Electronic Supplementary Material (ESI) for Green Chemistry.


**SUPPORTING INFORMATION**

# Heterogeneous Copper-Catalyzed Direct Reduction of C-Glycosidic Enones to Saturated Alcohols in Water

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## 1. Experimental Section

### *a. General Experimental*

Chemicals and solvents were purchased from Sigma-Aldrich, Alfa-Aesar, JT Baker or TCI and used as received. Compound **1a** (Octulose) was obtained from L'Oreal as a solution in $H_2O$, and concentrated *in vacuo* before use. All hydrogenation reactions under $H_2$ atmosphere were set-up in a 100 mL stainless-steel Parr reactor equipped with a mechanical stirrer. The reactions were pressurized under Hydrogen Atmosphere (*Airgas,* Ultra High Purity). The loaded reactor was placed on a bench-top Parr stand equipped with a Parr 4843 reactor controller. Proton nuclear magnetic resonance ($^1$H NMR) spectra were acquired using Agilent DD2 400 MHz, Agilent DD2 500 MHz, Agilent DD2 600 MHz or Varian Inova 500 MHz spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) and are calibrated to the residual solvent peak. Coupling constants (*J*) are reported in Hz. Multiplicities are reported using the following abbreviations: s = singlet; d = doublet; t = triplet; m = multiplet (range of multiplet is given). Carbon nuclear magnetic resonance ($^{13}$C NMR) spectra were acquired using Agilent DD2 600 MHz or Agilent DD2 400 MHz spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) and are calibrated to the residual solvent peak. X-Ray Powder Diffraction (XRPD) measurements were performed on a Bruker D8-focus X-Ray diffractometer equipped with a Cu line-focus sealed tube, a divergent beam geometer and a NaI scintillation detector. Measurements were made with a 40 kV, 40 mA beam in the range 2θ from 3$^o$ to 80$^o$ locked couple scan type, a step size of 0.05$^o$ and a scan speed of 1 second/step. Analytical thin layer chromatography was performed on pre-coated 250 µm layer thickness silica gel 60 $F_{254}$ Plates (EMD Chemicals Inc.). Visualization was performed by ultraviolet light and/or by staining with potassium permanganate or ceric ammonium molybdate (CAM) solutions. Purifications by column chromatography were performed using SilicaFlash F60 silica gel (40-63 µm, 230-400 mesh, Silicycle). Elemental analyses were performed using inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Perkin Elmer Optima 3000 equipped with a Scott nebulizer. The Sc standard was measured at 361.384 nm, Cu at 324.754 nm, Mg at 279.079 nm and Al at 308.215 nm. Samples were prepared for ICP-OES by

dissolving a known solid amount in 2 mL of 6 M nitric acid and diluting to 50 mL with DI $H_2O$. Elemental components were quantified by comparison with purchased calibration standards. High resolution mass spectra (HRMS) were recorded using an Agilent 6550A QTOF by electrospray ionization time of flight experiments.

*b. Synthesis of the Cu-PMO Catalyst*

A solution of $Al(NO_3)_3.9H_2O$ (18.8 g, 0.05 mol, 1 equiv.), $Mg(NO_3)_2.6H_2O$ (30.76 g, 0.12 mol, 2.4 equiv.) and $Cu(NO_3)_2.2.5H_2O$ (7.0g, 0.03 mol, 0.6 equiv.) in 300 mL distilled (DI) water was added dropwise over four hours to a stirring solution of $Na_2CO_3.H_2O$ (6.2 g, 0.05 mol, 1 equiv.) in 375 mL distilled water. The pH was kept constant at pH ~ 10 by adding aliquots of 1 M NaOH aqueous solution. Upon completion of the addition, the mixture is allowed to stir vigorously at room temperature for three days. The blue precipitate is collected by vacuum filtration and washed with 1.5 L distilled water. The filter cake is then suspended in a solution of $Na_2CO_3$ solution (62 g, 0.5 mol, 10 equiv.) in DI $H_2O$ (250 mL, 2M) and allowed to stir at room temperature overnight. Upon completion, the precipitate is collected by vacuum filtration and washed with DI $H_2O$ (2.5 L). The filter is left to dry overnight in a 105$^oC$ oven to obtain copper-doped hydrotalcite. The solid is ground by mortar and pestle and subjected to calcination at 460$^oC$ in air for 24 h to obtain Cu-PMO (9.21 g) as a green powder. The Cu-PMO was analyzed by XRPD (Figure S1), showing the expected loss of hydrotalcite features[1]. Elemental analysis of Cu-PMO was performed by ICP-OES (Table S1) and confirms incorporation of the metals in the expected ratio.

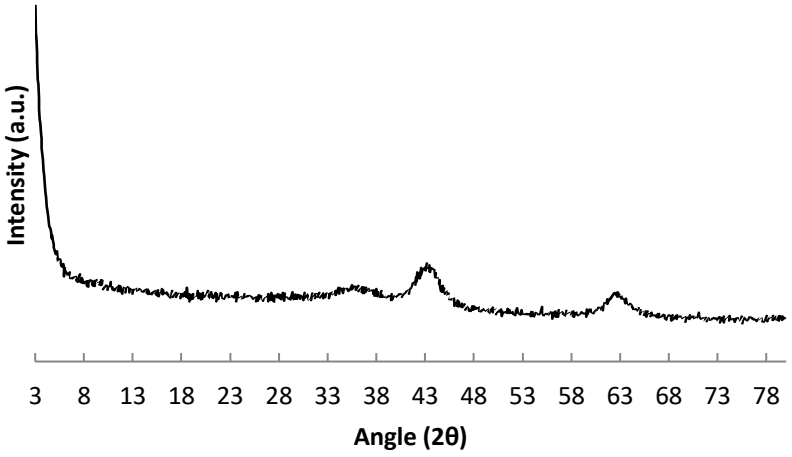



**Figure S1:** XPRD of Cu-PMO catalyst

**Table S1:** Metal Ion Composition of Cu-PMO determined by ICP-OES

| | Cu | Mg | Al |
|---|---|---|---|
| Concentration (mg/L) | 26.09 | 39.37 | 19.36 |
| Mass in solution (mg) | 1.305 | 1.969 | 0.968 |
| Amount in solution (mmol) | 0.0205 | 0.0806 | 0.0359 |
| Normalized Ratio of Metals | 0.57 | 2.25 | 1.00 |

*c. Synthesis of the Hydrotalcite (HTC) catalyst*

A solution of $Al(NO_3)_3.9H_2O$ (18.8 g, 0.05 mol, 1 equiv.) and $Mg(NO_3)_2.6H_2O$ (38.46 g, 0.15 mol, 3 equiv.) in 300 mL distilled (DI) water was added dropwise over four hours to a stirring solution of $Na_2CO_3.H_2O$ (6.2 g, 0.05 mol, 1 equiv.) in 375 mL distilled water. The pH was kept constant at pH ~ 10 by adding aliquots of 1 M NaOH aqueous solution. Upon completion of the addition, the mixture is allowed to stir vigorously at 40°C for three days. The white precipitate is collected by vacuum filtration and washed with 1.5 L distilled water. The filter cake is then suspended in a solution of $Na_2CO_3$ solution (62 g, 0.5 mol, 10 equiv.) in DI $H_2O$ (250 mL, 2M) and allowed to stir at 40°C overnight. Upon completion, the precipitate is collected by vacuum filtration and washed with DI $H_2O$ (2.5 L). The filter is left to dry overnight in a 105°C oven to obtain hydrotalcite (HTC). The HTC was analyzed by XRPD (Figure S2) and is identical to literature reports[1].

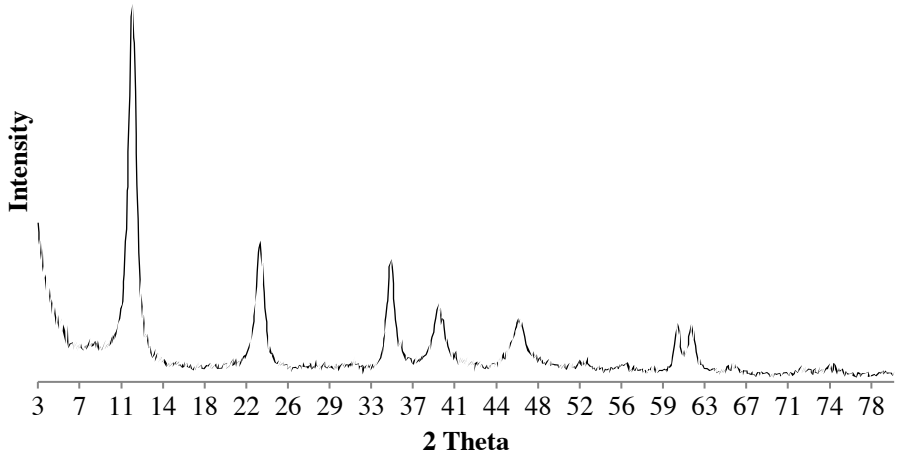
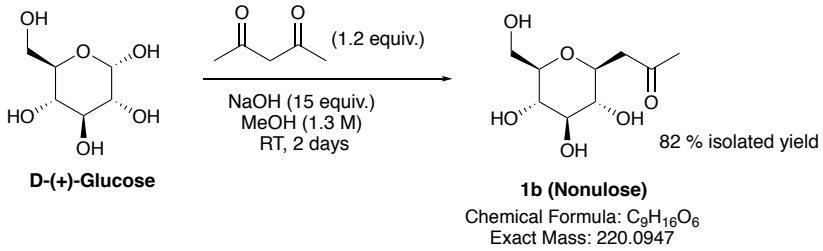



**Figure S2**: XRPD of HTC catalys

*d. Synthesis of Lubineau's ketone **1b***

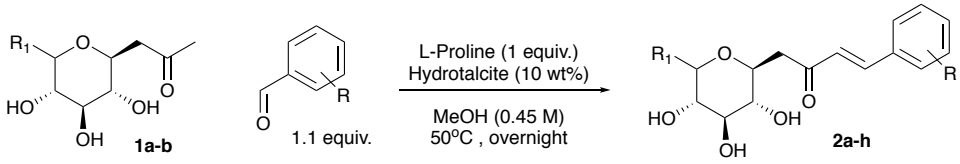



Synthesis of Nonulose **1b** was performed according to a modified procedure by Cavezza et al.[2] D-(+)-Glucose (10 g, 55.51 mmol, 1 equiv.) and 2,4-pentanedione (6.8 mL, 6.65 g, 66.53 mmol, 1.2 equiv.) were added to a 100 mL round bottom flask equipped with a Teflon coated stir bar. MeOH (20.7 mL) was added by syringe. A solution of NaOH (3.33 g, 83.25 mmol, 15 equiv.) in MeOH (22 mL) and $H_2O$ (10 mL) was prepared. After full dissolution of NaOH, the solution was added to the round bottom flask by pouring. The mixture was allowed to stir at room temperature for two days. Upon completion, the flask was placed in an ice bath and the basic mixture was quenched by dropwise addition of concentrated HCl (6.8 mL). The resulting crude mixture was evaporated *in vacuo* to obtain the crude product. Column chromatography (silica gel, EtOAc:MeOH:$H_2O$, 30:8:2) furnished pure product **1b** as a brown oil in 82 % yield (11.284 g, 45.46 mmol).

**$R_f$** = 0.14 (silica gel, 8:1 DCM:MeOH); **$^1$H NMR** (400 MHz, Methanol-$d_4$) δ 3.77 (dd, *J* = 12.0, 2.1 Hz, 1H), 3.61 (ddd, *J* = 20.2, 10.6, 5.7 Hz, 2H), 3.37 – 3.17 (m, 3H), 3.05 (t, *J* = 9.1 Hz, 1H), 2.86 (dd, *J* = 16.0, 3.0 Hz, 1H), 2.57 (dd, *J* = 16.0, 9.1 Hz, 1H), 2.18 (s, 3H). **$^{13}$C NMR** (101 MHz, $cd_3od$) δ 208.83, 80.24, 78.19, 75.84, 73.69, 70.30, 61.38, 45.76, 29.19.

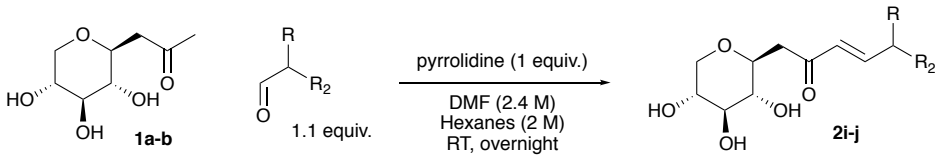
Analytical data is identical to that reported in the literature.[3]

*e. General Procedure A for synthesis of C-glycosidic substrates **2a-g***



Representative Procedure A: The procedure developed by de Winter et al. was replicated with alterations to afford targeted substrates.[4] The hygroscopicity of the starting material varied the true amount weighed out. Hence, an internal standard (biphenyl) was utilized to quantify amount of starting material added by $^1$H NMR, which is used to correct product yields. It follows that this variation in starting material content affects the relative amounts of reagents and reactants. C-glycoside ketone **1a-b** (1 equiv.) was added to a round bottom flask equipped with a Teflon coated stir bar. MeOH (0.45 M) and biphenyl (0.05 equivalents, internal standard) were added by syringe and the mixture was stirred until complete dissolution of the starting material. An aliquot was removed and analyzed by $^1$H NMR to determine the amount of C-glycoside **1a-b** added. L-Proline (1 equiv.), benzylic aldehyde (1.1 equiv.) and MgO (10 wt% of C-glycoside) were added to the stirring mixture. The reaction was allowed to proceed at 50°C with stirring until completion as observed by TLC analysis. The mixture was filtered over filter paper, then mixed with silica gel and concentrated *in vacuo.* Crude product was purified over a short-path silica plug, after dry loading, by first flushing the internal standard (biphenyl) and excess aldehyde with a small amount of ethyl acetate, then collecting product with acetone as liquid phase.

### *f. General Procedure B for synthesis of C-Glycosidic Substrates **2i-j***

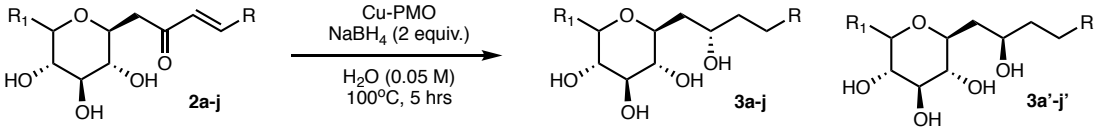



Representative Procedure B: The procedure developed by Foley et al. was replicated with minor alterations to afford aliphatic C-glycosidic enones.[5]

C-glycoside ketone **1a** (1 equiv.) and biphenyl (0.05 equiv., internal standard) were added to a round bottom flask equipped with a Teflon coated stir bar. DMF (2.4 M) was added by syringe and the mixture was stirred until complete dissolution of the starting material. An aliquat was removed for $^1$H NMR analysis of starting material amount. Then, hexanes (2 M), pyrrolidine (1 equiv.) and aliphatic aldehyde (1 equiv.) were added to the stirring mixture. The reaction was allowed to proceed at room temperature with stirring until completion as observed by TLC

analysis. The mixture was treated with Amberlite IR-120 H+ resin, filtered, and concentrated *in vacuo.* Crude product was purified by column chromatography (silica gel, 450:50 DCM:MeOH).

*g. <u>Optimized General Procedure C for the full catalytic hydrogenation of C-glycosidic Enones **2a-j**</u>*




<u>Representative Procedure C</u>: C-glycosidic enone **2a-j** (0.5 mmol, 1 equiv.) was added to a 25 mL round-bottom flask equipped with a Teflon coated stir bar. $H_2O$ (10 mL, 0.05 M) was added by syringe. Cu-PMO (see below section 1i. for amounts) and $NaBH_4$ (37.8 mg, 1.0 mmol, 2 equiv.) were added to the mixture in single portions. The mixture was allowed to stir at reflux (100°C) for 5 hours. Upon completion, the mixture was cooled and treated with Amberlite IR-120 H+ resin. The heterogeneous mixture was filtered over cellulose filter paper and the retentate was washed with methanol (~ 20 mL). The combined organic fractions were concentrated *in vacuo*. $CHCl_3$ (0.04 mL, 59.69 mg, 0.5 mmol, 1 equiv., internal standard) were added to the residue, and the mixture was completely dissolved in deuterated methanol for $^{1}H$ and $^{11}B$ NMR analysis. Once the NMR yield was obtained and the absence of boron salts was confirmed by NMR, the mixture was evaporated *in vacuo* and placed under high vacuum before weighing (if complete conversion to desired product). If boron salts were present, the mixture was re-dissolved in methanol and evaporated *in vacuo,* and the process was repeated until the absence of boron salts was confirmed by NMR. Once the NMR yield was obtained and the absence of boron salts was confirmed by NMR, the mixture was evaporated *in vacuo* and placed under high vacuum before weighing (if complete conversion to desired product). When desired, produced diastereomers were separated by column chromatography (silica gel, 450:50 DCM:MeOH).

*h. <u>Procedures and Amounts for the optimization of the one-step enone full reduction (c.f. Table 1)</u>*

Optimization of the one-step reduction of enone *under $H_2$ pressure* was performed according to the following representative procedure D: C-Glycosidic enone **2a** (1 equiv.) was added to a 100 mL stainless-steel Parr reactor. If required, $NaBH_4$, LiCl, NaCl, and/or Cu-PMO catalyst were added to the Parr reactor (see Table S2 for amounts). Solvent (30 mL) was added to the reactor by syringe. The reactor was closed once all reaction components were added and subsequently pressurized under $H_2$ pressure. The reactor was placed on a stand and connected to a temperature controller. Heating was turned on at time t=0. The reaction was allowed to stir for the targeted amount of time (see Table S2). Upon completion, the reactor was cooled to room temperature under a stream of water. Once cool, the reactor was depressurized and opened in a fumehood. Caution: flammable gas is released! The mixture was treated with Amberlite IR-120H+ resin and filtered over cellulose paper before concentrating *in vacuo*. DMF or $CHCl_3$ (1 equiv., internal standard) was added to the residue, and the mixture was completely dissolved in deuterated methanol for $^1$H NMR analysis.

Optimization of the one-step reduction of enone *without $H_2$ pressure* was performed according to the following representative procedure E: C-glycosidic enone **2a** (1 equiv.) was added to a 25 mL round-bottom flask equipped with a Teflon coated stir bar. Solvent was added by syringe. If required, $NaBH_4$, LiCl, NaCl, and/or Cu-PMO catalyst were added to the mixture in single portions. If using CuCl, the mixture was allowed to stir for 15 minutes, then CuCl was added (0.5 eq.). The mixture was allowed to stir at the chosen temperature for a set amount of time (*c.f.* Table 1). Upon completion, the mixture was brought to room temperature and treated with Amberlite IR-120 H+ resin. The heterogeneous mixture was filtered over cellulose filter paper and the retentate was washed with methanol. The combined organic fractions were concentrated *in vacuo*. DMF or $CHCl_3$ (1 equiv., internal standard) was added to the residue, and the mixture was completely dissolved in deuterated methanol for $^1$H NMR analysis.

**Table S2.** Amounts in each reaction towards the optimization of the direct Cu-catalyzed full reduction of enones (*c.f.* Table 1 in manuscript)

| Entry from Table 1 | Compound 2a | Catalyst | Additive | Solvent | Internal Standard |
|---|---|---|---|---|---|
| 1 | 0.3 mmol, 83.5 mg | Cu-PMO 10 mg | - | MeOH (30 mL, 0.01 M) | DMF (23 µL, 1 eq.) |
| 2 | 0.3 mmol, 83.5 mg | Cu-PMO 10 mg | - | $H_2O$ (30 mL, 0.01 M) | DMF (23 µL, 1 eq.) |

| | | | | | |
|---|---|---|---|---|---|
| 3 | 0.3 mmol, 83.5 mg | Cu-PMO 10 mg | LiCl (0.3 mmol, 12.7 mg) | MeOH (30 mL, 0.01 M) | DMF (23 µL, 1 eq.) |
| 4 | 0.3 mmol, 83.5 mg | Cu-PMO 10 mg | NaCl (0.3 mmol, 17.5 mg) | MeOH (30 mL, 0.01 M) | DMF (23 µL, 1 eq.) |
| 5 | 0.38 mmol, 106.7 mg | CuCl 19.0 mg | $NaBH_4$ (3.8 mmol, 143.8 mg) | MeOH (3.8 mL, 0.1 M) | DMF (28 µL, 1 eq.) |
| 6 | 0.38 mmol, 106.7 mg | CuCl 19.0 mg | $NaBH_4$ (3.8 mmol, 143.8 mg) | MeOH (3.8 mL, 0.1 M) | DMF (28 µL, 1 eq.) |
| 7 | 0.3 mmol, 83.5 mg | Cu-PMO 10 mg | $NaBH_4$ (0.6 mmol, 22.7 mg) | MeOH (30 mL, 0.01 M) | DMF (23 µL, 1 eq.) |
| 8 | 0.3 mmol, 83.5 mg | Cu-PMO 10 mg | $NaBH_4$ (0.6 mmol, 22.7 mg) | MeOH (30 mL, 0.01 M) | DMF (23 µL, 1 eq.) |
| 9 | 0.3 mmol, 83.5 mg | Cu-PMO 10 mg | $NaBH_4$ (0.6 mmol, 22.7 mg) | MeOH (30 mL, 0.01 M) | DMF (23 µL, 1 eq.) |
| 10 | 0.3 mmol, 83.5 mg | Cu-PMO 10 mg | $NaBH_4$ (0.6 mmol, 22.7 mg) | MeOH (30 mL, 0.01 M) | DMF (23 µL, 1 eq.) |
| 11 | 1.5 mmol, 417.5 mg | Cu-PMO 55 mg | $NaBH_4$ (3.0 mmol, 113.5 mg) | MeOH (30 mL, 0.05 M) | DMF (110 µL, 1 eq.) |
| 12 | 1.5 mmol, 417.5 mg | Cu-PMO 55 mg | $NaBH_4$ (3.0 mmol, 113.5 mg) | MeOH (30 mL, 0.05 M) | DMF (110 µL, 1 eq.) |
| 13 | 1.5 mmol, 417.5 mg | Cu-PMO 55 mg | $NaBH_4$ (3.0 mmol, 113.5 mg) | MeOH (30 mL, 0.05 M) | DMF (110 µL, 1 eq.) |
| 14 | 1.5 mmol, 417.5 mg | Cu-PMO 55 mg | $NaBH_4$ (3.0 mmol, 113.5 mg) | MeOH (30 mL, 0.05 M) | DMF (110 µL, 1 eq.) |
| 15 | 1.5 mmol, 417.5 mg | Cu-PMO 25 mg | $NaBH_4$ (3.0 mmol, 113.5 mg) | MeOH (30 mL, 0.05 M) | DMF (110 µL, 1 eq.) |
| 16 | 0.725 mmol, 201.8 mg | Cu-PMO 26.5 mg | $NaBH_4$ (1.45 mmol, 55 mg) | $H_2O$ (14.5 mL, 0.05 M) | DMF (56 µL, 1 eq.) |
| 17 | 1.5 mmol, 417.5 mg | Cu-PMO 55 mg | $NaBH_4$ (3.0 mmol, 113.5 mg) | $H_2O$ (30 mL, 0.05 M) | DMF (110 µL, 1 eq.) |
| 18 | 1.5 mmol, 417.5 mg | Cu-PMO 55 mg | $NaBH_4$ (3.0 mmol, 113.5 mg) | $H_2O$ (30 mL, 0.05 M) | DMF (110 µL, 1 eq.) |
| 19 | 0.5 mmol, 139.2 mg | Cu-PMO 16.5 mg | $NaBH_4$ (0.25 mmol, 9.5 mg) | $H_2O$ (10 mL, 0.05 M) | $CHCl_3$ (40 µL, 1 eq.) |
| 20 | 1.2 mmol, 333.9 mg | - | $NaBH_4$ (2.4 mmol, 90 mg) | $H_2O$ (24 mL, 0.05 M) | DMF (93 µL, 1 eq.) |

*i. Procedure for the large-scale reduction of Aromatic Enone **2e***

C-glycosidic enone **2e** (8.12 g, 25 mmol, 1 equiv.) and water (500 ml, 0.05 M) were charged to a 1 L double-jacketed reactor equipped with a mechanical stirrer. To this suspension were added Cu-PMO (892 mg, 11 mol%) and $NaBH_4$ (1.89 g, 50 mmol, 2 equiv.) in single portions. The reaction mixture was allowed to stir at reflux (100°C) for 5 hours. Upon completion, the dark brown homogeneous solution was cooled and treated with Amberlite IR-120 H+ resin (~ 180 g). The suspension was filtered over cellulose filter paper and the retentate was washed with methanol (~ 1 L). The combined organic and aqueous fractions were evaporated to dryness under vacuum. The crude residue was purified by filtration over silica (eluting with EtOAc:MeOH 80:20), followed by a carbon black treatment at reflux in ethanol for one hour. After concentration *in vacuo*, the solid was diluted with water, filtered, and lyophilized, furnishing pure product **3e** (mixture of diastereomers) as a beige powder in 72.9% isolated yield (6 g, 18.27 mmol). $^{1}H$ and $^{13}C$ NMR data are consistent with those from the smaller scale results reported in Section 1.j.

*j. Catalyst Recycling Studies*

C-glycosidic enone **2e** (162.2 mg, 0.5 mmol, 1 equiv.) was added to a 25 mL round-bottom flask equipped with a Teflon coated stir bar. $H_2O$ (10 mL, 0.05 M) was added by syringe. Cu-PMO (Trial 1: 16.5 mg, 10wt% and afterwards as recovered from previous run) and $NaBH_4$ (37.8 mg, 1.0 mmol, 2 equiv.) were added to the mixture in single portions. The mixture was allowed to stir at reflux (100°C) for 5 hours. Upon completion, the mixture was cooled and treated with Amberlite IR-120 H+ resin. The heterogeneous mixture was filtered over cellulose filter paper and the retentate was washed with methanol (~ 20 mL). The combined organic fractions were concentrated *in vacuo*. $CHCl_3$ (0.04 mL, 59.69 mg, 0.5 mmol, 1 equiv., internal standard) were added to the residue, and the mixture was completely dissolved in deuterated methanol for $^{1}H$ and $^{11}B$ NMR analysis. Once the NMR yield was obtained and the absence of boron salts was confirmed by NMR, the mixture was evaporated *in vacuo* and placed under high vacuum before

weighing to obtain the isolated yield. The recovered catalyst was placed in a dessicator until further use.

**Table S3.** Product yields after catalyst recycling

| | **2e Conversion[a] (%)** | **NMR Yield 3e/3e'[a] (%)** | **Isolated Yield 3e/3e' (%)** |
|---|---|---|---|
| **Cycle 1** | 100 | > 95 | 93 |
| **Cycle 2** | 100 | 94 | 97 |
| **Cycle 3** | 100 | > 95 | 85 |
| **Cycle 4** | 100 | > 95 | 92 |
| **Cycle 5** | 100 | > 95 | 93 |

[a]Conversion and NMR yields determined by $^1$H NMR using $CHCl_3$ as internal standard.

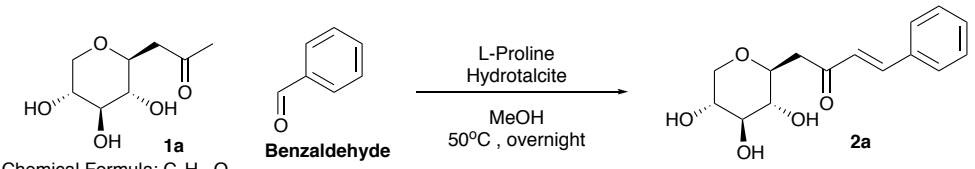
*k. Amberlite IR-120H$^+$ regeneration and reuse*

Amberlite IR-120 H$^+$ can be recuperated after reaction through a simple vacuum filtration. After recuperation Amberlite IR-120 H$^+$ can be reused after treatment to re-generate its acidity. To do so, spent Amberlite IR-120 H+ is placed in an Erlenmeyer containing a Teflon coated stir bar. The solid was covered with concentrated sulfuric acid and allowed to stir at room temperature for 30 minutes. After completion, the resin was filtered out of the solution and washed with DI water. The resin was placed in a dessicator for further drying until use.

Use of recycled resin did not alter reduction results. **2a** (0.5 mmol) was reduced using our optimized conditions with Cu-PMO (11 wt%) and $NaBH_4$ (2 equiv.) in MeOH (0.05 M) at 100$^o$C for 5 hours. After completion, recycled Amberlite IR-120 H$^+$ resin was added to the mixture to acidify until pH = 5. The mixture was filtered, washed with MeOH, and evaporated *in vacuo* to generate product **3a**, as a diastereomeric mixture, in > 95% NMR yield.

*l. Substrates Syntheses, Isolations and Characterizations*

*i. C-Glycosidic Aromatic Enones **2a-h***



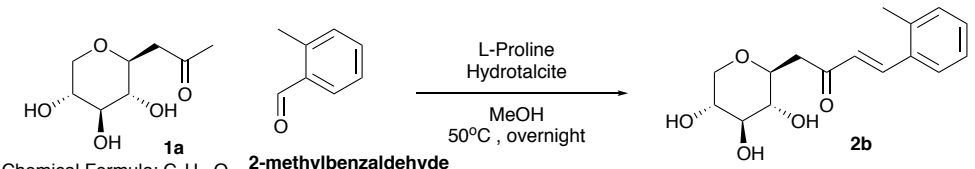

**1a**
Chemical Formula: $C_8H_{14}O_5$
Exact Mass: 190.08412

**2a**
Chemical Formula: $C_{15}H_{18}O_5$
Exact Mass: 278.11542

**2a** was synthesized following general procedure A with Octulose **1a** (1125 mg, 5.918 mmol), benzaldehyde (0.85 mL, 921.1 mg, 8.68 mmol), L-Proline (908.5 mg, 7.891 mmol), biphenyl (61.4 mg, internal standard) and MgO (150 mg) in methanol (17.5 mL). Crude product was isolated from internal standard, L-proline and excess aldehyde by short path silica plug (EtOAc, then acetone) to obtain **2a** as an off-white solid in 85 % isolated yield.

**$R_f$** = 0.32 (silica gel, 8:1 DCM:MeOH); **$^1$H NMR** (400 MHz, Methanol-*$d_4$*) δ 7.65 – 7.56 (m, 3H), 7.42 – 7.33 (m, 3H), 6.84 (d, *J* = 16.3 Hz, 1H), 3.77 (dd, *J* = 11.1, 5.4 Hz, 1H), 3.64 (t, *J* = 9.4, 1H), 3.42 (dd, *J* = 10.5, 8.9, 1H), 3.27 (t, *J* = 3.2, 1H), 3.17 – 3.02 (m, 3H), 2.84 (dd, *J* = 15.8, 9.2 Hz, 1H); **$^{13}$C NMR** (151 MHz, Methanol-*$d_4$*) δ 199.98, 143.97, 135.11, 130.85, 129.19, 128.67, 126.66, 78.95, 77.65, 74.31, 70.67, 70.18, 43.36. **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{15}H_{19}O_5$ $[M+H]^+$ 279.12325 Found 279.12345.

Analytical data is identical to that reported in the literature.[6]



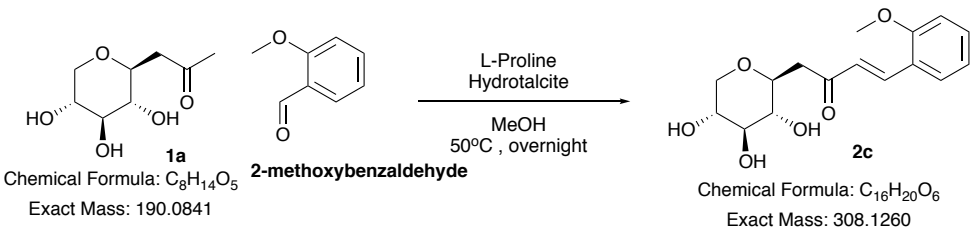

**1a**
Chemical Formula: $C_8H_{14}O_5$
Exact Mass: 190.08412

**2b**
Chemical Formula: $C_{16}H_{20}O_5$
Exact Mass: 292.13107

**2b** was synthesized following general procedure A with Octulose **1a** (324.9 mg, 1.710 mmol), 2-methylbenzaldehyde (0.34 mL, 347.23 mg, 2.89 mmol), L-Proline (302.8 mg, 2.63 mmol), biphenyl (23.6 mg, 0.123 mmol) and MgO (50 mg) in methanol (5.8 mL). Crude product was isolated from internal standard, L-proline and excess aldehyde by short path silica plug (Ethyl acetate, then acetone) to obtain **2b** as a yellow oil in 86 % isolated yield.

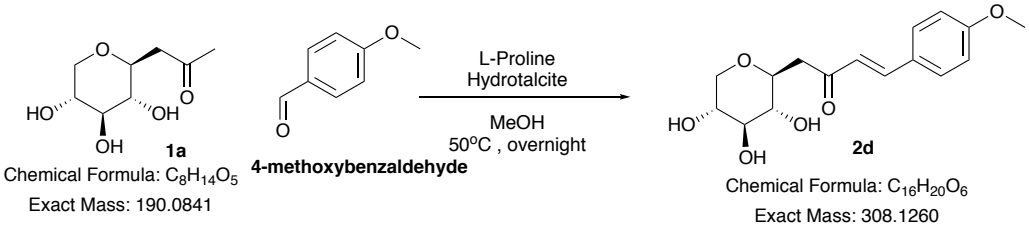
**$R_f$** = 0.36 (silica gel, 8:1 DCM:MeOH); **$^1$H NMR** (400 MHz, Methanol-*$d_4$*) δ 7.93 (d, *J* = 16.0 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.34 – 7.24 (m, 1H), 7.24 – 7.11 (m, 2H), 6.77 (d, *J* = 16.0 Hz, 1H), 3.80 (dd, *J* = 11.1, 5.4 Hz, 1H), 3.66 (td, *J* = 9.4, 2.5 Hz, 1H), 3.49 – 3.40 (m, 1H), 3.33 – 3.24 (m, 1H), 3.19 –

3.05 (m, 3H), 2.84 (dd, *J* = 15.8, 9.2 Hz, 1H), 2.42 (s, 3H). **$^{13}$C NMR** (101 MHz, $cd_3od$) δ 199.43, 140.75, 137.97, 133.17, 130.43, 130.06, 126.92, 126.09, 126.01, 78.34, 77.13, 73.69, 70.07, 69.61, 43.09, 18.29. **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{16}H_{21}O_5$ $[M+H]^+$ 293.13890 Found 293.13829.




**2c** was synthesized following general procedure A with Octulose **1a** (349.9 mg, 1.841mmol), 2-methoxybenzaldehyde (0.35 mL, 394 mg, 2.89 mmol), L-Proline (302.8 mg, 2.63 mmol), biphenyl (21.0 mg, 0.136 mmol, internal standard) and MgO (50 mg) in methanol (5.8 mL). Crude product was isolated from internal standard, L-proline and excess aldehyde by short path silica plug (Ethyl acetate, then acetone) to obtain **2c** as a brown solid in 77 % isolated yield.

**$R_f$** = 0.60 (silica gel, 8:1 DCM:MeOH); **$^1$H NMR** (400 MHz, Methanol-$d_4$) δ 7.94 (d, *J* = 16.4 Hz, 1H), 7.61 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.38 (ddd, *J* = 8.8, 7.4, 1.7 Hz, 1H), 7.03 (dd, *J* = 8.5, 1.0 Hz, 1H), 6.96 (td, *J* = 7.5, 1.0 Hz, 1H), 6.89 (d, *J* = 16.3 Hz, 1H), 3.89 (s, 3H), 3.83 – 3.75 (m, 2H), 3.66 (td, *J* = 9.4, 2.5 Hz, 1H), 3.44 (ddd, *J* = 10.6, 9.0, 5.4 Hz, 1H), 3.20 – 3.02 (m, 3H), 2.82 (dd, *J* = 15.9, 9.3 Hz, 1H). **$^{13}$C NMR** (101 MHz, $cd_3od$) δ 199.78, 158.65, 138.52, 131.86, 128.16, 126.18, 122.92, 120.43, 111.02, 78.34, 77.05, 73.70, 70.08, 69.59, 54.68, 42.76. **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{16}H_{21}O_6$ $[M+H]^+$ 309.13381 Found 309.13310.

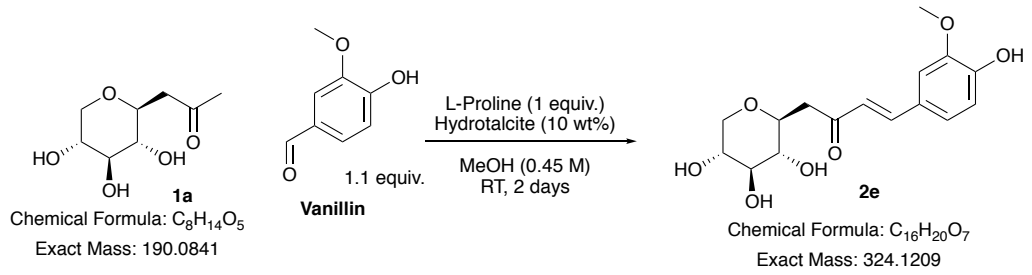



**2d** was synthesized following general procedure A with Octulose **1a** (349.9 mg, 1.841 mmol), 4-methoxybenzaldehyde (0.35 mL, 394 mg, 2.89 mmol), L-Proline (302.8 mg, 2.63 mmol), biphenyl (20.3 mg, 0.132 mmol, internal standard) and MgO (50 mg) in methanol (5.8 mL). Crude product

was isolated from internal standard, L-proline and excess aldehyde by short path silica plug (Ethyl acetate, then acetone) to obtain **2d** as an off-white solid in 79 % isolated yield.

**$R_f$** = 0.34 (silica gel, 8:1 DCM:MeOH); **$^1$H NMR** (400 MHz, Methanol-*$d_4$*) δ 7.64 – 7.52 (m, 3H), 6.94 (dd, *J* = 9.1, 2.5 Hz, 2H), 6.72 (d, *J* = 16.1, 1H), 3.83 – 3.71 (m, 4H), 3.64 (td, *J* = 9.4, 2.5 Hz, 1H), 3.53 – 3.40 (m, 1H), 3.30 – 3.21 (m, 1H), 3.19 – 2.98 (m, 3H), 2.87 – 2.73 (m, 1H); **$^{13}$C NMR** (151 MHz, Methanol-*$d_4$*) δ 199.75, 162.17, 143.79, 130.21, 127.19, 123.98, 114.31, 78.61, 77.37, 73.97, 70.32, 69.80, 54.74, 42.89. **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{16}H_{21}O_6$ $[M+H]^+$ 309.13381 Found 309.13324.

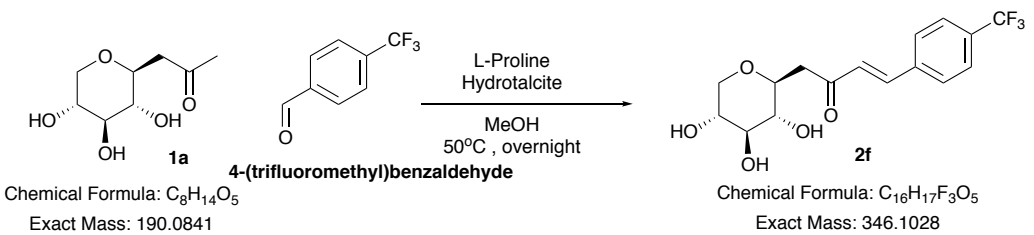
Analytical data is identical to that reported in the literature.[7]




**2e** was synthesized following general procedure A with Octulose **1a** (1500 mg, 7.891 mmol, 1 equiv.), vanillin (1320.2 mg, 8.68 mmol, 1.1 equiv.), L-Proline (908.5 mg, 7.891 mmol, 1 equiv.) and HTC (150 mg, 10 wt%) in methanol (17.5 mL). Pure product precipitated out of the reaction mixture and was filtered to obtain **2e** as an off-white solid in 63 % isolated yield.

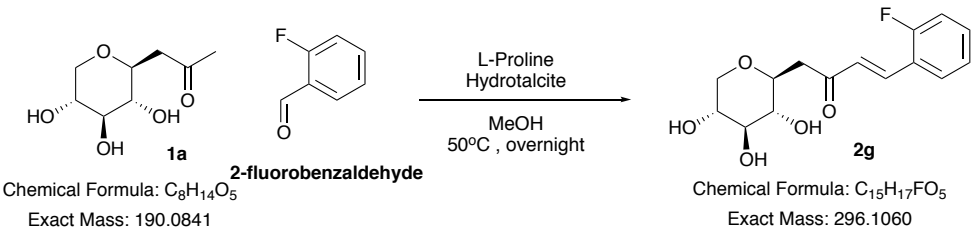
**$R_f$** = 0.24 (silica gel, 8:1 DCM:MeOH); **$^1$H NMR** (400 MHz, Methanol-*$d_4$*) δ 7.57 (d, *J* = 16.1 Hz, 1H), 7.21 (d, *J* = 1.9 Hz, 1H), 7.11 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 6.71 (d, *J* = 16.1 Hz, 1H), 3.88 (s, 3H), 3.79 (dd, *J* = 11.1, 5.4 Hz, 1H), 3.65 (td, *J* = 9.4, 2.6 Hz, 1H), 3.44 (ddd, *J* = 10.5, 8.9, 5.3 Hz, 1H), 3.29 (p, *J* = 1.6 Hz, 1H), 3.17 – 3.00 (m, 3H), 2.82 (dd, *J* = 15.7, 9.3 Hz, 1H). **$^{13}$C NMR** (101 MHz, $cd_3od$) δ 199.58, 147.98, 144.38, 126.30, 123.26, 123.13, 115.11, 110.42, 78.36, 77.20, 73.76, 70.08, 69.58, 54.97, 42.58. **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{16}H_{21}O_7$ $[M+H]^+$ 325.12873 Found 325.12751.

Analytical data is identical to that reported in the literature.[7]




**2f** was synthesized following general procedure A with Octulose **1a** (624.9 mg, 3.285 mmol), 4-trifluoromethylbenzaldehyde (0.67 mL, 854.3 mg, 4.906 mmol), L-Proline (506.6 mg, 4.400 mmol), biphenyl (19.8 mg, 0.128 mmol, internal standard) and MgO (50 mg) in methanol (9.8 mL). Crude product was isolated from internal standard, L-proline and excess aldehyde by short path silica plug (Ethyl acetate, then acetone) to obtain **2f** as a brown solid in 71 % isolated yield.

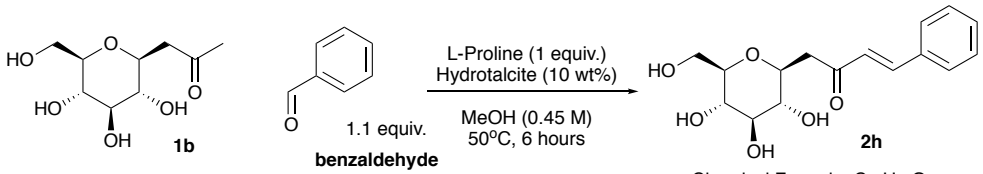
**$R_f$** = 0.37 (silica gel, 8:1 DCM:MeOH); **$^1$H NMR** (400 MHz, Methanol-$d_4$) δ 7.81 (d, *J* = 8.1 Hz, 2H), 7.72 – 7.61 (m, 3H), 6.97 (d, *J* = 16.3 Hz, 1H), 3.79 (dd, *J* = 11.1, 5.4 Hz, 1H), 3.67 (td, *J* = 9.4, 2.7 Hz, 1H), 3.44 (ddd, *J* = 10.5, 8.9, 5.4 Hz, 1H), 3.20 – 3.05 (m, 4H), 2.87 (dd, *J* = 15.9, 9.2 Hz, 1H). **$^{13}$C NMR** (151 MHz, cd$_3$od) δ 199.01, 141.04, 138.41, 138.40, 128.51, 131.61, 131.39, 131.18, 130.96, 128.48, 125.48, 125.44, 125.41, 125.39, 78.35, 76.98, 73.70, 70.07, 69.60, 43.01. **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{16}H_{18}F_3O_5$ $[M+H]^+$ 347.11063 Found 347.10976.




**2g** was synthesized following general procedure A with Octulose **1a** (500 mg, 2.63 mmol), 2-fluorobenzaldehyde (0.45 mL, 530.1 mg, 4.271 mmol), L-Proline (455 mg, 3.952 mmol), biphenyl (19.9 mg, 0.128 mmol, internal standard) and MgO (75 mg) in methanol (8.8 mL). Crude product was isolated from internal standard, L-proline and excess aldehyde by short path silica plug (Ethyl acetate, then acetone) to obtain **2g** as a yellow solid in 93 % isolated yield.

**$R_f$** = 0.37 (silica gel, 8:1 DCM:MeOH); **$^1$H NMR** (400 MHz, Methanol-$d_4$) δ 7.76 – 7.68 (m, 2H), 7.43 (dddd, *J* = 8.5, 7.2, 5.3, 1.7 Hz, 1H), 7.25 – 7.11 (m, 2H), 6.94 (d, *J* = 16.3 Hz, 1H), 3.79 (dd, *J* = 11.1, 5.4 Hz, 1H), 3.66 (td, *J* = 9.4, 2.6 Hz, 1H), 3.44 (ddd, *J* = 10.5, 8.9, 5.4 Hz, 1H), 3.29 (dt, *J* = 3.1, 1.5

Hz, 1H), 3.17 – 3.04 (m, 3H), 2.83 (dd, *J* = 15.9, 9.2 Hz, 1H).**$^{13}$C NMR** (151 MHz, $cd_3od$) δ 199.14, 162.30, 160.63, 135.03, 135.01, 132.07, 132.01, 128.76, 128.74, 128.21, 128.17, 124.49, 124.47, 122.31, 122.24, 115.72, 115.58, 78.33, 76.99, 73.67, 70.06, 69.59, 43.09. **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{15}H_{18}FO_5$ $[M+H]^+$ 297.11383 Found 297.11360.

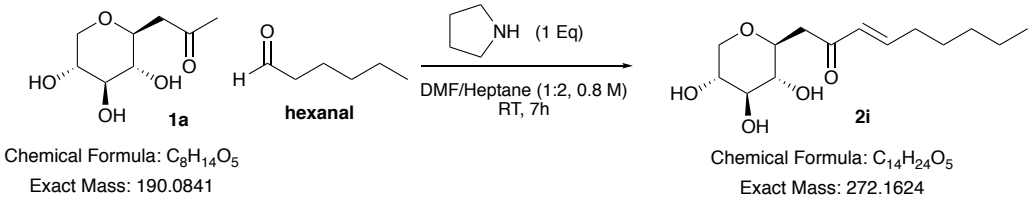



**2h** was synthesized following general procedure A with Nonulose **1b** (106.3 mg, 0.483 mmol), benzaldehyde (0.23 mL, 235 mg, 2.21 mmol), L-Proline (232 mg, 2.01 mmol), biphenyl (16.4 mg, 0.106 mmol, internal standard) and MgO (50 mg) in methanol (4.5 mL). Crude product was isolated from internal standard, L-proline and excess aldehyde by short path silica plug (Ethyl acetate, then acetone) to obtain **2h** as a beige powder in 66 % isolated yield.

**$R_f$** = 0.18 (silica gel, 9:1 DCM:MeOH); **$^1$H NMR** (400 MHz, Methanol-$d_4$) δ 7.67 – 7.61 (m, 3H), 7.42 – 7.37 (m, 3H), 6.90 (d, *J* = 16.2 Hz, 1H), 3.80 – 3.71 (m, 2H), 3.64 – 3.58 (m, 1H), 3.38 – 3.31 (m, 2H), 3.21 (ddd, *J* = 9.3, 5.1, 2.3 Hz, 1H), 3.18 – 3.06 (m, 2H), 2.89 (dd, *J* = 15.9, 8.9 Hz, 1H). **$^{13}$C NMR** (101 MHz, $cd_3od$) δ 199.56, 143.40, 134.56, 130.24, 128.59, 128.10, 126.03, 80.19, 78.29, 76.03, 73.70, 70.24, 61.3, 42.92.

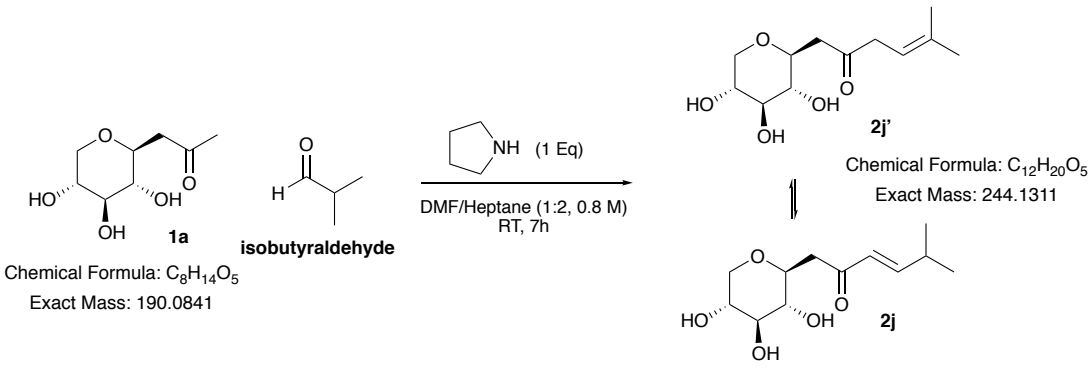
Analytical data is identical to that reported in the literature.[4]

*ii. Aliphatic C-glycosidic Enones **2i-j***



**2i** was synthesized following general procedure B with Octulose **1a** (1000 mg, 5.26 mmol, 1 equiv.), pyrrolidine (0.44 mL, 374.1 mg, 5.26 mmol, 1 equiv.) and hexanal (0.64 mL, 526.8 mg, 5.26 mmol, 1 equiv.) in hexanes (2.68 mL) and DMF (2.2 mL) at room temperature overnight. The crude mixture was purified by column chromatography (silica gel, DCM:MeOH, 450:50) to afford **2i** as an orange oil in 36 % yield.

**$R_f$** = 0.43 (silica gel, 8:1 DCM:MeOH); **$^1$H NMR** (400 MHz, Methanol-$d_4$) δ 6.91 (dt, *J* = 15.8, 7.0 Hz, 1H), 6.13 (dt, *J* = 15.9, 1.5 Hz, 1H), 3.76 (dd, *J* = 11.1, 5.4 Hz, 1H), 3.58 (td, *J* = 9.4, 2.5 Hz, 1H), 3.42 (ddd, *J* = 10.6, 8.9, 5.4 Hz, 1H), 3.31 – 3.21 (m, 1H), 3.14 – 3.02 (m, 2H), 2.99 – 2.89 (m, 1H), 2.71 (dd, *J* = 15.9, 9.3 Hz, 1H), 2.28 – 2.19 (m, 2H), 1.54 – 1.43 (m, 2H), 1.42 – 1.23 (m, 4H), 0.97 – 0.85 (m, 3H). **$^{13}$C NMR** (101 MHz, $cd_3od$) δ 201.24, 150.63, 131.87, 79.99, 78.59, 75.30, 71.71, 71.21, 43.61, 33.74, 32.74, 29.12, 23.71, 14.54. **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{14}H_{25}O_5$ $[M+H]^+$ 273.17020 Found 273.16922.

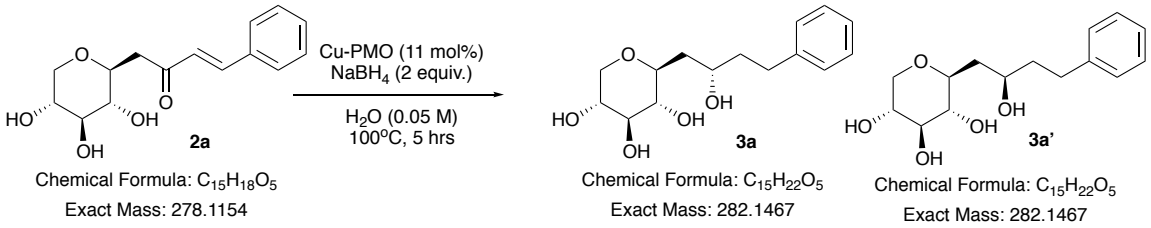



**2j** was synthesized following general procedure B with Octulose **1a** (250 mg, 1.315 mmol, 1 equiv.), pyrrolidine (0.11 mL, 93.5 mg, 1.315 mmol, 1 equiv.) and isobutyraldehyde (0.12 mL, 94.8 mg, 1.315 mmol, 1 equiv.) in heptane (0.66 mL) and DMF (0.55 mL) at room temperature overnight. The crude mixture was purified by column chromatography (silica gel, DCM:MeOH, 450:50) to afford **2j** (mixture of trans isomer **2j** and deconjugated isomer **2j'**) as an orange oil in 70% yield. **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{12}H_{21}O_5$ $[M+H]^+$ 245.13890 Found 245.13824.

**2j: $R_f$** = 0.5 (silica gel, 8:1 DCM:MeOH); **$^1$H NMR** (400 MHz, Methanol-$d_4$) δ 6.87 (dd, *J* = 16.0, 6.8 Hz, 1H), 6.09 (dd, *J* = 16.0, 1.4 Hz, 1H), 3.77 (dt, *J* = 11.1, 5.5 Hz, 1H), 3.57 (dtd, *J* = 14.5, 9.4, 2.7 Hz, 1H), 3.41 (dddd, *J* = 10.7, 8.9, 5.4, 1.9 Hz, 1H), 3.24 (dt, *J* = 8.9, 4.5 Hz, 1H), 3.08 (m, 2H), 2.94 (dd, *J* = 16.0, 2.5 Hz, 1H), 2.72 (dd, *J* = 16.0, 9.3 Hz, 1H), 2.59 – 2.42 (m, 1H), 1.07 (d, *J* = 6.8 Hz, 6H). **$^{13}$C NMR** (101 MHz, $cd_3od$) δ 201.26, 156.10, 128.85, 79.77, 78.29, 75.07, 71.48, 70.99, 43.49, 32.44, 21.62.

**2j': $R_f$** = 0.5 (silica gel, 8:1 DCM:MeOH); **$^1$H NMR** (400 MHz, Methanol-*d*$_4$) δ 5.26 (dddd, *J* = 8.6, 7.2, 2.9, 1.5 Hz, 1H), 3.77 (dt, *J* = 11.1, 5.5 Hz, 1H), 3.57 (dtd, *J* = 14.5, 9.4, 2.7 Hz, 1H), 3.41 (dddd, *J* = 10.7, 8.9, 5.4, 1.9 Hz, 1H), 3.17 (d, *J* = 7.3 Hz, 2H), 3.08 (m, 2H) 2.83 (dd, *J* = 15.9, 2.9 Hz, 1H), 2.59 – 2.42 (m, 1H), 1.67 (dd, *J* = 46.4, 1.4 Hz, 6H). **$^{13}$C NMR** (101 MHz, cd$_3$od) δ 210.04, 136.69, 117.02, 79.71, 78.18, 75.05, 71.46, 70.97, 45.83, 44.04, 25.83, 18.08.

*iii. C-Glycosidic Alcohols **3a-j** and **3a'-j'***



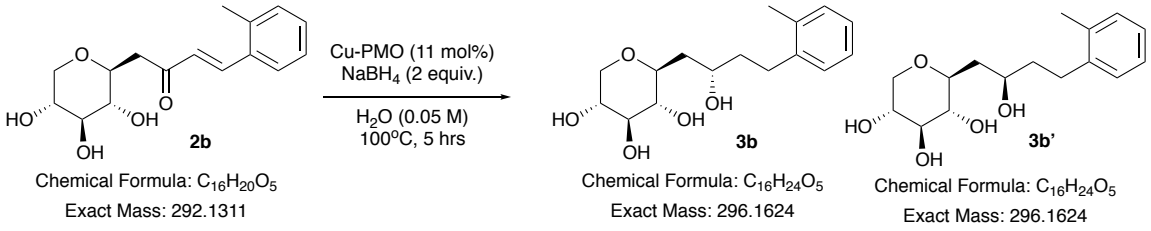

**3a** and **3a'** were synthesized following general procedure C with **2a** (139.2 mg, 0.5 mmol, 1 equiv.), Cu-PMO (16.5 mg, 11 mol%) and $NaBH_4$ (37.8 mg, 1.0 mmol, 2 equiv.) in $H_2O$ (10 mL) at reflux for 5 hours. The mixture containing only **3a** and **3a'** was fully dissolved in MeOD and an internal standard ($CHCl_3$, 40 µL, 1 equiv.) was added to obtain the NMR yield. Boron NMR was measured to verify the absence of boron salts in the crude mixture. After evaporation *in vacuo*, the product was weighed to show 89% isolated yield. The diastereomers were separated by column chromatography (silica gel, DCM:MeOH, 450:50) to afford **3a** and **3a'** as clear oils in 10% yield for each.

