

Electronic Supplementary Information

Stereoselective Synthesis of (+)-5-Thiosucrose and (+)-5-Thioisosucrose

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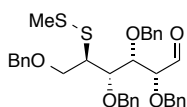
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1. General procedures and methods

^1H NMR chemical shifts (δ) are reported in parts per million (ppm) relative to the resonance of the solvent or to tetramethylsilane (0.00 ppm). $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shifts are reported in ppm relative to the resonance of the solvent or to acetonitrile (1.47 ppm) when D_2O was used. For the assignment of protons in ^1H NMR spectra, protons of pyranoside ring are numbered as 1', 2', etc. ^1H -NMR signal assignments were done using gCOSY analysis. Low- and high-resolution mass spectra (LRMS and HRMS) were measured using fast atom bombardment (FAB) ionization with double-focusing high-resolution magnetic sector or using electrospray ionization (ESI) in TOF mode. Silica gel (230–400 mesh) was used for flash column chromatography. Analytical thin-layer chromatography (TLC) was performed on glass pre-coated with silica gel (0.25 mm thickness). Compounds were observed in UV-light at 254 nm and then visualized with *p*-anisaldehyde/sulfuric acid in EtOH stain or molybdatephosphoric acid in EtOH stain. All moisture-sensitive reactions were carried out under an argon atmosphere. THF was dried over sodium/benzophenone ketyl, and CH_2Cl_2 was dried over P_2O_5 , and they were distilled prior to use.

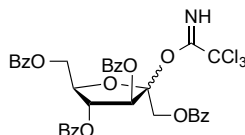
2. Synthesis outlined in Scheme 1



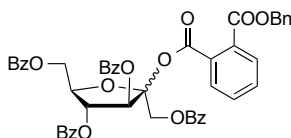
Glycosylation of 6 with 3. A mixture of acceptor **6** (35.0 mg, 63.0 μmol), donor **3** (100 mg, 126 μmol), and 2,6-di-*tert*-butyl-4-methylpyridine (12.9 mg, 63.0 μmol) in CH_2Cl_2 (6 mL) was stirred for 15 min at room temperature in presence of activated powdered molecular sieves 4 Å (0.3 g). To the mixture was dropped a solution of dimethyl(methylthio)sulfonium trifluoromethanesulfonate (0.5 M in CH_2Cl_2 , 0.504 mL, 252 μmol) at room temperature and the mixture was stirred for 2 h at room temperature. The reaction was quenched with triethylamine (0.3 mL), diluted with CH_2Cl_2 , filtered through a Celite pad, and evaporated. The residue was purified by flash column chromatography on silica gel eluted with 10% EtOAc in *n*-hexane to afford 2,3,4,6-tetra-*O*-benzyl-5-deoxy-5-methyldisulphenyl-D-glucose **7** (33.4 mg) in 88% yield. Colorless oil. $R_f = 0.67$ (30% EtOAc in *n*-hexane). $[\alpha]_{\text{D}}^{20} +7.3$ (c 0.47, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ : 9.68 (1H, s, H-1), 7.38–7.21 (20H, m), 4.82 (1H, d, $J = 12.1$ Hz, *CHHP*h), 4.68 (1H, d, $J = 11.4$ Hz, *CHHP*h), 4.59 (1H, d, $J = 11.0$ Hz, *CHHP*h), 4.55 (1H, d, $J = 11.4$ Hz, *CHHP*h), 4.52 (1H, d, $J = 12.0$ Hz, *CHHP*h), 4.50 (1H, d, $J = 12.1$ Hz, *CHHP*h), 4.48 (1H, d, $J = 11.0$ Hz, *CHHP*h), 4.47 (1H, d, $J = 12.0$ Hz, *CHHP*h), 4.28 (1H, dd, $J_{2,3} = 5.2$, $J_{3,4} = 3.8$ Hz, H-3), 4.10 (1H, dd, $J_{4,5} = 7.1$, $J_{3,4} = 3.8$ Hz, H-4), 3.89 (1H, d, $J_{2,3} = 5.2$ Hz, H-2), 3.87 (1H, dd, $J_{6a,6b} = 9.9$, $J_{5,6a} = 5.7$ Hz, H-6a), 3.77 (1H, dd, $J_{6a,6b} = 9.9$, $J_{5,6b} = 5.7$ Hz, H-6b), 3.29 (1H, ddd, $J_{4,5} = 7.1$, $J_{5,6a} = J_{5,6b} = 5.7$ Hz, H-5), 2.32 (3H, s, SCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ : 200.3, 137.8, 137.7, 137.4, 137.3, 128.5,

128.5, 128.5, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 127.6, 80.5, 80.1, 78.2, 74.2, 74.0, 73.2, 73.1, 68.8, 52.6, 23.8. IR (film): 2859, 1728, 1496, 1454 cm^{-1} . MS (FAB) m/z : 625 $[\text{M}+\text{Na}]^+$. HRMS (FAB) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{35}\text{H}_{38}\text{O}_5\text{S}_2\text{Na}$, 625.2058; found, 625.2052.

3. Synthesis outlined in Scheme 2

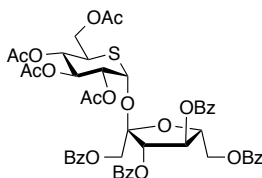


1,3,4,6-Tetra-*O*-benzoyl-D-fructofuranosyl trichloroacetimidate (8b). To a solution of fructose **8a** (1.80 g, 3.02 mmol) and trichloroacetonitrile (2.9 mL, 29 mmol) in 15 mL of CH_2Cl_2 was added cesium carbonate (1.00 g, 3.07 mmol) and the reaction mixture was stirred overnight at room temperature. After which the reaction mixture was filtered through a Celite pad, and the filtrate was concentrated. The residue was purified on basic aluminium oxide column (20% EtOAc in *n*-hexane) to give imidate **8b** (1.50 g) in 66% yield with 2:1 α/β anomeric ratio. Colorless oil. $R_f = 0.32$ (20% EtOAc in *n*-hexane). ^1H NMR (300 MHz, C_6D_6) δ (α -anomer): 8.62 (1H, s, NH), 8.18–7.92 (8H, m), 7.11–6.82 (13H, m, ArH, H-3), 5.87 (1H, dd, $J_{4,5} = 5.1$, $J_{3,4} = 2.2$ Hz, H-4), 5.67 (1H, d, $J_{1a,1b} = 12.1$ Hz, H-1a), 5.27 (1H, d, $J_{1a,1b} = 12.1$ Hz, H-1b), 5.00–4.63 (3H, m, H-5, 6a, 6b); δ (β -anomer): 8.51 (1H, s, NH), 8.18–7.92 (8H, m), 7.11–6.82 (12H, m), 6.49 (1H, d, $J_{3,4} = 6.2$ Hz, H-3), 6.37 (1H, t, $J_{3,4} = 6.2$, $J_{4,5} = 6.2$ Hz, H-4), 5.48 (1H, d, $J_{1a,1b} = 11.7$ Hz, H-1a), 5.17 (1H, d, $J_{1a,1b} = 11.7$ Hz, H-1b), 5.00–4.63 (3H, m, H-5, 6a, 6b). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6) δ (α - and β -anomer): 166.0 (β), 165.9 (α), 165.7 (α), 165.7 (β), 165.5 (α), 165.4 (β), 165.2 (β), 164.8 (α), 159.1 (α), 158.4 (β), 133.5, 133.3, 133.1, 133.0, 132.8, 130.4, 130.3, 130.3, 130.2, 130.1, 130.0, 129.5, 129.4, 129.3, 129.2, 128.7, 128.6, 128.5, 128.5, 128.4, 128.3, 128.0, 127.7, 112.2 (α), 107.9 (β), 92.3 (β), 91.8 (α), 83.7 (α), 80.7 (β), 80.4 (α), 78.5 (2C, α and β), 77.7 (β), 65.0 (β), 64.6 (β), 63.6 (α), 61.6 (α). IR (film): 3460, 1720, 1451 cm^{-1} . MS (FAB) m/z : 762 $[\text{M}+\text{Na}]^+$. HRMS (FAB) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{36}\text{H}_{28}\text{Cl}_3\text{NO}_{10}\text{Na}$, 762.0676; found, 762.0673.



Benzyl (1,3,4,6-tetra-*O*-benzoyl-D-fructofuranosyl) phthalate (8d). To a mixture of fructose **8a** (1.00 g, 1.68 mmol) and benzyl hydrogen phthalate (1.29 g, 5.04 mmol) in CH_2Cl_2 (10 mL) at 0 $^\circ\text{C}$ were added *N,N'*-dicyclohexylcarbodiimide (1.04 g, 5.04 mmol) and 4-(dimethylamino)pyridine (DMAP, 205 mg, 1.68 mmol), and the reaction mixture was stirred for 1 h at room temperature. The reaction mixture was filtered through a Celite pad, which was washed with CH_2Cl_2 (100 mL). The

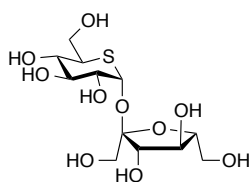
organic filtrate was washed with 5% aqueous Na₂CO₃ solution (20 mL × 2) followed by water (20 mL), dried over Na₂SO₄, and concentrated under vacuum. The residue was purified by silica gel flash column chromatography eluted with 20% EtOAc in *n*-hexane to give phthalate **8d** (1.08 g) in 77% yield as an anomeric mixture (α : β = 1:1.2). Colorless syrup. R_f = 0.21 (20% EtOAc in *n*-hexane). ¹H NMR (400 MHz, CDCl₃) δ (α -anomer): 8.05–7.90 (8H, m), 7.79–7.76 (2H, m), 7.59–7.17 (19H, m), 6.40 (1H, d, $J_{3,4}$ = 2.4 Hz, H-3), 5.73 (1H, dd, $J_{4,5}$ = 4.8, $J_{3,4}$ = 2.4 Hz, H-4), 5.35 (1H, d, J = 12.1 Hz), 5.22 (1H, d, J = 12.3 Hz), 5.14 (1H, d, J = 12.3 Hz), 4.99 (1H, ddd, $J_{5,6b}$ = 4.9, $J_{4,5}$ = 4.8, $J_{5,6a}$ = 3.5 Hz, H-5), 4.98 (1H, d, J = 12.1 Hz), 4.80 (1H, dd, $J_{6a,6b}$ = 12.1, $J_{5,6a}$ = 3.5 Hz, H-6a), 4.72 (1H, dd, $J_{6a,6b}$ = 12.1, $J_{5,6b}$ = 4.9 Hz, H-6b); δ (β -anomer): 8.05–7.90 (8H, m), 7.68–7.63 (2H, m), 7.59–7.17 (19H, m), 6.33 (1H, d, $J_{3,4}$ = 6.4 Hz, H-3), 6.27 (1H, dd, $J_{3,4}$ = 6.4, $J_{4,5}$ = 5.9 Hz, H-4), 5.32 (1H, d, J = 12.3 Hz), 5.26 (1H, d, J = 12.3 Hz), 5.07 (1H, d, J = 11.7 Hz), 5.01 (1H, d, J = 11.7 Hz), 4.88–4.73 (3H, m, H-5, 6a, 6b). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ (α - and β -anomer): 167.0, 166.7, 166.1, 166.0, 165.5, 165.5, 165.4, 165.4, 165.4, 165.2, 164.7, 164.4, 135.5, 135.3, 133.7, 133.5, 133.5, 133.4, 133.2, 133.1, 133.0, 132.9, 132.5, 132.0, 131.6, 131.5, 131.3, 131.3, 131.0, 130.9, 130.0, 129.9, 129.8, 129.7, 129.7, 129.7, 129.7, 129.5, 129.4, 129.4, 129.3, 129.2, 129.1, 129.0, 129.0, 128.8, 128.8, 128.6, 128.6, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 128.2, 128.2, 128.2, 128.1, 110.1 (α -C-2), 106.1 (β -C-2), 82.9, 80.4, 79.9, 77.5, 77.4, 77.0, 67.5, 67.4, 64.7, 64.7, 63.5, 62.1. IR (KBr): 3065, 1727, 1601, 1491, 1452 cm⁻¹. MS (FAB) m/z : 857 [M+Na]⁺. HRMS (FAB) m/z : [M+Na]⁺ Calcd for C₄₉H₃₈O₁₃Na, 857.2210; found, 857.2206.



Preparation of 1,3,4,6-Tetra-*O*-benzoyl- α -D-fructofuranosyl 2,3,4,6-tetra-*O*-acetyl-5-thio- α -D-glucopyranoside (10). Glycosylation of 9 with 8b. Donor **8b** (17 mg, 0.023 mmol, α : β = 2:1) and acceptor **9** (45 mg, 0.12 mmol) were dissolved in CH₂Cl₂ (5 mL) containing powdered molecular sieves (4Å, 0.1 g). The mixture was stirred under argon for 15 min after which trimethylsilyl trifluoromethanesulfonate (TMSOTf, 9 μ L, 0.05 mmol) was added at -40 °C. The reaction was monitored by TLC and was quenched by adding triethylamine (0.1 mL), diluted with CH₂Cl₂, filtered through a Celite pad, and the filtrate was concentrated. The residue was purified by flash column chromatography on silica gel (30% EtOAc in *n*-hexane) to give glycoside **10** (16 mg) in 73% yield. **Glycosylation of 9 with 8c.** Donor **8c**^{16c} (71 mg, 0.10 mmol, α : β = 3:1) and acceptor **9** (0.22 g, 0.60 mmol) were dissolved in CH₂Cl₂ (10 mL) containing powdered molecular sieves (4Å, 0.4 g). The mixture was stirred under argon for 15 min after which TMSOTf (18 μ L, 0.10 mmol)

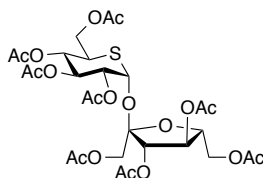
was added at $-40\text{ }^{\circ}\text{C}$. The reaction was monitored by TLC and was quenched by adding triethylamine (0.5 mL), diluted with CH_2Cl_2 , filtered through a Celite pad, and the filtrate was concentrated. The residue was purified by flash column chromatography on silica gel (30% EtOAc in *n*-hexane) to give glycoside **10** (75 mg) in 80% yield. **Glycosylation of 9 with 8d**. Acceptor **9** (50.0 mg, 137 μmol) and donor **8d** (137 mg, 164 μmol , $\alpha:\beta = 1:1.2$) were azeotropically dried with toluene (5 mL) three times and further dried on P_2O_5 under vacuum for 1 h. The resultant mixture was dissolved in CH_2Cl_2 (3 mL) and cooled to $-40\text{ }^{\circ}\text{C}$, then dropped TMSOTf (29.6 μL , 164 μmol). The reaction mixture was stirred for 2 h and then quenched by adding triethylamine (0.5 mL) and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (30% EtOAc in *n*-hexane) to give glycoside **10** (90.4 mg) in 70% yield. Colorless syrup. $R_f = 0.34$ (40% EtOAc in *n*-hexane). $[\alpha]_D^{26} +117.4$ (c 1.20, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 8.18–8.15 (2H, m), 8.02–7.99 (2H, m), 7.96–7.92 (2H, m), 7.85–7.82 (2H, m), 7.64–7.59 (1H, m), 7.57–7.48 (5H, m), 7.43–7.39 (2H, m), 7.31–7.27 (4H, m), 6.12 (1H, d, $J = 1.1$ Hz), 5.68 (1H, dd, $J = 10.2, 9.3$ Hz), 5.59 (1H, dd, $J = 4.9, 1.1$ Hz), 5.41 (1H, d, $J = 3.1$ Hz), 5.35 (1H, dd, $J = 10.2, 3.1$ Hz), 5.27 (1H, dd, $J = 10.9, 9.3$ Hz), 5.09 (1H, d, $J = 12.2$ Hz), 4.88 (1H, dd, $J = 12.1, 2.9$ Hz), 4.71 (1H, dd, $J = 12.1, 5.2$ Hz), 4.63 (1H, ddd, $J = 5.2, 4.9, 2.9$ Hz), 4.46 (1H, d, $J = 12.2$ Hz), 4.00 (1H, dd, $J = 12.3, 4.0$ Hz), 3.59 (1H, ddd, $J = 10.9, 4.0, 2.9$ Hz), 3.11 (1H, dd, $J = 12.3, 2.9$ Hz), 2.02 (3H, s), 1.98 (3H, s), 1.85 (3H, s), 1.70 (3H, s). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 170.2, 169.6, 169.3, 169.2, 166.1, 166.0, 165.1, 164.5, 133.7, 133.6, 133.5, 133.2, 130.3, 129.7, 129.6, 129.4, 129.4, 128.8, 128.7, 128.6, 128.6, 128.4, 128.4, 109.0, 83.0, 81.0, 79.0, 74.2, 71.9, 71.5, 71.4, 63.5, 60.7, 60.3, 39.3, 20.5 (2C), 20.4, 20.3. IR (film): 2965, 1729, 1601, 1452 cm^{-1} . MS (FAB) m/z : 965 $[\text{M}+\text{Na}]^+$. HRMS (FAB) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{48}\text{H}_{46}\text{O}_{18}\text{SNa}$, 965.2303; found, 965.2310.

4. Synthesis outlined in Scheme 3



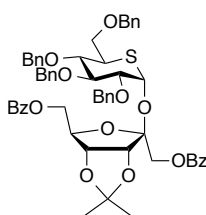
α -D-Fructofuranosyl 5-thio- α -D-glucopyranoside (2). To a solution of compound **10** (68 mg, 0.072 mmol) in MeOH (2 mL) was added sodium methoxide (2 mg, 0.04 mmol). The mixture was stirred at room temperature for 4 h after which the solvent was removed and the residue was purified on Cosmosil 140C₁₈-OPN with water as an eluent to give **2** (23 mg) in 90% yield. White solid. $R_f = 0.50$ (25% H_2O in MeCN). $[\alpha]_D^{25} +247.3$ (c 0.90, H_2O). $^1\text{H NMR}$ (400 MHz, D_2O) δ : 5.23 (1H, d, $J = 3.1$ Hz), 4.25 (1H, ddd, $J = 6.0, 3.8, 3.3$ Hz), 4.20 (1H, d, $J = 2.0$ Hz), 4.10 (1H, d, $J = 12.2$ Hz), 4.02 (1H, dd, $J = 3.3, 2.0$ Hz), 3.93 (1H, dd, $J = 12.3, 5.5$ Hz), 3.90 (1H, dd, $J = 12.3,$

3.5 Hz), 3.82 (1H, d, $J = 12.2$ Hz), 3.79–3.76 (1H, m), 3.78 (1H, dd, $J = 12.1, 3.8$ Hz), 3.70 (1H, dd, $J = 12.1, 6.0$ Hz), 3.65–3.59 (2H, m), 3.29 (1H, ddd, $J = 10.6, 5.5, 3.3$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, D_2O) δ : 110.3, 85.8, 79.6, 77.4, 75.1, 74.2, 73.1, 72.3, 61.5, 59.9, 58.7, 43.7. IR (KBr): 3422, 2935 cm^{-1} . MS (FAB) m/z : 381 $[\text{M}+\text{Na}]^+$. HRMS (FAB) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{12}\text{H}_{22}\text{O}_{10}\text{SNa}$, 381.0831; found, 381.0836.



