Electronic Supporting Information

anti-Dihydroxylation of olefins enabled by *in situ* generated peroxyacetic acid

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General information

All commercially available chemicals were purchased from Acros Organics, Sigma-Aldrich, and Fluka and used without further purification. All reactions were carried out in oven-dried glassware under air with a closed cap. Since reactions require higher temperatures, they were heated with an oil bath over a Heidolph heating plate, where the temperature was set and monitored via an external thermometer. Necessary technical quality solvents like acetic acid, cyclohexane, ethyl acetate, and others were bought and used for performing the reactions and chromatography. Cyclohexane and ethyl acetate were used for extraction and chromatography steps after their purification via distillation.

Merck pre-coated TLC plates (TLC 100 µm silica gel 60 F_{254}) were used for thin-layer chromatography (TLC) analysis. Visualisation of the UV active and UV non-active spots was accomplished by UV light (λ = 254 nm) and a basic potassium permanganate stain ($KMnO_4$: 3 g potassium permanganate, 20 g potassium carbonate, 5 g sodium hydroxide, 1000 mL water) with subsequent heating, respectively. Flash column chromatography was performed on VWR silica gel (40-63 µm) used as the stationary phase, applying medium pressure (0.5-1 bar, compressed air), and the eluent used is reported in the respective experiments. Abbreviations are as follows: PE: Petroleum ether, CH: Cyclohexane, EA: Ethyl acetate, DCM: Dichloromethane, MeOH: Methanol, HOAc: Acetic acid, and Et_3N: Triethylamine.

All Nuclear magnetic resonance spectroscopy (NMR) spectra (^1H at 400 MHz or 600 MHz, ^{13}C at 101 MHz or 151 MHz) were recorded by a Bruker (Avance III 600 and Avance 400) NMR spectrometer at an ambient temperature unless stated. NMR chemical shifts were referenced via residual proton and carbon resonances of the corresponding deuterated solvent. Coupling constants (J) are reported in Hertz (Hz). Peak values were reported downfield to TMS in ppm (parts per million/ δ scale). Standard abbreviations were used to define multiplicities. High-resolution mass spectra (HRMS) were carried out using ESI or APCI ionisation (positive) on a micrOTOF mass spectrometer from Bruker with the liquid chromatograph from Agilent Technologies (1100). GC-FID measurements were performed on an Agilent 7890A GC-System with a flame ionisation detector.

Reactions in continuous flow were carried out using the syringe pump (HLL LA-120), 3-way valve (T-mixer), water bath, and ETFE pipes with commercially available connections. The general setup of the self-made flow reactor is shown in Figure S1.

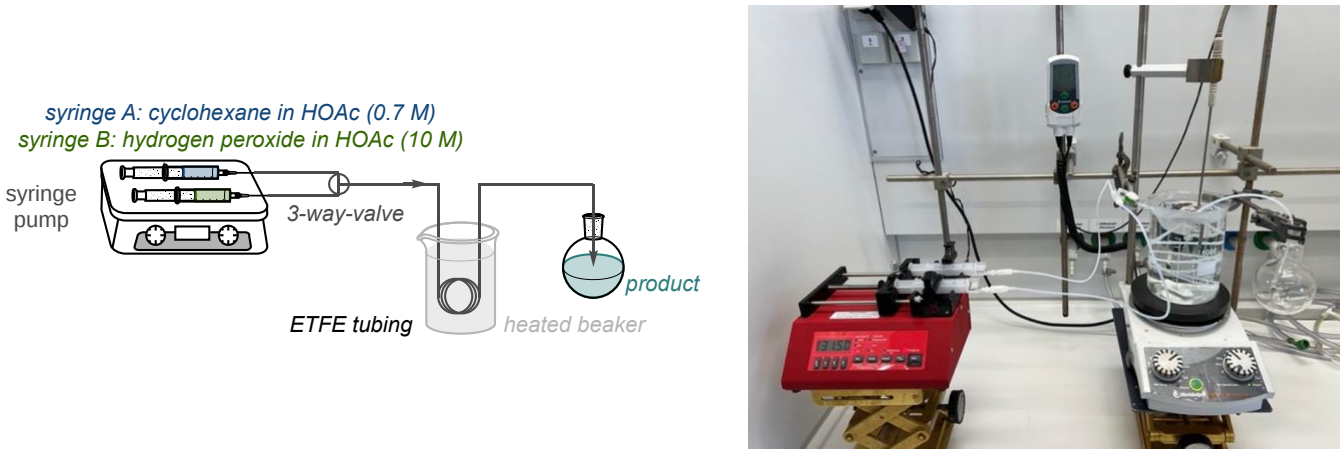
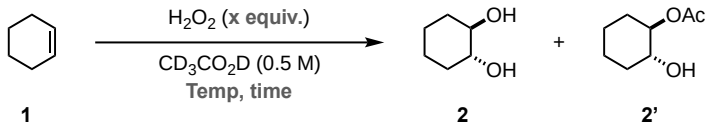


Figure S1. Flow reaction setup.

Optimisation of the reaction conditions in a batch

General protocol: In a 1.5 mL glass vial equipped with a magnetic stirring bar, cyclohexene **1** (10.1 µL, 0.10 mmol, 1.0 equiv.) was taken and dissolved in acetic acid-d_4 (0.20 mL, 0.5 M) as the solvent, different amounts of 35% hydrogen peroxide (1.25 – 8.0 equiv.) were added as the oxidant. The mixture was stirred at either 50°C or 70°C for varying times (2 – 24 hours). After completion, additional acetic acid-d_4 (0.3 mL) was added. Finally, the relative amounts of starting material and formed products were analysed using ^{1}H NMR spectroscopy with trichloroethylene (9.0 µL, 0.10 mmol, 1.0 equiv.) as the internal standard.

Table S1. Optimisation studies in batch.



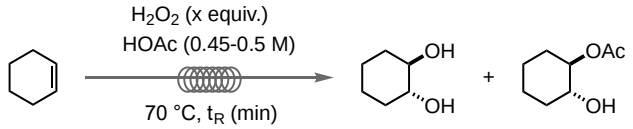
1 **2** **2'**

Entry	Solvent	H_2O_2 (equiv.)	Temp. (°C)	Time (h)	2 (%)	2' (%)	1 (%)
1	CD_3COOD	8	50	3	40	25	0
2	CD_3COOD	2	70	2	13	44	22
3	CD_3COOD	2	70	16	15	60	0
4	CD_3COOD	2	70	6	20	56	0
5	CD_3COOD	2	50	24	30	54	0
6	CD_3COOD	2	50	6	12	29	38
7	CD_3COOD	2	50	16	25	66	0
8	CD_3COOD	1.5	50	24	23	67	0
9	CD_3COOD	1.5	50	16	15	49	20
10	CD_3COOD	1.25	50	24	17	60	25
11	CD_3COOD	0	50	24	0	0	100

Optimisation of the reaction conditions in a continuous flow

General protocol: Syringes A and B of 24 mL were filled with cyclohexene **1** (0.506 mL, 5.0 mmol, 1.0 equiv.) in acetic acid and 35% aqueous H_2O_2 (2.0 – 8.0 equiv.) with acetic acid respectively and mounted on the same syringe pump. The amount of solution in both syringes was maintained equal to ensure the proper mixing at a 3-way-valve (T-mixer). The flow rates were varied to obtain various residence times. As it departs the T-mixer, the mixture was allowed to pass through 1.5 m long ETFE tubing immersed in a water bath at 70 °C with a residence time of 20 – 39 mins, followed by the collection of the mixture of **2** and **2'** in a 100 mL round bottom flask. After completion, the relative amounts of starting material and formed products were analysed using ^{1}H NMR spectroscopy with trichloroethylene (0.45 mL, 5.0 mmol, 1.0 equiv.) as the internal standard.

Table S2. Optimisation studies in a continuous flow. Yields mentioned in parentheses are the isolated yield followed by the saponification step.

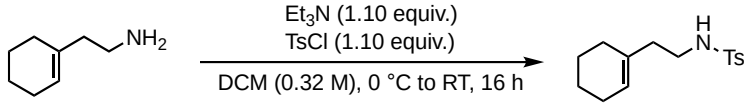


1 **2** **2'**

Entry	HOAc (M)	H_2O_2 (equiv.)	Temp. (°C)	Residence time t_R (min)	2 (%)	2' (%)	1 (%)
1	0.5	2	50	39	5	5	59
2	0.5	8	50	39	19	4	20
3	0.5	2	70	39	12	16	38
4	0.5	4	70	39	24	18	14
5	0.5	6	70	39	42 (65)	24	1
6	0.5	5	70	39	34	22	5
7	0.45	8	70	20	(67)	-	-
8	0.5	8	70	25	31	10	8
9	0.5	8	70	29	34	11	2
10	0.45	8	70	39	(85)	-	0

Synthesis & Characterisation of Substrates

N-(2-cyclohex-1-enyl-ethyl)-4-methyl-benzenesulfonamide



Synthesised according to literature procedures[1]: In an oven-dried round bottom flask equipped with a magnetic stirring bar was charged with 2-cyclohex-1-enyl-ethylamine (1.00 g, 7.8 mmol, 1.0 equiv.), Et_3N (1.19 mL, 8.6 mmol, 1.1 equiv.) and dichloromethane, DCM (16 mL) under nitrogen. The mixture was cooled to 0 °C, and 4-methyl-benzene sulfonyl chloride (1.66 g, 8.6 mmol, 1.1 equiv.) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 16 h. After the completion of the reaction, H_2O (25 mL) was added, and the mixture was extracted with DCM (25 mL ×3). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtrated and concentrated in a vacuum. The residue was purified using flash chromatography over silica gel (PE/EA 100:1→2:1) to obtain the desired product as a white solid in 88% yield (1.93 g, 6.91 mmol).

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.73 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 5.38 – 5.30 (m, 1H), 4.70 (s, 1H), 2.96 (t, *J* = 6.8 Hz, 2H), 2.40 (s, 3H), 2.03 (t, 2H), 1.91 (s, 2H), 1.68 (s, 2H), 1.56 – 1.41 (m, 4H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ [ppm] = 143.3, 136.9, 133.5, 129.7, 127.1, 124.6, 40.7, 37.4, 27.6, 25.2, 22.7, 22.2, 21.5.

Synthesis & Characterisation of Dihydroxylated Derivatives

General procedure 1 (GP1):

Step 1: In an oven-dried round bottom flask equipped with a magnetic stirring bar, respective alkenes (0.50 mmol, 1.0 equiv.) were taken and dissolved in acetic acid (1.0 mL, 0.5 M) as the solvent. To this mixture, 35% aqueous H_2O_2 (85.6 µL, 1.0 mmol, 2.0 equiv.) was added as the oxidant, and the reaction was stirred in an oil bath preheated at 50 °C until complete conversion of the starting alkene was achieved.

Step 2: For the saponification step, the excess H_2O_2 was quenched by adding 1 M aqueous $Na_2S_2O_3$ solution (1.0 mL) to the same flask. The potassium-iodine starch paper was used to monitor the absence of H_2O_2. Following this, 5 M aqueous NaOH (5.0 mL) was added to the solution and stirred until the complete conversion of side products yielded one single dihydroxylated product spot on TLC. After completion of the reaction, the solution was neutralised with the addition of sat. aqueous NH_4Cl and extracted with ethyl acetate six times. The organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated in a vacuum. The residue was later purified using flash chromatography over silica gel to yield the desired product.

General procedure 2 (GP2):

Step 1: In an oven-dried round bottom flask equipped with a magnetic stirring bar, respective alkenes (0.50 mmol, 1.0 equiv.) were taken and dissolved in acetic acid (1.0 mL, 0.5 M) as the solvent. To this mixture, 35% aqueous H_2O_2 (0.343 mL, 4.0 mmol, 8.0 equiv.) was added as the oxidant, and the reaction was stirred in an oil bath preheated at 50 °C until the complete conversion was achieved.

Step 2: For the saponification step, the excess H_2O_2 was quenched by adding 1 M aqueous $Na_2S_2O_3$ solution (8.0 mL) to the same flask. The potassium-iodine starch paper was used to monitor the absence of H_2O_2. Following this, 5 M aqueous NaOH (5.0 mL) was added to the solution and stirred until the complete conversion of side products yielded one single dihydroxylated product spot on TLC. After completion of the reaction, the solution was neutralised with the addition of sat. aqueous NH_4Cl and extracted with ethyl acetate six times. The organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated in a vacuum. The residue was later purified using flash chromatography over silica gel to yield the desired product.

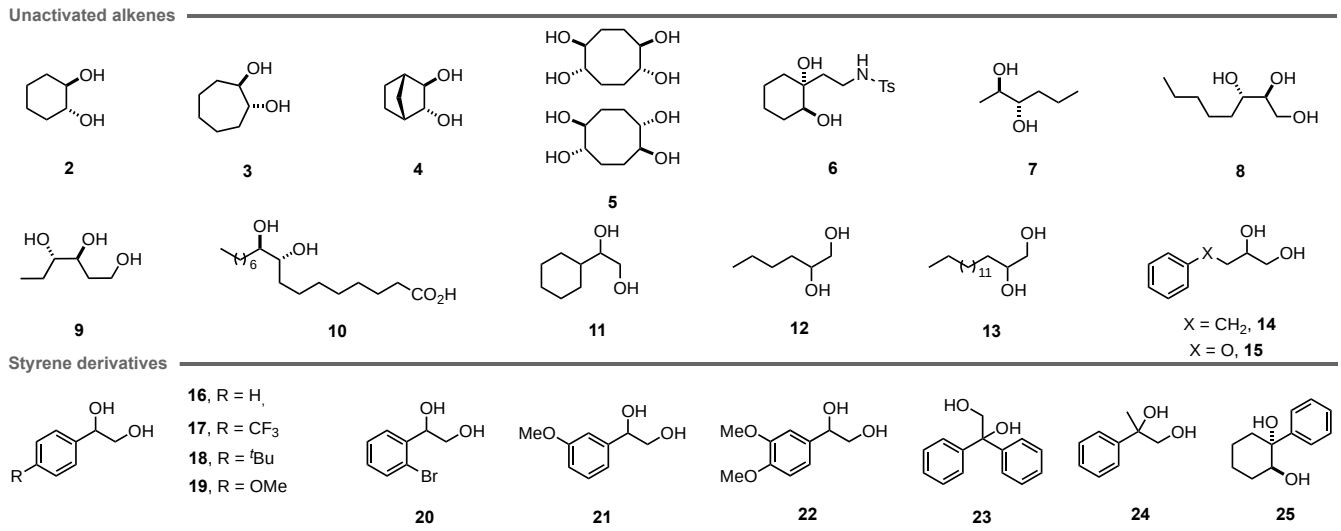
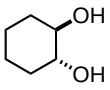


Figure S2. Synthesised dihydroxylated derivatives.

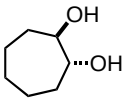
(±)-*trans*-Cyclohexane-1,2-diol, 2



Synthesised following **GP1** using cyclohexene (50.6 µL, 0.50 mmol, 1.0 equiv.) and 35% H_2O_2 (85.6 µL, 1.0 mmol, 2.0 equiv.). The desired product **2** was isolated after flash chromatography over silica gel (CH/EA 3:7) as a white solid in 90% yield (52.3 mg, 0.45 mmol).

^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 3.71 (br s, 2H), 3.38 – 3.27 (m, 2H), 1.94 (d, *J* = 5.9 Hz, 2H), 1.74 – 1.60 (m, 2H), 1.23 (d, *J* = 5.5 Hz, 4H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ [ppm] = 75.8, 33.0, 24.5.
HRMS (APCI): [m/z] calculated for $C_6H_{12}NaO_2$ ([M+Na]$^+$): 139.0730; Found: 139.0732.
All the characterisation data are consistent with the literature.[2]

(±)-*trans*-Cycloheptane-1,2-diol, 3

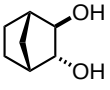


Synthesised following **GP1** using cycloheptene (58.4 µL, 0.50 mmol, 1.0 equiv.) and 35% H_2O_2 (85.6 µL, 1.0 mmol, 2.0 equiv.). The desired product **3** was isolated after flash chromatography over silica gel (CH/EA 2:3) as a white solid in 67% yield (43.3 mg, 0.33 mmol).

Synthesised following **GP2** using cycloheptene (58.4 µL, 0.50 mmol, 1.0 equiv.) and 35% H_2O_2 (0.343 mL, 4.0 mmol, 8.0 equiv.). The desired product **3** was isolated after flash chromatography over silica gel (CH/EA 2:3) as a white solid in 77% yield (50.0 mg, 0.38 mmol).

^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 3.49 – 3.36 (m, 2H), 3.16 (br s, 2H), 1.92 – 1.80 (m, 2H), 1.65 (dq, *J* = 13.7, 6.2 Hz, 2H), 1.55 – 1.38 (m, 6H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ [ppm] = 78.0, 32.6, 26.6, 22.3.
HRMS (ESI): [m/z] calculated for $C_7H_{14}NaO_2$ ([M+Na]$^+$): 153.0886; Found: 153.0887.
All the characterisation data are consistent with the literature.[3]

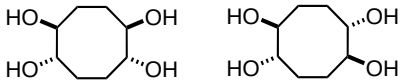
(±)-*trans*-2,3-Dihydroxynorbornane, 4



Synthesised following **GP1** using 2-norbornene (47.5 mg, 0.50 mmol, 1.0 equiv.) and 35% H_2O_2 (85.6 µL, 1.0 mmol, 2.0 equiv.). The desired product **4** was isolated after flash chromatography over silica gel (CH/EA 7:3) as a white solid in 47% yield (30.0 mg, 0.23 mmol).

^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 4.03 (s, 1H), 3.86 (t, *J* = 4.7 Hz, 1H), 3.12 (br s, 2H), 2.18 (s, 1H), 2.09 (d, *J* = 5.1 Hz, 1H), 1.88 (d, *J* = 6.2 Hz, 2H), 1.55 (tt, *J* = 12.5, 4.2 Hz, 1H), 1.50 – 1.43 (m, 1H), 1.03 (td, *J* = 11.1, 3.6 Hz, 1H), 0.97 (ddd, *J* = 12.2, 10.3, 4.7 Hz, 1H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ [ppm] = 81.0, 76.3, 46.4, 41.0, 39.8, 25.3, 21.7.
HRMS (ESI): [m/z] calculated for $C_7H_{12}NaO_2$ ($[M+Na]^+$): 151.0730; Found: 151.0729.
All the characterisation data are consistent with the literature.[4,5]

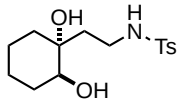
(±)-(1R,2R,5S,6S)-Cyclooctane-1,2,5,6-tetraol and (±)-(1S,2S,5S,6S)-Cyclooctane-1,2,5,6-tetraol, 5



Synthesised following **GP2** using (1Z,5Z)-cycloocta-1,5-diene (61.3 µL, 0.50 mmol, 1.0 equiv.) and 35% H_2O_2 (0.343 mL, 4.0 mmol, 8.0 equiv.). The desired products **5** was isolated after flash chromatography over silica gel (CH/EA 1:4) as a colourless highly viscous liquid mixture of cis- and trans- products in 84% yield (74.0 mg, 0.42 mmol).

^{1}H NMR (400 MHz, Acetone-d_6): δ [ppm] = 4.34 – 4.25 (m, 2H), 3.96 (br s, OH), 3.87 (tdd, *J* = 5.6, 3.7, 1.9 Hz, 4H), 3.79 (br s, OH), 3.65 – 3.58 (m, 2H), 2.22 (qd, *J* = 7.1, 1.6 Hz, 2H), 2.11 – 2.06 (m, 2H), 1.85 – 1.69 (m, 8H), 1.63 (dtd, *J* = 3.8, 2.7, 1.5 Hz, 4H).
^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6): δ [ppm] = 81.8, 72.4, 70.7, 69.0, 29.7, 29.5, 24.8, 22.9.
HRMS (APCI): [m/z] calculated for $C_8H_{15}O_3$ ($[M-H_2O]^+$): 159.1016; Found: 159.1015.
All the characterisation data are consistent with the literature.[6]

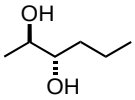
(±)-*trans*- *N*-(2-(1,2-dihydroxycyclohexyl)ethyl)-4-methylbenzenesulfonamide, 6



Synthesised following **GP1** using 2-(cyclohex-1-en-1-yl)ethan-1-amine (140 mg, 0.50 mmol, 1.0 equiv.) and 35% H_2O_2 (85.6 µL, 1.0 mmol, 2.0 equiv.). The desired product **6** was isolated after flash chromatography over silica gel (MeOH/EA 1:10) as a white solid in 36% yield (56.1 mg, 0.18 mmol).

^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 7.75 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.49 (dd, *J* = 9.3, 4.1 Hz, 1H), 3.24 (br s, 2H), 3.16 – 3.04 (m, 2H), 2.42 (s, 3H), 1.95 – 1.85 (m, 1H), 1.85 – 1.78 (m, 1H), 1.74 – 1.59 (m, 3H), 1.55 – 1.45 (m, 1H), 1.39 – 1.12 (m, 5H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ [ppm] = 143.5, 136.9, 129.8, 127.3, 76.6, 75.4, 38.8, 34.9, 30.6, 23.2, 22.4, 21.6.
HRMS (ESI): [m/z] calculated for $C_{15}H_{23}NNaO_4S$ ($[M+Na]^+$): 336.1240; Found: 336.1240.

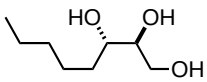
(±)-*trans*-Hexane-2,3-diol, 7



Synthesised following **GP1** using hex-2-ene (64.9 µL, 0.50 mmol, 1.0 equiv.) and 35% H_2O_2 (85.6 µL, 1.0 mmol, 2.0 equiv.). The desired product **7** was isolated after flash chromatography over silica gel (CH/EA 3:2) as a colourless liquid in 66% yield (39.1 mg, 0.33 mmol).

^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 3.77 (qd, *J* = 6.4, 3.2 Hz, 1H), 3.62 (dt, *J* = 8.3, 3.7 Hz, 1H), 2.30 (br s, 2H), 1.53 (ddt, *J* = 11.7, 9.5, 4.9 Hz, 1H), 1.44 – 1.29 (m, 3H), 1.13 (d, *J* = 6.5 Hz, 3H), 0.94 (t, *J* = 7.1 Hz, 3H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ [ppm] = 74.8, 70.6, 34.1, 19.3, 16.7, 14.2.
HRMS (ESI): [m/z] calculated for $C_6H_{14}NaO_2$ ($[M+Na]^+$): 141.0886; Found: 141.0889.
All the characterisation data are consistent with the literature.[7]

(±)-Octane-1,2,3-triol, 8

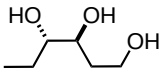


Synthesised following **GP1** using (E)-oct-2-en-1-ol (76.1 µL, 0.50 mmol, 1.0 equiv.) and 35% H_2O_2 (85.6 µL, 1.0 mmol, 2.0 equiv.). The desired product **8** was isolated after flash chromatography over silica gel (CH/EA 3:7) as a white solid in 50% yield (40.6 mg, 0.25 mmol).

Synthesised following **GP2** using (E)-oct-2-en-1-ol (76.1 µL, 0.50 mmol, 1.0 equiv.) and 35% H_2O_2 (0.343 mL, 4.0 mmol, 8.0 equiv.). The desired product **8** was isolated after flash chromatography over silica gel (CH/EA 3:7) as a white solid in 86% yield (69.7 mg, 0.43 mmol).

^{1}H NMR (600 MHz, DMSO-d_6): δ [ppm] = 4.34 (d, *J* = 5.3 Hz, 1H), 4.28 (d, *J* = 5.5 Hz, 1H), 4.27 (br s, 1H), 3.51 (ddd, *J* = 10.5, 5.9, 4.0 Hz, 1H), 3.37 – 3.30 (m, 1H), 3.29 – 3.25 (m, 1H), 3.21 (p, *J* = 6.0 Hz, 1H), 1.54 (tt, *J* = 12.1, 3.4 Hz, 1H), 1.49 – 1.39 (m, 1H), 1.33 – 1.16 (m, 6H), 0.86 (t, *J* = 7.0 Hz, 3H).
^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6): δ [ppm] = 74.8, 71.4, 63.5, 32.7, 31.5, 24.9, 22.2, 13.9.
HRMS (ESI): [m/z] calculated for $C_8H_{18}NaO_3$ ([M+Na]$^+$): 185.1148; Found: 185.1150.
All the characterisation data are consistent with the literature.[8]

(±)-Hexane-1,3,4-triol, 9

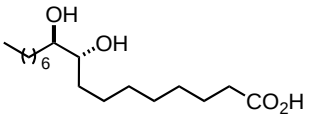


Synthesised following **GP1** using cis-hex-3-en-1-ol (61.0 µL, 0.50 mmol, 1.0 equiv.) and 35% H_2O_2 (85.6 µL, 1.0 mmol, 2.0 equiv.). The desired product **9** was isolated after flash chromatography over silica gel (MeOH/EA 1:10) as a white solid in 58% yield (39.1 mg, 0.29 mmol).

Synthesised following **GP2** using cis-hex-3-en-1-ol (61.0 µL, 0.50 mmol, 1.0 equiv.) and 35% H_2O_2 (0.343 mL, 4.0 mmol, 8.0 equiv.). The desired product **9** was isolated after flash chromatography over silica gel (MeOH/EA 1:10) as a white solid in 80% yield (53.4 mg, 0.40 mmol).

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 3.92 – 3.82 (m, 2H), 3.74 – 3.68 (m, 1H), 3.39 (dt, *J* = 8.9, 4.6 Hz, 1H), 2.78 (br s, 3H), 1.76 (dq, *J* = 12.3, 4.7 Hz, 2H), 1.58 (ddd, *J* = 14.0, 7.4, 4.3 Hz, 1H), 1.47 (dt, *J* = 13.5, 7.5 Hz, 1H), 0.99 (t, *J* = 7.4 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ [ppm] = 75.9, 73.6, 60.9, 35.1, 26.3, 9.9.
HRMS (ESI): [m/z] calculated for $C_6H_{14}NaO_3$ ([M+Na]$^+$): 157.0869; Found: 157.0870.
All the characterisation data are consistent with the literature.[9]

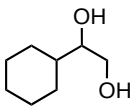
(±)-*trans*-9,10-Dihydroxyoctadecanoic acid, 10



Synthesised following **GP2** using oleic acid (151 µL, 0.50 mmol, 1.0 equiv.) and 35% H_2O_2 (0.343 mL, 4.0 mmol, 8.0 equiv.). The desired product **10** was isolated by recrystallisation using ethyl acetate as a white solid in 78% yield (0.117 g, 0.39 mmol).

^{1}H NMR (600 MHz, DMSO-d_6): δ [ppm] = 11.93 (s, 1H), 4.13 – 4.09 (m, 2H), 3.19 (d, *J* = 6.0 Hz, 2H), 2.18 (t, *J* = 7.4 Hz, 2H), 1.48 (br s, 2H), 1.41 – 1.34 (m, 4H), 1.24 (h, *J* = 7.5 Hz, 20H), 0.86 (t, *J* = 6.8 Hz, 3H).
^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6): δ [ppm] = 174.4, 73.1, 33.6, 32.2, 31.3, 29.2, 29.1, 29.0, 28.8, 28.7, 28.5, 25.6 (d, *J* = 3.6 Hz), 24.5, 22.0, 13.9.
HRMS (ESI): [m/z] calculated for $C_{18}H_{36}NaO_4$ ([M+Na]$^+$): 339.2495; Found: 339.2506.
All the characterisation data are consistent with the literature.[10]

(±)-1-Cyclohexylethane-1,2-diol, 11

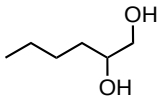


Synthesised following **GP1** using vinylcyclohexane (68.5 µL, 0.50 mmol, 1.0 equiv.) and 35% H_2O_2 (85.6 µL, 1.0 mmol, 2.0 equiv.). The desired product **11** was isolated after flash chromatography over silica gel (CH/EA 3:2) as a white solid in 67% yield (48.0 mg, 0.33 mmol).

Synthesised following **GP2** using vinylcyclohexane (68.5 µL, 0.50 mmol, 1.0 equiv.) and 35% H_2O_2 (0.343 mL, 4.0 mmol, 8.0 equiv.). The desired product **11** was isolated after flash chromatography over silica gel (CH/EA 3:2) as a white solid in 79% yield (57.0 mg, 0.40 mmol).

^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 3.71 (s, 1H), 3.55 – 3.49 (m, 1H), 3.44 (td, *J* = 7.4, 2.9 Hz, 1H), 2.41 (br s, 2H), 1.86 (d, *J* = 12.7 Hz, 1H), 1.80 – 1.70 (m, 2H), 1.69 – 1.61 (m, 2H), 1.40 (dtd, *J* = 11.6, 7.5, 3.3 Hz, 1H), 1.29 – 1.09 (m, 3H), 1.04 (t, *J* = 12.1 Hz, 2H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ [ppm] = 76.7, 65.0, 29.1, 28.8, 26.5, 26.2, 26.1.
HRMS (ESI): [m/z] calculated for $C_8H_{16}NaO_2$ ([M+Na]$^+$): 167.1052; Found: 167.1043.
All the characterisation data are consistent with the literature.[11]

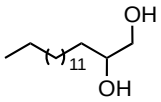
(±)-Hexane-1,2-diol, 12



Synthesised following **GP1** using hex-1-ene (62.5 µL, 0.50 mmol, 1.0 equiv.) and 35% H_2O_2 (85.6 µL, 1.0 mmol, 2.0 equiv.). The desired product **12** was isolated after flash chromatography over silica gel (CH/EA 1:1) as a colourless liquid in 81% yield (47.6 mg, 0.40 mmol).

^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 3.68 (tt, *J* = 7.3, 3.0 Hz, 1H), 3.62 (dd, *J* = 11.2, 3.0 Hz, 1H), 3.41 (dd, *J* = 11.3, 7.8 Hz, 1H), 3.04 (br s, 2H), 1.46 – 1.23 (m, 6H), 0.90 (t, *J* = 7.1 Hz, 3H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ [ppm] = 72.5, 66.9, 33.0, 27.9, 22.8, 14.1.
HRMS (ESI): [m/z] calculated for $C_6H_{14}NaO_2$ ([M+Na]$^+$): 141.0886; Found: 141.0885.
All the characterisation data are consistent with the literature.[2]

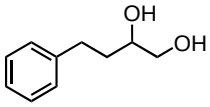
(±)-1,2-Hexadecanediol, 13



Synthesised following **GP2** using hexadec-1-ene (143.7 µL, 0.50 mmol, 1.0 equiv.) and 35% H_2O_2 (0.343 mL, 4.0 mmol, 8.0 equiv.). The desired product **13** was isolated after flash chromatography over silica gel (CH/EA 3:2) as a yellow oil in 81% yield (105 mg, 0.41 mmol).

