Supporting information

Selective Catalytic Oxidation of Diglycerol

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1 General information

All reagents were used as received without further purification unless otherwise noted. Diglycerol (mixture of isomer, >80% α,α-diglycerol) was purchased from Tokyo Chemical Industry, palladium(II) acetate, neocuproine, glycerol, 1,1,1,3,3,3-hexafluoroisopropanol, 2,2,2,-trifluoroethanol, cyclopentyl methyl ether, 2-methyltetrahydrofuran, tetrahydrofuran, 1,4-dioxane, (trifluoromethyl)benzene, styrene, dimethyl carbonate, potassium carbonate, mesitylene, benzyl alcohol, Benzoyl chloride and Amberlyst 15 hydrogen form were supplied by Sigma-Aldrich or Alfa-Aesar. Palladium, 10% on activated wood carbon was purchased from Strem Chemicals. Reactions were monitored by TLC (thin-layer chromatography) using aluminium silica gel ($60F_{254}$) and chromatography was performed using silica 60M (0.04–0.063 mm). ^{1}H and ^{13}C NMR spectra were recorded on a Brüker DRX 300 or Brüker ALS 300 in $CDCl_3$, DMSO-d_6 or CD_3OD solutions using tetramethylsilane (TMS) as an internal standard. Electrospray ionization (ESI), High resolution mass spectra (HRMS) were recorded on a MicroTOFQ-II, Bruker Daltonics spectrometer instrument using standard conditions (ESI, 70 eV).

2 Procedure for the purification of α,α-diglycerol

2.1 Procedure to purify α,α-diglycerol.[1]

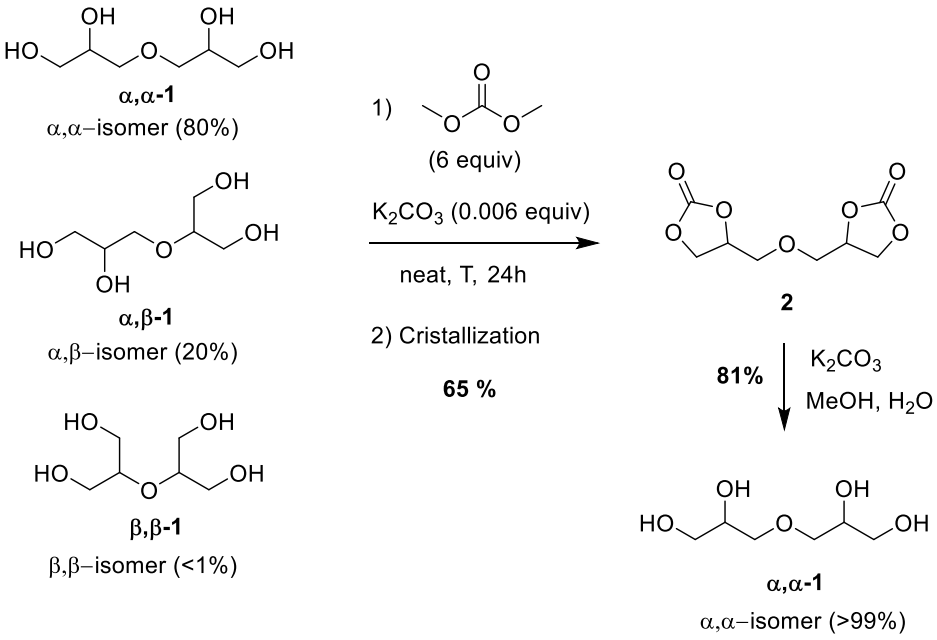
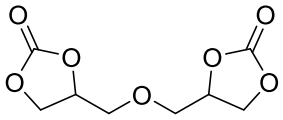


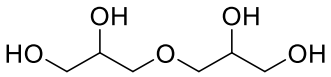
Figure S1. Preparation of α,α-diglycerol from commercially available diglycerol

2.1.1 Synthesis of **α,α-diglycerol dicarbonate** (**2**)



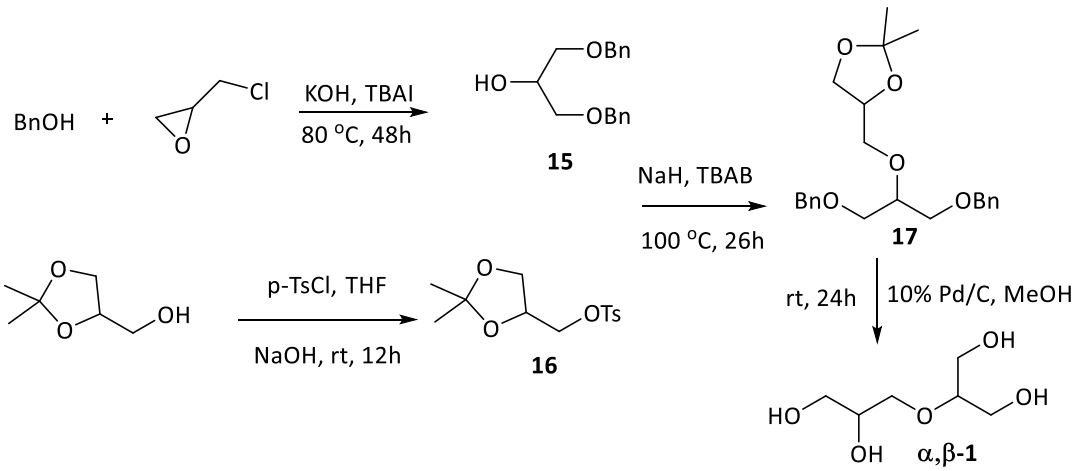
Following a reported procedure,[1] in a 250 mL round bottom flask equipped with a magnetic stirrer and a reflux condenser, a mixture of diglycerol isomers (40 g, 240.1 mmol) and dimethyl carbonate (32.1 g, 142.4 mmol, 120 mL, 6 equiv) were placed followed by K_2CO_3 (200 mg, 1.44 mmol, 0.006 equiv). The reaction mixture was heated at 70 °C for 24 h. Then, the solvent mixture of dimethyl carbonate and methanol was removed by evaporation. Cold ethyl acetate (200 mL) was added into flask, to precipitate K_2CO_3. The precipitated catalyst was filtered off and washed with ethyl acetate (200 mL). The filtrate was evaporated to dryness and crystallized from methanol. The product **2** (33.9 g, 65%) was obtained as a white solid. ^{1}H NMR (300 MHz, CD_3OD): δ = 4.94 (dddd, *J* = 8.8, 6.2, 4.5, 2.6 Hz, 2H, 2CH), 4.52 (t, *J* = 8.5 Hz, 2H, CH_2), 4.24 (ddd, *J* = 8.3, 7.3, 6.1 Hz, 2H, CH_2), 3.76 (ddd, *J* = 11.6, 3.6, 2.7 Hz, 2H, $CH_2O\ C\underline{H}_2$), 3.68 (ddd, *J* = 11.6, 4.3, 3.0 Hz, 2H, $C\underline{H}_2O\ CH_2$). ^{13}C NMR (75 MHz, CD_3OD): δ = 154.86 (Cq), 154.81 (Cq), 75.40 (CH_2), 75.34 (CH_2), 70.40 (CH), 70.35 (CH), 65.88 (2 CH_2).

2.1.2 Hydrolysis of α,α-diglycerol decarbonate to synthesize **α,α–isomer (α,α-1)**

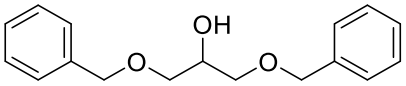


Following a reported procedure,[1] in a 250 mL round bottom flask equipped with a magnetic stirrer and a reflux condenser, α,α-diglycerol dicarbonate **2** (10 g, 45.9 mmol), methanol (50 mL) and H_2O (50 mL) were placed followed by K_2CO_3 (2 g, 14.5 mmol, 50 mL, 0.32 equiv). The reaction mixture was heated at reflux (90 °C) for 2 h. The mixture was evaporated to dryness. The residue was dissolved in cold methanol (100 mL). K_2CO_3 was filtrated off and then the solution was evaporated to dryness. The product **α,α-1** was obtained as a light viscous oil with 81% yield (6.2 g). ^{1}H NMR (300 MHz, CD_3OD): δ = 3.81-3.74 (m, 2H, $CH_2C\underline{H}CH_2$), 3.61-3.44 (m, 8H, $OC\underline{H}_2$). ^{13}C NMR (75 MHz, CD_3OD): δ = 73.83 (2 $O\underline{C}H_2$), 72.20 (2 $\underline{C}H$), 64.31 (2 $\underline{C}H_2OH$).

2.2 Procedure to prepare **α,β–isomer (α,β-1)**

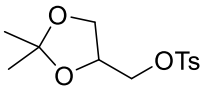


2.2.1 Synthesis of **1,3-Di-*O*-benzylglycerol** (**15**).[2]



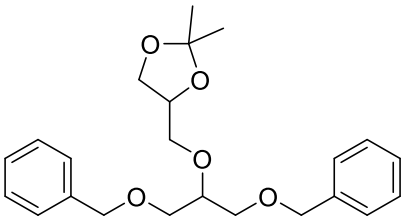
Following a reported procedure,[2] in a 250 mL round bottom flask equipped with a magnetic stirrer and a reflux condenser, epichlorohydrin (23 g, 0.25 mol,) was added dropwise to a mixture of benzyl alcohol (108 g, 1.0 mol, 104 mL, 4 equiv), tetra-n-butylammonium iodide (18.45 g, 0.05 mol, 0.2 equiv), KOH (42 g, 0.75 mol, 3 equiv) and water (3 mL). The mixture was then stirred at 80 °C for 40 h. After cooling, the reaction mixture was partitioned in dichloromethane (150 mL) and water (150 mL). The organic phase was washed with water for three times and then dry with $MgSO_4$. Then, the solvent was removed under reduced pressure, and the residue was purified by column chromatography (cyclohexane/EtOAc, 30 : 1, v/v) to give **15** as a pale yellow oil with 73% yield (68 g). ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.35-7.27 (m, 10 H, H-Ph), 4.49 (s, 4 H, 2 CH_2-Ph), 3.83 (p, J = 5.4 Hz, 1H, CH OH), 3.47 (dd, J = 9.8, 5.0 Hz, 2H, CHCH_2), 3.40 (dd, J = 9.8, 5.8 Hz, 2H, CHCH_2). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 138.54 (2 Cq), 128.18 (4 CH), 127.45 (2 CH), 127.32 (4 CH), 72.27(2 CH_2), 71.86 (2 CH_2-Ph), 68.58 (CHOH).

2.2.2 Synthesis of **toluene-4-sulfonic acid 2,2-(dimethyl-[1,3]dioxolan-4-ylmethyl ester)** (**16**). [3]



Following a reported procedure,[3] a solution of NaOH (5N, 60 mL) was added to a solution of solketal (5 g, 37.6 mmol) in THF (40 mL). The mixture was cooled to 0 °C (ice bath). Then, a solution of tosyl chloride (10.8 g, 56.7 mmol, 1.5 equiv) in THF (33 mL) was added dropwise. The mixture was stirred overnight at room temperature. The solvent was evaporated to dryness. Then, water was added and the mixture was extracted with ether (200 mL). The organic layer was dried over anhydrous sodium sulfate, filtrated and concentrated under reduced pressure to give **16** as a white solid with 92% yield (9.9 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, J = 8.3 Hz, 2H, Ar-H), 7.35 (d, J = 8.0 Hz, 1H, Ar-H), 4.27 (dddd, J = 5.2 Hz, 5.2 Hz, 5.2 Hz, 5.2 Hz, 1H, CH_2-CH- CH_2), 4.04 (dd, J = 5.8, 3.0 Hz, 2H, CH_2), 3.97 (dd, J = 10.1, 6.2 Hz, 1H, CH_2), 4.04 (dd, J = 5.8, 3.0 Hz, 1H, CH_2), 2.45 (s, 3H, Ar-CH_3), 1.34 (s, 3H, CH_3), 1.31 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.16 (C-SO_2), 132.72 (C-CH_3), 130.00 (2 CH), 128.05 (2 CH), 110.10 ((CH_3)$_2$-C), 72.98 (CH), 69.60 (CH_2), 66.22 (CH_2), 26.69 (CH_3), 25.21 (CH_3), 21.71 (CH_3-Ar).

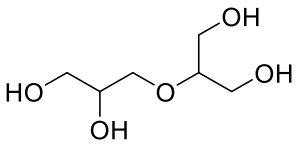
2.2.3 Synthesis of **6-*O*-Benzyl-5-benzyloxymethyl-1,2-*O*-isopropylidene-4-oxahexane- 1,2,6-triol** (**17**).[4]



Following a reported procedure,[4] in a 100 mL round bottom flask equipped with a magnetic stirrer and a reflux condenser, compound **15** (2.923 g, 10.7 mmol) was added dropwise into the solution of NaH (60% in mineral oil, 514 mg, 21.4 mmol, 2 equiv) in DMF (29.3 mL) at room temperature. The

mixture was stirred for 30 min and tetrabutylammonium bromide (691 mg, 2.14 mmol, 0.2 equiv) was added and the mixture was stirred for additional 30 min. Then compound **16** (3.68 mg, 12.9 mmol, 1.2 equiv) was added in one portion. The mixture was heated at 100 °C for 26 h. Then, water (120 mL) was added and extracted with dichloromethane (120 mL). The organic layer was washed with $NaHCO_3$ solution twice (2*80 mL) and dry with $MgSO_4$. Then, the solvent was removed under reduced pressure, and the residue was purified by column chromatography. (cyclohexane/EtOAc, 30 : 1, v/v) to give **17** as a pale yellow oil with 56% yield (2.3 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38-7.23 (m, 10H, Ar-H), 4.55 (s, 4H, 2CH_2-Ar), 4.28 (dddd, *J* = 6.2, 6.0, 5.8, 6.1 Hz, 1H, Cq-OCH), 4.05 (dd, *J* = 8.3, 6.4 Hz, 1H), 3.80-3.72 (m, 3 H, CH_2), 3.68-3.54 (m, 5 H, CH_2), 1.42 (s, 3 H, CH_3), 1.37 (s, 3 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.22 (Cq), 137.77 (Cq), 128.45 (2 CH), 128.36 (2 CH),127.80 (CH), 127.75 (CH), 127.73 (CH), 127.62 (2 CH), 127.61 (CH), 109.27 (Cq), 78.81 (CH), 74.82 (CH), 73.47 (CH_2-Ar), 73.38 (CH_2-Ar), 71.55 (CH_2), 70.23 (CH_2), 70.20 (CH_2), 66.96 (CH_2) 26.81 (CH_3), 25.41 (CH_3).

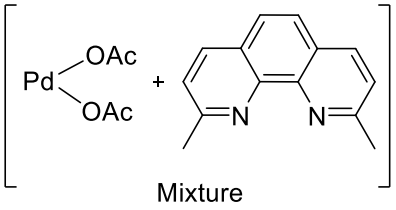
2.2.4 Synthesis of α,β– 1.



Following a reported procedure,[4] in a 30 mL round bottom flask equipped with a magnetic stirrer and a reflux condenser, compound **17** (654 mg, 1.7 mmol), MeOH (10 mL) and [Pd/C (Palladium 10% on activated wood carbon, 65.4 mg, 0.17 mmol, 10 wt %)] was added. In the presence of 1 atm of hydrogen (balloon) the mixture was stirred for 24 h at room temperature. Then, after filtration to remove the catalyst and the solvent was evaporated under reduced pressure (150 mbar) to give **α,β-1** as a pale-yellow oil with 97% yield (272 mg). ^{1}H NMR (300 MHz, CD_3OD): δ = 3.82-3.75 (m, 1H, CHOH), 3.72-3.52 (m, 8H, 4CH_2), 3.46-3.39 (m, 1H, OCH). ^{13}C NMR (75 MHz, CD_3OD): δ = 82.96 (OCH), 72.43 (OCH_2), 72.39 (CHOH), 64.12 ($CHCH_2OH$), 62.38 ($2CH_2OH$).

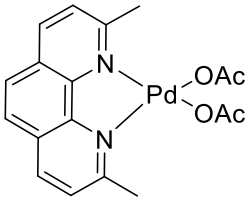
3 Procedure for the preparation of palladium-based catalyst.

3.1 Procedure for the preparation of **Pd-1**



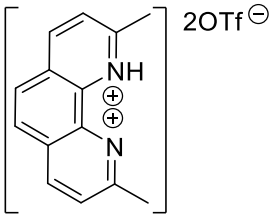
Pd-1 $Pd(OAc)_2$ (10 mg, 0.045 mmol) and neocuproine (9.36 mg, 0.045 mmol) were mixed to give catalyst **Pd-1** .

3.2 Procedure for the preparation of **Pd-2.** [6]

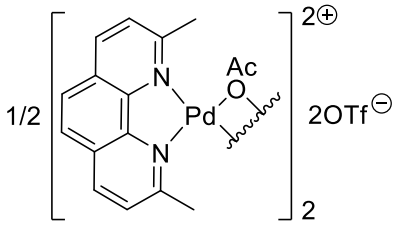


(Neocuproine)Pd(OAc)$_2$ (Pd-2) In a 500 mL round bottom flask equipped with a magnetic stirrer, a solution of neocuproine (2.50 g, 11 mmol) in anhydrous CH_2Cl_2 (40 mL) was added to a solution of $Pd(OAc)_2$ (2.24 g, 11 mmol, 1eq) in anhydrous toluene (200 mL) at room temperature under Argon. The mixture was stirred overnight and petroleum ether (40 – 60 ^oC) was added to precipitate the complex. After filtration, the solid was collected and washed with acetone (45 mL), dried under vacuum to give a yellow solid with 75% yield (3.34 g). Spectroscopic data was identical to previously published data.

3.3 Procedure for the preparation of **Pd-3.** [7]



[NeocuproineH$_2$][OTf]$_2$ (18) In a 25 mL round bottom flask equipped with a magnetic stirrer, triflic acid (2.94 mL, 33.3 mmol) was added dropwise to a solution of neocuproine (1.74 g, 8.4 mmol) in acetone (41 mL) under a nitrogen atmosphere at room temperature for 30 min. Then, the reaction mixture turned to cloudy yellow and diethyl ether (~30 mL) was added to precipitate a white solid, which was collected by filtration and washed with diethyl ether (100 mL). The white solid was dried under vacuum to get [NeocuproineH$_2$][OTf]$_2$ **17** as a white power (3.3 g, 78%). Other spectroscopic data were identical to previously published data.



Pd-3 (19) In a 25 mL round bottom flask equipped with a magnetic stirrer, $Pd(OAc)_2$ (785 mg, 3.5 mmol) was added to the solution of neocuproine (730 mg, 3.5 mmol) and [NeocuproineH$_2$][OTf]$_2$ **18** (1.78 mg, 3.5 mmol) in acetone (70 mL), the reaction mixture was stirred at room temperature for 48 h. The solution turned to dark brown with an orange precipitate. Then, the precipitate was collected by filtration, washed with diethyl ether, and dried in vacuum to give the product **19** as an orange powder (1.13 g, 62%). ^{1}H NMR (300 MHz, CD_3CN, saturated solution to favor dimer; dimer peaks), δ = 8.26 (d, J = 8.4 Hz, 4H), 7.70 (s, 4H), 7.37 (d, J = 8.4 Hz, 4H), 2.63 (s, 12H), 2.24 (s, 6H). monomer peaks: δ = 8.60 (d, J = 8.5 Hz, 2H, 2CH), 8.01 (s, 2H, 2CH), 7.73 (s, 2H, 2CH), 2.80 (s, 6H, $2CH_3$), 1.99 (s, 3H, CH_3). Other spectroscopic data was identical to previously published data.

4 Procedure for the oxidation of diglycerol.

In a 30-mL-stainless steel reactor equipped with a magnetic stirrer, diglycerol **α, α-1** or **α, β-1** (75 mg, 0.45 mmol) dissolved in HFIP (5.5 mL), **Pd-3** (6 mg, 2.5 mol%) and styrene (236 mg, 5 equiv) were added. The reactor was purged twice with O_2 and was charged with 3 bar of oxygen. The reactor was heated at 50 °C for 18 h. After cooling to room temperature, the O_2 pressure was released, the solvent was removed under reduced pressure, and the residue was purified by column chromatography (CH_2Cl_2/MeOH, 10: 1, v/v) to give α,α-diglycerose **3** or α,β-diglycerose **7**.

Study of the influence of the temperature:

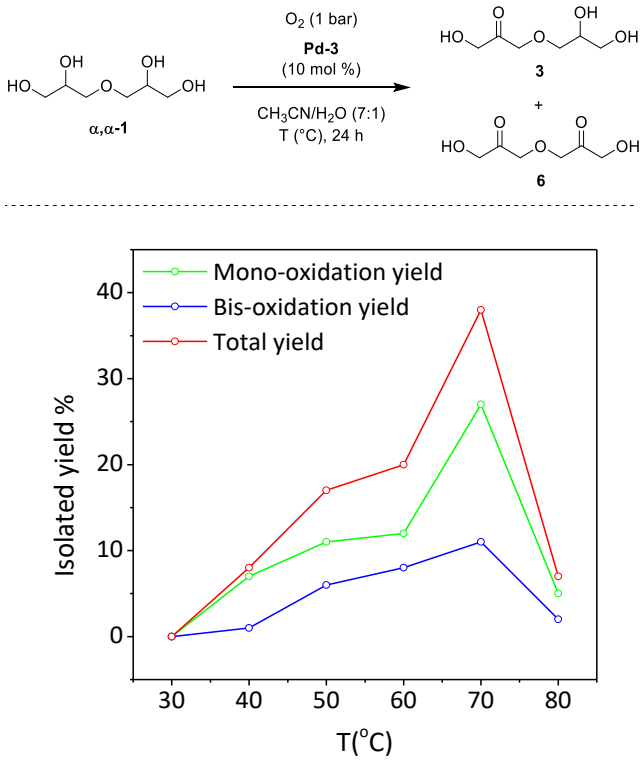
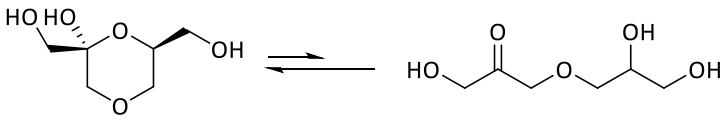


Figure S2. Effect of the temperature for the oxidation of diglycerol. Reaction conditions: diglycerol (0.45 mmol), Palladium-based catalyst **Pd-3** (10 mol%), O_2 (1 bar), CH_3CN/H_2O (v/v 7:1, 5.5 mL), 24 h. Yields are isolated yields.

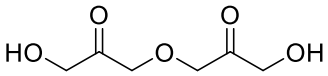
5 Derivatization procedure for kinetics studies.

The sample was silylated before analysis: the crude mixture (0.13 mmol) was diluted in THF (0.7 mL), then 1 mL of the silylating reagent (pyridine:hexamethyldisilazane (HMDS):chlorotrimethylsilane (TMSCl) = 1 mL :0.2 mL:0.1 mL) was added into the solution. Then the mixture was stirred vigorously at 70°C for 10 min. Next, the sample was diluted in 6 mL of THF solution, and add methyl oleate (0.13 mmol, internal standard) . Finally, the sample was filtrated by a syringe filter (PTFE; 0.2 μm) before injection in GC.

