Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Deuterium Labelling to Extract Local Stereochemical Information by VCD Spectroscopy in C-D Stretching Region: A Case Study of Sugars

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Supporting Information

Supporting Figures

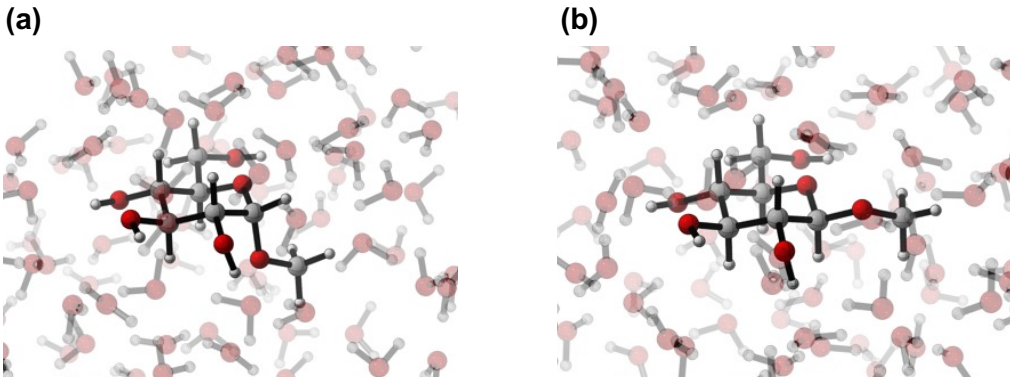


Fig. S1 Representative MD snapshots for (a) **CD_3-α-D-Glc** and (b) **CD_3-β-D-Glc** with explicit water molecules.

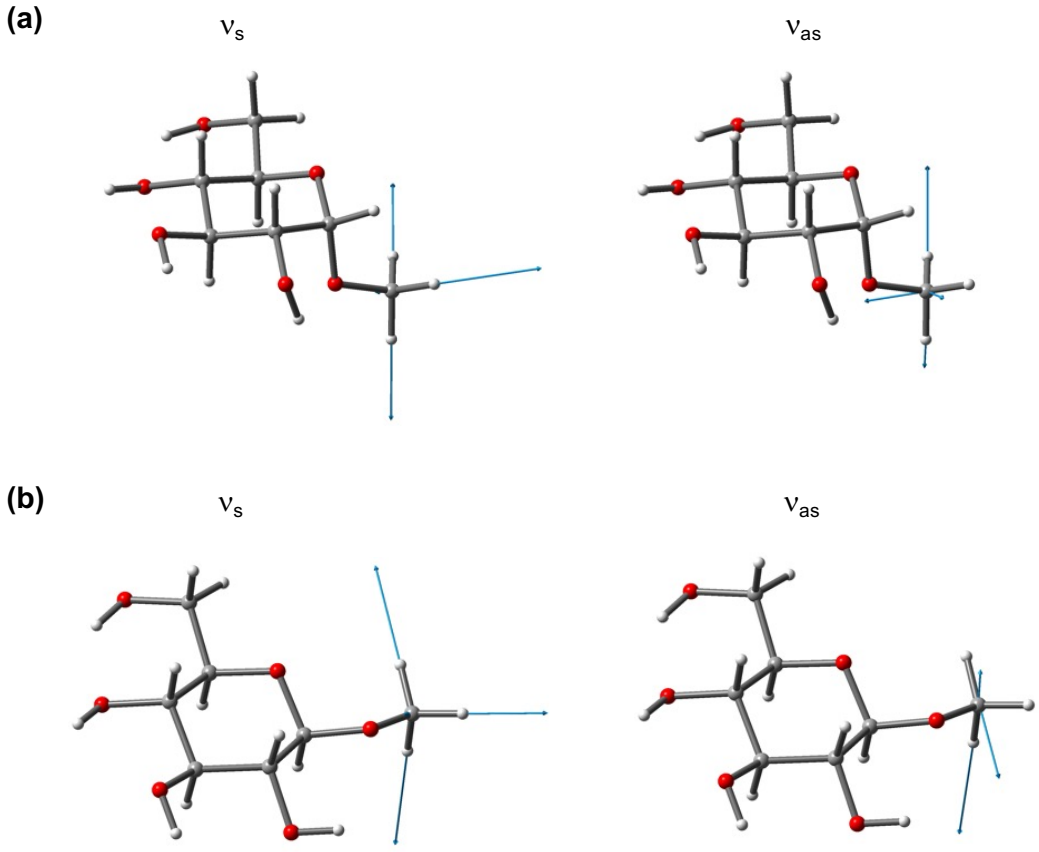


Fig. S2 Vibrational modes of ν_s (left) and ν_{as} (right) CD_3 group of (a) **CD_3-α-D-Glc** and (b) **CD_3-β-D-Glc** calculated at DFT/B3LYP/6-31G(d)/PCM(water). Displacement vectors (arbitrary length) of each atom are shown as arrows.

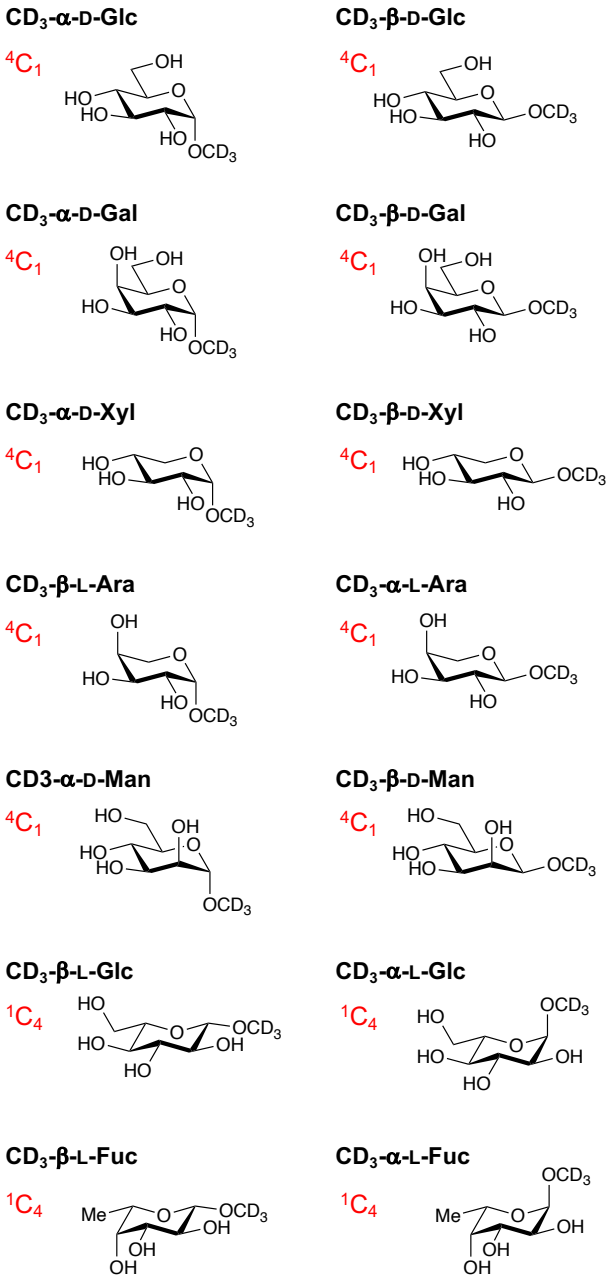


Fig. S3 Preferred pyranose conformations of the studied methyl-d_3 glycopyranosides in polar solvents.

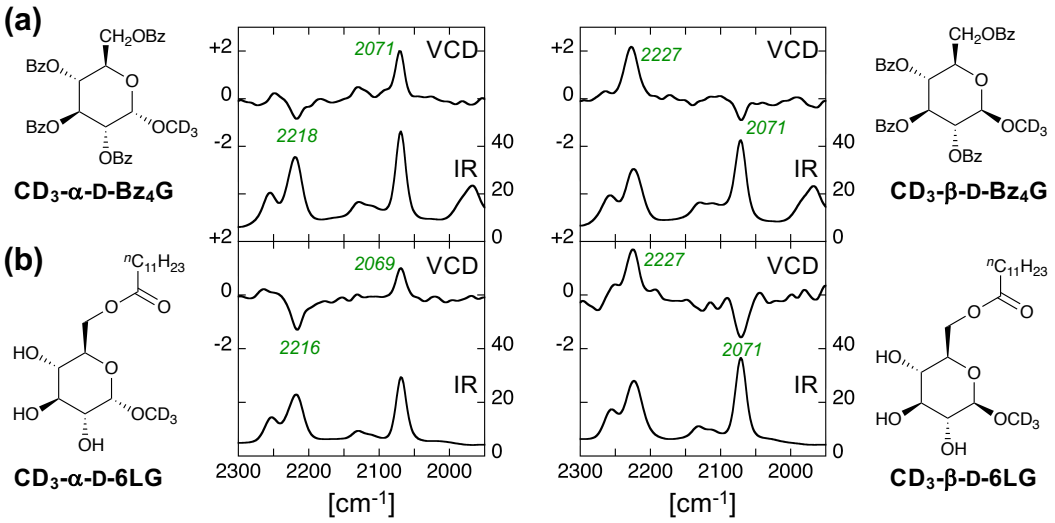


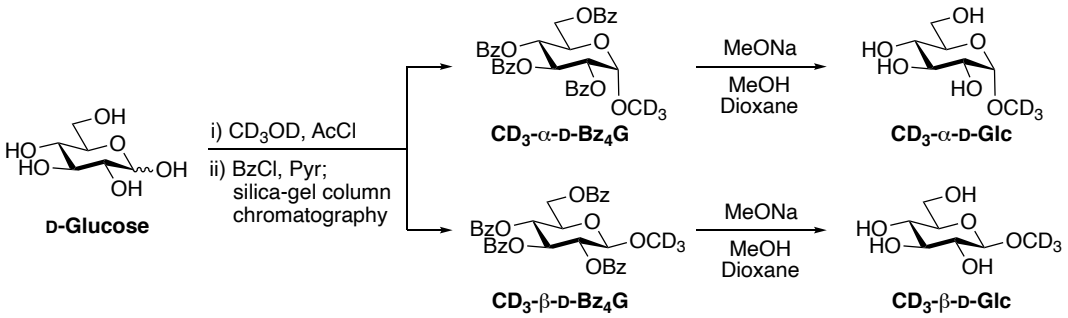
Fig. S4 VCD and IR spectra of (a) **CD_3-α-** and **β-D-Bz_4G** and (b) **CD_3-α-** and **β-D-6LG** measured in $CHCl_3$ (*c* 0.5 or 1.0 M, *l* 50 μm). Wavenumbers of VCD signal extrema for ν_s CD_3 (lower frequency) and ν_{as} CD_3 (higher frequency) are labelled in italic (green).

Experimental Details

General Experimental Details

^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Varian Inova instrument at 25 °C. Chemical shift values (δ) are reported in ppm relative to tetramethylsilane, $CDCl_3$ (^{13}C, δ 77.00), CD_3OD (^{1}H, δ 3.31), or D_2O (^{1}H, δ 4.75). The following abbreviations were used for signal multiplicities: s = singlet; d = doublet; t = triplet; and m = multiplet. Electrospray ionization mass spectrometry was measured on an Exactive Plus (Thermo Scientific). For vibrational spectroscopy, each sample was dissolved in $CHCl_3$, DMSO-h_6 or H_2O and placed in a 25-μm CaF_2 cell or a 50-μm BaF_2 cell. VCD and IR spectra were recorded using a JASCO FVS-6000 spectrometer with 8 cm^{-1} resolution for 1500 and 16 scans, respectively. To detect VCD signals in the 2300-1900 cm^{-1} region with higher S/N, the spectrometer was inserted an optical filter that passes through 2400-1900 cm^{-1} light and the signal was detected with an InSb detector.[1] The modulation frequency of the photoelastic modulator was set to 2127 cm^{-1}. All the VCD and IR spectra except the raw spectra in Fig. 2b were corrected by solvent spectra obtained under the identical measurement conditions.

Synthesis of **CD_3-α-D-Glc**, **CD_3-β-D-Glc**, **CD_3-α-D-Bz_4G**, and **CD_3-β-D-Bz_4G** and General Procedures



(A) General procedure for Fischer glycosidation

CD_3OD (1 mL) was added AcCl (10 μL) and D-glucose (200 mg, 1.11 mmol) and the mixture was stirred overnight. After removal of the solvent, the crude mixture was used for the next reaction without purification unless otherwise noted.

(B) General procedure for benzoylation and the following chromatographic separation

A crude mixture obtained by the procedure (A) was added pyridine (5 mL) and benzoyl chloride (1 mL) and stirred overnight at 70 °C. The mixture was diluted with EtOAc, washed sequentially with 2M HCl aq, 2M NaOH aq, and brine, and then dried over $MgSO_4$. After removal of the solvent, the mixture was purified by silica-gel column chromatography (hexane-EtOAc = 3:1), which afforded **CD_3-α-D-Bz_4G** (302 mg, 45% in 2 steps) and **CD_3-β-D-Bz_4G** (130 mg, 19% in 2 steps).

The ^{1}H NMR spectra of these compounds were virtually the same as those reported for methyl-h_3 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranoside and methyl-h_3 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside except for the absence of the -OCH_3 signal.[2]

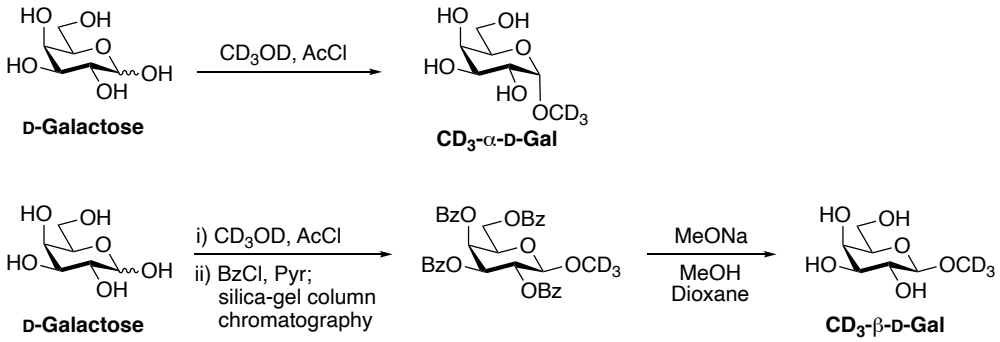
CD_3-α-D-Bz_4G: ^{1}H NMR ($CDCl_3$) δ 8.05 (d, ArH, *J* = 7.2 Hz, 2H), 7.99 (d, ArH, *J* = 7.2 Hz, 2H), 7.94 (d, ArH, *J* = 7.2 Hz, 2H), 7.87 (d, ArH, *J* = 7.2 Hz, 2H), 7.58-7.47 (m, ArH, 3H), 7.45-7.32 (m, ArH, 7H), 7.32-7.25 (m, ArH, 2H), 6.19 (dd, H-3, *J* = 10.0, 10.0 Hz, 1H), 5.69 (dd, H-4, *J* = 9.8, 9.8 Hz, 1H), 5.31 (dd, H-2, *J* = 3.4, 10.2 Hz, 1H), 5.26 (d, H-1, *J* = 3.7 Hz, 1H), 4.62 (dd, H-6a, *J* = 2.8, 12.1 Hz, 1H), 4.49 (dd, H-6b, *J* = 5.3, 12.2 Hz, 1H), 4.43 (m, H-5, 1H); **CD_3-β-D-Bz_4G**: ^{1}H NMR ($CDCl_3$) δ 8.02 (m, ArH, 2H), 7.97 (m, ArH, 2H), 7.90 (m, ArH, 2H), 7.82 (m, ArH, 2H), 7.57-7.47 (m, ArH, 3H), 7.44-7.32 (m, ArH, 7H), 7.30-7.26 (m, ArH, 2H), 5.91 (dd, H-3, *J* = 9.6, 9.6 Hz, 1H), 5.68 (dd, H-4, *J* = 9.8, 9.8 Hz, 1H), 5.52 (dd, H-2, *J* = 7.9, 9.8 Hz, 1H), 4.77 (d, H-1, *J* = 7.9 Hz, 1H), 4.65 (dd, H-6a, *J* = 3.2, 12.1 Hz, 1H), 4.51 (dd, H-6b, *J* = 5.4, 12.1 Hz, 1H), 4.16 (m, H-5, 1H).

(C) General procedure for deprotection of benzoyl or acetyl groups

CD_3-β-D-Bz_4G (125 mg, 204 μmol) in MeOH (2 mL) and 1,4-dioxane (2 mL) was added MeONa (20 μL) and stirred overnight at room temperature. The mixture was neutralized using Amberlite® 120IR (hydrogen form), then filtered and evaporated. The crude residue was added H_2O and Et_2O and the aqueous layer was collected and evaporated, which afforded **CD_3-β-D-Glc** (34 mg, 85%).[3]

CD_3-α-D-Glc[3] was prepared in a similar manner starting from **CD_3-α-D-Bz_4G**.

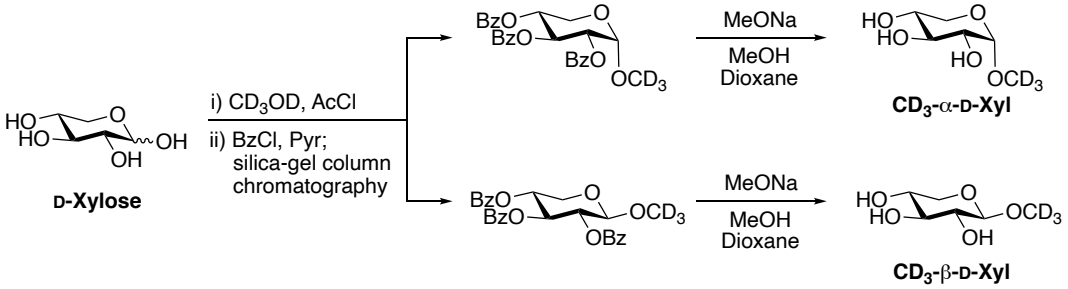
Synthesis of **CD_3-α-D-Gal** and **CD_3-β-D-Gal**



CD_3-α-D-Gal was obtained starting from D-galactose using the general procedure (A) and the following silica-gel column chromatography separation (chloroform-MeOH = 5:1). Its ^{1}H NMR spectrum was virtually the same as that observed for commercially available methyl-h_3 α-D-galactopyranoside except for the absence of the -OCH_3 signal. **CD_3-α-D-Gal**: ^{1}H NMR (D_2O) δ 4.81 (d, H-1, *J* = 2.4 Hz, 1H), 3.94 (dd, *J* = 1.3, 2.5 Hz, H-4, 1H), 3.87 (m, H-5, 1H), 3.83-3.76 (m, H-2, H-3, 2H), 3.74-3.69 (m, H-6a, H-6b, 2H).

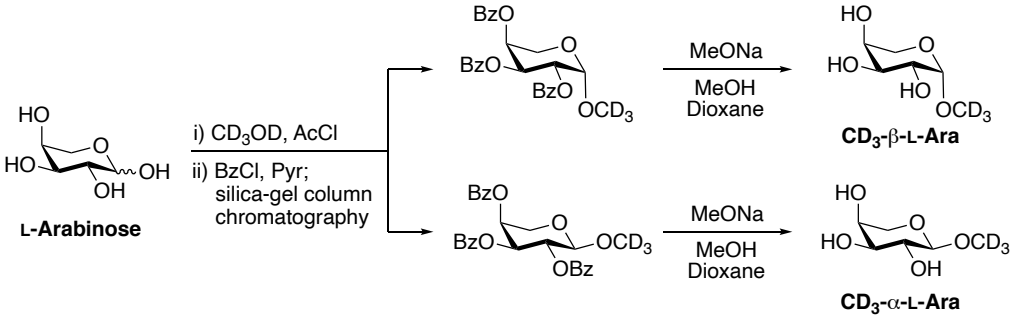
CD_3-β-D-Gal was obtained starting from D-galactose using the general procedures (A)-(C). The ^{1}H NMR spectra of methyl-d_3 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranoside and **CD_3-β-D-Gal** were virtually the same as those reported for methyl-h_3 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranoside[2,4] and observed for commercially available methyl-h_3 β-D-galactopyranoside, respectively, except for the absence of the -OCH_3 signal. Methyl-d_3 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranoside: ^{1}H NMR ($CDCl_3$) δ 8.09 (m, ArH, 2H), 8.03 (m, ArH, 2H), 7.97 (m, ArH, 2H), 7.78 (m, ArH, 2H), 7.65-7.54 (m, ArH, 2H), 7.53-7.36 (m, ArH, 8H), 7.25-7.21 (m, ArH, 2H), 6.00 (dd, H-4, *J* = 1.2, 3.5 Hz, 1H), 5.79 (dd, *J* = 7.9, 10.4 Hz, H-2, 1H), 5.61 (dd, H-3, *J* = 3.4, 10.3 Hz, 1H), 4.75 (d, H-1, *J* = 7.8 Hz, 1H), 4.70 (dd, H-6a, *J* = 6.6, 11.3 Hz, 1H), 4.43 (dd, H-6b, *J* = 6.7, 11.4 Hz, 1H), 4.33 (m, H-5, 1H). **CD_3-β-D-Gal**: ^{1}H NMR (CD_3OD) δ 4.13 (d, H-1, *J* = 7.1 Hz, 1H), 3.83 (d, H-4, *J* = 2.1 Hz, 1H), 3.79-3.70 (m, H-6a, H-6b, 2H), 3.53-3.43 (m, H-2, H-3, H-5, 3H).

Synthesis of **CD_3-α-D-Xyl** and **CD_3-β-D-Xyl**



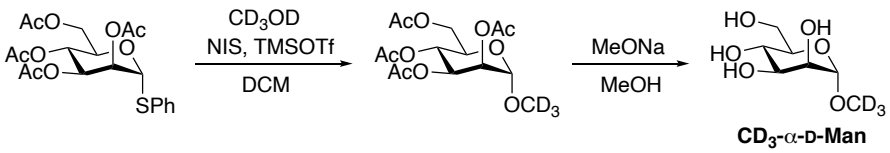
CD_3-α-D-Xyl and **CD_3-β-D-Xyl** were obtained starting from D-xylose using the general procedures (A)-(C). The ^{1}H NMR spectra of tribenzoyl synthetic intermediates were virtually the same as those reported for methyl-h_3 2,3,4-tri-*O*-benzoyl-α- and β-D-xylopyranoside except for the absence of the -OCH_3 signal,[5] while those of **CD_3-α-D-Xyl** and **CD_3-β-D-Xyl** were virtually the same as those observed for commercially available methyl-h_3 α- and β-D-xylopyranoside except for the absence of the -OCH_3 signal. Methyl-d_3 2,3,4-tri-*O*-benzoyl-α-D-xylopyranoside: ^{1}H NMR ($CDCl_3$) δ 7.98 (m, ArH, 4H), 7.92 (m, ArH, 2H), 7.51 (m, ArH, 2H), 7.44 (m, ArH, 1H), 7.38 (m, ArH, 4H), 7.31 (m, ArH, 2H), 6.16 (dd, H-3, *J* = 9.8, 9.8 Hz, 1H), 5.42 (m, H-4, 1H), 5.26 (dd, H-2, *J* = 3.4, 10.1 Hz, 1H), 5.17 (d, H-1, *J* = 3.5 Hz, 1H), 4.10 (dd, H-5a, *J* = 6.0, 10.8 Hz, 1H), 3.84 (dd, H-5b, *J* = 10.7, 10.7 Hz, 1H). Methyl-d_3 2,3,4-tri-*O*-benzoyl-β-D-xylopyranoside: ^{1}H NMR ($CDCl_3$) δ 8.02-7.94 (m, ArH, 6H), 7.55-7.45 (m, ArH, 3H), 7.40-7.31 (m, ArH, 6H), 5.80 (dd, H-3, *J* = 7.6, 7.6 Hz, 1H), 5.40 (dd, H-2, *J* = 5.7, 7.6 Hz, 1H), 5.33 (m, H-4, 1H), 4.74 (d, H-1, *J* = 5.7 Hz, 1H), 4.44 (dd, H-5a, *J* = 4.4, 12.0 Hz, 1H), 3.71 (dd, H-5b, *J* = 7.4, 12.2 Hz, 1H).**CD_3-α-D-Xyl**: ^{1}H NMR (CD_3OD) δ 4.61 (d, H-1, *J* = 3.6 Hz, 1H), 3.58-3.51 (m, H-3, H-4, 2H), 3.49-3.41 (m, H-5a, H-5b, 2H), 3.36 (dd, H-2, *J* = 3.6, 9.5 Hz, 1H). **CD_3-β-D-Xyl**: ^{1}H NMR (D_2O) δ 4.29 (d, H-1, *J* = 7.8 Hz, 1H), 3.93 (dd, H-5a, *J* = 5.2, 11.7, 1H), 3.58 (m, H-4, 1H), 3.40 (dd, H-3, *J* = 9.3, 9.3 Hz, 1H), 3.29 (dd, H-5b, *J* = 11.0, 11.0 Hz, 1H), 3.21 (dd, H-2, *J* = 7.8, 9.1 Hz, 1H).

Synthesis of **CD_3-β-L-Ara** and **CD_3-α-L-Ara**



CD_3-β-L-Ara and **CD_3-α-L-Ara** were obtained starting from L-arabinose using the general procedures (A)-(C). The ^{1}H NMR spectra of tribenzoyl synthetic intermediates and **CD_3-β-L-Ara** were virtually the same as those reported for methyl-h_3 2,3,4-tri-*O*-benzoyl-β- and α-L-arabinopyranoside[4] and methyl-h_3 β-L-arabinopyranoside,[6] respectively, except for the absence of the -OCH_3 signal. The ^{1}H NMR spectrum of **CD_3-α-L-Ara** was virtually the same as that observed for commercially available methyl-h_3 α-L-arabinopyranosid except for the absence of the -OCH_3 signal. Methyl-d_3 2,3,4-tri-*O*-benzoyl-β-L-arabinopyranoside: ^{1}H NMR ($CDCl_3$) δ 8.11 (d, ArH, *J* = 7.3 Hz, 2H), 8.00 (d, ArH, *J* = 7.3 Hz, 2H), 7.85 (d, ArH, *J* = 7.3 Hz, 2H), 7.59 (t, ArH, *J* = 7.4 Hz, 1H), 7.54-7.40 (m, ArH, 5H), 7.37 (t, ArH, *J* = 7.7 Hz, 1H), 7.26 (t, ArH, *J* = 7.9 Hz, 2H), 5.96 (dd, H-3, *J* = 3.5, 10.7 Hz, 1H), 5.78-5.71 (m, H-2, H-4, 2H), 5.25 (d, H-1, *J* = 3.5 Hz, 1H), 4.18 (m, H-5a, 1H), 4.12 (dd, H-5b, *J* = 1.6, 13.3 Hz, 1H). Methyl-d_3 2,3,4-tri-*O*-benzoyl-α-L-arabinopyranoside: ^{1}H NMR ($CDCl_3$) δ 8.09-7.99 (m, ArH, 4H), 7.94-7.88 (d, ArH, *J* = 7.5 Hz, 2H), 7.60-7.51 (m, ArH, 2H), 7.50-7.38 (m, ArH, 5H), 7.35-7.29 (t, ArH, *J* = 7.8 Hz, 2H), 5.76-5.68 (m, H-2, H-4, 2H), 5.61 (dd, H-3, *J* = 3.4, 8.8 Hz, 1H), 4.67 (dd, H-1, *J* = 6.2 Hz, 1H), 4.33 (dd, H-5a, *J* = 3.7, 13.1 Hz, 1H), 3.91 (dd, H-5b, *J* = 1.6, 12.8 Hz, 1H). **CD_3-β-L-Ara**: ^{1}H NMR (D_2O) δ 4.79 (d, H-1, *J* = 2.4 Hz, 1H), 3.96 (m, H-4, 1H), 3.83 (d, H-5a, *J* = 11.6 Hz, 1H), 3.81-3.78 (m, H-2, H-3, 2H), 3.61 (dd, H-5b, *J* = 1.8, 12.7 Hz, 1H). **CD_3-α-L-Ara**: ^{1}H NMR (D_2O) δ 4.23 (d, H-1, *J* = 7.6 Hz, 1H), 3.93-3.86 (m, H-4, H-5a, 2H), 3.66-3.61 (m, H-3, H-5b, 2H), 3.50 (m, H-2, 1H).

