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# Supporting Information

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## A Fluorescence Polarization Activity-Based Protein Profiling Assay in the Discovery of Potent, Selective Inhibitors for Human Non-lysosomal Glucosylceramidase

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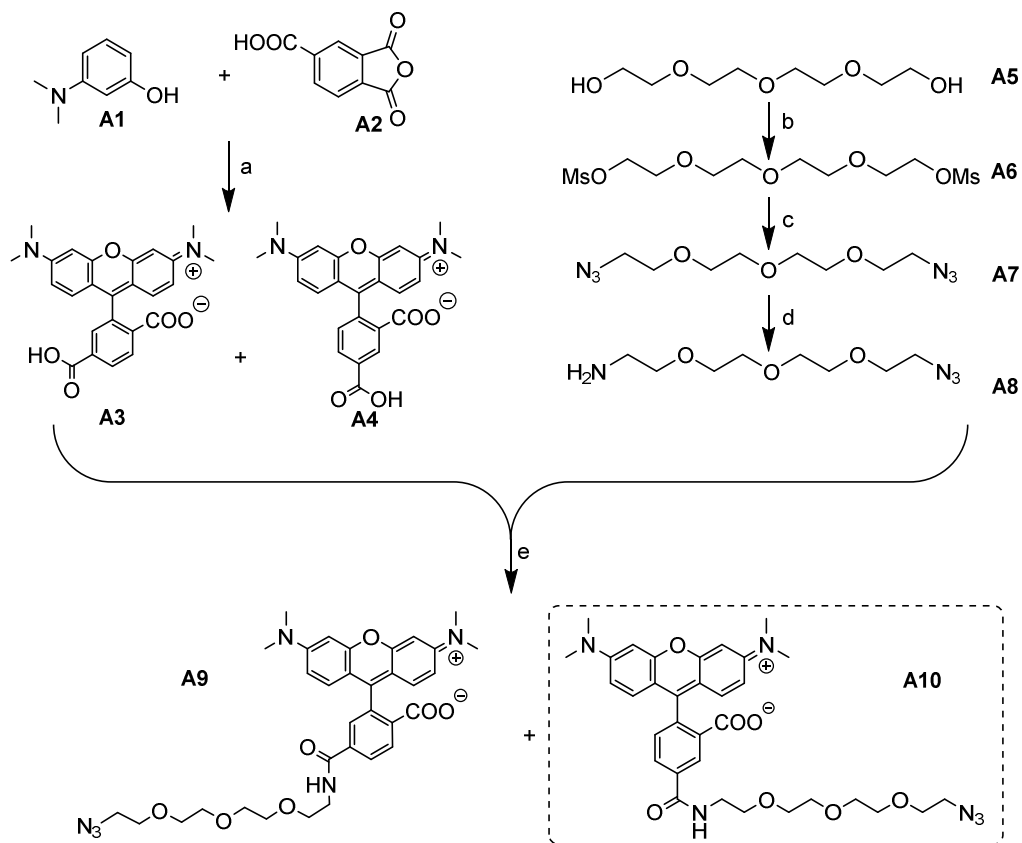
## S1. Chemistry - General Information

### Chemicals, materials and methods

All solvents and reagents were obtained commercially and used as received unless stated otherwise. Dichloromethane (DCM), dimethylformamide (DMF), tetrahydrofuran (THF) and methanol (MeOH) were dried over molecular sieves (4Å/3Å) for at least 12 hours before use. Moisture sensitive reactions were performed under argon atmosphere and carried out in oven dried glassware. Reactions were monitored by TLC analysis using sheets with pre-coated silica with detection by UV-absorption (254 nm) wherever applicable and by spraying with 20% H<sub>2</sub>SO<sub>4</sub> in MeOH, an aqueous solution containing KMnO<sub>4</sub> (5 g/L) and K<sub>2</sub>CO<sub>3</sub> (95 g/L) or a solution of ninhydrine (6 g/L) in AcOH:MeOH (1:9, v/v) followed by charring at ≈ 200°C. Flash column chromatography was performed on silica gel (40-63 μm). For LC/MS analysis a HPLC-system (detection simultaneously at 213 nm, 254 nm and evaporative light detection) equipped with an analytical C-18 column (4.6 mmD × 250 mmL, 5 μm particle size) in combination with buffers A: H<sub>2</sub>O, B: acetonitrile, C: 1.0% aqueous trifluoroacetic acid and coupled with an electrospray interface (ESI) was used. For RP-HPLC purifications, an automated HPLC system equipped with a semi-preparative S2 C18 column (5 μm C18, 10Å, 150 × 21.2 mm) was used. The applied buffers were A: H<sub>2</sub>O + trifluoroacetic acid (1%) and B: MeCN. HPLC-MS purification was performed on an Agilent Technologies 1200 series automated HPLC system with a Quadropole MS 6130, equipped with a semi-preparative Gemini C18 column (Phenomex, 250 × 10, 5 μm) using buffers A: H<sub>2</sub>O + K<sub>2</sub>CO<sub>3</sub> (1%) and B: MeCN. Compounds are characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, COSY and HSQC NMR experiments. NMR spectra were recorded on a Bruker DPX-300, DMX-400, AV-400, AV-600 and AV-850 spectrometer in mentioned solvent. Chemical shifts are given in ppm (δ) relative to tetramethylsilane or the deuterated solvent as the internal standard. High resolution mass spectra were recorded by direct injection (2 μL of a 2 μM solution in water/acetonitrile/*tert*-butanol, 1:1:1, v/v) on a mass spectrometer (Thermo Finnigan LTQ Orbitrap) equipped with an electrospray ion source with resolution R = 60000 at m/z 400 (mass range m/z = 150-2000). IR spectra were recorded on a Shimadzu FTIR-8300 fitted with a single bounce Durasample IR diamond crystal ATR-element and are reported in cm<sup>-1</sup>. Optical rotation were measured on an automatic polarimeter of sodium D-line, at λ = 589 nm. Size-exclusion purifications were performed on an ÄKTA-explorer provided by GE-Healthcare (polymere HW-40S from Toyopearl. The column used, had a d = 26 mm; l = 60 mm and the eluents used was NH<sub>4</sub>HCO<sub>3</sub> (0.15 M) in H<sub>2</sub>O, with a flow of 1.5 mL/min.

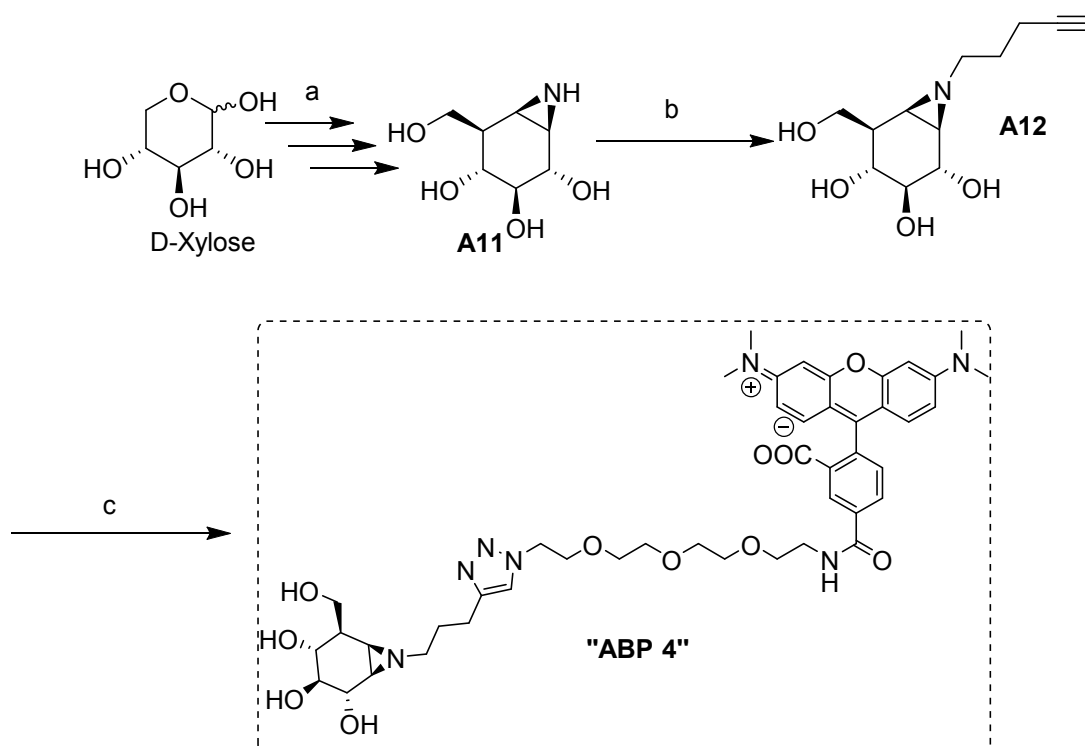
## S2. Synthesis and Characterization of ABP 4

Reaction between dimethylaminophenol **A1** and trimellitic anhydride **A2** in acetic acid as solvent using a catalytic amount of sulfuric acid produced stereoisomers **A3** and **A4**. Synthesis of the polyethylene-glycol-(PEG)-linker was obtained from di-alcohol **A5** through subsequent mesylation, azide formation, and (selective) reductive amination. Overall yield for the synthesis of linker **A8** was 33% over three steps. **A8** was attached to stereoisomers **A3** and **A4** in the presence of BOP.PF<sub>6</sub> and *N,N*-diisopropylethylamine (DIPEA), affording a mixture containing **A9** and **A10**. Desired product **A10**, 5-TAMRA-PEG3-azide, was isolated (2%) using HPLC (scheme S1).



**Scheme S1:** Synthesis of 5-TAMRA-PEG3-azide [a] cat. H<sub>2</sub>SO<sub>4</sub> in AcOH under reflux; [b] MsCl, Et<sub>3</sub>N in THF, 45%; [c] NaN<sub>3</sub> in DMF under reflux, 95%; [d] PPh<sub>3</sub> in 5% HCl (aq), 77%; [e] BOP.PF<sub>6</sub>, DIPEA in DMSO, 2% over two steps

Synthesis of gluco-aziridine **A11** from the D-xylose was afforded according to experimental procedures described by Madsen et al.<sup>1</sup> and Kallemeijn et al.<sup>2</sup> Crude aziridine **A11** was alkylated using iodo-pentyne and sodium bicarbonate. Copper(I)-catalyzed azide-alkyne cycloaddition of 5-TAMRA-PEG3-azide **A10** with **A12** provided “**ABP 4**” (scheme S2).



**Scheme S2:** Synthetic route towards gluco-cyclophellitol aziridine-type **ABP4**, [a] synthesis of **A11** described in references 1 and 2; [b] 5-iodo-pentyne, NaHCO<sub>3</sub> in DMF; [c] **A10**, sodium ascorbate, CuSO<sub>4</sub> in H<sub>2</sub>O, 6% over three steps

**((oxybis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl) dimethanesulfonate (**A6**)**

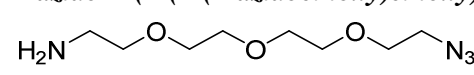
A mixture of triethylamine (11.2 g, 110 mmol, 2.2 eq.) in THF (10 mL) was added dropwisely at 0°C into a mixture containing tetra-ethylene glycol (9.7 g, 50 mmol) and mesylchloride (12.6 g, 110 mmol, 2.2 eq.) dissolved in dry THF (50 mL). After 30 minutes the cooling bath was removed and the reaction was stirred for 4 more hours at ambient temperature. THF was removed under reduced pressure. Subsequently a mixture H<sub>2</sub>O (100 mL), aqueous HCl (100 mL, 1 M) and DCM (200 mL) was poured into the residue. The organic layer was washed with saturated bicarbonate (3 × 100 mL), dried with MgSO<sub>4</sub> and filtrated. Purification via flash column chromatography (DCM → 5% MeOH/DCM) afforded **A6** (7.943 g, 22.62 mmol, 45%) as a brown oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 4.27 - 4.14 (m, 4H), 3.66 - 3.57 (m, 4H), 3.50 (s, 8H), 2.93 (s, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 70.1, 69.3, 68.5, 37.1. HRMS: found 351.0773 [M+H]<sup>+</sup>, calculated for [C<sub>10</sub>H<sub>22</sub>O<sub>9</sub>S<sub>2</sub>+H]<sup>+</sup> 351.0778.

**1-azido-2-(2-(2-(2-azidoethoxy)ethoxy)ethoxy)ethane (**A7**)**

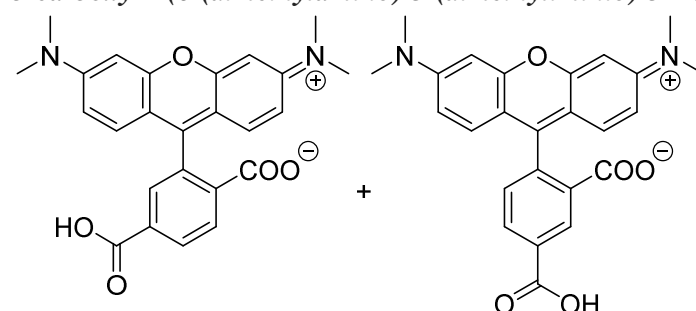
A mixture of **A6** (7.1 g, 20 mmol) with sodium azide (5.3 g, 82 mmol, 4 eq.) in absolute ethanol (40 mL) and DMF (10 mL) was refluxed overnight. This mixture was poured into a mixture of H<sub>2</sub>O/DCM (200 mL, 1:1, v/v). The organic layer was washed subsequently with H<sub>2</sub>O (3 × 100 mL) and brine (3 × 100 mL). The organic layer was dried over MgSO<sub>4</sub> and filtered. A yellow oil (4.7 g, 19 mmol, 95%) was obtained after removing the solvents under reduced pressure. R<sub>F</sub> = 0.85 (MeOH:DCM, 1:9, v/v). <sup>1</sup>H NMR (300

MHz, CDCl<sub>3</sub>) δ 3.62 - 3.54 (m, 12H), 3.36 - 3.23 (m, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 70.6, 70.0, 50.6. HRMS: found 245.1358 [M+H]<sup>+</sup>, calculated for [C<sub>8</sub>H<sub>16</sub>O<sub>3</sub>N<sub>6</sub>+H]<sup>+</sup> 245.1357.

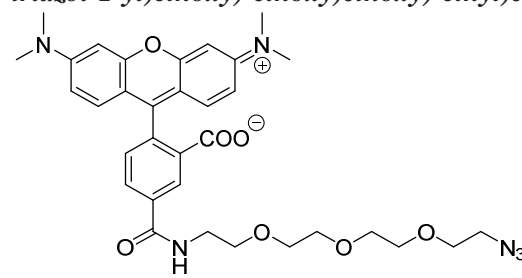
**1-azido-2-(2-(2-(2-azidoethoxy)ethoxy)ethoxy)ethane (A8)**

 Triphenylphosphine (0.8 g, 3 mmol, 0.9 eq.) dissolved in ether (15 mL) was added into a solution of **A7** (0.8 g, 3.3 mmol) in 5% aqueous HCl (10 mL). Addition was performed in 30 minutes at room temperature and the reaction was stirred for an additional 2.5 hours. Phases were separated using a separation funnel and the aqueous layer was washed using DCM (3 × 25 mL). The aqueous layer was adjusted to pH 10 using KOH pellets. Product was extracted with DCM (4 × 50 mL). Combined organic layers were dried over MgSO<sub>4</sub> and filtered. After removal of the organic solvents under reduced pressure a yellow oil (4.7 g, 19 mmol, 77%) was afforded. *R*<sub>F</sub> = 0.2 (MeOH:DCM, 1:9, v/v). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 3.73 - 3.49 (m, 10H), 3.45 (t, *J* = 5.2 Hz, 2H), 3.36 - 3.28 (m, 2H), 2.80 (t, *J* = 5.1 Hz, 2H), 1.44 (s, 2H). <sup>13</sup>C NMR (75 MHz, D<sub>2</sub>O) δ 73.5, 70.7 - 70.1, 50.8, 41.9. HRMS: found 219.1452 [M+H]<sup>+</sup>, calculated for [C<sub>8</sub>H<sub>16</sub>O<sub>3</sub>N<sub>4</sub>+H]<sup>+</sup> 219.1452.

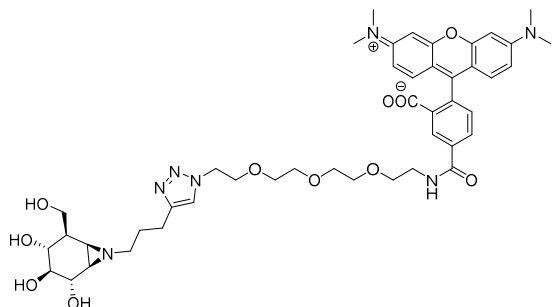
**5-carboxy-2-(6-(dimethylamino)-3-(dimethyliminio)-3H-xanthen-9-yl)benzoate (A3& A4)**

 Dimethylaminophenol (6.9 g, 50 mmol) and trimellitic anhydride (4.8 g, 25 mmol) were dissolved in AcOH (400 mL). After adding a catalytic amounts of concentrated H<sub>2</sub>SO<sub>4</sub> (ca. 0.5 mL) the mixture was refluxed overnight. Reaction mixture was concentrated under reduced pressure and pre-purified over column chromatography (DCM → 50% MeOH/DCM) to isolate 2.7 g of a mixture containing desired of regio-isomers.

**2-(6-(dimethylamino)-3-(dimethyliminio)-3H-xanthen-9-yl)-5-((2-(2-(2-(2-(4-(3-((1*R*,2*S*,3*S*,4*R*,5*R*,6*R*)-2,3,4-trihydroxy-5-(hydroxymethyl)-7-azabicyclo[4.1.0]heptan-7-yl)propyl)-1*H*-1,2,3-triazol-1-yl)ethoxy)-ethoxy)ethoxy)-ethyl)carbamoyl)benzoate (A10)**

 BOP.PF6 (74 mg, 0.168 mmol) and DIPEA (54 μL, 0.31 mmol) were added into a mixture containing isomers **A3** and **A4** (60 mg) and linker **A8** (30 mg, 0.14 mmol) dissolved in DMSO (2 mL). The reaction was stirred for 24 hours at ambient temperature. Desired stereoisomeric product **A10** (7.41 mg, 11.7 μmol, 2% estimated yield over two steps) was isolated using HPLC purification. <sup>1</sup>H NMR (600 MHz, MeOD) δ 8.79 (d, *J* = 1.7 Hz, 1H), 8.31 - 8.25 (m, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.15 (d, *J* = 9.5 Hz, 2H), 7.07 (dd, *J* = 9.5, 2.5 Hz, 2H), 7.00 (d, *J* = 2.4 Hz, 2H), 3.77 - 3.60 (m, 14H), 3.35 - 3.33 (m, 2H), 3.32 (s, 12H). <sup>13</sup>C NMR (150 MHz, MeOD) δ 168.6, 167.7, 161.0, 159.4, 159.3, 138.4, 138.0, 133.2, 132.7, 132.2, 132.2, 131.7, 115.9, 115.0, 97.8, 72.0 - 70.8, 52.0, 49.9, 41.5, 41.2. HRMS: found 631.2877 [M+H]<sup>+</sup>, calculated for [C<sub>33</sub>H<sub>38</sub>O<sub>7</sub>N<sub>6</sub>+H]<sup>+</sup> 631.2875.

**2-(6-(dimethylamino)-3-(dimethyliminio)-3H-xanthen-9-yl)-5-((2-(2-(2-(2-(4-(3-((1R,2S,3S,4R,5R,6R)-2,3,4-trihydroxy-5-(hydroxymethyl)-7-azabicyclo[4.1.0]heptan-7-yl)propyl)-1H-1,2,3-triazol-1-yl)ethoxy)ethoxy)ethoxy)ethyl)carbamoyl)benzoate (ABP4)**

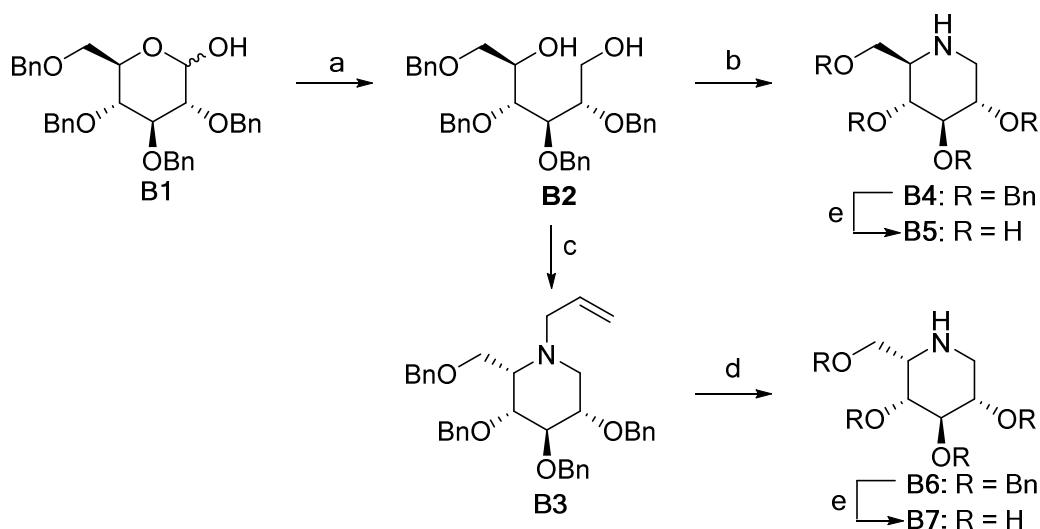


Sodium bicarbonate (4.8 mg, 57  $\mu\text{mol}$ ) and iodo-pentyne (2.9 mg, 15  $\mu\text{mol}$ ) were added into a roundbottomflask containing crude aziridine **A11** (5 mg) dissolved in dry DMF (0.5 mL). The reaction was stirred for 24h at ca. 60°C. The volatiles were removed under reduced pressure, the residue was dissolved in water (10 mL) and washed with DCM (3  $\times$  10 mL) and EtOAc (3  $\times$  10 mL). The aqueous layer was concentrated under reduced pressure. The residue containing compound **A12** was redissolved in H<sub>2</sub>O

(0.5 mL). Sodium ascorbate and CuSO<sub>4</sub> (5  $\mu\text{L}$  of 1 M solution) were added into the aqueous solution containing **A12**. After the mixture turned yellow-green TAMRA **A10** (1.25 mg, 1.98  $\mu\text{mol}$  dissolved in 1.5 mL H<sub>2</sub>O) was added. The reaction was completed after 3 days according to LC/MS analysis. Solvents were evaporated and product **ABP4** (1.457 mg, 1.670  $\mu\text{mol}$ , 6% yield over three steps) was isolated as a purple solid after HPLC-purification.  $R_F = 0.1$  (MeOH:DCM, 1:3, v/v). <sup>1</sup>H NMR (600 MHz, MeOD)  $\delta$  8.56 (s, 1H), 8.07 (d,  $J = 7.9$  Hz, 1H), 7.81 (s, 1H), 7.38 (d,  $J = 7.9$  Hz, 1H), 7.26 (d,  $J = 9.5$  Hz, 2H), 7.04 (d,  $J = 9.5$  Hz, 2H), 6.96 (s, 2H), 4.60 (s, 2H), 4.52 (t,  $J = 5.1$  Hz, 2H), 4.00 (dd,  $J = 10.1, 4.4$  Hz, 1H), 3.88 (t,  $J = 5.1$  Hz, 2H), 3.74 (t,  $J = 5.3$  Hz, 2H), 3.72 - 3.60 (m, 14H), 3.31 (d,  $J = 3.7$  Hz, 12H), 3.12 (dd,  $J = 9.9, 8.2$  Hz, 1H), 3.03 (t,  $J = 9.8$  Hz, 1H), 2.81 - 2.71 (m, 2H), 2.45 - 2.37 (m, 1H), 2.24 - 2.16 (m, 1H), 2.03 - 1.99 (m, 1H), 1.96 - 1.85 (m, 3H), 1.61 (d,  $J = 12.0$  Hz, 1H). <sup>13</sup>C NMR (150 MHz, MeOD)  $\delta$  169.2, 169.0, 162.9, 159.0, 158.7, 137.0, 136.9, 132.8, 132.6, 130.8, 129.5, 129.5, 124.1, 115.0, 114.8, 102.0, 97.3, 79.0, 74.0, 71.6 - 70.4, 70.14, 63.7, 61.2, 51.3, 49.8, 49.6, 45.5, 45.5, 43.1, 41.2, 40.8, 30.2, 24.1. HRMS: found 872.4184 [M+H]<sup>+</sup>, calculated for [C<sub>45</sub>H<sub>57</sub>O<sub>11</sub>N<sub>7</sub>+H]<sup>+</sup> 872.4189.

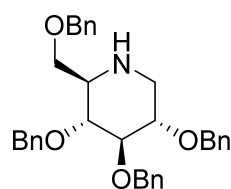
### S3. Synthetic Procedure and Spectral Data of Second Generation Deoxynojirimycins

#### Synthesis of *D*-gluco and *L*-ido Deoxynojirimycins



**Scheme S3:** Synthesis of 1-deoxynojirimycin and *L*-ido-1-deoxynojirimycin [a]  $\text{LiAlH}_4$ , THF; [b]  $(\text{COCl})_2$ , DMSO, DCM,  $\text{CHOONH}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaBH}_3\text{CN}$ , MeOH, 12% 2 steps; [c]  $\text{MsCl}$ , pyridine, allyl amine, reflux, 78% 2 steps; [d]  $\text{KOtBu}$ , DMSO, HCl, 92%; [e]  $\text{Pd/C}$ ,  $\text{H}_2$ , 82% (**B5**), 76% (**B7**).

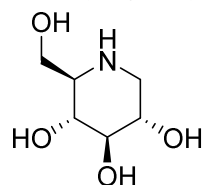
#### 2,3,4,6-Tetra-*O*-benzyl-1-deoxynojirimycin (**B4**)



A solution of  $(\text{COCl})_2$  (0.70 mL, 8.16 mmol) in dry DCM (5 mL) under argon atmosphere, was cooled to  $-78^\circ\text{C}$ . DMSO (0.71 mL, 10.0 mmol) dissolved in dry DCM (5 mL) was added dropwise. After 40 minutes **B2** (1.02 g, 1.88 mmol), which was co-evaporated 3 times with toluene, in dry DCM (3 mL), was added dropwise to the mixture. The reaction was stirred for 2 hours at  $-78^\circ\text{C}$ , after which  $\text{Et}_3\text{N}$  (3.40 mL, 24.4 mmol) was added dropwise to quench the reaction.

The mixture was gradually warmed to  $-5^\circ\text{C}$  after which it was poured into a cooled ( $0^\circ\text{C}$ ) MeOH solution (50 mL) of  $\text{NaCNBH}_3$  (0.503 g, 8.00 mmol),  $\text{HCOONH}_4$  (2.53 g, 40.1 mmol), and  $\text{Na}_2\text{SO}_4$  (0.887 g, 6.24 mmol). The mixture was stirred overnight allowing the temperature to reach rt. TLC analysis showed complete consumption of the starting material (PE:EtOAc = 1:1,  $R_F$  = 0.36). After filtration, the solvent was evaporated, as the residue was dissolved in EtOAc (70 mL), washed with sat aq.  $\text{NaHCO}_3$  solution (70 mL). The organic layer was dried over  $\text{Na}_2\text{SO}_4$  and after filtration and concentration, the residue was purified with silica gel column (2:1  $\rightarrow$  1:2, PE:EtOAc) to give the pure product **B4** in 12% overall yield (0.114 g, 0.218 mmol).  $R_F$  = 0.36 (1:1, PE:EtOAc).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 - 7.22 (m, 20H), 5.09 (d,  $J$  = 10.9 Hz, 1H), 4.96 (t,  $J$  = 10.4 Hz, 2H), 4.82 - 4.72 (m, 2H), 4.65 - 4.48 (m, 3H), 3.77 (dd,  $J$  = 9.0, 2.6 Hz, 1H), 3.71 - 3.56 (m, 3H), 3.47 (t,  $J$  = 9.2 Hz, 1H), 3.35 (dd,  $J$  = 12.3, 4.9 Hz, 1H), 2.83 (ddd,  $J$  = 9.8, 5.8, 2.6 Hz, 1H), 2.61 (dd,  $J$  = 12.3, 10.2 Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  138.9, 138.5, 138.4, 138.0, 128.4, 128.4, 128.4, 128.4, 128.0, 128.0, 127.9, 127.8, 127.8, 127.7, 127.7, 127.5, 87.3, 80.6, 80.1, 75.7, 75.2, 73.4, 72.8, 70.2, 59.7, 48.1.

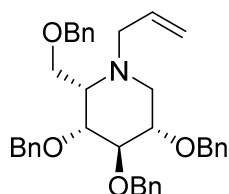
#### 1-deoxynojirimycin (**B5**)



**B4** (2.00 g, 3.82 mmol) was dissolved in EtOH (120 mL) and pH was adjusted to 2 with HCl solution (1 M). The solution was flushed with argon for 3 times, after which two spatula tips of  $\text{Pd/C}$  (20%) was added. Then the solution was exposed to

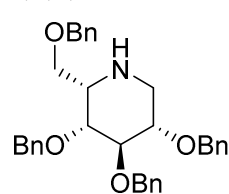
H<sub>2</sub> atmosphere (4 bar) for 24 hours. The product was purified on silica gel column (4:1, EtOAc:MeOH + 1% NH<sub>4</sub>OH → 6:4:1, EtOH:H<sub>2</sub>O:NH<sub>4</sub>OH) to give the **B5** in 82% yield (511 mg, 3.13 mmol). <sup>1</sup>H NMR (400 MHz, MeOD) δ 3.92 (dd, *J* = 10.9, 3.1 Hz, 1H), 3.68 (dd, *J* = 10.9, 6.5 Hz, 1H), 3.57 - 3.44 (m, 1H), 3.34 - 3.21 (m, 2H), 3.18 (dd, *J* = 12.1, 5.1 Hz, 1H), 2.68 - 2.42 (m, 2H). <sup>13</sup>C NMR (100 MHz, MeOD) δ 81.5, 74.2, 73.4, 63.9, 63.7, 51.9.

### 2,3,4,6-Tetra-*O*-benzyl-*L*-ido-*N*-allyl-1-deoxynojimycin (**B3**)



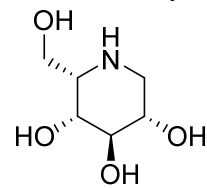
MsCl (4.2 mL, 53.1 mmol) was added dropwise to a cooled solution (0°C) of pyridine (90 mL) and **B2** (11.5 g, 21.2 mmol) was kept under argon atmosphere. The mixture was stirred for 3 hours at r.t., after which TLC analysis (2:1, PE:EtOAc, *R<sub>F</sub>* = 0.13) showed complete consumption of the starting material. Water (60 mL) was added and the solution was concentrated. Then after adding EtOAc (130 mL) it was washed with HCl (100 mL, 1M, 2 times), sat. aq. NaHCO<sub>3</sub> (100 mL) and brine (100 mL) successively. The organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and concentrated, and then it was co-evaporated 3 times with toluene. Allylamine (90 mL) was added to dissolve the methanesulfonylated product, and the solution was heated to reflux for 14 hours. The reaction was then stirred for 2 more hours at rt until TLC analysis (2:1, PE:EtOAc) showed complete consumption of the starting material. After concentrating, EtOAc (110 mL) was added and was washed with sat aq. NaHCO<sub>3</sub> (100 mL, 2 ×) and brine (100 mL). The organic layer was dried on Na<sub>2</sub>SO<sub>4</sub> and after filtering and concentrating, the residue was purified on silica gel column (17:3, PE:EtOAc) to give **B3** in 78% yield (9.30 g, 16.5 mmol). *R<sub>F</sub>* = 0.76 (2:1, PE:EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.33 - 7.23 (m, 20H), 5.77 (ddt, *J* = 16.8, 10.3, 6.3 Hz, 1H), 5.12 (dd, *J* = 23.6, 6.2 Hz, 2H), 4.90 - 4.46 (m, 8H), 3.84 (dd, *J* = 10.2, 6.8 Hz, 1H), 3.72 (dd, *J* = 10.2, 2.5 Hz, 1H), 3.69 (dd, *J* = 7.6, 4.2 Hz, 1H), 3.60 - 3.50 (m, 2H), 3.42 (ddd, *J* = 10.1, 5.8, 1.6 Hz, 1H), 3.37 (dd, *J* = 6.9, 2.0 Hz, 1H), 3.18 (dd, *J* = 14.1, 6.9 Hz, 1H), 2.92 (dd, *J* = 11.9, 4.9 Hz, 1H), 2.53 (dd, *J* = 11.8, 9.8 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 139.3, 138.8, 138.7, 138.6, 136.3, 128.5, 117.2, 83.1, 80.3, 78.9, 75.5, 73.4, 73.1, 72.8, 64.8, 60.1, 58.1, 49.2.

### 2,3,4,6-Tetra-*O*-benzyl-*L*-ido-1-deoxynojirimycin (**B6**)



A mixture of DMSO (35 mL), tBuOK (1.00 g, 8.91 mmol) and **B3** (9.30 g, 16.5 mmol), which was co-evaporated 3 times with toluene, were stirred and heated to 100°C under argon atmosphere. After 1 hour stirring, HCL solution (30 mL, 1M) was added and the heating resource was removed. After 30 minutes, the mixture was poured into sat aq. NaHCO<sub>3</sub> (100 mL). Sat aq. NaHCO<sub>3</sub> (200 mL) and Et<sub>2</sub>O (150 mL) was added to the reaction mixture and the organic layer were separated. The water layer was re-extracted with Et<sub>2</sub>O (150 mL, 2 ×) and the combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>) filtered and concentrated. The residue was purified with silica gel column (2:1 → 1:2 → 0:1, PE:EtOAc) to give the pure product **B6** with a yield of 92% (7.93 g, 15.1 mmol). *R<sub>F</sub>* = 0.13 (1:1, PE:EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.54 - 7.17 (m, 20H), 4.69 - 4.43 (m, 8H), 3.82 (t, *J* = 5.2 Hz, 1H), 3.69 - 3.54 (m, 3H), 3.50 (q, *J* = 4.7 Hz, 1H), 3.31 (td, *J* = 6.8, 3.6 Hz, 1H), 3.01 (dd, *J* = 13.5, 3.6 Hz, 1H), 2.94 (dd, *J* = 13.5, 5.1 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 140.7, 140.6, 140.5, 140.4, 130.3, 130.2, 130.1, 129.9, 129.8, 129.6, 129.6, 129.5, 77.6, 77.0, 75.3, 75.1, 74.4, 73.6, 56.4, 46.4.

### *L*-Ido-1-deoxynojimycin (**B7**)



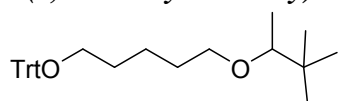
**B6** (2.30 g, 4.39 mmol) was dissolved in EtOH (150 mL) and pH was adjusted to 2 with HCl solution (1 M). The solution was flushed with argon for 3 times, after which two spatula tips of Pd/C (20%) was added. Then the solution was exposed to H<sub>2</sub> atmosphere (4 bar) for 24 hours. The product was purified with silica gel column (4:1, EtOAc:MeOH + 1% NH<sub>4</sub>OH → 6:4:1, EtOH:H<sub>2</sub>O:NH<sub>4</sub>OH) to give the **B7** in 76% yield (840 mg, 3.32 mmol). <sup>1</sup>H NMR (400 MHz, MeOD) δ 3.94 (ddd, *J* = 6.5, 3.9, 2.6 Hz, 2H), 3.89 (dd, *J* = 5.7, 2.0 Hz, 1H), 3.85 (dd, *J* = 11.0, 2.1 Hz, 1H), 3.81 (dd, *J* = 11.7, 5.1 Hz, 1H), 3.51 (ddd, *J* = 8.9, 5.0, 1.9 Hz, 1H), 3.41 (dd, *J* = 13.2, 2.0 Hz, 1H), 3.27 (dd, *J* = 13.2, 1.7 Hz, 1H). <sup>13</sup>C NMR (100 MHz, MeOD) δ 70.1, 69.2, 68.7, 61.5, 59.1, 47.9.





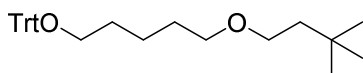
2H), 1.44 (ddd,  $J = 8.9, 7.5, 4.3$  Hz, 2H), 0.90 (s, 3H), 0.88 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.6, 128.8, 127.7, 126.9, 86.4, 77.9, 71.0, 63.6, 30.0, 29.7, 28.5, 23.1, 19.5. IR/ $\text{cm}^{-1}$ : 3061, 2930, 2901, 2866, 1597, 1489, 1448, 1392, 1364, 1176, 1072, 902.

#### 5-(3,3-dimethyl-2-butoxy)-1-trityloxypentane (B15)



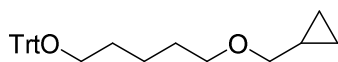
Compound **B10** (4.43 mmol) was subjected to general procedure A, using 3,3-dimethyl-2-butanol (5.06 mmol) to provide **B15** (0.95 g, 2.21 mmol) in a 50% yield, as thick oil, after silica gel column purification.  $R_F = 0.79$  (5% EtOAc in PE).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 - 7.36 (m, 6H), 7.28 - 7.11 (m, 12H), 3.53 (dt,  $J = 9.4, 5.8$  Hz, 1Ha), 3.21 (dd,  $J = 9.2, 6.2$  Hz, 1H), 3.06 (t,  $J = 6.6$  Hz, 2H), 2.93 (q,  $J = 6.3$  Hz, 1H, H-6), 1.74 - 1.35 (m, 6H), 1.01 (d,  $J = 6.3$  Hz, 3H), 0.87 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.7, 129.1, 127.9, 127.0, 86.5, 83.4, 69.9, 63.8, 35.3, 30.3, 26.2, 23.4, 14.2. IR/ $\text{cm}^{-1}$ : 3059, 3022, 2936, 2866, 1597, 1489, 1448, 1389, 1362, 1219, 1090, 1072, 899.

#### 5-(3,3-dimethyl-1-butoxy)-1-trityloxypentane (B16)



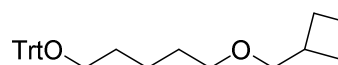
Compound **B10** (4.41 mmol) was subjected to general procedure A, using 3,3-dimethyl-1-butanol (5.07 mmol) to provide **B16** (1.02 g, 2.36 mmol) in a 54% yield, as thick oil, after silica gel column purification.  $R_F = 0.67$  (5% EtOAc in PE).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (dt,  $J = 8.3, 2.2$  Hz, 6H), 7.25 - 7.16 (m, 6H), 7.16 - 7.10 (m, 3H), 3.41 (t,  $J = 7.4$  Hz, 2H), 3.34 (t,  $J = 6.4$  Hz, 2H), 3.06 (td,  $J = 6.9, 3.0$  Hz, 2H), 1.63 (p,  $J = 6.8$  Hz, 2H), 1.52 (q,  $J = 7.2$  Hz, 4H), 1.48 - 1.38 (m, 2H), 0.90 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.7, 128.9, 127.9, 127.0, 71.0, 68.3, 63.7, 43.2, 30.1, 29.8, 23.3. IR/ $\text{cm}^{-1}$ : 3057, 3022, 2936, 2864, 1597, 1489, 1448, 1364, 1219, 1111, 1072, 899.

#### 5-(cyclopropylmethoxy)-1-trityloxypentane (B17)



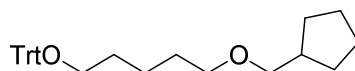
Compound **B10** (4.41 mmol) was subjected to general procedure A, using cyclopropylmethanol (5.02 mmol) to provide **B17** (0.10 g, 2.49 mmol) in a 56% yield, as thick oil, after silica gel column purification.  $R_F = 0.63$  (10% EtOAc in PE).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 - 7.41 (m, 6H, Trt), 7.28 - 7.19 (m, 6H), 7.20 - 7.13 (m, 3H), 3.38 (t,  $J = 6.6$  Hz, 2H), 3.20 (d,  $J = 6.9$  Hz, 2H), 3.06 (t,  $J = 6.6$  Hz, 2H), 1.65 (p,  $J = 6.8$  Hz, 2H), 1.55 (dq,  $J = 8.9, 6.3$  Hz, 2H), 1.47 - 1.38 (m, 2H), 1.08 - 0.97 (m, 1H), 0.52 - 0.45 (m, 2H), 0.16 (dt,  $J = 6.0, 4.5$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.6, 128.8, 127.8, 126.9, 86.4, 75.7, 70.7, 63.7, 30.1, 29.8, 23.1, 10.9, 3.2. IR/ $\text{cm}^{-1}$ : 3082, 3057, 3022, 2933, 2862, 1732, 1597, 1489, 1448, 1382, 1219, 1087, 1074, 899.

#### 5-(cyclobutylmethoxy)-1-trityloxypentane (B18)



Compound **B10** (4.40 mmol) was subjected to general procedure A, using cyclobutylmethanol (5.01 mmol) to provide **B18** (0.79 g, 1.91 mmol) in a 43% yield, as thick oil, after silica gel column purification.  $R_F = 0.74$  (10% EtOAc in PE).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 - 7.43 (m, 6H) 7.22 - 7.17 (m, 6H), 7.14 - 7.10 (m, 3H), 3.37 - 3.32 (m, 4H), 3.07 (t, 2H), 2.56 - 2.49 (m, 1H), 2.04 - 1.97 (m, 2H), 1.86 - 1.79 (m, 2H), 1.75 - 1.40 (m, 8H,  $\text{H}_2$ -2).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.6, 128.8, 127.8, 126.9, 86.4, 75.5, 71.0, 63.6, 60.3, 35.3, 29.7, 25.2, 23.1, 18.8. IR/ $\text{cm}^{-1}$ : 3084, 3059, 2934, 2862, 1597, 1489, 1448, 1363, 1219, 1111, 1072, 898.

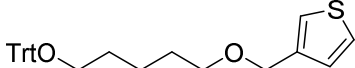
#### 5-(cyclopentylmethoxy)-1-trityloxypentane (B19)



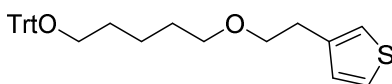
Compound **B10** (4.43 mmol) was subjected to general procedure A, using cyclopentylmethanol (5.09 mmol) to provide **B19** (1.29 g, 3.02 mmol) in a 68% yield, as thick oil after silica gel column purification.  $R_F = 0.77$  (10% EtOAc in PE).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (m, 6H), 7.18 - 7.06 (m, 9H), 3.39 - 3.29 (m, 2H), 3.21 (dd,  $J = 7.0, 1.0$  Hz, 2H), 3.05 (dt,  $J = 11.1, 6.5$  Hz, 2H), 2.10 (q,  $J = 7.4$  Hz, 1H), 1.74 - 1.57 (m, 4H), 1.57 - 1.36 (m, 8H), 1.31 - 1.17 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.4 -

125.6, 75.2, 70.6, 63.3, 38.4, 29.4, 28.7, 25.3, 25.1, 22.8. IR/cm<sup>-1</sup> : 3084, 3057, 3022, 2939, 2864, 1597, 1489, 1448, 1367, 1176, 1072.

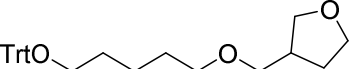
#### 5-(thiophen-3-methoxy)-1-trityloxypentane (**B20**)

 Compound **B10** (4.56 mmol) was subjected to general procedure A, using 3-thiophenmethanol (4.57 mmol) to provide **B20** (0.73 g, 2.13 mmol) in a 56% yield, as thick oil, after silica gel column purification.  $R_F = 0.79$  (15% EtOAc in PE). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45 - 7.38 (m, 6H), 7.28 - 7.20 (m, 6H), 7.20 - 7.14 (m, 3H), 7.12 (dq,  $J = 3.0, 1.0$  Hz, 1H), 7.04 (dd,  $J = 4.9, 1.3$  Hz, 1H), 7.02 (dd,  $J = 4.9, 1.3$  Hz, 1H), 4.44 (d,  $J = 0.8$  Hz, 2H), 3.40 (t,  $J = 6.5$  Hz, 2H), 3.05 (t,  $J = 6.6$  Hz, 2H), 1.70 - 1.49 (m, 4H), 1.51 - 1.36 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 144.6, 128.9, 127.9, 127.4, 127.0, 126.0, 122.6, 114.7, 86.5, 70.4, 68.3, 63.7, 30.0, 29.8, 23.1. IR/cm<sup>-1</sup> : 3501, 3088, 3059, 3024, 2938, 2864, 2316, 1734, 1448, 1364, 1242, 1068, 1034.

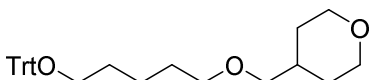
#### 5-(thiophen-3-ethoxy)-1-trityloxypentane (**B21**)

 Compound **B10** (4.56 mmol) was subjected to general procedure A, using 3-thiophenethanol (4.57 mmol) to provide **B21** (0.97 g, 1.65 mmol) in a 47% yield as oil after silica gel column purification.  $R_F = 0.70$  (10% EtOAc in PE). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.58 - 7.38 (m, 6H), 7.33 - 7.26 (m, 6H), 7.25 - 7.11 (m, 3H), 7.04 - 6.81 (m, 2H), 4.10 (q,  $J = 7.1$  Hz, 2H), 3.59 (t,  $J = 7.0$  Hz, 2H), 3.41 (t,  $J = 6.5$  Hz, 2H), 3.05 (t,  $J = 6.6$  Hz, 2H), 2.88 (t,  $J = 7.0$  Hz, 2H), 1.63 (q,  $J = 7.1$  Hz, 2H), 1.59 - 1.48 (m, 2H), 1.42 (qd,  $J = 7.3, 4.0$  Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 144.5, 128.8, 128.0, 127.8, 126.9, 125.2, 121.1, 114.6, 86.4, 71.1, 71.0, 63.6, 30.8, 29.9, 29.6, 23.0. IR/cm<sup>-1</sup> : 3524, 3086, 3057, 2934, 2862, 1738, 1717, 1489, 1447, 1387, 1364, 1242, 1159, 1113, 1069, 1034.

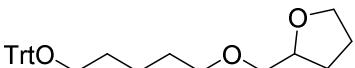
#### 5-(*R/S*-tetrahydrofuran-3-ylmethoxy)-1-trityloxypentane (**B11**)

 Compound **B10** (4.61 mmol) was subjected to General procedure A, using *R/S* tetrahydrofuran-3-ylmethanol (4.96 mmol) to provide **B11** (1.11 g, 2.58 mmol) in a 56% yield as oil after silica gel column purification.  $R_F = 0.40$  (15% EtOAc in PE). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.48 - 7.40 (m, 6H), 7.21 (dd,  $J = 8.5, 6.8$  Hz, 6H), 7.16 - 7.10 (m, 3H), 3.75 (ddd,  $J = 12.1, 8.3, 6.2$  Hz, 2H), 3.68 - 3.55 (m, 1H), 3.53 (dd,  $J = 8.7, 5.4$  Hz, 1H), 3.40 - 3.18 (m, 4H), 3.07 (t,  $J = 6.5$  Hz, 2H), 2.49 - 2.35 (m, 1H), 1.87 (ddt,  $J = 13.9, 8.1, 4.0$  Hz, 1H), 1.62 (p,  $J = 6.8$  Hz, 2H), 1.51 (m, 3H), 1.46 - 1.37 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 144.6, 128.8, 127.0, 86.4, 73.0, 71.1, 71.1, 67.8, 39.4, 30.0, 29.6, 29.2, 23.1. IR/cm<sup>-1</sup> : 3445, 2934, 2866, 2347, 1716, 1489, 1448, 1339, 1163, 1074.

#### 5-(tetrahydro-2H-pyran-4-ylmethoxy)-1-trityloxypentane (**B22**)

 Compound **B10** (4.68 mmol) was subjected to general procedure A, using tetrahydro-2H-pyran-4-ylmethanol (4.34 mmol) to provide **B22** (0.79 g, 1.78 mmol) in a yield of 38% as oil after silica gel column purification.  $R_F = 0.48$  (15% EtOAc in PE). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.50 - 7.38 (m, 6H), 7.29 - 7.12 (m, 11H), 3.90 (ddd,  $J = 11.5, 4.6, 1.8$  Hz, 2H), 3.39 - 3.26 (m, 4H), 3.20 (d,  $J = 6.5$  Hz, 2H), 3.06 (t,  $J = 6.5$  Hz, 2H), 1.89 - 1.71 (m, 1H), 1.70 - 1.57 (m, 4H), 1.57 - 1.47 (m, 2H), 1.47 - 1.38 (m, 2H), 1.35 - 1.25 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 144.5, 128.7, 127.7, 126.9, 86.4, 75.9, 71.1, 67.7, 63.5, 35.5, 30.1, 29.9, 29.6, 23.0. IR/cm<sup>-1</sup> : 3085, 3056, 3023, 2932, 2849, 1558, 1506, 1506, 1489, 1227, 1163, 1097.

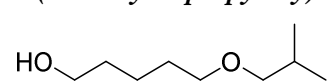
#### 5-(*R/S*-tetrahydrofuran-1-ylmethoxy)-1-trityloxypentane (**B23**)

 Compound **B10** (5.03 mmol) was subjected to general procedure A, using *R/S* tetrahydrofuran-1-ylmethanol (5.73 mmol) to provide **B23** (1.06 g, 2.46 mmol) in a yield of 49% as oil after silica gel column purification.  $R_F = 0.52$  (15% EtOAc in PE). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45 - 7.37 (m, 6H), 7.32 - 7.23 (m, 6H), 7.23 - 7.16 (m, 3H), 4.02 (tt,  $J = 7.3, 5.3$  Hz, 1H), 3.85 (ddd,  $J = 8.2, 6.9, 6.1$  Hz, 1H),

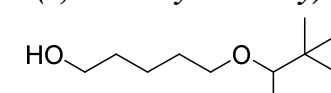
3.73 (ddd,  $J = 8.2, 7.2, 6.3$  Hz, 1H), 3.53 - 3.37 (m, 4H), 3.05 (t,  $J = 6.6$  Hz, 2H), 1.96 - 1.77 (m, 3H), 1.69 - 1.60 (m, 2H), 1.60 - 1.52 (m, 3H), 1.47 - 1.37 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.5, 128.7, 127.7, 126.9, 86.3, 77.9, 73.6, 71.6, 68.4, 63.6, 30.0, 29.6, 28.2, 25.7, 22.9. IR/ $\text{cm}^{-1}$ : 3084, 3055, 3022, 2934, 2862, 1597, 1489, 1448, 1373, 1219, 1111, 1074.

**General Procedure B: Deprotection of the trityl-group.** To a solution of alkyloxy-1-trityloxypentane (2.0 mmol) in toluene/MeOH (1:1, 20 mL, 0.1 M) was added  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (3.0 mmol, 1.5 eq). This mixture was stirred for 1.5 h at r.t. After completion of the starting material (TLC monitored), the mixture was diluted with EtOAc (30 mL) and washed with sat. aq.  $\text{NaHCO}_3$  (50 mL). The water layer was re-extracted with EtOAc ( $3 \times 30$  mL) and the combined organic layers were dried ( $\text{MgSO}_4$ ), filtered, concentrated and the residue purified by silica gel column chromatography (1:9  $\rightarrow$  1:4  $\rightarrow$  1:1  $\rightarrow$  1:0, EtOAc:PE) to give target alcohol chains.

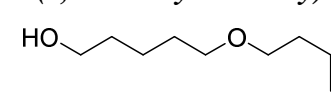
#### 5-(2-methyl-1-propyloxy)-1-pentanol (B24)

 Compound **B14** (3.56 mmol) was subjected to general procedure B to provide **B24** (0.33 g, 2.07 mmol) in a yield of 73% as oil after silica gel column purification.  $R_F = 0.24$  (20% EtOAc in PE).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.46 (t,  $J = 6.6$  Hz, 2H), 3.29 (t,  $J = 6.5$  Hz, 2H), 3.04 (d,  $J = 6.8$  Hz, 2H), 1.73 (dt,  $J = 13.4, 6.7$  Hz, 1H), 1.62 - 1.39 (m, 4H), 1.38 - 1.22 (m, 2H), 0.78 (d,  $J = 0.8$  Hz, 3H), 0.76 (d,  $J = 0.8$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  77.8, 70.8, 62.1, 32.3, 29.3, 28.2, 22.3, 19.3. IR/ $\text{cm}^{-1}$ : 3335, 2934, 2859, 1470, 1383, 1366, 1115, 1055, 1007.

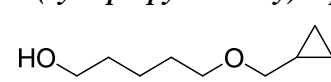
#### 5-(3,3-dimethyl-2-butoxy)-1-pentanol (B25)

 Compound **B15** (2.21 mmol) was subjected to general procedure B to provide **B27** (0.2089 g, 1.11 mmol) in a 50% yield as an oil after silica gel column purification.  $R_F = 0.32$  (20% EtOAc in PE).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.64 (t,  $J = 6.6$  Hz, 2H), 3.57 (dt,  $J = 9.2, 6.1$  Hz, 1H), 3.26 (dt,  $J = 9.2, 6.6$  Hz, 1H), 2.95 (q,  $J = 6.3$  Hz, 1H), 1.64 - 1.51 (m, 4H), 1.50 - 1.36 (m, 2H), 1.03 (d,  $J = 6.3$  Hz, 3H), 0.87 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  83.4, 69.8, 62.8, 35.1, 32.5, 29.8, 26.0, 22.5, 14.0. IR/ $\text{cm}^{-1}$ : 3296, 2938, 2866, 1474, 1456, 1388, 1371, 1339, 1209, 1099, 1057.

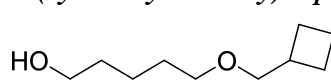
#### 5-(3,3-dimethyl-1-butoxy)-1-pentanol (B26)

 Compound **B16** (2.36 mmol) was subjected to general procedure B to provide **B26** (0.2142 g, 1.14 mmol) in a yield of 48% as oil after silica gel column purification.  $R_F = 0.22$  (20% EtOAc in PE).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.63 (t,  $J = 6.5$  Hz, 2H), 3.51 - 3.36 (m, 4H), 1.60 (dq,  $J = 14.6, 6.6$  Hz, 4H), 1.54 - 1.49 (m, 2H), 1.48 - 1.37 (m, 2H), 0.92 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  70.9, 68.2, 62.6, 42.9, 32.4, 29.7, 29.6, 29.5, 22.5. IR/ $\text{cm}^{-1}$ : 3345, 2938, 2864, 1472, 1364, 1244, 1194, 1113, 1055.

#### 5-(cyclopropylmethoxy)-1-pentanol (B27)

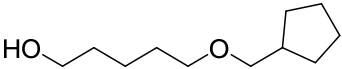
 Compound **B17** (2.49 mmol) was subjected to general procedure B to provide **B27** (0.19 g, 1.19 mmol) in a yield of 48% as oil after silica gel column purification.  $R_F = 0.27$  (30% EtOAc in PE).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.63 (t,  $J = 6.5$  Hz, 2H), 3.45 (t,  $J = 6.6$  Hz, 2H), 3.25 (d,  $J = 6.9$  Hz, 2H), 1.61 (m, 4H), 1.49 - 1.36 (m, 2H), 1.12 - 0.98 (m, 1H), 0.59 - 0.47 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  75.6, 70.6, 62.5, 32.4, 29.4, 22.4, 10.6, 3.0. IR/ $\text{cm}^{-1}$ : 3348, 2934, 2858, 1456, 1382, 1339, 1107, 1051.

#### 5-(cyclobutylmethoxy)-1-pentanol (B28)

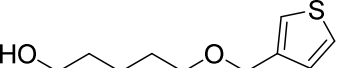
 Compound **B18** (1.91 mmol) was subjected to general procedure B to provide **B28** (0.18 g, 1.02 mmol) in a yield of 53% as oil after silica gel

column purification.  $R_F = 0.41$  (30% EtOAc in PE).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.61 (t,  $J = 6.6$  Hz, 2H), 3.42 (t,  $J = 6.5$  Hz, 2H), 3.27 (d,  $J = 7.2$  Hz, 2H), 2.12 - 2.18 (m, 1H), 1.81 - 1.68 (m, 1H), 1.64 - 1.50 (m, 7H), 1.47 - 1.37 (m, 2H), 1.26 - 1.15 (m, 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  75.6, 70.9, 62.4, 39.3, 32.4, 29.6, 29.3, 25.4, 22.4, 18.6.  $\text{IR}/\text{cm}^{-1}$ : 3360, 2933, 2858, 1456, 1364, 1113, 1057.

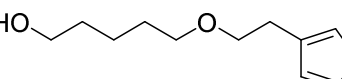
#### 5-(cyclopentylmethoxy)-1-pentanol (B29)

 Compound **B19** (3.02 mmol) was subjected to general procedure B to provide **B29** (0.27 g, 1.43 mmol) in a yield of 47% as oil after silica gel column purification.  $R_F = 0.45$  (30% EtOAc in PE).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.63 (t,  $J = 6.5$  Hz, 2H), 3.45 - 3.37 (m, 4H), 2.56 (p,  $J = 7.5$  Hz, 1H), 2.11 - 2.00 (m, 2H), 1.97 - 1.79 (m, 2H), 1.77 - 1.65 (m, 2H), 1.59 (dq,  $J = 14.6, 6.6$  Hz, 4H), 1.46 - 1.37 (m, 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  75.6, 70.9, 62.6, 35.1, 32.4, 29.7, 29.3, 25.2, 22.4.  $\text{IR}/\text{cm}^{-1}$ : 3333, 2939, 2862, 1456, 1373, 1361, 1115, 1057.

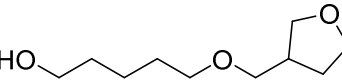
#### 5-(thiophen-3-methoxy)-1-pentanol (B30)

 Compound **B20** (2.13 mmol) was subjected to general procedure B to provide **B30** (0.23 g, 1.15 mmol) in a yield of 69% as oil after silica gel column purification.  $R_F = 0.27$  (30% EtOAc in PE).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 (dd,  $J = 4.9, 3.0$  Hz, 1H), 7.19 (ddt,  $J = 2.1, 1.5, 0.9$  Hz, 1H), 7.06 (dd,  $J = 4.9, 1.3$  Hz, 1H), 4.49 (s, 2H), 3.57 (t,  $J = 6.6$  Hz, 2H), 3.46 (t,  $J = 6.5$  Hz, 2H), 1.66 - 1.57 (m, 2H), 1.57 - 1.50 (m, 2H), 1.45 - 1.36 (m, 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  139.6, 127.3, 125.9, 122.7, 70.2, 68.1, 62.4, 32.4, 29.4, 22.4.

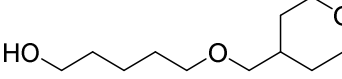
#### 5-(thiophen-3-ethoxy)-1-pentanol (B31)

 Compound **B21** (1.65 mmol) was subjected to General procedure B to provide **B31** (0.3318 g, 1.55 mmol) in a 73% yield as an oil after silica gel column purification.  $R_F = 0.30$  (30% EtOAc in PE).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23 (dd,  $J = 4.9, 3.0$  Hz, 1H), 7.00 - 7.03 (m, 1H), 6.97 (dd,  $J = 4.9, 1.3$  Hz, 1H), 3.62 (m, 4H), 3.45 (t,  $J = 6.5$  Hz, 2H), 2.90 (td,  $J = 7.0, 0.8$  Hz, 2H), 1.65 - 1.52 (m, 4H), 1.45 - 1.35 (m, 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  139.3, 128.5, 125.2, 121.1, 71.0, 70.9, 62.6, 32.4, 30.7, 29.4, 22.4.  $\text{IR}/\text{cm}^{-1}$ : 3360, 2934, 2860, 1456, 1418, 1348, 1250, 1225, 1155, 1094, 1053.

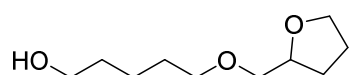
#### 5-(*R/S*-tetrahydrofuran-3-ylmethoxy)-1-pentanol (B12)

 Compound **B11** (3.56 mmol) was subjected to general procedure B to provide **B12** (0.48 g, 2.56 mmol) in a yield of 72% as oil, after silica gel column purification.  $R_F = 0.33$  (2:1, EtOAc:PE).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.82 (ddd,  $J = 8.4, 6.2, 2.4$  Hz, 2H), 3.72 (dt,  $J = 8.4, 7.3$  Hz, 1H), 3.63 - 3.52 (m, 3H), 3.47 - 3.36 (m, 3H), 3.31 (dd,  $J = 9.2, 7.9$  Hz, 1H), 2.58 - 2.42 (m, 1H), 2.04 - 1.93 (m, 1H), 1.59 (dddd,  $J = 16.3, 14.7, 8.0, 4.7$  Hz, 5H), 1.41 (tdd,  $J = 12.4, 6.5, 3.4$  Hz, 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  73.0, 71.0, 67.8, 62.4, 39.2, 32.5, 29.4, 29.1, 22.5.  $\text{IR}/\text{cm}^{-1}$ : 3385, 2934, 2858, 1456, 1375, 1211, 1113, 1072, 1056.

#### 5-(tetrahydro-2H-pyran-4-ylmethoxy)-1-pentanol (B32)

 Compound **B23** (1.78 mmol) was subjected to general procedure B to provide **B32** (0.1409 g, 0.697 mmol) in a yield of 39% as oil after silica gel column purification.  $R_F = 0.31$  (2:1, EtOAc:PE).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.96 (m, 2H), 3.60 (t,  $J = 6.6$  Hz, 2H), 3.45 - 3.34 (m, 4H), 3.25 (d,  $J = 6.6$  Hz, 2H), 1.83 (t,  $J = 3.4$  Hz, 1H), 1.70 - 1.51 (m, 6H), 1.46 - 1.36 (m, 2H), 1.36 - 1.21 (m, 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  75.9, 71.0, 67.6, 62.3, 35.3, 32.4, 29.9, 29.3, 22.4.  $\text{IR}/\text{cm}^{-1}$ : 3445, 2931, 2851, 1437, 1364, 1236, 1117, 1092, 1012, 987.

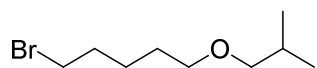
#### 5-(*R/S*-tetrahydrofuran-1-ylmethoxy)-1-pentanol (B33)



Compound **B25** (2.46 mmol) was subjected to general procedure B to provide **B33** (0.35 g, 1.86 mmol) in a yield of 76% as oil after silica gel column purification.  $R_F = 0.28$  (2:1, EtOAc:PE).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.04 (ddd,  $J = 12.4, 6.9, 5.2$  Hz, 1H), 3.87 (dt,  $J = 8.3, 6.6$  Hz, 1H), 3.81 - 3.71 (m, 1H), 3.61 (t,  $J = 6.5$  Hz, 2H), 3.48 (td,  $J = 6.6, 2.2$  Hz, 2H), 3.44 - 3.39 (m, 2H), 2.02 - 1.79 (m, 3H), 1.66 - 1.54 (m, 5H), 1.48 - 1.36 (m, 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  77.8, 73.4, 71.4, 68.2, 62.3, 32.4, 29.3, 28.0, 25.5, 22.3. IR/ $\text{cm}^{-1}$ : 3410, 2934, 2858, 1645, 1454, 1375, 1109, 1072, 1055.

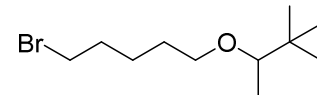
**General Procedure C: Bromination.** To a solution of alkyloxy-1-pentanol (1 mmol) in DCM (100 mL, 0.01 M) was added  $\text{PPh}_3$  (0.40 g, 1.5 mmol, 1.5 eq) and cooled to 0 °C. Then  $\text{CBr}_4$  (0.5 g, 1.5 mmol, 1.5 eq) was added and the reaction mixture was kept stirred at 0 °C until TLC monitored the completion of starting compound. After which Celite was added and the volatiles were evaporated. The residue was purified with silica gel column chromatography (0 - 100% toluene in heptane  $\rightarrow$  2 - 20% EtOAc in toluene) to give the bromide spacers.

#### *1-bromo-5-(2-methyl-1-propyloxy)pentane (B34)*



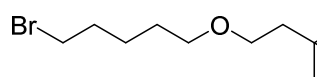
Alcohol **B24** (2.07 mmol) was subjected to general procedure C to provide **B34** (0.24 g, 1.08 mmol) in a yield of 52% after silica gel column purification.  $R_F = 0.71$  (100% tol)  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.41 (t,  $J = 6.9$  Hz, 2H), 3.40 (t,  $J = 6.3$  Hz, 2H), 3.16 (d,  $J = 6.7$  Hz, 2H), 1.90 - 1.85 (m, 3H), 1.65 - 1.56 (m, 2H), 1.56 - 1.47 (m, 2H), 0.90 (d,  $J = 6.7$  Hz, 6H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  77.9, 70.6, 33.7, 32.6, 28.9, 28.4, 25.0, 19.4. IR/ $\text{cm}^{-1}$ : 2940, 2863, 1473, 1363, 1332, 1100.

#### *1-bromo-5-(3,3-dimethyl-2-butoxy)pentane (B35)*



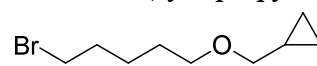
Alcohol **B25** (1.11 mmol) was subjected to general procedure C to provide **B35** (0.2477 g, 0.986 mmol) in a yield of 89% after silica gel column purification.  $R_F = 0.71$  (1:1, PE:tol).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.56 (dt,  $J = 9.5, 5.8$  Hz, 1H), 3.41 (t,  $J = 6.9$  Hz, 2H), 3.24 (dt,  $J = 9.5, 6.1$  Hz, 1H), 2.94 (q,  $J = 6.3$  Hz, 1H), 1.88 (p,  $J = 7.0$  Hz, 2H), 1.64 - 1.44 (m, 4H), 1.03 (d,  $J = 6.3$  Hz, 3H), 0.87 (s, 9H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  83.3, 69.3, 35.1, 33.8, 32.7, 29.3, 26.0, 25.1, 13.9. IR/ $\text{cm}^{-1}$ : 2938, 2866, 1477, 1369, 1335, 1099.

#### *1-bromo-5-(3,3-dimethyl-1-butoxy)pentane (B36)*



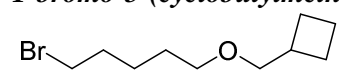
Alcohol **B26** (1.14 mmol) was subjected to general procedure C to provide **B36** (0.14 g, 0.54 mmol) in a yield of 48% after silica gel column purification.  $R_F = 0.71$  (100% tol).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.52 - 3.36 (m, 6H), 2.00 - 1.79 (m, 2H), 1.65 - 1.55 (m, 2H), 1.55 - 1.47 (m, 4H), 0.92 (s, 9H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  70.6, 68.2, 43.0, 33.7, 32.7, 29.8, 29.6, 29.0, 25.0. IR/ $\text{cm}^{-1}$ : 2951, 2862, 1734, 1486, 1364, 1111.

#### *1-bromo-5-(cyclopropylmethoxy)pentane (B37)*

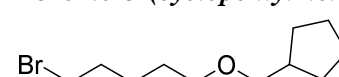


Alcohol **B27** (1.19 mmol) was subjected to general procedure C to provide **B37** (0.12 g, 0.54 mmol) in a yield of 46% after silica gel column purification.  $R_F = 0.52$  (100% tol).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.44 (t,  $J = 6.4$  Hz, 2H), 3.42 (t,  $J = 6.8$  Hz, 2H), 3.25 (d,  $J = 6.9$  Hz, 2H), 1.89 (dt,  $J = 14.8, 7.0$  Hz, 2H), 1.67 - 1.56 (m, 2H), 1.58 - 1.47 (m, 2H), 1.13 - 0.98 (m, 1H), 0.58 - 0.49 (m, 2H), 0.20 (dt,  $J = 6.1, 4.5$  Hz, 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  75.6, 70.3, 33.8, 32.6, 28.9, 24.9, 10.6, 3.0. IR/ $\text{cm}^{-1}$ : 2934, 2857, 1732, 1456, 1381, 1337, 1250, 1107, 1016.

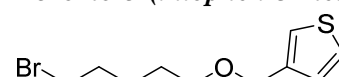
### ***1-bromo-5-(cyclobutylmethoxy)pentane (B38)***

 Alcohol **B28** (1.02 mmol) was subjected to general procedure C to provide **B38** (0.1276 g, 0.54 mmol) in a yield of 53% after silica gel column purification.  $R_F = 0.67$  (100% tol)  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.41, (t,  $J = 6.7$  Hz, 2H), 3.41 (t,  $J = 6.9$  Hz, 2H), 3.38 (d,  $J = 6.8$  Hz, 2H), 2.55 - 2.59 (m, 1H), 2.14 - 2.01 (m, 2H), 1.97 - 1.81 (m, 4H), 1.80 - 1.67 (m, 2H), 1.66 - 1.56 (m, 2H), 1.56 - 1.45 (m, 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  75.6, 70.7, 35.2, 33.8, 32.6, 28.9, 25.2, 24.9, 18.6. IR/ $\text{cm}^{-1}$ : 2932, 2855, 1732, 1456, 1364, 1246, 1111.

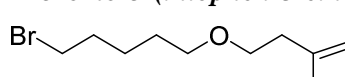
### ***1-bromo-5-(cyclopentylmethoxy)pentane (B39)***

 Alcohol **B29** (1.43 mmol) was subjected to general procedure C to provide **B39** (0.25 g, 1.01 mmol) in a yield of 71% after silica gel column purification.  $R_F = 0.71$  (100% tol)  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.43 (dd,  $J = 6.7, 6.0$  Hz, 2H), 3.43 (t,  $J = 6.8$  Hz, 1H), 3.27 (d,  $J = 7.1$  Hz, 2H), 2.13 (dq,  $J = 14.8, 7.4$  Hz, 1H), 1.89 (dt,  $J = 14.1, 7.0$  Hz, 2H), 1.79 - 1.66 (m, 2H), 1.64 - 1.45 (m, 8H), 1.29 - 1.16 (m, 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  75.6, 70.6, 39.5, 33.8, 32.6, 29.6, 28.9, 25.4, 25.0. IR/ $\text{cm}^{-1}$ : 2940, 2857, 1734, 1452, 1366, 1250, 1111.


### ***1-bromo-5-(thiophen-3-methoxy)pentane (B40)***

 Alcohol **B30** (1.15 mmol) was subjected to general procedure C to provide **B40** (0.19 g, 0.74 mmol) in a yield of 45% after silica gel column purification.  $R_F = 0.67$  (100% tol).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 (dd,  $J = 5.0, 3.0$  Hz, 1H), 7.23 (dd,  $J = 2.9, 1.2$  Hz, 1H), 7.10 (dd,  $J = 5.0, 1.2$  Hz, 1H), 4.56 - 4.51 (s, 2H), 3.50 (t,  $J = 6.3$  Hz, 2H), 3.44 (t,  $J = 6.8$  Hz, 2H), 1.90 (p,  $J = 7.0$  Hz, 2H), 1.72 - 1.59 (m, 2H), 1.62 - 1.48 (m, 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  139.7, 127.3, 126.0, 122.6, 70.0, 68.2, 33.8, 32.6, 28.9, 25.0. IR/ $\text{cm}^{-1}$ : 3000, 2934, 2857, 1732, 1153, 1096.

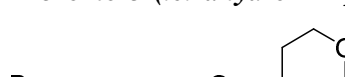
### ***1-bromo-5-(thiophen-3-ethoxy)pentane (B41)***

 Alcohol **B31** (1.55 mmol) was subjected to general procedure C to provide **B41** (0.28 g, 0.99 mmol) in a yield of 46% after silica gel column purification.  $R_F = 0.67$  (100% tol).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25 - 7.21 (m, 1H), 7.00 (dq,  $J = 3.0, 1.0$  Hz, 1H), 6.97 (dd,  $J = 4.9, 1.3$  Hz, 1H), 3.62 (t,  $J = 7.0$  Hz, 2H), 3.44 (t,  $J = 6.3$  Hz, 2H), 3.39 (t,  $J = 6.8$  Hz, 2H), 2.90 (td,  $J = 7.0, 0.8$  Hz, 2H), 1.92 - 1.79 (m, 2H), 1.64 - 1.54 (m, 2H), 1.53 - 1.44 (m, 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  139.4, 128.5, 125.2, 121.1, 71.1, 70.6, 33.9, 32.6, 30.8, 28.9, 25.0. IR/ $\text{cm}^{-1}$ : 3102, 2934, 2857, 1734, 1109.

### ***1-bromo-5-(R/S-tetrahydrofuran-3-ylmethoxy)pentane (B13)***

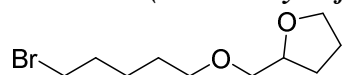
 Alcohol **B12** (1.86 mmol) was subjected to general procedure C to provide **B13** (0.58 g, 2.32 mmol) in a yield of 91% after silica gel column purification.  $R_F = 0.33$  (5% EtOAc in PE).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.87 - 3.78 (m, 2H), 3.78 - 3.66 (m, 1H), 3.56 (dd,  $J = 8.7, 5.4$  Hz, 1H), 3.46 - 3.25 (m, 6H), 2.51 (tt,  $J = 7.1, 1.4$  Hz, 1H), 2.06 - 1.94 (m, 1H), 1.92 - 1.83 (m, 2H), 1.65 - 1.54 (m, 3H), 1.54 - 1.45 (m, 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  73.2, 71.2, 71.0, 68.0, 39.4, 33.9, 32.8, 29.3, 29.0, 25.1. IR/ $\text{cm}^{-1}$ : 2934, 2857, 1486, 1111, 1076.

### ***1-bromo-5-(tetrahydro-2H-pyran-4-ylmethoxy)pentane (B42)***

 Alcohol **B32** (0.31 mmol) was subjected to general procedure C to provide **B42** (0.061 g, 0.23 mmol) in a 33% yield after silica gel column purification.  $R_F = 0.35$  (5% EtOAc in PE).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.01 - 3.94 (m, 2H), 3.45 - 3.35 (m, 6H), 3.25 (d,  $J = 6.6$  Hz, 2H), 1.93 - 1.77 (m, 3H), 1.68 - 1.55 (m, 4H), 1.55 - 1.46 (m, 2H), 1.42 - 1.19 (m, 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  76.0, 70.8, 67.8, 35.5, 33.8, 32.6, 30.0, 28.9, 24.9. IR/ $\text{cm}^{-1}$ : 2924, 2845, 1734, 1384,

1115, 1092.

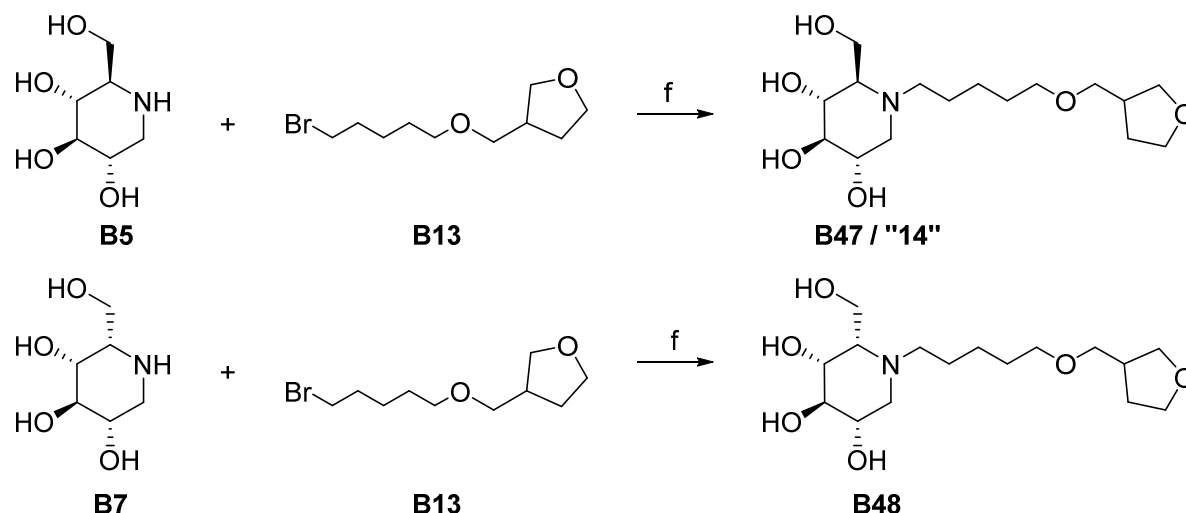
***1-bromo-5-(R/S-tetrahydrofuran-1-ylmethoxy) pentane (B43)***



Alcohol **B33** (1.86 mmol) was subjected to general procedure C to provide **B43** (0.33 g, 1.30 mmol) in a yield of 70% after silica gel column purification.  $R_F = 0.33$  (5% EtOAc in PE).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.04 (m, 1H), 3.88 (m, 1H), 3.75 (m, 1H), 3.49 (m, 2H), 3.47 - 3.39 (m, 4H), 1.99-1.83 (m, 5H), 1.66 - 1.62 (m, 3H), 1.61 - 1.53 (m, 2H).  $^{13}\text{C NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  77.9, 73.6, 71.2, 68.3, 33.8, 32.6, 28.8, 28.1, 25.6, 24.9. IR/ $\text{cm}^{-1}$ : 2938, 2860, 1456, 1437, 1117, 1070.



## Synthesis of the Alkylated Iminosugars



**Scheme S5:** *N*-Alkylation strategy of DNM and *L*-ido DNM: [a] TrtCl, TEA, EtOAc, 85°C, 3h, 99%; [b] *p*-TsCl, TEA, DMAP, DCM, 0°C to r.t., 2h, 70%; [c] 1) THF-3-yl-methanol, NaH, DMF, rt, 90 min; 2) **15**, 75°C, 1h, 56%; [d] BF<sub>3</sub>·OEt<sub>2</sub>, toluene/MeOH (1:1), 1.5h, 72%; [e] 1) PPh<sub>3</sub>, DCM, rt, 0 °C; 2) CBr<sub>4</sub>, Ar, 2h, 91%; [f] DMF, K<sub>2</sub>CO<sub>3</sub>, 80 °C, 88% (**B47**), 30% (**B48**).

**General Procedure D: Alkylation of iminosugars.** To a mixture of the 1-bromo-5-alkyloxy-pentane (0.3 mmol, 1.5 eq) and di-isopropylethylamine (DiPEA, 0.1 mL, 0.6 mmol, 3 eq) was added a solution of iminosugar (0.03 g, 0.2 mmol) in DMF (1 mL). This was stirred overnight at 70 °C. After cooling to r.t., the mixture was filtered and concentrated. The crude compound was purified using HPLC.

### *N*-[5-(2-methyl-1-propyloxy)pentyl]-1-deoxynojirimycin (**B44/11**)

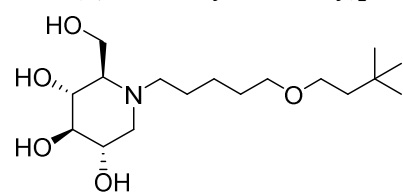
Bromide chain **B34** (0.19 mmol) was subjected to general procedure D with 1-deoxynojirimycin (0.20 mmol) to provide **B44** (28 mg, 0.092 mmol, yield 46%). <sup>1</sup>H NMR (400 MHz, MeOD) δ 4.07 (d, *J* = 12.4 Hz, 1H), 3.93 (dd, *J* = 12.5, 2.9 Hz, 1H), 3.67 (td, *J* = 10.1, 4.5 Hz, 1H), 3.58 (t, *J* = 9.6 Hz, 1H), 3.47 (t, *J* = 6.3 Hz, 3H), 3.43 - 3.24 (m, 3H), 3.22 (d, *J* = 6.6 Hz, 2H), 3.10 (br s, 1H), 2.92 - 2.74 (m, 2H), 1.81 - 1.89 (m, 2H), 1.80 - 1.72 (m, 2H), 1.71 - 1.62 (m, 2H), 1.54 - 1.41 (m, 2H), 0.93 (d, *J* = 6.7 Hz, 6H), <sup>13</sup>C NMR (100 MHz, MeOD) δ 77.6, 77.2, 70.2, 68.1, 67.0, 66.1, 55.5, 54.0, 52.6, 28.9, 28.2, 23.3, 22.9, 18.3. [α]<sub>D</sub><sup>20</sup>: -7.17, (c = 0.56, MeOH). IR/cm<sup>-1</sup>: 3333, 2871, 1670, 1432, 1383, 1201, 1131, 1031. HRMS: found 306.2276 [M+H]<sup>+</sup>, calculated for [C<sub>15</sub>H<sub>31</sub>NO<sub>5</sub>+H]<sup>+</sup> 306.2275.

### *N*-[5-(3,3-dimethyl-2-butoxy)pentyl]-1-deoxynojirimycin (**B45/13**)

Bromide chain **B35** (0.32 mmol) was subjected to general procedure D with 1-deoxynojirimycin (0.20 mmol) to provide **B45** (31 mg, 0.094 mmol, yield 47%). <sup>1</sup>H NMR (400 MHz, MeOD) δ 4.14 (d, *J* = 12.4 Hz, 1H), 3.93 (dd, *J* = 12.6, 2.7 Hz, 1H), 3.72 (td, *J* = 10.4, 4.9 Hz, 1H), 3.68 - 3.58 (m, 3H), 3.48 (dd, *J* = 12.0, 4.9 Hz, 1H), 3.43 -

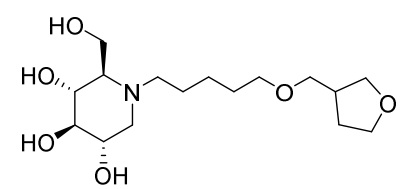
3.35 (m, 3H), 3.22 (td,  $J = 12.2, 5.1$  Hz, 1H), 3.07 (br d,  $J = 9.8$  Hz, 1H), 3.03 (d,  $J = 6.3$  Hz, 2H), 3.01 (dd,  $J = 12.5, 10.9$  Hz, 1H), 1.81 (dt,  $J = 11.1, 5.7$  Hz, 2H), 1.65 (dt,  $J = 8.8, 5.8$  Hz, 2H), 1.57 - 1.44 (m, 2H), 1.07 (d,  $J = 6.3$  Hz, 3H), 0.90 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz, MeOD)  $\delta$  83.3, 76.7, 68.9, 67.4, 66.4, 66.0, 53.5, 53.5, 52.9, 34.6, 29.3, 25.0, 23.2, 22.6, 12.8.  $[\alpha]_{\text{D}}^{20}$ : -6.94 ( $c = 0.63$ , MeOH). IR/cm $^{-1}$ : 3330, 2956, 2875, 1672, 1439, 1203, 1134, 1029. HRMS: found 334.2588  $[\text{M}+\text{H}]^+$ , calculated for  $[\text{C}_{17}\text{H}_{35}\text{NO}_5+\text{H}]^+$  334.2588.

#### *N*-[5-(3,3-dimethyl-1-butoxy)pentyl]-1-deoxynojirimycin (**B46**)



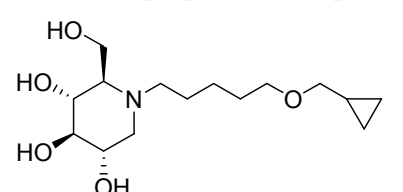
Bromide chain **B36** (0.299 mmol) was subjected to general procedure D with 1-deoxynojirimycin (0.20 mmol) to provide **B46** (28 mg, 0.085 mmol, yield 43%).  $^1\text{H}$  NMR (400 MHz, MeOD)  $\delta$  4.12 (d,  $J = 12.5$  Hz, 1H), 3.93 (dd,  $J = 12.3, 2.8$  Hz, 1H), 3.71 (td,  $J = 10.4, 10.0, 4.4$  Hz, 1H), 3.62 (t,  $J = 9.7$  Hz, 1H), 3.50 (t,  $J = 7.3$  Hz, 2H), 3.50 (dd,  $J = 9.0, 1.5$  Hz, 1H), 3.46 (t,  $J = 6.3$  Hz, 3H), 3.43 - 3.36 (m, 2H), 3.22 (td,  $J = 12.1, 5.2$  Hz, 1H), 3.07 (br d,  $J = 10.3$  Hz, 1H), 3.00 (t,  $J = 11.7$  Hz, 1H), 1.90 - 1.71 (m, 2H), 1.65 (ddd,  $J = 13.7, 7.5, 6.0$  Hz, 2H), 1.51 (t,  $J = 7.4$  Hz, 2H), 1.53 - 1.43 (m, 2H), 0.94 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz, MeOD)  $\delta$  76.7, 70.0, 67.9, 67.4, 66.4, 66.0, 53.4, 53.3, 52.9, 42.6, 29.7, 28.7, 25.8, 25.0, 22.6.  $[\alpha]_{\text{D}}^{20}$ : +0.56 ( $c = 0.57$ , MeOH). IR/cm $^{-1}$ : 3343, 2954, 2870, 1673, 1433, 1203, 1134. HRMS: found 334.2589  $[\text{M}+\text{H}]^+$ , calculated for  $[\text{C}_{17}\text{H}_{35}\text{NO}_5+\text{H}]^+$  334.2588.

#### *N*-[5-(*R/S*-tetrahydrofuran-3-ylmethoxy)pentyl]-1-deoxynojirimycin (**B47/14**)



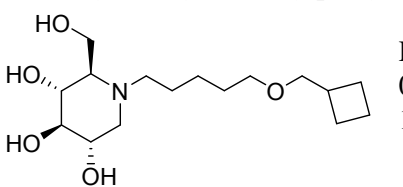
Bromide chain **B13** (0.29 mmol) was subjected to general procedure D with 1-deoxynojirimycin (0.20 mmol) to provide **B47** (58.5 mg, 0.17 mmol, yield 88%).  $^1\text{H}$  NMR (400 MHz, MeOD)  $\delta$  4.14 (d,  $J = 12.6$  Hz, 1H), 3.93 (dd,  $J = 12.4, 3.0$  Hz, 1H), 3.85 (dd,  $J = 8.3, 5.5$  Hz, 1H), 3.83 (dd,  $J = 8.7, 7.2$  Hz, 1H), 3.78 - 3.69 (m, 2H), 3.63 (t,  $J = 9.8$  Hz, 1H), 3.58 (dd,  $J = 8.6, 5.5$  Hz, 2H), 3.52 - 3.47 (m, 1H), 3.50 (td,  $J = 6.3, 1.7$  Hz, 2H), 3.44 (dd,  $J = 9.2, 6.3$  Hz, 1H), 3.43 - 3.35 (m, 3H), 3.22 (td,  $J = 12.2, 5.2$  Hz, 1H), 3.07 (br d,  $J = 9.9$  Hz, 1H), 3.01 (t,  $J = 11.7$  Hz, 1H), 2.59 - 2.48 (m, 1H), 2.04 (dddd,  $J = 12.8, 8.5, 7.7, 5.5$  Hz, 1H), 1.91 - 1.72 (m, 2H), 1.72 - 1.60 (m, 3H), 1.53 - 1.47 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz, MeOD)  $\delta$  76.7, 72.5, 70.5, 70.3, 67.4, 67.3, 66.4, 66.0, 53.5, 53.5, 52.9, 39.0, 28.7, 28.5, 23.1, 22.5. IR/cm $^{-1}$ : 3346, 2970, 2942, 1738, 1670, 1430, 1366, 1199, 1132, 898.  $[\alpha]_{\text{D}}^{20}$ : -1.89 ( $c = 1.17$ , MeOH). HRMS: found 334.2228  $[\text{M}+\text{H}]^+$ , calculated for  $[\text{C}_{16}\text{H}_{31}\text{NO}_6+\text{H}]^+$  334.2224.

#### *N*-[5-(cyclopropylmethoxy)pentyl]-1-deoxynojirimycin (**B49**)



Bromide chain **B37** (0.30 mmol) was subjected to General Procedure D with 1-deoxynojirimycin (0.20 mmol) to provide **B49** (30 mg, 0.097 mmol, yield 49%).  $^1\text{H}$  NMR (400 MHz, MeOD)  $\delta$  4.13 (d,  $J = 12.6$  Hz, 1H), 3.94 (dd,  $J = 12.7, 3.1$  Hz, 1H), 3.73 (td,  $J = 10.3, 4.7$  Hz, 1H), 3.64 (t,  $J = 9.8$  Hz, 1H), 3.52 (t,  $J = 6.3$  Hz, 2H), 3.51 - 3.46 (m, 1H), 3.40 (t,  $J = 9.2$  Hz, 1H), 3.40 - 3.36 (m, 1H), 3.30 (d,  $J = 6.9$  Hz, 2H), 3.23 (td,  $J = 12.3, 5.3$  Hz, 1H), 3.08 (br d,  $J = 10.1$  Hz, 1H), 3.01 (t,  $J = 11.7$  Hz, 1H), 1.91 - 1.73 (m, 2H), 1.72 - 1.63 (m, 2H), 1.55 - 1.45 (m, 2H), 1.06 (dddd,  $J = 13.3, 6.9, 5.0, 2.6$  Hz, 1H), 0.57 - 0.51 (m, 2H), 0.22 (dt,  $J = 6.1, 4.4$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz, MeOD)  $\delta$  76.7, 75.3, 69.8, 67.4, 66.4, 66.0, 53.6, 53.4, 52.9, 28.7, 23.1, 22.5, 10.0, 2.1.  $[\alpha]_{\text{D}}^{20}$ : -6.08 ( $c = 0.59$ , MeOH). IR/cm $^{-1}$ : 3346, 2866, 1672, 1430, 1202, 1134, 1032. HRMS: found 304.2119  $[\text{M}+\text{H}]^+$ , calculated for  $[\text{C}_{15}\text{H}_{29}\text{NO}_5+\text{H}]^+$  304.2118.

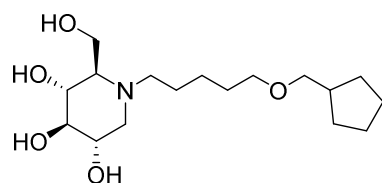
#### *N*-[5-(cyclobutylmethoxy)pentyl]-1-deoxynojirimycin (**B50**)



Bromide chain **B38** (0.31 mmol) was subjected to general procedure D with 1-deoxynojirimycin (0.20 mmol) to provide **B50** (25 mg, 0.079 mmol, yield 39%).  $^1\text{H}$  NMR (400 MHz, MeOD)  $\delta$  4.14 (d,  $J = 12.5$  Hz, 1H), 3.93 (dd,  $J = 12.7, 3.1$  Hz, 1H), 3.71 (td,  $J = 10.7, 10.2,$

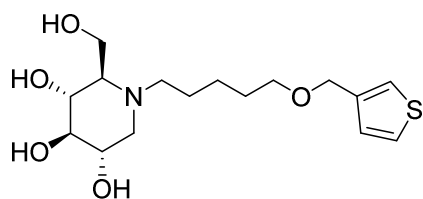
4.7 Hz, 1H), 3.63 (t,  $J = 9.8$  Hz, 1H), 3.49 (t,  $J = 6.2$  Hz, 2H), 3.48 (dd,  $J = 11.8, 5.2$  Hz, 1H), 3.43 (d,  $J = 6.8$  Hz, 2H), 3.43 - 3.36 (m, 1H), 3.39 (t,  $J = 9.4$  Hz, 1H), 3.22 (td,  $J = 12.3, 5.3$  Hz, 1H), 3.06 (br d,  $J = 11.2$  Hz, 1H), 3.01 (t,  $J = 11.7$  Hz, 1H), 2.58 (dq,  $J = 14.6, 7.3$  Hz, 1H), 2.14 - 2.03 (m, 2H), 2.03 - 1.91 (m, 2H), 1.91 - 1.72 (m, 4H), 1.67 (ddd,  $J = 13.7, 7.5, 5.9$  Hz, 2H), 1.49 (td,  $J = 10.6, 7.2$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz, MeOD)  $\delta$  76.7, 75.2, 70.2, 67.4, 66.4, 66.0, 53.5, 53.4, 52.9, 35.1, 28.7, 24.6, 23.1, 22.5, 18.0.  $[\alpha]_{\text{D}}^{20}$ : -6.02 ( $c = 0.50$ , MeOH). IR/cm $^{-1}$ : 3341, 2938, 2865, 1673, 1431, 1202, 1135, 1031. HRMS: found 318.2276  $[\text{M}+\text{H}]^+$ , calculated for  $[\text{C}_{16}\text{H}_{31}\text{NO}_5+\text{H}]^+$  318.2275.

#### *N*-[5-(cyclopentylmethoxy)pentyl]-1-deoxynojirimycin (**B51**)



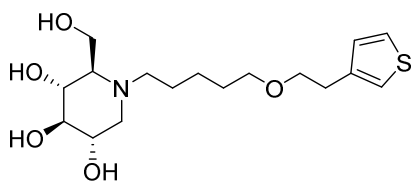
Bromide chain **B39** (0.30 mmol) was subjected to general procedure D with 1-deoxynojirimycin (0.20 mmol) to provide **B51** (23 mg, 0.069 mmol, yield 35%).  $^1\text{H}$  NMR (400 MHz, MeOD)  $\delta$  4.13 (d,  $J = 12.5$  Hz, 1H), 3.93 (dd,  $J = 12.6, 3.1$  Hz, 1H), 3.72 (dt,  $J = 14.7, 4.6$  Hz, 1H), 3.63 (t,  $J = 9.7$  Hz, 1H), 3.52 - 3.44 (m, 1H), 3.49 (t,  $J = 6.2$  Hz, 2H), 3.43 - 3.35 (m, 2H), 3.33 (d,  $J = 7.1$  Hz, 2H), 3.22 (td,  $J = 12.3, 5.3$  Hz, 1H), 3.07 (d,  $J = 9.5$  Hz, 1H), 3.00 (t,  $J = 11.7$  Hz, 1H), 2.21 - 2.12 (m, 1H), 1.88 - 1.71 (m, 4H), 1.71 - 1.54 (m, 6H), 1.50 (qd,  $J = 7.9, 5.1$  Hz, 2H), 1.35 - 1.22 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz, MeOD)  $\delta$  76.7, 75.3, 70.1, 67.4, 66.4, 66.0, 53.5, 53.5, 52.8, 39.3, 29.2, 28.7, 25.0, 23.1, 22.7.  $[\alpha]_{\text{D}}^{20}$ : -4.76 ( $c = 0.46$ , MeOH). IR/cm $^{-1}$ : 3346, 2950, 2867, 1673, 1433, 1203, 1133, 1032. HRMS: found 332.2432  $[\text{M}+\text{H}]^+$ , calculated for  $[\text{C}_{17}\text{H}_{33}\text{NO}_5+\text{H}]^+$  332.2432.

#### *N*-[5-(thiophen-3-methoxy)pentyl]-1-deoxynojirimycin (**B52**)



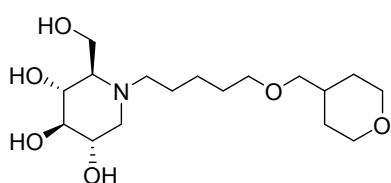
Bromide chain **B40** (0.29 mmol) was subjected to general procedure D with 1-deoxynojirimycin (0.20 mmol) to provide **B52** (41 mg, 0.12 mmol, yield 59%).  $^1\text{H}$  NMR (400 MHz, MeOD)  $\delta$  7.41 (dd,  $J = 5.0, 3.0$  Hz, 1H), 7.34 - 7.31 (m, 1H), 7.10 (dd,  $J = 5.0, 1.2$  Hz, 1H), 4.54 (s, 2H), 4.12 (d,  $J = 12.2$  Hz, 1H), 3.92 (dd,  $J = 12.7, 3.1$  Hz, 1H), 3.71 (td,  $J = 10.1, 4.5$  Hz, 1H), 3.62 (t,  $J = 9.8$  Hz, 1H), 3.54 (t,  $J = 6.2$  Hz, 2H), 3.46 (dd,  $J = 12.1, 4.8$  Hz, 1H), 3.43 - 3.36 (m, 2H), 3.21 (td,  $J = 12.3, 5.2$  Hz, 1H), 3.11 - 3.02 (m, 1H), 2.99 (t,  $J = 11.7$  Hz, 1H), 1.89 - 1.74 (m, 2H), 1.69 (ddd,  $J = 13.6, 7.5, 6.0$  Hz, 2H), 1.53 - 1.45 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz, MeOD)  $\delta$  139.5, 127.1, 125.6, 122.6, 76.7, 69.3, 67.6, 67.4, 66.4, 66.0, 53.5, 53.5, 52.9, 28.6, 23.1, 22.5.  $[\alpha]_{\text{D}}^{20}$ : -3.16 ( $c = 0.82$ , MeOH). IR/cm $^{-1}$ : 3346, 2963, 2867, 1672, 1429, 1366, 1202, 1133, 1032. HRMS: found 346.1684  $[\text{M}+\text{H}]^+$ , calculated for  $[\text{C}_{16}\text{H}_{27}\text{NO}_5\text{S}+\text{H}]^+$  346.1684.

#### *N*-[5-(thiophen-3-ethoxy)pentyl]-1-deoxynojirimycin (**B53**)



Bromide chain **B41** (0.29 mmol) was subjected to general procedure D with 1-deoxynojirimycin (0.20 mmol) to provide **B53** (10 mg, 0.028 mmol, yield 14%).  $^1\text{H}$  NMR (400 MHz, MeOD)  $\delta$  7.33 (dd,  $J = 5.0, 2.9$  Hz, 1H), 7.11 (dd,  $J = 3.0, 1.1$  Hz, 1H), 7.02 (dd,  $J = 4.9, 1.3$  Hz, 1H), 4.12 (d,  $J = 12.5$  Hz, 1H), 3.92 (d,  $J = 12.3$  Hz, 1H), 3.74 - 3.70 (m, 1H), 3.68 (t,  $J = 6.7$  Hz, 2H), 3.62 (t,  $J = 9.7$  Hz, 1H), 3.52 (t,  $J = 6.2$  Hz, 2H), 3.45 (dd,  $J = 12.1, 4.8$  Hz, 1H), 3.42 - 3.34 (m, 2H), 3.23 - 3.13 (m, 1H), 3.06 - 3.00 (m, 1H), 2.97 (t,  $J = 11.7$  Hz, 1H), 2.91 (dd,  $J = 7.1, 6.3$  Hz, 2H), 1.86 - 1.70 (m, 2H), 1.70 - 1.62 (m, 2H), 1.52 - 1.40 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz, MeOD)  $\delta$  139.3, 128.1, 124.7, 120.7, 76.8, 70.8, 69.9, 67.5, 66.4, 66.0, 53.4, 53.0, 30.2, 28.7, 24.0, 23.1.  $[\alpha]_{\text{D}}^{20}$ : -9.09 ( $c = 0.20$ , MeOH). IR/cm $^{-1}$ : 3358, 3018, 2943, 2870, 1736, 1677, 1439, 1366, 1205, 1134, 1031. HRMS: found 360.1849  $[\text{M}+\text{H}]^+$ , calculated for  $[\text{C}_{17}\text{H}_{29}\text{NO}_5\text{S}+\text{H}]^+$  360.1839.

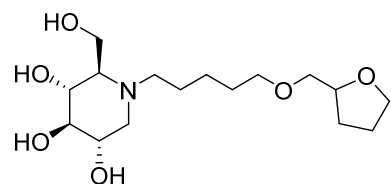
#### *N*-[5-(tetrahydro-2H-pyran-4-ylmethoxy)pentyl]-1-deoxynojirimycin (**B54**)



Bromide chain **B42** (0.29 mmol) was subjected to general procedure D with 1-deoxynojirimycin (0.20 mmol) to provide **B54** (35 mg, 0.10 mmol, yield 50%).  $^1\text{H}$  NMR (400 MHz, MeOD)  $\delta$  4.14 (d,  $J = 12.5$  Hz, 1H), 3.92 (dd,  $J = 11.8, 2.6$  Hz, 1H), 3.99 -

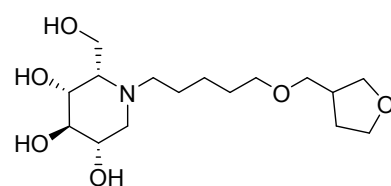
3.94 (m, 2H), 3.70 (ddd,  $J = 11.2, 9.3, 4.9$  Hz, 1H), 3.62 (dd,  $J = 10.4, 9.2$  Hz, 1H), 3.49 (t,  $J = 6.2$  Hz, 2H), 3.48 - 3.35 (m, 5H), 3.31 (d,  $J = 6.4$  Hz, 2H), 3.23 (dd,  $J = 12.1, 5.3$  Hz, 1H), 3.06 (dd,  $J = 10.3, 2.7$  Hz, 1H), 3.01 (t,  $J = 11.7$  Hz, 1H), 1.92 - 1.84 (m, 1H), 1.84 - 1.72 (m, 2H), 1.72 - 1.62 (m, 4H), 1.57 - 1.45 (m, 2H), 1.30 - 1.38 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz, MeOD)  $\delta$  76.8, 75.5, 70.2, 67.3, 67.3, 66.4, 66.0, 53.5, 53.4, 52.8, 35.2, 29.6, 28.7, 23.1, 22.5.  $[\alpha]_{\text{D}}^{20}$ : -4.01 ( $c = 0.70$ , MeOH). IR/cm $^{-1}$ : 3333, 2923, 2859, 1671, 1433, 1387, 1200, 1136, 1088, 1032. HRMS: found 348.2381  $[\text{M}+\text{H}]^+$ , calculated for  $[\text{C}_{17}\text{H}_{33}\text{NO}_6+\text{H}]^+$  348.2381.

***N*-[5-(*R/S*-tetrahydrofuran-1-ylmethoxy)pentyl]-1-deoxynojirimycin (B55/15)**



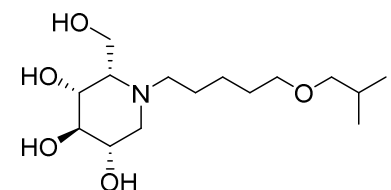
Bromide chain **B43** (0.29 mmol) was subjected to general procedure D with 1-deoxynojirimycin (0.20 mmol) to provide **B55** (10 mg, 0.030 mmol, yield 15%).  $^1\text{H}$  NMR (600 MHz, MeOD)  $\delta$  4.12 (d,  $J = 11.5$  Hz, 1H), 4.07 - 4.01 (m, 1H), 3.91 (dd,  $J = 12.5, 3.2$  Hz, 1H), 3.85 (dt,  $J = 8.2, 6.7$  Hz, 1H), 3.76 (td,  $J = 7.7, 6.1$  Hz, 1H), 3.64 - 3.72 (m, 1H), 3.60 (dd,  $J = 12.7, 6.6$  Hz, 1H), 3.51 (td,  $J = 6.2, 3.8$  Hz, 1H), 3.47 - 3.34 (m, 5H), 3.20 (td,  $J = 12.4, 5.0$  Hz, 1H), 3.04 (d,  $J = 9.9$  Hz, 1H), 2.99 (t,  $J = 11.7$  Hz, 1H), 2.01 - 1.95 (m, 1H), 1.94 - 1.87 (m, 1H), 1.87 - 1.71 (m, 2H), 1.66 (tt,  $J = 7.5, 5.9$  Hz, 2H), 1.63 - 1.57 (m, 1H), 1.54 - 1.43 (m, 2H).  $^{13}\text{C}$  NMR (150 MHz, MeOD)  $\delta$  80.3, 79.0, 75.4, 72.8, 70.1, 69.6, 68.7, 68.3, 63.2, 55.8, 55.2, 33.7, 30.8, 29.8, 27.4, 25.4. IR/cm $^{-1}$ : 3367, 2964, 2902, 1674, 1396, 1066.  $[\alpha]_{\text{D}}^{20}$ : -9.8 ( $c = 0.20$ , MeOH). HRMS: found 334.2227  $[\text{M}+\text{H}]^+$ , calculated for  $[\text{C}_{16}\text{H}_{31}\text{NO}_6+\text{H}]^+$  334.2224.

***N*-[5-(*R/S*-tetrahydrofuran-3-ylmethoxy)pentyl]-L-ido-1-deoxynojirimycin (B48)**



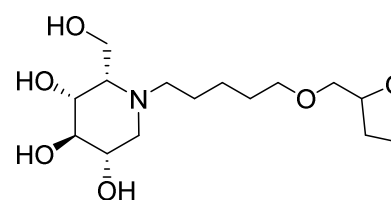
Bromide chain **B13** (0.29 mmol) was subjected to general procedure D with L-ido-1-deoxynojirimycin (0.20 mmol) to provide **B48** (20 mg, 0.060 mmol, yield 30%).  $^1\text{H}$  NMR (400 MHz, MeOD)  $\delta$  4.05 - 3.95 (m, 3H), 3.90 (t,  $J = 3.0$  Hz, 1H), 3.88 - 3.80 (m, 2H), 3.77 - 3.70 (m, 1H), 3.58 (dd,  $J = 8.6, 5.5$  Hz, 1H), 3.56 - 3.52 (m, 2H), 3.50 (td,  $J = 6.3, 1.8$  Hz, 2H), 3.44 (dd,  $J = 9.3, 6.2$  Hz, 1H), 3.41 - 3.32 (m, 4H), 2.50 - 2.58 (m, 1H), 2.00 - 2.08 (m, 2H), 1.97 - 1.72 (m, 2H), 1.71 - 1.60 (m, 2H), 1.48 (p,  $J = 7.6$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz, MeOD)  $\delta$  72.5, 70.9, 70.5, 70.3, 67.5, 67.3, 66.7, 62.4, 60.0, 53.7, 53.0, 39.0, 28.7, 28.5, 23.1, 21.9. IR/cm $^{-1}$ : 3355, 2971, 1674, 1201, 1132, 1066.  $[\alpha]_{\text{D}}^{20}$ : +10.50 ( $c = 0.40$ , MeOH). HRMS: found 334.2230  $[\text{M}+\text{H}]^+$ , calculated for  $[\text{C}_{16}\text{H}_{31}\text{NO}_6+\text{H}]^+$  334.2224.

***N*-[5-(2-methyl-1-propyloxy)pentyl]-L-ido-1-deoxynojirimycin (B56/12)**



Bromide chain **B34** (0.19 mmol) was subjected to general procedure D with L-ido-1-deoxynojirimycin (0.20 mmol) to provide **B56** (28 mg, 0.092 mmol, yield 46%).  $^1\text{H}$  NMR (400 MHz, MeOD)  $\delta$  3.85 (t,  $J = 5.7$  Hz, 2H), 3.72 (dd,  $J = 8.9, 5.2$  Hz, 1H), 3.61 - 3.51 (m, 1H), 3.46 (t,  $J = 6.5$  Hz, 2H), 3.43 - 3.37 (m, 1H), 3.21 (d,  $J = 6.7$  Hz, 2H), 3.05 (q,  $J = 5.3$  Hz, 1H), 2.85 - 2.73 (m, 2H), 2.71 - 2.64 (m, 1H), 2.59 (dd,  $J = 12.4, 9.7$  Hz, 1H), 1.68 - 1.50 (m, 6H), 1.41 (p,  $J = 7.4$  Hz, 3H), 0.94 (s, 3H), 0.92 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz, MeOD)  $\delta$  79.8, 76.8, 73.6, 72.8, 72.1, 65.2, 58.5, 56.4, 53.7, 31.5, 30.4, 29.3, 25.8, 20.6.  $[\alpha]_{\text{D}}^{20}$ : +1.73 ( $c = 0.69$ , MeOH). IR/cm $^{-1}$ : 3345, 2870, 1673, 1430, 1381, 1198, 1132, 1028. HRMS: found 320.2432  $[\text{M}+\text{H}]^+$ , calculated for  $[\text{C}_{16}\text{H}_{33}\text{NO}_5+\text{H}]^+$  320.2431.

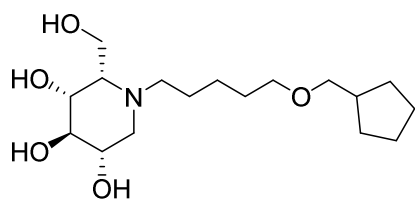
***N*-[5-(*R/S*-tetrahydrofuran-1-ylmethoxy)pentyl]-L-ido-1-deoxynojirimycin (B57)**



Bromide chain **B43** (0.29 mmol) was subjected to General Procedure D with L-ido-1-deoxynojirimycin (0.20 mmol) to provide **B57** (23 mg, 0.069 mmol, yield 34%).  $^1\text{H}$  NMR (400 MHz, MeOD)  $\delta$  4.12 - 3.94 (m, 5H), 3.93 - 3.83 (m, 2H), 3.82 - 3.74 (m, 1H), 3.58 - 3.48 (m, 5H), 3.48 - 3.29 (m, 3H), 2.08 - 1.85 (m, 4H), 1.85 - 1.73 (m, 1H), 1.70 - 1.59 (m, 3H), 1.50 (q,  $J$

= 7.5 Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz, MeOD)  $\delta$  78.0, 73.1, 70.9, 70.6, 67.8, 67.6, 66.7, 62.4, 59.9, 53.7, 53.0, 28.6, 27.5, 25.2, 23.1, 21.8. IR/cm $^{-1}$ : 3346, 2871, 1673, 1432, 1200, 1132, 1071.  $[\alpha]_{\text{D}}^{20}$ : +12.5 (c = 0.46, MeOH). HRMS: found 334.2228  $[\text{M}+\text{H}]^+$ , calculated for  $[\text{C}_{16}\text{H}_{31}\text{NO}_6+\text{H}]^+$  334.2224.

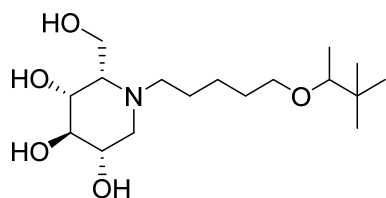
***N*-[5-(cyclopentylmethoxy)pentyl]-L-ido-1-deoxynojirimycin (B58)**



Bromide chain **B39** (0.30 mmol) was subjected to General Procedure D with L-ido-1-deoxynojirimycin (0.20 mmol) to provide **B58** (23 mg, 0.069 mmol, yield 35%).  $^1\text{H}$  NMR (400 MHz, MeOD)  $\delta$  4.05 (br s, 1H), 4.03 - 3.94 (m, 3H), 3.90 (br s, 1H), 3.60 - 3.51 (m, 2H), 3.49 (t,  $J$  = 6.3 Hz, 2H), 3.40 - 3.33 (m, 5H), 2.17 (dt,  $J$  = 14.9, 7.6 Hz, 1H), 1.96 - 1.72 (m, 4H), 1.71 - 1.54 (m, 6H), 1.48 (p,  $J$  = 7.7 Hz, 2H), 1.24 - 1.32 (m, 2H).  $^{13}\text{C}$

NMR (100 MHz, MeOD)  $\delta$  75.3, 70.9, 70.2, 67.5, 66.6, 62.4, 60.0, 53.6, 53.0, 39.3, 29.2, 28.7, 25.0, 23.1, 21.9. IR/cm $^{-1}$ : 3374, 2953, 2873, 1678, 1440, 1205, 1136, 1072.  $[\alpha]_{\text{D}}^{20}$ : +4.33 (c = 0.46, MeOH). HRMS: found 332.2436  $[\text{M}+\text{H}]^+$ , calculated for  $[\text{C}_{17}\text{H}_{33}\text{NO}_5+\text{H}]^+$  332.2432.

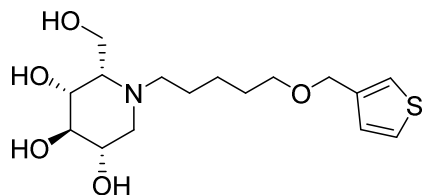
***N*-[5-(3,3-dimethyl-2-butoxy)pentyl]-L-ido-1-deoxynojirimycin (B59)**



Bromide chain **B35** (0.32 mmol) was subjected to general procedure D with L-ido-1-deoxynojirimycin (0.20 mmol) to provide **B59** (14 mg, 0.042 mmol, yield 21%).  $^1\text{H}$  NMR (400 MHz, MeOD)  $\delta$  4.05 (br s, 1H), 4.03 - 3.95 (m, 3H), 3.93 - 3.86 (m, 1H), 3.64 (ddd,  $J$  = 8.9, 7.6, 4.7 Hz, 1H), 3.58 - 3.47 (m, 2H), 3.41 - 3.30 (m, 4H), 3.04 (q,  $J$  = 6.3 Hz, 1H), 1.95 - 1.72 (m, 2H), 1.66 (dt,  $J$  = 12.9, 6.2 Hz, 2H), 1.56 - 1.44 (m, 2H), 1.08 (d,  $J$  = 6.4 Hz, 3H),

0.91 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz, MeOD)  $\delta$  83.3, 70.9, 68.9, 67.5, 66.6, 62.4, 60.0, 53.7, 53.0, 34.6, 29.4, 25.0, 23.3, 22.0, 12.8. IR/cm $^{-1}$ : 3372, 2972, 1673, 1393, 1203, 1139, 1066.  $[\alpha]_{\text{D}}^{20}$ : +1.44 (c = 0.28, MeOH). HRMS: found 334.2594  $[\text{M}+\text{H}]^+$ , calculated for  $[\text{C}_{17}\text{H}_{35}\text{NO}_5+\text{H}]^+$  334.2588.

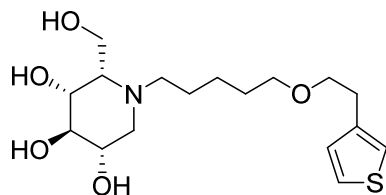
***N*-[5-(thiophen-3-methoxy)pentyl]-L-ido-1-deoxynojirimycin (B60)**



Bromide chain **B40** (0.29 mmol) was subjected to general procedure D with L-ido-1-deoxynojirimycin (0.20 mmol) to provide **B60** (14 mg, 0.042 mmol, yield 21%).  $^1\text{H}$  NMR (400 MHz, MeOD)  $\delta$  7.41 (dd,  $J$  = 5.0, 2.9 Hz, 1H), 7.33 (dd,  $J$  = 2.8, 1.2 Hz, 1H), 7.11 (dd,  $J$  = 5.0, 1.2 Hz, 1H), 4.54 (d,  $J$  = 0.7 Hz, 2H), 4.04 (br s, 1H), 4.01 - 3.93 (m, 3H), 3.89 (t,  $J$  = 3.7 Hz,

1H), 3.54 (t,  $J$  = 6.2 Hz, 2H), 3.55 - 3.44 (m, 2H), 3.39 - 3.28 (m, 3H), 1.98 - 1.72 (m, 2H), 1.69 (dt,  $J$  = 8.3, 6.3 Hz, 2H), 1.50 (q,  $J$  = 7.6 Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz, MeOD)  $\delta$  139.5, 127.1, 125.6, 122.6, 70.9, 69.3, 67.6, 67.5, 66.6, 62.4, 60.0, 53.6, 53.0, 28.7, 23.1, 21.8. IR/cm $^{-1}$ : 3346, 2970, 1673, 1409, 1201, 1133, 1066.  $[\alpha]_{\text{D}}^{20}$ : +8.28 (c = 0.29, MeOH). HRMS: found 346.1682  $[\text{M}+\text{H}]^+$ , calculated for  $[\text{C}_{16}\text{H}_{27}\text{NO}_5\text{S}+\text{H}]^+$  346.1683.

***N*-[5-(thiophen-3-ethoxy)pentyl]-L-ido-1-deoxynojirimycin (B61)**



Bromide chain **B41** (0.29 mmol) was subjected to general procedure D with L-ido-1-deoxynojirimycin (0.20 mmol) to provide **B61** (36 mg, 0.099 mmol, yield 49%).  $^1\text{H}$  NMR (400 MHz, MeOD)  $\delta$  7.33 (dd,  $J$  = 4.9, 3.0 Hz, 2H), 7.14 - 7.09 (m, 1H), 7.02 (dd,  $J$  = 4.9, 1.3 Hz, 1H), 4.05 (br s, 1H), 4.01 - 3.95 (m, 3H), 3.90 (t,  $J$  = 3.7 Hz, 1H), 3.68 (t,  $J$  = 6.7 Hz, 2H), 3.56 - 3.47 (m, 2H), 3.52 (t,  $J$  = 6.2 Hz, 2H), 3.38 - 3.28 (m, 3H), 2.94 - 2.88 (m, 2H),

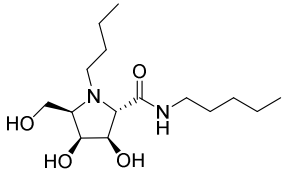
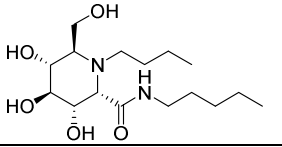
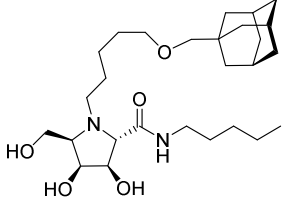
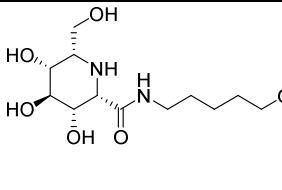
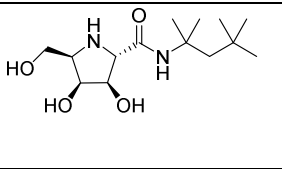
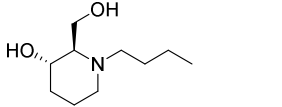
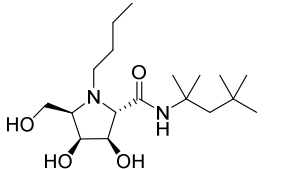
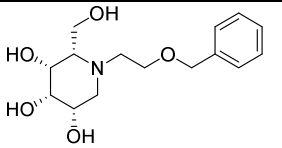
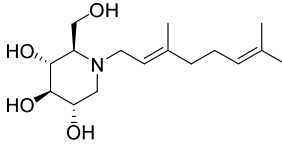
1.93 - 1.70 (m, 2H), 1.67 (dq,  $J$  = 8.3, 6.3 Hz, 2H), 1.53 - 1.37 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz, MeOD)  $\delta$  139.3, 128.1, 124.7, 120.7, 70.9, 70.8, 70.0, 67.5, 66.6, 62.4, 60.0, 53.7, 53.0, 30.2, 28.7, 23.1, 21.8. IR/cm $^{-1}$ : 3355, 2971, 1674, 1394, 1202, 1066.  $[\alpha]_{\text{D}}^{20}$ : +2.52 (c = 0.71, MeOH). HRMS: found 360.1840  $[\text{M}+\text{H}]^+$ , calculated for  $[\text{C}_{17}\text{H}_{29}\text{NO}_5\text{S}+\text{H}]^+$  360.1839.

## S4. Synthetic Procedure and Spectral Data of Iminosugar Library Compounds

The synthesis of deoxynojirimycin congeners was performed similar as described in previous section (procedure D). For non *D-gluco* or *L-ido* configured iminosugars the procedure was slightly adjusted with the use of the proper configured deoxynojirimycin in order to obtain the desired products.<sup>3, 4 & 5</sup> The following list contains the chemical structures and names for all entries in the library. The spectral data are given for unpublished iminosugar derivatives (table S1).