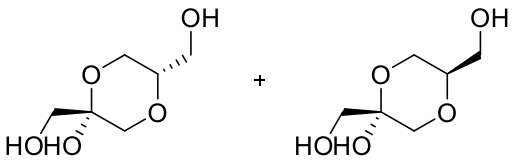
6 Characterization of oxidation and dehydration products



α,α-diglycerose (3). In a 30 mL reactor equipped with a magnetic stirrer, α,α-diglycerol (750 mg 4.5 mmol) was dissolved in HFIP (55 mL), **Pd-3** (60 mg, 2.5 mol%) and styrene (2.36 g, 5 equiv) were added. The reactor was purged twice with O_2 and was charged with 3 bar of oxygen. The reactor was heated at 50 °C for 18 h. After cooling to room temperature, the O_2 pressure was released, the solvent was removed under reduced pressure, and the residue was purified by column chromatography (CH_2Cl_2/MeOH, 10: 1, v/v) to give α,α-diglycerose **3** with 76% yield (562 mg). ^{1}H NMR (300 MHz, CD_3OD): *δ (cyclic form)* = 4.16 (dtd, *J* = 10.9, 4.5, 2.9 Hz, 1H, CH), 3.80 (dd, *J* = 11.4, 2.8 Hz, 1H, CHC<u>H</u>$_2$O), 3.66 (d, *J* = 11.5 Hz, 1H, Cq-C<u>H</u>$_2$O), 3.55 (d, *J* = 11.6 Hz, 1H, Cq-C<u>H</u>$_2$O), 3.55 (d, *J* = 4.6 Hz, 2H, CHC<u>H</u>$_2$OH), 3.46 (d, *J* = 11.6 Hz, 2H, CqC<u>H</u>$_2$OH), 3.38 (d, *J* = 11.2 Hz, 1H, CHC<u>H</u>$_2$O). *δ (open form, visible peaks)* = 4.35 (s, 2H, Cq-C<u>H</u>$_2$OH), 4.30 (s, 2H, Cq-C<u>H</u>$_2$O). ^{13}C NMR (75 MHz, CD_3OD): *δ (cyclic form)* = 94.61 (Cq), 70.2 (OCH_2), 69.94 (CH), 68.58 (OCH_2), 67.04 (CH_2OH), 62.89 (CH_2OH). *δ (open form)* = 210.45 (Cq), 75.34 (Cq-<u>C</u>H$_2$O), 74.01 (<u>C</u>HOH), 73.74 (CH<u>C</u>H$_2$O), 71.98 (Cq-<u>C</u>H$_2$OH), 68.07 (CH<u>C</u>H$_2$OH). HRMS (ESI$^+$): calcd. for $C_6H_{12}NaO_5$ [M + Na]$^+$, 187.0577, found 187.0576.



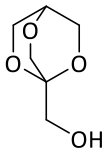
3,3'-oxybis(1-hydroxypropan-2-one) (6) In a 30 mL reactor equipped with a magnetic stirrer, **α,α-1** (750 mg 4.5 mmol) dissolved in acetonitrile/water (7:1, v/v, 5.5 mL) and **Pd-3** (24 mg, 10 mol%) was added. The reactor was heated at 70 °C for 24 h. After cooling to room temperature, the solvent was removed under reduced pressure, and the residue was purified by column chromatography (CH_2Cl_2/MeOH, 10: 1, v/v) to give α,α-diglycerose **3** with 27% yield (199 mg) and **6** with 11% yield (80 mg). ^{1}H NMR (300 MHz, CD_3OD): *δ*= 4.86 (s, 4 H, 2 CH_2), 4.31 (s, 4H, 2 CH_2). ^{13}C NMR (75 MHz, CD_3OD): *δ*= 212.09 (2 Cq), 66.81 (2 CH_2), 83.13 (2 CH_2OH). HRMS (ESI$^+$): calcd for $C_6H_{10}NaO_5$ [M + Na]$^+$, 185.0420, found 185.0412; calcd for $C_7H_{14}NaO_6$ [M + MeOH + Na]$^+$, 217.0683, found 217.0672.



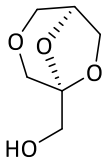
88% 12%

α,β-diglycerose (7). In a 100 mL flask equipped with a magnetic stirrer, **α,β-1** (750 mg 4.5 mmol) was dissolved in HFIP (55 mL) and **Pd-3** (60 mg, 2.5 mol%) and styrene (2.36 g, 5 equiv) were added. The

flask was equipped with 1 balloon (1 atm) of oxygen. The flask was heated at 50 °C for 18 h. After cooling to room temperature, the solvent was removed under reduced pressure, and the residue was purified by column chromatography (CH_2Cl_2/MeOH, 10: 1, v/v) to give **7** with 51% yield (377 mg) and **8** with 10% yield (66 mg). **(7)** ^{1}H NMR (500 MHz, CD_3OD): *δ (major isomer)* = 3.91 (t, *J* = 10.9 Hz, 1H, CH_2), 3.76 (d, *J* = 11.6 Hz, 1H, CH_2), 3.68 (d, *J* = 11.6 Hz, 1H, CH_2), 3.64-3.61 (m, 1 H, CH), 3.59 (d, *J* = 10.6 Hz, 1H, CH_2), 3.55 (dd, *J* = 13.2, 6.9 Hz, 2H, C$\underline{H_2}$OH), 3.43 (d, *J* = 11.7 Hz, 1H, CqC$\underline{H_2}$OH), 3.38 (d, *J* = 11.6 Hz, 1H, CqC$\underline{H_2}$OH). ^{13}C NMR (125 MHz, CD_3OD): *δ (major isomer)* = 93.72 (Cq), 76.72 (CH), 71.03 (CH_2), 66.96 (CH_2OH), 62.83 (CH_2OH), 62.37 (CH_2). *δ (minor isomer)* = 94.42 (Cq), 75.23 (CH), 68.09 (Cq$\underline{CH_2}$O), 63.86 (Cq$\underline{CH_2}$OH), 63.51 (CH$\underline{CH_2}$O), 61.55 (CH$\underline{CH_2}$OH). HRMS (ESI$^+$): calcd. for $C_6H_{12}NaO_5$ $[M + Na]^+$, 187.0577, found 187.0581.

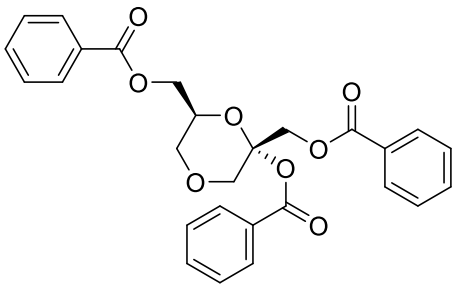


(8) ^{1}H NMR (300 MHz, CD_3OD): *δ* = 4.31 (dd, *J* = 2.2, 1.0 Hz, 1H, CHC$\underline{H_2}$), 4.28 (dd, *J* = 2.2, 1.1 Hz, 1H, CHC$\underline{H_2}$), 4.19 (s, 2H, $\underline{CH_2}$OH), 4.14 (dd, *J* = 2.9, 1.7 Hz, 1H, CH_2), 4.11 (dd, *J* = 2.9, 1.7 Hz, 1H, CH_2), 3.89 (ddd, *J* = 3.5, 2.2, 1.3 Hz, 1H, CH), 3.41 (s, 2H, Cq$\underline{CH_2}$O). ^{13}C NMR (75 MHz, CD_3OD): *δ* = 94.75 (Cq), 72.71 (CH), 70.16 (2 CH$\underline{CH_2}$), 66.20 (CH_2), 64.80 (CH_2OH). HRMS (ESI$^+$): calcd. for $C_6H_{10}NaO_4$ $[M + Na]^+$, 169.0471, found 169.0471.

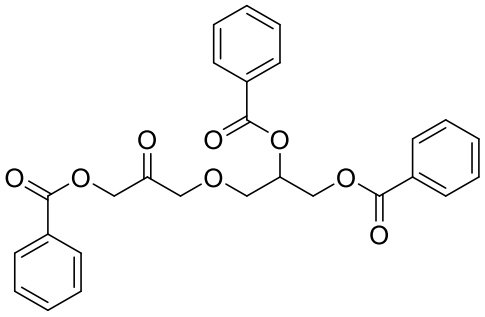


((1S,5R)-3,6,8-trioxabicyclo[3.2.1]octan-5-yl)methanol (9). In a 50 mL round bottom flask equipped with a magnetic stirrer, α,α-diglycerose **3** (200 mg, 5.5 mmol) was dissolved in dichloromethane (10 mL) and the reaction mixture was stirred at room temperature for 3 h. Then the catalyst was removed by filtration and the filtrate was collected. The filtrate was dried with Na_2SO_4. Then, the solvent was removed under reduced pressure, and the residue was purified by column chromatography (cyclohexane/EtOAc, 1: 3, v/v) to give compound **9** as a colorless oil with 48% yield (84 mg). ^{1}H NMR (300 MHz, CD_3OD): *δ* = 4.50 (dd, *J* = 4.2, 1.0 Hz, 1H, CH), 4.22 (d, *J* = 7.1 Hz, 1H, OC$\underline{H_2}$-CH), 3.85 (dd, *J* = 12.0, 1.0 Hz, 1H, OC$\underline{H_2}$-CH), 3.83 (dt, *J* = 12.1, 1.2 Hz, 1H, OC$\underline{H_2}$-CH), 3.65 (d, *J* = 11.0 Hz, 1H, C-C$\underline{H_2}$-O), 3.63 (dd, *J* = 11.6, 1.2 Hz, 1H, OC$\underline{H_2}$-CH), 3.59 (s, 2H, C$\underline{H_2}$-OH), 3.59 (d, *J* = 11.6 Hz, 1H, C-C$\underline{H_2}$-O). ^{1}H NMR (300 MHz, CD_3OD): *δ* = 106.64 (Cq), 76.19 (CH), 70.90 (CH_2), 69.93 (CH_2), 69.04 (CH_2), 63.53 (CH_2OH).

7 Characterization of other products

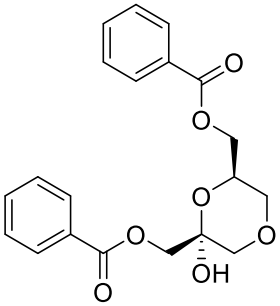


(2-(benzoyloxy)-1,4-dioxane-2,6-diyl)bis(methylene) dibenzoate (10) In a 50 mL round bottom flask equipped with a magnetic stirrer, α,α-diglycerose **3** (900 mg, 5.5 mmol) in pyridine (5 mL) was added dropwise into a cooled (-10°C) mixture of pyridine (5 mL), chloroform (10 mL) and benzoyl chloride (3.08 g, 22 mmol, 4 equiv) followed by warming to room temperature for 3 h. Then, water (30 mL) was added and the mixture was extracted with dichloromethane (30 mL). The organic layer was washed with $NaHCO_3$ solution twice (80 mL*2) and dried with $MgSO_4$. Then, the solvent was removed under reduced pressure, and the residue was purified by column chromatography (cyclohexane/EtOAc, 3: 1, v/v) to give compound **10** as a colorless oil with 65% yield (1.7 g), compound **11** as a colorless oil with 9% yield (235 mg) and compound **12** as a colorless oil with 3% yield (61 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.14-8.11 (m, 2H, H-Ar), 8.04-7.97 (m, 4H, H-Ar), 7.61-7.33 (m, 9H, H-Ar), 5.05 (d, J = 11.9 Hz, 1H, COOC$\underline{H}_2$Cq), 4.81 (d, J = 11.9 Hz, 1H, COOC$\underline{H}_2$Cq), 4.58 (d, J = 12.3 Hz, 2H, CH, CH_2), 4.43 (t, J = 4.9 Hz, 2H, COOC$\underline{H}_2$CH), 4.03 (dd, J = 11.6, 2.8 Hz, 1H, CHC$\underline{H}_2$O), 3.75 (d, J = 12.3 Hz, 1H, CqC$\underline{H}_2$), 3.67 (t, J = 11.3 Hz, 1H, CqC$\underline{H}_2$O). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.13 (C=O), 165.66 (C=O), 164.53 (C=O), 133.42 (Cq), 133.26 (2 Cq), 130.25 (CH), 129.91 (2 CH), 129.74 (2 CH), 129.73 (2 CH), 129.65 (CH), 129.51 (CH), 128.54 (2 CH), 128.49 (2 CH), 128.47 (2 CH), 100.25 (Cq), 68.46 (CH_2), 68.06 (CH), 67.52 (CH_2), 64.07 (CH_2), 63.46 (CH_2). HRMS (ESI$^+$): calcd. for $C_{27}H_{24}NaO_8$ $[M + Na]^+$, 499.1363, found 499.1349.

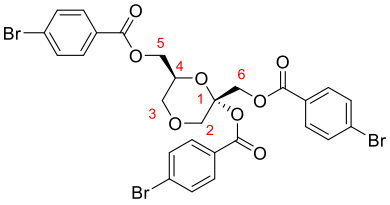


3-(3-(benzoyloxy)-2-oxopropoxy)propane-1,2-diyl dibenzoate (11). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.09-8.01 (m, 6H, H-Ar), 7.54-7.51 (m, 3H, H-Ar), 7.44-7.38 (m, 6H, H-Ar), 5.67 (dddd, J = 4.9, 5.7, 4.4, 5.1 Hz, 1H), 5.09 (s, 2H, COOC$\underline{H}_2$O), 4.74 (dd, J = 12.0, 4.1 Hz, 1H, CHC$\underline{H}_2$O), 4.65 (dd, J = 11.9, 6.1 Hz, 1H, CHC$\underline{H}_2$O), 4.36 (d, J = 16.9 Hz, 1H, OC$\underline{H}_2$CO), 4.29 (d, J = 16.9 Hz, 1H, OC$\underline{H}_2$CO), 3.97 (dd, J = 10.3, 5.1 Hz, 1H, OC$\underline{H}_2$CH), 3.92 (dd, J = 10.0, 4.1 Hz, 1H, OC$\underline{H}_2$CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 201.40 (C=O), 166.05 (C=O), 165.75 (C=O), 165.71 (C=O), 133.38 (CH), 133.30 (CH), 133.18 (CH), 129.81 (2 CH), 129.73 (2 CH), 129.63 (2 CH), 129.58 (2 Cq), 129.09 (Cq) 128.45 (2 CH), 128.43 (2 CH), 128.42 (2 CH),

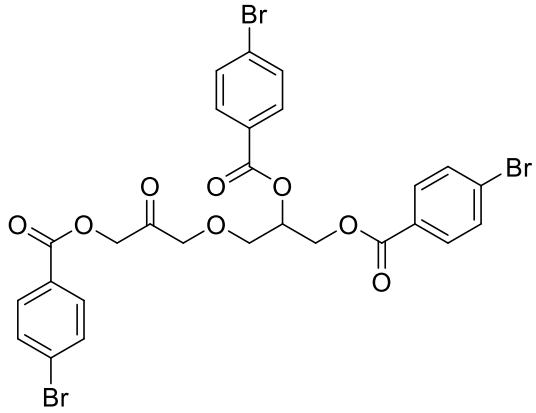
75.12 (CH_2), 70.64 (CH), 70.31 (CH_2), 67.06 (CH_2), 63.04 (CH_2). HRMS (ESI^+): calcd. for $C_{27}H_{24}NaO_8$ [M + Na]$^+$, 499.1363, found 499.1347.



(2-hydroxy-1,4-dioxane-2,6-diyl)bis(methylene) dibenzoate (12) ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.06-7.94 (m, 4H, H-Ar), 7.59-7.53 (m, 2H, H-Ar), 7.45-7.35 (m, 4H, H-Ar), 4.57 (dtd, *J* = 10.9, 4.8, 3.0 Hz, 1H, CH), 4.41 (d, *J* = 11.7 Hz, 1H, C*H*$_2$), 4.37-4.31 (m, 2H, CH_2), 4.28 (d, *J* = 11.7Hz, 1H, C*H*$_2$), 3.98 (dd, *J* = 11.5, 2.9 Hz, 1H, CH_2), 3.90 (d, *J* = 11.6 Hz, 1H, CH_2), 3.62 (d, *J* = 11.6 Hz, 1H, C$\underline{H}_2$), 3.53 (t, *J* = 11.2 Hz, 1H, C$\underline{H}_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.33 (2 C=O), 133.45 (2 CH), 133.32 (2 Cq), 129.85 (2 CH), 129.77 (2 CH), 128.58 (2 CH), 128.55 (2 CH), 93.14 (Cq), 70.14 (CH_2), 68.20 (CH), 67.08 (CH_2), 66.91 (CH_2), 63.95 (C$\underline{H}$C$\underline{H}_2$). HRMS (ESI^+): calcd. for $C_{20}H_{20}NaO_7$ [M + Na]$^+$, 395.1101, found 395.1107.



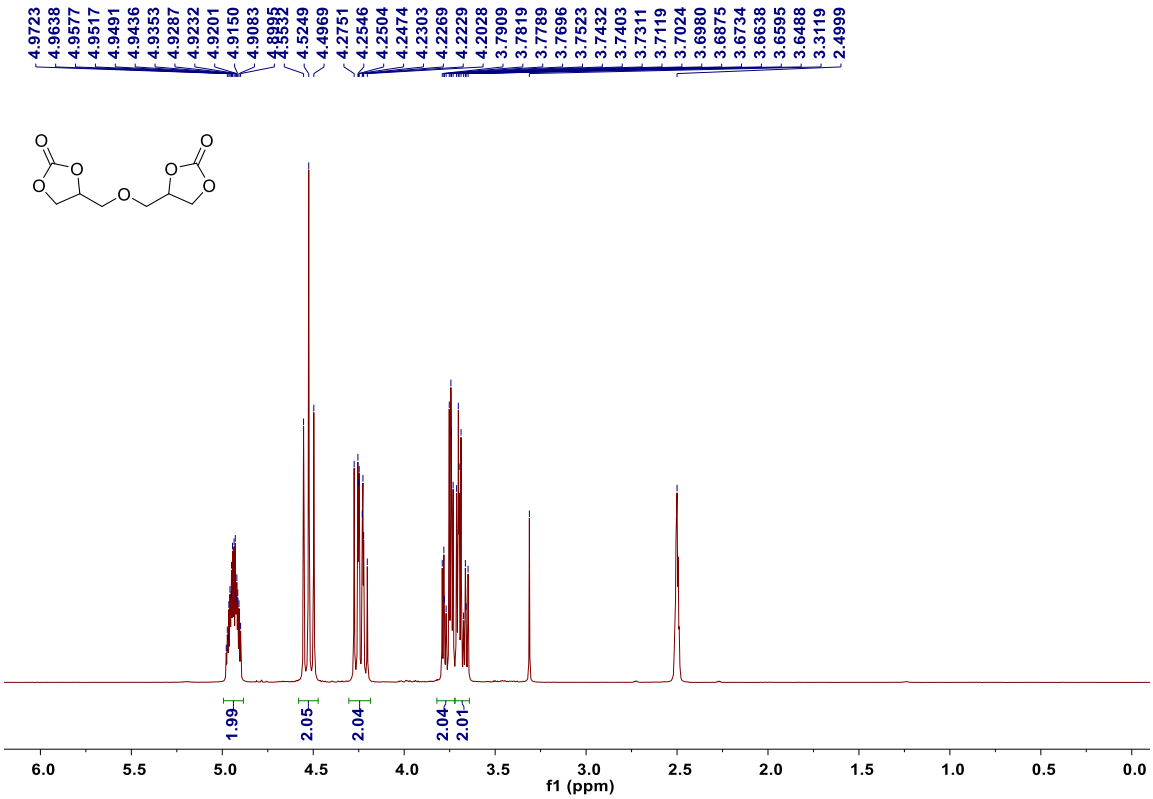
(2-((3-bromobenzoyl)oxy)-1,4-dioxane-2,6-diyl)bis(methylene) bis(4-bromobenzoate) (13) In a 50 mL round bottom flask equipped with a magnetic stirrer, α,α-diglycerose **3** (300 mg, 5.5 mmol) in pyridine (5 mL) was added dropwise into a cooled (-10°C) mixture of pyridine (5 mL), chloroform (10 mL) and benzoyl chloride (4.80 g, 22 mmol, 4 equiv) followed by warming to room temperature for 3 h. Then water (60 mL) was added and extracted with dichloromethane (60 mL). The organic layer was washed with $NaHCO_3$ solution twice (60 mL*2) and dried with $MgSO_4$. Then, the solvent was removed under reduced pressure, and the residue was purified by column chromatography. (cyclohexane/EtOAc, 3: 1, v/v) to give compound **13** as a white solid with 45% yield (583 mg), and compound **14** as a white solid with 6% yield (78 mg). **(13)** ^{1}H NMR (500 MHz, $CDCl_3$): 7.93 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.83 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.78 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.60 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.55 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.50 (d, *J* = 8.6 Hz, 2H, Ar-H), 4.96 (d, *J* = 11.9 Hz, 1H, H_6), 4.76 (d, *J* = 11.9 Hz, 1H, H_6), 4.51 (d, *J* = 12.2 Hz, 2H, H_4, H_2), 4.39 (d, *J* = 4.7 Hz, 2H, H_5), 3.99 (dd, *J* = 11.7, 2.9 Hz, 1H, H_3), 3.69 (d, *J* = 12.4 Hz, 1H, H_2), 3.62 (t, *J* = 11.3 Hz, 1H, H_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.48 (CO), 164.98 (CO), 163.87 (CO), 132.05 (2 CH), 131.98 (4 CH), 131.44 (2 CH), 131.27 (4 CH), 129.07 (Cq), 128.87 (Cq),128.72 (Cq), 128.67 (Cq), 128.51 (Cq), 128.34 (Cq), 100.45 (C_1), 68.54 (C_4), 68.07 (C_2), 67.46 (C_3), 64.10 (C_6), 63.57 (C_5). HRMS (ESI^+): calcd. for $C_{27}H_{21}Br_3NaO_8$ [M + Na]$^+$, 732.8679, found 732.8695.