^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 3.77 – 3.69 (m, 1H), 3.66 (dd, *J* = 11.0, 3.0 Hz, 1H), 3.44 (dd, *J* = 11.0, 7.6 Hz, 1H), 1.76 (s, 3H), 1.44 (s, 2H), 1.37 – 1.21 (m, 23H), 0.88 (t, *J* = 6.9 Hz, 3H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ [ppm] = 72.3, 66.8, 33.2, 31.9, 29.6 (d, J = 5.5 Hz), 29.5, 29.5, 29.3, 25.5, 22.6, 14.0.
HRMS (ESI): [m/z] calculated for $C_{16}H_{34}NaO_2$ ([M+Na]$^+$): 281.2451; Found: 281.2452.
All the characterisation data are consistent with the literature.[12]

(±)-4-Phenylbutane-1,2-diol, 14

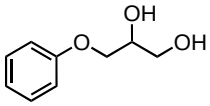


Synthesised following **GP1** using 4-phenyl-1-butene (76.7 µL, 0.50 mmol, 1.0 equiv.) and 35% H_2O_2 (85.6 µL, 1.0 mmol, 2.0 equiv.). The desired product **14** was isolated after flash chromatography over silica gel (CH/EA 1:5) as a white solid in 57% yield (47.4 mg, 0.28 mmol).

Synthesised following **GP2** using 4-phenyl-1-butene (76.7 µL, 0.50 mmol, 1.0 equiv.) and 35% H_2O_2 (0.343 mL, 4.0 mmol, 8.0 equiv.). The desired product **14** was isolated after flash chromatography over silica gel (CH/EA 1:5) as a white solid in 85% yield (71.0 mg, 0.29 mmol).

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.38 – 7.28 (m, 2H), 7.27 – 7.23 (m, 3H), 3.76 (tdd, *J* = 7.8, 5.0, 2.9 Hz, 1H), 3.67 (dd, *J* = 11.3, 2.9 Hz, 1H), 3.62 (br s, 1H), 3.50 (dd, *J* = 11.3, 7.8 Hz, 1H), 2.79 (dddd, *J* = 52.1, 13.8, 9.0, 6.7 Hz, 2H), 1.88 – 1.70 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ [ppm] = 141.8, 128.5 (d, *J* = 4.0 Hz), 126.0, 71.7, 66.8, 34.7, 31.9.
HRMS (ESI): [m/z] calculated for $C_{10}H_{14}NaO_2$ ([M+Na]$^+$): 189.0886; Found: 189.0886.
All the characterisation data are consistent with the literature.[13]

(±)-3-Phenoxypropane-1,2-diol, 15

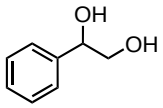


Synthesised following **GP2** using allyl phenyl ether (68.6 µL, 0.50 mmol, 1.0 equiv.) and 35% H_2O_2 (342.5 µL, 4.0 mmol, 8.0 equiv.). The desired product **15** was isolated after flash chromatography over silica gel (CH/EA 2:3) as a yellow oil in 74% yield (62.2 mg, 0.37 mmol).

^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 7.32 – 7.24 (m, 2H), 6.98 (t, *J* = 7.3 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 2H), 4.15 – 4.06 (m, 1H), 4.05 (t, *J* = 4.6 Hz, 2H), 3.85 (dd, *J* = 11.4, 3.9 Hz, 1H), 3.76 (dd, *J* = 11.4, 5.5 Hz, 1H), 2.26 (br s, 2H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ [ppm] = 158.6, 129.7, 121.5, 114.7, 70.5, 69.3, 63.8.
HRMS (ESI): [m/z] calculated for $C_9H_{12}NaO_3$ ([M+Na]$^+$): 191.0705; Found: 191.0706.

All the characterisation data are consistent with the literature.[14]

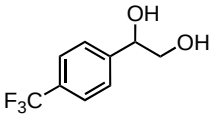
(±)-1-Phenylethane-1,2-diol, 16



Synthesised following **GP1** using styrene (57.2 µL, 0.50 mmol, 1.0 equiv.) and 35% H_2O_2 (85.6 µL, 1.0 mmol, 2.0 equiv.). The desired product **16** was isolated after flash chromatography over silica gel (CH/EA 7:3) as a white solid in 68% yield (47.0 mg, 0.34 mmol).

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.42 – 7.27 (m, 5H), 4.83 (dd, *J* = 8.1, 3.5 Hz, 1H), 3.77 (dd, *J* = 11.4, 3.5 Hz, 1H), 3.67 (dd, *J* = 11.3, 8.2 Hz, 1H), 2.28 (br s, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ [ppm] = 140.6, 128.7, 128.2, 126.2, 74.8, 68.2.
HRMS (APCI): [m/z] calculated for $C_8H_{10}NaO_2$ ([M+Na]$^+$): 161.0573; Found: 161.0571.
All the characterisation data are consistent with the literature.[15]

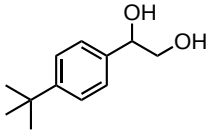
(±)-1-(4-(Trifluoromethyl)phenyl)ethane-1,2-diol, 17



Synthesised following **GP2** using 4-(Trifluormethyl)styrol (73.9 µL, 0.50 mmol, 1.0 equiv.) and 35% H_2O_2 (0.343 mL, 4.0 mmol, 8.0 equiv.). The desired product **17** was isolated after flash chromatography over silica gel (CH/EA 2:3) as a colourless liquid in 40% yield (41.3 mg, 0.20 mmol).

^{1}H NMR (400 MHz, DMSO-d_6): δ [ppm] = 7.67 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 5.47 (br s, 1H), 4.80 (br s, 1H), 4.63 (t, *J* = 6.0 Hz, 1H), 3.46 (dd, *J* = 7.4, 5.9 Hz, 2H).
^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ [ppm] = 148.6, 127.8, 127.5, 124.9, 124.9, 124.8, 124.8, 73.4, 67.3.
^{19}F{^{1}H} NMR (376 MHz, DMSO-d_6): δ [ppm] = -60.73.
HRMS (ESI): [m/z] calculated for $C_9H_9F_3NaO_2$ ([M+Na]$^+$): 229.0452; Found 229.0453.
All the characterisation data are consistent with the literature.[16]

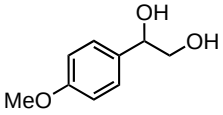
(±)-1-(4-(*tert*-Butyl)phenyl)ethane-1,2-diol, 18



Synthesised following **GP1** using 4-tert-butylstyrene (90.6 µL, 0.50 mmol, 1.0 equiv.) and 35% H_2O_2 (85.6 µL, 1.0 mmol, 2.0 equiv.). The desired product **18** was isolated after flash chromatography over silica gel (CH/EA 3:2) as a white solid in 72% yield (70.0 mg, 0.36 mmol).

^{1}H NMR (600 MHz, $CDCl_3$): δ [ppm] = 7.39 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.80 (dd, *J* = 8.3, 3.5 Hz, 1H), 3.87 – 3.52 (m, 2H), 2.40 (br s, 2H), 1.32 (s, 9H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ [ppm] = 151.0, 137.5, 125.8, 125.4, 74.5, 67.9, 34.5, 31.3.
HRMS (ESI): [m/z] calculated for $C_{12}H_{18}NaO_2$ ([M+Na]$^+$): 217.1200; Found: 217.1199.
All the characterisation data are consistent with the literature.[17]

(±)-1-(4-Methoxyphenyl)ethane-1,2-diol, 19

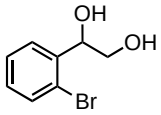


Synthesised following **GP1** using 4-Vinylanisole (67.0 µL, 0.50 mmol, 1.0 equiv.) and 35% H_2O_2 (85.6 µL, 1.0 mmol, 2.0 equiv.). The desired product **19** was isolated after flash chromatography over silica gel (CH/EA 1:1) as a white solid in 52% yield (44.0 mg, 0.26 mmol).

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.25 – 7.20 (m, 2H), 6.88 – 6.82 (m, 2H), 4.70 (dd, *J* = 8.3, 3.6 Hz, 1H), 3.77 (s, 3H), 3.64 (dd, *J* = 11.4, 3.7 Hz, 1H), 3.58 (dd, *J* = 11.5, 8.3 Hz, 1H), 3.40 (s, 2H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ [ppm] = 159.4, 132.8, 127.5, 114.0, 74.4, 68.1, 55.4.
HRMS (ESI): [m/z] calculated for $C_9H_{12}NaO_3$ ($[M+Na]^+$): 191.0679; Found: 191.0678.
All the characterisation data are consistent with the literature.[15]

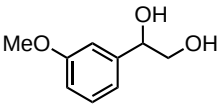
(±)-1-(2-Bromophenyl)ethane-1,2-diol, 20



Synthesised following **GP2** using 2-bromostyrene (62.7 µL, 0.50 mmol, 1.0 equiv.) and 35% H_2O_2 (0.343 mL, 4.0 mmol, 8.0 equiv.). The desired product **20** was isolated after flash chromatography over silica gel (CH/EA 1:1) as a colourless liquid in 42% yield (46.0 mg, 0.21 mmol).

^1H NMR (600 MHz, DMSO-d_6): δ [ppm] = 7.59 – 7.51 (m, 2H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.22 – 7.15 (m, 1H), 5.45 (br s, 1H), 4.86 (dd, *J* = 7.6, 3.4 Hz, 1H), 3.51 (dd, *J* = 11.2, 3.4 Hz, 1H), 3.38 – 3.26 (m, 2H).
$^{13}C\{^1H\}$ NMR (151 MHz, DMSO-d_6): δ [ppm] = 141.9, 132.0, 128.9, 128.6, 127.5, 121.6, 72.9, 65.8.
HRMS (ESI): [m/z] calculated for $C_8H_9BrNaO_2$ ($[M+Na]^+$): 238.9678; Found: 238.9678.
All the characterisation data are consistent with the literature.[15]

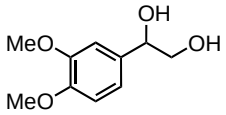
(±)-1-(3-Methoxyphenyl)ethane-1,2-diol, 21



Synthesised following **GP2** using 3-Vinylanisole (71.5 µL, 0.50 mmol, 1.0 equiv.) and 35% H_2O_2 (0.343 mL, 4.0 mmol, 8.0 equiv.). The desired product **21** was isolated after flash chromatography over silica gel (CH/EA 6:4) as a yellowish-white solid in 45% yield (38.0 mg, 0.23 mmol).

^1H NMR (600 MHz, $CDCl_3$): δ [ppm] = 7.27 (t, *J* = 7.9 Hz, 1H), 6.93 (d, *J* = 7.1 Hz, 2H), 6.84 (dd, *J* = 8.9, 2.3 Hz, 1H), 4.79 (dd, *J* = 8.1, 3.5 Hz, 1H), 3.81 (s, 3H), 3.75 (dd, *J* = 11.4, 3.5 Hz, 1H), 3.65 (dd, *J* = 11.4, 8.1 Hz, 1H), 2.47 (br s, 2H).
$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ [ppm] = 160.0, 142.3, 129.7, 118.5, 113.6, 111.8, 74.7, 68.2, 55.4.
HRMS (ESI): [m/z] calculated for $C_9H_{12}NaO_3$ ($[M+Na]^+$): 191.0679; Found: 191.0678.
All the characterisation data are consistent with the literature.[15]

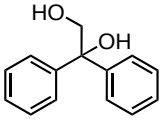
(±)-1-(3,4-Dimethoxyphenyl)ethane-1,2-diol, 22



Synthesised following **GP1** using 3,4-Dimethoxystyrol (74.0 µL, 0.50 mmol, 1.0 equiv.) and 35% H_2O_2 (85.6 µL, 1.0 mmol, 2.0 equiv.). The desired product **22** was isolated after flash chromatography over silica gel (CH/EA 4:6) as a white solid in 57% yield (56.0 mg, 0.28 mmol).

^1H NMR (400 MHz, $CDCl_3$): δ [ppm] = 6.87 (s, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 4.70 (dd, *J* = 8.4, 3.5 Hz, 1H), 3.83 (s, 6H), 3.66 (dd, *J* = 11.2, 3.3 Hz, 1H), 3.60 (dd, *J* = 11.7, 8.6 Hz, 1H), 3.35 (br s, 2H).
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ [ppm] = 149.1, 148.7, 133.2, 118.4, 111.1, 109.3, 74.5, 68.2, 56.0, 55.9.
HRMS (ESI): [m/z] calculated for $C_{10}H_{14}NaO_4$ ($[M+Na]^+$): 221.0784; Found: 221.0787.
All the characterisation data are consistent with the literature.[16]

(±)-1,1-Diphenylethane-1,2-diol, 23

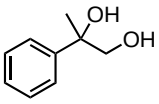


Synthesised following **GP2** using 1,1-Diphenylethylene (90.1 µL, 0.50 mmol, 1.0 equiv.) and 35% H_2O_2 (0.343 mL, 4.0 mmol, 8.0 equiv.). The desired product **23** was isolated after flash chromatography over silica gel (CH/EA 1:1) as a white solid in 65% yield (69.4 mg, 0.32 mmol).

^1H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.48 – 7.37 (m, 4H), 7.37 – 7.31 (m, 4H), 7.29 – 7.25 (m, 2H), 4.15 (s, 2H), 2.30 (br s, 2H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ [ppm] = 143.6, 129.0, 128.8, 128.3, 127.3, 126.2, 78.4, 69.2.
HRMS (ESI): [m/z] calculated for $C_{14}H_{14}NaO_2$ ($[M+Na]^+$): 237.0889; Found: 237.0889.
All the characterisation data are consistent with the literature.[15]

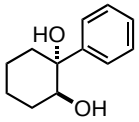
(±)-2-Phenylpropane-1,2-diol, 24



Synthesised following **GP1** using alpha-methylstyrene (65.2 µL, 0.50 mmol, 1.0 equiv.) and 35% H_2O_2 (85.6 µL, 1.0 mmol, 2.0 equiv.). The desired product **24** was isolated after flash chromatography over silica gel (CH/EA 2:3) as a white solid in 71% yield (54.1 mg, 0.36 mmol).

^1H NMR (600 MHz, $CDCl_3$): δ [ppm] = 7.44 (d, *J* = 6.6 Hz, 2H), 7.39 – 7.32 (m, 2H), 7.28 (d, *J* = 7.4 Hz, 1H), 3.75 (d, *J* = 11.1 Hz, 1H), 3.60 (d, *J* = 11.2 Hz, 1H), 2.66 (br s, 2H), 1.51 (s, 3H).
$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ [ppm] = 144.9, 128.3, 127.0, 125.0, 74.8, 70.9, 25.9.
HRMS (ESI): [m/z] calculated for $C_9H_{12}NaO_2$ ($[M+Na]^+$): 175.0730; Found: 175.0730.
All the characterisation data are consistent with the literature.[15]

(±)-1-Phenylcyclohexane-1,2-diol, 25



Synthesised following **GP1** using 1-Phenyl-1-Cyclohexene (79.6 µL, 0.50 mmol, 1.0 equiv.) and 35% H_2O_2 (85.6 µL, 1.0 mmol, 2.0 equiv.). The desired product **25** was isolated after flash chromatography over silica gel (CH/EA 4:1) as a yellow solid in 83% yield (79.6 mg, 0.41 mmol).

^1H NMR (600 MHz, $CDCl_3$): δ [ppm] = 7.54 – 7.49 (m, 2H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.30 – 7.24 (m, 1H), 3.99 (dd, *J* = 11.1, 4.6 Hz, 1H), 2.05 (br s, 2H), 1.93 – 1.81 (m, 3H), 1.81 – 1.62 (m, 3H), 1.59 – 1.51 (m, 1H), 1.42 (dt, *J* = 13.2, 3.7 Hz, 1H).
$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ [ppm] = 146.3, 128.4, 126.9, 125.0, 75.7, 74.4, 38.4, 29.2, 24.3, 21.0.
HRMS (ESI): [m/z] calculated for $C_{12}H_{16}NaO_2$ ($[M+Na]^+$): 215.1049; Found: 215.1043.
All the characterisation data are consistent with the literature.[18]

Additive-Based Screening of the Reaction

The test of functional group compatibility of our method was conducted via additive-based screening.[19] All calibrations were performed using gas chromatography analysis, whose method is as follows:

Column: HP-5 (Agilent 19091J-413) GC column.

Method: Initial temperature 80 °C, hold 2 min, increment 25 °C/min, and the final temperature 280 °C, hold 5 min.

Detection: Flame ionisation detection.

Calibration for additives: The retention times of additives (**A–P**) were determined through individual analysis using gas chromatography. Three calibration solutions were prepared with three different amounts of each additive (up to 4 compounds in one group), i.e., 1, 0.5 and 0.2 mmol of compounds in 20 mL of ethyl acetate each, along with 1 mmol of methyl laurate as the internal standard. It was also ensured that compounds with similar retention times were separated. Later, standard gas chromatography 3-point calibration lines were plotted for each additive separately using area relative to the methyl laurate.

Calibration for yields of the products: The retention times of products **2** and **2'** were determined through individual analysis using gas chromatography. Five calibration solutions were prepared with five different amounts of both products, i.e., 1, 0.8, 0.6, 0.4 and 0.2 mmol of compounds in 20 mL of ethyl acetate each, along with 1 mmol of methyl laurate as the internal standard. Later, standard gas chromatography 5-point calibration lines were plotted for each product using area relative to the methyl laurate.

With the calibration lines in hand, a control experiment without any additive was performed to obtain the maximum possible yield of products in our reaction condition.

In a 4 mL glass vial equipped with a magnetic stirring bar, 0.6 mL from a stock solution of cyclohexene **1** in acetic acid (0.5 M) and 35% hydrogen peroxide (2.0 equiv.) were added as the oxidant. The mixture was stirred at 50°C for 16 hours. After completion, methyl

Laurate (0.3 mmol, 1.0 equiv.) was added as the internal standard from a stock solution of methyl laurate in ethyl acetate (0.5 M). Then, an aliquot of 60 µL was taken out from the reaction vial and passed through a pad of Na_2SO_4 in a glass pipette with several washing while collecting the mixture in a 1.5 mL glass vial. This glass vial is then used to determine the relative amounts of formed products using GC-FID. It was found that the maximum possible yield for the reaction is 94% under our standard conditions.

General protocol for screening:

In a 4 mL glass vial equipped with a magnetic stirring bar, an additive (0.3 mmol, 1.0 equiv.) was weighed. 0.6 mL from a stock solution of cyclohexene **1** in acetic acid (0.5 M) and 35% hydrogen peroxide (2.0 equiv.) were added as the oxidant. The mixture was stirred at 50°C for 16 hours. After completion, methyl Laurate (0.3 mmol, 1.0 equiv.) was added as the internal standard from a stock solution of methyl laurate in ethyl acetate (0.5 M). Then, an aliquot of 60 µL was taken out from the reaction vial and passed through a pad of Na_2SO_4 in a glass pipette with several washing while collecting the mixture in a 1.5 mL glass vial. This glass vial is then used to determine the relative amounts of formed products and additives using GC-FID.

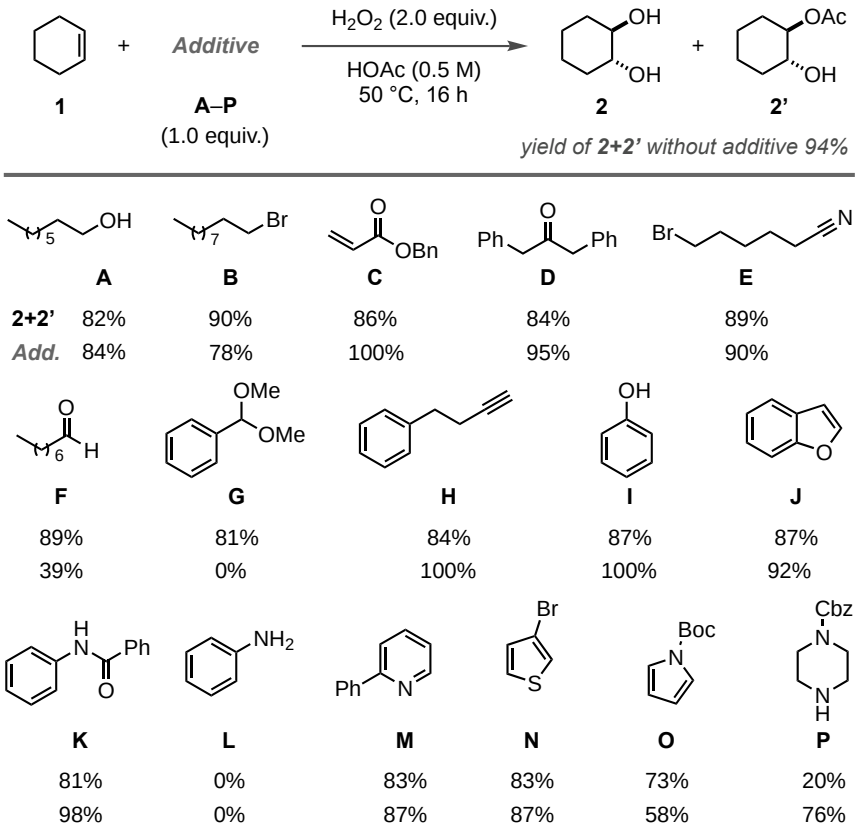
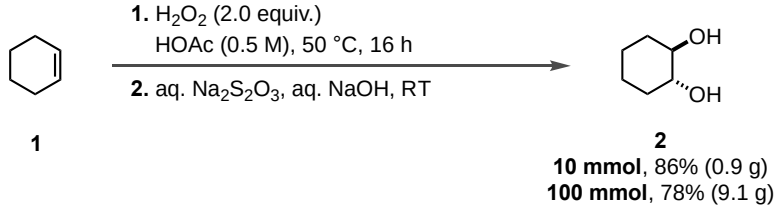


Figure S3. Additive screening of the reaction.

Scale-up Synthesis of 2 in a Batch



For 10 mmol:

Step 1: In an oven-dried round bottom flask equipped with a magnetic stirring bar, for the following reaction, cyclohexene **1** (1.01 mL, 10 mmol, 1.0 equiv.) was taken and dissolved in acetic acid (20 mL, 0.5 M) as the solvent. To this mixture, 35% aqueous H_2O_2 (1.71 mL, 20 mmol, 2.0 equiv.) was added as the oxidant, and the reaction was stirred in an oil bath preheated at 50 °C until the complete conversion was achieved.

Step 2: For the saponification step, the excess H_2O_2 was quenched by a dropwise addition of 1M aqueous $Na_2S_2O_3$ solution (12 mL) to the same flask. The potassium-iodine starch paper was used to monitor the absence of H_2O_2. Following this, 5M aqueous NaOH (96

mL) was added dropwise to the solution and stirred until the complete conversion of side products yielded one single dihydroxylated product spot on TLC. **Caution:** If the reaction is performed on a larger scale, adding 1M aqueous $Na_2S_2O_3$ and 5M aqueous NaOH should be performed dropwise to ensure safety, as it's an exothermic reaction during addition due to pH changes. After completion of the reaction, the solution was neutralised with the addition of sat. aqueous NH_4Cl and extracted with ethyl acetate six times. The organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated in a vacuum. The residue was later purified using flash chromatography over silica gel in cyclohexane/ethyl acetate to yield the desired product in 86% yield as a yellowish-white solid (0.993 g, 8.55 mmol).

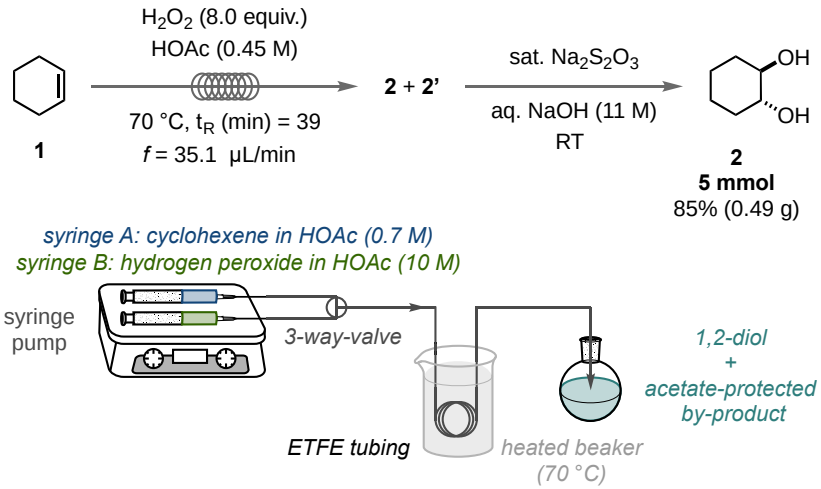
Alternatively, for the saponification step, the excess H_2O_2 was quenched by a dropwise addition of 1M aqueous $Na_2S_2O_3$ solution (12 mL) to the same flask. The potassium-iodine starch paper was used to monitor the absence of H_2O_2. Acetic acid was distilled off under vacuum. Following this, 5M aqueous NaOH (13 mL) was added dropwise to the solution and stirred until the complete conversion of side products yielded one single dihydroxylated product spot on TLC. After completion of the reaction, the solution was neutralised with the addition of sat. aqueous NH_4Cl and extracted with ethyl acetate six times. The organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated in a vacuum. The residue was later purified using flash chromatography over silica gel in cyclohexane/ethyl acetate to yield the desired product in 83% yield as a white solid (0.966 g, 8.32 mmol).

For 100 mmol:

Step 1: In an oven-dried round bottom flask equipped with a magnetic stirring bar, for the following reaction, cyclohexene **1** (10.1 mL, 0.10 mol, 1.0 equiv.) was taken and dissolved in acetic acid (0.20 L, 0.5 M) as the solvent. To this mixture, 35% aqueous H_2O_2 (17.1 mL, 0.20 mol, 2.0 equiv.) was added as the oxidant, and the reaction was stirred in an oil bath preheated at 50 °C until the complete conversion was achieved.

Step 2: For the saponification step, the excess H_2O_2 was quenched by a dropwise addition of saturated aq. $Na_2S_2O_3$ solution (100 mL) to the same flask. The potassium-iodine starch paper was used to monitor the absence of H_2O_2. Following this, 11M aqueous NaOH (383 mL) was added dropwise to the solution and stirred until the complete conversion of side products yielded one single dihydroxylated product spot on TLC. **Caution:** If the reaction is performed on a larger scale, adding saturated aq. $Na_2S_2O_3$ and 11M aqueous NaOH should be performed dropwise to ensure safety, as it's an exothermic reaction during addition due to pH changes. After completion of the reaction, the solution was neutralised with the addition of 6M HCl and extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated in a vacuum. The residue was later purified using flash chromatography over silica gel in cyclohexane/ethyl acetate to yield the desired product in 78% yield as a white solid (9.11 g, 78.5 mmol).

Scale-up Synthesis of 2 in a Continuous Flow



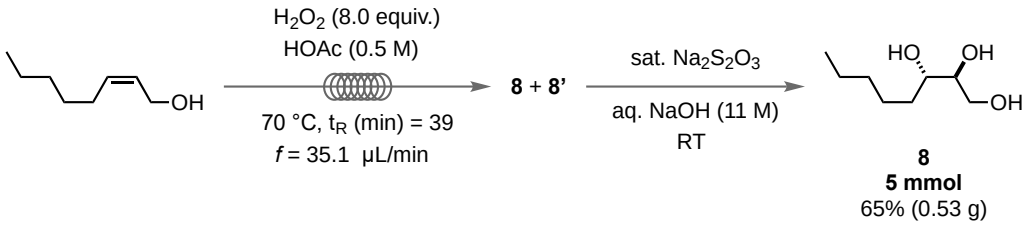
For 5 mmol:

Step 1: Syringes A and ååB of 24 mL were filled with cyclohexene **1** (0.506 mL, 5.0 mmol, 1.0 equiv.) with acetic acid (7.00 mL) and 35% aqueous H_2O_2 (3.43 mL, 40 mmol, 8.0 equiv.) with acetic acid (4.0 mL) respectively and mounted on the same syringe pump. The amount of solution in both syringes was maintained equal to ensure the proper mixing at a 3-way-valve (T-mixer). The flow rate was adjusted to 31.5 µL min^{-1}. As it departs the T-mixer, the mixture was allowed to pass through 1.5 m long ETFE tubing immersed in a water bath at 70 °C with a residence time of 39 mins, followed by the collection of the mixture of **2** and **2'** in a 250 mL round bottom flask.

Step 2: For the saponification step, the excess H_2O_2 was quenched by a dropwise addition of saturated aq. $Na_2S_2O_3$ solution (20 mL) to the same flask. The potassium-iodine starch paper was used to monitor the absence of H_2O_2. Following this, 11 M aqueous NaOH

(40 mL) was added dropwise to the solution and stirred until the complete conversion of side products yielded one single dihydroxylated product spot on TLC. **Caution:** If the reaction is performed on a larger scale, adding saturated aq. $Na_2S_2O_3$ and 11 M aqueous NaOH should be performed dropwise to ensure safety, as it's an exothermic reaction during addition due to pH changes. After completion of the reaction, the solution was neutralised with the addition of sat. aqueous NH_4Cl and extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated in a vacuum. The residue was later purified using flash chromatography over silica gel in cyclohexane/ethyl acetate to yield the desired product in 85% yield as a white solid (0.492 g, 4.24 mmol).

Scale-up Synthesis of 8 in a Continuous Flow



For 5 mmol:

Step 1: Syringes A and B of 24 mL were filled with (E)-oct-2-en-1-ol (0.760 mL, 5.0 mmol, 1.0 equiv.) with acetic acid (6.33 mL) and 35% aqueous H_2O_2 (3.43 mL, 40 mmol, 8.0 equiv.) with acetic acid (3.67 mL) respectively and mounted on the same syringe pump. The amount of solution in both syringes was maintained equal to ensure the proper mixing at a 3-way-valve (T-mixer). The flow rate was adjusted to 31.5 µL min^{-1}. As it departs the T-mixer, the mixture was allowed to pass through 1.5 m long ETFE tubing immersed in a water bath at 70 °C with a residence time of 39 mins, followed by the collection of the mixture of **8** and **8'** in a 250 mL round bottom flask.

