Online Supporting Information I

Modular synthesis of *N*-glycans and arrays for hetero-ligand binding analysis of HIV antibodies

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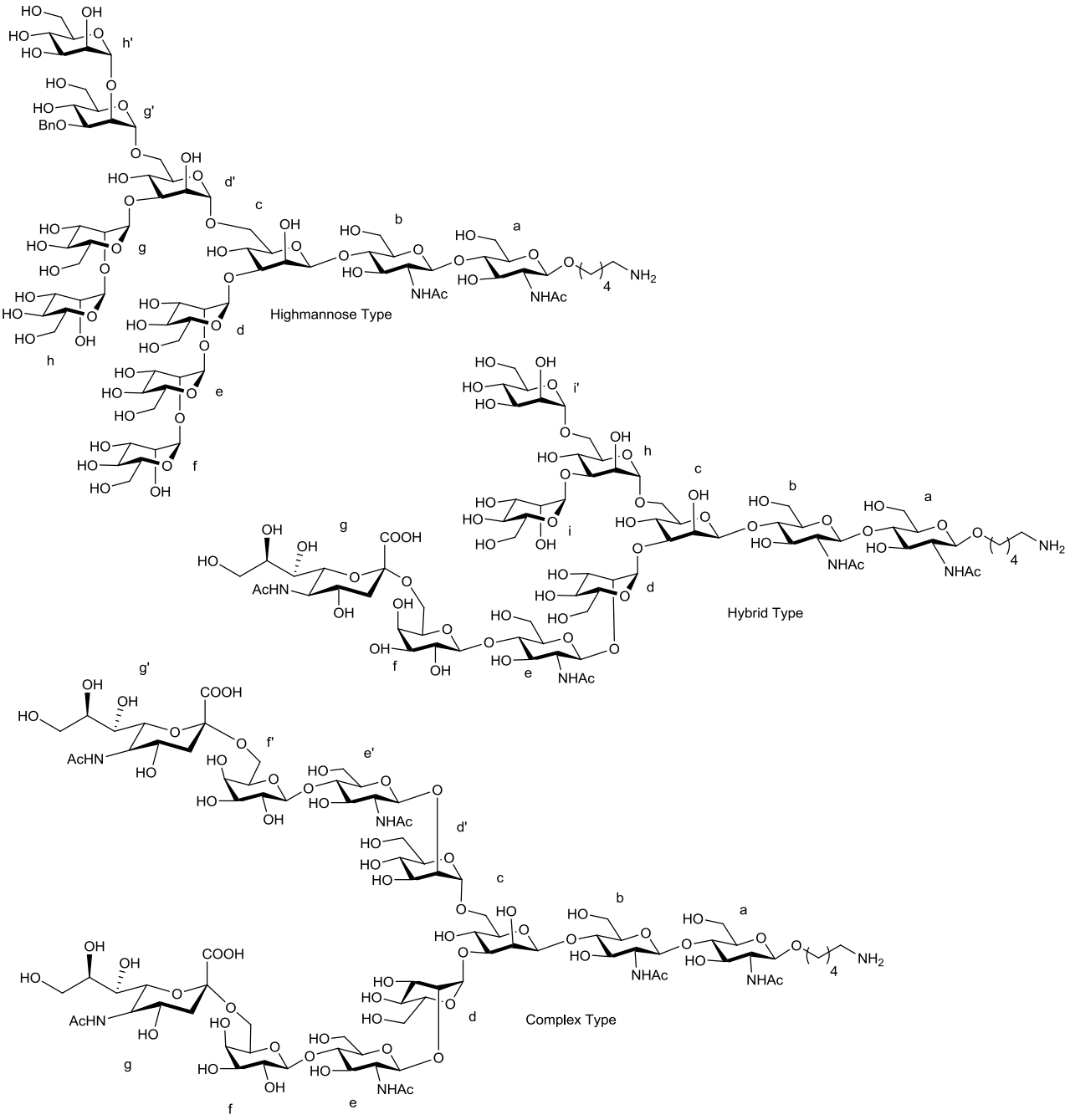
1. Chemial Synthesis

i. Materials and Methods

All reagents were purchased from Sigma Aldrich, Across and used without further purification. Dry solvents were purchased from a commercial source without further distillation. Pulverized Molecular Sieves MS-4 Å (Aldrich) for glycosylation was activated by heating at 350 ^{o}C for 3 h. Reactions were monitored by analytical thin-layer chromatography (TLC) in EM silica gel 60 F254 plates and visualized under UV (254 nm) and/or by staining with acidic ceric ammonium molybdate or *p*-anisadehyde. Flash chromatography was performed on silica gel (Merck) of 40-63 μm particle size. ^{1}H NMR spectra were recorded on a Bruker AVANCE 600 (600 MHz) spectrometer at 25 ºC. All ^{1}H Chemical shifts (in ppm) were assigned according to $CDCl_3$ (δ = 7.24 ppm) and D_2O (δ = 4.80 ppm). ^{13}C NMR spectra were obtained with Bruker AVANCE 600 spectrometer and were calibrated with $CDCl_3$ (δ = 77.00 ppm). Coupling constants (*J*) are reported in hertz (Hz). Splitting patterns are described by using the following abbreviations: s, singlet; brs, broad singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublet; m, multiplet. ^{1}H NMR spectra are reported in the following order: chemical shift, multiplicity, coupling constant(s) and number(s) of protons. All NMR signals were assigned on the basis of ^{1}H NMR, COSY, HSQC, HMQC, TOCSY, and ^{13}C experiments. High resolution ESI mass spectra were recorded on a Bruker Daltonics spectrometer. NHS coated glass slides were purchased from SCHOTT (Nexterion H). Broadly neutralizing HIV antibodies PG9, PG16 and PGT141-145 were kindly gifted by Prof. Peter Kwong, NIH (PG9/PG16 also purchased from Polymun, Vienna Austria). PGT128 was kindly gifted by Prof. Dennis Burton, TSRI. Secondary antibody DyLight649-conjugated donkey anti-Human IgG was purchased from Jackson Immuno Research. Cytidine 5'-triphosphate (CTP), N-Acetylneuraminic acid (Neu5Ac), UDP galactose, L-fucose and Phospho (enol) pyruvic acid (PEP) were purchase from Sigma-Aldrich.

NMR Nomenclature. The individual sugar residues of highmannose, hybrid and compelx type oligosaccharides have been labeled as shown bellow.



ii. General Procedures.

1. Enzyme expression, purification and reactions:

The functional domain of α-2,3 sialyltransferase (JTFAJ-16)[1] and α-2,6 sialyltransferase (JT-ISH-224)[2] were obtained according to our previous report[3]. Enzymes β-1, 4 galactosyl transferases from bovine milk was purchased from Sigma. Enzyme α-1, 2 fucosyl transferases (Human Fut2 derived from HEK-293 cells) was purchansed from R&D SYSTEMS. The enzymes used in this work including *Bacteroides fragilis* L-fucokinase/GDP-fucose pyrophosphorylase (FKP), pyruvate kinase (PK), pyrophosphatase (PPA), cytidine monophosphate kinase (CMK), CMP-sialic acid synthetases (CSS) and α 1–3-fucosyltransferase from Helicobacter pylori (Hp1–3FTΔ26695) are examples of suitable recombinant enzymes that are expressed and purified in our laboratory. Enzymatic reactions with cofactor regeneration were carried out according to the procedure reported previously from our group[4].

2. Global deprotection:

Method 1 (for glycans with -Nphthallamide protection at all glucosamine residues): A mixture of protected glycans (50 mmol) and 10 mL of ethylene diamine: *n*BuOH (1:4) was stirred at 90 ^{o}C for overnight. Volatiles were then evaporated and the crude product was reacted with 10 mL Ac_2O/pyridine (1:2) for overnight. The solvents were removed using high vacuum and product was purified by flash column chromatography (acetone: toluene, 2/8, v/v). Product was de-acetylated using sodium methoxide in MeOH (10 mL) for overnight. The reaction mixture was neutralized by using IR-120, filtered and concentrated in *vacuo.* The residue was purified by flash column chromatography (acetone: toluene, 3/7, v/v). Product was dissolved in 10 mL MeOH: H_2O: HCOOH (6:3:1), $Pd(OH)_2$ (50% by weight) was added and the reaction mixture was hydrogenated for overnight. The reaction mixture was filtered through Celite and concentrated in *vacuo.* The residue was purified by Bio-Gel P-2 (BIO-RAD) column chromatography using water as eluent, and the product was the lyophilized to get desired oligosaccharides as a white color powder.

Method 2 (for glycans with -NHTroc protection at all glucosamine residues): A mixture of protected glycans (50 mmol) and lithium hydroxide (250 mmol) in 10 mL of 1, 4 dioxane: H_2O (4:1) was stirred at 90 ^oC for overnight. Volatiles were then evaporated and the crude product was reacted with 10 mL Ac_2O: pyridine (1:2) for overnight. The solvents were removed using high vacuum and product was purified by C18 gel column chromatography (MeOH: H_2O as an eluent). The product was de-acetylated using sodium methoxide in MeOH (10 mL) for overnight. The reaction mixture was neutralized by using IR-120, filtered and concentrated in *vacuo.* The residue was purified by C18 gel column chromatography (MeOH: H_2O as an eluent). The product was dissolved in 10 mL MeOH: H_2O: HCOOH (6:3:1), $Pd(OH)_2$ (50% by weight) was added and the mixture was hydrogenated for overnight. The reaction mixture was filtered through Celite and concentrated in *vacuo.* The residue was purified by Bio-Gel P-2 (BIO-RAD) column chromatography using water as eluent. The product was the lyophilized to get desired oligosaccharides as a white color powder.

3. Enzymatic sialylation with cofactor regeneration: Glycans (5 µmol), Neu5Ac (10 µmol), ATP (0.05 µmol), CTP (1 µmol), phosphoenolpyruvate (10 µmol, monopotassium salt), cytidine monophosphate kinase (CMK, 80 units), CMP-sialic acid synthetases (CSS, 120 units), pyruvate kinase (PK, 40 units), pyrophosphatase (PPA, 40 units) and α 2,6/2,3 sialyltransferase (150 units) were dissolved in 50 µmol Tris buffer (25 mM, pH 7.5). The reaction was incubated at 37 ℃ with gentle agitation. Complete consumption of starting material was confirmed by mass spectrometric analysis. The reaction mixture was centrifuged and the supernatant subjected to gel filtration over P2-Biogel (eluent water). Fractions containing the product were combined and lyophilized to give the respective products as amorphous white solids.

4. Enzymatic β-1, 4-galactosylation:

Glycans (1 eq.) and UDP galactose (2 eq. per galactose) were dissolved in Tris buffer (25 mM, pH 7.5) containing $MnCl_2$ (10 mM). Enzyme β-1, 4-GalT-1 (150 units) was added to achieve a final concentration of glycan ranging from 2-5 mM. The resulting reaction mixture was incubated at 37 ^oC for 24 h. In di-galactosylation case, when TLC showed mono-galactosylated

intermediate, additional UDP-galactose (2eq), β-1,4-GalT (100 units) were added and incubated at 37 ^{o}C until complete consumption of intermidiate. The reaction mixture was centrifuged and the supernatant was subjected to gel filtration over P2-Biogel (eluent water). Fractions containing the product were combined and lyophilized to give the respective products as amorphous white solids.

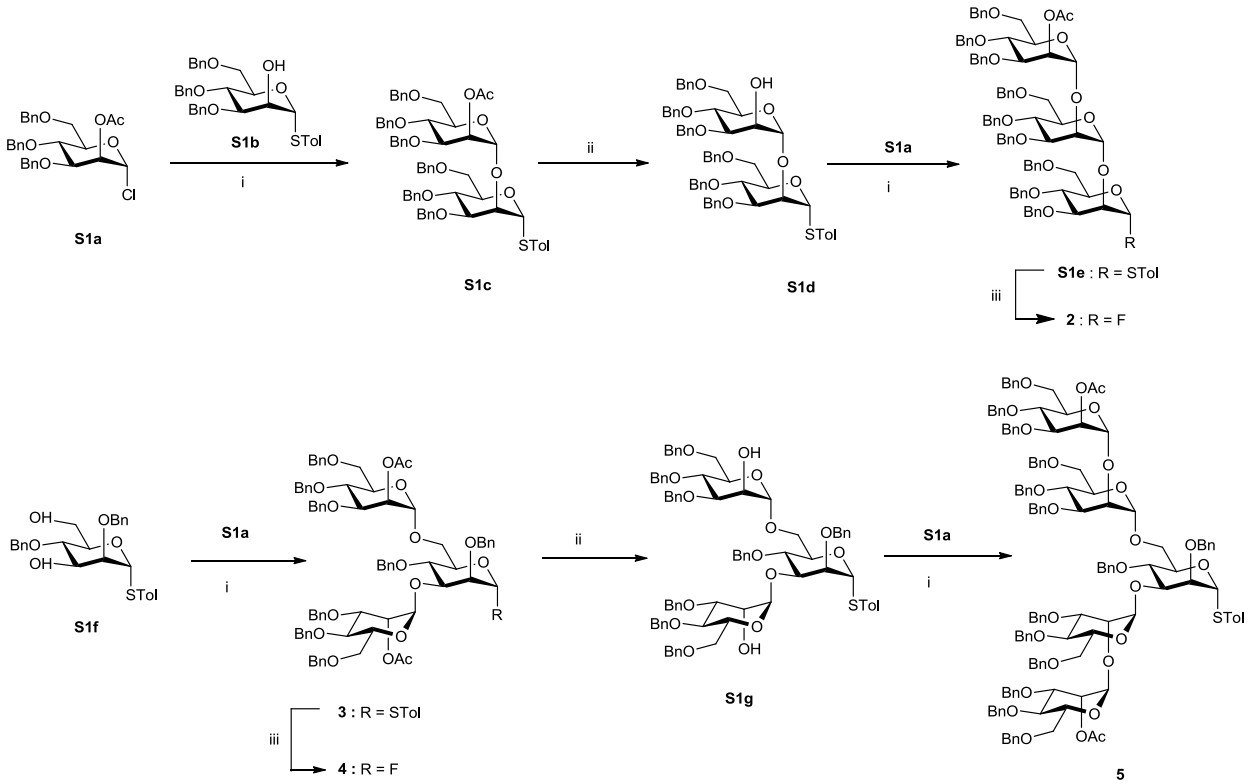
5. Enzymatic α–1,2/1,3-fucosylation : To a solution of glycans (5 µmol), L-fucose (5 µmol), ATP (0.5 µmol), of GTP (0.5 µmol), PEP (10 µmol), and 10 mM $MnCl_2$ in a 25 mM Tris buffer (pH 7.4) was added L-fucokinase/GDP-fucose pyrophosphorylase (FKP, 200 units), PK (200 units), PPA (200 units), and α-1,2/1,3-fucosyltransferase (200 units), and the mixture was incubated at 37 ℃ for overnight. The reaction mixture was centrifuged and the supernatant was subjected to gel filtration over P2-Biogel (eluent water). Fractions containing the product were combined and lyophilized to give the respective products as amorphous white solids.

iii. Synthesis of builing blocks 1-13.

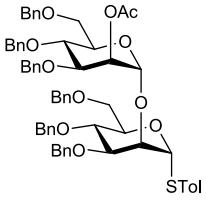
Synthesis of mono-, tri- and pentasaccharide builing blocks 1-5.

The mannosyl trichloroacetimidate building block **1** was obtained by reported procedure[5]. The preparation of D1 arm trisaccharide **2** of $Man_9GlcNAc_2$ began by glycosylation of mannosyl chloride **S1a**[6] and thioglycoside acceptor **S1b**[7] under the treatment of 2,6-di-*tert*-butylpyridine (DTBP) and silver triflate (AgOTf) to obtain disaccharide **S1c** (Scheme S1). Zemplén deacetylation of **S1c** at 2-O position followed by glycosylation with **S1a** by employing DTBP and AgOTf gave desired trisaccharide **S1e** in 93% yield. The leaving group modification of **S1e** from thioglycoside to glycosyl fluoride **2** was performed under the action of *N*-bromosuccinimide (NBS) and diethylaminosulfur trifluoride (DAST). The fluoride transformation provided us better results in terms of α-selectivity and excellent yield during glycosylation with chitobiose trisaccharide. Under the activation of AgOTf, the condensation of donor **S1a**[6] and acceptor **S1f**[7] was performed to afford trimannose **3,** which was subsequently deacetylated and further di-glycosylated with **S1a** to afford D2/D3 arm pentasaccharide **5** in 71% yield. Compound **3** was next subjected to leaving group modification to trimannosyl fluoride **4**

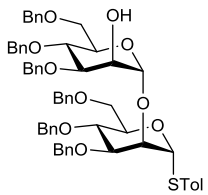
by using NBS and DAST in 68% yield. Careful observation of our strategy revealed that a single mannosyl chloride donor **S1a** and a unique DTBP/AgOTf mediated glycosylation condition was utilized to get D1, D2/D3 arm tri- and pentasaccharide intermediates in excellent yield.



Scheme S1 | Preparation of compound 1-5. **i,** DTBP, AgOTf, 4 Å MS, CH_2Cl_2, -30 ^oC to RT, overnight; **S1c**: 93%, **S1e**: 91%, **3**: 66%, **5**: 74%; **ii**, NaOMe, MeOH: CH_2Cl_2 = 1/1; **S1d**: 89%, **S1g**: 90%; **iii**, N-bromo succinimide (NBS), DAST, CH_2Cl_2, -30 ℃ to -10 ℃; **2**: 58%, **4**:61%. DTBP: 2, 6-di-tert-butylpyridine; DAST: Diethylaminosulfur trifluoride; AgOTf: Silver trifluromethanesulfonate.

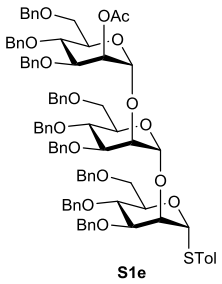


***p*-Tolyl-2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-1-thio-α-D-mannopyranoside (S1c):** To a solution of acceptor **S1b** (1.70 g, 3.05 mmol) and donor **S1a** (2.34 g, 4.58 mmol) in 20 mL CH_2Cl_2 was added activated 4 Å molecular sieves and stirred for 1 h at RT. In a separate flask, AgOTf (1.19 g, 4.58 mmol) and DTBP (1.03 mL, 4.58 mmol) in 10 mL of CH_2Cl_2 were stirred with 4 Å MS for 1 h. The flask containing the AgOTf/DTBP was cooled to -30 ℃ and solution containing mixture of donor and acceptor was added over 5 min. The solution was stirred with gradual warming up to room temperature over 24 h. TLC (ethyl acetate: hexane, 2/8) indicated formation of product with consumption of starting material, the reaction was quenched with Et_3N, filtered through Celite, the filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL) and a brine (50 mL) solution. The organic layer was dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (0% → 15% EA in hexane) to afford **S1c** (2.90 g, 93%) as colorless foam. TLC (ethyl acetate: hexane = 2/8 v/v): R_f = 0.35; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38-7.16 (m, 30H, Ar-H), 7.11-7.09 (m, 2H, Ar-H), 7.00 (d, *J* = 8.4 Hz, 2H, Ar-H), 5.44 (s, 1H, H-1^a), 5.51 (d, *J* = 2.4 Hz, 1H), 5.06 (s, 1H, H-1^b), 4.88 (d, *J* = 11.8 Hz, 1H), 4.81 (d, *J* = 11.2 Hz, 1H), 4.73-4.37 (m, 10H), 4.29 (t, *J* = 8.9 Hz, 1H), 4.22 (s, 1H), 3.96-3.88 (m, 4H), 3.83-3.71 (m, 2H), 3.69-3.63 (m, 2H), 3.55 (d, *J* = 12.1 Hz, 1H), 2.26 (s, 3H, -C(O)CH_3), 2.13 (s, 3H, -CH_3 of STol); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.49, 138.75, 138.67, 138.62, 138.42, 138.32, 138.24, 137.87, 132.55, 130.51, 128.77, 128.64, 128.61, 128.56, 128.52, 128.39, 128.29, 128.20, 128.15, 128.03, 127.99, 127.94, 127.78, 127.63, 99.99, 87.78, 80.19, 78.35, 76.88, 75.48, 75.32, 75.03, 74.56, 73.46, 73.08, 72.47, 72.21, 72.18, 68.48, 69.02, 68.85, 21.42, 21.36; ESI-MS: *m/z* calcd for $C_{63}H_{66}O_{11}S$; 1030.4218; found 1053.4228 $(M + Na)^+$.