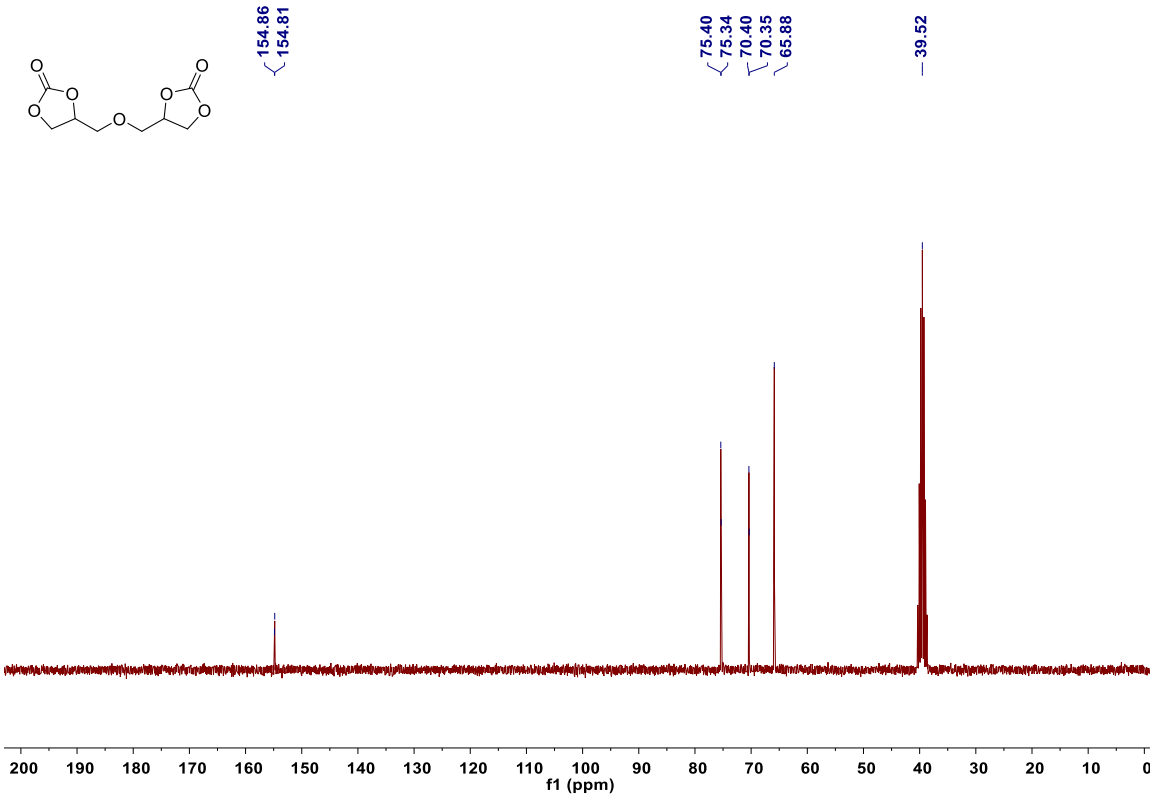
3-(3-((4-bromobenzoyl)oxy)-2-oxopropoxy)propane-1,2-diyl bis(4-bromobenzoate) (14) ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.97-7.84 (m, 6H, Ar-H), 7.63-7.54 (m, 6H, Ar-H), 5.63 (td, *J* = 9.2, 5.0 Hz, 1H, $CH_2\underline{C}HCH_2$), 5.06 (s, 2H, Ar-COO-C$\underline{H}_2$), 4.71 (dd, *J* = 12.0, 4.0 Hz, 1H, CHC$\underline{H}_2$COO), 4.62 (dd, *J* = 12.0, 6.3 Hz, 1H, CHC$\underline{H}_2$COO), 4.34 (d, *J* = 16.8 Hz, 1H, $COCH_2$), 4.27 (d, *J* = 16.8 Hz, 1H, $COCH_2$), 3.95 (dd, *J* = 9.2, 3.9 Hz, 1H, CHC$\underline{H}_2$), 3.90 (dd, *J* = 9.2, 3.5 Hz, 1H, CHC$\underline{H}_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 201.08 (CH_2-$\underline{C}$O-CH_2), 165.57 (Ar-$\underline{C}$O), 165.29 (Ar-$\underline{C}$O), 165.26 (Ar-$\underline{C}$O), 132.06 (2 CH), 132.04 (2 CH), 132.03 (2 CH), 131.53 (2 CH), 131.41 (2 CH), 131.33 (2 CH), 128.91 (Cq), 128.84 (Cq), 128.69 (Cq), 128.51 (Cq), 128.49(Cq), 128.06 (Cq), 75.27 (CO-$\underline{C}H_2$-O), 70.94 (CH), 70.39 (O-$\underline{C}H_2$-CH), 67.28 (O-$\underline{C}H_2$-CO), 63.32(CH$\underline{C}H_2$O). HRMS (ESI$^+$): calcd. for $C_{27}H_{21}Br_3NaO_8$ $[M + Na]^+$, 732.8679, found 732.8669.

8 ^{1}H and ^{13}C NMR spectra:

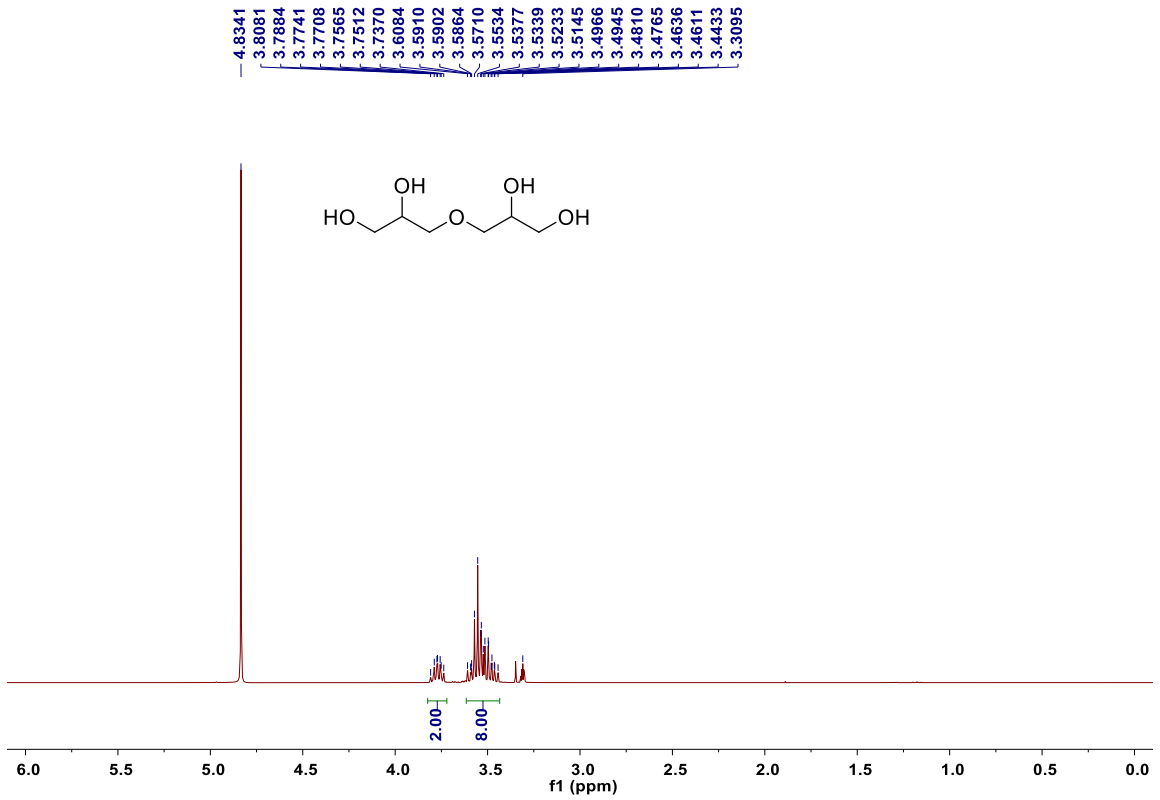
^{1}H NMR (300 MHz, DMSO-$_{d6}$) of α,α-diglycerol dicarbonate (**2**)



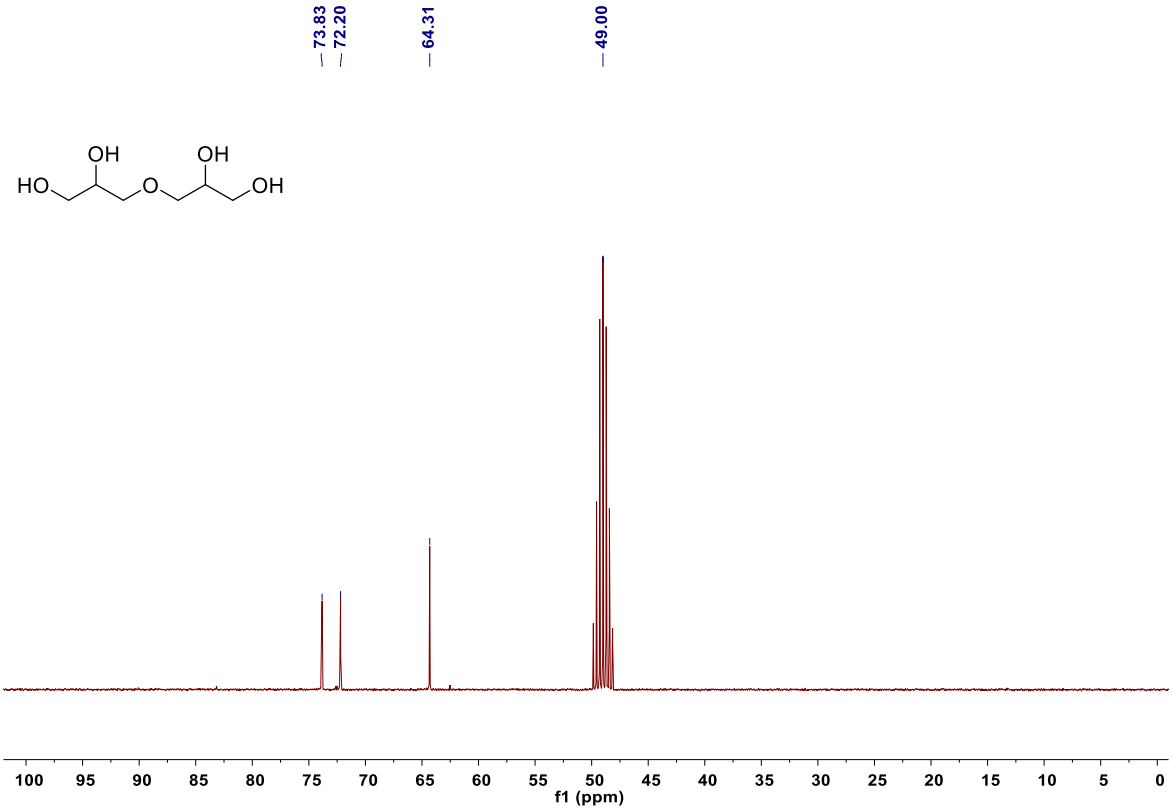
^{13}C N MR (75 MHz, DMSO-$_{d6}$) of α,α-diglycerol dicarbonate (**2**)



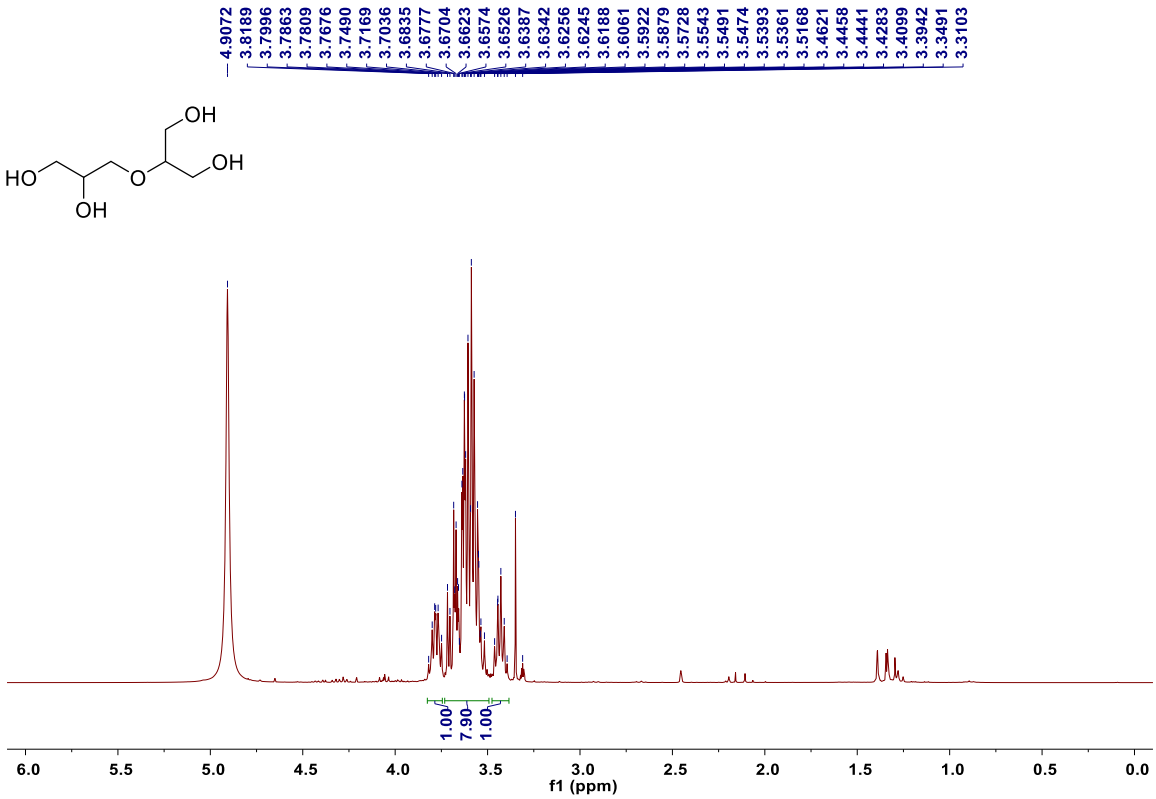
^{1}H NMR (300 MHz, CD_3OD) of α,α-diglycerol (**α,α-1**)



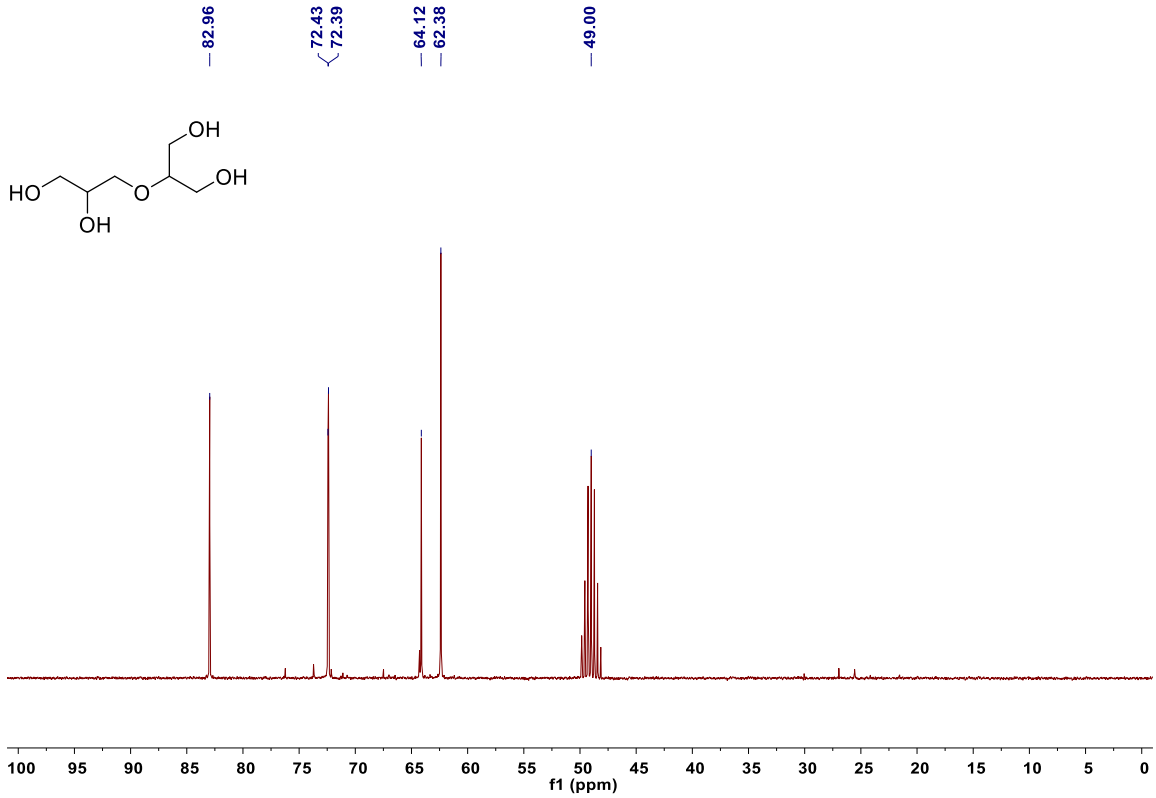
^{13}C NMR (75 MHz, CD_3OD) of α,α-diglycerol (**α,α–1**)



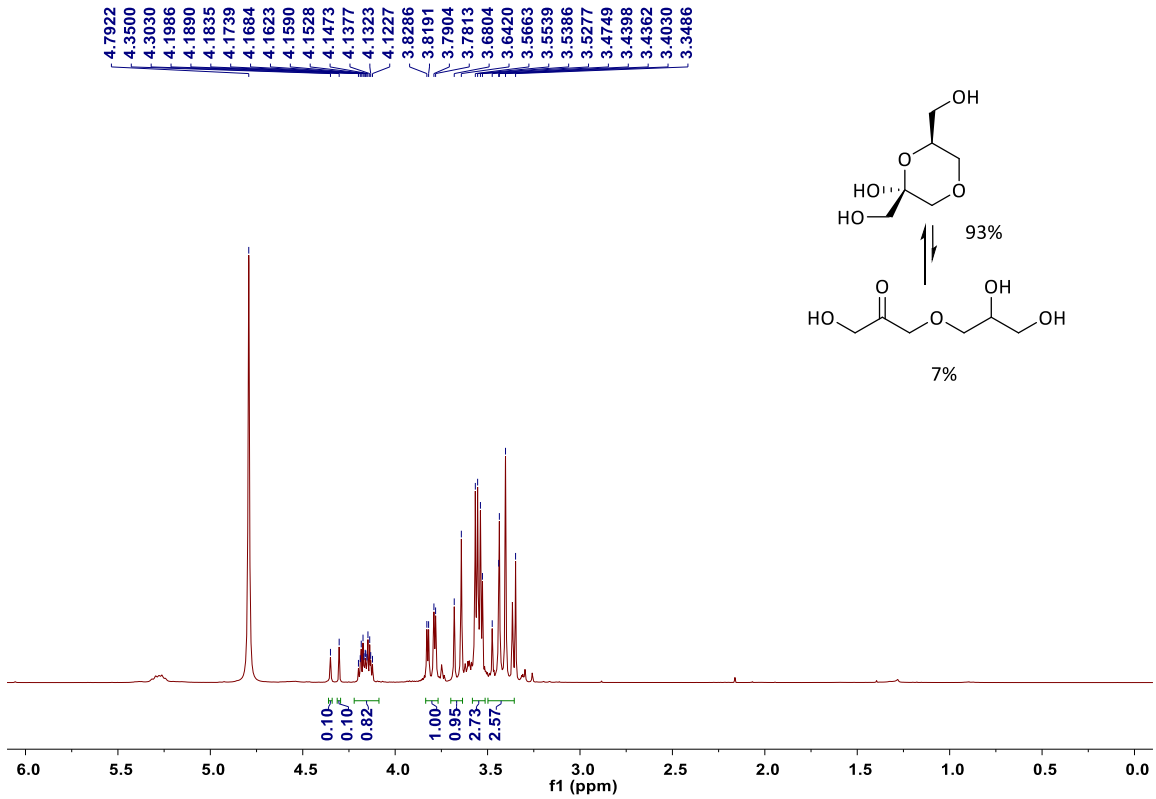
^{1}H NMR (300 MHz, CD_3OD) of α,β-diglycerol (**α,β–1**)



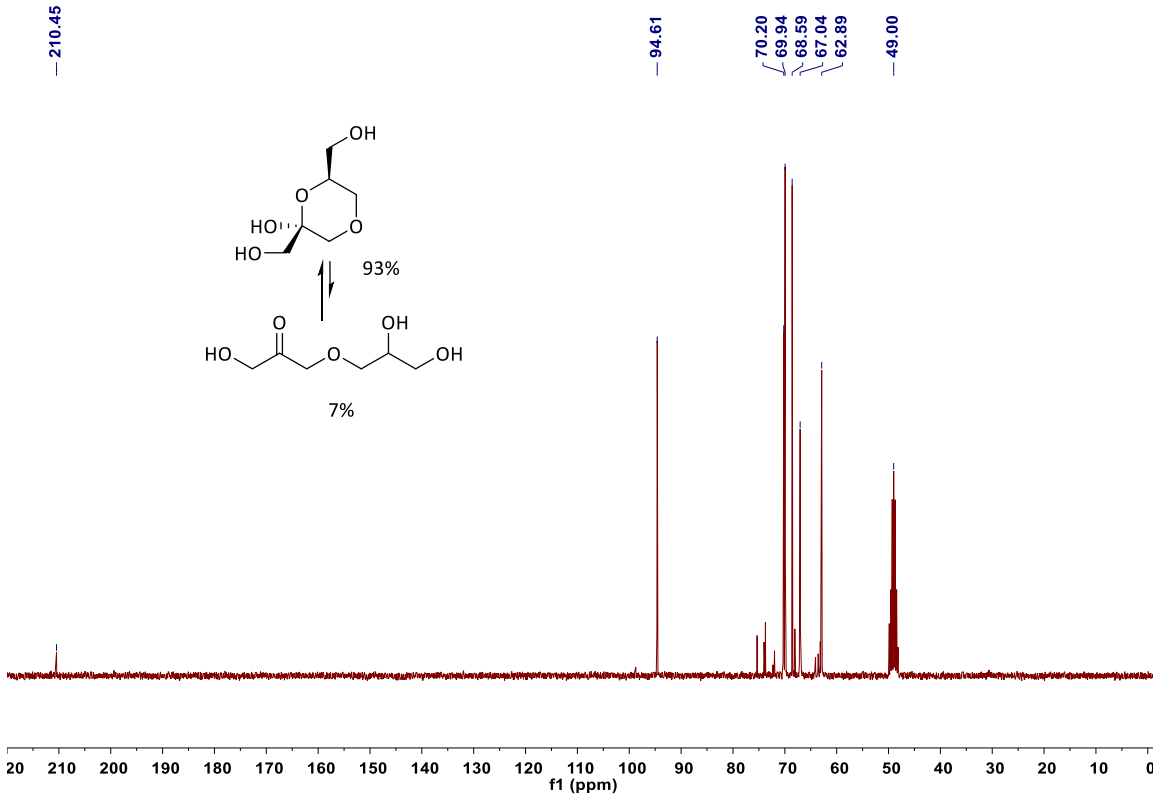
^{13}C NMR (75 MHz, CD_3OD) of α,β-diglycerol (**α,β–1**)



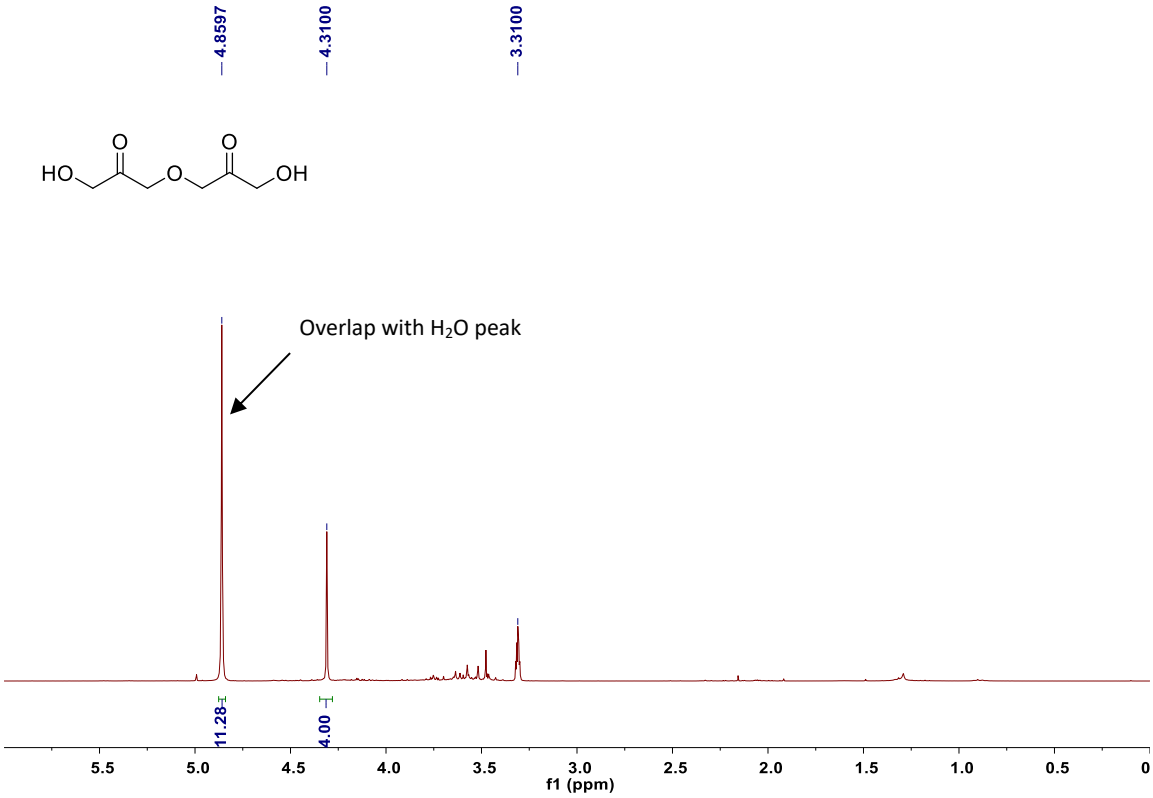
^{1}H NMR (300 MHz, CD_3OD) of α,α- diglycerose (**3**)



