixture was extracted with 3 × 20 mL of MTBE. The organic extracts were washed once with a 30 mL portion of saturated $Na_2CO_3$ 30 mL and once with a 30 mL portion of brine. The extracts were then dried over $Na_2SO_4$, the solvent was evaporated and the products were purified by column chromatography.

**3-Undecanol** Table 1, entry 1



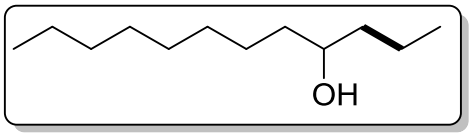

Purified by column chromatography using $CH_2Cl_2$/Hexanes 3:1. Clear oil, 147 mg, 85%.
**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S29) δ 0.87 (t, $^3J_{H-H}$ = 6.9 Hz, 3H), 0.93 (t, $^3J_{H-H}$ = 7.5 Hz, 3H), 1.27–1.52 (m, 16H), 1.59 (bs, 1H), 3.51 (m, 1H). **$^{13}$C{$^1$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S30) δ 10.0 (s), 14.2 (s), 22.8 (s), 25.8 (s), 29.4 (s), 29.7 (s), 29.9 (s), 30.2 (s), 32.0 (s), 37.1 (s), 73.4 (s). **HR-MS (ESI+)** calc. for $C_{11}H_{24}O_1Na_1$ $[M+Na]^+$ 195.1719, found: 195.1720.

**4-Dodecanol** Table 1, entry 2



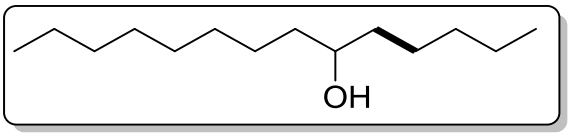

Purified by column chromatography using $CH_2Cl_2$/Hexanes 3:1. Clear oil, 156 mg, 84%.
**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S31) δ 0.86 (t, $^3J_{H-H}$ = 7.0 Hz, 3H), 0.91 (t, $^3J_{H-H}$ = 7.0 Hz, 3H), 1.26–1.50 (m, 18H), 1.66 (bs, 1H), 3.57 (m, 1H). **$^{13}$C{$^1$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S32) δ 14.2 (s), 14.2 (s), 18.9 (s), 22.8 (s), 25.8 (s), 29.4 (s), 29.7 (s), 29.9 (s), 32.0 (s), 37.6 (s), 39.8 (s), 71.8 (s). **HR-MS (ESI+)** calc. for $C_{12}H_{26}O_1Na_1$ $[M+Na]^+$ 209.1876, found: 209.1877.

**4-Dodecanol** Table 1, entry 3



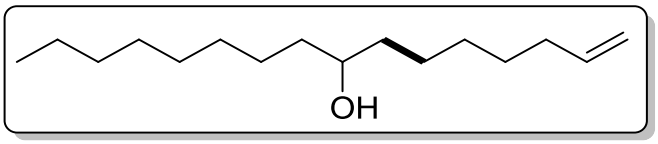

Ethylmagnesium bromide was used in this case. Clear oil, 149 mg, 80%. Figure NMR-S33.

**6-Tetradecanol** Table 1, entry 4




Purified by column chromatography using neat $CHCl_3$. Clear oil, 185 mg, 86%.
**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S34) δ 0.88 – 0.90 (overlapping triplets, 6H), 1.28 – 1.42 (m, 23H), 3.58 (m, 1H). **$^{13}$C{$^1$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S35) δ 14.2 (s), 14.3 (s), 22.8 (s), 22.8 (s), 25.5 (s), 25.8 (s), 29.4 (s), 29.75 (s), 29.9 (s), 32.0 (s), 32.1 (s), 37.6 (s), 37.6 (s), 72.2 (s), 77.2 (s). **HR-MS (ESI+)** calc. for $C_{14}H_{30}O_1Na_1$ $[M+Na]^+$ 237.2189, found: 237.2188.

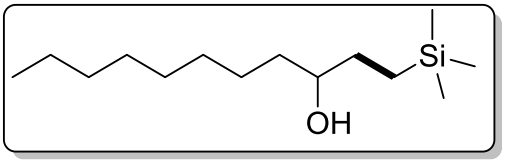
**1-Hexadecene-8-ol** Table 1, entry 5




Purified by column chromatography using $CH_2Cl_2$/Hexanes 3:1. White solid, 198 mg, 82%.

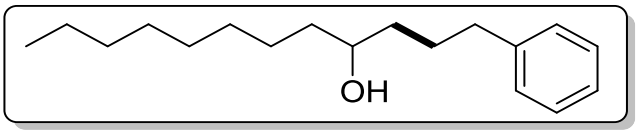
**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S36) δ 0.89 (t, $^3J_{H-H}$ = 6.7 Hz, 3H), 1.28 – 1.43 (m, 21H), 2.05 (m, 2H), 3.58 (m, 1H), 1.65 (bs, 1H), 3.48 (m, 1H), 4.95 (m, 1H), 5.01 (dq, $^{trans}J_{H-H}$ = 17.0 Hz, $^{vic}J_{H-H}$ = 1.7 Hz, 1H), 5.81(ddt, $^{trans}J_{H-H}$ = 17.0 Hz, $^{cis}J_{H-H}$ = 10.0 Hz, $^3J_{H-H}$ = 6.7 Hz, 1H). **$^{13}$C{$^1$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S37) δ 14.3 (s), 22.8 (s), 25.7 (s), 25.8 (s), 29.0 (s), 29.3 (s), 29.4 (s), 29.7 (s), 29.9 (s), 32.0 (s), 33.9 (s), 37.5 (s), 37.6 (s), 72.1 (s), 114.4 (s), 139.2 (s). **HR-MS (ESI+)** calc. for $C_{16}H_{32}O_1Na_1$ $[M+Na]^+$ 263.2345, found 263.2345.

**1-(Trimethylsilyl)-3-undecanol** Table 1, entry 6



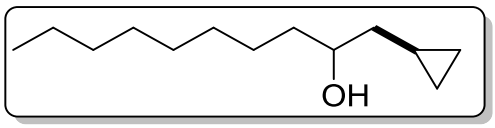

Purified by column chromatography using $CH_2Cl_2$/Hexanes 3:1. Clear oil, 197 mg, 80%.
**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S38) δ –0.02 (s, 9H), 0.41 (dt, $J_{H-H}$ = 13.9, 4.5 Hz, 1H), 0.60 (dt, $J_{H-H}$ = 13.4, 4.4 Hz, 1H), 0.87 (t, $^3J_{H-H}$ = 6.4 Hz, 3H), 1.28 – 1.47 (m, 16H), 1.65 (bs, 1H), 3.48 (m, 1H). **$^{13}$C{$^1$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S39) δ –1.7 (s), 12.1(s), 14.2 (s), 22.8 (s), 25.9 (s), 29.4 (s), 29.7 (s), 29.9 (s), 31.6 (s), 32.0 (s), 36.9 (s), 74.3 (s). **HR-MS (ESI+)** calc. for $C_{14}H_{32}O_1Si_1Na_1$ $[M+Na]^+$ 267.2115, found: 267.2115.

**1-Phenyldodecan-4-ol** Table 1, entry 7



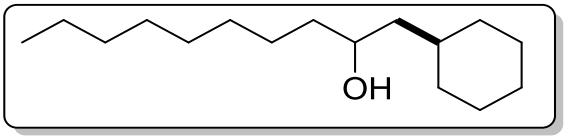

$CH_2Cl_2$/Hexanes 3:1. Clear oil, 103 mg, 40%
**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S40) δ 0.91 (t, $^3J_{H-H}$ = 6.9 Hz, 3H), 1.30 (m, 11H), 1.44 – 1.56 (m, 6H), 1.69 (m, 1H), 1,79 (m, 1H), 2.65 (m, 2H), 3.62 (m, 1H), 7.23 – 7.19 (m, 3H), 7.32 – 7.28 (m, 2H). **$^{13}$C{$^1$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S41) δ 14.3 (s), 22.8 (s), 25.8 (s), 27.6 (s), 29.4 (s), 29.7 (s), 29.8 (s), 32.0 (s), 36.0 (s), 37.1 (s), 37.6 (s), 71.9 (s), 125.8 (s), 128.4 (s), 128.5 (s), 142.5 (s). **HR-MS (ESI+)** calc. for $C_{18}H_{30}O_1Na_1$ $[M+Na]^+$ 285.2189, found: 285.2189.

**1-Cyclopropyl-2-decanol** Table 1, entry 8



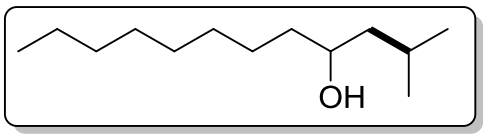

Purified by column chromatography using $CH_2Cl_2$/Hexanes 3:1. Clear oil, 170 mg, 85%.
**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S42) δ 0.03 (m, 1H), 0.09 (m, 1H), 0.44 (m, 2H), 0.73 (m, 1H), 0.86 (t, $^3J_{H-H}$ = 6.6 Hz, 3H), 1.26 – 1.48 (m, 16H), 1.86 (bs, 1H), 3.68 (m, 1H). **$^{13}$C{$^1$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S43) δ 3.8 (s), 4.6 (s), 7.6 (s), 14.2 (s), 22.8 (s), 25.8 (s), 29.4 (s), 29.7 (s), 29.9 (s) 32.0 (s), 37.3 (s), 42.4 (s), 72.6 (s). **HR-MS (ESI+)** calc. for $C_{13}H_{26}O_1Na_1$ $[M+Na]^+$ 221.1876, found: 221.1876.

**1-Cyclohexyl-2-decanol** Table 1, entry 9



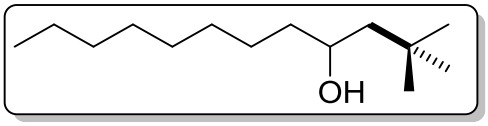

Purified by column chromatography using $CH_2Cl_2$/Hexanes 3:1. Clear oil, 183 mg, 76%.
**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S44) δ 0.83 (m, 1H), 0.87 (t, $^3J_{H-H}$ = 6.9 Hz, 3H), 0.94 (m, 1H), 1.13 – 1.80 (m, 26H), 3.68 (m, 1H). **$^{13}$C{$^1$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S45) δ 14.2 (s), 22.8 (s), 25.8 (s), 26.3 (s), 26.5 (s), 26.7 (s), 29.4 (s), 29.7 (s), 29.9 (s), 32.0 (s), 33.0 (s), 34.2 (s), 34.4 (s), 38.3 (s), 45.6 (s), 69.4 (s). **HR-MS (ESI+)** calc. for $C_{16}H_{32}O_1Na_1$ $[M+Na]^+$ 236.2345, found: 263.2345.

**2-Methyl-4-dodecanol** Table 1, entry 10



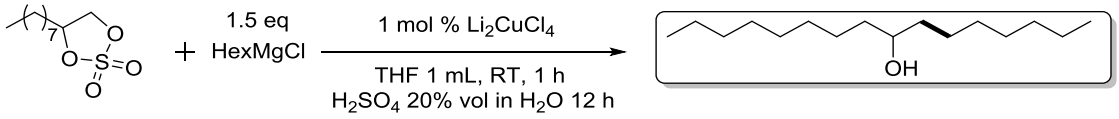

Purified by column chromatography using $CH_2Cl_2$/Hexanes 3:1. Clear oil, 129 mg, 65%.
**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S46) δ 0.88 (t, $^3J_{H-H}$ = 7.0 Hz, 3H), 0.90 (d, $^3J_{H-H}$ = 6.4 Hz, 3H), 0.92 (d, $^3J_{H-H}$ = 6.5 Hz, 3H) 1.20 – 1.43 (m, 17H), 1.77 (m, 1H), 3.66 (ddd, $J_{H-H}$ = 8.9, 7.3, 4.2 Hz, 1H). **$^{13}$C{$^1$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S47) δ 14.2 (s), 22.2 (s), 22.8 (s), 23.7 (s), 24.7 (s), 25.8 (s), 29.4 (s), 29.75 (s), 29.9 (s), 32.0 (s), 38.2 (s), 46.9 (s), 70.1 (s). **HR-MS (ESI+)** calc. for $C_{13}H_{28}O_1Na_1$ $[M+Na]^+$ 223.2032, found: 223.2034.

**2,2-Dimethyl-4-dodecanol** Table 1, entry 11



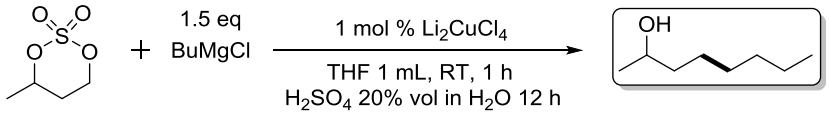

Purified by column chromatography using $CH_2Cl_2$/Hexanes 3:1. Clear oil, 52 mg, 27%.
**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S48) δ 0.88 (t, $^3J_{H-H}$ = 7.0 Hz, 3H), 0.96 (s, 9H), 1.28–1.45 (m, 16H), 3.73 (m, 1H). **$^{13}$C{$^1$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S49) δ 14.3 (s), 22.8 (s), 25.8 (s), 29.4 (s), 29.7 (s), 29.8 (s), 30.3 (s), 30.4 (s), 32.0 (s), 39.8 (s), 51.5 (s), 69.8 (s). **HR-MS (ESI+)** calc. for $C_{14}H_{30}O_1Na_1$ $[M+Na]^+$ 237.2189, found: 237.2188.

**8-Hexadecanol**



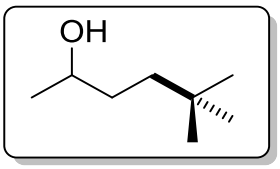

Purified by column chromatography using $CH_2Cl_2$/Hexanes 3:1. White solid, 198 mg, 82%.
**$^1$H NMR** (300 MHz, $CDCl_3$) (Figure NMR-S50) δ 0.89 (t, $^3J_{H-H}$ = 7.1 Hz, 6H), 1.25 – 1.51 (m, 27H), 3.50 – 3.71 (m, 1H). **$^{13}$C{$^1$H} NMR** (75 MHz, $CDCl_3$) (Figure NMR-S51) δ 14.2 (s), 22.8 (s), 25.8 (s), 29.4 (s), 29.5 (s), 29.8 (s), 29.8 (s), 29.9 (s), 32.0 (s), 32.1 (s), 37.7 (s), 72.2 (s). **HR-MS (ESI+)** calc. for $C_{16}H_{34}O_1Na_1$, 265.2502, found: 265.2503.

**2-Octanol**



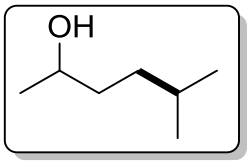

Clear oil, 93.5 mg, 72%.
**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S52) δ 0.85 (t, $^3J_{H-H}$ = 6.6 Hz, 3H), 1.14 (d, $^3J_{H-H}$ = 6.2 Hz, 3H), 1.26-1.43 (m, 10H), 2.03 (b, 1H), 3.75 (m, 1H). **$^{13}$C{$^1$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S53) δ 14.2 (s). 22.7 (s), 23.5 (s), 25.9 (s), 29.4 (s), 31.9 (s), 39.5 (s), 68.1 (s).

**5,5-Dimethylhexan-2-ol** Table 2, entry 1



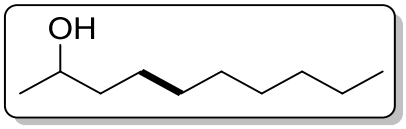

Purified by column chromatography using neat $CH_2Cl_2$.Clear oil, 85.3 mg, 66%.
**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S54) δ 0.88 (s, 9H), 1.15 (td, $J_{H-H}$ = 12.4, 4.6 Hz, 1H), 1.19 (d, $^3J_{H-H}$ = 6.2 Hz, 3H), 1.31 (td, $J_{H-H}$ = 12.4, 4.7 Hz, 1H), 1.35 – 1.49 (m, 2H), 1.55 (s, 1H), 3.81 – 3.68 (m, 1H). **$^{13}$C{$^1$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S55) δ 23.6 (s), 29.5 (s), 30.2 (s), 34.5 (s), 40.1 (s), 69.1 (s). **HR-MS (ESI+)** calc. for $C_8H_{18}O_1Na_1$ $[M+Na]^+$ 153.1250, found 153.1249.

**5-Methyl-2-hexanol** Table 2, entry 2



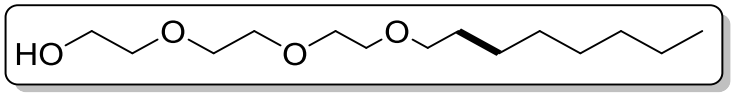

Purified by column chromatography using neat $CHCl_3$. Clear oil, 71%
**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S56) δ 0.89 (dd, *J* = 6.6, 2.3 Hz, 6H), 1.19 (d, *J* = 6.2 Hz, 3H), 1.25 – 1.34 (m, 2H), 1.39 – 1.49 (m, 2H), 1.48 – 1.59 (m, 1H), 1.59 (s, 1H), 3.77 (h, *J* = 6.2 Hz, 1H). **$^{13}$C{$^1$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S57) δ 22.7 (s), 22.8 (s), 23.6 (s), 28.2 (s), 35.1 (s), 37.3 (s), 68.7 (s).

**2-Decanol** Table 2, entry 3



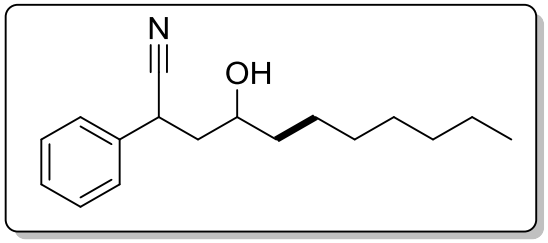

Purified by column chromatography using pentane/MTBE 3:1. Clear oil, 138 mg, 87%
**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S58) δ 0.88 (t, $^3J_{H-H}$ = 6.9 Hz, 3H), 1.19 (d, $J_{H-H}$ = 6.2 Hz, 3H), 1.29 – 1.48 (m,15H), 3.79 (m, 1H). **$^{13}$C{$^1$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S59) δ 14.3 (s), 22.8 (s), 23.6 (s), 25.9 (s), 29.4 (s), 29.7 (s), 29.8 (s), 32.0 (s), 39.5 (s), 68.3 (s).

**2-(2-(2-(Octyloxy)ethoxy)ethoxy)ethan-1-ol** Table 2, entry 4



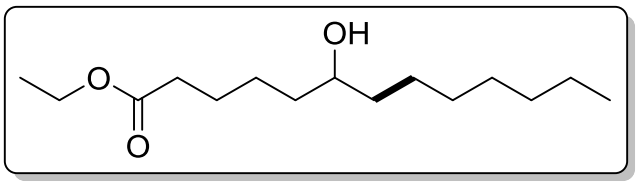

Purified by column chromatography using $CH_2Cl_2$/MTBE 4:1. White solid, 186 mg, 71%
**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S60) δ 0.83 (t, $^3J_{H-H}$ = 6.8 Hz, 3H). 1.23 – 1.29 (m, 10H), 1.54 (p, $J_{H-H}$ = 6.9 Hz, 2H), 2.91(bs, 1H), 3.41 (t, $J_{H-H}$ = 6.8 Hz, 2H), 3.53 – 3.69 (m, 12H). **$^{13}$C{$^1$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S61) δ 14.2 (s), 22.8 (s), 26.2 (s), 29.4 (s), 29.6 (s), 29.7 (s), 31.9 (s), 61.9 (s), 70.1 (s), 70.5 (s), 70.7 (s), 70.8 (s), 71.7 (s), 72.7 (s). **HR-MS (ESI+)** calc. for $C_{14}H_{30}O_4Na_1$ $[M+Na]^+$ 285.2036, found: 285.2034.

**4-Hydroxy-2-phenylundecanenitrile** Table 2, entry 5



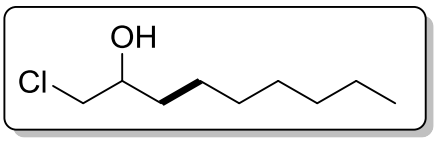

Purified by column chromatography using neat $CH_2Cl_2$.Clear oil, 58 mg, 50%.
**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S62) δ 0.89 (t, $^3J_{H-H}$ = 7.0 Hz, 3H), 1.26 – 1.32 (m, 10H), 1.43 – 1.52 (m, 2H), 1.84 (ddd, $J_{H-H}$ = 13.9, 10.6, 4.4 Hz, 1H), 2.02 (ddd, *J* = 14.0, 11.6, 2.4 Hz, 1H), 3.97 (m, 1H), 4.21 (dd, *J* = 11.6, 4.4 Hz, 1H), 7.32 – 7.41 (m, 5H). **$^{13}$C{$^1$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S63) δ 14.2 (s), 22.8 (s), 25.6 (s), 29.3 (s), 29.6 (s), 31.9 (s), 34.5 (s), 38.0 (s), 43.7 (s), 69.4 (s), 120.9 (s), 127.3 (s), 128.1 (s), 129.3 (s), 136.3 (s)**. HR-MS (ESI–)** calc. for $C_{17}H_{24}O_1N_1$ $[M]^-$ 258.1863, found: 258.1866.

**Ethyl 6-hydroxytridecanoate** Table 2, entry 6



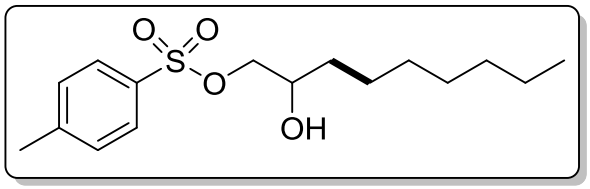

Purified by column chromatography using $CH_2Cl_2$/Ethyl acetate 3:1.10:1. Clear oil, 191.7 mg, 74%
**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S64) δ 0.87 (t, $J_{H-H}$ = 7.1 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.26 – 1.30 (m, 9H), 1.33 – 1.49 (m, 7H), 1.56 – 1.69 (m, 3H), 2.30 (t, *J* = 7.5 Hz, 2H), 3.58 (dt, *J* = 7.2, 3.9 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 2H). **$^{13}$C{$^1$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S65) δ 14.2 (s) 14.4 (s), 22.8 (s), 25.0 (s), 25.3 (s), 25.8 (s), 29.4 (s), 29.8 (s), 31.9 (s), 34.4 (s), 37.1 (s), 37.6 (s), 60.4 (s), 71.8 (s), 173.9 (s). **HR-MS (ESI+)** calc. for $C_{15}H_{30}O_3Na_1$ $[M+Na]^+$ 281.2087, found: 281.2087.

**1-Chloro-2-nonanol** Table 2, entry 7



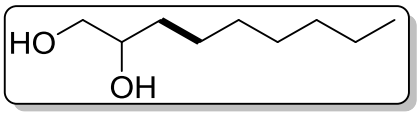

Purified by column chromatography using neat $CH_2Cl_2$. Clear oil, 133 mg, 74%
**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S66) δ 0.88 (t, $^3J_{H-H}$ = 6.9 Hz, 3H), 1.28 – 1.55 (m,12H), 2.27 (s, 1H), 3.48 (dd, $J_{H-H}$ = 11.1, 7.1 Hz, 1H), 3.62 (dd, $J_{H-H}$ = 11.0, 3.3 Hz, 1H), 3.80 (tdd, *J* = 7.2, 5.4, 3.3 Hz, 1H). **$^{13}$C{$^1$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S67) δ 14.2 (s), 22.8 (s), 25.7 (s), 29.3 (s), 29.6 (s), 31.9 (s), 34.3 (s), 50.7 (s), 71.6 (s). **HR-MS (ESI+)** calc. for $C_9H_{19}Cl_1O_1Na_1$ $[M+Na]^+$ 201.1017, found: 201.1017.

**4-Hydroxynonyl tosylate** Table 2, entry 8



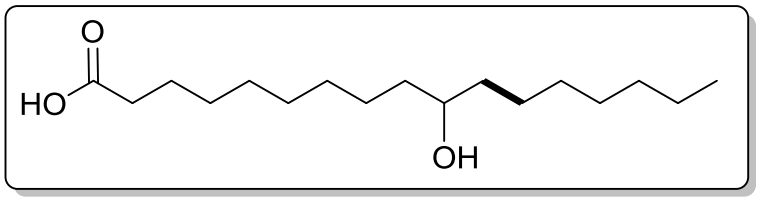
Purified by column chromatography using neat $CH_2Cl_2$.Clear oil, 291 mg, 91%.
**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S68) δ 0.87 (t, $^3J_{H-H}$ = 7.0 Hz, 3H), 1.25 (m, 9H), 1.41 (m, 3H), 2.11 (s, 1H), 2.45 (s, 3H), 3.82 (m, 1H), 3.89 (dd, *J* = 9.9, 7.1 Hz, 1H), 4.03 (dd, *J* = 9.9, 2.9 Hz, 1H), 7.36 (m, 2H), 7.79 (m, 2H). **$^{13}$C{$^1$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S69) δ 14.2 (s), 21.8 (s), 22.7 (s), 25.3 (s), 29.2 (s), 29.5 (s), 31.8 (s), 32.8 (s), 69.6 (s), 74.1 (s), 128.1 (s), 130.1 (s), 132.8 (s), 145.2 (s). **HR-MS (ESI+)** calc. for $C_{16}H_{26}O_4Na_1$ $[M+Na]^+$ 337.1444, found 337.1442.

**1,2-Nonanediol** Table 2, entry 9



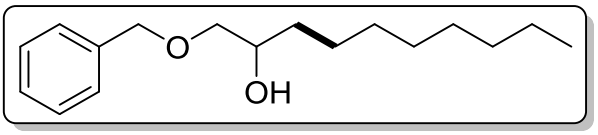
2.5 equivalents of butylmagnesium chloride were used in this case.
Purified by column chromatography using a 2:1 mixture of ethyl acetate and pentane.Clear oil, 110 mg, 69%.
**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S70) δ 0.87 (t, $^3J_{H-H}$ = 6.8 Hz, 3H), 1.26 – 1.29 (m, 9H), 1.44 – 1.38 (m, 3H), 3.39 (dd, $J_{H-H}$ = 11.2, 7.9, 1H), 3.51 – 3.56 (b, 2H), 3.62 (dd, *J* = 11.4, 2.9 Hz, 1H), 3.64 – 3.67 (m, 1H). **$^{13}$C{$^1$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S71) δ 14.2 (s), 22.8 (s), 25.8 (s), 29.4 (s), 29.8 (s), 32.0 (s), 33.2(s), 66.9 (s), 72.5 (s). **HR-MS (ESI+)** calc. for $C_9H_{20}O_2Na_1$ $[M+Na]^+$ 183.1355, found 183.1356.

**10-Hydroxyheptadecanoic acid** Table 2, entry 10



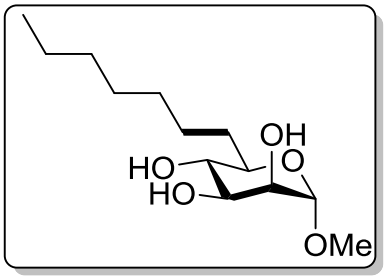
2.5 equivalents of butylmagnesium chloride were used in this case.
Purified by column chromatography using a solution of 10% MeOH in $CH_2Cl_2$.White solid, 79.3 mg, 78%.
**$^1$H NMR** (500.81 MHz, $CD_2Cl_2$) (Figure NMR-S72) δ 0.88 (t, $J_{H-H}$ = 6.9 Hz, 3H), 1.21 – 1.44 (m, 24H), 1.59 – 1.63 (m, 3H), 2.34 (t, $J_{H-H}$ = 7.5 Hz, 2H), 3.54 – 3.56 (m, 1H). **$^{13}$C{$^1$H} NMR** (125.94 MHz, $CD_2Cl_2$) (Figure NMR-S73) δ 14.5 (s), 23.3 (s), 25.3 (s), 26.2 (s), 26.2 (s), 29.6 (s), 29.7 (s), 29.89 (s), 29.95 (s), 30.17 (s), 30.26 (s), 32.4 (s), 34.5 (s), 38.0 (s), 38.1 (s), 72.5 (s), 179.7 (s). **HR-MS (ESI–)** calc. for $C_{17}H_{33}O_3$ $[M]^-$ 285.2435, found 285.2436.

**1-(Benzyloxy)-2-nonanol** Table 2, entry 11



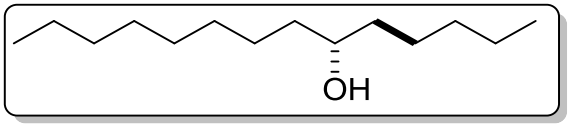

Purified by column chromatography using an eluent mixture of 10:10:1 $CHCl_3/CH_2Cl_2$/MTBE.Clear oil, 192 mg, 80%.
**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S74) δ 0.89 (t, $^3J_{H-H}$ = 7.0 Hz, 3H), 1.29 – 1.36 (m, 8H), 2.27 (s, 1H), 1.41 – 1.49 (m, 3H), 2.33 (bs, 1H), 3.34 (dd, *J* = 9.4, 7.9 Hz, 1H), 3.51 (dd, *J* = 9.4, 3.0 Hz, 1H), 3.82 (m, 1H), 4.57 (s, 2H), 7.31 – 7.39 (m, 5H). **$^{13}$C{$^1$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S75) δ 14.2 (s), 22.8 (s), 25.7 (s), 29.3 (s), 29.8 (s), 31.9 (s), 33.3 (s), 70.6 (s), 73.4 (s), 74.9 (s), 127.8 (s), 127.9(s), 128.6 (s), 138.1 (s). **HR-MS (ESI+)** calc. for $C_{16}H_{26}O_2Na_1$ $[M+Na]^+$ 273.1825, found: 273.1825.

**Methyl 6-hexyl-6-deoxy-α-D-mannopyranoside** Table 2, entry 12




The product was isolated exclusively as the alpha anomer. Purified by column chromatography using a polarity gradient ranging from neat ethyl acetate to neat acetone. 22 mg, 53%.
**$^1$H NMR** (500.81 MHz, $D_2O$) (Figure NMR-S76) δ 0.85 (s, 3H), 1.22–1.35 (m, 9H), 1.45–1.58 (m, 2H), 1.87–2.01 (m, 1H), 3.38 (s, $–OCH_3$, 3H), 3.62 (td, $J_{H-H}$ = 9.6, 2.2 Hz, 1H), 3.91 (dd, $J_{H-H}$ = 9.1, 3.4 Hz, 1H), 3.96 (dd, $J_{H-H}$ = 3.5, 1.9 Hz, 1H), 4.23 (t, $J_{H-H}$ = 9.3 Hz, 1H), 4.70 (d, $J_{H-H}$ = 2.0 Hz, $^1J_{C-H}$ = 170.2 Hz, –C*H*–OMe, 100% α-anomer, 1H). **$^{13}$C{$^1$H} NMR** (125.94 MHz, $D_2O$) (Figure NMR-S77- NMR-S78) δ 13.5 (s), 22.2 (s), 25.0 (s), 28.6 (s), 28.6 (s), 30.4 (s), 31.2 (s), 54.7 (s), 69.7 (s), 70.0 (s), 70.1 (s), 79.0 (s), 100.3 (s, anomeric –*C*HOMe). **HR-MS (ESI+)** calc. for $C_{13}H_{26}O_5Na_1$ $[M+Na]^+$ 285.167244, found: 285.167470. Specific rotation $[\alpha]_D^{25}$ +56.00° (*c* 0.7, $H_2O$).
Assignment was made on the basis of comparison of anomeric carbon $^{13}$C NMR chemical shifts and $^1J_{C-H}$ coupling constants between the isolated compound and pure, commercially available methyl-α-D-mannopyranoside (δ = 100.8 ppm, $^1J_{C-H}$ =171.1 Hz).

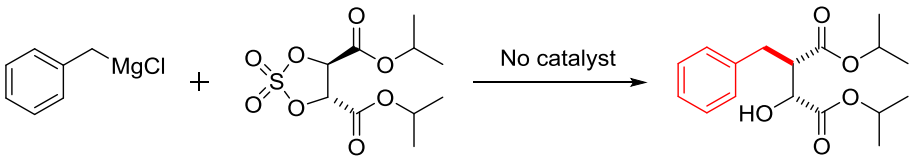
**(R)-6-Tetradecanol** Table 2, entry 13




White solid. 174 mg, 81%.
Specific rotation $[\alpha]_D^{25}$ –1.0 degcm$^3$g$^{-1}$dm$^{-1}$ (*c* 0.78 gcm$^{-3}$, $CHCl_3$). Enantiomeric excess: 96.7%
Initially, determination of the enantiopurity of this compound was attempted through $^{19}$F NMR analysis of its Mosher ester, however, the signals for each enantiomer in the racemic mixture showed a considerable amount of overlapping, rendering the method unreliable in this particular case. Enantiopurity was ascertained through a chiral HPLC separation of the Mosher ester, already in hand (Chiralpak AD-3, n-heptane/2-propanol 99:1 v/v, 1.0 mLmin$^{-1}$). $t_R$ = 3.33 min, $t_R$ = 4.07 min.

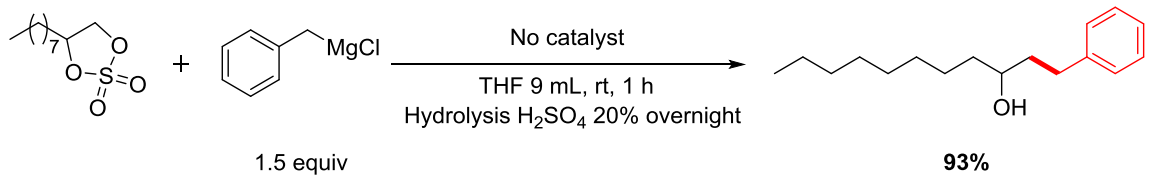
Synthesis of the Mosher ester.
Inside a dry box, a 10 mL dram vial equipped with a magnetic stir bar was charged with (S)-(–)-α-methoxy α-trifluoromethylphenylacetic acid (109.23 mg, 0.47 mmol,2.00 equiv) and $CH_2Cl_2$ (8 mL). N,N'-dicyclohexylcarbodiimide (96.24 mg, 0.47 mmol, 2.00 equiv) was added followed by DMAP (2.85 mg, 0.023 mmol, 0.10 equiv) and enantiopure 6-tetradecanol (0.20 g, 0.95 mmol, 1.00 equiv) in $CH_2Cl_2$ (2 mL). Gas chromatographic analysis confirmed complete conversion after stirring overnight. The reaction mixture was filtered through a plug of Celite, solvents removed *in vacuo* to obtain an oily residue that was purified by column chromatography using neat pentane to obtain a clear oil. Yield: 74 mg, 96%.

# Control reactions




This reaction was carried out following previously reported reaction conditions minus the catalyst.[1] (–)-Diisopropyl tartrate-2,3-cyclic sulfate (prepared following literature procedures[1]) (151.6 mg, 0.512 mmol) and 4.5 mL of dry THF were charged in a vial equipped with a PTFE-coated stir bar. The vial was placed in an acetone/dry ice cooling bath, and benzylmagnesium chloride (0.77 mmol, 770 μL of a 1.0 M solution), was added via syringe in a single portion. The mixture was kept in the cooling bath for 2 h, then quenched with 2 mL of 20% aqueous $H_2SO_4$ solution and stirred overnight to effect complete hydrolysis of the organic sulfate. The reaction mixture was extracted with 3 × 30 mL portions of MTBE. The organic extracts were collected, washed once with 20 mL of a saturated solution of $Na_2CO_3$, dried over $Na_2SO_4$ and concentrated *in vacuo*. The crude oil was purified by column chromatography using neat $CH_2Cl_2$.

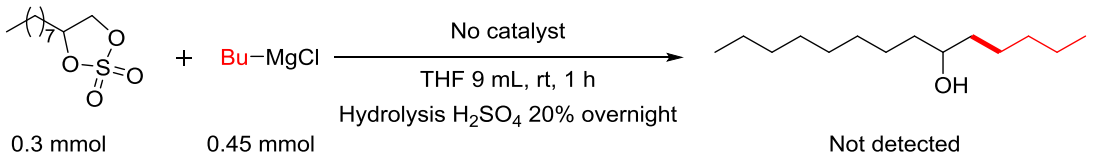
Clear oil, 129 mg, 82%.
**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S79) δ 1.15 (d, $^3J_{H-H}$ = 6.3 Hz, 3H), 1.21 (d, $^3J_{H-H}$ = 6.3 Hz, 3H), 1.26 (d, $^3J_{H-H}$ = 6.3 Hz, 3H), 1.28 (d, $^3J_{H-H}$ = 6.3 Hz, 3H), 2.99 (dd, *J* = 13.3, 8.8 Hz, 1H), 3.12 (m, 1H), 3.17 (m, 1H), 3.28 (d, *J* = 7.2 Hz, 1H), 4.06 (m, 1H), 5.00 (hept, *J* = 6.3 Hz, 1H), 5.09 (hept, *J* = 6.2 Hz, 1H), 7.21 – 7.26 (m, 1H), 7.27– 7.34 (m, 4H). **$^{13}$C{$^1$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S80) δ 21.8 (s), 21.9 (s), 34.2 (s), 50.3 (s), 68.7 (s), 69.9 (s), 70.0 (s), 126.7 (s), 128.7 (s), 129.4 (s), 138.7 (s), 171.8 (s), 173.2 (s). Specific rotation $[\alpha]_D^{25}$ –9.02° (*c* 0.51, $CHCl_3$). **HR-MS (ESI+)** calc. for $C_{17}H_{24}O_5Na_1$ $[M+Na]^+$ 331.1516, found. 331.1515.




Inside of a dry box, 1,2-decanediol cyclic sulfate (0.81 mmol) and 9 mL of dry THF were charged in a 14 mL dram vial equipped with a PTFE-lined stir bar. The vial was closed with a septum screw cap and was then removed from the dry box. Benzylmagnesium chloride (1.21 mmol, 1.21 mL of a 1.0 M solution) was added quickly and in a single portion at room temperature to the solution, under vigorous stirring to allow for fast mixing. After 1 h the reaction mixture was quenched with 2 mL of 20% aqueous $H_2SO_4$, and the mixture was stirred overnight. Next morning, the mixture was extracted with three 10 mL portions of MTBE, the organic extracts washed with one 5 mL portion of saturated $Na_2CO_3$ and dried over $MgSO_4$.

Purified by column chromatography using an eluent mixture of 8:1 pentane/MTBE.Clear oil, 187 mg, 93%.
**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure NMR-S81) $\delta$ 0.91 (t, $^3J_{H-H}$ = 7.0 Hz, 3H), 1.25 – 1.41 (m, 12H), 1.63 – 1.40 (m, 3H), 1.70 – 1.90 (m, 2H), 2.61 – 2.77 (m, 1H), 2.77 – 2.90 (m, 1H), 3.64 (tt, *J* = 8.2, 3.7 Hz, 1H), 7.18 – 7.25 (m, 3H), 7.28 – 7.33 (m, 2H). **$^{13}$C{$^1$H} NMR** (125.94 MHz, $CDCl_3$) (Figure NMR-S82) $\delta$ 14.2 (s), 22.8 (s), 25.7 (s), 29.4 (s), 29.7 (s), 29.8 (s), 32.0 (s), 32.2 (s), 37.7 (s), 39.2 (s), 71.5 (s), 125.9 (s), 128.5 (s), 128.5 (s), 142.4 (s). **HR-MS (ESI+)** calc. for $C_{17}H_{28}O_1Na_1$ $[M+Na]^+$ 271.2032, found 271.2033.

Inside of a dry box, 1,2-decanediol cyclic sulfate (0.3 mmol) and 2 mL of dry THF were charged in a 14 mL dram vial equipped with a PTFE-lined stir bar. The vial was closed with a septum screw cap and was then removed from the dry box. The appropriate alkylmagnesium chloride reagent (0.45 mmol) was added quickly and in a single portion at room temperature to the reaction mixture, under vigorous stirring to allow for fast mixing. After 1 h the reaction mixture was quenched with 1 mL of 20% aqueous $H_2SO_4$, and the mixture was stirred overnight. Next morning, the mixture was extracted with 5 mL of MTBE, the organic fraction dried over $Na_2SO_4$ and used for gas chromatographic analysis.



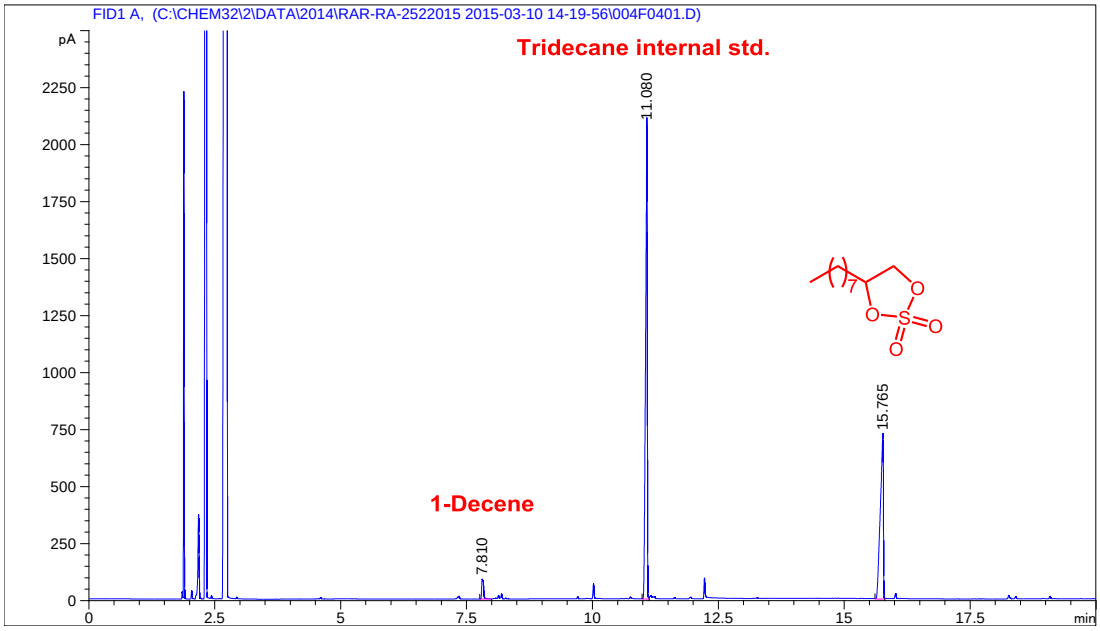
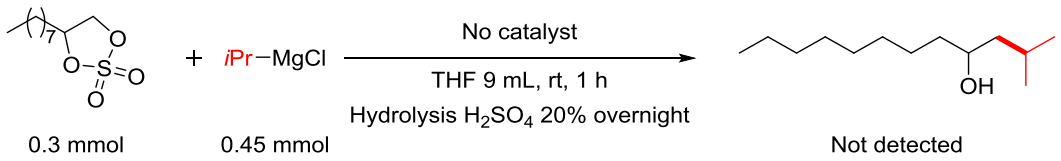




**Figure S1.** GC chromatogram of the reaction mixture formed after treating the 1,2-decanediol cyclic sulfate with butylmagnesium chloride in the absence of catalyst. Retention time of the respective coupling product: 13.9 min.



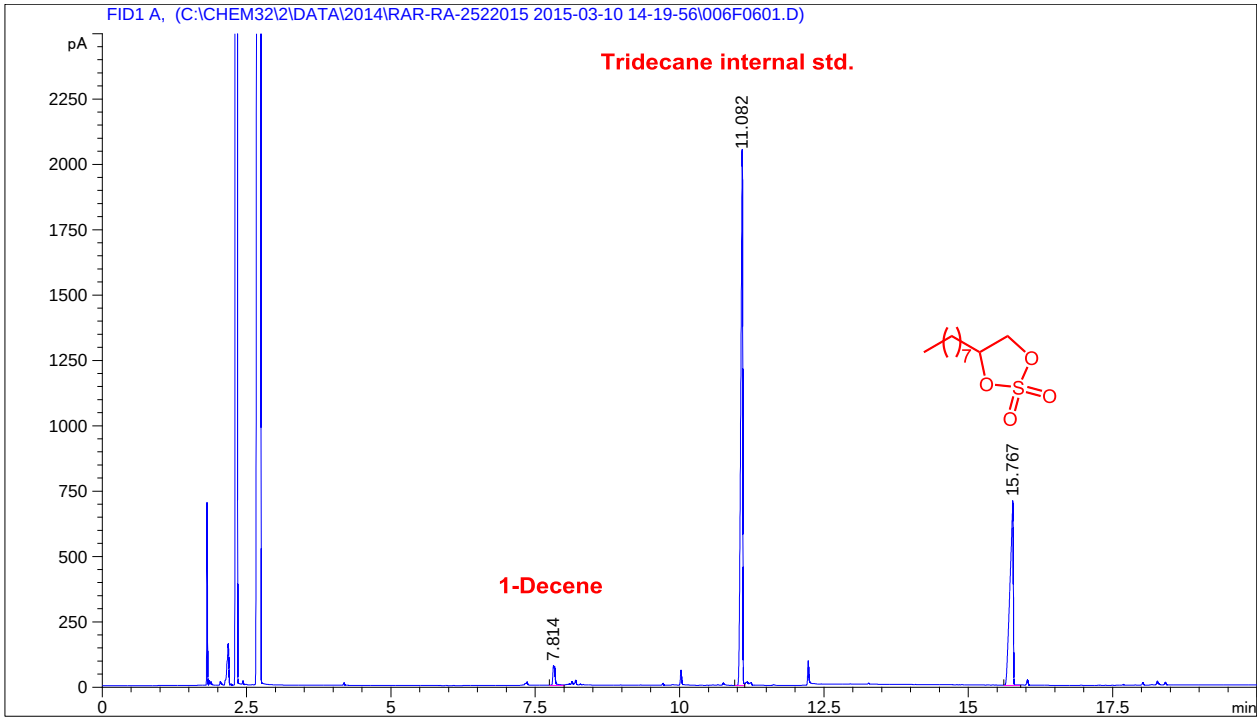
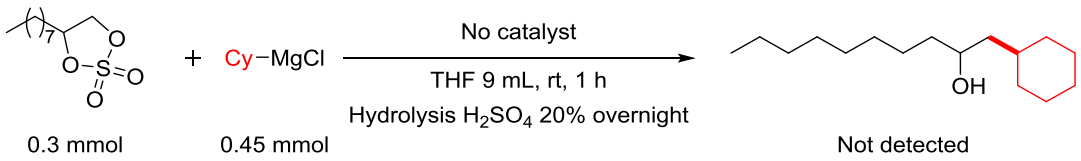




**Figure S2.** GC chromatogram of the reaction mixture formed after treating the 1,2-decanediol cyclic sulfate with isopropylmagnesium chloride in the absence of catalyst. Retention time of the respective coupling product: 12.5 min.