Mixture **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{15}H_{23}O_5$ $[M+H]^+$ 283.15455 Found 283.15364.

**3a $R_f$ =** 0.6 (silica gel, 8:1 DCM:MeOH, developed with CAM); **$^1$H NMR** (400 MHz, Methanol-*d*$_4$) δ 7.26 – 7.15 (m, 5H), 3.82 (dd, *J* = 11.1, 5.6 Hz, 3H), 3.51 – 3.37 (m, 1H), 3.37 – 2.95 (m, 2H), 2.76 (ddd, *J* = 15.1, 10.0, 5.3 Hz, 2H), 2.62 (ddd, *J* = 13.6, 9.8, 6.5 Hz, 2H), 2.01 (ddd, *J* = 14.4, 5.9, 2.8 Hz, 1H), 1.78 (dddd, *J* = 14.1, 10.4, 6.4, 4.1 Hz, 1H), 1.59 (ddd, *J* = 15.0, 9.0, 6.6 Hz, 1H); **$^{13}$C NMR** (101 MHz, Methanol-*d*$_4$) δ 142.25, 128.00, 127.89, 125.26, 78.95, 78.30, 74.37, 70.02, 69.49, 68.71, 39.19, 38.42, 31.36. **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{15}H_{22}O_5$ $[M+H]^+$ 283.15455 Found 283.15347.

**3a' $R_f$ =** 0.49 (silica gel, 8:1 DCM:MeOH, developed with CAM); **$^1$H NMR** (400 MHz, Methanol-*d*$_4$) 7.22 (t, *J* = 7.5 Hz, 2H), 7.17 (d, *J* = 6.7 Hz, 2H), 7.14 – 7.07 (m, 1H), 3.87 – 3.70 (m, 2H), 3.43 (ddd,

*J* = 11.0, 9.0, 5.4 Hz, 1H), 3.38 – 3.20 (m, 2H), 3.12 (t, *J* = 10.9 Hz, 1H), 3.00 (t, *J* = 9.1 Hz, 1H), 2.80 – 2.54 (m, 2H), 1.92 (ddd, *J* = 14.8, 9.9, 2.3 Hz, 1H), 1.76 – 1.66 (m, 2H), 1.45 (ddd, *J* = 14.7, 9.6, 2.5 Hz, 1H); **$^{13}$C NMR** (101 MHz, Methanol-*d*$_4$) 142.25, 127.99, 127.87, 125.24, 78.49, 77.21, 74.33, 70.21, 69.48, 66.67, 39.73, 39.67, 31.65. **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{15}H_{22}O_5$ $[M+H]^+$ 283.15455 Found 283.15411.



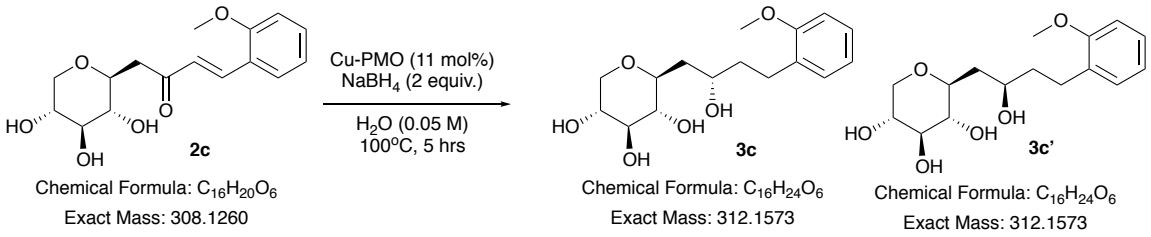

**3b** and **3b'** were synthesized following general procedure C with **2b** (146.2 mg, 0.5 mmol, 1 equiv.), Cu-PMO (16.5 mg, 11 mol%) and $NaBH_4$ (37.8 mg, 1.0 mmol, 2 equiv.) in $H_2O$ (10 mL) at reflux for 5 hours. The crude mixture containing only **3b** and **3b'** was fully dissolved in MeOD and an internal standard ($CHCl_3$, 40 µL, 1 equiv.) was added to obtain the NMR yield. Boron NMR was measured to verify the absence of boron salts in the crude mixture. After evaporation *in vacuo*, the product was weighed to show quantitative yield. The diastereomers were separated by column chromatography (silica gel, DCM:MeOH, 450:50) to afford **3b** and **3b'** as clear oils in 17.6 % and 4.5 %, respectively.

Mixture **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{16}H_{25}O_5$ $[M+H]^+$ 297.17020 Found 297.16939.

**3b** $R_f$ = 0.32 (silica gel, 8:1 DCM:MeOH); **$^1$H NMR** (400 MHz, Methanol-*d*$_4$) δ 7.05 (dqd, *J* = 19.4, 8.0, 7.2, 3.8 Hz, 4H), 3.84 (td, *J* = 11.3, 5.9 Hz, 2H), 3.43 (ddd, *J* = 10.5, 8.8, 5.3 Hz, 1H), 3.27 – 3.16 (m, 2H), 3.15 – 2.99 (m, 2H), 2.76 (ddd, *J* = 14.0, 10.6, 5.2 Hz, 1H), 2.61 (ddd, *J* = 13.8, 10.5, 6.0 Hz, 1H), 2.37 – 2.30 (m, 1H), 2.28 (s, 3H), 2.02 (ddd, *J* = 14.4, 6.0, 2.8 Hz, 1H), 1.72 (tdd, *J* = 14.9, 7.2, 4.1 Hz, 1H), 1.61 (ddt, *J* = 17.9, 9.4, 6.5 Hz, 2H). **$^{13}$C NMR** (101 MHz, cd$_3$od) δ 140.28, 135.40, 129.62, 128.39, 125.51, 125.41, 78.94, 78.29, 74.37, 70.02, 69.51, 69.01, 39.14, 37.09, 28.72, 17.95. **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{16}H_{23}O_5Na$ $[M+Na]^+$ 319.15214 Found 319.13670.

**3b'** $R_f$ = 0.23 (silica gel, 8:1 DCM:MeOH); **$^1$H NMR** (400 MHz, Methanol-*d*$_4$) δ 7.12 – 6.99 (m, 4H), 3.82 (dddd, *J* = 14.6, 9.1, 6.6, 3.6 Hz, 2H), 3.44 (dddd, *J* = 12.7, 7.7, 5.4, 2.3 Hz, 1H), 3.38 – 3.06 (m, 4H), 3.05 – 2.97 (m, 1H), 2.75 (dt, *J* = 13.7, 8.2 Hz, 1H), 2.61 (dt, *J* = 13.6, 8.0 Hz, 1H), 2.31 (d, *J* = 2.7 Hz, 1H), 2.28 (s, 3H), 2.00 – 1.87 (m, 1H), 1.70 – 1.58 (m, 2H), 1.47 (ddd, *J* = 14.4, 9.7, 2.6 Hz,

1H).**$^{13}$C NMR** (101 MHz, $cd_3od$) δ 140.26, 135.38, 129.64, 128.43, 125.53, 125.43, 78.44, 77.17, 74.32, 70.20, 69.48, 66.98, 39.63, 38.47, 29.01, 17.97. **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{16}H_{24}O_5$ $[M+H]^+$ 297.17020 Found 297.17004.



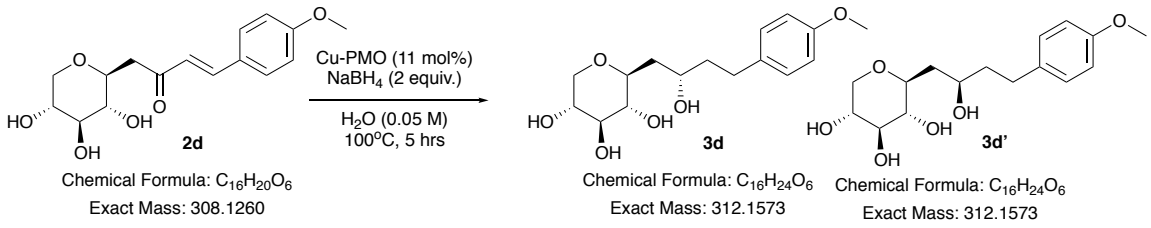

**3c** and **3c'** were synthesized following general procedure C with **2c** (154.2 mg, 0.5 mmol, 1 equiv.), Cu-PMO (16.5 mg, 11 mol%) and $NaBH_4$ (37.8 mg, 1.0 mmol, 2 equiv.) in $H_2O$ (10 mL) at reflux for 5 hours. The mixture containing only **3c** and **3c'** was fully dissolved in MeOD and an internal standard ($CHCl_3$, 40 µL, 1 equiv.) was added to obtain the NMR yield. Boron NMR was measured to verify the absence of boron salts in the crude mixture. After evaporation *in vacuo*, the product was weighed to show quantitative yield. The diastereomers were separated by column chromatography (silica gel, DCM:MeOH, 450:50) to afford **3c** and **3c'** as clear oils in 22 % and 35 % yield, respectively.

Mixture **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{16}H_{25}O_6$ $[M+H]^+$ 313.16511 Found 313.16422.

**3c $R_f$** = 0.41 (silica gel, 8:1 DCM:MeOH); **$^1$H NMR** (400 MHz, Methanol-$d_4$) δ 7.15 – 7.06 (m, 2H), 6.89 – 6.84 (m, 1H), 6.81 (td, *J* = 7.4, 1.1 Hz, 1H), 3.85 – 3.74 (m, 5H), 3.43 (ddd, *J* = 10.6, 8.9, 5.4 Hz, 1H), 3.27 – 3.14 (m, 2H), 3.06 (dt, *J* = 17.3, 10.0 Hz, 2H), 2.75 (ddd, *J* = 13.5, 10.1, 5.4 Hz, 1H), 2.60 (ddd, *J* = 13.4, 9.9, 6.2 Hz, 1H), 2.01 (ddd, *J* = 14.3, 5.8, 2.9 Hz, 1H), 1.75 (dddd, *J* = 14.2, 10.4, 6.2, 4.4 Hz, 1H), 1.68 – 1.51 (m, 2H). **$^{13}$C NMR** (101 MHz, $cd_3od$) δ 157.43, 130.27, 129.40, 126.68, 120.00, 109.94, 79.05, 78.30, 74.38, 70.02, 69.51, 69.14, 54.28, 39.08, 36.61, 25.98. **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{16}H_{24}O_6$ $[M+H]^+$ 313.16511 Found 313.14989.

**3c' $R_f$** = 0.38 (silica gel, 8:1 DCM:MeOH); **$^1$H NMR** (400 MHz, Methanol-$d_4$) δ 7.16 – 7.05 (m, 2H), 6.88 – 6.84 (m, 1H), 6.81 (td, *J* = 7.4, 1.1 Hz, 1H), 3.86 – 3.73 (m, 5H), 3.44 (ddd, *J* = 10.6, 8.9, 5.4 Hz, 1H), 3.37 – 3.20 (m, 2H), 3.13 (t, *J* = 10.8 Hz, 1H), 3.06 – 2.96 (m, 1H), 2.78 – 2.66 (m, 1H), 2.60 (dt, *J* = 13.5, 7.7 Hz, 1H), 1.91 (ddd, *J* = 14.5, 10.0, 2.4 Hz, 1H), 1.73 – 1.60 (m, 2H), 1.47 (ddd, *J* = 14.5, 9.7, 2.5 Hz, 1H). **$^{13}$C NMR** (101 MHz, $cd_3od$) δ 157.40, 130.25, 129.40, 126.68, 120.00, 109.94,

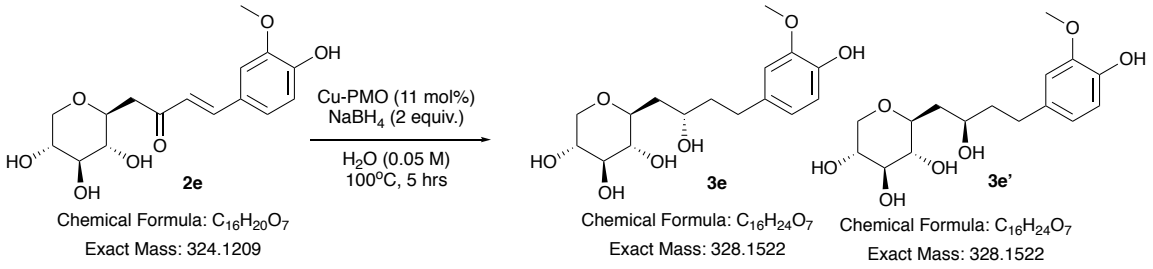
78.48, 77.21, 74.36, 70.21, 69.47, 67.04, 54.28, 39.59, 37.99, 26.24. **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{16}H_{24}O_6$ $[M+H]^+$ 313.16511 Found 313.16446.




**3d** and **3d'** were synthesized following general procedure C with **2d** (308.33 mg, 1.0 mmol, 1 equiv.), Cu-PMO (33 mg, 11 mol%) and $NaBH_4$ (75.6 mg, 2.0 mmol, 2 equiv.) in $H_2O$ (20 mL) at reflux for 5 hours. The crude mixture containing only **3d** and **3d'** was fully dissolved in MeOD and an internal standard ($CHCl_3$, 80 µL, 1 equiv.) was added to obtain the NMR yield. Boron NMR was measured to verify the absence of boron salts in the crude mixture. After evaporation *in vacuo*, the product was weighed to show quantitative yield. The diastereomers were separated by column chromatography (silica gel, DCM:MeOH, 450:50) to afford **3d** and **3d'** as clear oils in 14% and 30% yield, respectively. Mixture **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{16}H_{25}O_6$ $[M+H]^+$ 313.16511 Found 313.16428.

**3d** $R_f$ = 0.55 (silica gel, 8:1 DCM:MeOH); **$^1$H NMR** (400 MHz, Methanol-$d_4$) δ 7.11 – 7.06 (m, 2H), 6.82 – 6.76 (m, 2H), 3.80 (ddd, *J* = 13.7, 10.3, 4.3 Hz, 2H), 3.73 (s, 3H), 3.42 (ddd, *J* = 10.5, 9.0, 5.4 Hz, 1H), 3.25 – 3.15 (m, 2H), 3.10 (d, *J* = 10.9 Hz, 1H), 3.08 – 2.98 (m, 1H), 2.69 (ddd, *J* = 13.7, 10.0, 5.3 Hz, 1H), 2.56 (ddd, *J* = 13.7, 9.8, 6.5 Hz, 1H), 1.99 (ddd, *J* = 14.4, 5.9, 2.8 Hz, 1H), 1.81 – 1.53 (m, 3H). **$^{13}$C NMR** (101 MHz, $cd_3od$) δ 157.80, 134.18, 128.86, 113.29, 78.94, 78.26, 74.37, 70.01, 69.49, 68.63, 54.18, 39.20, 38.58, 30.42. **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{16}H_{24}O_6$ $[M+H]^+$ 313.16511 Found 313.16445.

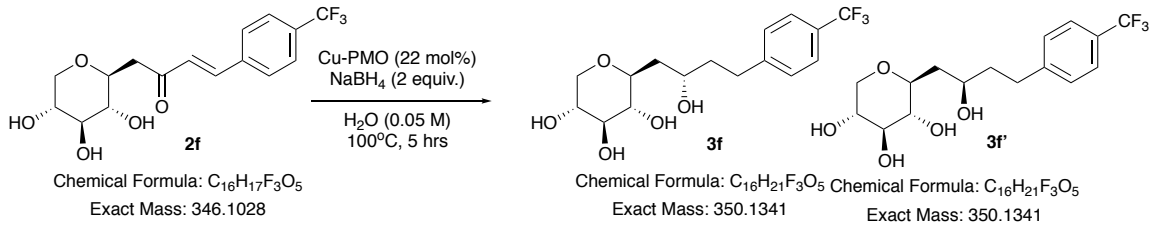
**3d'** $R_f$ = 0.45 (silica gel, 8:1 DCM:MeOH); **$^1$H NMR** (400 MHz, Methanol-$d_4$) δ 7.12 – 7.02 (m, 2H), 6.86 – 6.73 (m, 2H), 3.88 – 3.73 (m, 2H), 3.43 (ddd, *J* = 10.5, 8.9, 5.4 Hz, 1H), 3.37 – 3.21 (m, 3H), 3.12 (t, *J* = 10.8 Hz, 1H), 3.00 (t, *J* = 9.1 Hz, 1H), 2.74 – 2.63 (m, 1H), 2.56 (dt, *J* = 13.8, 8.2 Hz, 1H), 1.99 – 1.82 (m, 1H), 1.67 (td, *J* = 8.1, 5.8 Hz, 2H), 1.44 (ddd, *J* = 14.5, 9.7, 2.6 Hz, 1H). **$^{13}$C NMR** (101 MHz, $cd_3od$) δ $^{13}$C NMR (101 MHz, $cd_3od$) δ 157.78, 134.18, 128.88, 113.30, 78.45, 77.15, 74.32, 70.20, 69.47, 66.53, 54.19, 39.94, 39.69, 30.73. **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{16}H_{24}O_6$ $[M+H]^+$ 313.16511 Found 313.16386.




**3e** and **3e'** were synthesized following general procedure C with **2e** (162.2 mg, 0.5 mmol, 1 equiv.), Cu-PMO (16.5 mg, 11 mol%) and $NaBH_4$ (37.8 mg, 1.0 mmol, 2 equiv.) in $H_2O$ (10 mL) at reflux for 5 hours. The crude mixture containing only **3e** and **3e'** was fully dissolved in MeOD and an internal standard ($CHCl_3$, 40 µL, 1 equiv.) was added to obtain the NMR yield. Boron NMR was measured to verify the absence of boron salts in the crude mixture. After evaporation *in vacuo*, the product was weighed to show 93 % isolated yield. Attempts to separate diastereomers by column chromatography (silica gel, 15:4:1 EtOAc:MeOH:$H_2O$), precipitation/recrystallization and preparatory thin layer chromatography (silica gel, 9:1 DCM:MeOH) were unsuccessful. Characterization data reported below is assessed from analysis of a mixture of **3e** and **3e'**. Mixture **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{16}H_{25}O_7$ $[M+H]^+$ 329.16003 Found 329.15889.

**3e** $R_f$ = 0.64 (silica gel, 15:4:1 EtOAc:MeOH:$H_2O$); **$^1$H NMR** (400 MHz, Methanol-$d_4$) δ 6.73 (dd, *J* = 3.3, 1.9 Hz, 1H), 6.68 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.60 (dt, *J* = 8.0, 2.0 Hz, 1H), 3.90 – 3.73 (m, 5H), 3.52 – 3.39 (m, 1H), 3.31 – 2.98 (m, 4H), 2.66 (ddt, *J* = 15.2, 10.1, 5.8 Hz, 1H), 2.53 (ddd, *J* = 13.8, 9.0, 6.9 Hz, 1H), 2.01 (ddd, *J* = 14.4, 5.8, 2.7 Hz, 1H), 1.81 – 1.53 (m, 3H). **$^{13}$C NMR** (101 MHz, $cd_3od$) δ 147.35, 143.93, 133.84, 120.36, 114.67, 111.74, 78.97, 77.18, 74.32, 70.01, 69.48, 68.71, 66.61, 54.93, 39.19, 38.63, 30.94.

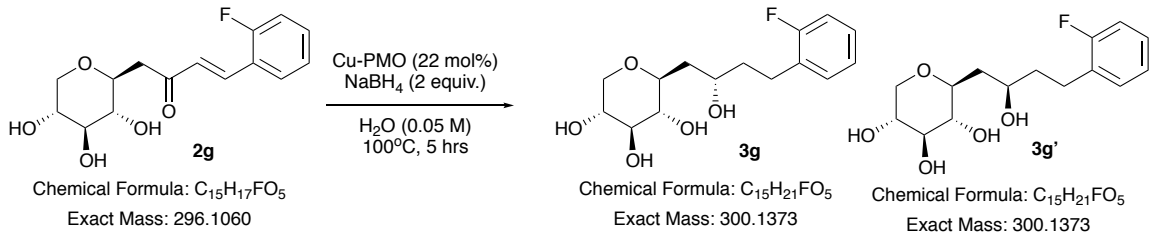
**3e'** $R_f$ = 0.64 (silica gel, 15:4:1 EtOAc:MeOH:$H_2O$); **$^1$H NMR** (400 MHz, Methanol-$d_4$) δ 6.73 (dd, *J* = 3.3, 1.9 Hz, 1H), 6.68 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.60 (dt, *J* = 8.0, 2.0 Hz, 1H), 3.90 – 3.73 (m, 5H), 3.52 – 3.39 (m, 1H), 3.31 – 2.98 (m, 4H), 2.66 (ddt, *J* = 15.2, 10.1, 5.8 Hz, 1H), 2.53 (ddd, *J* = 13.8, 9.0, 6.9 Hz, 1H), 1.96 – 1.86 (m, 1H), 1.81 – 1.53 (m, 2H), 1.47 (ddd, *J* = 14.7, 9.7, 2.5 Hz, 1H). **$^{13}$C NMR** (101 MHz, $cd_3od$) δ 147.34, 143.93, 133.84, 120.36, 114.67, 111.72, 78.45, 78.26, 74.36, 70.20, 69.48, 68.71, 54.95, 39.95, 39.65, 31.25.




**3f** and **3f'** were synthesized following general procedure C with **2f** (173.15 mg, 0.5 mmol, 1 equiv.), Cu-PMO (33 mg, 22 mol%) and $NaBH_4$ (37.8 mg, 1.0 mmol, 2 equiv.) in $H_2O$ (10 mL) at reflux for 5 hours. The crude mixture was fully dissolved in MeOD and an internal standard ($CHCl_3$, 40 µL, 1 equiv.) was added to obtain the NMR yield. Boron NMR was measured to verify the absence of boron salts in the crude mixture. After evaporation *in vacuo*, the product was weighed to show 87 % isolated yield. Diastereomers were separated by column chromatography (silica gel, DCM:MeOH, 450:50) to afford **3f** and **3f'** as clear oils in 44% and 18% yield, respectively. Mixture **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{16}H_{22}F_3O_5$ $[M+H]^+$ 351.14193 Found 351.14087

**3f** $R_f$ = 0.31 (silica gel, 8:1 DCM:MeOH); **$^1$H NMR** (600 MHz, Methanol-$d_4$) δ $^1$H NMR (600 MHz, Methanol-$d_4$) δ 7.56 – 7.53 (m, 2H), 7.41 – 7.36 (m, 2H), 3.87 – 3.77 (m, 2H), 3.42 (ddd, *J* = 10.6, 8.9, 5.4 Hz, 1H), 3.26 – 3.16 (m, 3H), 3.14 – 3.07 (m, 1H), 3.02 (dt, *J* = 11.9, 9.4 Hz, 1H), 2.86 (ddd, *J* = 14.7, 10.1, 5.0 Hz, 1H), 2.73 (ddd, *J* = 13.7, 10.1, 6.7 Hz, 1H), 2.06 – 1.95 (m, 1H), 1.88 – 1.78 (m, 1H), 1.70 (dddd, *J* = 13.6, 10.0, 8.4, 5.1 Hz, 1H), 1.60 (ddd, *J* = 14.3, 9.1, 6.4 Hz, 1H). **$^{13}$C NMR** (151 MHz, $cd_3od$) δ 147.06, 128.67, 124.78, 124.75, 124.73, 124.70, 78.76, 78.26, 74.37, 70.00, 69.48, 68.36, 39.20, 37.89, 31.15. **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{16}H_{22}F_3O_5$ $[M+H]^+$ 351.14193 Found 351.14106.

**3f'** $R_f$ = 0.38 (silica gel, 8:1 DCM:MeOH); **$^1$H NMR** (400 MHz, Methanol-$d_4$) δ 7.53 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 3.86 – 3.72 (m, 2H), 3.43 (ddd, *J* = 10.6, 9.0, 5.3 Hz, 1H), 3.37 – 3.19 (m, 2H), 3.18 – 3.07 (m, 1H), 3.00 (t, *J* = 9.1 Hz, 1H), 2.91 – 2.80 (m, 1H), 2.72 (dt, *J* = 13.8, 8.1 Hz, 1H), 1.94 (ddd, *J* = 14.5, 10.0, 2.4 Hz, 1H), 1.80 – 1.68 (m, 2H), 1.45 (ddd, *J* = 14.4, 9.8, 2.7 Hz, 1H). **$^{13}$C NMR** (101 MHz, $cd_3od$) δ 147.03, 128.68, 124.80, 124.77, 124.73, 124.69, 78.42, 77.09, 74.29, 70.18, 69.46, 66.40, 39.65, 39.24, 31.46. **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{16}H_{22}F_3O_5$ $[M+H]^+$ 351.14193 Found 351.14075.



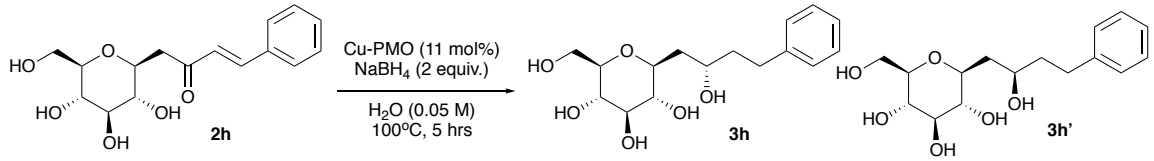

Chemical Formula: $C_{15}H_{17}FO_5$
Exact Mass: 296.1060

Chemical Formula: $C_{15}H_{21}FO_5$
Exact Mass: 300.1373

Chemical Formula: $C_{15}H_{21}FO_5$
Exact Mass: 300.1373

**3g** and **3g'** were synthesized following general procedure C with **2g** (173.15 mg, 0.5 mmol, 1 equiv.), Cu-PMO (33 mg, 22 mol%) and $NaBH_4$ (37.8 mg, 1.0 mmol, 2 equiv.) in $H_2O$ (10 mL) at reflux for 5 hours. The crude mixture containing **3g** and **3g'** was fully dissolved in MeOD and an internal standard ($CHCl_3$, 40 µL, 1 equiv.) was added to obtain the NMR yield. Boron NMR was measured to verify the absence of boron salts in the crude mixture. After evaporation *in vacuo*, the product was weighed to show 92% yield. The diastereomers were separated by column chromatography (silica gel, DCM:MeOH, 450:50) to afford **3g'** as a clear oil in 1% yield. Unfortunately, diastereomer **3g** could not be isolated separately from **3g'**. Further optimization of separation of the diastereomers is required. Mixture **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{15}H_{22}FO_5$ $[M+H]^+$ 301.14513 Found 301.14436.

**3g' $R_f$** = 0.52 (silica gel, 8:1 DCM:MeOH); **$^1$H NMR** (600 MHz, Methanol-$d_4$) δ 7.23 (td, *J* = 7.6, 1.8 Hz, 1H), 7.16 (tdt, *J* = 10.3, 7.0, 3.4 Hz, 1H), 7.05 (td, *J* = 7.5, 1.3 Hz, 1H), 6.99 (ddd, *J* = 9.8, 8.3, 1.2 Hz, 1H), 3.86 – 3.73 (m, 2H), 3.43 (ddd, *J* = 10.6, 9.0, 5.3 Hz, 1H), 3.35 – 3.30 (m, 1H), 3.25 (t, *J* = 8.9 Hz, 1H), 3.17 – 3.07 (m, 1H), 3.04 – 2.96 (m, 1H), 2.84 – 2.73 (m, 1H), 2.72 – 2.63 (m, 1H), 1.98 – 1.88 (m, 1H), 1.75 – 1.66 (m, 2H), 1.45 (ddd, *J* = 14.4, 9.8, 2.6 Hz, 1H). **$^{13}$C NMR** (151 MHz, $cd_3od$) δ 130.45, 130.41, 128.89, 128.79, 127.28, 127.22, 123.74, 123.71, 114.64, 114.49, 78.44, 77.10, 74.32, 70.20, 69.47, 66.65, 39.63, 38.18, 24.93, 24.91. **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{15}H_{22}FO_5$ $[M+H]^+$ 301.14513 Found 301.14439.




Chemical Formula: $C_{16}H_{20}O_6$
Exact Mass: 308.1260

Chemical Formula: $C_{16}H_{24}O_6$
Exact Mass: 312.1573

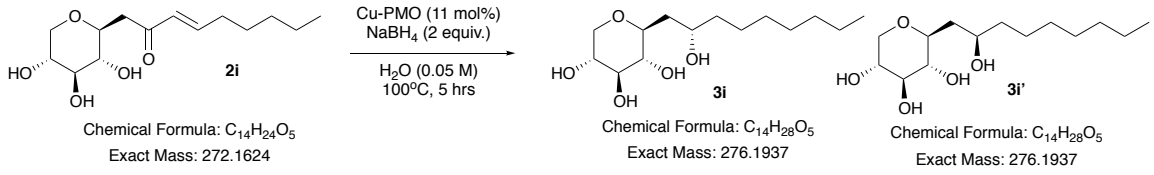
Chemical Formula: $C_{16}H_{24}O_6$
Exact Mass: 312.1573

**3h** and **3h'** were synthesized following general procedure C with **2h** (154.2 mg, 0.5 mmol, 1 equiv.), Cu-PMO (16.5 mg, 11 wt%) and $NaBH_4$ (37.8 mg, 1.0 mmol, 2 equiv.) in $H_2O$ (10 mL) at

reflux for 5 hours. The crude mixture was fully dissolved in MeOD and an internal standard ($CHCl_3$, 40 µL, 1 equiv.) was added to obtain the NMR yield. Boron NMR was measured to verify the absence of boron salts in the crude mixture. After evaporation *in vacuo*, the product was weighed to show 92% yield. The diastereomers were separated by column chromatography (silica gel, DCM:MeOH, 450:50) to afford **3h** and **3h'** as clear oils in 11.7% and 36% yield, respectively. Mixture **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{15}H_{25}O_6$ $[M+H]^+$ 313.16511 Found 313.16428

**3h** $R_f$ = 0.22 (silica gel, 8:1 DCM:MeOH); **$^1$H NMR** (400 MHz, Methanol-$d_4$) δ 7.25 – 7.14 (m, 4H), 7.12 (d, *J* = 7.1 Hz, 1H), 3.90 – 3.71 (m, 2H), 3.57 (dd, *J* = 11.8, 5.4 Hz, 1H), 3.31 – 3.15 (m, 4H), 3.06 (t, *J* = 9.0 Hz, 1H), 2.76 (ddd, *J* = 13.6, 10.1, 5.4 Hz, 1H), 2.63 (ddd, *J* = 13.6, 9.8, 6.5 Hz, 1H), 2.09 – 1.96 (m, 1H), 1.85 – 1.64 (m, 2H), 1.60 (ddd, *J* = 14.5, 9.2, 7.3 Hz, 1H). **$^{13}$C NMR** (101 MHz, $cd_3od$) δ 142.26, 128.01, 127.89, 125.25, 80.20, 78.51, 78.21, 74.33, 70.48, 69.17, 61.61, 38.93, 38.67, 31.34. **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{15}H_{25}O_6$ $[M+H]^+$ 313.16511 Found 313.16406.

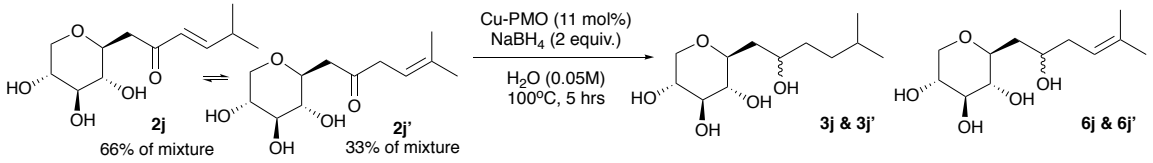
**3h'** $R_f$ = 0.18 (silica gel, 8:1 DCM:MeOH); **$^1$H NMR** (400 MHz, Methanol-$d_4$) δ 7.25 – 7.15 (m, 4H), 7.15 – 7.07 (m, 1H), 3.93 – 3.74 (m, 2H), 3.61 (dd, *J* = 11.7, 5.2 Hz, 1H), 3.40 (td, *J* = 9.5, 2.5 Hz, 1H), 3.36 – 3.18 (m, 3H), 3.04 (t, *J* = 9.1 Hz, 1H), 2.77 (dt, *J* = 13.5, 7.9 Hz, 1H), 2.62 (dt, *J* = 13.6, 8.1 Hz, 1H), 1.93 (ddd, *J* = 14.4, 9.9, 2.5 Hz, 1H), 1.72 (td, *J* = 8.3, 6.4 Hz, 2H), 1.53 (ddd, *J* = 14.4, 9.6, 2.6 Hz, 1H). **$^{13}$C NMR** (101 MHz, $cd_3od$) δ 142.35, 128.00, 127.89, 125.25, 80.05, 78.39, 76.26, 74.30, 70.58, 66.65, 61.68, 39.73, 39.53, 31.78. **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{15}H_{25}O_6$ $[M+H]^+$ 313.16511 Found 313.16411.




**3i** and **3i'** were synthesized following general procedure C with **2i** (136.1 mg, 0.5 mmol), Cu-PMO (16.5 mg, 11 mol%) and $NaBH_4$ (37.8 mg, 1.0 mmol, 2 equiv.) in $H_2O$ (10 mL, 0.05 M) at reflux for 5 hours. Because the starting material is very hygroscopic, we verified the true added amount of starting material **2i** present in a stock solution by NMR using $CHCl_3$ (0.04 mL, 0.5 mmol) as internal standard**.** After reaction, the crude mixture fully dissolved in MeOD and an internal standard ($CHCl_3$, 40 µL, 1 equiv.) was added to obtain the NMR yield. Boron NMR was measured to verify the absence of boron salts in the crude mixture. After evaporation *in vacuo*, the product was

weighed to show quantitative yield. The diastereomers were separated by column chromatography (silica gel, DCM:MeOH, 450:50) to afford **3i'** as a clear oil in 8.2% yield. Unfortunately, diastereomer **3i** could not be isolated separately from **3i'**. Further optimization of separation of the diastereomers is required. Mixture **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{14}H_{28}O_5Na$ $[M+Na]^+$ 299.18344 Found 299.14731.

**3i' $R_f$** = 0.42 (silica gel, 8:1 DCM:MeOH); **$^1$H NMR** (400 MHz, Methanol-$d_4$) 3.84 (dd, *J* = 11.1, 5.4 Hz, 1H), 3.78 (dd, *J* = 7.1, 4.2 Hz, 1H), 3.43 (ddd, *J* = 10.3, 9.0, 5.4 Hz, 1H), 3.27 – 3.15 (m, 2H), 3.11 (t, *J* = 10.8 Hz, 1H), 3.03 (t, *J* = 9.1 Hz, 1H), 1.96 (ddd, *J* = 14.4, 5.8, 2.8 Hz, 1H), 1.54 (ddd, *J* = 15.1, 9.0, 6.7 Hz, 1H), 1.50 – 1.23 (m, 12H), 0.89 (t, *J* = 6.9 Hz, 3H). **$^{13}$C NMR** (151 MHz, cd$_3$od) δ 79.08, 78.28, 74.41, 70.01, 69.52, 69.34, 39.25, 36.35, 31.60, 29.34, 29.00, 25.09, 22.30, 13.01. **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{14}H_{28}O_5Na$ $[M+Na]^+$ 299.18344 Found 299.16790.




**3j** and **3j'** were synthesized following general procedure C with **2j** (122.2 mg, 0.5 mmol, 1 equiv.), Cu-PMO (16.5 mg, 11 mol%) and $NaBH_4$ (37.8 mg, 1.0 mmol, 2 equiv.) in $H_2O$ (10 mL, 0.05 M) at reflux for 5 hours. Because the starting material is very hygroscopic, we verified the true added amount of starting material **2j** present in a stock solution by NMR using $CHCl_3$ (0.04 mL, 0.5 mmol) as internal standard**.** After reaction, the crude mixture fully dissolved in MeOD and an internal standard ($CHCl_3$, 40 µL, 1 equiv.) was added to obtain the NMR yield. Boron NMR was measured to verify the absence of boron salts in the crude mixture. The diastereomers were separated by column chromatography (silica gel, DCM:MeOH, 450:50) to afford **3j'** as a clear oil in 10.2% yield. Unfortunately, diastereomer **3j** could not be isolated separately from **3j'**. Further optimization of separation of the diastereomers is required. Mixture **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{12}H_{25}O_5$ $[M+H]^+$ 249.17020 Found 249.16894.

**3j' $R_f$** = 0.25 (silica gel, 8:1 DCM:MeOH); **$^1$H NMR** (400 MHz, Methanol-$d_4$) δ 3.82 (dd, *J* = 11.0, 5.4 Hz, 2H), 3.75 – 3.65 (m, 1H), 3.43 (ddd, *J* = 10.5, 8.9, 5.4 Hz, 2H), 3.35 – 3.20 (m, 13H), 3.18 – 3.07 (m, 1H), 3.00 (q, *J* = 9.2, 8.8 Hz, 1H), 1.91 – 1.78 (m, 1H), 1.57 – 1.46 (m, 1H), 1.46 – 1.37 (m, 2H), 1.36 – 1.22 (m, 2H), 1.23 – 1.10 (m, 2H), 1.01 – 0.93 (m, 2H), 0.88 (dd, *J* = 6.6, 2.5 Hz, 7H).**$^{13}$C NMR**

(151 MHz, $cd_3od$) δ 78.46, 77.19, 74.38, 70.21, 69.48, 67.46, 39.63, 35.55, 34.66, 27.84, 21.68, 21.53. **HR-MS (ESI$^+$, m/*z*):** Calcd for $C_{12}H_{24}O_5$ $[M+Na]^+$ 271.15214 Found 271.12140.

## 2. Procedures and tables for calculated geometries

The proton and carbon NMR shifts were calculated computationally in methanol and compared with experimental data of the separated isomers in methanol using Smith and Goodman's CP3 parameter and related probability factor.[8] The full procedure for the calculations of the NMR chemical shifts can be found in the ESI. Several conformers of each diastereomer were generated using the Tinker 8.2 program,[9] and the most stable geometries of all conformers were calculated using Gaussian 16. Ground state geometries were optimized in methanol by using the self-consistent reaction field (SCRF) method combined with the polarized continuum (PCM) solvation model[10] with ωB97XD[11] and the def2TZVP[12,13] basis set. NMR shielding constants for proton and carbon nuclei were calculated using GIAO method as implemented in Gaussian 16.

To obtain the conformers for the two diastereomers of the compound, **3a** and **3a'**, for the NMR shift calculations, we have performed conformational search using Tinker 8.2 program. Initial structures for the conformational search, DA1 and DB1, were obtained from the gas phase optimization of the two diastereomers (Figure S3). MMFF force field in gas phase with rms gradient cutoff of 1 kcal/mol was used to obtain ten structures for each diastereomer with sufficiently different conformations. For each of the conformers ground state geometries were optimized using ωB97XD/def2TZVP method in methanol, and then energies and GIAO shielding constants were calculated.

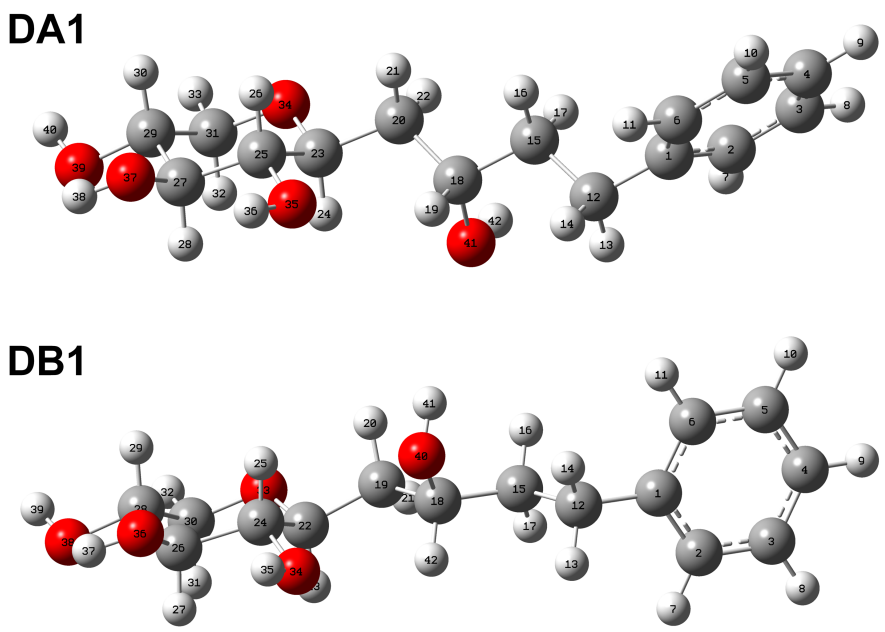



**Figure S3**. Initial structures of the two diastereomers used for the conformational search with the numbering of the atoms; white – hydrogen, red – oxygen, gray – carbon.

*a. <u>Coordinates for the optimized geometries</u>*

The following geometries were optimized by Gaussian 16 using ωB97XD/def2TZVP method in methanol:

**DA1**

| # | Atom | X | Y | Z |
|---|---|---|---|---|
| 1 | C | 4.28515 | 0.178973 | 0.357223 |
| 2 | C | 5.075972 | -0.96701 | 0.375162 |
| 3 | C | 6.325913 | -0.98155 | -0.22697 |
| 4 | C | 6.807443 | 0.155907 | -0.85984 |
| 5 | C | 6.029495 | 1.304995 | -0.88435 |
| 6 | C | 4.78007 | 1.313288 | -0.28102 |
| 7 | H | 4.707272 | -1.85889 | 0.869883 |
| 8 | H | 6.926703 | -1.88232 | -0.19903 |
| 9 | H | 7.783727 | 0.147884 | -1.32792 |
| 10 | H | 6.397657 | 2.199041 | -1.37248 |
| 11 | H | 4.178574 | 2.21542 | -0.30294 |
| 12 | C | 2.910011 | 0.17536 | 0.968693 |
| 13 | H | 2.885884 | -0.50415 | 1.82223 |

| | | | | |
|---|---|---|---|---|
| 14 | H | 2.67107 | 1.173379 | 1.345701 |
| 15 | C | 1.837998 | -0.24542 | -0.03736 |
| 16 | H | 1.851129 | 0.441547 | -0.88811 |
| 17 | H | 2.076814 | -1.2394 | -0.43409 |
| 18 | C | 0.432428 | -0.26907 | 0.550497 |
| 19 | H | 0.200556 | 0.712943 | 0.96417 |
| 20 | C | -0.59898 | -0.6253 | -0.51761 |
| 21 | H | -0.46238 | 0.023065 | -1.38708 |
| 22 | H | -0.4052 | -1.64953 | -0.85173 |
| 23 | C | -2.04641 | -0.56527 | -0.0541 |
| 24 | H | -2.10677 | -0.89674 | 0.991608 |
| 25 | C | -2.67094 | 0.826803 | -0.16433 |
| 26 | H | -2.59508 | 1.150928 | -1.21185 |
| 27 | C | -4.14111 | 0.780132 | 0.215644 |
| 28 | H | -4.21453 | 0.504466 | 1.277258 |
| 29 | C | -4.86978 | -0.26956 | -0.59887 |
| 30 | H | -4.87545 | 0.043211 | -1.64897 |
| 31 | C | -4.13 | -1.59735 | -0.47035 |
| 32 | H | -4.19369 | -1.94645 | 0.569585 |
| 33 | H | -4.58147 | -2.35152 | -1.11526 |
| 34 | O | -2.78523 | -1.46313 | -0.87085 |
| 35 | O | -1.97225 | 1.723495 | 0.673467 |
| 36 | H | -2.48268 | 2.537791 | 0.70415 |
| 37 | O | -4.66667 | 2.078435 | 0.018185 |
| 38 | H | -5.58933 | 2.068215 | 0.284651 |
| 39 | O | -6.19071 | -0.35308 | -0.09734 |
| 40 | H | -6.75142 | -0.7695 | -0.75452 |
| 41 | O | 0.345962 | -1.15666 | 1.660781 |
| 42 | H | 0.566246 | -2.04145 | 1.356249 |

**DA2**

| # | Atom | X | Y | Z |
|---|---|---|---|---|
| 1 | C | 4.368153 | -0.312942 | 0.298696 |
| 2 | C | 5.019186 | -0.790124 | -0.83608 |
| 3 | C | 6.268212 | -0.307235 | -1.198915 |
| 4 | C | 6.889416 | 0.666055 | -0.428707 |
| 5 | C | 6.251614 | 1.150075 | 0.704874 |
| 6 | C | 5.002172 | 0.663665 | 1.062297 |
| 7 | H | 4.540729 | -1.552386 | -1.441159 |
| 8 | H | 6.759035 | -0.694158 | -2.08352 |
| 9 | H | 7.865441 | 1.042334 | -0.708229 |
| 10 | H | 6.729463 | 1.906978 | 1.314719 |
| 11 | H | 4.510837 | 1.04535 | 1.950598 |

| | | | | |
|---|---|---|---|---|
| 12 | C | 2.993453 | -0.806392 | 0.661417 |
| 13 | H | 2.882455 | -1.848479 | 0.358387 |
| 14 | H | 2.863475 | -0.770195 | 1.74656 |
| 15 | C | 1.894011 | 0.027255 | 0.00072 |
| 16 | H | 2.00016 | 1.071234 | 0.307813 |
| 17 | H | 2.014222 | -0.002908 | -1.08703 |
| 18 | C | 0.492851 | -0.442305 | 0.352308 |
| 19 | H | 0.376083 | -0.394306 | 1.446079 |
| 20 | C | -0.571848 | 0.448698 | -0.280574 |
| 21 | H | -0.346982 | 1.491156 | -0.050095 |
| 22 | H | -0.537539 | 0.33598 | -1.368978 |
| 23 | C | -1.978684 | 0.165821 | 0.209948 |
| 24 | H | -2.006552 | 0.252425 | 1.306298 |
| 25 | C | -3.012114 | 1.128349 | -0.372218 |
| 26 | H | -2.969515 | 1.060722 | -1.468104 |
| 27 | C | -4.40917 | 0.738439 | 0.080366 |
| 28 | H | -4.466407 | 0.871187 | 1.170159 |
| 29 | C | -4.690795 | -0.71856 | -0.233402 |
| 30 | H | -4.716624 | -0.844926 | -1.321303 |
| 31 | C | -3.575672 | -1.580572 | 0.349 |
| 32 | H | -3.593746 | -1.511958 | 1.444289 |
| 33 | H | -3.704857 | -2.623936 | 0.063588 |
| 34 | O | -2.322031 | -1.167065 | -0.155237 |
| 35 | O | -2.694547 | 2.436124 | 0.052198 |
| 36 | H | -3.434236 | 3.001993 | -0.186213 |
| 37 | O | -5.317583 | 1.611661 | -0.55987 |
| 38 | H | -6.20261 | 1.390875 | -0.258686 |
| 39 | O | -5.945802 | -1.036675 | 0.336077 |
| 40 | H | -6.295502 | -1.822057 | -0.088908 |
| 41 | O | 0.363592 | -1.793427 | -0.071302 |
| 42 | H | -0.581096 | -1.99122 | -0.07958 |

**DA3**

| # | Atom | X | Y | Z |
|---|---|---|---|---|
| 1 | C | -4.07347 | 0.302679 | -0.22945 |
| 2 | C | -4.43612 | -0.39215 | -1.37993 |
| 3 | C | -5.74147 | -0.82184 | -1.57179 |
| 4 | C | -6.70841 | -0.56205 | -0.61093 |
| 5 | C | -6.35934 | 0.130067 | 0.540475 |
| 6 | C | -5.05264 | 0.557001 | 0.727214 |
| 7 | H | -3.686 | -0.59694 | -2.13586 |
| 8 | H | -6.00446 | -1.35825 | -2.47517 |

| | | | | |
|---|---|---|---|---|
| 9 | H | -7.72816 | -0.89413 | -0.75958 |
| 10 | H | -7.10755 | 0.340653 | 1.294716 |
| 11 | H | -4.78723 | 1.098282 | 1.628689 |
| 12 | C | -2.64613 | 0.724505 | -0.00344 |
| 13 | H | -2.17189 | 0.919527 | -0.96739 |
| 14 | H | -2.63559 | 1.662984 | 0.557504 |
| 15 | C | -1.8574 | -0.34397 | 0.759616 |
| 16 | H | -2.37079 | -0.56274 | 1.699565 |
| 17 | H | -1.85413 | -1.27012 | 0.177417 |
| 18 | C | -0.41153 | 0.024575 | 1.086858 |
| 19 | H | 0.035293 | -0.82204 | 1.607258 |
| 20 | C | 0.417484 | 0.327461 | -0.15942 |
| 21 | H | 0.225215 | -0.43291 | -0.92125 |
| 22 | H | 0.092143 | 1.283949 | -0.57822 |
| 23 | C | 1.912908 | 0.437668 | 0.098639 |
| 24 | H | 2.077137 | 0.862979 | 1.098662 |
| 25 | C | 2.650019 | -0.89943 | 0.00642 |
| 26 | H | 2.472084 | -1.31559 | -0.9952 |
| 27 | C | 4.145098 | -0.69355 | 0.178892 |
| 28 | H | 4.327567 | -0.32139 | 1.197037 |
| 29 | C | 4.656307 | 0.340798 | -0.80367 |
| 30 | H | 4.556682 | -0.0607 | -1.81825 |
| 31 | C | 3.813771 | 1.605863 | -0.67469 |
| 32 | H | 3.977094 | 2.047951 | 0.317861 |
| 33 | H | 4.102581 | 2.337377 | -1.42948 |
| 34 | O | 2.447543 | 1.321903 | -0.87599 |
| 35 | O | 2.152779 | -1.77873 | 0.992969 |
| 36 | H | 2.736048 | -2.54294 | 1.011176 |
| 37 | O | 4.764753 | -1.9534 | 0.008254 |
| 38 | H | 5.708871 | -1.83993 | 0.143253 |
| 39 | O | 6.01644 | 0.581737 | -0.49513 |
| 40 | H | 6.444373 | 0.985694 | -1.25235 |
| 41 | O | -0.33816 | 1.096625 | 2.022955 |
| 42 | H | -0.61061 | 1.907508 | 1.586305 |

**DA4**

| # | Atom | X | Y | Z |
|---|---|---|---|---|
| 1 | C | 3.726994 | 0.189311 | 0.084951 |
| 2 | C | 3.840012 | -0.809781 | 1.04865 |
| 3 | C | 4.682777 | -1.894881 | 0.856603 |
| 4 | C | 5.429378 | -1.999387 | -0.308911 |
| 5 | C | 5.325953 | -1.010821 | -1.277346 |
| 6 | C | 4.481057 | 0.072102 | -1.07959 |

| | | | | |
|---|---|---|---|---|
| 7 | H | 3.260729 | -0.733589 | 1.962323 |
| 8 | H | 4.759181 | -2.659336 | 1.620086 |
| 9 | H | 6.089859 | -2.843983 | -0.459765 |
| 10 | H | 5.906848 | -1.081304 | -2.188786 |
| 11 | H | 4.40676 | 0.841764 | -1.839984 |
| 12 | C | 2.775802 | 1.339155 | 0.277828 |
| 13 | H | 2.710095 | 1.592104 | 1.337603 |
| 14 | H | 3.155473 | 2.222994 | -0.241947 |
| 15 | C | 1.373682 | 1.017186 | -0.2401 |
| 16 | H | 1.422894 | 0.799532 | -1.311612 |
| 17 | H | 1.007892 | 0.111579 | 0.252084 |
| 18 | C | 0.380974 | 2.153923 | -0.006329 |
| 19 | H | 0.823443 | 3.073768 | -0.400071 |
| 20 | C | -0.938788 | 1.966033 | -0.761552 |
| 21 | H | -1.624506 | 2.762396 | -0.459782 |
| 22 | H | -0.731731 | 2.111046 | -1.824627 |
| 23 | C | -1.6697 | 0.630667 | -0.663827 |
| 24 | H | -0.987812 | -0.194205 | -0.913602 |
| 25 | C | -2.312074 | 0.325617 | 0.692432 |
| 26 | H | -2.9515 | 1.172421 | 0.972905 |
| 27 | C | -3.16423 | -0.929344 | 0.618107 |
| 28 | H | -2.499682 | -1.781856 | 0.41835 |
| 29 | C | -4.166771 | -0.84142 | -0.513228 |
| 30 | H | -4.886216 | -0.046205 | -0.28891 |
| 31 | C | -3.41839 | -0.501183 | -1.796827 |
| 32 | H | -2.748689 | -1.332115 | -2.057313 |
| 33 | H | -4.116154 | -0.349083 | -2.620202 |
| 34 | O | -2.694673 | 0.698556 | -1.644944 |
| 35 | O | -1.298919 | 0.139736 | 1.668187 |
| 36 | H | -1.721688 | -0.203482 | 2.461692 |
| 37 | O | -3.778208 | -1.083821 | 1.88238 |
| 38 | H | -4.275426 | -1.905452 | 1.873698 |
| 39 | O | -4.816604 | -2.095019 | -0.596894 |
| 40 | H | -5.633537 | -1.994379 | -1.089057 |
| 41 | O | 0.191676 | 2.409887 | 1.375419 |
| 42 | H | -0.272455 | 1.639624 | 1.738557 |

**DA5**

| # | Atom | X | Y | Z |
|---|---|---|---|---|
| 1 | C | -3.737352 | -0.050669 | 0.305211 |
| 2 | C | -4.613741 | 0.370725 | -0.691266 |
| 3 | C | -5.481804 | -0.522408 | -1.302917 |
| 4 | C | -5.487144 | -1.857909 | -0.925514 |

| | | | | |
|---|---|---|---|---|
| 5 | C | -4.618878 | -2.290846 | 0.067022 |
| 6 | C | -3.752612 | -1.393323 | 0.674357 |
| 7 | H | -4.616921 | 1.413378 | -0.989497 |
| 8 | H | -6.157972 | -0.173819 | -2.073882 |
| 9 | H | -6.16573 | -2.556056 | -1.399202 |
| 10 | H | -4.617915 | -3.330297 | 0.371422 |
| 11 | H | -3.077993 | -1.738452 | 1.450242 |
| 12 | C | -2.763582 | 0.910316 | 0.932133 |
| 13 | H | -3.192805 | 1.913028 | 0.953511 |
| 14 | H | -2.575154 | 0.619792 | 1.969261 |
| 15 | C | -1.432981 | 0.945993 | 0.178654 |
| 16 | H | -1.019142 | -0.06513 | 0.151206 |
| 17 | H | -1.605042 | 1.243501 | -0.862627 |
| 18 | C | -0.410626 | 1.884494 | 0.807081 |
| 19 | H | -0.234408 | 1.569514 | 1.837484 |
| 20 | C | 0.922126 | 1.909558 | 0.061192 |
| 21 | H | 0.758343 | 2.281249 | -0.953937 |
| 22 | H | 1.581239 | 2.620971 | 0.566203 |
| 23 | C | 1.628196 | 0.571646 | -0.035798 |
| 24 | H | 1.015911 | -0.137801 | -0.610929 |
| 25 | C | 2.982818 | 0.683212 | -0.736171 |
| 26 | H | 3.599427 | 1.40682 | -0.185162 |
| 27 | C | 3.691137 | -0.6604 | -0.723064 |
| 28 | H | 3.104172 | -1.364383 | -1.330171 |
| 29 | C | 3.773023 | -1.208715 | 0.688109 |
| 30 | H | 4.42468 | -0.55718 | 1.280858 |
| 31 | C | 2.376122 | -1.219175 | 1.301413 |
| 32 | H | 1.744362 | -1.929835 | 0.751023 |
| 33 | H | 2.417667 | -1.530794 | 2.345024 |
| 34 | O | 1.811323 | 0.072542 | 1.277562 |
| 35 | O | 2.771452 | 1.126026 | -2.059902 |
| 36 | H | 3.605085 | 1.032127 | -2.529387 |
| 37 | O | 4.966578 | -0.471592 | -1.303502 |
| 38 | H | 5.413946 | -1.321539 | -1.316543 |
| 39 | O | 4.317454 | -2.512142 | 0.601536 |
| 40 | H | 4.657006 | -2.769588 | 1.460651 |
| 41 | O | -0.917473 | 3.210426 | 0.919003 |
| 42 | H | -1.101648 | 3.537406 | 0.034214 |