Synthesis of **CD_3-α-D-Man**

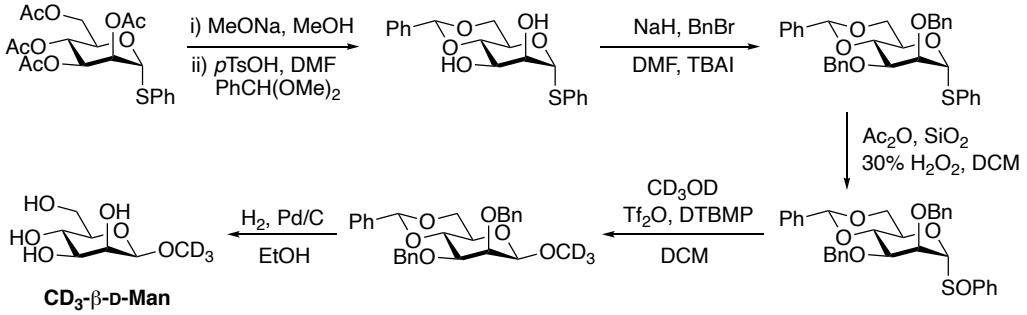


A solution of phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyranoside (570 mg, 1.30 mmol) in CH_2Cl_2 (5 mL) was added CD_3OD (160 μL) and stirred at 0 °C. To this mixture was added a solution of *N*-iodosuccinimide (750 mg) in THF (2.5 mL) dropwise, trimethylsilyl

trifluoromethanesulfonate (25 μL) dropwise and stirred at 0 °C for 40 mins. The mixture was added triethylamine (20 μL), diluted with EtOAc, washed sequentially with a 1:1 mixed solution of 10% $Na_2S_2O_3$ aq and sat $NaHCO_3$ aq and then brine, and dried over $MgSO_4$. After removal of the solvent, the mixture was purified by silica-gel column chromatography (hexane-EtOAc = 5:2 to 1:1), which provided methyl-d_3 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside (122 mg, 26%). Its ^{1}H NMR spectrum was virtually the same as that observed for commercially available methyl-h_3 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside except for the absence of the -OCH_3 signal. Methyl-d_3 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside: ^{1}H NMR ($CDCl_3$) δ 5.34 (dd, H-3, *J* = 3.6, 9.8 Hz, 1H), 5.28 (dd, H-4, *J* = 9.8, 9.8 Hz, 1H), 5.24 (dd, H-2, *J* = 1.7, 3.2 Hz, 1H), 4.72 (d, H-1, *J* = 1.5 Hz, 1H), 4.29 (dd, H-6a, *J* = 5.4, 12.2 Hz, 1H), 4.13 (dd, H-6b, *J* = 2.4, 12.2 Hz, 1H), 3.97 (ddd, H-5, *J* = 2.4, 5.4, 9.8 Hz, 1H), 2.16 (s, Ac, 3H), 2.11 (s, Ac, 3H), 2.04 (s, Ac, 3H), 1.99 (s, Ac, 3H).

In a similar manner to the general procedure (C) without the use of 1,4-dioxane, methyl-d_3 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside (104 mg, 285 μmol) was converted to **CD_3-α-D-Man** (31 mg, 55%). Its ^{1}H NMR spectrum was virtually the same as that observed for commercially available methyl-h_3 α-D-mannopyranoside except for the absence of the -OCH_3 signal. **CD_3-α-D-Man**: ^{1}H NMR (D_2O) δ 4.74 (d, H-1, *J* = 1.5 Hz, 1H), 3.90 (dd, H-2, *J* = 2.0, 3.4 Hz, 1H), 3.87 (dd, H-6a, *J* = 2.0, 12.2 Hz, 1H), 3.75-3.71 (m, H-3, H-6b, 2H), 3.64-3.56 (m, H-4, H-5, 2H).

Synthesis of **CD_3-β-D-Man**



In a similar manner to the general procedure (C) without the use of 1,4-dioxane, phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyranoside (2.20 g, 5.00 mmol) was deacetylated. A solution of the crude compound in DMF (25 mL) was added benzaldehyde dimethoxy acetal (1 mL) and a catalytic amount of *p*-TsOH•H_2O and stirred overnight at room temperature. The mixture was diluted with $CHCl_3$, washed sequentially with sat $NaHCO_3$ aq. and brine, and dried over $MgSO_4$. After removal of the solvent, the mixture was purified by recrystallization using EtOAc, which afforded phenyl 4,6-*O*-benzylidine-1-thio-α-D-mannopyranoside[7] (1.36 g, 67%).

A solution of phenyl 4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (720 mg, 2.00 mmol) in DMF (25 mL) was added 60% NaH in mineral oil (200 mg) and stirred at room temperature. After 15 mins, benzyl bromide (0.7 mL) was added dropwise followed by the addition of a catalytic amount of tetra-*n*-butylammonium iodide and stirred overnight at room temperature. The mixture

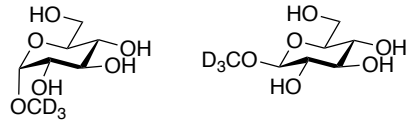
was quenched with H_2O and was diluted with EtOAc. The organic phase was washed with brine and dried over $MgSO_4$. After removal of the solvent, the mixture was purified by silica-gel column chromatography (hexane-EtOAc = 25:1 to 15:1), which afforded phenyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidine-1-thio-α-D-mannopyranoside[8] (293 mg, 27%).

A solution of phenyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidine-1-thio-α-D-mannopyranoside (270 mg, 500 μmol) in CH_2Cl_2 (5 mL) was added SiO_2 (100 mg), acetic anhydride (50 μL), and 30% H_2O_2 aq (110 μL) and stirred overnight at room temperature. The mixture was filtered through cotton, diluted with EtOAc, washed sequentially with 10% $Na_2S_2O_3$ aq, sat $NaHCO_3$ aq and brine, and dried over $MgSO_4$. After removal of the solvent, the residue was washed with methanol and hexane to yield phenyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidine-1-thio-α-D-mannopyranoside *S*-oxide[9] (128 mg, 46%).

A solution of phenyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidine-1-thio-α-D-mannopyranoside *S*-oxide (116 mg, 209 μmol) in CH_2Cl_2 (5 mL) was added 2,6-di-*tert*-butyl-4-methylpyridine (86 mg), trifluoromethanesulfonic anhydride (34 μL), CD_3OD (68 μL) and stirred at -78 °C. After 30 mins the reaction was quenched with the addition of Et_3N, diluted with EtOAc, washed sequentially with sat NH_4Cl aq, sat $NaHCO_3$ aq, and brine and dried over $MgSO_4$. After removal of the solvent, the mixture was purified by silica-gel column chromatography (hexane-EtOAc = 10:1 to 5:2), which provided methyl-d_3 2,3-di-*O*-benzyl-4,6-*O*-benzylidine-β-D-mannopyranoside (51 mg, 52%). Its ^{1}H NMR spectrum was virtually the same as that reported for methyl-h_3 2,3-di-*O*-benzyl-4,6-*O*-benzylidine-β-D-mannopyranoside except for the absence of the -OCH_3 signal.[10] ^{1}H NMR ($CDCl_3$) δ 7.53-7.44 (m, ArH, 4H), 7.40-7.23 (m, ArH, 11H), 5.62 (s, CH, 1H), 4.96 (d, CH_2, *J* = 12.2 Hz, 1H), 4.84 (d, CH_2, *J* = 12.2 Hz, 1H), 4.68 (d, CH_2, *J* = 12.7, 1H), 4.58 (d, CH_2, *J* = 12.7, 1H), 4.47 (s, H-1, 1H), 4.32 (dd, H-6a, *J* = 4.9, 10.7 Hz, 1H), 4.20 (dd, H-4, *J* = 9.3, 9.8 Hz, 1H), 3.97-3.90 (m, H-2, H-6b, 2H), 3.58 (dd, H-3, *J* = 3.2, 10.0 Hz, 1H), 3.33 (ddd, H-5, *J* = 4.6, 9.6, 9.6 Hz, 1H).

A solution of methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidine-β-D-mannopyranoside (49 mg, 105 μmol) in EtOH (20 mL) was added a catalytic amount of 10% Pd/C and stirred at room temperature for 24 hours under hydrogen atmosphere. The suspension was filtered through Celite and the filtrate was dried in vacuo to yield **CD_3-β-D-Man** (17 mg, 82%). Its ^{1}H NMR spectrum was virtually the same as that observed for commercially available methyl-h_3 β -D-mannopyranoside except for the absence of the -OCH_3 signal. ^{1}H NMR (D_2O) δ 4.55 (d, H-1, *J* = 1.0 Hz, 1H), 3.96 (dd, H-2, *J* = 1.0, 3.4 Hz, 1H), 3.91 (dd, H-6a, *J* = 2.4, 12.2 Hz, 1H), 3.71 (dd, H-6b, *J* = 6.8, 12.2 Hz, 1H), 3.61 (dd, H-3, *J* = 3.5, 9.6 Hz, 1H), 3.54 (dd, H-4, *J* = 9.7, 9.7 Hz, 1H), 3.34 (m, H-5, 1H).

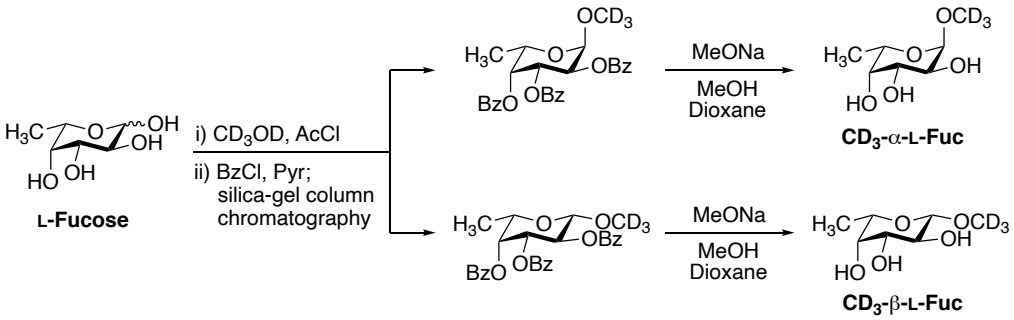
Synthesis of **CD_3-α-L-Glc** and **CD_3-β-L-Glc**



CD_3-α-L-Glc **CD_3-β-L-Glc**

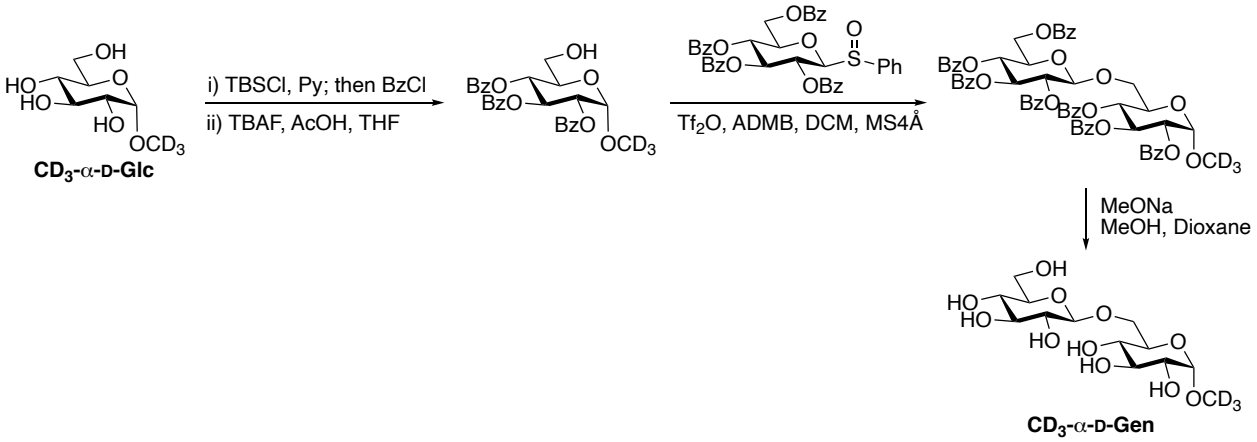
CD_3-α-L-Glc and **CD_3-β-L-Glc** were obtained starting from L-glucose in a similar manner to the synthesis of **CD_3-α-D-Glc** and **CD_3-β-D-Glc**.

Synthesis of **CD_3-α-L-Fuc** and **CD_3-β-L-Fuc**



CD_3-α-L-Fuc and **CD_3-β-L-Fuc** were obtained starting from L-fucose using the general procedures (A)-(C). The ^{1}H NMR spectra of methyl-d_3 2,3,4-tri-*O*-benzoyl-α-D-fucopyranoside, **CD_3-α-L-Ara**, and **CD_3-β-L-Fuc** were virtually the same as those reported for methyl-h_3 2,3,4-tri-*O*-benzoyl-α-D-fucopyranoside[11], methyl-h_3 α-L-fucopyranoside,[12] and methyl-h_3 β-L-fucopyranoside,[13] respectively, except for the absence of the -OCH_3 signal. Methyl-d_3 2,3,4-tri-*O*-benzoyl-α-L-fucopyranoside: ^{1}H NMR ($CDCl_3$) δ 8.13-8.08 (m, ArH, 2H), 8.00-7.95 (m, ArH, 2H), 7.82-7.76 (m, ArH, 2H), 7.61 (m, ArH, 1H), 7.53-7.34 (m, ArH, 6H), 7.28-7.20 (m, ArH, 2H), 5.96 (dd, H-3, *J* = 3.5, 10.7 Hz, 1H), 5.76 (d, H-4, *J* = 2.2 Hz, 1H), 5.64 (dd, H-2, *J* = 3.5, 10.7 Hz, 1H), 5.24 (d, H-1, *J* = 3.5 Hz, 1H), 4.40 (m, H-5, 1H), 1.29 (d, H_3-6, *J* = 6.5 Hz, 3H). Methyl-d_3 2,3,4-tri-*O*-benzoyl-β-L-fucopyranoside: ^{1}H NMR ($CDCl_3$) δ 8.13-8.08 (m, ArH, 2H), 7.99-7.94 (m, ArH, 2H), 7.81-7.75 (m, ArH, 2H), 7.61 (m, ArH, 1H), 7.53-7.35 (m, ArH, 6H), 7.25-7.20 (m, ArH, 2H), 5.78-5.68 (m, H-2, H-4, 2H), 5.56 (dd, H-3, *J* = 3.4, 10.3 Hz, 1H), 4.68 (d, H-1, *J* = 7.9 Hz, 1H), 4.09 (m, H-5, 1H), 1.37 (d, H_3-6, *J* = 6.4 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 166.2 (C=O), 165.9 (C=O), 165.6 (C=O), 133.6 (Ar), 133.3 (Ar), 133.3 (Ar), 130.1 (Ar), 130.0 (Ar), 129.9 (Ar), 129.4 (Ar), 129.0 (Ar), 129.0 (Ar), 128.7 (Ar), 128.5 (Ar), 128.4 (Ar), 110.9 (C-1), 109.2 (OCD_3), 102.4 (C-2), 72.3 (C-4), 71.2 (C-3), 69.9 (C-5), 16.3 (C-6); $[\alpha]_D$ -206.3 (*c* 1.0, $CHCl_3$); HRMS (ESI) *m/z* calcd for $C_{28}H_{23}D_3O_8Na$ $[M+Na]^+$ 516.1708, found 516.1693. **CD_3-α-L-Fuc**: ^{1}H NMR (CD_3OD) δ 4.63 (d, H-1, *J* = 2.7 Hz, 1H), 3.91 (m, H-5, 1H), 3.75-3.68 (m, H-2, H-3, 2H), 3.65 (s, H-4, 1H), 1.22 (d, H_3-6, *J* = 6.6 Hz, 3H). **CD_3-β-L-Fuc**: ^{1}H NMR (D_2O) δ 4.27 (d, H-1, *J* = 7.8 Hz, 1H), 3.77 (m, H-5, 1H), 3.71 (d, H-4, *J* = 2.7 Hz, 1H), 3.61 (dd, H-3, *J* = 3.5, 10.1 Hz, 1H), 3.53-3.41 (m, H-2, 1H), 1.23 (d, H_3-6, *J* = 6.6 Hz, 3H).

Synthesis of **CD_3-α-D-Gen**



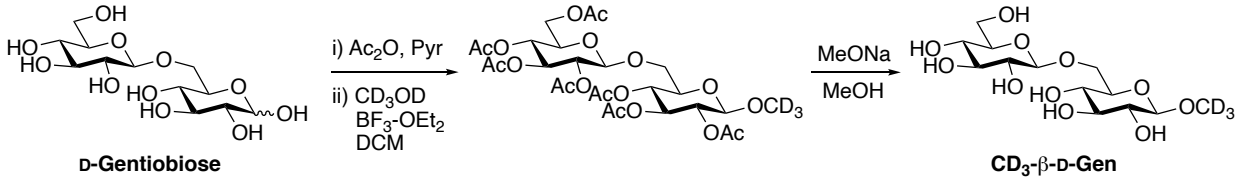
CD_3-α-D-Glc was added pyridine (5 mL) and TBSCl (224 mg) and stirred overnight at room temperature. To this mixture additional TBSCl (180 mg) was added and stirred at room temperature for 3 hours, which led to the complete consumption of the **CD_3-α-D-Glc** on TLC. To this solution BzCl (1.2 mL) was then added and the mixture was stirred at room temperature for 1.5 hours. The mixture was diluted with Et_2O, washed sequentially with 2 M HCl aq, 2 M NaOH aq, and brine, and then dried over $MgSO_4$. After removal of the solvent, the mixture was added ca. 1 M THF solution of TBAF (3 mL) and AcOH (200 μL) and stirred overnight at room temperature. The mixture was diluted with Et_2O, washed with brine, and dried over $MgSO_4$. After removal of the solvent, the mixture was purified by silica-gel column chromatography (hexane-EtOAc = 2:3 to 1:5), which afforded methyl-d_3 2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (303 mg, 45% in 3 steps). Its ^{1}H NMR spectrum was virtually the same as that reported for methyl-h_3 2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside except for the absence of the -OCH_3 signal.[14] Methyl-d_3 2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside: ^{1}H NMR ($CDCl_3$) δ 8.00-7.96 (m, ArH, 4H), 7.88 (m, ArH, 2H), 7.53 (m, ArH, 1H), 7.50 (m, ArH, 1H), 7.43-7.35 (m, ArH, 5H), 7.28 (m, ArH, 2H), 6.24 (dd, H-3, *J* = 9.8, 9.8 Hz, 1H), 5.51 (dd, H-4, *J* = 9.9, 9.9 Hz, 1H), 5.30 (dd, H-2, *J* = 3.7, 10.0 Hz, 1H), 5.27 (d, H-1, *J* = 3.7 Hz, 1H), 4.05 (ddd, H-5, *J* = 2.3, 3.9, 10.2 Hz, 1H), 3.84 (dd, H-6a, *J* = 2.3, 13.0 Hz, 1H), 3.75 (dd, H-6b, *J* = 3.8, 12.9 Hz, 1H), 2.78 (br s, OH-6, 1H).

To a 2-neck flask was added methyl-d_3 2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (48 mg, 94 μmol), phenyl 2,3,4,6-tetra-O-benzoyl-1-sulfinyl-β-D-glucopyranoside[15] (65 mg, 92 μmol), and 4-allyl-1,2-dimethoxybenzene (21 μL). This mixture was dried under vacuum for 1 hour and then added 4 Å molecular sieves (0.3 g). This flask was further dried under vacuum and then purged with N_2. To this flask was added CH_2Cl_2 (2 mL), stirred for 15 mins at room temperature and then cooled to -78 °C. The mixture was then added Tf_2O (16.9 μL) and stirred for 15 mins at this temperature, and then the temperature was slowly raised to -40 °C over 30 mins. The reaction was then quenched with triethylamine (50 μL), diluted with EtOAc, and filtered through cotton. The

filtrate was washed sequentially with sat NH_4Cl aq, sat $NaHCO_3$ aq, and brine, and then dried over $MgSO_4$. After removal of the solvent, the mixture was purified by silica-gel column chromatography (hexane-EtOAc = 2:1 to 4:5), which afforded methyl-d_3 2′,3′,4′,6′-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1′→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (71 mg, 71%). Its ^{1}H NMR spectrum was virtually the same as that reported for methyl-h_3 2′,3′,4′,6′-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1′→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside except for the absence of the -OCH_3 signal.[16] Methyl-d_3 2′,3′,4′,6′-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1′→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside: ^{1}H NMR ($CDCl_3$) δ 8.01-7.77 (m, ArH, 14H), 7.56-7.24 (m, ArH, 21H), 6.06 (dd, H-3, *J* = 9.7, 10.0 Hz, 1H), 5.91 (dd, H-3′, *J* = 9.7, 9.7 Hz, 1H), 5.65 (dd, H-4′, *J* = 9.7, 9.7 Hz, 1H), 5.56 (dd, H-2′, *J* = 7.8, 9.8 Hz, 1H), 5.31 (dd, H-4, *J* = 9.5, 10.3 Hz, 1H), 5.08 (dd, H-2, *J* = 3.6, 10.2 Hz, 1H), 4.97 (d, H-1′, *J* = 7.9 Hz, 1H), 4.93 (d, H-1, *J* = 3.6 Hz, 1H), 4.60 (dd, H-6′a, *J* = 3.2, 12.2 Hz, 1H), 4.44 (dd, H-6′b, *J* = 5.1, 12.1 Hz, 1H), 4.22 (ddd, H-5, *J* = 1.9, 7.6, 10.0 Hz, 1H), 4.14 (ddd, H-5′, *J* = 3.3, 5.1, 9.8 Hz, 1H), 4.10 (dd, H-6a, *J* = 2.0, 11.5 Hz, 1H), 3.78 (dd, H-6b, *J* = 7.8, 11.4 Hz, 1H).

Using the general procedure (C), methyl-d_3 2′,3′,4′,6′-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1′→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (51 mg, 47 μmol) was converted to **CD_3-α-D-Gen** (17 mg, quant). Its ^{1}H NMR spectrum was virtually the same as that reported for methyl-h_3 β-D-glucopyranosyl-(1′→6)-α-D-glucopyranoside except for the absence of the -OCH_3 signal.[17] **CD_3-α-D-Gen**: ^{1}H NMR (D_2O) δ 4.78 (d, H-1, *J* = 3.8 Hz, 1H), 4.47 (d, H-1′, *J* = 7.9 Hz, 1H), 4.14 (dd, H-6a, *J* = 2.1, 11.5 Hz, 1H), 3.91-3.85 (m, H-6b, H-6′a, 2H), 3.77 (ddd, H-5, *J* = 2.1, 5.0, 10.1 Hz, 1H), 3.70 (dd, H-6′b, *J* = 5.9, 12.3 Hz, 1H), 3.64 (dd, H-3, *J* = 9.5, 9.5 Hz, 1H), 3.54 (dd, H-2, *J* = 3.8, 9.8 Hz, 1H), 3.49 (dd, H-3′, *J* = 9.1, 10.1 Hz, 1H), 3.46 (dd, H-4, *J* = 9.1, 9.1 Hz, 1H), 3.43 (ddd, H-5′, *J* = 2.3, 5.9, 9.9 Hz, 1H), 3.36 (dd, H-4′, *J* = 9.0, 9.8 Hz, 1H), 3.28 (dd, H-2′, *J* = 7.9, 9.4 Hz, 1H).

Synthesis of **CD_3-β-D-Gen**

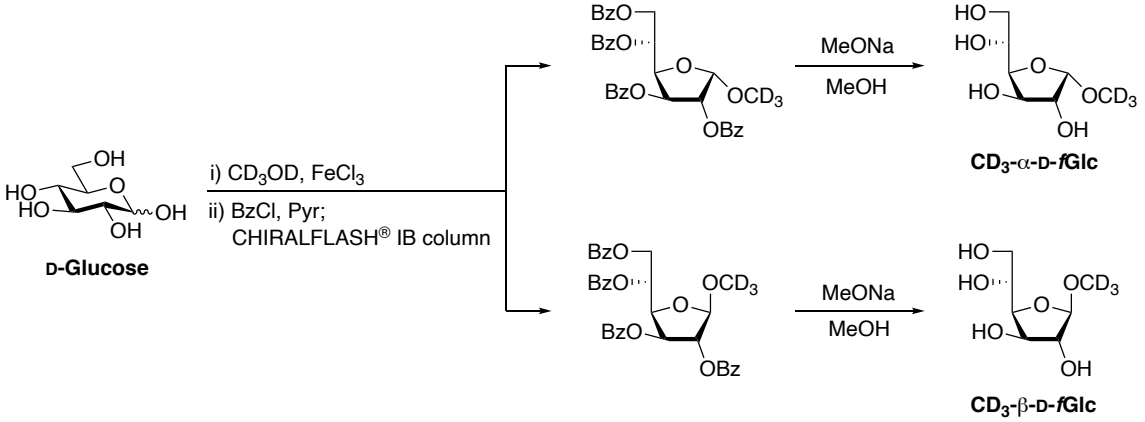


D-gentiobiose (118 mg, 345 μmol) was added pyridine (4 mL) and acetic anhydride (2 mL) at 80 °C, and stirred overnight at 50 °C. The mixture was then dried in vacuo, which provided pure D-gentiobiose octaacetate (234 mg, quant). Part of this product (224 mg, 330 μmol) was dissolved in CH_2Cl_2 (3 mL), added CD_3OD (54 μL) and BF_3-OEt_2 (103 μL) at 0 °C, and stirred overnight at room temperature. The mixture was diluted with EtOAc, washed sequentially with sat $NaHCO_3$ aq and brine, and then dried over $MgSO_4$. After removal of the solvent, the mixture was purified by silica-gel column chromatography (hexane-EtOAc = 1:1 to 1:4), which provided methyl-d_3

2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyl-(1′→6)-2,3,4-tri-*O*-acetyl-β-D-glucopyranoside (87 mg, 40%). Its ^{1}H NMR spectrum was virtually the same as that reported for methyl-h_3 2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyl-(1′→6)-2,3,4-tri-*O*-acetyl-β-D-glucopyranoside except for the absence of the -OCH_3 signal.[18] Methyl-d_3 2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyl-(1′→6)-2,3,4-tri-*O*-acetyl-β-D-glucopyranoside: ^{1}H NMR ($CDCl_3$) δ 5.19 (dd, H-3, *J* = 9.5, 9.5 Hz, 1H), 5.18 (dd, H-3′, *J* = 9.5, 9.5 Hz, 1H), 5.07 (dd, H-4′, *J* = 9.7, 9.7 Hz, 1H), 5.00 (dd, H-2′, *J* = 8.0, 9.6 Hz, 1H), 4.93 (dd, H-2, *J* = 8.0, 9.7 Hz, 1H), 4.89 (dd, H-4, *J* = 9.6, 9.6 Hz, 1H), 4.60 (d, H-1′, *J* = 7.9 Hz, 1H), 4.39 (d, H-1, *J* = 7.9 Hz, 1H), 4.27 (dd, H-6′a, *J* = 4.8, 12.3 Hz, 1H), 4.13 (dd, H-6′b, *J* = 2.4, 12.3 Hz, 1H), 3.88 (dd, H-6a, *J* = 2.0, 11.0 Hz, 1H), 3.72–3.66 (m, H-5, H-5′, 2H), 3.62 (dd, H-6b, *J* = 7.5, 11.0 Hz, 1H), 2.09 (s, Ac, 3H), 2.05 (s, Ac, 3H), 2.04 (s, Ac, 3H), 2.03 (s, Ac, 3H), 2.02 (s, Ac, 3H), 2.00 (s, Ac, 3H), 1.99 (s, Ac, 3H).