S1d

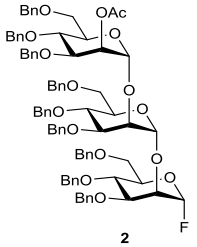
***p*-Tolyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-1-thio-α-D-manno pyranoside (S1d):** To a solution of compound **S1c** (1.01 g, 0.970 mmol) in 20 mL of methanol: CH_2Cl_2 (1/1) was added sodium methoxide (0.024 g, 0.42 mmol), stirred at RT until TLC (ethyl acetate: hexane, 3/7) indicated formation of a product with consumption of the starting material. The reaction mixture was neutralized with IR-120, filtered and concentrated *in vacuo* and the residue was purified by silica gel column chromatography (0% → 30% EA in hexane) to afford **S1d** (0.859 g, 89%) as a colorless oil. TLC (ethyl acetate: hexane = 3/7 v/v): R_f = 0.29; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33-7.10 (m, 32H, Ar-H), 6.96 (d, *J* = 7.8 Hz, 2H, Ar-H), 5.56 (s, 1H, H-1), 5.11 (s, 1H, H-1), 4.85 (d, *J* = 10.8 Hz, 1H), 4.75 (d, *J* = 10.8 Hz, 1H), 4.69-4.62 (m, 3H), 4.52-4.38 (m, 6H), 4.37 (d, *J* = 12.1 Hz, 1H), 4.25 (d, *J* = 12 Hz, 2H), 4.09 (s, 1H), 3.90-3.77 (m, 6H), 3.70 (d, *J* = 10.8 Hz, 1H), 3.62 (dd, *J* = 4.8, 8.2 Hz, 1H), 3.54 (d, *J* = 10.2 Hz, 1H), 2.23 (s, 3H, CH_3, STol); ^{13}C NMR (150 MHz, $CDCl_3$): δ 138.61, 138.42, 138.33, 138.24, 137.97, 137.51, 132.18, 130.38, 129.73, 128.55, 128.47, 128.38, 128.29, 128.24, 127.93, 127.91, 127.89, 127.86, 127.85, 127.78, 127.68, 127.57, 127.48, 127.45, 127.33, 101.23, 87.62, 80.06, 79.99, 76.52, 75.18, 75.01, 74.95, 94.35, 73.21, 73.18, 72.87, 72.38, 72.18, 71.69, 69.28, 68.70, 68.56, 19.45; ESI-MS: *m/z* calcd for $C_{61}H_{64}O_{10}S$; 988.4112; found 1011.4125 $(M + Na)^+$.



S1e

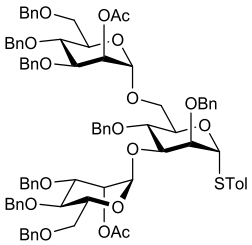
***p*-Tolyl-2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-1-thio-α-D-mannopyranoside (S1e):** To a solution of acceptor **S1d** (2.6 g, 2.62 mmol) and donor **S1a** (2.01 g, 3.94 mmol) in 10 mL CH_2Cl_2 was added activated 4 Å molecular sieves and stirred for 1 h at RT. In a separate flask,

AgOTf (1.02 g, 3.94 mmol) and DTBP (893 µL, 3.94 mmol) in 30 mL of CH_2Cl_2 were stirred with activated 4 Å molecular sieves for 1 h. The mixture of AgOTf /DTBP was cooled to -30 °C and a solution of donor and acceptor was added over 5 min. The solution was stirred with gradual warming up to RT over 24 h until TLC (ethyl acetate: hexane, 2/8) indicated formation of product with consumption of starting material. The reaction was quenched with Et_3N, filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL) and a brine (50 mL) solution. The organic layer was dried over Na_2SO_4, filtered and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (0% → 20% EA in hexane) to afford **S1e** (3.50 g, 91%) as colorless foam. TLC (ethyl acetate: hexane = 2/8 v/v): R_f = 0.41; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34-7.11 (m, 45H, Ar-H), 7.05-7.03 (m, 2H, Ar-H), 6.93 (d, *J* = 7.2 Hz, 2H, Ar-H), 5.65 (s, 1H, H-1), 5.50 (d, *J* = 3.0 Hz, 1H, H-1), 5.10 (d, *J* = 3.2 Hz, 1H, H-1), 4.82 (dd, *J* = 3.1, 10.2 Hz, 2H), 4.75 (d, *J* = 12.1 Hz, 1H), 4.68 (s, 2H), 4.60-4.54 (m, 8H), 4.35-4.19 (m, 9H), 3.90-3.84 (m, 4H), 3.78-3.72 (m, 2H), 3.66-3.63 (m, 3H), 3.55-3.52 (m, 1H), 3.46 (d, *J* = 4.2 Hz, 1H), 3.41 (dd, *J* = 3.4, 9.2 Hz, 1H), 3.31 (d, *J* = 9.8 Hz, 1H), 2.20 (s, 3H, -C(O)CH_3), 2.05 (s, 3H, CH_3, STol); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.84, 139.12, 138.85, 138.79, 138.65, 138.60, 138.52, 138.37, 138.25, 137.94, 137.60, 132.30, 130.75, 129.97, 129.90, 128.98, 128.63, 128.52, 128.33, 128.20, 128.03, 127.88, 127.64, 100.79, 96.52, 88.06, 80.83, 80.45, 76.45, 76.42, 76.04, 75.65, 75.21. 75.14, 74.69, 73.63, 73.05, 73.01, 72.95, 71.99, 71.87, 71.43, 69.66, 69.51, 69.35, 68.40, 68.34, 21.40, 21.36, 21.31; ESI-MS: *m/z* calcd for $C_{90}H_{94}O_{16}S$; 1462.6155; found 1485.6190 $(M + Na)^+$.



2

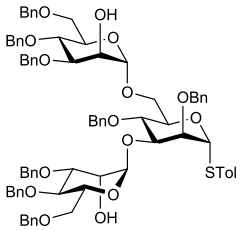
2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-1-α-D-mannopyranosyl fluoride (2): To a solution of trisaccharide **S1e** (0.6 g, 0.410 mmol) in CH_2Cl_2 (10 mL) at -30 ^oC was added NBS (0.218 mg, 1.23 mmol), stirred for 10 minutes. DAST (324 µL, 2.46 mmol) was added slowly and the resulting reaction mixture was stirred at -10 ℃ for 6 h. TLC (ethyl acetate: hexane, 3/7) indicated formation of product with consumption of starting material, the reaction was quenched with aq.$NaHCO_3$, and the filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL) and a brine (50 mL) solution. The organic layer was dried over Na_2SO_4, filtered and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (0% → 25% EA in hexane) to afford fluoride **2** (0.320 g, 58%) as white foam and 0.200 g alcohol (anomeric-OH) as side product. TLC (ethyl acetate: hexane = 3/7, v/v): R_f = 0.31; ^{1}H NMR (600 MHz, $CHCl_3$): δ 7.32-7.12 (m, 45H, Ar-H), 5.67 (d, *J* = 50.4 Hz, 1H, Ar-H), 5.49 (s, 1H, H-1), 5.16 (s, 1H, H-1), 4.99 (s, 1H, H-1), 4.82-4.77 (m, 3H), 4.65-4.38 (m, 15H), 4.30 (d, *J* = 12.1 Hz, 1H), 4.03 (s, 1H), 3.97-3.94 (m, 3H), 3.90-3.64 (m, 12H), 3.54 (d, *J* = 10.2 Hz, 1H), 2.11 (s, 3H, -C(O)CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.44, 138.77, 138.64, 138.60, 138.54, 138.46, 138.41, 138.28, 128.76, 128.64, 128.61, 128.54, 128.44, 128.31, 128.19, 128.13, 128.09, 128.04, 128.01, 127.95, 127.90, 127.87, 127.84, 127.79, 127.73, 107.65, 106.19, 101.04, 99.72, 78.56, 78.31, 75.45, 75.41, 75.31, 74.86, 74.59, 74.31, 74.10, 73.86, 73.68, 73.65, 73.57, 72.69, 72.49, 72.38, 72.17, 69.51, 69.31, 69.01, 68.95, 21.44; ESI-MS: *m/z* calcd for $C_{83}H_{87}FO_{16}$; 1358.5870; found 1381.5891 $(M + Na)^+$.



3

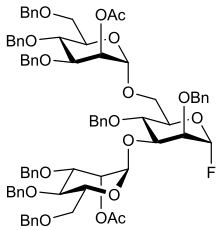
***p*-Tolyl-2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→3)-2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→6)-2,4-di-O-benzyl-1-thio-α-D-mannopyranoside (3):** To a

solution of acceptor **S1f** (0.54 g, 1.23 mmol) and donor **S1a** (1.57 g, 3.07 mmol) in CH_2Cl_2 (10 mL) was added 4 Å activated MS and stirred for 1 h at room temperature. In a separate flask, AgOTf (0.787 g, 3.07 mmol) and DTBP (690 µL, 3.07 mmol) in 10 mL of CH_2Cl_2 were stirred with MS 4 Å. After stirring for 1 h, the flask containing the AgOTf /DTBP was cooled to -30 °C and a solution containing a mixture of donor and acceptor was added over 5 min. The solution was stirred with gradual warming up to room temperature over 24 h. TLC (ethyl acetate: hexane, 2/8) indicated formation of product with consumption of starting material. The reaction was quenched with Et_3N, filtered through Celite, the filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL) and a brine (50 mL) solution. The organic layer was dried over Na_2SO_4, filtered and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (0% → 20% EA in hexane) to afford **3** (1.10 g, 66%) as colorless foam. TLC (ethyl acetate: hexane = 2/8, v/v): R_f = 0.36; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35-7.10 (m, 42H, Ar-H), 7.05 (d, *J* = 8.0 Hz, 2H, Ar-H), 5.51 (s, 1H), 5.47 (s, 1H, H-1), 5.45 (dd, *J* = 2.0, 2.8 Hz, 1H), 5.21 (s, 1H, H-1), 4.91 (d, *J* = 1.5 Hz, 1H, H-1), 4.86 (t, *J* = 10.2 Hz, 2H), 4.75 (d, *J* = 11.2 Hz, 1H), 4.67-4.58 (m, 5H), 4.54-4.36 (m, 8H), 4.23 (dd, *J* = 3.9, 9.6 Hz, 1H), 4.12-4.06 (m, 2H), 4.01 (dd, *J* = 3.2, 9.2 Hz, 1H), 3.97-3.86 (m, 5H), 3.82 (t, *J* = 9.2 Hz, 1H) 3.79-3.75 (m, 1H), 3.72 (dd, *J* = 3.9, 10.7 Hz, 1H), 3.70-3.56 (m, 4H), 2.17 (s, 3H, -C(O)CH_3), 2.13 (s, 3H, -C(O)CH_3), 2.09 (s, 3H, CH_3, STol); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.27, 170.10, 138.57, 138.53, 138.18, 138.16, 137.81, 137.77, 137.42, 131.46, 130.85, 129.83, 128.44, 128.42, 128.36, 128.27, 128.21, 128.06, 127.81, 127.72, 127.68, 127.63, 127.53, 127.48, 99.83, 98.17, 85.23, 78.98, 78.08, 77.76, 75.15, 74.98, 74.89, 74.32, 74.15, 73.52, 73.30, 72.23, 72.05, 71.85, 71.48, 71.43, 71.36, 69.05, 68.72, 68.60, 68.41, 66.60, 60.39, 21.15, 21.00, 20.94; ESI-MS: *m/z* calcd for $C_{85}H_{90}O_{17}S$; 1414.5791; found 1437.5821 $(M + Na)^+$.



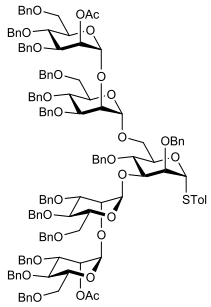
S1g

***p*-Tolyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→3)-3,4,6-tri-O-benzyl-α-D-manno pyranosyl-(1→6)]-2,4-di-O-benzyl-1-thio-α-D-mannopyranoside (S1g):** To a solution of trisaccharide **3** (1.30 g, 0.918 mmol) in 10 mL methanol: CH_2Cl_2 (1/1) was added sodium methoxide (0.024 g, 0.459 mmol), stirred at RT until TLC (ethyl acetate: hexane, 3/7) indicated formation of a product with consumption of the starting material. The reaction mixture was neutralized with IR-120, filtered and concentrated *in vacuo* and the residue was purified by silica gel column chromatography (0% → 25% EA in hexane) to afford **S1g** (1.10 g, 90%) as a colorless oil. TLC (ethyl acetate : hexane = 3/7, v/v): R_f = 0.26; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36-7.12 (m, 42H, Ar-H), 7.06 (d, *J* = 8.0 Hz, 2H, Ar-H), 5.46 (s, 1H, H-1), 5.24 (s, 1H, H-1), 5.01 (d, *J* = 1.1 Hz, 1H, H-1), 4.82 (t, *J* = 11.1 Hz, 2H), 4.69 (d, *J* = 11.6 Hz, 1H), 4.65-4.44 (m, 13H), 4.23 (dd, *J* = 4.1, 9.6 Hz, 1H), 4.16 (s, 1H), 4.07 (dd, *J* = 2.8, 9.4 Hz, 1H), 4.03 (d, *J* = 10.1 Hz, 1H), 3.96-3.88 (m, 4H), 3.87-3.81 (m, 3H), 3.80-3.75 (m, 1H), 3.73-3.64 (m, 4H), 3.62 (dd, *J* = 1.6, 10.8 Hz, 1H), 2.38 (s, 1H), 2.34 (s, 1H, -C(O)CH_3), 2.19 (s, 3H, CH_3, STol); ^{13}C NMR (150 MHz, $CDCl_3$): δ 138.12, 138.11, 137.69, 131.75, 130.12, 128.82, 128.76, 128.73, 128.67, 128.63, 128.57, 128.54, 128.53, 128.41, 128.35, 128.29, 128.19, 128.12, 128.08, 128.03, 127.95, 128.92, 127.82, 124.43, 99.90, 85.55, 80.32, 80.00, 78.49, 79.46, 75.46, 75.41, 75.27, 75.19, 75.13, 74.66, 74.50, 74.39, 73.85, 73.81, 73.62, 72.32, 72.24, 71.85, 71.71, 71.40, 71.33, 69.48, 69.00, 68.96, 68.90, 68.32, 66.51, 21.15; ESI-MS: *m/z* calcd for $C_{81}H_{86}O_{15}S$; 1330.5580; found 1353.5614 $(M + Na)^+$.



4

2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→3)-2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→6)-2,4-di-O-benzyl-α-D-mannopyranosyl fluoride (4): To a solution of compound **3** (0.270 g, 0.197 mmol) in CH_2Cl_2 (10 mL) at -30 ^oC was added NBS (0.052 g, 0.296 mmol), stirred for 10 min. DAST (52 µL, 0.395 mmol) was then added slowly and the resulting reaction mixture was stirred for 4 h at -10 ℃. TLC (ethyl acetate: hexane, 3/7) indicated formation of product with consumption of starting material. The reaction mixture was quenched with aq.$NaHCO_3$, and the filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL) and a brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (0% → 8% EA in toluene) to afford **4** (0.150 g, 61%) as white foam. TLC (ethyl acetate: toluene =1/9, v/v): R_f = 0.19; ^1H NMR (600 MHz, $CHCl_3$): δ 7.29-7.10 (m, 40H, Ar-H), 5.50 (s, 1H, H-1), 5.47 (d, *J* = 50 Hz, 1H, H-1), 5.46 (s, 1H, H-1), 5.18 (s, 1H), 4.92 (s, 1H), 4.86 (d, *J* = 11.2 Hz, 1H), 4.83 (d, *J* = 10.8 Hz, 1H), 4.72 (d, *J* = 10.0 Hz, 1H), 4.72-4.56 (m, 6H), 4.48-4.40 (m, 7H), 4.10 (d, *J* = 8.9 Hz, 1H), 4.00-3.92 (m, 4H), 4.90-3.77 (m, 5H), 3.71-3.64 (m, 5H), 3.57 (d, *J* = 7.2 Hz, 1H), 2.13 (s, 3H, -C(O)CH_3), 2.06 (s, 3H, -C(O)CH_3); ^{13}C NMR (150 MHz, $CHCl_3$): δ 170.56, 170.36, 138.80, 138.74, 138.50, 138.39, 138.11, 138.04, 137.89, 137.88, 129.70, 128.81, 128.70, 128.68, 128.65, 128.58, 128.56, 128.54, 128.43, 128.27, 128.18, 128.12, 128.07, 128.04, 128.00, 127.97, 127.89, 127.82, 126.55, 106.66, 105.18, 100.02, 98.84, 98.81, 78.31, 77.70, 76.31, 76.03, 75.42, 75.37, 75.23, 74.62, 74.41, 74.27, 73.90, 73.80, 73.65, 73.16, 72.66, 72.14, 71.92, 71.58, 69.42, 68.96, 68.70, 68.61, 66.53, 42.20, 32.21, 29.98, 29.65, 22.98, 21.63, 21.44, 21.27, 14.71, 14.41; ESI-MS: *m/z* calcd for $C_{78}H_{83}O_{17}F$; 1310.5507; found 1333.5536 $(M + Na)^+$.



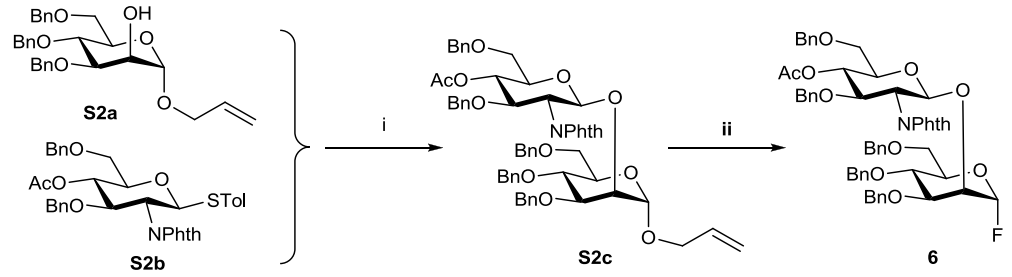
5

***p*-Tolyl-2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→3)-[2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→6)]-2,4-di-O-benzyl-1-thio-α-D-mannopyranoside (5):** To a solution of acceptor **S1g** (1.01 g, 0.739 mmol) and donor **S1a** (0.947 g, 1.84 mmol) in 20 mL CH_2Cl_2 was added 4 Å activated MS and stirred for 1 h at room temperature. In a separate flask, AgOTf (0.472 g, 1.85 mmol) and DTBP (415 µL, 1.85 mmol) in 10 mL of CH_2Cl_2 were stirred with MS 4 Å. After stirring for 1 h, the flask containing the AgOTf /DTBP was cooled to -30 °C and a solution containing a mixture of donor and acceptor in CH_2Cl_2 was added over 5 min. The solution was stirred with gradual warming up to room temperature over 24 h. TLC (ethyl acetate: hexane, 3/7) indicated formation of product with consumption of starting material. The reaction was then quenched with Et_3N, filtered through Celite, and the filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL) and a brine (50 mL) solution. The organic layer was dried over Na_2SO_4, filtered and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (0% → 25% EA in hexane) to afford **5** (1.25 g, 74%) as white solid. TLC (ethyl acetate: hexane =3/7, v/v): R_f = 0.33; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.27-7.04 (m, 72H, Ar-H), 7.02 (d, *J* = 8.0 Hz, 2H, Ar-H), 5.52 (d, *J* = 1.5 Hz, 2H, 2 x H-1), 5.46 (s, 1H, H-1), 5.18 (s, 1H, H-1), 5.04 (d, *J* = 8.2 Hz, 1H), 4.85 (t, *J* = 11.0 Hz, 2H), 4.78 (t, *J* = 11.1 Hz, 2H), 4.72-4.44 (m, 18H), 4.41-4.30 (m, 8H), 4.27 (d, *J* = 12.3 Hz, 2H), 4.20 (s, 2H), 4.05-3.92 (m, 6H), 3.91-3.73 (m, 8H), 3.68-3.56 (m, 10H), 3.48 (d, *J* = 10.1 Hz, 1H), 3.40 (d, *J* = 10.3 Hz, 1H), 3.34 (d, *J* =

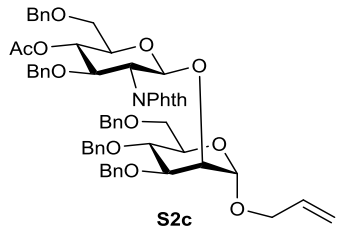
10.5 Hz, 1H), 2.10 (s, 6H, -C(O)CH_3), 2.01 (s, 3H, CH_3, STol); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.22, 152.99, 152.78, 152.57, 138.43, 138.38, 138.24, 138.05, 138.02, 137.86, 137.81, 131.15, 129.80, 128.44, 128.30, 128.20, 128.05, 127.95, 127.85, 127.72, 127.70, 127.62, 127.55, 127.53, 127.47, 127.41, 127.38, 127.35, 127.23, 126.94, 101.16, 99.37, 98.86, 84.97, 79.24, 78.07, 78.02, 75.22, 74.99, 74.87, 74.77, 74.55, 74.47, 74.29, 74.17, 73.94, 73.82, 73.38, 73.24, 73.18, 73.01, 72.58, 71.93, 71.85, 71.77, 71.60, 71.55, 71.47, 70.99, 69.41, 68.64, 68.57, 68.46, 68.01, 29.69, 21.22, 20.91; ESI-MS: *m/z* calcd for $C_{139}H_{146}O_{27}S$; 2279.9698; found 2302.9747 $(M + Na)^+$.

Synthesis of disaccharides builing block 6.

Condensation of acceptor **S2a**[8] with donor **S2b**[9] mediated by NIS and TfOH supplied the disaccharide **S2c** with exclusively *β*-linkage ($J_{1',2'}$ = 8.5 Hz) in 64% yield. Compound **S2c** was next modified to fluoride **6** via anomeric deallylation followed by conversion of free -OH to -F in presence of DAST (Scheme S2).

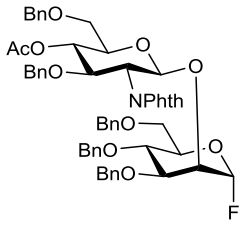


Scheme S2 | Preparation of compound 6. i, NIS, TfOH, CH_2Cl_2, 4 Å MS, -40 ℃, 2h, 64%; **ii**, (1) $PdCl_2$, MeOH: CH_2Cl_2 = 1/1, (2) DAST, CH_2Cl_2, -30 ℃ to -10 ℃, 3-5 h, 61%.