Step 2: For the saponification step, the excess H_2O_2 was quenched by a dropwise addition of saturated aq. $Na_2S_2O_3$ solution (20 mL) to the same flask. The potassium-iodine starch paper was used to monitor the absence of H_2O_2. Following this, 11 M aqueous NaOH (40 mL) was added dropwise to the solution and stirred until the complete conversion of side products yielded one single dihydroxylated product spot on TLC. **Caution:** If the reaction is performed on a larger scale, adding saturated aq. $Na_2S_2O_3$ and 11 M aqueous NaOH should be performed dropwise to ensure safety, as it's an exothermic reaction during addition due to pH changes. After completion of the reaction, the solution was neutralised with the addition of sat. aqueous NH_4Cl and extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated in a vacuum. The residue was later purified using flash chromatography over silica gel in cyclohexane/ethyl acetate to yield the desired product in 65% yield as a white solid (0.525 g, 3.24 mmol).

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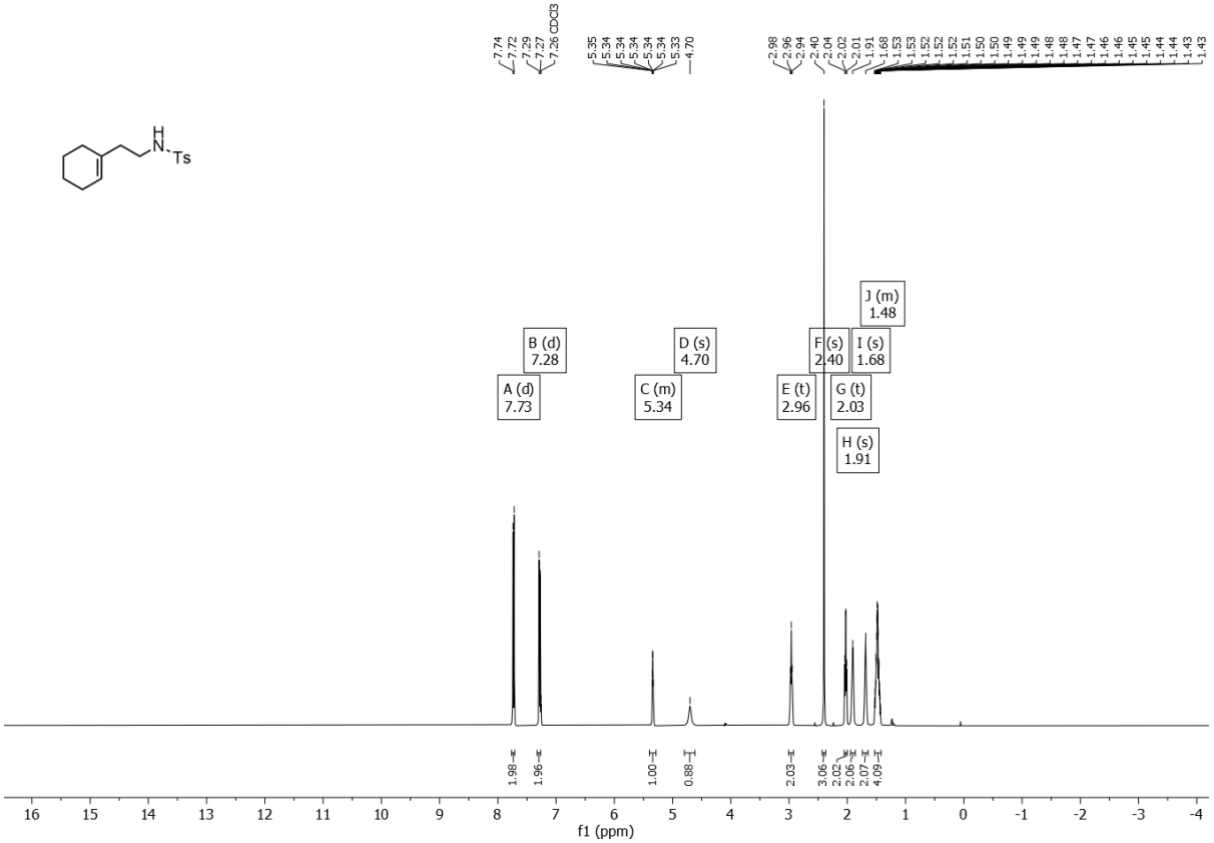
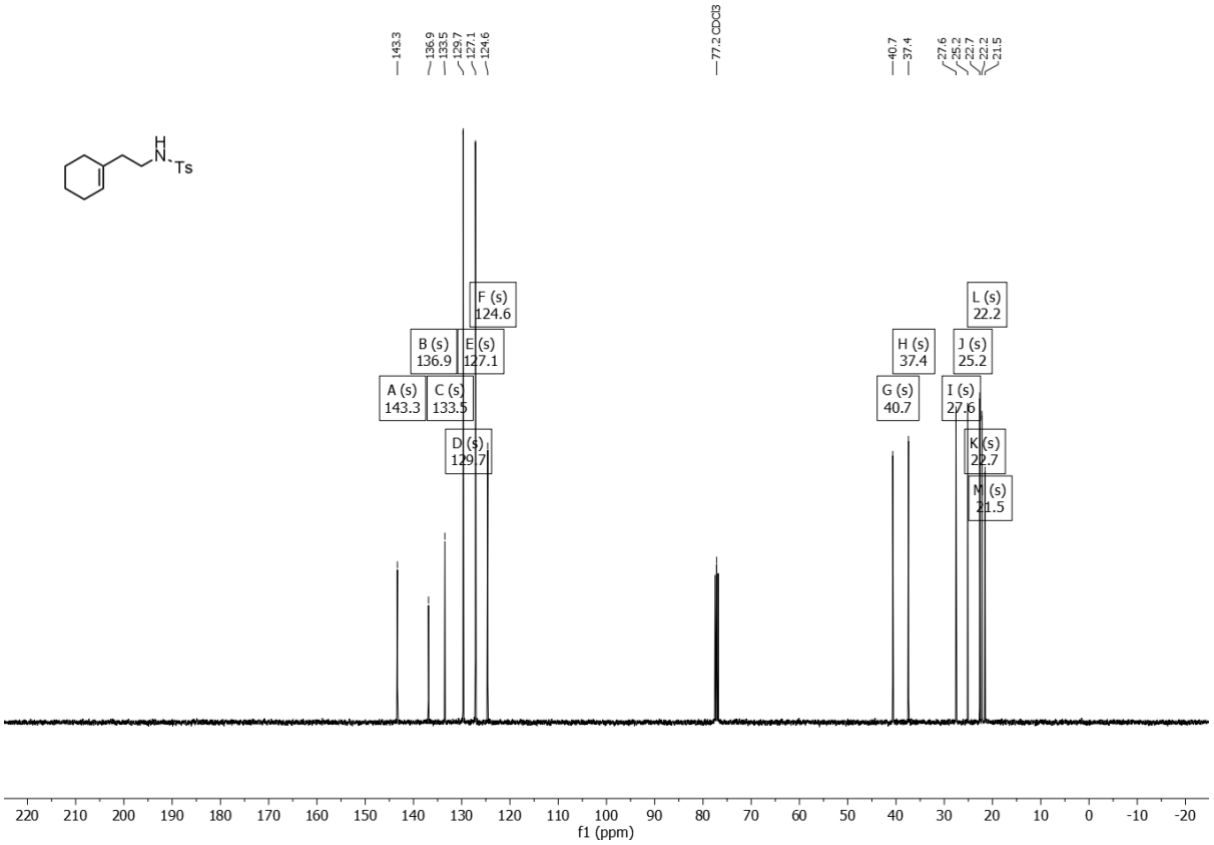
^{1}H, ^{13}C NMR Spectra

(*N*-(2-cyclohex-1-enyl-ethyl)-4-methyl-benzenesulfonamide)

^{1}H NMR (400 MHz, $CDCl_3$)

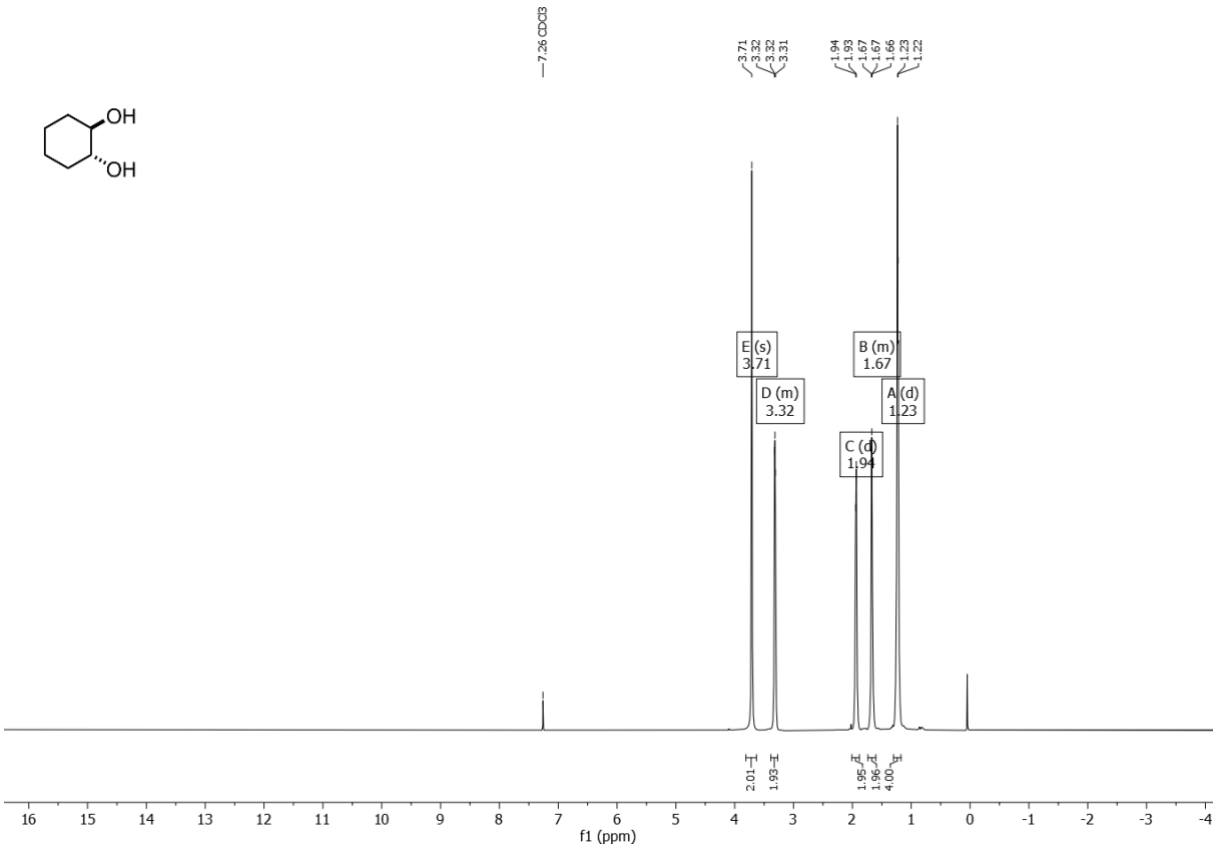


^{13}C NMR (151 MHz, $CDCl_3$)

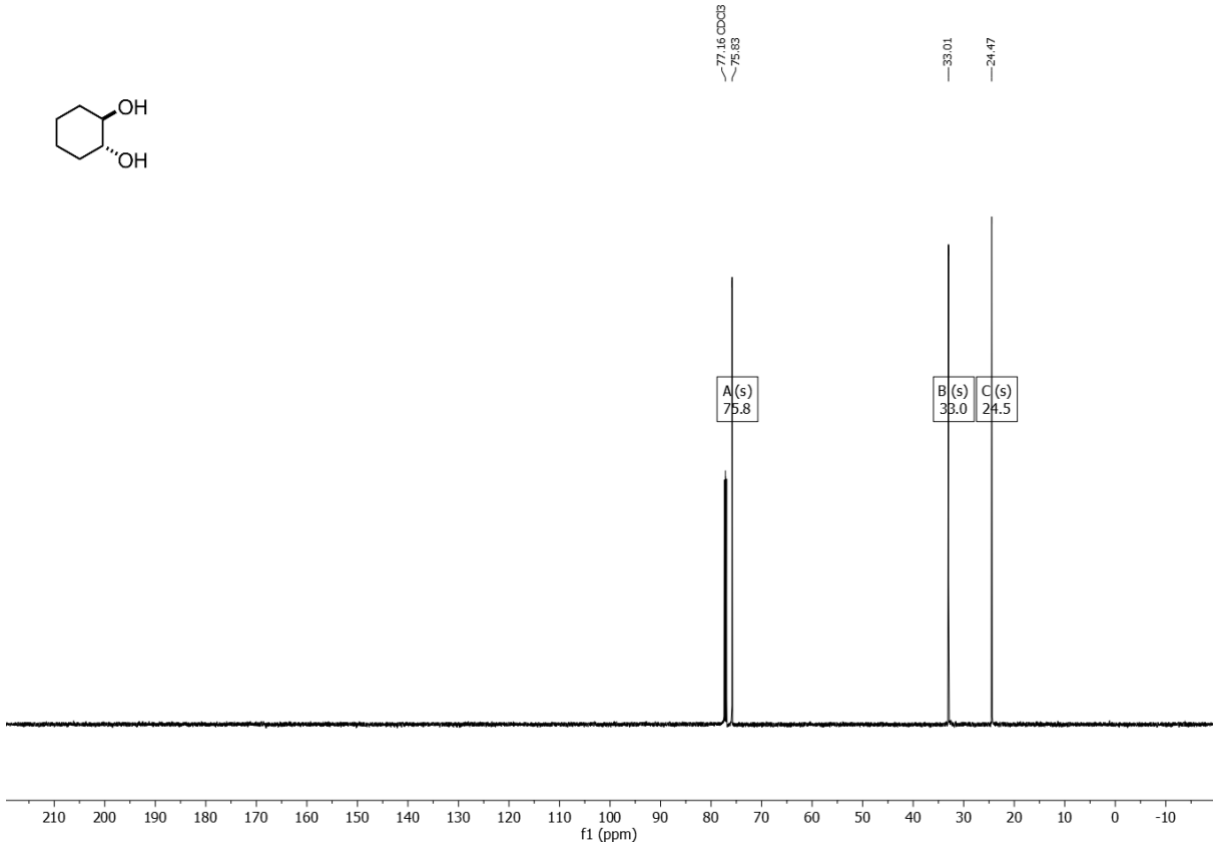


(±)-*trans*-Cyclohexane-1,2-diol, 2

^{1}H NMR (600 MHz, $CDCl_3$)

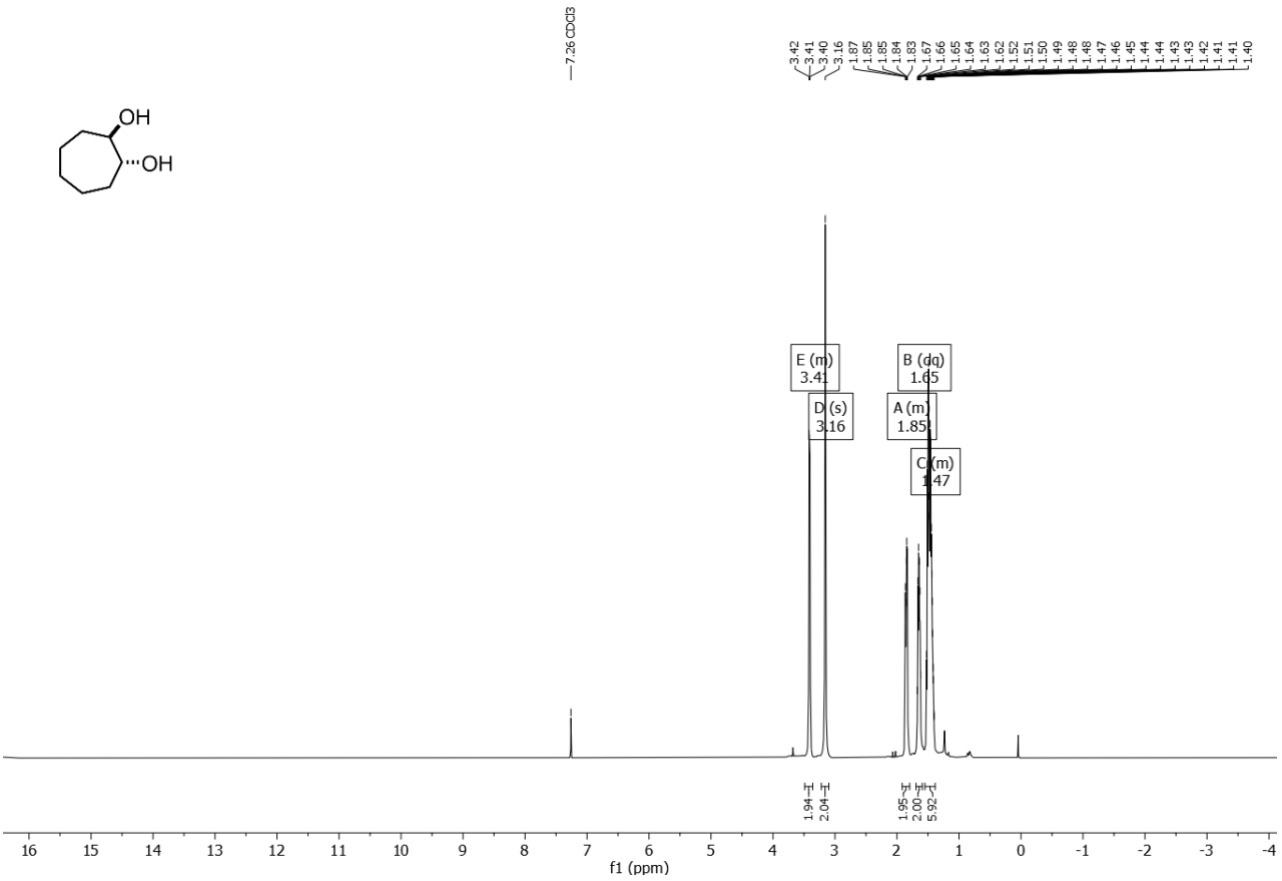


^{13}C NMR (151 MHz, $CDCl_3$)

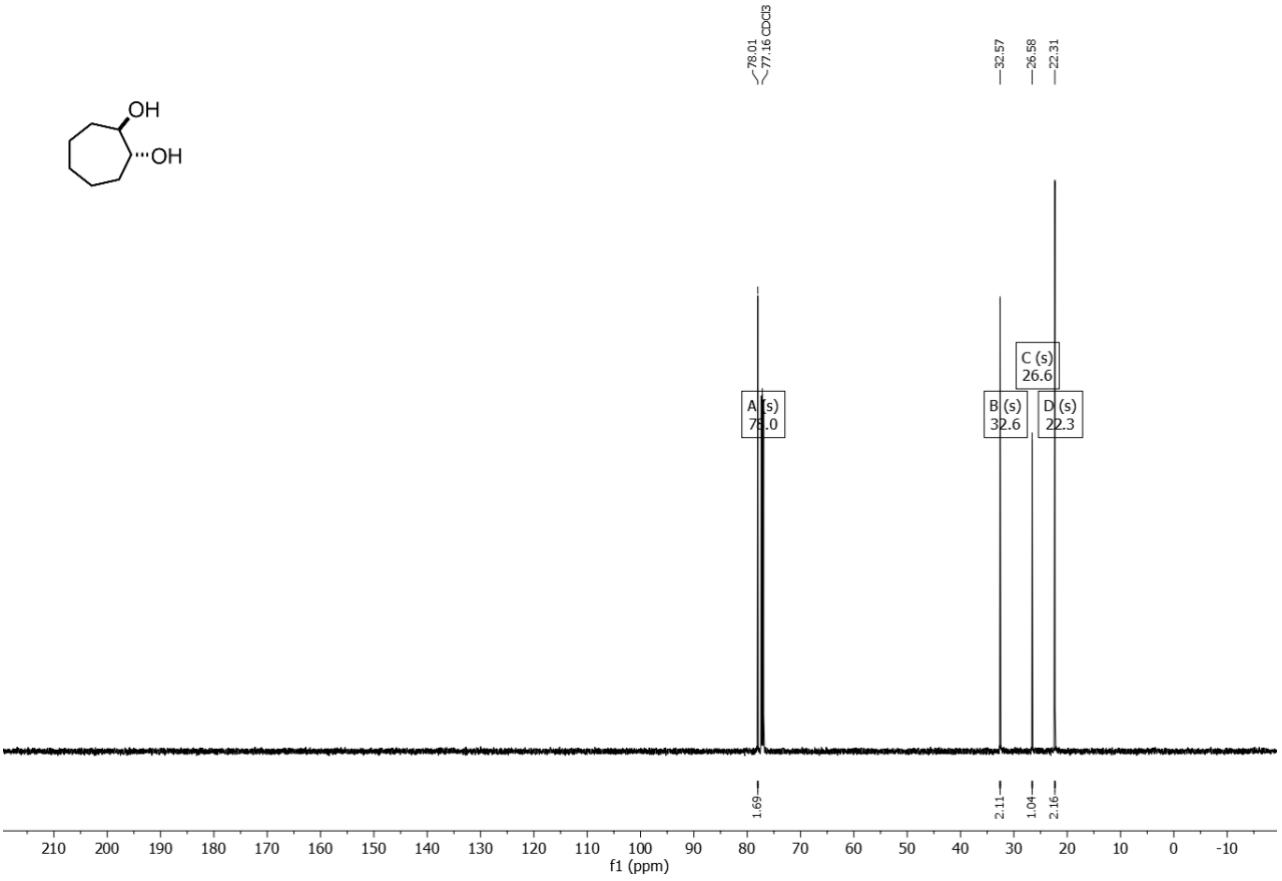


(±)-*trans*-Cycloheptane-1,2-diol, 3

^{1}H NMR (600 MHz, $CDCl_3$)

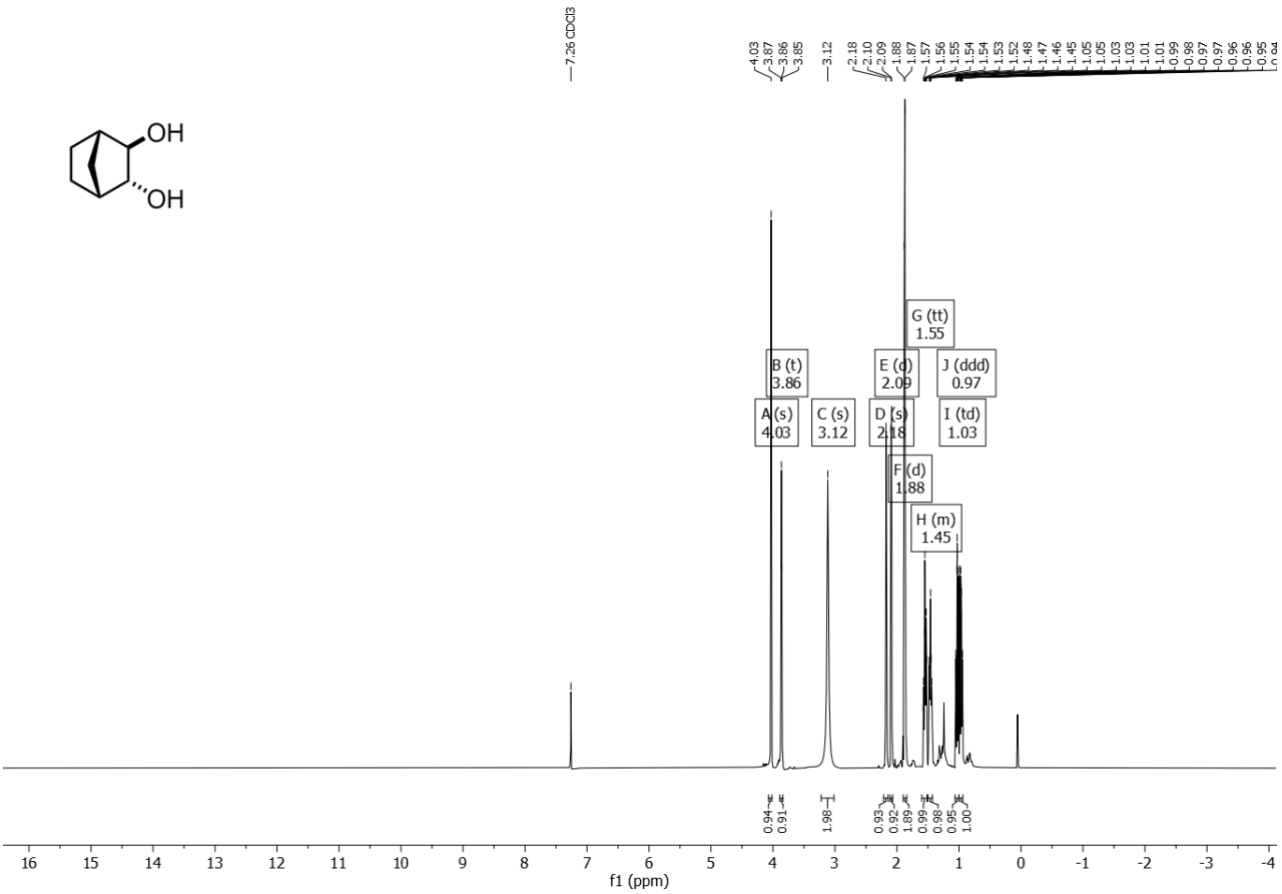


^{13}C NMR (151 MHz, $CDCl_3$)

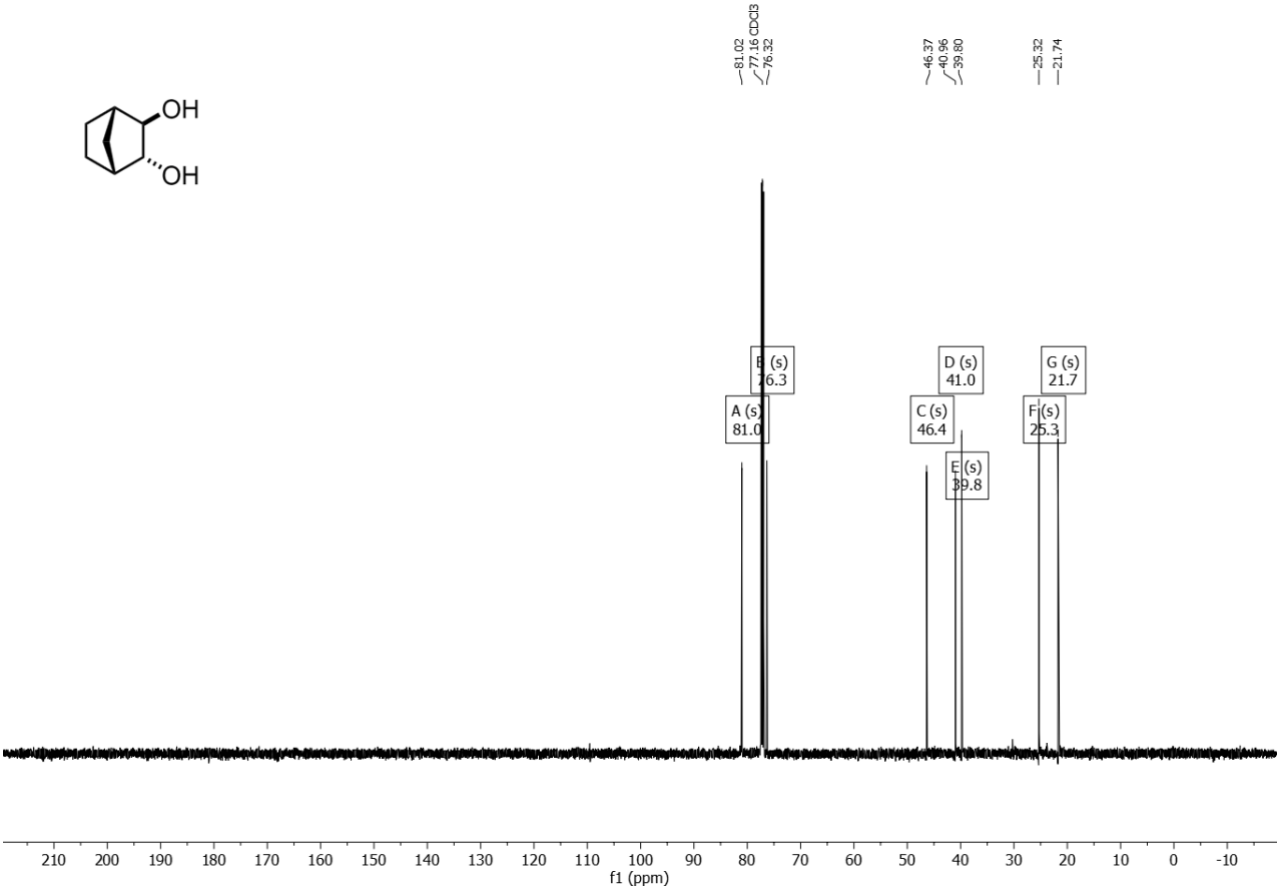


(±)-*trans*-2,3-Dihydroxynorbornane, 4

^{1}H NMR (600 MHz, $CDCl_3$)