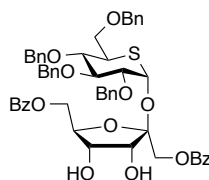
1,3,4,6-Tetra-*O*-acetyl- α -D-fructofuranosyl 2,3,4,6-tetra-*O*-acetyl-5-thio- α -D-glucopyranoside (11). The mixed solution of compound **2** (7.0 mg, 0.019 mmol) and DMAP (1 mg) in pyridine (1 mL) and acetic anhydride (0.2 mL) was stirred at room temperature for 2 h. The reaction mixture was diluted with EtOAc, and washed with saturated aqueous NaHCO_3 solution, water, and brine, dried over MgSO_4 , and concentrated. The residue was purified by flash column chromatography on silica gel (40% EtOAc in *n*-hexane) to give **11** (12 mg) in 89% yield. Colorless syrup. $R_f = 0.45$ (60% EtOAc in *n*-hexane). $[\alpha]_D^{26} +147.8$ (c 0.66, CHCl_3). ^1H NMR (400 MHz, C_6D_6) δ : 5.73 (1H, dd, $J_{2,3} = 10.2, J_{3,4} = 9.3$ Hz, H-3), 5.69 (1H, d, $J_{3',4'} = 0.5$ Hz, H-3'), 5.56 (1H, dd, $J_{4,5} = 11.0, J_{3,4} = 9.3$ Hz, H-4), 5.35 (1H, dd, $J_{2,3} = 10.2, J_{1,2} = 2.9$ Hz, H-2), 4.95 (1H, d, $J_{1,2} = 2.9$ Hz, H-1), 4.87 (1H, dd, $J_{4',5'} = 3.3, J_{3',4'} = 0.5$ Hz, H-4'), 4.55 (1H, ddd, $J_{5',6'b} = 7.7, J_{4',5'} = 4.1, J_{5',6'a} = 3.3$ Hz, H-5'), 4.54 (1H, dd, $J_{6'a,6'b} = 12.6, J_{5',6'a} = 4.1$ Hz, H-6'a), 4.52 (1H, dd, $J_{6a,6b} = 12.0, J_{5,6a} = 4.4$ Hz, H-6a), 4.52 (1H, d, $J_{1'a,1'b} = 12.3$ Hz, H-1'a), 4.30 (1H, dd, $J_{6'a,6'b} = 12.6, J_{5',6'b} = 7.7$ Hz, H-6'b), 4.29 (1H, d, $J_{1'a,1'b} = 12.3$ Hz, H-1'b), 3.80 (1H, dd, $J_{6a,6b} = 12.0, J_{5,6b} = 3.1$ Hz, H-6b), 3.59 (1H, ddd, $J_{4,5} = 11.0, J_{5,6a} = 4.4, J_{5,6b} = 3.1$ Hz, H-5), 2.01 (3H, s), 1.79 (3H, s), 1.72 (3H, s), 1.71 (3H, s), 1.71 (3H, s), 1.69 (3H, s), 1.65 (3H, s), 1.63 (3H, s). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 170.7, 170.4, 170.4, 169.6 (2C), 169.4, 169.3, 168.5, 108.6, 82.2, 79.0, 78.2, 74.6, 72.1, 71.4, 71.0, 63.3, 61.2, 59.4, 39.3, 20.7, 20.6, 20.6, 20.5, 20.5, 20.4, 20.4, 20.4. IR (film): 2959, 1743 cm^{-1} . MS (FAB) m/z : 717 $[\text{M}+\text{Na}]^+$. HRMS (FAB) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{28}\text{H}_{38}\text{O}_{18}\text{SNa}$, 717.1677; found, 717.1672.

5. Synthesis outlined in Scheme 4



2,3,4,6-Tetra-*O*-benzyl-5-thio- α -D-glucopyranosyl 1,6-di-*O*-benzoyl-3,4-*O*-isopropylidene- β -D-psicofuranoside (13). A mixture of glycosyl acceptor **6** (200 mg, 360 μ mol) and donor **12** (288 mg, 432 μ mol) was azeotropically dried with toluene three times and further dried under reduced pressure on P₂O₅ for 1 h. The mixture was dissolved in CH₂Cl₂ (14.4 mL), cooled to -40 °C and then dropped TMSOTf (78.1 μ L, 432 μ mol). The whole was stirred for 40 min at -40 to -20 °C, then quenched with saturated aqueous NaHCO₃ solution, extracted with CH₂Cl₂, washed with water, dried over MgSO₄ and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluted with 15% EtOAc in *n*-hexane to give glycoside **13** (262 mg) in 76% yield. Colorless syrup. R_f = 0.52 (30% EtOAc in *n*-hexane). $[\alpha]_D^{26} +92.2$ (*c* 0.54, CHCl₃). ¹H NMR (400 MHz, C₆D₆) δ : 8.29–8.26 (2H, m), 8.08–8.06 (2H, m), 7.49–7.46 (2H, m), 7.25–6.92 (24H, m), 5.25 (1H, d, J = 11.5 Hz), 5.15 (1H, d, J = 11.5 Hz), 5.04 (1H, d, J = 12.3 Hz), 5.04 (1H, d, J = 11.7 Hz), 4.90 (1H, d, J = 12.3 Hz), 4.81 (1H, $J_{3,4}$ = 6.0 Hz, H-3), 4.80 (1H, d, $J_{1',2'}$ = 2.9 Hz, H-1'), 4.75 (1H, dd, $J_{6a,6b}$ = 10.6, $J_{5,6a}$ = 8.2 Hz, H-6a), 4.69 (1H, d, J = 11.7 Hz), 4.68 (1H, dd, $J_{5,6a}$ = 8.2, $J_{5,6b}$ = 5.3, $J_{4,5}$ = 1.7 Hz, H-5), 4.64 (1H, d, J = 10.8 Hz), 4.53 (1H, dd, $J_{6a,6b}$ = 10.6, $J_{5,6b}$ = 5.3 Hz, H-6b), 4.42 (1H, dd, $J_{3,4}$ = 6.0, $J_{4,5}$ = 1.7 Hz, H-4), 4.28 (1H, d, J = 10.8 Hz), 4.26 (1H, dd, $J_{2',3'}$ = 9.5, $J_{3',4'}$ = 9.2 Hz, H-3'), 4.18 (1H, d, J = 12.1 Hz), 4.12 (1H, d, J = 12.1 Hz), 4.12 (1H, dd, $J_{4',5'}$ = 10.6, $J_{3',4'}$ = 9.2 Hz, H-4'), 3.91 (1H, dd, $J_{6'a,6'b}$ = 9.9, $J_{5',6'a}$ = 3.7 Hz, H-6'a), 3.73 (1H, dd, $J_{2',3'}$ = 9.5, $J_{1',2'}$ = 2.9 Hz, H-2'), 3.62 (1H, ddd, $J_{4',5'}$ = 10.6, $J_{5',6'a}$ = 3.7, $J_{5',6'b}$ = 2.2 Hz, H-5'), 3.13 (1H, dd, $J_{6'a,6'b}$ = 9.9, $J_{5',6'b}$ = 2.2 Hz, H-6'b), 1.38 (3H, s), 1.07 (3H, s). ¹³C {¹H} NMR (75 MHz, CDCl₃) δ : 166.0, 165.9, 139.0, 138.3, 137.9, 137.7, 133.1, 132.8, 130.2, 129.8, 129.7, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.6, 127.6, 127.6, 127.5, 127.2, 113.6, 109.9, 84.2, 84.1, 83.9, 83.7, 82.2, 81.7, 75.9, 75.5, 73.9, 73.9, 73.2, 67.3, 64.7, 63.5, 42.1, 26.5, 24.9. IR (KBr): 2924, 1720, 1602, 1496 cm⁻¹. MS (FAB) m/z : 989 [M+Na]⁺. HRMS (FAB) m/z : [M+Na]⁺ Calcd for C₅₇H₅₈O₁₂SNa, 989.3547; found, 989.3555.

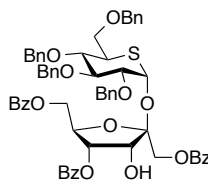
6. Synthesis outlined in Scheme 5



2,3,4,6-Tetra-*O*-benzyl-5-thio- α -D-glucopyranosyl 1,6-di-*O*-benzoyl- β -D-psicofuranoside (14).

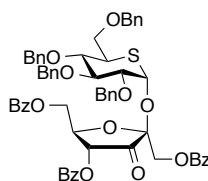
The mixed solution of compound **13** (368 mg, 381 μ mol) and *p*-toluenesulfonic acid monohydrate (145 mg, 762 μ mol) in MeOH–CH₂Cl₂ (1:1, 8 mL) was stirred at room temperature for 2 days. The resultant mixture was quenched with saturated aqueous NaHCO₃ solution and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine, dried (Na₂SO₄)

and concentrated to dryness. The crude residue was purified by silica gel flash column chromatography eluted with 35% EtOAc in *n*-hexane to give **14** (200 mg) in 57% yield along with 70.5 mg (19% rsm) of recovered starting material. Colorless syrup. $R_f = 0.38$ (40% EtOAc in *n*-hexane). $[\alpha]_D^{26} +77.8$ (c 0.88, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ : 8.07–8.02 (4H, m), 7.57–7.53 (1H, m), 7.47–7.41 (3H, m), 7.31–7.23 (15H, m), 7.19–7.16 (5H, m), 7.10–7.07 (2H, m), 5.24 (1H, d, $J_{1',2'} = 2.5$ Hz, H-1'), 4.86–4.80 (1H, m, H-5), 4.82 (1H, d, $J = 10.6$ Hz), 4.70 (1H, d, $J = 11.9$ Hz), 4.70–4.66 (1H, m, H-6a), 4.68 (1H, d, $J = 10.8$ Hz), 4.66 (1H, d, $J = 11.4$ Hz), 4.60 (1H, d, $J = 10.8$ Hz), 4.58 (1H, d, $J = 11.4$ Hz), 4.52 (1H, d, $J = 10.6$ Hz), 4.51 (1H, d, $J = 12.1$ Hz), 4.44 (1H, d, $J = 12.1$ Hz), 4.40–4.35 (2H, m, H-3, H-6b), 4.35 (1H, d, $J = 11.9$ Hz), 4.30 (1H, br s, 4-OH), 4.12–4.11 (1H, m, H-4), 3.92 (1H, dd, $J_{6'b,6'b} = 9.9$, $J_{5',6'a} = 4.4$ Hz, H-6'a), 3.86–3.80 (2H, m, H-3', 4'), 3.77 (1H, dd, $J_{2',3'} = 9.6$, $J_{1',2'} = 2.5$ Hz, H-2'), 3.58 (1H, dd, $J_{6'a,6'b} = 9.9$, $J_{5',6'b} = 2.6$ Hz, H-6'b), 3.34 (1H, ddd, $J_{4',5'} = 10.0$, $J_{5',6'a} = 4.4$, $J_{5',6'b} = 2.6$ Hz, H-5'), 2.90 (1H, br s, 3-OH). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ : 167.3, 166.5, 138.8, 138.2, 137.8, 137.7, 133.3, 133.1, 130.0, 129.9, 129.7, 129.5, 128.4, 128.3, 128.3, 128.3, 128.3, 128.2, 128.2, 127.9, 127.7, 127.7, 127.7, 127.6, 127.4, 127.3, 107.6, 84.0, 83.5, 82.1, 81.8, 75.8, 75.6, 74.3, 73.3, 73.2, 71.9, 71.7, 67.8, 65.5, 62.6, 42.0. IR (film): 3440, 3032, 2863, 1722, 1602 cm^{-1} . MS (FAB) m/z : 949 $[\text{M}+\text{Na}]^+$. HRMS (FAB) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{54}\text{H}_{54}\text{O}_{12}\text{SNa}$, 949.3234; found, 949.3226.

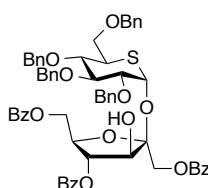


2,3,4,6-Tetra-*O*-benzyl-5-thio- α -D-glucopyranosyl 1,4,6-tri-*O*-benzoyl- β -D-psicofuranoside (15). A stirred mixture of compound **14** (200 mg, 216 μmol) and di-*n*-butyltin (IV) oxide (56.5 mg, 227 μmol) in MeOH (7 mL) was heated at reflux for 45 min. The reaction mixture was cooled to 0 $^\circ\text{C}$, added benzoyl chloride (251 μL , 2.16 mmol) and triethylamine (300 μL , 2.16 mmol), and stirred for 10 min at the same temperature, and then the solvent was removed under reduced pressure. The residue was purified by silica gel flash column chromatography eluted with 20% EtOAc in *n*-hexane to yield **15** (138 mg) in 62% yield. Colorless syrup. $R_f = 0.43$ (30% EtOAc in *n*-hexane). $[\alpha]_D^{21} +55.0$ (c 1.00, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ : 8.10–7.99 (6H, m), 7.59–7.11 (29H, m), 5.55 (1H, dd, $J_{4,5} = 7.8$, $J_{3,4} = 4.7$ Hz, H-4), 5.22 (1H, d, $J_{1',2'} = 2.6$ Hz, H-1'), 4.91–4.86 (3H, m), 4.73–4.44 (12H, m), 4.00 (1H, dd, $J_{6'a,6'b} = 10.0$, $J_{5',6'a} = 4.4$ Hz, H-6'a), 3.91 (1H, dd, $J_{2',3'} = 9.3$, $J_{3',4'} = 9.2$ Hz, H-3'), 3.84 (1H, dd, $J_{4',5'} = 10.2$, $J_{3',4'} = 9.2$ Hz, H-4'), 3.79 (1H, dd, $J_{2',3'} = 9.3$, $J_{1',2'} = 2.6$ Hz, H-2'), 3.66 (1H, dd, $J_{6'a,6'b} = 10.0$, $J_{5',6'b} = 2.4$ Hz, H-6'b), 3.53 (1H, ddd, $J_{4',5'} = 10.2$, $J_{5',6'a} = 4.4$, $J_{5',6'b} = 2.4$ Hz, H-5'). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ : 166.8, 166.1, 165.6, 138.9, 138.3, 137.9, 137.8, 133.5, 133.2, 133.1, 130.0, 129.8, 129.7, 129.7, 129.7,

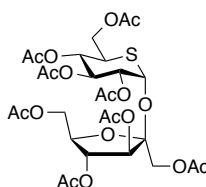
129.0, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 128.2, 127.9, 127.7, 127.6, 127.5, 127.3, 108.4, 83.7, 83.5, 81.8, 79.0, 75.8, 75.6, 73.8, 73.3, 73.3, 73.1, 72.3, 67.8, 65.0, 62.3, 42.0. IR (film): 3452, 3030, 1724, 1602, 1495 cm^{-1} . MS (FAB) m/z : 1053 $[\text{M}+\text{Na}]^+$. HRMS (FAB) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{61}\text{H}_{58}\text{O}_{13}\text{SNa}$, 1053.3496; found, 1053.3502.



1,4,6-Tri-*O*-benzoyl- β -D-erythro-2,3-hexodiulofuranosyl 2,3,4,6-tetra-*O*-benzyl-5-thio- α -D-glucopyranoside (16). To a solution of oxalyl chloride (117 μL , 1.34 mmol) in CH_2Cl_2 (2 mL) was slowly added dimethyl sulfoxide (190 μL , 2.68 mmol) in CH_2Cl_2 (0.5 mL) at -78°C , and stirred for 30 min at the same temperature. A solution of compound **15** (138 mg, 134 μmol) in CH_2Cl_2 (2.5 mL) was added into the reaction mixture and the whole was stirred for 1 h at -78 to -60°C . After addition of triethylamine (559 μL , 4.02 mmol) at -78°C , the resultant mixture was further stirred for 1 h. The reaction was quenched with saturated aqueous NH_4Cl solution, extracted with EtOAc, dried over MgSO_4 and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel eluted with 20% EtOAc in *n*-hexane to give **16** (111 mg) in 81% yield. Colorless syrup. $R_f = 0.50$ (30% EtOAc in *n*-hexane). $[\alpha]_D^{22} +130.5$ (c 1.18, CHCl_3). ^1H NMR (500 MHz, CDCl_3) δ : 8.01–7.94 (6H, m), 7.60–7.56 (1H, m), 7.52–7.47 (2H, m), 7.41–7.37 (2H, m), 7.35–7.31 (2H, m), 7.28–7.11 (22H, m), 6.33 (1H, d, $J = 7.6$ Hz), 5.42 (1H, d, $J = 3.2$ Hz), 4.90 (1H, d, $J = 10.7$ Hz), 4.89 (1H, dd, $J = 12.2, 2.7$ Hz), 4.82 (1H, d, $J = 10.4$ Hz), 4.75 (1H, d, $J = 10.4$ Hz), 4.73 (1H, dd, $J = 12.2, 4.6$ Hz), 4.69 (1H, ddd, $J = 7.6, 4.6, 2.7$ Hz), 4.65 (1H, d, $J = 11.0$ Hz), 4.60 (1H, d, $J = 11.0$ Hz), 4.56–4.47 (2H, m), 4.55 (1H, d, $J = 11.9$ Hz), 4.48 (1H, d, $J = 11.6$ Hz), 4.36 (1H, d, $J = 11.9$ Hz), 3.96 (1H, dd, $J = 10.2, 3.5$ Hz), 3.86 (1H, dd, $J = 9.2, 9.0$ Hz), 3.82 (1H, dd, $J = 10.1, 9.2$ Hz), 3.66 (1H, dd, $J = 9.0, 3.2$ Hz), 3.36 (1H, dd, $J = 10.2, 2.4$ Hz), 3.04 (1H, ddd, $J = 10.1, 3.5, 2.4$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ : 207.2, 166.1, 165.2, 165.1, 138.8, 138.2, 137.9, 137.8, 133.8, 133.4, 133.3, 130.0, 129.8, 129.7, 129.2, 128.6, 128.5, 128.4, 128.3, 128.3, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 98.1, 83.1, 82.9, 81.1, 76.8, 76.1, 75.6, 73.0, 72.4, 72.1, 70.2, 67.3, 67.0, 63.4, 42.2. IR (film): 2864, 1779, 1728, 1601, 1495 cm^{-1} . MS (FAB) m/z : 1051 $[\text{M}+\text{Na}]^+$. HRMS (FAB) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{61}\text{H}_{56}\text{O}_{13}\text{SNa}$, 1051.3339; found, 1051.3348.