S2c

Allyl-O-4-O-acetyl-3,6-O-di-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→2)-O-3,4,6-tri-O-benzyl-α-D-mannopyranoside (S2c): A mixture of thioglycoside donor **S2b** (2.33 g, 3.65 mmol), acceptor **S2a**(1.50 g, 3.05 mmol) and activated 4 Å molecular sieves in 30 mL dry CH_2Cl_2 was stirred for 1h at room temperature. NIS (1.35 g, 6.01 mmol) and TfOH (66.2 µL, 0.75 mmol) were added slowly at -40 ^oC and stirred for 2 h until TLC (ethyl acetate: toluene, 1/9) indicated formation of product with consumption of starting material. The reaction mixture was quenched with Et_3N, filtered through Celite, and the filtrate was washed with aq. $NaHCO_3$ (2 x 50 mL), aq.$Na_2S_2O_3$ (2 x 50 mL) and finally with brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 10% EA in toluene) to afford **S2c** (2.10 g, 64%) as white solid. TLC (ethyl acetate: toluene = 1/9, v/v): R_f = 0.29; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52-7.50 (m, 4H, Ar-H), 7.33-7.10 (m, 16H, Ar-H), 7.10-7.09 (m, 2H, Ar-H), 7.00-6.90 (m, 2H, Ar-H), 5.73-5.71 (m, 1H, -OCH_2-C<u>H</u>=CH_2), 5.26 (d, *J* = 8.4 Hz, 1H,H-1), 5.14-5.06 (m, 3H), 4.71 (t, *J* = 7.8 Hz, 2H), 4.58 (d, *J* = 12.1 Hz, 1H), 4.50-4.39 (m, 6H), 4.34 (d, *J* = 4.8 Hz, 1H), 4.32 (d, *J* = 6.6 Hz, 1H), 4.10 (t, *J* = 8.6 Hz, 1H), 4.07-4.00 (q, 2H), 3.78 (dd, *J* = 3.2, 6.1 Hz, 1H), 3.81-3.78 (m, 2H), 3.71-3.70 (dd, *J* =3.2, 6.3 Hz, 1H), 3.65-3.60 (m, 1H), 3.58 (dd, *J* = 3.1, 6.5 Hz, 1H), 3.56 (t, *J* = 8.9 Hz, 1H), 3.48 (t, *J* = 10.2 Hz, 1H), 3.39 (d, *J* = 8.4 Hz, 1H), 2.97-2.96 (m, 1H), 1.93 (s, 3H, -C(O)CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.9, 138.69, 138.6, 138.5, 137.9, 137.9, 134., 133.8, 133.7, 131.9, 130.3, 128.5, 128.4, 128.4, 128.3, 128.2, 128.0, 127.9, 127.7, 127.7, 127.6, 127.5, 127.5, 123.3, 117.5, 97.1, 96.4, 77.9, 76.9, 75.1, 74.8, 73.9, 73.8, 73.8, 73.05, 72.8, 71.9, 71.0, 70.4, 70.1, 68.1, 55.5, 28.7, 21.5, 21.1; ESI-MS: *m/z* calcd for $C_{60}H_{61}NO_{13}$; 1003.4035 found 1026.4043 $(M + Na)^+$.



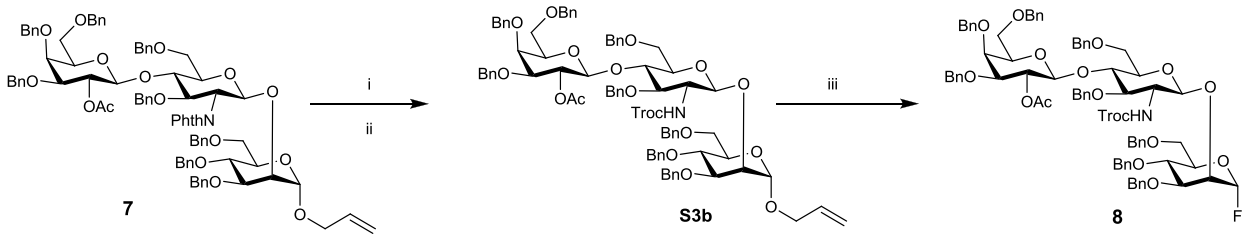
6

4-O-acetyl-3,6-O-di-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→2)-O-3,4,6-tri-O-benzyl-α-D-mannopyranosyl fluoride (6): To a solution of **S2c** (0.750 g, 0.747 mmol) in 10 mL CH_2Cl_2: MeOH (1/1) was added $PdCl_2$ (0.02 g) and stirred at rt for overnight until TLC (ethyl acetate: toluene, 2/8) indicated formation of a product with consumption of the starting material. The reaction mixture was then concentrated in *vacuo,* and the residue was purified by flash column chromatography to afford alcohol **(**0.6 g, 80%) as colorless foam. To a solution of alcohol (0.270 g, 0.197 mmol) in CH_2Cl_2 (10 mL) at -30 ^oC was DAST (52 µL, 0.395 mmol) and the resulting reaction mixture was stirred at -10 ℃ for 8 h until TLC indicated formation of product with consumption of starting material. The reaction was quenched with aq.$NaHCO_3$, and the filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL) and a brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (0% → 25% EA in hexane) to afford **6** (0.150 g, 61%) as white foam. TLC (ethyl acetate: hexane =3/7, v/v): R_f = 0.45; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.57-7.55 (m, 4H, Ar-H), 7.35-7.21 (m, 11H, Ar-H), 7.07 (d, *J* = 6.4 Hz, 4H, Ar-H), 6.99 (d, *J* = 7.2 Hz, 2H, Ar-H), 6.88-6.82 (m, 3H, Ar-H), 5.30 (d, *J* = 50.4 Hz, 1H, H-1^{Man}), 5.30 (d, *J* = 12.2 Hz, 1H, H-1^{GlcNAc}), 4.88 (d, *J* = 11.2 Hz, 1H), 4.80-4.71 (m, 3H), 4.64 (d, *J* = 11.3 Hz, 1H), 4.49-4.46 (m, 2H), 4.43 (d, *J* = 11.8 Hz, 2H), 4.34-4.28 (m, 3H), 4.23 (dd, *J* = 6.1, 11.3 Hz, 1H), 4.16 (s, 1H), 4.06 (d, *J* = 12.1 Hz, 1H), 4.02 (d, *J* = 12.3 Hz, 1H), 3.76-3.57 (m, 5H), 3.32 (d, *J* = 10.8

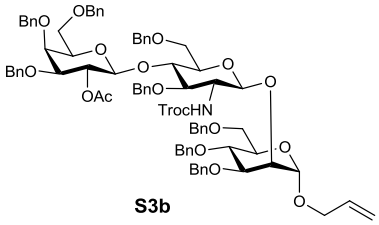
Hz, 1H), 3.02 (dd, *J* = 4.2, 11.3 Hz, 1H), 1.97 (s, 3H, -C(O)CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.99, 138.40, 138.28, 138.16, 137.94, 137.70, 133.94, 131.82, 128.90, 128.63, 128.57, 128.47, 128.40, 128.31, 128.27, 128.04, 127.89, 127.89, 127.76, 123.54, 106.33, 104.85, 97.45, 79.55, 78.48, 75.43, 75.23, 74.09, 73.84, 73.70, 73.16, 72.78, 72.54, 71.36, 69.18, 63.40, 55.80, 31.21, 29.98, 21.11; ESI-MS: *m/z* calcd for $C_{57}H_{56}FNO_{12}$; 965.3679 found 988.3690 $(M + Na)^+$.

Synthesis of trisaccharide builing blocks 7 and 8.

Builing block **7** (Figure **2a**) was obtained according to previous report[3]. The N-pthallamide protection at Glcucosamine residues was modified to NH-Troc to prepare builing block **8** (Scheme S3).

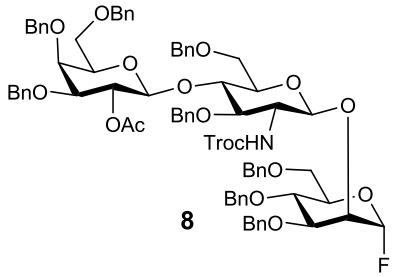


Scheme S3 | Preparation of compound 8. i, (1) EDA, n-BuOH, 90 ^oC, (2) Troc-Cl, $NaHCO_3$, CH_2Cl_2, **ii**, Ac_2O, pyridine, RT, overnight, 72% over 3 steps; **iii**, (1) $PdCl_2$, MeOH: CH_2Cl_2, (2) DAST, CH_2Cl_2, -30 ^oC, 66% over 2 steps.



Allyl-O-2-O-acetyl-3,4,6-O-tri-benzyl-β-D-galactopyranosyl-(1→4)-O-3,6-O-di-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranosyl-(1→2)-O-3,4,6-tri-O-

benzyl-α-D-mannopyranoside (S3b): A mixture of compound **S3a** (1 g, 0.693 mmole) and 10 mL of ethylene diamine: *n*-BuOH (1:4) was stirred at 90 ^{o}C overnight. Volatiles were evaporated, and the crude product was dried using high vacuum. It was then dissolved in CH_2Cl_2 (20 mL), $NaHCO_3$ (0.376 g, 6.93 mmol) and 2,2,2-trichloro ethyl chloroformate (0.665 mL, 6.93 mmol) were added at 0 ^{o}C, allowed it to warm to rt and stirred for overnight. TLC (ethyl acetate: toluene, 2/8) indicated formation of product with consumption of starting material. The reaction mixture was diluted with CH_2Cl_2 (100 mL), washed with water (2 x 50 mL) and brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (0% $\rightarrow$ 15% EA in toluene). The product was then acetylated using 10 mL of pyridine/acetic anhydride (6:4) until TLC indicated (ethyl acetate: toluene, 2/8) complete consumption of starting material. The reaction mixture was then concentrated *in vacuo* and purified by silica gel column chromatography to afford **S3b** (0.760 g, 72%) as a white foam. TLC (ethyl acetate: toluene = 2/8, v/v): R_f = 0.64; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34-7.13 (m, 40H, -Ph), 5.86-5.77 (m, 1H, allyl -C<u>H</u>), 5.30-5.28 (t, *J* = 8.2 *Hz*, 1H, $H2^{gal}$), 5.25 (bd, 1H, -N<u>H</u>Troc), 5.16 (d, *J* = 17.6 Hz, 1H, Troc), 5.10 (d, *J* = 10.2 Hz, 1H), 4.90 (t, 3H), 4.82-4.76 (m, 3H), 4.74 (s, 1H), 4.65-4.61 (dd, *J* = 8.4 & 2.8 Hz, 3H), 4.55-4.41 (m, 8H), 4.30 (d, *J* = 12.3 Hz, 2H), 4.20 (d, *J* = 12.2 Hz, 2H), 4.10-4.01 (m, 3H), 3.90-3.84 (m, 5H), 3.76-3.61 (m, 5H), 3.55-3.40 (m, 3H), 3.35-3.30 (m, 2H), 3.13 (d, *J* = 7.2 Hz, 1H), 1.92 (s, 3H, -C(O)CH_3) ; ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.23, 154.11, 139.17, 138.98, 138.75, 138.25, 138.20, 134.04, 127.41, 100.7, 97.5, 96.80, 80.55, 78.53, 75.36, 72.87, 73.55, 72.78, 72.49, 72.10, 71.96, 69.98, 68.90, 68.65, 57.64, 41.51, 21.30. ESI-MS: *m/z* calcd for $C_{82}H_{88}Cl_3N_1O_{18}$; 1458.4960 found 1504.4956 $(M + Na)^{+}$



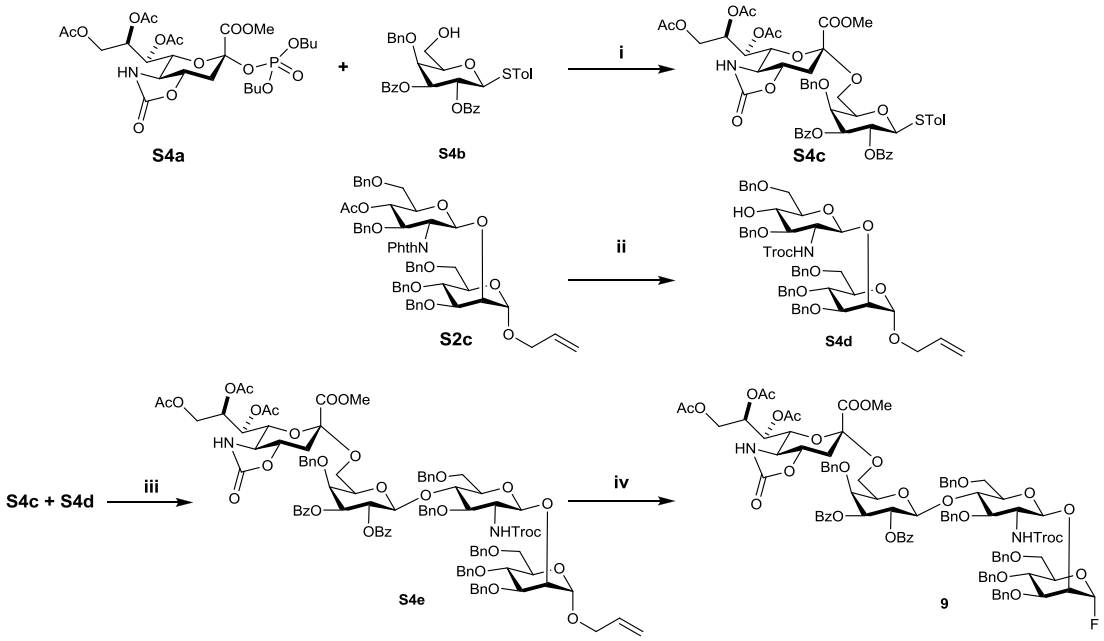
8

2-O-acetyl-3,4,6-O-tri-benzyl-β-D-galactopyranosyl-(1→4)-O-3,6-O-di-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranosyl-(1→2)-O-3,4,6-tri-O-benzyl-α-D-mannopyranosyl fluoride (8): $PdCl_2$ (0.030 g) was added to a solution of **S3b** (1.3 g, 0.942 mmol) in 10 mL of CH_2Cl_2: MeOH (1:1). The reaction mixture was stirred at room temperature for 2 h until TLC (ethyl acetate: toluene, 2/8) indicated formation of product with consumption of the starting material. The reaction mixture was then filtered through Celite and concentrated in *vacuo.* The residue was purified by flash column chromatography to afford 1-OH compound (0.980 g) as white color foam. The residue (0.850 g, 0.608 mmol) was dissolved in CH_2Cl_2 (10 mL) at -30 ^oC, then DAST (160 µL, 1.21 mmol) was added slowly. The resulting reaction mixture was stirred for 1 h. When TLC (ethyl acetate: toluene, 2/8) indicated formation of product with consumption of starting material, the reaction was quenched with aq. $NaHCO_3$. The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL) and brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (0% → 15% EA in toluene) to afford **8** (0.700 g, 66% over 2 steps) as white foam. TLC (ethyl acetate: toluene = 2/8, v/v): R_f = 0.64; ^1H NMR (600 MHz, $CDCl_3$): δ 7.35-7.10 (m, 40H), 4.57 (d, *J* = 51.4 Hz, 1H), 5.33 (t, *J* = 10.2 Hz, 1H), 5.22 (d, *J* = 8.2 Hz, 1H), 4.99-4.91 (m, 3H), 4.82 (d, *J* = 7.8 Hz, 1H), 4.75 (t, *J* = 10.3 Hz, 1H), 4.64-4.44 (m, 12H), 4.38 (dd, *J* = 3.4 & 10.2 Hz, 2H), 4.26 (s, 2H), 4.06-4.33 (m, 5H), 3.76-3.64 (m, 4H), 3.54-3.46 (m, 2H), 3.40-3.34 (m, 3H), 3.12 (d, *J* = 8.4 Hz, 1H), 1.65 (S, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.5, 154.0, 139.0, 138.8, 138.7, 138.5, 138.4, 138.3, 138.1, 129.4, 128.7, 128.6, 128.4, 128.2, 128.0, 127.9, 127.7, 127.5, 127.4, 127.2, 127.1, 125.5, 107.6, 105.4, 100.7, 98.7, 95.8, 80.5, 77.4,

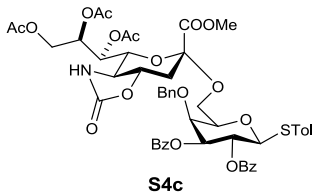
74.3, 73.6, 73.3, 73.1, 72.3, 72.1, 72.0, 71.9, 68.9, 68.7, 68.3, 57.4, 41.4, 21.7, 21.2; ESI-MS: *m/z* calcd for $C_{79}H_{83}Cl_3FN_1O_{17}$; 1443.4602 found 1466.4608 $(M + Na)^+$.

Synthesis of complex type D1 arm tetrasaccharide 9.

Preparation of sialylated D1 arm was achieved through coupling of two main builing units S4c and S4d. Use of sialyl phosphate donor **S4a** for the α-2,6 glycosyaltion of Gal **S4b** resulted in complete α-selectivity[10]. The N-Phth protection at glucosamine of S2c was modified NHTroc, while doing so, the 4-OAc group was removed to afford the desired **S4d**. At last the coupling of **S4c** and **S4d** afforded the desired tetrasaccharide, which further underwent anomeric modification to get donor **9**.

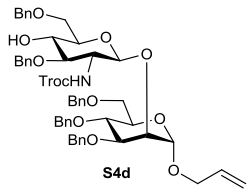


Scheme S4 | Preparation of compound 9. i, TMSOTf, CH_2Cl_2, -50 ^oC, 64%; **ii**, (1) EDA, n-BuOH, 90 ^oC, (2) Troc-Cl, $NaHCO_3$, CH_2Cl_2, 78% over 2 steps; **iii**, NIS, TfOH, CH_2Cl_2, -50 ^oC, 65%; **iv**, (1) $PdCl_2$, MeOH: CH_2Cl_2, (2) DAST, CH_2Cl_2, -30 ^oC, 55% over 2 steps.

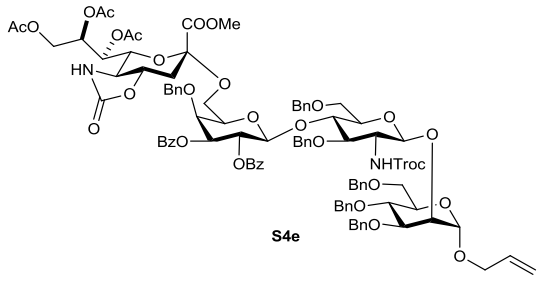


S4c

Methyl-5-acetamido-7,8,9-tri-O-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonate-(2→6)-*p*-tolyl-4-O-benzyl-2,3-di-O-benzoyl-1-thio-β-D-glacto-pyranoside (S4c): A mixture of donor **S4a** (0.113 g, 0.178 mmol), acceptor **S4b** (0.220 g, 0.119 mmol) and activated 4 Å molecular sieves in dry CH_2Cl_2 (10 mL) was stirred at rt for 1 h. The reaction was cooled to -50 ^oC, trimethylsilyl triflate (12 µL, 0.06 mmol) was added slowly and the resulting reaction mixture was stirred for 2 h. The reaction was quenched by adding Et_3N, diluted with CH_2Cl_2, filtered through Celite, extracted with saturated $NaHCO_3$, dried over sodium sulfate and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 25% EA in hexane) to afford **S4c** (0.190 g, 64%) as colorless foam. TLC: (ethyl acetate: hexane = 3/7, v/v): R_f = 0.46; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.93 (d, *J* = 7.8 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.50-7.45 (m, 2H), 7.42-7.30 (m, 6H), 7.24-7.13 (m, 5H), 7.04 (d, *J* = 8.2 Hz, 2H), 5.80 (t, *J* = 10.3 Hz, 1H), 5.47 (d, *J* = 8.9 Hz, 1H), 5.37 (s, 3H), 5.32 (dd, *J* = 4.2 & 7.8 Hz, 1H), 5.12 (dd, *J* = 4.1 & 7.2 Hz, 1H), 4.90 (d, *J* = 12.2 Hz, 1H), 4.65 (d, *J* = 12.1 Hz, 1H), 4.20 (dd, *J* = 3.2 & 7.8 Hz, 1H), 4.18 (d, *J* = 6.8 Hz, 1H), 3.94-3.91 (m, 3H), 3.74-3.72 (m, 3H), 3.71 (s, 3H), 3.65 (dd, *J* = 3.2 & 7.8 Hz, 1H), 3.06 (t, *J* = 10.2 Hz, 2H), 2.87 (dd, *J* = 3.6 & 8.6 Hz, 1H), 2.33 (s, 3H), 2.17 (s, 3H), 2.15 (t, *J* = 7.8 Hz, 1H), 2.13 (s, 3H), 2.10 (S, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.9, 170.8, 169.8, 168.2, 166.8, 165.2, 159.2, 138.1, 133.7, 133.3, 130.0, 129.8, 129.4, 129.3, 129.2, 128.7, 128.6, 128.5, 128.4, 127.8, 127.7, 125.5, 100, 5, 86.8, 76.8, 76.1, 74.7, 73.8, 68.9, 68.5, 68.3, 67.2, 63.7, 62.0, 58.1, 53.3, 37.7, 25.88, 21.7, 21.5, 21.3, 21.0, 20.9 ; ESI-MS: *m/z* calcd for $C_{51}H_{53}NO_{18}S$; 999.2876 found 1022.2882 $(M + Na)^+$.