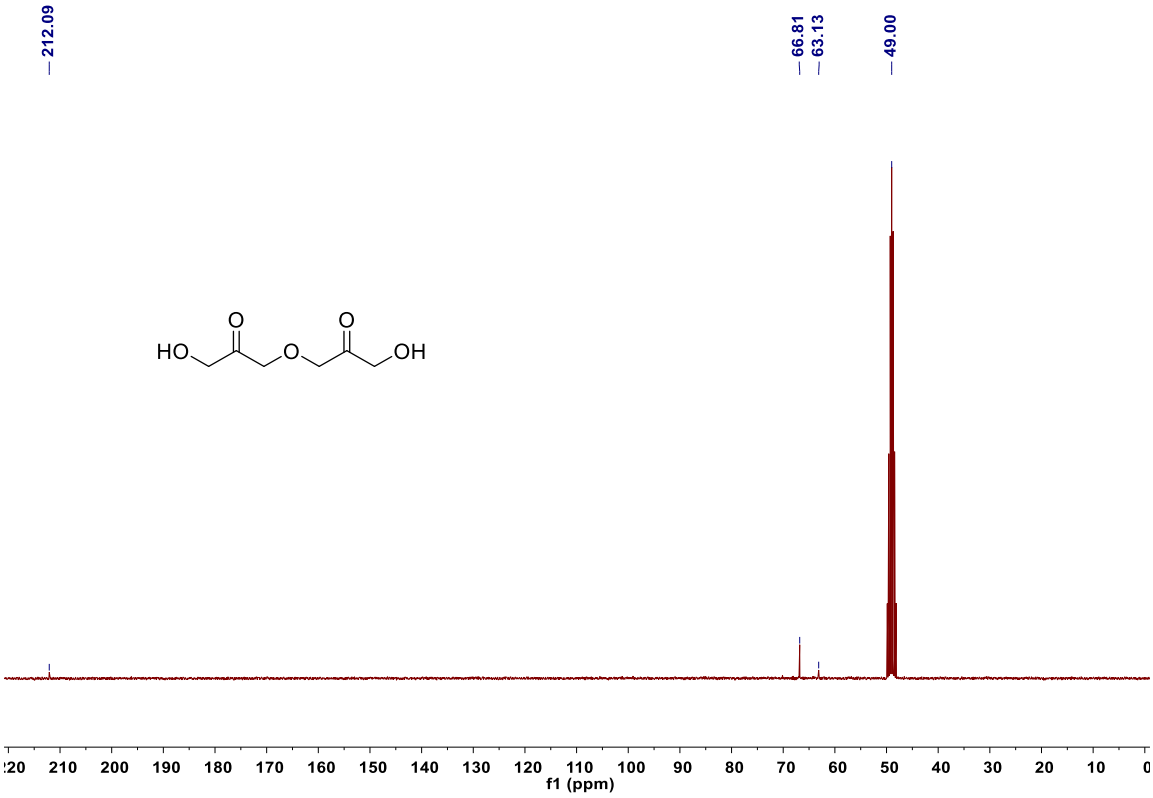
^{13}C NMR (75 MHz, CD_3OD) of α,α-diglycerose (**3**)



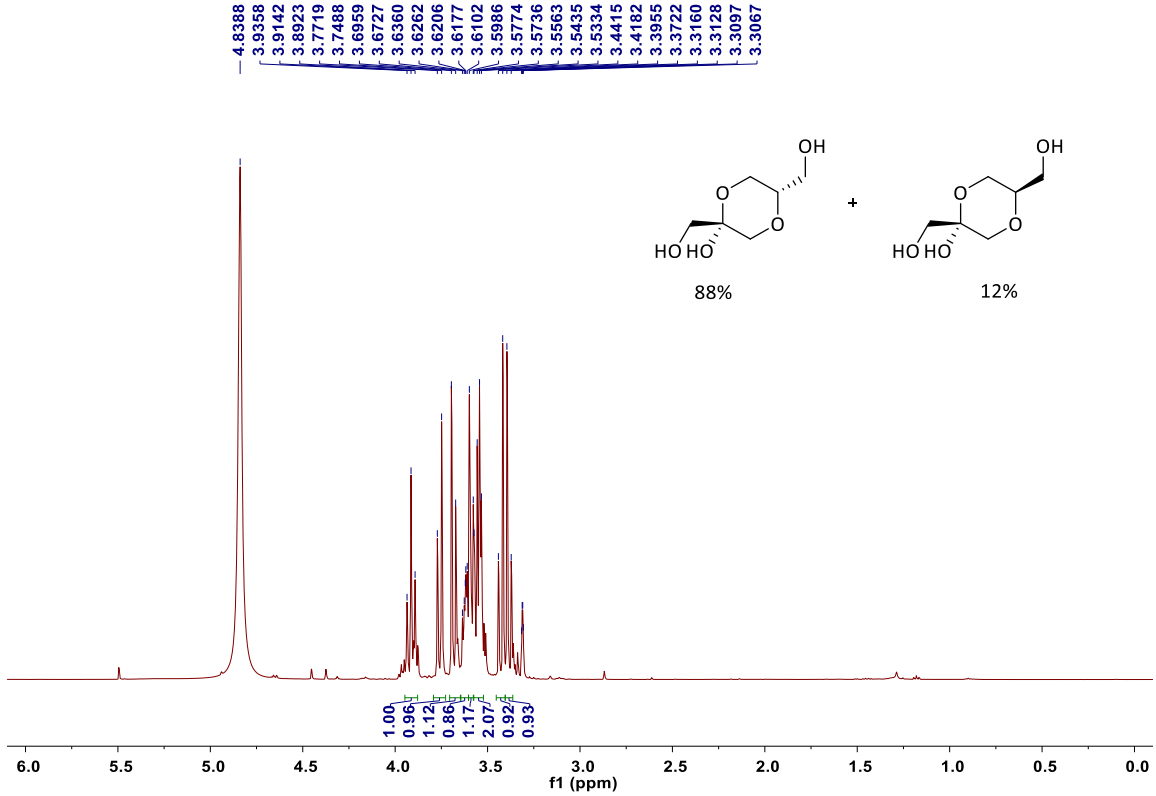
^{1}H NMR (300 MHz, CD_3OD) of 3,3'-oxybis(1-hydroxypropan-2-one) **(6)**



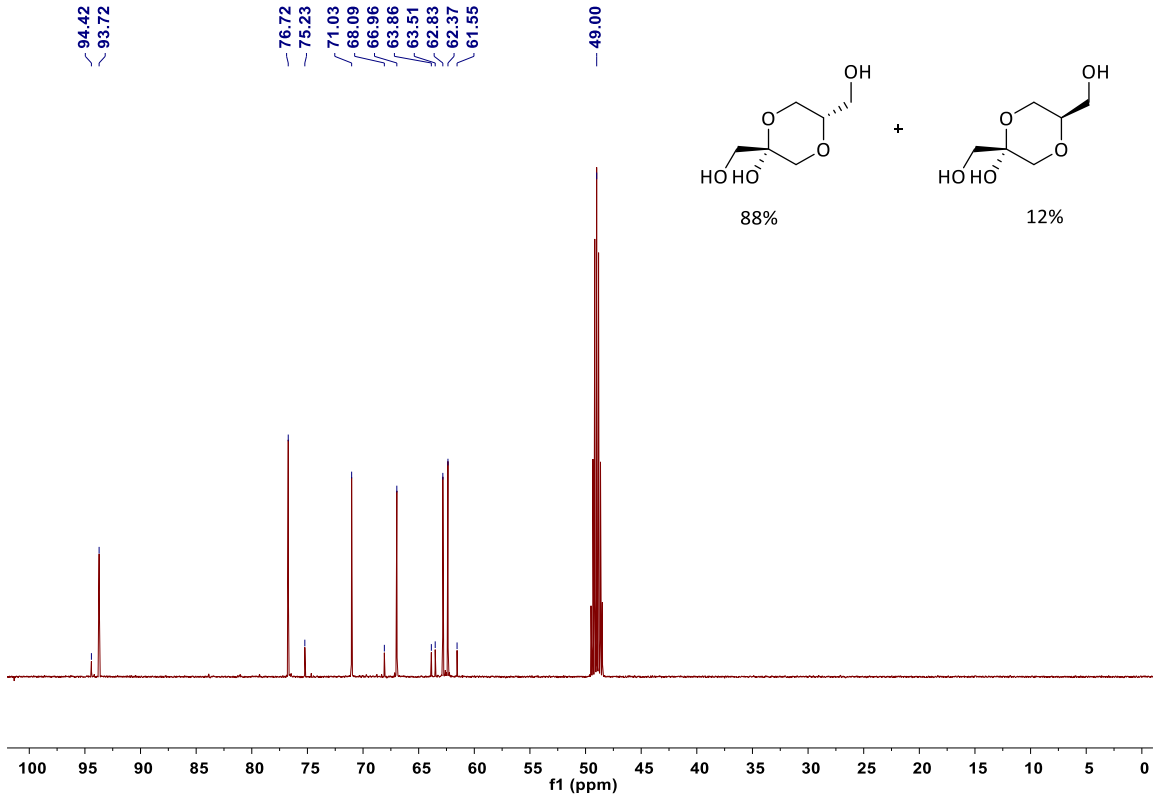
^{13}C NMR (75 MHz, CD_3OD) of 3,3'-oxybis(1-hydroxypropan-2-one) **(6)**



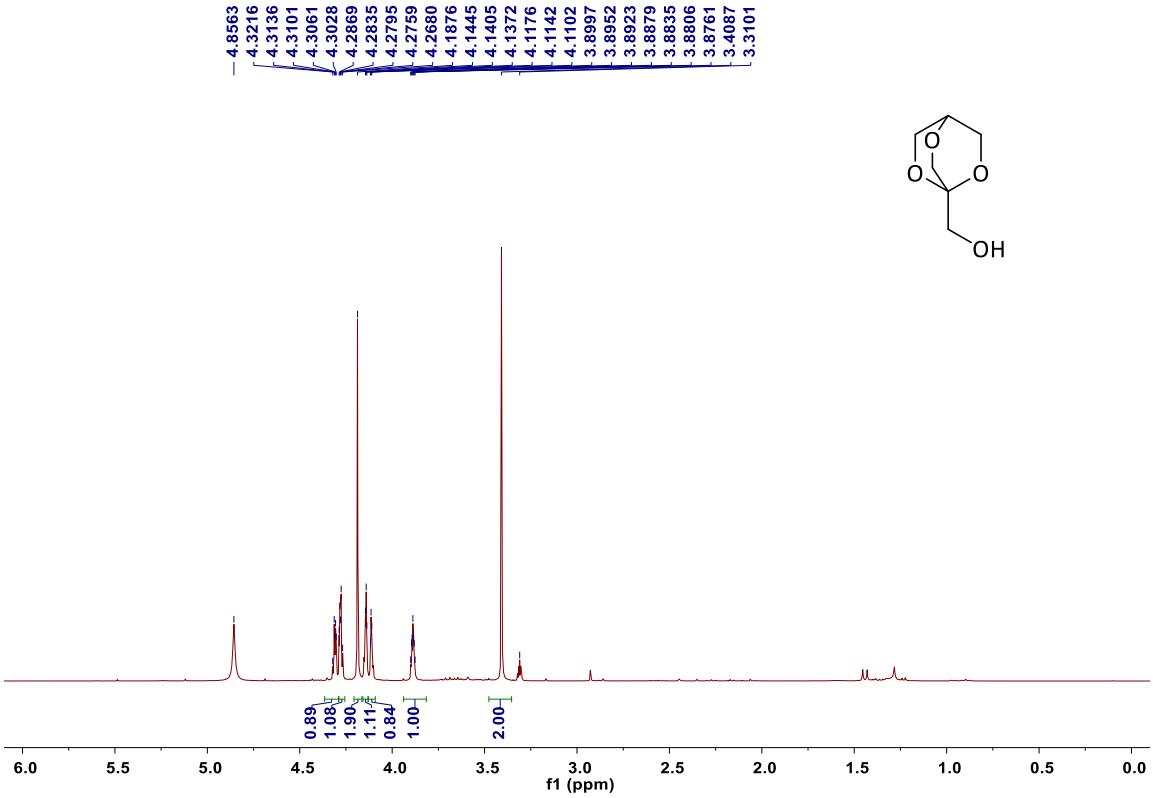
^{1}H NMR (500 MHz, CD_3OD) of α,β-diglycerose (**7**)



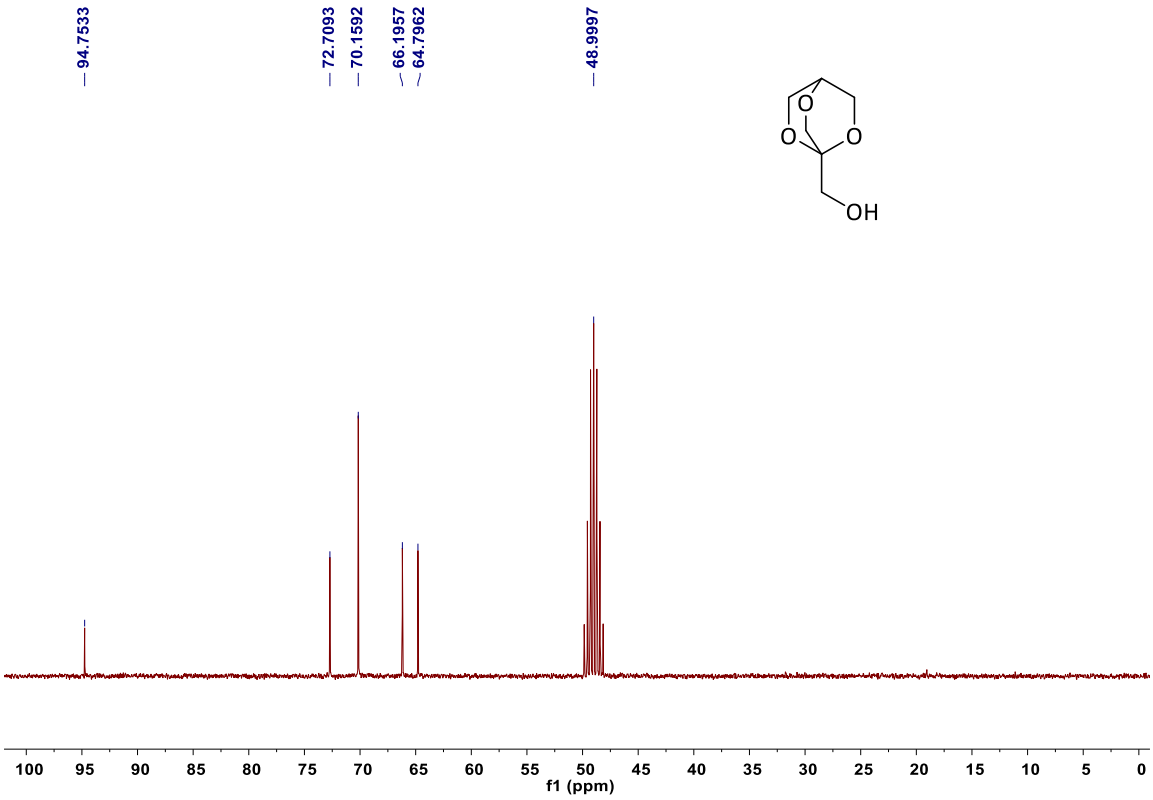
^{13}C NMR (125 MHz, CD_3OD) of α,β-diglycerose (**7**)



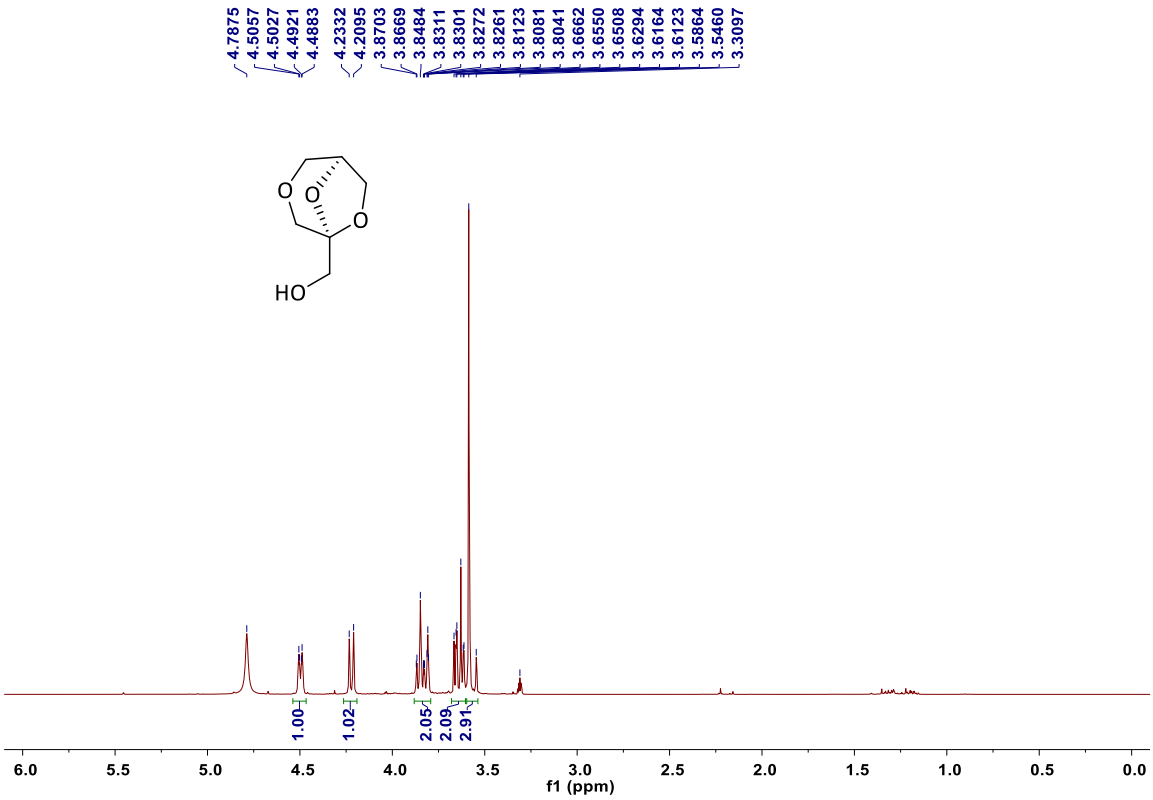
^{1}H NMR (300 MHz, CD_3OD) of (2,5,7-trioxabicyclo[2.2.2]octan-1-yl)methanol (**8**)



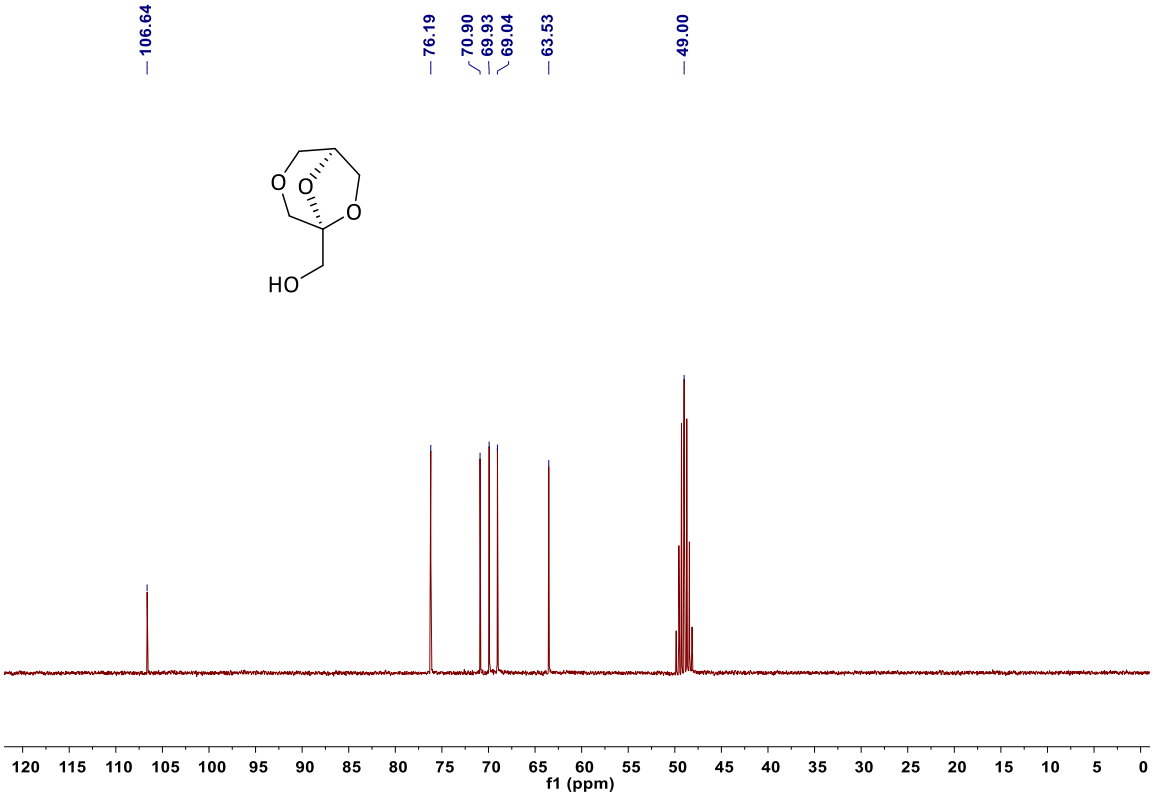
^{13}C NMR (75 MHz, CD_3OD) of (2,5,7-trioxabicyclo[2.2.2]octan-1-yl)methanol (**8**)