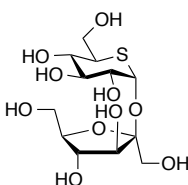


1,4,6-Tri-*O*-benzoyl- β -D-fructofuranosyl 2,3,4,6-tetra-*O*-benzyl-5-thio- α -D-glucopyranoside (17). To a mixed solution of compound **16** (111 mg, 108 μ mol) in MeOH-CH₂Cl₂ (1:1, 3 mL) was added sodium borohydride (8.2 mg, 0.22 mmol) at 0 °C and the reaction was stirred for 30 min at the same temperature. After addition of saturated aqueous NH₄Cl solution, aqueous phase was extracted with EtOAc and the organic extracts were washed with brine, dried (Na₂SO₄), and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (eluent: 15% EtOAc in *n*-hexane) to afford **17** (98.4 mg) in 89% yield. Colorless syrup. R_f = 0.48 (30% EtOAc in *n*-hexane). $[\alpha]_D^{20}$ +63.2 (*c* 0.90, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ : 8.08–8.03 (4H, m), 7.99–7.96 (2H, m), 7.61–7.20 (27H, m), 7.17–7.15 (2H, m), 5.67 (1H, dd, $J_{3',4'} = J_{4',5'} = 7.1$ Hz, H-4'), 5.47 (1H, d, $J_{1,2} = 2.9$ Hz, H-1), 4.88 (1H, d, $J = 10.6$ Hz), 4.81 (1H, d, $J = 10.8$ Hz), 4.79–4.53 (9H, m), 4.52 (1H, d, $J = 12.1$ Hz), 4.45–4.40 (1H, m), 4.44 (1H, d, $J = 12.1$ Hz), 3.96 (1H, dd, $J_{6a,6b} = 10.1$, $J_{5,6a} = 4.2$ Hz, H-6a), 3.90 (1H, dd, $J_{2,3} = 9.1$, $J_{3,4} = 9.0$ Hz, H-3), 3.86 (1H, dd, $J_{4,5} = 9.9$, $J_{3,4} = 9.0$ Hz, H-4), 3.77 (1H, dd, $J_{2,3} = 9.1$, $J_{1,2} = 2.9$ Hz, H-2), 3.74 (1H, d, $J = 9.2$ Hz, OH), 3.60 (1H, dd, $J_{6a,6b} = 10.1$, $J_{5,6b} = 2.6$ Hz, H-6b), 3.47 (1H, ddd, $J_{4,5} = 9.9$, $J_{5,6a} = 4.2$, $J_{5,6b} = 2.6$ Hz, H-5). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ : 166.0, 165.8, 165.7, 138.6, 138.2, 137.7, 137.4, 133.5, 133.2, 133.0, 129.9, 129.8, 129.7, 129.6, 129.5, 129.0, 128.5, 128.4, 128.4, 128.3, 128.2, 128.2, 127.9, 127.8, 127.7, 127.6, 127.6, 127.4, 104.6, 83.5, 83.1, 81.5, 78.1, 77.7, 77.3, 76.0, 75.6, 73.2, 73.1, 73.1, 67.5, 64.5, 64.0, 42.3. IR (film): 3438, 3030, 2864, 1730, 1602, 1495 cm⁻¹. MS (FAB) m/z : 1053 [M+Na]⁺. HRMS (FAB) m/z : [M+Na]⁺ Calcd for C₆₁H₅₈O₁₃SNa, 1053.3496; found, 1053.3491.



1,3,4,6-Tetra-*O*-acetyl- β -D-fructofuranosyl 2,3,4,6-tetra-*O*-acetyl-5-thio- α -D-glucopyranoside (18). Metal sodium (approximately 50 mg, 2.2 mmol) was added to liquid ammonia (4 mL) at -78 °C. To the resultant dark blue solution was added compound **17** (98.4 mg, 95.4 μ mol) in THF (4 mL) solution and the reaction was vigorously stirred for 5 min at the same temperature. MeOH (4 mL) was added to the reaction, which was stirred for 15 min prior to the addition of Acetic acid (1 mL), then warmed to room temperature and evaporated. The residue obtained after removal of the solvent was diluted with pyridine (5 mL) and acetic anhydride (2 mL, 21.2 mmol), and then stirred at room temperature for 2 h in the presence of DMAP (20 mg, 0.16 mmol). The residue obtained after co-evaporation with toluene was purified by flash column chromatography on silica gel eluted with 45% EtOAc in *n*-hexane to give **18** (57.7 mg) in 87% yield. Colorless syrup. R_f = 0.11 (40% EtOAc in *n*-hexane). $[\alpha]_D^{21}$ +67.6 (*c* 0.90, CHCl₃). ¹H NMR (300 MHz, C₆D₆) δ : 5.76

(1H, dd, $J_{2,3} = 10.2$, $J_{3,4} = 9.7$ Hz, H-3), 5.71 (1H, d, $J_{3',4'} = 5.9$ Hz, H-3'), 5.62 (1H, dd, $J_{3',4'} = 5.9$, $J_{4',5'} = 5.6$ Hz, H-4'), 5.54 (1H, dd, $J_{4,5} = 10.8$, $J_{3,4} = 9.7$ Hz, H-4), 5.36 (1H, d, $J_{1,2} = 2.8$ Hz, H-1), 5.23 (1H, dd, $J_{2,3} = 10.2$, $J_{1,2} = 2.8$ Hz, H-2), 4.52 (2H, d, $J_{5',6'} = 5.5$ Hz, H-6'), 4.44 (1H, dd, $J_{6a,6b} = 12.0$, $J_{5,6a} = 5.4$ Hz, H-6a), 4.38 (1H, d, $J_{1'a,1'b} = 12.1$ Hz, H-1'a), 4.28 (1H, d, $J_{1'a,1'b} = 12.1$ Hz, H-1'b), 4.22 (1H, dt, $J_{4',5'} = 5.6$, $J_{5',6'} = 5.5$ Hz, H-5'), 4.14 (1H, dd, $J_{6a,6b} = 12.0$, $J_{5,6b} = 3.1$ Hz, H-6b), 3.80 (1H, ddd, $J_{4,5} = 10.8$, $J_{5,6a} = 5.4$, $J_{5,6b} = 3.1$ Hz, H-5), 1.99 (3H, s), 1.87 (3H, s), 1.83 (3H, s), 1.77 (3H, s), 1.75 (3H, s), 1.68 (3H, s), 1.65 (3H, s), 1.57 (3H, s). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) δ : 170.5, 170.4, 170.1, 170.0, 169.9, 169.8, 169.6, 169.5, 103.9, 78.8, 75.7, 74.7, 74.5, 72.1, 71.9, 70.4, 63.6, 63.4, 61.2, 39.2, 20.8, 20.7, 20.6, 20.6 (2C), 20.5 (2C), 20.5. IR (film): 2960, 1747 cm^{-1} . MS (FAB) m/z : 717 $[\text{M}+\text{Na}]^+$. HRMS (FAB) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{28}\text{H}_{38}\text{O}_{18}\text{SNa}$, 717.1677; found, 717.1669.

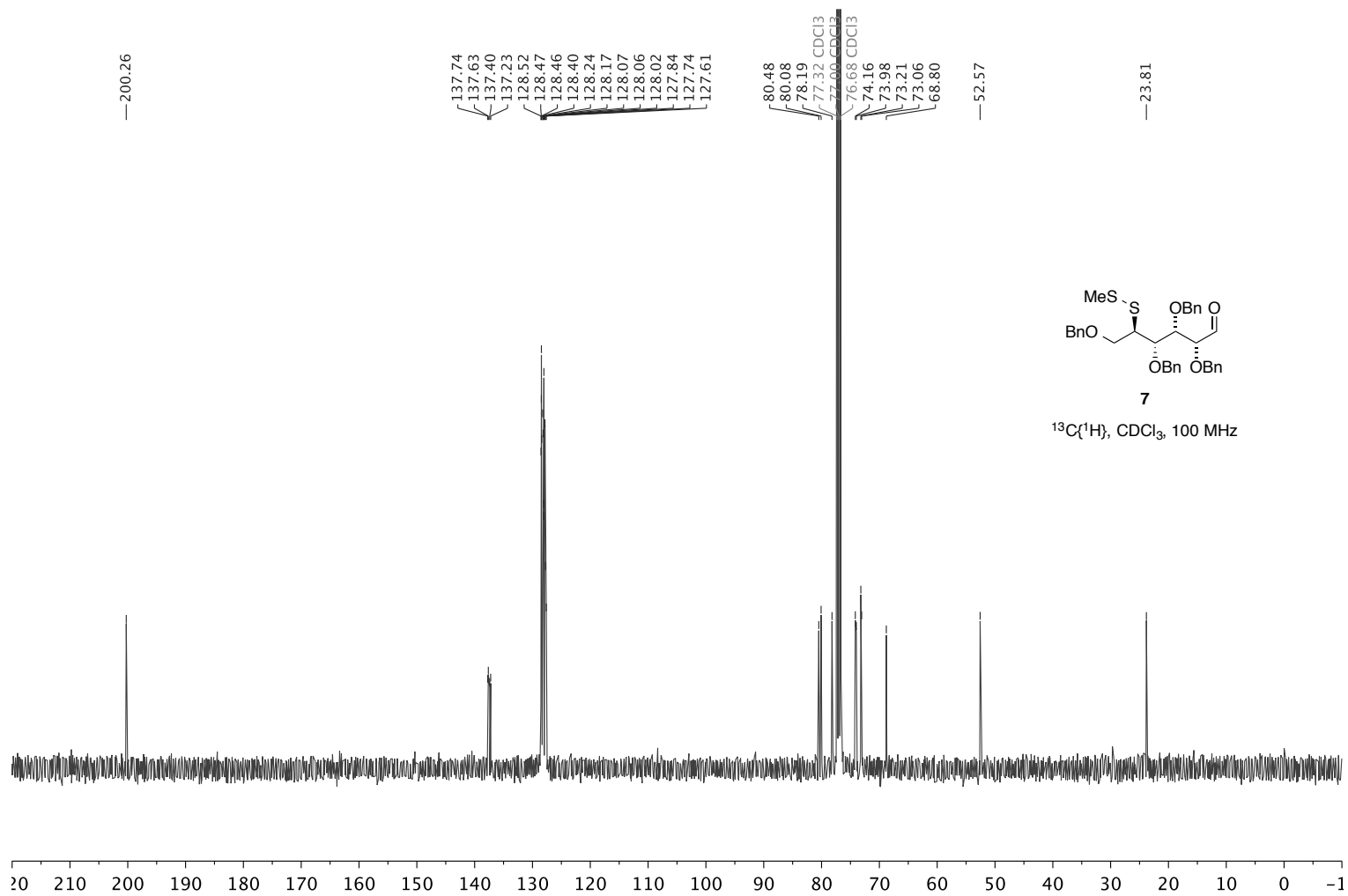
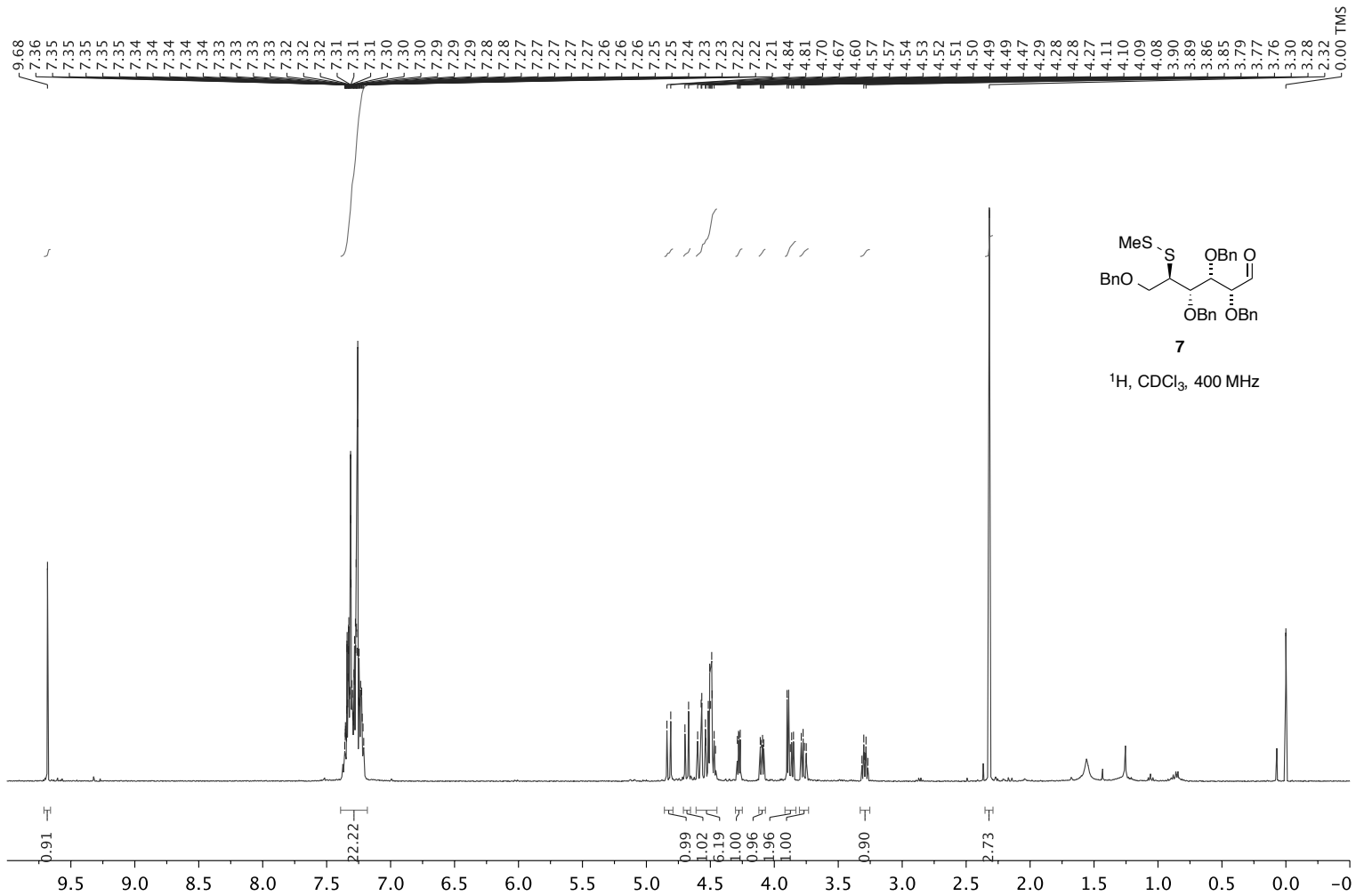