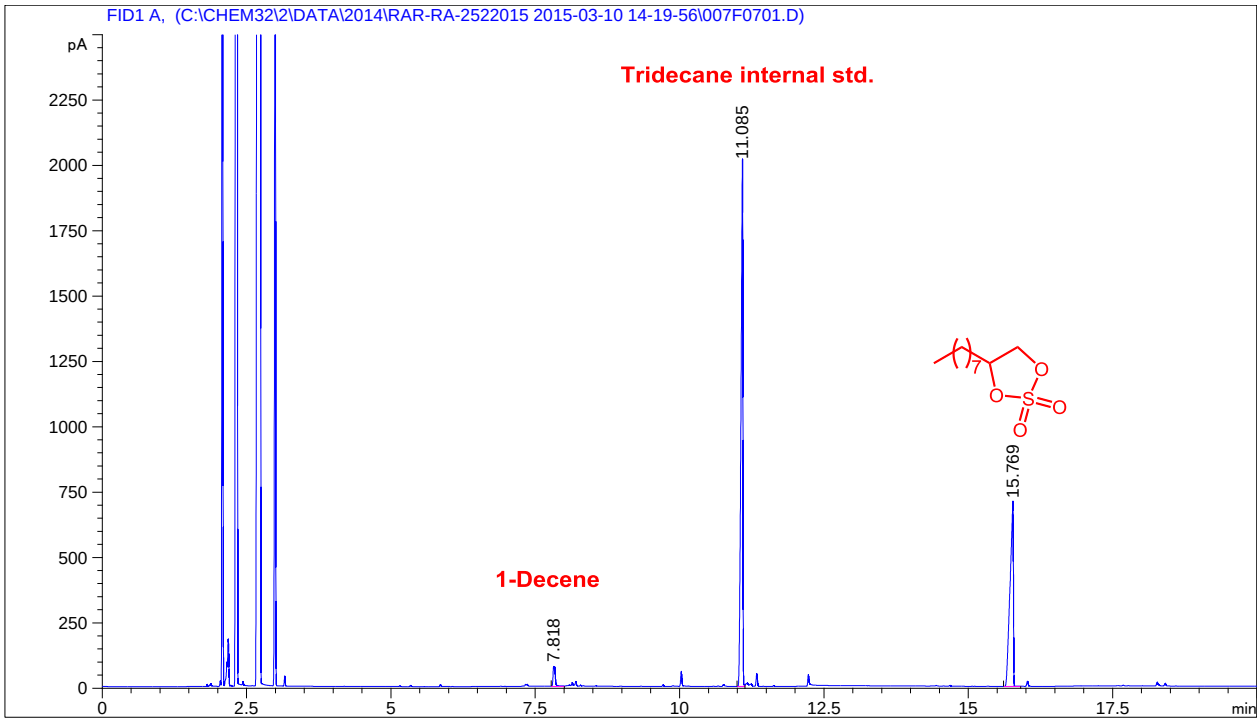
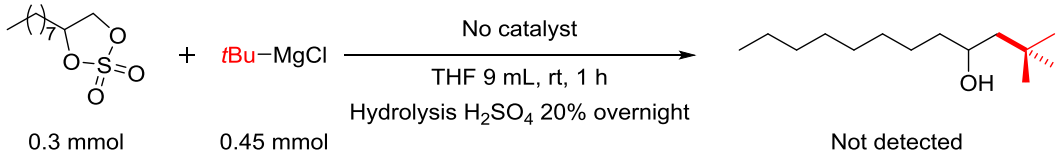




**Figure S3.** GC chromatogram of the reaction mixture formed after treating the 1,2-decanediol cyclic sulfate with cyclohexylmagnesium chloride in the absence of catalyst. Retention time of the respective coupling product: 16.1 min.



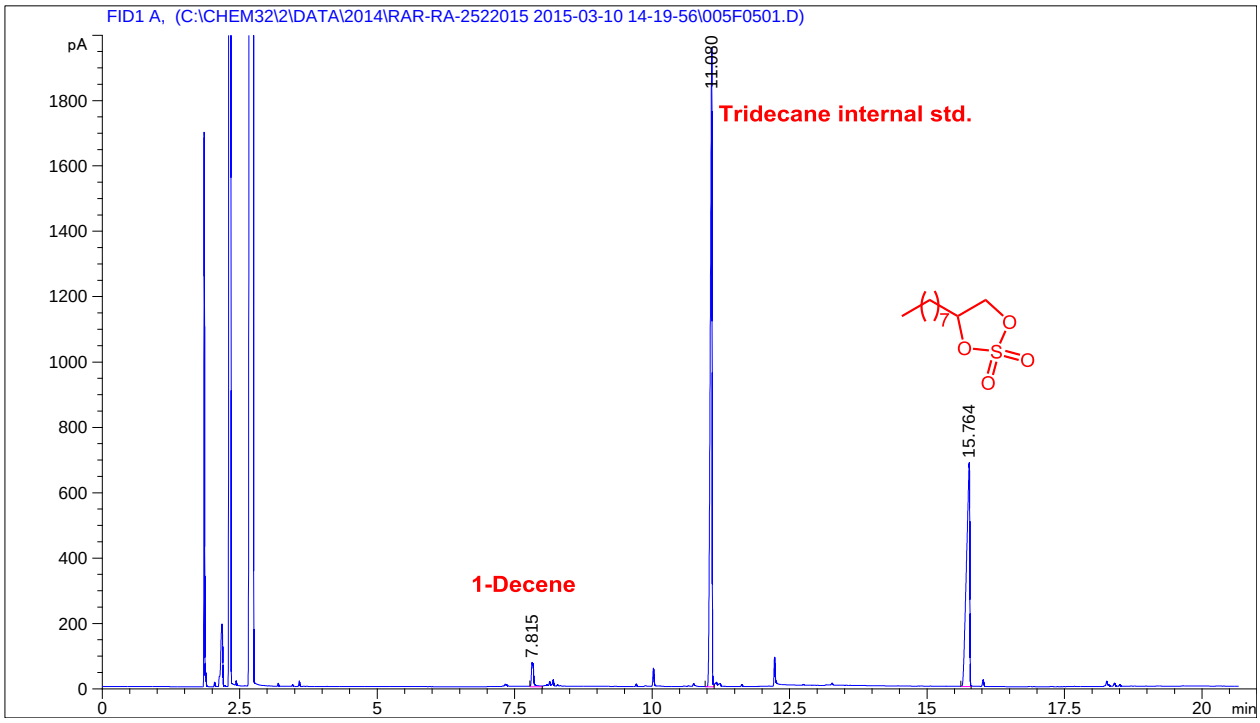
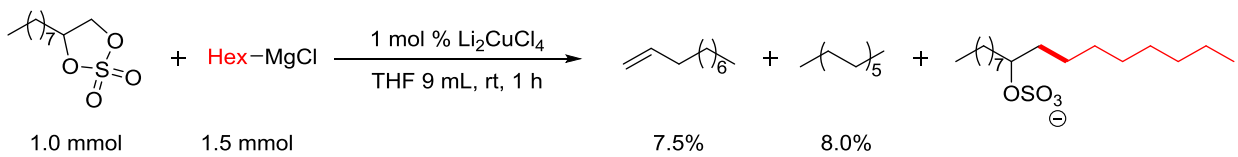




**Figure S4.** GC chromatogram of the reaction mixture formed after treating the 1,2-decanediol cyclic sulfate with cyclohexylmagnesium chloride in the absence of catalyst. Retention time of the respective coupling product: 12.9 min.

# Observation of formation of 1-decene and homocoupling products from 1,2-decanediol cyclic sulfate from catalytic reactions

Inside of a dry box, 1,2-decanediol cyclic sulfate (1.0 mmol) and 9 mL of dry THF were charged in a 14 mL dram vial equipped with a PTFE-lined stir bar. The vial was closed with a septum screw cap and was then removed from the dry box. $Li_2CuCl_4$ (1% mol, 100 μL of a 0.1 M commercial solution in THF) and tridecane (94.0 mg, 0.5 mmol) were charged and the vial was placed on a stir plate. The appropriate alkylmagnesium chloride reagent (1.5 mmol) was added quickly and in a single portion to the reaction mixture under vigorous stirring to allow for fast mixing. An aliquot of 1 mL was taken 1 h after addition of the organomagnesium reagent, and quenched with 100 μL of methanol. Any solids that may have formed were removed by filtration through a Millipore® filter and 1 μL of the sample was injected into the gas chromatograph. The amounts of 1-decene, dodecane and 2,2,4,4-tetramethylbutane formed during the reactions were determined quantitatively by means of the relative ratio of the relevant signal intensity and the signal intensity of a known amount of tridecane added to the reaction mixture.



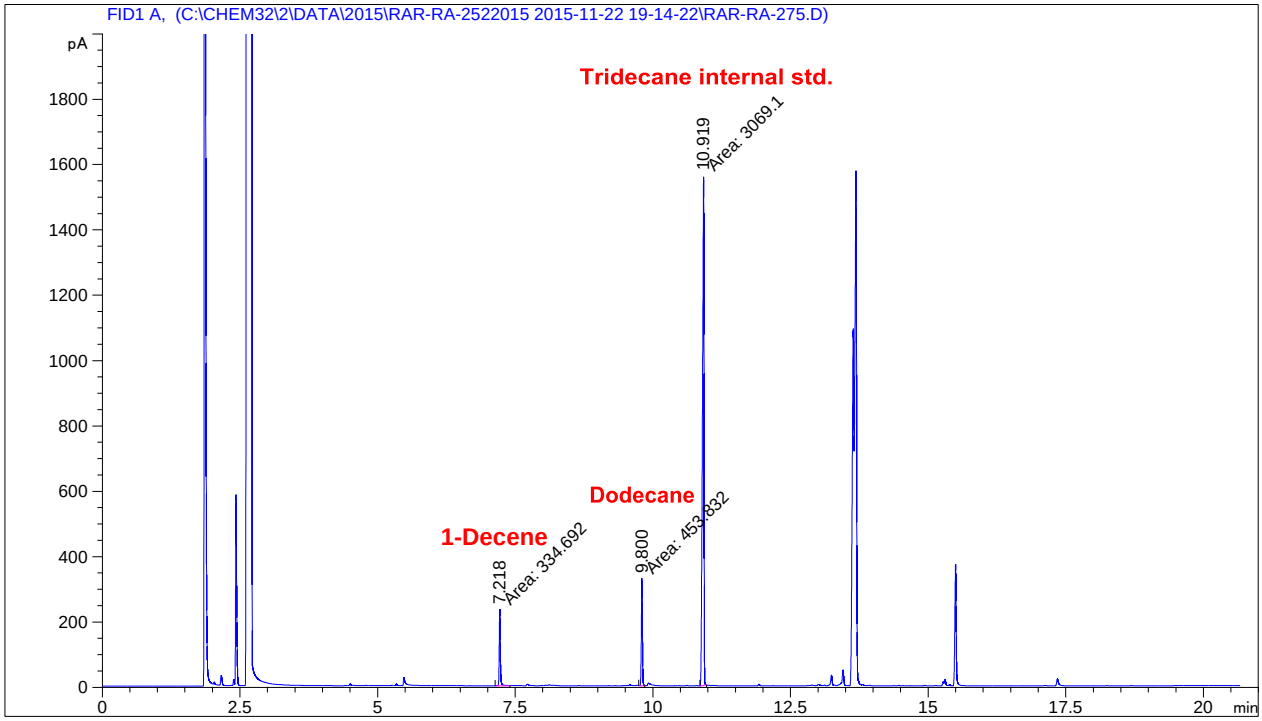
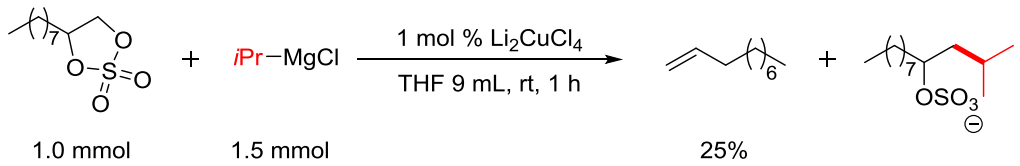




**Figure S5.** GC chromatogram of the reaction mixture formed after treating the 1,2-decanediol cyclic sulfate with hexylmagnesium chloride.



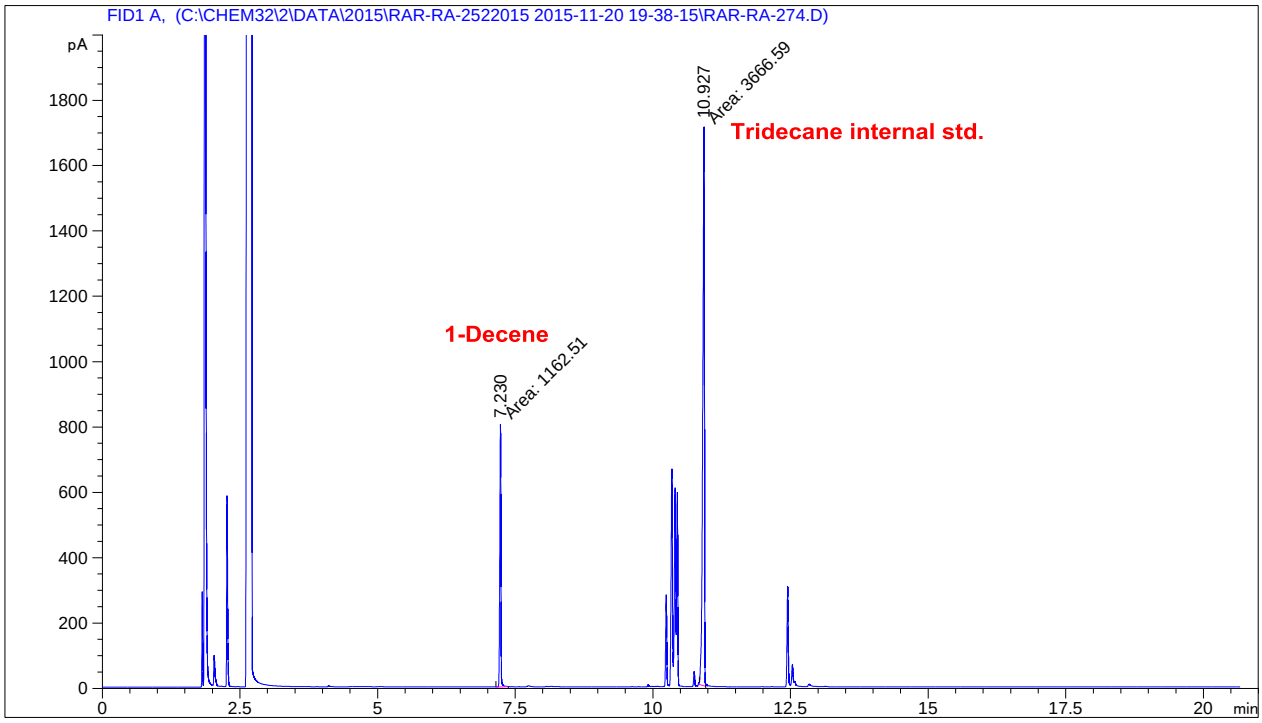
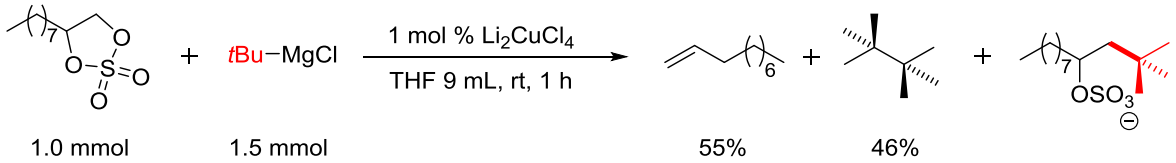




**Figure S6.** GC chromatogram of the reaction mixture formed after treating the 1,2-decanediol cyclic sulfate with isopropylmagnesium chloride.



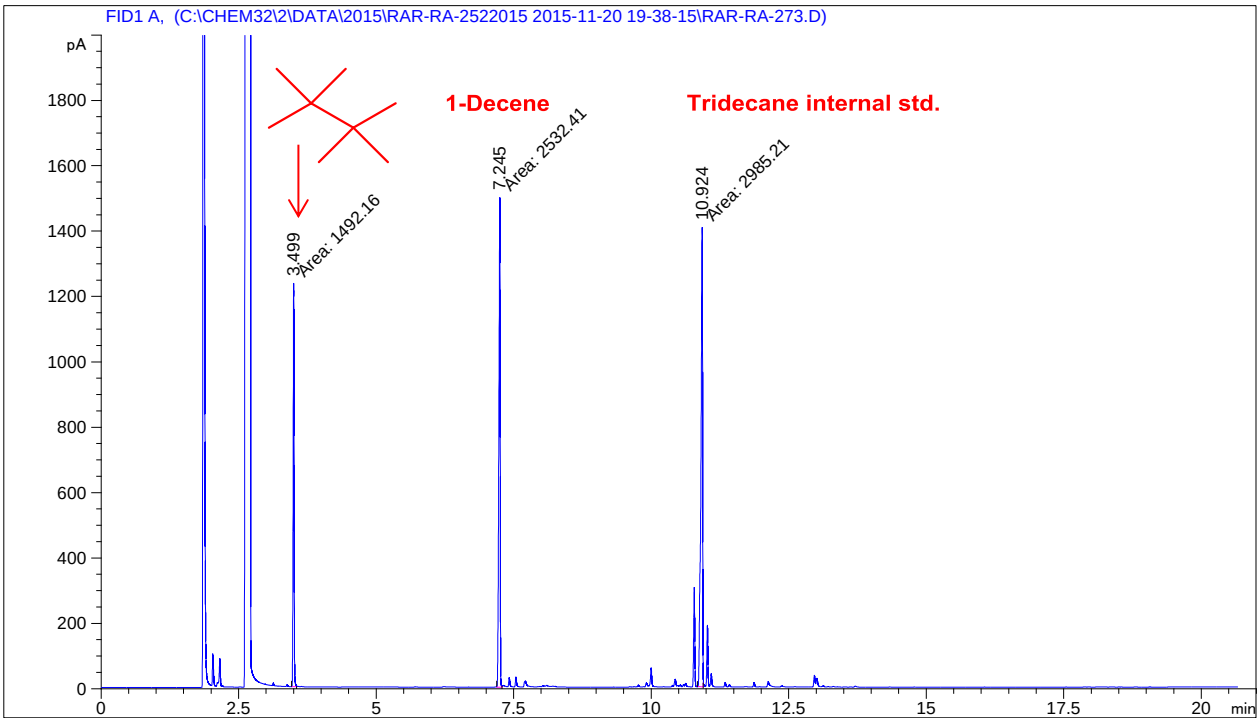
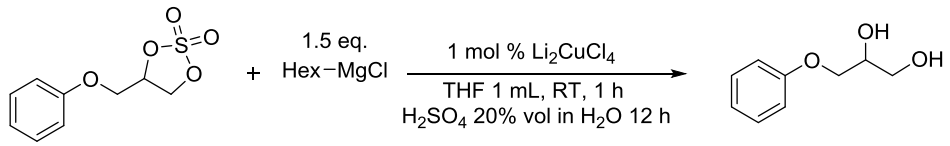




**Figure S7.** GC chromatogram of the reaction mixture formed after treating the 1,2-decanediol cyclic sulfate with *tert*-butylmagnesium chloride.

## Observation of desulfuration of the cyclic sulfate




**2a** **3a**

Inside of a dry box, 5-hexene-1,2-diol cyclic sulfate (1.13 mmol, 261 mg) and 9 mL of dry THF were charged in a 14 mL dram vial equipped with a PTFE-lined stir bar. The vial was closed with a septum screw cap and was then removed from the dry box. $Li_2CuCl_4$ (10 μmol, 100 μL of a 0.1 M commercial solution in THF) was charged and the vial was placed on a stir plate. Hexylmagnesium chloride (1.50 mmol, 750 μL of a 2.0 M solution) was added quickly and in a single portion to the reaction mixture under vigorous stirring to allow for fast mixing. After 1 h, the reaction mixture was quenched with 2 mL of a 20% aqueous solution of $H_2SO_4$ and the mixture was stirred overnight to effect complete hydrolysis of the resulting sulfate. This mixture was extracted with 3 × 20 mL of MTBE. The organic extracts were washed once with a 30 mL portion of saturated $Na_2CO_3$ 30 mL and once with a 30 mL portion of brine. The extracts were then dried over $Na_2SO_4$, the solvent was evaporated and the components of the reaction mixture were purified by column chromatography, using a mixture of $CHCl_3$/ $CH_2Cl_2$/MTBE 10:10:1. White solid, 180 mg, 94%

**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure S8) δ2.62 (s, 2H), 3.76 (dd, *J* = 11.5, 5.6 Hz, 1H), 3.85 (dd, *J* = 11.5, 3.8 Hz, 1H), 4.04 (d, *J* = 2.5 Hz, 1H), 4.05 (s, 1H), 4.16 – 4.08 (m, 1H), 6.95 – 6.89 (m, 2H), 7.03 – 6.95 (m, 1H), 7.34 – 7.28 (m, 2H).

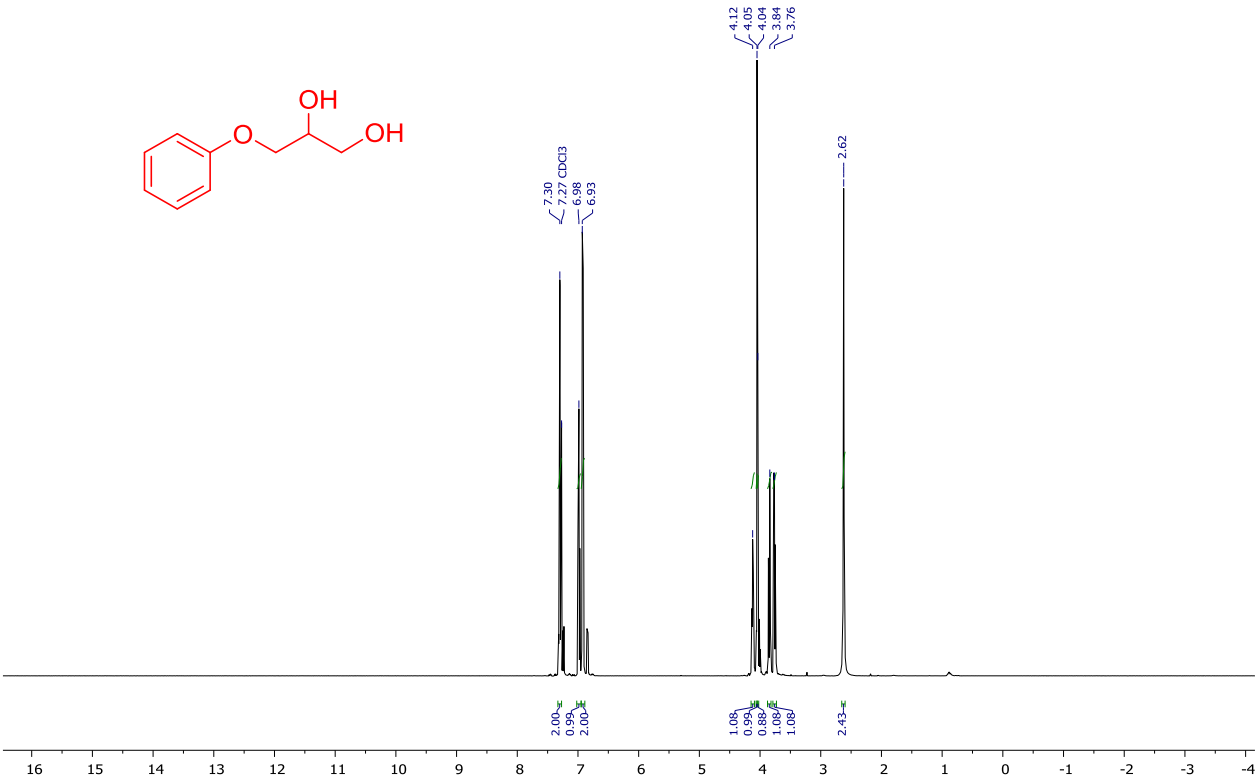



**Figure S8.** 500 MHz $^1$H NMR spectrum of 3-phenoxypropane-1,2-diol (**3a**), by-product of the coupling reaction between 3-phenoxypropane-1,2-diol cyclic sulfate with hexylmagensium chloride.

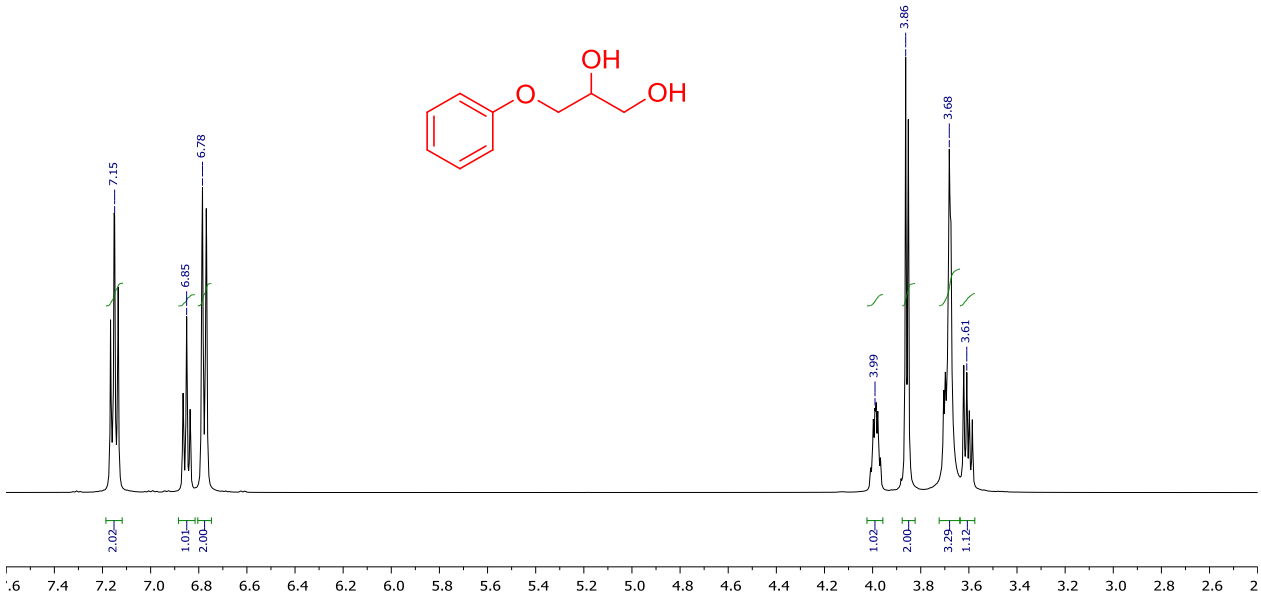
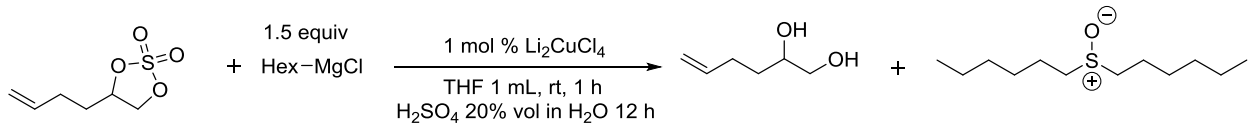



**Figure S9.** 500 MHz $^{1}$H NMR spectrum of an authentic sample of 3-phenoxypropane-1,2-diol (**3a**).




**2b** **3b**

Inside of a dry box, 5-hexene-1,2-diol cyclic sulfate (0.31 mmol, 55.5 mg) and 2 mL of dry THF were charged in a 14 mL dram vial equipped with a PTFE-lined stir bar. The vial was closed with a septum screw cap and was then removed from the dry box. $Li_2CuCl_4$ (1% mol, 31 μL of a 0.1 M commercial solution in THF) was charged and the vial was placed on a stir plate. Hexylmagnesium chloride (0.47 mmol, 230 μL of a 2.0 M solution) was added quickly and in a single portion to the reaction mixture under vigorous stirring to allow for fast mixing. After 1 h, the reaction mixture was quenched with 2 mL of a 20% aqueous solution of $H_2SO_4$ and the mixture was stirred overnight to effect complete hydrolysis of the resulting sulfate. This mixture was extracted with 3 × 20 mL of MTBE. The organic extracts were washed once with a 30 mL portion of saturated $Na_2CO_3$ 30 mL and once with a 30 mL portion of brine. The extracts were then dried over $Na_2SO_4$, the solvent was evaporated and the components of the reaction mixture were purified by column chromatography, starting with MTBE, followed by mixtures of $CH_2Cl_2/CH_3OH$ with progressively increasing polarity until all products had eluted.

Isolated mass of 5-hexene-1,2-diol: 0.258 mmol, 30 mg.
**$^1$H NMR** (500.81 MHz, $CDCl_3$) (Figure S10) δ 1.44 – 1.59 (m, 2H), 3.27 – 3.38 (m, 2H), 2.29 (bs, 2H), 3.42 (dd, *J* = 11.3, 7.7 Hz, 1H), 3.62 (dd, *J* = 11.3, 2.9 Hz, 1H), 3.70 (tdd, *J* = 7.9, 5.1, 2.9 Hz, 1H), 5.04 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.95 – 5.00 (m, 1H), 5.82 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H).

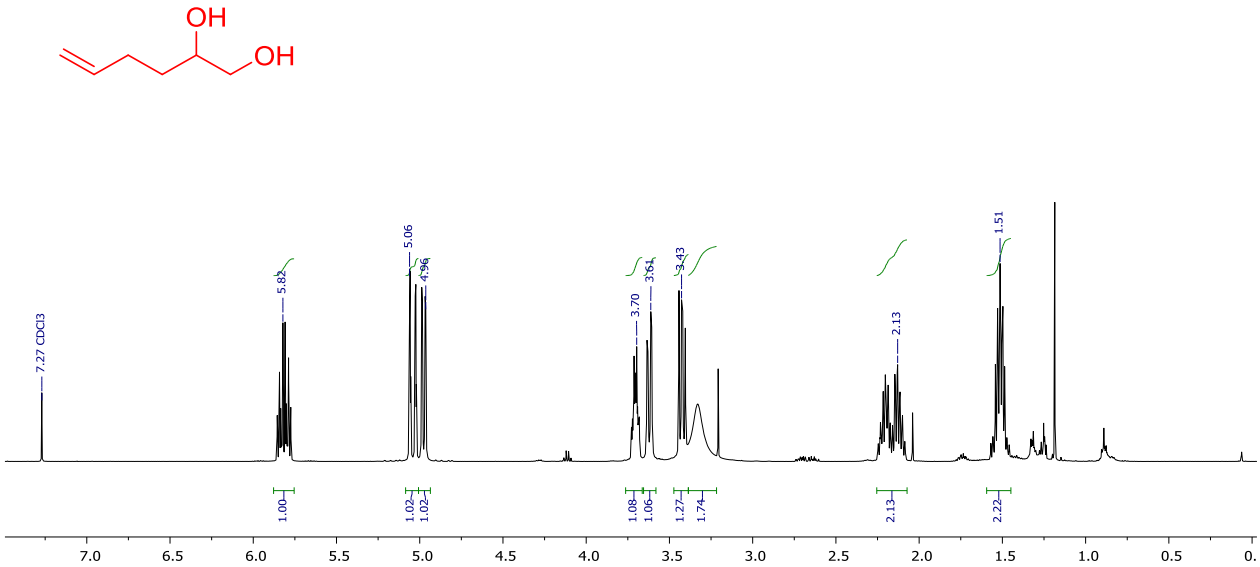



**Figure S10.** 500 MHz $^1$H NMR spectrum of 5-hexene-1,2-diol (**3b**) recovered from the reaction mixture.

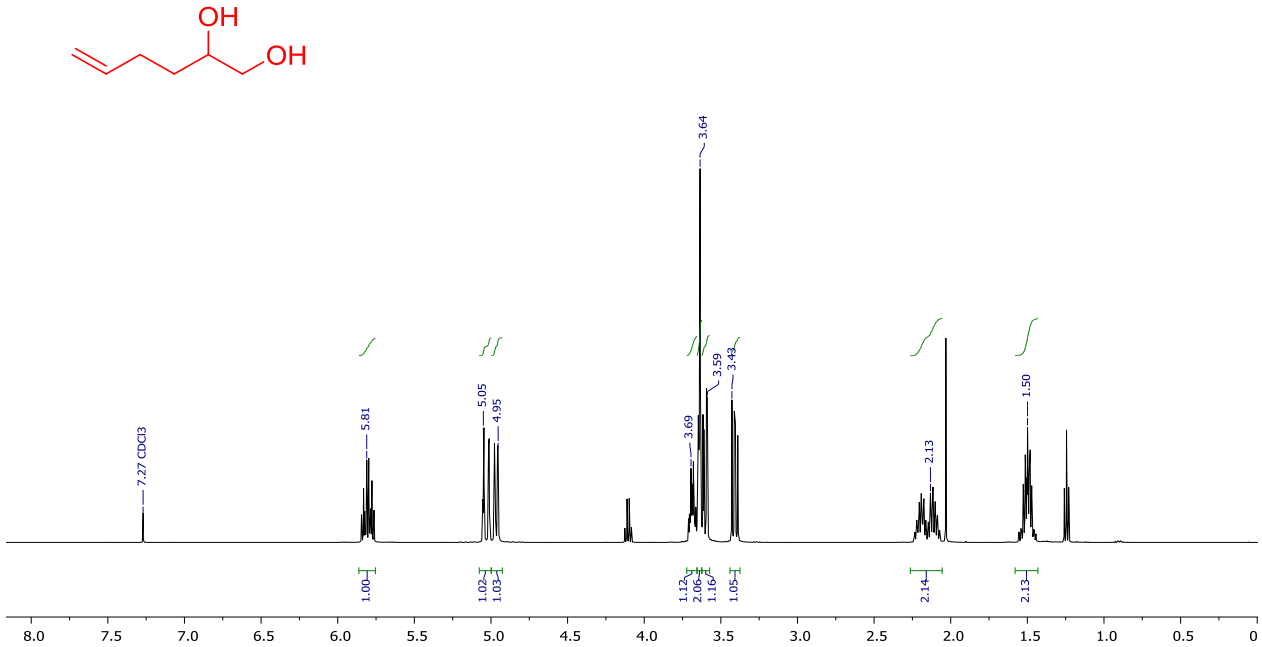



**Figure S11.** 500 MHz $^{1}$H NMR spectrum of an authentic sample of 5-hexene-1,2-diol (**3b**).

Isolated mass of dihexylsulfoxide: 0.163 mmol, 35.6 mg.
**$^{1}$H NMR** (500.81 MHz, $CDCl_3$) (Figure S12) δ 0.90 (t, *J* = 7.3 Hz, 6H), 1.26 – 1.37 (m, 8H), 1.38 – 1.54 (m, 4H), 1.71 – 1.83 (m, 4H), 2.53 – 2.74 (m, 4H). ). **$^{13}$C{$^{1}$H} NMR** (125.94 MHz, $CDCl_3$) (Figure S13) δ 14.1 (s), 22.6 (s), 22.7 (s), 28.7 (s), 31.5 (s), 52.7 (s),

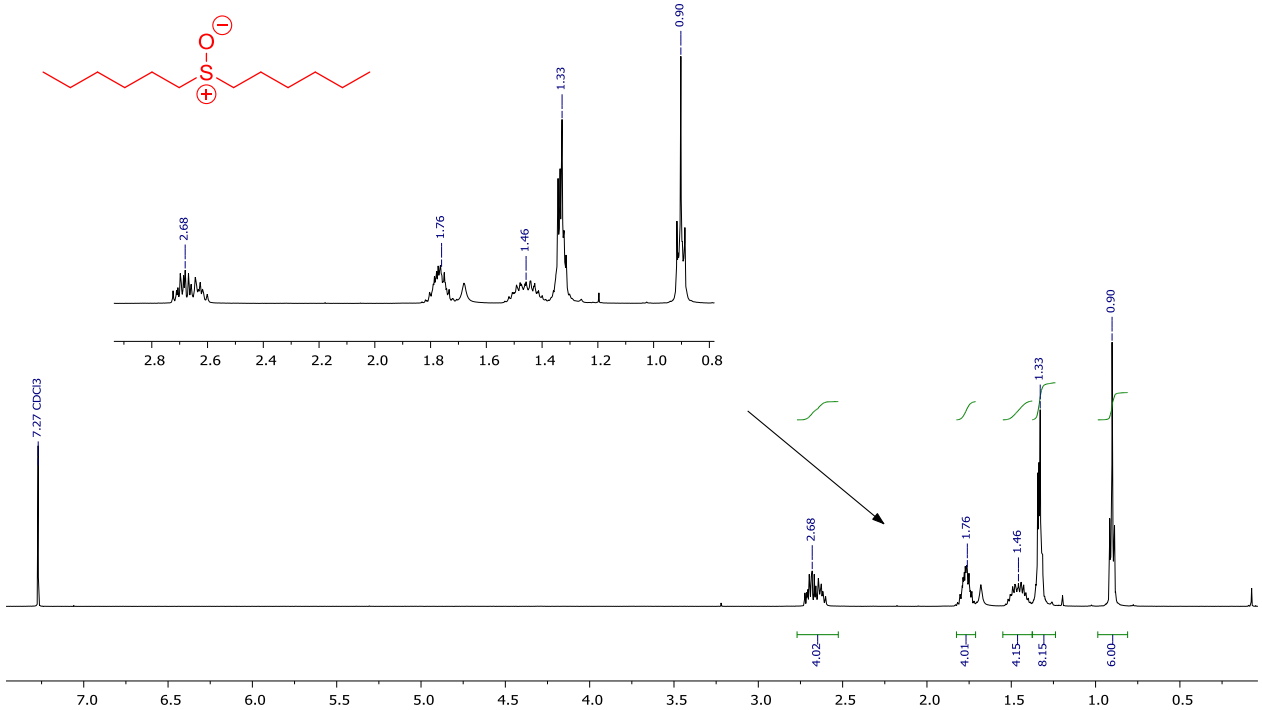



**Figure S12.** 500 MHz $^{1}$H NMR spectrum of dihexyl sulfoxide recovered from the reaction mixture.

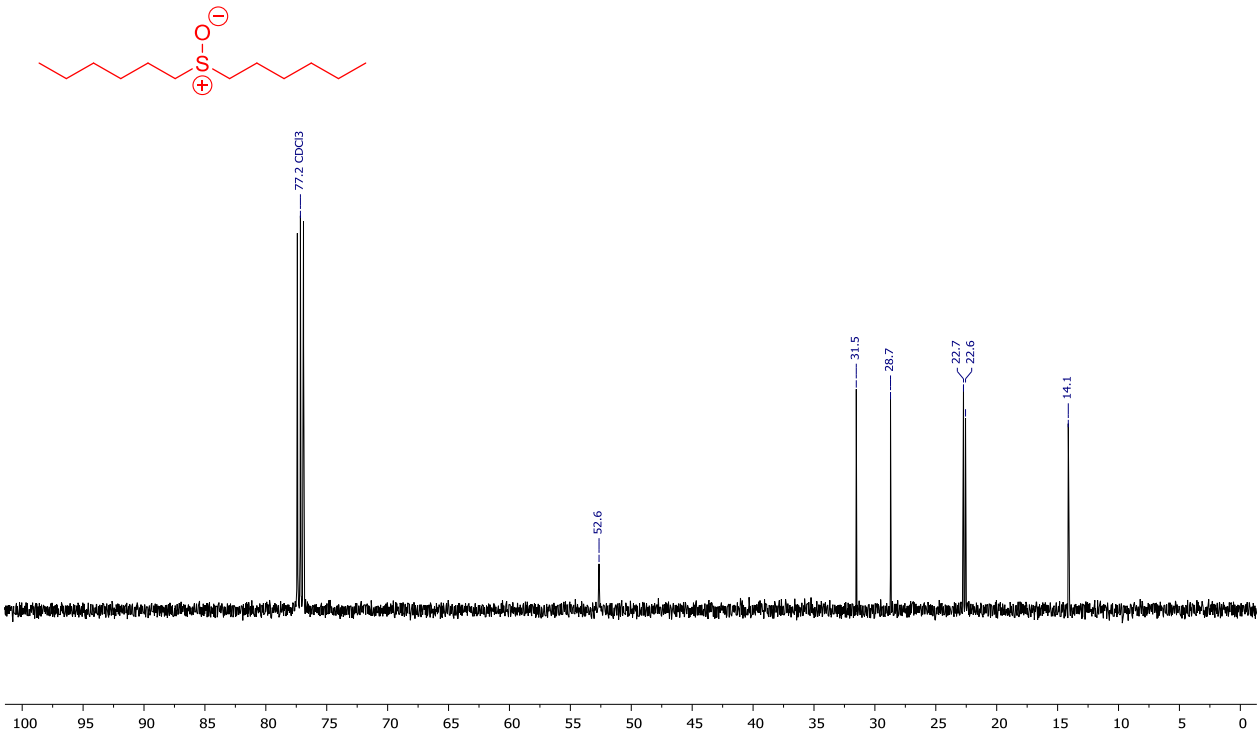



**Figure S13.** 125.94 MHz $^{13}C\{^{1}H\}$ NMR spectrum of dihexylsulfoxide.

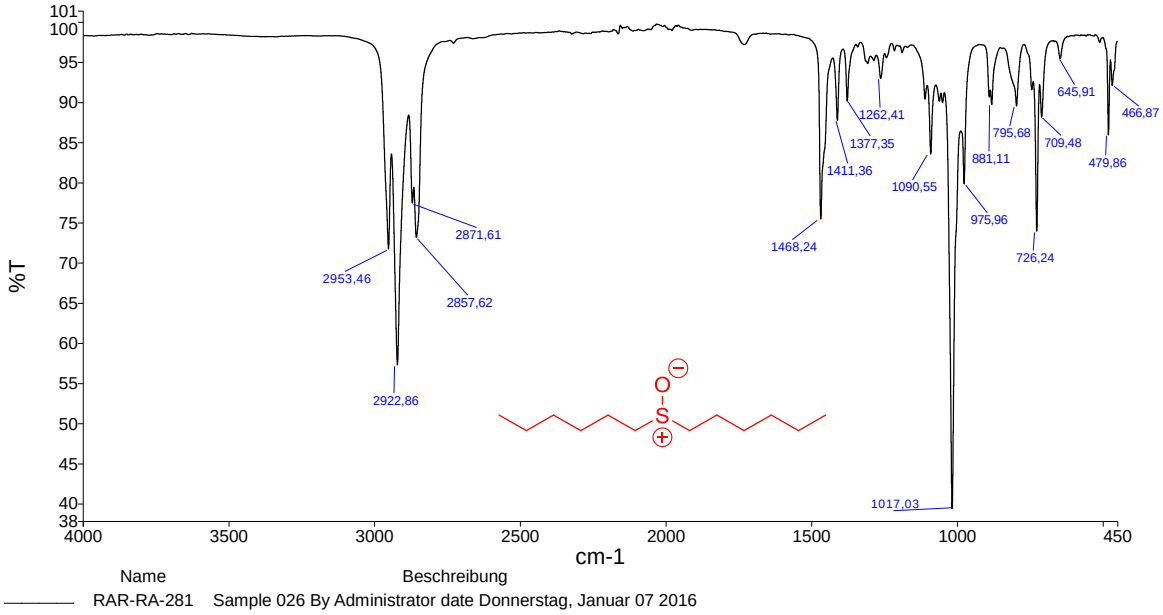
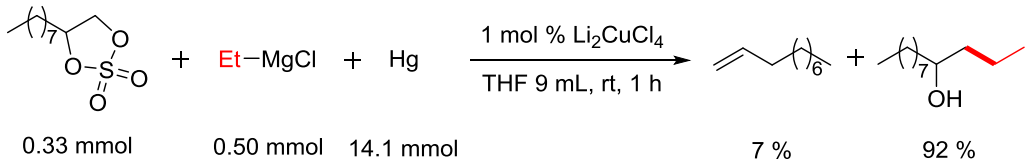



**Figure S14.** FT-IR spectrum of dihexyl sulfoxide recovered from the reaction mixture.

# Mercury drop test

Inside of a dry box, 1,2-decanediol cyclic sulfate (0.33 mmol), mercury (2.8 g, 14.1 mmol) and 3 mL of dry THF were charged in a 14 mL dram vial equipped with a PTFE-lined stir bar. The vial was closed with a septum screw cap and was then removed from the dry box. $Li_2CuCl_4$ (1% mol, 33 μL of a 0.1 M commercial solution in THF) and tridecane (42.6 mg, 0.23 mmol) were charged and the vial was placed on a stir plate. The appropriate ethylmagnesium chloride reagent (250 μL of a 2.0 M solution, 0.50 mmol) was added quickly and in a single portion to the reaction mixture under vigorous stirring to allow for fast mixing. After 1 h, the reaction mixture was quenched with 2 mL of a 20% aqueous solution of $H_2SO_4$ and the mixture was stirred overnight to effect complete hydrolysis of the resulting sulfate. This mixture was extracted with 5 mL of MTBE. The organic extract was washed once with a 5 mL portion of saturated $Na_2CO_3$, dried over $MgSO_4$ and analyzed by GC chromatography.



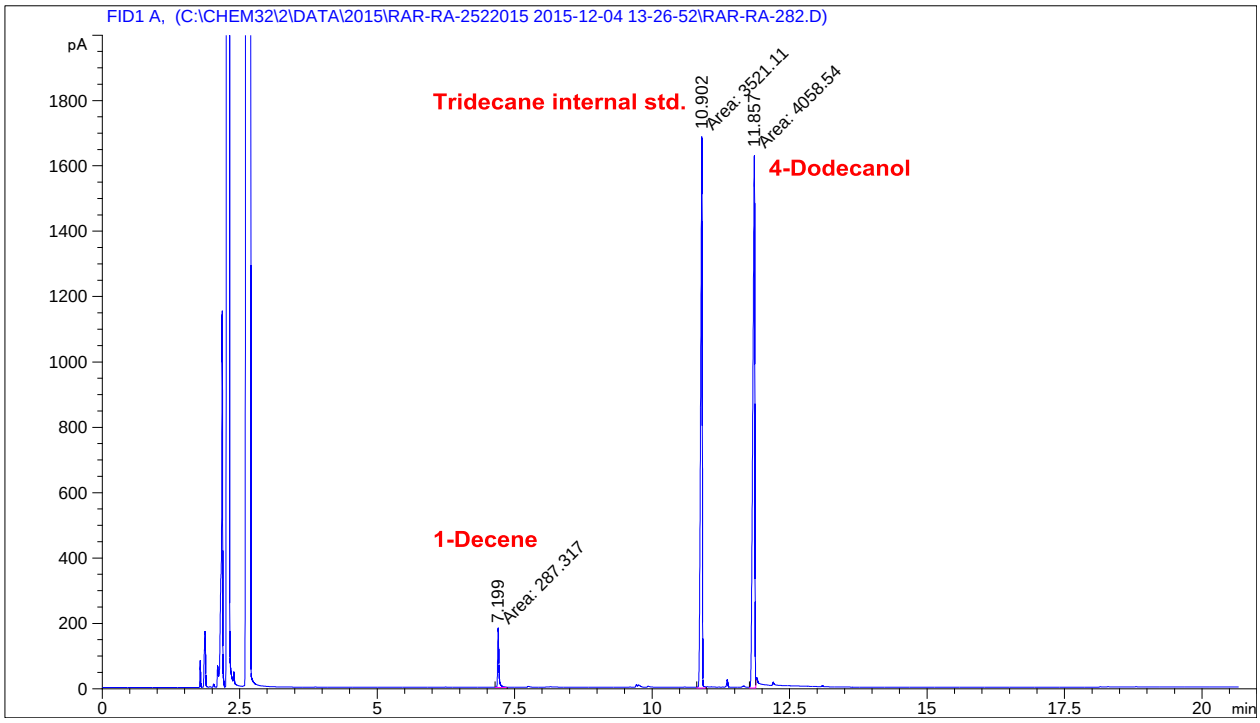
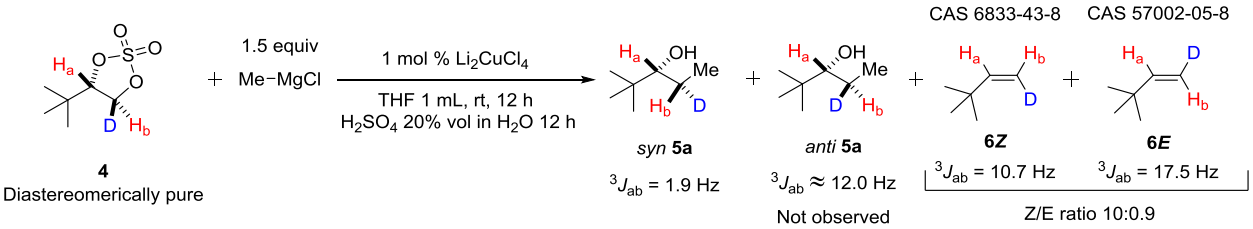



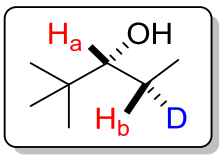

**Figure S15.** GC chromatogram of the reaction mixture formed after treating the 1,2-decanediol cyclic sulfate with ethylmagnesium chloride in the presence of excess mercury.

