Supporting Information

Synthesis of Sialidase-Resistant Oligosaccharide and Antibody Glycoform Containing α2,6-Linked 3F^{ax}-Neu5Ac.

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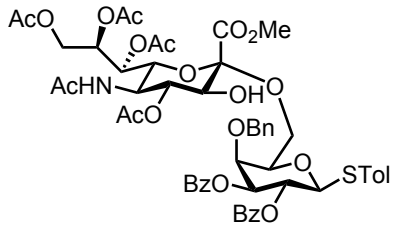
General Information. All reactions were carried out under an inert atmosphere unless mentioned otherwise, and standard syringe–septa techniques were followed. Solvents were purchased from commercial sources and used without further purification. Pulverized molecular sieves 4Å (EMD Millipore) were grounded in powder and activated before use. The progress of all the reactions was monitored by TLC, using TLC glass plates precoated with silica gel 60 F254 (Merck KGaA). The TLC was visualized by UV light (254 nm), *p*-anisaldehyde and/or ceric ammonium molybdate stains. Column chromatography was performed on Across silica gel (particle size 0.035– 0.070 mm, 60Å). ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded with Bruker AVIII-600, DRX-500, AV-400, DPX-400, AVANCE 500 AV and AVANCE 600 spectrometers at 25 ^{o}C and chemical shifts were measured in δ (ppm) with residual solvent peaks as internal standards (δ, ppm: 7.24 ($CHCl_3$), 4.80 (H_2O) in ^{1}H NMR; and 77 ($CDCl_3$) in ^{13}C NMR). Coupling constants (*J*) were measured in Hz. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad). High-resolution mass spectra (HRMS) were recorded on an Agilent LC/MSD TOF mass spectrometer by electrospray ionization time-of-flight (ESI-TOF) reflectron experiments. The single crystal X-ray diffraction studies were carried out on a Bruker D8 Platinum-^{135} CCD diffractometer equipped with Cu K_α radiation (λ = 1.5478). HPLC measurements were performed on a Hitachi HPLC D-7000 system. RRV measurements were recorded using a normal-phase ZORBAX RX-SIL, 5μm, 4.6 x 250mm (Colloidal Silica, Agilent Technologies) using the solvent system EtOAc/hexanes with 1 mL/min flow rate, and visualized at 254 nm.

Experimental Procedures and Characterization Data

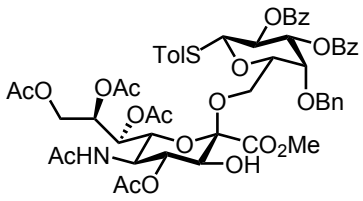
Synthesis of 3F^{ax}-Neu5Ac-Terminated Bi-Antennary *N*-Glycan



***p*-Tolyl [methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-5-deoxy-D-erythro-*α*-L-gluco-non-2-ulopyranosonate]-(2→6)-2,3-di-*O*-benzoyl-4-*O*-benzyl-1-thio-*β*-D-galactopyranoside 6*α*.** mixture of acceptor **3** (1.05 g, 1.80 mmol, 1 equiv.) and donor **5** (1.02 mg, 1.80 mmol, 1 equiv.) in anhydrous toluene (60 mL) was stirred under argon atmosphere for 10 min. Then, the reaction mixture was cooled to -50 °C and dry Na_2HPO_4 (1.07 g, 7.54 mmol, 4.2 equiv.) was added, followed by addition of AgOTf (692 mg, 2.69 mmol, 1.5 equiv., in toluene 18 mL) with stirring. Upon completion (TLC indicated the disappearance of starting materials after 24 hrs)., the reaction mixture was diluted with EtOAc (80 mL), washed with 20% aq. $Na_2S_2O_3$ (10 mL), satd. aq. $NaHCO_3$ (5 mL) and brine (5 mL), then the organic layer was dried over $MgSO_4$, filtered, and concentrated. The obtained residue was purified by silica gel column chromatography using acetone/toluene (3:7) as eluent to give compound **6** (*α*:*β* = 13:1) as a white powder (680 mg, 35%) along with recovered acceptor **3** (670 mg, 99% brsm).

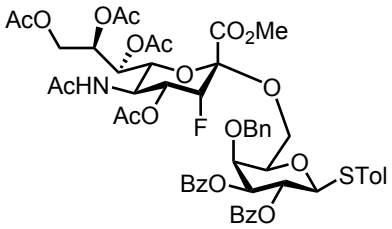
α-anomer **6α**: R_f = 0.36 (silica gel, $CHCl_3$:MeOH = 20:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.96-7.94 (m, 2H, Ar-H), 7.91-7.90 (m, 2H, Ar-H), 7.50-7.47 (m, 2H, Ar-H), 7.40-7.39 (m, 2H, Ar-H), 7.37-7.32 (m, 5H, Ar-H), 7.25-7.18 (m, 4H, Ar-H), 7.06-7.04 (m, 2H, Ar-H), 5.81 (dd, *J* = 10.2. 9.6 Hz, 1H), 5.59 (d, *J* = 10.2 Hz, 1H), 5.38 (dd, *J* = 9.0, 3.0 Hz, 1H), 5.35-5.32 (m, 1H), 5.25 (dd, *J* = 10.2, 9.6 Hz, 1H), 5.24 (d, *J* = 7.8, 2.4 Hz, 1H), 4.92 (d, *J* = 9.6 Hz, 1H, C1-H_β), 4.71 (d, *J* = 12.0 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.49 (dd, *J* = 10.8, 1.8 Hz, 1H), 4.30 (dd, *J* = 12.6, 3.0 Hz, 1H), 4.26 (ddd, *J* = 10.2, 10.2, 10.2 Hz, 1H), 4.20 (d, *J* = 3.0 Hz, 1H), 4.10 (dd, *J* = 10.2, 7.2 Hz, 1H), 4.04 (dd, *J* = 12.6, 6.6 Hz, 1H), 4.00 (dd, *J* = 6.6, 6.6 Hz, 1H), 3.86 (d, *J* = 9.6 Hz, 1H), 3.82-3.73 (m, 2H), 3.75 (s, 3H, -CH_3), 2.30 (s, 3H, -CH_3), 2.09 (s, 3H, -CH_3), 2.07 (s, 3H, -CH_3), 2.06 (s, 3H, -CH_3), 1.96 (s, 3H, -CH_3), 1.89 (s, 3H, -CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.6,

170.6, 170.3, 170.1, 169.5, 168.5, 165.8, 165.1, 138.0, 137.9, 133.4, 133.1, 129.8, 129.7, 129.6, 128.9, 128.6, 128.4, 128.3, 128.2, 127.7, 127.6, 100.3, 86.6, 75.9, 74.5, 73.7, 73.2, 73.1, 72.5, 68.8, 68.3, 63.1, 62.5, 52.8, 48.4, 23.1, 21.2, 20.9, 20.8, 20.7, 20.7; HRMS (ESI-TOF) m/e : Calcd for $C_{54}H_{59}NO_{20}SNa$ $[M+Na]^+$: 1096.3243 found 1096.3241.



***p*-Tolyl [methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-5-deoxy-D-erythro-*β*-L-gluco-non-2-ulopyranosonate]-(2→6)-2,3-di-*O*-benzoyl-4-*O*-benzyl-1-thio-*β*-D-galactopyranoside 6β.**

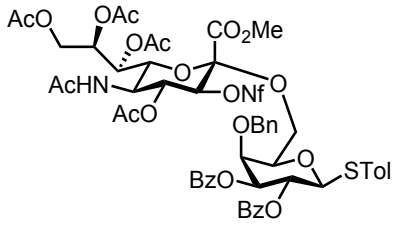
β-anomer **6β** R_f = 0.42 (silica gel, $CHCl_3$:MeOH = 20:1); ^1H NMR (600 MHz, $CDCl_3$): δ 7.94-7.92 (m, 4H, Ar-H), 7.50-7.47 (m, 2H, Ar-H), 7.43-7.40 (m, 6H, Ar-H), 7.37-7.31 (m, 5H, Ar-H), 7.13-7.12 (m, 2H, Ar-H), 5.81 (dd, *J* = 10.2. 10.2 Hz, 1H), 5.51 (dd, *J* = 10.2, 3.0 Hz, 1H), 5.22 (ddd, *J* = 6.0, 6.0, 3.0 Hz, 1H), 5.14 (d, *J* = 13.2 Hz, 1H), 5.07 (dd, *J* = 6.0, 2.4 Hz, 1H), 4.90 (d, *J* = 10.2 Hz, 1H, C1-H_β), 4.66-4.62 (m, 2H), 4.55 (dd, *J* = 12.6, 2.4 Hz, 1H), 4.29 (d, *J* = 1.8 Hz, 1H), 4.14 (dd, *J* = 7.8, 7.2 Hz, 1H), 4.08 (ddd, *J* = 10.8, 10.8, 10.8 Hz, 1H), 3.98 (dd, *J* = 12.6, 6.6 Hz, 1H), 3.92-3.88 (m, 2H), 3.85-3.77 (m, 3H), 3.83 (s, 3H, $-CH_3$), 3.53 (dd, *J* = 10.8, 2.4 Hz, 1H), 2.32 (s, 3H, $-CH_3$), 2.26 (s, 3H, $-CH_3$), 2.07 (s, 3H, $-CH_3$), 2.04 (s, 3H, $-CH_3$), 1.97 (s, 3H, $-CH_3$), 1.68 (s, 3H, $-CH_3$); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.4, 170.6, 170.3, 169.8, 169.8, 166.6, 165.8, 165.2, 139.2, 138.4, 133.5, 133.4, 133.1, 129.9, 129.8, 129.5, 128.9, 128.5, 128.3, 127.2, 126.0, 99.6, 86.9, 76.0, 75.5, 74.3, 73.1, 72.5, 71.7, 70.3, 68.4, 67.2, 62.1, 62.0, 53.3, 47.5, 22.9, 21.5, 21.2, 20.8, 20.7, 20.7; HRMS (ESI-TOF) m/e : Calcd for $C_{54}H_{59}NO_{20}S$ $[M+H]^+$: 1074.3424 found 1074.3458.



***p*-Tolyl [methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-3-fluoro-D-erythro- *α*-L-manno-non-2-ulopyranosonate]-(2→6)-2,3-di-*O*-benzoyl-4-*O*-benzyl-1-thio-*β*-D-galactopyranoside 4.** To a solution of compound **6α** (500 mg, 0.47 mmol, 1 equiv.) in toluene (5 mL) in a screw-capped vial containing a stirring bar were added DBU (0.28 mL, 1.86 mmol, 4 equiv.), perfluoro-1-butanesulfonyl fluoride (0.33 mL, 1.86 mmol, 4 equiv.) and TASF (256 mg, 0.93 mmol, 2 equiv.). The reaction vial was sealed and stirred at 40 °C. After 24 h, the reaction was treated with the additional amounts of DBU (0.28 mL, 1.86 mmol, 4 equiv.), perfluoro-1-butanesulfonyl fluoride (0.33 mL, 1.86 mmol, 4 equiv.) and TASF (256 mg, 0.93 mmol, 2 equiv.), then stirred at 40 °C for another 24 h. The reaction mixture was directly loaded onto the silica gel column chromatography and eluted with acetone/toluene (7:3). The disaccharide **4** was obtained as a light yellow powder (300 mg, 60%) along with perfluoro-1-butanesulfonyl compound **7** as a light yellow powder (50 mg, 8%).

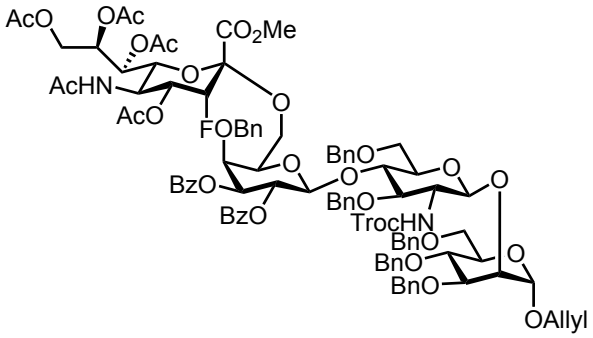
***Synthesis of the disaccharide* 4 *from* 7**: To a compound **7** (730 mg, 0.54 mmol, 1 equiv.) dissolved in toluene (7 mL) in a screw-capped vial containing a stirring bar were added DBU (0.64 mL, 4.31 mmol, 8 equiv.) and perfluoro-1-butanesulfonyl fluoride (0.77 mL, 4.31 mmol, 8 equiv.). The container was sealed and stirred at 40 °C for 15 days. The reaction mixture was directly loaded onto the silica gel column chromatography and eluted with acetone/toluene (7:3) as eluent disaccharide **4** was isolated as a light yellow powder (282 mg, 49%) along with perfluoro-1-butanesulfonyl compound **7** as a light yellow powder (267 mg, 77% brsm). R_f = 0.43 (silica gel, acetone/toluene = 2:3); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.95-7.93 (m, 2H, Ar-H), 7.87-7.85 (m, 2H, Ar-H), 7.48-7.44 (m, 2H, Ar-H), 7.41-7.39 (m, 2H, Ar-H), 7.35-7.33 (m, 2H, Ar-H), 7.31-7.29 (m, 2H, Ar-H), 7.25-7.24 (m, 2H, Ar-H), 7.21-7.19 (m, 2H, Ar-H), 7.16-7.14 (m, 1H, Ar-H), 7.04-7.03 (m, 2H, Ar-H), 5.79 (dd, *J* = 10.2. 9.6 Hz, 1H), 5.49 (ddd, *J* = 9.0, 5.4, 2.4 Hz, 1H), 5.42 (dd, *J* = 10.2, 3.0 Hz, 1H), 5.31-5.28 (m, 2H), 5.20 (dd, *J* = 27.0, 11.4 Hz, 1H, sia-C4-H), 5.01 (dd, *J* = 51.6, 1.8 Hz, 1H, sia-C3-H), 4.97 (d, *J* = 10.2 Hz, 1H, C1-H_β), 4.66 (d, *J* = 11.4 Hz, 1H), 4.58 (d, *J* = 11.4 Hz, 1H), 4.37 (dd, *J* = 12.6, 2.4 Hz, 1H), 4.28-4.26 (m, 2H), 4.17 (dd, *J* = 12.6, 5.4 Hz, 1H), 4.09-4.05 (m, 2H), 3.98 (dd, *J* = 10.2, 6.0 Hz, 1H), 3.74 (dd, *J* = 10.2, 8.4 Hz, 1H), 3.72 (s, 3H, -CH_3), 2.29 (s, 3H, -CH_3), 2.17 (s, 3H, -CH_3), 2.16 (s, 3H, -CH_3), 2.09 (s, 3H, -CH_3), 1.98 (s, 3H, -CH_3), 1.91 (s, 3H, -CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.9, 170.7, 170.4, 170.2, 169.8, 165.6, 165.3, 138.3, 137.6, 133.2, 133.0, 132.6, 129.8, 129.8, 129.7, 129.5, 129.3, 129.1,

128.4, 128.3, 128.1, 127.5, 127.3, 98.2 (d, J = 16.4 Hz, 1C, sia-C2), 87.5 (d, J = 193.0 Hz, 1C, sia-C3), 86.4, 76.2, 75.6, 74.6, 74.0, 71.4, 69.2, 69.0, 68.5, 68.0, 67.3, 63.4, 62.5, 53.2, 45.5, 23.4, 21.2, 21.2, 20.8, 20.7, 20.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ -215.9; HRMS (ESI-TOF) m/e : Calcd for $C_{54}H_{58}FNO_{19}SNa$ $[M+Na]^+$: 1098.3200 found 1098.3212.



***p*-Tolyl [methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-5-deoxy-3-*O*-(perfluoro-1-butane) sulfonyl-D-erythro-*α*-L-gluco-non-2-ulopyranosonate]-(2→6)-2,3-di-*O*-benzoyl-4-*O*-benzyl-1-thio-*β*-D-galactopyranoside 7.**

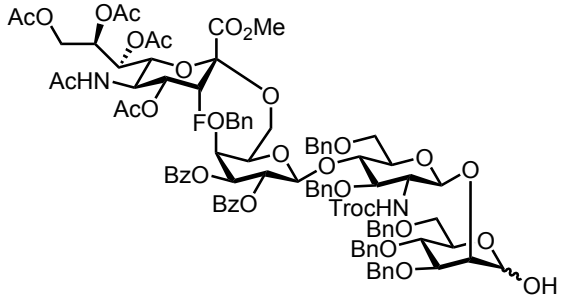
R_f = 0.59 (silica gel, acetone:toluene = 2:3); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.95-7.94 (m, 2H, Ar-H), 7.90-7.89 (m, 2H, Ar-H), 7.49-7.45 (m, 2H, Ar-H), 7.40-7.39 (m, 2H, Ar-H), 7.36-7.30 (m, 4H, Ar-H), 7.27-7.26 (m, 2H, Ar-H), 7.25-7.18 (m, 3H, Ar-H). 7.04-7.03 (m, 2H, Ar-H), 5.82 (dd, J = 10.2. 9.6 Hz, 1H), 5.62-5.38 (m, 4H), 5.26 (d, J = 9.0 Hz, 1H), 4.96-4.94 (m, 2H, C1-H_β), 4.70-4.64 (m, 3H), 4.35-4.30 (m, 1H), 4.22-4.20 (m, 2H), 4.09 (dd, J = 9.6, 6.0 Hz, 1H), 4.02 (dd, J = 12.6, 6.0 Hz, 1H), 3.98 (dd, J = 6.6, 6.0 Hz, 1H), 3.93 (dd, J = 10.2, 7.2 Hz, 1H), 3.76 (s, 3H, -CH_3), 2.29 (s, 3H, -CH_3), 2.17 (s, 3H, -CH_3), 2.09 (s, 3H, -CH_3), 2.06 (s, 3H, -CH_3), 1.94 (s, 3H, -CH_3), 1.90 (s, 3H, -CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.6, 170.2, 170.1, 169.3, 167.0, 165.7, 165.2, 138.1, 137.7, 133.2, 133.0, 132.5, 129.8, 129.7, 129.7, 129.5, 129.1, 129.0, 128.4, 128.3, 128.1, 128.0, 127.5, 127.4, 97.8, 86.5, 83.4, 75.7, 74.6, 74.2, 72.6, 70.0, 68.4, 67.9, 66.5, 64.5, 62.4, 53.1, 49.0, 23.0, 21.1, 20.9., 20.7, 20.6, 20.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ -126.2, -126.2, -121.5, -121.5, -110.4, -110.4, -81.0, -80.9, -80.9; HRMS (ESI-TOF) m/e : Calcd for $C_{58}H_{58}F_9NO_{22}S_2Na$ $[M+Na]^+$: 1378.2640 found 1378.2644.



Allyl [methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-3-fluoro-D-erythro-*α*-L-manno-non-2-ulopyranosonate]-(2→6)-[2,3-di-*O*-benzoyl-4-*O*-benzyl-1-*β*-D-galactopyranosyl]-(1→4)-[3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranosyl]-(1→2)-3,4,6-tri-*O*-benzyl-*α*-D-mannopyranoside 9. A mixture of acceptor **8** (1.04 g, 1.03 mmol, 1 equiv.), donor **4** (1.39 g, 1.29 mmol, 1.25 equiv.) and activated pulverized 4 Å MS (0.70 g) in anhydrous CH_2Cl_2 (7 mL) were stirred under argon atmosphere for 1 h. Then, the reaction mixture was cooled to −40 °C and NIS (465 mg, 2.06 mmol, 2 equiv.) was added, followed by addition of TfOH (0.5 M in Et_2O, 0.62 mL, 0.31 mmol, 0.3 equiv.) with stirring. Upon completion (TLC indicated the disappearance of starting materials after ~2 hrs)., the reaction mixture was quenched with Et_3N (0.4 mL) and filtered through a pad of Celite. The filtrate was diluted with CH_2Cl_2 (30 mL), washed with 20% aq. $Na_2S_2O_3$ (10 mL), satd. aq. $NaHCO_3$ (15 mL) and brine (8 mL). The separated organic layer was dried over $MgSO_4$, and concentrated. The obtained residue was purified by silica gel column chromatography using acetone/toluene (1:2) as eluent to give compound **9** as a white powder (1.30 g, 64%).

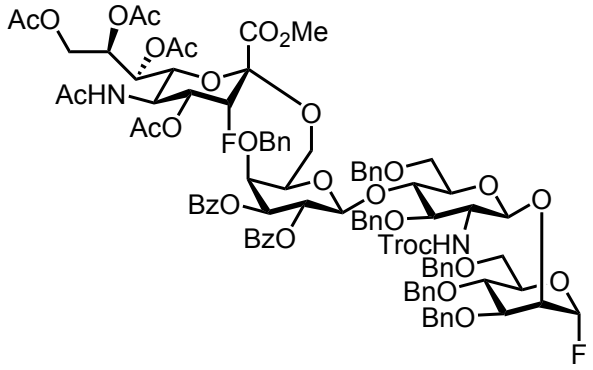
R_f = 0.51 (silica gel, acetone:toluene = 2:3); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.90-7.88 (m, 4H, Ar-H), 7.48-7.45 (m, 2H, Ar-H), 7.34-7.22 (m, 24H, Ar-H), 7.18-7.13 (m, 10H, Ar-H), 5.85-5.78 (m, 2H), 5.47-5.44 (m, 1H), 5.35-5.32 (m, 4H), 5.24-5.16 (m, 2H), 5.11 (dd, *J* = 10.2, 1.2 Hz, 1H), 5.06-4.97 (m, 3H, C1-H_β, sia-C3-H), 4.85-4.73 (m, 4H, C1-H_α, C1-H_β), 4.70-4.54 (m, 6H), 4.53-4.42 (m, 4H), 4.33-4.26 (m, 2H), 4.23-4.18 (m, 3H), 4.14-4.04 (m, 3H), 3.97-3.93 (m, 1H), 3.89-3.81 (m, 5H), 3.73-3.58 (m, 10H), 3.45-3.43 (m, 1H), 3.32-3.30 (m, 1H), 2.16 (s, 3H, -CH_3), 2.13 (s, 3H, -CH_3), 2.10 (s, 3H, -CH_3), 2.01 (s, 3H, -CH_3), 1.92 (s, 3H, -CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.7, 170.6, 170.4, 170.2, 169.8, 165.6, 165.4, 165.4, 165.1, 153.8, 138.8, 138.6, 138.5, 138.2, 138.2, 138.1, 133.7, 133.2, 133.1, 133.1, 130.8, 130.0, 129.8, 129.6, 129.4, 129.0, 128.4,

128.3, 128.3, 128.2, 128.2, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.6, 127.6, 127.5, 127.4, 127.3, 127.2, 125.2, 117.1, 100.0, 98.3, 98.2, 96.9, 95.6, 87.4 (d, J = 193.2 Hz, 1C, sia-C3), 77.9, 75.0, 74.7, 74.6, 74.5, 74.2, 74.1, 73.9, 73.4, 73.3, 73.1, 73.0, 72.4, 71.9, 71.4, 70.9, 70.9, 69.5, 69.2, 69.1, 69.0, 68.0, 67.9, 67.2, 62.9, 62.3, 57.2, 53.2, 45.5, 23.3, 21.0, 20.7, 20.7, 20.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ -215.6; HRMS (ESI-TOF) m/e : Calcd for $C_{100}H_{108}Cl_3FN_2O_{31}Na$ $[M+Na]^+$: 1979.5878 found 1979.5889.



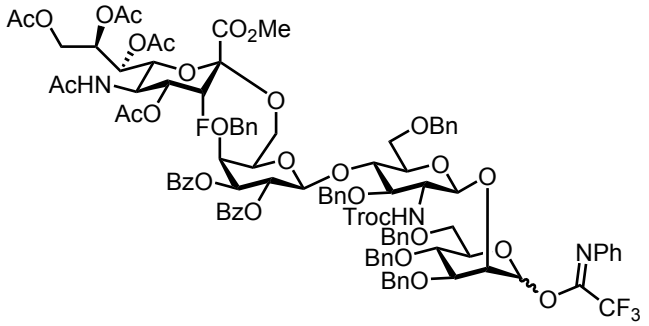
[Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-3-fluoro-D-erythro-*α*-L-manno-non-2-ulopyranosonate]-(2→6)-[2,3-di-*O*-benzoyl-4-*O*-benzyl-1-*β*-D-galactopyranosyl]-(1→4)-[3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranosyl]-(1→2)-3,4,6-tri-*O*-benzyl-*α*-D-mannopyranoside 10. To a stirred solution of tetrasaccharide **9** (578 mg, 0.30 mmol, 1 equiv.) in acetic acid (6.0 mL, acetic acid/water, 10:1 = *v/v*) was added CH_3COONa (121 mg, 1.48 mmol, 5 equiv.) followed by addition of $PdCl_2$ (105 mg, 0.59 mmol, 2 equiv.) at room temperature. After 20 hrs, when TLC indicated the disappearance of starting material, the reaction mixture was diluted with ethyl acetate (20 mL) and poured into satd. aq. $NaHCO_3$ (20 mL). The aqueous layer was extracted with ethyl acetate (2×10 mL), and the combined organic phases were dried over $MgSO_4$, and concentrated. The obtained residue was purified by silica gel column chromatography using acetone/hexane (2:3) as eluent to give compound **10** as a white powder (465 mg, 82%). R_f = 0.23 (silica gel, acetone:hexane = 2:3); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.90-7.87 (m, 4H, Ar-H), 7.48-7.45 (m, 2H, Ar-H), 7.34-7.20 (m, 24H, Ar-H), 7.19-7.12 (m, 10H, Ar-H), 5.80-5.75 (m, 1H), 5.45-5.43 (m, 1H), 5.33-5.28 (m, 3H), 5.21-4.89 (m, 5H , man-C1-H_α, man-C1-H_β, C1-H_β, sia-C3-H), 4.84-4.30 (m, 15H, C1-H_β), 4.27-3.79 (m, 12H), 3.78-3.43 (m, 12H), 2.13-2.12 (m, 6H, -2CH_3), 2.09-2.08 (m, 3H, -CH_3), 2.02-2.00 (m, 3H, -CH_3), 1.91 (br, 3H, -CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ170.8, 170.7, 170.7, 170.7, 170.6, 170.5, 170.4, 170.3, 170.3, 170.2, 169.9, 169.8, 165.6, 165.6, 165.4, 165.2, 165.2, 154.0,

138.6, 138.5, 138.3, 138.2, 138.1, 133.2, 133.1, 129.8, 129.6, 129.5, 129.0, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.2, 128.1, 128.0, 127.9, 127.9, 127.7, 127.7, 127.6, 127.5, 127.5, 127.4, 127.4, 127.3, 100.0, 99.5, 98.3, 98.2, 98.1, 95.8, 95.7, 92.3, 87.5 (d, J = 193.2 Hz, 1C, sia-C3), 76.1, 74.8, 74.7, 74.6, 74.6, 74.3, 74.2, 74.2, 73.9, 73.8, 73.3, 73.2, 73.1, 73.1, 72.7, 72.6, 72.4, 72.3, 71.6, 71.4, 71.2, 70.9, 70.8, 69.9, 69.5, 69.3, 69.2, 69.1, 69.0, 68.1, 68.0, 67.2, 67.1, 63.0, 62.3, 62.2, 62.1, 53.3, 53.3, 45.5, 45.4, 26.3, 23.3, 21.1, 20.8, 20.7, 20.7, 20.6, 20.6 ; ^{19}F NMR (376 MHz, $CDCl_3$): δ -215.2, -215.7; HRMS (ESI-TOF) m/e : Calcd for $C_{97}H_{104}Cl_3FN_2O_{31}Na$ $[M+Na]^+$: 1939.5565 found 1939.5619.



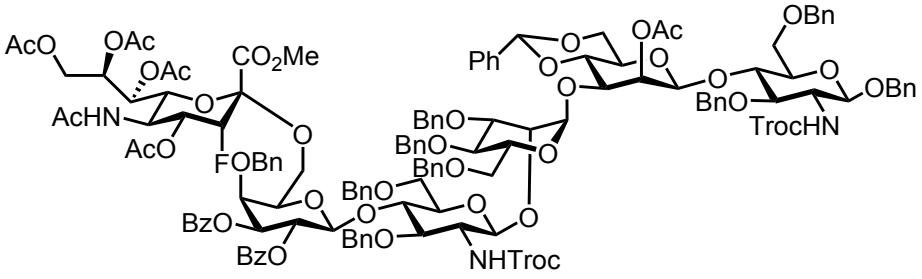
[Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-3-fluoro-D-erythro-*α*-L-manno-non-2-ulopyranosonate]-(2→6)-[2,3-di-*O*-benzoyl-4-*O*-benzyl-1-*β*-D-galactopyranosyl]-(1→4)-[3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranosyl]-(1→2)-3,4,6-tri-*O*-benzyl-*α*-D-mannopyranosyl fluoride 11. To a well-stirred solution of hemiacetal **10** (395 mg, 0.21 mmol, 1 equiv.) in anhydrous CH_2Cl_2 (12 mL) was added DAST (81.6 μL, 0.62 mmol, 3 equiv.) at -20 ^oC. The reaction mixture was vigorously stirred until TLC indicated the disappearance of starting material (3 h). Upon completion, the reaction mixture was diluted with CH_2Cl_2 (10 mL) and washed with satd. aq. $NaHCO_3$ (5 mL) and brine (4 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated. The obtained residue was purified by silica gel column chromatography using acetone/hexane (3:4) as eluent to give compound **11** as a white powder (289 mg, 73%). R_f = 0.32 (silica gel, acetone:hexane = 3:4); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.89-7.88 (m, 4H, Ar-H), 7.47-7.45 (m, 2H, Ar-H), 7.33-7.22 (m, 22H, Ar-H), 7.17-7.12 (m, 12H, Ar-H), 5.78 (dd, J = 10.2, 7.8 Hz, 1H), 5.53-5.40 (m, 2H), 5.33-5.29 (m, 3H, C1-H_α), 5.21 (dd, J = 27.6, 11.4 Hz, 1H, sia-C4-H), 5.00 (dd, J = 51.0, 1.8 Hz, 1H,

sia-C3-H), 5.00 (d, J = 7.8 Hz, 1H, C1-H_β), 4.94 (d, J = 11.4 Hz, 1H), 4.82-4.79 (m, 4H, C1-H_β), 4.75-4.72 (m, 1H), 4.68-4.59 (m, 3H), 4.58-4.54 (m, 2H), 4.50-4.48 (m, 2H), 4.30 (dd, J = 12.6, 3.0 Hz, 1H), 4.26 (d, J = 10.2 Hz, 1H), 4.23-4.15 (m, 4H), 4.08-4.04 (m, 2H), 3.95 (dd, J = 9.0, 8.4 Hz, 1H), 3.89-3.78 (m, 5H), 3.72-3.57 (m, 9H), 3.50-3.48 (m, 1H), 3.35 (d, J = 0.6 Hz, 1H) 2.14 (s, 3H, -CH_3), 2.12 (s, 3H, -CH_3), 2.09 (s, 3H, -CH_3), 2.00 (s, 3H, -CH_3), 1.91 (s, 3H, -CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.8, 170.7, 170.4, 170.2, 169.9, 165.6, 165.4, 165.2, 153.9, 138.2, 138.1, 137.8, 133.2, 133.1, 129.8, 129.6, 129.4, 129.0, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.6, 127.6, 127.4, 127.3, 127.3, 106.9, 105.4, 99.8, 99.2, 98.3, 98.2, 95.6, 87.5 (d, J = 192.7 Hz, 1C, sia-C3), 74.9, 74.8, 74.2, 74.0, 73.9, 73.8, 73.3, 73.2, 72.5, 71.4, 71.3, 70.9, 69.1, 69.1, 68.9, 68.0, 67.3, 62.8, 62.3, 56.9, 53.3, 45.6, 23.4, 21.1, 20.8 (2 C), 20.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ -138.6, -215.7; HRMS (ESI-TOF) m/e : Calcd for $C_{97}H_{103}Cl_3F_2N_2O_{30}Na$ $[M+Na]^+$: 1941.5521 found 1941.5521.



(*N*-Phenyl)-2,2,2-trifluoroacetimidate [methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl- 3,5-dideoxy-3-fluoro-D-erythro-*α*-L-manno-non-2-ulopyranosonate]-(2→6)-[2,3-di-*O*-benzoyl-4-*O*-benzyl-1-*β*-D-galactopyranosyl]-(1→4)-[3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranosyl]-(1→2)-3,4,6-tri-*O*-benzyl-D-mannopyranoside 12. To a well-stirred solution of hemiacetal **10** (395 mg, 0.21 mmol, 1 equiv.) in anhydrous CH_2Cl_2 (12 mL) were added Cs_2CO_3 (83.2 mg, 0.26 mmol, 2 equiv.) and 2,2,2-trifluoro-*N*-phenyl- acetimidoyl chloride (41 μL, 0.26 mmol, 2 equiv.) at 0 °C with stirring, and then the mixture was warmed up to room temperature and stirred for 3 hrs. Upon completion, the reaction mixture was diluted with CH_2Cl_2 (10 mL), filtered through a pad of Celite, and concentrated. The obtained residue was purified by silica gel column chromatography using acetone/hexane (1:2) as eluent to give compound **12** as a white foam (150 mg, 56%); anomeric mixture (α:β = 1:1). R_f = 0.55 (silica gel, acetone:hexane = 1:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ

7.93-7.88 (m, 4H, Ar-H), 7.49-7.45 (m, 2H, Ar-H), 7.40-7.12 (m, 38H, Ar-H), 6.75-6.71 (m, 1H, Ar-H), 5.82-5.78 (m, 1H), 5.46-5.42 (m, 1H), 5.36-5.30 (m, 3H), 5.24-5.16 (m, 1H), 5.08-4.81 (m, 5H, 0.5man-C1-H_α, 2C1-H_β, sia-C3-H), 4.78-4.74 (m, 1H), 4.69-4.41 (m, 9H, 0.5man-C1-H_β), 4.33-4.06 (m, 7H), 3.95-3.82 (m, 5H), 3.69-3.36 (m, 10H), 2.16-2.10 (m, 9H, -$3CH_3$), 2.01-1.99 (m, 3H, -CH_3), 1.92 (s, 3H, -CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.7, 170.7, 170.7, 170.7, 170.4, 170.2, 169.9, 169.9, 165.6, 165.6, 165.4, 165.2, 165.1, 154.1, 153.9, 143.3, 143.1, 138.7, 138.5, 138.3, 138.2, 138.2, 138.1, 138.0, 138.0, 137.8, 137.7, 133.2, 133.1, 133.1, 129.8, 129.6, 129.4, 129.3, 129.0, 128.7, 128.4, 128.4, 128.3, 128.3, 128.3, 128.2, 128.2, 128.1, 128.1, 128.1, 128.0, 127.9, 127.7, 127.7, 127.6, 127.5, 127.5, 127.5, 127.4, 127.3, 119.4, 119.2, 102.3, 100.2, 100.0, 98.3, 98.2, 95.6, 95.5, 87.4 (d, J = 193.2 Hz, 1C, sia-C3), 80.0, 79.3, 75.9, 75.0, 74.7, 74.7, 74.5, 74.3, 74.2, 73.8, 73.8, 73.5, 73.3, 73.2, 73.1, 72.8, 72.4, 72.3, 71.5, 71.4, 71.1, 71.0, 70.9, 70.1, 69.8, 69.3, 69.1, 68.2, 67.2, 67.2, 62.8, 62.3, 62.2, 53.3, 53.2, 45.5, 23.3, 21.0, 21.0, 20.7, 20.7, 20.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ -65.2, -65.4, -65.5, -65.6, -65.6, -65.7, -215.6, -215.7; HRMS (ESI-TOF) m/e : Calcd for $C_{105}H_{108}Cl_3F_4N_3O_{31}Na$ $[M+Na]^+$: 2110.5860 found 2110.5865.

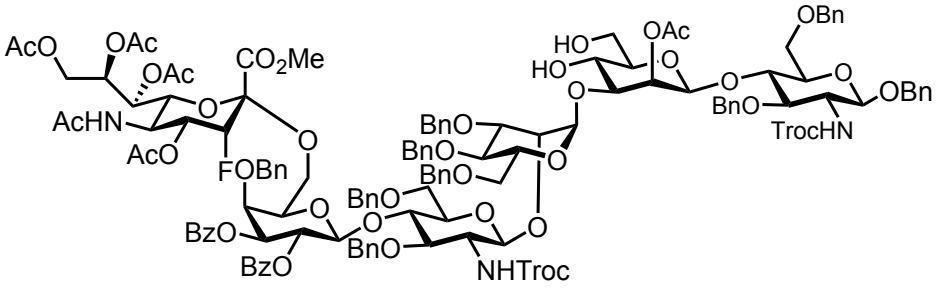


Benzyl [methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-3-fluoro-D-erythro-*α*-L-manno-non-2-ulopyranosonate]-(2→6)-[2,3-di-*O*-benzoyl-4-*O*-benzyl-1-*β*-D-galactopyranosyl]-(1→4)-[3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranosyl]-(1→2)-[3,4,6-tri-*O*-benzyl-*α*-D-mannopyranosyl]-(1→3)-[2-*O*-acetyl-4,6-*O*-benzylidine-*β*-D-mannopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside 14. A mixture AgOTf (194 mg, 0.75 mmol, 6 equiv. with respect to acceptor), bis Cp_2HfCl_2 (167 mg, 0.44 mmol, 3.5 equiv. with respect to acceptor), and freshly activated 4 Å MS (1.50 g) in anhydrous toluene (15 mL) was stirred at room temperature under argon atmosphere for 1 h. Then, the reaction mixture was cooled to -20 °C and treated with a solution of donor **11** (290 mg, 0.15 mmol,

1.2 equiv.) and acceptor **13** (115 mg, 0.13 mmol, 1 equiv.) in anhydrous toluene (8 mL). The reaction mixture was stirred at 0 ^{o}C until TLC indicated the disappearance of starting material (3 hrs). Upon completion, the reaction mixture was quenched with Et_3N (0.25 mL), diluted with EtOAc (25 mL), and filtered through a pad of Celite. The filtrate was washed twice with satd. aq. $NaHCO_3$ (10 mL) and brine (6 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated. The obtained residue was purified by silica gel column chromatography using acetone/toluene (1:2) as eluent to give compound **14** as a white powder (299 mg, 85%).

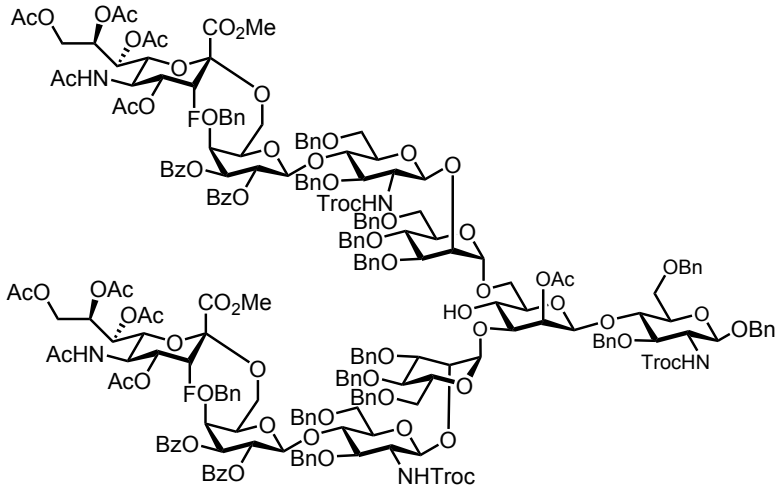
One-pot Synthesis: A mixture of acceptor **18** (40.0 mg, 0.037 mmol, 1 equiv.), donor **4** (60.1 mg, 0.056 mmol, 1.5 equiv.) and activated pulverized 4 Å MS (0.25 g) in anhydrous CH_2Cl_2 (1.25 mL) was stirred under argon atmosphere for 1 h. Then, the reaction mixture was cooled to −40 °C and NIS (12.6 mg, 0.056 mmol, 1.5 equiv.) was added, followed by addition of TfOH (0.5 M in Et_2O, 22.3 µL, 0.011 mmol, 0.3 equiv.) and the mixture was then allowed to stir to -20 ^{o}C for 2 hrs. Next, upon disappearance of starting materials (monitored by TLC), the reaction mixture was treated sequentially with acceptor **13** (34.2 mg, 0.037 mmol, 1 equiv.) in anhydrous CH_2Cl_2 (1.25 mL) with stirring for 10 min under argon; NIS (16.8 mg, 0.075 mmol, 2 equiv.); and TfOH (0.5 M in Et_2O, 22.3 µL, 0.011 mmol, 0.3 equiv.). Upon addition of all the reagents, the mixture was allowed to warm up to -10 ^{o}C and continued to stir until TLC indicated the disappearance of starting materials (1 h). Upon completion, the reaction was quenched with Et_3N (0.4 mL) and filtered through a pad of Celite. The filtrate was diluted with CH_2Cl_2 (10 mL), washed with 20% aq. $Na_2S_2O_3$ (3 mL), satd. aq. $NaHCO_3$ (2 mL) and brine (2 mL). The separated organic layer was dried over $MgSO_4$, filtered and concentrated in *vacuo*. The obtained residue was purified by silica gel column chromatography using acetone/toluene (1:2) as eluent, followed by a second column using acetone/hexane (3:4) eluent to give compound **14** as a white powder (27 mg, 26%).
R_f = 0.43 (silica gel, acetone:toluene = 3:5); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.96-7.95 (m, 2H, Ar-H), 7.91-7.90 (m, 2H, Ar-H), 7.51-7.47 (m, 2H, Ar-H), 7.36-7.26 (m, 35H, Ar-H), 7.23-7.10 (m, 19H, Ar-H), 5.84 (dd, *J* = 10.2, 7.8 Hz, 1H), 5.45-5.42 (m, 1H), 5.34-5.27 (m, 4H), 5.21-5.15 (m, 2H), 5.04-4.94 (m, 4H, C1-H_α, C1-H_β, sia-C3-H), 4.87-4.78 (m, 4H), 4.71-4.50 (m, 14H, 2C1-H_β), 4.46-4.34 (m, 5H), 4.31-4.21 (m, 4H), 4.16 (dd, *J* = 12.6, 5.4 Hz, 1H), 4.13-4.06 (m, 2H), 3.98-3.95 (m, 4H, C1-H_β), 3.84-3.57 (m, 17H), 3.51-3.41 (m, 4H), 3.36-3.35 (m, 2H), 3.15 (br, 1H), 2.93 (br, 1H), 2.68-2.67 (m, 1H), 2.12 (s, 3H, -CH_3), 2.11 (s, 3H, -CH_3), 2.09 (s, 3H, -CH_3), 1.99

(s, 3H, -CH_3), 1.91 (s, 3H, -CH_3), 1.85 (s, 3H, -CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ170.8, 170.7, 170.4, 170.2, 169.7, 169.4, 165.6, 165.4, 165.2, 153.7, 153.6, 138.9, 138.7, 138.4, 138.3, 137.9, 137.1, 133.2, 129.8, 129.7, 129.5, 129.1, 128.9, 128.6, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.9, 127.8, 127.8, 127.6, 127.6, 127.6, 127.5, 127.4, 127.4, 127.3, 127.2, 126.3, 102.1, 100.1, 99.0, 98.7, 98.6, 95.8, 95.5, 87.6 (d, *J* = 192.6 Hz, 1C, sia-C3), 78.8, 78.4, 74.8, 74.5, 74.3, 74.2, 73.9, 73.8, 73.3, 72.9, 72.3, 71.9, 71.4, 71.1, 70.7, 70.3, 69.2, 69.1, 69.0, 68.4, 68.3, 67.9, 67.2, 66.2, 63.2, 62.3, 57.4, 56.8, 53.3, 45.5, 23.3, 21.0, 20.8, 20.7, 20.6, 20.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ -215.6; HRMS (ESI-TOF) m/e : Calcd for $C_{142}H_{150}Cl_6FN_3O_{43}Na$ $[M+Na]^+$: 2836.7650 found 2836.7685.



Benzyl [methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-3-fluoro-D-erythro-*α*-L-manno-non-2-ulopyranosonate]-(2→6)-[2,3-di-*O*-benzoyl-4-*O*-benzyl-1-*β*-D-galactopyranosyl]-(1→4)-[3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranosyl]-(1→2)-[3,4,6-tri-*O*-benzyl-*α*-D-mannopyranosyl]-(1→3)-[2-*O*-acetyl-*β*-D-mannopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside 15. To a stirred solution of starting material **14** (318 mg, 0.11 mmol, 1 equiv.) in acetonitrile (12 mL) was added *p*-TsOH^xH_2O (21.5 mg, 0.11 mmol, 1 equiv.). The reaction mixture was vigorously stirred until TLC indicated the disappearance of starting material (6 hrs). Upon completion, the reaction mixture was quenched with Et_3N (0.3 mL) and concentrated under high vacuum. The obtained residue was purified by silica gel column chromatography using acetone/toluene (3:5) as eluent to give compound **15** as a white powder (231 mg, 75%). R_f = 0.25 (silica gel, acetone:toluene = 1:2); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.88-7.87 (m, 4H, Ar-H), 7.46 (dd, *J* = 7.2, 7.2 Hz, 1H, Ar-H), 7.43 (dd, *J* = 7.2, 7.2 Hz, 1H, Ar-H), 7.33-7.13 (m, 47H, Ar-H), 7.09-7.08 (m, 2H, Ar-H), 6.01 (br, 1H), 5.76 (dd, *J* = 10.2, 7.8 Hz, 1H), 5.46-5.43 (m, 1H), 5.38 (d, *J* = 8.4 Hz, 1H), 5.31-5.29 (m, 3H),

5.19-5.13 (m, 2H, C1-H_α), 5.05-4.96 (m, 3H, C1-H_β, sia-C3-H), 4.89-4.79 (m, 4H, C1-H_β), 4.69-4.60 (m, 8H, C1-H_β), 4.57-4.49 (m, 8H, C1-H_β), 4.45 (d, J = 12.0 Hz, 1H), 4.40-4.36 (m, 2H), 4.31 (dd, J = 12.6, 2.4 Hz, 1H), 4.24-4.16 (m, 4H), 4.12-4.09 (m, 2H), 4.02 (br, 1H), 3.98-3.93 (m, 2H), 3.91-3.86 (m, 2H), 3.80 (dd, J = 7.8, 6.0 Hz, 1H), 3.76-3.69 (m, 6H), 3.66-3.37 (m, 18H), 2.96-2.93 (m, 1H), 2.13 (s, 3H, -CH_3), 2.11 (s, 3H, -CH_3), 2.09 (s, 3H, -CH_3), 1.98 (s, 3H, -CH_3), 1.93 (s, 3H, -CH_3), 1.90 (s, 3H, -CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.8, 170.7, 170.4, 170.3, 170.2, 169.8, 165.6, 165.5, 165.3, 154.3, 153.8, 138.6, 138.4, 138.3, 138.1, 138.0, 137.8, 137.2, 133.3, 133.1, 129.8, 129.6, 129.4, 129.0, 128.5, 128.4, 128.3, 128.2, 128.2, 127.9, 127.9, 127.8, 127.7, 127.6, 127.5, 127.5, 127.4, 127.4, 127.3, 100.1, 99.1, 98.3, 98.2, 98.1, 95.7, 95.5, 87.6 (d, J = 193.2 Hz, 1C, sia-C3), 78.6, 78.2, 75.4, 75.1, 74.8, 74.7, 74.4, 74.2, 74.1, 73.8, 73.3, 73.2, 72.6, 71.9, 71.8, 71.5, 71.4, 70.9, 70.6, 69.5, 62.3, 57.2, 56.8, 53.8, 53.3, 45.4, 23.3, 21.1, 21.0, 20.7 (2C), 20.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ -215.6; HRMS (ESI-TOF) m/e : Calcd for $C_{135}H_{146}Cl_6FN_3O_{43}Na$ $[M+Na]^+$: 2748.7337 found 2748.7373.



Benzyl [methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-3-fluoro-D-erythro-*α*-L-manno-non-2-ulopyranosonate-(2→6)-2,3-di-*O*-benzoyl-4-*O*-benzyl-1-*β*-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-*α*-D-mannopyranosyl-(1→3)]-[methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-3-fluoro-D-erythro-*α*-L-manno-non-2-ulopyranosonate-(2→6)-2,3-di-*O*-benzoyl-4-*O*-benzyl-1-*β*-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranosyl-(1→2)-3,4,6-

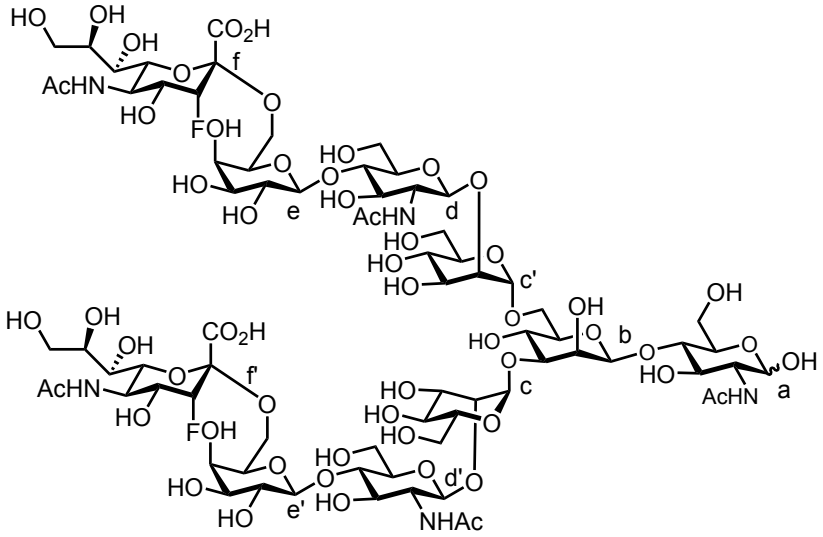
tri-*O*-benzyl-*α*-D-mannopyranosyl-(1→6)]-[2-*O*-acetyl-*β*-D-mannopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside 16.

From fluoride donor: A mixture of AgOTf (142 mg, 0.55 mmol, 8 equiv. with respect to acceptor), Cp_2HfCl_2 (105 mg, 0.28 mmol, 4 equiv. with respect to acceptor), and freshly activated 4 Å MS (1 g) in anhydrous toluene (10 mL) was stirred at room temperature under argon atmosphere for 1 h. Then, the reaction mixture was cooled to -40 °C and a solution of donor **11** (232 mg, 0.12 mmol, 1.75 equiv.) and acceptor **15** (188 mg, 0.069 mmol, 1 equiv.) in anhydrous toluene (1 mL) was added. Stirring was continued at -15 °C for 3 hrs. The reaction mixture was quenched with Et_3N (0.20 mL), diluted with EtOAc (20 mL), and filtered through a pad of Celite. The filtrate was washed twice with satd. aq. $NaHCO_3$ (8 mL) and brine (4 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated in *vacuo*. The obtained residue was purified by silica gel column chromatography using acetone/toluene (2:3) as eluent to give compound **16** as a white powder (223 mg, 70%) along with the recovered **15** (23.0 mg, 80% brsm).

From trifluoroacetimidate donor: A mixture of acceptor **15** (32.0 mg, 0.012 mmol, 1 equiv.), donor **12** (42.9 mg, 0.021 mmol, 1.75 equiv.) and activated pulverized 4 Å MS (200 mg) in anhydrous CH_2Cl_2 (2 mL) were stirred under argon atmosphere for 30 min. Then, the reaction mixture was cooled to -60 °C and treated with TfOH (0.5 M in Et_2O, 5.86 µL, 2.93 µmol, 0.25 equiv. with respect to acceptor). After stirring at -20 °C for 3 hrs. the reaction mixture was quenched with Et_3N (0.10 mL), diluted with CH_2Cl_2 (10 mL), and filtered through a pad of Celite. The filtrate was washed twice with satd. aq. $NaHCO_3$ (4 mL) and brine (3 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated. The obtained residue was purified by silica gel column chromatography using acetone/toluene (2:3) as eluent to give compound **16** as a white powder (18.0 mg, 33%) along with the recovered acceptor (12.6 mg, 55% brsm).

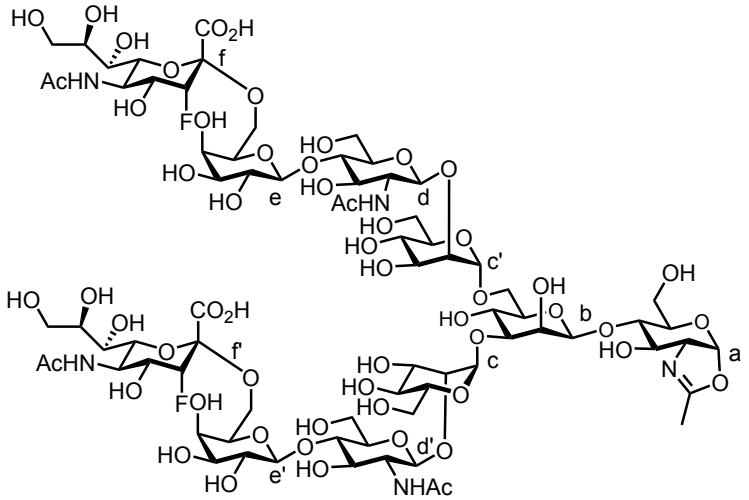
R_f = 0.17 (silica gel, acetone:toluene = 1:2); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.91-7.86 (m, 8H, Ar-H), 7.48-7.42 (m, 4H, Ar-H), 7.33-7.11 (m, 83H, Ar-H), 5.81-5.75 (m, 2H), 5.43-5.38 (m, 3H), 5.31-5.07 (m, 11H, 2C1-H_α), 5.03-4.78 (m, 9H, 2C1-H_β, 2sia-C3-H), 4.75-4.08 (m, 48H, 4C1-H_β), 4.05-3.89 (m, 7H), 3.87-2.99 (m, 40H), 2.13-2.12 (m, 6H, -2CH_3), 2.10-2.07 (m, 15H, -5CH_3), 1.99-1.97 (s, 6H, -2CH_3), 1.90-1.88 (m, 6H, -2CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.7, 170.6, 170.6, 170.4, 170.2, 169.8, 169.7, 169.6, 165.6, 165.5, 165.4, 165.4, 165.1, 154.0, 153.6, 139.1, 138.8, 138.4, 138.3, 138.1, 138.0, 137.7, 133.2, 133.1, 129.8, 129.8, 129.7, 129.6, 129.6, 129.5,

129.5, 129.1, 129.1, 128.4, 128.4, 128.3, 128.2, 128.2, 128.0, 128.0, 127.8, 127.8, 127.8, 127.7, 127.7, 127.5, 127.4, 127.4, 127.3, 127.2, 127.1, 100.1, 99.8, 98.8, 98.4, 98.2, 95.7, 88.1, 87.5 (d, J = 192.7 Hz, 2C, sia-C3), 78.3, 77.8, 75.3, 74.7, 74.5, 74.4, 74.3, 74.2, 74.0, 73.9, 73.4, 73.3, 73.3, 73.2, 73.1, 73.0, 72.9, 72.5, 72.4, 72.0, 71.9, 71.5, 71.0, 71.0, 70.9, 70.9, 70.7, 69.5, 69.4, 69.2, 69.1, 69.0, 69.0, 68.5, 68.1, 68.1, 68.0, 67.2, 62.9, 62.2, 57.5, 57.2, 53.8, 53.2, 53.2, 45.5, 45.3, 23.3, 21.0, 21.0, 20.8, 20.7, 20.7, 20.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ -215.6 (2F); HRMS (ESI-TOF) m/e : Calcd for $C_{232}H_{255}Cl_9F_2N_6O_{74}$ $[M+H_3O+NH_4]^{2+}$: 2330.6770 found 2330.6724.



[5-Acetamido-3,5-dideoxy-3-fluoro-D-erythro-*α*-L-manno-non-2-ulopyranosonate-(2→6)-*β*-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-*β*-D-glucopyranosyl-(1→2)-*α*-D-mannopyranosyl-(1→3)]-[5-acetamido-3,5-dideoxy-3-fluoro-D-erythro-*α*-L-manno-non-2-ulopyranosonate-(2→6)-*β*-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-*β*-D-glucopyranosyl-(1→2)-*α*-D-mannopyranosyl-(1→6)]-[*β*-D-mannopyranosyl]-(1→4)-2-acetamido-2-deoxy-D-glucopyranoside 17. A well-stirred solution of protected glycan **16** (103 mg, 0.022 mmol, 1 equiv.) and LiOH (51.5 mg, 50% by S.M. wt) in a mixture of 1,4-dioxane/H_2O (3 mL, 4:1 = *v/v*) was stirred at 90 °C for 16 hrs. The reaction mixture was concentrated under high vacuum and subjected to the acetylation conditions (pyridine (2.5 mL), Ac_2O (1.5 mL), r.t., 16 hrs). After the solvent was removed, the crude residue was purified by LiChroprep® RP-18 reverse-phase column chromatography using H_2O/MeOH (1:5) as eluent. The product was deacetylated

by stirring with NaOMe in MeOH (3 mL, 0.5 M) for 16 hrs. The reaction mixture was neutralized with IR-120, filtered, and concentrated in *vacuo*. The residue was purified by LiChroprep® RP-18 reverse-phase column chromatography using H_2O/MeOH (1:4) as eluent. The crude product of deacetylation step was dissolved in a mixture of MeOH/H_2O/HCOOH (3 mL, 6:3:1 = *v/v/v*) and treated with $Pd(OH)_2$ (51.5 mg, 50% by S.M. wt) for 20 hrs. The reaction mixture was filtered through a pad of Celite and concentrated in *vacuo*. The residue was purified by (BIO-RAD) Biogel P-2 column chromatography (eluting with water), followed by purification with LiChroprep® RP-18 reverse-phase column chromatography (eluting with water) to give compound **17** as a white powder (18.3 mg, 40%); anomeric mixture (α:β = 0.65:0.35). ^{1}H NMR (600 MHz, D_2O): δ 5.23 (d, *J* = 3.0 Hz, 0.65H, a-C1-H_α), 5.14 (d, *J* = 52.8 Hz, 2H, sia-C3-H), 5.14 (br, 1H, c-C1-H_α), 4.96 (br, 1H, c'-C1-H_α), 4.79 (br, 1H, b-C1-H_β), 4.73 (br, 0.35H, a-C1-H_β), 4.60 (d, *J* = 7.8 Hz, 2H, dd'-C1-H_β), 4.48 (d, *J* = 7.8 Hz, 2H, ee'-C1-H_β), 4.28-4.21 (m, 4H), 4.13 (br, 1H), 4.00-3.51 (m, 57H), 2.09-2.08 (m, 9H, -3CH_3), 2.05 (br, 6H, -2CH_3); ^{13}C NMR (150 MHz, D_2O): δ 174.5, 174.2, 174.1, 102.7, 102.6, 100.0, 99.1, 98.9, 98.9, 98.7, 98.6, 96.6, 94.4, 90.4 (d, *J* = 183.2 Hz, 2C, sia-C3), 90.0, 80.0, 79.7, 79.3, 78.9, 76.0, 75.8, 74.1, 74.0, 73.9, 73.1, 72.9, 72.7, 72.4, 71.9, 71.9, 71.6, 71.5, 71.1, 70.3, 69.8, 69.4, 69.2, 69.1, 69.0, 68.7, 68.0, 67.8, 66.9, 66.8, 65.4, 65.2, 63.6, 62.2, 61.2, 61.2, 59.7, 59.6, 55.6, 54.4, 53.1, 46.3, 21.9, 21.6; ^{19}F NMR (376 MHz, D_2O): δ -217.4, -217.4; HRMS (ESI-TOF) m/e : Calcd for $C_{76}H_{121}F_2N_5O_{57}$ $[M-2H]^{-2}$: 1026.8351 found 1026.8299.

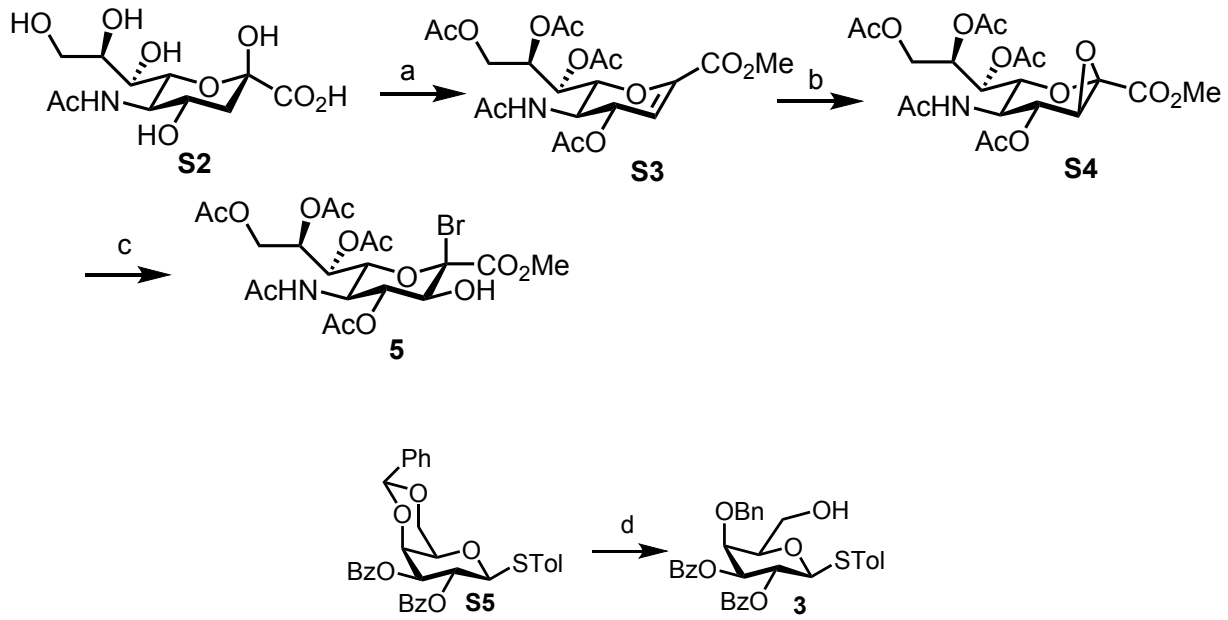


[5-Acetamido-3,5-dideoxy-3-fluoro-D-erythro-*α*-L-manno-non-2-ulopyranosonate-(2→6)-*β*-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-*β*-D-glucopyranosyl-(1→2)-*α*-D-

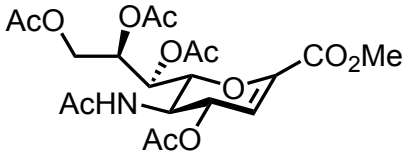
mannopyranosyl-(1→3)]-[5-acetamido-3,5-dideoxy-3-fluoro-D-erythro-*α*-L-manno-non-2-ulopyranosonate-(2→6)-*β*-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-*β*-D-glucopyranosyl-(1→2)-*α*-D-mannopyranosyl-(1→6)]-[*β*-D-mannopyranosyl]-(1→4)-(2-acetamido-1,2-dideoxy-D-glucopyrano)-[2,1-*d*]-2-methyloxazoline S1. *A representative synthesis of glycan oxazoline*. A solution of glycan **17** (14.5 mg, 7.05 μmol, 1 equiv.), 2-Chloro-1,3-dimethyl-1H-benzimidazol-3-ium chloride (CDMBI) (12.2 mg, 0.056 mmol, 8 equiv.) and Et_3N (19.9 μL) in water (121.1 μL) was stirred at 4 °C for 1 h. The reaction mixture was subjected to gel filtration chromatography on a Sephadex G-25 column eluting with 0.05% aq. Et_3N. The fractions containing product (glycan oxazoline) were combined and lyophilized to give the desired product **S1** as a white powder (12.6 mg, yield 87%). ^{1}H NMR (600 MHz, D_2O + 0.05% Et_3N): δ 6.09 (d, J = 7.2 Hz, 1H, oxa-C1-H_α), 5.12 (d, J = 52.2 Hz, 2H, sia-C3-H), 5.11 (br, 1H, c-C1-H_α), 4.95 (br, 1H, c'-C1-H_α), 4.74 (br, 1H, b-C1-H_β), 4.60-4.57 (m, 2H, dd'-C1-H_β), 4.46-4.45 (m, 2H, ee'-C1-H_β), 4.39 (br, 1H), 4.22-4.15 (m, 5H), 3.98-3.49 (m, 55H), 3.43-3.40 (m, 1H), 2.07-2.02 (m, 15H, -5CH_3); ^{13}C NMR (150 MHz, D_2O + 0.05% Et_3N): δ 174.9, 174.7, 174.7, 170.7, 170.7, 168.5, 103.1, 103.1, 101.4, 99.9, 99.5, 99.4, 99.2, 99.1, 99.0, 96.5, 90.8 (d, J = 183.2 Hz, 2C, sia-C3), 80.4, 79.4, 77.9, 76.4, 76.0, 74.6, 74.2, 73.4, 73.4, 72.8, 72.4, 72.3, 72.0, 71.9, 71.5, 70.8, 70.7, 70.2, 69.6, 69.5, 69.4, 69.1, 68.5, 68.2, 67.2, 65.8, 65.7, 65.1, 64.1, 62.6, 61.6, 61.6, 60.1, 54.9, 46.7, 22.4, 22.0, 12.9; ^{19}F NMR (470 MHz, D_2O + 0.05% Et_3N): δ -217.3 (d, J_{FH} = 51.3 Hz), -217.3 (d, J_{FH} = 51.3 Hz); HRMS (ESI-TOF) m/e : Calcd for $C_{76}H_{120}F_2N_5O_{56}$ $[M-H]^-$: 2036.6658 found 2036.6672.

Synthesis of Building Blocks 3, 5, 8, 13, and 18

Scheme S1. Synthesis of Building Block 3 and 5.

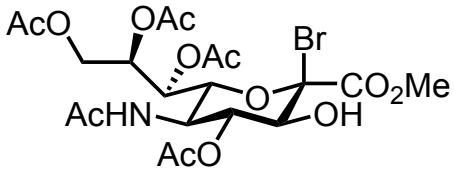


Reagents and conditions: (a) TFA, MeOH, 60 °C, 16 h, then AcCl, r.t., 2 d, then Na_2HPO_4, CH_3CN, reflux, 20 h, 92 %. (b) ref. 3, 80 % (three steps). (c) $TiBr_4$, dichloroethane, r.t., 10 min., 92 %. (d) BH_3, $Cu(OTf)_2$, THF, r.t., 8 h, 96%.



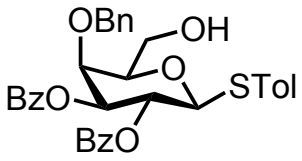
Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2,6-anhydro-D-glycero-D-galacto -non-2-enonate S3[1]. To a stirred solution of compound **S2** (20 g, 64.7 mmol, 1 equiv.) in MeOH (600 mL) was added TfOH (4.95 mL, 64.7 mmol, 1 equiv.). The reaction mixture was allowed to stir at 60 °C for 16 hrs. The solvent was removed by rotary evaporation under reduced pressure and co-evaporated with toluene twice to remove traces of water. Thus obtained residue was dissolved in AcCl (200 mL) at 0 °C in a round bottom flask, sealed and stirred to room temperature for 2 days. Upon removal of solvent, the obtained residue was diluted with anhydrous acetonitrile

(200 mL) and then Na_2HPO_4 (19.6 g, 155 mmol, 2.4 equiv.) was added under argon atmosphere. The reaction mixture was vigorously stirred at 90 ^oC until TLC indicated the disappearance of starting material (16 hrs). The solution was filtered through a pad of Celite, dried ($MgSO_4$), and concentrated in *vacuo*. The obtained residue was purified by silica gel column chromatography using EtOAc/hexane (4:1) as eluent to give compound **S3** as a brown foam (28.2 g, 92%). Spectroscopic data was agreed with reported in the literature previously.[1] R_f = 0.30 (silica gel, EtOAc); ^1H NMR (600 MHz, $CDCl_3$): δ 5.95 (d, *J* = 3.0 Hz, 1H), 5.81 (d, *J* = 9.0 Hz, 1H), 5.47-5.44 (m, 2H), 5.32-5.30 (m, 1H), 4.59 (dd, *J* = 12.0, 3.0 Hz, 1H), 4.38-4.33 (m, 2H), 4.15 (d, *J* = 12.0, 7.2 Hz, 1H), 3.76 (s, 3H, $-CH_3$), 2.08 (s, 3H, $-CH_3$), 2.03 (s, 3H, $-CH_3$), 2.02 (s, 3H, $-CH_3$), 2.01 (s, 3H, $-CH_3$), 1.88 (s, 3H, $-CH_3$); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.7, 170.5, 170.1, 170.1, 170.0, 161.6, 145.0, 107.9, 70.6, 67.8, 67.6, 61.9, 52.5, 46.5, 23.1, 20.8, 20.7, 20.7; HRMS (ESI-TOF) m/e : Calcd for $C_{20}H_{27}NO_{12}Na$ $[M+Na]^+$: 496.1425 found 496.1435.



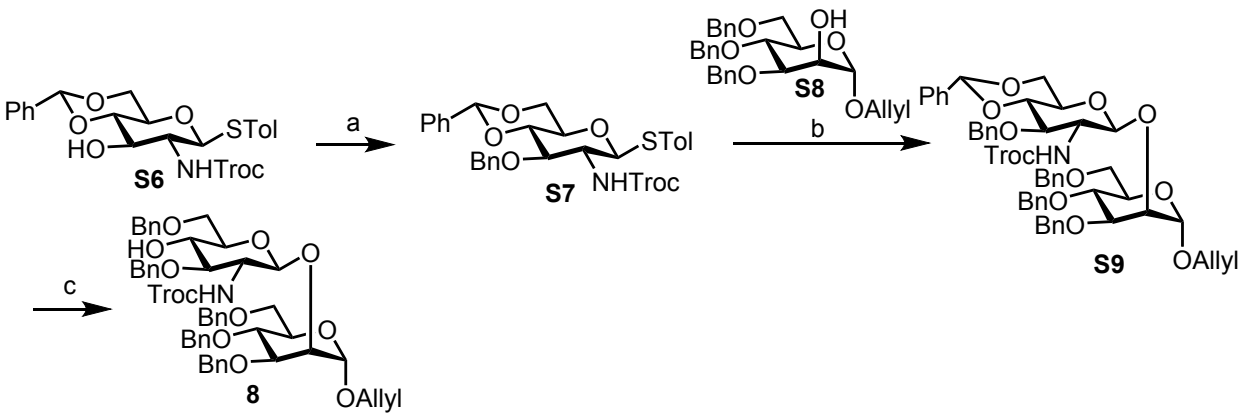
Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-2-bromo-2,5-dideoxy-D-erythro-*α*-L-gluco-non -2-ulopyranosonate 3.[2] The synthesis of the epoxide **S4** was performed from sialic acid using reported procedures.[3] To a stirred solution of epoxide compound **S4** (1.10 g, 2.25 mmol, 1 equiv.) in anhydrous 1,2-dichloroethane (18 mL), was added $TiBr_4$ (0.91 g, 2.47 mmol, 1.1 equiv.) under argon atmosphere for 10 min. The solvent was removed by rotary evaporation under high vacuum. The obtained residue was diluted with EtOAc (30 mL), washed with saturated aq. Na_2SO_4 (10 mL), 5% aq. $NaHCO_3$ (10 mL), and then brine (5 mL). The separated organic layer was dried over $MgSO_4$, and concentrated in *vacuo*. The obtained residue was purified by silica gel column chromatography using acetone/hexane (2:1) as eluent to give compound **3** as a white powder (1.18 g, 92%). Spectroscopic data and protocol were identical to that reported previously.[2] R_f = 0.23 (silica gel, acetone:toluene = 1:1); ^1H NMR (600 MHz, $CDCl_3$): δ 5.99 (d, *J* = 7.2 Hz, 1H), 5.42 (dd, *J* = 7.2, 1.2 Hz, 1H), 5.21-5.18 (m, 1H), 5.10 (ddd, *J* = 6.0, 6.0, 2.4 Hz, 1H), 4.38 (dd, *J* = 12.6, 2.4 Hz, 1H), 4.32-4.30 (m, 2H), 3.99 (dd, *J* = 12.6, 6.0 Hz, 1H), 3.86 (s, 3H, $-CH_3$), 3.78 (d, *J* = 9.0 Hz, 1H), 3.66 (br, 1H, -OH), 2.07 (s, 3H, $-CH_3$), 2.06 (s, 3H, $-CH_3$), 2.05 (s, 3H, $-CH_3$),

2.01 (s, 3H, -CH_3), 1.84 (s, 3H, -CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.4, 170.6, 170.3, 169.8, 169.7, 167.0, 98.0, 75.0, 72.8, 72.2, 69.9, 66.5, 61.9, 54.0, 47.2, 22.9, 21.0, 20.7, 20.6; HRMS (ESI-TOF) m/e : Calcd for $C_{20}H_{29}BrNO_{13}$ $[M+H]^+$: 570.0817 found 570.0822.