In a similar manner to the general procedure (C) without the use of 1,4-dioxane, methyl-d_3 2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyl-(1′→6)-2,3,4-tri-*O*-acetyl-β-D-glucopyranoside (87 mg, 133 μmol) was converted to **CD_3-β-D-Gen** (25 mg, 52%). Its ^{1}H NMR spectrum was virtually the same as that reported for methyl-h_3 β-D-glucopyranosyl-(1′→6)-β-D-glucopyranoside except for the absence of the -OCH_3 signal.[17] **CD_3-β-D-Gen**: ^{1}H NMR (D_2O) δ 4.49 (d, H-1′, *J* = 7.9 Hz, 1H), 4.36 (d, H-1, *J* = 8.0 Hz, 1H), 4.19 (dd, H-6a, *J* = 2.1, 11.7 Hz, 1H), 3.90 (dd, H-6′a, *J* = 2.3, 12.3 Hz, 1H), 3.84 (dd, H-6b, *J* = 5.8, 11.7 Hz, 1H), 3.70 (dd, H-6′b, *J* = 5.8, 12.3 Hz, 1H), 3.59 (ddd, H-5, *J* = 2.0, 5.8, 9.7 Hz, 1H), 3.50-3.40 (m, H-3, H-4, H-3′, H-5′, 4H), 3.37 (dd, H-4′, *J* = 8.9, 9.8 Hz, 1H), 3.29 (dd, H-2′, *J* = 8.0, 9.4 Hz, 1H), 3.24 (dd, H-2, *J* = 8.0, 9.2 Hz, 1H).

Synthesis of **CD_3-α-D-*f*Glc** and **CD_3-β-D-*f*Glc**



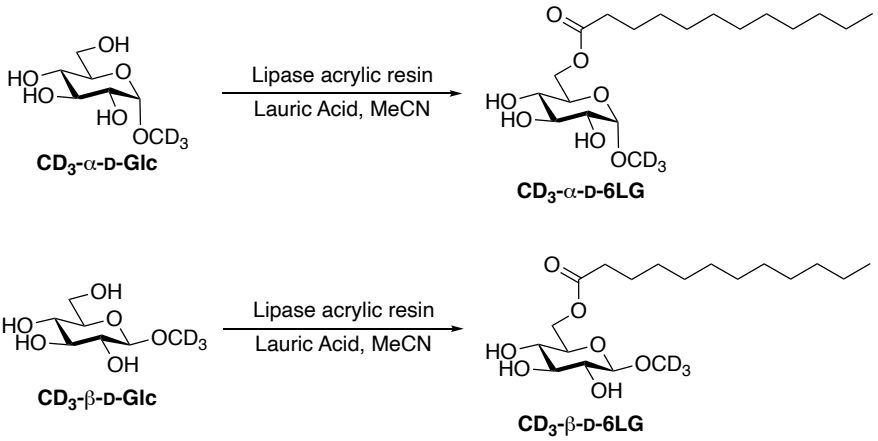
CD_3-α-D-*f*Glc and **CD_3-β-D-*f*Glc** were synthesized in a similar manner to a reported procedure.[19] A solution of $FeCl_3$ (389 mg, 2.40 mmol) in CD_3OD (10 mL) was added D-glucose (324 mg, 1.80 mmol) and stirred at 40 °C for 2 days. This mixture was added Celite and then sat $NaHCO_3$ aq (10 mL) and then filtered through a pad of Celite, which was washed with MeOH. After removal of the solvent, the residue was dissolved in THF, and the solution was filtered and evaporated. The crude mixture was purified by silica-gel column chromatography ($CHCl_3$-MeOH

= 7:1 to 3:1), which provided a mixture of methyl-d_3 α- and β-D-glucofuranosides (225 mg, 63%, α/β = 3:2). The mixture (200 mg, 1.01 mmol) was used for the next reaction using the general procedures (B) to produce the tetrabenzoyl synthetic intermediates (375 mg, 62%, α/β = 2:3).

The enantioseperation of tetrabenzoyl synthetic intermediates was carried out on a Daicel CHIRALPAK® IB column (10 mm ϕ × 250 mm) using hexane-EtOAc = 88:12, which led to the first-eluted methyl-d_3 2,3,4,6-tetra-*O*-benzoyl-α-D-glucofuranoside and the second-eluted methyl-d_3 2,3,4,6-tetra-*O*-benzoyl-β-D-glucofuranoside. Methyl-d_3 2,3,4,6-tetra-*O*-benzoyl-α-D-glucofuranoside: ^{1}H NMR ($CDCl_3$) δ 8.08 (d, ArH, *J* = 7.3 Hz, 2H), 8.01 (d, ArH, *J* = 7.3 Hz, 2H), 7.84 (d, ArH, *J* = 7.3 Hz, 2H), 7.77 (d, ArH, *J* = 7.3 Hz, 2H), 7.59-7.52 (m, ArH, 2H), 7.50-7.39 (m, ArH, 6H), 7.33-7.27 (m, ArH, 4H), 6.16 (dd, H-3, *J* = 4.9, 5.7 Hz, 1H), 5.79 (m, H-5, 1H), 5.41 (d, H-1, *J* = 4.6 Hz, 1H), 5.37 (dd, H-2, *J* = 4.5, 4.5 Hz, 1H), 4.93-4.86 (m, H-4, H-6a, 2H), 4.71 (dd, H-6b, *J* = 5.1, 12.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 166.1 (C=O), 165.8 (C=O), 165.3 (C=O), 165.1 (C=O), 133.4 (Ar), 133.3 (Ar), 133.1 (Ar), 133.0 (Ar), 130.0 (Ar), 129.8 (Ar), 129.7 (Ar), 129.5 (Ar), 129.3 (Ar), 129.1 (Ar), 128.6 (Ar), 128.4 (Ar), 128.4 (Ar), 128.2 (Ar), 128.2 (Ar), 102.1 (OCD_3), 100.7 (C-1), 78.7 (C-2), 75.0 (C-3), 73.4 (C-4), 69.6 (C-5), 63.7 (C-6); $[\alpha]_D$ +45.9 (*c* 1.0, $CHCl_3$); HRMS (ESI) *m/z* calcd for $C_{35}H_{27}D_3O_{10}Na$ $[M+Na]^+$ 636.1920, found 636.1907. Methyl-d_3 2,3,4,6-tetra-*O*-benzoyl-β-D-glucofuranoside: ^{1}H NMR ($CDCl_3$) δ 8.07 (d, ArH, *J* = 7.3 Hz, 2H), 8.02 (d, ArH, *J* = 6.8 Hz, 2H), 7.86 (d, ArH, *J* = 7.3 Hz, 2H), 7.75 (d, ArH, *J* = 7.3 Hz, 2H), 7.63-7.58 (m, ArH, 1H), 7.57-7.52 (m, ArH, 1H), 7.51-7.39 (m, ArH, 6H), 7.34-7.26 (m, ArH, 4H), 5.93 (d, H-3, *J* = 5.4 Hz, 1H), 5.81 (m, H-5, 1H), 5.48 (s, H-2, 1H), 5.16 (s, H-1, 1H), 5.04 (dd, H-4, *J* = 5.6, 9.0 Hz, 1H), 4.98 (dd, H-6a, *J* = 2.0, 12.2 Hz, 1H), 4.73 (dd, H-6b, *J* = 4.6, 12.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 166.1 (C=O), 165.1 (C=O), 165.0 (C=O), 165.0 (C=O), 133.6 (Ar), 133.3 (Ar), 133.0 (Ar), 133.0 (Ar), 129.9 (Ar), 129.9 (Ar), 129.8 (Ar), 129.7 (Ar), 129.5 (Ar), 129.3 (Ar), 129.0 (Ar), 128.7 (Ar), 128.5 (Ar), 128.4 (Ar), 128.2 (Ar), 128.1 (Ar), 107.5 (C-1), 100.3 (OCD_3), 81.0 (C-2), 78.4 (C-4), 74.6 (C-3), 70.2 (C-5), 64.0 (C-6); $[\alpha]_D$ -39.5 (*c* 1.0, $CHCl_3$); HRMS (ESI) *m/z* calcd for $C_{35}H_{27}D_3O_{10}Na$ $[M+Na]^+$ 636.1920, found 636.1902.

In a similar manner to the general procedure (C) without the use of 1,4-dioxane, methyl-d_3 2,3,4,6-tetra-*O*-benzoyl-α-D-glucofuranoside (52 mg, 87 μmol) and methyl-d_3 2,3,4,6-tetra-*O*-benzoyl-β-D-glucofuranoside (57 mg, 95 μmol) were converted to **CD_3-α-D-*f*Glc** (10 mg, 58%) and **CD_3-β-D-*f*Glc** (12 mg, 63%), respectively. Their ^{1}H NMR spectra were virtually the same as those reported for methyl-h_3 α- and β-D-glucofuranoside except for the absence of the -OCH_3 signal.[20] **CD_3-α-D-*f*Glc** ^{1}H NMR (D_2O) δ 5.06 (d, H-1, *J* = 4.4 Hz, 1H), 4.27 (dd, H-3, *J* = 3.4, 4.7 Hz, 1H), 4.14 (dd, H-2, *J* = 3.7, 3.7 Hz, 1H), 4.08 (dd, H-4, *J* = 4.6, 8.1 Hz, 1H), 3.86 (m, H-5, 1H), 3.78 (dd, H-6a, *J*= 2.7, 12.0 Hz, 1H), 3.64 (dd, H-6b, *J* = 6.4, 12.2 Hz, 1H). **CD_3-β-D-*f*Glc**: ^{1}H NMR (D_2O) δ 4.86 (s, H-1, 1H), 4.22 (d, H-3, *J* = 4.4 Hz, 1H), 4.16 (dd, H-4, *J* = 4.6, 9.0 Hz, 1H), 4.12 (s, H-2, 1H), 3.94 (m, H-5, 1H), 3.85 (dd, H-6a, *J* = 2.8, 12.0 Hz, 1H), 3.69 (dd, *J* = 6.1, 12.0 Hz, H-6b, 1H).

Enzymatic preparation of **CD_3-α-D-*f*Glc** and **CD_3-β-D-*f*Glc**



CD_3-α-D-6LG was synthesized in a similar manner to a reported procedure.[21] A solution of **CD_3-α-D-Glc** (97 mg, 0.50 mmol) in MeCN (1.5 mL), was added lauric acid (100 mg), thermally activated pulverized 4 Å molecular sieves (80 mg) and lipase acrylic resin (≥5,000 U/g, recombinant, expressed in *Aspergillus niger*) purchased from Sigma-Aldrich (0.49g, 50% w/w of sugar). The reaction mixture was incubated in a shaking incubator S1-300C (from AS ONE) at 60 °C with rotational speed of 300 rpm for 3 days. The reaction mixture was diluted with EtOAc and then filtered, and the filtrate was evaporated. The residue was purified by silica-gel column chromatography ($CHCl_3$-MeOH = 15:1 to 9:1), which provided **CD_3-α-D-6LG**, (53 mg, 28%). Its ^{1}H NMR spectrum was virtually the same as that reported for methyl-h_3 6-lauroyl-α-D-glucopyranoside except for the absence of the -OCH_3 signal. [22] **CD_3-α-D-6LG**: ^{1}H NMR ($CDCl_3$) δ 4.79 (d, H-1, J = 3.9 Hz, 1H), 4.57 (dd, H-6a, J = 4.2, 12.5, Hz, 1H), 4.22 (dd, H-6b, J = 2.0, 12.2 Hz, 1H), 3.76-3.69 (m, H-3, H-5, 2H), 3.53 (dd, H-2, J = 3.9, 9.3 Hz, 1H), 3.34 (dd, H-4, J = 9.3, 9.3, Hz, 1H), 2.38 (t, CH_2, J = 7.6 Hz, 2H), 1.64 (m, CH_2, 2H), 1.22-1.35 (m, CH_2 × 8, 16H), 0.88 (t, CH_3, J = 6.8 Hz, 3H).

CD_3-β-D-Glc (89 mg, 0.45 mmol) was converted to **CD_3-β-D-6LG** (60 mg, 32%) in a similar manner. Its ^{1}H NMR spectrum was similar to that reported for methyl-h_3 6-lauroyl-β-D-glucopyranoside, but the signal assignment and some of chemical shifts were slightly different from ours.[22] **CD_3-β-D-6LG**: ^{1}H NMR ($CDCl_3$) δ 4.59 (dd, H-6a, J = 3.9, 12.2 Hz, 1H), 4.26 (dd, H-6b, J = 2.0, 12.2 Hz, 1H), 4.21 (d, H-1, J = 7.8 Hz, 1H), 3.59 (dd, H-3, J = 9.1, 9.1, 1H), 3.45 (m, H-5, 1H), 3.41-3.34 (m, H-2, H-4, 2H), 2.38 (t, CH_2, J = 7.6 Hz, 2H), 1.63 (m, CH_2, 2H), 1.22-1.34 (m, CH_2 × 8, 16H), 0.88 (t, CH_3, J = 6.8 Hz, 3H).

Computational Details

DFT calculations were carried out on Gaussian 16 software.[23]

Gas phase and PCM Solvent effects

Molecular mechanics conformational search was performed for each molecule on Spartan'18 software.[24] Obtained geometries within 20 kJ/mol from the most stable for each molecule were submitted to DFT optimization. Geometry optimization and IR and VCD calculations on the isolated conformers were computed at the level of B3LYP/6-31G(d). The effects of water and DMSO were included using a polarizable continuum model (PCM). The calculated frequencies were converted to IR and VCD spectra on GaussView6 software using a peak half-width a half height of 10 cm^{-1}. When applicable, the VCD spectra of each conformer were averaged according to the Boltzmann populations simulated at 298 K.

CD_3-α- and **β-D-Glc** with Explicit Water Molecules

Geometry optimization of initial structures of each epimer was performed at the level of B3LYP/6-31G(d). Obtained structures were submitted to MD simulation on AMBER18 program[25] using periodic boundary conditions and an octahedron cell. ff14SB[26] was chosen as the force field, whereas water molecules were included by the TIP3P potential.[27] Before performing the MD simulation, the energy minimization of an octahedron model was carried out with steepest descent and conjugate gradient method. Then, *NVT* and *NPT* equilibration and MD simulation were successively performed. Electrostatic interactions were calculated with the particle-mesh Ewald method.[28] The cutoff distance of the van der Waals and electrostatic interactions was 8 Å. The Langevin method for temperature (300 K) was applied to the simulation system. The time step for the integration was set to 0.5 ps. During *NVT* and *NPT* equilibration, the system was relaxed for 20 ps. After equilibration, the system was simulated for 1.8 ns, and 12 snapshots were taken every 25 ps (from 500-775 ps).

Next, geometry optimizations of the 12 snapshots were performed. A two-layer ONIOM method was used for the QM/MM calculations. The high layer consisting of solute was treated at the B3LYP/6-31G(d) level, and the low layer consisting of water molecules was described by AMBER force field including TIP3P parameters. After optimizations, IR and VCD calculations were performed at the same level of theory used for optimizations. As with the gas phase and PCM hydration, the calculated frequencies were converted to IR and VCD spectra on the GaussView6 software with the peak half width and half height at 10 cm^{-1}.