**Table S1: Compound Numbering and Structures of the Iminosugar Library**

| Entry | Name   | Structure | Reference or Spectral Data |
|-------|--|-----------|----------------------------|
| C1    | (2 <i>S</i> ,3 <i>S</i> ,4 <i>S</i> ,5 <i>R</i> ,6 <i>S</i> )-1-(5-(((3 <i>S</i> ,5 <i>S</i> ,7 <i>S</i> )-adamantan-1-yl)methoxy)pentyl)-3,4,5-trihydroxy-6-(hydroxymethyl)- <i>N</i> -(2,4,4-trimethylpentan-2-yl)piperidine-2-carboxamide |           | 6                          |
| C2    | (2 <i>S</i> ,3 <i>S</i> ,4 <i>S</i> ,5 <i>R</i> ,6 <i>S</i> )- <i>N</i> -(5-(((3 <i>S</i> ,5 <i>S</i> ,7 <i>S</i> )-adamantan-1-yl)methoxy)pentyl)-3,4,5-trihydroxy-6-(hydroxymethyl)piperidine-2-carboxamide                                |           | 6                          |
| C3    | (2 <i>S</i> ,3 <i>S</i> ,4 <i>S</i> ,5 <i>R</i> ,6 <i>R</i> )-1-(5-(((3 <i>S</i> ,5 <i>S</i> ,7 <i>S</i> )-adamantan-1-yl)methoxy)pentyl)-3,4,5-trihydroxy-6-(hydroxymethyl)piperidine-2-carboxylic acid                                     |           | 6                          |
| C4    | (2 <i>S</i> ,3 <i>S</i> ,4 <i>S</i> ,5 <i>R</i> ,6 <i>S</i> )- <i>N</i> -(5-(((3 <i>S</i> ,5 <i>S</i> ,7 <i>S</i> )-adamantan-1-yl)methoxy)pentyl)-1-butyl-3,4,5-trihydroxy-6-(hydroxymethyl)piperidine-2-carboxamide                        |           | 6                          |
| C5    | (2 <i>S</i> ,3 <i>S</i> ,4 <i>S</i> ,5 <i>R</i> ,6 <i>S</i> )- <i>N</i> ,1-bis(5-(((3 <i>S</i> ,5 <i>S</i> ,7 <i>S</i> )-adamantan-1-yl)methoxy)pentyl)-3,4,5-trihydroxy-6-(hydroxymethyl)piperidine-2-carboxamide                           |           | 6                          |
| C6    | (2 <i>S</i> ,3 <i>R</i> ,4 <i>S</i> ,5 <i>R</i> )-3,4-dihydroxy-5-(hydroxymethyl)- <i>N</i> -pentylpyrrolidine-2-carboxamide   |           | 7                          |
| C7    | (2 <i>R</i> ,3 <i>R</i> ,4 <i>R</i> ,5 <i>S</i> )-1-butyl-2-(hydroxymethyl)piperidine-3,4,5-triol  |           | 8                          |

|     |  |   |   |
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| C8  | (2S,3R,4S,5R)-1-butyl-3,4-dihydroxy-5-(hydroxymethyl)-N-pentylpyrrolidine-2-carboxamide  |    | 7   |
| C9  | (2S,3S,4S,5R,6R)-1-butyl-3,4,5-trihydroxy-6-(hydroxymethyl)-N-pentylpiperidine-2-carboxamide                                     |    | 6   |
| C10 | (2S,3R,4S,5R)-1-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-3,4-dihydroxy-5-(hydroxymethyl)-N-pentylpyrrolidine-2-carboxamide |    | 7   |
| C11 | (2S,3S,4S,5R,6S)-N-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-3,4,5-trihydroxy-6-(hydroxymethyl)piperidine-2-carboxamide     |    | 6   |
| C12 | (2S,3R,4S,5R)-3,4-dihydroxy-5-(hydroxymethyl)-N-(2,4,4-trimethylpentan-2-yl)pyrrolidine-2-carboxamide                            |   | 7   |
| C13 | (2R,3S)-1-butyl-2-(hydroxymethyl)piperidin-3-ol  |  | 9   |
| C14 | (2S,3R,4S,5R)-1-butyl-3,4-dihydroxy-5-(hydroxymethyl)-N-(2,4,4-trimethylpentan-2-yl)pyrrolidine-2-carboxamide                    |  | 7   |
| C15 | (2S,3R,4S,5S)-1-(2-(benzyloxy)ethyl)-2-(hydroxymethyl)piperidine-3,4,5-triol   |  | <sup>1</sup> H NMR (400 MHz, D <sub>2</sub> O) δ 7.51 - 7.31 (m, 5H), 4.58 (s, 2H), 4.22 (s, 1H), 4.17 (s, 1H), 3.99 (m, 2H), 3.94 - 3.85 (m, 2H), 3.82 (s, 1H), 3.74 - 3.43 (m, 4H), 3.36 (d, J = 13.1 Hz, 1H). <sup>13</sup> C NMR (100 MHz, D <sub>2</sub> O) δ 136.86, 128.90, 128.66, 128.61, 73.08, 69.88, 66.98, 66.52, 65.60, 63.00, 59.17, 55.91, 52.75. [α] <sub>D</sub> <sup>25</sup> = +13.0 (c = 0.4, MeOH). IR/cm <sup>-1</sup> : 3341, 1674, 1435, 1200, 1130, 1042. LCMS: 10 - 50, R <sub>t</sub> 3.10 min, [M+H] <sup>+</sup> = 298.13. HRMS : calcd for [C <sub>15</sub> H <sub>23</sub> NO <sub>5</sub> +H] <sup>+</sup> 298.1649, found 298.1656 [M+H] <sup>+</sup> . |
| C16 | (2R,3R,4R,5S)-2-(hydroxymethyl)-1-((2E,6E)-3,7,11-trimethyldodeca-2,6,10-trien-1-yl)piperidine-                                  |  | <sup>1</sup> H NMR (400 MHz, MeOD) δ 5.48 - 5.29 (m, 1H), 5.27 - 5.02 (m, 2H), 4.23 - 4.05 (m, 1H), 4.04 - 3.85 (m, 2H), 3.83 - 3.73 (m, 1H), 3.73 - 3.62   |

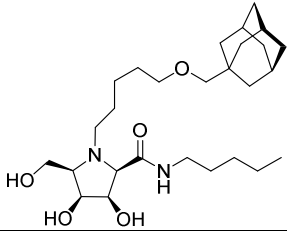
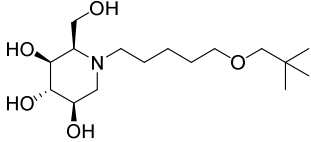
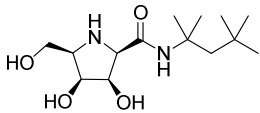
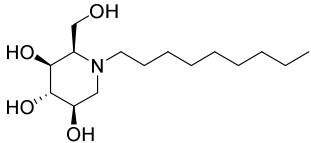
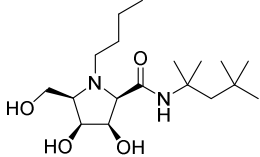
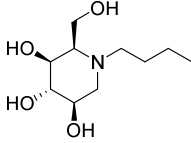
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|     | 3,4,5-triol   |  | (m, 1H), 3.62 - 3.51 (m, 1H), 3.46 - 3.33 (m, 2H), 3.05 - 2.88 (m, 1H), 2.86 - 2.66 (m, 1H), 2.40 - 1.91 (m, 8H), 1.91 - 1.46 (m, 12H). <sup>13</sup> C NMR (50 MHz, MeOD) δ 149.1, 137.0, 132.3, 125.5, 124.8, 114.0, 78.6, 69.3, 68.2, 67.3, 55.7, 54.6, 51.7, 41.0, 40.9, 27.9, 27.3, 26.0, 17.9, 17.2, 16.3. [α] <sub>D</sub> <sup>20</sup> = -1.3 (c = 0.9, MeOH). IR/cm <sup>-1</sup> : 3333, 2962, 2924, 1643, 1443, 1381, 1080, 1026. HRMS: calcd for [C <sub>21</sub> H <sub>37</sub> O <sub>4</sub> N+H] <sup>+</sup> 368.2795 found 368.2820 [M+H] <sup>+</sup> . |
| C17 | (2R,3R,4R,5S)-2-(hydroxymethyl)-1-pentylpiperidine-3,4,5-triol  |  | 8  |
| C18 | N-((3S,5S,7S)-adamantan-1-yl)-6-((2R,3R,4R,5S)-3,4,5-trihydroxy-2-(hydroxymethyl)piperidin-1-yl)hexanamide  |  | 10   |
| C19 | (2R,3R,4R,5S)-1-(5-butoxypentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol  |  | 8  |
| C20 | (2R,3R,4R,5S)-2-(hydroxymethyl)-1-(5-(pentyloxy)pentyl)piperidine-3,4,5-triol   |  | 8  |
| C21 | (2R,3R,4R,5S)-1-(5-(hexyloxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol  |  | 8  |
| C22 | (2S,3R,4R,5S)-1-(5-(((3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol |  | 10   |
| C23 | (2R,3R,4R,5S)-1-(5-(heptyloxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol   |  | 8  |



|     |  |  |  |
|-----|--|--|--|
| C24 | (2S,3S,4R,5R)-1-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol   |  | <sup>1</sup> H NMR (400 MHz, D <sub>2</sub> O) δ 4.14 (s, 1H), 4.08 - 3.94 (m, 2H), 3.94 - 3.80 (m, 2H), 3.39 (t, <i>J</i> = 6.2 Hz, 2H), 3.31 - 3.10 (m, 5H), 2.97 (s, 2H), 1.91 (s, 3H), 1.63 (m, 10H), 1.49 (s, 6H), 1.42 - 1.30 (m, 2H). <sup>13</sup> C NMR (100 MHz, D <sub>2</sub> O) δ 81.7, 71.4, 69.5, 64.7, 63.8, 60.3, 53.6, 53.0, 48.9, 40.0, 37.0, 33.8, 28.4, 28.2, 22.8, 22.2. [α] <sub>D</sub> <sup>25</sup> = +3.5 (c = 1.3, MeOH). IR/cm <sup>-1</sup> : 3368, 2901, 2847, 1670, 1454, 1188, 1134, 1080. LCMS: 10-50, <i>R</i> <sub>t</sub> 9.55 min, [M+H] <sup>+</sup> = 398.33. HRMS : calcd for [C <sub>22</sub> H <sub>39</sub> NO <sub>5</sub> +H] <sup>+</sup> 398.2901, found 398.2900 [M+H] <sup>+</sup> . |
| C25 | (2R,3R,4R,5S)-2-(hydroxymethyl)-1-(5-(octyloxy)pentyl)piperidine-3,4,5-triol                             |  | 8  |
| C26 | (2S,3R,4R,5S)-2-(hydroxymethyl)-1-(5-(neopentyloxy)pentyl)piperidine-3,4,5-triol                         |  | <sup>1</sup> H NMR (400 MHz, MeOD) δ 3.89 (d, <i>J</i> = 5.3 Hz, 2H), 3.82 (dd, <i>J</i> = 7.2, 4.2 Hz, 1H), 3.71 - 3.64 (m, 1H), 3.56 (t, <i>J</i> = 7.0 Hz, 1H), 3.43 (t, <i>J</i> = 6.3 Hz, 1H), 3.27 - 3.18 (m, 1H), 3.07 (s, 2H), 3.10 - 2.87 (m, 4H), 1.82 - 1.53 (m, 4H), 1.51 - 1.37 (m, 2H), 0.90 (s, 9H). <sup>13</sup> C NMR (100 MHz, MeOD) δ 82.4, 72.4, 72.3, 70.3, 64.0, 55.8, 55.3, 53.3, 32.9, 30.4, 26.7, 24.8, 13.3. IR/cm <sup>-1</sup> : 3369, 2935, 2860, 1066. LC/MS analysis: <i>R</i> <sub>t</sub> 4.98 min (linear gradient 10-90% B), ES: = 320.3 [M+H] <sup>+</sup> . HRMS : calcd for [C <sub>16</sub> H <sub>33</sub> O <sub>5</sub> N+H] <sup>+</sup> 320.2432 found 320.2431 [M+H] <sup>+</sup> .      |
| C27 | (2R,3R,4R,5S)-2-(hydroxymethyl)-1-(5-(nonyloxy)pentyl)piperidine-3,4,5-triol                             |  | 8  |
| C28 | (2R,3S,4R,5R,6R)-2-(4-(((3R,5R,7R)-adamantan-1-yl)methoxy)butyl)-6-(hydroxymethyl)piperidine-3,4,5-triol |  | 11   |
| C29 | (2R,3R,4R,5S)-1-hexyl-2-(hydroxymethyl)piperidine-3,4,5-triol  |  | 8  |

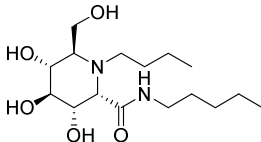
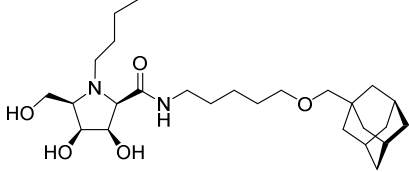
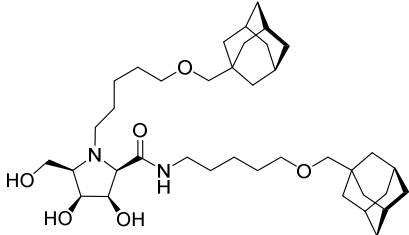
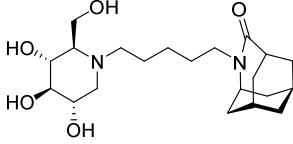
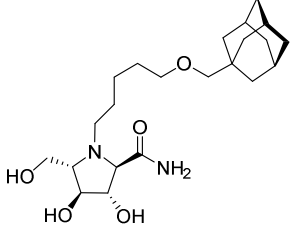
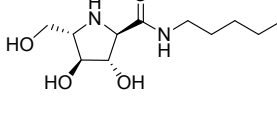
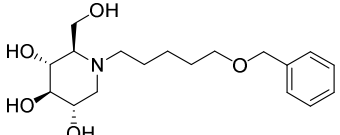
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| C30 | (2R,3S,4S,5R)-2-((E)-5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pent-2-en-1-yl)piperidine-3,4,5-triol                                |  | 11 |
| C31 | (2R,3R,4R,5S)-1-heptyl-2-(hydroxymethyl)piperidine-3,4,5-triol  |  | 8  |
| C32 | (2R,3R,4R,5S)-1-(6-((3R,5R,7R)-adamantan-1-yl)hexyl)-2-(hydroxymethyl)piperidine-3,4,5-triol                                    |  | 10 |
| C33 | (2R,3R,4R,5S)-2-(hydroxymethyl)-1-octylpiperidine-3,4,5-triol   |  | 8  |
| C34 | (2S,3R,4S,5R)-N-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-1-butyl-3,4-dihydroxy-5-(hydroxymethyl)pyrrolidine-2-carboxamide |  | 7  |
| C35 | (2R,3R,4R,5S)-1-(5-((3-fluoro-[1,1'-biphenyl]-4-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol                      |  | 10 |
| C36 | (2S,3S,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)-N-pentylpiperidine-2-carboxamide  |  | 6  |
| C37 | (2R,3R,4R,5S)-1-(5-((2-fluoro-[1,1'-biphenyl]-4-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol                      |  | 10 |
| C38 | (2S,3R,4S,5R)-N,1-bis(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-3,4-dihydroxy-5-(hydroxymethyl)pyrrolidine-2-carboxamide    |  | 7  |
| C39 | (2S,3R,4R,5S)-2-(hydroxymethyl)-1-(5-((3-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)methoxy)pentyl)piperidine-3,4,5-triol           |  | 10 |

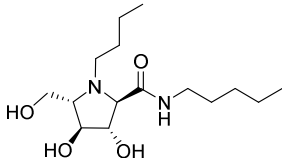
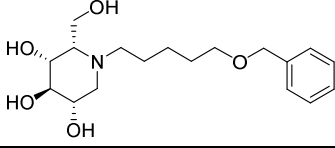
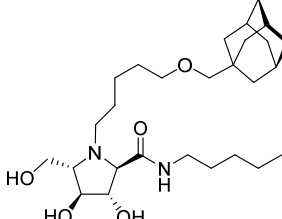
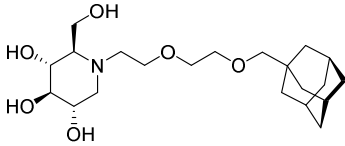
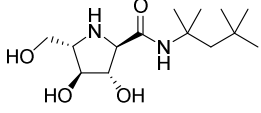
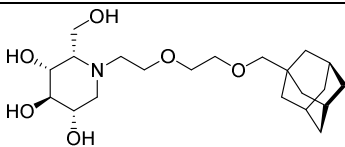
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| C40 | (2R,3R,4S,5R)-1-butyl-3,4-dihydroxy-5-(hydroxymethyl)pyrrolidine-2-carboxamide  |  | 7   |
| C41 | (2S,3R,4R,5S)-2-(hydroxymethyl)-1-(5-((2-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)methoxy)pentyl)piperidine-3,4,5-triol   |  | 10  |
| C42 | (2R,3R,4S,5R)-1-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-3,4-dihydroxy-5-(hydroxymethyl)pyrrolidine-2-carboxamide |  | 7   |
| C43 | (2S,3R,4R,5S)-1-(5-((3-fluoro-[1,1'-biphenyl]-4-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol              |  | 10  |
| C44 | (2S,3R,4S,5R)-3,4-dihydroxy-5-(hydroxymethyl)-N-pentylpyrrolidine-2-carboxamide   |  | 7   |
| C45 | (2S,3R,4R,5S)-1-(5-((2-fluoro-[1,1'-biphenyl]-4-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol              |  | 10  |
| C46 | (2R,3R,4S,5R)-1-butyl-3,4-dihydroxy-5-(hydroxymethyl)-N-pentylpyrrolidine-2-carboxamide                                 |  | 7   |
| C47 | (2R,3S,4S,5R)-1-(5-(benzyloxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol   |  | <sup>1</sup> H NMR (400 MHz, MeOD) δ 7.42 -7.24 (m, 5H), 4.60 (s, 2H), 4.05 - 3.76 (m, 5H), 3.76 - 3.27 (m, 5H). <sup>13</sup> C NMR (100 MHz, MeOD) δ 138.7, 129.6, 129.1, 129.0, 74.1, 71.63, 68.7, 68.6, 64.5, 64.1, 60.2, 54.6, 54.1. [α] <sub>D</sub> <sup>20</sup> = -0.02 (c = 0.5, MeOD). IR/cm <sup>-1</sup> : 3363, 1674, 1203, 1134, 1072. LC/MS analysis: R <sub>t</sub> 3.03 min (linear gradient 10-90% B), ES : = 298.1 [M+H] <sup>+</sup> . HRMS : calcd for [C <sub>15</sub> H <sub>23</sub> O <sub>5</sub> N+H] <sup>+</sup> 298.1655 found 298.1660 [M+H] <sup>+</sup> . |

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| C48 | (2R,3R,4S,5R)-1-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-3,4-dihydroxy-5-(hydroxymethyl)-N-pentylpyrrolidine-2-carboxamide |    | 7   |
| C49 | (2R,3S,4S,5R)-2-(hydroxymethyl)-1-(5-(neopentyloxy)pentyl)piperidine-3,4,5-triol   |    | <sup>1</sup> H NMR (400 MHz, MeOD) δ 4.08 (m, 4H), 3.84 (br s, 1H), 3.53 - 3.32 (m, 7H), 3.08 (s, 2H), 1.87 - 1.73 (m, 2H), 1.69 - 1.59 (m, 2H), 1.51 - 1.43 (m, 2H), 0.91 (s, 9H). <sup>13</sup> C NMR (100 MHz, MeOD) δ 82.2, 71.8, 71.7, 68.6, 68.1, 63.4, 60.8, 54.4, 53.9, 29.9, 26.7, 24.1, 23.1. [α] <sub>D</sub> <sup>20</sup> = -0.04 (c = 0.6, MeOD). IR/cm <sup>-1</sup> : 3444, 1680, 1199, 1134, 1068. LC/MS analysis: R <sub>t</sub> 4.51 min (linear gradient 10-90% B), ES: = 320.3 [M+H] <sup>+</sup> . HRMS : calcd for [C <sub>16</sub> H <sub>33</sub> O <sub>5</sub> N+H] <sup>+</sup> found 320.2437 [M+H] <sup>+</sup> . |
| C50 | (2R,3R,4S,5R)-3,4-dihydroxy-5-(hydroxymethyl)-N-(2,4,4-trimethylpentan-2-yl)pyrrolidine-2-carboxamide                            |   | 7   |
| C51 | (2R,3S,4S,5R)-2-(hydroxymethyl)-1-nonylpiperidine-3,4,5-triol  |  | <sup>1</sup> H NMR (400 MHz, MeOD) δ 4.03 - 3.87 (m, 4H), 3.82 (br s, 1H), 3.52 - 3.26 (m, 5H), 1.85 - 1.67 (m, 2H), 1.41 - 1.28 (m, 12H), 0.90 (t, J = 7.0 Hz, 3H). <sup>13</sup> C NMR (100 MHz, MeOD) δ 71.8, 68.8, 68.0, 63.6, 60.7, 54.7, 53.7, 33.0 - 23.7, 14.4. [α] <sub>D</sub> <sup>20</sup> = -0.05 (c = 0.5, MeOD). IR/cm <sup>-1</sup> : 3363, 1670, 1203, 1134, 1068. LC/MS analysis: R <sub>t</sub> 5.02 min (linear gradient 10-90% B), ES: = 290.3 [M+H] <sup>+</sup> . HRMS: calcd for [C <sub>16</sub> H <sub>31</sub> O <sub>4</sub> N+H] <sup>+</sup> 290.2331 found 290.2335 [M+H] <sup>+</sup> .                         |
| C52 | (2R,3R,4S,5R)-1-butyl-3,4-dihydroxy-5-(hydroxymethyl)-N-(2,4,4-trimethylpentan-2-yl)pyrrolidine-2-carboxamide                    |  | 7   |
| C53 | (2R,3S,4S,5R)-1-butyl-2-(hydroxymethyl)piperidine-3,4,5-triol  |  | <sup>1</sup> H NMR (400 MHz, MeOD) δ 4.02 - 3.76 (m, 5H), 3.52 - 3.22 (m, 5H), 1.77 - 1.65 (m, 2H), 1.47 - 1.37 (m, 2H), 1.01 (t, J = 7.4 Hz, 3H). <sup>13</sup> C NMR (100 MHz, MeOD) δ 72.6, 69.0, 64.3, 63.9, 61.1, 54.7, 25.7, 21.1, 14.0. [α] <sub>D</sub> <sup>20</sup> = -0.01 (c = 0.2, MeOD). IR/cm <sup>-1</sup> : 3363, 1670, 1203, 1134, 1068. LC/MS analysis:  |

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|     |  |  | $R_t$ 0.73 min (linear gradient 10-90% B), ES: = 220.0 [M+H] <sup>+</sup> . HRMS: calcd for [C <sub>10</sub> H <sub>21</sub> O <sub>4</sub> N+H] <sup>+</sup> 220.1549 found 220.1551 [M+H] <sup>+</sup> .   |
| C54 | (2S,3R,4S,5R)-2-(hydroxymethyl)-1-((2E,6E)-3,7,11-trimethyldodeca-2,6,10-trien-1-yl)piperidine-3,4,5-triol |  | <sup>1</sup> H NMR (400 MHz, MeOD) δ 5.32 (t, <i>J</i> = 6.9, 1H), 5.17 - 5.01 (m, 2H), 3.91 (d, <i>J</i> = 5.2, 2H), 3.87 - 3.78 (m, 1H), 3.73 - 3.63 (m, 1H), 3.63 - 3.46 (m, 3H), 3.26 - 3.12 (m, 1H), 3.07 - 2.93 (m, 1H), 2.92 - 2.71 (m, 1H), 2.22 - 1.95 (m, 8H), 1.73 (s, 3H), 1.67 (s, 3H), 1.61 (s, 3H), 1.60 (s, 3H). <sup>13</sup> C NMR (100 MHz, MeOD) δ 136.7, 132.3, 125.6, 125.1, 72.7, 70.6, 64.1, 59.1, 53.1, 53.0, 41.1, 41.0, 27.9, 27.5, 26.0, 17.9, 16.9, 16.3. IR/cm <sup>-1</sup> : 3317, 2962, 2916, 2862, 1666, 1443, 1381, 1242, 1072, 1042, 980. MS: found 368.5 [M+H] <sup>+</sup> , calculated for [C <sub>21</sub> H <sub>37</sub> O <sub>4</sub> N+H] <sup>+</sup> 368.3. |
| C55 | (2S,3R,4S,5R)-2-(hydroxymethyl)-1-pentylpiperidine-3,4,5-triol   |  | 8  |
| C56 | (2S,3R,4R,5S)-1-(6-(((3S,5S,7S)-adamantan-1-yl)methoxy)hexyl)-2-(hydroxymethyl)piperidine-3,4,5-triol      |  | 3  |
| C57 | (2S,3R,4R,5S)-1-(5-butoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol                                  |  | 8  |
| C58 | (2R,3R,4R,5S)-2-(hydroxymethyl)-1-(5-(naphthalen-2-ylmethoxy)pentyl)piperidine-3,4,5-triol                 |  | 10   |
| C59 | (2S,3R,4R,5S)-2-(hydroxymethyl)-1-(5-(pentyloxy)pentyl)piperidine-3,4,5-triol                              |  | 8  |
| C60 | (2S,3R,4R,5S)-2-(hydroxymethyl)-1-(5-(naphthalen-2-ylmethoxy)pentyl)piperidine-3,4,5-triol                 |  | 10   |
| C61 | (2S,3R,4R,5S)-1-(5-(hexyloxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol                               |  | 8  |

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| C62 | (2R,3R,4R,5S)-1-(5-([1,1'-biphenyl]-4-ylmethoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol  |  | 10 |
| C63 | (2S,3R,4R,5S)-1-(5-(heptyloxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol  |  | 8  |
| C64 | (2S,3R,4R,5S)-1-(5-([1,1'-biphenyl]-4-ylmethoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol  |  | 10 |
| C65 | (2S,3R,4R,5S)-2-(hydroxymethyl)-1-(5-(octyloxy)pentyl)piperidine-3,4,5-triol   |  | 8  |
| C66 | (2R,3R,4R,5S)-2-(hydroxymethyl)-1-(5-(phenanthren-9-ylmethoxy)pentyl)piperidine-3,4,5-triol  |  | 10 |
| C67 | (2S,3R,4R,5S)-2-(hydroxymethyl)-1-(5-(nonyloxy)pentyl)piperidine-3,4,5-triol   |  | 8  |
| C68 | (2S,2'S,3R,3'R,4R,4'R,5S,5'S)-1,1'-((2-((3S,5S,7S)-adamantan-1-yl)propane-1,3-diyl)bis(oxy))bis(pentane-5,1-diyl))bis(2-(hydroxymethyl)piperidine-3,4,5-triol) |  | 12 |
| C69 | (2S,3R,4R,5S)-1-hexyl-2-(hydroxymethyl)piperidine-3,4,5-triol  |  | 8  |
| C70 | N-((3R,5R,7R)-adamantan-1-yl)-6-((2S,3R,4R,5S)-3,4,5-trihydroxy-2-(hydroxymethyl)piperidin-1-yl)hexanamide   |  | 10 |
| C71 | (2S,3R,4R,5S)-1-heptyl-2-(hydroxymethyl)piperidine-3,4,5-triol   |  | 8  |
| C72 | (2S,3R,4R,5S)-2-(hydroxymethyl)-1-octylpiperidine-3,4,5-triol  |  | 8  |

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| C73 | (2S,3S,4S,5R,6R)-1-butyl-3,4,5-trihydroxy-6-(hydroxymethyl)-N-pentylpiperidine-2-carboxamide   |    | 6  |
| C74 | (2R,3R,4S,5R)-N-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-1-butyl-3,4-dihydroxy-5-(hydroxymethyl)pyrrolidine-2-carboxamide              |    | 7  |
| C75 | (2R,3R,4S,5R)-N,1-bis(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-3,4-dihydroxy-5-(hydroxymethyl)pyrrolidine-2-carboxamide                 |    | 7  |
| C76 | (1R,3R,8S)-4-(5-(((2R,3R,4R,5S)-3,4,5-trihydroxy-2-(hydroxymethyl)piperidin-1-yl)pentyl)-4-azatricyclo[4.3.1.1 <sup>3,8</sup> ]undecan-5-one |    | <sup>1</sup> H NMR (400 MHz, MeOD) δ 4.02 (dd, <i>J</i> = 11.6, 76.8, 2H), 3.85 - 3.74 (m, 3H), 3.68 - 3.59 (m, 1H), 3.54 - 3.30 (m, 6H), 3.16-3.07 (m, 1H), 2.79 ( <i>t</i> , <i>J</i> = 4.0, 1H), 2.08 - 2.01 (m, 4H), 1.88 (s, 4H), 1.82 (d, <i>J</i> = 13.6, 4H), 1.77 (s, 2H), 1.62 ( <i>t</i> , <i>J</i> = 7.2, 2H), 1.45 - 1.37 (m, 2H). <sup>13</sup> C NMR (100 MHz, MeOD) δ 181.0, 68.4, 67.3, 67.0, 60.6, 58.2, 55.1, 54.5, 49.2, 46.8, 43.4, 36.2, 36.2, 34.9, 31.7, 27.7, 27.1, 24.3. [α] <sub>D</sub> <sup>20</sup> = - 0.00 (c = 0.4, MeOD). IR/cm <sup>-1</sup> : 3363, 1666, 1203, 1134, 1091, 1029. LC/MS analysis: <i>R</i> <sub>t</sub> 4.02 min (linear gradient 10-90% B), ES: = 397.3 [M+H] <sup>+</sup> . HRMS: calcd for [C <sub>21</sub> H <sub>36</sub> O <sub>5</sub> N <sub>2</sub> +H] <sup>+</sup> 397.2702 found 397.2702 [M+H] <sup>+</sup> . |
| C77 | (2R,3S,4S,5S)-1-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-3,4-dihydroxy-5-(hydroxymethyl)pyrrolidine-2-carboxamide                      |  | 7  |
| C78 | (2R,3S,4S,5S)-3,4-dihydroxy-5-(hydroxymethyl)-N-pentylpyrrolidine-2-carboxamide  |  | 7  |
| C79 | (2R,3R,4R,5S)-1-(5-(benzyloxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol  |  | 10   |

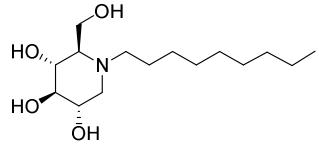
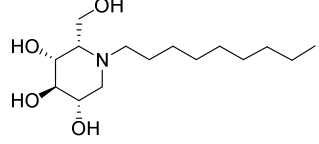
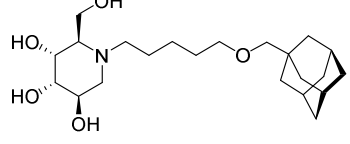
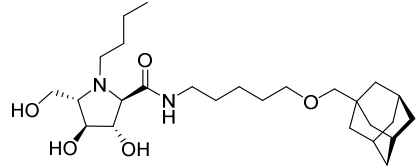
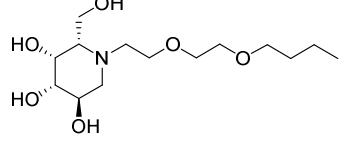
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| C80 | (2R,3S,4S,5S)-1-butyl-3,4-dihydroxy-5-(hydroxymethyl)-N-pentylpyrrolidine-2-carboxamide  |    | 7  |
| C81 | (2S,3R,4R,5S)-1-(5-(benzyloxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol  |    | 10   |
| C82 | (2R,3S,4S,5S)-1-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-3,4-dihydroxy-5-(hydroxymethyl)-N-pentylpyrrolidine-2-carboxamide |    | 7  |
| C83 | (2R,3R,4R,5S)-1-(2-(2-(((3R,5R,7R)-adamantan-1-yl)methoxy)ethoxy)ethyl)-2-(hydroxymethyl)piperidine-3,4,5-triol                  |    | <sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) δ 3.94 (dd, <i>J</i> = 12.2, 2.6 Hz, 1H), 3.86 (dd, <i>J</i> = 12.2, 2.5 Hz, 1H), 3.66 (t, <i>J</i> = 5.4 Hz, 2H), 3.63 - 3.58 (m, 2H), 3.57 - 3.52 (m, 3H), 3.50 (ddd, <i>J</i> = 10.4, 9.3, 4.8 Hz, 1H), 3.39 (t, <i>J</i> = 9.3 Hz, 1H), 3.17 (t, <i>J</i> = 9.1 Hz, 1H), 3.15 - 3.06 (m, 2H), 2.81 (dt, <i>J</i> = 14.4, 4.8 Hz, 1H), 2.40 (t, <i>J</i> = 11.0 Hz, 1H), 2.33 (dt, <i>J</i> = 9.5, 2.4 Hz, 1H), 1.95 (s, 3H), 1.82 - 1.64 (m, 6H), 1.57 (m, 6H). <sup>13</sup> C NMR (100 MHz, MeOD) δ 83.5, 80.2, 72.2, 71.5, 71.4, 70.3, 69.1, 67.7, 58.8, 58.2, 52.8, 40.7, 38.3, 35.1, 29.7. [α] <sub>D</sub> <sup>20</sup> = -0.01 (c = 1.3, MeOD). IR/cm <sup>-1</sup> : 3363, 2900, 2846, 1454, 1246, 1091, 1037, 1014. LC/MS analysis: <i>R</i> <sub>t</sub> 5.20 min (linear gradient 10-90% B), ES: = 400.3 [M+H] <sup>+</sup> . HRMS: calcd for [C <sub>21</sub> H <sub>37</sub> NO <sub>6</sub> +H] <sup>+</sup> : 400.2699. found 400.2700 [M+H] <sup>+</sup> . |
| C84 | (2R,3S,4S,5S)-3,4-dihydroxy-5-(hydroxymethyl)-N-(2,4,4-trimethylpentan-2-yl)pyrrolidine-2-carboxamide                            |  | 7  |
| C85 | (2S,3R,4R,5S)-1-(2-(2-(((3S,5S,7S)-adamantan-1-yl)methoxy)ethoxy)ethyl)-2-(hydroxymethyl)piperidine-3,4,5-triol                  |  | <sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) δ 4.03-3.86 (br m, 6H), 3.82 (br s, 1H), 3.68 - 3.44 (m, 9H), 3.04 (s, 2H), 1.95 (b s, 3H), 1.78 - 1.67 (m, 6H), 1.57 (m, 6H). <sup>13</sup> C NMR (100 MHz, CDCl <sub>3</sub> ) δ 83.2, 71.9, 71.7, 71.2, 68.9, 68.8, 65.9, 64.2, 59.9, 54.1, 40.3, 37.9, 29.3. [α] <sub>D</sub> <sup>20</sup> = 0.03 (c = 0.7, MeOD). IR/cm <sup>-1</sup> : 3313, 2900, 2846, 1674, 1203, 1134, 1080. LC/MS analysis: <i>R</i> <sub>t</sub>   |

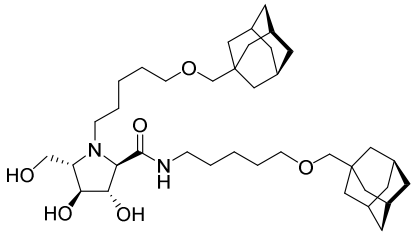
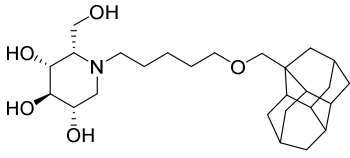
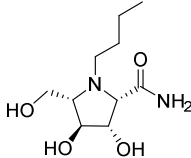
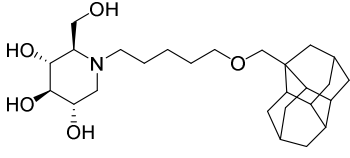


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|     |  |  | 5.32 min (linear gradient 10-90% B), ES: = 400.3 [M+H] <sup>+</sup> . HRMS: calcd for [C <sub>21</sub> H <sub>37</sub> O <sub>6</sub> N+H] <sup>+</sup> 400.2699 found 400.2698 [M+H] <sup>+</sup> .  |
| C86 | (2R,3S,4S,5S)-1-butyl-3,4-dihydroxy-5-(hydroxymethyl)-N-(2,4,4-trimethylpentan-2-yl)pyrrolidine-2-carboxamide  |  |   |
| C87 | (2S,3R,4R,5S)-1-(2-(2-(cyclohexylmethoxy)ethoxy)ethyl)-2-(hydroxymethyl)piperidine-3,4,5-triol   |  | <sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) δ 4.08 (d, <i>J</i> = 12.8 Hz, 1H), 3.98 (dd, <i>J</i> = 12.5, 3.0 Hz, 1H), 3.88 (t, <i>J</i> = 4.8 Hz, 2H), 3.71 (ddd, <i>J</i> = 11.0, 9.2, 5.0 Hz, 1H), 3.67 - 3.58 (m, 6H), 3.55 (dd, <i>J</i> = 12.3, 4.8 Hz, 1H), 3.43 (dt, <i>J</i> = 14.9, 4.9 Hz, 1H), 3.36 (t, <i>J</i> = 9.2 Hz, 1H), 3.29 (d, <i>J</i> = 6.6 Hz, 2H), 3.13 (d, <i>J</i> = 10.0 Hz, 1H), 3.06 (t, <i>J</i> = 11.7 Hz, 1H), 1.81 - 1.65 (m, 4H), 1.63 - 1.56 (m, 1H), 1.33 - 1.19 (m, 4H), 1.01 - 0.88 (m, 2H). <sup>13</sup> C NMR (100 MHz, MeOD) δ 78.3, 78.2, 71.4, 71.30, 68.9, 68.3, 67.8, 65.8, 55.3, 55.1, 53.4, 39.14, 31.11, 27.69, 26.92. [α] <sub>D</sub> <sup>20</sup> = 0.07 (c = 1.2, MeOD). IR/cm <sup>-1</sup> : 3390, 2924, 1670, 1203, 1134, 1091, 1037. LC/MS analysis: <i>R</i> <sub>t</sub> 4.37 min (linear gradient 10-90% B), ES: = 348.3 [M+H] <sup>+</sup> . HRMS: calcd for [C <sub>17</sub> H <sub>33</sub> NO <sub>6</sub> +H] <sup>+</sup> : 348.2386. found: 348.2385. |
| C88 | (2R,3S,4S,5S)-1-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-3,4-dihydroxy-5-(hydroxymethyl)-N-(2,4,4-trimethylpentan-2-yl)pyrrolidine-2-carboxamide |  |   |
| C89 | (2R,3R,4R,5S)-2-(hydroxymethyl)-1-(2-(2-(neopentyloxy)ethoxy)ethyl)piperidine-3,4,5-triol  |  | <sup>1</sup> H NMR (400 MHz, MeOD) δ 3.94 (dd, <i>J</i> = 12.2, 2.7 Hz, 1H), 3.87 (dd, <i>J</i> = 12.2, 2.6 Hz, 1H), 3.71 - 3.66 (m, 2H), 3.64 - 3.61 (m, 2H), 3.59 - 3.56 (m, 2H), 3.51 (ddd, <i>J</i> = 10.6, 9.2, 4.9 Hz, 1H), 3.40 (t, <i>J</i> = 9.4 Hz, 1H), 3.18 (t, <i>J</i> = 9.1 Hz, 1H), 3.17 - 3.11 (m, 3H), 2.93 - 2.77 (m, 1H), 2.44 (t, <i>J</i> = 11.1 Hz, 1H), 2.38 (dt, <i>J</i> = 9.9, 2.3 Hz, 1H), 0.91 (s, 9H). <sup>13</sup> C NMR (100 MHz, MeOD) δ 82.9, 80.1, 72.10, 71.54, 71.2, 70.1, 68.9, 67.8, 58.6, 58.0, 52.9, 27.1. IR/cm <sup>-1</sup> : 3367, 2954, 2904, 2866, 2461, 1658, 1087.  |

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|     |   |  | 1037. LC/MS analysis: $R_t$ 3.77 min (linear gradient 10-90% B), ES: = 322.2 $[M+H]^+$ . HRMS: calcd for $[C_{15}H_{31}O_6N+H]^+$ 322.2230 found 322.2230 $[M+H]^+$ .   |
| C90 | (2R,3R,4R,5S)-2-(hydroxymethyl)-1-(5-(((2E,6E)-3,7,11-trimethyldodeca-2,6,10-trien-1-yl)oxy)pentyl)piperidine-3,4,5-triol |  | 10  |
| C91 | (2R,3R,4R,5S)-1-butyl-2-(hydroxymethyl)piperidine-3,4,5-triol   |  | 8   |
| C92 | (2S,3R,4R,5S)-2-(hydroxymethyl)-1-(5-(((2E,6E)-3,7,11-trimethyldodeca-2,6,10-trien-1-yl)oxy)pentyl)piperidine-3,4,5-triol |  | 10  |
| C93 | (2S,3R,4R,5S)-1-butyl-2-(hydroxymethyl)piperidine-3,4,5-triol   |  | 8   |
| C94 | (2R,3S,4S,5R,6S)-3,4,5-trihydroxy-6-(hydroxymethyl)-N-(2,4,4-trimethylpentan-2-yl)piperidine-2-carboxamide                |  | 6   |
| C95 | (2R,3R,4S,5R)-1-(5-([1,1'-biphenyl]-4-ylmethoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol                           |  | $^1H$ NMR (400 MHz, $D_2O$ ) $\delta$ 7.19 - 7.09 (m, 4H), 6.99 (d, $J$ = 8.0 Hz, 2H), 6.93 (dd, $J$ = $J$ = 7.5 Hz, 2H), 6.90 - 6.82 (m, 1H), 4.13 (s, 2H), 4.07 (dd, $J$ = 10.5, 2.1 Hz, 1H), 4.03 - 3.88 (m, 3H), 3.76 (d, $J$ = 12.1 Hz, 1H), 3.20 (d, $J$ = 12.4 Hz, 1H), 3.15 - 2.92 (m, 6H), 1.49 - 1.24 (m, 4H), 1.13 - 0.95 (m, 2H). $^{13}C$ NMR (100 MHz, $D_2O$ ) $\delta$ 140.0, 139.6, 137.1, 128.7, 128.4, 127.2, 126.6, 71.8, 69.6, 68.0, 66.1, 62.9, 61.3, 54.1, 52.8, 51.2, 28.4, 22.6, 21.7. $[\alpha]_D^{20}$ = -2.8 (c = 0.5, MeOH). IR/ $cm^{-1}$ : 3366, 2920, 2862, 1674, 1204, 1134, 1090, 1076. LCMS: 10-50, $R_t$ 7.84 min, $[M+H]^+$ = 416.2. |
| C96 | (2S,3S,4S,5R,6S)-3,4,5-trihydroxy-6-(hydroxymethyl)-N-(2,4,4-trimethylpentan-2-yl)piperidine-2-carboxamide                |  | 6   |

|      |   |  |  |
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| C97  | (2R,3S,4R,5R,6R)-2-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-6-(hydroxymethyl)piperidine-3,4,5-triol   |  | 11   |
| C98  | (2R,3S,4R,5R,6R)-2-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-6-(hydroxymethyl)-1-nonylpiperidine-3,4,5-triol   |  | 11   |
| C99  | (2R,2'R,3R,3'R,4R,4'R,5S,5'S)-1,1'-((((1S,3S,5R,7R)-adamantane-1,3-diyl)bis(methylene))bis(oxy))bis(pentane-5,1-diyl)bis(2-(hydroxymethyl)piperidine-3,4,5-triol) |  | 12   |
| C100 | (2R,3R,4R,5S)-2-(hydroxymethyl)-1-(5-((3-methylbut-2-en-1-yl)oxy)pentyl)piperidine-3,4,5-triol  |  | <sup>1</sup> H NMR (600 MHz, CDCl <sub>3</sub> ) δ 5.28 - 5.21 (m, 1H), 5.10 - 5.01 (m, 1H), 3.93 - 3.87 (m, 2H), 3.56 - 3.40 (m, 3H), 3.30 - 3.16 (m, 2H), 3.05 (dd, <i>J</i> = 11.1, 4.3 Hz, 1H), 2.26 - 2.18 (m, 2H), 2.11 - 2.00 (m, 4H), 1.66 (s, 6H), 1.59 (s, 3H). <sup>13</sup> C NMR (150 MHz, CDCl <sub>3</sub> ) δ 142.4, 133.1, 125.0, 118.8, 80.3, 71.6, 70.4, 66.8, 59.0, 57.2, 51.4, 41.3, 27.7, 26.8, 18.8, 17.5. [α] <sub>D</sub> <sup>20</sup> = -14.72 (c = 0.98, CHCl <sub>3</sub> ). LC/MS analysis: <i>R</i> <sub>t</sub> 5.17 min (linear gradient 0-90% B), ES: = 300.3 [M+H] <sup>+</sup> , 599.4 [2M + H] <sup>+</sup> . HRMS: calcd for [C <sub>16</sub> H <sub>31</sub> NO <sub>5</sub> +H] <sup>+</sup> 300.2169, found 300.2169 [M+H] <sup>+</sup> . |
| C101 | (2S,3S,4S,5R,6S)-1-butyl-3,4,5-trihydroxy-6-(hydroxymethyl)-N-(2,4,4-trimethylpentan-2-yl)piperidine-2-carboxamide  |  | 6  |
| C102 | (2S,3R,4R,5S)-2-(hydroxymethyl)-1-(5-((3-methylbut-2-en-1-yl)oxy)pentyl)piperidine-3,4,5-triol  |  | <sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) δ 5.31 - 5.25 (m, 1H), 5.17 - 5.10 (m, 1H), 3.93 - 3.83 (m, 2H), 3.87 (dd, <i>J</i> = 5.1, 8.6, 1H), 3.60-3.52 (m, 1H), 3.45 (t, <i>J</i> = 7.1, 1H), 3.40-3.29 (m, 2H), 3.03 (dd, <i>J</i> = 5.2, 10.6, 1H), 2.83 (dd, <i>J</i> = 4.8, 12.4, 1H), 2.58 (dd, <i>J</i> = 9.3, 12.4, 1H), 2.19 - 2.03 (m, 4H), 1.71 (s, 6H), 1.63 (s, 3H). <sup>13</sup> C NMR (100 MHz, CDCl <sub>3</sub> ) δ 132.5, 125.2, 122.7, 75.8, 72.7, 71.2, 64.1, 57.9, 53.0, 52.3, 40.9, 40.1, 27.5, 25.9, 17.8, 16.5. [α] <sub>D</sub> <sup>20</sup> = +4.71 (c = 0.42, CHCl <sub>3</sub> ). LC/MS analysis: <i>R</i> <sub>t</sub> 5.48 min (linear   |

|      |   |   |   |
|------|---|---|---|
|      |   |   | gradient 0-90% B), ES: = 300.3 [M+H] <sup>+</sup> , 599.8 [2M + H] <sup>+</sup> . HRMS: calcd for [C <sub>16</sub> H <sub>31</sub> NO <sub>5</sub> +H] <sup>+</sup> 300.2169, found 300.2169 [M+H] <sup>+</sup> .   |
| C103 | (2R,3R,4R,5S)-2-(hydroxymethyl)-1-nonylpiperidine-3,4,5-triol   |    | 8   |
| C104 | (2S,3R,4R,5S)-2-(hydroxymethyl)-1-nonylpiperidine-3,4,5-triol   |    | 8   |
| C105 | (2R,3R,4S,5R)-1-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol                          |    | <sup>1</sup> H NMR (400 MHz, D <sub>2</sub> O) δ 4.17 - 4.08 (m, 2H), 4.09 - 3.89 (m, 3H), 3.48 (d, <i>J</i> = 12.5 Hz, 1H) 3.42 (t, <i>J</i> = 6.2 Hz, 2H), 3.37 - 3.21 (m, 4H), 3.00 (s, 2H), 1.92 (s, 3H), 1.82 - 1.54 (m, 10H), 1.50 (s, 6H), 1.45 - 1.31 (m, 2H). <sup>13</sup> C NMR (100 MHz, D <sub>2</sub> O) δ 81.7, 71.4, 68.0, 66.1, 62.9, 61.3, 54.2, 53.0, 514, 39.3, 36.9, 33.74, 28.31, 28.14, 22.74, 21.81. [α] <sub>D</sub> <sup>20</sup> = +1.0 (c = 0.5, MeOH). IR/cm <sup>-1</sup> : 3368, 2901, 2847, 1674, 1458, 1204, 1134, 1092. HRMS: calcd for [C <sub>22</sub> H <sub>39</sub> NO <sub>5</sub> +H] <sup>+</sup> 398.2901, found 398.2896 [M+H] <sup>+</sup> . |
| C106 | (2R,3S,4S,5S)-N-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-1-butyl-3,4-dihydroxy-5-(hydroxymethyl)pyrrolidine-2-carboxamide |  | 7   |
| C107 | (2S,3R,4S,5R)-1-(2-(2-butoxyethoxy)ethyl)-2-(hydroxymethyl)piperidine-3,4,5-triol   |  | <sup>1</sup> H NMR (400 MHz, MeOD) δ 4.04 - 3.78 (m, 7H), 3.69 - 3.58 (m, 6H), 3.53 - 3.58 (m, 5H), 1.64 - 1.49 (m, 2H), 1.46 - 1.32 (m, 2H), 0.94 (t, <i>J</i> = 7.4 Hz, 3H). <sup>13</sup> C NMR (100 MHz, MeOD) δ 72.4, 72.2, 71.4, 71.1, 69.2, 67.7, 66.1, 64.7, 60.8, 54.5, 32.8, 20.3, 14.3. [α] <sub>D</sub> <sup>20</sup> = 0.03 (c = 0.5, MeOD). IR/cm <sup>-1</sup> : 3398, 2958, 2495, 1670, 1458, 1203, 1138, 1087. LC/MS analysis: <i>R</i> <sub>t</sub> 3.07 min (linear gradient 10-90% B), ES: = 308.2 [M+H] <sup>+</sup> . HRMS: calcd for [C <sub>14</sub> H <sub>29</sub> O <sub>6</sub> N+H] <sup>+</sup> 308.2073 found 308.2074 [M+H] <sup>+</sup> .                |

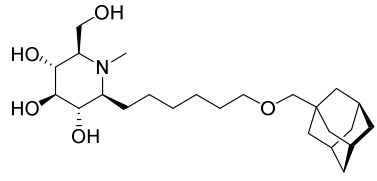
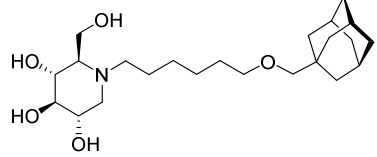
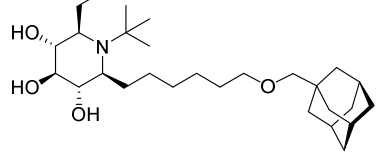
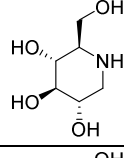
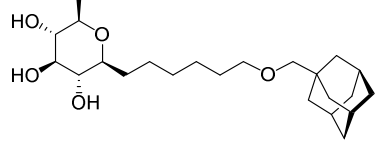
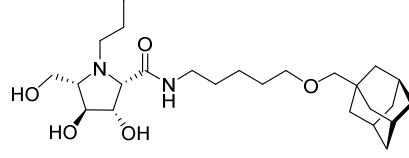
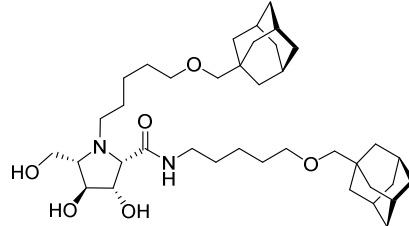
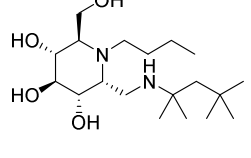
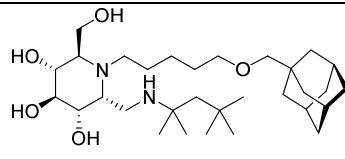
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|------|--|---|--|
| C108 | (2R,3S,4S,5S)-N,1-bis(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-3,4-dihydroxy-5-(hydroxymethyl)pyrrolidine-2-carboxamide   |    | 7  |
| C109 | (2S,3R,4R,5S)-2-(hydroxymethyl)-1-(5-(((2S,4s,4aR,6R,8R,8aS,10S,11R)-octahydro-2,8,4,6-(epibutane[1,2,3,4]tetra-yl)naphthalen-4(1H)-yl)methoxy)pentyl)piperidine-3,4,5-triol |    | <sup>1</sup> H NMR (400 MHz, MeOD) δ 4.04 - 3.83 (m, 5H), 3.55 - 3.29 (m, 9H), 2.09 - 2.03 (m, 2H), 1.89 - 1.55 (m, 19H), 1.49 - 1.42 (m, 4H). <sup>13</sup> C NMR (100 MHz, MeOD) δ 77.5, 72.0, 71.9, 68.8, 68.5, 63.5, 60.9, 54.5, 53.7, 42.2, 40.2, 39.8, 39.6, 39.3, 39.8, 39.0, 34.1, 31.1, 30.2, 28.8, 27.3, 24.7, 24.1. [α] <sub>D</sub> <sup>20</sup> = 0.04 (c = 0.7, MeOD). IR/cm <sup>-1</sup> : 3363, 2900, 2866, 1674, 1435, 1203, 1134, 1072. LC/MS analysis: R <sub>t</sub> 6.50 min (linear gradient 10-90% B), ES: = 450.4 [M+H] <sup>+</sup> . HRMS: calcd for [C <sub>26</sub> H <sub>43</sub> O <sub>5</sub> N+H] <sup>+</sup> 450.3219 found 450.3214 [M+H] <sup>+</sup> .  |
| C110 | (2S,3S,4S,5S)-1-butyl-3,4-dihydroxy-5-(hydroxymethyl)pyrrolidine-2-carboxamide   |   | 7  |
| C111 | (2R,3R,4R,5S)-2-(hydroxymethyl)-1-(5-(((2R,4s,4aR,6S,8S,8aS,10S,11R)-octahydro-2,8,4,6-(epibutane[1,2,3,4]tetra-yl)naphthalen-4(1H)-yl)methoxy)pentyl)piperidine-3,4,5-triol |  | <sup>1</sup> H NMR (400 MHz, MeOD) δ 4.10 (d, J = 12.4 Hz, 1H), 3.90 (dd, J = 12.6, 2.8 Hz, 1H), 3.69 (qd, J = 9.6, 4.9 Hz, 1H), 3.60 (t, J = 9.7, 1H), 3.49 - 3.42 (m, 3H), 3.39 - 3.34 (m, 4H), 3.20 (td, J = 12.7, 5.2 Hz, 1H), 3.03 (d, J = 9.6 Hz, 1H), 2.97 (t, J = 11.7 Hz, 1H), 2.10 - 2.04 (m, 2H), 1.88 - 1.57 (m, 19H), 1.53 - 1.41 (m, 4H). <sup>13</sup> C NMR (100 MHz, MeOD) δ 78.1, 77.6, 72.0, 68.8, 67.8, 67.3, 54.9, 54.2, 42.2, 40.1, 39.8, 39.6, 39.2, 39.1, 39.0, 34.0, 31.1, 30.2, 28.8, 27.3, 24.6, 24.0. [α] <sub>D</sub> <sup>20</sup> = - 0.01 (c = 1.1, MeOD). IR/cm <sup>-1</sup> : 3340, 2900, 2866, 1670, 1438, 1203, 1184, 1134, 1033. LC/MS analysis: R <sub>t</sub> 6.34 min (linear gradient 10-90% B), ES: = 450.4 [M+H] <sup>+</sup> . HRMS: calcd for [C <sub>26</sub> H <sub>43</sub> O <sub>5</sub> N+H] <sup>+</sup> 450.3219 found 450.3216 [M+H] <sup>+</sup> . |

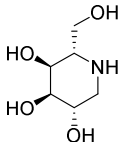
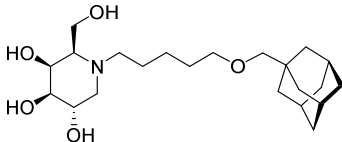
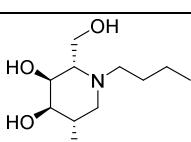
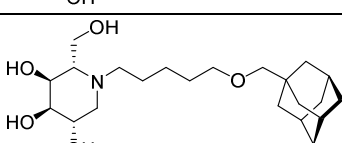
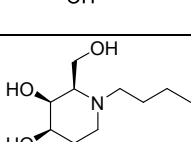
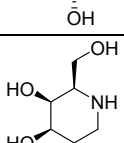
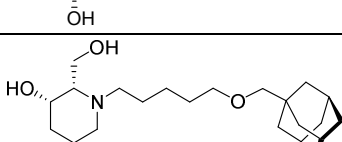
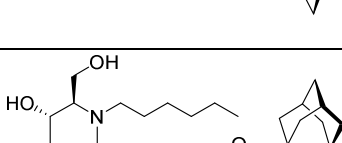
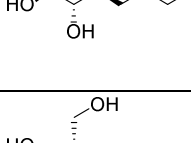
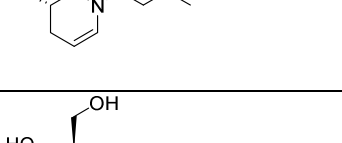
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|------|--|--|----|
| C112 | (2S,3S,4S,5S)-1-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-3,4-dihydroxy-5-(hydroxymethyl)pyrrolidine-2-carboxamide          |  | 7  |
| C113 | (2R,3R,4R,5S)-1-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol                           |  | 13 |
| C114 | (2S,3S,4S,5S)-3,4-dihydroxy-5-(hydroxymethyl)-N-pentylpyrrolidine-2-carboxamide  |  | 7  |
| C115 | (2R,3S)-1-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3-ol  |  | 9  |
| C116 | (2S,3S,4S,5S)-1-butyl-3,4-dihydroxy-5-(hydroxymethyl)-N-pentylpyrrolidine-2-carboxamide  |  | 7  |
| C117 | (2S,3S,4S,5S)-1-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-3,4-dihydroxy-5-(hydroxymethyl)-N-pentylpyrrolidine-2-carboxamide |  | 7  |
| C118 | (2R,3R,4R,5S)-2-(hydroxymethyl)-1-(5-(3-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)methoxy)pentyl)piperidine-3,4,5-triol             |  | 10 |
| C119 | (2S,3S,4S,5S)-3,4-dihydroxy-5-(hydroxymethyl)-N-(2,4,4-trimethylpentan-2-yl)pyrrolidine-2-carboxamide                            |  | 7  |
| C120 | (2R,3R,4R,5S)-2-(hydroxymethyl)-1-(5-(2-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)methoxy)pentyl)piperidine-3,4,5-triol             |  | 10 |
| C121 | (2S,3S,4S,5S)-1-butyl-3,4-dihydroxy-5-(hydroxymethyl)-N-(2,4,4-trimethylpentan-2-yl)pyrrolidine-2-carboxamide                    |  | 7  |

|      |  |  |   |
|------|--|--|---|
| C122 | (2R,3S,4S,5R)-1-(5-([1,1'-biphenyl]-4-ylmethoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol  |  | 10  |
| C123 | (2S,3S,4S,5S)-1-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-3,4-dihydroxy-5-(hydroxymethyl)-N-(2,4,4-trimethylpentan-2-yl)pyrrolidine-2-carboxamide |  | 7   |
| C124 | (2R,3S,4S,5R)-1-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol   |  | <sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) δ 4.03 - 3.87 (br m, 4H), 3.84 (br s, 1H), 3.53 - 3.33 (m, 7H), 2.98 (s, 2H), 1.94 (b s, 3H), 1.77 - 1.62 (m, 8H), 1.55 (m, 6H), 1.49 - 1.44 (m, 4H). <sup>13</sup> C NMR (100 MHz, CDCl <sub>3</sub> ) δ 83.1, 71.7, 71.7, 68.5, 68.0, 63.8, 60.5, 54.4, 53.7, 40.8, 38.3, 35.1, 31.1, 30.1, 24.6, 23.3. [α] <sub>D</sub> <sup>20</sup> = -0.07 (c = 0.9, MeOD). IR/cm <sup>-1</sup> : 3363, 2904, 2846, 1670, 1199, 1134, 1072. LC/MS analysis: R <sub>t</sub> 5.77 min (linear gradient 10-90% B), ES: = 398.3 [M+H] <sup>+</sup> . HRMS: calcd for [C <sub>22</sub> H <sub>39</sub> O <sub>5</sub> N+H] <sup>+</sup> 398.2906, found 398.2902 [M+H] <sup>+</sup> . |
| C125 | (2S,3R,4R,5S)-1-(5-(((1S,3S,5S,7S)-adamantan-2-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol  |  | 10  |
| C126 | (2S,3S,4R,5R,6R)-1-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-2-butyl-6-(hydroxymethyl)piperidine-3,4,5-triol                                      |  | 11  |
| C127 | (2R,3R,4R,5S)-1-(5-(cyclohexylmethoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol  |  | 10  |
| C128 | (2S,3S,4R,5R,6R)-2-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-1-benzyl-6-(hydroxymethyl)piperidine-3,4,5-triol                                     |  | 11  |
| C129 | (2S,3R,4R,5S)-1-(5-(cyclohexylmethoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol  |  | 10  |

|      |   |  |    |
|------|---|--|----|
| C130 | (2S,3S,4R,5R,6R)-2-(4-(((3S,5S,7S)-adamantan-1-yl)methoxy)butyl)-6-(hydroxymethyl)piperidine-3,4,5-triol          |  | 11 |
| C131 | (2R,3R,4R,5S)-1-((Z)-6-((3R,5R,7R)-adamantan-1-yl)hex-5-en-1-yl)-2-(hydroxymethyl)piperidine-3,4,5-triol          |  | 10 |
| C132 | (2S,3S,4R,5R,6R)-2-(4-(((3S,5S,7S)-adamantan-1-yl)methoxy)butyl)-6-(hydroxymethyl)-1-methylpiperidine-3,4,5-triol |  | 11 |
| C133 | (2S,3R,4R,5S)-1-((Z)-6-((3S,5S,7S)-adamantan-1-yl)hex-5-en-1-yl)-2-(hydroxymethyl)piperidine-3,4,5-triol          |  | 10 |
| C134 | (2S,3S,4R,5R,6R)-2-(4-(((3S,5S,7S)-adamantan-1-yl)methoxy)butyl)-1-butyl-6-(hydroxymethyl)piperidine-3,4,5-triol  |  | 11 |
| C135 | (2S,3S)-1-(4-(((3S,5S,7S)-adamantan-1-yl)methoxy)butyl)-2-(hydroxymethyl)-1,2,3,6-tetrahydropyridin-3-ol          |  | 9  |
| C136 | (2S,3R,4R,5S,6R)-2-(4-(((3S,5S,7S)-adamantan-1-yl)methoxy)butyl)-6-(hydroxymethyl)tetrahydro-2H-pyran-3,4,5-triol |  | 11 |
| C137 | (2S,3R)-2-(hydroxymethyl)piperidin-3-ol   |  | 9  |
| C138 | (2S,3S,4R,5R,6R)-2-(6-(((3S,5S,7S)-adamantan-1-yl)methoxy)hexyl)-6-(hydroxymethyl)piperidine-3,4,5-triol          |  | 11 |
| C139 | (2R,3R,4R,5S)-1-(5-(benzyloxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol                                     |  | 10 |



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| C140 | (2S,3S,4R,5R,6R)-2-(6-(((3S,5S,7S)-adamantan-1-yl)methoxy)hexyl)-6-(hydroxymethyl)-1-methylpiperidine-3,4,5-triol                                       |    | 11 |
| C141 | (2R,3R,4R,5S)-1-(6-(((3R,5R,7R)-adamantan-1-yl)methoxy)hexyl)-2-(hydroxymethyl)piperidine-3,4,5-triol   |    | 10 |
| C142 | (2S,3S,4R,5R,6R)-2-(6-(((3S,5S,7S)-adamantan-1-yl)methoxy)hexyl)-1-(tert-butyl)-6-(hydroxymethyl)piperidine-3,4,5-triol                                 |    | 11 |
| C143 | (2R,3R,4R,5S)-2-(hydroxymethyl)piperidine-3,4,5-triol   |    | 3  |
| C144 | (2S,3R,4R,5S,6R)-2-(6-(((3S,5S,7S)-adamantan-1-yl)methoxy)hexyl)-6-(hydroxymethyl)tetrahydro-2H-pyran-3,4,5-triol                                       |   | 11 |
| C145 | (2S,3S,4S,5S)-N-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-1-butyl-3,4-dihydroxy-5-(hydroxymethyl)pyrrolidine-2-carboxamide                         |  | 7  |
| C146 | (2S,3S,4S,5S)-N,1-bis(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-3,4-dihydroxy-5-(hydroxymethyl)pyrrolidine-2-carboxamide                            |  | 7  |
| C147 | (2R,3R,4R,5S,6R)-1-butyl-2-(hydroxymethyl)-6-(((2,4,4-trimethylpentan-2-yl)amino)methyl)piperidine-3,4,5-triol  |  | 11 |
| C148 | (2R,3R,4R,5S,6R)-1-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-2-(hydroxymethyl)-6-(((2,4,4-trimethylpentan-2-yl)amino)methyl)piperidine-3,4,5-triol |  | 11 |

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| C149 | (2S,3S,4R,5S)-2-(hydroxymethyl)piperidine-3,4,5-triol   |    | 3  |
| C150 | (2R,3S,4R,5S)-1-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol            |    | 3  |
| C151 | (2S,3S,4R,5S)-1-butyl-2-(hydroxymethyl)piperidine-3,4,5-triol   |    | 3  |
| C152 | (2S,3S,4R,5S)-1-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol            |    | 3  |
| C153 | (2R,3S,4R,5S)-1-butyl-2-(hydroxymethyl)piperidine-3,4,5-triol   |    | 3  |
| C154 | (2R,3S,4R,5S)-2-(hydroxymethyl)piperidine-3,4,5-triol   |   | 3  |
| C155 | (2S,3S)-1-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3-ol                         |  | 9  |
| C156 | (2S,3S,4R,5R,6R)-2-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-1-hexyl-6-(hydroxymethyl)piperidine-3,4,5-triol |  | 11 |
| C157 | (2S,3S)-1-butyl-2-(hydroxymethyl)-1,2,3,4-tetrahydropyridin-3-ol  |  | 9  |
| C158 | (2R,3S,4R,5R,6R)-2-(6-(((3R,5R,7R)-adamantan-1-yl)methoxy)hexyl)-6-(hydroxymethyl)piperidine-3,4,5-triol          |  | 11 |

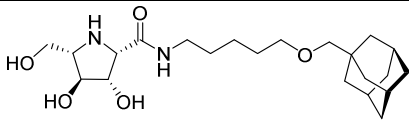
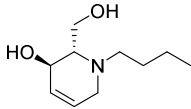
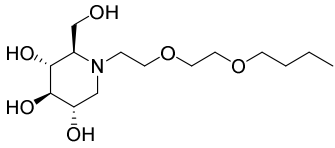
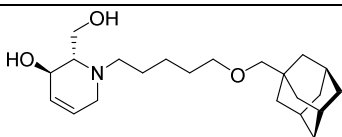
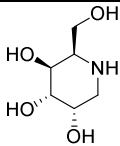
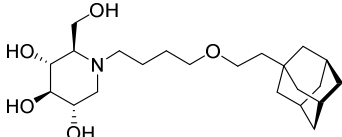
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| C159 | (2R,3S,4R,5R,6R)-2-((E)-5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pent-2-en-1-yl)-6-(hydroxymethyl)piperidine-3,4,5-triol |  | 11 |
| C160 | (2S,3S)-1-butyl-2-(hydroxymethyl)piperidine-3-ol  |  | 9  |
| C161 | (2R,3S,4R,5R,6S)-2-(4-(((3R,5R,7R)-adamantan-1-yl)methoxy)butyl)-6-(hydroxymethyl)piperidine-3,4,5-triol              |  | 11 |
| C162 | (2S,3R,4R)-2-(hydroxymethyl)piperidine-3,4-diol   |  | 9  |
| C163 | (2R,3S,4R,5R,6S)-2-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-6-(hydroxymethyl)piperidine-3,4,5-triol             |  | 11 |
| C164 | (2S,3R,4R)-1-butyl-2-(hydroxymethyl)piperidine-3,4-diol   |  | 9  |
| C165 | (2R,3S,4R,5R,6S)-2-(6-(((3R,5R,7R)-adamantan-1-yl)methoxy)hexyl)-6-(hydroxymethyl)piperidine-3,4,5-triol              |  | 11 |
| C166 | (2S,3R,4R)-1-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4-diol                      |  | 9  |
| C167 | (2R,3S,4R,5R,6S)-2-((E)-5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pent-2-en-1-yl)-6-(hydroxymethyl)piperidine-3,4,5-triol |  | 11 |
| C168 | (2S,3R)-2-(hydroxymethyl)-1,2,3,4-tetrahydropyridin-3-ol  |  | 9  |

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| C169 | (2R,3S,4S,5R)-2-(4-(((3R,5R,7R)-adamantan-1-yl)methoxy)butyl)piperidine-3,4,5-triol  |  | 11   |
| C170 | (2R,3R,4R,5S)-1-(5-(2-((3R,5R,7R)-adamantan-1-yl)ethoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol  |  | <sup>1</sup> H NMR (600 MHz, MeOD) δ 3.89 - 3.82 (m, 2H), 3.51 - 3.44 (m, 3H), 3.42 (t, <i>J</i> = 6.5 Hz, 2H), 3.36 (t, <i>J</i> = 9.3 Hz, 1H), 3.14 (t, <i>J</i> = 9.1 Hz, 1H), 3.01 (dd, <i>J</i> = 11.1, 4.7 Hz, 1H), 2.86 - 2.79 (m, 1H), 2.66 - 2.56 (m, 1H), 2.21 (t, <i>J</i> = 10.7 Hz, 1H), 2.15 (d, <i>J</i> = 7.4 Hz, 1H), 1.93 (s, 3H), 1.77 - 1.65 (m, 6H), 1.62 - 1.48 (m, 8H), 1.35 (m, 4H). <sup>13</sup> C NMR (150 MHz, MeOD) δ 80.4, 71.8, 71.7, 70.6, 67.8, 67.4, 59.4, 59.2, 53.7, 44.8, 48.3, 38.2 (CH <sub>2</sub> ), 32.8, 30.6, 30.2, 25.2, 24.9. [α] <sub>D</sub> <sup>20</sup> = 11.2 (c = 0.8, MeOD). IR/cm <sup>-1</sup> : 3360, 2360, 2341, 1097, 1089, 1033, 1012. LC/MS analysis: <i>R</i> <sub>t</sub> 5.77 min (linear gradient 10-90% B), ES: = 412.1 [M+H] <sup>+</sup> . HRMS: calcd for [C <sub>22</sub> H <sub>40</sub> NO <sub>5</sub> +H] <sup>+</sup> : 412.3057. found: 412.3057 |
| C171 | (2R,3S,4S,5R)-2-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)piperidine-3,4,5-triol   |  | 11   |
| C172 | (2R,3S,4S,5R)-2-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)piperidine-3,4,5-triol   |  | 11   |
| C173 | 1-((2S,3S,4S,5R,6S)-1-butyl-3,4,5-trihydroxy-6-(hydroxymethyl)piperidin-2-yl)-3,3,5,5-tetramethylhexan-1-one   |  | 6  |
| C174 | (2S,3R,4R,5S)-1-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol   |  | 3  |
| C175 | (2S,3R,4S,5R)-1-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-3,4-dihydroxy-5-(hydroxymethyl)-N-(2,4,4-trimethylpentan-2-yl)pyrrolidine-2-carboxamide |  | 7  |

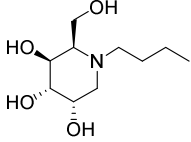
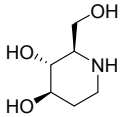
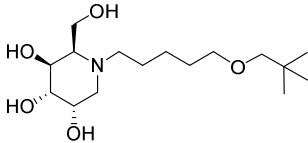
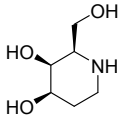
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| C176 | (2S,3R,4S,5R)-N-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-3,4-dihydroxy-5-(hydroxymethyl)pyrrolidine-2-carboxamide                                |  | 7  |
| C177 | (2R,3R,4S,5R)-1-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-3,4-dihydroxy-5-(hydroxymethyl)-N-(2,4,4-trimethylpentan-2-yl)pyrrolidine-2-carboxamide |  | 7  |
| C178 | (2R,3R,4S,5R)-N-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-3,4-dihydroxy-5-(hydroxymethyl)pyrrolidine-2-carboxamide                                |  | 7  |
| C179 | (2R,3S,4S,5S)-N-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-3,4-dihydroxy-5-(hydroxymethyl)pyrrolidine-2-carboxamide                                |  | 7  |
| C180 | (2S,3S,4S,5R,6R)-1-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-3,4,5-trihydroxy-6-(hydroxymethyl)-N-pentylpiperidine-2-carboxamide                  |  | 6  |
| C181 | (2S,3S,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)-1-methyl-N-(2,2,4,4-tetramethylpentyl)piperidine-2-carboxamide                                     |  | 6  |
| C182 | (2S,3R,4R,5S)-1-butyl-2-(hydroxymethyl)piperidine-3,4,5-triol  |  | 3  |
| C183 | (2R,3S,4R,5R,6S)-2-(4-(((3R,5R,7R)-adamantan-1-yl)methoxy)butyl)-6-(hydroxymethyl)piperidine-3,4,5-triol   |  | 11 |
| C184 | (2R,3S,4R,5R,6S)-2-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-6-(hydroxymethyl)piperidine-3,4,5-triol  |  | 11 |

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| C185 | (2S,3S,4R,5R,6R)-2-((Z)-5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pent-1-en-1-yl)-1-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-6-(hydroxymethyl)piperidine-3,4,5-triol |  | 11   |
| C186 | (2S,3S,4R,5R,6R)-1-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-2-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-6-(hydroxymethyl)piperidine-3,4,5-triol             |  | 11   |
| C187 | (2S,3S,4R,5R,6R)-2-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pent-1-yn-1-yl)-6-(hydroxymethyl)piperidine-3,4,5-triol  |  | 11   |
| C188 | (2R,3R,4S,5R)-1-butyl-2-(hydroxymethyl)piperidine-3,4,5-triol  |  | <sup>1</sup> H NMR (400 MHz, D <sub>2</sub> O) δ 4.13 - 4.04 (m, 2H), 4.02 - 3.88 (m, 3H), 3.44 (d, <i>J</i> = 13.1 Hz, 1H), 3.32 - 3.14 (m, 4H), 1.73 - 1.54 (m, 2H), 1.32 (h, <i>J</i> = 7.1 Hz, 2H), 0.87 (t, <i>J</i> = 7.4 Hz, 3H). <sup>13</sup> C NMR (100 MHz, D <sub>2</sub> O) δ 68.1, 66.0, 62.9, 61.2, 54.1, 53.0, 51.3, 23.8, 19.3, 12.7. [α] <sub>D</sub> <sup>20</sup> = -0.5 (c = 0.4, MeOH). IR/cm <sup>-1</sup> : 3333, 2955, 1674, 1200, 1134, 1072. HRMS: calcd for [C <sub>10</sub> H <sub>21</sub> NO <sub>4</sub> +H] <sup>+</sup> 220.15433, found 220.15434 [M+H] <sup>+</sup> .                                    |
| C189 | (2S,3S,4R,5R,6R)-2-((E)-5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pent-1-en-1-yl)-6-(hydroxymethyl)piperidine-3,4,5-triol  |  | 11   |
| C190 | (2R,3R,4S,5R)-2-(hydroxymethyl)-1-nonylpiperidine-3,4,5-triol  |  | <sup>1</sup> H NMR (400 MHz, D <sub>2</sub> O) δ 4.22 - 4.12 (m, 2H), 4.11 - 3.98 (m, 3H), 3.54 (d, <i>J</i> = 12.1 Hz, 1H), 3.46 - 3.21 (m, 4H), 1.95 - 1.63 (m, 2H), 1.52 - 1.15 (m, 12H), 0.97 - 0.76 (t, <i>J</i> = 7.2 Hz, 3H). <sup>13</sup> C NMR (100 MHz, D <sub>2</sub> O) δ 68.2, 66.1, 63.0, 61.2, 54.2, 53.3, 51.4, 31.2, 28.4, 28.4, 28.2, 25.8, 22.1, 21.8, 13.4. [α] <sub>D</sub> <sup>20</sup> = 0.0 (c = 1.0, MeOH). IR/cm <sup>-1</sup> : 3225, 2928, 2859, 1670, 1435, 1184, 1134, 1072. HRMS: calcd for [C <sub>15</sub> H <sub>29</sub> NO <sub>4</sub> +H] <sup>+</sup> 290.2326, found 290.2326 [M+H] <sup>+</sup> . |

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| C191 | (2S,3S,4R,5R,6R)-2-((Z)-5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pent-1-en-1-yl)-6-(hydroxymethyl)piperidine-3,4,5-triol      |  | 11  |
| C192 | (2R,3R,4S,5S)-1-butyl-2-(hydroxymethyl)piperidine-3,4,5-triol  |  | <sup>1</sup> H NMR (400 MHz, D <sub>2</sub> O) δ 4.20 (s, 1H), 4.14 - 3.96 (m, 3H), 3.90 (dd, <i>J</i> = 10.7, 2.4 Hz, 1H), 3.45 - 3.18 (m, 5H), 1.90 - 1.62 (m, 2H), 1.41 (m, 2H), 0.95 (t, <i>J</i> = 7.4 Hz, 3H). <sup>13</sup> C NMR (100 MHz, D <sub>2</sub> O) δ 69.5, 64.8, 63.9, 60.2, 53.4, 53.2, 48.8, 24.4, 19.3, 12.8. [ $\alpha$ ] <sub>D</sub> <sup>20</sup> = -3.2 (c = 0.5, MeOH). IR/cm <sup>-1</sup> : 3372, 1670, 1458, 1423, 1184, 1134, 1076, 1043. LCMS: 00-20, RT 1.47 min, [M+H] <sup>+</sup> = 220.1. HRMS: calcd for [C <sub>10</sub> H <sub>21</sub> NO <sub>4</sub> +H] <sup>+</sup> 220.1543, found 220.1544 [M+H] <sup>+</sup> .    |
| C193 | (2S,3S,4R,5R,6R)-2-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-6-(hydroxymethyl)piperidine-3,4,5-triol                  |  | 11  |
| C194 | (2R,3R,4S,5S)-2-(hydroxymethyl)-1-nonylpiperidine-3,4,5-triol  |  | <sup>1</sup> H NMR (400 MHz, D <sub>2</sub> O) δ 4.20 (s, 1H), 4.15 - 3.84 (m, 4H), 3.43 - 3.17 (m, 5H), 1.75 (s, 2H), 1.46 - 1.20 (m, 12H), 0.88 (t, <i>J</i> = 6.6 Hz, 3H). <sup>13</sup> C NMR (100 MHz, D <sub>2</sub> O) δ 69.6, 64.8, 63.9, 60.2, 53.6, 53.2, 48.9, 31.6, 29.2, 28.9, 28.8, 26.2, 22.2, 13.7. [ $\alpha$ ] <sub>D</sub> <sup>20</sup> = -5.0 (c = 1.0, MeOH). IR/cm <sup>-1</sup> : 3352, 2955, 2926, 2857, 1670, 1456, 1200, 1184, 1134, 1076, 1043. LCMS: 10-50, RT 6.67 min, [M+H] <sup>+</sup> = 290.3. HRMS: calcd for [C <sub>15</sub> H <sub>31</sub> NO <sub>4</sub> +H] <sup>+</sup> 290.2332, found 290.2326 [M+H] <sup>+</sup> . |
| C195 | (2S,3S,4R,5R,6R)-2-butyl-6-(hydroxymethyl)piperidine-3,4,5-triol   |  | 11  |
| C196 | (2R,3S,4S)-1-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4-diol                           |  | 9   |
| C197 | (2R,2'R,3R,3'R,4R,4'R,5S,5'S)-1,1'-(((2-(((3R,5R,7R)-adamantan-1-yl)propane-1,3-diyl)bis(oxy))bis(pentane-5,1-diyl))bis(2- |  | 12  |

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|------|---|---|---|
|      | (hydroxymethyl)piperidine-3,4,5-triol   |   |   |
| C198 | (2S,3S,4S,5S)-N-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-3,4-dihydroxy-5-(hydroxymethyl)pyrrolidine-2-carboxamide |    | 7   |
| C199 | (2S,3R)-1-butyl-2-(hydroxymethyl)-1,2,3,6-tetrahydropyridin-3-ol  |    | 9   |
| C200 | (2R,3R,4R,5S)-1-(2-(2-butoxyethoxy)ethyl)-2-(hydroxymethyl)piperidine-3,4,5-triol                                       |    | <sup>1</sup> H NMR (400 MHz, MeOD) δ 4.04 (dd, <i>J</i> = 12.5, 2.0 Hz, 1H), 3.98 (dd, <i>J</i> = 12.5, 2.9 Hz, 1H), 3.83 (t, <i>J</i> = 5.0 Hz, 2H), 3.69 (ddd, <i>J</i> = 11.0, 9.2, 4.8 Hz, 1H), 3.66 (m, 2H), 3.60 (m, 3H), 3.57 (dd, <i>J</i> = 9.9, 9.2 Hz, 1H), 3.50 (t, <i>J</i> = 6.7 Hz, 2H), 3.48 (dd, <i>J</i> = 12.0, 4.8 Hz, 1H), 3.36 (t, <i>J</i> = 9.2 Hz, 1H), 2.98 (d, <i>J</i> = 9.9 Hz, 1H), 2.92 (t, <i>J</i> = 11.5 Hz, 1H), 1.64 - 1.52 (m, 2H), 1.45 - 1.31 (m, 2H), 0.94 (t, <i>J</i> = 7.4 Hz, 3H). <sup>13</sup> C NMR (100 MHz, MeOD) δ 78.5, 72.1, 71.3, 70.9, 69.4, 68.3, 68.2, 66.5, 56.2, 56.1, 53.5, 32.7, 20.3, 14.3. [ $\alpha$ ] <sub>D</sub> <sup>20</sup> = 0.10 ( <i>c</i> = 1.9, MeOD). IR/cm <sup>-1</sup> : 3379, 2958, 2931, 2873, 2515, 1631, 1458, 1249, 1091, 1033. LC/MS analysis: <i>R</i> <sub>t</sub> 2.86 min (linear gradient 10-90% B), ES: = 308.2 [M+H] <sup>+</sup> . HRMS: calcd for [C <sub>14</sub> H <sub>29</sub> O <sub>6</sub> N+H] <sup>+</sup> 308.2073 found 308.2071 [M+H] <sup>+</sup> . |
| C201 | (2S,3R)-1-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-2-(hydroxymethyl)-1,2,3,6-tetrahydropyridin-3-ol               |  | 9   |
| C202 | (2R,3S,4S,5S)-2-(hydroxymethyl)piperidine-3,4,5-triol   |  | 4   |
| C203 | (2R,3R,4R,5S)-1-(4-(2-((3R,5R,7R)-adamantan-1-yl)ethoxy)butyl)-2-(hydroxymethyl)piperidine-3,4,5-triol                  |  | <sup>1</sup> H NMR (600 MHz, D <sub>2</sub> O) δ 3.98 (d, <i>J</i> = 12.6 Hz, 1H), 3.88 (d, <i>J</i> = 12.6 Hz, 1H), 3.73 - 3.69 (m, 1H), 3.56 (t, <i>J</i> = 9.6, 1H), 3.49 - 3.45 (m, 4H), 3.41 (dd, <i>J</i> = 9.6, 9.0, 1H), 3.35 (m, 1H), 3.16 (br m, 1H), 3.06 (br m, 1H), 2.86 (d, <i>J</i> = 9.6 Hz, 1H), 2.81 (t, <i>J</i> = 11.4 Hz, 1H), 1.90 (s, 3H), 1.67 - 1.52 (m, 10H), 1.51 (s,  |

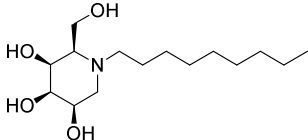
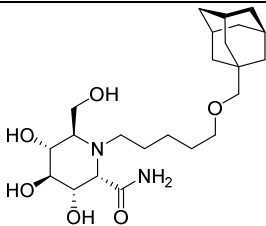
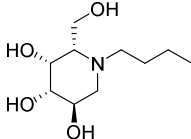
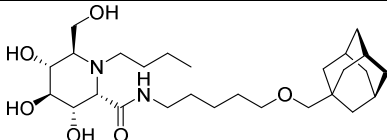
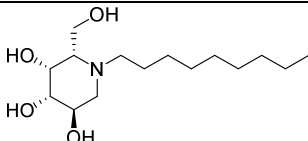


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|      |  |   | 6H), 1.35 (t, $J = 7.2$ Hz). $^{13}\text{C}$ NMR (150 MHz, $\text{D}_2\text{O}$ ) $\delta$ 77.7, 71.1, 68.9, 67.9, 67.7, 66.3, 56.0, 54.9, 53.4, 44.1, 43.4, 38.1, 32.4, 27.7, 27.6, 20.7. IR/ $\text{cm}^{-1}$ : 3358, 2899, 2846, 1647, 1450, 1023. LC/MS analysis: $R_t$ 4.60 min (linear gradient 10-90% B), ES: = 398.2 $[\text{M}+\text{H}]^+$ . HRMS: calcd for $[\text{C}_{22}\text{H}_{39}\text{O}_5\text{N}+\text{H}]^+$ 398.2901, found 398.2899 $[\text{M}+\text{H}]^+$ .  |
| C204 | (2R,3S,4S,5S)-1-butyl-2-(hydroxymethyl)piperidine-3,4,5-triol                    |    | $^1\text{H}$ NMR (400 MHz, MeOD) $\delta$ 4.20 (ddd, $J = 10.5, 5.6, 2.7$ Hz, 1H), 4.08 (dd, $J = 4.3, 1.7$ Hz, 1H), 4.01 - 3.85 (m, 3H), 3.46 - 3.44 (m, 1H), 3.30 - 3.11 (m, 4H), 1.89 - 1.63 (m, 2H), 1.41 (h, $J = 7.4$ Hz, 2H), 1.00 (t, $J = 7.4$ Hz, 3H). $^{13}\text{C}$ NMR (100 MHz, MeOD) $\delta$ 72.3, 70.0, 64.1, 61.8, 61.1, 54.9, 51.2, 25.2, 20.9, 13.9. $[\alpha]_{\text{D}}^{20} = -93.1$ ( $c = 0.08$ , MeOD). IR/ $\text{cm}^{-1}$ : 3653, 3002, 1669, 1429, 1184, 1131, 800, 722. HRMS: calcd for $[\text{C}_{10}\text{H}_{21}\text{NO}_4+\text{H}]^+$ 220.1543, found 220.1544 $[\text{M}+\text{H}]^+$ .  |
| C205 | (2R,3R,4R)-2-(hydroxymethyl)piperidine-3,4-diol                                  |  | 9  |
| C206 | (2R,3S,4S,5S)-2-(hydroxymethyl)-1-(5-(neopentyloxy)pentyl)piperidine-3,4,5-triol |  | $^1\text{H}$ NMR (400 MHz, MeOD) $\delta$ 4.20 (ddd, $J = 10.8, 5.3, 2.7$ Hz, 1H), 4.08 (dd, $J = 4.4, 1.8$ Hz, 1H), 4.00 - 3.82 (m, 3H), 3.46 - 3.43 (m, 1H), 3.44 (t, $J = 6.2$ Hz, 2H), 3.30 - 3.11 (m, 4H), 3.08 (s, 2H), 1.91 - 1.69 (m, 2H), 1.65 (q, $J = 7.3$ Hz, 2H), 1.47 (q, $J = 7.3$ Hz, 2H), 0.90 (s, 9H). $^{13}\text{C}$ NMR (100 MHz, MeOD) $\delta$ 82.5, 72.3, 72.1, 70.1, 64.1, 61.8, 61.2, 55.0, 51.2, 30.2, 27.1, 24.6, 23.1. $[\alpha]_{\text{D}}^{20} = -14.6$ ( $c = 0.49$ , MeOD). IR/ $\text{cm}^{-1}$ : 3648, 2954, 1669, 1184, 1135, 839, 799, 722. HRMS: calcd for $[\text{C}_{16}\text{H}_{33}\text{NO}_5+\text{H}]^+$ 320.2431, found 320.2431 $[\text{M}+\text{H}]^+$ . |
| C207 | (2R,3S,4R)-2-(hydroxymethyl)piperidine-3,4-diol                                  |  | 9  |

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| C208 | (2R,3S,4S,5S)-1-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol |  | <sup>1</sup> H NMR (400 MHz, MeOD) δ 4.20 (ddd, <i>J</i> = 9.3, 6.2, 2.7 Hz, 1H), 4.07 (dd, <i>J</i> = 4.5, 1.9 Hz, 1H), 3.96 (d, <i>J</i> = 4.7 Hz, 2H), 3.88 (dd, <i>J</i> = 4.6, 2.7 Hz, 1H), 3.48 (dt, <i>J</i> = 5.1, 2.5 Hz, 1H), 3.41 (t, <i>J</i> = 6.1 Hz, 2H), 3.28 (dd, <i>J</i> = 7.2, 4.1 Hz, 2H), 3.20 (d, <i>J</i> = 9.9 Hz, 2H), 2.98 (s, 2H), 1.96 - 1.94 (m, 3H), 1.83 - 1.60 (m, 10H), 1.57 - 1.56 (m, 6H), 1.46 (q, <i>J</i> = 7.4 Hz, 2H). <sup>13</sup> C NMR (100 MHz, MeOD) δ 83.1, 72.1, 71.9, 70.1, 64.0, 62.0, 60.6, 54.6, 51.2, 40.8, 38.3, 35.1, 31.1, 30.1, 29.7, 24.6. [α] <sub>D</sub> <sup>20</sup> = - 12.2 (c = 0.53, MeOD). IR/cm <sup>-1</sup> : 3668 - 2902, 1669, 1186, 1136, 800, 722, 611. HRMS: calcd for [C <sub>22</sub> H <sub>39</sub> NO <sub>5</sub> +H] <sup>+</sup> 398.2901, found: 398.2887 [M+H] <sup>+</sup> . |
| C209 | (2R,3S,4S)-1-butyl-2-(hydroxymethyl)piperidine-3,4-diol  |  | <sup>9</sup>   |
| C210 | (2R,3S,4S,5S)-1-(5-([1,1'-biphenyl]-4-ylmethoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol        |  | <sup>1</sup> H NMR (400 MHz, MeOD) δ 7.61 (d, <i>J</i> = 8.4 Hz, 4H), 7.43 (d, <i>J</i> = 8.4 Hz, 4H), 7.38 - 7.29 (m, 1H), 4.55 (s, 2H), 4.19 (ddd, <i>J</i> = 11.1, 5.2, 2.8 Hz, 1H), 4.07 (dd, <i>J</i> = 4.4, 1.8 Hz, 1H), 4.01 - 3.84 (m, 3H), 3.56 (t, <i>J</i> = 6.2 Hz, 2H), 3.46 - 3.44 (m, 1H), 3.32 - 3.21 (m, 2H), 3.23 - 3.07 (m, 2H), 1.95 - 1.61 (m, 4H), 1.50 (q, <i>J</i> = 8.1 Hz, 2H). <sup>13</sup> C NMR (100 MHz, MeOD) δ 142.1, 141.9, 138.9, 129.9, 129.4, 128.4, 128.0, 127.9, 73.7, 72.4, 71.0, 70.1, 64.1, 61.7, 61.1, 55.0, 51.2, 30.2, 24.6, 23.0. [α] <sub>D</sub> <sup>20</sup> = - 10.0 (c = 0.20, MeOH). IR/cm <sup>-1</sup> : 3718, 2989, 1673, 1179, 1134. HRMS: calcd for [C <sub>24</sub> H <sub>33</sub> NO <sub>5</sub> +H] <sup>+</sup> 416.2431, found 416.2430 [M+H] <sup>+</sup> .  |
| C211 | (2R,3R,4R)-1-butyl-2-(hydroxymethyl)piperidine-3,4-diol  |  | <sup>9</sup>   |
| C212 | (2R,3S,4S,5S)-2-(hydroxymethyl)-1-nonylpiperidine-3,4,5-triol  |  | <sup>1</sup> H NMR (400 MHz, MeOD) δ 4.20 (ddd, <i>J</i> = 10.4, 5.4, 2.7 Hz, 1H), 4.08 (dd, <i>J</i> = 4.4, 1.8 Hz, 1H), 4.01 - 3.81 (m, 3H), 3.46 (d, <i>J</i> = 4.8 Hz, 1H), 3.29 - 3.06 (m, 4H), 1.89 - 1.60 (m, 2H), 1.46 - 1.26 (m, 12H), 0.90 (t, <i>J</i> = 8.0 Hz,  |

|      |   |  |   |
|------|---|--|---|
|      |   |  | 3H). $^{13}\text{C}$ NMR (100 MHz, MeOD) $\delta$ 72.3, 70.1, 64.1, 61.7, 61.1, 55.1, 51.2, 33.0, 30.5, 30.3, 30.2, 27.7, 23.7, 23.2, 14.4. $[\alpha]_D^{20} = -15.4$ ( $c = 0.59$ , MeOD). IR/cm $^{-1}$ : 3685 - 2927, 1668, 1184, 1135, 838, 799, 722. HRMS: calcd for $[\text{C}_{15}\text{H}_{31}\text{NO}_4 + \text{H}]^+$ 290.2326, found 290.2323 $[\text{M} + \text{H}]^+$ .   |
| C213 | (2R,3R,4S)-1-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4-diol  |  | 9   |
| C214 | (2S,3S,4S)-1-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4-diol  |  | 9   |
| C215 | (2S,3R,4R,5S)-2-(hydroxymethyl)-1-(2-(2-(neopentyloxy)ethoxy)ethyl)piperidine-3,4,5-triol   |  | $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ ) $\delta$ 3.99-3.83 (m, 6H), 3.77 (br s, 1H), 3.69-3.67 (m, 2H), 3.63 - 3.59 (br m, 3H), 3.57 - 3.38 (br m, 4H $^*$ ), 3.14 (s, 2H neopentyl), 0.92 (s, 9H neopentyl). $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ ) $\delta$ 82.9, 71.9, 71.7, 71.3, 69.4, 69.0, 66.4, 64.3, 59.6, 54.2, 54.1, 27.1. IR/cm $^{-1}$ : 3394, 2954, 2515, 1674, 1458, 1199, 1134, 1091. LC/MS analysis: $R_t$ 3.88 min (linear gradient 10-90% B), ES: = 322.3 $[\text{M} + \text{H}]^+$ . HRMS: calcd for $[\text{C}_{15}\text{H}_{31}\text{O}_6\text{N} + \text{H}]^+$ 322.2230, found 322.2230 $[\text{M} + \text{H}]^+$ . |
| C216 | (2S,2'S,3R,3'R,4R,4'R,5S,5'S)-1,1'-((((1R,3R,5S,7S)-adamantane-1,3-diyl)bis(methylene))bis(oxy))bis(pentane-5,1-diyl)bis(2-(hydroxymethyl)piperidine-3,4,5-triol) |  | 12  |
| C217 | (2S,3R,4R,5R)-1-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol  |  | $^1\text{H}$ NMR (400 MHz, MeOD) $\delta$ 3.98 (ddd, $J = 3.3, 4.4, 9.7$ Hz, 1H), 3.92 (dd, $J = 2.6, 4.7$ Hz, 1H), 3.84 (dd, $J = 5.3, 11.5$ Hz, 1H), 3.79 (dd, $J = 4.7, 11.5$ Hz, 1H), 3.76 (dd, $J = 3.3, 4.7$ Hz, 1H), 3.39 (t, $J = 6.4$ Hz, 2H), 2.97 (s, 2H), 2.79 - 2.76 (m, 1H), 2.75 - 2.69 (m, 2H), 2.66 - 2.57 (m, 2H), 1.95 (s, 3H), 1.72 (dd, $J = 11.7, 30.9$ Hz, 6H), 1.63 - 1.50 (m, 10H), 1.39 - 1.27 (m, 2H). $^{13}\text{C}$ NMR (100 MHz, MeOD) $\delta$ 83.2, 73.1, 72.7, 72.3, 67.6, 61.7, 60.9, 55.0,  |

|      |  |  |   |
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|      |  |  | 53.2, 41.0, 38.5, 35.3, 30.7, 29.9, 25.5, 25.4. $[\alpha]_D^{20} = +24.5$ (c = 0.4, MeOH). IR/cm <sup>-1</sup> : 3359, 2902, 2848, 1453, 1065, 1057. HRMS: calcd for [C <sub>22</sub> H <sub>39</sub> O <sub>5</sub> N+H] <sup>+</sup> 398.2901, found 398.2899 [M+H] <sup>+</sup> .  |
| C218 | (2R,3R,4R,5S)-1-((5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)oxy)-2-(hydroxymethyl)piperidine-3,4,5-triol                  |  | <sup>1</sup> H NMR (400 MHz, MeOD) δ 3.93 (dd, <i>J</i> = 3.1, 11.2 Hz, 1H), 3.87 - 3.78 (m, 1H), 3.75 (t, <i>J</i> = 6.3 Hz, 2H), 3.50 - 3.44 (m, 1H), 3.47 (dd, <i>J</i> = 4.5, 11.4 Hz, 1H), 3.39 (t, <i>J</i> = 6.3 Hz, 2H), 3.19 (dd, <i>J</i> = 8.9 Hz, 1H), 2.97 (s, 2H), 2.50 - 2.36 (m, 1H), 1.95 (s, 3H), 1.72 (dd, <i>J</i> = 11.6, 30.4 Hz, 6H), 1.63 - 1.52 (m, 10H), 1.47 - 1.38 (m, 2H). <sup>13</sup> C NMR (100 MHz, MeOD) δ 83.2, 80.4, 74.0, 72.7, 70.6, 69.2, 61.4, 60.2, 41.0, 38.5, 35.3, 30.7, 29.8, 29.9, 24.3. $[\alpha]_D^{20} = +1.0$ (c = 0.4, MeOH). IR/cm <sup>-1</sup> : 3359, 2902, 2849, 1453, 1105, 1043. HRMS: calcd for [C <sub>22</sub> H <sub>39</sub> O <sub>6</sub> N+H] <sup>+</sup> 414.2850, found 414.2848 [M+H] <sup>+</sup> .   |
| C219 | (2R,3S,4R,5R)-1-butyl-2-(hydroxymethyl)piperidine-3,4,5-triol  |  | <sup>1</sup> H NMR (400 MHz, D <sub>2</sub> O) δ 4.29 - 4.24 (m, 1H), 4.22 (s, 1H), 3.99 (qd, <i>J</i> = 12.9, 5.0 Hz, 2H), 3.83 (t, <i>J</i> = 3.4 Hz, 1H), 3.55 (dd, <i>J</i> = 13.5, 3.3 Hz, 1H), 3.45 (m, 1H), 3.42 - 3.33 (dd, <i>J</i> = 13.5, 1.2 Hz, 1H), 3.28 (m, Hz, 2H), 1.70 (m, 2H), 1.35 (h, <i>J</i> = 7.4 Hz, 2H), 0.91 (t, <i>J</i> = 7.4 Hz, 3H). <sup>13</sup> C NMR (100 MHz, D <sub>2</sub> O) δ 69.95, 66.93, 66.85, 64.44, 59.20, 55.40, 53.17, 23.88, 19.31, 12.78. $[\alpha]_D^{20} = -13.5$ (c = 0.6, MeOH). IR/cm <sup>-1</sup> : 3310, 2967, 2878, 1671, 1420, 1200, 1130, 1103, 1065. LCMS: 0-20, <i>R</i> <sub>t</sub> 2.11 min, [M+H] <sup>+</sup> = 220.00. HRMS: calcd for [C <sub>10</sub> H <sub>21</sub> NO <sub>4</sub> +H] <sup>+</sup> 220.1543, found 220.1547 [M+H] <sup>+</sup> . |
| C220 | (2S,3S,4S,5R,6R)-N-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-3,4,5-trihydroxy-6-(hydroxymethyl)piperidine-2-carboxamide |  | 6   |

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| C221 | (2R,3S,4R,5R)-2-(hydroxymethyl)-1-nonylpiperidine-3,4,5-triol  |    | $^1\text{H NMR}$ (400 MHz, $\text{D}_2\text{O}$ ) $\delta$ 4.25 (s, 1H), 4.20 (s, 1H), 3.97 (m, 2H), 3.82 (t, $J = 3.1$ Hz, 1H), 3.51 (dd, $J = 13.4$ , 2.8 Hz, 1H), 3.42 (s, 1H), 3.35 (d, $J = 12.8$ Hz, 1H), 3.29 - 3.21 (m, 2H), 1.70 (m, 2H), 1.27 (m, 12H), 0.86 - 0.78 (m, 3H). $^{13}\text{C NMR}$ (100 MHz, $\text{D}_2\text{O}$ ) $\delta$ 70.0, 66.9, 66.9, 64.5, 59.3, 55.5, 53.4, 31.3, 28.7, 28.6, 28.4, 25.9, 22.2, 21.8, 13.50. $[\alpha]_{\text{D}}^{20} = -15.8$ (c = 0.5, MeOH). IR/ $\text{cm}^{-1}$ : 3310, 2995, 2928, 2859, 1670, 1420, 1200, 1185, 1130, 1069. HRMS: calcd for $[\text{C}_{15}\text{H}_{31}\text{NO}_4 + \text{H}]^+$ 290.2326, found 290.2332 $[\text{M} + \text{H}]^+$ .  |
| C222 | (2S,3S,4S,5R,6R)-1-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-3,4,5-trihydroxy-6-(hydroxymethyl)piperidine-2-carboxamide         |    | <sup>6</sup>  |
| C223 | (2S,3R,4S,5R)-1-butyl-2-(hydroxymethyl)piperidine-3,4,5-triol  |   | $^1\text{H NMR}$ (400 MHz, $\text{D}_2\text{O}$ ) $\delta$ 4.27 (s, 1H), 4.08 (td, $J = 11.0$ , 5.2 Hz, 1H), 3.98 (m, 2H), 3.60 (dd, $J = 9.8$ , 3.0 Hz, 1H), 3.52 (dd, $J = 12.2$ , 5.2 Hz, 1H), 3.45 (t, $J = 4.1$ Hz, 1H), 3.29 (dt, $J = 11.7$ , 6.5 Hz, 1H), 3.21 (td, $J = 13.4$ , 12.5, 5.4 Hz, 1H), 2.98 (t, $J = 11.8$ Hz, 1H), 1.74 - 1.64 (m, 2H), 1.41 - 1.32 (m, 2H), 0.92 (t, $J = 7.4$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, $\text{D}_2\text{O}$ ) $\delta$ 72.6, 69.9, 64.5, 63.9, 59.1, 53.3, 53.2, 23.8, 19.3, 12.7. $[\alpha]_{\text{D}}^{20} = -6.9$ (c = 0.5, MeOH). IR/ $\text{cm}^{-1}$ : 3333, 2970, 2940, 2878, 1674, 1420, 1200, 1134, 1084. LCMS: 0-20, $R_t$ 1.91 min, $[\text{M} + \text{H}]^+ = 220.07$ . HRMS: calcd for $[\text{C}_{10}\text{H}_{21}\text{NO}_4 + \text{H}]^+$ 220.1543, found 220.1547 $[\text{M} + \text{H}]^+$ . |
| C224 | (2S,3S,4S,5R,6R)-N-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-1-butyl-3,4,5-trihydroxy-6-(hydroxymethyl)piperidine-2-carboxamide |  | <sup>6</sup>  |
| C225 | (2S,3R,4S,5R)-2-(hydroxymethyl)-1-nonylpiperidine-3,4,5-triol  |  | $^1\text{H NMR}$ (400 MHz, $\text{D}_2\text{O}$ ) $\delta$ 4.23 (m, 1H), 4.04 (td, $J = 10.6$ , 5.1 Hz, 1H), 3.94 (d, $J = 4.4$ Hz, 2H), 3.56 (dd, $J = 9.7$ , 2.9 Hz, 1H), 3.47 (dd, $J = 12.2$ , 5.1 Hz, 1H), 3.41 (t, $J = 4.2$ Hz, 1H), 3.21 (m, 2H), 2.94 (t, $J = 11.8$ Hz, 1H), 1.77   |

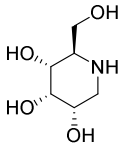
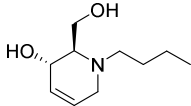
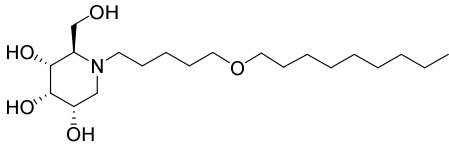
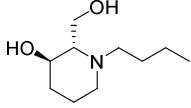
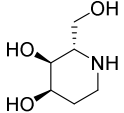
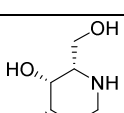
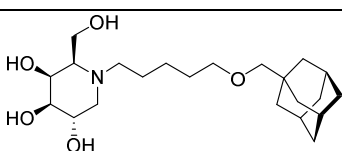
|      |   |  |  |
|------|---|--|--|
|      |   |  | - 1.57 (m, 2H), 1.38 - 1.16 (m, 12H - H <sub>2</sub> -8), 0.80 (t, <i>J</i> = 6.4 Hz, 3H). <sup>13</sup> C NMR (100 MHz, D <sub>2</sub> O) δ 72.6, 69.9, 64.5, 63.8, 59.1, 53.4, 53.3, 31.1, 28.4, 28.3, 28.1, 25.6, 22.0, 21.6, 13.4. [α] <sup>20</sup> <sub>D</sub> = - 0.5 (c = 0.6, MeOH). IR/cm <sup>-1</sup> : 3333, 2928, 2855, 1674, 1204, 1184, 1134, 1080. LCMS: 0-50, R <sub>t</sub> 8.96 min, [M+H] <sup>+</sup> = 290.20. HRMS: calcd for [C <sub>15</sub> H <sub>31</sub> NO <sub>4</sub> +H] <sup>+</sup> 290.2326, found 290.2331 [M+H] <sup>+</sup> .   |
| C226 | (2S,3S,4S,5R,6R)-N,1-bis(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-3,4,5-trihydroxy-6-(hydroxymethyl)piperidine-2-carboxamide |  | 6  |
| C227 | (2S,3R,4S,5R)-1-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol                            |  | <sup>1</sup> H NMR (400 MHz, D <sub>2</sub> O) δ 4.24 (s, 1H), 4.06 (td, <i>J</i> = 10.5, 4.9 Hz, 1H), 3.95 (d <i>J</i> = 4.0 Hz, 2H), 3.58 (d, <i>J</i> = 7.9 Hz, 1H), 3.58 - 3.41 (m, 4H), 3.30 - 3.19 (m, 2H), 3.01 (s, 2H), 2.94 (t, <i>J</i> = 11.6 Hz, 1H), 1.90 (s, 3H, CH), 1.72 - 1.54 (m, 10H), 1.48 (s, 6H), 1.43 - 1.28 (m, 2H). <sup>13</sup> C NMR (100 MHz, D <sub>2</sub> O) δ 81.6, 72.5, 71.3, 69.8, 64.4, 64.1, 59.2, 53.4, 53.2, 39.2, 36.8, 33.6, 28.1, 28.0, 22.6, 21.7. [α] <sup>20</sup> <sub>D</sub> = -5.7 (c = 0.4, MeOH). IR/cm <sup>-1</sup> : 3310, 2901, 2847, 1674, 1454, 1204, 1184, 1334. LCMS: 10-50, R <sub>t</sub> 9.59 min, [M+H] <sup>+</sup> = 398.33. HRMS: calcd for [C <sub>22</sub> H <sub>39</sub> NO <sub>5</sub> +H] <sup>+</sup> 398.2901, found 398.2901 [M+H] <sup>+</sup> . |
| C228 | (2S,3S,4S,5R,6S)-3,4,5-trihydroxy-6-(hydroxymethyl)-N-pentylpiperidine-2-carboxamide  |  | 6  |
| C229 | (2S,3S,4R,5R)-1-butyl-2-(hydroxymethyl)piperidine-3,4,5-triol   |  | <sup>1</sup> H NMR (400 MHz, D <sub>2</sub> O) δ 4.15 (s, 1H), 4.08 - 3.90 (m, 3H), 3.85 (dd, <i>J</i> = 10.7, 2.4 Hz, 1H), 3.41 - 3.10 (m, 5H), 1.82 - 1.57 (m, 2H), 1.40 - 1.32 (m, 2H), 0.90 (t, <i>J</i> = 7.4 Hz, 3H). <sup>13</sup> C NMR (100 MHz, D <sub>2</sub> O) δ 69.6, 64.8, 63.9, 60.2, 53.4, 53.2, 48.8, 24.4, 19.3, 12.8. [α] <sup>20</sup> <sub>D</sub> = +4.2 (c = 0.6, MeOH). IR/cm <sup>-1</sup> : 3333, 2970, 2940, 2882, 1674, 1435, 1200, 1134, 1080, 1045. LCMS: 0-20, R <sub>t</sub> 2.21 min, [M+H] <sup>+</sup> = 220.07. HRMS: calcd for [C <sub>10</sub> H <sub>21</sub> NO <sub>4</sub> +H] <sup>+</sup> 220.1543,   |

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|      |   |  | found 220.1547 [M+H] <sup>+</sup> .  |
| C230 | (2S,3S,4S,5R,6S)-1-butyl-3,4,5-trihydroxy-6-(hydroxymethyl)-N-pentylpiperidine-2-carboxamide  |  | 6  |
| C231 | (2S,3S,4R,5R)-2-(hydroxymethyl)-1-nonylpiperidine-3,4,5-triol   |  | <sup>1</sup> H NMR (400 MHz, D <sub>2</sub> O) δ 4.13 (s, 1H), 4.08 - 3.93 (m, 2H), 3.93 - 3.78 (m, 2H), 3.35 - 3.07 (m, 5H), 1.68 (s, 2H), 1.26 (m, 12H), 0.82 (t, <i>J</i> = 6.6 Hz, 3H). <sup>13</sup> C NMR (100 MHz, D <sub>2</sub> O) δ 69.6, 64.8, 63.9, 60.2, 53.6, 53.2, 48.9, 31.6, 29.2, 28.9, 28.8, 26.2, 22.4, 13.7. [α] <sub>D</sub> <sup>20</sup> = 5.2 (c = 0.9, MeOH). IR/cm <sup>-1</sup> : 3310, 2928, 2859, 1670, 1420, 1184, 1130, 1076, 1045. LCMS: 0-50, R <sub>t</sub> 8.81 min, [M+H] <sup>+</sup> = 290.13. HRMS: calcd for [C <sub>15</sub> H <sub>31</sub> NO <sub>4</sub> +H] <sup>+</sup> 290.2326, found 290.2332 [M+H] <sup>+</sup> .                    |
| C232 | (2S,3S,4S,5R,6S)-1-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-3,4,5-trihydroxy-6-(hydroxymethyl)-N-pentylpiperidine-2-carboxamide |  | 6  |
| C233 | (2R,3R)-2-(hydroxymethyl)piperidin-3-ol   |  | 9  |
| C234 | (2R,3R,4R,5R)-2-(hydroxymethyl)-1-(5-(neopentyloxy)pentyl)piperidine-3,4,5-triol  |  | <sup>1</sup> H NMR (400 MHz, MeOD) δ 4.16 - 4.02 (m, 2H), 4.01 - 3.85 (m, 2H), 3.59 - 3.50 (m, 1H), 3.45 (t, <i>J</i> = 6.2 Hz, 2H), 3.44 - 3.43 (m, 1H), 3.32 - 3.28 (m, 3H), 3.29 (s, 2H), 3.05 - 2.96 (m, 1H), 1.81 - 1.74 (m, 2H), 1.65 (q, <i>J</i> = 8.2 Hz, 2H), 1.47 (q, <i>J</i> = 8.2 Hz, 2H), 0.90 (s, 9H). <sup>13</sup> C NMR (100 MHz, MeOD) δ 82.5, 74.3, 72.0, 67.8, 67.2, 67.0, 56.1, 54.5, 32.9, 30.2, 27.1, 24.6. [α] <sub>D</sub> <sup>20</sup> = -21.2 (c = 0.15, MeOD). IR/cm <sup>-1</sup> : 3634, 2956, 1669, 1172, 1204, 1113. HRMS : calcd for [C <sub>16</sub> H <sub>33</sub> NO <sub>5</sub> +H] <sup>+</sup> 320.2431, found 320.2429 [M+H] <sup>+</sup> . |

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| C235 | (2R,3S)-1-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-2-(hydroxymethyl)-1,2,3,6-tetrahydropyridin-3-ol |  | 9   |
| C236 | (2R,3R,4R,5R)-1-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol    |  | <sup>1</sup> H NMR (400 MHz, MeOD) δ 4.16 - 4.00 (m, 2H), 4.01 - 3.87 (m, 2H), 3.55 (dd, <i>J</i> = 9.1, 3.0 Hz, 1H), 3.50 - 3.35 (m, 4H), 3.12 - 2.99 (m, 1H), 2.98 (s, 2H), 1.95 (s, 3H), 1.83 - 1.60 (m, 10H), 1.57 - 1.55 (m, 6H), 1.46 (q, <i>J</i> = 8.2 Hz, 2H). <sup>13</sup> C NMR (100 MHz, MeOD) δ 83.1, 74.2, 72.1, 67.8, 67.2, 66.9, 56.0, 54.5, 40.9, 38.3, 35.1, 30.2, 29.8, 24.6, 23.5. [ $\alpha$ ] <sub>D</sub> <sup>20</sup> = -16.8 (c = 0.19, MeOD). IR/cm <sup>-1</sup> : 3685, 2997, 1669, 1200, 1129, 831, 800, 719. HRMS: calcd for [C <sub>22</sub> H <sub>39</sub> NO <sub>5</sub> +H] <sup>+</sup> 298.2901, found 298.2891 [M+H] <sup>+</sup> .  |
| C237 | (2R,3R)-1-butyl-2-(hydroxymethyl)-1,2,3,6-tetrahydropyridin-3-ol  |  | 9   |
| C238 | (2S,3R,4R,5S)-1-(4-(2-((3S,5S,7S)-adamantan-1-yl)ethoxy)butyl)-2-(hydroxymethyl)piperidine-3,4,5-triol    |  | <sup>1</sup> H NMR (600 MHz, D <sub>2</sub> O) δ 3.82 - 3.79 (m, 2H), 3.68 (dd, <i>J</i> = 8.4, 4.8 Hz, 1H), (ddd, <i>J</i> = 10.2, 9.0, 5.4 Hz, 1H), 3.47 (t, <i>J</i> = 7.2 Hz, 2H), 3.41 (br s, 2H), 3.37 (dd, <i>J</i> = 8.4, 7.8 Hz, 1H), 3.02 (m, 1H), 2.80 - 2.75 (m, 2H), 2.66 (br m, 1H), 2.57 (dd, <i>J</i> = 12.0, 10.2 Hz, 1H), 1.92 (s, 3H), 1.75 - 1.66 (m, 6H), 1.56 - 1.35 (m, 10H), 1.35 (t, <i>J</i> = 7.2 Hz, 2H). <sup>13</sup> C NMR (150 MHz, MeOD) δ 75.8, 72.8, 71.7, 71.3, 67.8, 64.4, 57.7, 55.3, 52.8, 44.8, 43.9, 38.2, 32.8, 30.2, 28.5, 25.4. IR/cm <sup>-1</sup> : 3342, 2899, 2846, 1654, 1450, 1062. LC/MS analysis: <i>R</i> <sub>t</sub> 7.27 min (linear gradient 10-90% B), ES: = 398.2 [M+H] <sup>+</sup> . HRMS: calcd for [C <sub>22</sub> H <sub>39</sub> O <sub>5</sub> N <sub>1</sub> +H] <sup>+</sup> 398.2901, found 398.2899 [M+H] <sup>+</sup> . |
| C239 | (2R,3R,4R,5R)-2-(hydroxymethyl)-1-nonylpiperidine-3,4,5-triol   |  | <sup>1</sup> H NMR (400 MHz, MeOD) δ 4.15 - 4.03 (m, 2H), 4.02 - 3.82 (m, 2H), 3.59 - 3.49 (m, 1H), 3.44 (dd, <i>J</i> = 12.8, 3.8 Hz, 1H), 3.34 - 3.32 (m, 3H), 3.03 - 3.0 (m, 1H), 1.83 - 1.60 (m, 2H), 1.54 - 1.13 (m, 12H), 0.90 (t, <i>J</i> = 8.2 Hz, 3H). <sup>13</sup> C NMR (100 MHz, MeOD) δ 74.2, 67.8, 67.2, 67.0, 56.0, 54.6, 33.0, 30.5,  |



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|      |  |  | 30.3, 30.2, 27.6, 23.7. $[\alpha]_D^{20} = -20.8$ (c = 0.17, MeOH). IR/cm <sup>-1</sup> : 3560, 2924, 1669, 1207, 1175, 1127. HRMS: calcd for [C <sub>15</sub> H <sub>31</sub> NO <sub>4</sub> +H] <sup>+</sup> 290.2326, found: 290.2328 [M+H] <sup>+</sup> .   |
| C240 | (2R,3R,4R)-1-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4-diol |  | 9  |
| C241 | (2R,3R,4R,5R)-2-(hydroxymethyl)piperidine-3,4,5-triol  |  | <sup>1</sup> H NMR (600 MHz, D <sub>2</sub> O) δ 4.17 (s, 1H), 3.91 (d, J = 12.6 Hz, 1H), 3.80 - 3.74 (m, 2H), 3.61 (d, J = 9.3 Hz, 1H), 3.33 (d, J = 13.5 Hz, 1H), 3.17 (d, J = 13.5 Hz, 1H), 3.09 - 3.06 (m, 1H). <sup>13</sup> C NMR (150 MHz, D <sub>2</sub> O) δ 73.2, 66.6, 61.2, 58.9, 48.4. $[\alpha]_D^{20} = -2.1$ (c = 0.17 MeOH). IR/cm <sup>-1</sup> : 3678, 2619, 1629, 1442, 1033. HRMS: calcd for [C <sub>6</sub> H <sub>13</sub> NO <sub>4</sub> + H] <sup>+</sup> 164.0917, found: 164.0916 [M+H] <sup>+</sup> . |
| C242 | (2R,3R,4S)-1-butyl-2-(hydroxymethyl)piperidine-3,4-diol  |  | 9  |
| C243 | (2R,3R,4R,5R)-1-(2-hydroxyethyl)-2-(hydroxymethyl)piperidine-3,4,5-triol                         |  | <sup>1</sup> H NMR (600 MHz, MeOD) δ 4.15 - 4.06 (m, 2H), 4.01 - 3.98 (m, 2H), 3.97 - 3.93 (m, 2H), 3.64 - 3.52 (m, 3H), 3.46 - 3.44 (m, 1H), 3.37 - 3.35 (m, 1H), 3.18 - 3.17 (m, 1H). <sup>13</sup> C NMR (150 MHz, MeOD) δ 74.2, 68.6, 67.1, 67.0, 56.6, 56.4, 55.9, 55.7. $[\alpha]_D^{20} = -20.7$ (c = 0.05, MeOD). IR/cm <sup>-1</sup> : 3741 - 2786, 1635, 1084, 611. HRMS: calcd for [C <sub>8</sub> H <sub>17</sub> NO <sub>5</sub> +H] <sup>+</sup> 208.1185, found 208.1180 [M+H] <sup>+</sup> .                       |
| C244 | (2R,3S,4R)-1-butyl-2-(hydroxymethyl)piperidine-3,4-diol  |  | 9  |