**DA6**

| # | Atom | X | Y | Z |
|---|---|---|---|---|
| 1 | C | 4.077917 | 0.254556 | 0.337274 |
| 2 | C | 5.015965 | -0.567662 | 0.955943 |

| | | | | |
|---|---|---|---|---|
| 3 | C | 6.363849 | -0.474209 | 0.641256 |
| 4 | C | 6.79653 | 0.446957 | -0.302596 |
| 5 | C | 5.871469 | 1.272183 | -0.926261 |
| 6 | C | 4.524544 | 1.174476 | -0.60721 |
| 7 | H | 4.685103 | -1.288457 | 1.695574 |
| 8 | H | 7.078464 | -1.120244 | 1.136231 |
| 9 | H | 7.8483 | 0.523229 | -0.548031 |
| 10 | H | 6.199456 | 1.996501 | -1.661658 |
| 11 | H | 3.80744 | 1.824063 | -1.096888 |
| 12 | C | 2.610956 | 0.119133 | 0.647976 |
| 13 | H | 2.482241 | -0.161984 | 1.696633 |
| 14 | H | 2.126681 | 1.088854 | 0.516086 |
| 15 | C | 1.938482 | -0.93101 | -0.238188 |
| 16 | H | 2.034366 | -0.64631 | -1.290747 |
| 17 | H | 2.46181 | -1.883243 | -0.118075 |
| 18 | C | 0.470712 | -1.170149 | 0.0819 |
| 19 | H | 0.375399 | -1.333024 | 1.166328 |
| 20 | C | -0.418863 | 0.007641 | -0.304816 |
| 21 | H | -0.011989 | 0.926814 | 0.117562 |
| 22 | H | -0.416032 | 0.116141 | -1.394308 |
| 23 | C | -1.848239 | -0.114627 | 0.186435 |
| 24 | H | -1.847704 | -0.252182 | 1.277887 |
| 25 | C | -2.690676 | 1.117167 | -0.140093 |
| 26 | H | -2.672246 | 1.270504 | -1.227973 |
| 27 | C | -4.131265 | 0.900145 | 0.291184 |
| 28 | H | -4.15208 | 0.812648 | 1.386891 |
| 29 | C | -4.681786 | -0.385527 | -0.295914 |
| 30 | H | -4.740245 | -0.277906 | -1.384532 |
| 31 | C | -3.741047 | -1.535546 | 0.048095 |
| 32 | H | -3.735653 | -1.692003 | 1.13443 |
| 33 | H | -4.064296 | -2.457259 | -0.434291 |
| 34 | O | -2.437244 | -1.25943 | -0.42187 |
| 35 | O | -2.131228 | 2.230472 | 0.522507 |
| 36 | H | -2.754135 | 2.957615 | 0.436378 |
| 37 | O | -4.867611 | 2.035688 | -0.115921 |
| 38 | H | -5.776291 | 1.918212 | 0.17262 |
| 39 | O | -5.969073 | -0.582715 | 0.256083 |
| 40 | H | -6.465597 | -1.181132 | -0.305236 |
| 41 | O | 0.088024 | -2.355404 | -0.604474 |
| 42 | H | -0.877226 | -2.370875 | -0.615389 |

**DA7**

| # | Atom | X | Y | Z |
|---|---|---|---|---|

| | | | | |
|---|---|---|---|---|
| 1 | C | -4.038816 | -0.059869 | -0.369022 |
| 2 | C | -4.538426 | -1.340479 | -0.147702 |
| 3 | C | -5.90142 | -1.561278 | -0.009362 |
| 4 | C | -6.790733 | -0.498992 | -0.090065 |
| 5 | C | -6.305699 | 0.782736 | -0.310616 |
| 6 | C | -4.941926 | 0.997327 | -0.447767 |
| 7 | H | -3.849589 | -2.175853 | -0.08579 |
| 8 | H | -6.269916 | -2.565777 | 0.158923 |
| 9 | H | -7.854863 | -0.669072 | 0.01488 |
| 10 | H | -6.991784 | 1.618061 | -0.378872 |
| 11 | H | -4.570108 | 2.001205 | -0.621165 |
| 12 | C | -2.557124 | 0.182743 | -0.471826 |
| 13 | H | -2.077732 | -0.699107 | -0.901998 |
| 14 | H | -2.363243 | 1.018334 | -1.146694 |
| 15 | C | -1.939639 | 0.492454 | 0.894873 |
| 16 | H | -2.483484 | 1.323489 | 1.352555 |
| 17 | H | -2.065571 | -0.369426 | 1.556006 |
| 18 | C | -0.463782 | 0.863705 | 0.858084 |
| 19 | H | -0.135519 | 0.995584 | 1.899345 |
| 20 | C | 0.412323 | -0.215979 | 0.226804 |
| 21 | H | 0.148994 | -1.185362 | 0.653586 |
| 22 | H | 0.222501 | -0.265686 | -0.849147 |
| 23 | C | 1.895485 | 0.001882 | 0.45439 |
| 24 | H | 2.092558 | 0.077097 | 1.534071 |
| 25 | C | 2.752137 | -1.129447 | -0.110924 |
| 26 | H | 2.536453 | -1.224122 | -1.184168 |
| 27 | C | 4.227659 | -0.808072 | 0.056282 |
| 28 | H | 4.453567 | -0.77939 | 1.131819 |
| 29 | C | 4.552055 | 0.552259 | -0.530917 |
| 30 | H | 4.406049 | 0.510484 | -1.615852 |
| 31 | C | 3.610055 | 1.592469 | 0.065951 |
| 32 | H | 3.80378 | 1.686999 | 1.14221 |
| 33 | H | 3.762194 | 2.564795 | -0.401191 |
| 34 | O | 2.265189 | 1.22773 | -0.168319 |
| 35 | O | 2.418342 | -2.322589 | 0.564664 |
| 36 | H | 3.066208 | -2.986113 | 0.311446 |
| 37 | O | 4.957935 | -1.848267 | -0.561995 |
| 38 | H | 5.893205 | -1.665267 | -0.441185 |
| 39 | O | 5.902839 | 0.833477 | -0.21923 |
| 40 | H | 6.232392 | 1.505019 | -0.819301 |
| 41 | O | -0.342219 | 2.104504 | 0.173786 |
| 42 | H | 0.594331 | 2.216504 | -0.02983 |

**DA8**

| # | Atom | X | Y | Z |
|---|---|---|---|---|
| 1 | C | 4.014283 | -0.502404 | -0.331745 |
| 2 | C | 4.313913 | 0.567672 | -1.167505 |
| 3 | C | 5.115965 | 1.613841 | -0.731923 |
| 4 | C | 5.635818 | 1.604591 | 0.55385 |
| 5 | C | 5.350759 | 0.537873 | 1.396357 |
| 6 | C | 4.550893 | -0.504289 | 0.954009 |
| 7 | H | 3.907087 | 0.586667 | -2.172231 |
| 8 | H | 5.333482 | 2.438826 | -1.399351 |
| 9 | H | 6.260954 | 2.419472 | 0.896785 |
| 10 | H | 5.756212 | 0.516673 | 2.400598 |
| 11 | H | 4.338852 | -1.33397 | 1.619459 |
| 12 | C | 3.156295 | -1.648668 | -0.805056 |
| 13 | H | 2.940494 | -1.523908 | -1.869382 |
| 14 | H | 3.739346 | -2.569587 | -0.715783 |
| 15 | C | 1.837814 | -1.858449 | -0.051535 |
| 16 | H | 1.459271 | -2.849713 | -0.311981 |
| 17 | H | 2.013944 | -1.860938 | 1.028369 |
| 18 | C | 0.741163 | -0.853091 | -0.366471 |
| 19 | H | 0.618882 | -0.811982 | -1.46026 |
| 20 | C | -0.593202 | -1.279142 | 0.242878 |
| 21 | H | -0.796106 | -2.316433 | -0.027266 |
| 22 | H | -0.524755 | -1.228873 | 1.334406 |
| 23 | C | -1.77435 | -0.450957 | -0.225672 |
| 24 | H | -1.82549 | -0.479827 | -1.324336 |
| 25 | C | -3.105366 | -0.956085 | 0.328686 |
| 26 | H | -3.047825 | -0.949435 | 1.425969 |
| 27 | C | -4.23745 | -0.037721 | -0.099456 |
| 28 | H | -4.334067 | -0.098633 | -1.192819 |
| 29 | C | -3.932646 | 1.401765 | 0.26812 |
| 30 | H | -3.91523 | 1.489385 | 1.359947 |
| 31 | C | -2.565815 | 1.782663 | -0.290799 |
| 32 | H | -2.600733 | 1.765213 | -1.387699 |
| 33 | H | -2.281274 | 2.783496 | 0.032464 |
| 34 | O | -1.575688 | 0.896468 | 0.190062 |
| 35 | O | -3.318759 | -2.268276 | -0.144496 |
| 36 | H | -4.221954 | -2.509891 | 0.079223 |
| 37 | O | -5.418597 | -0.510851 | 0.515872 |
| 38 | H | -6.144888 | 0.050396 | 0.23254 |
| 39 | O | -4.961368 | 2.202552 | -0.280724 |
| 40 | H | -4.984491 | 3.044737 | 0.177297 |
| 41 | O | 1.138829 | 0.425038 | 0.108008 |

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|---|---|---|---|---|
| 42 | H | 0.34451 | 0.973273 | 0.121838 |

**DA9**

| # | Atom | X | Y | Z |
|---|---|---|---|---|
| 1 | C | -4.038655 | -0.059964 | -0.368915 |
| 2 | C | -4.538256 | -1.340407 | -0.146557 |
| 3 | C | -5.901267 | -1.561176 | -0.008444 |
| 4 | C | -6.790632 | -0.499015 | -0.090391 |
| 5 | C | -6.305609 | 0.782541 | -0.311896 |
| 6 | C | -4.941796 | 0.9971 | -0.448831 |
| 7 | H | -3.849376 | -2.175673 | -0.083635 |
| 8 | H | -6.269751 | -2.565548 | 0.160626 |
| 9 | H | -7.854783 | -0.669091 | 0.014353 |
| 10 | H | -6.991708 | 1.617777 | -0.381081 |
| 11 | H | -4.570013 | 2.000862 | -0.622967 |
| 12 | C | -2.556935 | 0.182542 | -0.471542 |
| 13 | H | -2.07754 | -0.699589 | -0.901158 |
| 14 | H | -2.362919 | 1.017746 | -1.146859 |
| 15 | C | -1.939635 | 0.492907 | 0.895033 |
| 16 | H | -2.483442 | 1.324196 | 1.352307 |
| 17 | H | -2.065684 | -0.368656 | 1.556554 |
| 18 | C | -0.463726 | 0.864006 | 0.858281 |
| 19 | H | -0.135493 | 0.995921 | 1.899541 |
| 20 | C | 0.412248 | -0.215731 | 0.226928 |
| 21 | H | 0.148806 | -1.18516 | 0.653524 |
| 22 | H | 0.222395 | -0.265187 | -0.849042 |
| 23 | C | 1.895431 | 0.00191 | 0.454547 |
| 24 | H | 2.092512 | 0.076875 | 1.534243 |
| 25 | C | 2.751915 | -1.129416 | -0.111012 |
| 26 | H | 2.536063 | -1.223974 | -1.184228 |
| 27 | C | 4.227521 | -0.808268 | 0.055969 |
| 28 | H | 4.45368 | -0.779976 | 1.131452 |
| 29 | C | 4.551992 | 0.55219 | -0.530887 |
| 30 | H | 4.405836 | 0.510716 | -1.615817 |
| 31 | C | 3.610177 | 1.592339 | 0.066369 |
| 32 | H | 3.803994 | 1.686543 | 1.142643 |
| 33 | H | 3.762397 | 2.564791 | -0.40049 |
| 34 | O | 2.265244 | 1.227847 | -0.16789 |
| 35 | O | 2.4181 | -2.32259 | 0.564535 |
| 36 | H | 3.065281 | -2.986423 | 0.310384 |
| 37 | O | 4.957478 | -1.848408 | -0.562831 |
| 38 | H | 5.892807 | -1.66605 | -0.441552 |
| 39 | O | 5.902838 | 0.833191 | -0.219299 |

| | | | | |
|---|---|---|---|---|
| 40 | H | 6.232122 | 1.505498 | -0.818667 |
| 41 | O | -0.341959 | 2.104792 | 0.173975 |
| 42 | H | 0.594555 | 2.216409 | -0.02997 |

**DA10**

| # | Atom | X | Y | Z |
|---|---|---|---|---|
| 1 | C | -3.233047 | 0.071892 | 0.440079 |
| 2 | C | -4.554639 | 0.485668 | 0.305698 |
| 3 | C | -5.545422 | -0.407221 | -0.079926 |
| 4 | C | -5.226583 | -1.732343 | -0.339135 |
| 5 | C | -3.910967 | -2.157328 | -0.209087 |
| 6 | C | -2.925734 | -1.261149 | 0.176622 |
| 7 | H | -4.811512 | 1.519621 | 0.507912 |
| 8 | H | -6.569168 | -0.066815 | -0.175909 |
| 9 | H | -5.998261 | -2.430608 | -0.63797 |
| 10 | H | -3.652729 | -3.190539 | -0.406562 |
| 11 | H | -1.898682 | -1.593889 | 0.277594 |
| 12 | C | -2.143215 | 1.039791 | 0.814053 |
| 13 | H | -2.564513 | 1.869828 | 1.387171 |
| 14 | H | -1.420309 | 0.532246 | 1.454142 |
| 15 | C | -1.42799 | 1.584278 | -0.422336 |
| 16 | H | -1.036053 | 0.751461 | -1.011482 |
| 17 | H | -2.148614 | 2.112609 | -1.052162 |
| 18 | C | -0.296903 | 2.547587 | -0.100746 |
| 19 | H | -0.702966 | 3.365658 | 0.508831 |
| 20 | C | 0.874974 | 1.94161 | 0.673384 |
| 21 | H | 1.635196 | 2.717794 | 0.787063 |
| 22 | H | 0.559326 | 1.667556 | 1.68291 |
| 23 | C | 1.516533 | 0.73007 | 0.021373 |
| 24 | H | 1.483277 | 0.842178 | -1.072081 |
| 25 | C | 2.978672 | 0.550493 | 0.43046 |
| 26 | H | 3.027006 | 0.466818 | 1.525169 |
| 27 | C | 3.540757 | -0.722845 | -0.177822 |
| 28 | H | 3.555808 | -0.600325 | -1.270281 |
| 29 | C | 2.661521 | -1.913681 | 0.149893 |
| 30 | H | 2.70648 | -2.097201 | 1.229187 |
| 31 | C | 1.223499 | -1.594908 | -0.247015 |
| 32 | H | 1.16194 | -1.485472 | -1.338471 |
| 33 | H | 0.554941 | -2.401032 | 0.056315 |
| 34 | O | 0.781824 | -0.42405 | 0.400005 |
| 35 | O | 3.710433 | 1.676103 | -0.008283 |
| 36 | H | 4.642609 | 1.479418 | 0.119316 |
| 37 | O | 4.860222 | -0.878412 | 0.307067 |

| | | | | |
|---|---|---|---|---|
| 38 | H | 5.228952 | -1.671158 | -0.090875 |
| 39 | O | 3.172885 | -3.022732 | -0.565568 |
| 40 | H | 2.847114 | -3.832052 | -0.167439 |
| 41 | O | 0.143886 | 3.071617 | -1.350631 |
| 42 | H | 0.857418 | 3.692221 | -1.186082 |

**DB1**

| # | Atom | X | Y | Z |
|---|---|---|---|---|
| 1 | C | 4.294699 | -0.36284 | -0.15292 |
| 2 | C | 4.895617 | 0.186247 | -1.28254 |
| 3 | C | 6.170219 | 0.731219 | -1.21973 |
| 4 | C | 6.866828 | 0.737117 | -0.01947 |
| 5 | C | 6.279069 | 0.193242 | 1.114264 |
| 6 | C | 5.004821 | -0.351 | 1.045036 |
| 7 | H | 4.358037 | 0.183531 | -2.2244 |
| 8 | H | 6.621399 | 1.149809 | -2.11097 |
| 9 | H | 7.86244 | 1.159566 | 0.031509 |
| 10 | H | 6.815985 | 0.189543 | 2.054927 |
| 11 | H | 4.553033 | -0.7769 | 1.934215 |
| 12 | C | 2.894947 | -0.91246 | -0.21165 |
| 13 | H | 2.696493 | -1.31106 | -1.21025 |
| 14 | H | 2.793227 | -1.74207 | 0.489655 |
| 15 | C | 1.847461 | 0.152383 | 0.114523 |
| 16 | H | 2.039343 | 0.564039 | 1.113004 |
| 17 | H | 1.946975 | 0.983016 | -0.58956 |
| 18 | C | 0.414146 | -0.36855 | 0.054313 |
| 19 | C | -0.58096 | 0.746167 | 0.379061 |
| 20 | H | -0.68523 | 0.803236 | 1.467382 |
| 21 | H | -0.16639 | 1.704603 | 0.059199 |
| 22 | C | -1.98187 | 0.664797 | -0.21746 |
| 23 | H | -1.93359 | 0.855648 | -1.30005 |
| 24 | C | -2.714 | -0.66813 | -0.0283 |
| 25 | H | -2.60845 | -0.98729 | 1.016356 |
| 26 | C | -4.19665 | -0.54304 | -0.35343 |
| 27 | H | -4.28749 | -0.39189 | -1.4387 |
| 28 | C | -4.83391 | 0.647534 | 0.32772 |
| 29 | H | -4.81741 | 0.496178 | 1.412821 |
| 30 | C | -4.01715 | 1.883459 | -0.02157 |
| 31 | H | -4.05831 | 2.056014 | -1.10595 |
| 32 | H | -4.41273 | 2.765261 | 0.482869 |
| 33 | O | -2.68941 | 1.720822 | 0.416305 |

| | | | | |
|---|---|---|---|---|
| 34 | O | -2.13228 | -1.617 | -0.89935 |
| 35 | H | -2.60922 | -2.44249 | -0.78352 |
| 36 | O | -4.80569 | -1.7667 | 0.012099 |
| 37 | H | -5.7375 | -1.70814 | -0.21411 |
| 38 | O | -6.16566 | 0.737194 | -0.14432 |
| 39 | H | -6.6742 | 1.289941 | 0.451998 |
| 40 | O | 0.239224 | -1.48604 | 0.918934 |
| 41 | H | 0.451804 | -1.20314 | 1.812449 |
| 42 | H | 0.2227 | -0.76042 | -0.94553 |

**DB2**

| # | Atom | X | Y | Z |
|---|---|---|---|---|
| 1 | C | 3.487878 | -0.314061 | -0.331546 |
| 2 | C | 3.056219 | 0.482323 | -1.388424 |
| 3 | C | 3.316421 | 1.845668 | -1.408015 |
| 4 | C | 4.016799 | 2.43622 | -0.366193 |
| 5 | C | 4.454811 | 1.652924 | 0.693253 |
| 6 | C | 4.190981 | 0.291422 | 0.707614 |
| 7 | H | 2.50095 | 0.026522 | -2.200066 |
| 8 | H | 2.971456 | 2.44761 | -2.239758 |
| 9 | H | 4.222658 | 3.499127 | -0.380098 |
| 10 | H | 5.006306 | 2.103612 | 1.509277 |
| 11 | H | 4.537547 | -0.313903 | 1.538225 |
| 12 | C | 3.162985 | -1.784222 | -0.282235 |
| 13 | H | 2.96219 | -2.150484 | -1.289765 |
| 14 | H | 4.026804 | -2.335446 | 0.095688 |
| 15 | C | 1.9599 | -2.096425 | 0.615221 |
| 16 | H | 1.81756 | -3.179844 | 0.663047 |
| 17 | H | 2.168949 | -1.751007 | 1.631443 |
| 18 | C | 0.664191 | -1.456036 | 0.146907 |
| 19 | C | -0.481923 | -1.757482 | 1.108172 |
| 20 | H | -0.664952 | -2.835286 | 1.11682 |
| 21 | H | -0.179575 | -1.479637 | 2.120319 |
| 22 | C | -1.794812 | -1.050545 | 0.805633 |
| 23 | H | -2.533469 | -1.352301 | 1.561107 |
| 24 | C | -1.706751 | 0.48103 | 0.825726 |
| 25 | H | -0.978236 | 0.817155 | 0.080175 |
| 26 | C | -3.056568 | 1.080109 | 0.46758 |
| 27 | H | -3.778026 | 0.798766 | 1.248064 |
| 28 | C | -3.544387 | 0.52665 | -0.85784 |
| 29 | H | -2.857659 | 0.86323 | -1.645449 |
| 30 | C | -3.53156 | -0.992937 | -0.808976 |

| | | | | |
|---|---|---|---|---|
| 31 | H | -4.269535 | -1.341847 | -0.075381 |
| 32 | H | -3.786668 | -1.40683 | -1.782997 |
| 33 | O | -2.247495 | -1.47606 | -0.475853 |
| 34 | O | -1.364669 | 0.969504 | 2.109564 |
| 35 | H | -0.410458 | 1.00638 | 2.195523 |
| 36 | O | -2.993585 | 2.486222 | 0.352028 |
| 37 | H | -2.660831 | 2.832802 | 1.184347 |
| 38 | O | -4.862788 | 0.93775 | -1.144824 |
| 39 | H | -4.892974 | 1.894973 | -1.066067 |
| 40 | O | 0.388102 | -1.928475 | -1.165158 |
| 41 | H | -0.544715 | -1.753799 | -1.339787 |
| 42 | H | 0.82105 | -0.369169 | 0.108021 |

**DB3**

| # | Atom | X | Y | Z |
|---|---|---|---|---|
| 1 | C | -3.767125 | -0.316259 | 0.186337 |
| 2 | C | -3.514108 | 0.90246 | 0.809928 |
| 3 | C | -3.90832 | 2.098297 | 0.226311 |
| 4 | C | -4.56568 | 2.094038 | -0.995554 |
| 5 | C | -4.824887 | 0.885497 | -1.627766 |
| 6 | C | -4.42745 | -0.306389 | -1.040134 |
| 7 | H | -2.992705 | 0.910248 | 1.759988 |
| 8 | H | -3.70138 | 3.035771 | 0.727793 |
| 9 | H | -4.876072 | 3.025694 | -1.451707 |
| 10 | H | -5.340852 | 0.871083 | -2.579997 |
| 11 | H | -4.635221 | -1.246642 | -1.539326 |
| 12 | C | -3.300696 | -1.61277 | 0.795178 |
| 13 | H | -3.200925 | -1.495079 | 1.875198 |
| 14 | H | -4.05218 | -2.386327 | 0.623061 |
| 15 | C | -1.966921 | -2.095335 | 0.215657 |
| 16 | H | -1.729092 | -3.08086 | 0.632224 |
| 17 | H | -2.069508 | -2.227516 | -0.864988 |
| 18 | C | -0.796806 | -1.151148 | 0.478243 |
| 19 | C | 0.495551 | -1.705895 | -0.120547 |
| 20 | H | 0.940658 | -2.395918 | 0.603555 |
| 21 | H | 0.258611 | -2.299308 | -1.006363 |
| 22 | C | 1.574129 | -0.714042 | -0.542233 |
| 23 | H | 1.24606 | -0.173858 | -1.44295 |
| 24 | C | 1.954979 | 0.342398 | 0.500963 |
| 25 | H | 2.097636 | -0.150084 | 1.471127 |
| 26 | C | 3.243838 | 1.06123 | 0.124667 |
| 27 | H | 3.031989 | 1.685077 | -0.755535 |

| | | | | |
|---|---|---|---|---|
| 28 | C | 4.346739 | 0.097842 | -0.253624 |
| 29 | H | 4.625551 | -0.49664 | 0.623645 |
| 30 | C | 3.813641 | -0.825705 | -1.339761 |
| 31 | H | 3.561228 | -0.235675 | -2.231697 |
| 32 | H | 4.561008 | -1.568857 | -1.618501 |
| 33 | O | 2.691929 | -1.529651 | -0.862988 |
| 34 | O | 0.906845 | 1.288186 | 0.572427 |
| 35 | H | 1.162129 | 1.950827 | 1.218925 |
| 36 | O | 3.594951 | 1.883638 | 1.221218 |
| 37 | H | 4.393489 | 2.361933 | 0.983652 |
| 38 | O | 5.443892 | 0.871926 | -0.702557 |
| 39 | H | 6.236979 | 0.333 | -0.685915 |
| 40 | O | -0.652267 | -0.892746 | 1.871352 |
| 41 | H | -0.523081 | -1.734776 | 2.316028 |
| 42 | H | -1.018433 | -0.178236 | 0.040171 |

**DB4**

| # | Atom | X | Y | Z |
|---|---|---|---|---|
| 1 | C | -2.42523 | -0.00765 | -0.52919 |
| 2 | C | -2.18392 | -1.29937 | -0.07009 |
| 3 | C | -3.2263 | -2.11468 | 0.349953 |
| 4 | C | -4.53208 | -1.64889 | 0.315864 |
| 5 | C | -4.78701 | -0.36325 | -0.14313 |
| 6 | C | -3.7421 | 0.446822 | -0.56035 |
| 7 | H | -1.1684 | -1.679 | -0.03933 |
| 8 | H | -3.01592 | -3.11698 | 0.702286 |
| 9 | H | -5.34684 | -2.28349 | 0.640942 |
| 10 | H | -5.80378 | 0.008145 | -0.17886 |
| 11 | H | -3.94992 | 1.448388 | -0.92065 |
| 12 | C | -1.29524 | 0.894746 | -0.94685 |
| 13 | H | -0.41026 | 0.300226 | -1.17677 |
| 14 | H | -1.56118 | 1.416217 | -1.87027 |
| 15 | C | -0.96274 | 1.944944 | 0.119949 |
| 16 | H | -1.8041 | 2.63605 | 0.197489 |
| 17 | H | -0.86154 | 1.474812 | 1.10154 |
| 18 | C | 0.281606 | 2.771235 | -0.20827 |
| 19 | C | 1.569195 | 2.359984 | 0.514257 |
| 20 | H | 2.336398 | 3.088643 | 0.236353 |
| 21 | H | 1.411553 | 2.459117 | 1.590208 |
| 22 | C | 2.150052 | 0.977345 | 0.244989 |
| 23 | H | 3.199281 | 0.99282 | 0.576212 |
| 24 | C | 1.478233 | -0.16701 | 1.010819 |

| | | | | |
|---|---|---|---|---|
| 25 | H | 0.416105 | -0.21308 | 0.758201 |
| 26 | C | 2.101411 | -1.49672 | 0.623495 |
| 27 | H | 3.143777 | -1.5072 | 0.97271 |
| 28 | C | 2.106006 | -1.6688 | -0.88297 |
| 29 | H | 1.069402 | -1.73762 | -1.23352 |
| 30 | C | 2.773906 | -0.45596 | -1.52225 |
| 31 | H | 3.829987 | -0.42348 | -1.22133 |
| 32 | H | 2.725908 | -0.51966 | -2.60922 |
| 33 | O | 2.110723 | 0.730559 | -1.14898 |
| 34 | O | 1.633138 | 0.081609 | 2.392069 |
| 35 | H | 1.31463 | -0.69365 | 2.862341 |
| 36 | O | 1.362493 | -2.51085 | 1.275453 |
| 37 | H | 1.746106 | -3.3578 | 1.033553 |
| 38 | O | 2.804662 | -2.8655 | -1.16616 |
| 39 | H | 2.579572 | -3.16153 | -2.0502 |
| 40 | O | -0.0213 | 4.119188 | 0.155249 |
| 41 | H | 0.742887 | 4.666191 | -0.04096 |
| 42 | H | 0.453933 | 2.726332 | -1.28912 |

**DB5**

| # | Atom | X | Y | Z |
|---|---|---|---|---|
| 1 | C | -3.86344 | -0.40234 | 0.060083 |
| 2 | C | -3.78529 | 0.590768 | 1.03221 |
| 3 | C | -4.20972 | 1.885571 | 0.767018 |
| 4 | C | -4.7217 | 2.208472 | -0.48115 |
| 5 | C | -4.80664 | 1.226959 | -1.45962 |
| 6 | C | -4.38028 | -0.06457 | -1.1888 |
| 7 | H | -3.38056 | 0.344923 | 2.007446 |
| 8 | H | -4.14012 | 2.643394 | 1.537712 |
| 9 | H | -5.05496 | 3.217219 | -0.69021 |
| 10 | H | -5.20876 | 1.467998 | -2.43601 |
| 11 | H | -4.45129 | -0.82578 | -1.95815 |
| 12 | C | -3.36139 | -1.79631 | 0.331113 |
| 13 | H | -3.33684 | -1.97353 | 1.407044 |
| 14 | H | -4.05372 | -2.5228 | -0.10012 |
| 15 | C | -1.96674 | -2.0537 | -0.24954 |
| 16 | H | -1.68852 | -3.0957 | -0.0649 |
| 17 | H | -1.99244 | -1.91775 | -1.33408 |
| 18 | C | -0.88302 | -1.15347 | 0.319292 |
| 19 | C | 0.454202 | -1.40109 | -0.37176 |
| 20 | H | 0.729114 | -2.4522 | -0.25931 |
| 21 | H | 0.341755 | -1.20225 | -1.44162 |

| | | | | |
|---|---|---|---|---|
| 22 | C | 1.5879 | -0.55028 | 0.161967 |
| 23 | H | 1.720945 | -0.74697 | 1.238503 |
| 24 | C | 2.919963 | -0.84119 | -0.53879 |
| 25 | H | 2.78763 | -0.70358 | -1.61529 |
| 26 | C | 3.996247 | 0.120909 | -0.05083 |
| 27 | H | 4.186493 | -0.08136 | 1.014733 |
| 28 | C | 3.528044 | 1.557947 | -0.17451 |
| 29 | H | 3.402862 | 1.790604 | -1.23992 |
| 30 | C | 2.18456 | 1.707494 | 0.521903 |
| 31 | H | 2.310337 | 1.535456 | 1.599597 |
| 32 | H | 1.79291 | 2.713235 | 0.376259 |
| 33 | O | 1.240772 | 0.811764 | -0.01954 |
| 34 | O | 3.343093 | -2.18188 | -0.37539 |
| 35 | H | 3.413537 | -2.37402 | 0.564584 |
| 36 | O | 5.194865 | -0.01314 | -0.78646 |
| 37 | H | 5.45802 | -0.93699 | -0.75543 |
| 38 | O | 4.433943 | 2.459693 | 0.424092 |
| 39 | H | 5.303979 | 2.288131 | 0.054226 |
| 40 | O | -0.79608 | -1.40727 | 1.720273 |
| 41 | H | -0.45871 | -0.62302 | 2.155878 |
| 42 | H | -1.17054 | -0.10936 | 0.16365 |

**DB6**

| # | Atom | X | Y | Z |
|---|---|---|---|---|
| 1 | C | 3.701258 | 0.180996 | 0.357074 |
| 2 | C | 3.727133 | -0.94712 | 1.173277 |
| 3 | C | 4.595704 | -1.99702 | 0.912944 |
| 4 | C | 5.455876 | -1.93601 | -0.1747 |
| 5 | C | 5.439828 | -0.81775 | -0.9964 |
| 6 | C | 4.569368 | 0.229704 | -0.73036 |
| 7 | H | 3.058858 | -1.00118 | 2.025735 |
| 8 | H | 4.602919 | -2.86384 | 1.562305 |
| 9 | H | 6.136187 | -2.75323 | -0.3787 |
| 10 | H | 6.109294 | -0.75906 | -1.8458 |
| 11 | H | 4.564136 | 1.101416 | -1.37543 |
| 12 | C | 2.723785 | 1.295755 | 0.615454 |
| 13 | H | 2.549012 | 1.38909 | 1.690919 |
| 14 | H | 3.143874 | 2.243807 | 0.276099 |
| 15 | C | 1.386565 | 1.052375 | -0.08549 |
| 16 | H | 1.543915 | 0.973541 | -1.16757 |
| 17 | H | 0.978156 | 0.091337 | 0.233307 |
| 18 | C | 0.35671 | 2.139787 | 0.188619 |

| | | | | |
|---|---|---|---|---|
| 19 | C | -1.00579 | 1.873299 | -0.4486 |
| 20 | H | -1.64394 | 2.729017 | -0.22419 |
| 21 | H | -0.90397 | 1.816167 | -1.53733 |
| 22 | C | -1.70667 | 0.61303 | 0.027252 |
| 23 | H | -1.47092 | 0.437441 | 1.090885 |
| 24 | C | -3.23219 | 0.705661 | -0.10871 |
| 25 | H | -3.47774 | 0.928789 | -1.15044 |
| 26 | C | -3.87909 | -0.61838 | 0.2801 |
| 27 | H | -3.69951 | -0.78792 | 1.353367 |
| 28 | C | -3.25514 | -1.77173 | -0.48128 |
| 29 | H | -3.49163 | -1.65157 | -1.54639 |
| 30 | C | -1.7456 | -1.72612 | -0.30623 |
| 31 | H | -1.49212 | -1.90797 | 0.74709 |
| 32 | H | -1.27027 | -2.4954 | -0.91316 |
| 33 | O | -1.23626 | -0.48478 | -0.73658 |
| 34 | O | -3.78615 | 1.76436 | 0.649212 |
| 35 | H | -3.54828 | 1.64377 | 1.573515 |
| 36 | O | -5.26738 | -0.62367 | 0.01889 |
| 37 | H | -5.65398 | 0.137394 | 0.460419 |
| 38 | O | -3.71483 | -3.02085 | -0.01174 |
| 39 | H | -4.67537 | -3.00311 | -0.02752 |
| 40 | O | 0.831964 | 3.421719 | -0.20791 |
| 41 | H | 1.014034 | 3.395013 | -1.15119 |
| 42 | H | 0.218065 | 2.223347 | 1.27135 |

**DB7**

| # | Atom | X | Y | Z |
|---|---|---|---|---|
| 1 | C | 2.973505 | -0.13611 | 0.449475 |
| 2 | C | 2.817109 | -1.21587 | -0.417 |
| 3 | C | 3.89987 | -2.00262 | -0.77834 |
| 4 | C | 5.164133 | -1.71962 | -0.27799 |
| 5 | C | 5.333301 | -0.64605 | 0.583984 |
| 6 | C | 4.245027 | 0.138274 | 0.942671 |
| 7 | H | 1.831657 | -1.43672 | -0.81156 |
| 8 | H | 3.757272 | -2.84018 | -1.45011 |
| 9 | H | 6.010993 | -2.33395 | -0.55683 |
| 10 | H | 6.314935 | -0.41851 | 0.98111 |
| 11 | H | 4.384538 | 0.974456 | 1.61882 |
| 12 | C | 1.794006 | 0.728893 | 0.803031 |

| | | | | |
|---|---|---|---|---|
| 13 | H | 0.924406 | 0.09224 | 0.964872 |
| 14 | H | 1.989022 | 1.254508 | 1.740935 |
| 15 | C | 1.493752 | 1.757946 | -0.29079 |
| 16 | H | 2.355035 | 2.42537 | -0.37552 |
| 17 | H | 1.380543 | 1.250717 | -1.25283 |
| 18 | C | 0.265121 | 2.629323 | -0.01507 |
| 19 | C | -1.06286 | 2.072606 | -0.52984 |
| 20 | H | -1.83299 | 2.808147 | -0.29365 |
| 21 | H | -1.01983 | 1.984089 | -1.62081 |
| 22 | C | -1.50782 | 0.732682 | 0.02529 |
| 23 | H | -1.24118 | 0.661889 | 1.093207 |
| 24 | C | -3.02536 | 0.533744 | -0.09236 |
| 25 | H | -3.31379 | 0.653297 | -1.14011 |
| 26 | C | -3.41273 | -0.86516 | 0.372145 |
| 27 | H | -3.19827 | -0.94217 | 1.449636 |
| 28 | C | -2.59061 | -1.92055 | -0.34145 |
| 29 | H | -2.85296 | -1.90104 | -1.40705 |
| 30 | C | -1.1147 | -1.58801 | -0.19517 |
| 31 | H | -0.82137 | -1.66991 | 0.860875 |
| 32 | H | -0.51156 | -2.28652 | -0.77384 |
| 33 | O | -0.84555 | -0.29665 | -0.69079 |
| 34 | O | -3.76197 | 1.509191 | 0.61986 |
| 35 | H | -3.5131 | 1.472225 | 1.548421 |
| 36 | O | -4.77703 | -1.14175 | 0.133027 |
| 37 | H | -5.29684 | -0.44584 | 0.544253 |
| 38 | O | -2.8053 | -3.20729 | 0.196418 |
| 39 | H | -3.75228 | -3.37009 | 0.195266 |
| 40 | O | 0.445632 | 3.939175 | -0.54745 |
| 41 | H | 0.546362 | 3.86433 | -1.50006 |
| 42 | H | 0.182669 | 2.785328 | 1.064839 |

**DB8**

| # | Atom | X | Y | Z |
|---|---|---|---|---|
| 1 | C | -3.59617 | -0.26452 | -0.86901 |
| 2 | C | -4.55498 | -1.11986 | -0.32692 |
| 3 | C | -5.70699 | -0.61913 | 0.257662 |
| 4 | C | -5.92286 | 0.752225 | 0.312911 |
| 5 | C | -4.98043 | 1.614372 | -0.2252 |
| 6 | C | -3.8278 | 1.107654 | -0.81308 |
| 7 | H | -4.39199 | -2.19115 | -0.36275 |
| 8 | H | -6.43978 | -1.30007 | 0.67233 |
| 9 | H | -6.82203 | 1.144099 | 0.770933 |

| | | | | |
|---|---|---|---|---|
| 10 | H | -5.14005 | 2.684777 | -0.19053 |
| 11 | H | -3.09468 | 1.787923 | -1.23154 |
| 12 | C | -2.32226 | -0.81591 | -1.45664 |
| 13 | H | -2.56318 | -1.65686 | -2.11075 |
| 14 | H | -1.85313 | -0.05248 | -2.08192 |
| 15 | C | -1.30497 | -1.29262 | -0.41254 |
| 16 | H | -1.72611 | -2.10533 | 0.186695 |
| 17 | H | -0.449 | -1.70921 | -0.9488 |
| 18 | C | -0.81305 | -0.20926 | 0.547667 |
| 19 | C | 0.486619 | -0.6109 | 1.236639 |
| 20 | H | 0.60943 | 0.003101 | 2.13234 |
| 21 | H | 0.401924 | -1.64751 | 1.571142 |
| 22 | C | 1.722196 | -0.49989 | 0.352129 |
| 23 | H | 1.44004 | -0.61588 | -0.70517 |
| 24 | C | 2.45636 | 0.839342 | 0.496492 |
| 25 | H | 2.751493 | 0.96132 | 1.545173 |
| 26 | C | 3.707681 | 0.843004 | -0.3651 |
| 27 | H | 3.400529 | 0.775416 | -1.41877 |
| 28 | C | 4.573871 | -0.35918 | -0.04298 |
| 29 | H | 4.943825 | -0.25168 | 0.984886 |
| 30 | C | 3.736271 | -1.62554 | -0.13523 |
| 31 | H | 3.429726 | -1.78215 | -1.17853 |
| 32 | H | 4.319421 | -2.48731 | 0.186443 |
| 33 | O | 2.608389 | -1.54952 | 0.707214 |
| 34 | O | 1.667877 | 1.938536 | 0.075311 |
| 35 | H | 1.126424 | 2.242814 | 0.805722 |
| 36 | O | 4.483857 | 2.006226 | -0.16284 |
| 37 | H | 3.919677 | 2.765154 | -0.33443 |
| 38 | O | 5.653305 | -0.48497 | -0.94366 |
| 39 | H | 6.11843 | 0.355607 | -0.96032 |
| 40 | O | -1.74691 | 0.043957 | 1.592777 |
| 41 | H | -2.58715 | 0.290815 | 1.195541 |
| 42 | H | -0.64695 | 0.715959 | -0.01897 |

**DB9**

| # | Atom | X | Y | Z |
|---|---|---|---|---|
| 1 | C | 3.673742 | -0.21094 | 0.147739 |
| 2 | C | 4.604789 | -0.45109 | -0.85843 |
| 3 | C | 5.499575 | 0.534184 | -1.25256 |
| 4 | C | 5.474692 | 1.780965 | -0.6445 |
| 5 | C | 4.549931 | 2.033482 | 0.359813 |
| 6 | C | 3.659052 | 1.044894 | 0.750244 |

| | | | | |
|---|---|---|---|---|
| 7 | H | 4.630904 | -1.42358 | -1.33747 |
| 8 | H | 6.219068 | 0.326271 | -2.03498 |
| 9 | H | 6.172914 | 2.550448 | -0.94893 |
| 10 | H | 4.524237 | 3.002731 | 0.842451 |
| 11 | H | 2.939289 | 1.248566 | 1.535553 |
| 12 | C | 2.671933 | -1.26125 | 0.545698 |
| 13 | H | 3.07156 | -2.25556 | 0.329021 |
| 14 | H | 2.495045 | -1.21336 | 1.621228 |
| 15 | C | 1.343233 | -1.08054 | -0.19 |
| 16 | H | 0.946181 | -0.08529 | 0.020901 |
| 17 | H | 1.517584 | -1.13145 | -1.2675 |
| 18 | C | 0.313973 | -2.14601 | 0.15849 |
| 19 | C | -0.99634 | -2.01673 | -0.62822 |
| 20 | H | -0.75946 | -1.65945 | -1.63312 |
| 21 | H | -1.43319 | -3.0103 | -0.74881 |
| 22 | C | -2.12538 | -1.13669 | -0.0815 |
| 23 | H | -2.54297 | -1.58718 | 0.831522 |
| 24 | C | -1.75403 | 0.318738 | 0.262977 |
| 25 | H | -1.17224 | 0.736734 | -0.57081 |
| 26 | C | -2.99848 | 1.178434 | 0.445033 |
| 27 | H | -3.48044 | 0.863691 | 1.382105 |
| 28 | C | -4.00008 | 0.980093 | -0.67424 |
| 29 | H | -3.56777 | 1.348864 | -1.61121 |
| 30 | C | -4.29378 | -0.50415 | -0.8116 |
| 31 | H | -4.74727 | -0.88112 | 0.115362 |
| 32 | H | -4.98309 | -0.69173 | -1.63503 |
| 33 | O | -3.10171 | -1.19109 | -1.10943 |
| 34 | O | -1.01507 | 0.406875 | 1.463825 |
| 35 | H | -0.61783 | -0.45581 | 1.665673 |
| 36 | O | -2.60074 | 2.531176 | 0.539138 |
| 37 | H | -3.40644 | 3.056119 | 0.550349 |
| 38 | O | -5.15334 | 1.727488 | -0.33061 |
| 39 | H | -5.67295 | 1.886755 | -1.12064 |
| 40 | O | 0.099341 | -2.10444 | 1.574182 |
| 41 | H | -0.44986 | -2.84765 | 1.834518 |
| 42 | H | 0.75194 | -3.11828 | -0.09074 |

**DB10**

| # | Atom | X | Y | Z |
|---|---|---|---|---|
| 1 | C | -2.01762 | -1.56247 | -0.02527 |
| 2 | C | -1.48471 | -2.04159 | -1.21624 |
| 3 | C | -0.42146 | -2.93514 | -1.2169 |

| | | | | |
|---|---|---|---|---|
| 4 | C | 0.119498 | -3.37461 | -0.01902 |
| 5 | C | -0.42123 | -2.92597 | 1.179164 |
| 6 | C | -1.47996 | -2.03285 | 1.17222 |
| 7 | H | -1.89653 | -1.7031 | -2.16025 |
| 8 | H | -0.01339 | -3.28318 | -2.15765 |
| 9 | H | 0.953464 | -4.06491 | -0.01689 |
| 10 | H | -0.01264 | -3.26916 | 2.121427 |
| 11 | H | -1.88638 | -1.68008 | 2.113625 |
| 12 | C | -3.13032 | -0.54201 | -0.00105 |
| 13 | H | -3.51857 | -0.39243 | -1.01161 |
| 14 | H | -3.95587 | -0.95163 | 0.58457 |
| 15 | C | -2.73715 | 0.810597 | 0.618854 |
| 16 | H | -3.61036 | 1.243955 | 1.109731 |
| 17 | H | -1.99431 | 0.655272 | 1.402278 |
| 18 | C | -2.25014 | 1.866658 | -0.37277 |
| 19 | C | -1.09244 | 1.497488 | -1.30099 |
| 20 | H | -1.28008 | 0.499299 | -1.69461 |
| 21 | H | -1.12593 | 2.169849 | -2.16168 |
| 22 | C | 0.359373 | 1.512077 | -0.80323 |
| 23 | H | 0.743238 | 2.543326 | -0.79657 |
| 24 | C | 0.618277 | 0.929348 | 0.592984 |
| 25 | H | 0.106509 | -0.03627 | 0.675663 |
| 26 | C | 2.104264 | 0.693333 | 0.822161 |
| 27 | H | 2.600527 | 1.672733 | 0.869546 |
| 28 | C | 2.723587 | -0.08978 | -0.31264 |
| 29 | H | 2.254963 | -1.08191 | -0.36128 |
| 30 | C | 2.436378 | 0.654412 | -1.60417 |
| 31 | H | 2.912995 | 1.643801 | -1.57261 |
| 32 | H | 2.832418 | 0.106882 | -2.45869 |
| 33 | O | 1.047336 | 0.767345 | -1.79886 |
| 34 | O | 0.206608 | 1.8003 | 1.630666 |
| 35 | H | -0.54395 | 2.339264 | 1.331463 |
| 36 | O | 2.335806 | -0.01739 | 2.024601 |
| 37 | H | 1.972125 | 0.500052 | 2.74756 |
| 38 | O | 4.122664 | -0.20793 | -0.16387 |
| 39 | H | 4.291323 | -0.51004 | 0.732869 |
| 40 | O | -1.95456 | 3.030528 | 0.410765 |
| 41 | H | -1.75088 | 3.762859 | -0.17652 |
| 42 | H | -3.09968 | 2.095686 | -1.02549 |

*b. Procedure for calculating NMRs*

To calculate NMR shifts for each of the diastereomers, following the procedure by Smith and Goodman[8], we have averaged the shielding constants in each conformer using Boltzmann averaging over the conformers *i* using following equation:

$$\sigma^x = \frac{\sum_i \sigma_i^x \exp(-E_i/RT)}{\sum_i \exp(-E_i/RT)}$$

where $\sigma^x$ is the Boltzmann averaged shielding constant for nucleus *x*, $\sigma_i^x$ is the shielding constant for nucleus *x* in conformer *i*, and E is the potential energy of conformer *i* (relative to the global minimum), obtained from the calculation. The temperature T was taken as 298 K.

Averaged shielding constants for each nuclei of the two diastereomers were then scaled using following equation:

$$\delta_{scaled} = \frac{\sigma_{calc} - intercept}{slope}$$

where the slope and intercept (Table S4) were obtained from a plot of the calculated *vs* experimental data for a test set of molecules used by Pierens[14].

**Table S4**. Intercept and slope values calculated for the test set of molecules[14] using ωB97XD/def2TZVP method in methanol.

| | ***intercept*** | ***slope*** | ***R*** |
|---|---|---|---|
| ***$^1$H*** | 32.041 | -1.081 | 0.9947 |
| ***$^{13}$C*** | 188.78 | -1.048 | 0.9987 |

**Table S5.** NMR shielding constants calculated using GIAO method with ωB97XD/def2TZVP in methanol for the conformers of DA with scaled values

| | | DA1 | DA2 | DA3 | DA4 | DA5 | DA6 | DA7 | DA8 | DA9 | DA10 | $\overline{DA}$ | Scaled |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | C | 35.418 | 35.213 | 35.710 | 35.068 | 35.296 | 35.880 | 34.978 | 34.336 | 34.980 | 35.019 | 35.210 | 146.550 |
| 2 | C | 53.531 | 53.380 | 53.265 | 53.419 | 53.510 | 53.200 | 53.242 | 52.479 | 53.239 | 53.696 | 53.323 | 129.265 |
| 3 | C | 53.269 | 53.310 | 53.227 | 53.274 | 53.276 | 53.174 | 53.344 | 54.067 | 53.344 | 53.364 | 53.352 | 129.237 |
| 4 | C | 56.806 | 56.866 | 56.696 | 56.912 | 56.773 | 56.658 | 56.920 | 57.624 | 56.920 | 56.874 | 56.893 | 125.858 |
| 5 | C | 53.234 | 53.253 | 53.152 | 53.291 | 53.169 | 53.312 | 53.190 | 54.041 | 53.190 | 53.452 | 53.314 | 129.274 |
| 6 | C | 53.132 | 53.224 | 53.372 | 53.205 | 53.067 | 53.392 | 53.299 | 54.199 | 53.301 | 53.083 | 53.302 | 129.285 |
| 7 | H | 24.218 | 24.207 | 24.210 | 24.212 | 24.206 | 24.164 | 24.209 | 24.219 | 24.209 | 24.215 | 24.208 | 7.249 |
| 8 | H | 24.118 | 24.117 | 24.117 | 24.112 | 24.111 | 24.100 | 24.126 | 24.224 | 24.126 | 24.131 | 24.126 | 7.324 |
| 9 | H | 24.254 | 24.256 | 24.245 | 24.254 | 24.240 | 24.242 | 24.259 | 24.331 | 24.259 | 24.258 | 24.259 | 7.202 |
| 10 | H | 24.117 | 24.118 | 24.104 | 24.118 | 24.095 | 24.118 | 24.111 | 24.143 | 24.111 | 24.107 | 24.115 | 7.335 |
| 11 | H | 24.181 | 24.183 | 24.200 | 24.184 | 24.153 | 24.206 | 24.203 | 24.140 | 24.203 | 24.122 | 24.178 | 7.276 |
| 12 | C | 151.360 | 151.625 | 157.817 | 150.687 | 151.524 | 151.978 | 156.559 | 149.623 | 156.559 | 152.913 | 152.801 | 34.334 |
| 13 | H | 28.812 | 28.857 | 29.309 | 28.772 | 28.772 | 29.368 | 29.281 | 29.281 | 29.280 | 29.525 | 29.077 | 2.743 |
| 14 | H | 29.341 | 29.391 | 29.328 | 29.410 | 29.367 | 29.302 | 29.011 | 28.797 | 29.011 | 28.949 | 29.220 | 2.611 |
| 15 | C | 140.036 | 141.652 | 142.654 | 143.498 | 143.913 | 142.647 | 143.517 | 146.063 | 143.522 | 146.041 | 142.937 | 43.748 |
| 16 | H | 30.241 | 30.407 | 30.095 | 30.335 | 30.017 | 30.483 | 30.163 | 30.133 | 30.163 | 30.204 | 30.241 | 1.666 |
| 17 | H | 30.645 | 30.418 | 30.298 | 30.251 | 30.775 | 30.212 | 30.313 | 29.999 | 30.313 | 30.229 | 30.376 | 1.541 |
| 18 | C | 114.962 | 111.499 | 116.847 | 115.453 | 115.309 | 110.637 | 112.987 | 108.473 | 112.988 | 114.429 | 113.334 | 71.998 |
| 19 | H | 27.837 | 27.956 | 27.677 | 28.240 | 28.139 | 27.984 | 27.802 | 27.907 | 27.802 | 27.866 | 27.917 | 3.816 |
| 20 | C | 139.021 | 146.634 | 141.975 | 141.124 | 144.145 | 149.039 | 149.373 | 146.294 | 149.371 | 149.873 | 145.215 | 41.574 |
| 21 | H | 30.062 | 29.972 | 29.943 | 30.044 | 30.242 | 29.466 | 29.852 | 29.986 | 29.851 | 29.804 | 29.938 | 1.946 |
| 22 | H | 30.479 | 30.556 | 30.175 | 29.918 | 30.068 | 30.654 | 30.234 | 30.588 | 30.234 | 30.002 | 30.329 | 1.585 |
| 23 | C | 109.999 | 102.739 | 109.250 | 109.816 | 108.624 | 102.576 | 102.628 | 102.749 | 102.633 | 110.445 | 106.177 | 78.827 |
| 24 | H | 28.259 | 28.394 | 28.356 | 28.525 | 28.776 | 28.398 | 28.427 | 28.467 | 28.427 | 28.249 | 28.411 | 3.359 |
| 25 | C | 107.099 | 110.986 | 107.017 | 109.583 | 110.141 | 110.869 | 110.822 | 111.002 | 110.822 | 111.855 | 109.859 | 75.313 |
| 26 | H | 28.532 | 28.653 | 28.509 | 28.573 | 28.702 | 28.570 | 28.567 | 28.707 | 28.567 | 28.597 | 28.597 | 3.187 |
| 27 | C | 106.158 | 106.512 | 106.201 | 106.661 | 106.215 | 106.495 | 106.490 | 106.578 | 106.487 | 105.784 | 106.355 | 78.658 |
| 28 | H | 28.426 | 28.474 | 28.430 | 28.478 | 28.565 | 28.448 | 28.458 | 28.522 | 28.458 | 28.425 | 28.465 | 3.309 |
| 29 | C | 112.925 | 113.609 | 112.911 | 113.319 | 113.175 | 113.605 | 113.570 | 113.712 | 113.568 | 112.977 | 113.326 | 72.005 |
| 30 | H | 28.328 | 28.291 | 28.297 | 28.325 | 28.324 | 28.276 | 28.273 | 28.380 | 28.273 | 28.215 | 28.300 | 3.462 |
| 31 | C | 114.715 | 115.319 | 114.671 | 115.141 | 114.912 | 115.341 | 115.300 | 115.446 | 115.300 | 115.403 | 115.132 | 70.281 |
| 32 | H | 28.661 | 28.606 | 28.643 | 28.801 | 28.766 | 28.603 | 28.613 | 28.715 | 28.613 | 28.578 | 28.656 | 3.133 |
| 33 | H | 28.097 | 27.983 | 28.060 | 28.131 | 28.038 | 27.990 | 27.980 | 28.140 | 27.980 | 27.805 | 28.024 | 3.718 |
| 34 | O | 276.811 | 278.871 | 276.281 | 277.675 | 283.299 | 278.289 | 279.229 | 279.458 | 279.237 | 276.586 | 278.453 | |
| 35 | O | 301.618 | 301.084 | 301.983 | 291.476 | 301.318 | 300.815 | 301.059 | 301.024 | 301.050 | 300.357 | 300.372 | |
| 36 | H | 29.729 | 29.858 | 29.777 | 29.046 | 29.909 | 29.776 | 29.799 | 29.865 | 29.799 | 29.808 | 29.746 | 2.124 |
| 37 | O | 300.850 | 300.417 | 300.873 | 300.742 | 300.338 | 300.365 | 300.366 | 300.389 | 300.358 | 299.661 | 300.468 | |
| 38 | H | 29.601 | 29.571 | 29.604 | 29.576 | 29.616 | 29.541 | 29.544 | 29.595 | 29.545 | 29.538 | 29.575 | 2.282 |
| 39 | O | 304.728 | 305.014 | 304.747 | 304.758 | 304.725 | 305.172 | 305.120 | 305.157 | 305.102 | 304.579 | 304.904 | |
| 40 | H | 30.635 | 30.571 | 30.618 | 30.644 | 30.627 | 30.557 | 30.558 | 30.632 | 30.559 | 30.529 | 30.595 | 1.339 |
| 41 | O | 282.471 | 279.035 | 286.101 | 279.502 | 276.535 | 274.885 | 281.411 | 273.449 | 281.411 | 276.442 | 279.392 | |
| 42 | H | 32.235 | 28.324 | 31.349 | 27.673 | 31.870 | 28.450 | 28.669 | 28.895 | 28.668 | 31.472 | 29.844 | 2.033 |

**Table S6**. NMR shielding constants calculated using GIAO method with ωB97XD/def2TZVP in methanol for the conformers of DB with scaled values

| | | DB1 | DB2 | DB3 | DB4 | DB5 | DB6 | DB7 | DB8 | DB9 | DB10 | $\overline{DB}$ | Scaled |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | C | 35.378 | 37.066 | 37.182 | 36.493 | 37.026 | 35.188 | 35.626 | 37.046 | 35.872 | 35.128 | 36.201 | 145.604 |
| 2 | C | 53.148 | 51.512 | 51.328 | 53.741 | 51.678 | 53.093 | 53.216 | 52.440 | 53.377 | 50.930 | 52.445 | 130.103 |
| 3 | C | 53.226 | 53.971 | 54.066 | 53.142 | 53.949 | 53.193 | 53.405 | 52.142 | 53.203 | 53.312 | 53.361 | 129.229 |
| 4 | C | 56.839 | 56.663 | 56.721 | 56.463 | 56.662 | 56.841 | 56.722 | 55.411 | 56.681 | 55.964 | 56.497 | 126.237 |
| 5 | C | 53.300 | 53.152 | 53.235 | 53.087 | 53.096 | 53.296 | 53.284 | 52.267 | 53.243 | 52.120 | 53.008 | 129.566 |
| 6 | C | 53.497 | 53.307 | 53.356 | 53.065 | 53.360 | 53.605 | 53.711 | 53.672 | 53.184 | 51.642 | 53.240 | 129.345 |
| 7 | H | 24.183 | 24.059 | 24.082 | 23.967 | 24.137 | 24.157 | 24.091 | 24.040 | 24.195 | 24.223 | 24.113 | 7.336 |
| 8 | H | 24.118 | 24.116 | 24.150 | 24.121 | 24.138 | 24.100 | 24.102 | 24.015 | 24.116 | 24.144 | 24.112 | 7.338 |
| 9 | H | 24.256 | 24.231 | 24.246 | 24.232 | 24.241 | 24.248 | 24.252 | 24.165 | 24.240 | 24.208 | 24.232 | 7.227 |
| 10 | H | 24.117 | 24.087 | 24.093 | 24.082 | 24.089 | 24.118 | 24.127 | 24.072 | 24.092 | 24.019 | 24.090 | 7.358 |
| 11 | H | 24.218 | 24.191 | 24.197 | 24.147 | 24.190 | 24.220 | 24.196 | 24.129 | 24.161 | 24.010 | 24.166 | 7.288 |
| 12 | C | 151.244 | 154.774 | 154.385 | 151.544 | 154.244 | 151.070 | 151.570 | 149.957 | 151.447 | 155.040 | 152.530 | 34.593 |
| 13 | H | 29.366 | 28.967 | 28.926 | 28.913 | 28.878 | 29.368 | 29.156 | 28.782 | 29.420 | 29.555 | 29.133 | 2.691 |
| 14 | H | 28.862 | 29.138 | 29.169 | 29.123 | 29.104 | 28.823 | 29.352 | 29.289 | 28.797 | 28.744 | 29.040 | 2.777 |
| 15 | C | 138.919 | 145.718 | 143.272 | 144.909 | 147.124 | 141.593 | 139.987 | 147.007 | 143.772 | 150.505 | 144.286 | 42.461 |
| 16 | H | 30.475 | 30.164 | 30.214 | 29.958 | 30.163 | 30.734 | 30.114 | 30.371 | 29.580 | 29.580 | 30.135 | 1.763 |
| 17 | H | 30.327 | 30.552 | 30.419 | 30.221 | 30.451 | 29.889 | 30.118 | 29.731 | 30.424 | 29.818 | 30.195 | 1.708 |
| 18 | C | 116.779 | 121.735 | 121.637 | 116.042 | 122.481 | 110.833 | 112.337 | 113.397 | 114.781 | 112.965 | 116.302 | 69.165 |
| 19 | C | 138.613 | 150.169 | 139.272 | 147.005 | 145.128 | 145.416 | 144.005 | 142.856 | 144.150 | 149.632 | 144.633 | 42.129 |
| 20 | H | 30.632 | 30.159 | 30.662 | 29.954 | 30.056 | 29.418 | 29.323 | 30.263 | 30.460 | 30.013 | 30.093 | 1.802 |
| 21 | H | 29.940 | 30.421 | 30.087 | 29.850 | 30.851 | 30.735 | 30.589 | 30.391 | 29.429 | 29.742 | 30.204 | 1.700 |
| 22 | C | 107.873 | 104.470 | 108.024 | 107.530 | 108.929 | 106.129 | 107.086 | 108.304 | 108.536 | 109.096 | 107.595 | 77.474 |
| 23 | H | 28.550 | 28.555 | 28.869 | 28.412 | 28.735 | 28.993 | 28.745 | 28.991 | 28.414 | 28.757 | 28.702 | 3.090 |
| 24 | C | 110.682 | 113.472 | 110.884 | 114.787 | 108.429 | 109.517 | 109.309 | 105.870 | 111.256 | 113.993 | 110.820 | 74.397 |
| 25 | H | 28.253 | 28.626 | 28.329 | 27.774 | 29.090 | 29.056 | 28.949 | 28.654 | 28.581 | 30.173 | 28.749 | 3.046 |
| 26 | C | 104.871 | 106.394 | 104.967 | 105.426 | 103.714 | 103.615 | 103.618 | 106.144 | 104.940 | 103.431 | 104.712 | 80.225 |
| 27 | H | 28.450 | 28.588 | 28.596 | 28.427 | 28.678 | 28.663 | 28.598 | 28.484 | 28.449 | 28.884 | 28.582 | 3.201 |
| 28 | C | 113.595 | 114.365 | 113.632 | 113.052 | 114.066 | 114.146 | 114.153 | 113.971 | 113.336 | 115.879 | 114.021 | 71.342 |
| 29 | H | 28.353 | 28.259 | 28.406 | 27.858 | 28.362 | 28.315 | 28.103 | 28.247 | 28.427 | 29.156 | 28.349 | 3.417 |
| 30 | C | 116.126 | 116.255 | 116.190 | 114.735 | 116.707 | 117.078 | 116.786 | 116.052 | 116.120 | 117.398 | 116.345 | 69.124 |
| 31 | H | 28.749 | 28.717 | 28.862 | 28.627 | 28.744 | 28.770 | 28.569 | 28.627 | 28.745 | 28.997 | 28.741 | 3.054 |
| 32 | H | 28.165 | 27.914 | 28.221 | 27.938 | 28.109 | 28.181 | 27.676 | 27.972 | 28.167 | 28.303 | 28.064 | 3.680 |
| 33 | O | 277.171 | 280.739 | 277.358 | 280.987 | 283.220 | 276.278 | 278.248 | 276.673 | 276.848 | 279.114 | 278.667 | |
| 34 | O | 294.824 | 304.884 | 294.746 | 300.218 | 299.916 | 297.959 | 297.636 | 305.825 | 285.610 | 292.277 | 297.399 | |
| 35 | H | 29.877 | 30.981 | 30.015 | 29.816 | 31.930 | 31.823 | 31.781 | 30.291 | 26.828 | 27.175 | 30.054 | 1.839 |
| 36 | O | 299.772 | 300.740 | 299.797 | 299.262 | 300.016 | 299.231 | 299.204 | 301.272 | 296.751 | 302.594 | 299.866 | |
| 37 | H | 29.592 | 29.696 | 29.653 | 29.393 | 29.609 | 29.591 | 29.544 | 29.513 | 29.600 | 30.062 | 29.625 | 2.236 |
| 38 | O | 304.195 | 303.840 | 304.278 | 303.703 | 303.586 | 303.334 | 303.135 | 303.304 | 304.996 | 306.911 | 304.128 | |
| 39 | H | 30.626 | 29.994 | 30.674 | 30.479 | 30.069 | 30.054 | 29.958 | 29.998 | 30.603 | 30.209 | 30.266 | 1.643 |
| 40 | O | 269.833 | 282.227 | 271.289 | 270.523 | 298.437 | 272.454 | 257.246 | 269.539 | 278.286 | 270.583 | 274.059 | |
| 41 | H | 32.160 | 28.700 | 32.205 | 31.558 | 30.741 | 31.797 | 31.325 | 32.164 | 30.295 | 30.491 | 31.141 | 0.833 |
| 42 | H | 27.882 | 28.324 | 28.323 | 27.945 | 28.435 | 28.398 | 28.450 | 27.975 | 27.673 | 27.736 | 28.114 | 3.634 |

*c. Calculation of the CP3 and the probability parameters*

Using the applet available at http://www-jmg.ch.cam.ac.uk/tools/nmr/ we have calculated the values of the CP3 parameter and corresponding probability for the assignment of the pair of diastereoisomers developed by Smith and Goodman[8]. The CP3 parameter is based on comparing differences in experimental and calculated NMR shifts and combined with Bayes' theorem to obtain quantifiable confidence of diastereomer assignment. Values for the CP3 parameter obtained from the applet are shown in Table S7.