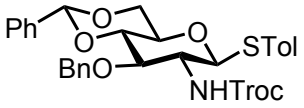


***p*-Tolyl 2,3-di-*O*-benzoyl-4-*O*-benzyl-1-thio-*β*-D-galactopyranoside 5**.[4] To a stirred solution of starting material **S5**[5] (4.00 g, 6.86 mmol, 1 equiv.) in BH_3-THF complex (1M in THF, 34.3 mL, 34.3 mmol, 5 equiv.) was added $Cu(OTf)_2$ (124 mg, 0.34 mmol, 0.05 equiv.) and the reaction mixture was stirred at room temperature for 8 hrs. Upon completion, the reaction was carefully neutralized with TEA (0.96 mL, 6.86 mmol, 1 equiv.) at 0 °C, then diluted with MeOH (15 mL). After removal of solvent in *vacuo,* the obtained residue was purified by silica gel column chromatography using EtOAc/hexane (1:2) as an eluent to give compound **5** as a white powder (3.85 g, 96%). Spectroscopic data was agreed with reported in the literature previously.[4] R_f = 0.45 (silica gel, EtOAc:hexane = 1:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.97-7.94 (m, 4H, Ar-H), 7.51-7.48 (m, 2H, Ar-H), 7.38-7.34 (m, 6H, Ar-H), 7.27-7.21 (m, 5H, Ar-H), 5.85 (dd, *J* = 10.2, 10.2 Hz, 1H), 5.36 (dd, *J* = 9.6, 3.0 Hz, 1H), 4.87 (d, *J* = 9.6 Hz, 1H, C1-H_β), 4.74 (d, *J* = 12.0 Hz, 1H), 4.47 (d, *J* = 12.0 Hz, 1H), 4.16 (d, *J* = 2.4 Hz, 1H), 3.91 (d, *J* = 11.4, 7.2 Hz, 1H), 3.76 (dd, *J* = 6.0, 6.0 Hz, 1H), 3.61 (dd, *J* = 11.4, 5.4 Hz, 1H), 2.30 (s, 3H, -CH_3), 1.83 (br, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.9, 165.2, 138.1, 137.4, 133.4, 133.1, 133.0, 129.8, 129.7, 129.6, 129.5, 128.9, 128.7, 128.5, 128.4, 128.3, 128.1, 127.9, 86.8, 79.0, 76.0, 74.6, 73.7, 68.5, 61.9, 21.1; HRMS (ESI-TOF) m/e : Calcd for $C_{34}H_{32}O_7SNa$ $[M+Na]^+$: 607.1761 found 607.1770.

Scheme S2. Synthesis of Building Block 8.



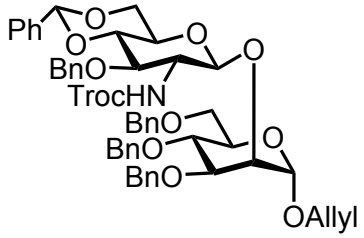
Reagents and conditions: (a) TESOTf, BnCHO, TESH, toluene, THF, 2 h, -20 °C, 90%. (b) NIS, TfOH, 4Å MS, -40 °C, 1.5 h, CH_2Cl_2, 75%. (c) $NaBH_3CN$, HCl/ether, AW-300, THF, 0 °C to r.t., 16 h, 85%.



***p*-Tolyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-1-thio-2-(2,2,2-trichloroethoxy) carbamoylamino-*β*-D-glucopyranoside S7**.

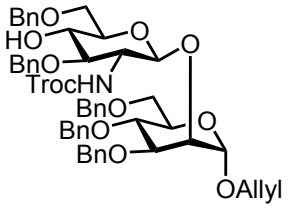
To a stirred solution of starting material **S6**[6] (5.17 g, 9.42 mmol, 1 equiv.) in a mixture of THF/toluene (45 mL, 1:2 = *v/v*) was added TESOTf (4.26 mL, 18.8 mmol, 2 equiv.) at -20 °C under argon atmosphere. After stirring for 45 min at -20 °C, benzaldehyde (4.79 mL, 47.1 mmol, 5 equiv.) and triethylsilane (2.26 mL, 14.1 mmol, 1.5 equiv.) were added dropwise to the mixture with stirring. After 2 hrs at -20 °C, TLC indicated the disappearance of starting material and the reaction was quenched with satd. aq. Na_2CO_3, diluted with EtOAc (100 mL) and washed with satd. aq. Na_2CO_3 (30 mL), and brine. The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography using CH_2Cl_2/toluene (1:4) to EtOAc/toluene (1:10) as eluents to give compound **S7** as a white solid (5.40 g, 90%). R_f = 0.50 (silica gel, EtOAc:toluene = 1:25); ^{1}H NMR (600 MHz, Acetone-d6): δ 7.52-7.50 (m, 2H, Ar-H), 7.42-7.36 (m, 4H, Ar-H), 7.32-7.31 (m, 2H, Ar-H), 7.29-7.22 (m, 4H, Ar-H), 7.18-7.15 (m, 2H, Ar-H), 5.72 (s, 1H, Ph-CH), 5.03 (d, J = 10.8 Hz, 1H, C1-H_β), 4.90-

4.82 (m, 3H), 4.74 (d, J = 12.0 Hz, 1H), 4.30 (dd, J = 10.2, 5.4 Hz, 1H), 3.95 (dd, J = 9.6, 9.0 Hz, 1H), 3.84-3.71 (m, 3H), 3.56 (ddd, J = 9.6, 9.6, 4.8 Hz, 1H), 2.83 (s, 2H), 2.32 (s, 3H, -CH_3); ^{13}C NMR (150 MHz, Acetone-d6): δ 155.3, 139.8, 139.4, 138.6, 133.3, 130.7, 130.5, 129.8, 129.6, 129.1, 129.0, 129.0, 128.5, 128.2, 127.1, 101.8, 97.1, 88.6, 82.7, 80.8, 75.0, 75.0, 71.2, 69.1, 57.4, 21.1; HRMS (ESI-TOF) m/e : Calcd for $C_{30}H_{30}Cl_3NO_6SNa$ $[M+Na]^+$: 660.0752 found 660.0749.



Allyl [3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxy) carbonylamino-*β*-D -glucopyranosyl]-(1→2)-3,4,6-tri-*O*-benzyl-*α*-D-mannopyranoside S9. A mixture of acceptor **S8**[7] (523 mg, 0.94 mmol, 1 equiv.), donor **S7** (900 mg, 1.41 mmol, 1.5 equiv.) and activated pulverized 4 Å MS (2.00 g) in anhydrous CH_2Cl_2 (20 mL) was stirred under argon atmosphere for 1 h. Then, the reaction mixture was cooled to −40 °C and treated with NIS (423 mg, 1.88 mmol, 2 equiv.) and TfOH (0.5 M in Et_2O, 0.47 mL, 0.23 mmol, 0.25 equiv.). After stirring at that temperature for 1.5h, the TLC indicated the disappearance of starting materials and the reaction mixture was quenched with Et_3N (0.2 mL), and filtered through a pad of Celite. The filtrate was diluted with CH_2Cl_2 (20 mL), washed with 20% aq. $Na_2S_2O_3$ (5 mL), satd. aq. $NaHCO_3$ (10 mL) and brine (5 mL). The separated organic layer was dried over $MgSO_4$ and concentrated in *vacuo*. The obtained residue was purified by silica gel column chromatography using EtOAc/toluene (1:10) as eluent to give compound **S9** as a white foam (710 mg, 75%). R_f = 0.36 (silica gel, EtOAc:toluene = 1:10); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.50-7.48 (m, 2H, Ar-H), 7.39-7.36 (m, 6H, Ar-H), 7.33-7.25 (m, 15H, Ar-H), 7.23-7.22 (m, 2H, Ar-H), 5.84 (ddd, J = 16.2. 10.8, 5.4 Hz, 1H), 5.55 (s, 1H, Ph-CH), 5.26 (d, J = 1.2 Hz, 1H), 5.23-5.20 (m, 1H), 5.16 (dd, J = 10.8, 1.2 Hz, 1H), 5.01 (d, J = 7.8 Hz, 1H, C1-H_β), 4.90 (d, J = 10.8 Hz, 1H), 4.83 (d, J = 11.4 Hz, 1H), 4.75-4.62 (m, 6H, C1-H_α), 4.55-4.51 (m, 3H), 4.33-4.29 (m, 2H), 4.13-4.10 (m, 1H), 4.08 (dd, J = 2.4, 2.4 Hz, 1H), 4.00-3.97 (m, 1H), 3.94 (dd, J = 9.6, 3.0 Hz, 1H), 3.89 (dd, J = 13.2, 6.0 Hz, 1H), 3.82-3.78 (m, 2H), 3.72-3.66 (m, 3H), 3.50-3.46 (m, 1H), 3.12 (d, J = 6.0 Hz, 1H); ^{13}C NMR (150

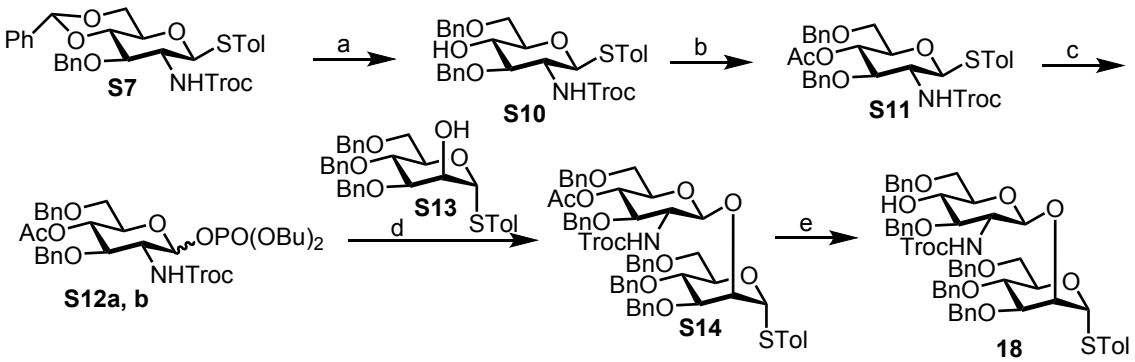
MHz, $CDCl_3$): δ 153.8, 138.6, 138.5, 138.3, 138.1, 137.3, 133.7, 129.0, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.6, 127.6, 127.4, 126.0, 117.2, 101.2, 98.9, 96.9, 95.5, 82.4, 78.5, 75.6, 75.2, 74.6, 74.4, 74.2, 73.3, 72.2, 72.2, 69.2, 68.6, 68.0, 66.1, 58.1; HRMS (ESI-TOF) m/e : Calcd for $C_{53}H_{56}Cl_3NO_{12}Na$ $[M+Na]^+$: 1026.2760 found 1026.2780.



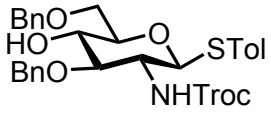
Allyl [3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranosyl] -(1→2)-3,4,6-tri-*O*-benzyl-*α*-D-mannopyranoside 8.[8] To a stirred solution of starting material **S9** (500 mg, 0.50 mmol, 1 equiv.) in anhydrous THF (12 mL) was added activated pulverized AW 300 MS (1.20 g) under argon atmosphere. Then, the reaction mixture was cooled to 0 °C and $NaCNBH_3$ (313 mg, 4.97 mmol, 10 equiv.) was added, followed by a slow addition of HCl • Et_2O (2 M in Et_2O, 2.24 mL, 4.48 mmol, 9 equiv.), and the mixture was continued to stir until TLC indicated the disappearance of starting materials (16 hrs). Upon completion, the reaction mixture was quenched with satd. aq. $NaHCO_3$ (0.5 mL) and filtered through a pad of Celite. The filtrate was diluted with CH_2Cl_2 (20 mL) then washed with satd. aq. $NaHCO_3$ (8 mL) and brine (5 mL). The separated organic layer was dried over $MgSO_4$ and concentrated. The obtained residue was purified by silica gel column chromatography using EtOAc/toluene (1:5) as an eluent to give compound **8** as a white foam (425 mg, 85%). The spectroscopic data matched the literature precedent.[8] R_f = 0.17 (silica gel, EtOAc:toluene = 1:10); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36-7.23 (m, 23H, Ar-H), 7.20-7.19 (m, 2H, Ar-H), 5.84 (ddd, *J* = 16.2. 10.2, 6.0 Hz, 1H), 5.35 (br, 1H), 5.21 (dd, *J* = 16.2, 1.2 Hz, 1H), 5.14 (dd, *J* = 10.2, 1.2 Hz, 1H), 4.95 (d, *J* = 7.2 Hz, 1H, C1-H_β), 4.88 (d, *J* = 10.8 Hz, 1H), 4.78 (d, *J* = 1.8 Hz, 1H, C1-H_α), 4.75 (d, *J* = 11.4 Hz, 1H), 4.70-4.63 (m, 5H), 4.60 (d, *J* = 11.4 Hz, 1H), 4.55-4.49 (m, 4H), 4.14-4.07 (m, 3H), 3.96-3.87 (m, 3H), 3.77 (dd, *J* = 10.8, 4.2 Hz, 1H), 3.73-3.70 (m, 3H), 3.66 (dd, *J* = 10.8, 1.8 Hz, 1H), 3.61 (dd, *J* = 9.6, 8.4 Hz, 1H), 3.54-3.51 (m, 1H), 3.08 (m, 1H), 2.71 (m, 1H, -OH); ^{13}C NMR (150 MHz, $CDCl_3$): δ 154.0, 138.5, 138.5, 138.4, 138.1, 137.6, 133.7, 128.5, 128.5, 128.3, 128.3, 128.3, 128.2, 128.0, 128.0, 127.8, 127.7, 127.7, 127.6, 127.6, 127.5, 117.3, 79.2, 78.2, 75.1, 74.6, 74.3, 74.2, 73.8, 73.7,

73.4, 73.3, 72.0, 71.7, 70.9, 69.3, 68.0, 57.5; HRMS (ESI-TOF) m/e : Calcd for $C_{53}H_{58}Cl_3NO_{12}Na$ $[M+Na]^+$: 1028.2917 found 1028.2927.

Scheme S3. Synthesis of Building Block 18.

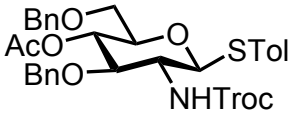


Reagents and conditions: (a) $NaBH_3CN$, HCl/ether, AW-300, THF, 0 °C to r.t., 16 h, 90%. (b) Ac_2O, pyridine, r.t., 16 h, 98%. (c) NIS, TfOH, $HOPO(OBu)_2$, 4Å MS, -30 °C, 2 h, CH_2Cl_2, 90%. (d) TMSOTf, 4Å MS, -50 °C, 1 h, CH_2Cl_2, 87%. (e) NaOMe, MeOH/CH_2Cl_2, 0 °C to r.t., 76%.

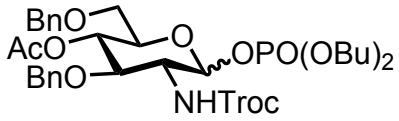


***p*-Tolyl 3,6-di-*O*-benzyl-2-deoxy-1-thio-2-(2,2,2-trichloroethoxy)carbamoylamino-*β*-D-glucopyranoside S10**.[9] To a stirred solution of starting material **S7** (1.00 g, 1.56 mmol, 1 equiv.) in anhydrous THF (30 mL) was added activated pulverized AW 300 MS (3.00 g) under argon atmosphere. Then, the reaction mixture was cooled to 0 °C and $NaCNBH_3$ (0.98 g, 15.6 mmol, 10 equiv.) was added, followed by a slow addition of HCl • Et_2O (2 M in Et_2O, 7.04 mL, 14.1 mmol, 9 equiv.), and the mixture was continued to stir until TLC indicated the disappearance of starting materials (16 hrs). Upon completion, the reaction mixture was quenched with satd. aq. $NaHCO_3$ (0.5 mL) and filtered through a pad of Celite. The filtrate was diluted with CH_2Cl_2 (50 mL) then washed with satd. aq. $NaHCO_3$ (15 mL) and brine (10 mL). The separated organic layer was dried over $MgSO_4$ and concentrated. The obtained residue was purified by silica gel column chromatography using EtOAc/hexane/CH_2Cl_2 (1:3:1) as eluent to give compound **S10** as a white foam (902 mg, 90%). The spectroscopic data matched the literature precedent.[9] R_f = 0.29 (silica gel, EtOAc:hexane = 1:3); ^1H NMR (600 MHz, $CDCl_3$): δ 7.40-7.38 (m, 2H, Ar-H), 7.36-7.27 (m, 10H, Ar-H), 7.04-7.03 (m, 2H, Ar-H), 5.20 (d, *J* = 7.8 Hz, 1H), 4.84 (d, *J* = 10.2 Hz, 1H, C1-H_β), 4.77-4.72 (m, 4H), 4.58-4.52 (m, 2H), 3.76 (d, *J* = 4.8 Hz, 2H), 3.71-3.64 (m, 2H), 3.50-3.49 (m,

1H), 3.42-3.38 (m, 1H), 2.90 (br, 1H, -OH), 2.29 (s, 3H, $-CH_3$); ^{13}C NMR (150 MHz, $CDCl_3$): δ 153.8, 138.1, 138.1, 137.7, 133.0, 129.6, 128.6, 128.5, 128.4, 128.1, 127.9, 127.8, 127.7, 95.5, 86.1, 81.9, 78.0, 74.5, 74.4, 73.6, 72.5, 70.4, 55.9, 21.1; HRMS (ESI-TOF) m/e : Calcd for $C_{30}H_{32}Cl_3NO_6SNa$ $[M+Na]^+$: 662.0908 found 662.0919.



***p*-Tolyl 4-*O*-acetyl-3,6-di-*O*-benzyl-2-deoxy-1-thio-2-(2,2,2-trichloroethoxy)carbamoylamino -*β*-D-glucopyranoside S11**. To a stirred solution of starting material **S10** (0.97 g, 1.51 mmol, 1 equiv.) in pyridine (12 mL) was added Ac_2O (6 mL). The reaction mixture was vigorously stirred for 16 hrs at room temperature. The reaction mixture was then concentrated in *vacuo* and purified by silica gel column chromatography using EtOAc/hexane/CH_2Cl_2 (1:4:1) as eluent to give compound **S11** as a white powder (1.01 g, 98%). R_f = 0.47 (silica gel, EtOAc:hexane = 1:3); ^1H NMR (600 MHz, $CDCl_3$): δ 7.41-7.40 (m, 2H, Ar-H), 7.34-7.25 (m, 8H, Ar-H), 7.22-7.21 (m, 2H, Ar-H), 7.03-7.01 (m, 2H, Ar-H), 5.29 (d, *J* = 7.2 Hz, 1H), 5.04 (d, *J* = 10.2 Hz, 1H, C1-H_β), 4.98 (dd, *J* = 9.6, 9.6 Hz, 1H), 4.78 (d, *J* = 12.0 Hz, 1H), 4.70 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 11.4 Hz, 1H), 4.57 (d, *J* = 11.4 Hz, 1H), 4.50 (br, 2H), 4.05 (dd, *J* = 9.6, 9.0 Hz, 1H), 3.65-3.63 (m, 1H), 3.59-3.55 (m, 2H), 3.33 (ddd, *J* = 9.6, 9.6, 9.6 Hz, 1H), 2.29 (s, 3H, $-CH_3$), 1.87 (s, 3H, $-CH_3$); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.8, 153.7, 138.4, 138.0, 137.7, 133.3, 129.8, 128.6, 128.5, 128.4, 128.2, 128.1, 128.1, 127.9, 127.9, 127.7, 95.5, 85.3, 79.4, 77.7, 74.4, 73.6, 71.4, 69.7, 56.5, 21.1, 20.9; HRMS (ESI-TOF) m/e : Calcd for $C_{32}H_{34}Cl_3NO_7SNa$ $[M+Na]^+$: 704.1014 found 104.1031.

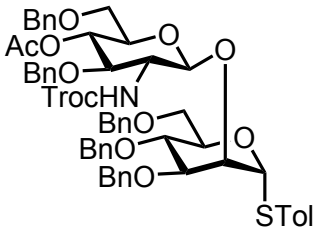


Dibutyl 4-*O*-acetyl-3,6-di-*O*-benzyl-2-deoxy-1-thio-2-(2,2,2-trichloroethoxy) carbamoylamino-*α* or *β*-D-glucopyranoside phosphate S12a, b. A mixture of the compound **S11** (990 mg, 1.45 mmol, 1 eq.), dibutyl phosphate (1.15 mL, 5.80 mmol, 3 eq.) and activated pulverized 4 Å MS (1.80 g) in anhydrous CH_2Cl_2 (18 mL) was stirred under argon atmosphere for

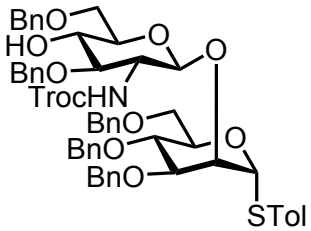
1 h. Then it was cooled to -30 °C with stirring, and NIS (978 mg, 4.35 mmol, 2 eq.) was added followed by TfOH (0.5 M in Et_2O, 0.87 mL, 0.43 mmol, 0.3 eq.). After 2hrs, the TLC analysis indicated the disappearance of starting materials and the reaction mixture was quenched by satd. aq. $NaHCO_3$ (0.5 mL) and filtered through a pad of Celite. The filtrate was diluted with CH_2Cl_2 (50 mL), washed with 20% aq. $Na_2S_2O_3$ (10 mL), satd. aq. $NaHCO_3$ (5 mL) and brine (5 mL). The separated organic layer was dried over $MgSO_4$ and concentrated in *vacu*o. The obtained residue was purified by silica gel column chromatography using EtOAc/toluene (1:3) as eluent to give compound **S12** as a white foam (1.00 g, 90%); anomeric mixture (α : β= 1:3).

β-anomer **S12b**: R_f = 0.32 (silica gel, EtOAc:toluene = 1:3); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30-7.22 (m, 10H, Ar-H), 5.81 (br, 1H), 5.35 (dd, *J* = 7.8, 7.8 Hz, 1H, C1-H_β), 5.09 (dd, *J* = 9.6, 9.0 Hz, 1H), 4.74 (d, *J* = 12.0 Hz, 1H), 4.65-4.58 (m, 3H), 4.49-4.44 (m, 2H), 4.06-3.97 (m, 4H), 3.88 (dd, *J* = 9.6, 9.0 Hz, 1H), 3.77-3.74 (m, 1H), 3.69 (ddd, *J* = 9.6, 4.2, 4.2 Hz, 1H), 3.53-3.52 (m, 2H), 1.83 (s, 3H, -CH_3), 1.61-1.54 (m, 4H), 1.36-1.31 (m, 4H), 0.93-0.85 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.5, 154.2, 137.6, 137.6, 128.5, 128.4, 128.3, 127.9, 127.9, 127.7, 127.7, 96.5, 95.3, 78.3, 74.5, 73.9, 73.6, 73.5, 70.6, 69.2, 68.1, 68.1, 68.1, 68.0, 57.2, 57.2, 32.1, 32.0, 32.0, 20.7, 18.6, 18.6, 13.5; HRMS (ESI-TOF) m/e : Calcd for $C_{33}H_{45}Cl_3NO_{11}PNa$ $[M+Na]^+$: 790.1688 found 790.1685.

α-anomer **S12a**: R_f = 0.44 (silica gel, EtOAc:toluene = 1:3); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31-7.22 (m, 10H, Ar-H), 5.67 (dd, *J* = 6.0, 3.6 Hz, 1H, C1-H_α), 5.21-5.16 (m, 2H), 4.75 (d, *J* = 12.0 Hz, 1H), 4.62-4.56 (m, 3H), 4.49-4.44 (m, 2H), 4.11-3.99 (m, 6H), 3.77 (dd, *J* = 10.2, 9.6 Hz, 1H), 3.50-3.49 (m, 2H), 1.89 (s, 3H, -CH_3), 1.60-1.55 (m, 4H), 1.35-1.31 (m, 4H), 0.92-0.86 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.3, 154.0, 137.4, 137.4, 128.4, 128.2, 127.8, 127.8, 127.8, 127.6, 127.6, 127.6, 96.4, 96.3, 95.2, 76.4, 74.6, 73.6, 73.5, 71.1, 70.1, 68.6, 68.1, 68.0, 68.0, 67.9, 54.4, 54.3, 32.1, 32.0, 20.7, 18.5, 18.5, 13.5; HRMS (ESI-TOF) m/e : Calcd for $C_{33}H_{45}Cl_3NO_{11}PNa$ $[M+Na]^+$: 790.1688 found 790.1688.



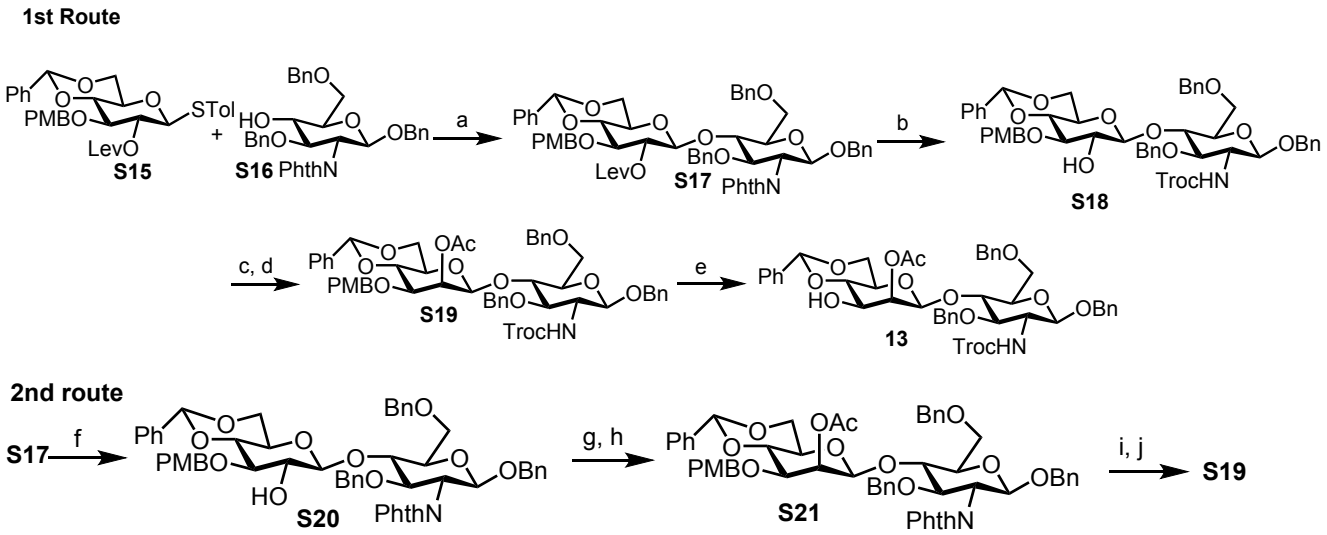
***p*-Tolyl [4-*O*-acetyl-3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranosyl]-(1→2)-3,4,6-tri-*O*-benzyl-1-thio-*α*-D-mannopyranoside S14.** A mixture of acceptor **S13**[10] (407 mg, 0.73 mmol, 1 equiv.) and donor **S12** (900 mg, 1.17 mmol, 1.6 equiv.) and activated pulverized 4 Å molecular sieves (200 mg) in anhydrous CH_2Cl_2 (2 mL) was stirred under argon atmosphere for 30 min. Then it was cooled to -50 °C and followed by addition of TMSOTf (0.21 mL, 1.17 μmol, 1.6 equiv. with respect to acceptor) with stirring until TLC analysis indicated disappearance of starting materials (1 h). The reaction mixture was quenched with Et_3N (0.30 mL), diluted with CH_2Cl_2 (20 mL), and filtered through a pad of Celite. The filtrate was washed twice with satd aq. $NaHCO_3$ (8 mL) and brine (4 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated in vacuo. The obtained residue was purified by silica gel column chromatography using EtOAc/hexane (1:3) as eluent to give compound **S14** as a white powder (710 mg, 87%). R_f = 0.26 (silica gel, EtOAc:hexane = 1:3); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37-7.36 (m, 2H, Ar-H), 7.33-7.14 (m, 25H, Ar-H), 7.05-7.03 (m, 2H, Ar-H), 5.33 (d, *J* = 1.8 Hz, 1H, C1-H_α), 5.26 (d, *J* = 4.8 Hz, 1H), 5.07 (d, *J* = 9.0 Hz, 1H, C1-H_β), 4.93-4.90 (m, 2H), 4.77 (d, *J* = 11.4 Hz, 1H), 4.60-4.52 (m, 5H), 4.46-4.34 (m, 5H), 4.27 (dd, *J* = 8.4, 8.4 Hz, 1H), 4.19 (dd, *J* = 9.6, 2.4 Hz, 1H), 4.15 (d, *J* = 12.0 Hz, 1H), 4.07 (dd, *J* = 9.6, 9.0 Hz, 1H), 3.84-3.81 (m, 2H), 3.64-3.63 (m, 2H), 3.57 (dd, *J* = 10.8, 6.0 Hz, 1H), 3.51 (dd, *J* = 11.4, 3.0 Hz, 1H), 3.01 (dd, *J* = 6.6 Hz, 1H), 2.28 (s, 3H, -CH_3), 1.82 (s, 3H, -CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.7, 154.2, 138.5, 138.3, 138.0, 137.8, 137.7, 137.6, 132.5, 130.3, 129.8, 129.7, 129.0, 128.4, 128.4, 128.3, 128.2, 128.2, 128.2, 128.2, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.6, 127.4, 125.2, 97.1, 95.4, 86.2, 78.3, 75.2, 75.1, 74.5, 74.1, 74.0, 73.6, 73.4, 73.1, 72.5, 71.7, 71.3, 70.0, 69.2, 58.1, 21.1, 20.8; HRMS (ESI-TOF) m/e : Calcd for $C_{59}H_{62}Cl_3NO_{12}SNa$ $[M+Na]^+$: 1136.2950 found 1136.2978.



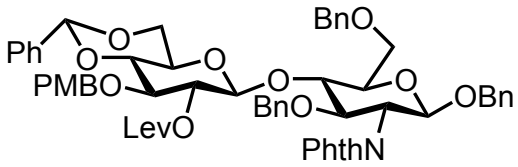
***p*-Tolyl [3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranosyl]-(1→2)-3,4,6-tri-*O*-benzyl-1-thio-*α*-D-mannopyranoside 18.** To a well-stirred solution of compound **S14** (203 mg, 0.18 mmol, 1 equiv.) in a mixture of CH_2Cl_2/MeOH (10 mL,

1:1 = *v/v*) was added NaOMe (2.95 mg, 0.055 mmol, 0.3 equiv.) at 0 °C. After 20 min, the ice bath was removed and the reaction mixture was warmed up to room temperature with stirring until TLC analysis indicated the disappearance of starting materials (4 hrs). Upon completion, the reaction mixture was neutralized with IR-120, filtered, and concentrated in *vacuo*. The obtained residue was purified by silica gel column chromatography using EtOAc/hexane (1:2) as eluent to give compound **18** as a white foam (149 mg, 76%). R_f = 0.14 (silica gel, EtOAc:hexane = 1:3); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39-7.37 (m, 2H, Ar-H), 7.34-7.24 (m, 25H, Ar-H), 7.06-7.05 (m, 2H, Ar-H), 5.33 (d, *J* = 1.8 Hz, 1H, C1-H_α), 5.24 (d, *J* = 4.8 Hz, 1H), 5.00 (d, *J* = 7.8 Hz, 1H, C1-H_β), 4.93 (d, *J* = 10.8 Hz, 1H), 4.78 (d, *J* = 11.4 Hz, 1H), 4.69-4.64 (m, 2H), 4.61 (d, *J* = 11.4 Hz, 2H), 4.57-4.51 (m, 4H), 4.43 (d, *J* = 11.4 Hz, 1H), 4.34 (dd, *J* = 2.4, 2.4 Hz, 1H), 4.22-4.20 (m, 2H), 4.07-4.04 (m, 2H), 3.84-3.82 (m, 2H), 3.77-3.72 (m, 2H), 3.67-3.65 (m, 1H), 3.59-3.54 (m, 2H), 3.01 (d, *J* = 7.2 Hz, 1H), 2.68 (br, 1H, -OH), 2.30 (s, 3H, -CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 154.2, 138.5, 138.4, 138.3, 137.9, 137.7, 137.6, 132.5, 130.3, 129.8, 128.5, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 127.5, 97.5, 95.4, 86.2, 79.1, 78.4, 75.3, 75.2, 74.6, 74.4, 74.2, 73.8, 73.8, 73.2, 73.1, 72.5, 71.4, 70.9, 69.3, 57.8, 21.1; HRMS (ESI-TOF) m/e : Calcd for $C_{57}H_{60}Cl_3NO_{11}SNa$ $[M+Na]^+$: 1094.2845 found 1094.2881.

Scheme S4. Synthesis of the Disaccharide Core 13.

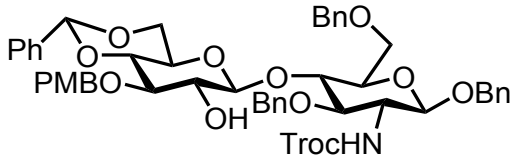


Reagents and conditions: (a) NIS, TfOH, 4 Å MS, -40 °C, 1 h, CH_2Cl_2, 93%. (b) ethylenediamine/BuOH (1:4), 90 °C, 2 h, then $NaHCO_3$, TrocCl, CH_2Cl_2, 0 °C, 3 h, 81%. (c) Tf_2O, pyridine, CH_2Cl_2, 0 °C, 4h. (d) Bu_4NOAc, toluene, sonication, r.t., 8h, then $NaHCO_3$, TrocCl, CH_2Cl_2, 0 °C, 3 h, 61% (2 steps). (e) DDQ, CH_2Cl_2, phosphate buffer (pH = 7), 0 °C to r.t., 3h, 85%. (f) hydrazine acetate , THF, r.t., 16h, 92%. (g) Tf_2O, pyridine, CH_2Cl_2, 0 °C, 2h. (h) Bu_4NOAc, toluene, sonication, r.t., 8h, 93% (2 steps). (i) ethylenediamine/BuOH (1:4), 90 °C, 2 h, then $NaHCO_3$, TrocCl, CH_2Cl_2, 0 °C, 3 h. (j) Ac_2O, pyridine, CH_2Cl_2, r.t., 16h, 83% (2 steps).



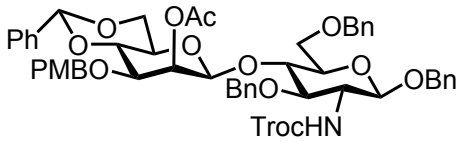
Benzyl [4,6-*O*-benzylidine-3-*O*-*p*-methoxy-benzyl-2-*O*-levulinoyl-*β*-D-glucopyranosyl]-(1→4) -3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranoside S17. A mixture of acceptor **S16**[11] A mixture of acceptor **S16**[11] (1.59 g, 2.74 mmol, 1 equiv.), donor **S15**[7] (2.11 g, 3.57 mmol, 1.3 equiv.) and activated pulverized 4 Å MS (5.00 g) in anhydrous CH_2Cl_2 (50 mL) was stirred under argon atmosphere for 1 h. Then, the reaction mixture was cooled to −40 °C and NIS (1.23 g, 5.49 mmol, 2 equiv.) was added, followed by addition of TfOH (0.5 M in Et_2O, 1.37 mL, 0.69 mmol, 0.25 equiv.) until TLC indicated the disappearance of starting materials (2 hrs). Upon

completion, the reaction mixture was quenched with Et_3N (0.7 mL) and filtered through a pad of Celite. The filtrate was diluted with CH_2Cl_2 (50 mL), washed with 20% aq. $Na_2S_2O_3$ (15 mL), satd. aq. $NaHCO_3$ (20 mL), and brine (10 mL). The separated organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography using EtOAc/hexane (2:3) as eluent to give compound **S17** as a white foam (2.68 g, 93%). R_f = 0.43 (silica gel, acetone:toluene = 1:6); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.75 (br, 1H, Ar-H), 7.63 (br, 2H, Ar-H), 7.50 (br, 1H, Ar-H), 7.46-7.45 (m, 2H, Ar-H), 7.39-7.32 (m, 7H, Ar-H), 7.29-7.26 (m, 1H, Ar-H), 7.20-7.18 (m, 2H, Ar-H), 7.07-7.05 (m, 1H, Ar-H), 7.02-7.01 (m, 4H, Ar-H), 6.98-6.97 (m, 2H, Ar-H), 6.87-6.83 (m, 5H, Ar-H), 5.44 (s, 1H, Ph-CH), 5.10-5.08 (m, 1H, C1-H_β), 4.92 (dd, *J* = 9.0, 8.4 Hz, 1H), 4.81-4.71 (m, 4H), 4.58 (d, *J* = 7.8 Hz, 1H, C1-H_β), 4.56 (d, *J* = 4.2 Hz, 1H), 4.47 (d, *J* = 6.0 Hz, 1H), 4.45 (d, *J* = 6.6 Hz, 1H), 4.36 (d, *J* = 12.6 Hz, 1H), 4.23 (dd, *J* = 10.2, 4.8 Hz, 1H), 4.20-4.19 (m, 2H), 4.09-4.06 (m, 1H), 3.87 (dd, *J* = 11.4, 3.0 Hz, 1H), 3.79-3.78 (m, 1H), 3.78 (s, 3H, -CH_3), 3.59 (dd, *J* = 9.6, 9.0 Hz, 1H), 3.55-3.51 (m, 2H), 3.43 (dd, *J* = 10.2, 10.2 Hz, 1H), 3.17 (ddd, *J* = 9.6, 9.6, 4.8 Hz, 1H), 2.81-2.76 (m, 1H), 2.70-2.65 (m, 1H), 2.50-2.38 (m, 2H), 2.20 (s, 3H, -CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 206.2, 171.1, 159.2, 138.6, 138.1, 137.3, 133.5, 131.6, 130.4, 129.4, 129.0, 128.5, 128.2, 128.1, 127.9, 127.8, 127.7, 127.5, 127.5, 127.0, 126.0, 123.1, 113.6, 101.1, 100.6, 97.4, 81.7, 78.0, 77.9, 76.6, 74.8, 74.5, 73.7, 73.6, 70.7, 68.6, 67.7, 65.8, 55.7, 55.3, 37.7, 29.9, 27.8; HRMS (ESI-TOF) m/e : Calcd for $C_{61}H_{61}NO_{15}Na$ $[M+Na]^+$: 1070.3933 found 1070.3933.



Benzyl [4,6-*O*-benzylidine-3-*O*-*p*-methoxy-benzyl-*β*-D-glucopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside S18. A solution of disaccharide **S17** (625 mg, 0.596 mmol, 1 equiv.) in ethylene diamine/*n*-BuOH (7 mL, 2:8 = *v/v*) was stirred at 90 °C for 2 hrs. The solvent was removed by rotary evaporation under high vacuum and co-evaporated with toluene twice to remove traces of water. The obtained residue was dissolved in anhydrous CH_2Cl_2 (15 mL) and treated with $NaHCO_3$ (250 mg, 2.98 mmol, 5 equiv.) and 2,2,2-trichloro ethyl chloroformate (0.41 mL, 2.98 mmol, 5 equiv.) at 0 °C under argon

atmosphere for 3rs. Upon completion, the reaction mixture was diluted with CH_2Cl_2 (20 mL), washed with water (20 mL) and brine (10 mL). The organic layer was dried over $MgSO_4$ and concentrated in *vacuo*. The obtained residue was purified by silica gel column chromatography using EtOAc/toluene (1:4) as eluent to give compound **S18** as a white powder (481 mg, 81%). R_f = 0.60 (silica gel, EtOAc:toluene = 1:2); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.47-7.46 (m, 2H, Ar-H), 7.40-7.25 (m, 20H, Ar-H), 6.86-6.85 (m, 2H, Ar-H), 5.46 (s, 1H, Ph-CH), 5.12 (br, 1H), 4.88-4.85 (m, 3H), 4.71-4.55 (m, 9H, 2C1-H_β), 4.06-4.03 (m, 2H), 3.99 (dd, *J* = 11.4, 3.6 Hz, 1H), 3.87 (br, 1H), 3.80 (dd, *J* = 11.4, 1.8 Hz, 1H), 3.78 (s, 3H, -CH_3), 3.56 (dd, *J* = 9.6, 9.0 Hz, 1H), 3.52-3.45 (m, 5H), 3.15 (ddd, *J* = 9.6, 9.6, 4.8 Hz, 1H), 3.03 (br, 1H, -OH); ^{13}C NMR (150 MHz, $CDCl_3$): δ 159.3, 153.8, 138.4, 137.7, 137.3, 137.2, 130.4, 129.6, 128.9, 128.4, 128.4, 128.3, 128.2, 128.0, 127.8, 127.8, 127.6, 127.4, 126.0, 113.8, 103.2, 101.1, 99.2, 95.5, 81.3, 79.9, 79.2, 77.7, 74.9, 74.5, 74.3, 74.2, 73.5, 70.7, 68.6, 68.2, 66.2, 57.6, 55.2; HRMS (ESI-TOF) m/e : Calcd for $C_{51}H_{54}Cl_3NO_{13}Na$ $[M+Na]^+$: 1016.2553 found 1016.2554.

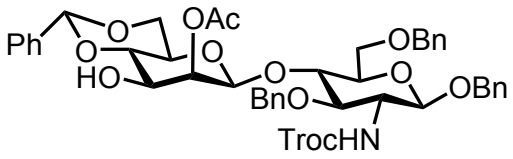


Benzyl [2-*O*-acetyl-4,6-*O*-benzylidine-3-*O*-*p*-methoxy-benzyl-*β*-D-mannopyranosyl]- (1→4)-3,6-di-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside S19.

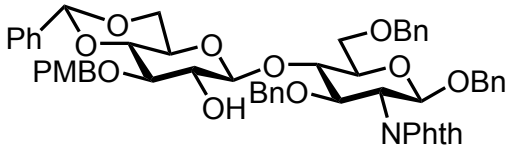
From **S18**: To a stirred solution of disaccharide **S18** (1.02 g, 1.02 mmol, 1 equiv.) in anhydrous CH_2Cl_2 (13 mL) was added anhydrous pyridine (0.58 mL, 7.17 mmol, 7 equiv.), followed by dropwise addition of Tf_2O (0.30 mL, 1.79 mmol, 1.75 equiv.) at 0 °C under argon atmosphere. The reaction mixture was stirred at 0 °C until TLC indicated the disappearance of starting material (4 hrs). Upon completion, it was diluted with CH_2Cl_2 (20 mL), washed with 0.5N HCl (20 mL) and brine (10 mL). The separated organic layer was dried over $MgSO_4$ and concentrated in *vacuo*. The crude residue was mixed with Bu_4NOAc (927 mg, 3.07 mmol, 3 equiv.) and dissolved in toluene (20 mL). The solvent was removed in *vacuo* and the residue was co-evaporated with toluene twice; then, redissolved in anhydrous toluene (13 mL) and the mixture was sonicated for 8 hrs. During this time, we observed a partial deprotection of NHTroc and the reaction mixture was concentrated under high vacuum. Thus obtained residue was dissolved in CH_2Cl_2 (13 mL) and treated with

$NaHCO_3$ (430 mg, 5.12 mmol, 5 equiv.) and 2,2,2-trichloro ethyl chloroformate (0.71 mL, 5.12 mmol, 5 equiv.) at 0 ^oC under argon atmosphere. After stirring for 3hrs, the reaction mixture was diluted with CH_2Cl_2 (20 mL), washed with water (20 mL) and brine (10 mL). The separated organic layer was dried over $MgSO_4$ and concentrated in *vacuo*. The obtained residue was purified by silica gel column chromatography using EtOAc/toluene (1:5) as eluent to give compound **S19** as a white powder (650 mg, 61%).

From **S21**: A solution of disaccharide **S21** (1.20 g, 1.21 mmol, 1 equiv.) in ethylene diamine/*n*-BuOH (15 mL, 2:8 = *v/v*) was stirred at 90 ^oC for 2 h. After removal of solvent, the crude product was co-evaporated with toluene twice. The obtained residue was dissolved in CH_2Cl_2 (30 mL) and treated with $NaHCO_3$ (508 mg, 6.05 mmol, 5 equiv.) and 2,2,2-trichloro ethyl chloroformate (0.83 mL, 6.05 mmol, 5 equiv.) at 0 ^oC under argon atmosphere. After 3 hrs, the reaction mixture was diluted with CH_2Cl_2 (45 mL), washed with water (30 mL) and brine (15 mL). The organic layer was dried over $MgSO_4$, concentrated, co-evaporated with toluene twice, evaporated in *vacuo* and the obtained residue was subjected directly to the acetylation conditions (Ac_2O (7 mL), pyridine (14 mL), 0 ^oC to room temperature, 16 hrs). The reaction mixture was concentrated under high vacuum and purified by silica gel column chromatography using acetone/toluene (1:5) as eluent to give compound **S19** as a white powder (1.04 g, 83%). R_f = 0.54 (silica gel, EtOAc:toluene = 1:3); ^1H NMR (600 MHz, $CDCl_3$): δ 7.48-7.46 (m, 2H, Ar-H), 7.39-7.35 (m, 3H, Ar-H), 7.33-7.25 (m, 14H, Ar-H), 7.24-7.21 (m, 3H, Ar-H), 6.84-6.82 (m, 2H, Ar-H), 5.50 (s, 1H, Ph-CH), 5.41 (d, *J* = 3.0 Hz, 1H), 5.09 (br, 1H), 4.92 (d, *J* = 10.8 Hz, 1H), 4.88 (d, *J* = 12.0 Hz, 1H), 4.72-4.62 (m, 5H, 2C1-H_β), 4.58-4.56 (m, 3H), 4.47-4.44 (m, 2H), 4.08 (dd, *J* = 10.2, 4.8 Hz, 1H), 4.04 (dd, *J* = 9.0, 8.4 Hz, 1H), 3.87-3.84 (m, 2H), 3.78-3.72 (m, 5H, -CH_3), 3.59 (dd, *J* = 10.2, 10.2 Hz, 1H), 3.45-3.43 (m, 2H), 3.38 (ddd, *J* = 8.4, 8.4, 8.4 Hz, 1H), 3.10 (ddd, *J* = 9.6, 9.6, 4.8 Hz, 1H), 2.07 (s, 3H, -CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.3, 159.3, 153.8, 138.4, 137.8, 137.4, 137.1, 129.7, 129.2, 128.9, 128.5, 128.4, 128.3, 128.2, 128.0, 128.0, 127.9, 127.8, 127.7, 126.1, 113.8, 101.4, 99.1, 99.1, 77.8, 75.3, 74.4, 73.5, 71.4, 70.8, 69.1, 68.5, 68.4, 67.0, 57.5, 55.2, 21.0; HRMS (ESI-TOF) m/e : Calcd for $C_{53}H_{56}Cl_3NO_{14}Na$ $[M+Na]^+$: 1058.2658 found 1058.2657.

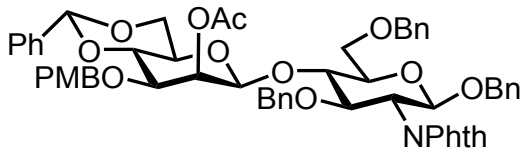


Benzyl [2-*O*-acetyl-4,6-*O*-benzylidine-*β*-D-mannopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy -2-(2,2,2-trichloroethoxy)carbonylamino-*β*-D-glucopyranoside 13. To a stirred solution of **S19** (120 mg, 0.12 mmol, 1 equiv.) in a mixture of CH_2Cl_2/phosphate buffer (pH = 7) (3 mL, 9:1 = *v/v*) was added 2,3-dichloro-5,6-dicyanobenzoquinone (52.5 mg, 0.23 mmol, 2.2 equiv.) at 0 °C. The reaction mixture was vigorously stirred until TLC indicated the disappearance of starting material (3 hrs). Upon completion, the reaction mixture was diluted with CH_2Cl_2 (10 mL), washed with satd. aq. $NaHCO_3$ (8 mL) and brine (4 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated. The obtained residue was purified by silica gel column chromatography using EtOAc/toluene (1:4) as eluent to give compound **13** as a white powder (90 mg, 85%). R_f = 0.29 (silica gel, EtOAc:toluene = 1:3); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.45-7.44 (m, 2H, Ar-H), 7.39-7.34 (m, 7H, Ar-H), 7.33-7.26 (m, 11H, Ar-H), 5.47 (s, 1H, Ph-CH), 5.23 (d, *J* = 3.6 Hz, 1H), 5.06 (br, 1H), 4.91 (d, *J* = 11.4 Hz, 1H), 4.87 (d, *J* = 12.0 Hz, 1H), 4.74 (d, *J* = 12.0 Hz, 1H), 4.68-4.61 (m, 4H, 2C1-H_β), 4.58-4.56 (m, 2H), 4.48 (d, *J* = 12.0 Hz, 1H), 4.08 (dd, *J* = 10.2, 4.8 Hz, 1H), 4.04 (dd, *J* = 9.0, 9.0 Hz, 1H), 3.83 (br, 1H), 3.78 (dd, *J* = 11.4, 3.0 Hz, 1H), 3.73-3.70 (m, 2H), 3.64 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.56 (dd, *J* = 10.2, 10.2 Hz, 1H), 3.43-3.36 (m, 2H), 3.11 (ddd, *J* = 9.6, 9.6, 4.8 Hz, 1H), 2.21 (d, *J* = 3.6 Hz, 1H), 2.11 (s, 3H, -CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.5, 153.8, 138.5, 137.8, 137.1, 137.0, 129.3, 128.6, 128.6, 128.4, 128.4, 128.3, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7, 126.2, 102.1, 99.1, 99.0, 78.5, 78.2, 74.4, 74.4, 73.6, 71.2, 70.8, 69.7, 68.4, 68.4, 66.7, 57.5; HRMS (ESI-TOF) m/e : Calcd for $C_{45}H_{49}Cl_3NO_{13}$ $[M+H]^+$: 916.2264 found 916.2252.



Benzyl [4,6-*O*-benzylidine-3-*O*-*p*-methoxy-benzyl-*β*-D-glucopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranoside S20. To a stirred solution of starting

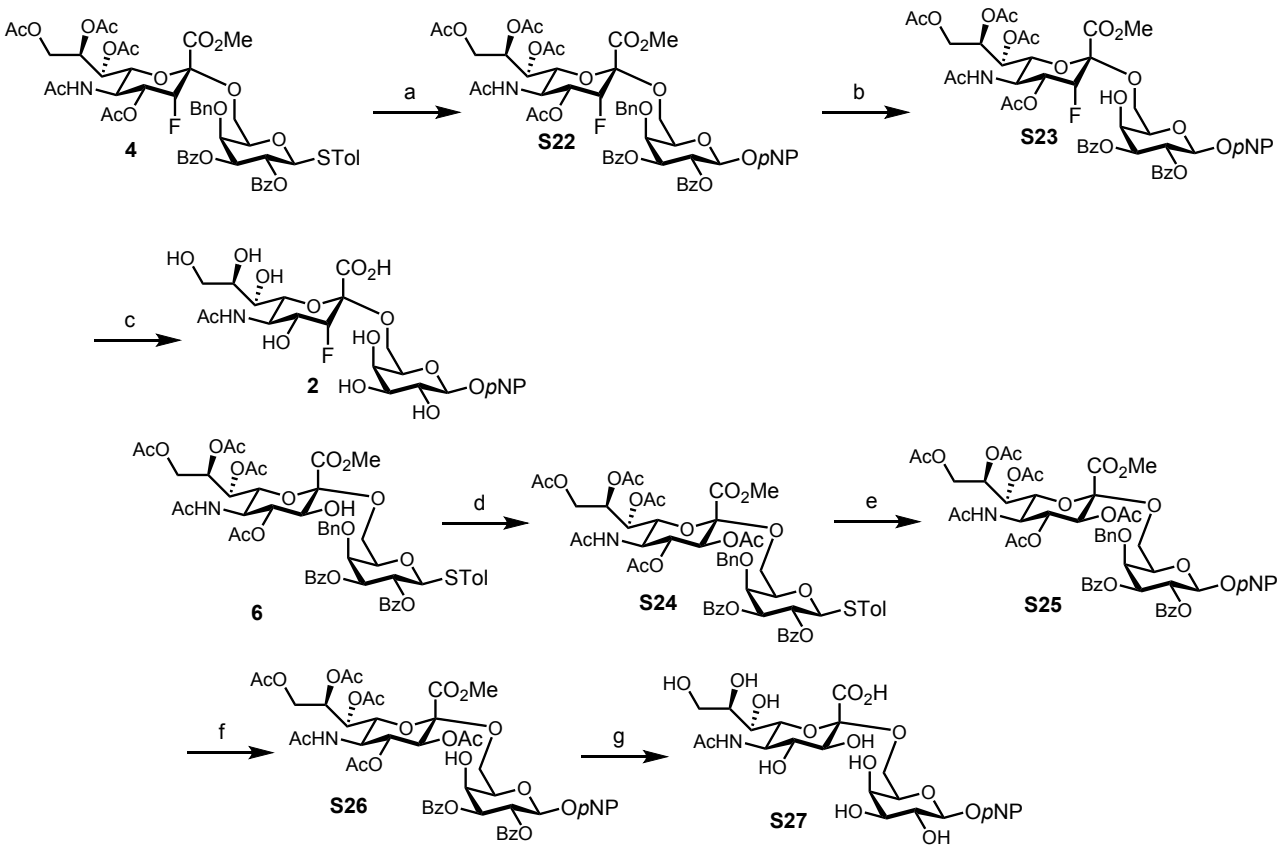
material **S17** (2.48 g, 2.37 mmol, 1 equiv.) in anhydrous THF (55 mL) was added hydrazine acetate (327 mg, 3.55 mmol, 1.5 equiv.) at room temperature under argon atmosphere. The reaction mixture was vigorously stirred until TLC indicated the disappearance of starting material (16 hrs). Upon completion, the reaction mixture was diluted with EtOAc (150 mL), washed with water (60 mL) and brine (30 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated in *vacuo*. The obtained residue was purified by silica gel column chromatography using EtOAc/Hexane (1:2) as eluent to give compound **S20** as a white foam (2.07 g, 92%). R_f = 0.54 (silica gel, EtOAc:hexane = 1:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.79-7.54 (m, 4H, Ar-H), 7.51-7.44 (m, 2H, Ar-H), 7.38-7.33 (m, 7H, Ar-H), 7.30-7.27 (m, 3H, Ar-H), 7.08-7.04 (m, 1H, Ar-H), 7.02-7.01 (m, 4H, Ar-H), 6.98-6.97 (m, 2H, Ar-H), 6.89-6.81 (m, 5H, Ar-H), 5.46 (s, 1H, Ph-CH), 5.09 (d, *J* = 8.4 Hz, 1H, C1-H_β), 4.85 (d, *J* = 11.4 Hz, 1H), 4.77 (d, *J* = 12.6 Hz, 1H), 4.75 (d, *J* = 4.2 Hz, 1H), 4.73 (d, *J* = 4.2 Hz, 1H), 4.68 (d, *J* = 11.4 Hz, 1H), 4.62 (d, *J* = 7.2 Hz, 1H, C1-H_β), 4.56 (d, *J* = 12.0 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 4.38 (d, *J* = 12.0 Hz, 1H), 4.32 (dd, *J* = 10.8, 8.4 Hz, 1H), 4.21 (d, *J* = 10.8, 8.4 Hz, 1H), 4.15-4.10 (m, 2H), 4.04 (dd, *J* = 11.4, 3.0 Hz, 1H), 3.82 (dd, *J* = 11.4, 1.8 Hz, 1H), 3.78 (s, 3H, -CH_3), 3.61 (ddd, *J* = 9.6, 3.0, 3.0 Hz, 1H), 3.56 (dd, *J* = 3.0, 3.0 Hz, 1H), 3.52-3.45 (m, 3H), 3.18 (ddd, *J* = 9.6, 9.6, 4.8 Hz, 1H), 2.98 (br, 1H, -OH); ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.9, 159.3, 138.4, 137.8, 137.3, 137.2, 133.6, 131.6, 130.5, 129.7, 128.9, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.5, 127.4, 127.1, 126.0, 123.2, 113.8, 103.4, 101.1, 97.5, 81.3, 79.5, 78.8, 77.8, 75.0, 74.7, 74.5, 74.2, 73.6, 70.8, 68.6, 68.2, 66.2, 55.8, 55.3; HRMS (ESI-TOF) m/e : Calcd for $C_{56}H_{55}NO_{13}Na$ $[M+Na]^+$: 972.3565 found 972.3567.



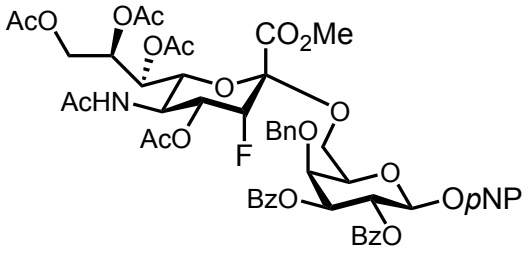
Benzyl [2-*O*-acetyl-4,6-*O*-benzylidine-3-*O*-*p*-methoxy-benzyl-*β*-D-mannopyranosyl]-(1→4) -3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranoside S21. To a stirred solution of disaccharide **S20** (936 mg, 0.985 mmol, 1 equiv.) in anhydrous CH_2Cl_2 (12 mL) was added anhydrous pyridine (0.56 mL, 6.90 mmol, 7 equiv.), then trifluoromethanesulfonic anhydride (0.29 mL, 1.72 mmol, 1.75 equiv.) was added dropwise at 0 °C under argon atmosphere and the mixture was stirred at 0 °C until TLC indicated the disappearance of starting material (2 h). Upon

completion, the reaction mixture was diluted with CH_2Cl_2 (20 mL), washed with 0.5 N HCl (20 mL) and brine (10 mL). The separated organic layer was dried over $MgSO_4$, concentrated in *vacuo* and the obtained residue was used as is for further steps. The above-obtained residue was added Bu_4NOAc (594 mg, 1.97 mmol, 2 equiv.) and dissolved in toluene (18 mL). The solvent was removed in *vacuo* and the residue was co-evaporated with toluene twice to remove traces of water. The residue was redissolved in anhydrous toluene (12 mL) and the mixture was sonicated for 8 h. Upon completion, the reaction mixture was diluted with EtOAc (20 mL), washednd with water (20 mL) and brine (10 mL). The separated organic layer was dried over $MgSO_4$, and concentrated. The obtained residue was purified by silica gel column chromatography. Using EtOAc/hexane (1:2) as eluent to give compound **S21** as white powder (913 mg, 93%). R_f = 0.29 (silica gel, EtOAc:hexane = 1:2); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.76-7.49 (m, 4H, Ar-H), 7.48-7.46 (m, 2H, Ar-H), 7.39-7.31 (m, 7H, Ar-H), 7.26-7.22 (m, 3H, Ar-H), 7.10-7.06 (m, 1H, Ar-H), 7.04-7.03 (m, 4H, Ar-H), 6.99-6.98 (m, 2H, Ar-H), 6.90-6.84 (m, 5H, Ar-H), 5.49 (s, 1H, Ph-CH), 5.44 (d, *J* = 3.0 Hz, 1H), 5.09 (d, *J* = 7.8 Hz, 1H, C1-H_β), 4.82-4.76 (m, 3H), 4.68 (s, 1H, C1-H_β), 4.58 (d, *J* = 12.0 Hz, 1H), 4.49-4.44 (m, 3H), 4.38 (d, *J* = 12.6 Hz, 1H), 4.26-4.19 (m, 2H), 4.17-4.11 (m, 2H), 3.86-3.82 (m, 2H), 3.78 (s, 3H, -CH_3), 3.78-3.76 (m, 1H), 3.57-3.54 (m, 2H), 3.44 (dd, *J* = 10.2, 3.6 Hz, 1H), 3.13 (ddd, *J* = 9.6, 9.6, 4.8 Hz, 1H), 2.15 (s, 3H, -CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.2, 167.8, 159.2, 138.5, 137.8, 137.4, 137.1, 133.6, 131.5, 129.7, 129.2, 128.9, 128.5, 128.1, 128.1, 127.9, 127.9, 127.8, 127.7, 127.6, 127.5, 127.1, 126.0, 123.1, 113.8, 101.4, 99.5, 97.3, 79.1, 77.7, 76.9, 75.4, 74.5, 74.3, 73.5, 71.3, 70.7, 69.1, 68.4, 68.3, 66.9, 55.6, 55.2, 21.0; HRMS (ESI-TOF) m/e : Calcd for $C_{58}H_{57}NO_{14}Na$ $[M+Na]^+$: 1014.3671 found 1014.3699.

Scheme S5. Synthesis of 2 and S27.

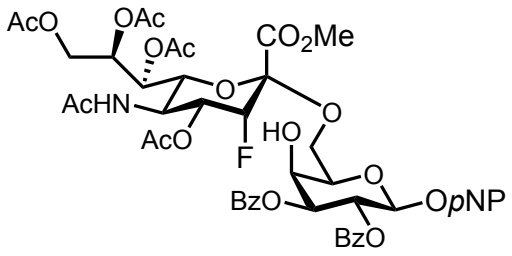


Reagents and conditions: (a) Br_2, CH_2Cl_2, 0 °C, 10 min., then *p*-nitrophenol, Ag_2O, CH_3CN, 1h, 73%. (b) $NaBrO_3$, $Na_2S_2O_4$, H_2O, EtOAc, r.t., 1.5h, 93%. (c) $LiOH{\cdot}H_2O$, MeOH, r.t., 16h, 84%. (d) Ac_2O, pyridine, r.t., 16 h, 90%. (e) Br_2, CH_2Cl_2, 0 °C, 10 min., then *p*-nitrophenol, Ag_2O, CH_3CN, 1h, 74%. (f) $NaBrO_3$, $Na_2S_2O_4$, H_2O, EtOAc, r.t., 1.5h, 97% (g) $LiOH{\cdot}H_2O$, MeOH, r.t., 16h, 94%.

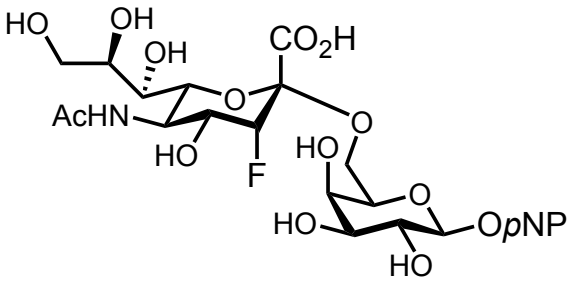


***p*-Nitrophenyl [methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-3-fluoro-D-erythro -*α*-L-manno-non-2-ulopyranosonate]-(2→6)-2,3-di-*O*-benzoyl-4-*O*-benzyl-*β*-D-**

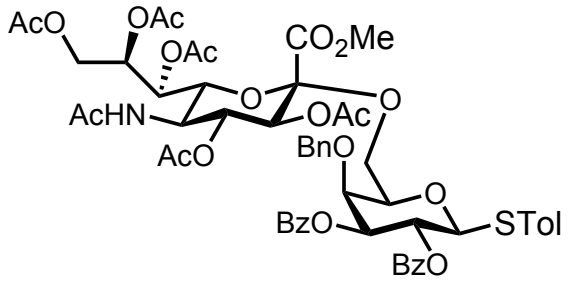
galactopyranoside S22. To a stirred solution of thioglycoside **4** (115 mg, 0.11 mmol, 1 equiv.) in anhydrous CH_2Cl_2 (2 mL) at 0 °C was added bromine (6.02 µL, 0.12 mmol, 1.1 equiv.). After the reaction mixture was vigorously stirred for 10 min, the solvent was removed in *vacuo* and the residue was co-evaporated with toluene twice to remove traces of water. Thus obtained residue was dissolved in anhydrous CH_3CN (2 mL) and treated with 4-nitrophenol (25.3 mg, 0.18 mmol, 1.7 equiv.) and Ag_2O (124 mg, 0.53 mmol, 5 equiv.). The reaction mixture was vigorously stirred in the dark under N_2 until TLC indicated the disappearance of starting material (1 h). Upon completion, the reaction mixture was diluted with EtOAc (10 mL) and filtered through a pad of Celite. The filtrate was washed twice with satd. aq. $NaHCO_3$ (4 mL) and brine (3 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated in *vacuo*. The obtained residue was purified by silica gel column chromatography using acetone/toluene (1:2) as eluent to give compound **S22** as a white powder (85 mg, 73%). R_f = 0.46 (silica gel, acetone:toluene = 2:3); ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.13-8.11 (m, 2H, Ar-H), 7.96-7.94 (m, 2H, Ar-H), 7.91-7.89 (m, 2H, Ar-H), 7.49-7.44 (m, 2H, Ar-H), 7.35-7.30 (m, 6H, Ar-H), 7.24-7.22 (m, 2H, Ar-H), 7.20-7.18 (m, 2H, Ar-H), 7.13-7.11 (m, 1H, Ar-H), 6.09 (dd, *J* = 10.2, 7.8 Hz, 1H), 5.65-5.59 (dd, *J* = 10.2, 3.0 Hz, 1H, C1-H_β), 5.35 (d, *J* = 9.6 Hz, 1H), 5.28 (dd, *J* = 9.6, 1.8 Hz, 1H), 5.19 (dd, *J* = 27.0, 10.8 Hz, 1H, sia-C4-H), 5.04 (dd, *J* = 51.0, 1.8 Hz, 1H, sia-C3-H), 4.72-4.67 (m, 2H), 4.44 (dd, *J* = 12.6, 3.6 Hz, 1H), 4.40 (d, *J* = 3.0 Hz, 1H), 4.37 (dd, *J* = 8.4, 6.6 Hz, 1H), 4.31 (d, *J* = 10.8 Hz, 1H), 4.18 (ddd, *J* = 4.2, 4.2, 4.2 Hz, 1H), 4.08 (dd, *J* = 12.6, 6.6 Hz, 1H), 3.89-3.80 (m, 5H, -CH_3), 2.26 (s, 6H, -2CH_3), 2.10 (s, 3H, -CH_3), 1.93 (s, 3H, -CH_3), 1.92 (s, 3H, -CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.1, 170.8, 170.4, 170.3, 170.2, 165.5, 165.5, 165.4, 165.3, 161.8, 142.6, 138.0, 133.2, 133.1, 129.8, 129.7, 129.4, 129.0, 128.4, 128.3, 128.2, 128.1, 128.0, 127.5, 125.6, 116.8, 98.8 (d, *J* = 15.9 Hz, 1C, sia-C2), 98.2, 87.5 (d, *J* = 193.1 Hz, 1C, sia-C3), 75.0, 73.9, 73.7, 73.2, 71.6, 69.7, 69.1, 69.0, 67.3, 67.2, 63.4, 63.3, 53.4, 45.1, 23.3, 21.2, 20.8, 20.7, 20.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ -215.5; HRMS (ESI-TOF) m/e : Calcd for $C_{53}H_{55}FN_2O_{22}Na$ $[M+Na]^+$: 1113.3123 found 1113.3131.



***p*-Nitrophenyl [methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-3-fluoro-D-erythro-*α*-L-manno-non-2-ulopyranosonate]-(2→6)-2,3-di-*O*-benzoyl-*β*-D-galactopyranoside S23.** To a well-stirred solution of compound **S22** (63.0 mg, 0.058 mmol, 1 equiv.) in EtOAc (0.8 mL) was added $NaBrO_3$ (85 %, 39.2 mg, 0.26 mmol, 4.5 equiv.) in H_2O (0.6 mL) followed by a slow addition of $Na_2S_2O_4$ (40.2 mg, 0.23 mmol, 4 equiv.) in H_2O (1.2 mL) at room temperature. The reaction mixture was stirred until TLC indicated the disappearance of the starting material (1.5 h). Upon completion of the reaction, the reaction mixture was diluted with EtOAc (10 mL), washed with 20% aq. $Na_2S_2O_3$ (5 mL) and brine (3 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated in *vacuo*, and the obtained residue was purified by silica gel column chromatography using acetone/toluene (3:5) as eluent to give compound **S23** as a white powder (54 mg, 93%). R_f = 0.40 (silica gel, acetone:toluene = 2:3); ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.13-8.12 (m, 2H, Ar-H), 7.99-7.98 (m, 2H, Ar-H), 7.95-7.94 (m, 2H, Ar-H), 7.50-7.46 (m, 2H, Ar-H), 7.37-7.32 (m, 4H, Ar-H), 7.19-7.18 (m, 2H, Ar-H), 6.05 (dd, *J* = 10.2, 9.8 Hz, 1H), 5.53 (ddd, *J* = 9.0, 6.0, 3.0 Hz, 1H), 5.49-5.45 (m, 2H, C1-H_β), 5.36 (d, *J* = 9.0 Hz, 1H), 5.27 (dd, *J* = 9.0, 1.8 Hz, 1H), 5.19 (dd, *J* = 27.0, 11.4 Hz, 1H, sia-C4-H), 5.05 (dd, *J* = 51.6, 1.8 Hz, 1H, sia-C3-H), 4.47 (d, *J* = 3.0 Hz, 1H), 4.37 (dd, *J* = 12.6, 3.0 Hz, 1H), 4.26 (dd, *J* = 10.8, 1.2 Hz, 1H), 4.18 (dd, *J* = 6.6, 6.6 Hz, 1H), 4.13-4.07 (m, 1H), 4.05 (dd, *J* = 12.6, 6.6 Hz, 1H), 3.99-3.98 (m, 2H), 3.85 (s, 3H, -CH_3), 2.99 (br, 1H, -OH), 2.17 (s, 3H, -CH_3), 2.08 (s, 3H, -CH_3), 2.07 (s, 3H, -CH_3), 1.93 (s, 3H, -CH_3), 1.88 (s, 3H, -CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.9, 170.8, 170.5, 170.3, 165.6, 165.6, 165.3, 161.8, 142.9, 133.4, 133.3, 129.8, 129.7, 129.2, 129.1, 129.0, 128.4, 128.4, 128.2, 125.6, 125.3, 117.1, 99.0, 98.1 (d, *J* = 15.8 Hz, 1C, sia-C2), 87.7 (d, *J* = 192.4 Hz, 1C, sia-C3), 73.9, 73.3, 71.6, 69.2, 69.1, 69.0, 67.9, 67.2, 66.5, 63.6, 62.9, 53.4, 45.1, 23.3, 21.1, 20.7, 20.6, 20.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ -216.0; HRMS (ESI-TOF) m/e : Calcd for $C_{46}H_{50}FN_2O_{22}$ $[M+H]^+$: 1001.2834 found 1001.2833.

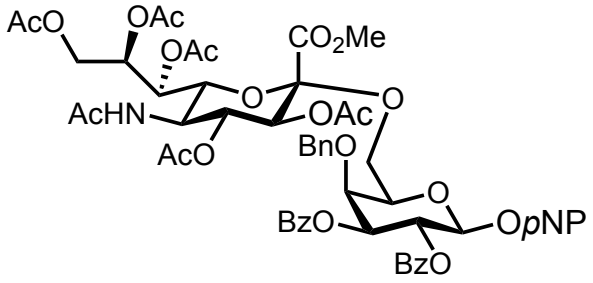


***p*-Nitrophenyl [methyl 5-acetamido-3,5-dideoxy-3-fluoro-D-erythro-*α*-L-manno-non-2 -ulopyranosonate]-(2→6)-*β*-D-galactopyranoside 2.** To a solution of compound **S23** (53 mg, 0.053 mmol, 1 equiv.) in methanol (5 mL) was added $LiOH \cdot H_2O$ (22.2 mg, 0.53 mmol, 10 equiv.) in water (1 mL). After stirring for 16 hrs at room temperature, the reaction mixture was neutralized with IR-120, filtered, and concentrated in *vacuo*. The obtained residue was purified by (BIO-RAD) Biogel P-2 column chromatography (eluting with water) to give compound **2** (27 mg, 84%). ^{1}H NMR (600 MHz, D_2O): δ 8.29-8.28 (m, 2H, Ar-H), 7.30-7.29 (m, 2H, Ar-H), 5.21 (dd, *J* = 51.6, 2.4 Hz, 1H, sia-C3-H), 5.18 (d, *J* = 7.8 Hz, C1-H_β), 4.17 (dd, *J* = 9.0, 9.0 Hz, 1H), 4.07-4.00 (m, 3H), 3.91-3.77 (m, 7H), 3.63 (dd, *J* = 12.0, 6.6 Hz, 1H), 3.57 (dd, *J* = 9.0, 1.8 Hz, 1H), 2.04 (s, 3H, -CH_3); ^{13}C NMR (150 MHz, D_2O): δ 175.0, 170.8, 161.9, 142.5, 126.1, 116.5, 100.0, 98.9 (d, *J* = 13.9 Hz, 1C, sia-C2), 91.0 (d, *J* = 183.2 Hz, 1C, sia-C3), 73.9, 72.4, 72.4, 71.6, 70.3, 69.7, 69.5, 68.4, 68.1, 63.7, 62.6, 46.8, 46.8, 22.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ -217.6; HRMS (ESI-TOF) m/e : Calcd for $C_{23}H_{32}FN_2O_{16}$ $[M+H]^+$: 611.1730 found 611.1732.