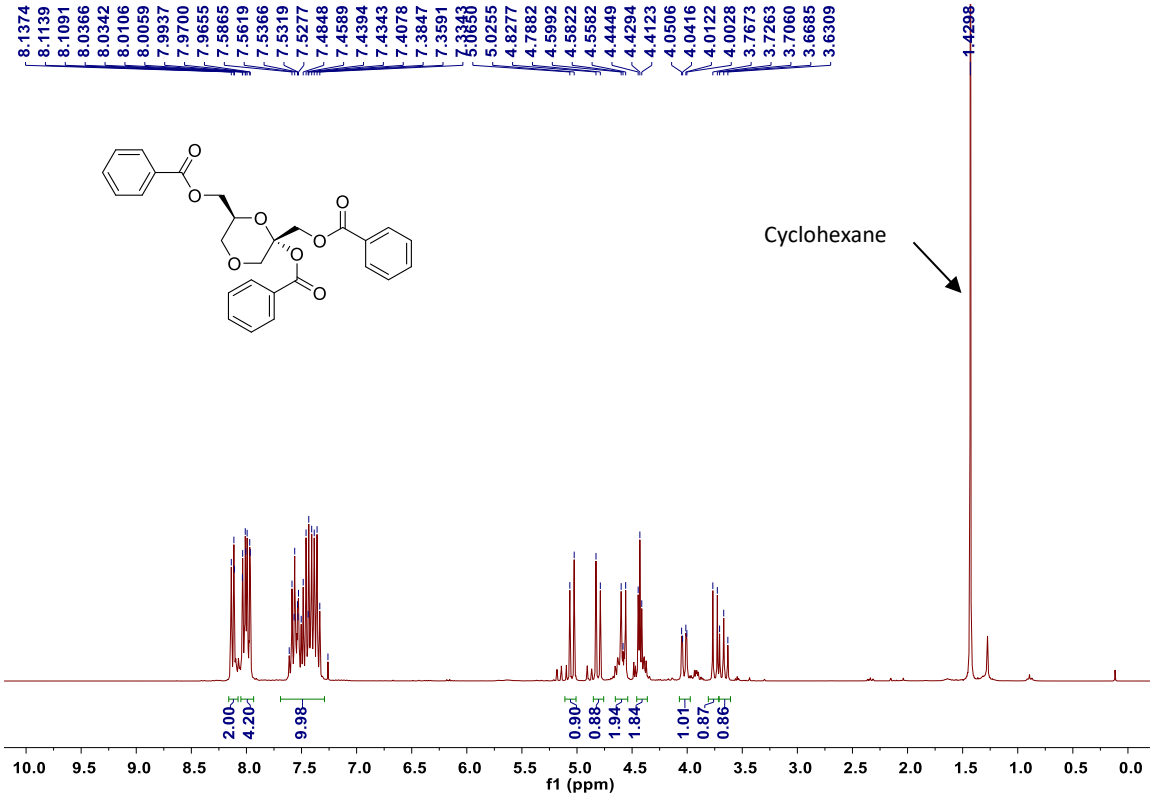
^{1}H NMR (300 MHz, CD_3OD) of (3,6,8-trioxabicyclo[3.2.1]octan-5-yl)methanol (**9**)



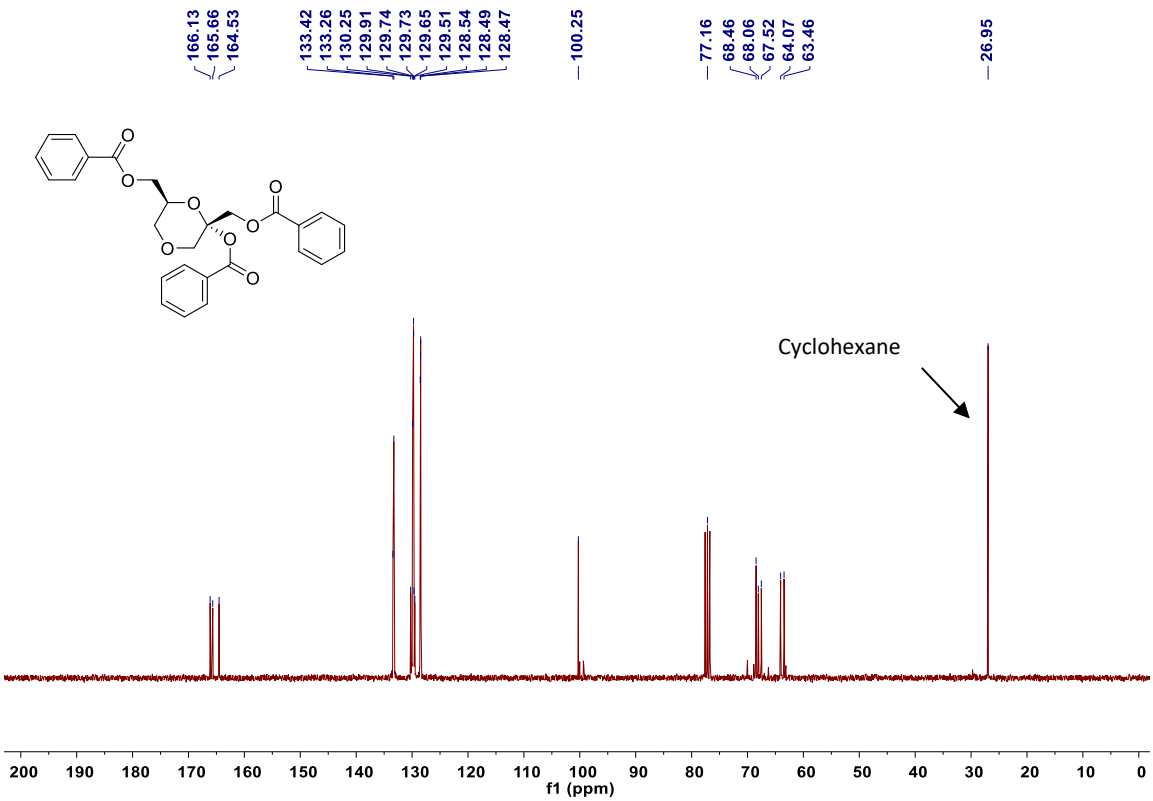
^{13}C NMR (75 MHz, CD_3OD) of (3,6,8-trioxabicyclo[3.2.1]octan-5-yl)methanol (**9**)



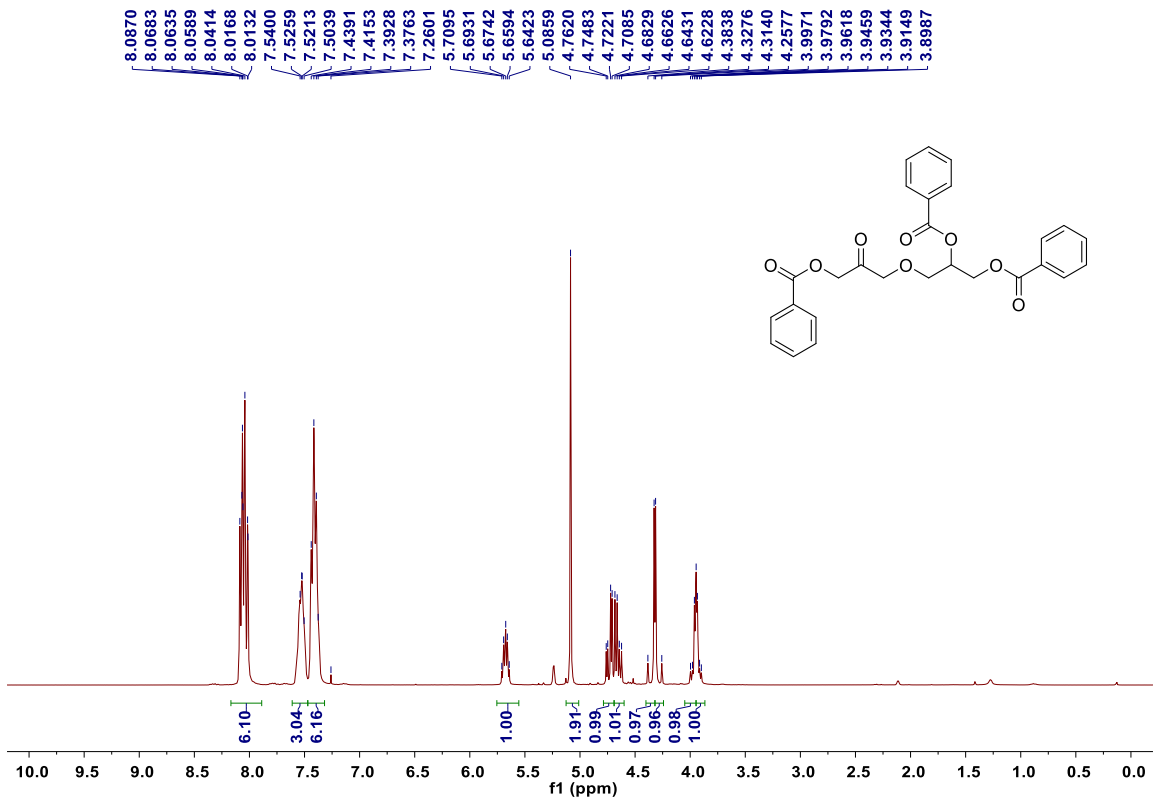
^{1}H NMR (300 MHz, $CDCl_3$) of (2-(benzyloxy)-1,4-dioxane-2,6-diyl) dimethanol (**10**)



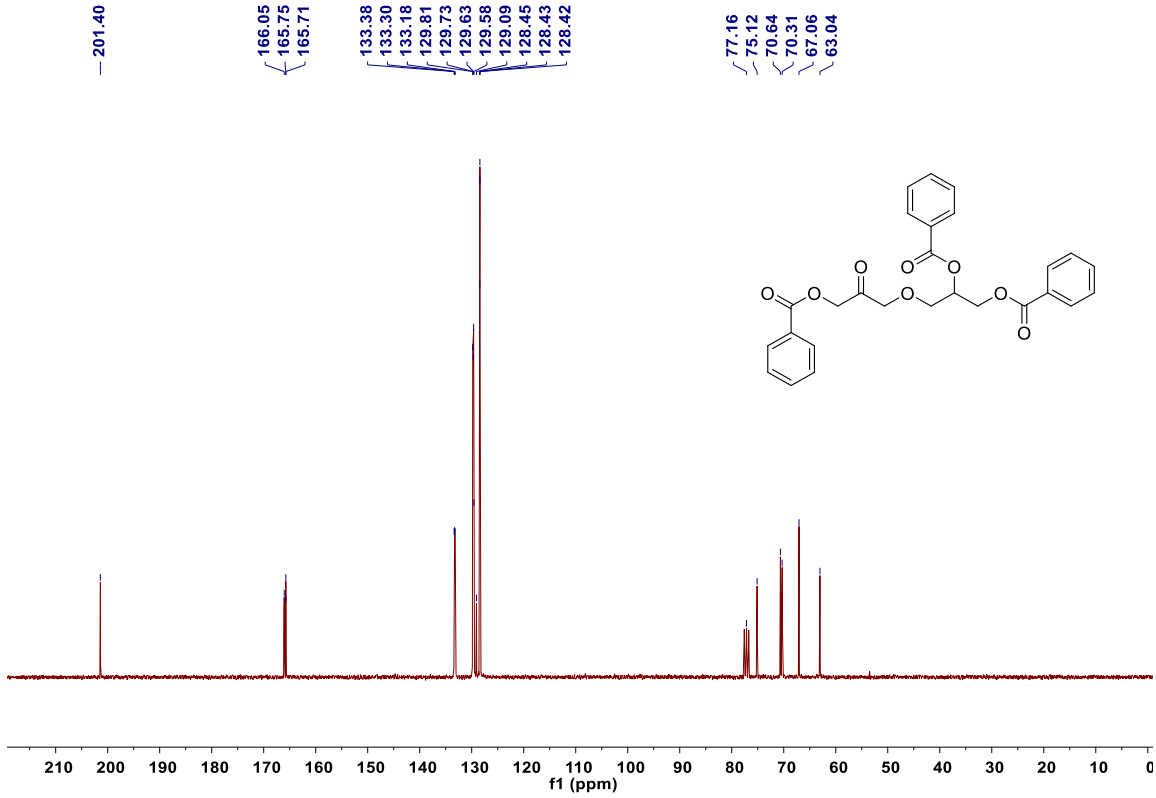
^{13}C NMR (75 MHz, $CDCl_3$) of (2-(benzyloxy)-1,4-dioxane-2,6-diyl) dimethanol (**10**)



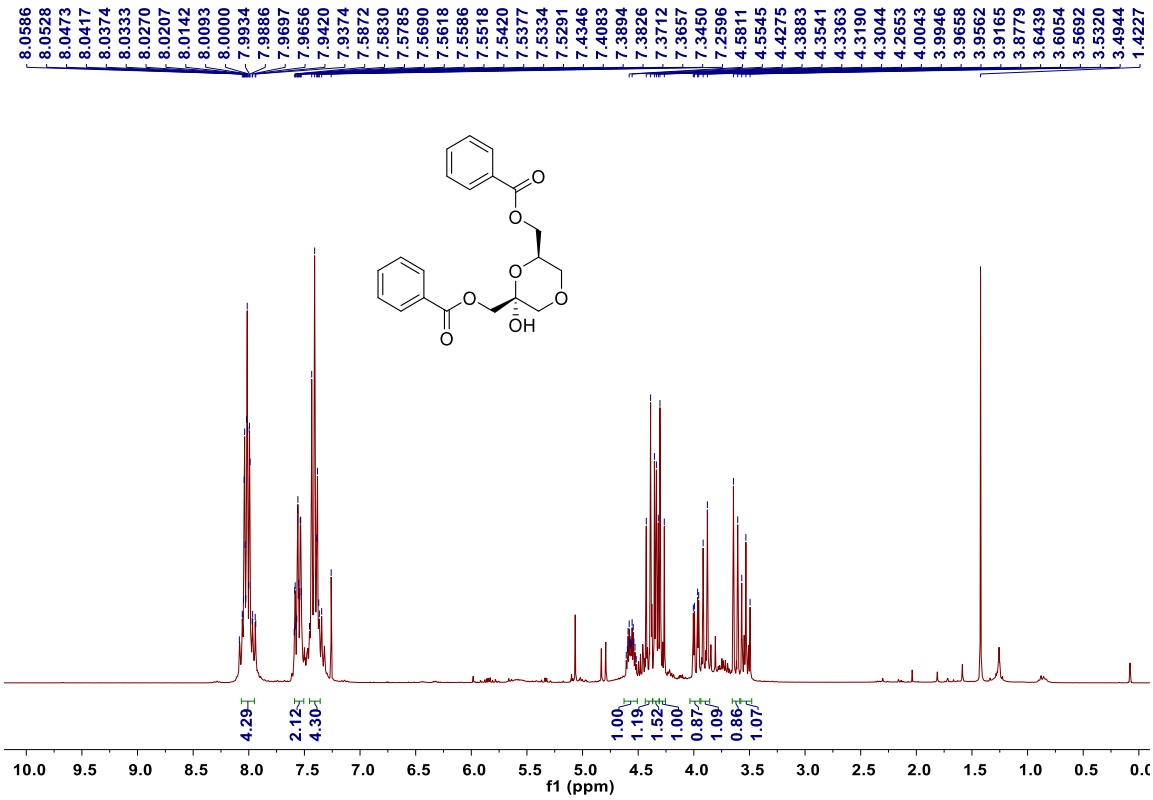
^{1}H NMR (300 MHz, $CDCl_3$) of (2-(benzyloxy)-1,4-dioxane-2,6-diyl) dimethanol (**11**)



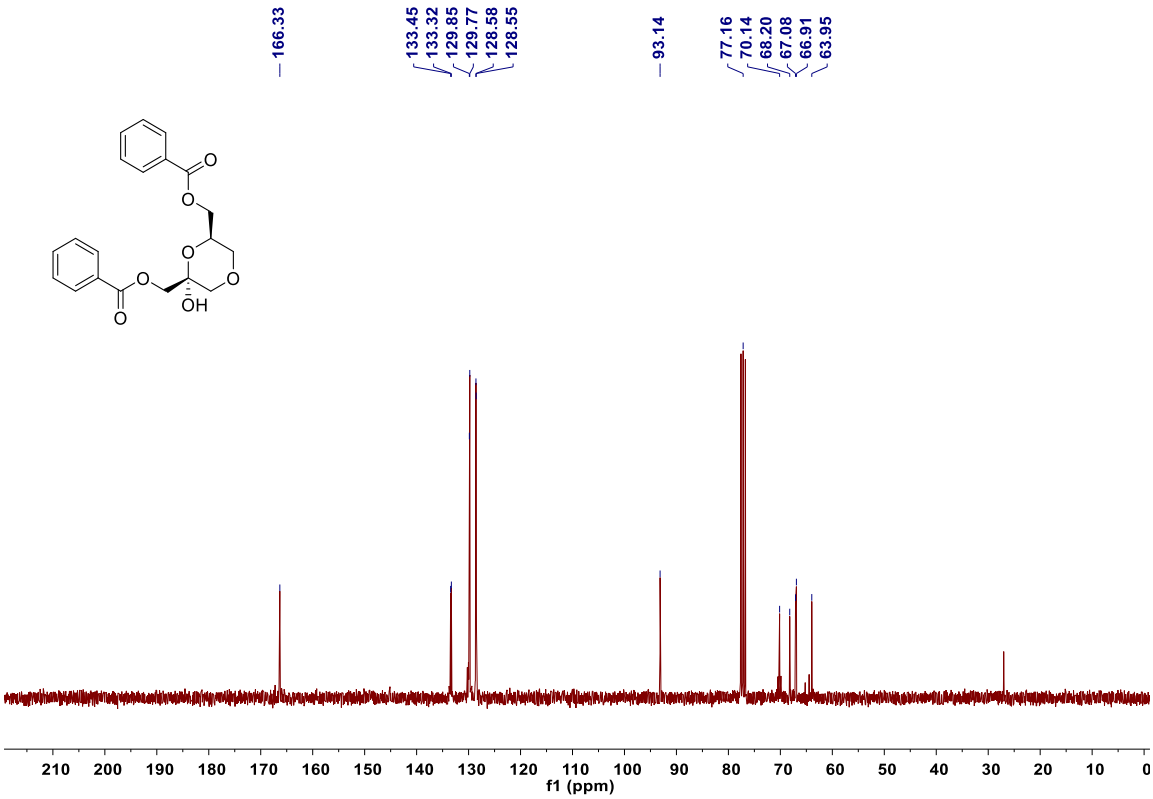
^{13}C NMR (75 MHz, $CDCl_3$) of (2-(benzyloxy)-1,4-dioxane-2,6-diyl) dimethanol (**11**)



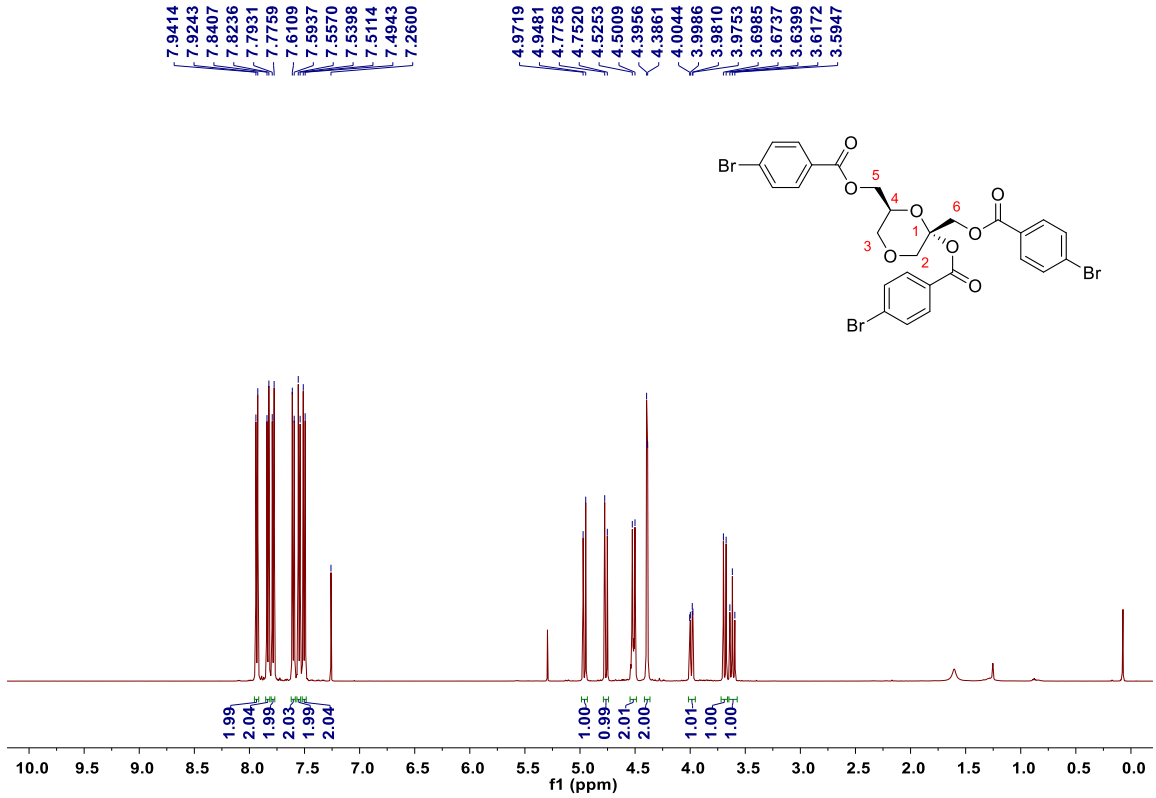
^{1}H NMR (300 MHz, $CDCl_3$) of (2-hydroxy-1,4-dioxane-2,6-diyl)bis(methylene) dibenzoate (**12**)



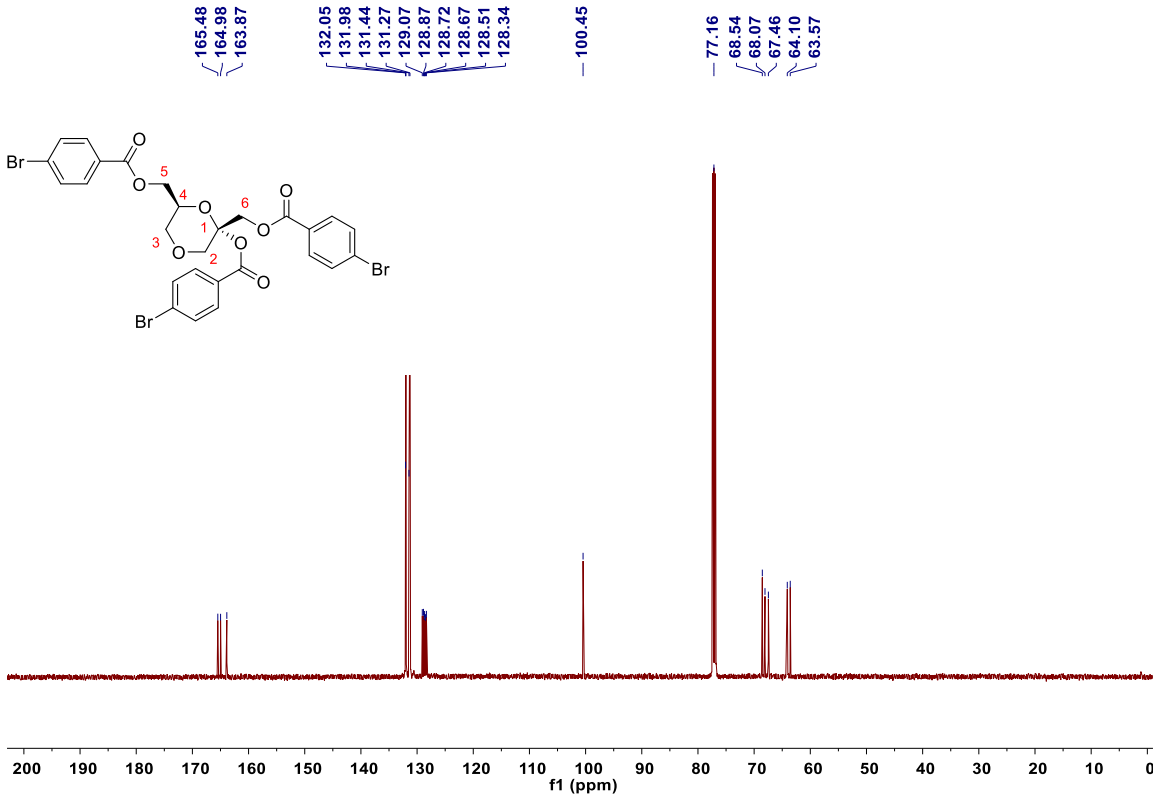
^{13}C NMR (75 MHz, $CDCl_3$) of (2-hydroxy-1,4-dioxane-2,6-diyl)bis(methylene) dibenzoate (**12**)