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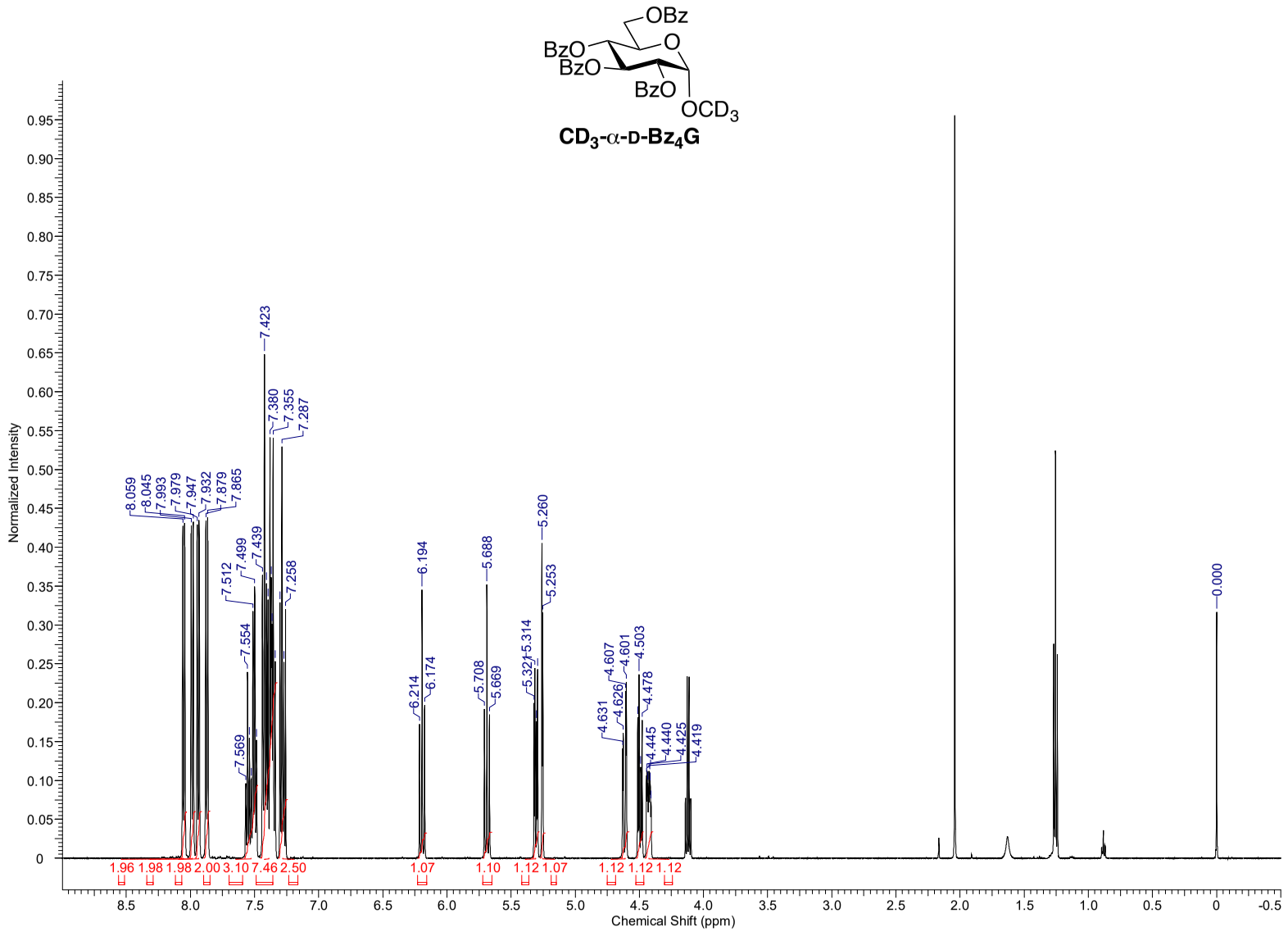
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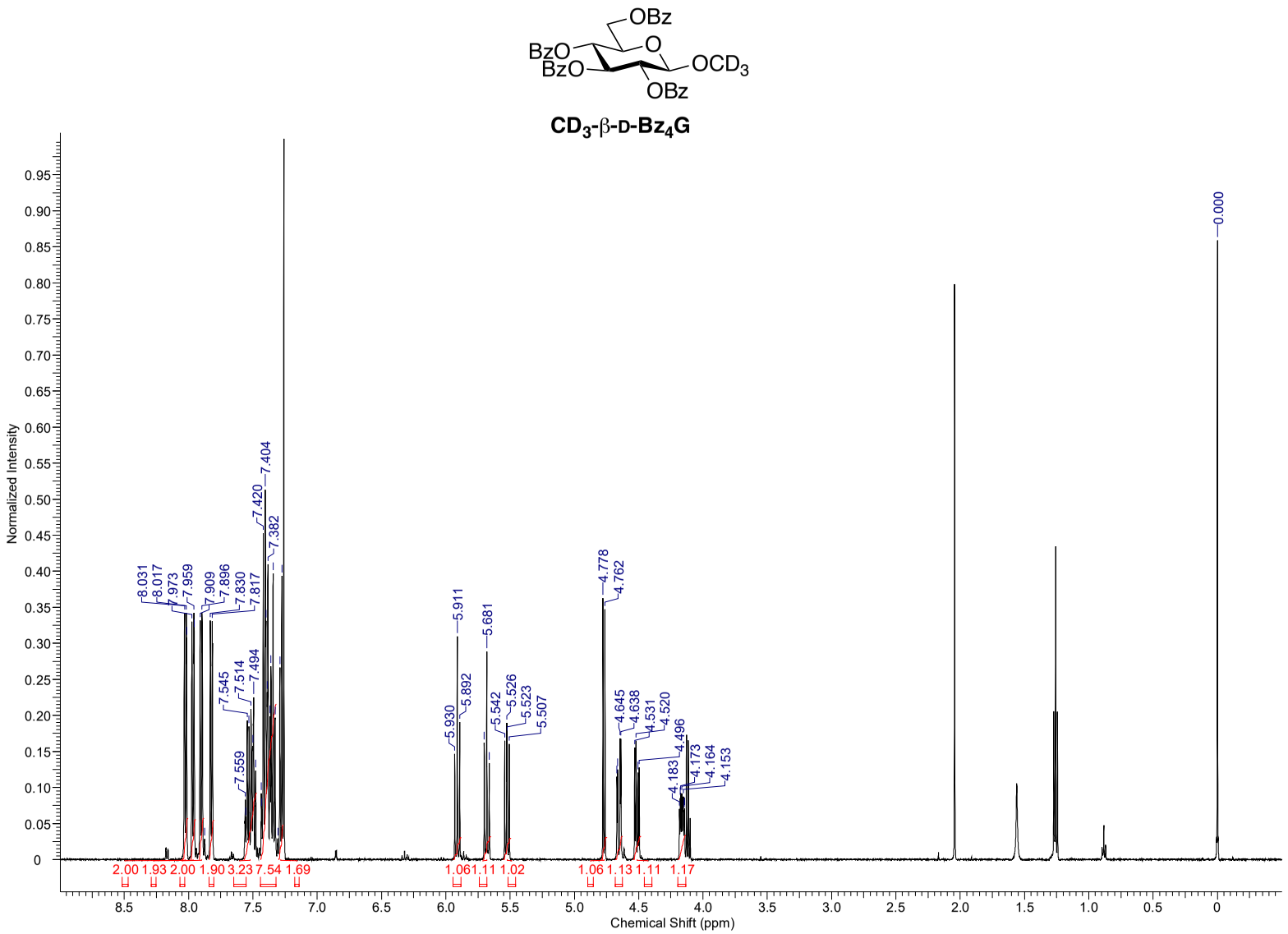
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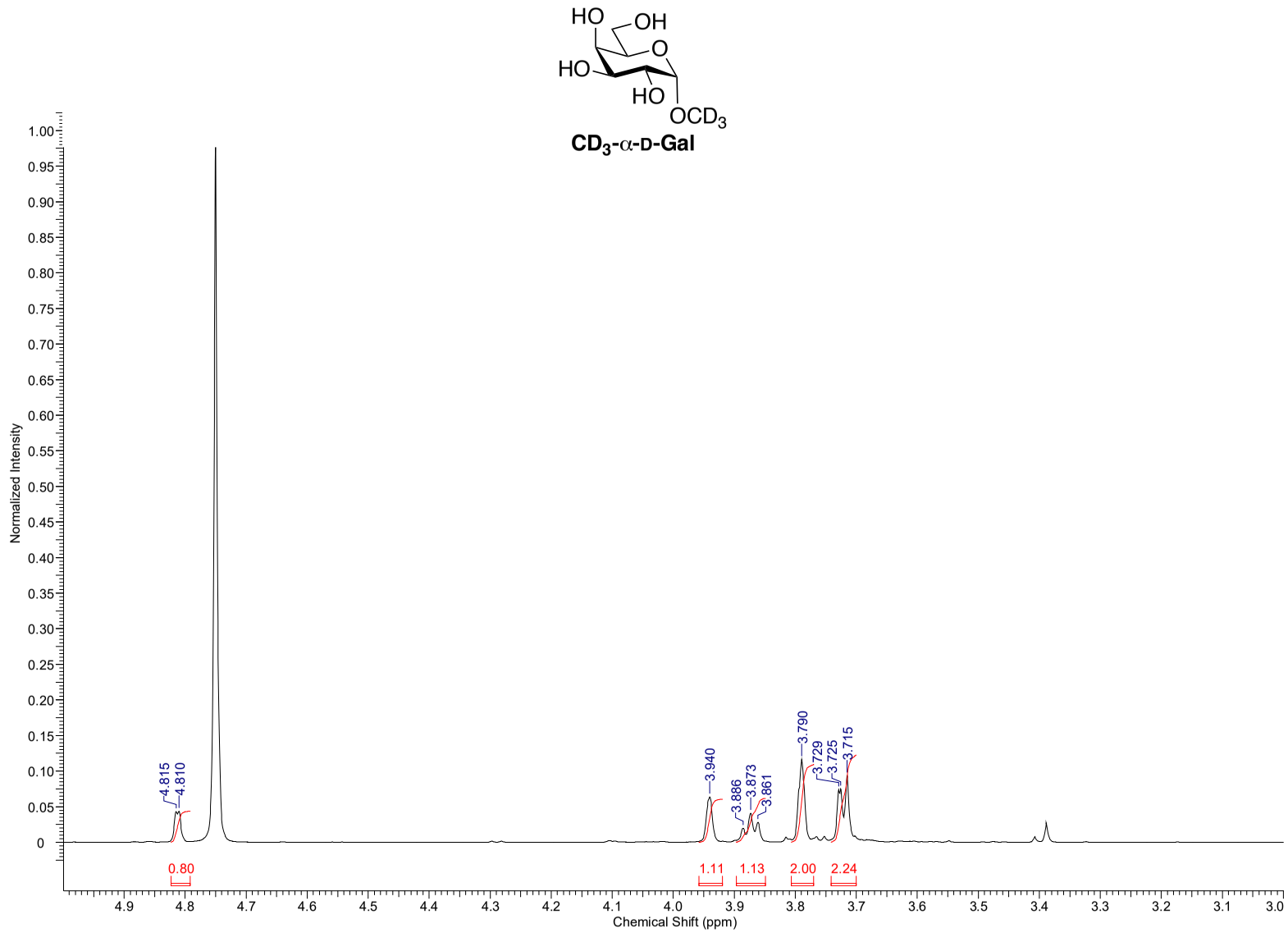
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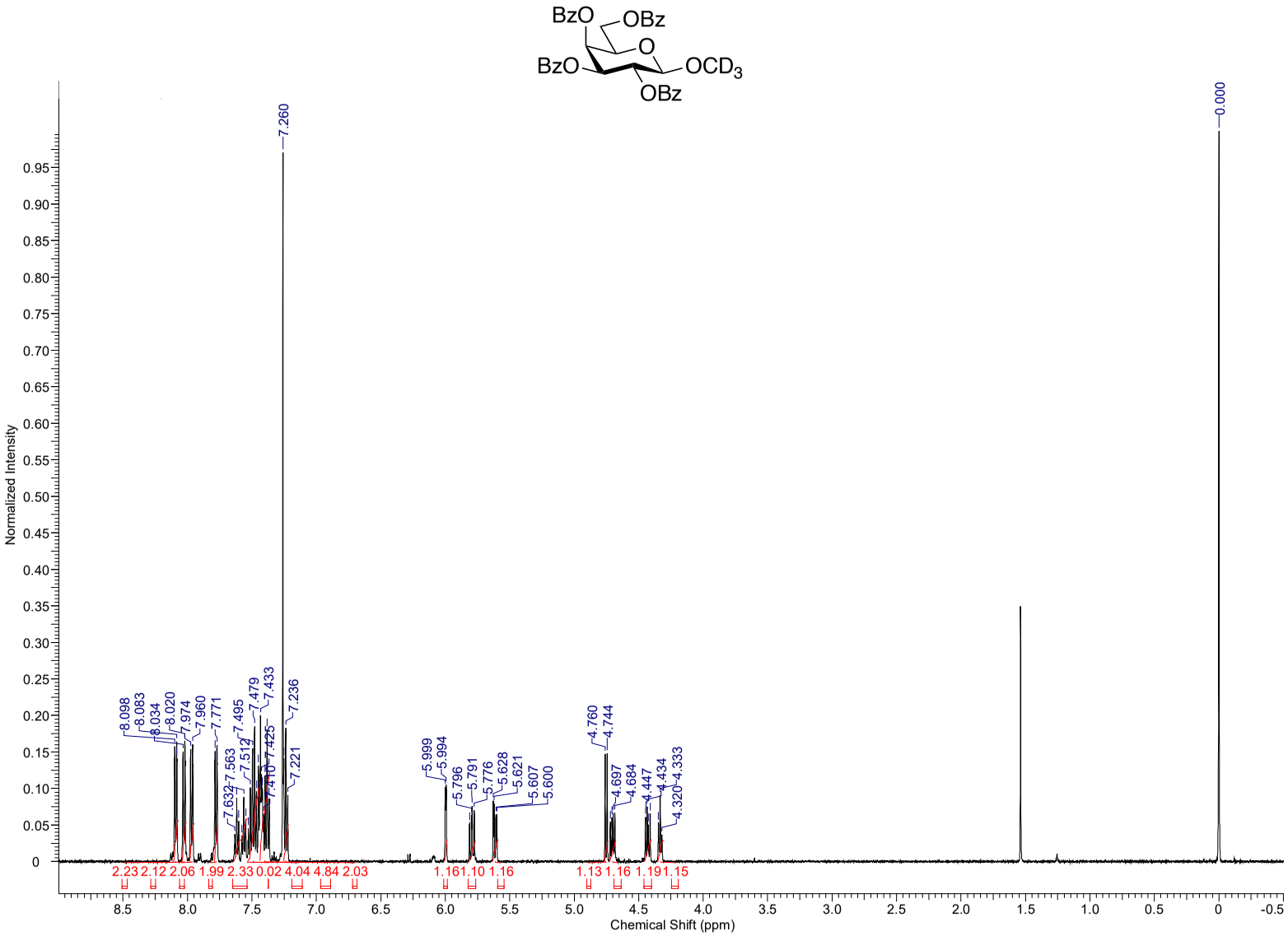
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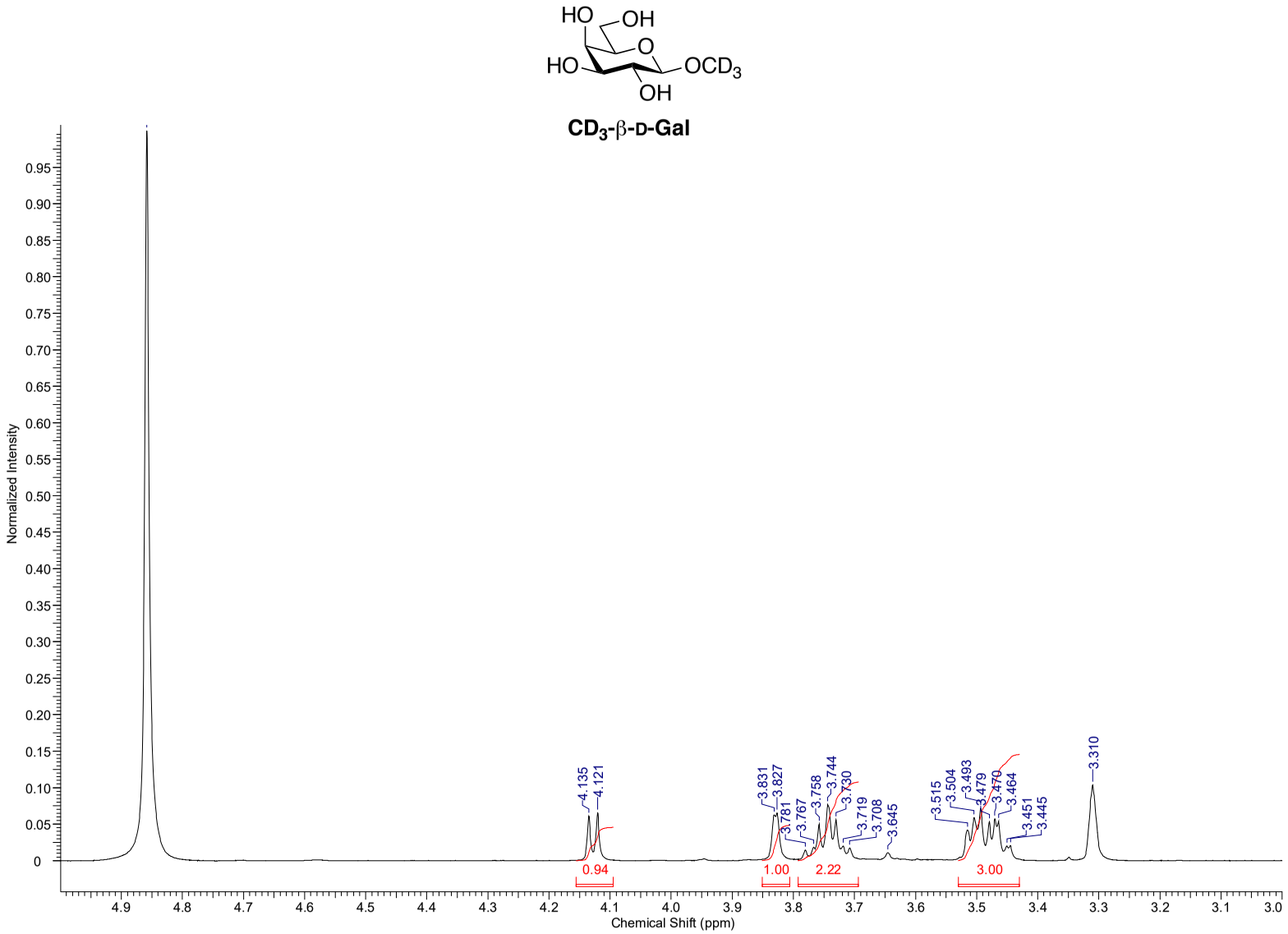
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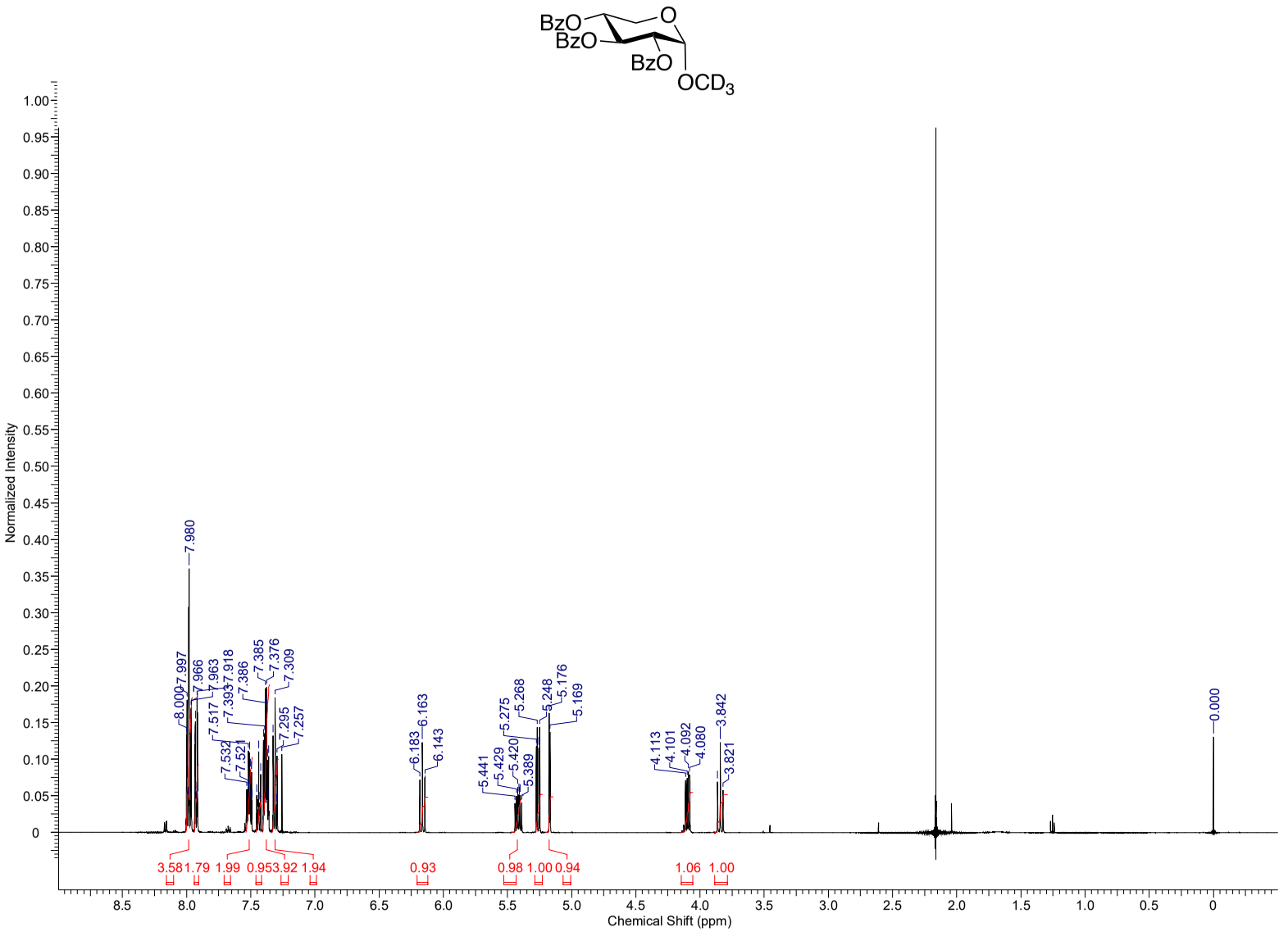
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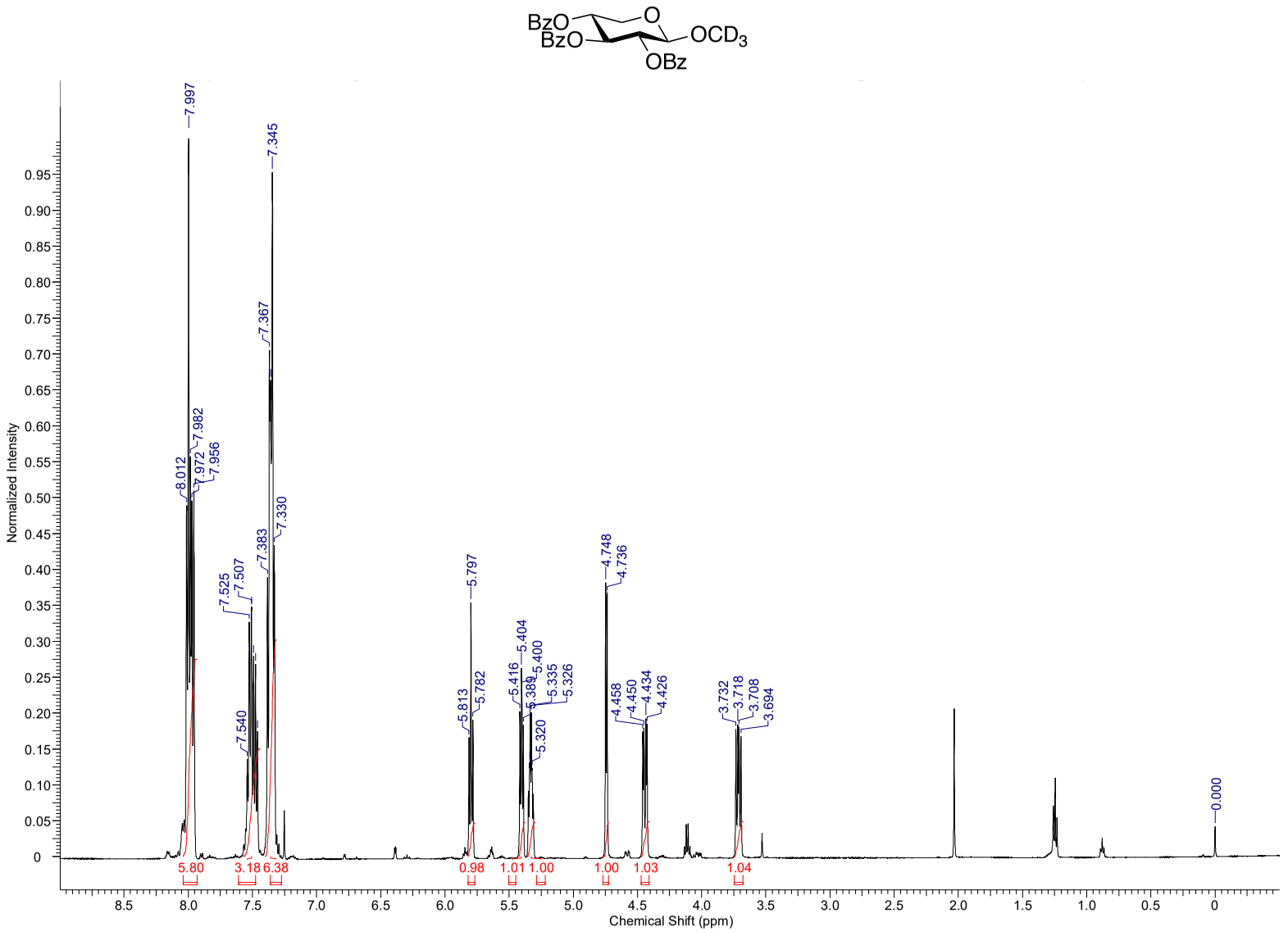
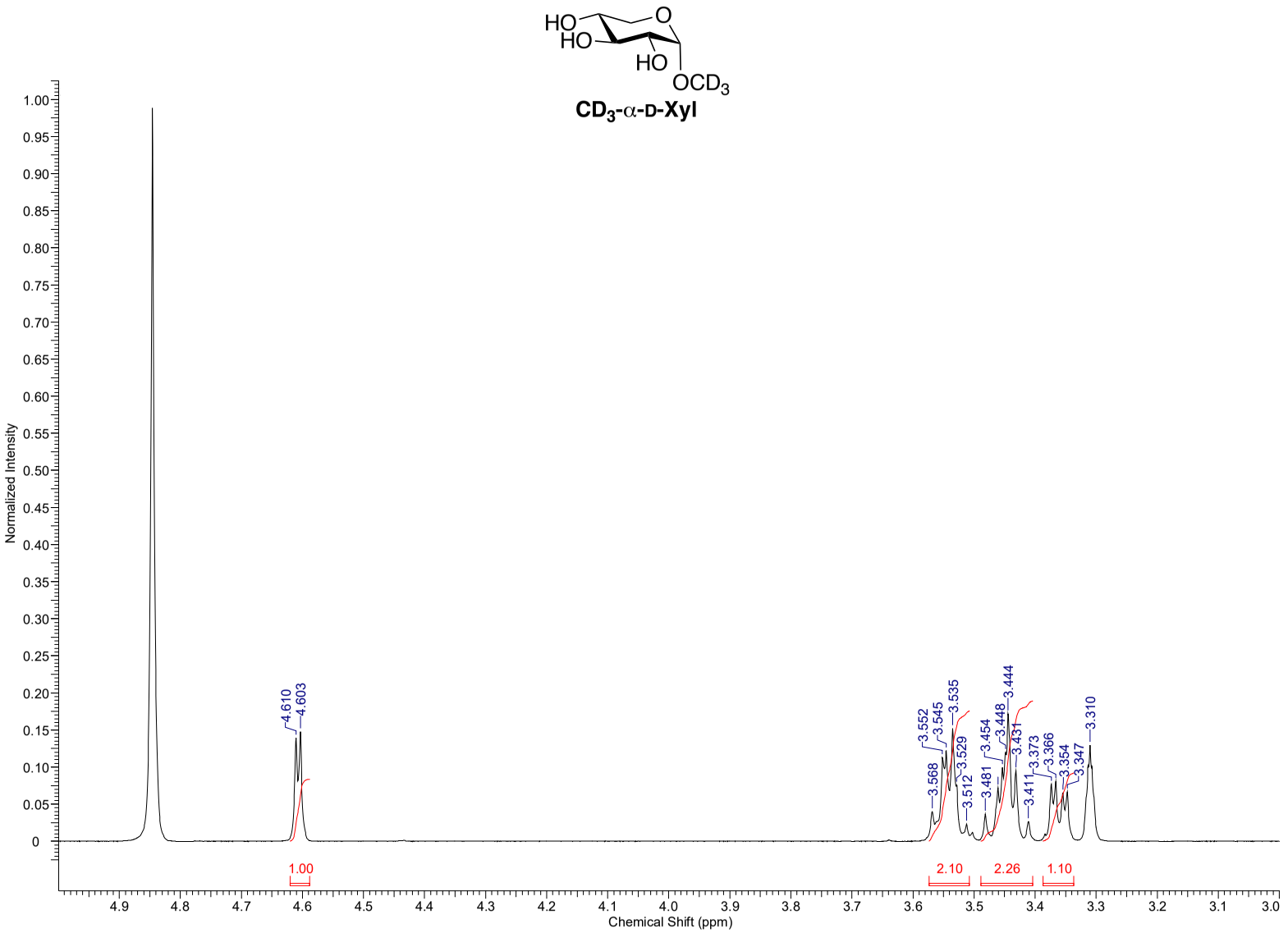
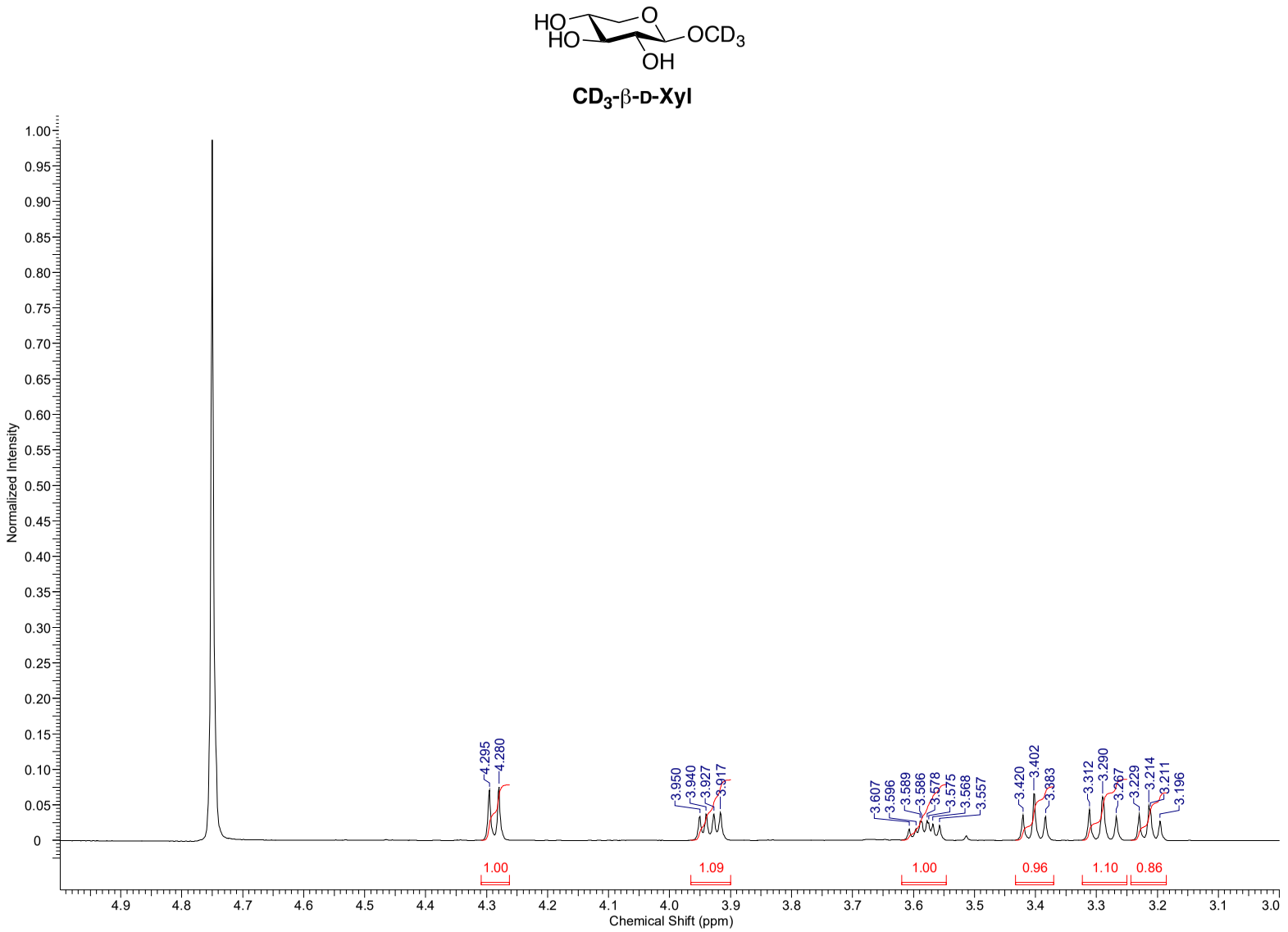
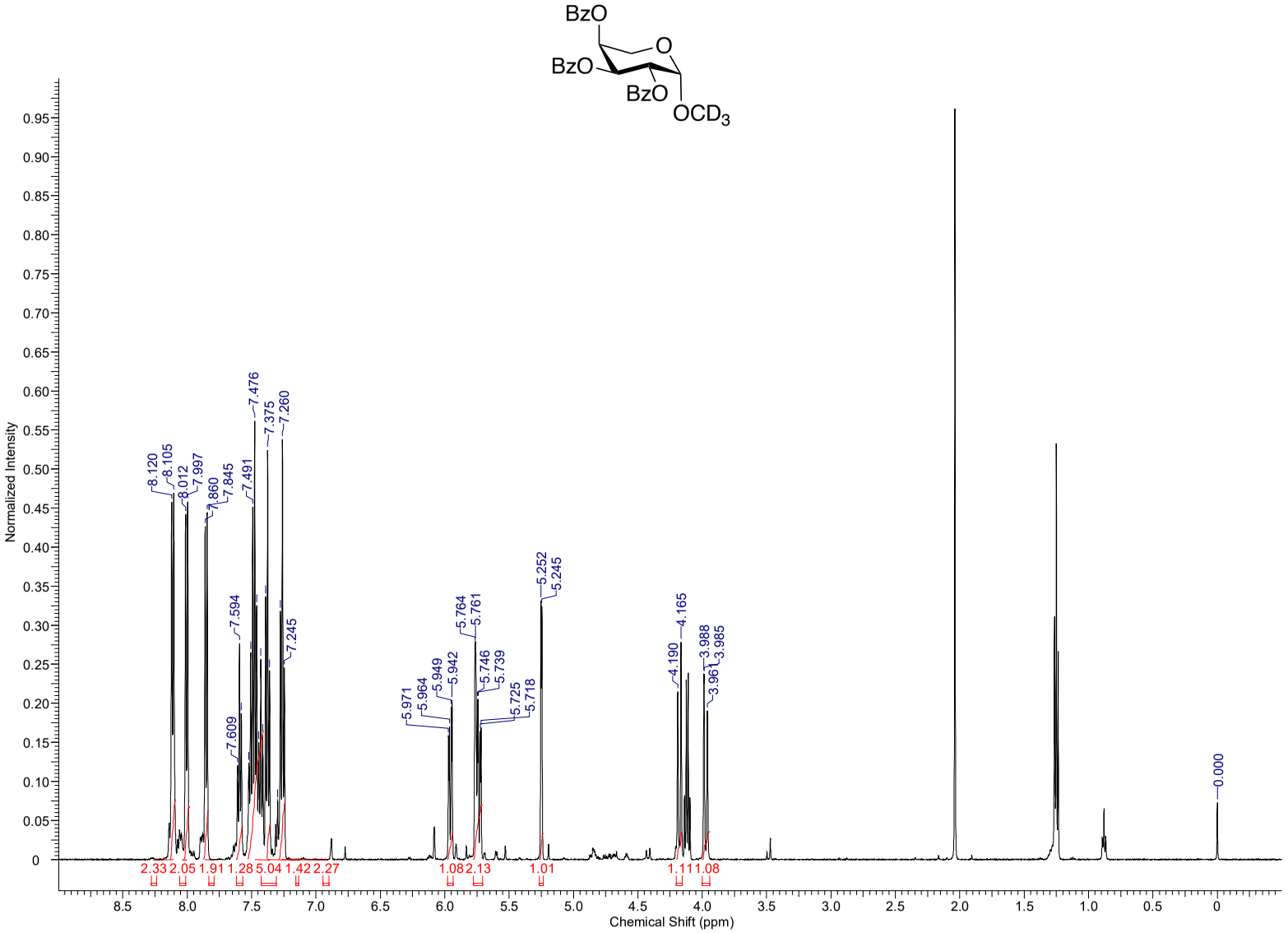
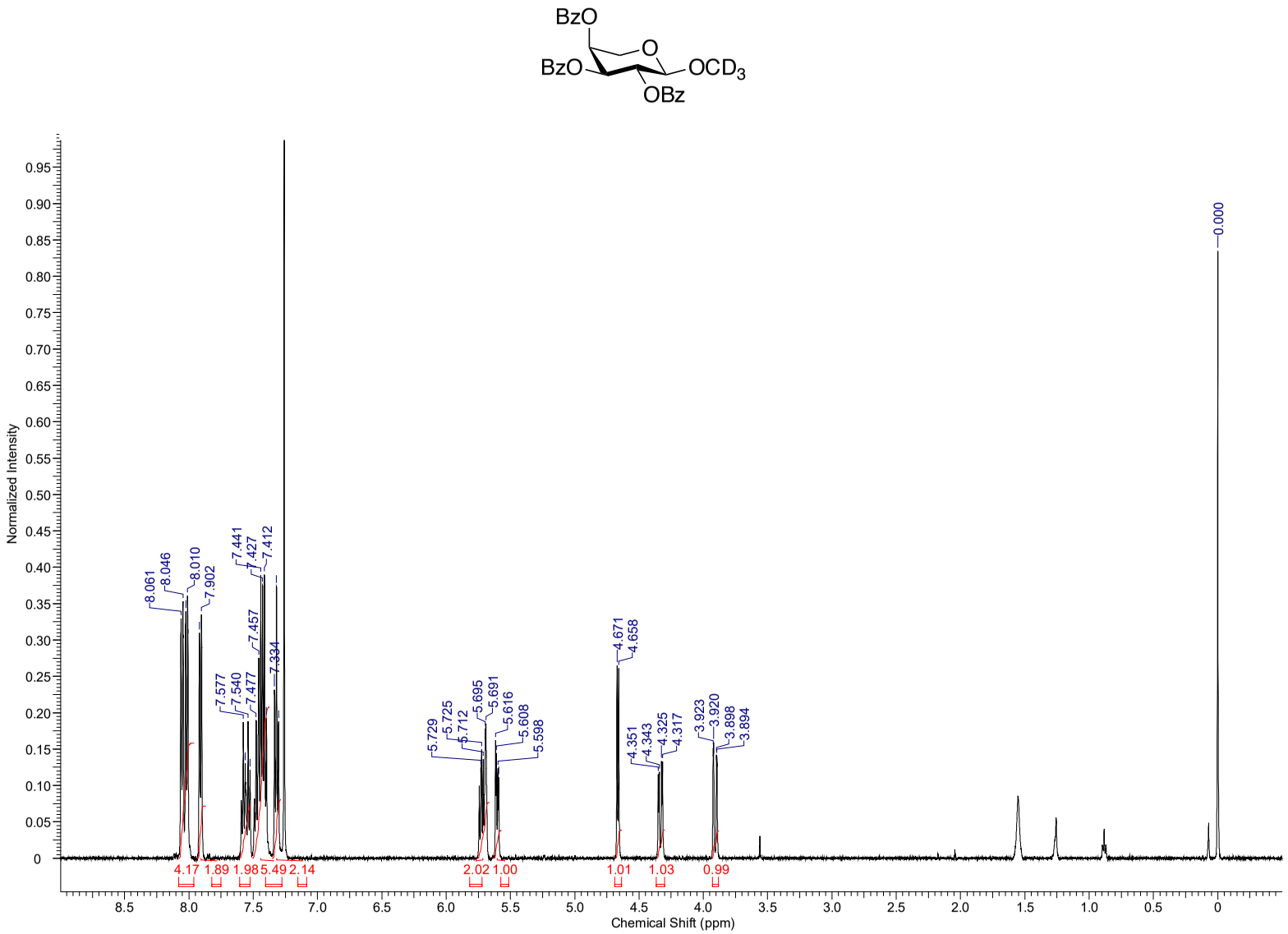
0.98 1.00 0.94
1.06 1.00