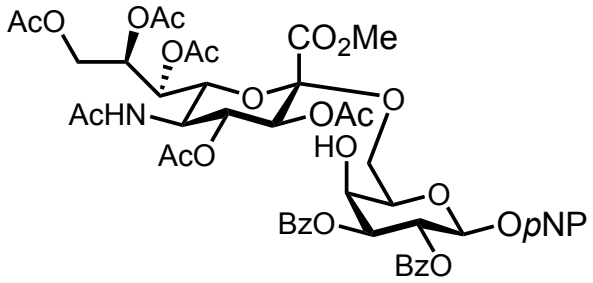
***p*-Tolyl [methyl 5-acetamido-3,4,7,8,9-penta-*O*-acetyl-5-deoxy-D-erythro-*α*-L-gluco-non -2-ulopyranosonate]-(2→6)-2,3-di-*O*-benzoyl-4-*O*-benzyl-1-thio-*β*-D-galactopyranoside S24**. To a stirred solution of starting material **6** (174 mg, 0.16 mmol, 1 equiv.) in pyridine (2 mL) was added Ac_2O (1 mL). The reaction mixture was vigorously stirred for 16 hrs at room temperature,

then concentrated under high vacuum. The obtained residue was purified by silica gel column chromatography using acetone/toluene (1:2) as eluent to give compound **S24** as a white powder (162 mg, 90%). R_f = 0.49 (silica gel, acetone:toluene = 2:3); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.94-7.92 (m, 2H, Ar-H), 7.88-7.87 (m, 2H, Ar-H), 7.48-7.44 (m, 2H, Ar-H), 7.40-7.38 (m, 2H, Ar-H), 7.35-7.27 (m, 6H, Ar-H), 7.23-7.20 (m, 2H, Ar-H), 7.18-7.16 (m, 1H, Ar-H), 7.05-7.03 (m, 2H, Ar-H), 5.80 (dd, *J* = 10.2. 9.6 Hz, 1H), 5.44-5.42 (m, 2H), 5.35-5.29 (m, 3H), 5.25 (dd, *J* = 8.4, 1.8 Hz, 1H), 4.95 (d, *J* = 10.2 Hz, 1H, C1-H_β), 4.67-4.61 (m, 3H), 4.33 (ddd, *J* = 10.2, 10.2, 10.2 Hz, 1H), 4.25-4.22 (m, 2H), 4.03-3.97 (m, 3H), 3.92-3.89 (m, 1H), 3.75 (s, 3H, -CH_3), 2.29 (s, 3H, -CH_3), 2.15 (s, 3H, -CH_3), 2.07 (s, 3H, -CH_3), 2.00 (s, 3H, -CH_3), 1.95 (s, 3H, -CH_3), 1.94 (s, 3H, -CH_3), 1.89 (s, 3H, -CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.0, 170.5, 170.3, 170.0, 169.3, 168.5, 168.0, 165.7, 165.2, 138.4, 137.6, 133.1, 132.9, 132.5, 129.8, 129.7, 129.7, 129.5, 129.2, 129.1, 128.3, 128.2, 128.0, 127.4, 127.2, 98.9, 86.5, 76.9, 75.5, 74.6, 74.3, 72.7, 71.6, 71.5, 68.5, 68.3, 66.9, 62.6, 62.5, 52.7, 48.4, 23.0, 21.1, 20.8, 20.7, 20.6, 20.6, 20.5; HRMS (ESI-TOF) m/e : Calcd for $C_{56}H_{61}NO_{21}SNa$ $[M+Na]^+$: 1138.3349 found 1138.3358.



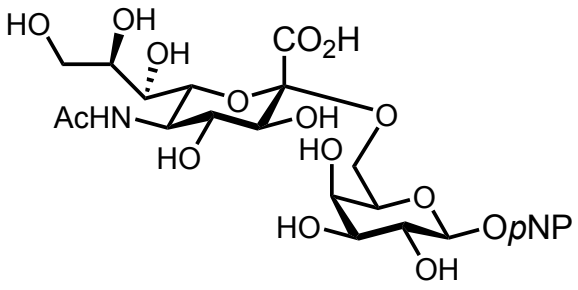
***p*-Nitrophenyl [methyl 5-acetamido-3,4,7,8,9-penta-*O*-acetyl-5-deoxy-D-erythro-*α*-L-gluco-non-2-ulopyranosonate]-(2→6)-2,3-di-*O*-benzoyl-4-*O*-benzyl-*β*-D-galactopyranoside S25.** To a stirred solution of thioglycoside **S24** (132 mg, 0.12 mmol, 1 equiv.) in anhydrous CH_2Cl_2 (2.5 mL) at 0 °C was added bromine (6.67 µL, 0.13 mmol, 1.1 equiv.). After vigorously stirring for 10 min, the solvent was removed in *vacuo* and the residue was co-evaporated with toluene twice to remove traces of water. The obtained residue was dissolved in anhydrous CH_3CN (2.5 mL) and treated with 4-nitrophenol (28.0 mg, 0.20 mmol, 1.7 equiv.) and Ag_2O (137 mg, 0.59 mmol, 5 equiv.). The reaction mixture was vigorously stirred in the dark under N_2 until TLC indicated the disappearance of starting material (1 h). Upon completion of the reaction, the reaction mixture was diluted with EtOAc (12 mL), and filtered through a pad of Celite. The filtrate was washed twice

with satd. aq. $NaHCO_3$ (5 mL) and brine (3 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated in *vacuo*, and the obtained residue was purified by silica gel column chromatography using acetone/toluene (3:5) as eluent to give compound **S25** as a white powder (99 mg, 74%). R_f = 0.51 (silica gel, acetone:toluene = 2:3); ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.15-8.13 (m, 2H, Ar-H), 7.95-7.92 (m, 4H, Ar-H), 7.50-7.44 (m, 2H, Ar-H), 7.36-7.31 (m, 6H, Ar-H), 7.24-7.19 (m, 2H, Ar-H), 7.17-7.15 (m, 3H, Ar-H), 6.10 (dd, *J* = 10.2, 7.8 Hz, 1H), 5.54 (dd, *J* = 10.2, 3.0 Hz, 1H), 5.52 (d, *J* = 7.8 Hz, 1H, C1-H_β), 5.48 (ddd, *J* = 10.2, 7.2, 3.0 Hz, 1H), 5.39 (d, *J* = 10.2 Hz, 1H), 5.31-5.29 (m, 2H), 5.23 (dd, *J* = 9.6, 1.8 Hz, 1H), 4.73 (dd, *J* = 10.8, 2.4 Hz, 1H), 4.71-4.65 (m, 2H), 4.32-4.30 (m, 3H), 4.19 (dd, *J* = 7.2, 7.2 Hz, 1H), 3.97 (dd, *J* = 12.6, 7.2 Hz, 1H), 3.88-3.86 (m, 2H), 3.83 (s, 3H, -CH_3), 2.24 (s, 3H, -CH_3), 2.12 (s, 3H, -CH_3), 2.01 (s, 3H, -CH_3), 1.98 (s, 3H, -CH_3), 1.90 (s, 3H, -CH_3), 1.88 (s, 3H, -CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.0, 170.7 (2C), 170,0, 169.6, 168.5, 168.3, 165.7, 165.3, 161.7, 142.7, 137.9, 133.3, 133.2, 129.9, 129.7, 129.3, 128.9, 128.4, 128.3, 128.2, 128.0, 127.6, 125.7, 116.8, 99.7, 98.4, 75.1, 74.1, 74.0, 73.9, 72.8, 71.6, 71.1, 69.7, 67.6, 67.0, 63.8, 63.3, 52.9, 48.4, 23.0, 20.9, 20.8, 20.7, 20.6; HRMS (ESI-TOF) m/e : Calcd for $C_{55}H_{59}N_2O_{24}$ $[M+H]^+$: 1131.3452 found 1131.3440.



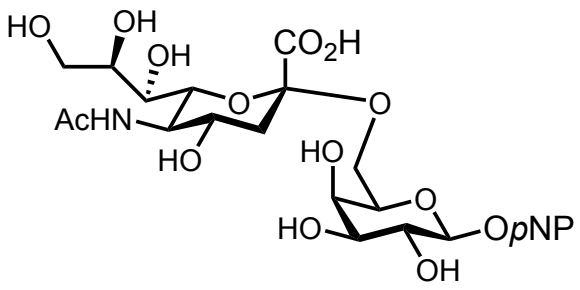
***p*-Nitrophenyl [methyl 5-acetamido-3,4,7,8,9-penta-*O*-acetyl-5-deoxy-D-erythro-*α*-L-gluco-non-2-ulopyranosonate]-(2→6)-2,3-di-*O*-benzoyl-*β*-D-galactopyranoside S26.** To a well-stirred solution of compound **S25** (91.0 mg, 0.080 mmol, 1 equiv.) in EtOAc (1.2 mL) was added $NaBrO_3$ (54.6 mg, 0.36 mmol, 4.5 equiv.) in H_2O (0.9 mL) followed by a slow addition of $Na_2S_2O_4$ (85 %, 56.0 mg, 0.32 mmol, 4 equiv.) in H_2O (1.8 mL) at room temperature. The reaction mixture was stirred until TLC indicated the disappearance of the starting material (1.5 h). Upon completion, the reaction mixture was diluted with EtOAc (15 mL), washed with 20% aq. $Na_2S_2O_3$ (7 mL) and brine (4 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated in *vacuo*. The obtained residue was purified by silica gel column chromatography using acetone/toluene (3:5) as

eluent to give compound **S26** as a white powder (81 mg, 97%). R_f = 0.23 (silica gel, acetone:toluene = 2:3); ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.18-8.16 (m, 2H, Ar-H), 8.00-7.99 (m, 2H, Ar-H), 7.94-7.93 (m, 2H, Ar-H), 7.51-7.46 (m, 2H, Ar-H), 7.38-7.32 (m, 4H, Ar-H), 7.15-7.13 (m, 2H, Ar-H), 6.07 (dd, *J* = 10.2, 7.8 Hz, 1H), 5.46-5.34 (m, 5H, C1-H_β), 5.30 (d, *J* = 10.2 Hz, 1H), 5.22 (dd, *J* = 7.8, 1.8 Hz, 1H), 4.60 (dd, *J* = 10.8, 1.8 Hz, 1H), 4.43 (d, *J* = 3.0 Hz, 1H), 4.33 (dd, *J* = 12.6, 2.4 Hz, 1H), 4.26 (ddd, *J* = 10.2, 10.2, 10.2 Hz, 1H), 4.12 (dd, *J* = 6.6, 6.6 Hz, 1H), 4.05 (dd, *J* = 10.2, 6.6 Hz, 1H), 3.99 (dd, *J* = 10.2, 6.6 Hz, 1H), 3.93 (dd, *J* = 12.6, 7.2 Hz, 1H), 3.83 (s, 3H, -CH_3), 3.17 (br, 1H, -OH), 2.14 (s, 3H, -CH_3), 2.05 (s, 3H, -CH_3), 2.02 (s, 3H, -CH_3), 2.00 (s, 3H, -CH_3), 1.87 (s, 3H, -CH_3), 1.85 (s, 3H, -CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.1, 171.0, 170.4, 170.0, 169.9, 168.8, 167.9, 165.8, 165.2, 161.7, 142.9, 133.4, 133.3, 129.9, 129.7, 129.3, 129.1, 128.4, 128.4, 125.8, 116.9, 99.1, 98.9, 74.0, 73.9, 73.0, 71.1, 70.6, 69.2, 68.7, 67.2, 66.5, 63.0, 62.5, 53.0, 48.5, 23.0, 20.8, 20.7, 20.6, 20.6; HRMS (ESI-TOF) m/e : Calcd for $C_{48}H_{53}N_2O_{24}$ $[M+H]^+$: 1041.2983 found 1041.2976.



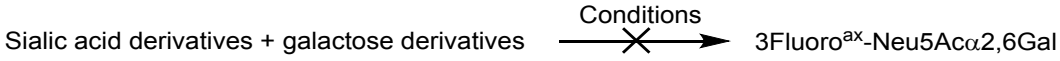
***p*-Nitrophenyl [5-acetamido-5-deoxy-D-erythro-*α*-L-gluco-non-2-ulopyranosonate]-(2→6)-*β*-D-galactopyranoside S27.** To a solution of compound **S26** (75 mg, 0.072 mmol, 1equiv.) in methanol (5 mL) was added LiOH·H_2O (30 mg, 0.72 mmol, 10 equiv.) in water (1 mL). After stirring for 16 h at room temperature, the reaction mixture was neutralized with IR-120, filtered, and concentrated. The obtained residue was purified by (BIO-RAD) Biogel P-2 column chromatography using water as eluent to give compound **S27** (41 mg, 94%). ^{1}H NMR (600 MHz, D_2O): δ 8.29-8.28 (m, 2H, Ar-H), 7.28-7.27 (m, 2H, Ar-H), 5.20 (d, *J* = 7.2 Hz, C1-H_β), 4.09-4.06 (m, 2H), 4.01 (dd, *J* = 10.8, 7.8 Hz, 1H), 3.92-3.79 (m, 6H), 3.71 (d, *J* = 10.8 Hz, 1H), 3.64-3.60 (m, 2H), 3.53 (d, *J* = 9.6 Hz, 1H), 3.49 (d, *J* = 9.6 Hz, 1H), 2.02 (s, 3H, -CH_3); ^{13}C NMR (150 MHz, D_2O): δ 174.8, 173.0, 161.9, 142.5, 126.1, 116.4, 99.9, 98.1, 76.1, 73.9, 73.5, 72.4, 72.2, 71.5, 70.3, 68.4, 68.0, 63.0, 62.6, 50.7, 21.9; HRMS (ESI-TOF) m/e : Calcd for $C_{23}H_{33}N_2O_{17}$

$[M+H]^+$: 609.1774 found 609.1774.



***p*-Nitrophenyl [5-acetamido-5-deoxy-D-glycero-*α*-D-galacto-non-2-ulopyranosylonate]- (2→6)-*β*-D-galactopyranoside 1.** Neu5Ac-α2,6-Gal-*p*NP: Neu5Ac-α2,6-Gal-*p*NP was synthesized by mixing commercial pNP-β-Gal (1.0 mmol), sialic acid (1.2 mmol), cytidine triphosphate (1.2 mmol), CMP-sialic acid synthetases (CSS, 12 U), pyrophosphatase (PPA, 1U) and α-2,6-sialyltransferase (SiaT, 15U) in a 15 mL Tris buffer (pH 7.0) with 5 mM $MgCl_2$ and 5 mM $MnCl_2$. After removal of the proteins by heating and centrifugation, it was purified by (BIO-RAD) Biogel P-2 column chromatography using water as eluents. The fractions containing Neu5Ac-α2,6-Gal-*p*NP were collected, and lyophilized to give compound **1** (50%). ^{1}H NMR (600 MHz, D_2O): δ 8.33-8.32 (m, 2H, Ar-H), 7.31-7.29 (m, 2H, Ar-H), 5.23 (d, J = 7.8 Hz, C1-H_β), 4.06-4.04 (m, 2H), 3.99 (dd, J = 10.2, 8.4 Hz, 1H), 3.90-3.86 (m, 3H), 3.83 (dd, J = 10.2, 3.6 Hz, 1H), 3.80-3.76 (m, 1H), 3.73-3.69(m, 3H), 3.65-3.62 (m, 2H), 3.57 (d, J = 8.4 Hz, 1H), 2.79 (dd, J = 12.6, 4.8 Hz, 1H), 2.04 (s, 3H, -CH_3), 1.68 (dd, J = 12.6, 12.0 Hz, 1H); ^{13}C NMR (150 MHz, D_2O): δ 174.6, 173.1, 161.4, 142.1, 125.7, 116.0, 99.8, 99.4, 73.6, 72.1, 71.9, 71.3, 69.8, 68.0, 67.7, 67.7, 62.5, 62.2, 51.4, 39.8, 21.6; HRMS (ESI-TOF) m/e : Calcd for $C_{23}H_{33}N_2O_{16}$ $[M+H]^+$: 593.1825 found 593.1825.

Table S1. Failed Attempts for the Synthesis of 3F^{ax}-Neu5Ac-α2,6-Gal Disaccharide.



entry	donor Neu5Ac	acceptor Gal	Conditions	results
1	**S28**	**3**	TMSOTf, EtCN, -78 °C , 2 h	S.M. [a]
2	**S29**	**S30**	Cs_2CO_3, DCM/ACN, TBAI, reflux	S.M. [a]
3	**S28**	**S31**	TMSOTf, EtCN, 4Å MS, -78 °C to r.t., 16 h	S.M. [a]
4	**S32**	**3**	Cp_2HfCl_2, AgOTf, 4Å MS, toluene, -30 °C to r.t., 2 d	S.M. [a]
5	**S33**	**3**	Selectfluor® , CH_3NO_2, r.t., 24 h	S.M. [a]
6	**S33**	**3**	Selectfluor® , DMF, 60 °C, 4 d	S.M. [a]

[a]Starting material was recovered.

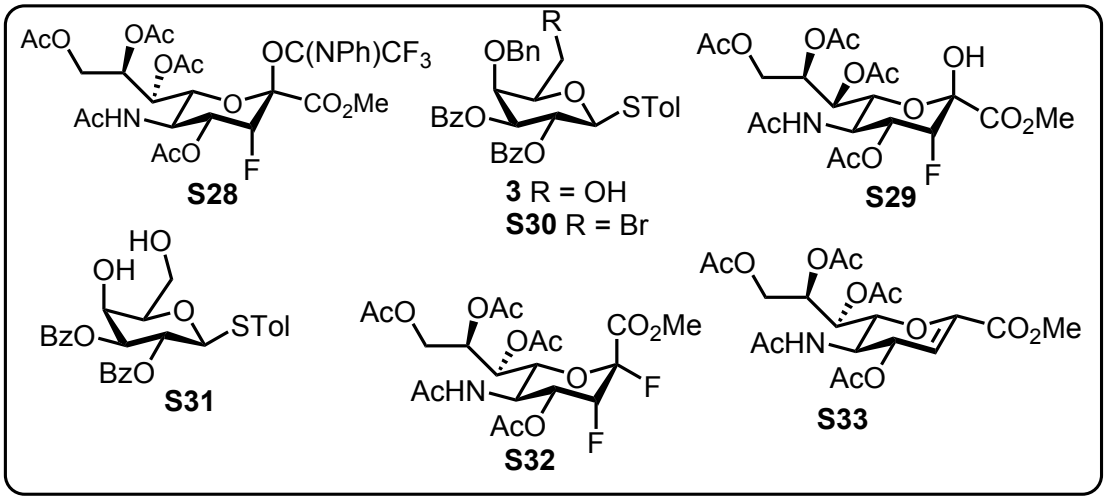
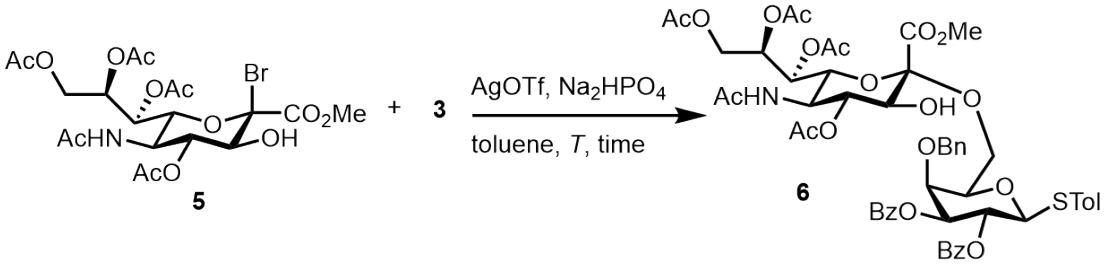


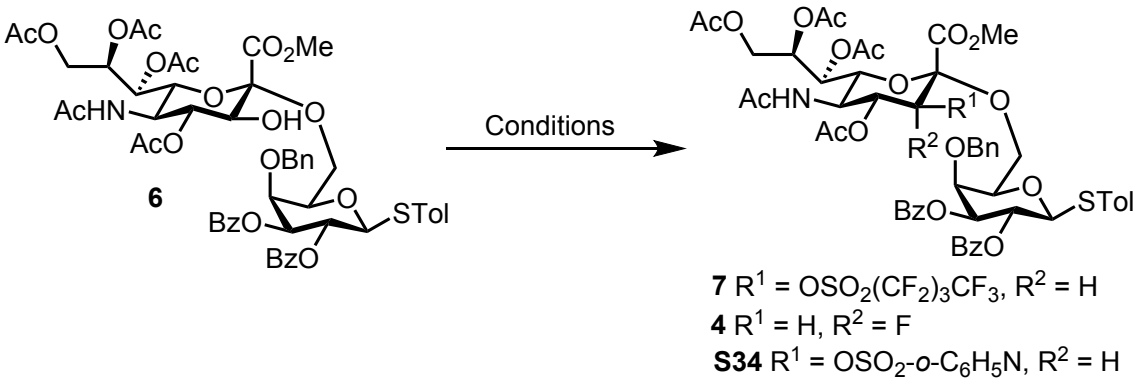
Table S2. Optimization of the Glycosylation Step.



entry	**5**/**3**/AgOTf/Na_2HPO_4	*T* (°C)	Time (h)	α:β[a]	Yield[b] (%) (brsm)[c]
1	1/1.1/1/4.6	-10	0.5	3.1:1	15[d]
2[e]	1.1/1/1.1/--	-78 to -20	3	2.7:1	21[d]
3	0.8/1/1.6/4.5	-50	16	5.2:1	46(94)
4	0.7/1/1.5/4.2	-50 to -35	16	3.8:1	53(99)
5	0.7/1/1.5/4.2	-50 to -15	16	1.8:1	72(99)
6	1/1.25/1.5/4.2	-50	16	16:1	28
7	1/1/1.5/4.2	-50	16	13:1	35(99)
8[f]	1/1/1.5/--	-50	16	11:1	33(99)
9[g]	1/1/1.5/4.2	-50	24	13:1	35(99)

[a]Determined by ^{1}H NMR. [b]Yield of isolated product. [c]Yield based on the recovered starting material (brsm), acceptor. [d]The donor and acceptor were not completely consumed. [e]Using CH_2Cl_2 with 4Å MS. [f]With 4Å MS. [g]Gram-scale.

Table S3. Screen of Fluorinating Conditions (6 -> 4).

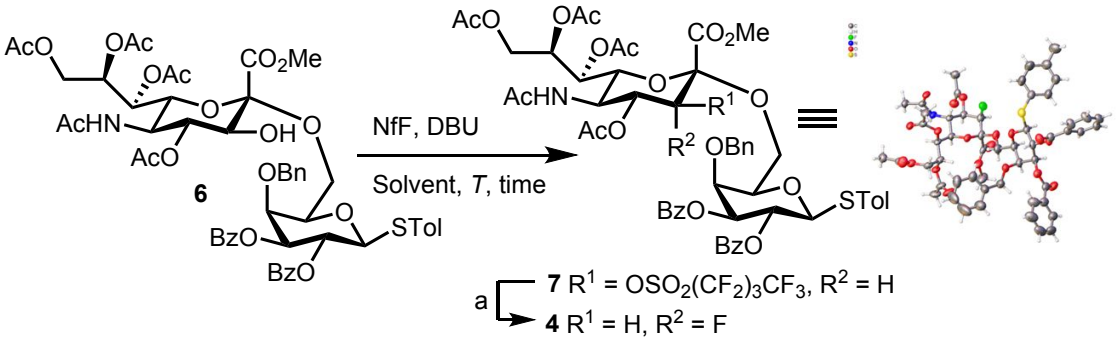


entry	Conditions	Results(%)[a]
1	a. Tf_2O, Pyridine, CH_2Cl_2, - 5 °C, 20 min.. b. TSAF, THF, reflux, 1 d.	decomposed[b]
2	DAST, CH_2Cl_2, -40 to 25 °C, 2 d.	decomposed[b]
3	a. MsCl, Et_3N, - 5 °C, 20 min.. b. TSAF or TBAF, THF, reflux, 16 h.	decomposed[c]
4	a. MsCl, Et_3N, - 5 °C, 20 min.. b. KF, 18-C-6 or Kryptofix®222, CH_3CN, 90 °C, 1 d.	decomposed[c,]
5[12]	Phenofluor™, DIPEA, KF, toluene, 80 °C, 1.5 d.	S.M.[d]
6[13]	XtalFluor-M® Et_3N • 3HF, Et_3N, CH_2Cl_2, -78 to 25 °C, 20 h.	no reaction
7[14]	TFFH, Et_3N • 3HF, Et_3N, EtOAc, 0 to 25 °C, 1 d	no reaction
8[15]	Deoxo-Fluor®, DCM, CH_2Cl_2, -40 to 25 °C, 1 d.	S.M.[d]
9[16]	PyFlour (4 equiv.), DBU (4 equiv.), toluene, 40 °C, 2 d.	**S34** (80)
10	NfF (6 equiv.), DBU (6 equiv.), toluene, 25 to 90 °C, 2 d.	**4** (5.8)[e]
11	NfF (6 equiv.), DBU (6 equiv.), THF, 25 to 90 °C, 2 d.	**4** (4.0)[e]
12	NfF (6 equiv.), DBU (6 equiv.), CH_3CN, 25 to 90 °C, 2 d.	**4** (2.0)[e]
13	NfF (4 equiv.), DBU (4 equiv.), toluene, 40 °C, 7 d.	**4** (30) **7** (52)
14	NfF (4 equiv.), DBU (4 equiv.), toluene, 40 °C, 17 d.	**4** (36) **7** (44)
15	NfF (4 equiv.), DBU (4 equiv.), toluene, 40 °C, 6 h, sonication.	**6** (32) **7** (66)
16	NfF (3 equiv.), DBU (6 equiv.), toluene, 40 °C, 3 d.	**6** (40) **7** (20)
17	NfF (6 equiv.), DBU (3 equiv.), toluene, 40 °C, 3 d.	**6** (80) **7** (15)
18[f]	NfF (12 equiv.), DBU (12 equiv.), toluene, 40 °C, 4.5 d.	**4** (33) **7** (59)
19	NfF (10 equiv.), DBU (10 equiv.), toluene, 40 °C, 3 d.	**4** (31) **7** (50)
20	NfF (10 equiv.), DBU (10 equiv.), DMF, 40 °C, 9 d.	decomposed
21	NfF (4 equiv.), DBU (4 equiv.), toluene, 40 °C, 3 d then TASF (2 equiv.), 8 d.	**4** (24) **7** (35)
22[g]	NfF (10 equiv.), DBU (10 equiv.), toluene, 40 °C, 5 d.	**4** (4.0)
23	NfF (4 equiv.), DBU (4 equiv.), toluene, 40 °C, 4Å MS, 5 d.	**4** (4.3) **7** (78)
24	NfF (4 equiv.), DBU (4 equiv.), toluene, 50 °C, 6 d.	**4** (7.5) **7** (71)

25[h]	NfF (10 equiv.), DBU (10 equiv.), toluene, 40 °C, 17 d.	**4** (46) **7** (5)
26[f]	NfF (8 equiv.), DBU (8 equiv.), toluene, 40 °C, 15 d.	**4** (63) **7** (15)
27[f, i]	NfF (8 equiv.), DBU (8 equiv.), toluene, 40 °C, 15 d.	**4** (63) **7** (10)
28[j]	NfF (8 equiv.), DBU (8 equiv.), TASF(4 equiv.), toluene, 40 °C, 2 d.	**4** (60) **7** (8)
29	NfF (4 equiv.), $Et_3N \cdot 3HF$(4 equiv.), toluene, 40 °C, 6 d.	No reaction

[a]Yield of isolated product. [b]No R-OTf formation was observed. [c]Intermediate R-OMs was isolated in 88% yield, but no product was observed in 2nd (S_N2) step. [d]Starting material was recovered in 50 % [e]Two major unidentified compounds. [f]Portion-wise addition of NfF (4 equiv./day) and DBU (4 equiv./day). [g]The solvent was gradually evaporated to dryness. [h]Elimination product was observed. [i]Gram-scale synthesis. [j]Portion-wise addition of NfF (4 equiv./day), DBU (4 equiv./day) and tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF) (2 equiv./day).

Table S4. Optimization of the Fluorination Step.



entry	NfF/DBU, (equiv.)	solvent	T (°C)	time (day)	Yield [b](%)	
					4	**7**
1	6/6	THF	25 to 90	2	4	
2	6/6	CH_3CN	25 to 90	2	2	
3	6/6	toluene	25 to 90	2	2	
4	4/4	DMF	40	9	--[c]	
5	4/4	toluene	50	6	8	71
6	4/4	toluene	40	7	30	52
7	4/4	toluene	40	17	36	44
8[d]	8/8	toluene	40	15	63	15
9[e]	8/8	toluene	40	2	60	8

[a]Reagents and conditions: (a) NfF, DBU, toluene, 40 °C, 15 d, 49% (77% brsm). [b]Yield of isolated product. [c]No product observed. [d]Portion-wise addition of NfF (4 equiv./day) and DBU (4 equiv./day) followed by stirring for 14 days. [e] Portion-wise addition of NfF (4 equiv./day), DBU (4 equiv./day) and tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF) (2 equiv./day).

Protocols for the Sialidase-Catalyzed Hydrolysis and Sialidase Inhibition.[17]

Materials:

β-Galactosidase of *Aspergillus oryzae* (G5160) and sialidases from *Vibrio cholerae* (11080725001) and *Clostridium perfringens* (11585886001) were received from Sigma Aldrich.

Enzymatic Assays for Sialidases:

The assays were carried out at 37 °C in duplicates in 96-well plates in a final volume of 50 µL containing a substrate (0-20 mM), and β-galactosidase (100 mU). The assay conditions for the two sialidases were as follows: *C. perfringens* (1 mU), sodium acetate buffer (50 mM) pH 5.0 and $CaCl_2$ (10 mM); *V. cholerae* (2 mU), sodium acetate buffer (50 mM) pH 5.5, $CaCl_2$ (10 mM) and NaCl (150 mM). The reactions were carried out for 40 min to 2 hrs for *C. perfringens* and overnight for *V. cholerae*. The assays were stopped by adding 65 µL of CAPS buffer (*N*-cyclohexyl-3-aminopropane sulfonic acid, 0.5 M, pH 10.5). The amount of the *para*-nitrophenolate formed was determined by measuring the A_{405nm} of the reaction mixtures using a microplate reader. Three compounds (Neu5Ac-α2,6-Galβ-*p*NP (**1**), $3F^{ax}$-Neu5Ac-α2,6-Galβ-*p*NP (**2**) and $3OH^{eq}$-Neu5Ac-α2,6-Galβ-*p*NP (**S27**)) were tested as substrates for the enzymes. All three compounds have the backgound absorbance of A_{405nm} at 20 mM after incubation for 1 hr at 37 °C in the ansence of sialidase. The absorbance of compounds **1**, **2** and **S27** were 0.044, 0.129 and 0.072, respectively. The results are presented in Figure S1A.

Inhibition Assays for Sialidases:

The assays were carried out at 37 °C in duplicates in 96-well plates in a final volume of 50 µL containing the substrate Neu5Ac-α2,6-Galβ*p*NP (**1**) (0.6 mM), β-galactosidase (100 mU), and sialidase in the absence or presence of an inhibitor (**2** or **S27**) at varied concentrations (0-20 mM). Reactions were allowed to proceed for 40 min to 2 hrs for *C. perfringens* and overnight for *V. cholera.* The assays were stopped by adding CAPS buffer (65 uL, 0.5 M, pH 10.5). The results are presented in Figure S1B.

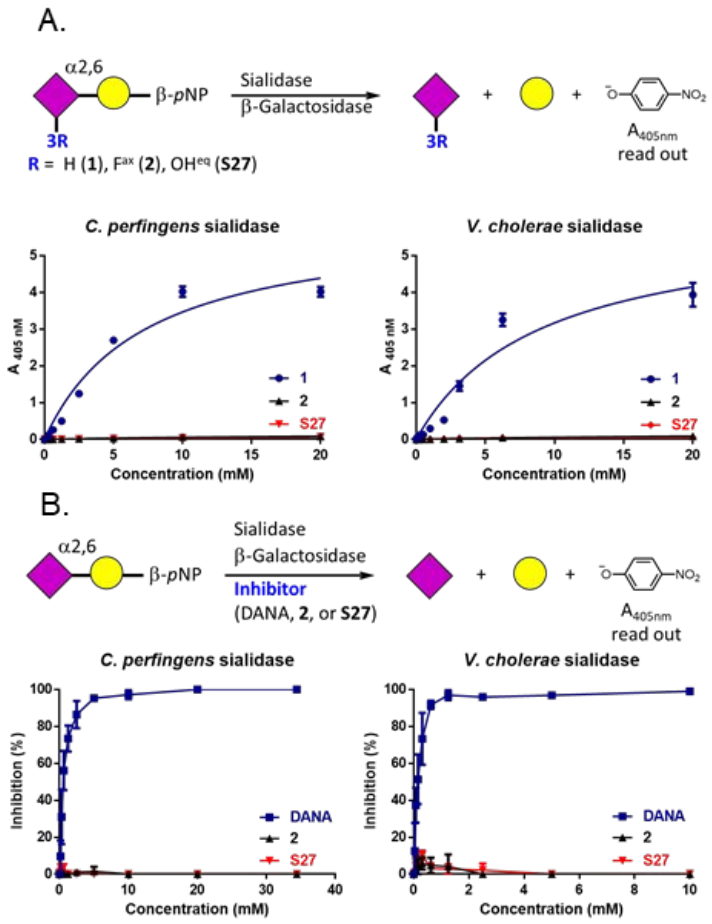


Figure S1. (A) Enzyme-catalyzed hydrolysis of **1** (control), **2** and **S27**. (B) Testing of the inhibition of sialidases with DANA, **2** and **S27**.

Protocols for Preparation of Homogeneous mAb Modified with α2,6-F-SCT to Study the Effect on Binding to FcγRIIIa by Surface Plasmon Resonance (SPR) Analysis.

Expression of enzymes. The *endo*-glycosidases Endo-S, Endo-S2, Endo-S2 mutant (D184Q), and the α-L-fucosidase from *Bacteroides fragilis* NCTC 9343 (BfFucH) were expressed in *Escherichia coli* and the purification of enzymes was performed using Ni-NTA agarose beads.

Preparation of mono-GlcNAc-Rituximab. As described previously,[18] Rituximab (3.0 mg; Rituxan® Roche) in a Tris-HCl buffer (50 mM, pH 7.4, 1.5 mL) was incubated with Endo-S (120 μg), Endo-S2 (240 μg) and BfFucH (4.5 mg) at 37 °C for 24 hrs. LC-MS and SDS-PAGE analyses indicated the complete cleavage of the *N*-glycans on the heavy chain. The reaction mixture was subjected to affinity chromatography on a column of protein A-agarose resin (1 mL; GE Healthcare) pre-equilibrated with a Tris-HCl buffer (50 mM, pH 7.4). Then, the column was washed with a Tris-HCl buffer (50 mM, pH 7.4, 20 mL). The bound IgG was released with glycine-HCl (100 mM, pH 3.0, 10 mL), and the elution fractions were immediately neutralized with Tris-HCl buffer (1.0 M, pH 8.3). The fractions containing the antibody were combined and concentrated by centrifugal filtration (Amicon Ultra centrifugal filter, Millipore, Billerica, MA) to give mono-GlcNAc Rituximab (2.4 mg). A sample of the product was trypsinized, and the glycopeptides, TKPREEQYNSTYR (m/z=1391.58) and EEQYNSTYR (m/z=1873.88) were analyzed using nanospray LCMS to confirm the glycosylation pattern of mono-GlcNAc.

Transglycosylation of mono-GlcNAc Rituximab with glycan oxazolines. A glycan oxazoline was added to the mixture of an Endo-S2 (D184Q) and mono-GlcNAc Rituximab in 50 mM Tris buffer (pH 7.4). The solution was incubated for 30 min at 37 ^{o}C. Then, the reaction mixture was purified with protein-A affinity column, followed by an anion exchange column of Capto Q (GE Healthcare) to collect the desired product.

SDS-PAGE detection of glycoengineered retuximab antibodies. All the SDS–PAGE analyses were performed with NuPAGE® Novex® 4–12% Bis-Tris gel (Invitrogen) in MOPS buffer with 2-mercaptoethanol present in samples (Figure S2).

MS spectrometry analysis of glycoengineered mAb. For the analysis of trypsinized glycopeptides, high resolution and high mass accuracy nanoflow LC-MS/MS experiments were performed on a LTQFT Ultra (linear quadrupole ion trap Fourier transform ion cyclotron resonance) mass spectrometer (Thermo Electron, San Jose, CA) equipped with a nanoelectrospray

ion source (New Objective, Inc.), an Agilent 1100 Series binary high-performance liquid chromatography pump (Agilent Technologies, Palo Alto, CA), and a Famos autosampler (LC Packings, San Francisco, CA). The digestion solution (6 µL) was injected at the 10 µL/min flow rate to a self-packed precolumn (150 µm I.D. x 20 mm, 5 µm, 100 Å). The chromatographic separation was performed on a self-packed reversed phase C18 nano-column (75 µm I.D. x 300 mm, 5 µm, 100 Å) using 0.1% formic acid in water as a mobile phase A and 0.1% formic acid in 80% acetonitrile as mobile phase B operated at 300 nL/min flow rate. Survey of the full-scan MS conditions: mass range m/z 320-2000, resolution 100,000 at m/z 400. The ten most intense ions were sequentially isolated for MS2 by LTQ. Electrospray voltage was maintained at 1.8 kV and the capillary temperature was set at 200 ^{o}C (Figure S3 and Table S5).

Surface Plasmon Resonance (SPR) Analysis. All the SPR experiments were performed with the single cycle kinetic method by BIACORE T200 at 25 °C using HBS-EP (10mM HEPES pH7.4, 0.15M NaCl, 3mMEDTA, 0.005% surfactant P20) as running buffer. FcγRIIIa was transfected into HEK-293 cells to express the complex-type glycosylated recombinant protein as analyte. For the analysis of rituximab's binding to FcγRIIIa receptor, anti-human Fab antibodies in human Fab capture kit (GE Healthcare) were immobilized onto both the reference and active channels of CM5 sensor chip, and then Rituximabs were captured on the active channel for interacting with the serial dilutions of FcγRIIIa analyte (2.5, 5, 10, 20, 40nM for 2,6-FluoSCT and 2,6-SCT; 8, 24, 72, 216, 648 nM for the commercial rituximab) at 30 µl/min for association of 240 seconds followed by dissociation time of 420 seconds. The data were processed with double referencing for background subtraction and were fitted to 1:1 Langmuir binding model in BiaEvaluation software (GE Healthcare) to obtain the kinetic/affinity constants (Table S6).

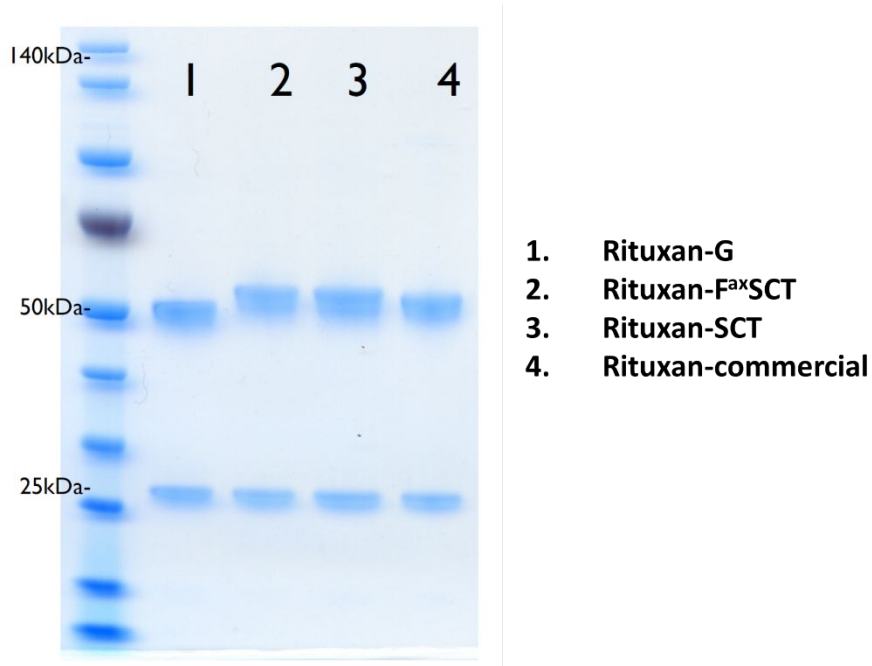
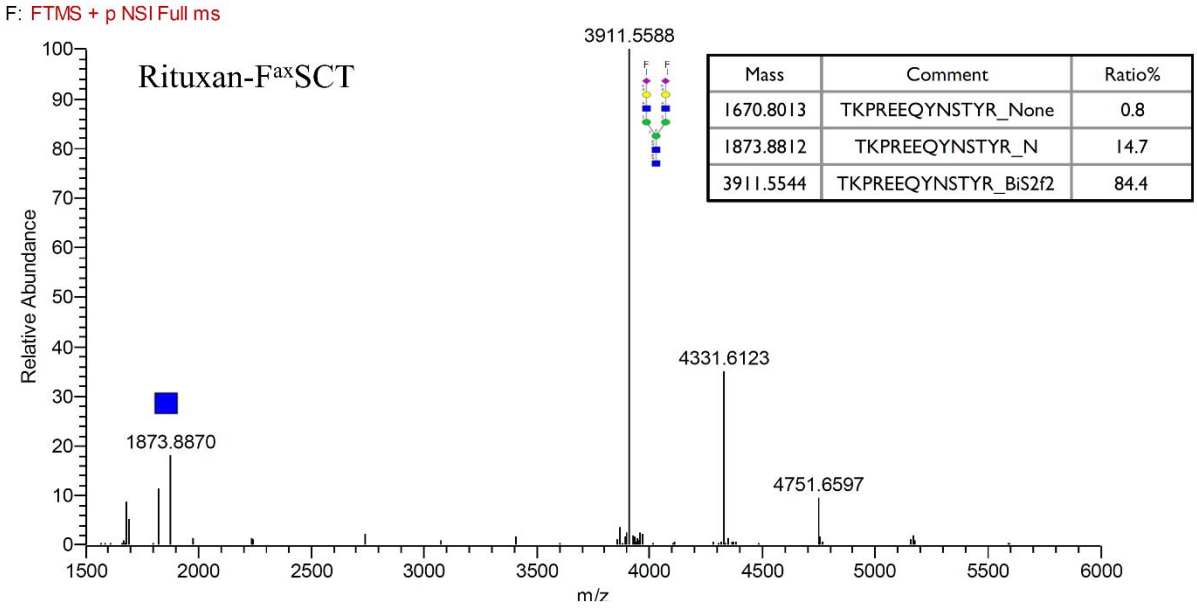
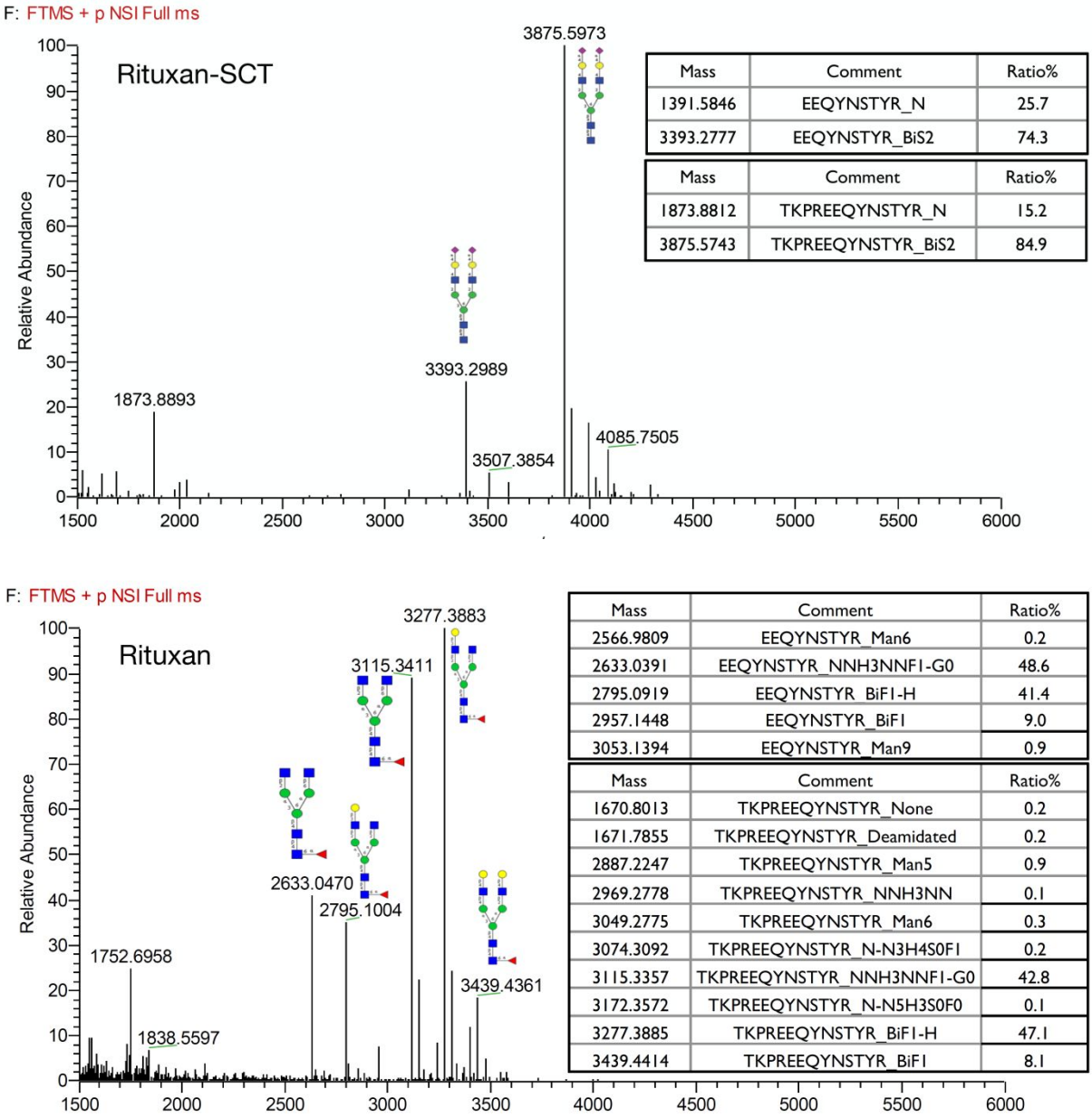


Figure S2. SDS-PAGE of Rit-G, Rit-F^{ax}SCT, Rit-SCT, Rit-commercial concentration (25 kDa band corresponds to the light chain, whereas 50 kDa band corresponds to the heavy chain).



Mass	Comment	Ratio%
1670.8013	TKPREEQYNSTYR_None	0.8
1873.8812	TKPREEQYNSTYR_N	14.7
3911.5544	TKPREEQYNSTYR_BiS2f2	84.4



Mass	Comment	Ratio%
1391.5846	EEQYNSTYR_N	25.7
3393.2777	EEQYNSTYR_BiS2	74.3

Mass	Comment	Ratio%
1873.8812	TKPREEQYNSTYR_N	15.2
3875.5743	TKPREEQYNSTYR_BiS2	84.9

Mass	Comment	Ratio%
2566.9809	EEQYNSTYR_Man6	0.2
2633.0391	EEQYNSTYR_NNH3NNF1-G0	48.6
2795.0919	EEQYNSTYR_BiF1-H	41.4
2957.1448	EEQYNSTYR_BiF1	9.0
3053.1394	EEQYNSTYR_Man9	0.9

Mass	Comment	Ratio%
1670.8013	TKPREEQYNSTYR_None	0.2
1671.7855	TKPREEQYNSTYR_Deamidated	0.2
2887.2247	TKPREEQYNSTYR_Man5	0.9
2969.2778	TKPREEQYNSTYR_NNH3NN	0.1
3049.2775	TKPREEQYNSTYR_Man6	0.3
3074.3092	TKPREEQYNSTYR_N-N3H4S0F1	0.2
3115.3357	TKPREEQYNSTYR_NNH3NNF1-G0	42.8
3172.3572	TKPREEQYNSTYR_N-N5H3S0F0	0.1
3277.3885	TKPREEQYNSTYR_BiF1-H	47.1
3439.4414	TKPREEQYNSTYR_BiF1	8.1

Figure S3. Distribution of *N*-glycan on mass spectroscopy analysis.

Table S5. *N*-glycan Relative Abundance[19]

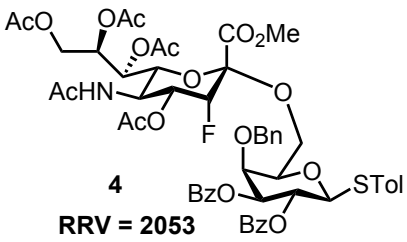
Sample composition (glycan at N297)	Rit-F^{ax}SCT	Rit-SCT
none	1.0%	-
GlcNAc	1.7%	1.8%
α2,6-SCT	0.0%	98.2%
α2,6-F-SCT	97.3%	-

Table S6. Binding Avidity of Glycoengineered Rituximab IgG1 to FcγRIIIa Measured by SPR. Analyzed antibodies were captured by the Human Fab capture kit and detected with the single cycle kinetic method

Sample	ka (1/Ms)	kd (1/s)	KD (M)	Rmax (RU)	Fold
Rituximab	2.31E+05	0.07054	3.06E-07	32.33	1-fold
α2,6-F-SCT	2.44E+05	0.001996	8.18E-09	71.28	37.4-fold
α2,6-SCT	2.68E+05	0.002059	7.67E-09	60.64	39.9-fold

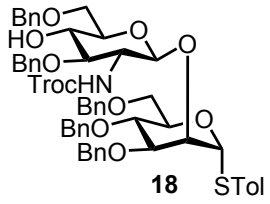
Relative reactivity values (RRV) of compounds 4 and 18

The RRVs were measured in triplicates by following the experimental procedure reported previously.[20] The RRV (2053) of disaccharide donor **4** was measured against a competition reference donor **S34**[5] (RRV = 1791). The RRV (537) of disaccharide donor **18** was measured against a competition reference donor **S**[5] (RRV = 286).



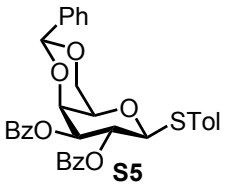
4

RRV = 2053



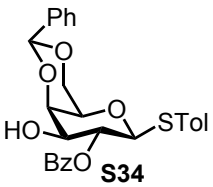
18

RRV = 537



S5

RRV = 286



S34

RRV = 1791

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Experimental Summary for the Crystal Structure of Compound 4

The single crystal X-ray diffraction studies were carried out on a Bruker D8 Platinum[135] CCD diffractometer equipped with Cu K_α radiation (λ = 1.5478). A 0.457 x 0.095 x 0.091 mm piece of a colorless rod was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ϖ scans. Crystal-to-detector distance was 40 mm using variable exposure time (2s-5s) depending on θ with a scan width of 1.0°. Data collection was 99.2% complete to 68.00° in θ. A total of 88061 reflections were collected covering the indices, -20<=h<=25, -25<=k<=24, -23<=l<=26. 10475 reflections were found to be symmetry independent, with a R_{int} of 0.0427. Indexing and unit cell refinement indicated a primitive, hexagonal lattice. The space group was found to be $P6_1$. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Due to unmodelable solvent disorder, Platon SQUEEZE was used to remove the electron density from the lattice due to the disordered solvent contribution. Solvent appeared to be toluene. One void was found with approximately 275 electrons. The absolute stereochemistry of the molecule was established by anomalous dispersion using the Parson's method with a Flack parameter of -0.004(7). Crystallographic data are summarized in Table S7.

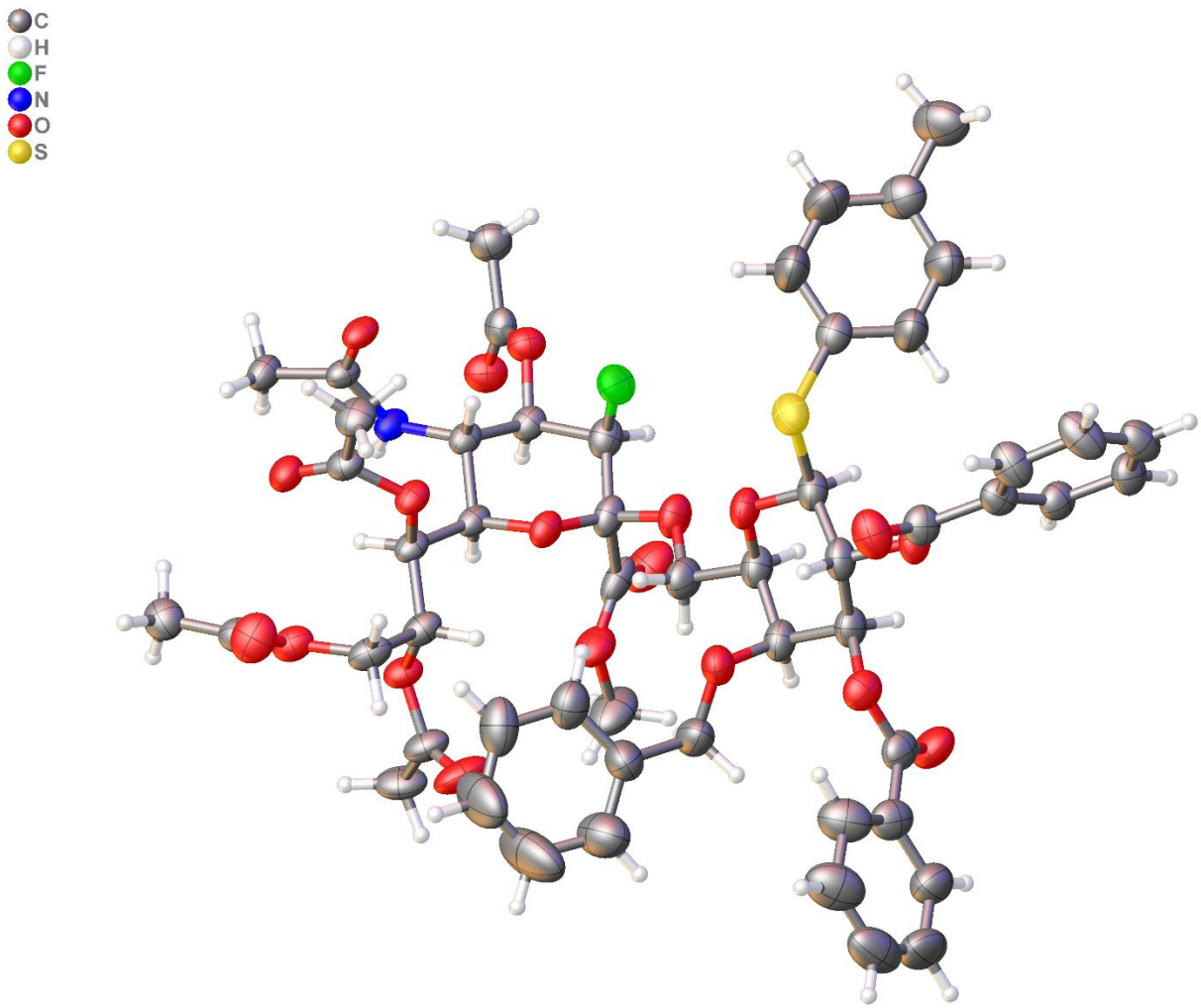

C
H
F
N
O
S

Table S7. Crystal data and structure refinement for compound **4**.

Report date	2018-05-01	
Identification code	Jay-1-144	
Empirical formula	C54 H58 F N O19 S	
Molecular formula	C54 H58 F N O19 S	
Formula weight	1076.07	
Temperature	100.0 K	
Wavelength	1.54178 Å	
Crystal system	Hexagonal	
Space group	$P6_1$	
Unit cell dimensions	a = 21.1703(5) Å	α= 90°.
	b = 21.1703(5) Å	β= 90°.
	c = 22.7806(6) Å	γ = 120°.
Volume	8842.0(5) $Å^3$	
Z	6	
Density (calculated)	1.213 Mg/m^3	
Absorption coefficient	1.107 mm^{-1}	
F(000)	3396	
Crystal size	0.457 x 0.095 x 0.091 mm^3	
Crystal color, habit	Colorless Rod	
Theta range for data collection	2.410 to 68.329°.	
Index ranges	-20<=h<=25, -25<=k<=24, -23<=l<=26	
Reflections collected	88061	
Independent reflections	10475 [R(int) = 0.0427, R(sigma) = 0.0250]	
Completeness to theta = 68.000°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.3201 and 0.2175	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10475 / 181 / 786	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0343, wR2 = 0.0933	
R indices (all data)	R1 = 0.0386, wR2 = 0.0970	
Absolute structure parameter	-0.004(7)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.361 and -0.167 e.$Å^{-3}$	

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for compound **4** U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	4204(1)	9887(1)	4780(1)	52(1)
F(1)	6840(1)	10138(1)	5829(1)	52(1)
O(1)	4495(1)	9048(1)	5444(1)	46(1)
O(2)	2731(1)	8957(1)	5446(1)	47(1)
O(3)	2349(7)	7501(7)	5677(4)	48(2)
O(3B)	2368(15)	7478(16)	5824(9)	48(2)
O(4)	3622(1)	7501(1)	5414(1)	50(1)
O(5)	5631(1)	9009(1)	6130(1)	49(1)
O(6)	6358(1)	8686(2)	7170(1)	72(1)
O(7)	5792(1)	7733(1)	6563(1)	58(1)
O(8)	6298(1)	8615(1)	5620(1)	38(1)
O(9)	8182(1)	10461(1)	6140(1)	43(1)
O(10)	6831(1)	8532(1)	4508(1)	38(1)
O(11)	6475(4)	7023(5)	5480(4)	41(1)
O(11B)	6362(17)	7080(20)	5502(15)	41(1)
O(12)	6726(1)	6929(1)	4303(1)	44(1)
O(13)	2395(1)	8789(1)	4490(1)	60(1)
O(14)	2079(6)	7228(6)	6631(5)	64(2)
O(14B)	2205(15)	7292(16)	6803(9)	80(5)
O(15)	8865(1)	10253(1)	6781(1)	50(1)
O(16)	8542(1)	10065(1)	4620(1)	40(1)
O(17)	7768(1)	8505(1)	4050(1)	46(1)
O(18)	5311(2)	6135(3)	5586(2)	73(1)
O(18B)	5196(8)	6437(10)	5724(7)	73(1)
O(19)	6366(1)	6755(2)	3366(1)	63(1)
N(1)	8284(1)	9380(1)	5441(1)	34(1)
C(1)	3988(2)	9306(2)	5421(1)	44(1)
C(2)	3216(2)	8673(2)	5369(1)	45(1)
C(3)	3045(2)	8128(2)	5860(1)	45(1)
C(4)	3633(2)	7914(2)	5911(1)	46(1)

C(5)	4378(2)	8594(2)	5940(1)	46(1)
C(6)	4965(2)	8388(2)	5941(2)	53(1)
C(7)	6152(2)	8425(2)	6692(1)	50(1)
C(8)	6243(2)	8923(2)	6151(1)	43(1)
C(9)	6895(2)	9688(2)	6245(1)	45(1)
C(10)	7614(1)	9710(2)	6144(1)	39(1)
C(11)	7608(1)	9368(1)	5554(1)	34(1)
C(12)	6959(1)	8588(1)	5559(1)	34(1)
C(13)	6899(1)	8155(1)	5010(1)	35(1)
C(14)	6245(2)	7380(2)	5030(1)	42(1)
C(15)	6090(2)	6969(2)	4463(1)	47(1)
C(16)	4616(2)	10777(2)	5080(1)	48(1)
C(17)	5270(2)	11298(2)	4855(2)	80(1)
C(18)	5564(3)	12016(3)	5034(3)	92(2)
C(19)	5217(2)	12244(2)	5417(2)	67(1)
C(20)	4558(2)	11703(2)	5636(2)	73(1)
C(21)	4261(2)	10983(2)	5472(2)	66(1)
C(22)	5511(3)	13029(2)	5574(2)	89(1)
C(23)	2392(2)	9032(2)	4966(1)	47(1)
C(24)	2011(2)	9437(2)	5116(1)	44(1)
C(25)	1749(2)	9674(2)	4658(2)	57(1)
C(26)	1410(2)	10073(2)	4774(2)	64(1)
C(27)	1304(2)	10206(2)	5340(2)	55(1)
C(28)	1551(2)	9962(2)	5804(2)	51(1)
C(29)	1915(2)	9584(2)	5685(1)	47(1)
C(30)	1956(6)	7062(6)	6128(4)	50(2)
C(30B)	1993(16)	7074(17)	6305(12)	64(4)
C(31)	1367(5)	6343(4)	5906(5)	56(2)
C(31B)	1344(9)	6398(10)	6178(11)	68(4)
C(32)	1306(6)	6162(4)	5314(4)	73(2)
C(32B)	1123(9)	6187(9)	5607(14)	73(4)
C(33)	773(6)	5474(5)	5114(6)	90(3)
C(33B)	513(11)	5505(11)	5463(14)	110(7)
C(34)	295(5)	4994(5)	5511(6)	88(3)
C(34B)	67(13)	5062(13)	5996(18)	116(9)
C(35)	337(5)	5180(6)	6098(7)	89(3)

C(35B)	329(9)	5273(10)	6539(16)	113(7)
C(36)	871(4)	5855(4)	6294(5)	71(2)
C(36B)	945(9)	5934(10)	6632(13)	84(5)
C(37)	3490(6)	6817(5)	5617(4)	65(2)
C(37B)	3152(6)	6697(6)	5417(5)	65(2)
C(38)	3518(2)	6394(2)	5060(2)	63(1)
C(39)	4057(2)	6774(2)	4637(2)	66(1)
C(40)	4220(3)	6394(3)	4232(2)	78(1)
C(41)	3856(4)	5664(3)	4227(2)	112(2)
C(42)	3375(5)	5289(3)	4663(3)	133(3)
C(43)	3186(3)	5649(3)	5063(2)	89(1)
C(44)	5571(3)	7229(3)	7055(2)	84(1)
C(45)	8792(2)	10655(2)	6454(1)	41(1)
C(46)	9362(2)	11426(2)	6325(2)	54(1)
C(47)	8693(1)	9713(1)	4966(1)	34(1)
C(48)	9332(2)	9598(2)	4865(1)	43(1)
C(49)	7304(2)	8674(1)	4054(1)	40(1)
C(50)	7149(2)	9051(2)	3570(1)	51(1)
C(51)	5946(3)	6394(3)	5720(2)	51(1)
C(51B)	5799(10)	6581(11)	5827(8)	51(1)
C(52)	6261(4)	6086(3)	6146(2)	60(1)
C(52B)	6074(14)	6244(13)	6242(10)	60(1)
C(53)	6807(2)	6834(2)	3730(1)	48(1)
C(54)	7513(2)	6862(2)	3616(2)	55(1)

Table S9. Bond lengths [Å] and angles [°] for compound **4**.

S(1)-C(1)	1.814(3)	O(15)-C(45)	1.197(4)
S(1)-C(16)	1.771(3)	O(16)-C(47)	1.231(3)
F(1)-C(9)	1.389(4)	O(17)-C(49)	1.202(4)
O(1)-C(1)	1.428(3)	O(18)-C(51)	1.210(6)
O(1)-C(5)	1.423(4)	O(18B)-C(51B)	1.18(2)
O(2)-C(2)	1.438(3)	O(19)-C(53)	1.196(4)
O(2)-C(23)	1.358(4)	N(1)-C(11)	1.441(3)
O(3)-C(3)	1.465(13)	N(1)-C(47)	1.344(3)
O(3)-C(30)	1.355(11)	C(1)-C(2)	1.514(4)
O(3B)-C(3)	1.41(3)	C(2)-C(3)	1.514(4)
O(3B)-C(30B)	1.37(3)	C(3)-C(4)	1.527(4)
O(4)-C(4)	1.424(4)	C(4)-C(5)	1.515(5)
O(4)-C(37)	1.410(10)	C(5)-C(6)	1.509(4)
O(4)-C(37B)	1.481(11)	C(7)-C(8)	1.569(4)
O(5)-C(6)	1.432(4)	C(8)-C(9)	1.529(4)
O(5)-C(8)	1.396(3)	C(9)-C(10)	1.519(4)
O(6)-C(7)	1.200(4)	C(10)-C(11)	1.522(4)
O(7)-C(7)	1.303(5)	C(11)-C(12)	1.532(4)
O(7)-C(44)	1.454(4)	C(12)-C(13)	1.518(4)
O(8)-C(8)	1.405(3)	C(13)-C(14)	1.530(4)
O(8)-C(12)	1.437(3)	C(14)-C(15)	1.499(4)
O(9)-C(10)	1.436(3)	C(16)-C(17)	1.366(5)
O(9)-C(45)	1.349(3)	C(16)-C(21)	1.372(5)
O(10)-C(13)	1.443(3)	C(17)-C(18)	1.384(7)
O(10)-C(49)	1.363(3)	C(18)-C(19)	1.375(7)
O(11)-C(14)	1.491(7)	C(19)-C(20)	1.382(6)
O(11)-C(51)	1.356(9)	C(19)-C(22)	1.498(6)
O(11B)-C(14)	1.33(3)	C(20)-C(21)	1.377(6)
O(11B)-C(51B)	1.35(4)	C(23)-C(24)	1.481(4)
O(12)-C(15)	1.439(4)	C(24)-C(25)	1.388(4)
O(12)-C(53)	1.345(4)	C(24)-C(29)	1.373(5)
O(13)-C(23)	1.202(4)	C(25)-C(26)	1.379(5)
O(14)-C(30)	1.190(10)	C(26)-C(27)	1.362(6)
O(14B)-C(30B)	1.22(3)	C(27)-C(28)	1.389(5)

C(28)-C(29)	1.386(4)	C(37)-O(4)-C(4)	107.8(4)
C(30)-C(31)	1.493(12)	C(8)-O(5)-C(6)	116.3(2)
C(30B)-C(31B)	1.43(3)	C(7)-O(7)-C(44)	116.4(3)
C(31)-C(32)	1.391(13)	C(8)-O(8)-C(12)	114.22(19)
C(31)-C(36)	1.366(11)	C(45)-O(9)-C(10)	118.6(2)
C(31B)-C(32B)	1.38(3)	C(49)-O(10)-C(13)	117.2(2)
C(31B)-C(36B)	1.39(2)	C(51)-O(11)-C(14)	117.2(6)
C(32)-C(33)	1.399(11)	C(14)-O(11B)-C(51B)	121(2)
C(32B)-C(33B)	1.41(3)	C(53)-O(12)-C(15)	116.5(2)
C(33)-C(34)	1.361(16)	C(47)-N(1)-C(11)	121.8(2)
C(33B)-C(34B)	1.54(4)	O(1)-C(1)-S(1)	107.85(18)
C(34)-C(35)	1.383(18)	O(1)-C(1)-C(2)	110.4(2)
C(34B)-C(35B)	1.34(4)	C(2)-C(1)-S(1)	109.3(2)
C(35)-C(36)	1.380(14)	O(2)-C(2)-C(1)	107.5(2)
C(35B)-C(36B)	1.37(3)	O(2)-C(2)-C(3)	106.3(2)
C(37)-C(38)	1.572(10)	C(3)-C(2)-C(1)	111.0(2)
C(37B)-C(38)	1.475(11)	O(3)-C(3)-C(2)	103.3(4)
C(38)-C(39)	1.399(6)	O(3)-C(3)-C(4)	110.7(6)
C(38)-C(43)	1.368(6)	O(3B)-C(3)-C(2)	116.2(8)
C(39)-C(40)	1.376(6)	O(3B)-C(3)-C(4)	107.3(12)
C(40)-C(41)	1.338(8)	C(2)-C(3)-C(4)	111.3(2)
C(41)-C(42)	1.358(9)	O(4)-C(4)-C(3)	110.8(2)
C(42)-C(43)	1.370(8)	O(4)-C(4)-C(5)	108.0(2)
C(45)-C(46)	1.495(4)	C(5)-C(4)-C(3)	109.7(3)
C(47)-C(48)	1.506(4)	O(1)-C(5)-C(4)	110.8(2)
C(49)-C(50)	1.492(4)	O(1)-C(5)-C(6)	107.8(2)
C(51)-C(52)	1.497(7)	C(6)-C(5)-C(4)	109.9(3)
C(51B)-C(52B)	1.47(3)	O(5)-C(6)-C(5)	108.0(3)
C(53)-C(54)	1.488(5)	O(6)-C(7)-O(7)	126.5(3)
		O(6)-C(7)-C(8)	120.6(3)
C(16)-S(1)-C(1)	103.51(14)	O(7)-C(7)-C(8)	112.7(3)
C(5)-O(1)-C(1)	112.2(2)	O(5)-C(8)-O(8)	109.1(2)
C(23)-O(2)-C(2)	118.7(2)	O(5)-C(8)-C(7)	107.7(2)
C(30)-O(3)-C(3)	113.7(7)	O(5)-C(8)-C(9)	105.7(2)
C(30B)-O(3B)-C(3)	123.6(19)	O(8)-C(8)-C(7)	112.0(3)
C(4)-O(4)-C(37B)	119.9(5)	O(8)-C(8)-C(9)	111.9(2)

C(9)-C(8)-C(7)	110.1(2)	C(29)-C(24)-C(23)	122.2(3)
F(1)-C(9)-C(8)	106.9(2)	C(29)-C(24)-C(25)	119.8(3)
F(1)-C(9)-C(10)	107.6(2)	C(26)-C(25)-C(24)	120.0(3)
C(10)-C(9)-C(8)	111.7(2)	C(27)-C(26)-C(25)	120.0(3)
O(9)-C(10)-C(9)	107.8(2)	C(26)-C(27)-C(28)	120.7(3)
O(9)-C(10)-C(11)	108.9(2)	C(29)-C(28)-C(27)	119.2(3)
C(9)-C(10)-C(11)	110.4(2)	C(24)-C(29)-C(28)	120.2(3)
N(1)-C(11)-C(10)	112.0(2)	O(3)-C(30)-C(31)	111.0(8)
N(1)-C(11)-C(12)	111.5(2)	O(14)-C(30)-O(3)	123.9(10)
C(10)-C(11)-C(12)	107.2(2)	O(14)-C(30)-C(31)	125.1(9)
O(8)-C(12)-C(11)	108.8(2)	O(3B)-C(30B)-C(31B)	115(2)
O(8)-C(12)-C(13)	108.4(2)	O(14B)-C(30B)-O(3B)	121(3)
C(13)-C(12)-C(11)	113.8(2)	O(14B)-C(30B)-C(31B)	123(2)
O(10)-C(13)-C(12)	108.7(2)	C(32)-C(31)-C(30)	121.6(7)
O(10)-C(13)-C(14)	109.3(2)	C(36)-C(31)-C(30)	119.1(9)
C(12)-C(13)-C(14)	112.3(2)	C(36)-C(31)-C(32)	119.3(8)
O(11)-C(14)-C(13)	102.4(4)	C(32B)-C(31B)-C(30B)	120.9(18)
O(11)-C(14)-C(15)	109.3(4)	C(32B)-C(31B)-C(36B)	119.1(17)
O(11B)-C(14)-C(13)	104.5(16)	C(36B)-C(31B)-C(30B)	120(2)
O(11B)-C(14)-C(15)	117.3(16)	C(31)-C(32)-C(33)	121.2(9)
C(15)-C(14)-C(13)	114.4(2)	C(31B)-C(32B)-C(33B)	122.6(19)
O(12)-C(15)-C(14)	108.1(2)	C(34)-C(33)-C(32)	118.2(9)
C(17)-C(16)-S(1)	118.5(3)	C(32B)-C(33B)-C(34B)	114(2)
C(17)-C(16)-C(21)	118.8(3)	C(33)-C(34)-C(35)	120.8(8)
C(21)-C(16)-S(1)	122.2(3)	C(35B)-C(34B)-C(33B)	120.0(19)
C(16)-C(17)-C(18)	119.6(4)	C(36)-C(35)-C(34)	120.7(9)
C(19)-C(18)-C(17)	123.1(4)	C(34B)-C(35B)-C(36B)	121(2)
C(18)-C(19)-C(20)	115.6(4)	C(31)-C(36)-C(35)	119.7(10)
C(18)-C(19)-C(22)	122.9(4)	C(35B)-C(36B)-C(31B)	123(2)
C(20)-C(19)-C(22)	121.5(4)	O(4)-C(37)-C(38)	106.1(6)
C(21)-C(20)-C(19)	122.2(4)	C(38)-C(37B)-O(4)	107.5(7)
C(16)-C(21)-C(20)	120.6(4)	C(39)-C(38)-C(37)	118.7(4)
O(2)-C(23)-C(24)	110.8(2)	C(39)-C(38)-C(37B)	125.7(5)
O(13)-C(23)-O(2)	124.0(3)	C(43)-C(38)-C(37)	120.5(5)
O(13)-C(23)-C(24)	125.2(3)	C(43)-C(38)-C(39)	117.9(4)
C(25)-C(24)-C(23)	118.0(3)	C(40)-C(39)-C(38)	119.7(4)

C(41)-C(40)-C(39)	120.8(5)
C(40)-C(41)-C(42)	120.0(4)
C(41)-C(42)-C(43)	120.1(5)
C(38)-C(43)-C(42)	120.9(5)
O(9)-C(45)-C(46)	110.9(3)
O(15)-C(45)-O(9)	123.9(3)
O(15)-C(45)-C(46)	125.2(3)
O(16)-C(47)-N(1)	122.6(2)
O(16)-C(47)-C(48)	121.6(2)
N(1)-C(47)-C(48)	115.7(2)
O(10)-C(49)-C(50)	110.2(2)
O(17)-C(49)-O(10)	124.0(2)
O(17)-C(49)-C(50)	125.7(3)
O(11)-C(51)-C(52)	111.2(5)
O(18)-C(51)-O(11)	121.8(5)
O(18)-C(51)-C(52)	127.0(4)
O(11B)-C(51B)-C(52B)	109(2)
O(18B)-C(51B)-O(11B)	121(2)
O(18B)-C(51B)-C(52B)	130.1(18)
O(12)-C(53)-C(54)	111.3(3)
O(19)-C(53)-O(12)	123.0(3)
O(19)-C(53)-C(54)	125.7(3)