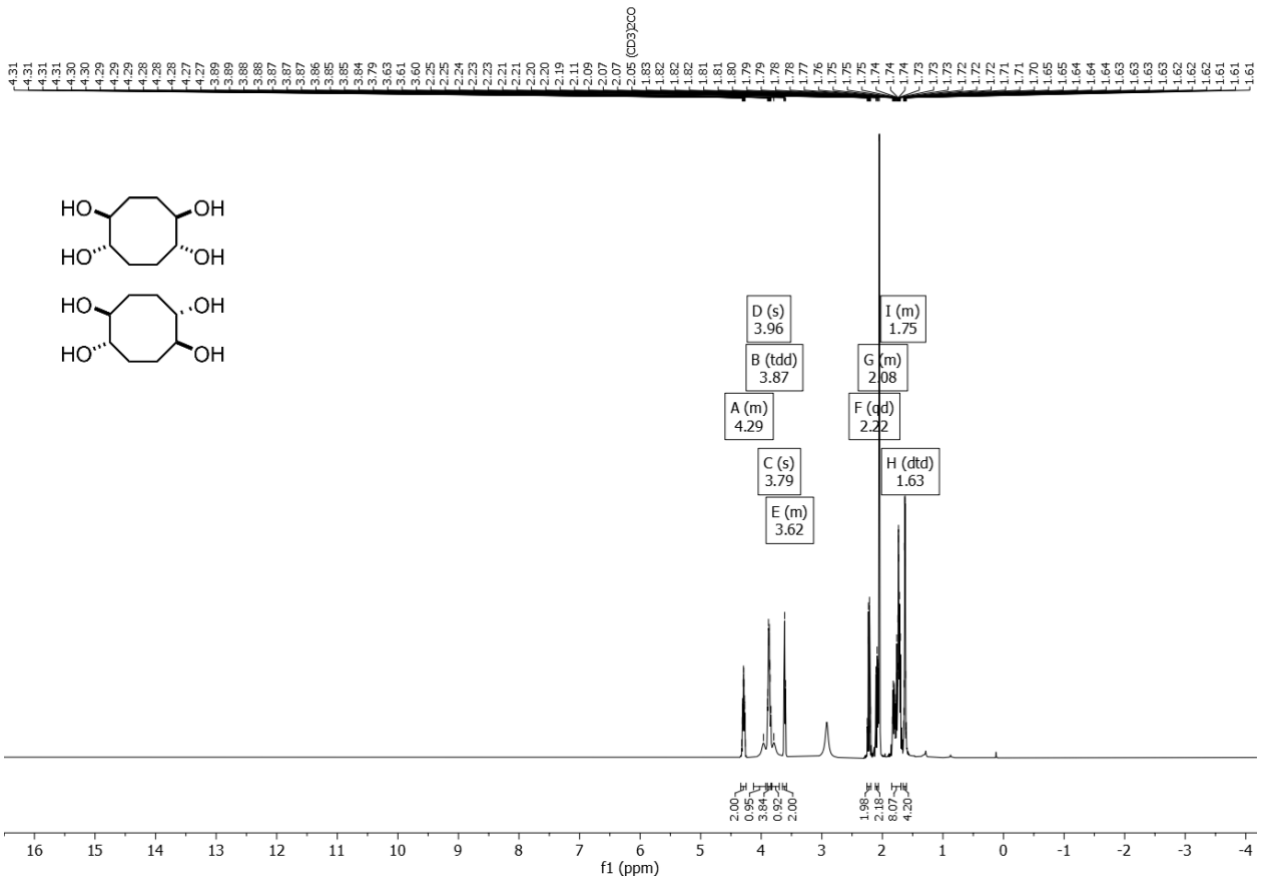


^{13}C NMR (151 MHz, $CDCl_3$)

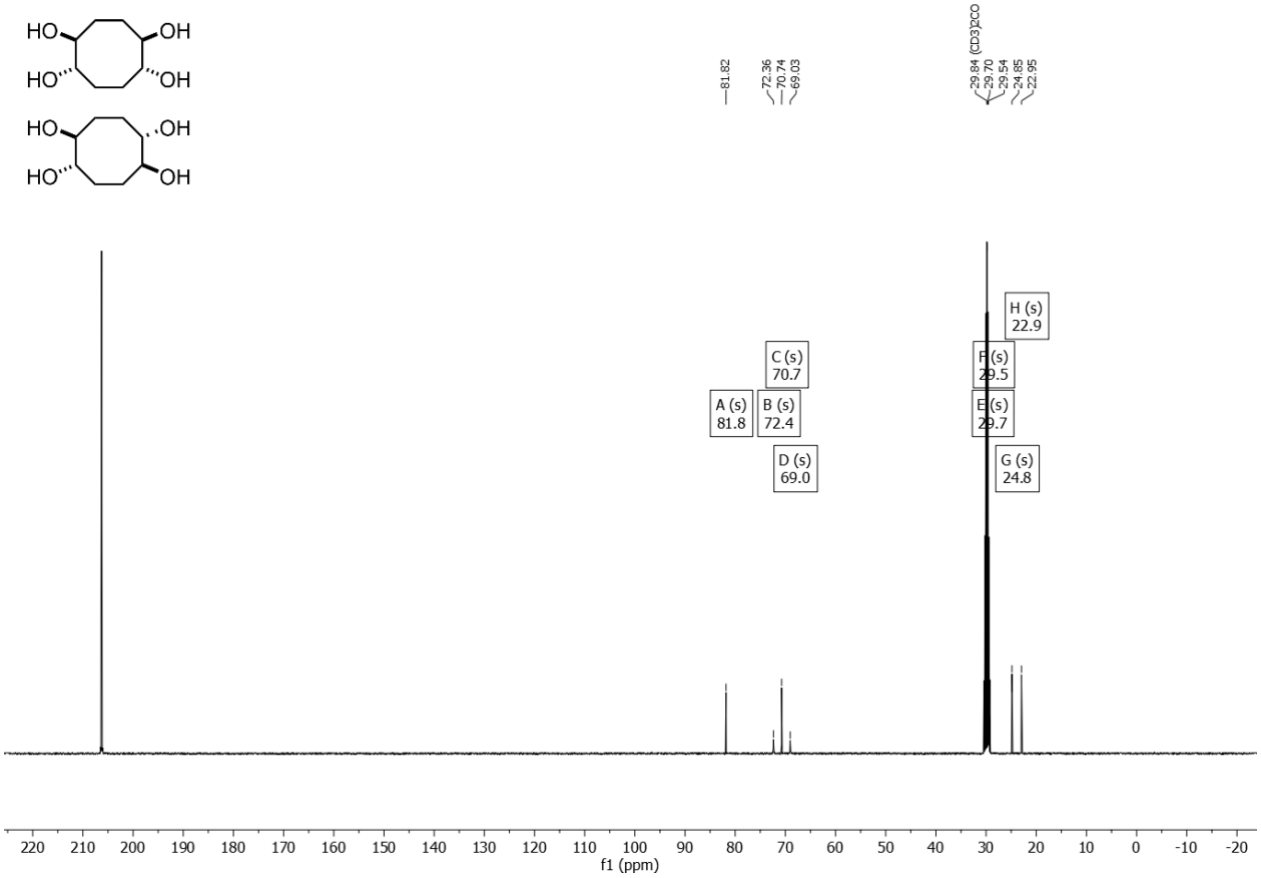


(±)-(1R,2R,5S,6S)-Cyclooctane-1,2,5,6-tetraol and (±)-(1S,2S,5S,6S)-Cyclooctane-1,2,5,6-tetraol, 5

^{1}H NMR (600 MHz, Acetone-d_6)

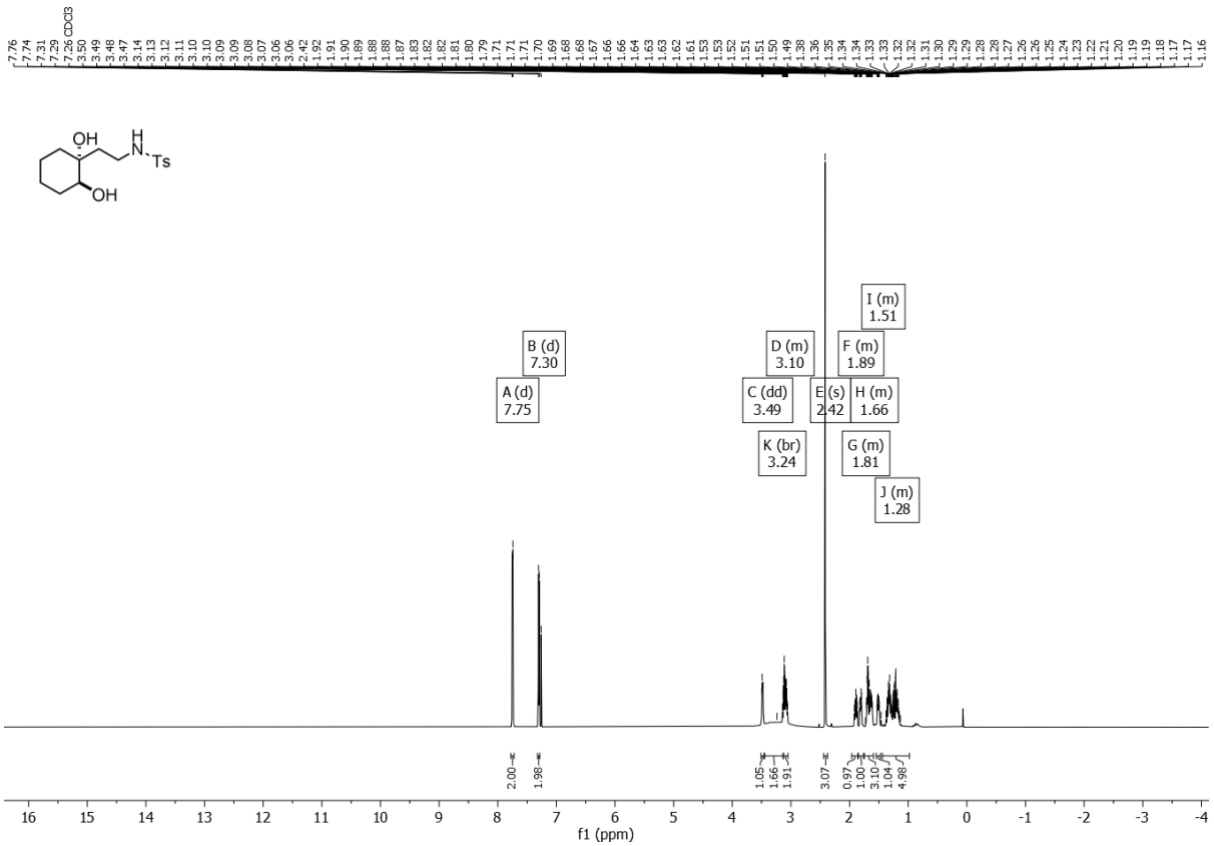


^{13}C NMR (151 MHz, Acetone-d_6)

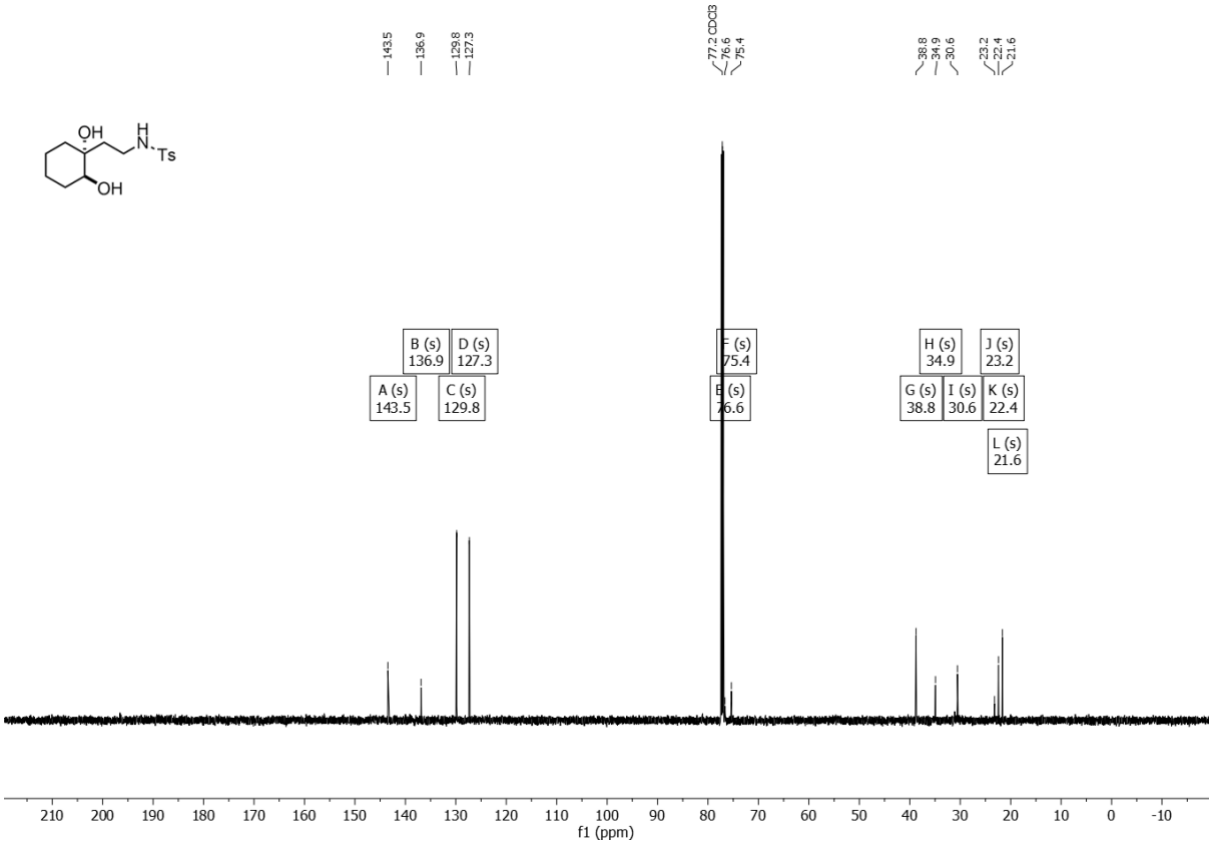


(±)-*trans*- *N*-(2-(1,2-dihydroxycyclohexyl)ethyl)-4-methylbenzenesulfonamide, 6

^{1}H NMR (600 MHz, $CDCl_3$)

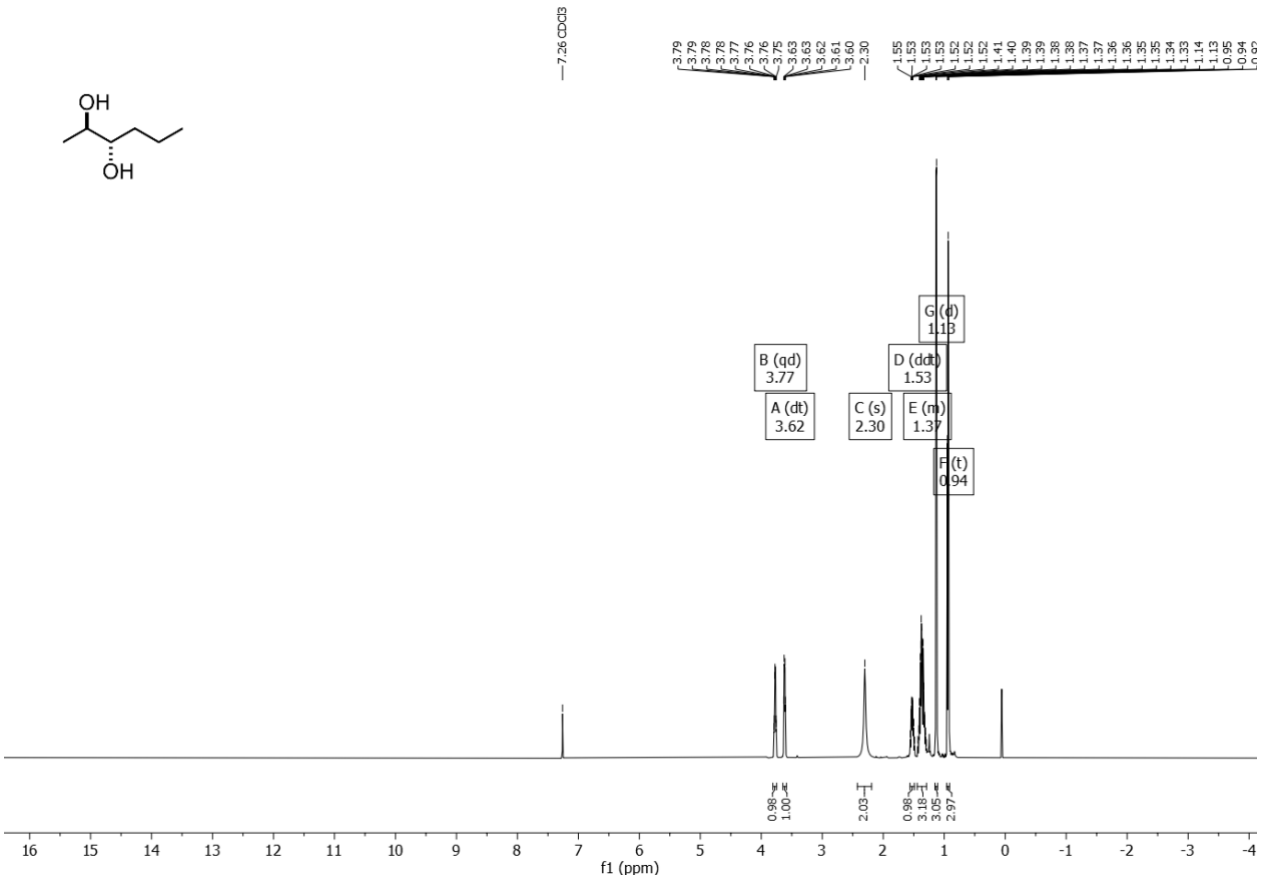


^{13}C NMR (151 MHz, $CDCl_3$)

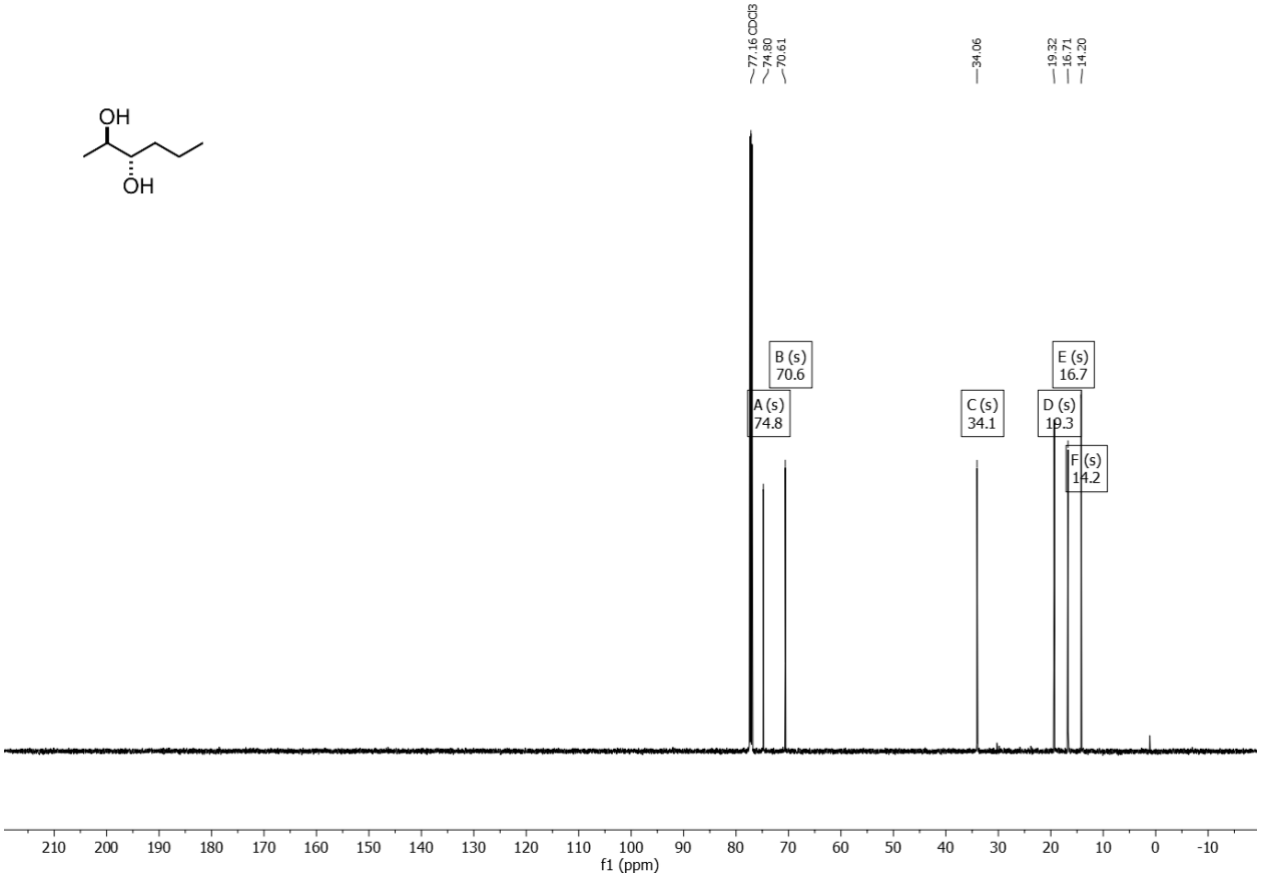


(±)-*trans*-Hexane-2,3-diol, 7

^{1}H NMR (600 MHz, $CDCl_3$)

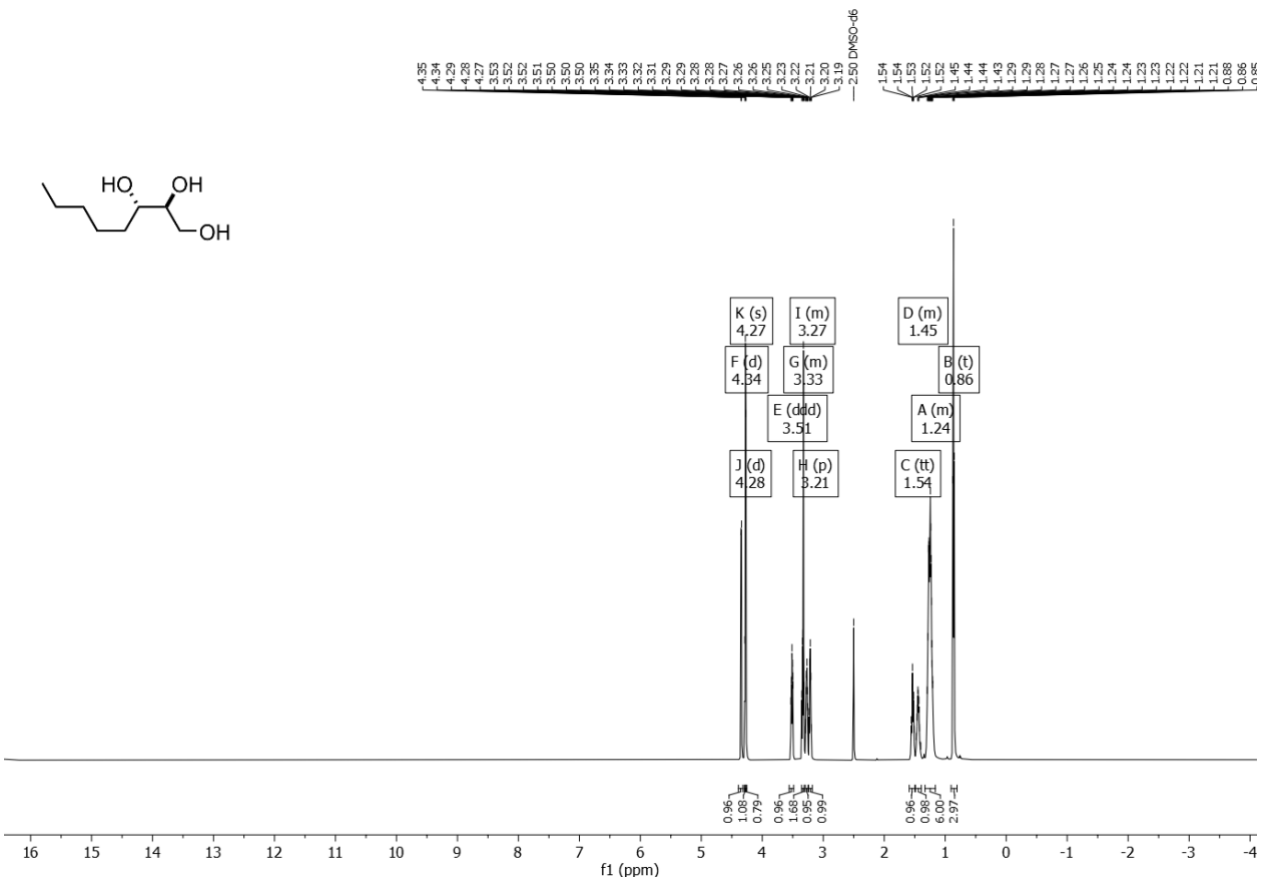


^{13}C NMR (151 MHz, $CDCl_3$)

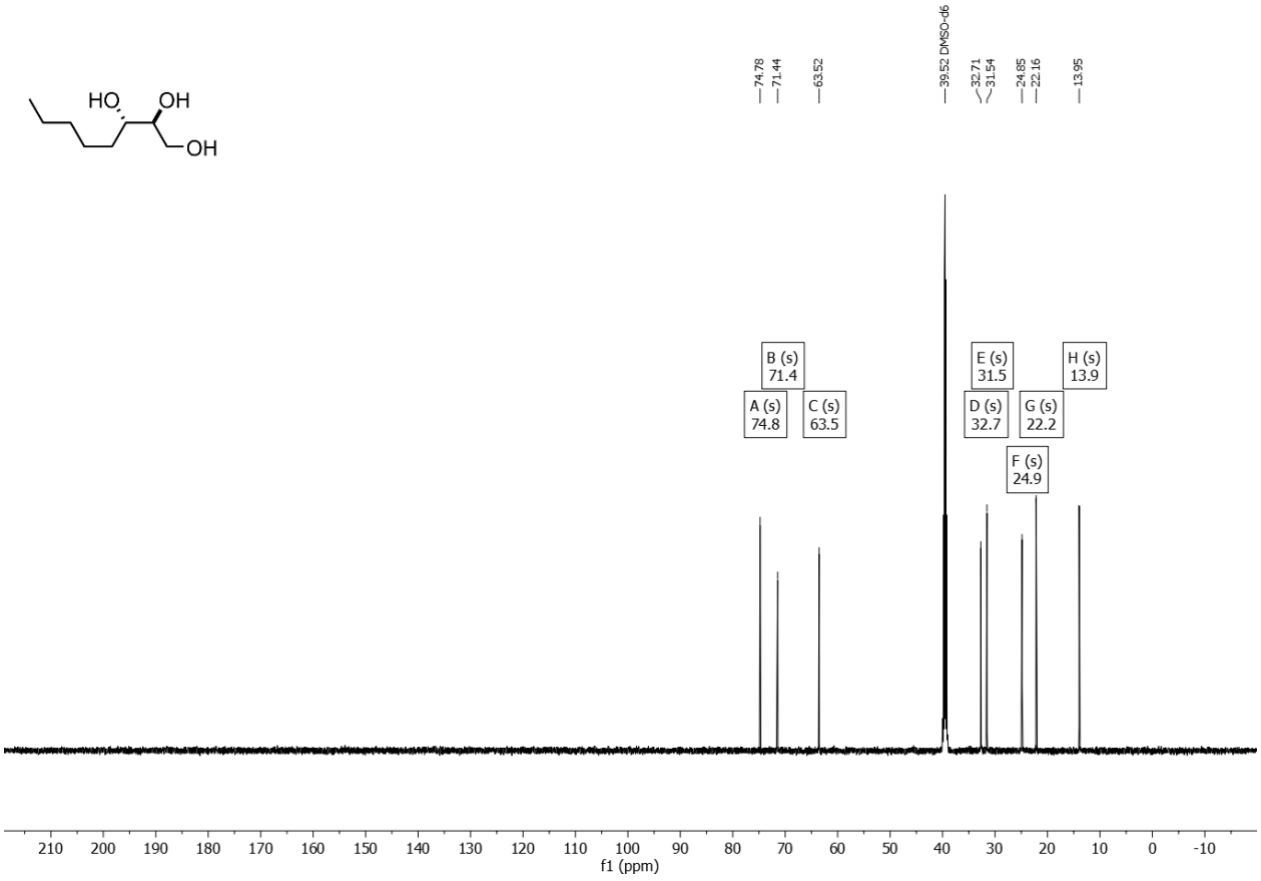


(±)-Octane-1,2,3-triol, 8

^{1}H NMR (600 MHz, DMSO-d_6)

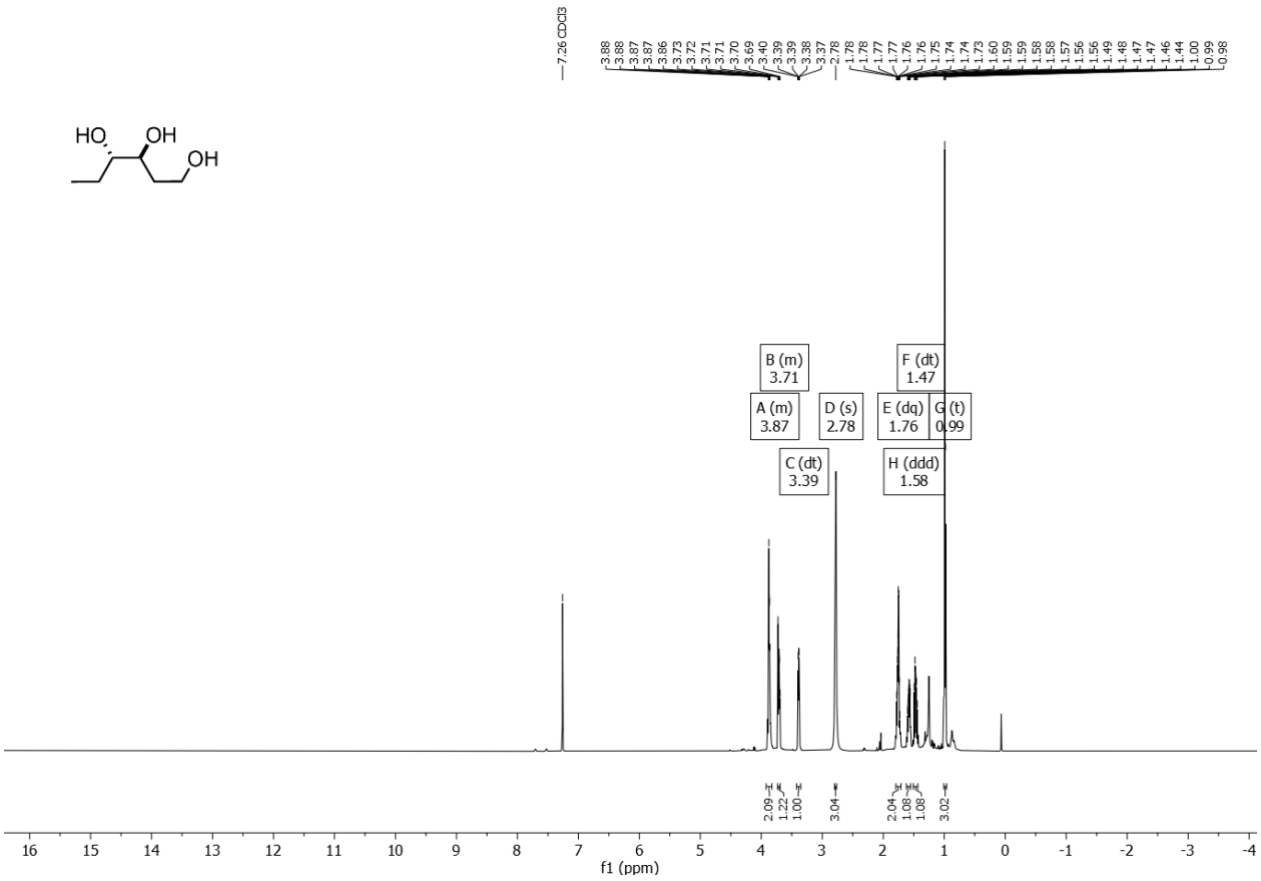


^{13}C NMR (151 MHz, DMSO-d_6)