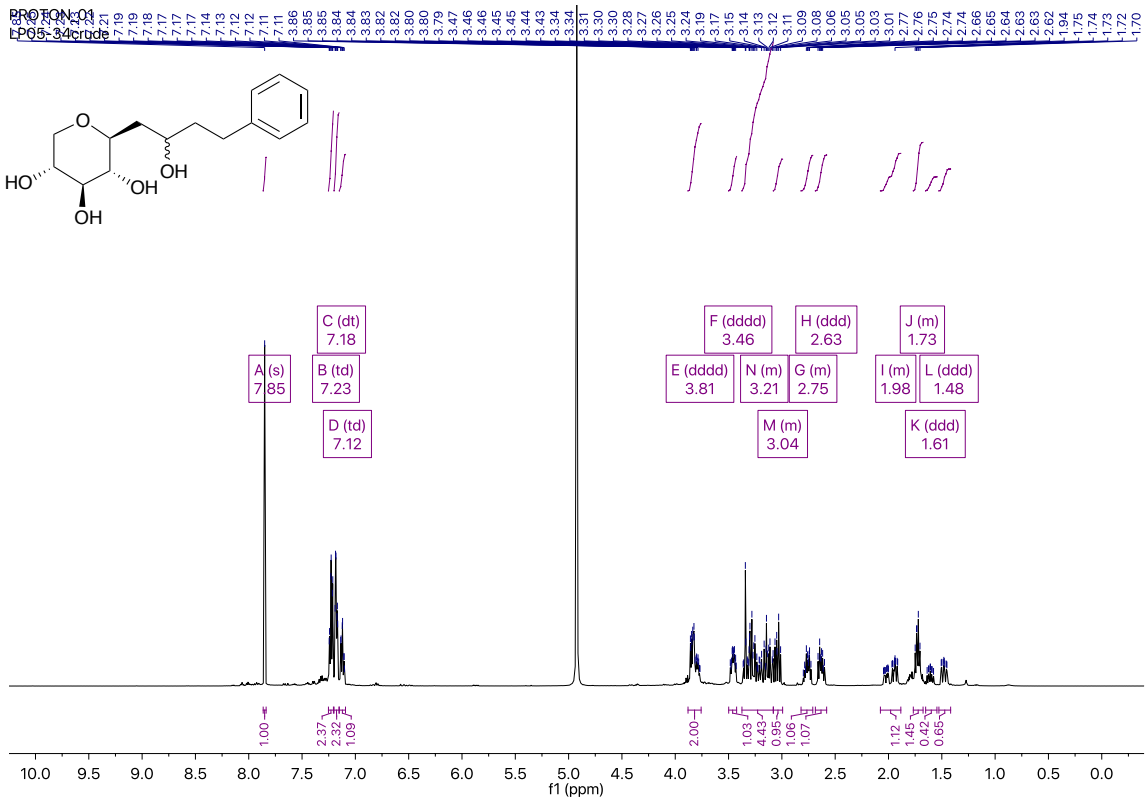
**Table S7**. CP3 parameter and the probability factor obtained from the Smith and Goodman calculations.

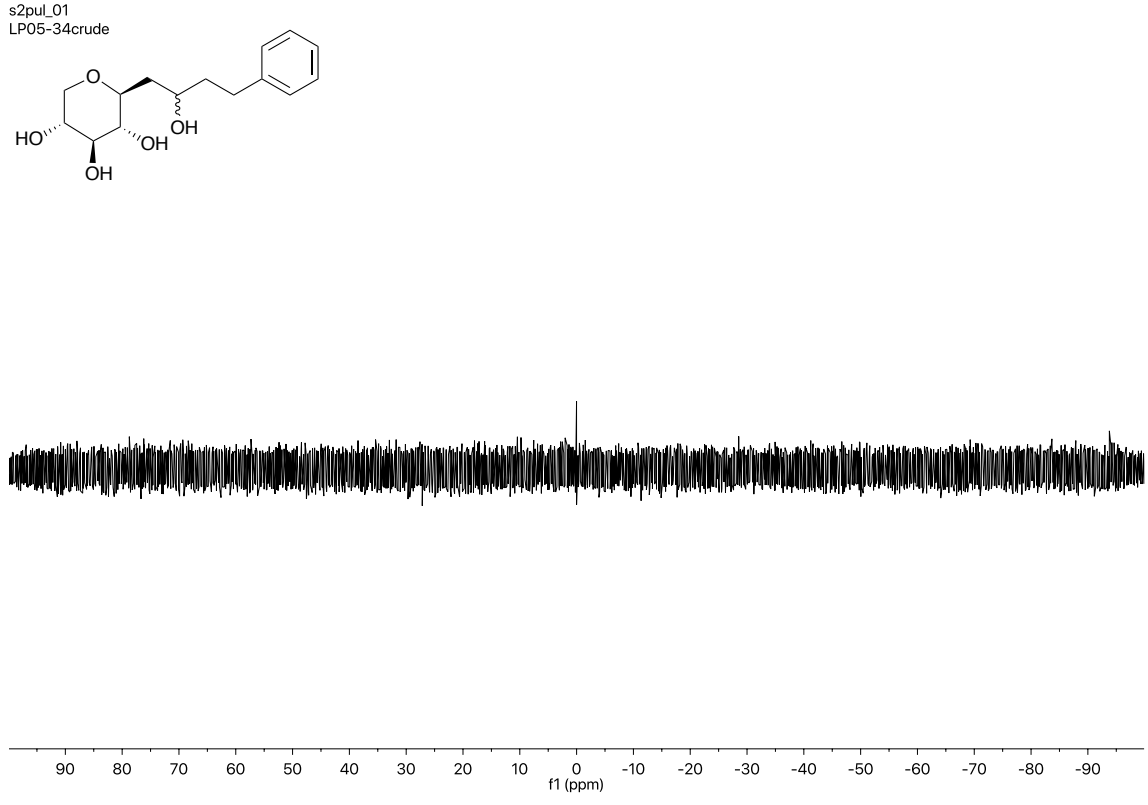
| ***CP3*** | ***C data*** | ***H data*** | ***All data*** |
|---|---|---|---|
| ***3a-DA & 3a'-DB*** | 0.36 | 0.29 | 0.33 |
| ***3a-DB & 3a'-DA*** | -0.57 | -0.45 | -0.51 |
| ***probability*** | | | |
| ***3a-DA & 3a'-DB*** | 100.0% | 98.3% | 100.0% |
| ***3a-DB & 3a'-DA*** | 0.0% | 1.7% | 0.0% |

## 3. NMRs

*a. $^{1}H$ and $^{11}B$ NMRs of crude reaction mixtures (Schemes 3-5)*

All of the following NMRs are taken in MeOD using quartz NMR tubes unless otherwise reported, and use $CHCl_3$ as internal standard (1 equivalent).


PROTON-01
LP05-34crude
HO
OH
OH
OH
A (s) 7.85
B (td) 7.23
C (dt) 7.18
D (td) 7.12
E (dddd) 3.81
F (dddd) 3.46
G (m) 2.75
H (ddd) 2.63
I (m) 1.98
J (m) 1.73
K (ddd) 1.61
L (ddd) 1.48
M (m) 3.04
N (m) 3.21
1.00
2.37
2.32
1.09
2.00
1.03
4.43
0.95
1.06
1.07
1.12
1.45
0.42
0.65
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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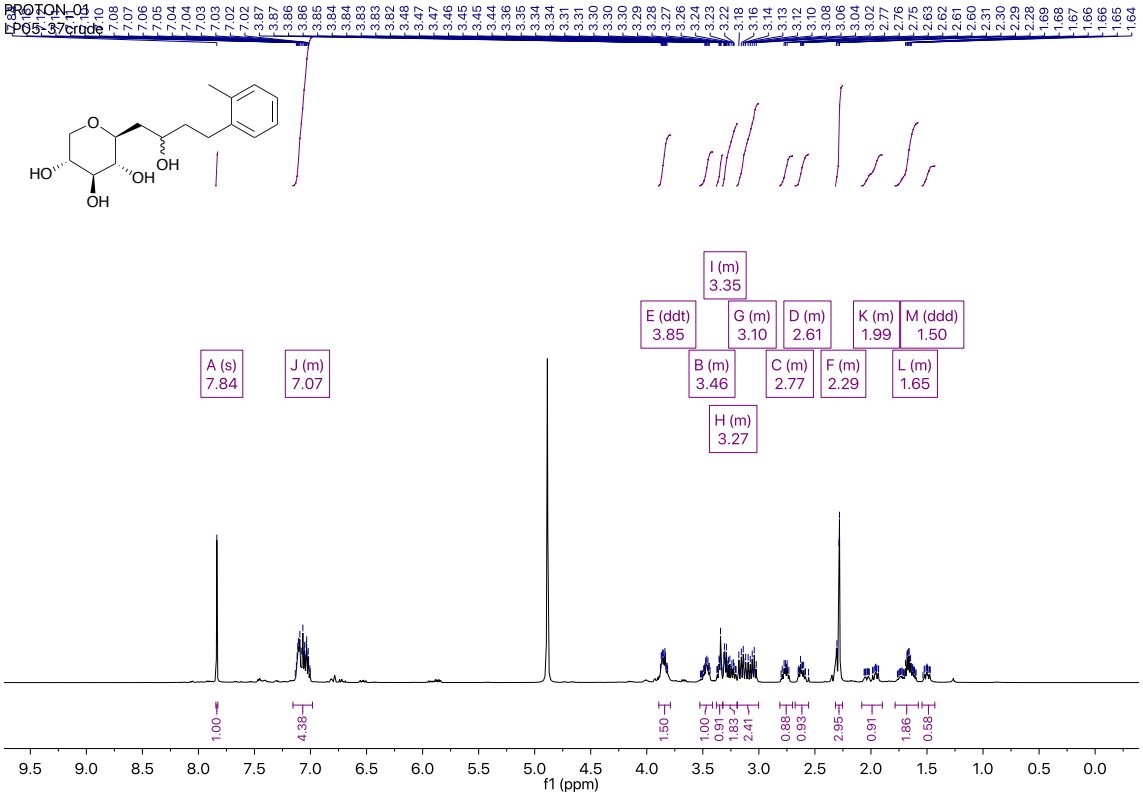
LP05-34crude
HO
OH
OH
OH
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)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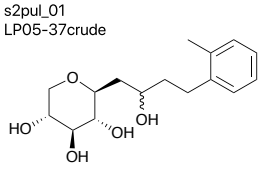
LP05-37crude
HO
OH
OH
OH
I (m)
3.35
E (ddt)
3.85
G (m)
3.10
D (m)
2.61
K (m)
1.99
M (ddd)
1.50
A (s)
7.84
J (m)
7.07
B (m)
3.46
C (m)
2.77
F (m)
2.29
L (m)
1.65
H (m)
3.27
1.00
4.38
1.50
1.00
0.91
1.83
2.41
0.88
0.93
2.95
0.91
1.86
0.58
f1 (ppm)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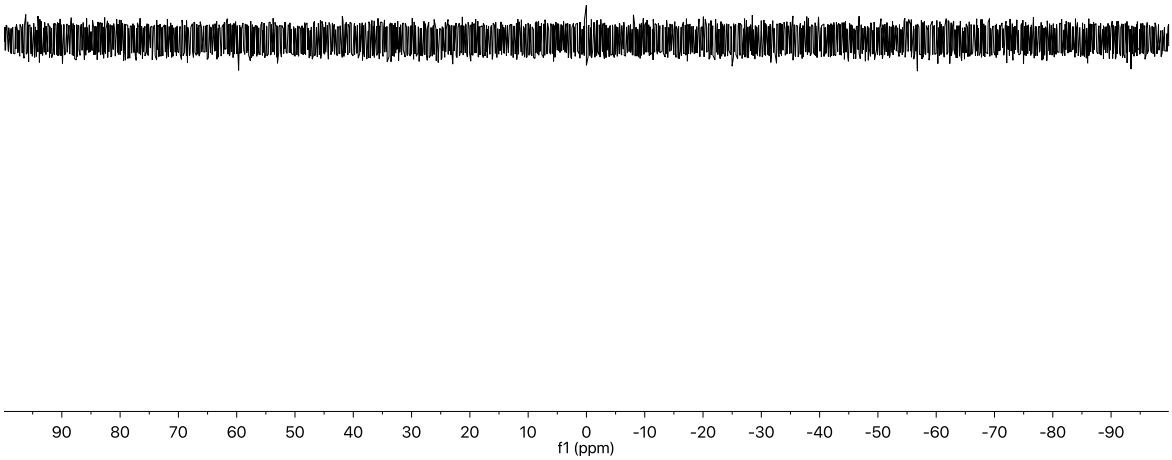
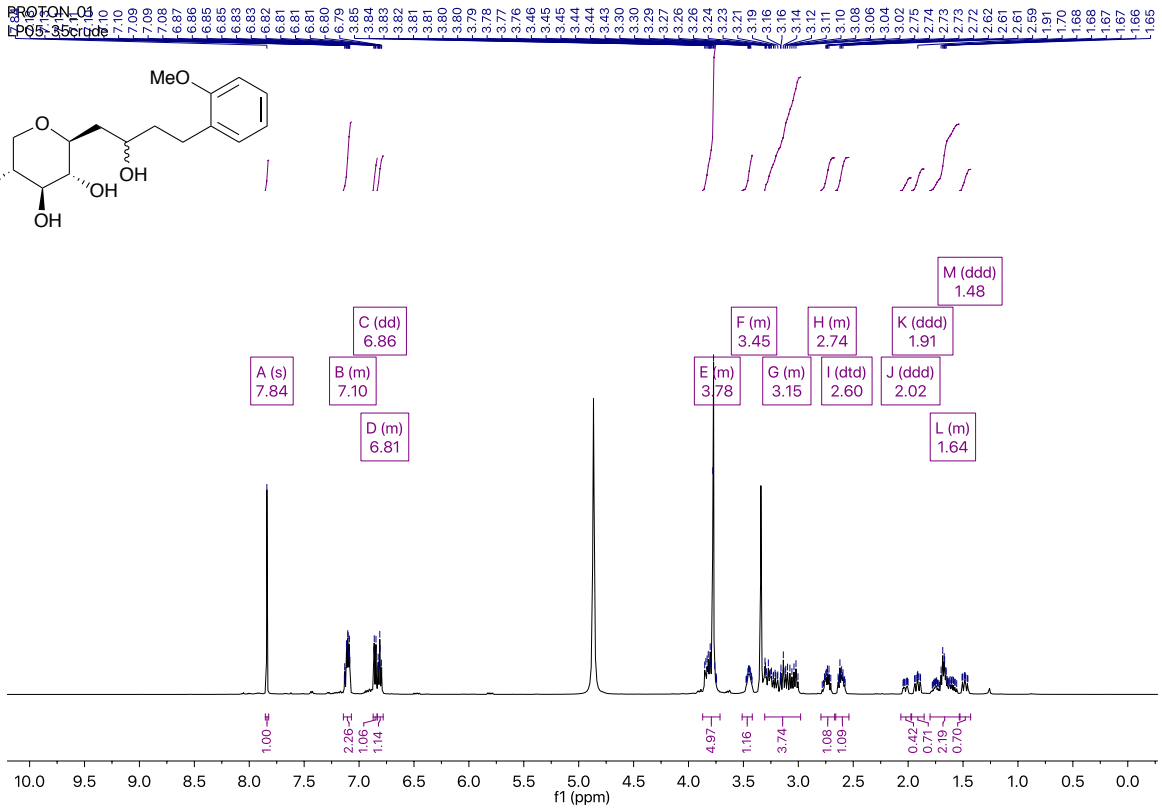
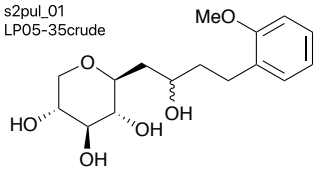
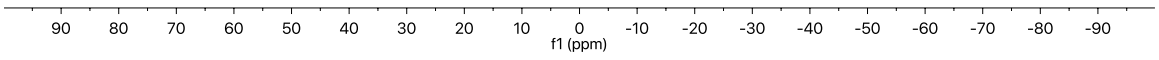
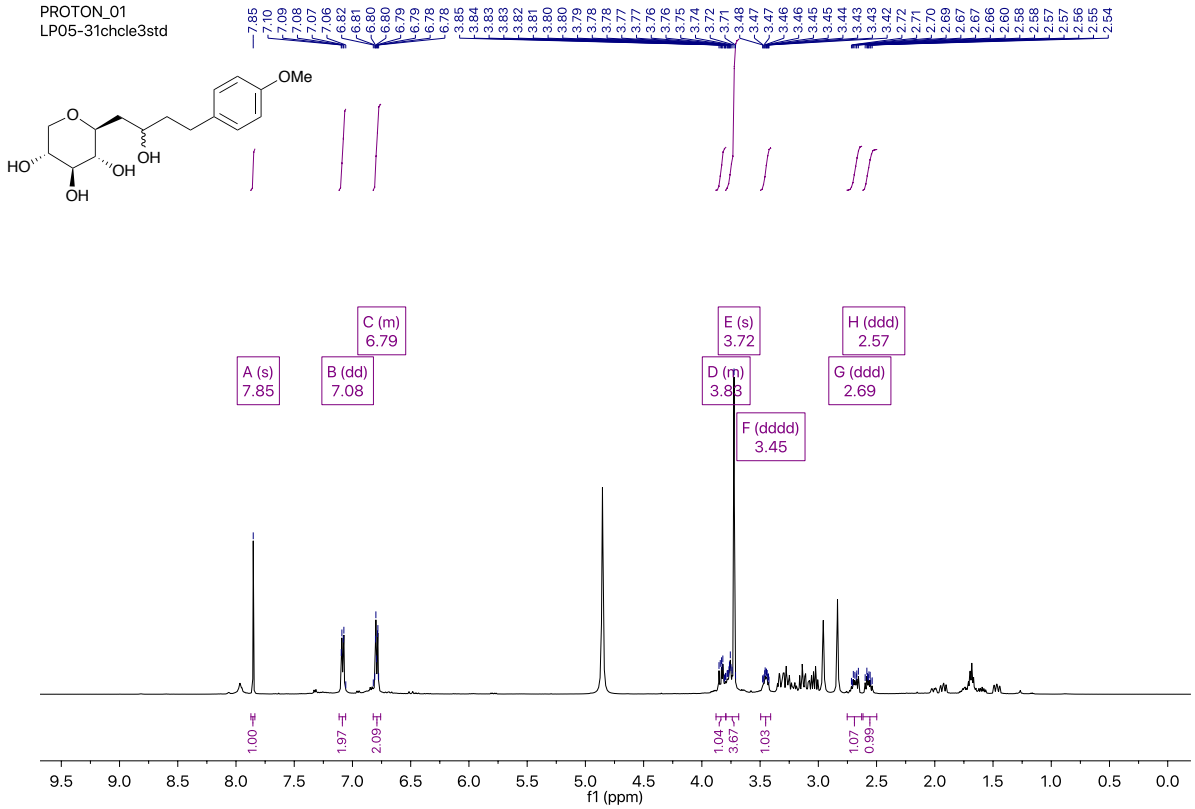
LP05-37crude
HO
OH
OH
OH


f1 (ppm)


PROTON_01
LP05-35crude
MeO
O
HO
OH
OH
OH
A (s)
7.84
B (m)
7.10
C (dd)
6.86
D (m)
6.81
E (m)
3.78
F (m)
3.45
G (m)
3.15
H (m)
2.74
I (dtd)
2.60
J (ddd)
2.02
K (ddd)
1.91
L (m)
1.64
M (ddd)
1.48
1.00
2.26
1.06
1.14
4.97
1.16
3.74
1.08
1.09
0.42
0.71
2.19
0.70
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


s2pul_01
LP05-35crude
MeO
O
HO
OH
OH
OH


90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)


PROTON_01
LP05-31chcle3std
OMe
HO
OH
OH
OH
A (s)
7.85
B (dd)
7.08
C (m)
6.79
D (m)
3.83
E (s)
3.72
F (dddd)
3.45
G (ddd)
2.69
H (ddd)
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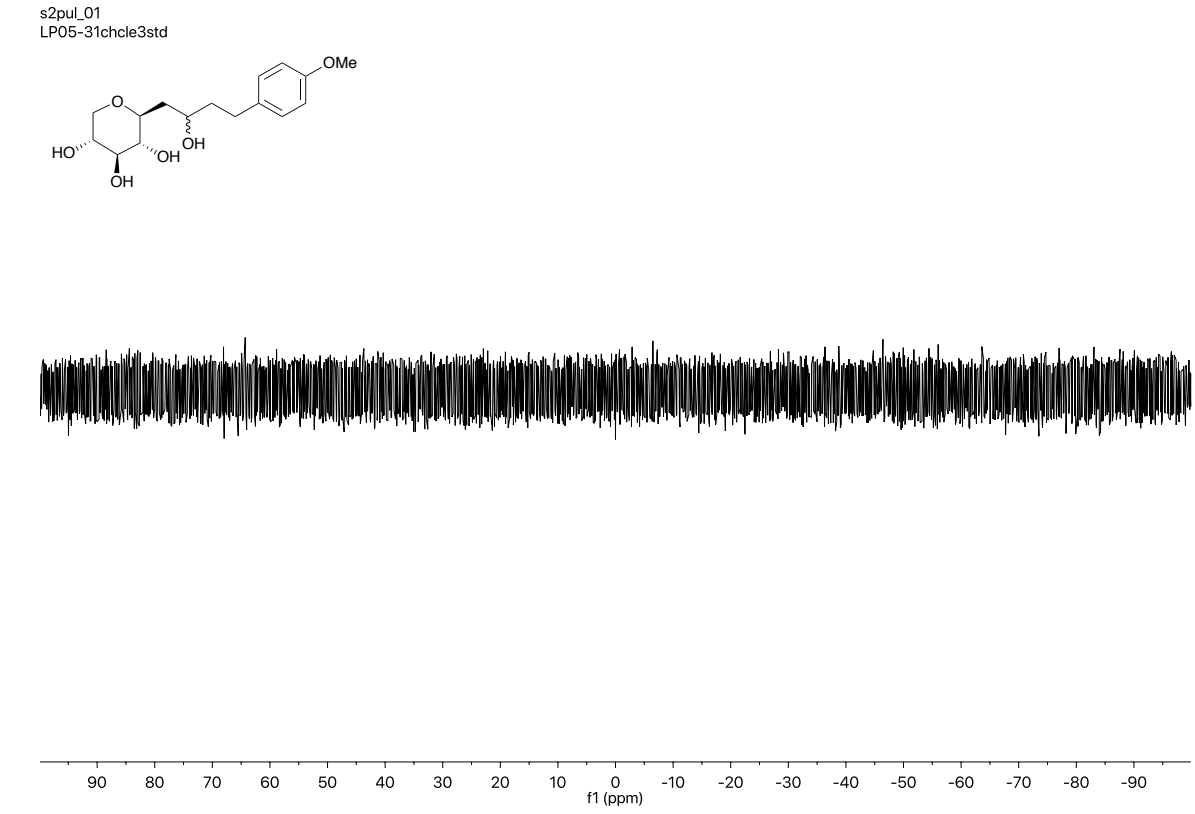
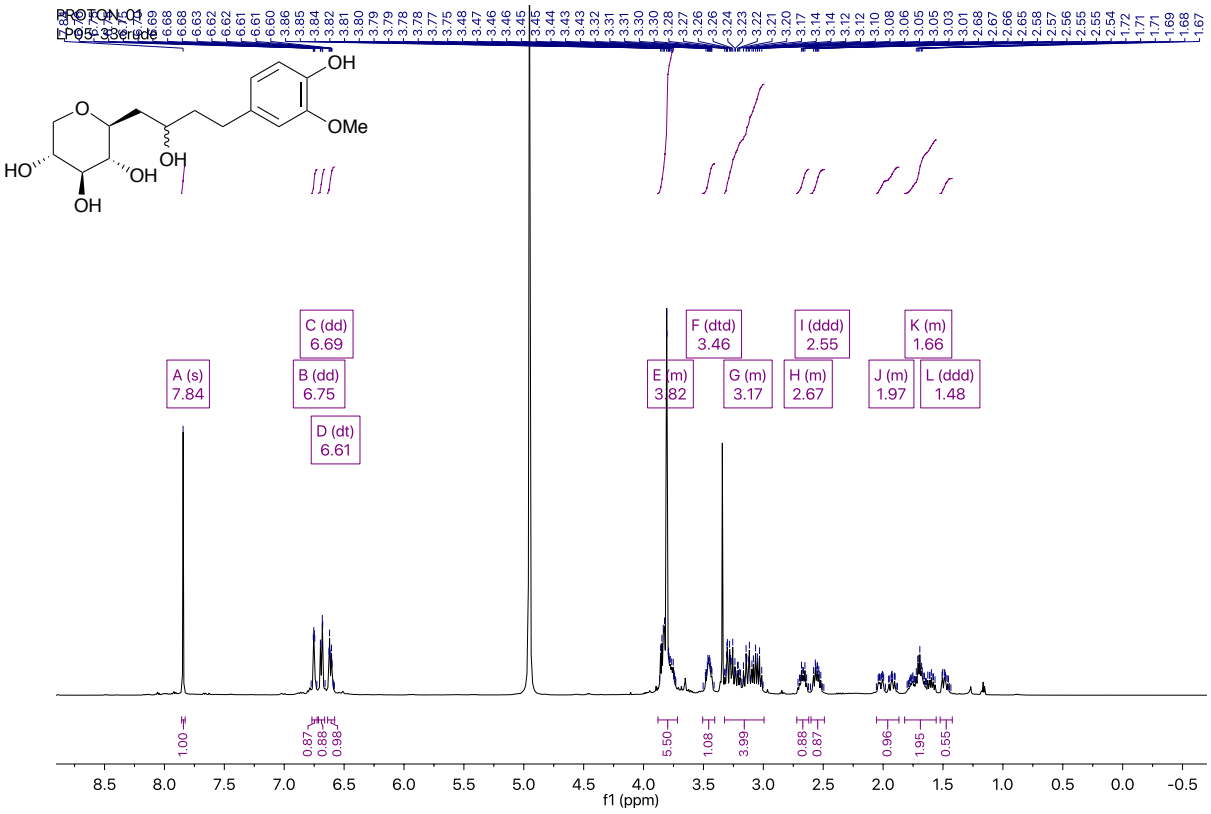
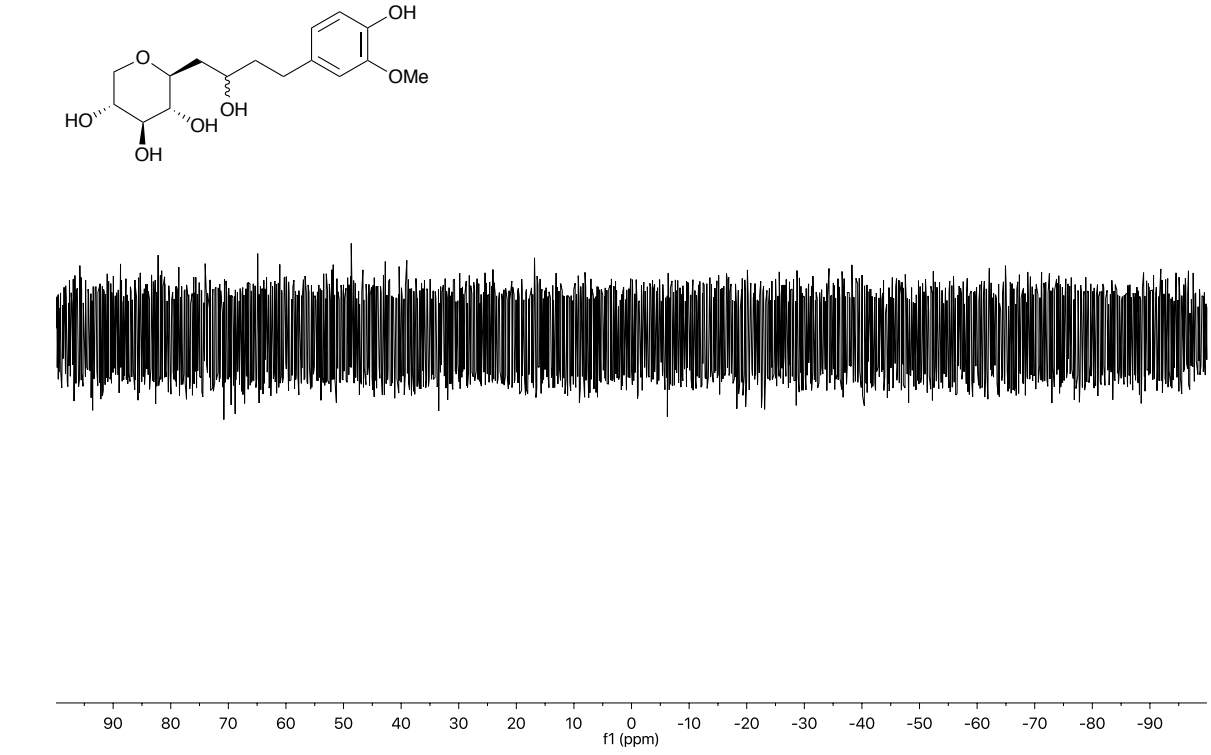
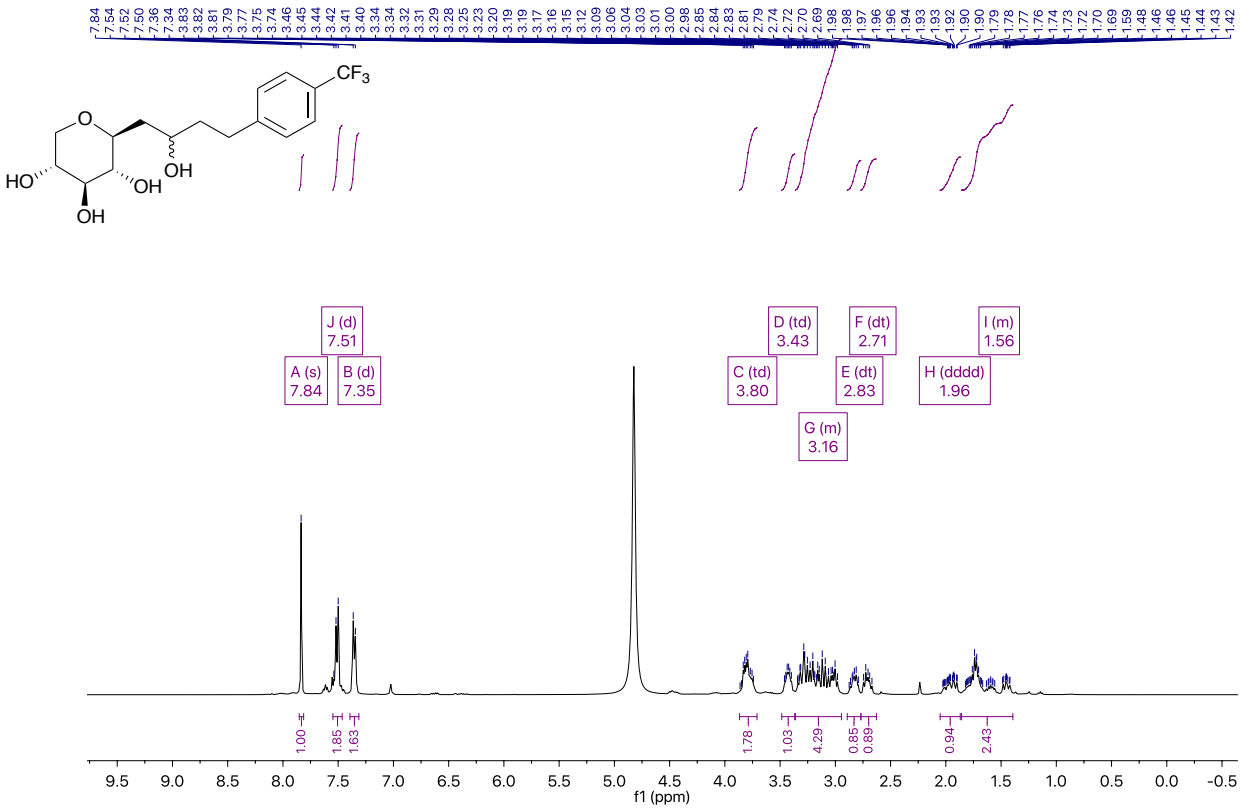
1.00
1.97
2.09
1.04
3.67
1.03
1.07
0.99
f1 (ppm)

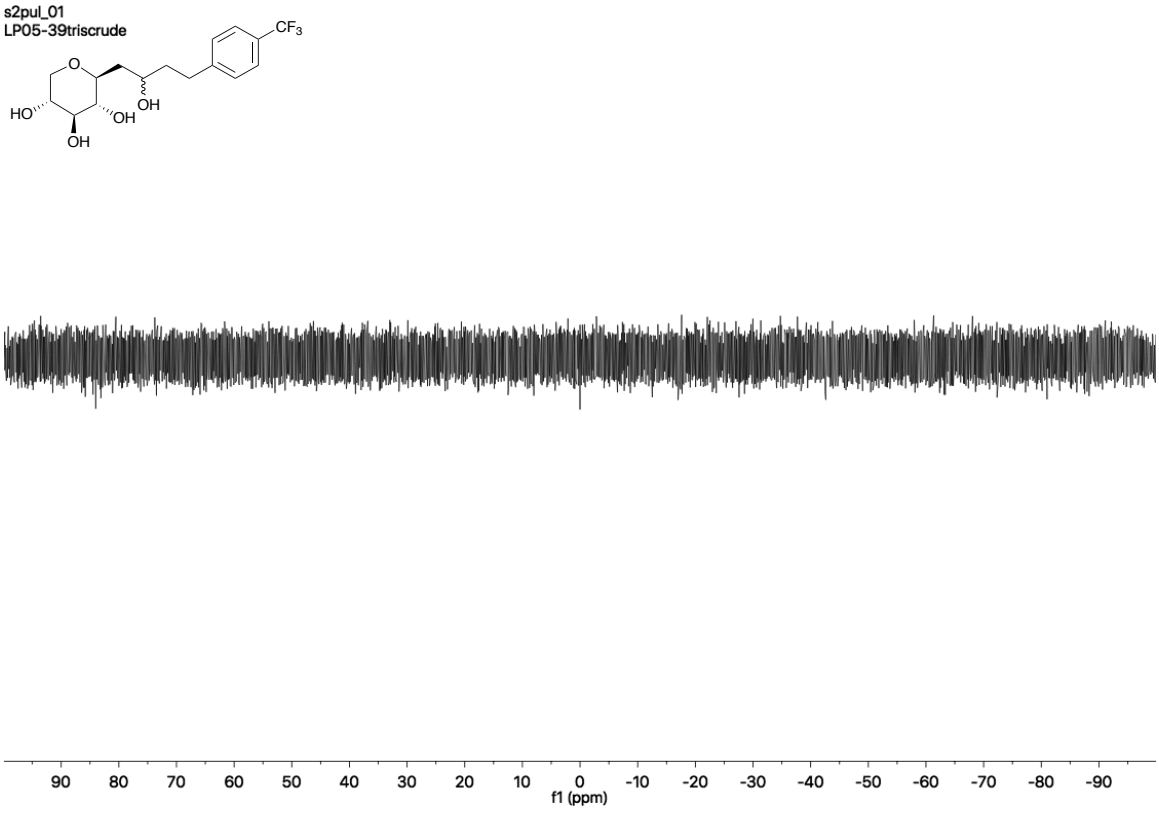

s2pul_01
LP05-31chcle3std
OMe
HO
OH
OH
OH
f1 (ppm)

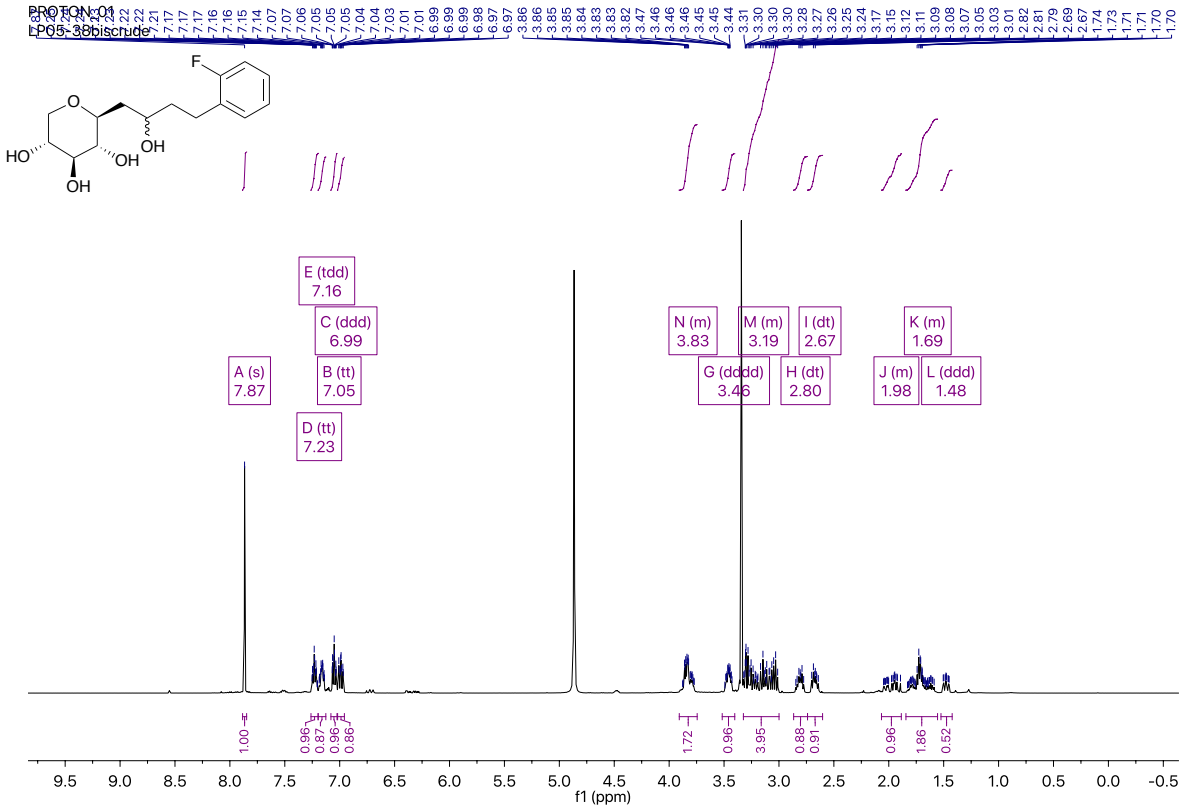


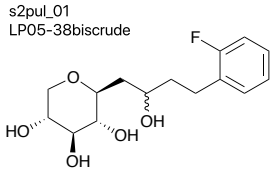

s2pul_01
LP05-33crude

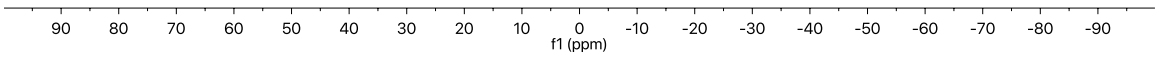


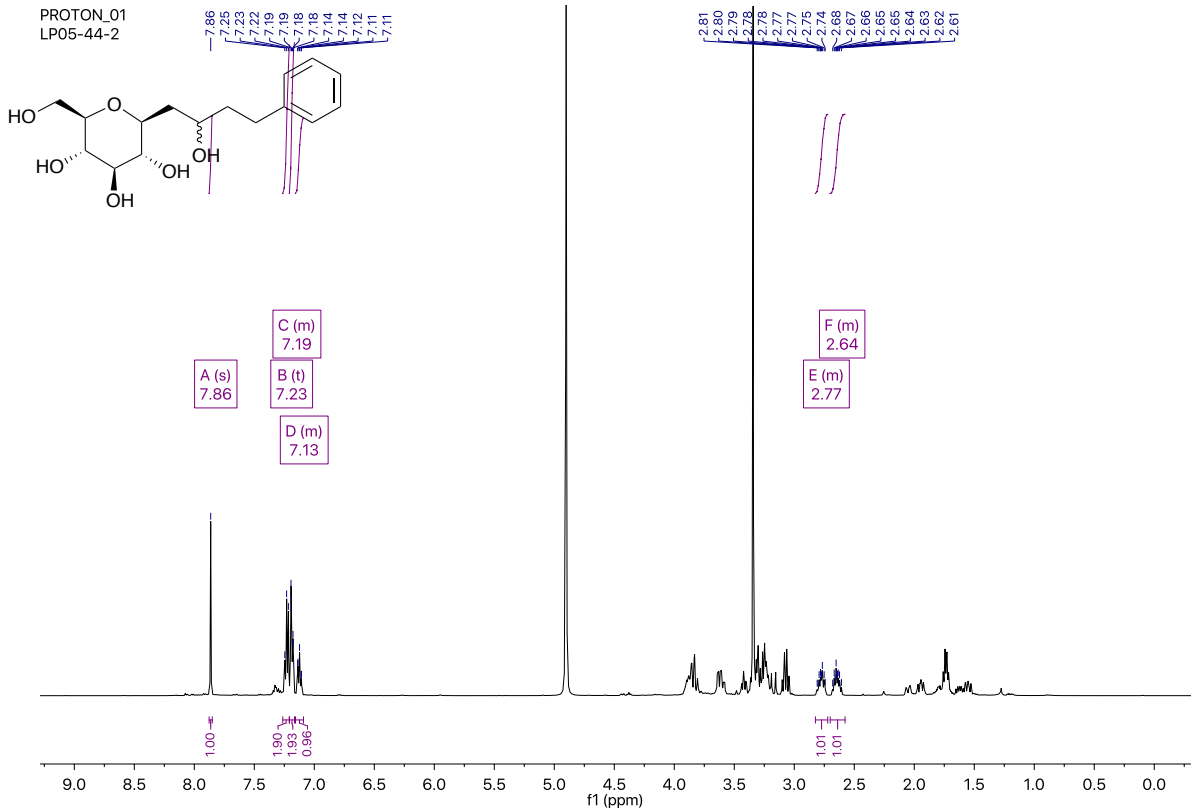

7.84 7.54 7.52 7.50 7.36 7.34 3.83 3.82 3.81 3.79 3.77 3.75 3.74 3.46 3.45 3.44 3.42 3.41 3.40 3.34 3.34 3.32 3.31 3.29 3.28 3.25 3.23 3.20 3.19 3.19 3.17 3.16 3.15 3.12 3.09 3.06 3.04 3.03 3.01 3.00 2.98 2.85 2.84 2.83 2.81 2.79 2.74 2.72 2.70 2.69 1.98 1.98 1.97 1.96 1.96 1.94 1.93 1.93 1.92 1.90 1.90 1.79 1.78 1.77 1.76 1.74 1.73 1.72 1.70 1.69 1.59 1.48 1.46 1.46 1.45 1.44 1.43 1.42
CF3
O
OH
HO
OH
OH
J (d) 7.51
A (s) 7.84
B (d) 7.35
D (td) 3.43
C (td) 3.80
F (dt) 2.71
E (dt) 2.83
G (m) 3.16
I (m) 1.56
H (dddd) 1.96
1.00
1.85
1.63
1.78
1.03
4.29
0.85
0.89
0.94
2.43
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

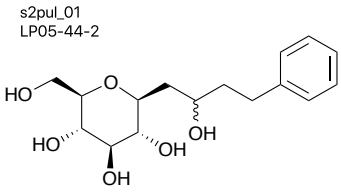

s2pul_01
LP05-39triscrude
CF3
O
OH
HO
OH
OH
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

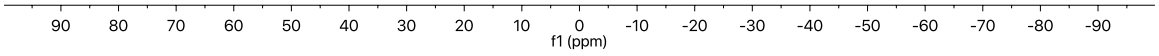

PROTON-01
LP05-38biscrude
F
O
HO
OH
OH
OH
E (tdd)
7.16
C (ddd)
6.99
A (s)
7.87
B (tt)
7.05
D (tt)
7.23
N (m)
3.83
M (m)
3.19
I (dt)
2.67
K (m)
1.69
G (dddd)
3.46
H (dt)
2.80
J (m)
1.98
L (ddd)
1.48
1.00
0.96
0.87
0.96
0.86
1.72
0.96
3.95
0.88
0.91
0.96
1.86
0.52
f1 (ppm)

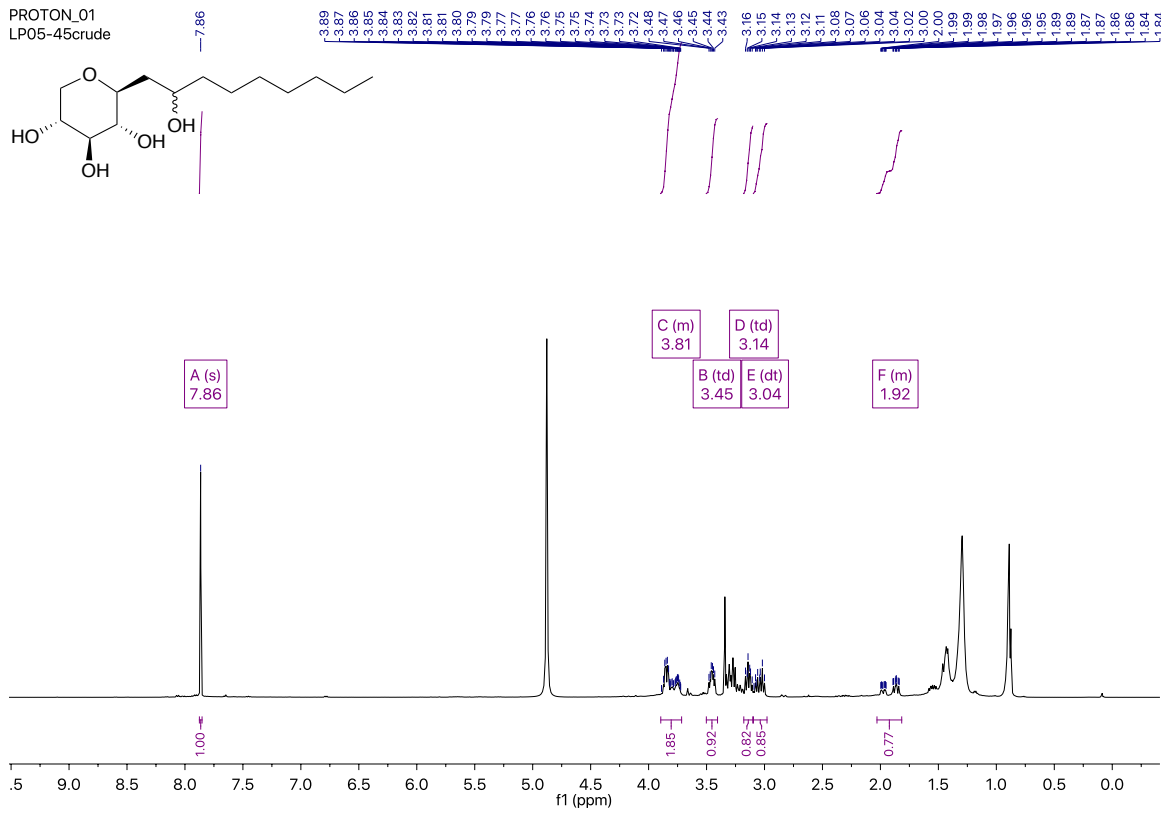

s2pul_01
LP05-38biscrude
F
O
HO
OH
OH
OH

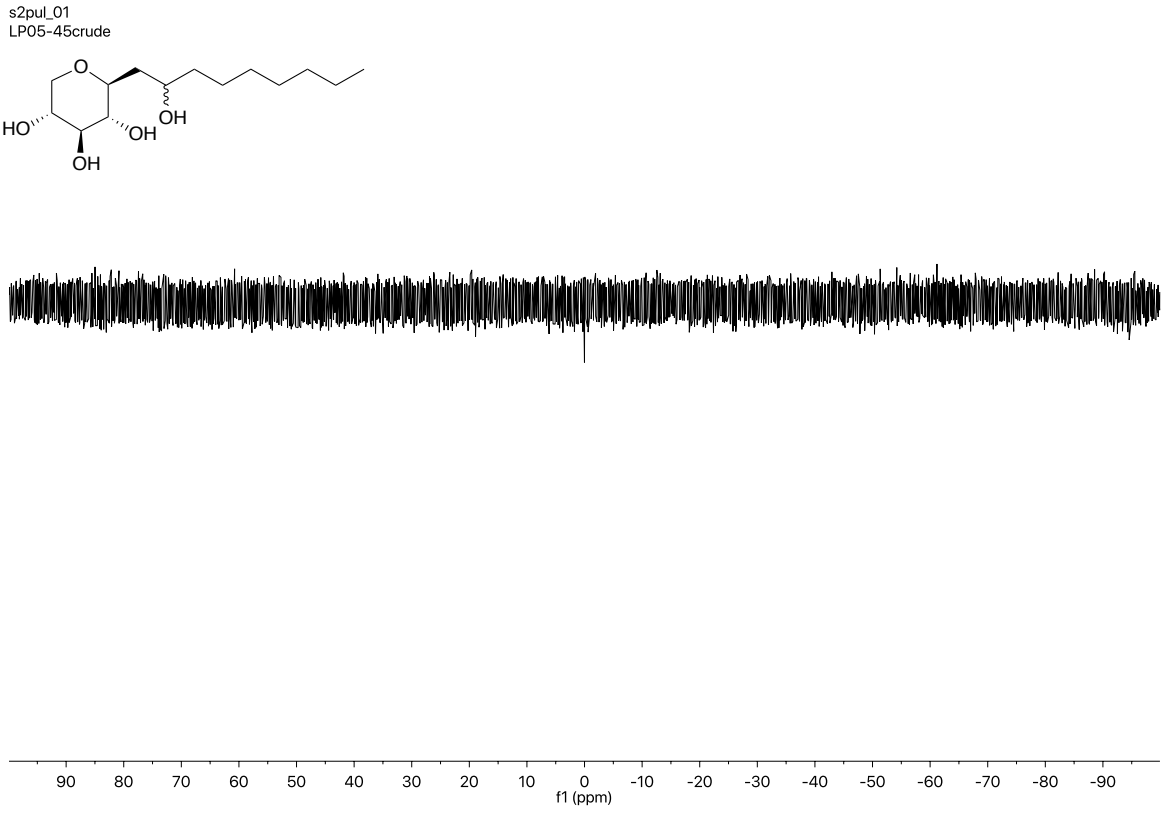

f1 (ppm)