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| C245 | (2R,3R,4S,5S)-2-(hydroxymethyl)piperidine-3,4,5-triol                                   |    | <sup>1</sup> H NMR (600 MHz, D <sub>2</sub> O) δ 4.02 (s, 1H), 3.85 (ddd, <i>J</i> = 11.8, 4.8, 2.3 Hz, 1H), 3.79 (dd, <i>J</i> = 12.7, 2.9 Hz, 1H), 3.75 - 3.64 (m, 2H), 3.22 - 3.15 (m, 1H), 3.12 (dd, <i>J</i> = 11.8, 4.8 Hz, 1H), 2.98 (t, <i>J</i> = 11.8 Hz, 1H). <sup>13</sup> C NMR (150 MHz, D <sub>2</sub> O) δ 70.7, 66.1, 65.3, 58.4, 55.5, 42.3. [α] <sub>D</sub> <sup>20</sup> = + 8.2 (c = 0.12, MeOH). IR/cm <sup>-1</sup> : 3690, 3018, 1634, 1061, 1033, 1015. HRMS: calcd for [C <sub>6</sub> H <sub>13</sub> NO <sub>4</sub> +H] <sup>+</sup> 164.0917, found 164.0916 [M+H] <sup>+</sup> .   |
| C246 | (2R,3S)-1-butyl-2-(hydroxymethyl)-1,2,3,6-tetrahydropyridin-3-ol                        |    | 9  |
| C247 | (2R,3R,4S,5S)-2-(hydroxymethyl)-1-(5-(nonyloxy)pentyl)piperidine-3,4,5-triol            |    | <sup>1</sup> H NMR (400 MHz, MeOD) δ 4.05 - 4.02 (m, 2H), 3.91 (dd, <i>J</i> = 12.4, 3.2 Hz, 1H), 3.83 (ddd, <i>J</i> = 9.4, 7.1, 2.4 Hz, 1H), 3.75 (dd, <i>J</i> = 10.3, 2.4 Hz, 1H), 3.47 - 3.41 (m, 4H), 3.28 - 3.22 (m, 1H), 3.18 - 3.11 (m, 4H), 1.86 - 1.65 (m, 2H), 1.63 (q, <i>J</i> = 6.7 Hz, 2H), 1.55 (q, <i>J</i> = 6.8 Hz, 2H), 1.46 (dt, <i>J</i> = 11.4, 7.8 Hz, 2H), 1.38 - 1.14 (m, 12H), 0.90 (t, <i>J</i> = 8.0 Hz, 3H). <sup>13</sup> C NMR (100 MHz, MeOD) δ 72.1, 71.5, 67.1, 66.1, 62.2, 55.6, 54.1, 50.9, 33.1, 30.8, 30.7, 30.6, 30.4, 30.2, 27.3, 24.6, 24.2, 23.7, 14.5. [α] <sub>D</sub> <sup>20</sup> = - 8.6 (c = 0.17, MeOD). IR/cm <sup>-1</sup> : 3663, 3016, 1668, 1185, 1116. HRMS: calcd for [C <sub>20</sub> H <sub>41</sub> NO <sub>5</sub> +H] <sup>+</sup> 376.3057, found 376.3058 [M+H] <sup>+</sup> . |
| C248 | (2S,3R)-1-butyl-2-(hydroxymethyl)piperidin-3-ol   |  | 9  |
| C249 | (2S,3S,4R)-2-(hydroxymethyl)piperidine-3,4-diol   |  | 9  |
| C250 | (2S,3R,4S)-2-(hydroxymethyl)piperidine-3,4-diol   |  | 9  |
| C251 | (2R,3S,4R,5S)-1-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-2-(hydroxymethyl)piperid |  | 3  |

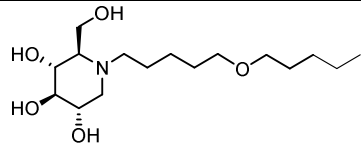
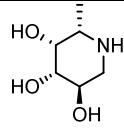
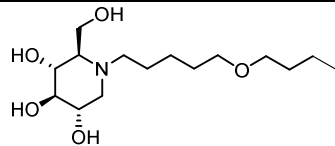
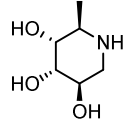
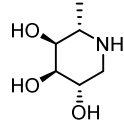
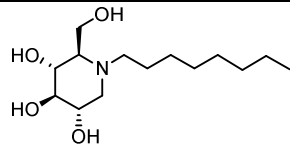
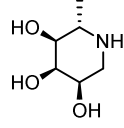
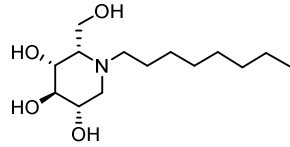
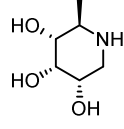
|      |   |  |   |
|------|---|--|---|
|      | ine-3,4,5-triol   |  |   |
| C252 | 1-((2R,3S,4S,5R,6S)-1-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-3,4,5-trihydroxy-6-(hydroxymethyl)piperidin-2-yl)-3,3,5,5-tetramethylhexan-1-one |  | 6   |
| C253 | (2R,3R,4S,5S)-1-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol  |  | <sup>1</sup> H NMR (400 MHz, D <sub>2</sub> O) δ 4.15 (s, 1H), 4.08 - 3.95 (m, 2H), 3.95 - 3.83 (m, 2H), 3.39 (t, <i>J</i> = 6.2 Hz, 2H), 3.35 - 3.09 (m, 5H), 2.98 (s, 2H), 1.91 (s, 3H), 1.65 (m, 10H), 1.50 (s, 6H), 1.43 - 1.29 (m, 2H). <sup>13</sup> C NMR (100 MHz, D <sub>2</sub> O) δ 81.8, 71.5, 69.6, 64.8, 63.9, 60.4, 53.7, 53.0, 49.0, 39.5, 37.1, 33.9, 28.6, 28.3, 22.9, 22.4. [α] <sub>D</sub> <sup>20</sup> = +2.8 (c = 1.2, MeOH). IR/cm <sup>-1</sup> : 3333, 2901, 2847, 1674, 1454, 1204, 1134, 1080, 1053. LCMS: 0-50, <i>R</i> <sub>t</sub> 10.36 min, [M+H] <sup>+</sup> = 398.33. HRMS: calcd for [C <sub>22</sub> H <sub>39</sub> NO <sub>5</sub> +H] <sup>+</sup> 398.2901, found 398.2901 [M+H] <sup>+</sup> .                                     |
| C254 | (2R,3S,4S,5R,6S)-N-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-3,4,5-trihydroxy-6-(hydroxymethyl)piperidine-2-carboxamide                          |  | 6   |
| C255 | (2S,3R,4S,5S)-1-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol  |  | <sup>1</sup> H NMR (400 MHz, D <sub>2</sub> O) δ 4.25 (s, 1H), 4.21 (s, 1H), 3.98 (m, 2H), 3.82 (s, 1H), 3.52 (d, <i>J</i> = 11.6 Hz, 1H), 3.41 (m, 3H), 3.35 (d, <i>J</i> = 13.2 Hz, 1H), 3.28 (m, 2H), 2.99 (s, 2H), 1.91 (s, 3H), 1.81 - 1.52 (m, 10H), 1.49 (s, 6H), 1.36 (m, 2H). <sup>13</sup> C NMR (100 MHz, D <sub>2</sub> O) δ 81.7, 71.4, 70.0, 66.9, 66.8, 64.7, 59.4, 55.5, 53.2, 39.3, 36.9, 33.7, 28.3, 28.1, 22.7, 21.8. [α] <sub>D</sub> <sup>20</sup> = 12.5 (c = 0.6, MeOH). IR/cm <sup>-1</sup> : 3368, 2901, 2847, 1674, 1539, 1184, 1130, 1069. LCMS: 10-50, <i>R</i> <sub>t</sub> 9.47 min, [M+H] <sup>+</sup> = 398.33. HRMS: calcd for [C <sub>22</sub> H <sub>39</sub> NO <sub>5</sub> +H] <sup>+</sup> 398.2901, found 398.2901 [M+H] <sup>+</sup> . |

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|------|--|--|--|
| C256 | (2R,3R,4S,5R)-1-(2-(benzyloxy)ethyl)-2-(hydroxymethyl)piperidine-3,4,5-triol   |  | $^1\text{H NMR}$ (400 MHz, $\text{D}_2\text{O}$ ) $\delta$ 7.99 - 7.10 (m, 5H), 4.60 (s, 2H), 4.14 (d, $J = 7.9$ Hz, 1H), 4.12 - 4.05 (m, 1H), 4.05 - 3.94 (m, 3H), 3.91 (s, 2H), 3.67 - 3.40 (m, 4H), 3.33 (d, $J = 14.1$ Hz, 1H). $^{13}\text{C NMR}$ (100 MHz, $\text{D}_2\text{O}$ ) $\delta$ 136.7, 128.7, 128.4, 73.0, 67.9, 65.7, 63.0, 62.7, 62.1, 54.0, 52.3, 51.9. $[\alpha]_{\text{D}}^{20} = +2.5$ ( $c = 0.8$ , MeOH). IR/ $\text{cm}^{-1}$ : 3356, 1674, 1520, 1454, 1200, 1134, 1072, 1026. HRMS: calcd for $[\text{C}_{15}\text{H}_{23}\text{NO}_5 + \text{H}]^+$ 298.1649, found 298.1656 $[\text{M} + \text{H}]^+$ . |
| C257 | (2R,3S,4R,5S)-2-(hydroxymethyl)-1-nonylpiperidine-3,4,5-triol  |  | 8  |
| C258 | (2S,3S,4S,5R,6R)-1-butyl-3,4,5-trihydroxy-6-(hydroxymethyl)piperidine-2-carboxylic acid  |  | 6  |
| C259 | (2R,3S,4R,5S)-1-(5-([1,1'-biphenyl]-4-ylmethoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol                                  |  | 10   |
| C260 | (2S,3S,4S,5R,6S)-1-butyl-3,4,5-trihydroxy-6-(hydroxymethyl)piperidine-2-carboxamide  |  | 6  |
| C261 | (2S,3S,4R,5S)-1-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol                           |  | 3  |
| C262 | (2S,3S,4S,5R,6S)-1-butyl-3,4,5-trihydroxy-6-(hydroxymethyl)piperidine-2-carboxylic acid  |  | 6  |
| C263 | (2S,3S,4S,5R,6S)-1-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-3,4,5-trihydroxy-6-(hydroxymethyl)piperidine-2-carboxylic acid |  | 6  |

|      |   |  |   |
|------|---|--|---|
| C264 | (2R,3R,4S,5S)-1-(5-([1,1'-biphenyl]-4-ylmethoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol |  | <sup>1</sup> H NMR (400 MHz, D <sub>2</sub> O) δ 7.07 (dd, <i>J</i> = 7.5, 3.8 Hz, 4H), 6.92 (d, <i>J</i> = 8.0 Hz, 2H), 6.86 (t, <i>J</i> = 7.4 Hz, 2H), 6.78 (t, <i>J</i> = 7.2 Hz, 1H), 4.11 (s, 1H), 4.08 (s, 2HPh), 3.99 - 3.85 (m, 2H), 3.80 (dd, <i>J</i> = 10.7, 1.9 Hz, 1H), 3.69 (d, <i>J</i> = 12.0 Hz, 1H), 3.18 - 2.91 (m, 6H), 2.90 - 2.76 (m, 1H), 1.57 - 1.35 (m, 2H), 1.35 - 1.17 (m, 2H), 1.11 - 0.88 (m, 2H). <sup>13</sup> C NMR (100 MHz, D <sub>2</sub> O) δ 139.9, 139.5, 137.0, 128.6, 128.2, 127.1, 126.5, 71.8, 69.6, 69.4, 64.6, 63.7, 60.2, 53.4, 52.7, 48.8, 28.4, 22.6, 22.1. [α] <sub>D</sub> <sup>20</sup> = -3.5 (c = 1.1, MeOH). IR/cm <sup>-1</sup> : 3310, 3028, 2936, 1674, 1539, 1508, 1458, 1204, 1134, 1057. LCMS: 0-50, <i>R</i> <sub>t</sub> 9.82 min, [M+H] <sup>+</sup> = 416.20. HRMS: calcd for [C <sub>24</sub> H <sub>33</sub> NO <sub>5</sub> +H] <sup>+</sup> 416.2432, found 416.2334 [M+H] <sup>+</sup> . |
| C265 | (2S,3S,4S,5R,6S)-3,4,5-trihydroxy-6-(hydroxymethyl)-N-pentylpiperidine-2-carboxamide            |  | 6   |
| C266 | (2R,3R,4S,5S)-1-(2-(benzyloxy)ethyl)-2-(hydroxymethyl)piperidine-3,4,5-triol                    |  | <sup>1</sup> H NMR (400 MHz, MeOD) δ 7.54 - 7.17 (m, 5H), 4.53 (s, 2H), 4.07 - 3.99 (m, 2H), 3.93 (dd, <i>J</i> = 10.6, 2.0 Hz, 1H), 3.88 - 3.78 (m, 3H), 3.75 (d, <i>J</i> = 10.4 Hz, 1H), 3.58 (d, <i>J</i> = 14.0 Hz, 1H), 3.46 (d, <i>J</i> = 14.0 Hz, 1H), 3.37 - 3.18 (m, 3H). <sup>13</sup> C NMR (100 MHz, MeOD) δ 139.9, 130.9, 130.4, 130.3, 75.7, 72.6, 67.8, 66.9, 65.9, 64.3, 56.2, 55.2, 52.6. [α] <sub>D</sub> <sup>20</sup> = +7.6 (c = 1.0, MeOH). IR/cm <sup>-1</sup> : 3333, 2909, 2886, 1674, 1454, 1420, 1200, 1134, 1080, 1045. LCMS: 0-20, <i>R</i> <sub>t</sub> 7.90 min, [M+H] <sup>+</sup> = 298.07. HRMS: calcd for [C <sub>15</sub> H <sub>23</sub> NO <sub>5</sub> +H] <sup>+</sup> 298.1649, found 298.1657 [M+H] <sup>+</sup> .  |
| C267 | (2S,3S,4S,5R,6S)-1-butyl-3,4,5-trihydroxy-6-(hydroxymethyl)-N-pentylpiperidine-2-carboxamide    |  | 6   |
| C268 | (2R,3R,4R,5S)-2-(hydroxymethyl)-1-(5-(neopentyloxy)pentyl)piperidine-3,4,5-triol                |  | <sup>1</sup> H NMR (400 MHz, MeOD) δ 4.01 (dd, <i>J</i> = 12.3, 2.0 Hz, 1H), 3.89 (dd, <i>J</i> = 12.3, 3.0 Hz, 1H), 3.62 (ddd, <i>J</i> = 10.8, 9.2, 4.9 Hz, 1H), 3.52 (t, <i>J</i> = 9.6 Hz, 1H), 3.44 (t, <i>J</i> = 6.2 Hz, 2H), 3.32 - 3.24 (m, 2H), 3.17 (td, <i>J</i> = 12.1, 11.5, 5.5  |

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|      |   |  | <p>Hz, 1H), 3.08 (s, 2H), 3.00 (td, <math>J = 12.7, 12.0, 5.4</math> Hz, 1H), 2.78 - 2.70 (m, 1H), 2.72 (t, <math>J = 11.4</math> Hz, 1H), 1.69 - 1.65 (m, 4H), 1.44 (ddd, <math>J = 17.2, 9.0, 5.9</math> Hz, 2H), 0.91 (s, 9H). <math>^{13}\text{C}</math> NMR (100 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 82.5, 79.0, 72.1, 69.9, 68.8, 67.4, 56.5, 55.7, 54.0, 32.9, 30.4, 27.1, 24.8, 24.4. IR/<math>\text{cm}^{-1}</math>: 3284, 2347, 2326, 1018. LC/MS analysis: <math>R_t</math> 4.89 min (linear gradient 10-90% B), ES: = 320.3 <math>[\text{M}+\text{H}]^+</math>. HRMS: calcd for <math>[\text{C}_{16}\text{H}_{33}\text{O}_5\text{N}+\text{H}]^+</math> 320.2432 found 320.2431 <math>[\text{M}+\text{H}]^+</math>.</p>  |
| C269 | (2S,3S,4S,5R,6S)-1-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-3,4,5-trihydroxy-6-(hydroxymethyl)-N-pentylpiperidine-2-carboxamide |  | 6  |
| C270 | (2S,3R,4R,5S)-1-(5-(2-((3S,5S,7S)-adamantan-1-yl)ethoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol                               |  | 3  |
| C271 | (2R,3S,4S,5S)-2-(hydroxymethyl)-1-(5-(nonyloxy)pentyl)piperidine-3,4,5-triol  |  | <p><math>^1\text{H}</math> NMR (600 MHz, MeOD) <math>\delta</math> 4.22 - 4.06 (m, 1H), 4.06 - 3.96 (m, 1H), 3.97 - 3.88 (m, 2H), 3.85 (dd, <math>J = 4.6, 2.8</math> Hz, 1H), 3.46 - 3.42 (m, 5 H), 3.22 - 3.13 (m, 2H), 3.13 - 3.03 (m, 2H), 1.86 - 1.67 (m, 2H), 1.55 (q, <math>J = 7.5</math> Hz, 2H), 1.55 (q, <math>J = 7.5</math> Hz, 2H), 1.43 (q, <math>J = 7.5</math> Hz, 2H), 1.38 - 1.22 (m, 12H), 0.90 (t, <math>J = 7.0</math> Hz, 3H). <math>^{13}\text{C}</math> NMR (150 MHz, MeOD) <math>\delta</math> 72.1, 72.1, 71.5, 70.6, 64.8, 61.7, 61.6, 54.9, 51.5, 33.1, 30.8, 30.8, 30.7, 30.6, 30.4, 30.3, 27.3, 24.7, 23.8, 14.5. <math>[\alpha]_D^{20} = -35.8</math> (<math>c = 0.06</math>, MeOD). IR/<math>\text{cm}^{-1}</math>: 3666 - 2994, 1672, 1201, 1127. HRMS: calcd for <math>[\text{C}_{20}\text{H}_{41}\text{NO}_5+\text{H}]^+</math> 376.3057, found 376.3059 <math>[\text{M}+\text{H}]^+</math>.</p> |
| C272 | (2S,3R,4R,5S)-2-(hydroxymethyl)-1-(5-(nonyloxy)pentyl)piperidine-3,4,5-triol  |  | 8  |
| C273 | (2S,3R,4R,5S)-1-(2-hydroxyethyl)-2-(hydroxymethyl)piperidine-3,4,5-triol  |  | 14   |

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|------|--|--|--|
| C274 | (2S,3R,4R,5S)-2-(hydroxymethyl)-1-(5-(octyloxy)pentyl)piperidine-3,4,5-triol     |  | 8  |
| C275 | (2R,3R,4R,5R)-1-butyl-2-(hydroxymethyl)piperidine-3,4,5-triol                    |  | 15   |
| C276 | (2R,3R,4R,5S)-1-(5-(heptyloxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol    |  | 8  |
| C277 | (2R,3R,4R,5R)-2-(hydroxymethyl)-1-(5-(neopentyloxy)pentyl)piperidine-3,4,5-triol |  | <sup>1</sup> H NMR (400 MHz, MeOD) δ 4.16 - 4.02 (m, 2H), 4.01 - 3.85 (m, 2H), 3.59 - 3.50 (m, 1H), 3.45 (t, <i>J</i> = 6.2 Hz, 2H), 3.44 - 3.43 (m, 1H), 3.32 - 3.28 (m, 3H), 3.29 (s, 2H), 3.05 - 2.96 (m, 1H), 1.81 - 1.74 (m, 2H), 1.65 (q, <i>J</i> = 8.2 Hz, 2H), 1.47 (q, <i>J</i> = 8.2 Hz, 2H), 0.90 (s, 9 H). <sup>13</sup> C NMR (100 MHz, MeOD) δ 82.5, 74.3, 72.0, 67.8, 67.2, 67.0, 56.1, 54.5, 32.9, 30.2, 27.1, 24.6. [α] <sub>D</sub> <sup>20</sup> = -21.2 (c = 0.15, MeOD). IR/cm <sup>-1</sup> : 3634, 2956, 1669, 1172, 1204, 1113. HRMS: calcd for [C <sub>16</sub> H <sub>33</sub> NO <sub>5</sub> +H] <sup>+</sup> 320.2431, found 320.2429 [M+H] <sup>+</sup> . |
| C278 | (2S,3R,4R,5S)-2-(hydroxymethyl)-1-(5-(pentyloxy)pentyl)piperidine-3,4,5-triol    |  | 8  |
| C279 | (2R,3R,4R,5R)-2-(hydroxymethyl)-1-(5-(nonyloxy)pentyl)piperidine-3,4,5-triol     |  | <sup>1</sup> H NMR (400 MHz, MeOD) δ 4.15 - 4.03 (m, 2H), 4.02 - 3.82 (m, 2H), 3.59 - 3.49 (m, 1H), 3.44 (dd, <i>J</i> = 12.8, 3.8 Hz, 1H), 3.34 - 3.32 (m, 3H), 3.03 - 3.0 (m, 1H), 1.83 - 1.60 (m, 2H), 1.54 - 1.13 (m, 12H), 0.90 (t, <i>J</i> = 8.2 Hz, 3H). <sup>13</sup> C NMR (100 MHz, MeOD) δ 74.2, 67.8, 67.2, 67.0, 56.0, 54.6, 33.0, 30.5, 30.3, 30.2, 27.6, 23.7. [α] <sub>D</sub> <sup>20</sup> = -20.8 (c = 0.17, MeOD). IR/cm <sup>-1</sup> : 3560, 2924, 1669, 1207, 1175, 1127. HRMS: calcd for [C <sub>15</sub> H <sub>31</sub> NO <sub>4</sub> +H] <sup>+</sup> 290.2326, found 290.2328 [M+H] <sup>+</sup> .  |
| C280 | (2R,3R,4S,5S)-2-(hydroxymethyl)-1-(5-(neopentyloxy)pentyl)piperidine-3,4,5-triol |  | <sup>1</sup> H NMR (400 MHz, MeOD) δ 4.14 - 4.01 (m, 2H), 3.92 (dd, <i>J</i> = 12.5, 3.1 Hz, 1H), 3.87 (d, <i>J</i> = 2.4 Hz, 1H), 3.82 - 3.75 (m, 1H), 3.45 (t, <i>J</i> = 6.1 Hz, 2H), 3.33 - 3.31 (m, 1H), 3.28 - 3.13 (m, 4H), 3.08 (s,  |

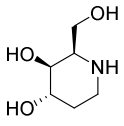
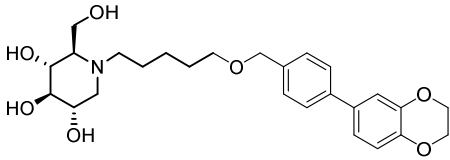
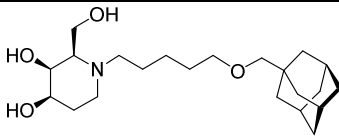
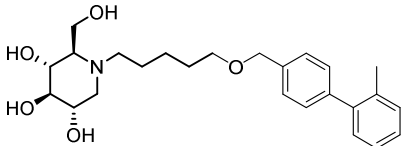
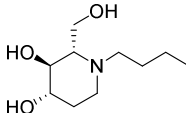
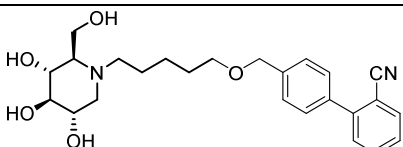
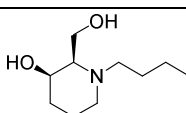
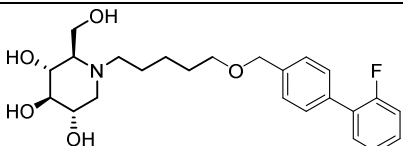
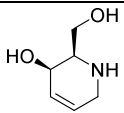
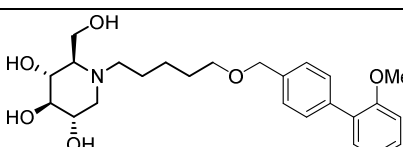
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|      |   |   | 2H), 1.90 - 1.70 (m, 2H), 1.70 - 1.59 (m, 2H), 1.50 - 1.48 (m, 2H), 0.91 (s, 9 H). <sup>13</sup> C NMR (100 MHz, MeOD) δ 82.5, 72.0, 71.4, 66.6, 65.7, 62.2, 55.0, 54.0, 50.7, 32.9, 30.2, 27.1, 24.6, 24.1. [α] <sub>D</sub> <sup>20</sup> = -3.5 (c = 0.23, MeOD). IR/cm <sup>-1</sup> : 3692, 2995, 1671, 1207, 1128. HRMS: calcd for [C <sub>16</sub> H <sub>33</sub> NO <sub>5</sub> +H] <sup>+</sup> 320.2431, found 320.2429 [M+H] <sup>+</sup> . |
| C281 | (2R,3R,4R,5S)-2-(hydroxymethyl)-1-(5-(pentyloxy)pentyl)piperidine-3,4,5-triol |    | 8  |
| C282 | (2S,3R,4S,5R)-2-methylpiperidine-3,4,5-triol                                  |    | 16   |
| C283 | (2R,3R,4R,5S)-1-(5-butoxypentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol      |    | 8  |
| C284 | (2R,3R,4S,5R)-2-methylpiperidine-3,4,5-triol                                  |   | 16   |
| C285 | (2S,3S,4R,5S)-2-methylpiperidine-3,4,5-triol                                  |  | 16   |
| C286 | (2R,3R,4R,5S)-2-(hydroxymethyl)-1-octylpiperidine-3,4,5-triol                 |  | 8  |
| C287 | (2S,3S,4R,5R)-2-methylpiperidine-3,4,5-triol                                  |  | 16   |
| C288 | (2S,3R,4R,5S)-2-(hydroxymethyl)-1-octylpiperidine-3,4,5-triol                 |  | 8  |
| C289 | (2R,3R,4S,5S)-2-methylpiperidine-3,4,5-triol                                  |  | 16   |



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| C290 | (2R,3R,4R,5S)-1-heptyl-2-(hydroxymethyl)piperidine-3,4,5-triol  |  | 8  |
| C291 | (2S,3R,4S,5R)-2-methylpiperidine-3,4,5-triol  |  | 16 |
| C292 | (2R,3S,4R,5S)-2-methylpiperidine-3,4,5-triol  |  | 16 |
| C293 | (2R,3R,4R,5S)-1-hexyl-2-(hydroxymethyl)piperidine-3,4,5-triol   |  | 8  |
| C294 | (2S,3R,4S,5S)-2-methylpiperidine-3,4,5-triol  |  | 16 |
| C295 | (2S,3R,4R,5S)-1-hexyl-2-(hydroxymethyl)piperidine-3,4,5-triol   |  | 8  |
| C296 | (2R,3S,4R,5R)-2-methylpiperidine-3,4,5-triol  |  | 16 |
| C297 | (2R,3R,4R,5S)-2-(hydroxymethyl)-1-pentylpiperidine-3,4,5-triol  |  | 8  |
| C298 | (2S,3R,4R,5S)-2-(hydroxymethyl)-1-pentylpiperidine-3,4,5-triol  |  | 8  |
| C299 | (2R,3S,4S,5R)-2-(hydroxymethyl)piperidine-3,4,5-triol   |  | 4  |
| C300 | (2S,3R)-2-(hydroxymethyl)-1,2,3,6-tetrahydropyridin-3-ol  |  | 9  |
| C301 | (2R,3R,4R,5S)-2-(hydroxymethyl)-1-(5-((4'-methyl-[1,1'-biphenyl]-4-yl)methoxy)pentyl)piperidine-3,4,5-triol |  | 10 |

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| C302 | (2R,3R,4R,5S)-2-(hydroxymethyl)-1-(5-((3'-methyl-[1,1'-biphenyl]-4-yl)methoxy)pentyl)piperidine-3,4,5-triol                  |  | 10 |
| C303 | (2R,3R,4R,5S)-1-(5-((4-(benzo[d][1,3]dioxol-5-yl)benzyl)oxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol                  |  | 10 |
| C304 | (2R,3R,4R,5S)-1-(5-((4-(3,4-dihydro-2H-benzo[b][1,4]dioxepin-7-yl)benzyl)oxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol |  | 10 |
| C305 | (2R,3R,4R,5S)-2-(hydroxymethyl)-1-(5-((4'-methoxy-[1,1'-biphenyl]-4-yl)methoxy)pentyl)piperidine-3,4,5-triol                 |  | 10 |
| C306 | (2R,3R,4R,5S)-2-(hydroxymethyl)-1-(5-((3'-methoxy-[1,1'-biphenyl]-4-yl)methoxy)pentyl)piperidine-3,4,5-triol                 |  | 10 |
| C307 | (2R,3R,4R,5S)-2-(hydroxymethyl)-1-(5-((4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)methoxy)pentyl)piperidine-3,4,5-triol       |  | 10 |
| C308 | (2R,3R,4R,5S)-1-(5-((3',5'-bis(trifluoromethyl)-[1,1'-biphenyl]-4-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol |  | 10 |
| C309 | 4'-(((5-((2R,3R,4R,5S)-3,4,5-trihydroxy-2-(hydroxymethyl)piperidin-1-yl)pentyl)oxy)methyl)-[1,1'-biphenyl]-4-carbonitrile    |  | 10 |
| C310 | 4'-(((5-((2R,3R,4R,5S)-3,4,5-trihydroxy-2-(hydroxymethyl)piperidin-1-yl)pentyl)oxy)methyl)-[1,1'-biphenyl]-3-carbonitrile    |  | 10 |
| C311 | (2R,3R,4R,5S)-1-(5-((4'-fluoro-[1,1'-biphenyl]-4-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol                  |  | 10 |

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| C312 | (2R,3R,4R,5S)-1-(5-((3'-fluoro-[1,1'-biphenyl]-4-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol |  | 10 |
| C313 | (2R,3R)-1-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-2-(hydroxymethyl)-1,2,3,6-tetrahydropyridin-3-ol   |  | 9  |
| C314 | (2R,3R,4R,5S)-1-(5-((4'-chloro-[1,1'-biphenyl]-4-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol |  | 10 |
| C315 | (2S,3R,4S)-1-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4-diol            |  | 9  |
| C316 | (2R,3R,4R,5S)-2-(hydroxymethyl)-1-(5-((4-(pyridin-4-yl)benzyl)oxy)pentyl)piperidine-3,4,5-triol             |  | 10 |
| C317 | (2S,3S,4R)-1-butyl-2-(hydroxymethyl)piperidine-3,4-diol   |  | 9  |
| C318 | (2R,3R,4R,5S)-2-(hydroxymethyl)-1-(5-((4-(pyridin-3-yl)benzyl)oxy)pentyl)piperidine-3,4,5-triol             |  | 10 |
| C319 | (2R,3R,4S)-2-(hydroxymethyl)piperidine-3,4-diol   |  | 9  |
| C320 | (2R,3R,4R,5S)-2-(hydroxymethyl)-1-(5-((4-(pyrimidin-5-yl)benzyl)oxy)pentyl)piperidine-3,4,5-triol           |  | 10 |
| C321 | (2S,3R,4S)-1-butyl-2-(hydroxymethyl)piperidine-3,4-diol   |  | 9  |
| C322 | (2R,3R,4R,5S)-1-(5-((4-(6-fluoropyridin-3-yl)benzyl)oxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol     |  | 10 |

|      |   |   |    |
|------|---|---|----|
| C323 | (2R,3S,4S)-2-(hydroxymethyl)piperidine-3,4-diol   |    | 9  |
| C324 | (2R,3R,4R,5S)-1-(5-((4-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)benzyl)oxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol    |    | 10 |
| C325 | (2R,3S,4R)-1-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4-diol                          |    | 9  |
| C326 | (2R,3R,4R,5S)-2-(hydroxymethyl)-1-(5-((2'-methyl-[1,1'-biphenyl]-4-yl)methoxy)pentyl)piperidine-3,4,5-triol               |    | 10 |
| C327 | (2S,3S,4S)-1-butyl-2-(hydroxymethyl)piperidine-3,4-diol   |   | 9  |
| C328 | 4'-((5-((2R,3R,4R,5S)-3,4,5-trihydroxy-2-(hydroxymethyl)piperidine-1-yl)pentyl)oxy)methyl)-[1,1'-biphenyl]-2-carbonitrile |  | 10 |
| C329 | (2R,3R)-1-butyl-2-(hydroxymethyl)piperidine-3-ol  |  | 9  |
| C330 | (2R,3R,4R,5S)-1-(5-((2'-fluoro-[1,1'-biphenyl]-4-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol               |  | 10 |
| C331 | (2R,3R)-2-(hydroxymethyl)-1,2,3,6-tetrahydropyridin-3-ol  |  | 9  |
| C332 | (2R,3R,4R,5S)-2-(hydroxymethyl)-1-(5-((2'-methoxy-[1,1'-biphenyl]-4-yl)methoxy)pentyl)piperidine-3,4,5-triol              |  | 10 |

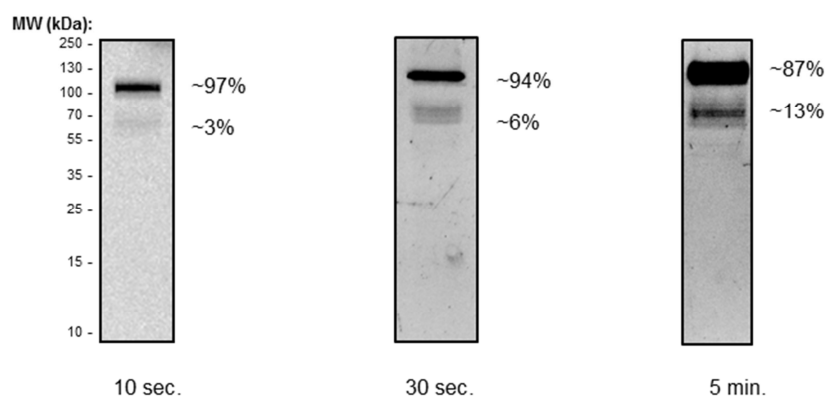
|      |   |  |    |
|------|---|--|----|
| C333 | (2R,3S)-2-(hydroxymethyl)piperidin-3-ol   |  | 9  |
| C334 | (2R,3R,4R,5S)-1-(5-((4-(2-fluoropyridin-4-yl)benzyl)oxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol |  | 10 |
| C335 | (2S,3S,4S)-2-(hydroxymethyl)piperidine-3,4-diol   |  | 9  |
| C336 | (2R,3R,4R,5S)-2-(hydroxymethyl)-1-(5-(5-phenylpyridin-2-yl)methoxy)pentyl)piperidine-3,4,5-triol        |  | 10 |
| C337 | (2S,3S)-2-(hydroxymethyl)-1,2,3,6-tetrahydropyridin-3-ol  |  | 9  |
| C338 | (2R,3R)-1-(5-(((3R,5R,7R)-adamantan-1-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidin-3-ol                |  | 9  |
| C339 | (2R,3R,4R,5S)-1-(5-([1,1'-biphenyl]-2-ylmethoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol         |  | 10 |
| C340 | (2R,3S)-2-(hydroxymethyl)-1,2,3,6-tetrahydropyridin-3-ol  |  | 9  |
| C341 | (2R,3R,4R,5S)-1-(5-([1,1'-biphenyl]-3-ylmethoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol         |  | 10 |
| C342 | (2S,3S,4R)-1-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4-diol        |  | 9  |
| C343 | (2R,3R,4R,5S)-1-(5-([1,1'-biphenyl]-4-ylmethoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol         |  | 10 |

|      |  |  |    |
|------|--|--|----|
| C344 | (2S,3S)-2-(hydroxymethyl)piperidine-3-ol   |  | 9  |
| C345 | (2R,3R,4R,5S)-1-(5-((R)-1-([1,1'-biphenyl]-4-yl)ethoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol       |  | 10 |
| C346 | (2S,3R)-1-(5-(((3S,5S,7S)-adamantan-1-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3-ol                    |  | 9  |
| C347 | (2R,3R,4R,5S)-1-(5-((S)-1-([1,1'-biphenyl]-4-yl)ethoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol       |  | 10 |
| C348 | (2R,3R,4R,5S)-1-(5-((4'-bromo-[1,1'-biphenyl]-4-yl)methoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol   |  | 10 |
| C349 | (2R,3R,4R,5S)-1-(5-([1,1'-biphenyl]-4-ylmethoxy)-4,4-difluoropentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol |  | 10 |
| C350 | (2R,3R,4R,5S)-1-(5-([1,1'-biphenyl]-4-ylmethoxy)-2,2-difluoropentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol |  | 10 |
| C351 | (2S,3R,4R,5S)-1-(5-([1,1'-biphenyl]-2-ylmethoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol              |  | 10 |
| C352 | (2S,3R,4R,5S)-1-(5-([1,1'-biphenyl]-3-ylmethoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol              |  | 10 |
| C353 | (2S,3R,4R,5S)-1-(5-([1,1'-biphenyl]-4-ylmethoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol              |  | 10 |

|      |  |  |    |
|------|--|--|----|
| C354 | (2S,3R,4R,5S)-1-(5-((R)-1-([1,1'-biphenyl]-4-yl)ethoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol       |  | 10 |
| C355 | (2S,3R,4R,5S)-1-(5-((S)-1-([1,1'-biphenyl]-4-yl)ethoxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol       |  | 10 |
| C356 | (2S,3R,4R,5S)-1-(5-((4-bromobenzyl)oxy)pentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol                       |  | 10 |
| C357 | (2S,3R,4R,5S)-1-(5-([1,1'-biphenyl]-4-ylmethoxy)-4,4-difluoropentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol |  | 10 |
| C358 | (2S,3R,4R,5S)-1-(5-([1,1'-biphenyl]-4-ylmethoxy)-2,2-difluoropentyl)-2-(hydroxymethyl)piperidine-3,4,5-triol |  | 10 |

## S5 Additional Biochemical Data for ABP 4

### *Prolonged Imaging Experiment*



**Figure S1.** Prolonged fluorescent scanning showing ca. 87% of signal originates from probe bound to GBA2 (102kDa) and approximately 13% from probe bound to GBA1 (60kDa). Intensities of the bands were quantified using Image Lab v4.1.

### *Potency and Selectivity of ABP 4*

Potency ( $IC_{50}$ ) of ABP 4 on GCS was determined as described by method described in the experimental section. The inhibition constants ( $K_i$ ) of ABP 4 were determined by the method described in Witte et al.<sup>17</sup> Values in table S2 are given in  $\mu$ M.

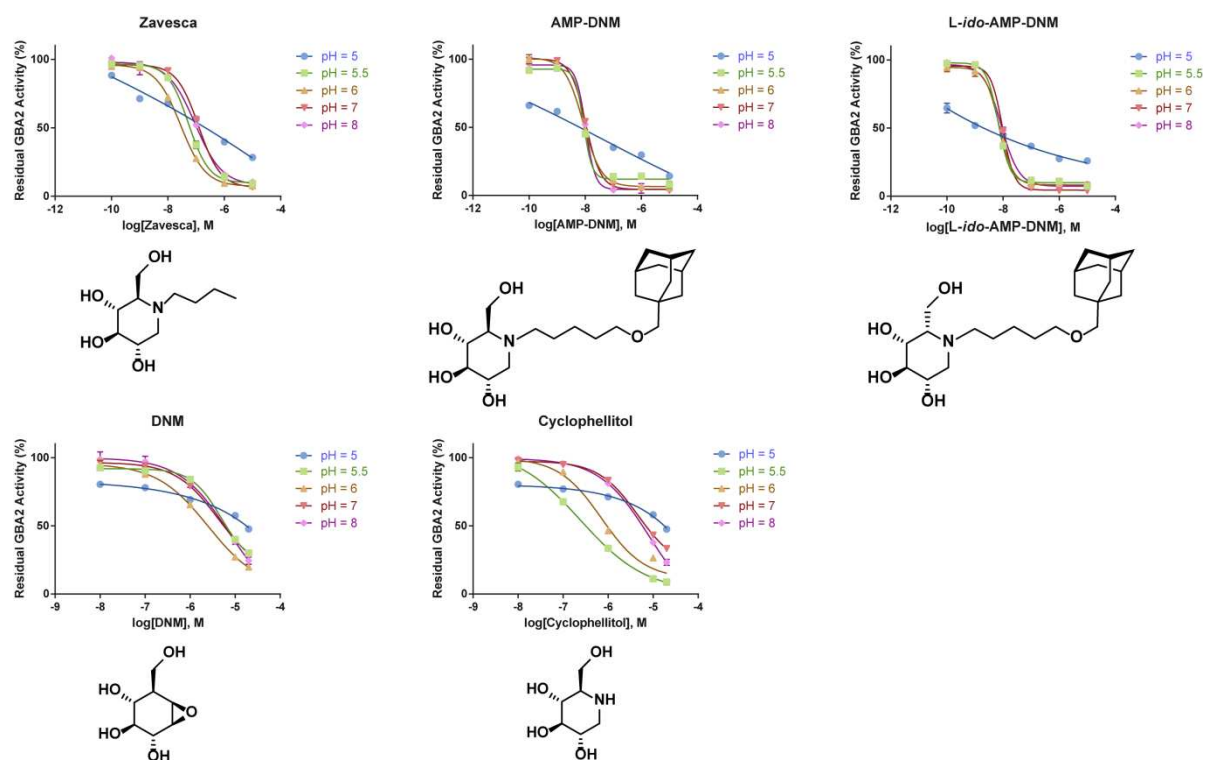
**Table S2: Potency and selectivity of the probe on GCS, GBA1, GBA2 and GBA3**

| GCS <sup>a</sup> | GBA1 <sup>b</sup> | GBA2 <sup>b</sup> | GBA3 <sup>b</sup> | Ratio GCS/GBA2 | Ratio GBA1/GBA2 | Ratio GBA3/GBA2 |
|------------------|-------------------|-------------------|-------------------|----------------|-----------------|-----------------|
| >200             | 0.249             | 0.008             | 0.054             | >25000         | 31              | 7               |

(a) *in situ* (b) *in vitro*



## S6 FluoPol-ABPP - pH Experiments on Established Competitors

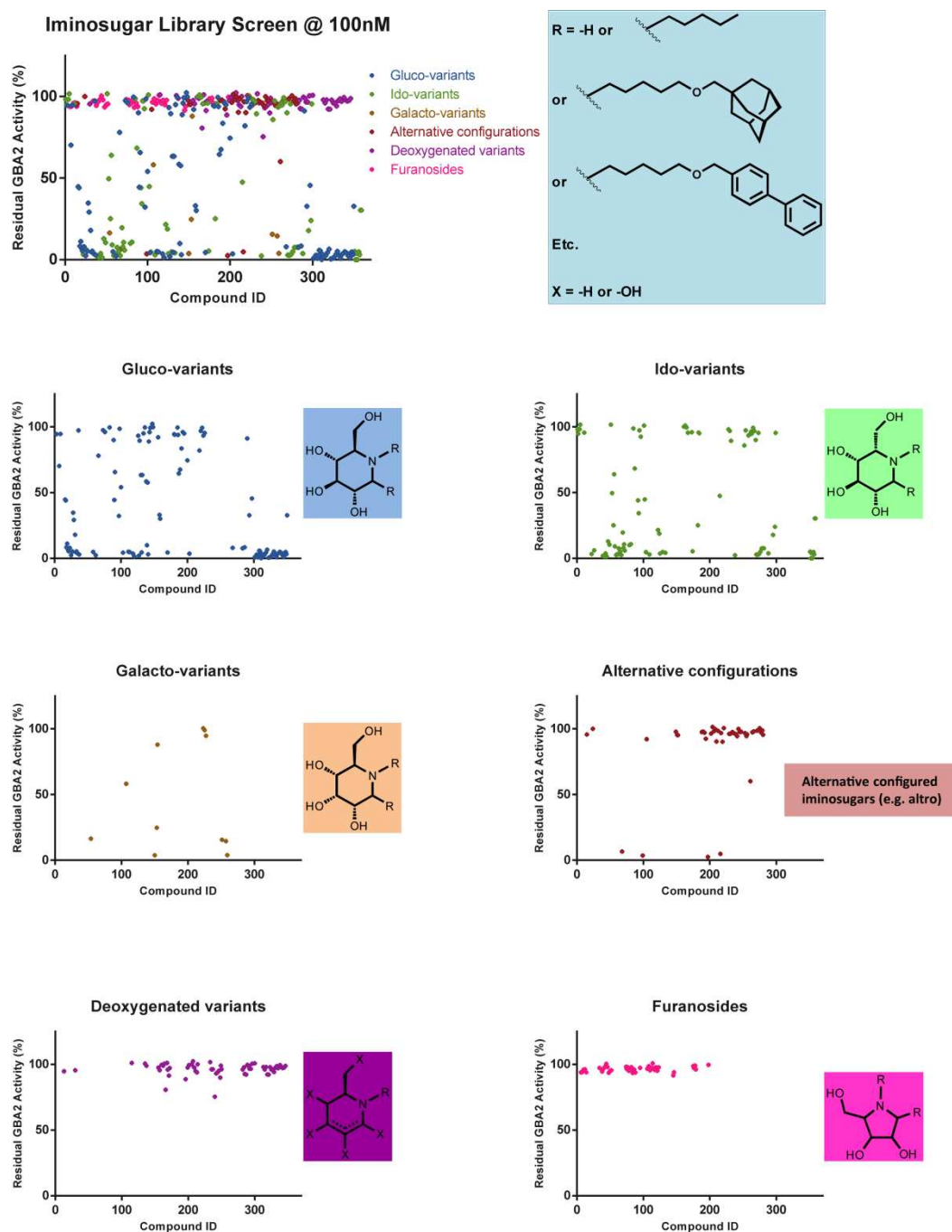


**Figure S2.** Inhibition by established inhibitors (1, 2, 6, 7 and 8) on GBA2 determined via FluoPol-ABPP. Curves represent experiments at a different pH, error bars represent standard error of the mean (SEM).

**Table S3: Inhibition values of established inhibitors on GBA2 determined via FluoPol-ABPP**

| pH  | Zavesca (1)   | AMP-DNM (2)     | L-ido-AMP-DNM (6) | DNM (7)      | Cyclophellitol (8) |
|-----|---------------|-----------------|-------------------|--------------|--------------------|
| 5.0 | 0.201 ± 0.006 | 0.0061 ± 0.0008 | 0.0027 ± 0.006    | 23.62 ± 0.76 | 26.70 ± 2.88       |
| 5.5 | 0.065 ± 0.003 | 0.0098 ± 0.0004 | 0.0072 ± 0.003    | 6.52 ± 0.40  | 0.35 ± 0.04        |
| 6.0 | 0.033 ± 0.002 | 0.0102 ± 0.0008 | 0.0072 ± 0.002    | 2.37 ± 0.08  | 1.16 ± 0.08        |
| 7.0 | 0.135 ± 0.001 | 0.0118 ± 0.0001 | 0.0095 ± 0.001    | 5.86 ± 0.24  | 7.48 ± 0.23        |
| 8.0 | 0.116 ± 0.001 | 0.106 ± 0.0004  | 0.0095 ± 0.001    | 5.54 ± 0.56  | 5.35 ± 0.01        |

## S7 FluoPol-ABPP Screen of the Iminosugar Library - Categorized based on Configuration



**Figure S3.** FluoPol-ABPP screen of the iminosugar library. Compounds are categorized based on its sugar configuration (*gluco*, *ido*, *galacto* and others are classified as ‘alternative configurations’), deoxygenated variants and furanosides.

## S8 Potency and Selectivity Assessment for D-gluco- and L-ido-deoxynojirimycins

The potency of D-gluco- and L-ido-deoxynojirimycins on GCS, GBA1 and GBA2 were determined by the method described in the manuscript. The data set displayed here is composed of published IC<sub>50</sub>-values which were confirmed in our experiments and for unknowns experimentally determined. Calculated ratios GCS/GBA2 and GBA1/GBA2 are colored in green. A stronger shade of green stands for a higher ratio and thus selectivity.

### Iminosugar Library

Table S4: Inhibition values of iminosugar library compounds on GCS, GBA1 and GBA2

| Entry: | GBA2 Inhibition (%) FluoPol | IC <sub>50</sub> on GCS (in situ) in $\mu$ M | IC <sub>50</sub> on GBA1 (in vitro) in $\mu$ M | IC <sub>50</sub> on GBA2 (in vitro) in $\mu$ M | Ratio GCS/GBA2 | Ratio GBA1/GBA2 |
|--------|-----------------------------|--|--|--|----------------|-----------------|
| C16    | 44.7                        | 2.9  | 2.17   | 0.025  | 116            | 87              |
| C17    | 44.1                        | 9.53   | 500  | 0.400  | 24             | 1250            |
| C18    | 8.4                         | 1  | 0.50   | 0.009  | 111            | 56              |
| C19    | 11.2                        | 4  | 30   | 0.060  | 67             | 500             |
| C20    | 6.9                         | 2  | 705  | 0.040  | 50             | 17625           |
| C21    | 5.5                         | 1  | 205  | 0.008  | 125            | 25625           |
| C22    | 3.3                         | 1  | 15   | 0.020  | 50             | 750             |
| C23    | 8.0                         | 0.3  | 1.75   | 0.015  | 20             | 117             |
| C25    | 2.4                         | 0.2  | 0.50   | 0.010  | 20             | 50              |
| C26    | 6.1                         | 2.77   | 100  | 0.007  | 413            | 14925           |
| C27    | 5.3                         | 0.1  | 0.50   | 0.040  | 3              | 13              |
| C28    | 34.7                        | 50   | 0.35   | 0.068  | 735            | 5               |
| C29    | 29.2                        | 20   | 80   | 0.110  | 182            | 727             |
| C31    | 18.0                        | 20   | 18.5   | 0.045  | 444            | 411             |
| C32    | 4.7                         | 40.03  | 0.06   | 0.010  | 4003           | 6               |
| C33    | 5.3                         | 4  | 4  | 0.020  | 200            | 200             |
| C35    | 3.6                         | 0.025  | 0.25   | 0.00008  | 313            | 3125            |
| C37    | 3.0                         | 0.025  | 0.20   | 0.00008  | 313            | 2500            |
| C39    | 1.9                         | 0.003  | 5  | 0.0001   | 30             | 50000           |
| C41    | 1.5                         | 0.003  | 6  | 0.0001   | 30             | 60000           |
| C43    | 3.8                         | 0.005  | 8  | 0.0004   | 13             | 20000           |
| C45    | 1.4                         | 0.0025                                       | 6  | 0.0006   | 4              | 10000           |
| C54    | 16.4                        | 1.94   | 100  | 0.0027   | 719            | 37037           |
| C55    | 25.2                        | 15   | 1000   | 0.250  | 60             | 4000            |
| C57    | 9.1                         | 2  | 1000   | 1.000  | 2              | 1000            |
| C58    | 4.9                         | 0.003  | 1  | 0.001  | 3              | 1000            |
| C59    | 2.5                         | 0.15   | 100  | 0.015  | 10             | 6667            |
| C60    | 3.1                         | 0.003  | 50   | 0.001  | 3              | 50000           |
| C61    | 3.1                         | 0.1  | 95   | 0.025  | 4              | 3800            |
| C62    | 2.3                         | 0.05   | 0.40   | 0.002  | 25             | 200             |
| C63    | 7.5                         | 0.05   | 40   | 0.015  | 3              | 2667            |
| C64    | 3.2                         | 0.008  | 20   | 0.003  | 3              | 6667            |
| C65    | 5.3                         | 0.05   | 15   | 0.015  | 3              | 1000            |

|      |      |       |       |         |      |       |
|------|------|-------|-------|---------|------|-------|
| C67  | 2.5  | 0.05  | 12    | 0.045   | 1    | 267   |
| C68  | 6.6  | 10    | 5     | 0.150   | 67   | 33    |
| C69  | 19.6 | 40    | 1000  | 0.140   | 286  | 7143  |
| C70  | 7.9  | 0.4   | 40    | 0.015   | 27   | 2667  |
| C71  | 10.7 | 4     | 700   | 0.040   | 100  | 17500 |
| C72  | 35.0 | 21.4  | 35.95 | 0.031   | 690  | 1160  |
| C73  | 5.9  | 4     | 25    | 0.020   | 200  | 1250  |
| C79  | 10.1 | 0.75  | 0.30  | 0.001   | 750  | 300   |
| C81  | 10.8 | 0.2   | 10    | 0.003   | 67   | 3333  |
| C90  | 44.4 | 0.5   | 1.5   | 0.004   | 125  | 375   |
| C92  | 44.1 | 2.5   | 50    | 0.100   | 25   | 500   |
| C93  | 34.3 | 20    | 1000  | 1.000   | 20   | 1000  |
| C97  | 32.2 | 50    | 0.07  | 0.300   | 167  | 0     |
| C99  | 3.6  | 20    | 0.34  | 0.010   | 2000 | 34    |
| C102 | 44.8 | 1.9   | 100   | 0.0058  | 328  | 17241 |
| C103 | 4.3  | 4     | 1.5   | 0.007   | 571  | 214   |
| C104 | 4.7  | 2     | 50    | 0.010   | 200  | 5000  |
| C109 | 3.0  | 0.43  | 11.97 | 0.0015  | 287  | 7980  |
| C111 | 5.0  | 0.39  | 0.84  | 0.001   | 390  | 840   |
| C113 | 4.8  | 0.2   | 0.1   | 0.002   | 100  | 50    |
| C118 | 3.6  | 0.025 | 0.2   | 0.00012 | 208  | 1667  |
| C120 | 1.4  | 0.025 | 0.1   | 0.00008 | 313  | 1250  |
| C122 | 3.7  | 0.08  | 10    | 0.002   | 40   | 5000  |
| C127 | 2.0  | 0.5   | 1.5   | 0.004   | 125  | 375   |
| C129 | 4.8  | 0.07  | 60    | 0.006   | 12   | 10000 |
| C131 | 4.5  | 35.2  | 0.5   | 0.005   | 7040 | 100   |
| C133 | 4.2  | 14.35 | 12    | 0.008   | 1794 | 1500  |
| C139 | 9.9  | 0.75  | 0.3   | 0.001   | 750  | 300   |
| C141 | 3.1  | 0.3   | 0.1   | 0.002   | 150  | 50    |
| C158 | 33.1 | 50    | 0.07  | 0.034   | 1471 | 2     |
| C159 | 30.2 | 10    | 0.25  | 0.020   | 500  | 13    |
| C170 | 4.4  | 5     | 0.19  | 0.005   | 1000 | 38    |
| C174 | 5.4  | 0.1   | 2     | 0.001   | 100  | 2000  |
| C182 | 25.2 | 3.88  | 1000  | 0.190   | 20   | 5263  |
| C197 | 2.6  | 40    | 0.38  | 0.008   | 5000 | 48    |
| C203 | 3.6  | 3.63  | 1.29  | 0.00415 | 875  | 311   |
| C215 | 47.6 | 12.06 | 100   | 0.0023  | 5243 | 43478 |
| C216 | 4.8  | 10    | 6     | 0.013   | 769  | 462   |
| C238 | 2.3  | 1.34  | 33.89 | 0.00058 | 2310 | 58431 |
| C268 | 8.0  | 5.05  | 6.2   | 0.00495 | 1020 | 1253  |
| C270 | 2.9  | 5     | 2     | 0.006   | 833  | 333   |
| C272 | 2.8  | 0.05  | 12    | 0.045   | 1    | 267   |
| C274 | 3.3  | 0.05  | 15    | 0.015   | 3    | 1000  |
| C276 | 4.9  | 0.3   | 1.75  | 0.015   | 20   | 117   |

|      |      |       |      |         |      |        |
|------|------|-------|------|---------|------|--------|
| C278 | 7.6  | 0.15  | 100  | 0.015   | 10   | 6667   |
| C281 | 7.7  | 2     | 705  | 0.040   | 50   | 17625  |
| C283 | 7.7  | 4     | 30   | 0.060   | 67   | 500    |
| C286 | 8.4  | 4     | 4    | 0.020   | 200  | 200    |
| C288 | 3.8  | 4     | 25   | 0.020   | 200  | 1250   |
| C293 | 32.8 | 20    | 80   | 0.110   | 182  | 727    |
| C295 | 17.9 | 40    | 1000 | 0.140   | 286  | 7143   |
| C297 | 45.6 | 20    | 500  | 0.400   | 50   | 1250   |
| C298 | 24.0 | 15    | 1000 | 0.250   | 60   | 4000   |
| C301 | 0.7  | 0.1   | 0.25 | 0.003   | 33   | 83     |
| C302 | 1.4  | 0.1   | 0.25 | 0.002   | 50   | 125    |
| C303 | 1.2  | 0.025 | 0.5  | 0.002   | 13   | 250    |
| C304 | 2.8  | 0.025 | 3    | 0.015   | 2    | 200    |
| C305 | 1.9  | 0.025 | 2.5  | 0.010   | 3    | 250    |
| C306 | 0.9  | 0.15  | 2.5  | 0.020   | 8    | 125    |
| C307 | 2.5  | 0.025 | 0.4  | 0.001   | 25   | 400    |
| C308 | 5.8  | 0.02  | 0.8  | 0.015   | 1    | 53     |
| C309 | 5.6  | 0.15  | 0.35 | 0.003   | 50   | 117    |
| C310 | 0.6  | 0.05  | 0.7  | 0.002   | 25   | 350    |
| C311 | 0.2  | 0.025 | 0.4  | 0.001   | 25   | 400    |
| C312 | 3.4  | 0.025 | 0.03 | 0.001   | 25   | 25     |
| C314 | 1.8  | 0.025 | 0.5  | 0.002   | 13   | 250    |
| C316 | 2.8  | 2     | 2    | 0.010   | 200  | 200    |
| C318 | 4.4  | 2     | 3    | 0.010   | 200  | 300    |
| C320 | 6.5  | 2     | 10   | 0.025   | 80   | 400    |
| C322 | 0.5  | 0.75  | 3    | 0.005   | 150  | 600    |
| C324 | 0.9  | 0.04  | 0.25 | 0.030   | 1    | 8      |
| C326 | 1.4  | 0.025 | 0.07 | 0.001   | 50   | 140    |
| C328 | 3.1  | 0.15  | 0.6  | 0.005   | 30   | 120    |
| C330 | 5.2  | 0.075 | 0.6  | 0.002   | 38   | 300    |
| C332 | 2.5  | 0.05  | 0.6  | 0.003   | 17   | 200    |
| C334 | 0.9  | 0.15  | 2    | 0.004   | 38   | 500    |
| C336 | 3.5  | 0.2   | 1.5  | 0.003   | 67   | 500    |
| C339 | 4.9  | 0.05  | 1.25 | 0.003   | 17   | 417    |
| C341 | 4.2  | 0.075 | 0.3  | 0.002   | 38   | 150    |
| C343 | 2.5  | 0.05  | 0.4  | 0.002   | 25   | 200    |
| C345 | 1.0  | 0.06  | 300  | 0.003   | 20   | 100000 |
| C347 | 4.6  | 0.07  | 400  | 0.003   | 23   | 133333 |
| C348 | 4.7  | 0.33  | 2.55 | 0.00004 | 7500 | 57955  |
| C349 | 3.2  | 0.06  | 0.3  | 0.001   | 60   | 300    |
| C350 | 32.8 | 1.25  | 0.13 | 0.010   | 125  | 13     |
| C351 | 5.1  | 0.025 | 15   | 0.003   | 8    | 5000   |
| C352 | 0.1  | 0.07  | 20   | 0.002   | 35   | 10000  |
| C353 | 3.9  | 0.008 | 20   | 0.003   | 3    | 6667   |

|             |      |       |      |         |    |        |
|-------------|------|-------|------|---------|----|--------|
| <b>C354</b> | 0.1  | 0.03  | 10   | 0.001   | 30 | 10000  |
| <b>C355</b> | 0.2  | 0.04  | 10   | 0.002   | 20 | 5000   |
| <b>C356</b> | 4.8  | 0.021 | 100  | 0.00025 | 84 | 401606 |
| <b>C357</b> | 3.1  | 0.015 | 12.5 | 0.002   | 8  | 6250   |
| <b>C358</b> | 30.4 | 0.02  | 500  | 0.002   | 10 | 250000 |

### *Second Generation Library*

**Table S5: Inhibition values of the second generation library compounds on GCS, GBA1 and GBA2**

| <b>Entry:</b> | <b>IC<sub>50</sub> on GCS<br/>(in situ) in uM</b> | <b>IC<sub>50</sub> on GBA1<br/>(in vitro) in uM</b> | <b>IC<sub>50</sub> on GBA2<br/>(in vitro) in uM</b> | <b>Ratio<br/>GCS/GBA2</b> | <b>Ratio<br/>GBA1/GBA2</b> |
|---------------|---|---|---|---------------------------|----------------------------|
| <b>B44</b>    | 4   | 23  | 0.0009  | 4444                      | 25556                      |
| <b>B45</b>    | 6   | 3   | 0.004   | 1500                      | 750                        |
| <b>B46</b>    | 0.76  | 4   | 0.005   | 152                       | 800                        |
| <b>B47</b>    | 53  | 156   | 0.042   | 1262                      | 3714                       |
| <b>B48</b>    | 1   | 1000  | 0.025   | 40                        | 40000                      |
| <b>B49</b>    | 7.2   | 51  | 0.018   | 400                       | 2833                       |
| <b>B50</b>    | 0.64  | 13  | 0.009   | 71                        | 1444                       |
| <b>B51</b>    | 0.12  | 13  | 0.009   | 13                        | 1444                       |
| <b>B52</b>    | 0.35  | 11  | 0.004   | 88                        | 2750                       |
| <b>B53</b>    | 0.38  | 6   | 0.002   | 190                       | 3000                       |
| <b>B54</b>    | 10  | 63  | 0.035   | 286                       | 1800                       |
| <b>B55</b>    | 50  | 325   | 0.12  | 417                       | 2708                       |
| <b>B56</b>    | 0.729   | 100   | 0.0006  | 1215                      | 166667                     |
| <b>B57</b>    | 2.5   | 1000  | 0.021   | 119                       | 47619                      |
| <b>B58</b>    | 0.1   | 176   | 0.003   | 33                        | 58667                      |
| <b>B59</b>    | 5   | 196   | 0.006   | 833                       | 32667                      |
| <b>B60</b>    | 0.053   | 328   | 0.007   | 8                         | 46857                      |
| <b>B61</b>    | 0.12  | 205   | 0.001   | 120                       | 205000                     |

## S9 Crystallography

### *Gene Expression and Protein Purification for TxGH116*

TxGH116 was expressed from a pET-30a plasmid described previously.<sup>18</sup> Competent *E. Coli* BL21 (DE3) cells were transformed and grown in LB media (with 30 µg/mL kanamycin) at 37 °C until an OD<sub>600</sub> of 0.6 had been reached. Expression of the TxGH116 gene was then induced with 0.5 mM IPTG and the cells incubated at 16 °C for 18 hr. Cells were lysed by sonication at 14-18 Hz, four runs of 40-50 seconds exposure, in buffer “A” (20 mM NaPO<sub>4</sub> pH 7.4, 150 mM NaCl). Cell debris was removed by centrifugation for 15 minutes in a Sorvall SS-34 rotor at 38000 g.

The resulting supernatant was heated at 65 °C for 20 minutes and the resulting precipitated protein removed by centrifugation. The remaining soluble fraction (containing the heat resistant TxGH116) was loaded onto a 5 mL GE sciences (GE healthcare) crude HisTrap column, equilibrated with buffer A. Unbound material was removed by washing with three column volumes of buffer A. Bound protein was eluted with a gradient into buffer B (20 mM NaPO<sub>4</sub> pH 7.4, 150 mM NaCl, 500 mM imidazole) across twenty column volumes. The fractions containing TxGH116 were pooled, concentrated and buffer exchanged into “Digest buffer” (20 mM Tris pH 8, 150 mM NaCl). The protein was digested with enterokinase (New England Bio Labs) as per the manufacturer’s instructions overnight, in order to remove the cleaved N terminal His and “S” tags, and then buffer exchanged into GF buffer using a 50 kDa MWCO centrifugal filter (Millipore Corp). The protein was then purified over a Superdex S200 gel filtration column, which had been equilibrated with GF buffer (20 mM Tris pH 8, 500 mM NaCl) and the fractions containing TxGH116 pooled, concentrated to 20 mg/mL in a 50 kDa MW cut-off centrifugal filter (Millipore Corp) and flash frozen at -80 °C.

### *Crystallization, Structure Solution and Refinement of TxGH116 in Complex with 5.*

TxGH116 was diluted to ~2 mg/mL and crystallization trials were set up using 350 nL of protein solution and 350 nL of mother liquor (0.2 M ammonium sulfate, 20% PEG 3350, 0.1M BisTris pH 5.5 - 6.7) in 48-well plate format sitting drop plates at 18°C. Crystals of TxGH116 were soaked in compound **5** ligand residue resuspended in the corresponding mother liquor (0.2 M ammonium sulfate, 20% PEG 3350, 0.1M BisTris pH 6.7) overnight to allow covalent binding. A cryoprotectant of 25% (v/v) glycerol together with the mother liquor was used. Diffraction data for the crystals was collected on beamline I03 beamline at the Diamond Light Source.

Data were processed using XDS<sup>20</sup> and the Aimless data reduction pipeline through the CCP4i2 software.<sup>20</sup> The previous TxGH116C PDB structure (5BVU)<sup>18</sup> was used to determine the phases and solve the structure. Refinement of the structures was performed using REFMAC<sup>21</sup> and model building completed using COOT, both programs run through the CCP4i2 software.<sup>22</sup> Ligand coordinates and restraints were built using JLigand.<sup>23</sup> Crystal structure illustrations were generated using CCP4mg.<sup>24</sup> Data collection and refinement statistics are shown in Table S7.

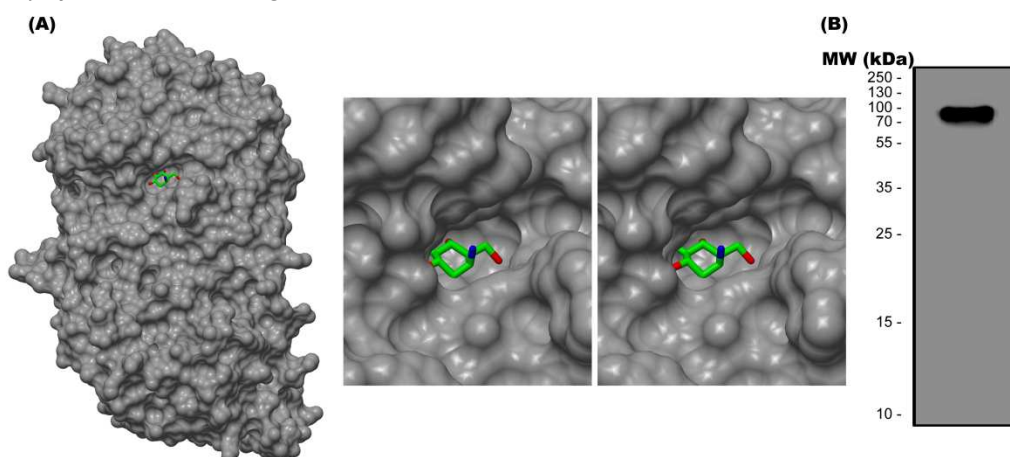
Final refined coordinates, and observed structure factor amplitudes, have been deposited on the PDB with accession code 5NCX.

**Table S6: Data collection and Refinement Statistics for the TxGH116 structure in complex with 5**

| <b>TxGH116 with 5</b>                               |                                 |
|---|---------------------------------|
| PDB Code  | 5NCX                            |
| <b>Data collection</b>                              |                                 |
| Space group   | P2 <sub>1</sub> 22 <sub>1</sub> |
| Cell dimensions                                     |                                 |
| <i>a, b, c</i> (Å)                                  | 53.62, 83.30, 177.48            |
| Resolution (Å)                                      | 60-1.70 (1.75 - 1.70) *         |
| <i>R</i> <sub>merge</sub>                           | 0.096 (1.00)                    |
| <i>R</i> <sub>pim</sub>                             | 0.044 (0.46)                    |
| CC(1/2)   | 0.998 (0.58)                    |
| <i>I</i> / $\sigma$ <i>I</i>                        | 12.4(1.7)                       |
| Completeness (%)                                    | 99.5(99.2)                      |
| Redundancy  | 5.7(5.6)                        |
| <b>Refinement</b>                                   |                                 |
| Resolution (Å)                                      | 88.90-1.70                      |
| No. reflections                                     | 87654/4371                      |
| <i>R</i> <sub>work</sub> / <i>R</i> <sub>free</sub> | 0.15/0.18                       |
| No. atoms   |                                 |
| Protein   | 6228                            |
| Ligand/ion  | 26                              |
| Water   | 371                             |
| <i>B</i> -factors (Å <sup>2</sup> )                 |                                 |
| Protein   | 20                              |
| Ligand/ion  | 34                              |
| Water   | 28                              |
| R.m.s. deviations                                   |                                 |
| Bond lengths (Å)                                    | 0.020                           |
| Bond angles (°)                                     | 1.99                            |

\*Values in parentheses are for highest-resolution shell.

**Accessibility of TxGH116 Binding Pocket**



**Figure S4.** Accessibility of TxGH116 binding pocket to ABPs and other molecules (A) Surface view of TxGH116, with a divergent (wall-eyed) stereo image close up of the enzyme binding pocket containing bound **5** (green). The TxGH116 binding pocket is freely accessible to solvent and can accommodate ABPs with larger linker moieties such as **4**. (B) Fluorescent gel of 0.5 µg/µL TxGH116 (~90kDa) after reaction with 500nM ABP **4**, illustrating that tagged ABPs can readily react with this enzyme.

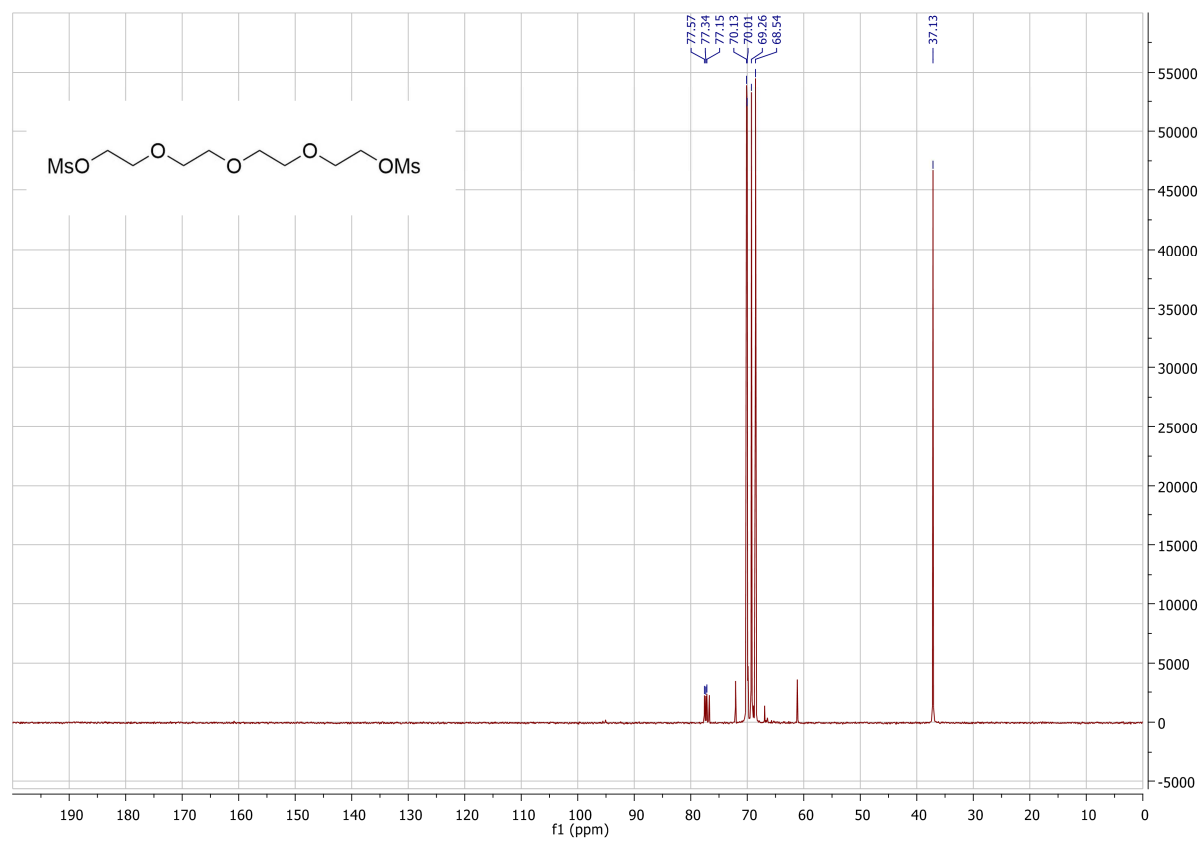
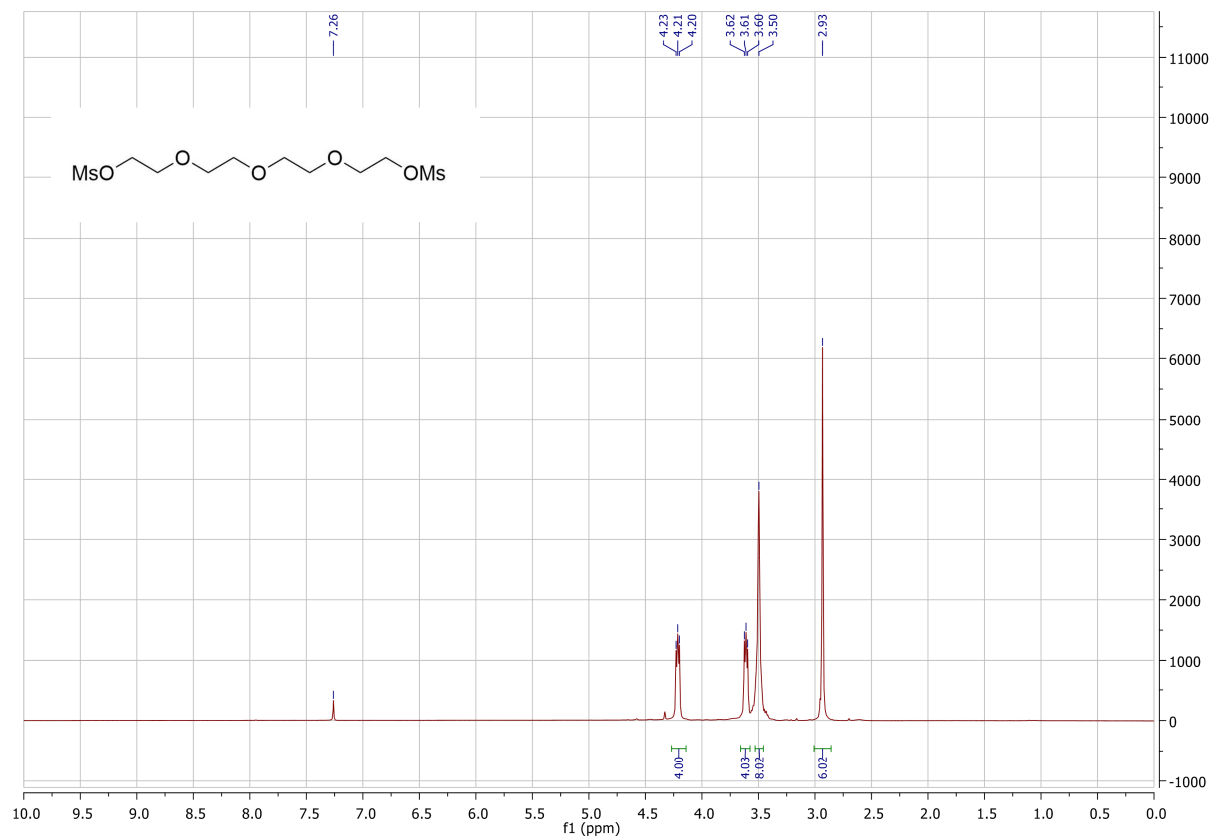


## References

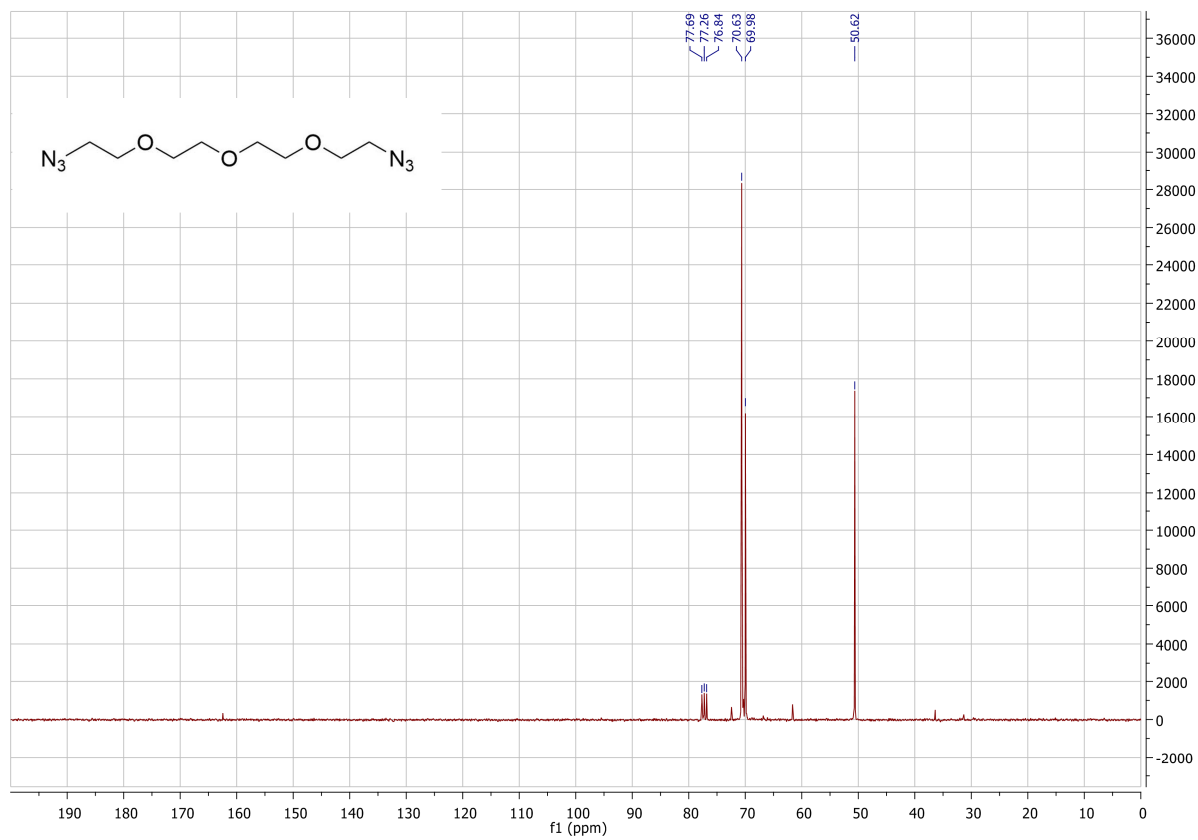
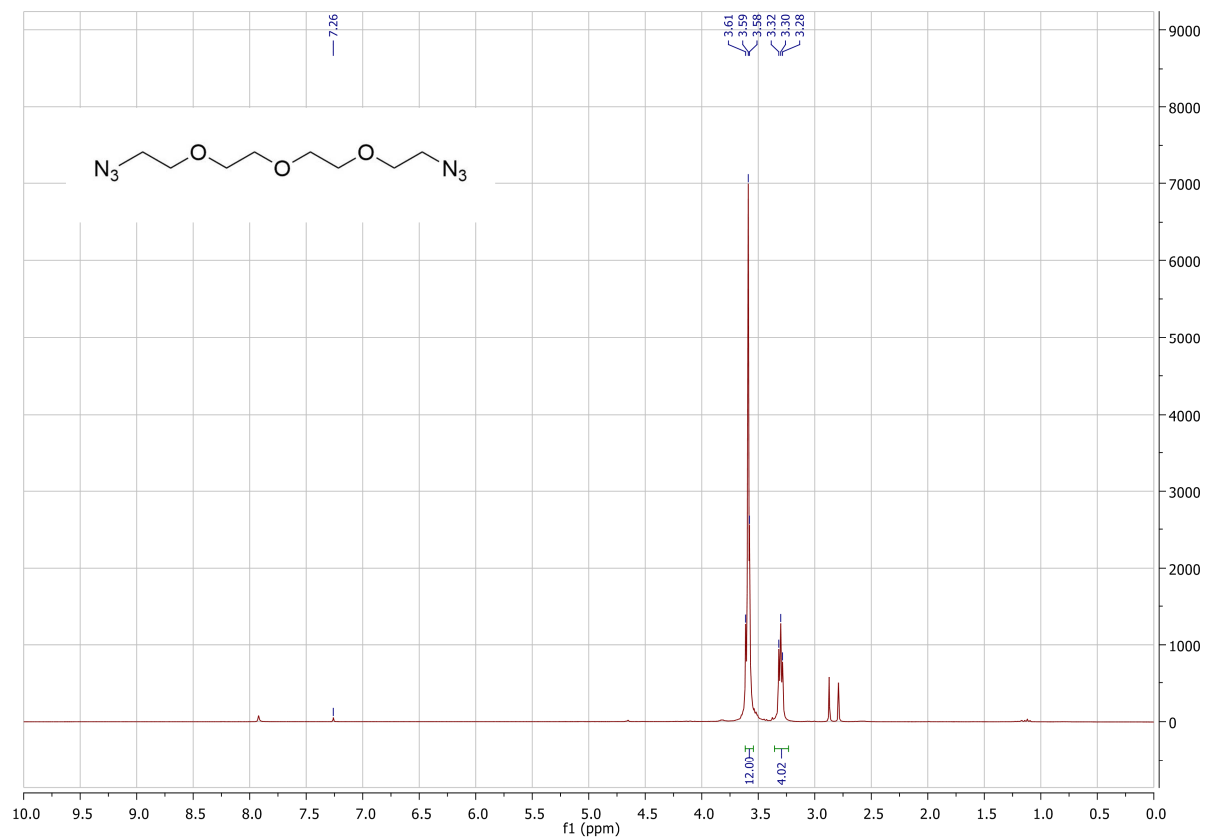
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## Appendix: Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra

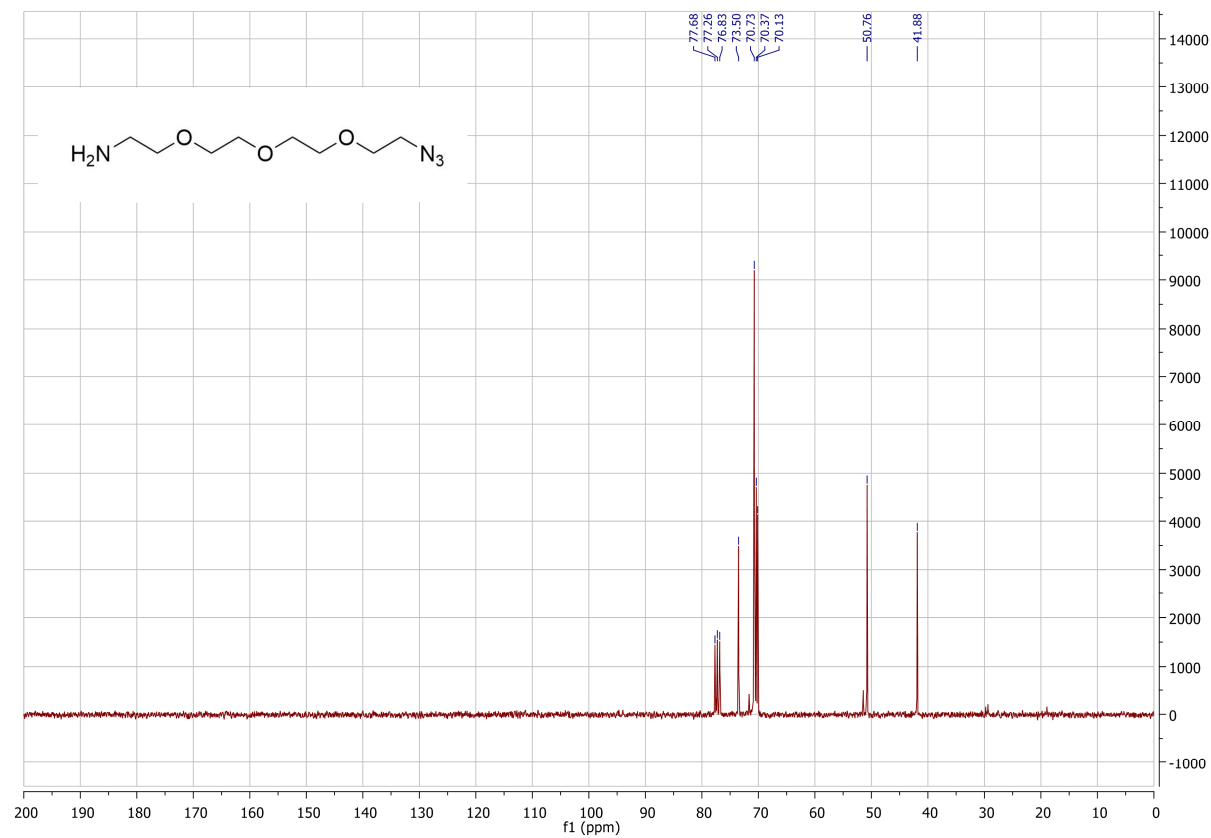
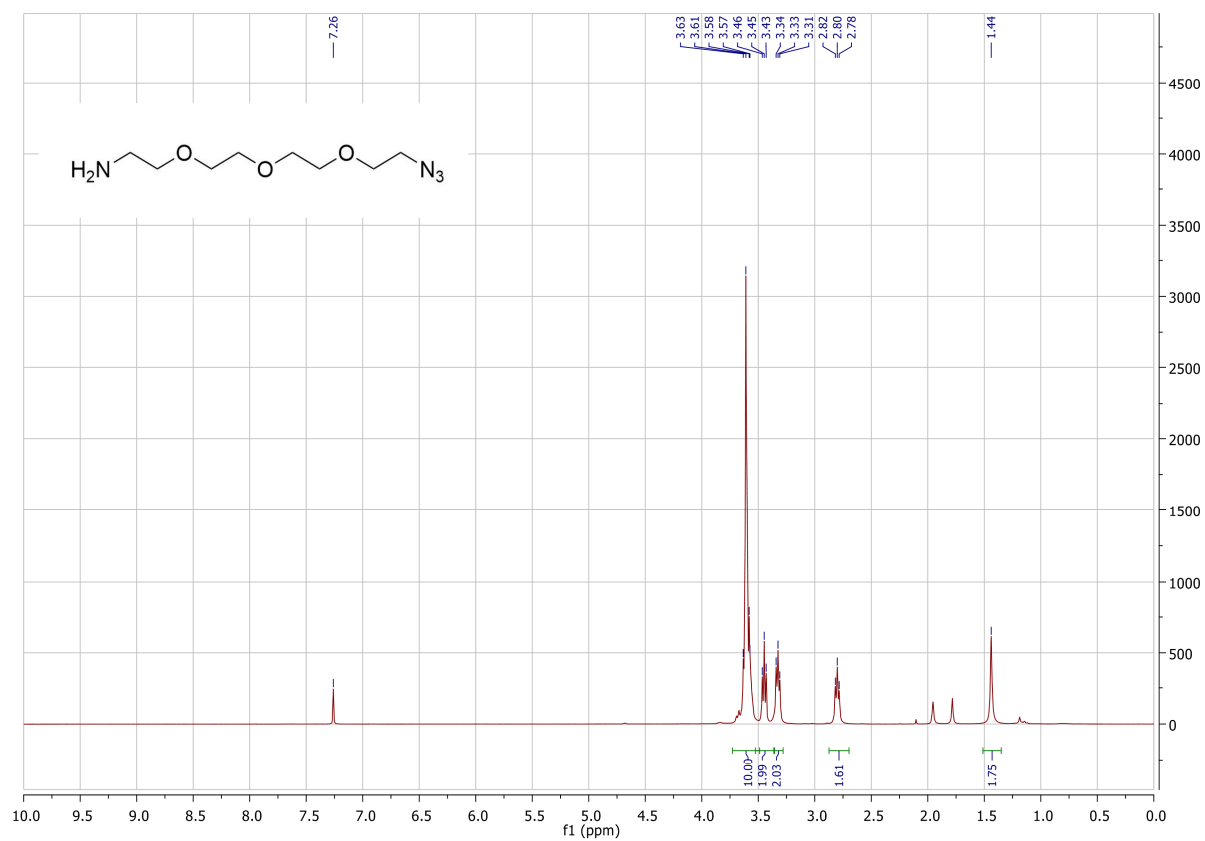
$^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR of compound A6 in  $\text{CDCl}_3$ .



<sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound A7 in CDCl<sub>3</sub>.

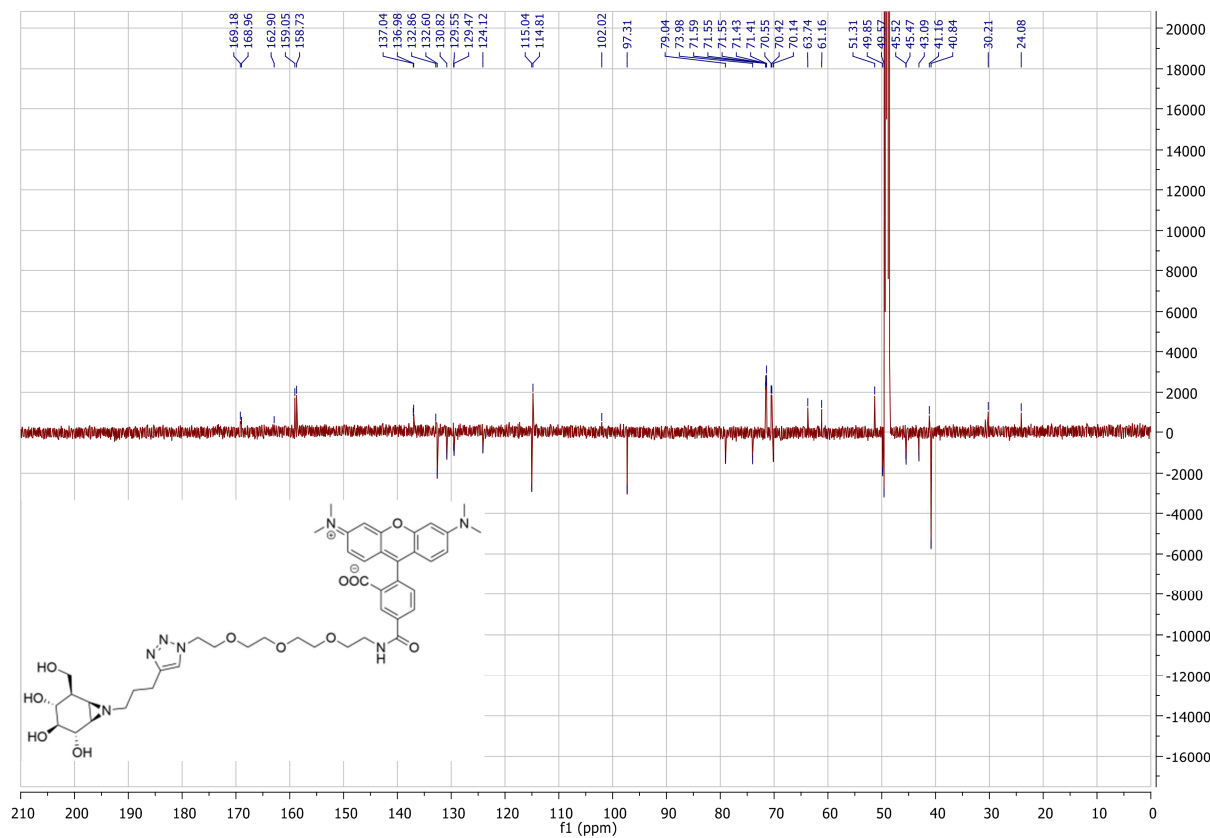
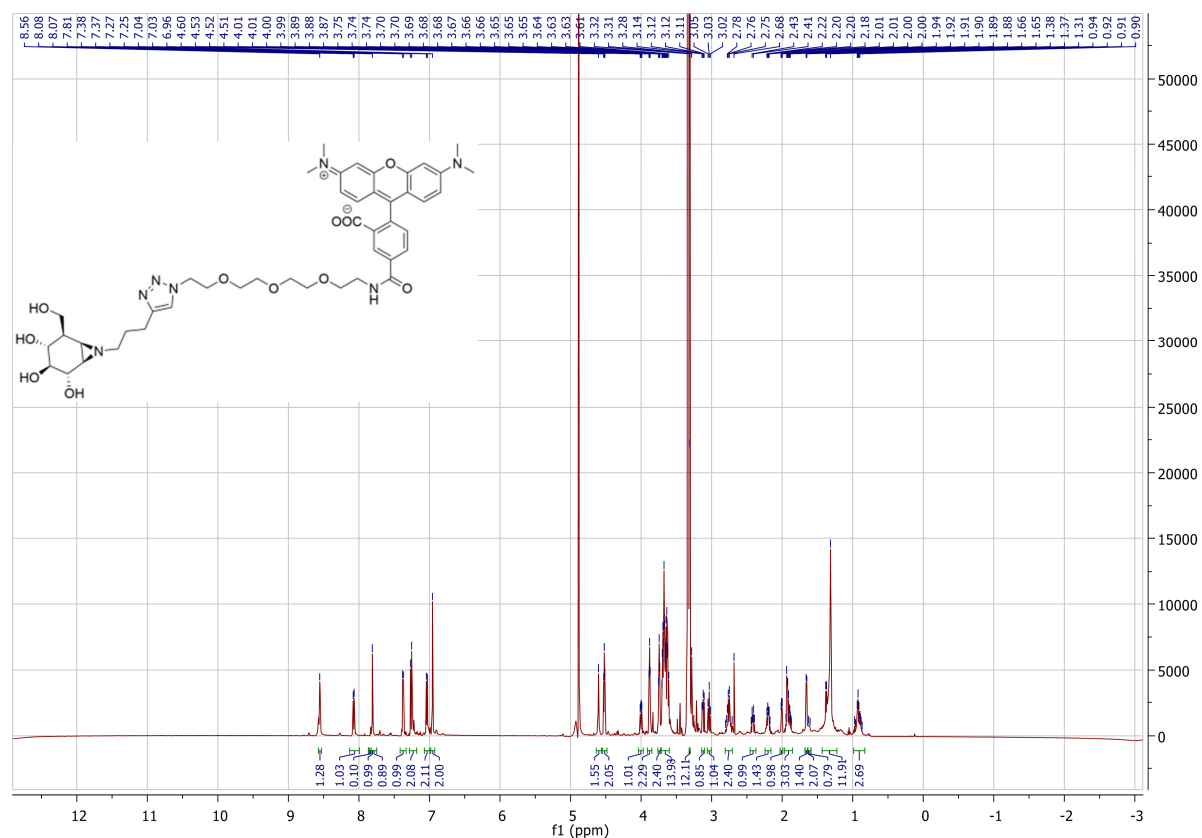


**<sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound A8 in CDCl<sub>3</sub>.**

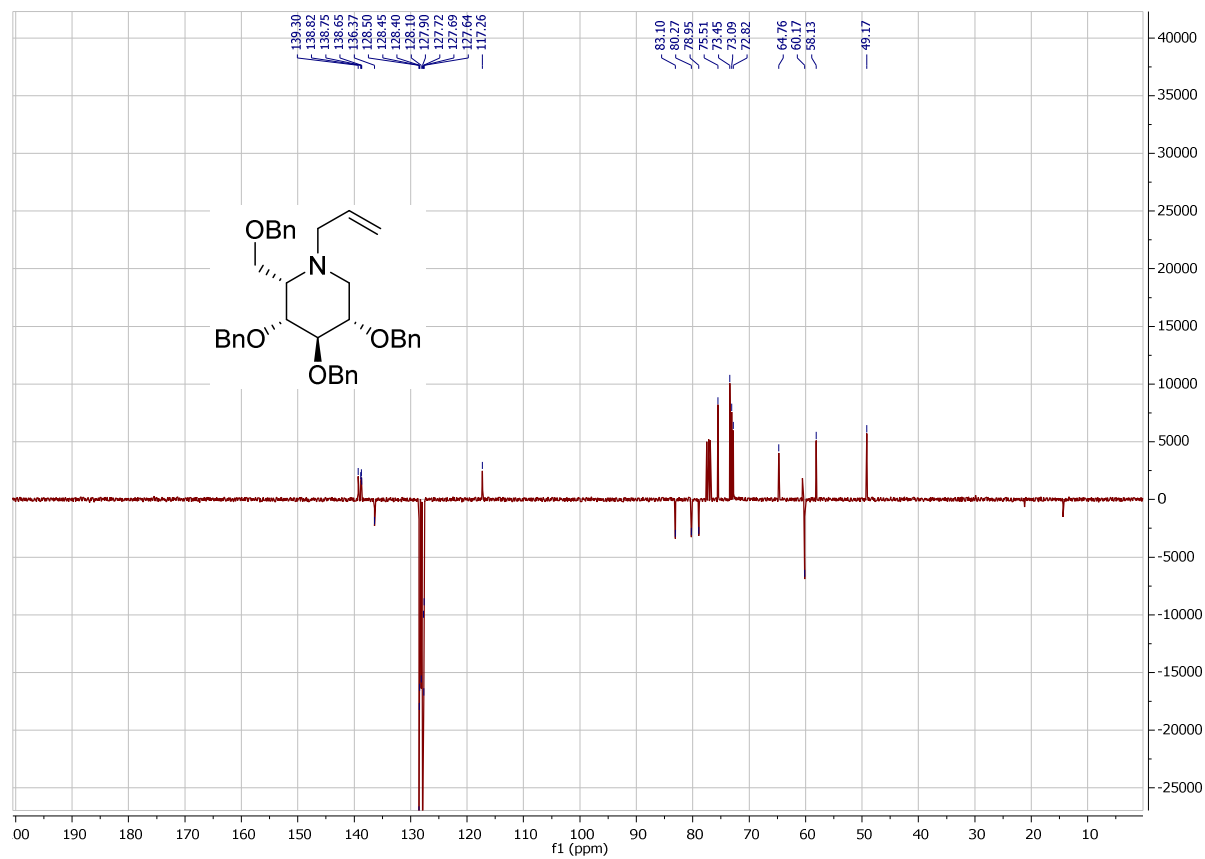
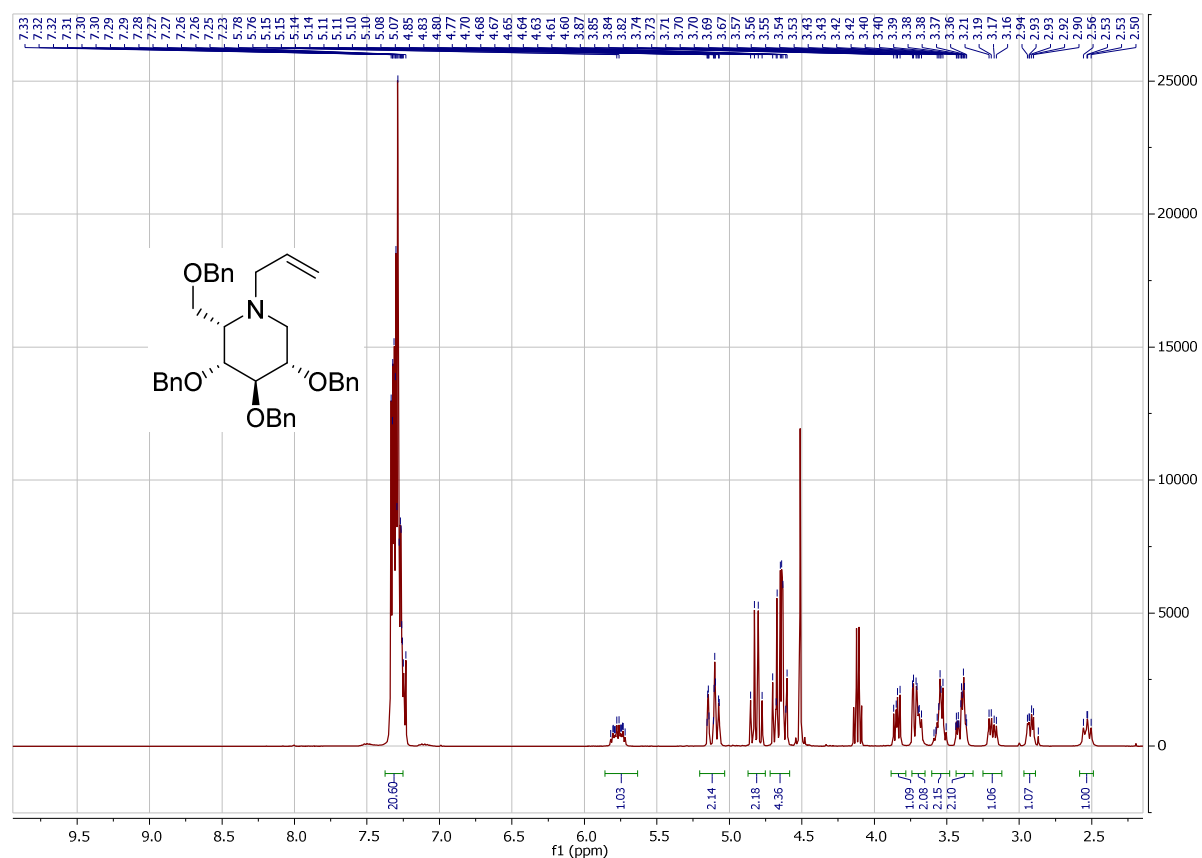




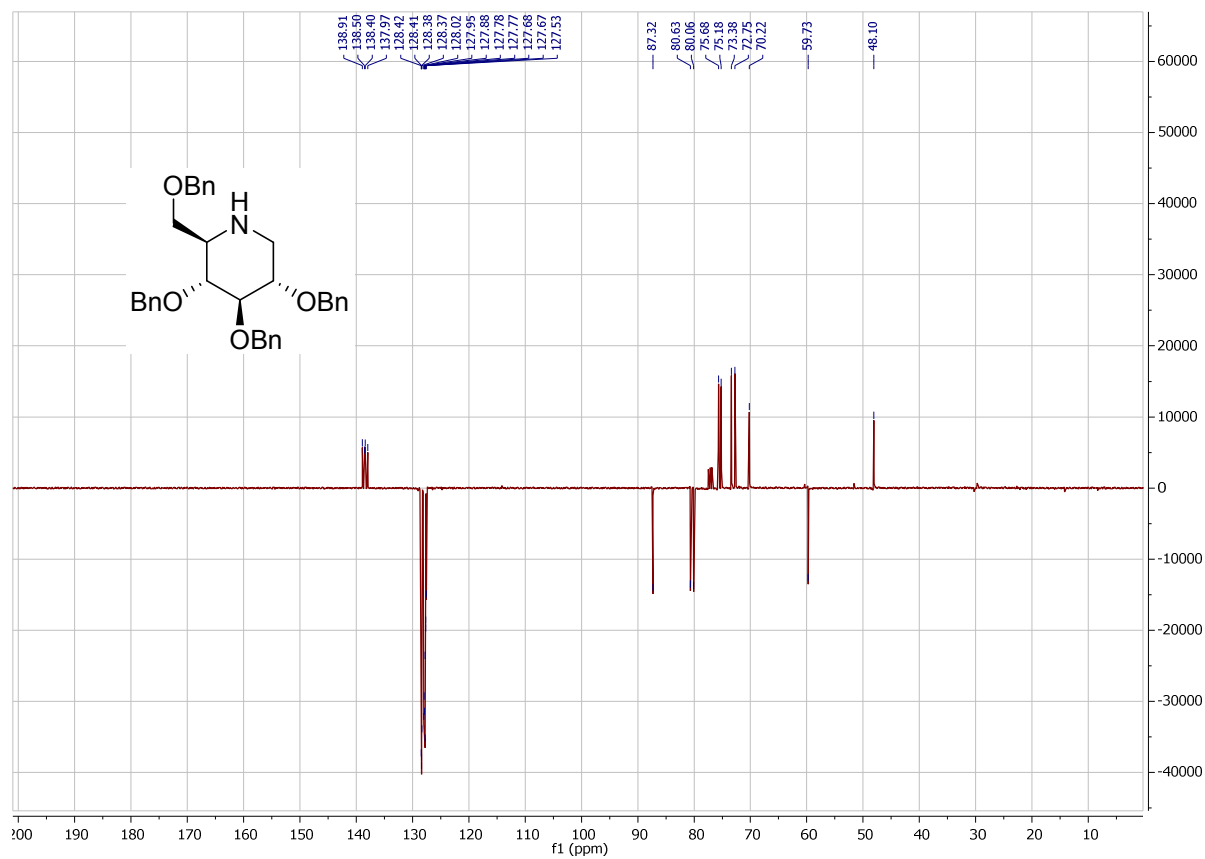
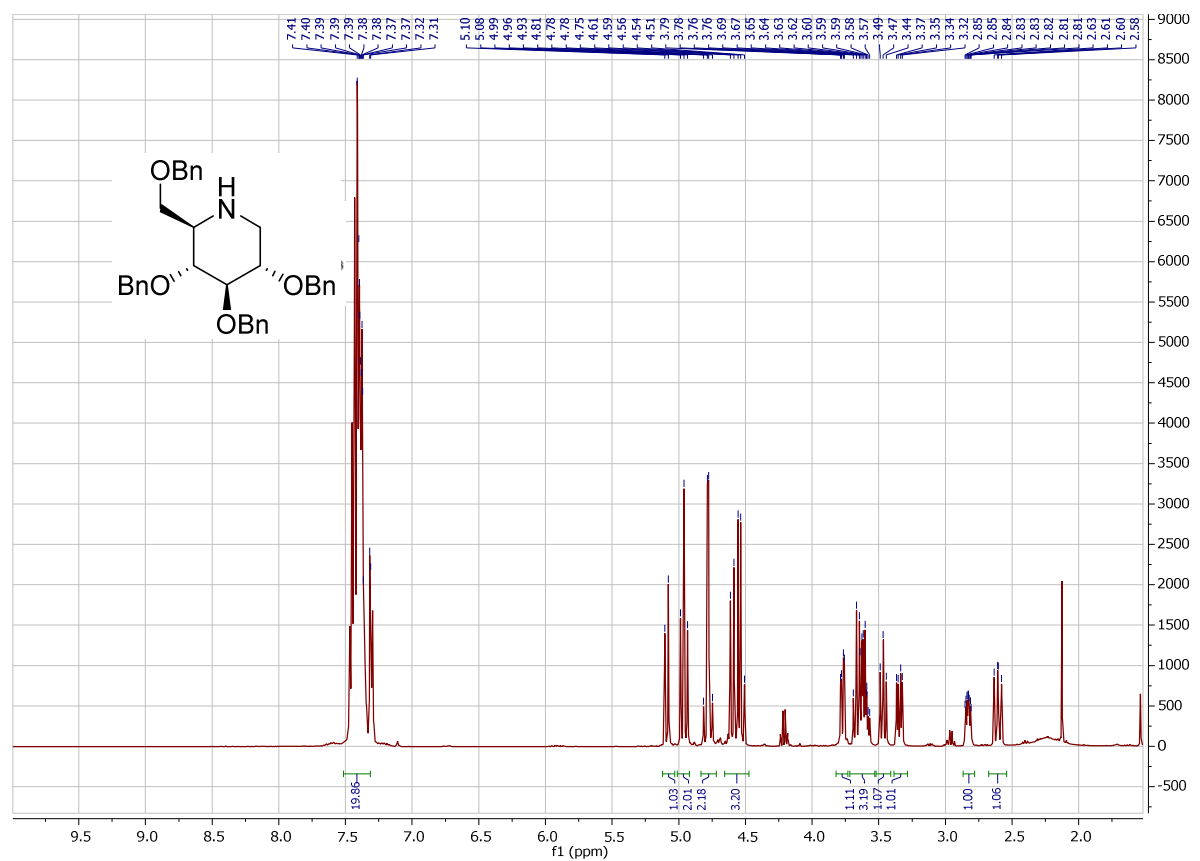
# <sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound ABP4 in CDCl<sub>3</sub>.