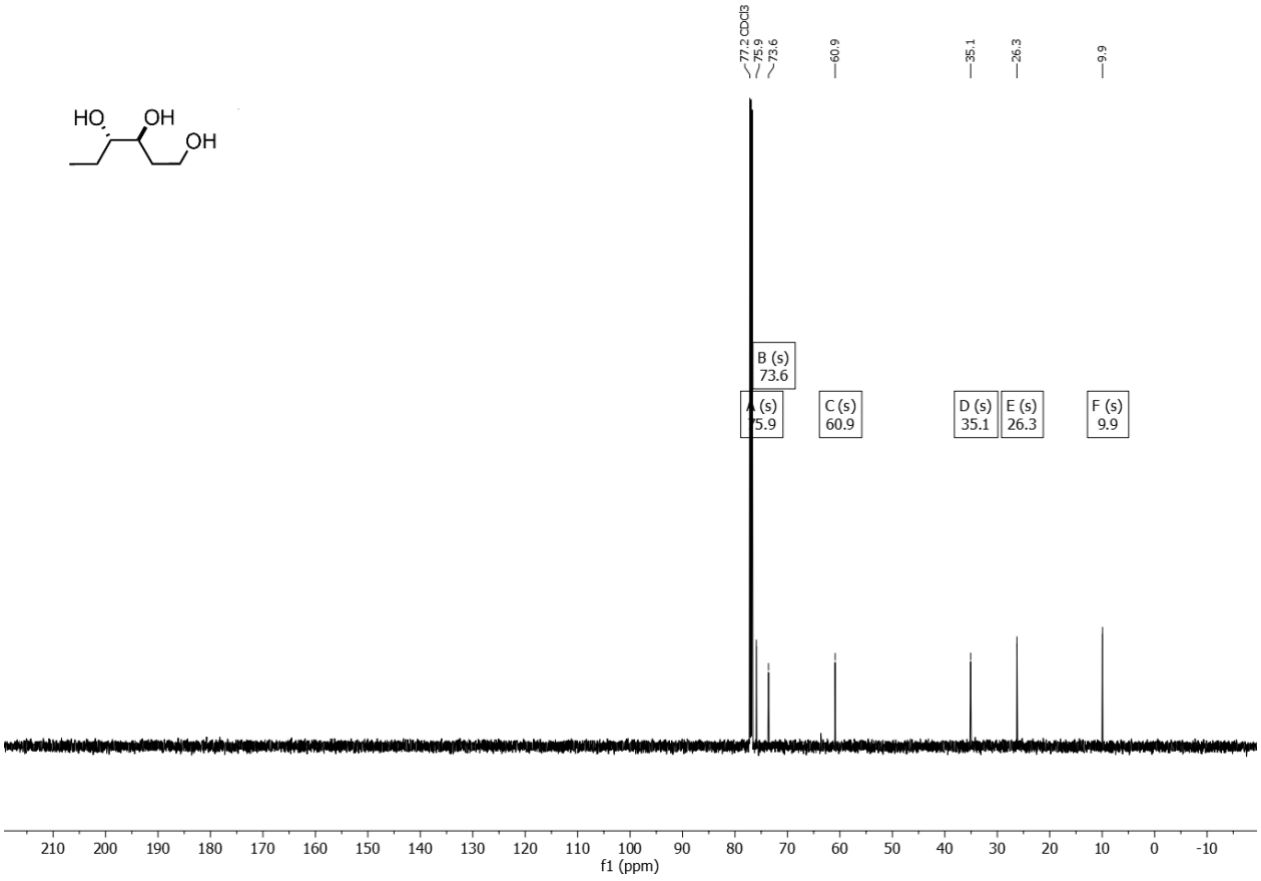


(±)-Hexane-1,3,4-triol, 9

^{1}H NMR (600 MHz, $CDCl_3$)

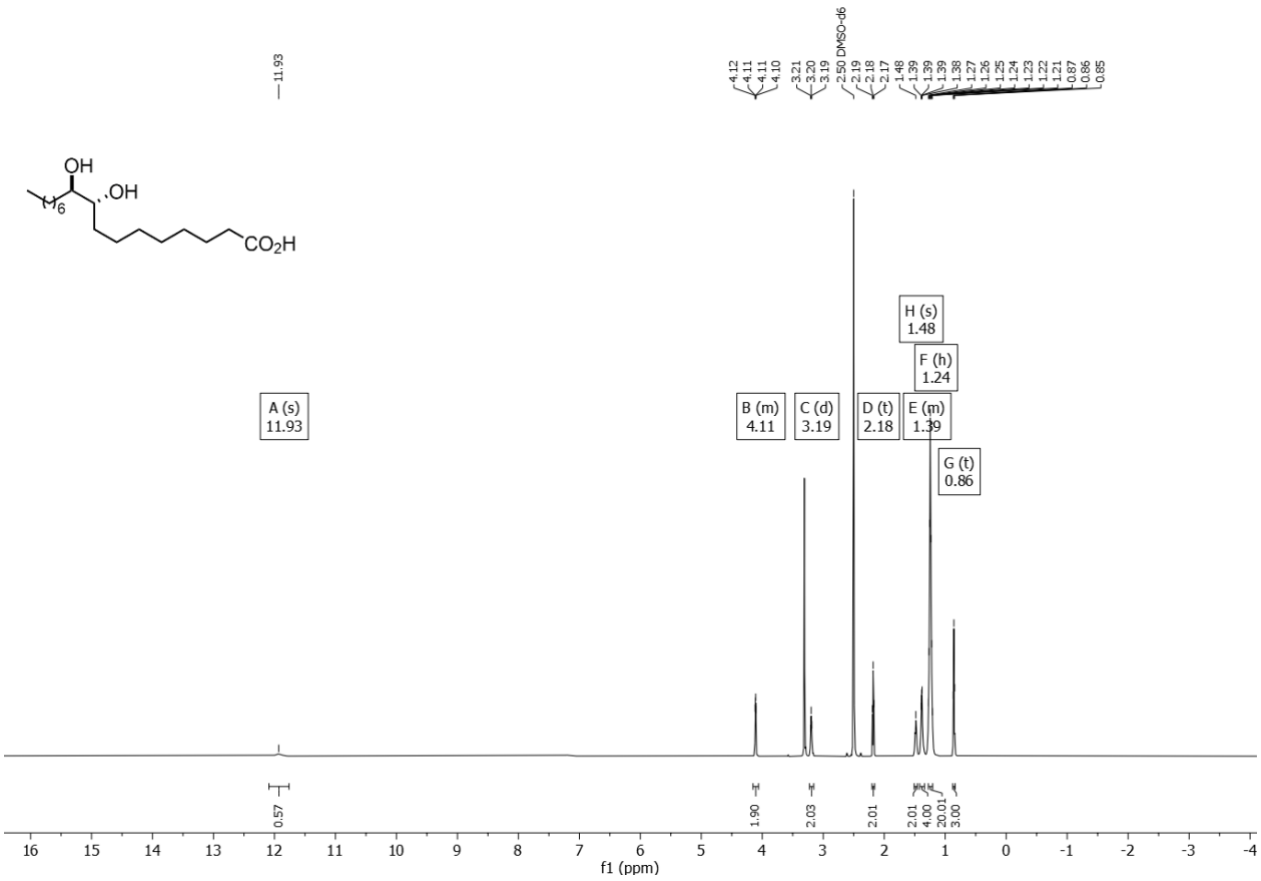


^{13}C NMR (151 MHz, $CDCl_3$)

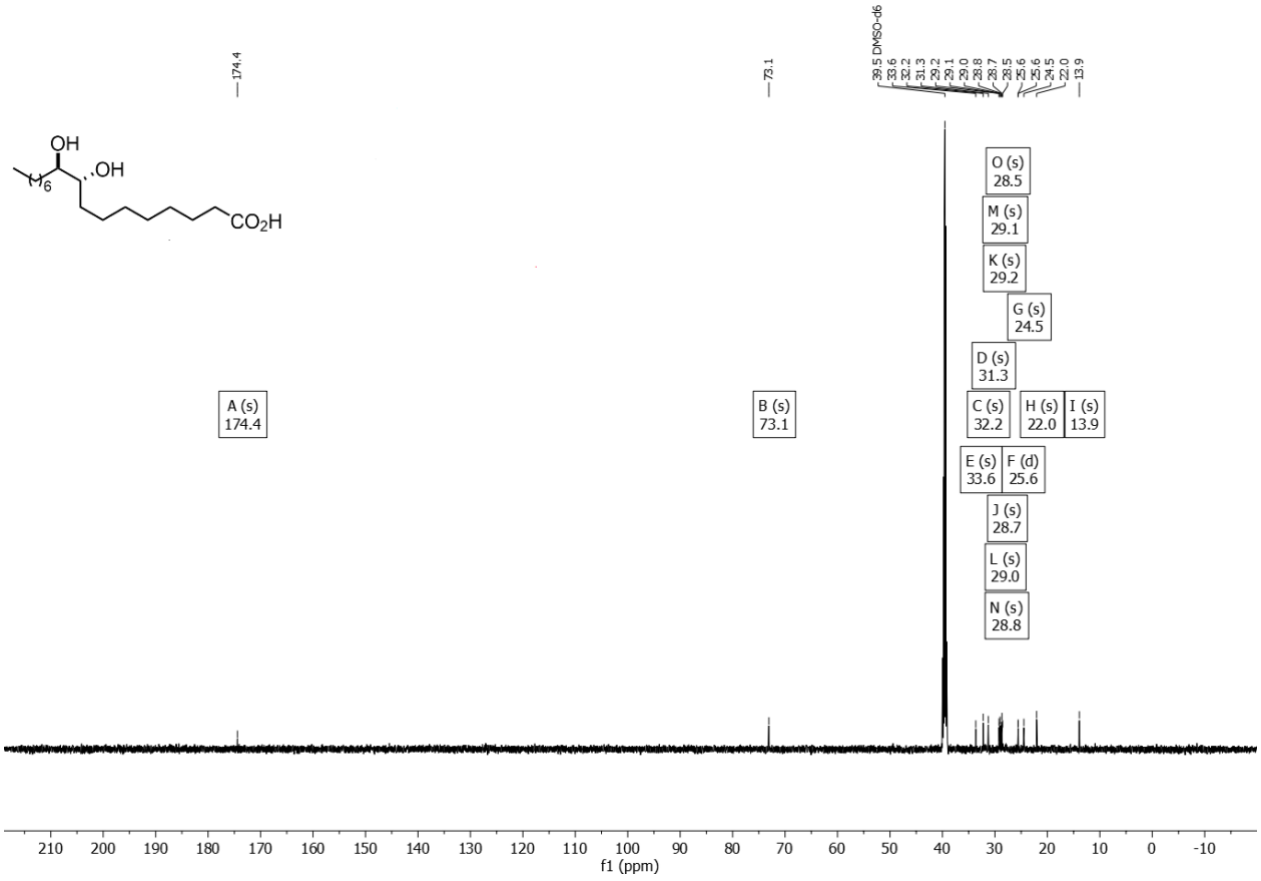


(±)-*trans*-9,10-Dihydroxyoctadecanoic acid, 10

^{1}H NMR (600 MHz, DMSO-d_6)

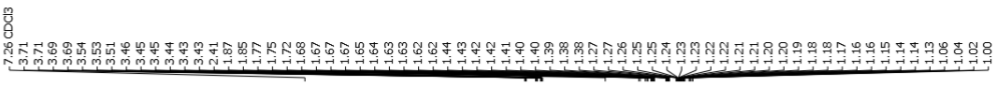


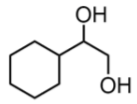
^{13}C NMR (151 MHz, DMSO-d_6)

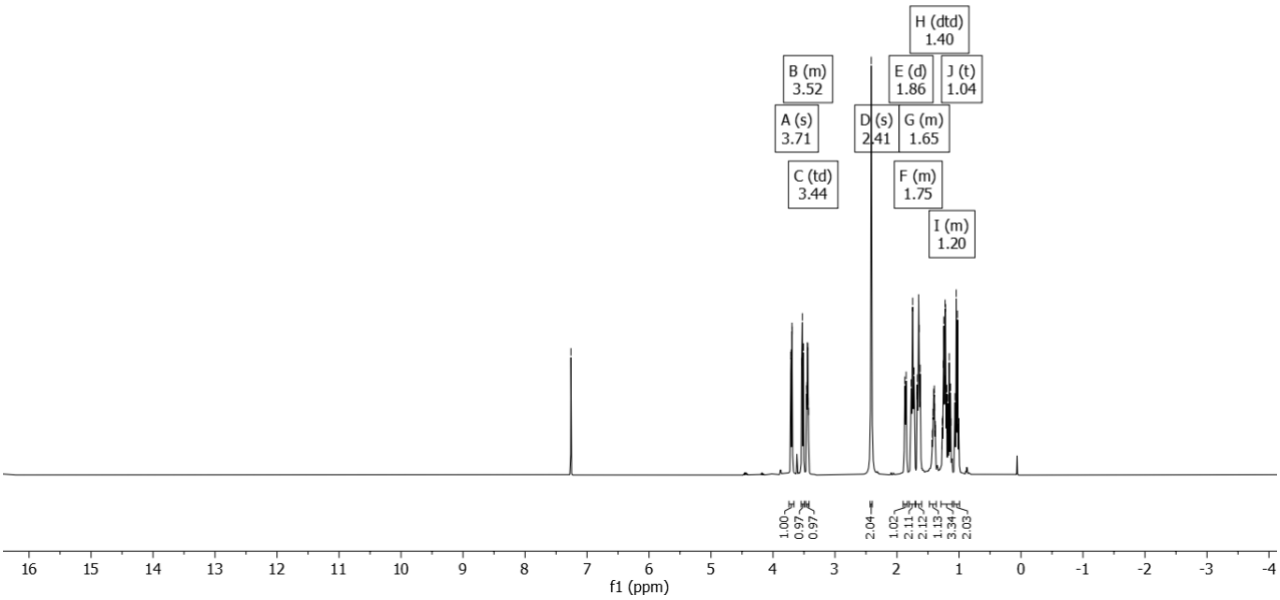


(±)-1-Cyclohexylethane-1,2-diol, 11

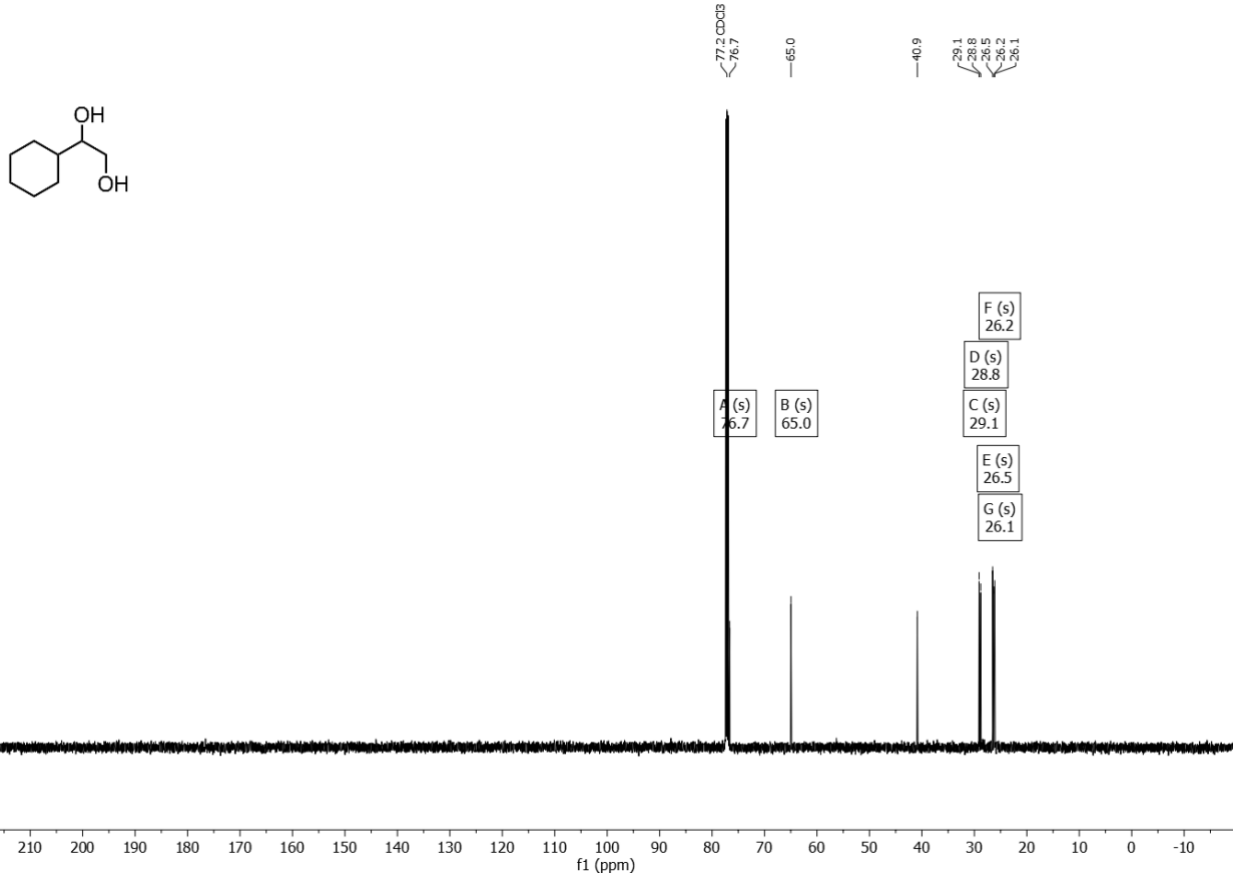
^{1}H NMR (600 MHz, $CDCl_3$)





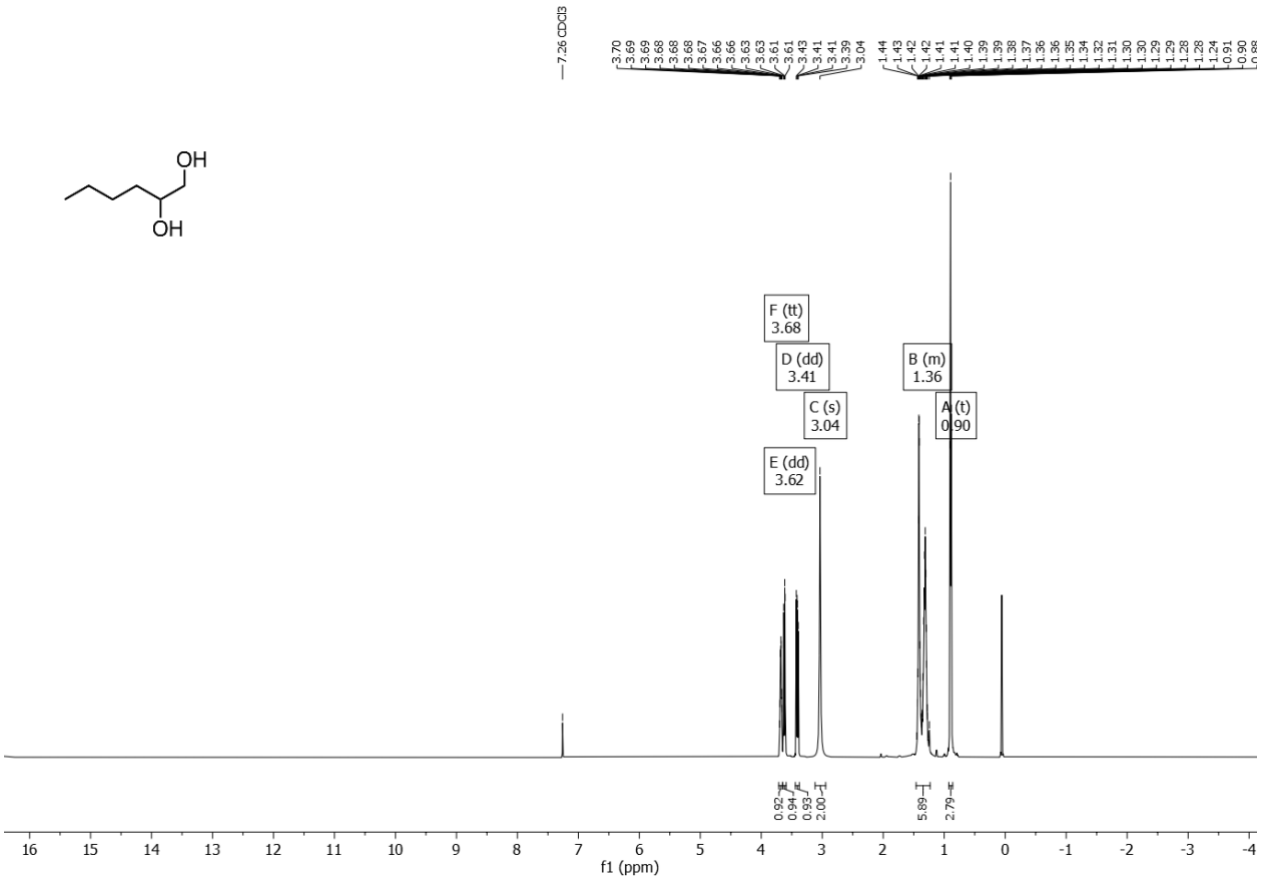


^{13}C NMR (151 MHz, $CDCl_3$)

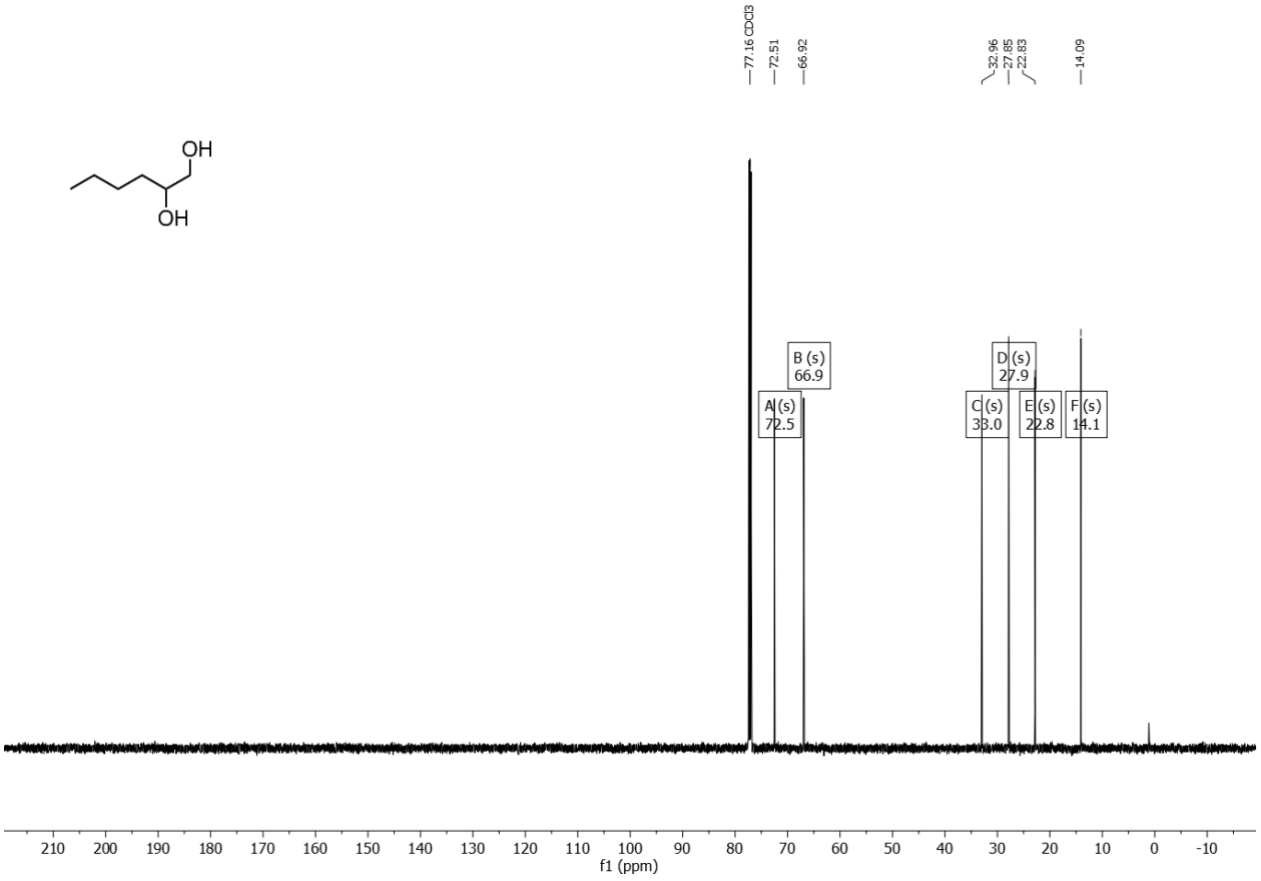


(±)-Hexane-1,2-diol, 12

^{1}H NMR (600 MHz, $CDCl_3$)

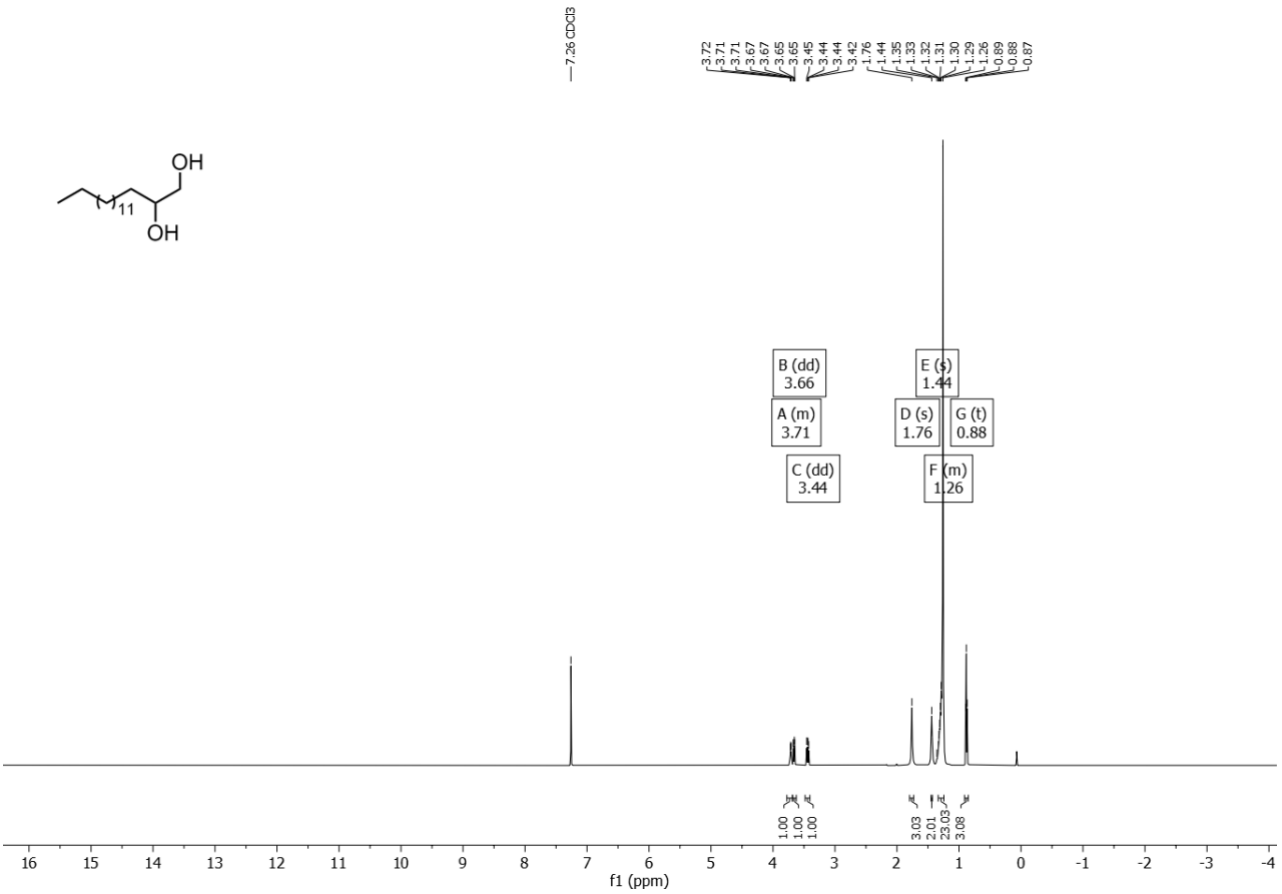


^{13}C NMR (151 MHz, $CDCl_3$)