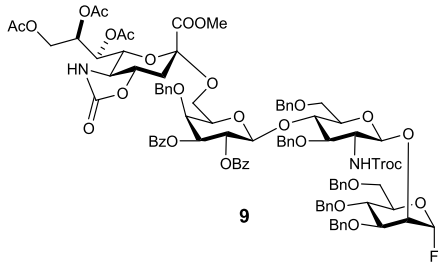


Allyl-O-3,6-O-di-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-gluco-pyranosyl-(1→2)-O-3,4,6-tri-O-benzyl-α-D-mannopyranoside (S4d): A mixture of compound S**2c** (2 g, 1.99 mmole) and 20 mL of ethylene diamine: *n*-BuOH (1:4) was stirred at 90 ^{o}C overnight. Volatiles were evaporated, and the crude product was dried using high vacuum. It was then dissolved in CH_2Cl_2 (20 mL), $NaHCO_3$ (1.05 g, 19.9 mmol) and 2,2,2-trichloro ethyl chloroformate (1.9 mL, 19.9 mmol) were added at 0 ^{o}C, allowed it to warm to rt and stirred for overnight until TLC (ethyl acetate: toluene, 1.5/8.5) indicated formation of product with consumption of starting material. The reaction mixture was diluted with CH_2Cl_2 (100 mL), washed with water (2 x 50 mL) and brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (0% → 10% EA in toluene) to afford **S4d** (1.5 g, 78%) as a white foam. TLC (ethyl acetate: toluene = 1.5/8.5, v/v): R_f = 0.44; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30-7.15 (m, 25H), 5.87-7.78 (m, 1H), 5.33 (d, *J* = 5.2 Hz, 1H), 5.21 (d, *J* = 3.2 Hz, 1H), 5.14 (d, *J* = 7.2 Hz, 1H), 4.94 (d, *J* = 5.8 Hz, 1H), 4.80 (d, *J* = 8.5 Hz, 1H), 4.73-4.44 (m, 10H), 4.12-4.06 (m, 4H), 3.97-3.86 (m, 4H), 3.78-3.49 (m, 7H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 153.97, 138.45, 138.37, 138.28, 137.98, 137.45, 133.63, 128.94, 128.43, 128.40, 128.26, 128.16, 127.97, 127.91, 127.78, 127.65, 127.53, 127.41, 125.20, 117.23, 97.93, 96.88, 95.50, 79.33, 79.08, 75.08, 74.47, 74.37, 73.53, 73.19, 73.00, 71.98, 71.65, 70.83, 69.16, 67.91, 57.41, 44.53; ESI-MS: *m/z* calcd for $C_{53}H_{58}Cl_3NO_{12}$; 1005.3025 found 1006.3089 $(M + H)^+$.



Allyl-[Methyl-5-acetamido-7,8,9-tri-O-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonate]-(2→6)-4-O-benzyl-2,3-di-O-benzoyl-1-β-D-galactopyranosyl-(1→4)-O-3,6-O-di-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranosyl-(1→2)-O-3,4,6-tri-O-benzyl-α-D-mannopyranoside (S4e): Activated 4 Å molecular sieves were added to a solution of acceptor **S4d** (0.208 g, 0.169 mmol) and donor **S4c** (0.310 g, 0.199 mmol) in anhydrous CH_2Cl_2 (10 mL). The mixture was stirred for 1 h at room temperature. The reaction mixture was cooled to -50 ^oC, NIS (0.076 g, 0.338 mmol) and TfOH (3.7 µL, 0.042 mmol) were added slowly. The resulting reaction mixture was stirred for 2 h. When TLC (ethyl acetate: toluene, 1.5/8.5) indicated formation of product with consumption of starting material, the reaction was quenched by adding Et_3N and filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL), aqueous $Na_2S_2O_3$ (2 x 50 mL), and brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 10% EA in toluene) to afford **S4e** (0.390 g, 65%) as clear foam. TLC (ethyl acetate: toluene = 1.5/8.5, v/v): R_f = 0.51; ^1H NMR (600 MHz, $CDCl_3$): δ 7.91-7.85 (m, 4H, Ph), 7.50-7.46 (m, 1H, Ph), 7.35-7.19 (m, 35H), 5.82-5.76 (m, 2H), 5.39-5.36 (m, 3H), 5.24 (d, *J* = 6.4 Hz, 1H), 5.22 (d, *J* = 7.2 Hz, 1H), 5.19 (d, *J* = 3.4 Hz, 1H), 5.15 (d, *J* = 3.4 Hz, 1H), 5.11-5.08 (dd, *J* = 6.3 & 3.1 Hz, 2H), 4.96 (d, *J* = 12.1 Hz, 2H), 4.83 (d, *J* = 12.1 Hz, 2H), 4.73-4.57 (m, 10H), 4.47-4.42 (m, 6H), 4.25-4.15 (m, 5H), 4.08-3.93 (m, 9H), 3.91 (s, 3H,), 3.39 (d, *J* = 7.8 Hz, 1H), 3.21 (bd, 1H), 2.93 (t, *J* = 7.8 Hz, 1H), 2.78 (dd, *J* = 3.6 & 7.8 Hz, 1H), 2.11 (s, 3H), 2.01 (s, 3H), 1.66 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.83, 170.84, 169.91, 168.03, 166.15, 165.43, 159.57, 154.17, 139.14, 138.85, 138.36, 134.08, 133.78, 132.66, 13.54,

129.67, 128.78, 128.43, 128.23, 127.78, 127.67, 127.56, 127.43, 127.23, 127.10, 117,53, 100.67, 100.32, 98.94, 97.18, 75.90, 78.31, 75.32, 74.95, 7.81, 74.43, 73.99, 73.58, 73.45, 73.33, 73.29, 73.23, 73.12, 69.90, 69.56, 68.66, 67.56, 58.70, 53.43, 21.28, 21.07, 20,98; ESI-MS: *m/z* calcd for $C_{97}H_{103}Cl_3N_2O_{13}$; 1982.5562 found 1905.5558 $(M + Na)^+$.



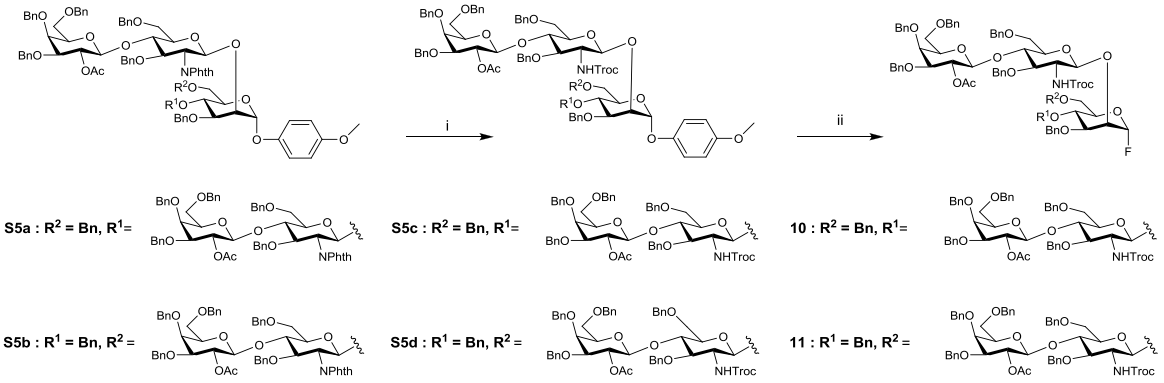
9

Methyl-5-acetamido-7,8,9-tri-O-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonate-(2→6)-4-O-benzyl-2,3-di-O-benzoyl-1-β-D-galactopyranosyl-(1→4)-O-3,6-O-di-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranosyl-(1→2)-O-3,4,6-tri-O-benzyl-α-D-mannopyranosyl fluoride (9): $PdCl_2$ (0.050 g) was added to a solution of **S4e** (2.7 g, 1.42 mmol) in 20 mL of CH_2Cl_2: MeOH (1:1). The reaction mixture was stirred at room temperature for 5 h until TLC (ethyl acetate: toluene, 2/8) indicated formation of product with consumption of the starting material. The reaction mixture was then filtered through Celite and concentrated in *vacuo.* The residue was purified by flash column chromatography (0% → 15% EA in toluene) to afford 1-OH compound (2.0 g) as white color foam. The residue (2 g, 1.07 mmol) was dissolved in CH_2Cl_2 (10 mL) at -30 ^oC, then DAST (284 μL, 2.14 mmol) was added slowly. The resulting reaction mixture was stirred for 1 h. When TLC (ethyl acetate: toluene, 2/8) indicated formation of product with consumption of starting material, the reaction was quenched with aq. $NaHCO_3$. The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL) and brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (0% → 15% EA in toluene) to afford **9** (1.45 g, 55% over 2 steps) as white foam. TLC (ethyl acetate: toluene = 2/8, v/v): R_f = 0.64; ^1H NMR (600 MHz, $CDCl_3$): δ 7.96 (m, 4H), 7.55 (m, 2H), 7.40-7.17 (m, 34H), 5.86 (t, *J* =

10.2Hz, 1H), 5.50 (d, *J* = 52Hz, 1H), 5.44-5.40 (m, 2H), 5.29 (dd, *J* = 1.6 & 7.8 Hz, 1H), 5.15 (dd, *J* = 1.7 & 7.2 Hz, 1H), 5.05-4.99 (m, 2H), 4.84-4.44 (m, 10H), 4.33-4.20 (m, 3H), 4.27-4.20 (m, 4H), 4.03-3.90 (m, 3H), 3.72-3.65 (s, 3H), 3.70-3.06 (m, 12H), 3.46-3.30 (m, 1H), 3.00 (t, *J* = 10.2 Hz, 1H), 2.86 (dd, *J* = 3.2 & 12.3 Hz, 1H), 2.19 (s, 3H), 2.16 (s, 3H), 2.12 (t, *J* = 8.4 Hz, 1H), 2.0 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.8, 170.0, 168.0, 166.1, 165.2, 159.5, 154.1, 138.9, 138.4, 138.2, 138.1, 133.7, 133.6, 133.4, 130.0, 129.9, 129.6, 129.3, 128.8, 128.6, 128.5, 128.4, 128.3, 128.1, 127.9, 127.5, 127.2, 125.5, 107.7, 100.7, 100.1, 99.2, 95.8, 78.1, 77.1, 76.6, 75.3, 74.9, 74.6, 74.4, 74.1, 73.9, 73.7, 73.5, 73.3, 73.0, 72.6, 72.5, 69.2, 69.0, 67.3, 63.2, 61.8, 58.1, 57.3, 53.4, 37.3, 21.7, 21.3, 21.0, 20.9 ; ESI-MS: *m/z* calcd for $C_{94}H_{98}Cl_3FN_2O_{29}$; 1844.5204 found 1867.5192 $(M + Na)^+$.

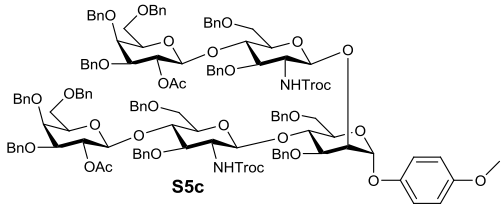
Synthesis of building blocks 10 and 11.

Pentasaccharides **S5a** and **S5b** were obtained according to our previous report[3], in which the functional group was further modified from N-pthallamide to N-Troc. Finally the anomeric *p*-methoxy phenyl group was removed and resulting –OH was changed to fluoride in presence of DAST.



Scheme S5 | Preparation of compound 10 and 11. i, (1) EDA, n-BuOH, 90 ^{o}C; (2) Troc-Cl, $NaHCO_3$, CH_2Cl_2; (3) Ac_2O, pyridine; **ii**, (1) CAN, ACN: Toluene: H_2O; (2) DAST, CH_2Cl_2,-30 ^{o}C.

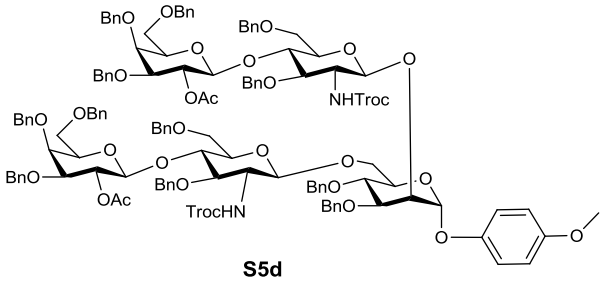
General procedure for step i: A mixture of compound **S5a** and **S5b** (0.500 g, 0.212 mmol) and 10 mL of ethylene diamine: *n*-BuOH (1:4) was stirred at 90 ^{o}C overnight. Volatiles were evaporated, and the crude product was dried using high vacuum. It was then dissolved in CH_2Cl_2 (20 mL), $NaHCO_3$ (0.114 g, 2.12 mmol) and 2,2,2-trichloro ethyl chloroformate (0.2 mL, 2.12 mmol) were added at 0 ^{o}C, allowed it to warm to RT and stirred for overnight. TLC (ethyl acetate: toluene, 2/8) indicated formation of product with consumption of starting material. The reaction mixture was diluted with CH_2Cl_2 (100 mL), washed with water (2 x 50 mL) and brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (0% → 15% EA in toluene). The product was then acetylated using 10 mL of pyridine/acetic anhydride (6:4) until TLC indicated (ethyl acetate: toluene, 2/8) complete consumption of starting material. The reaction mixture was then concentrated *in vacuo* and purified by silica gel column chromatography (0% → 15% EA in toluene) to afford **S5c** (0.332 g 65%) and **S5d** (0.340 g, 68%) as a colorless foam.



S5c

***p*-methoxyphenyl-O-2-O-acetyl-3,4,6-O-tri-benzyl-β-D-galactopyranosyl-(1→4)-O-3,6-O-di-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranosyl-(1→2)-[2-O-acetyl-3,4,6-O-tri-benzyl-β-D-galactopyranosyl-(1→4)-O-3,6-O-di-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranosyl-(1→4)]-3,6-O-di-benzyl-α-D-mannopyranoside (S5c):** Compounds **S5c** was prepared according to the above mentioned general procedure. TLC (ethyl acetate: toluene = 2/8, v/v): R_f = 0.64; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40-7.08 (m, 50H, Ar-H), 6.92-6.72 (m, 10H, Ar-H), 6.63-6.53 (m, 2H, PMP-H), 5.31-5.24 (m, 2H$^{'}$), 5.22 (d, *J* = 7.8 Hz, 1H), 5.15 (d, *J* = 8.4 Hz, 1H,), 4.94 (d, *J* = 3 Hz, 2H),

4.88 (d, *J* = 3.6 Hz, 1H), 4.86 (d, *J* = 3.6 Hz, 1H), 4.80-4.71 (m, 7H), 4.64-4.56 (m, 3H), 4.49-4.44 (m, 10H,), 4.39-4.10 (m, 14H), 4.15-4.05 (m, 2H), 4.03 (t, *J* = 8.4 Hz, 1H), 3.98-3.86 (m, 3H), 3.79-3.72 (m, 1H), 3.69 (s, 3H), 3.58-3.56 (m, 1H), 3.49-3.25 (m, 10H), 3.08 (d, *J* = 8.4 Hz, 1H), 3.05 (d, *J* = 8.9 Hz, 1H), 2.90 (bs, 1H), 1.93 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.5, 169.4, 168.3, 167.8, 154.8, 150.3, 139.2, 139.1, 139.0, 138.9, 138.8, 138.5, 138.3, 138.2, 138.0, 134.0, 133.6, 132.1, 131.9, 131.7, 129.2, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.4, 127.3, 127.1, 127.0, 126.8, 123.5, 123.4, 123.3, 118.1, 114.4, 108.9, 100.9, 100.7, 98.5, 97.6, 97.1, 80.5, 50.5, 79.7, 77.9, 77.8, 77.7, 77.4, 77.2, 75.4, 74.9, 74.6, 74.5, 73.7, 73.6, 73.6, 73.4, 73.3, 73.0, 72.8, 72.7, 72.2, 71.9, 71.8, 71.7, 71.2, 69.2, 68.5, 68.3, 68.2, 67.6, 67.3, 56.4, 55.9, 55.7, 21.3, 21.2, 21.2; ESI-MS: *m/z* calcd for $C_{131}H_{138}Cl_6N_2O_{31}$; 2449.7492; found 2449.7272 $(M + H)^+$.

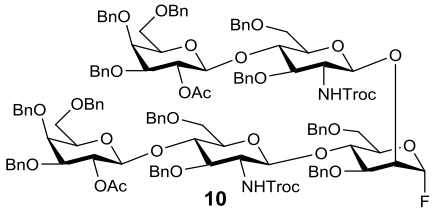


S5d

***p*-methoxyphenyl-O-2-O-acetyl-3,4,6-O-tri-benzyl-β-D-galactopyranosyl-(1→4)-O-3,6-O-di-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranosyl-(1→2)-[2-O-acetyl-3,4,6-O-tri-benzyl-β-D-galactopyranosyl-(1→4)-O-3,6-O-di-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranosyl-(1→6)]-3,6-O-di-benzyl-α-D-mannopyranoside (S5d):** Compounds **S5d** was prepared according to the above mentioned general procedure. TLC (ethyl acetate: toluene = 2/8, v/v): R_f = 0.61; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42-7.05 (m, 60H), 7.02 (d, *J* = 9.2 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 5.59 (s, 1H), 5.42 (bs, 1H), 5.39-5.29 (m, 2H), 5.15 (d, *J* = 3.8 Hz, 1H), 5.00-4.84 (m, 7H), 4.80-4.25 (m,

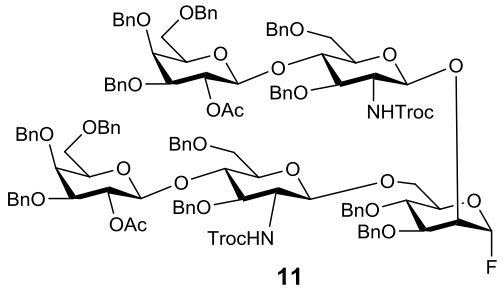
20H), 4.10 (dd, *J* = 3.8 & 7.8 Hz, 2H), 4.00-3.83 (m, 6H), 3.76 (s, 3H), 3.62-3.20 (m, 23H), 1.99 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.9, 169.5, 168.5, 155.0, 154.6, 150.1, 138.9, 138.4, 138.2, 138.1, 134.3, 132.0, 129.2, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.5, 127.3, 125.5, 123.6, 117.8, 117.2, 114.9, 106.1, 101.5, 100.9, 100.7, 98.3, 96.4, 95.7, 80.3, 80.1, 79.4, 78.3, 77.9, 78.3, 75.6, 74.8, 74.5, 74.4, 74.3, 73.6, 73.4, 73.2, 73.0, 72.6, 72.3, 71.8, 68.9, 68.1, 67.9, 67.5, 57.9, 56.7, 55.8, 41.3, 40.4, 37.7, 29.9, 21.6, 21.2, 21.1; ESI-MS: *m/z* calcd for $C_{131}H_{138}Cl_6N_2O_{31}$; 2448.7492 found 2449.7414 $(M + H)^+$.

General procedure for step ii: Cerium ammonium nitrate (0.616 g, 0.725 mmol) was added to a solution of compound **S5c** or **S5d** (0.350 g, 0.145 mmol) in 10 mL of acetonitrile: toluene: H_2O (4:2:1). The resulting reaction mixture was stirred at 0 ℃ for 2 h. The reaction was diluted with EtOAc (100 mL) and washed with H_2O (30 x 2 mL) and brine (30 mL). The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The product was purified by flash column chromatography (0% → 15% EA in toluene) to afford 1-**OH** compound (0.180 g) as clear foam. The residue (0.180 g, 0.078 mmol) was dissolved in CH_2Cl_2 (10 mL) at -30 ^oC. Then, DAST (30 µL, 0.234 mmol) was added slowly, and the resulting reaction mixture was stirred for 1 h. When TLC (ethyl acetate: toluene, 1/9) indicated formation of product with consumption of starting material, the reaction was quenched with aq. $NaHCO_3$. The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL) and brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (0% → 8% EA in toluene) to afford **10** (0.120 g, 34% over 2 steps) and **11** (0.150 g, 42 % over 2 steps).



10

2-O-acetyl-3,4,6-O-tri-benzyl-β-D-galactopyranosyl-(1→4)-O-3,6-O-di-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranosyl-(1→2)-[2-O-acetyl-3,4,6-O-tri-benzyl-β-D-galacto-pyranosyl-(1→4)-O-3,6-O-di-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy) carbonylamino-β-D-glucopyranosyl-(1→4)]-3,6-O-di-benzyl-α-D-mannopyranosyl fluoride (10): TLC (ethyl acetate: toluene =1/9, v/v): R_f = 0.34; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34-7.13 (m, 60H), 5.41 (s, 1H), 5.50 (d, *J* = 51.1Hz, 1H), 5.30-5.25 (m, 2H), 5.12 (d, *J* = 8.4 Hz, 1H), 4.92-4.85 (m, 5H), 4.69-4.38 (m, 20H), 4.32-4.14 (m, 8H), 3.91-3.77 (m, 7H), 3.70 (dd, *J* = 3.8 and 7.8 Hz, 1H), 3.60-3.56 (m, 3H), 3.49-3.24 (m, 14H), 2.03 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (150 MHz, $CHCl_3$): δ 169.68, 169.58, 154.31, 154.09, 139.06, 138.97, 138.93, 138.32, 138.29, 138.27, 138.20, 138.17, 129.32, 128.99, 128.69, 128.63, 128.50, 128.49, 128.45, 128.27, 128.24, 128.16, 128.15, 128.07, 128.05, 128.00, 127.97, 127.94, 127.91, 127.82, 127.72, 127.60, 127.57, 127.44, 125.58, 100.64, 100.45, 95.86, 80.54, 80.51, 76.81, 76.70, 76.03, 75.34, 75.08, 86, 74.77, 74.66, 74.57, 74.47, 73.74, 73.70, 73.67, 73.64, 73.58, 73.46, 73.42, 73.27, 72.90, 72.19, 72.17, 71.99, 71.95, 68.49, 68.27, 68.14, 68.01, 57.53, 21.40, 21.27; ESI-MS: *m/z* calcd for $C_{124}H_{131}Cl_6FN_2O_{29}$; 2340.6953 found 2363.7200 $(M + Na)^+$.