# Mechanistic experiments

Inside of a dry box, diastomerically pure 3,3-dimethylbutane-1-*d*-1,2-diol cyclic sulfate (0.5 mmol, 90.1 mg) and 1 mL of dry THF-$d_8$ were charged in a 14 mL dram vial equipped with a PTFE-lined stir bar. The vial was closed with a septum screw cap and was then removed from the dry box. $Li_2CuCl_4$ (1% mol, 50 μL of a 0.1 M solution in THF) was charged, followed by the appropriate alkylmagnesium chloride reagent (0.75 mmol, 250 μL of a 3.0 M of a methylmagnesium chloride solution, 375 μL of a 2.0 M solution of *i*-propylmagnesium chloride, and 750 μL of a 1.0 M solution of *t*-butylmagnesium chloride) was added quickly and in a single portion to the reaction mixture under vigorous stirring to allow for fast mixing. After stirring overnight, volatiles were vacuum transferred and NMR spectra were collected. The residue was hydrolyzed with 2 mL of a 20% solution of $H_2SO_4$ overnight, and was extracted ×3 with 5 mL of MTBE. The organic extracts were washed once with 2 mL of a saturated solution of $Na_2CO_3$, dried over $MgSO_4$, and the solvent removed in a rotary evaporator. Due to the low yield and low boiling points of the products, spectral analyses were performed on the crude products. NMR data for (Z)-3,3-dimethyl-1-butene-1-*d* (CAS 6833-43-8) and (E)-3,3-dimethyl-1-butene-1-*d* (CAS 57002-05-8) have been reported in the literature.[10]




**Syn *2,2-Dimethyl-3-pentanol-4*-d (*syn* 5a)**



**$^1$H NMR** (400.13 MHz, $CDCl_3$) (Figure S16 and S17) δ 0.89 (s, 9H), 1.00 (dt, $^3J_{H-H}$ = 7.6 Hz, $^3J_{H-D}$ = 1.1 Hz, 3H), 1.58 (qq, $^3J_{H-H}$ = 7.5 Hz, $^3J_{Ha-Hb}$ = 1.9 Hz, $^2J_{H-D}$ = 2.0 Hz, 1H), 3.09 (apparent quartet, *J* = 1.7 Hz, 1H). **$^{13}$C{$^1$H} NMR** (100.63 MHz, $CDCl_3$) (Figure S18 and S19) δ 11.6 (s) , 24.1 (s), 25.9 (s), 35.1 (s), 81.8 (s).

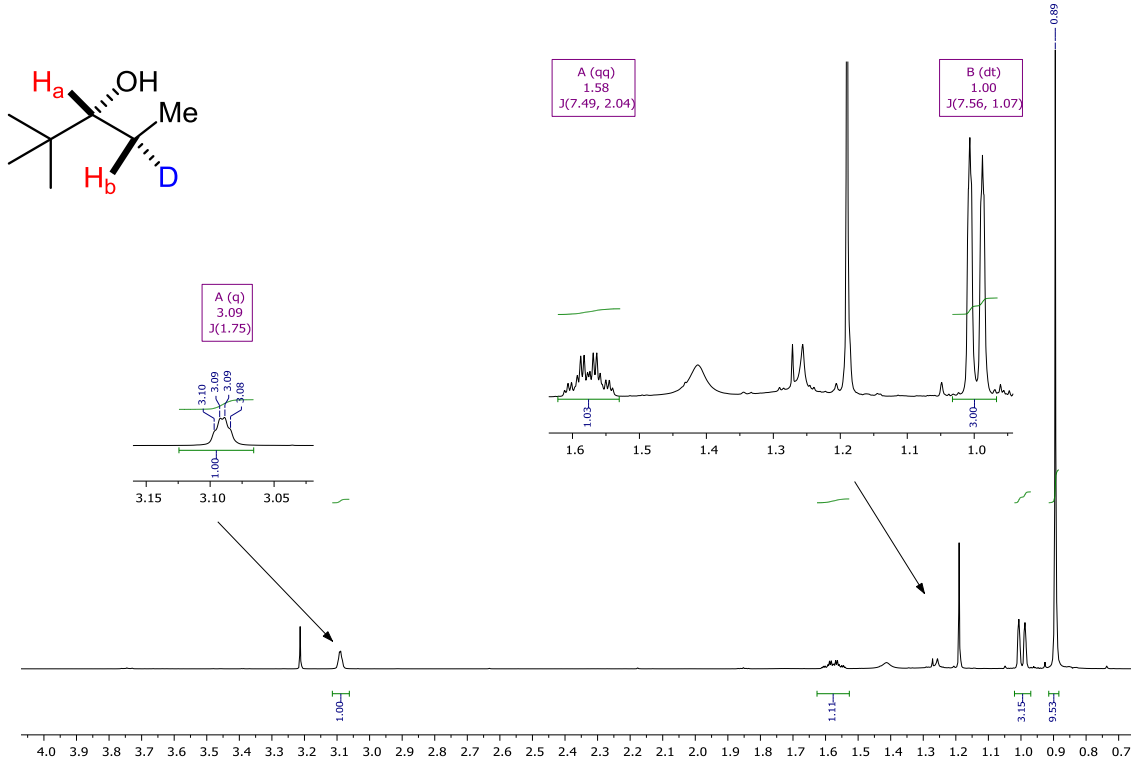



**Figure S16.** 400.13 MHz $^{1}$H NMR spectrum of *syn* 2,2-dimethyl-3-pentanol-4-*d* (***syn* 5a**).

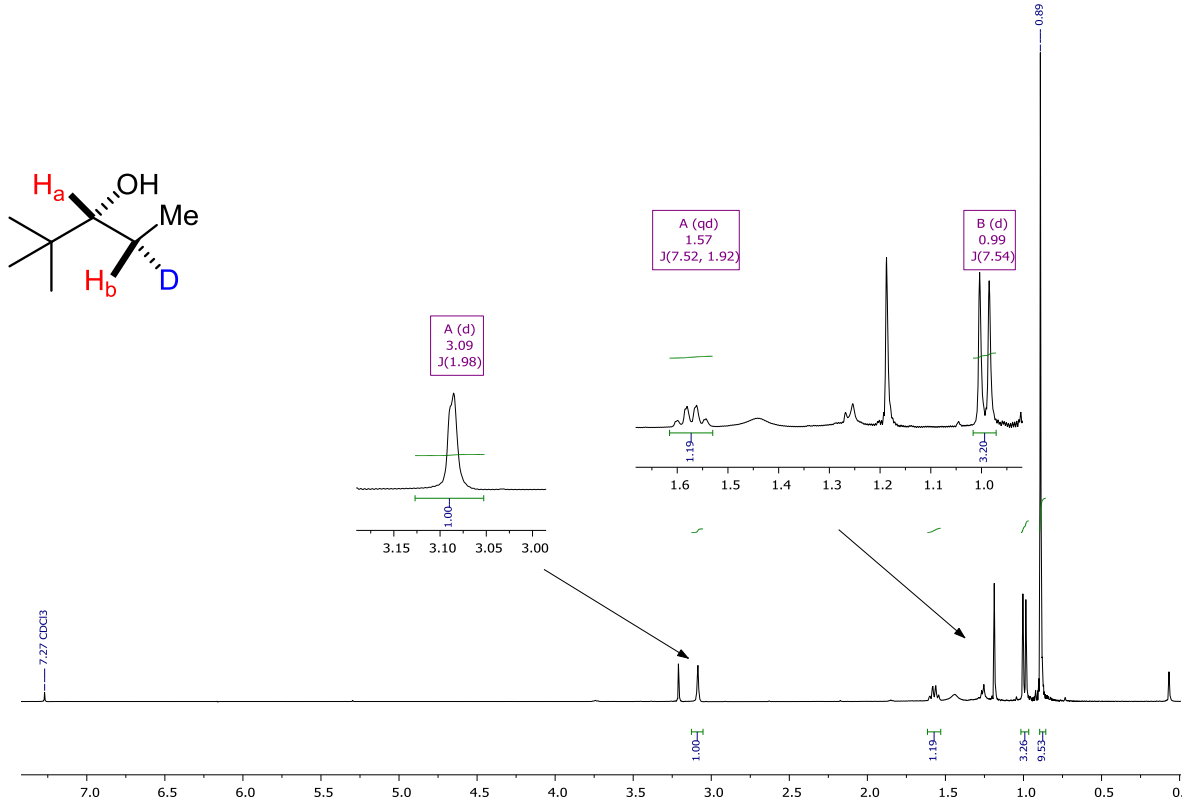



**Figure S17.** 400.13 MHz $^{1}$H{$^{2}$H} NMR spectrum of *syn* 2,2-dimethyl-3-pentanol-4-*d* (***syn* 5a**).

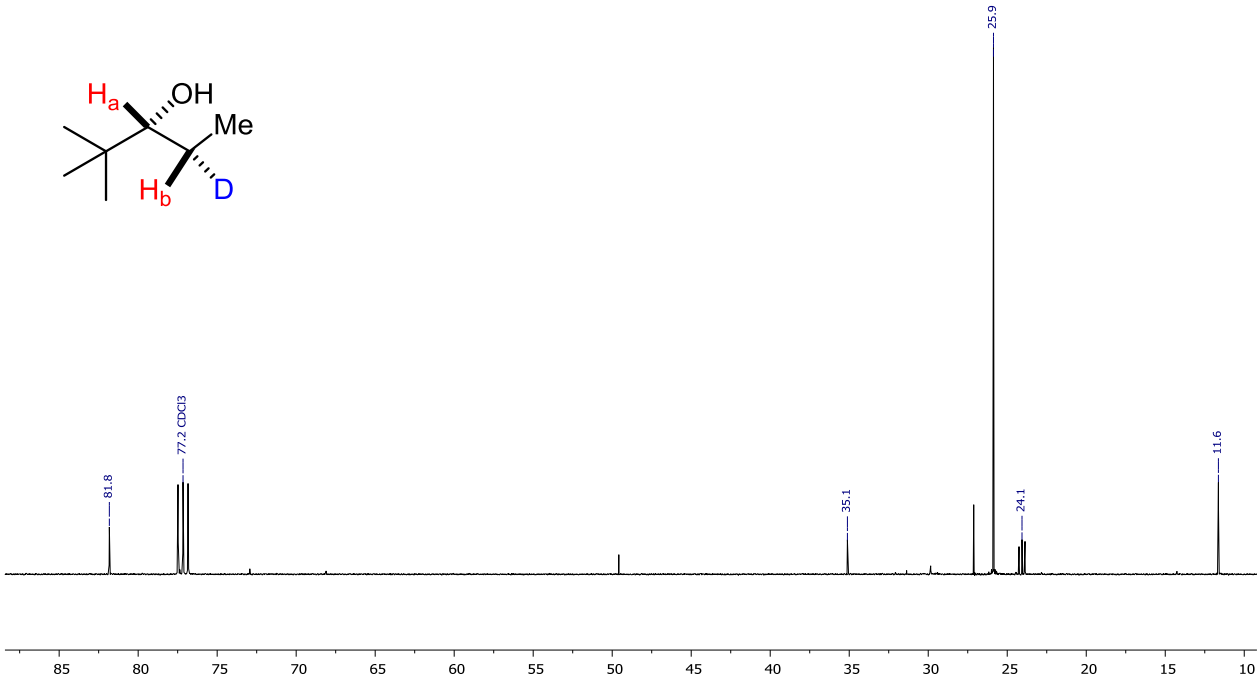



**Figure S18.** 100.63 MHz $^{13}C\{^{1}H\}$ NMR spectrum of *syn* 2,2-dimethyl-3-pentanol-4-*d* (***syn* 5a**).

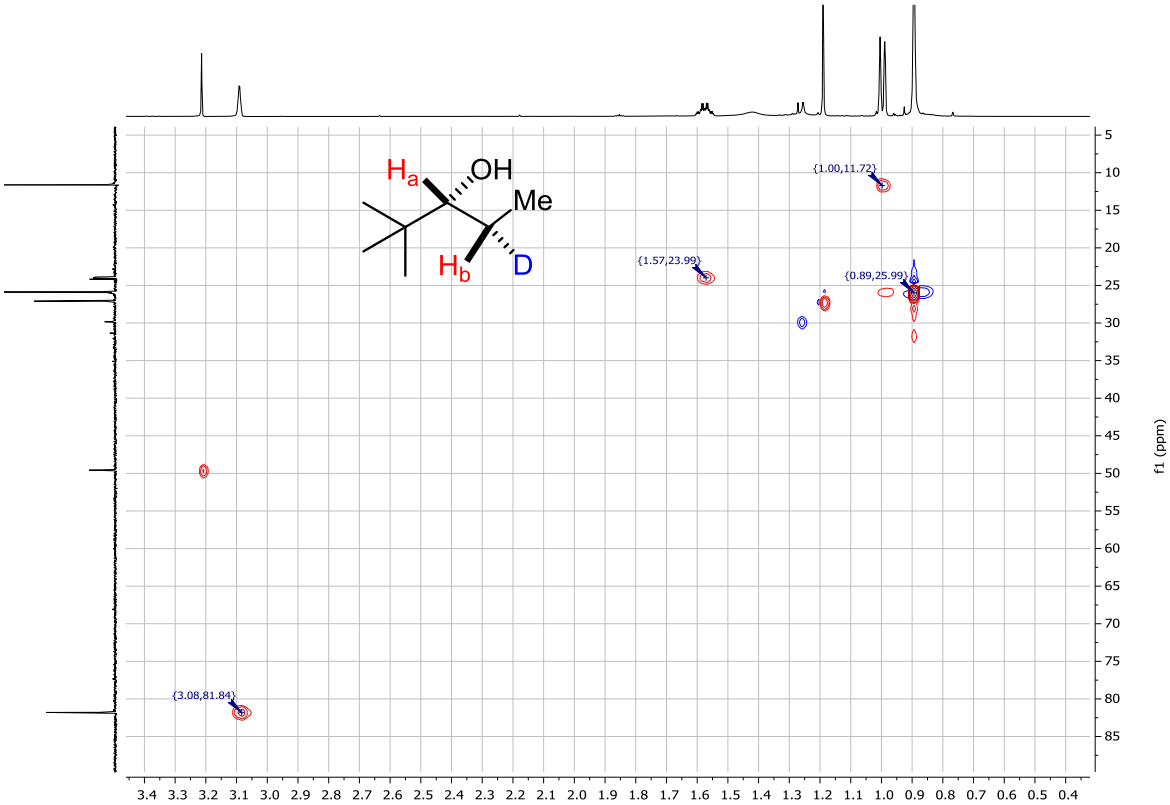



**Figure S19.** HSQC spectrum of *syn* 2,2-dimethyl-3-pentanol-4-*d* (***syn* 5a**).

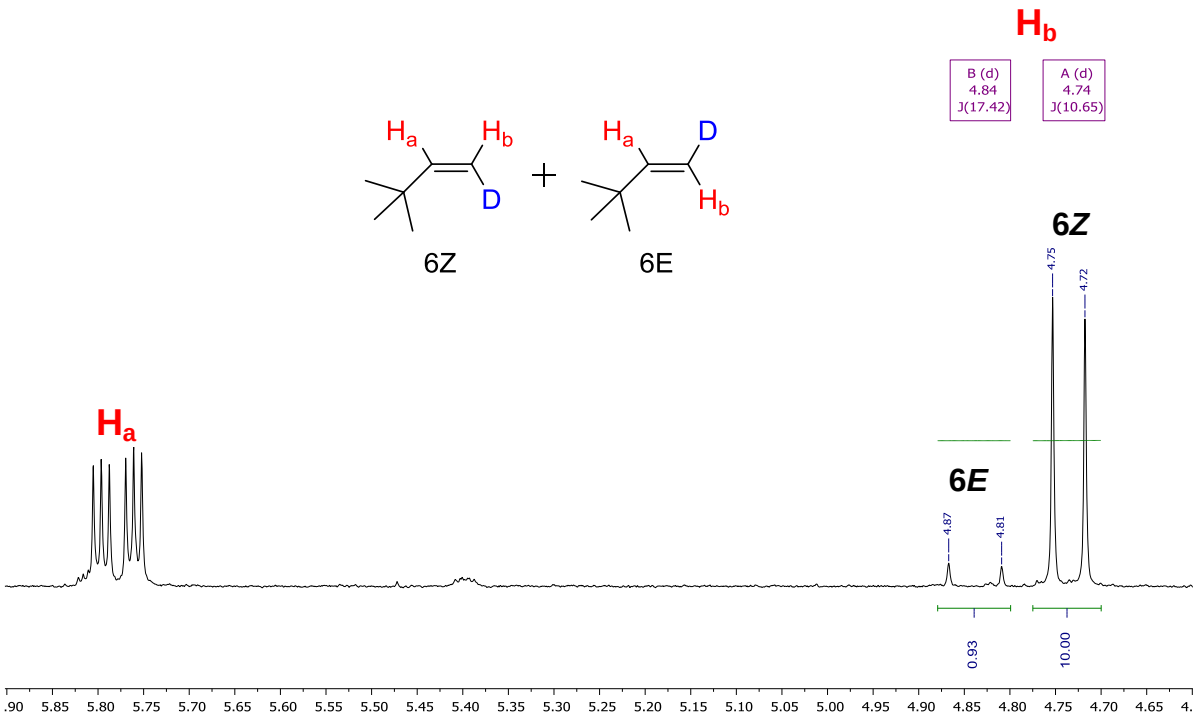
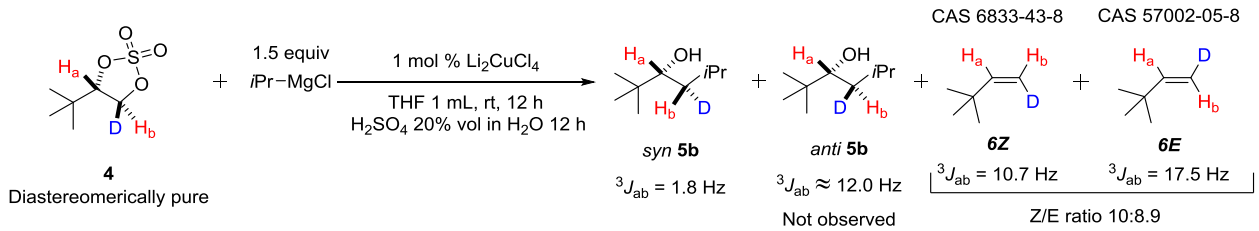
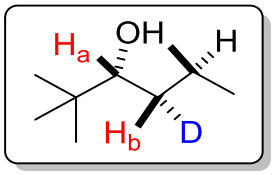



**Figure S20.** $^{1}$H 500 MHz NMR spectrum of the volatiles collected by vacuum transfer from the reaction mixture prior to quenching. Spectrum collected in THF-$d_8$.




**Syn *2,2,5-Trimethyl-3-hexanol-4*-d (*syn* 5b)**



**$^{1}$H NMR** (400.13 MHz, $CDCl_3$) (Figure S21) δ 0.89 (s, 9H), 0.90 (d, $^{3}J_{H\text{-}H}$ = 6.6 Hz, 3H), 0.95 (d, $^{3}J_{H\text{-}H}$ = 6.6 Hz, 3H), 1.21 (dq, $^{3}J_{Ha\text{-}Hb}$ = 2.0 Hz, $^{2}J_{H\text{-}D}$ = 2.0 Hz, $^{3}J_{H\text{-}H}$ = 10.0 Hz, 1H), 1.79 (dhept, $^{3}J_{H\text{-}H}$ = 6.6, 10.0 Hz, 1H), 3.28 (bs, 1H).
**$^{13}$C{$^{1}$H} NMR** (100.63 MHz, $CDCl_3$) (Figure S22 and S23) δ 21.4 (s), 24.3 (s), 25.0 (s), 25.8 (s), 35.0 (s), 40.5 (t, $^{1}J_{C\text{-}D}$ = 19.0 Hz), 77.7 (s).

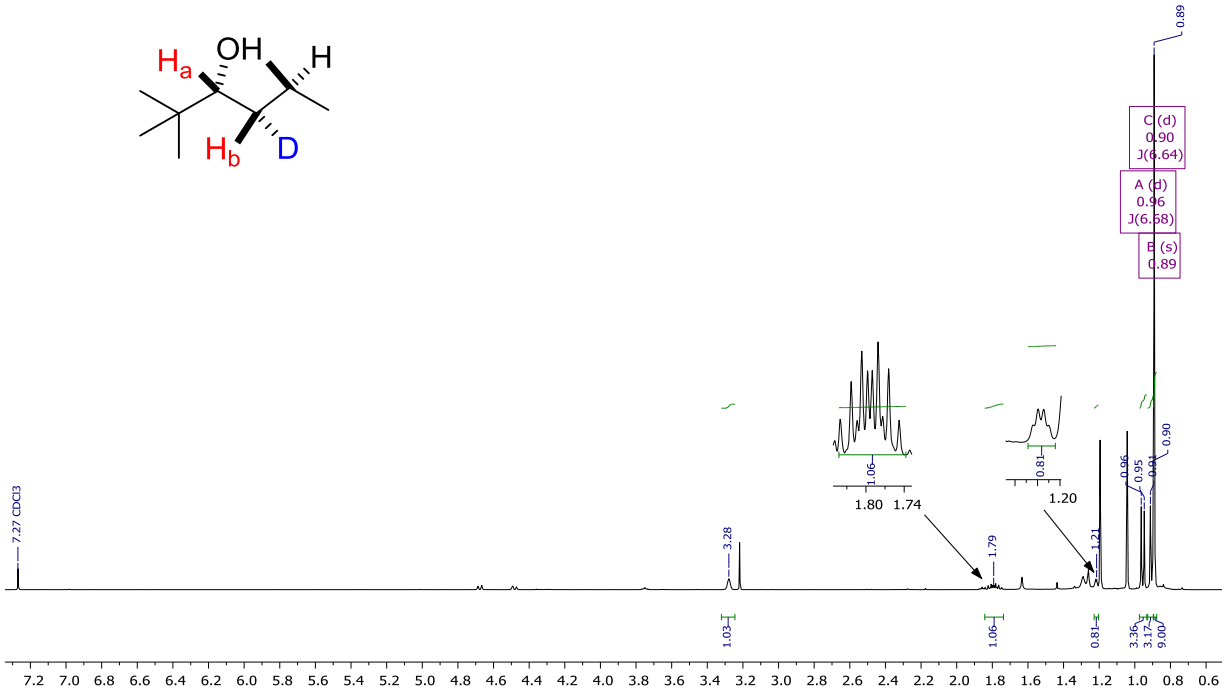



**Figure S21.** 400.13 MHz $^{1}$H NMR spectrum of *syn* 2,2,5-trimethyl-3-hexanol-4-*d* (***syn* 5b**). One of the components of the $H_b$ signal (δ = 1.21 ppm) is partially obscured by a residual solvent resonance. See Figure S25.

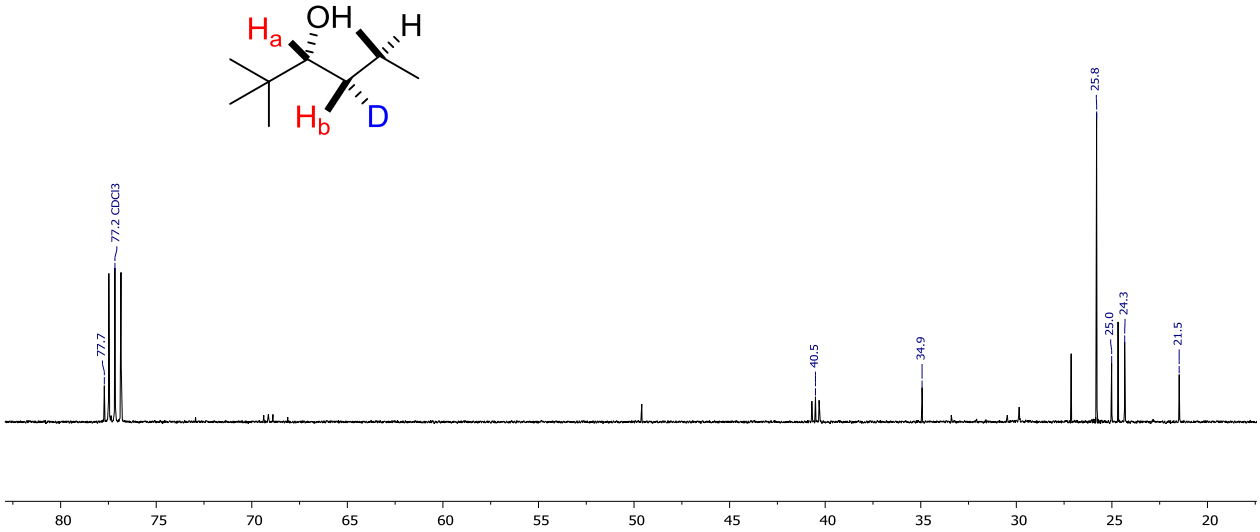



**Figure S22.** 100.63 MHz $^{13}C\{^{1}H\}$ NMR spectrum of *syn* 2,2,5-trimethyl-3-hexanol-4-*d* (***syn* 5b**).

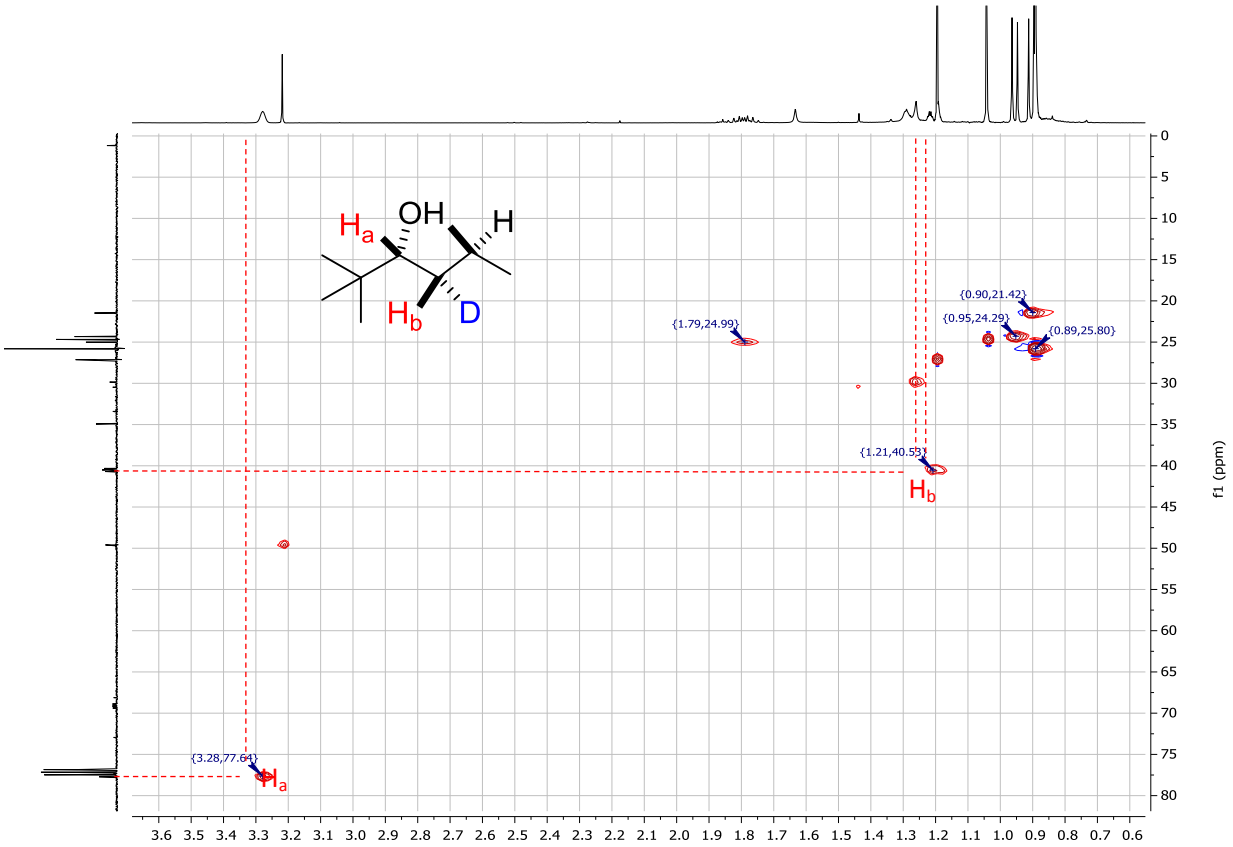



**Figure S23.** HSQC spectrum of *syn* 2,2,5-trimethyl-3-hexanol-4-*d* (***syn* 5b**).

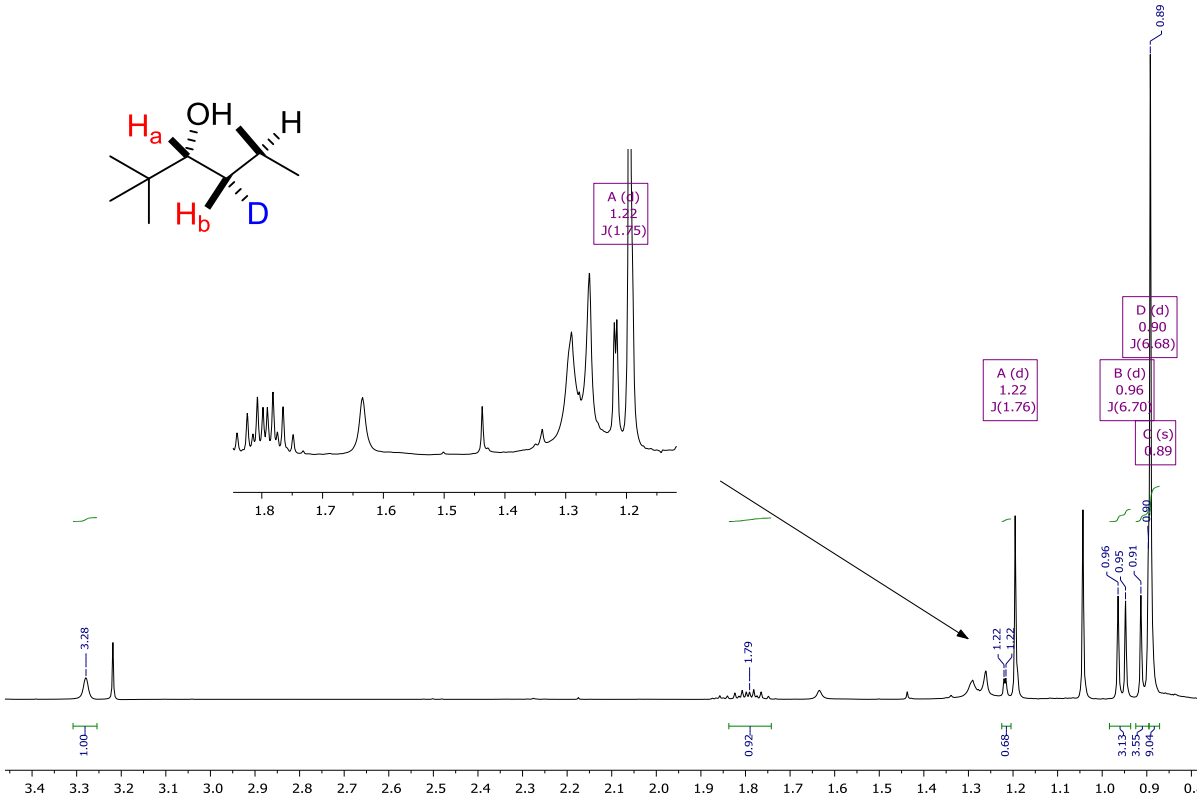



**Figure S24.** 400.13 MHz $^{1}H\{^{2}H\}$ NMR spectrum of *syn* 2,2,5-trimethyl-3-hexanol-4-*d* (***syn* 5b**).

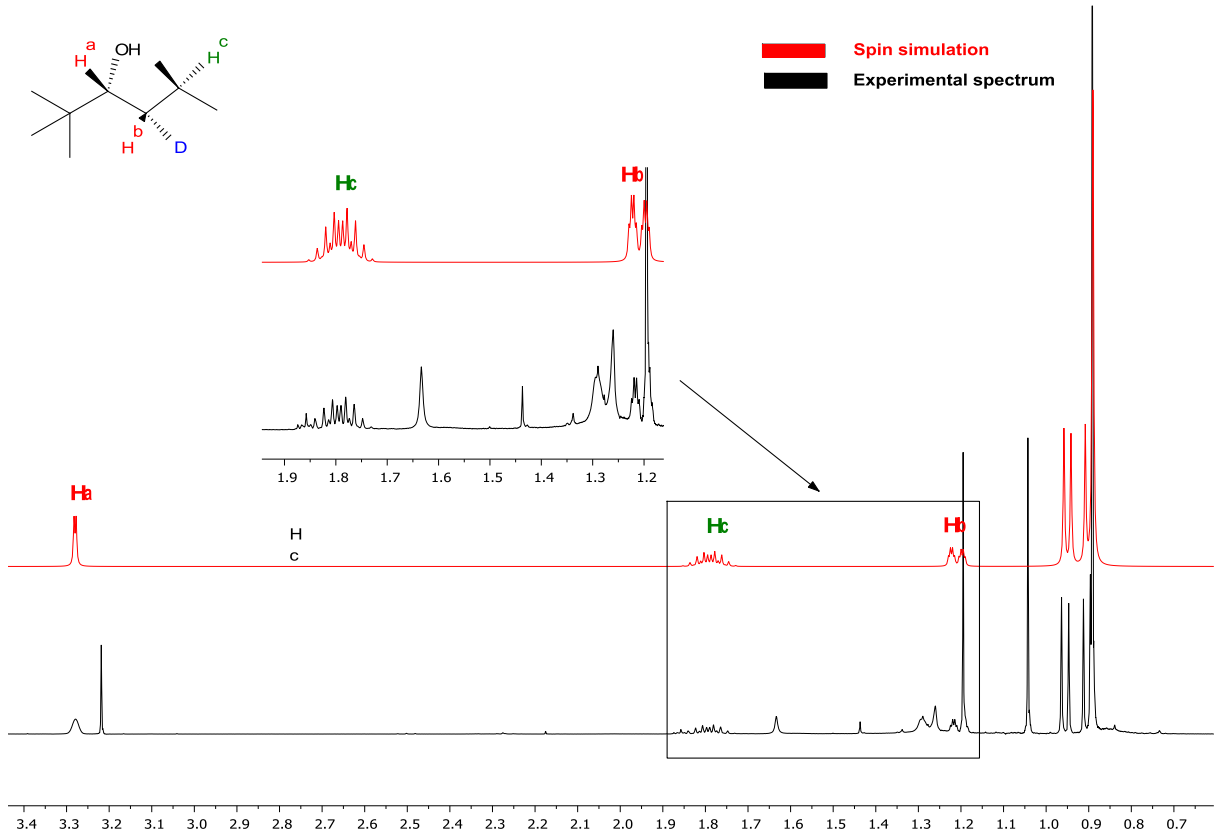



**Figure S25.** Spin simulation and experimental spectrum of the *syn* 2,2,5-trimethyl-3-hexanol-4-*d* (***syn* 5b**), showing the eclipsed multiplet at $\delta$ = 1.21 ppm.

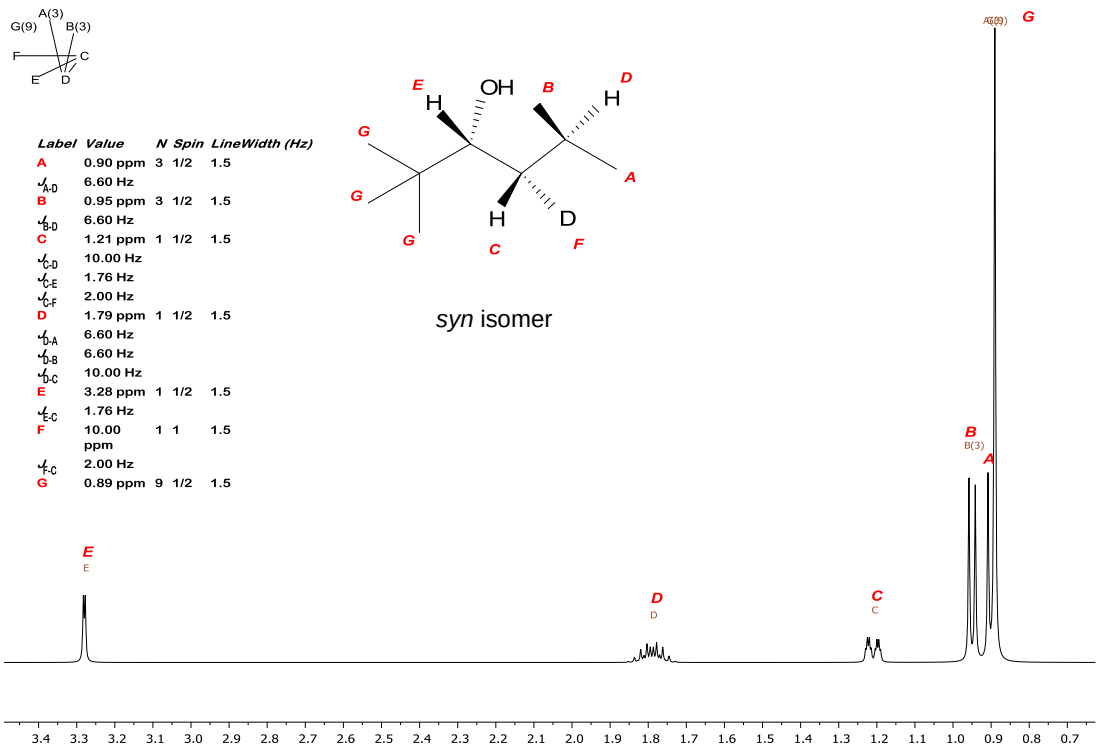



**Figure S26.** 400 MHz spectrum simulation of *syn* 2,2,5-trimethyl-3-hexanol-4-*d* (***syn* 5b**), calculated with MestreNova™ version 10.0.2. $J_{B\text{-}D}$, $J_{A\text{-}D}$, $J_{D\text{-}C}$ and $J_{C\text{-}F}$ coupling constants were obtained directly from experimental spectra.

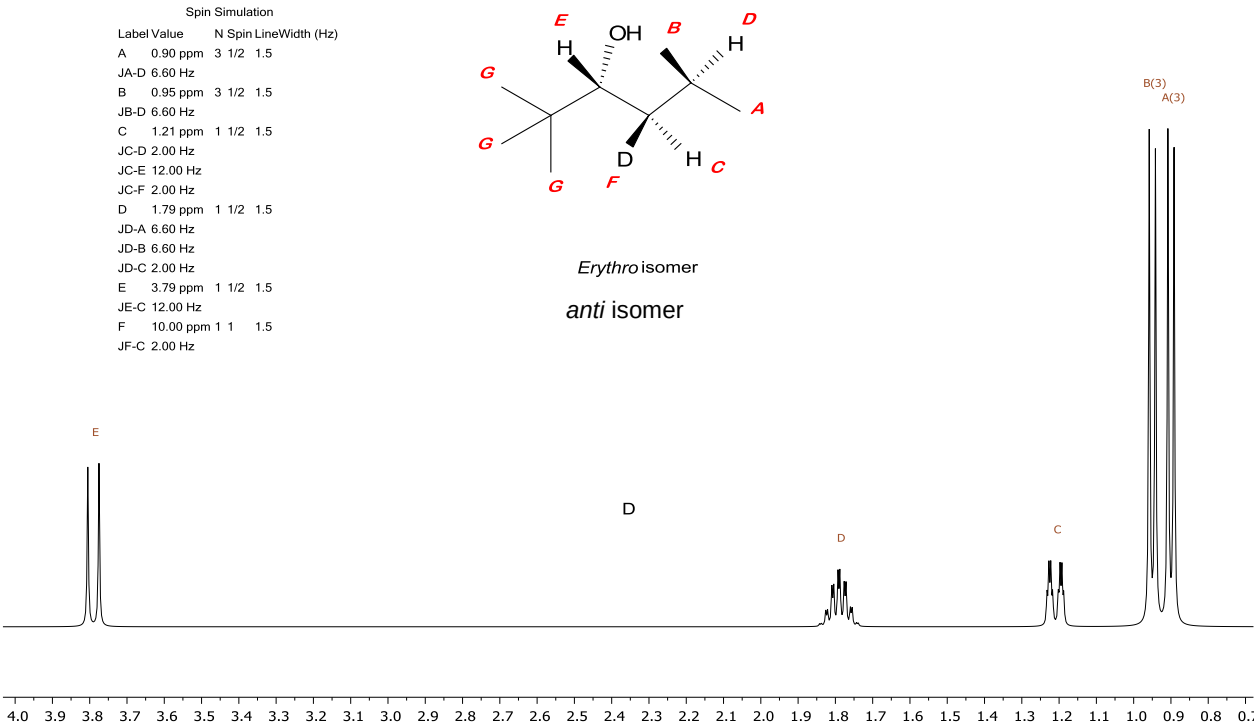



**Figure S27.** 400 MHz spectrum simulation of *anti* 2,2,5-trimethyl-3-hexanol-4-*d* (***anti* 5b**), calculated with MestreNova™ version 10.0.2. $J_{B\text{-}D}$, $J_{A\text{-}D}$, and $J_{C\text{-}F}$ coupling constants were obtained directly from experimental spectra.

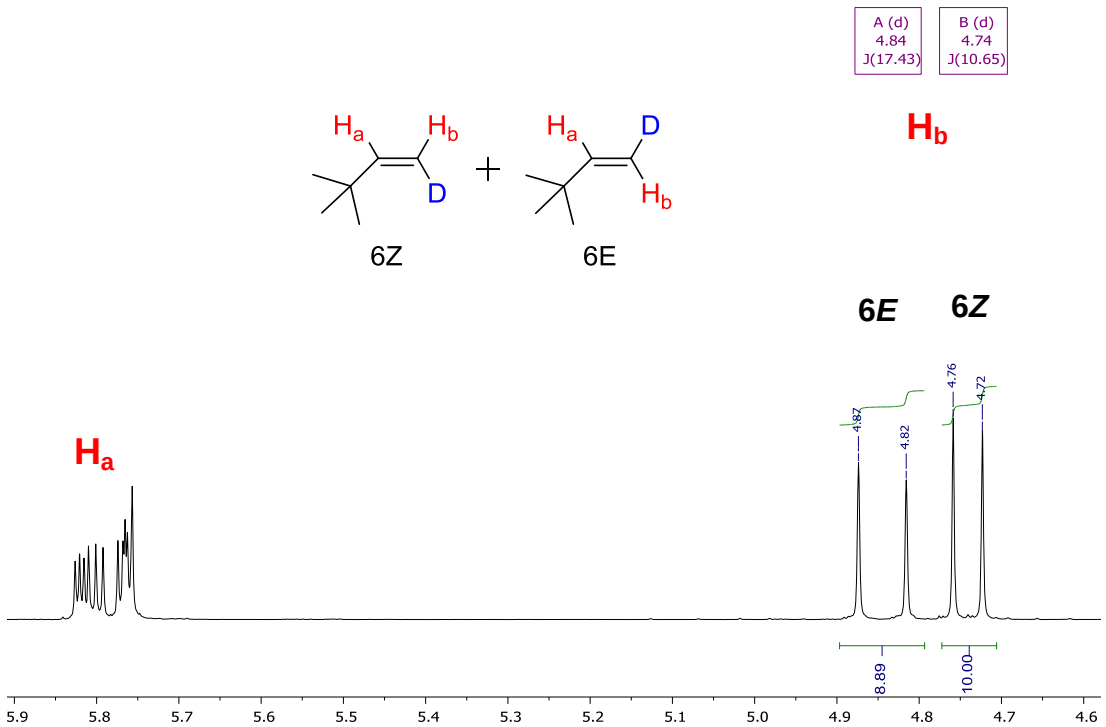
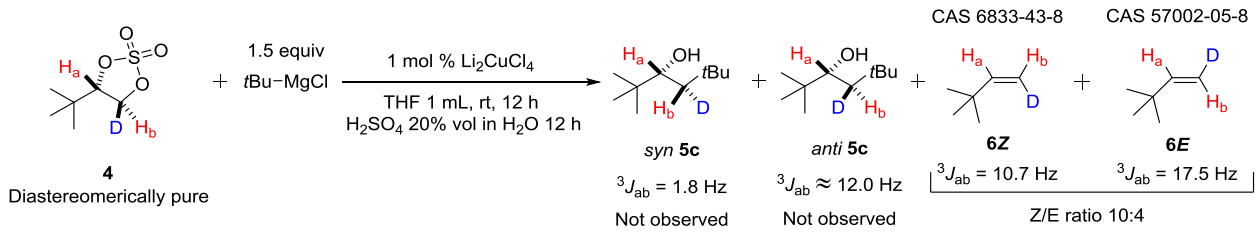



**Figure S28.** $^{1}$H 500 MHz NMR spectrum of the volatiles collected by vacuum transfer from the reaction mixture prior to quenching.



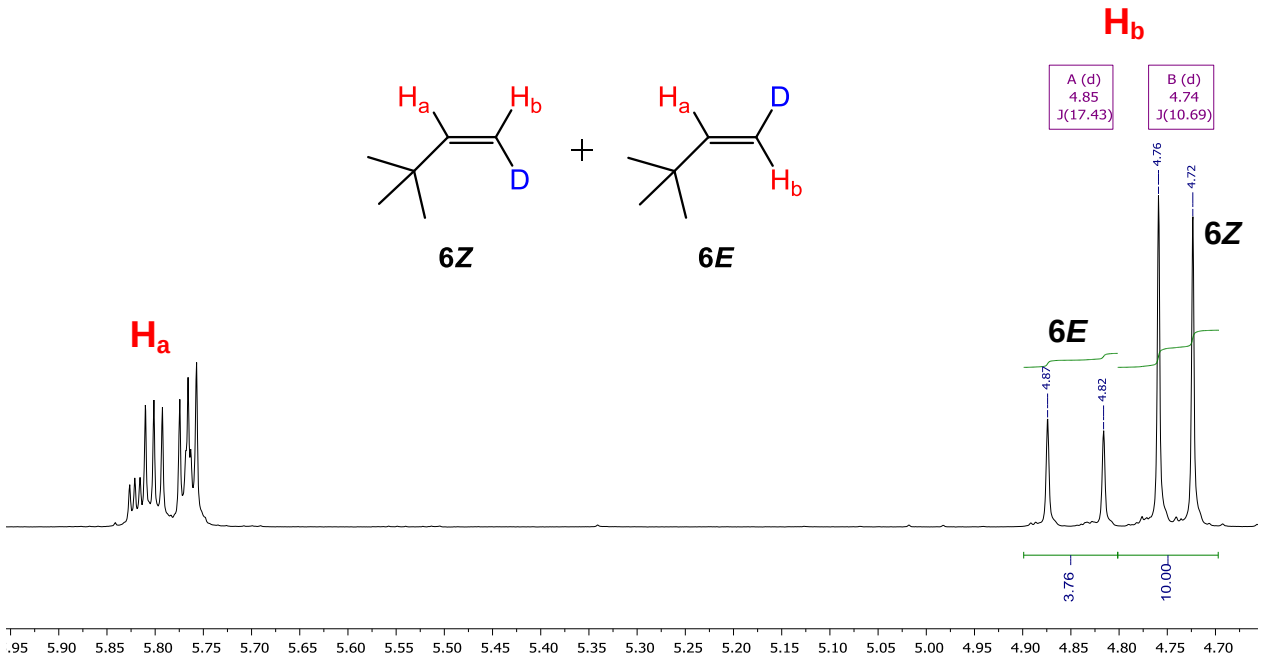
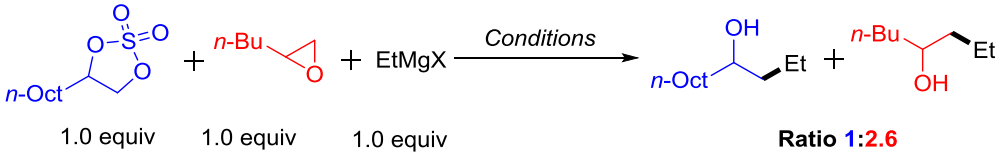




**Figure S29.** $^{1}$H 500 MHz NMR spectrum of the volatiles collected by vacuum transfer from the reaction mixture prior to quenching.