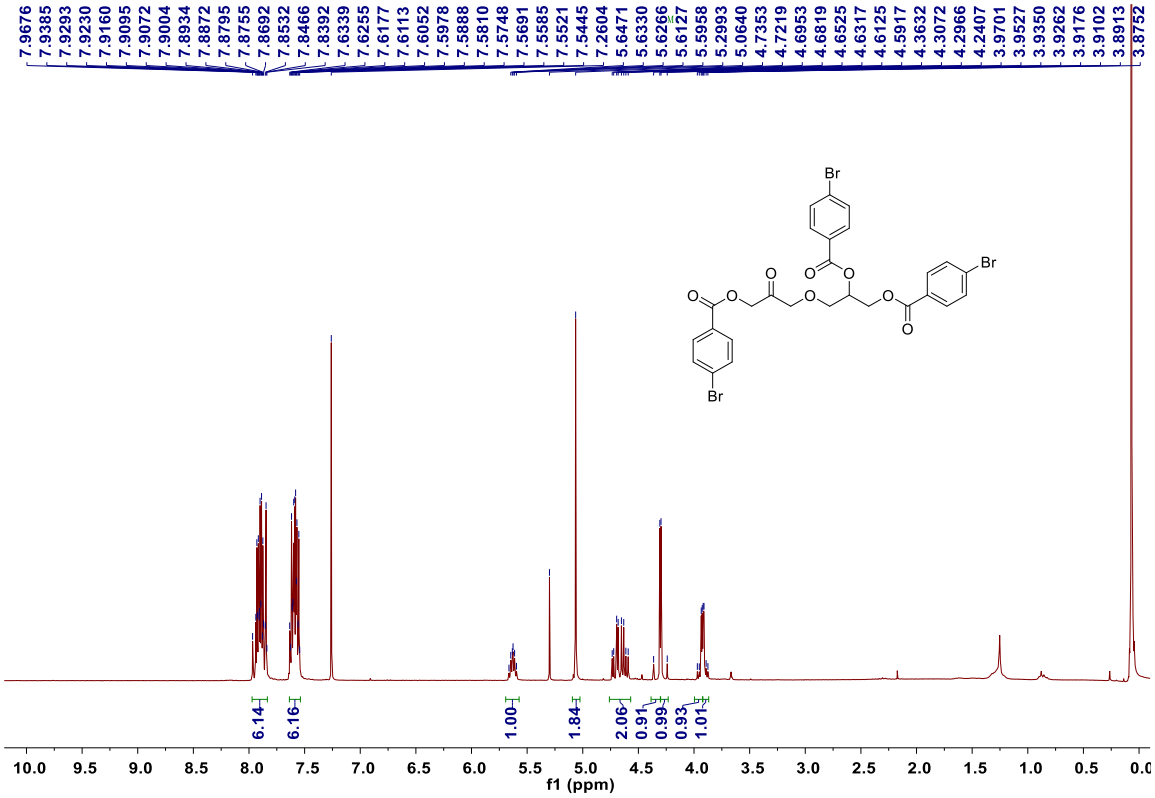
^{1}H NMR (500 MHz, $CDCl_3$) of (2-((4-bromobenzoyl)oxy)-1,4-dioxane-2,6-diyl)bis(methylene) bis(4-bromobenzoate) (**13**)



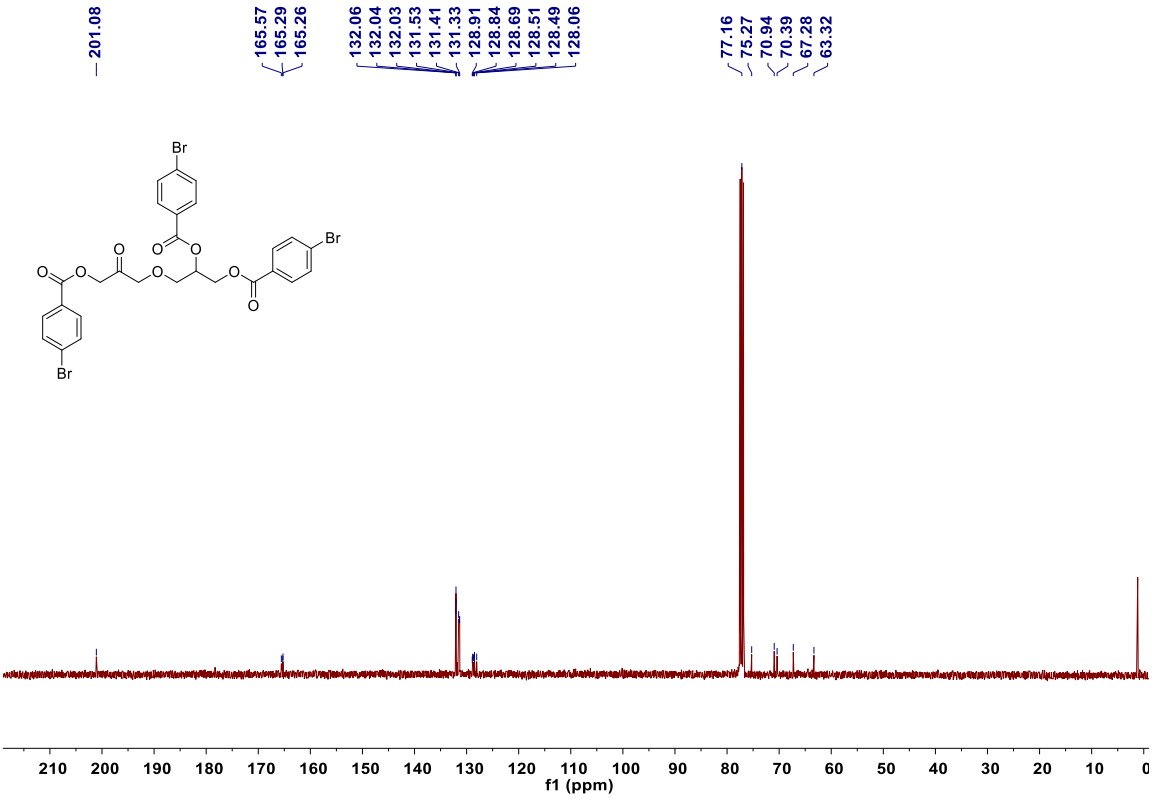
^{13}C NMR (125 MHz, $CDCl_3$) of (2-((4-bromobenzoyl)oxy)-1,4-dioxane-2,6-diyl)bis(methylene) bis(4-bromobenzoate) (**13**)



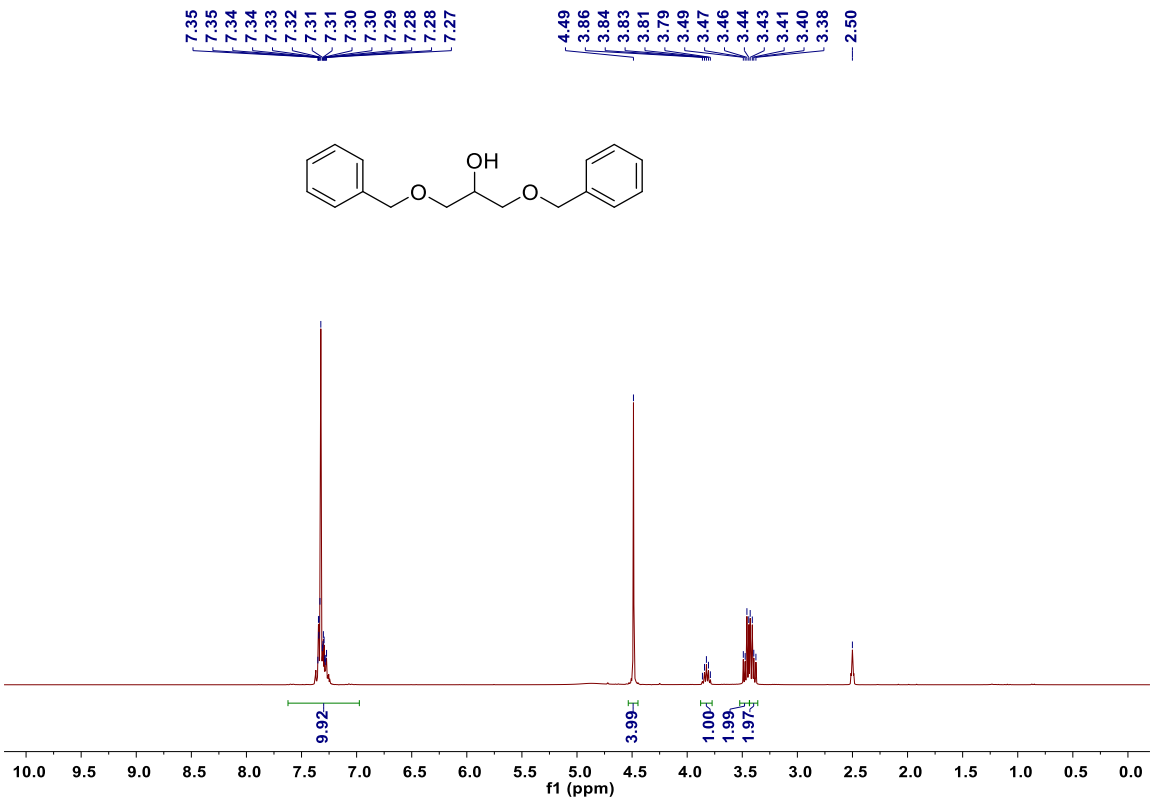
^{1}H NMR (300 MHz, $CDCl_3$) of 3-(3-((4-bromobenzoyl)oxy)-2-oxopropoxy)propane-1,2-diyl bis(4-bromobenzoate) **(14)**



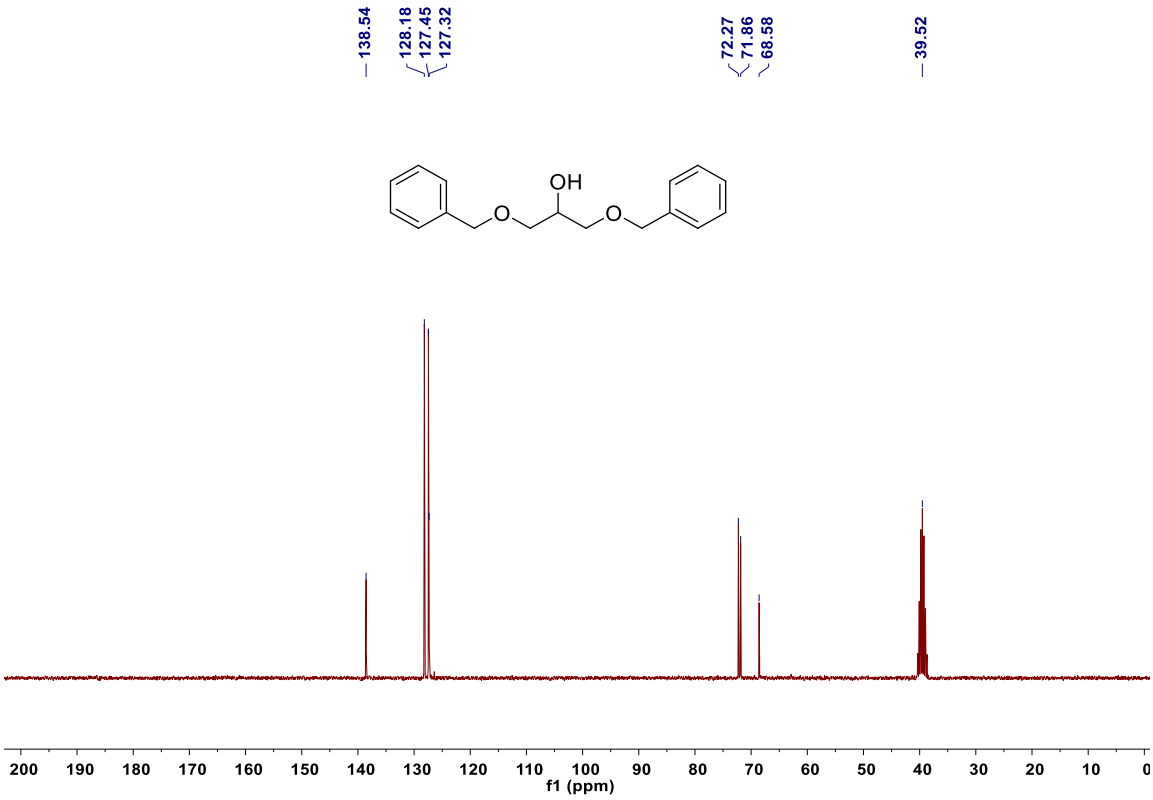
^{13}C NMR (75 MHz, $CDCl_3$) of 3-(3-((4-bromobenzoyl)oxy)-2-oxopropoxy)propane-1,2-diyl bis(4-bromobenzoate) **(14)**



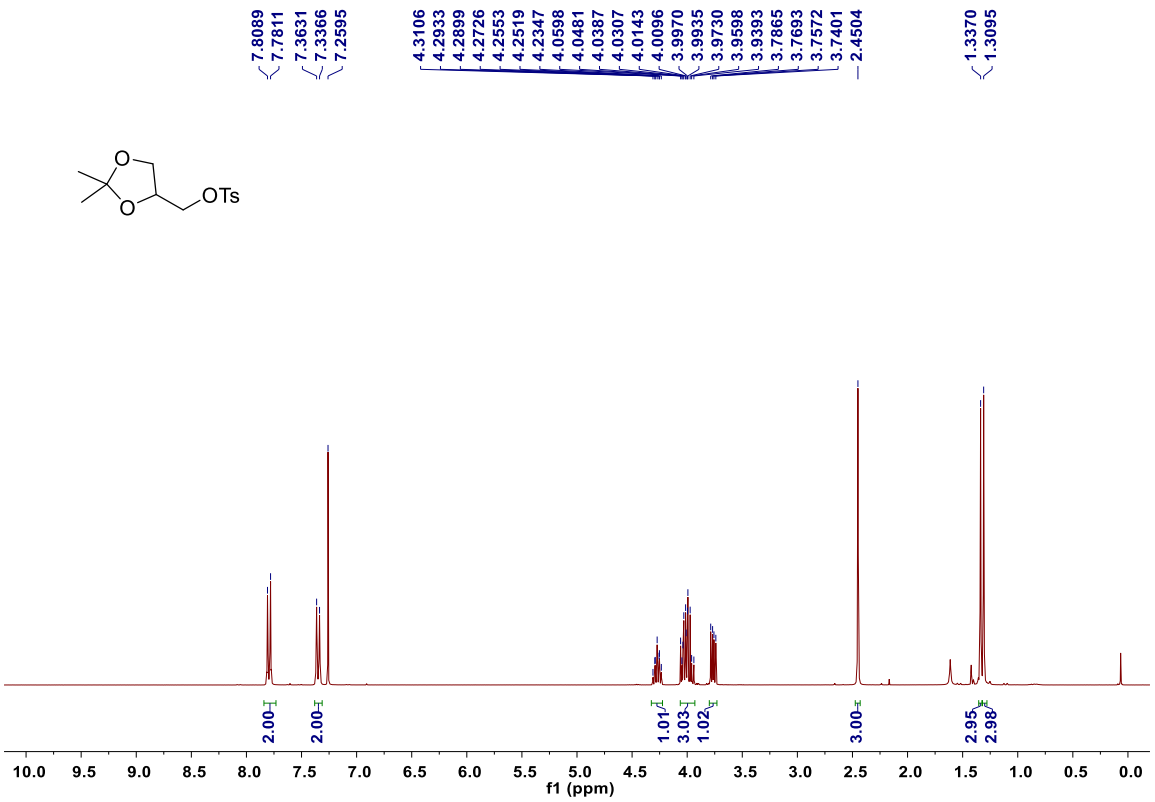
^{1}H NMR (300 MHz, DMSO-d_6) of 1,3-Di-*O*-benzylglycerol (**15**)



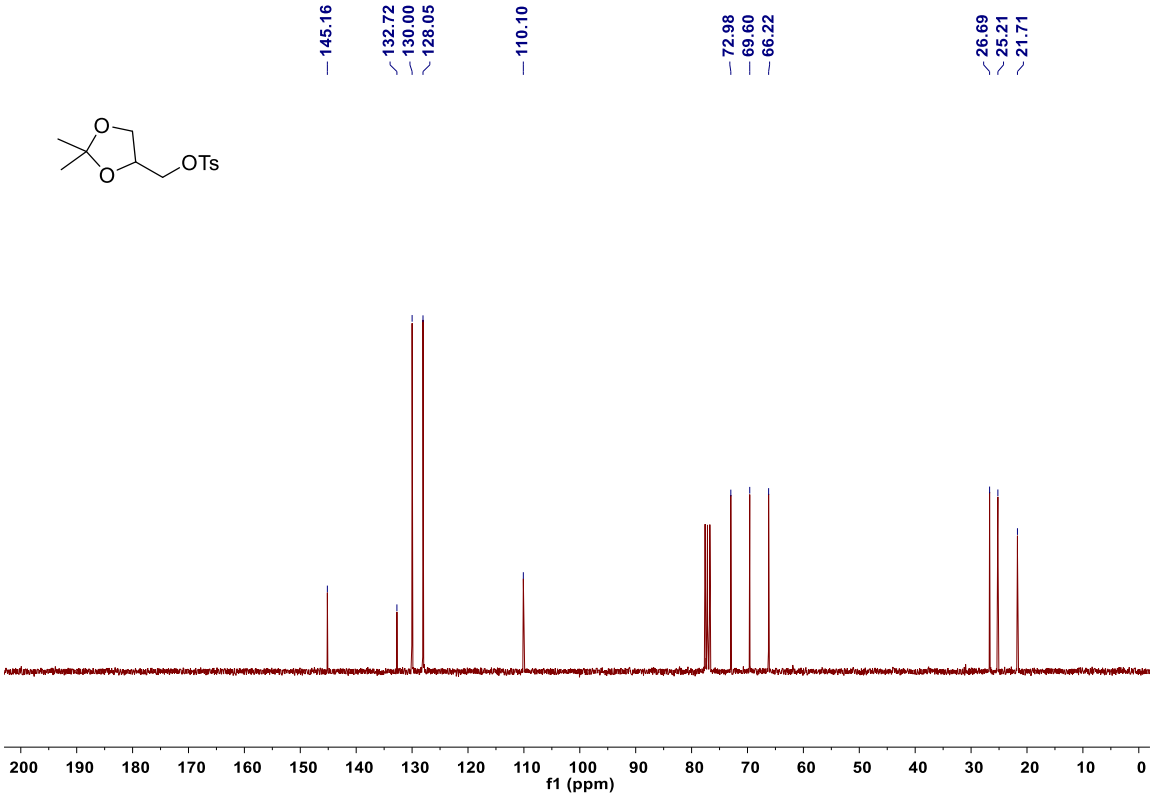
^{13}C NMR (75 MHz, DMSO-d_6) of 1,3-Di-*O*-benzylglycerol (**15**)



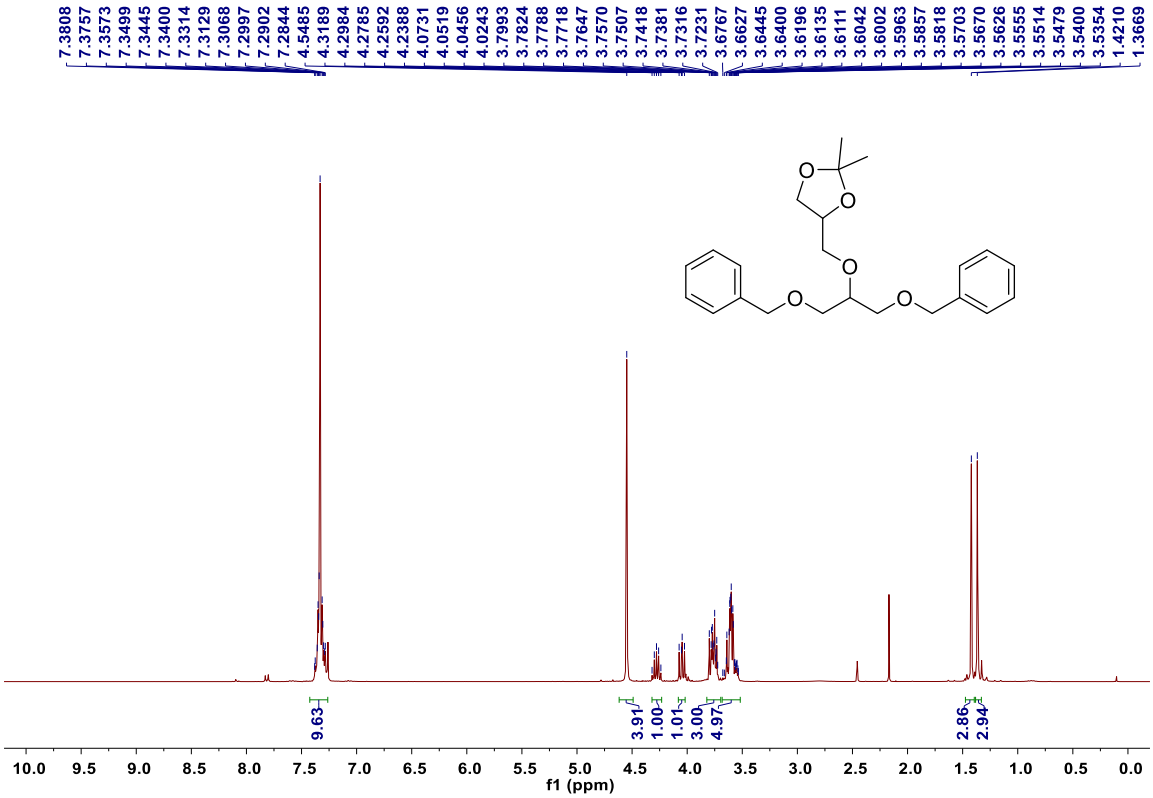
^{1}H NMR (300 MHz, $CDCl_3$) of toluene-4-sulfonic acid 2,2-(dimethyl-[1,3]dioxolan-4-ylmethyl ester) (**16**)



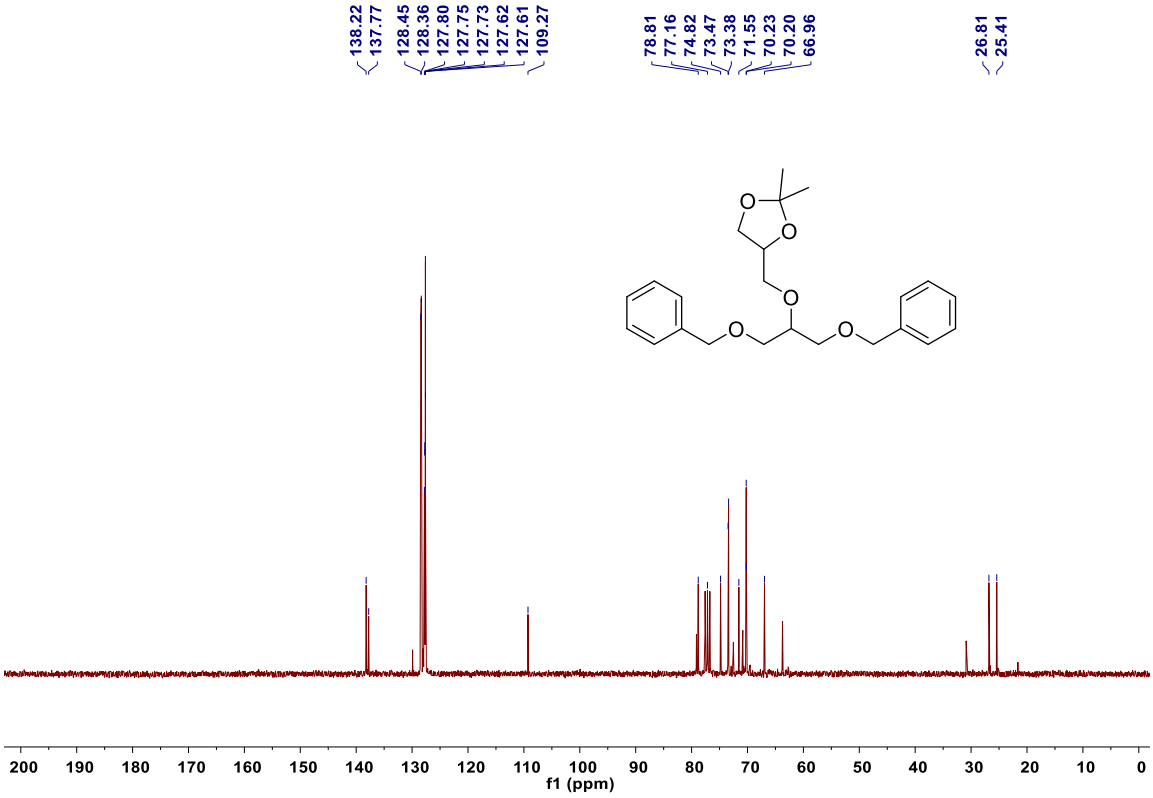
^{13}C NMR (75 MHz, $CDCl_3$) of toluene-4-sulfonic acid 2,2-(dimethyl-[1,3]dioxolan-4-ylmethyl ester) (**16**)