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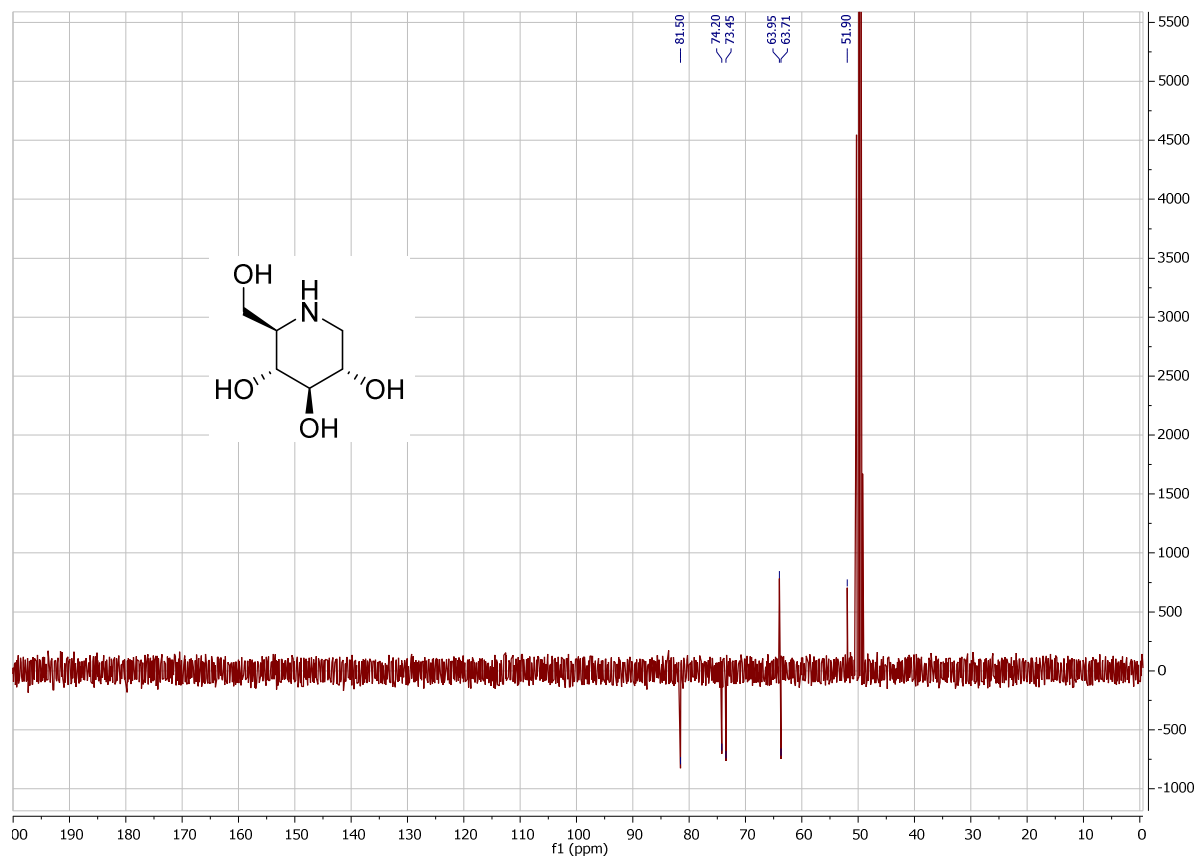
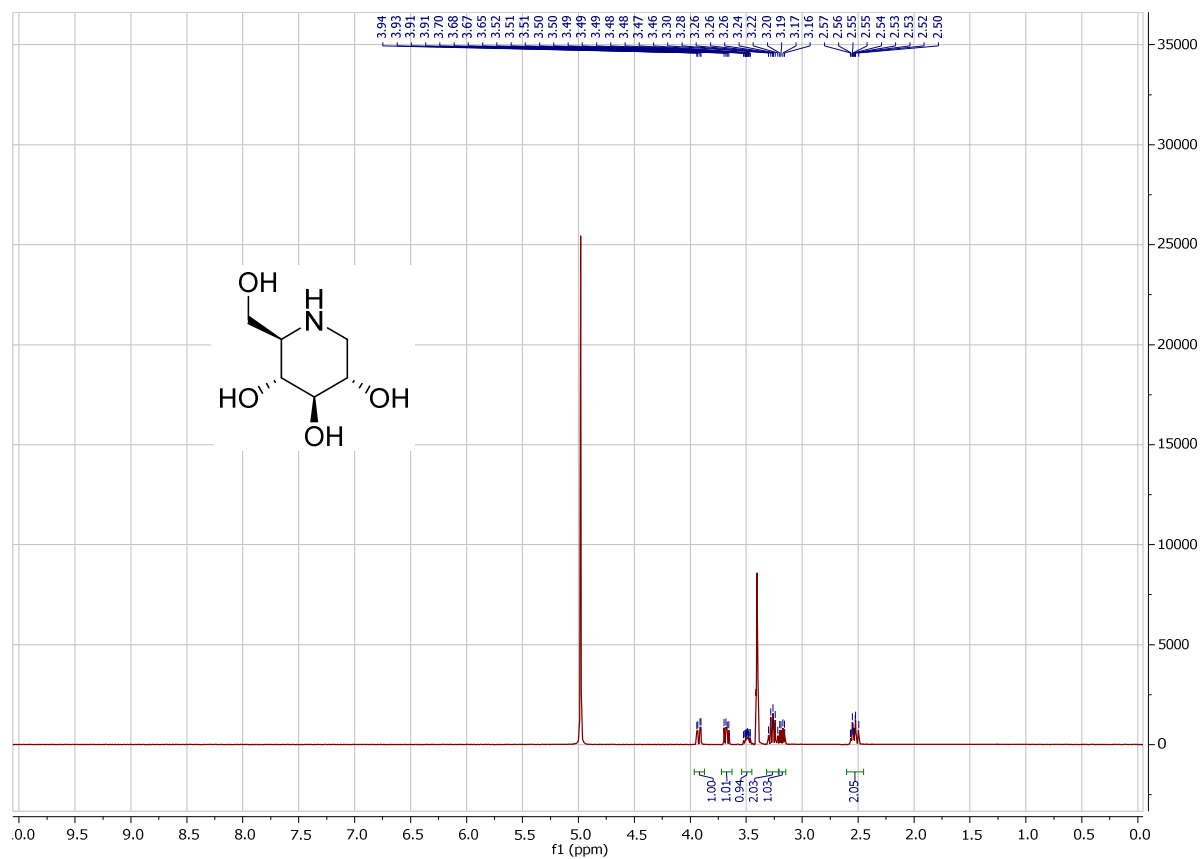


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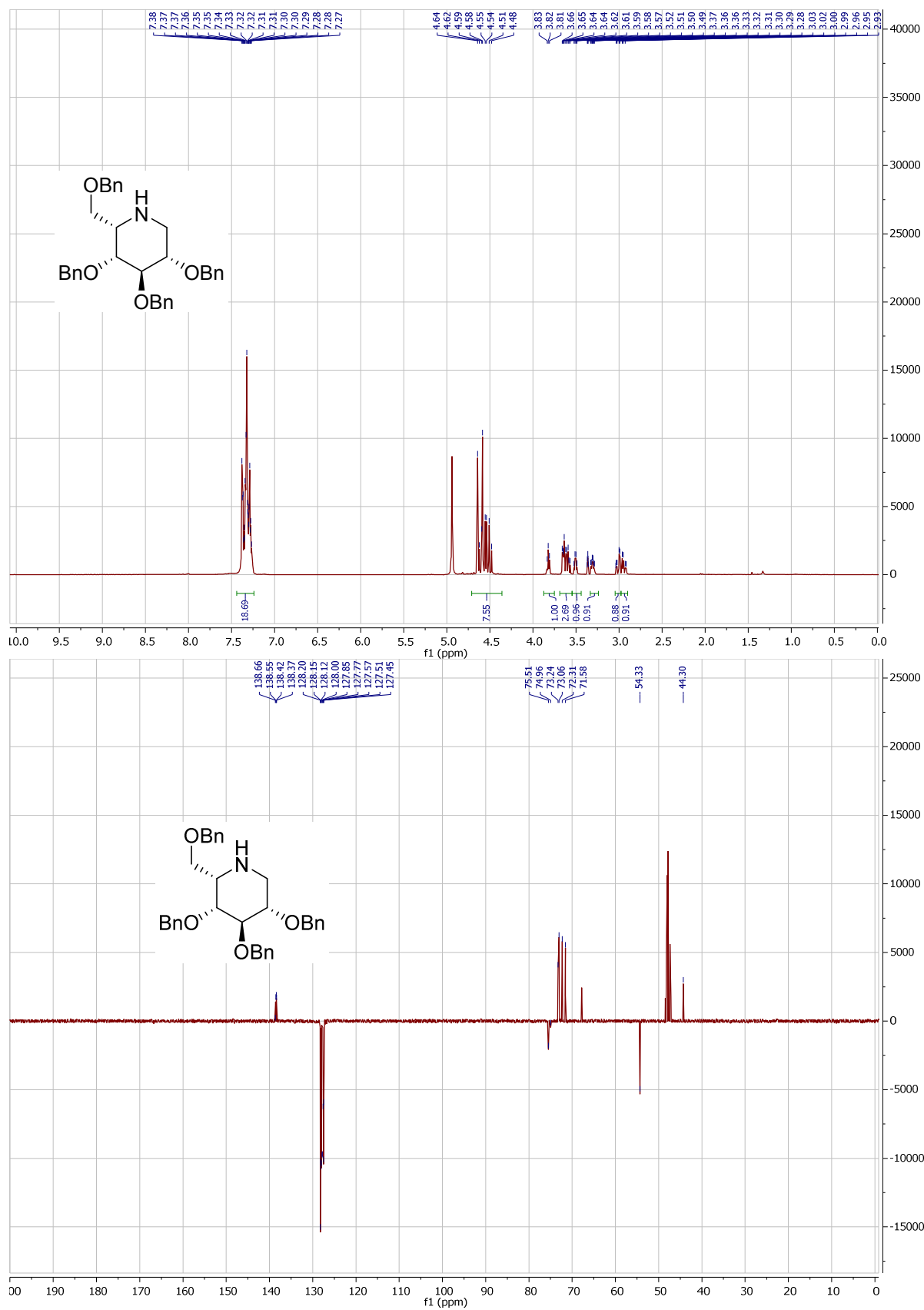




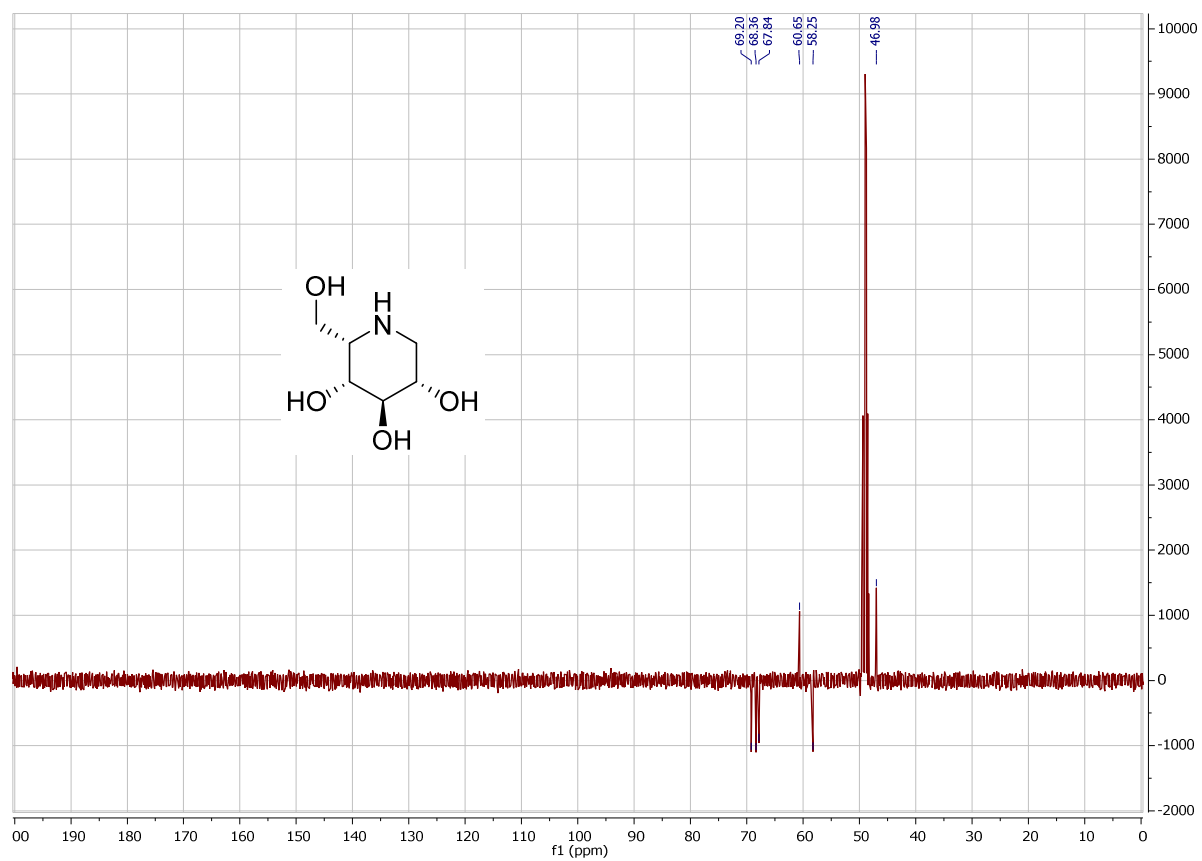
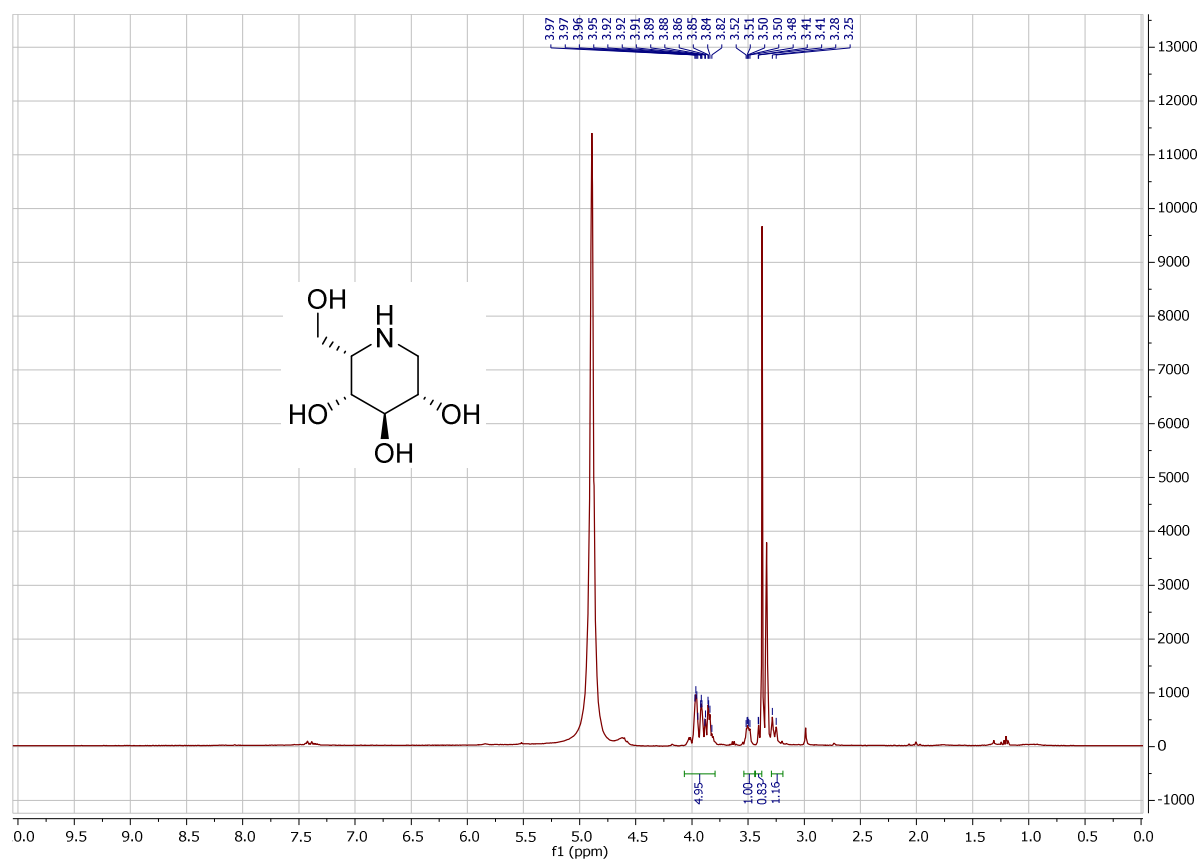
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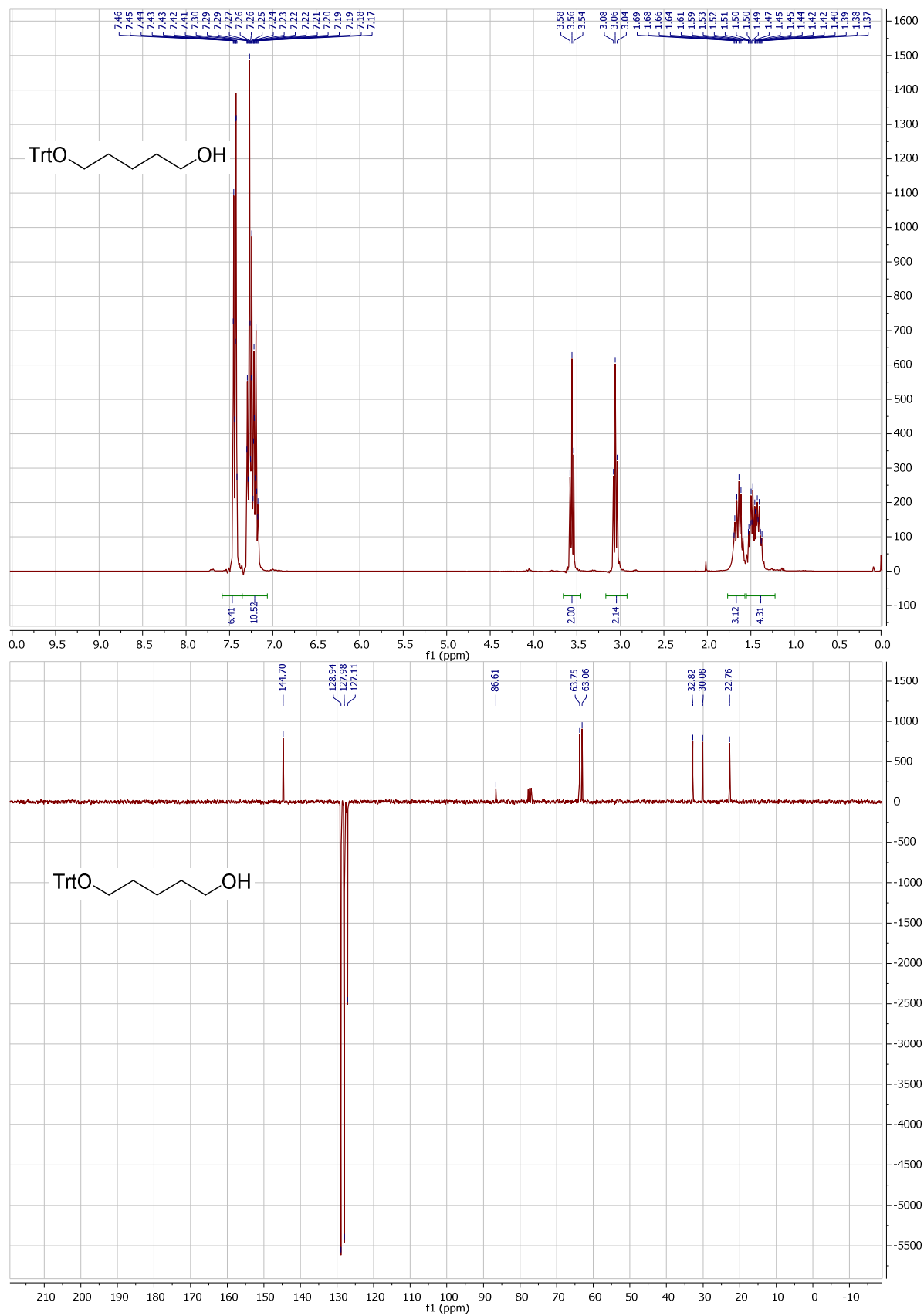
**$^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  of compound B6 in MeOD.**



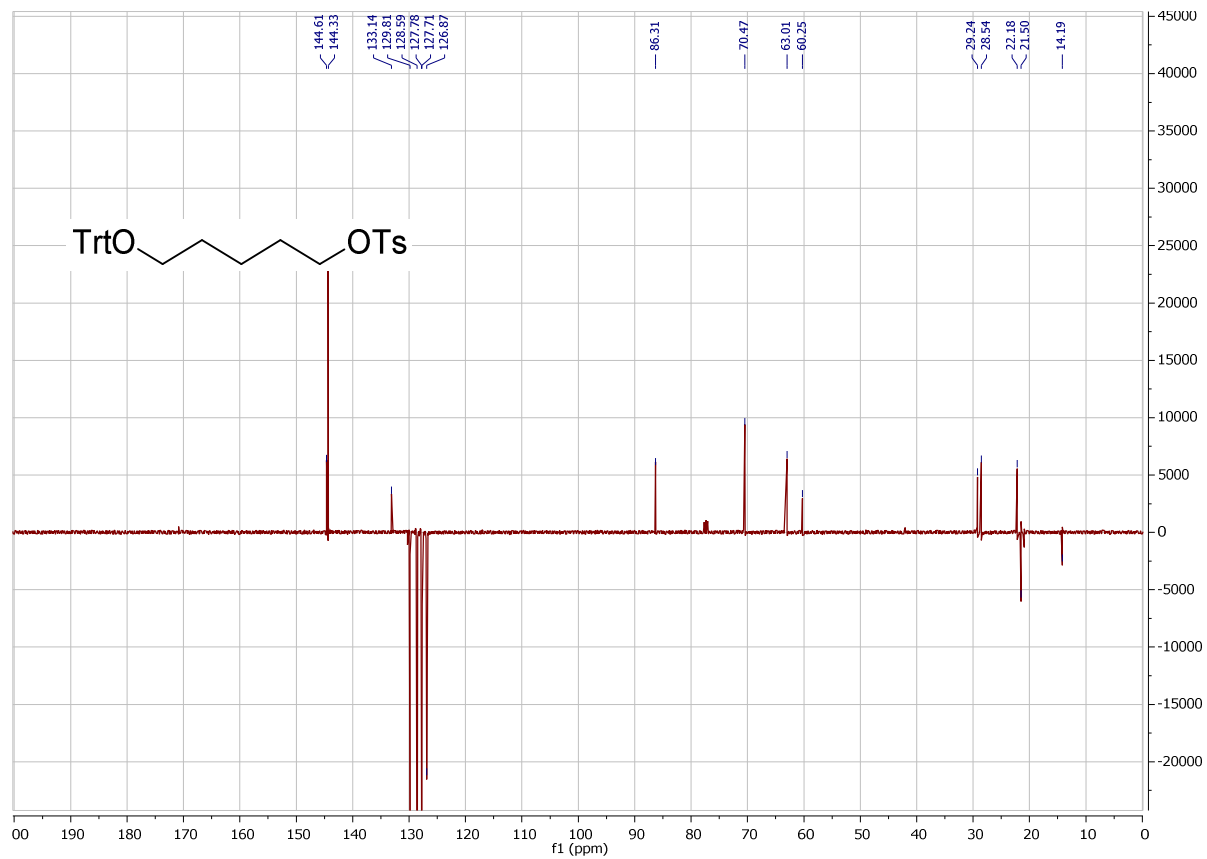
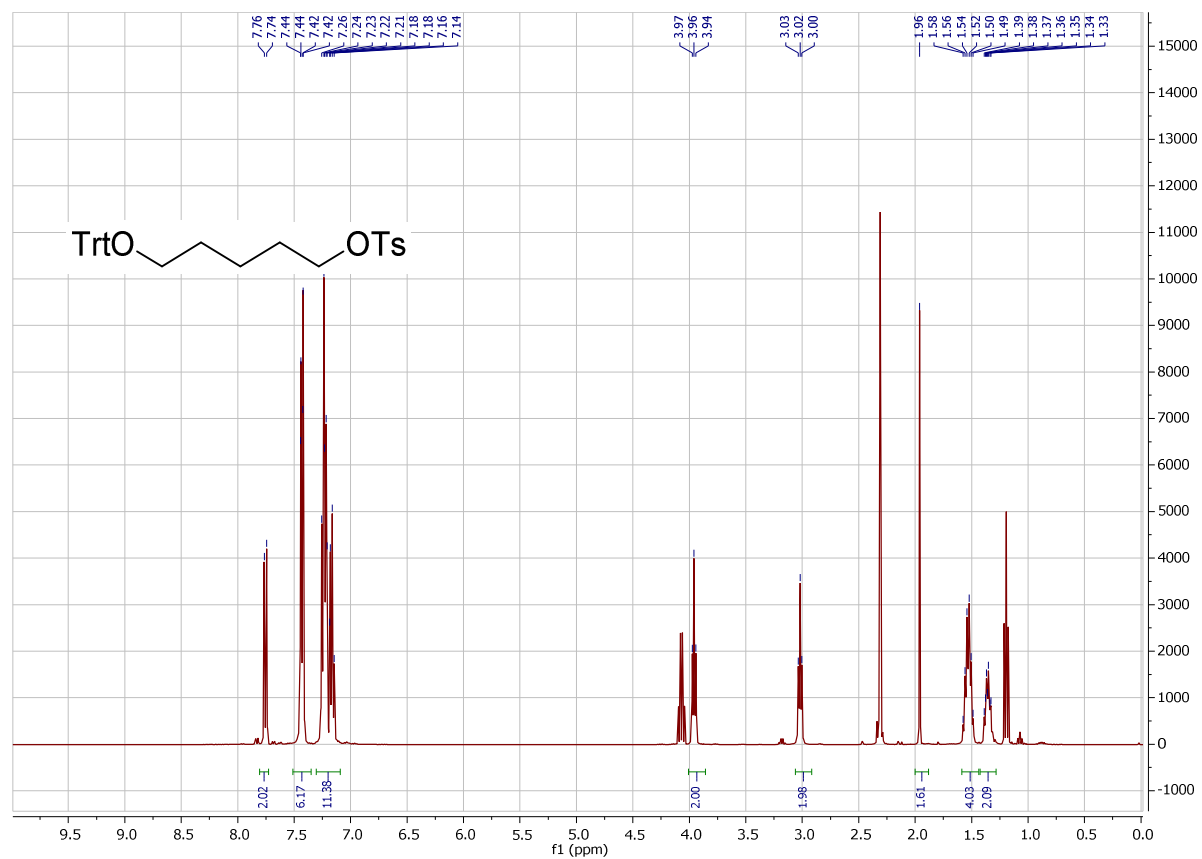
<sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound B7 in MeOD.



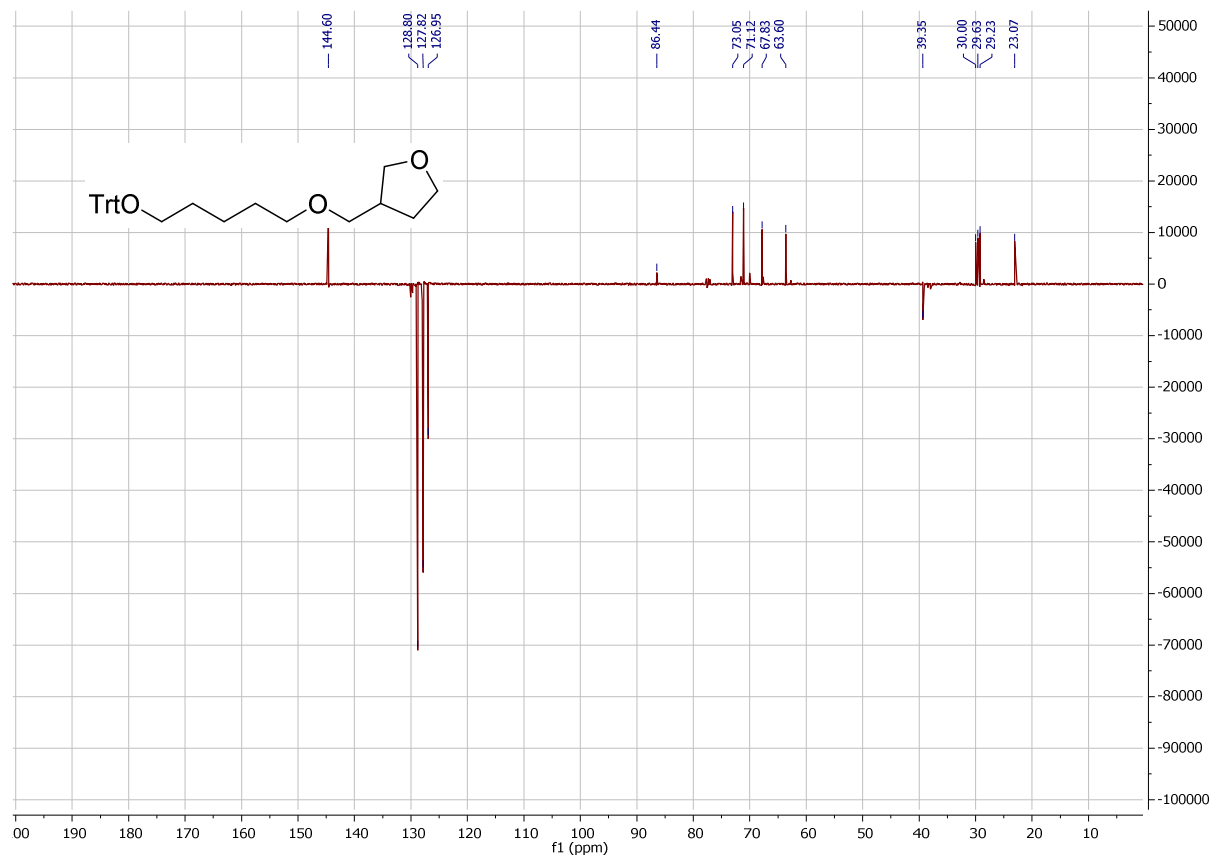
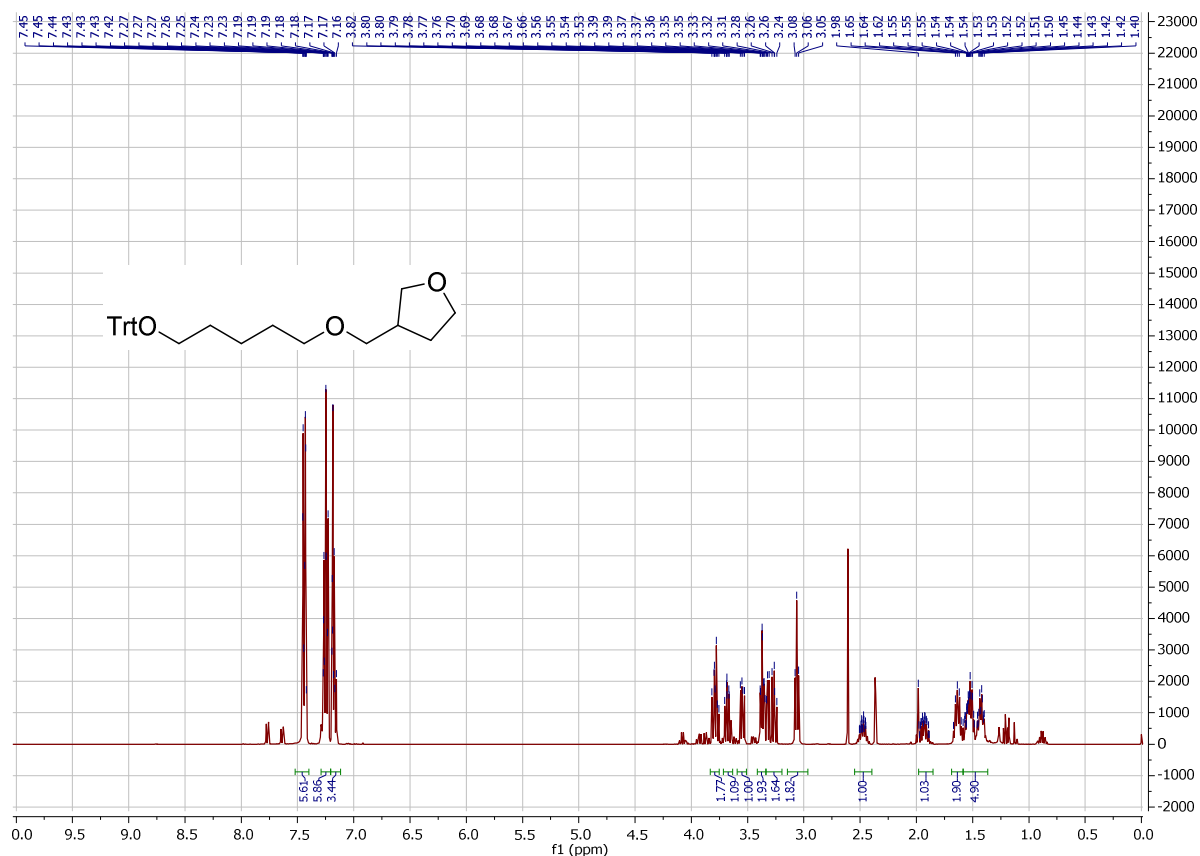
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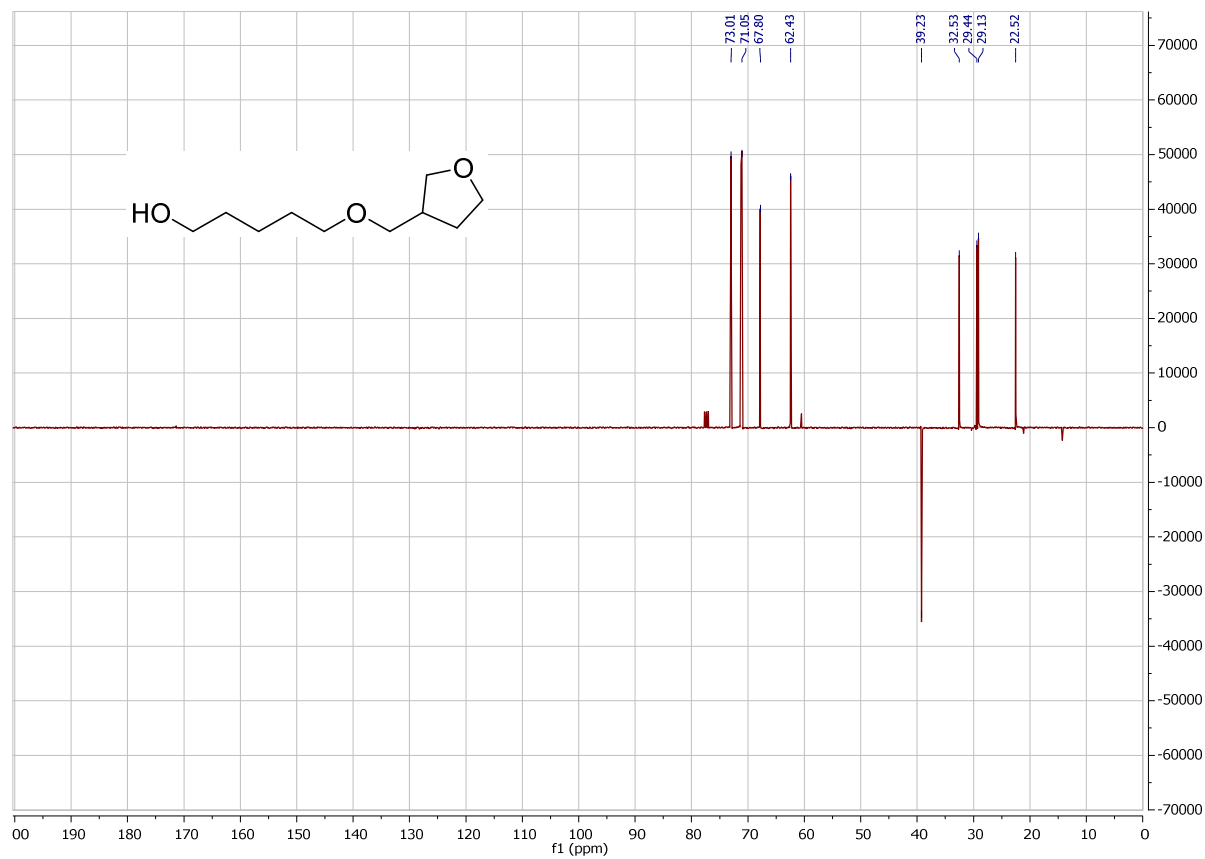
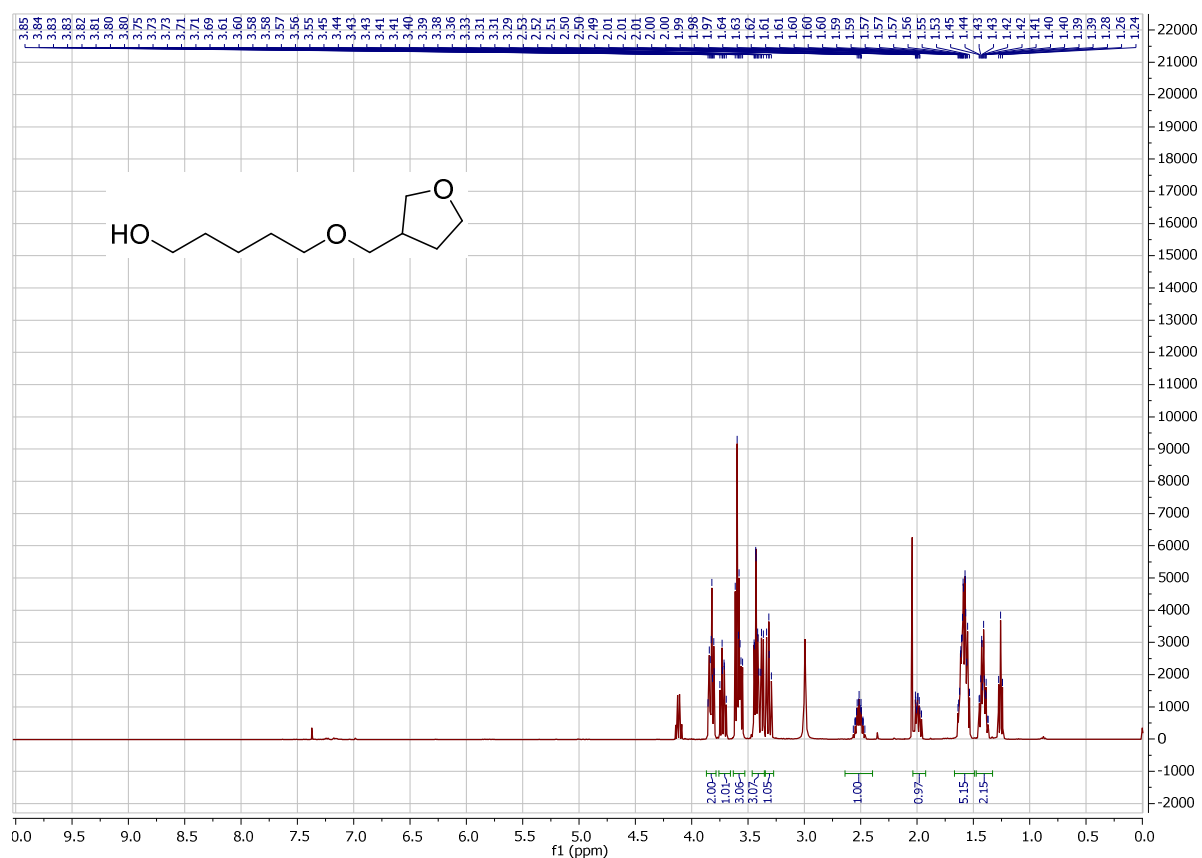
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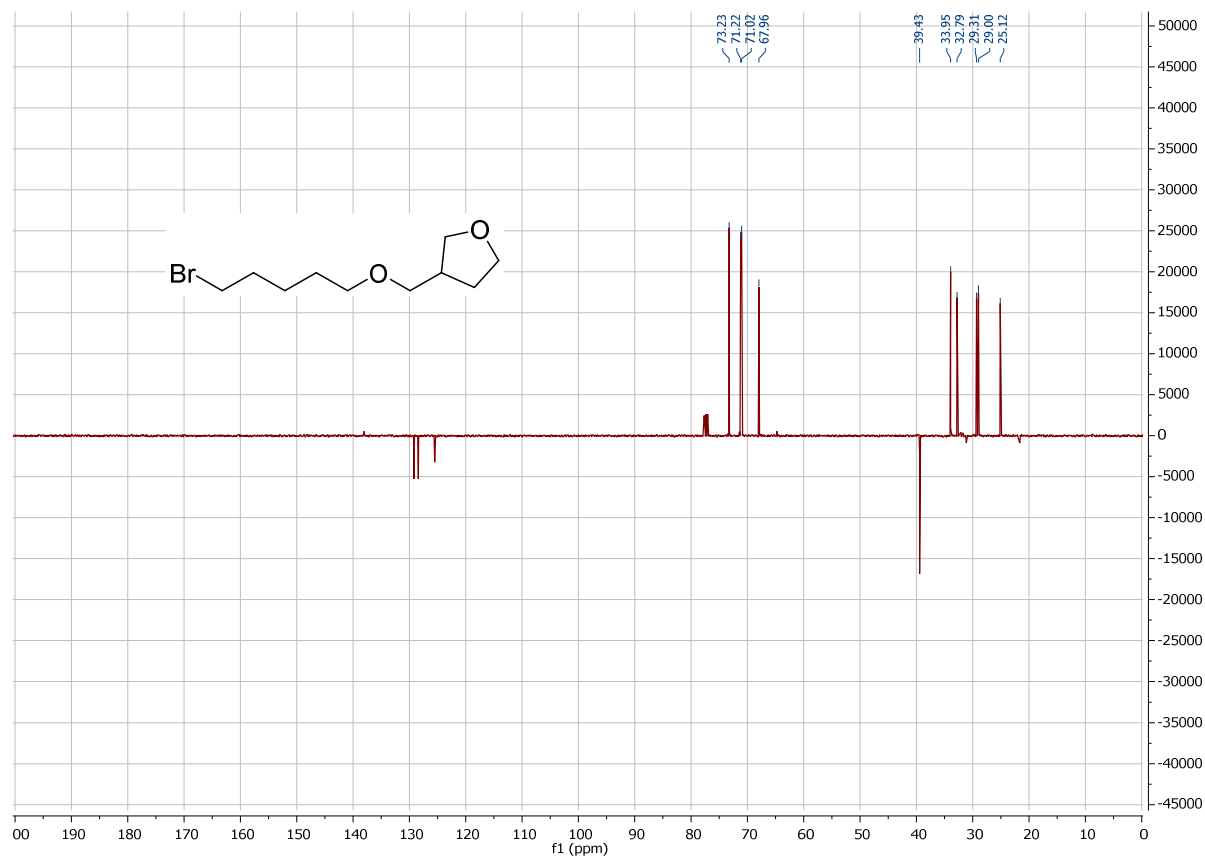
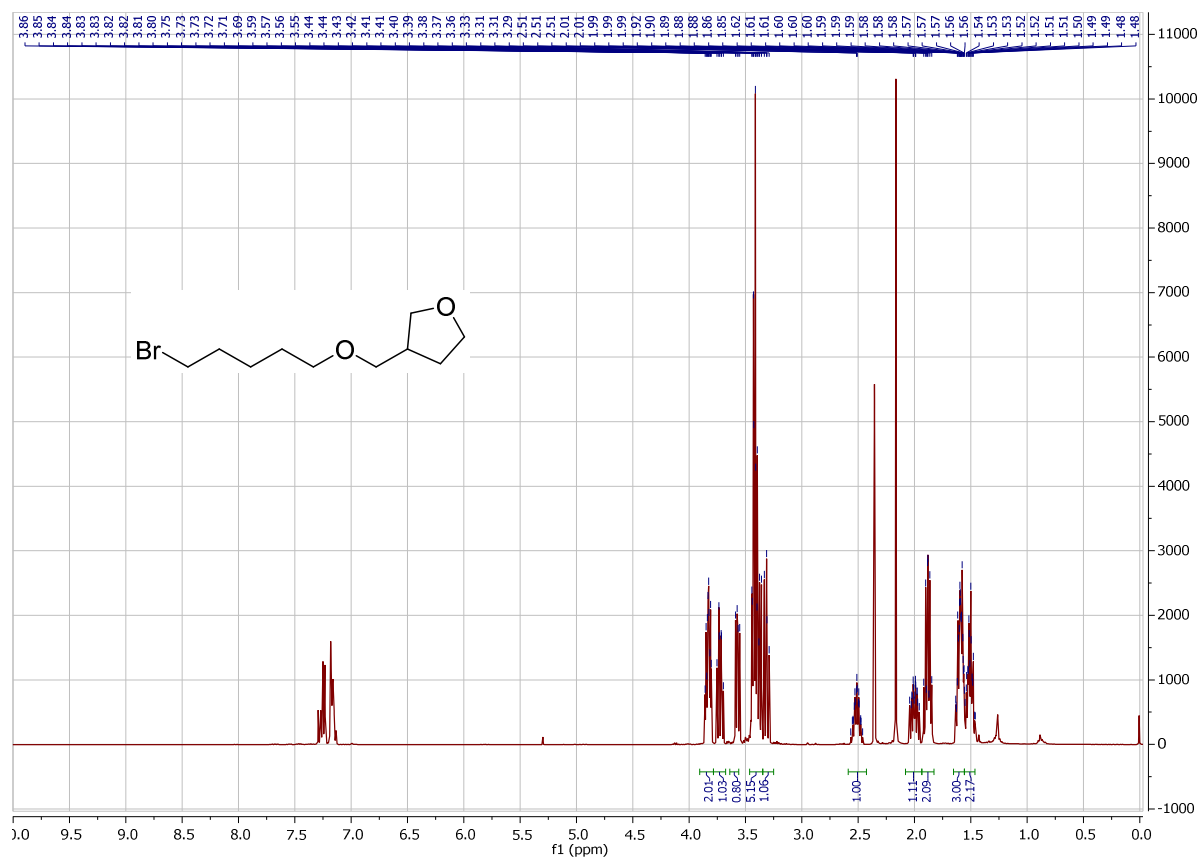
# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound B11 in $\text{CDCl}_3$ .



# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound B12 in $\text{CDCl}_3$ .



<sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound B13 in CDCl<sub>3</sub>.

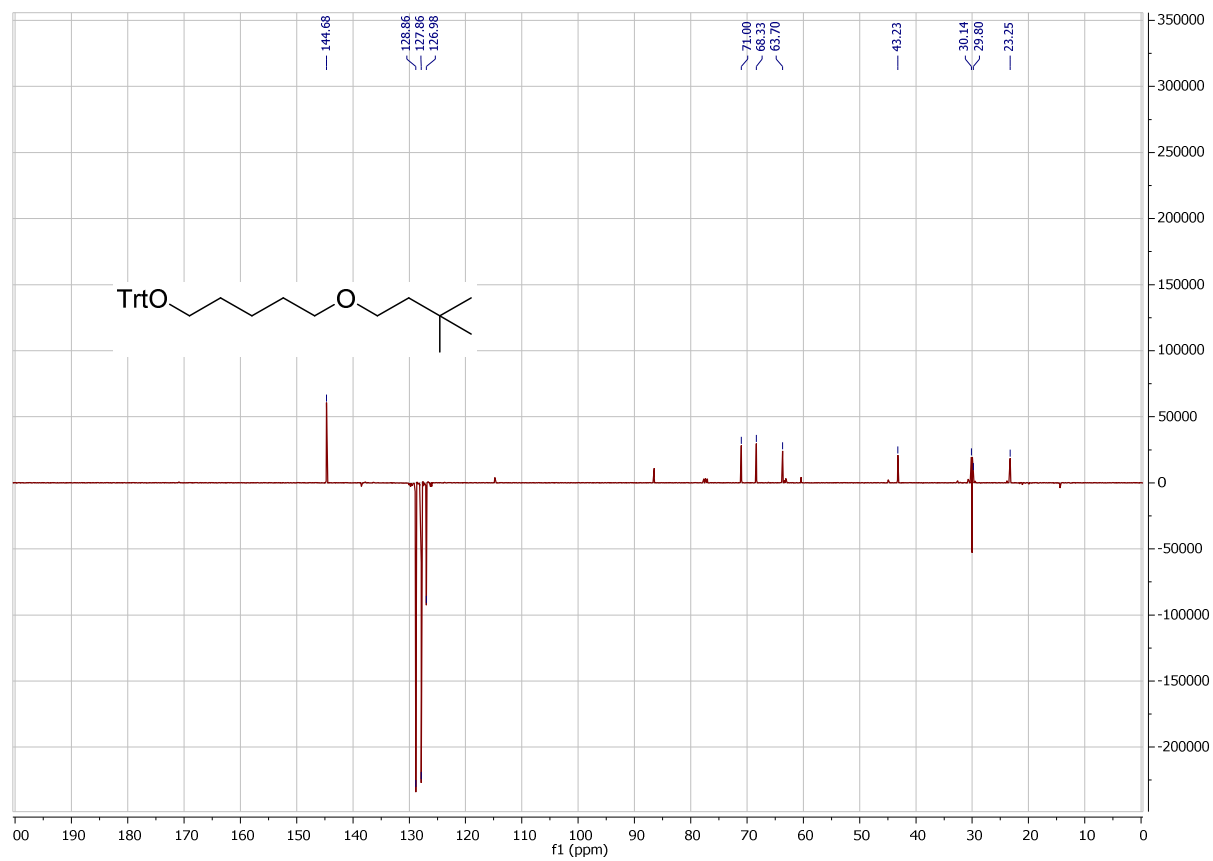
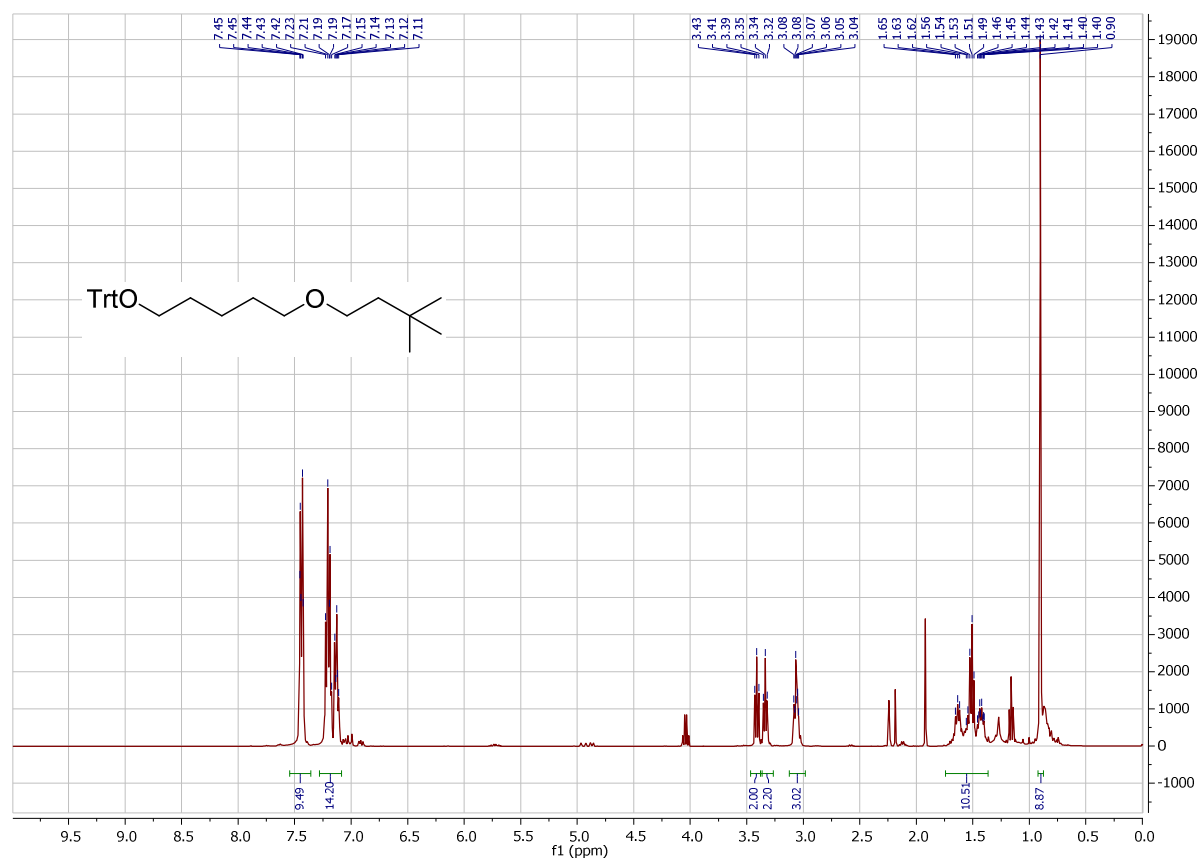




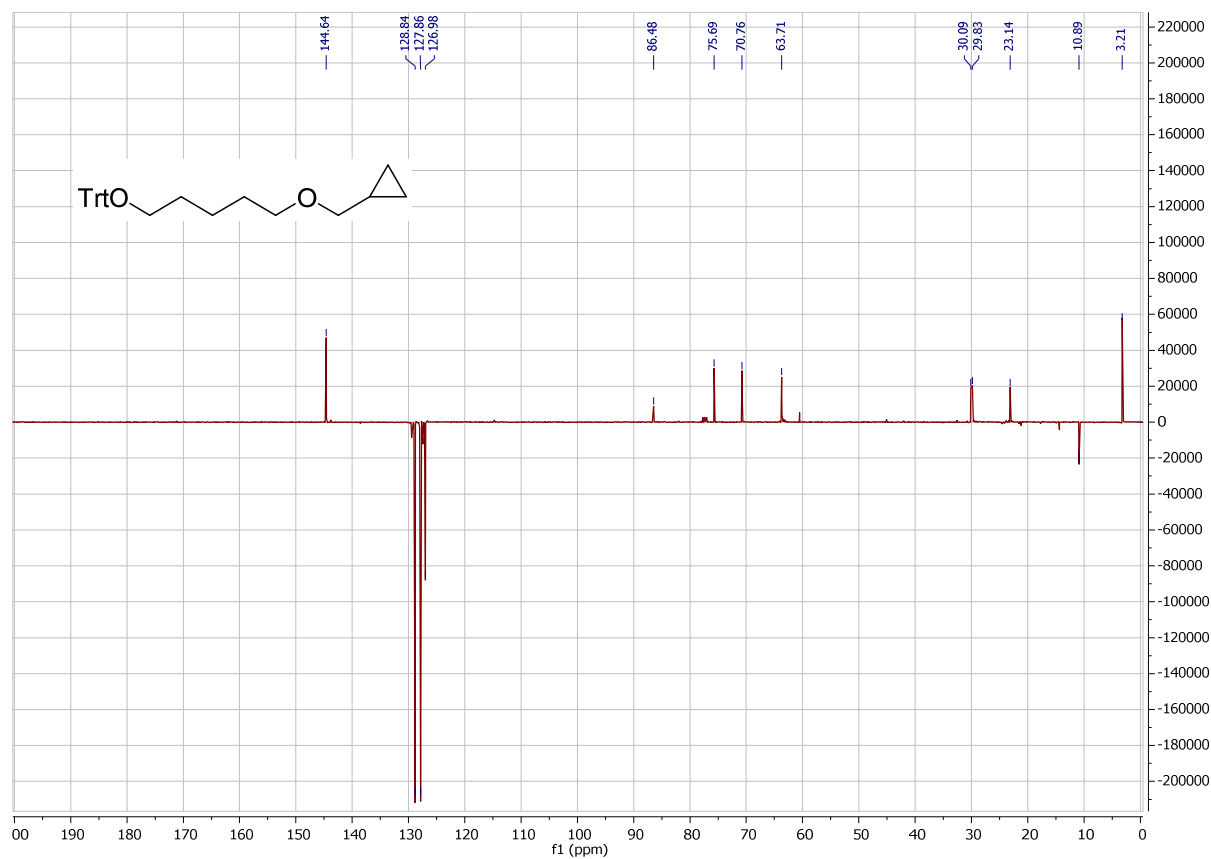
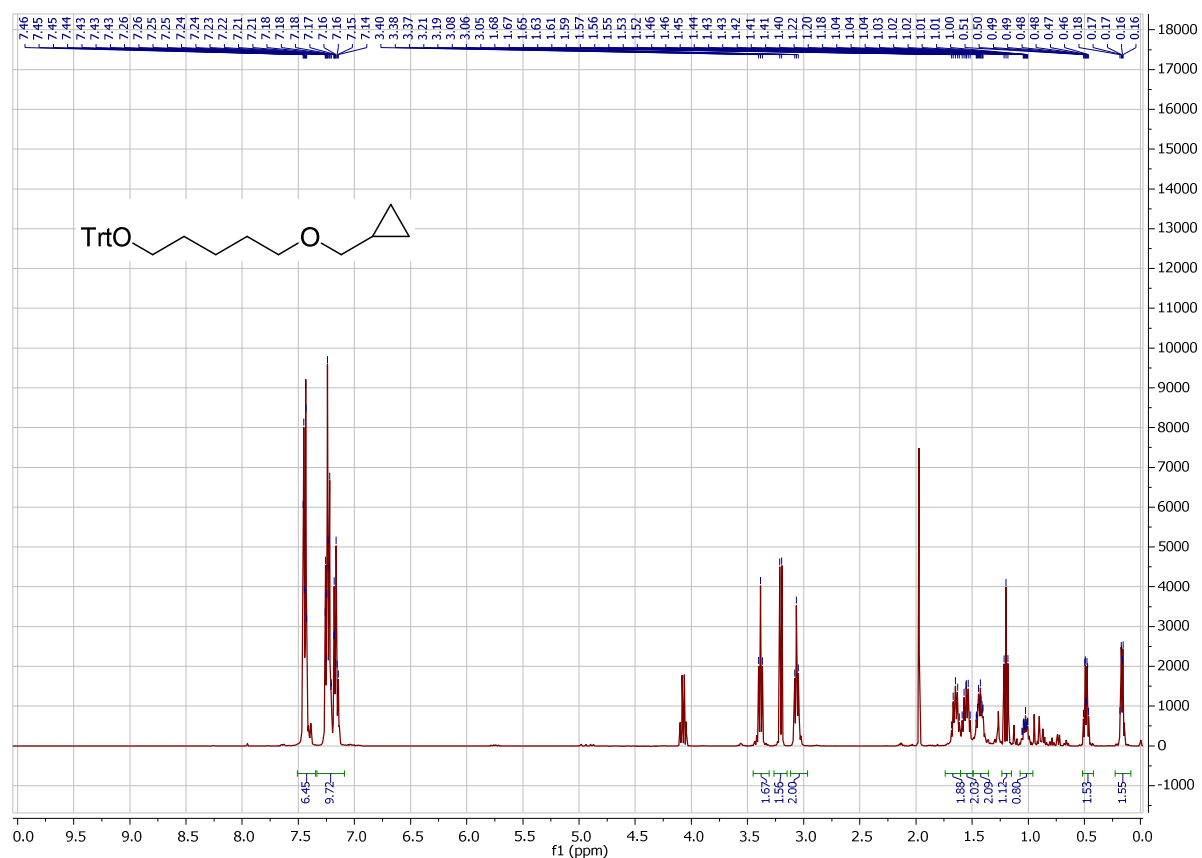




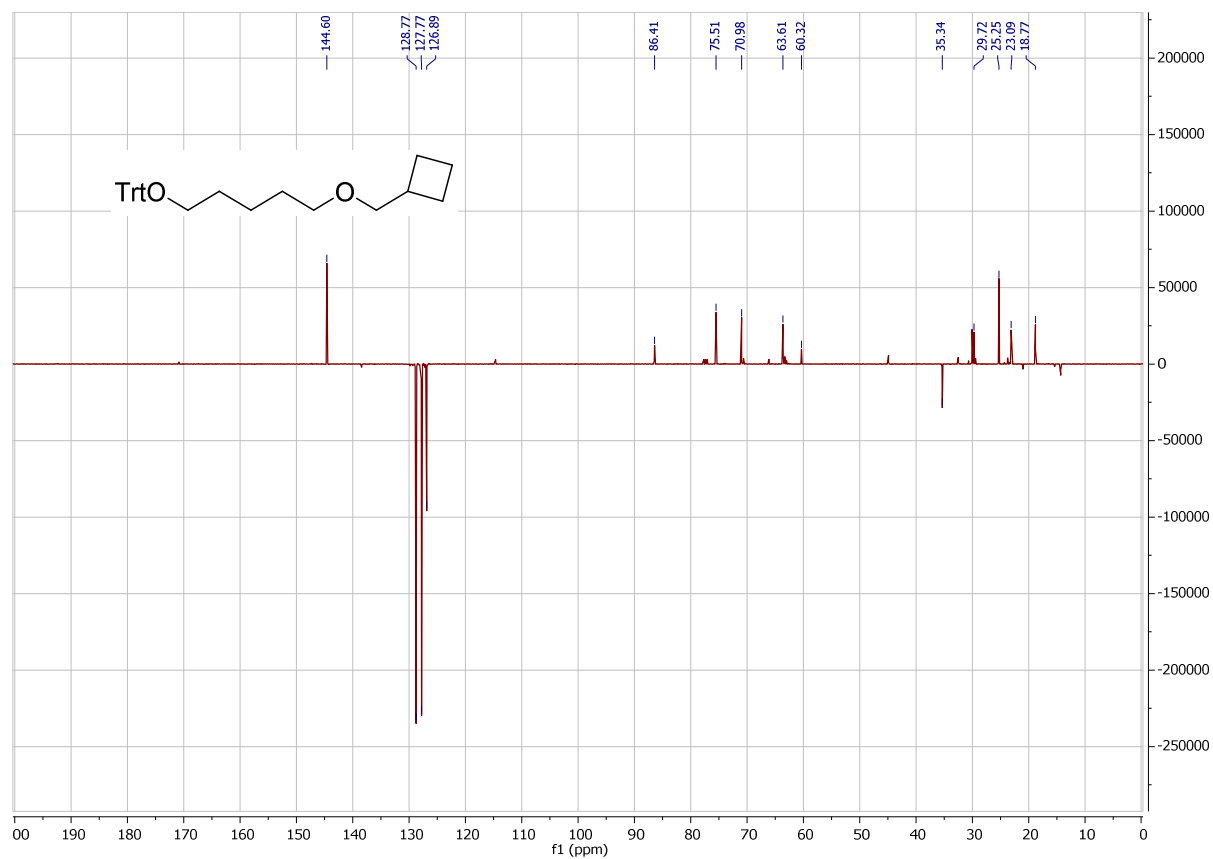
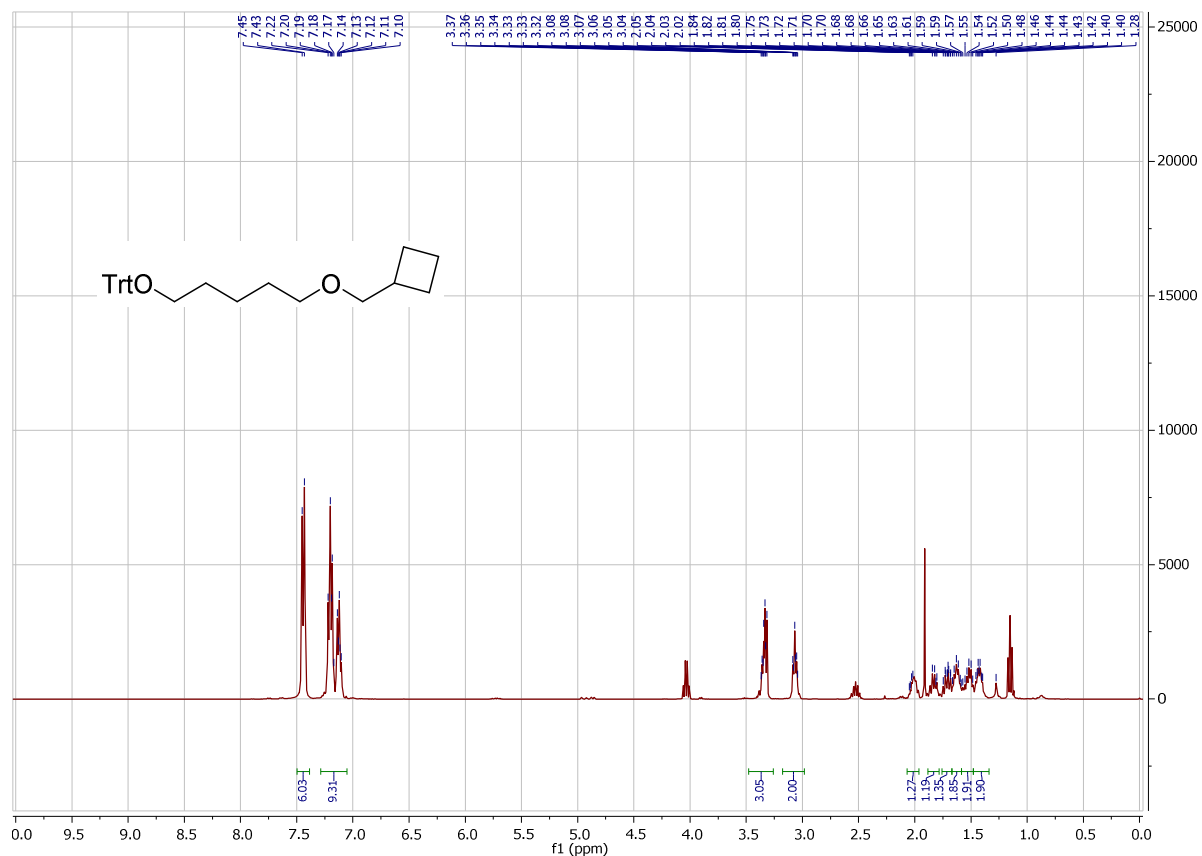
<sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound B16 in CDCl<sub>3</sub>.



# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound B17 in $\text{CDCl}_3$ .

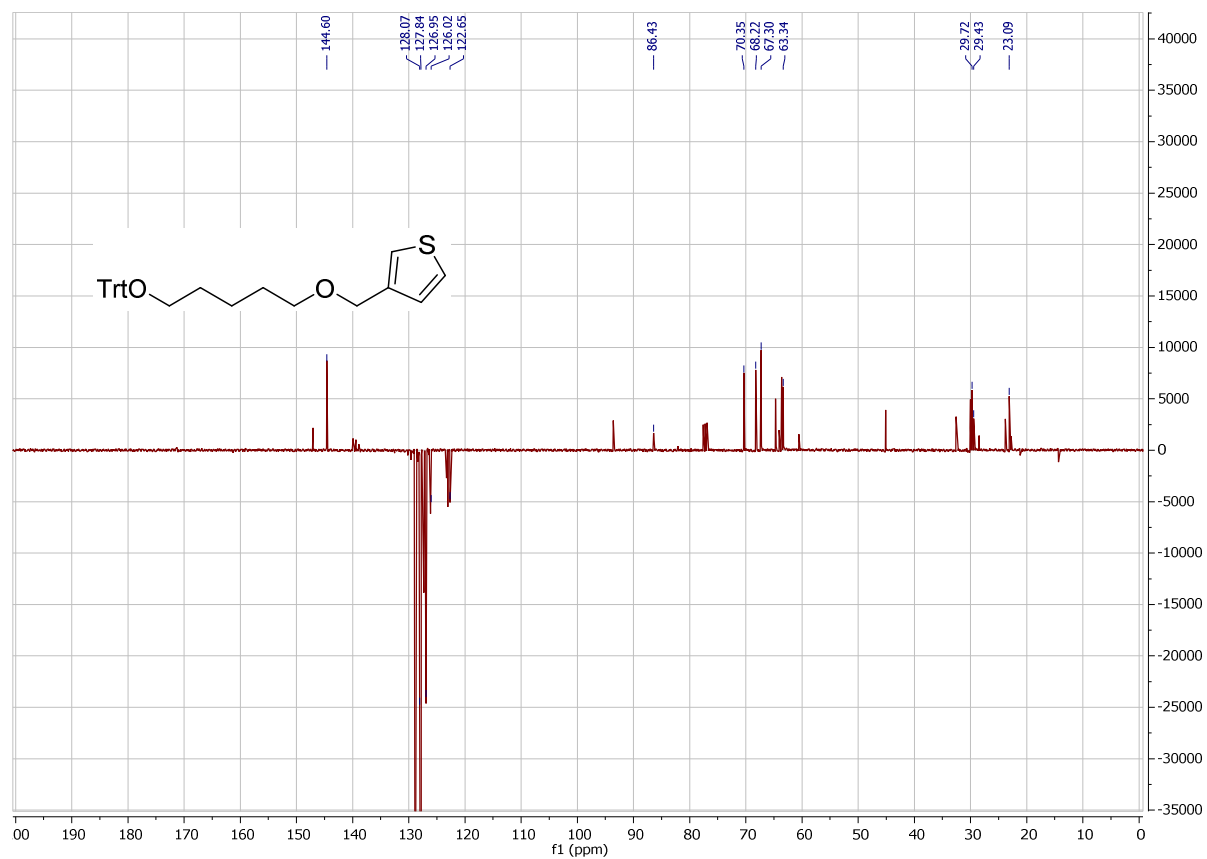
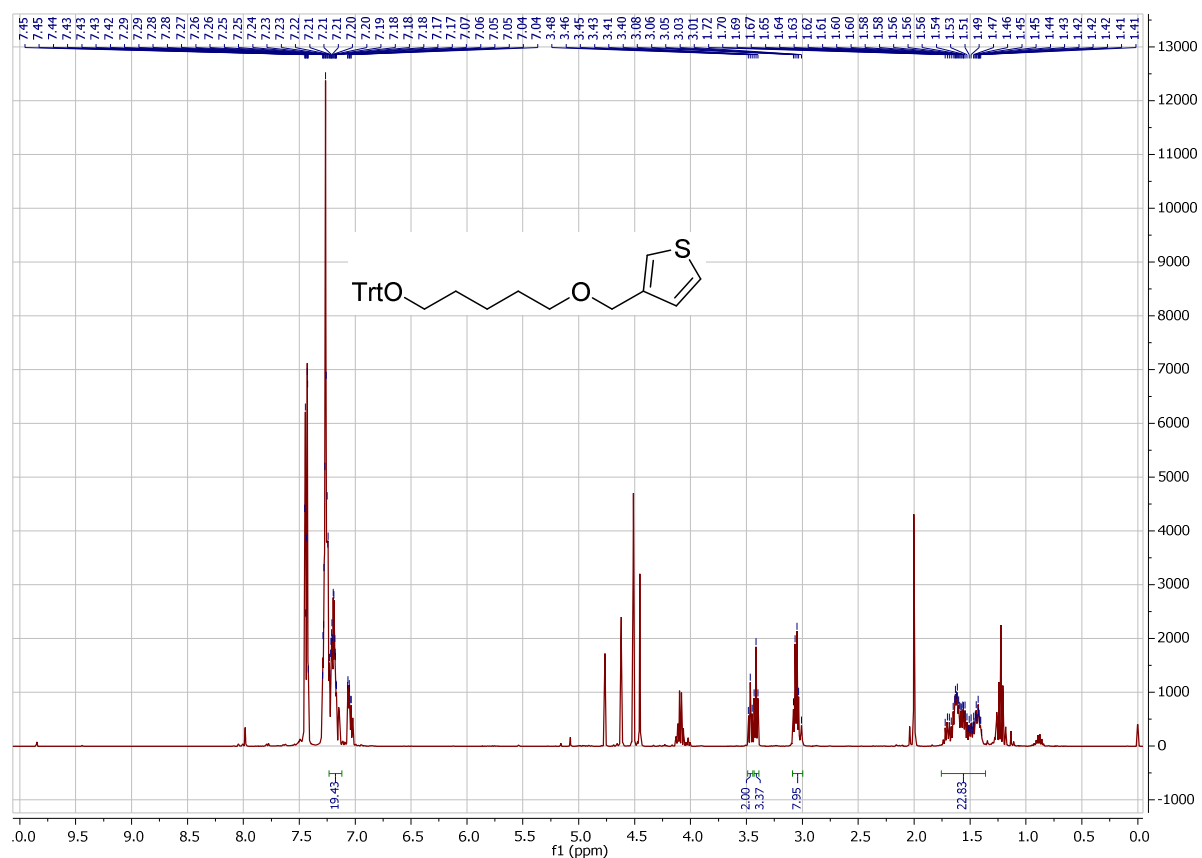


# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound B18 in $\text{CDCl}_3$ .

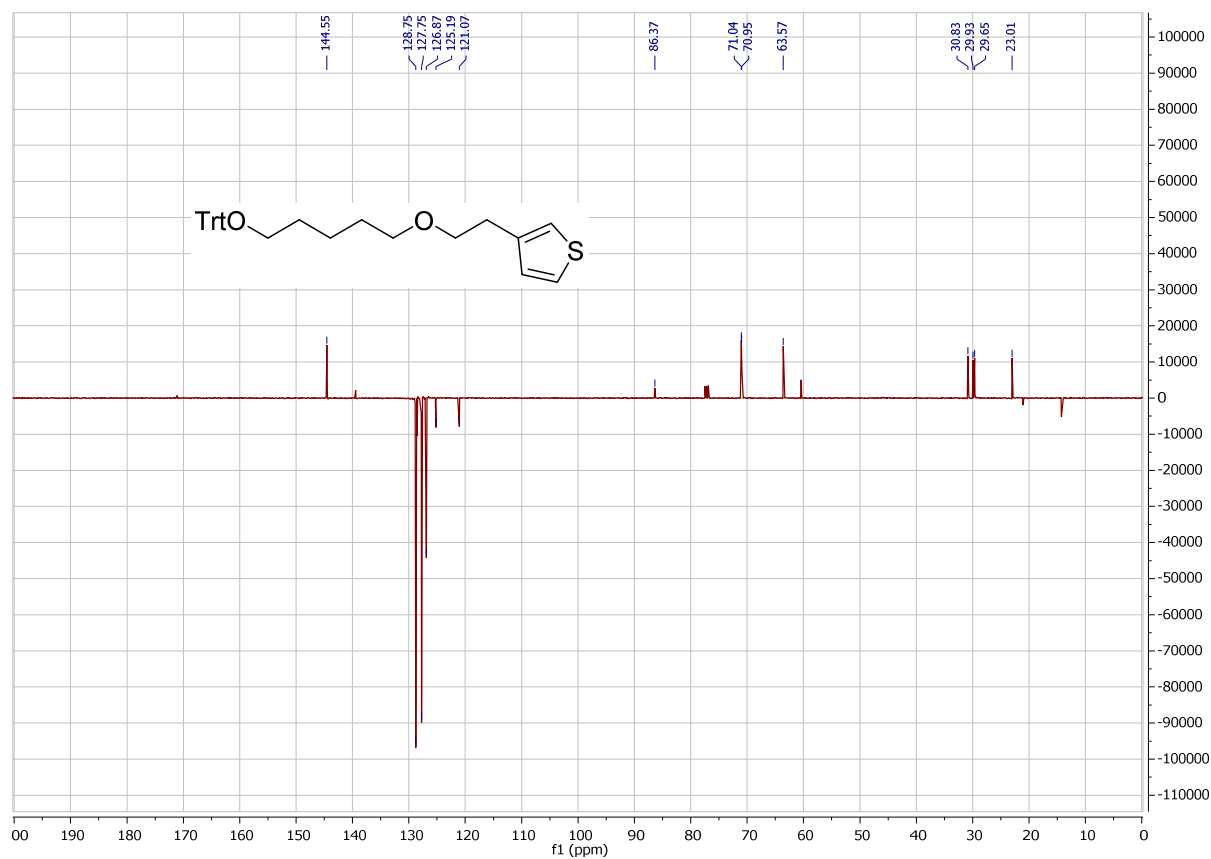
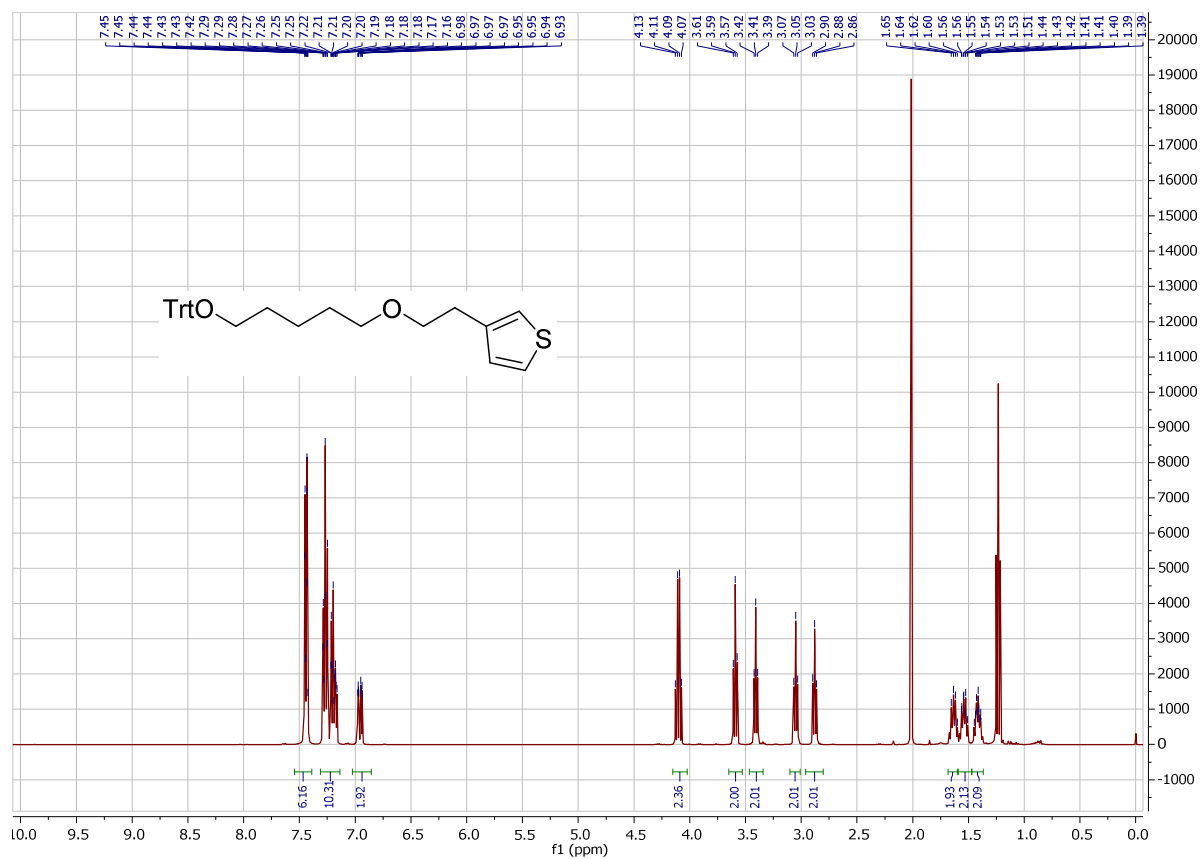




# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound B20 in $\text{CDCl}_3$ .

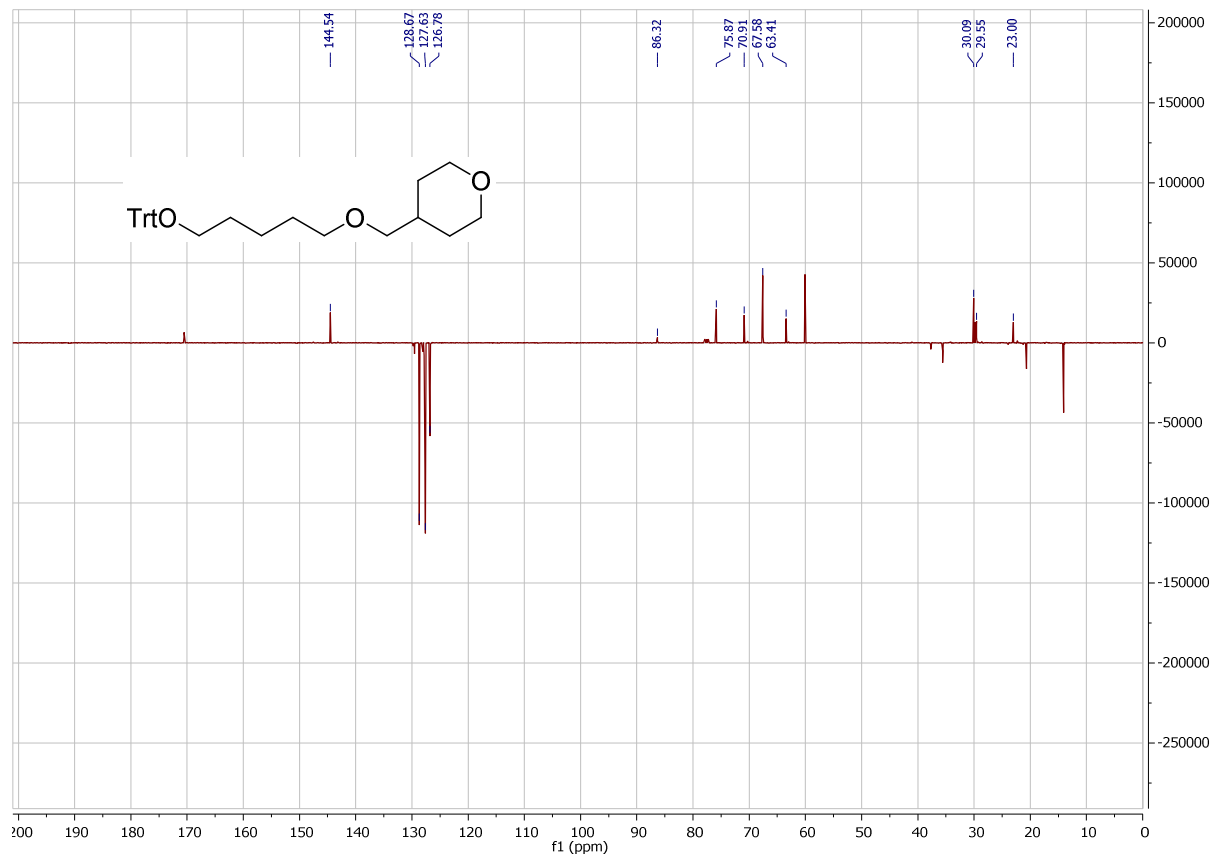
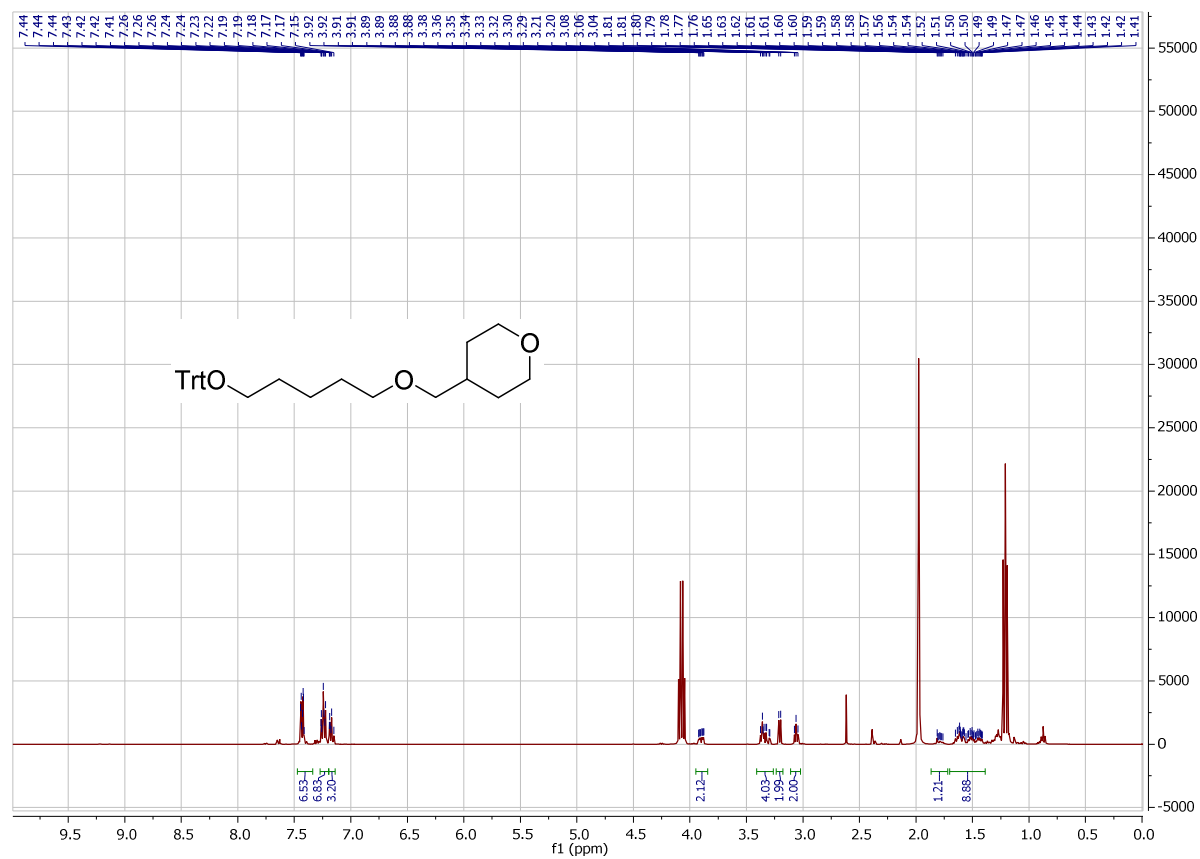


**$^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  of compound B21 in  $\text{CDCl}_3$ .**



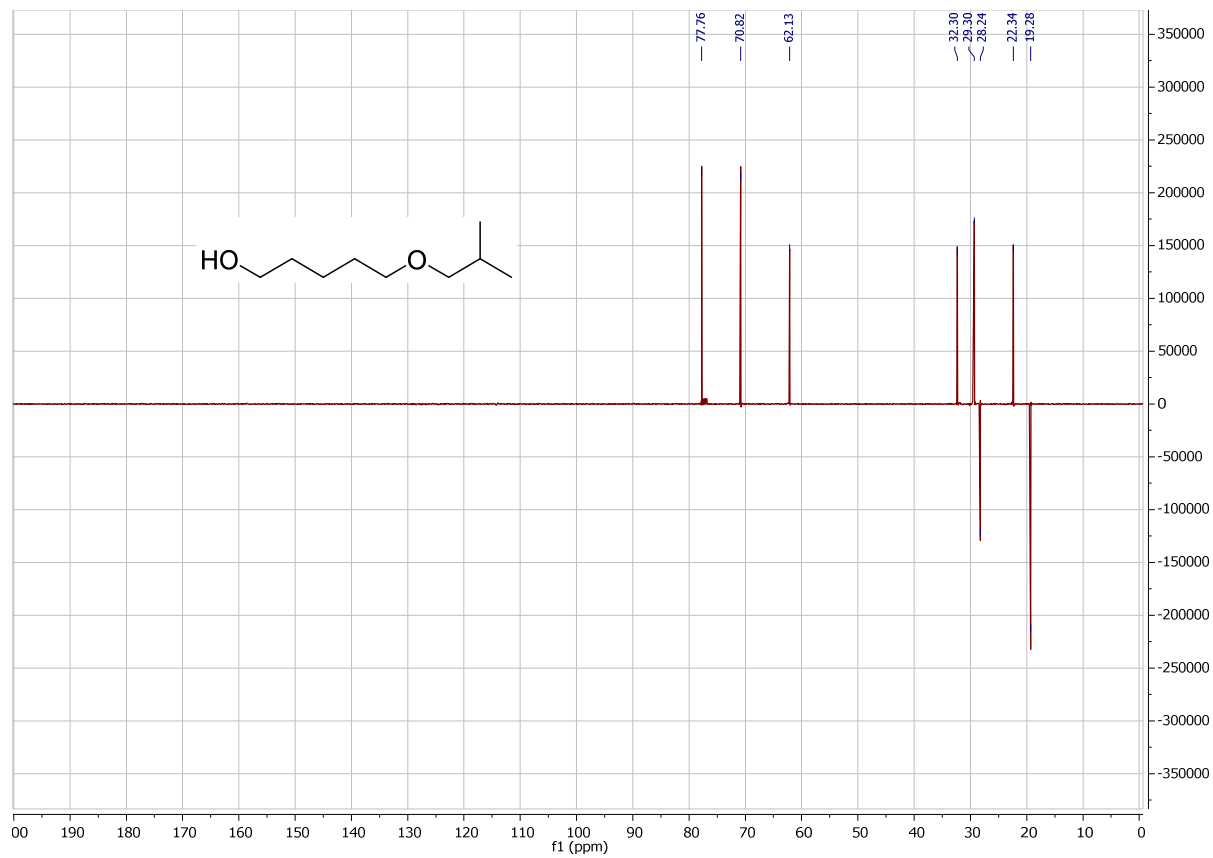
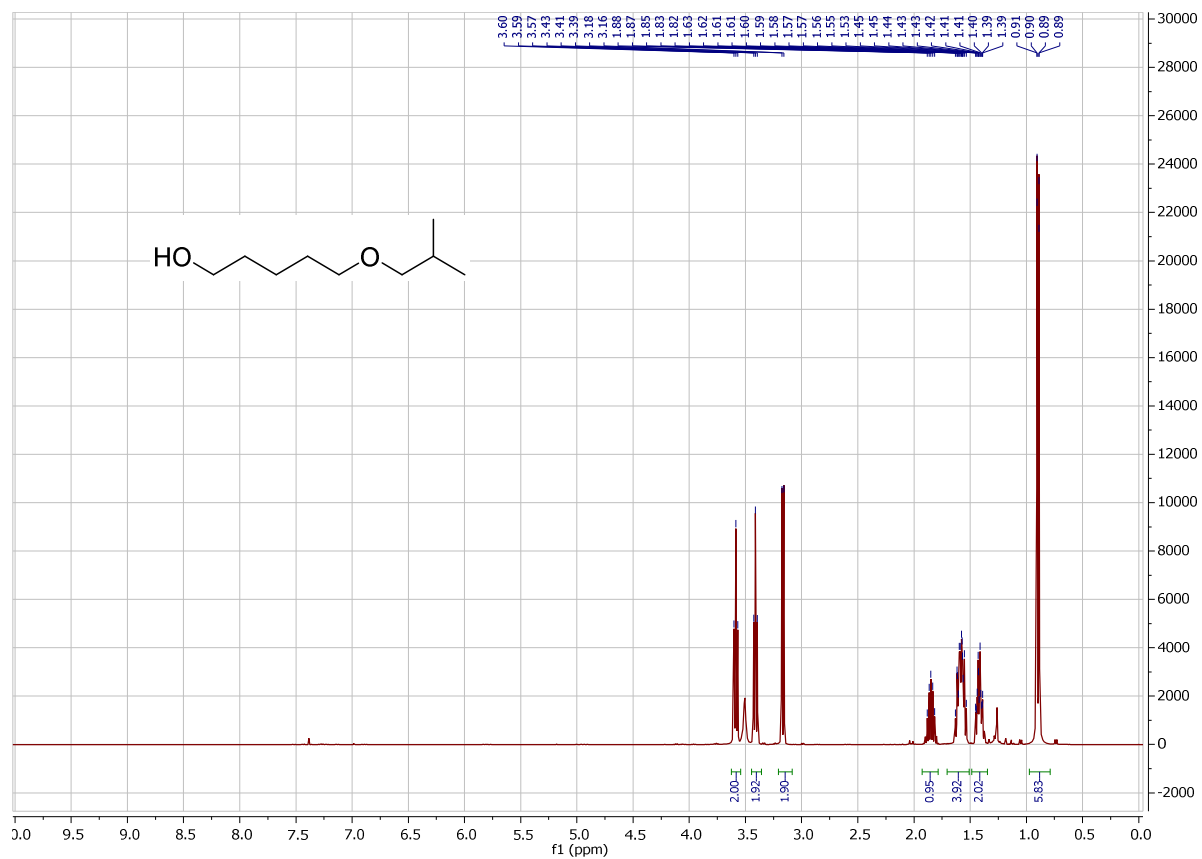


# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound B22 in $\text{CDCl}_3$ .

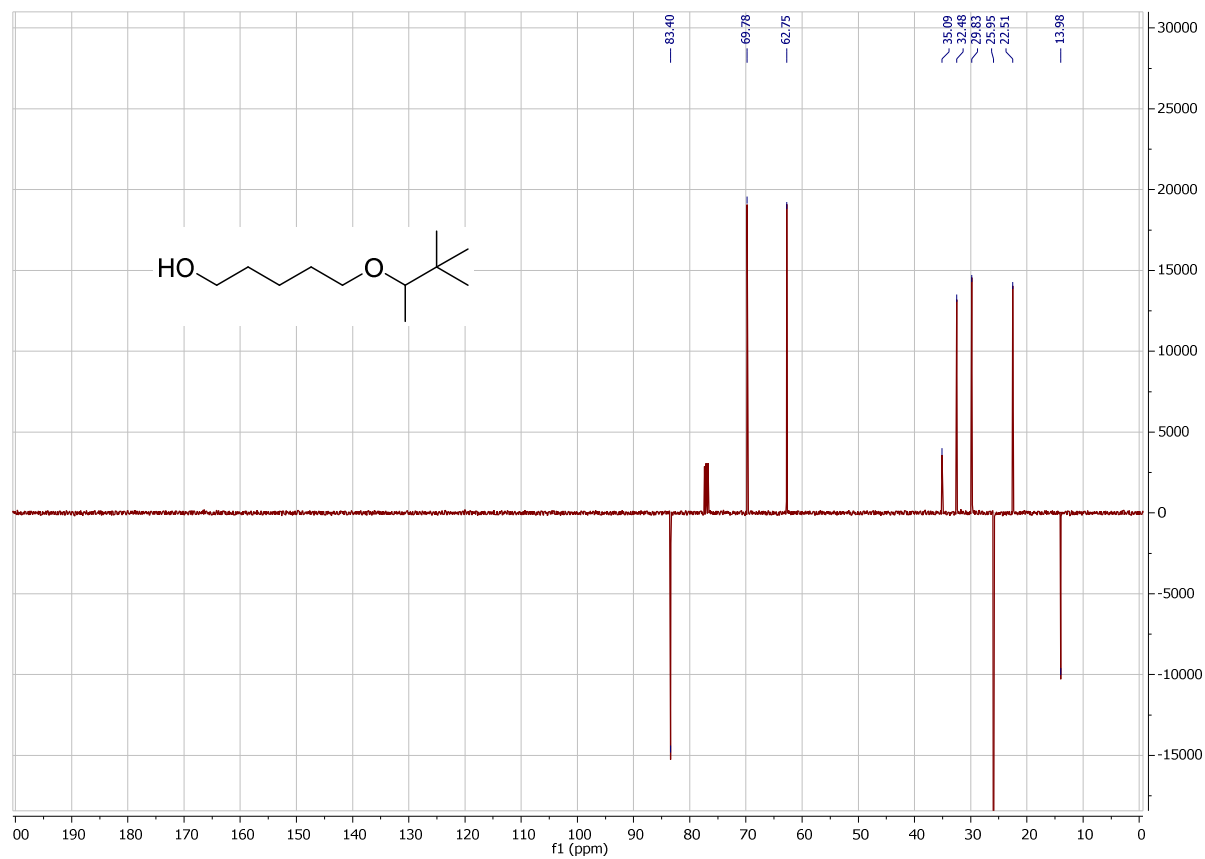
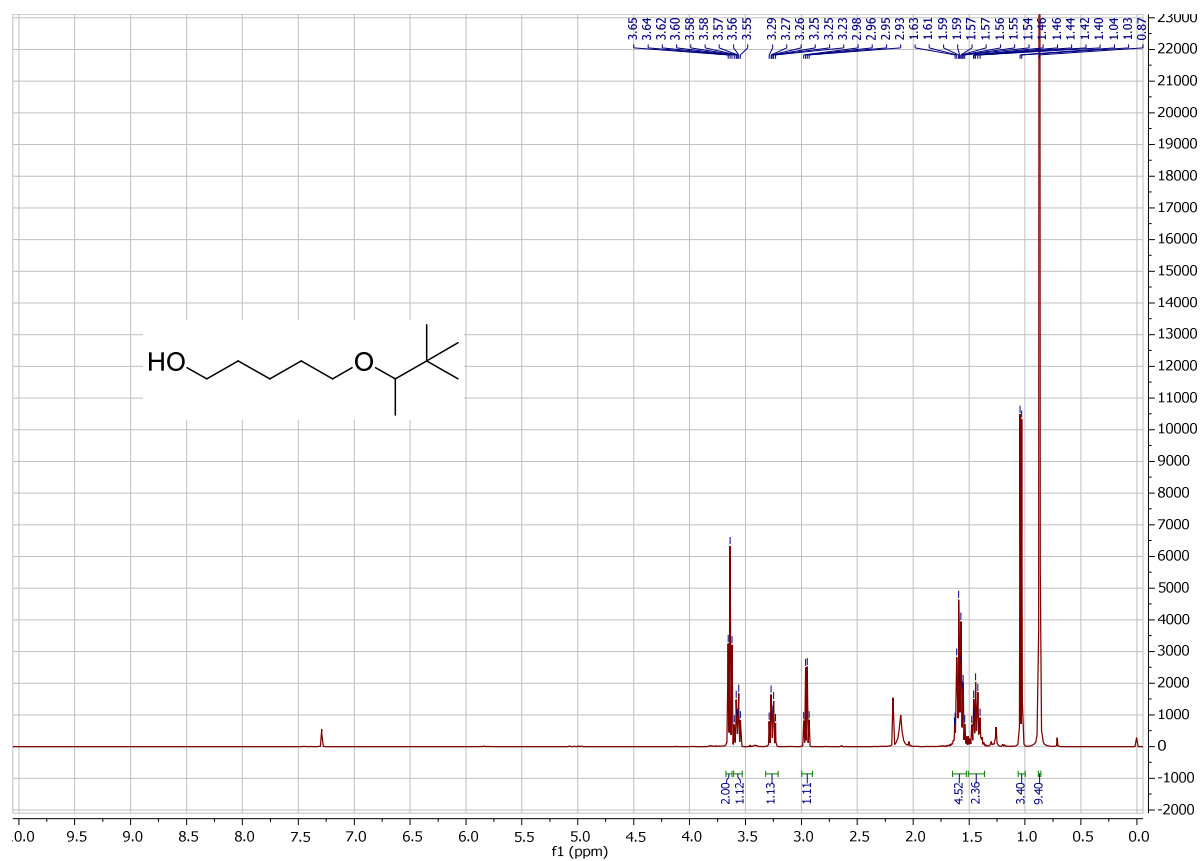




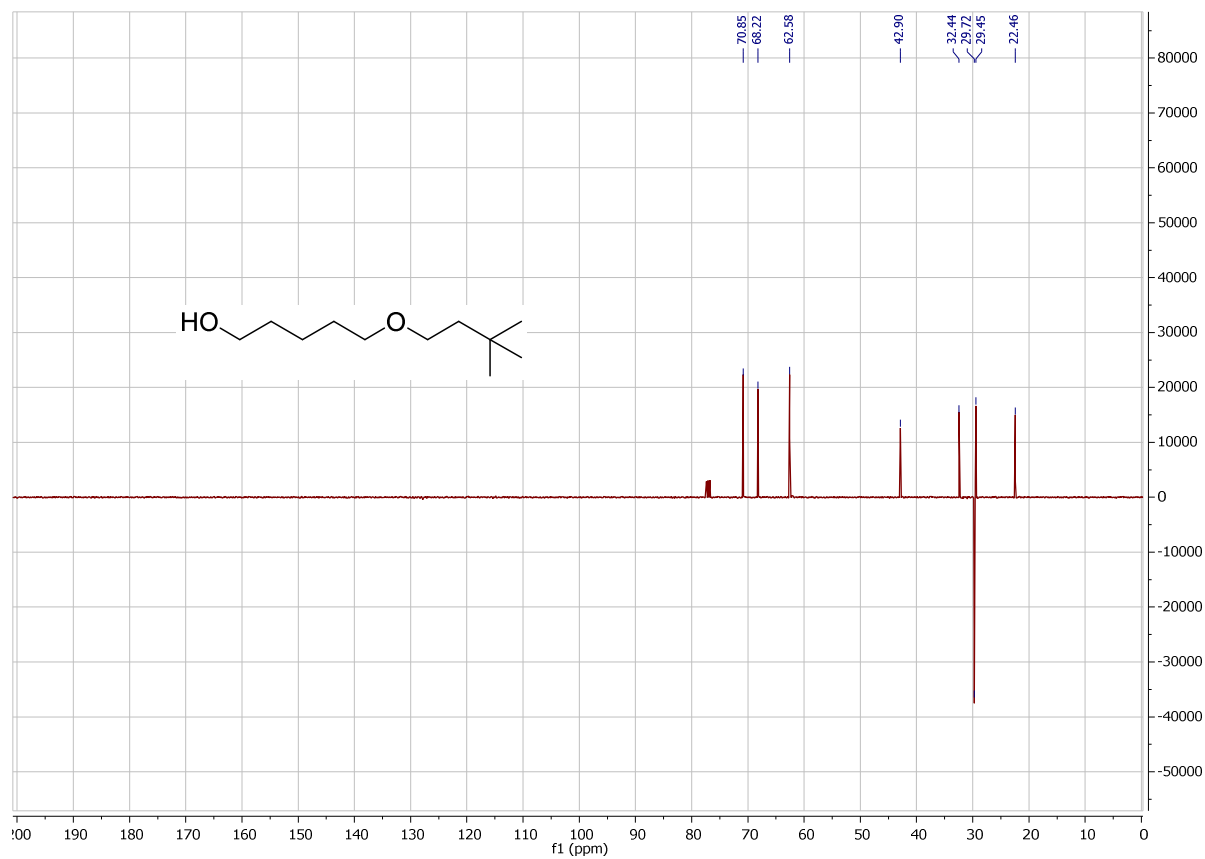
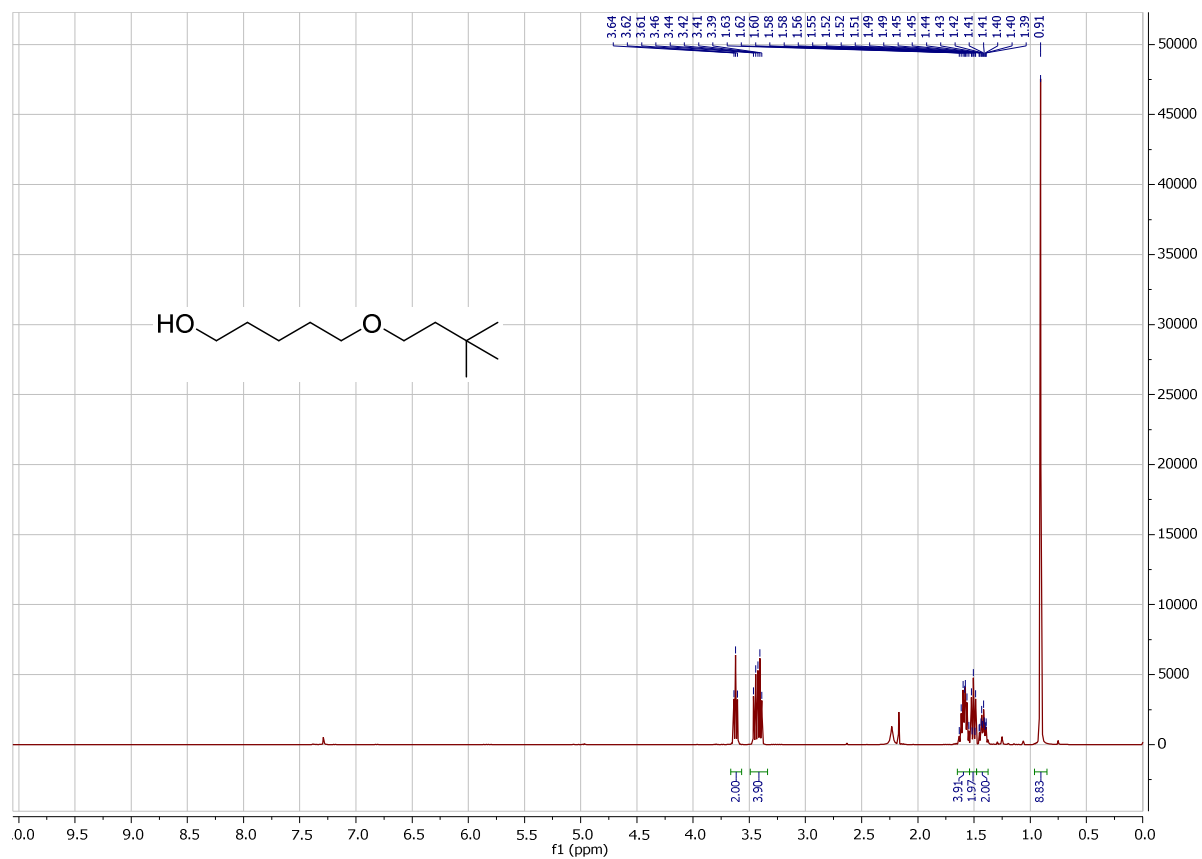
**<sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound B24 in CDCl<sub>3</sub>.**



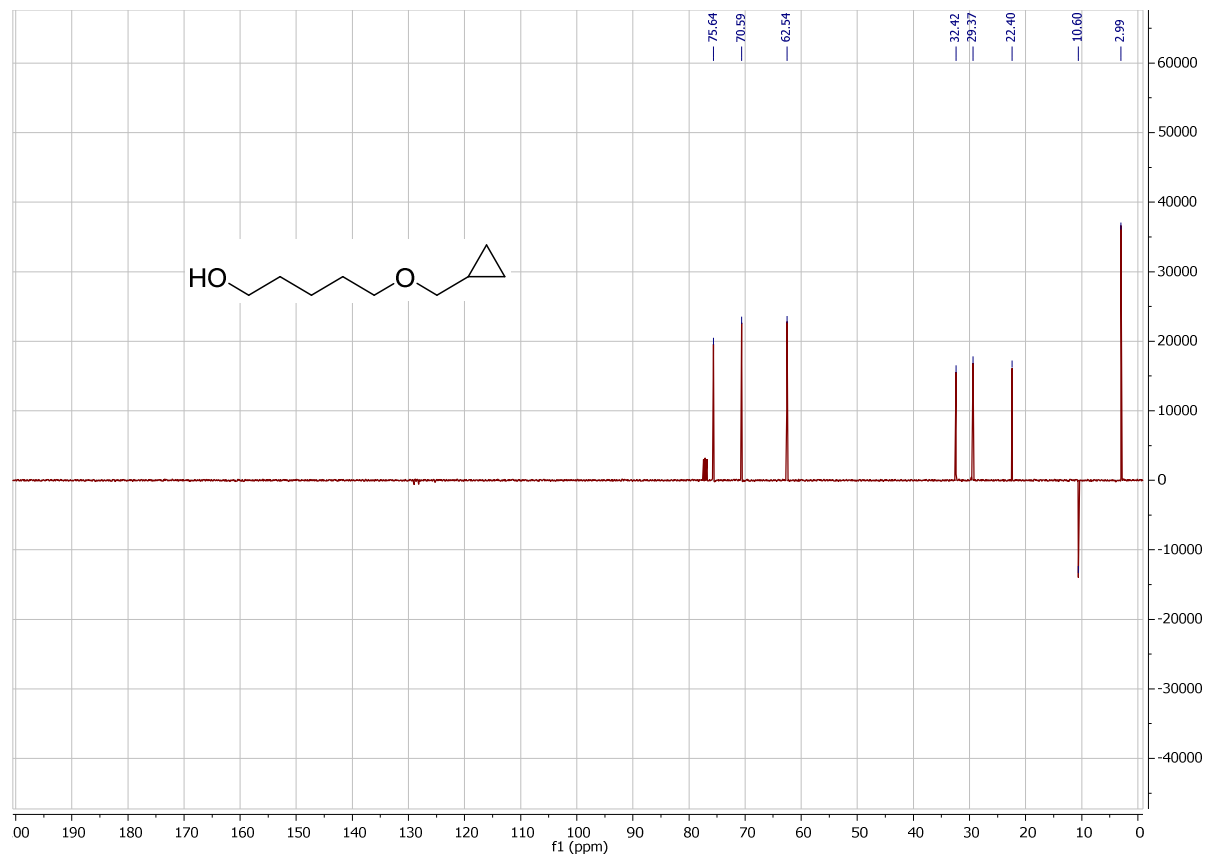
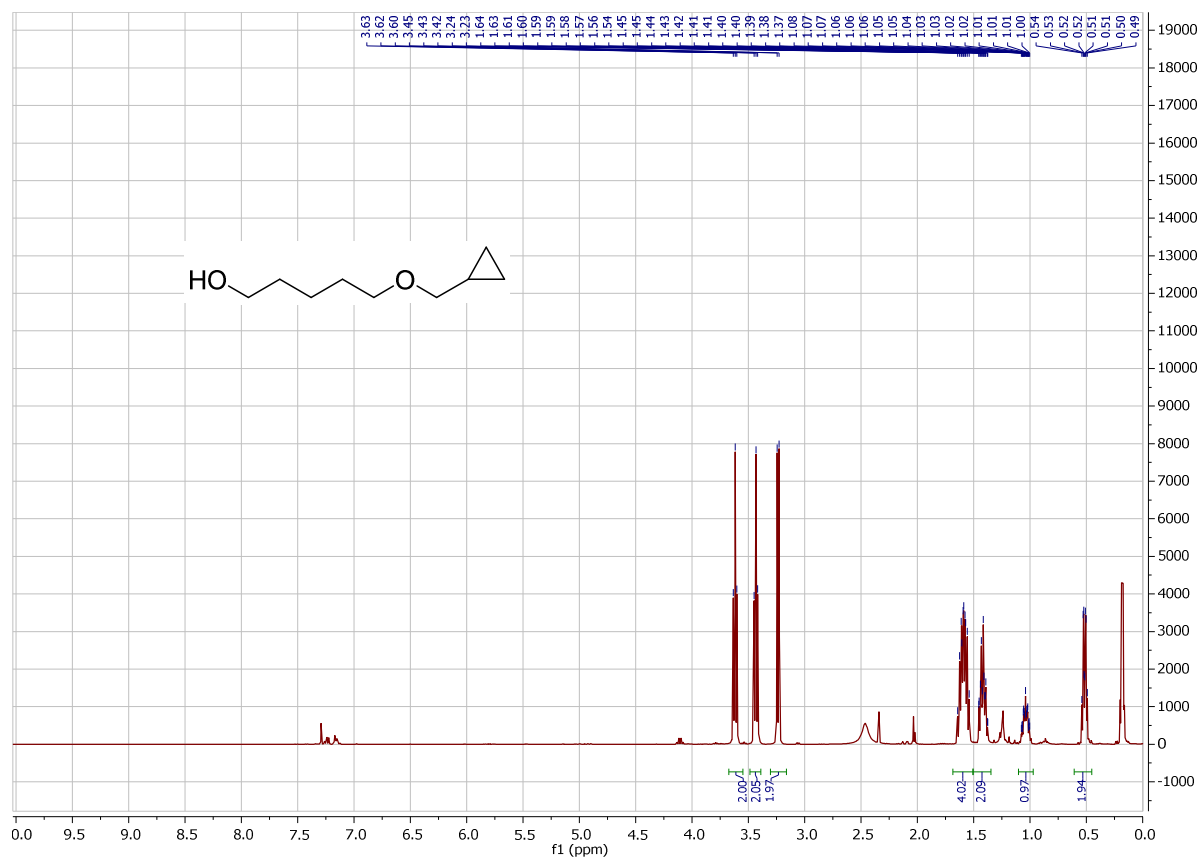
<sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound B25 in CDCl<sub>3</sub>.



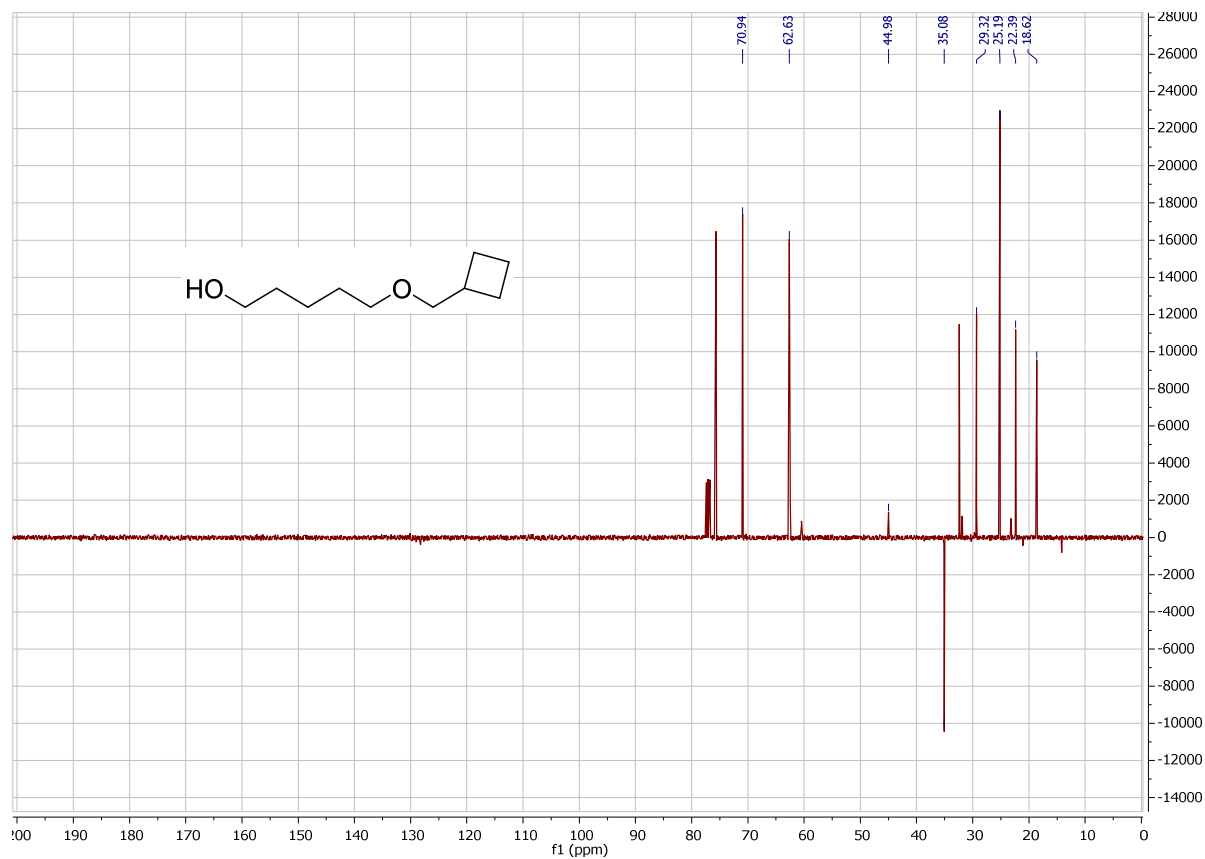
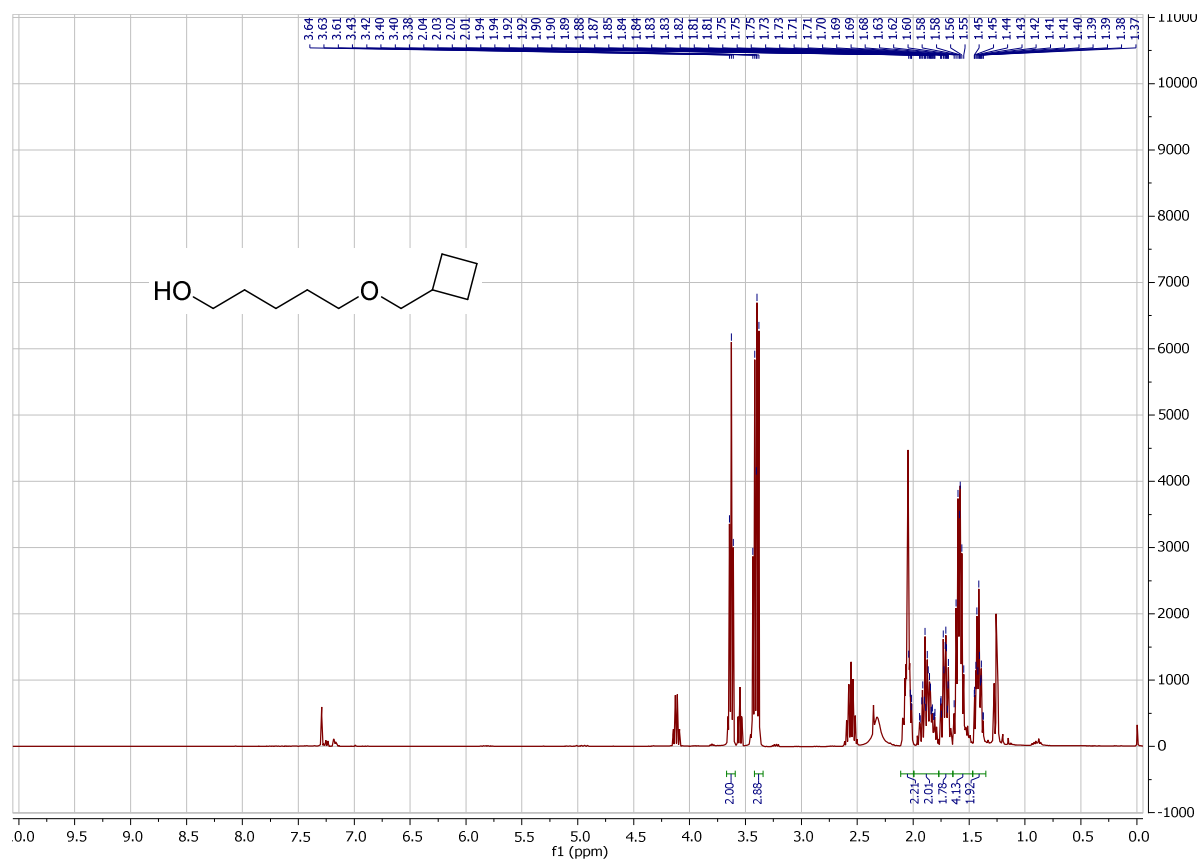
<sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound B26 in CDCl<sub>3</sub>.



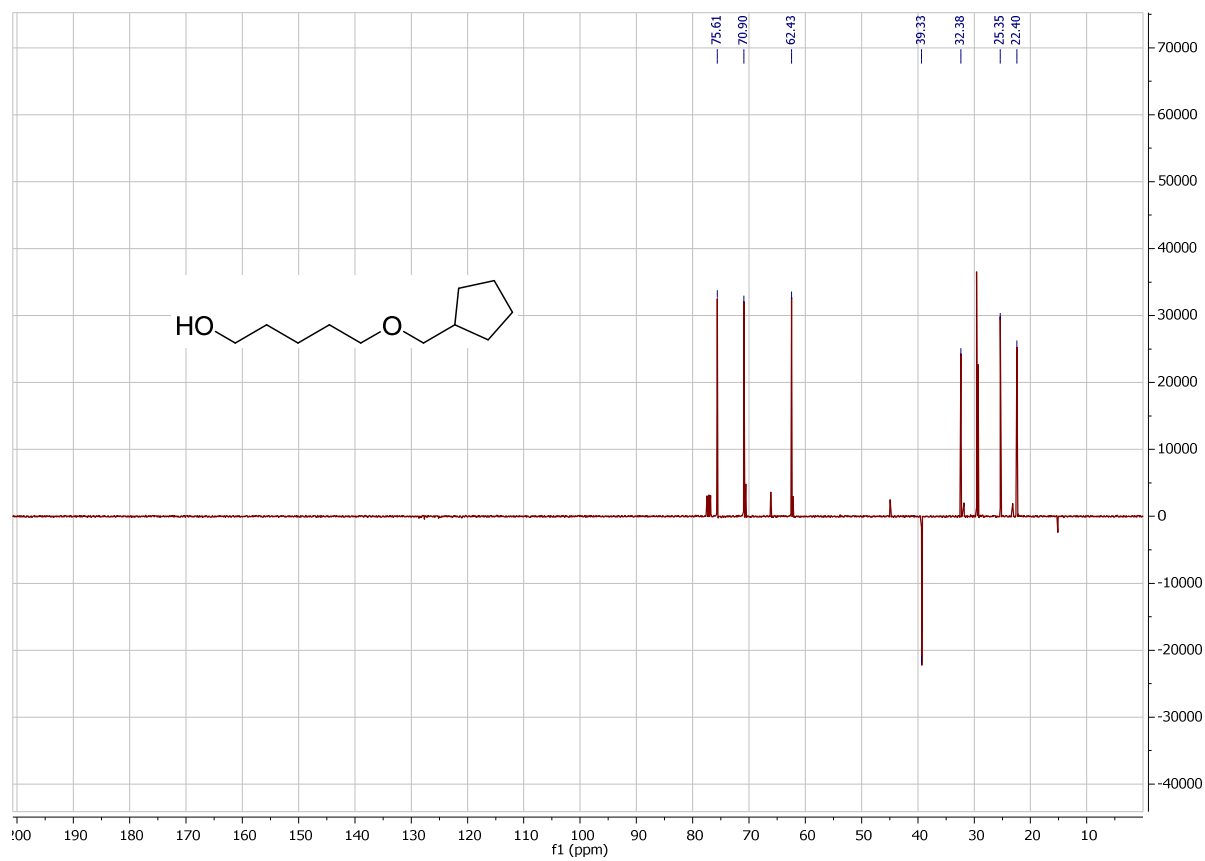
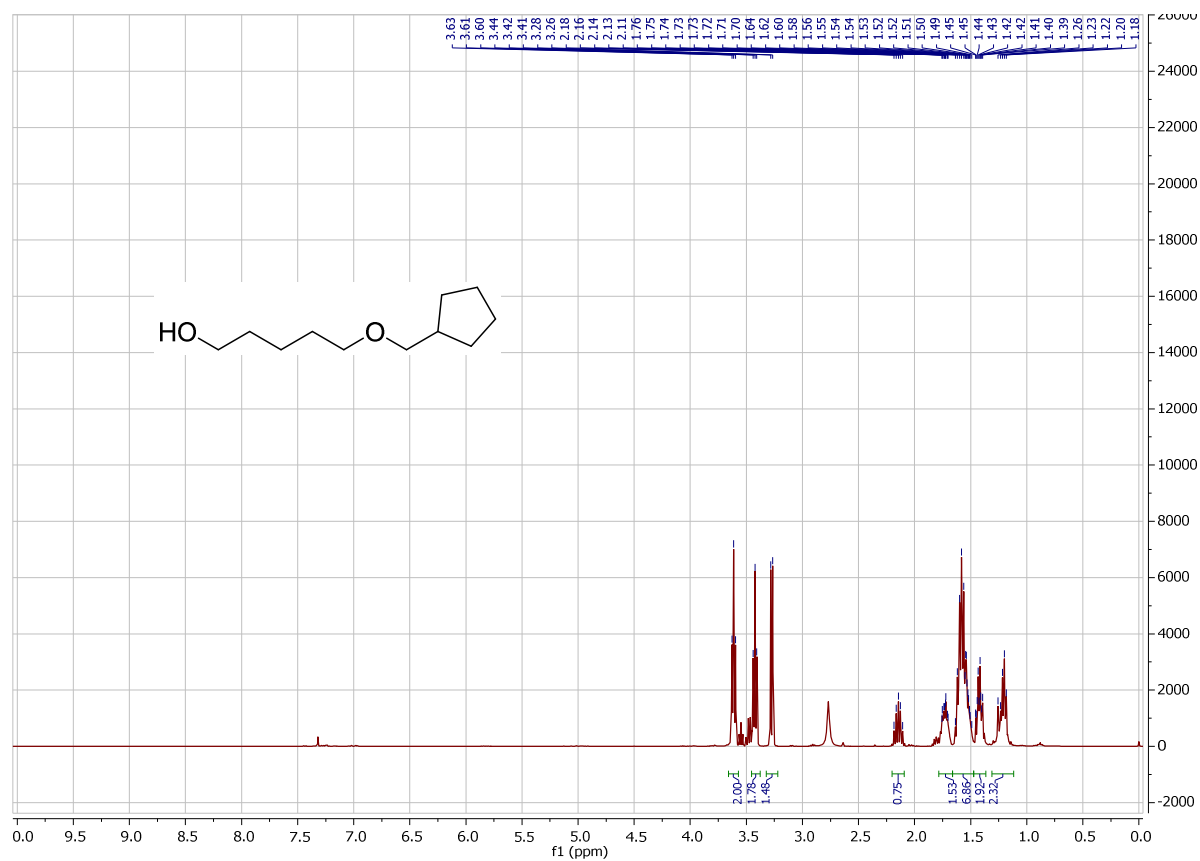
# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound B27 in $\text{CDCl}_3$ .



<sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound B28 in CDCl<sub>3</sub>.

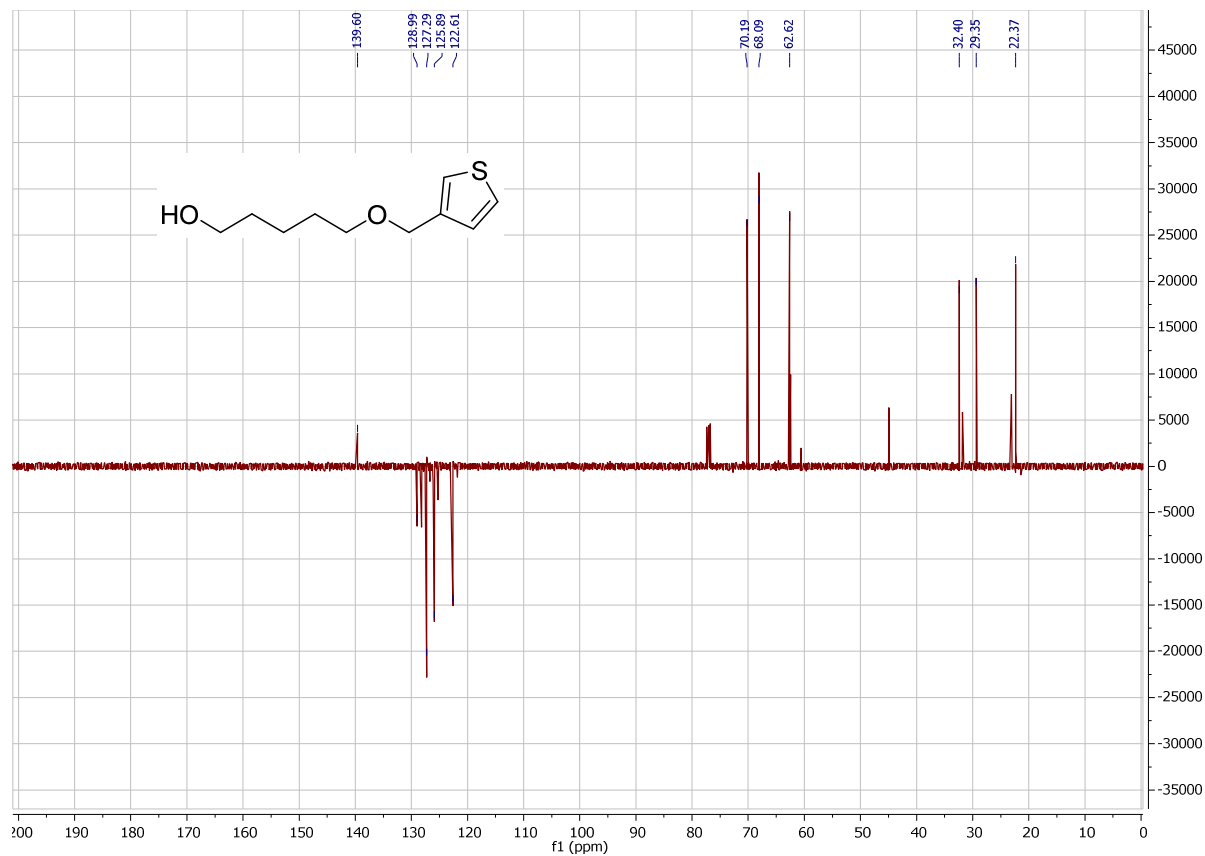
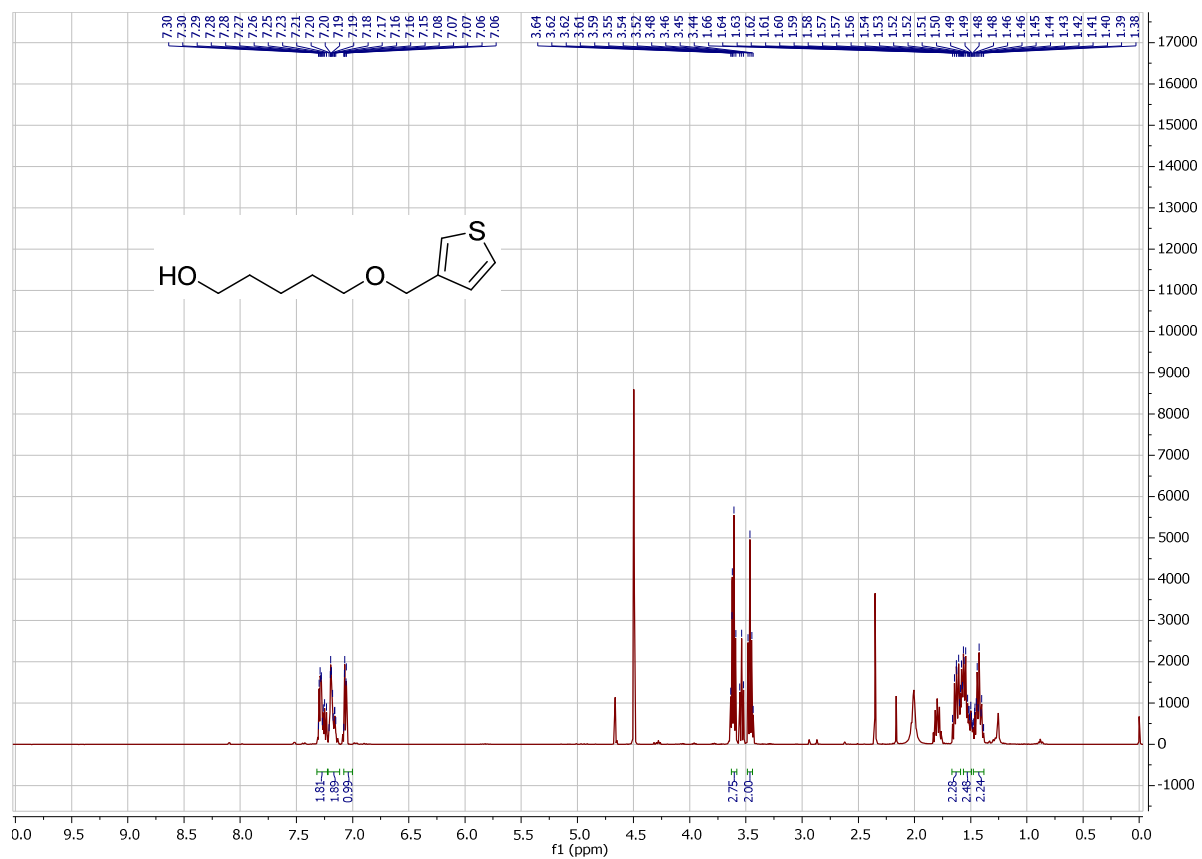


<sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound B29 in CDCl<sub>3</sub>.