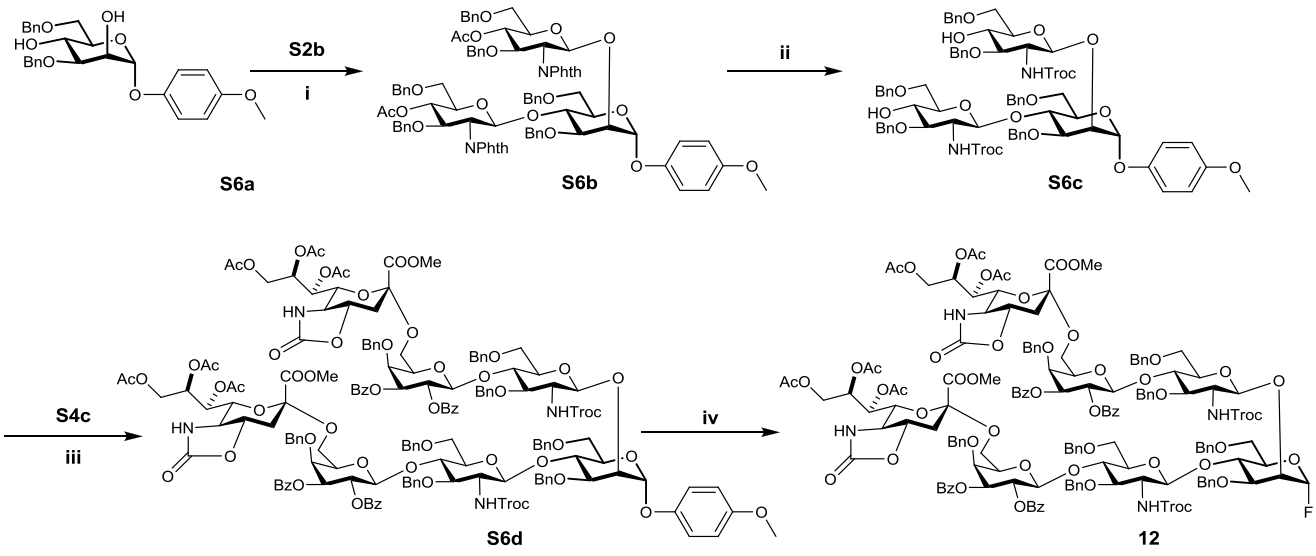
11

2-O-acetyl-3,4,6-O-tri-benzyl-β-D-galactopyranosyl-(1→4)-O-3,6-O-di-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranosyl-(1→2)-[2-O-acetyl-3,4,6-O-tri-benzyl-β-D-galacto-pyranosyl-(1→4)-O-3,6-O-di-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy) carbonylamino-β-D-glucopyranosyl-(1→4)]-3,6-O-di-benzyl-α-D-mannopyranosyl fluoride

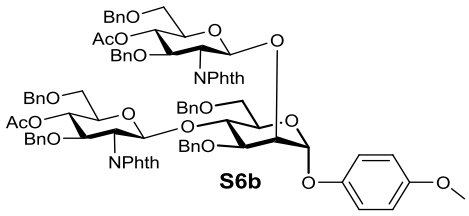
(11): TLC (ethyl acetate: toluene =1/9, v/v): R_f = 0.38; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33-7.09 (m, 60H), 5.60 (d, *J* = 52.1 Hz, 1H), 5.32- 5.28 (m, 2H), 5.10 (d, *J* = 2.1 Hz, 1H), 4.93-4.80 (m, 5H), 4.78 (d, *J* = 8.4 Hz, 1H), 4.74 (d, *J* = 8.2 Hz, 1H), 4.65-4.40 (m, 28H), 3.95 (dd, *J* = 8.4 Hz, 1H), 3.79-3.69 (m, 10H), 3.50-3.40 (m, 5H), 3.39-3.20 (m, 8H), 1.91 (s, 6H) ; ^{13}C NMR (150 MHz, $CHCl_3$): δ 169.69, 169.56, 154.72, 154.66, 139.55, 139.02, 139.00, 138.43, 138.34, 138.27, 138.20, 138.19, 128.93, 128.80, 128.76, 128.72, 128.65, 128.45, 128.41, 128.30, 128.28, 128.21, 127.67, 127.34, 127.10, 106.45, 105.33, 101.82, 101.21, 100.00, 97.86, 97.46, 95.60, 75.46, 75.27, 74.86, 74.58, 74.26, 74.10, 73.50, 73.47, 73.10, 72.90, 72.88, 72.37, 72.30, 71.40, 71.37, 71.09, 70.57, 70.35, 70.45, 69.78, 69.46, 29.99, 25.78, 22.87, 21.36, 21.29, 15.57, 14.49, 144.42; ESI-MS: *m/z* calcd for $C_{124}H_{131}Cl_6FN_2O_{29}$; 2340.6953 found 2362.7225 $(M + Na)^+$.

Synthesis of building blocks 12.

Preparation of disialylated antennae was commensed with β-1, 2 and β-1, 4 glycosylation of mannosyl acceptor **S6a** with donor **S2b**. Compound **S6b** was then modified to **S6c** and subsequently glycosylated with **S4c** to get desired heptasaccharide **S6d**. At last, the reducing end was modified to get donor **12**.

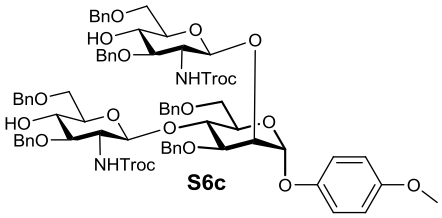


Scheme S6 | Preparation of compound 12. i, NIS, TfOH, CH_2Cl_2, -50 ^oC, 76%; **ii**, (1) EDA, n-BuOH, 90 ^oC, (2) Troc-Cl, $NaHCO_3$, CH_2Cl_2, 72% over 2 steps; **iii**, NIS, TfOH, CH_2Cl_2, -50 ^oC, 86%; **iv**, (1) CAN, ACN: Toluene: H_2O, (2) DAST, CH_2Cl_2, -30 ^oC, 40% over 2 steps.



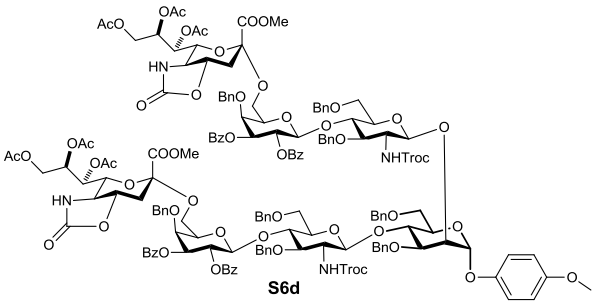
***p*-methoxyphenyl-O-4-O-acetyl-3,6-O-di-benzyl-2-deoxy-2-phthalimido-β-D-gluco pyranosyl-(1→2)-[4-O-acetyl-3,6-O-di-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)]-3,6-O-di-benzyl-α-D-mannopyranoside (S6b):** Activated 4 Å molecular sieves were added to a solution of acceptor **S6a** (0.560 g, 1.19 mmol) and donor **S2b** (1.74 g, 2.74 mmol) in anhydrous CH_2Cl_2 (10 mL). The reaction mixture was stirred for 1 h at room temperature then cooled to -50 ^oC. NIS (1.07 g, 4.75 mmol) and TfOH (52 µL, 0.595 mmol) were added slowly, and the resulting reaction mixture was stirred for 2 h. When TLC (ethyl acetate: toluene, 1.5/8.5) indicated formation of product with consumption of starting material, the reaction was quenched by adding Et_3N then filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL), aqueous $Na_2S_2O_3$ (2 x 50 mL), and brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 10% EA in toluene) to afford **S6b** (1.27 g, 76%) as clear foam. TLC (ethyl acetate : toluene = 1.5/8.5, v/v): R_f =0.57; ^1H NMR (600 MHz, $CDCl_3$): δ 7.70-7.68 (m, 8H), 7.66-7.16 (m, 18H), 6.97 (m, 12H), 6.66-6.49 (m, 4H), 5.25 (t, *J* = 10 Hz, 2H), 5.08-5.00 (dd, *J* = 9.6 & 3.4 Hz, 2H), 4.90 (d, *J* = 4.6 Hz, 1H), 4.69 (d, *J* = 12 Hz, 1H), 4.57 (t, 3H), 4.42-4.21 (m, 10H), 4.12 (dd, *J* = 3.2 & 8.4 Hz, 2H), 3.90 (dd, *J* = 3.2 & 7.8 Hz, 1H), 3.84-3.60 (m, 7H), 3.66 (s, 3H), 3.54-3.31 (m, 3H), 3.01 (d, *J* = 7.8Hz, 1H), 1.84 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.61, 169.12, 154.49, 150.07, 138.69, 138.21, 137.99, 137.77, 137.60, 133.52, 131.29, 128.28, 128.19, 127.99, 127.94, 127.91, 127.83, 127.68, 127.59, 127.47,

127.25, 127.08, 127.94, 123.17, 117.55, 114.08, 98.10, 97.37, 96.54, 78.89, 74.56, 73.56, 73.27, 72.98, 72.42, 72.32, 71.91, 71.43, 71.02, 69.91, 69.25, 68.90, 55.73, 55.45, 55.26, 20.80; ESI-MS: *m/z* calcd for $C_{77}H_{82}Cl_6N_2O_{21}$; 1585.3589 found 1586.5687 $(M + H)^+$.



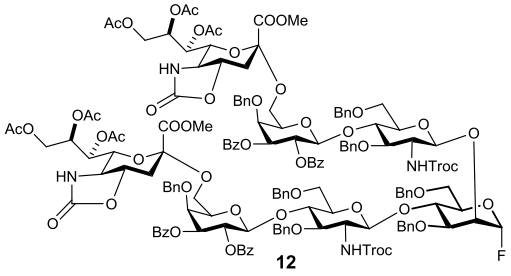
***p*-methoxyphenyl-O-3,6-O-di-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy) carbonylamino-β-D-glucopyranosyl-(1→2)-[3,6-O-di-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranosyl-(1→4)]-3,6-O-di-benzyl-α-D-mannopyranoside (S6c):** A mixture of compound **S6b** (1.9 g, 1.27 mmol) and 20 mL of ethylene diamine: *n*-BuOH (1:4) was stirred at 90 ^oC overnight. Volatiles were evaporated, and the crude product was dried using high vacuum. It was then dissolved in CH_2Cl_2 (20 mL), $NaHCO_3$ (0.687 g, 12.7 mmol) and 2,2,2-trichloro ethyl chloroformate (1.75 mL, 12.7 mmol) were added at 0 ^oC, allowed it to warm to rt and stirred for overnight until TLC (acetone: toluene, 1/9) indicated formation of product with consumption of starting material. The reaction mixture was diluted with CH_2Cl_2 (100 mL), washed with water (2 x 50 mL) and brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (0% → 8% EA in toluene) to afford **S6c** as a colorless solid (1.35 g, 72%). TLC (acetone: toluene = 1/9, v/v): R_f = 0.54; ^1H NMR (600 MHz, $CDCl_3$): δ 7.35-7.14 (m, 30H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 5.32 (d, *J* = 3.2 Hz, 1H), 5.27 (d, *J* = 7.2 Hz, 1H), 4.93 (d, *J* = 8.4 Hz, 1H), 4.73-4.58 (m, 10H), 4.48-4.43 (m, 7H), 4.19 (d, *J* = 7.2 Hz, 1H), 4.05-3.96 (m, 3H), 3.68 (s, 3H), 3.62-3.56 (m, 5H), 3.26 (q, 1H), 3.26-3.15 (m, 3H), 2.96 (s, 1H), 2.12 (s, 1H); ^{13}C NMR (150

MHz, $CDCl_3$): δ 155.26, 154.37, 154.27, 150.53, 138.93, 138.63, 138.48, 137.83, 137.74, 131.18, 128.96, 128.76, 128.67, 128.36, 128.21, 128.15, 127.89, 127.78, 118.00, 114, 85, 101.31, 98.79, 97.79, 95.81, 81.39, 79.59, 75.90, 74.70, 74.47, 74.01, 73.93, 73.53, 73.02, 72.83, 71.63, 71.37, 70.97, 68.99, 57.73, 57.40, 55.94 ; ESI-MS: *m/z* calcd for $C_{73}H_{78}Cl_6N_2O_{19}$; 1499.3338 found 1499.3419.



***p*-methoxyphenyl-O-[Methyl-5-acetamido-7,8,9-tri-O-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonate]-(2→6)-4-O-benzyl-2,3-di-O-benzoyl-1-β-D-galacto pyranosyl-(1→4)-O-3,6-O-di-benzyl-2-deoxy-2-(2,2,2-tri-chloroethoxy)carbonyl amino-β-D-glucopyranosyl-(1→2)-[Methyl-5-acetamido-7,8,9-tri-O-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonate]-(2→6)-4-O-benzyl-2,3-di-O-benzoyl-1-β-D-galacto pyranosyl-(1→4)-O-3,6-O-di-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranosyl-(1→4)-O-3,4,6-tri-O-benzyl-α-D-mannopyranoside (S6d):** Activated 4 Å molecular sieves were added to a solution of acceptor **S6c** (0.500 g, 0.341 mmol) and donor **S4c** (0.772 g, 0.751 mmol) in anhydrous CH_2Cl_2 (10 mL) . The mixture was stirred for 1 h at rt and then cooled to -50 ^oC. NIS (0.383 g, 1.70 mmol) and TfOH (15 µL, 0.170 mmol) were added slowly. The resulting reaction mixture was stirred for 2 h. When TLC (acetone: toluene, 2/8) indicated formation of product with consumption of starting material, the reaction was quenched by adding Et_3N and filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL), aqueous $Na_2S_2O_3$ (2 x 50 mL), and brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column

chromatography (0% → 15% EA in toluene) to afford **S6d** (0.950 g, 86%) as clear foam. TLC (acetone: toluene = 2/8, v/v): R_f = 0.48; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.90-7.87 (m, 7H), 7.81-7.79 (m, 3H), 7.50-7.07 (m, 50H), 6.98 (d, 2H), 6.40 (d, 2H), 5.78-5.73 (m, 2H), 5.36-5.26 (m, 4H), 5.20 (d, *J* = 8.6 Hz, 1H), 5.19-5.15 (dd, *J* = 3.2 & 8.4 Hz, 2H), 5.05 (dd, *J* = 4.3 & 8.4 Hz, 2H), 4.94-4.78 (m, 4H), 4.68-4.15 (m, 30H), 3.96-3.86 (m, 6H), 3.71 (S, 6H), 3.70-3.59 (m, 11H), 3.57 (s, 3H), 3.34-3.26 (m, 5H), 2.98-2.76 (m, 4H), 2.15 (s, 3H), 2.09 (s, 3H), 2.00 (S, 3H), 1.98 (s, 3H), 1.89 (S, 3H), 1.89 (S, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.56, 170.89, 169.56, 167.20, 165.28, 165.00, 159.11, 154.79, 138.78, 138.56, 138.21, 137.29, 137.00, 133,67, 133.24, 130.79, 129.70, 129.60, 129.26, 128.78, 128.56, 128.42, 128.32, 128.11, 127.69, 127.56, 127.44, 127.32, 127.14, 117.78, 100.89, 100.56, 99.87, 99.68, 95.41, 79.13, 75.56, 74.18, 73.48, 73.26, 73.12, 71.00, 72.90, 72.78, 71.76, 68.78, 68.40, 68.42, 61.78, 57.78, 57.33, 55.89, 53.80, 38.90, 38.7, 30.98, 30.76, 28.87, 23.89, 22.65, 20.87, 20.65, 20.54, 14.08, 10.86; ESI-MS: *m/z* calcd for $C_{161}H_{168}Cl_6N_4O_{55}$; 3251.8695 found 3252.8657 $(M)^+$.



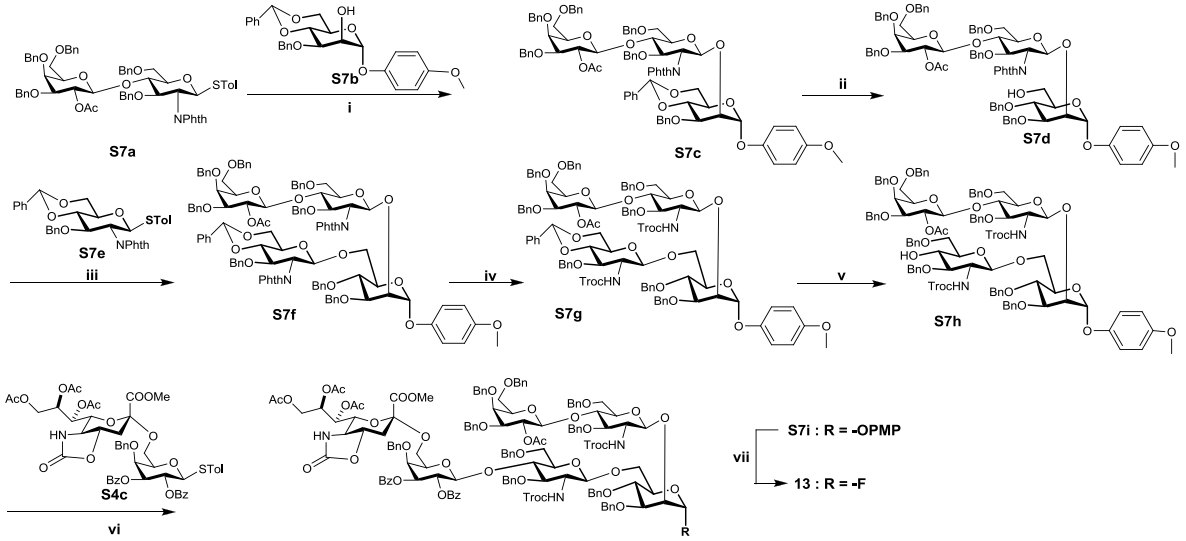
12

[Methyl-5-acetamido-7,8,9-tri-O-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonate]-(2→6)-4-O-benzyl-2,3-di-O-benzoyl-1-β-D-galacto pyranosyl-(1→4)-O-3,6-O-di-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranosyl-(1→2)-[Methyl-5-acetamido-7,8,9-tri-O-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonate]-(2→6)-4-O-benzyl-2,3-di-O-benzoyl-1-β-D-galactopyranosyl-(1→4)-O-3,6-O-di-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranosyl-(1→4)-O-3,4,6-tri-O-benzyl-α-D-mannopyranosyl fluoride (12): Cerium ammonium nitrate

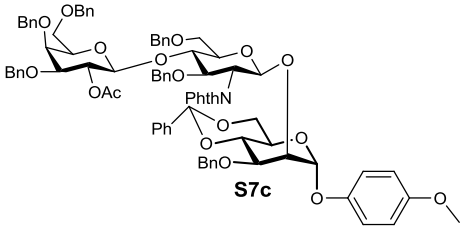
(0.470 g, 0.554 mmol) was added to a solution of compound **S6d** (0.300 g, 0.092 mmol) in 10 mL of acetonitrile: toluene: H_2O (4:2:1). The resulting reaction mixture was stirred at rt for 3 h. The reaction was diluted with EtOAc (100 mL) and washed with H_2O (30 x 2 mL) and brine (30 mL). The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The product was purified by flash column chromatography (0% → 20% EA in toluene) to afford 1-**OH** compound (0.180 g) as a foam. The residue (0.180 g, 0.057 mmol) was dissolved in CH_2Cl_2 (10 mL) at -30 ^oC. Then, DAST (22 µL, 0.171 mmol) was added slowly, and the resulting reaction mixture was stirred for 1 h. When TLC (acetone: toluene, 2/8) indicated formation of product with consumption of starting material, the reaction was quenched with aq. $NaHCO_3$. The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL) and brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (0% → 15% EA in toluene) to afford **13** (0.120 g, 41% over 2 steps) as white solid. TLC (acetone: toluene =2/8, v/v): R_f = 0.24; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.92-7.83 (m, 10H), 7.54-7.47 (m, 5H), 7.40-6.93 (m, 45H), 5.83 (m, 2H), 5.40-5.35 (m, 6H), 5.2 (dd, *J* = 3.2 & 7.8 Hz, 2H), 5.11 (dd, *J* = 4.3 & 8.4 Hz, 2H), 4.98-4.89 (m, 4H), 4.76-4.56 (m, 15H), 4.28-4.10 (m, 11H), 4.00-3.89 (m, 6H), 3.79-3.72 (m, 6H), 3.65 (s, 3H), 3.67 (s, 3H), 3.62-3.43 (m, 7H), 3.36-3.21 (m, 6H), 3.02-2.98 (m, 4H), 2.16 (s, 3H), 2.14 (s, 3H), 2.11 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.89-1.76 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.80, 170.85, 170.06, 168.03, 166.12, 165.41, 159.56, 154.16, 138.75, 138.34, 133.73, 130.11, 129.94, 129.57, 129.19, 128.79, 128.72, 128.50, 128.38, 128.03, 127.75, 127.56, 100.69, 100.00, 96.67, 95, 78, 95.35, 95.12, 74.91, 74.65, 74.29, 73.00, 70.91, 69.01, 67.35, 61.87, 58.15, 57.60, 53.42, 37.17, 21.28, 20.97; ESI-MS: *m/z* calcd for $C_{154}H_{161}Cl_6FN_4O_{53}$; 3147.6554 found 3169.8022 $(M + Na)^+$.