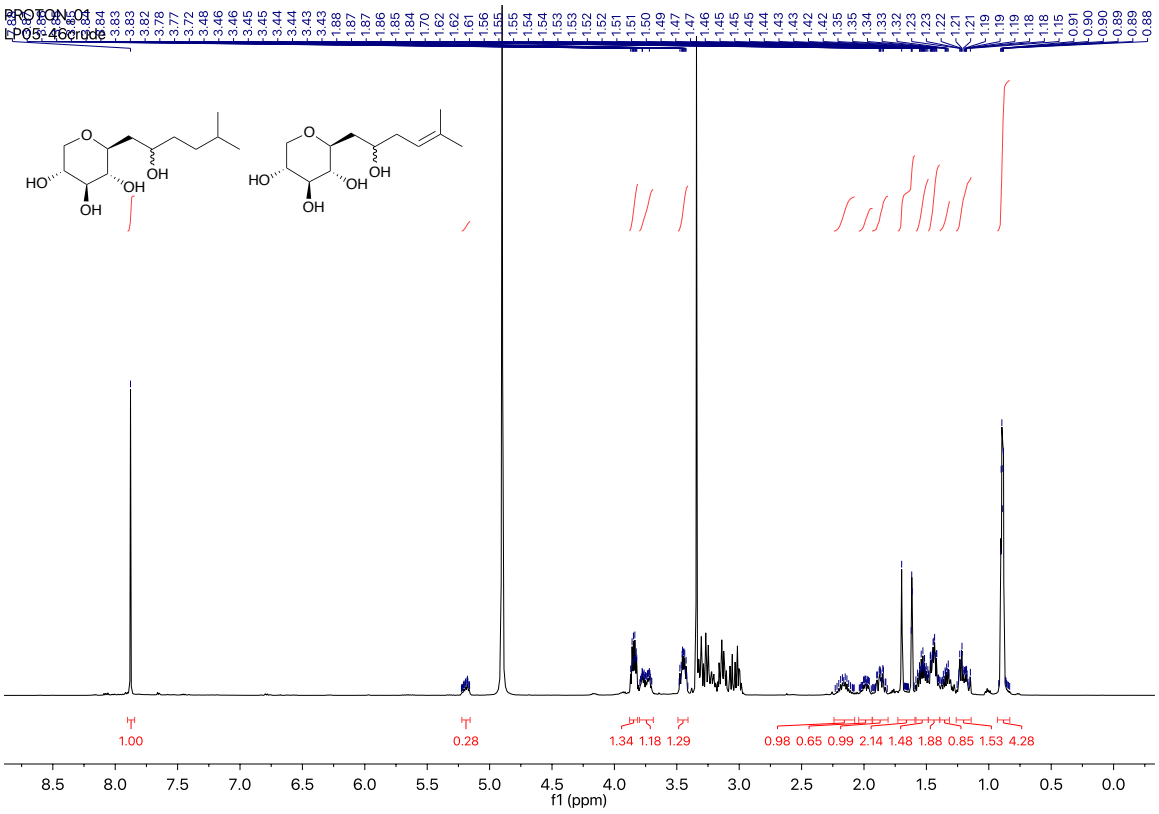

PROTON_01
LP05-44-2
HO
O
HO
OH
OH
OH
7.86
7.25
7.23
7.22
7.19
7.19
7.18
7.18
7.14
7.14
7.12
7.11
7.11
2.81
2.80
2.79
2.78
2.78
2.77
2.77
2.75
2.74
2.68
2.67
2.66
2.65
2.65
2.64
2.63
2.62
2.61
C (m)
7.19
A (s)
7.86
B (t)
7.23
D (m)
7.13
F (m)
2.64
E (m)
2.77
1.00
1.90
1.93
0.96
1.01
1.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

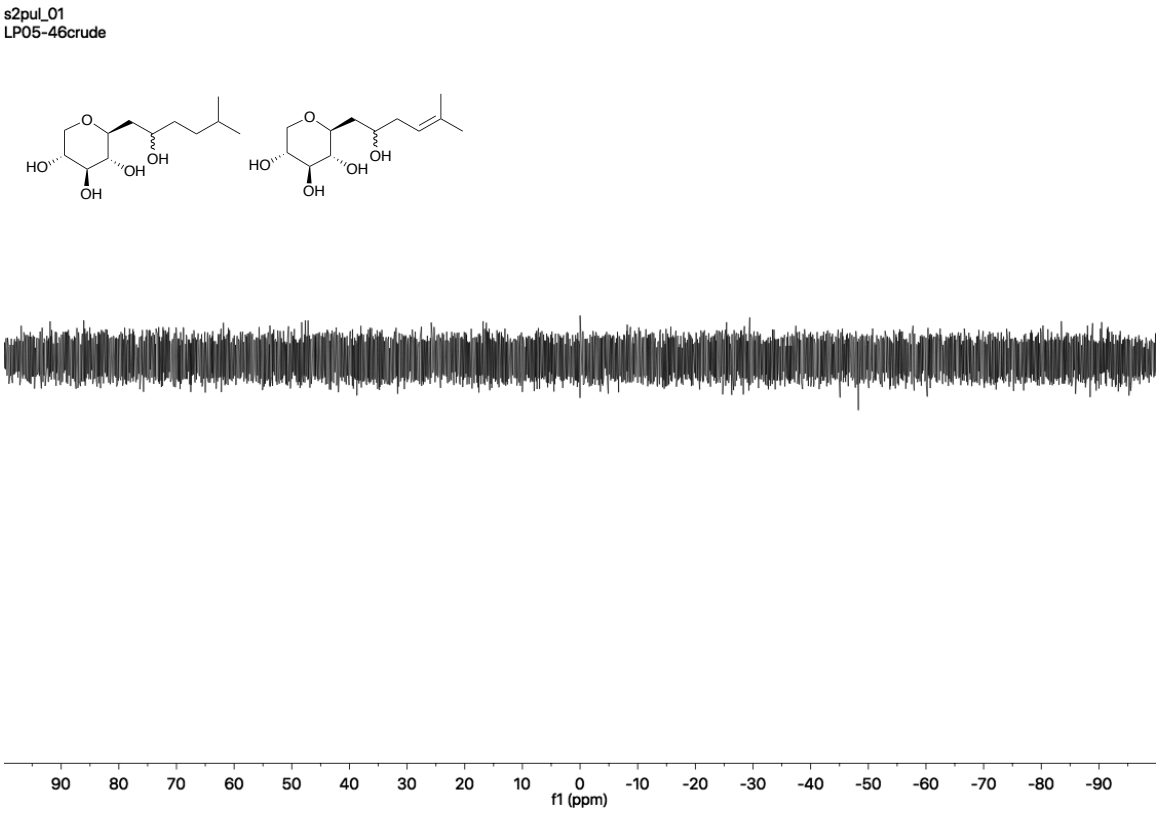

s2pul_01
LP05-44-2
HO
O
HO
OH
OH
OH


90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

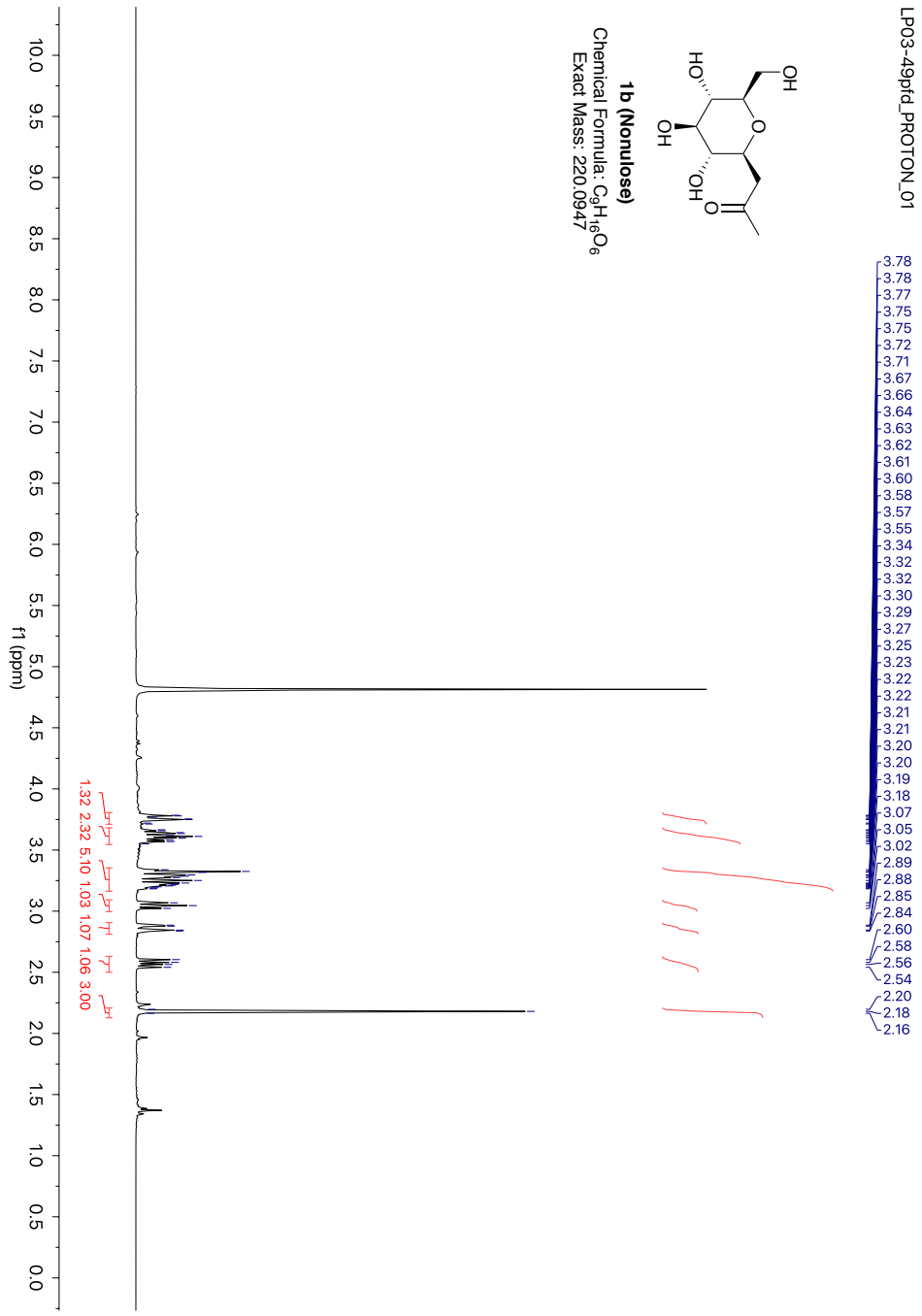

PROTON_01
LP05-45crude
A (s)
7.86
C (m)
3.81
D (td)
3.14
B (td)
3.45
E (dt)
3.04
F (m)
1.92
1.00
1.85
0.92
0.82
0.85
0.77
f1 (ppm)


s2pul_01
LP05-45crude
f1 (ppm)

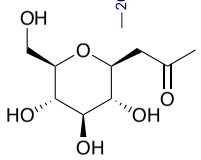

PROTON_01
LP05-46crude
HO
OH
OH
OH
1.00
0.28
1.34 1.18 1.29
0.98 0.65 0.99 2.14 1.48 1.88 0.85 1.53 4.28
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


s2pul_01
LP05-46crude
HO
OH
OH
OH
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

*b.* *$^{1}H$ and $^{13}C$ NMRs of purified compounds*



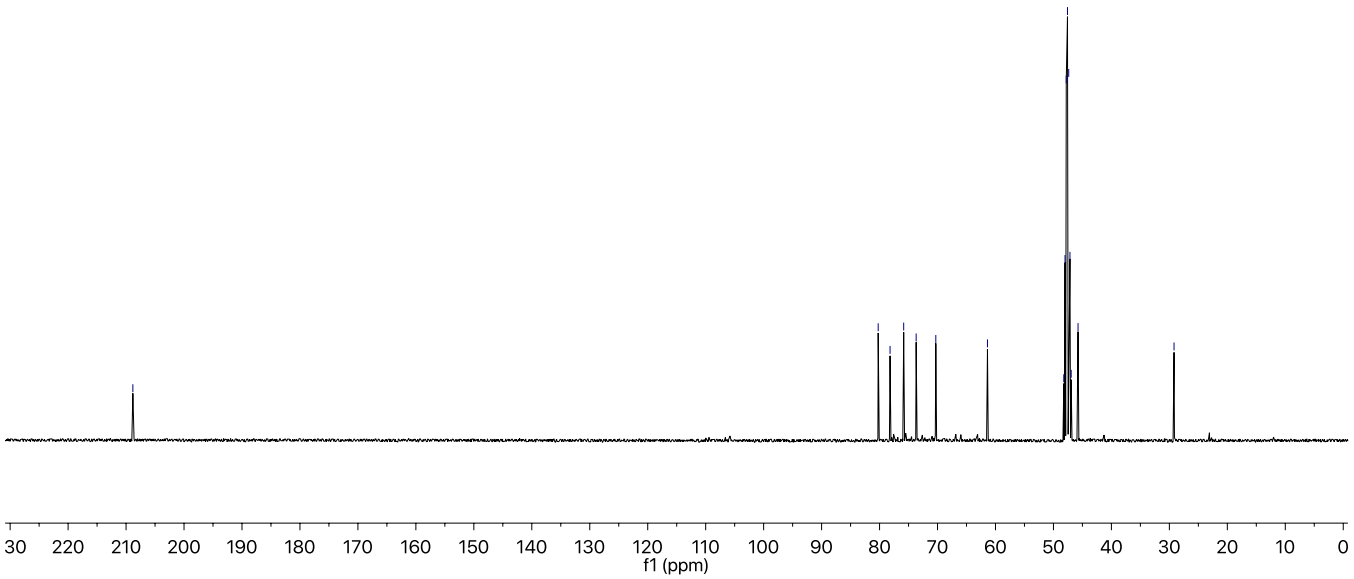
LP03-49pfd_CARBON_01

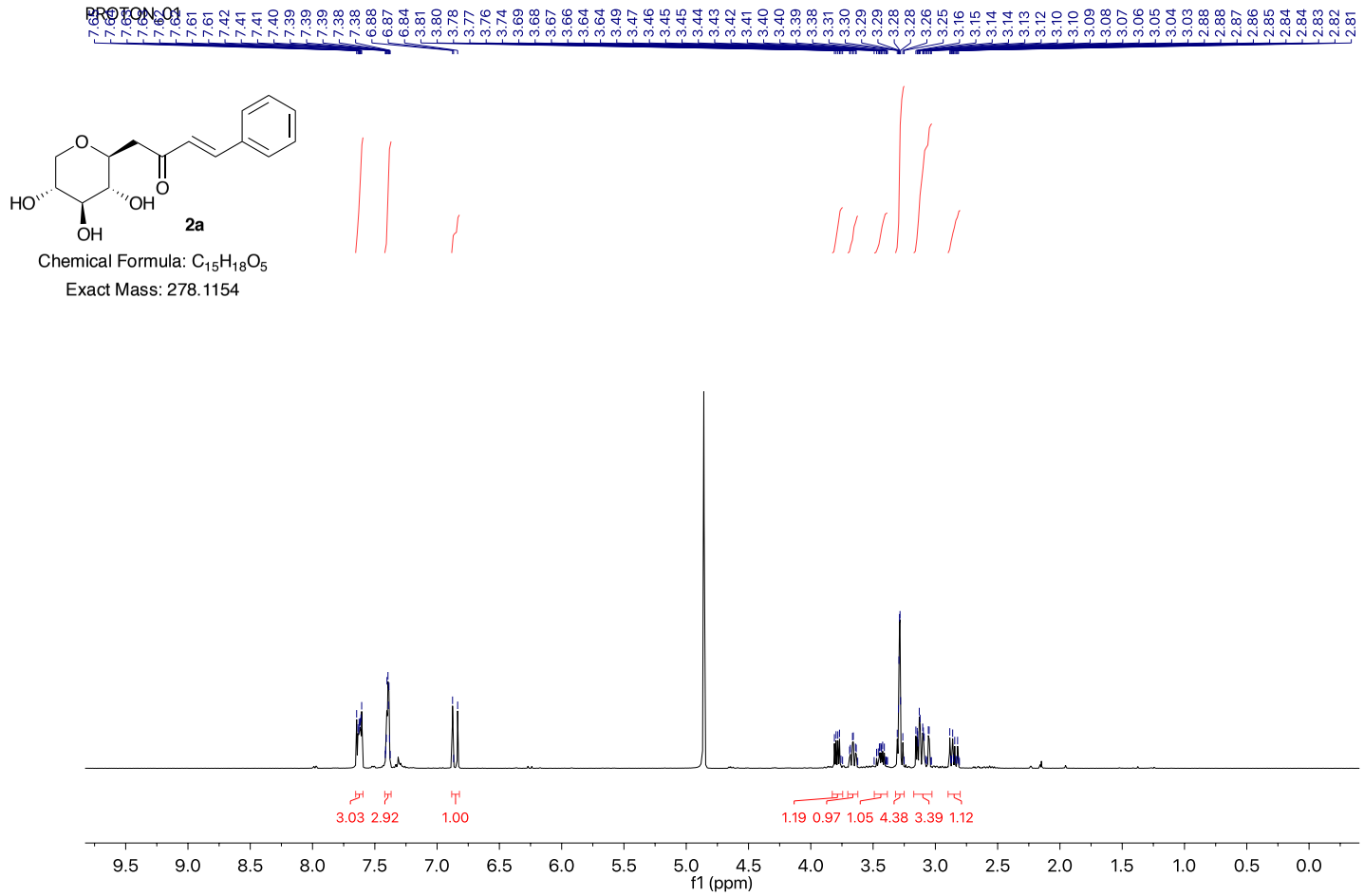


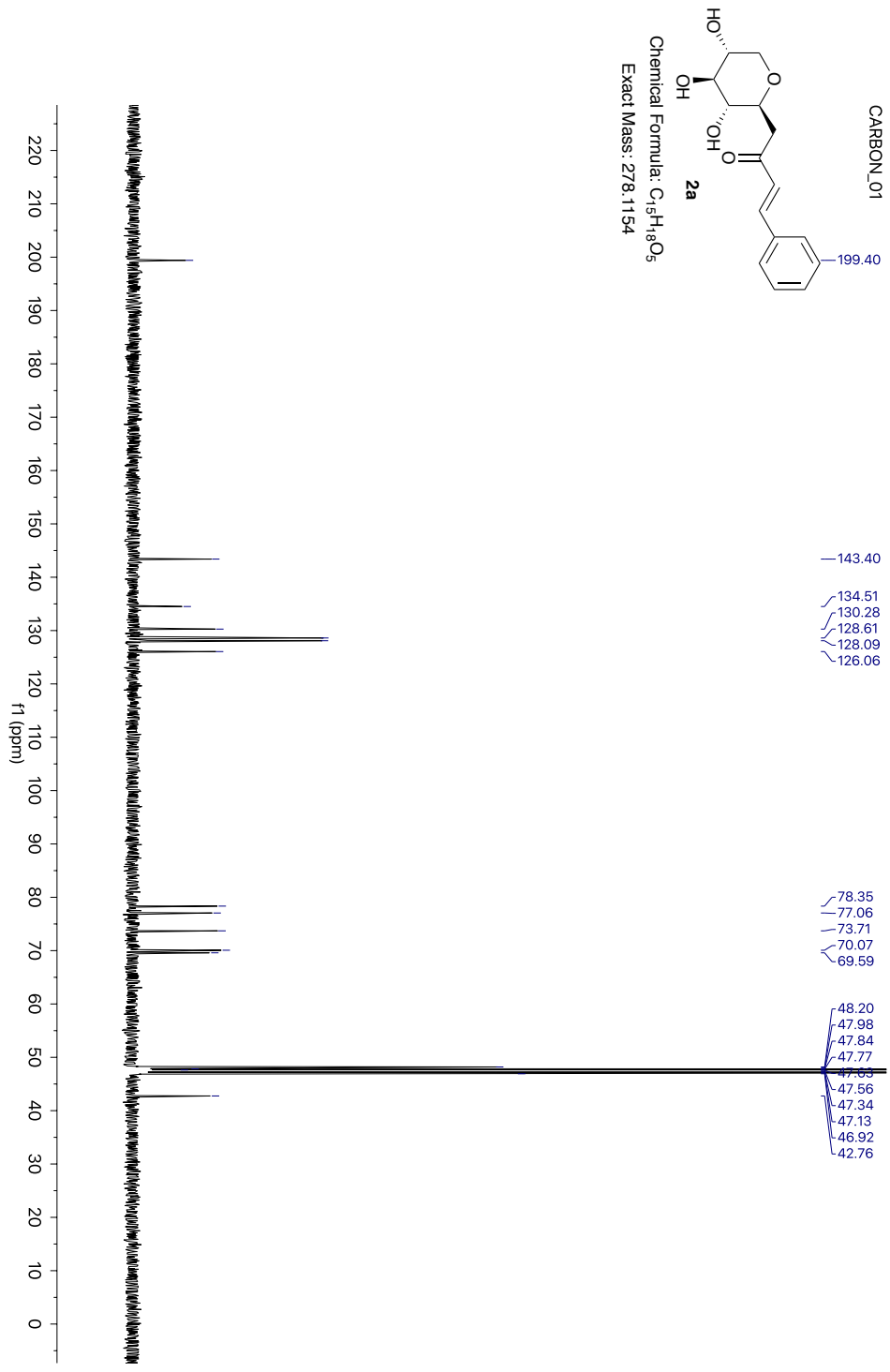

**1b (Nonulose)**

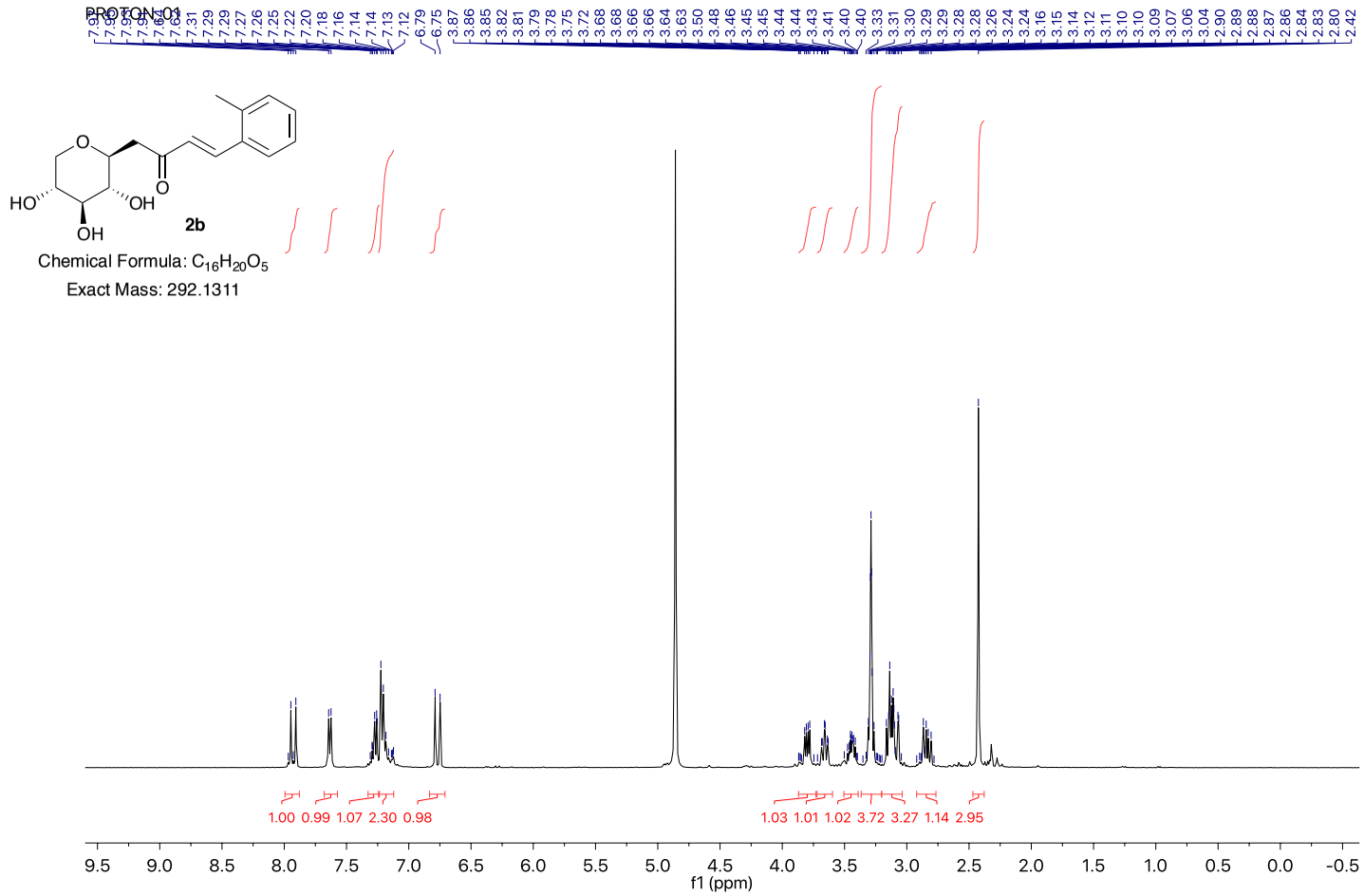
Chemical Formula: $C_9H_{16}O_6$
Exact Mass: 220.0947

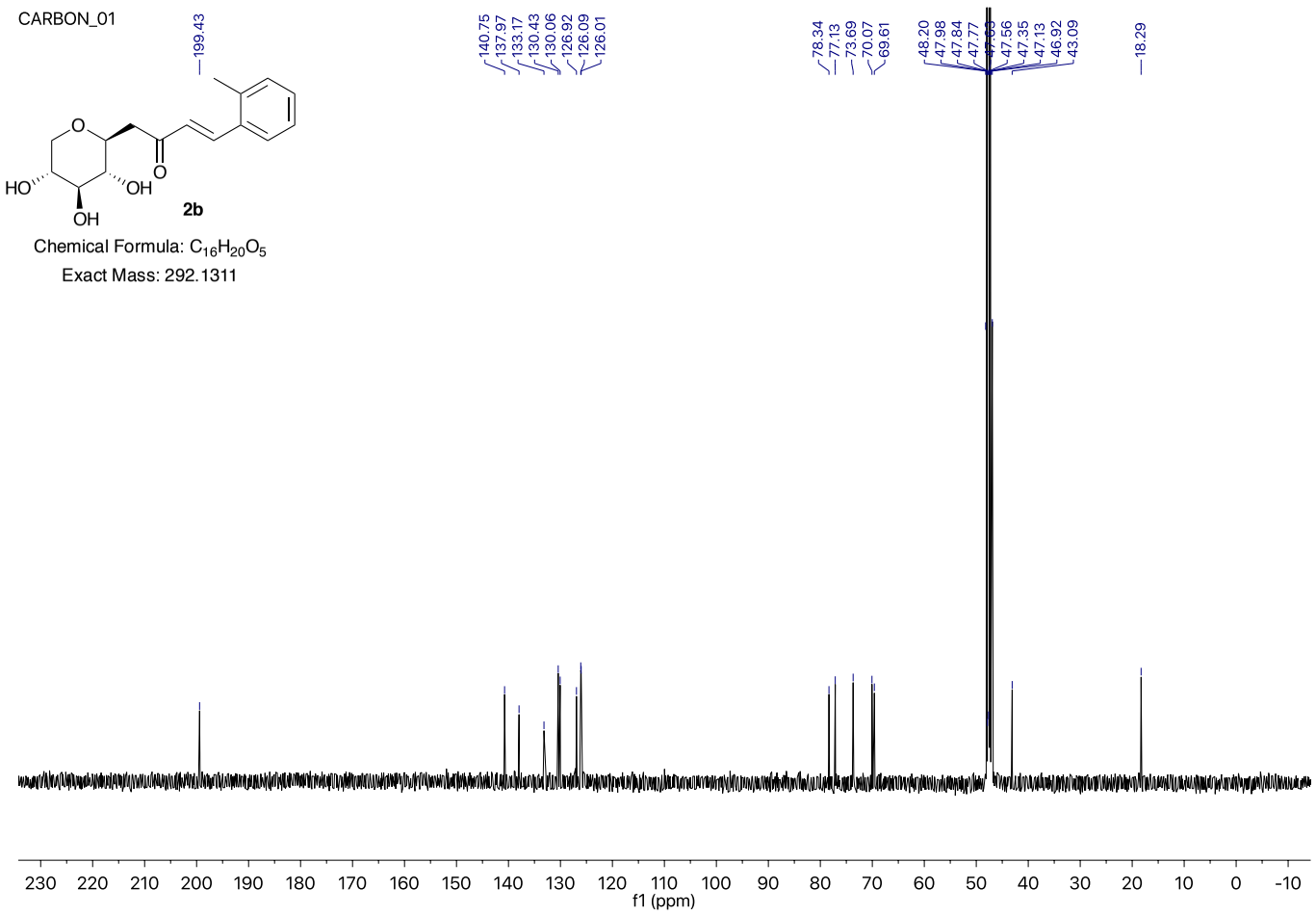
208.85
80.24
78.19
75.84
73.69
70.30
61.38
48.22
48.00
47.79
47.58
47.36
47.15
46.94
45.76
29.19

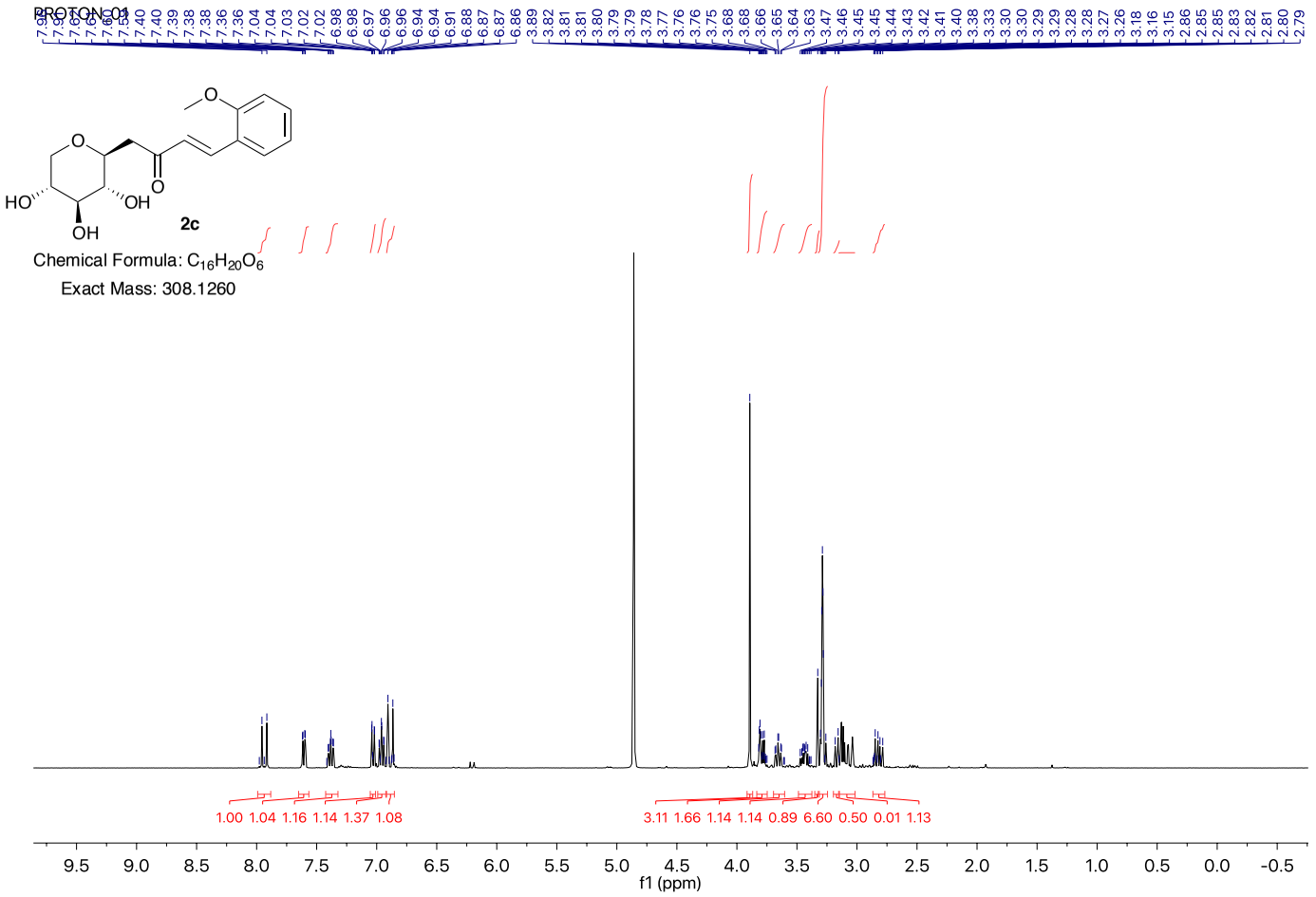


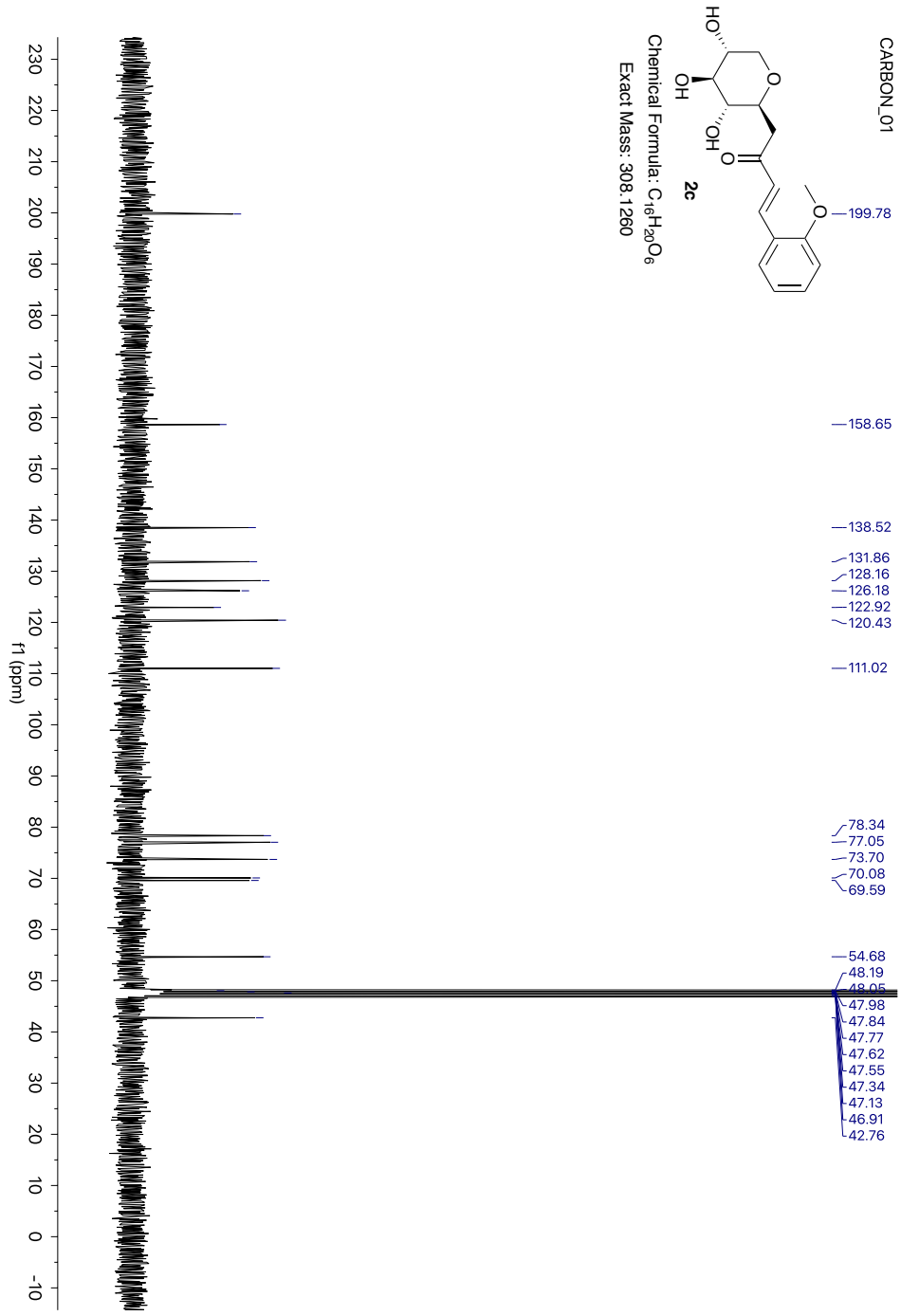

PROTON-01
HO
OH
OH
O
O
2a
Chemical Formula: $C_{15}H_{18}O_5$
Exact Mass: 278.1154
3.03 2.92 1.00 1.19 0.97 1.05 4.38 3.39 1.12
f1 (ppm)

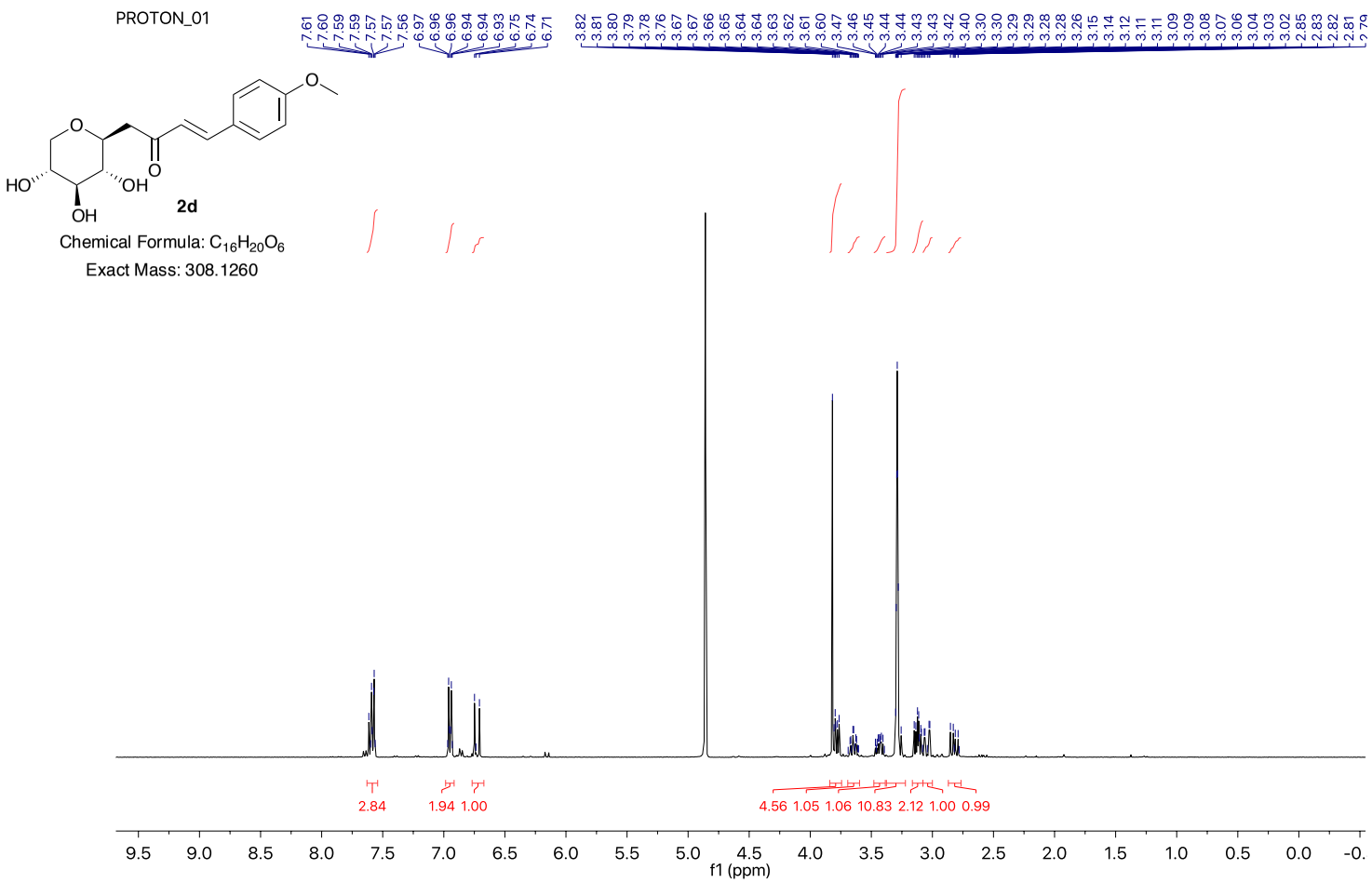

CARBON_01
199.40
143.40
134.51
130.28
128.61
128.09
126.06
78.35
77.06
73.71
70.07
69.59
48.20
47.98
47.84
47.77
47.56
47.34
47.13
46.92
42.76
HO
OH
OH
O
O
2a
Chemical Formula: C15H18O5
Exact Mass: 278.1154
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

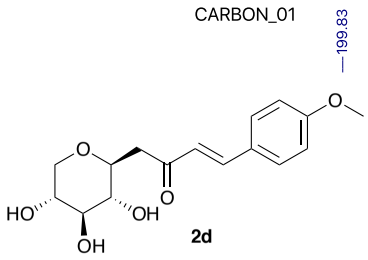

PROTON-01
HO
OH
OH
O
O
2b
Chemical Formula: C16H20O5
Exact Mass: 292.1311
1.00 0.99 1.07 2.30 0.98
1.03 1.01 1.02 3.72 3.27 1.14 2.95
f1 (ppm)


CARBON_01
199.43
140.75
137.97
133.17
130.43
130.06
126.92
126.09
126.01
78.34
77.13
73.69
70.07
69.61
48.20
47.98
47.84
47.77
47.56
47.35
47.13
46.92
43.09
18.29
O
O
HO
OH
OH
2b
Chemical Formula: C16H20O5
Exact Mass: 292.1311
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


PROTON-01
2c
Chemical Formula: C16H20O6
Exact Mass: 308.1260
1.00 1.04 1.16 1.14 1.37 1.08
3.11 1.66 1.14 1.14 0.89 6.60 0.50 0.01 1.13
f1 (ppm)


CARBON_01
Chemical Formula: C16H20O6
Exact Mass: 308.1260
2c
199.78
158.65
138.52
131.86
128.16
126.18
122.92
120.43
111.02
78.34
77.05
73.70
70.08
69.59
54.68
48.19
47.98
47.84
47.77
47.62
47.55
47.34
47.13
46.91
42.76
f1 (ppm)

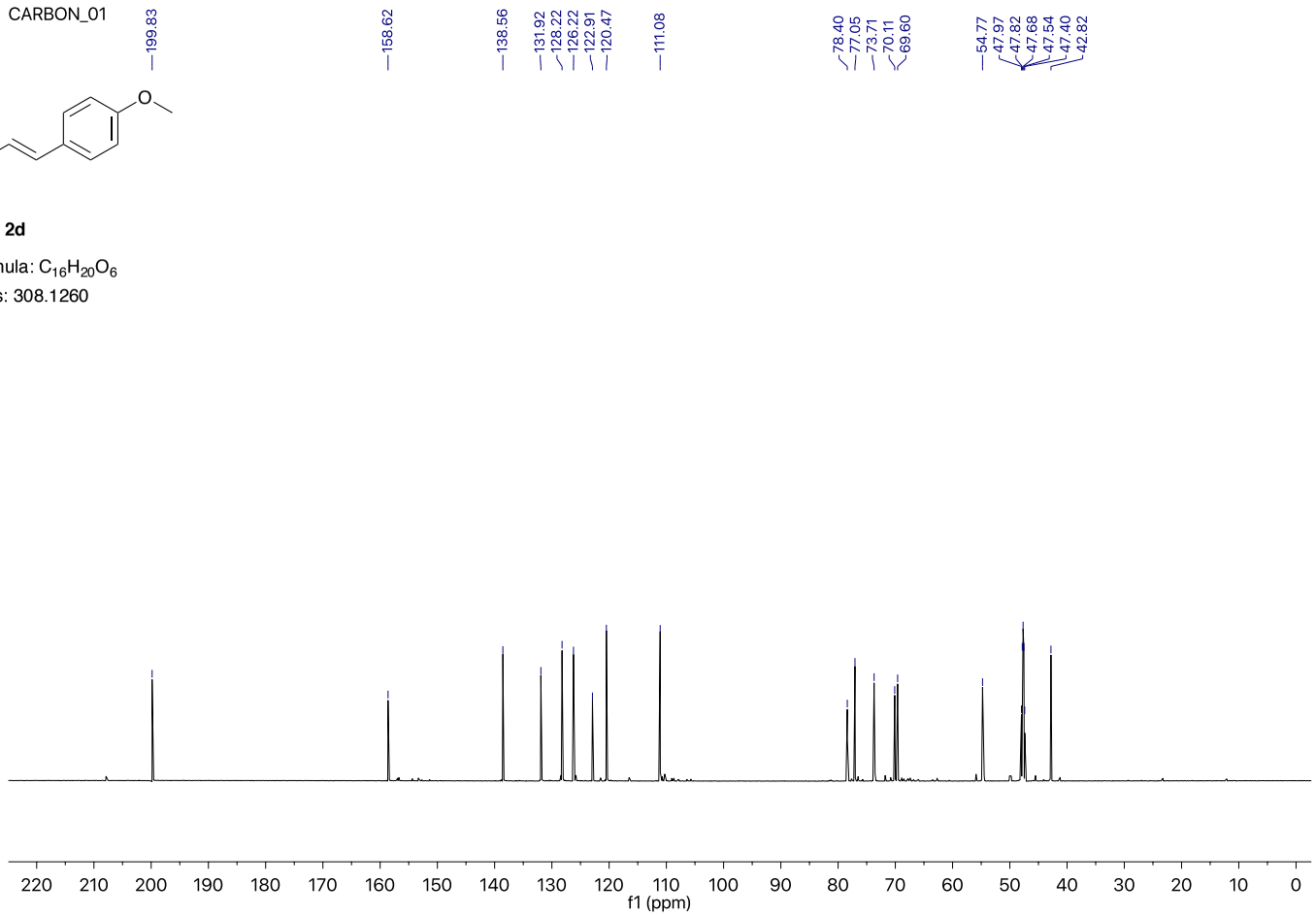

PROTON_01
7.61 7.60 7.59 7.59 7.57 7.57 7.56 6.97 6.96 6.96 6.94 6.94 6.93 6.75 6.74 6.71
3.82 3.81 3.80 3.79 3.78 3.76 3.67 3.67 3.66 3.65 3.64 3.64 3.63 3.62 3.61 3.60 3.47 3.46 3.45 3.44 3.44 3.43 3.42 3.40 3.30 3.30 3.29 3.29 3.28 3.28 3.26 3.15 3.14 3.12 3.11 3.11 3.09 3.09 3.08 3.07 3.06 3.04 3.03 3.02 2.85 2.83 2.82 2.81
HO
OH
OH
O
O
O
2d
Chemical Formula: C16H20O6
Exact Mass: 308.1260
2.84 1.94 1.00 4.56 1.05 1.06 10.83 2.12 1.00 0.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

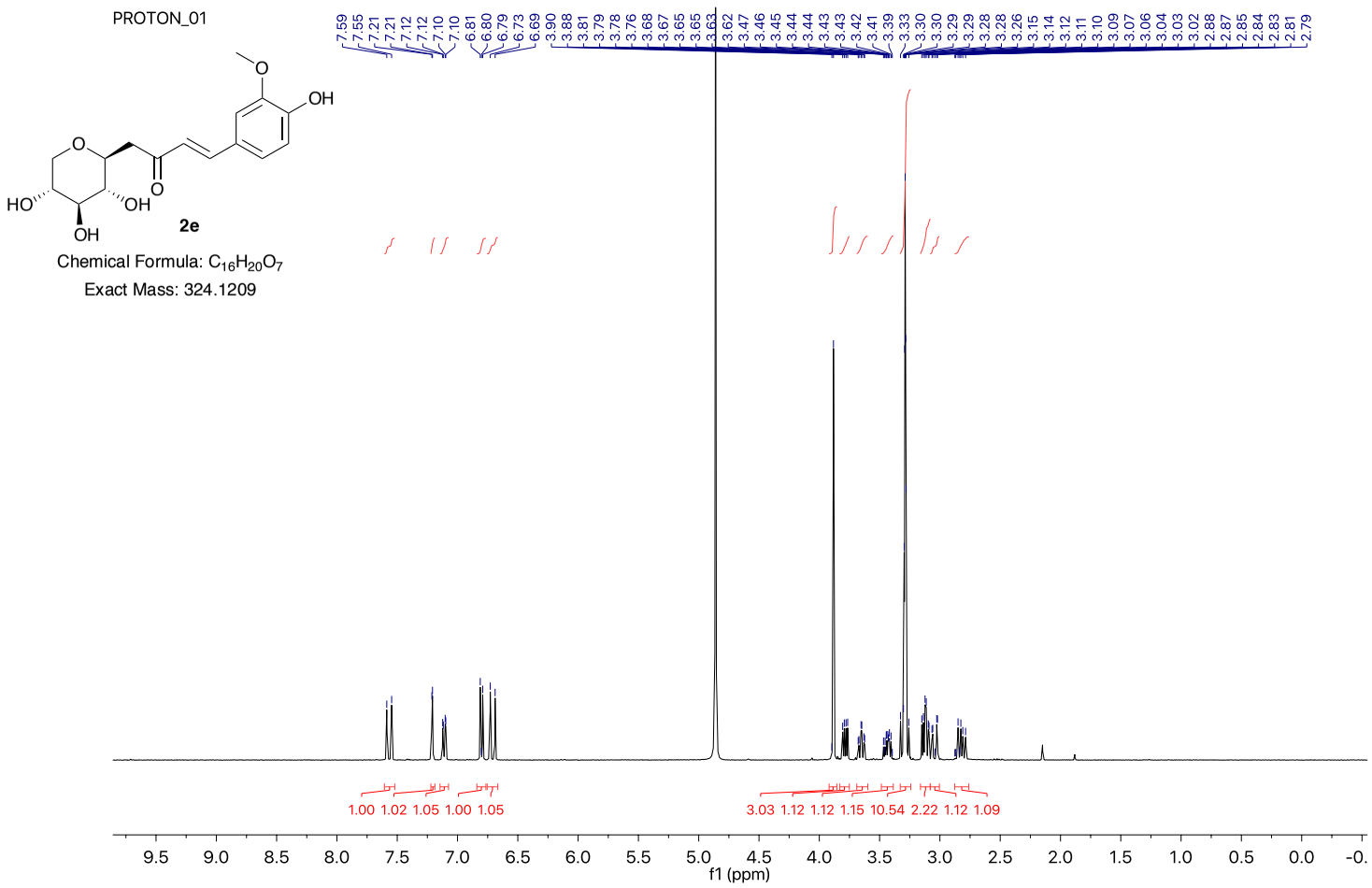



**2d**

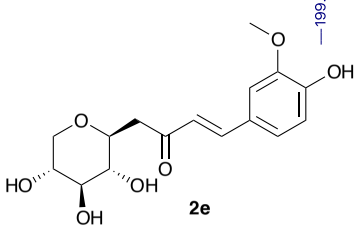
Chemical Formula: $C_{16}H_{20}O_6$

Exact Mass: 308.1260




PROTON_01
2e
Chemical Formula: C16H20O7
Exact Mass: 324.1209
1.00 1.02 1.05 1.00 1.05
3.03 1.12 1.12 1.15 10.54 2.22 1.12 1.09
f1 (ppm)