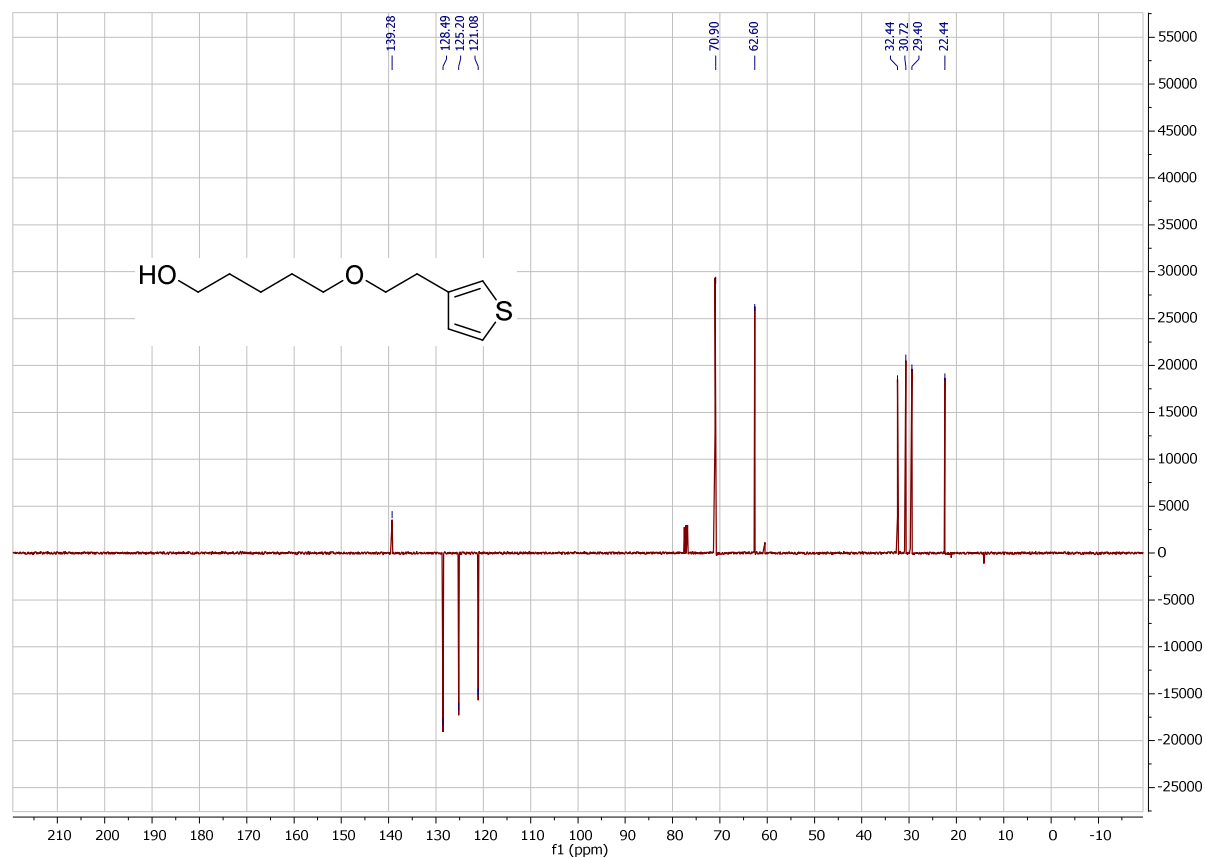
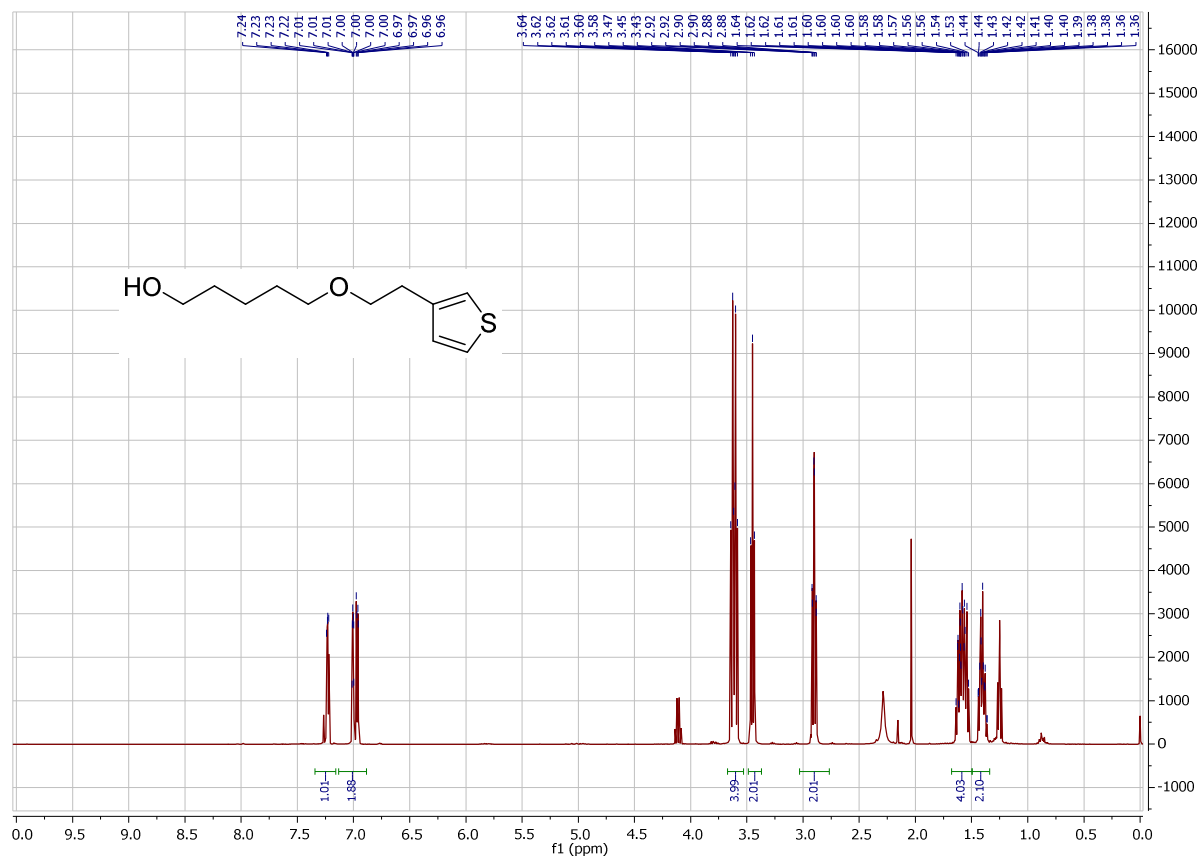




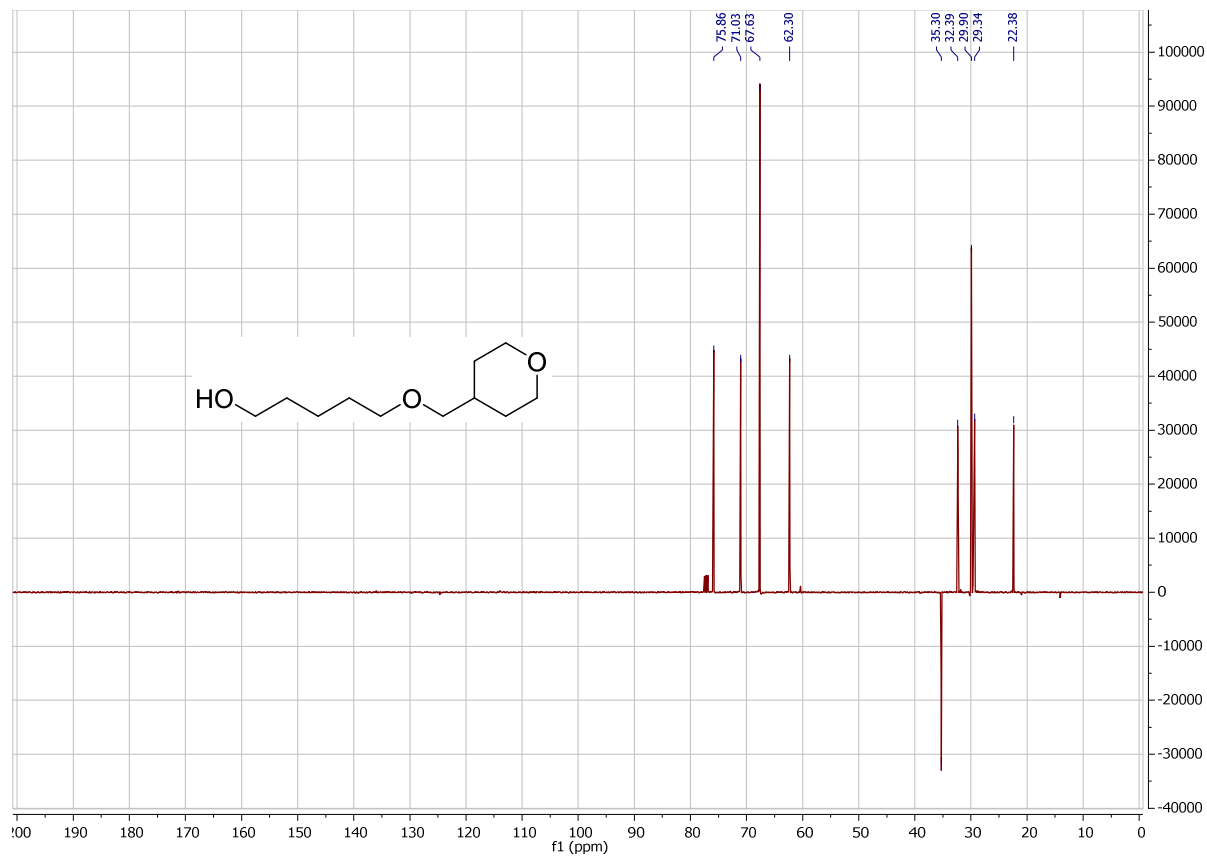
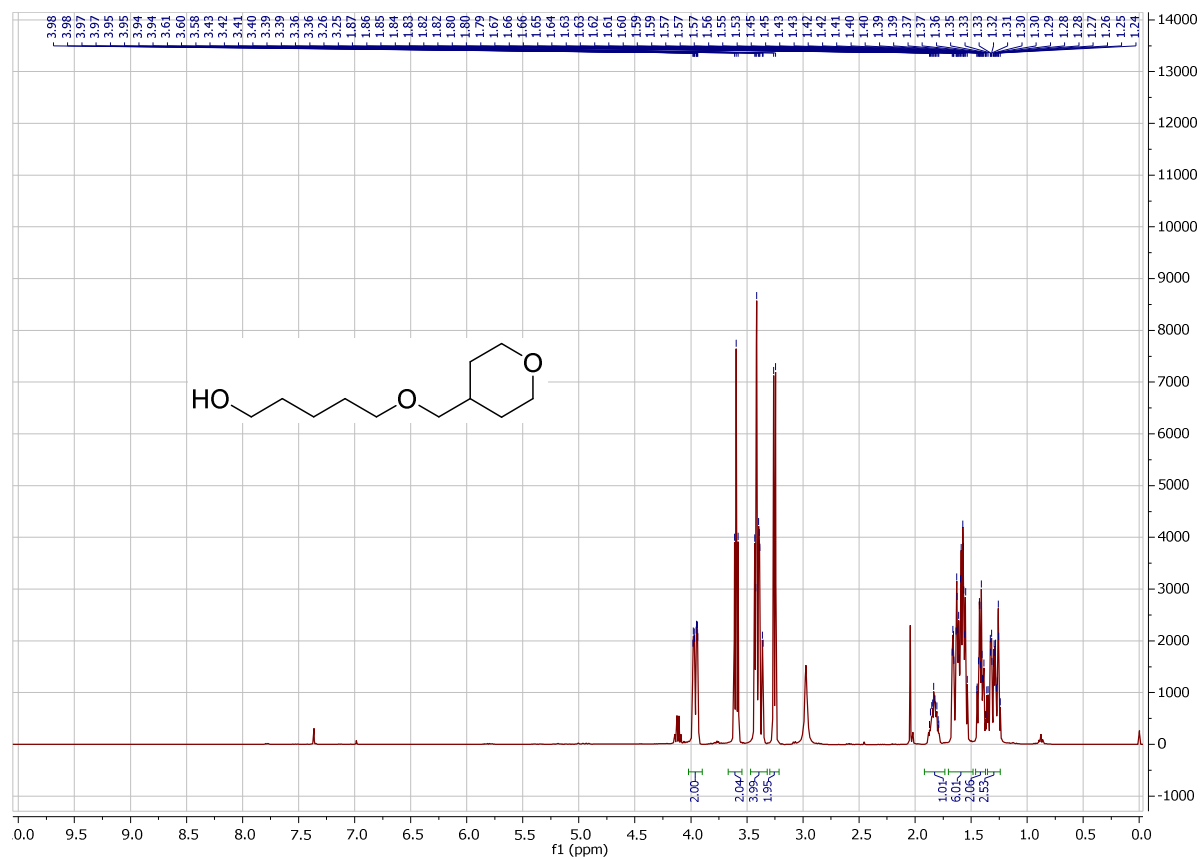
# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound B30 in $\text{CDCl}_3$ .



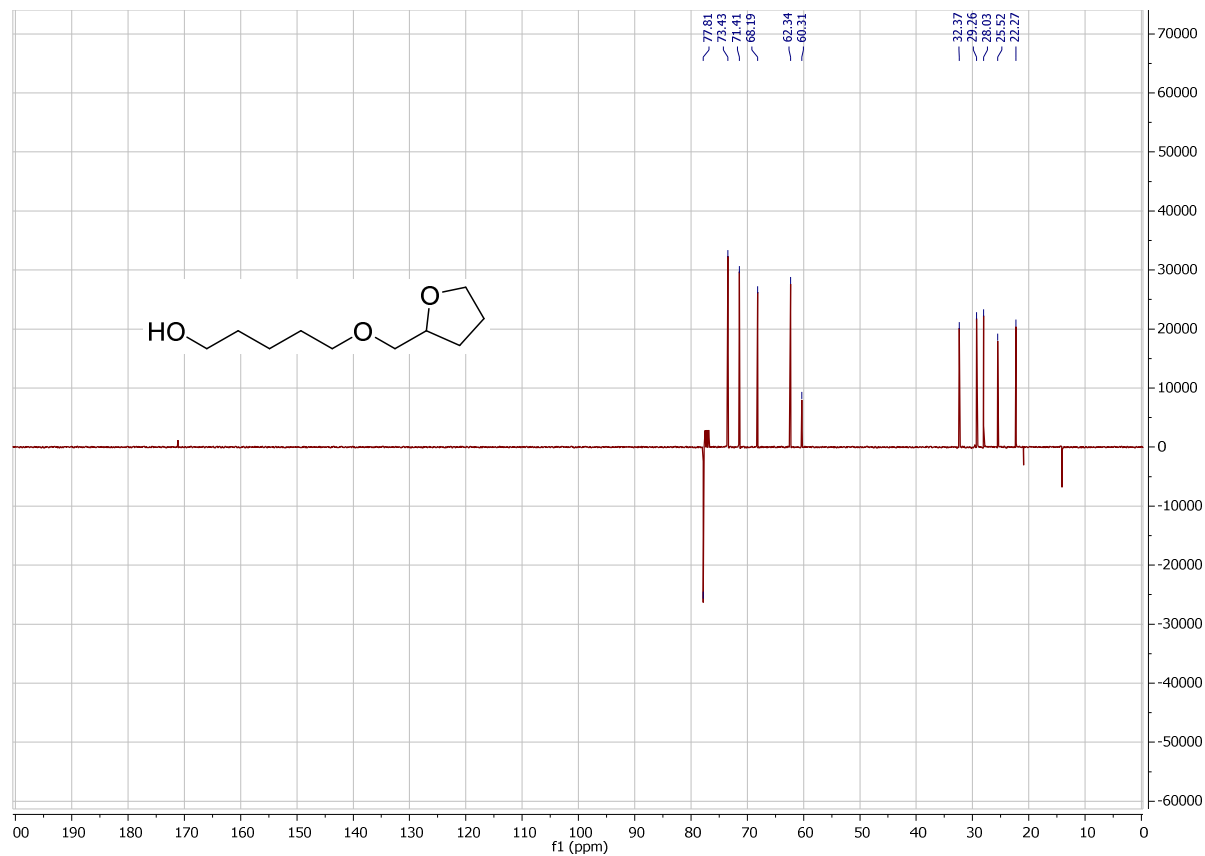
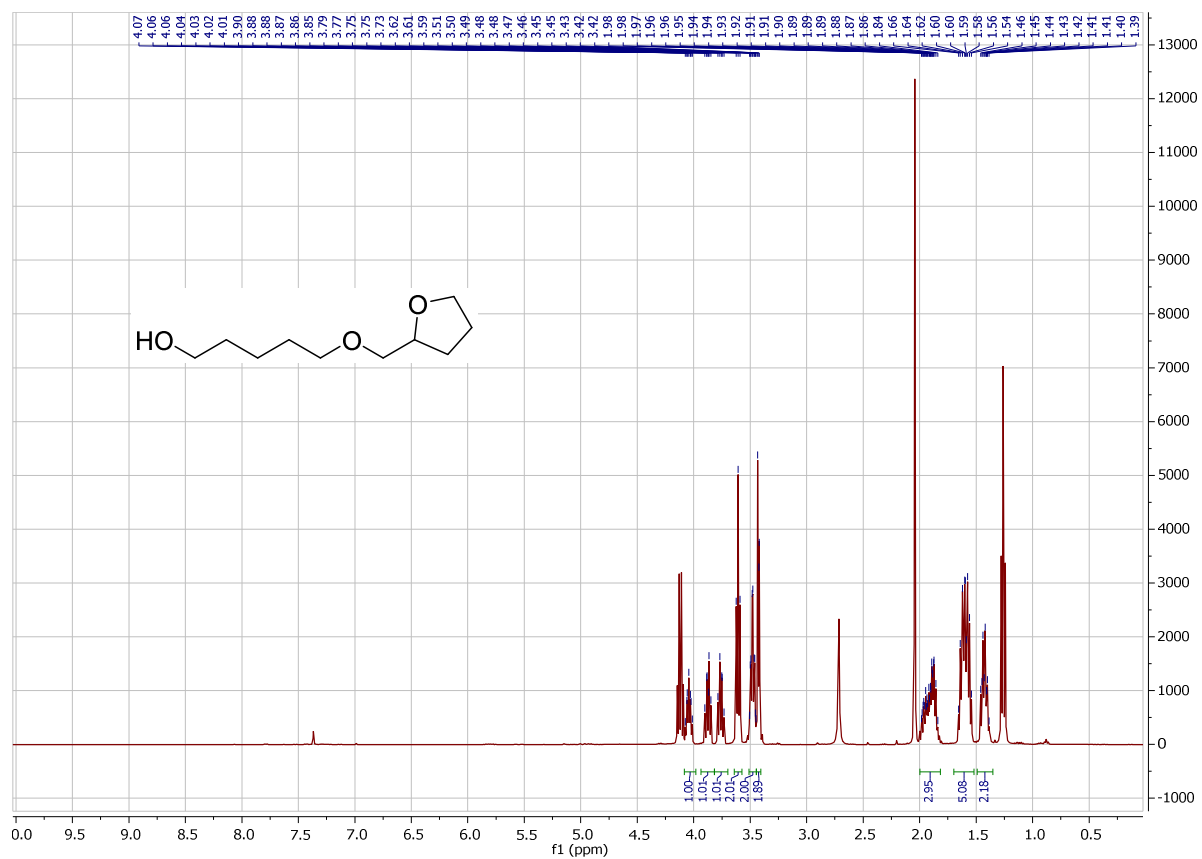
# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound B31 in $\text{CDCl}_3$ .



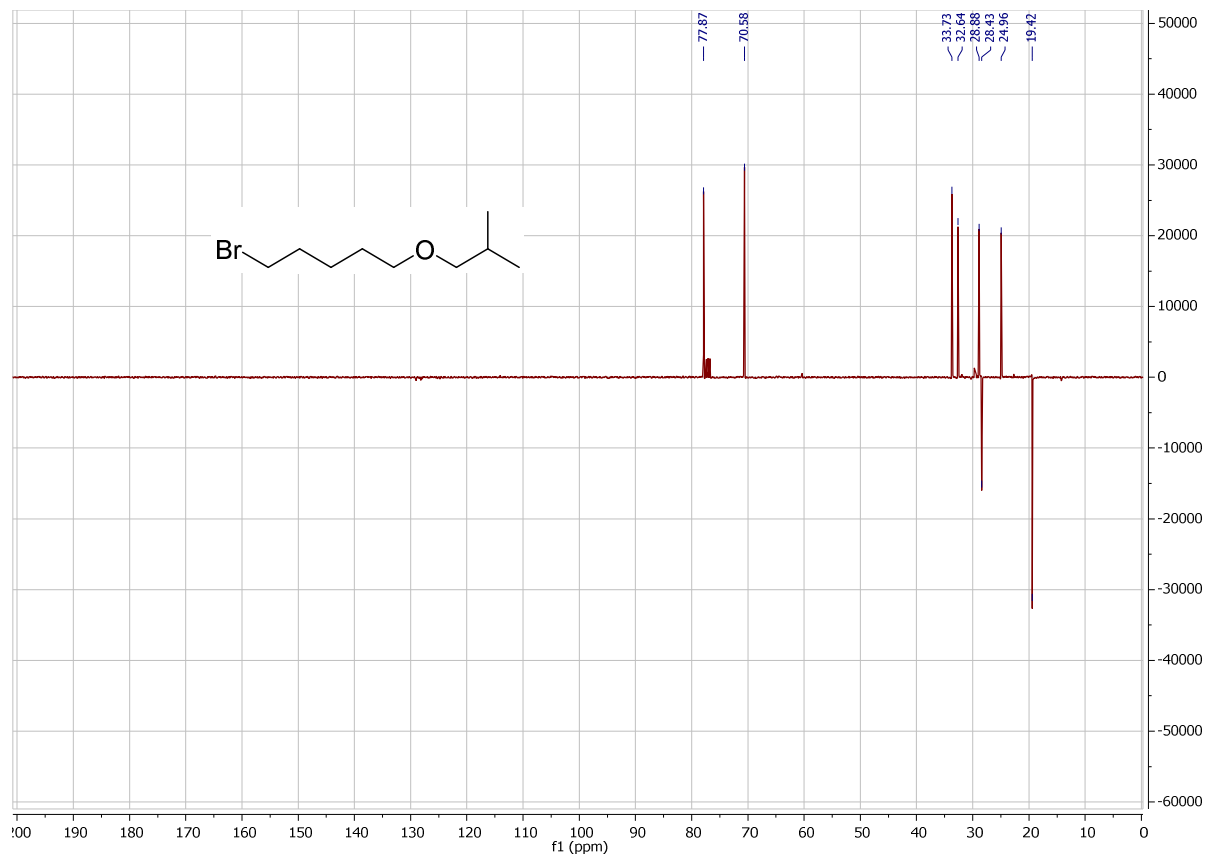
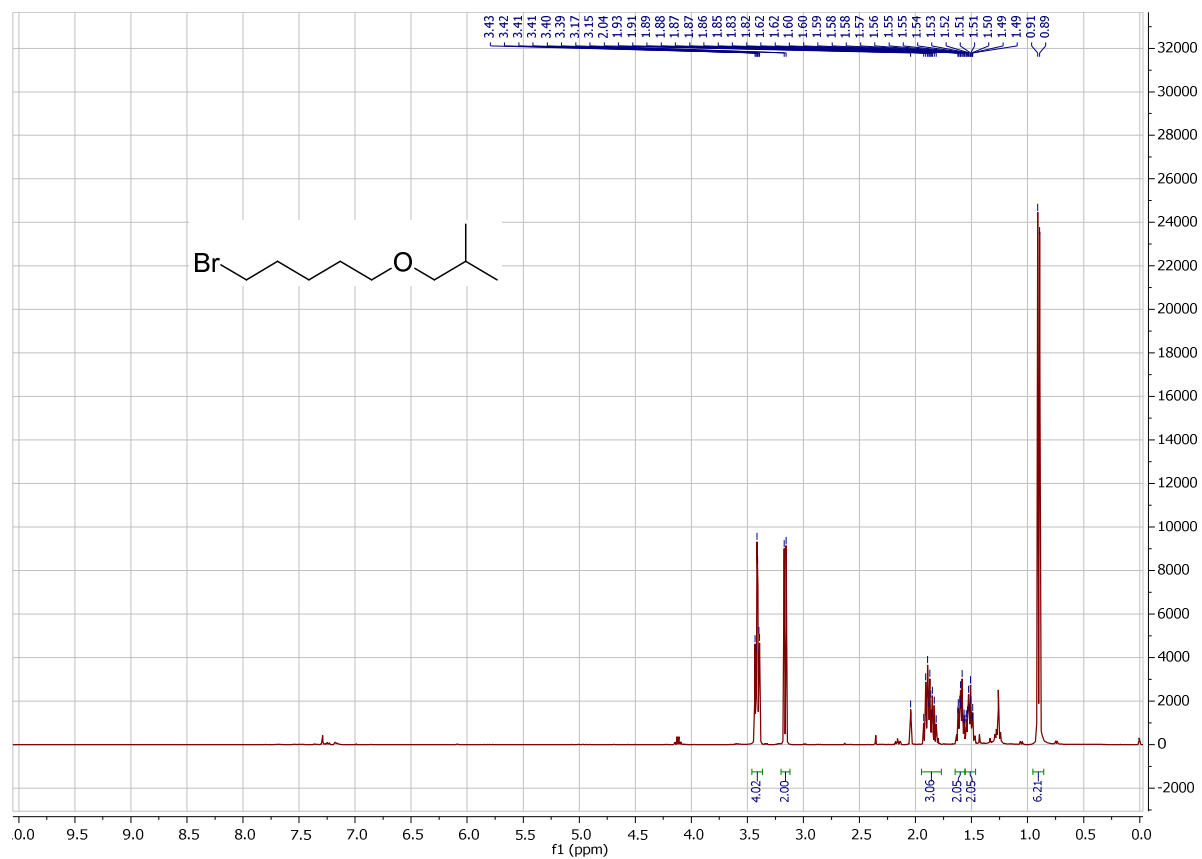
# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound B32 in $\text{CDCl}_3$ .



**$^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  of compound B33 in  $\text{CDCl}_3$ .**

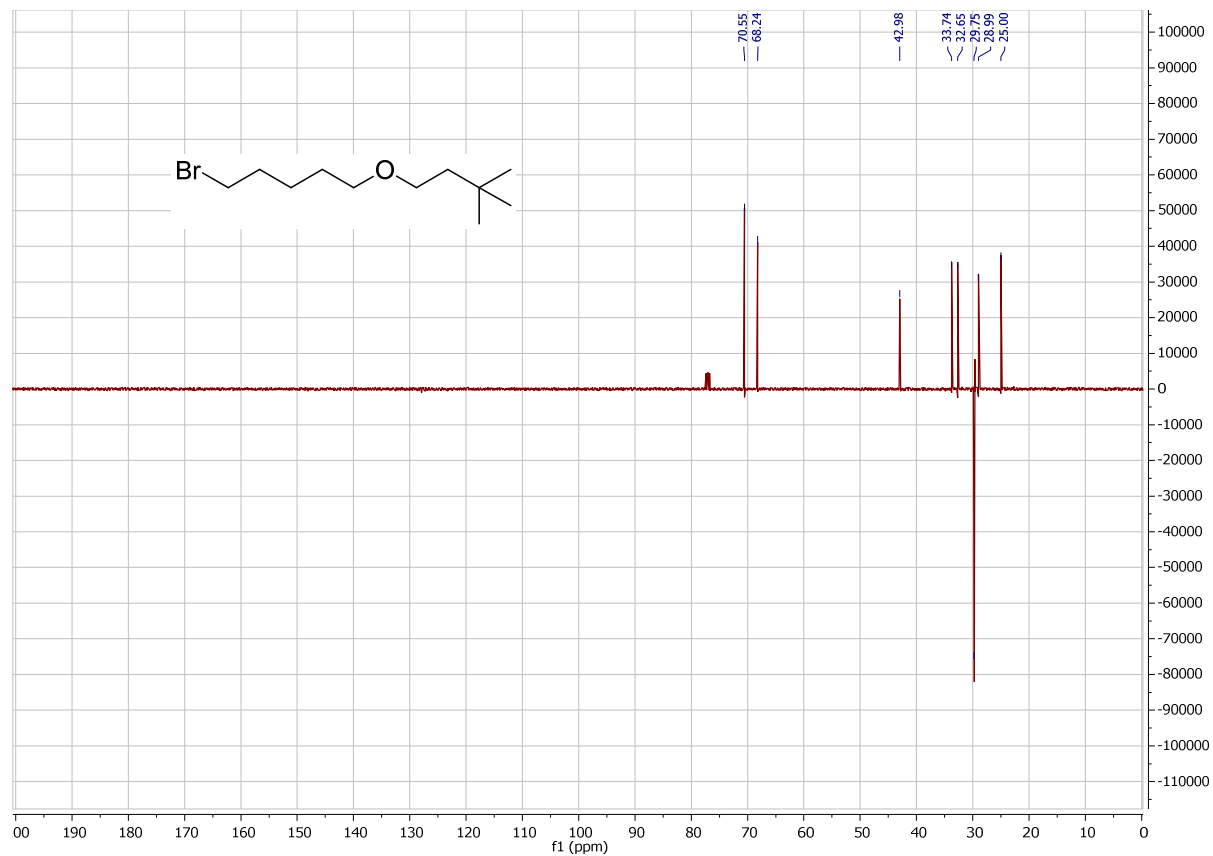
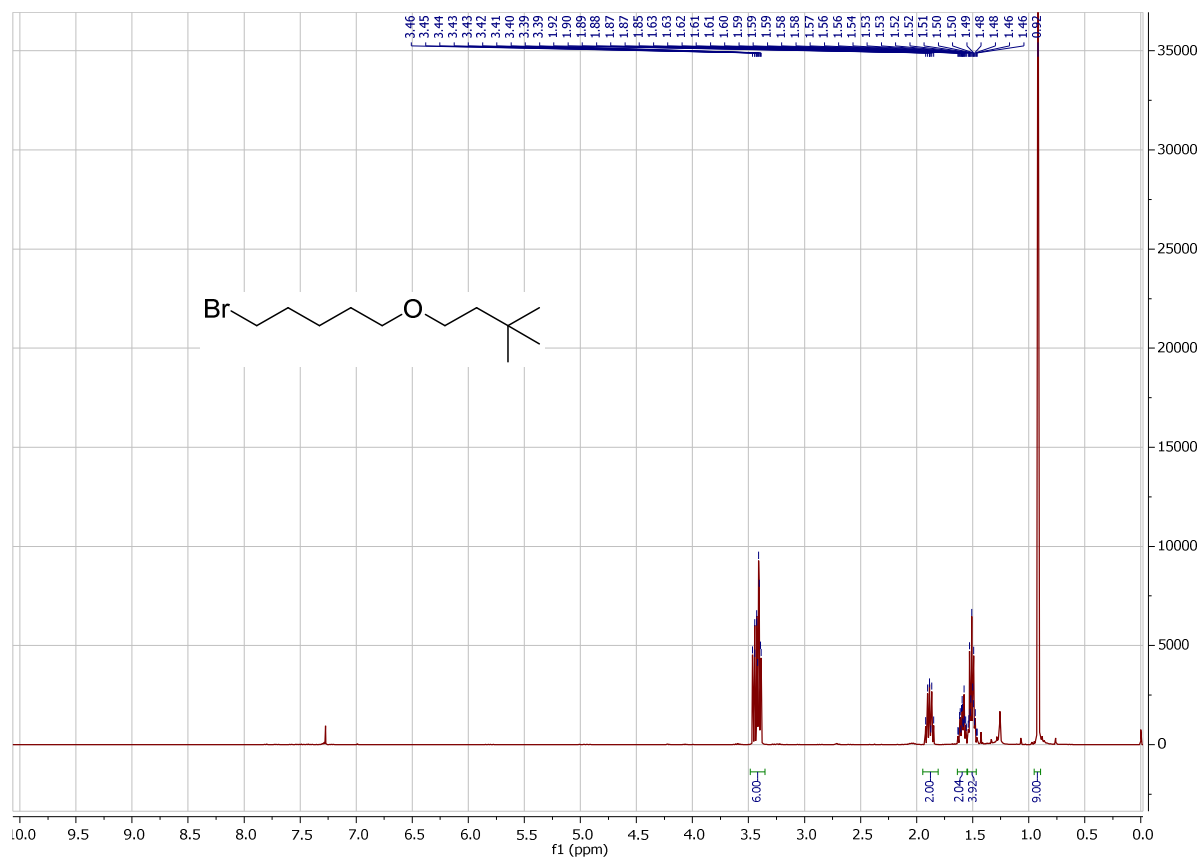


**$^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  of compound B34 in  $\text{CDCl}_3$ .**

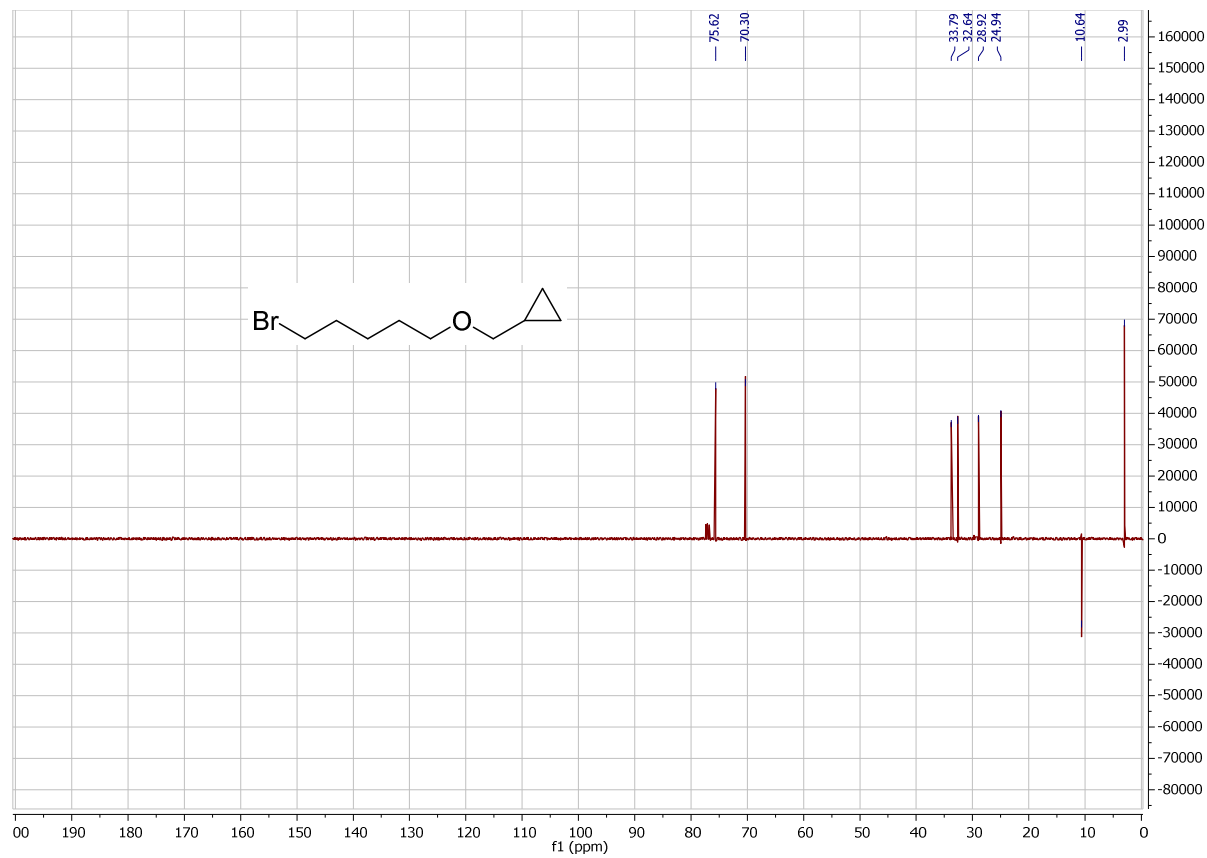
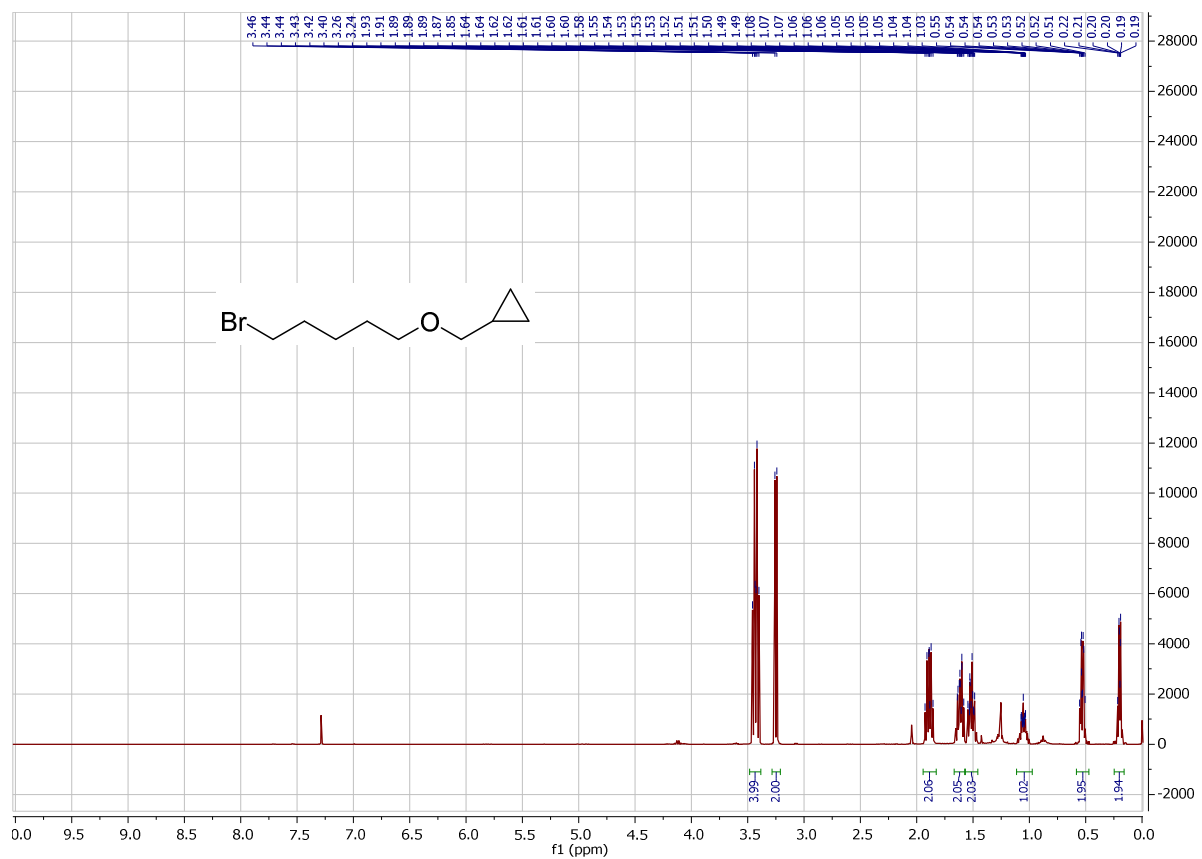




<sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound B36 in CDCl<sub>3</sub>.

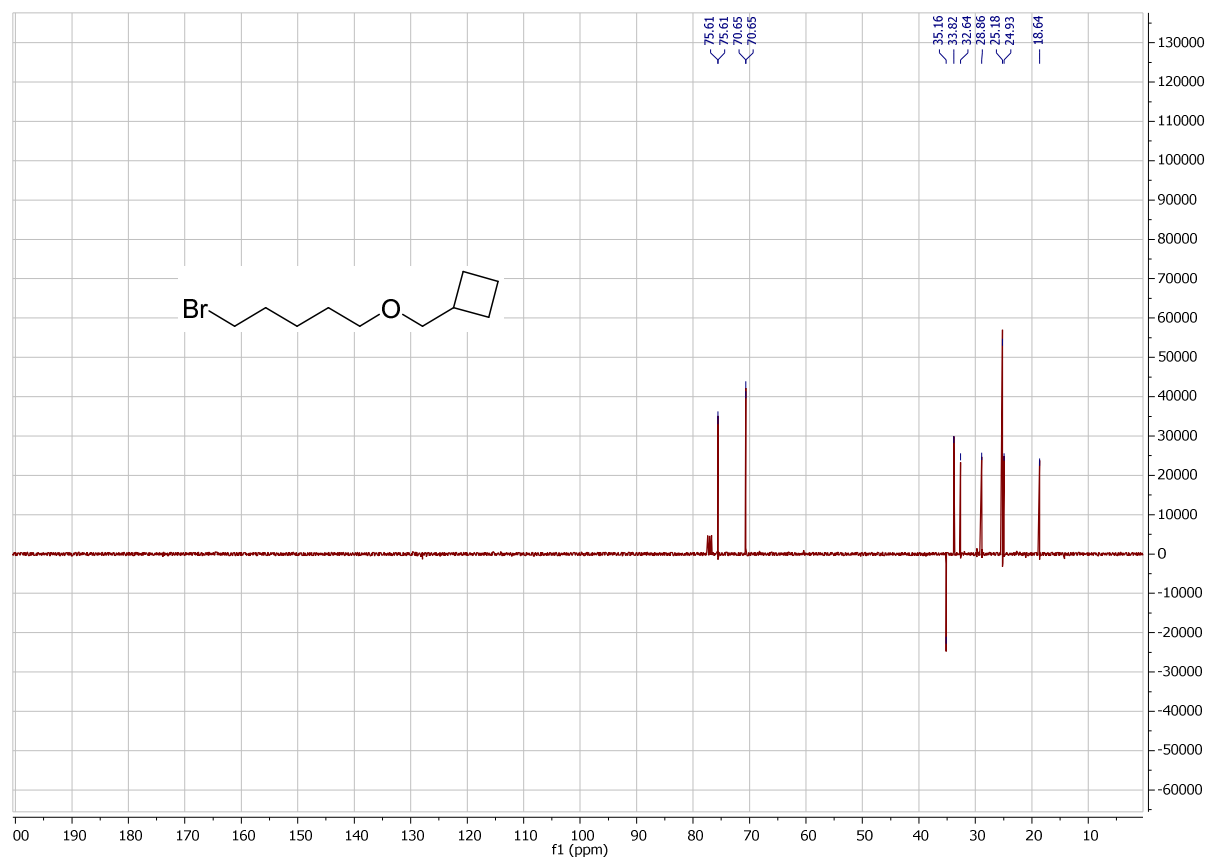
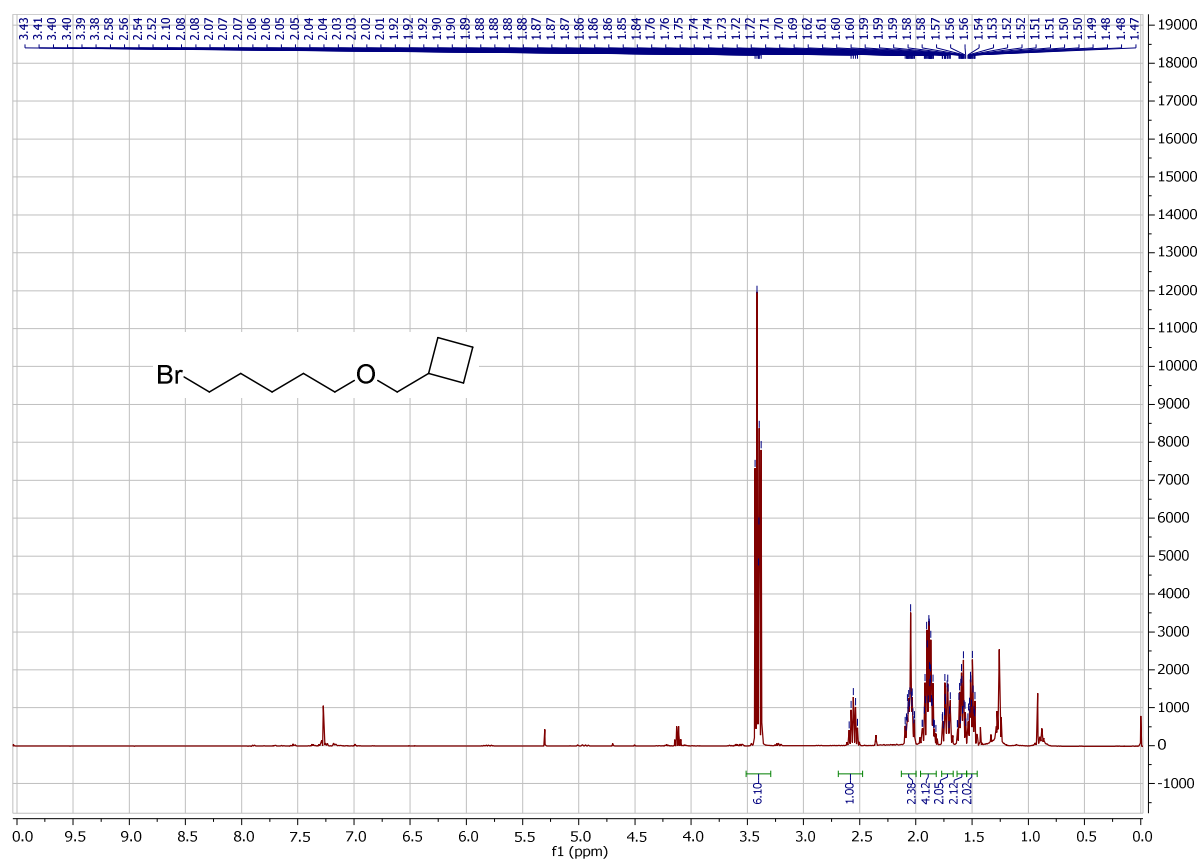


**$^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  of compound B37 in  $\text{CDCl}_3$ .**



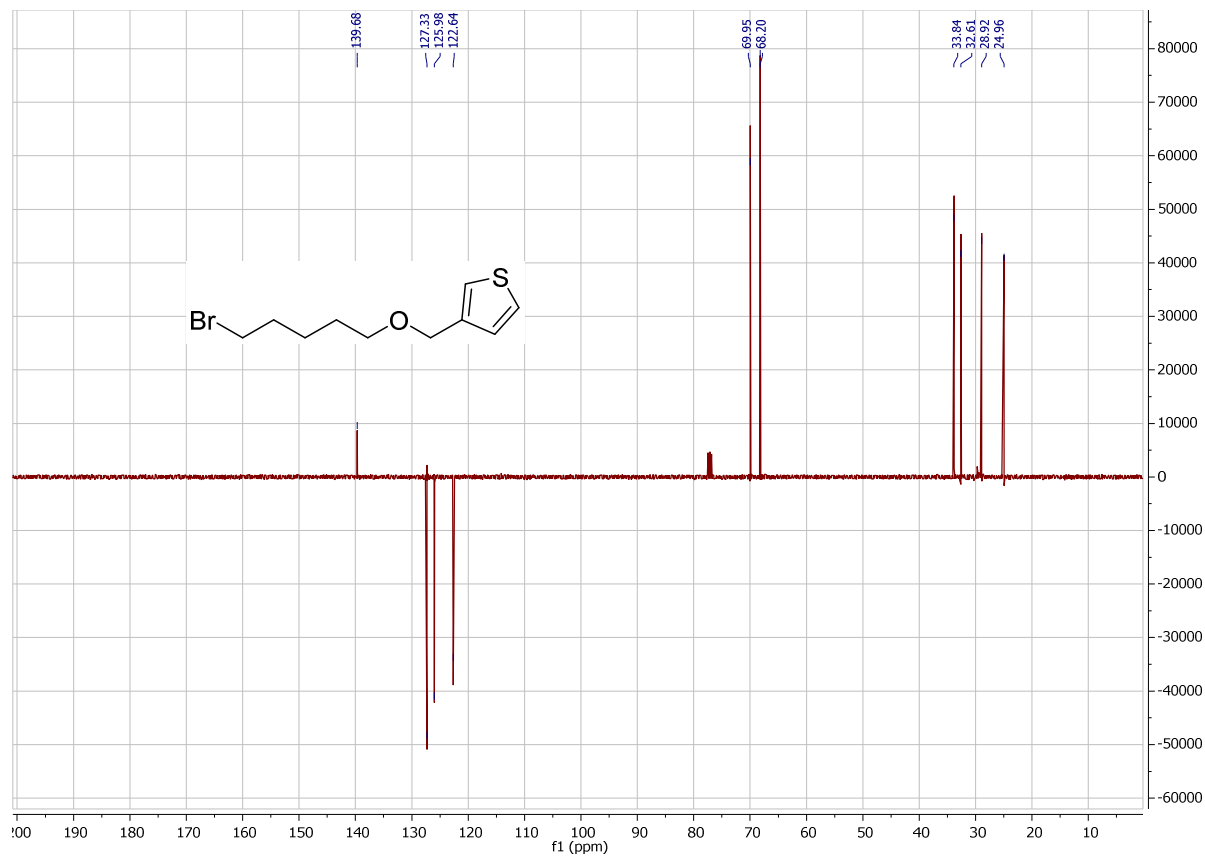
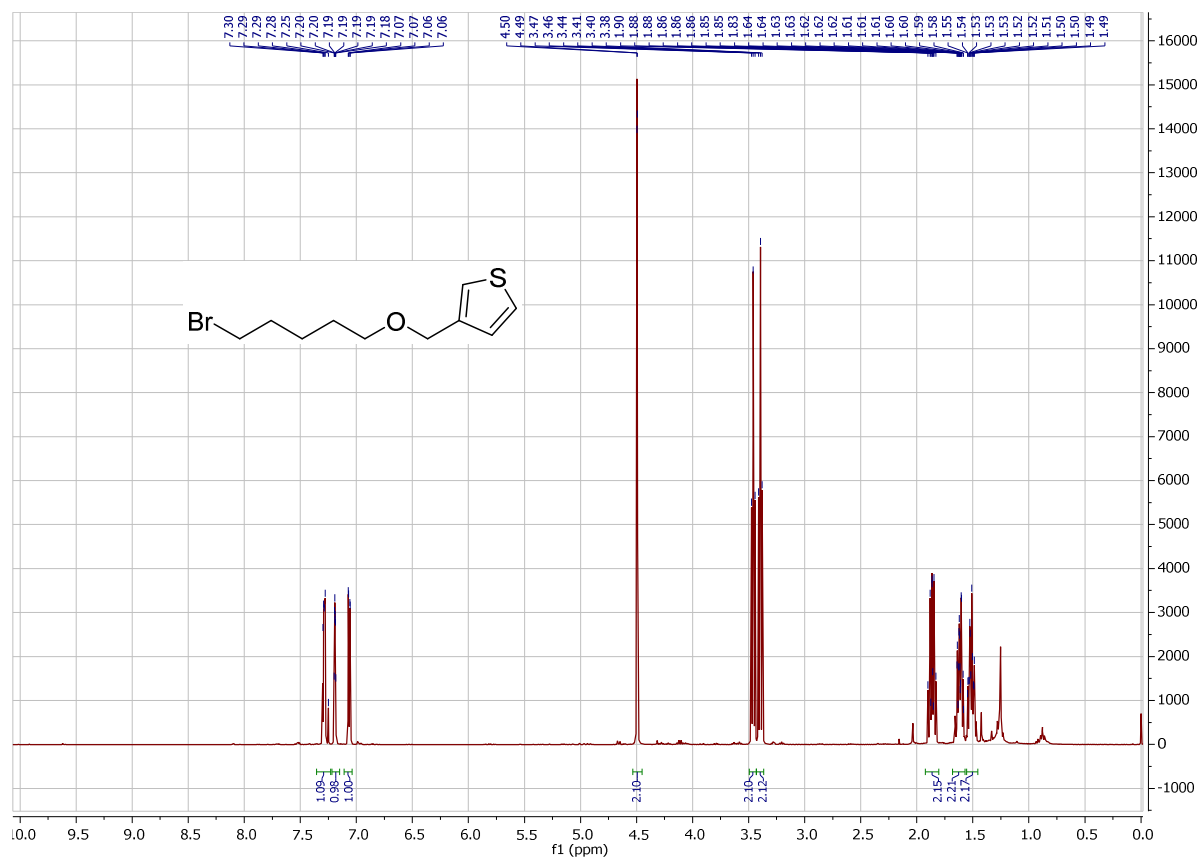


**$^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  of compound B38 in  $\text{CDCl}_3$ .**

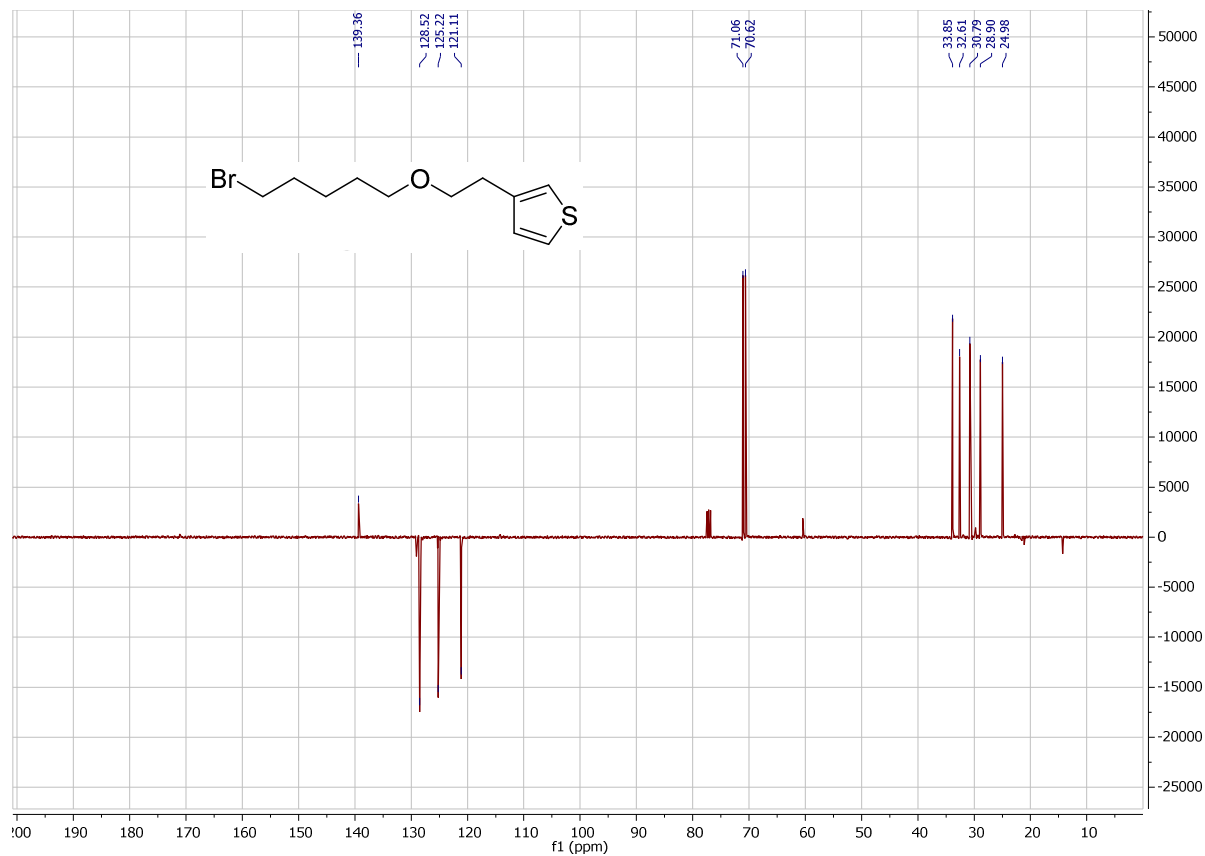
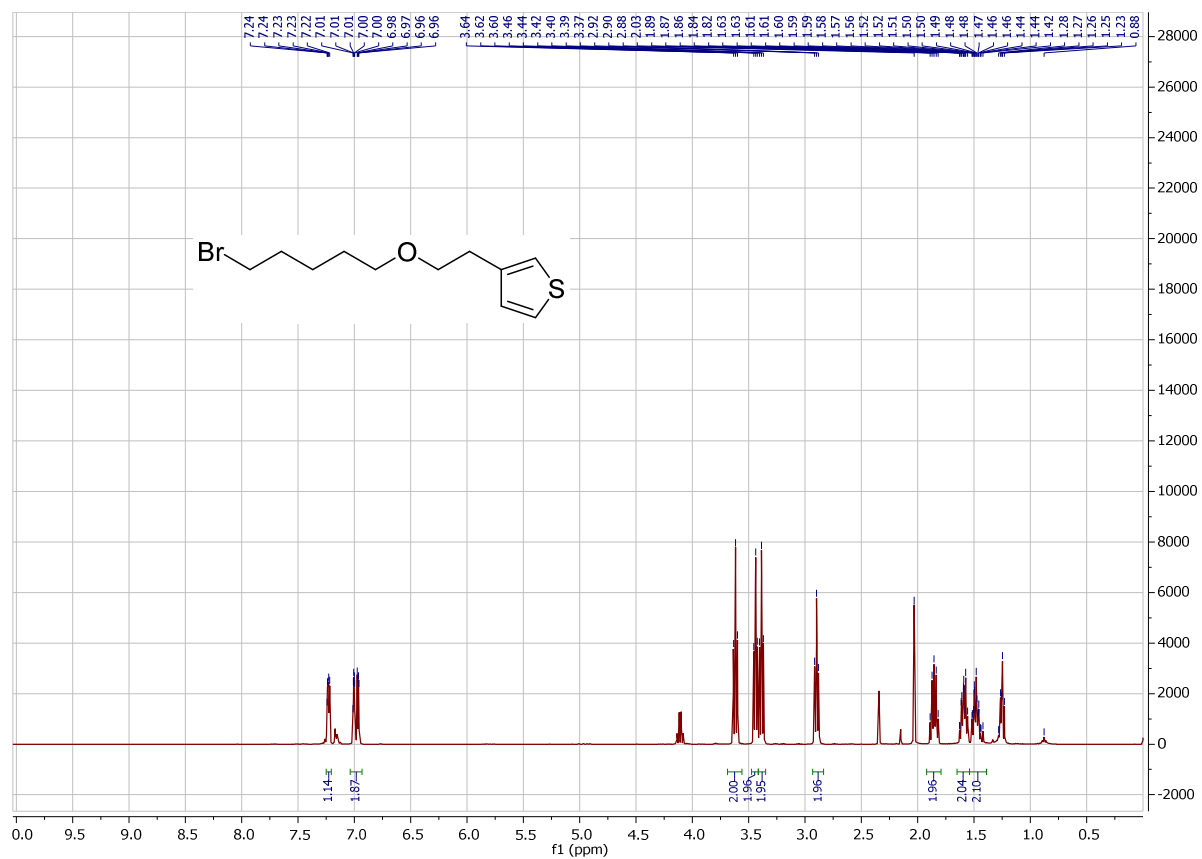




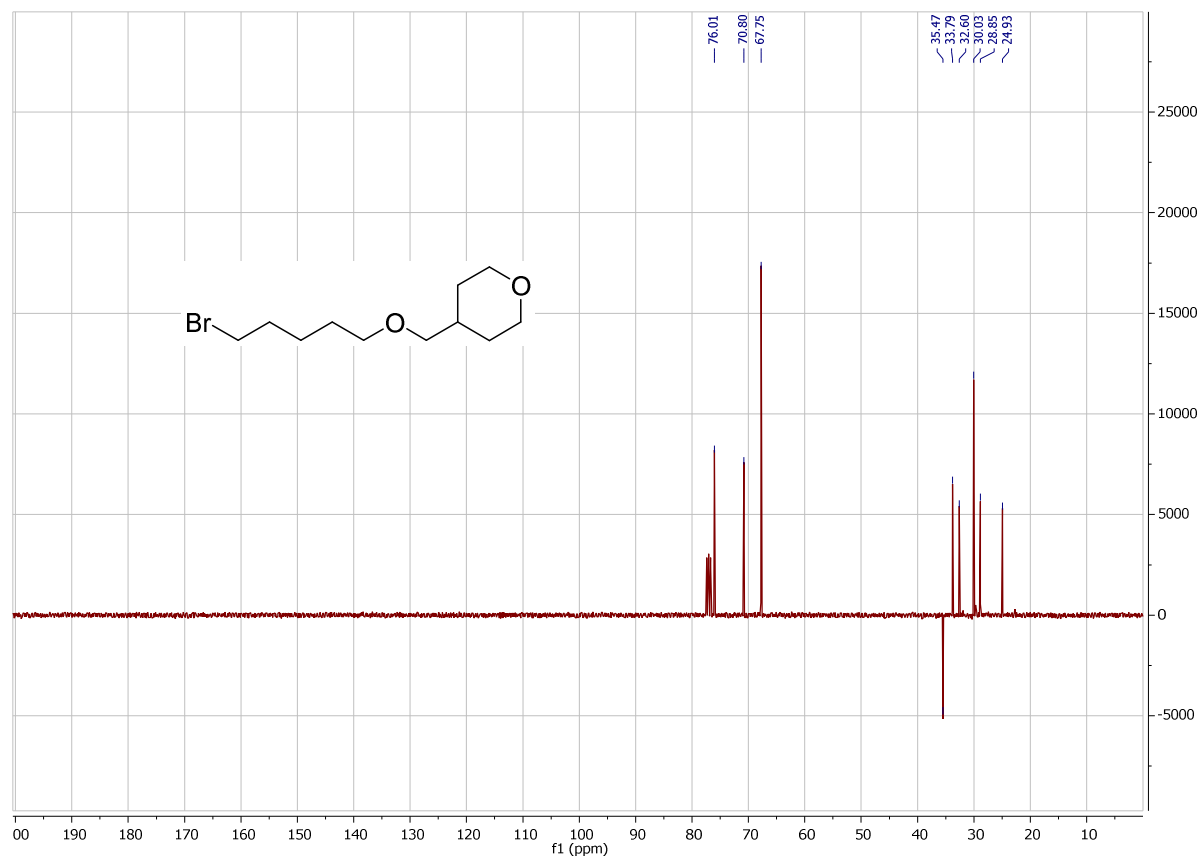
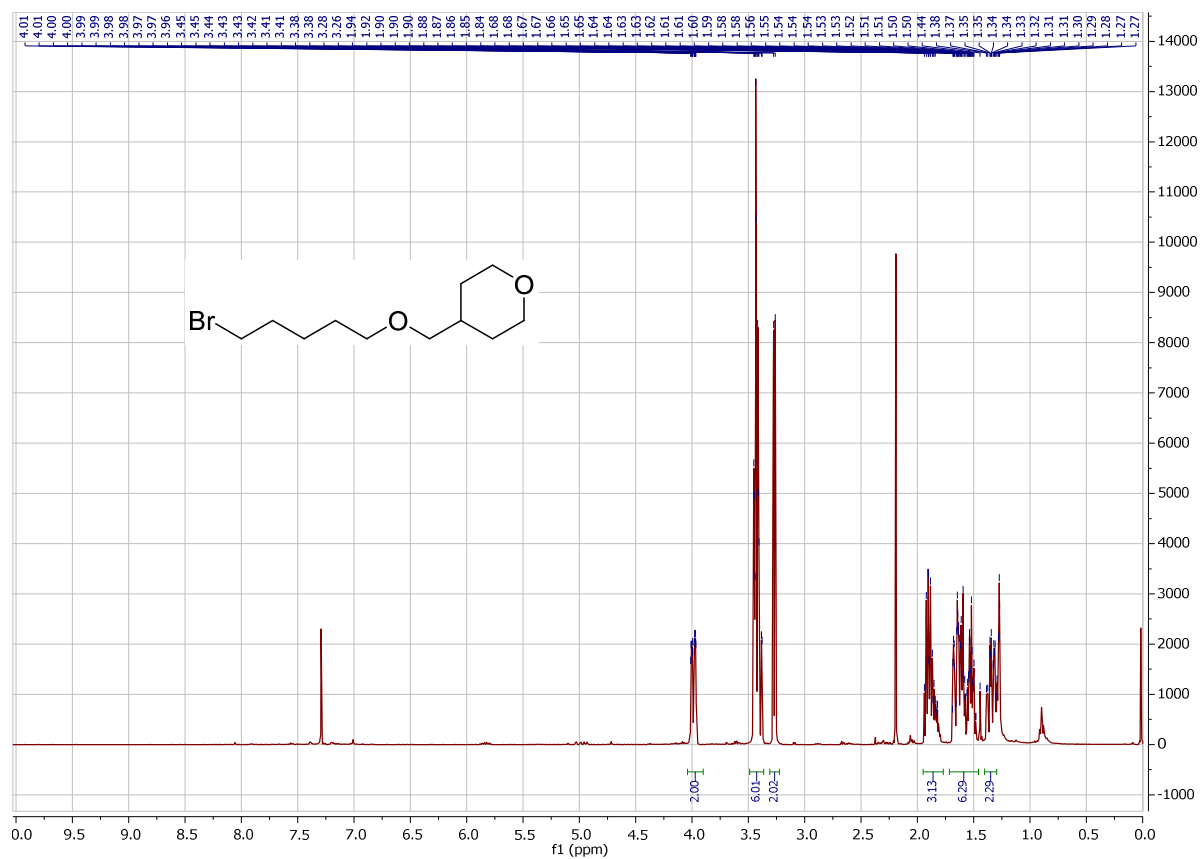
# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound B40 in $\text{CDCl}_3$ .



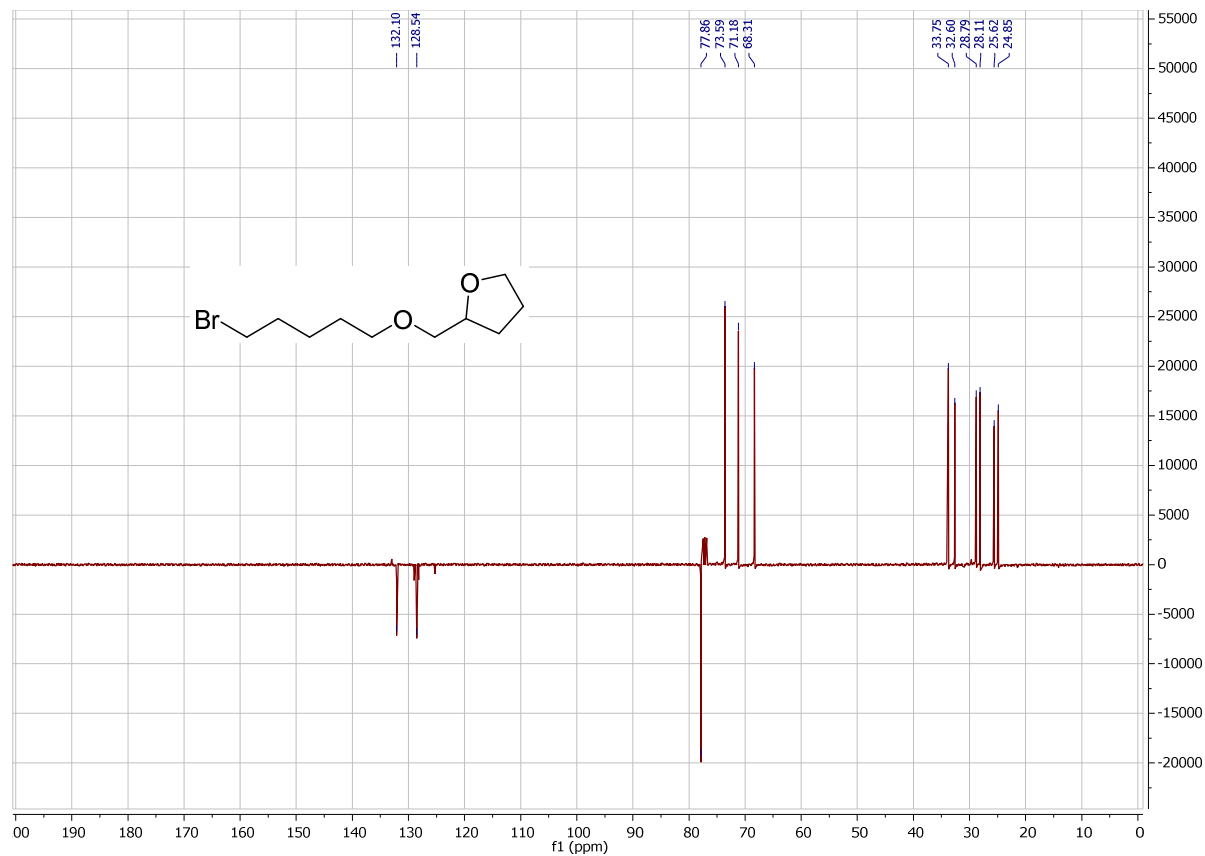
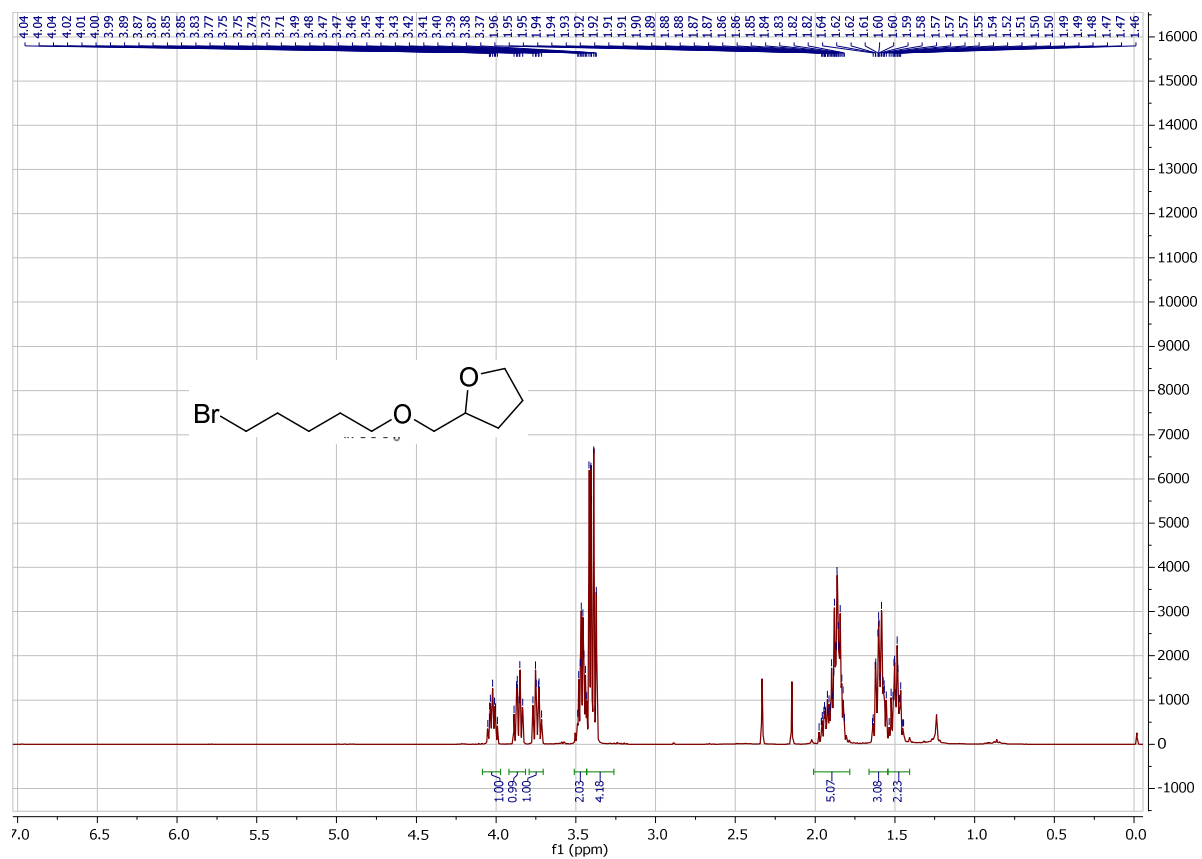
**$^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  of compound B41 in  $\text{CDCl}_3$ .**



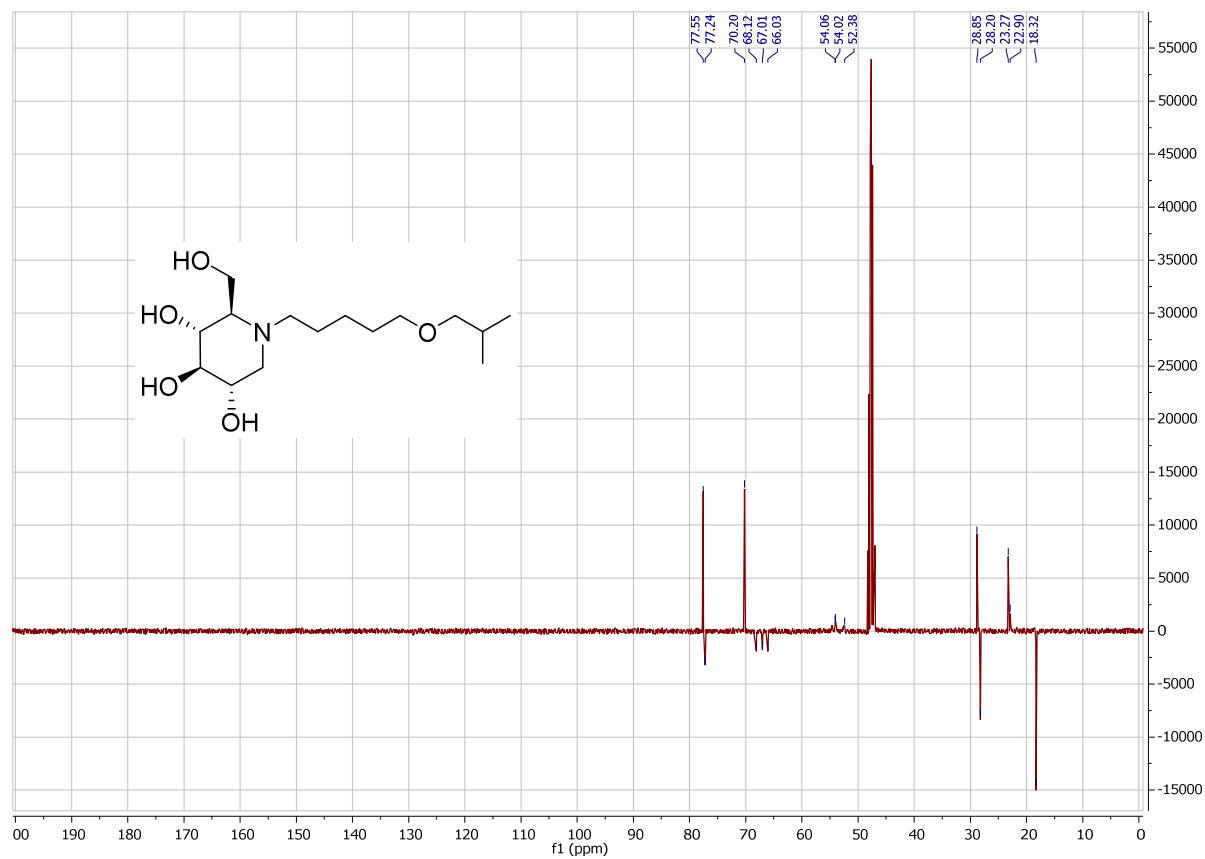
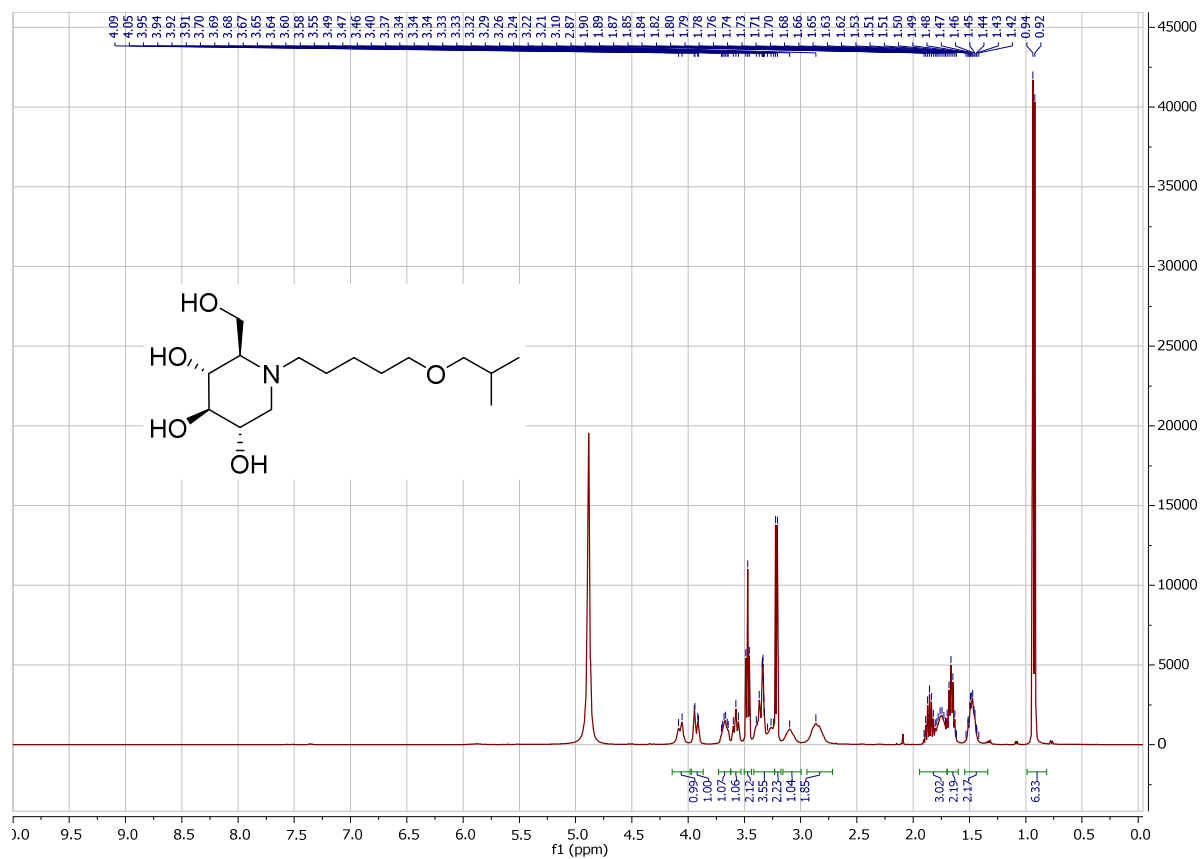
# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound B42 in $\text{CDCl}_3$ .



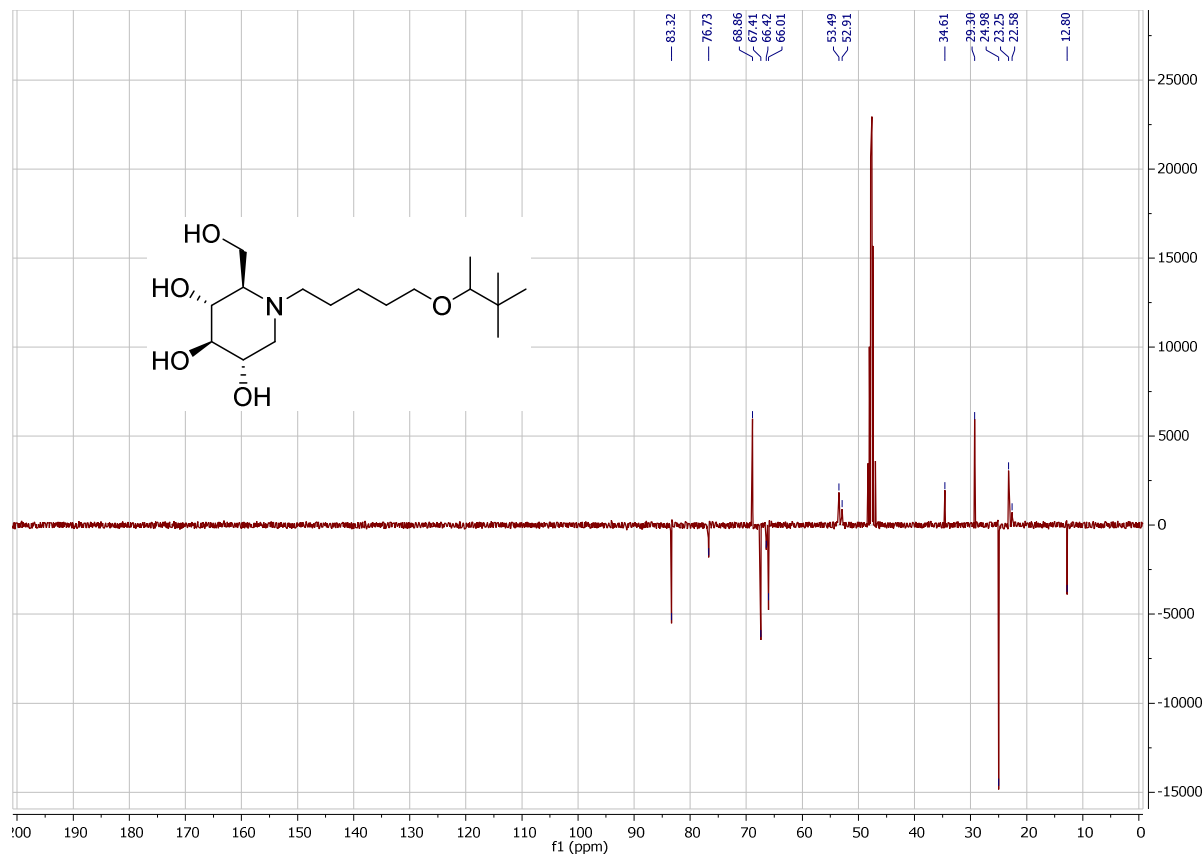
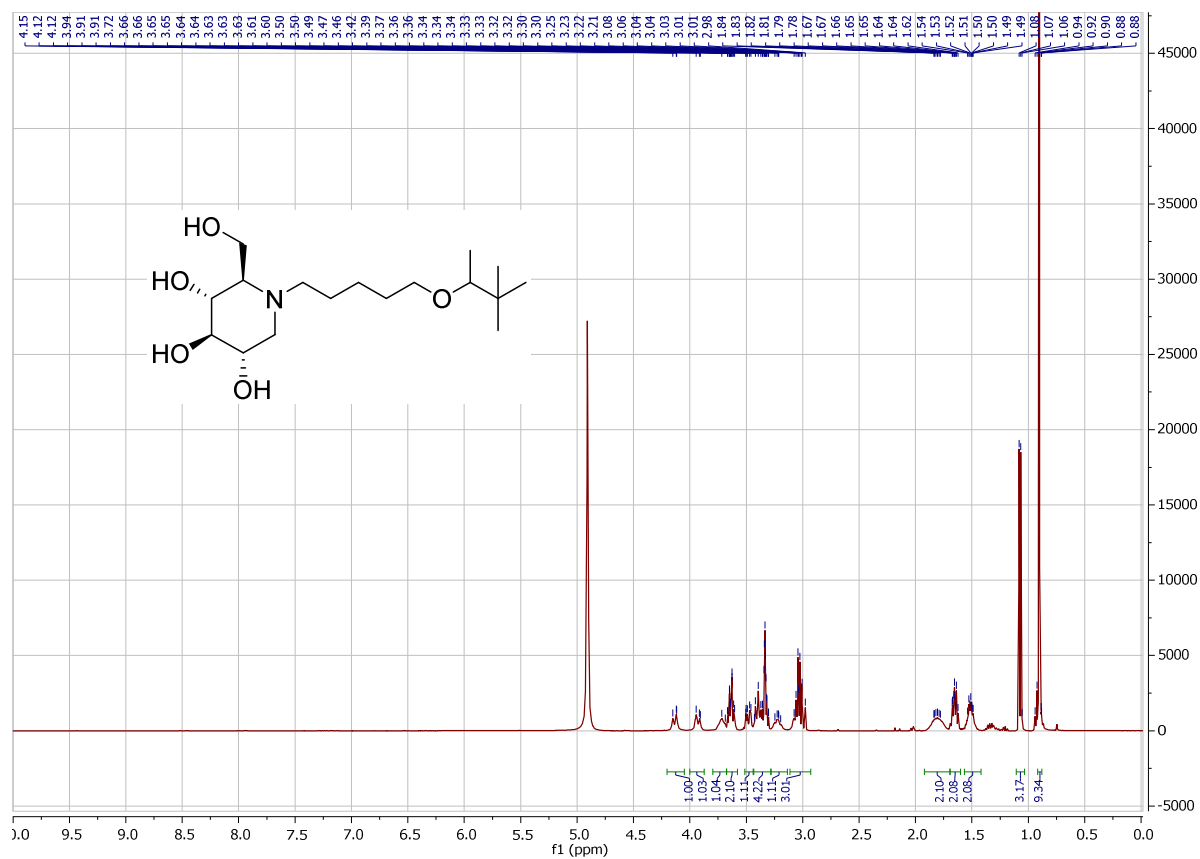
<sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound B43 in CDCl<sub>3</sub>.



**$^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  of compound B44/11 in MeOD.**

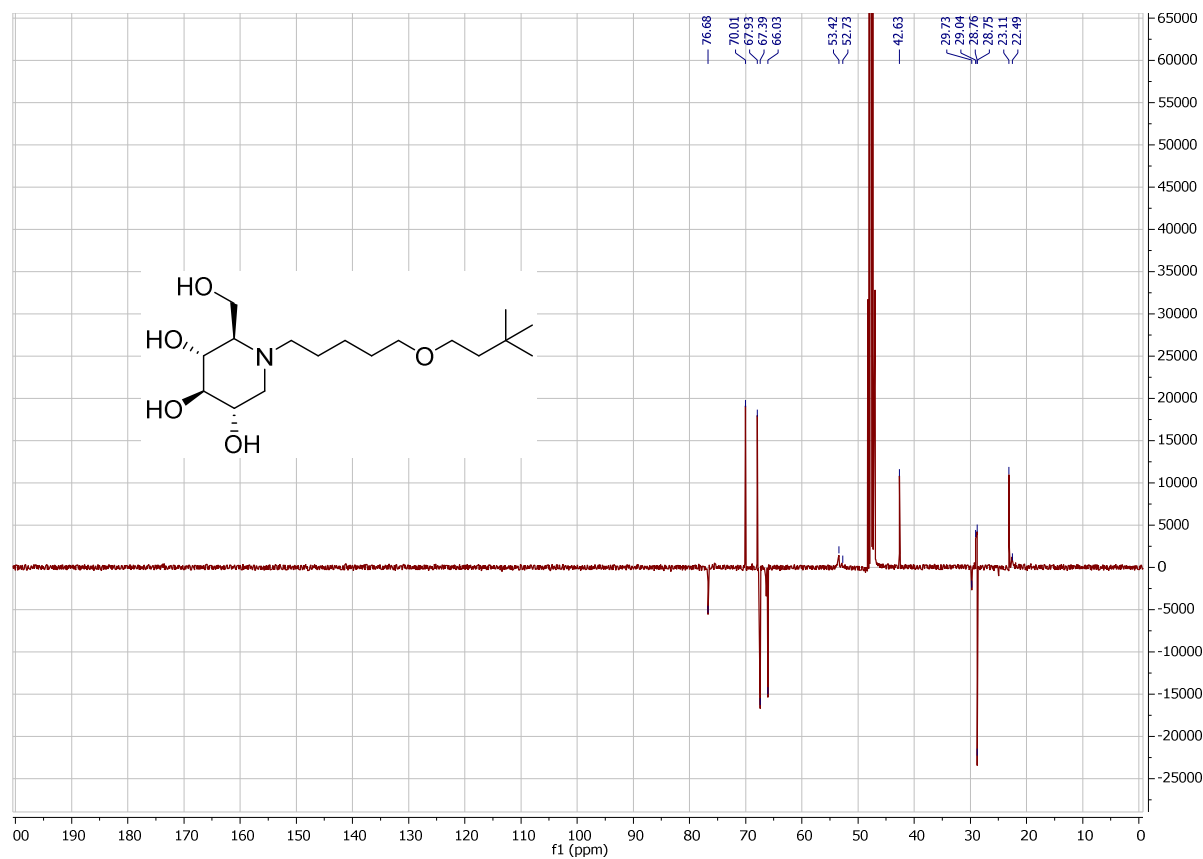
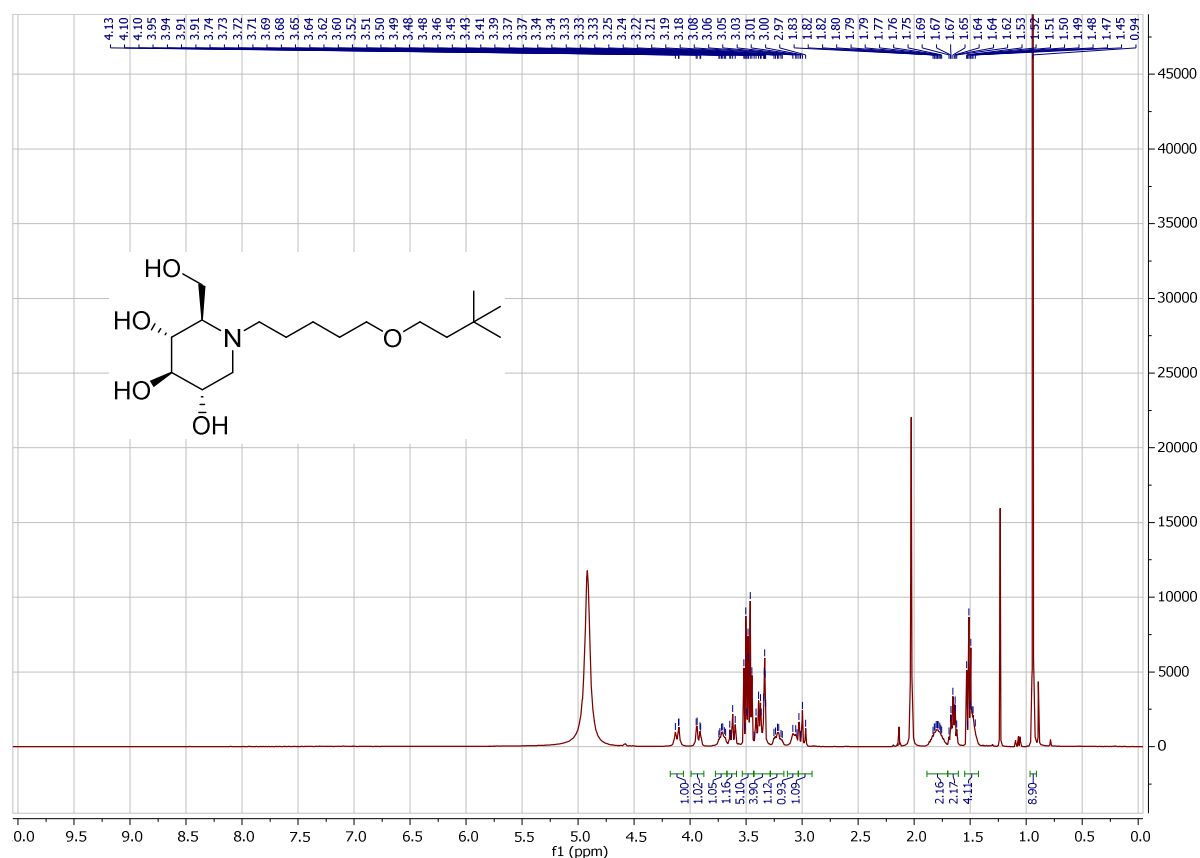


**$^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  of compound B45/13 in MeOD.**





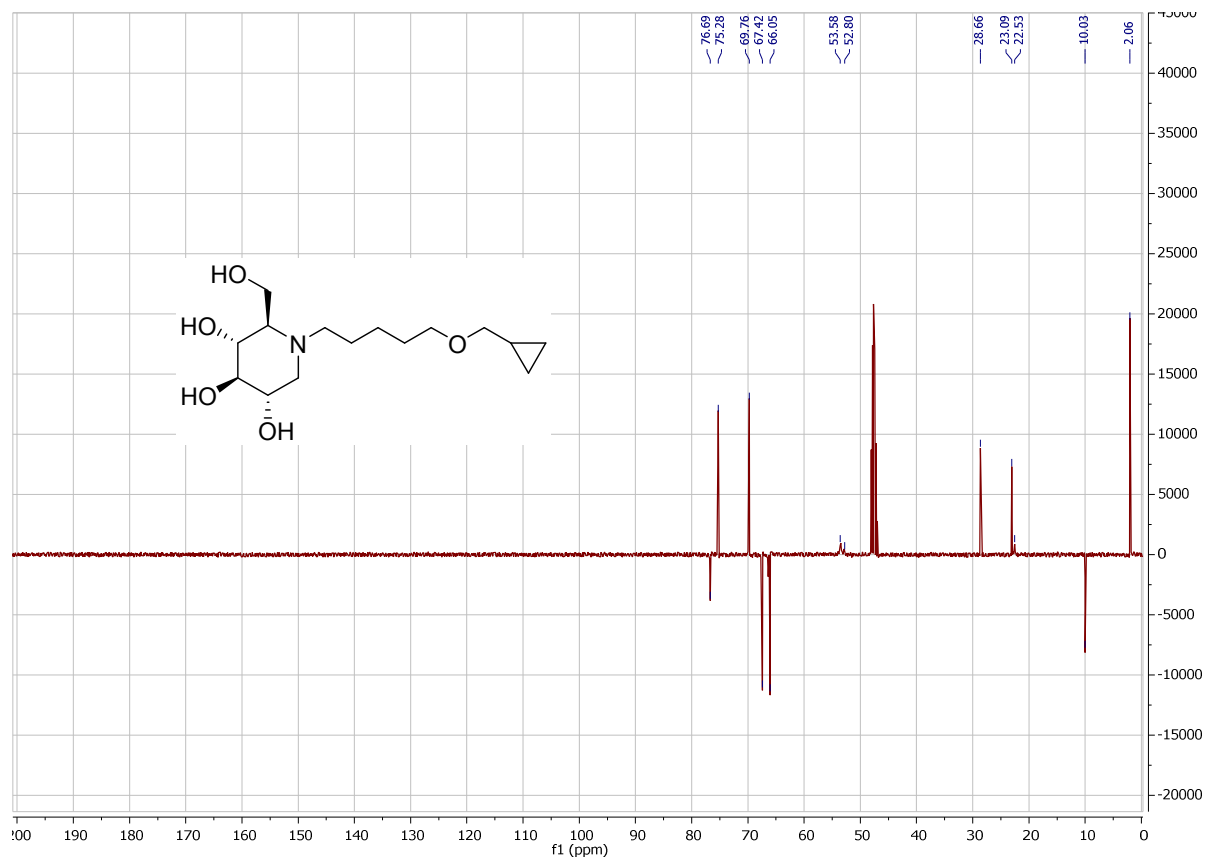
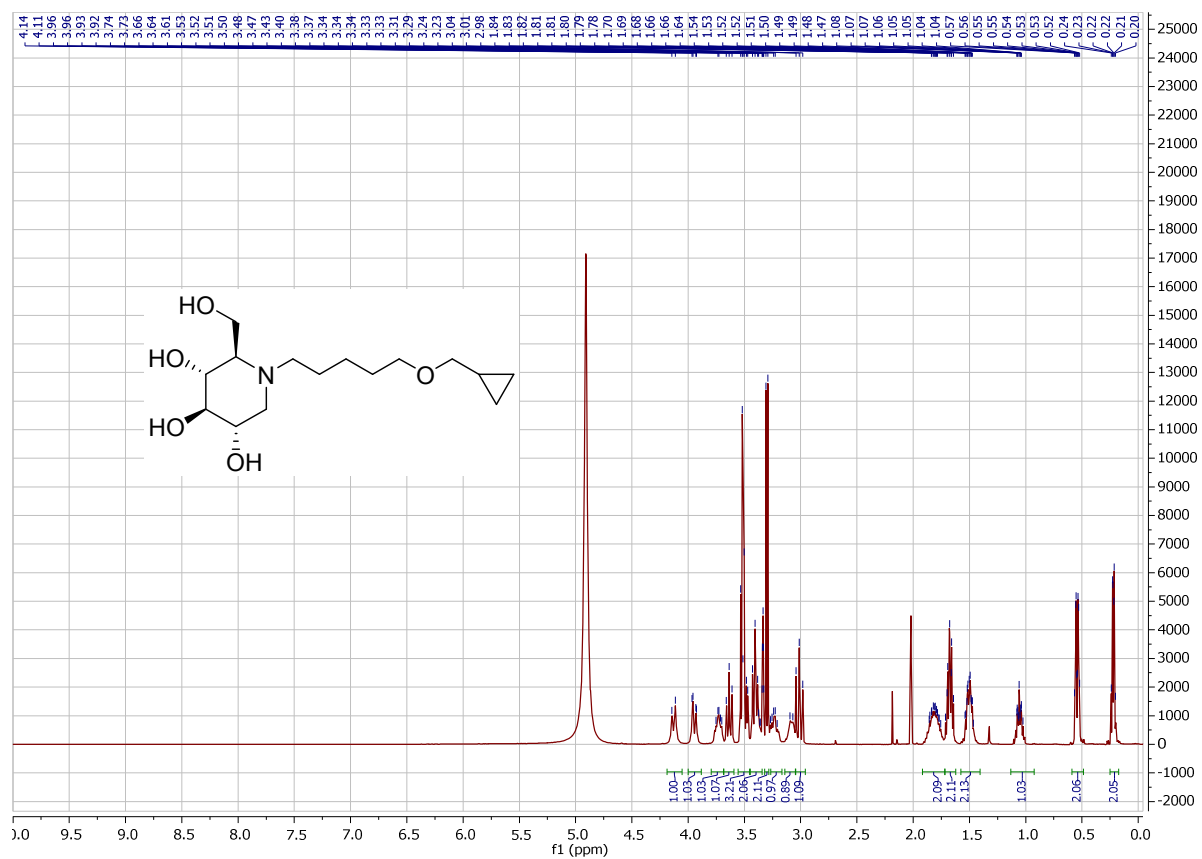
# <sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound B46 in MeOD.



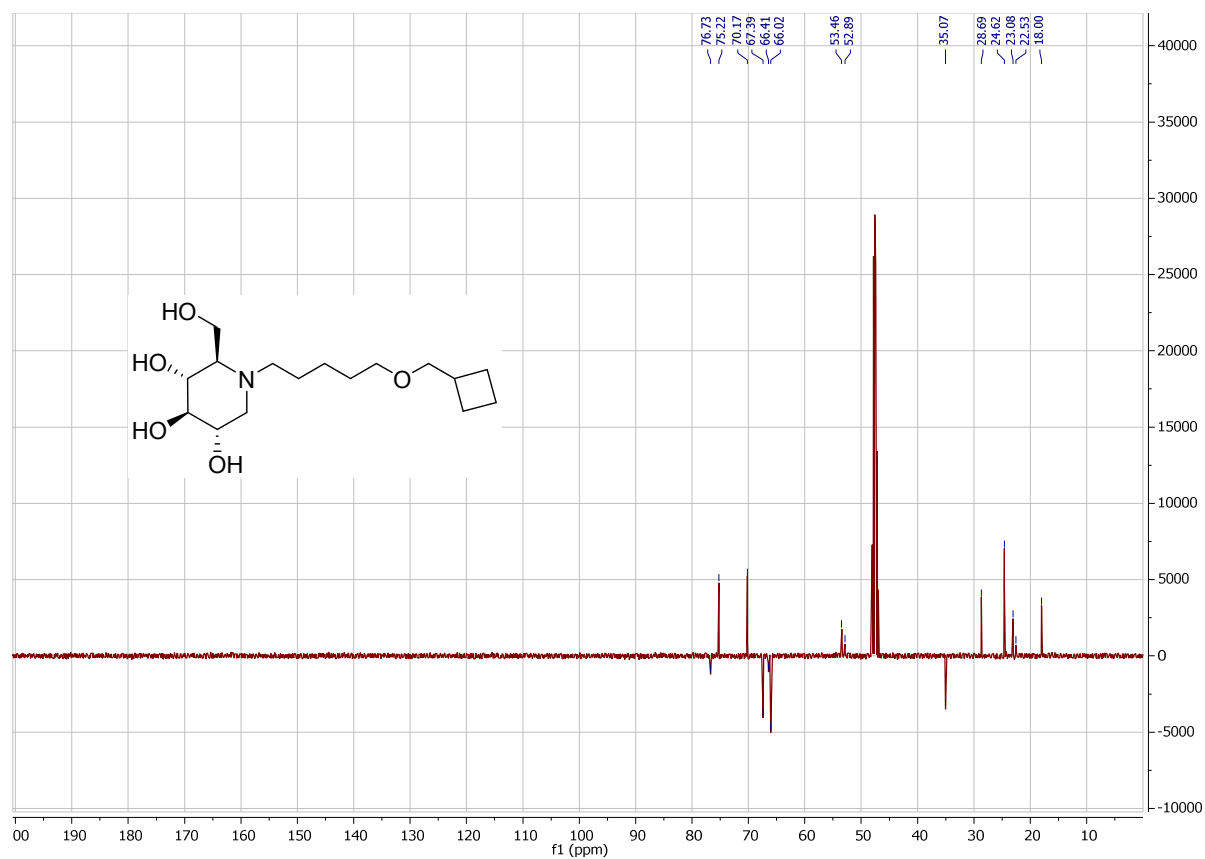
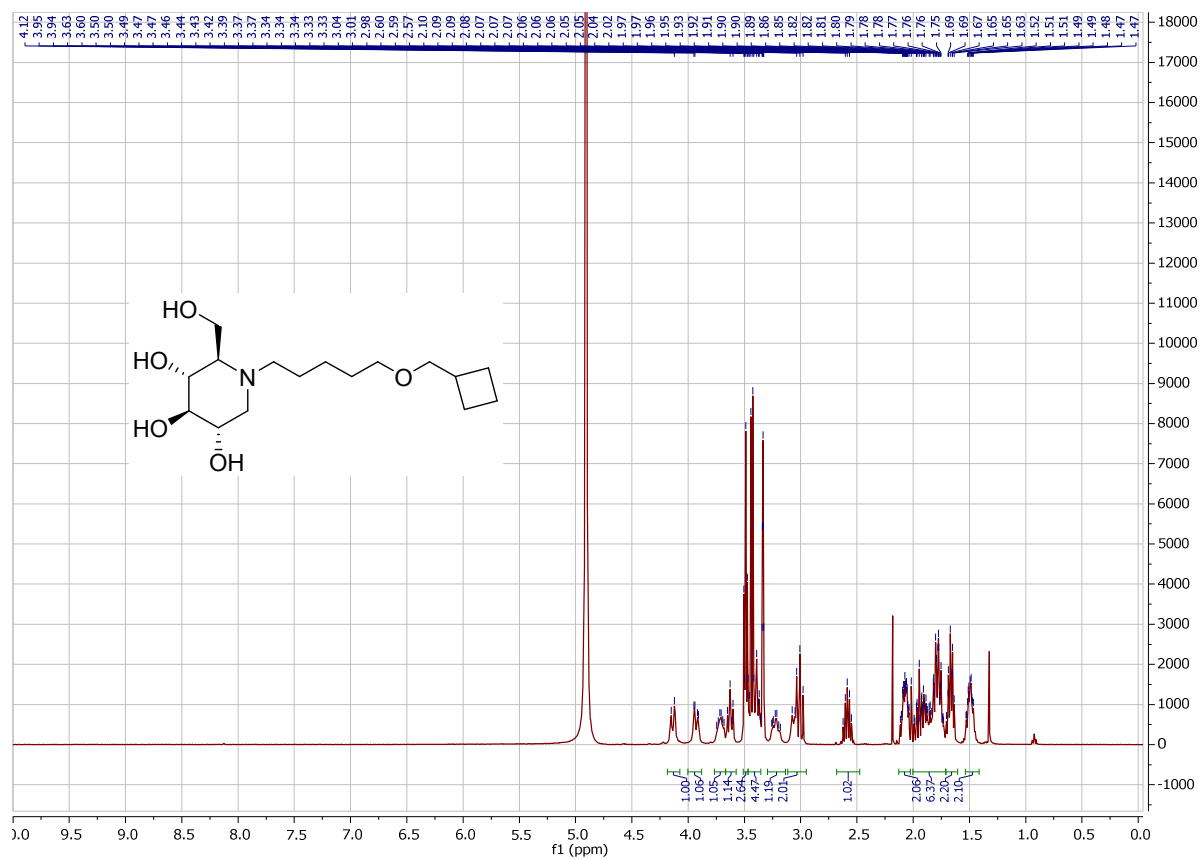




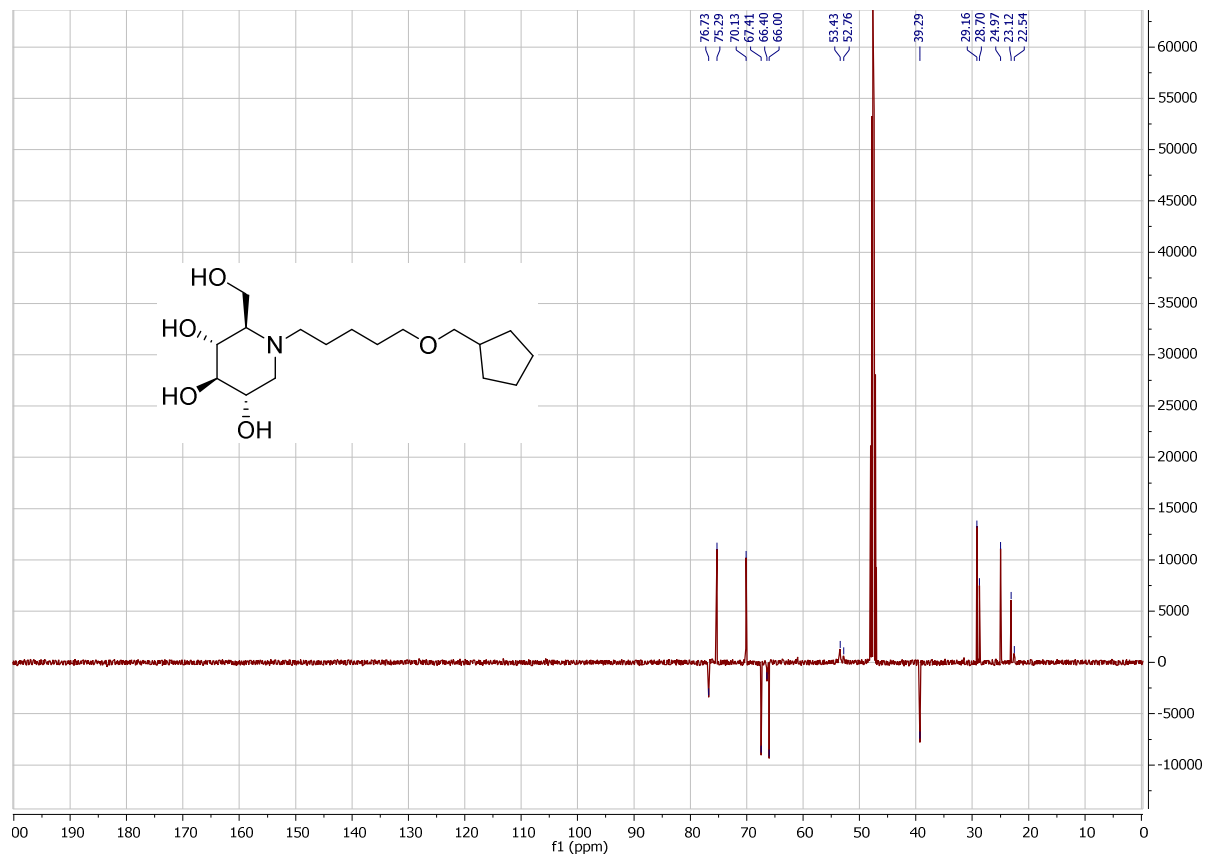
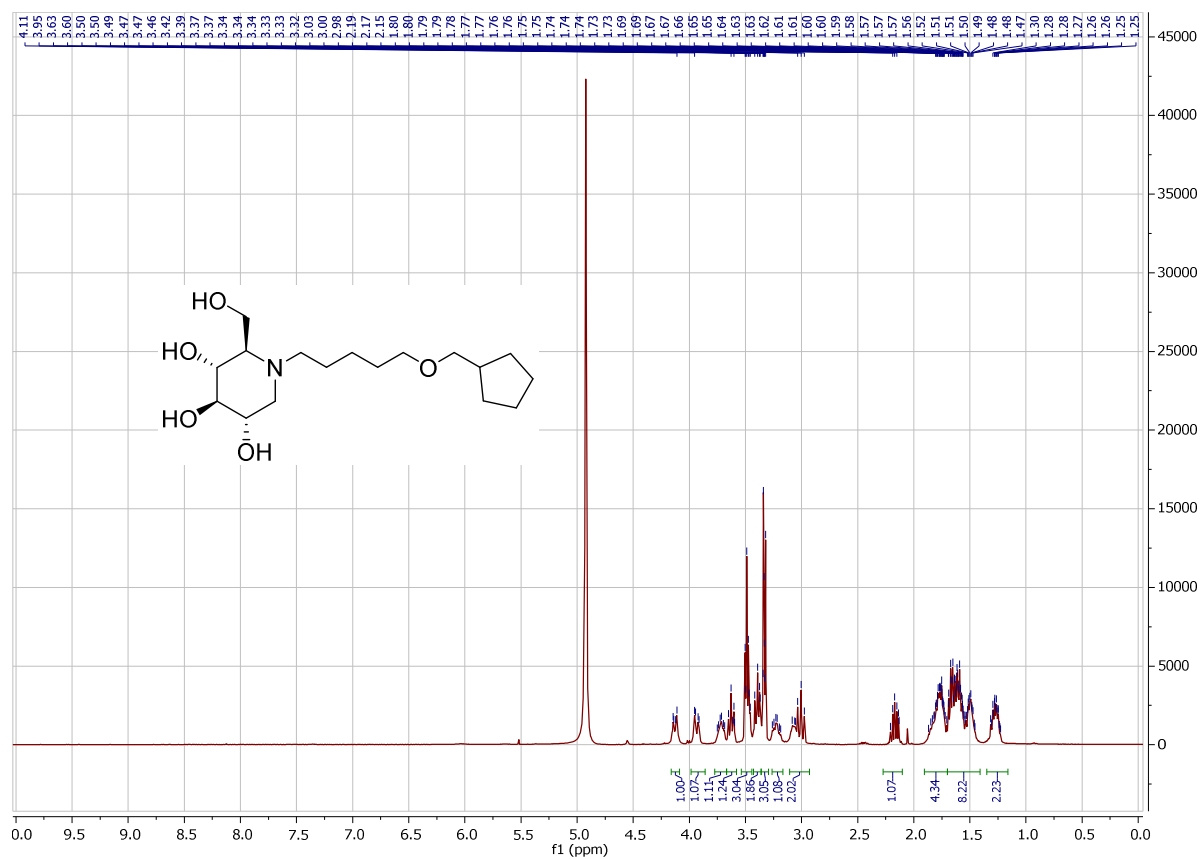
# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound B49 in MeOD.



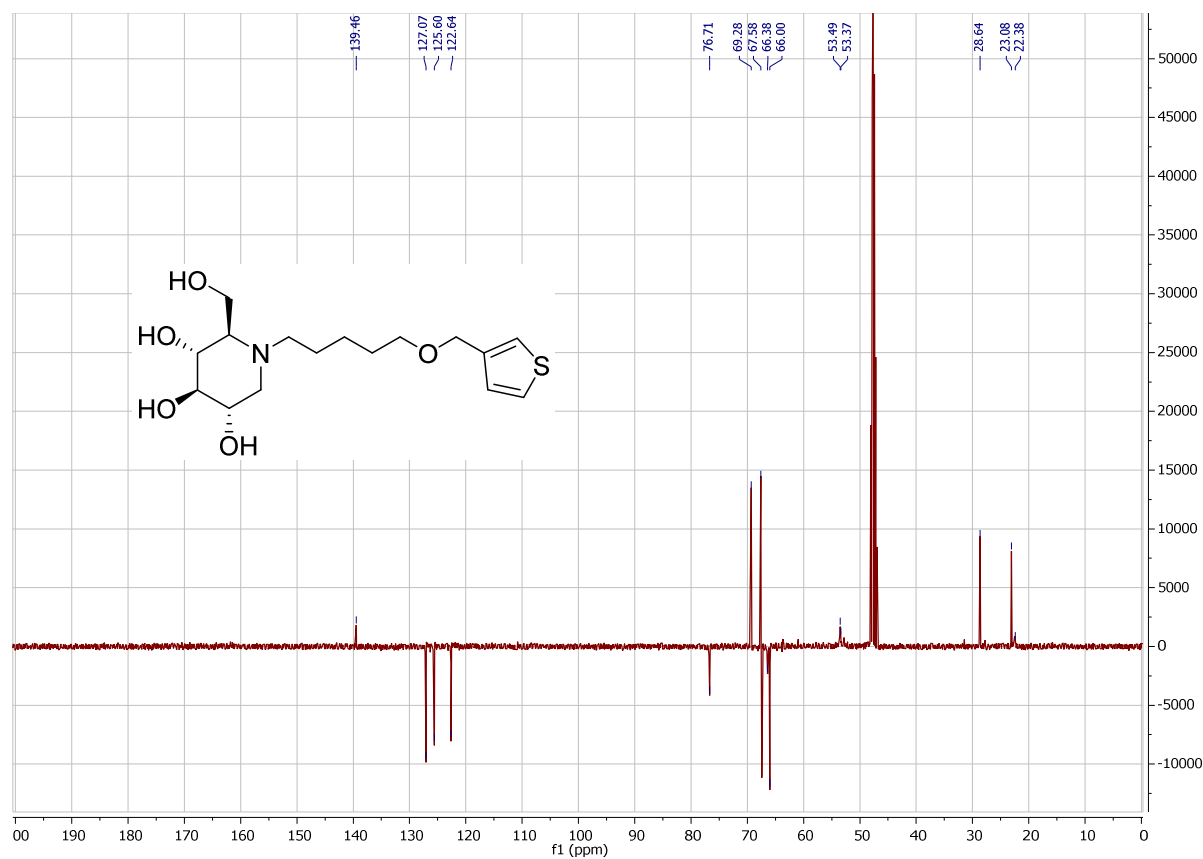
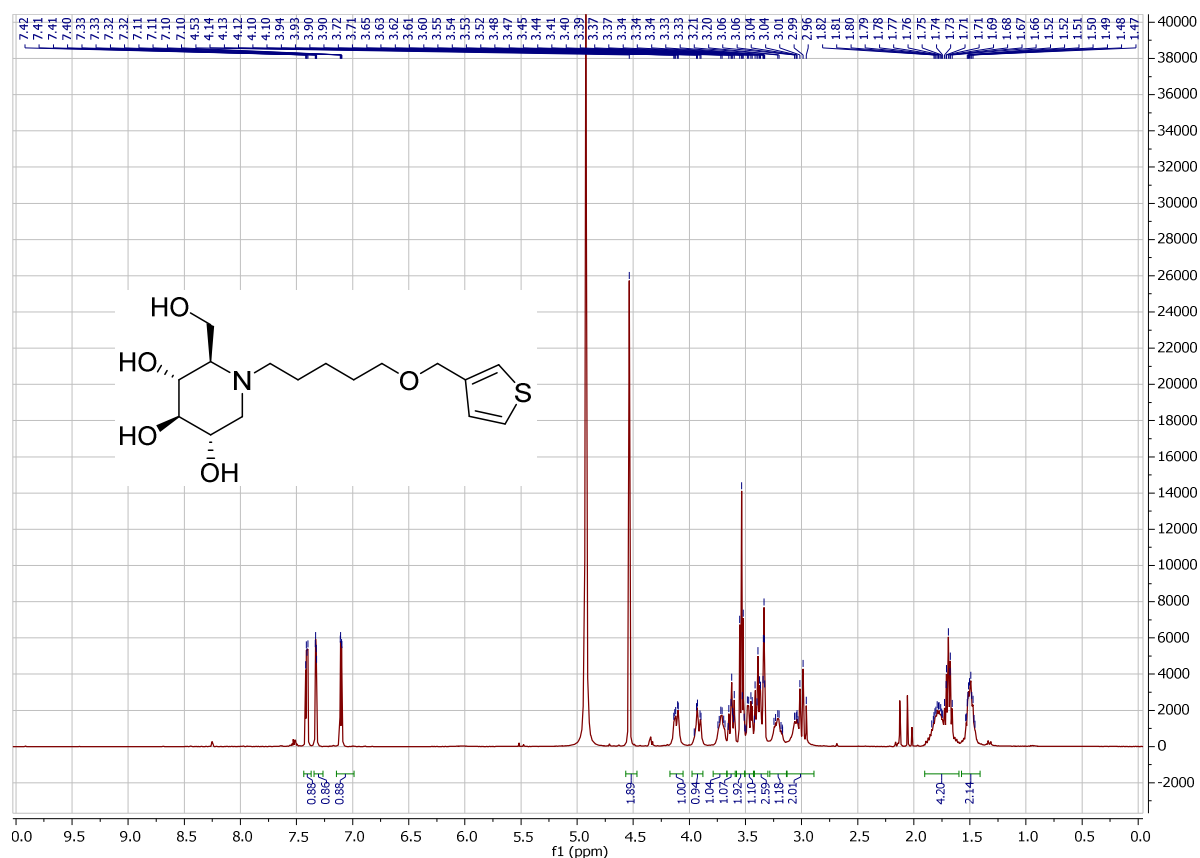
# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound B50 in MeOD.