Table S10. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for compound **4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	64(1)	60(1)	39(1)	0(1)	2(1)	37(1)
F(1)	51(1)	55(1)	60(1)	5(1)	-2(1)	34(1)
O(1)	40(1)	62(1)	45(1)	3(1)	6(1)	32(1)
O(2)	45(1)	68(1)	42(1)	-3(1)	-3(1)	39(1)
O(3)	41(1)	59(2)	47(5)	5(3)	-5(3)	27(1)
O(3B)	41(1)	59(2)	47(5)	5(3)	-5(3)	27(1)
O(4)	49(1)	53(1)	54(1)	0(1)	6(1)	31(1)
O(5)	38(1)	69(1)	47(1)	2(1)	0(1)	33(1)
O(6)	60(2)	104(2)	42(1)	17(1)	1(1)	32(1)
O(7)	62(1)	67(2)	53(1)	26(1)	16(1)	38(1)
O(8)	31(1)	51(1)	37(1)	8(1)	2(1)	23(1)
O(9)	42(1)	42(1)	43(1)	4(1)	-3(1)	20(1)
O(10)	36(1)	47(1)	30(1)	11(1)	2(1)	22(1)
O(11)	39(3)	40(2)	36(1)	11(1)	1(2)	14(1)
O(11B)	39(3)	40(2)	36(1)	11(1)	1(2)	14(1)
O(12)	42(1)	48(1)	34(1)	4(1)	-4(1)	15(1)
O(13)	67(1)	75(2)	51(1)	-17(1)	-18(1)	45(1)
O(14)	56(4)	68(3)	56(5)	11(4)	16(4)	23(3)
O(14B)	85(11)	95(9)	61(8)	16(6)	14(6)	47(8)
O(15)	49(1)	51(1)	46(1)	0(1)	-10(1)	22(1)
O(16)	35(1)	45(1)	41(1)	19(1)	7(1)	20(1)
O(17)	44(1)	50(1)	46(1)	11(1)	12(1)	24(1)
O(18)	45(2)	69(3)	73(2)	31(2)	4(2)	5(2)
O(18B)	45(2)	69(3)	73(2)	31(2)	4(2)	5(2)
O(19)	63(1)	88(2)	39(1)	-3(1)	-12(1)	37(1)
N(1)	30(1)	40(1)	31(1)	11(1)	1(1)	17(1)
C(1)	46(2)	58(2)	39(1)	2(1)	4(1)	34(1)
C(2)	45(2)	62(2)	41(2)	-4(1)	-2(1)	37(1)
C(3)	38(1)	56(2)	48(2)	-3(1)	-1(1)	28(1)
C(4)	45(2)	61(2)	42(2)	3(1)	4(1)	33(1)
C(5)	44(2)	63(2)	41(2)	1(1)	1(1)	34(1)
C(6)	41(2)	63(2)	64(2)	6(2)	2(1)	32(2)

C(7)	34(1)	87(2)	36(2)	16(2)	8(1)	35(2)
C(8)	37(1)	65(2)	36(1)	6(1)	3(1)	31(1)
C(9)	42(2)	60(2)	40(2)	3(1)	0(1)	30(1)
C(10)	37(1)	46(2)	33(1)	7(1)	0(1)	21(1)
C(11)	32(1)	41(1)	31(1)	10(1)	2(1)	20(1)
C(12)	28(1)	41(1)	34(1)	12(1)	2(1)	17(1)
C(13)	32(1)	42(1)	30(1)	12(1)	3(1)	18(1)
C(14)	35(1)	49(2)	35(1)	10(1)	1(1)	15(1)
C(15)	39(1)	46(2)	40(2)	7(1)	-3(1)	9(1)
C(16)	48(2)	62(2)	40(2)	3(1)	1(1)	30(2)
C(17)	65(2)	75(3)	97(3)	-7(2)	29(2)	32(2)
C(18)	64(2)	70(3)	118(4)	-6(2)	27(3)	15(2)
C(19)	72(2)	66(2)	53(2)	-6(2)	-2(2)	28(2)
C(20)	74(2)	67(2)	74(3)	-9(2)	18(2)	32(2)
C(21)	58(2)	63(2)	73(2)	-7(2)	18(2)	28(2)
C(22)	103(3)	65(3)	76(3)	-13(2)	-3(2)	25(2)
C(23)	43(2)	56(2)	45(2)	-3(1)	-7(1)	27(1)
C(24)	36(1)	46(2)	51(2)	-3(1)	-9(1)	21(1)
C(25)	65(2)	65(2)	51(2)	-14(1)	-19(2)	41(2)
C(26)	83(2)	66(2)	62(2)	-15(2)	-31(2)	51(2)
C(27)	50(2)	51(2)	72(2)	-11(2)	-16(2)	32(2)
C(28)	44(2)	61(2)	57(2)	-4(1)	-2(1)	32(2)
C(29)	38(1)	54(2)	52(2)	2(1)	-2(1)	26(1)
C(30)	41(3)	59(3)	60(5)	8(3)	3(3)	31(2)
C(30B)	53(7)	80(8)	62(9)	20(6)	16(6)	37(5)
C(31)	43(3)	59(3)	69(5)	8(3)	-7(3)	27(2)
C(31B)	52(6)	69(7)	96(10)	19(6)	12(6)	40(5)
C(32)	76(5)	64(4)	70(4)	0(3)	-20(4)	29(3)
C(32B)	55(7)	67(6)	107(11)	13(7)	-4(7)	38(5)
C(33)	85(5)	69(4)	108(6)	-12(4)	-34(4)	32(4)
C(33B)	86(10)	69(8)	166(16)	11(9)	-54(11)	32(7)
C(34)	61(4)	61(4)	143(7)	-15(4)	-26(4)	31(3)
C(34B)	59(11)	62(10)	210(20)	28(9)	-32(10)	16(8)
C(35)	50(5)	62(4)	140(7)	11(4)	20(6)	17(4)
C(35B)	57(7)	81(8)	186(18)	42(10)	-5(9)	22(6)
C(36)	57(4)	62(4)	90(6)	9(3)	13(4)	28(3)
C(36B)	56(6)	73(7)	120(12)	37(8)	18(7)	31(5)
C(37)	62(5)	49(3)	73(5)	-6(3)	18(3)	20(4)

C(37B)	62(5)	49(3)	73(5)	-6(3)	18(3)	20(4)
C(38)	70(2)	56(2)	70(2)	3(2)	13(2)	36(2)
C(39)	55(2)	79(2)	66(2)	-6(2)	2(2)	36(2)
C(40)	82(3)	117(4)	56(2)	-11(2)	-1(2)	66(3)
C(41)	195(7)	97(4)	68(3)	-2(2)	34(3)	90(4)
C(42)	238(9)	83(4)	86(4)	-13(3)	13(5)	86(5)
C(43)	112(4)	68(3)	78(3)	1(2)	12(3)	38(3)
C(44)	85(3)	104(3)	77(3)	50(3)	28(2)	58(3)
C(45)	42(1)	50(2)	32(1)	-5(1)	0(1)	25(1)
C(46)	50(2)	50(2)	53(2)	-2(1)	-4(1)	19(1)
C(47)	29(1)	34(1)	35(1)	7(1)	0(1)	13(1)
C(48)	36(1)	50(2)	44(2)	11(1)	6(1)	23(1)
C(49)	42(1)	39(1)	31(1)	5(1)	2(1)	16(1)
C(50)	60(2)	60(2)	35(1)	14(1)	5(1)	31(2)
C(51)	46(2)	46(3)	42(2)	13(2)	4(2)	9(2)
C(51B)	46(2)	46(3)	42(2)	13(2)	4(2)	9(2)
C(52)	70(3)	46(3)	48(2)	17(2)	-3(2)	17(2)
C(52B)	70(3)	46(3)	48(2)	17(2)	-3(2)	17(2)
C(53)	53(2)	44(2)	39(2)	3(1)	-4(1)	19(1)
C(54)	64(2)	61(2)	43(2)	2(1)	0(1)	34(2)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for compound **4**.

	x	y	z	U(eq)
H(1)	8432	9164	5690	40
H(1A)	4035	9593	5783	53
H(2)	3138	8431	4977	54
H(3A)	2988	8329	6240	54
H(3B)	3048	8375	6235	54
H(4)	3549	7619	6276	56
H(5)	4415	8871	6307	55
H(6A)	4829	7973	6211	64
H(6B)	5024	8240	5542	64
H(9)	6881	9864	6650	54
H(10)	7703	9443	6466	46

H(11)	7529	9648	5237	41
H(12)	7008	8326	5906	41
H(13)	7355	8127	4967	42
H(14)	5801	7389	5167	51
H(14A)	5808	7427	5119	51
H(15A)	5665	6472	4509	57
H(15B)	5975	7224	4152	57
H(17)	5521	11169	4578	96
H(18)	6027	12368	4885	110
H(20)	4301	11831	5908	88
H(21)	3807	10626	5633	79
H(22A)	5140	13166	5494	134
H(22B)	5947	13335	5339	134
H(22C)	5638	13101	5992	134
H(25)	1803	9562	4263	68
H(26)	1252	10255	4460	77
H(27)	1057	10469	5418	66
H(28)	1472	10053	6198	62
H(29)	2098	9426	5999	56
H(32)	1632	6512	5040	87
H(32B)	1392	6513	5298	88
H(33)	747	5346	4711	108
H(33B)	390	5335	5071	132
H(34)	-74	4525	5385	106
H(34B)	-396	4637	5939	139
H(35)	-5	4839	6369	107
H(35B)	87	4963	6863	136
H(36)	893	5980	6697	85
H(36B)	1104	6080	7024	100
H(37A)	3006	6548	5808	78
H(37B)	3867	6878	5904	78
H(37C)	3083	6509	5824	78
H(37D)	2668	6555	5249	78
H(39)	4309	7292	4629	79
H(40)	4597	6653	3953	93
H(41)	3933	5409	3918	135
H(42)	3169	4775	4690	159
H(43)	2820	5378	5346	107

H(44A)	5347	6728	6908	126
H(44B)	5218	7283	7298	126
H(44C)	6000	7338	7293	126
H(46A)	9638	11437	5976	80
H(46B)	9695	11627	6661	80
H(46C)	9128	11718	6255	80
H(48A)	9252	9316	4505	64
H(48B)	9379	9332	5198	64
H(48C)	9778	10072	4827	64
H(50A)	6679	8713	3389	77
H(50B)	7536	9216	3273	77
H(50C)	7132	9473	3728	77
H(52A)	6585	5956	5937	91
H(52B)	5865	5649	6331	91
H(52C)	6538	6450	6447	91
H(52D)	6332	6041	6025	91
H(52E)	5665	5853	6457	91
H(52F)	6410	6613	6519	91
H(54A)	7914	7364	3667	82
H(54B)	7517	6701	3214	82
H(54C)	7571	6541	3893	82

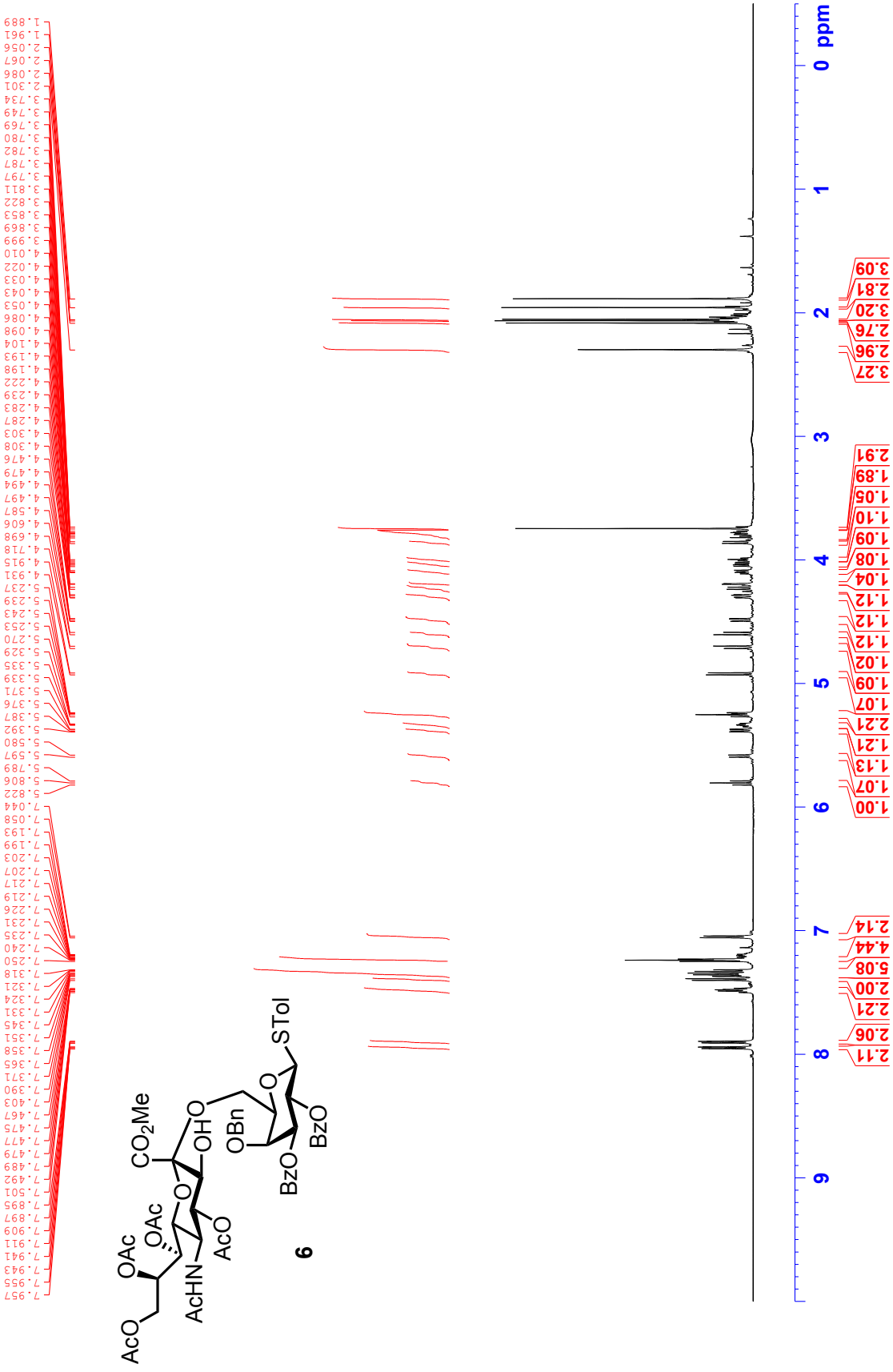
Table S9. Hydrogen bonds for compound **4** [Å and °].

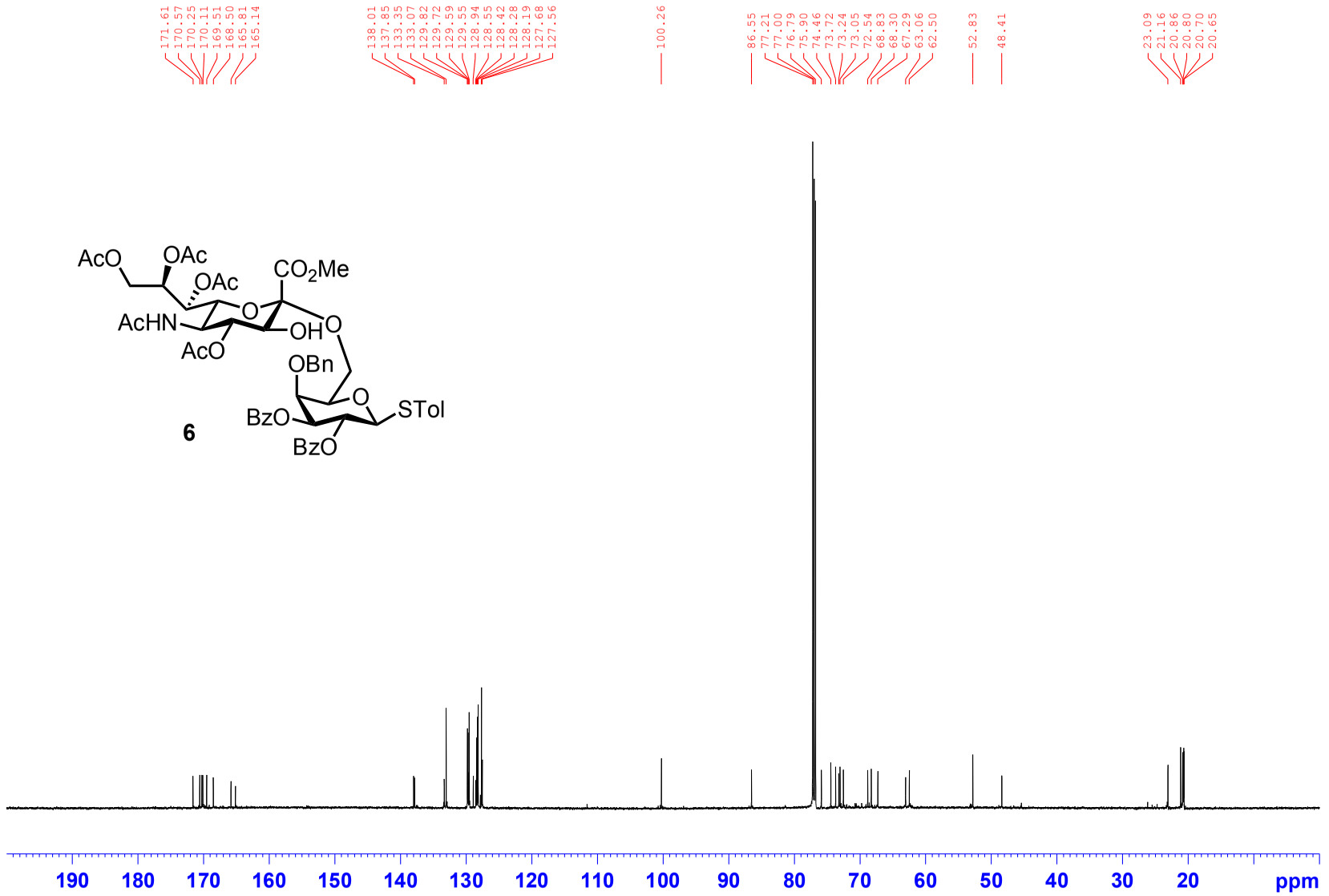
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(16)#1	0.88	1.93	2.785(3)	164.3

Symmetry transformations used to generate equivalent atoms:

#1 x-y+1,x,z+1/6

^{1}H and ^{13}C NMR Spectra

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62.50
52.83
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23.09
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20.80
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CO2Me
AcHN
O
OH
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OBn
O
STol
BzO
BzO
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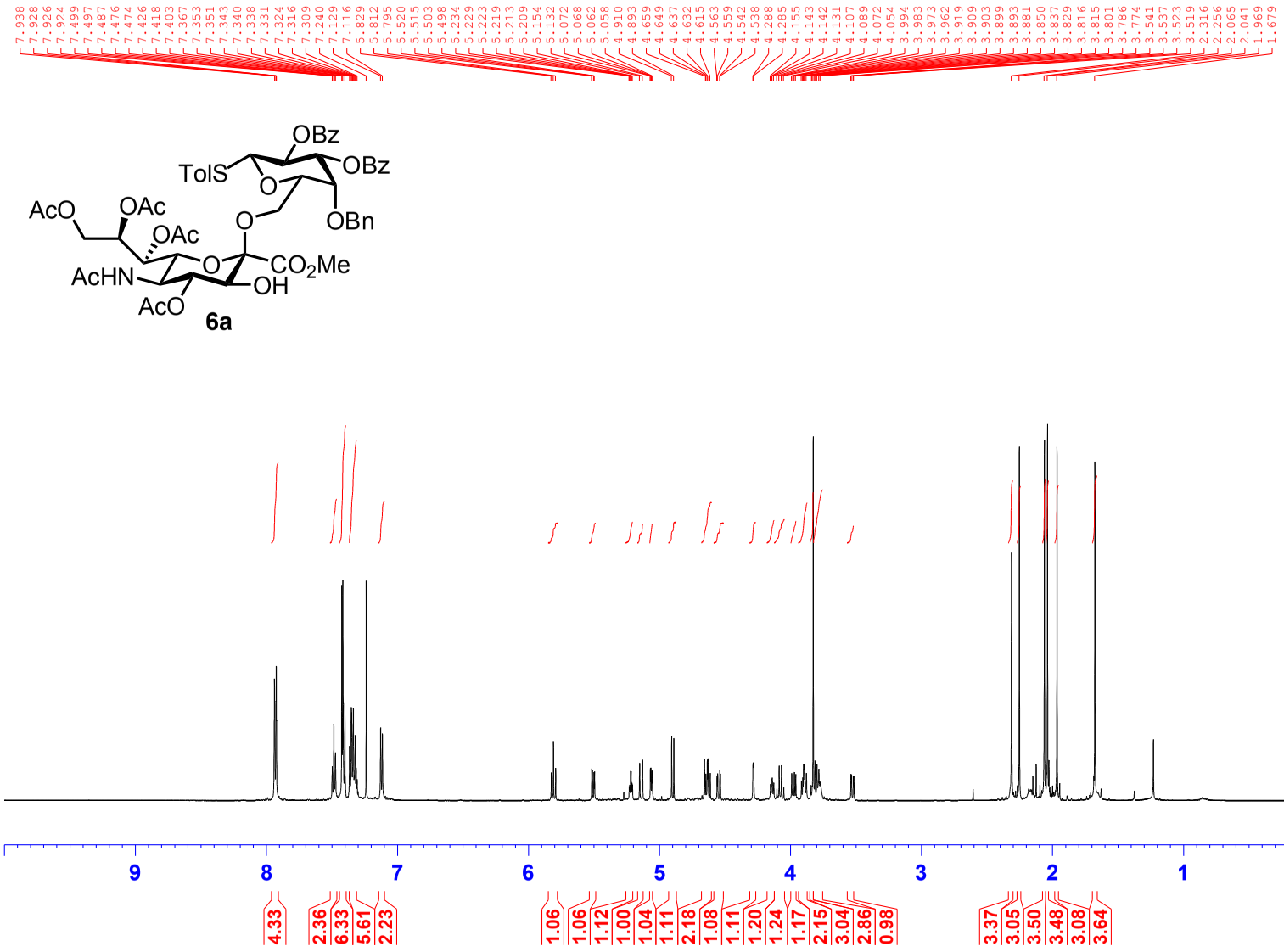
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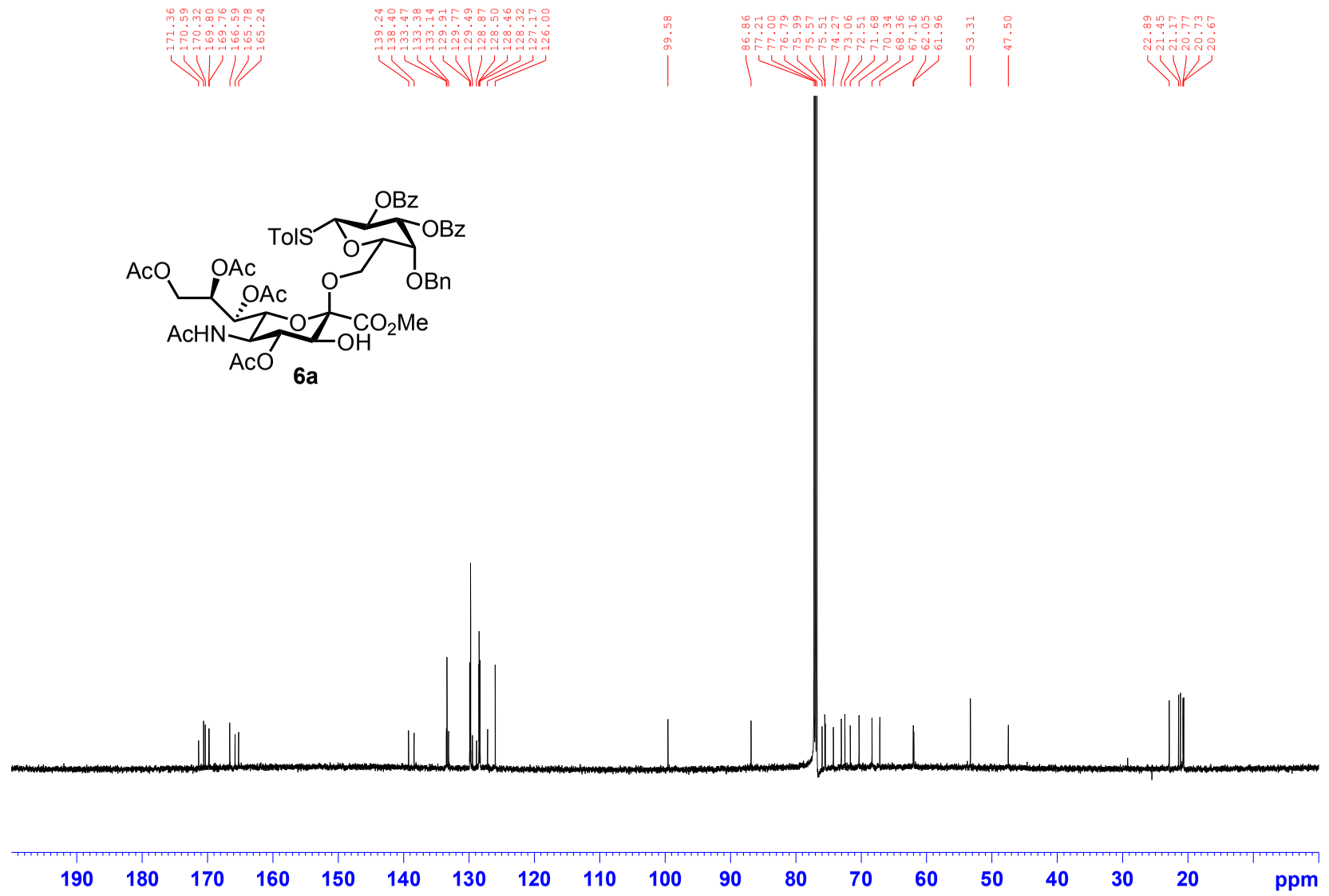
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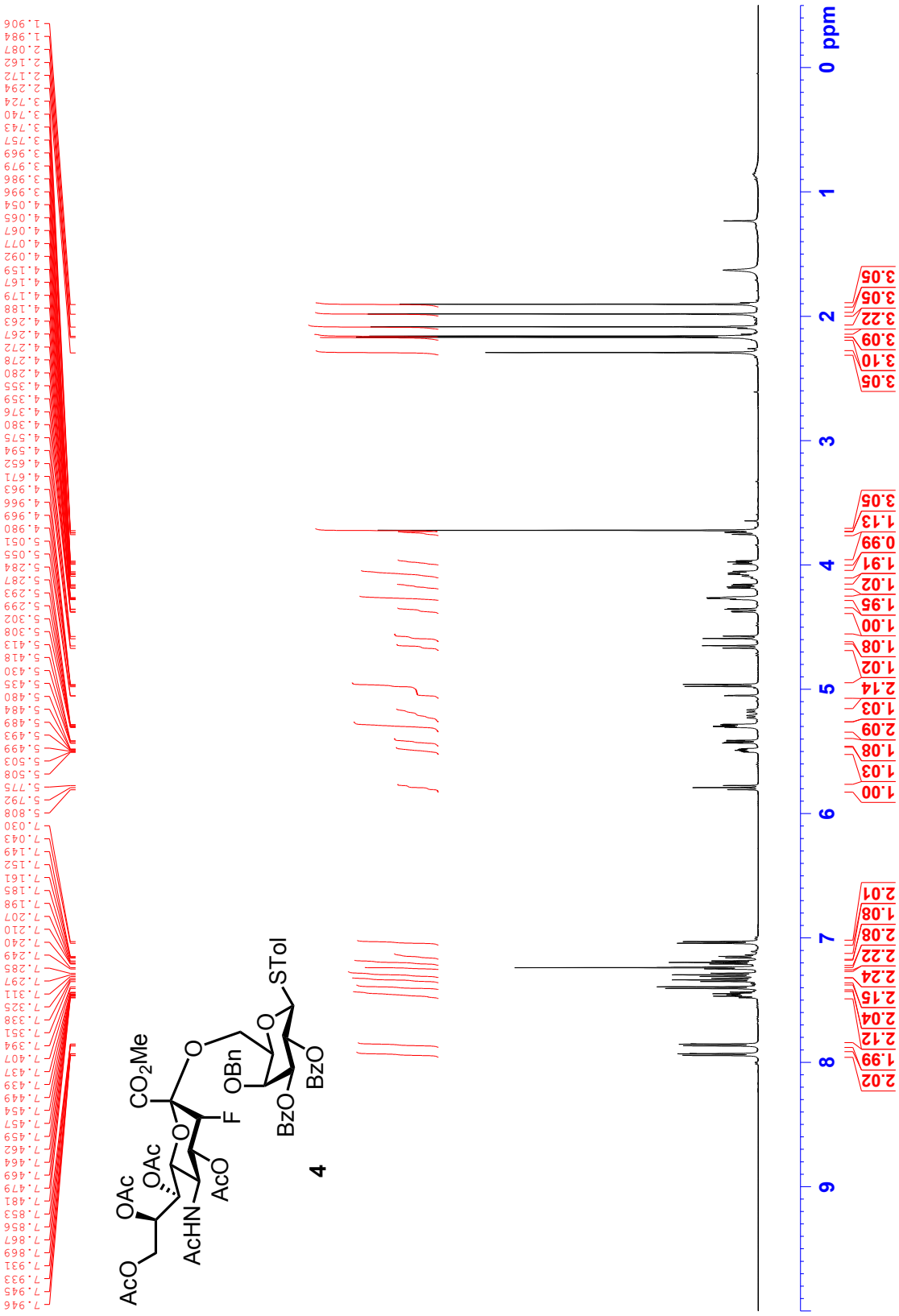
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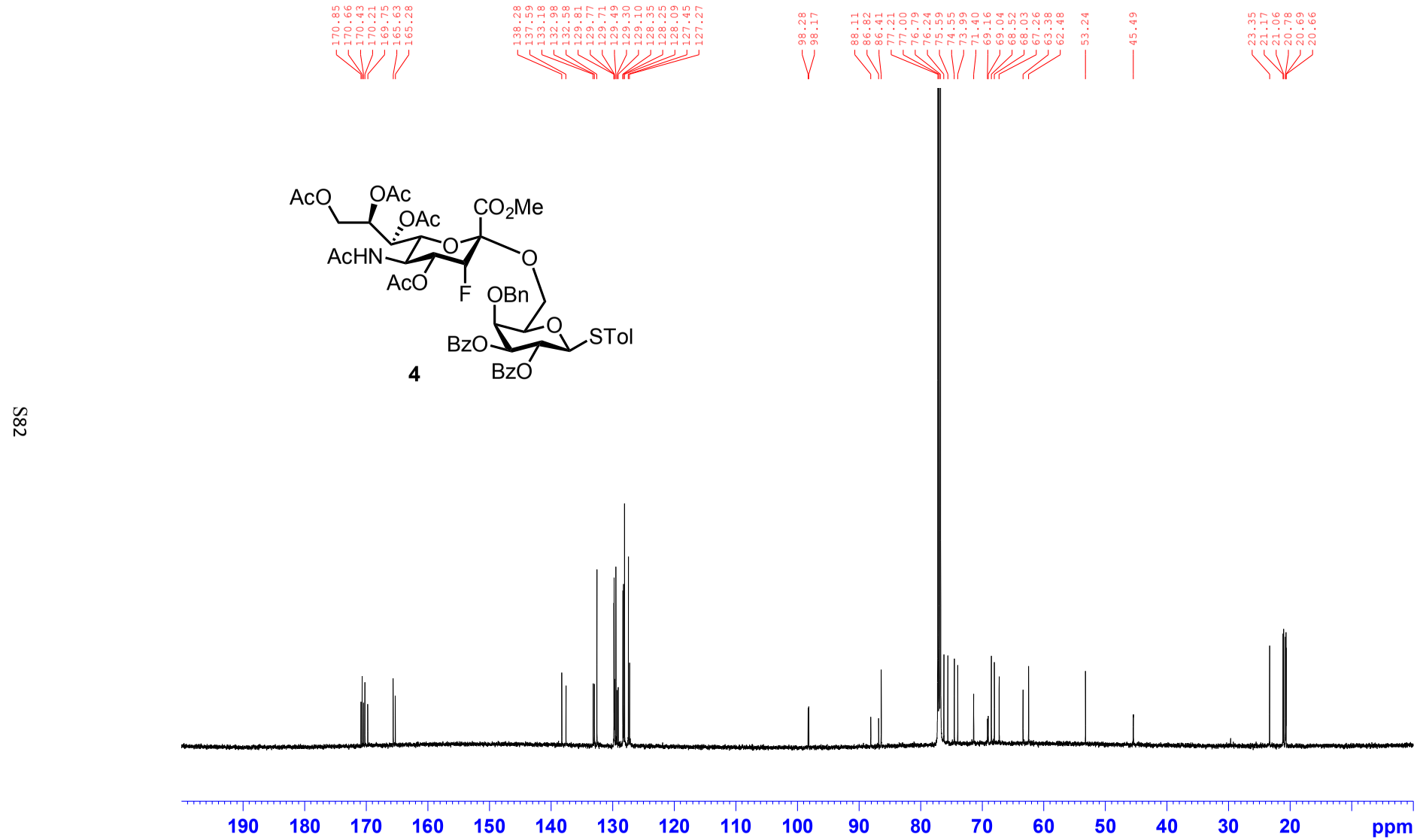
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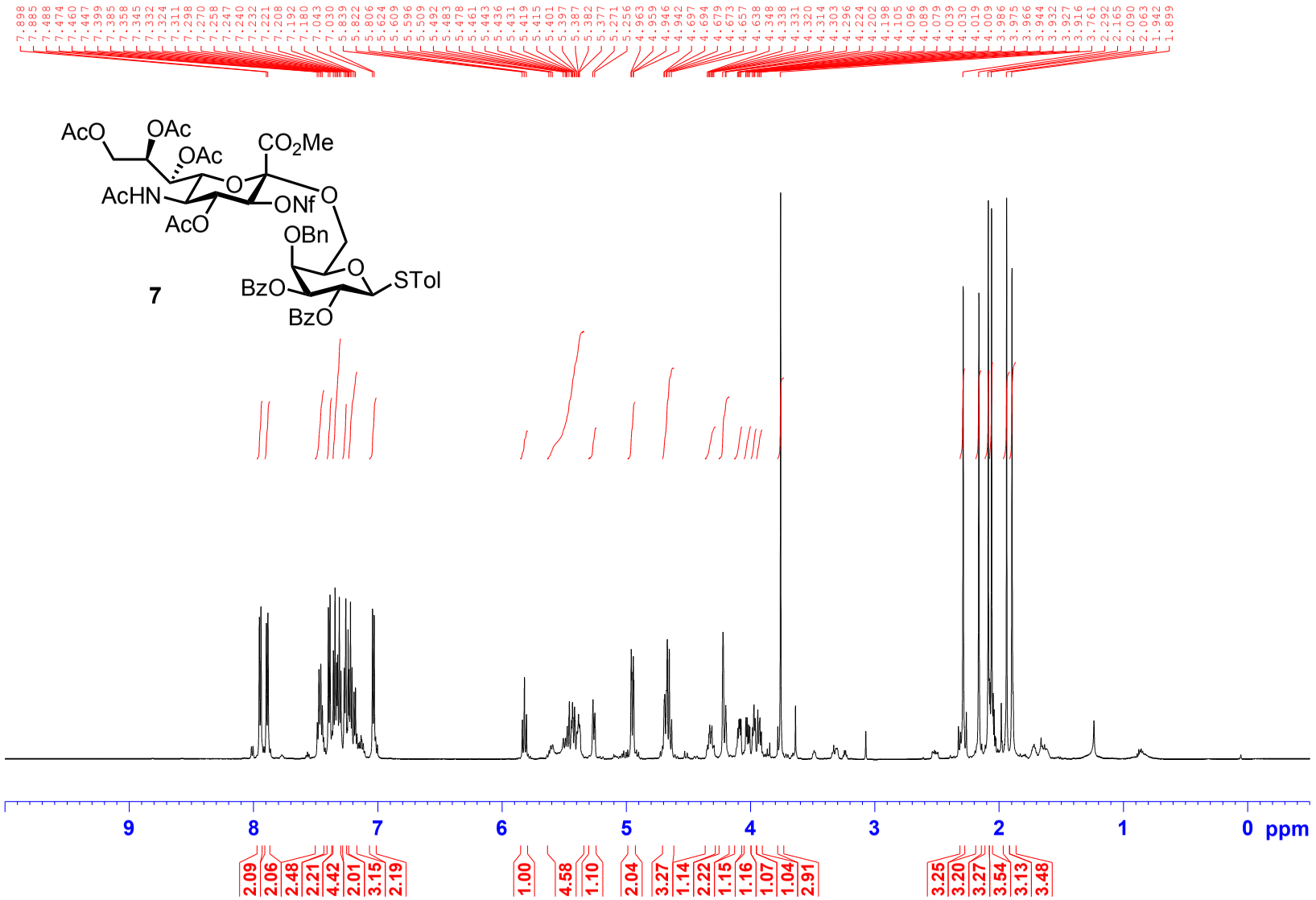
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7.298
7.270
7.258
7.247
7.240
7.232
7.221
7.208
7.192
7.180
7.043
7.030
5.839
5.822
5.806
5.624
5.609
5.596
5.509
5.492
5.483
5.478
5.461
5.443
5.436
5.431
5.419
5.415
5.401
5.397
5.387
5.382
5.377
5.271
5.256
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4.959
4.946
4.942
4.697
4.694
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4.673
4.657
4.638
4.348
4.338
4.331
4.320
4.314
4.303
4.296
4.224
4.202
4.198
4.105
4.096
4.089
4.079
4.039
4.030
4.019
4.009
3.986
3.975
3.966
3.944
3.932
3.927
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3.761
2.292
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2.090
2.063
1.942
1.899
AcO
OAc
OAc
CO2Me
AcHN
O
ONf
O
AcO
OBn
O
STol
BzO
BzO
7
9
8
7
6
5
4
3
2
1
0
ppm
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2.06
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2.21
4.42
2.01
3.15
2.19
1.00
4.58
1.10
2.04
3.27
1.14
2.22
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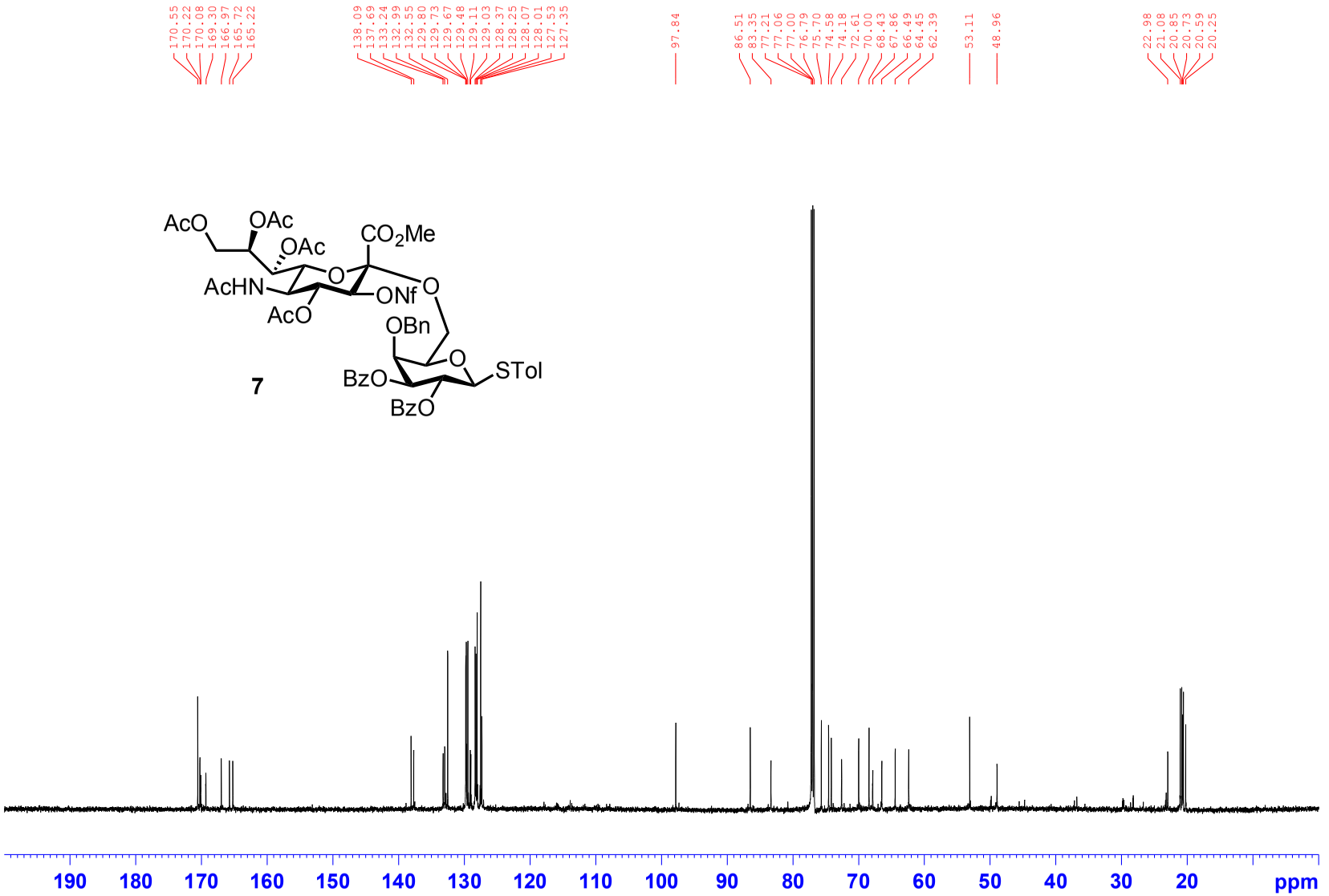
3.48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129.11
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127.35
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86.51
83.35
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74.58
74.18
72.61
70.00
68.43
67.86
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62.39
53.11
48.96
22.98
21.08
20.85
20.73
20.59
20.25
AcO
OAc
OAc
CO2Me
AcHN
O
ONf
O
AcO
OBn
O
STol
BzO
BzO
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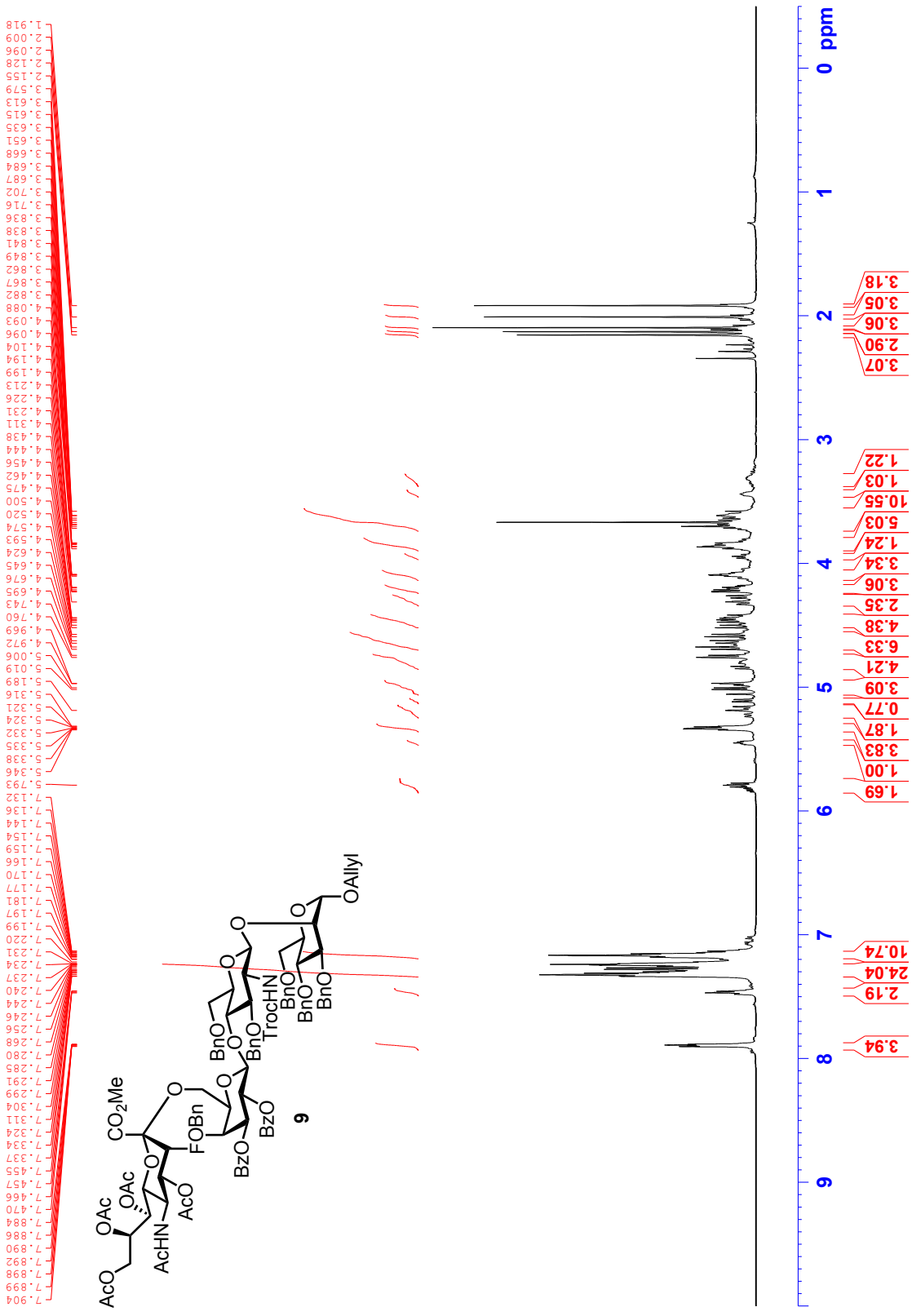
ppm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OAc
OAc
AcHN
AcO
CO2Me
FOBn
BzO
BzO
BnO
BnO
BnO
TrocHN
BnO
BnO
BnO
OAllyl
9
ppm
0
1
2
3
4
5
6
7
8
9
3.94
2.19
24.04
10.74
1.69
1.00
3.83
1.87
0.77
3.09
4.21
6.33
4.38
2.35
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5.03
10.55
1.03
1.22
3.07
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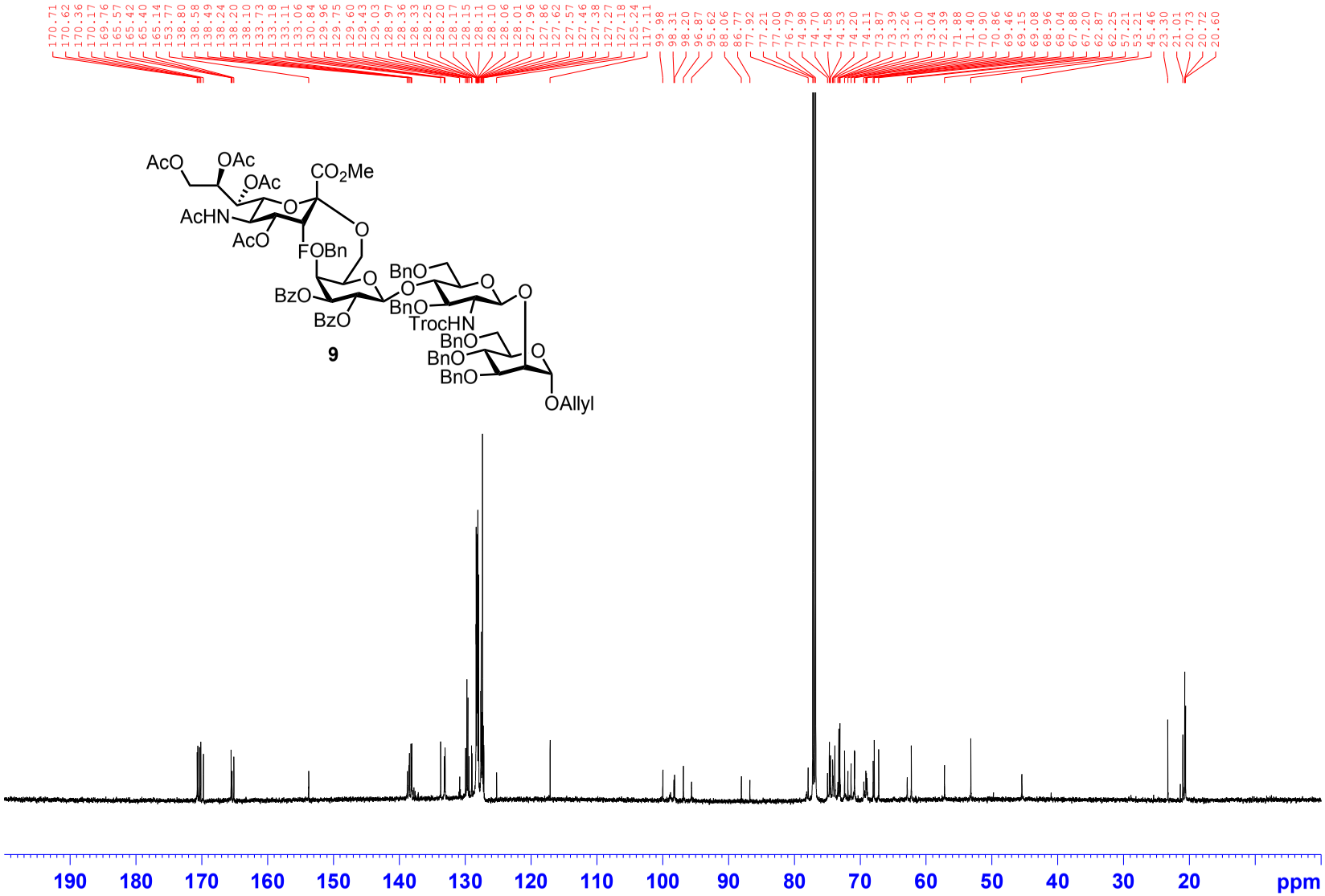
3.06
3.05
3.18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138.49
138.24
138.20
138.10
133.73
133.18
133.11
133.06
130.84
129.96
129.75
129.60
129.43
129.03
128.97
128.36
128.33
128.25
128.20
128.17
128.15
128.11
128.10
128.06
128.01
127.96
127.86
127.62
127.57
127.46
127.38
127.27
127.18
125.24
117.11
99.98
98.31
98.20
96.87
95.62
88.06
86.77
77.92
77.21
77.00
76.79
74.98
74.70
74.58
74.53
74.20
74.11
73.87
73.39
73.26
73.10
73.04
72.39
71.88
71.40
70.90
70.86
69.46
69.15
69.08
68.96
68.04
67.88
67.20
62.87
62.25
57.21
53.21
45.46
23.30
21.01
20.73
20.72
20.60
AcO
OAc
OAc
CO2Me
AcHN
AcO
O
FOBn
BzO
BzO
BnO
BnO
TrocHN
BnO
BnO
BnO
OAllyl
9
190
180
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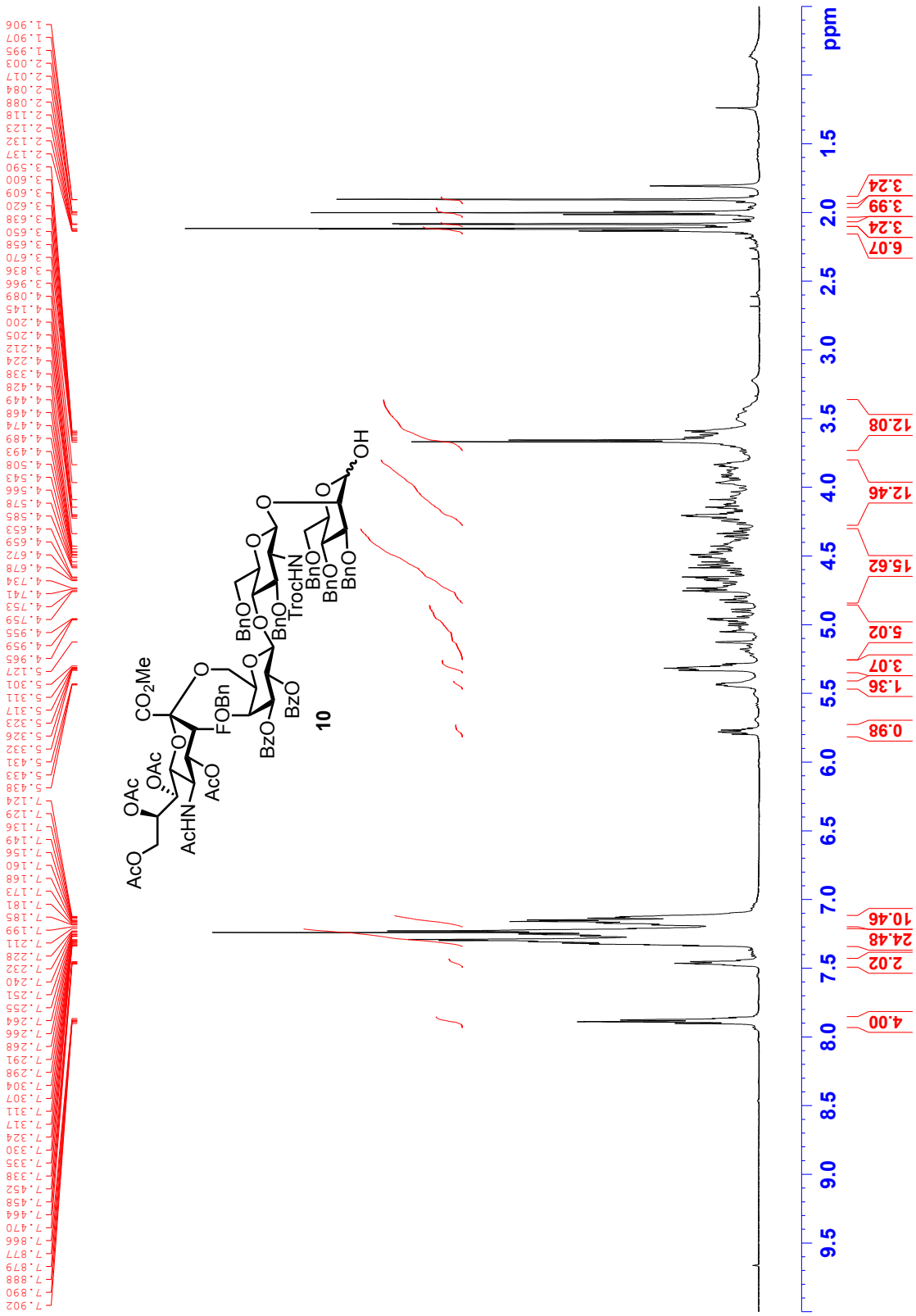
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


AcO
OAc
OAc
AcHN
AcO
CO2Me
O
FOBn
BzO
BzO
BnO
BnO
BnO
TrocHN
BnO
BnO
BnO
OH
10
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
4.00
2.02
24.48
10.46
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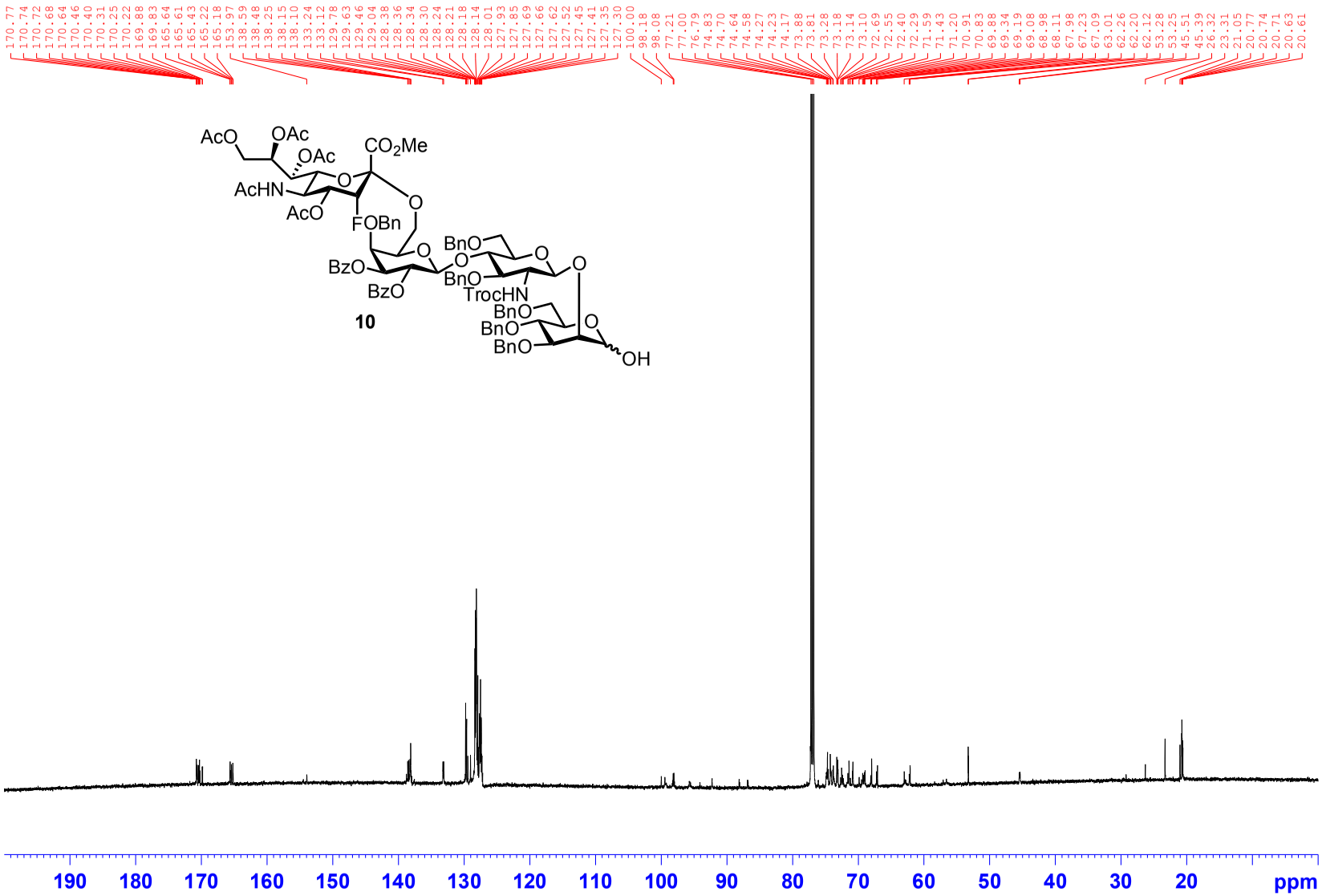
1.36
3.07
5.02
15.62
12.46
12.08
6.07
3.24
3.99
3.24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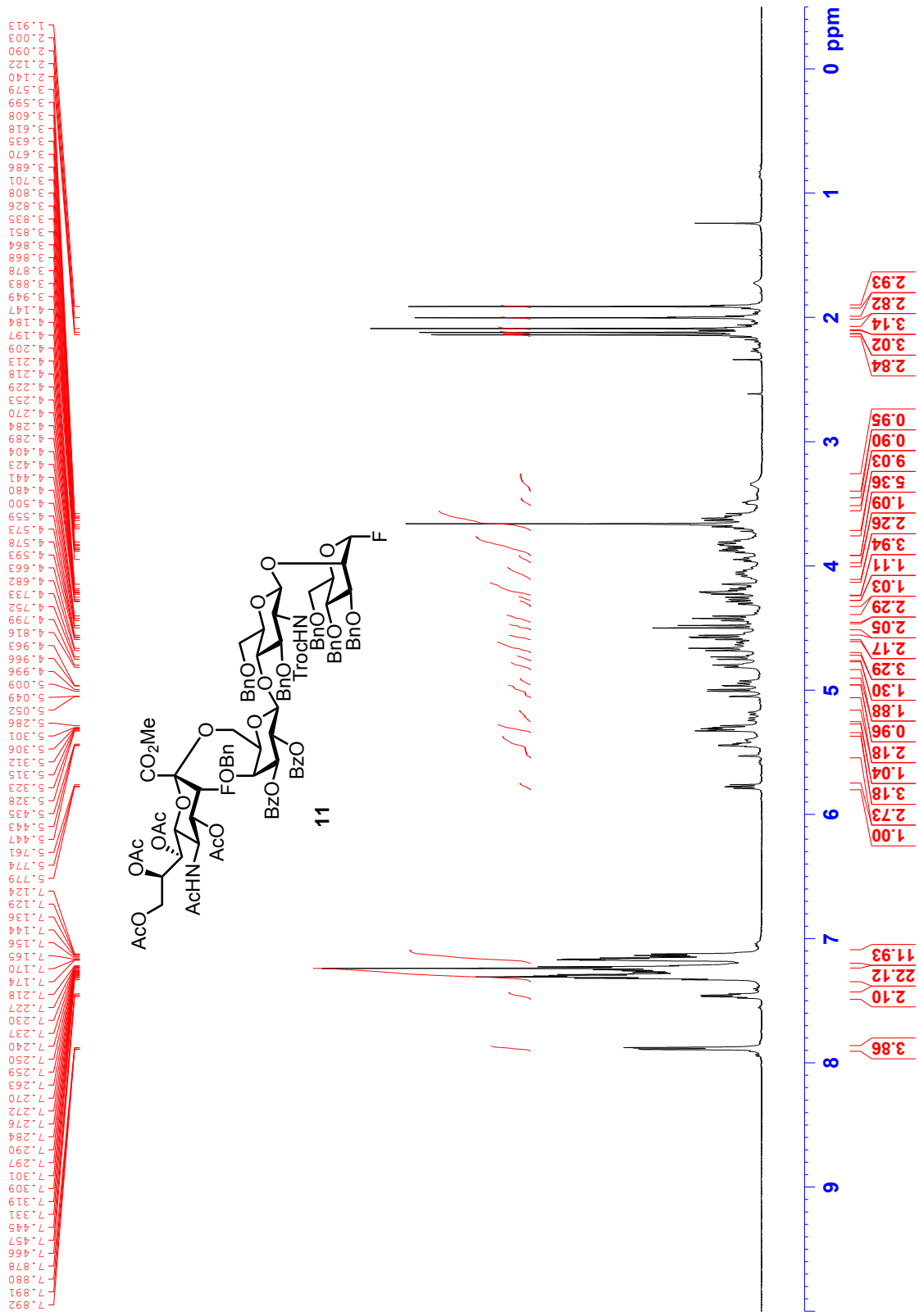
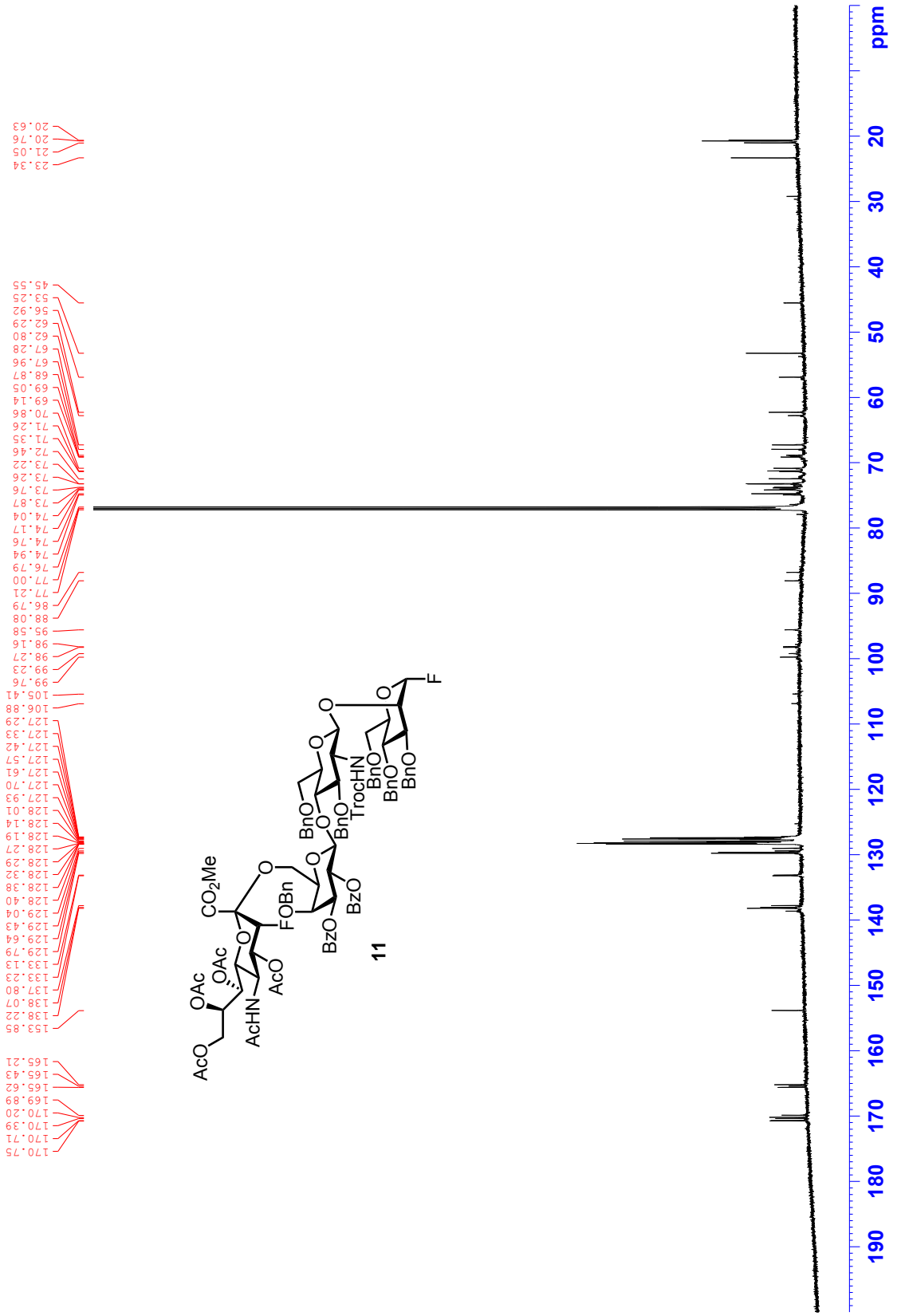
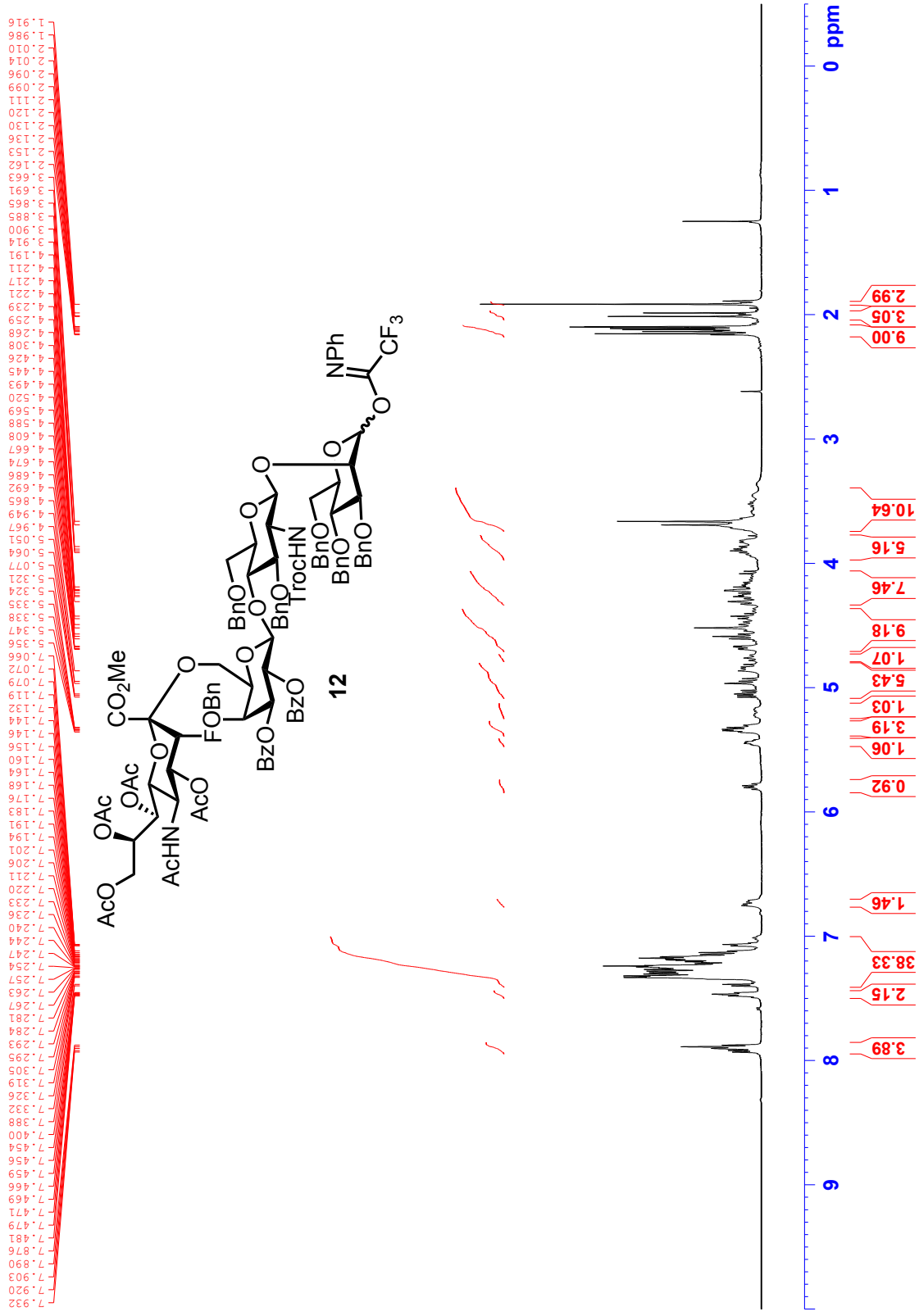
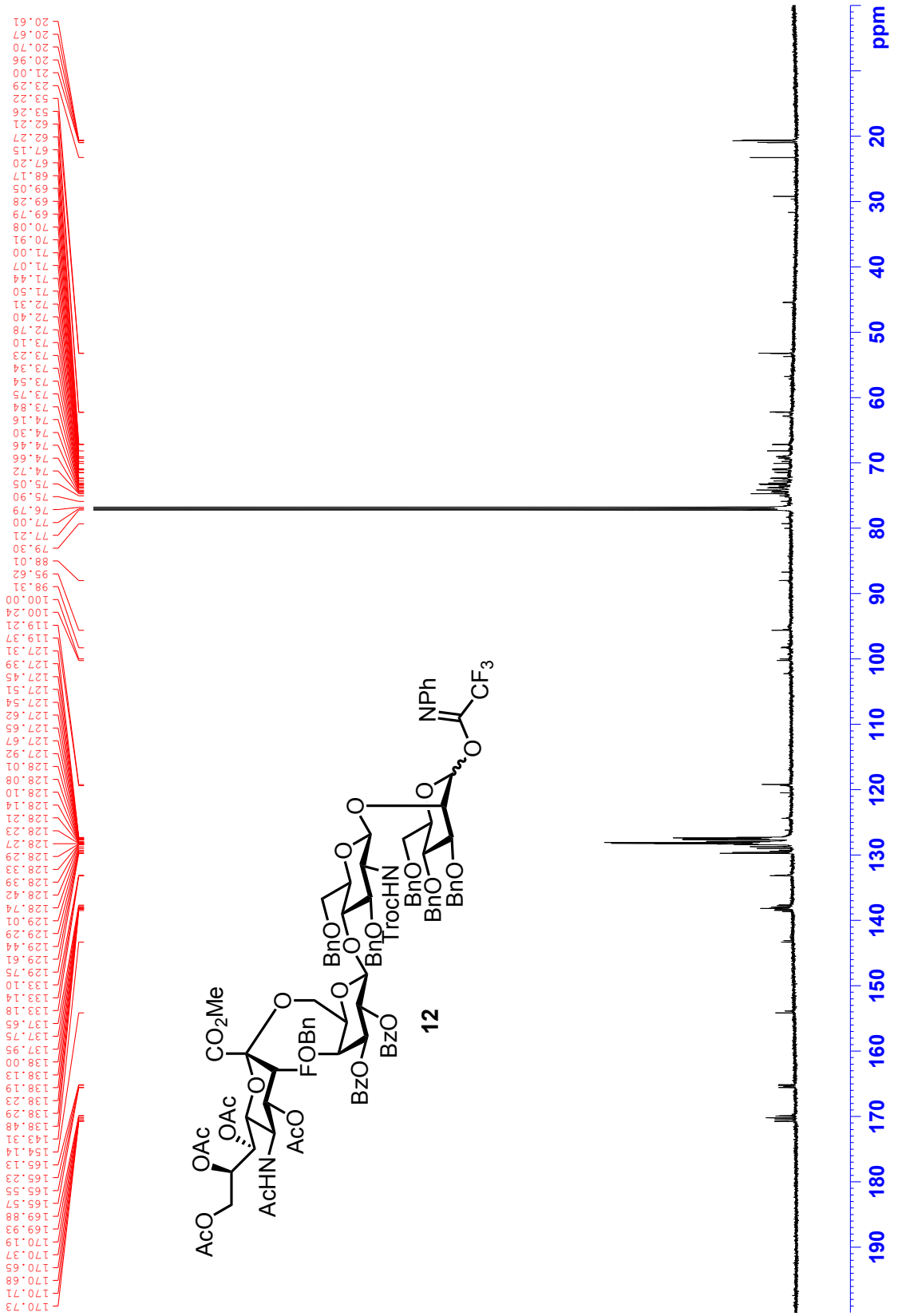
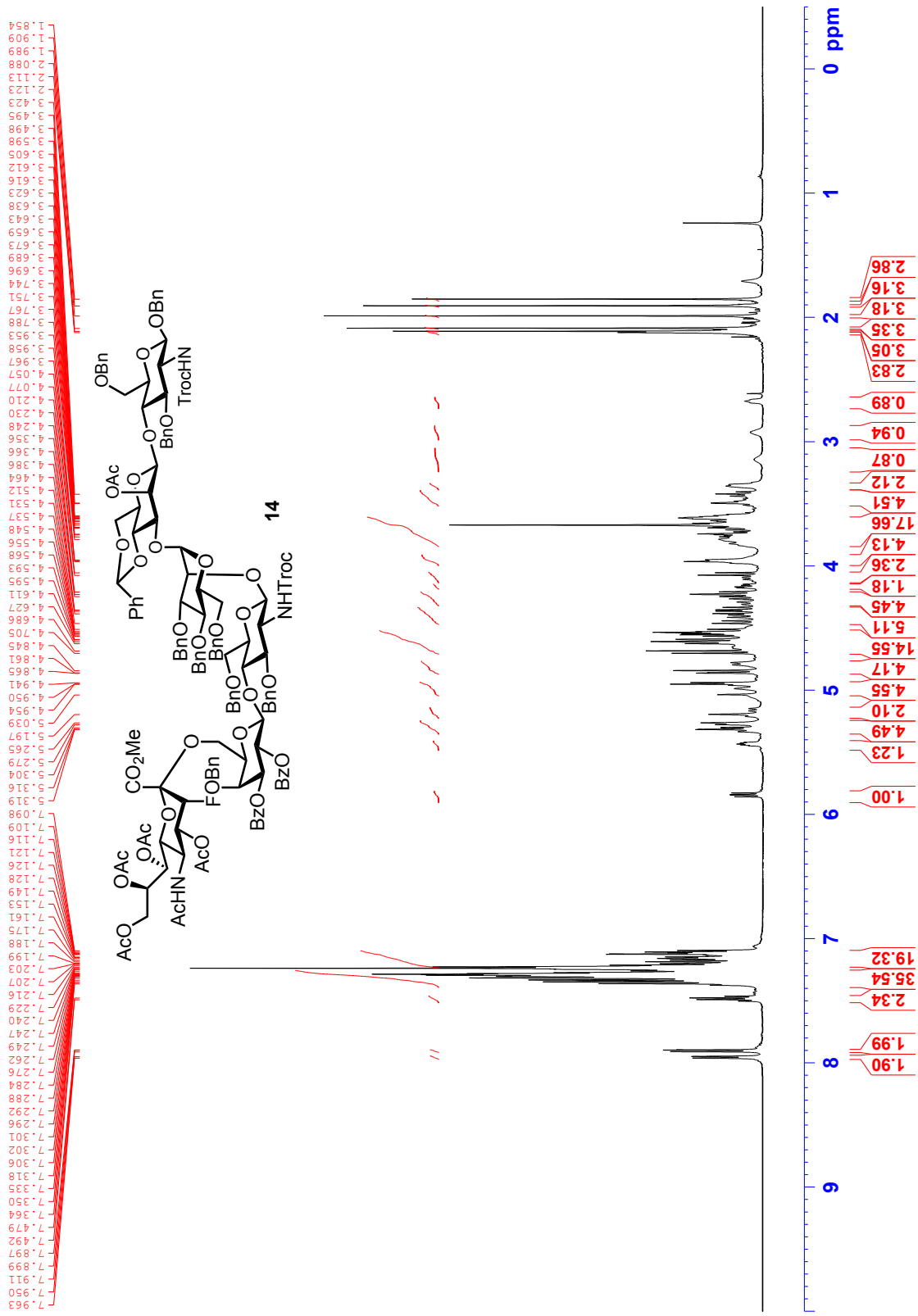
AcO
OAc
OAc
CO2Me
AcHN
AcO
FOBn
BzO
BzO
BnO
BnO
TrocHN
BnO
BnO
BnO
OH
10
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