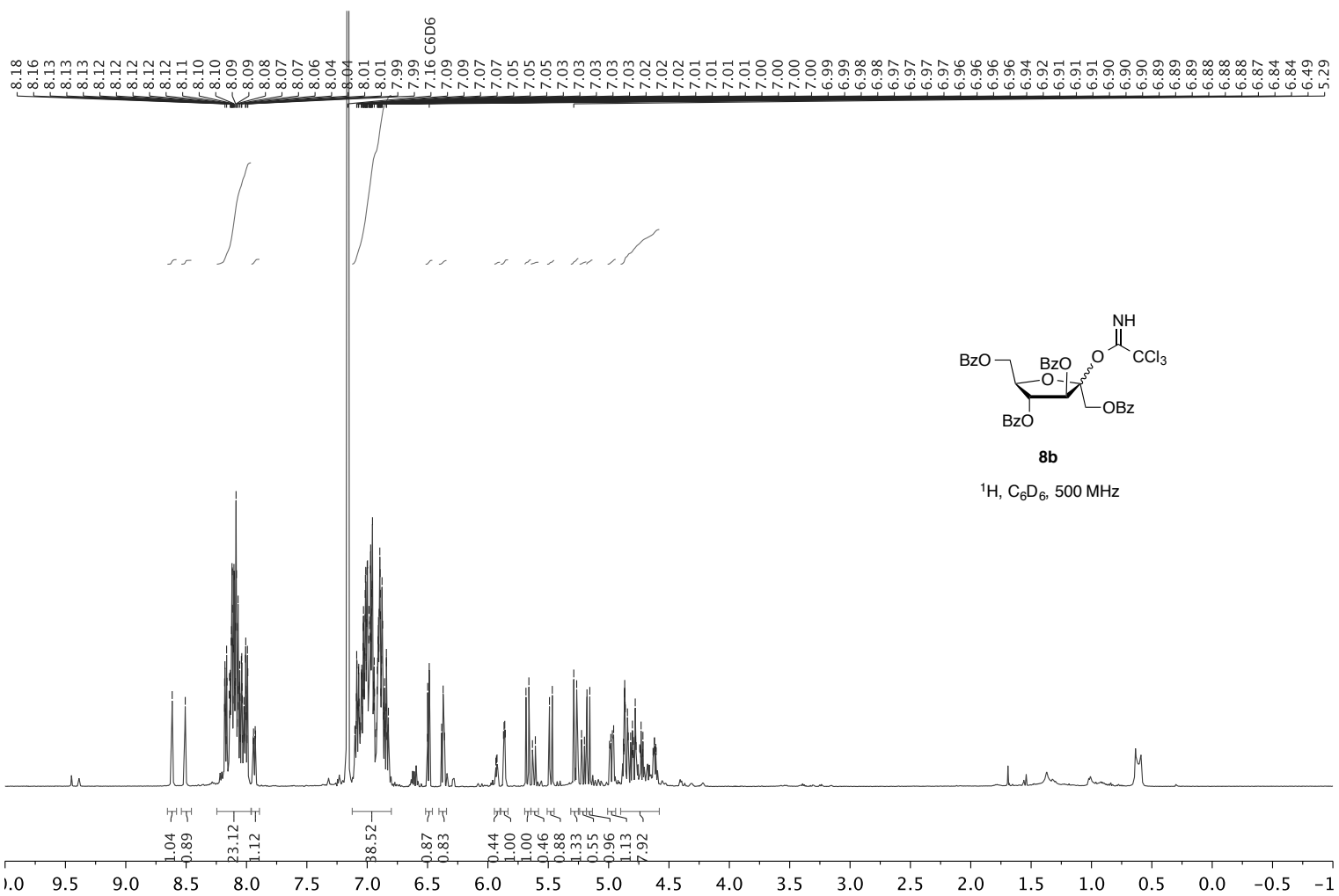
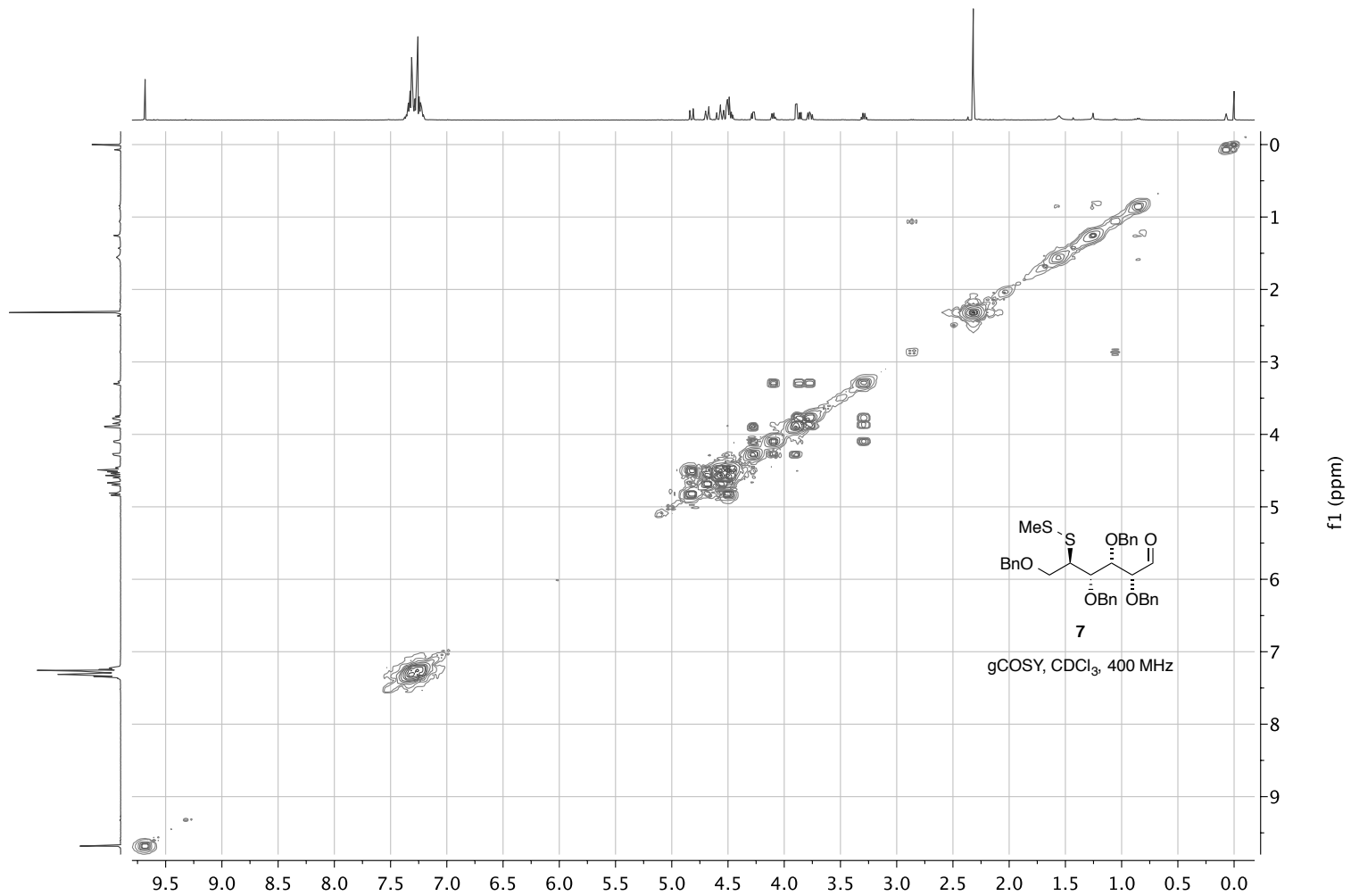
β -D-Fructofuranosyl 5-thio- α -D-glucopyranoside (1). To a solution of compound **18** (57.7 mg, 83.1 μmol) in MeOH (2.5 mL) was added 0.1 M solution of sodium methoxide in MeOH (83 μL , 8.3 μmol) and the reaction mixture was stirred for 3 h at room temperature. After neutralization with Amberlite FPC3500, the mixture was stirred for 10 min, then diluted with water and filtered through a membrane filter. Lyophilization of the aqueous solution afforded **1** (29.5 mg) in 99% yield. White solid. $R_f = 0.36$ (25% H_2O in MeCN). $[\alpha]_D^{20} +121.4$ (c 0.43, H_2O). ^1H NMR (400 MHz, D_2O) δ : 5.21 (1H, d, $J_{1,2} = 3.1$ Hz, H-1), 4.20 (1H, d, $J_{3',4'} = 8.8$ Hz, H-3'), 4.11 (1H, dd, $J_{3',4'} = 8.8$, $J_{4',5'} = 8.2$ Hz, H-4'), 4.07 (1H, dd, $J_{6'a,6'b} = 12.1$, $J_{5',6'a} = 7.3$ Hz, H-6'a), 3.93 (1H, dd, $J_{6a,6b} = 12.1$, $J_{5,6a} = 5.5$ Hz, H-6a), 3.89 (1H, ddd, $J_{4',5'} = 8.2$, $J_{5',6'a} = 7.3$, $J_{5',6'b} = 2.7$ Hz, H-5'), 3.89 (1H, dd, $J_{6a,6b} = 12.1$, $J_{5,6b} = 3.4$ Hz, H-6b), 3.83 (1H, dd, $J_{6'a,6'b} = 12.1$, $J_{5',6'b} = 2.7$ Hz, H-6'b), 3.78 (1H, dd, $J_{2,3} = 9.6$, $J_{1,2} = 3.1$ Hz, H-2), 3.75 (2H, s, H-1'), 3.70 (1H, dd, $J_{2,3} = 9.6$, $J_{3,4} = 8.9$ Hz, H-3), 3.62 (1H, dd, $J_{4,5} = 10.3$, $J_{3,4} = 8.9$ Hz, H-4), 3.26 (1H, ddd, $J_{4,5} = 10.3$, $J_{5,6a} = 5.5$, $J_{5,6b} = 3.4$ Hz, H-5). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, D_2O) δ : 103.8, 81.4, 77.0, 75.1, 74.2, 74.0, 73.8, 73.4, 62.1, 60.7, 60.1, 43.5. IR (KBr): 3398, 2931 cm^{-1} . MS (FAB) m/z : 381 $[\text{M}+\text{Na}]^+$. HRMS (FAB) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{12}\text{H}_{22}\text{O}_{10}\text{SNa}$, 381.0831; found, 381.0826.

7. Biological studies

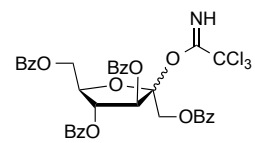
α -Glucosidase inhibitory assays⁵: Rat small intestinal brush border membrane vesicles were prepared and its suspension in a 0.1 M maleate buffer (pH 6.0) was used to determine the small

intestinal α -glucosidase enzyme activity of maltase and sucrase. The enzyme suspension was properly diluted to hydrolyze maltose and sucrose to produce ca. 0.30 and ca. 0.15 $\mu\text{mol}/\text{tube}$ of D-glucose, respectively, in the following reaction. The substrate solution in a 0.1 M maleate buffer (maltose: 74 mM or sucrose: 74 mM, 50 μL), test compound in a mixed solution of DMSO and 0.1 M maleate buffer (1:4, 25 μL), and the enzyme solution (pH 6.0, 25 μL) were incubated together at 37 °C. After 30 min of incubation, 0.4 mL of water was added to the test tube, and the test tube was immediately immersed in boiling water for 2 min to stop the reaction and then cooled with ice-water bath. The glucose concentration was determined using the glucose-oxidase method. Measurements were performed in duplicate.





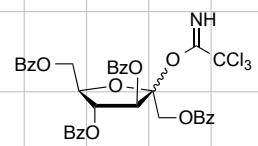
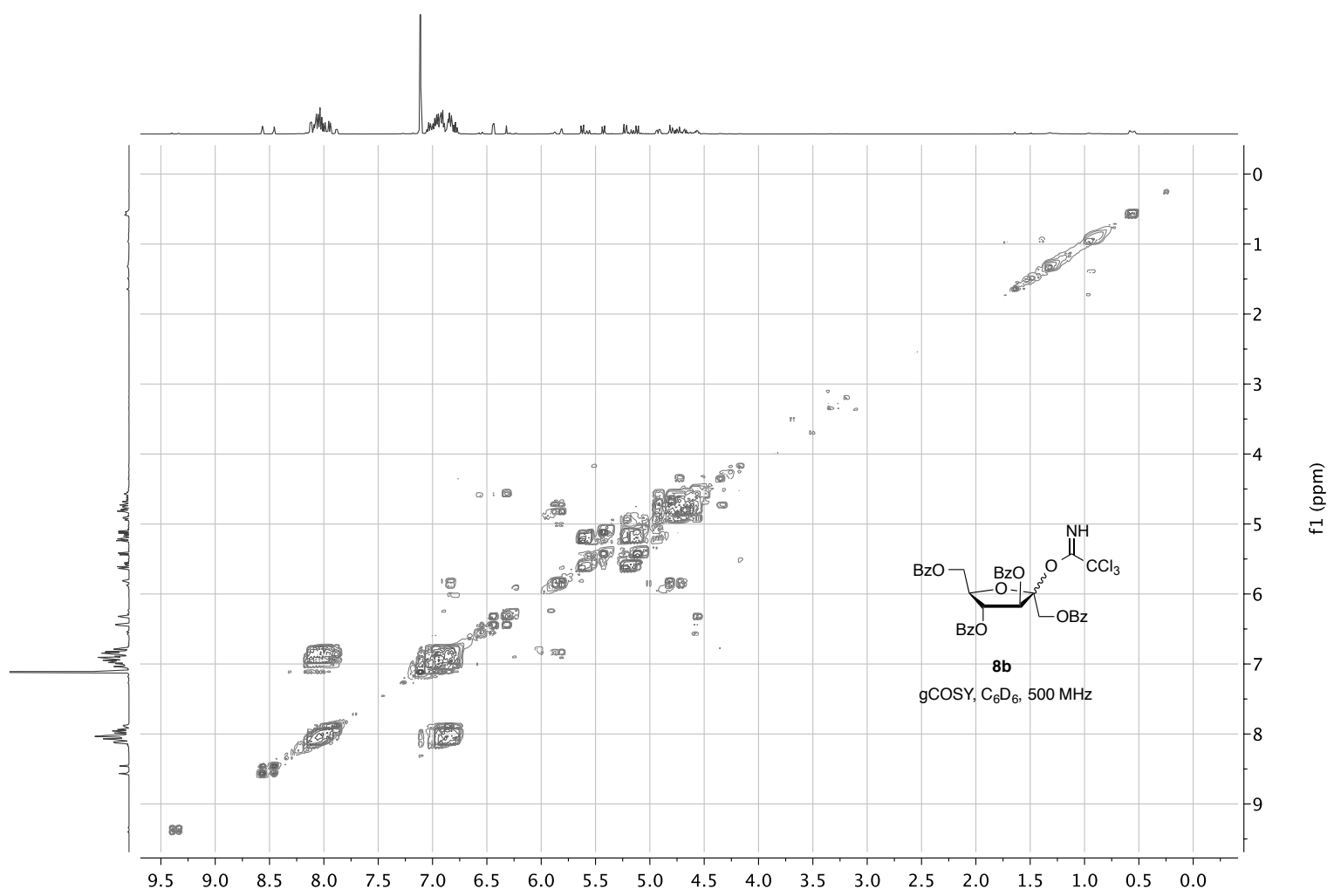
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133.49
133.16
133.04
132.99
132.88
130.49
130.40
130.38
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130.23
130.15
130.13
130.10
130.07
129.56
129.49
129.37
129.27
128.76
128.72
128.67
128.62
128.59
128.56
128.54
128.52
128.47
128.45
128.36
128.25 cdcl3
128.17
128.06 cdcl3
127.97
127.87 cdcl3
112.23
107.89
91.88
91.82
83.80
80.76
80.45
78.55
77.73
65.10
64.61
63.63
61.65