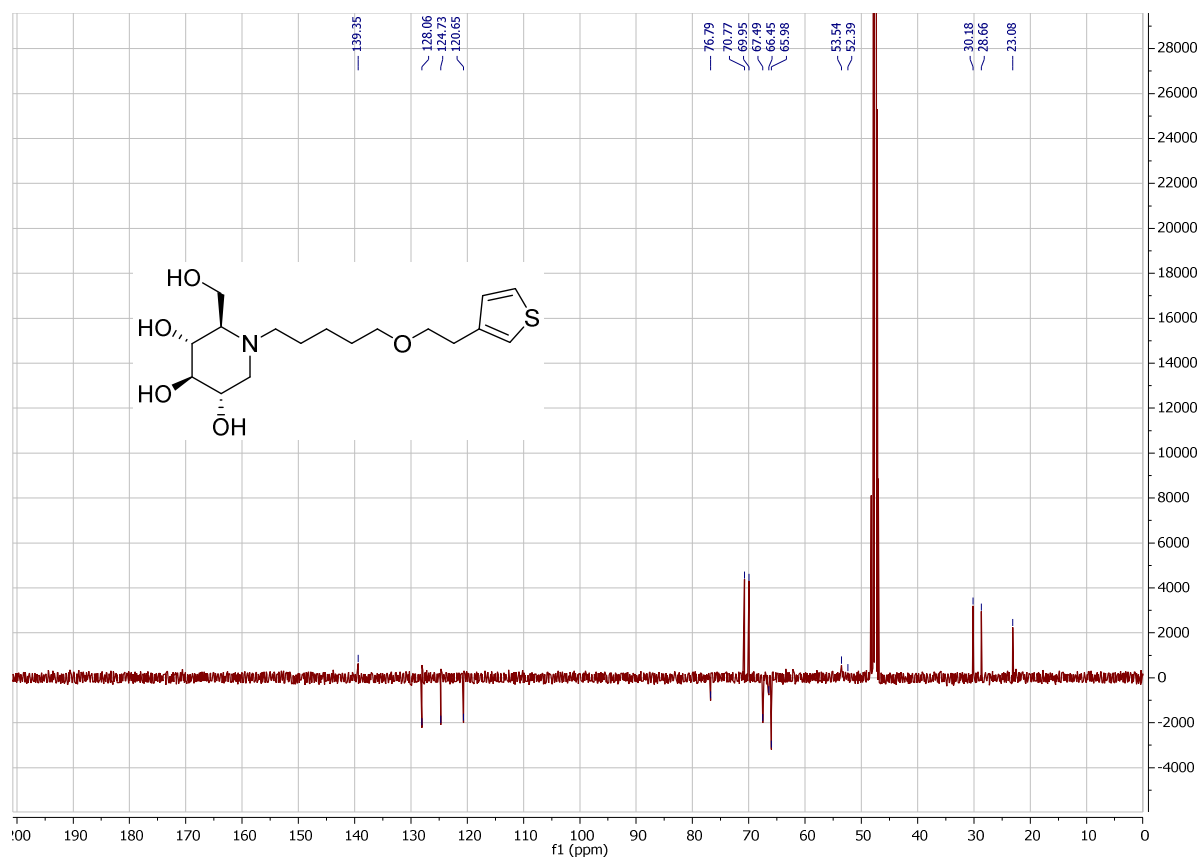
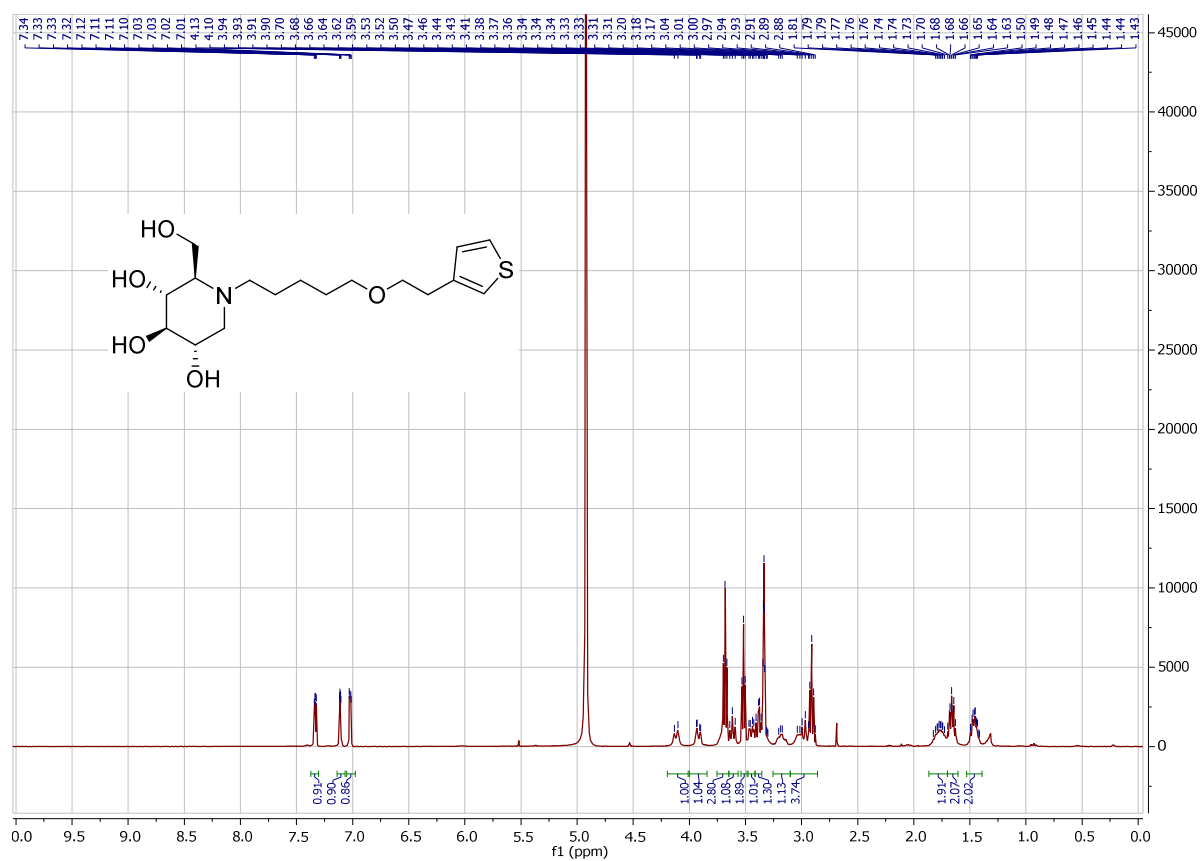
# <sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound B51 in MeOD.



# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound B52 in MeOD.



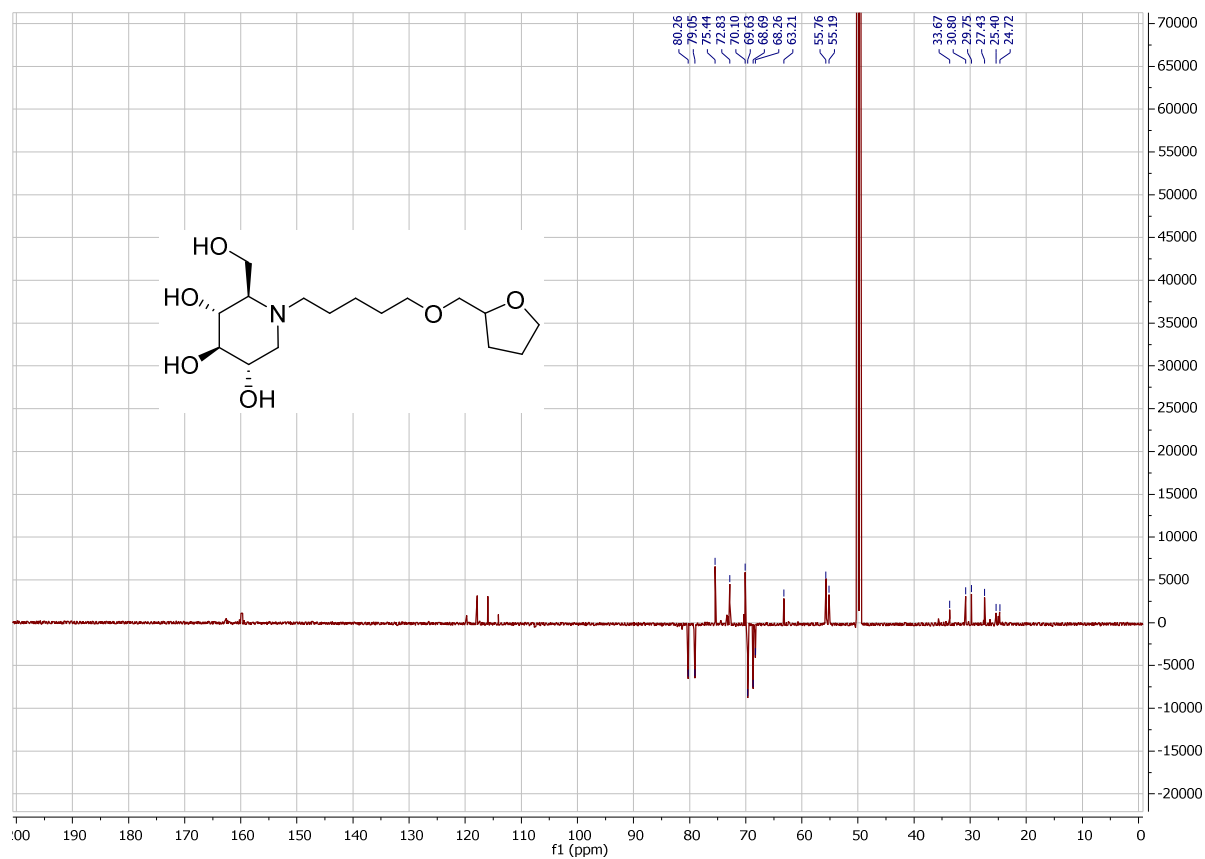
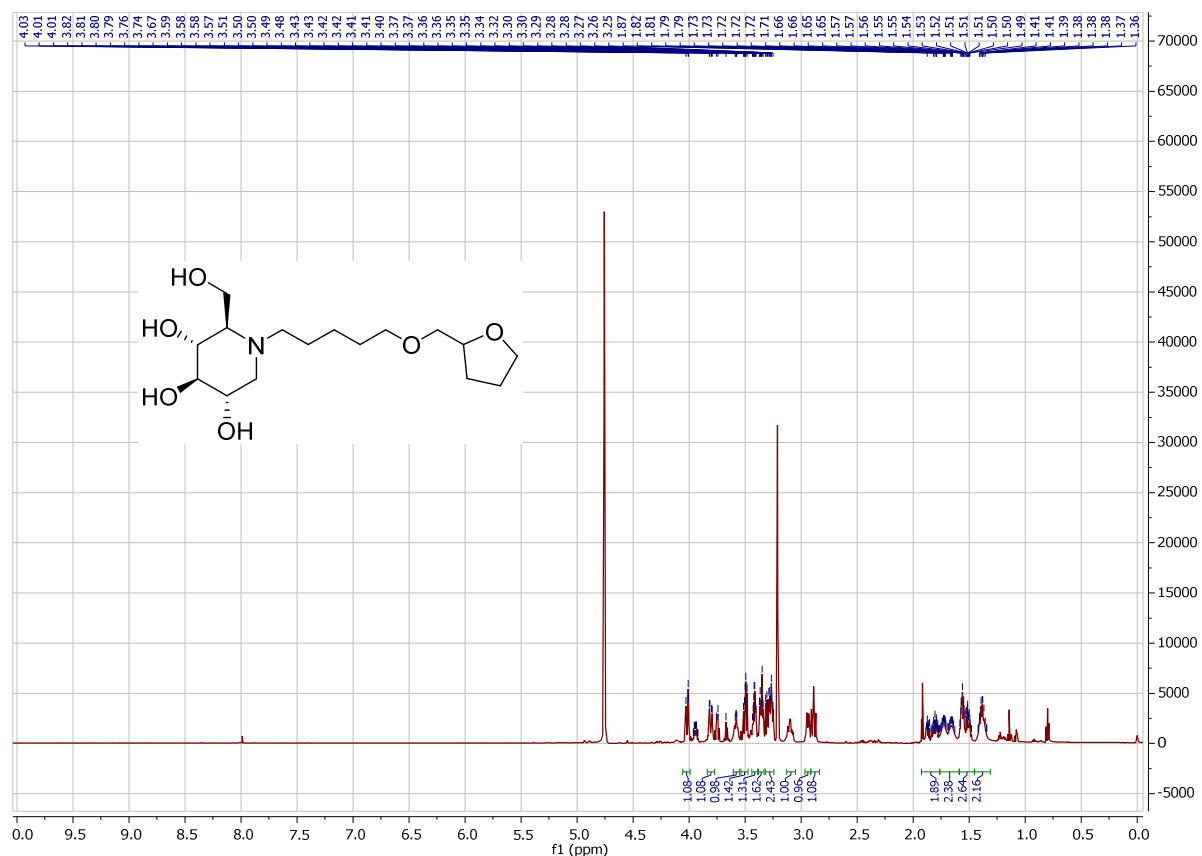
# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound B53 in MeOD.



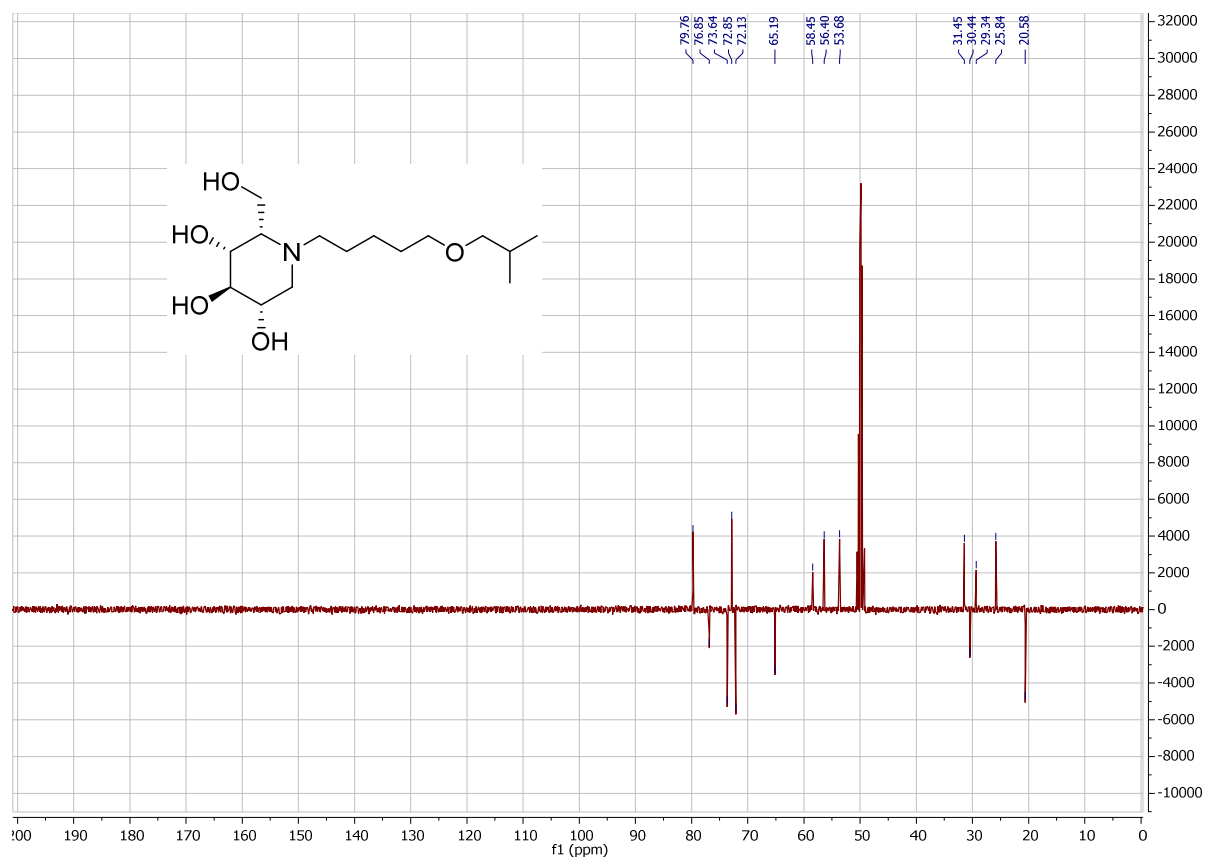
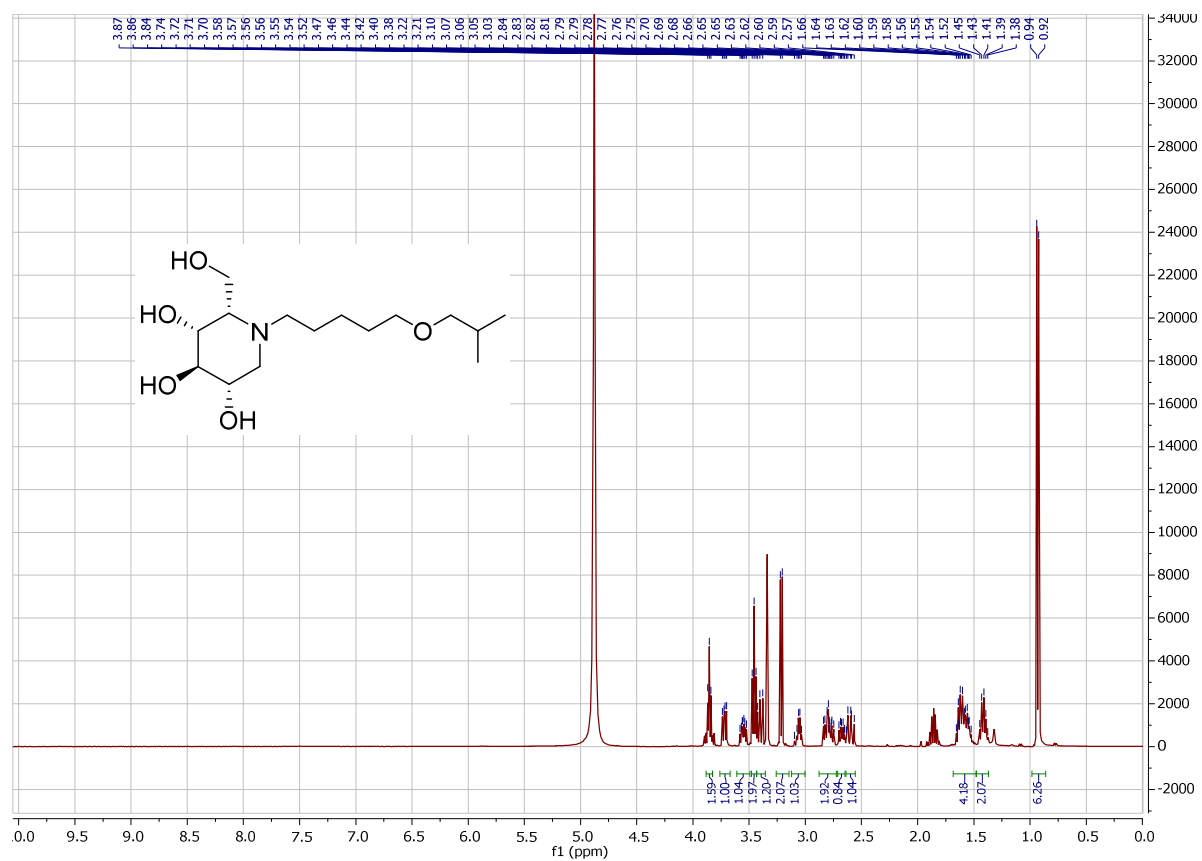




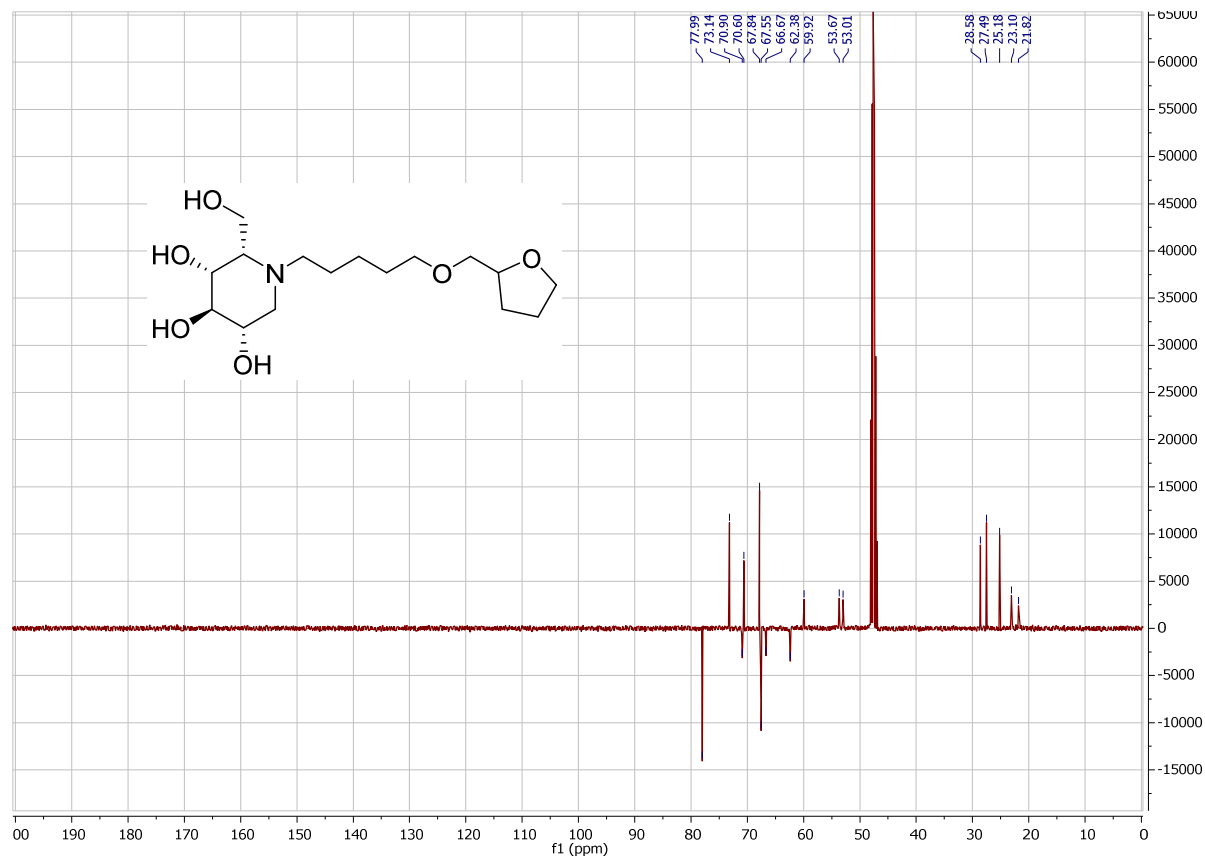
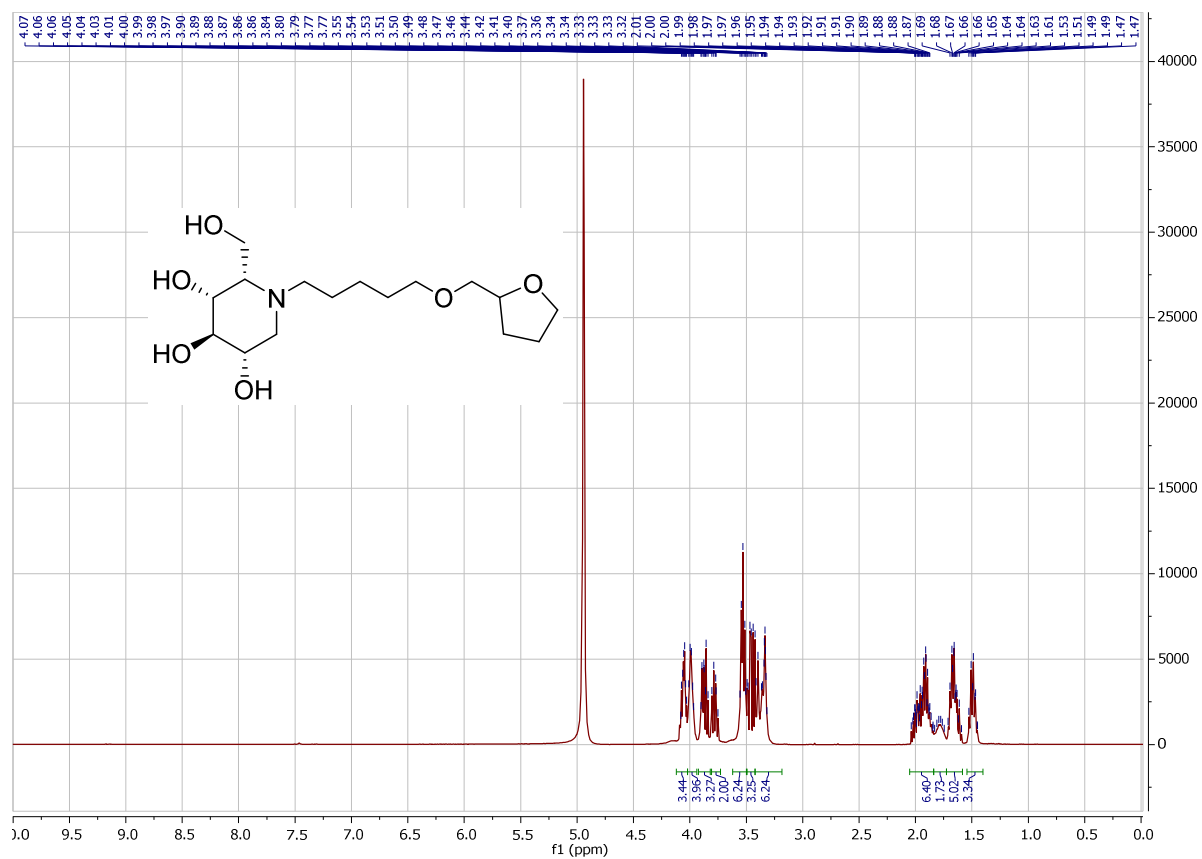
# <sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound B55/15 in MeOD.



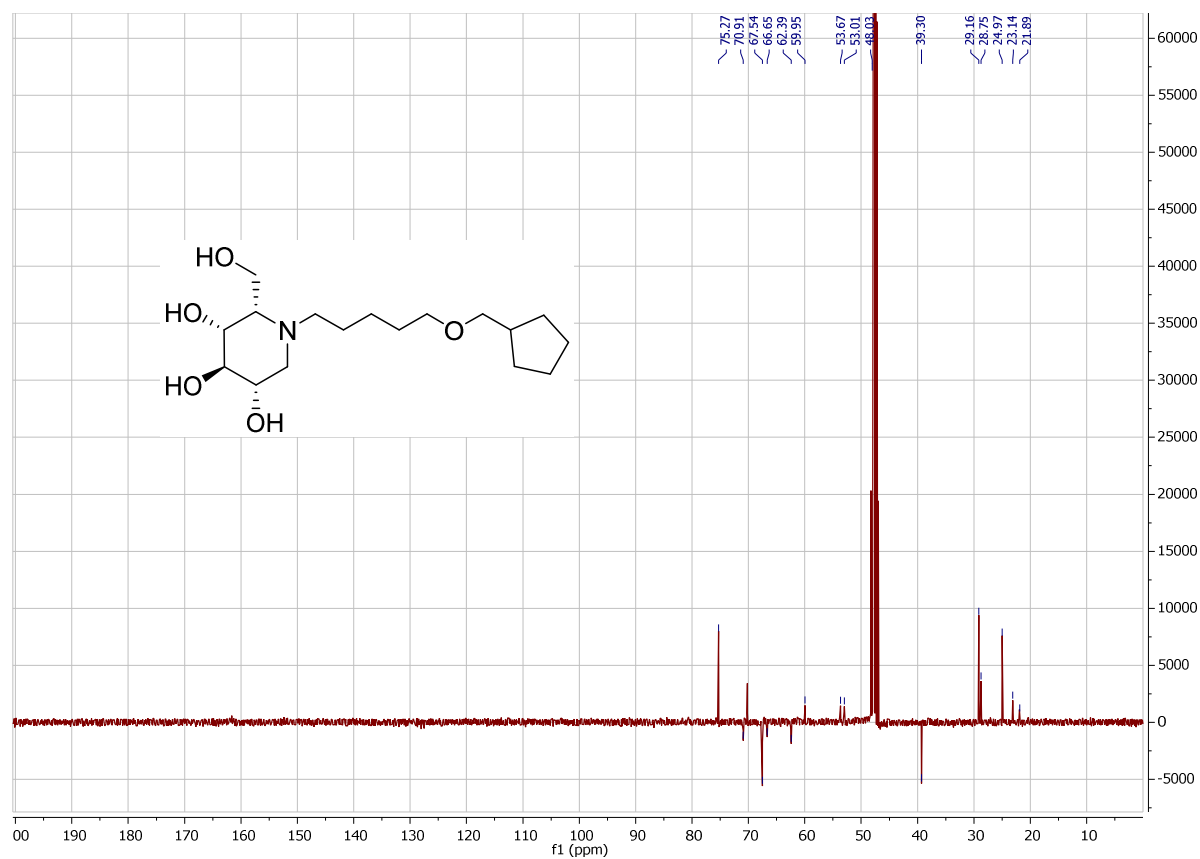
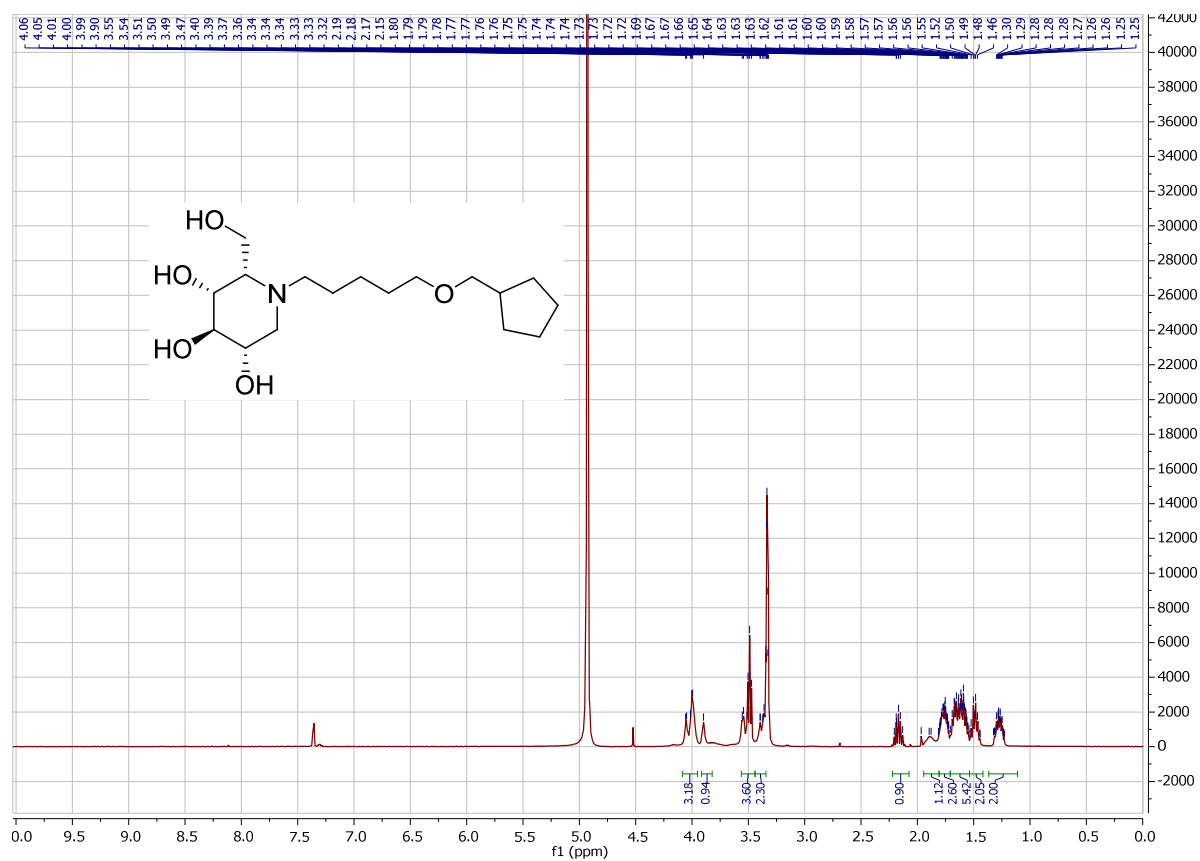
# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound B56/12 in MeOD.



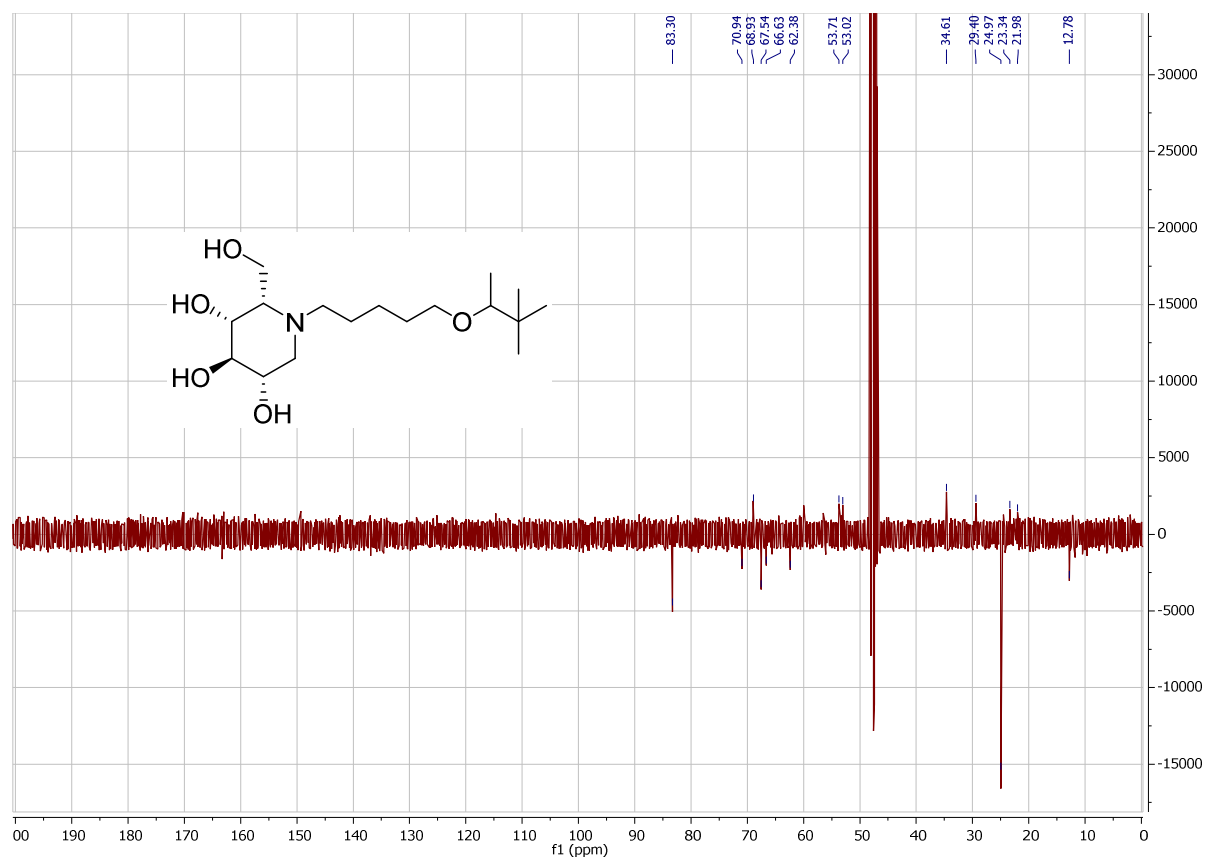
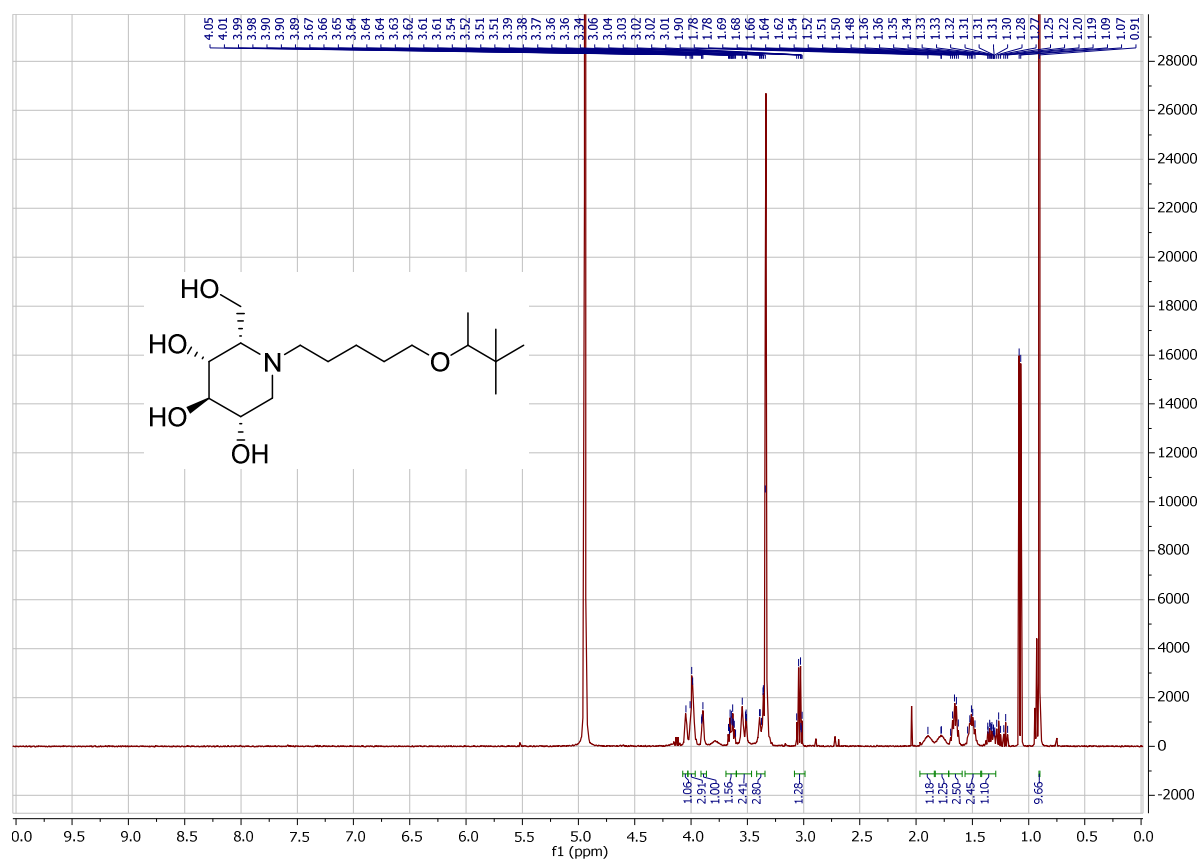
# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound B57 in MeOD.



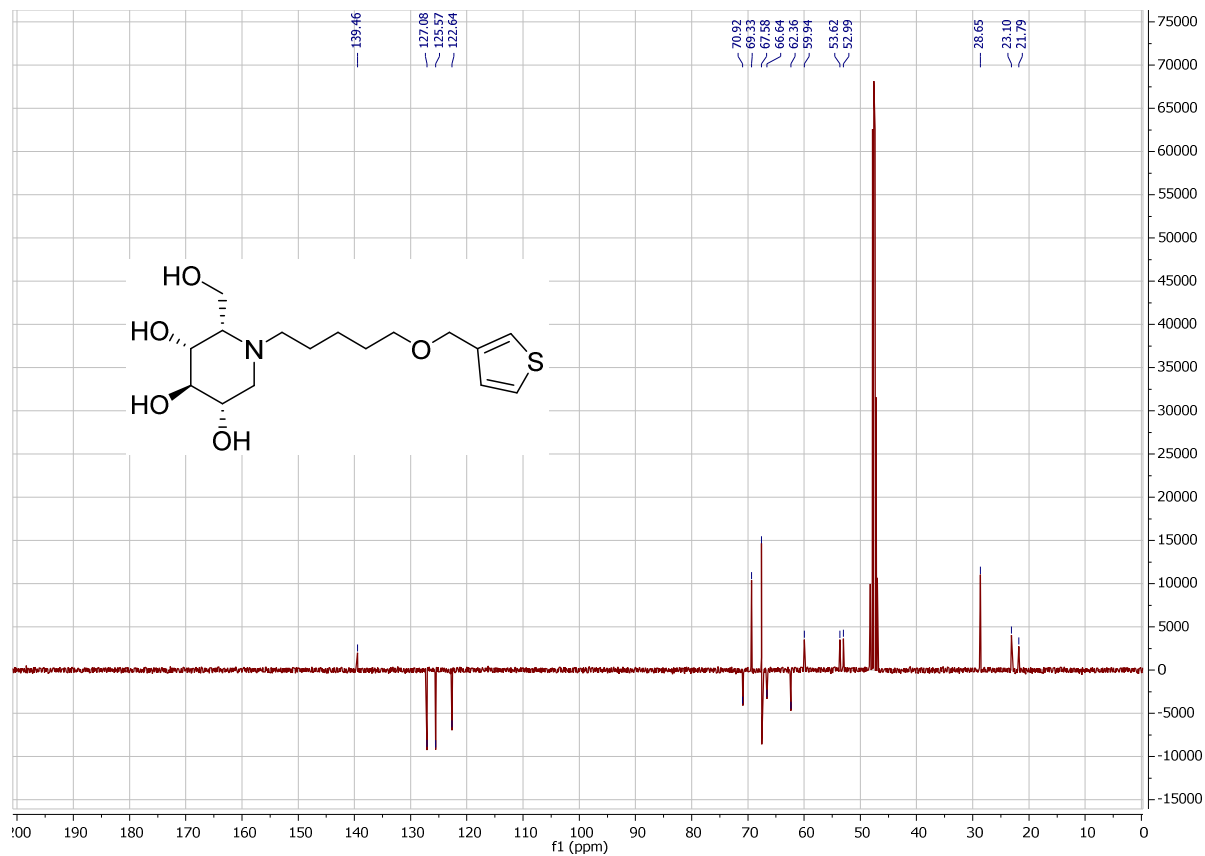
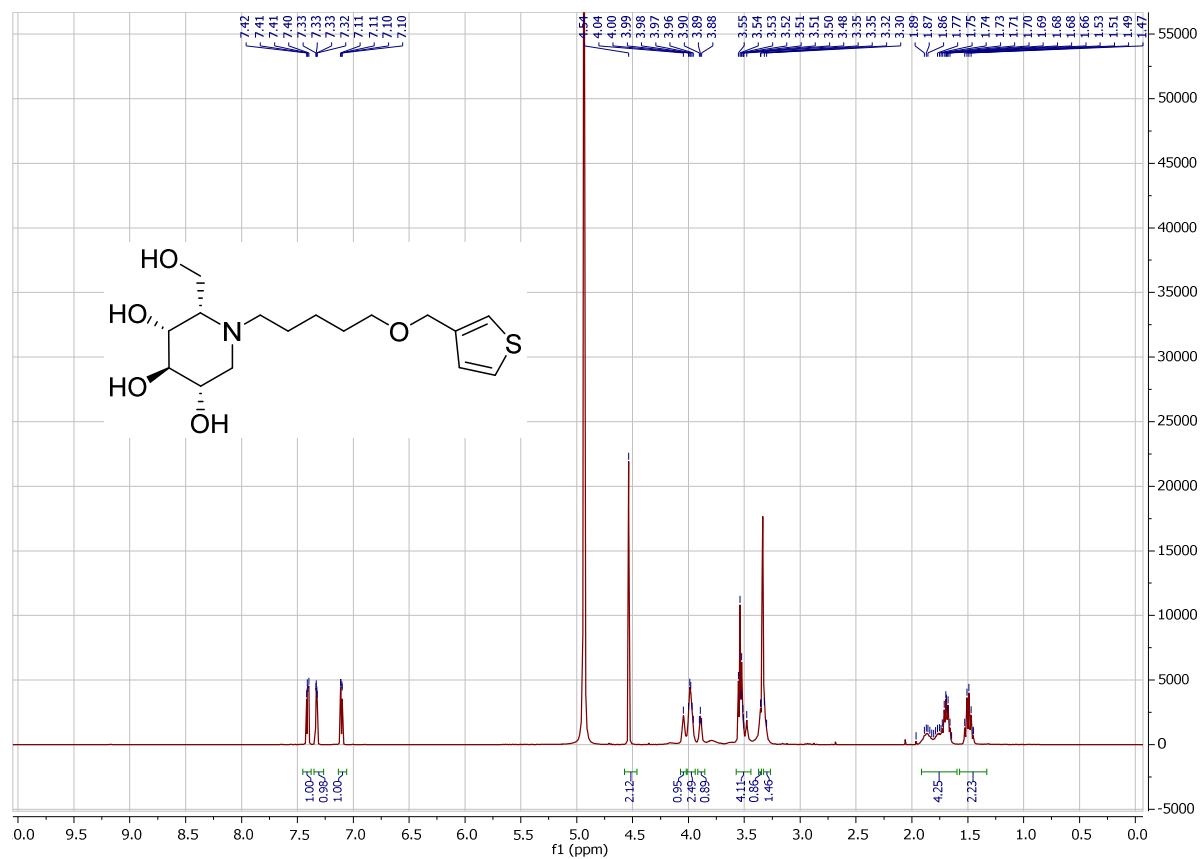
# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound B58 in MeOD.



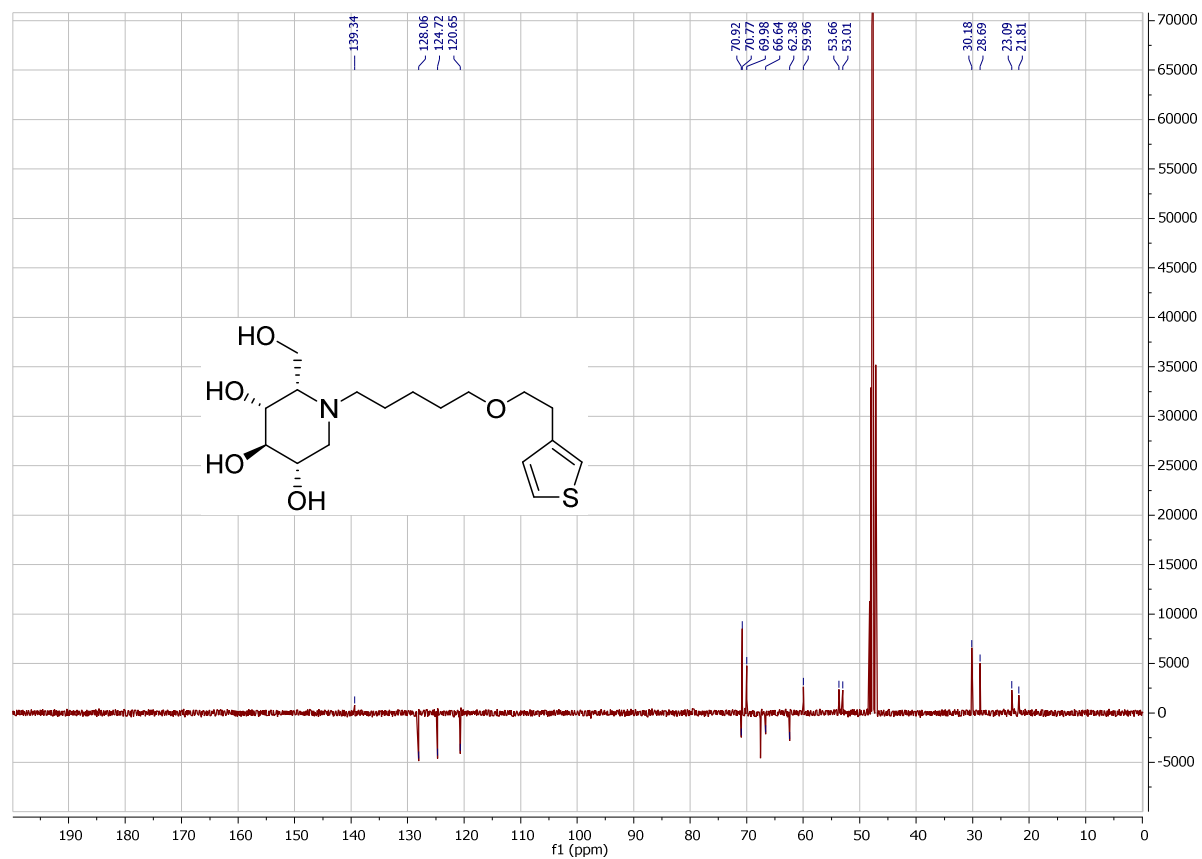
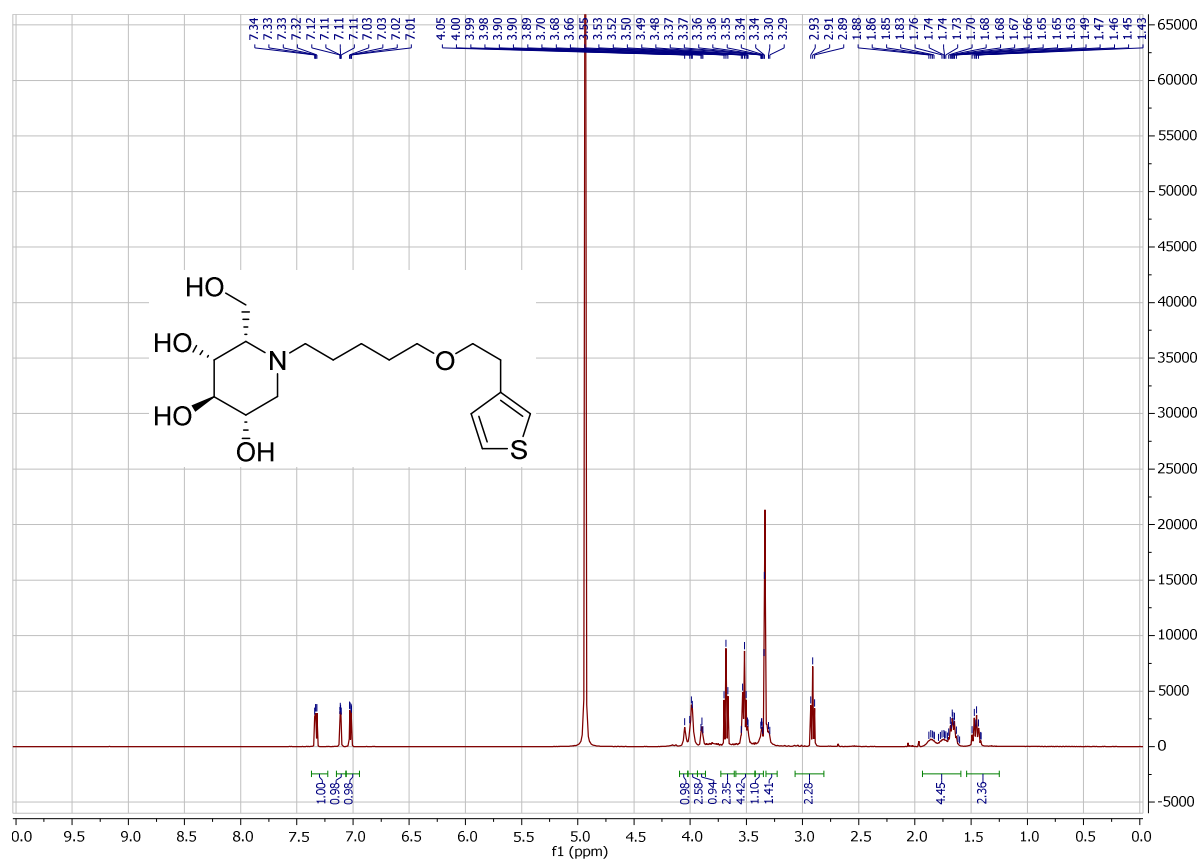
# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound B59 in MeOD.



# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound B60 in MeOD.

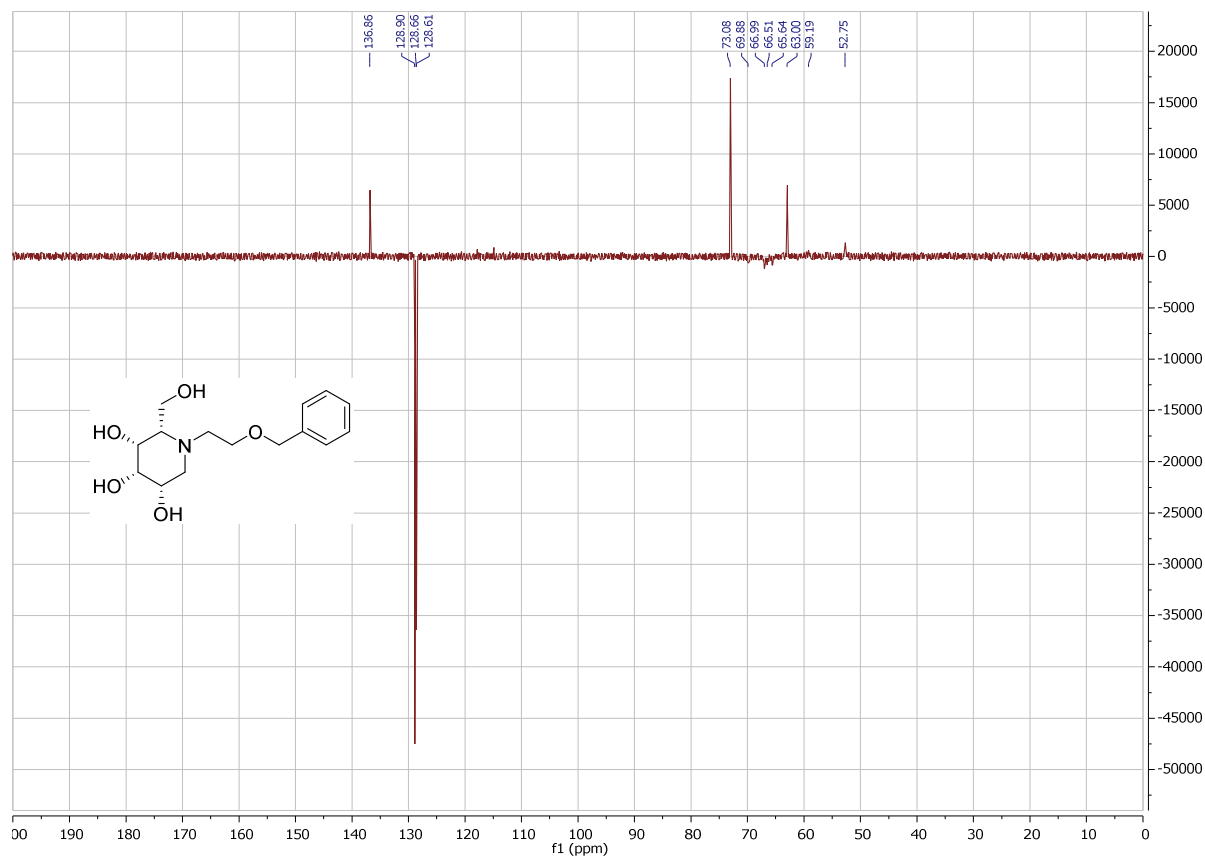
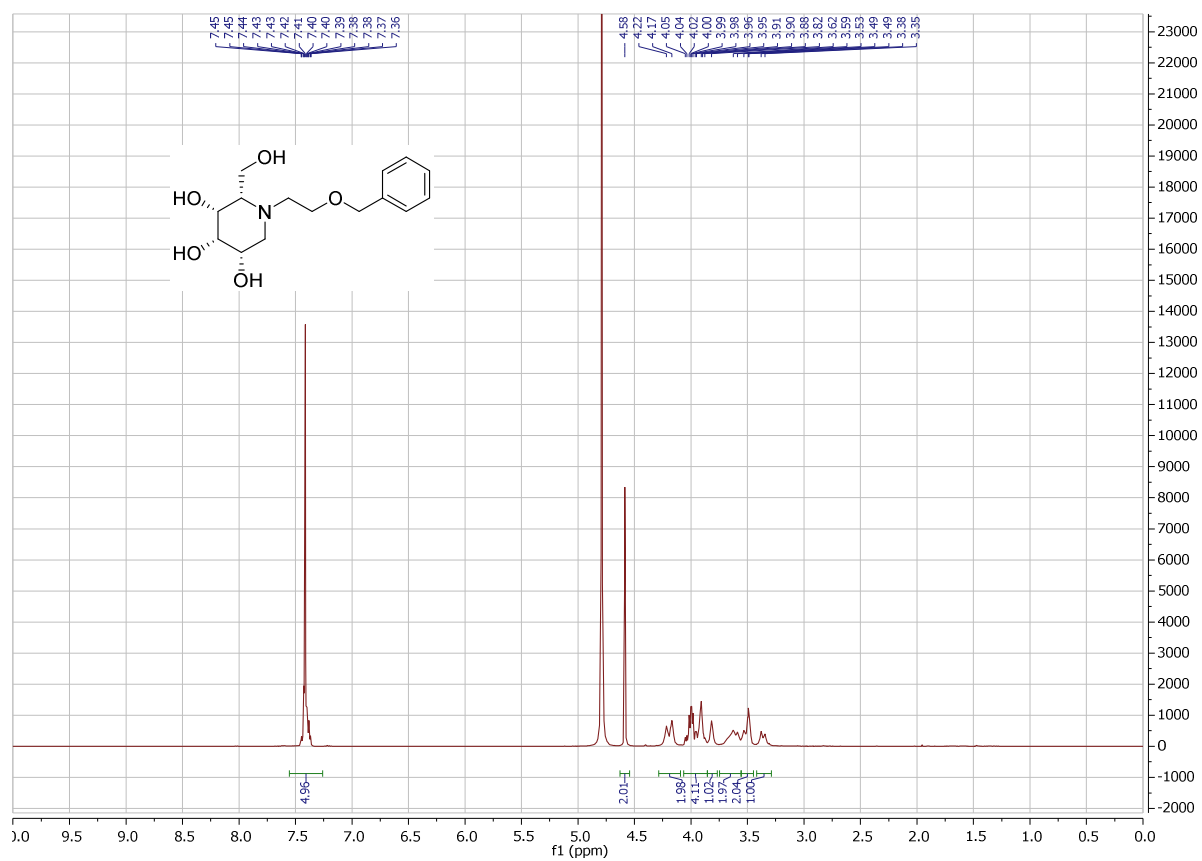


# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound B61 in MeOD.

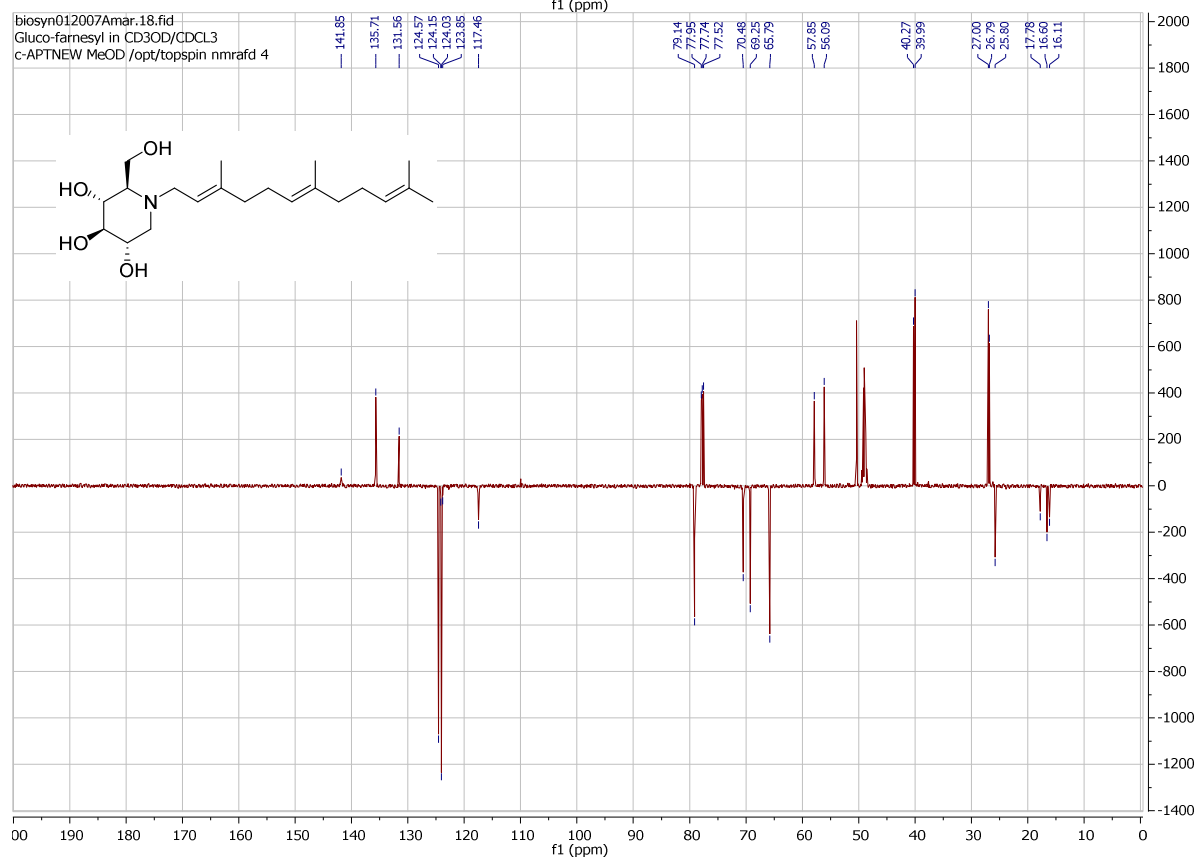
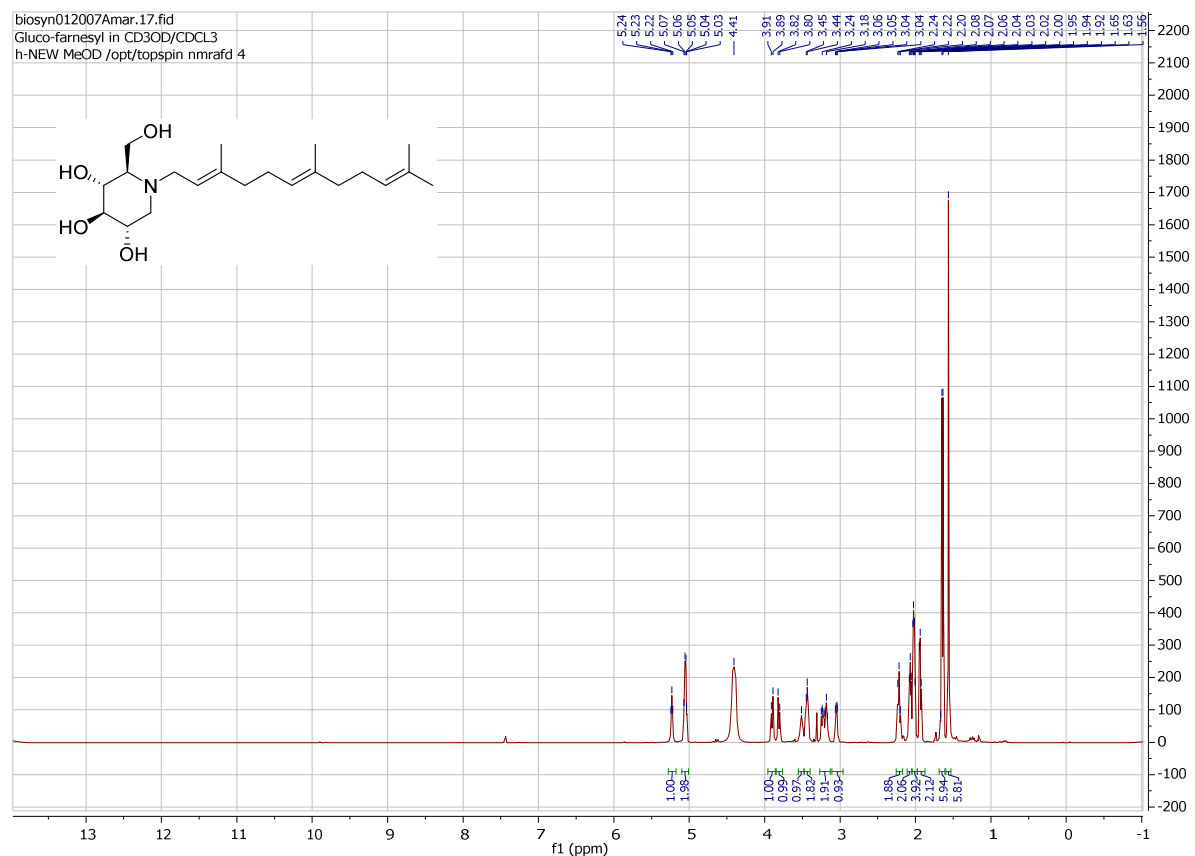




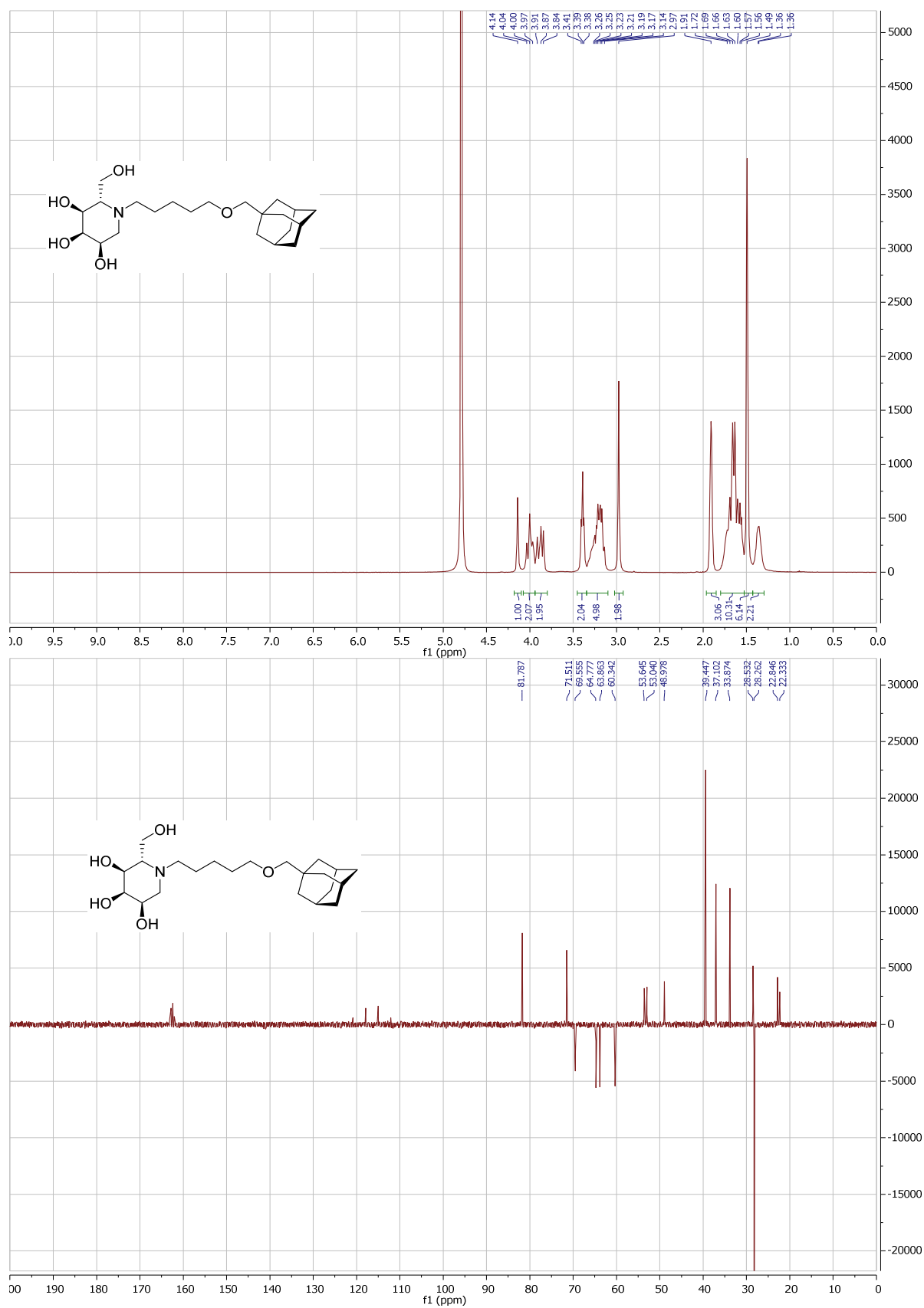
# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound C15.TFA in $\text{D}_2\text{O}$ .



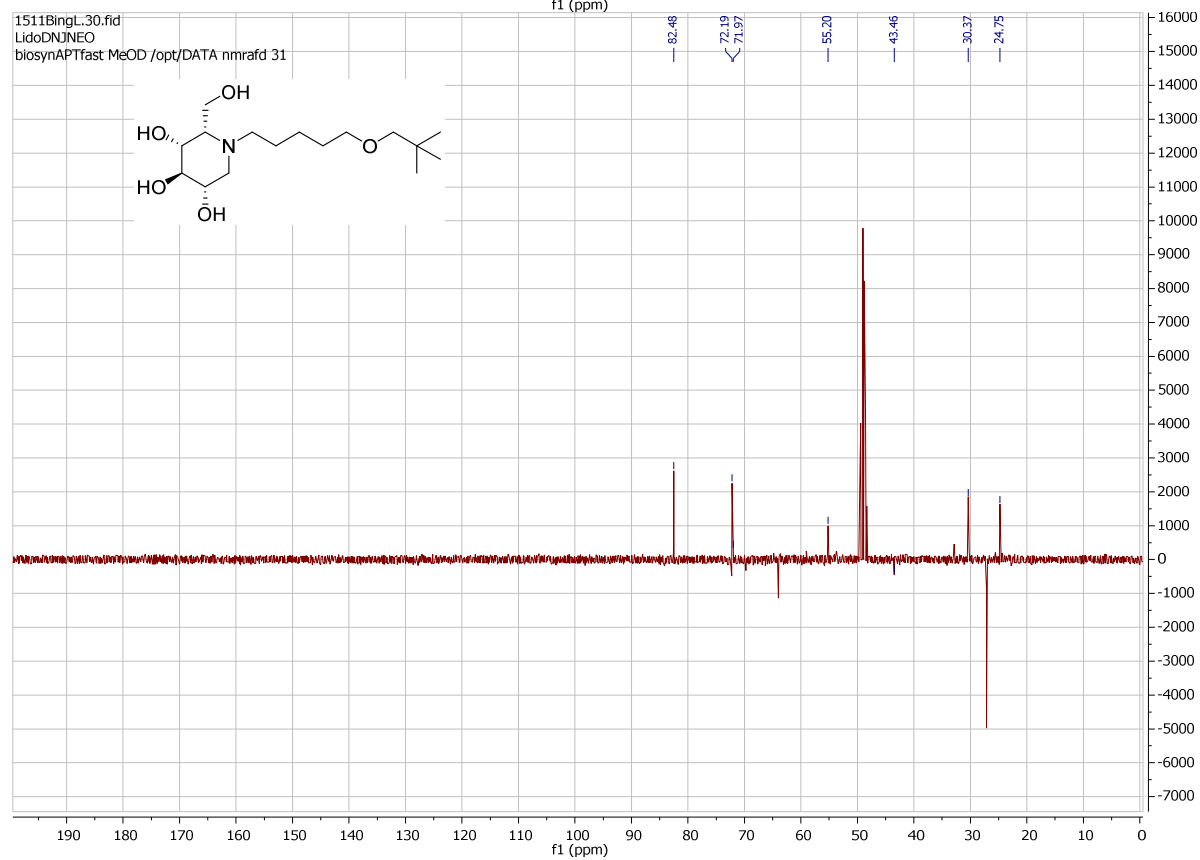
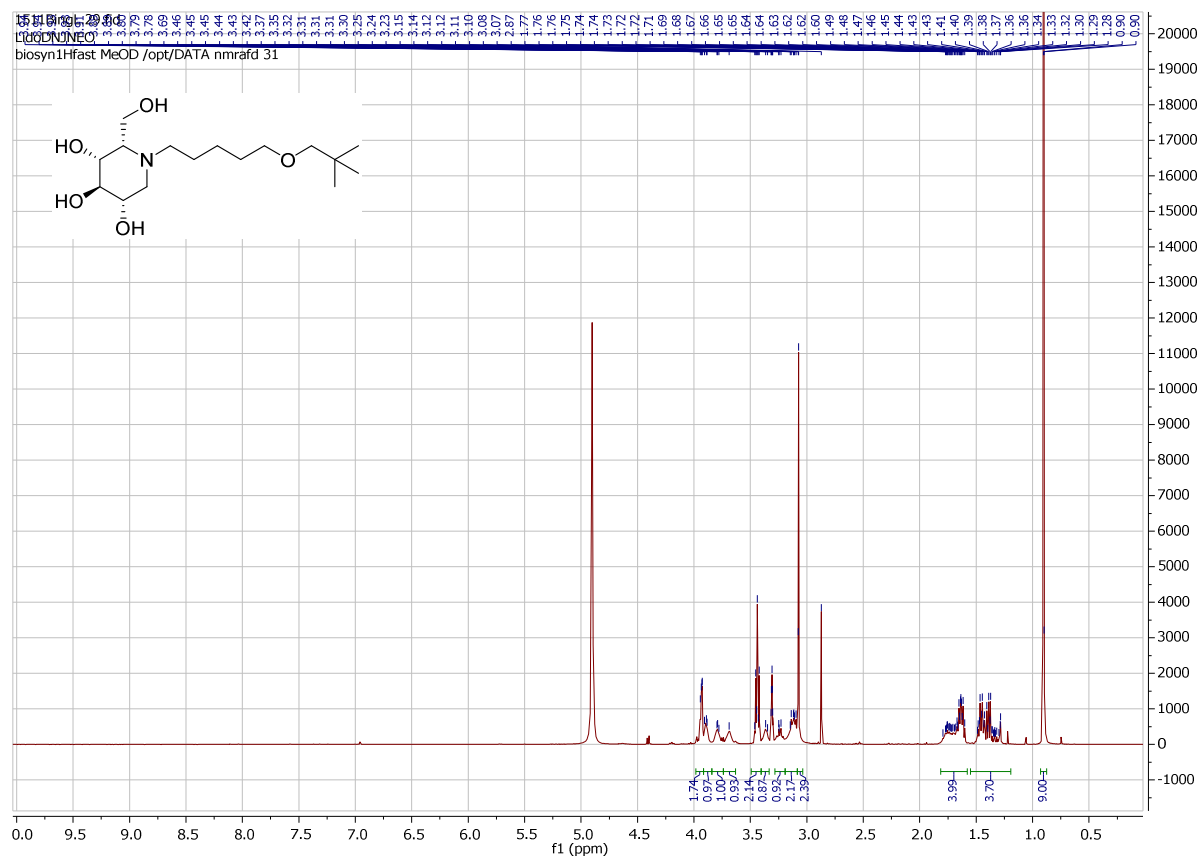
# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound C16.TFA in MeOD/ $\text{CDCl}_3$ .



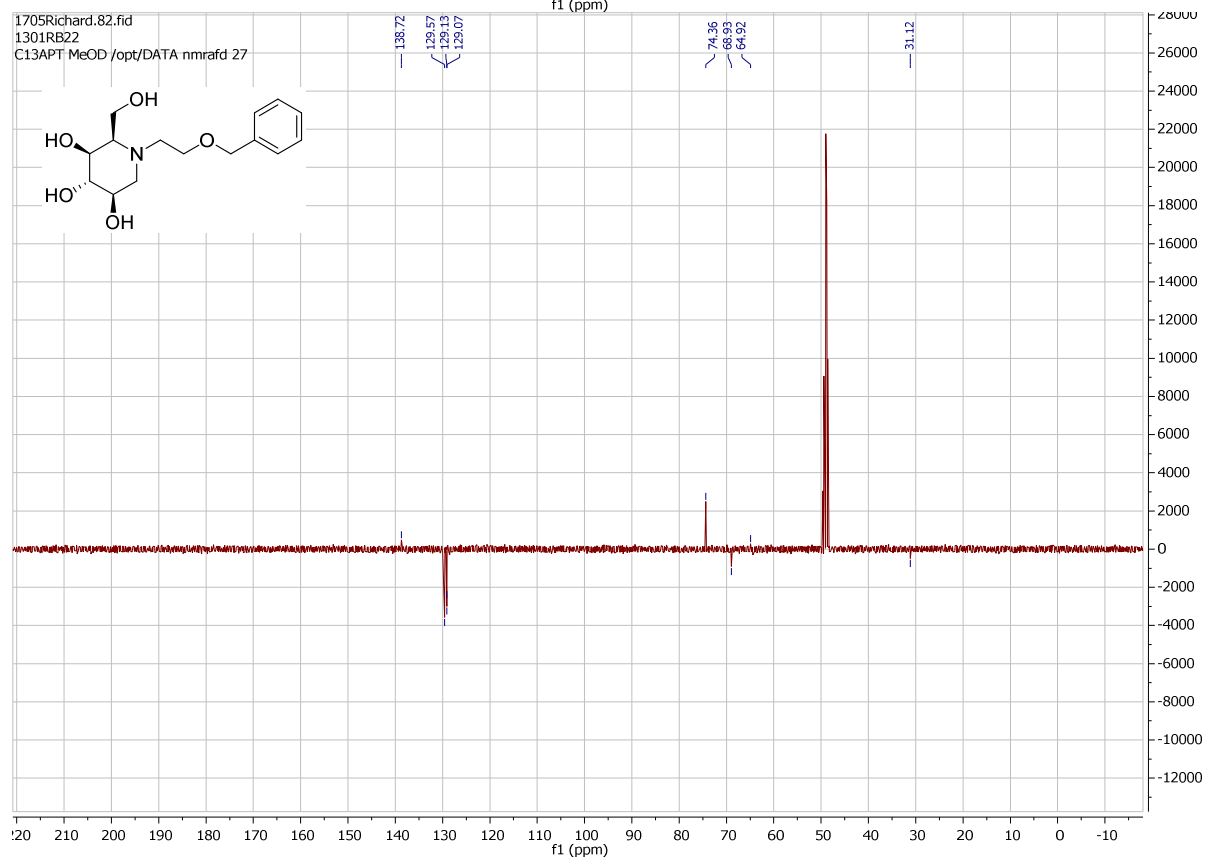
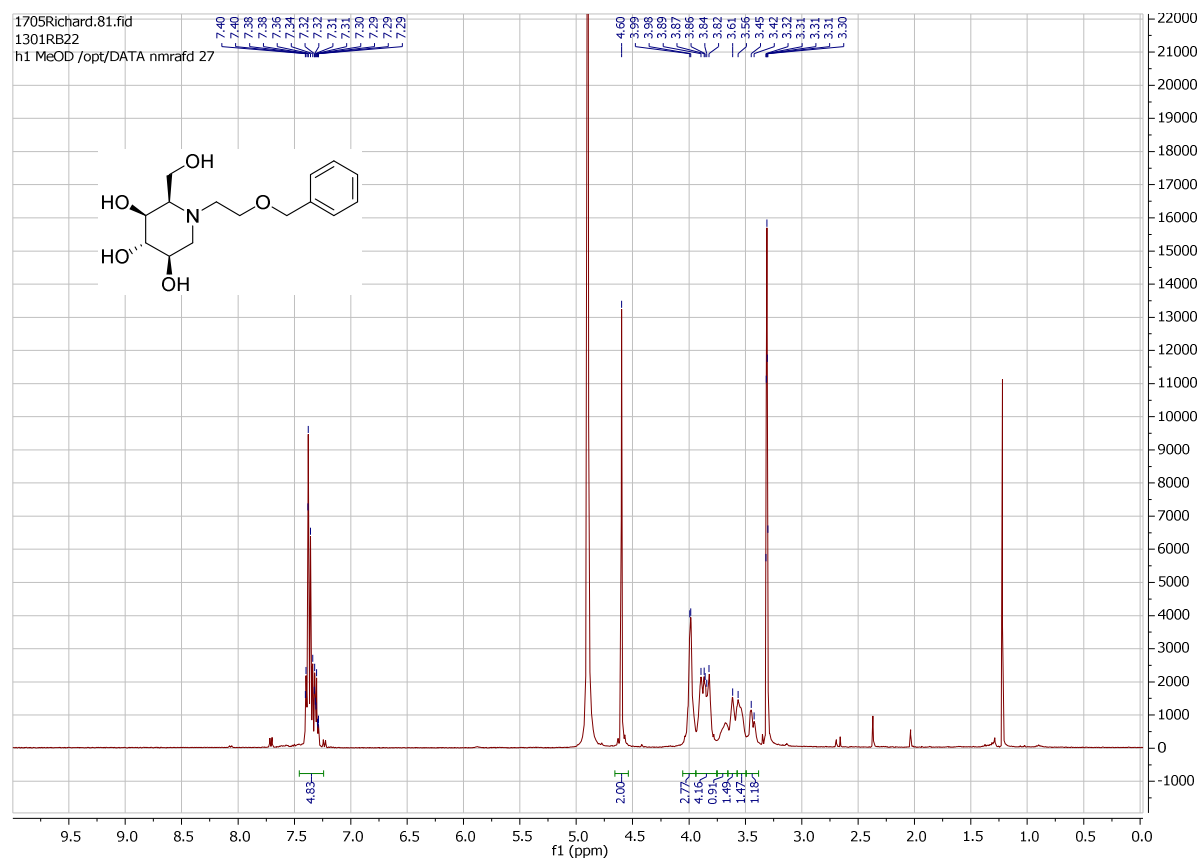
# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound C24.TFA in $\text{D}_2\text{O}$ .



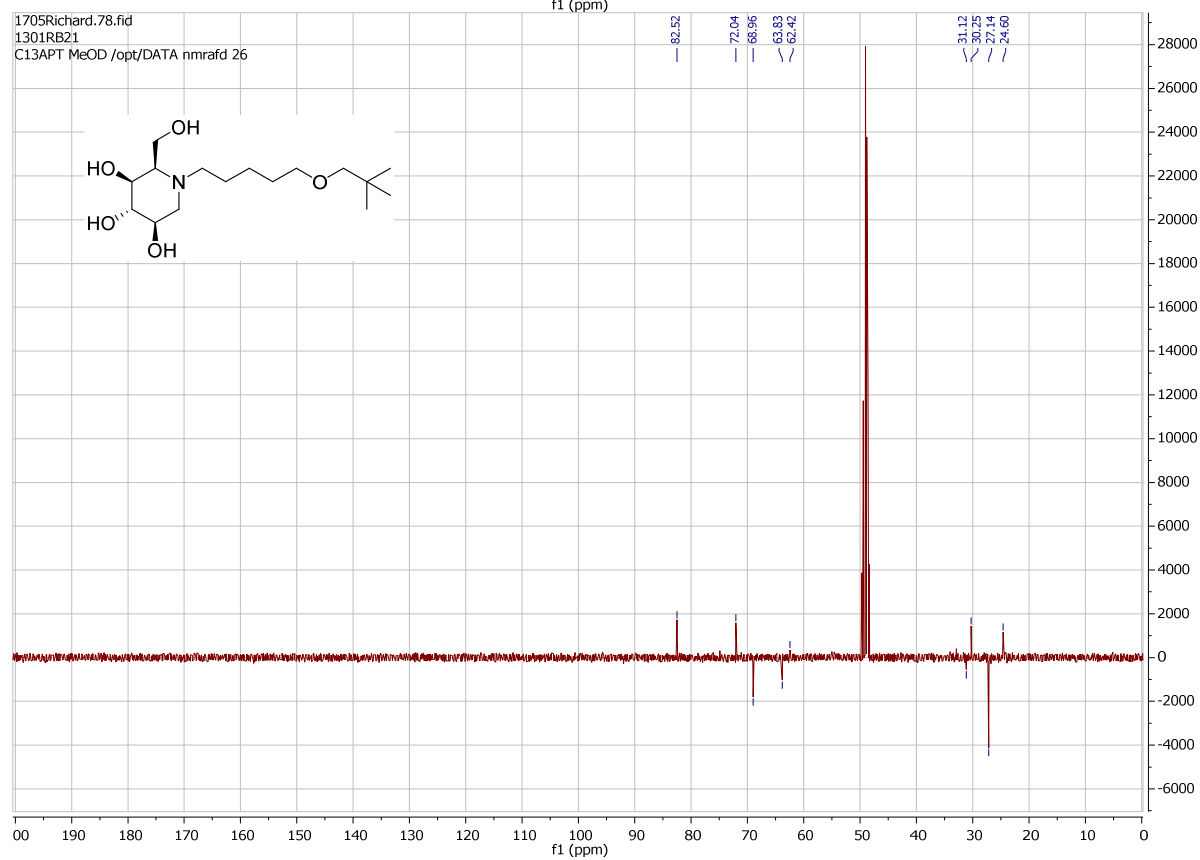
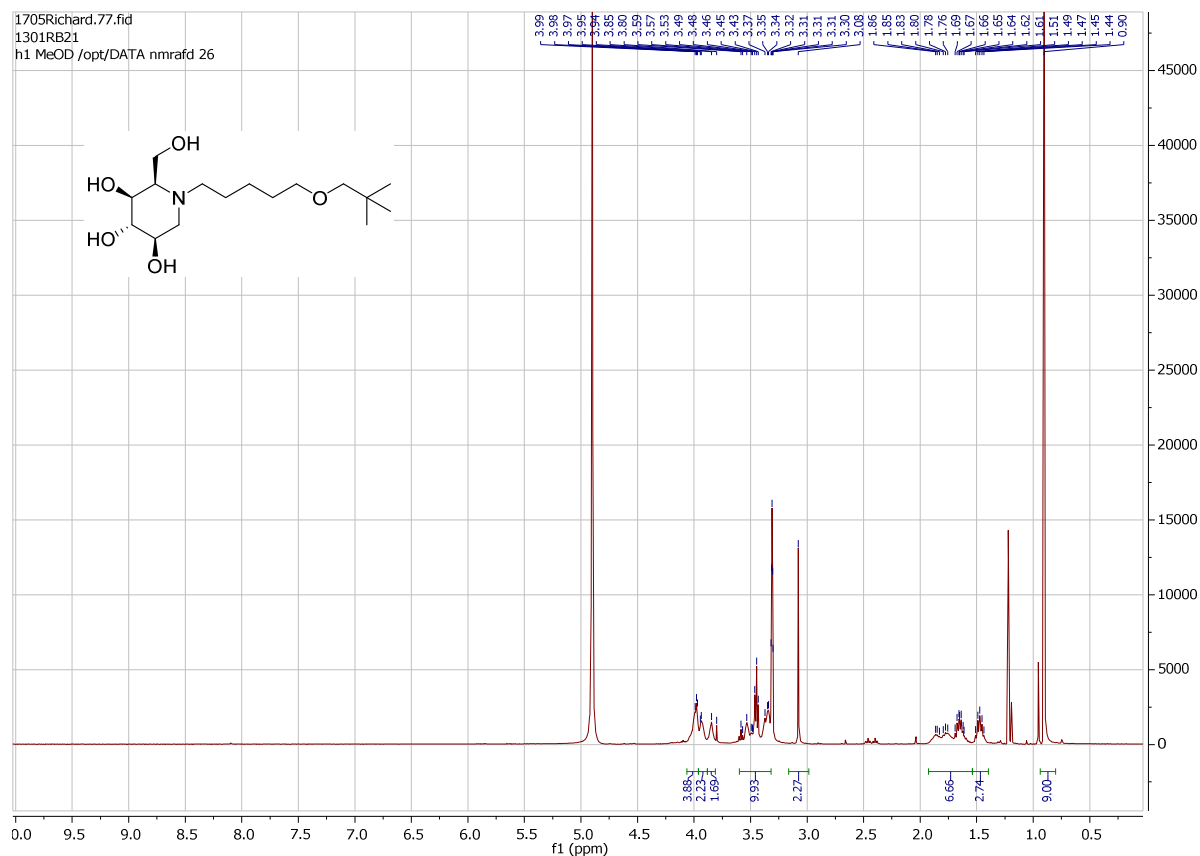
# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound C26.TFA in MeOD.



**<sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound C47.TFA in MeOD.**



# <sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound C49.TFA in MeOD.

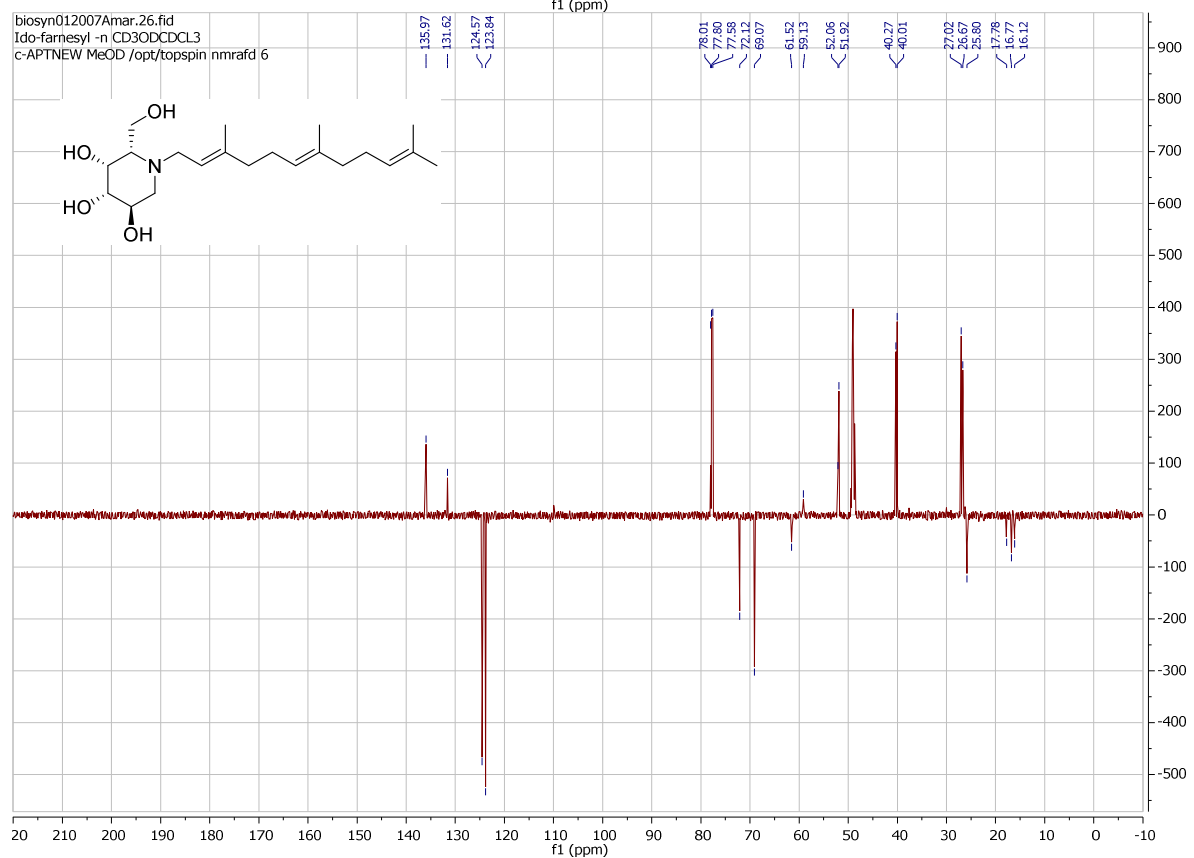
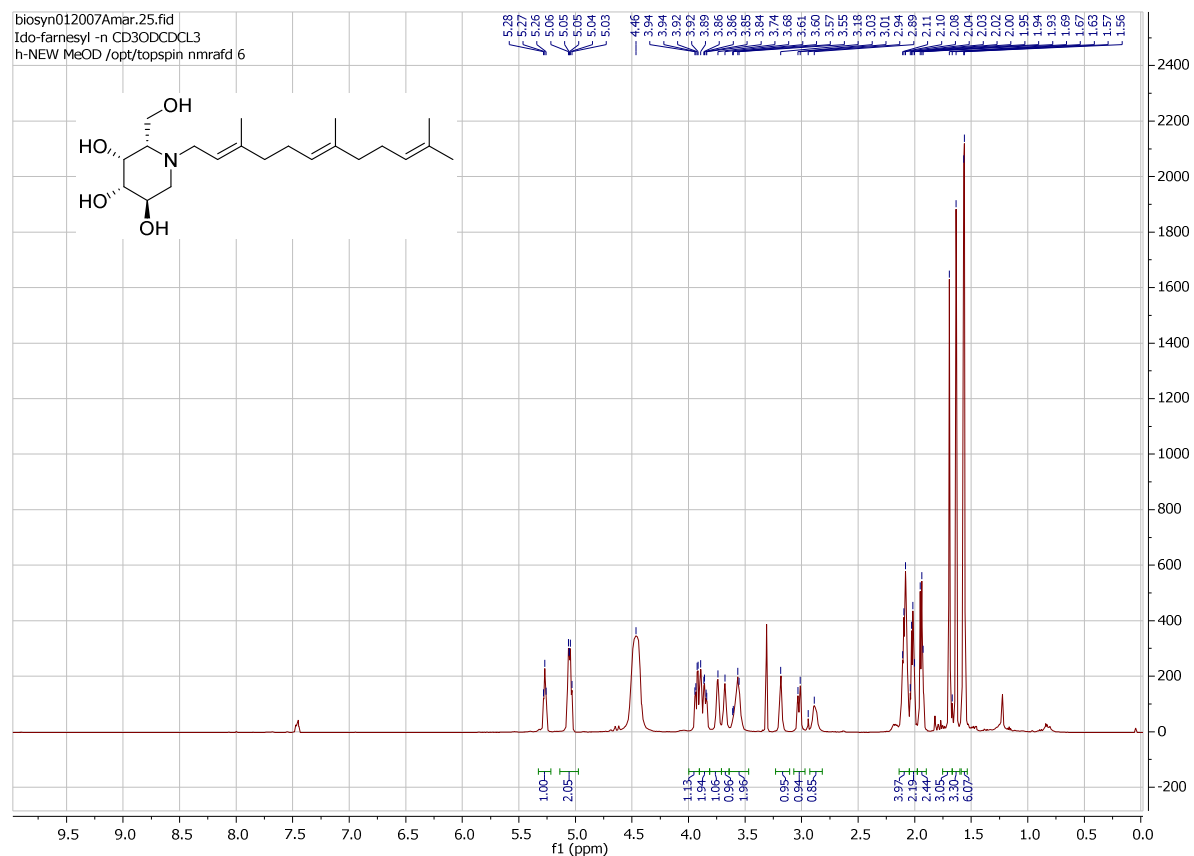




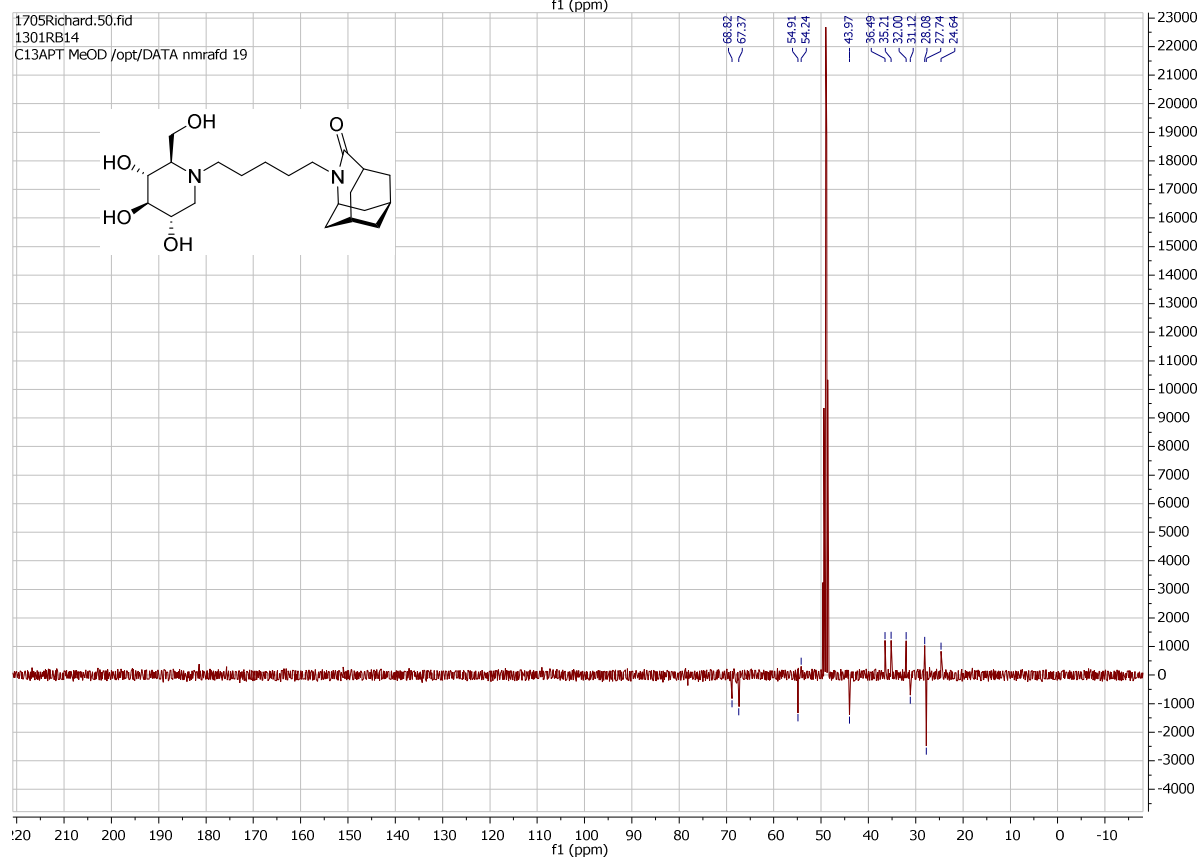
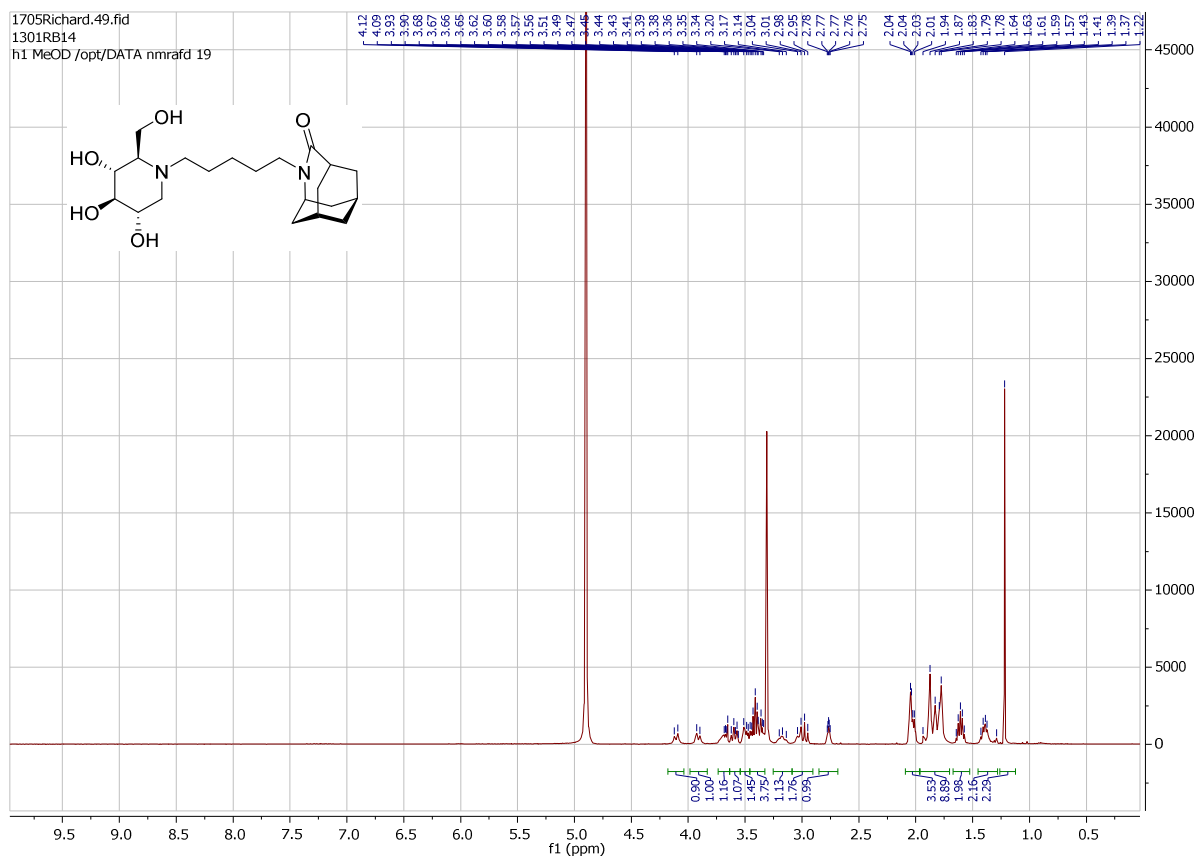




# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound C54.TFA in MeOD/ $\text{CDCl}_3$ .

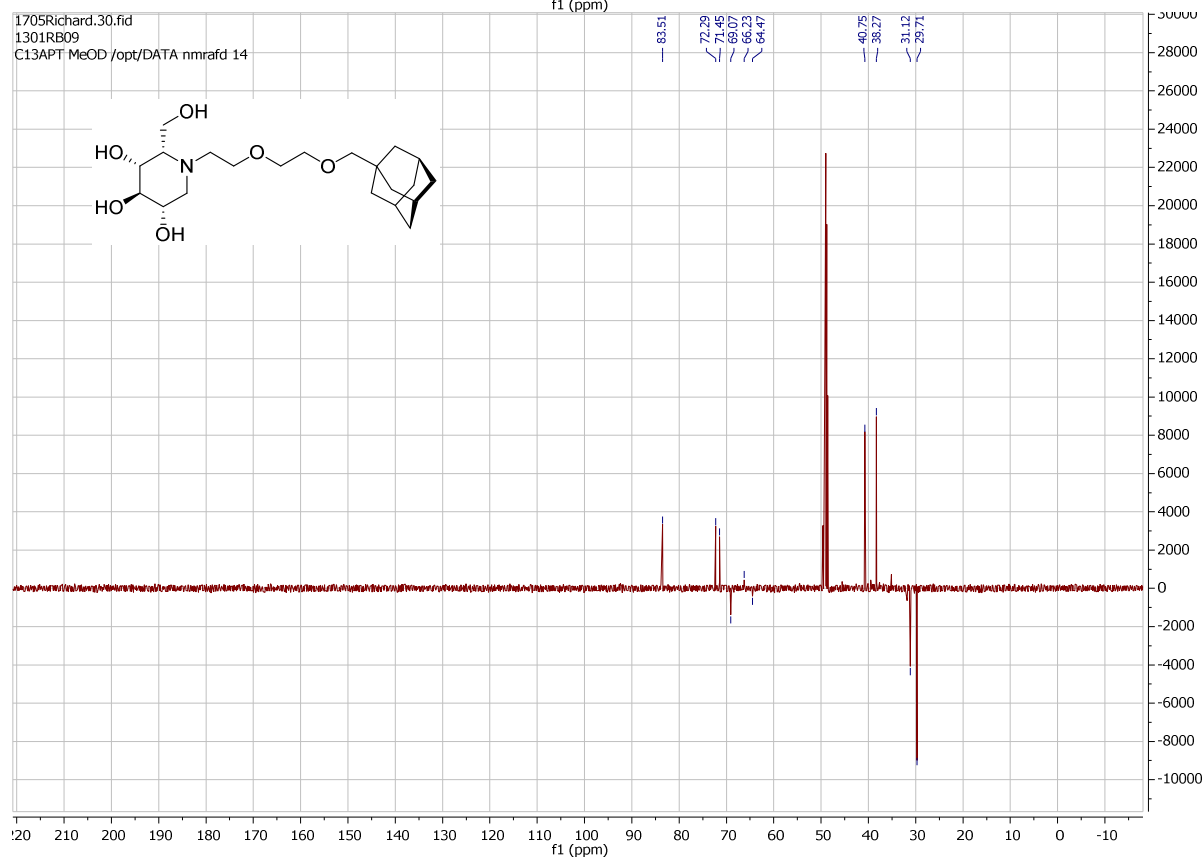
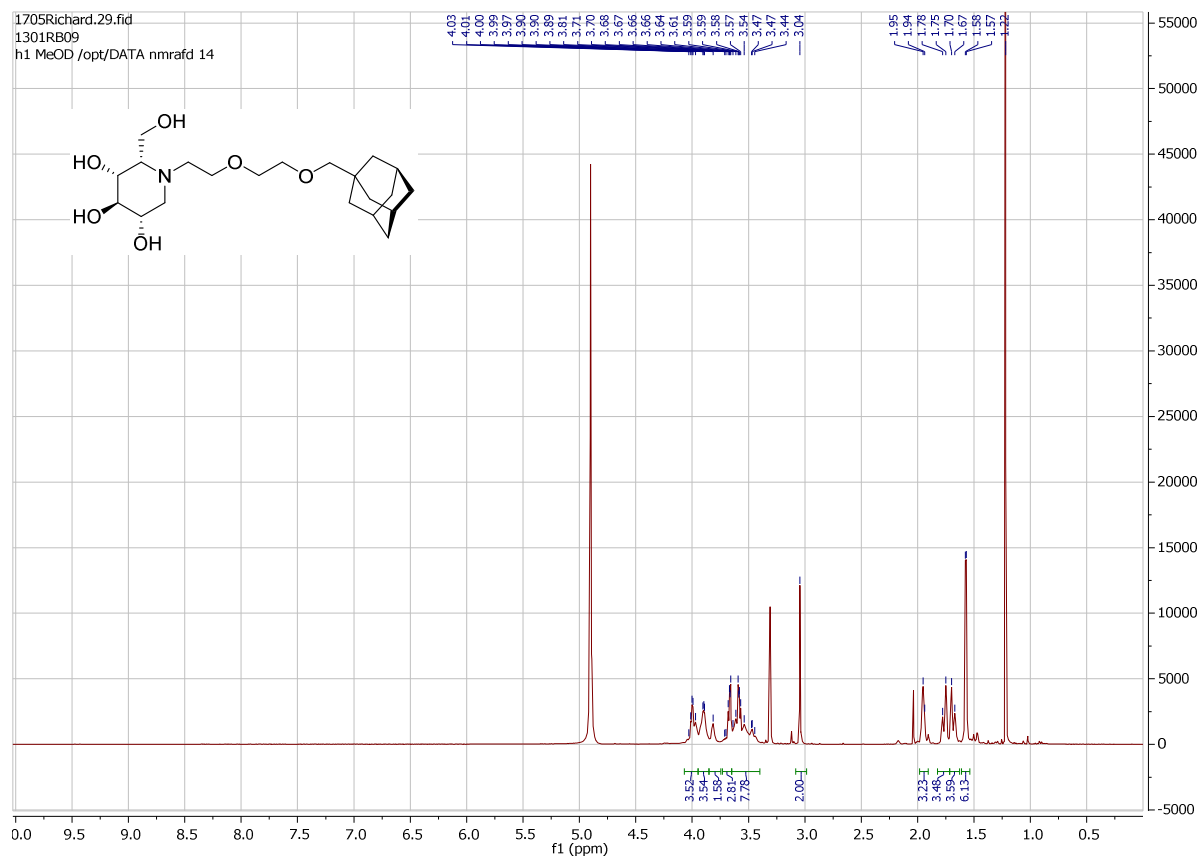


**<sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound C76.TFA in MeOD.**

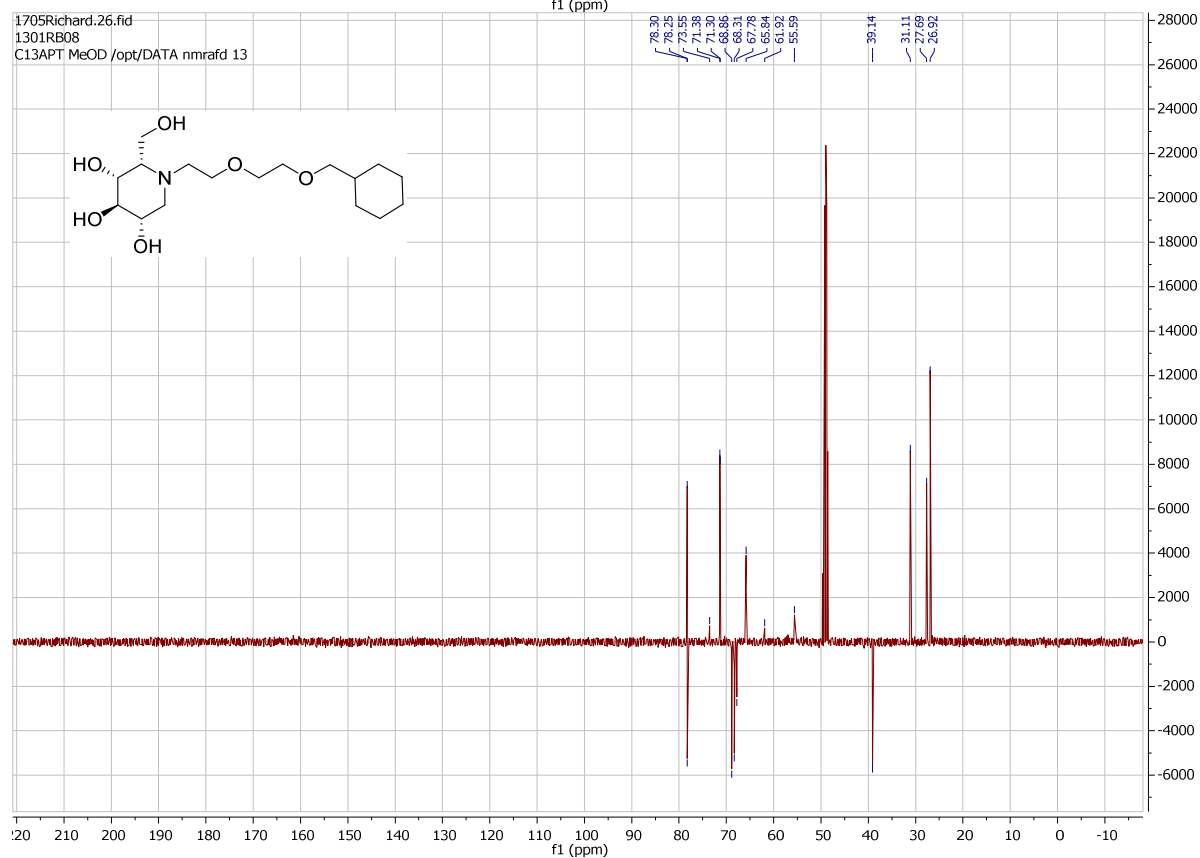
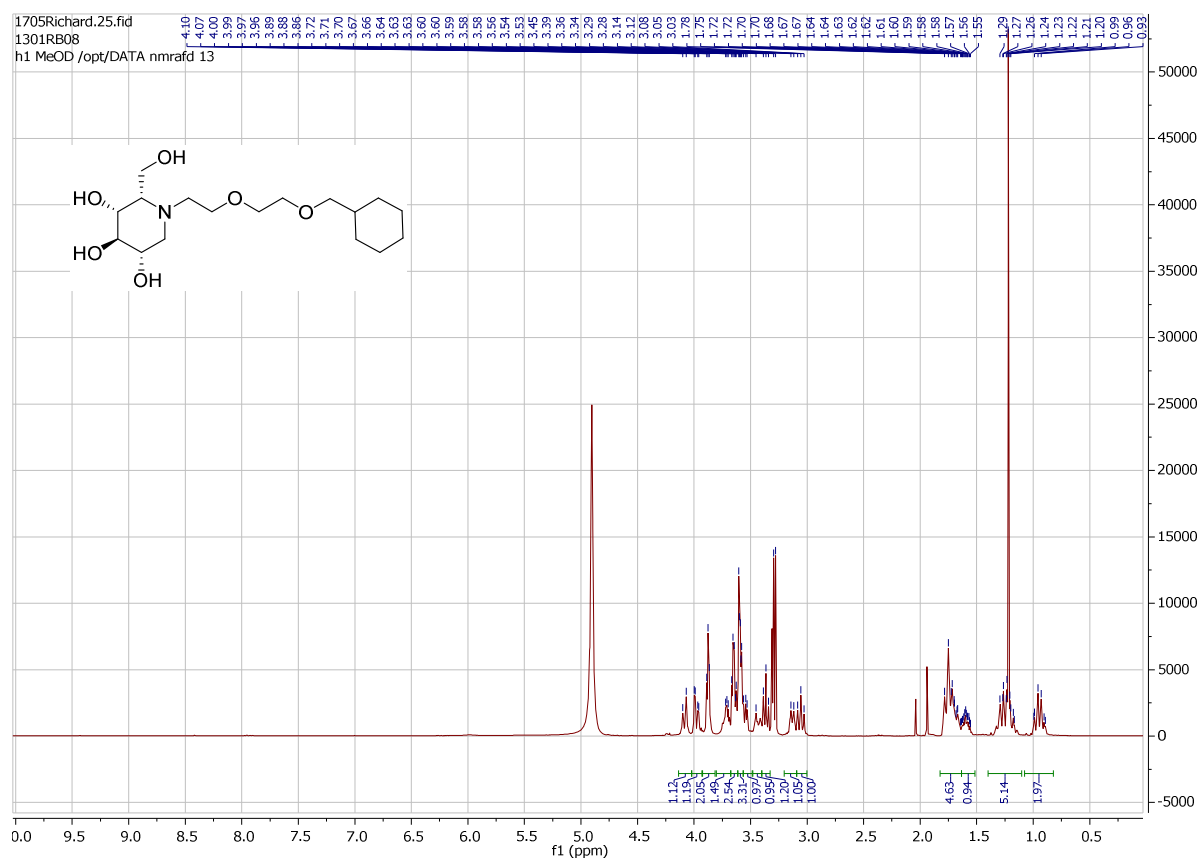




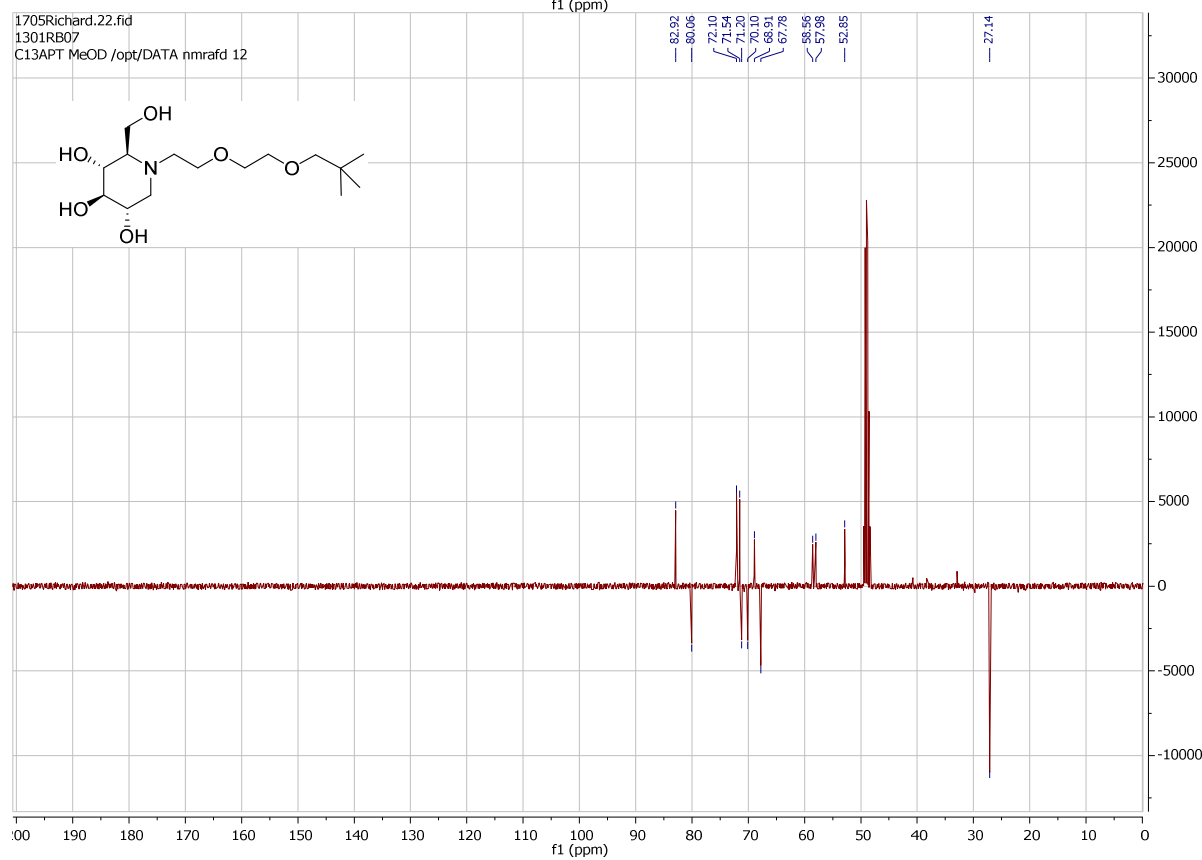
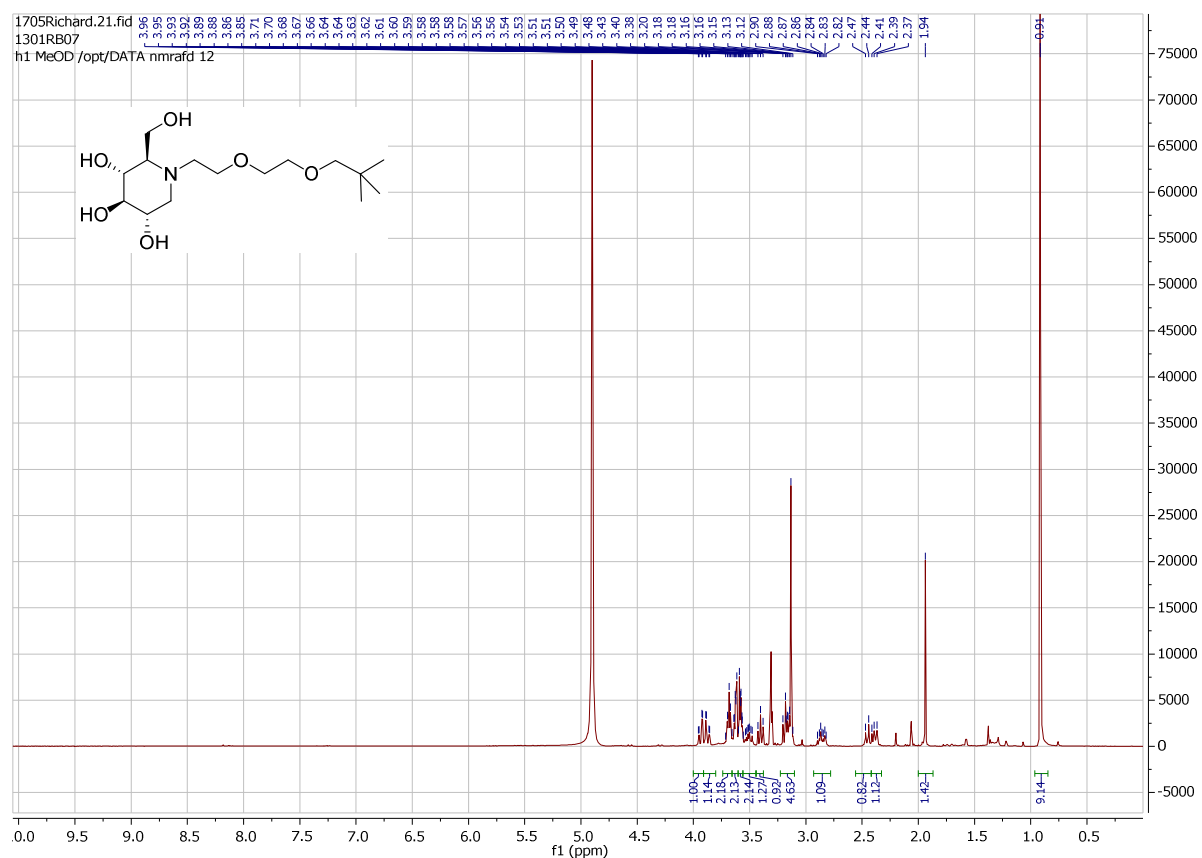
**<sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound C85.TFA in MeOD.**



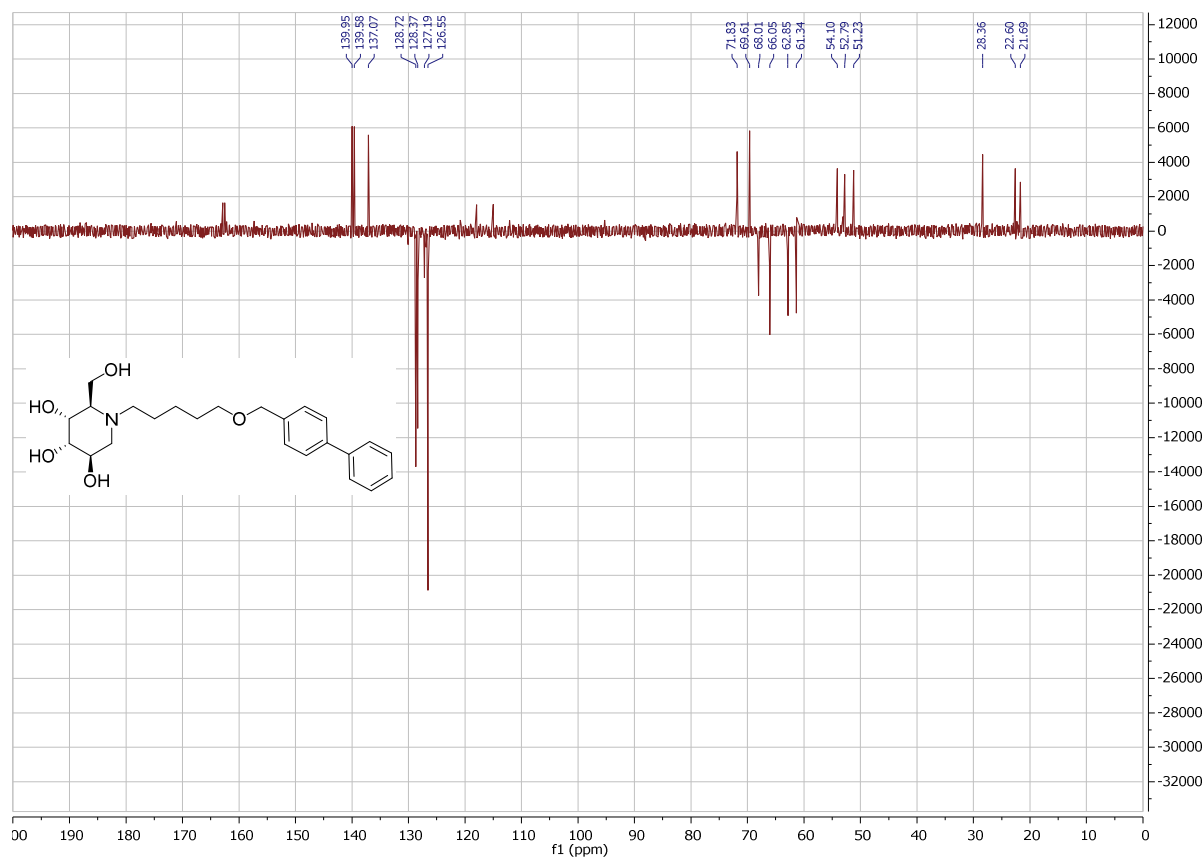
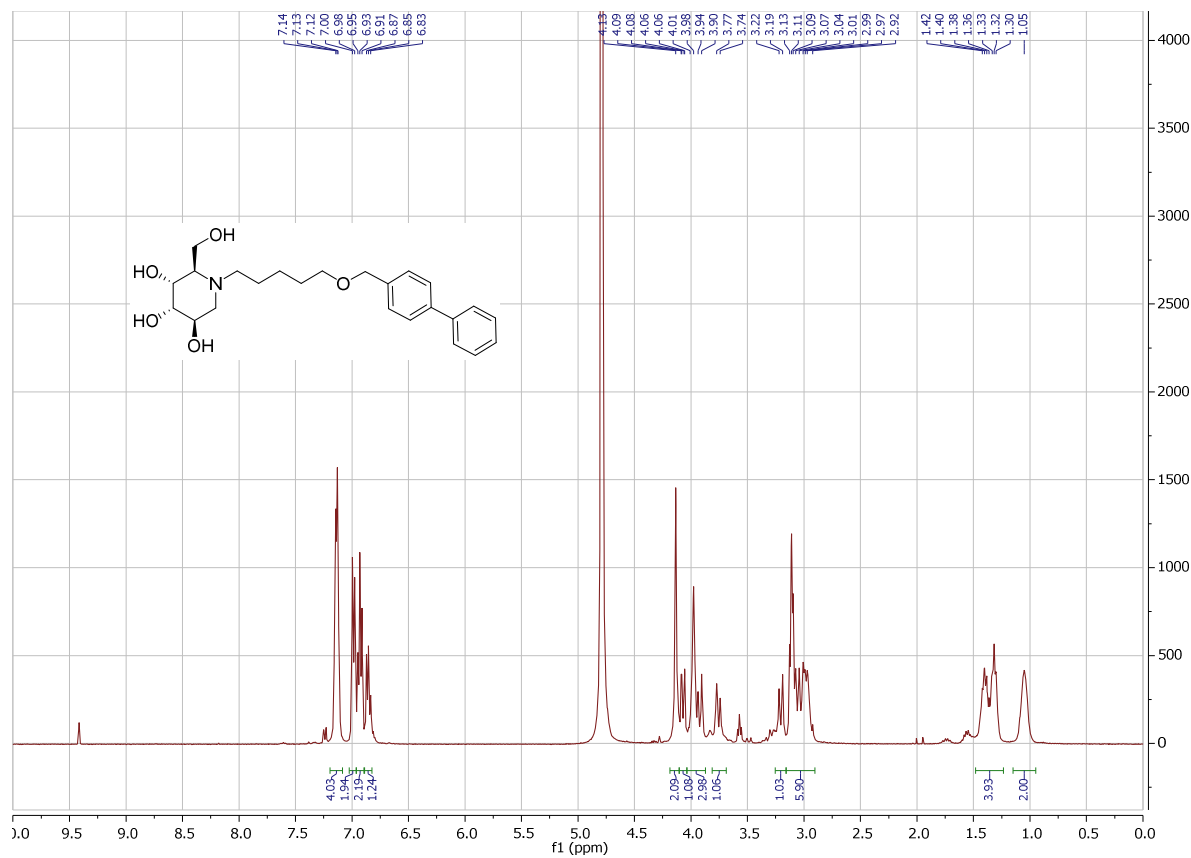
# <sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound C87.TFA in MeOD.