## Competition experiments




Inside of a dry box, 1,2-decanediol cyclic sulfate (0.3 mmol), 1,2-epoxyhexane (0.3 mmol), tridecane (0.3 mmol, 90 μL), and 4 mL of dry THF were charged in a 14 mL dram vial equipped with a PTFE-lined stir bar. The vial was closed with a septum screw cap and was then removed from the dry box. $Li_2CuCl_4$ (3.0 μmol, 30 μL of a 0.1 M commercial solution in THF) was charged and the vial was placed on a stir plate. Ethylmagnesium chloride (0.3 mmol, 150 μL of a 2.0 M solution) was added quickly and in a single portion to the reaction mixture under vigorous stirring to allow for fast mixing. After 1 h, the reaction mixture was quenched with 2 mL of a 20% aqueous solution of $H_2SO_4$ and the mixture was stirred overnight to effect complete hydrolysis of the resulting sulfate. This mixture was extracted with 3 × 10 mL of MTBE. The organic extracts were washed once with a 10 mL portion of saturated $Na_2CO_3$ and dried over $Na_2SO_4$. An aliquot from the extracts was transferred to an appropriate vial and subjected to GC analysis.

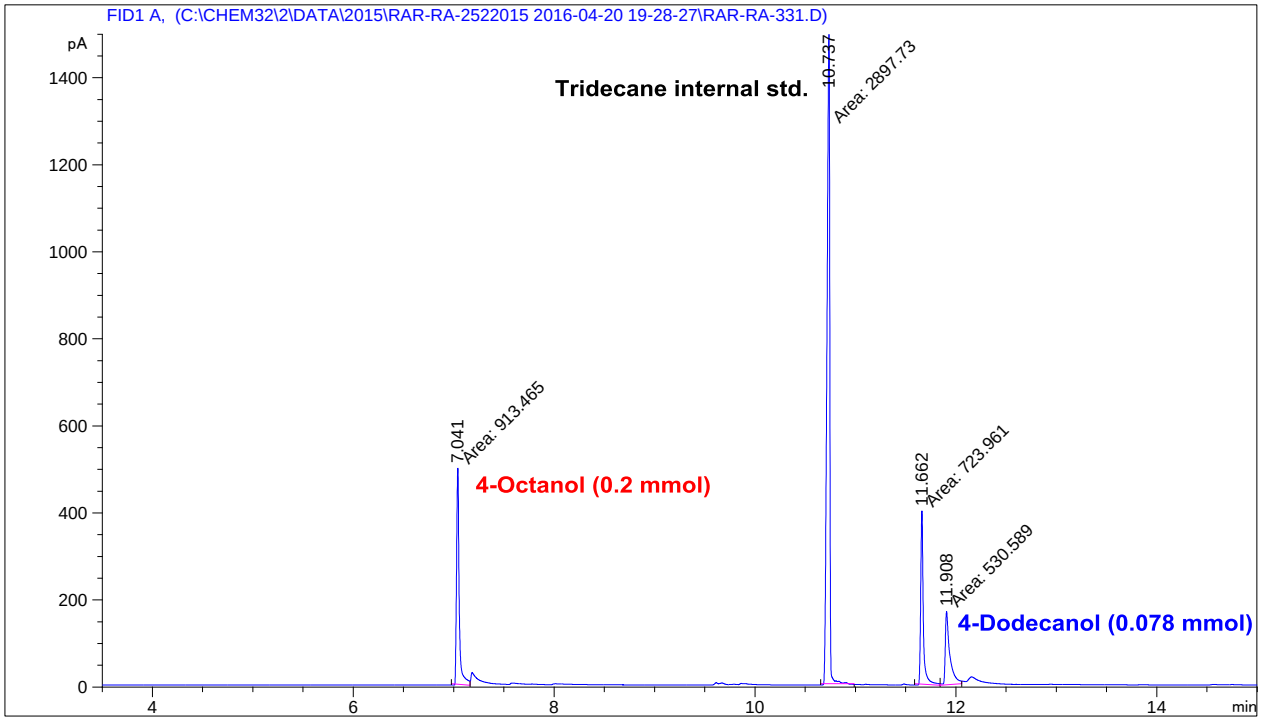



**Figure S30.** GC chromatogram of the reaction mixture formed after treating a 1:1 mixture of 1,2-decanediol cyclic sulfate and 1,2-epoxyethane with 1.0 equivalents of EtMgCl.

# NMR spectral data

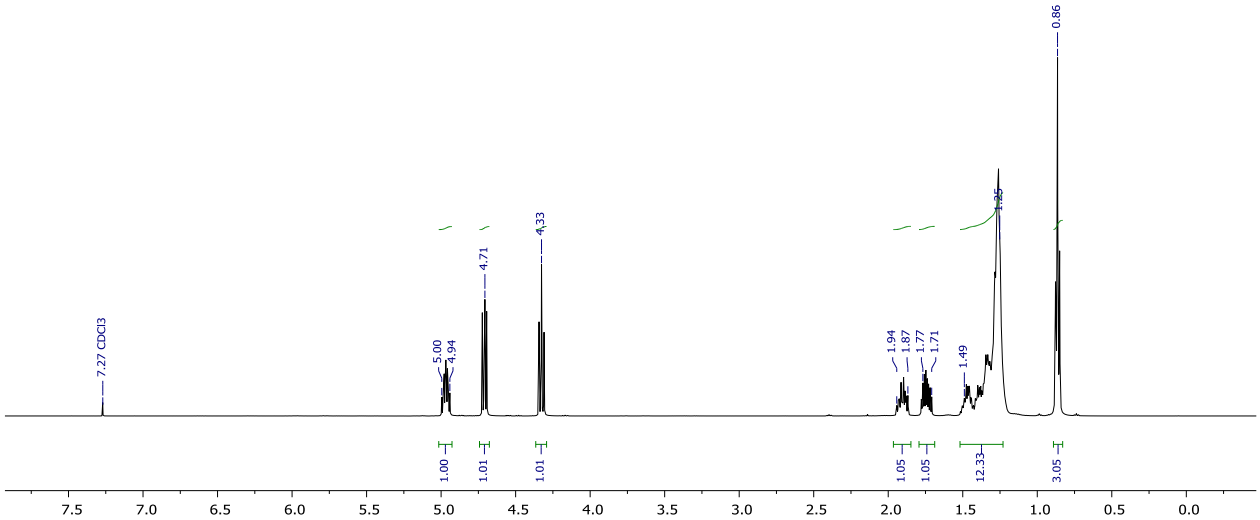



**Figure NMR-S1.** 500MHz $^{1}$H NMR spectrum of 4-octyl-1,3,2-dioxathiolane 2,2-dioxide .

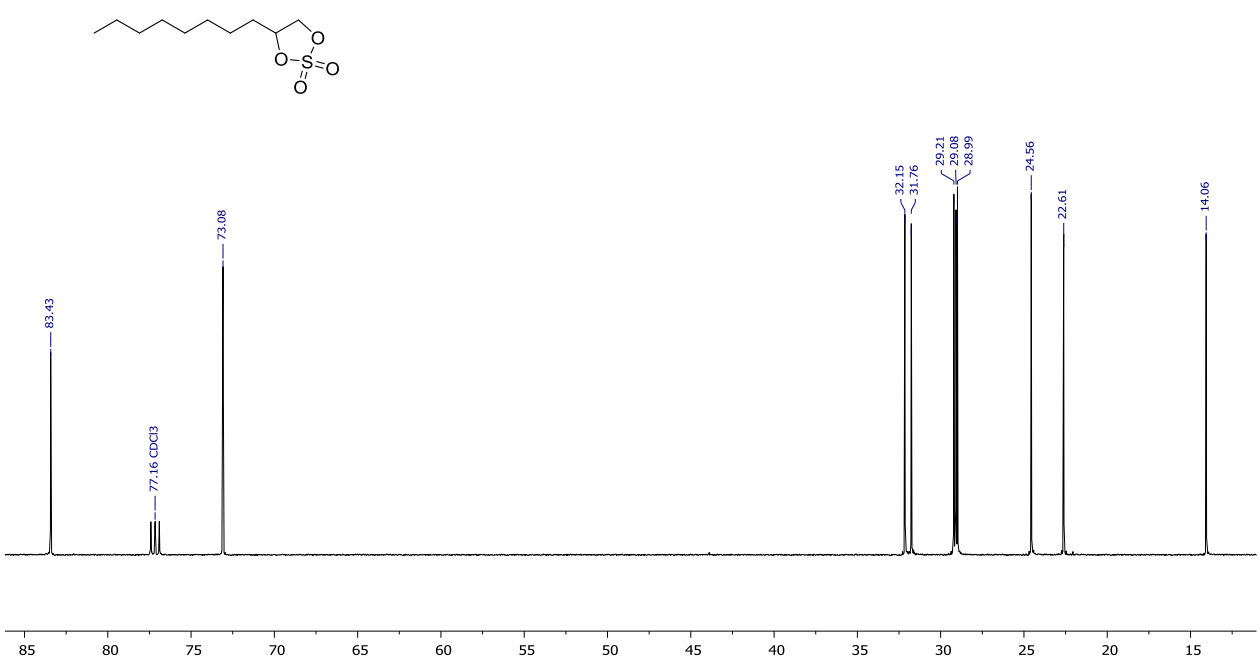



**Figure NMR-S2.** 125 MHz $^{13}$C{$^{1}$H} NMR spectrum of 4-octyl-1,3,2-dioxathiolane 2,2-dioxide .

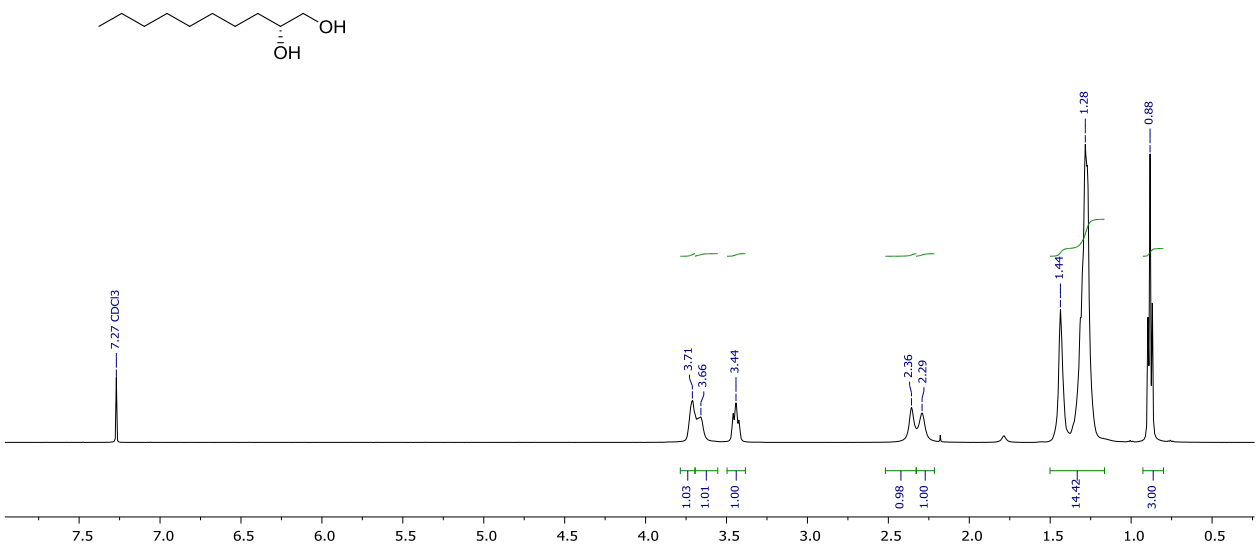



**Figure NMR-S3.** 500MHz $^{1}$H NMR spectrum of (R)-1,2-decanediol.

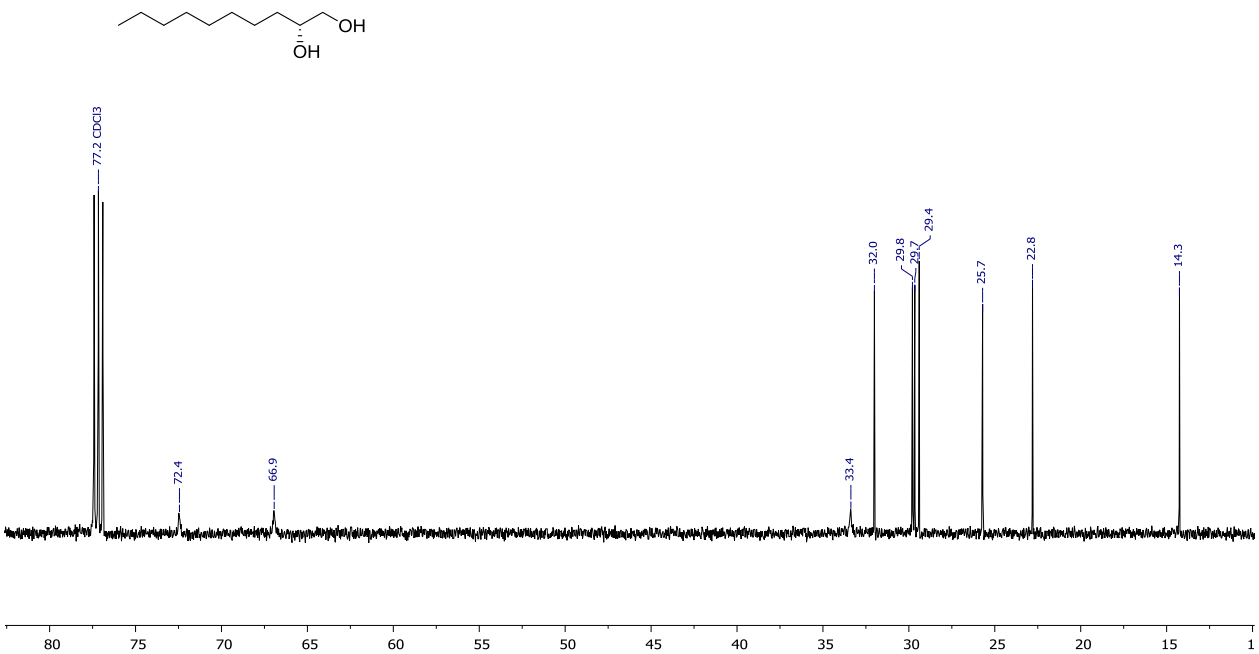



**Figure NMR-S4.** 125.94 MHz $^{13}$C{$^{1}$H} NMR spectrum of (R)-1,2-decanediol.

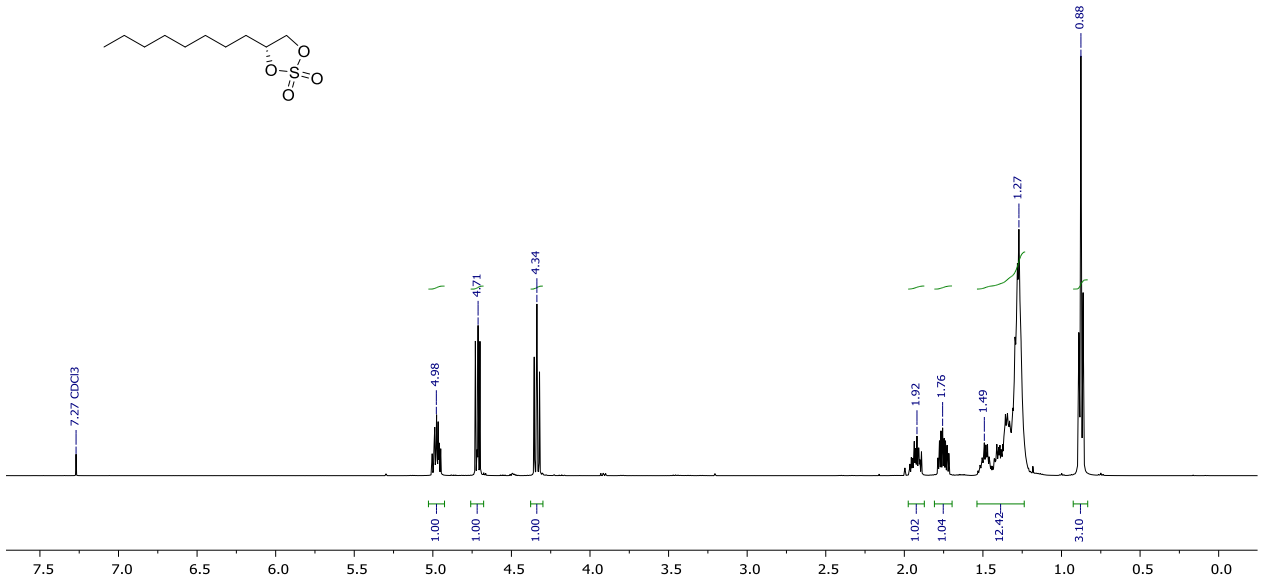



**Figure NMR-S5.** 500MHz $^{1}$H NMR spectrum of (R)-4-octyl-1,3,2-dioxothiolane-2,2-dioxide.

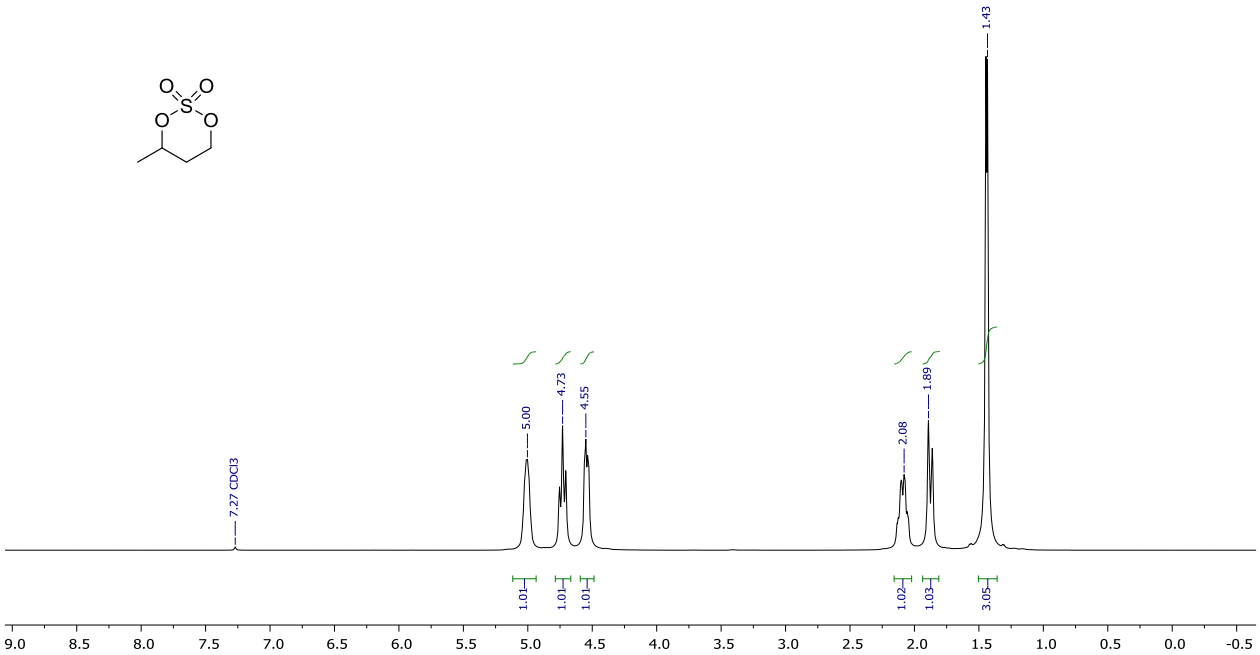



**Figure NMR-S6.** 500 MHz $^{1}$H NMR spectrum of 1,3-butanediol cyclic sulfate**.**

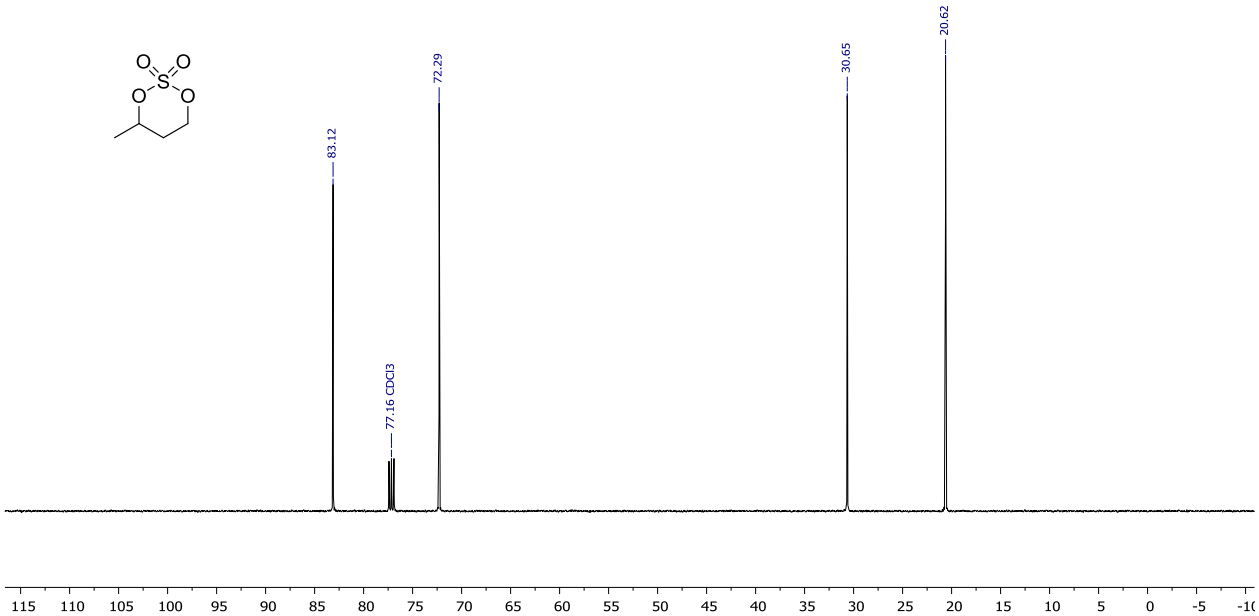



**Figure NMR-S7.** 125 MHz $^{13}C\{^{1}H\}$ NMR spectrum of 1,3-butanediol cyclic sulfate.

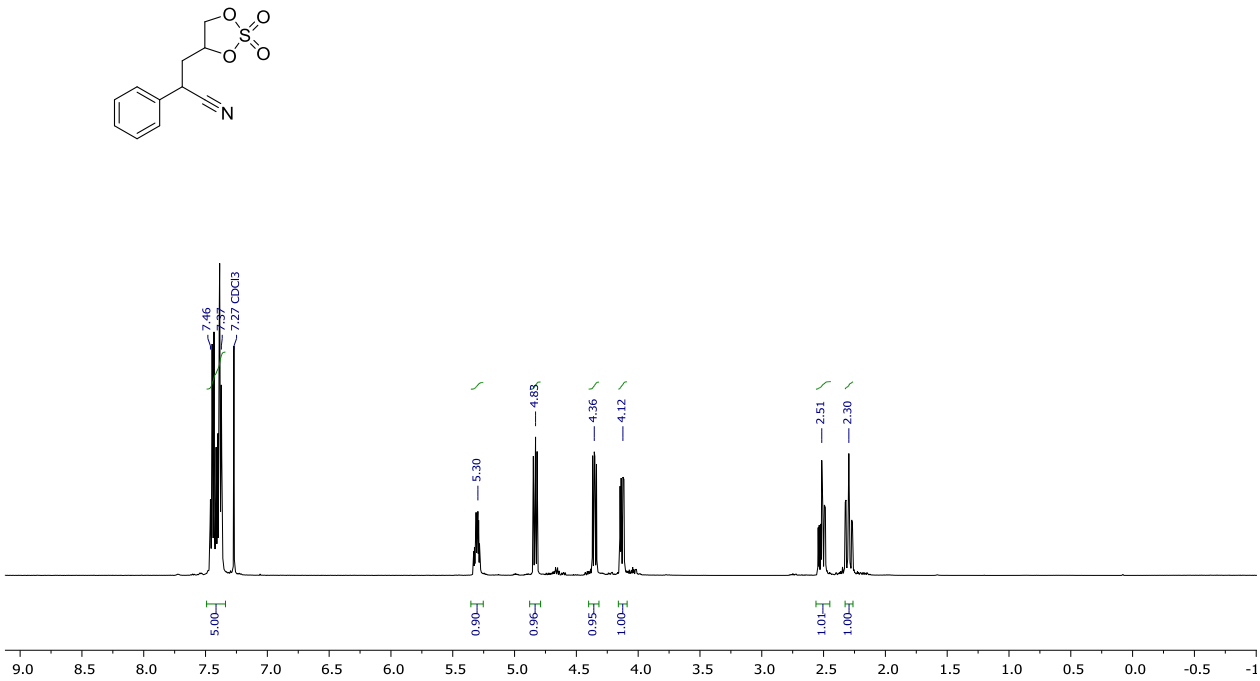



**Figure NMR-S8.** 500 MHz $^{1}H$ NMR spectrum of 3-(2,2-dioxido-1,3,2-dioxathiolan-4-yl)-2-phenylpropanenitrile.

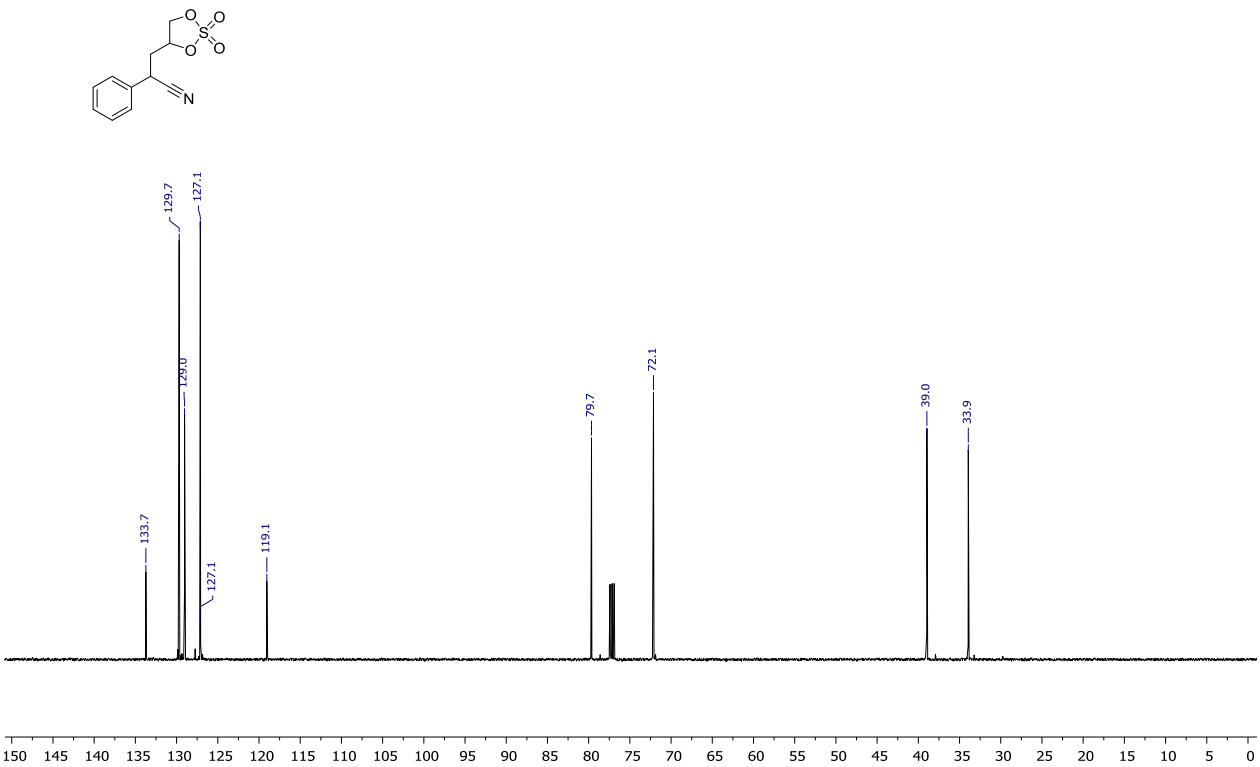
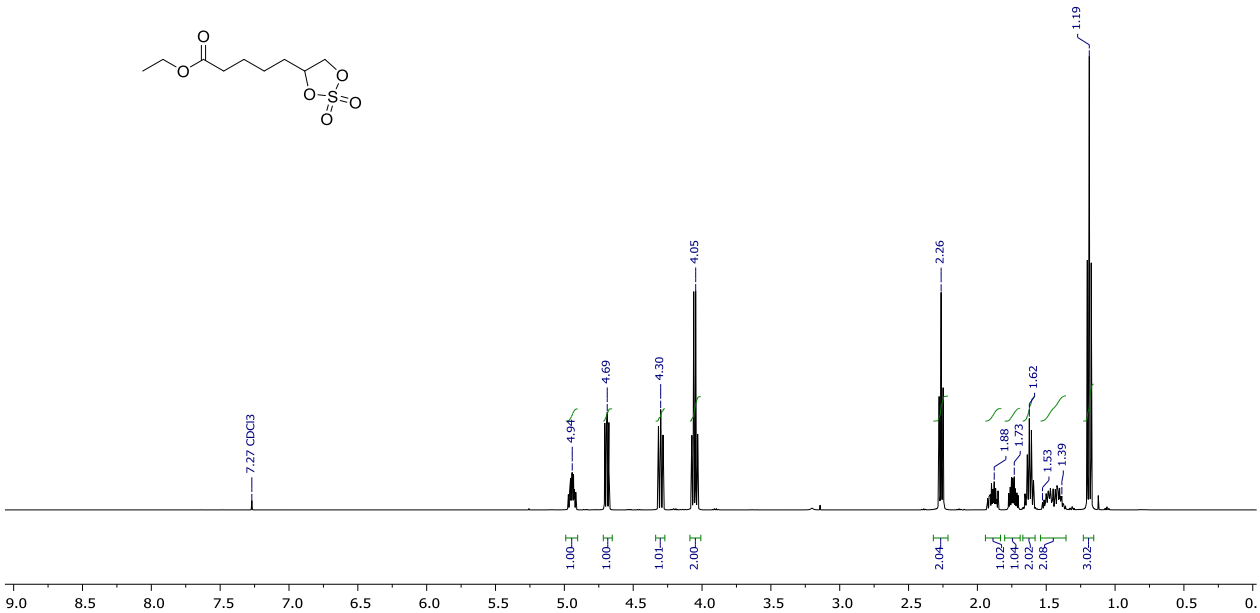



**Figure NMR-S9.** 125 MHz $^{13}C\{^{1}H\}$ NMR spectrum of 3-(2,2-dioxido-1,3,2-dioxathiolan-4-yl)-2-phenylpropanenitrile.




**fFigure NMR-S10.** 500 MHz $^{1}H$ NMR spectrum of ethyl 5-(2,2-dioxido-1,3,2-dioxathiolan-4-yl)pentanoate.

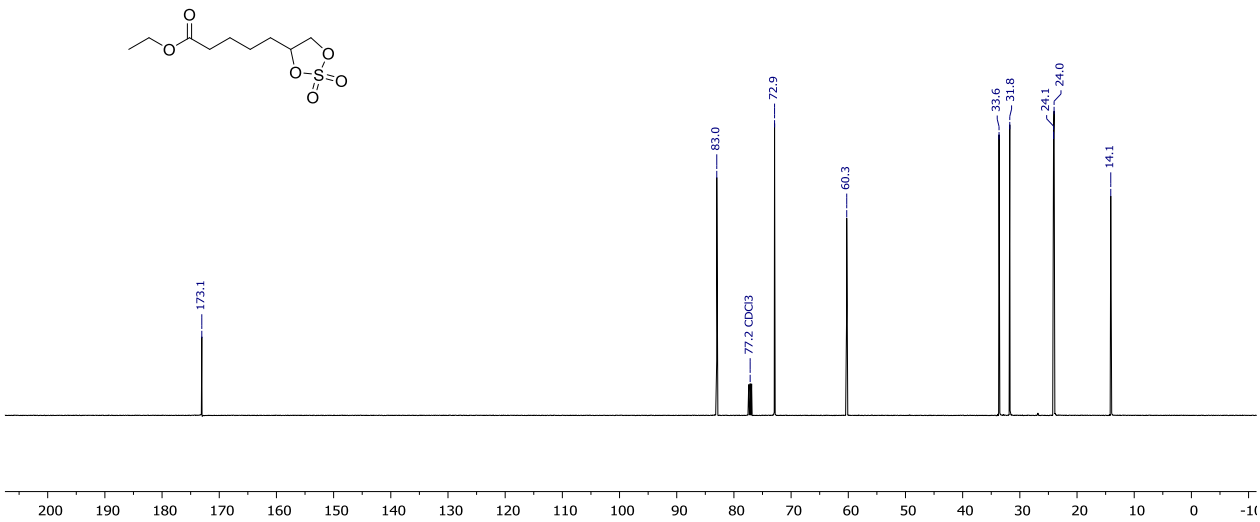



**Figure NMR-S11.** 125 MHz $^{13}C\{^{1}H\}$ NMR spectrum of ethyl 5-(2,2-dioxido-1,3,2-dioxathiolan-4-yl)pentanoate.

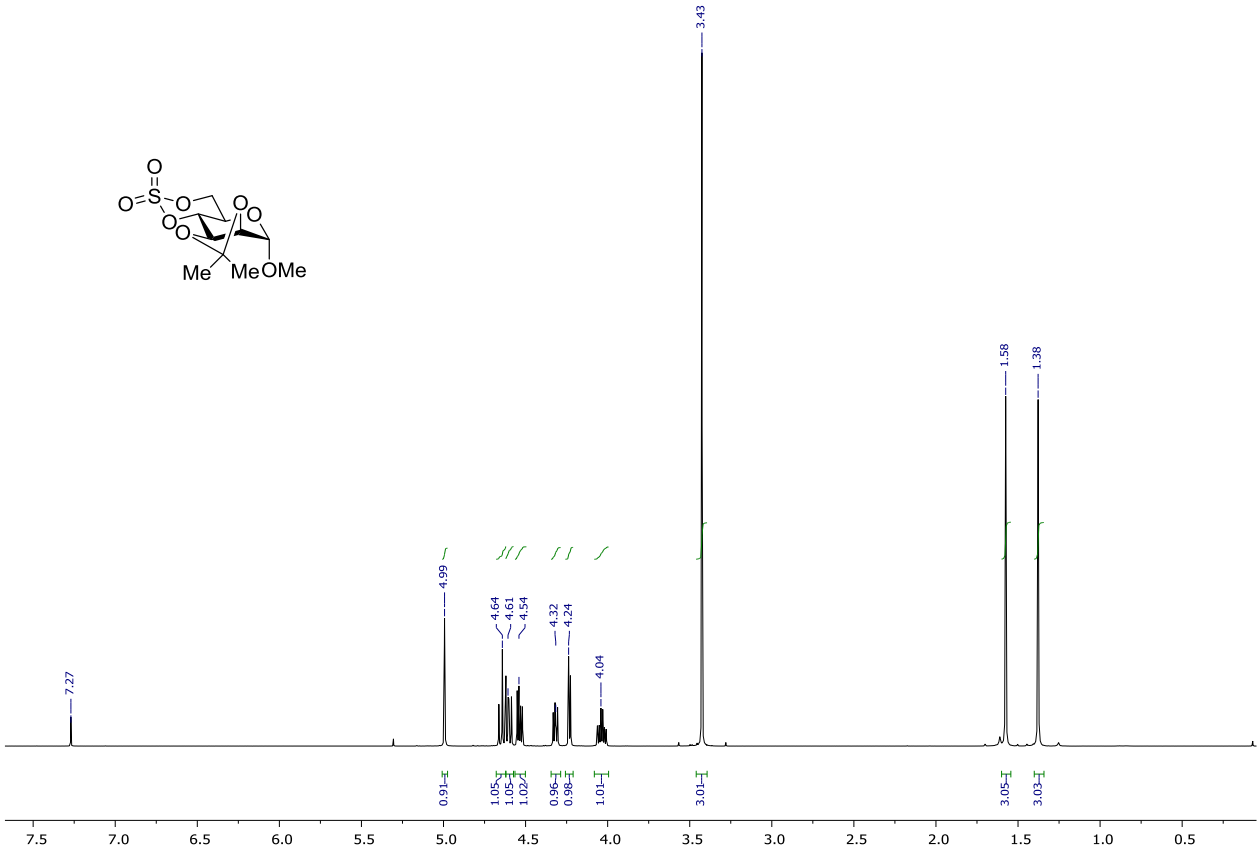



**Figure NMR-S12.** 500 MHz $^{1}H$ NMR spectrum of methyl-2,3-*O*-isopropylidene-α-d-mannopyranoside-1,3-cyclic sulfate.

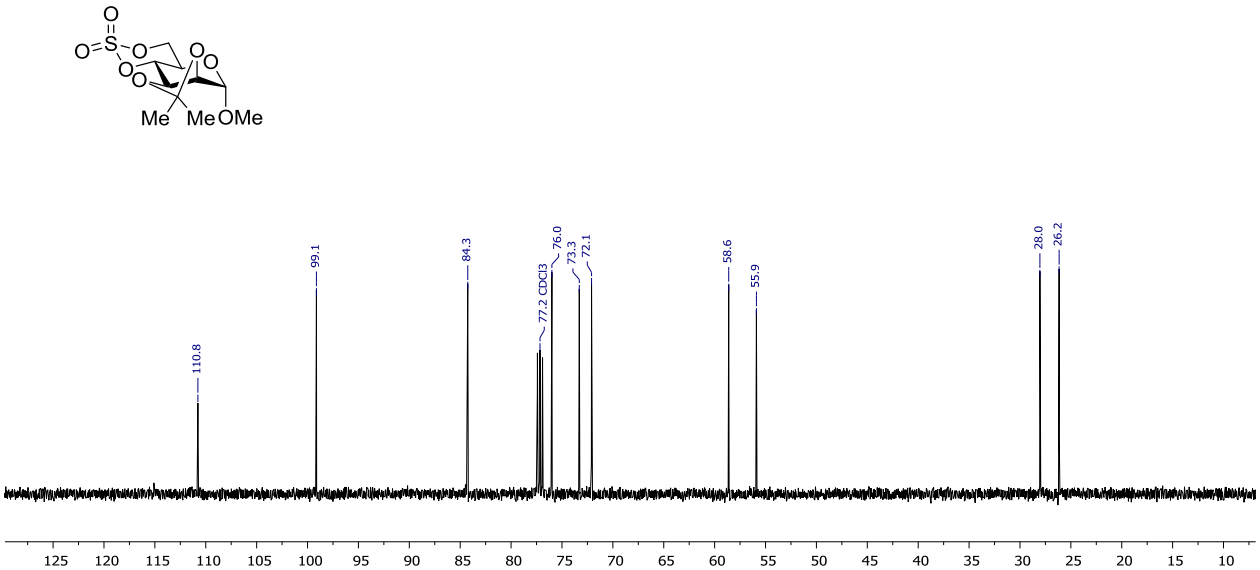



**Figure NMR-S13.** 125 MHz $^{13}C\{^{1}H\}$ NMR spectrum of methyl-2,3-*O*-isopropylidene-α-d-mannopyranoside-1,3-cyclic sulfate.

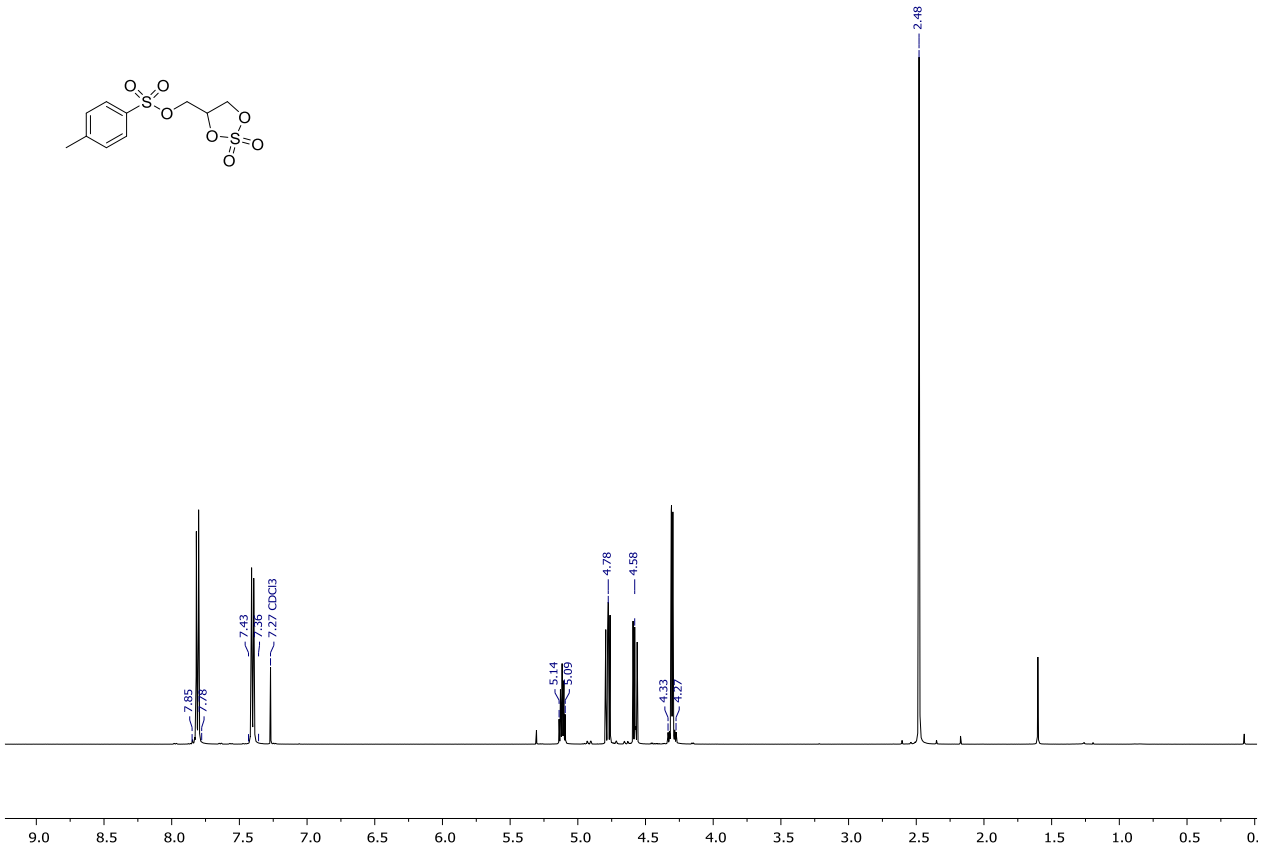



**Figure NMR-S14.** 500 MHz $^{1}H$ NMR spectrum of glycerol 3-tosyl-1,2-cyclic sulfate. Residual water observed at δ = 1.5 ppm.