8b

$^{13}\text{C}\{^1\text{H}\}$, C_6D_6 , 125 MHz

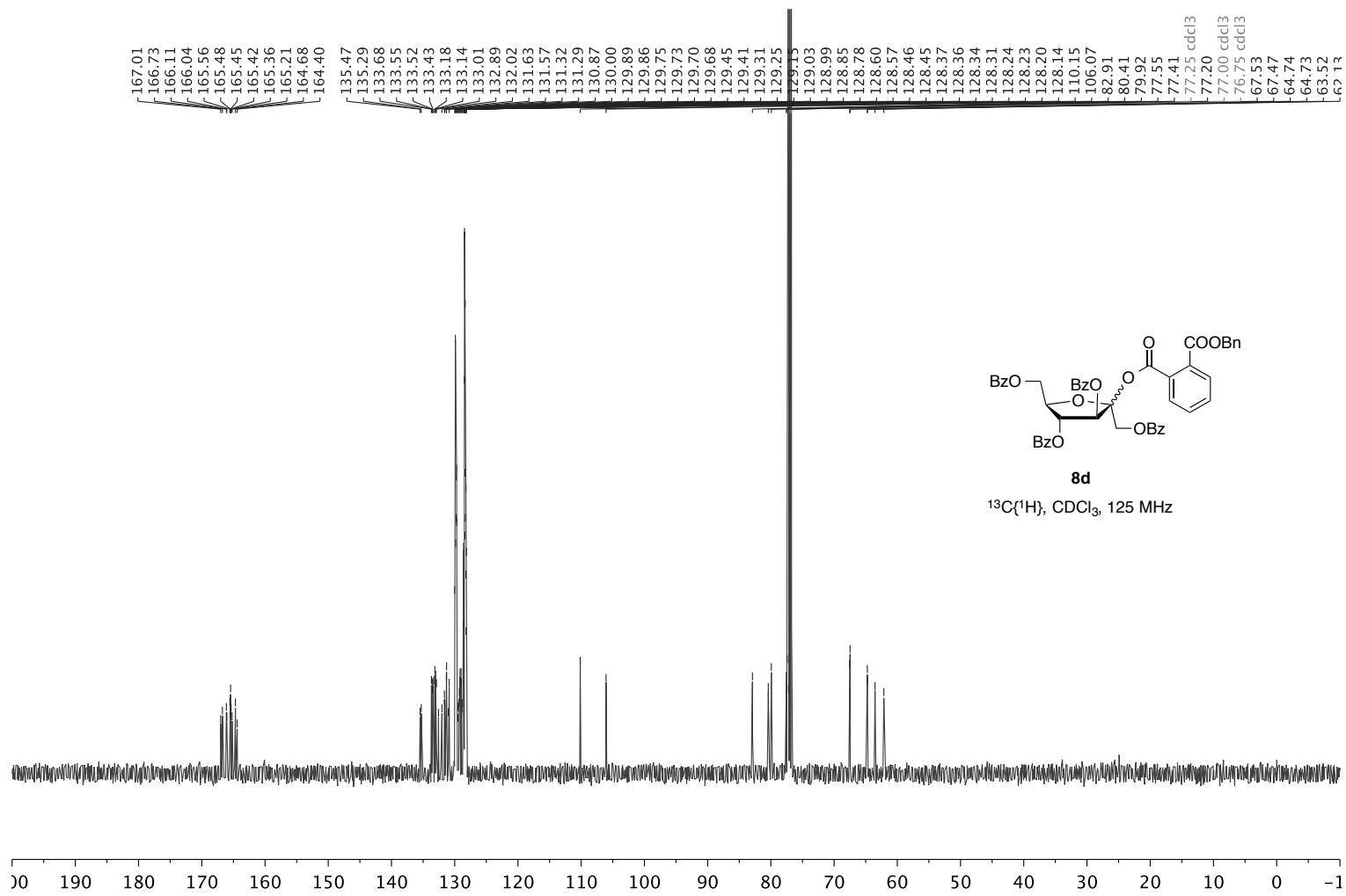
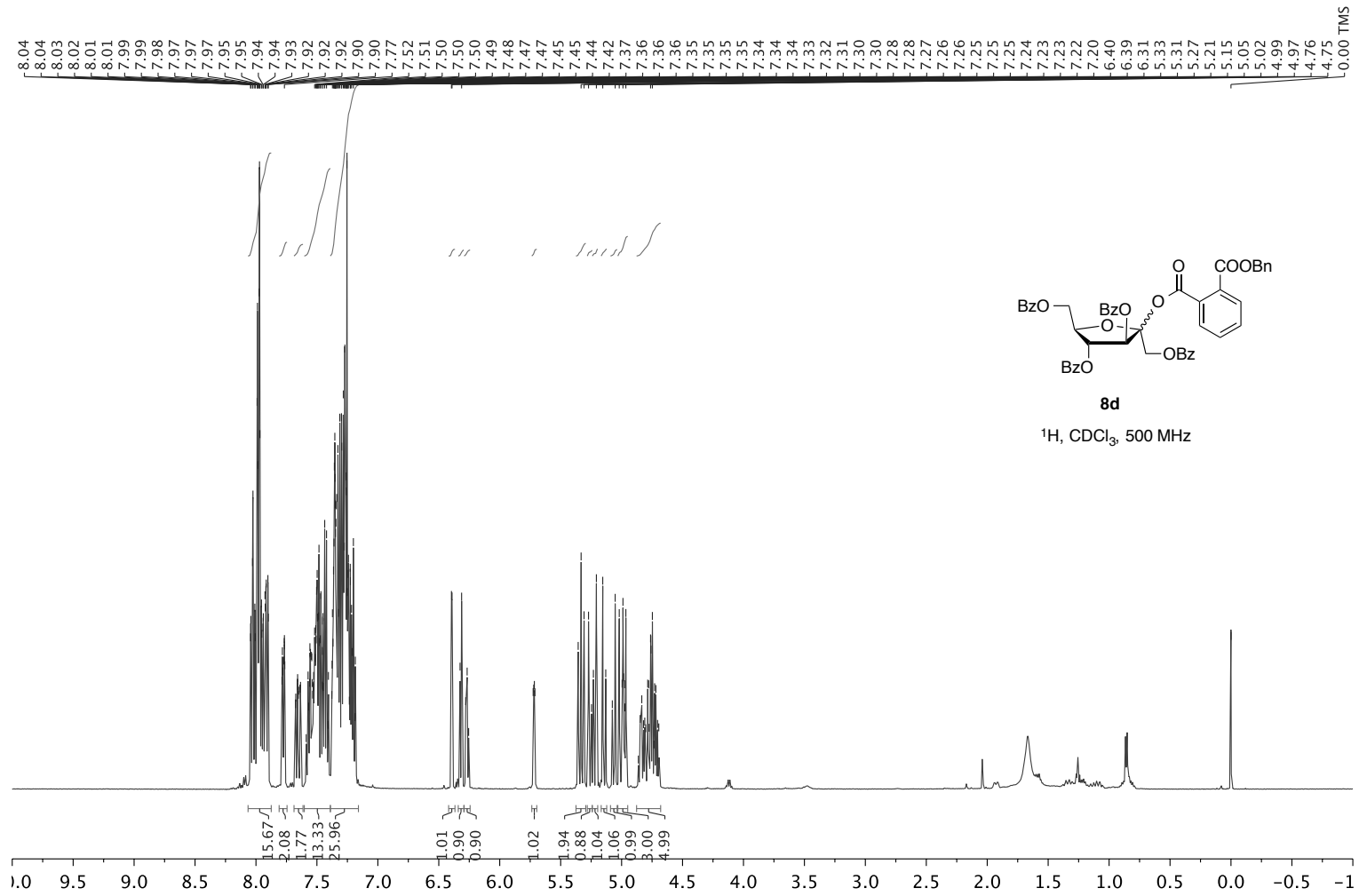
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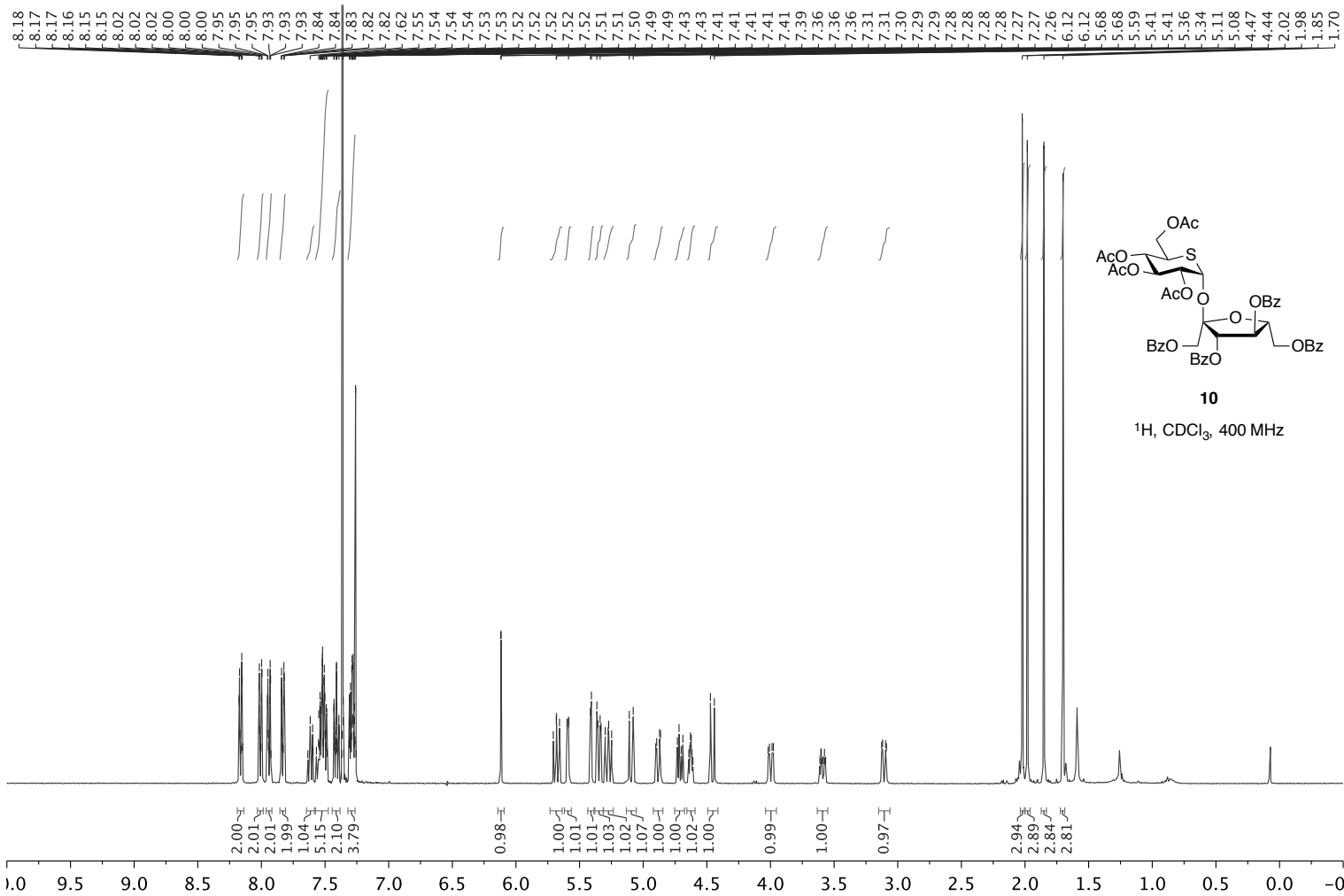
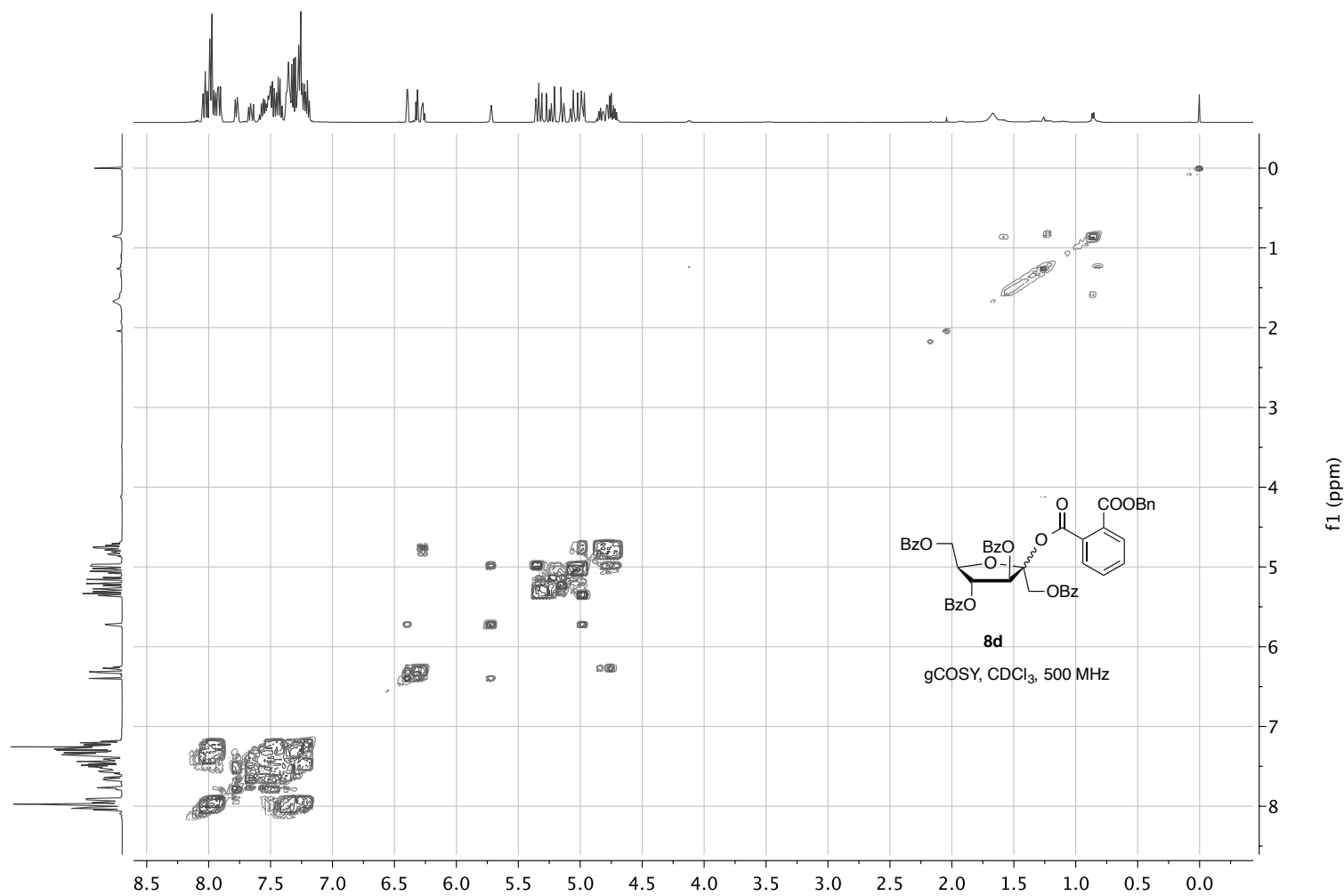


8b

gCOSY, C_6D_6 , 500 MHz

f1 (ppm)





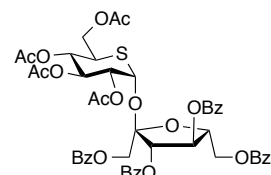
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169.37
169.24
166.08
166.06
165.11
164.53

133.71
133.66
133.57
133.22
130.28
129.70
129.65
129.41
129.37
128.79
128.72
128.59
128.42
128.40
128.30
109.00

83.09
81.00
79.06
77.32
77.00 CDCl₃
77.00 CDCl₃
76.68 CDCl₃
74.17
71.92
71.50
71.47
63.53
60.76
60.28

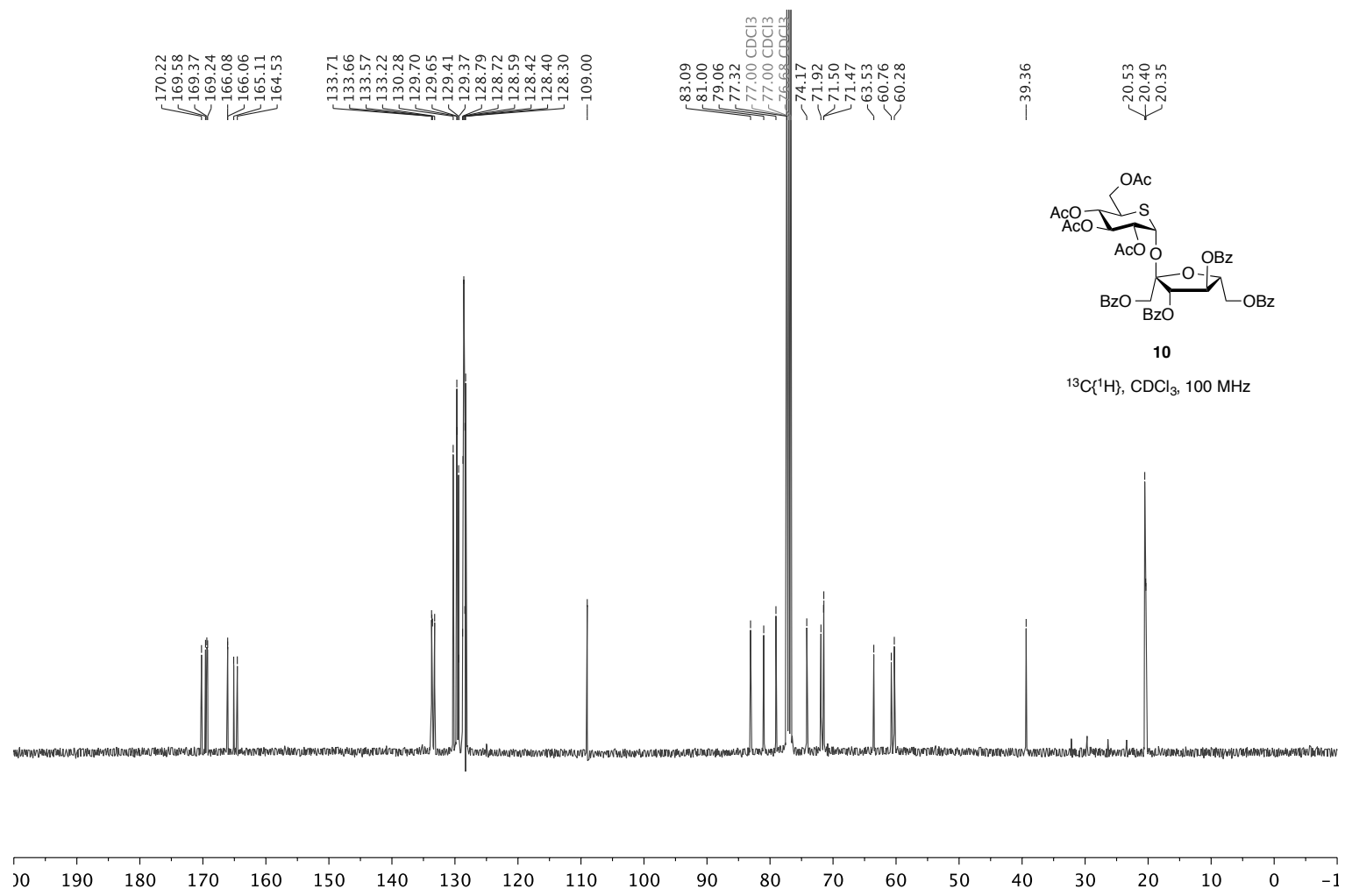
39.36

20.53
20.40
20.35



10

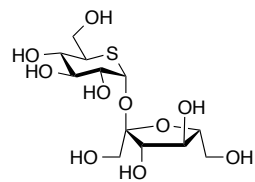
¹³C{¹H}, CDCl₃, 100 MHz



5.23
5.21

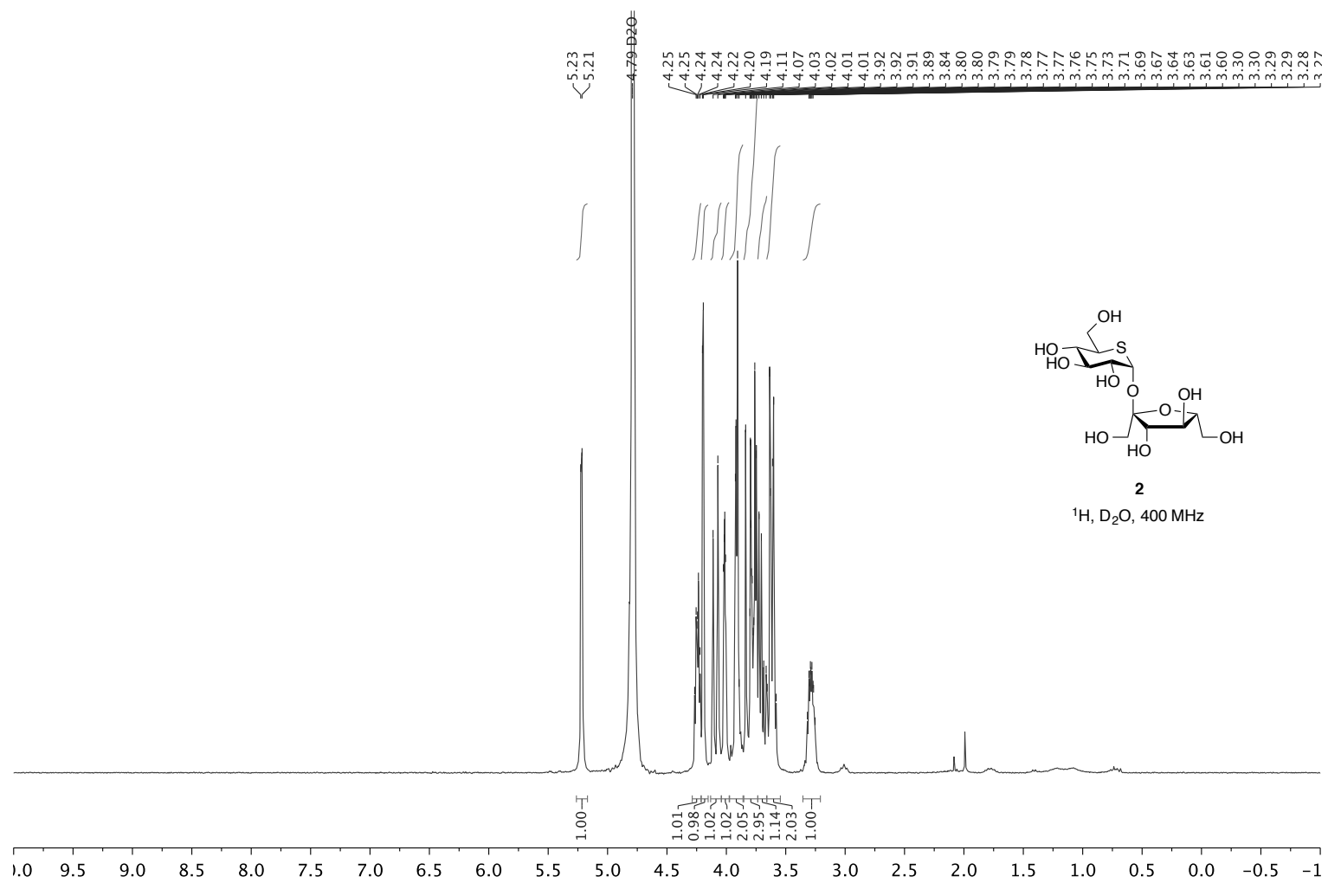
4.79
4.20

4.25
4.24
4.24
4.22
4.20
4.19
4.11
4.07
4.03
4.02
4.01
4.01
3.92
3.92
3.91
3.89
3.84
3.80
3.80
3.79
3.79
3.78
3.77
3.77
3.76
3.75
3.73
3.71
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3.30
3.30
3.29
3.29
3.28
3.27