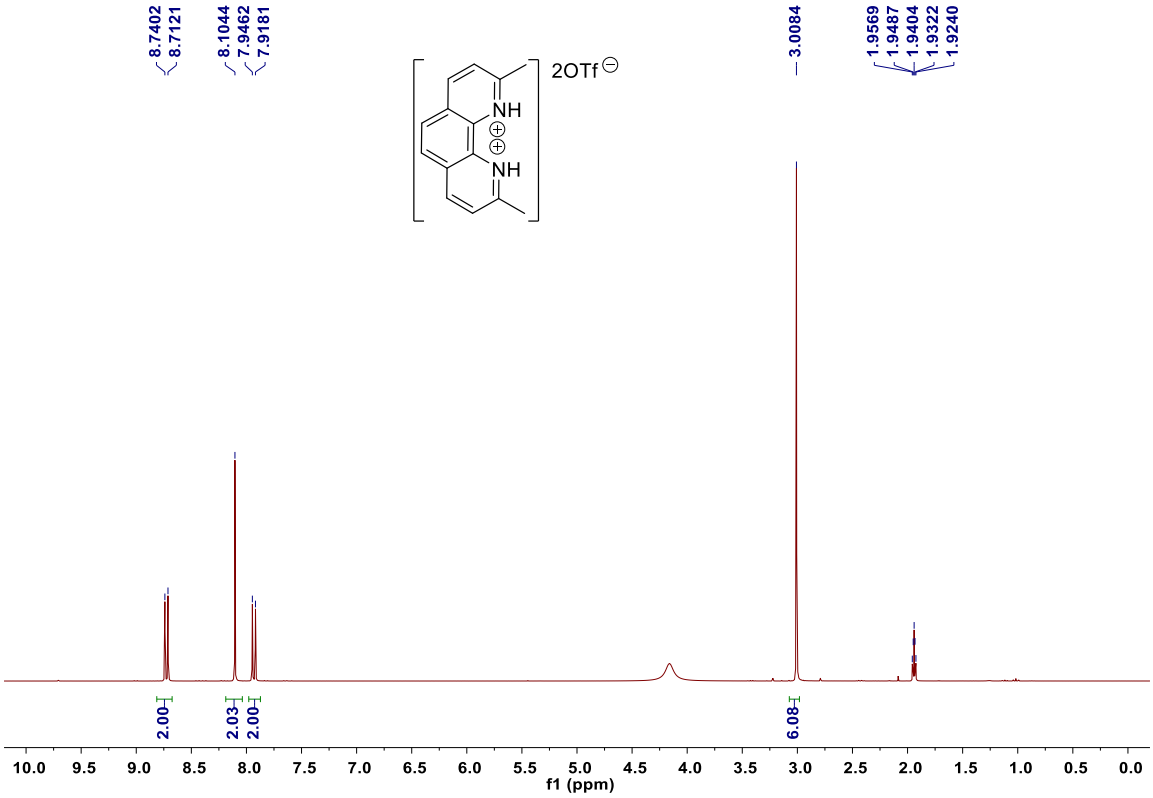
^{1}H NMR (300 MHz, $CDCl_3$) of 6-*O*-Benzyl-5-benzyloxymethyl-1,2-*O*-isopropylidene-4-oxahexane-1,2,6-triol (**17**)



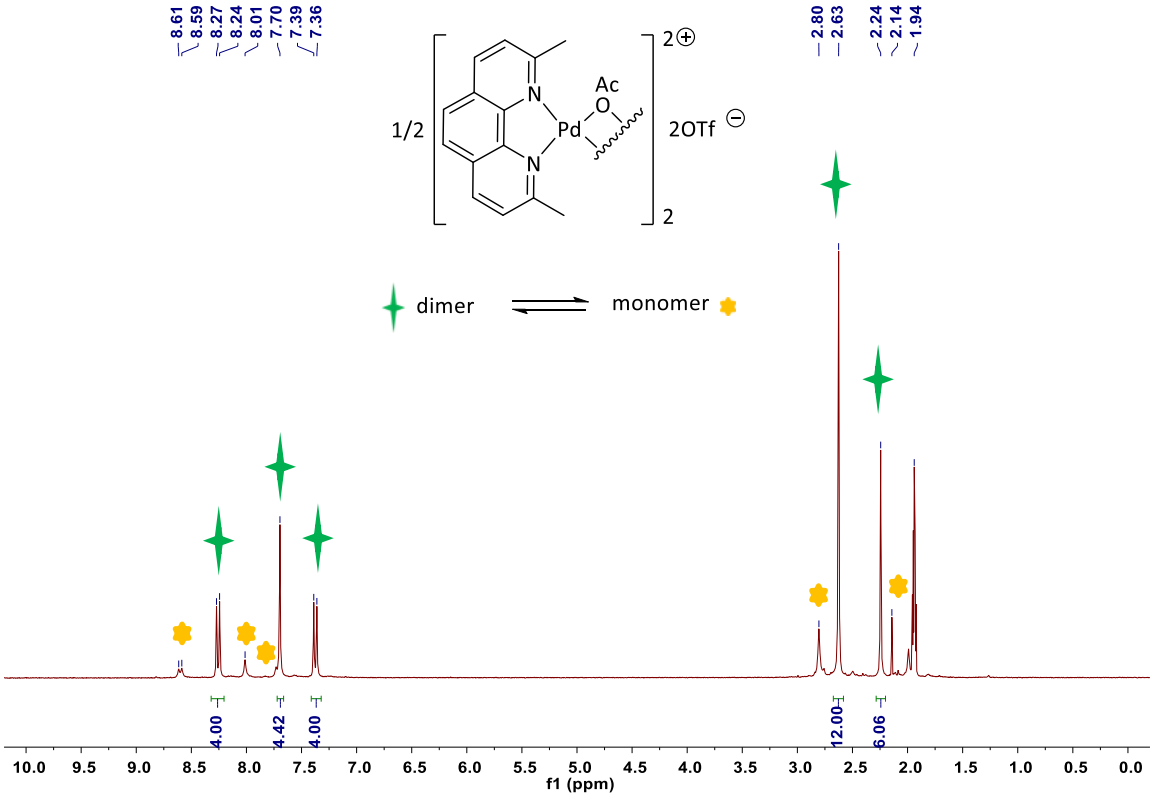
^{13}C NMR (75 MHz, $CDCl_3$) of 6-*O*-Benzyl-5-benzyloxymethyl-1,2-*O*-isopropylidene-4-oxahexane-1,2,6-triol (**17**)



^{1}H NMR (300 MHz, CD_3CN) of $[NeocuproineH_2][OTf]_2$ (**18**)

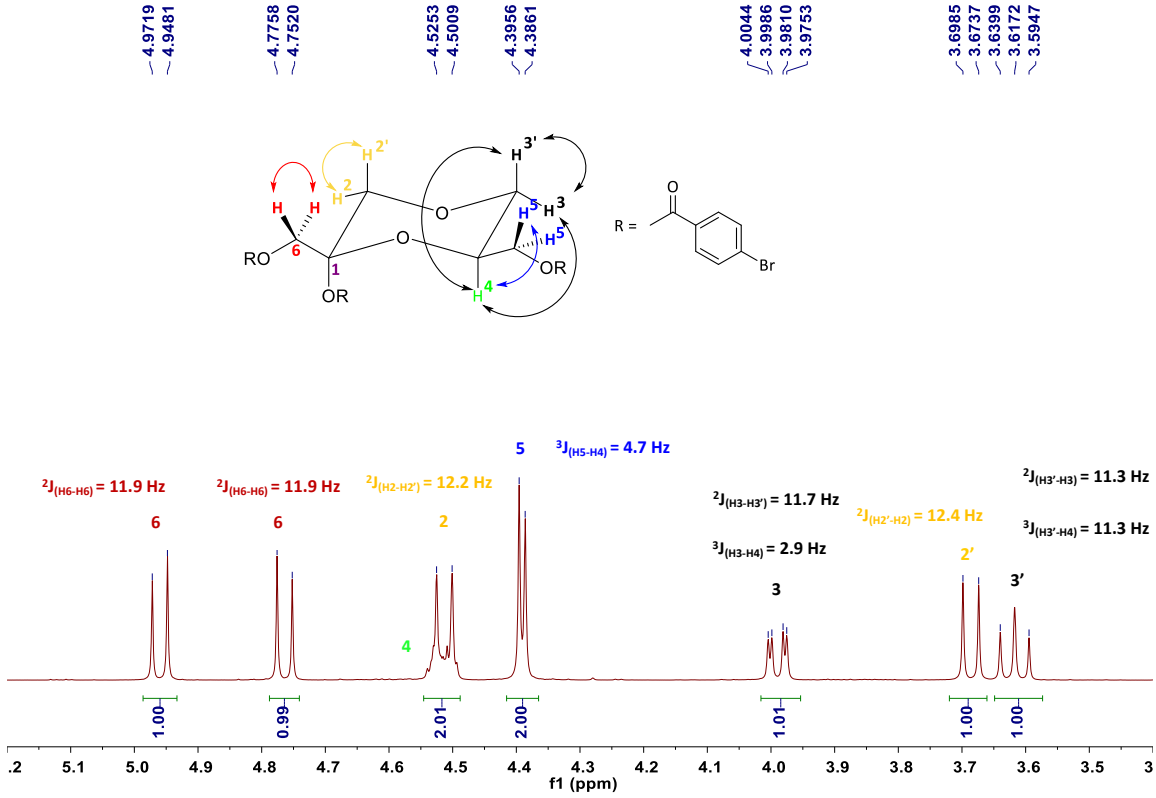


^{1}H NMR (300 MHz, CD_3CN) of **Pd-3** (**19**)

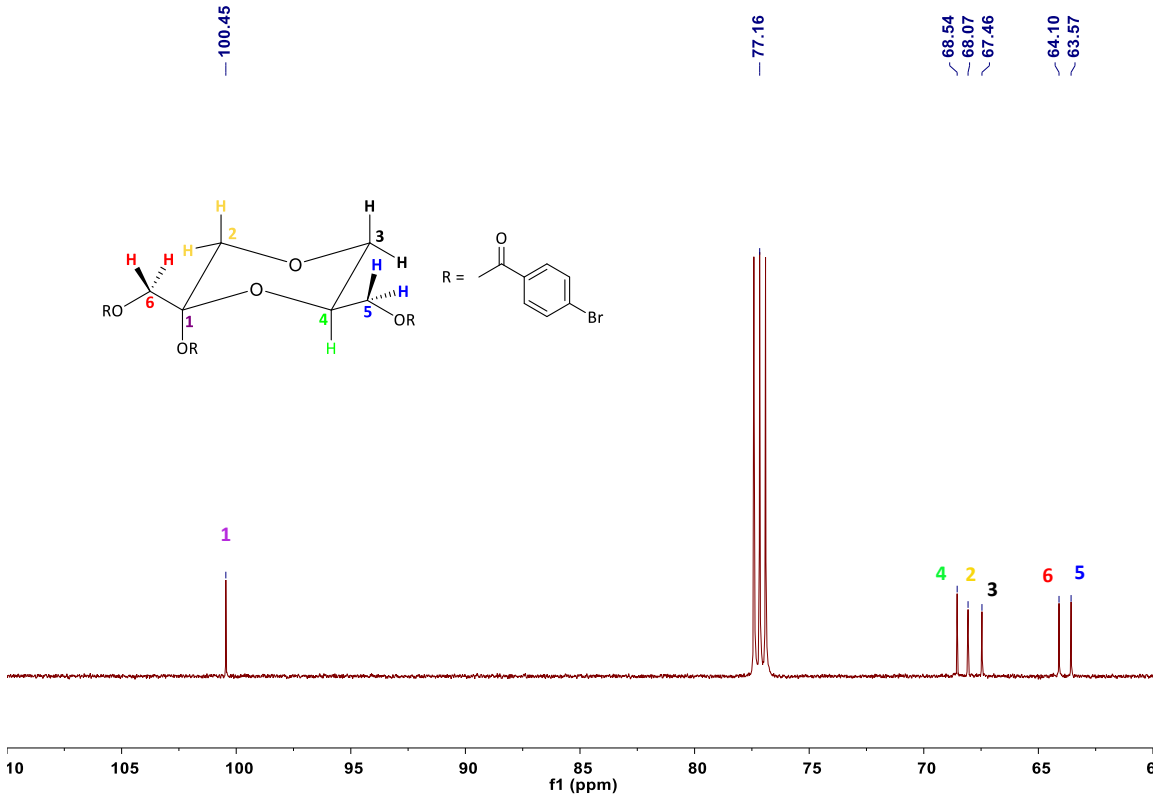


9 Structure analysis of oxidation products

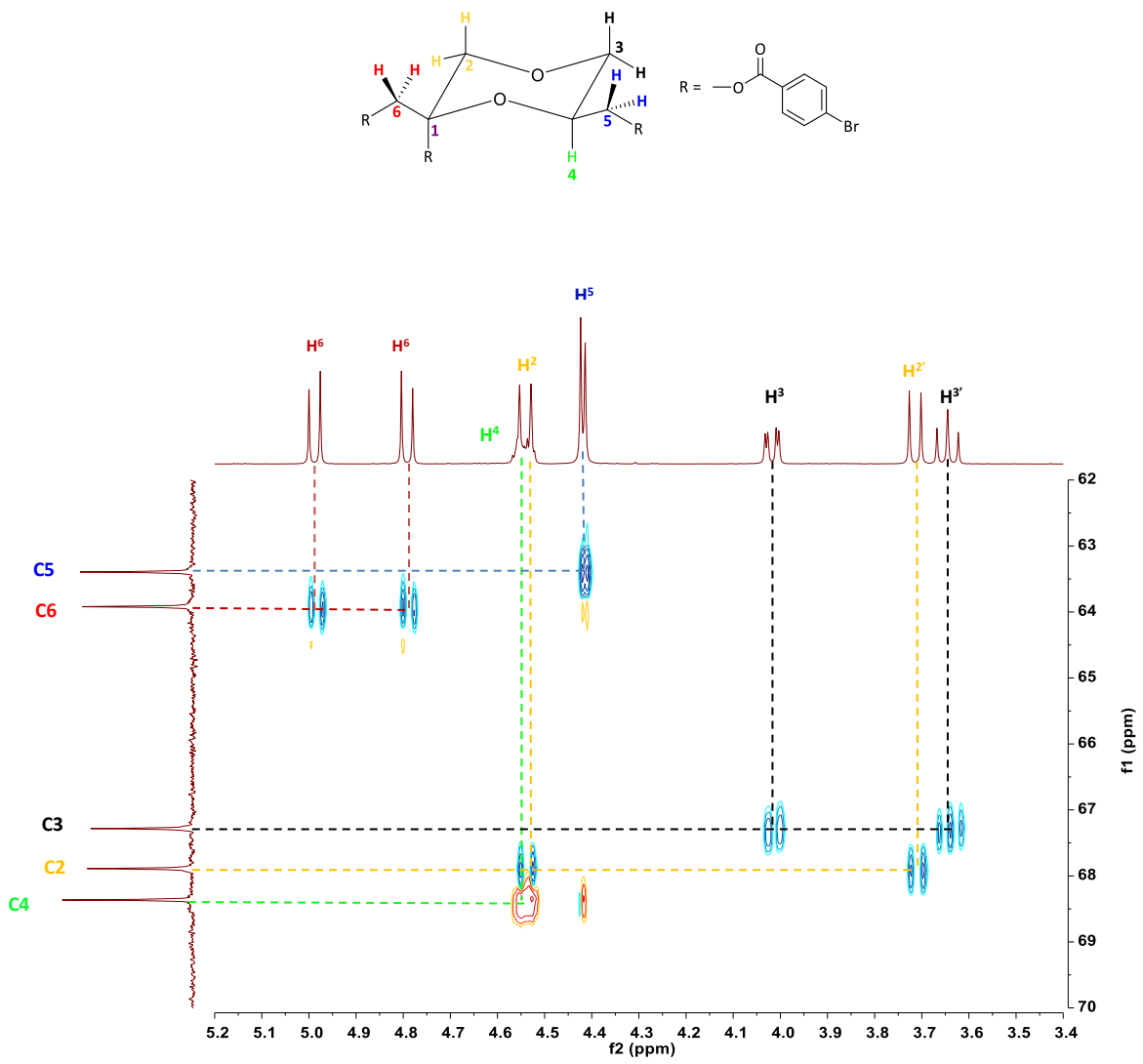
^{1}H NMR of **13** ($CDCl_3$, 500 MHz) Zoom 3.4-5.2 ppm



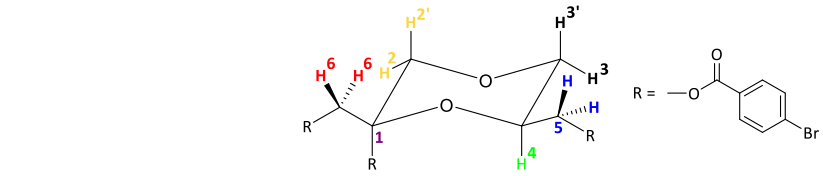
^{13}C NMR of **13** ($CDCl_3$, 125 MHz) Zoom 60-110 ppm