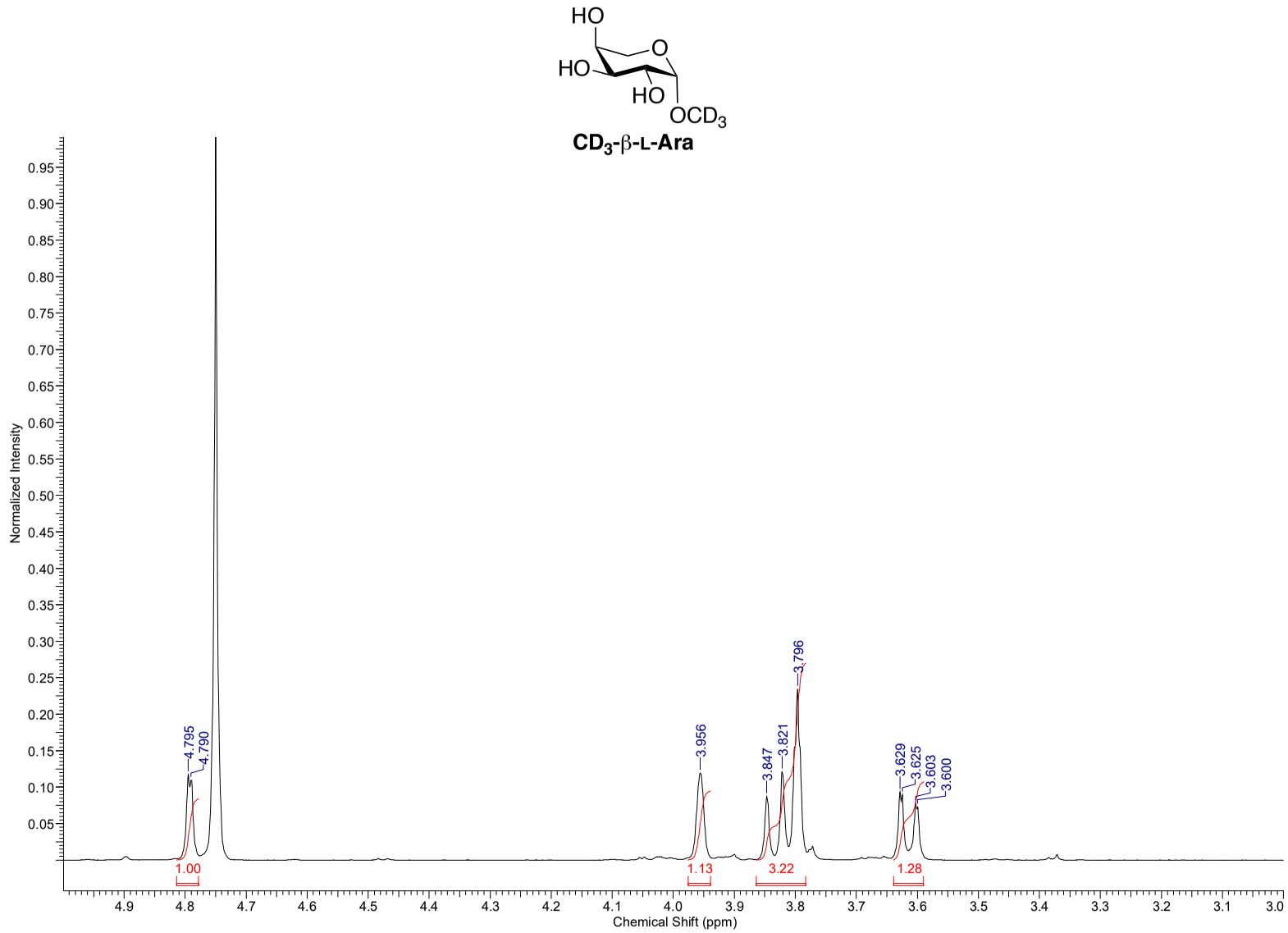

BzO
BzO
O
OCD3
OBz
Normalized Intensity
Chemical Shift (ppm)
8.012
7.997
7.982
7.972
7.956
7.540
7.525
7.507
7.383
7.367
7.345
7.330
5.813
5.797
5.782
5.416
5.404
5.389
5.400
5.335
5.326
5.320
4.748
4.736
4.458
4.450
4.434
4.426
3.732
3.718
3.708
3.694
0.000
5.80
3.18
6.38
0.98
1.01
1.00
1.00
1.03
1.04

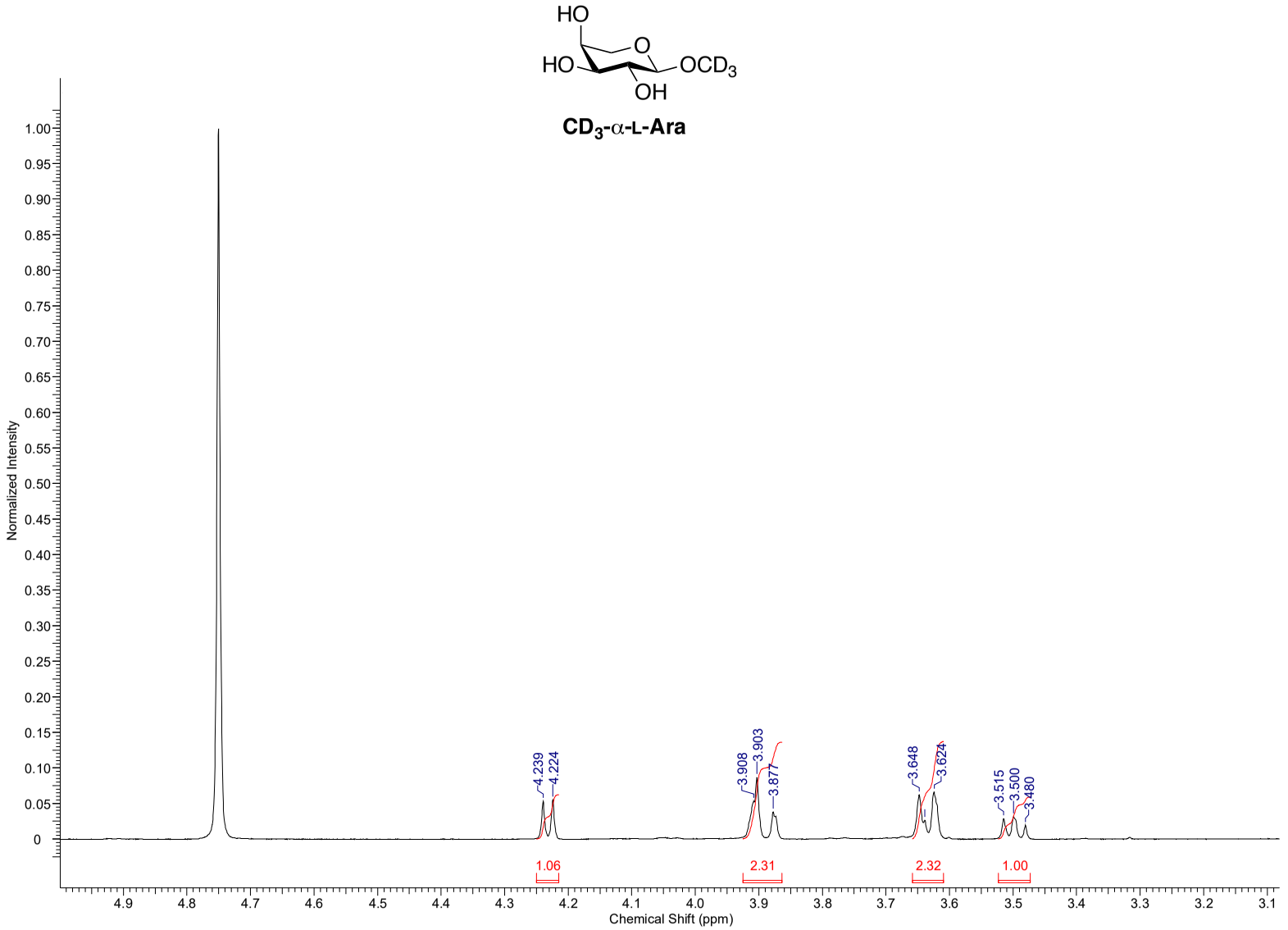

HO
HO
HO
O
OCD3
CD3-α-D-Xyl
Normalized Intensity
Chemical Shift (ppm)
4.610
4.603
3.568
3.552
3.545
3.535
3.529
3.512
3.481
3.454
3.448
3.444
3.431
3.411
3.373
3.366
3.354
3.347
3.310
1.00
2.10
2.26
1.10

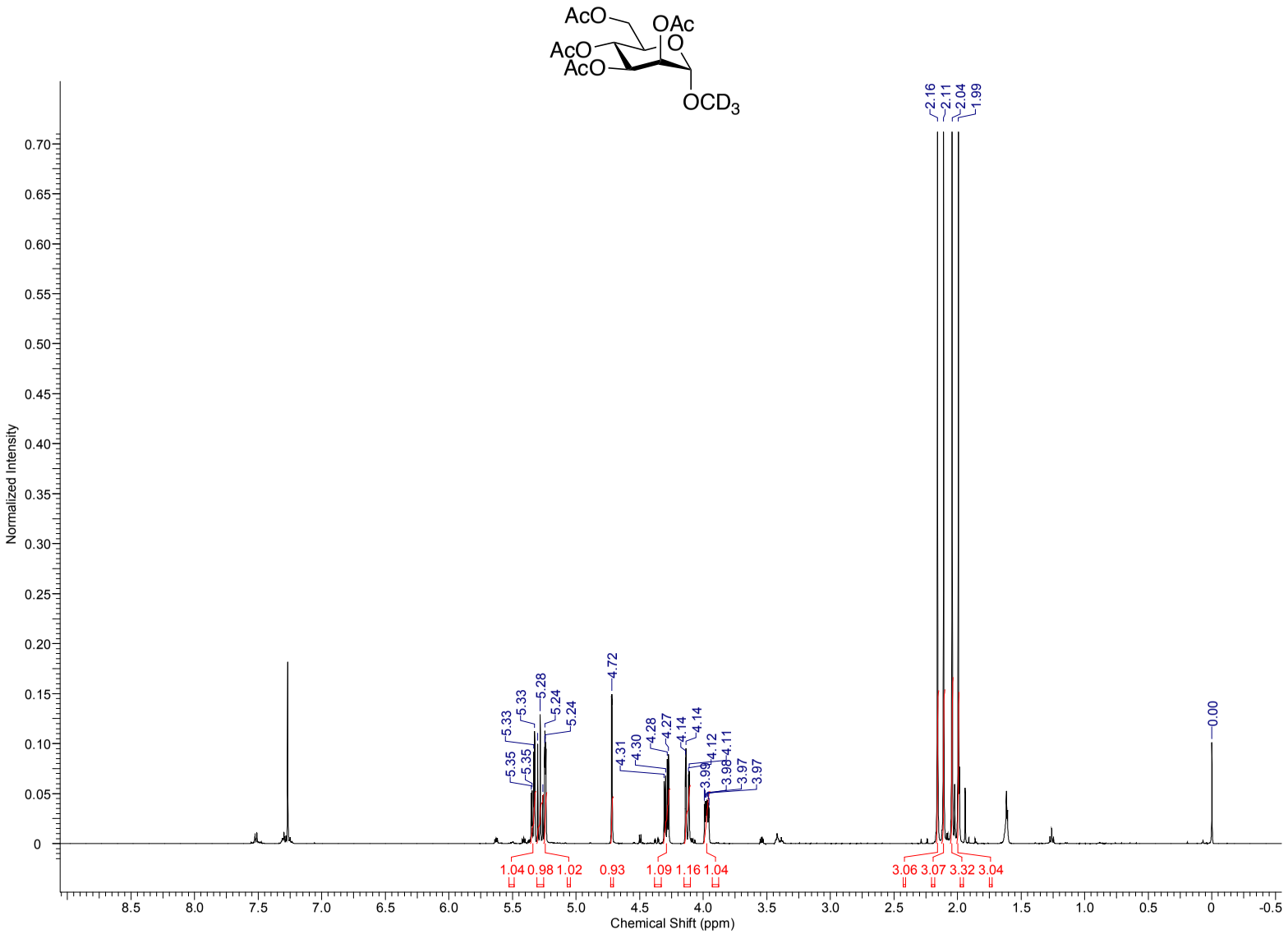

HO
HO
O
OCD3
OH
CD3-β-D-Xyl
Normalized Intensity
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
4.295
4.280
3.950
3.940
3.927
3.917
3.607
3.596
3.589
3.586
3.578
3.575
3.568
3.557
3.420
3.402
3.383
3.312
3.290
3.267
3.229
3.214
3.211
3.196
1.00
1.09
1.00
0.96
1.10
0.86
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
3.0
Chemical Shift (ppm)

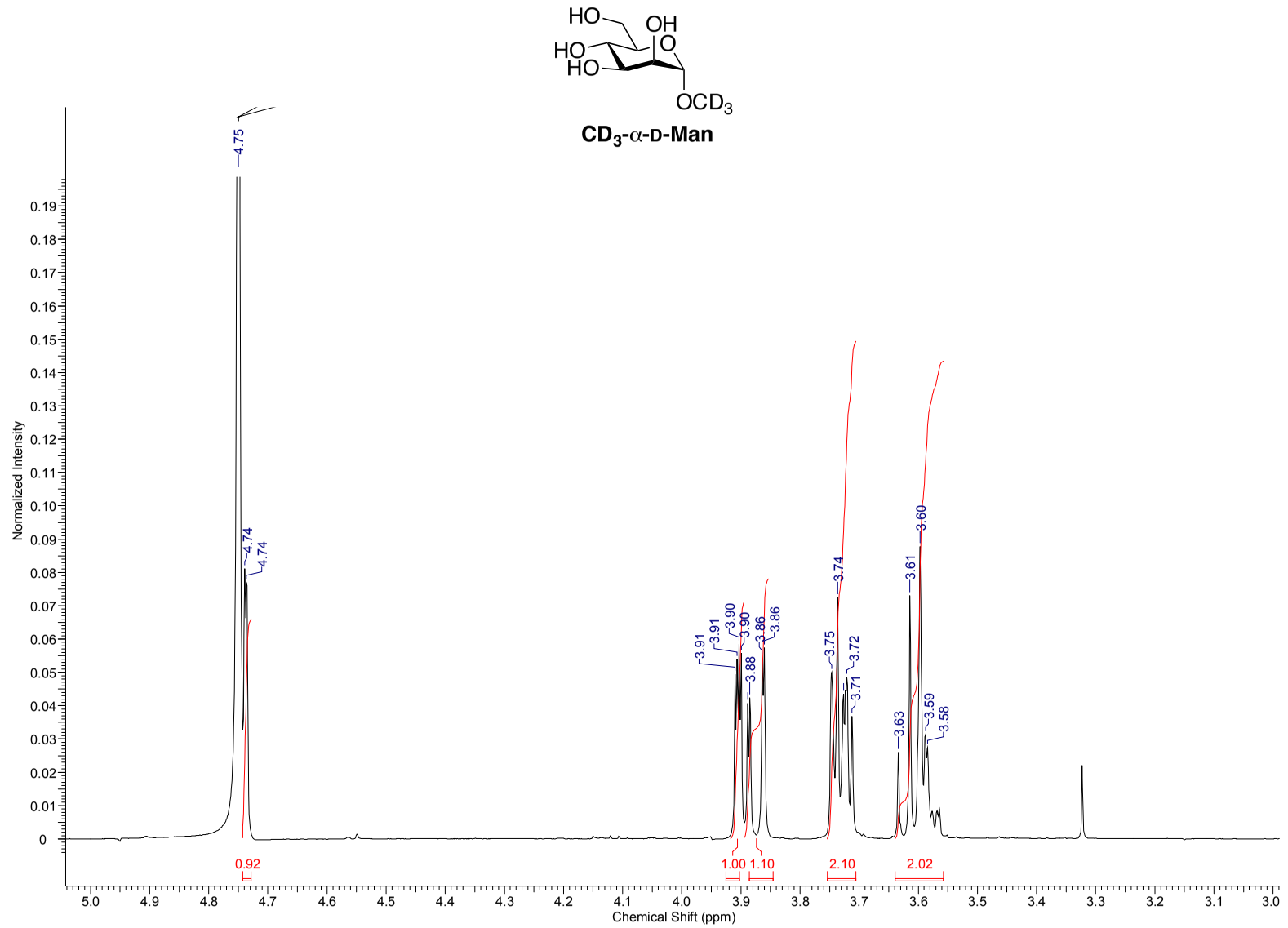

BzO
O
BzO
BzO
OCD3
Normalized Intensity
Chemical Shift (ppm)
8.120
8.105
8.012
7.997
7.860
7.845
7.609
7.594
7.491
7.476
7.375
7.260
7.245
5.971
5.964
5.949
5.942
5.764
5.761
5.746
5.739
5.725
5.718
5.252
5.245
4.190
4.165
3.988
3.985
3.961
0.000
2.33 2.05 1.91 1.28 5.04 1.42 2.27
1.08 2.13
1.01
1.11 1.08

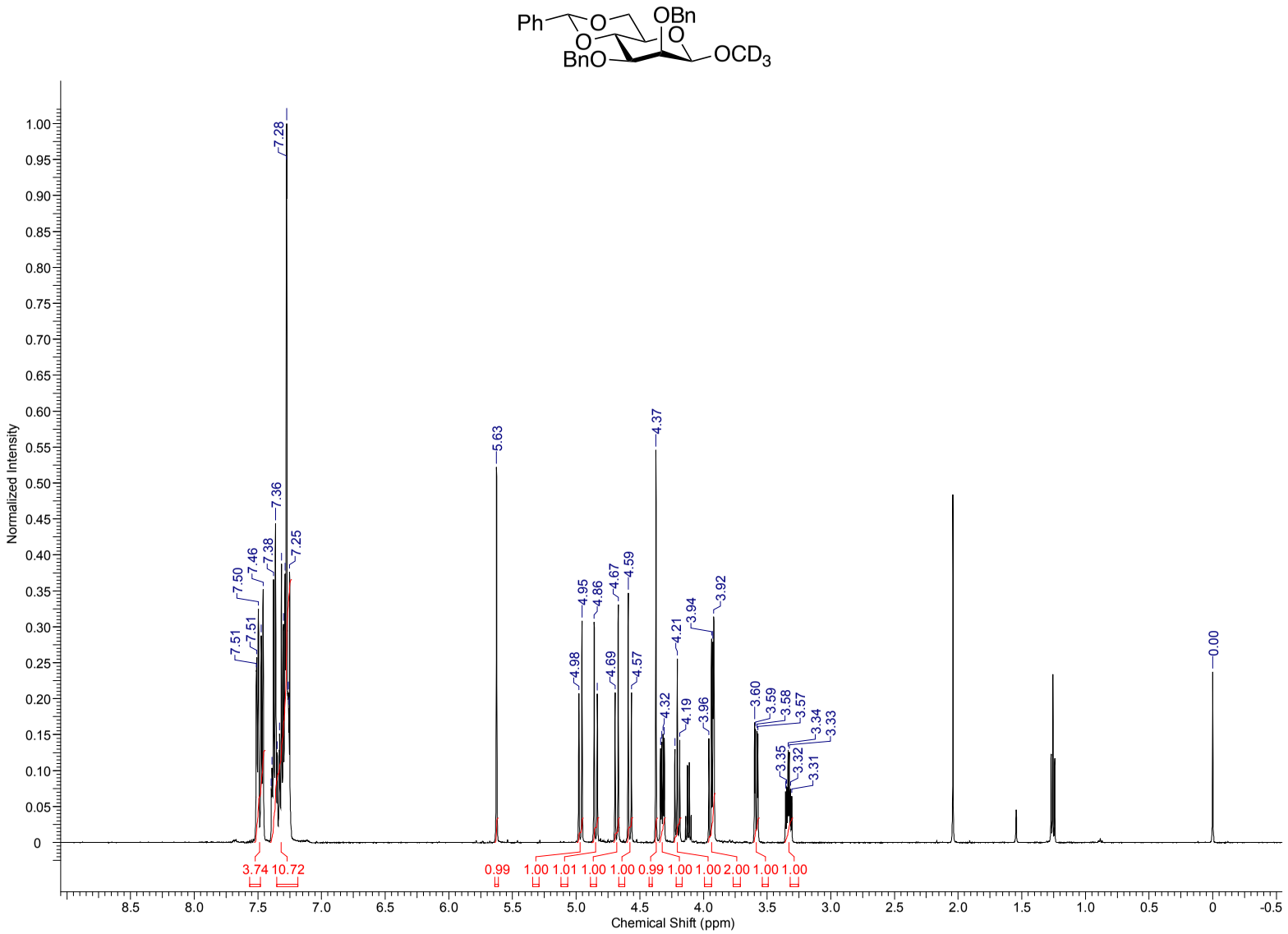

BzO
O
BzO
OCD3
OBz
Normalized Intensity
Chemical Shift (ppm)
8.061
8.046
8.010
7.902
7.577
7.540
7.477
7.457
7.441
7.427
7.412
7.334
5.729
5.725
5.712
5.695
5.691
5.616
5.608
5.598
4.671
4.658
4.351
4.343
4.325
4.317
3.923
3.920
3.898
3.894
0.000
4.17
1.89
1.98
5.49
2.14
2.02
1.00
1.01
1.03
0.99