Synthesis of building blocks 13.

Total chemical synthesis of partially sialylated antennae **13** is shown in scheme S7.

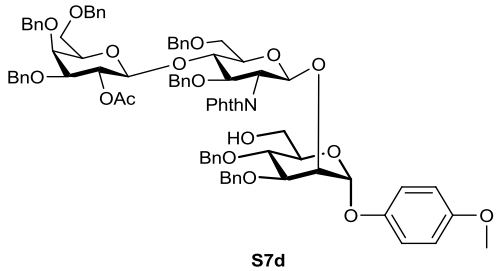


Scheme S7 | Preparation of compound 13. i, NIS, TfOH, CH_2Cl_2, -50 ^oC, 86%; **ii**, BH_3.THF, Bu_2BOTf, CH_2Cl_2, 65%; **iii**, NIS, TfOH, CH_2Cl_2, -50 ^oC, 76%; **iv**, (1) EDA, n-BuOH, 90 ^oC, (2) Troc-Cl, $NaHCO_3$, CH_2Cl_2; (3) Ac_2O, pyridine, 65% over 3 steps; **v**, Triethyl silane, TFA, CH_2Cl_2, 58%; **vi**, NIS, TfOH, CH_2Cl_2, -50 ^oC, 73%; **vii**, (1) CAN, ACN: Toluene: H_2O, (2) DAST, CH_2Cl_2, -30 ^oC, 30% over 2 steps.



***p*-methoxyphenyl-O-2-O-acetyl-3,4,6-O-tri-benzyl-β-D-galactopyranosyl-(1→4)-O-3,6-O-di-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→2)-O-3,4-O-benzyl-α-D-mannopyranoside (S7c):** Activated 4 Å molecular sieves were added to a solution of acceptor **S7a** (0.500 g, 1.07 mmol) and donor **S7b** (1.21 g, 1.28 mmol) in anhydrous CH_2Cl_2 (10 mL). The reaction mixture was stirred for 1 h at room temperature then cooled to -50 ^oC. NIS (0.481 g, 2.14 mmol) and TMSOTf (48 µL, 0.267 mmol) were added slowly, and the resulting reaction

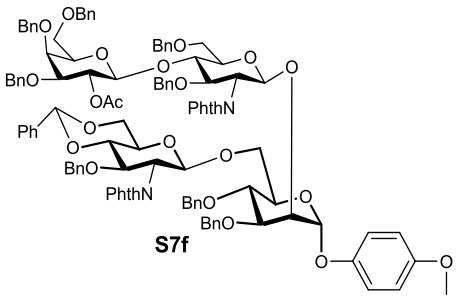
mixture was stirred for 3 h. When TLC (ethyl acetate: toluene, 1/9) indicated formation of product with consumption of starting material, the reaction was quenched by adding Et_3N then filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL), aqueous $Na_2S_2O_3$ (2 x 50 mL), and brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 10% EA in toluene) to afford **S7c** (1.30 g, 86%) as a pale yellow solid. TLC (ethyl acetate: toluene = 1/9, v/v): R_f = 0.59; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.80-7.77 (m, 4H), 7.75-7.65 (m, 5H), 7.37-7.15 (m, 30H), 6.98 (d, *J* = 8.1 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.70 (d, *J* = 8.4 Hz, 2H), 6.60 (d, *J* = 9.2 Hz, 2H), 5.39 (s, 1H), 5.34 (t, *J* = 10.2 Hz, 1H), 5.22 (dd, *J* = 7.2 & 2.8 Hz, 1H), 5.06 (d, *J* = 3.2 Hz, 1H), 4.89 (d, *J* = 11.4 Hz, 1H), 4.82 (d, *J* = 12.1 Hz, 1H), 4.75 (d, *J* = 11.8 Hz, 1H), 4.66-4.62 (m, 3H), 4.54-4.38 (m, 6H), 4.32 (d, *J* = 11.2 Hz, 1H), 4.29 (dd, *J* = 3.1 & 7.2 Hz, 2H), 4.27 (d, *J* = 10.8 Hz, 1H), 4.19 (t, *J* = 8.3 Hz, 1H), 4.00-3.89 (m, 4H), 3.72 (s, 3H), 3.58-3.33 (m, 4H), 3.0 (t, *J* = 8.7 Hz, 1H), 2.07 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.3, 154.9, 149.6, 138.8, 138.7, 138.6, 138.5, 138.1, 138.0, 137.9, 137.5, 133.6, 131.9, 128.7, 128.4, 128.4, 128.3, 128.2, 128.1, 128.1, 128.1, 128.0, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 127.6, 127.5, 127.4, 127.3, 127.2, 126.8, 126.0, 123.0, 117.03, 114.5, 101.4, 100.9, 97.0, 96.2, 96.2, 80.3, 78.1,78.0, 75.6,74.9, 74.5, 74.4, 73.7, 73.4, 73.3, 72.6, 72.6, 72.0, 71.7, 71.3, 68.4, 68.1, 68.1, 64.2, 55.6, 55.6, 55.6, 21.0; ESI-MS: *m/z* calcd for $C_{84}H_{83}NO_{19}$; 1409.5559 found 1432.5499 $(M + Na)^+$.



S7d

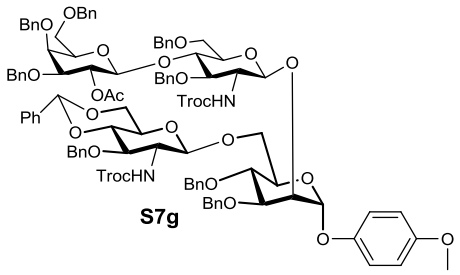
***p*-methoxyphenyl-O-2-O-acetyl-3,4,6-O-tri-benzyl-β-D-galactopyranosyl-(1→4)-O-3,6-O-di-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→2)-O-3,4-O-dibenzyl-α-D-**

mannopyranoside (S7d): To a mixture of compound **S7c** (1.30 g, 1.02 mmol) and activated molecular sieves in anhydrous CH_2Cl_2 (15 mL) was added borane.THF complex (0.978 mL of a 1M solution in THF, 10.2 mmol) and Bu_2BOTf (0.439 mL of a 1M solution in CH_2Cl_2, 10.2 mmol) were added at 0 ℃. The reaction mixture was allowed to stirred at room temperature for 4 h. TLC (acetone: toluene, 1/9) indicated formation of a product with consumption of the starting material. Triethyl amine was added to the reaction mixture followed by slow addition of methanol at 0 ℃. When no more hydrogen was produced, the reaction mixture was filtered through Celite, The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL), and brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% $\rightarrow$ 7% EA in toluene) to afford **S7d** (0.850 g, 65%) as clear foam. TLC (acetone: toluene = 1/9, v/v): R_f = 0.31; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.98-7.89 (m, 4H), 7.84-7.66 (m, 5H), 7.42-7.02 (m, 30H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.87 (t, *J* = 7.8 Hz, 2H), 6.67 (d, *J* = 12.1 Hz, 2H), 6.48 (d, *J* = 12.1 Hz, 2H), 5.39 (t, *J* = 10.2 Hz, 1H), 5.17 (d, *J* = 8.4 Hz, 1H), 4.93 (d, *J* = 12 Hz, 2H), 4.88 (d, *J* = 7.2 Hz, 1H), 4.85 (d, *J* = 12.1 Hz, 2H), 4.67 (dd, *J* = 4.3 & 8.4 Hz, 2H), 4.59-4.30 (m, 9H), 4.18 (t, *J* = 7.4 Hz, 1H), 4.01-3.96 (m, 3H), 3.84-3.78 (m, 3H), 3.76 (s, 3H), 3.68 (dd, *J* = 3.2 & 7.8 Hz, 1H), 3.54-3.34 (m, 3H), 3.25-3.20 (m, 1H), 2.01 (s, 3H) ; ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.3, 167.9, 154.7, 149.6, 138.9, 138.7, 138.4, 138.2, 138.0, 138.0, 137.9, 134.1, 133.6, 131.9, 131.5, 129.0, 128.4, 128.4, 128.4, 128.3, 128.2, 128.2, 128.1, 128.1, 127.9, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 127.6, 127.5, 127.3, 127.3, 126.8, 123.2, 123.0, 116.8, 114.4, 100.9, 97.6, 95.7, 80.3, 78.0, 76.9, 75.2, 75.1, 74.4, 74.4, 73.9, 73.6, 73.4, 73.3, 72.5, 72.3, 72.0, 71.6, 70.7, 68.6, 68.1, 62.2, 55.9, 55.6, 21.0; ESI-MS: *m/z* calcd for $C_{84}H_{85}NO_{19}$; 1411.5716 found 1412.5726 $(M + H)^+$.



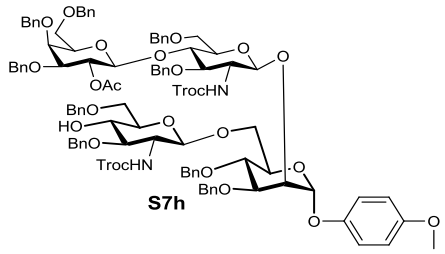
***p*-methoxyphenyl-O-[2-O-acetyl-3,4,6-O-tri-benzyl-β-D-galactopyranosyl-(1→4)-O-3,6-O-di-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl]-(1→2)-O-[3-O-benzyl-4,6-O-benzylidine-2-deoxy-2-phthalimido-β-D-glucopyranosyl]-(1→6)-3,4-O-dibenzyl-α-D-mannopyranoside (S7f):** Activated 4 Å molecular sieves were added to a solution of acceptor **S7d** (0.600 g, 0.470 mmol) and donor **S7e** (0.557 g, 0.940 mmol) in anhydrous CH_2Cl_2 (10 mL). The reaction mixture was stirred for 1 h at room temperature then cooled to -50 ^oC. NIS (0.211 g, 0.940 mmol) and TfOH (10.4 µL, 0.117 mmol) were added slowly, and the resulting reaction mixture was stirred for 2 h. When TLC (ethyl acetate: toluene, 2/8) indicated formation of product with consumption of starting material, the reaction was quenched by adding Et_3N then filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL), aqueous $Na_2S_2O_3$ (2 x 50 mL), and brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 15% EA in toluene) to afford **S7f** (0.610g, 76%) as clear foam. TLC (ethyl acetate: toluene = 2/8, v/v): R_f = 0.49; ^1H NMR (600 MHz, $CDCl_3$): δ 7.66 (m, 8H), 7.38-7.15 (m, 30H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.95-6.91 (m, 5H), 6.88-6.78 (m, 8H), 6.63 (d, *J* = 8.4 Hz, 2H), 6.50 (d, *J* = 8.8 Hz, 2H), 5.41 (s, 1H), 5.32 (t, *J* = 10.2 Hz, 1H), 5.11 (d, *J* = 8.4 Hz, 1H), 4.89 (d, *J* = 4.3 Hz, 1H), 4.87 (s, 1H), 4.80 (t, *J* = 8.8 Hz, 2H), 4.73 (s, 1H), 4.70 (s, 1H), 4.60 (t, *J* = 10.8 Hz, 3H), 4.57-4.40 (m, 5H), 4.35-4, 16 (m, 8H), 4.08 (t, *J* = 10.2 Hz, 1H), 4.00-3.89 (m, 4H), 3.85 (dd, *J* = 3.6 & 7.8 Hz, 1H), 3.78 (s, 3H), 3.70-3.61 (m, 3H), 3.52-3.41 (m, 4H), 3.40-3.28 (m, 4H), 3.20 (t, *J* = 10.2 Hz, 2H), 2.98 (m, 1H), 1.98 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.5, 164.8, 158.0, 153.0, 152.8, 151.6, 151.5, 150.6, 150.5, 149.2, 139.6, 138.9, 138.4, 138.1, 138.0, 137.4, 129.3, 129.2,

128.9, 128.9, 128.8, 128.9, 128.7, 128.5, 128.4, 128.2, 128.1, 128.0, 128.0, 127.9, 127.9, 127.7, 127.5, 127.4, 126.2, 125.5, 117.3, 114.9, 114.2, 102.2, 101.4, 100.9, 98.8, 96.5, 95.8, 95.7, 95.5, 95.3, 95.3, 95.0, 82.3, 80.6, 78.3, 76.2, 76.0, 75.8, 75.5,75.4, 75.2,74.9, 74.8,74.7, 74.7,74.2, 74.1, 73.8, 73.7, 73.5, 72.9, 72.3, 71.9, 68.9, 68.8, 68.2, 68.0, 66.4, 58.0, 57.1, 55.9, 44.3, 42.9, 40.8, 40.4, 40.3, 40.0, 21.7, 21.2; ESI-MS: *m/z* calcd for $C_{111}H_{108}N_2O_{24}$; 1882.7247 found 1882.7343.



***p*-methoxyphenyl-O-[2-O-acetyl-3,4,6-O-tri-benzyl-β-D-galactopyranosyl-(1→4)-O-3,6-O-di-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranosyl]-(1→2)-O-[3-O-benzyl-4,6-O-benzylidine-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranosyl]-(1→6)-3,4-O-dibenzyl-α-D-mannopyranoside (S7g):** A mixture of compound **S7f** (0.950 g, 0.545 mmol) and 10 mL of ethylene diamine: *n*-BuOH (2:8) was stirred at 90 ^oC overnight. Volatiles were evaporated, and the crude product was dried using high vacuum. It was then dissolved in CH_2Cl_2 (20 mL), $NaHCO_3$ (0.363 g, 5.45 mmol) and 2,2,2-trichloro ethyl chloroformate (0.86 mL, 5.45 mmol) were added at 0 ^oC, allowed it to warm to rt and stirred for overnight. TLC (ethyl acetate: toluene, 2/8) indicated formation of product with consumption of starting material. The reaction mixture was diluted with CH_2Cl_2 (100 mL), washed with water (2 x 50 mL) and brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (0% → 10% EA in toluene). The product was then acetylated using 10 mL of pyridine/acetic anhydride (6:4) until TLC indicated (ethyl acetate: toluene, 2/8) complete consumption of starting material. The reaction mixture was then concentrated *in vacuo* and purified by silica gel column chromatography (0% → 10% EA in toluene) to afford **S7g** as a white foam (0.650 g, 65%). TLC

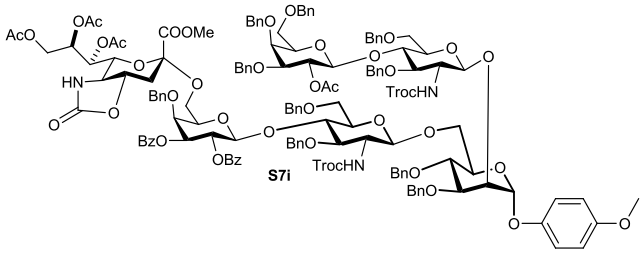
(ethyl acetate: toluene = 2/8, v/v): R_f = 0.64; H NMR (600 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.8 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.35-7.12 (m, 41H), 6.91 (d, *J* = 10.2 Hz, 2H), 6.87 (d, *J* = 10.3 Hz, 2H), 5.55 (s, 1H), 5.50 (s, 1H), 5.32 (t, *J* = 10.2 Hz, 1H), 4.94-4.89 (m, 8H), 4.83-4.67 (m, 10H), 4.64-4.66 (m, 5H), 4.54-4.50 (m, 3H), 4.36-4.22 (m, 6H), 4.06-3.87 (m, 6H), 3.83-3.46 (m, 6H), 3.38-3.34 (m, 3H), 3.20-3.10 (m, 2H), 2.33 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.5, 162.8, 155.0, 155.0, 154.8, 154.6, 154.51, 150.6, 150.5, 150.2, 139.6, 138.9, 138.4, 138.3, 138.3, 138.2, 138.1, 137.5, 129.3, 129.2, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 128.0, 127.9, 127.9, 127.7, 127.5, 127.4, 126.2, 125.5, 117.3, 114.9, 114.2, 102.2, 101.4, 100.8, 98.3, 9 6.5, 95. 8, 95.7, 95.5, 95.3, 95.3, 95.0, 82.3, 80.6, 78.3, 76.2, 76.0, 75.8, 75.5,75.4, 75.2,74.9, 74.8,74.7, 74.7,74.2, 74.1, 73.8, 73.7, 73.5, 72.9, 72.3, 71.9, 68.9, 68.8, 68.2, 68.0, 66.4, 58.0, 57.1, 55.9, 44.3, 42.9, 40.8, 40.4, 40.3, 40.0, 21.7, 21.2 ; ESI-MS: *m/z* calcd for $C_{102}H_{106}Cl_6N_2O_{25}$; 1972.6590 found 1973.5278 $(M + H)^+$.



S7h

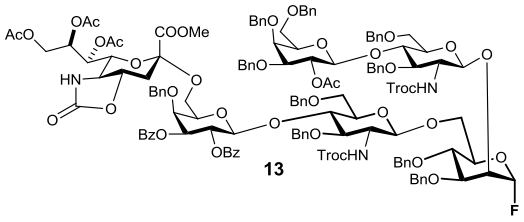
***p*-methoxyphenyl-O-[2-O-acetyl-3,4,6-O-tri-benzyl-β-D-galactopyranosyl-(1→4)-O-3,6-O-di-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranosyl]-(1→2)-O-[3,6-O-dibenzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranosyl]-(1→6)-3,4-O-dibenzyl-α-D-mannopyranoside (S7h):** To a solution of **S7g** (0.600 g, 0.328 mmol) in anhydrous CH_2Cl_2 (70 mL) was added triethyl silane (2.10 mL, 13.2 mmol) followed by trifluroacetic acid (0.953 mL, 13.2 mmol) at 0 ^oC. The resulting reaction mixture was stirred for 2 h. After 2 h, TLC (ethyl acetate: toluene, 1.5/8.5 v/v) indicated product formation with consumption of starting material. The reaction mixture was washed with sat. $NaHCO_3$ (2 x 50 mL). The aqueous layer was further extracted with CH_2Cl_2 (3 x 30 mL), and the combined

organic layer were washed with brine solution (100 mL), dried over $MgSO_4$, filtered and concentrated in *vacuo.* The residue was purified by flash column chromatography (0% → 10% EA in toluene) to afford **S7h** (0.350 g, 58%) as clear oil. TLC (ethyl acetate: toluene = 1.5/8.5, v/v): R_f = 0.35**;** ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33-7.04 (m, 45H), 6.92 (d, *J* = 8.2 Hz, 2H), 6.80 (d, *J* = 8.3 Hz, 2H), 5.55 (s, 1H), 5.31 (t, *J* = 10.1 Hz, 1H), 5.06 (d, *J* = 3.2 Hz, 1H), 4.93-4.80 (m, 4H), 4.47-4.35 (m, 13H), 4.35-4.18 (m, 8H), 4.05 (dd, *J* = 3.2 & 7.8 Hz, 2H), 3.82 (d, *J* = 8.4 Hz, 2H), 3.80-3.62 (m, 14H), 3.49-3.20 (m, 5H), 3.10 (bs, 2H), 2.08 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.5, 168.0, 155.3, 155.0, 154.7, 150.2, 138.9, 138.4, 138.3, 138.2, 137.8, 132.7, 131.1, 129.0, 128.7, 128.7, 128.6, 128.6, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 127.7, 127.5, 127.4, 117.3, 114.9, 101.5, 100.8, 95.7, 80.6, 78.5, 75.8, 75.3,74.9, 74.8, 74.6, 74.1, 74.0, 73.8, 73.7, 73.64, 73.5, 72.8, 72.3, 71.9, 71.1, 68.9, 68.8, 68.4, 68.2, 67.6, 58.0, 56.5, 55.9, 41.5, 39.0, 37.3, 33.7, 32.0, 31.4, 30.6, 29.9, 29.20, 26.6, 24.0, 23.2, 22.9, 21.2, 20.1, 14.6, 14.4, 14.3, 14.3, 11.2; ESI-MS: *m/z* calcd for $C_{102}H_{108}Cl_6N_2O_{25}$; 1974.6750 found 1975.5438 $(M + H)^+$.