LP03-66-goodcarbon_CARBON_01

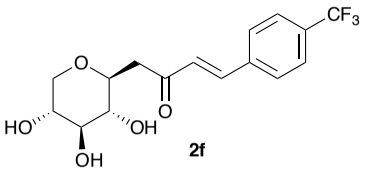



**2e**

Chemical Formula: $C_{16}H_{20}O_7$

Exact Mass: 324.1209

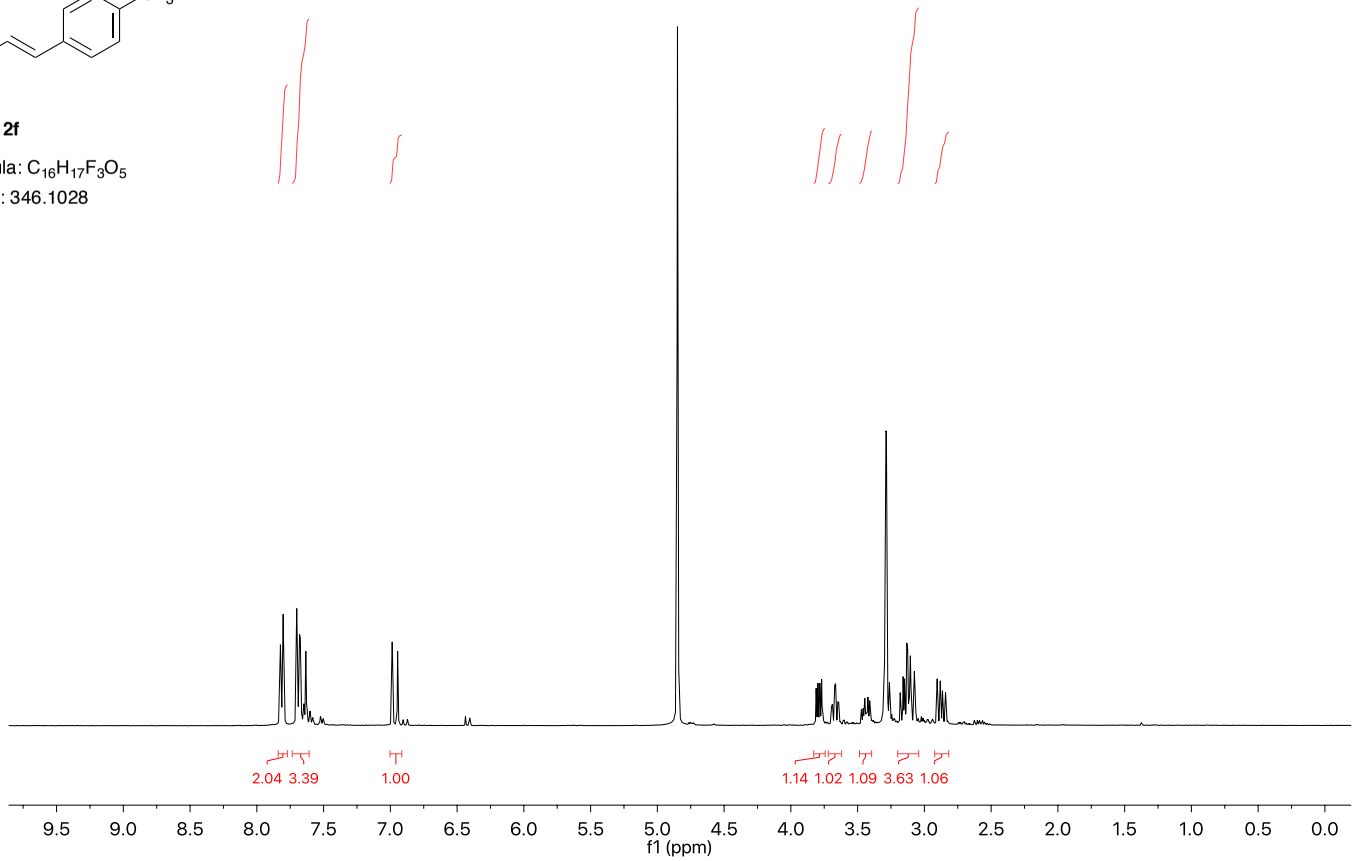
PROTON_01

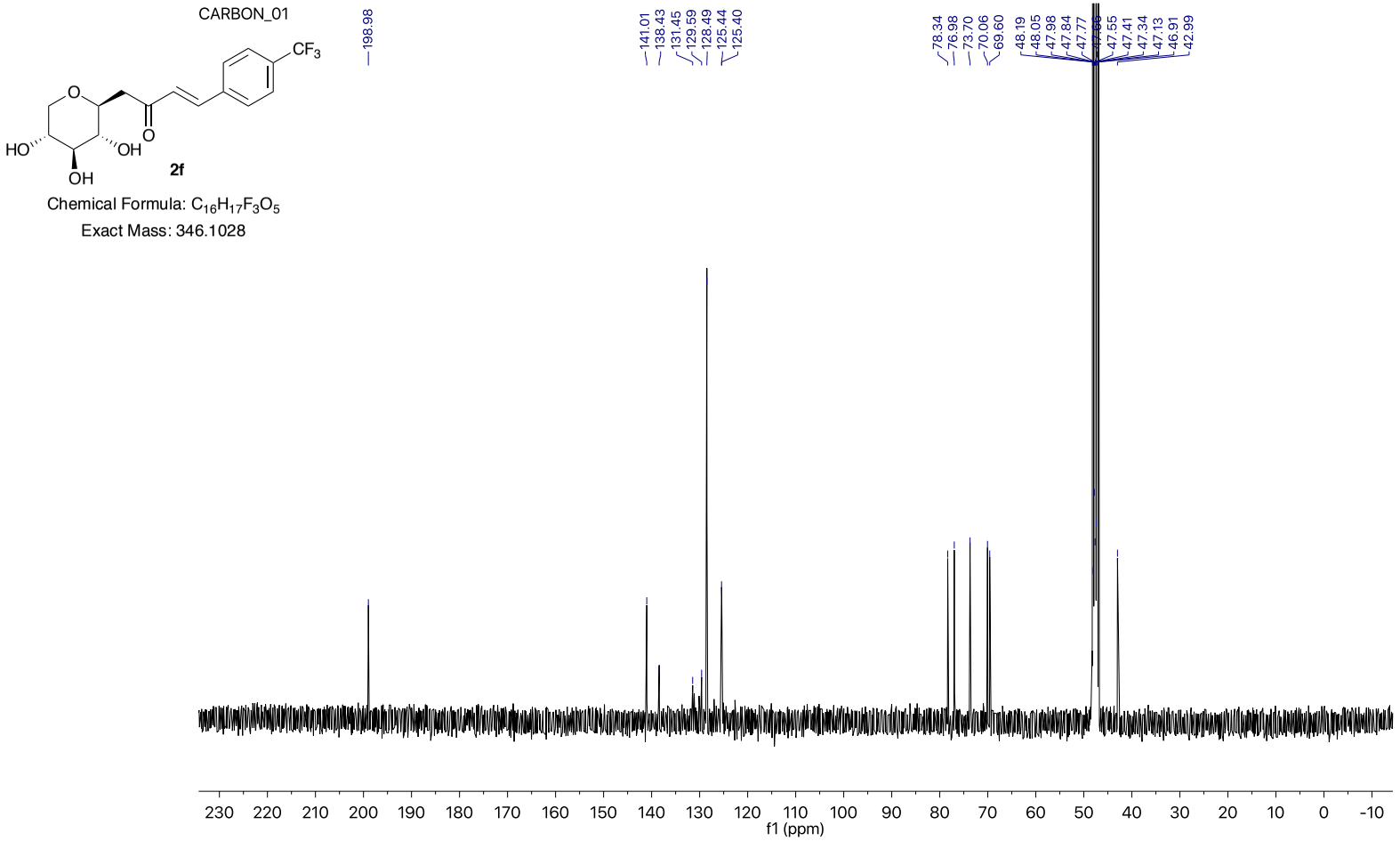


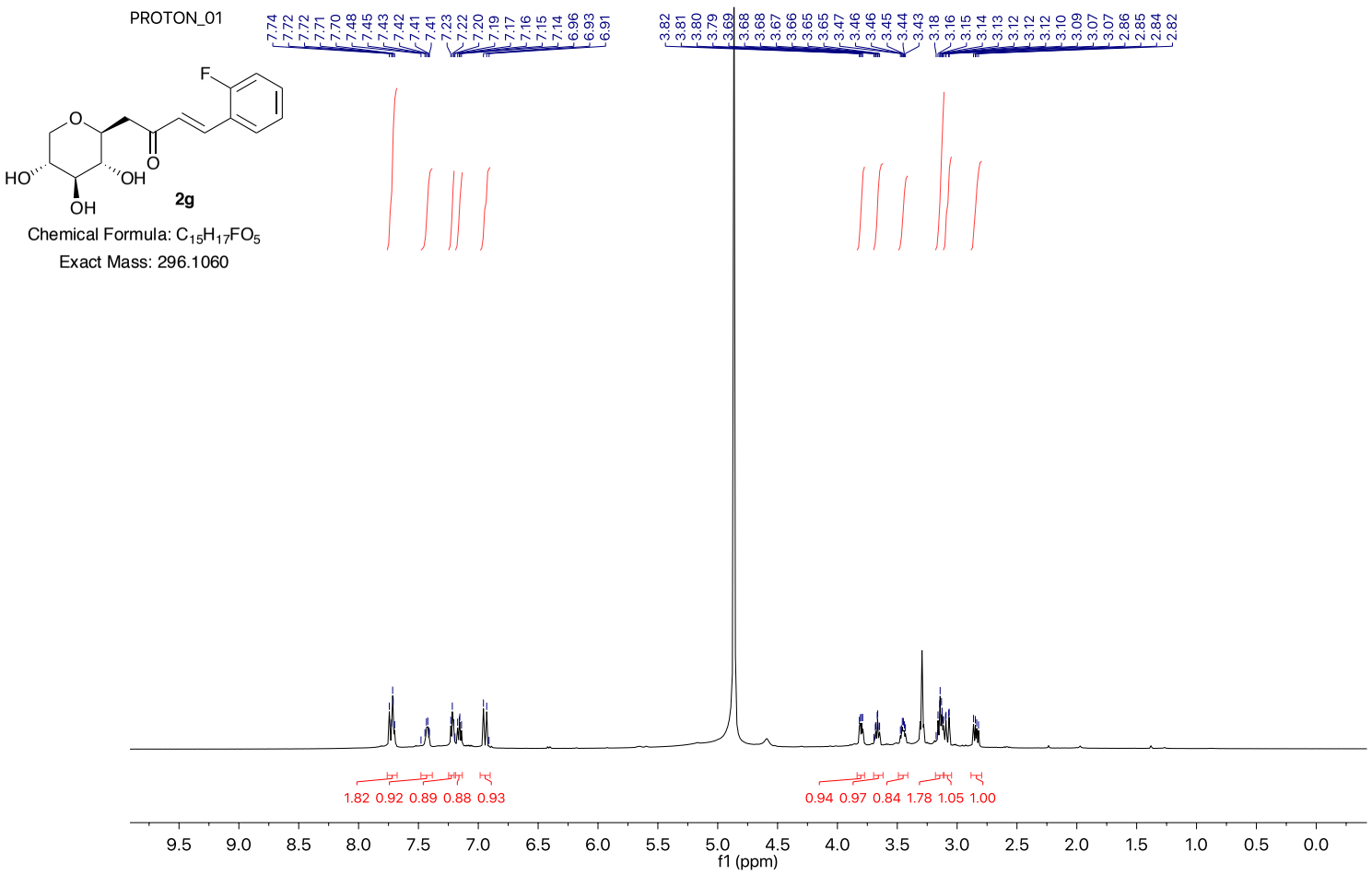

**2f**

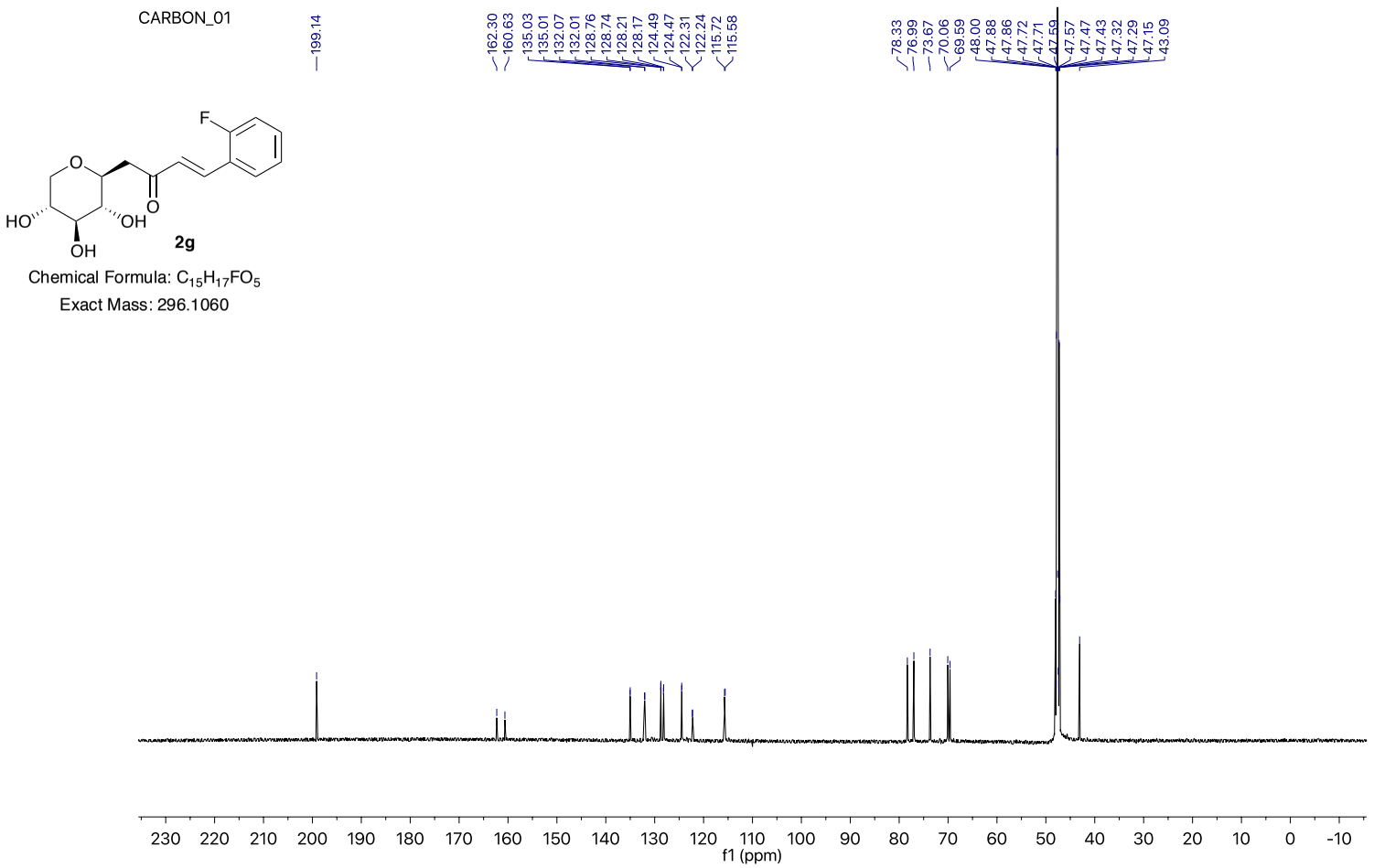
Chemical Formula: $C_{16}H_{17}F_3O_5$

Exact Mass: 346.1028



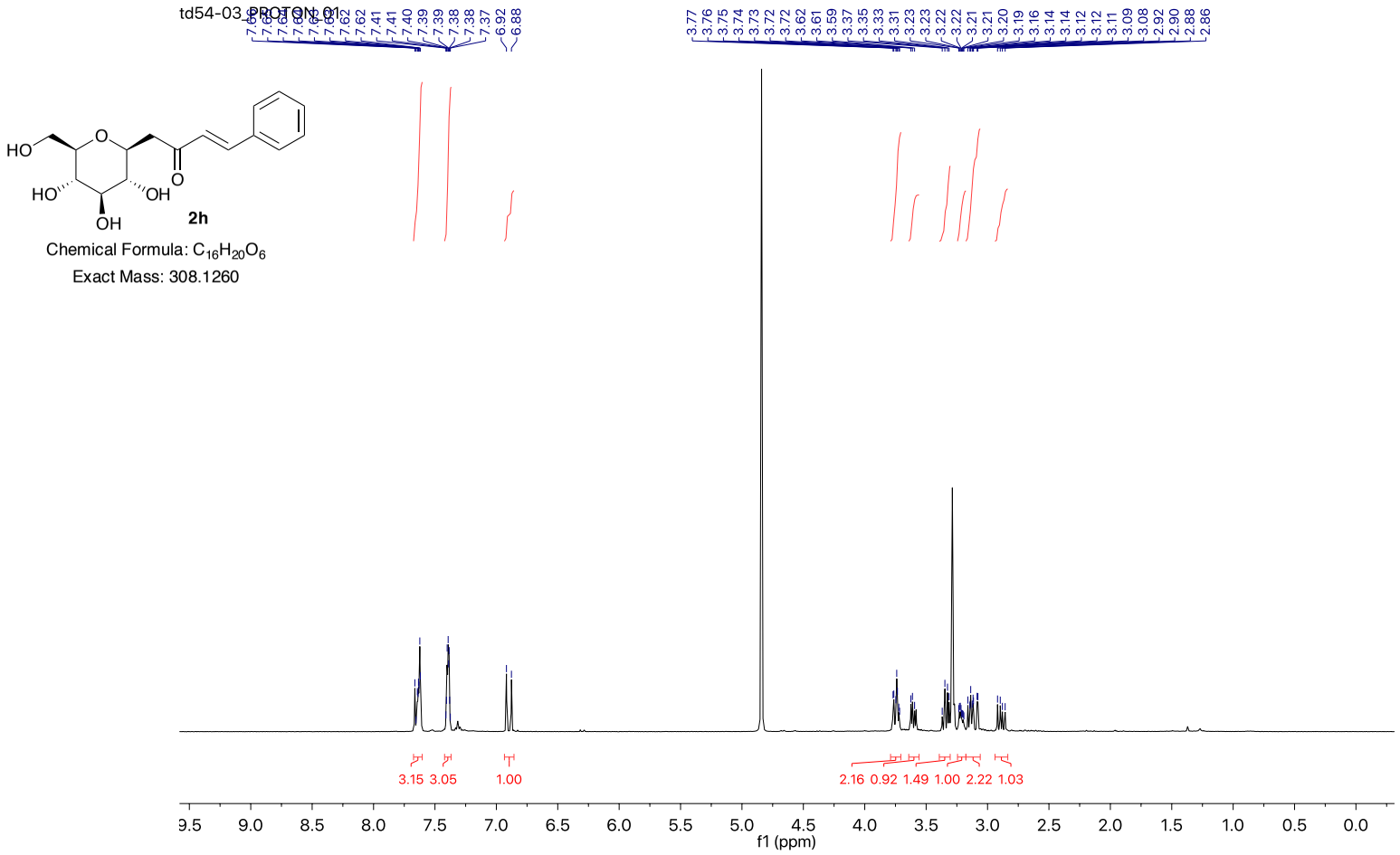

CARBON_01
198.98
141.01
138.43
131.45
129.59
128.49
125.44
125.40
78.34
76.98
73.70
70.06
69.60
48.19
48.05
47.98
47.84
47.77
47.55
47.41
47.34
47.13
46.91
42.99
CF3
O
O
HO
OH
OH
2f
Chemical Formula: C16H17F3O5
Exact Mass: 346.1028
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

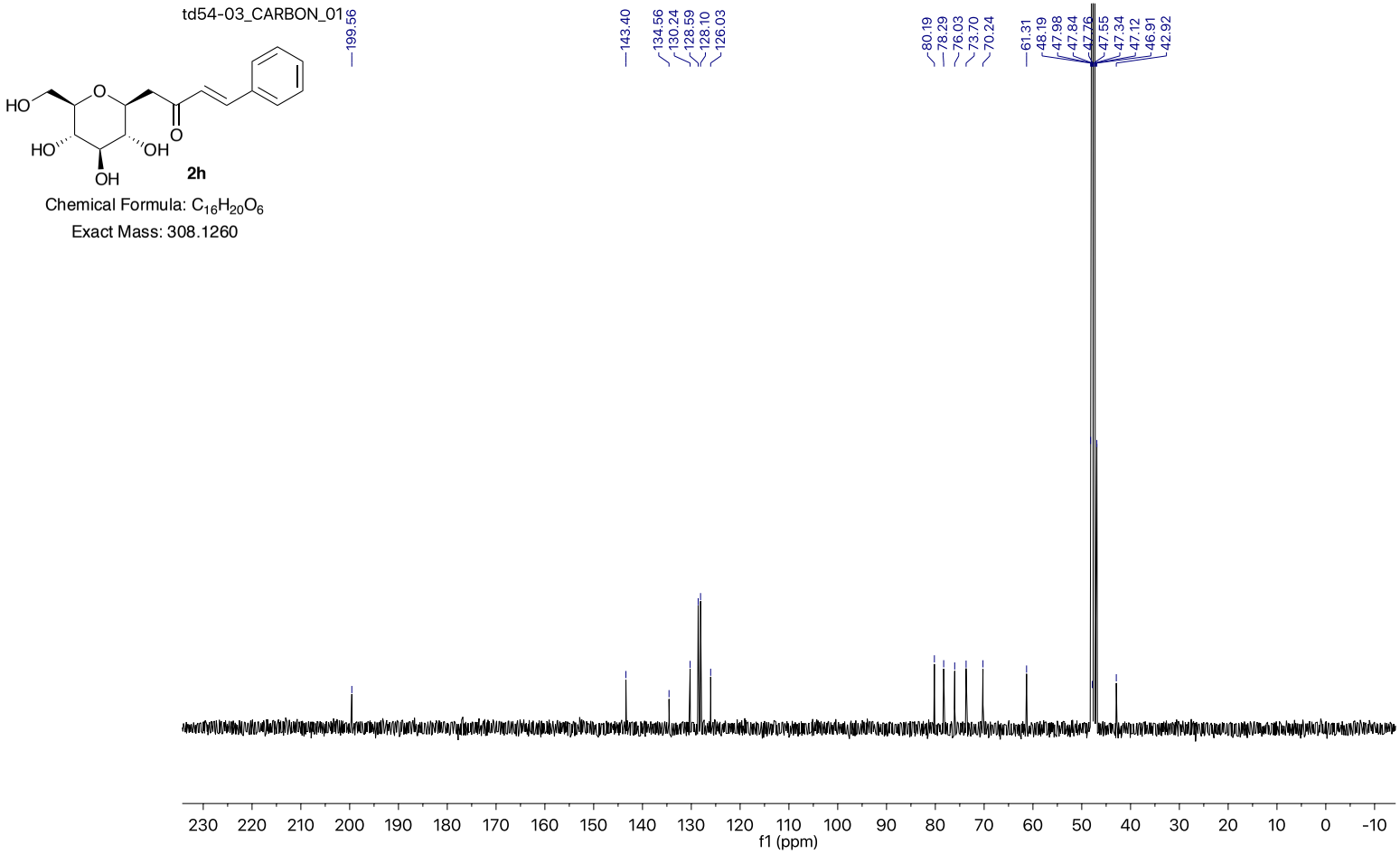

PROTON_01
7.74 7.72 7.72 7.71 7.70 7.48 7.45 7.43 7.42 7.41 7.41 7.23 7.22 7.20 7.19 7.17 7.16 7.15 7.14 6.96 6.93 6.91
3.82 3.81 3.80 3.79 3.69 3.68 3.68 3.67 3.66 3.65 3.65 3.47 3.46 3.46 3.45 3.44 3.43 3.18 3.16 3.15 3.14 3.13 3.12 3.12 3.12 3.10 3.09 3.07 3.07 2.86 2.85 2.84 2.82
F
O
HO
OH
OH
O
2g
Chemical Formula: C15H17FO5
Exact Mass: 296.1060
1.82 0.92 0.89 0.88 0.93
0.94 0.97 0.84 1.78 1.05 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

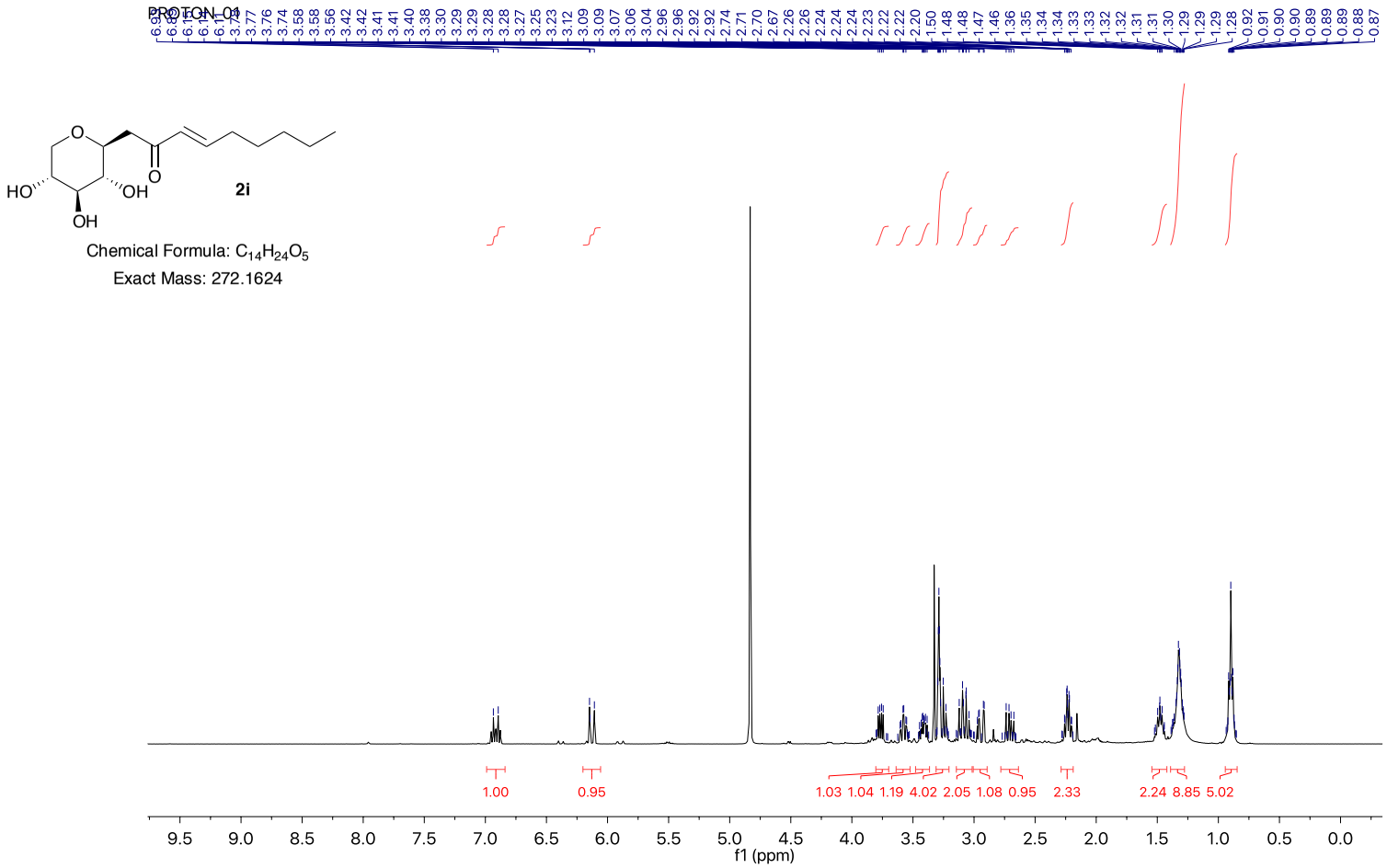


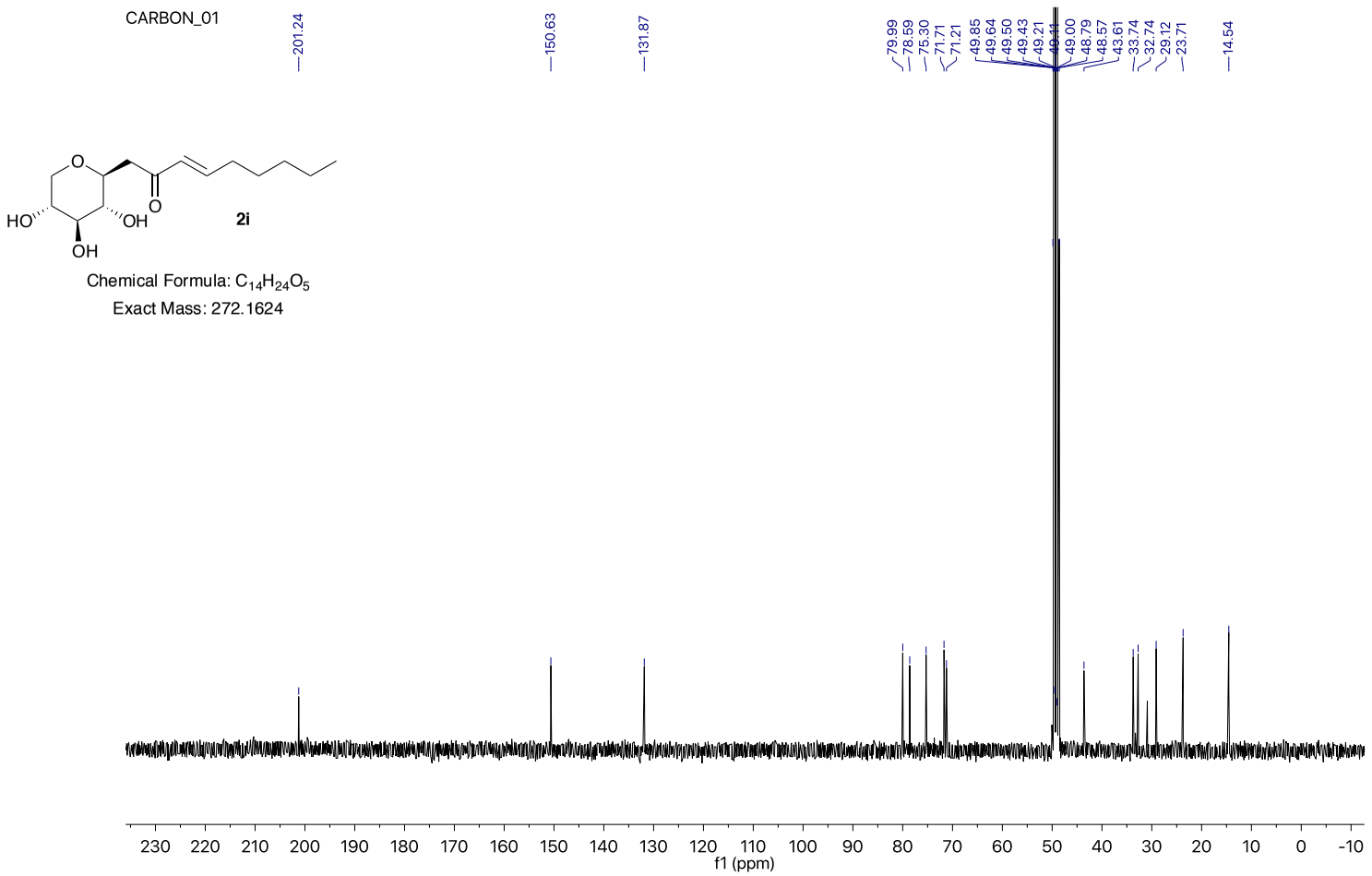

Chemical Formula: $C_{15}H_{17}FO_5$

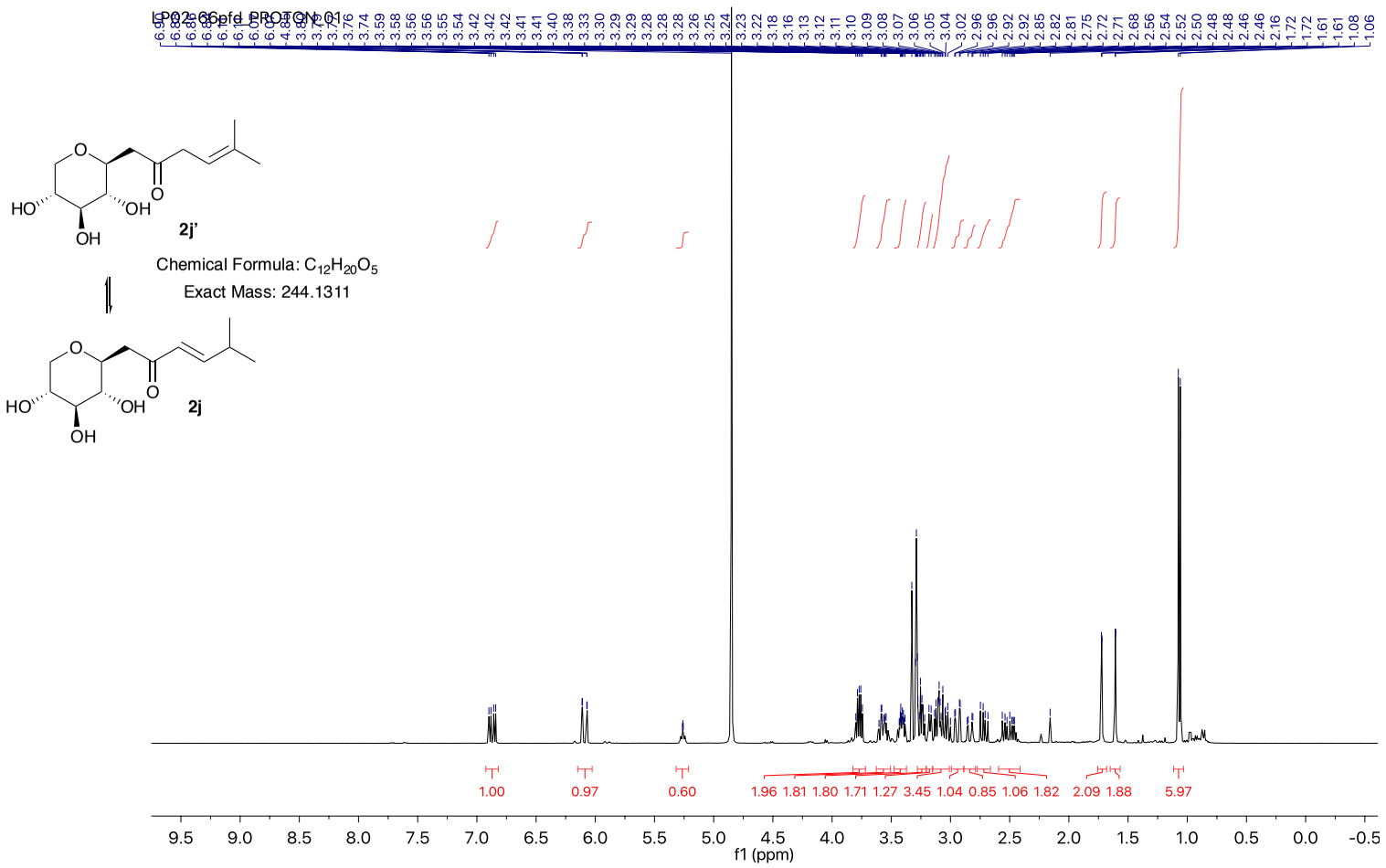
Exact Mass: 296.1060

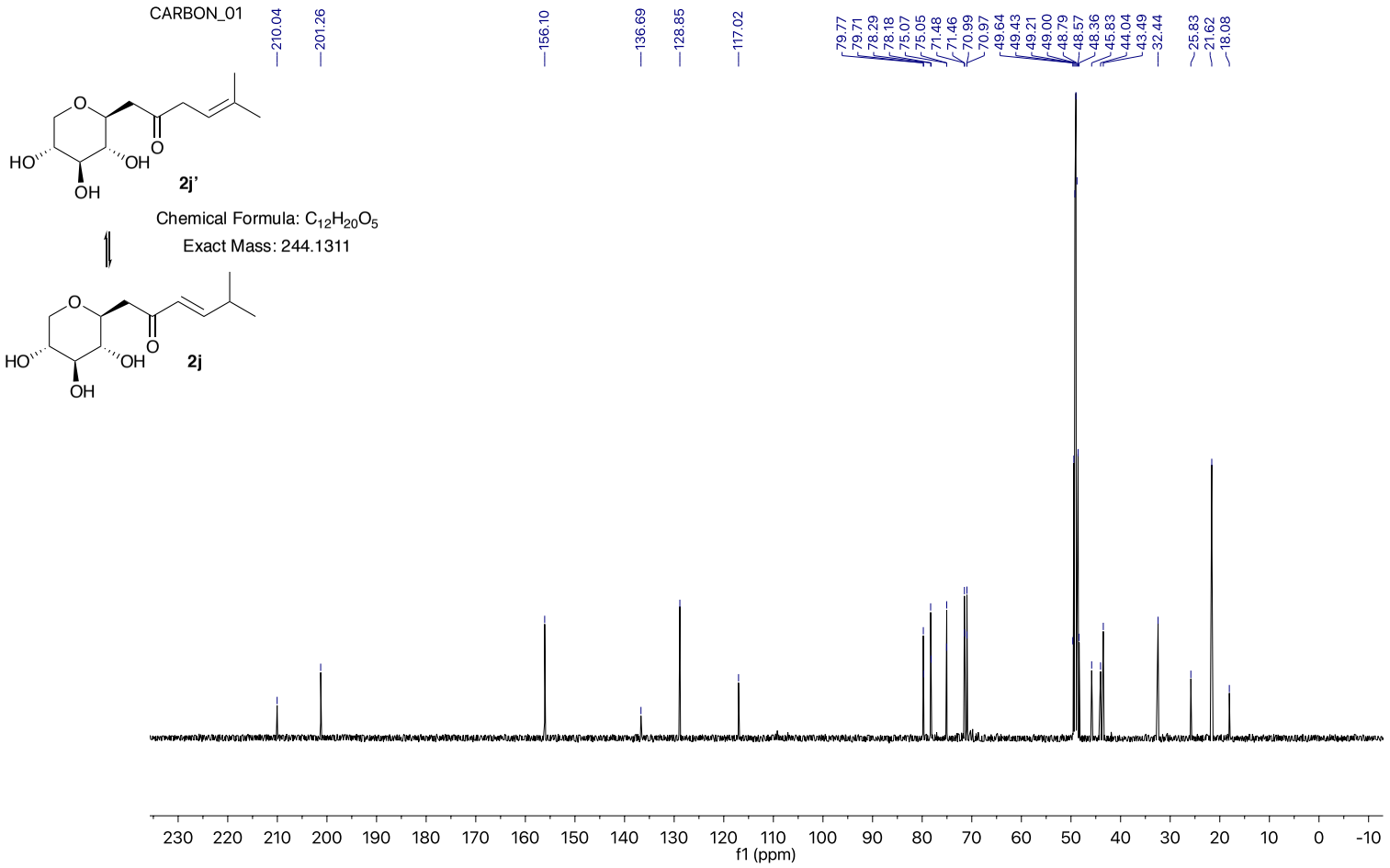

td54-03_PROTON-01
HO
HO
OH
OH
O
O
2h
Chemical Formula: C16H20O6
Exact Mass: 308.1260
3.15 3.05 1.00
2.16 0.92 1.49 1.00 2.22 1.03
f1 (ppm)

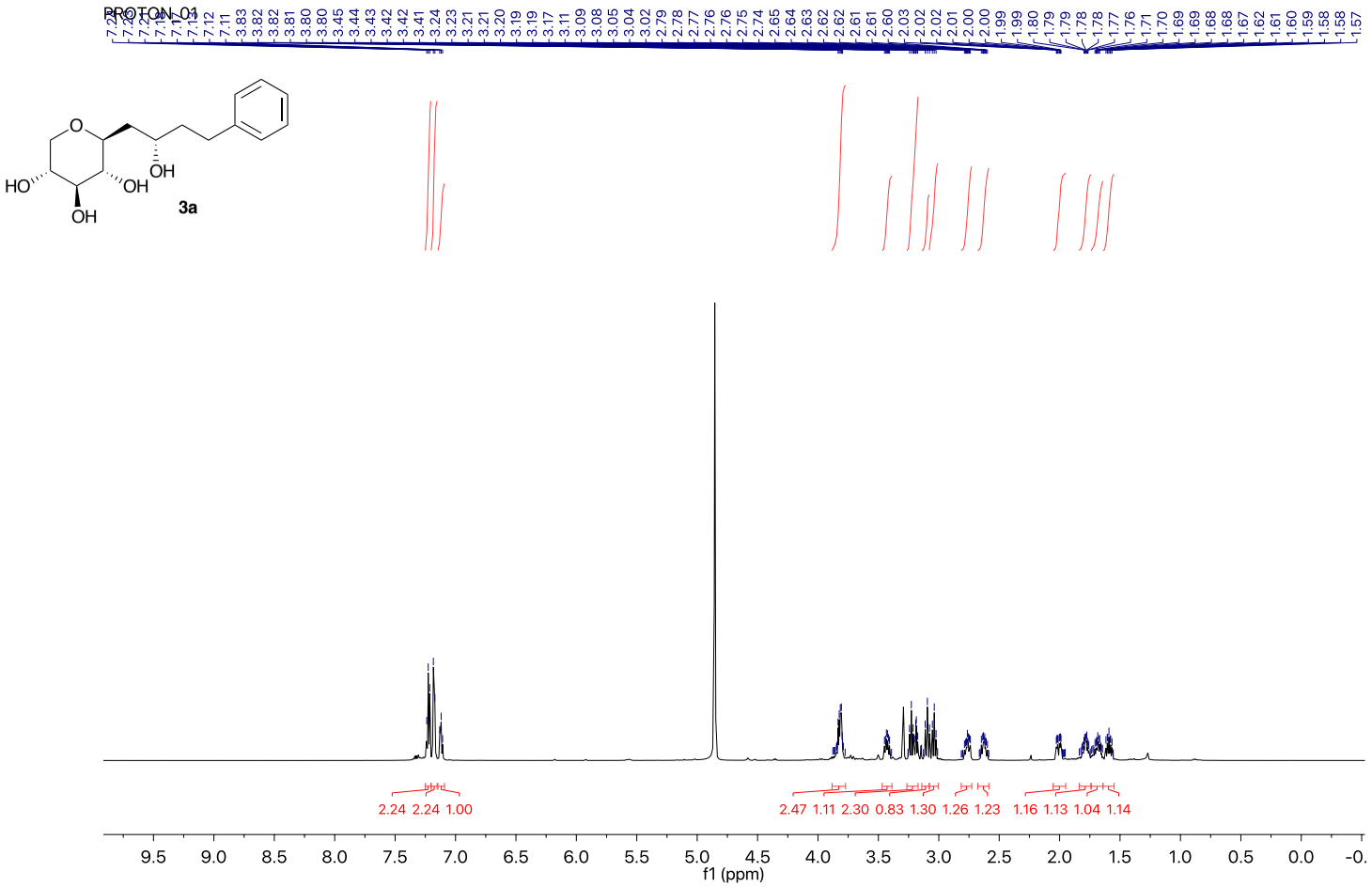

td54-03_CARBON_01
199.56
143.40
134.56
130.24
128.59
128.10
126.03
80.19
78.29
76.03
73.70
70.24
61.31
48.19
47.98
47.84
47.76
47.55
47.34
47.12
46.91
42.92
HO
O
HO
OH
OH
O
2h
Chemical Formula: C16H20O6
Exact Mass: 308.1260
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


PROTON_01
HO
OH
OH
O
O
2i
Chemical Formula: $C_{14}H_{24}O_5$
Exact Mass: 272.1624
1.00
0.95
1.03 1.04 1.19 4.02 2.05 1.08 0.95
2.33
2.24 8.85 5.02
f1 (ppm)

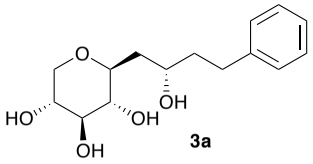

CARBON_01
201.24
150.63
131.87
79.99
78.59
75.30
71.71
71.21
49.85
49.64
49.50
49.43
49.21
49.00
48.79
48.57
43.61
33.74
32.74
29.12
23.71
14.54
HO
OH
OH
O
O
2i
Chemical Formula: C14H24O5
Exact Mass: 272.1624
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


LD02-66pfd PROTON 01
2j'
Chemical Formula: $C_{12}H_{20}O_5$
Exact Mass: 244.1311
2j
1.00
0.97
0.60
1.96 1.81 1.80 1.71 1.27 3.45 1.04 0.85 1.06 1.82
2.09 1.88
5.97
f1 (ppm)


CARBON_01
210.04
201.26
156.10
136.69
128.85
117.02
79.77
79.71
78.29
78.18
75.07
75.05
71.48
71.46
70.99
70.97
49.64
49.43
49.21
49.00
48.79
48.57
48.36
45.83
44.04
43.49
32.44
25.83
21.62
18.08
HO
OH
OH
O
O
2j'
Chemical Formula: C12H20O5
Exact Mass: 244.1311
HO
OH
OH
O
O
2j
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

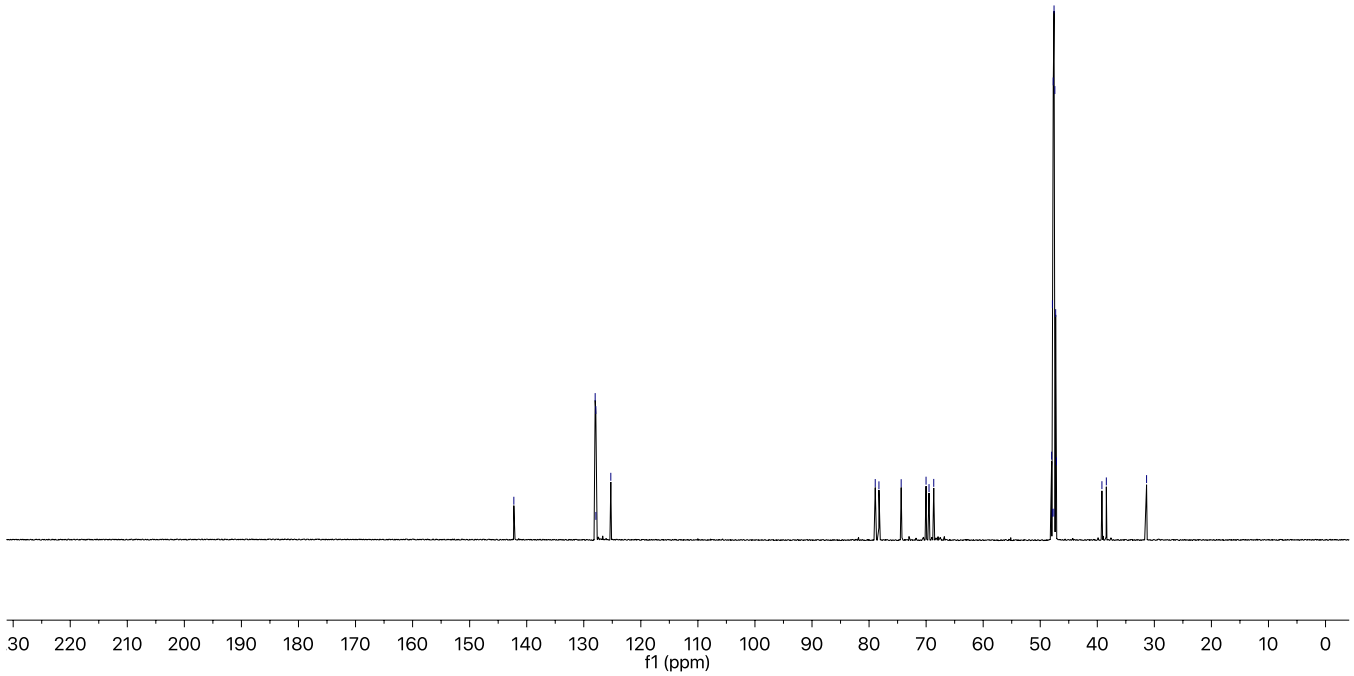

PROTON_01
HO
OH
OH
OH
O
3a
2.24 2.24 1.00
2.47 1.11 2.30 0.83 1.30 1.26 1.23
1.16 1.13 1.04 1.14
f1 (ppm)

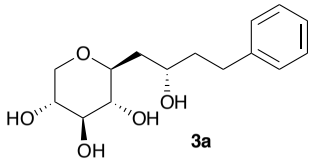
CARBON_01



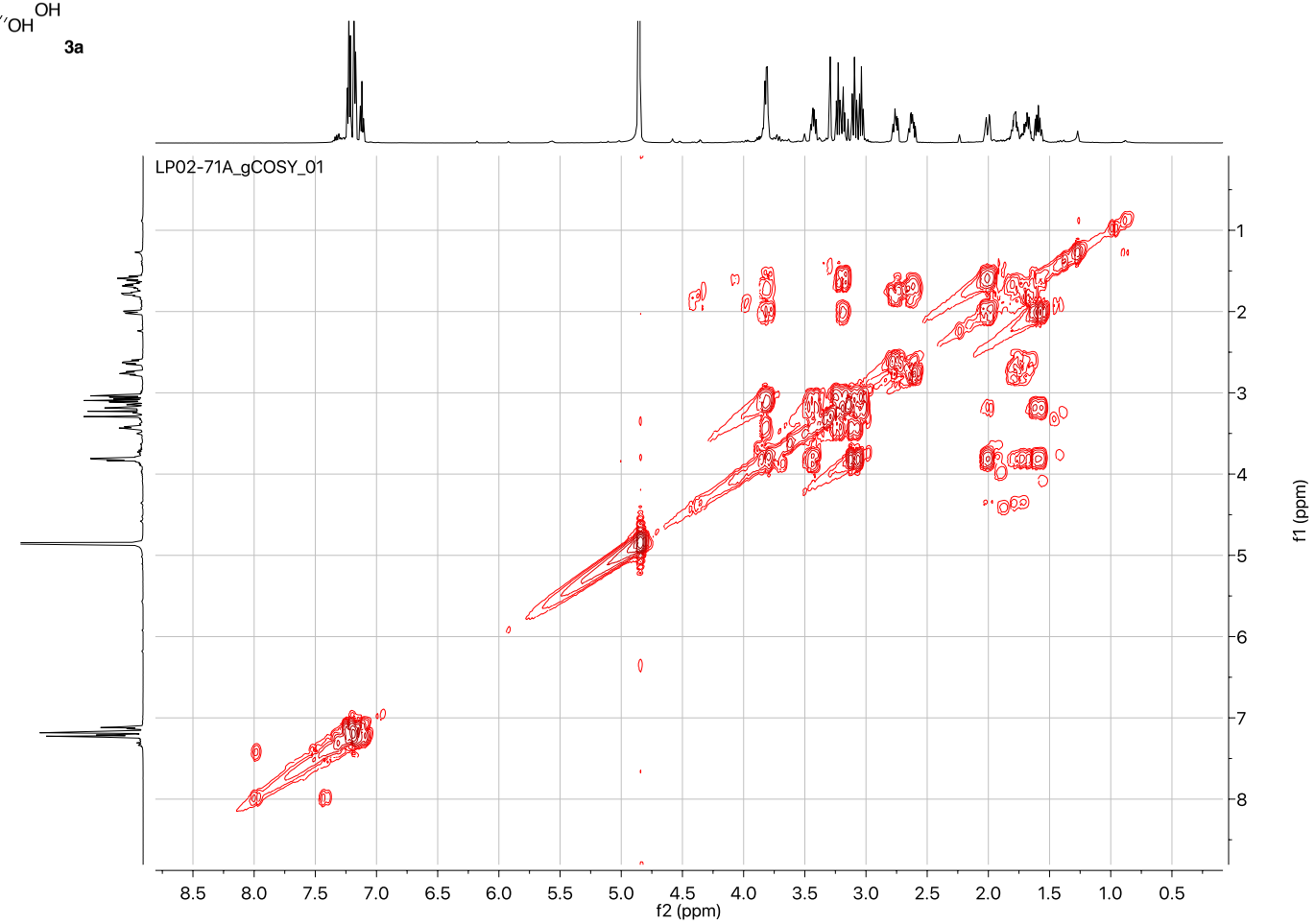

**3a**

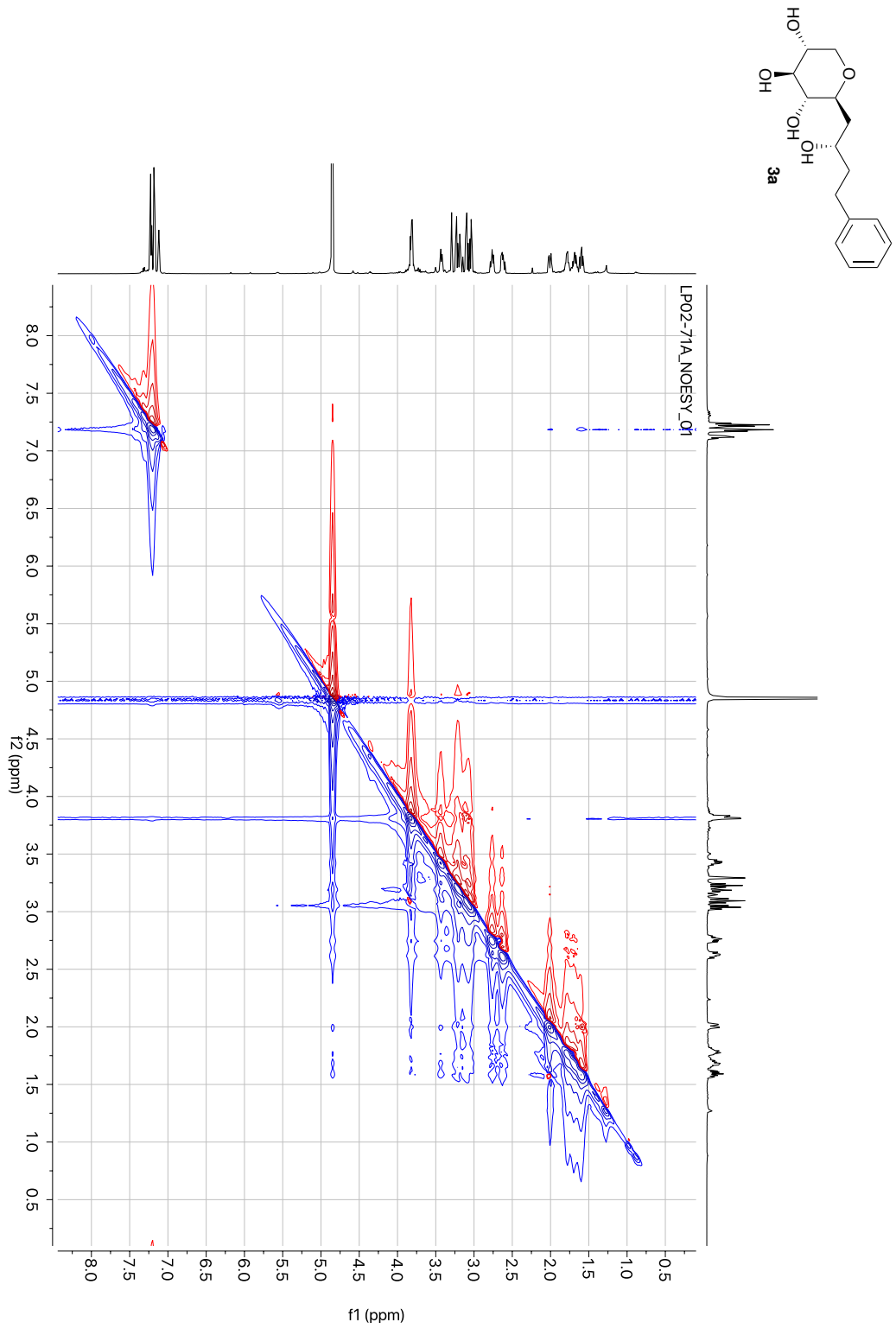
142.25
128.00
127.89
127.87
125.26
78.92
78.27
74.37
70.01
69.49
68.66
48.01
47.88
47.86
47.72
47.61
47.58
47.44
47.30
47.15
39.19
38.42
31.36

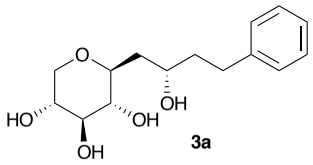



O
HO
OH
OH
OH

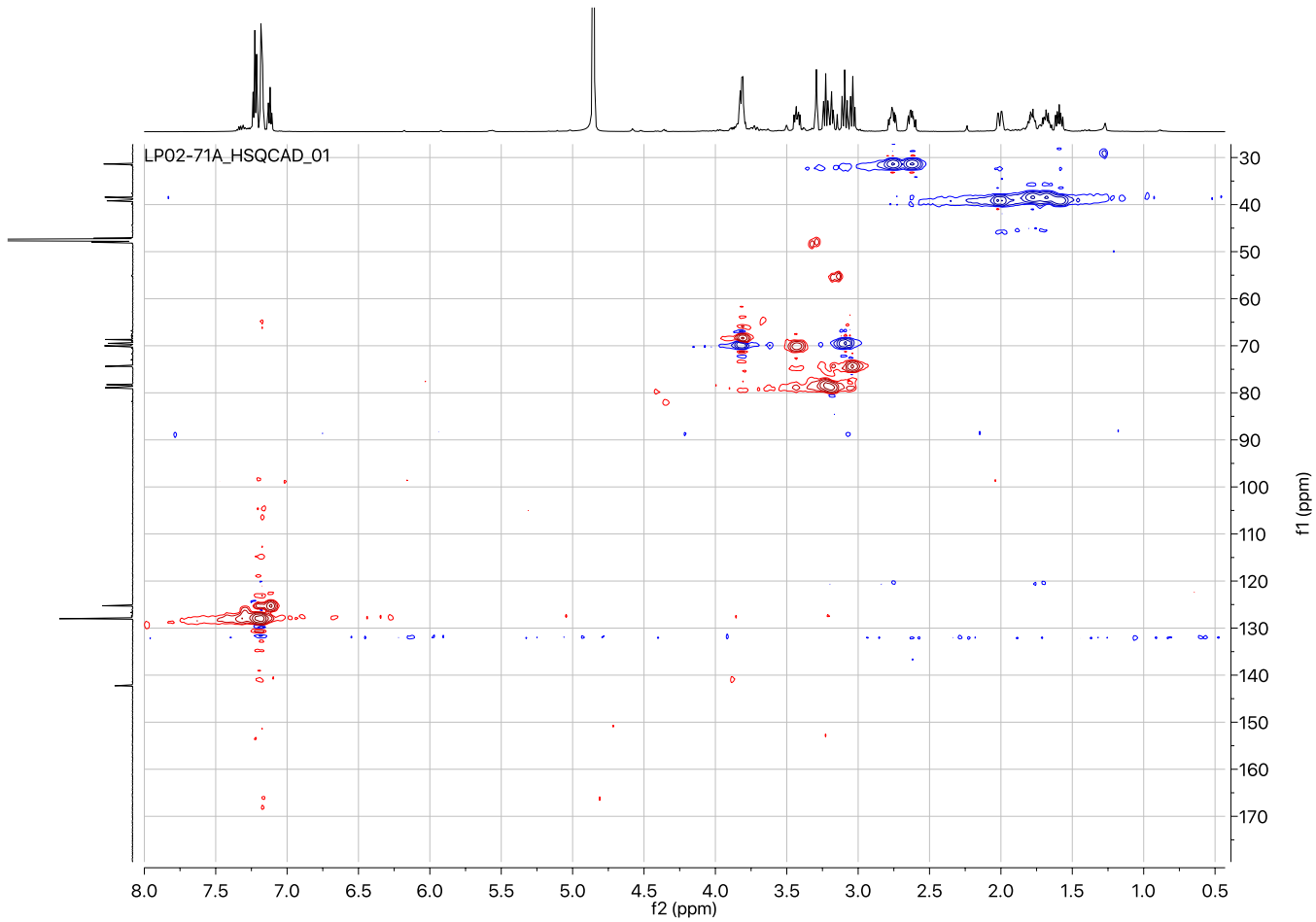
**3a**

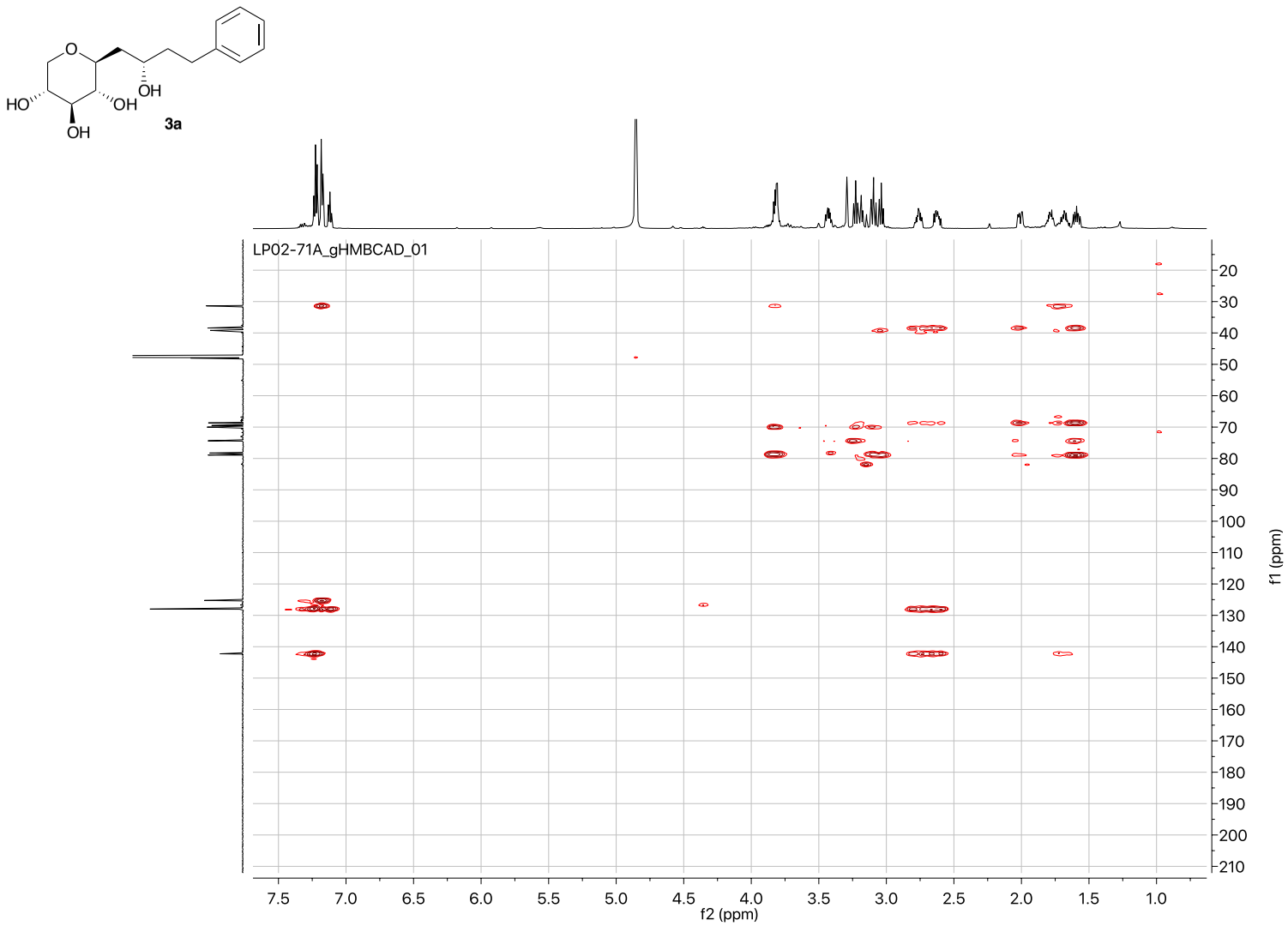

LP02-71A_gCOSY_01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
1
2
3
4
5
6
7
8
f1 (ppm)