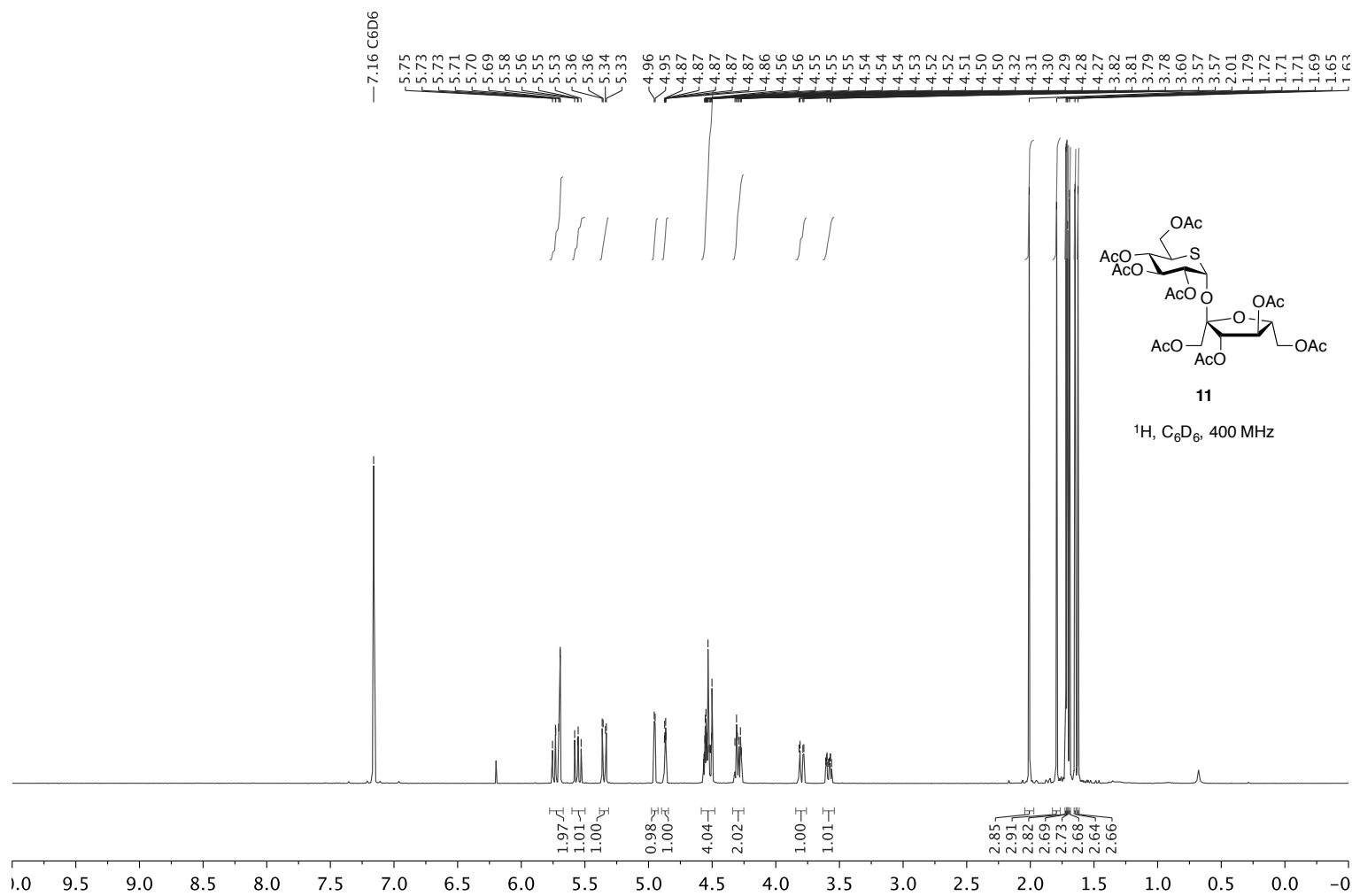
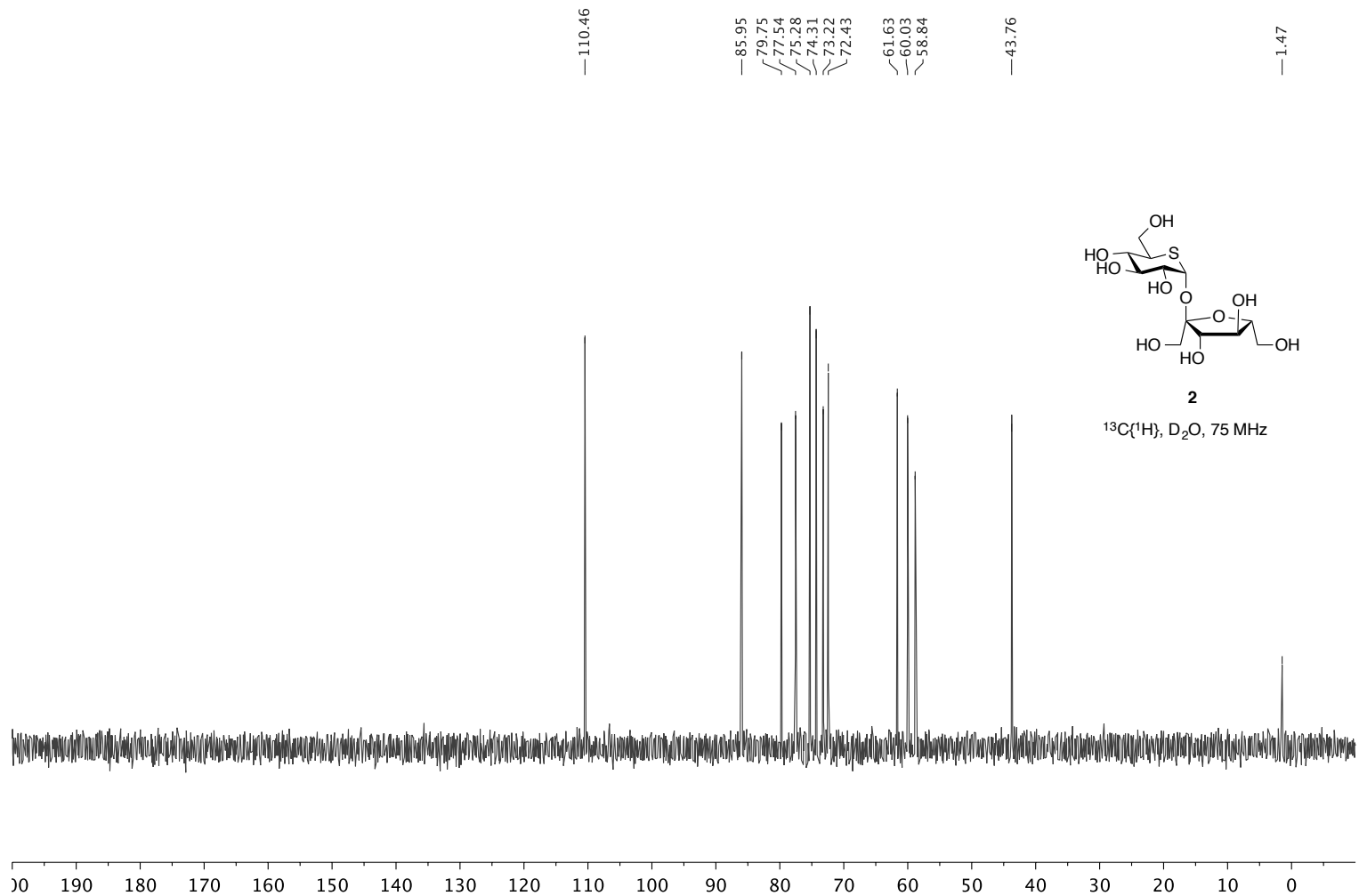


2

¹H, D₂O, 400 MHz



1.00
0.98
1.02
2.05
1.14
1.14
2.03
1.00



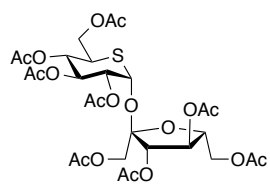
170.68
170.45
170.40
169.59
169.42
169.36
168.53

108.56

82.22
79.01
78.17
77.25 cdcl3
77.00 cdcl3
76.50 cdcl3
74.66
72.09
71.44
71.02
63.31
61.25
59.42

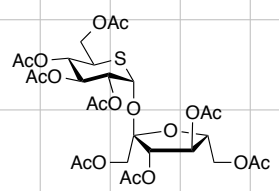
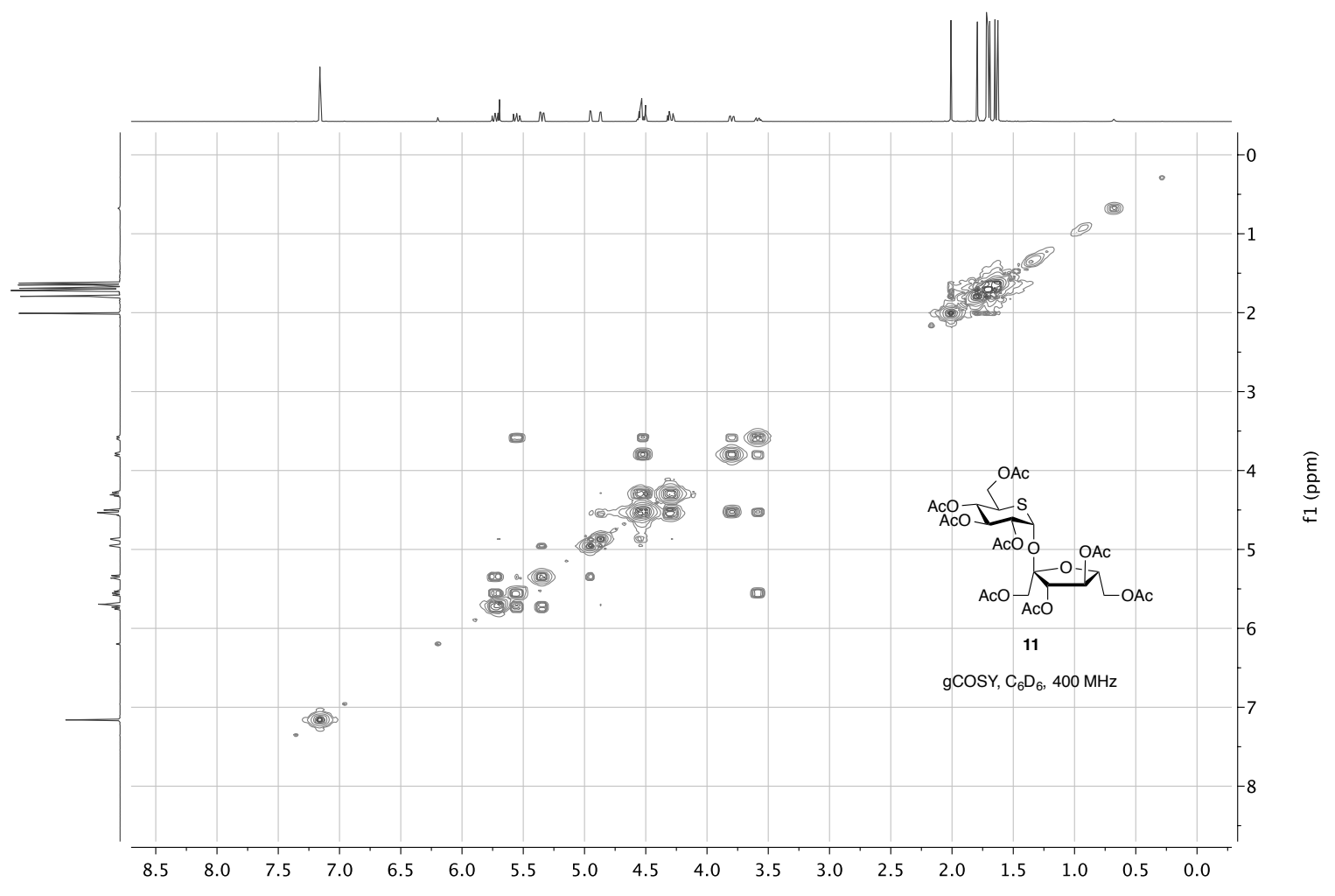
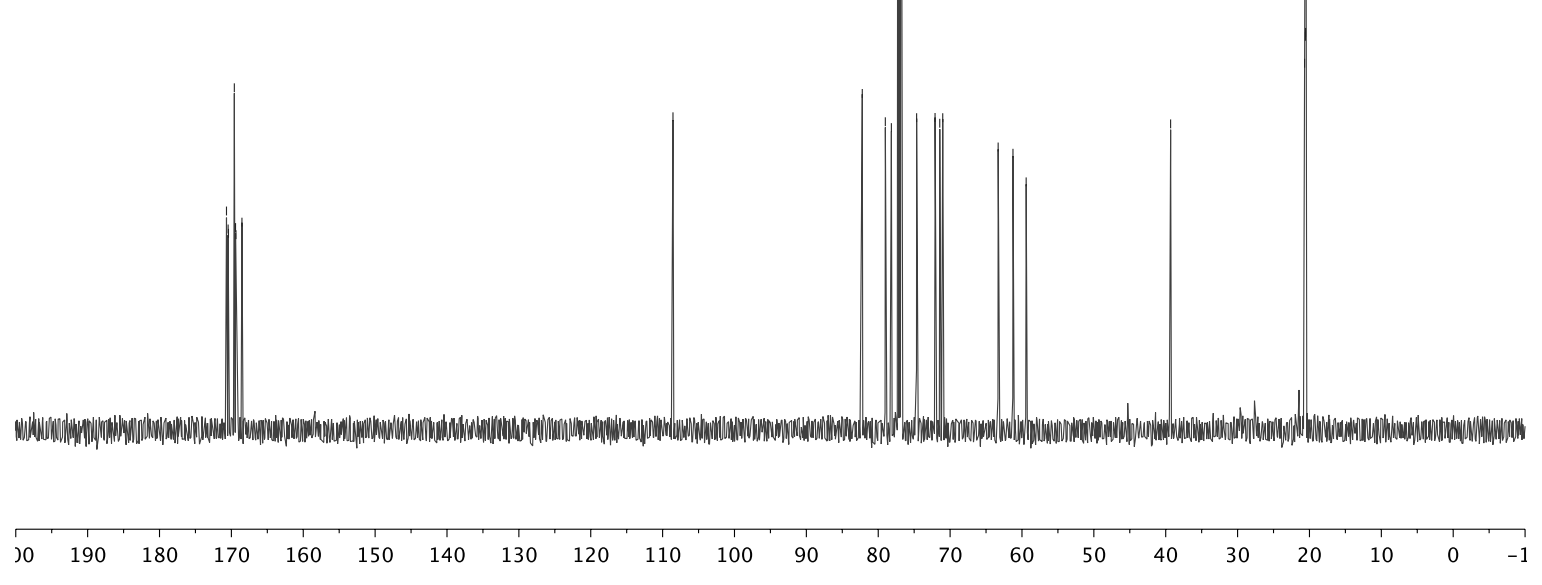
39.32