***p*-methoxyphenyl-O-[2-O-acetyl-3,4,6-O-benzyl-β-D-galactopyranosyl-(1→4)-O-3,6-O-di-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranosyl-(1→2)-[Methyl-5-acetamido-7,8,9-tri-O-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonate]-(2→6)-4-O-benzyl-2,3-di-O-benzoyl-1-β-D-galactopyranosyl-(1→4)-O-3,6-O-di-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranosyl-(1→6)-O-3,4,-di-O-benzyl-α-D-mannopyranoside (S7i):** A mixture of donor **S4c** (0.187 g, 0.182 mmol), acceptor **S7h** (0.300 g, 0.151 mmol) and activated 4 Å molecular sieves in dry

CH_2Cl_2 (10 mL) was stirred at room temperature for 1 h. The reaction mixture was cooled to -50 ^oC, NIS (0.067 g, 0.302 mmol) and TfOH (4 µL, 0.037 mmol) were added slowly and resulting reaction mixture was stirred for 2 h. The reaction was quenched by adding Et_3N, diluted with CH_2Cl_2, filtered through Celite, extracted with saturated $Na_2S_2O_3$ followed by $NaHCO_3$, dried over sodium sulfate and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 10% EA in toluene) to afford **S7i** (0.317 g, 73%) as colorless foam. TLC: (ethyl acetate: toluene = 1.5/8.5, v/v): R_f = 0.61; ^1H NMR (600 MHz, $CDCl_3$): δ 7.90 (m, 4H), 5.52-7.45 (m, 2H), 7.37-7.08 (m, 54H), 6.90 (d, *J* = 8.3 Hz, 2H), 6.80 (d, *J* = 8.3 Hz, 2H), 5.72 (t, *J* = 10.2 Hz, 1H), 5.53 (s, 1H), 5.35-5.32 (m, 3H), 5.20 (dd, *J* = 3.2 & 8.3 Hz, 1H), 5.08 (dd, *J* = 2.8 & 8.4 Hz, 2H), 4.99-4.79 (m, 7H), 4.70-4.18 (m, 25H), 4.06 (dd, *J* = 3.2 & 7.8 Hz, 1H), 3.94 (m, 2H), 3.90-3.84 (m, 16H), 3.74 (s, 3H), 2.60 (s, 3H), 2.59-2.57 (m, 3H), 3.45-3.32 (m, 6H), 3.20 (t, *J* = 9.8 Hz, 1H), 2.90 (t, *J* = 10.2 Hz, 2H), 2.83 (dd, *J* = 3.2 & 7.8 Hz, 1H), 2.08 (s, 3H), 2.06 (s, 3H), 2.02 (t, *J* = 10.1 Hz, 1H), 1.99 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.4, 170.5, 169.7, 169.1, 167.4, 165.7, 165.1, 159.1, 154.6, 159.8, 138.5, 138.2, 138.1, 137.9, 137.4, 133.3, 133.1, 132.3, 130.2, 129.8, 129.6, 129.4, 128.7, 128.5, 128.4, 128.1, 127.9, 127.5, 127.4, 127.1, 127.08, 116.9, 114.5, 101.3, 100.6, 100.4, 100.0, 95.3, 80.2, 79.9, 77.4, 75.5, 75.3, 74.5, 74.3, 74.1, 73.7, 73.4, 73.2, 73.1, 72.5, 72.1, 71.5, 71.2, 70.8, 68.6, 68.5, 68.3, 67.8, 67.5, 67.3, 63.1, 61.5, 57.8, 56.6, 55.5, 53.1, 38.6, 37.0, 36.8, 33.3, 32.0, 31.0, 30.9, 28.8, 26.2, 25.5, 23.6, 22.8, 22.5, 20.8, 20.6, 19.7, 14.3, 13.9, 10.8; ESI-MS: *m/z* calcd for $C_{146}H_{153}Cl_6N_3O_{43}$; 2850.5080 found 2850.8248.



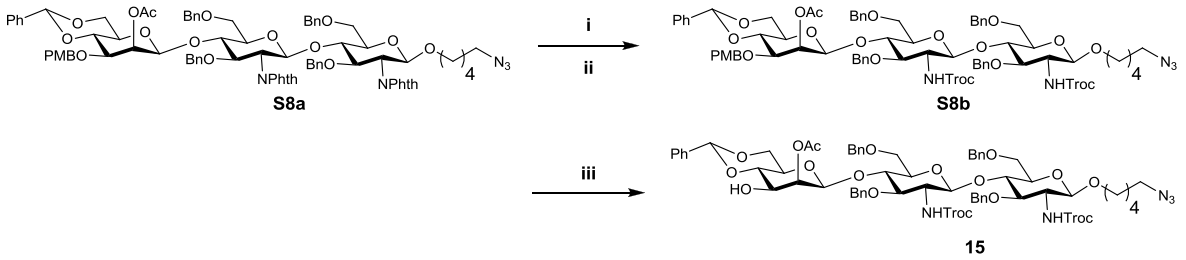
13

[2-O-acetyl-3,4,6-O-benzyl-β-D-galactopyranosyl-(1→4)-O-3,6-O-di-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranosyl-(1→2)-[Methyl-5-acetamido-7,8,9-tri-O-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonate]-(2→6)-4-O-benzyl-2,3-di-O-benzoyl-1-β-D-galactopyranosyl-(1→4)-O-3,6-O-di-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy) carbonylamino-β-D-glucopyranosyl-(1→6)-O-3,4,-di-O-benzyl-α-D-mannopyranosyl fluoride (13): To a solution of compound **S7i** (0.430 g, 0.150 mmol) in 10 mL of acetonitrile: toluene: H_2O (4:2:1) was added cerium ammonium nitrate (0.641 g, 0.754 mmol) and the resulting reaction mixture was stirred at 0 ℃ for 2 h. The reaction was diluted with EtOAc (100 mL) and washed with H_2O (30 x 2 mL) and brine (30 mL). The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The product was purified by flash column chromatography (0% → 20% EA in toluene) to afford 1-**OH** compound (0.240 g, 57%) as clear foam. The residue (0.200 g, 0.072 mmol) was dissolved in CH_2Cl_2 (10 mL) at -30 ^oC. Then, DAST (29 μL, 0.216 mmol) was added slowly, and the resulting reaction mixture was stirred for 2 h. When TLC (ethyl acetate: toluene, 2/8) indicated formation of product with consumption of starting material, the reaction was quenched with aq. $NaHCO_3$. The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL) and brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (0% → 10% EA in toluene) to afford **13** (0.104 g, 50%) as white foam. TLC (ethyl acetate: toluene =2/8, v/v): R_f = 0.44; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.95-7.90 (m, 4H), 7.58-7.49 (m, 2H), 7.39-7.18 (m, 54H), 5.82 (t, *J* = 10.2Hz, 1H), 5.65 (d, *J* = 51 Hz, 1H), 5.34 (t, *J* = 10.2 Hz, 2H), 5.21 (dd, *J* = 3.6 & 7.8 Hz, 1H), 5.13-4.19 (m, 30H), 4.10-4.09 (m, 5H), 4.02-3.74 (m, 12H), 3.65 (s, 3H), 3.64-3.27 (m, 14H), 3.02 (t, *J* = 10.2 Hz, 2H), 2.87 (dd, *J* = 3.2 & 7.8 Hz, 1H), 2.12 (s, 3H), 2.10 (s, 3H), 2.09 (t, *J* = 10.2 Hz, 1H), 2.00 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.4, 170.2, 169.7, 169.1, 167.4, 165.6, 165.1, 159.1, 154.4, 139.0, 138.8, 138.2, 138.1, 138.0, 137.7, 133.3, 129.8, 129.7, 129.2, 128.7, 128.4, 128.1, 127.9, 127.7, 127.6, 127.5, 127.4, 127.3, 127, 1, 127.0, 125.2, 101.4, 100.7, 100.4, 9.9, 97.3, 95.180.2, 79.6, 78.6, 75.5, 74.5, 74.3, 73.8, 73.5, 73.3, 73.1, 72.8, 71.3, 71.3, 70.7, 70.1, 68.6, 67.8, 66.9, 63.1,

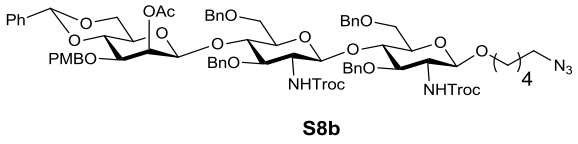
61.5, 57.8, 53.1, 37.1, 25.5, 21.3, 20.9, 20.5; ESI-MS: *m/z* calcd for $C_{139}H_{146}Cl_6FN_3O_{41}$; 2746.3454 found 2746.7604.

iv. Preparation of core trisaccharides 14-15

The reducing end trisaccharide (Man-β-1,4-GlcNAc-β-1,4-GlcNAc-β-linker) **14** with N-pthallamide protections was obtained according to our previous report[3]. Compound **14** was next modified to **15** as shown in scheme S8.

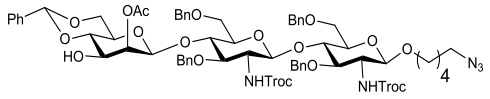


Scheme S8 | Preparation of compound 15. i, (1) EDA, n-BuOH, 90 ^{o}C, (2) Troc-Cl, $NaHCO_3$, CH_2Cl_2, 72% over 2 steps; **ii**, Ac_2O, pyridine, 79%; **iii**, DDQ, CH_2Cl_2 H_2O, 58%.



5-Azidopentyl-O-2-O-acetyl-3-O-*p*-methoxy-benzyl-4,6-O-benzylidine-β-D-manno-pyranosyl-(1→4)-O-(3,6-di-O-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranosyl)-(1→4)-O-3,6-di-O-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy) carbonylamino-β-D-glucopyranoside (S8b): A mixture of compound **S8a** (0.950 g, 0.545 mmol) and 10 mL of ethylene diamine: *n*-BuOH (2:8) was stirred at 90 ^{o}C overnight. Volatiles were evaporated, and the crude mixture was dried using high vacuum. It was then dissolved in CH_2Cl_2 (20 mL), $NaHCO_3$ (0.363 g, 5.45 mmol) and 2,2,2-trichloro ethyl chloroformate (0.86 mL, 5.45 mmol) were added at 0 ^{o}C, allowed it to warm to rt and stirred for overnight. TLC (ethyl acetate: toluene, 2/8) indicated formation of product with consumption of starting material.

Reaction was diluted with CH_2Cl_2 (100 mL), washed with water (2 x 50 mL) and brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (0% → 10% EA in toluene). The product was then acetylated using 10 mL of pyridine/acetic anhydride (6:4) until TLC indicated (ethyl acetate: toluene, 2/8) complete consumption of starting material. The reaction mixture was then concentrated *in vacuo* and purified by silica gel column chromatography (0% → 10% EA in toluene) to afford **S8b** as a white foam (0.650 g, 65%). TLC (ethyl acetate: toluene = 2/8, v/v): R_f = 0.64; ^{1}H NMR (600MHz, $CDCl_3$): δ 7.62-7.20 (m, 30H), 5.89 (s, 1H), 4.56 (d, *J* = 3.2 Hz, 1H), 4.23 (d, *J* = 8.9 Hz, 2H), 4.20-4.10 (m, 12H), 4.00-3.86 (m, 5H), 3.69-3.30 (m, 11H), 3.29 (s, 3H), 3.22-3.20 (m, 4H), 3.20-3.00 (m, 1H), 2.66 (s, 3H, -C(O)CH_3, 1.56-1.38 (m, 4H, -CCH_2C-, linker), 1.21-1.23(m, 2H, -CCH_2C-, linker) ; ^{13}C NMR (150 MHz, $CDCl_3$): δ 177.7, 169.6, 167.0, 138.5, 138.4, 138.3, 138.2, 137.2, 137.8, 137.5, 134.2, 133.2, 133.6, 131.7, 131.1, 131.45, 129.8, 129.06, 128.9, 128.2, 128.4, 128.2, 128.4, 128.7, 127.8, 127.87, 127.83, 127.4, 127.4, 127.0, 127.2, 127.29, 127.6, 127.20, 126.88, 126.24, 125.1, 123.6, 123.3, 101.5, 102.7, 99.7, 98.0, 97.1, 78.13, 78.55, 78.05, 75.82, 74.57, 75.38, 75.27,74.25, 74.30, 72.78, 72.26, 70.89, 66.85, 68,43, 68.25, 67.75, 66.87, 55.57, 53.71, 52.10, 28.97, 28.87, 23.80, 22.77, 20.12; ESI-MS: *m/z* calcd for $C_{74}H_{83}Cl_6N_5O_{20}$: 1575.1930 ; found 1576.235 $(M + H)^+$.



15

5-Azidopentyl-O-2-O-acetyl-4,6-O-benzylidine-β-D-mannopyranosyl-(1→4)-O-(3,6-di-O-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranosyl)-(1→4)-O-3,6-di-O-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranoside (15): To a solution of **S8a** (1.0 g, 0.673 mmol) in 10 mL (CH_2Cl_2 : H_2O, 10/1) was added DDQ (0.183 g, 0.808 mmol) at 0 ℃ and the resulting reaction mixture was stirred until TLC (ethyl acetate: toluene, 2/8) indicated formation of a product with consumption of the starting material. The

reaction mixture was then filtered and the organic layer washed with H_2O (2 x 30 mL). The aqueous layer was further extracted with CH_2Cl_2 (2 x 50 mL). The combined organic layers were washed with brine solution (40 mL), dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 15% EA in toluene) to afford **15** (0.652 g, 70%) as colorless foam**.** TLC (ethyl acetate: toluene =2/8 v/v): R_f = 0.24; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.44-7.16 (m, 25H), 5.44 (s, 1H), 5.15 (d, *J* = 3.2 Hz, 1H), 4.88 (t, *J* = 8.9 Hz, 2H), 4.54-4.40 (m, 12H), 4.08-3.58 (m, 3H), 3.56-3.40 (m, 14H), 3.25-3.20 (m, 4H), 3.02-3.00 (m, 1H), 2.16 (s, 3H, -C(O)CH_3, 1.51-1.47 (m, 4H, -CCH_2C-, linker), 1.30-0.99 (m, 2H, -CCH_2C-, linker); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.5, 168.6, 167.0, 138.7, 138.4, 138.38, 138.2, 137.2, 137.8, 137.5, 134.2, 133.2, 133.6, 131.7, 131.1, 131.45, 129.8, 129.06, 128.9, 128.2, 128.4, 128.2, 128.4, 128.7, 127.8, 127.87, 127.83, 127.4, 127.4, 127.0, 127.2, 127.29, 127.6, 127.20, 126.88, 126.24, 125.1, 123.6, 123.3, 101.5, 102.7, 99.7, 98.0, 97.1, 78.13, 78.55, 78.05, 75.82, 74.57, 74.37, 74.27,73.25, 73.30, 72.78, 71.26, 69.89, 68.85, 69,43, 68.25, 67.73, 66.67, 56.57, 55.71, 51.10, 28.67, 28.27, 23.00, 21.47, 21.02 ; ESI-MS: *m/z* calcd for $C_{66}H_{75}Cl_6N_5O_{19}$: 1455.0420; found 1478.3082 $(M + Na)^+$.

v. Synthesis of high-mannose type oligosaccharides (G1-G6)

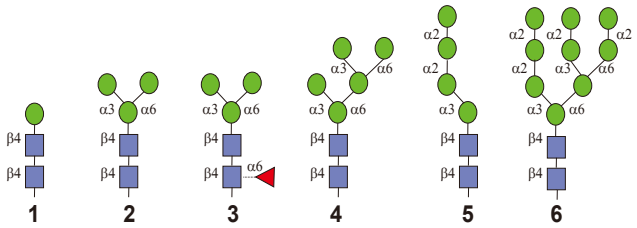
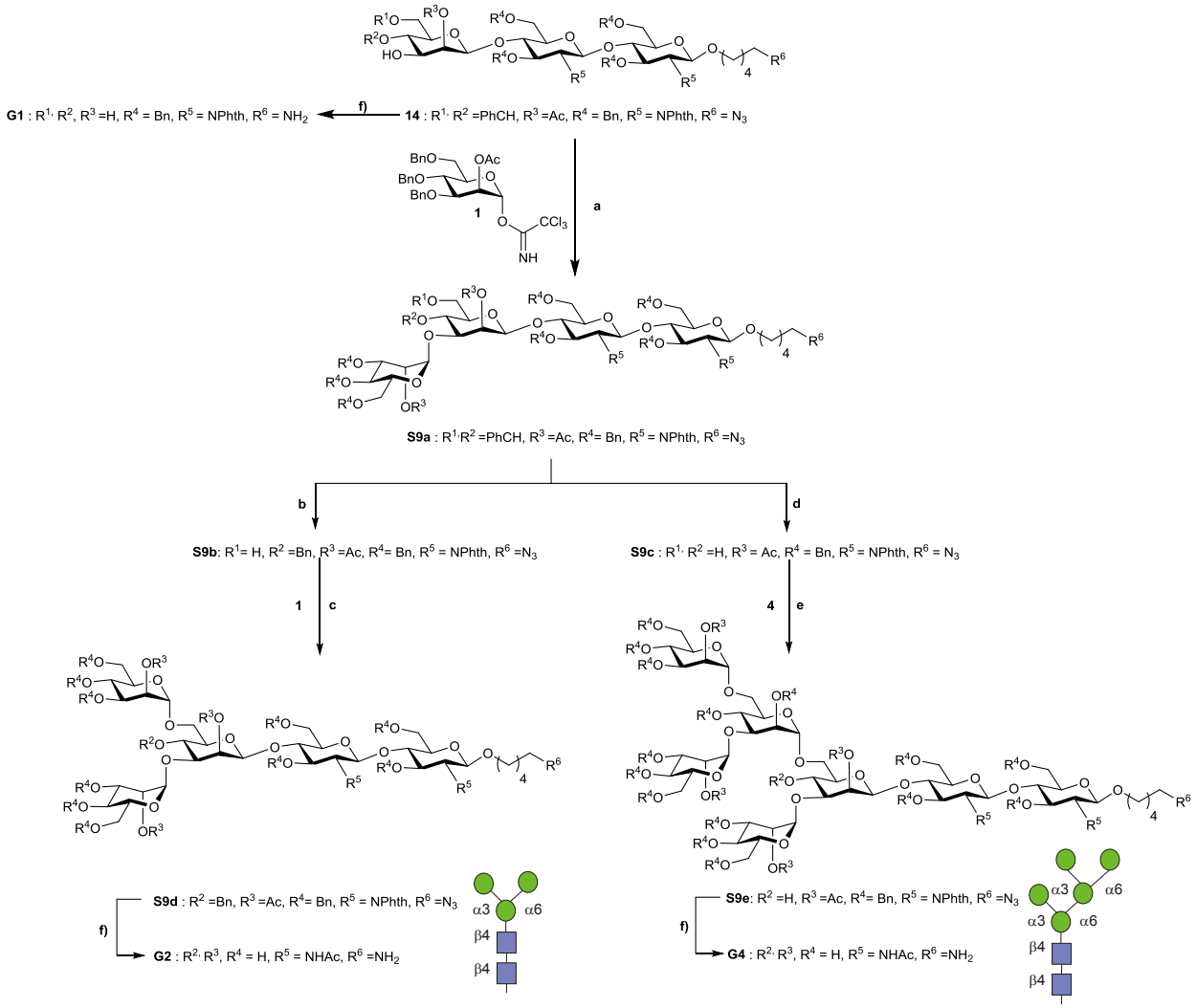


Figure S1 | Structures of high mannose type glycans and their fragments

With the donors **1-5** in hand, we investigated their glycosylation with core trisaccharide acceptor **14** and the coupling products (Scheme S9). The glycosylation of **14** with known imidate donor **1** to give tetrasaccharide **S9a** in 70% yield[11]. After selective benzylidene ring opening of **S9a,** the resulting 6"-OH **S9b** was glycosylated with **1** to afford the desired fully protected $Man_3GlcNAc_2$

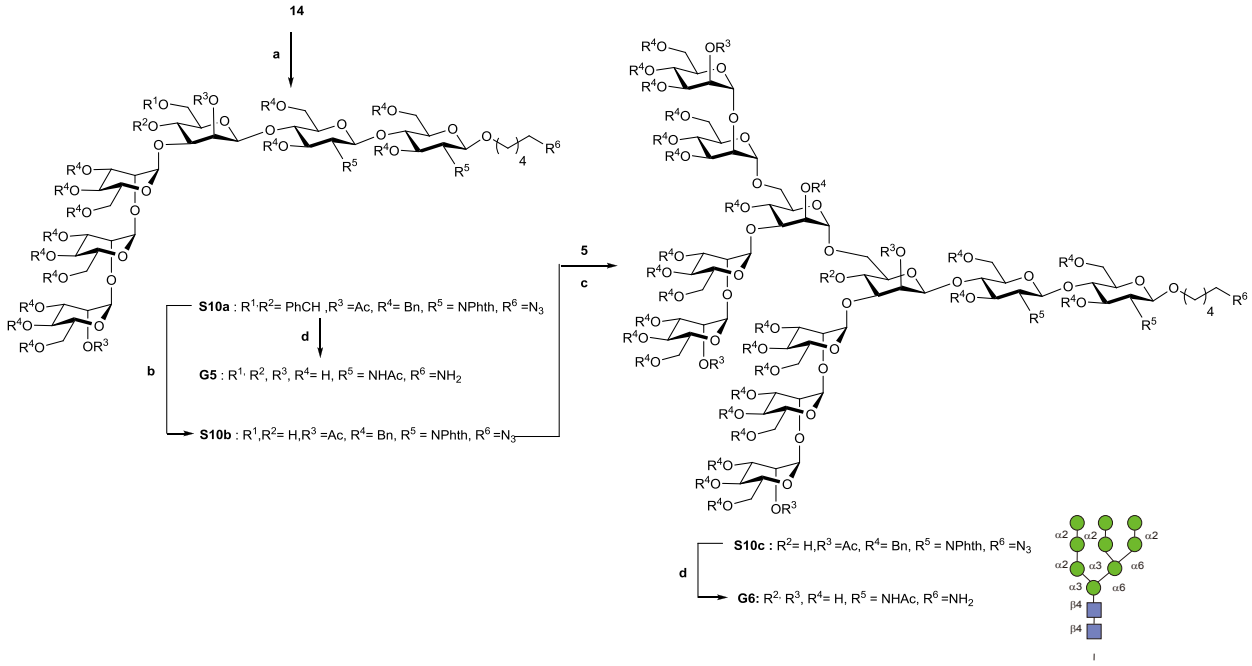
pentasaccharide **S9d,** an early intermediate in *N*-Glycan biosynthesis and thus a conserved motif in all *N*-glycans, in 60% yield. In another pathway, opening of the benzylidene group **S9a** resulted in diol **S9c**, which was further condensed with trimannosyl fluoride **4** by using Cp_2HfCl_2 and AgOTf to obtain heptasaccharide **S9e,** an intermediate in GlcNAc mediated branching in the Golgi apparatus, in 52% yield[11].