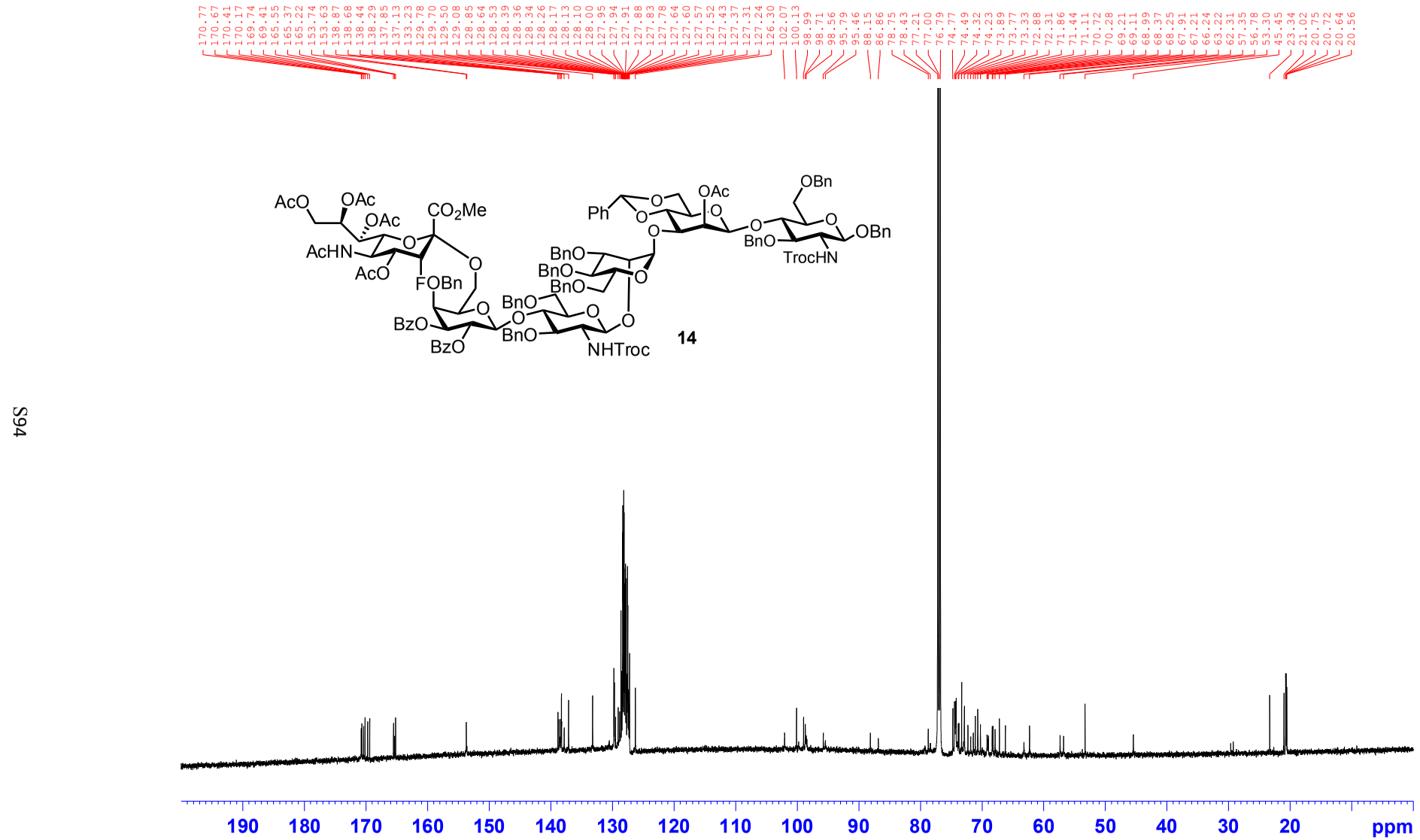

AcO
OAc
OAc
AcHN
AcO
CO2Me
FOBn
BzO
BzO
BnO
BnO
TrocHN
BnO
BnO
BnO
F
11
0 ppm


AcO
OAc
OAc
AcHN
AcO
CO2Me
FOBn
BzO
BzO
BnO
BnO
TrocHN
BnO
BnO
BnO
F
11
ppm


12
AcO
OAc
OAc
AcHN
AcO
CO2Me
O
FOBn
BzO
BnO
O
BnO
TrocHN
BnO
BnO
BnO
O
O
NPh
CF3
0 ppm
1
2
3
4
5
6
7
8
9
9.00
3.05
2.99
10.64
5.16
7.46
9.18
1.07
5.43
1.03
3.19
1.06
0.92
1.46
38.33
2.15
3.89


AcO
OAc
OAc
AcHN
AcO
CO2Me
FOBn
BzO
BzO
BnO
BnO
TrocHN
BnO
BnO
BnO
NPh
CF3
12
ppm


14
AcO
OAc
OAc
AcHN
AcO
CO2Me
FOBn
BzO
BzO
BnO
BnO
BnO
BnO
BnO
NHTroc
Ph
OAc
OBn
BnO
TrocHN
OBn
0 ppm
1.90
1.99
2.34
35.54
19.32
1.00
1.23
4.49
2.10
4.55
4.17
14.55
5.11
4.45
1.18
2.36
4.13
17.66
4.51
2.12
0.87
0.94
0.89
2.83
3.05
3.35
3.18
3.16
2.86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165.37
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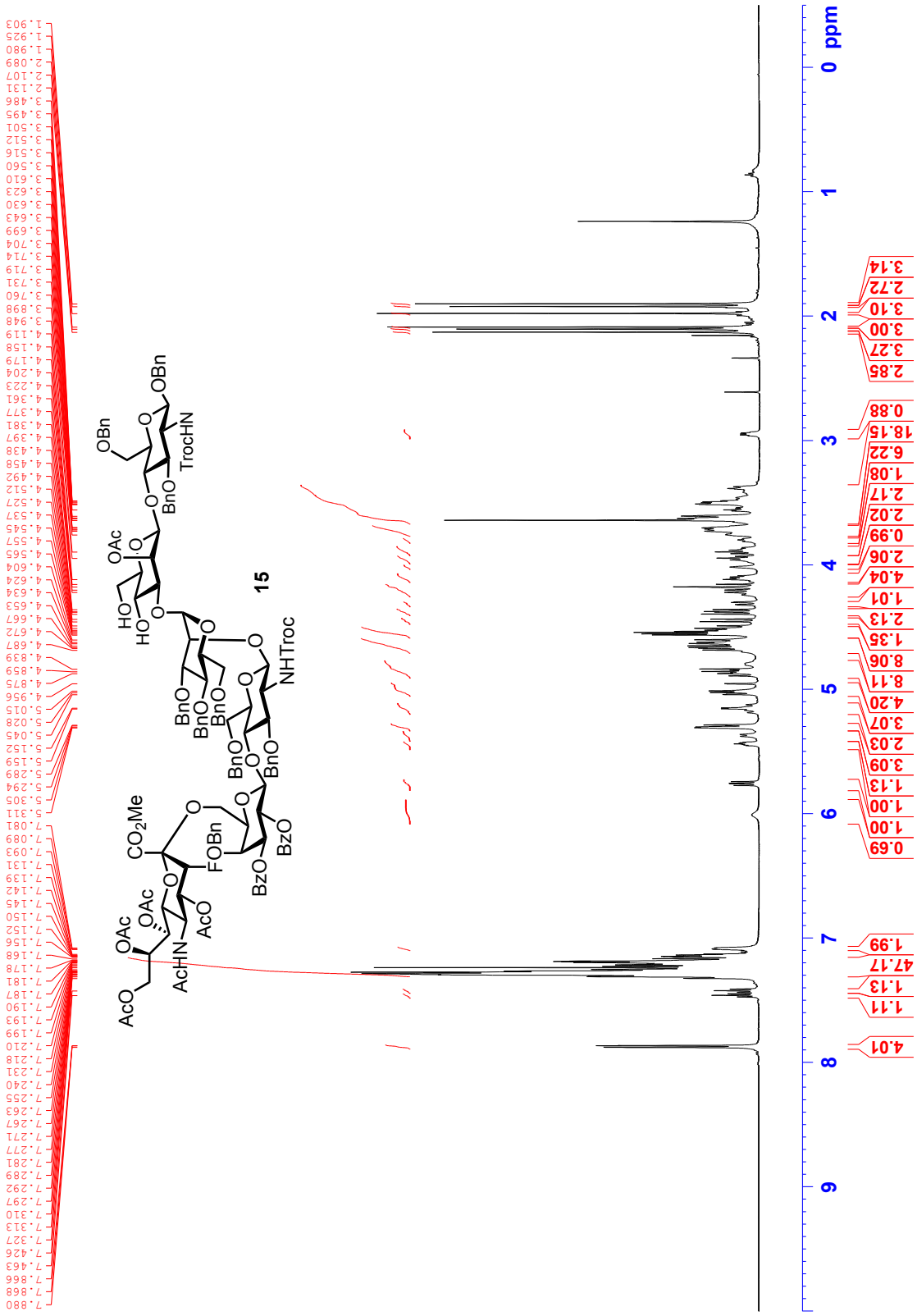
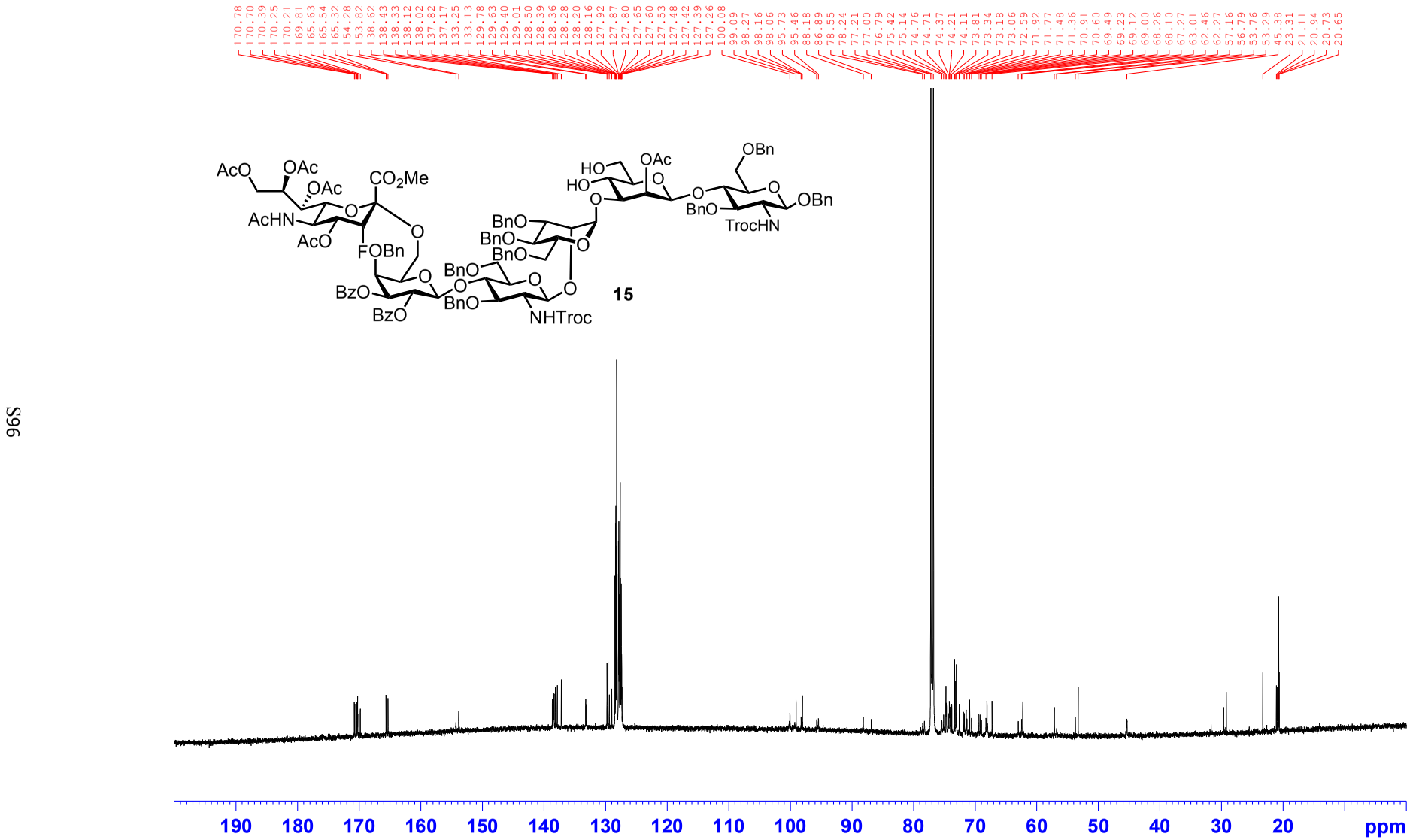
153.63
138.87
138.68
138.44
138.29
137.85
137.13
133.23
129.78
129.70
129.50
129.08
128.85
128.64
128.53
128.39
128.36
128.34
128.26
128.17
128.13
128.10
128.00
127.95
127.94
127.91
127.88
127.83
127.78
127.64
127.60
127.57
127.52
127.43
127.37
127.31
127.21
127.24
126.30
102.07
100.13
98.99
98.71
98.56
95.79
95.46
88.15
86.86
78.75
78.43
77.21
77.00
76.79
74.77
74.49
74.32
74.23
73.89
73.77
73.33
72.88
72.31
71.86
71.44
71.11
70.72
70.28
69.21
69.11
68.99
68.37
68.25
67.91
67.21
66.24
63.22
62.31
57.35
56.78
53.30
45.45
23.34
21.02
20.75
20.72
20.64
20.56
AcO
OAc
OAc
AcHN
AcO
CO2Me
FOBn
BzO
BzO
BnO
BnO
BnO
BnO
BnO
NHTroc
Ph
OAc
OBn
BnO
OBn
TrocHN
14
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


15
AcO
OAc
AcHN
OAc
AcO
CO2Me
FOBn
BzO
BnO
BnO
BnO
BnO
BnO
NHTroc
BzO
HO
HO
OAc
BnO
TrocHN
OBn
OBn
ppm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170.25
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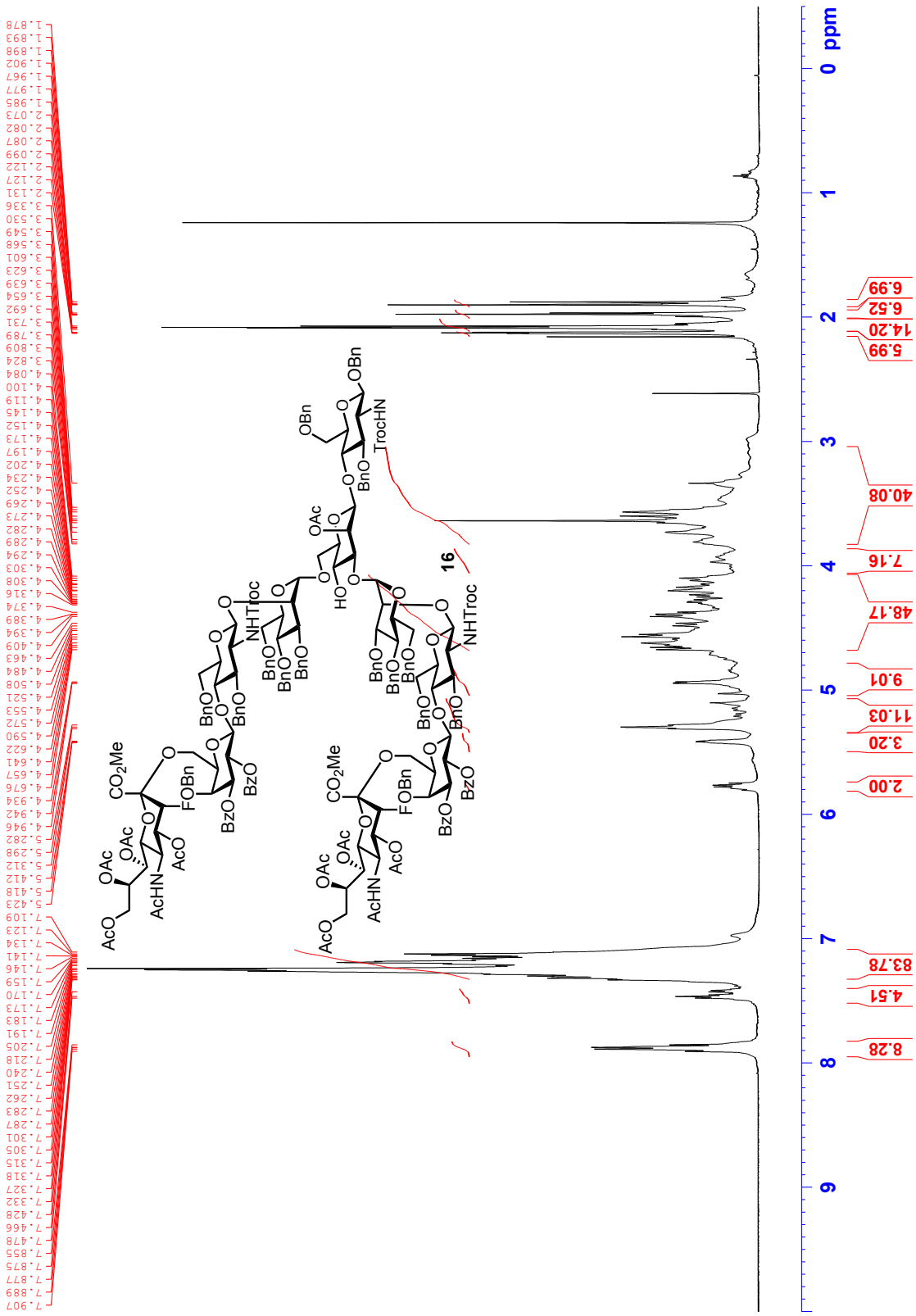
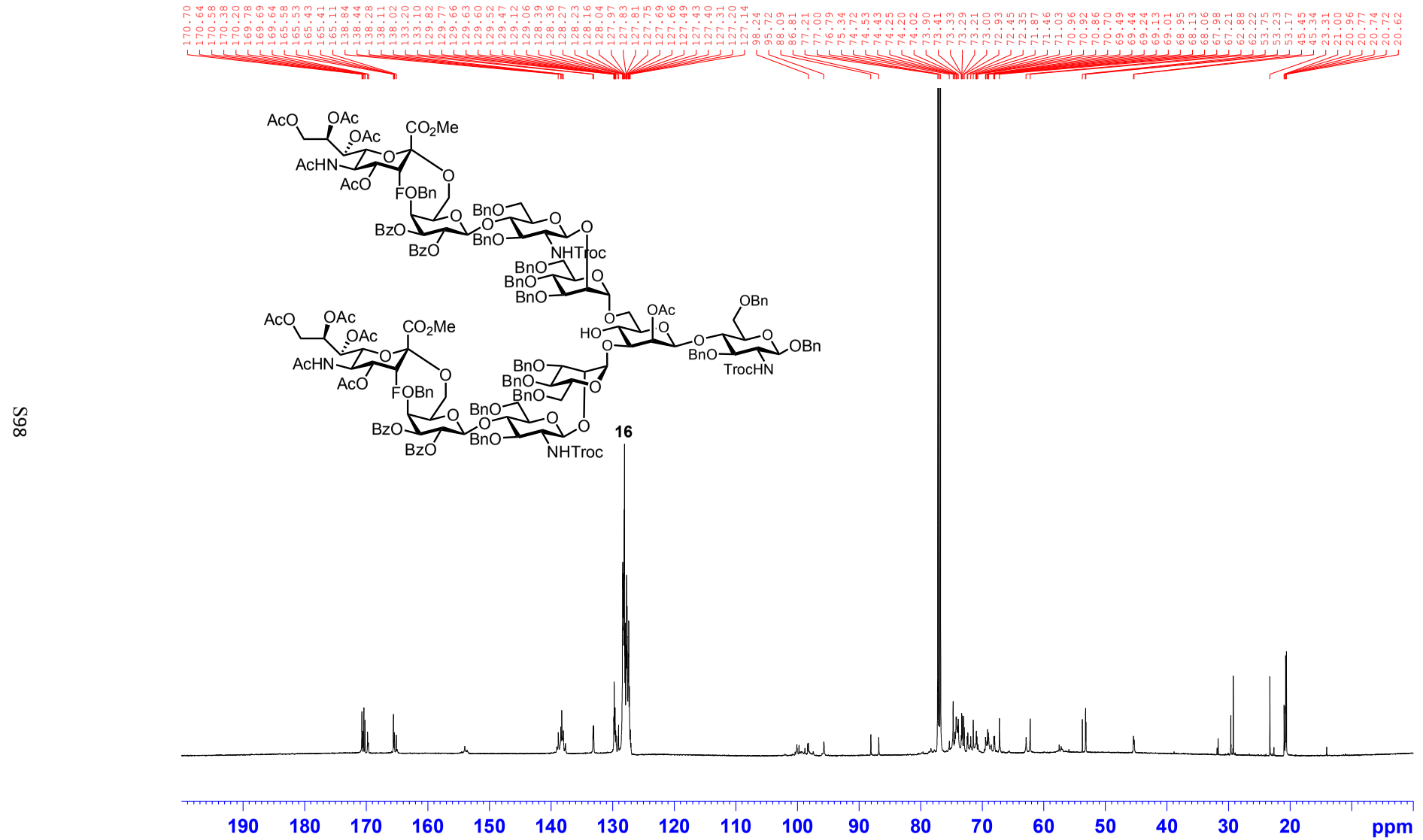
165.63
165.54
165.32
154.28
153.82
138.62
138.43
138.33
138.12
138.02
137.82
137.17
133.25
133.13
129.78
129.63
129.40
129.01
128.50
128.39
128.36
128.28
128.20
128.16
127.92
127.87
127.80
127.65
127.60
127.53
127.48
127.42
127.39
127.26
100.08
99.09
98.27
98.16
98.06
95.73
95.46
88.18
86.89
78.55
78.24
77.21
77.00
76.79
75.42
75.14
74.76
74.71
74.37
74.21
74.11
73.81
73.34
73.18
73.06
72.59
71.92
71.77
71.48
71.36
70.91
70.60
69.49
69.23
69.12
69.00
68.26
68.10
67.27
63.01
62.46
62.27
57.16
56.79
53.76
53.29
45.38
23.31
21.11
20.94
20.73
20.65
AcO
OAc
OAc
CO2Me
AcHN
AcO
FOBn
BzO
BzO
BnO
BnO
BnO
BnO
BnO
NHTroc
HO
HO
OAc
BnO
TrocHN
OBn
OBn
15
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


16
0 ppm
1
2
3
4
5
6
7
8
9
5.99
14.20
6.52
6.99
40.08
7.16
48.17
9.01
11.03
3.20
2.00
83.78
4.51
8.28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169.78
169.69
169.64
165.58
165.53
165.43
165.41
165.11
138.84
138.44
138.28
138.11
138.02
133.20
133.10
129.82
129.77
129.66
129.63
129.60
129.52
129.47
129.12
129.06
128.39
128.36
128.27
128.23
128.16
128.04
127.97
127.83
127.81
127.75
127.69
127.66
127.49
127.43
127.40
127.31
127.20
127.14
98.24
95.72
88.09
86.81
77.21
77.00
76.79
75.34
74.72
74.53
74.43
74.25
74.20
74.02
73.90
73.41
73.33
73.29
73.21
73.00
72.93
72.45
72.35
71.87
71.46
71.03
70.96
70.92
70.86
70.70
69.49
69.44
69.24
69.13
69.01
68.95
68.13
68.06
67.98
67.21
62.88
62.22
53.75
53.23
53.17
45.45
45.34
23.31
21.00
20.96
20.77
20.74
20.72
20.62
16
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180
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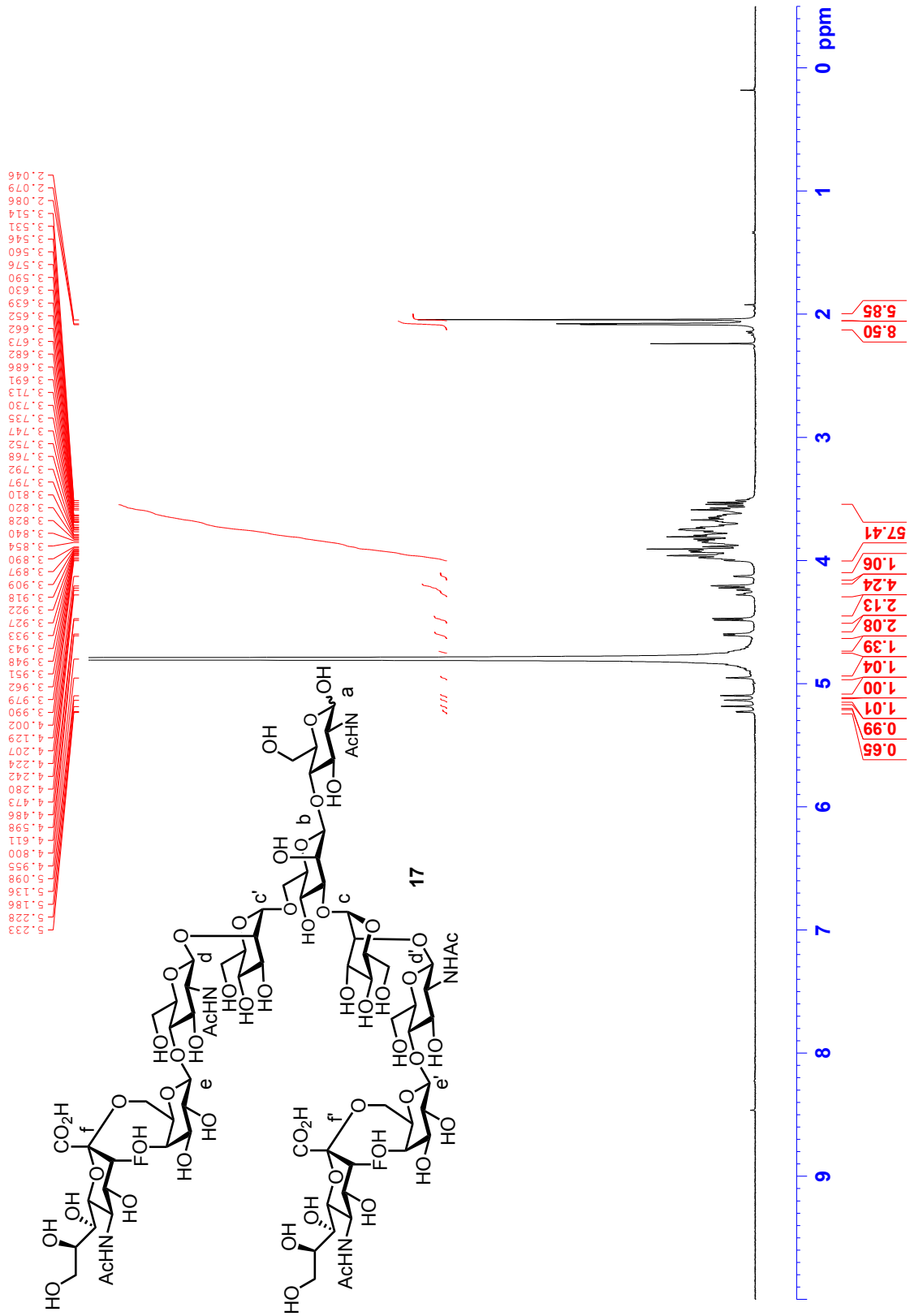
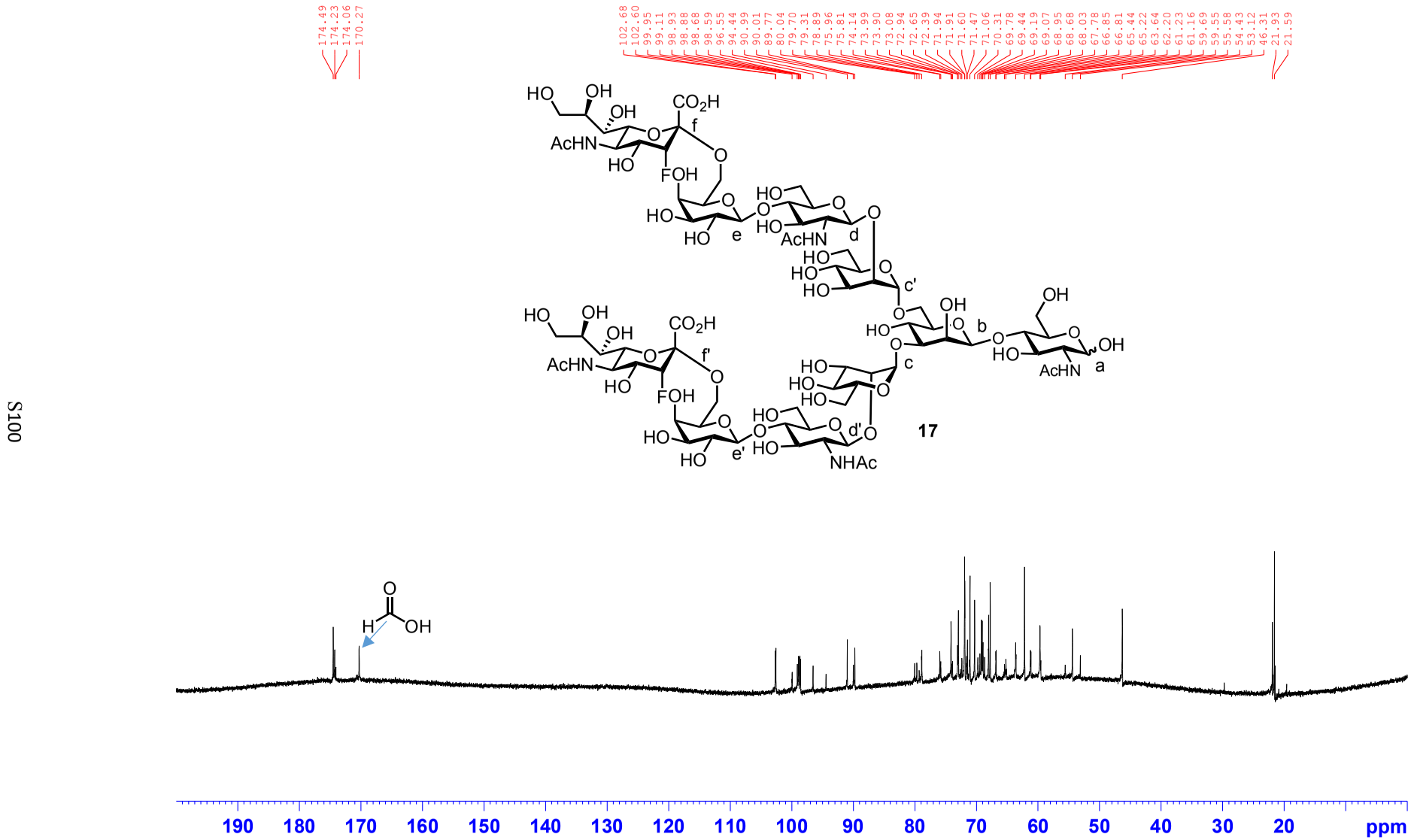
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


17
0.65
0.99
1.01
1.00
1.04
1.39
2.08
2.13
4.24
1.06
57.41
8.50
5.85
0 ppm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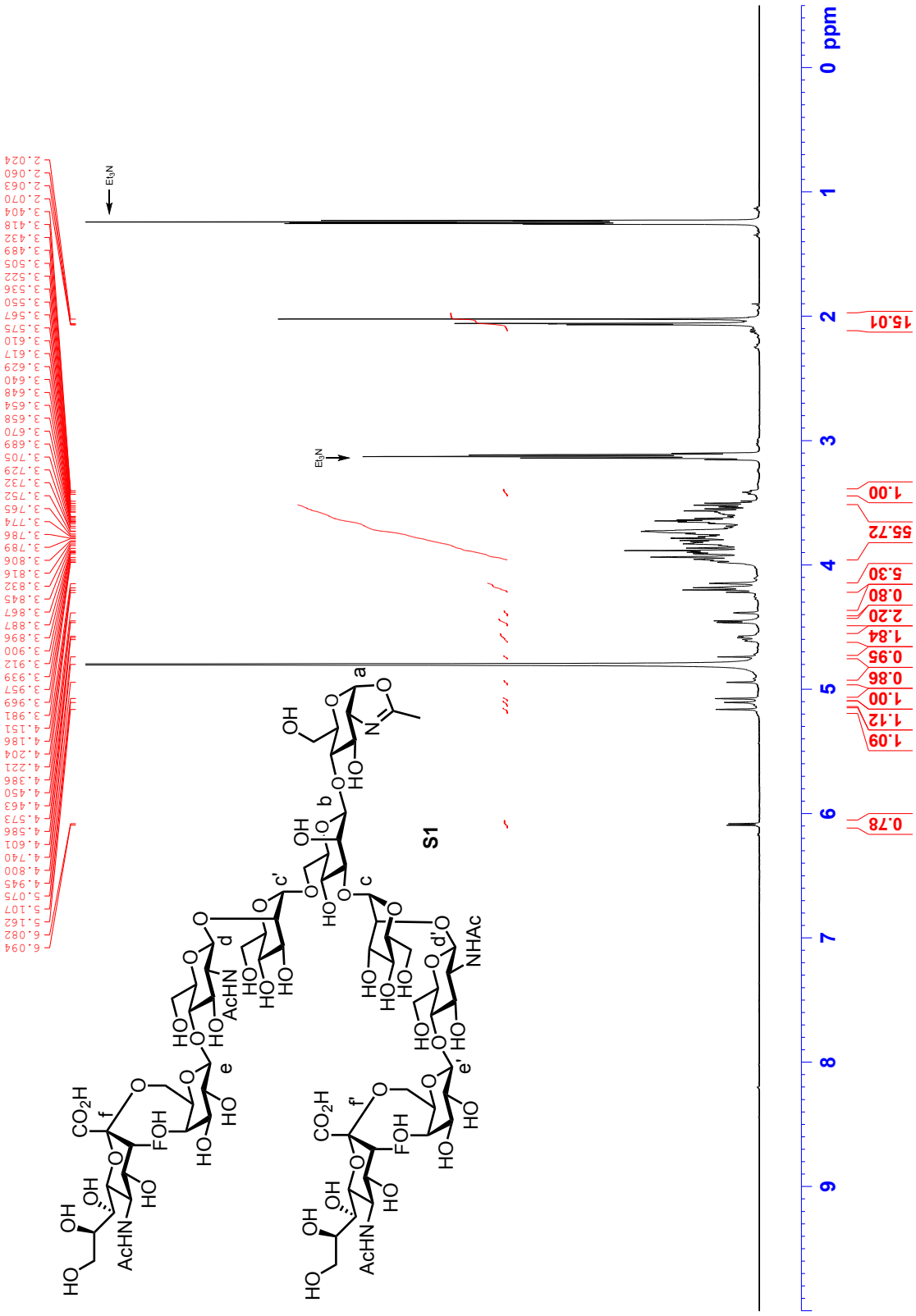
174.23
174.06
170.27
102.68
102.60
99.95
99.11
98.93
98.88
98.68
98.59
96.55
94.44
90.99
90.01
89.77
80.04
79.70
79.31
78.89
75.96
75.81
74.14
73.99
73.90
73.08
72.94
72.65
72.39
71.94
71.91
71.60
71.47
71.06
70.31
69.78
69.44
69.19
69.07
68.95
68.68
68.03
67.78
66.85
66.81
65.44
65.22
63.64
62.20
61.23
61.16
59.69
59.55
55.58
54.43
53.12
46.31
21.93
21.59
17
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


S1
Et3N
Et3N
15.01
1.00
55.72
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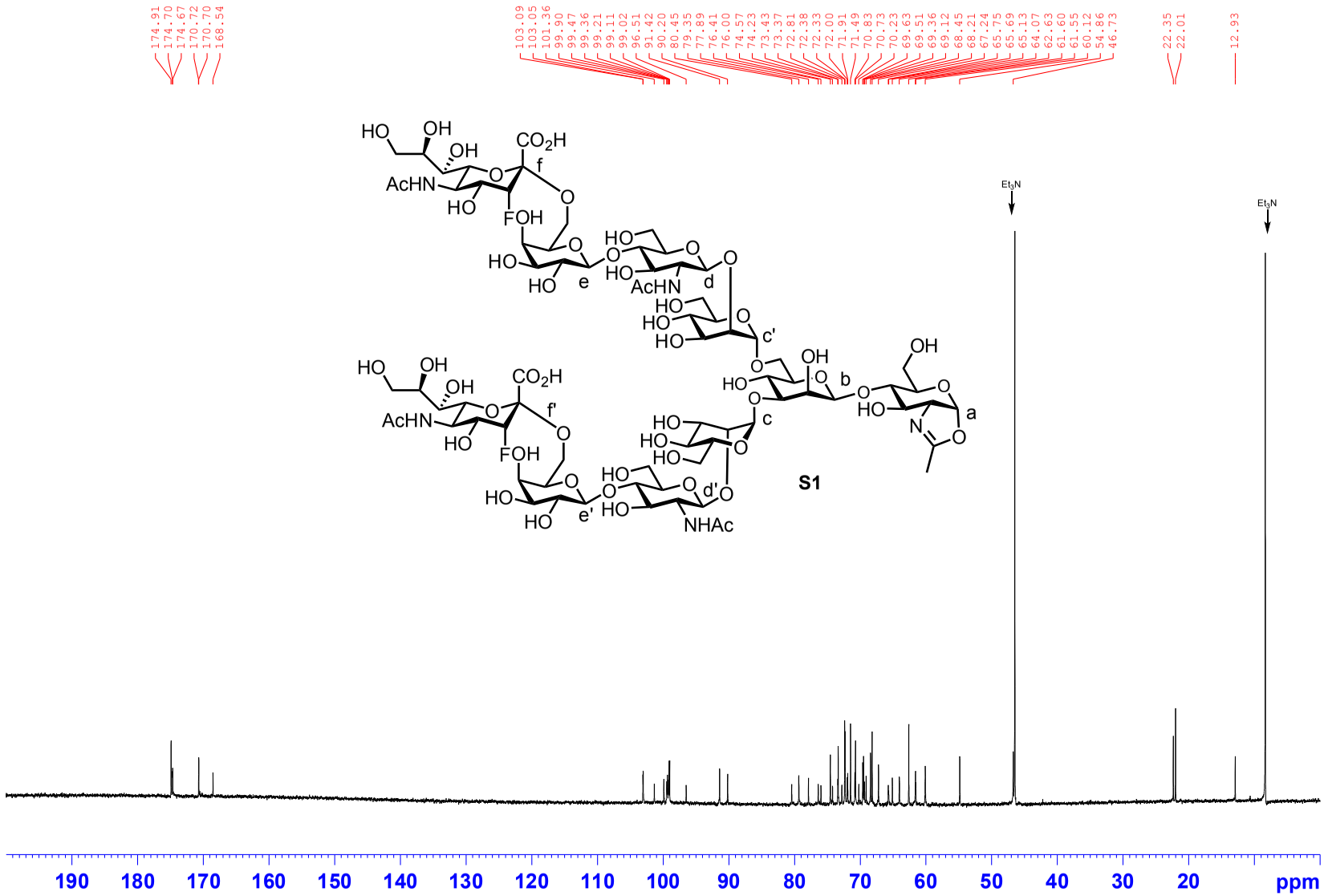
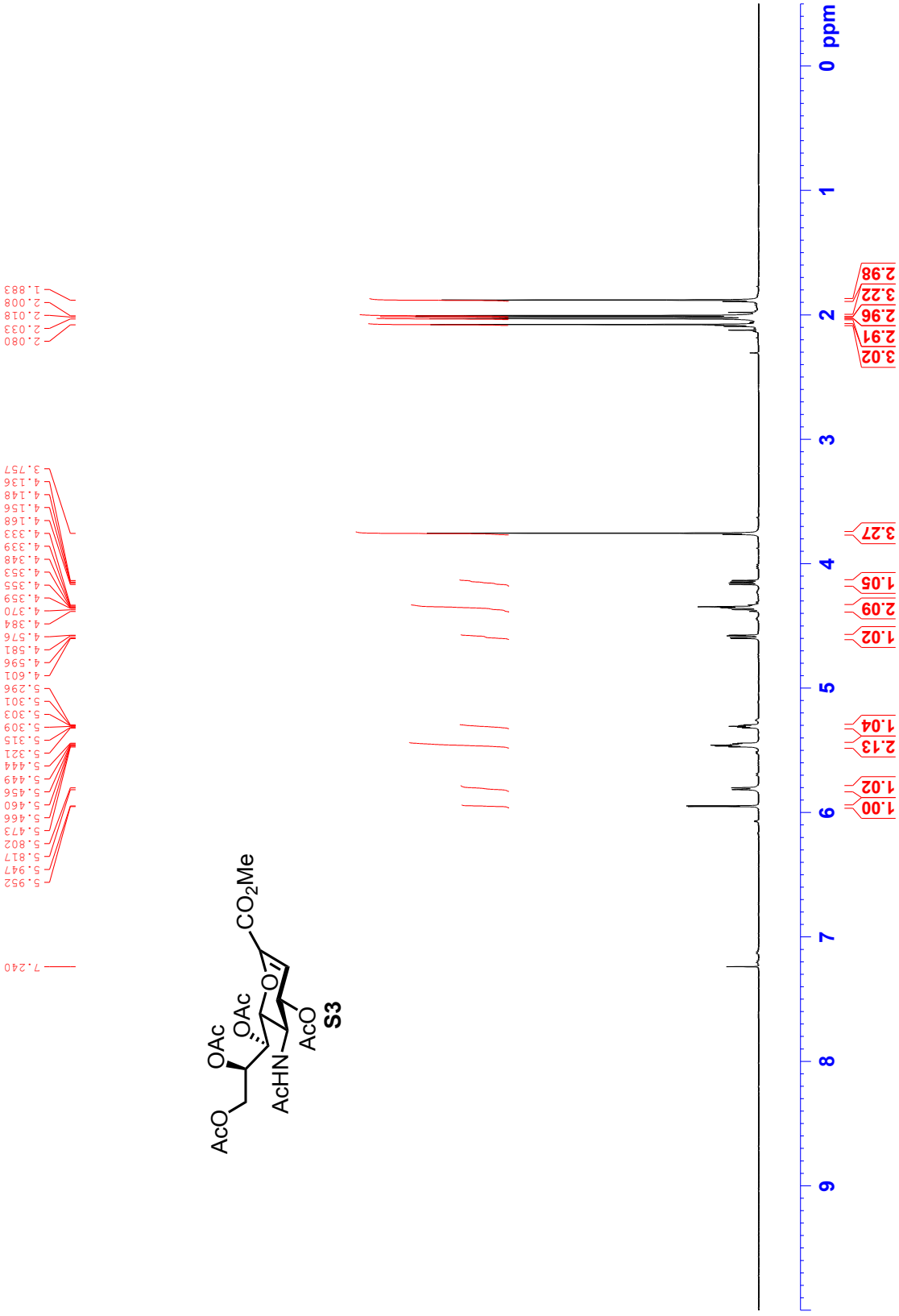
0.80
2.20
1.84
0.95
0.86
1.00
1.12
1.09
0.78
0 ppm


174.91
174.70
174.67
170.72
170.70
168.54
103.09
103.05
101.36
99.90
99.47
99.36
99.21
99.11
99.02
96.51
91.42
90.20
80.45
79.35
77.89
76.41
76.00
74.57
74.23
73.43
73.37
72.81
72.38
72.33
72.00
71.91
71.49
70.83
70.73
70.23
69.63
69.51
69.36
69.12
68.45
68.21
67.24
65.75
65.69
65.13
64.07
62.63
61.60
61.55
60.12
54.86
46.73
22.35
22.01
12.93
Et3N
Et3N
S1
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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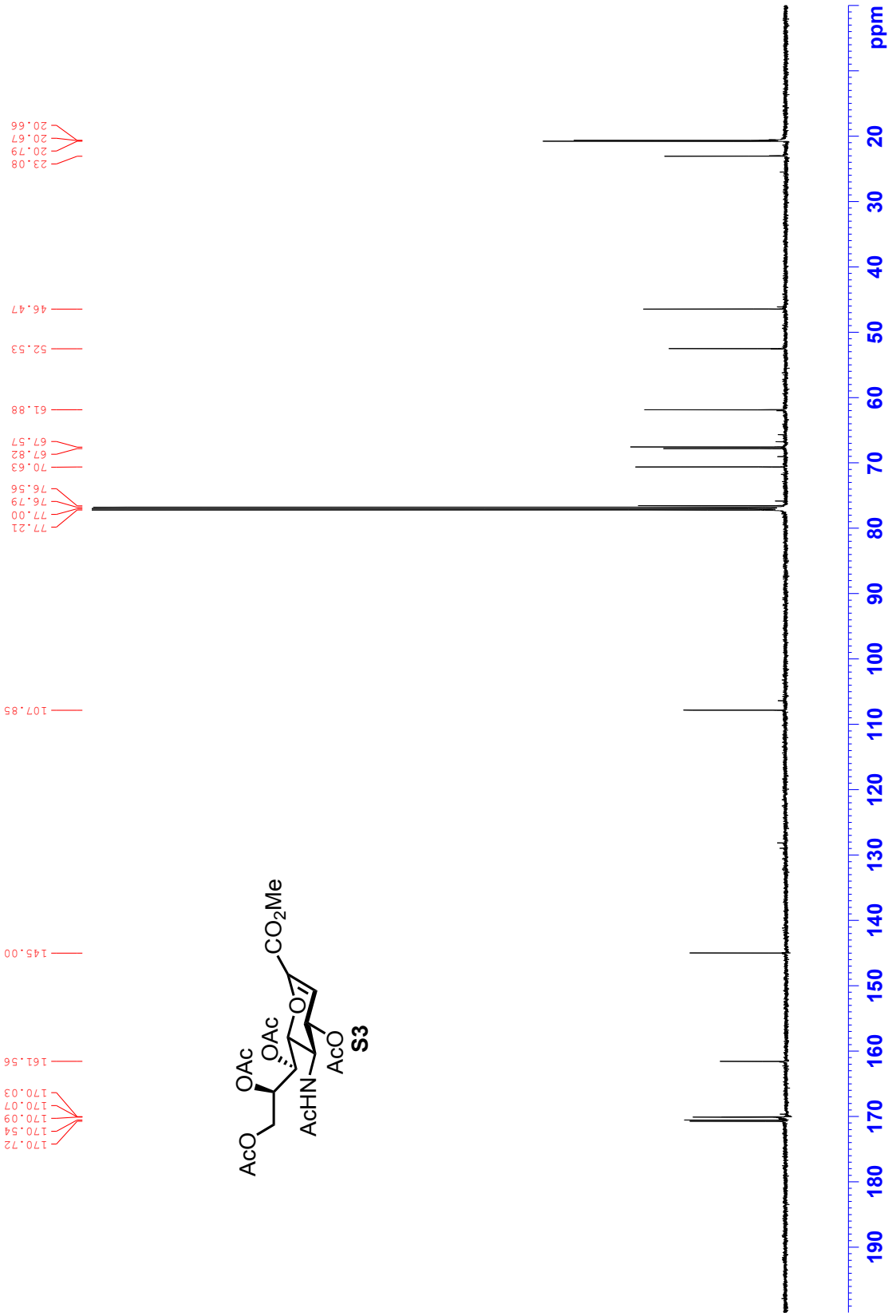
2.008
2.018
2.033
2.080
3.757
4.136
4.148
4.156
4.168
4.333
4.339
4.348
4.353
4.355
4.359
4.370
4.384
4.576
4.581
4.596
4.601
5.296
5.301
5.303
5.309
5.315
5.321
5.444
5.449
5.456
5.460
5.466
5.473
5.802
5.817
5.947
5.952
7.240
AcO
OAc
OAc
AcHN
O
CO2Me
AcO
S3
0 ppm
1
2
3
4
5
6
7
8
9
3.02
2.91
2.96
3.22
2.98
3.27
1.05
2.09
1.02
1.04
2.13
1.02
1.00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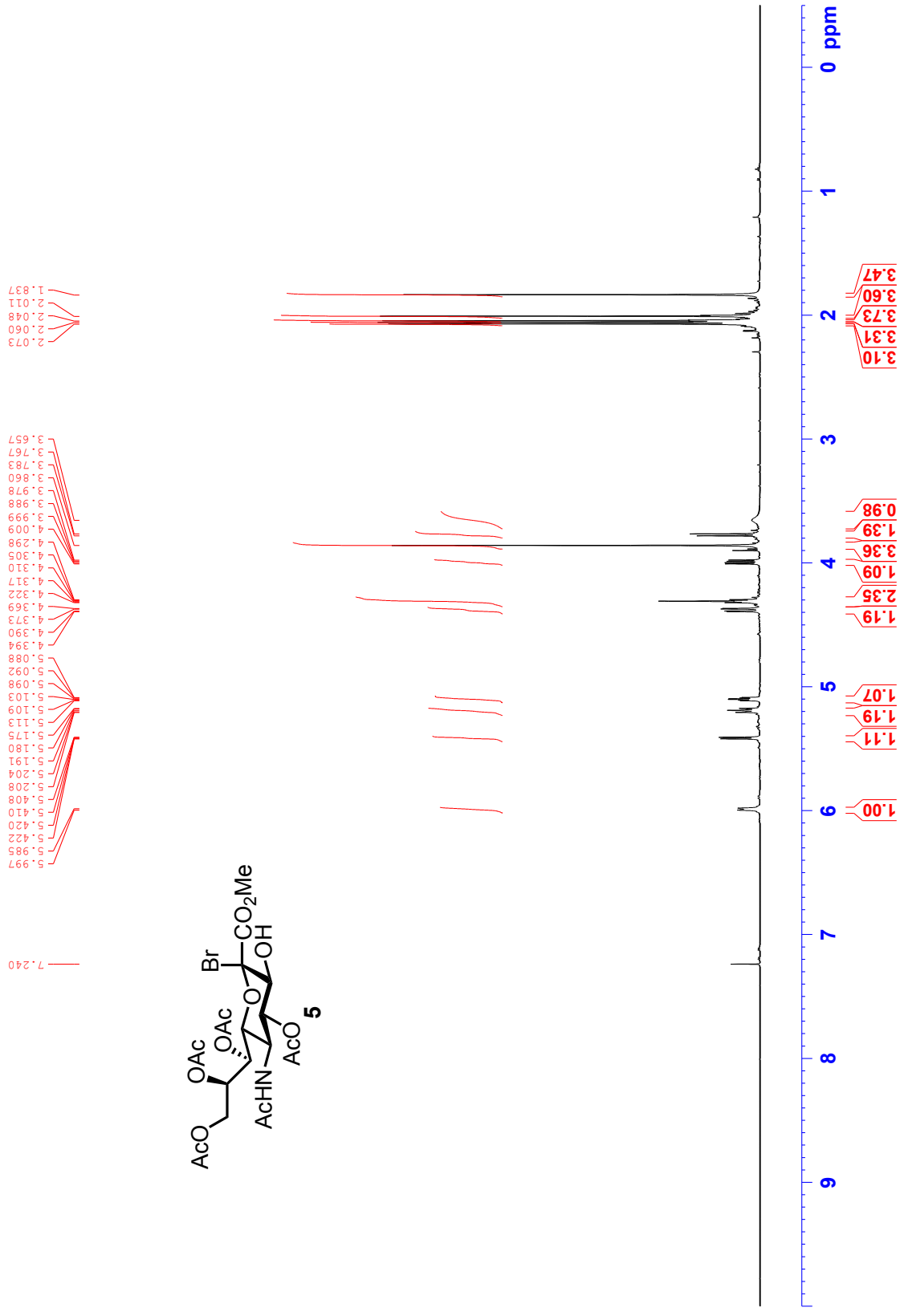
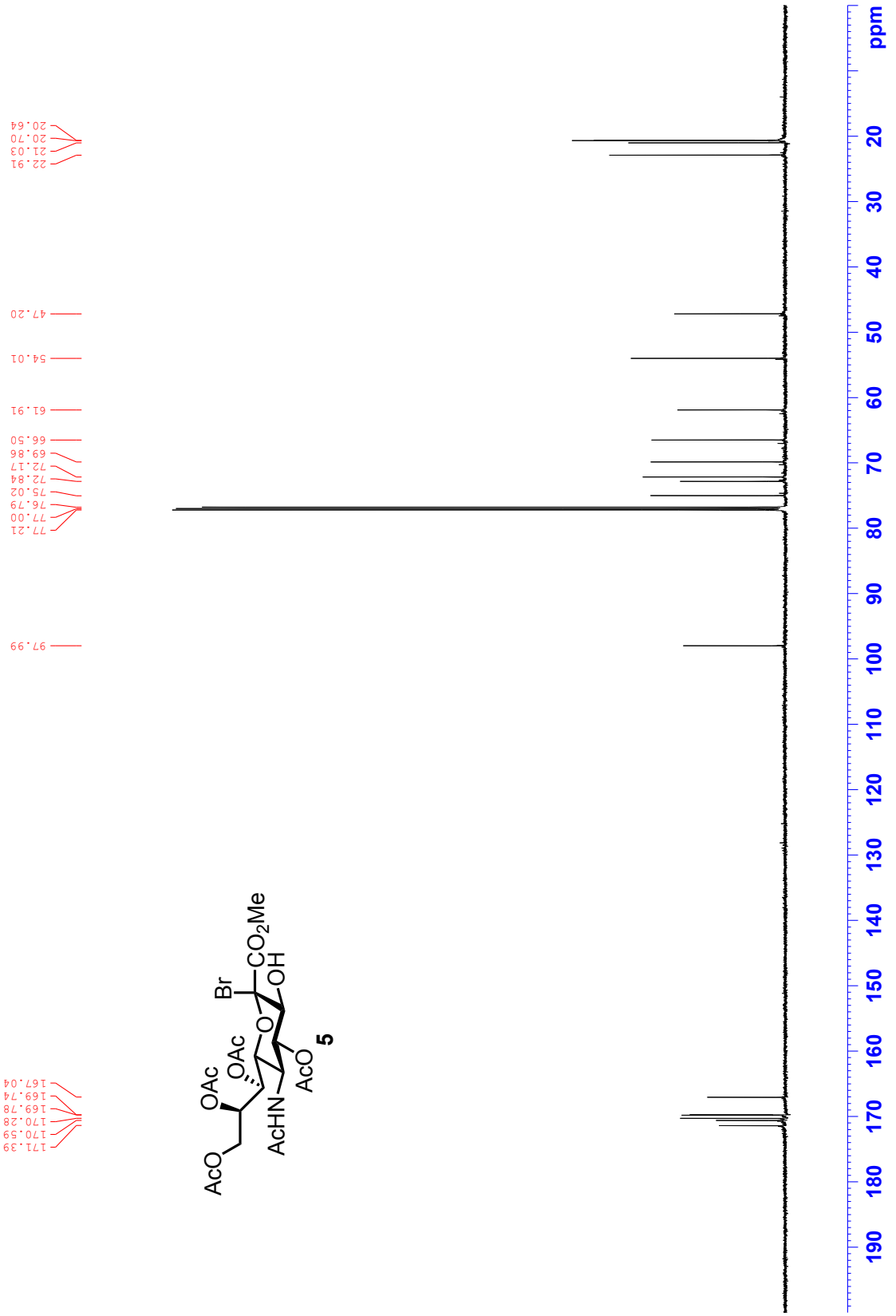
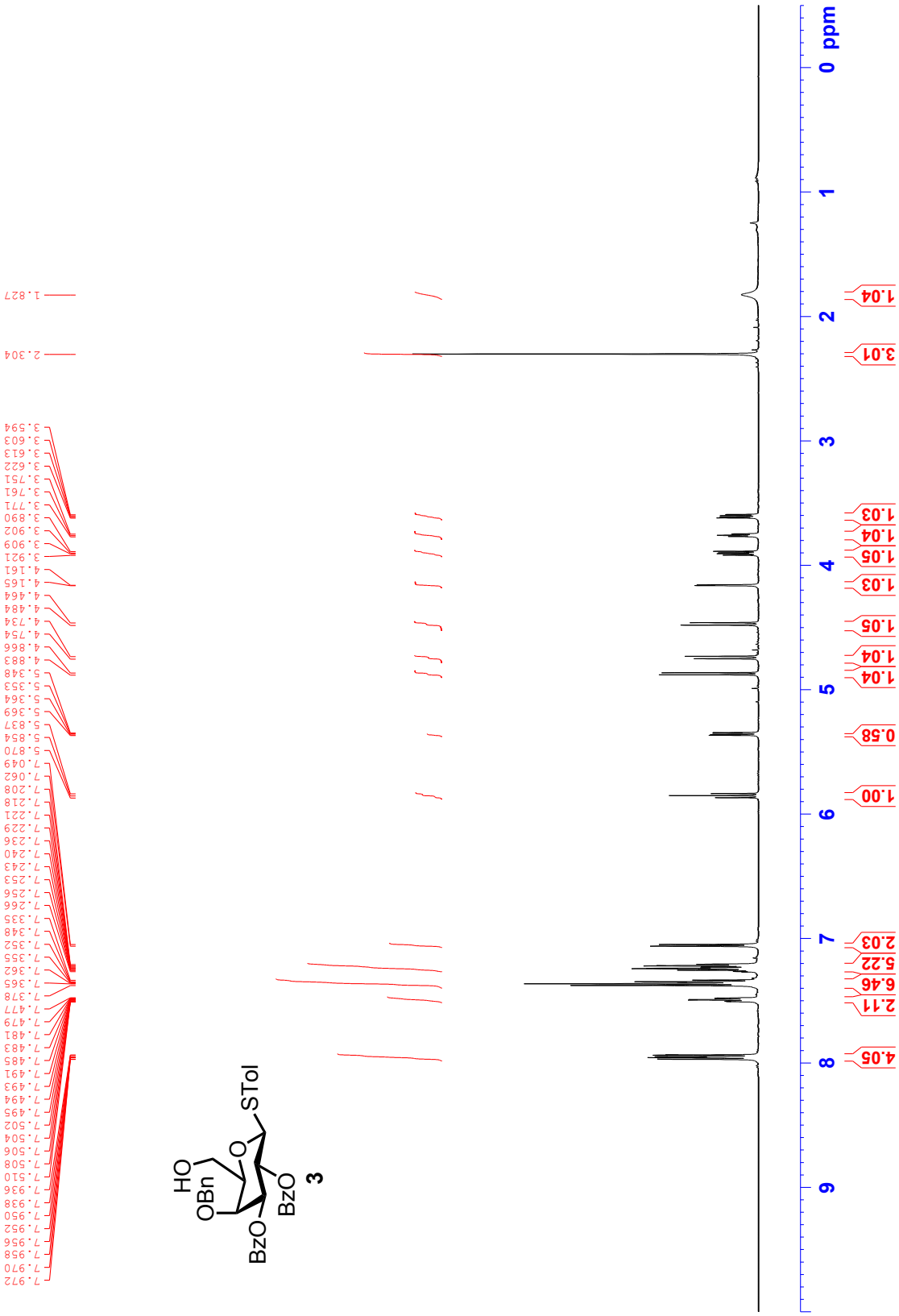
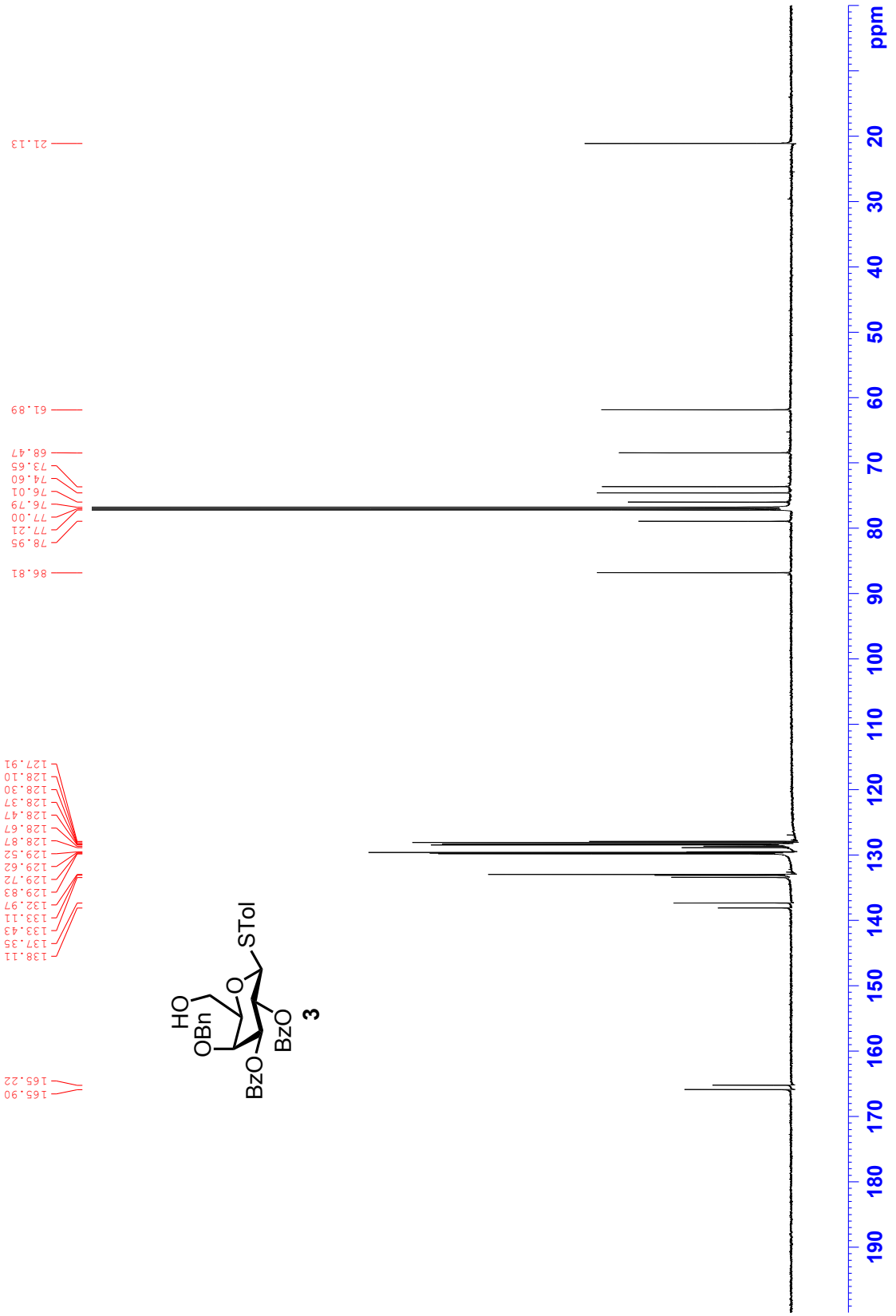
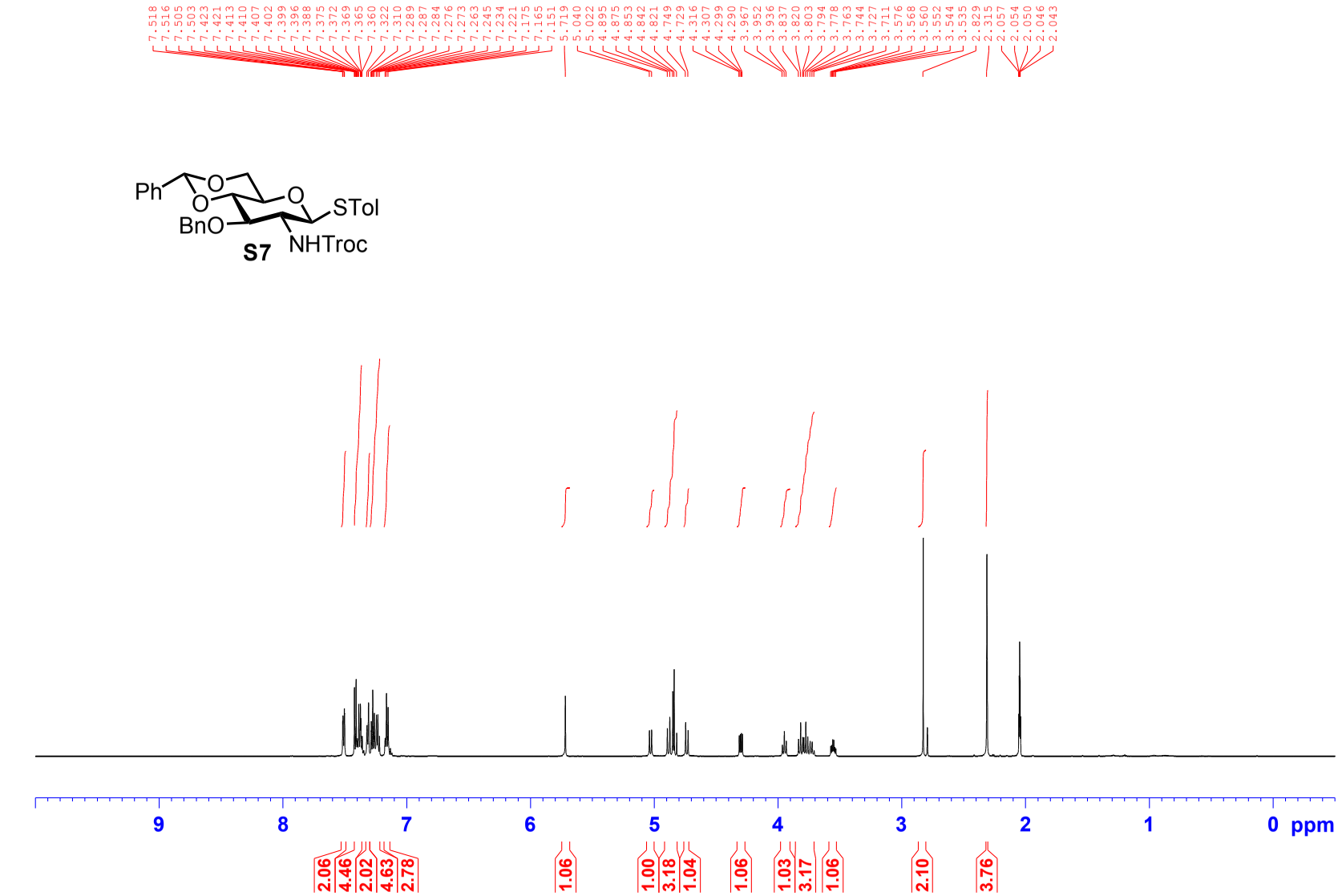
20.67
20.79
23.08
46.47
52.53
61.88
67.57
67.82
70.63
76.56
76.79
77.00
77.21
107.85
145.00
161.56
170.03
170.07
170.09
170.54
170.72
ppm
AcO
OAc
OAc
AcHN
O
CO2Me
AcO
S3

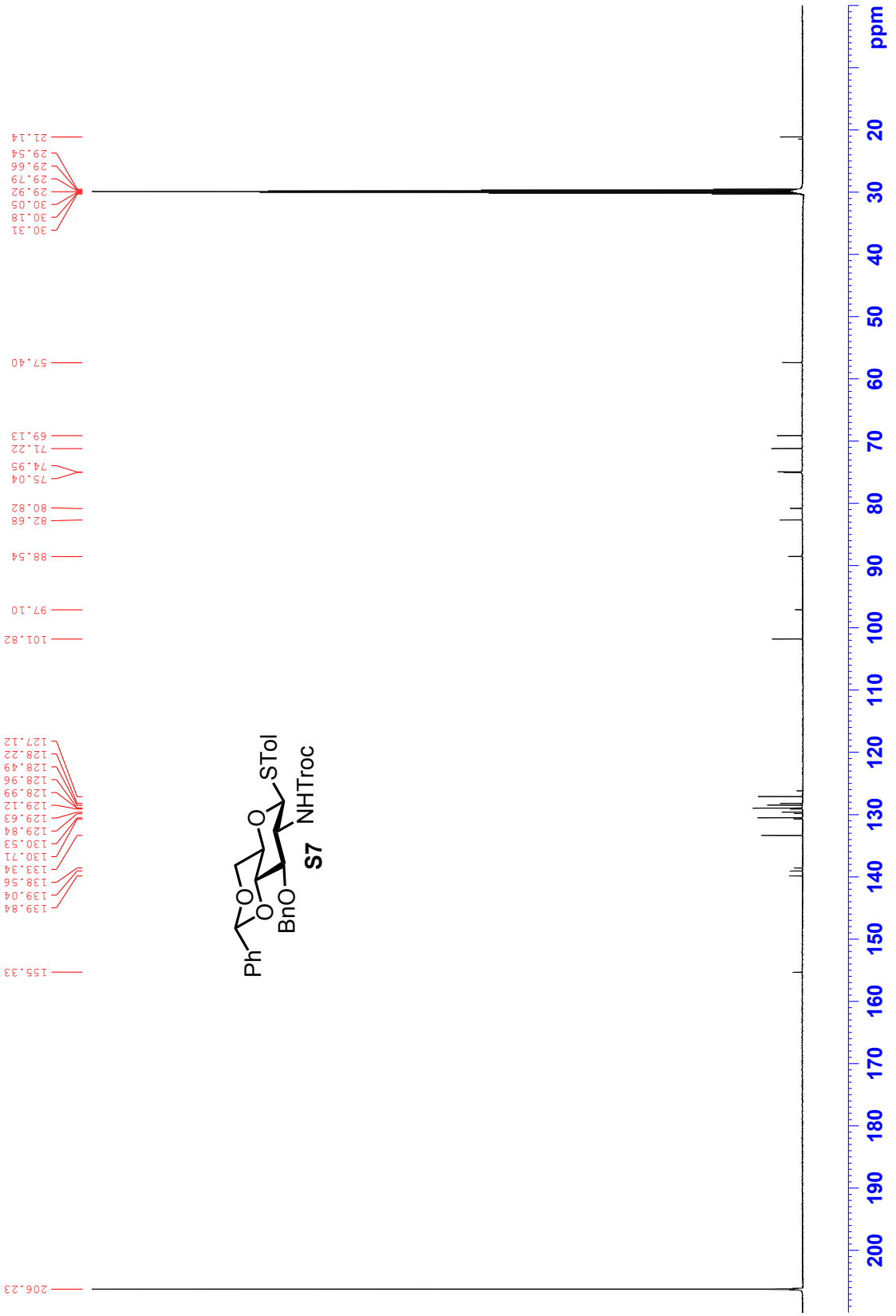

7.240
5.997
5.985
5.422
5.420
5.410
5.408
5.208
5.204
5.191
5.180
5.175
5.113
5.109
5.103
5.098
5.092
5.088
4.394
4.390
4.373
4.369
4.322
4.317
4.310
4.305
4.298
4.009
3.999
3.988
3.978
3.860
3.783
3.767
3.657
2.073
2.060
2.048
2.011
1.837
3.47
3.60
3.73
3.31
3.10
0.98
1.39
3.36
1.09
2.35
1.19
1.07
1.19
1.11
1.00
0 ppm
1
2
3
4
5
6
7
8
9
AcO
OAc
OAc
AcHN
AcO
O
Br
CO2Me
OH
5