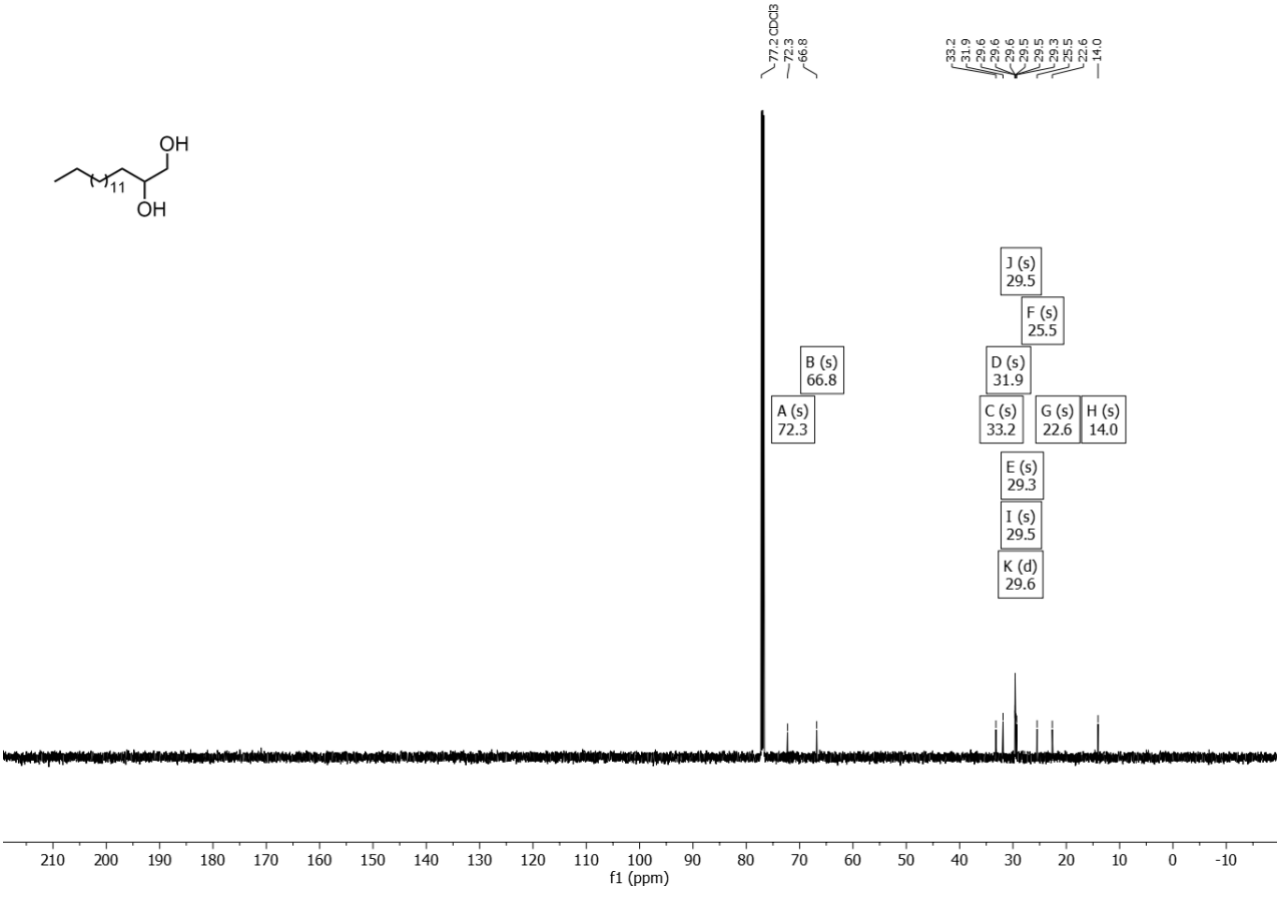


(±)-1,2-Hexadecanediol, 13

^{1}H NMR (600 MHz, $CDCl_3$)

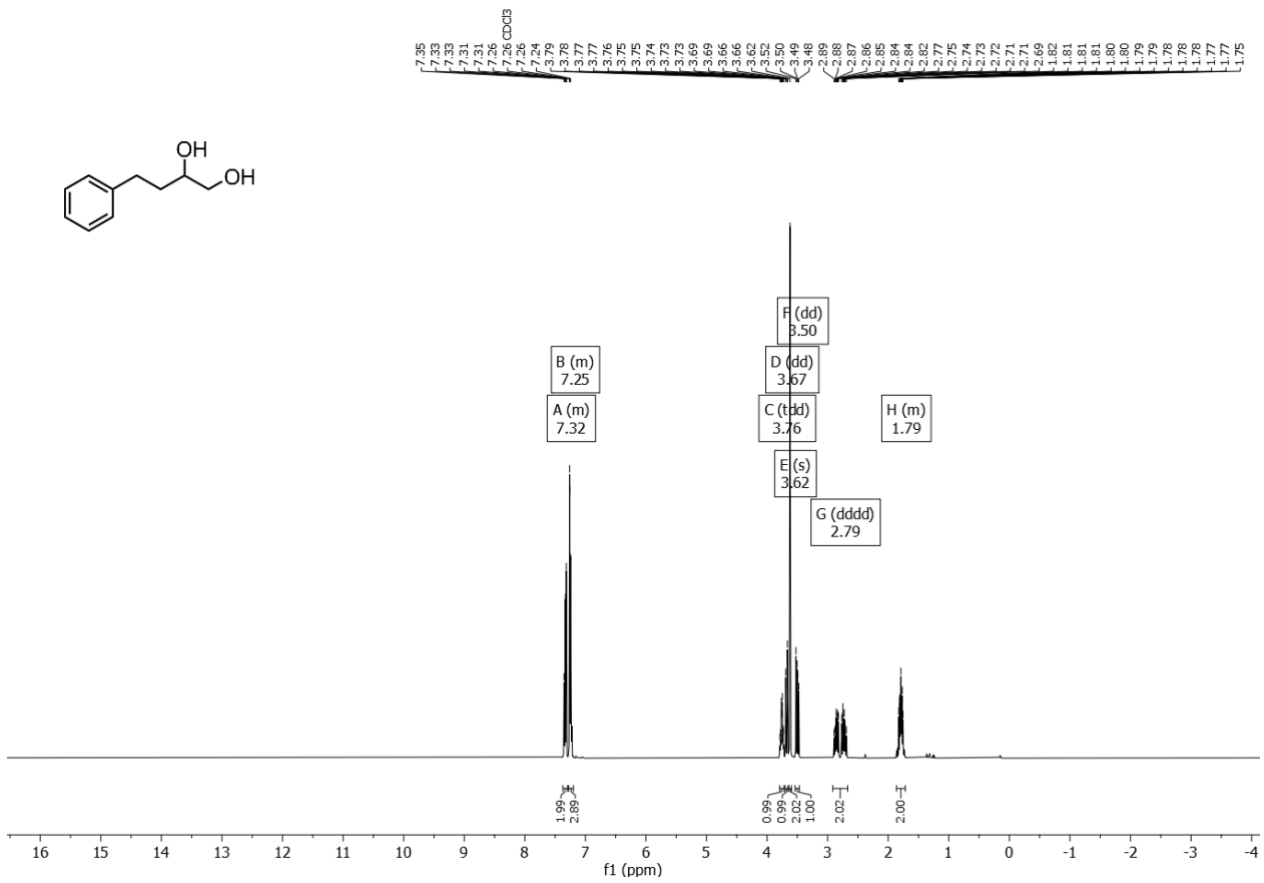


^{13}C NMR (151 MHz, $CDCl_3$)

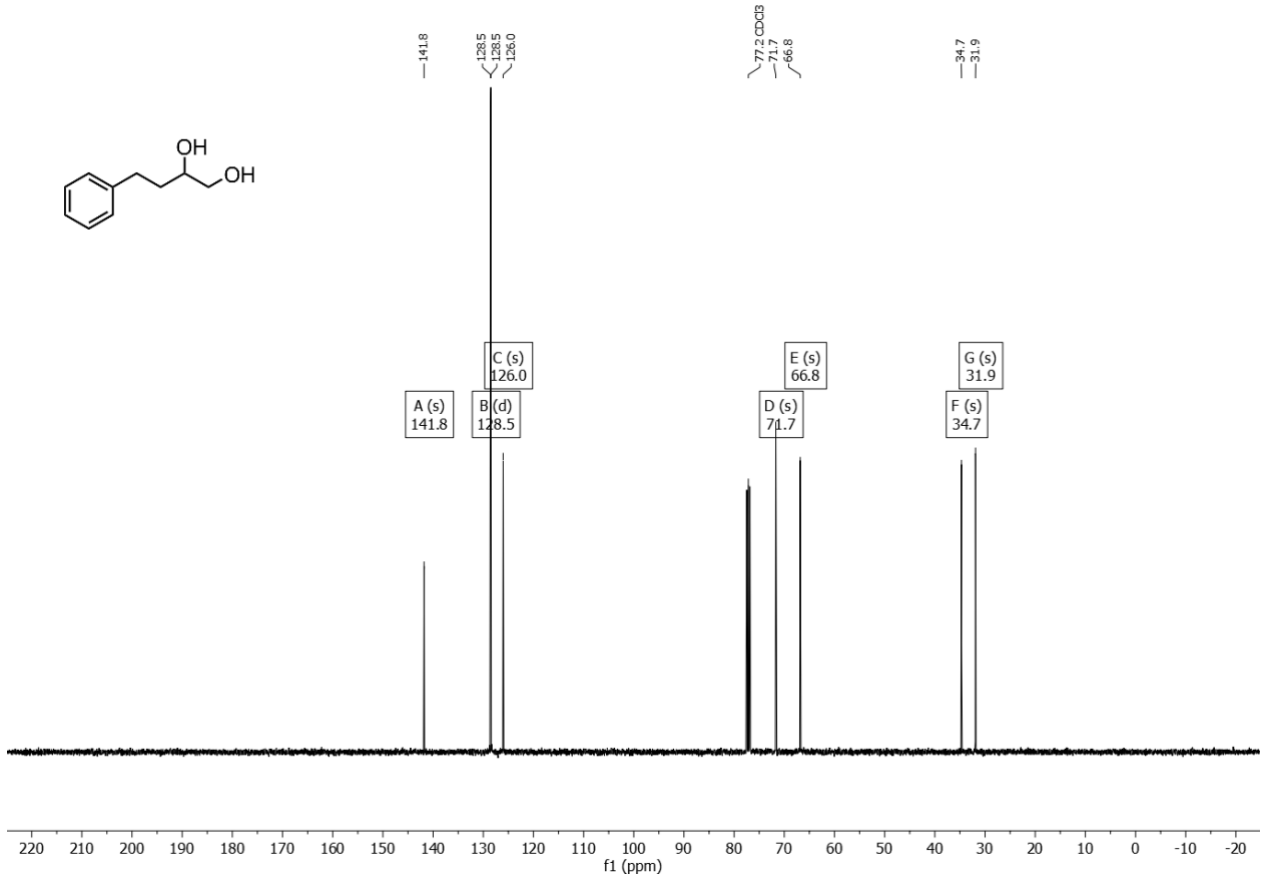


(±)-4-Phenylbutane-1,2-diol, 14

^{1}H NMR (600 MHz, $CDCl_3$)

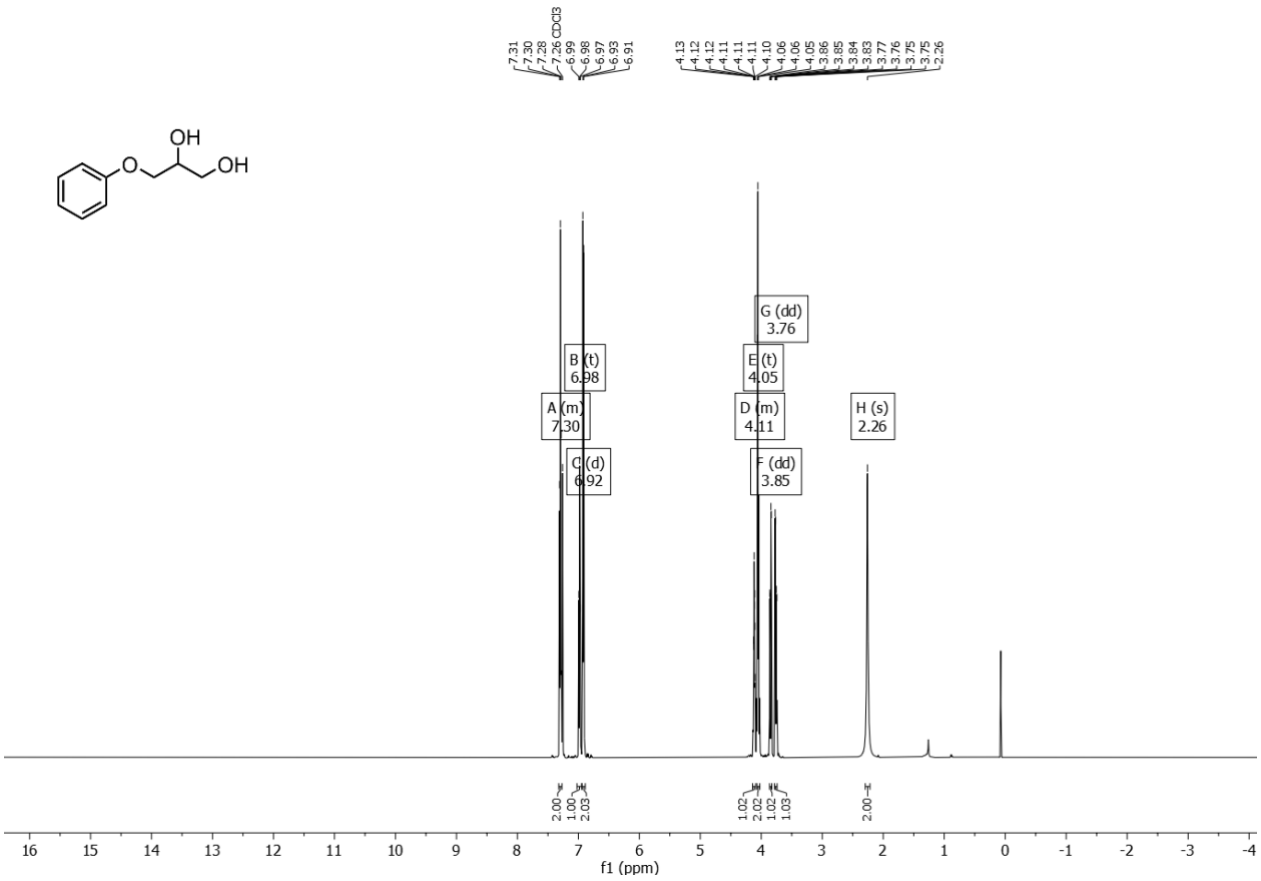


^{13}C NMR (151 MHz, $CDCl_3$)

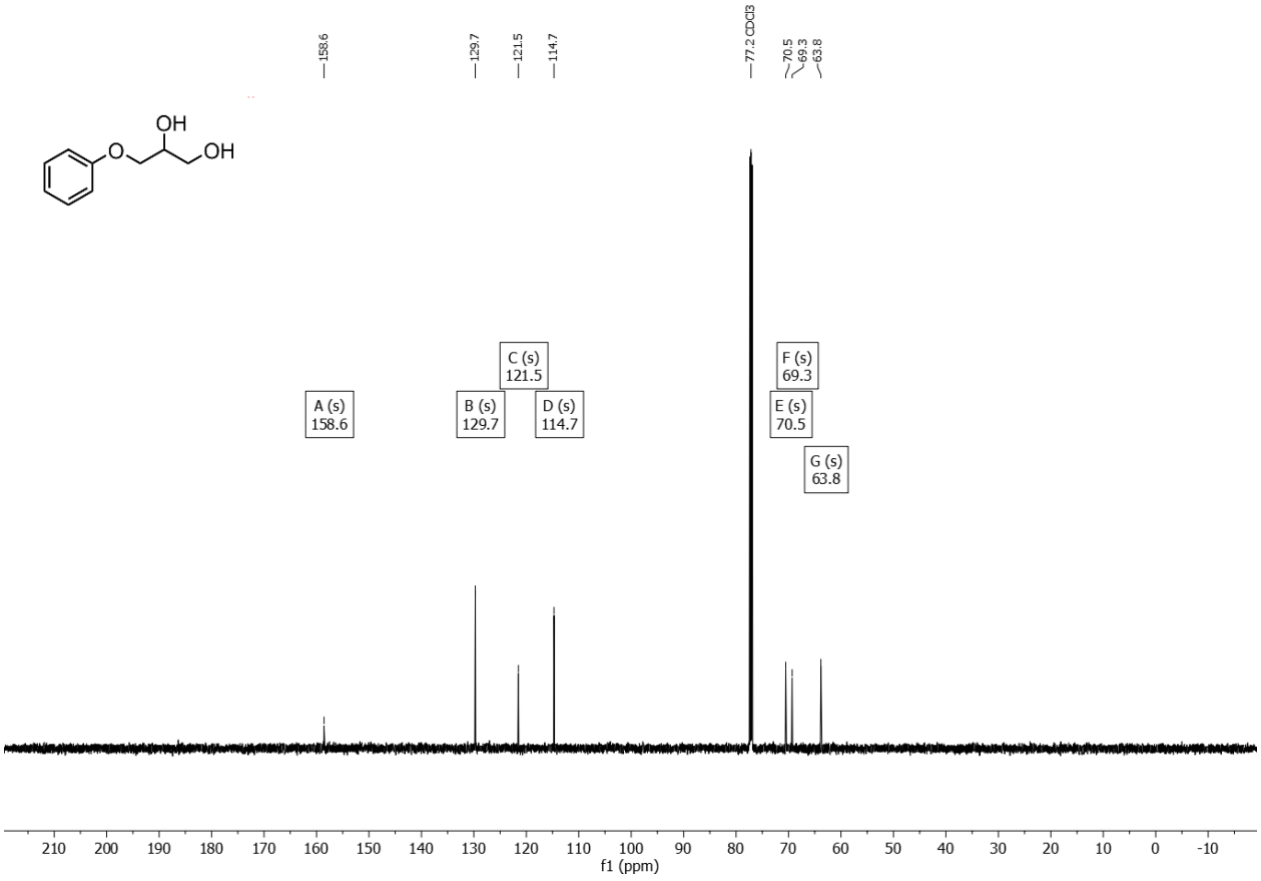


(±)-3-Phenoxypropane-1,2-diol, 15

^{1}H NMR (600 MHz, $CDCl_3$)

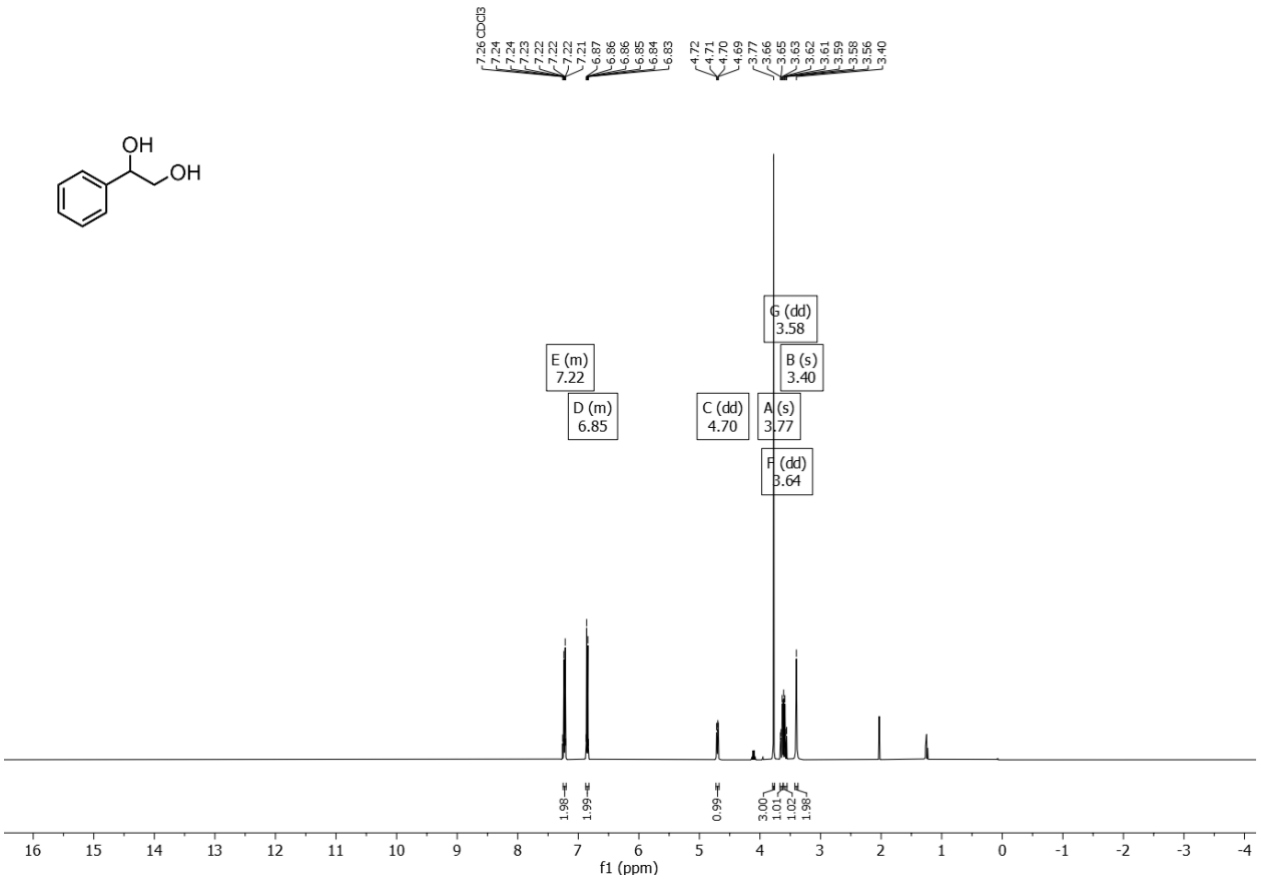


^{13}C NMR (151 MHz, $CDCl_3$)

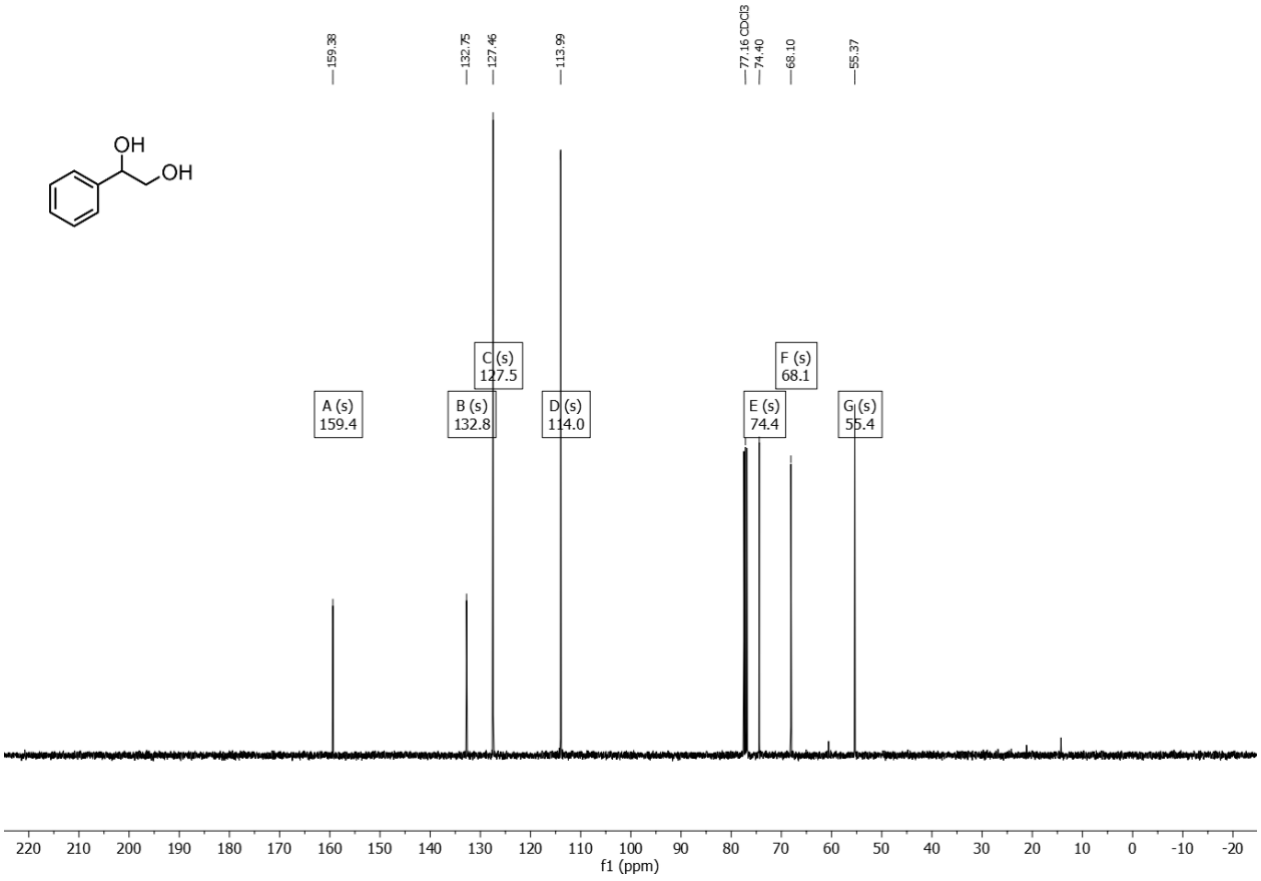


(±)-1-Phenylethane-1,2-diol, 16

^{1}H NMR (600 MHz, $CDCl_3$)

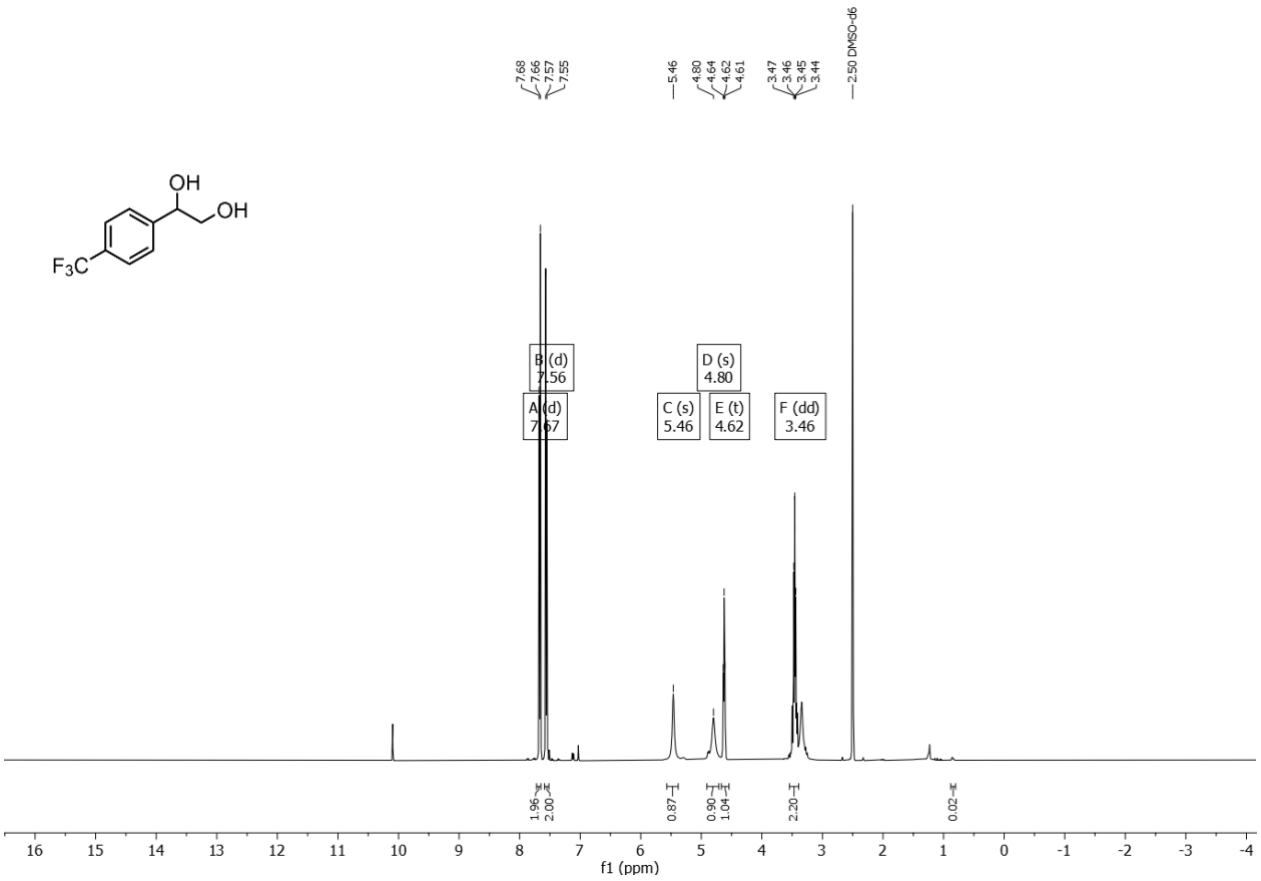


^{13}C NMR (151 MHz, $CDCl_3$)