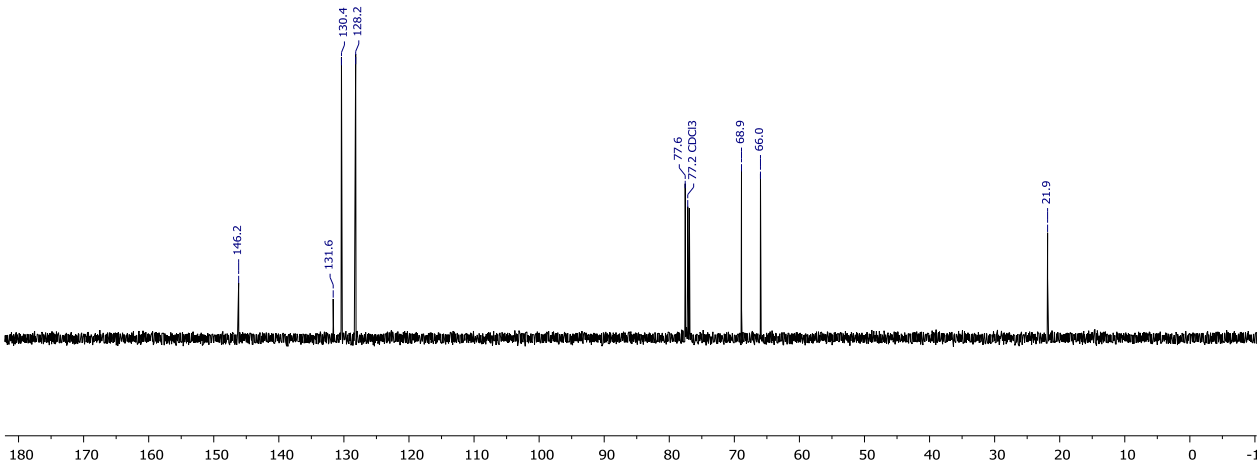



**Figure NMR-S15.** 125 MHz $^{13}C\{^{1}H\}$ NMR spectrum of glycerol 3-tosyl-1,2-cyclic sulfate.

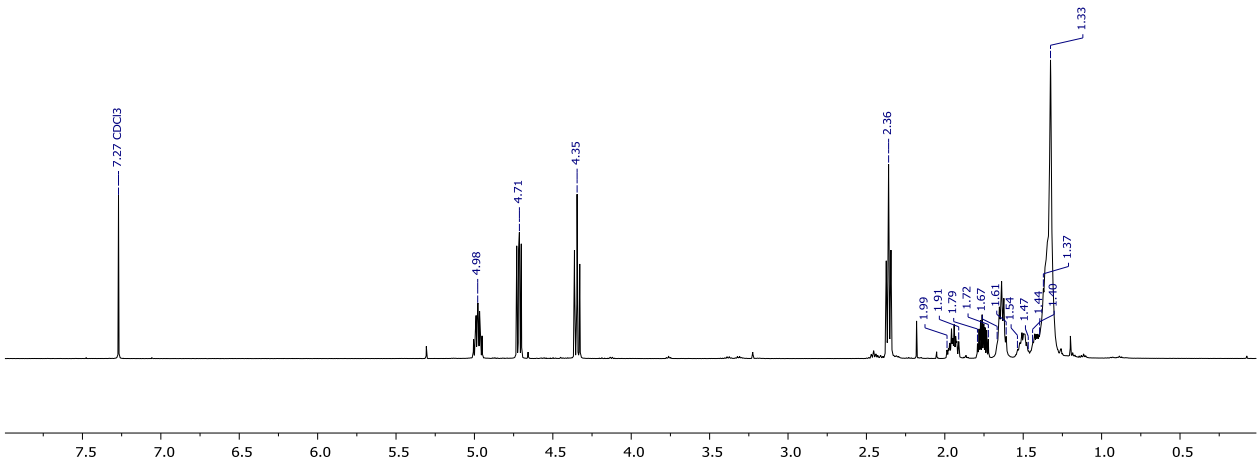



**Figure NMR-S16.** 500 MHz $^{1}H$ NMR spectrum of undecanoic acid 1,2-cyclic sulfate.

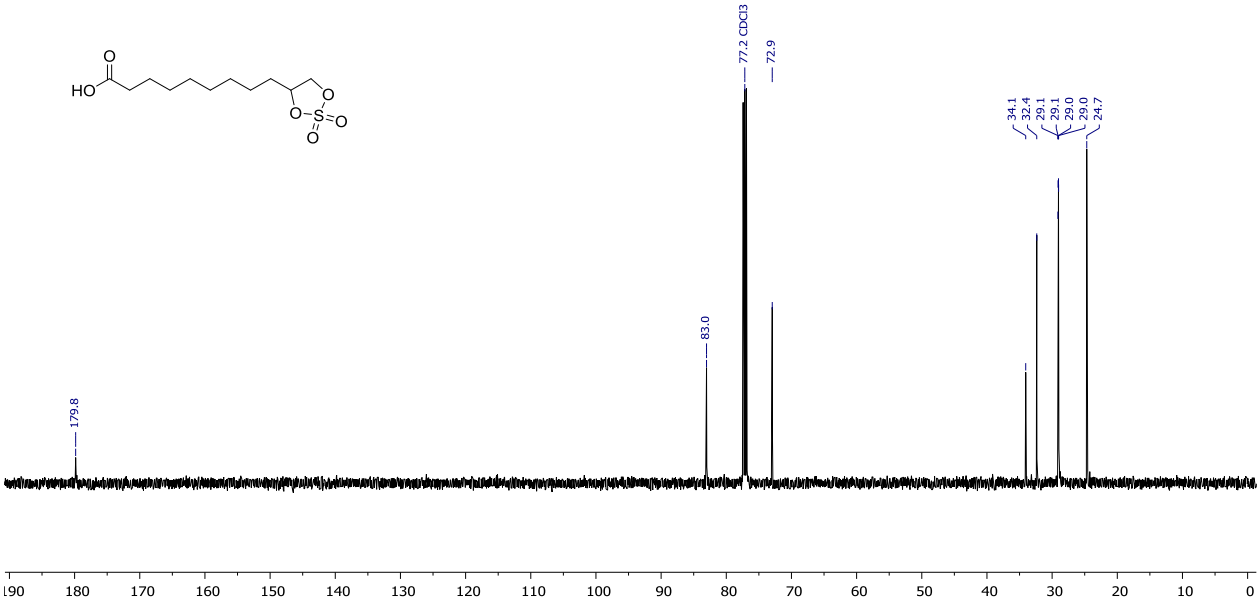



**Figure NMR-S17.** 125 MHz $^{13}C\{^{1}H\}$ NMR spectrum of undecanoic acid 1,2-cyclic sulfate.

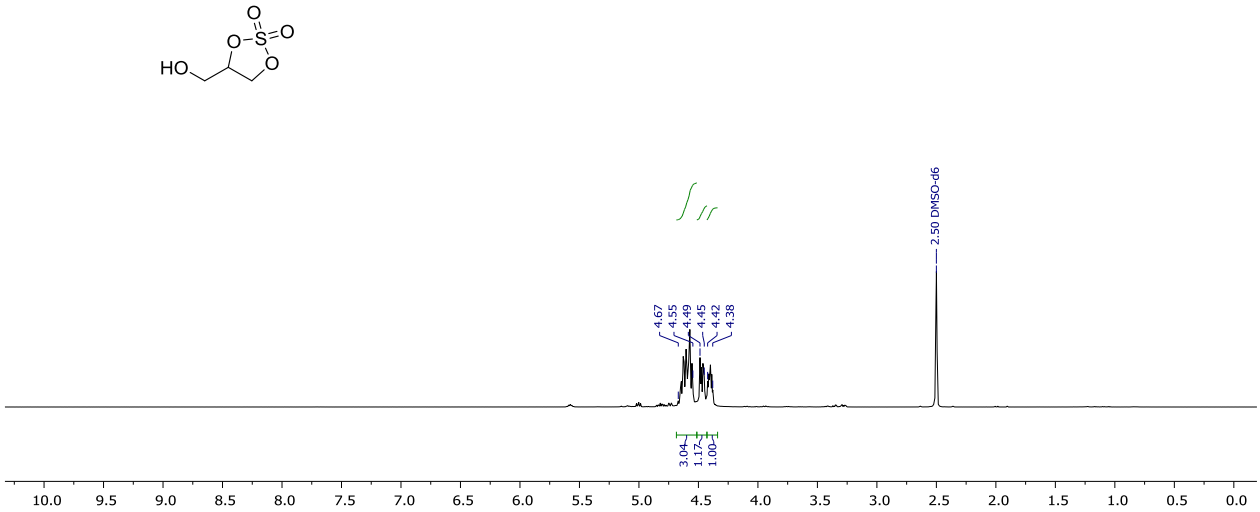



**Figure NMR-S18.** 500 MHz $^{1}H$ NMR spectrum of glycerol 1,2-cyclic sulfate.

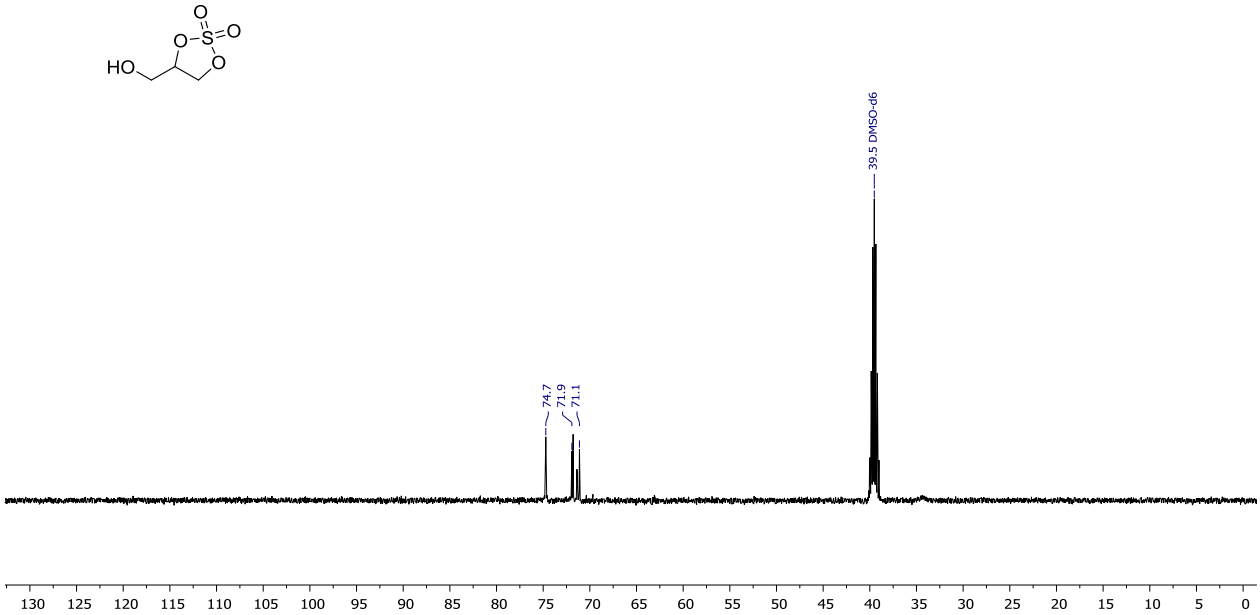



**Figure NMR-S19.** 125 MHz $^{13}C\{^{1}H\}$ NMR spectrum of glycerol 1,2-cyclic sulfate.

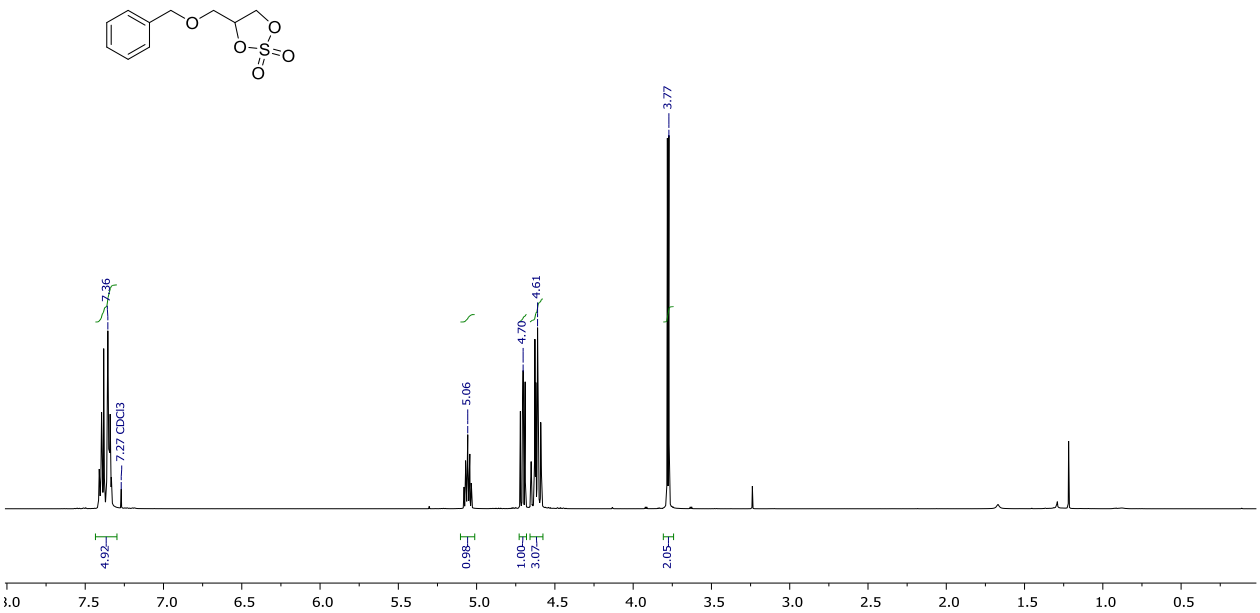



**Figure NMR-S20.** 500 MHz $^{1}H$ NMR spectrum of benzylglycerol 2,3-cyclic sulfate.

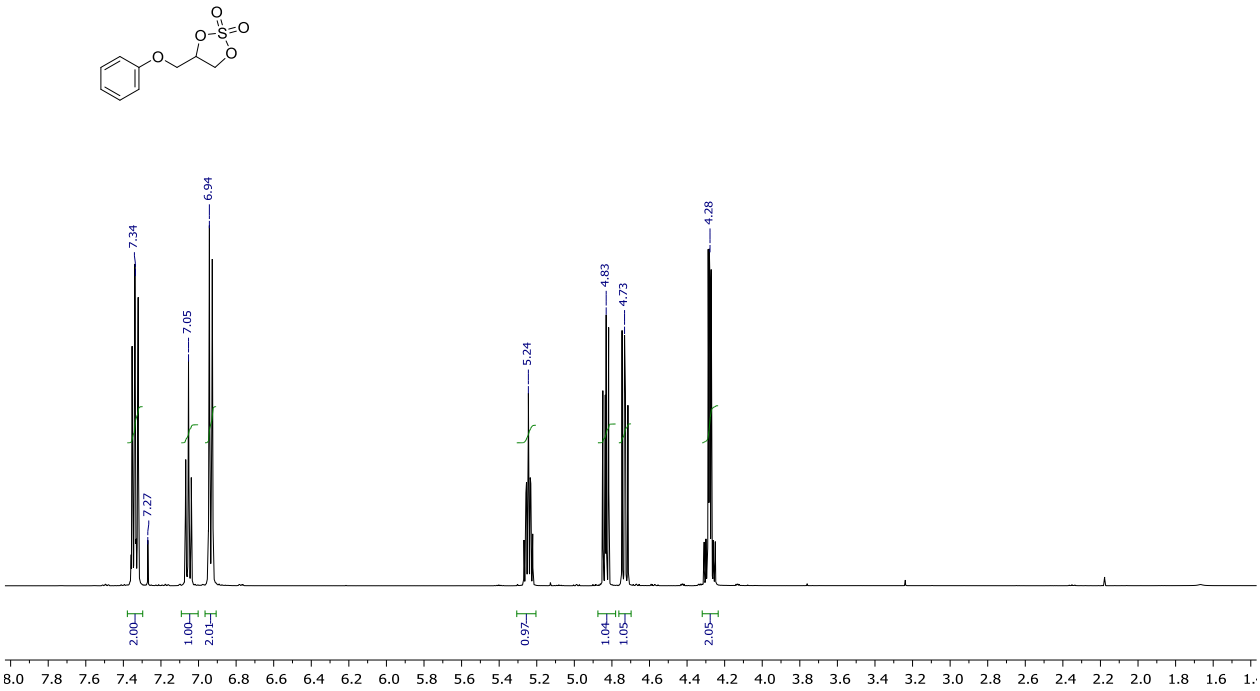



**Figure NMR-S21.** 500 MHz $^{1}$H NMR spectrum of phenylglycerol 2,3-cyclic sulfate**.**

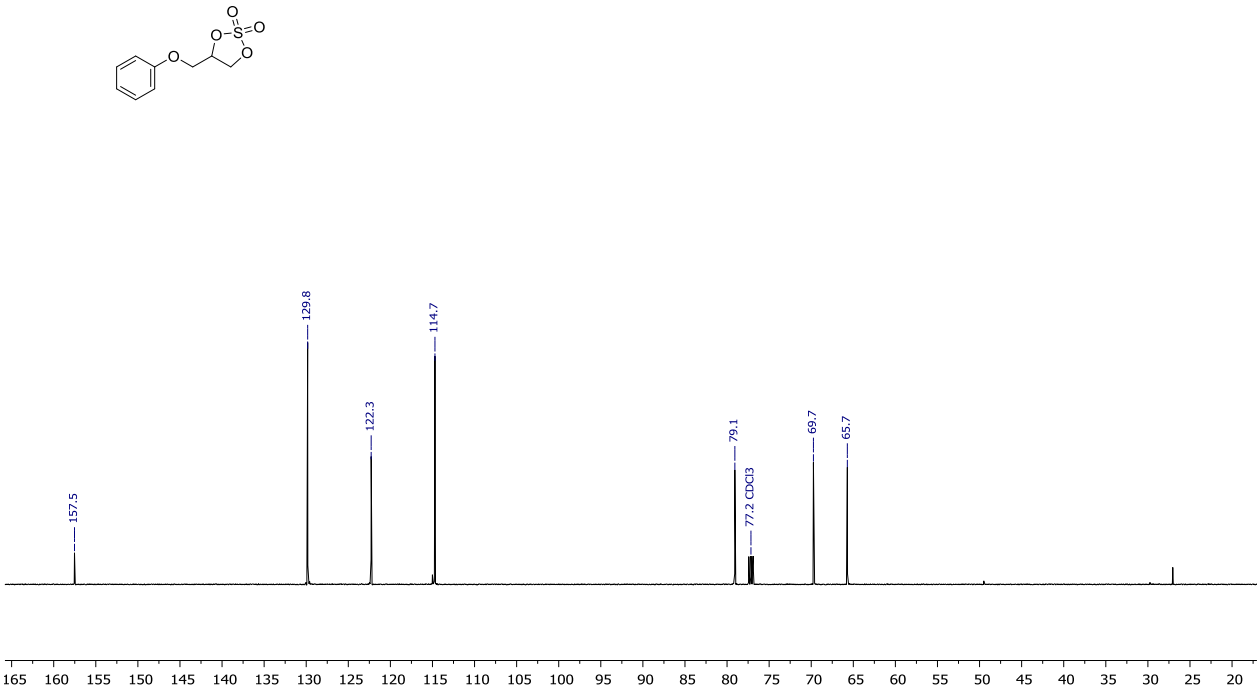



**Figure NMR-S22.** 125 MHz $^{13}$C{$^{1}$H} NMR spectrum of phenylglycerol 2,3-cyclic sulfate**.**

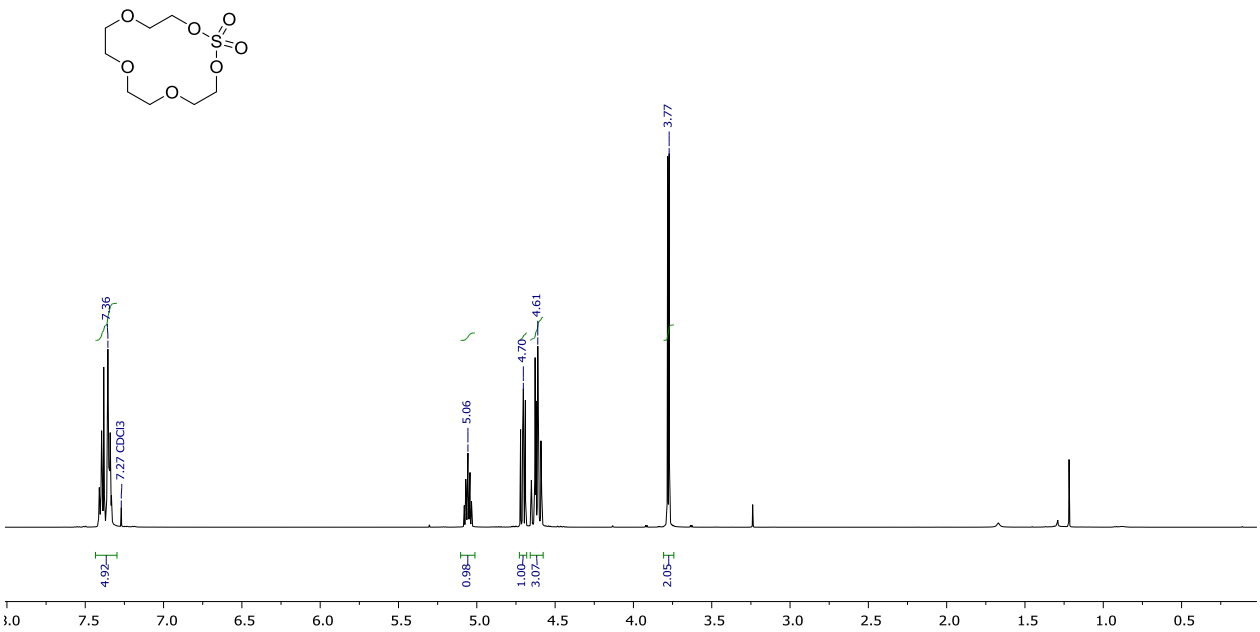



**Figure NMR-S23.** 500 MHz $^{1}$H NMR spectrum of tetraethylene glycol macrocyclic sulfate.

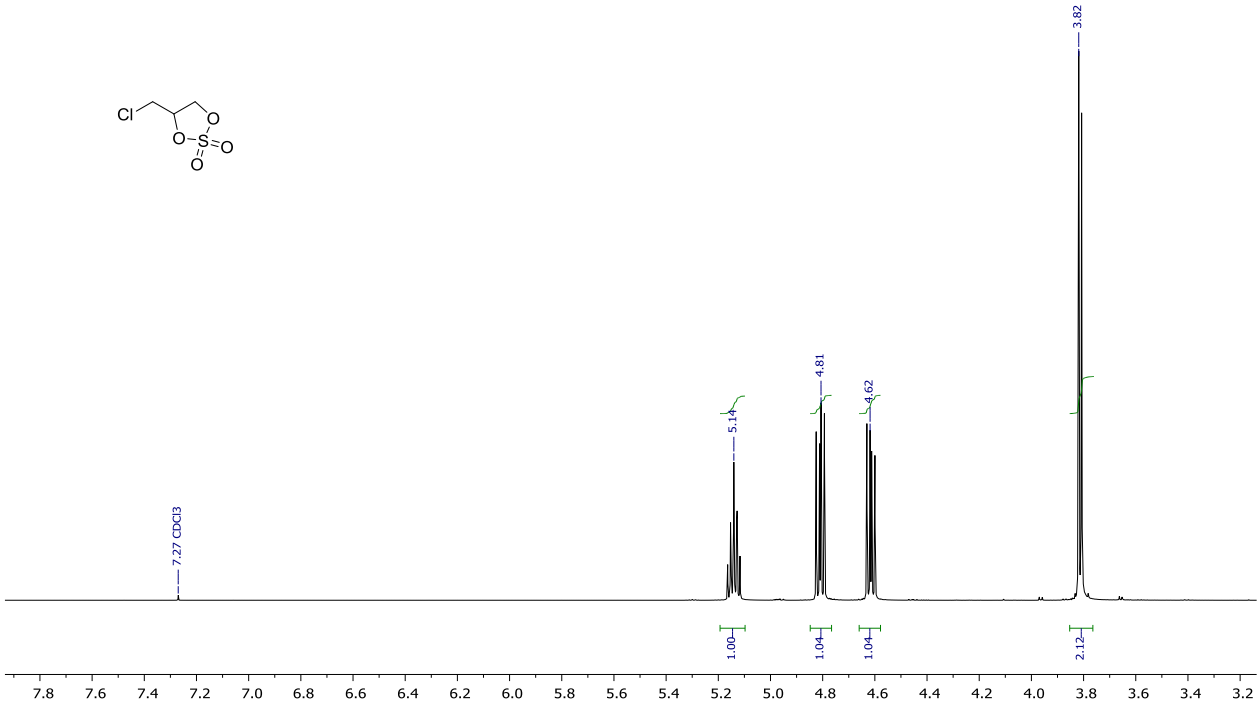
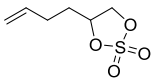



**Figure NMR-S24**. 500 MHz $^{1}$H NMR spectrum of 3-chloro-1,2-propanediol cyclic sulfate.



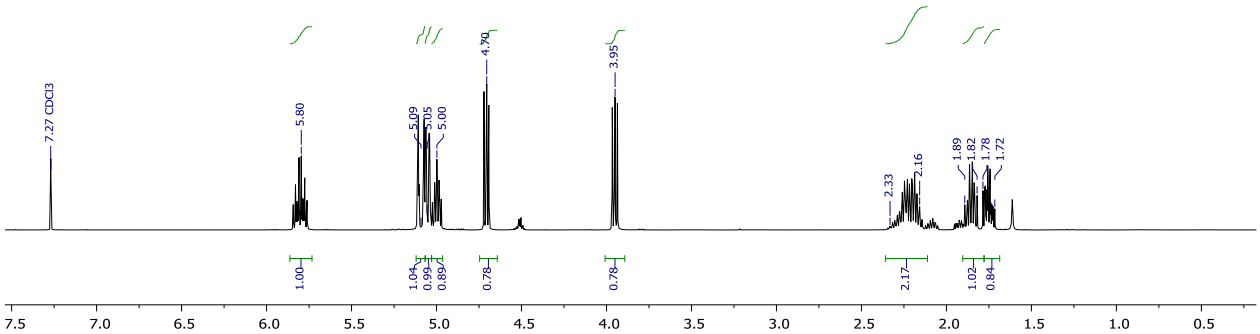
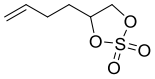