20.68
20.63
20.62
20.56
20.54
20.51
20.50



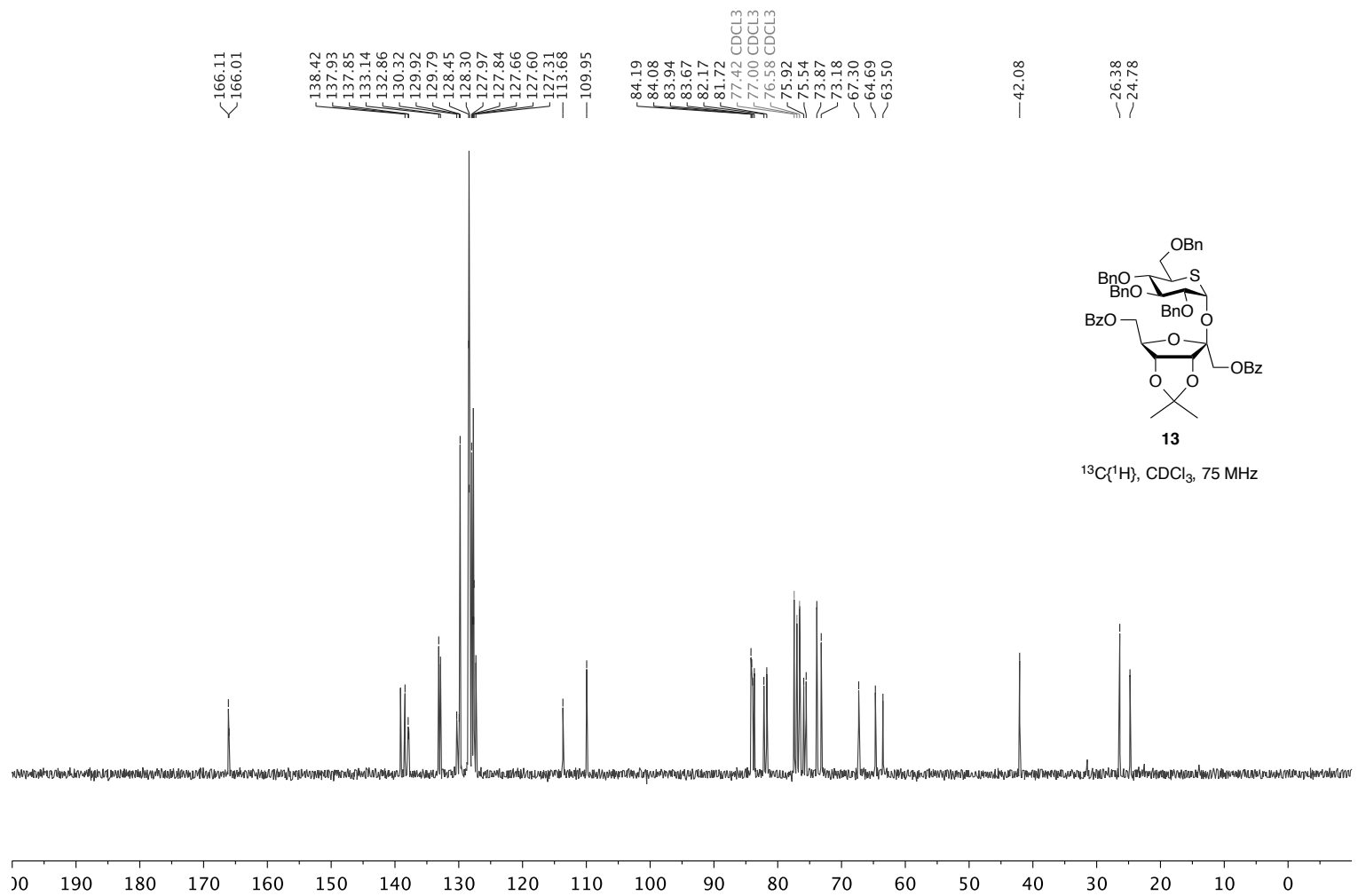
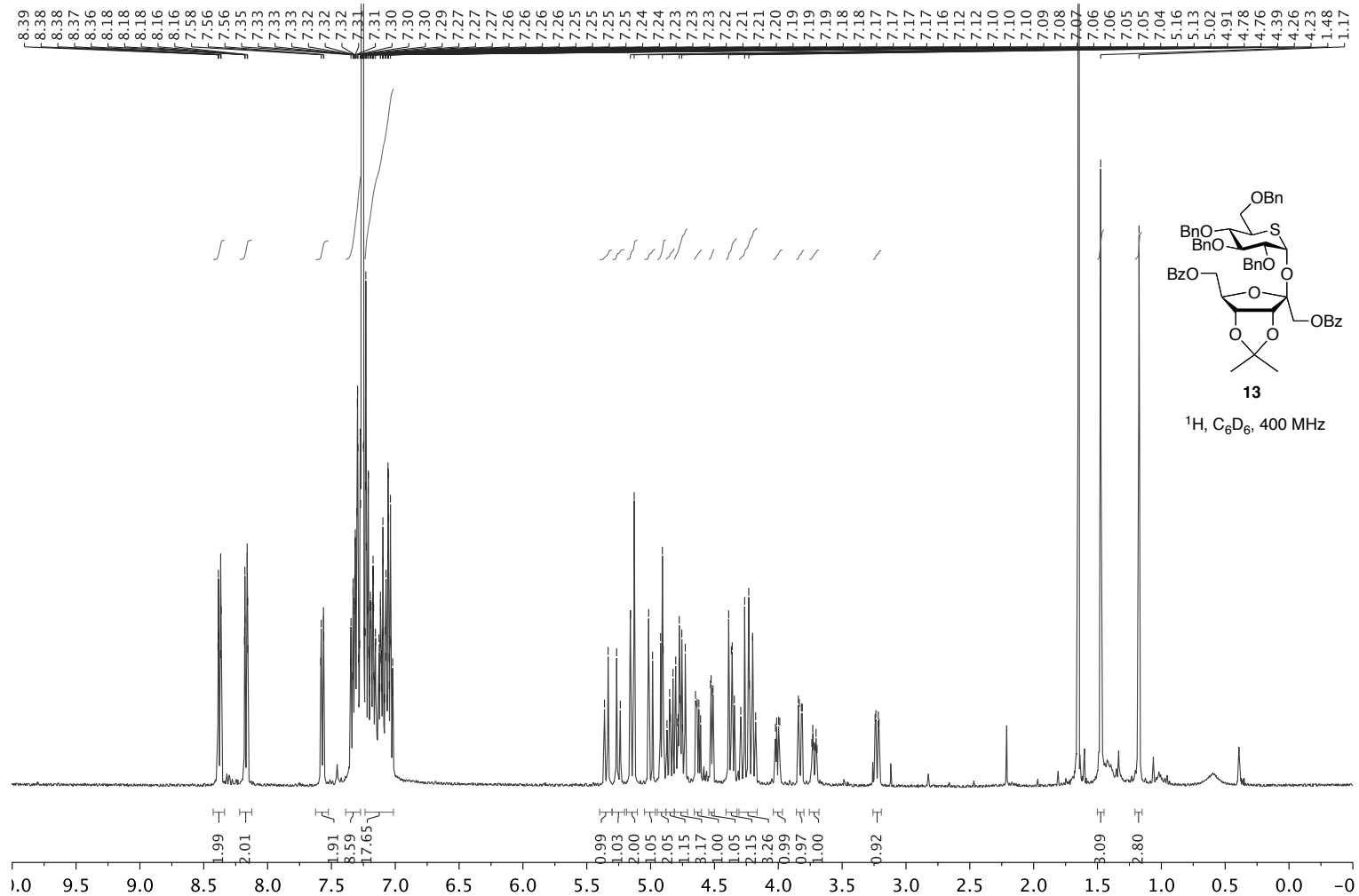
11

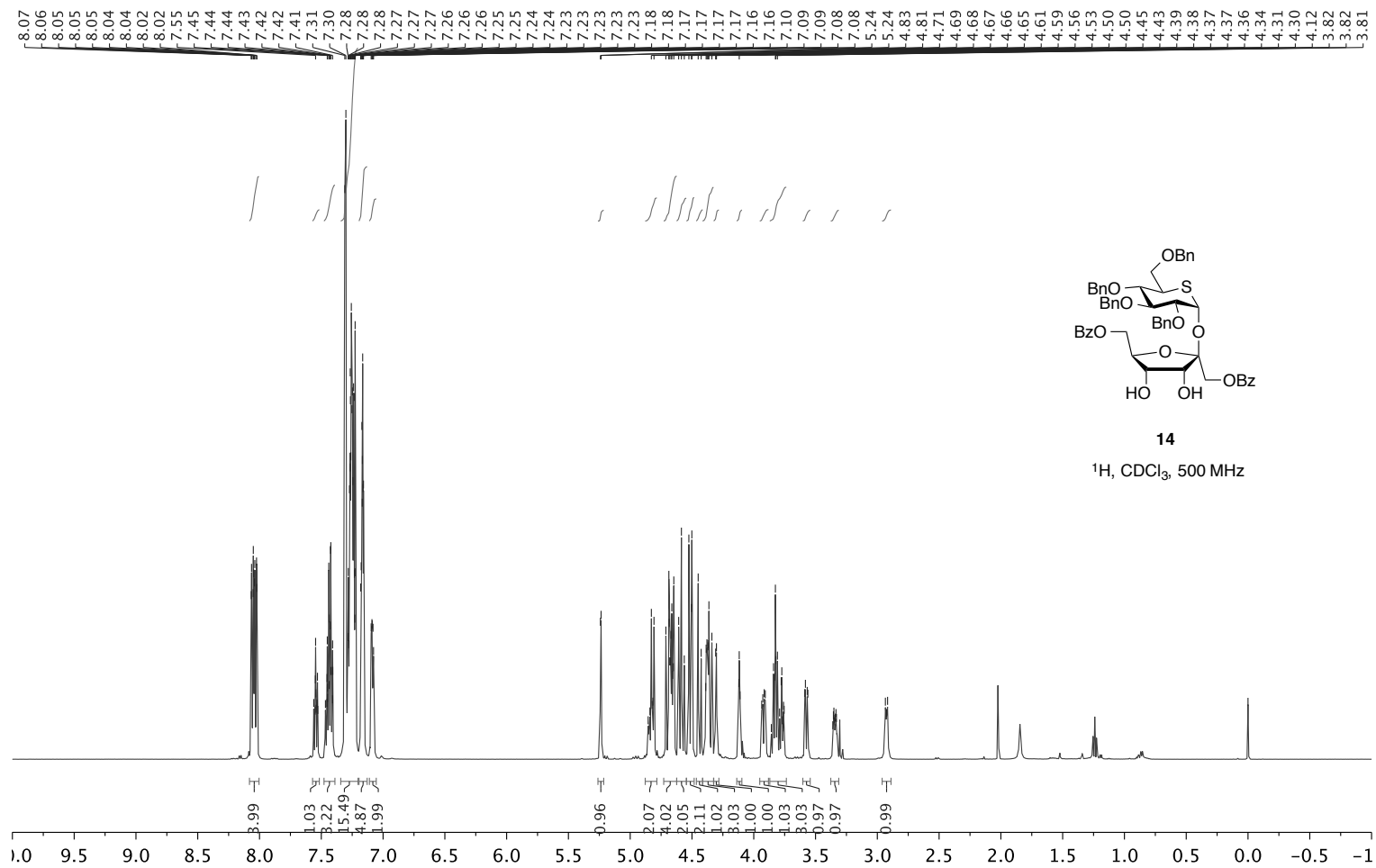
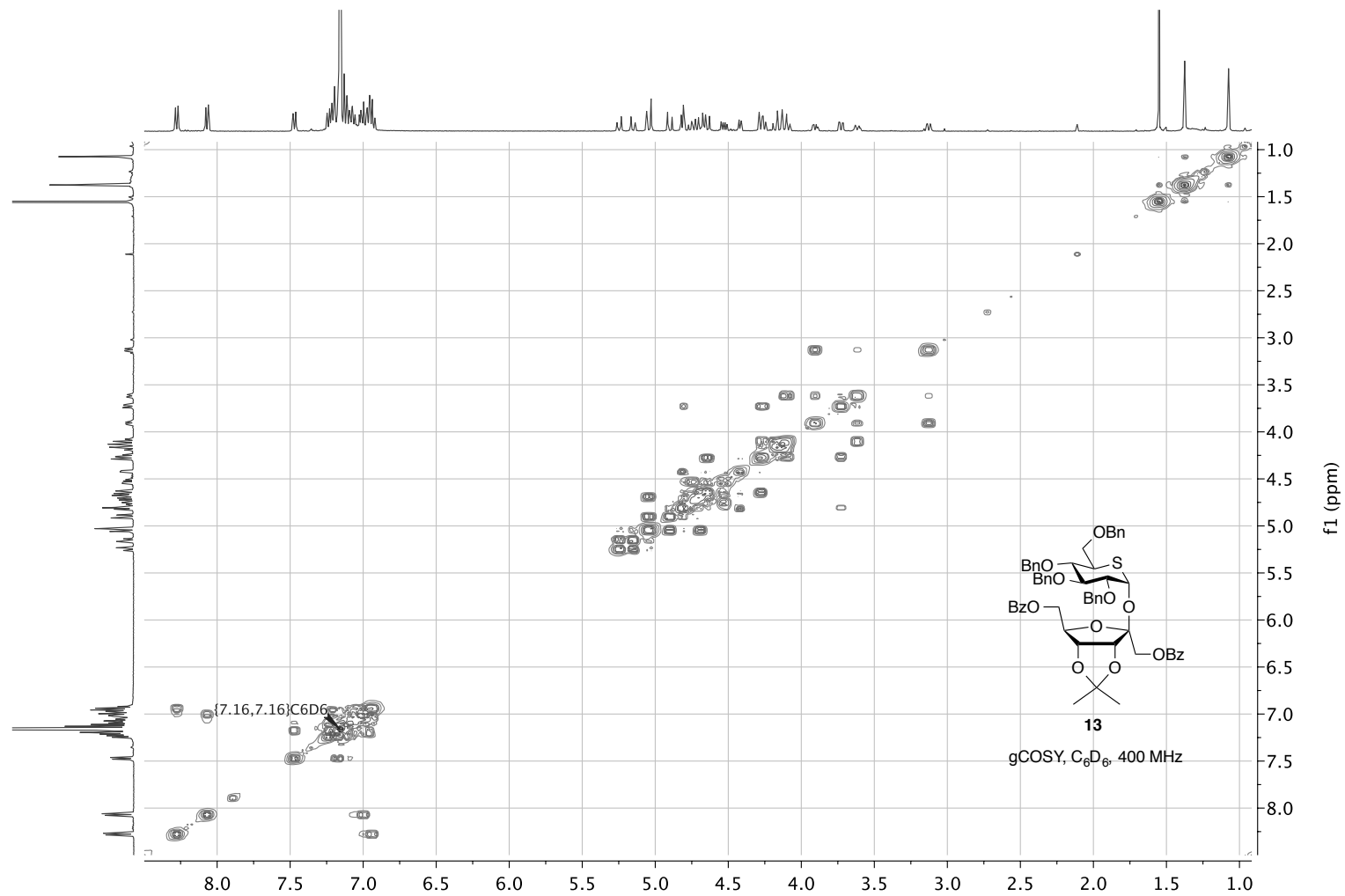
$^{13}\text{C}\{^1\text{H}\}$, CDCl_3 , 125 MHz



11

gCOSY, C_6D_6 , 400 MHz

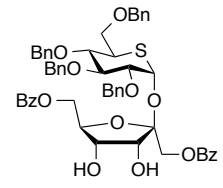




167.24
166.46
138.82
138.16
137.74
137.71
133.25
133.06
129.84
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129.54
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127.63
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127.29
107.64

83.97
83.44
82.03
81.77
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77.00 cdd13
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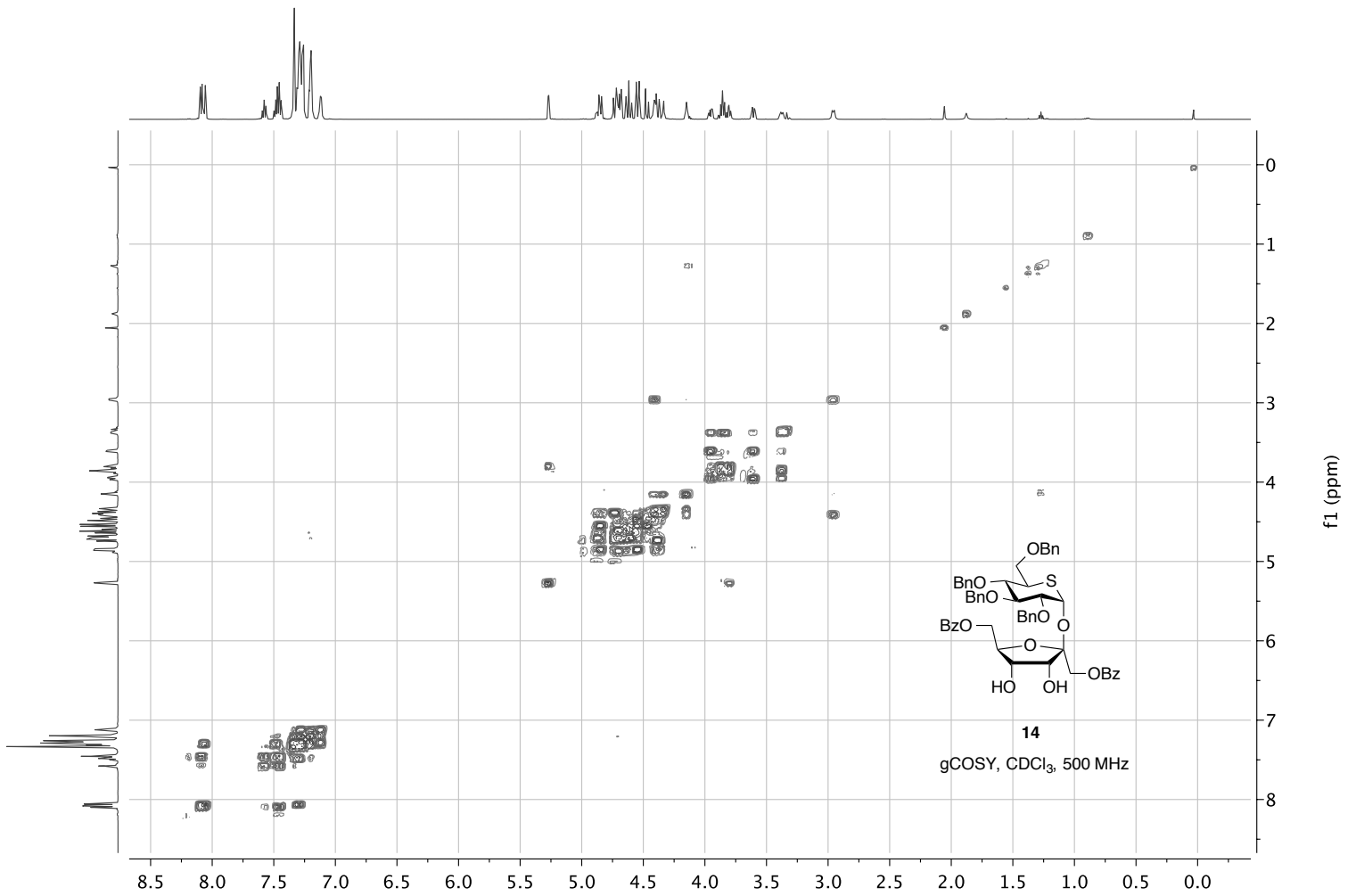
41.94