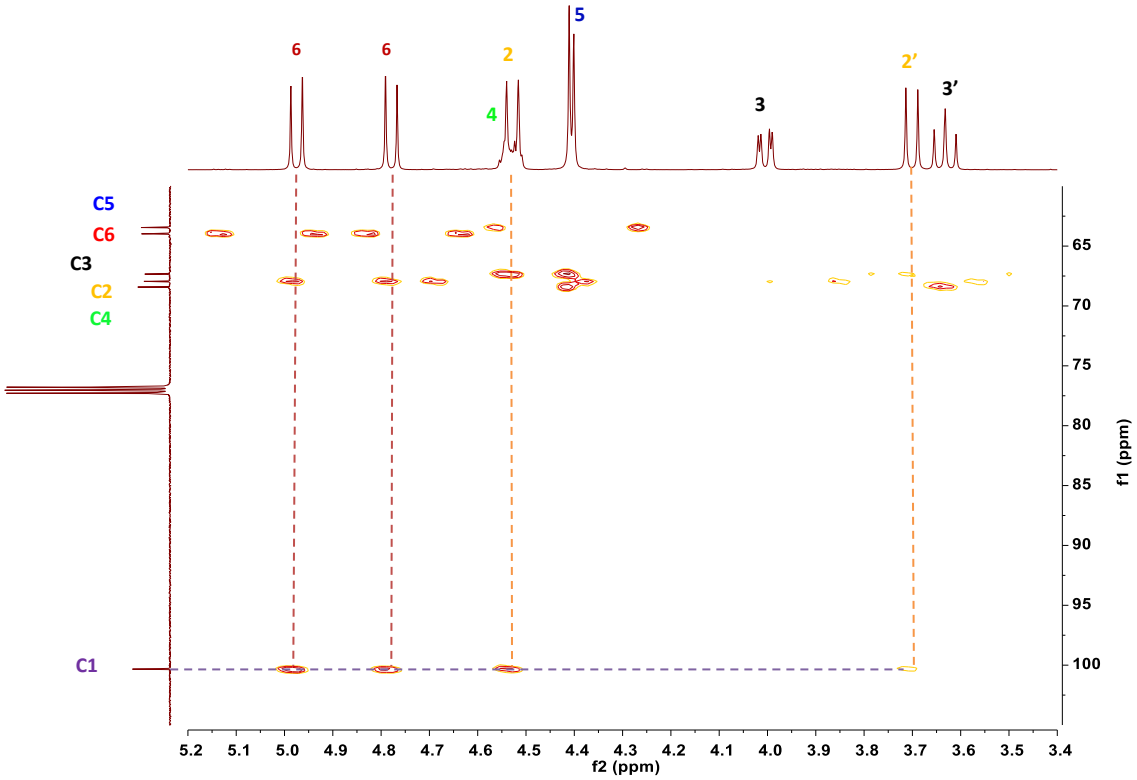


HSQC of **13** ($CDCl_3$, 500 Hz) Zoom 3.4-5.2ppm, 62-70 ppm

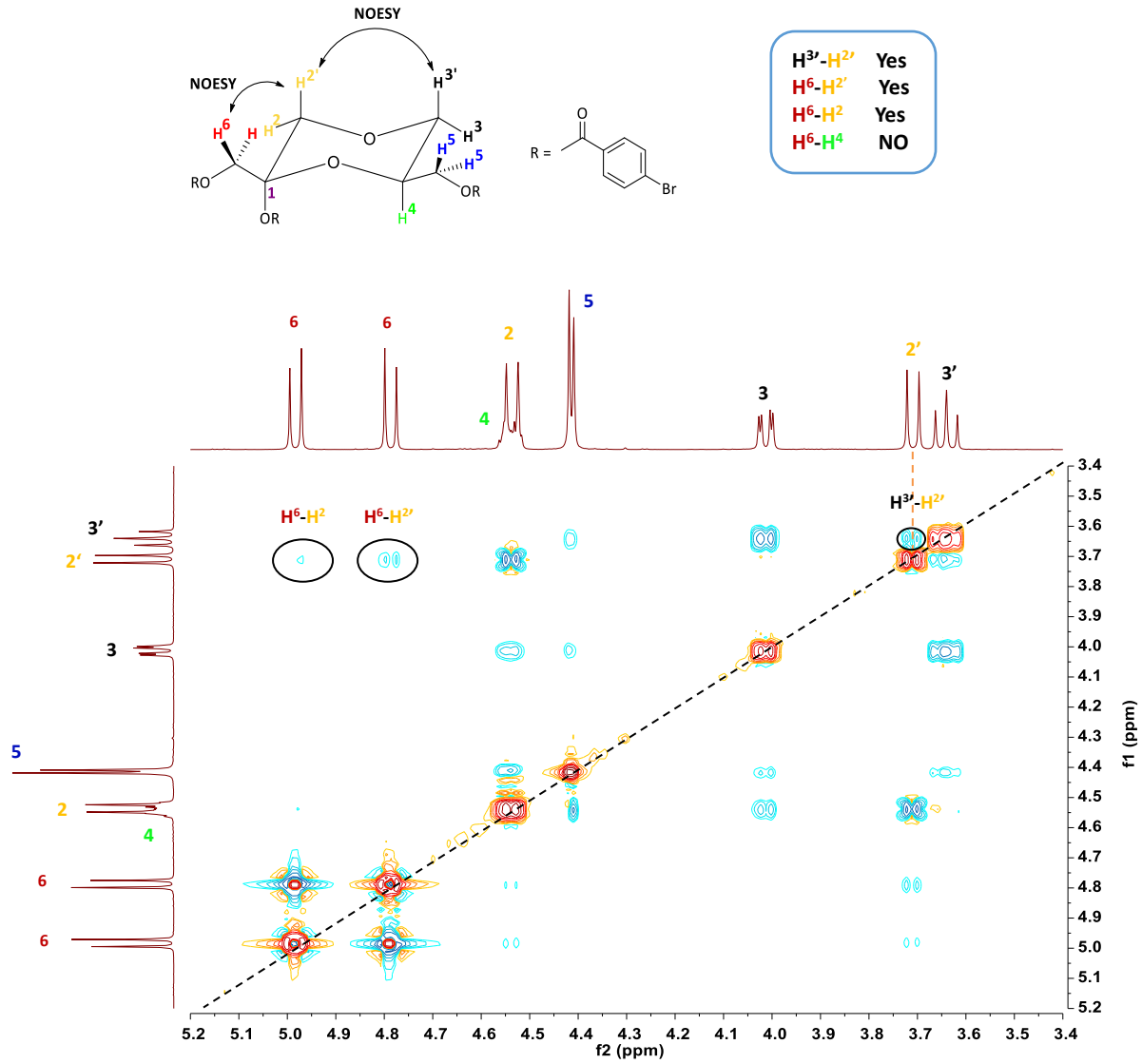


HMBC of **13** ($CDCl_3$, 500 Hz) Zoom 3.4-5.2ppm, 60-110 ppm

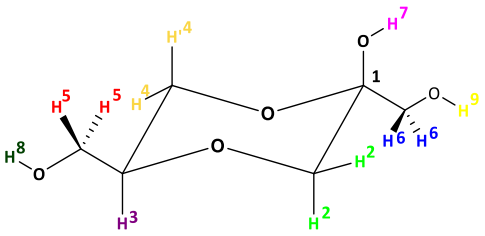


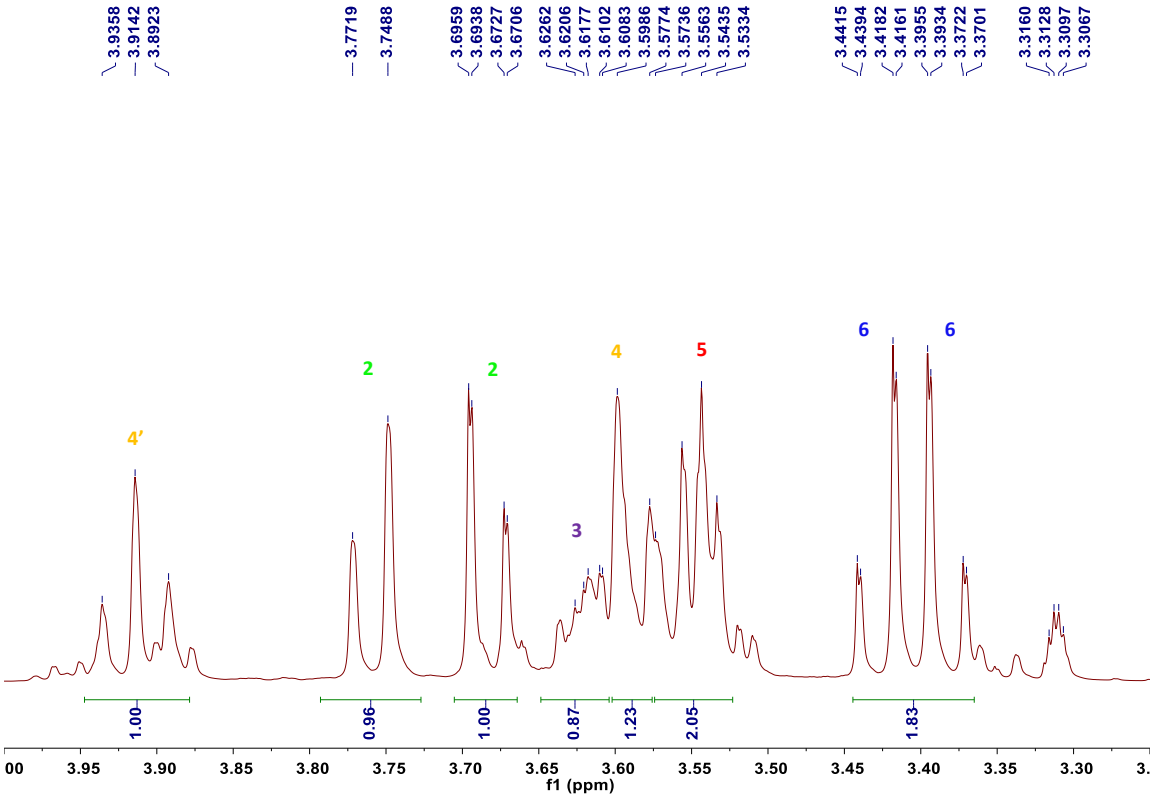


NOESY of **13** ($CDCl_3$, 500 Hz) Zoom 3.4-5.2ppm

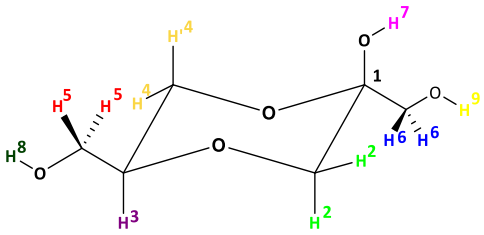


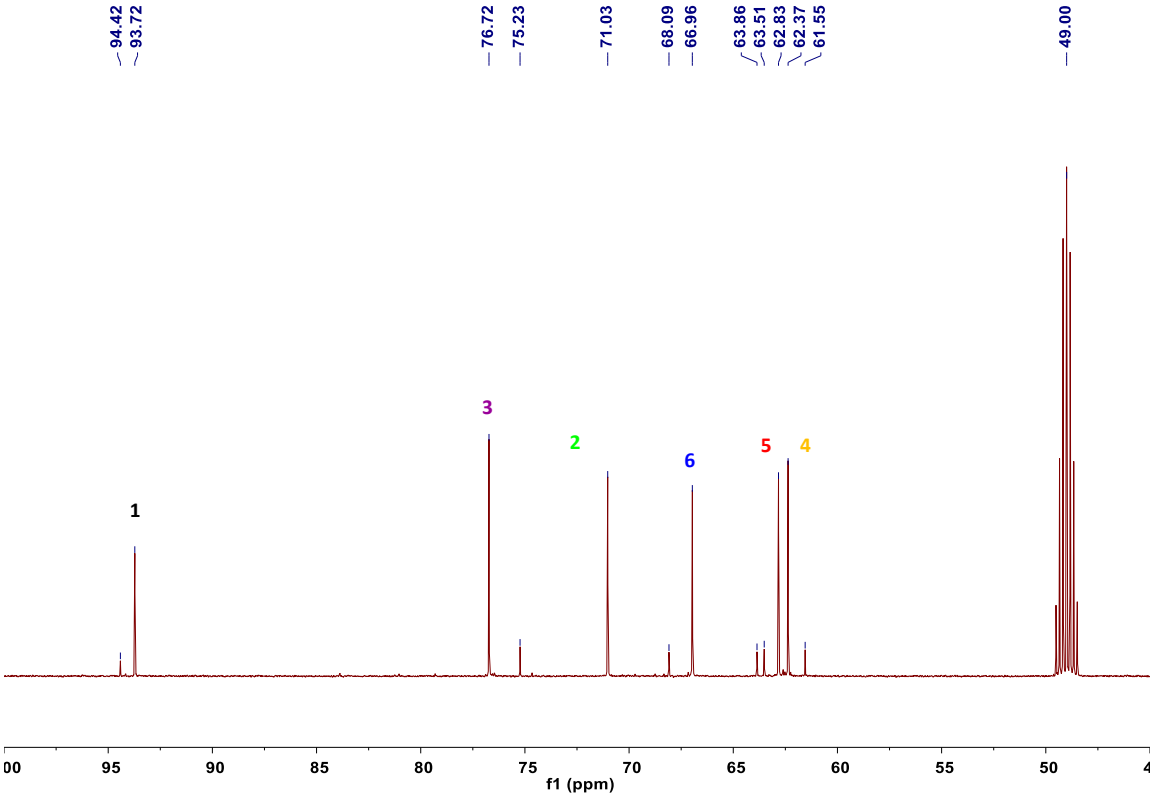
^{1}H NMR of **7** (CD_3OD, 500 Hz) Zoom 3.25-4.00 ppm



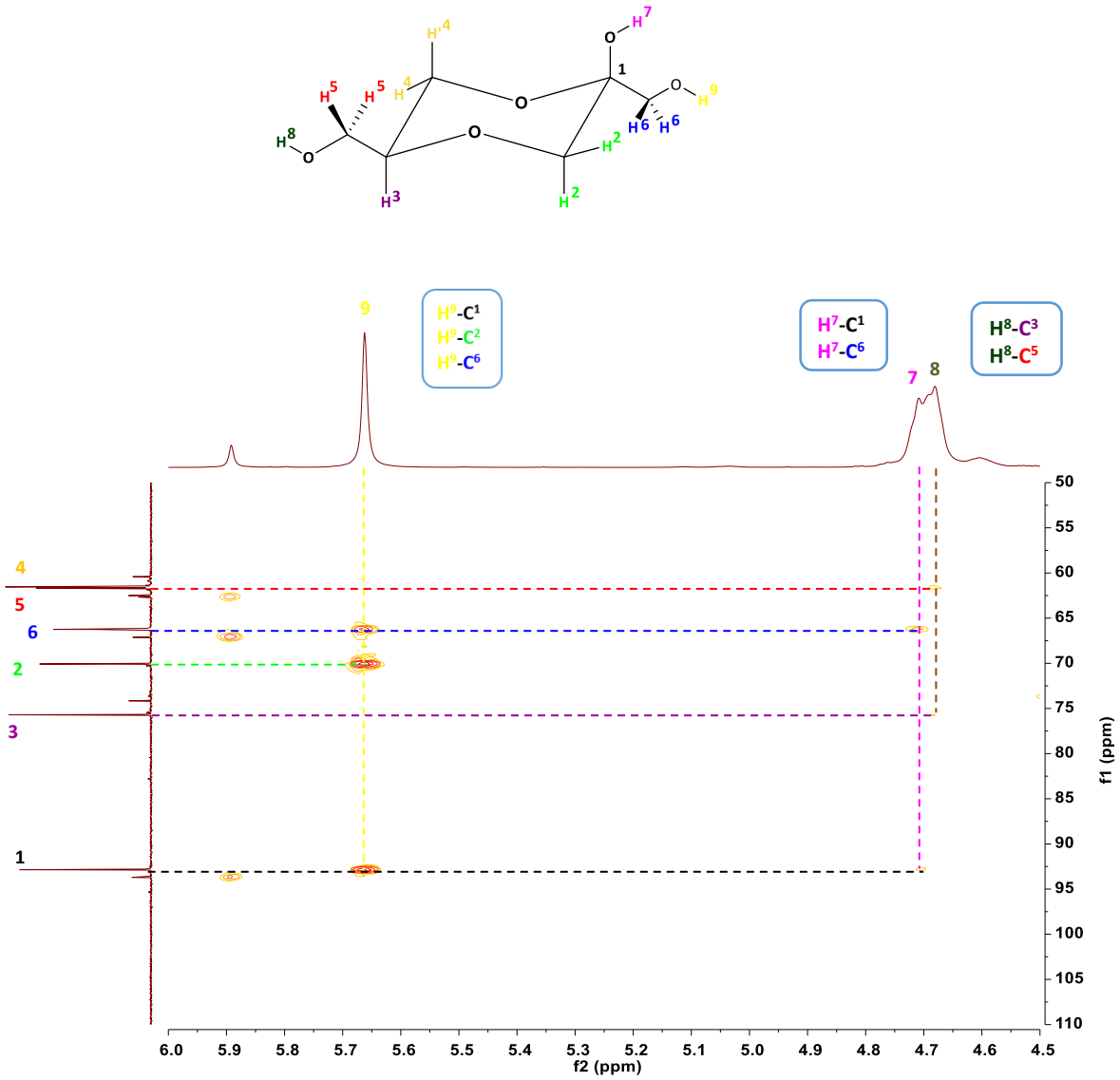


^{13}C NMR of **7** (CD_3OD, 125 Hz) Zoom 40-100 ppm

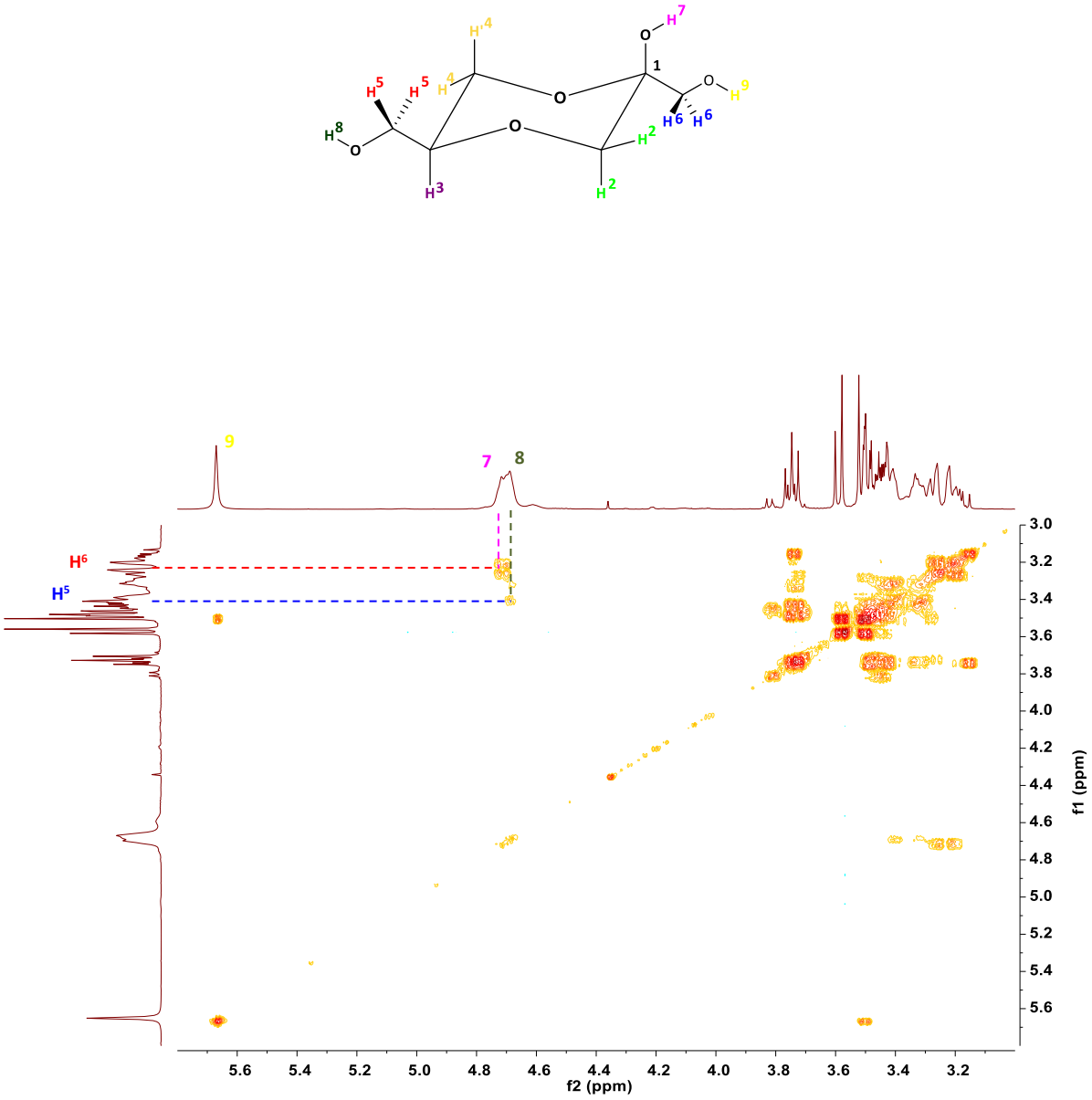




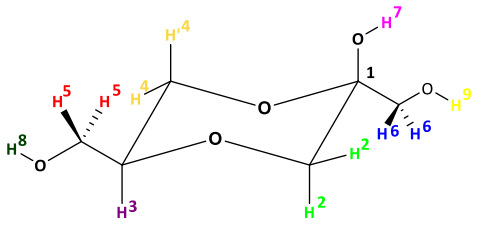
HMBC of **7** (DMSO-$_{d6}$, 500 Hz) Zoom 4.5-6.0ppm, 50-110 ppm

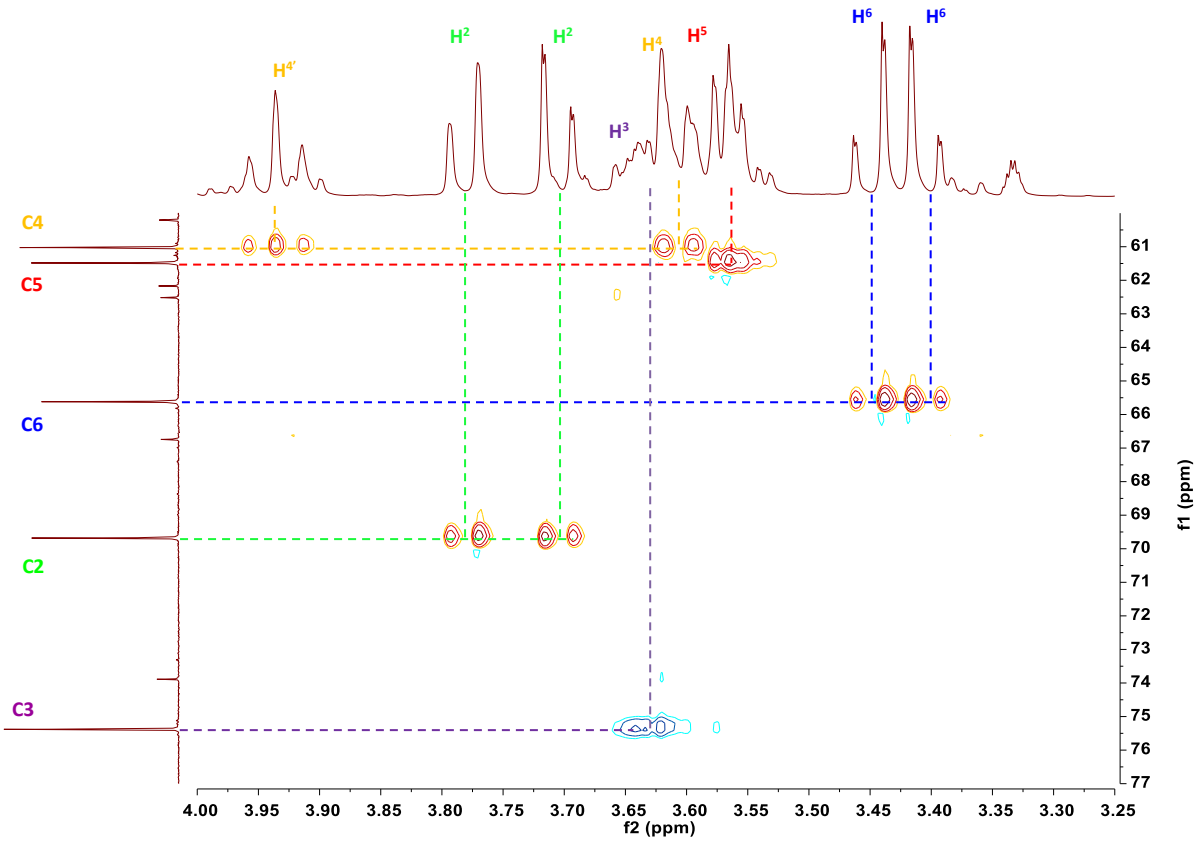


COSY of **7** (DMSO-$_{d6}$, 500 Hz) Zoom 3.00-5.80 ppm.

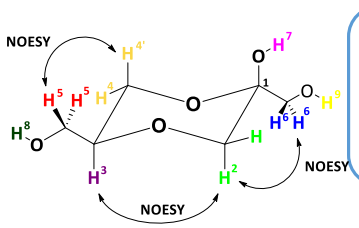


HSQC of **7** (CD_3OD, 500 Hz) Zoom 3.15-3.80 ppm, 60-77 ppm.

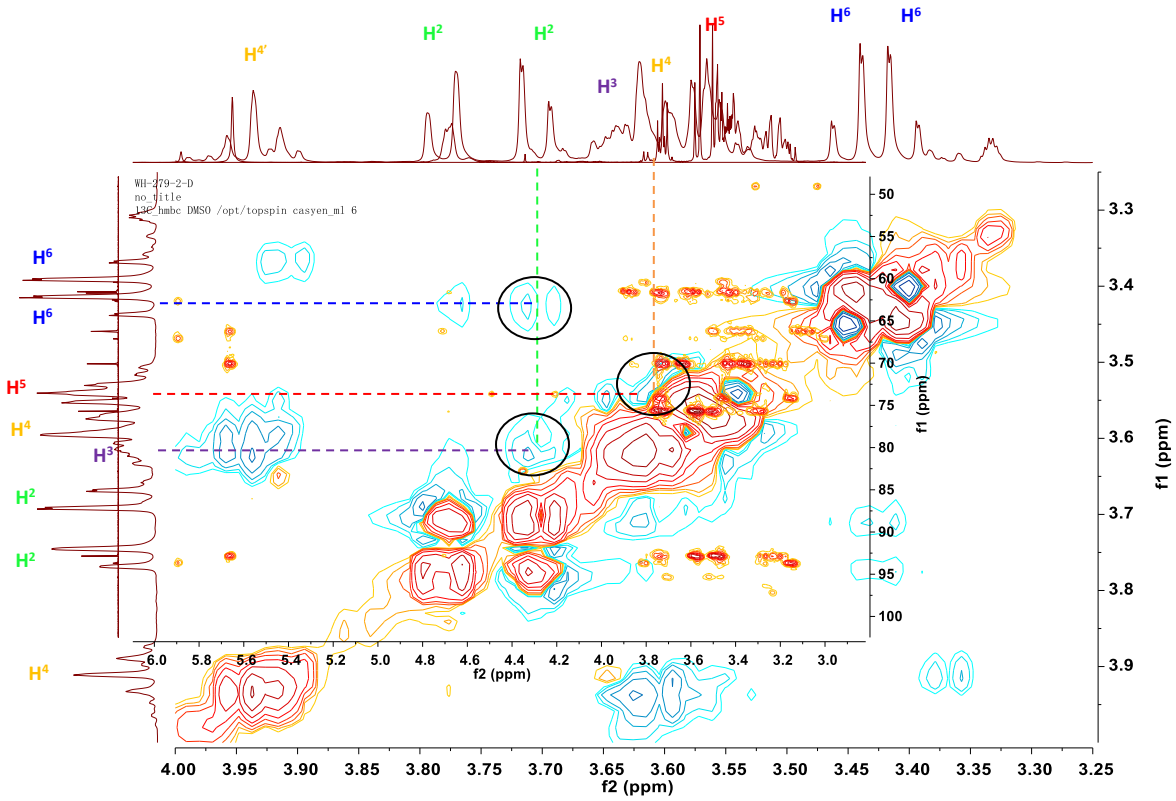




NOESY of **7** (CD_3OD, 500 Hz) Zoom 3.25-4.00 ppm



H^2-H^3	Yes
H^2-H^6	Yes
H^5-H^4	Yes
H^5-H^2	No



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