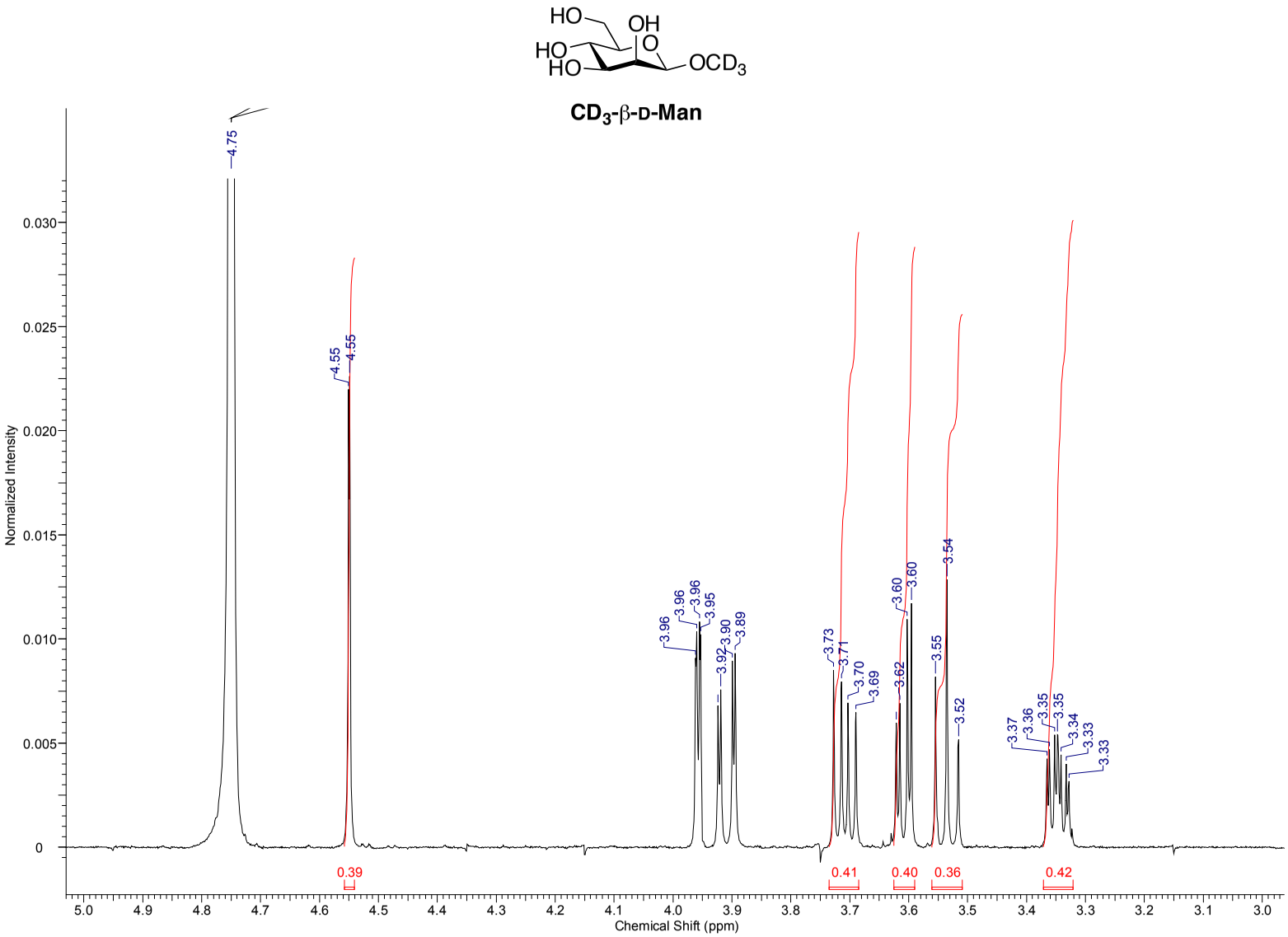

HO
O
HO
HO
OCD3
CD3-β-L-Ara
Normalized Intensity
Chemical Shift (ppm)
4.795
4.790
3.956
3.847
3.821
3.796
3.629
3.625
3.603
3.600
1.00
1.13
3.22
1.28

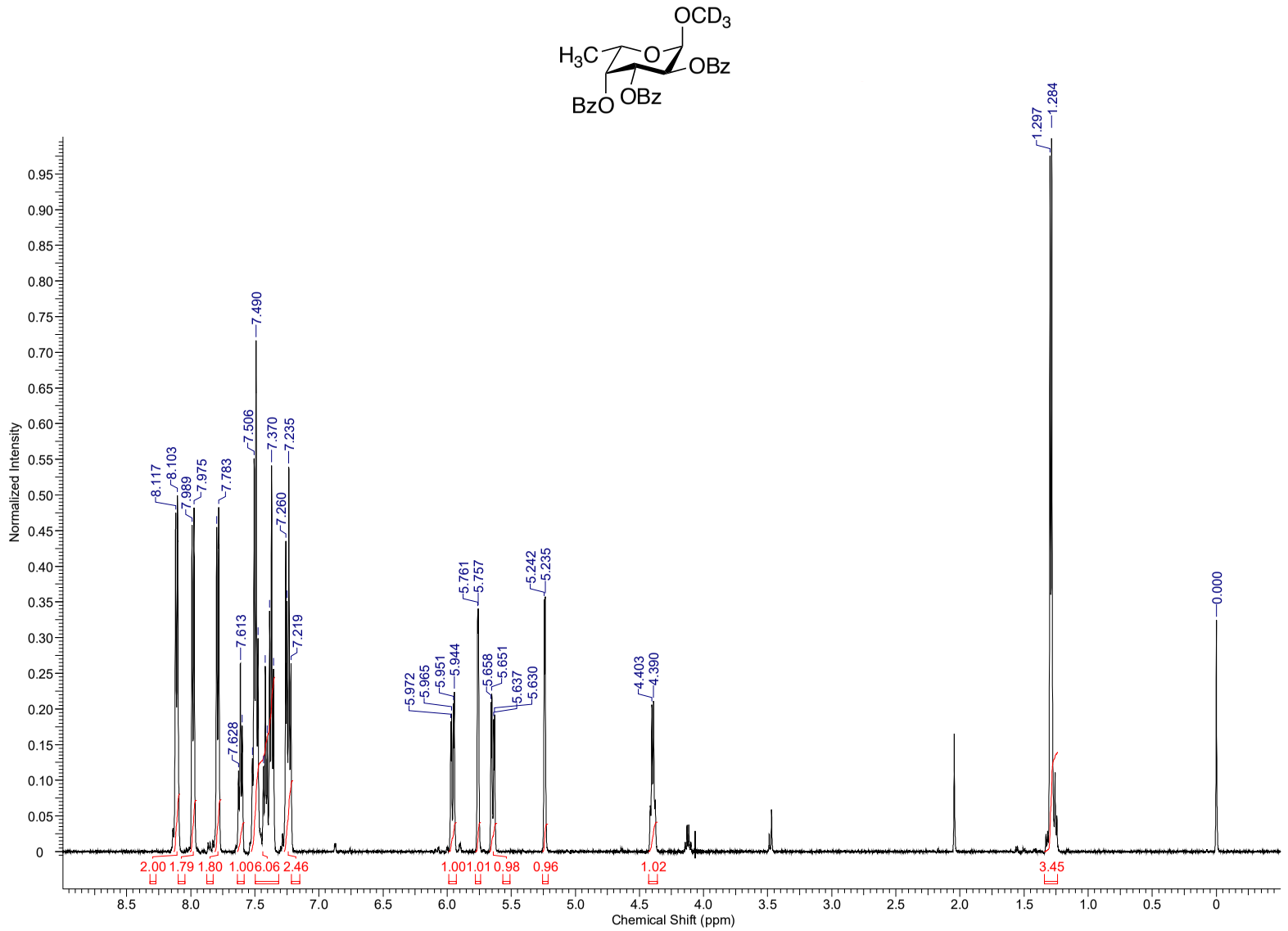

HO
O
HO
OCD3
OH
CD3-α-L-Ara
Normalized Intensity
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
4.239
4.224
3.908
3.903
3.877
3.648
3.624
3.515
3.500
3.480
1.06
2.31
2.32
1.00
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
Chemical Shift (ppm)

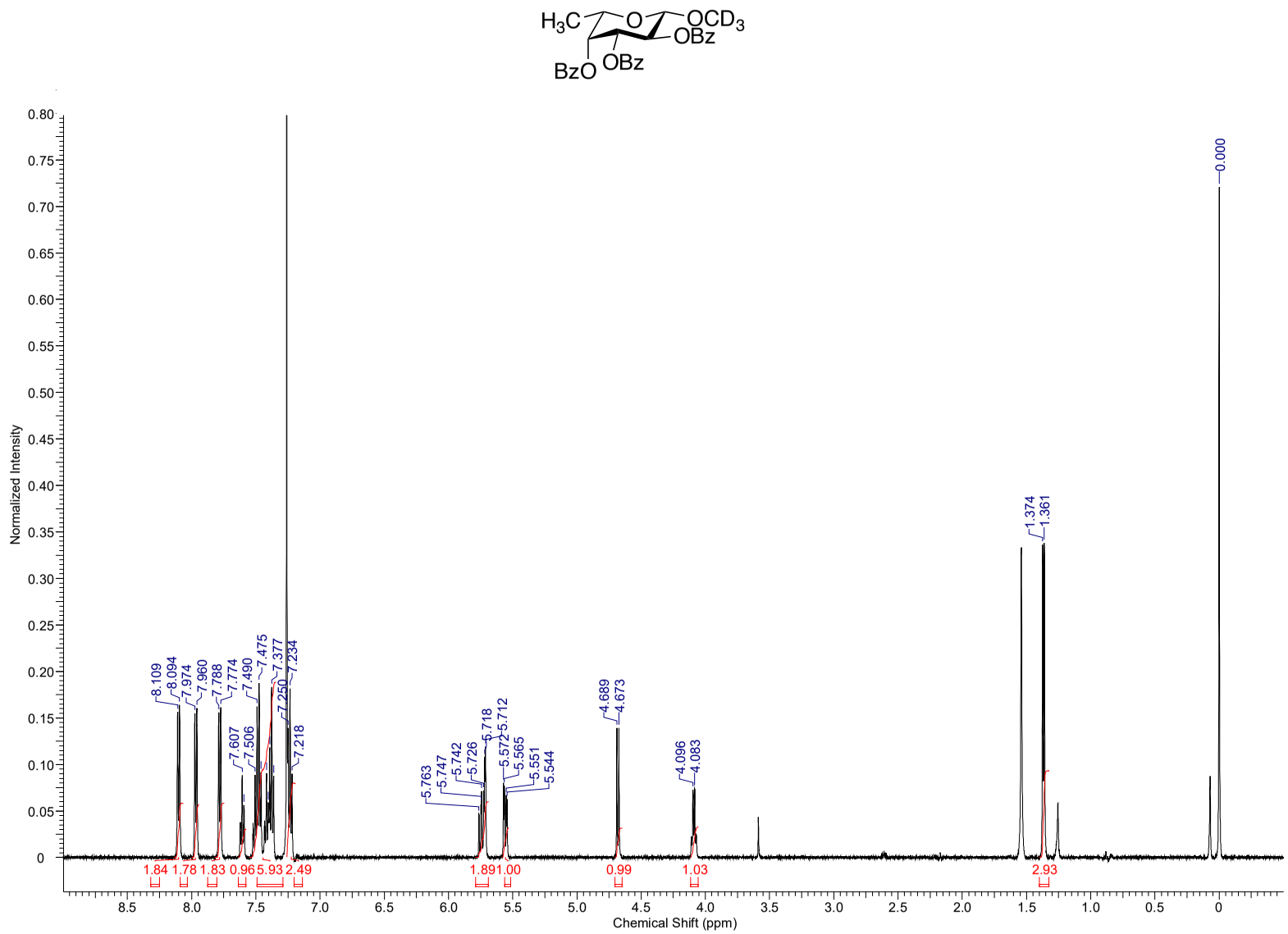

AcO
OAc
AcO
O
AcO
OCD3
Normalized Intensity
Chemical Shift (ppm)
5.35
5.33
5.33
5.28
5.24
5.24
5.35
4.72
4.31
4.30
4.28
4.27
4.14
4.14
4.12
3.99
3.98
4.11
3.97
3.97
2.16
2.11
2.04
1.99
0.00
1.04 0.98 1.02
0.93
1.09 1.16 1.04
3.06 3.07 3.32 3.04

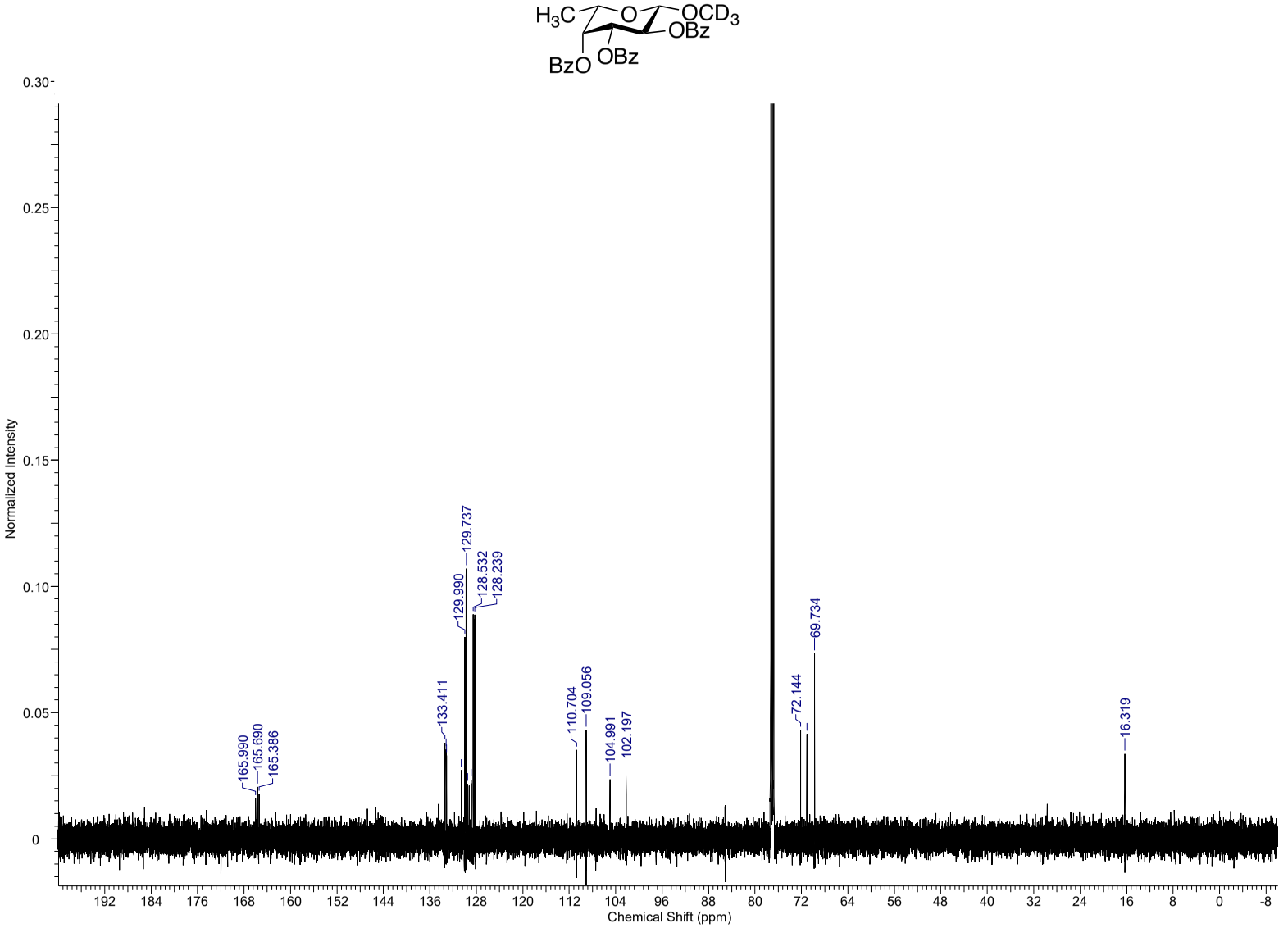

HO
OH
O
HO
HO
OCD3
CD3-α-D-Man
Normalized Intensity
Chemical Shift (ppm)
4.75
4.74
4.74
3.91
3.91
3.90
3.90
3.88
3.86
3.86
3.75
3.74
3.72
3.71
3.63
3.61
3.60
3.59
3.58
0.92
1.00
1.10
2.10
2.02

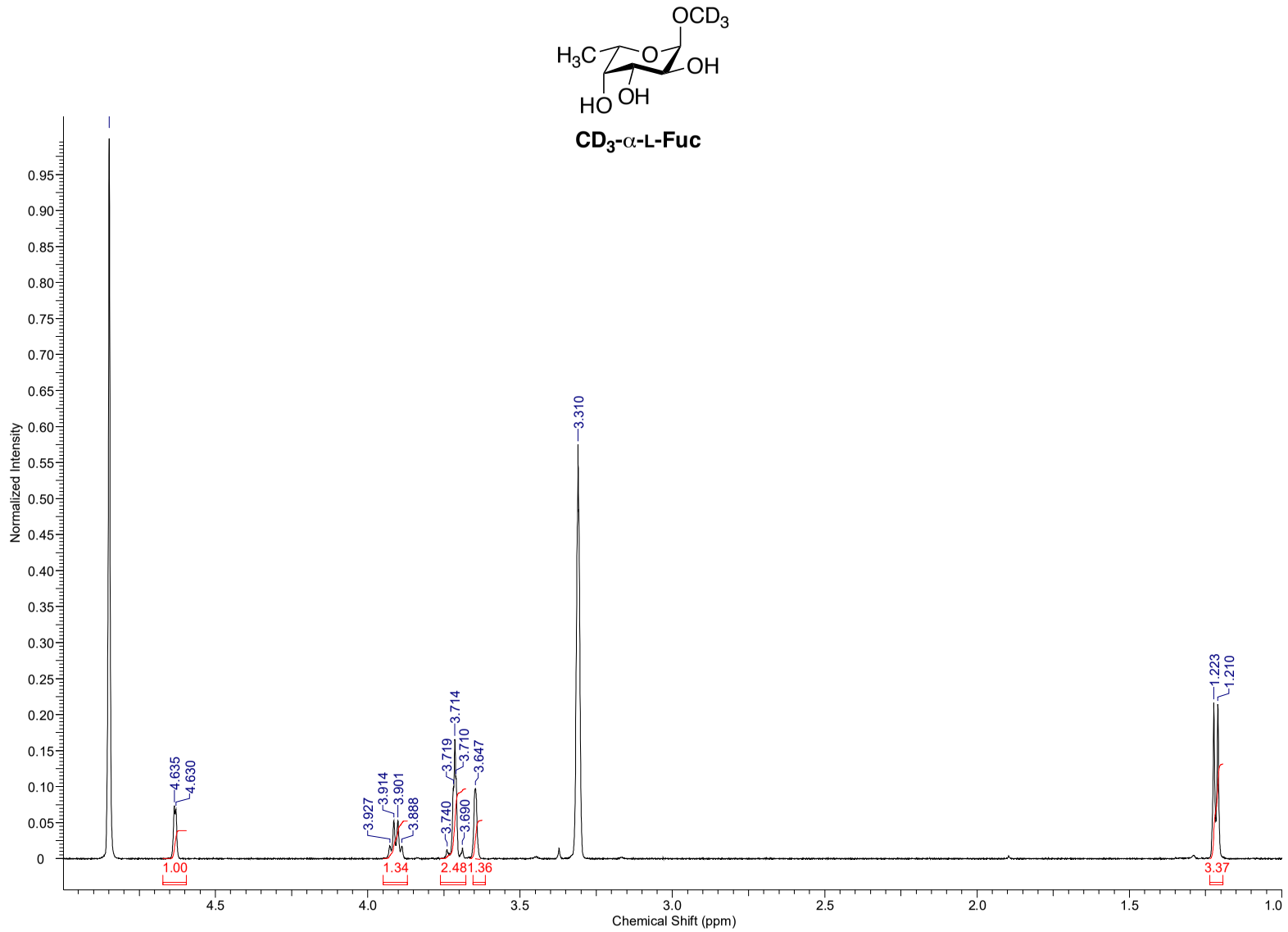

Ph
O
OBn
O
O
BnO
OCD3
Normalized Intensity
Chemical Shift (ppm)
7.28
7.51
7.50
7.51
7.46
7.38
7.36
7.25
5.63
4.98
4.95
4.86
4.69
4.67
4.59
4.57
4.37
4.32
4.21
4.19
3.96
3.94
3.92
3.60
3.59
3.58
3.57
3.35
3.34
3.33
3.32
3.31
0.00
3.74
10.72
0.99
1.00
1.01
1.00
1.00
0.99
1.00
1.00
2.00
1.00
1.00

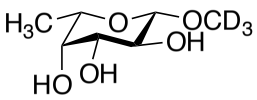

HO
OH
HO
O
HO
OCD3
CD3-β-D-Man
Normalized Intensity
0.030
0.025
0.020
0.015
0.010
0.005
0
4.75
4.55
4.55
3.96
3.96
3.96
3.95
3.92
3.90
3.89
3.73
3.71
3.70
3.69
3.60
3.62
3.60
3.55
3.54
3.52
3.37
3.36
3.35
3.35
3.34
3.33
3.33
0.39
0.41
0.40
0.36
0.42
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
3.0
Chemical Shift (ppm)


OCD3
H3C
O
OBz
BzO
OBz
Normalized Intensity
8.117
8.103
7.989
7.975
7.783
7.628
7.613
7.506
7.490
7.370
7.260
7.235
7.219
5.972
5.965
5.951
5.944
5.761
5.757
5.658
5.651
5.637
5.630
5.242
5.235
4.403
4.390
1.297
1.284
0.000
2.00 1.79 1.80 1.00 6.06 2.46
1.00 1.01 0.98
0.96
1.02
3.45
Chemical Shift (ppm)

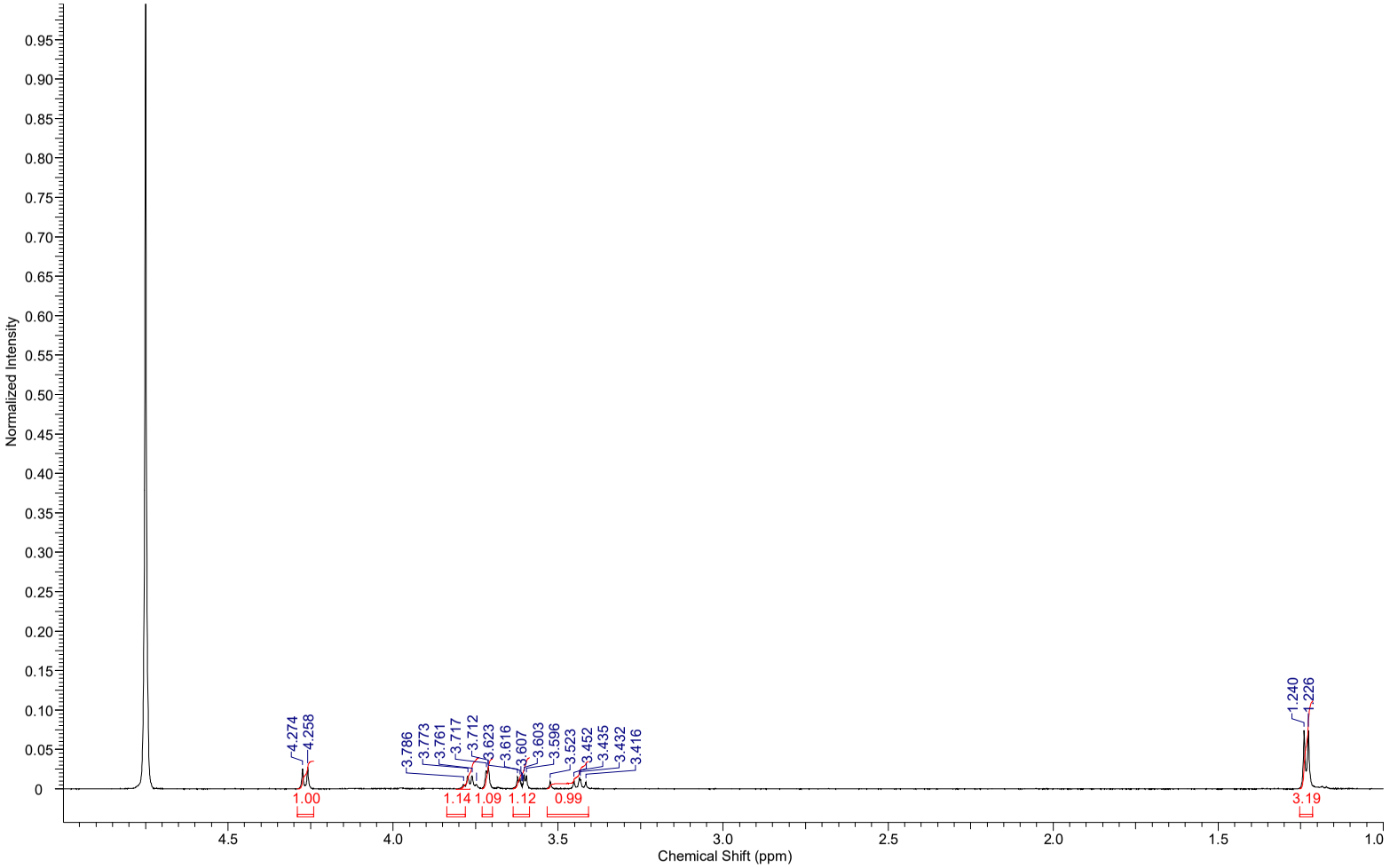

H3C
O
OCD3
OBz
BzO
OBz
Normalized Intensity
Chemical Shift (ppm)
8.109
8.094
7.974
7.960
7.788
7.774
7.490
7.475
7.377
7.250
7.234
7.218
7.607
7.506
5.763
5.747
5.742
5.726
5.718
5.712
5.572
5.565
5.551
5.544
4.689
4.673
4.096
4.083
1.374
1.361
0.000
1.84
1.78
1.83
0.96
5.93
2.49
1.89
1.00
0.99
1.03
2.93

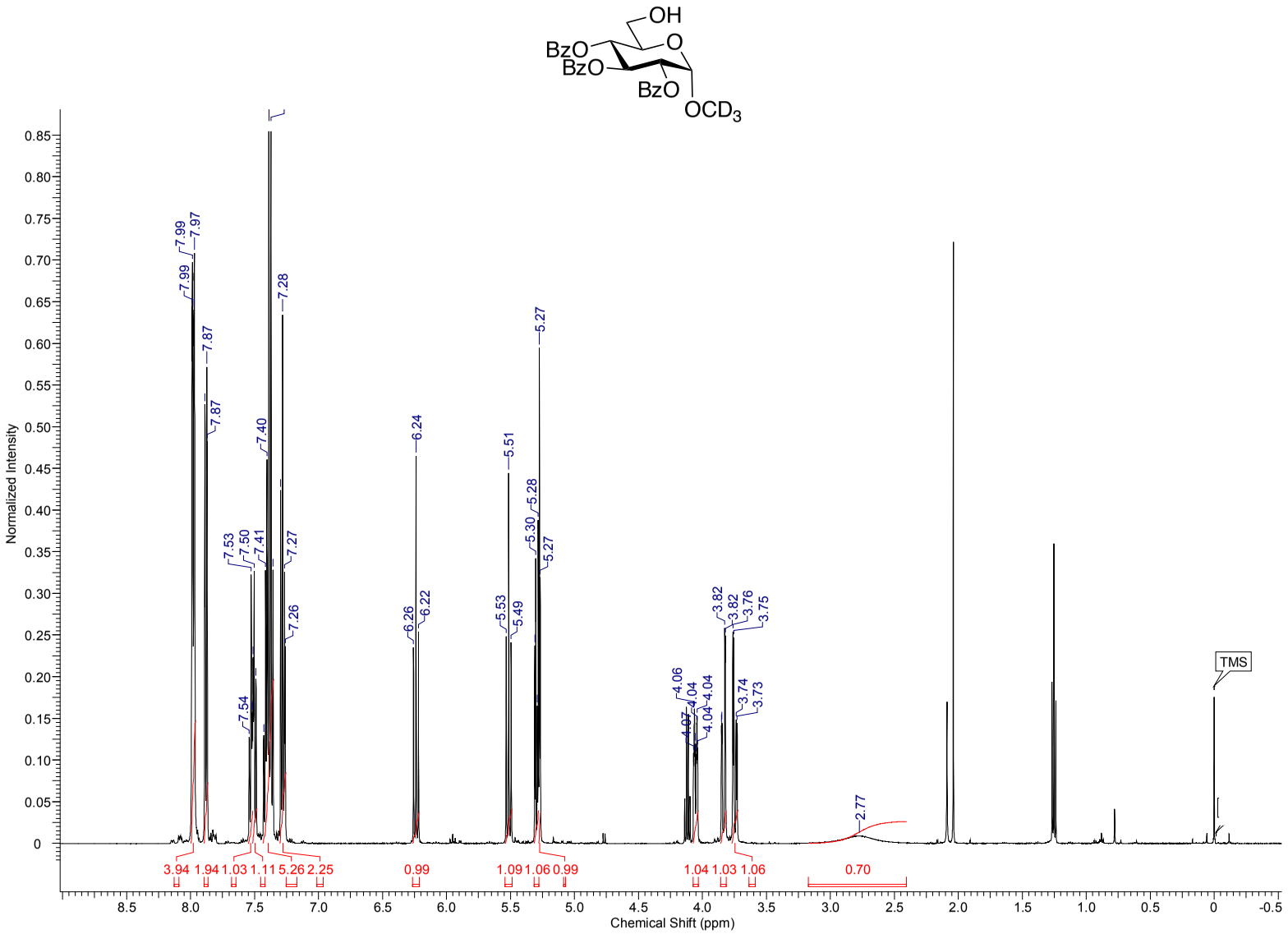

H3C
O
OCD3
OBz
BzO
OBz
Normalized Intensity
0.30
0.25
0.20
0.15
0.10
0.05
0
165.990
165.690
165.386
133.411
129.990
129.737
128.532
128.239
110.704
109.056
104.991
102.197
72.144
69.734
16.319
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
-8
Chemical Shift (ppm)