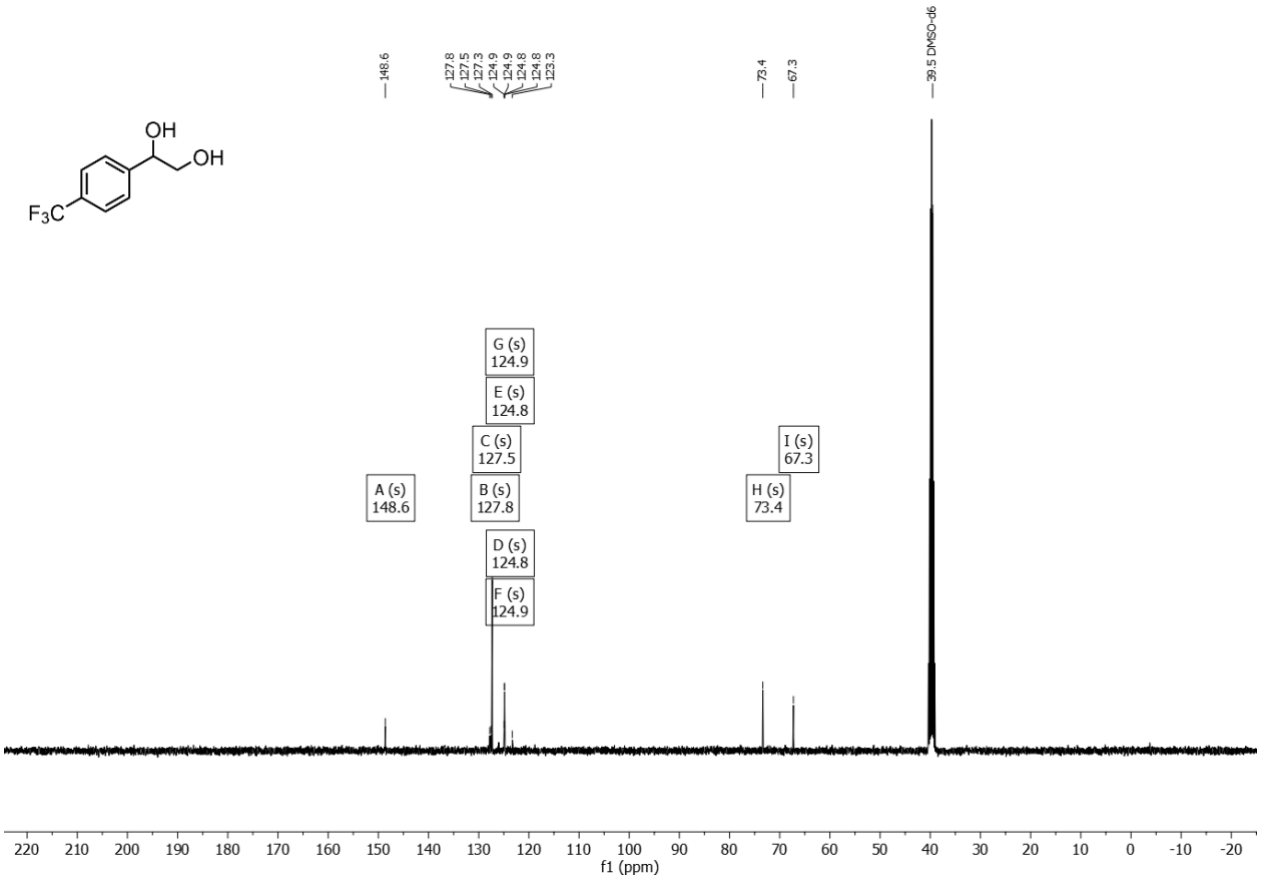


(±)-1-(4-(Trifluoromethyl)phenyl)ethane-1,2-diol, 17

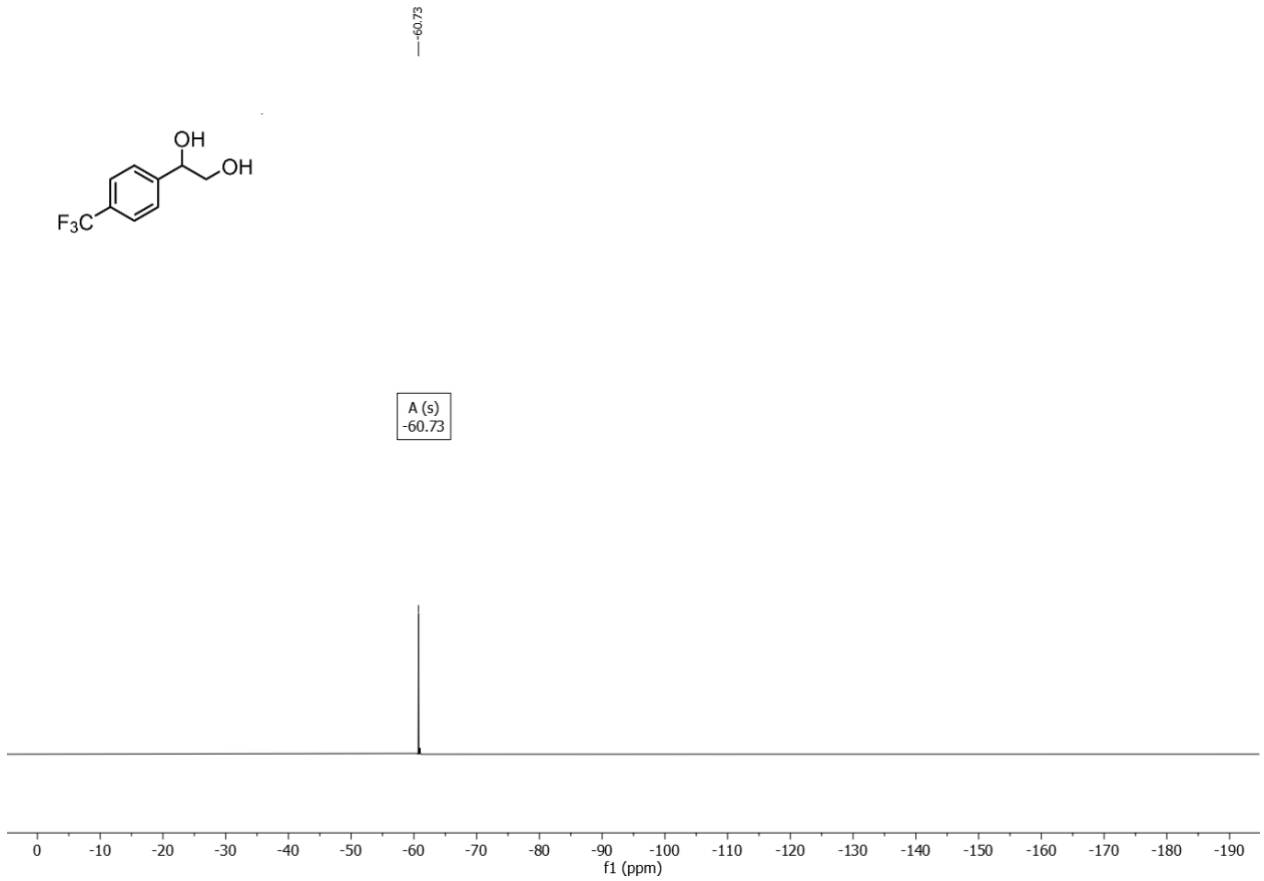
^{1}H NMR (600 MHz, DMSO-d_6)



^{13}C NMR (151 MHz, DMSO-d_6)

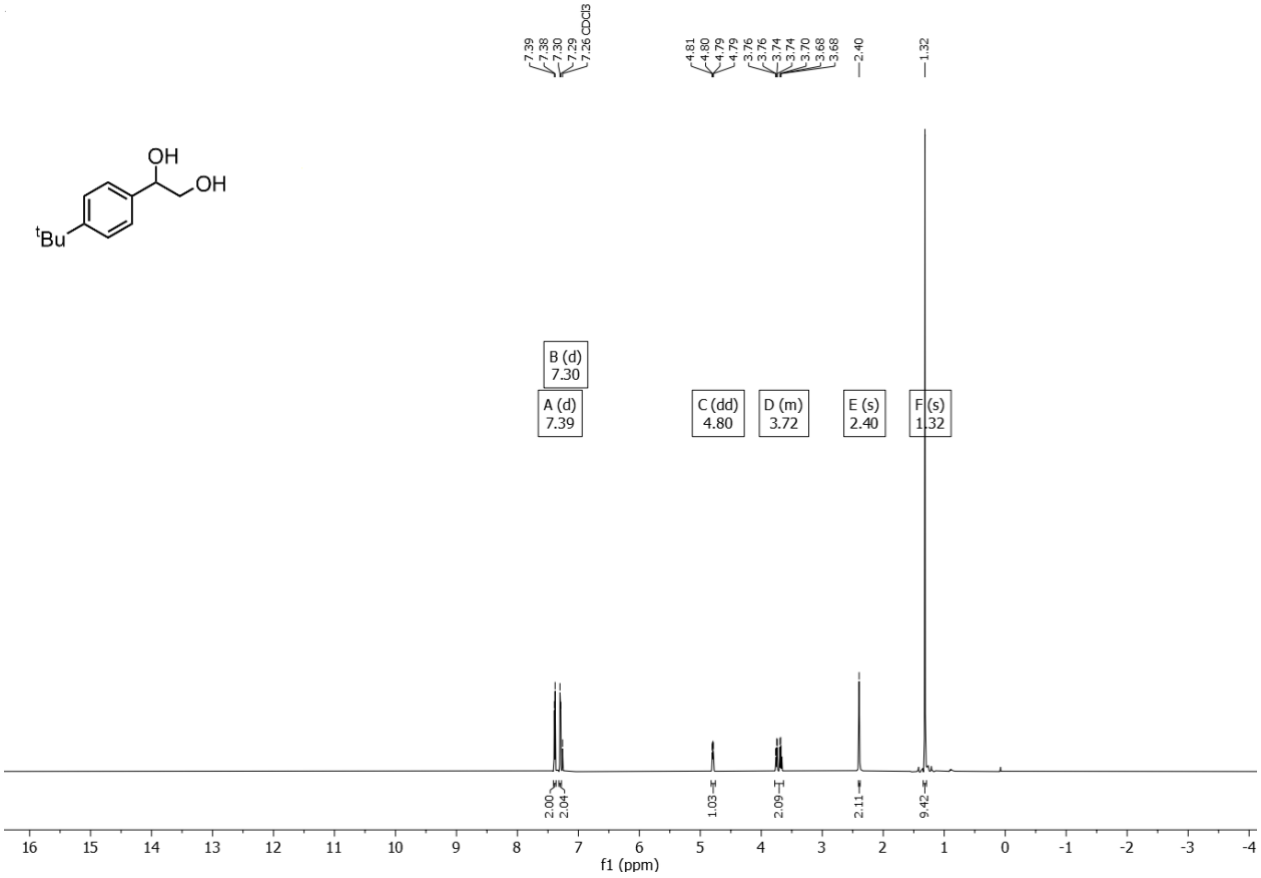


^{19}F NMR (151 MHz, DMSO-d_6)

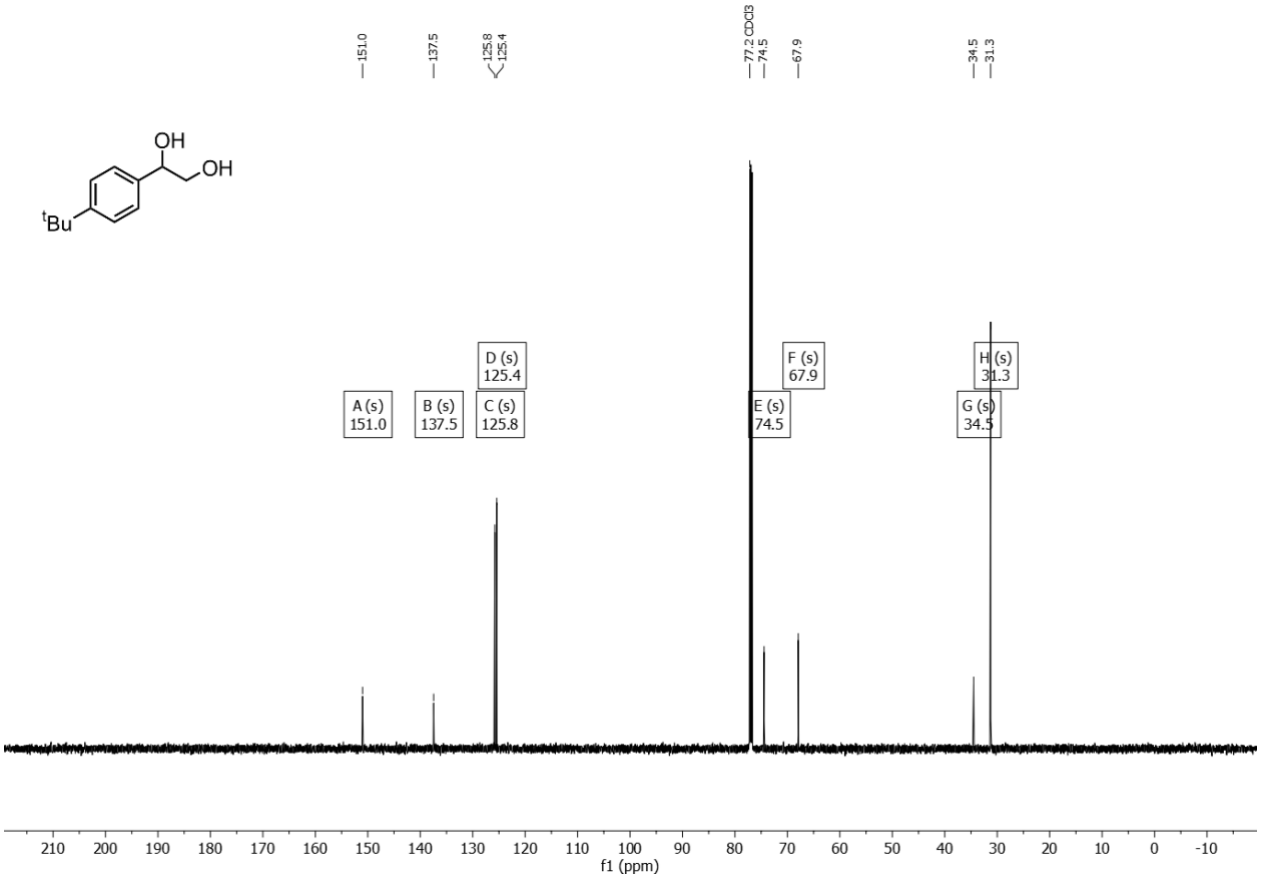


(±)-1-(4-(*tert*-Butyl)phenyl)ethane-1,2-diol, 18

^{1}H NMR (600 MHz, $CDCl_3$)

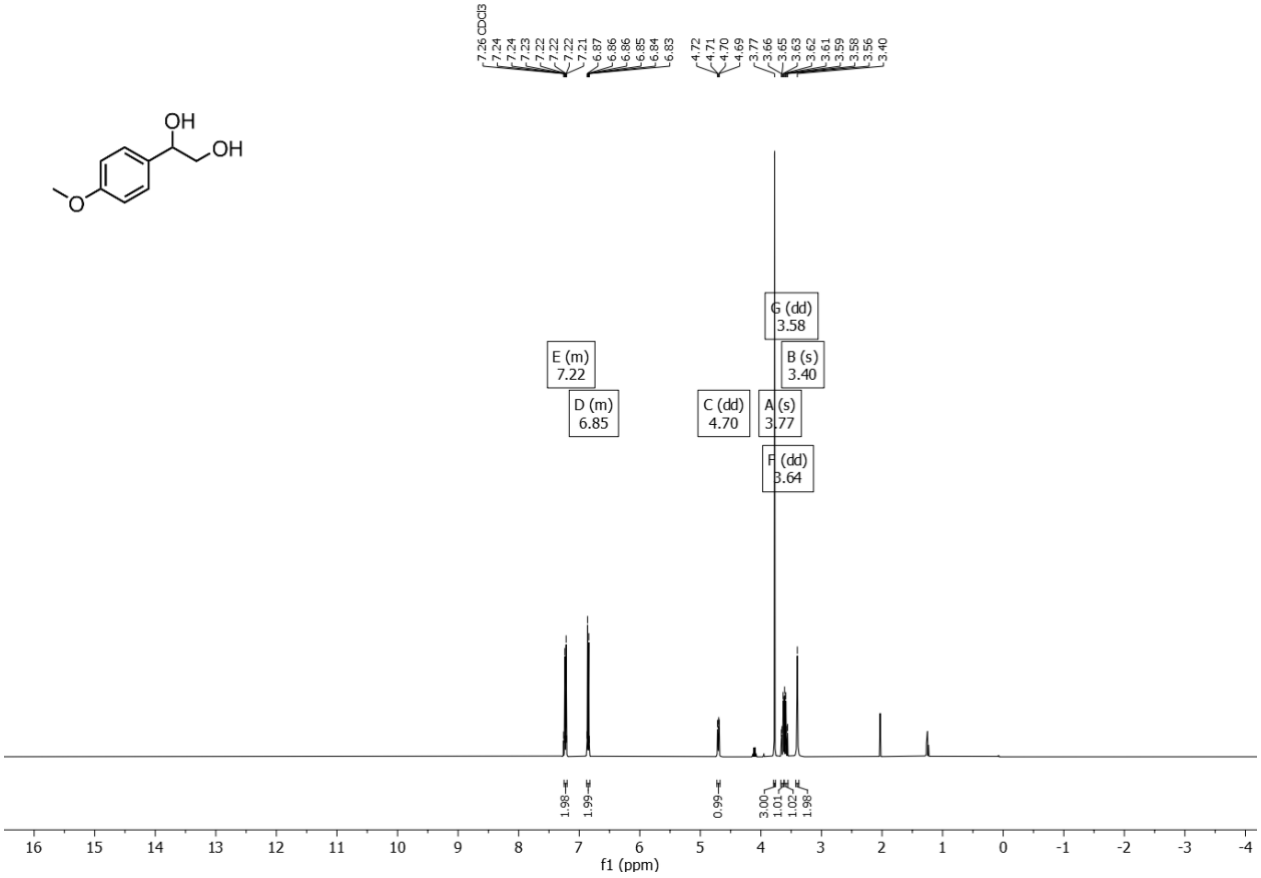


^{13}C NMR (151 MHz, $CDCl_3$)

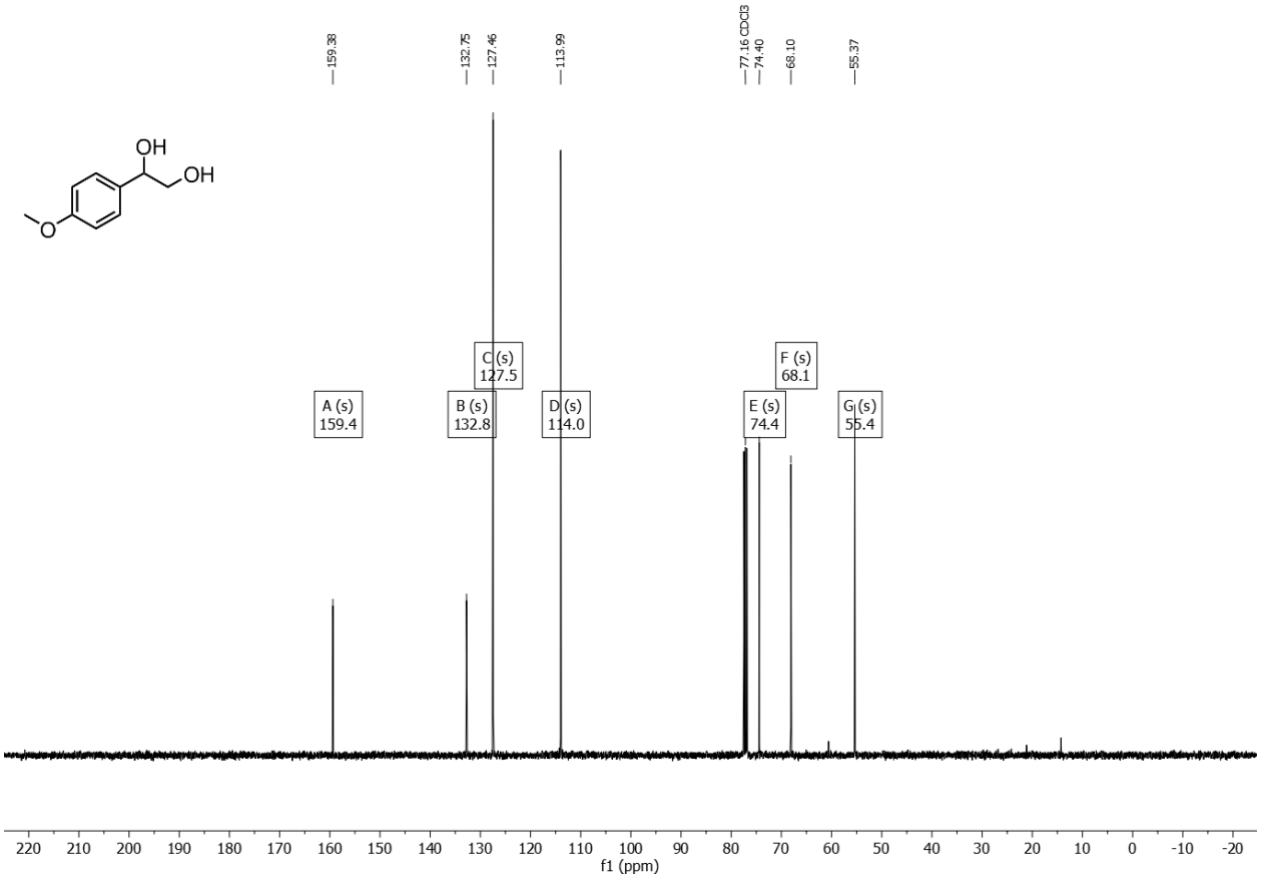


(±)-1-(4-Methoxyphenyl)ethane-1,2-diol, 19

^{1}H NMR (600 MHz, $CDCl_3$)

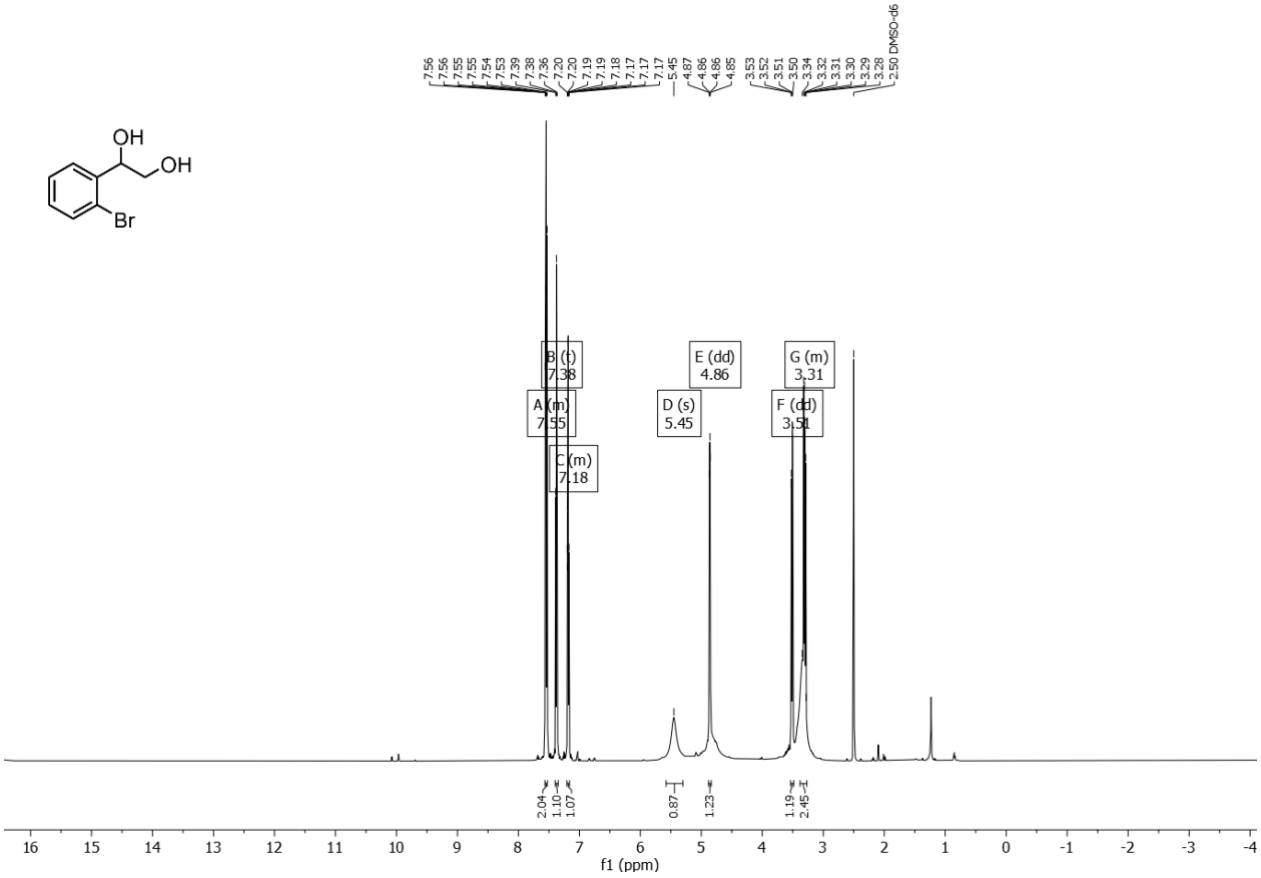


^{13}C NMR (151 MHz, $CDCl_3$)

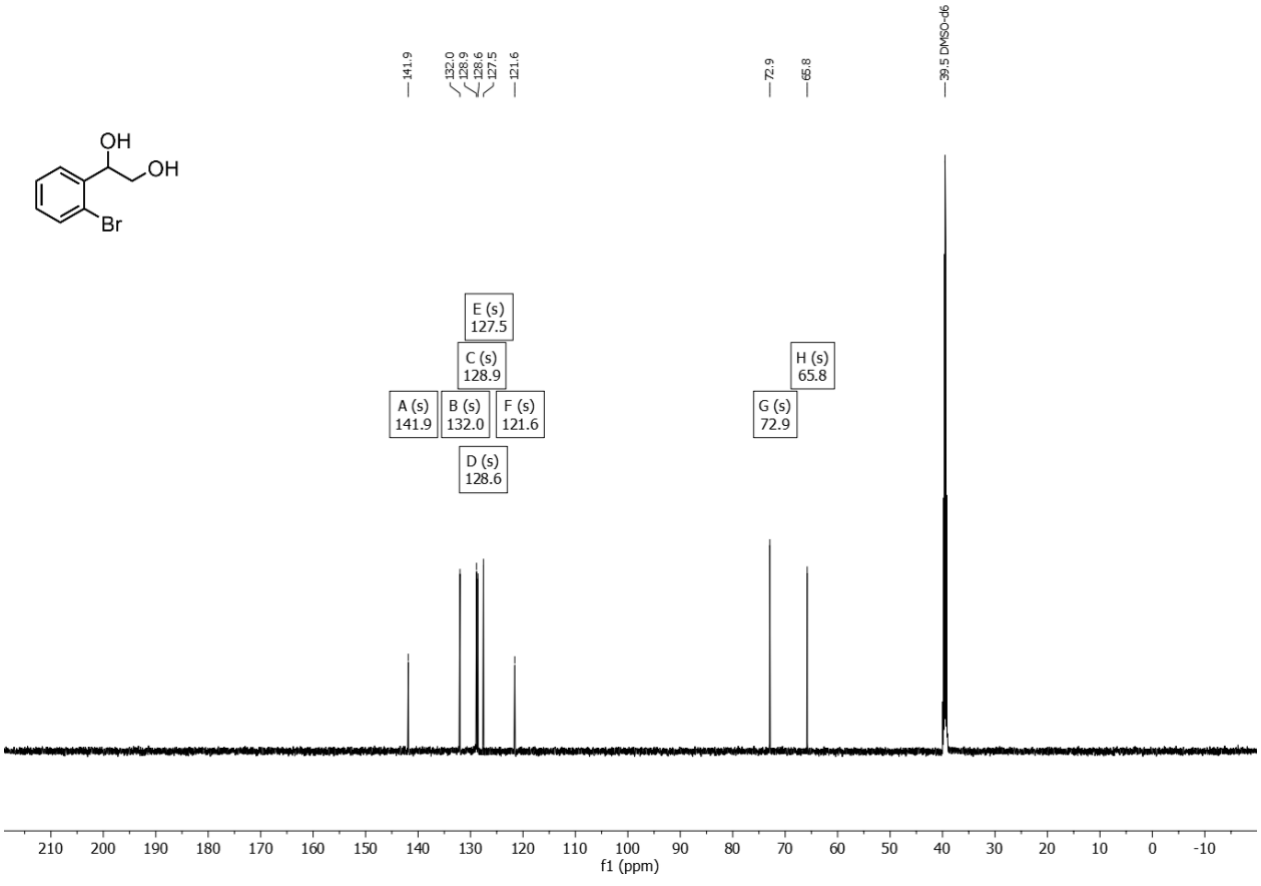


(±)-1-(2-Bromophenyl)ethane-1,2-diol, 20

^{1}H NMR (600 MHz, DMSO-d_6)

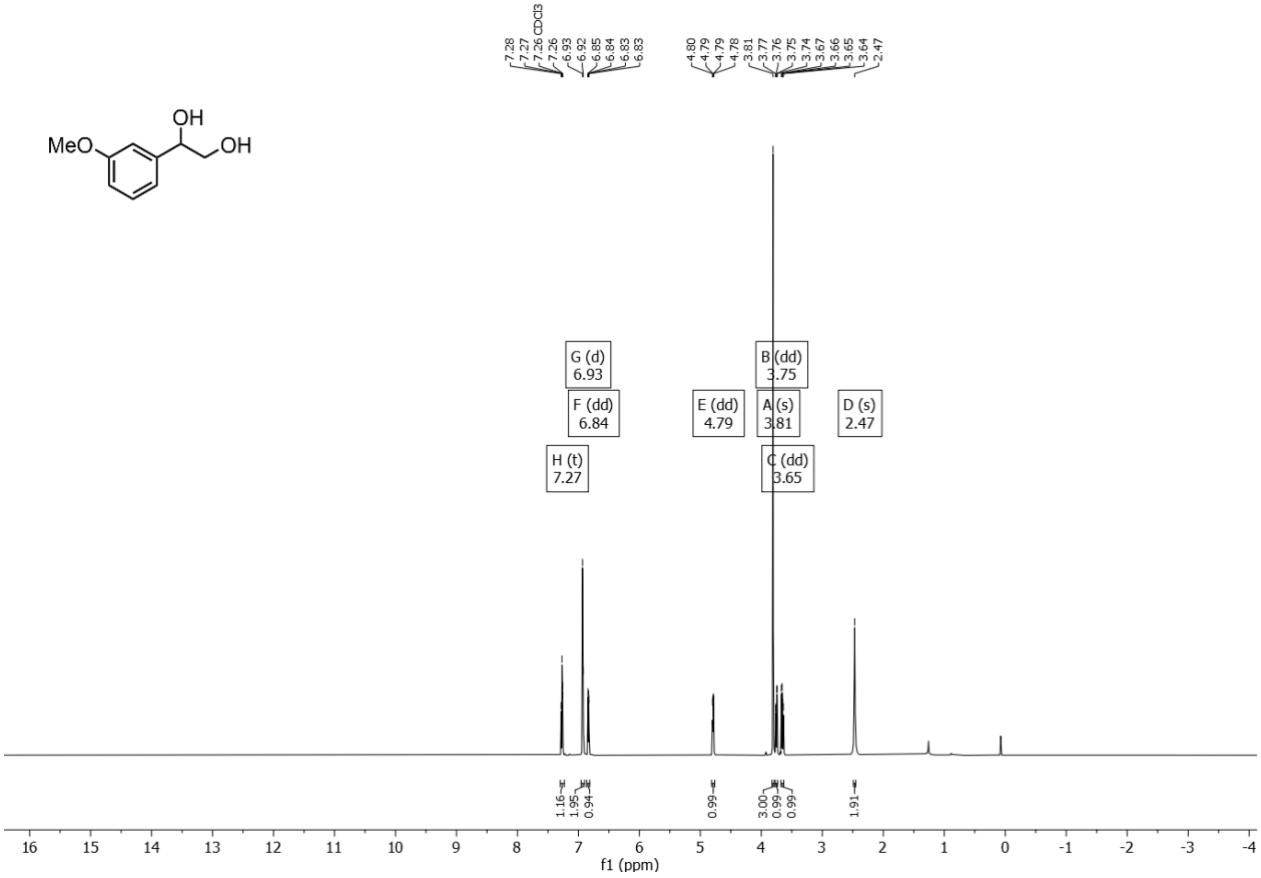


^{13}C NMR (151 MHz, DMSO-d_6)