**Figure NMR-S25.** 500 MHz $^{1}$H NMR spectrum of 6-hexene 1,2-cyclic sulfate.



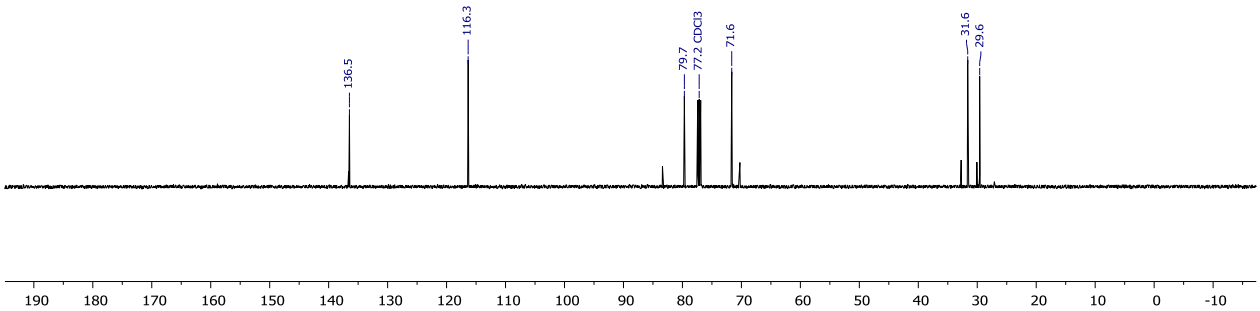



**Figure NMR-S26.** 125 MHz $^{13}$C{$^{1}$H} NMR spectrum of 6-hexene 1,2-cyclic sulfate.

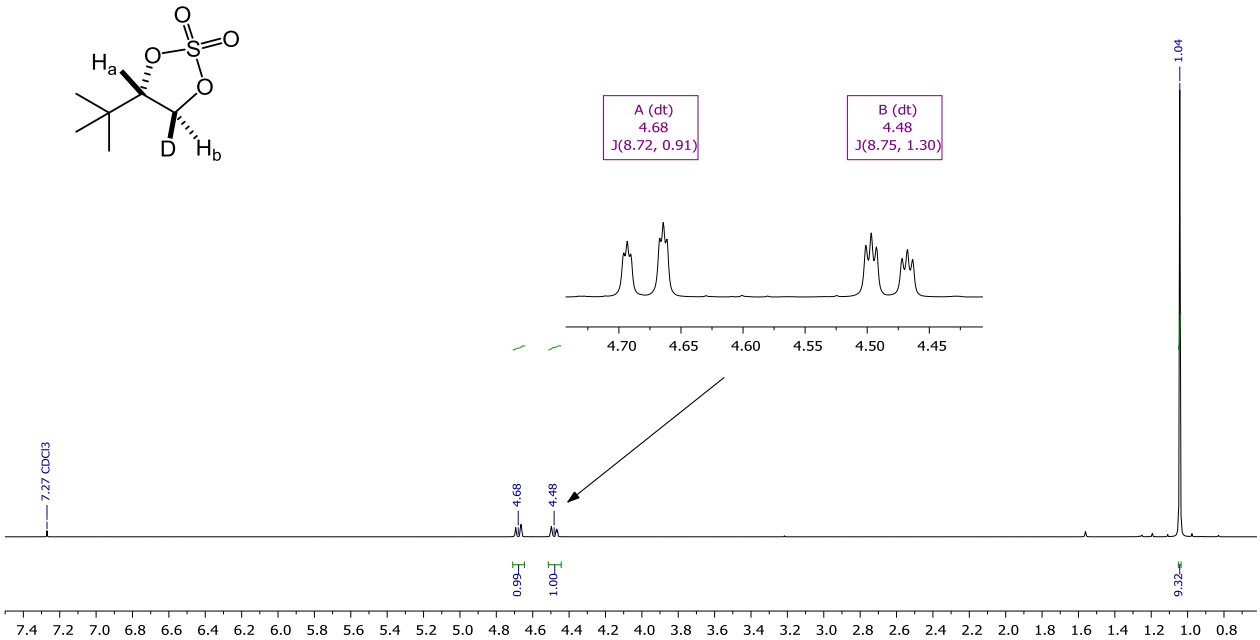



**Figure NMR-S27.** 300 MHz NMR spectrum of 4-(*tert*-butyl)-1,3,2-dioxathiolane 2,2-dioxide-5-*d*.

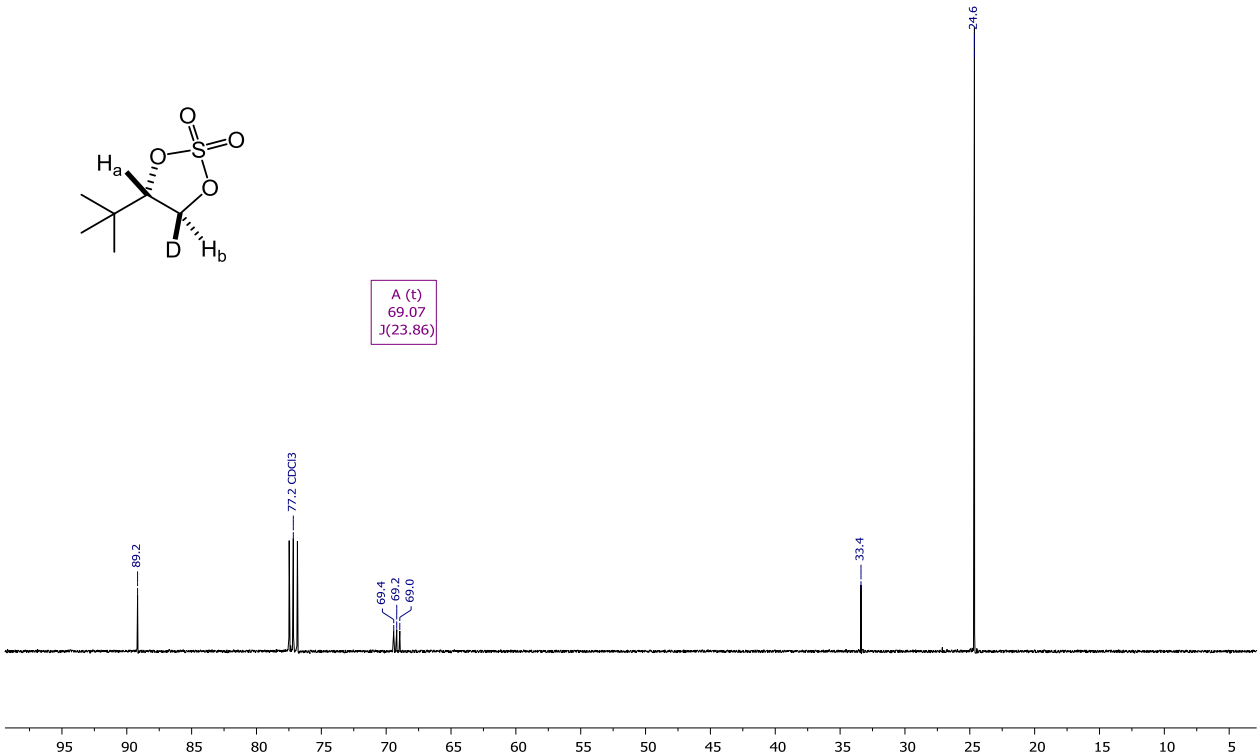



**Figure NMR-S28.** 100.63 MHz $^{13}C\{^{1}H\}$ NMR spectrum of 4-(*tert*-butyl)-1,3,2-dioxathiolane 2,2-dioxide-5-*d*.

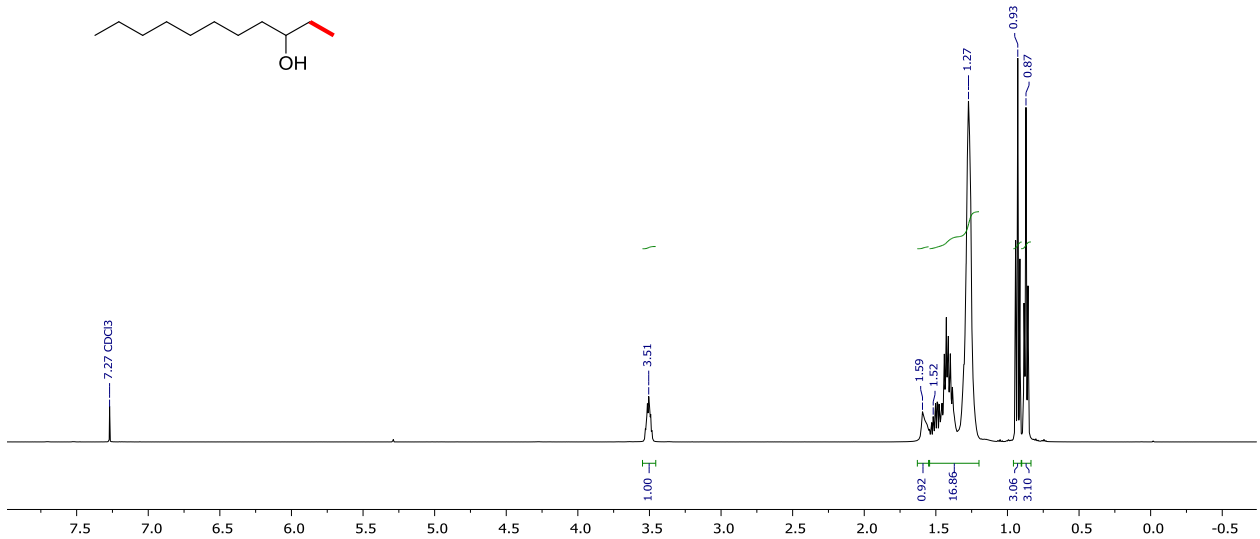



**Figure NMR-S29.** 500 MHz $^{1}$H NMR spectrum of 3-undecanol (table 1, entry 1).

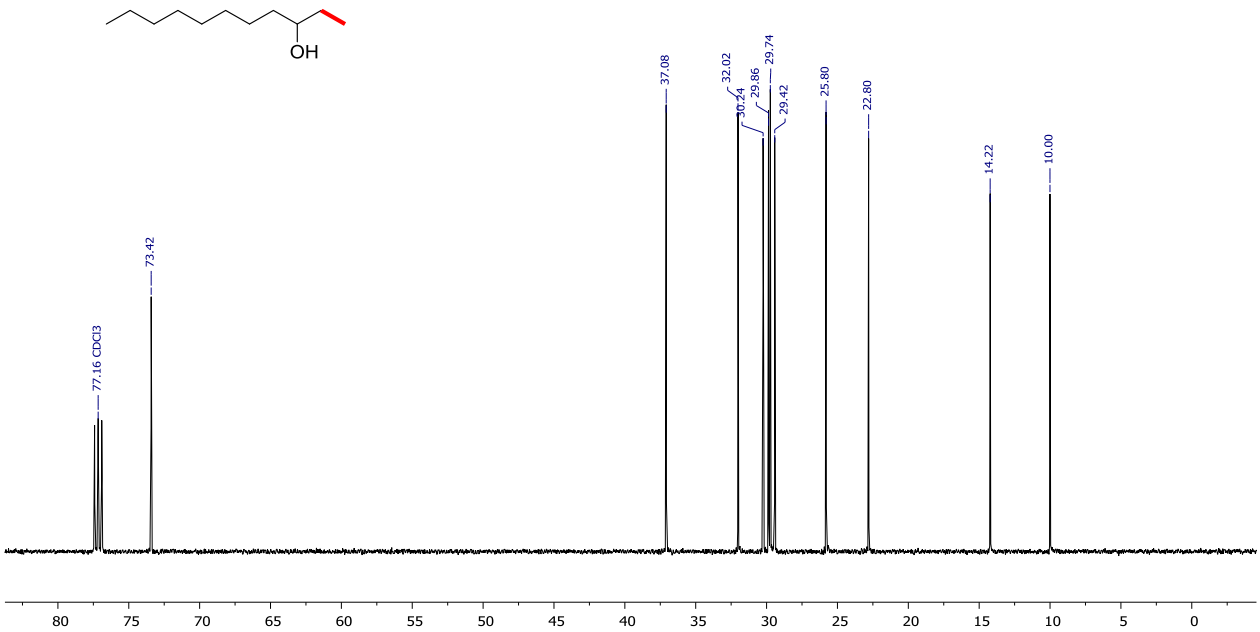



**Figure NMR-S30.** 125 MHz $^{13}$C{$^{1}$H} NMR spectrum of 3-undecanol (table 1, entry 1).

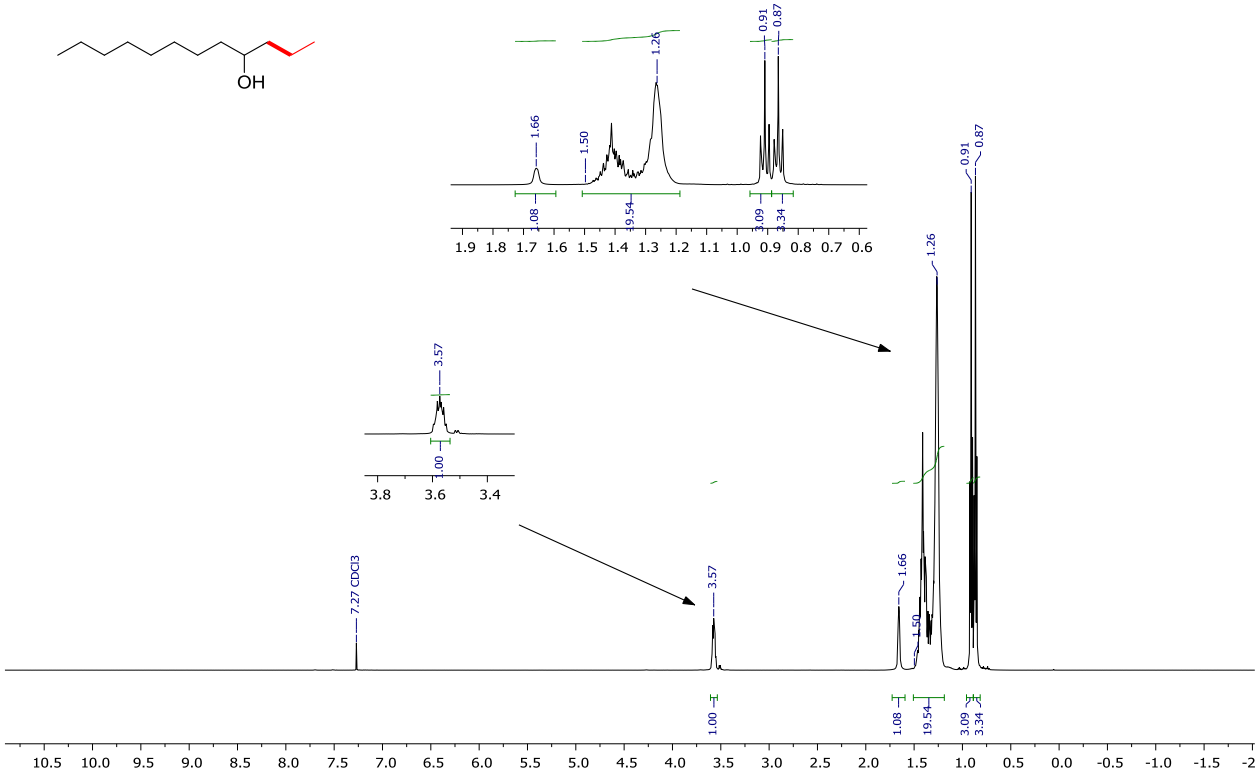



**Figure NMR-S31.** 500 MHz $^{1}$H NMR spectrum of 4-dodecanol (table 1, entry 2).

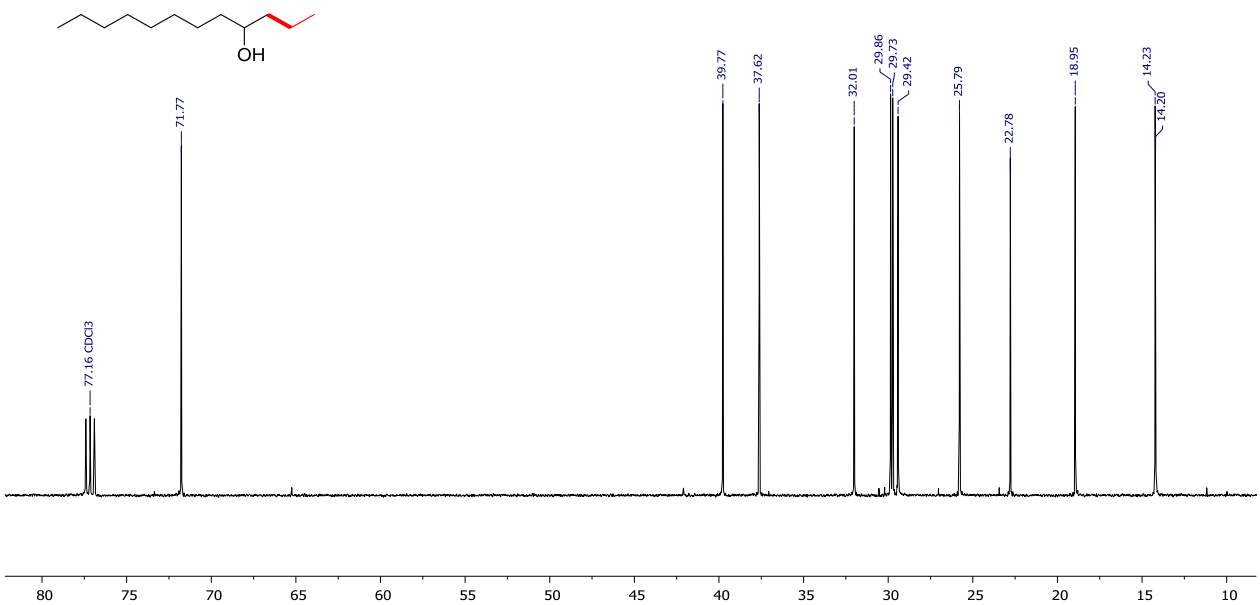



**Figure NMR-S32.** 125 MHz $^{13}$C{$^{1}$H} NMR spectrum of 4-dodecanol (table 1, entry 2).

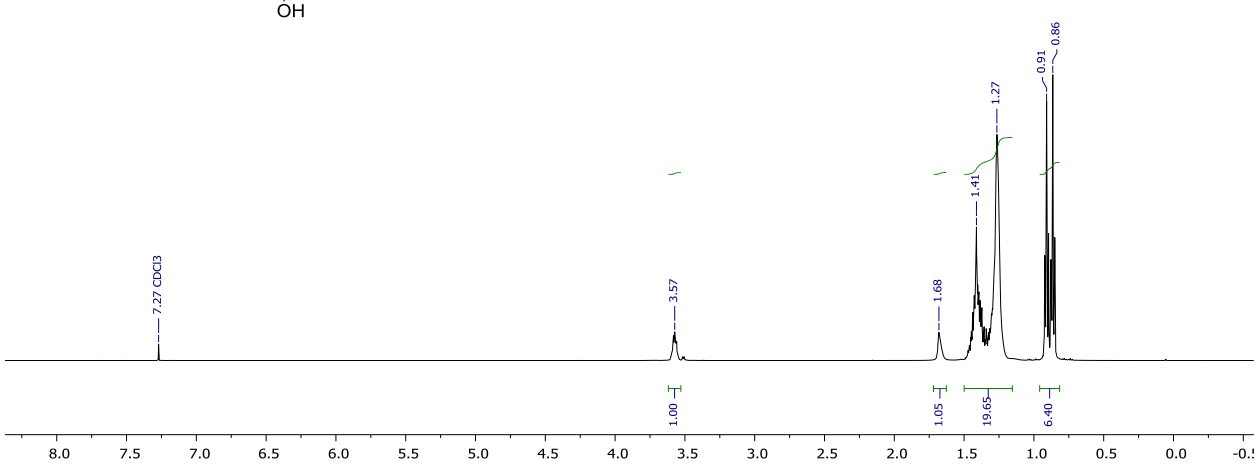



**Figure NMR-S33.** 500 MHz $^{1}$H NMR spectrum of 4-dodecanol, prepared using EtMgBr (table 1, entry 3).

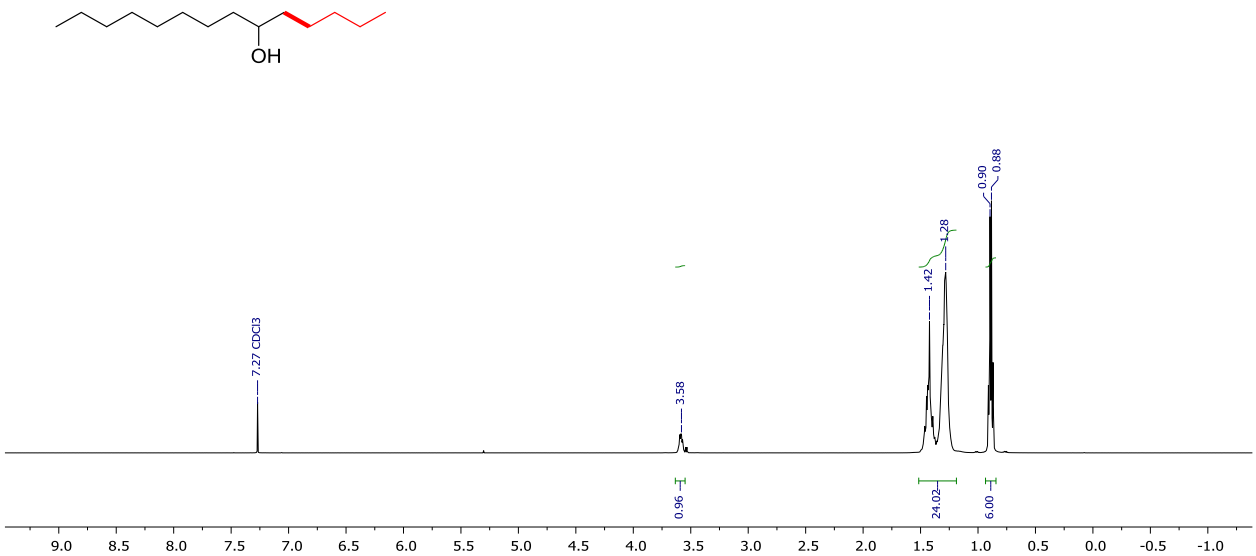



**Figure NMR-S34.** 500 MHz $^{1}$H NMR spectrum of 6-tetradecanol (table 1, entry 4).

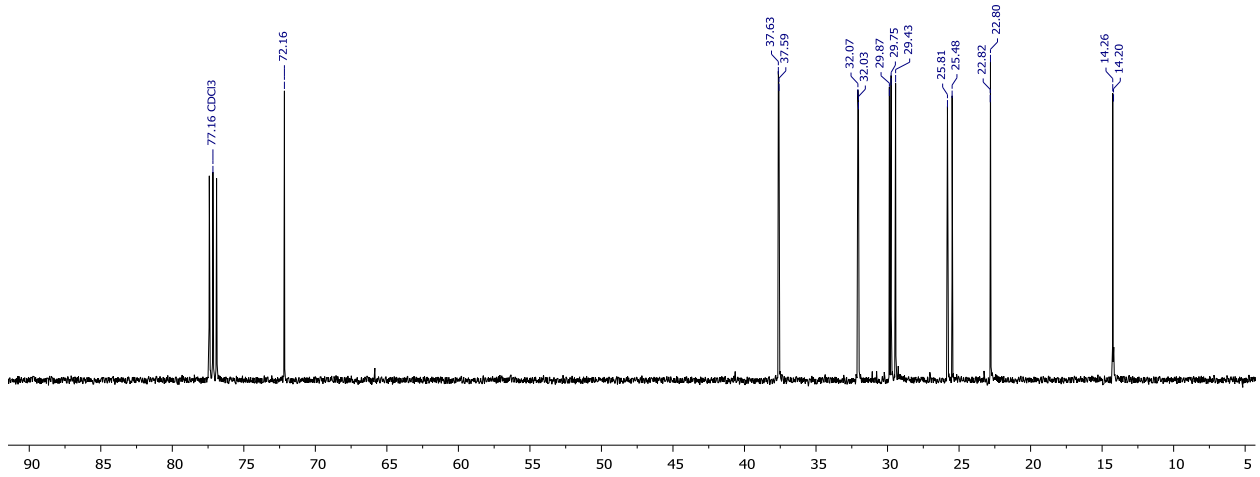



**Figure NMR-S35.** 125 MHz $^{13}C\{^{1}H\}$ NMR spectrum of 6-tetradecanol (table 1, entry 4).

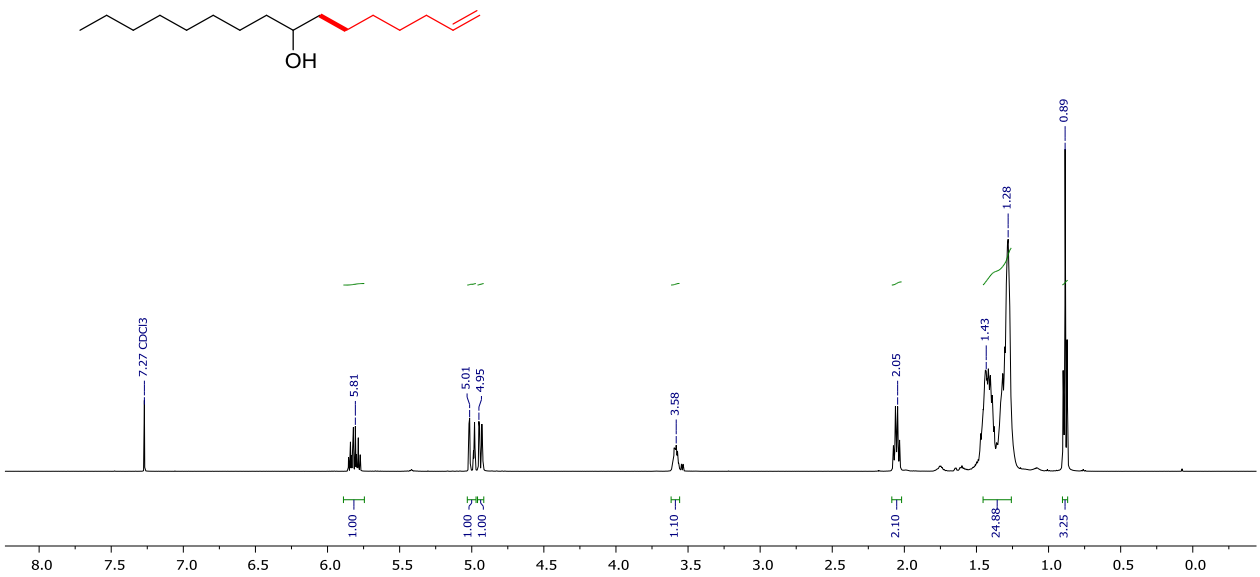



**Figure NMR-S36.** 500 MHz $^{1}H$ NMR spectrum of 1-hexadecene-8-ol (table 1, entry 5).

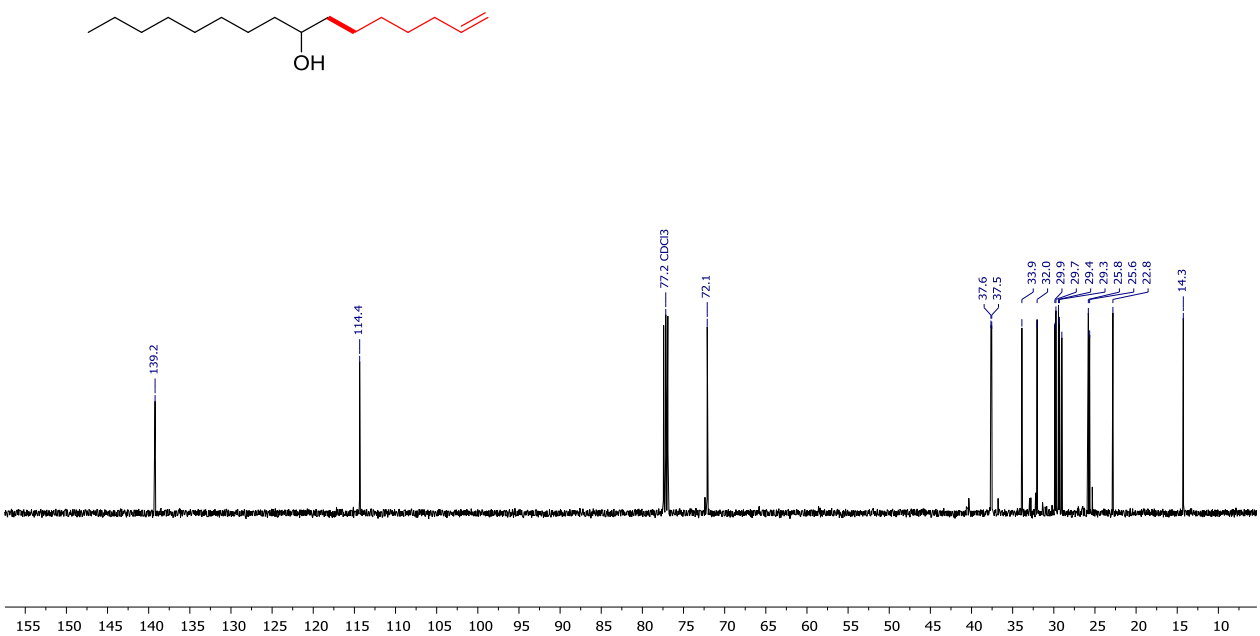



**Figure NMR-S37.** 125 MHz $^{13}C\{^{1}H\}$ NMR spectrum of 1-hexadecene-8-ol (table 1, entry 5).

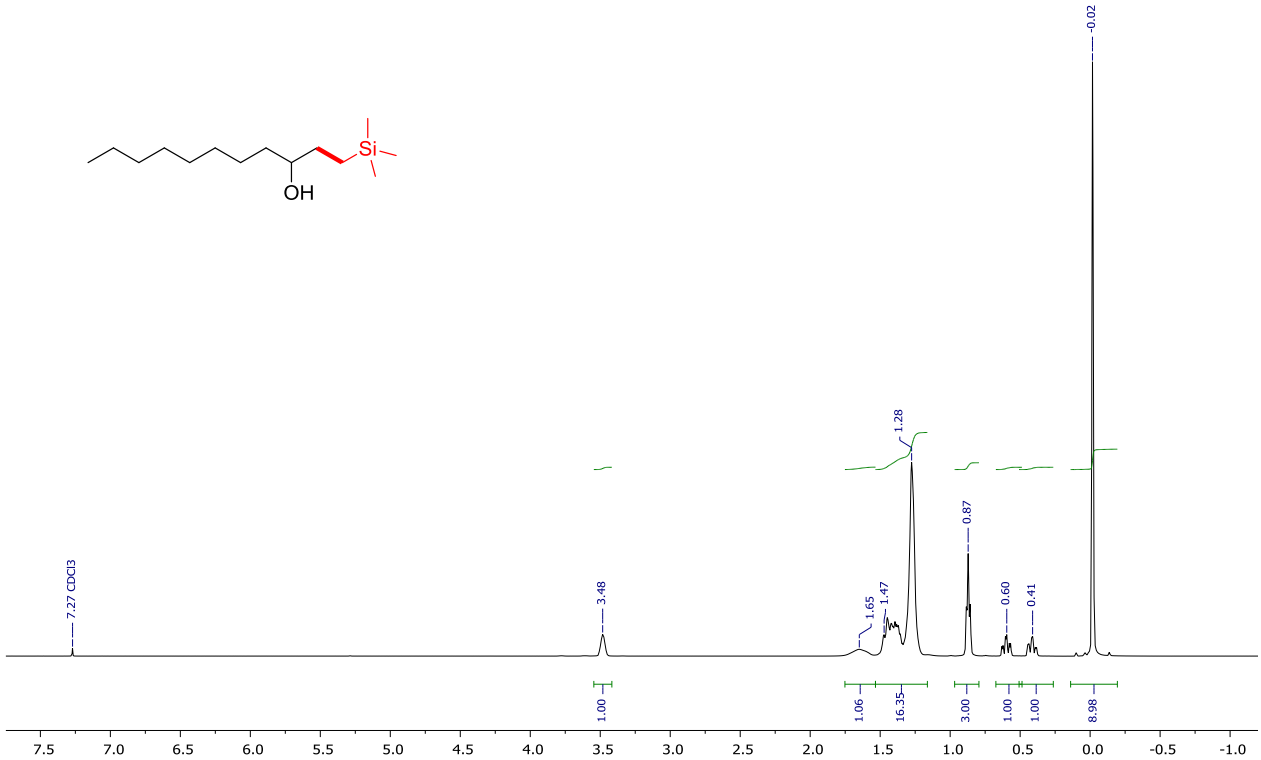



**Figure NMR-S38.** 500 MHz $^{1}H$ NMR spectrum of 1-(trimethylsilyl)-3-undecanol (table 1, entry 6).

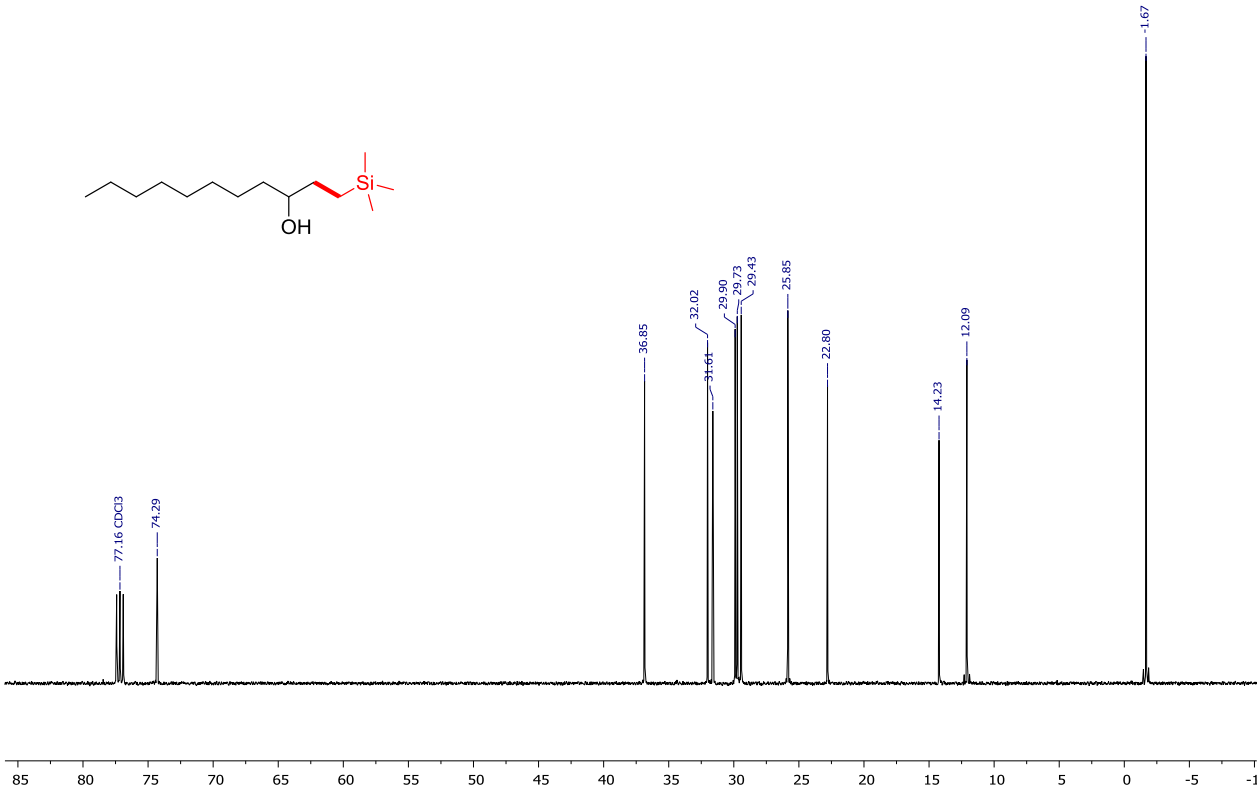



**Figure NMR-S39.** 125 MHz $^{13}C\{^{1}H\}$ NMR spectrum of 1-(trimethylsilyl)-3-undecanol (table 1, entry 6).

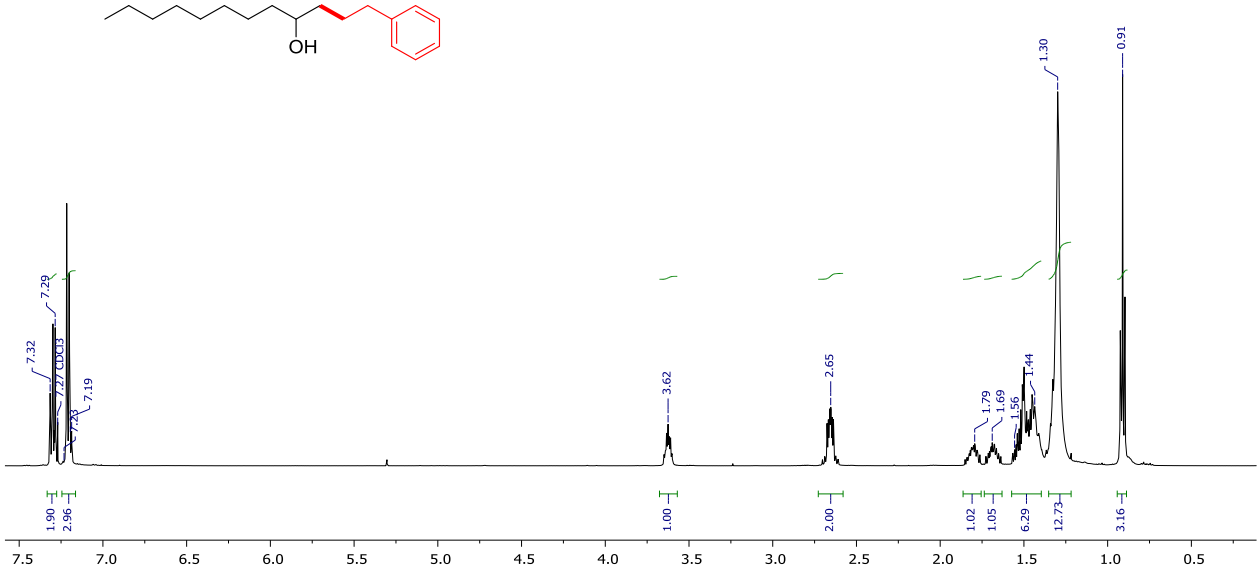



**Figure NMR-S40.** 500 MHz $^{1}H$ NMR spectrum of 1-phenyldodecan-4-ol (table 1, entry 7).

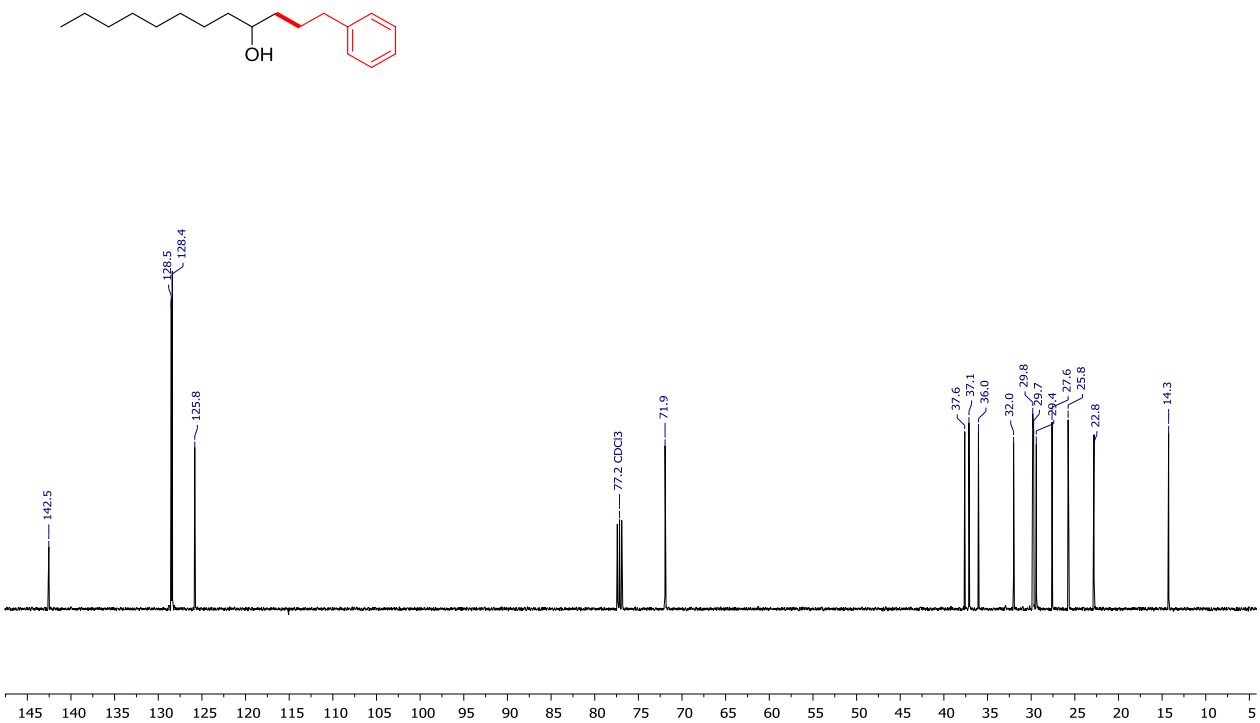



**Figure NMR-S41.** 125 MHz $^{13}C\{^{1}H\}$ NMR spectrum of 1-phenyldodecan-4-ol (table 1, entry 7).

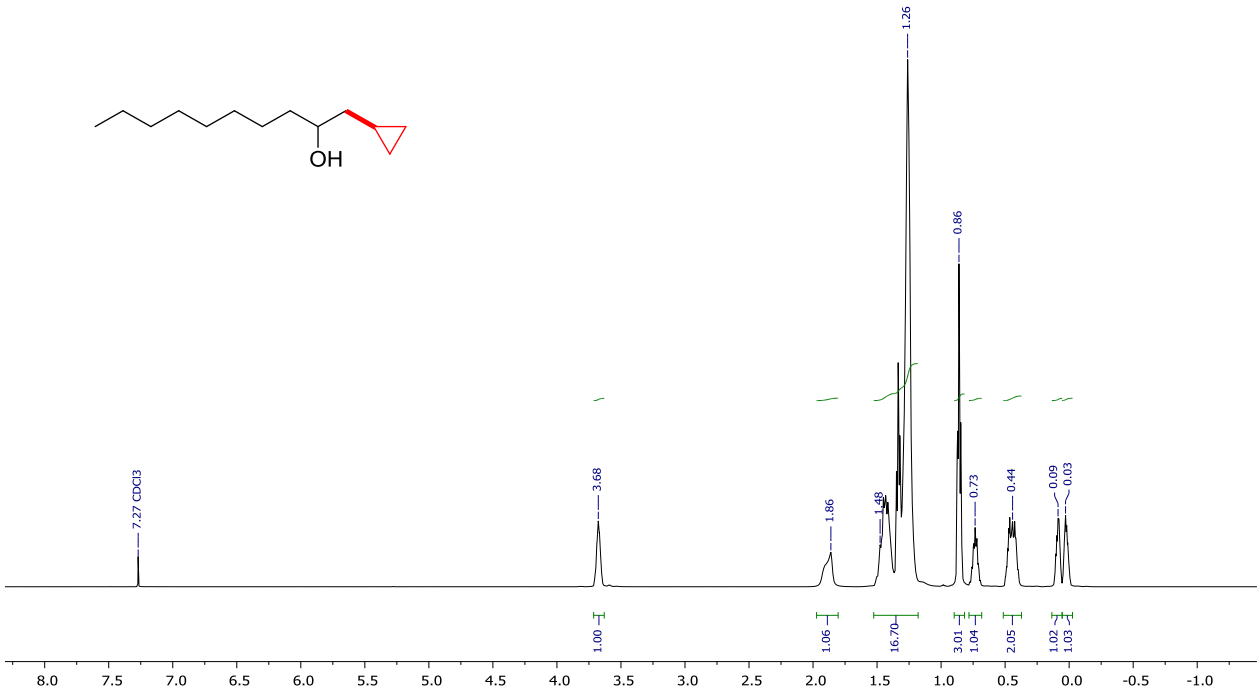



**Figure NMR-S42.** 500 MHz $^{1}H$ NMR spectrum of 1-cyclopropyl-2-decanol (table 1, entry 8)**.**

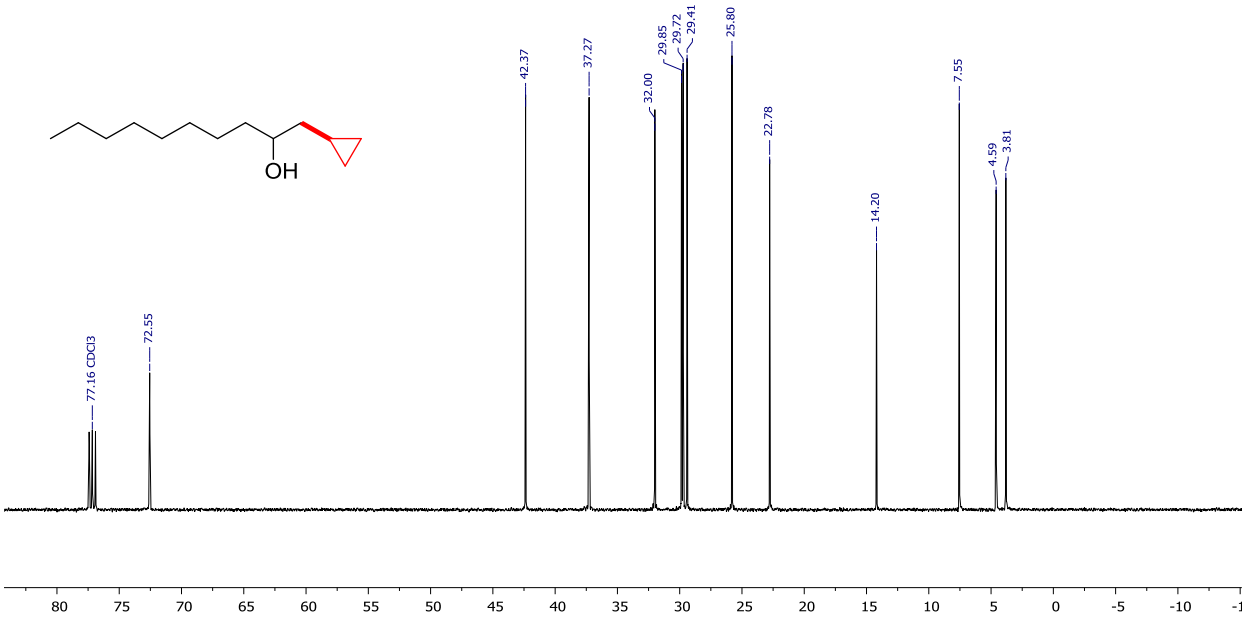