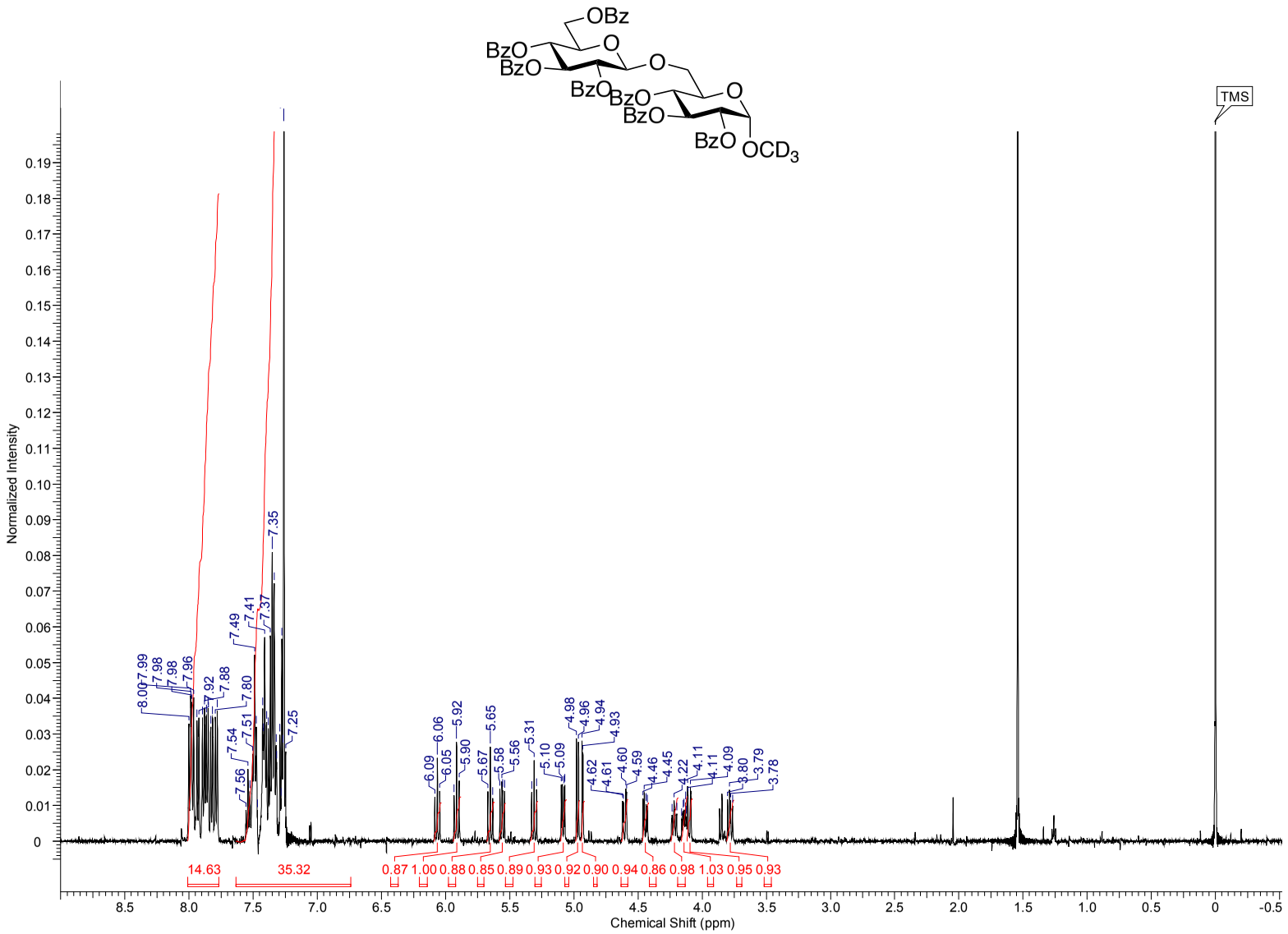

OCD3
H3C
O
OH
HO
OH
CD3-α-L-Fuc
Normalized Intensity
Chemical Shift (ppm)
4.635
4.630
3.927
3.914
3.901
3.888
3.740
3.719
3.714
3.710
3.690
3.647
3.310
1.223
1.210
1.00
1.34
2.48
1.36
3.37

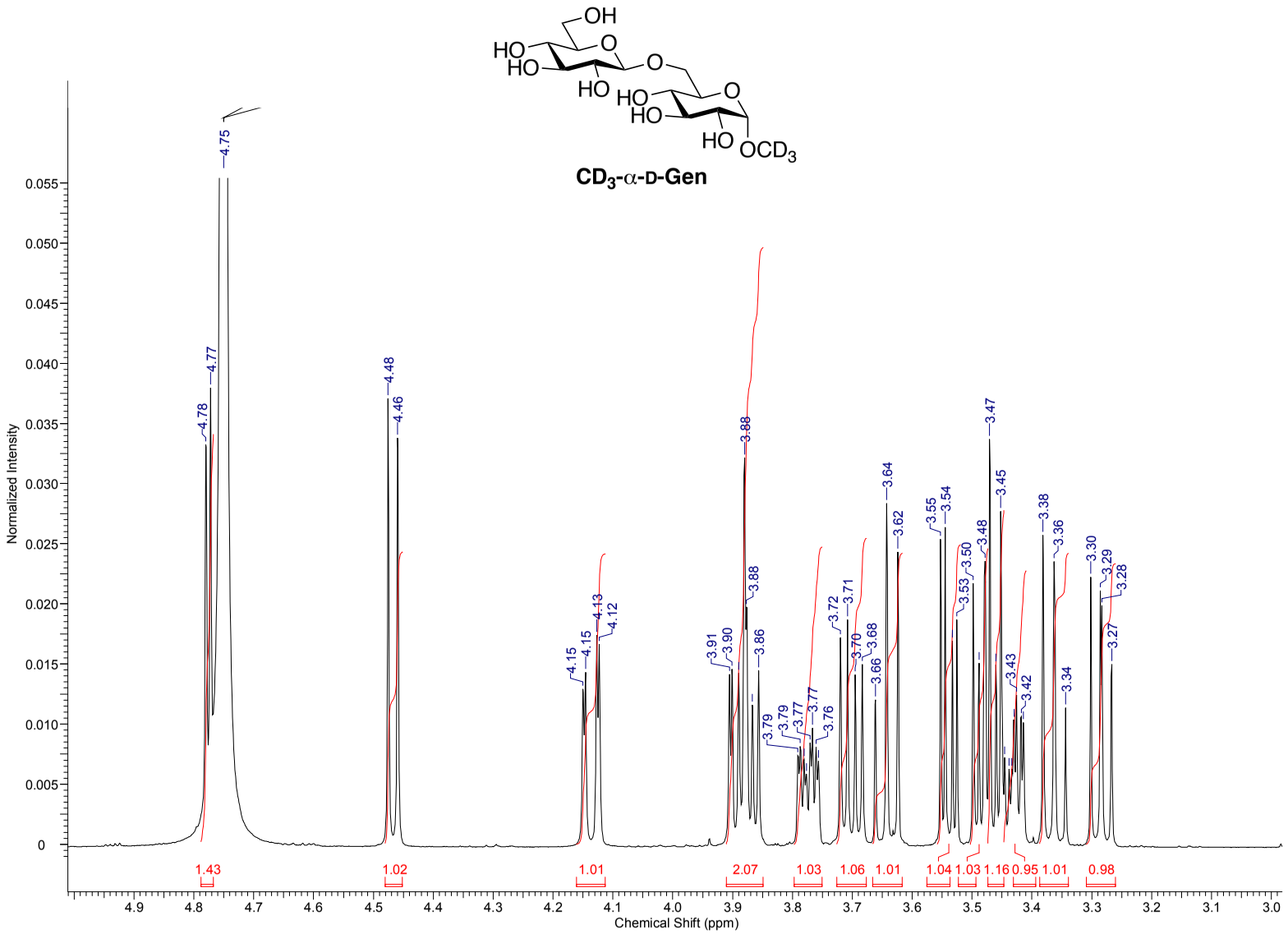

H3C
O
OCD3
OH
HO
OH

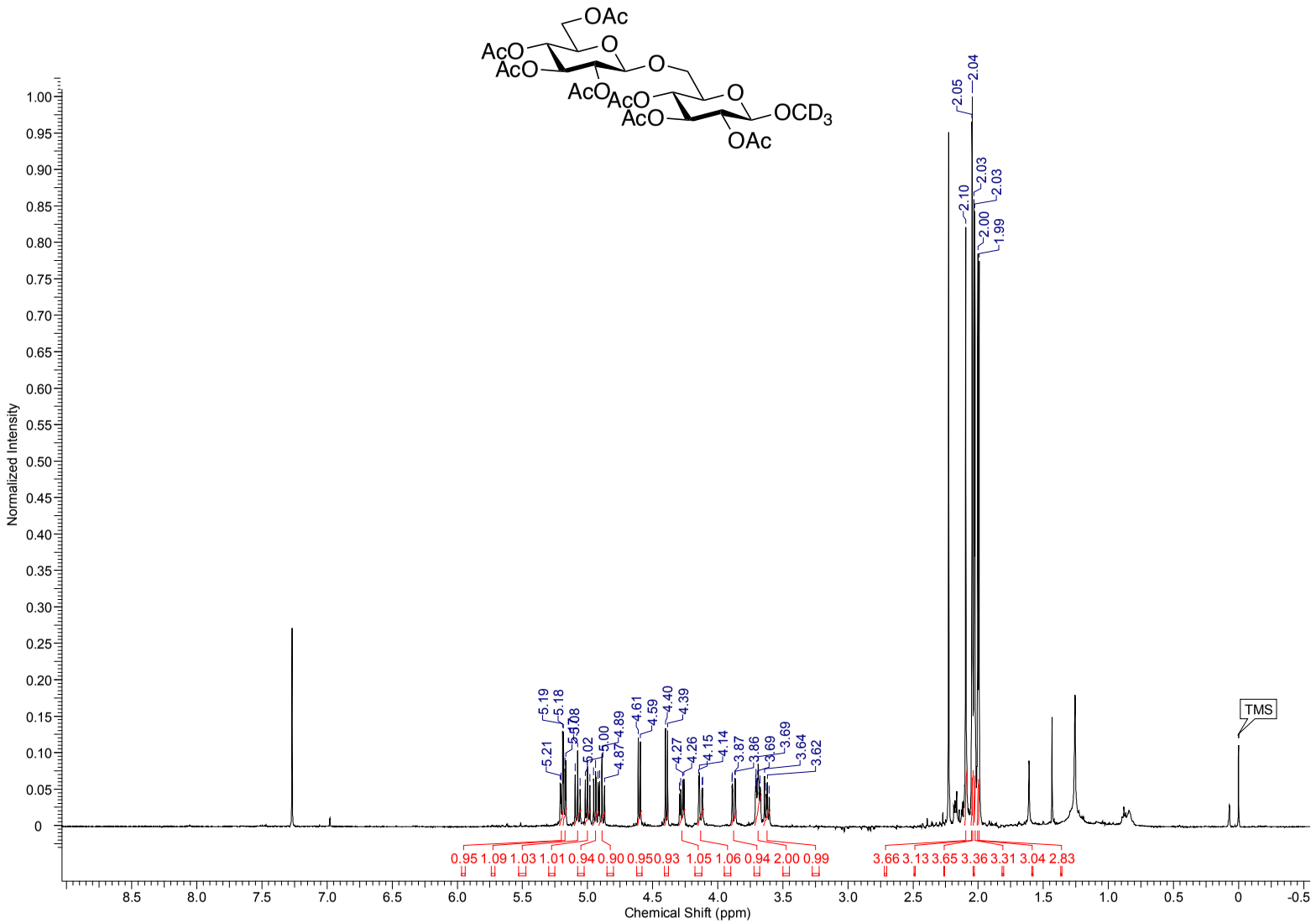
CD_3-β-L-Fuc

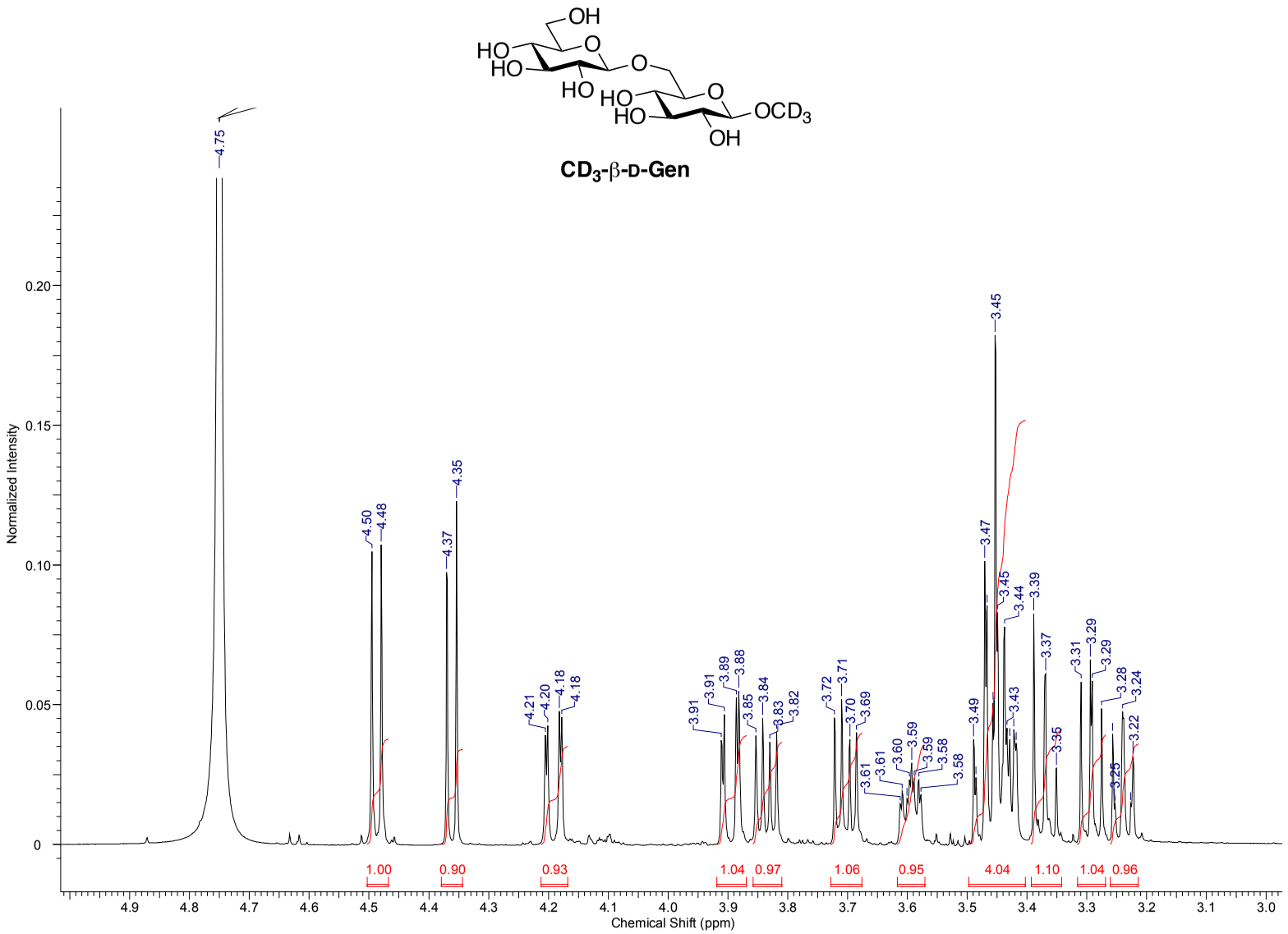

Normalized Intensity
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
4.274
4.258
3.786
3.773
3.761
3.717
3.712
3.623
3.616
3.607
3.603
3.596
3.523
3.452
3.435
3.432
3.416
1.240
1.226
1.00
1.14
1.09
1.12
0.99
3.19
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)

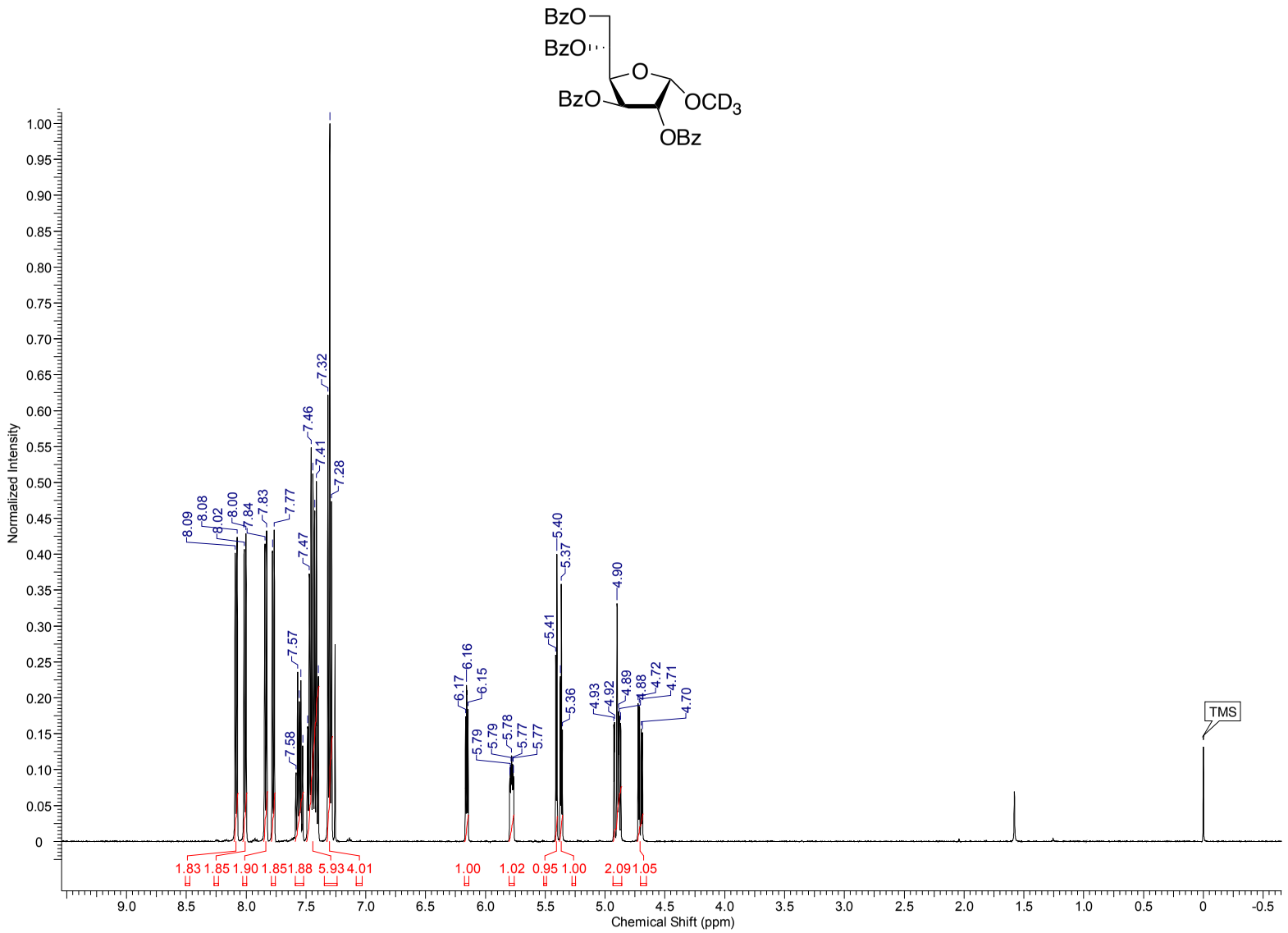

OH
BzO
O
BzO
BzO
OCD3
Normalized Intensity
Chemical Shift (ppm)
TMS
7.99
7.97
7.99
7.87
7.87
7.40
7.28
7.53
7.50
7.41
7.27
7.26
7.54
6.24
6.26
6.22
5.51
5.53
5.49
5.28
5.30
5.27
5.27
4.06
4.04
4.04
4.04
4.07
3.82
3.82
3.76
3.75
3.74
3.73
2.77
3.94 1.94 1.03 1.11 5.26 2.25
0.99
1.09 1.06 0.99
1.04 1.03 1.06
0.70

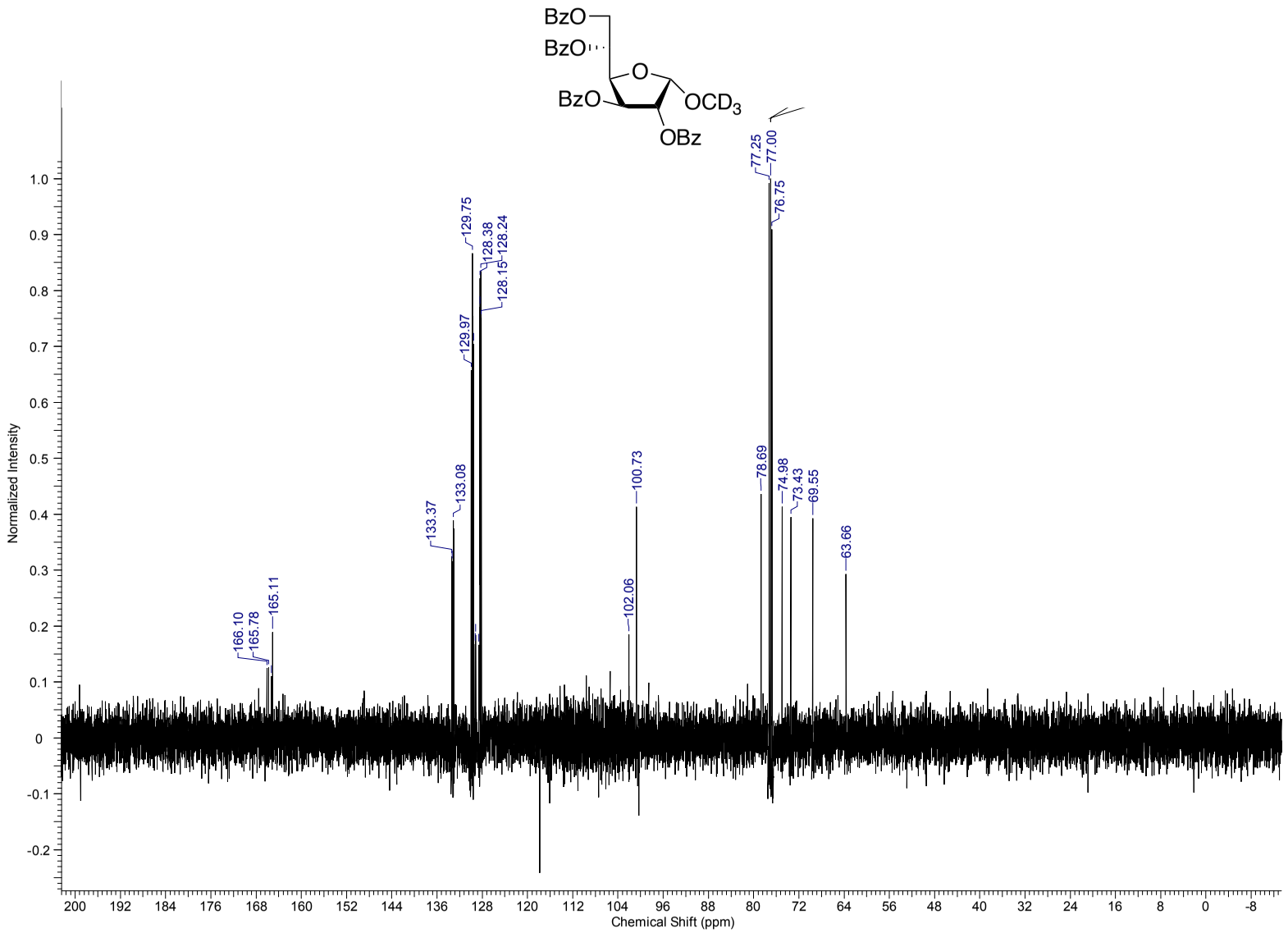

OBz
BzO
BzO
BzO
BzO
BzO
BzO
OCD3
TMS
Normalized Intensity
Chemical Shift (ppm)
8.00 7.99 7.98 7.98 7.96 7.92 7.88 7.80 7.56 7.54 7.51 7.49 7.41 7.37 7.35 7.25
6.09 6.06 6.05 5.92 5.90 5.67 5.65 5.58 5.56 5.31 5.10 5.09 4.98 4.96 4.94 4.93 4.62 4.61 4.60 4.59 4.46 4.45 4.22 4.11 4.11 4.09 3.80 3.79 3.78
14.63 35.32 0.87 1.00 0.88 0.85 0.89 0.93 0.92 0.90 0.94 0.86 0.98 1.03 0.95 0.93