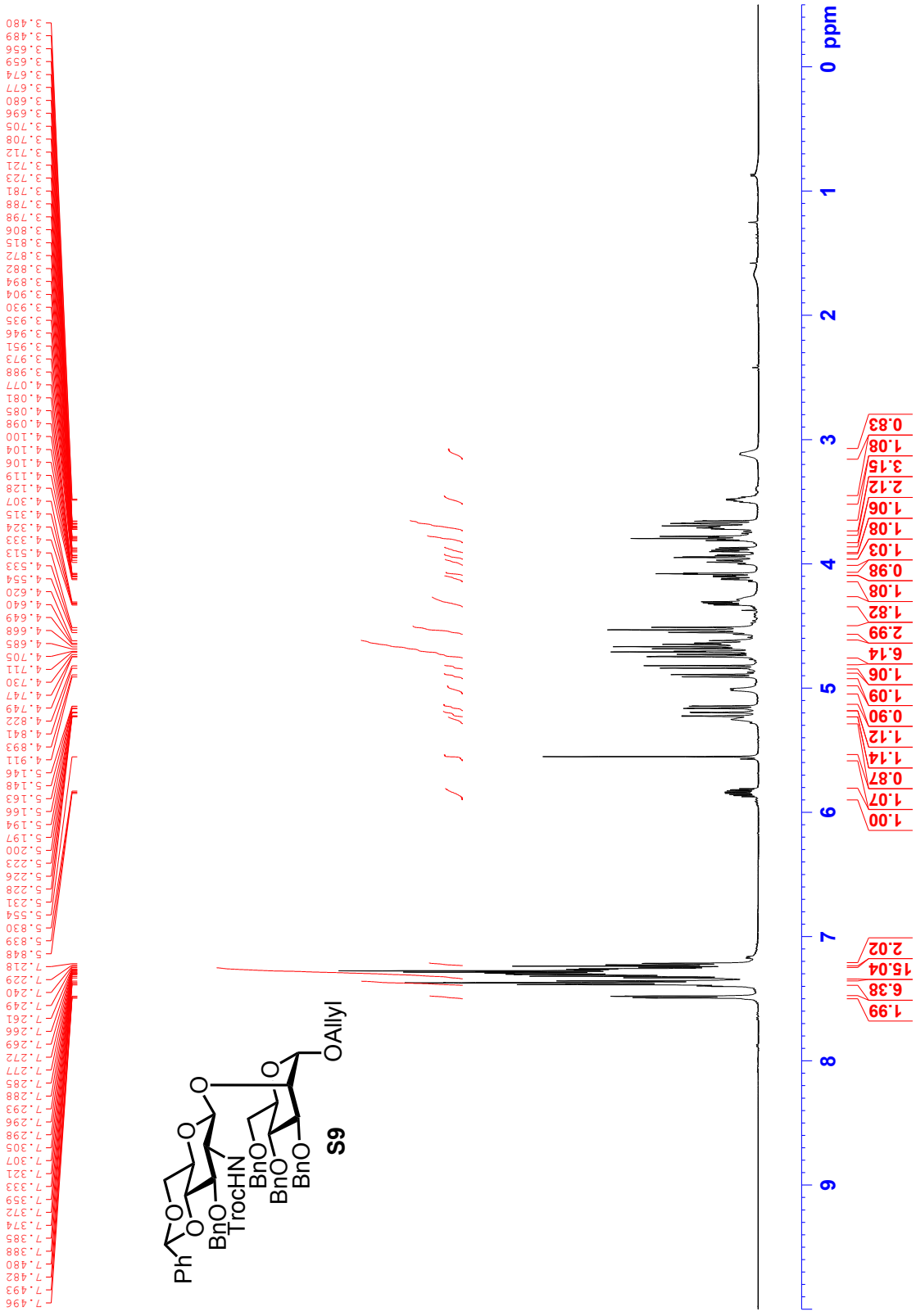

20.64
20.70
21.03
22.91
47.20
54.01
61.91
66.50
69.86
72.17
72.84
75.02
76.79
77.00
77.21
97.99
167.04
169.74
169.78
170.28
170.59
171.39
ppm
AcO
OAc
OAc
AcHN
O
Br
CO2Me
OH
AcO
5

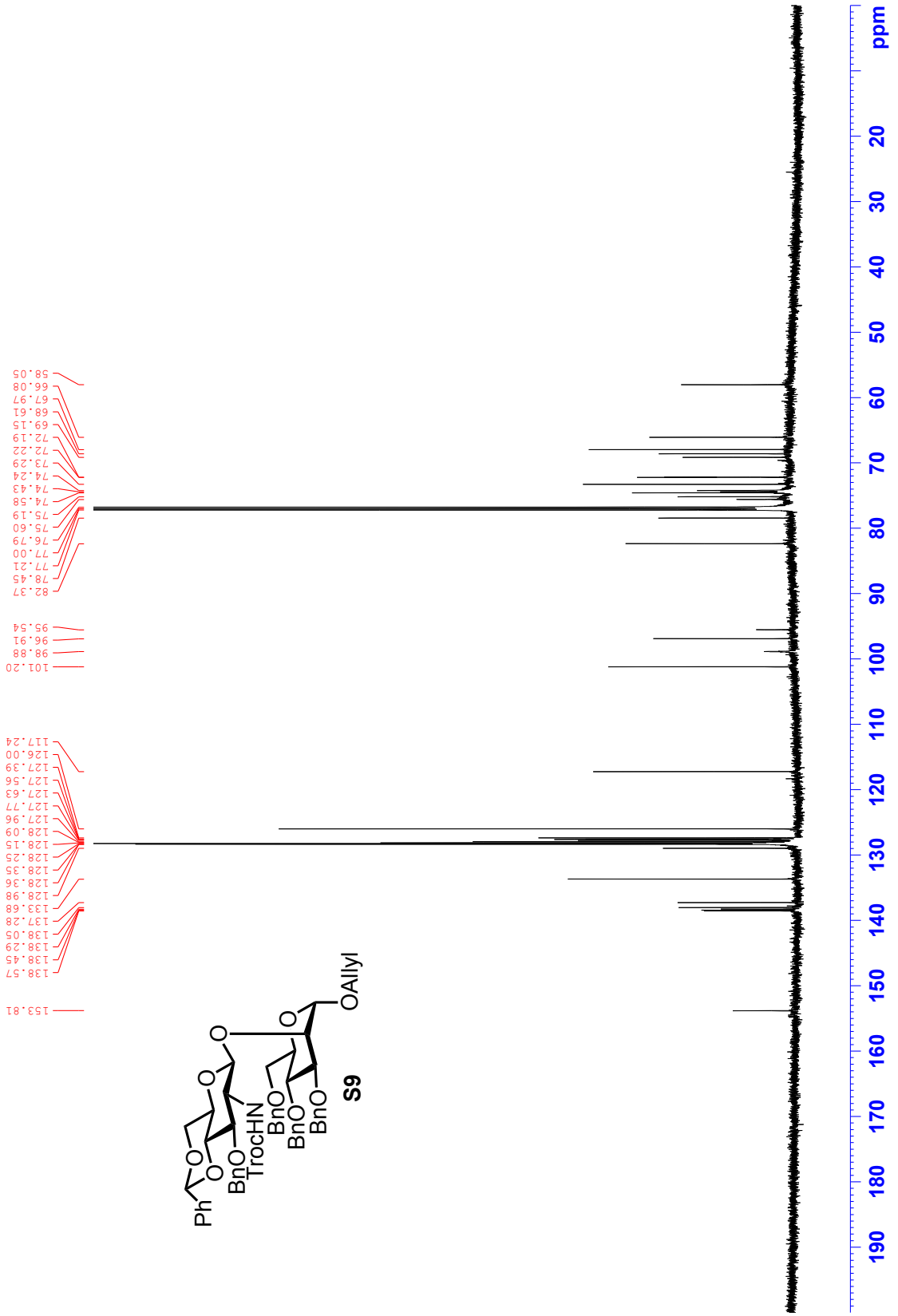

HO
OBn
O
STol
BzO
BzO
3
0 ppm
1
2
3
4
5
6
7
8
9
1.04
3.01
1.03
1.04
1.05
1.03
1.05
1.04
1.04
0.58
1.00
2.03
5.22
6.46
2.11
4.05

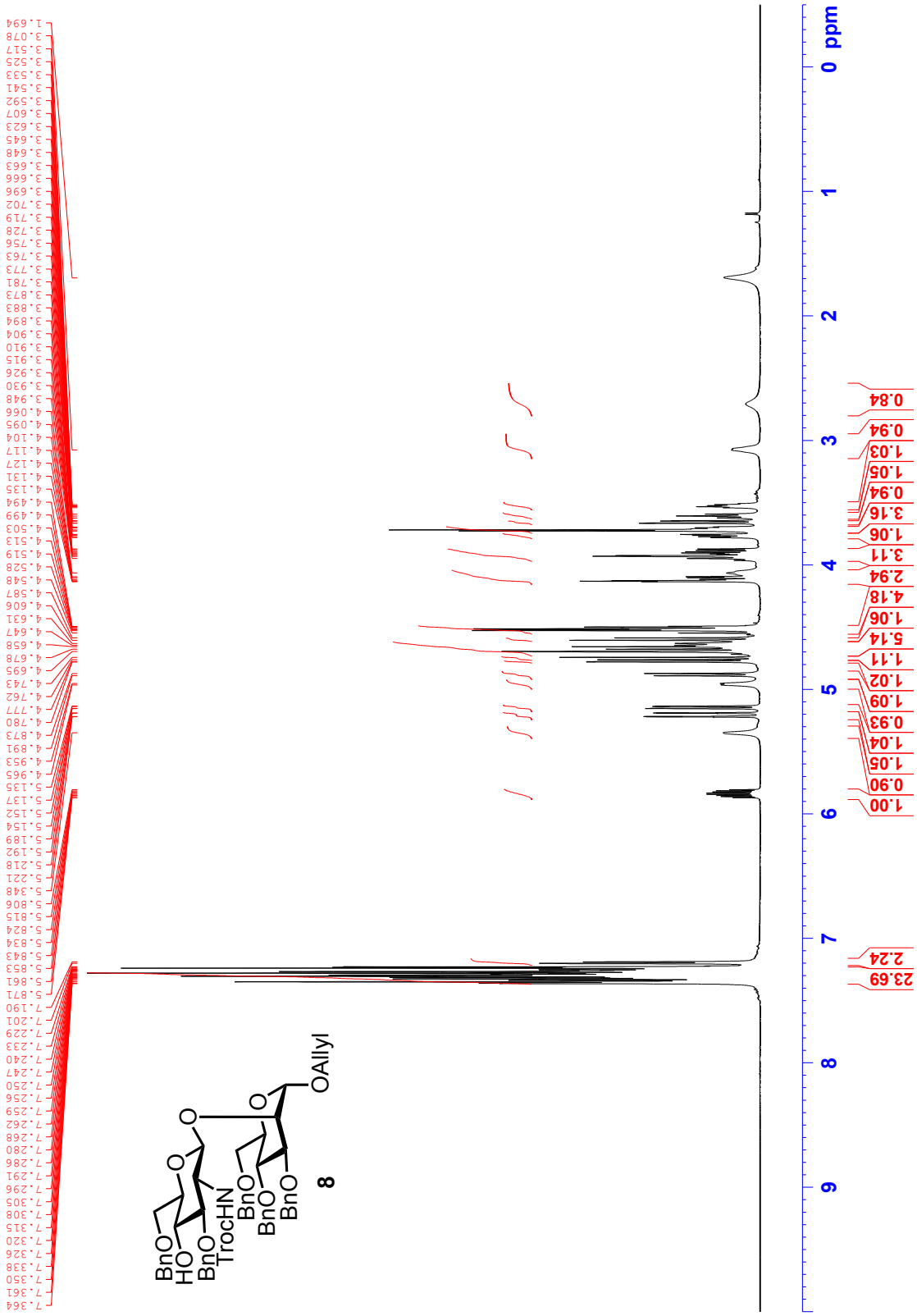

21.13
61.89
68.47
73.65
74.60
76.01
76.79
77.00
77.21
78.95
86.81
127.91
128.10
128.30
128.37
128.47
128.67
128.87
129.52
129.62
129.72
129.83
132.97
133.11
133.43
137.35
138.11
165.22
165.90
HO
OBn
O
STol
BzO
BzO
3
ppm
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190

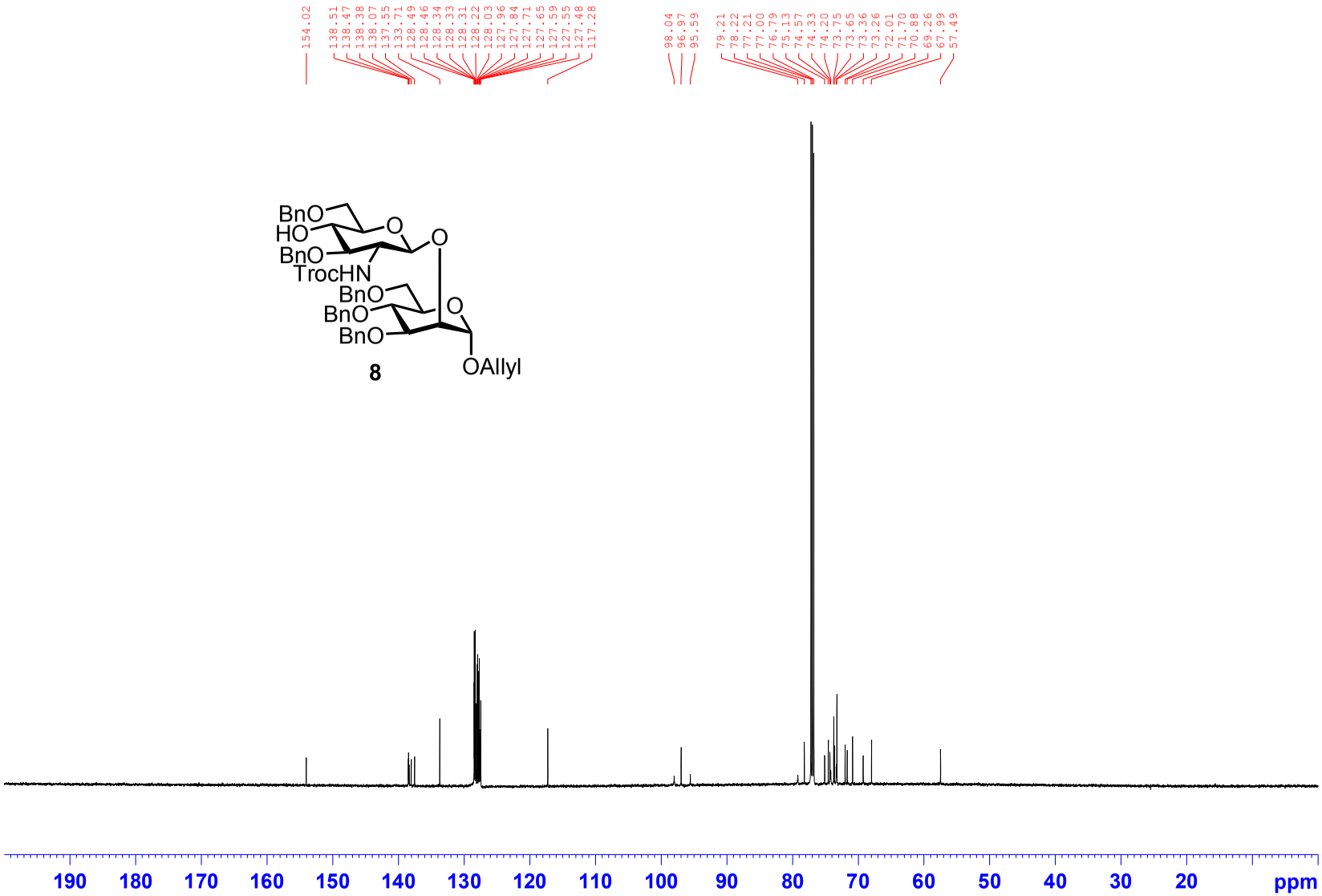

7.518
7.516
7.505
7.503
7.423
7.421
7.413
7.410
7.407
7.402
7.399
7.396
7.388
7.375
7.372
7.369
7.365
7.360
7.322
7.310
7.289
7.287
7.284
7.276
7.273
7.263
7.245
7.234
7.221
7.175
7.165
7.151
5.719
5.040
5.022
4.895
4.875
4.853
4.842
4.821
4.749
4.729
4.316
4.307
4.299
4.290
3.967
3.952
3.936
3.837
3.820
3.803
3.794
3.778
3.763
3.744
3.727
3.711
3.576
3.568
3.560
3.552
3.544
3.535
2.829
2.315
2.057
2.054
2.050
2.046
2.043
Ph
O
O
O
STol
BnO
NHTroc
S7
9
8
7
6
5
4
3
2
1
0 ppm
2.06
4.46
2.02
4.63
2.78
1.06
1.00
3.18
1.04
1.06
1.03
3.17
1.06
2.10
3.76

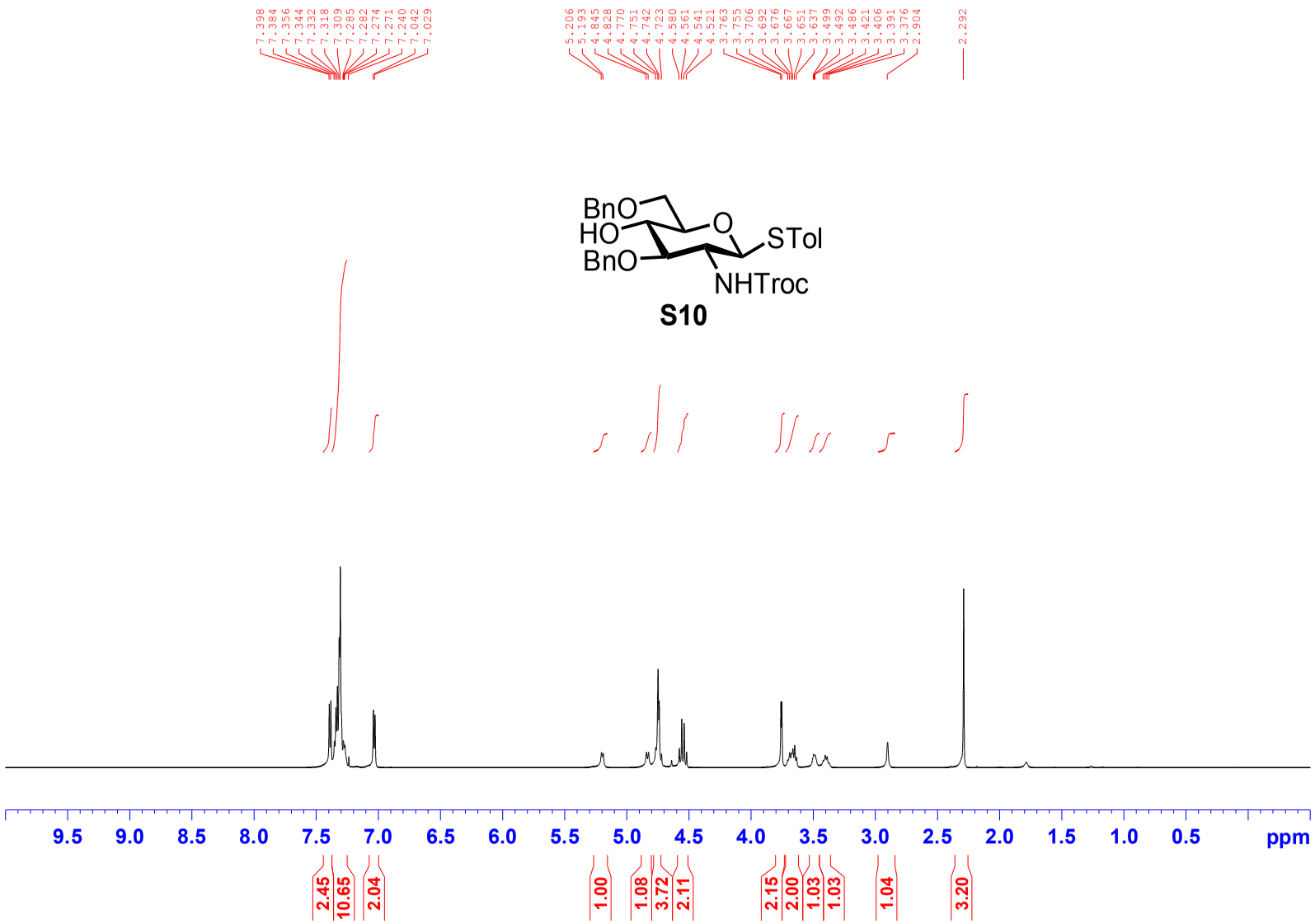

21.14
29.54
29.66
29.79
29.92
30.05
30.18
30.31
57.40
69.13
71.22
74.95
75.04
80.82
82.68
88.54
97.10
101.82
127.12
128.22
128.49
128.96
128.99
129.12
129.63
129.84
130.53
130.71
133.34
138.56
139.04
139.84
155.33
206.23
STol
NHTroc
BnO
Ph
S7
ppm


S9
Ph
BnO
TrocHN
BnO
BnO
BnO
OAllyl
ppm
0
1
2
3
4
5
6
7
8
9
1.00
1.07
0.87
1.14
1.12
0.90
1.09
1.06
6.14
2.99
1.82
1.08
0.98
1.03
1.08
1.06
2.12
3.15
1.08
0.83
1.99
6.38
15.04
2.02


153.81
138.57
138.45
138.29
138.05
137.28
133.68
128.98
128.36
128.35
128.25
128.15
128.09
127.96
127.77
127.63
127.56
127.39
126.00
117.24
101.20
98.88
96.91
95.54
82.37
78.45
77.21
77.00
76.79
75.60
75.19
74.58
74.43
74.24
73.29
72.22
72.19
69.15
68.61
67.97
66.08
58.05
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
Ph
O
O
O
BnO
TrocHN
O
BnO
BnO
BnO
O
OAllyl
S9


BnO
HO
BnO
TrocHN
BnO
BnO
BnO
O
OAllyl
8
ppm


154.02
138.51
138.47
138.38
138.07
137.55
133.71
128.49
128.46
128.34
128.33
128.31
128.22
128.03
127.96
127.84
127.71
127.65
127.59
127.55
127.48
117.28
98.04
96.97
95.59
79.21
78.22
77.21
77.00
76.79
75.13
74.57
74.33
74.20
73.75
73.65
73.36
73.26
72.01
71.70
70.88
69.26
67.99
57.49
BnO
HO
BnO
TrocHN
O
O
BnO
BnO
BnO
O
OAllyl
8
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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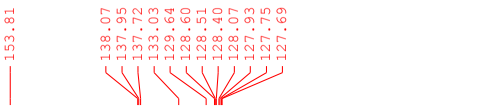
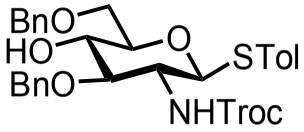
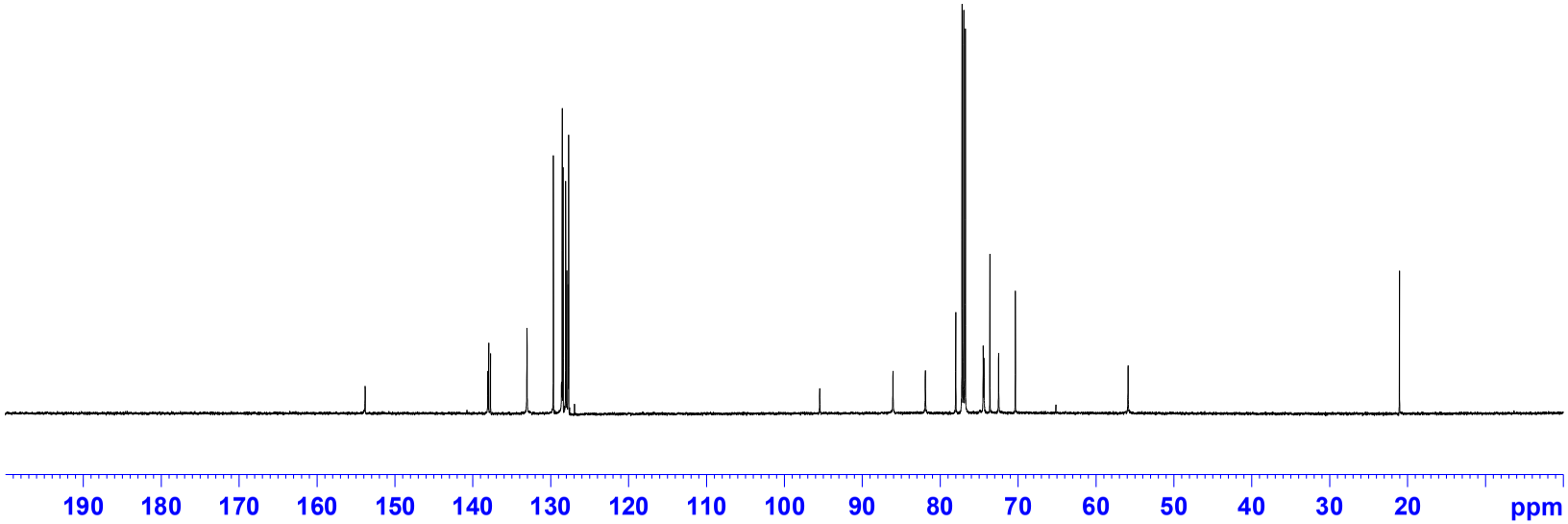
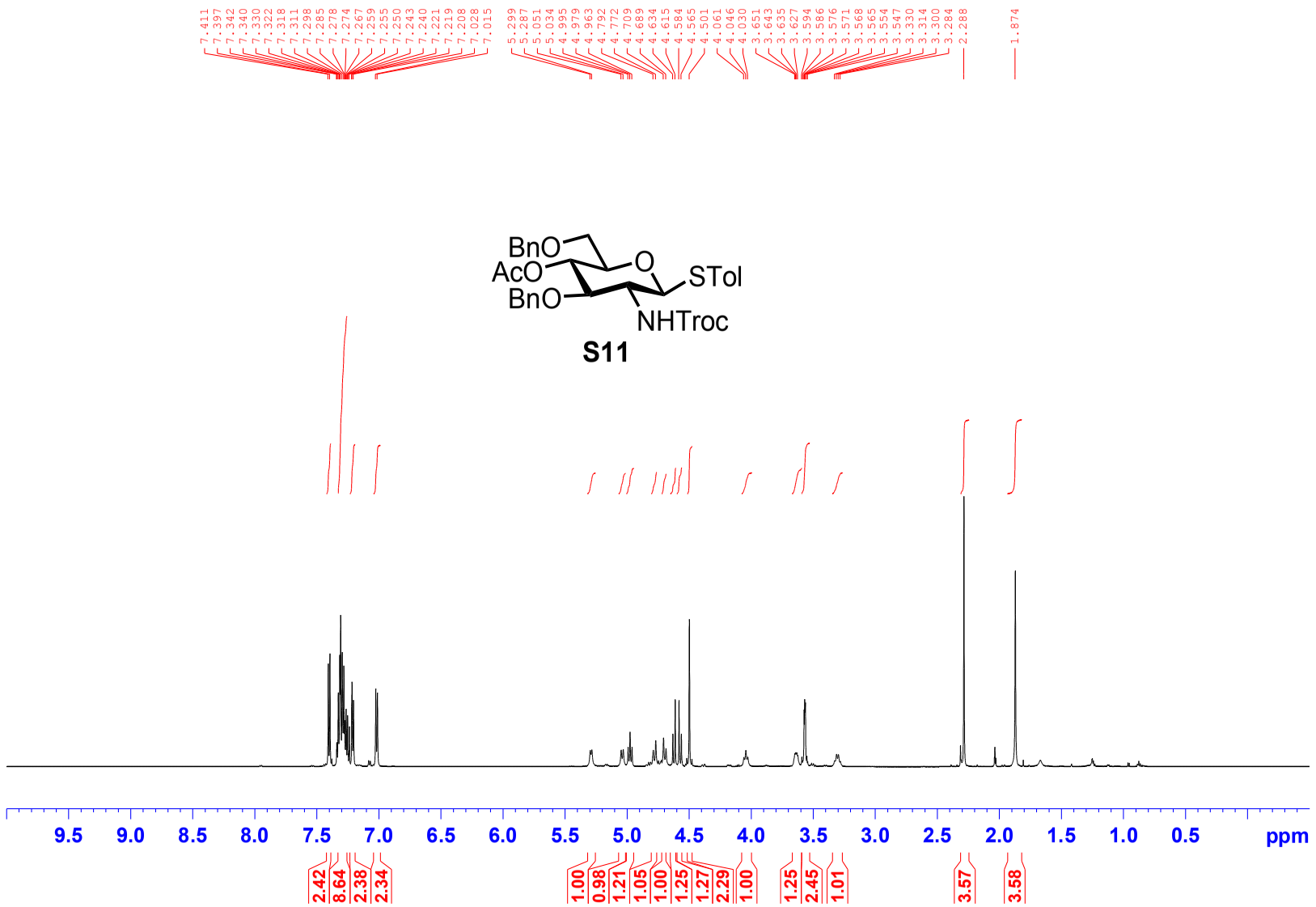
7.356
7.344
7.332
7.318
7.309
7.285
7.282
7.274
7.271
7.240
7.042
7.029
5.206
5.193
4.845
4.828
4.770
4.751
4.742
4.723
4.580
4.561
4.541
4.521
3.763
3.755
3.706
3.692
3.676
3.667
3.651
3.637
3.499
3.492
3.486
3.421
3.406
3.391
3.376
2.904
2.292
BnO
HO
BnO
O
STol
NHTroc
S10
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.45
10.65
2.04
1.00
1.08
3.72
2.11
2.15
2.00
1.03
1.03
1.04
3.20


153.81
138.07
137.95
137.72
133.03
129.64
128.60
128.51
128.40
128.07
127.93
127.75
127.69
95.45
86.08
81.92
78.02
77.21
77.00
76.79
74.50
74.40
73.63
72.51
70.37
55.90
21.06


BnO
HO
BnO
O
STol
NHTroc

S10


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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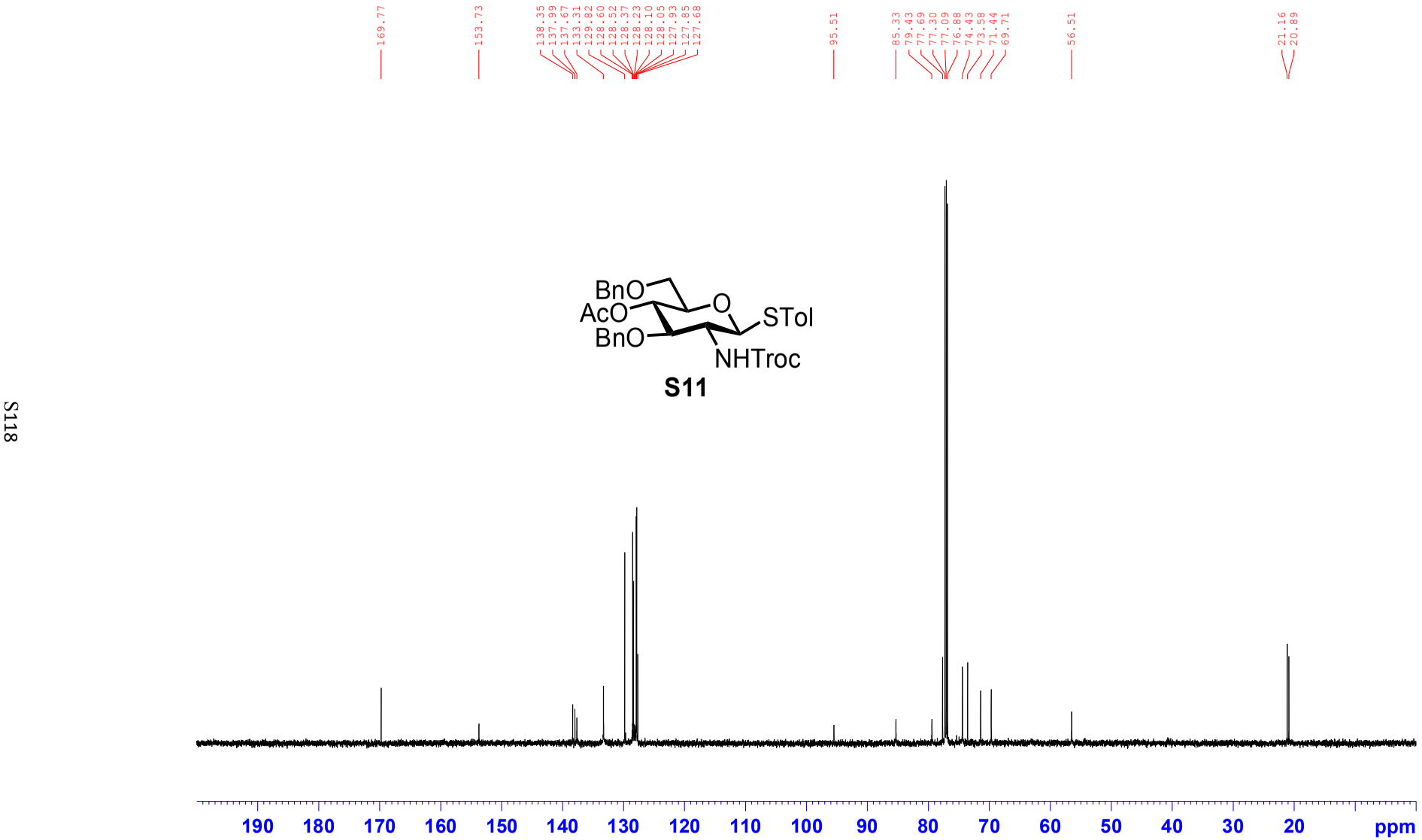
7.397
7.342
7.340
7.330
7.322
7.318
7.311
7.298
7.285
7.278
7.274
7.267
7.259
7.255
7.250
7.243
7.240
7.221
7.219
7.208
7.028
7.015
5.299
5.287
5.051
5.034
4.995
4.979
4.963
4.792
4.772
4.709
4.689
4.634
4.615
4.584
4.565
4.501
4.061
4.046
4.030
3.651
3.643
3.635
3.627
3.594
3.586
3.576
3.571
3.568
3.565
3.554
3.547
3.330
3.314
3.300
3.284
2.288
1.874
BnO
AcO
BnO
O
STol
NHTroc
S11
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.42
8.64
2.38
2.34
1.00
0.98
1.21
1.05
1.00
1.25
1.27
2.29
1.00
1.25
2.45
1.01
3.57
3.58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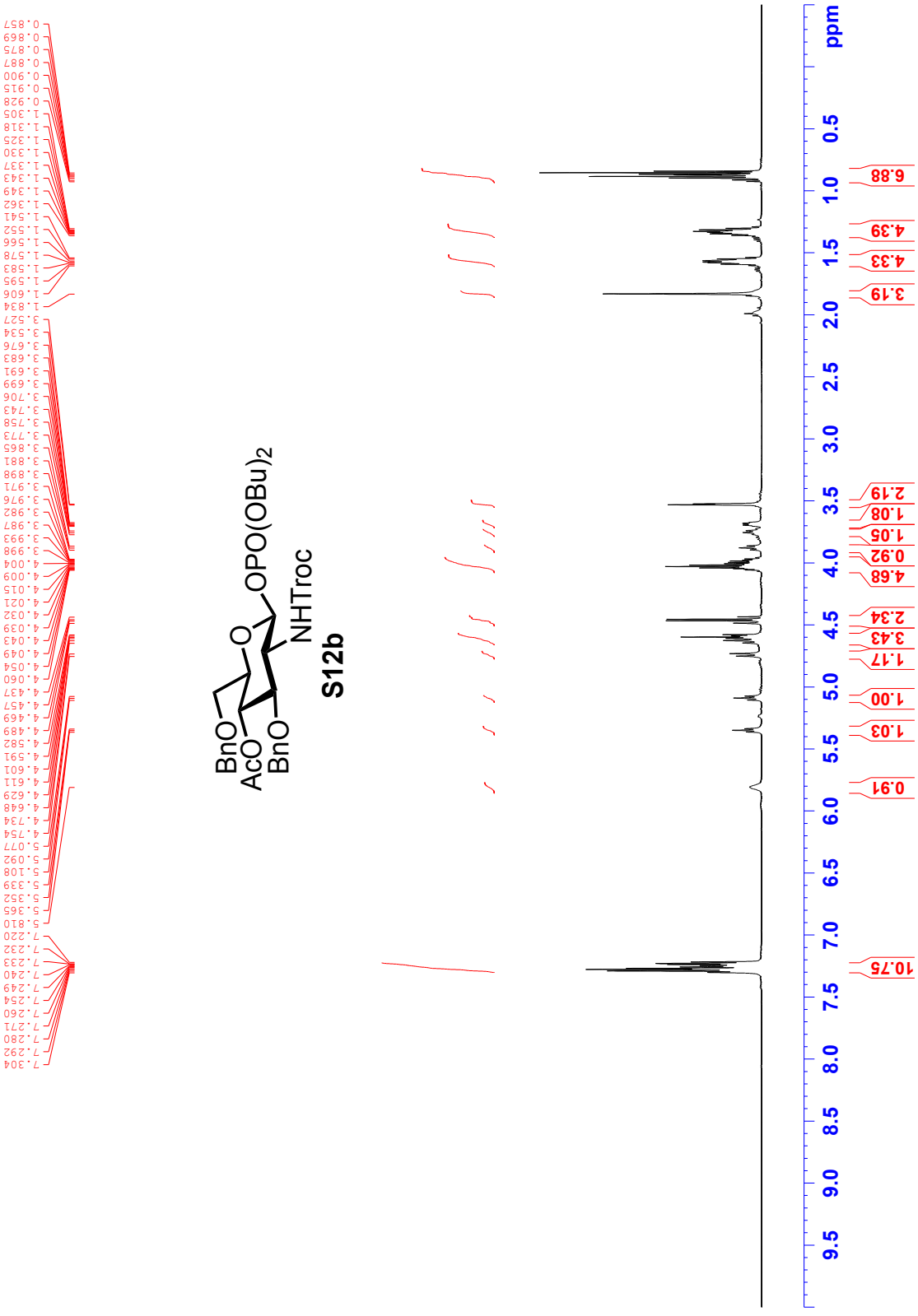
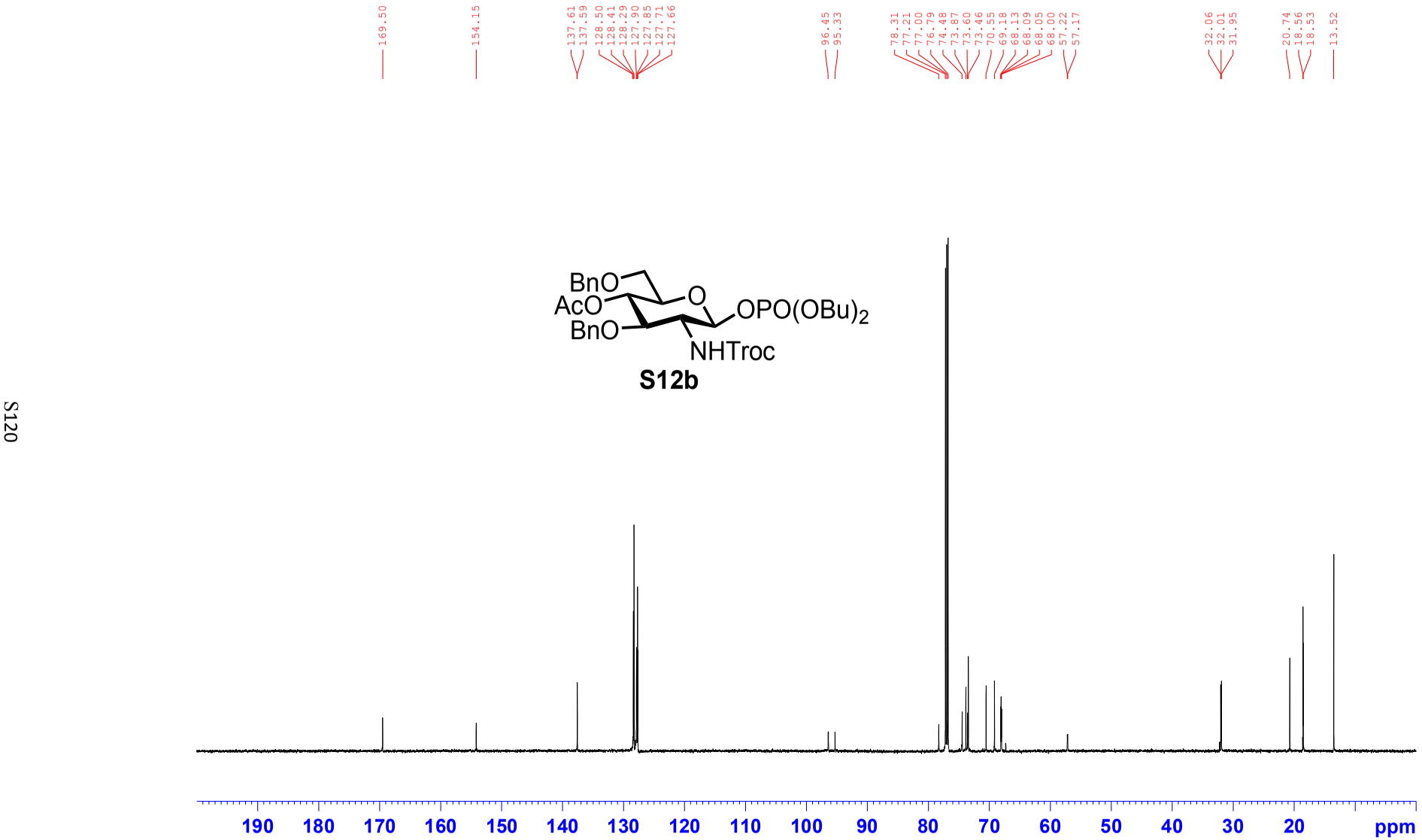
137.99
137.67
133.31
129.82
128.60
128.52
128.37
128.23
128.10
128.05
127.93
127.85
127.68
95.51
85.33
79.43
77.69
77.30
77.09
76.88
74.43
73.58
71.44
69.71
56.51
21.16
20.89
BnO
AcO
BnO
O
STol
NHTroc
S11
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


BnO
AcO
BnO
O
OPO(OBu)2
NHTroc
S12b
ppm
10.75
7.304
7.292
7.280
7.271
7.260
7.254
7.249
7.240
7.233
7.232
7.220
6.810
5.365
5.352
5.339
5.108
5.092
5.077
4.754
4.734
4.648
4.629
4.611
4.601
4.591
4.582
4.489
4.469
4.457
4.437
4.060
4.054
4.049
4.043
4.039
4.032
4.021
4.015
4.009
4.004
3.998
3.993
3.987
3.982
3.976
3.971
3.898
3.881
3.865
3.773
3.758
3.743
3.706
3.699
3.691
3.683
3.676
3.534
3.527
1.834
1.606
1.595
1.583
1.578
1.566
1.552
1.541
1.362
1.349
1.343
1.337
1.330
1.325
1.318
1.305
0.928
0.915
0.900
0.887
0.875
0.869
0.857
6.88
4.39
4.33
3.19
4.68
2.34
3.43
1.17
1.00
1.03
0.91
2.19
1.08
1.05
0.92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137.61
137.59
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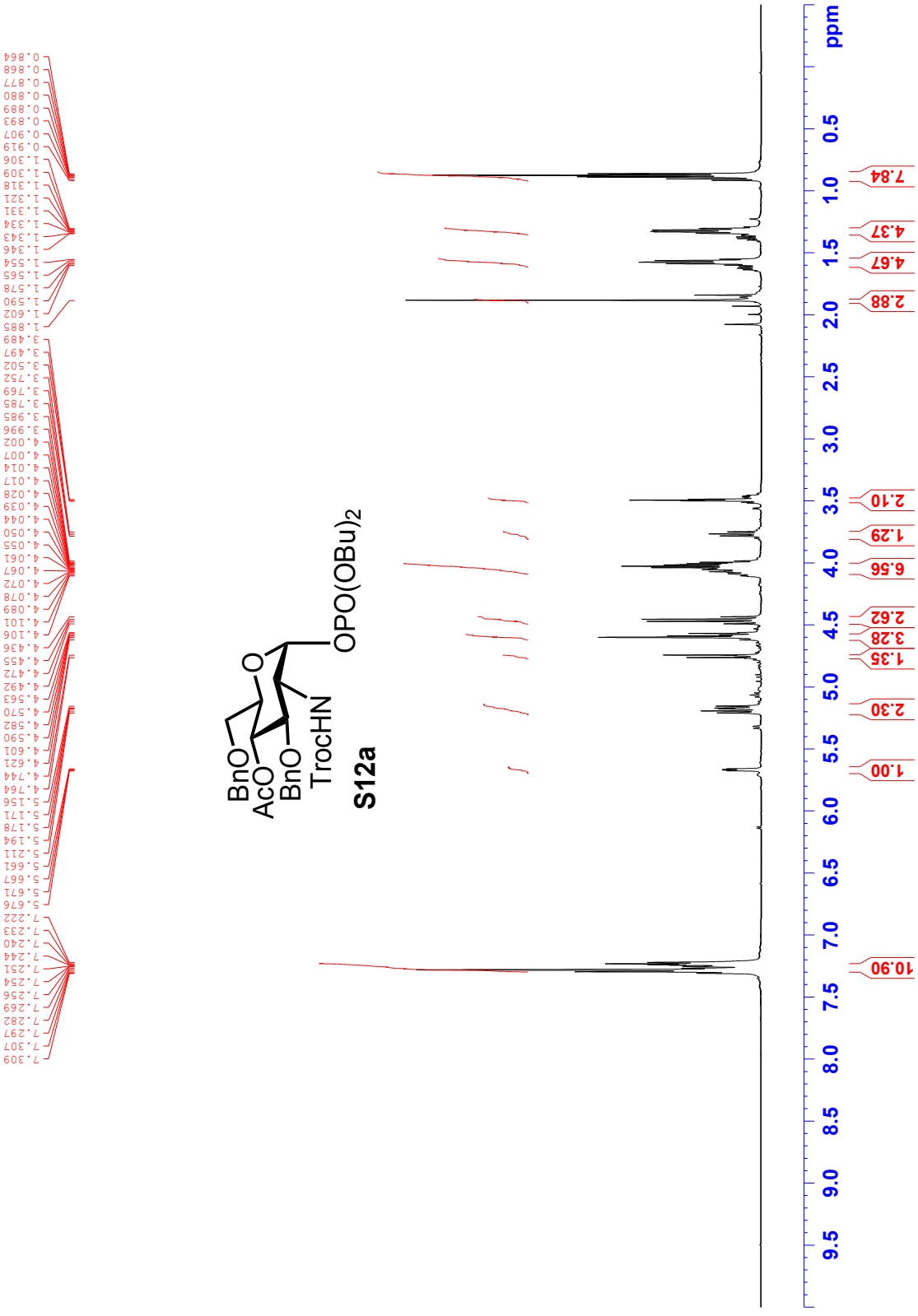
128.41
128.29
127.90
127.85
127.71
127.66
96.45
95.33
78.31
77.21
77.00
76.79
74.48
73.87
73.60
73.46
70.55
69.18
68.13
68.09
68.05
68.00
57.22
57.17
32.06
32.01
31.95
20.74
18.56
18.53
13.52
BnO
AcO
BnO
O
OPO(OBu)2
NHTroc
S12b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


BnO
AcO
BnO
TrocHN
OPO(OBu)2
S12a
ppm
10.90
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1.35
3.28
2.62
6.56
1.29
2.10
2.88
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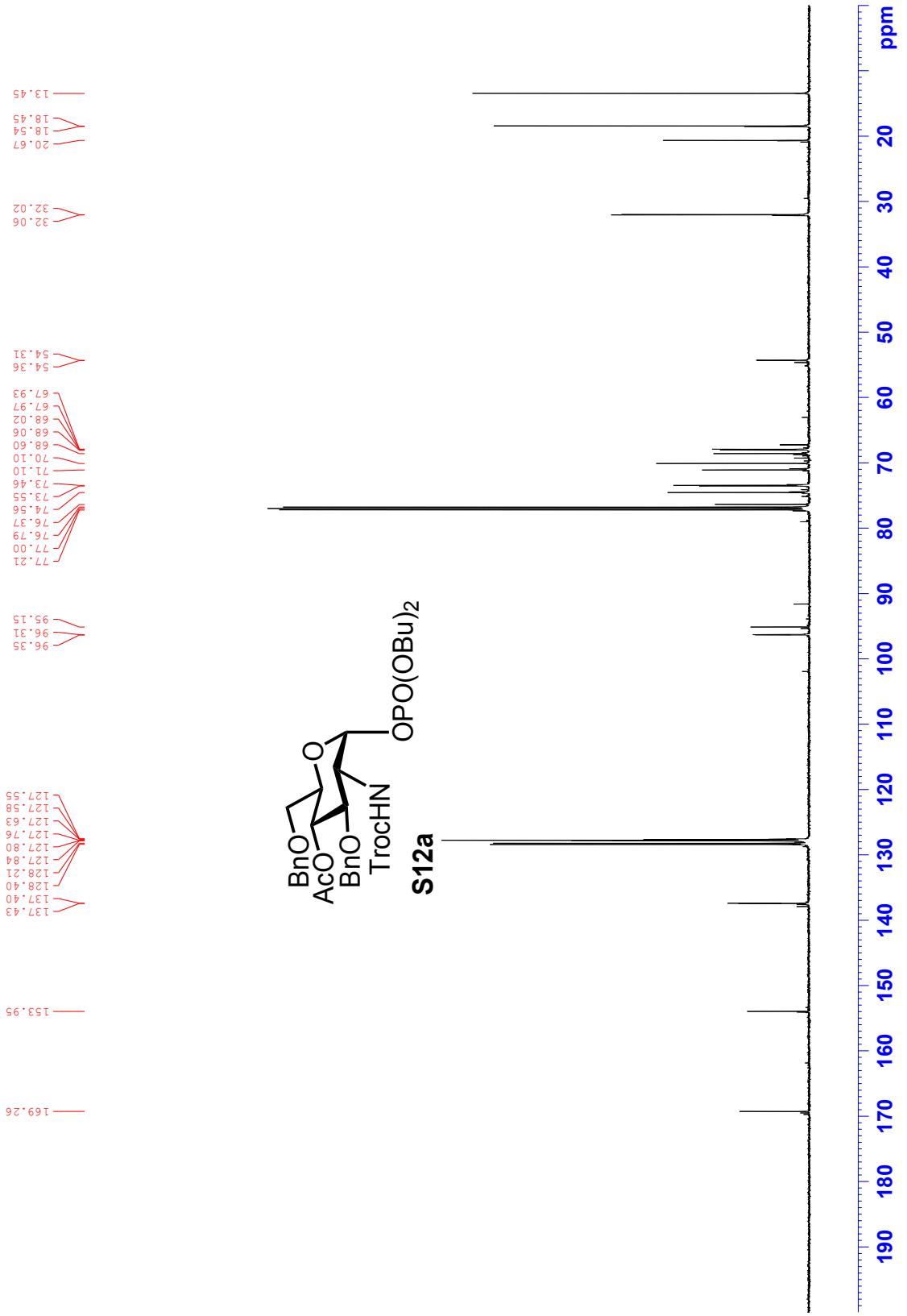
4.37
7.84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18.54
20.67
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32.06
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67.97
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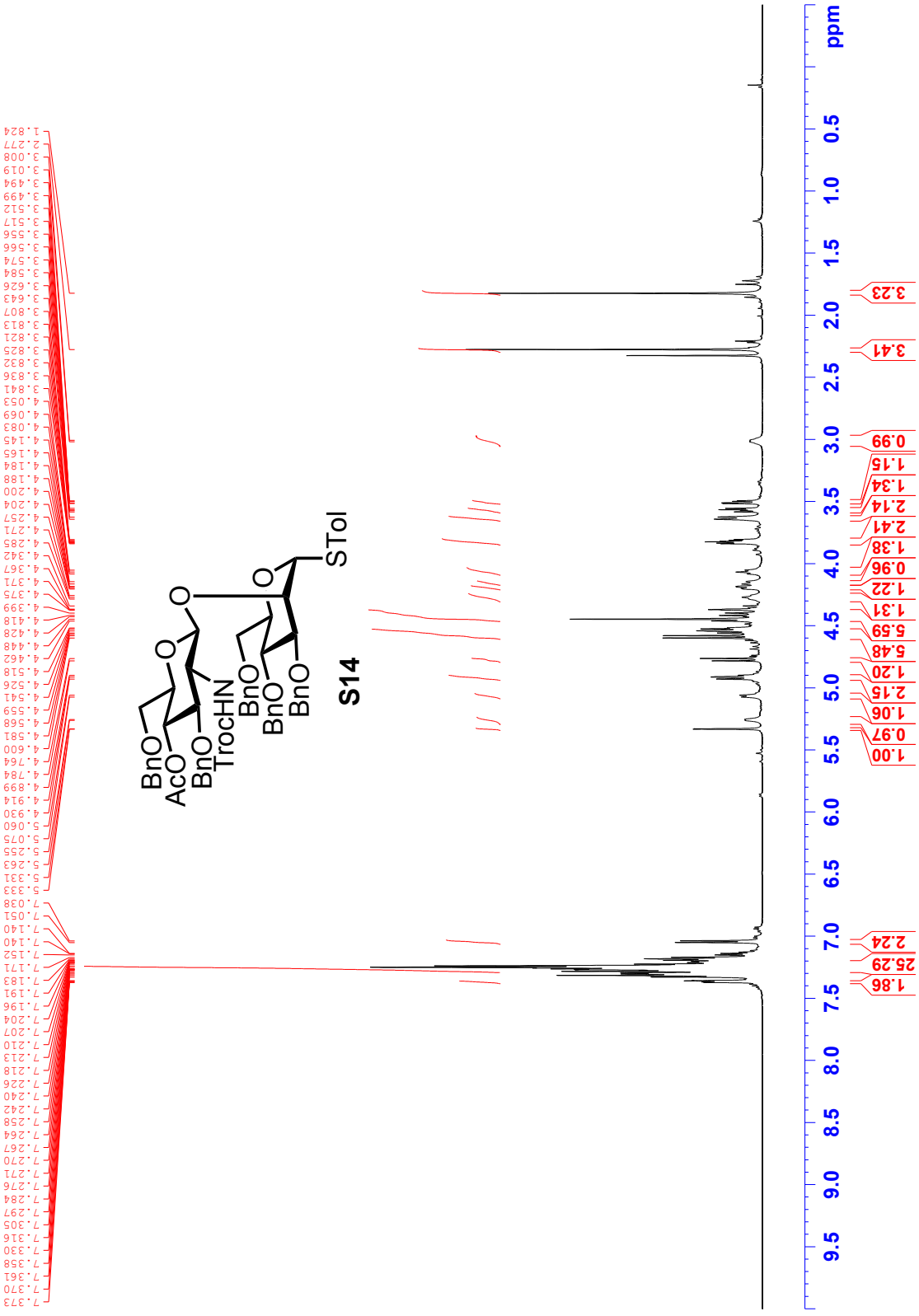
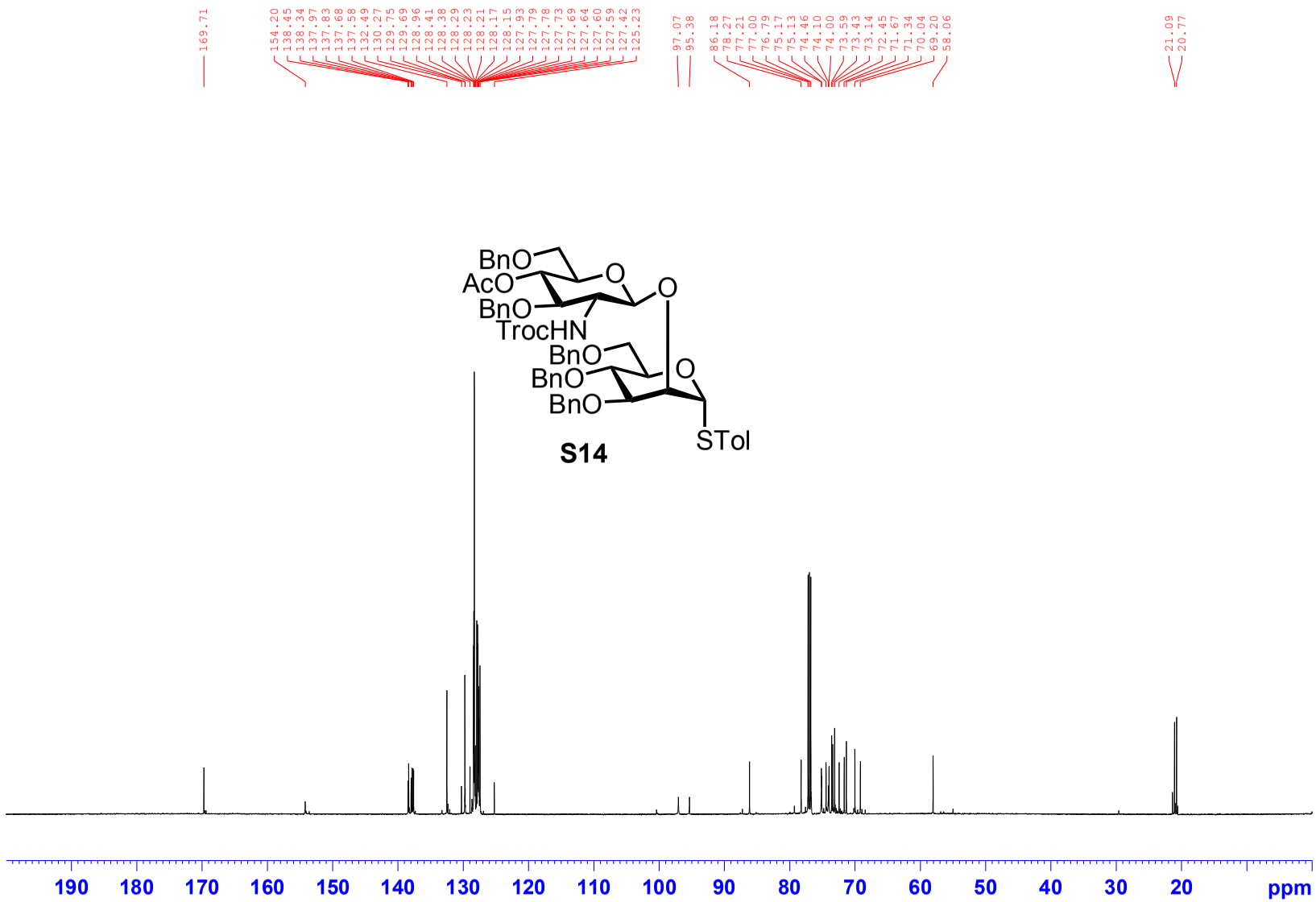
70.10
71.10
73.46
73.55
74.56
76.37
76.79
77.00
77.21
95.15
96.31
96.35
127.55
127.58
127.63
127.76
127.80
127.84
128.21
128.40
137.40
137.43
153.95
169.26
BnO
AcO
BnO
TrocHN
O
OPO(OBu)2
S12a
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20