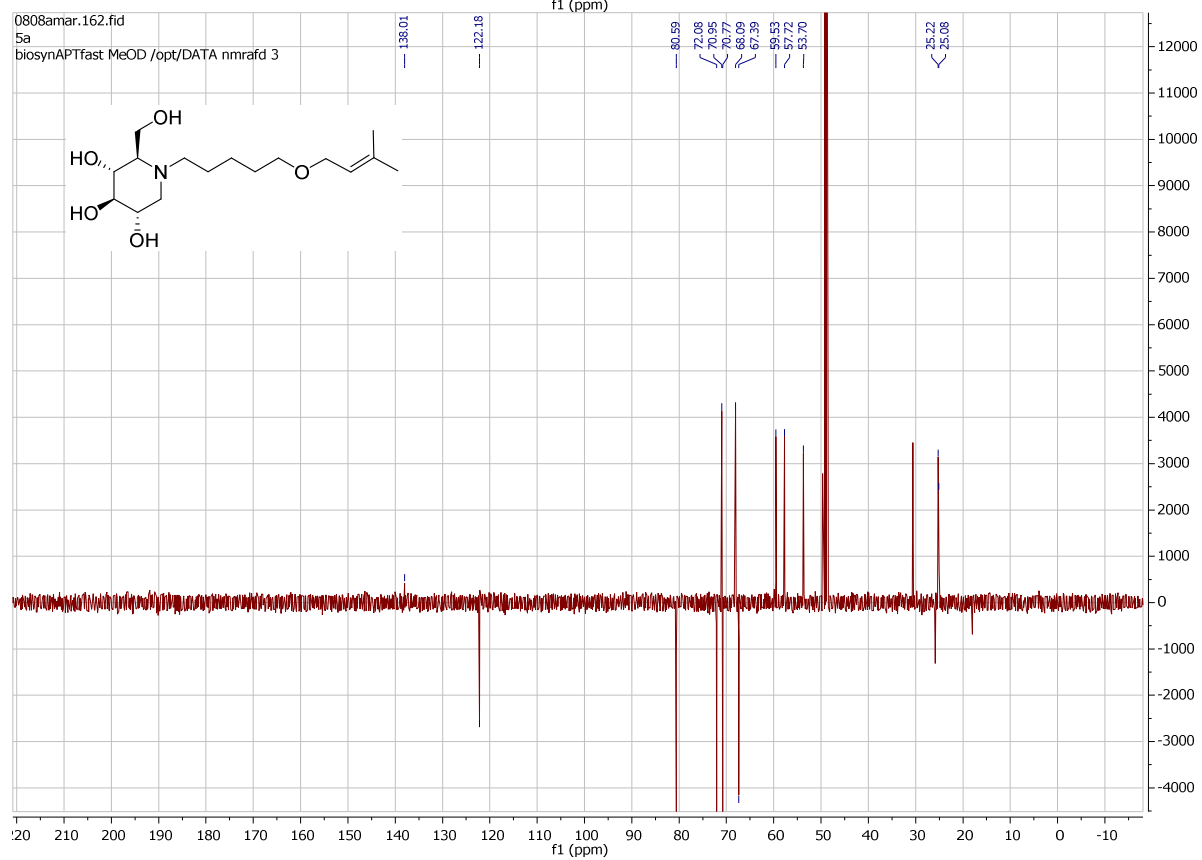
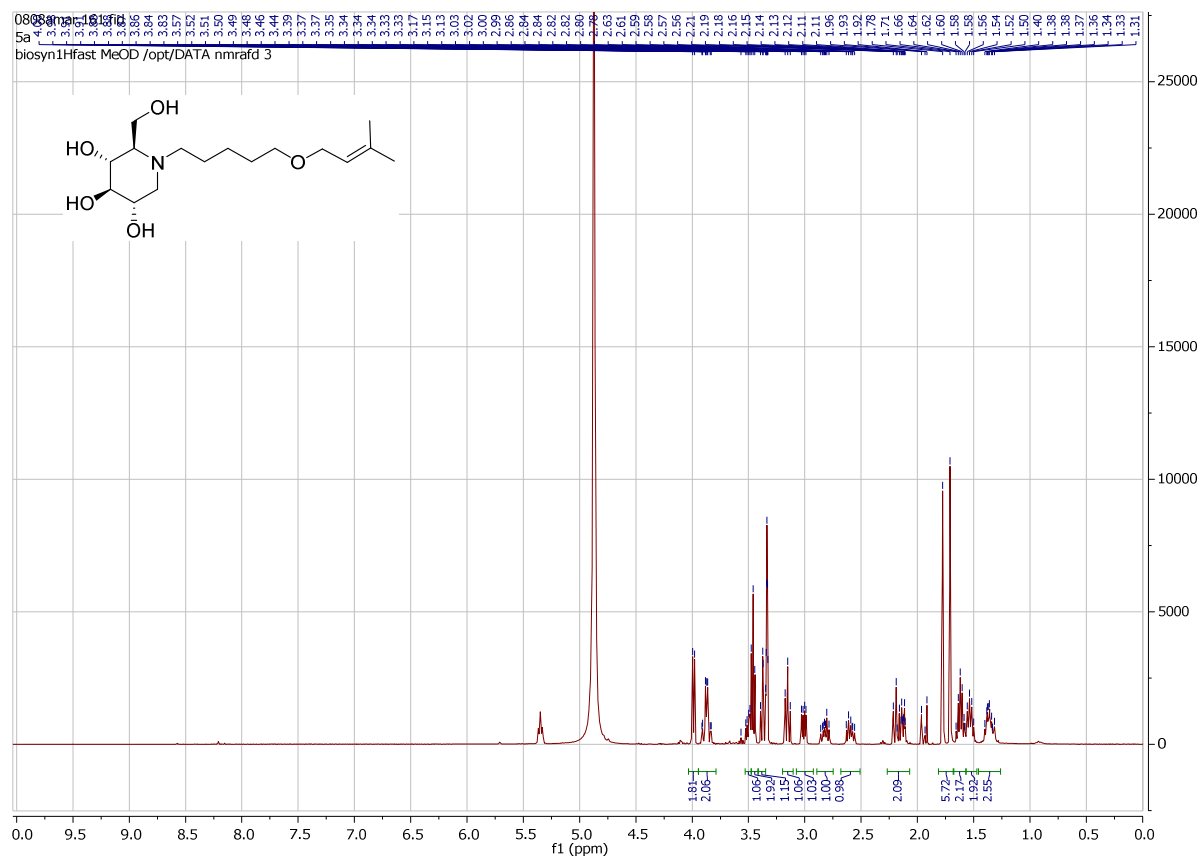
**<sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound C89.TFA in MeOD.**



**<sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound C95.TFA in D<sub>2</sub>O.**

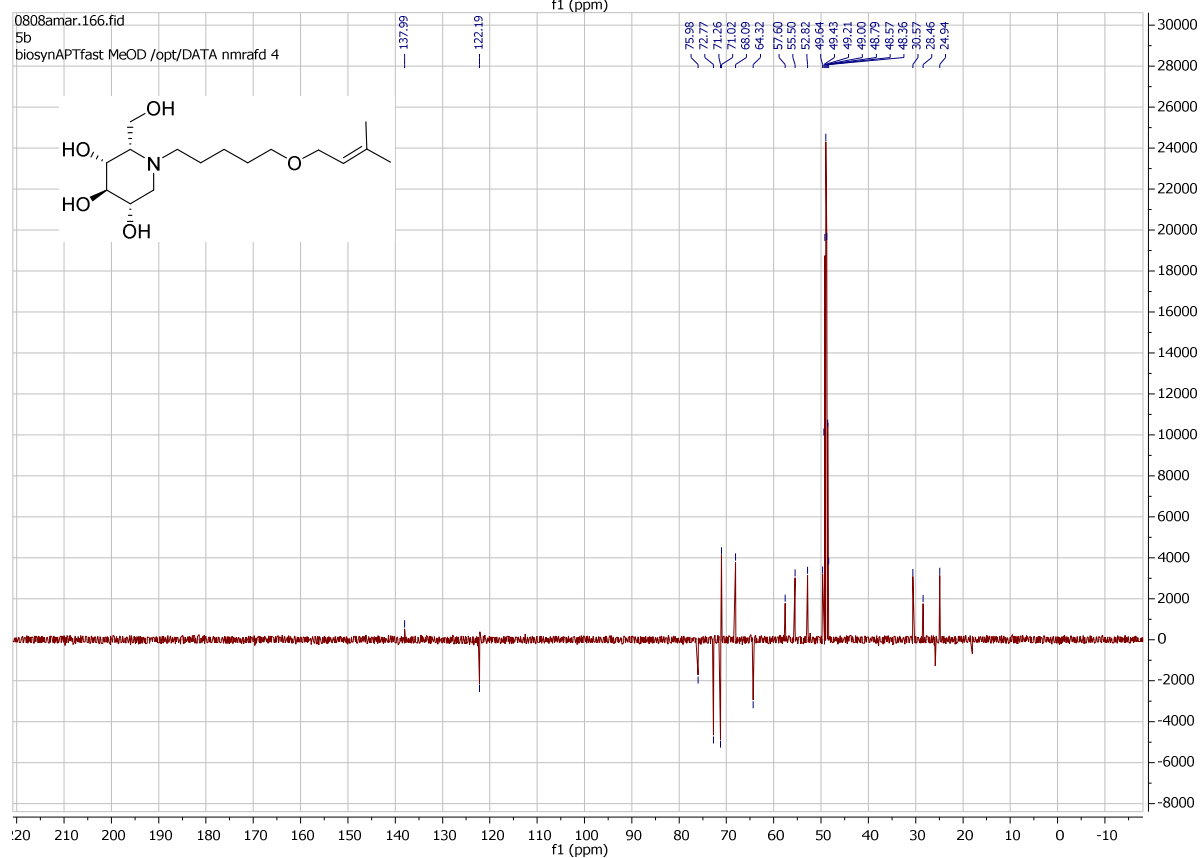
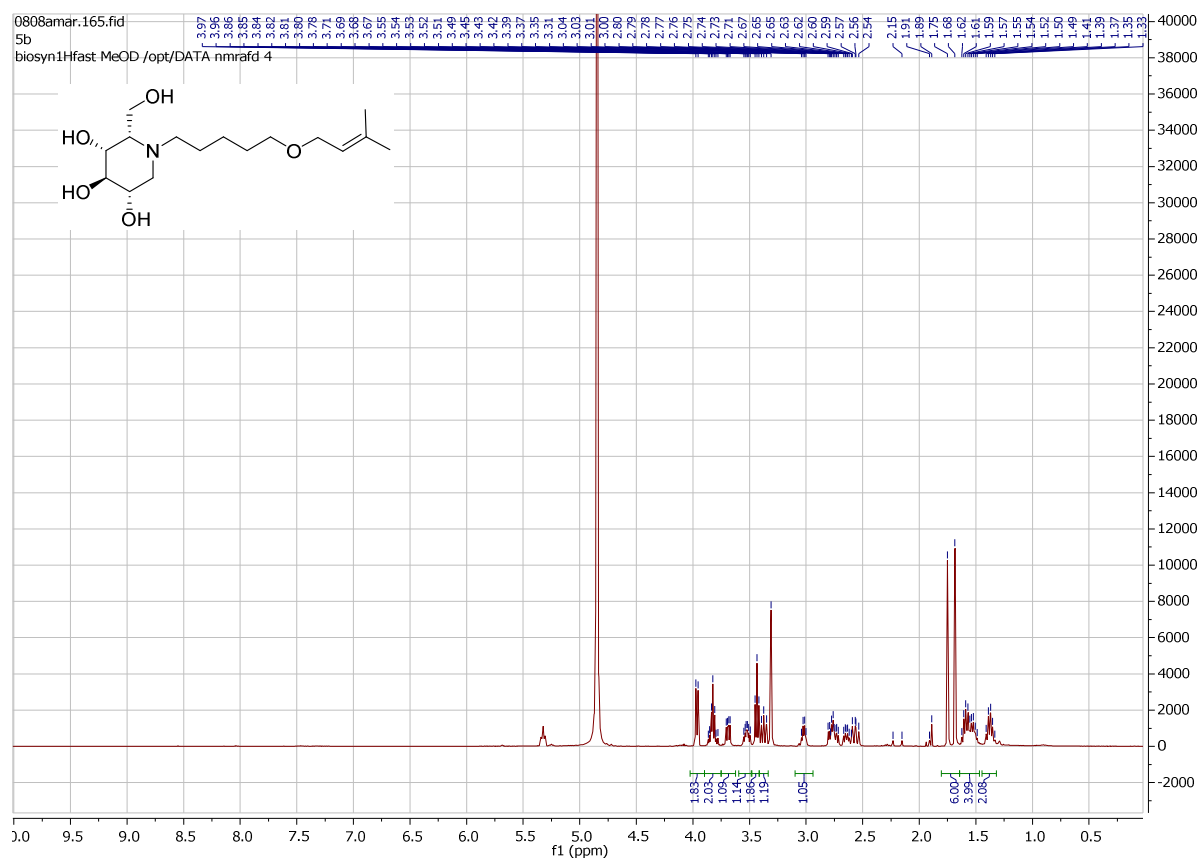


# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound C100.TFA in MeOD.

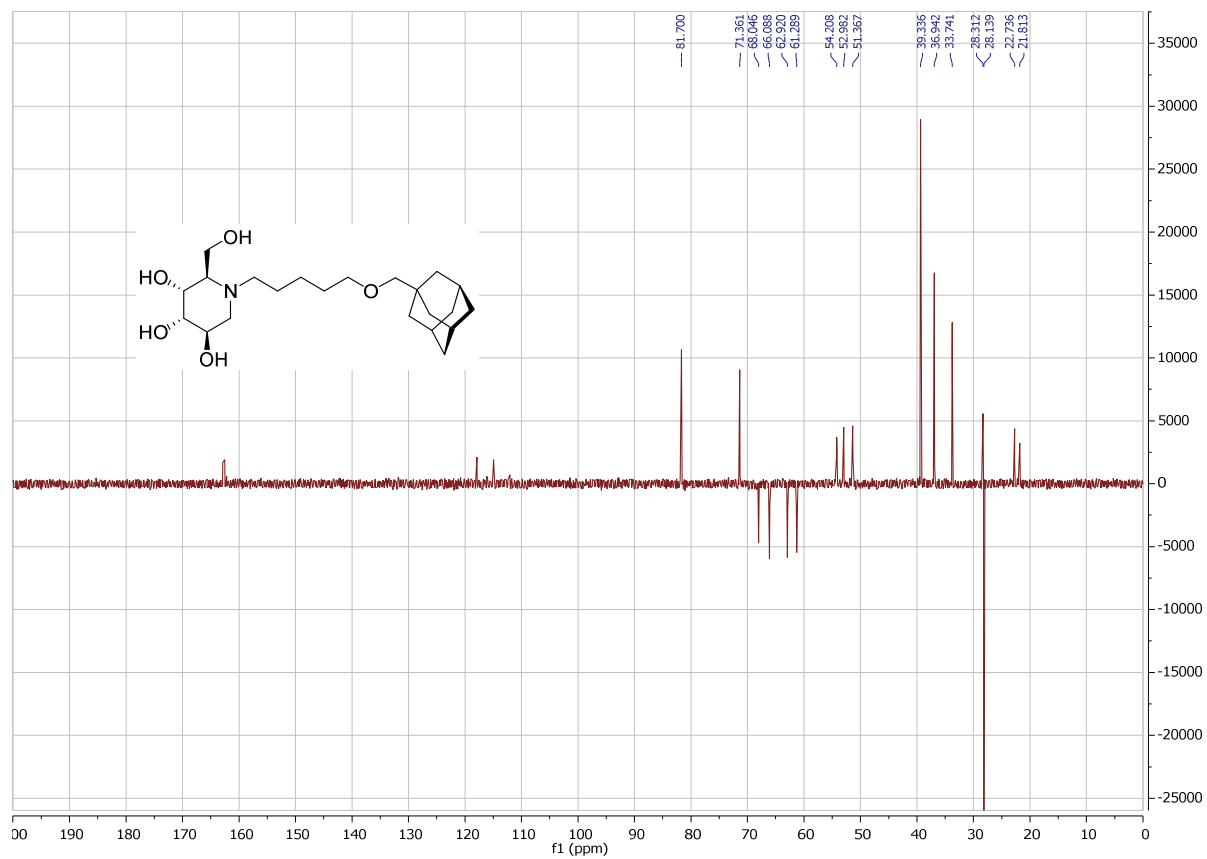
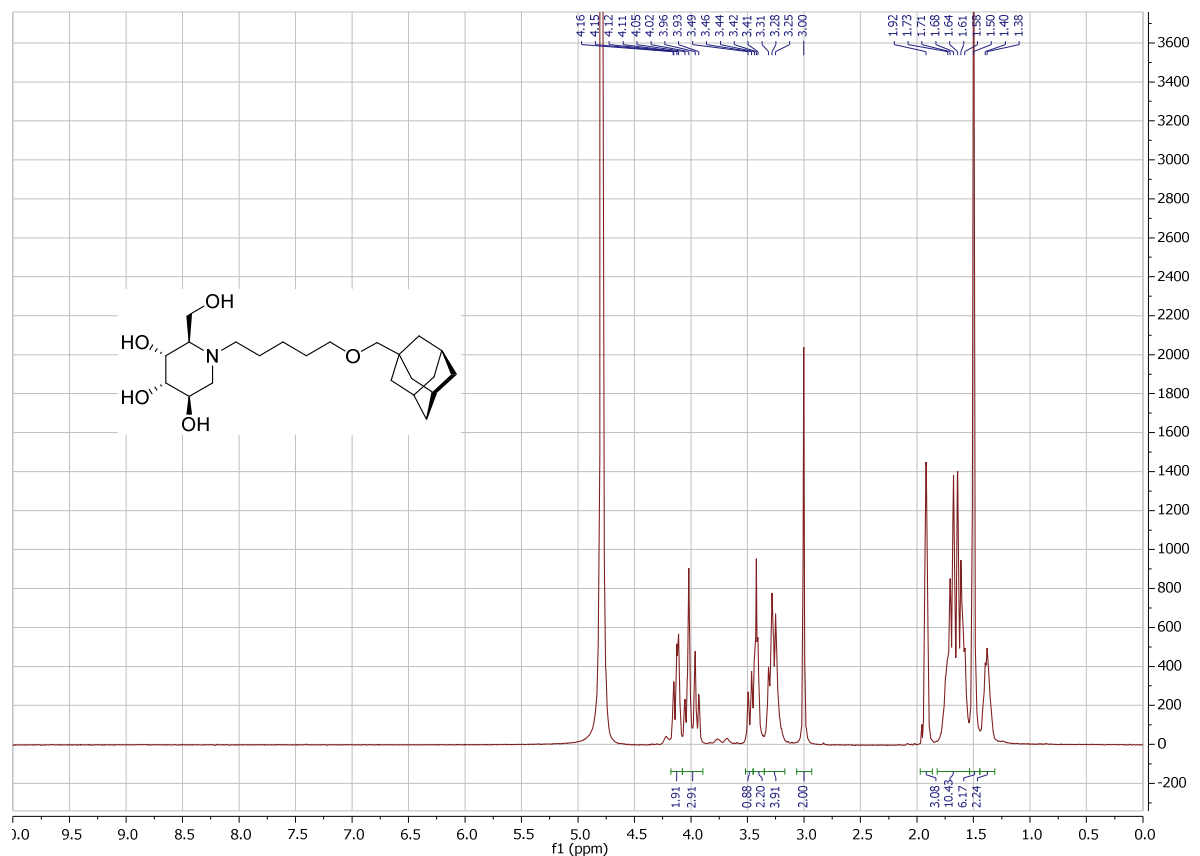




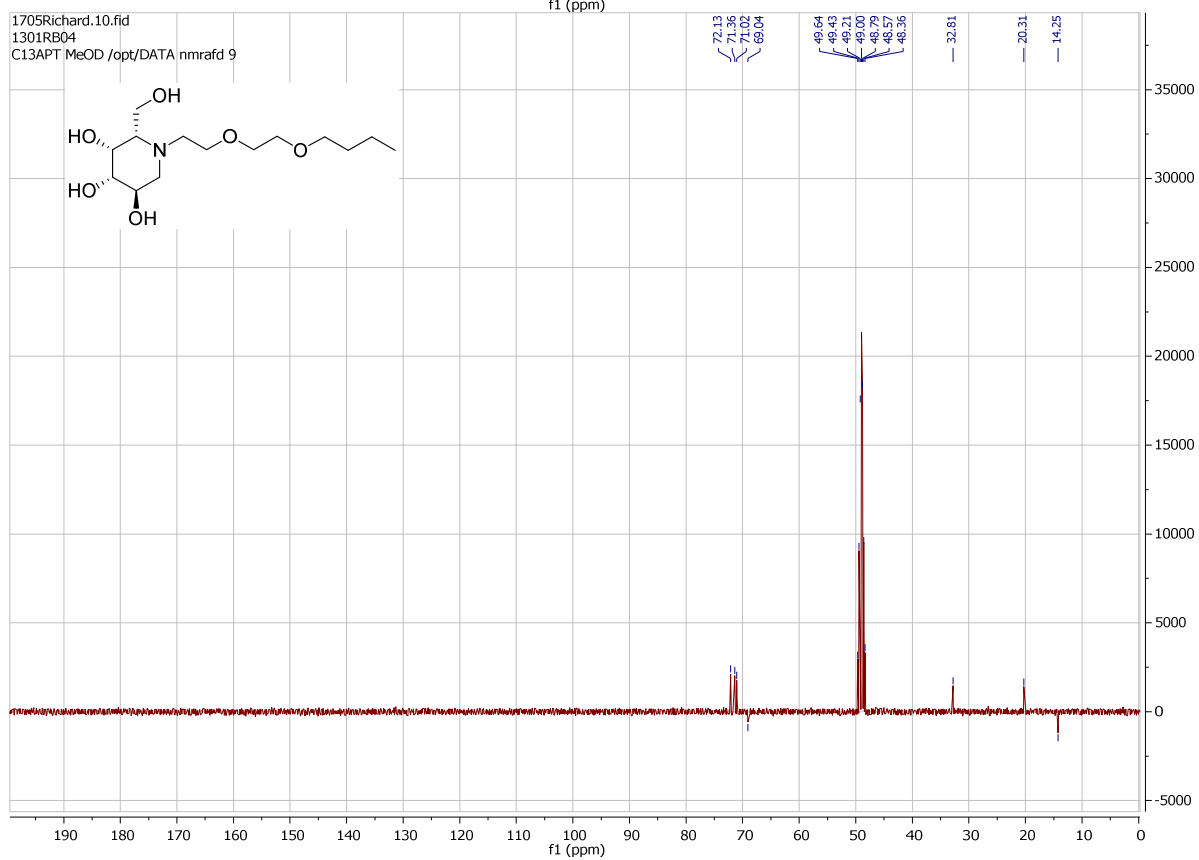
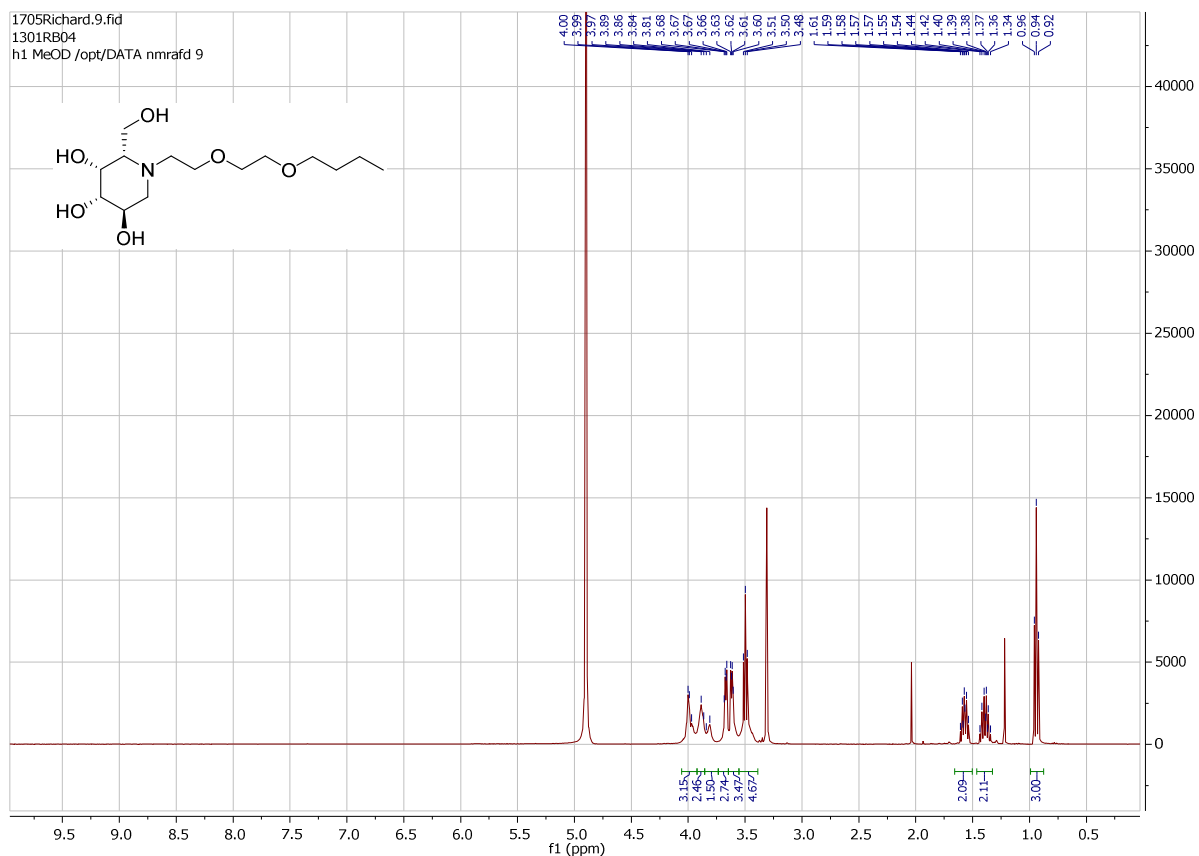
# <sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound C102.TFA in MeOD.



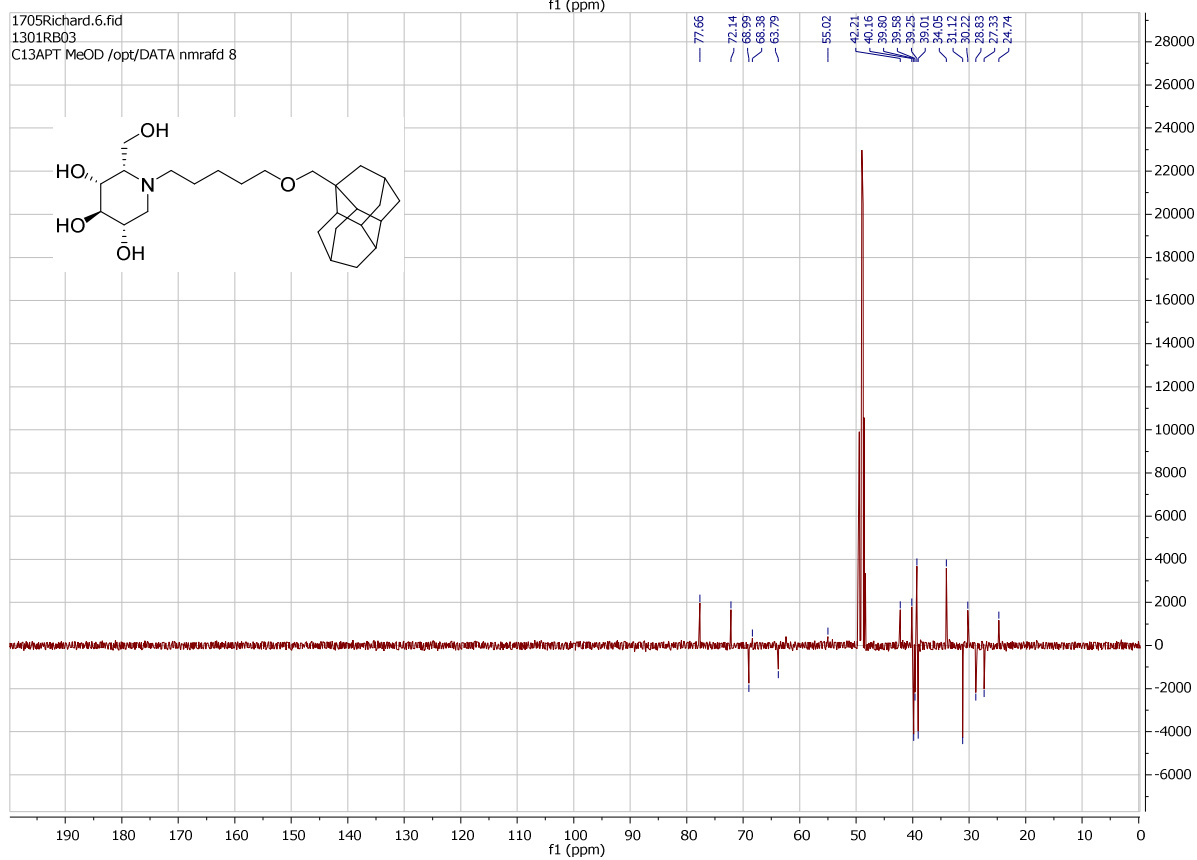
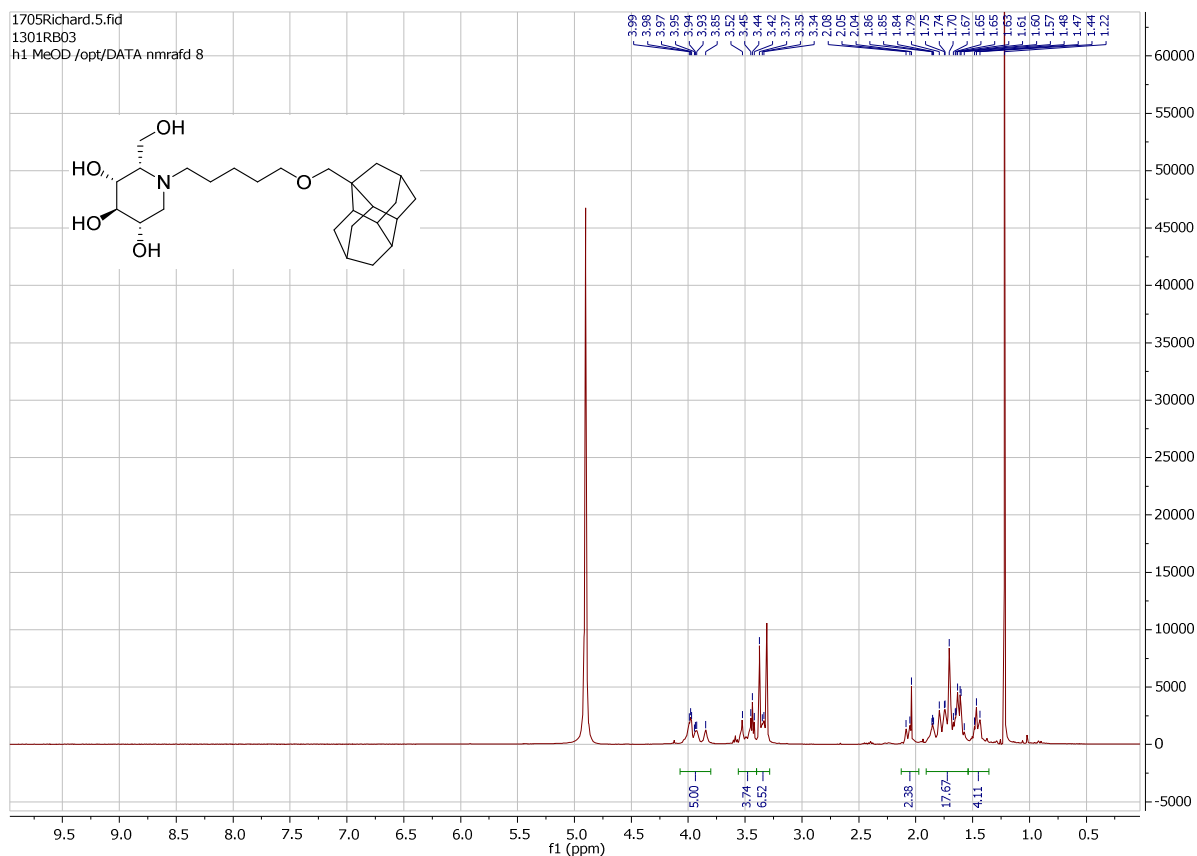
# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound C105.TFA in $\text{D}_2\text{O}$ .



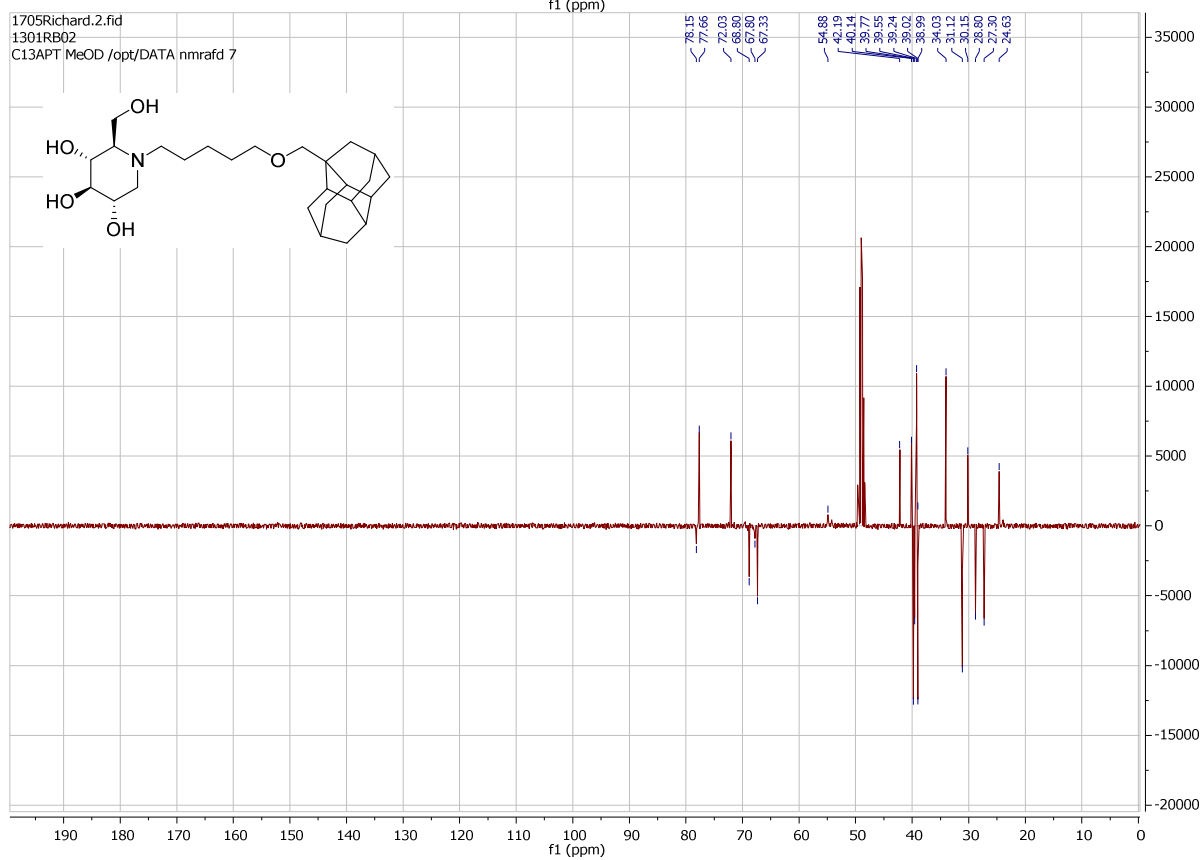
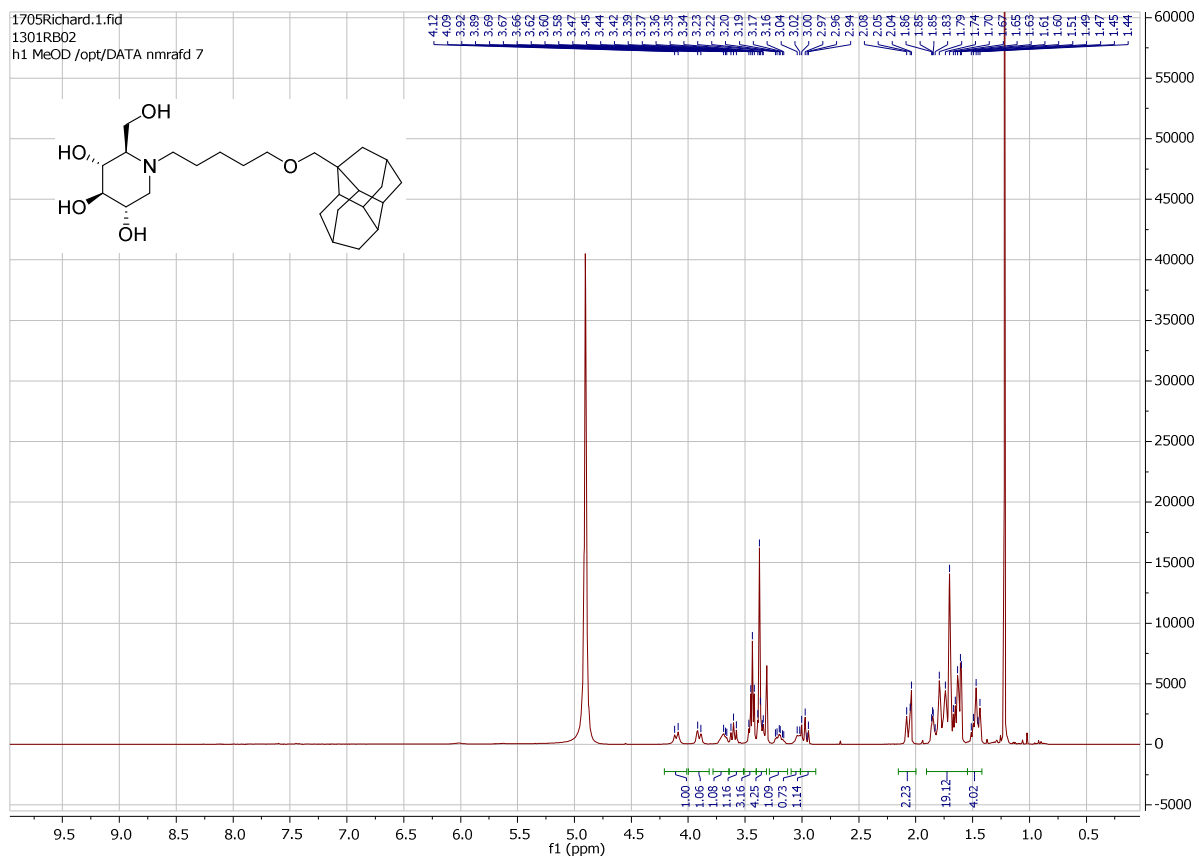
**<sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound C107.TFA in MeOD.**



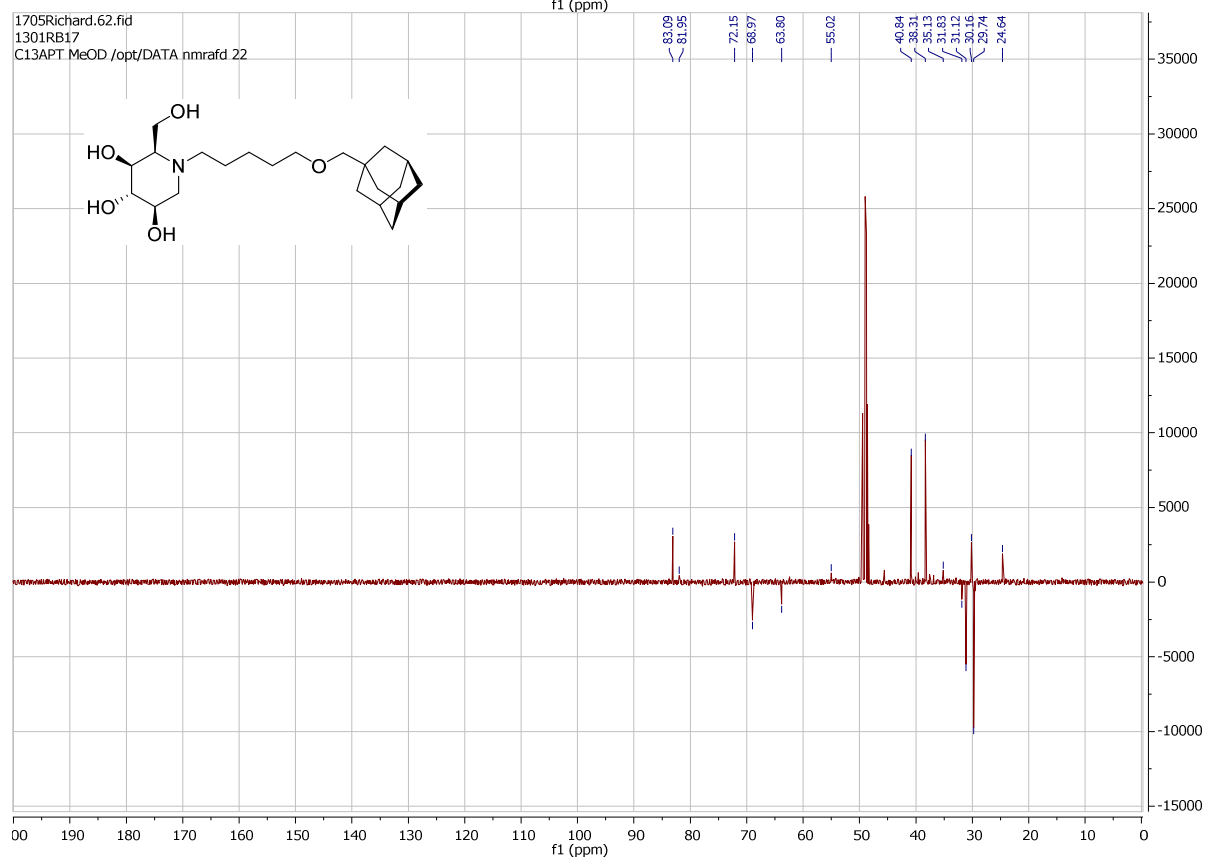
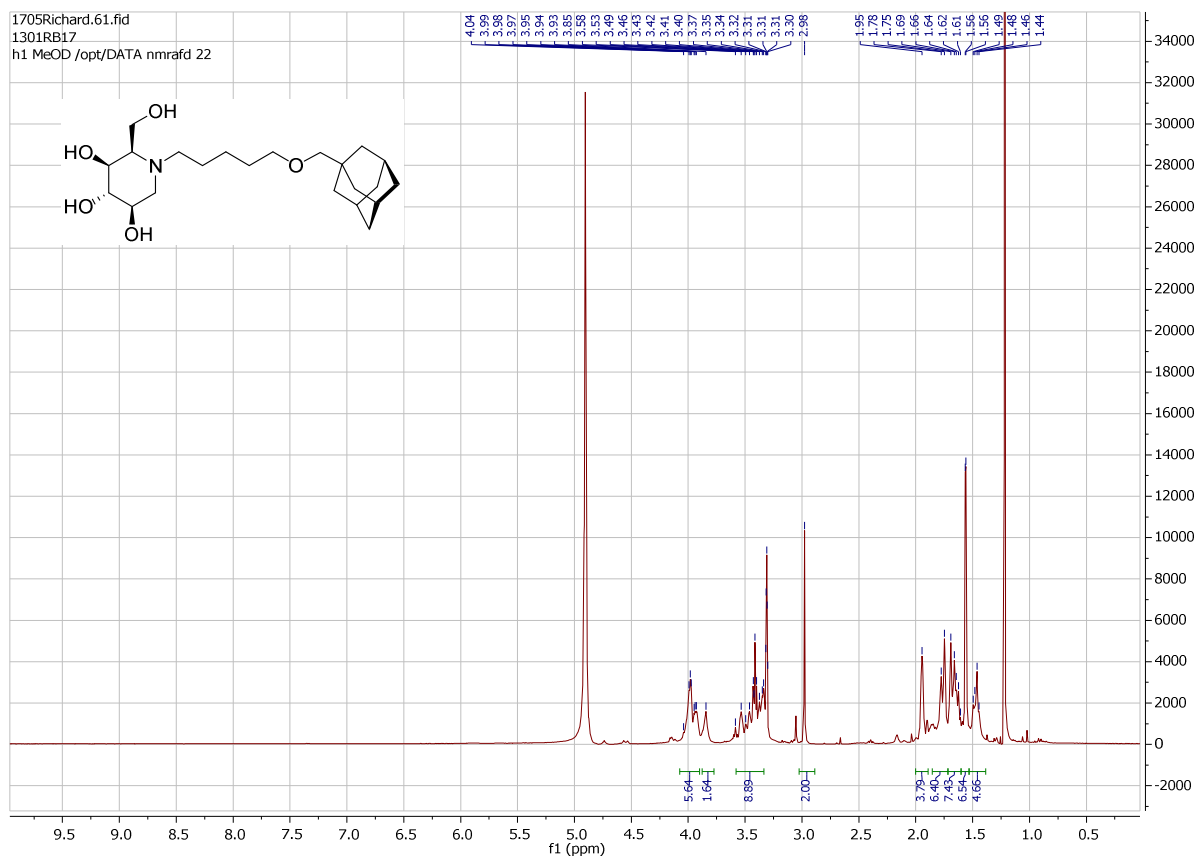
# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound C109.TFA in MeOD.



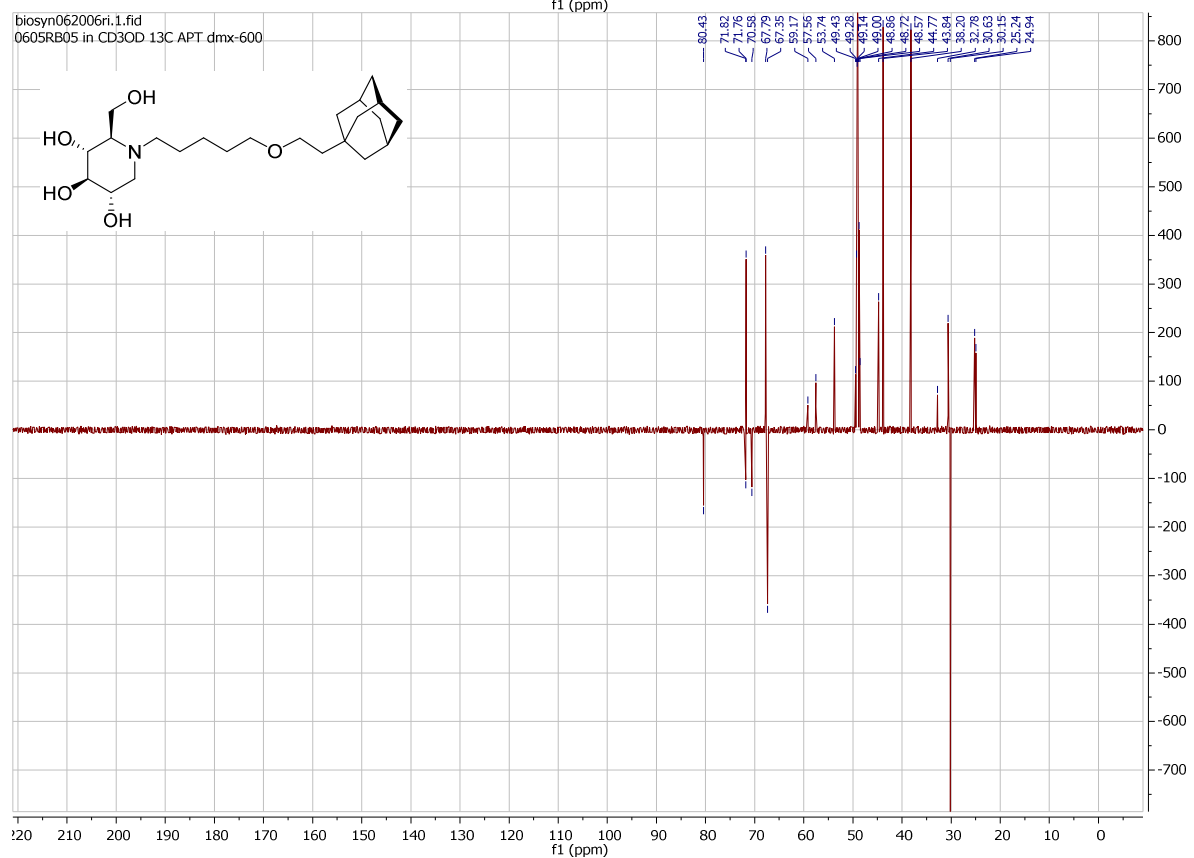
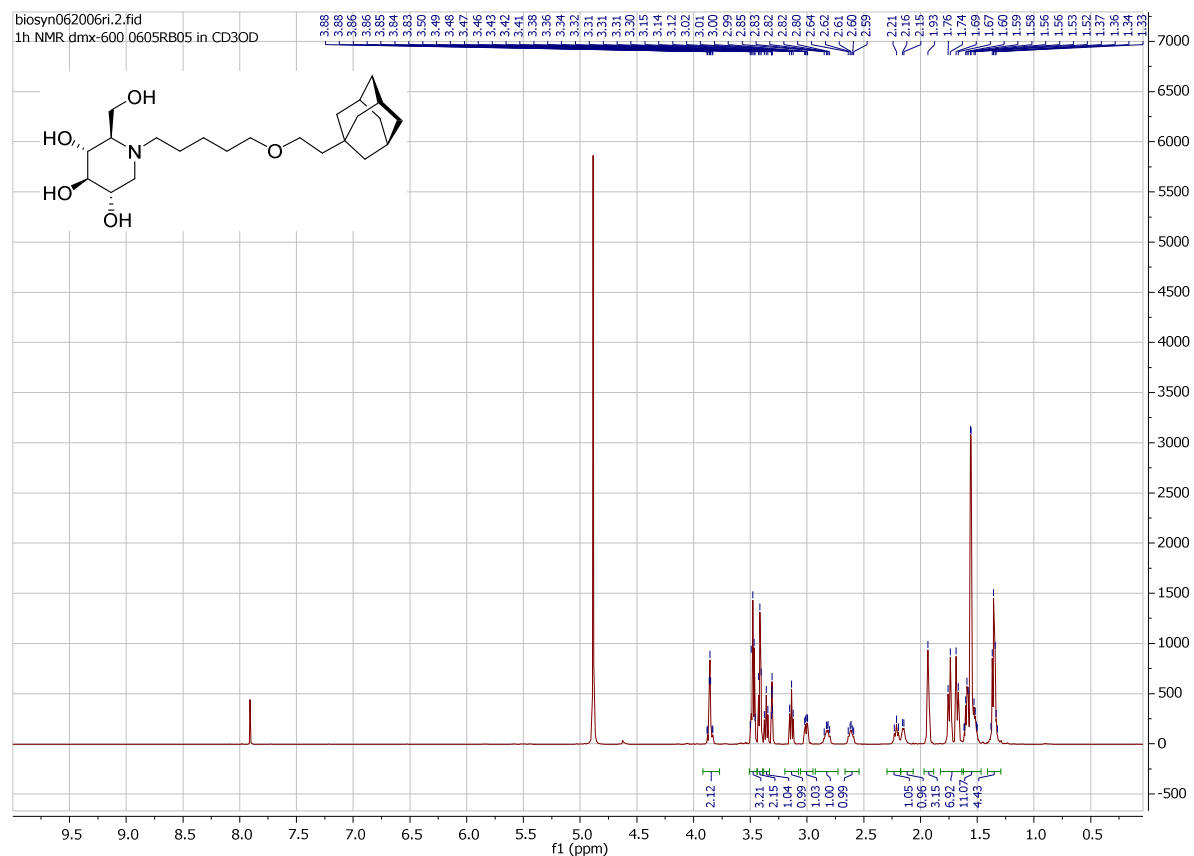
**<sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound C111.TFA in MeOD.**



# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound C124.TFA in MeOD.



# <sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound C170.TFA in MeOD.



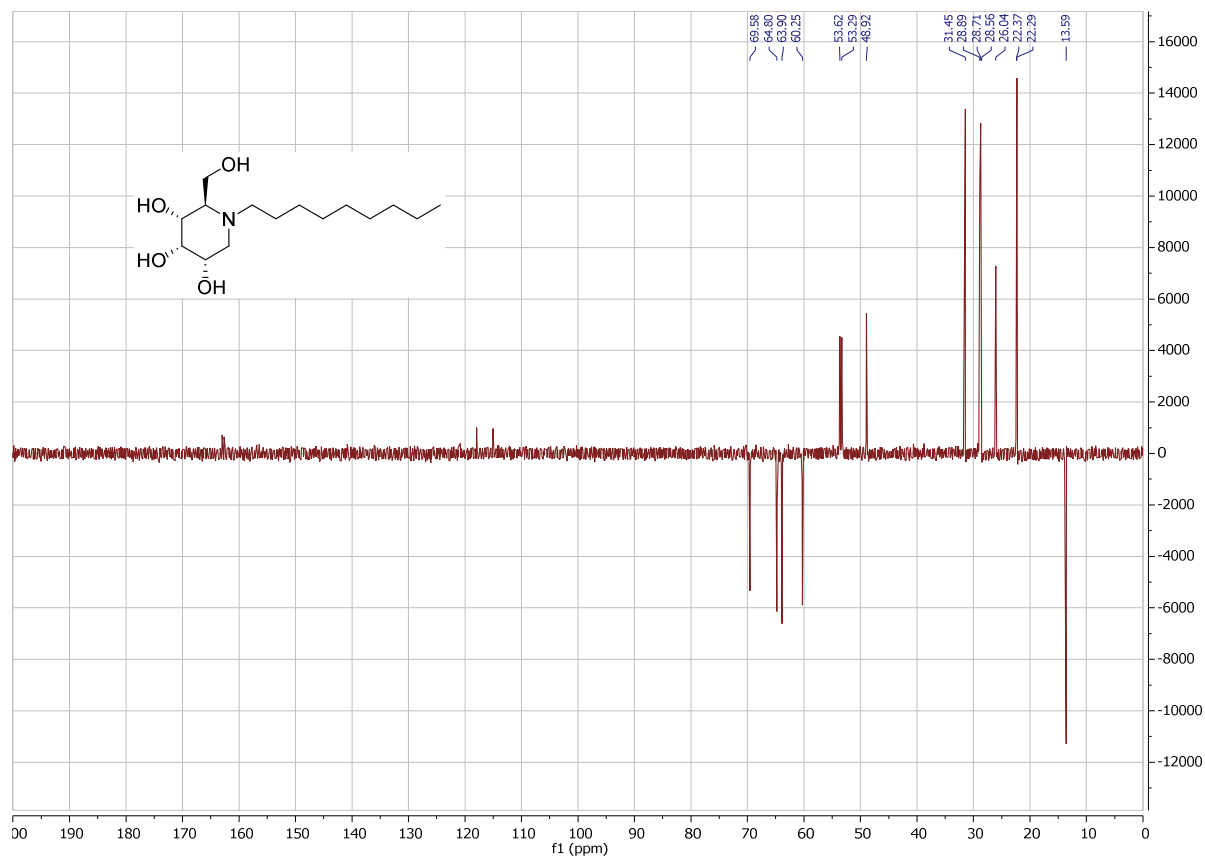
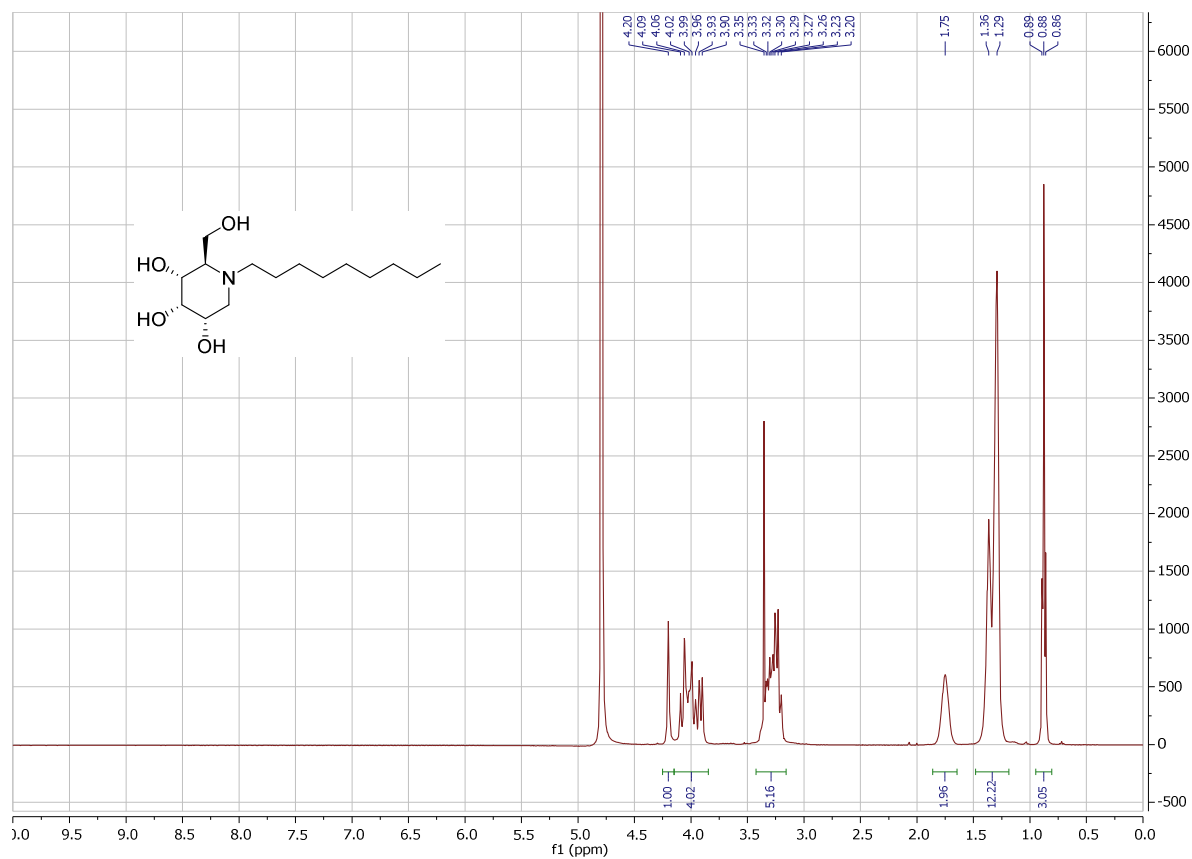




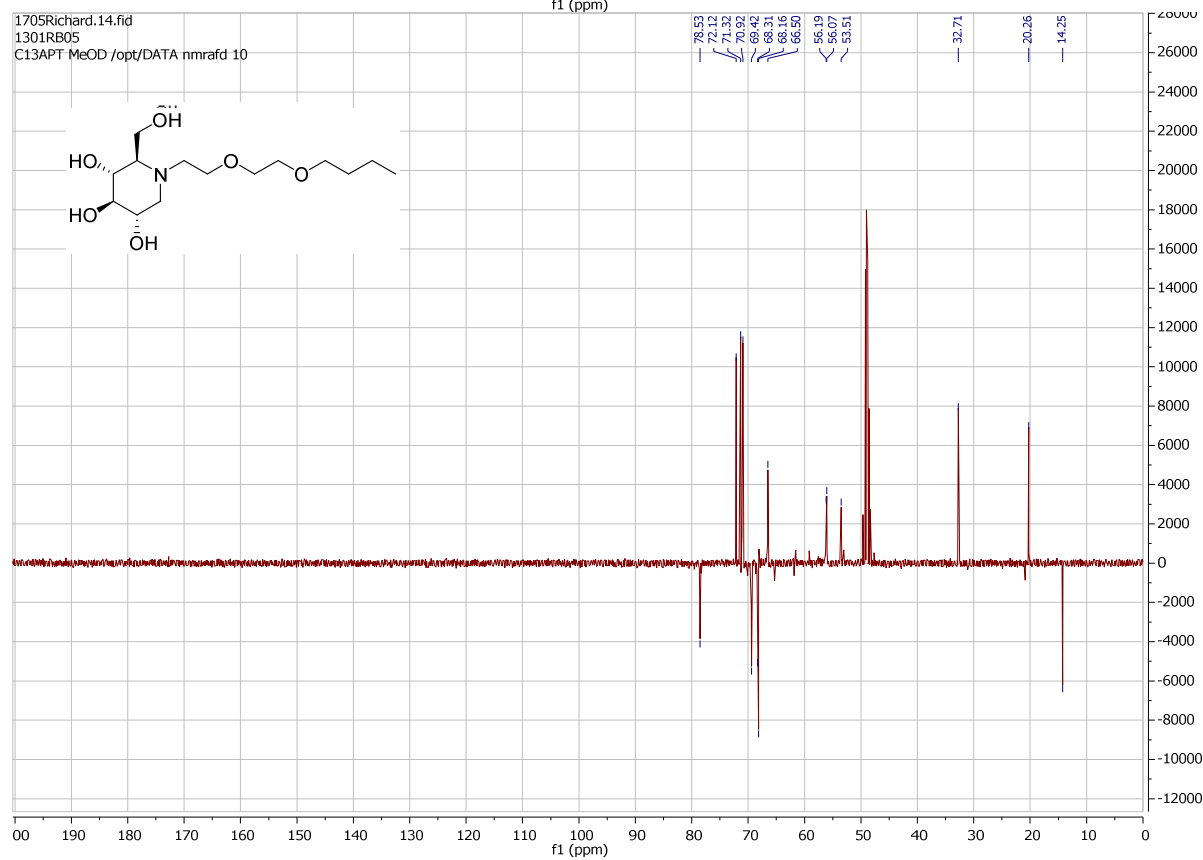
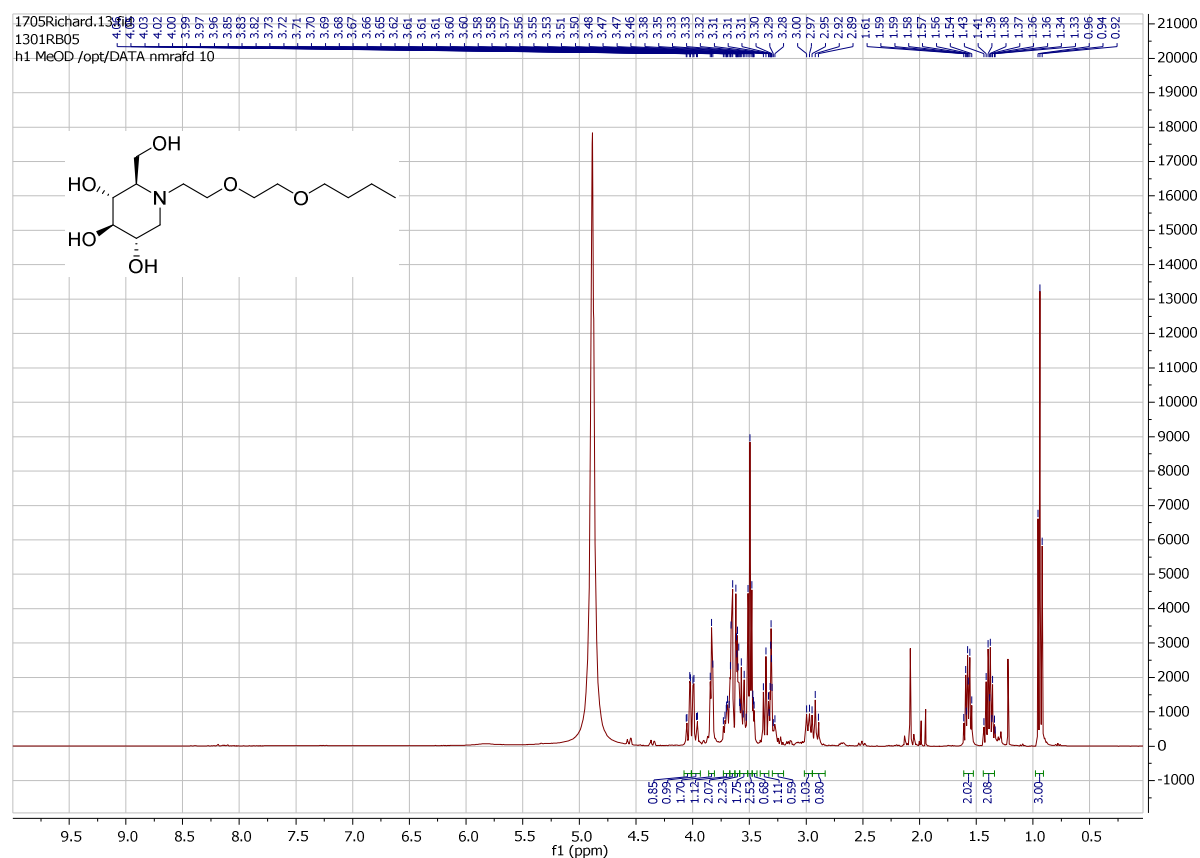




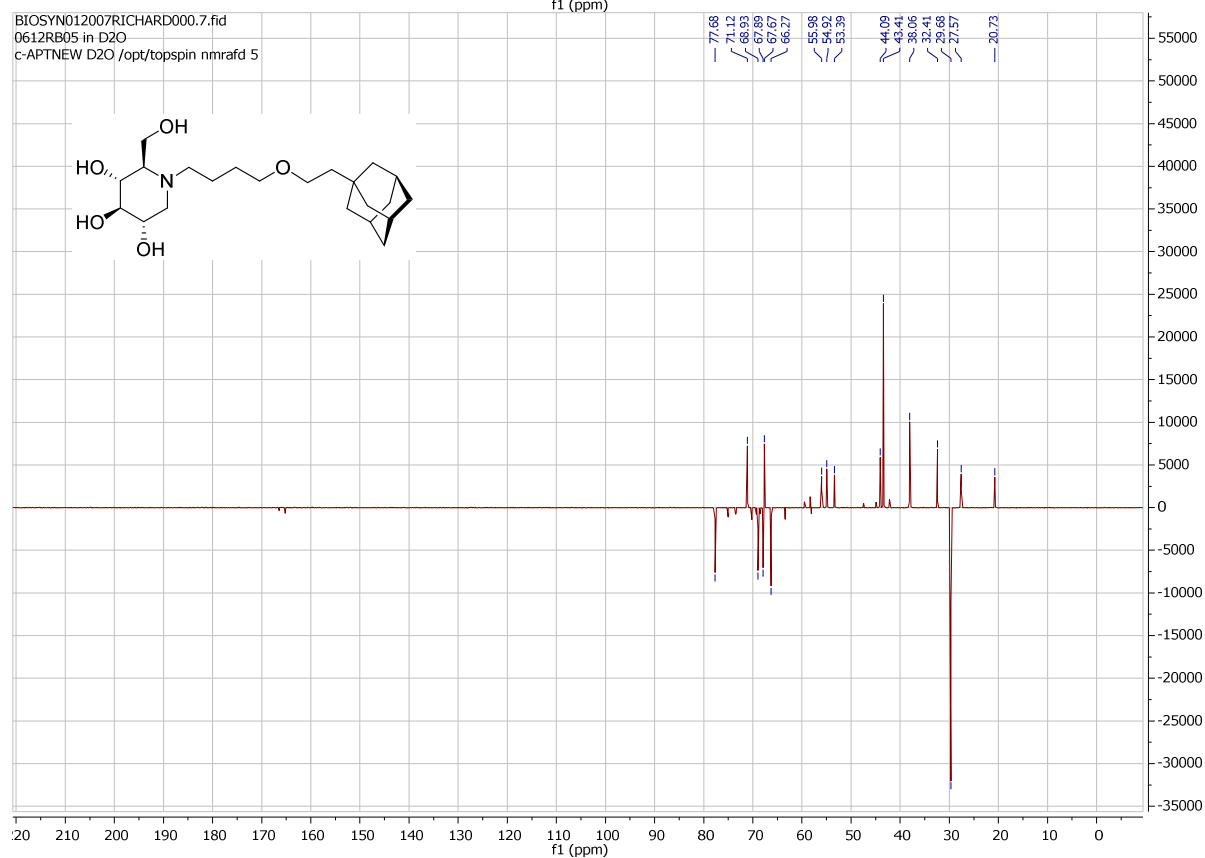
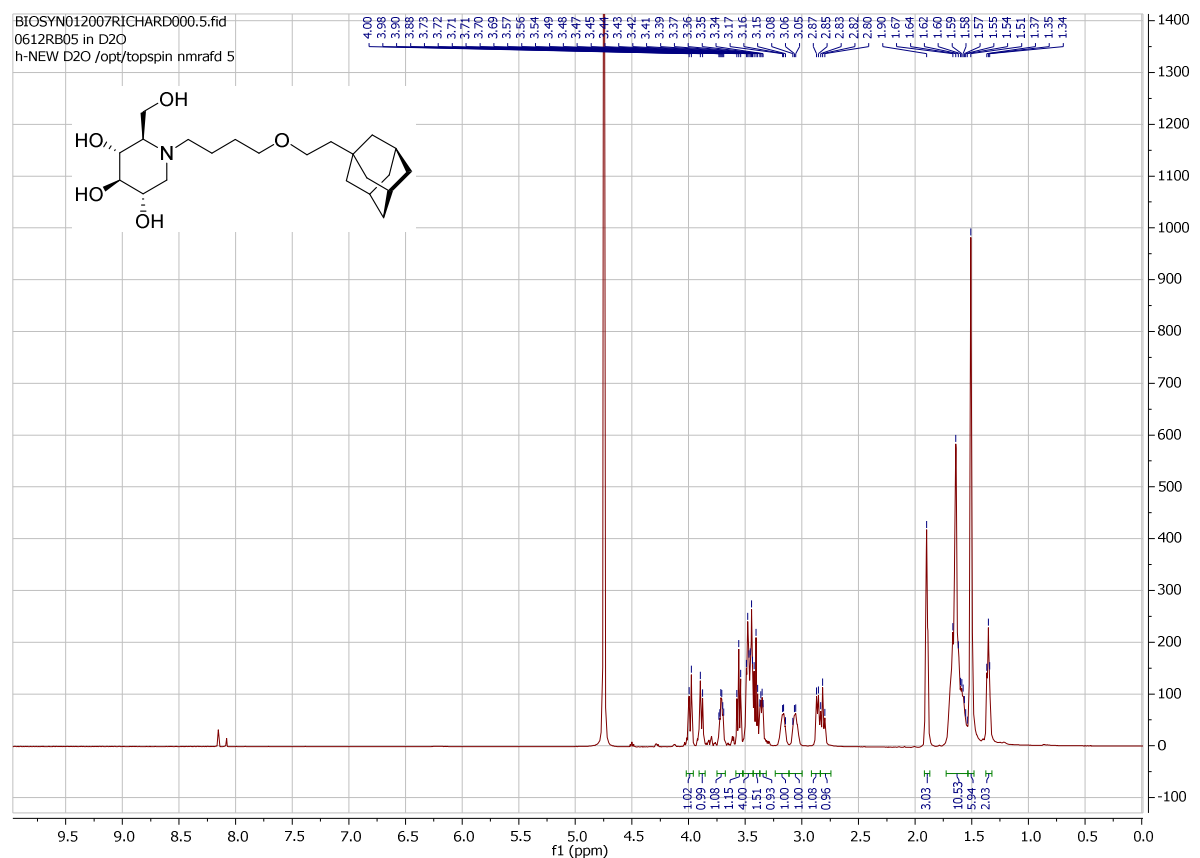
# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound C194.TFA in $\text{D}_2\text{O}$ .



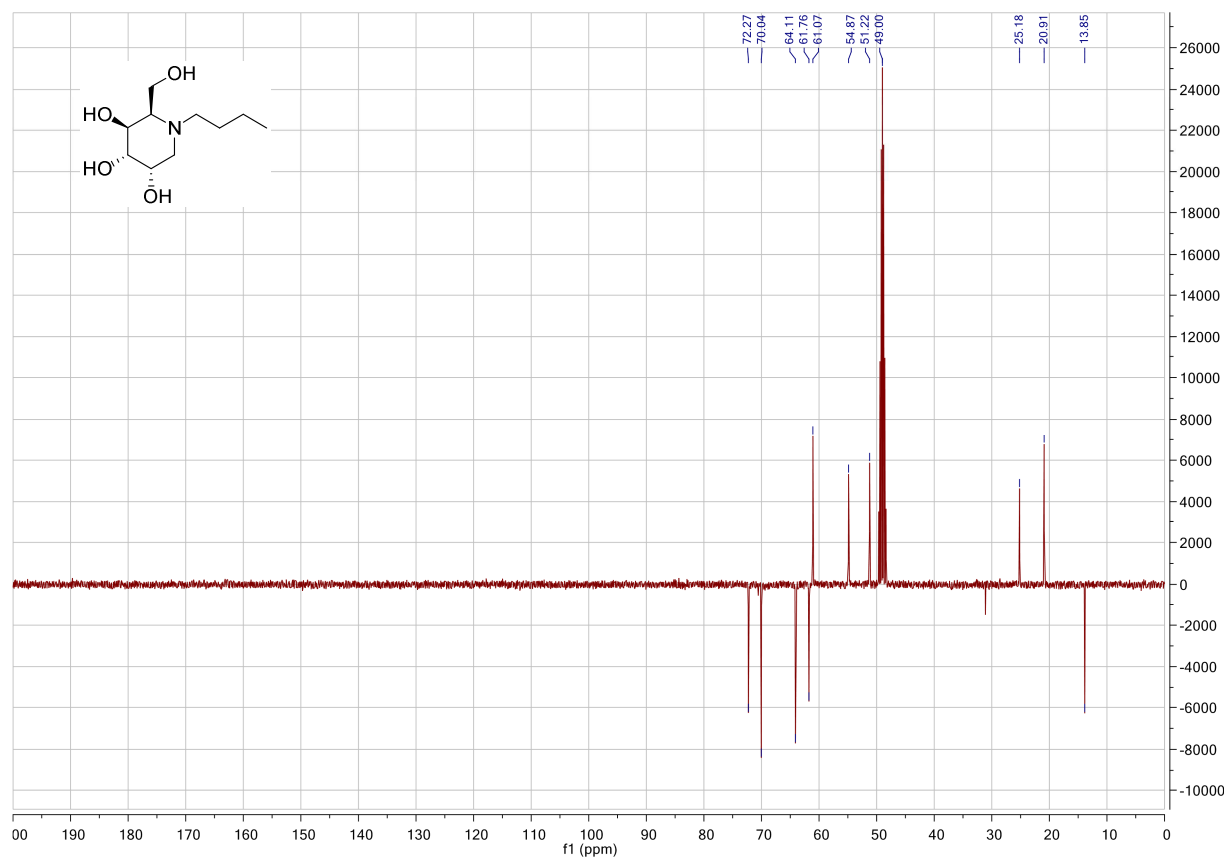
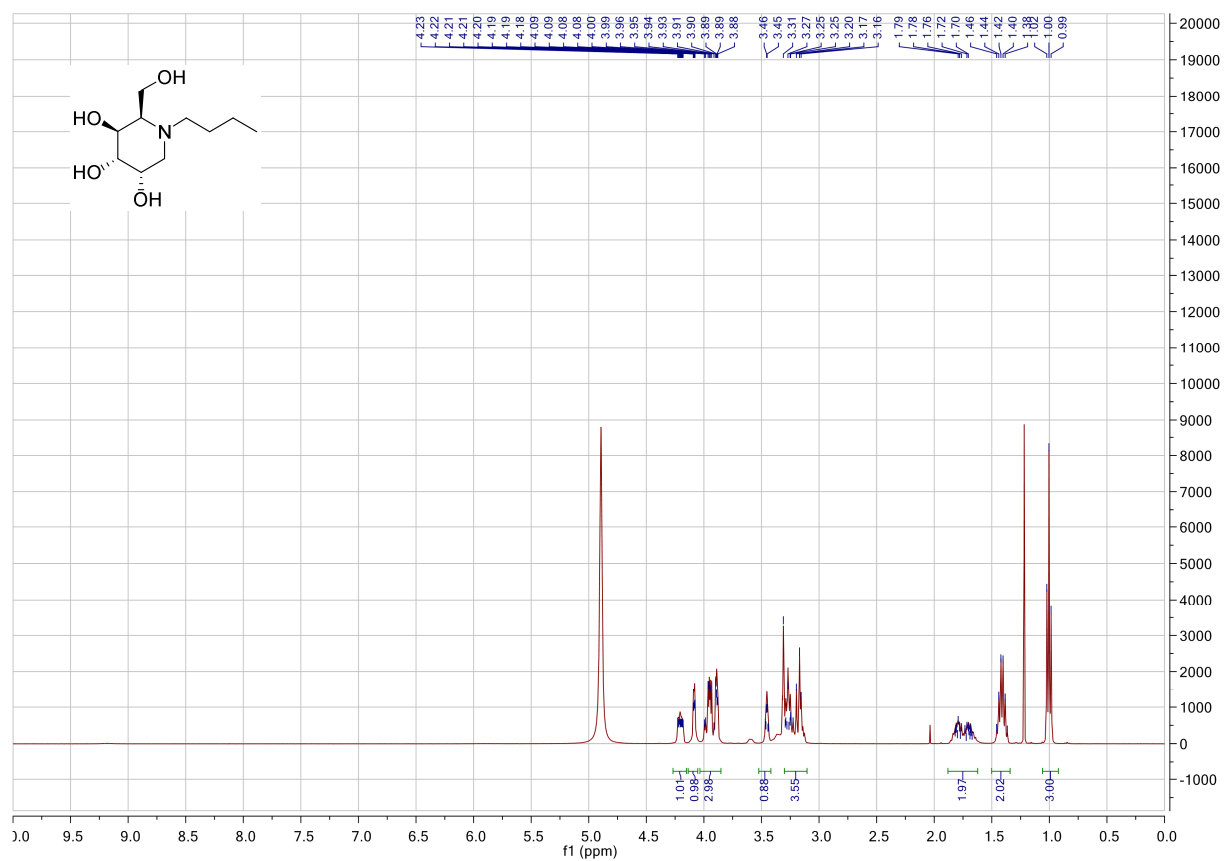
**<sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound C200.TFA in MeOD.**



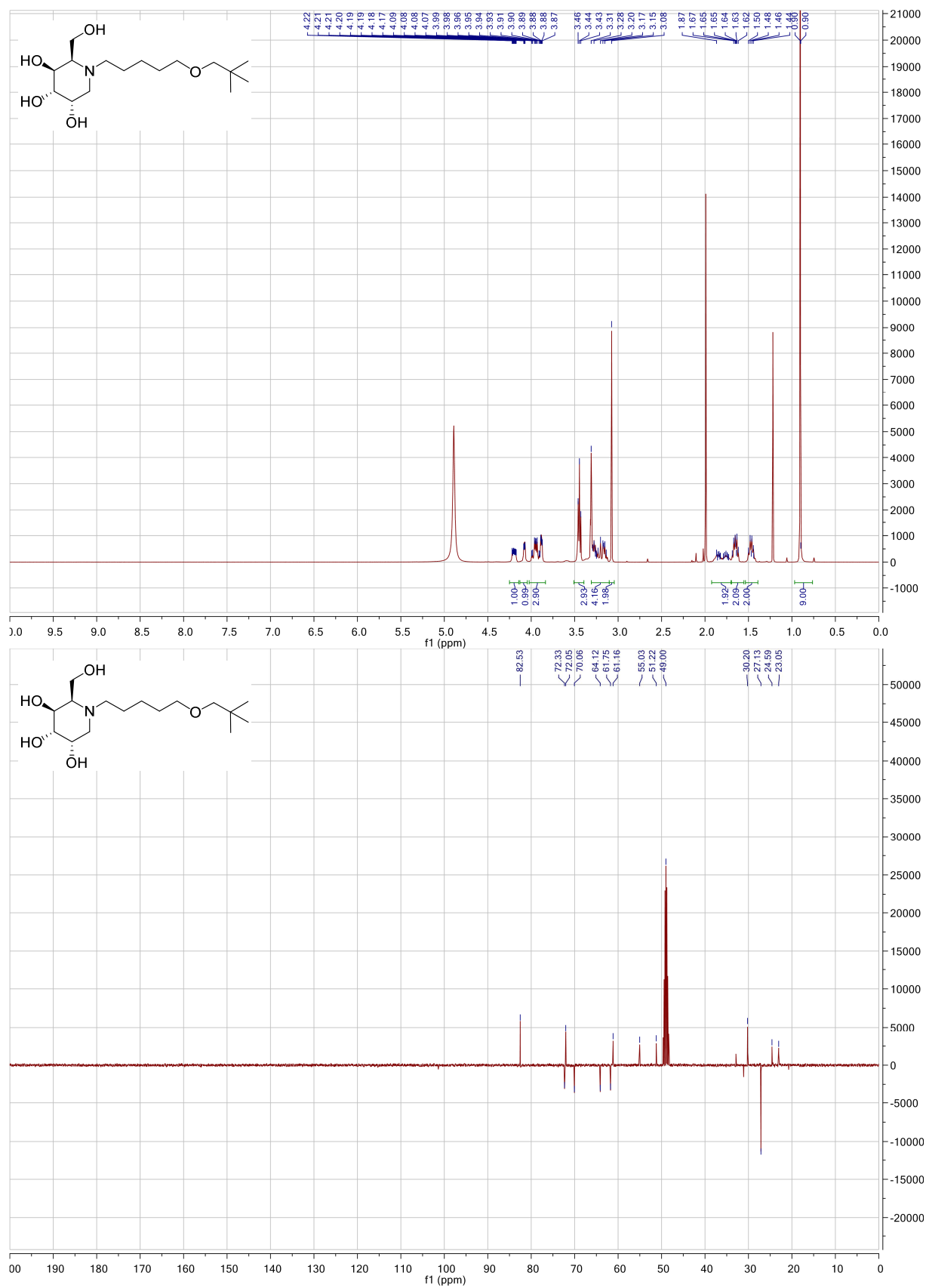
# <sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound C203.TFA in D<sub>2</sub>O.



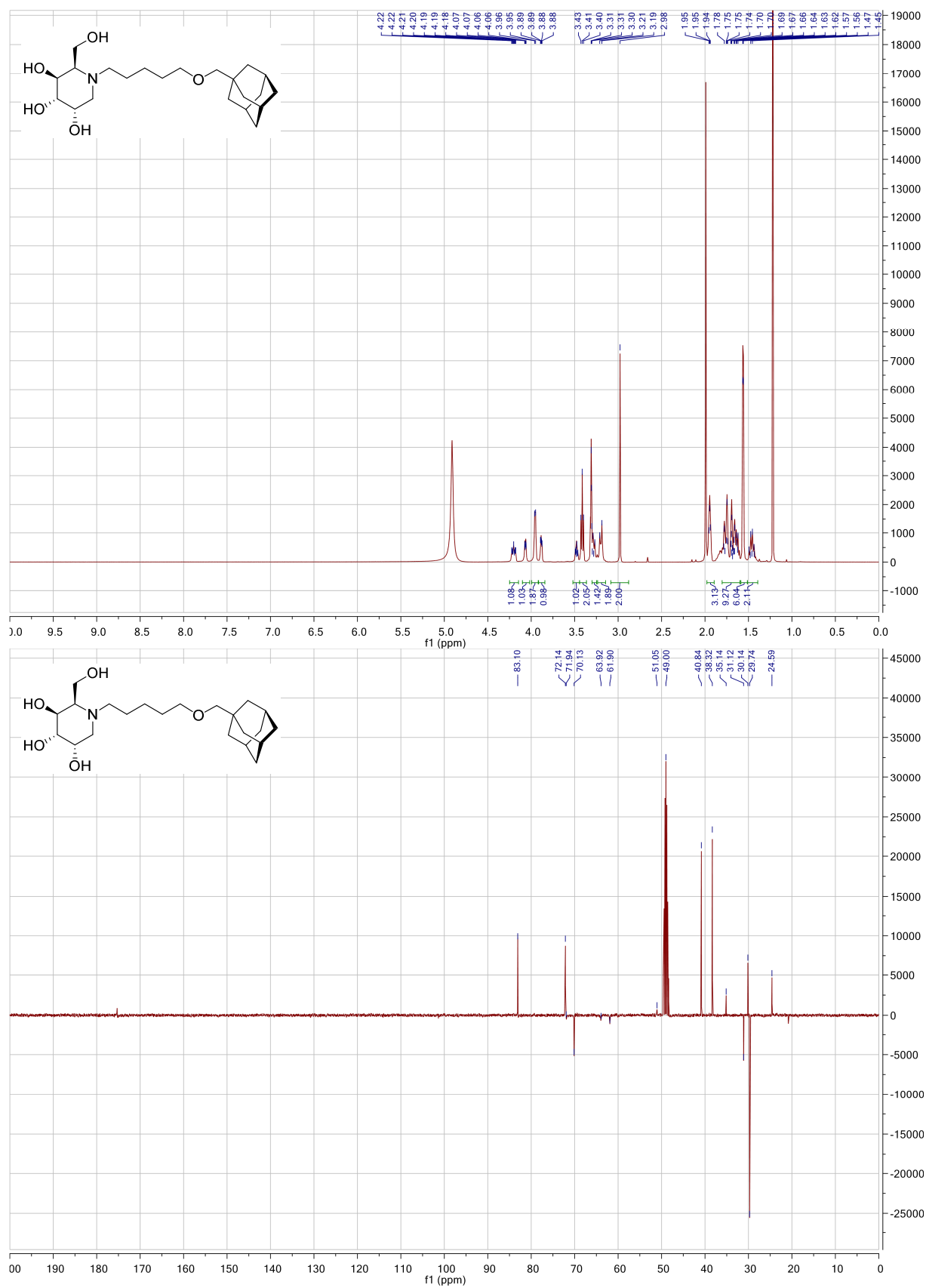
# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound C204.TFA in MeOD.



**<sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound C206.TFA in MeOD.**

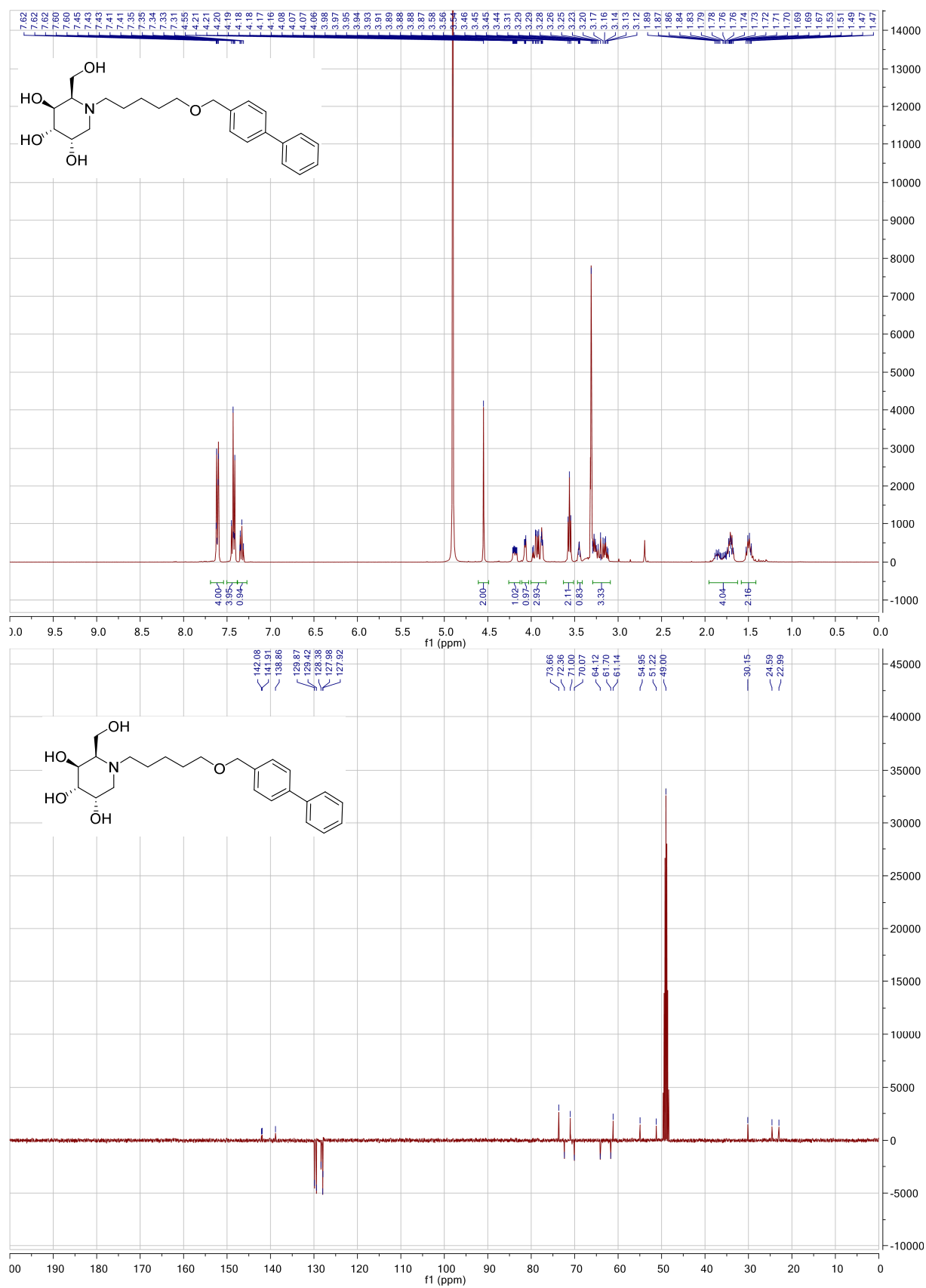


# <sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound C208.TFA in MeOD.





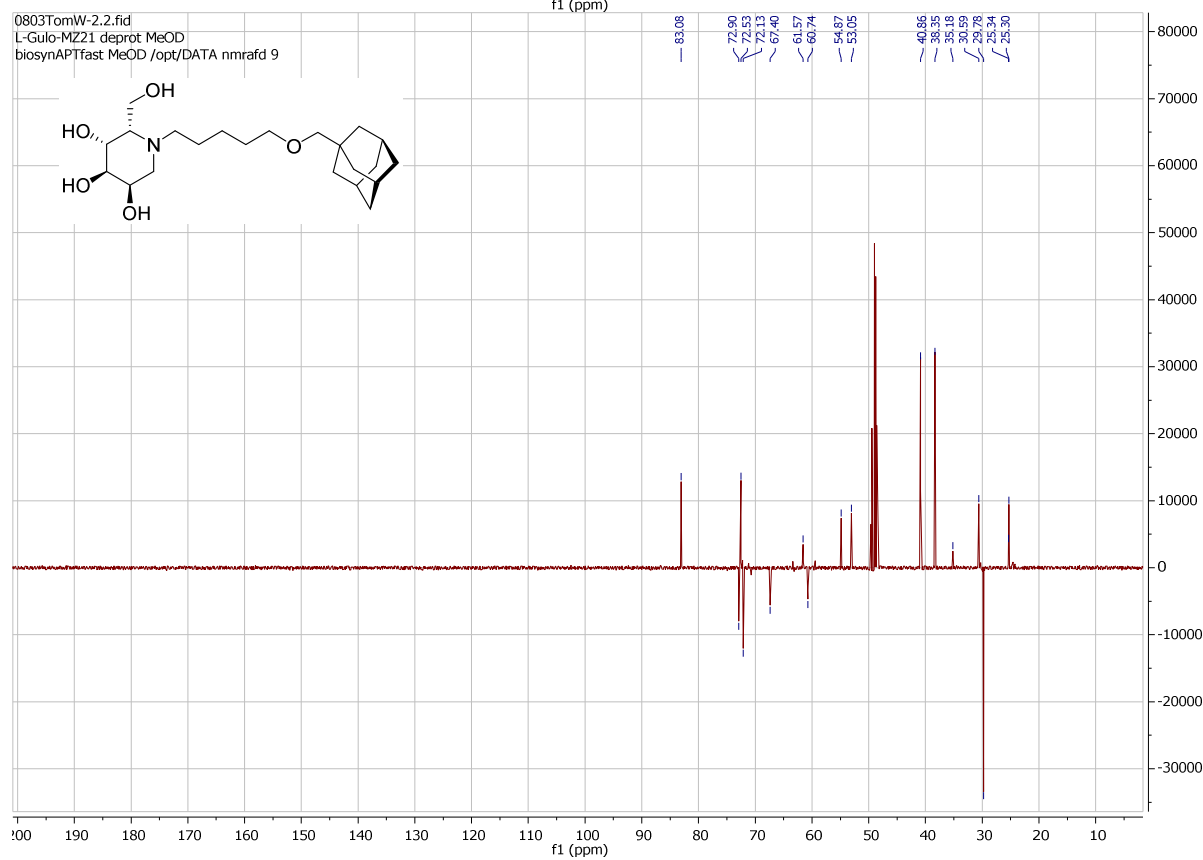
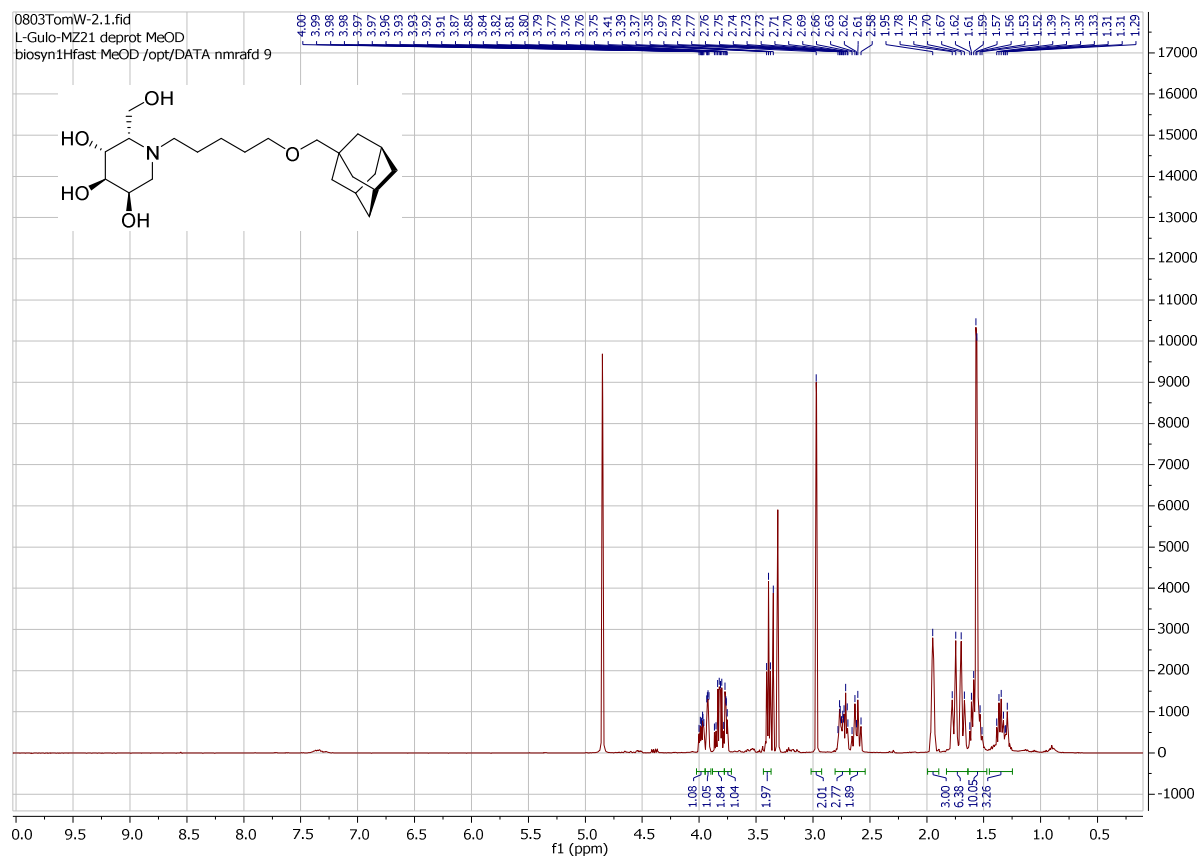
# <sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound C210.TFA in MeOD.



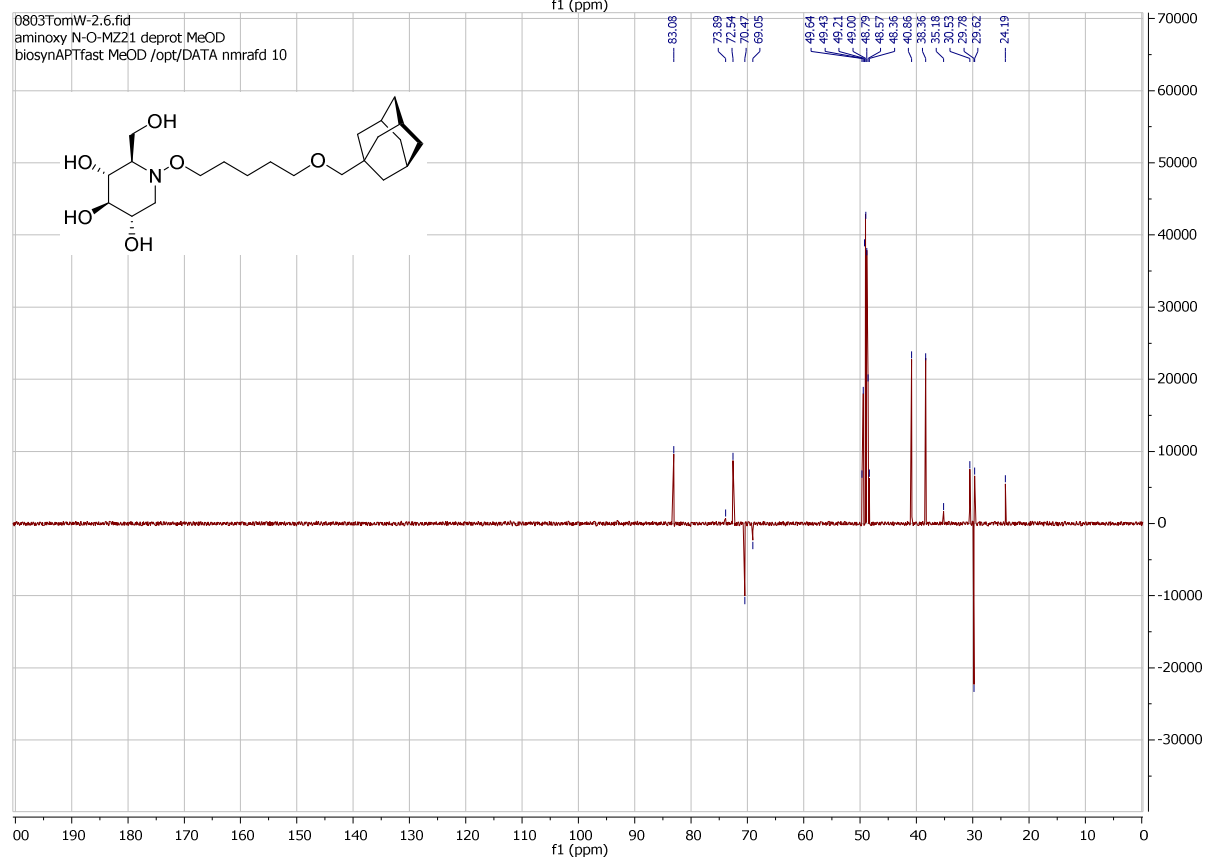
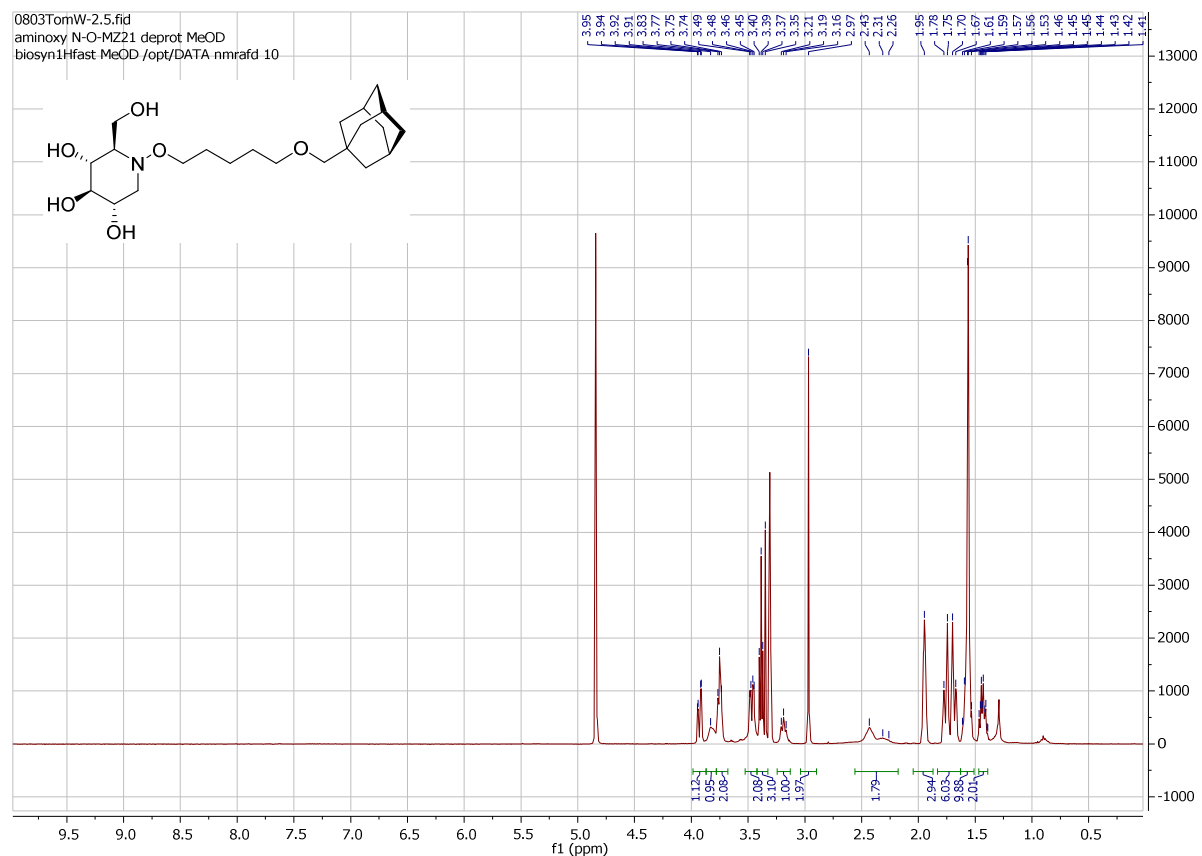




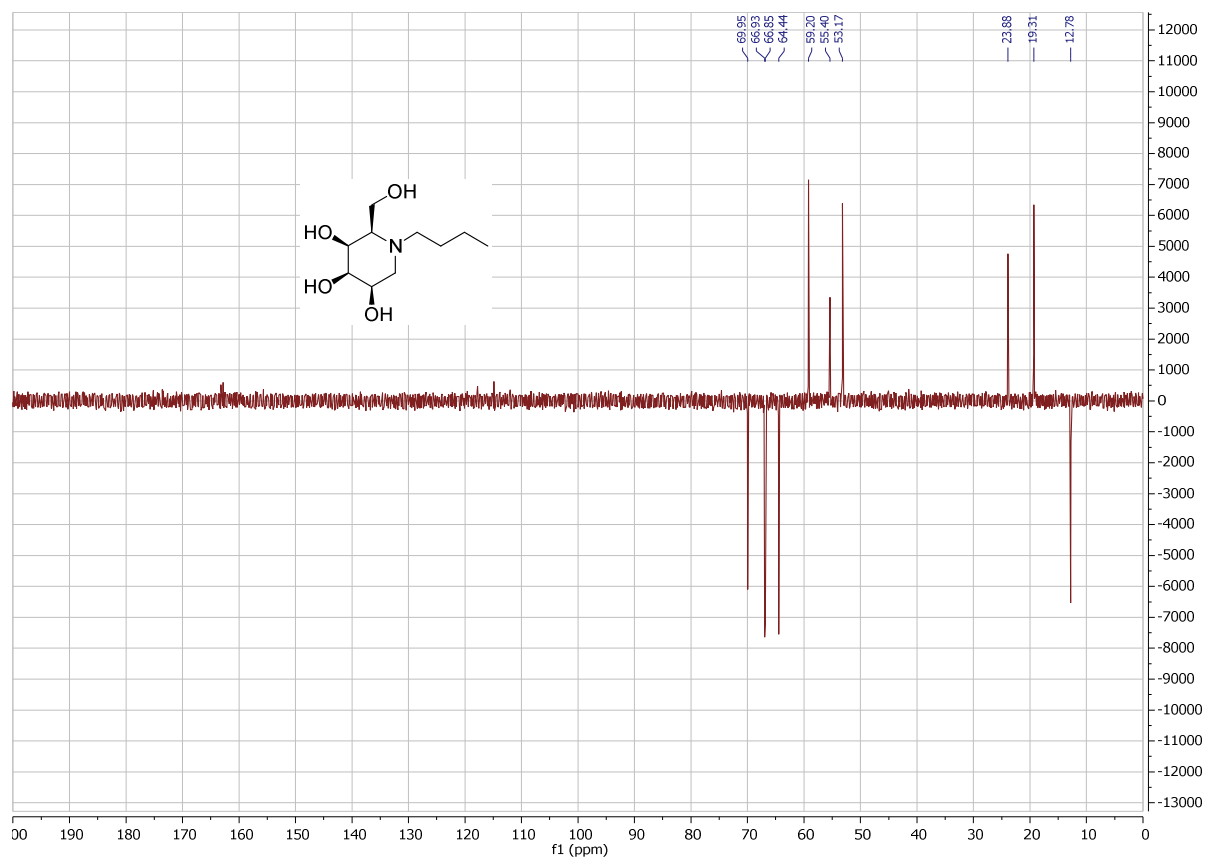
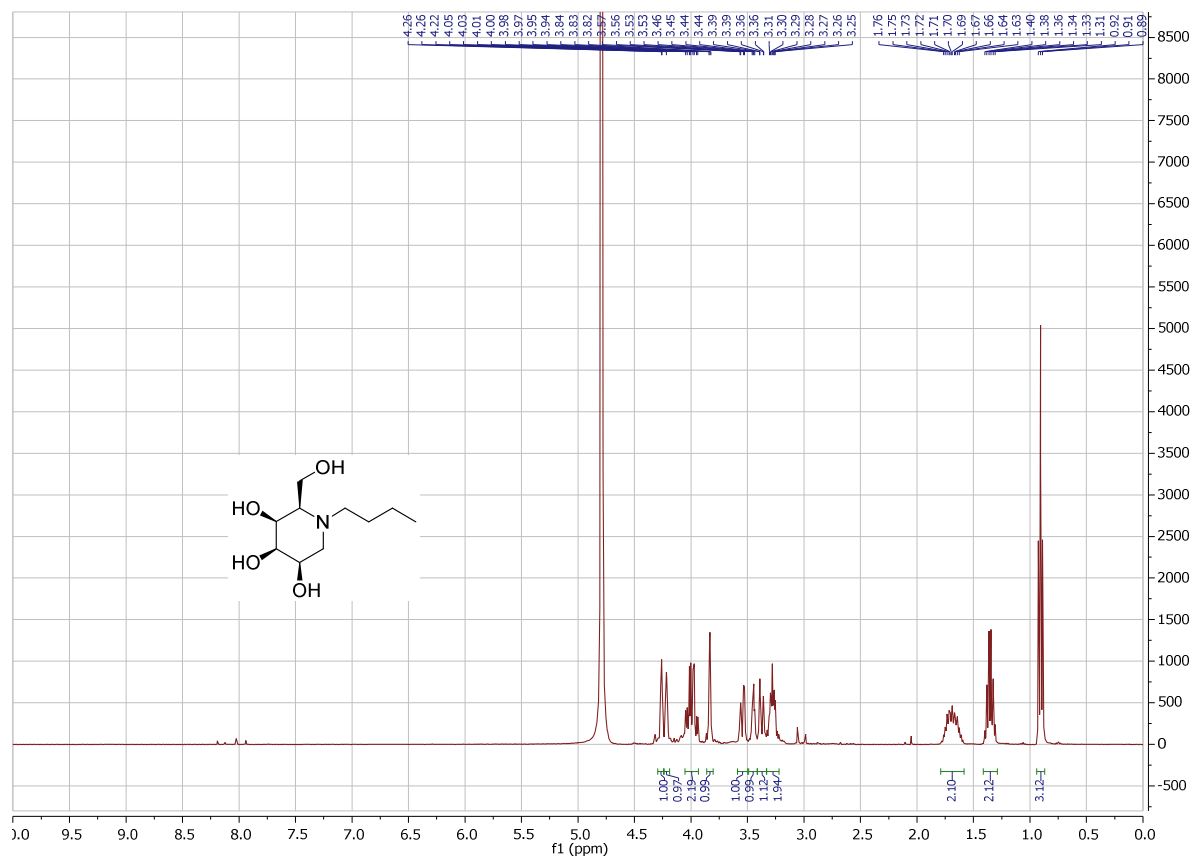
# <sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound C217 in MeOD.