**Figure NMR-S43.** 125 MHz $^{13}C\{^{1}H\}$ NMR spectrum of 1-cyclopropyl-2-decanol (table 1, entry 8)**.**

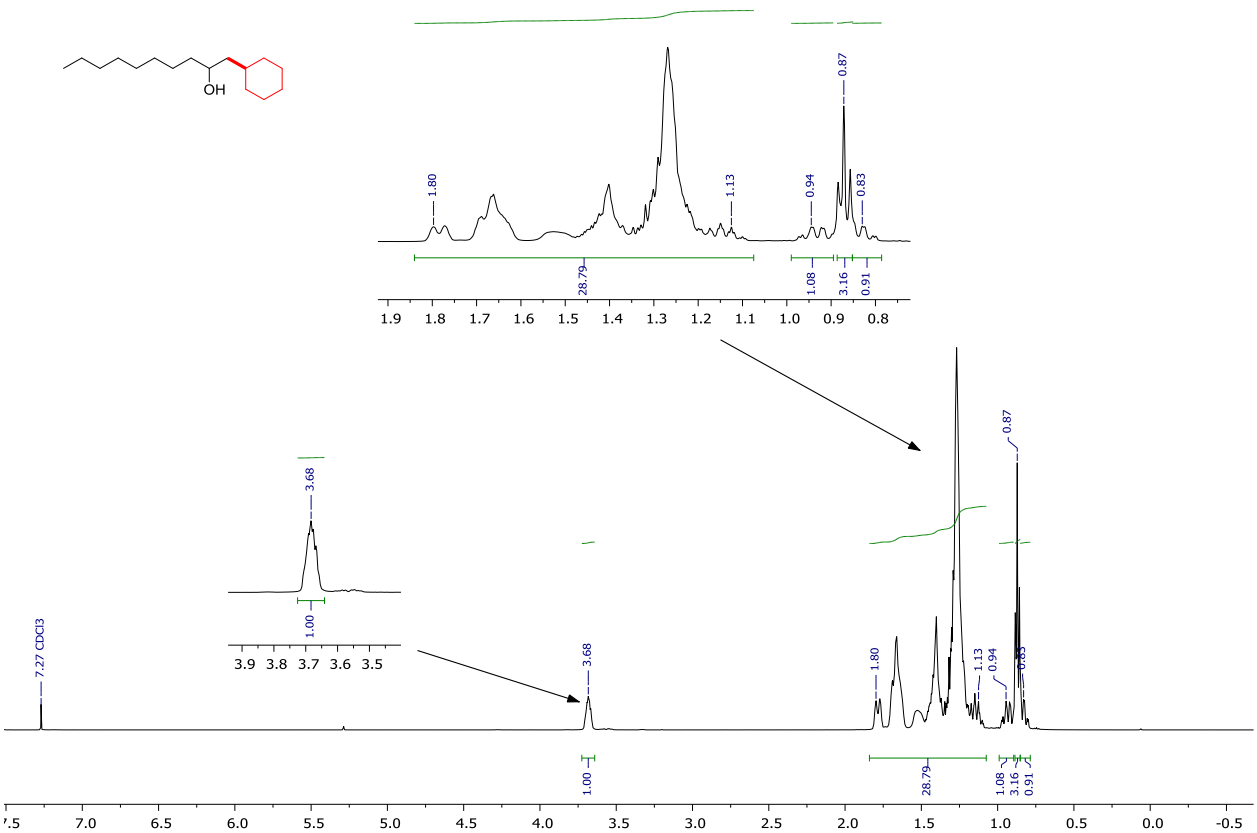



**Figure NMR-S44.** 500 MHz $^{1}H$ NMR spectrum of 1-cyclohexyl-2-decanol (table 1, entry 9)**.**

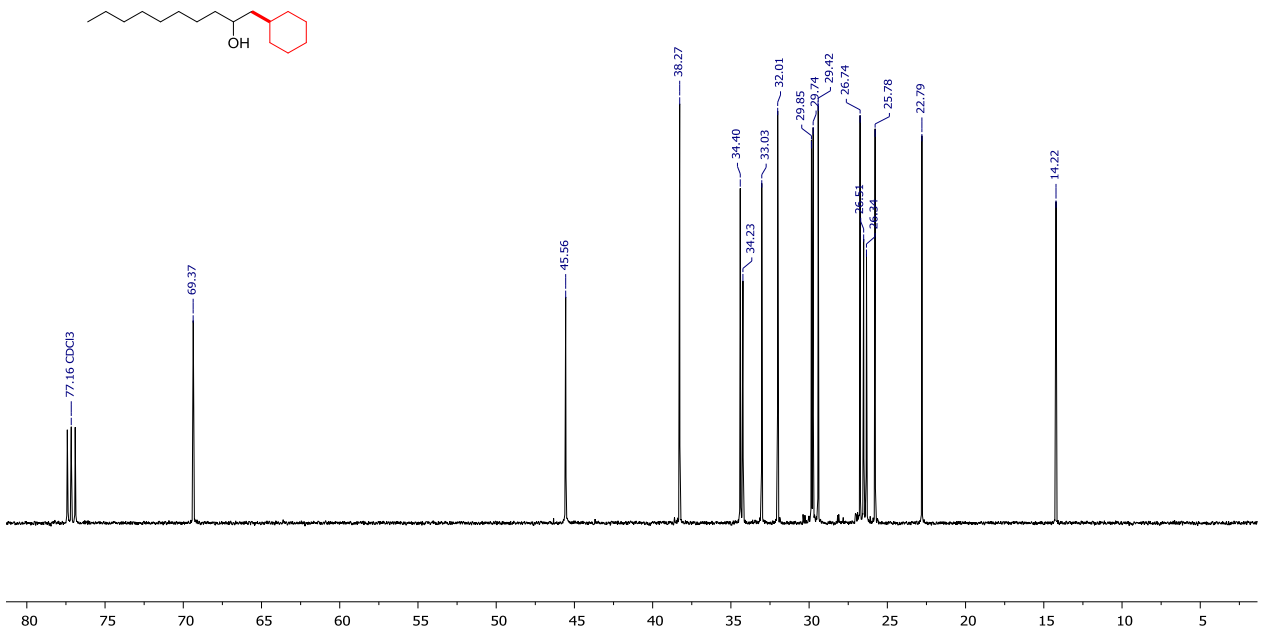



**Figure NMR-S45.** 125 MHz $^{13}C\{^{1}H\}$ NMR spectrum of 1-cyclohexyl-2-decanol (table 1, entry 9).

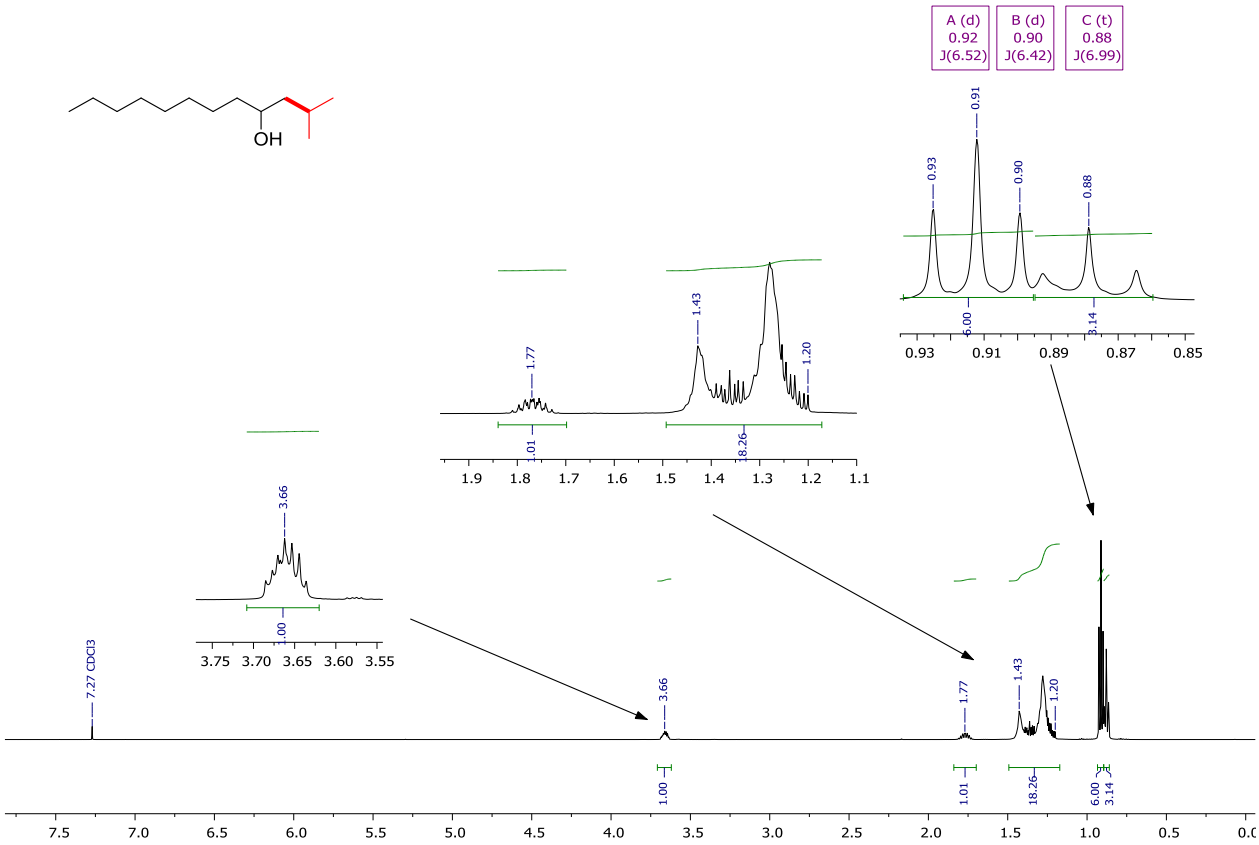



**Figure NMR-S46.** 500 MHz $^{1}H$ NMR spectrum of 2-methyl-4-dodecanol (table 1, entry 10).

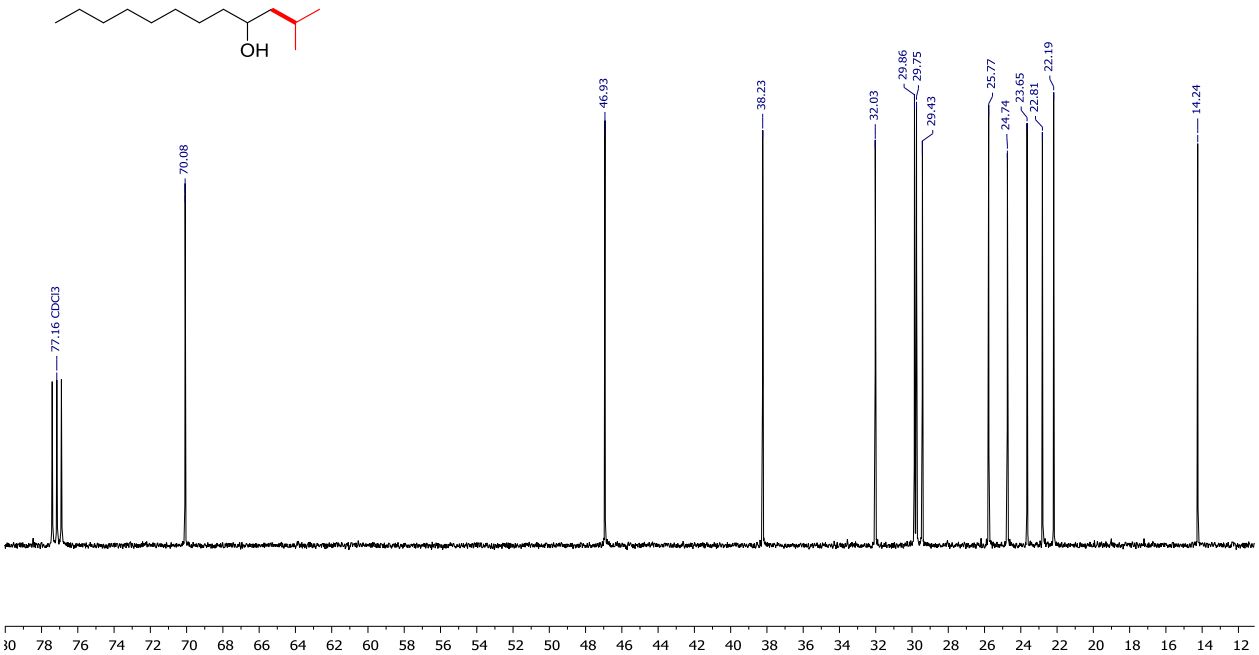



**Figure NMR-S47.** 125.94 MHz $^{13}C\{^{1}H\}$ NMR spectrum of 2-methyl-4-dodecanol (table 1, entry 10).

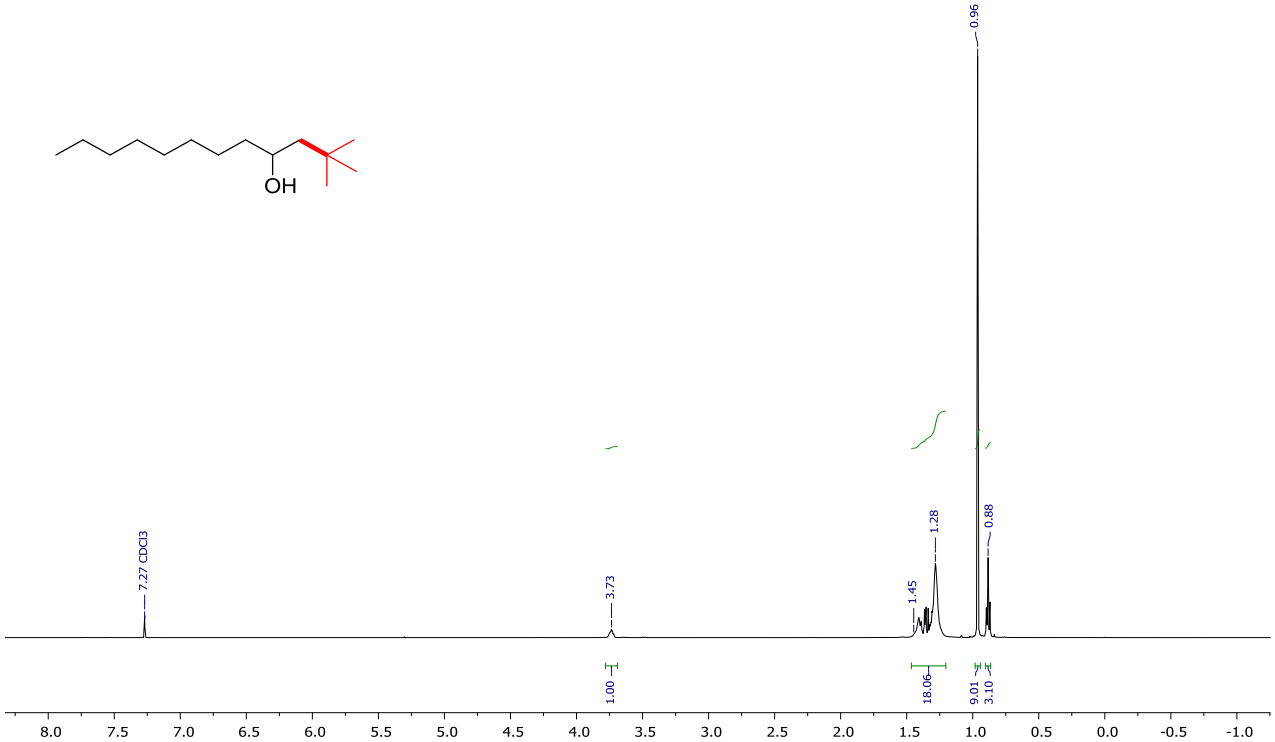



**Figure NMR-S48.** 500 MHz $^{1}H$ NMR spectrum of 2,2-Dimethyl-4-dodecanol (table 1, entry 11).

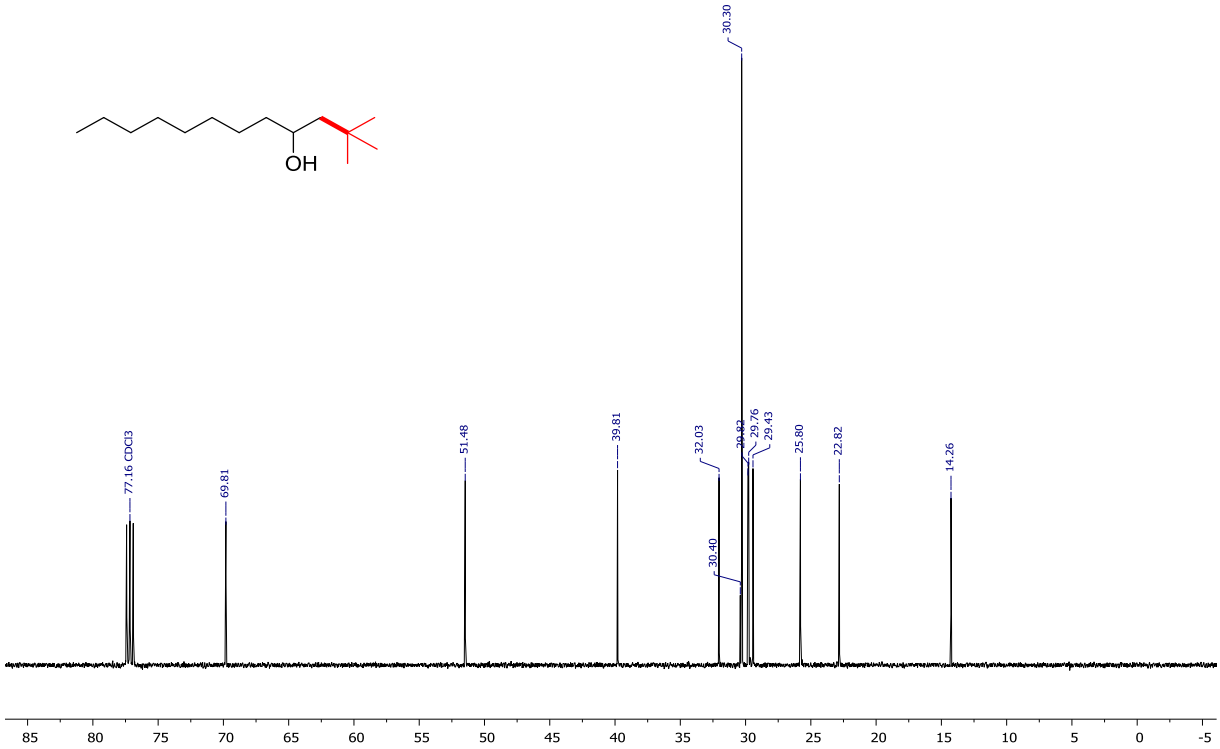



**Figure NMR-S49.** 125 MHz $^{13}C\{^{1}H\}$ NMR spectrum of 2,2-Dimethyl-4-dodecanol (table 1, entry 11).

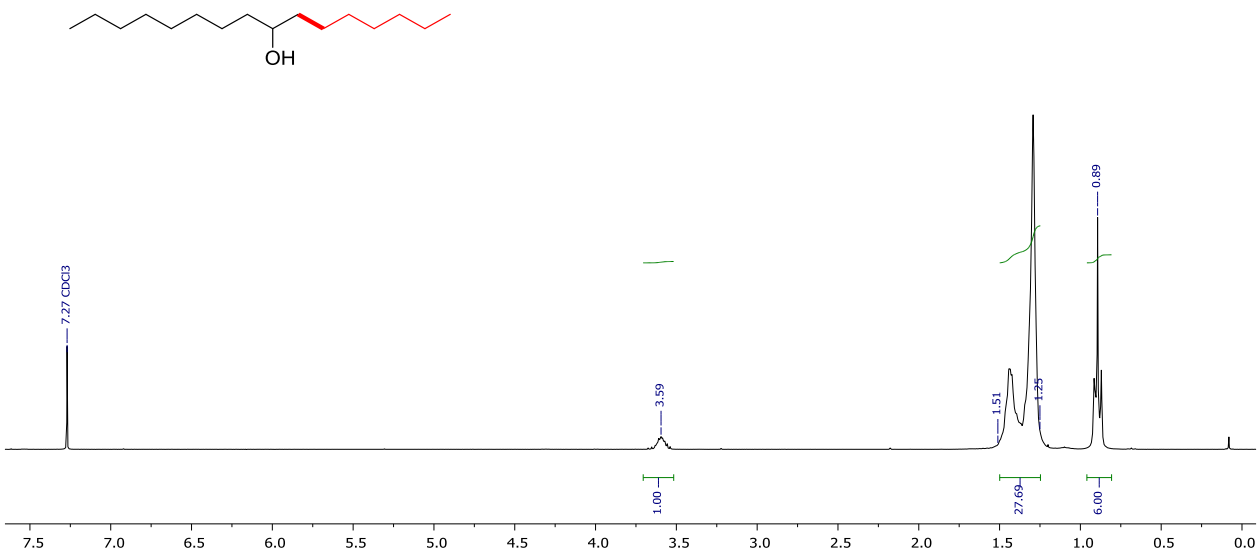



**Figure NMR-S50.** 300 MHz NMR spectrum of 8-hexadecanol.

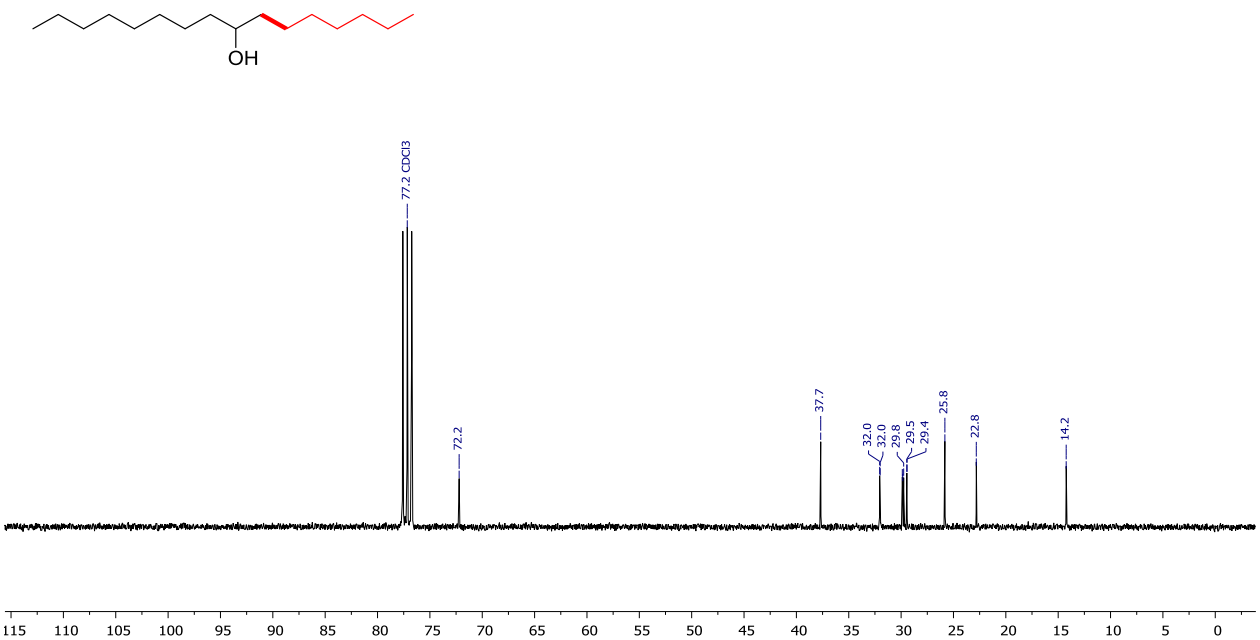



**Figure NMR-S51.** 75 MHz $^{13}C\{^{1}H\}$ NMR spectrum of 8-hexadecanol.

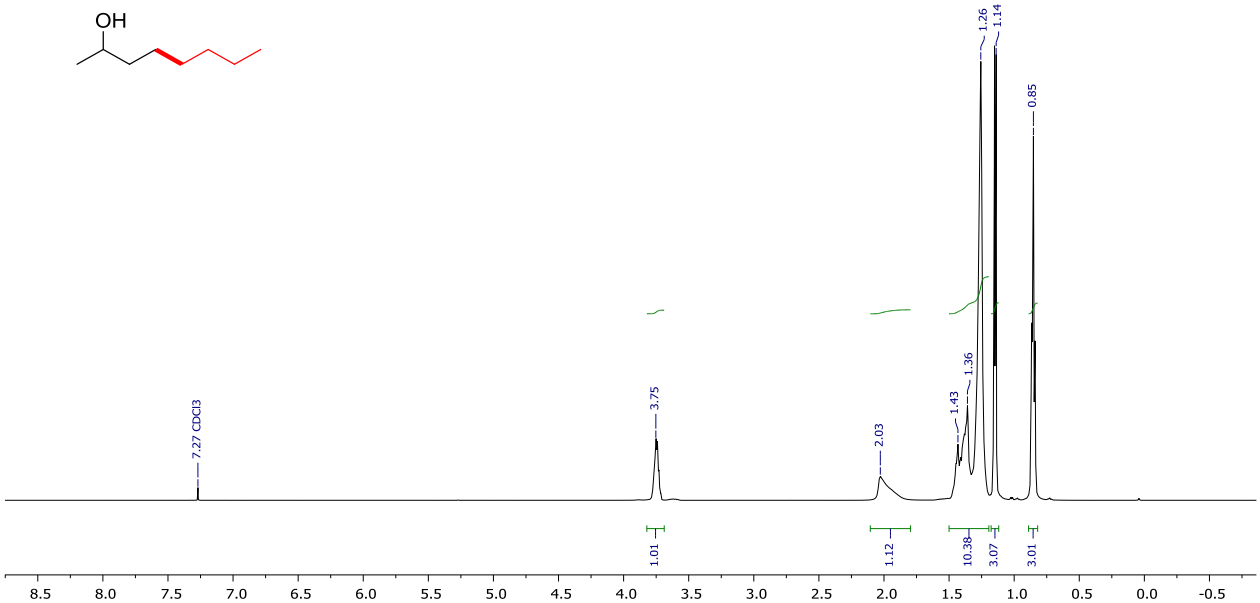



**Figure NMR-S52.** 500 MHz $^{1}H$ NMR spectrum of 2-octanol.

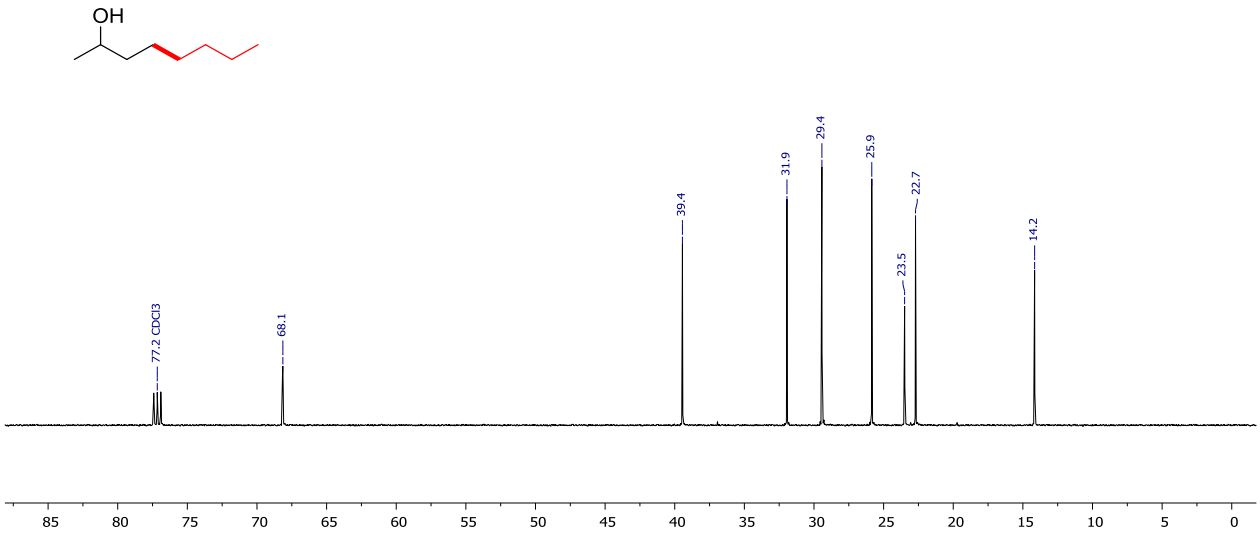



**Figure NMR-S53.** 125 MHz $^{13}C\{^{1}H\}$ NMR spectrum of 2-octanol.

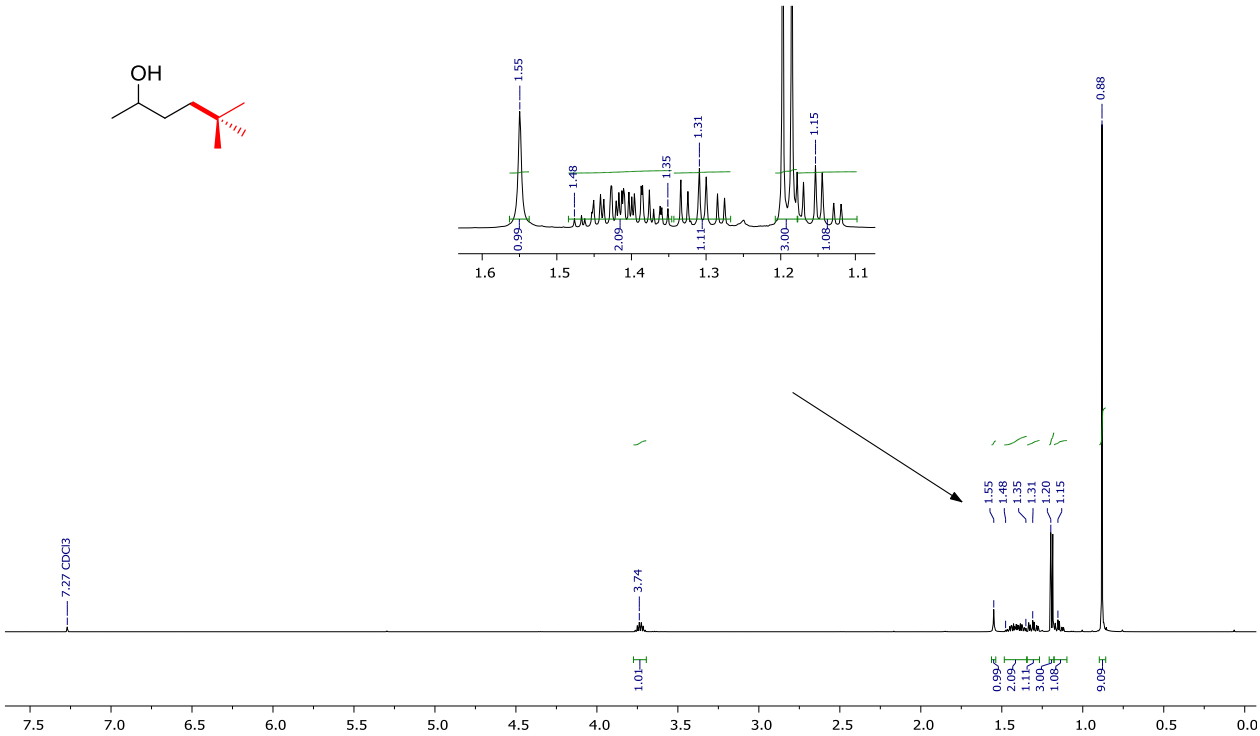



**Figure NMR-S54.** 500 MHz $^{1}H$ NMR spectrum of 5,5-dimethylhexan-2-ol (table 2, entry 1).

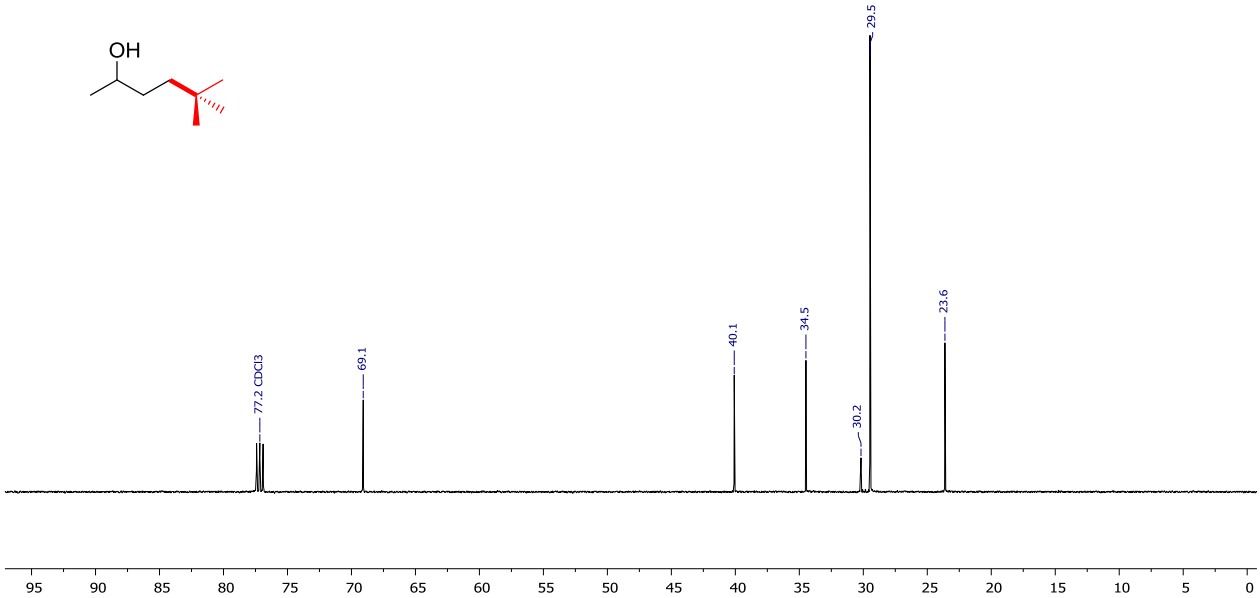



**Figure NMR-S55.** 125 MHz $^{13}C\{^{1}H\}$ NMR spectrum of 5,5-dimethylhexan-2-ol (table 2, entry 1).

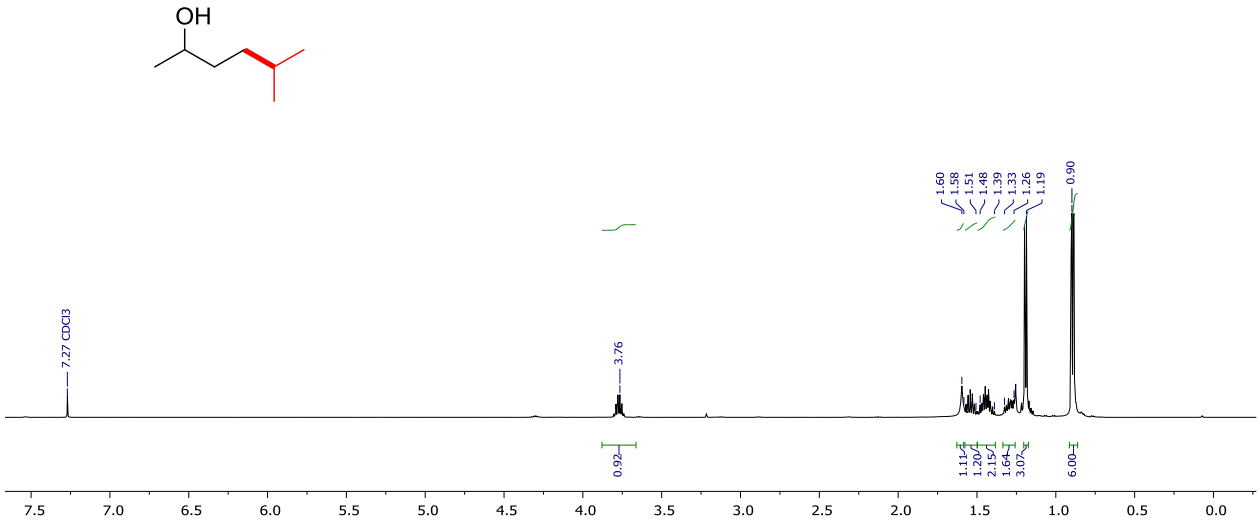



**Figure NMR-S56.** 500 MHz $^{1}H$ NMR spectrum of 5-methyl-2hexanol (table 2, entry 2).

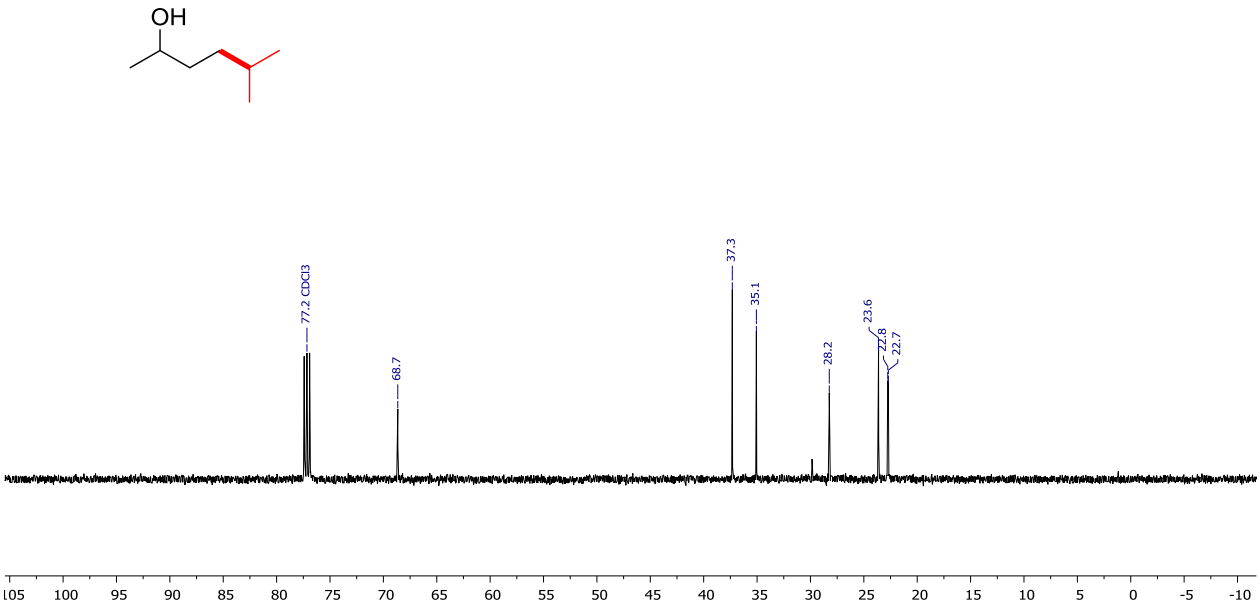



**Figure NMR-S57.** 125 MHz $^{13}C\{^{1}H\}$ NMR spectrum of 5-methyl-2hexanol (table 2, entry 2).

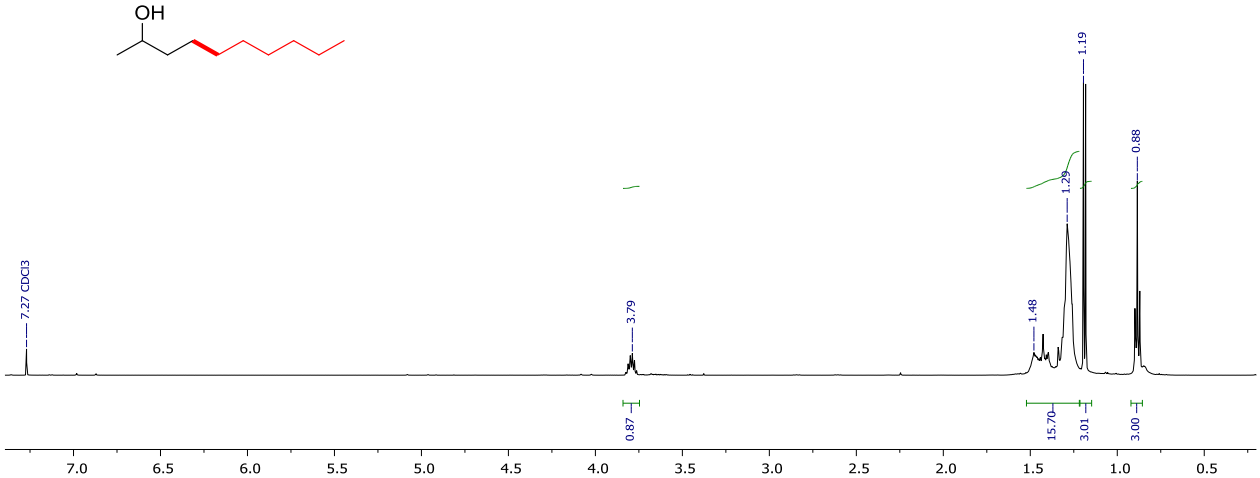



**Figure NMR-S58.** 500 MHz $^{1}H$ NMR spectrum of 2-decanol (table 2, entry 3).

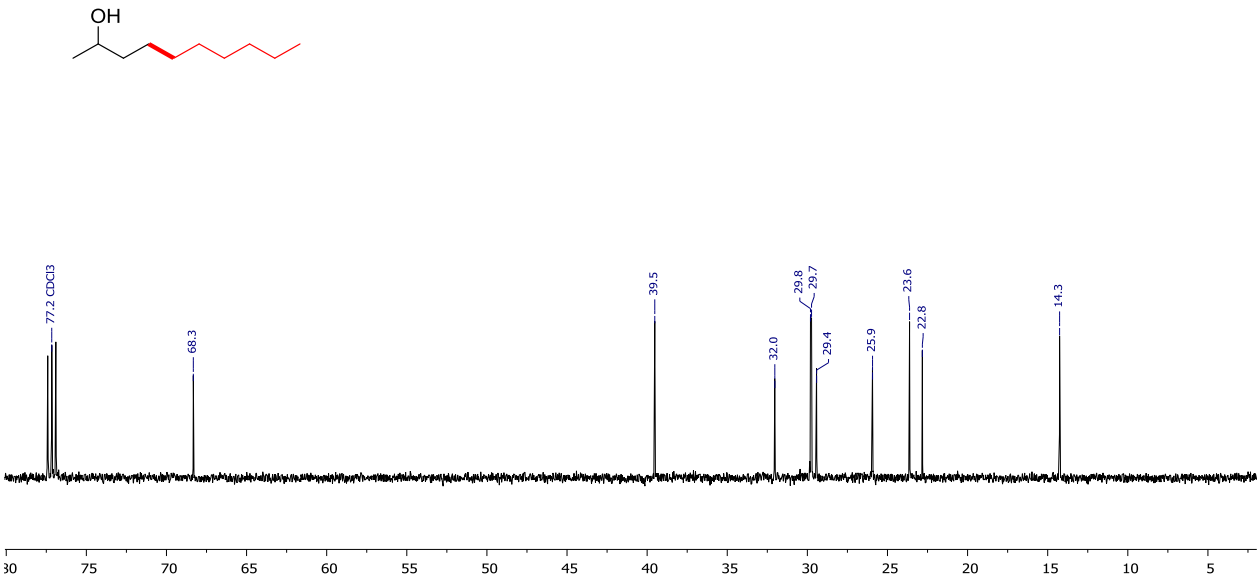



**Figure NMR-S59.** 125 MHz $^{13}C\{^{1}H\}$ NMR spectrum of 2-decanol (table 2, entry 3).

f

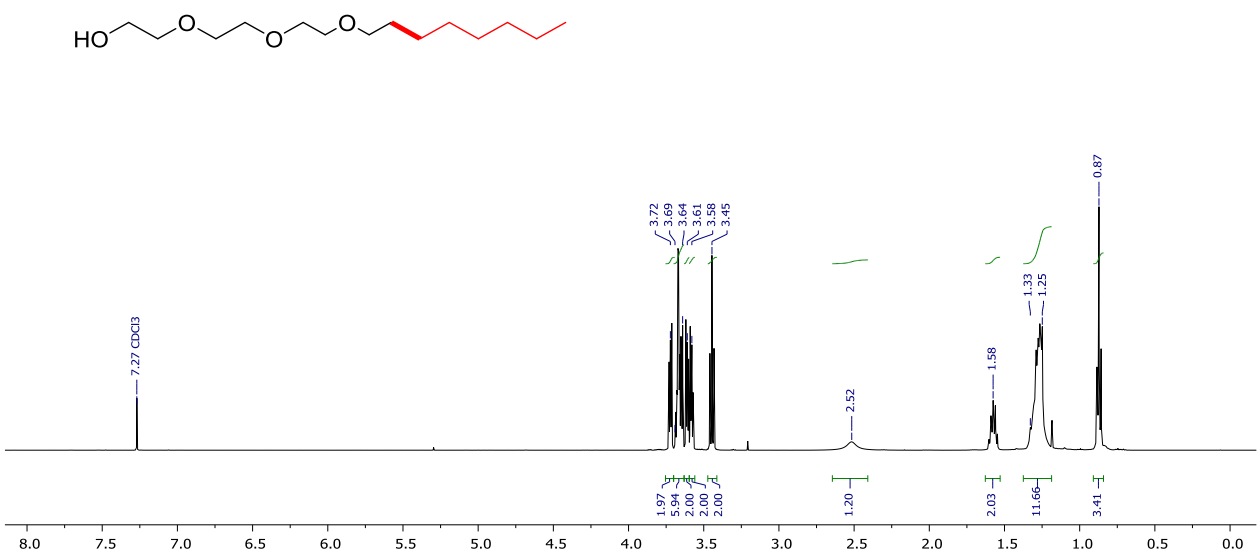



**Figure NMR-S60.** 500 MHz $^{1}H$ NMR of 2-(2-(2-(octyloxy)ethoxy)ethoxy)ethan-1-ol (table 2, entry 4).

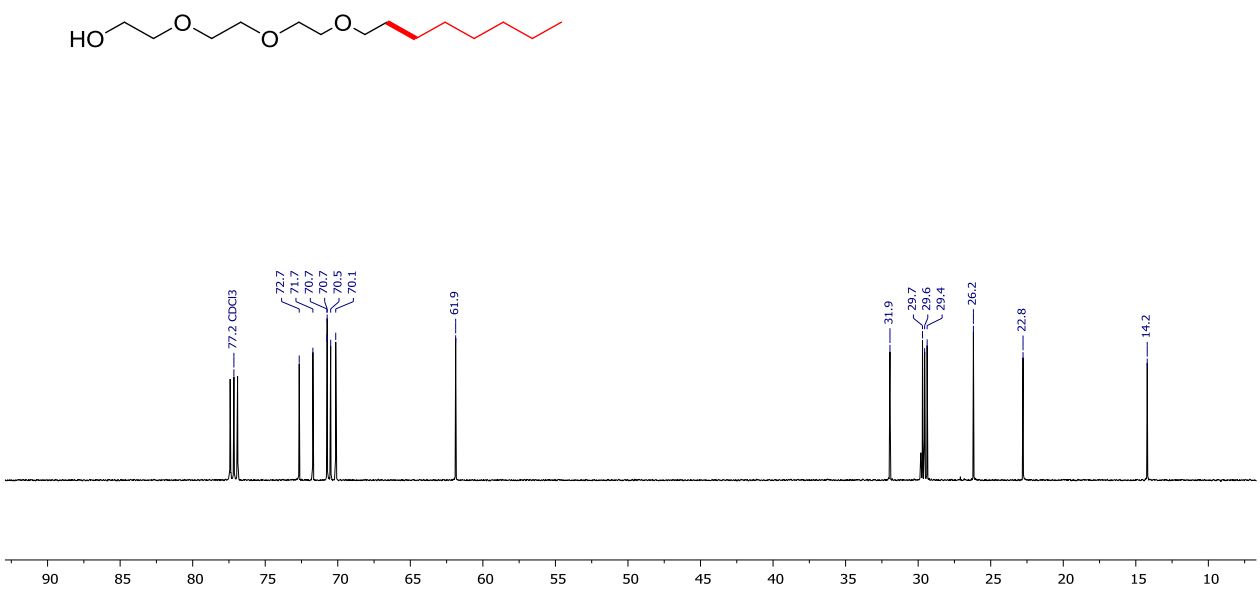



**Figure NMR-S61.** 125 MHz $^{13}C\{^{1}H\}$ NMR spectrum of 2-(2-(2-(octyloxy)ethoxy)ethoxy)ethan-1-ol (table 2, entry 4).