BnO
AcO
BnO
TrocHN
O
O
BnO
BnO
BnO
O
STol
S14
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
1.00
0.97
1.06
2.15
1.20
5.48
5.59
1.31
1.22
0.96
1.38
2.41
2.14
1.34
1.15
0.99
3.41
3.23
1.86
25.29
2.24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154.20
138.45
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137.97
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137.68
137.58
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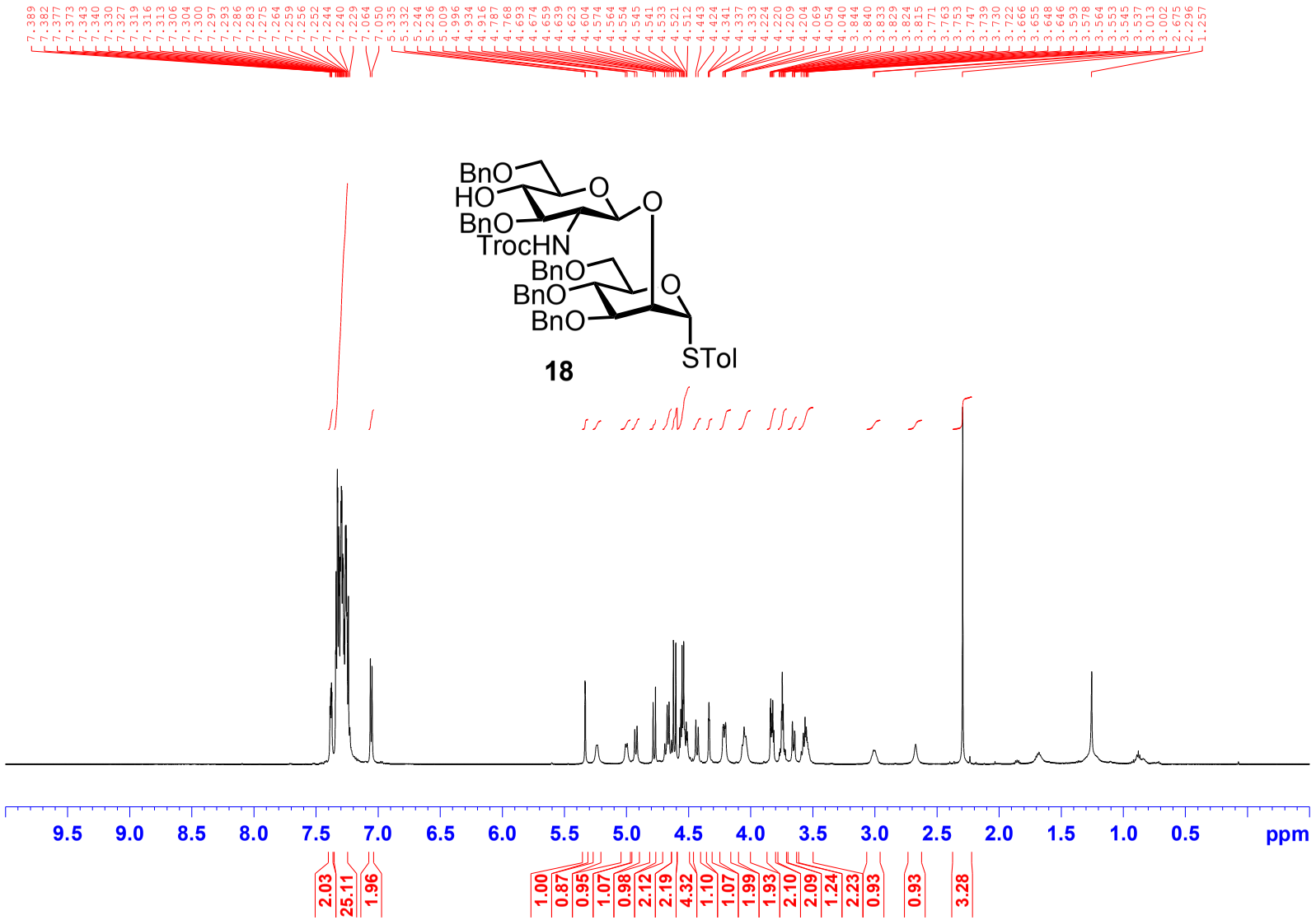
130.27
129.75
129.69
128.96
128.41
128.38
128.29
128.23
128.21
128.17
128.15
127.93
127.79
127.78
127.73
127.69
127.64
127.60
127.59
127.42
125.23
97.07
95.38
86.18
78.27
77.21
77.00
76.79
75.17
75.13
74.46
74.10
74.00
73.59
73.43
73.14
72.45
71.67
71.34
70.04
69.20
58.06
21.09
20.77
BnO
AcO
BnO
TrocHN
O
O
BnO
BnO
BnO
O
STol
S14
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.377
7.373
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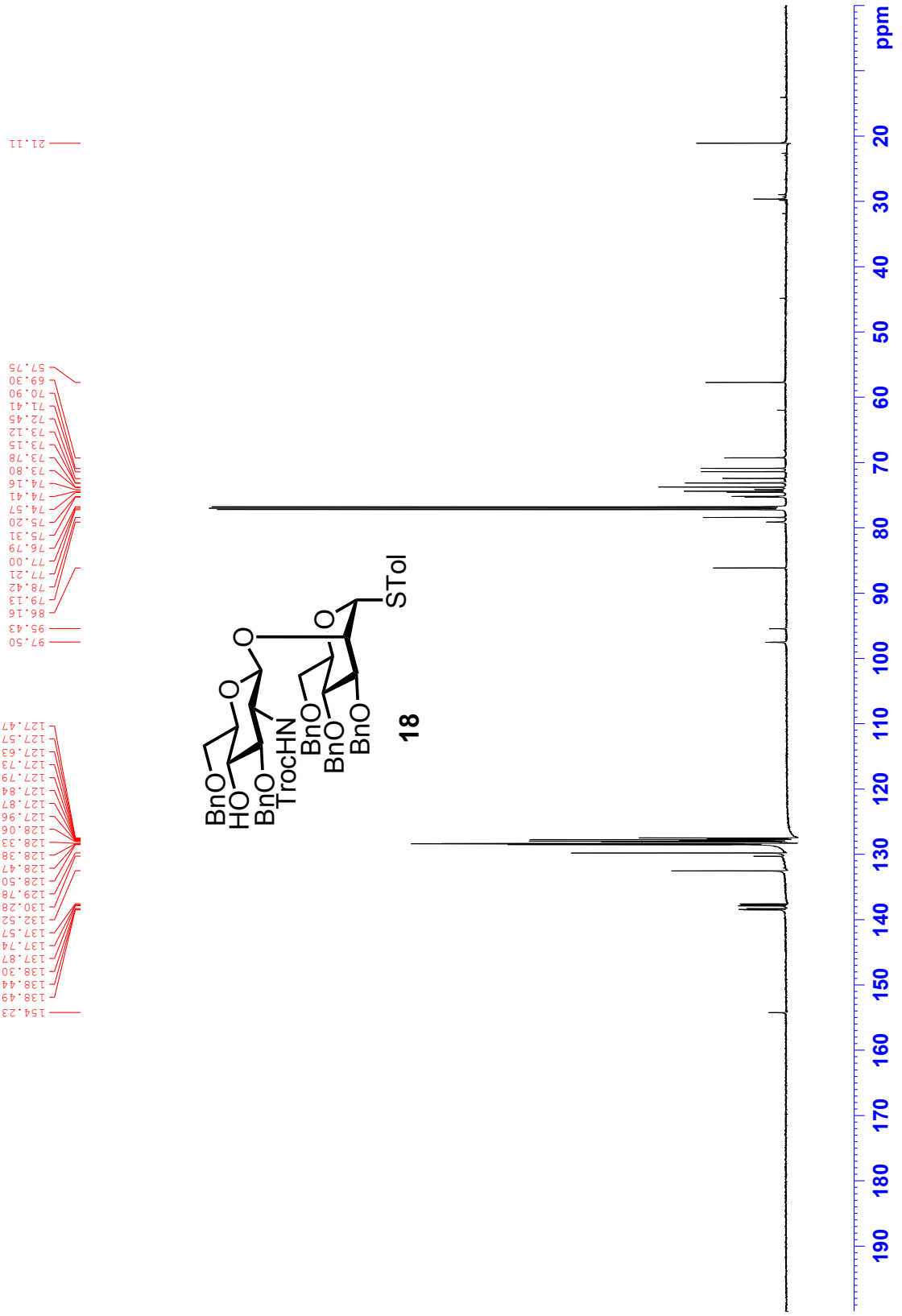
7.330
7.327
7.319
7.316
7.313
7.306
7.304
7.300
7.297
7.293
7.286
7.283
7.275
7.264
7.259
7.256
7.252
7.244
7.240
7.229
7.064
7.050
5.335
5.332
5.244
5.236
5.009
4.996
4.934
4.916
4.787
4.768
4.693
4.674
4.659
4.639
4.623
4.604
4.574
4.564
4.554
4.545
4.541
4.533
4.521
4.512
4.443
4.424
4.341
4.337
4.333
4.224
4.220
4.209
4.204
4.069
4.054
4.040
3.844
3.840
3.833
3.829
3.824
3.815
3.771
3.763
3.753
3.747
3.739
3.730
3.722
3.666
3.655
3.648
3.646
3.593
3.578
3.564
3.553
3.545
3.537
3.013
3.002
2.675
2.296
1.257
BnO
HO
BnO
TrocHN
O
O
BnO
BnO
BnO
O
STol
18
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.03
25.11
1.96
1.00
0.87
0.95
1.07
0.98
2.12
2.19
4.32
1.10
1.07
1.99
1.93
2.10
2.09
1.24
2.23
0.93
0.93
3.28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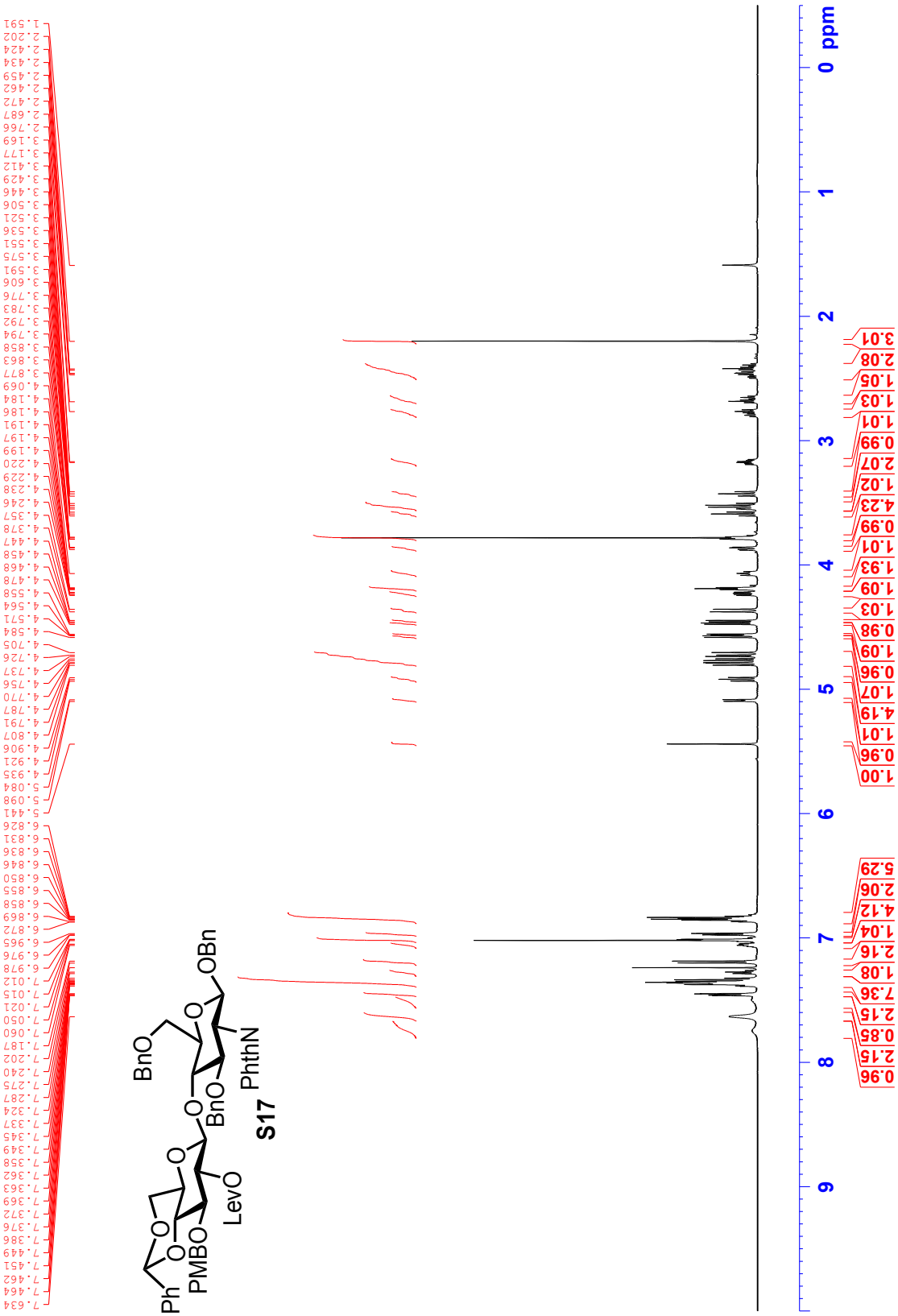
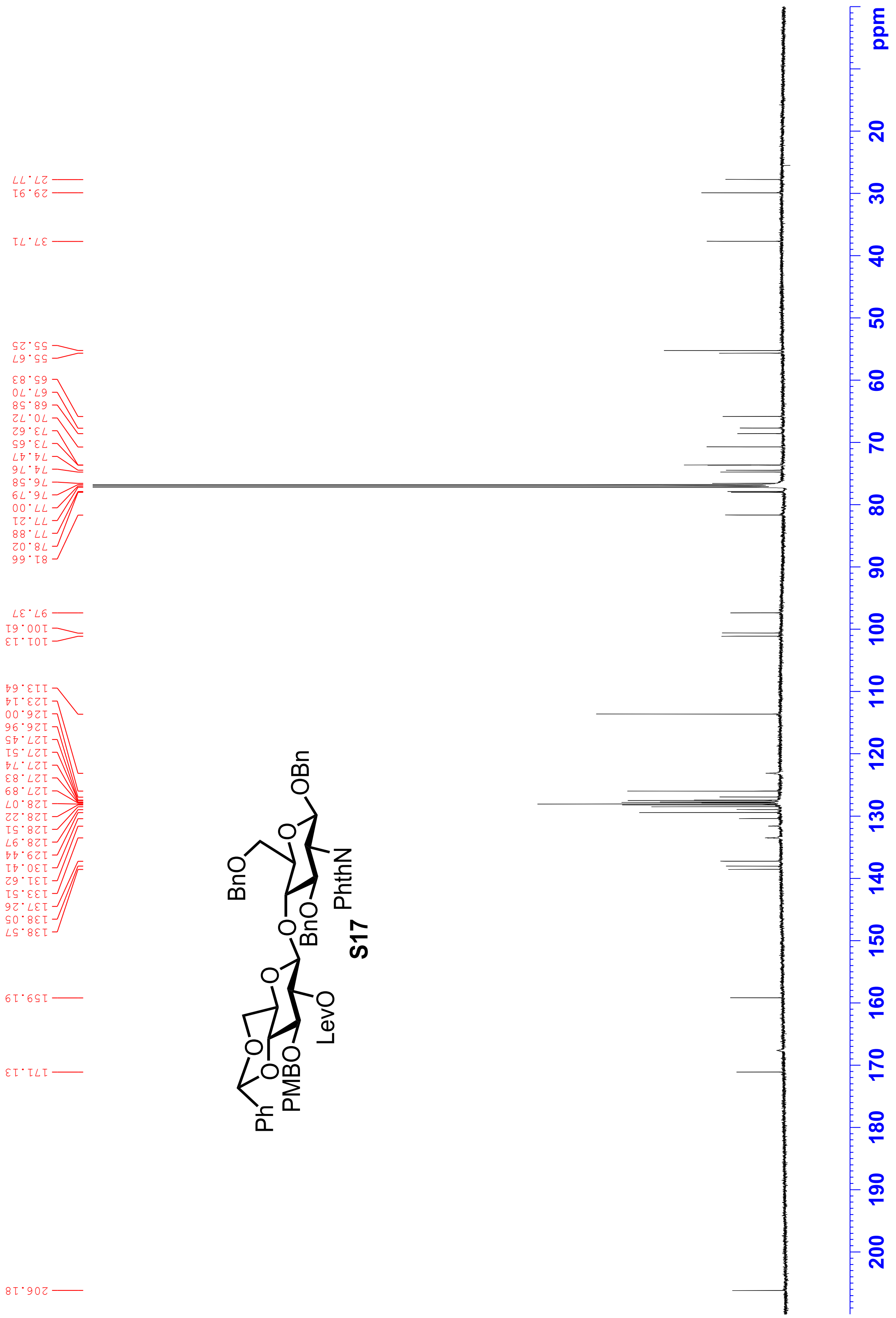
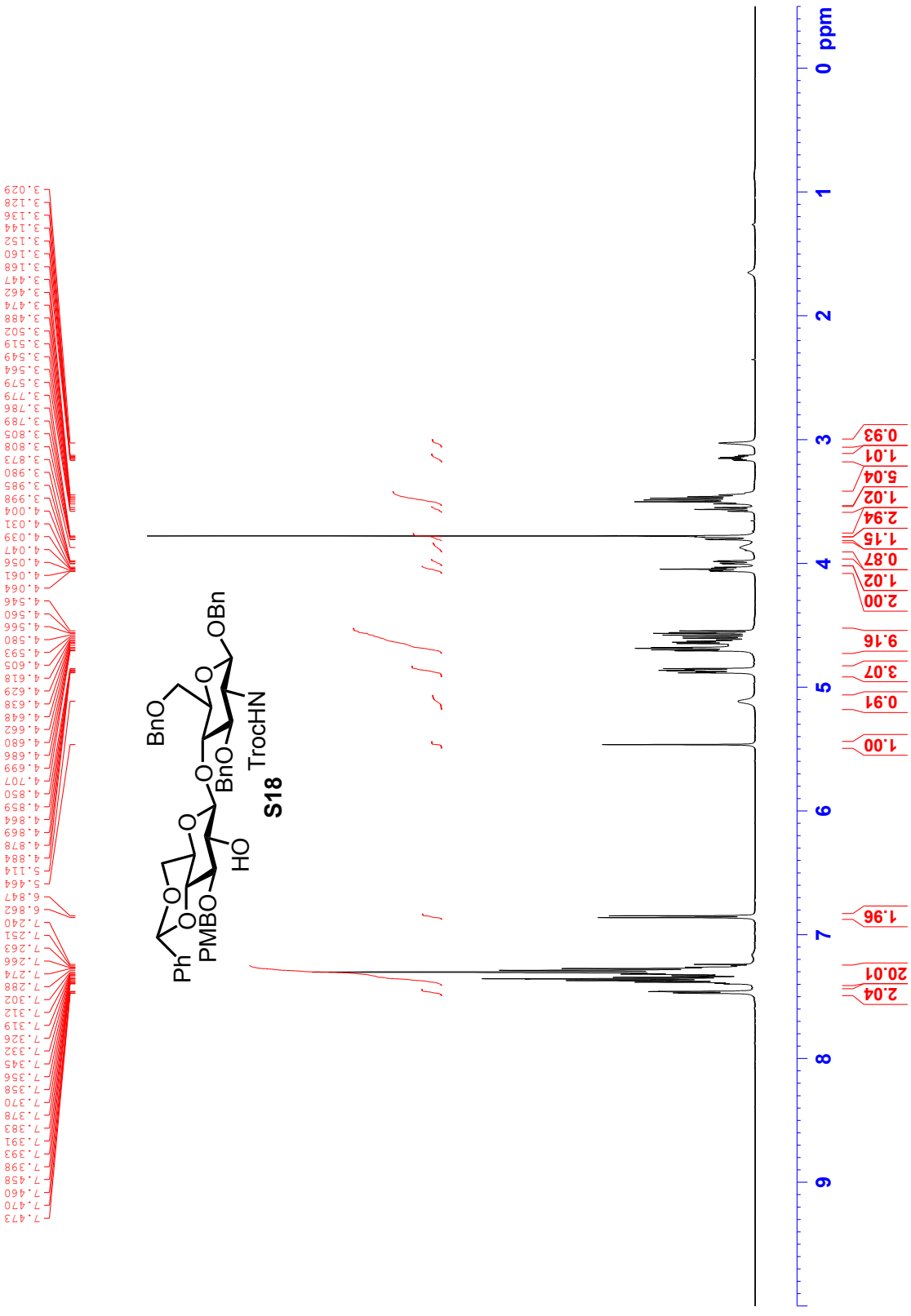
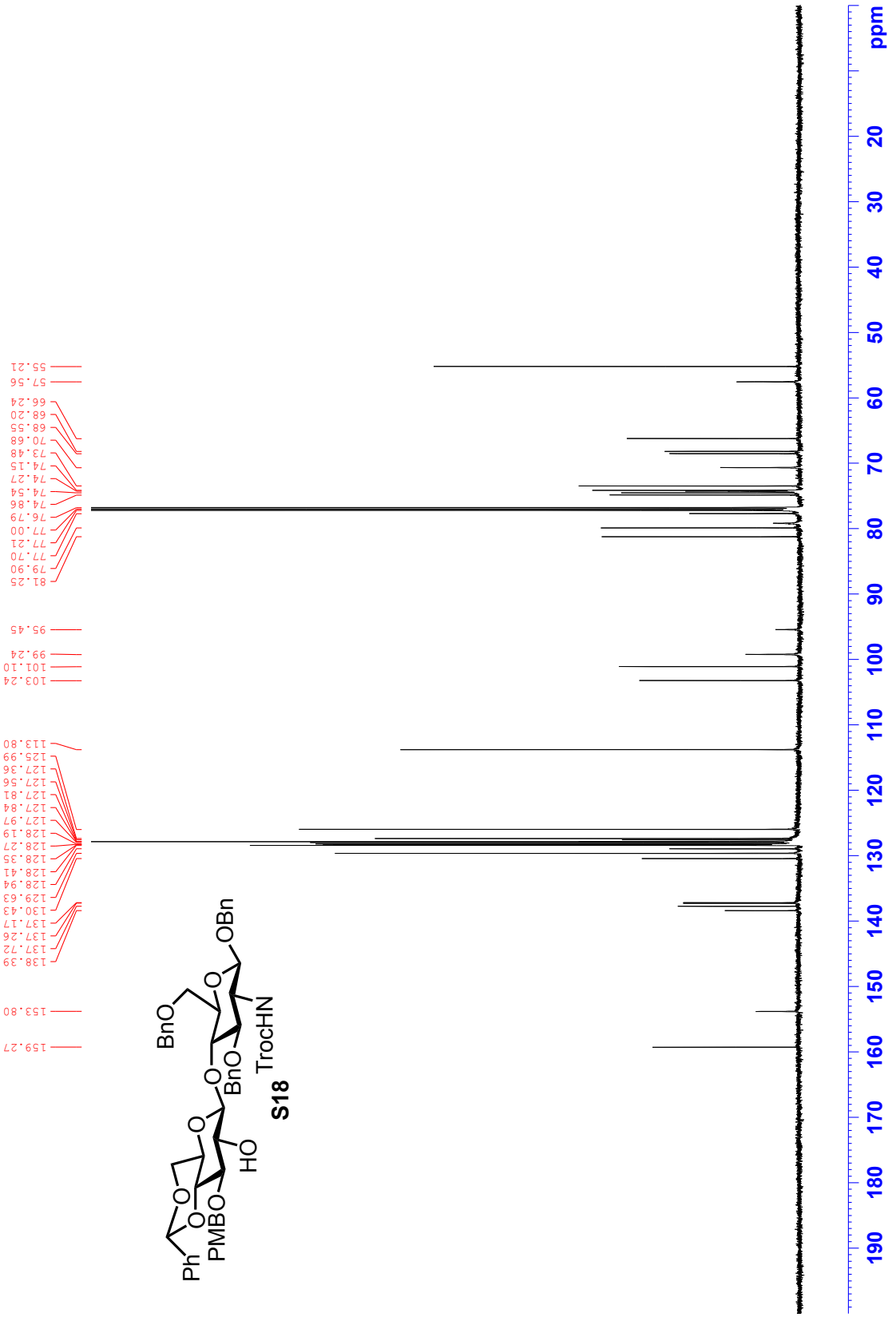
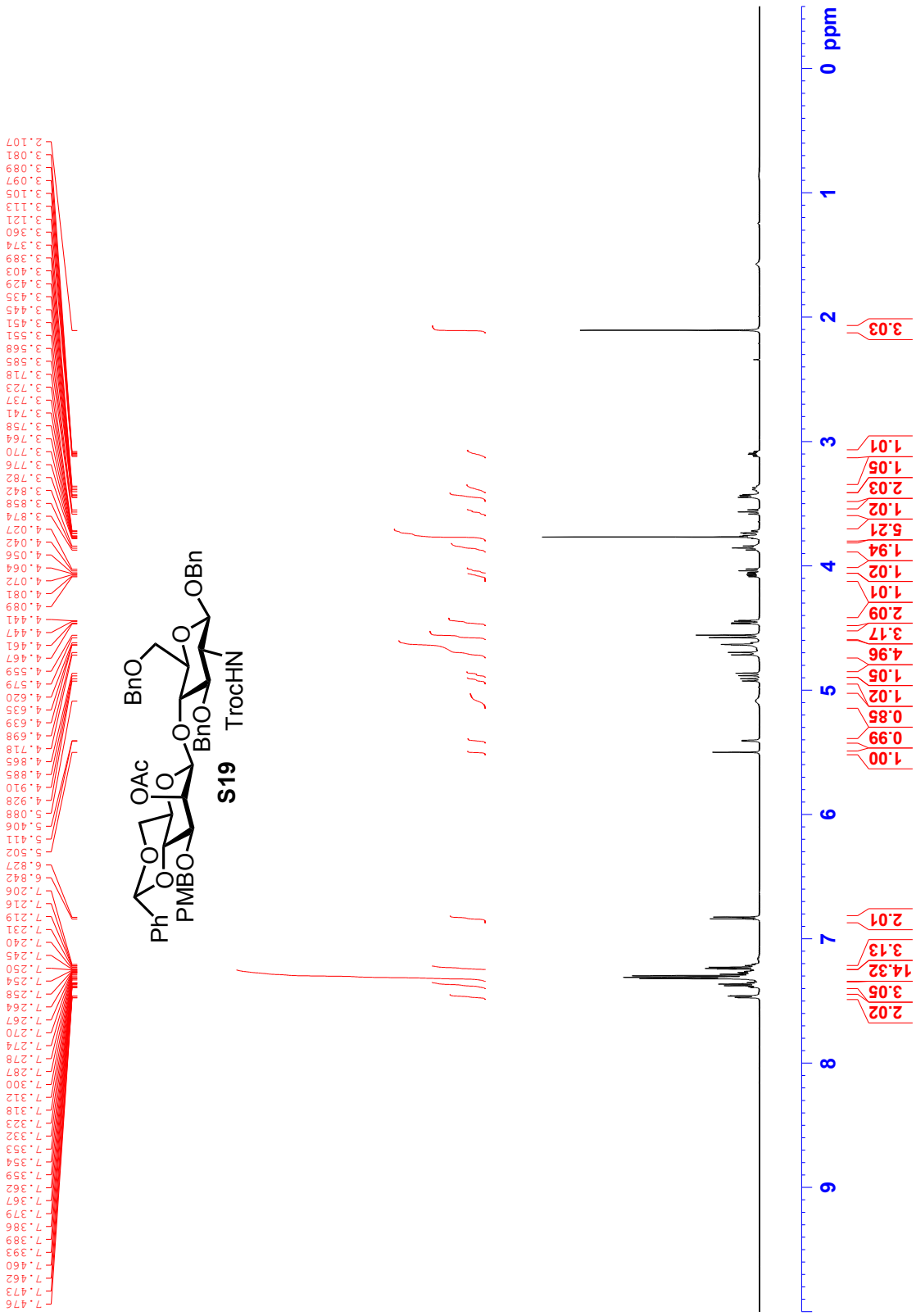
57.75
69.30
70.90
71.41
72.45
73.12
73.15
73.78
73.80
74.16
74.41
74.57
75.20
75.31
76.79
77.00
77.21
78.42
79.13
86.16
95.43
97.50
127.47
127.57
127.63
127.73
127.79
127.84
127.87
127.96
128.06
128.33
128.38
128.47
128.50
129.78
130.28
132.52
137.57
137.74
137.87
138.30
138.44
154.23
BnO
HO
BnO
TrocHN
O
O
BnO
BnO
BnO
O
STol
18
ppm
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190

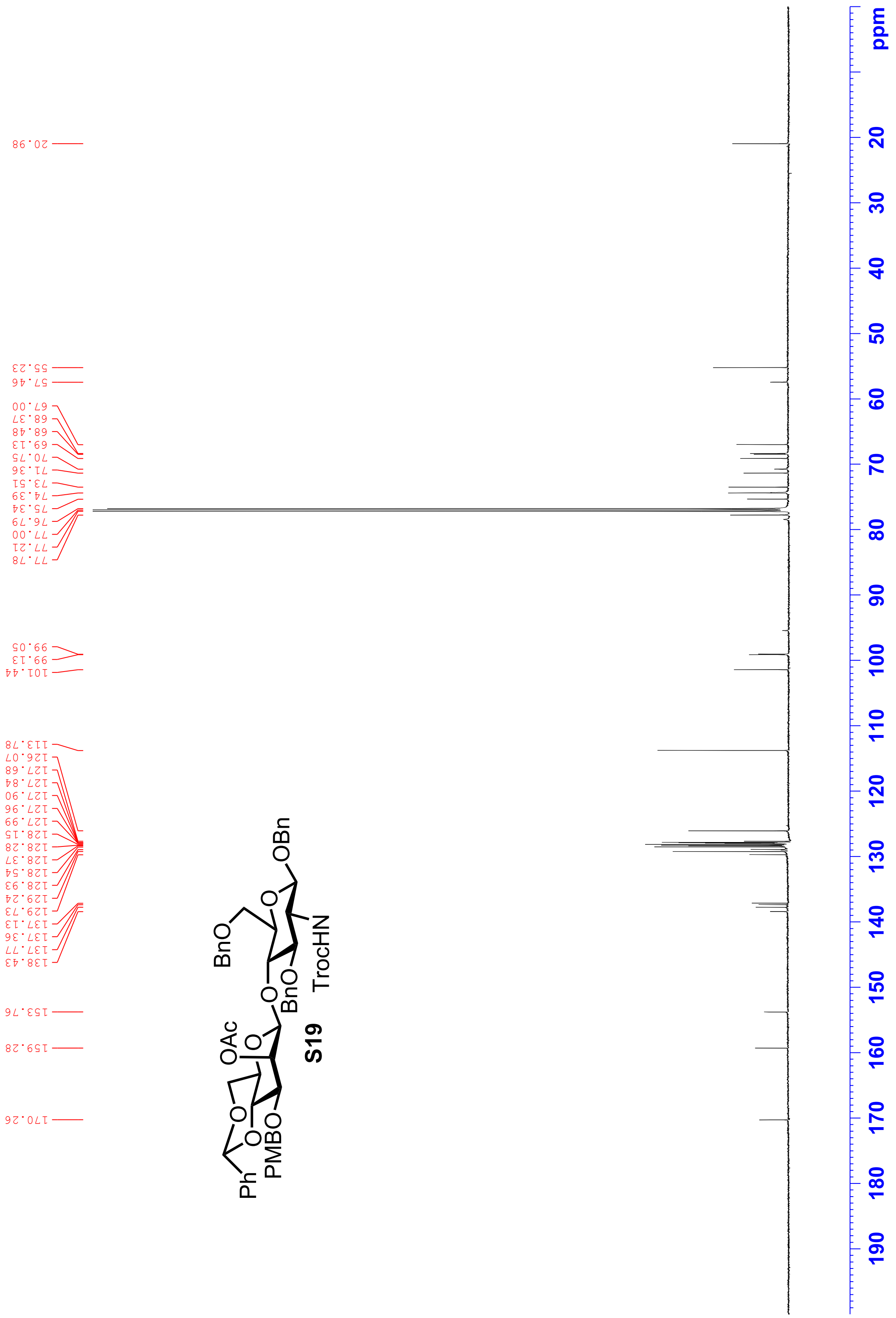

Ph
PMBO
LevO
BnO
BnO
OBn
PhthN
S17
0 ppm


27.77
29.91
37.71
55.25
55.67
65.83
67.70
68.58
70.72
73.62
73.65
74.47
74.76
76.58
76.79
77.00
77.21
77.88
78.02
81.66
97.37
100.61
101.13
113.64
123.14
126.00
126.96
127.45
127.51
127.74
127.83
127.89
128.07
128.22
128.51
128.97
129.44
130.41
131.62
133.51
137.26
138.05
138.57
159.19
171.13
206.18
OBn
BnO
O
PhthN
BnO
O
O
O
O
Ph
PMBO
LevO
S17
ppm
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200


S18
BnO
OBn
TrocHN
BnO
HO
PMBO
Ph
0 ppm
1 2 3 4 5 6 7 8 9
0.93
1.01
5.04
1.02
2.94
1.15
0.87
1.02
2.00
9.16
3.07
0.91
1.00
1.96
20.01
2.04


55.21
57.56
66.24
68.55
68.20
70.68
73.48
74.15
74.27
74.54
74.86
76.79
77.00
77.21
77.70
79.90
81.25
95.45
99.24
101.10
103.24
113.80
125.99
127.36
127.56
127.81
127.84
127.97
128.19
128.27
128.35
128.41
128.94
129.63
130.43
137.17
137.26
137.72
138.39
153.80
159.27
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
BnO
OBn
TrocHN
BnO
HO
PMBO
Ph
S18


S19
Ph
PMBO
OAc
BnO
BnO
BnO
TrocHN
ppm
0
1
2
3
4
5
6
7
8
9
3.03
1.01
1.05
2.03
1.02
5.21
1.94
1.02
1.01
2.09
3.17
4.96
1.05
1.02
0.85
0.99
1.00
2.01
3.13
14.32
3.05
2.02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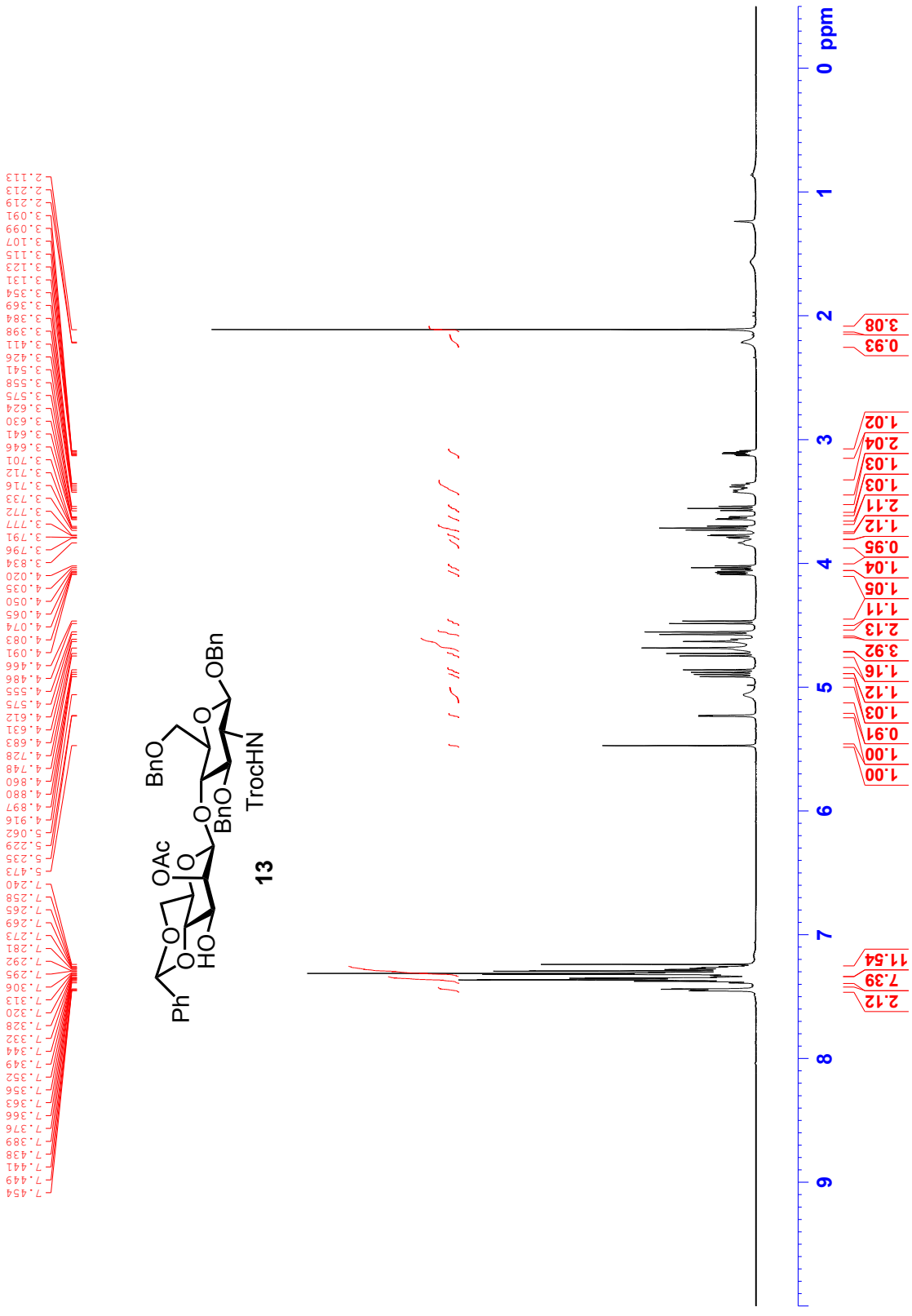
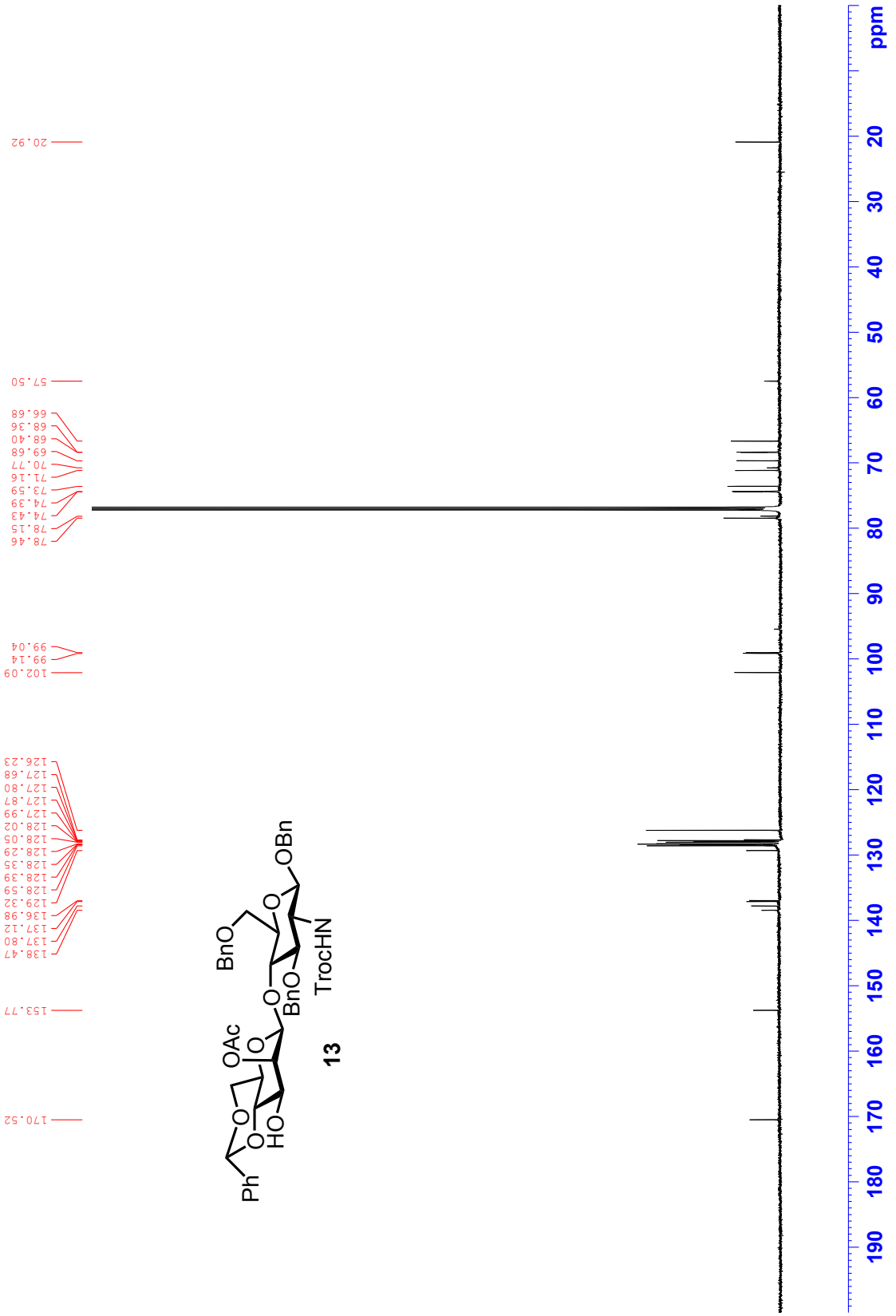
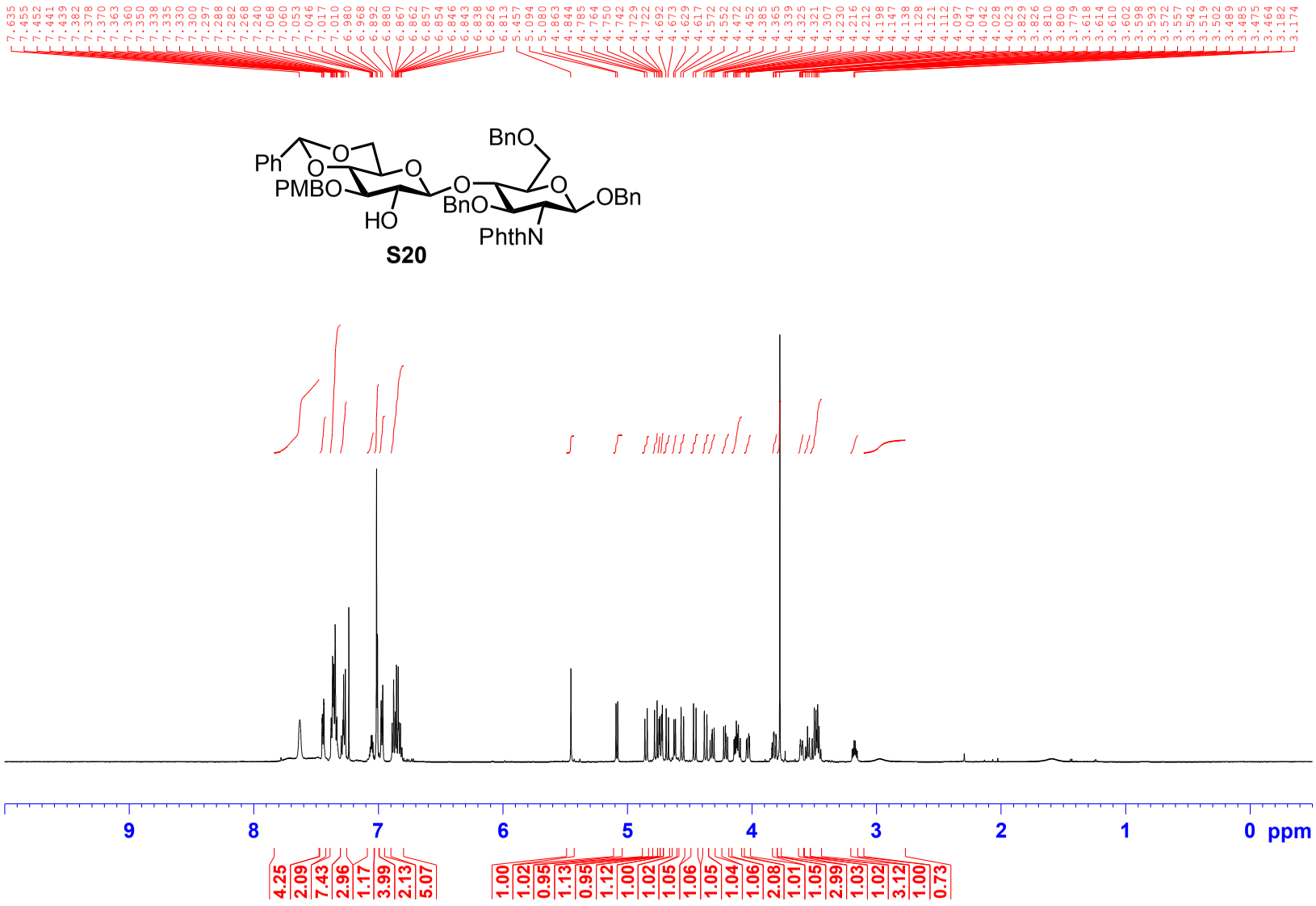
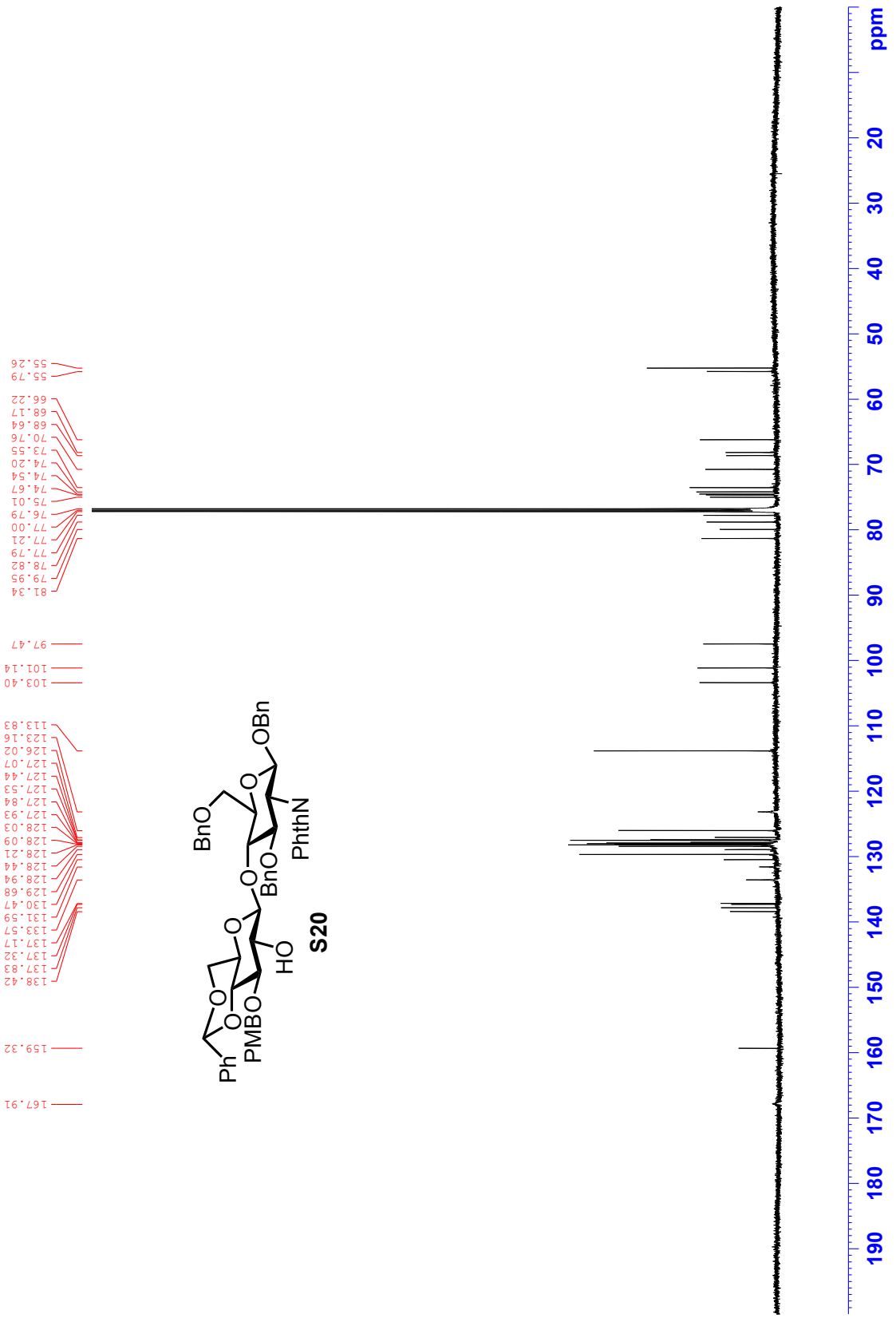
67.00
68.37
68.48
69.13
70.75
71.36
73.51
74.39
75.34
76.79
77.00
77.21
77.78
99.05
99.13
101.44
113.78
126.07
127.68
127.84
127.90
127.96
127.99
128.15
128.28
128.37
128.54
128.93
129.24
129.73
137.13
137.36
137.77
138.43
153.76
159.28
170.26
ppm
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
Ph
PMBO
OAc
BnO
OBn
TrocHN
S19


13
Ph
HO
OAc
BnO
BnO
BnO
OBn
TrocHN
0 ppm
1 2 3 4 5 6 7 8 9
1.00
1.00
0.91
1.03
1.12
1.16
3.92
2.13
1.11
1.05
1.04
0.95
1.12
2.11
1.03
1.03
2.04
1.02
0.93
3.08
2.12
7.39
11.54


20.92
57.50
66.68
68.36
68.40
69.68
70.77
71.16
73.59
74.39
74.43
78.15
78.46
99.04
99.14
102.09
126.23
127.68
127.80
127.87
127.99
128.02
128.05
128.29
128.35
128.39
128.59
129.32
136.98
137.12
137.80
138.47
153.77
170.52
BnO
OBn
TrocHN
BnO
OAc
HO
Ph
13
ppm
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190


7.635 7.455 7.452 7.441 7.439 7.382 7.378 7.370 7.363 7.360 7.350 7.338 7.335 7.330 7.300 7.297 7.288 7.282 7.268 7.240 7.068 7.060 7.053 7.046 7.017 7.010 6.980 6.968 6.892 6.880 6.867 6.862 6.857 6.854 6.846 6.843 6.838 6.826 6.813 5.457 5.094 5.080 4.863 4.844 4.785 4.764 4.750 4.742 4.729 4.722 4.692 4.673 4.629 4.617 4.572 4.552 4.472 4.452 4.385 4.365 4.339 4.325 4.321 4.307 4.230 4.216 4.212 4.198 4.147 4.138 4.128 4.121 4.112 4.097 4.047 4.042 4.028 4.023 3.829 3.826 3.810 3.808 3.779 3.618 3.614 3.610 3.602 3.598 3.593 3.572 3.557 3.542 3.519 3.502 3.489 3.485 3.475 3.464 3.182 3.174
Ph
O
O
O
PMBO
HO
O
BnO
BnO
O
OBn
PhthN
S20
9
8
7
6
5
4
3
2
1
0 ppm
4.25 2.09 7.43 2.96 1.17 3.99 2.13 5.07
1.00 1.02 0.95 1.13 0.95 1.12 1.00 1.02 1.05 1.06 1.05 1.04 1.06 2.08 1.01 1.05 2.99 1.03 1.02 3.12 1.00 0.73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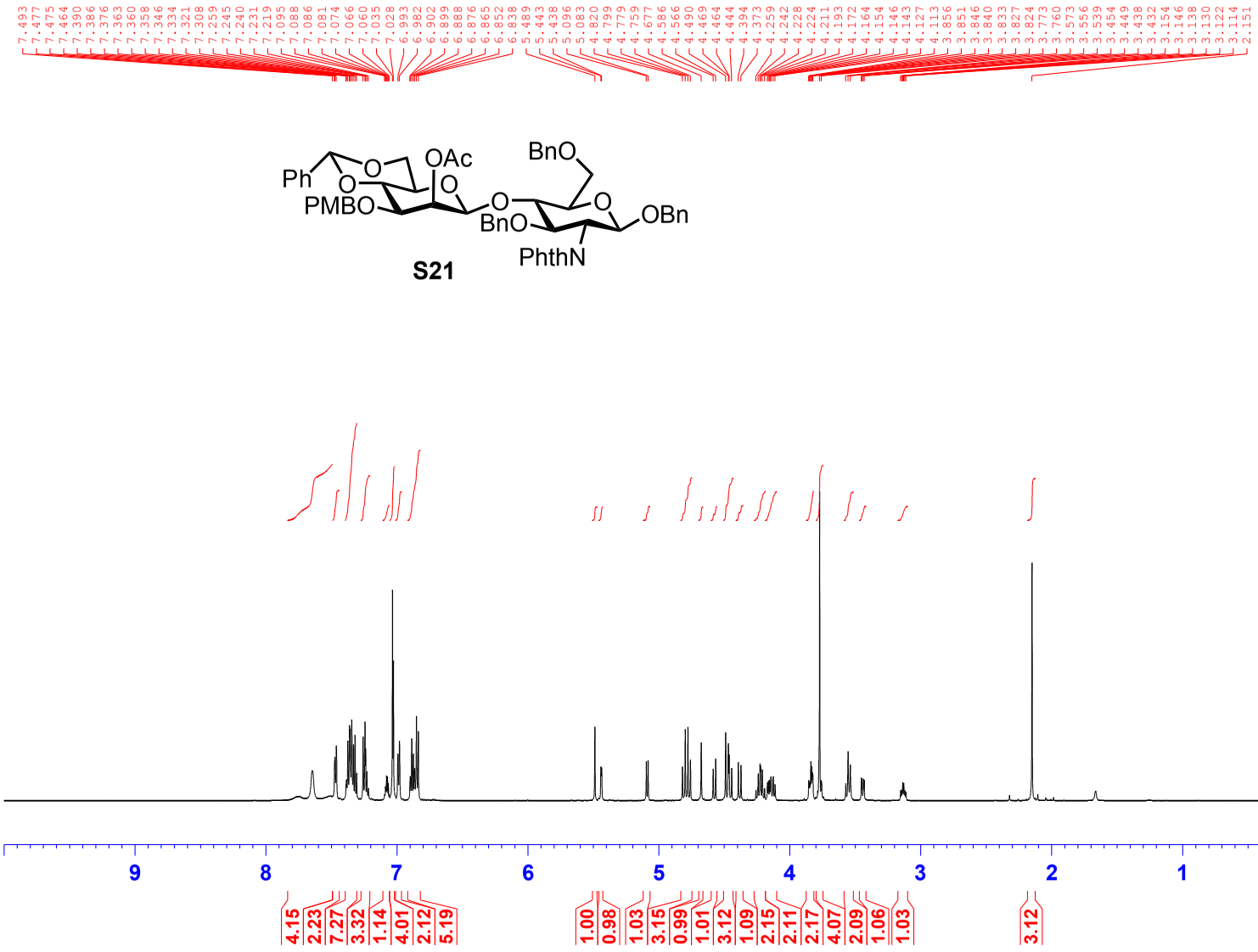
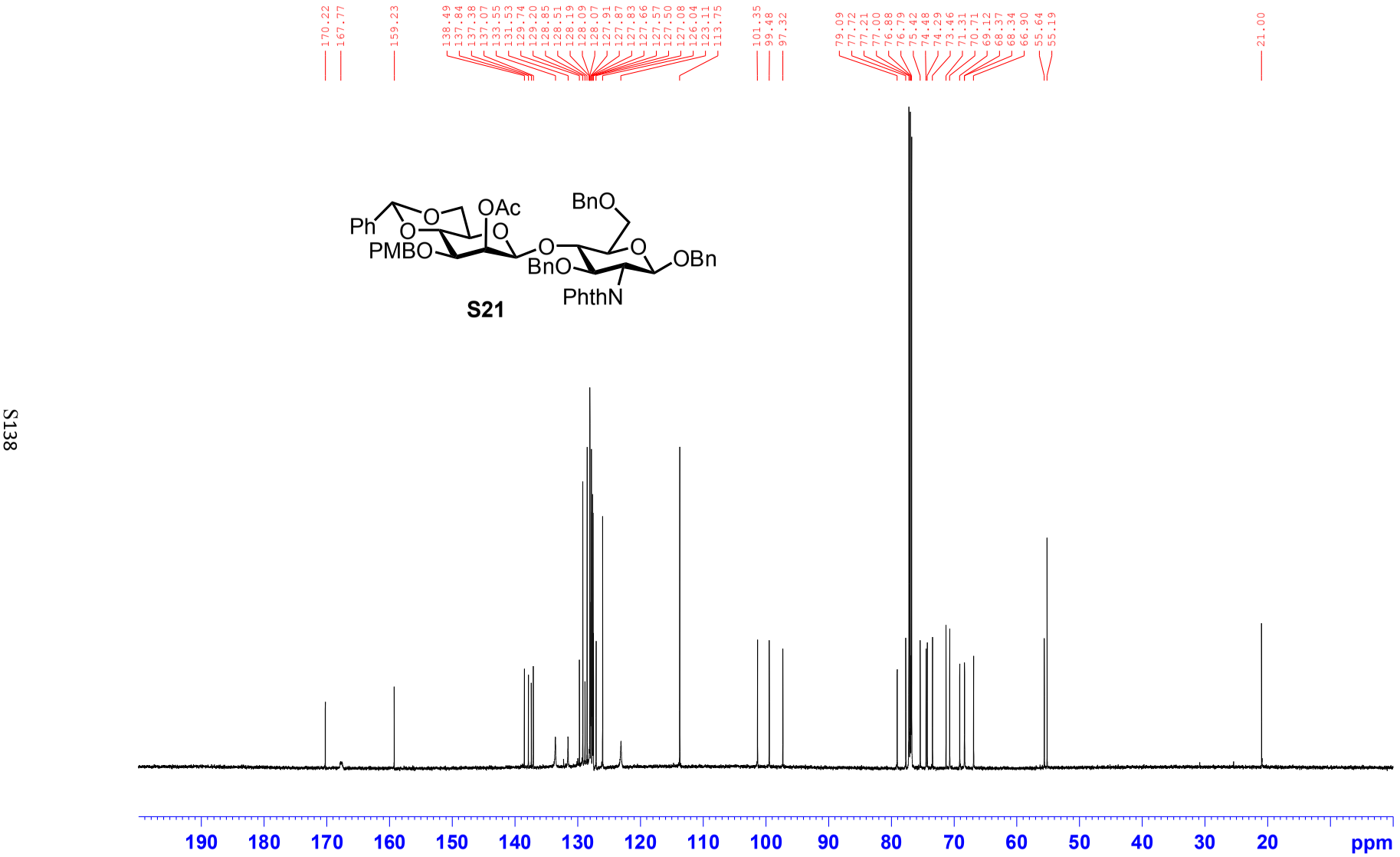
66.22
68.17
68.64
70.76
73.55
74.20
74.54
74.67
75.01
76.79
77.00
77.21
77.79
78.82
79.95
81.34
97.47
101.14
103.40
113.83
123.16
126.02
127.07
127.44
127.53
127.84
127.93
128.03
128.09
128.21
128.44
128.94
129.68
130.47
131.59
133.57
137.17
137.32
137.83
138.42
159.32
167.91
BnO
OBn
PhthN
BnO
HO
PMBO
Ph
S20
ppm
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190


7.493 7.477 7.475 7.464 7.390 7.386 7.376 7.363 7.360 7.358 7.346 7.334 7.321 7.308 7.259 7.245 7.240 7.231 7.219 7.095 7.088 7.086 7.081 7.074 7.066 7.060 7.035 7.028 6.993 6.982 6.902 6.899 6.888 6.876 6.865 6.852 6.838 5.489 5.443 5.438 5.096 5.083 4.820 4.799 4.779 4.759 4.677 4.586 4.566 4.490 4.469 4.464 4.444 4.394 4.373 4.259 4.242 4.228 4.224 4.211 4.193 4.172 4.164 4.154 4.146 4.143 4.127 4.113 3.856 3.851 3.846 3.840 3.833 3.827 3.824 3.773 3.760 3.573 3.556 3.539 3.454 3.449 3.438 3.432 3.154 3.146 3.138 3.130 3.122 3.114 2.151
Ph
O
OAc
O
PMBO
O
BnO
BnO
O
OBn
PhthN
S21
9
8
7
6
5
4
3
2
1
0 ppm
4.15 2.23 7.27 3.32 1.14 4.01 2.12 5.19
1.00 0.98 1.03 3.15 0.99 1.01 3.12 1.09 2.15 2.11 2.17 4.07 2.09 1.06 1.03
3.12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167.77
159.23
138.49
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137.38
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133.55
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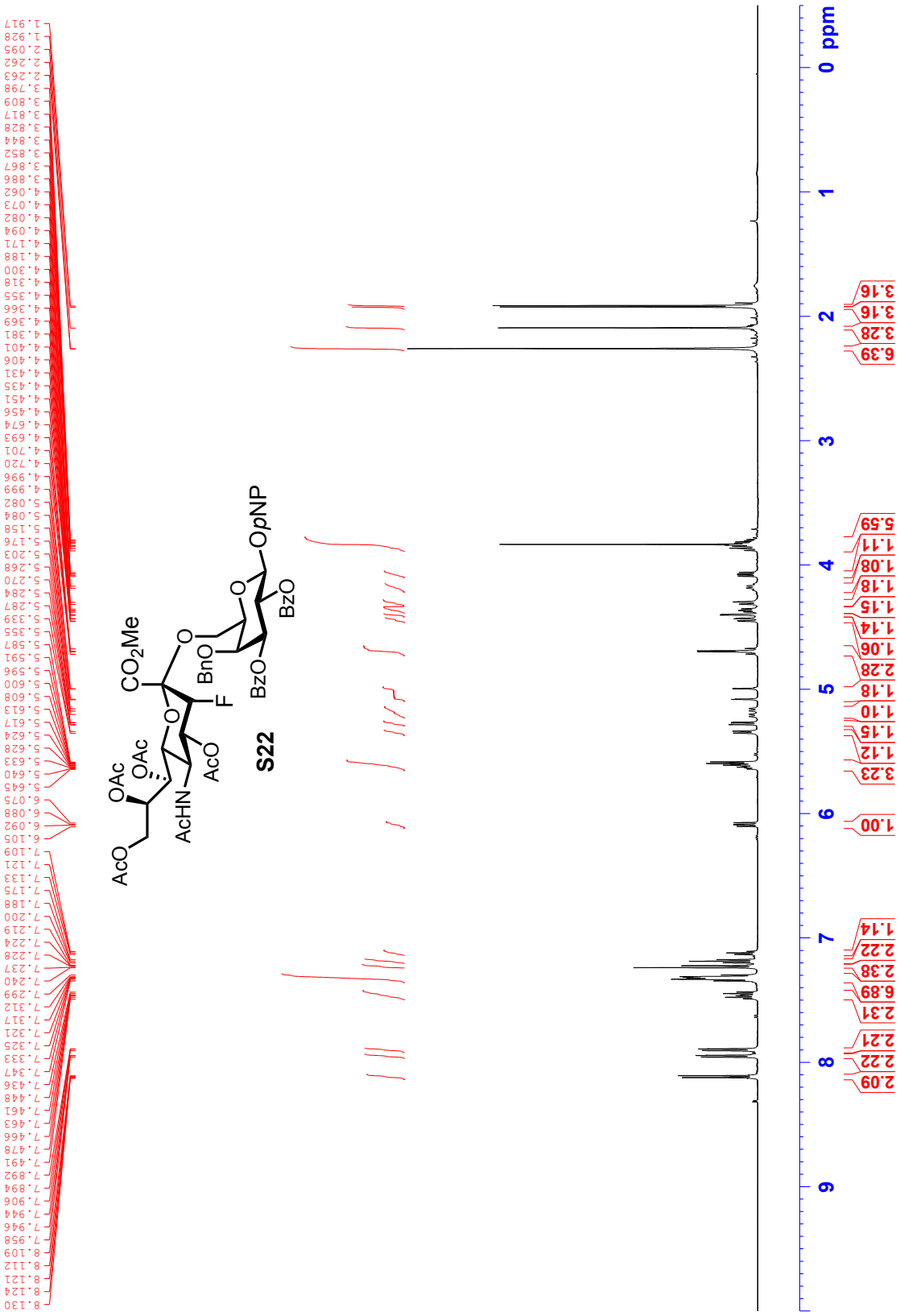
129.74
129.20
128.85
128.51
128.19
128.09
128.07
127.91
127.87
127.83
127.66
127.57
127.50
127.08
126.04
123.11
113.75
101.35
99.48
97.32
79.09
77.72
77.21
77.00
76.88
76.79
75.42
74.48
74.29
73.46
71.31
70.71
69.12
68.37
68.34
66.90
55.64
55.19
21.00
Ph
O
OAc
O
PMBO
O
BnO
BnO
O
OBn
PhthN
S21
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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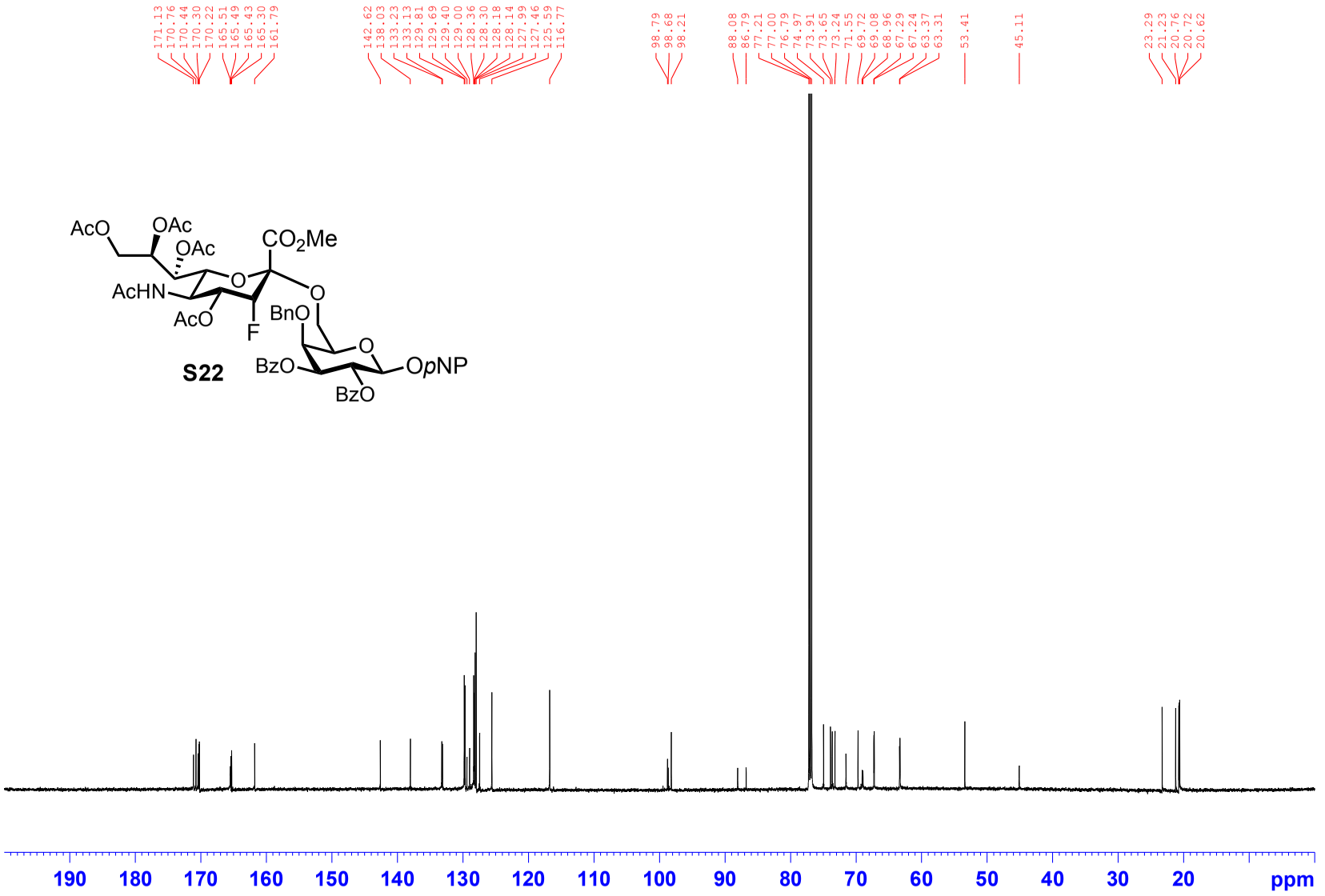
OAc
OAc
AcHN
AcO
CO2Me
O
O
BnO
F
O
BzO
OpNP
S22
0 ppm
1
2
3
4
5
6
7
8
9
6.39
3.28
3.16
3.16
5.59
1.11
1.08
1.18
1.15
1.14
1.06
2.28
1.18
1.10
1.15
1.12
3.23
1.00
1.14
2.22
2.38
6.89
2.31
2.21
2.22
2.09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170.76
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170.30
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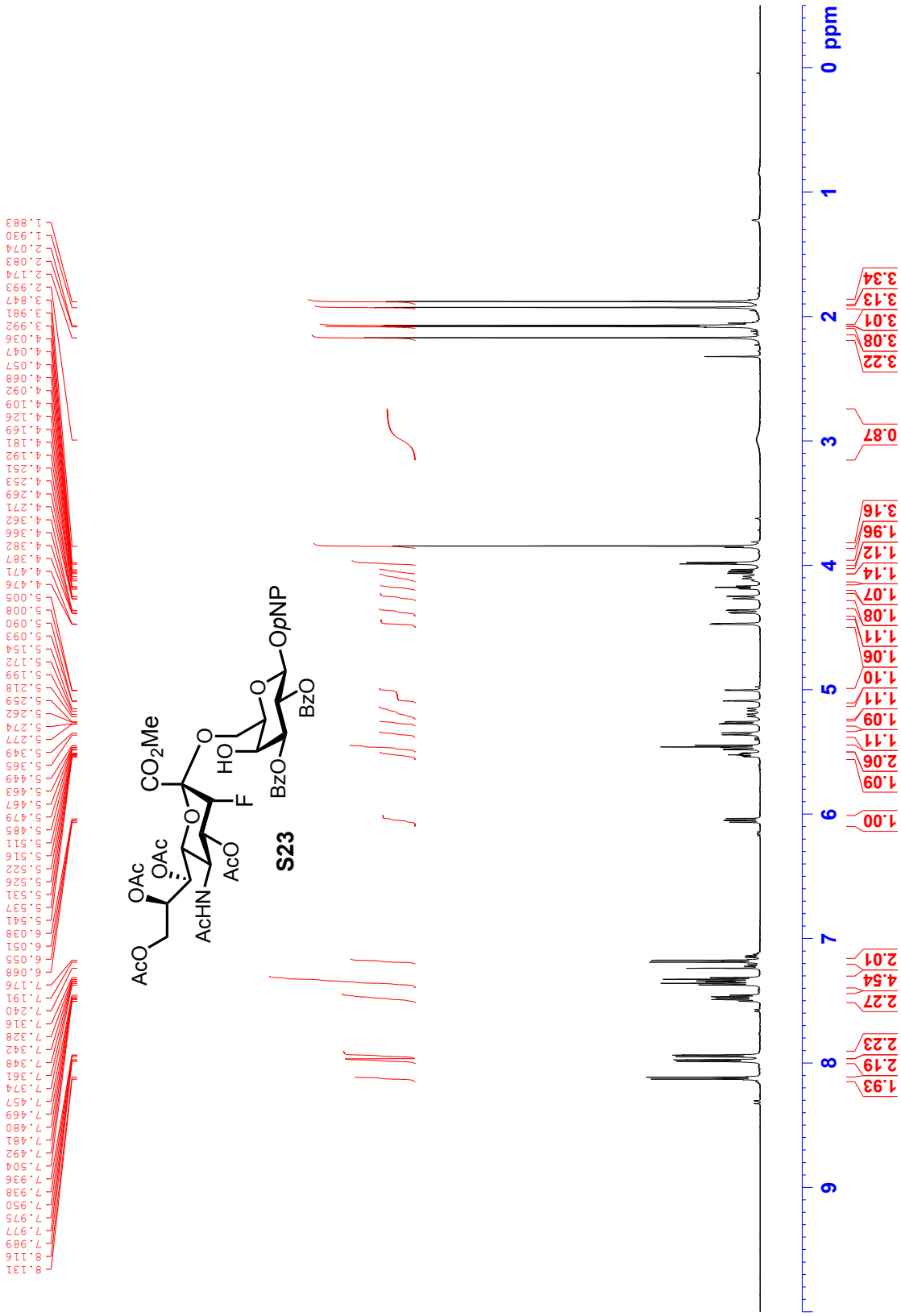
165.51
165.49
165.43
165.30
161.79
142.62
138.03
133.23
133.13
129.81
129.69
129.40
129.00
128.36
128.30
128.18
128.14
127.99
127.46
125.59
116.77
98.79
98.68
98.21
88.08
86.79
77.21
77.00
76.79
74.97
73.91
73.65
73.24
71.55
69.72
69.08
68.96
67.29
67.24
63.37
63.31
53.41
45.11
23.29
21.23
20.76
20.72
20.62
AcO
OAc
OAc
CO2Me
AcHN
O
O
AcO
F
BnO
O
BzO
OpNP
BzO
S22
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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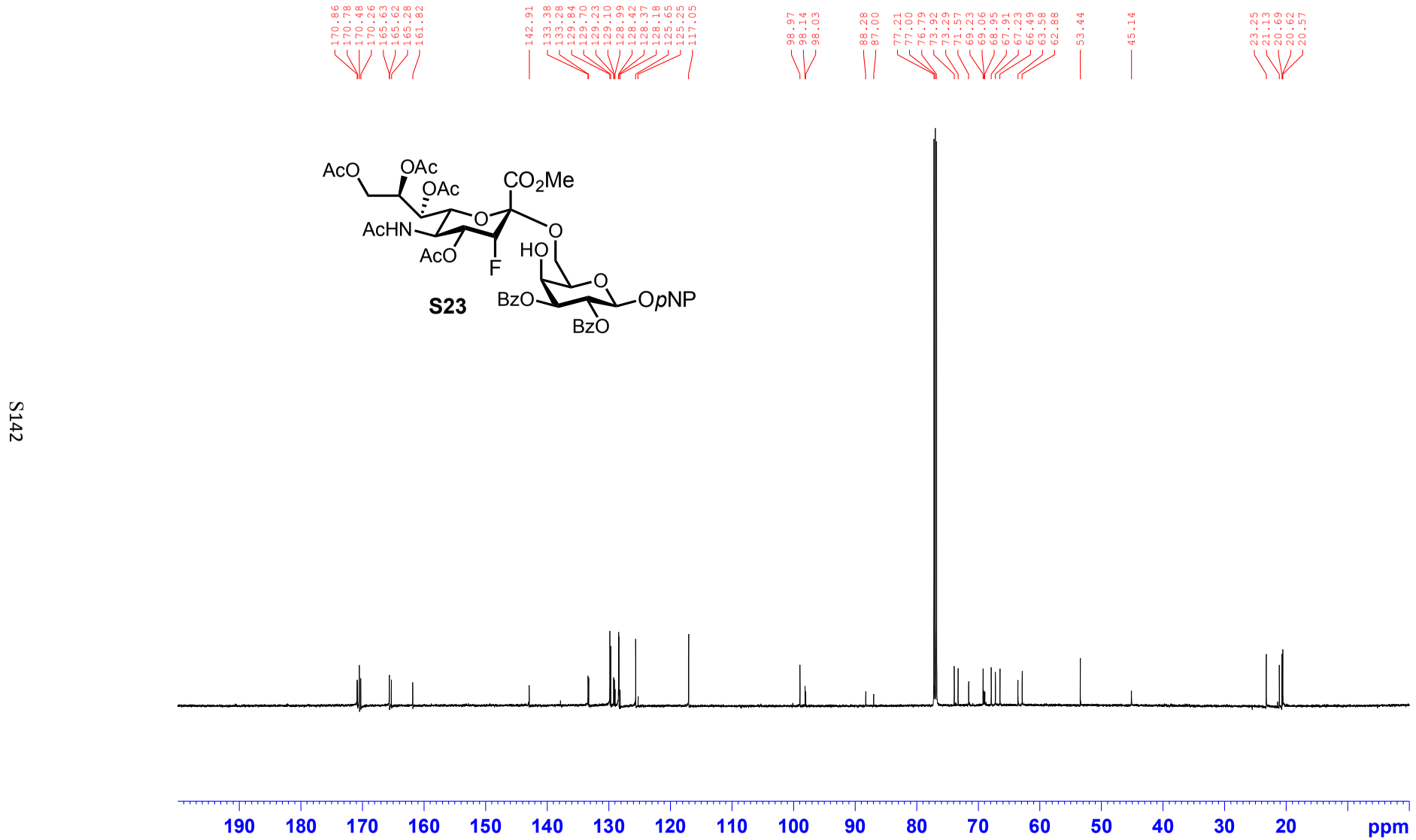
AcO
OAc
OAc
AcHN
AcO
F
HO
BzO
BzO
OpNP
CO2Me
0 ppm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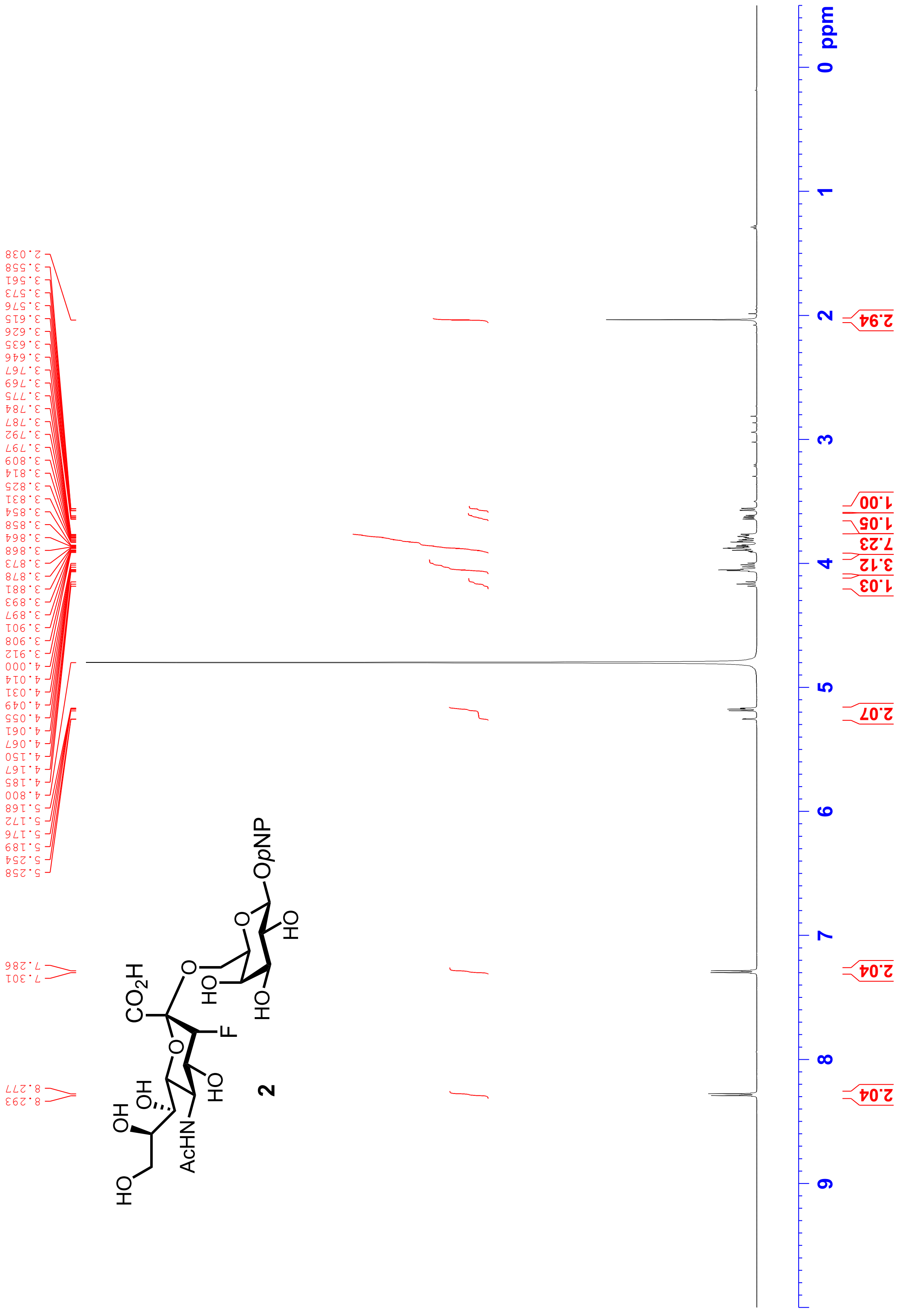
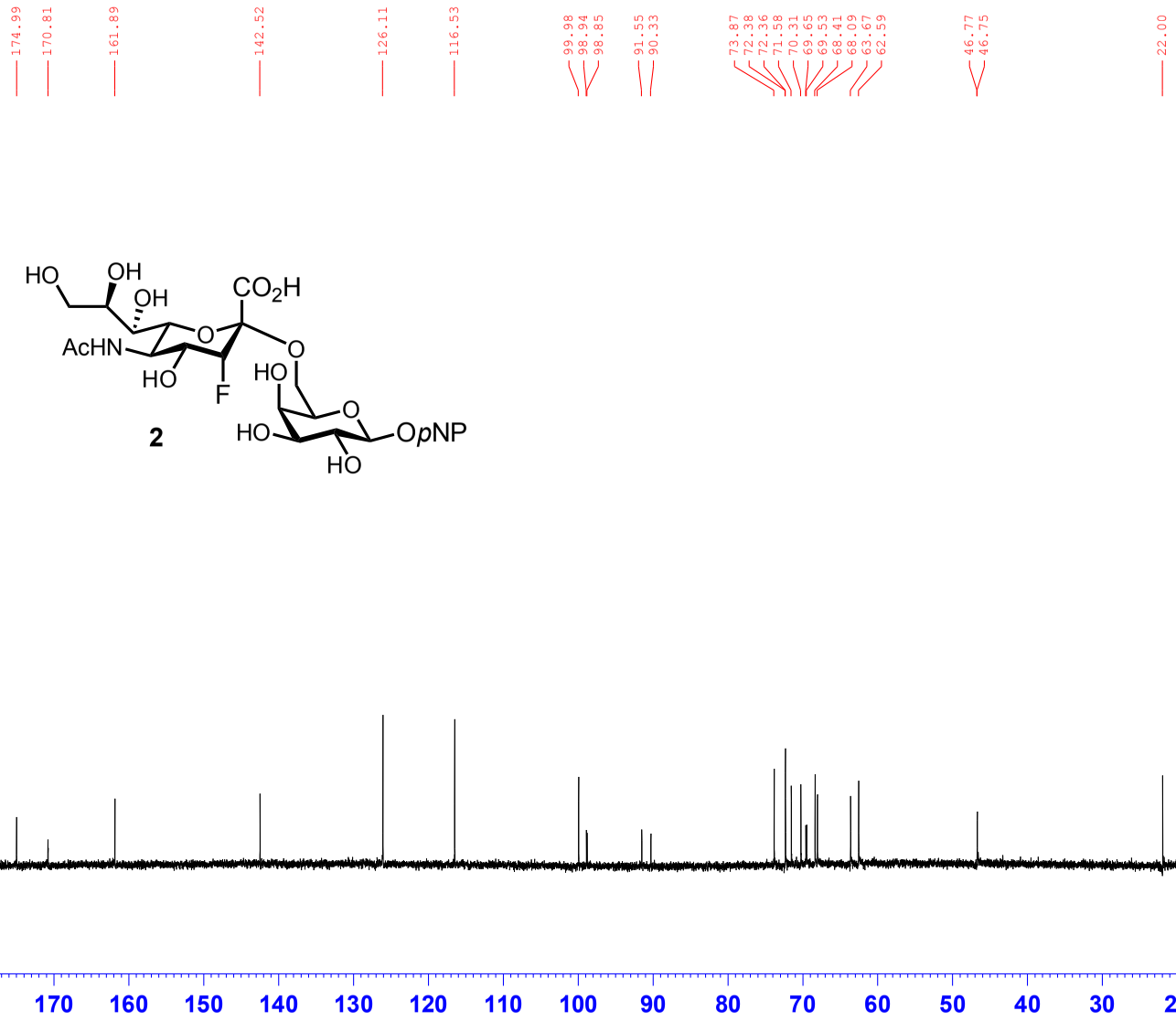
170.78
170.48
170.26
165.63
165.62
165.28
161.82
142.91
133.38
133.28
129.84
129.70
129.23
129.10
128.99
128.42
128.37
128.18
125.65
125.25
117.05
98.97
98.14
98.03
88.28
87.00
77.21
77.00
76.79
73.92
73.29
71.57
69.23
69.06
68.95
67.91
67.23
66.49
63.58
62.88
53.44
45.14
23.25
21.13
20.69
20.62
20.57
AcO
OAc
OAc
CO2Me
AcHN
O
O
AcO
F
HO
O
BzO
OpNP
BzO
S23
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