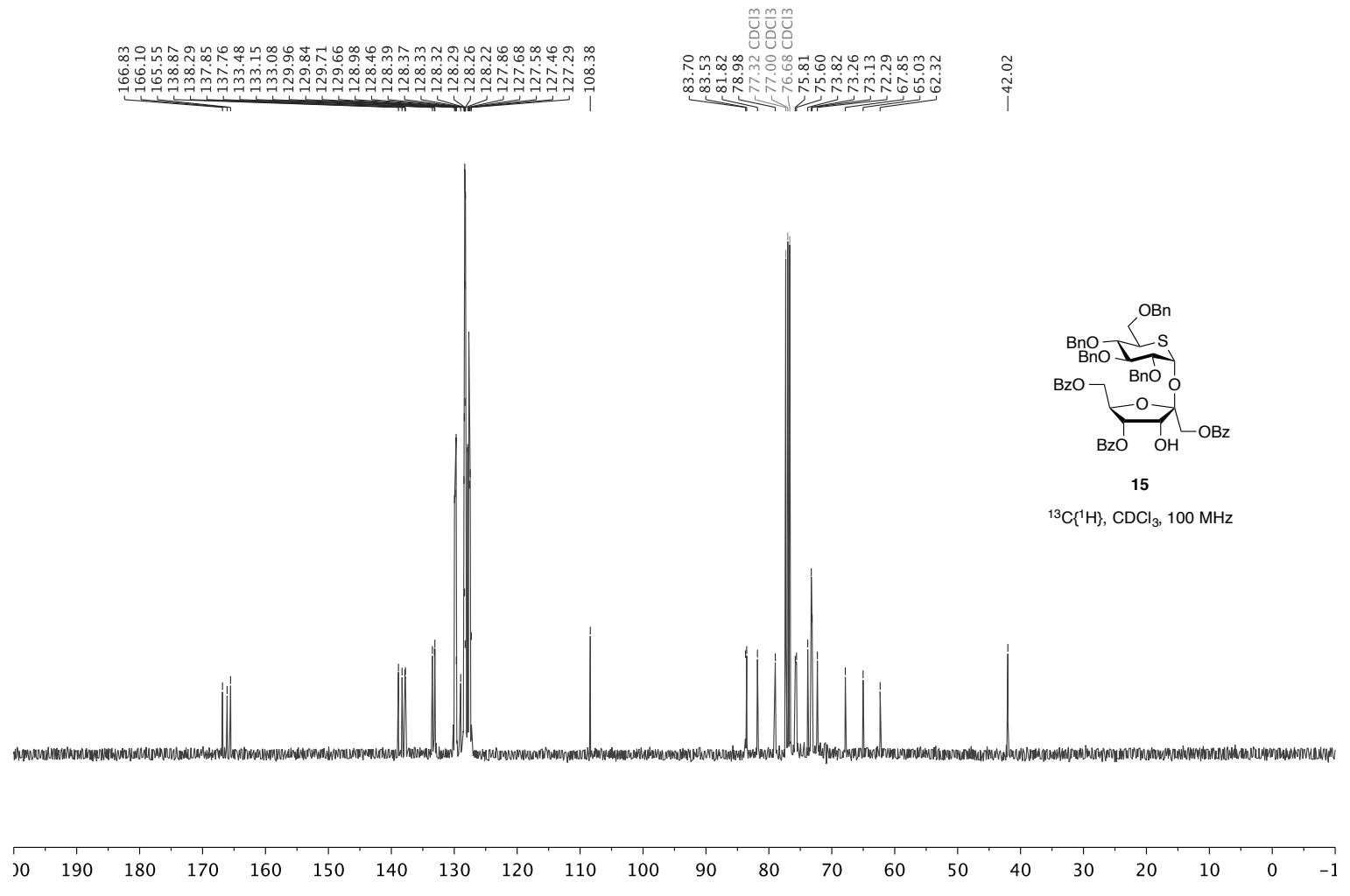
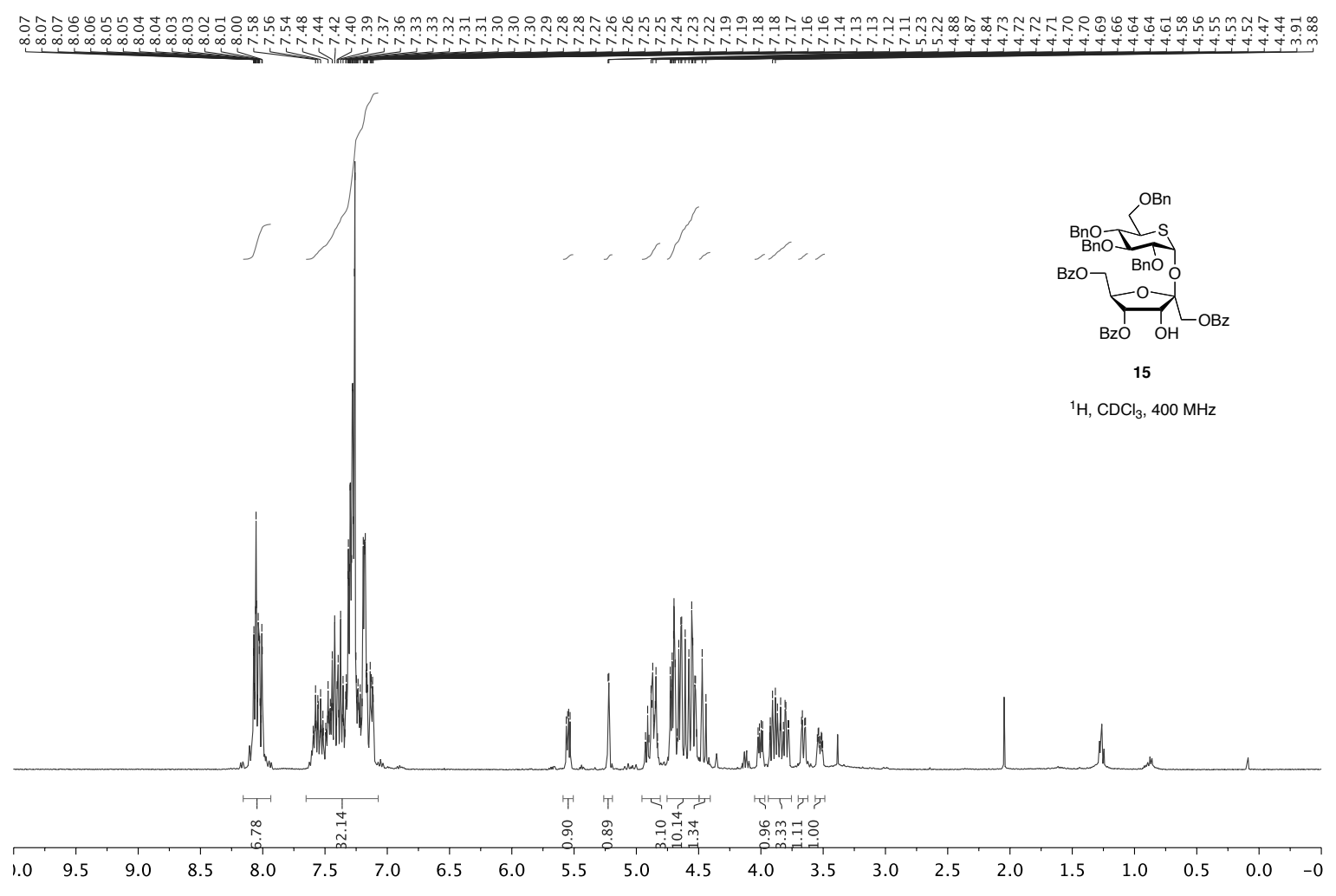


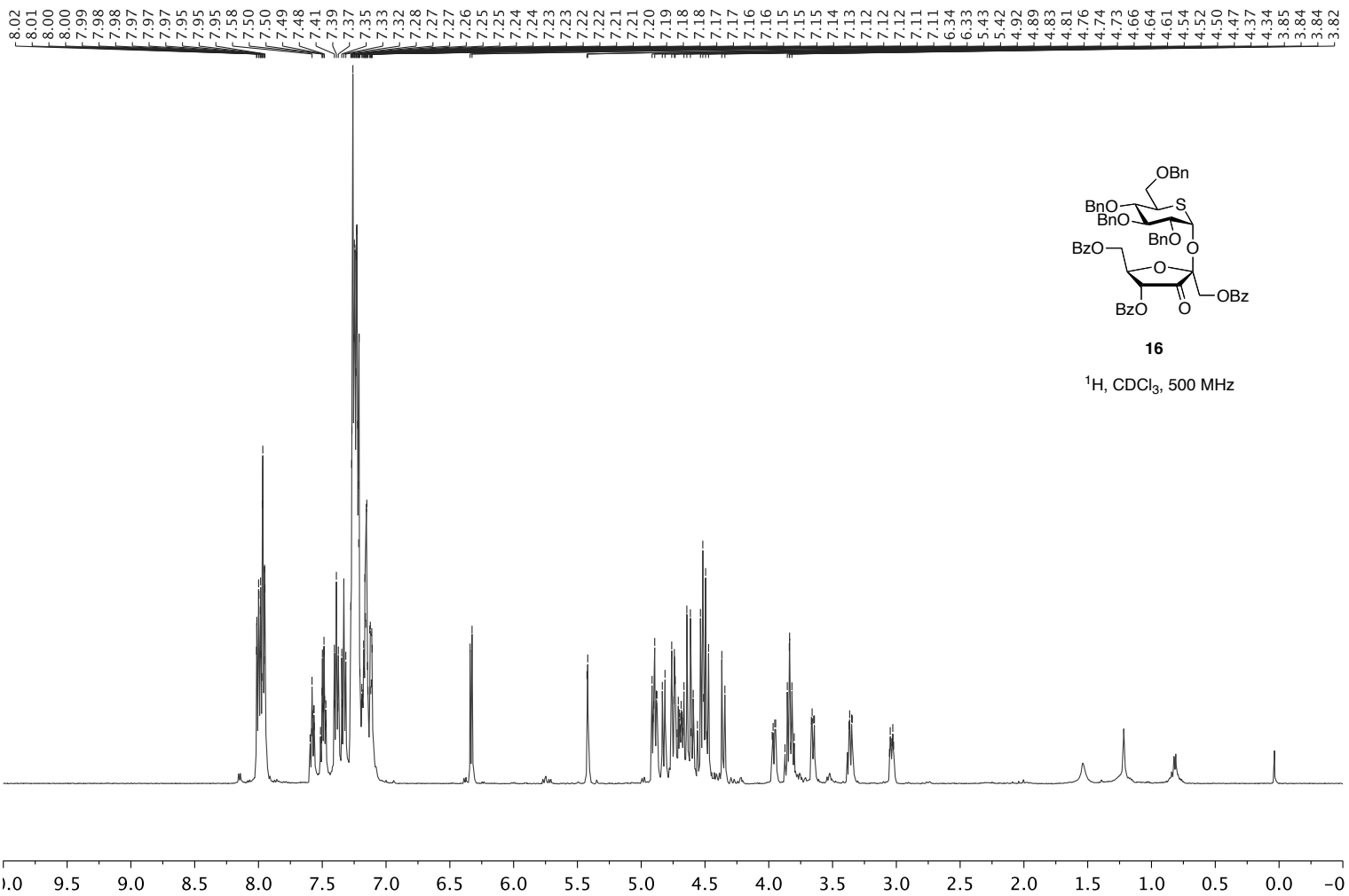
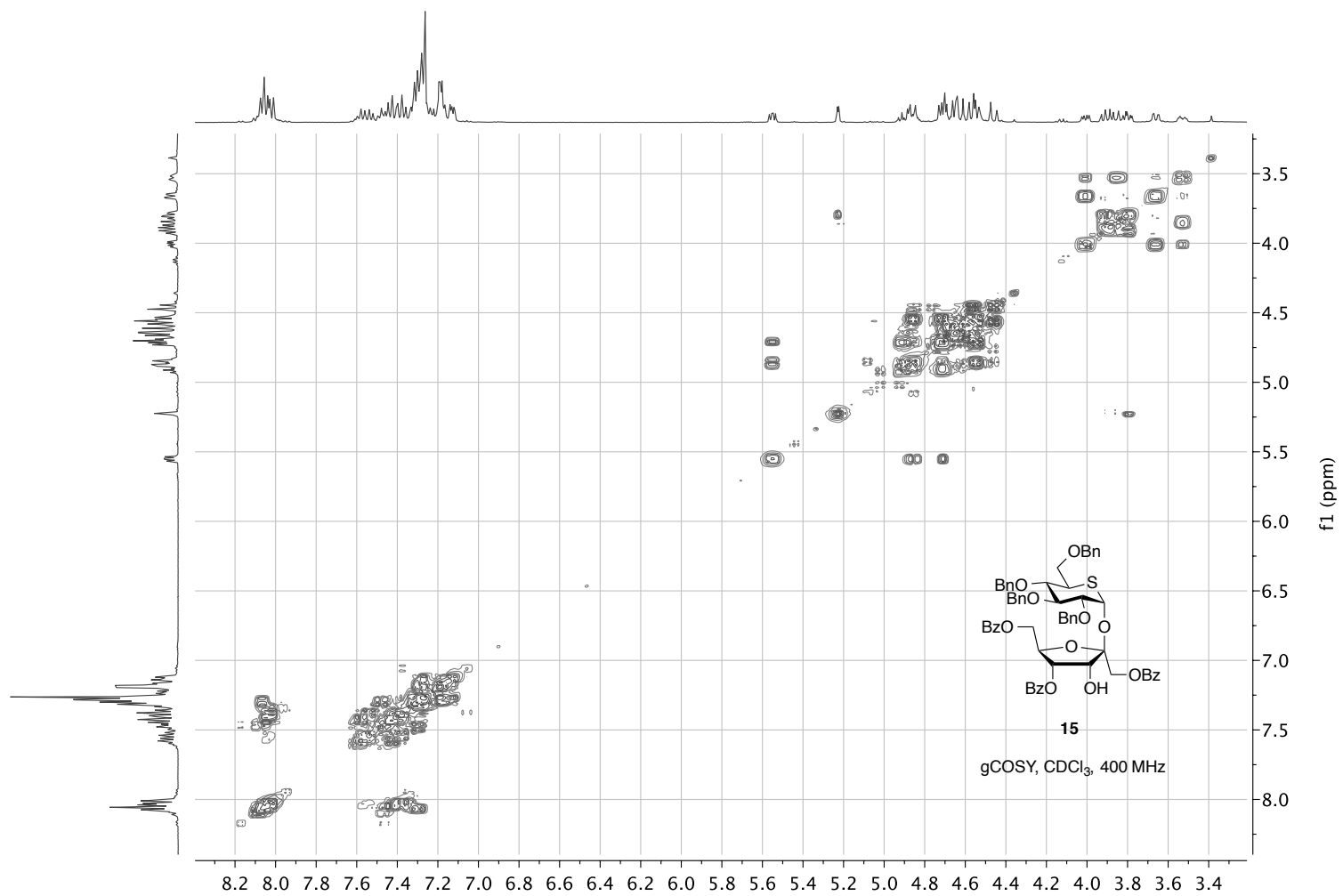
14

$^{13}\text{C}\{^1\text{H}\}$, CDCl_3 , 125 MHz

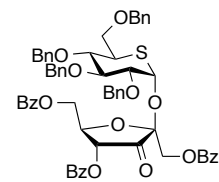
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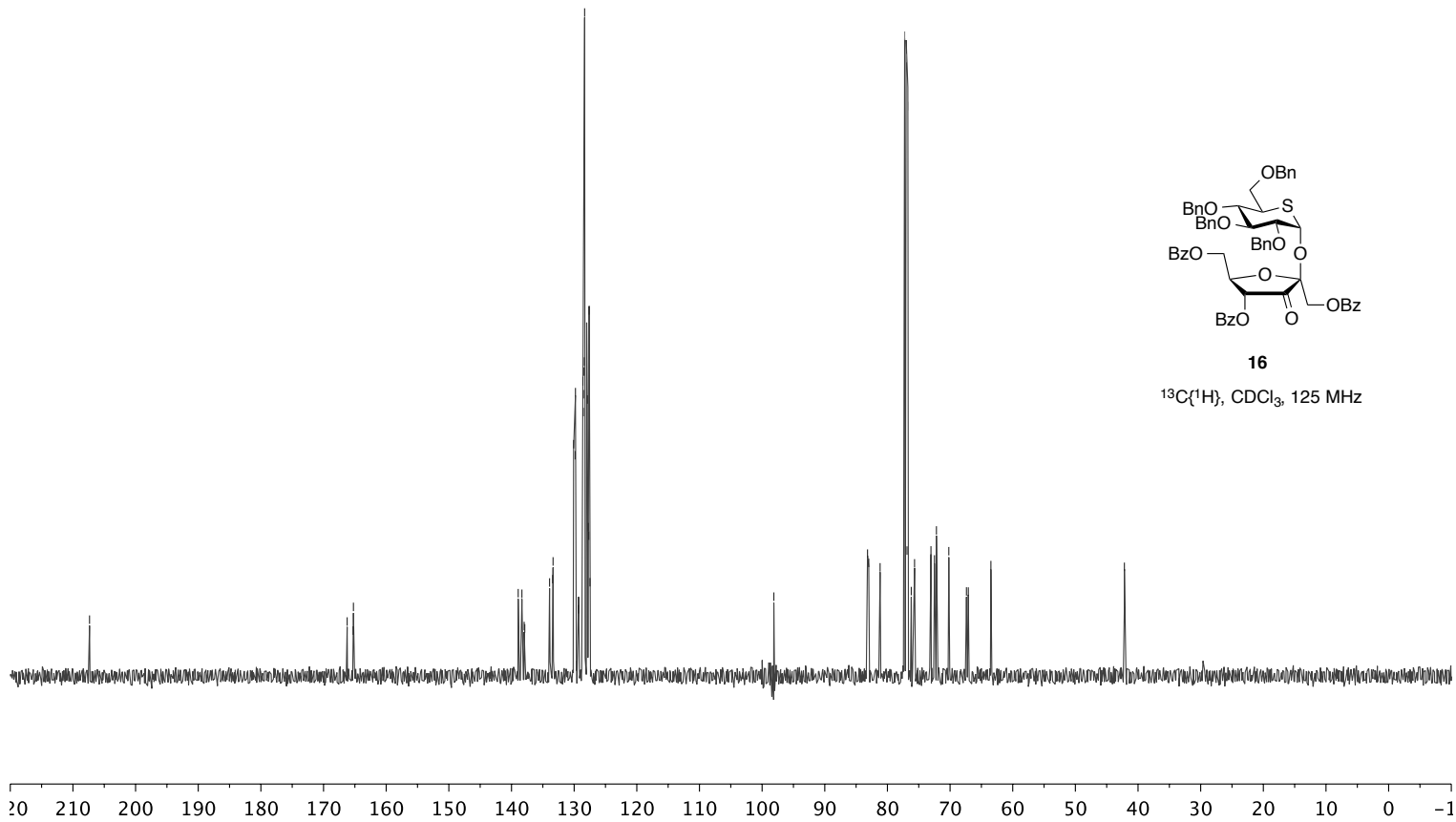


166.23
165.28
165.23
138.93
138.34
137.98
137.88
133.93
133.43
133.37
130.09
129.84
129.79
129.31
128.61
128.55
128.53
128.41
128.36
128.33
127.90
127.75
127.67
127.60
127.47
98.13
83.18
82.98
81.17
77.25 CDCl₃
77.00 CDCl₃
76.87
76.74 CDCl₃
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75.67
73.05
72.49
72.18
70.20
67.39
63.48



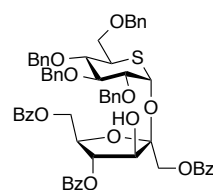
16

¹³C{¹H}, CDCl₃, 125 MHz



8.07
8.06
8.05
8.04
8.03
8.03
7.98
7.98
7.96
7.96
7.57
7.53
7.48
7.44
7.43
7.41
7.38
7.37
7.35
7.34
7.32
7.30
7.29
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7.28
7.27
7.26
7.26
7.26
7.25
7.24
7.23
7.23
7.22
7.22
7.21
7.21
7.21
7.20
7.20
7.16
7.15
7.14
7.14
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5.47
4.88
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4.75
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4.62
4.61
4.59
4.57
4.56
4.55
4.54
4.52
4.50
4.45
4.42
3.90
3.88
3.87
3.85
3.75
3.75
3.73

Integration values: 1.00, 0.99, 1.06, 3.11, 2.07, 2.05, 1.09, 2.05, 1.01, 1.04, 1.03, 1.03, 1.02



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¹H, CDCl₃, 500 MHz