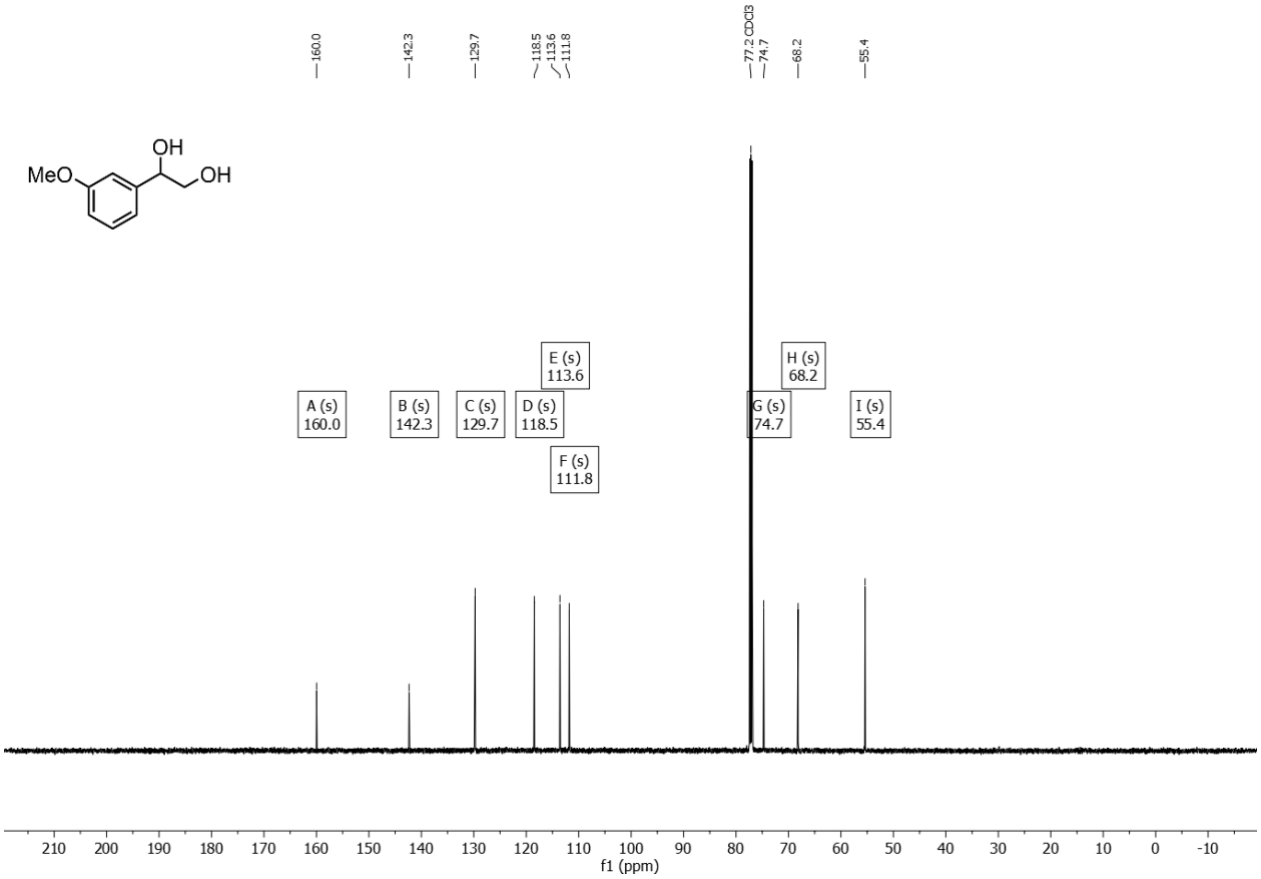


(±)-1-(3-Methoxyphenyl)ethane-1,2-diol, 21

^{1}H NMR (600 MHz, $CDCl_3$)

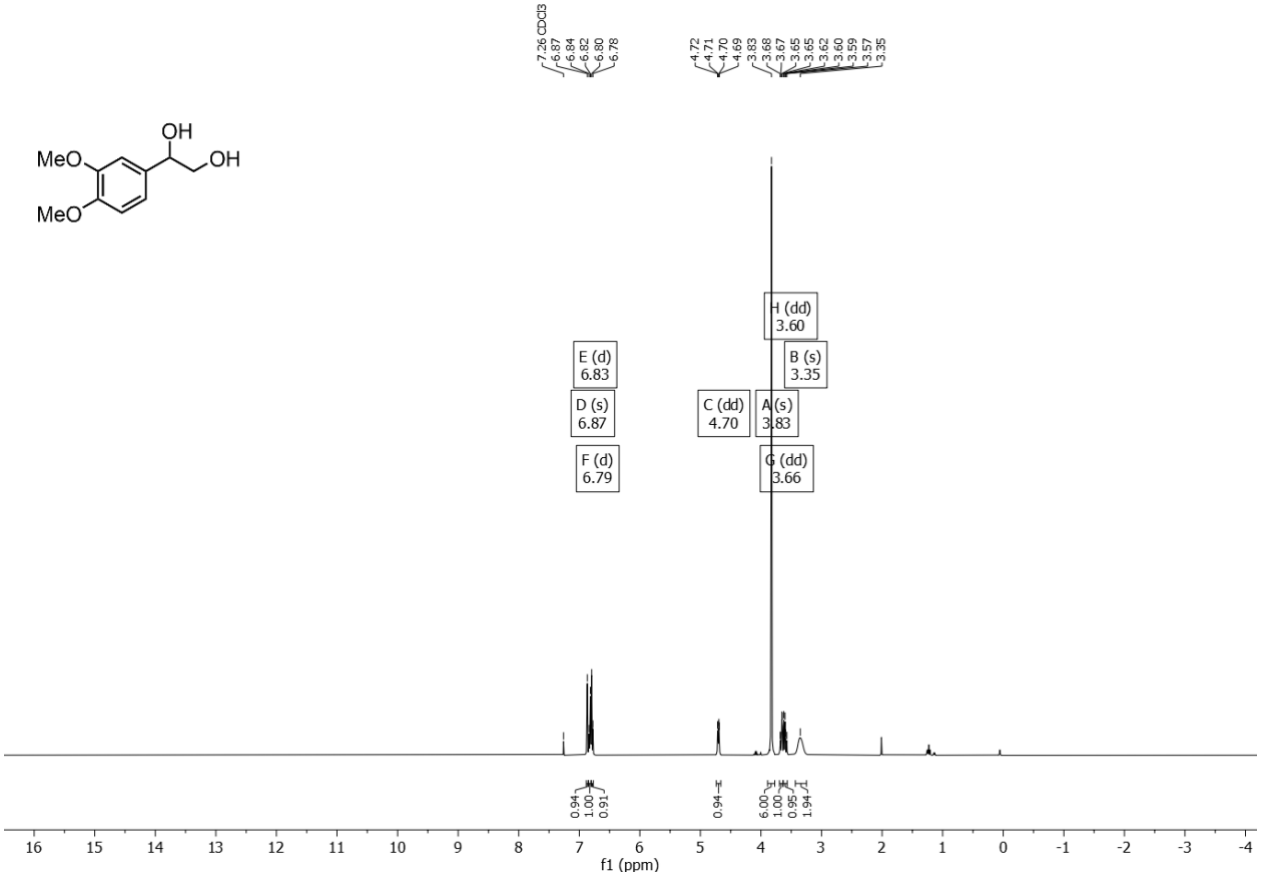


^{13}C NMR (151 MHz, $CDCl_3$)

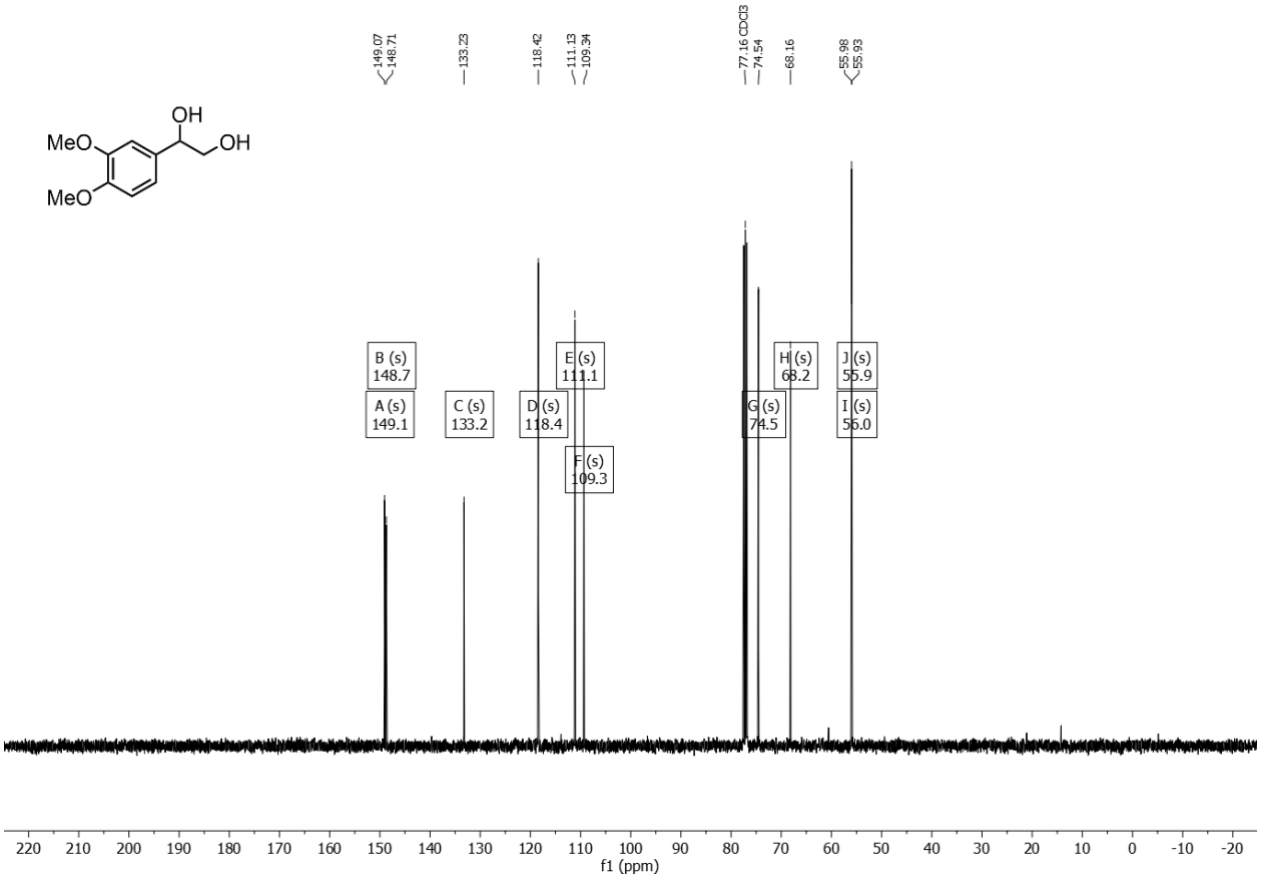


(±)-1-(3,4-Dimethoxyphenyl)ethane-1,2-diol, 22

^{1}H NMR (600 MHz, $CDCl_3$)

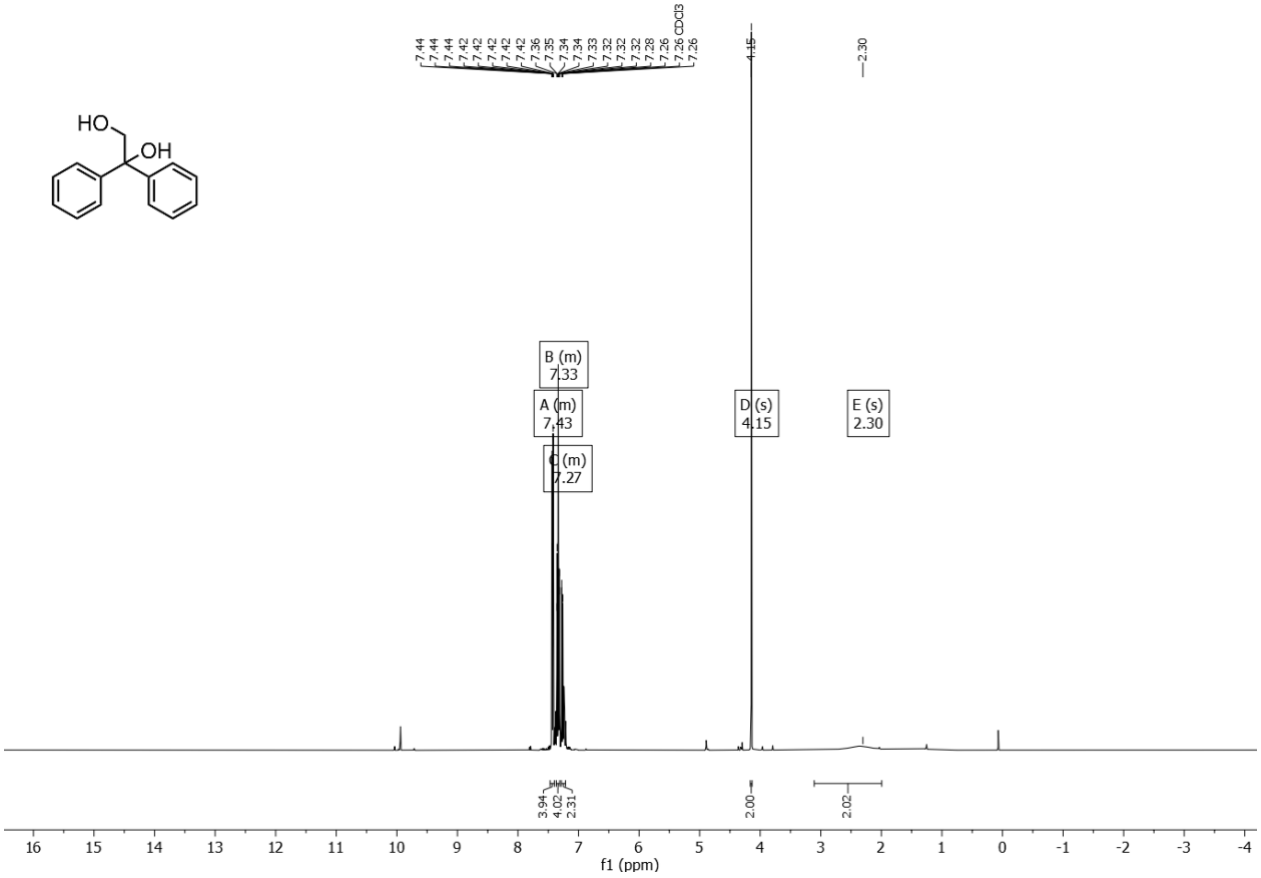


^{13}C NMR (151 MHz, $CDCl_3$)

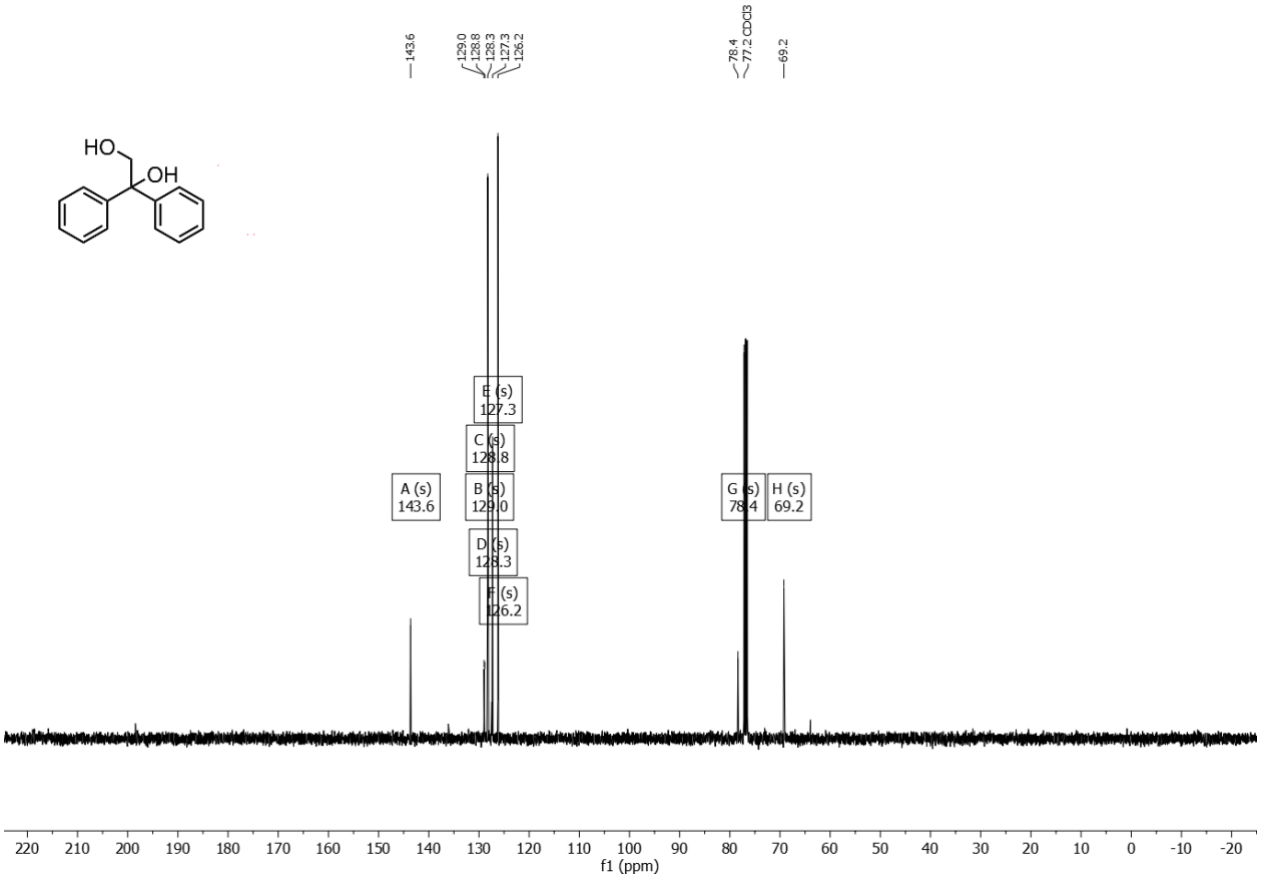


(±)-1,1-Diphenylethane-1,2-diol, 23

^{1}H NMR (600 MHz, $CDCl_3$)

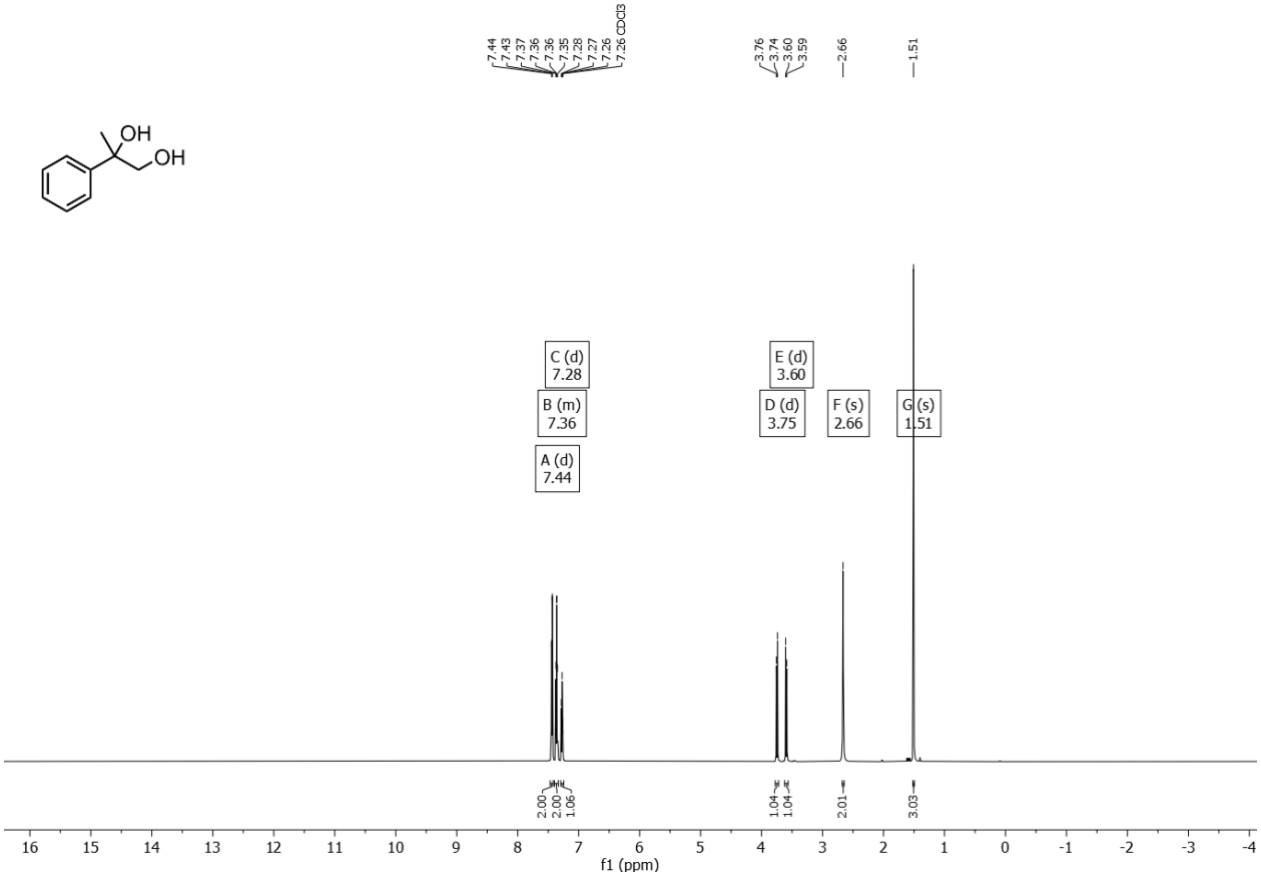


^{13}C NMR (151 MHz, $CDCl_3$)

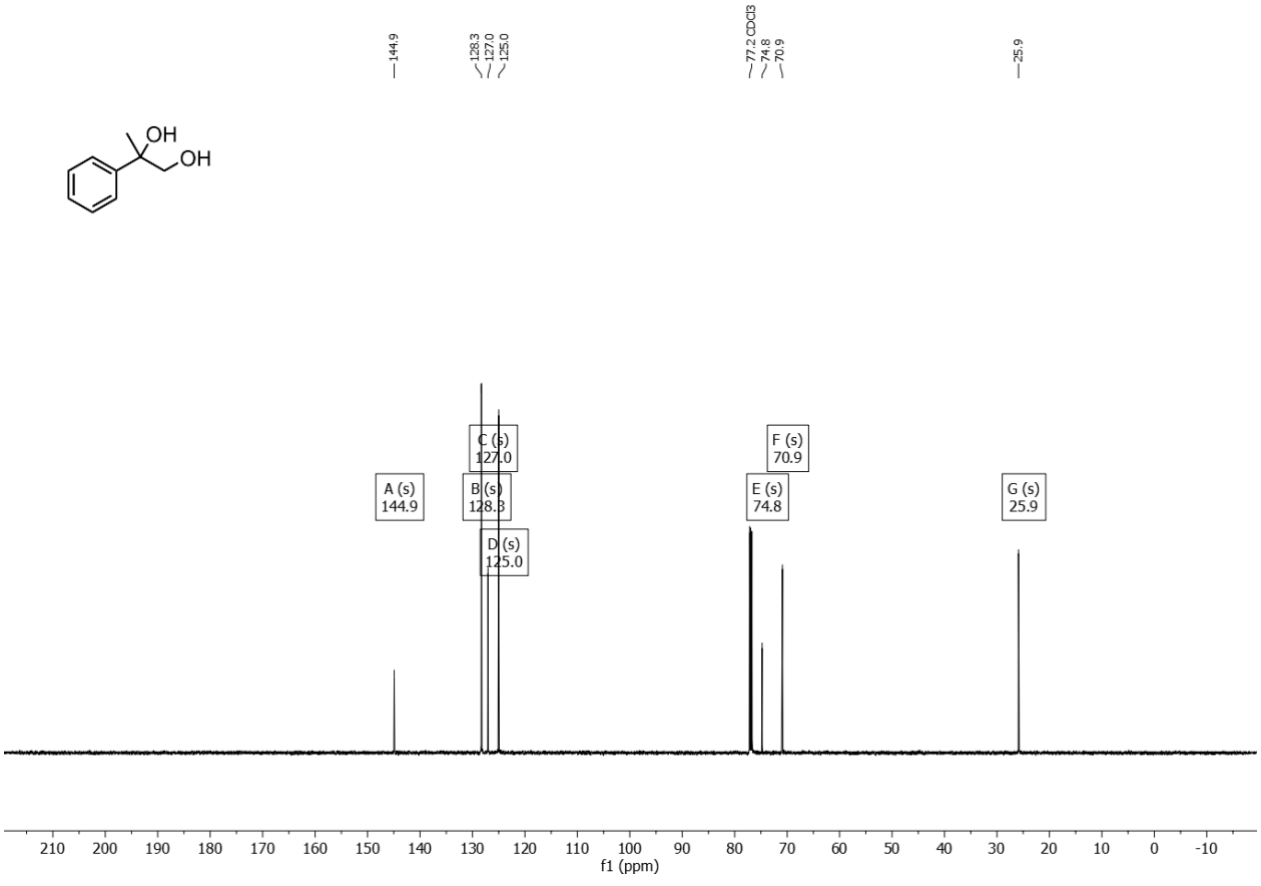


(±)-2-Phenylpropane-1,2-diol, 24

^{1}H NMR (600 MHz, $CDCl_3$)

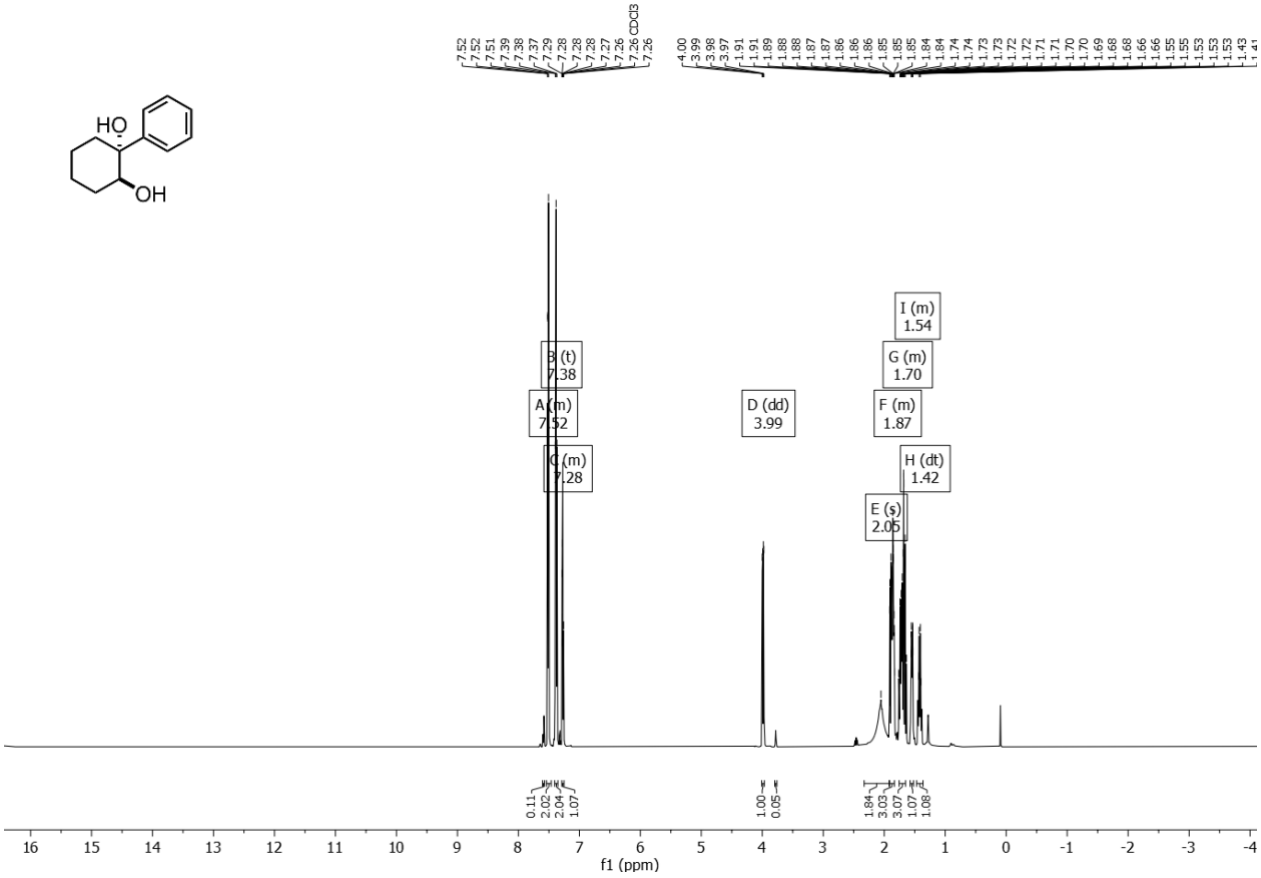


^{13}C NMR (151 MHz, $CDCl_3$)



(±)-1-Phenylcyclohexane-1,2-diol, 25

^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)