2.038
3.558
3.561
3.573
3.576
3.615
3.626
3.635
3.646
3.767
3.769
3.775
3.784
3.787
3.792
3.797
3.809
3.814
3.825
3.831
3.854
3.858
3.864
3.868
3.873
3.878
3.881
3.893
3.897
3.901
3.908
3.912
4.000
4.014
4.031
4.049
4.055
4.061
4.067
4.150
4.167
4.185
4.800
5.168
5.172
5.176
5.189
5.254
5.258
7.286
7.301
8.277
8.293
HO
OH
HO
AcHN
HO
CO2H
F
O
HO
HO
O
OpNP
HO
2
2.94
1.00
1.05
7.23
3.12
1.03
2.07
2.04
2.04
ppm
0
1
2
3
4
5
6
7
8
9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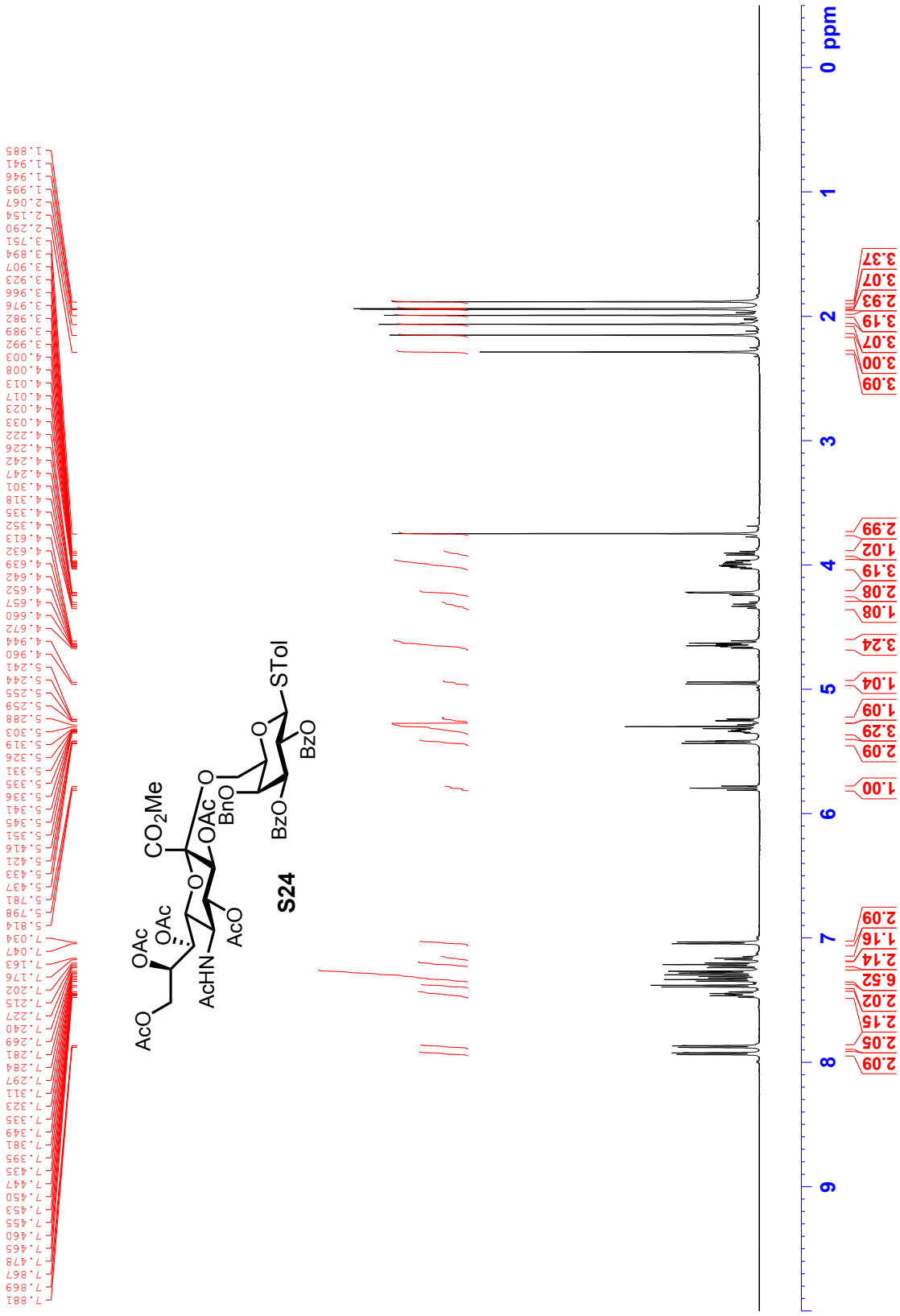
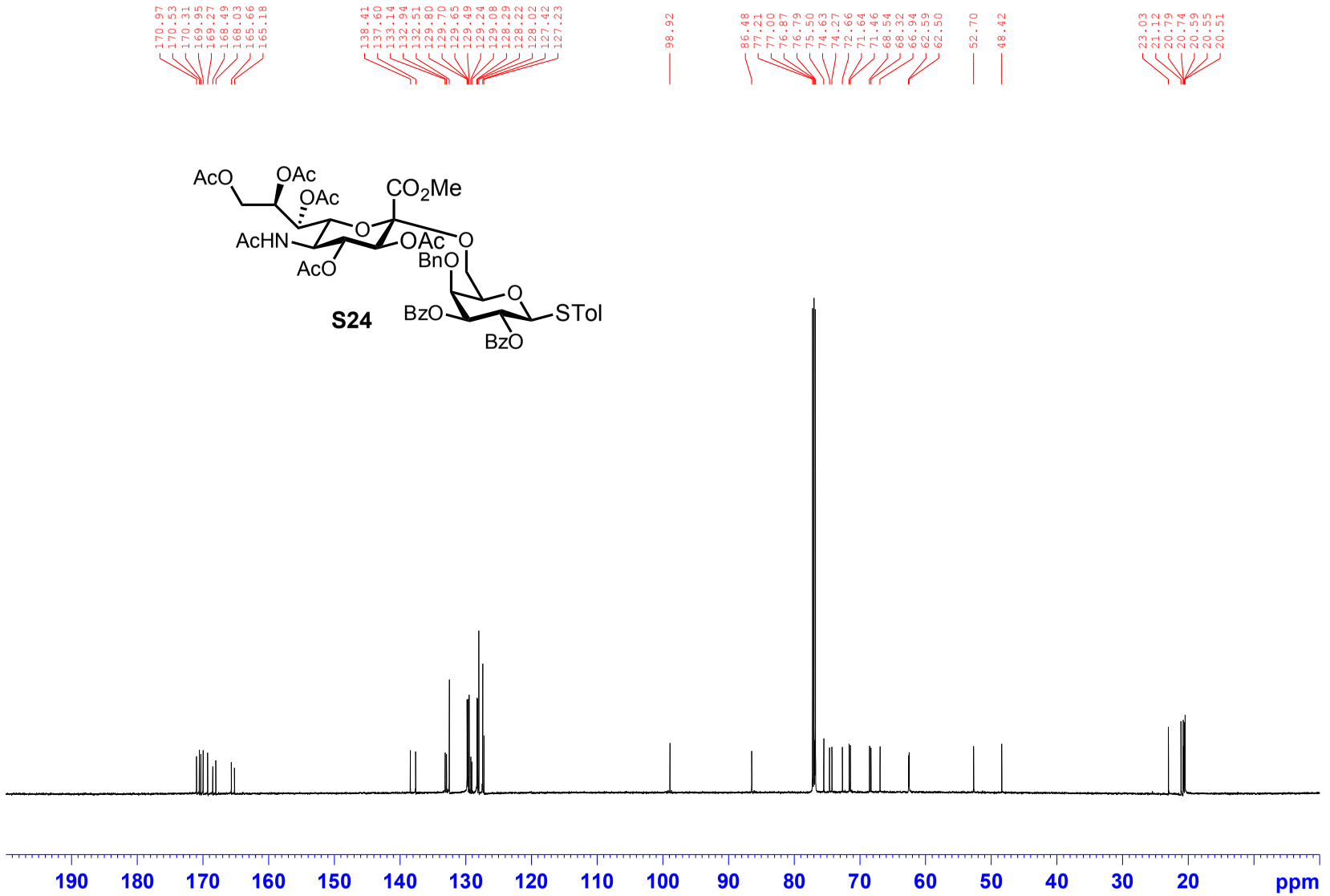
98.94
98.85
91.55
90.33
73.87
72.38
72.36
71.58
70.31
69.65
69.53
68.41
68.09
63.67
62.59
46.77
46.75
22.00
HO
OH
OH
CO2H
AcHN
O
O
HO
F
HO
O
HO
OpNP
HO
2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


S24
AcO
OAc
OAc
AcHN
AcO
CO2Me
OAc
BnO
BzO
BzO
STol
0 ppm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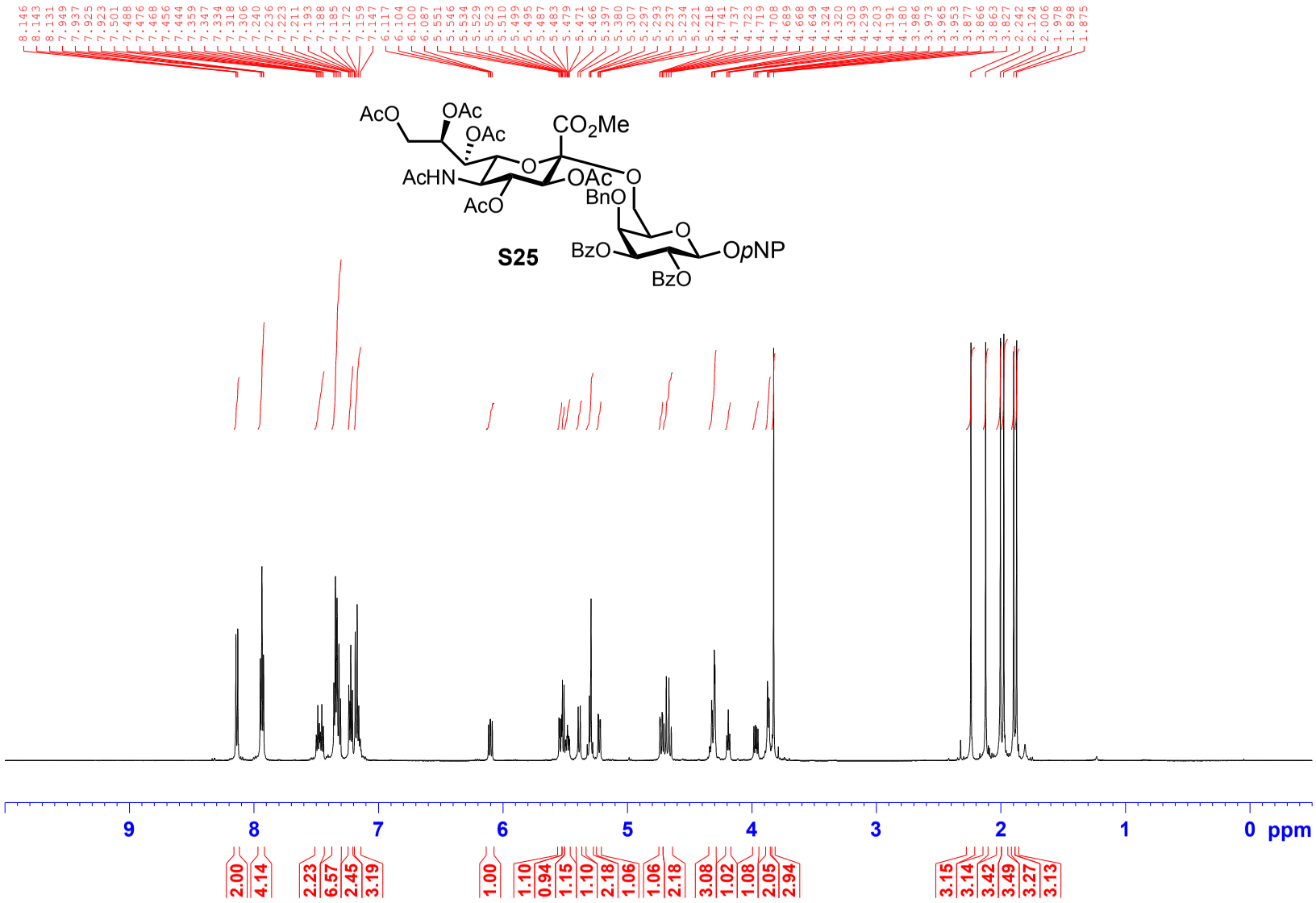
170.53
170.31
169.95
169.27
168.49
168.03
165.66
165.18
138.41
137.60
133.14
132.94
132.51
129.80
129.70
129.65
129.49
129.24
129.08
128.29
128.22
128.02
127.42
127.23
98.92
86.48
77.21
77.00
76.87
76.79
75.50
74.63
74.27
72.66
71.64
71.46
68.54
68.32
66.94
62.59
62.50
52.70
48.42
23.03
21.12
20.79
20.74
20.59
20.55
20.51
AcO
OAc
OAc
CO2Me
AcHN
O
OAc
O
AcO
BnO
O
BzO
STol
BzO
S24
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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8.131
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7.937
7.925
7.923
7.501
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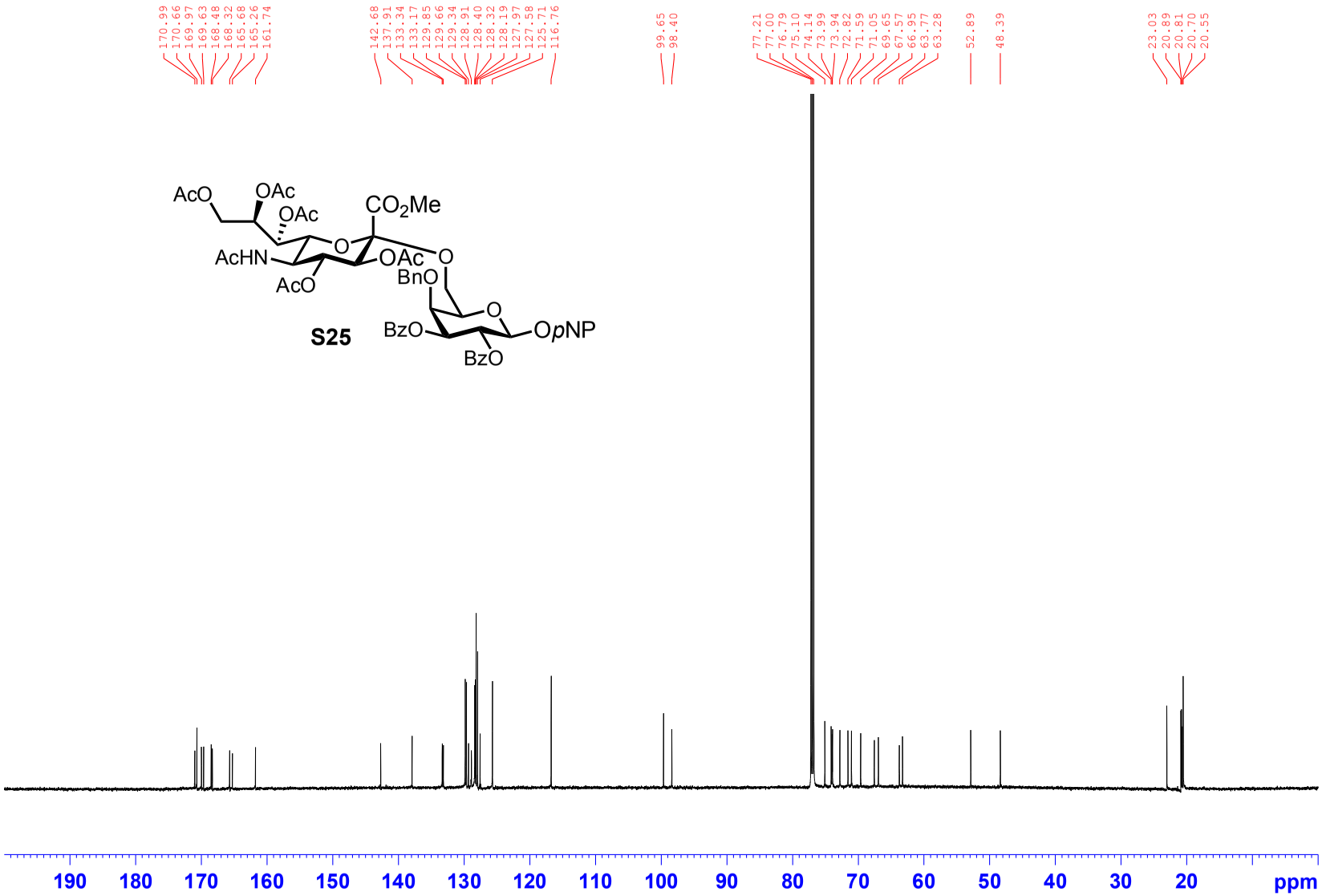
7.476
7.468
7.456
7.444
7.359
7.347
7.334
7.318
7.306
7.240
7.236
7.223
7.211
7.193
7.188
7.185
7.172
7.159
7.147
6.117
6.104
6.100
6.087
5.551
5.546
5.534
5.529
5.523
5.510
5.499
5.495
5.487
5.483
5.479
5.471
5.466
5.397
5.380
5.307
5.297
5.293
5.237
5.234
5.221
5.218
4.741
4.737
4.723
4.719
4.708
4.689
4.668
4.649
4.324
4.320
4.303
4.299
4.203
4.191
4.180
3.986
3.973
3.965
3.953
3.877
3.866
3.863
3.827
2.242
2.124
2.006
1.978
1.898
1.875
AcO
OAc
OAc
CO2Me
AcHN
O
OAc
O
AcO
BnO
O
BzO
OpNP
BzO
S25
9
8
7
6
5
4
3
2
1
0 ppm
2.00
4.14
2.23
6.57
2.45
3.19
1.00
1.10
0.94
1.15
1.10
2.18
1.06
1.06
2.18
3.08
1.02
1.08
2.05
2.94
3.15
3.14
3.42
3.49
3.27
3.13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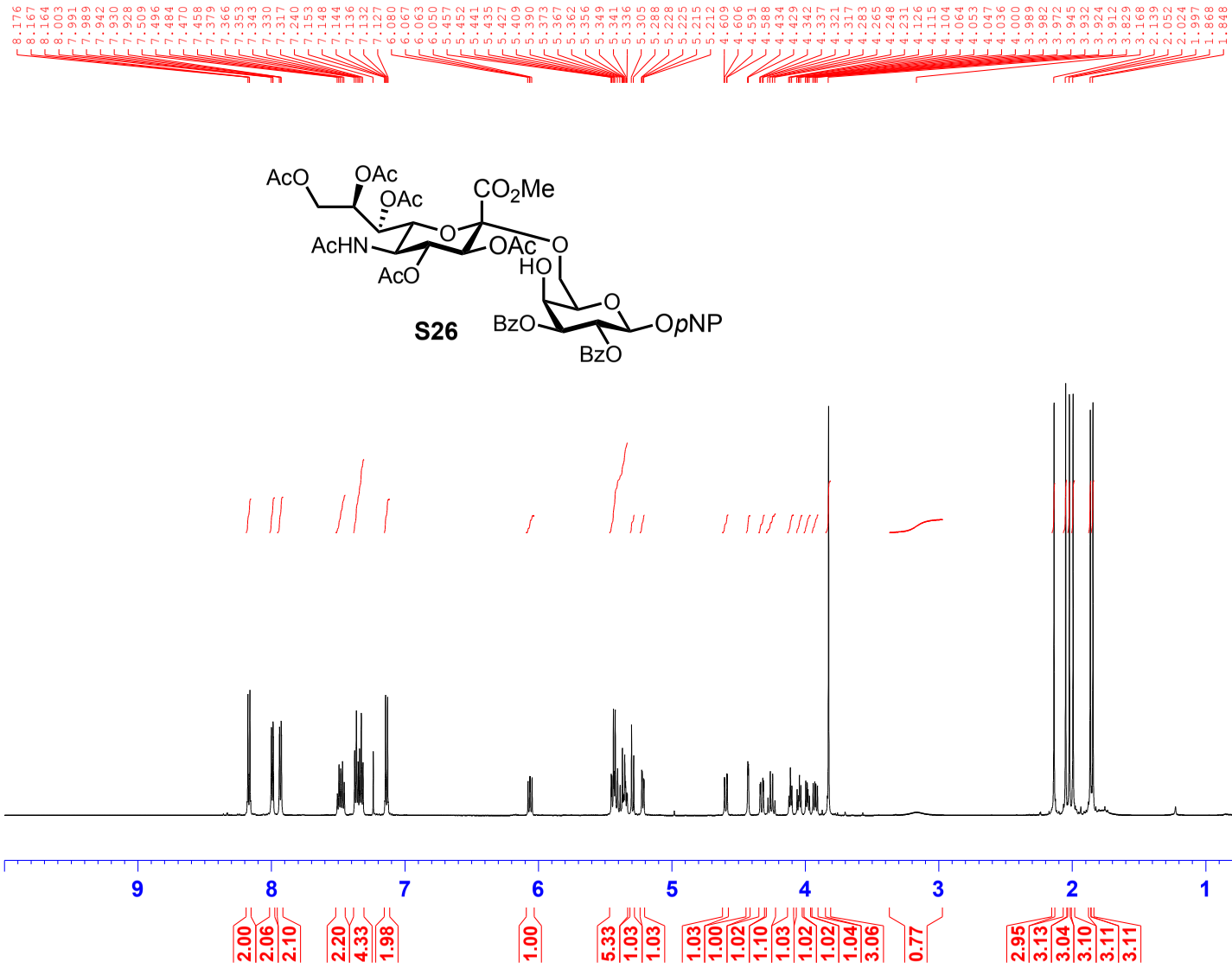
170.66
169.97
169.63
168.48
168.32
165.68
165.26
161.74
142.68
137.91
133.34
133.17
129.85
129.66
129.34
128.91
128.40
128.32
128.19
127.97
127.58
125.71
116.76
99.65
98.40
77.21
77.00
76.79
75.10
74.14
73.99
73.94
72.82
71.59
71.05
69.65
67.57
66.95
63.77
63.28
52.89
48.39
23.03
20.89
20.81
20.70
20.55
AcO
OAc
OAc
CO2Me
AcHN
O
OAc
O
BnO
AcO
O
BzO
OpNP
BzO
S25
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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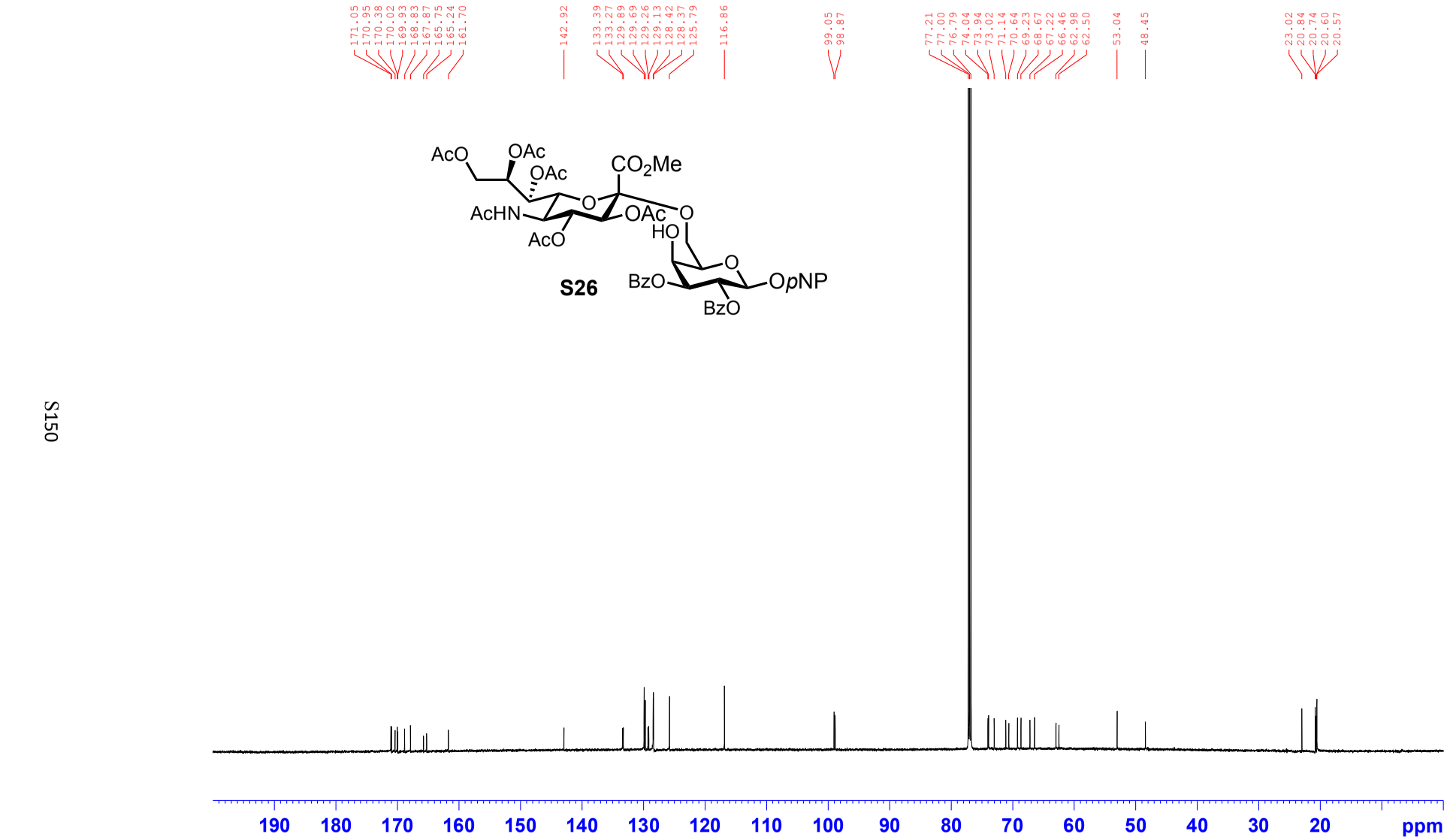
7.989
7.942
7.930
7.928
7.509
7.496
7.484
7.470
7.458
7.379
7.366
7.353
7.343
7.330
7.317
7.240
7.153
7.148
7.144
7.136
7.132
7.127
6.080
6.067
6.063
6.050
5.457
5.452
5.441
5.435
5.427
5.409
5.390
5.373
5.367
5.362
5.356
5.349
5.341
5.336
5.305
5.288
5.228
5.225
5.215
5.212
4.609
4.606
4.591
4.588
4.434
4.429
4.342
4.337
4.321
4.317
4.283
4.265
4.248
4.231
4.126
4.115
4.104
4.064
4.053
4.047
4.036
4.000
3.989
3.982
3.972
3.945
3.932
3.924
3.912
3.829
3.168
2.139
2.052
2.024
1.997
1.868
1.848
AcO
OAc
OAc
CO2Me
AcHN
O
OAc
O
HO
AcO
O
BzO
OpNP
BzO
S26
9
8
7
6
5
4
3
2
1
0 ppm
2.00
2.06
2.10
2.20
4.33
1.98
1.00
5.33
1.03
1.03
1.03
1.00
1.02
1.10
1.03
1.02
1.02
1.04
3.06
0.77
2.95
3.13
3.04
3.10
3.11
3.11


171.05
170.95
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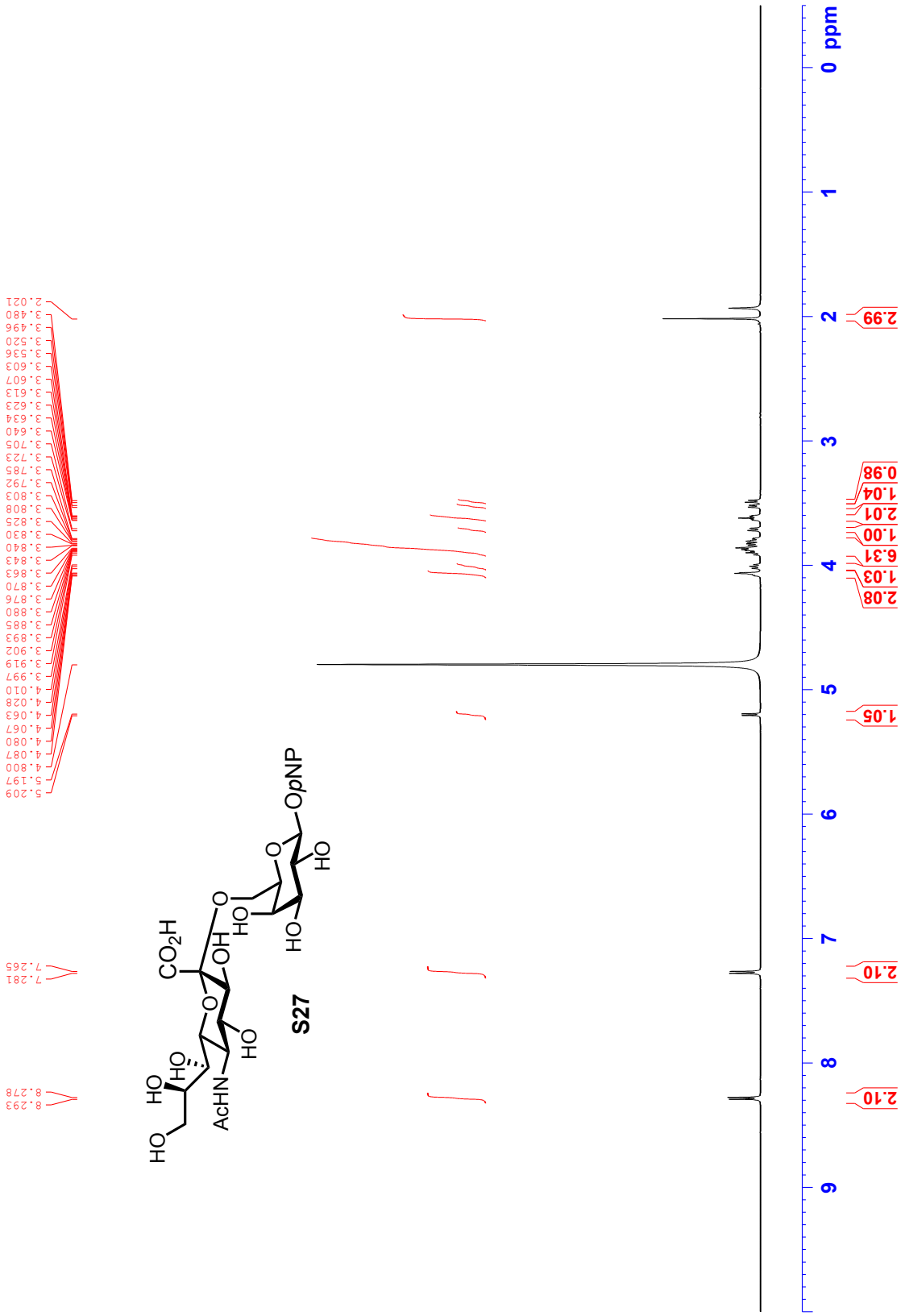
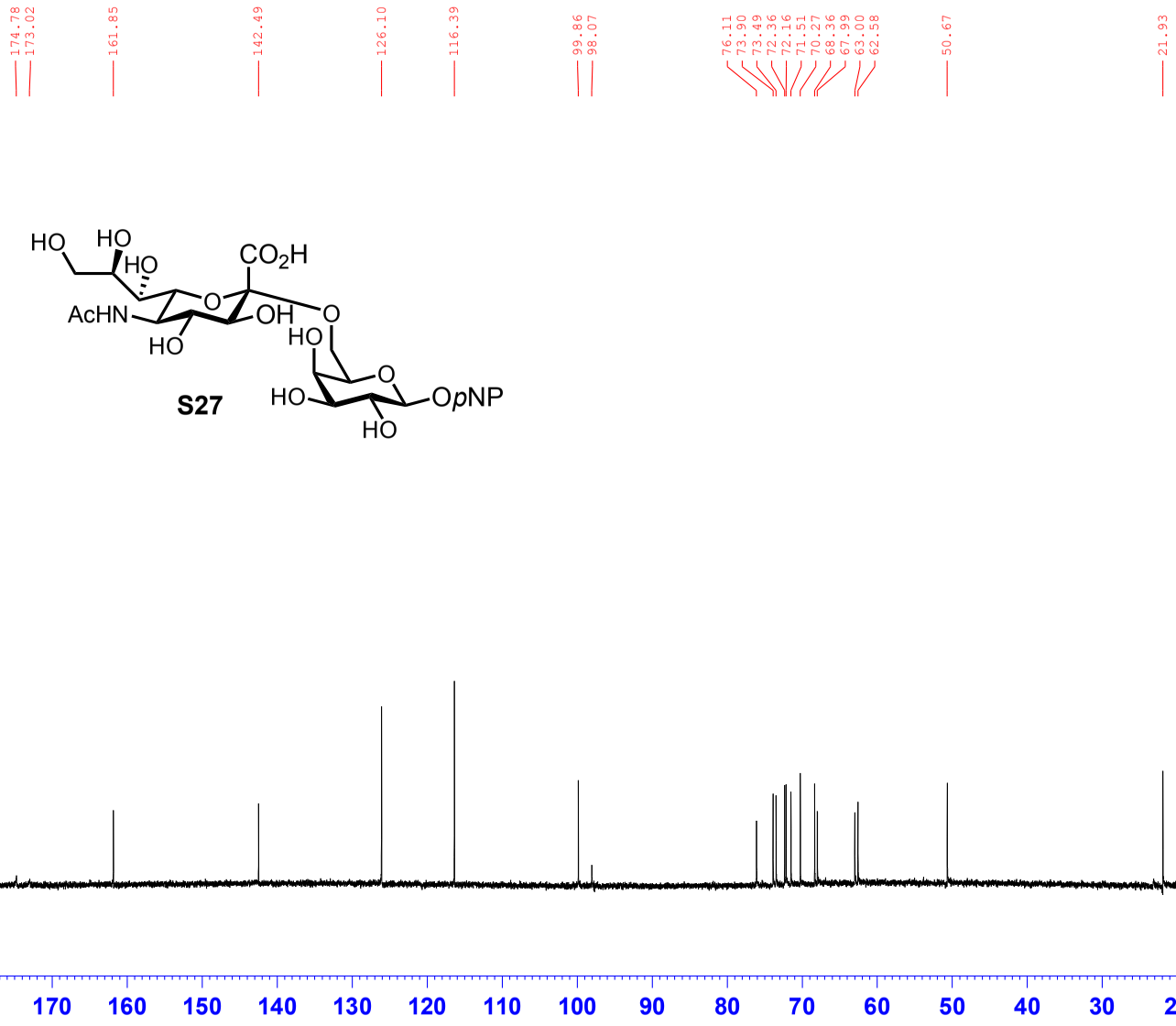
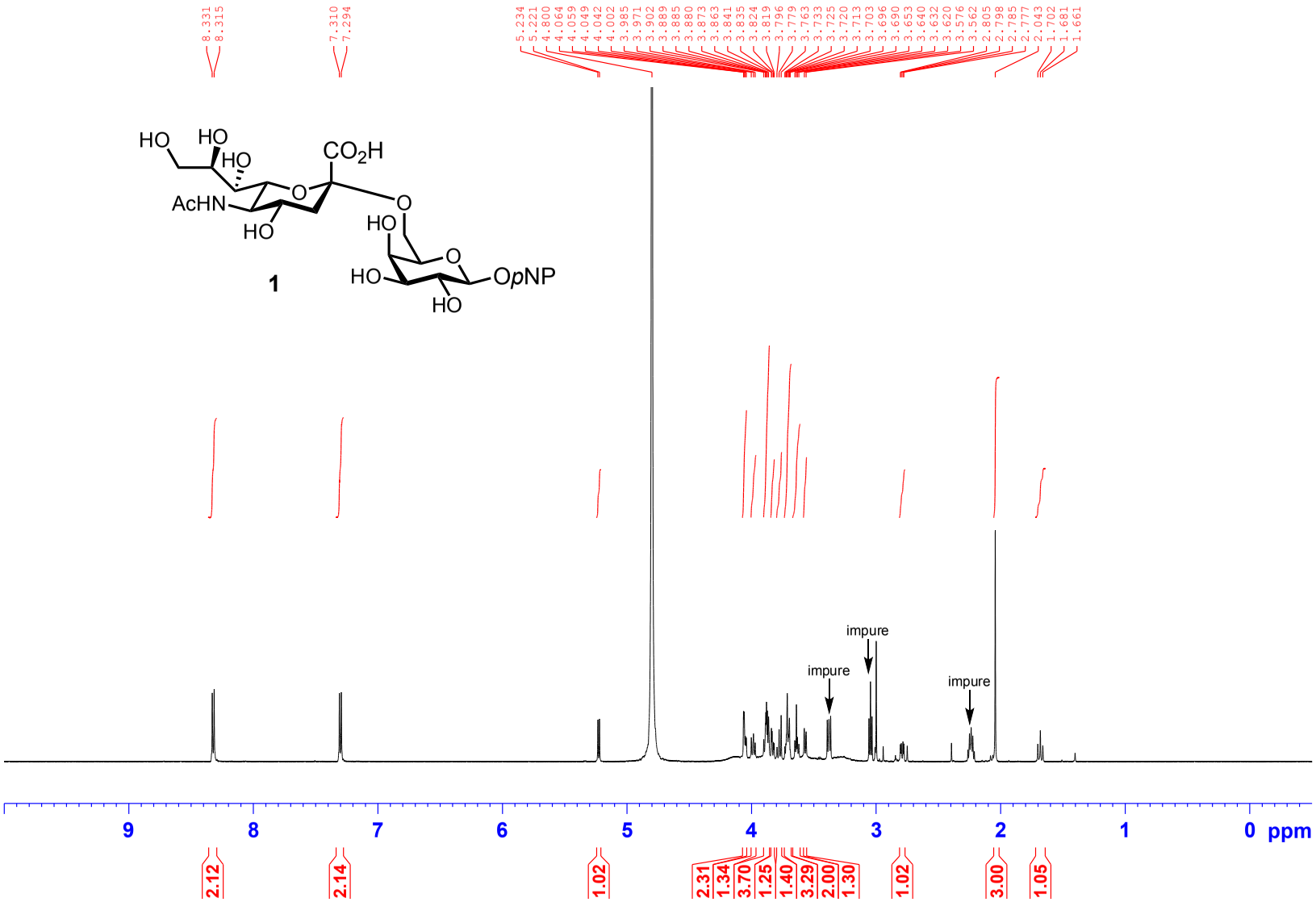
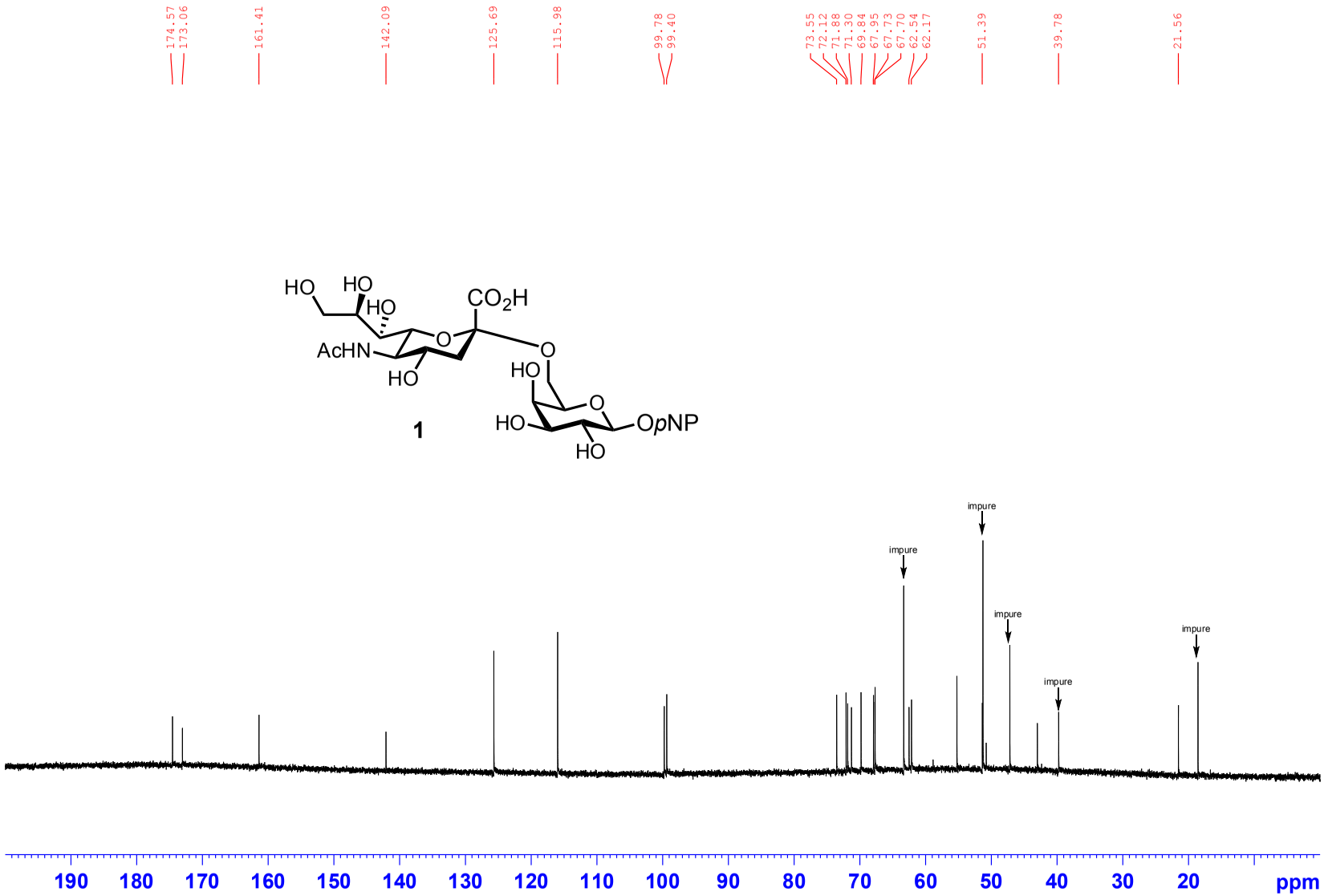
168.83
167.87
165.75
165.24
161.70
142.92
133.39
133.27
129.89
129.69
129.26
129.13
128.42
128.37
125.79
116.86
99.05
98.87
77.21
77.00
76.79
74.04
73.94
73.02
71.14
70.64
69.23
68.67
67.22
66.46
62.98
62.50
53.04
48.45
23.02
20.84
20.74
20.60
20.57
AcO
OAc
OAc
CO2Me
AcHN
O
OAc
O
HO
AcO
O
BzO
OpNP
BzO
S26
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

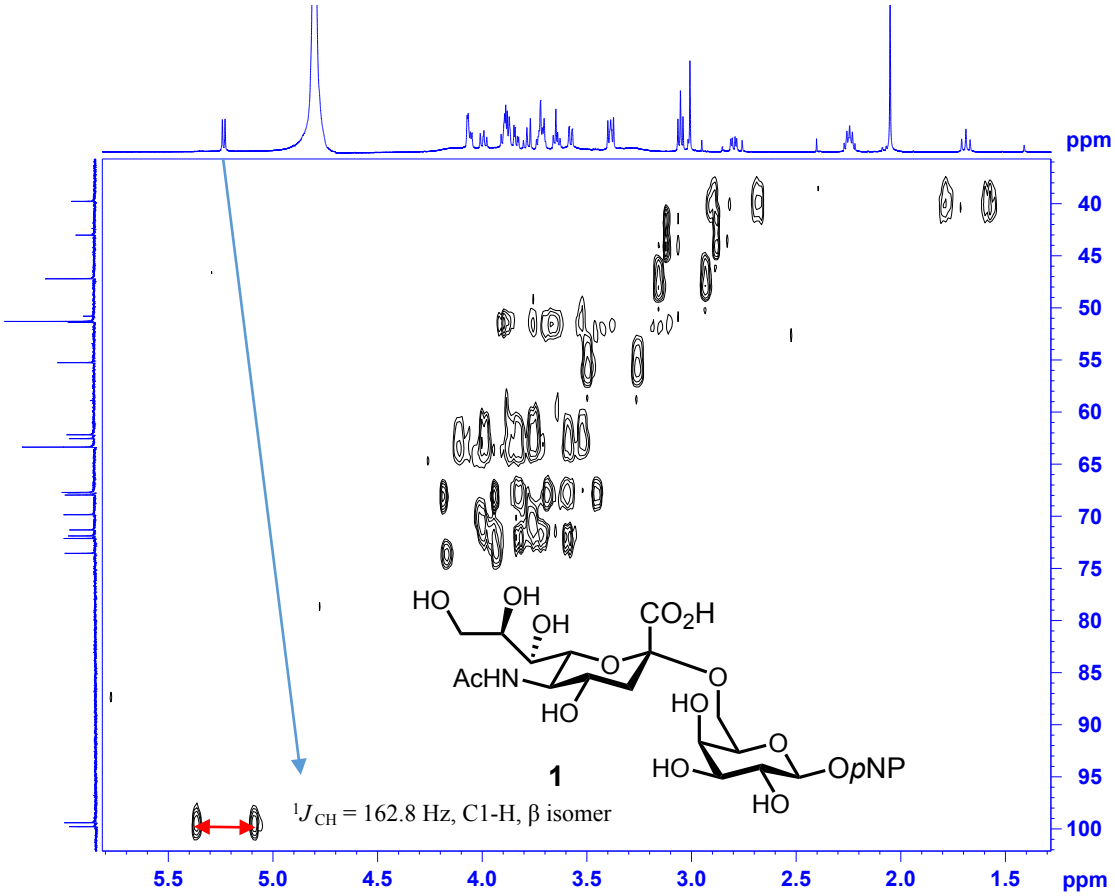

S27
OpNP
AcHN
CO2H
OH
HO
O
2.99
2.08
1.03
6.31
1.00
2.01
1.04
0.98
1.05
2.10
2.10
0 ppm

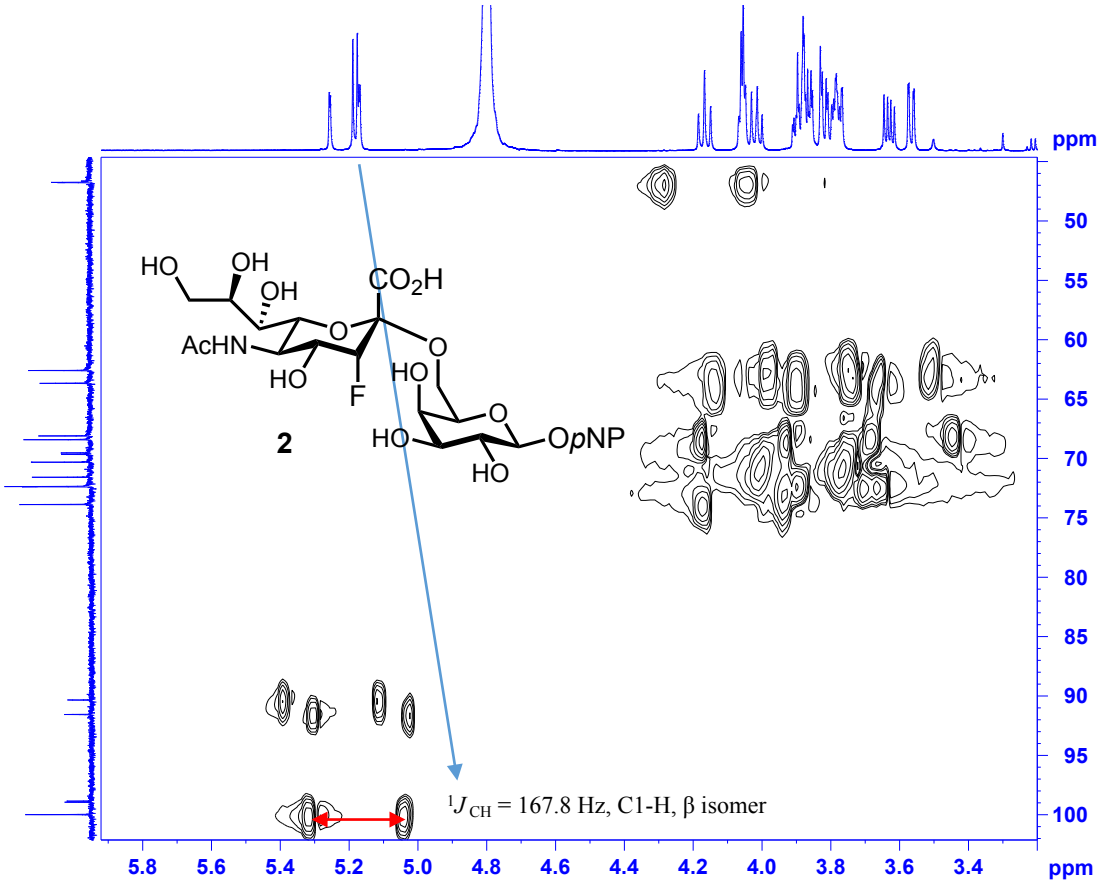

174.78
173.02
161.85
142.49
126.10
116.39
99.86
98.07
76.11
73.90
73.49
72.36
72.16
71.51
70.27
68.36
67.99
63.00
62.58
50.67
21.93
HO
HO
HO
AcHN
HO
O
CO2H
OH
O
HO
O
HO
OpNP
HO
S27
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

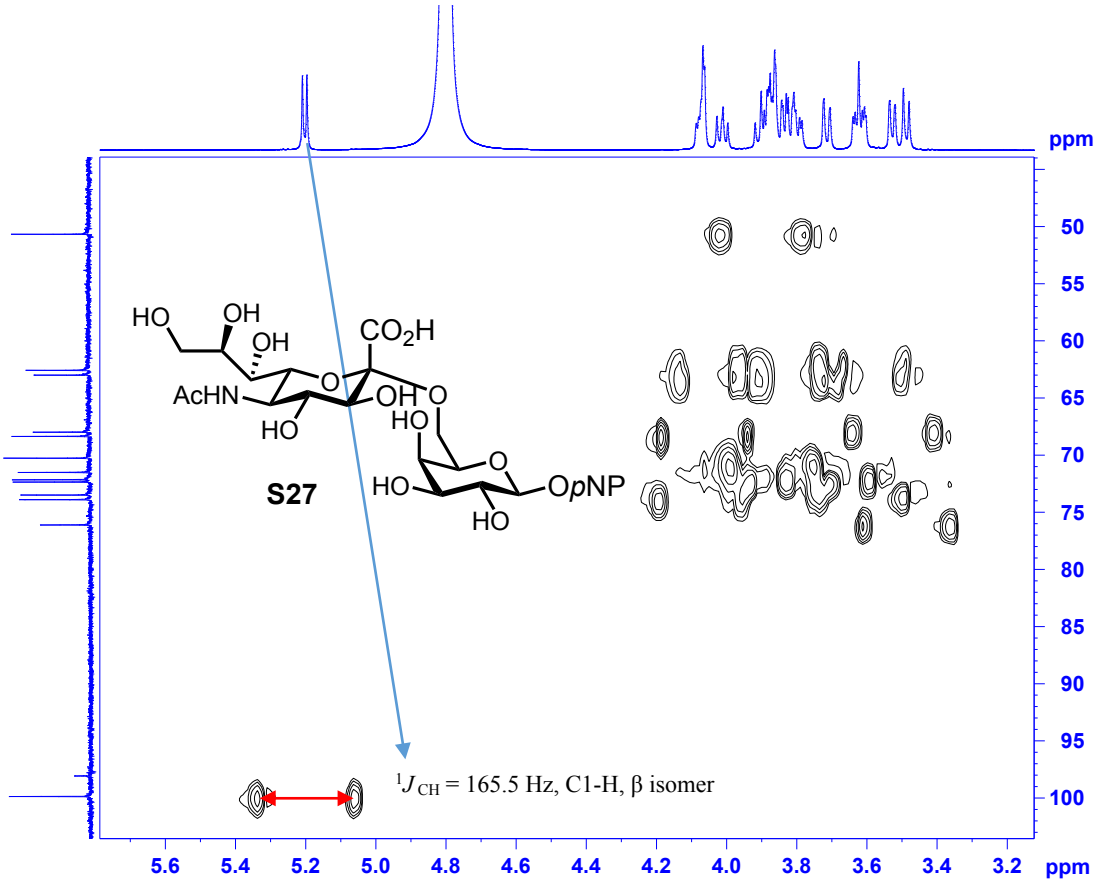

8.331
8.315
7.310
7.294
5.234
5.221
4.800
4.064
4.059
4.049
4.042
4.002
3.985
3.971
3.902
3.889
3.885
3.880
3.873
3.863
3.841
3.835
3.824
3.819
3.796
3.779
3.763
3.733
3.725
3.720
3.713
3.703
3.696
3.690
3.653
3.640
3.632
3.620
3.576
3.562
2.805
2.798
2.785
2.777
2.043
1.702
1.681
1.661
HO
HO
HO
CO2H
AcHN
HO
O
O
HO
HO
O
OpNP
HO
1
impure
impure
impure
9
8
7
6
5
4
3
2
1
0
ppm
2.12
2.14
1.02
2.31
1.34
3.70
1.25
1.40
3.29
2.00
1.30
1.02
3.00
1.05


174.57
173.06
161.41
142.09
125.69
115.98
99.78
99.40
73.55
72.12
71.88
71.30
69.84
67.95
67.73
67.70
62.54
62.17
51.39
39.78
21.56
HO
HO
HO
CO2H
AcHN
O
O
HO
HO
HO
O
OpNP
HO
1
impure
impure
impure
impure
impure
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

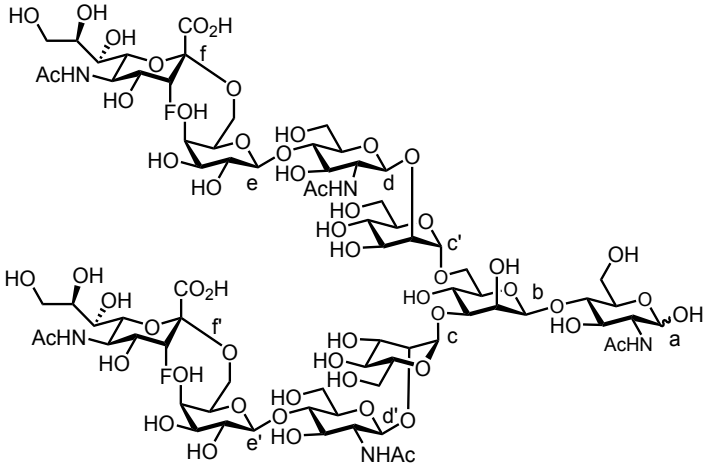
Coupled HSQC 2D NMR Spectra for Compound 1, 2 and S27.



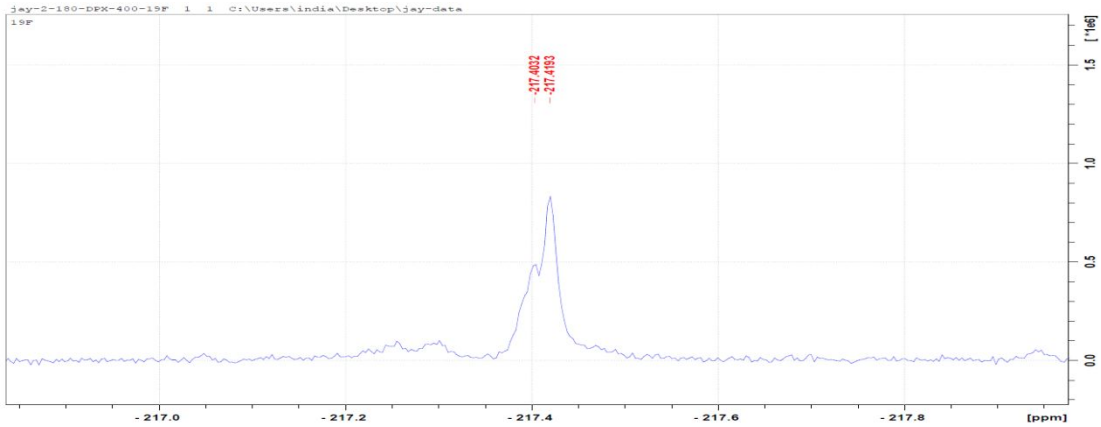



ppm
50
55
60
65
70
75
80
85
90
95
100
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
ppm
HO
OH
OH
AcHN
HO
O
CO2H
OH
O
HO
HO
O
HO
OpNP
HO
S27
1JCH = 165.5 Hz, C1-H, β isomer

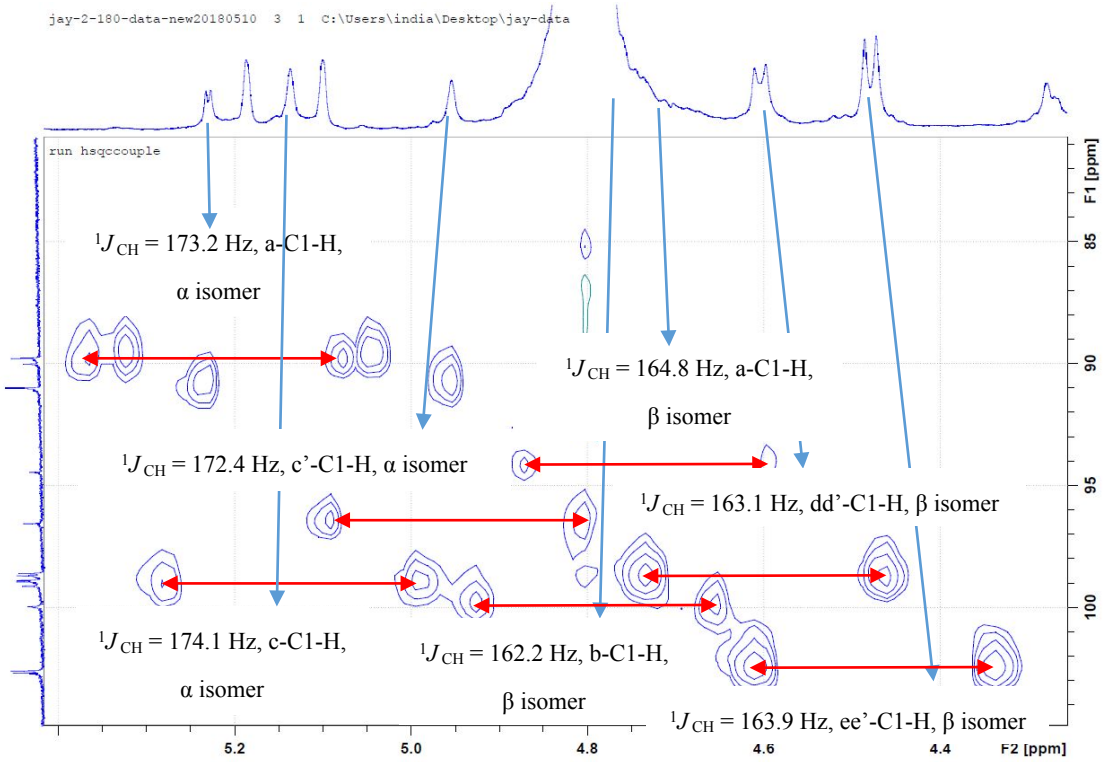
^{19}F and 2D NMR Spectra for Compound 17



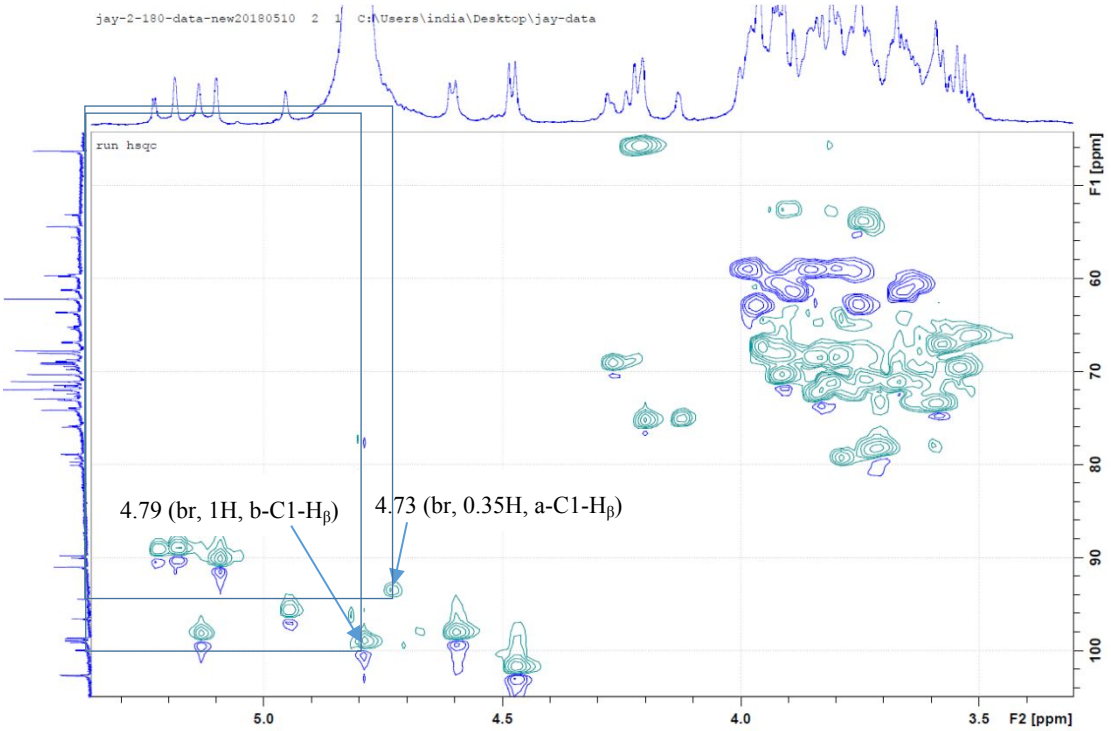
^{19}F



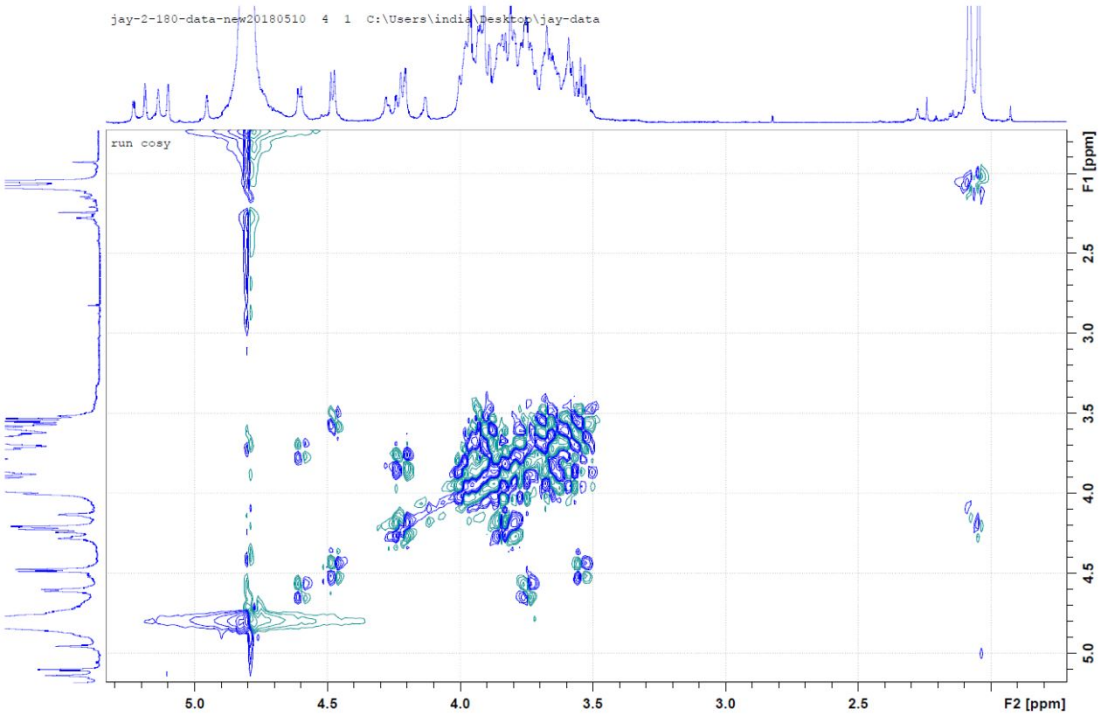
decoupling hsqc



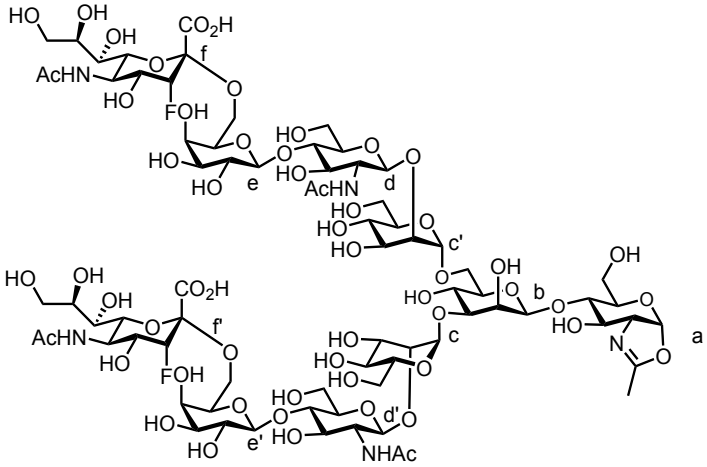
Hsqc


jay-2-180-data-new20180510 2 1 C:\Users\india\Desktop\jay-data
run hsqc
4.79 (br, 1H, b-C1-Hβ)
4.73 (br, 0.35H, a-C1-Hβ)
F1 [ppm]
F2 [ppm]

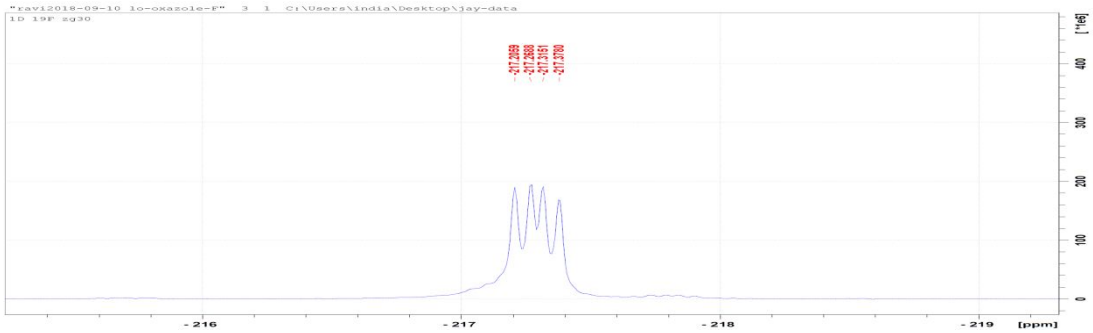
cosy


jay-2-180-data-new20180510 4 1 C:\Users\india\Desktop\jay-data
run cosy
F1 [ppm]
F2 [ppm]

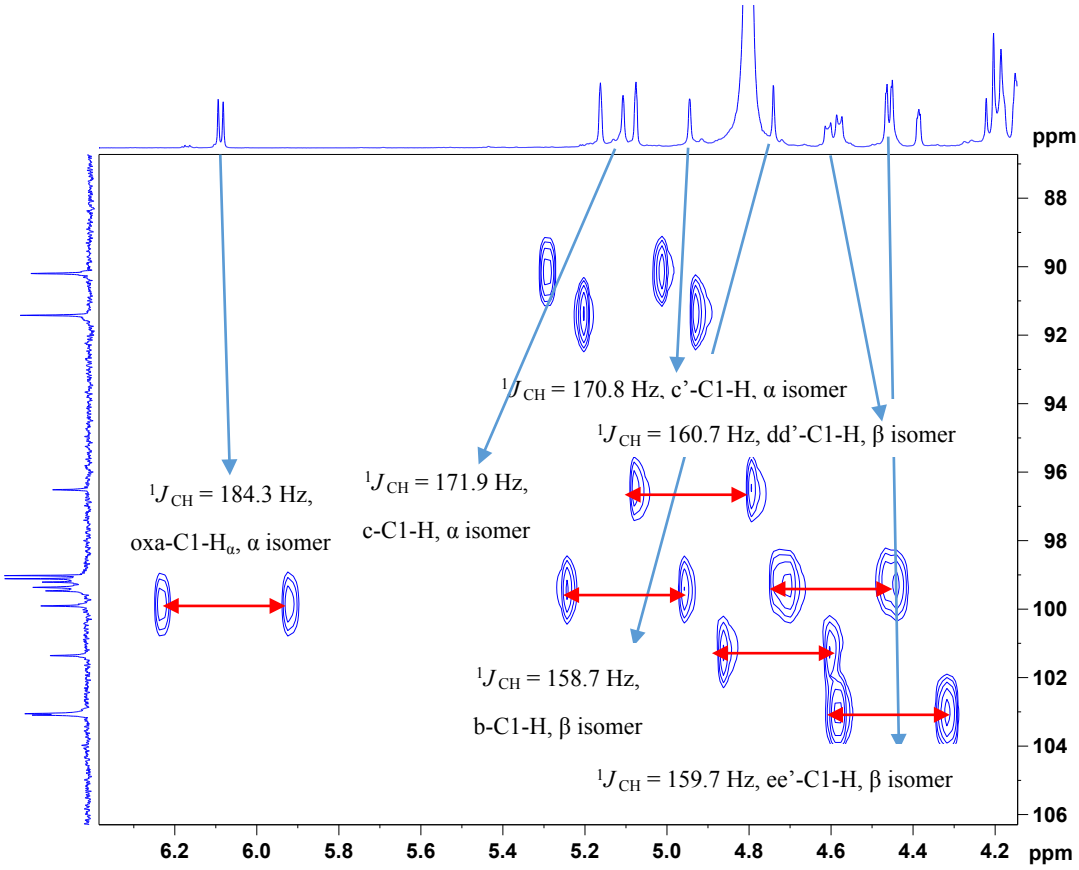
^{19}F and 2D NMR Spectra for Compound S1



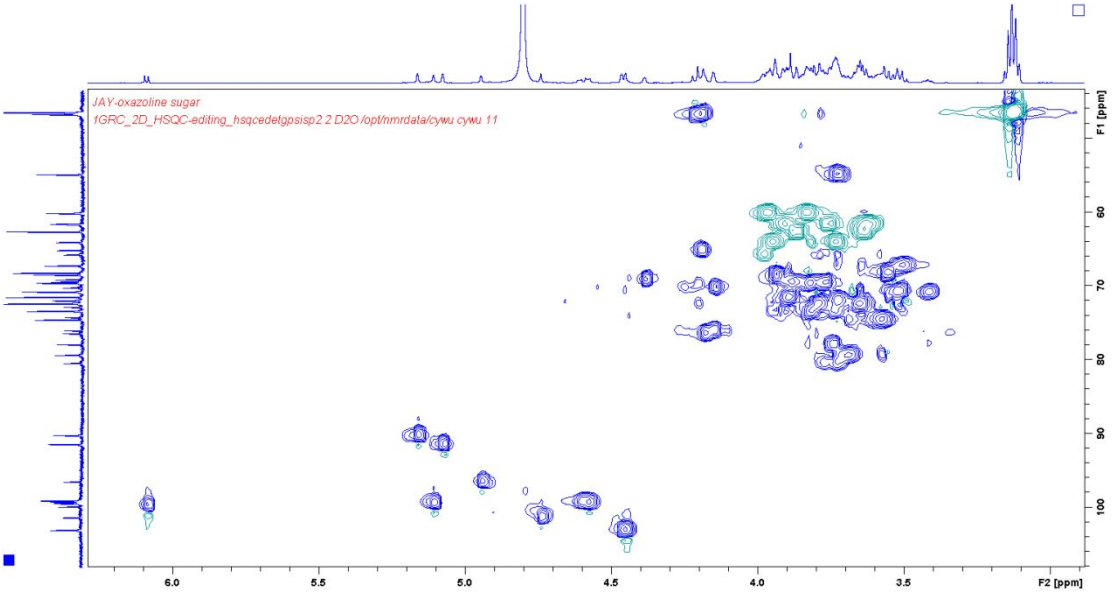
^{19}F



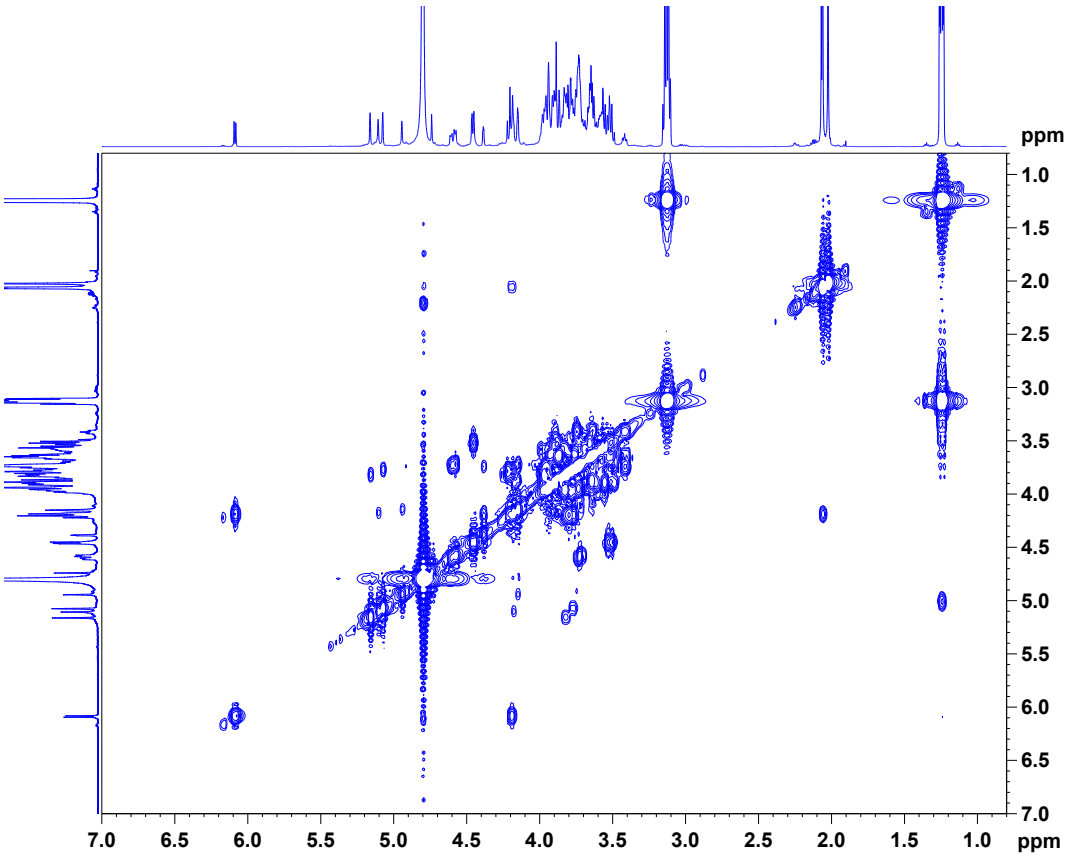
decoupling hsqc



Hsqc


JAY-oxazoline sugar
fGRC_2D_HSQC-editing_hsqcedetgpsisp2.2 D2O /opt/mmrdata/cywu cywu 11
F1 [ppm]
F2 [ppm]

cosy


ppm
ppm