# <sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound C218 in MeOD.

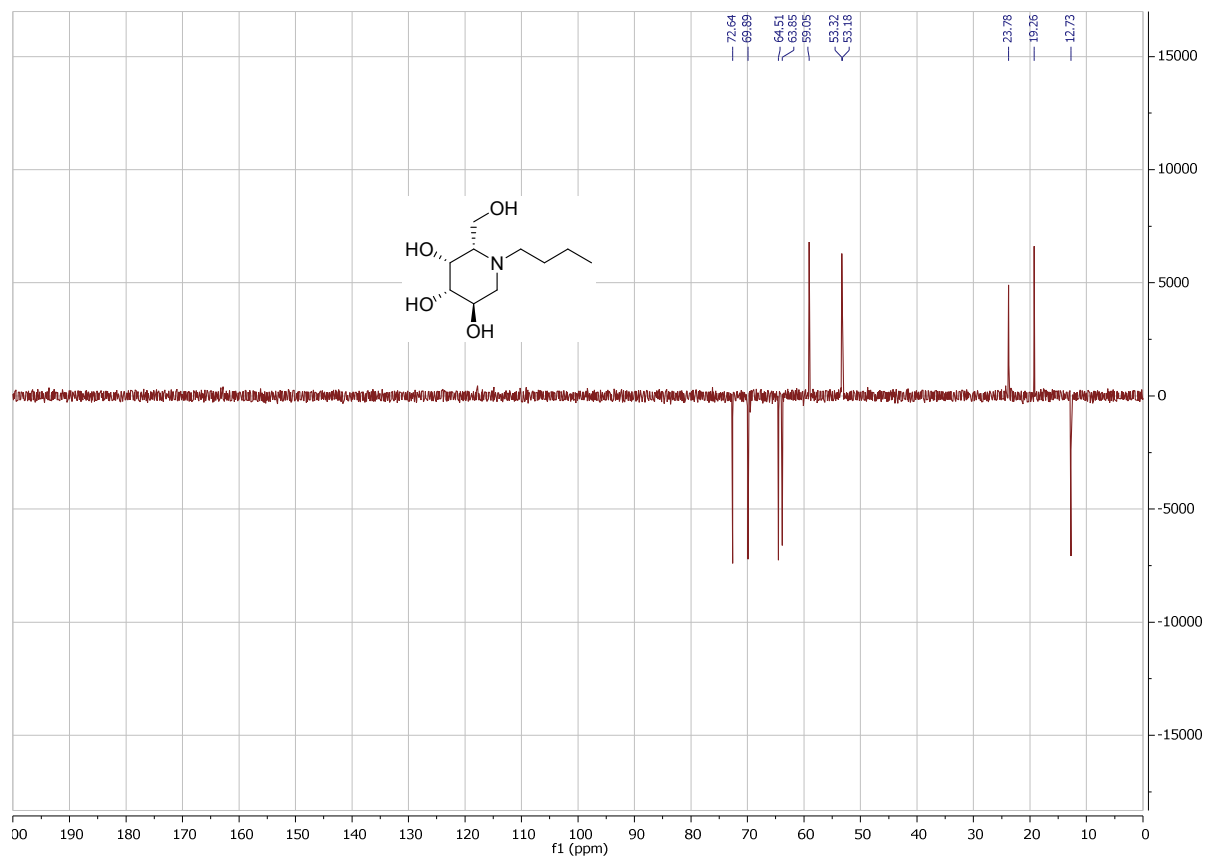
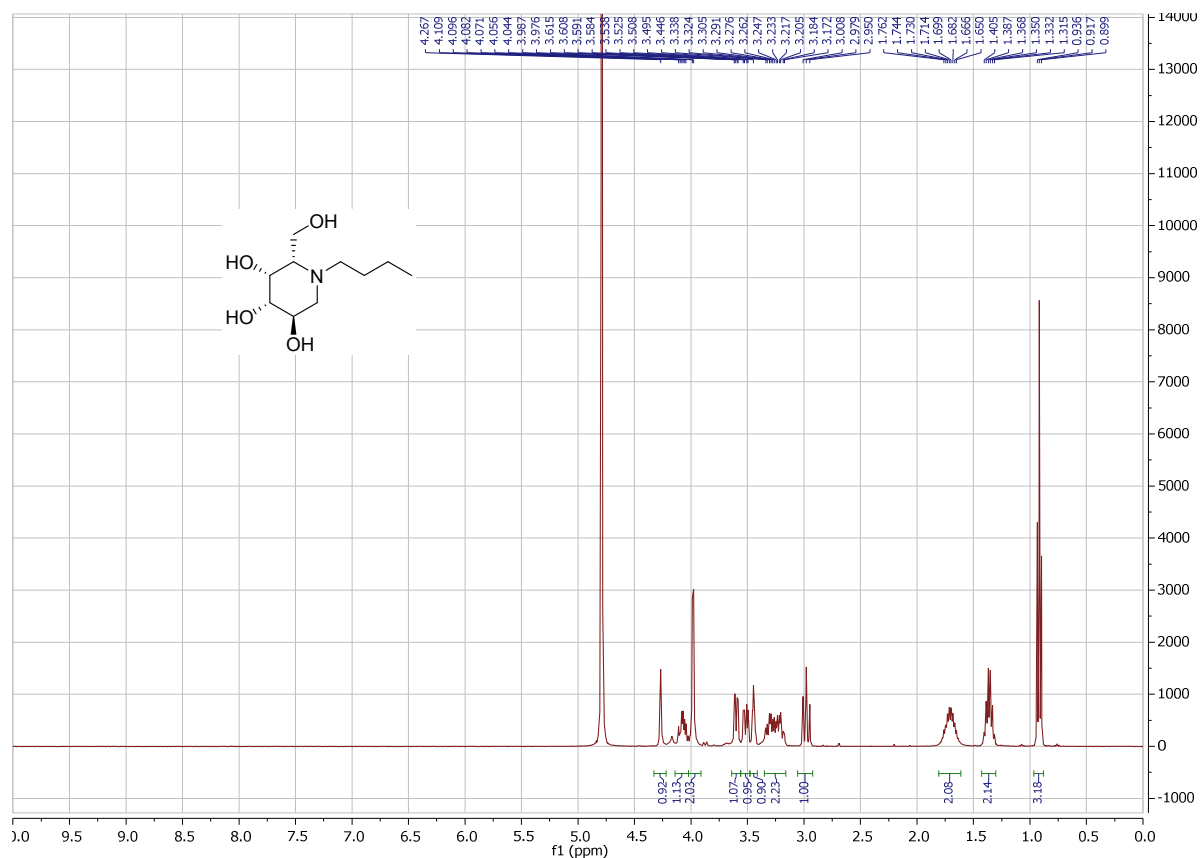


# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound C219.TFA in $\text{D}_2\text{O}$ .



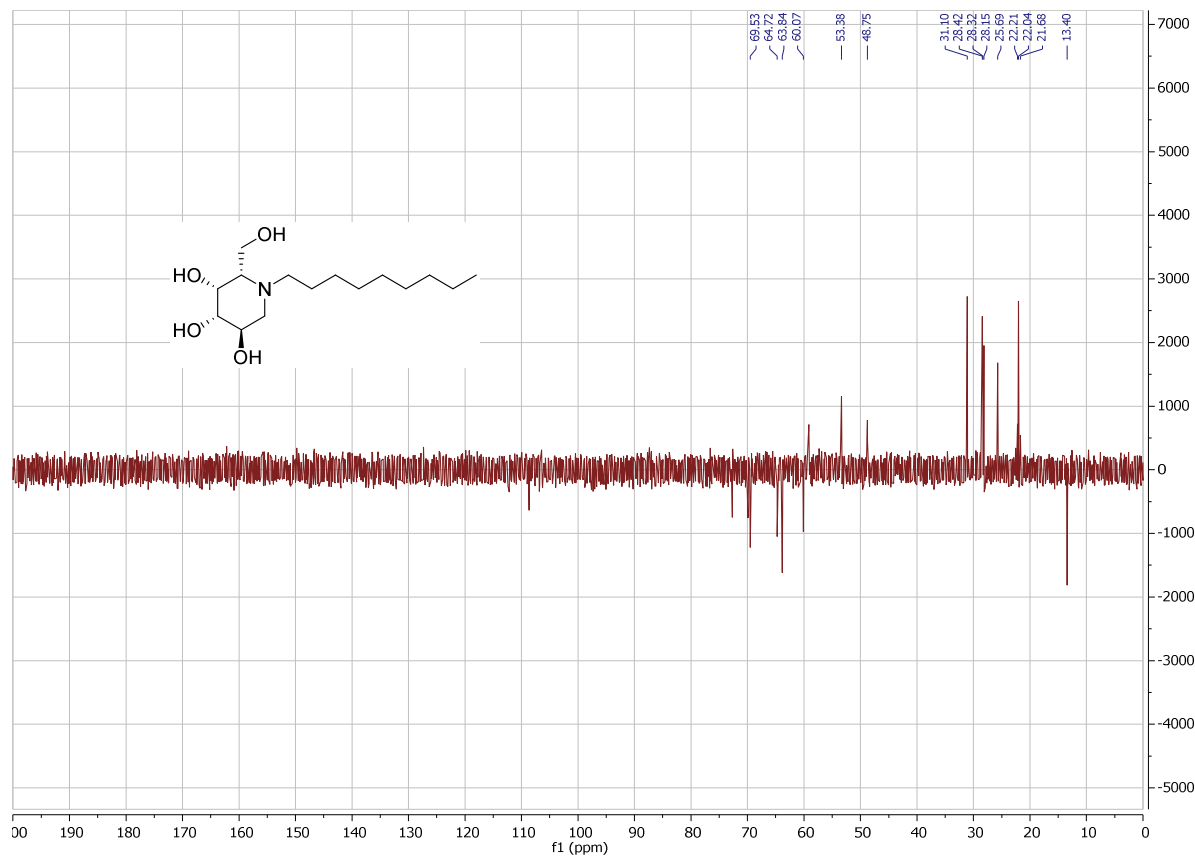
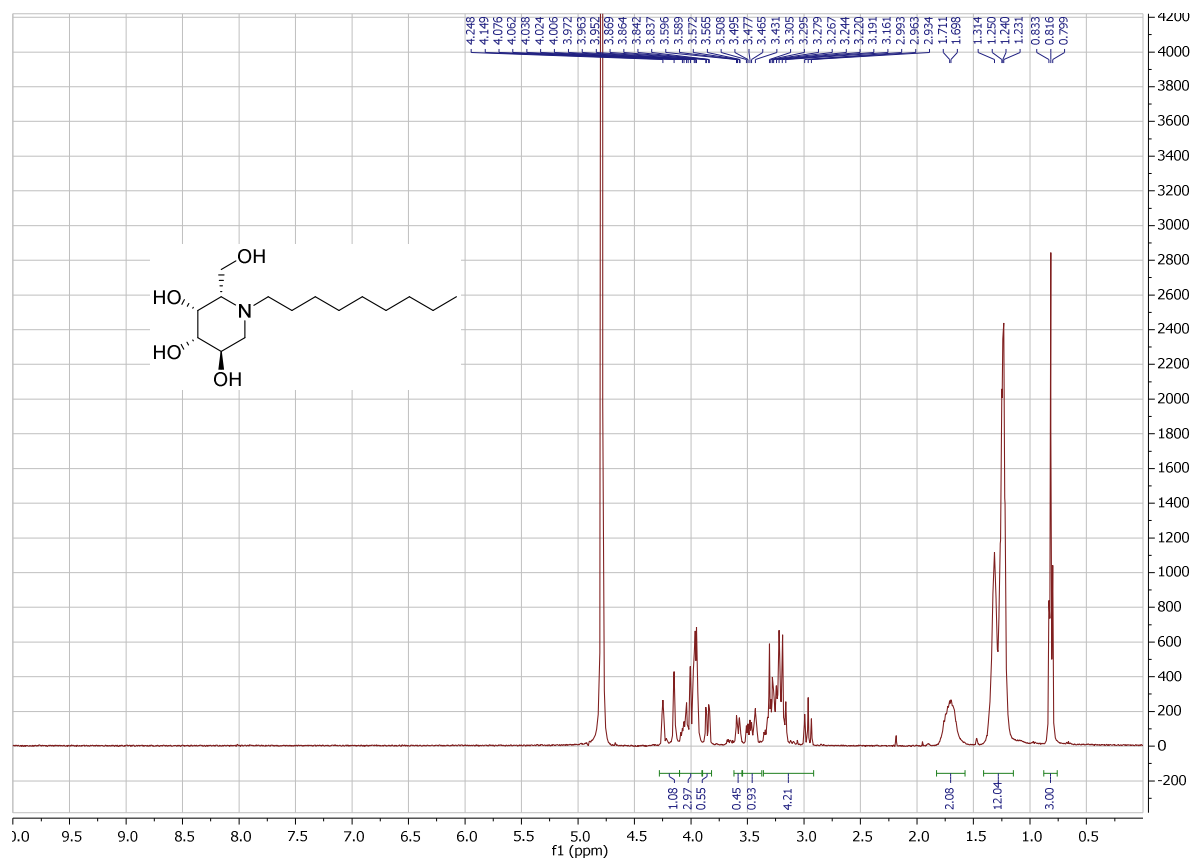


<sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound C223.TFA in D<sub>2</sub>O.

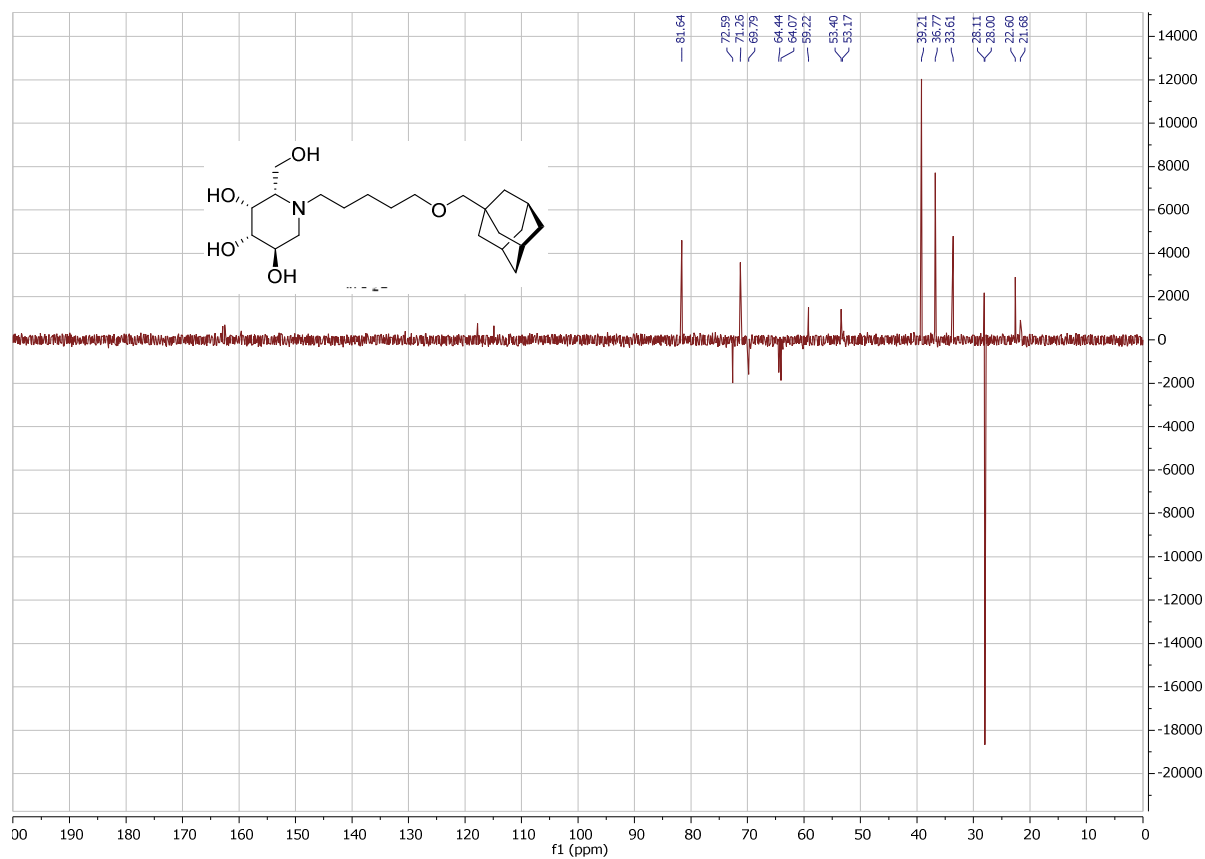
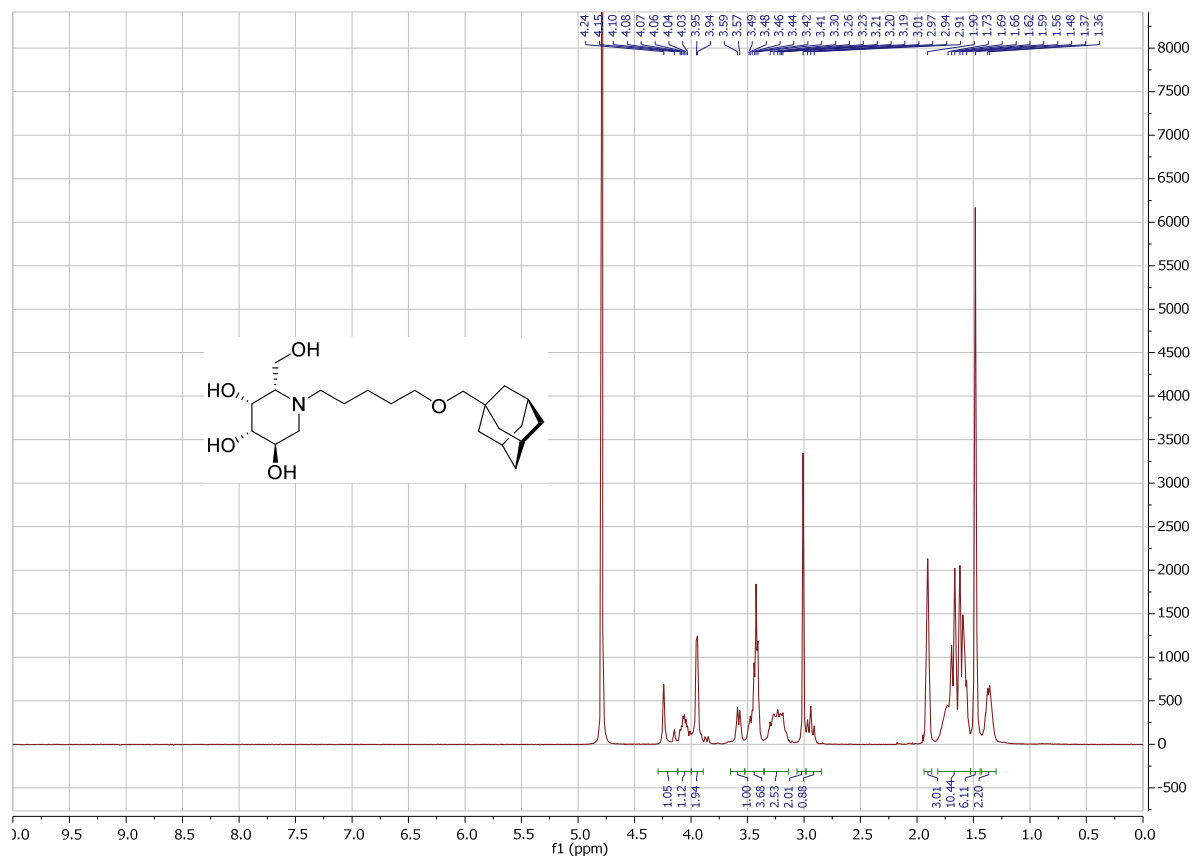




# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound C225.TFA in $\text{D}_2\text{O}$ .



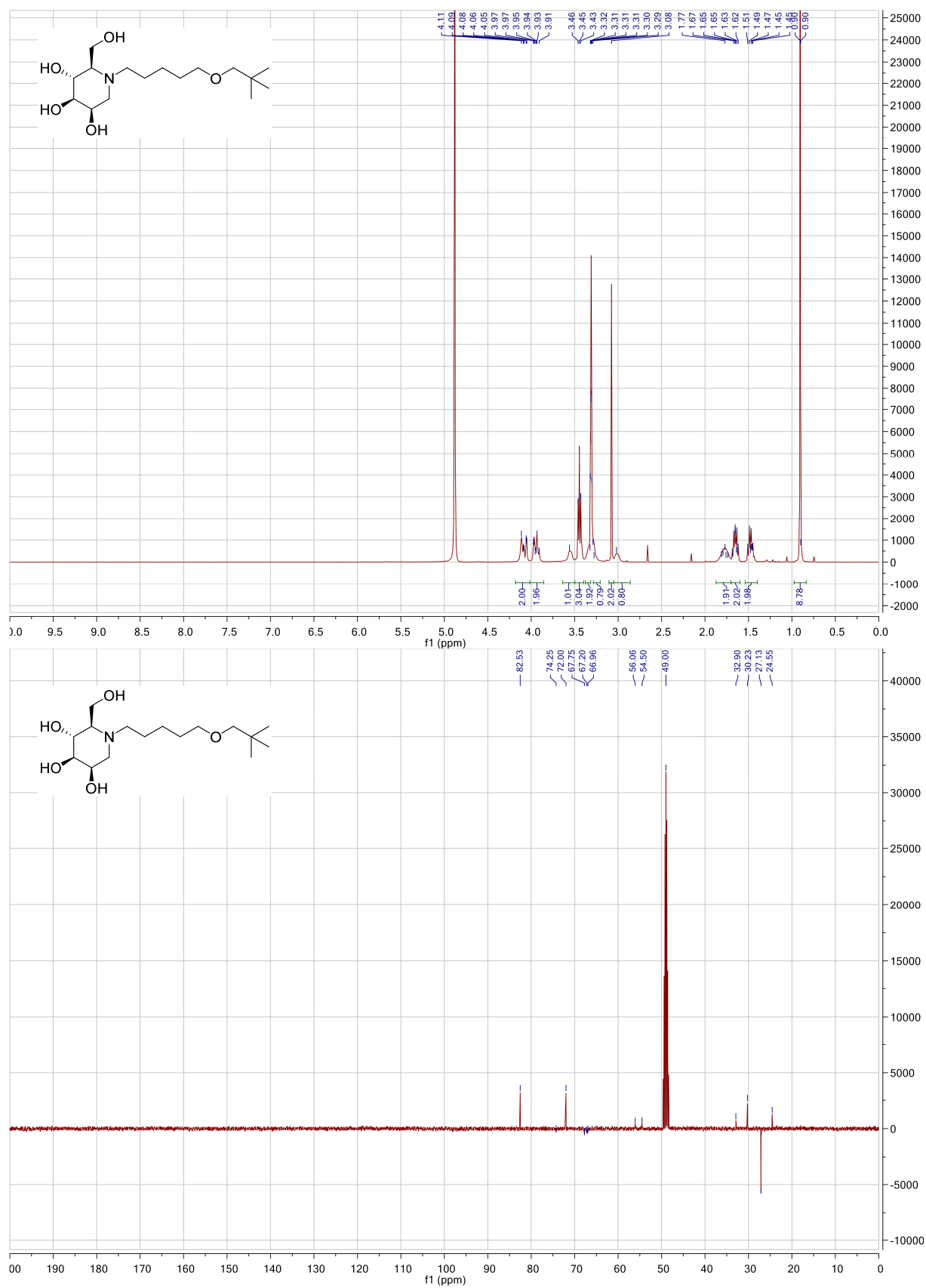
# <sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound C227.TFA in D<sub>2</sub>O.



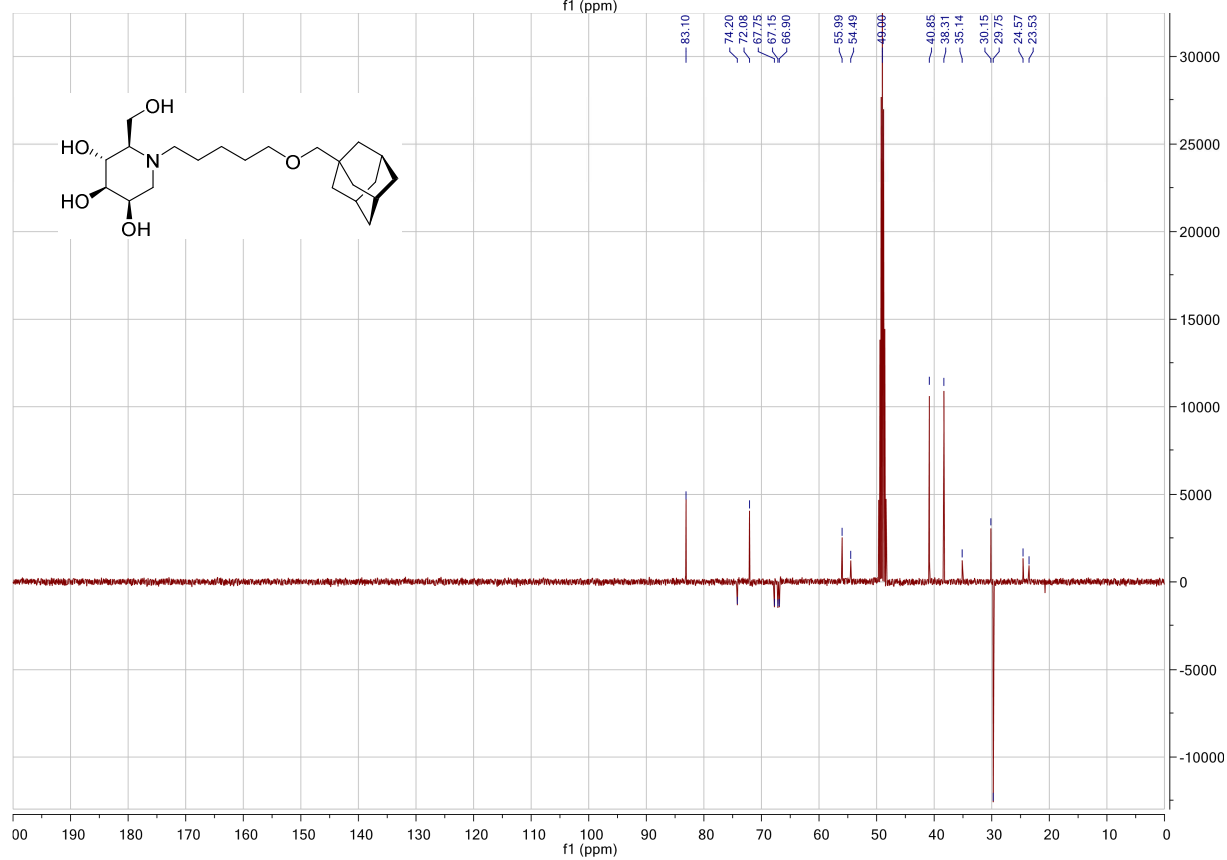
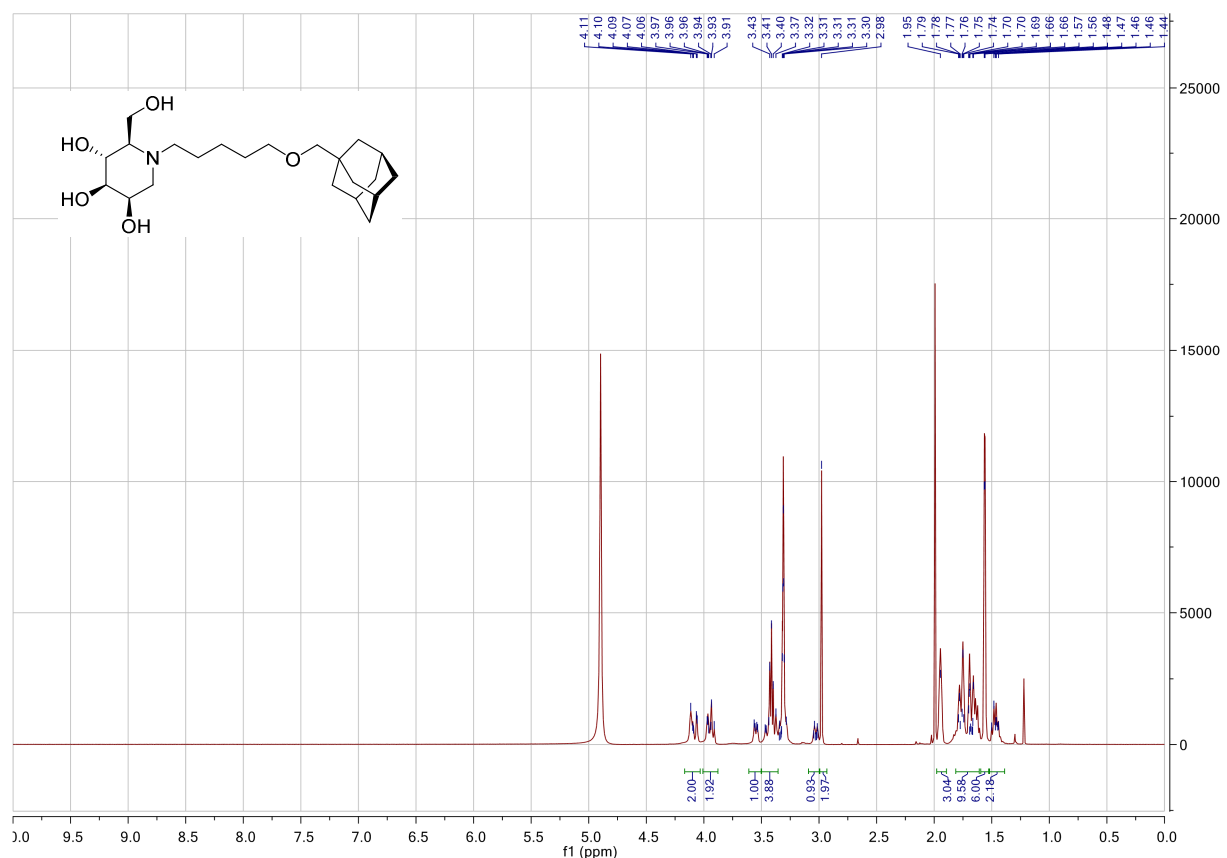




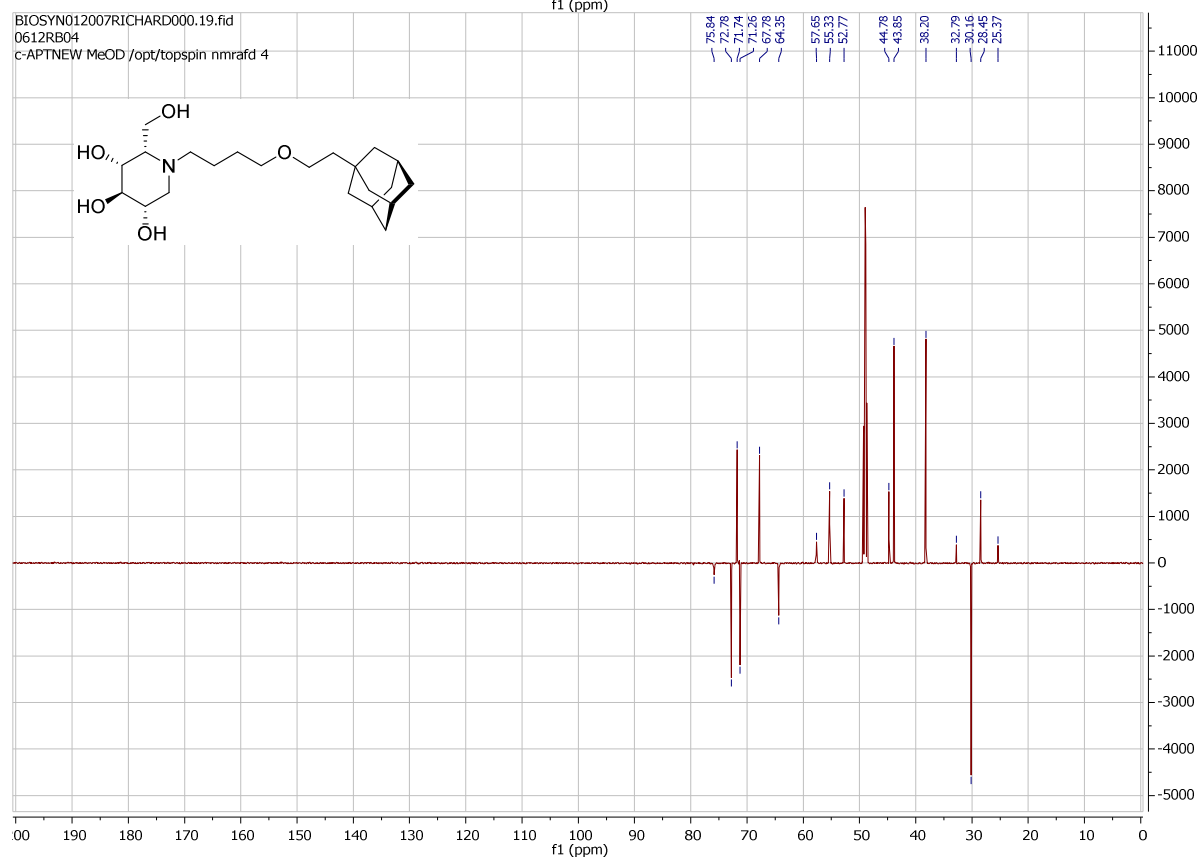
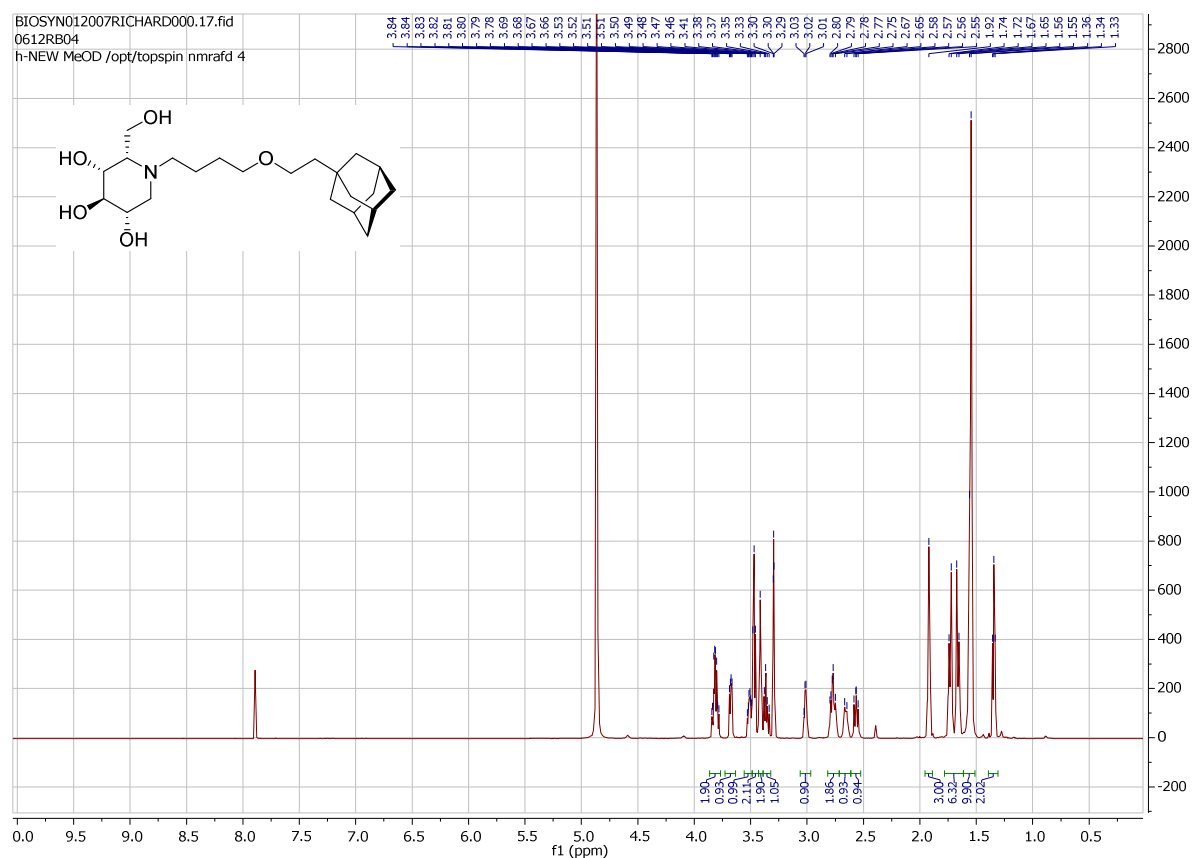
<sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound C234.TFA in MeOD.



**<sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound C236.TFA in MeOD.**



# <sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound C238.TFA in MeOD.

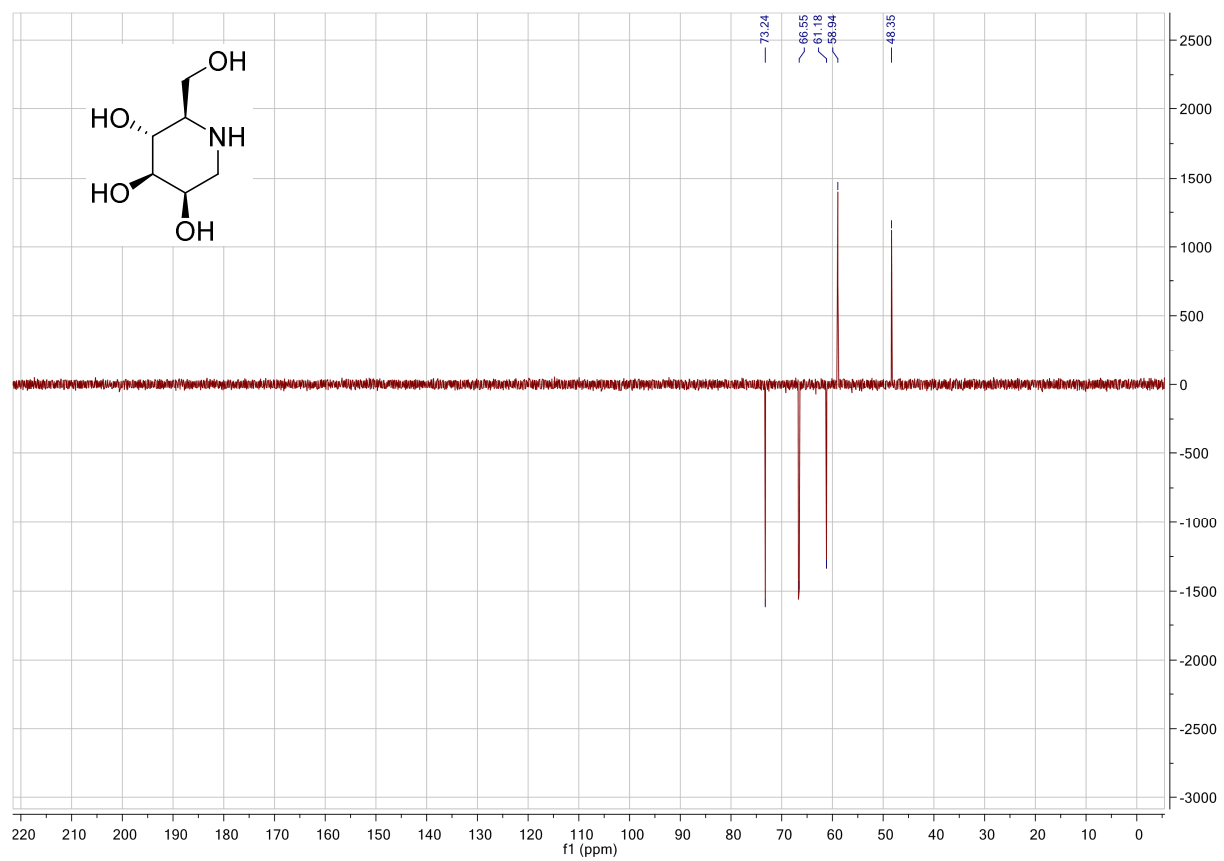
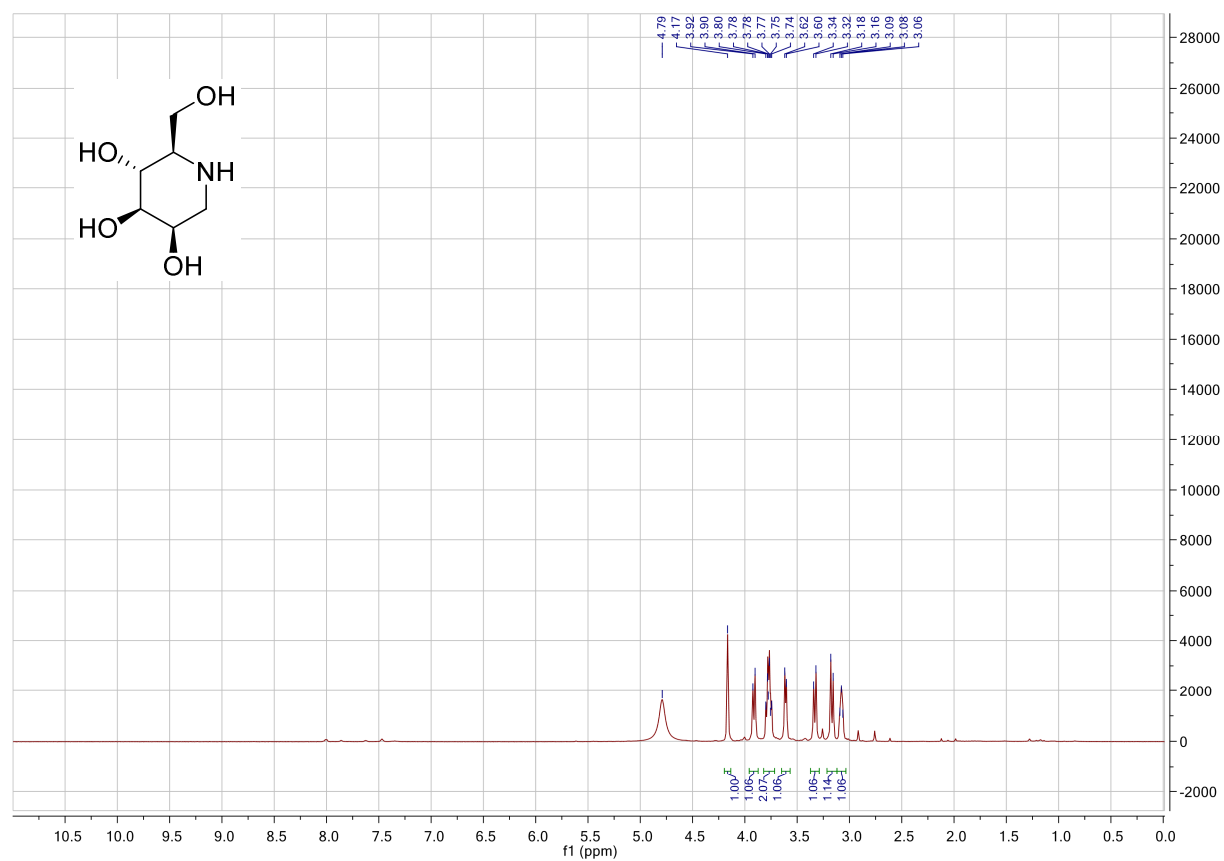


# <sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound C239.TFA in MeOD.

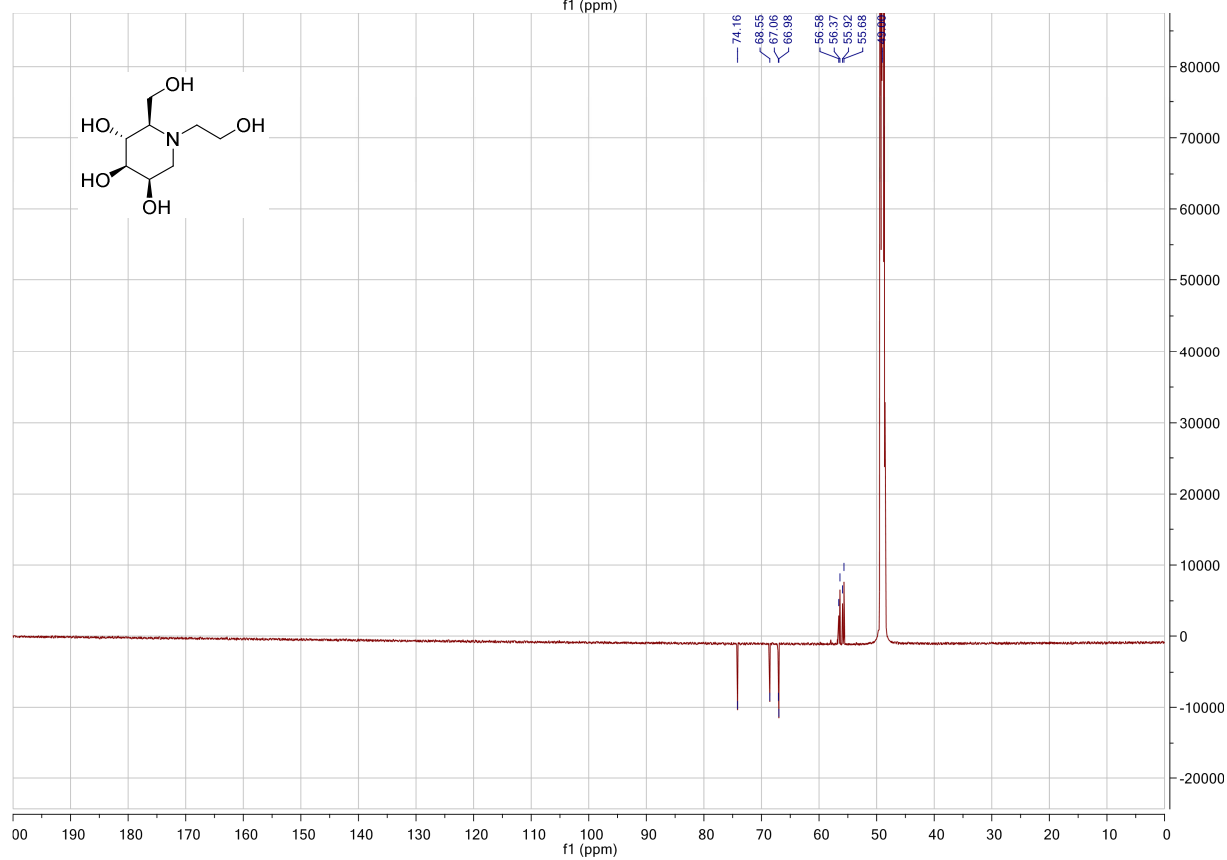
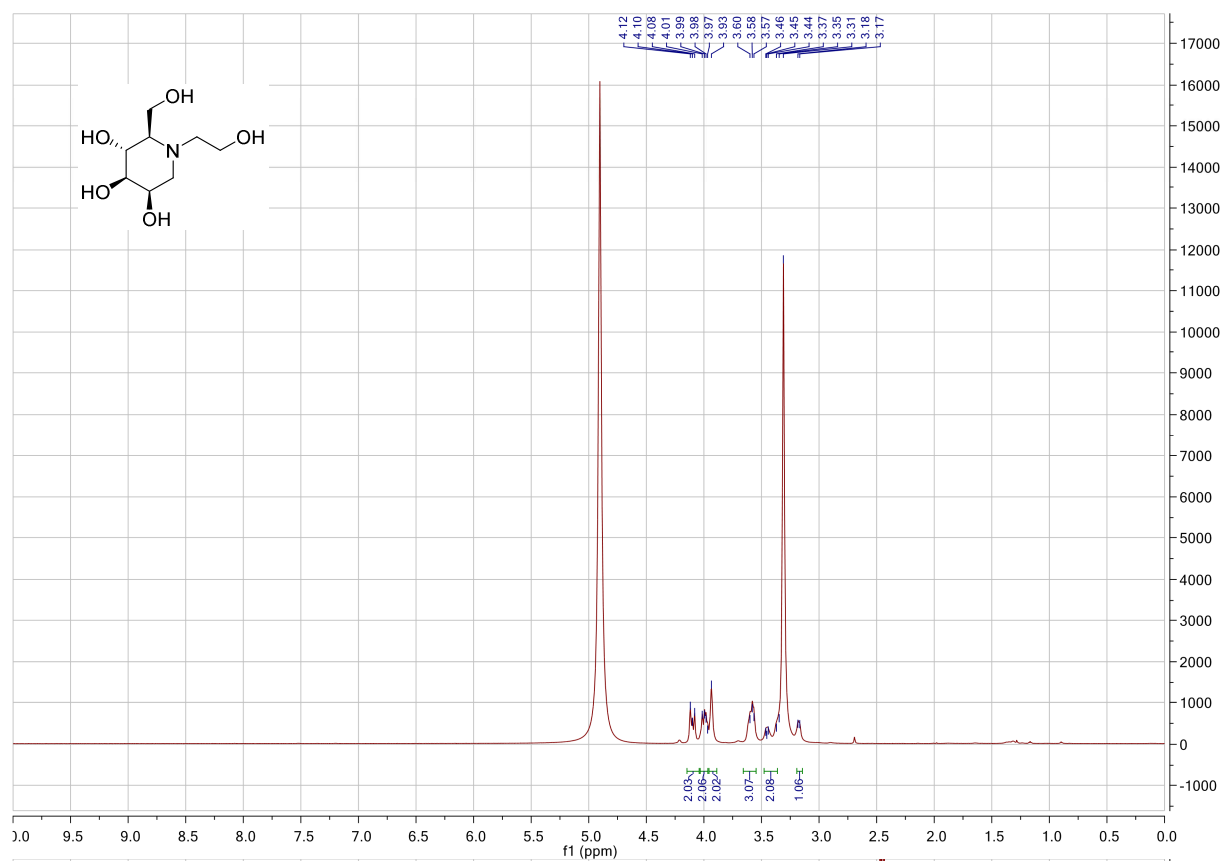




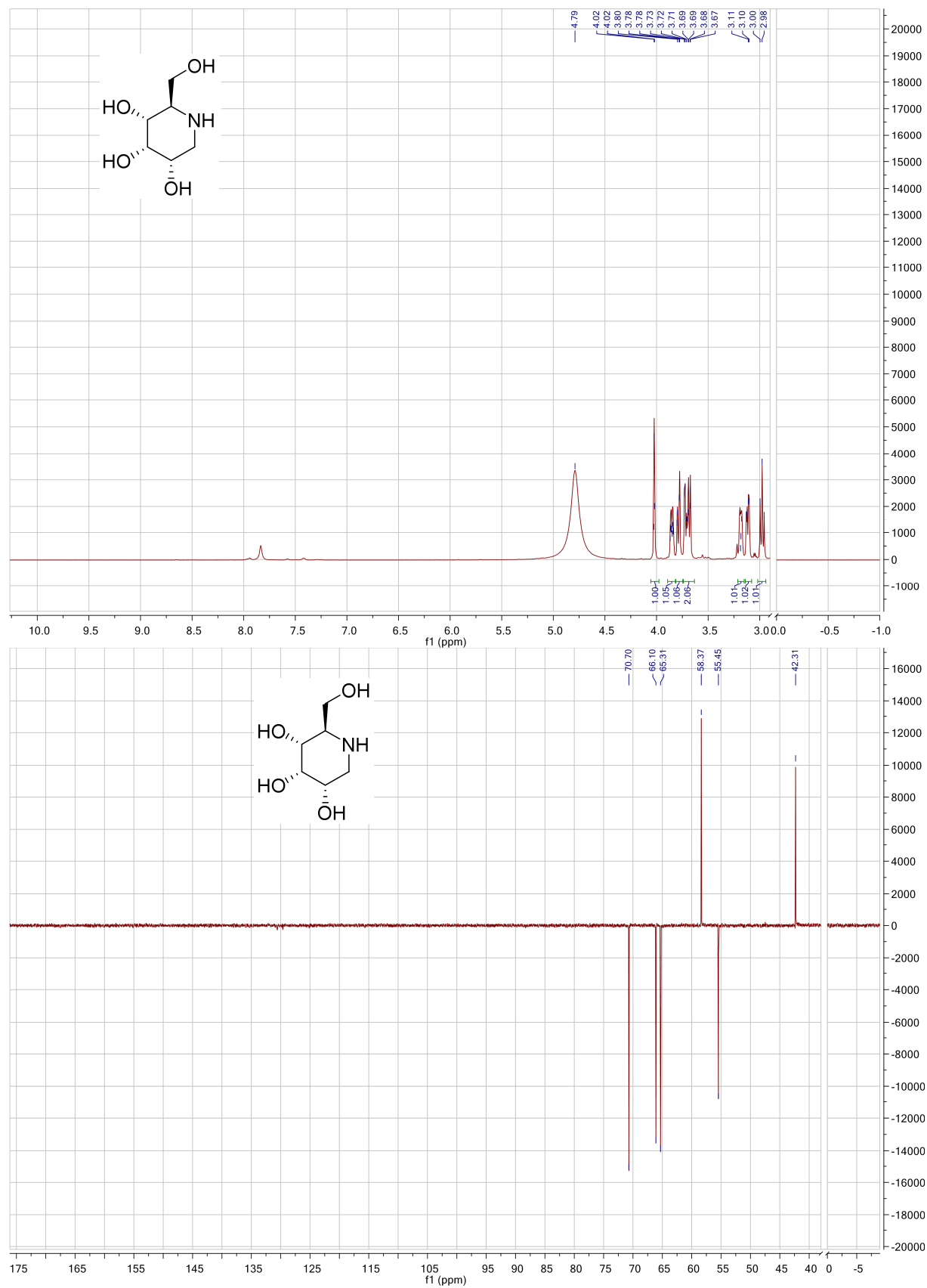
# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound C241 in $\text{H}_2\text{O}$ .



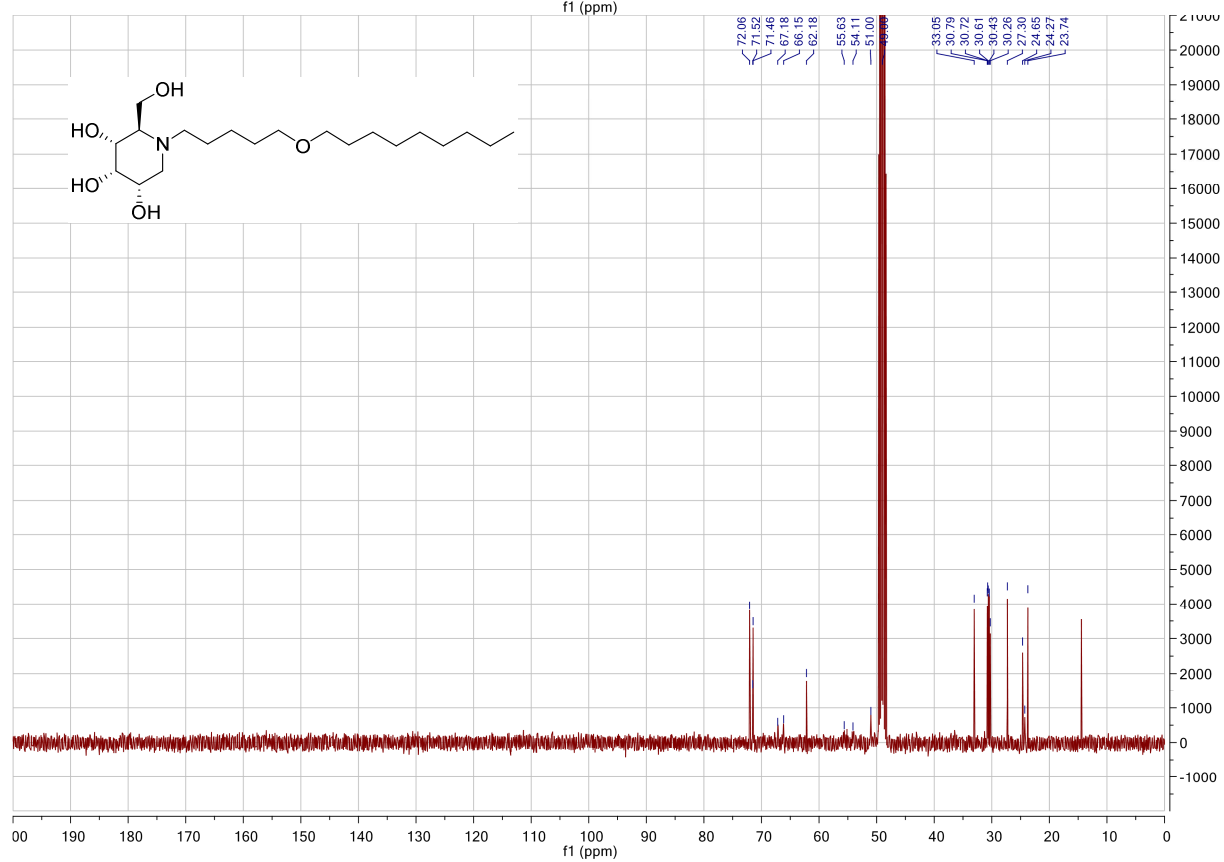
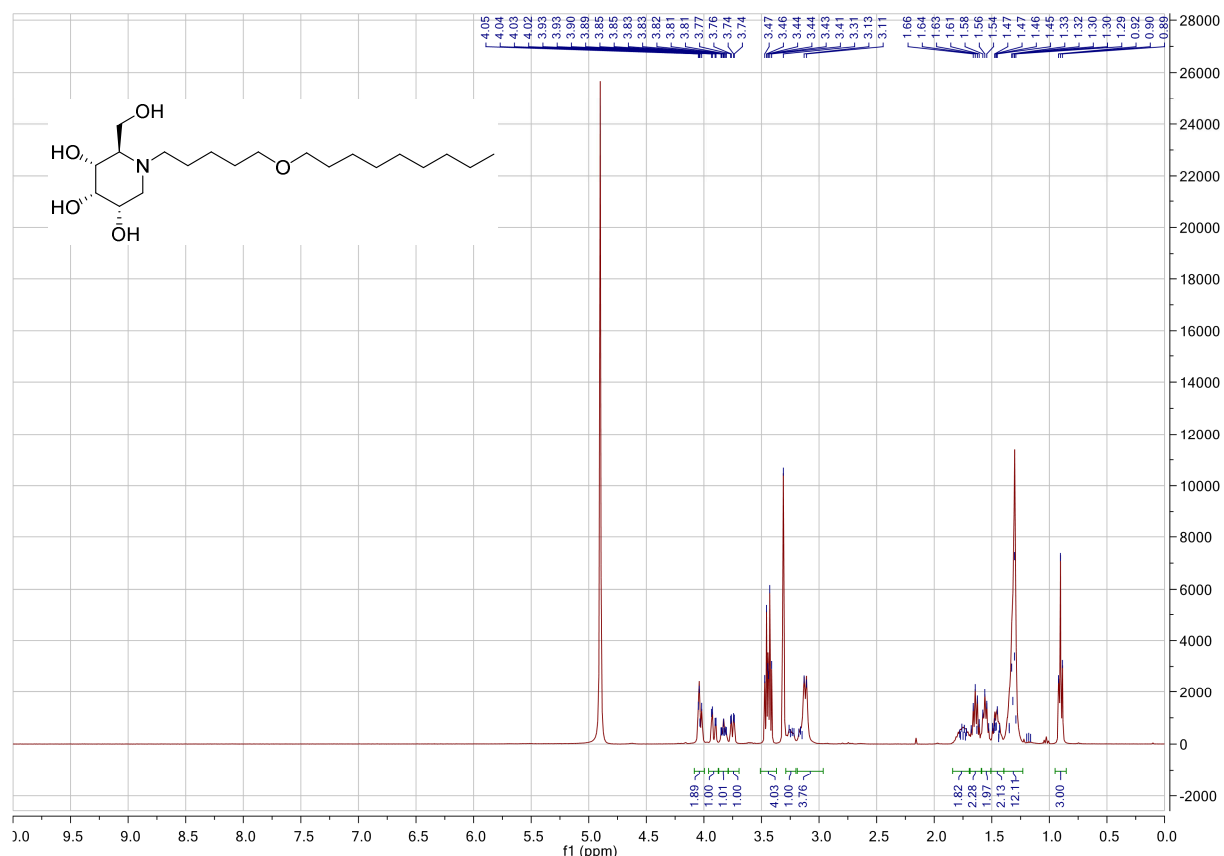
<sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound C243.TFA in MeOD.



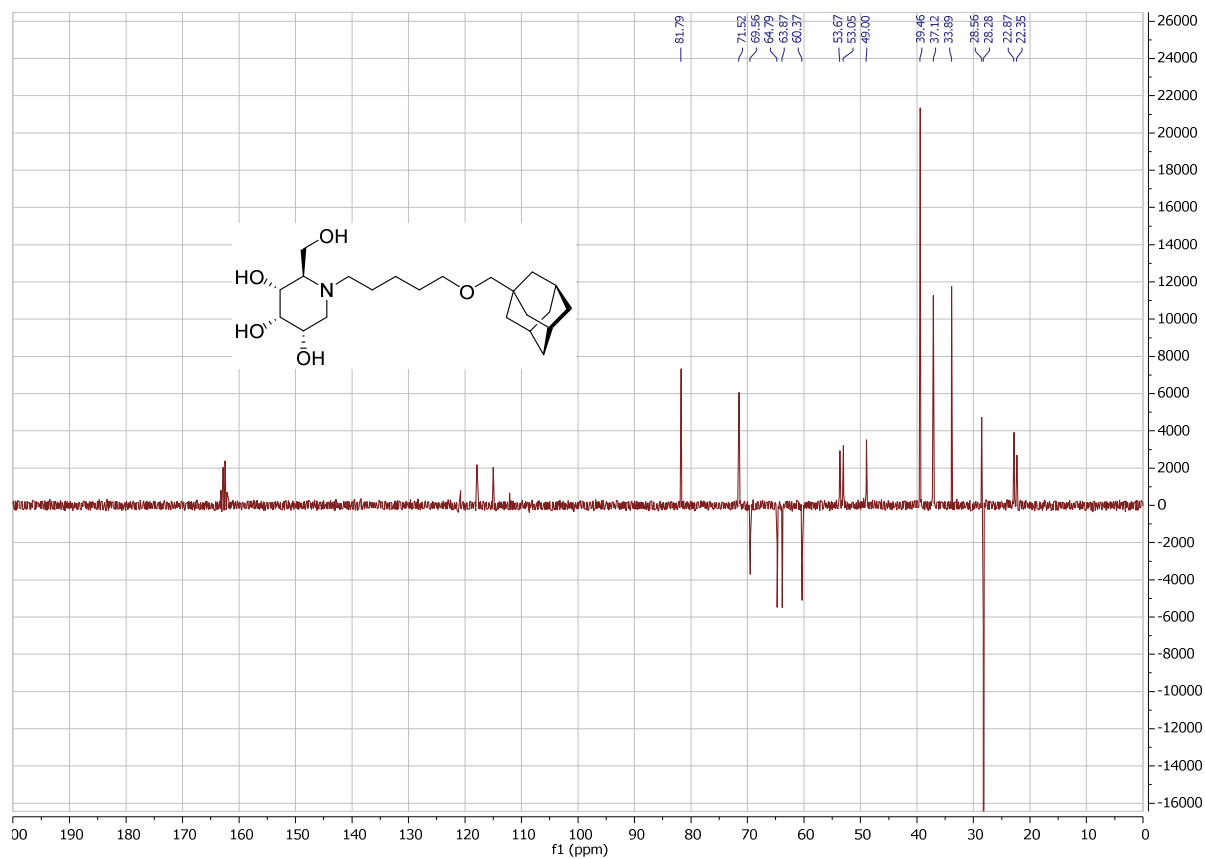
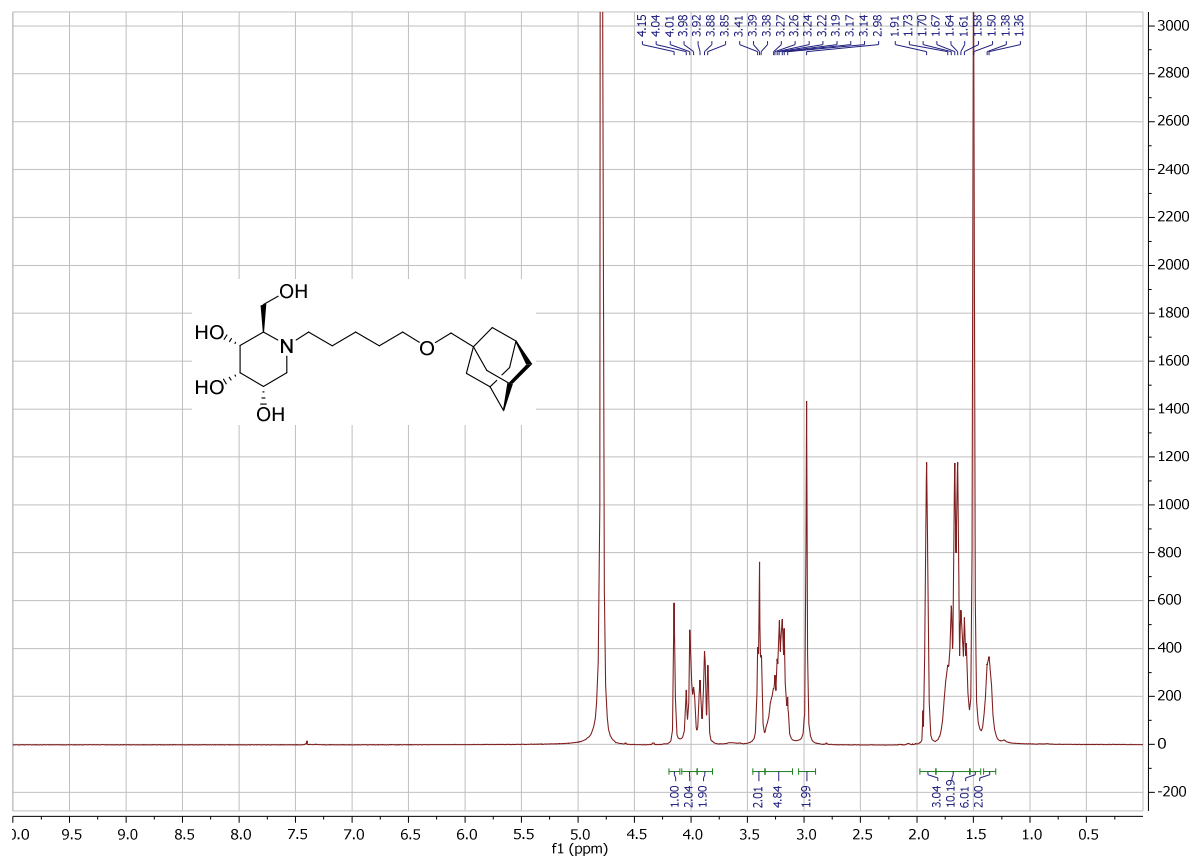
# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound C245 in $\text{D}_2\text{O}$ .



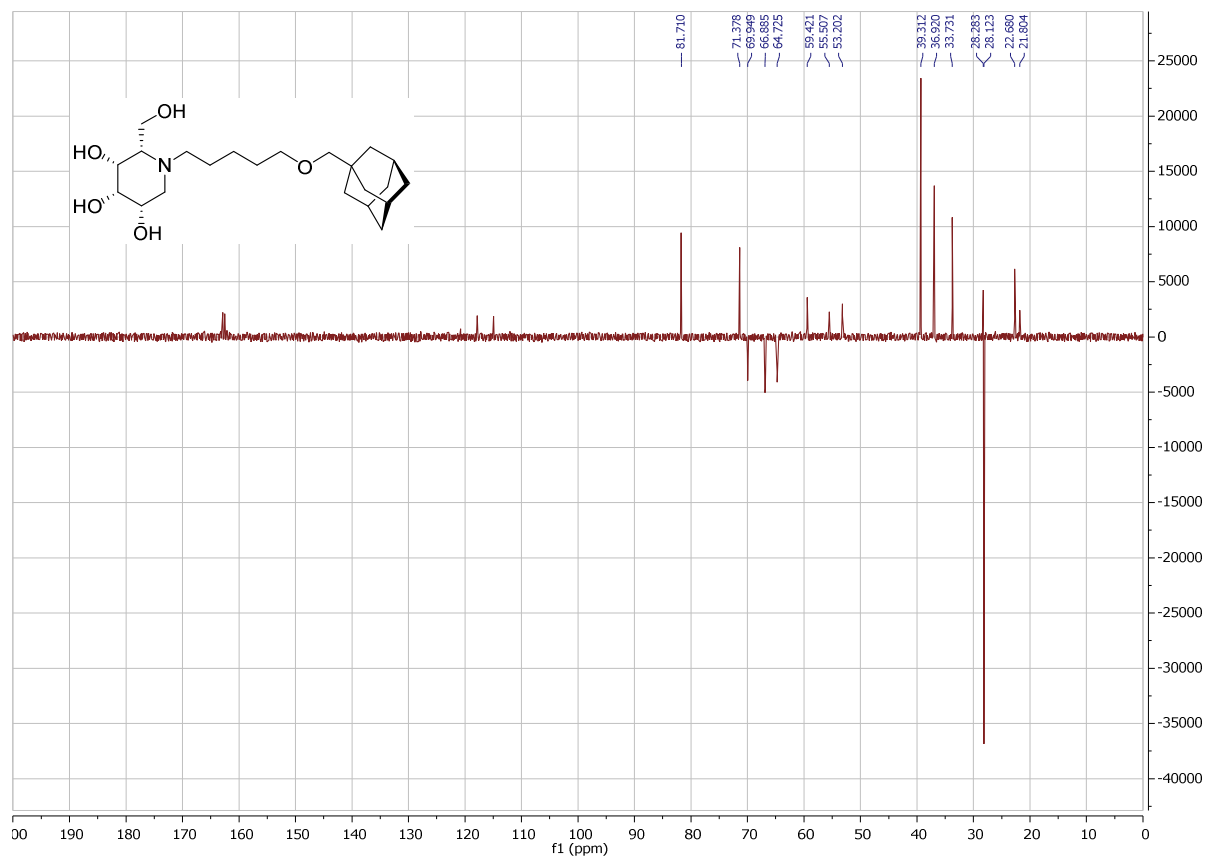
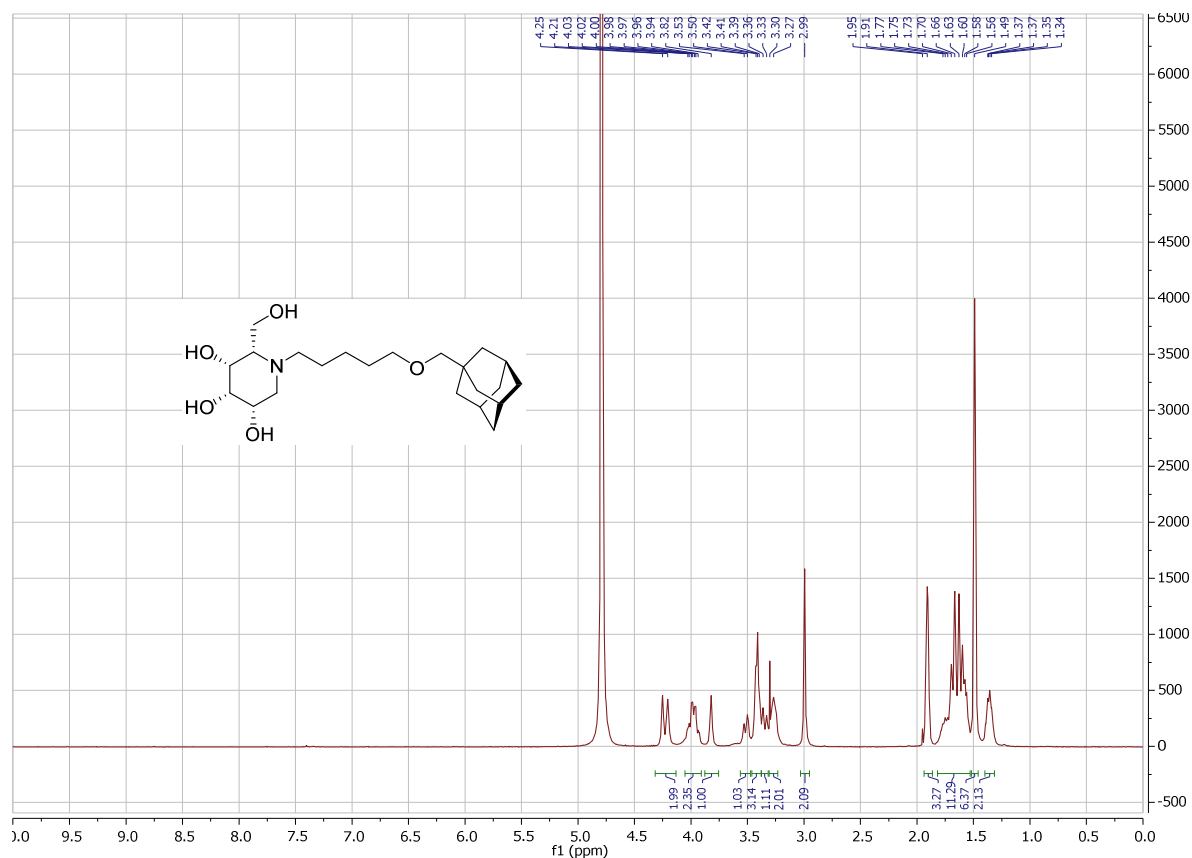
# <sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound C247.TFA in MeOD.



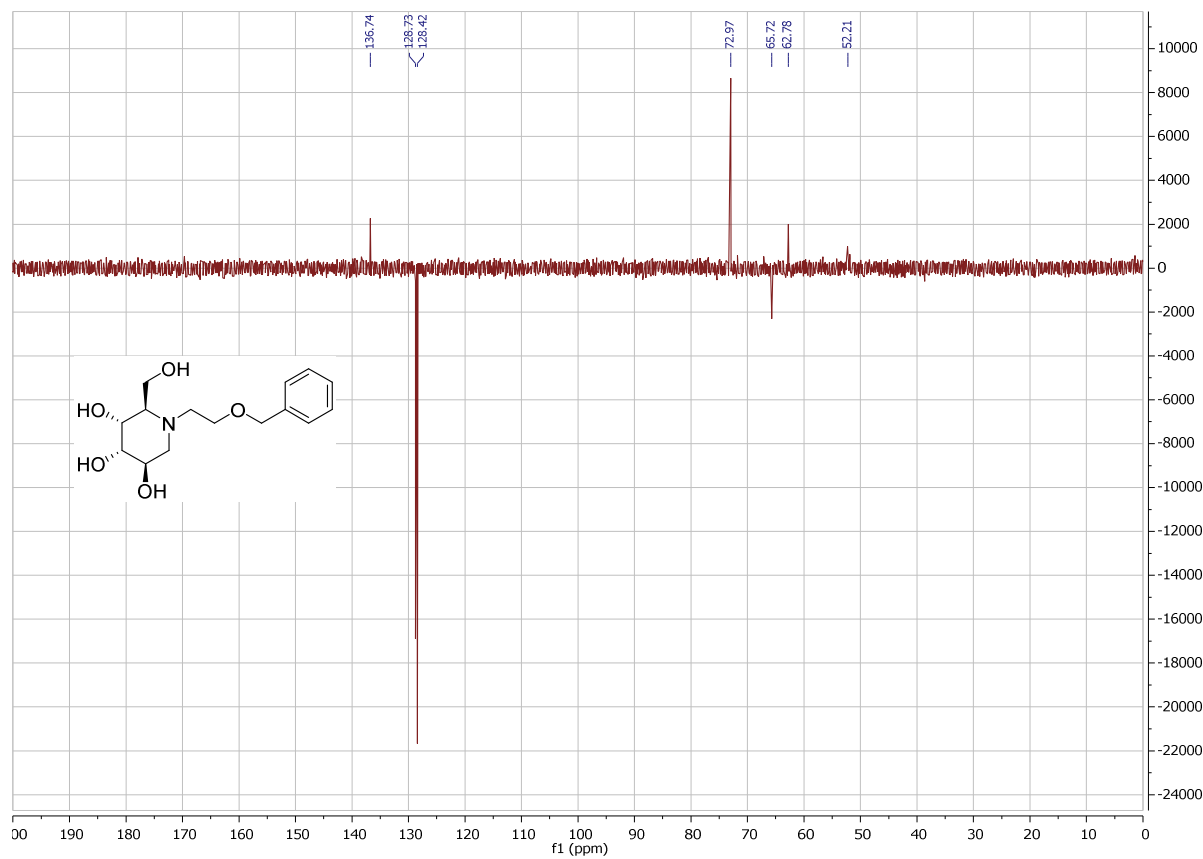
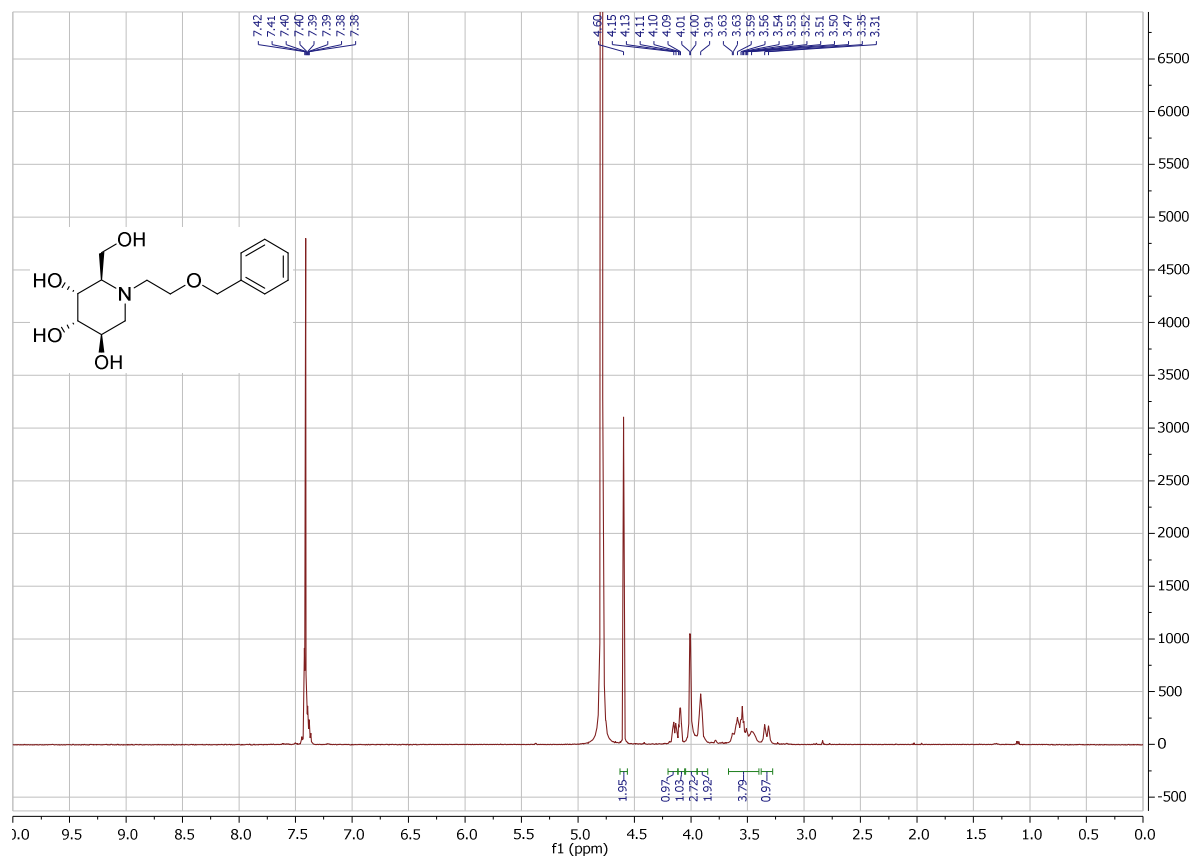
**$^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  of compound C253.TFA in  $\text{D}_2\text{O}$ .**



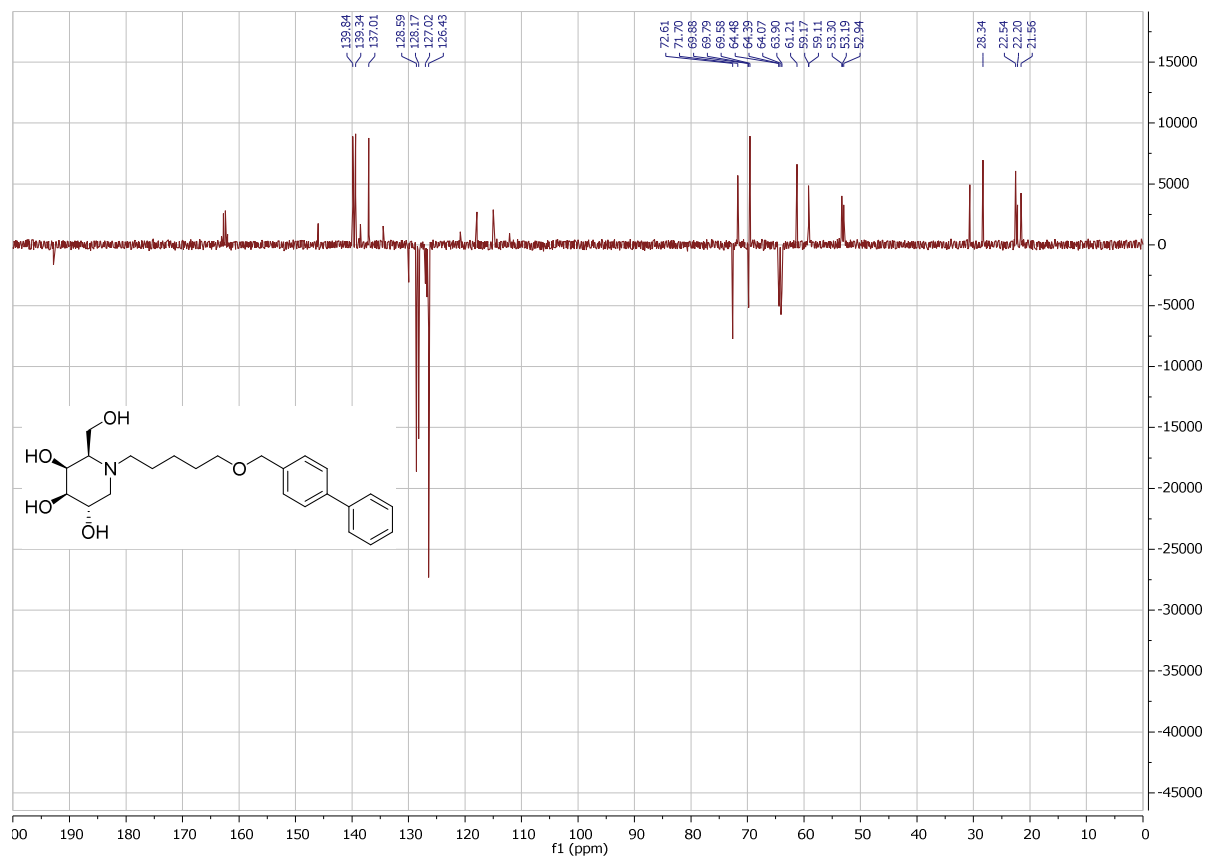
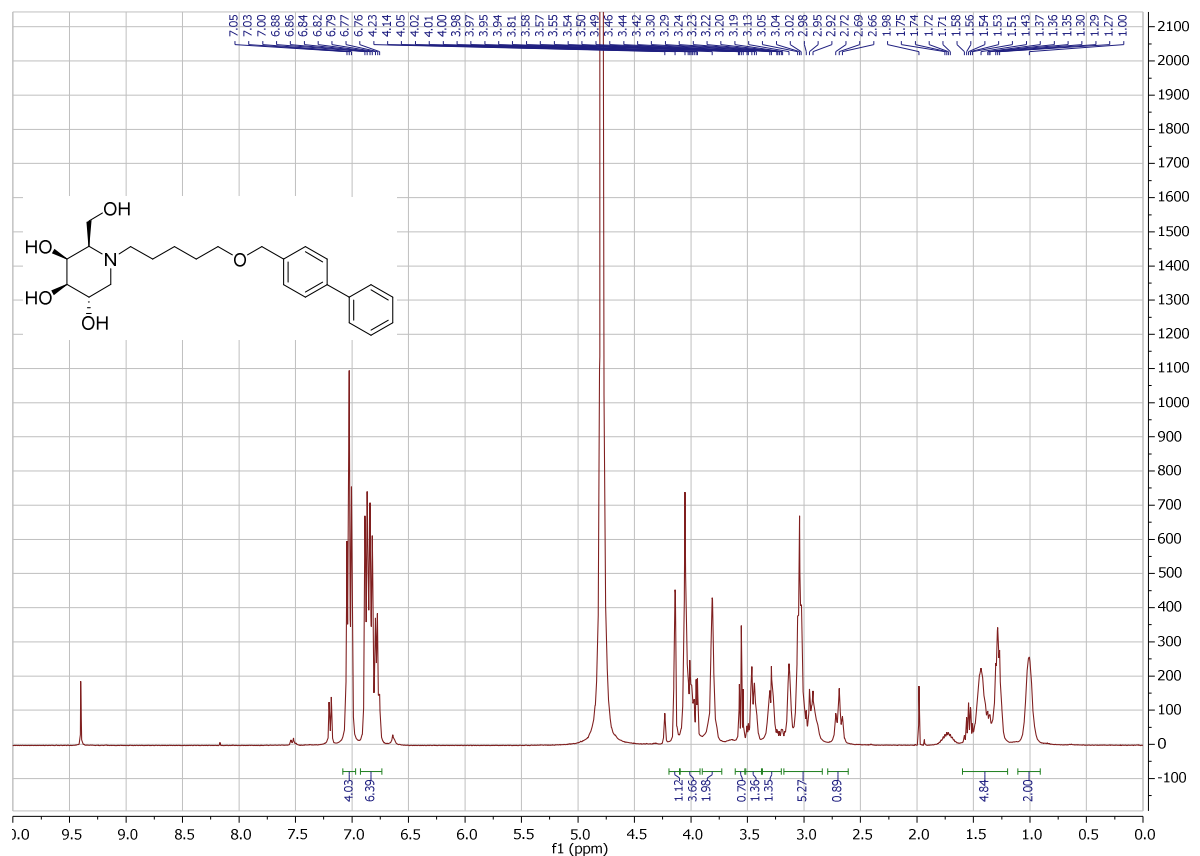
# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound C255.TFA in $\text{D}_2\text{O}$ .



# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound C256.TFA in $\text{D}_2\text{O}$ .

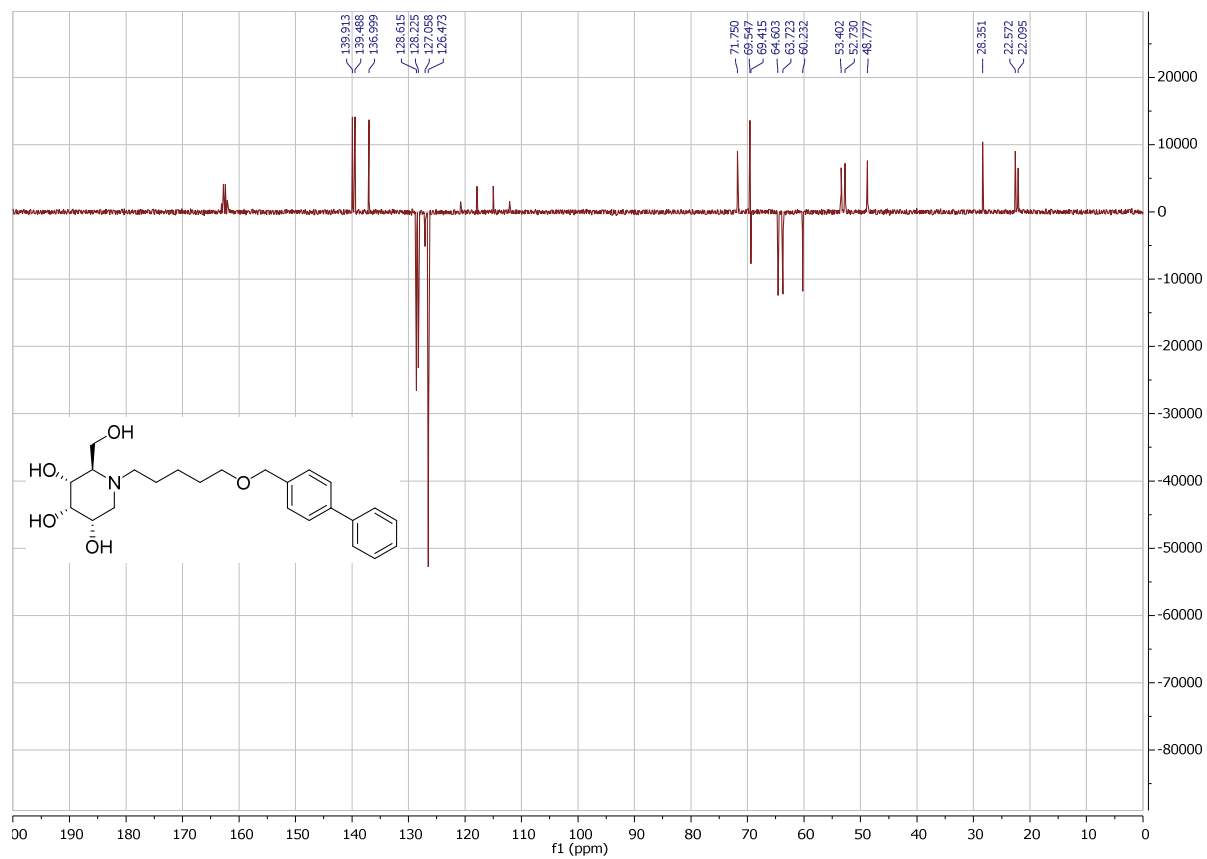
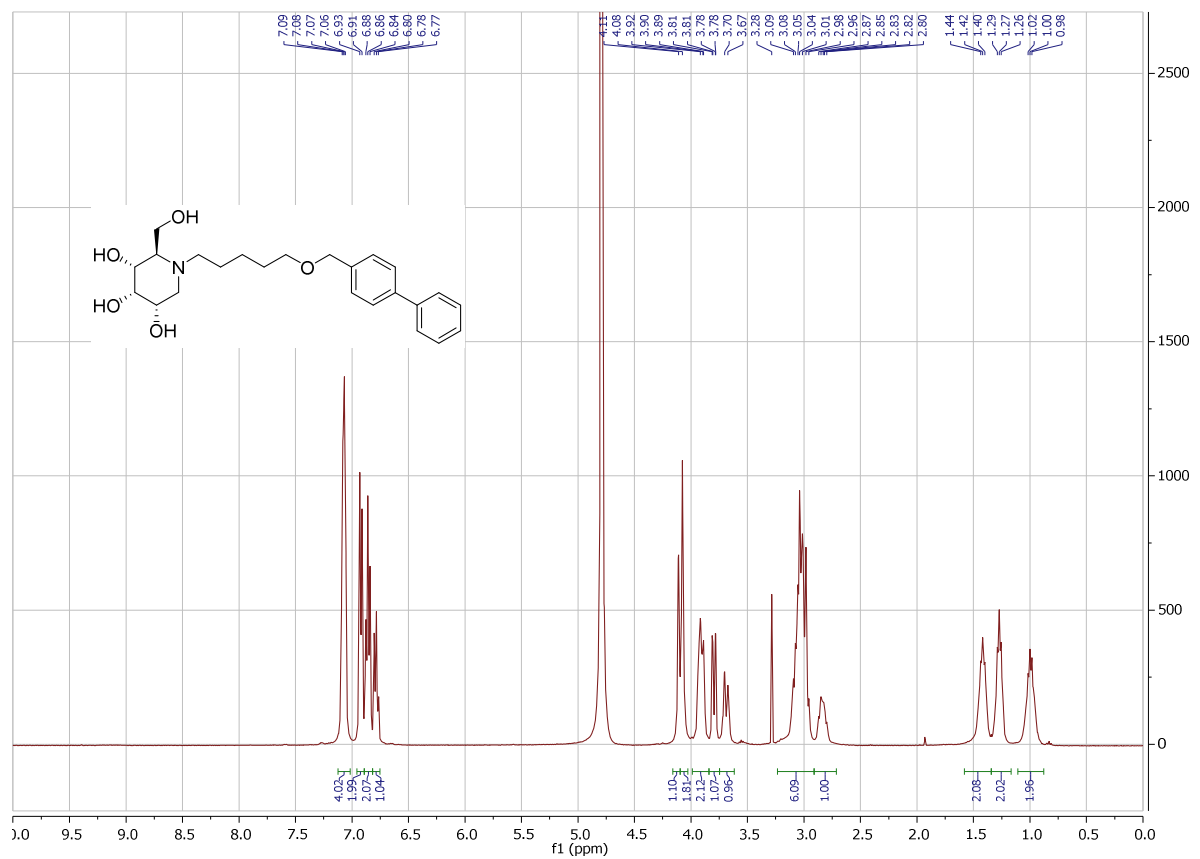


# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound C259.TFA in $\text{D}_2\text{O}$ .

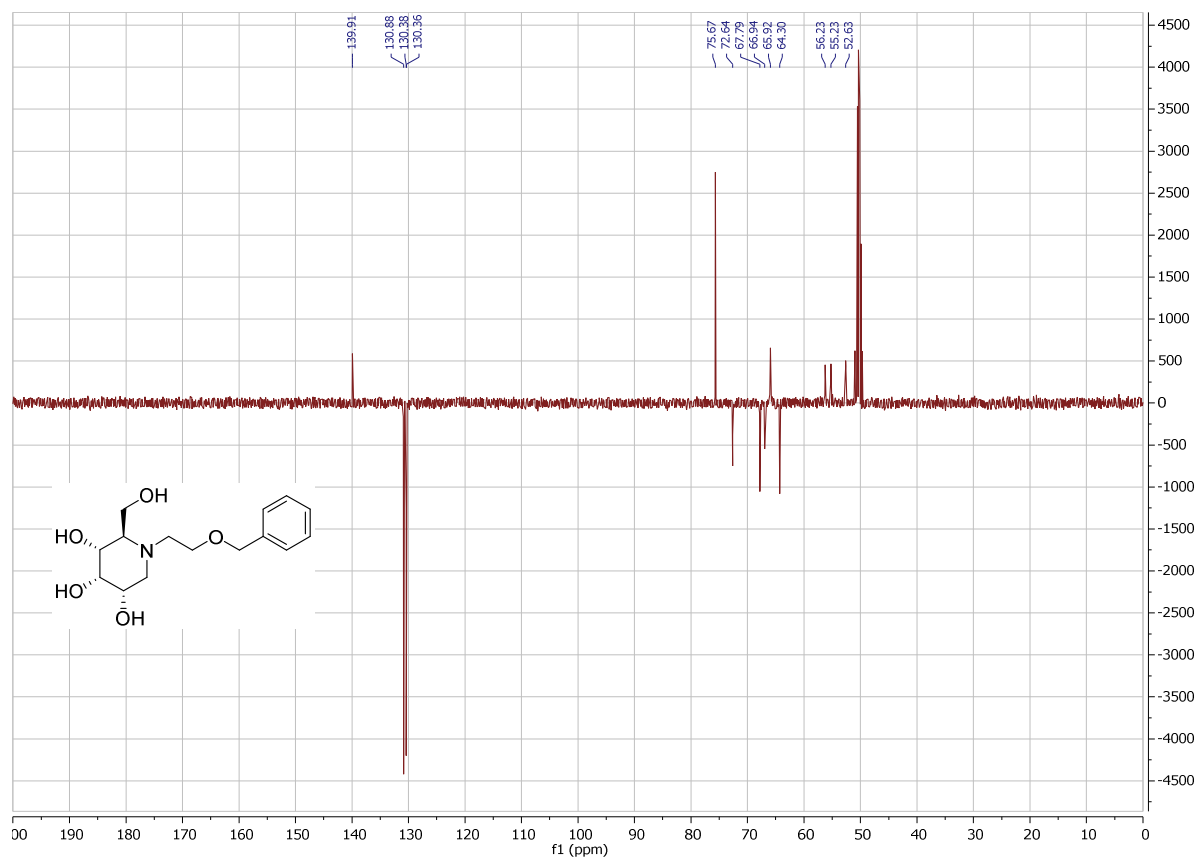
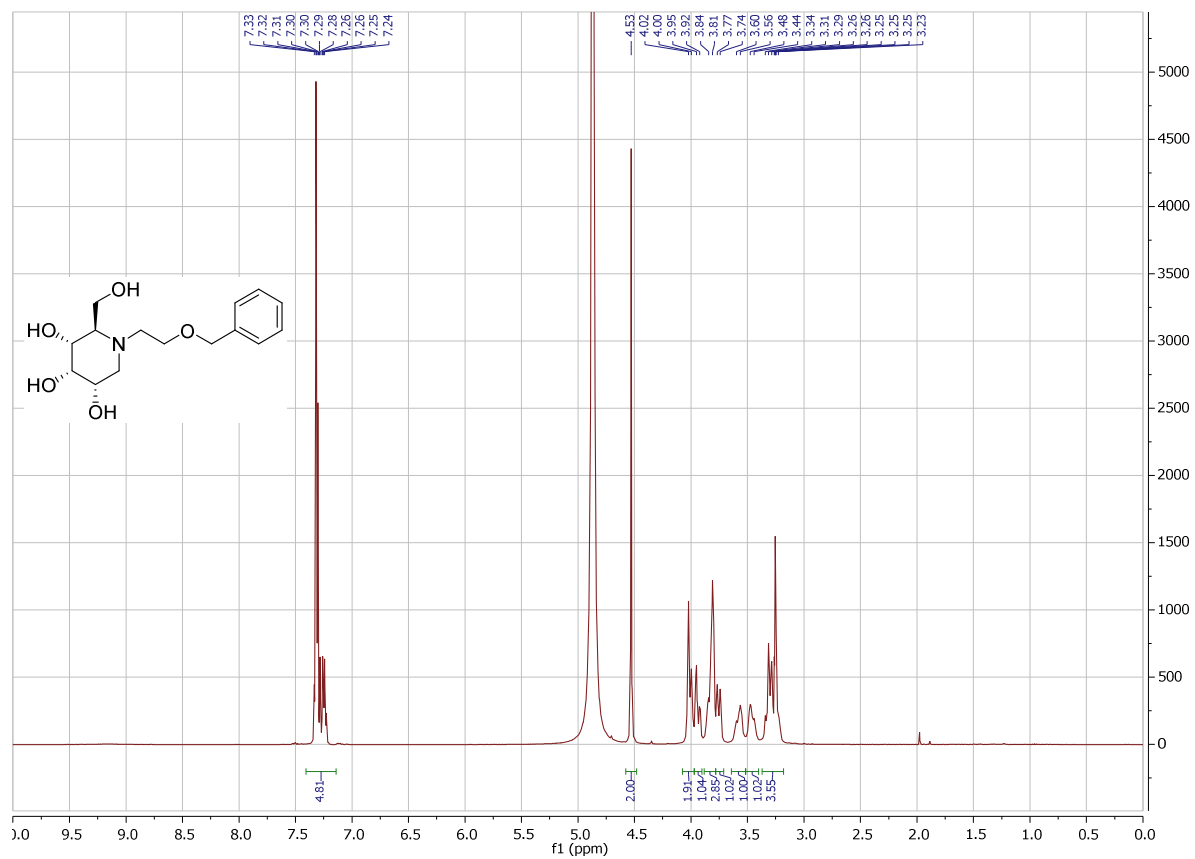




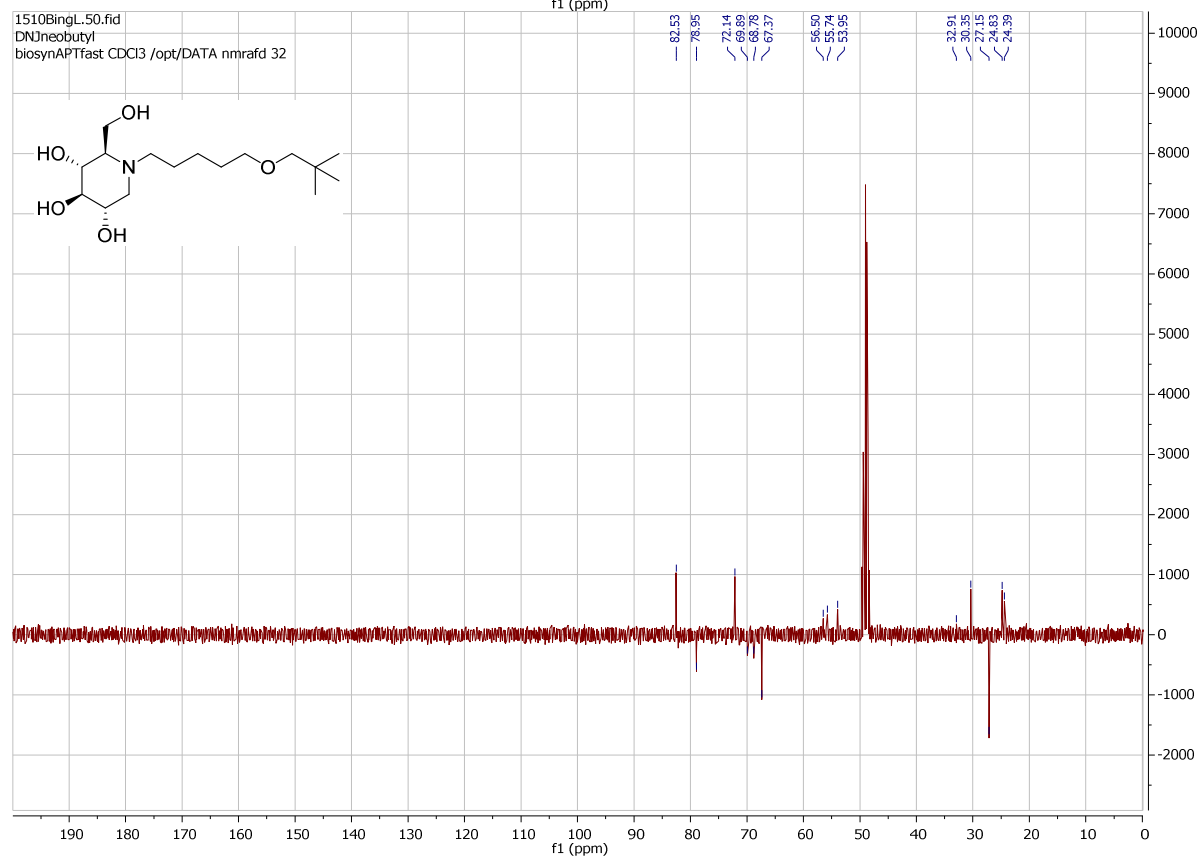
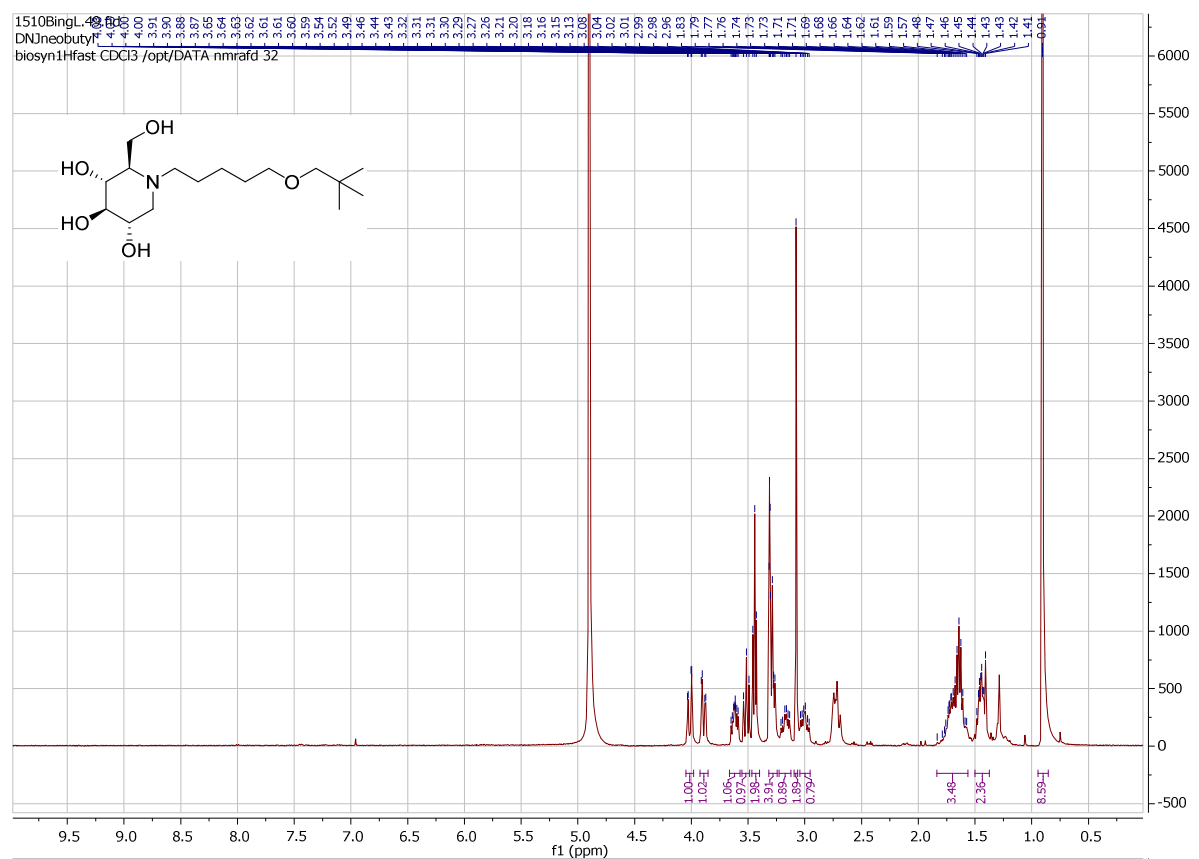
# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound C264.TFA in $\text{D}_2\text{O}$ .



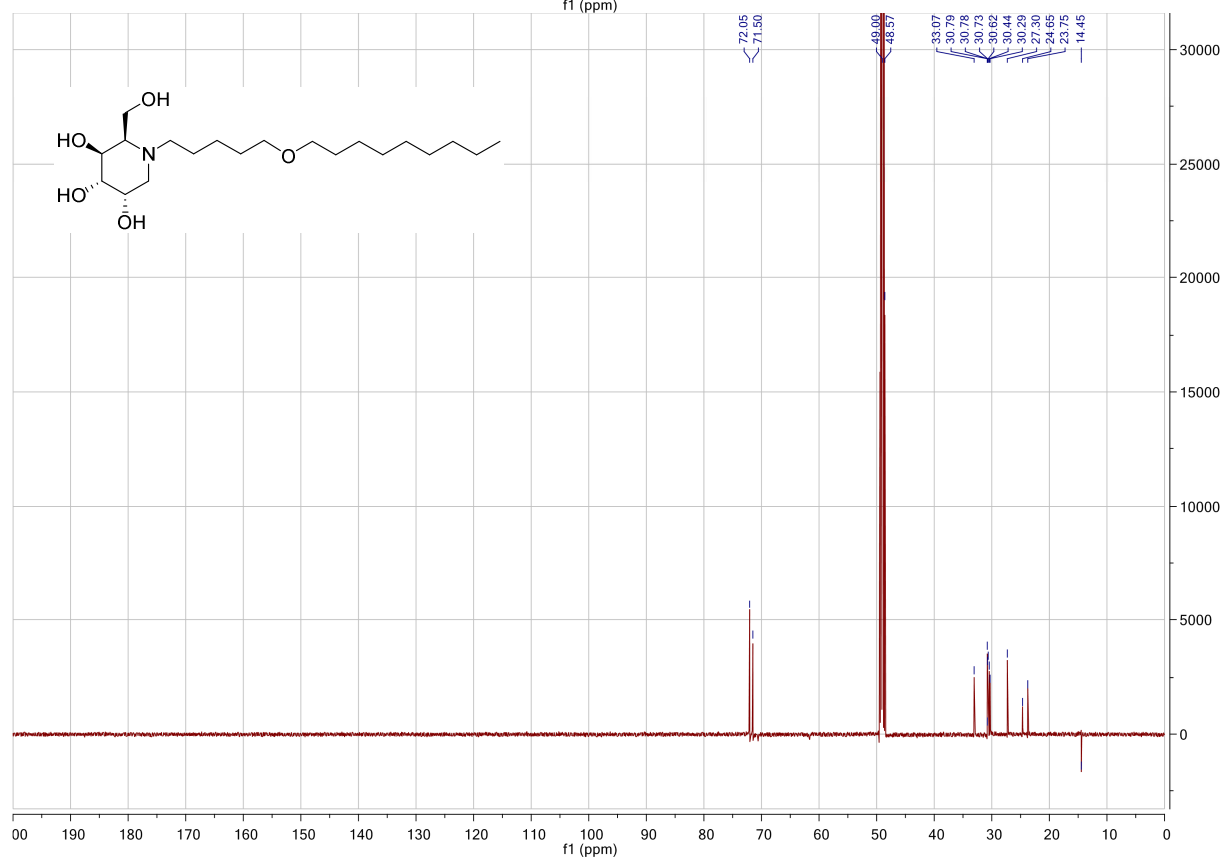
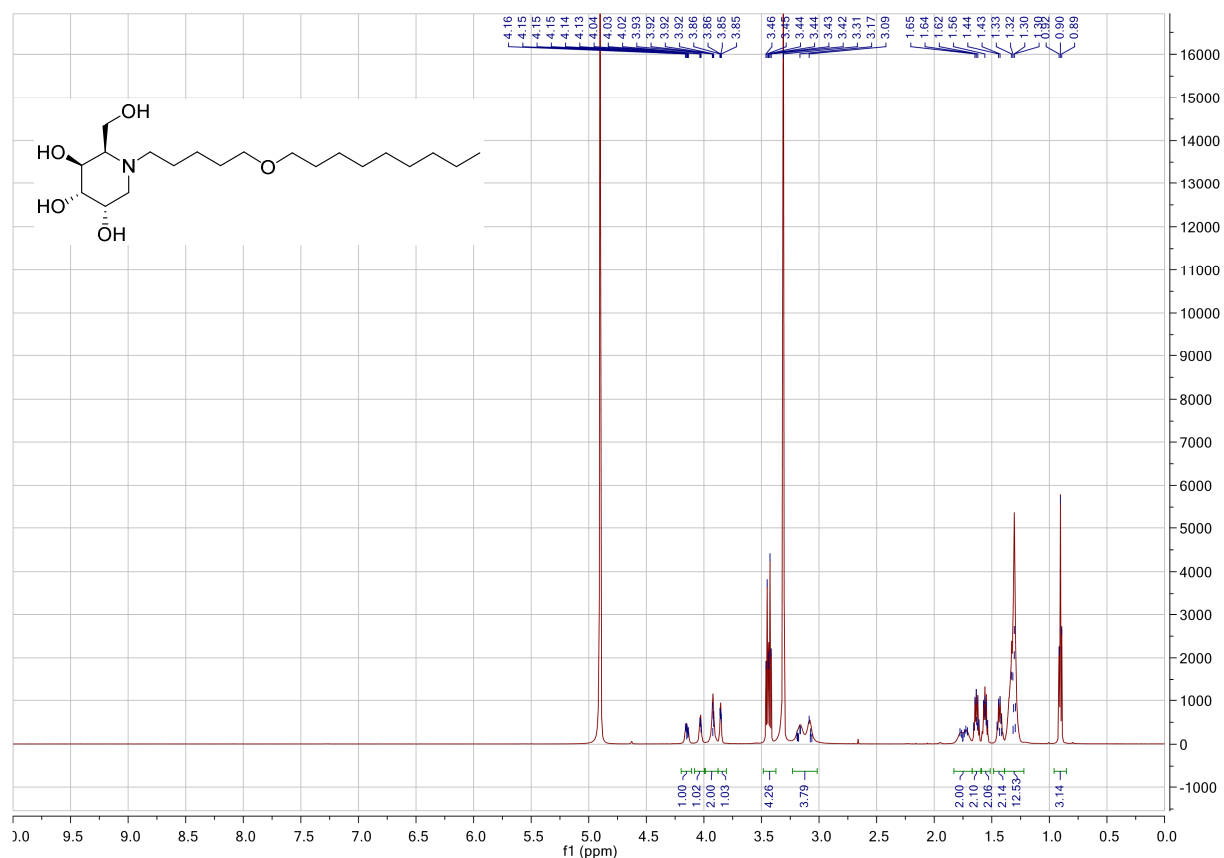
**$^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  of compound C266.TFA in MeOD.**



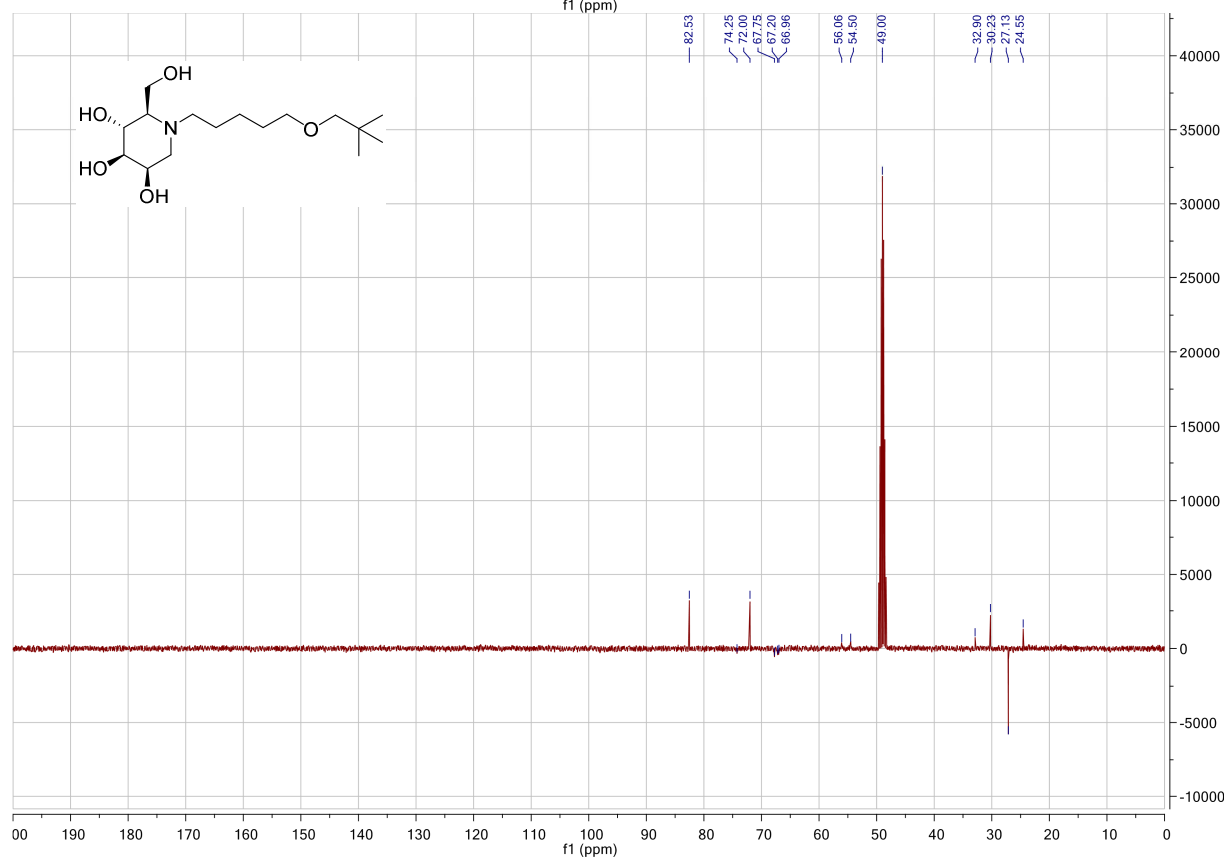
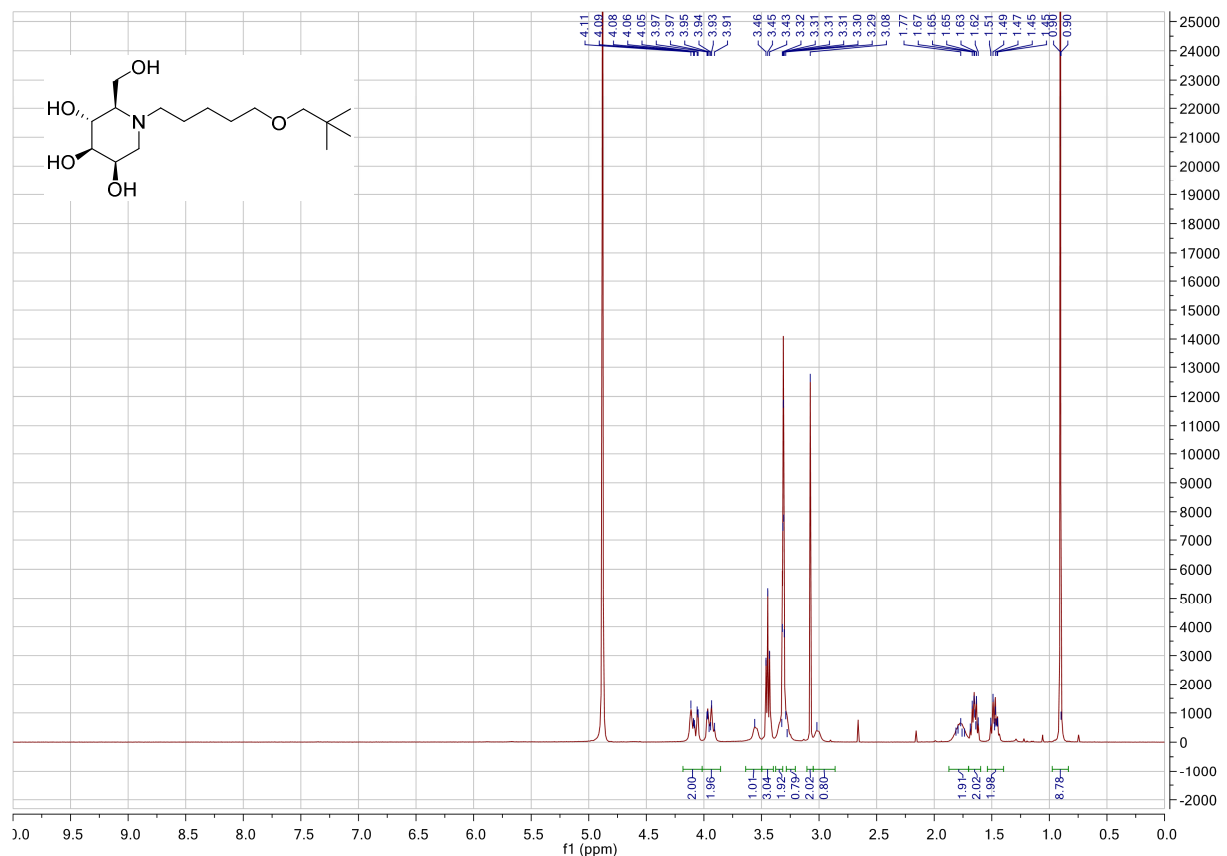
**<sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound C268.TFA in MeOD.**



**<sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound C271.TFA in MeOD.**



**<sup>1</sup>H-NMR and <sup>13</sup>C-NMR of compound C277.TFA in MeOD.**





# $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of compound C280.TFA in MeOD.