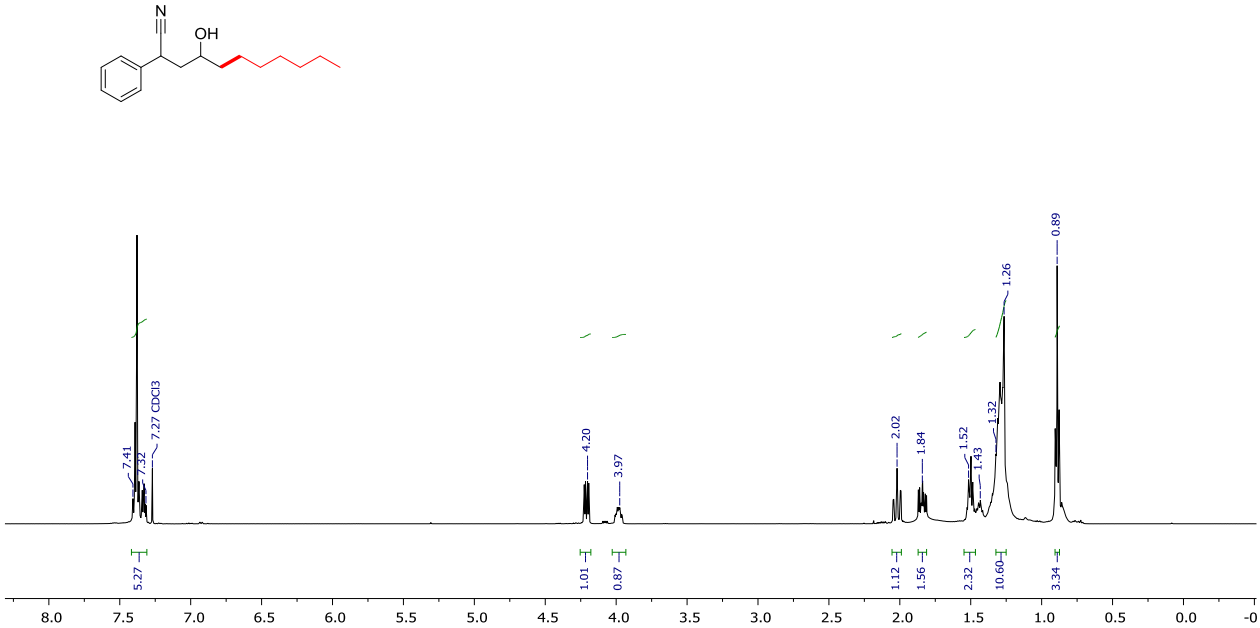



**Figure NMR-S62.** 500 MHz $^{1}H$ NMR spectrum of 4-Hydroxy-2-phenylundecanenitrile (table 2, entry 5).

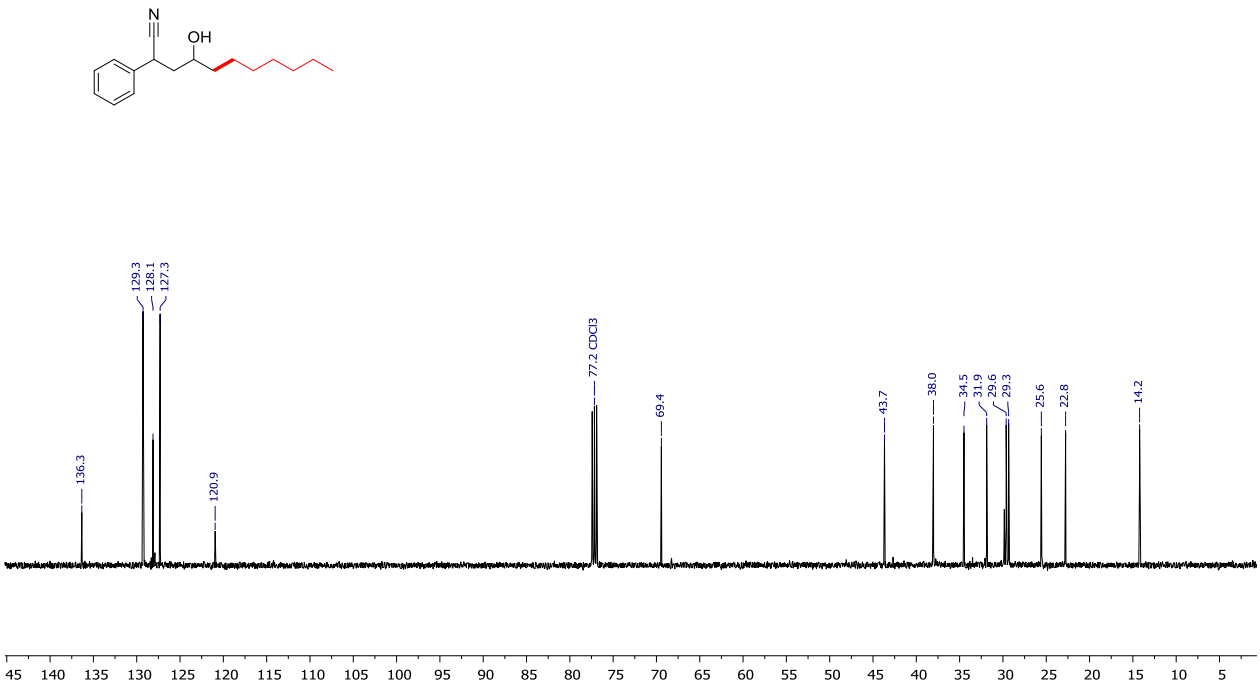



**Figure NMR-S63.** 125 MHz $^{13}C\{^{1}H\}$ NMR spectrum of 4-Hydroxy-2-phenylundecanenitrile (table 2, entry 5).

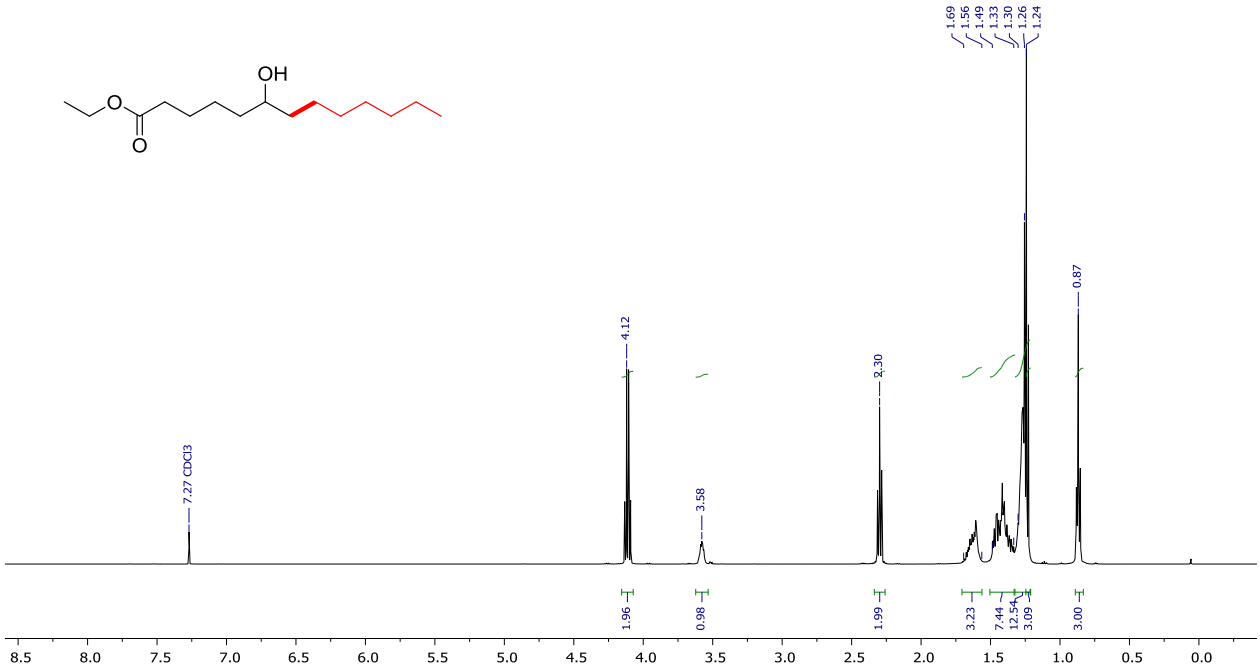



**Figure NMR-S64.** 500 MHz $^{1}H$ NMR spectrum of ethyl 6-hydroxytridecanoate (table 2, entry 6).

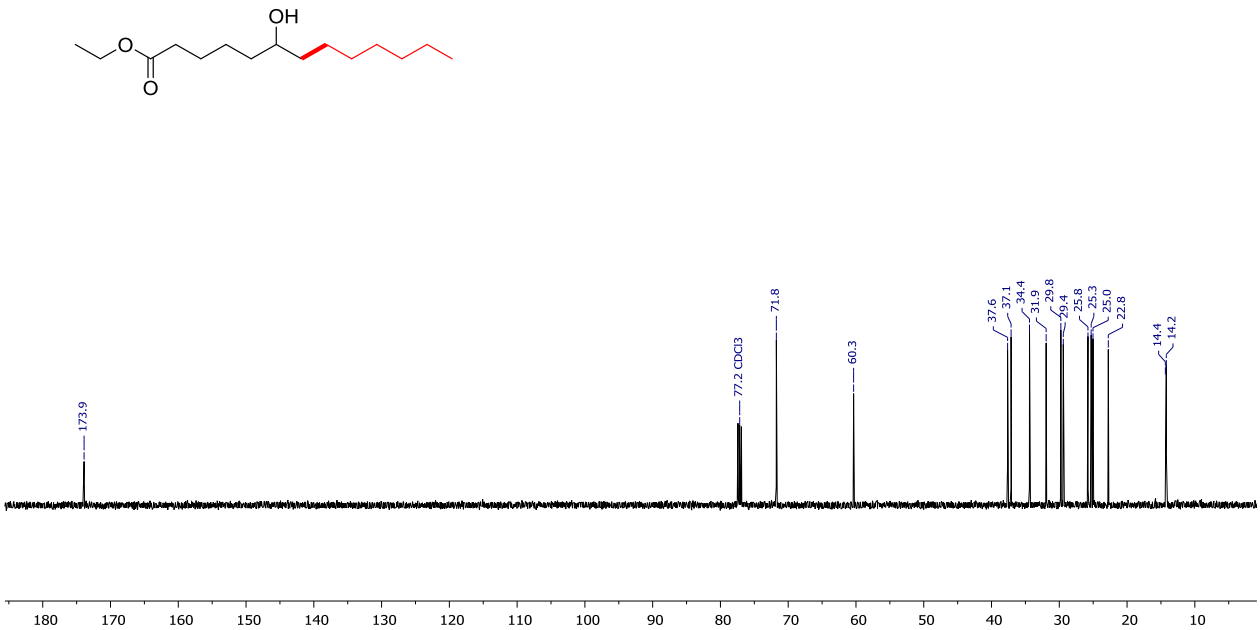



**Figure NMR-S65.** 125 MHz $^{13}C\{^{1}H\}$ NMR spectrum of ethyl 6-hydroxytridecanoate (table 2, entry 6).

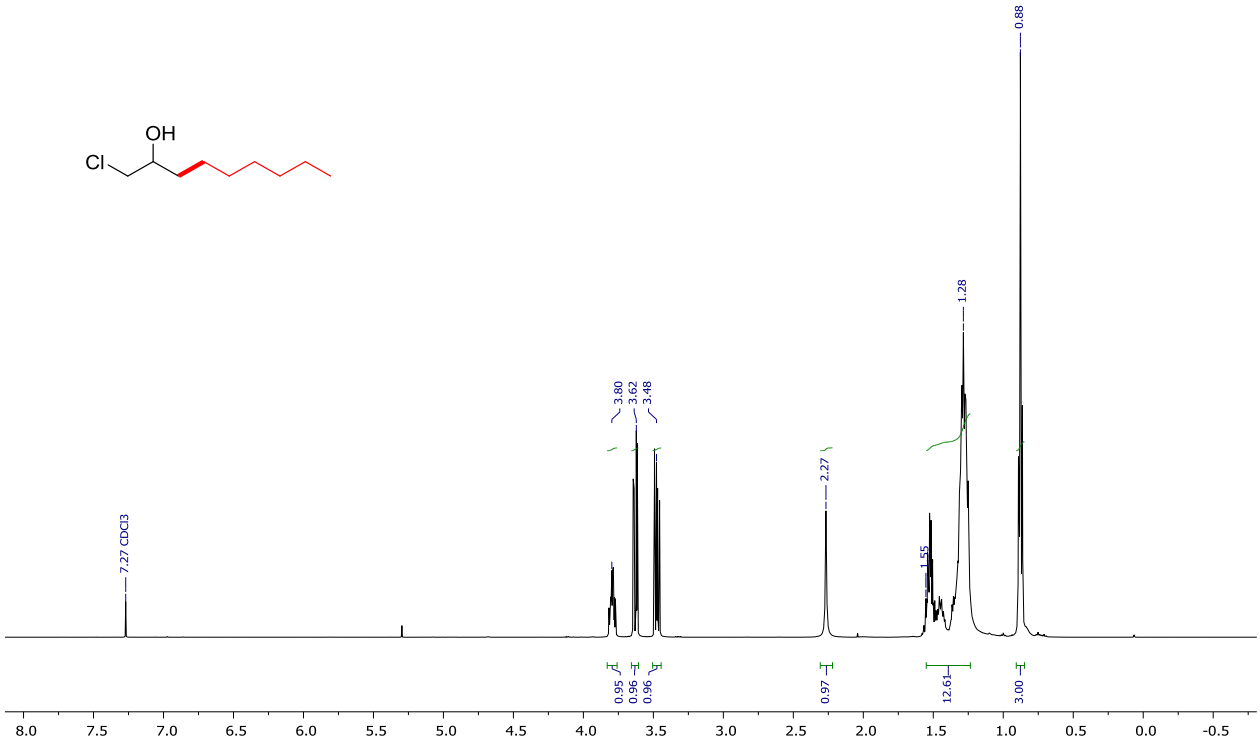



**Figure NMR-S66.** 500 MHz $^{1}H$ NMR spectrum of 1-chloro-2-nonanol (table 2, entry 7).

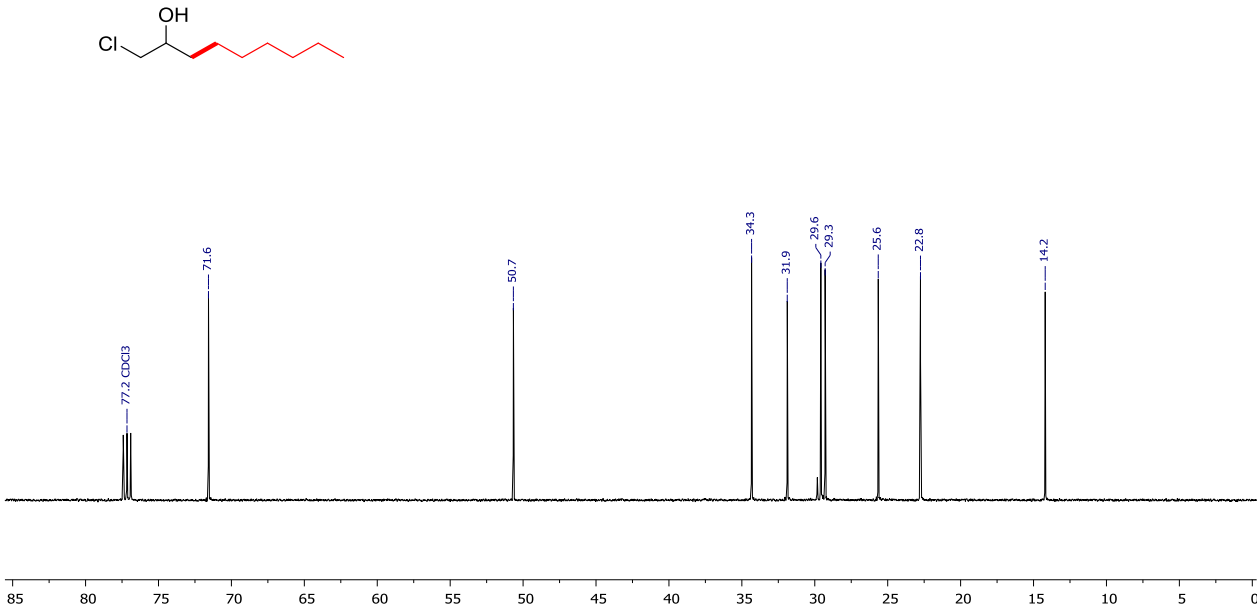



**Figure NMR-S67.** 125 MHz $^{13}C\{^{1}H\}$ NMR spectrum of 1-chloro-2-nonanol (table 2, entry 7).

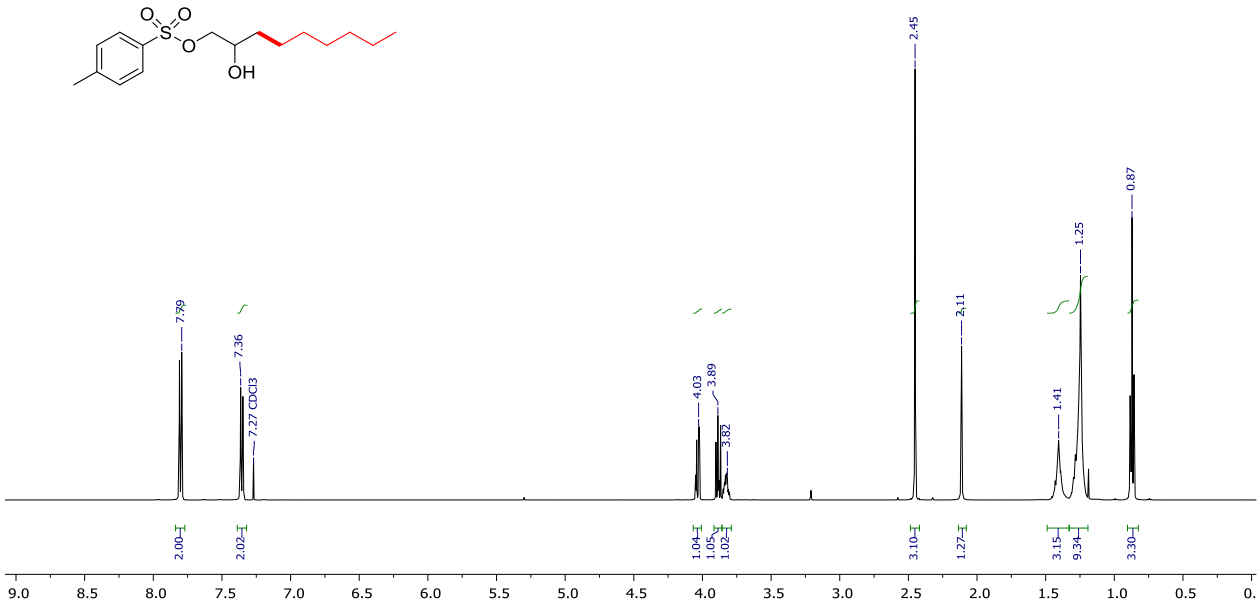



**Figure NMR-S68.** 500 MHz $^{1}H$ NMR spectrum of 4-hydroxynonyl tosylate (table 2, entry 8).

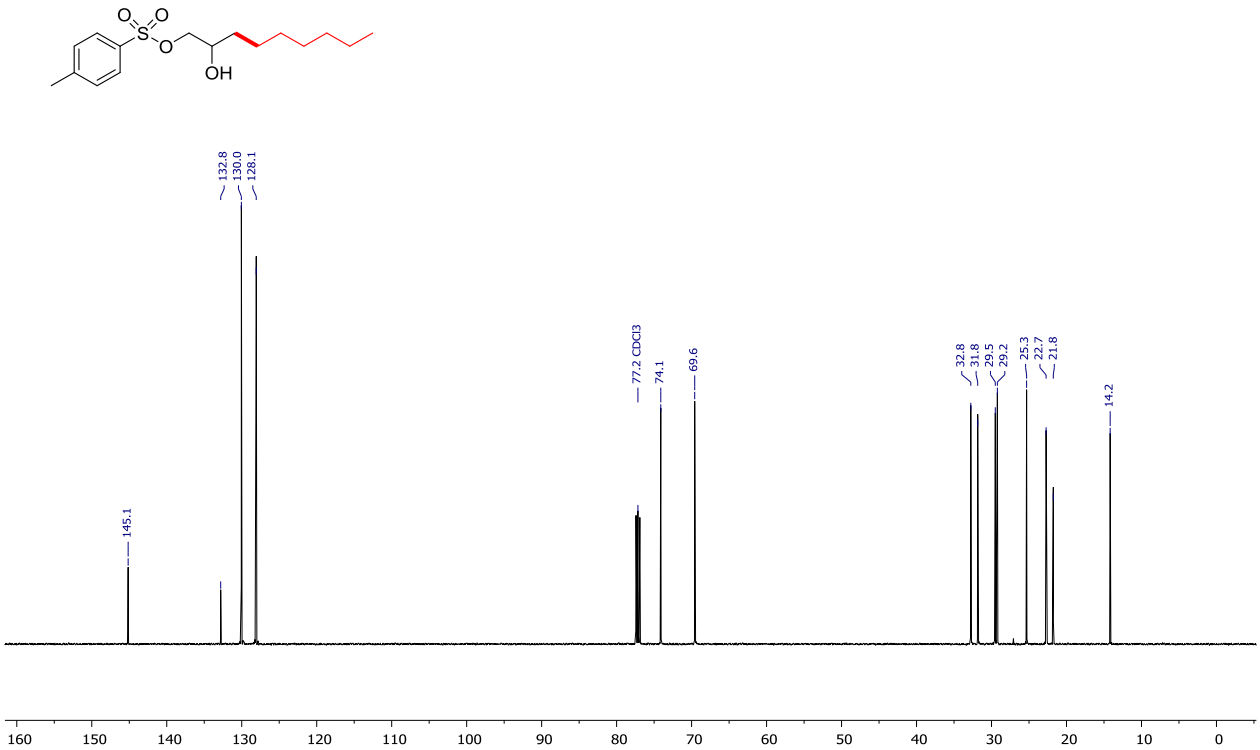



**Figure NMR-S69.** 125 MHz $^{13}C\{^{1}H\}$ NMR spectrum of 4-hydroxynonyl tosylate (table 2, entry 8).

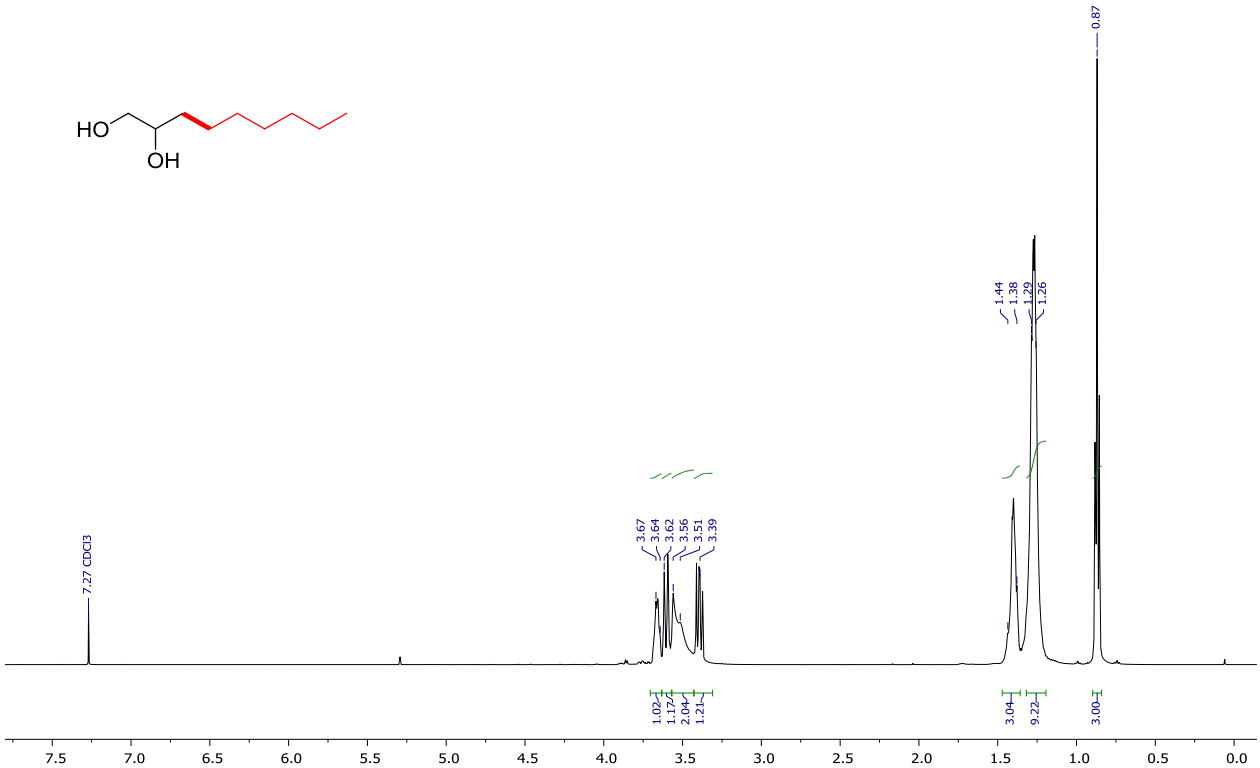



**Figure NMR-S70.** 500 MHz $^{1}H$ NMR spectrum of 1,2-nonanediol (table 2, entry 9).

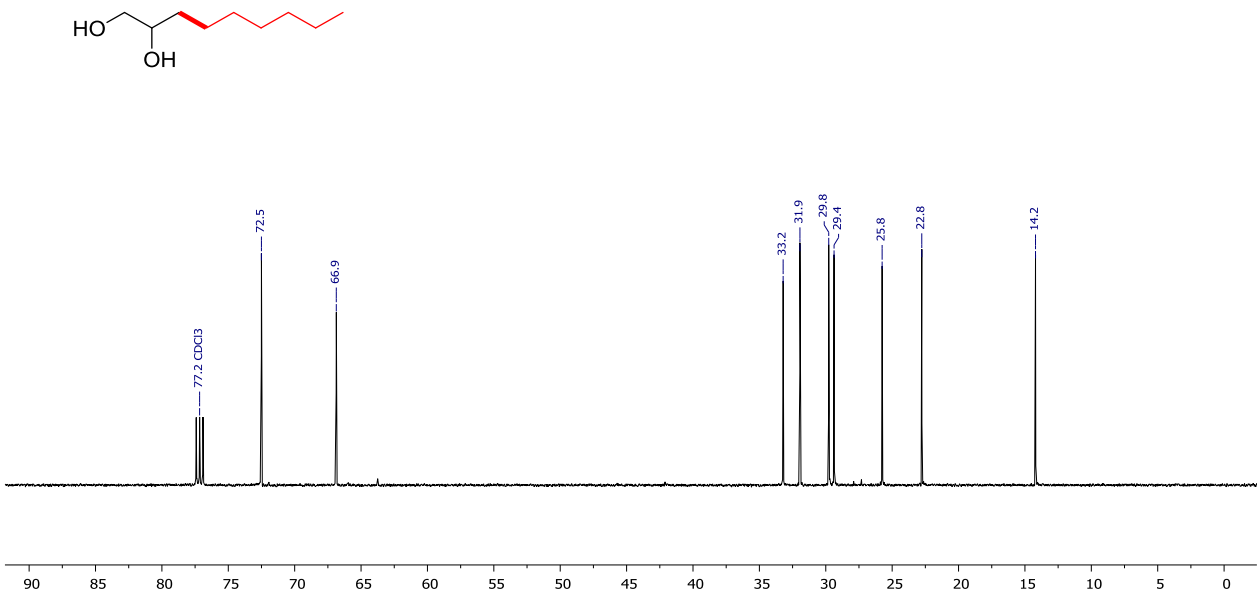



**Figure NMR-S71.** 125 MHz $^{13}C\{^{1}H\}$ NMR spectrum of 1,2-nonanediol (table 2, entry 9).

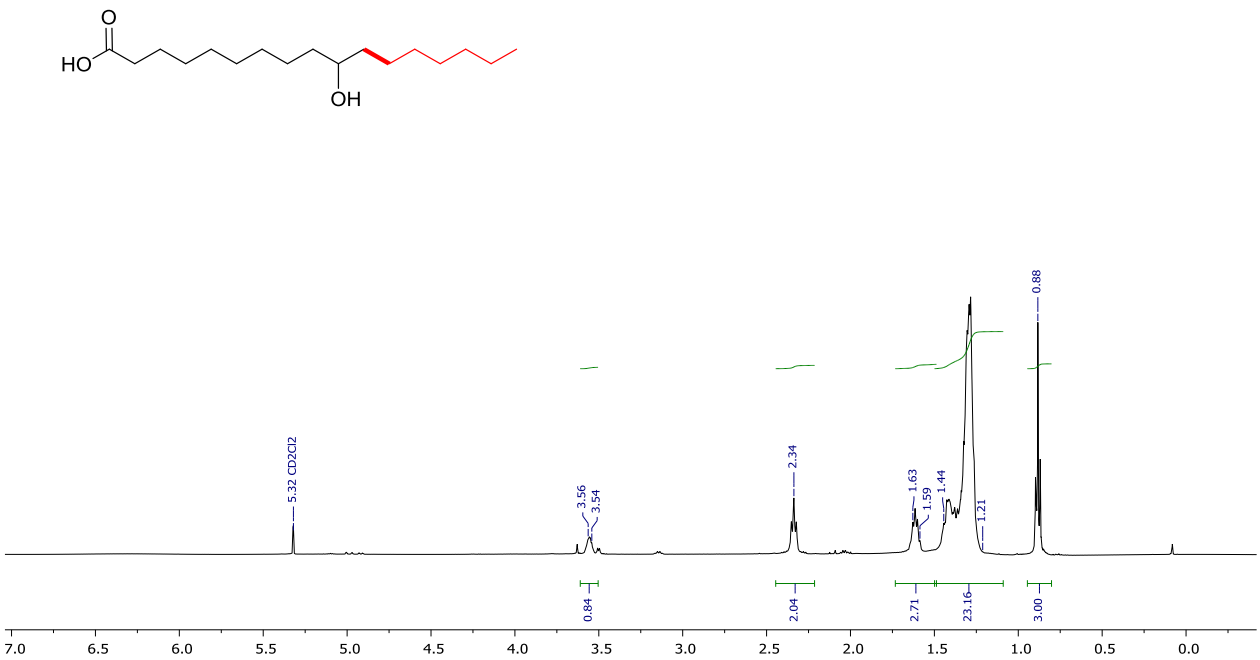



**Figure NMR-S72.** 500 MHz $^{1}H$ NMR spectrum of 10-hydroxyheptadecanoic acid (table 2, entry 10).

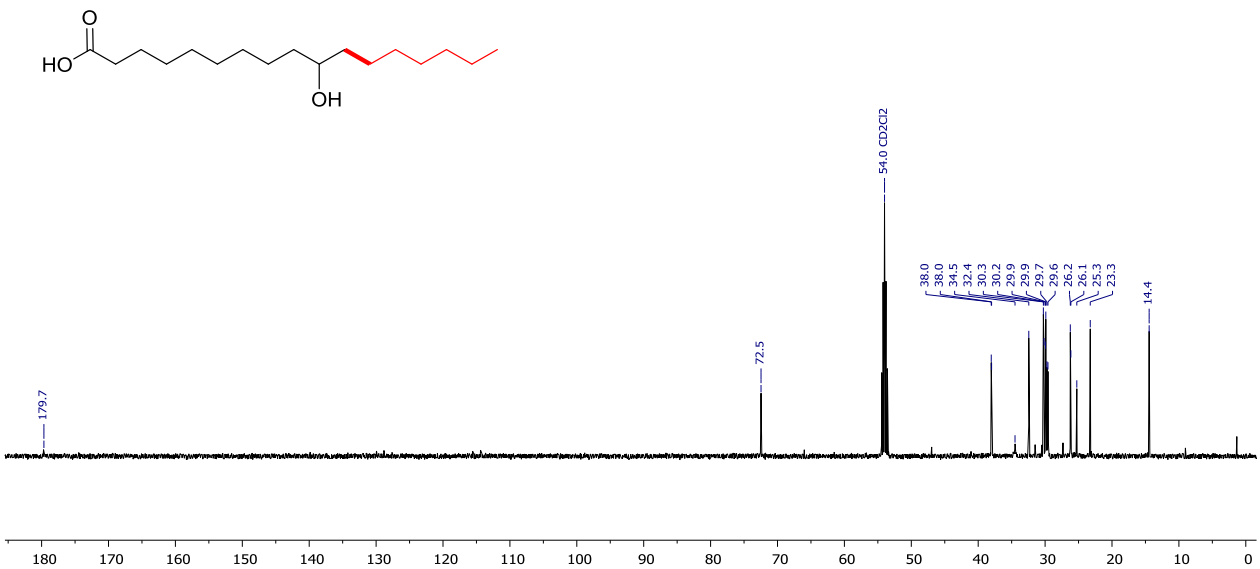



**Figure NMR-S73.** 125 MHz $^{13}C\{^{1}H\}$ NMR spectrum of 10-hydroxyheptadecanoic acid (table 2, entry 10).

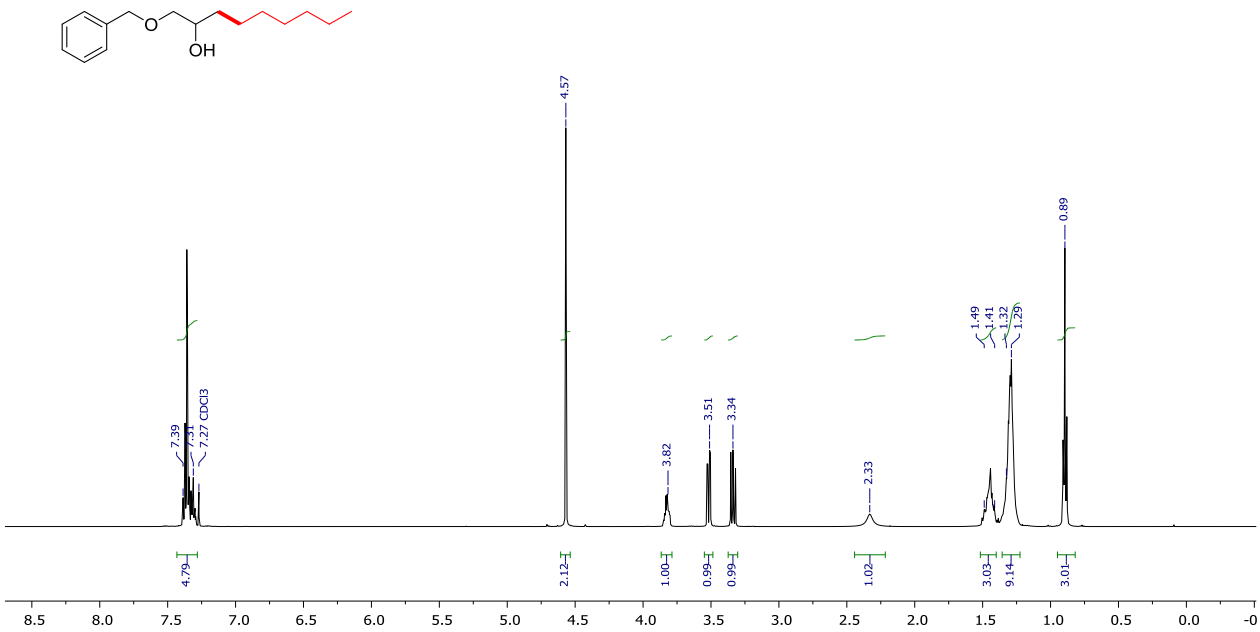



**Figure NMR-S74.** 500 MHz $^{1}H$ NMR spectrum of 1-(benzyloxy)-2-nonanol (table 2, entry 11).

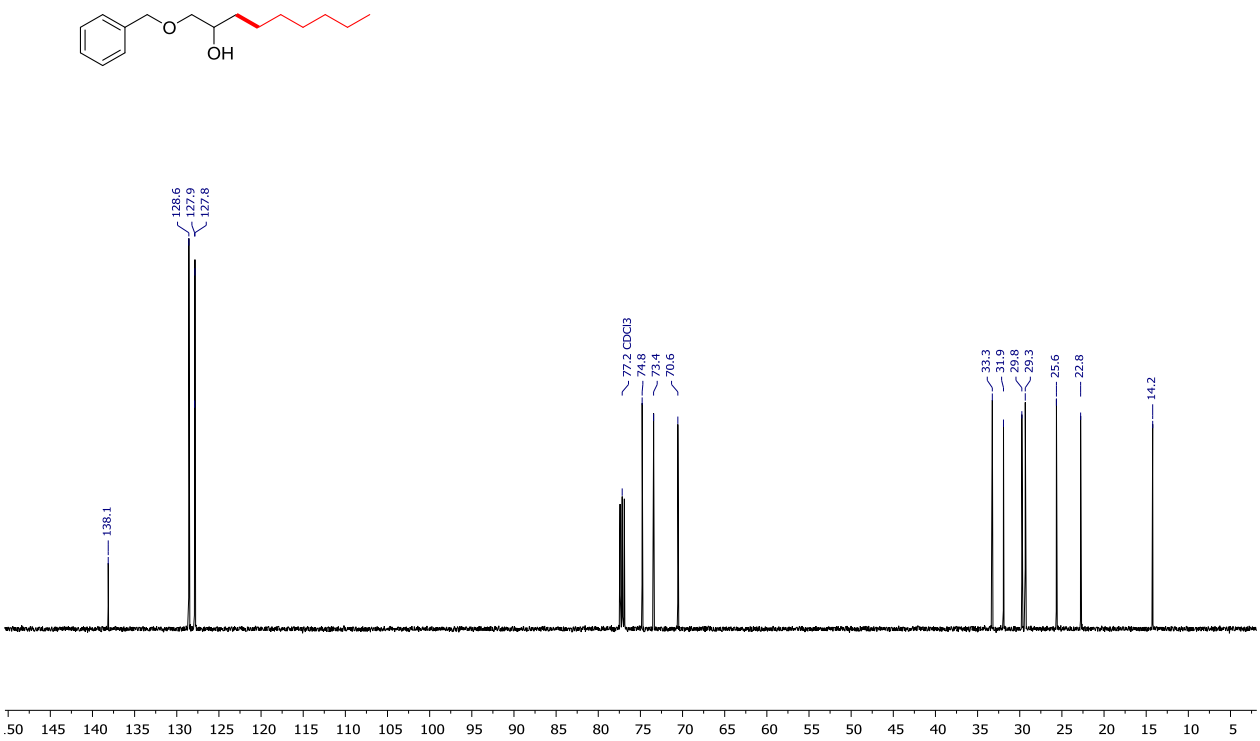



**Figure NMR-S75.** 125 MHz $^{13}C\{^{1}H\}$ NMR spectrum of 1-(benzyloxy)-2-nonanol (table 2, entry 11).

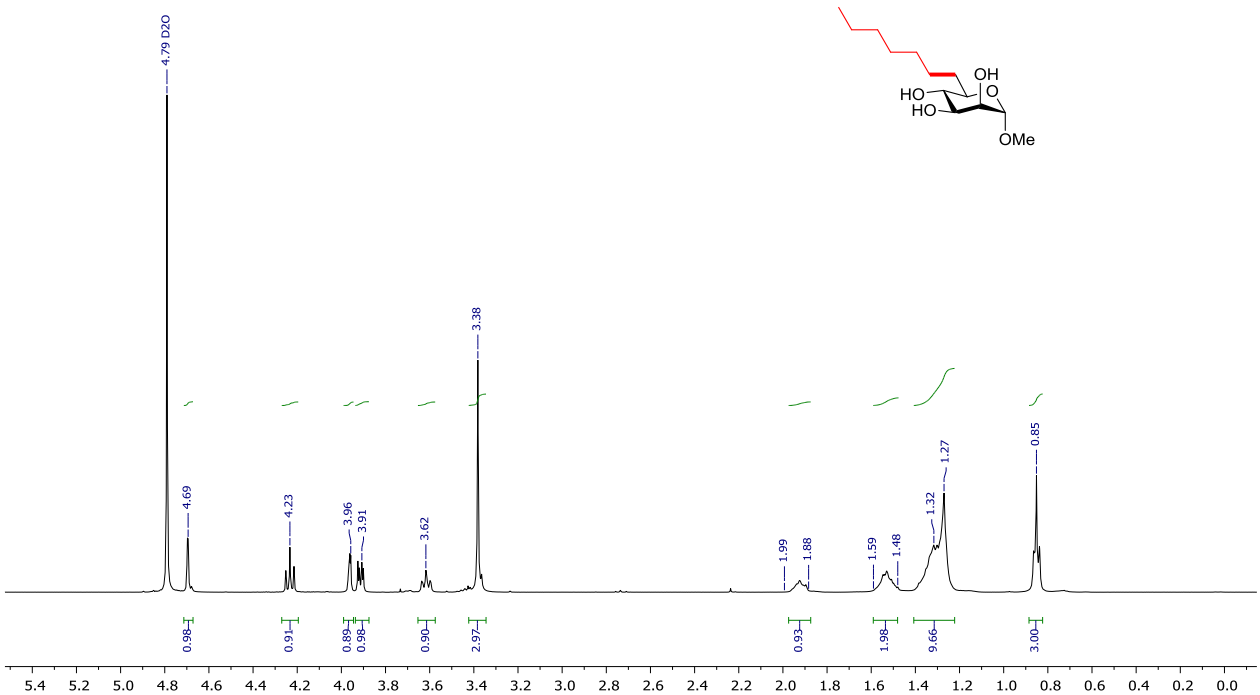



**Figure NMR-S76.** 500 MHz $^{1}H$ NMR spectrum of methyl 6-hexyl-6-deoxy-α-D-mannopyranoside (table 2, entry 12).

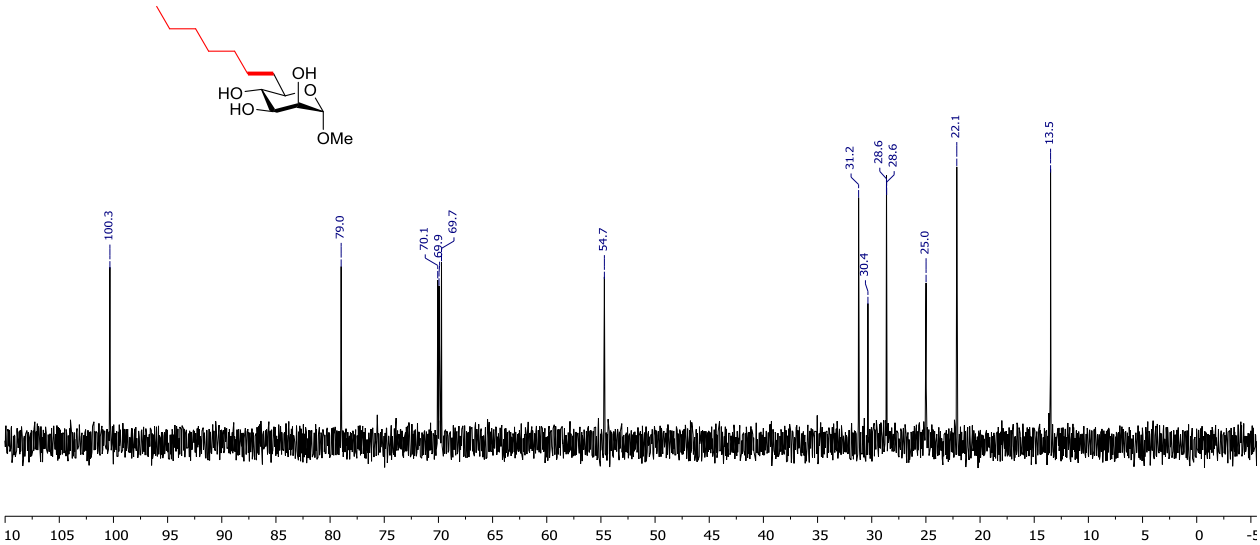



**Figure NMR-S77.** 125 MHz $^{13}C\{^{1}H\}$ NMR spectrum of methyl 6-hexyl-6-deoxy-α-D-mannopyranoside (table 2, entry 12).

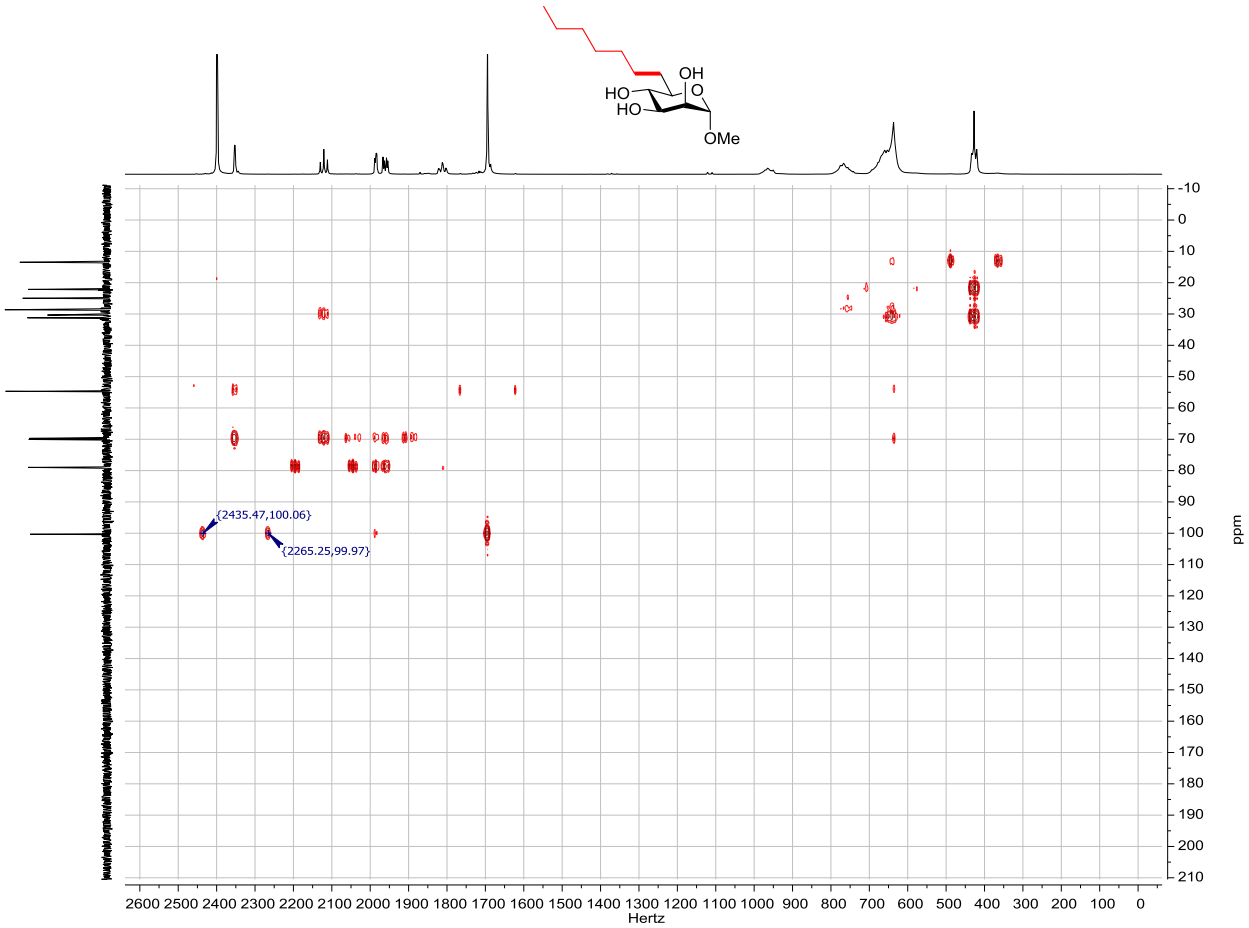



**Figure NMR-S78.** HMBC spectrum of methyl 6-hexyl-6-deoxy-α-D-mannopyranoside (table 2, entry 12).

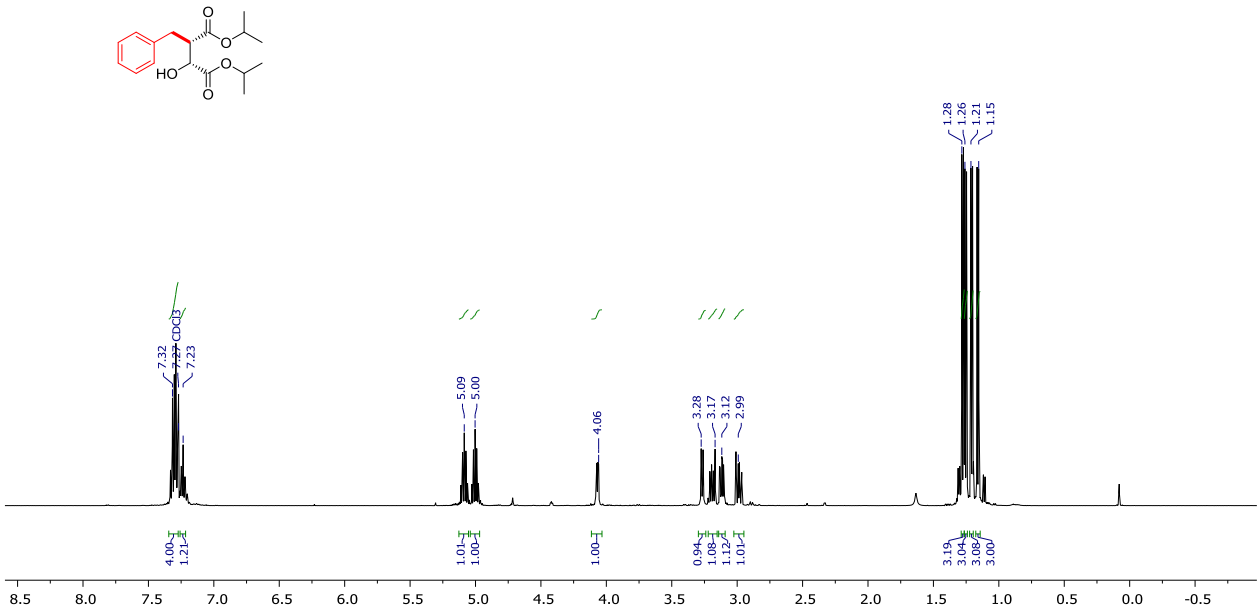



**Figure NMR-S79.** 500 MHz $^{1}$H NMR spectrum of diisopropyl-2-benzyl-3-hydroxysuccinate.

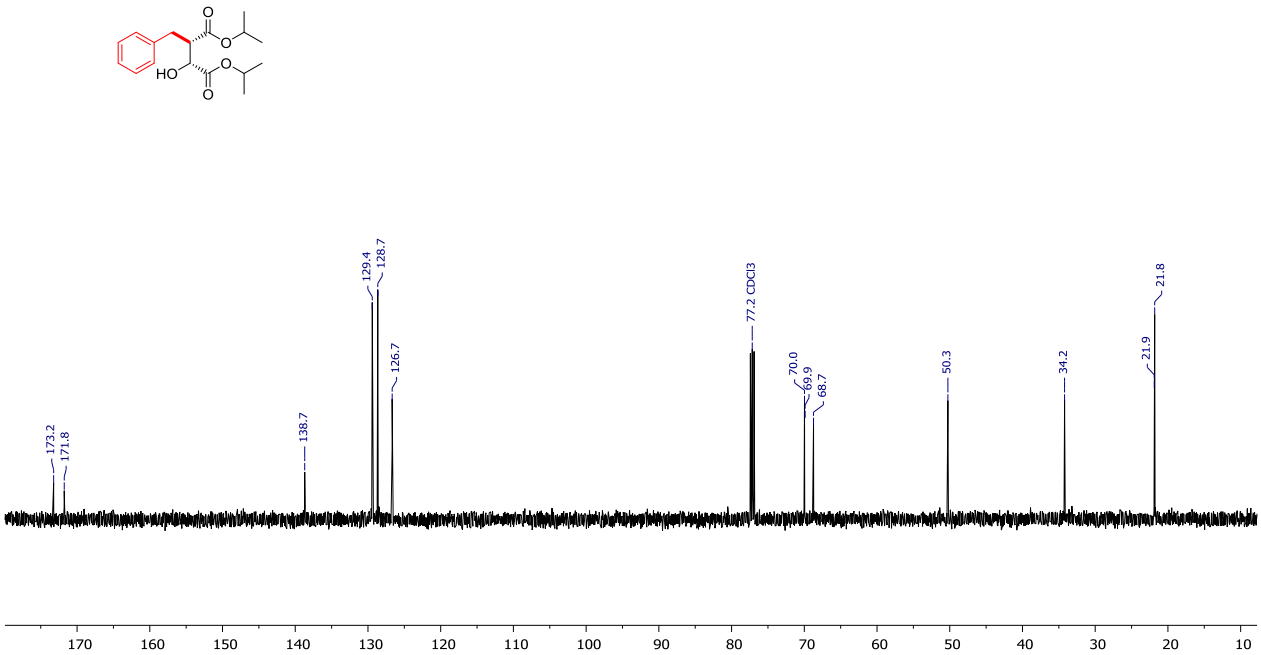



**Figure NMR-S80.** 125 MHz $^{13}$C{$^{1}$H} NMR spectrum of diisopropyl-2-benzyl-3-hydroxysuccinate.

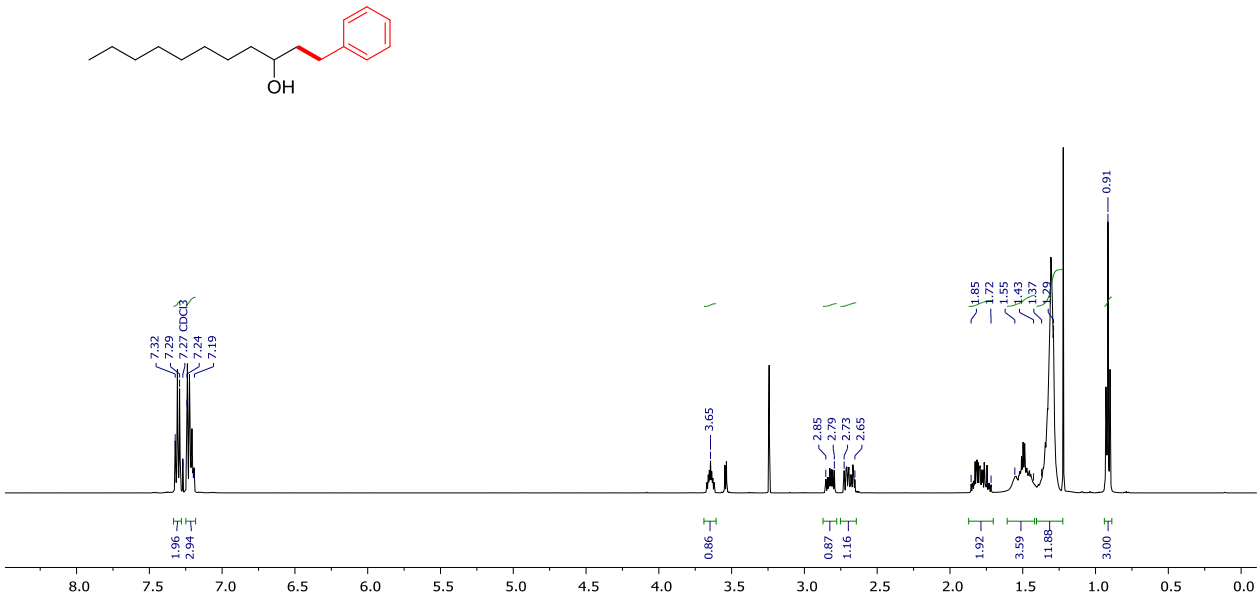



**Figure NMR-S81.** 500 MHz $^{1}$H NMR spectrum of 1-phenylundecan-3-ol. Residual MTBE observed at $\delta$ = 1.22 and 3.24 ppm.

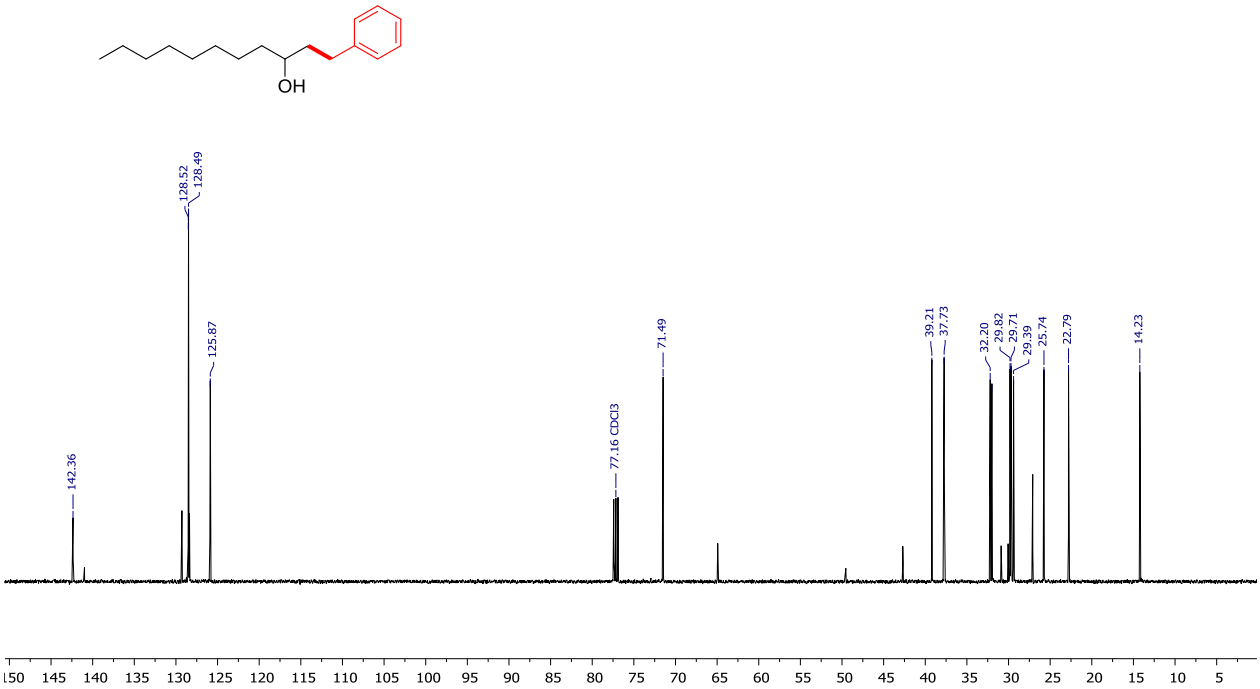
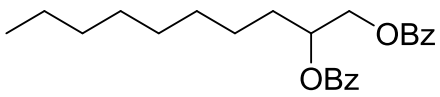
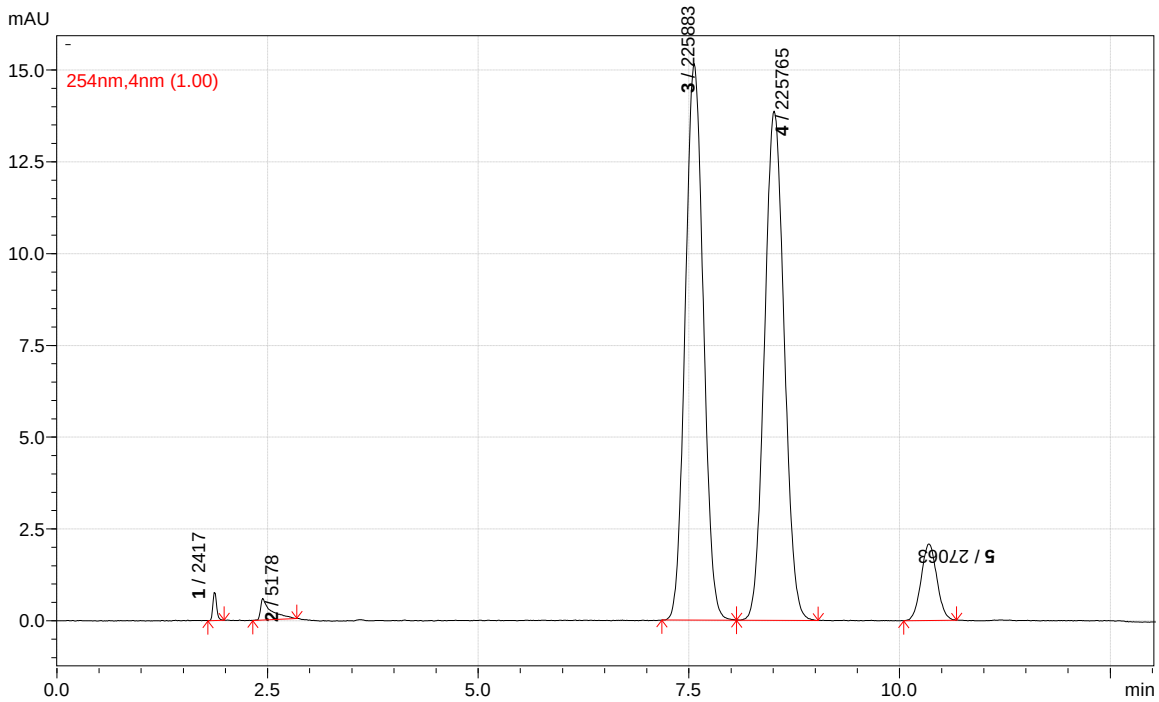



**Figure NMR-S82.** 125 MHz $^{13}$C{$^{1}$H} NMR spectrum of 1-phenylundecan-3-ol.

# Chiral HPLC chromatographic analyses




Chiralpak AD-3

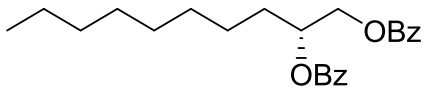
n-Heptane:Isopropanol 99:1

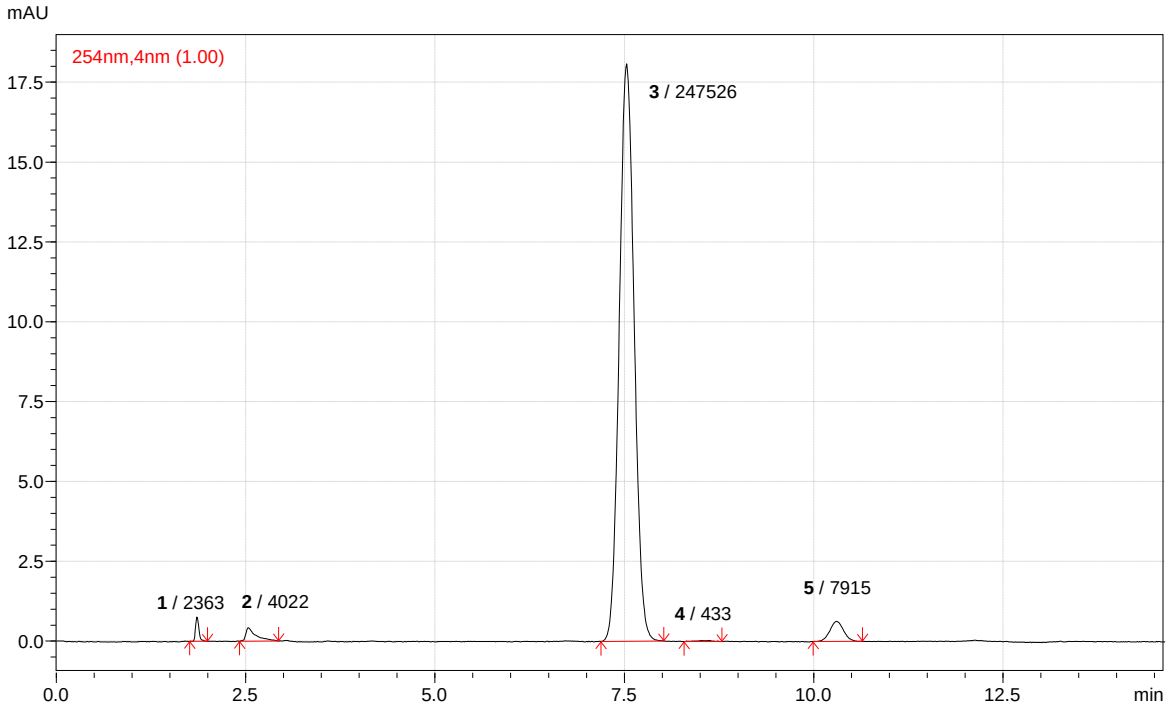
1.0 mL/min

[Peak Table(PDA-Ch1)]

# of Peaks 5

| Peak# | R.Time | I.Time | F.Time | Area | Height | A/H | |
|---|---|---|---|---|---|---|---|
| 1 | 1.866 | 1.792 | 1.984 | 2417 | 770 | 3.1390 | |
| 2 | 2.439 | 2.325 | 2.848 | 5178 | 588 | 8.8070 | |
| 3 | 7.557 | 7.179 | 8.064 | 225883 | 15150 | 14.9100 | Enantiomer 1 |
| 4 | 8.507 | 8.064 | 9.035 | 225765 | 13867 | 16.2810 | Enantiomer 2 |
| 5 | 10.343 | 10.048 | 10.677 | 27063 | 2083 | 12.9940 | |




Chiralpak AD-3

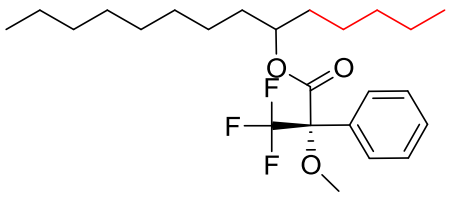
n-Heptane:Isopropanol 99:1

1.0 mL/min

[Peak Table(PDA-Ch1)]

# of Peaks 5

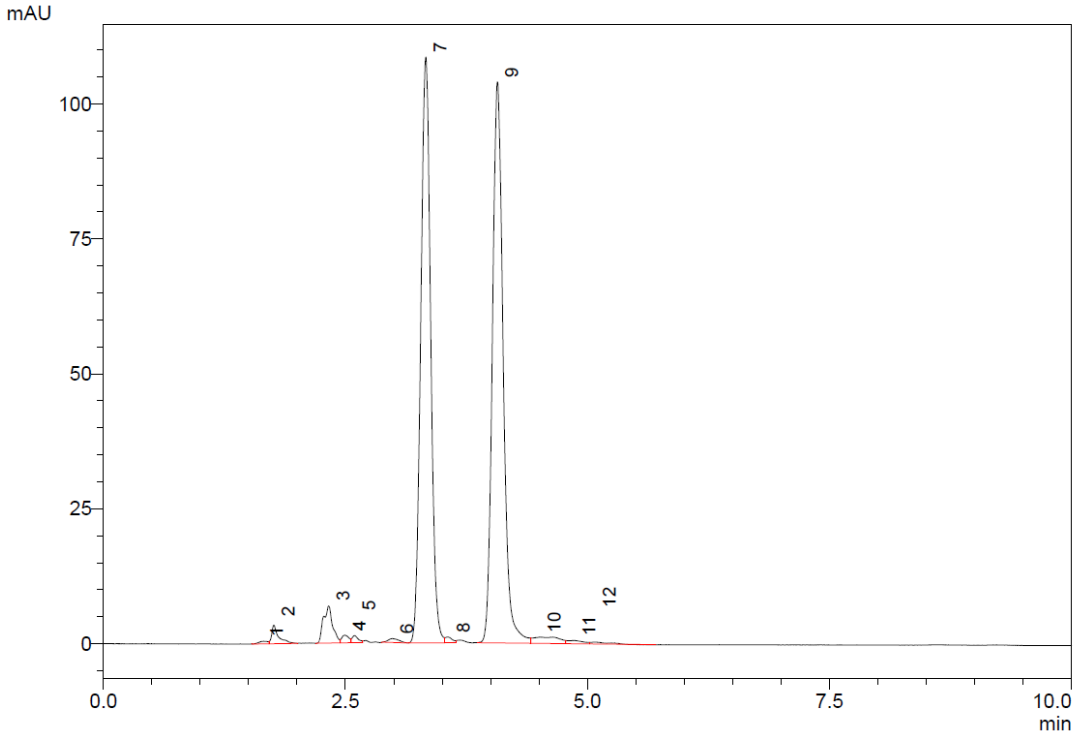
| Peak# | R.Time | I.Time | F.Time | Area | Height | A/H |
|---|---|---|---|---|---|---|
| 1 | 1.853 | 1.760 | 1.995 | 2363 | 764 | 3.0930 |
| 2 | 2.529 | 2.421 | 2.933 | 4022 | 423 | 9.4970 |
| 3 | 7.524 | 7.189 | 8.021 | 247526 | 18081 | 13.6890 Enantiomer 1 e.e. = 99.7% |
| 4 | 8.517 | 8.288 | 8.789 | 433 | 31 | 13.8820 Enantiomer 2 |
| 5 | 10.296 | 9.995 | 10.645 | 7915 | 630 | 12.5680 |



Vial # : 1
Injection Volume : 2 uL
Data File Name : RAR-RA-298-Rac-05.lcd
Method File Name : Ramirez.lcm

<<Oven>>
Valve L : 2
Valve R : 2

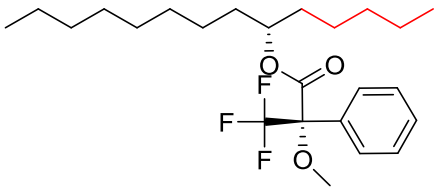
2 µL RAR-RA-298-Rac (1 µl in 0.5 ml n-Heptan)
150 mm Chiralpak AD-3, 4.6 mm i.D.; Säule 3
n-Heptan/2-Propanol = 99:1 (v/v)
1.0 ml/min, 5.2 MPa, 298 K
UV, 220 nm




1 220nm,4nm

PDA Ch1 220nm

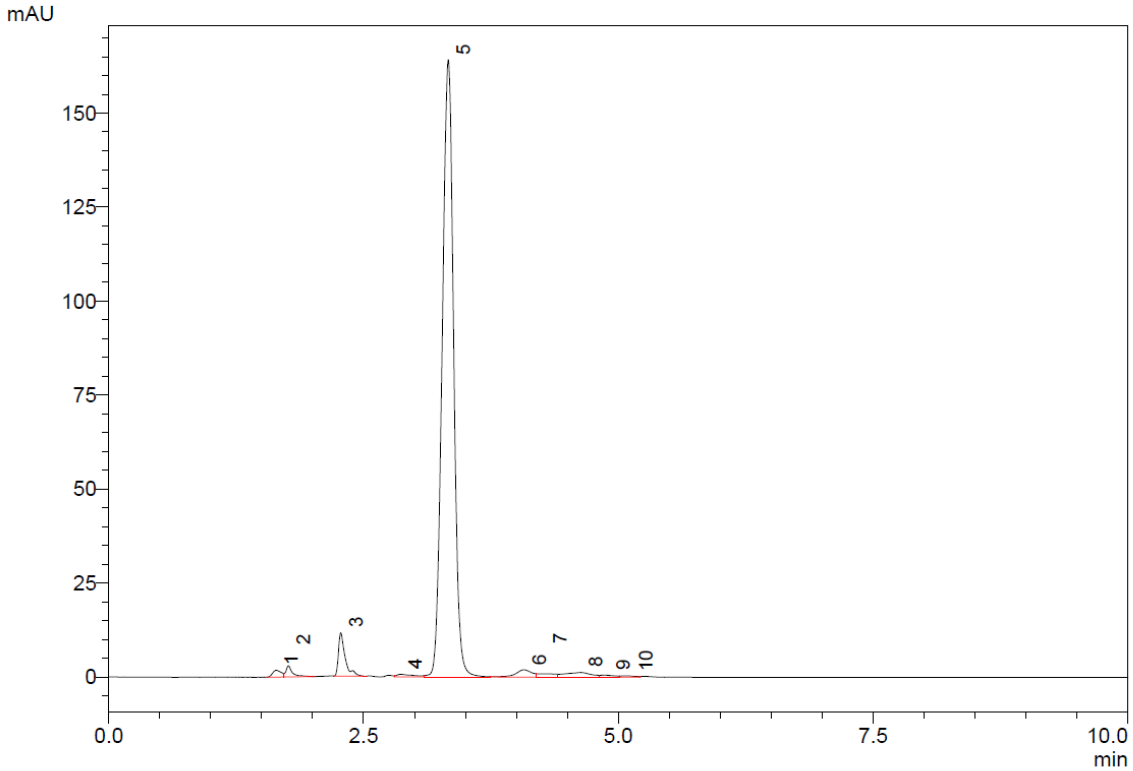
| Peak # | Ret. Time | Area % | Name |
|---|---|---|---|
| 1 | 1.64 | 0.19 | |
| 2 | 1.76 | 0.99 | |
| 3 | 2.33 | 2.66 | |
| 4 | 2.49 | 0.42 | |
| 5 | 2.59 | 0.33 | |
| 6 | 2.99 | 0.33 | |
| 7 | 3.33 | 45.43 | 1. Enantiomer |
| 8 | 3.57 | 0.31 | |
| 9 | 4.07 | 47.38 | 2. Enantiomer + Impurity |
| 10 | 4.51 | 1.30 | |
| 11 | 4.87 | 0.41 | |
| 12 | 5.08 | 0.24 | |
| Total | | 100.00 | |



Sample Name : RAR-RA-298-Enantiomer
Vial # : 2
Injection Volume : 2 uL
Data File Name : RAR-RA-298-E-02.lcd
Method File Name : Ramirez.lcm

<<Oven>>
Valve L : 2
Valve R : 2

2 µL RAR-RA-298-Enantiomer (1 µl in 0.5 ml n-Heptan
150 mm Chiralpak AD-3, 4.6 mm i.D.; Säule 3
n-Heptan/2-Propanol = 99:1 (v/v)
1.0 ml/min, 5.2 MPa, 298 K
UV, 220 nm




1 220nm,4nm

PDA Ch1 220nm

| Peak # | Ret. Time | Area % | Name | |
|---|---|---|---|---|
| 1 | 1.64 | 0.76 | | |
| 2 | 1.76 | 0.91 | | |
| 3 | 2.28 | 3.69 | | |
| 4 | 2.86 | 0.57 | | |
| 5 | 3.33 | 89.65 | 1. Enantiomer | = 96.7 % ee |
| 6 | 4.07 | 1.49 | 2. Enantiomer | |
| 7 | 4.28 | 0.74 | | |
| 8 | 4.63 | 1.59 | | |
| 9 | 4.90 | 0.35 | | |
| 10 | 5.12 | 0.25 | | |
| Total | | 100.00 | | |

# References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