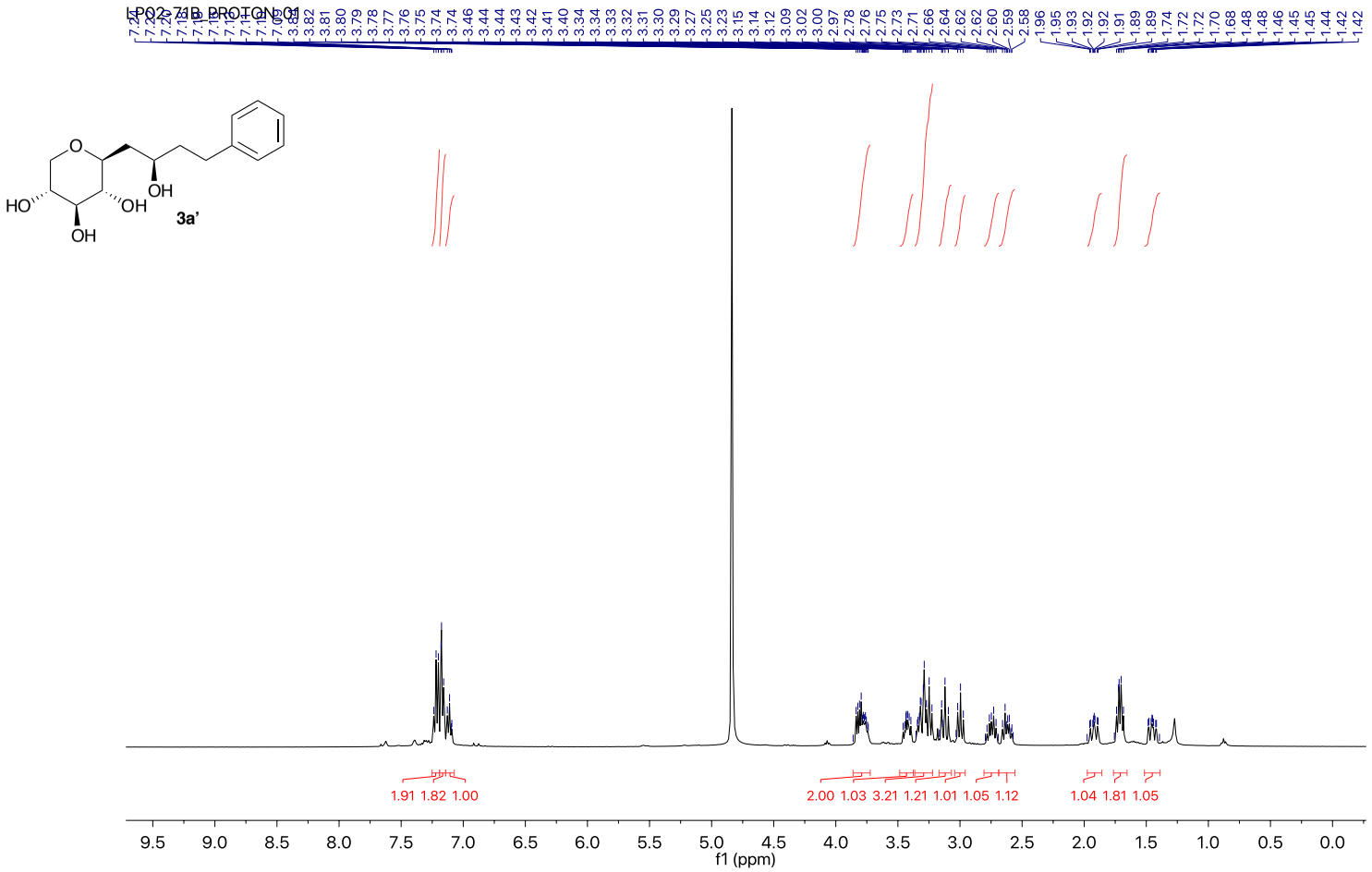

HO
O
OH
OH
OH
3a
LP02-71A_NOESY_01
f2 (ppm)
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

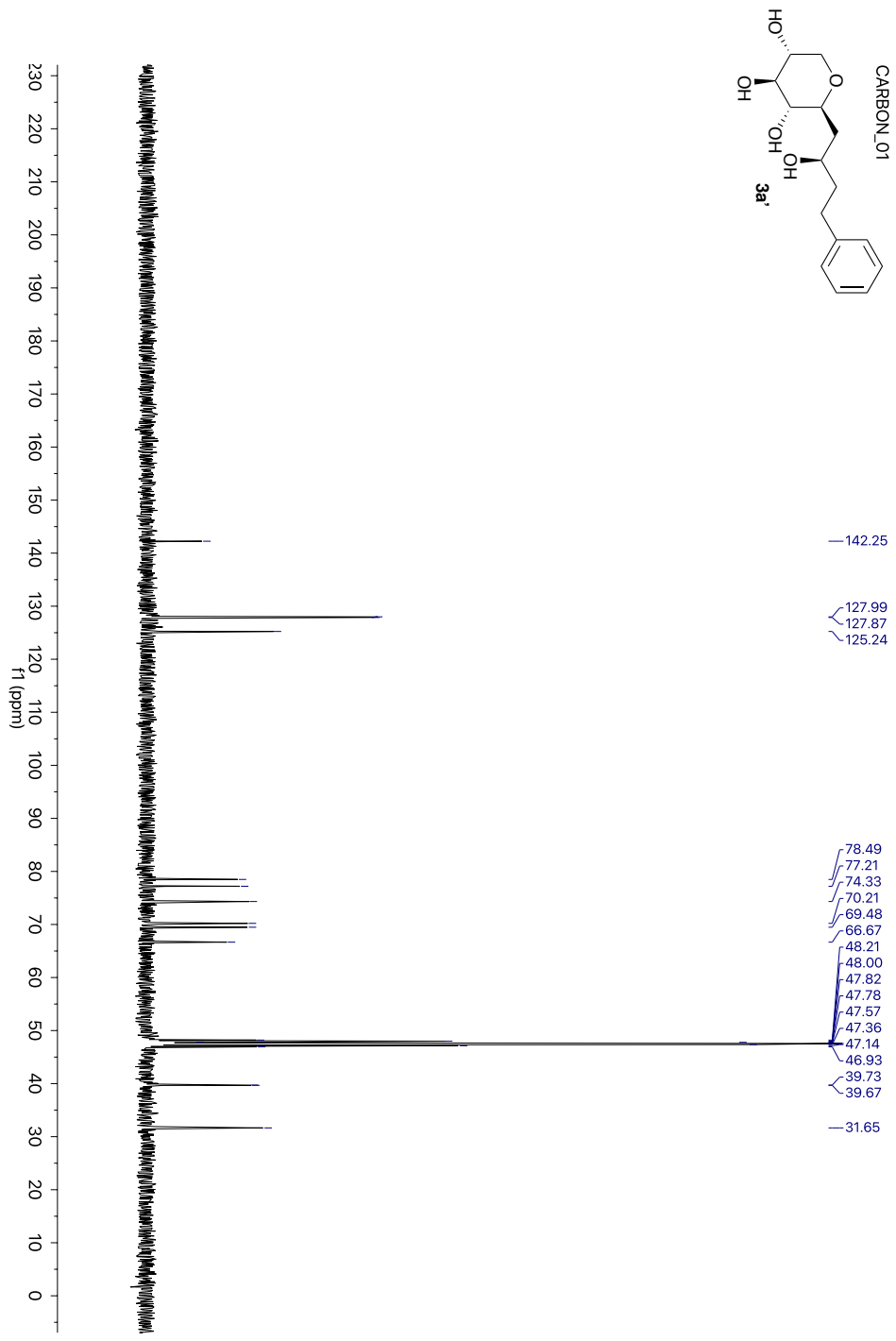

O
HO
OH
OH
OH

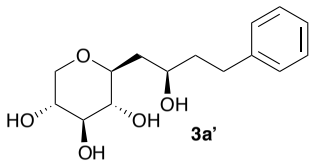
**3a**


LP02-71A_HSQCAD_01
f2 (ppm)
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170

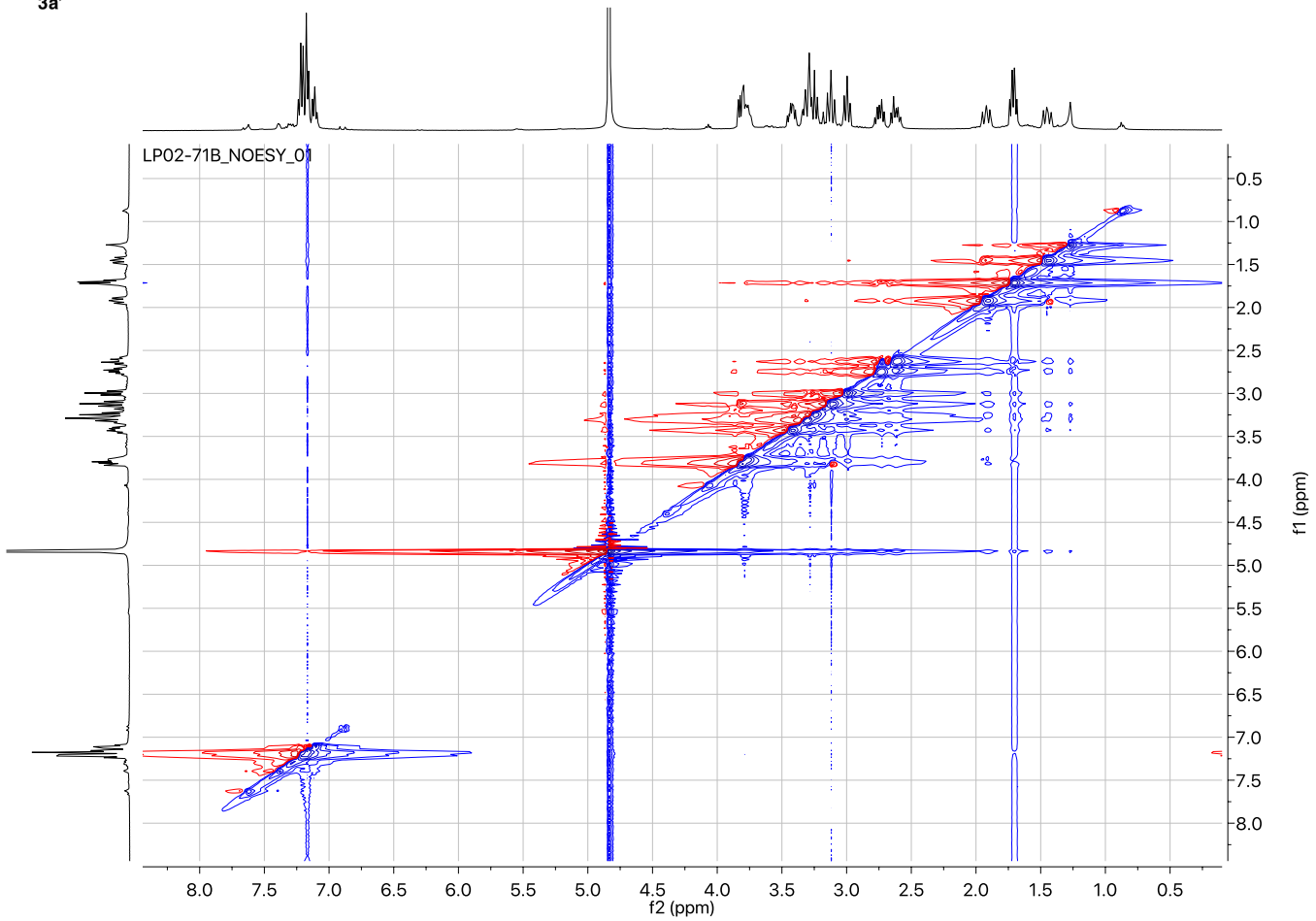

O
HO
OH
OH
OH
3a
LP02-71A_gHMBCAD_01
f2 (ppm)
f1 (ppm)

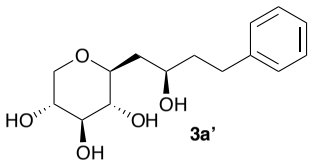

LPO2-71B PROTON-01
HO
OH
OH
OH
O
3a'
1.91 1.82 1.00
2.00 1.03 3.21 1.21 1.01 1.05 1.12
1.04 1.81 1.05
f1 (ppm)


CARBON_01
HO
OH
OH
OH
O
3a'
142.25
127.99
127.87
125.24
78.49
77.21
74.33
70.21
69.48
66.67
48.21
48.00
47.82
47.78
47.57
47.36
47.14
46.93
39.73
39.67
31.65
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

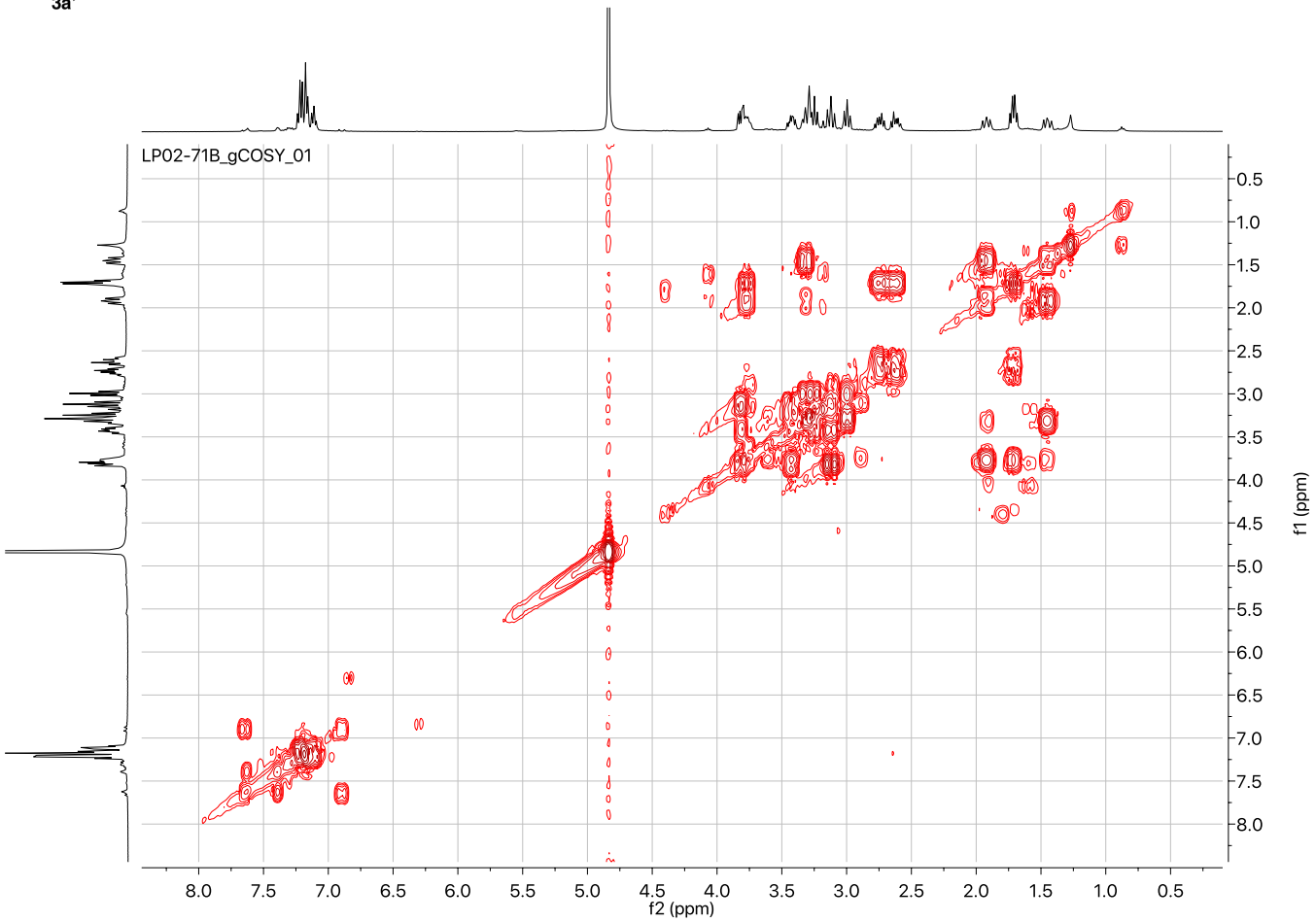

O
HO
OH
OH
OH

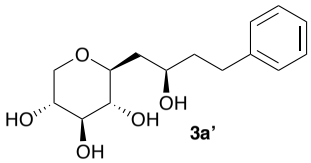
**3a'**

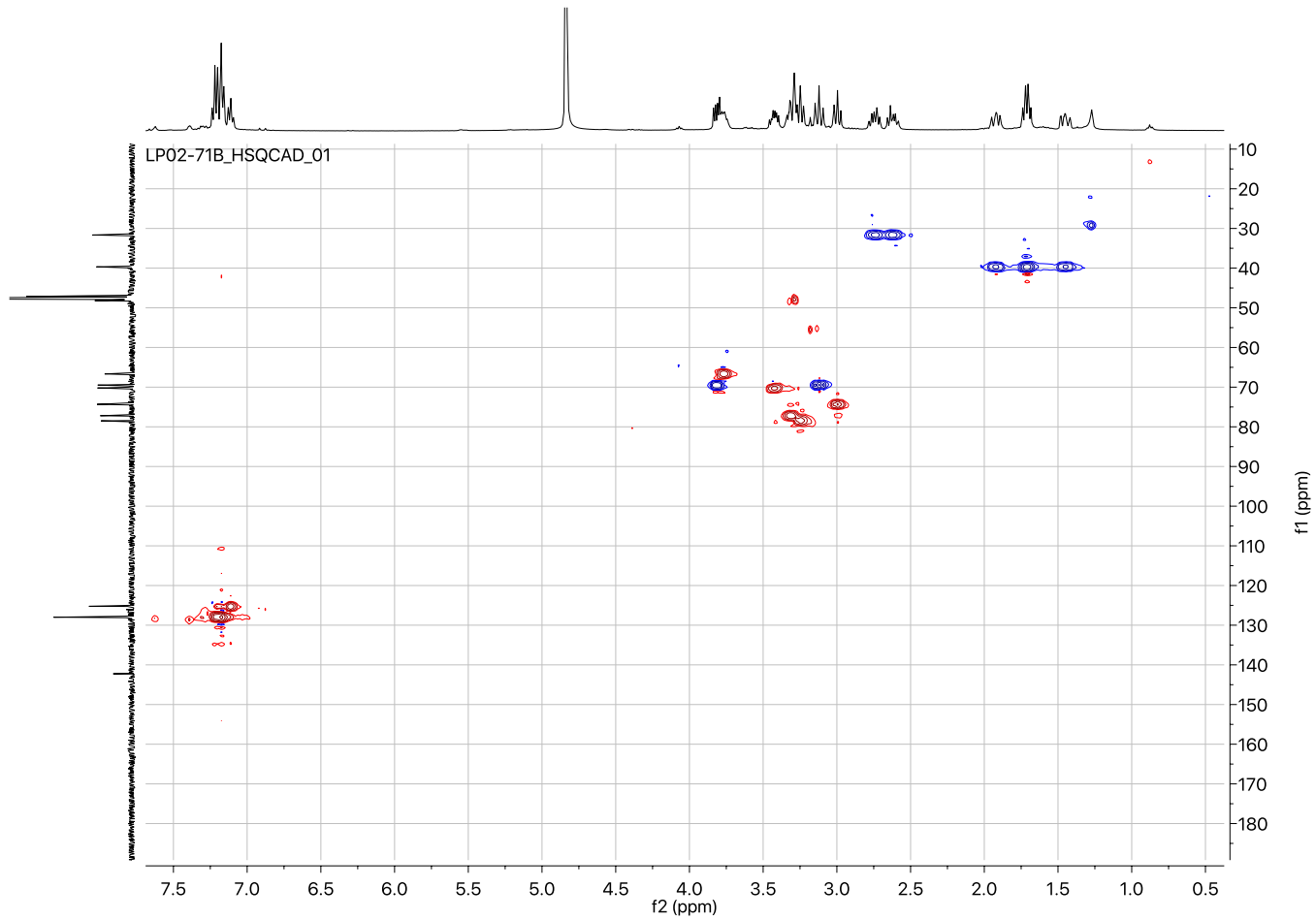

LP02-71B_NOESY_01
f2 (ppm)
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

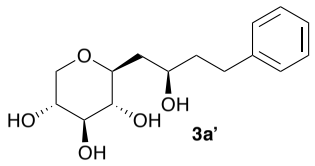

O
HO
OH
OH
OH

**3a'**

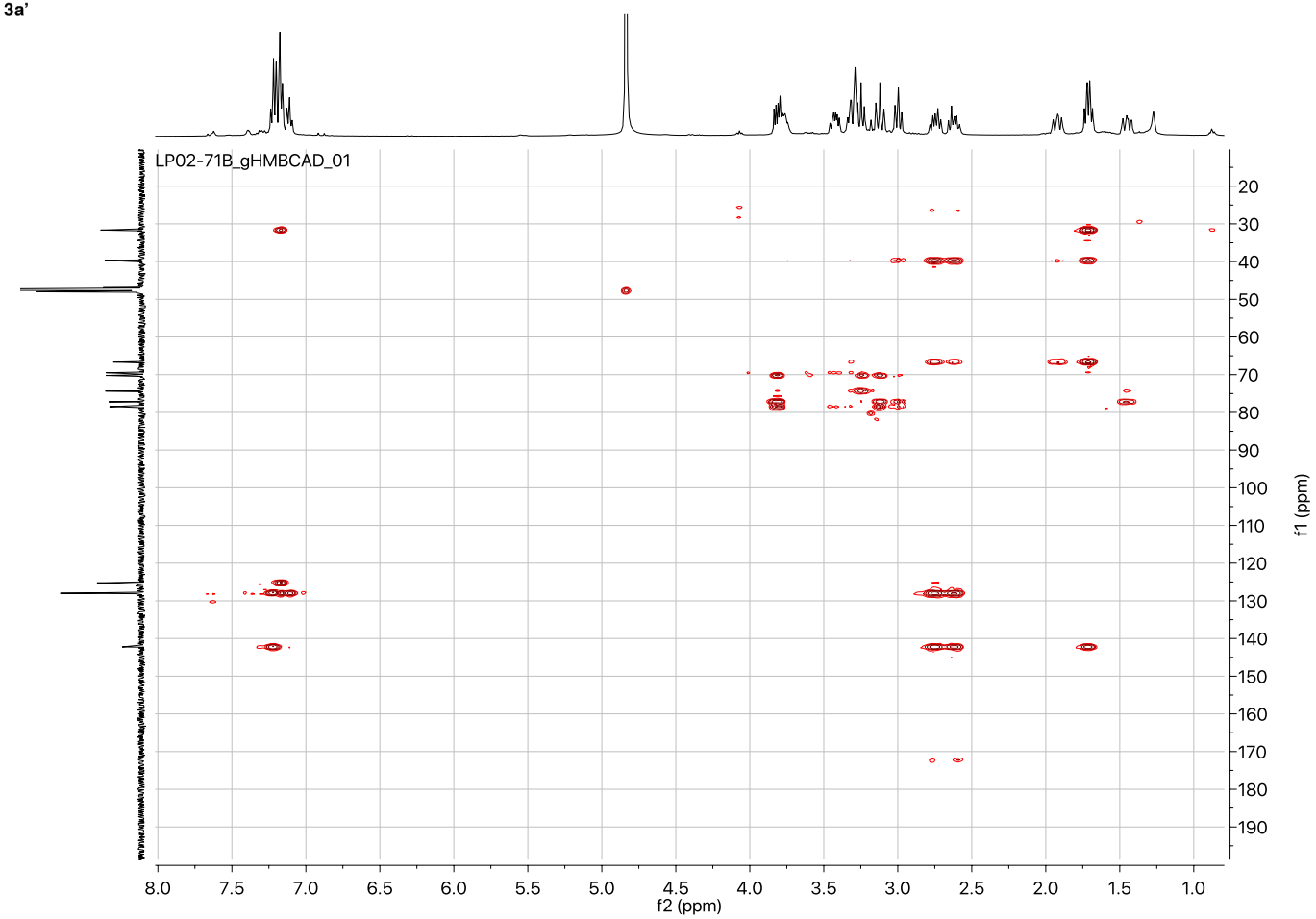

LP02-71B_gCOSY_01
f2 (ppm)
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

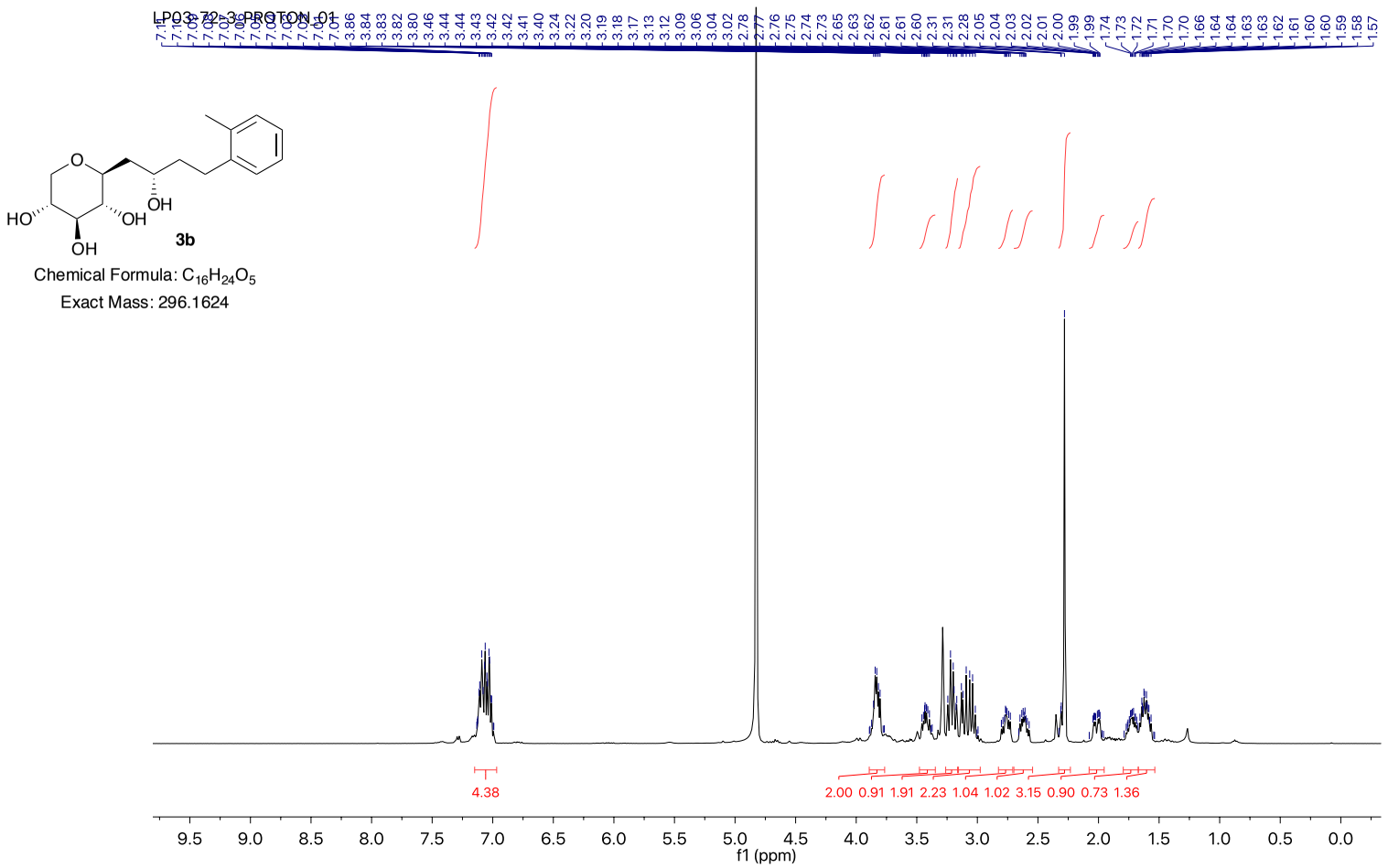

O
HO
OH
OH
OH
3a'


LP02-71B_HSQCAD_01
f2 (ppm)
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180

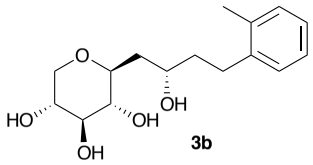



**3a'**




LP03-72-3-PROTON-01
HO
OH
OH
OH
O
3b
Chemical Formula: C16H24O5
Exact Mass: 296.1624
4.38
2.00 0.91 1.91 2.23 1.04 1.02 3.15 0.90 0.73 1.36
f1 (ppm)

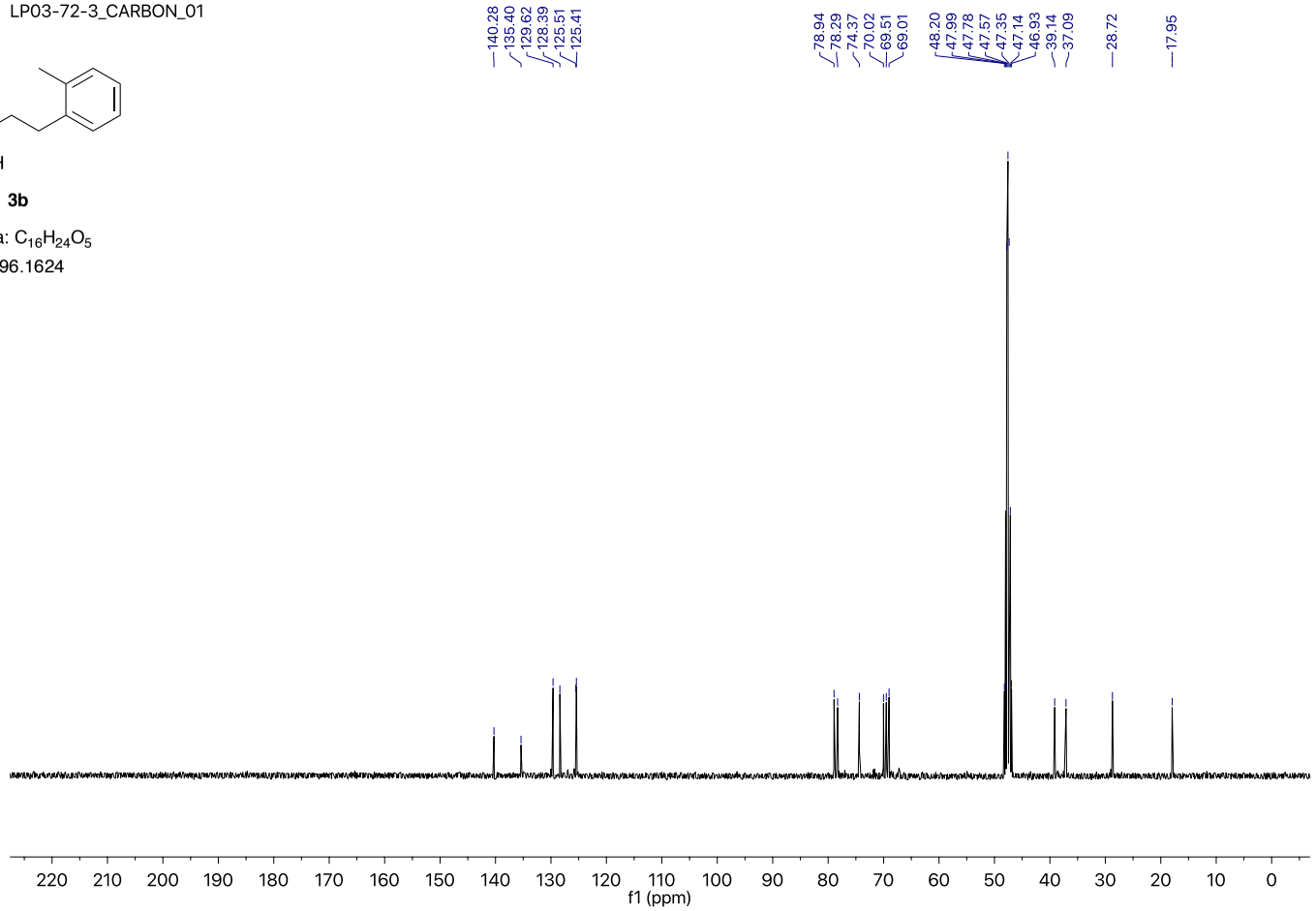
LP03-72-3_CARBON_01



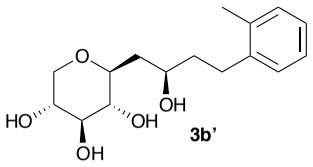

**3b**

Chemical Formula: $C_{16}H_{24}O_5$

Exact Mass: 296.1624



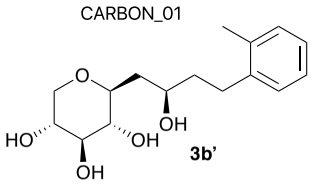
PROTON_01




**3b'**

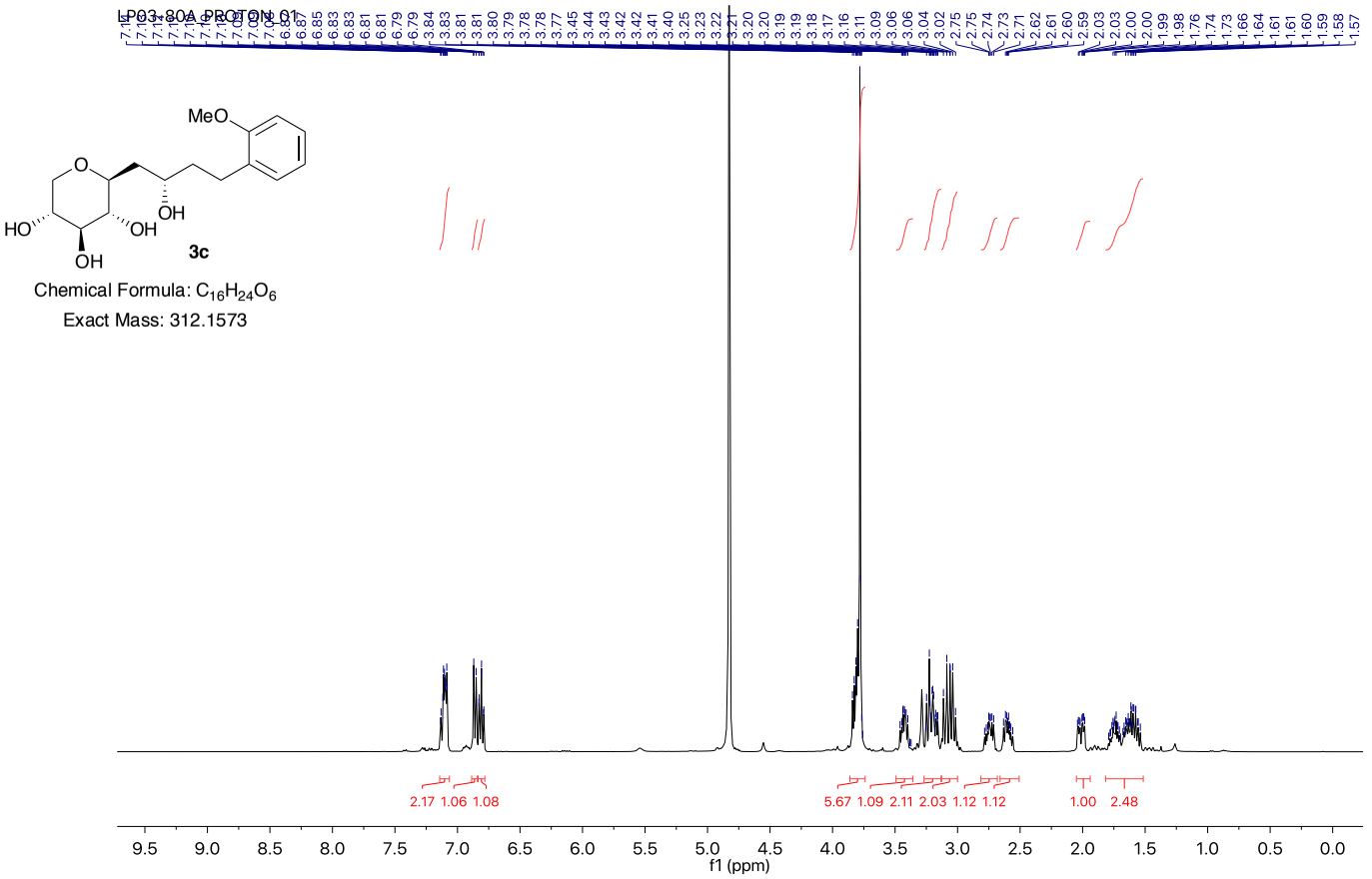
Chemical Formula: $C_{16}H_{24}O_5$

Exact Mass: 296.1624

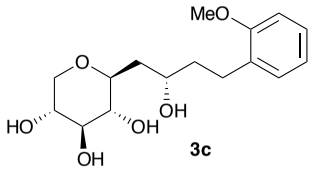



Chemical Formula: $C_{16}H_{24}O_5$

Exact Mass: 296.1624


LP03-80A PROTON 01
MeO
O
HO
OH
OH
OH
3c
Chemical Formula: $C_{16}H_{24}O_6$
Exact Mass: 312.1573
2.17 1.06 1.08
5.67 1.09 2.11 2.03 1.12 1.12
1.00 2.48
f1 (ppm)

LP03-80A_CARBON_01

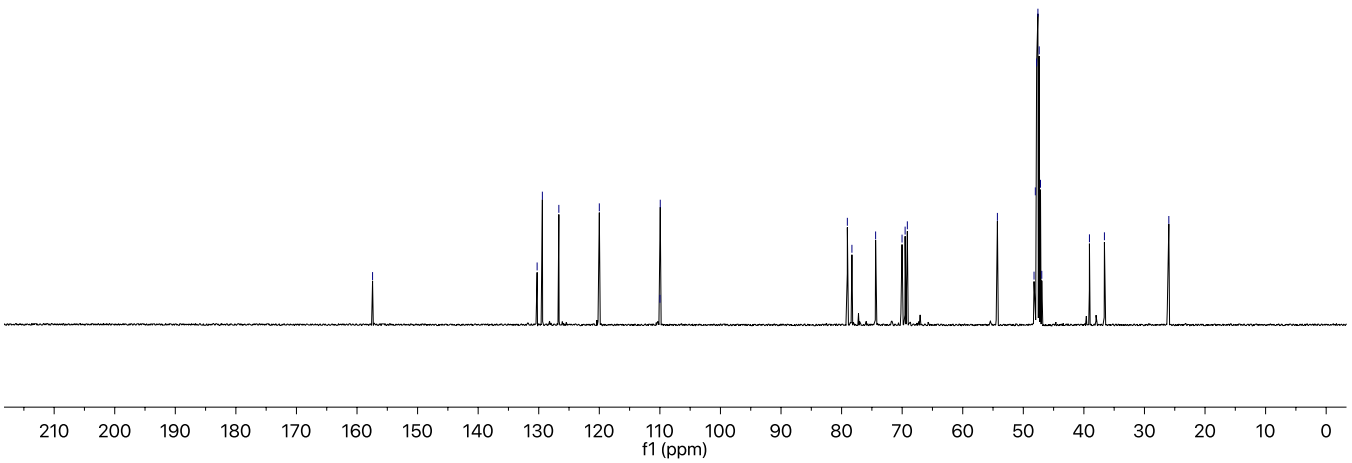


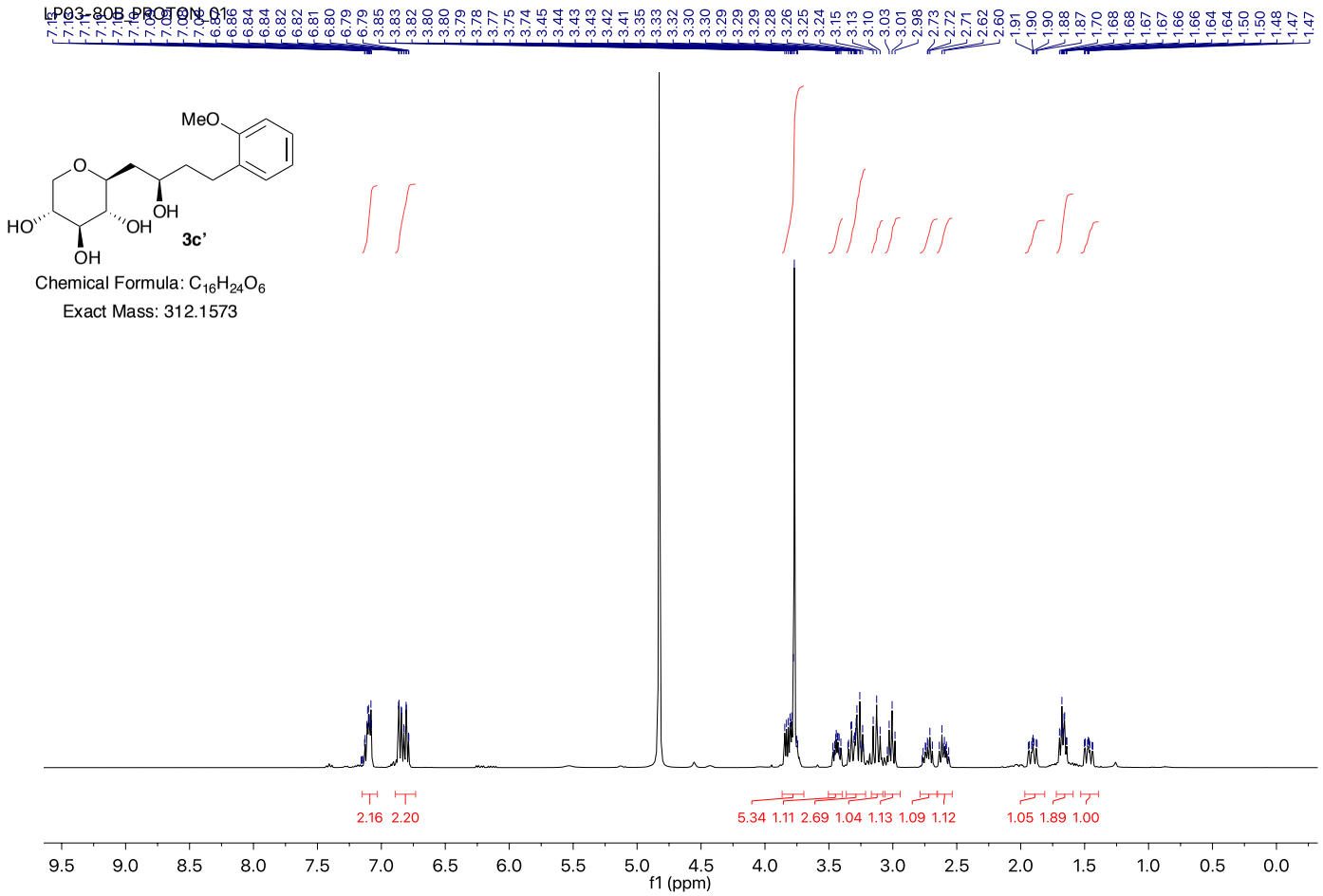

**3c**

Chemical Formula: $C_{16}H_{24}O_6$

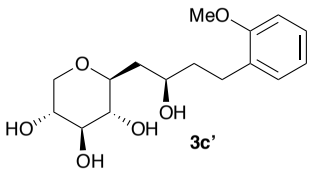
Exact Mass: 312.1573

157.43
130.27
129.40
126.68
120.00
109.99
109.94
79.05
78.30
74.38
70.02
69.51
69.14
54.28
48.23
48.02
47.80
47.59
47.38
47.16
46.95
39.08
36.61
25.98




LP03-80B PROTON 01
MeO
O
OH
HO
OH
OH
3c'
Chemical Formula: $C_{16}H_{24}O_6$
Exact Mass: 312.1573
2.16 2.20
5.34 1.11 2.69 1.04 1.13 1.09 1.12
1.05 1.89 1.00
f1 (ppm)

LP03-80B_CARBON_01

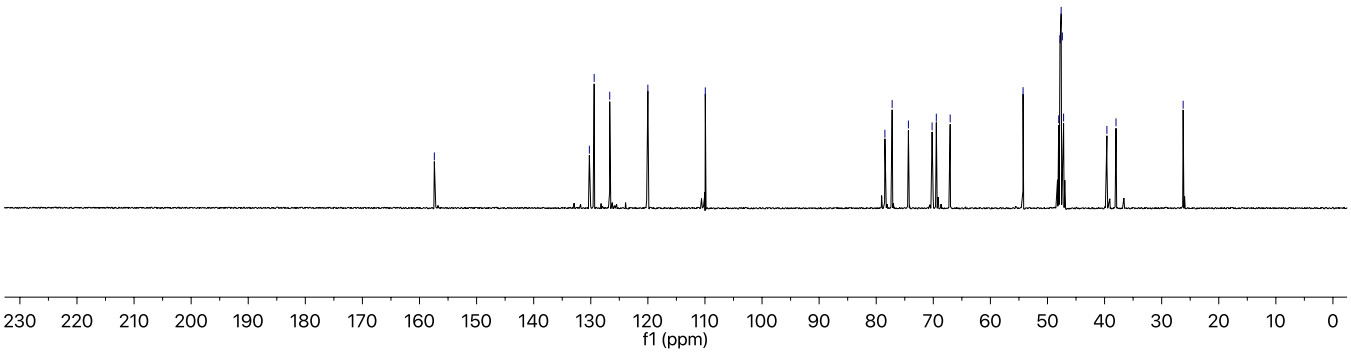


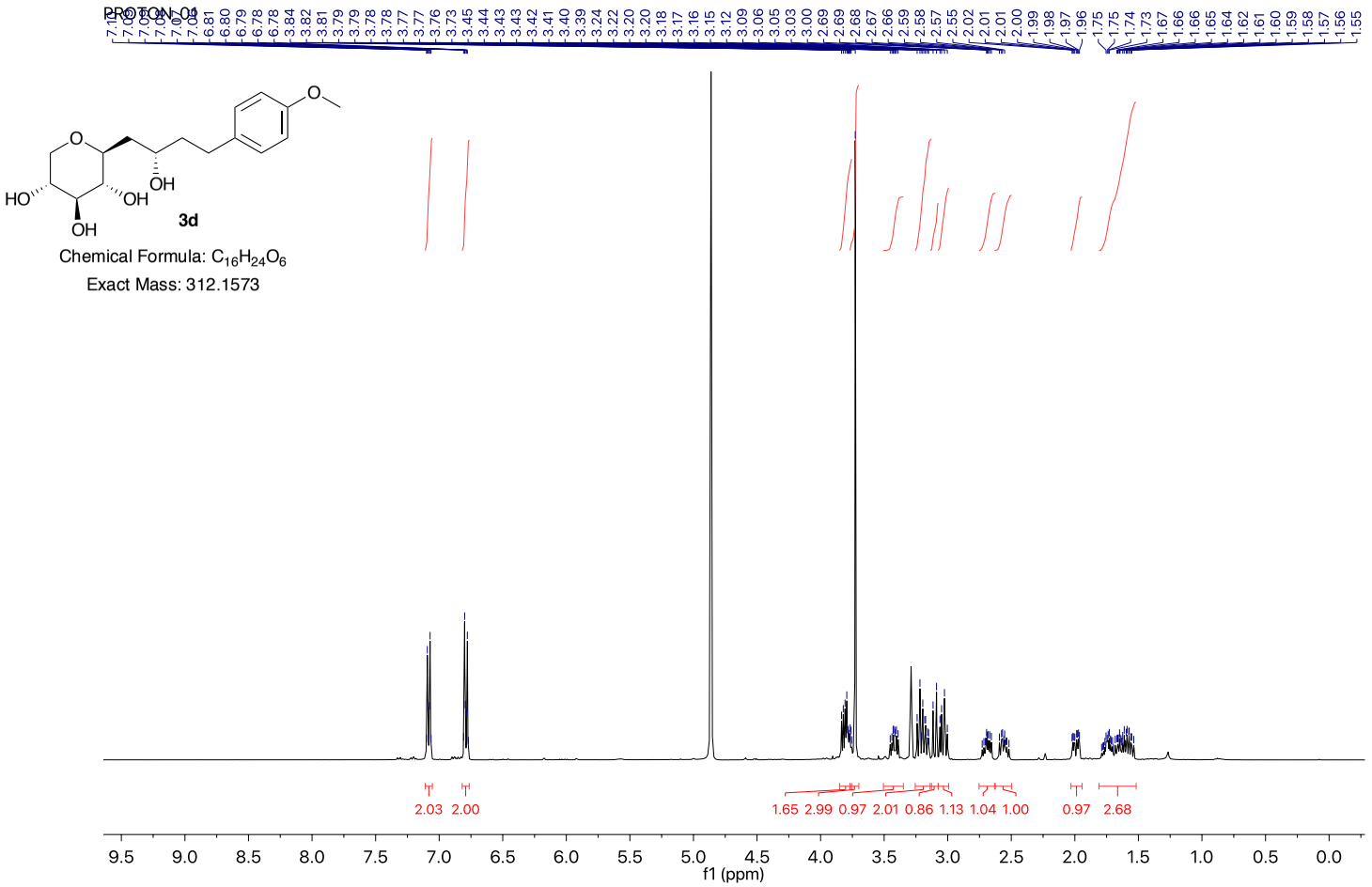

**3c'**

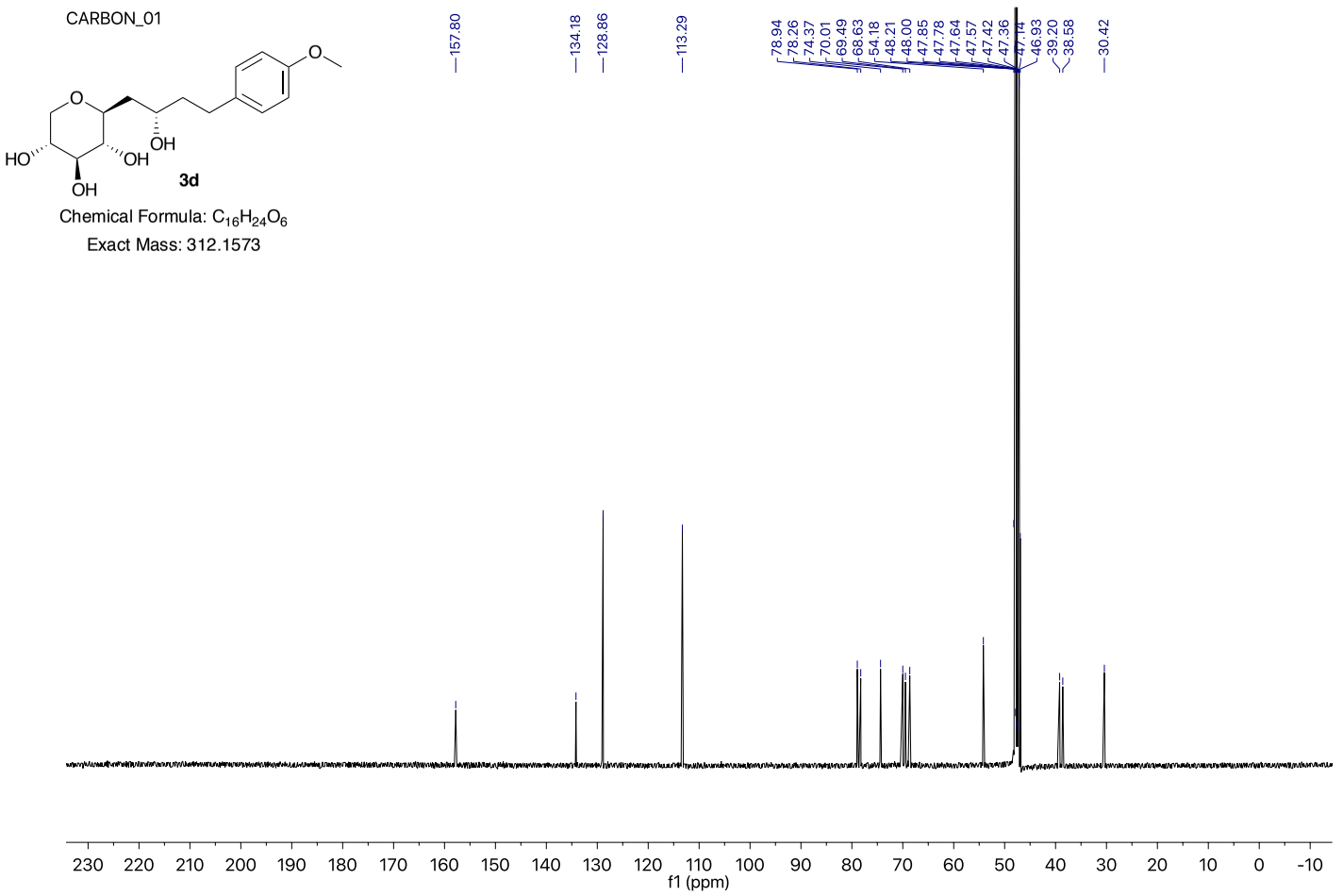
Chemical Formula: $C_{16}H_{24}O_6$

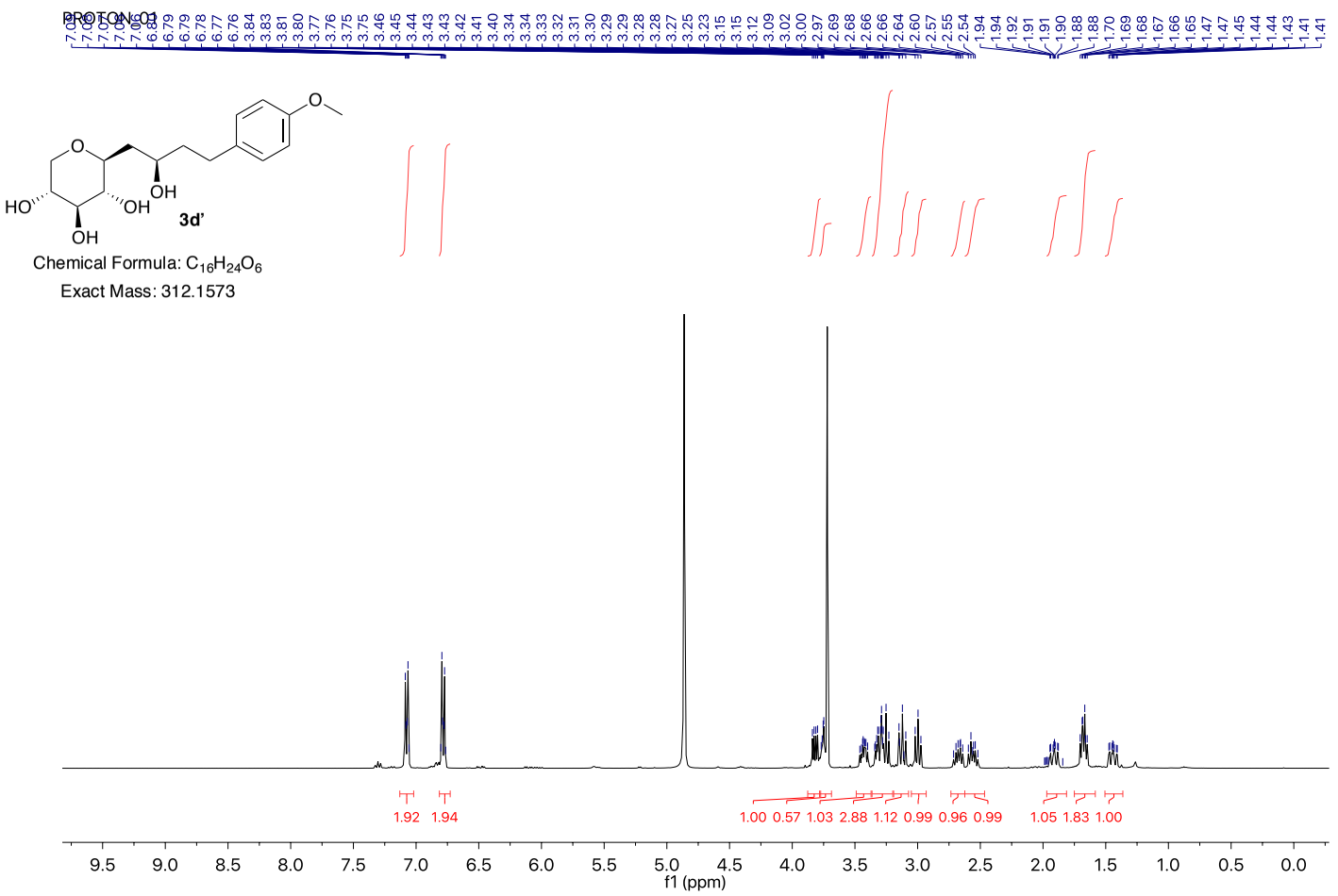
Exact Mass: 312.1573

157.40
130.25
129.40
126.68
120.00
109.94
78.48
77.21
74.36
70.21
69.47
67.04
54.28
48.03
47.82
47.61
47.39
47.18
39.59
37.99
26.24