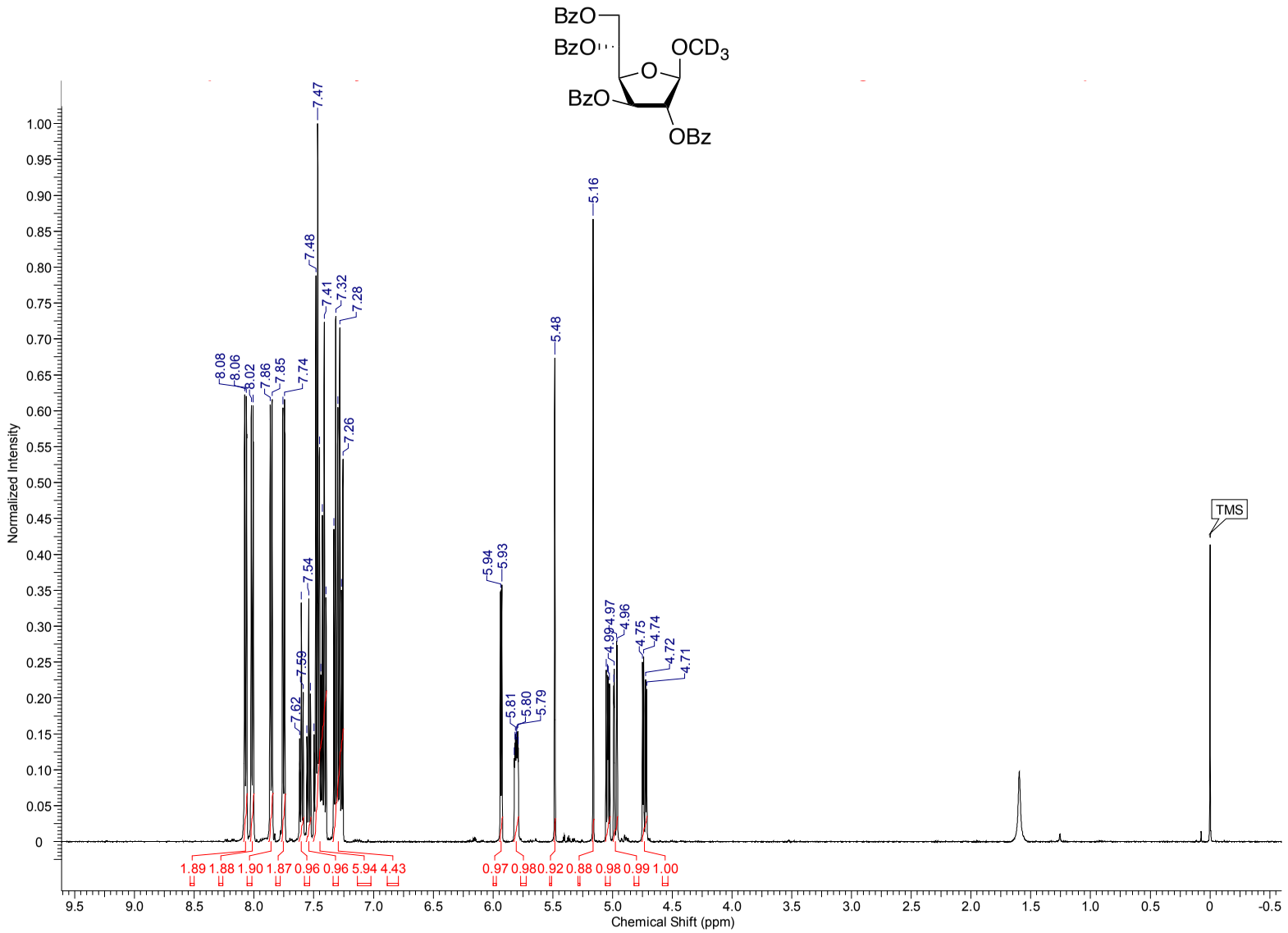

OH
HO
O
HO
O
HO
HO
HO
HO
O
HO
OCD3
CD3-α-D-Gen
Normalized Intensity
Chemical Shift (ppm)
4.75
4.78
4.77
4.48
4.46
4.15
4.13
4.12
3.91
3.90
3.88
3.86
3.79
3.77
3.76
3.72
3.71
3.70
3.68
3.66
3.64
3.62
3.55
3.54
3.53
3.50
3.48
3.47
3.45
3.43
3.42
3.38
3.36
3.34
3.30
3.29
3.28
3.27
1.43
1.02
1.01
2.07
1.03
1.06
1.01
1.04
1.03
1.16
0.95
1.01
0.98

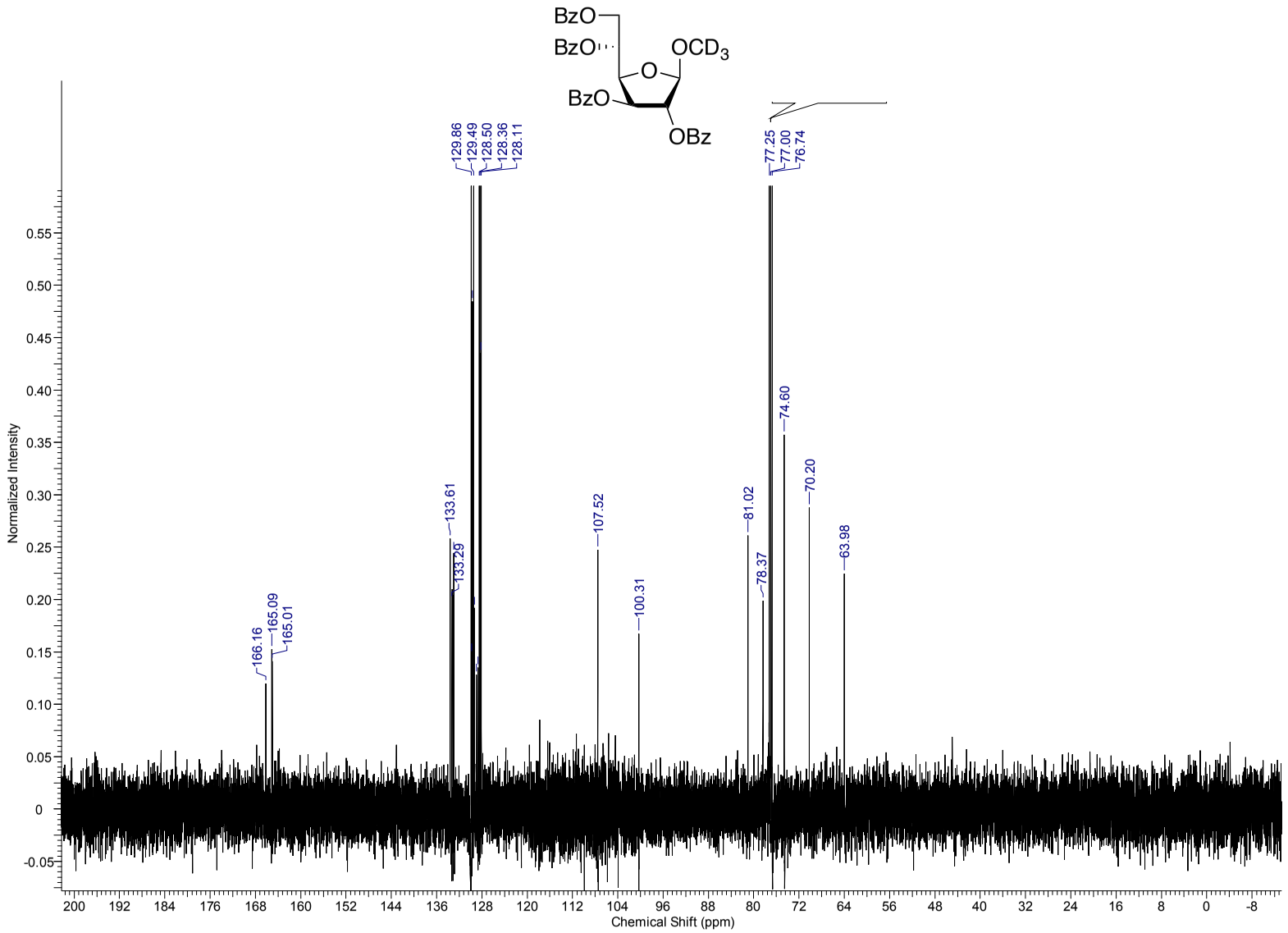

OAc
AcO
AcO
O
O
AcO
AcO
O
AcO
OCD3
OAc
Normalized Intensity
Chemical Shift (ppm)
TMS
2.05
2.04
2.10
2.03
2.03
2.00
1.99
5.19
5.18
5.21
5.08
5.02
5.00
4.89
4.87
4.61
4.59
4.40
4.39
4.27
4.26
4.15
4.14
3.87
3.86
3.69
3.69
3.64
3.62
0.95 1.09 1.03 1.01 0.94 0.90 0.95 0.93 1.05 1.06 0.94 2.00 0.99
3.66 3.13 3.65 3.36 3.31 3.04 2.83

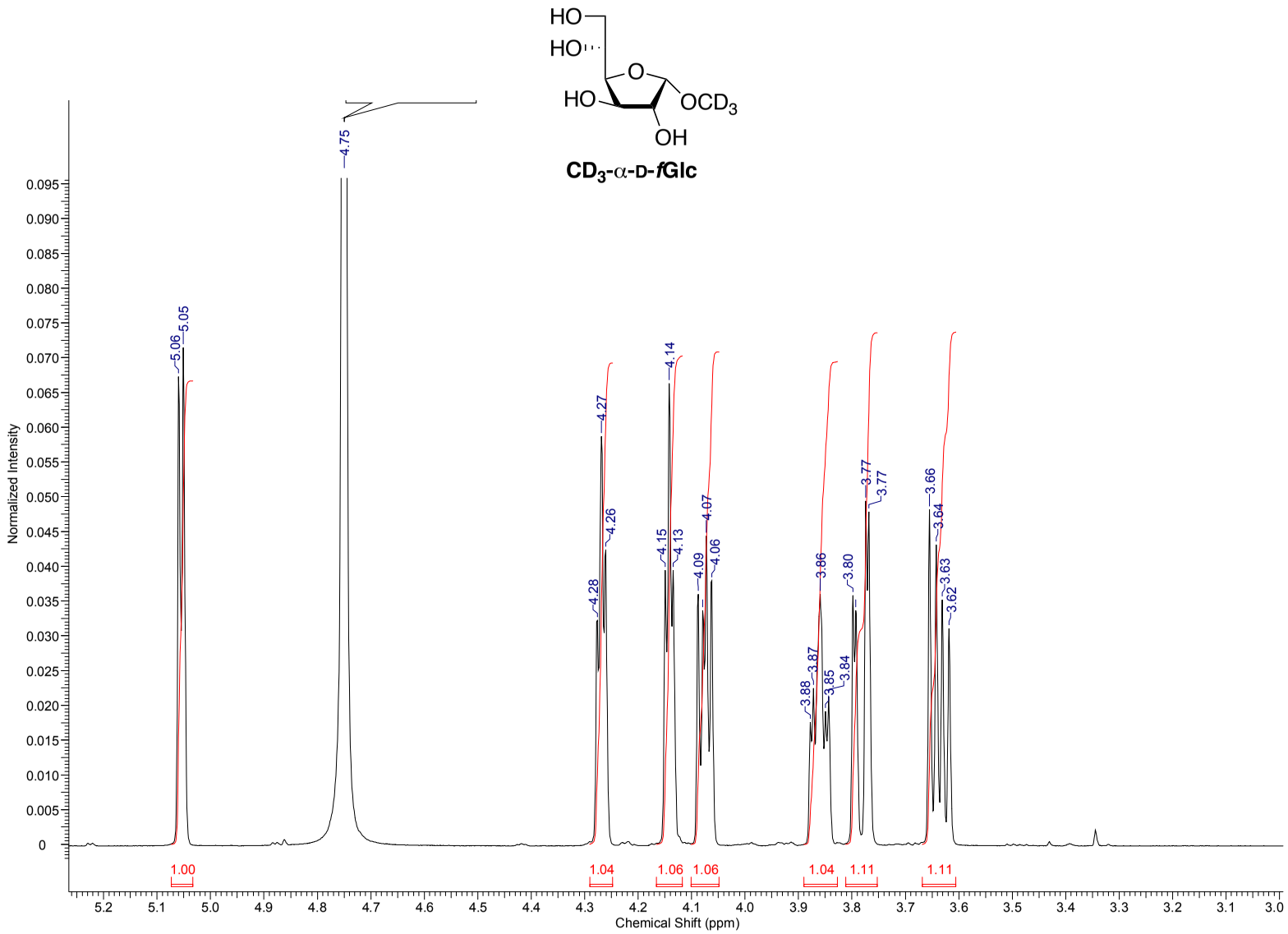

OH
HO
O
HO
HO
O
HO
HO
O
OCD3
OH
CD3-β-D-Gen
Normalized Intensity
0.20
0.15
0.10
0.05
0
4.75
4.50
4.48
4.37
4.35
4.21
4.20
4.18
4.18
3.91
3.91
3.89
3.88
3.85
3.84
3.83
3.82
3.72
3.71
3.70
3.69
3.61
3.61
3.60
3.59
3.59
3.58
3.58
3.49
3.47
3.45
3.45
3.44
3.43
3.39
3.37
3.35
3.31
3.29
3.29
3.28
3.25
3.24
3.22
1.00
0.90
0.93
1.04
0.97
1.06
0.95
4.04
1.10
1.04
0.96
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
3.0
Chemical Shift (ppm)

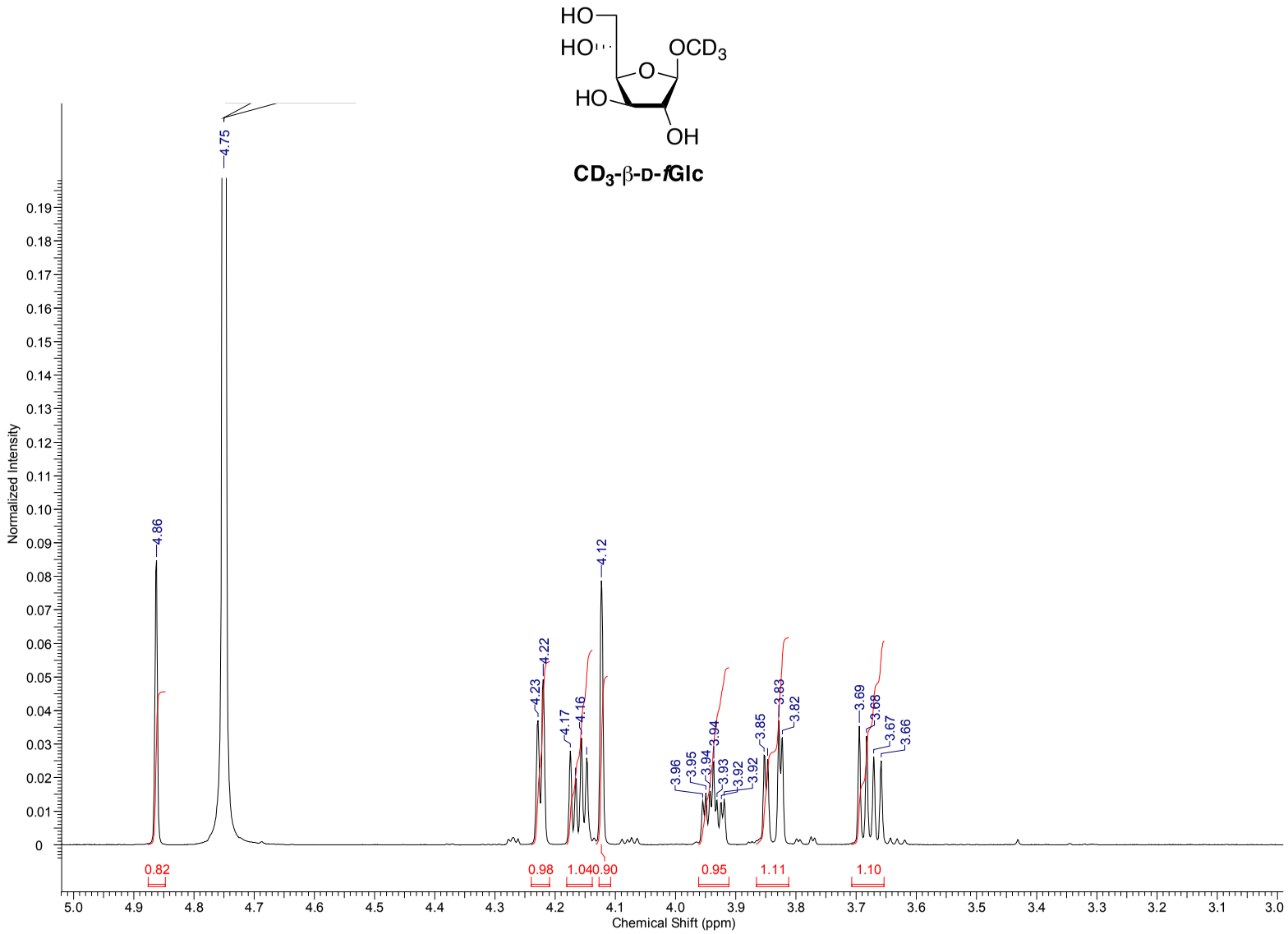

BzO
BzO
O
BzO
OCD3
OBz
Normalized Intensity
Chemical Shift (ppm)
TMS
8.09
8.08
8.02
8.00
7.84
7.83
7.77
7.58
7.57
7.47
7.46
7.41
7.32
7.28
6.17
6.16
6.15
5.79
5.79
5.78
5.77
5.77
5.41
5.40
5.37
5.36
4.93
4.92
4.90
4.89
4.88
4.72
4.71
4.70
1.83 1.85 1.90 1.85 1.88 5.93 4.01
1.00 1.02 0.95 1.00 2.09 1.05

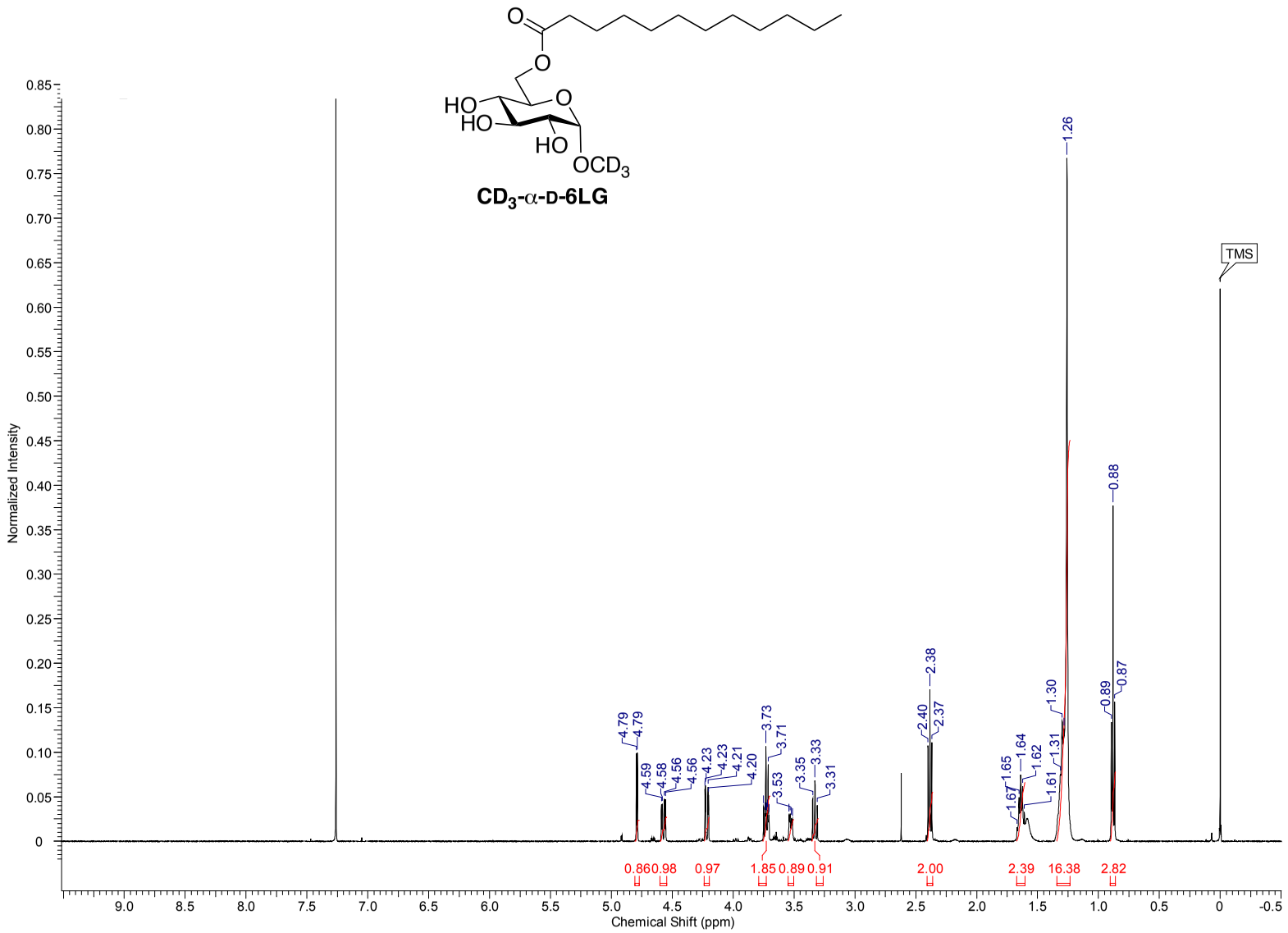

BzO
BzO
O
BzO
OCD3
OBz
Normalized Intensity
Chemical Shift (ppm)
166.10
165.78
165.11
133.37
133.08
129.97
129.75
128.38
128.24
128.15
102.06
100.73
78.69
77.25
77.00
76.75
74.98
73.43
69.55
63.66

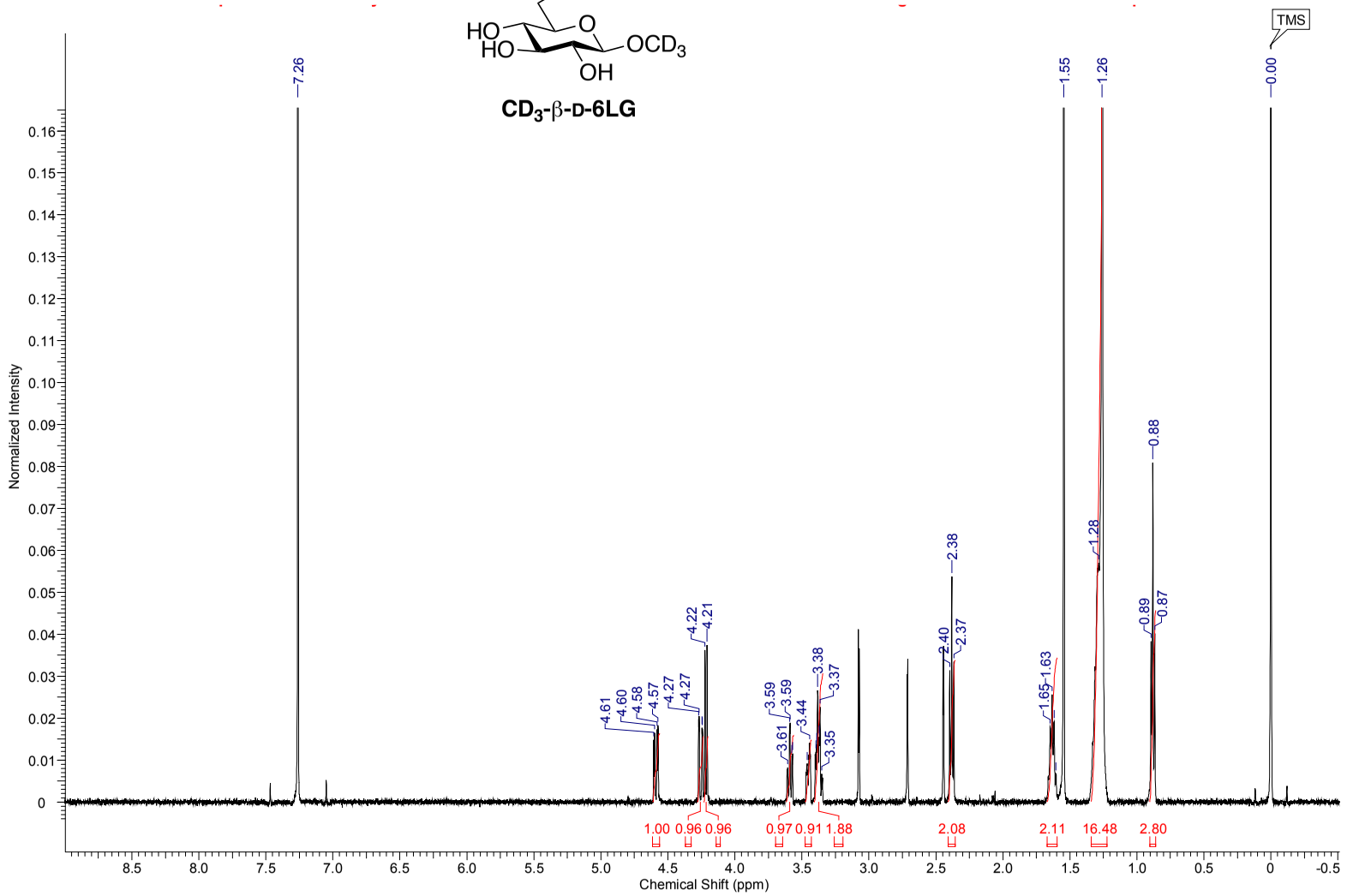

BzO
BzO
OCD3
O
BzO
OBz
Normalized Intensity
Chemical Shift (ppm)
TMS
8.08
8.06
8.02
7.86
7.85
7.74
7.62
7.59
7.54
7.48
7.47
7.41
7.32
7.28
7.26
5.94
5.93
5.81
5.80
5.79
5.48
5.16
4.99
4.97
4.96
4.75
4.74
4.72
4.71
1.89 1.88 1.90 1.87 0.96 0.96 5.94 4.43
0.97 0.98 0.92 0.88 0.98 0.99 1.00


BzO
BzO
OCD3
O
BzO
OBz
129.86
129.49
128.50
128.36
128.11
77.25
77.00
76.74
133.61
133.29
107.52
81.02
74.60
70.20
63.98
78.37
100.31
166.16
165.09
165.01
Normalized Intensity
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
-0.05
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
-8
Chemical Shift (ppm)


HO
HO
O
HO
OCD3
OH
CD3-α-D-fGlc
Normalized Intensity
Chemical Shift (ppm)
4.75
5.06
5.05
4.27
4.26
4.28
4.14
4.15
4.13
4.09
4.07
4.06
3.86
3.80
3.77
3.77
3.66
3.64
3.63
3.62
3.88
3.87
3.85
3.84
1.00
1.04
1.06
1.06
1.04
1.11
1.11


HO
HO
OCD3
O
HO
OH
CD3-β-D-fGlc
Normalized Intensity
Chemical Shift (ppm)
4.86
4.75
4.23
4.22
4.17
4.16
4.12
3.96
3.95
3.94
3.94
3.93
3.92
3.92
3.85
3.83
3.82
3.69
3.68
3.67
3.66
0.82
0.98
1.04
0.90
0.95
1.11
1.10


O
O
HO
HO
O
HO
OCD3
CD3-α-D-6LG
Normalized Intensity
Chemical Shift (ppm)
TMS
1.26
0.88
0.87
0.89
1.30
1.31
1.61
1.62
1.64
1.65
1.67
2.38
2.37
2.40
3.73
3.71
3.53
3.35
3.33
3.31
4.79
4.79
4.59
4.58
4.56
4.56
4.23
4.23
4.21
4.20
0.86 0.98 0.97 1.85 0.89 0.91 2.00 2.39 16.38 2.82


HO
HO
O
O
OCD3
OH
CD3-β-D-6LG
TMS
7.26
1.55
1.26
0.00
0.88
2.38
1.28
0.89
0.87
2.40
2.37
4.22
4.21
3.38
3.37
4.61
4.60
4.58
4.57
4.27
4.27
3.59
3.59
3.44
3.61
3.35
1.65
1.63
1.00
0.96
0.96
0.97
0.91
1.88
2.08
2.11
16.48
2.80
Normalized Intensity
Chemical Shift (ppm)