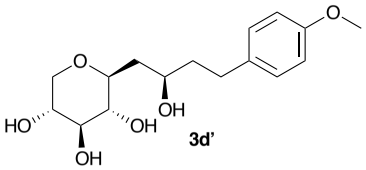



PROTON-01
3d
Chemical Formula: C16H24O6
Exact Mass: 312.1573
2.03 2.00
1.65 2.99 0.97 2.01 0.86 1.13 1.04 1.00
0.97 2.68
f1 (ppm)


CARBON_01
O
O
OH
HO
OH
OH
3d
Chemical Formula: C16H24O6
Exact Mass: 312.1573
157.80
134.18
128.86
113.29
78.94
78.26
74.37
70.01
69.49
68.63
54.18
48.21
48.00
47.85
47.78
47.64
47.57
47.42
47.36
47.14
46.93
39.20
38.58
30.42
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


PROTON-01
HO
OH
OH
OH
O
O
3d'
Chemical Formula: C16H24O6
Exact Mass: 312.1573
1.92 1.94
1.00 0.57 1.03 2.88 1.12 0.99 0.96 0.99
1.05 1.83 1.00
f1 (ppm)

CARBON_01

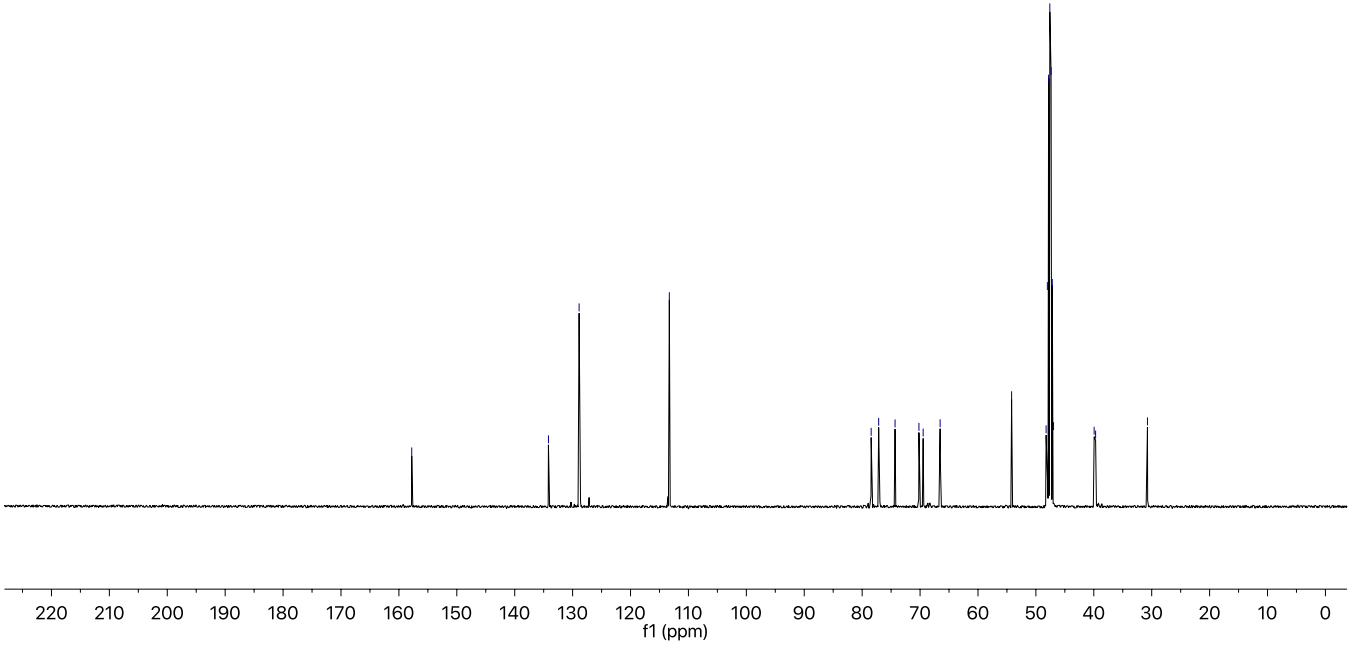


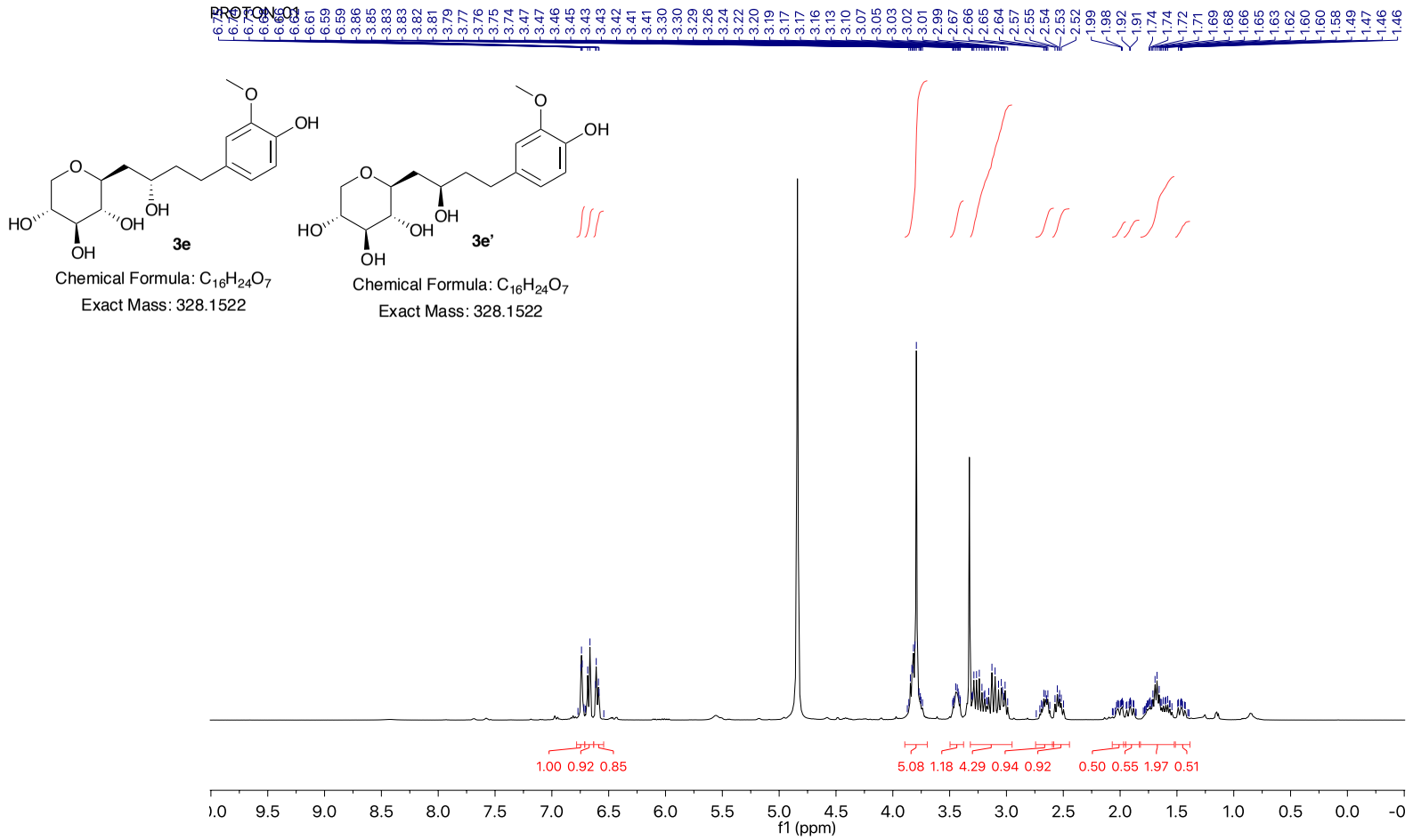

**3d'**

Chemical Formula: $C_{16}H_{24}O_6$

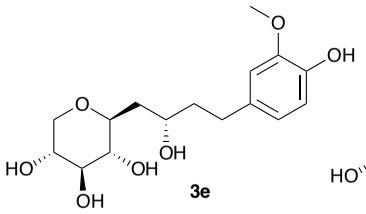
Exact Mass: 312.1573

157.78
134.18
128.88
113.30
78.45
77.15
74.32
70.20
69.47
66.53
54.19
48.23
48.02
47.81
47.59
47.38
47.17
46.95
39.94
39.69
30.73




PROTON-01
3e
Chemical Formula: C16H24O7
Exact Mass: 328.1522
3e'
Chemical Formula: C16H24O7
Exact Mass: 328.1522
1.00 0.92 0.85
5.08 1.18 4.29 0.94 0.92
0.50 0.55 1.97 0.51
f1 (ppm)

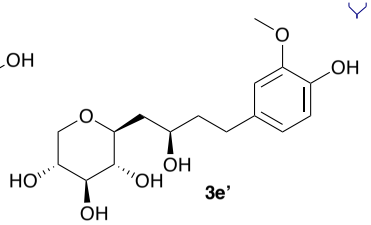
CARBON_01




**3e**

Chemical Formula: $C_{16}H_{24}O_7$

Exact Mass: 328.1522

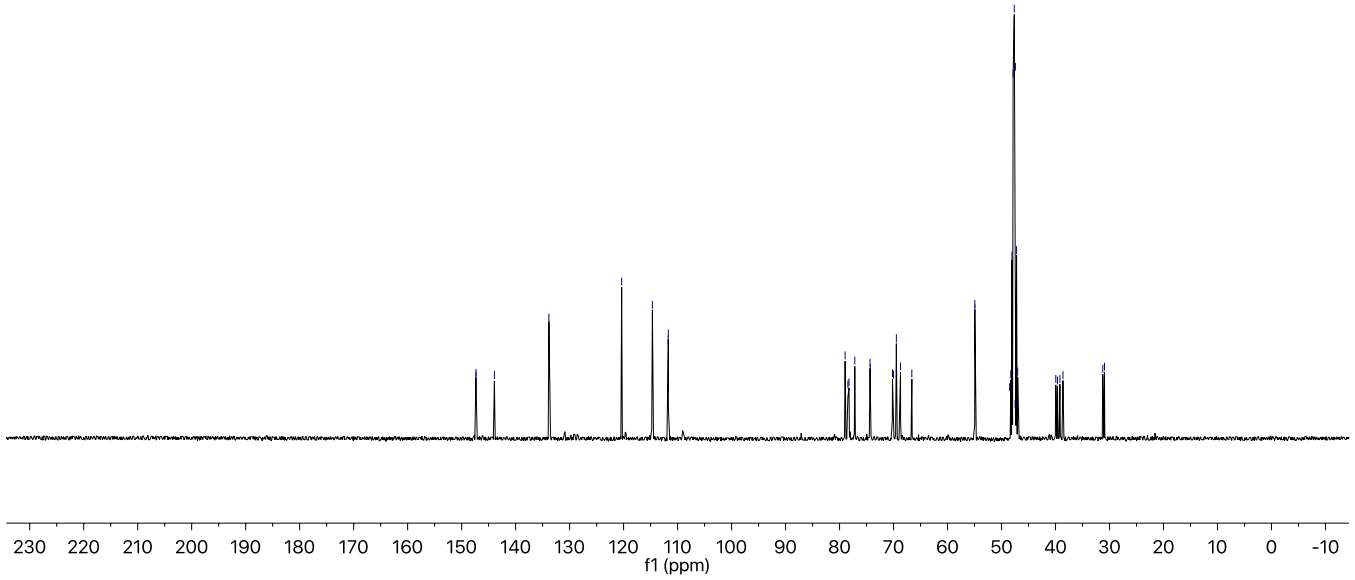


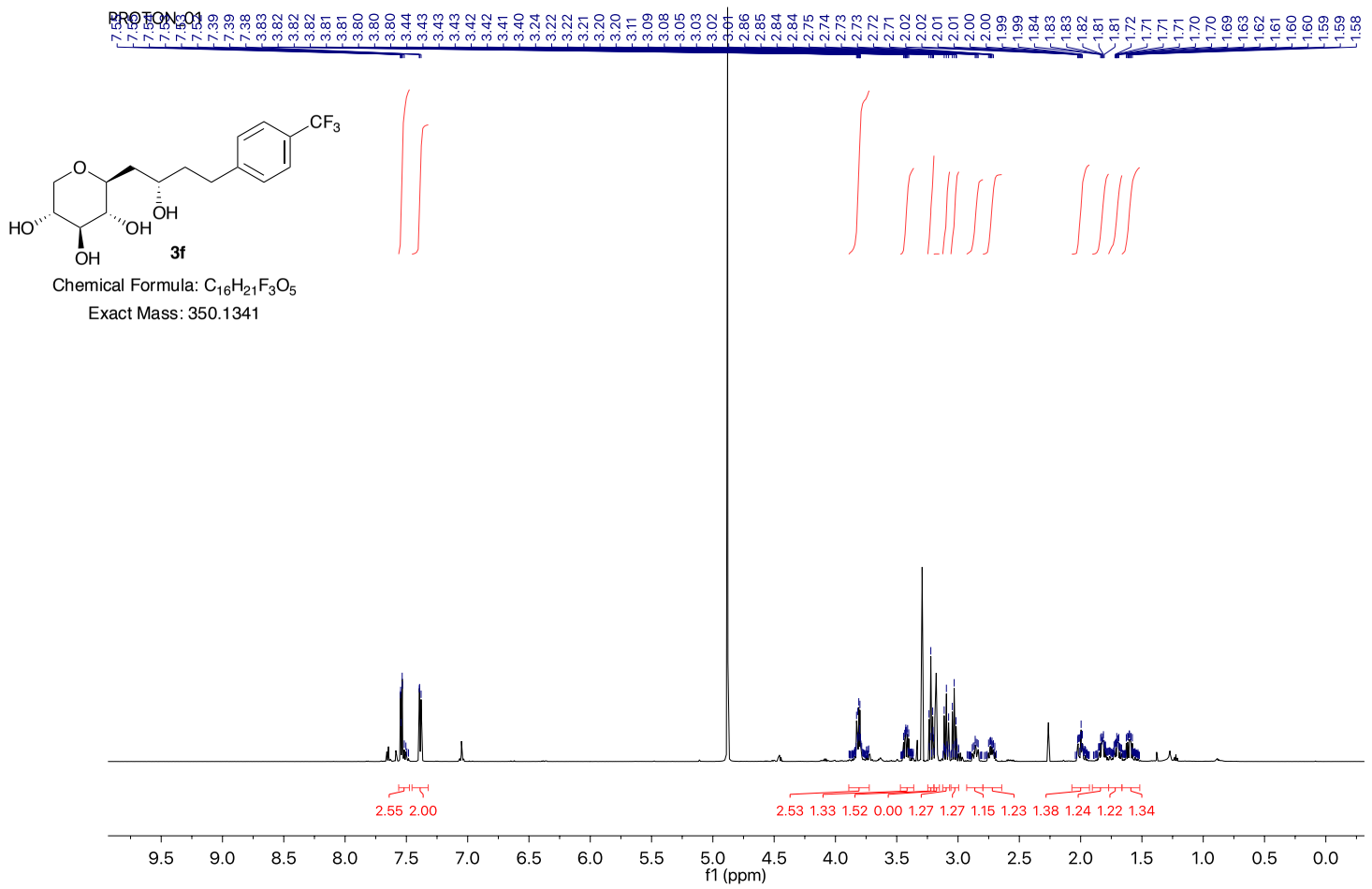

**3e'**

Chemical Formula: $C_{16}H_{24}O_7$

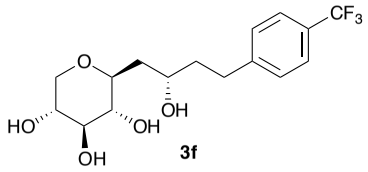
Exact Mass: 328.1522

147.35
147.34
143.93
133.84
120.36
114.67
111.74
111.72
78.97
78.45
78.26
77.18
74.36
74.32
70.20
70.01
69.48
68.71
66.61
54.95
54.93
48.49
48.28
48.07
47.86
47.64
47.48
47.43
47.22
47.00
39.95
39.65
39.19
38.63
31.25
30.94




PROTON-01
CF3
O
OH
HO
OH
OH
3f
Chemical Formula: C16H21F3O5
Exact Mass: 350.1341
2.55 2.00
2.53 1.33 1.52 0.00 1.27 1.27 1.15 1.23 1.38 1.24 1.22 1.34
f1 (ppm)

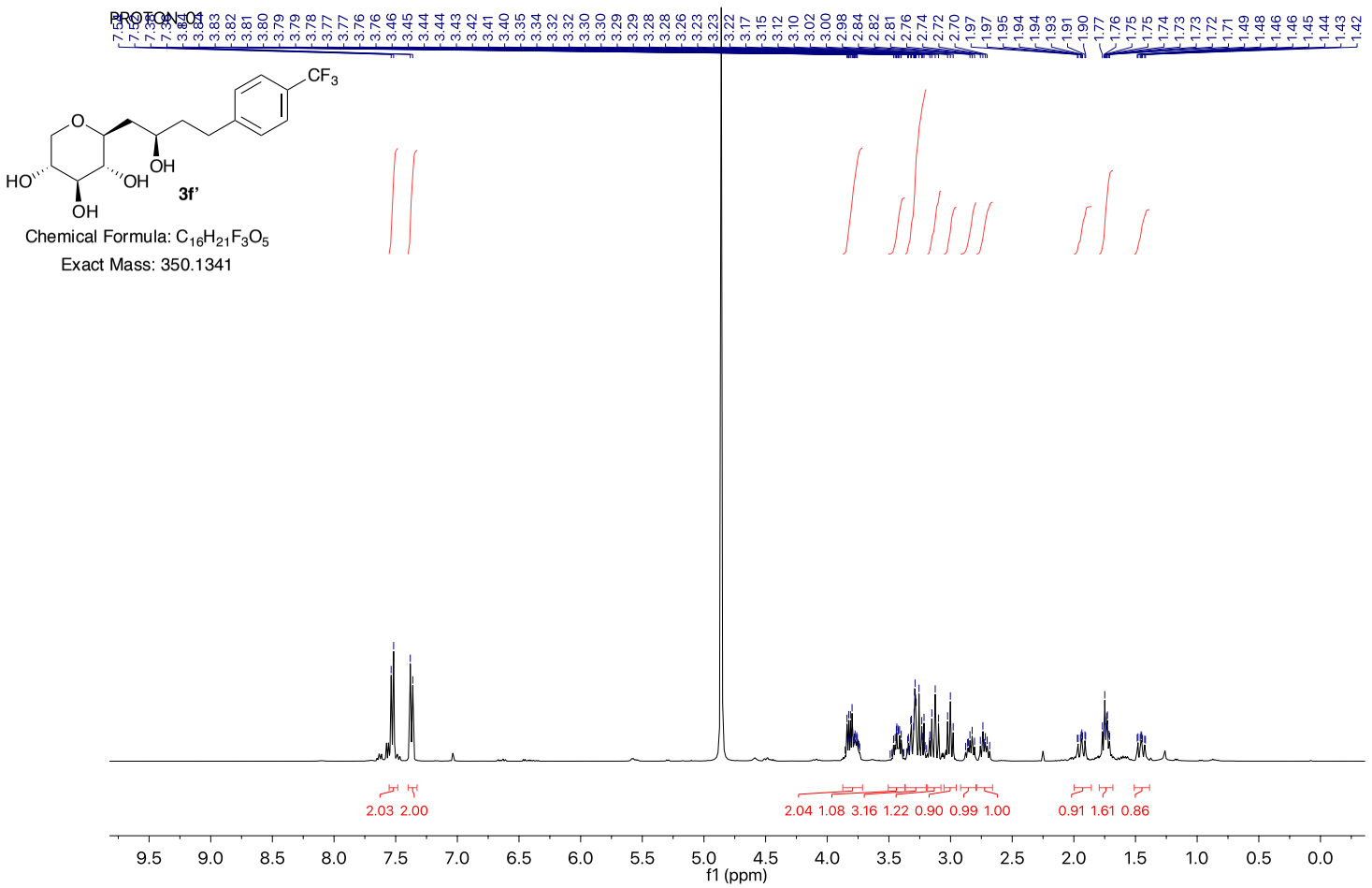
CARBON_01



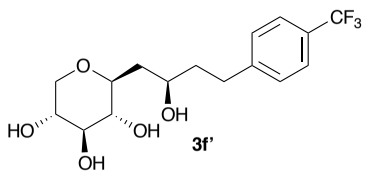

**3f**

Chemical Formula: $C_{16}H_{21}F_3O_5$

Exact Mass: 350.1341


PROTON-01
CF3
O
HO
OH
OH
OH
3f'
Chemical Formula: C16H21F3O5
Exact Mass: 350.1341
2.03 2.00
2.04 1.08 3.16 1.22 0.90 0.99 1.00
0.91 1.61 0.86
f1 (ppm)

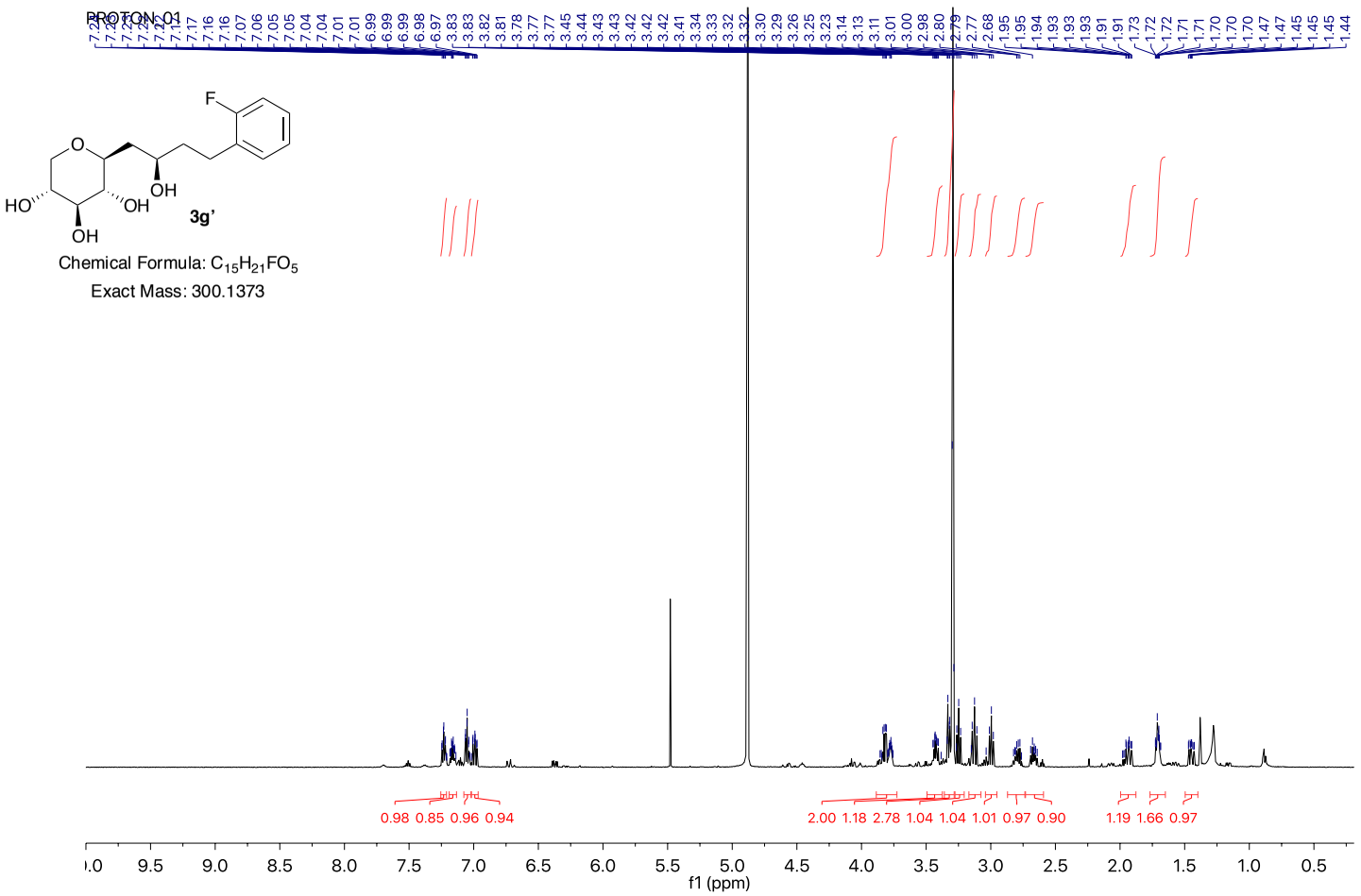
CARBON_01

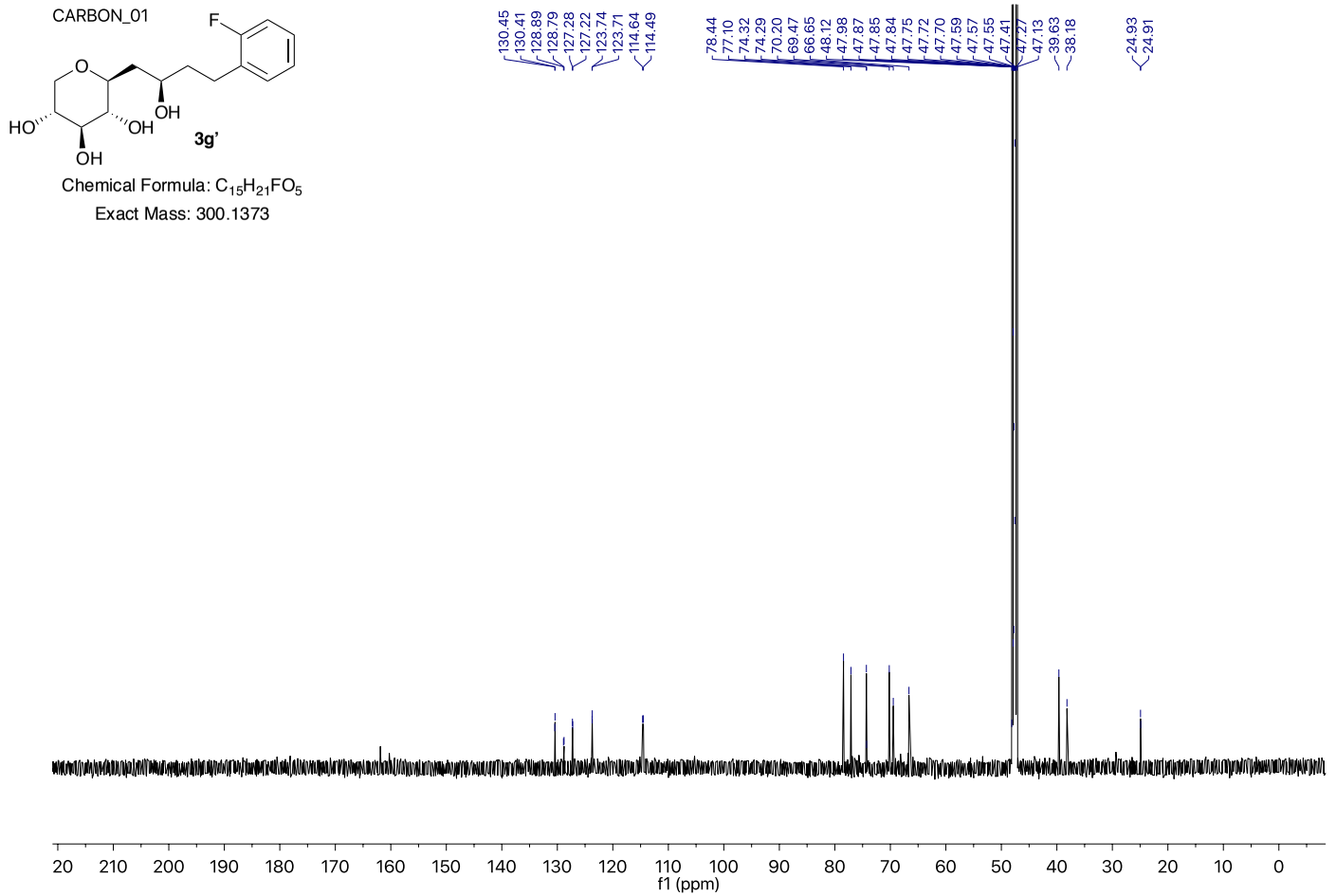


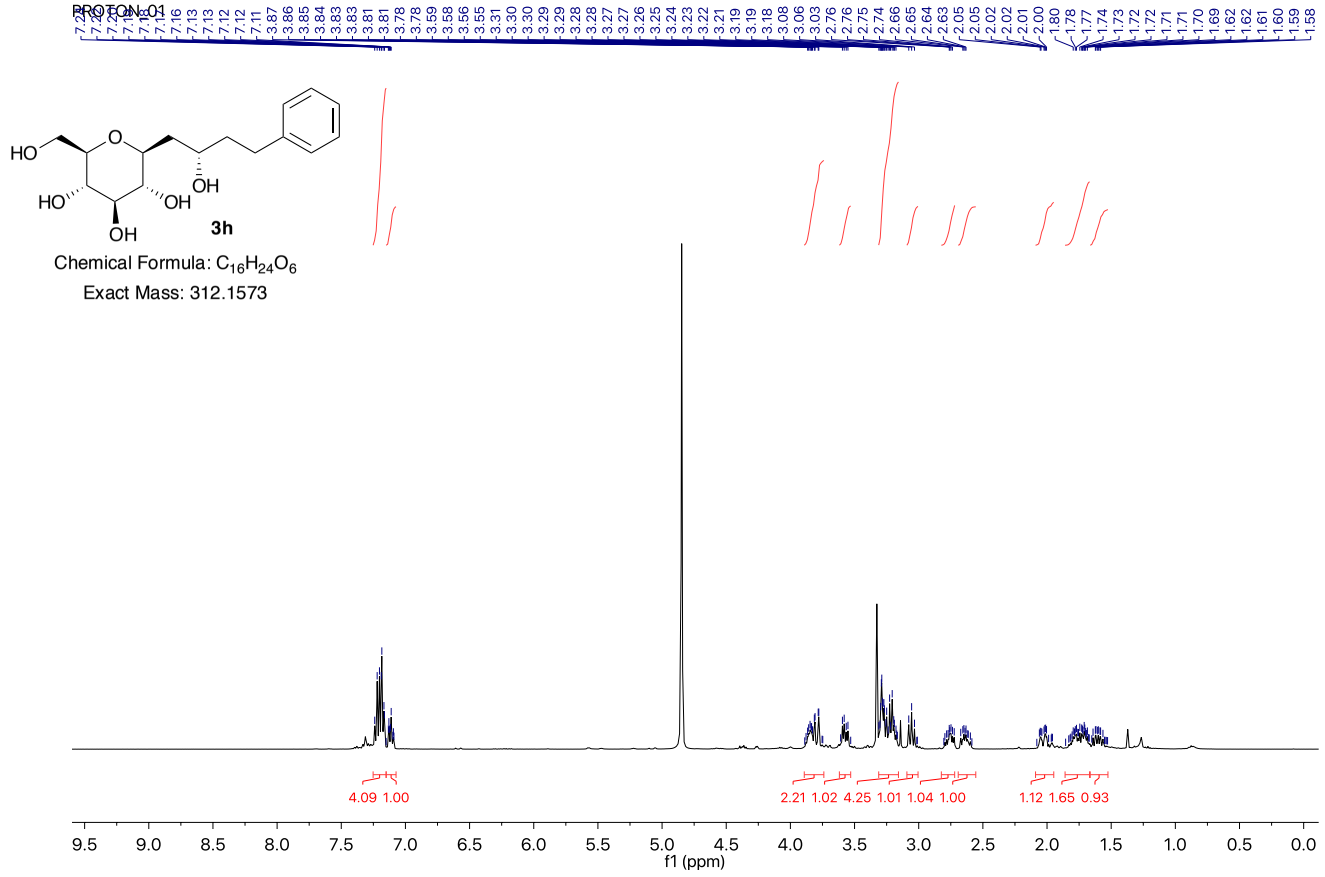

**3f'**

Chemical Formula: $C_{16}H_{21}F_3O_5$

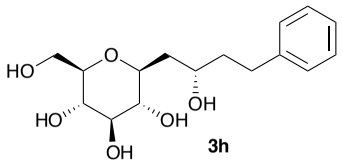
Exact Mass: 350.1341


PROTON-01
F
O
OH
HO
OH
OH
3g'
Chemical Formula: C15H21FO5
Exact Mass: 300.1373
0.98 0.85 0.96 0.94
2.00 1.18 2.78 1.04 1.04 1.01 0.97 0.90
1.19 1.66 0.97
f1 (ppm)


CARBON_01
F
O
HO
OH
OH
OH
3g'
Chemical Formula: C15H21FO5
Exact Mass: 300.1373
130.45
130.41
128.89
128.79
127.28
127.22
123.74
123.71
114.64
114.49
78.44
77.10
74.32
74.29
70.20
69.47
66.65
48.12
47.98
47.87
47.85
47.84
47.75
47.72
47.70
47.59
47.57
47.55
47.41
47.27
47.13
39.63
38.18
24.93
24.91
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


PROTON-01
HO
O
OH
HO
OH
OH
3h
Chemical Formula: C16H24O6
Exact Mass: 312.1573
4.09 1.00
2.21 1.02 4.25 1.01 1.04 1.00
1.12 1.65 0.93
f1 (ppm)

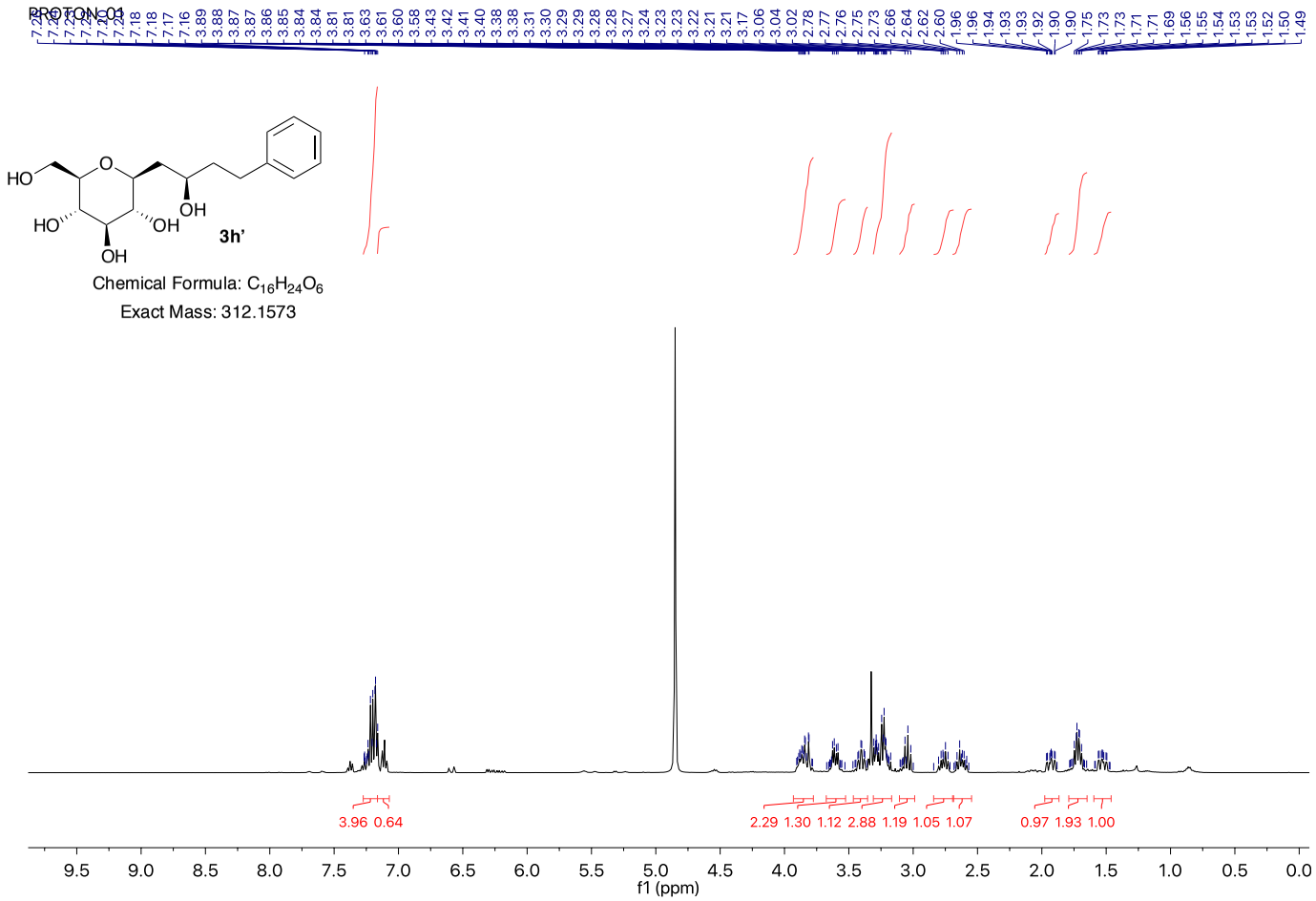
CARBON_01



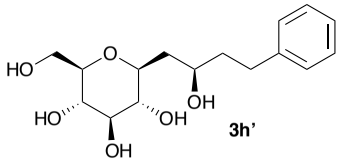

**3h**

Chemical Formula: $C_{16}H_{24}O_6$

Exact Mass: 312.1573


PROTON-01
HO
O
OH
HO
OH
OH
3h'
Chemical Formula: $C_{16}H_{24}O_6$
Exact Mass: 312.1573
3.96 0.64
2.29 1.30 1.12 2.88 1.19 1.05 1.07
0.97 1.93 1.00
f1 (ppm)

CARBON_01

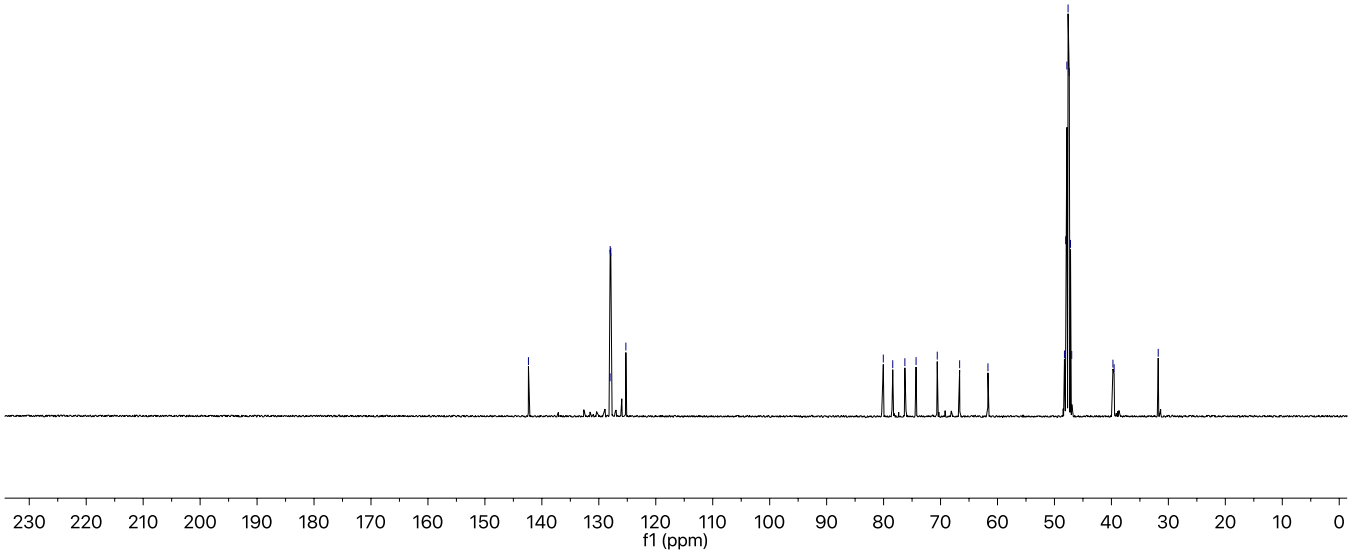


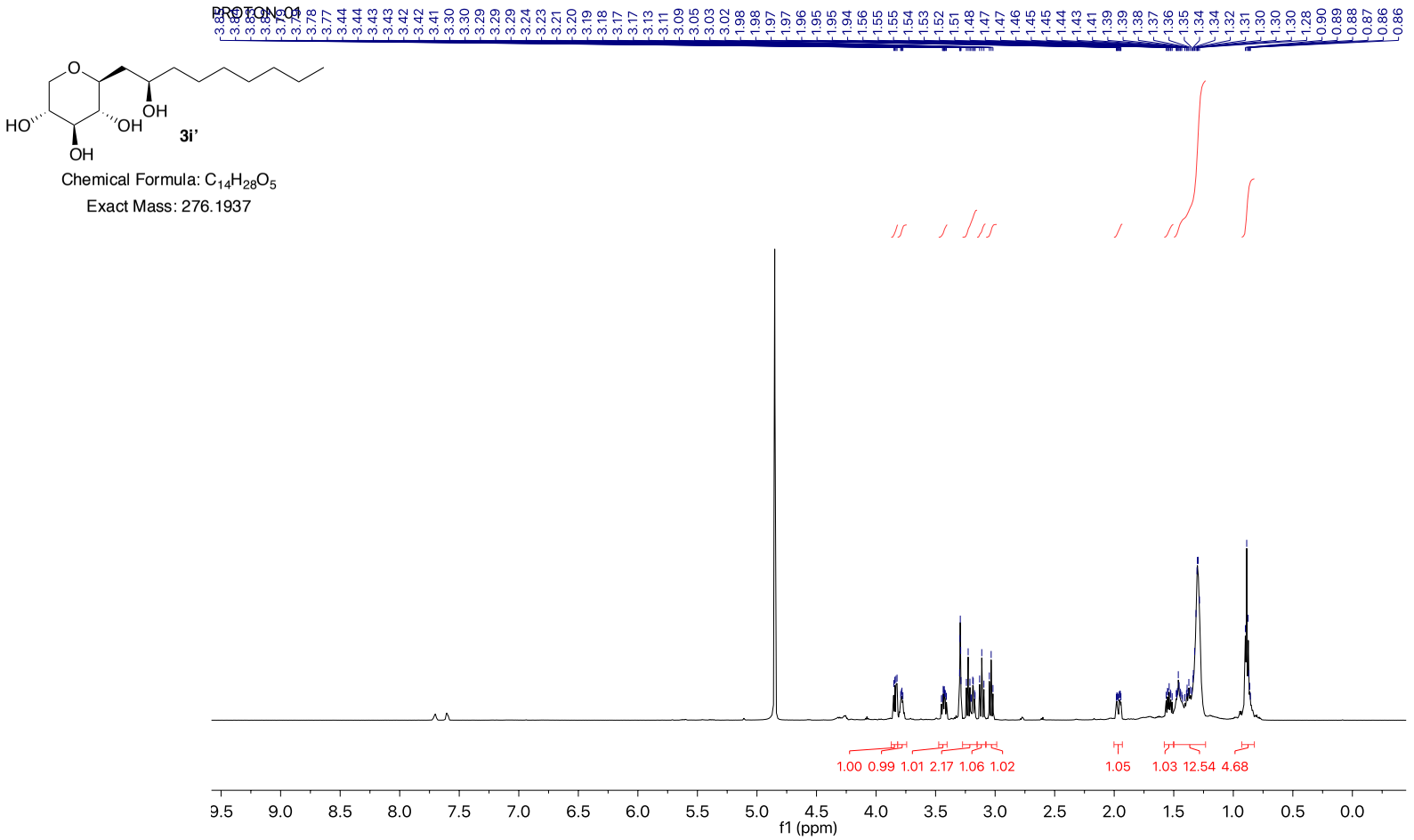

**3h'**

Chemical Formula: $C_{16}H_{24}O_6$

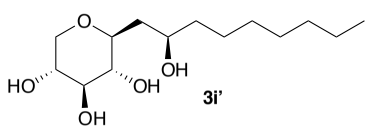
Exact Mass: 312.1573

142.35
128.02
128.00
127.89
125.25
80.05
78.39
76.26
74.30
70.58
66.65
61.68
48.25
48.03
47.82
47.61
47.40
47.18
46.97
39.73
39.53
31.78




PROTON-01
HO
OH
OH
OH
3i'
Chemical Formula: $C_{14}H_{28}O_5$
Exact Mass: 276.1937
1.00 0.99 1.01 2.17 1.06 1.02
1.05
1.03 12.54 4.68
f1 (ppm)

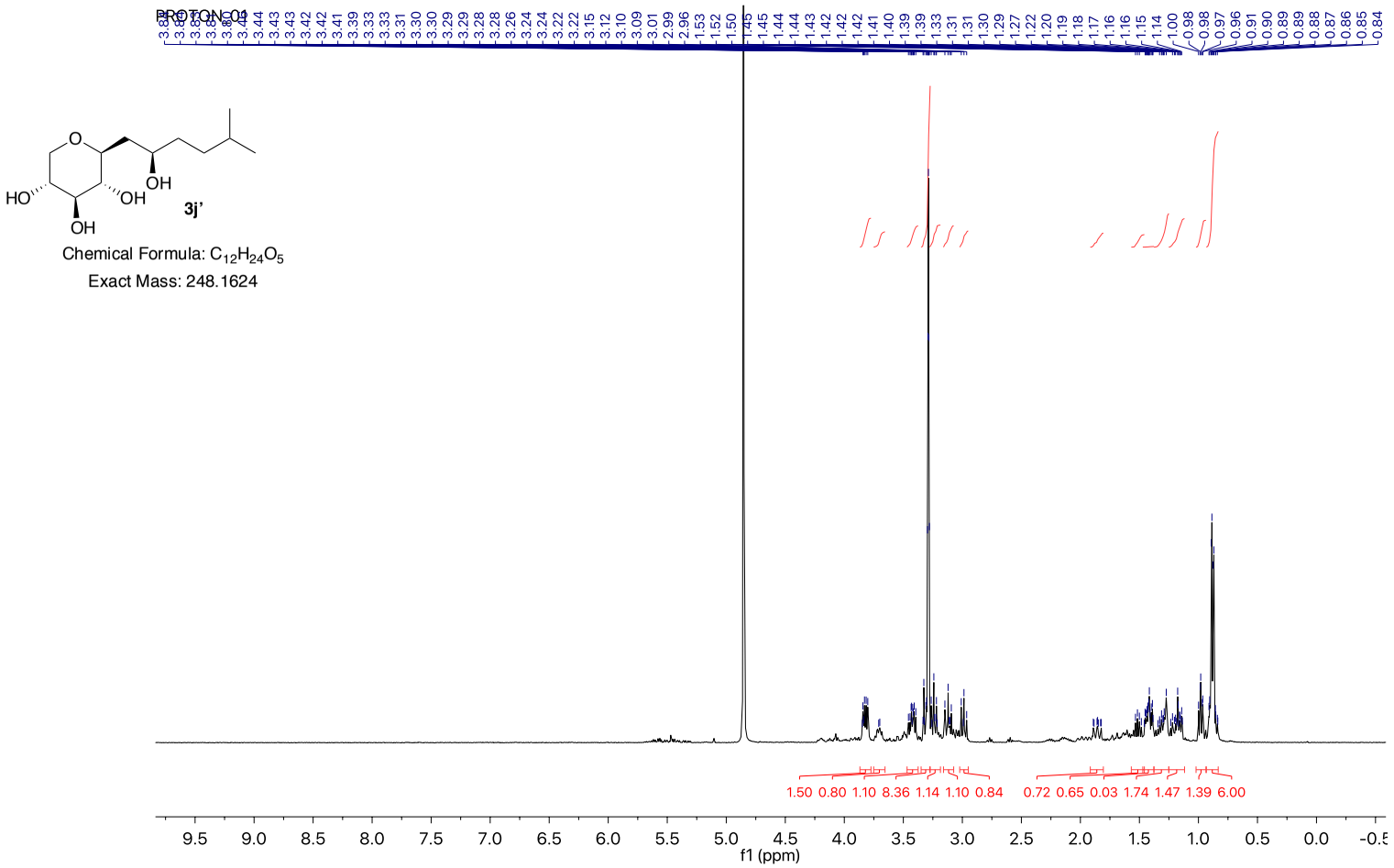
CARBON_01

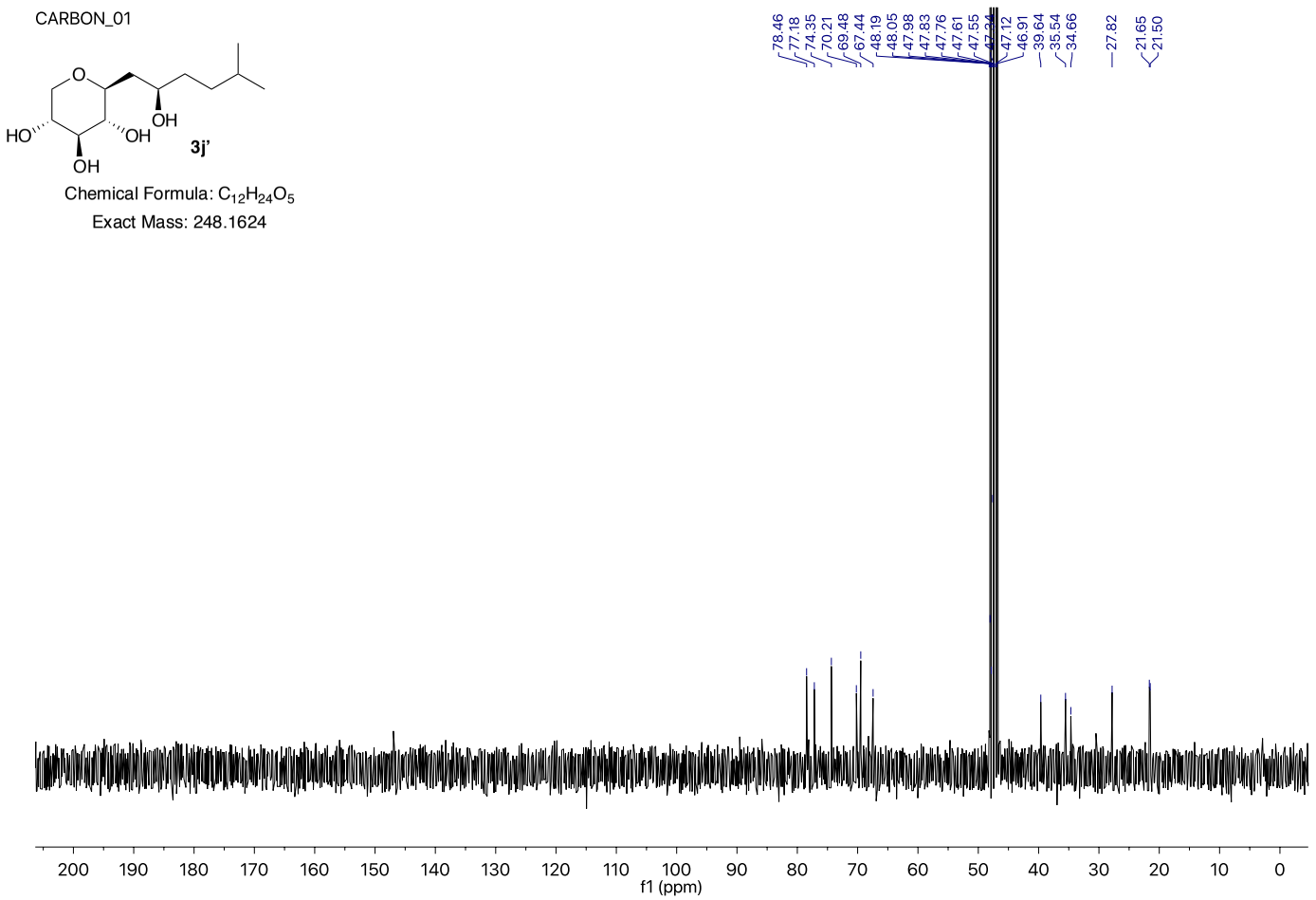



**3i'**

Chemical Formula: $C_{14}H_{28}O_5$

Exact Mass: 276.1937


PROTON.01
HO
OH
OH
OH
O
3j'
Chemical Formula: C12H24O5
Exact Mass: 248.1624
1.50 0.80 1.10 8.36 1.14 1.10 0.84
0.72 0.65 0.03 1.74 1.47 1.39 6.00
f1 (ppm)


CARBON_01
O
HO
OH
OH
OH
3j'
Chemical Formula: C12H24O5
Exact Mass: 248.1624
78.46
77.18
74.35
70.21
69.48
67.44
48.19
48.05
47.98
47.83
47.76
47.61
47.55
47.34
47.12
46.91
39.64
35.54
34.66
27.82
21.65
21.50
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

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