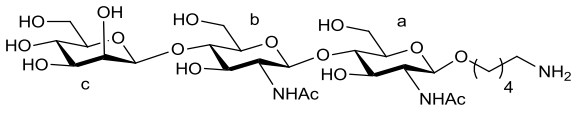
Scheme S9 | Preparation of Man_3 and $Man_5GlcNAc_2$. a, $BF_3.OEt_2$, CH_2Cl_2, 4 Å MS, -40 °C, 2 h, 70%; **b**, Triethyl silane, $PhBCl_2$, CH_2Cl_2, 4 Å MS, -78 °C, 1 h, 82%; **c**, **1**, $BF_3.OEt_2$, CH_2Cl_2, 4 Å MS, -60 °C to -20 °C, 2 h, 60%; **d**, *p*TsOH, CH_3CN, 2 h, 66%; **e**, **4**, AgOTf, Cp_2HfCl_2, Toluene, 4 Å MS, -40 °C, 2 h, 52%; **f**, (1) $NH_2CH_2CH_2NH_2$, *n*BuOH, 90 °C, overnight; (2) Ac_2O,

pyridine, overnight; (3) NaOMe, MeOH, overnight; (4) $Pd(OH)_2$, MeOH: H_2O: HCOOH (5:3:2), H_2; **G1**: 65%; **G2**: 52%; **G4**: 29%; Cp_2HfCl_2: Bis (cyclopentadienyl) hafnium Dichloride.

To synthesize $Man_9GlcNAc_2$, a major glycoform found on HIV-1 gp120 surface and an important component of epitope recognized by broadly neutralizing antibodies, compound **14** was subjected to 3"-O glycosylation with fluoride **2** under the promotion of Cp_2HfCl_2 /AgOTf to get hexasaccharide **S10a** in 65% yield. The *p*-toluene sulfonic acid mediated ring opening of **S10a** provided diol **S10b**, which was further glycosylated with **5** to afford undecasaccharide **S10c** (Scheme S10).

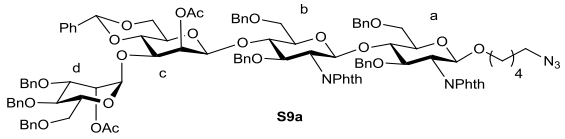


Scheme S10 | Preparation of Man_4 (G5) and $Man_9GlcNAc_2$ (G6). a, **2**, AgOTf, Cp_2HfCl_2, Toluene, 4 Å MS, -40 °C, 2 h, 58%; **b**, *p*-TsOH, CH_3CN, 2 h, 60%; **c**, **5**, $(BrC_6H_4)_3NSbCl_6$, CH_3CN, 4 Å MS, -10 °C to RT, 4 h, 52%; **d**, (1) $NH_2CH_2CH_2NH_2$, *n*BuOH, 90 °C, overnight; (2) Ac_2O, pyridine, overnight; (3) NaOMe, MeOH, overnight; (4) $Pd(OH)_2$, MeOH: H_2O: HCOOH (5:3:2), H_2; **G5**:42%; **SG6**: 26%; $(BrC_6H_4)_3NSbCl_6$: Tris (4-bromophenyl) ammoniumyl hexachloroantimonate.



G1

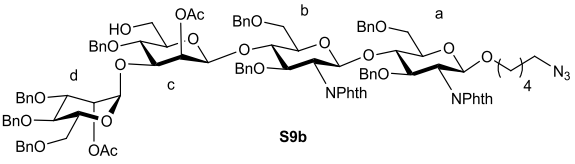
5-Aminopentyl-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (G1): Compound **14** (0.150 g, 0.110 mmol) was deprotected by following general procedure 2 (Method 1) to yield desired trisaccharide **G1** (0.045 g, 65%) as a white solid. ^{1}H NMR (600 MHz, D_2O): δ 4.72 (S, 1H, overlapped with D_2O, H-1^{c}), 4.60 (d, *J* = 7.8 Hz, 1H, H-1^{a}), 4.49 (d, *J* = 7.8 Hz, 1H, H-1^{b}), 4.06 (d, *J* = 3 Hz, 1H), 3.94-3.89 (m, 4H), 3.86-3.58 (m, 14H), 3.50-3.49 (m, 1H), 3.42-3.42 (m, 1H), 2.97 (t, *J* = 10.8 Hz, 2H, -CH_2NH_2, linker), 2.07 (s, 3H, -C(O)CH_3), 2.03 (s, 3H, -C(O)CH_3), 1.68-1.65 (m, 2H, -CCH_2C-, linker), 1.60-1.58 (m, 2H, -CCH_2C-, linker), 1.40-1.39 (m, 2H, -CCH_2C-, linker); ^{13}C NMR (150 MHz, D_2O): δ 177.32, 177.17, 173.76, 104.12 (C-1^{a}, $^{1}J_{C,H}$ = 163.1), 103.80 (C-1^{b}, $^{1}J_{C,H}$ = 162.2), 102.80 (C-1^{c}, $^{1}J_{C,H}$ = 160.2), 82.07, 81.35, 79.15, 77.31, 77.25, 75.49, 75.13, 74.68, 73.23, 72.84, 69.34, 63.65, 62.83, 62.77, 57.75, 57.72, 42.05, 30.78, 29.10, 24.86, 24.84, 24.83; ESI-MS: *m/z* calcd for $C_{27}H_{49}N_3O_{16}$: 671.3005; found 694.3115 $(M + Na)^+$.



S9a

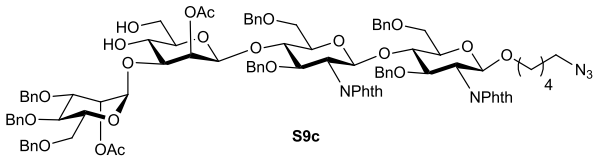
5-Azidopentyl-O-(2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→3)-2-O-acetyl-4,6-O-benzylidine-β-D-mannopyranosyl-(1→4)-O-(3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-O-3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-gluco-pyranoside (S91): A mixture of trichloroacetimidate **1** (0.278 g, 0.437 mmol), chitobiose acceptor **14** (0.300 g, 0.219 mmol) and activated 4 Å molecular sieves in dry CH_2Cl_2 (10 mL) was stirred at room temperature for 1 h. The reaction was cooled to -40 ^{o}C, boron trifluoride ethyl etherate (12 µL, 0.109 mmol) was then added slowly and the resulting reaction mixture was stirred for 2 h. The reaction was quenched by adding Et_3N, diluted with CH_2Cl_2, filtered through

Celite and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 15% EA in toluene) to afford **S9a** (0.310 g, 70%) as white foam. TLC (ethyl acetate: toluene = 2/8, v/v): R_f = 0.46; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.84-7.65 (m, 8H, Ar-H), 7.38-7.31 (m, 2H, Ar-H), 7.30-7.18 (m, 28H, Ar-H), 6.98-6.90 (m, 7H, Ar-H), 6.75-6.71 (m, 3H, Ar-H), 5.45 (s, 1H, Ph-C<u>H</u>, benzylidene), 5.43-5.43 (d, *J* = 3.4 Hz, 1H, H-2^d), 5.34 (d, *J* = 3.1 Hz, 1H, H-2^c), 5.21 (d, *J* = 8.1 Hz, 1H, H-1^a), 5.19 (d, *J* = 2.1 Hz, 1H, H-1^d), 4.90 (d, *J* = 8.1 Hz, 1H, H-1^a), 4.83-4.81 (m, 3H), 4.67 (s, 1H), 4.67-4.61 (m, 2H), 4.53-4.43 (m, 7H), 4.38-4.23 (q, 2H), 4.22-4.16 (m, 1H), 4.13-4.06 (m, 6H), 3.87-3.75 (m, 6H), 3.66-3.60 (m, 3H), 3.53-3.45 (m, 3H), 3.38 (dd, *J* = 4.2 & 12.0 Hz, 1H), 3.26-3.17 (m, 3H), 3.09-3.07 (m, 1H), 2.87-2.82 (m, 2H), 2.06 (s, 3H, -C(O)CH_3), 2.03 (s, 3H, -C(O)CH_3), 1.35-1.23 (m, 4H, -CCH_2C-, linker), 1.07-1.01 (m, 2H, -CCH_2C-, linker); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.87, 168.75, 167.83, 138.97, 138.47, 138.17, 137.36, 134.30, 134.10, 131.72, 129.12, 128.90, 128.64, 128.55, 128.51, 128.32, 128.23, 128.09, 127.84, 127.46, 128.14, 126.24, 123.40, 101.44, 99.38, 98.90, 98.37 (C-1^d, $^1J_{C,H}$ = 172 Hz), 97.31, 79.05, 78.84, 77.89, 76.14,7 5.02, 74.78, 73.70, 73.40, 73.06, 73.04, 72.37, 72.03, 71.00, 69.11, 69.85, 69.11, 68.85, 68.59. 68.50, 67.84, 66.70, 56.85, 55.99, 51.38, 28.95, 28.55, 23.28, 21.33, 21.16; ESI-MS: *m/z* calcd for $C_{105}H_{107}N_5O_{25}$: 1838.7180; found 1861.7223 (*M* + Na)$^+$.



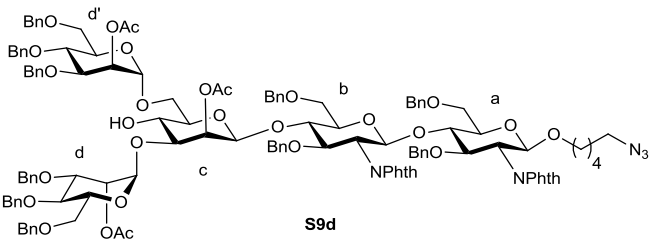
5-Azidopentyl-O-(2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→3)-2-O-acetyl-4-O-benzyl-β-D-mannopyranosyl-(1→4)-O-(3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-O-3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S9b): A mixture of tetrasaccharide **S9a** (0.280 g, 0.152 mmol) and 4 Å activated molecular

sieves in CH_2Cl_2 (10 mL) was stirred at room temperature for 1 h. Reaction was cooled to -78 ^oC, triethyl silane (73 µL, 0.456 mmol) and dichlorophenyl borane (69 µL, 0.532 mmol) were added and stirred for 1 h. The reaction was quenched by adding Et_3N, filtered through Celite and concentrated in *vacuo.* The residue was co-distilled with methanol 2-3 times before being purified by flash column chromatography (0% → 15% EA in toluene) to afford 6"-OH **S9b** (0.230 g, 82%). TLC: (ethyl acetate: toluene =2/8, v/v): R_f = 0.36; ^1H NMR (600 MHz, $CDCl_3$): δ 7.85-7.52 (m, 8H, Ar-H), 7.52-7.12 (m, 30H, Ar-H), 7.00-6.88 (m, 8H, Ar-H), 6.74-6.70 (m, 2H, Ar-H), 5.39 (d, *J* = 1.8 Hz, 1H, H-2^d), 5.32 (d, *J* = 3.6 Hz, 1H, H-2^c), 5.21 (d, *J* = 8.4 Hz, 1H, H-1^a), 5.10 (s, 1H, H-1^d), 4.90-4.81 (m, 4H), 4.67-4.61 (m, 2H, overlapped H-2^b), 4.59 (s, 1H, H-1^c), 4.59-4.44 (m, 9H), 4.37(d, *J* = 12 Hz, 2H), 4.24-4.12 (m, 3H), 4.10-4.05 (m, 3H), 3.90-3.77 (m, 3H), 3.69-3.58 (m, 7H), 3.49 (t, *J* = 11.5 Hz, 2H), 3.41-3.36 (dd, *J* = 6.1, 11.2 Hz, 2H), 3.26 (dd, *J* = 6.0, 9.2 Hz, 1H), 3.26-3.18 (m, 2H), 3.06-2.98 (m, 1H), 2.88-2.81 (m, 2H, linker), 2.06 (s, 3H, -C(O)CH_3), 2.04 (s, 3H, -C(O)CH_3), 1.37-1.22 (m, 4H, linker), 1.07 -1.00 (m, 2H, linker); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.45, 169.88, 168.78, 168.24, 167.86, 138.95, 138.92, 138.77, 138.58, 138.21, 138.11, 137.95, 137.37, 134.35, 134.16, 133.89, 132.09, 131.70, 128.90, 128.76, 128.71, 128.64, 128.58, 128.51, 128.41, 128.31, 128.08, 127.96, 127.81, 127.64, 127.13, 123.97, 123.46, 100.14, 98.40, 98.36, 97.36, 76.24, 75.52, 75.30, 74.96, 74.71, 74.51, 74.29, 73.41, 73.09, 72.55, 72.12, 69.41,69.20, 68.85, 68.48, 67.93, 67.71, 61.87, 56.78, 56.00, 51.38, 28.96, 28.55, 23.28, 21.37; ESI-MS: *m/z* calcd for $C_{105}H_{109}N_5O_{25}$: 1840.7337; found 1863.7383 $(M + Na)^+$.



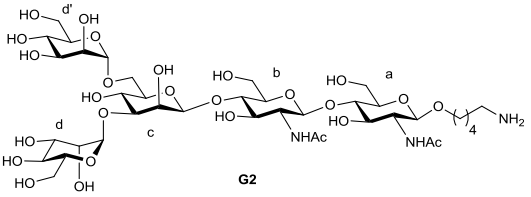
S9c

5-Azidopentyl-O-(2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→3)-2-O-acetyl-β-D-mannopyranosyl-(1→4)-O-(3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-gluco-pyranosyl)-(1→4)-O-3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S9c): *p*-Toluenesulfonic acid monohydrate (0.045 g, 0.239 mmol) was added to a stirred solution of tetrasaccharide **S9a** (0.220 g, 0.119 mmol) in acetonitrile (10 mL) at room temperature. After 8 h, the reaction mixture was quenched with Et_3N and concentrated in *vacuo.* The residue was purified by flash column chromatography (0% → 15% EA in toluene) to give the title diol **S9c** (0.140 g, 66%) as white solid. TLC: (ethyl acetate: toluene = 2/8, v/v): R_f = 0.26; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.85-7.52 (m, 8H, Ar-H), 7.32-7.17 (m, 25H, Ar-H), 6.98-6.91 (m, 7H, Ar-H), 6.75-6.71 (m, 3H, Ar-H), 5.30 (d, *J* = 3.6 Hz, 1H,), 5.21(d, *J* = 8.6 Hz, 1H, H-1^a), 5.20 (s, 2H, overlapped H-1^d), 4.89 (d, *J* = 8.4 Hz, 1H, H-1^b), 4.85-4.82 (m, 3H), 4.64-4.60 (m, 3H), 4.54-4.46 (m, 7H), 4.38 (d, *J* = 12.0 Hz, 1H), 4.34 (d, *J* = 12.2 Hz, 1H), 4.21-4.04 (m, 5H), 3.92 (m, 1H), 3.87-3.79 (m, 3H), 3.70-3.59 (m, 5H), 3.52-3.43 (m, 4H), 3.39 (dd, *J* = 3.2, 8.3 Hz, 1H), 3.28 (dd, *J* = 3.2, 8.2 Hz, 1H), 3.29-3.19 (m, 2H), 2.29 (m, 1H), 2.86-2.83 (m, 3H), 2.11 (s, 3H, -C(O)CH_3), 2.03 (s, 3H, -C(O)CH_3), 1.35-1.23 (m, 4H, -CCH_2C-, linker), 1.06-1.01 (m, 2H, -CCH_2C-, linker); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.76, 169.88, 138.92, 138.70, 138.62, 138.52, 138.12, 138.06, 134.27, 134.07, 133.81, 131.95, 131.64, 128.82, 128.64, 128.59, 128.52, 128.50, 128.39, 138.33, 128.20, 128.09, 128.06, 128.03, 128.01, 127.94, 127.81, 127.75, 127.54, 127.42, 127.29, 127.06, 123.90, 123.36, 98.51, 98.30, 98.24(C-1^d, $^1J_{C,H}$ = 173 Hz), 97.30, 79.07, 78.38, 77.60, 76.10, 75.52, 75.03, 74.79, 74.71, 74.59, 74.51, 73.39, 73.03, 72.07, 72.01, 71.30, 69.53, 69.27, 69.05, 68.44, 67.70, 67.17, 62.44, 56.74, 55.94, 51.32, 28.89, 28.49, 23.22, 21.31, 21.22; ESI-MS: *m/z* calcd for $C_{98}H_{103}N_5O_{25}$: 1750.6868; found 1773.6913 $(M + Na)^+$.

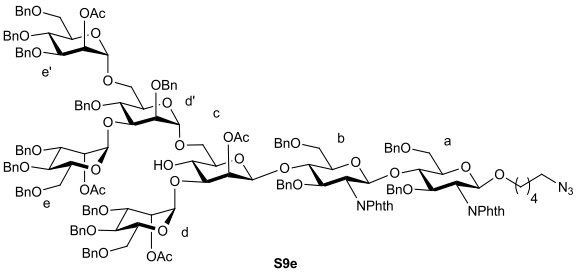


S9d

5-Azidopentyl-O-di-(2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→3), (1→6)-2-O-acetyl-4-O-benzyl-β-D-mannopyranosyl-(1→4)-O-(3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-O-3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S9d): A mixture of donor **1** (0.113 g, 0.178mmol), acceptor **S9b**(0.220 g, 0.119 mmol) and activated 4 Å molecular sieves in dry CH_2Cl_2 (10 mL) was stirred at room temperature for 1 h. The reaction was cooled to -60 ^oC, boron trifluoride ethyl etherate (12 µL, 0.109 mmol) was added slowly and the resulting reaction mixture was stirred for 2 h at -20 ℃. The reaction was quenched by adding Et_3N, diluted with CH_2Cl_2, filtered through Celite and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 20% EA in hexane) to afford **S9d** (0.170 g, 60%) as colorless foam. TLC: (ethyl acetate: hexane = 3/7, v/v): R_f = 0.46; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.77-7.59 (m, 8H, Ar-H), 7.32-7.16 (m, 37H, Ar-H), 7.14-7.08 (m, 2H, Ar-H), 6.91-6.89 (m, 5H, Ar-H), 6.73-6.67 (m, 6H, Ar-H), 5.45 (s, 1H, H-2^d), 5.34 (d, *J* = 3.1 Hz, 1H, H-2^c), 5.32 (s, 1H, H-2d$^{'}$),5.17 (d, *J* = 8.4 Hz, 1H, H-1^a), 5.09 (s, 1H, H-1^d), 5.0 (s, 1H, H-1$^{d'}$), 4.87 (d, *J* = 8.4 Hz, 1H, H-1^b), 4.83-4.78 (q, 2H), 4.74-4.71 (q, 2H), 4.65-4.61 (m, 4H), 4.56-4.42 (m, 15H), 4.31 (d, *J* = 9.2 Hz, 1H), 4.12-4.03 (m, 5H), 4.03-3.76 (m, 7H), 3.68-3.43 (m, 9H), 3.30 (dd, *J* = 3.2, 9.1 Hz, 1H), 3.21-3.15 (m, 2H), 3.13 (d, *J* = 9.2 Hz, 1H), 3.09 (d, *J* = 8.4 Hz, 1H), 2.89-2.79 (m, 2H, -CH_2N_3-, linker), 2.12 (s, 3H, -C(O)CH_3), 2.07 (s, 3H, -C(O)CH_3), 1.69 (s, 3H, -C(O)CH_3), 1.37-1.12 (m, 4H, -CCH_2C-, linker), 1.07-1.01 (m, 2H, -CCH_2C-, linker); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.45, 170.22, 170.18, 168.21, 167.71, 138.93, 138.72, 138.68, 138.50, 138.24, 138.22, 138.07, 133.83, 133.75, 128.87, 128.79, 128.67, 128.63, 128.58, 128.42, 128.21, 128.06, 127.99, 127.96, 127.81, 127.76, 127.70, 127.46, 127.08, 123.36, 100.13 (C-1^a, $^1J_{C,H}$ = 159.3 Hz), 99.39 (C-1$^{d'}$, $^1J_{C,H}$ = 171.5 Hz), 98.35 (C-1^b, $^1J_{C,H}$ = 162.3 Hz), 98.31(C-1^d, $^1J_{C,H}$ = 170 Hz), 97.16, 76.20, 76.05, 75.58, 75.21, 74.97, 74.89, 74.70, 74.47, 74.28, 73.94, 73.72, 73.00, 72.25,72.20, 71.70,71.50, 69.15,69.07, 69.04,68.99, 68.50, 68.45, 67.80, 65.45, 56.83, 51.37, 29.94, 23.27, 21.31, 21.28, 20.83; ESI-MS: *m/z* calcd for $C_{134}H_{139}N_5O_{31}$: 2314.9379; found 2337.9461 $(M + Na)^+$.

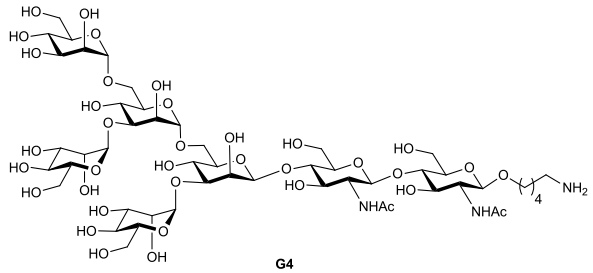


5-Aminopentyl-di-(α-D-mannopyranosyl)-(1→3),(1→6)-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-gluco-pyranoside (G2): Pentasaccharide **S9d** (0.090 g, 0.038 mmol) was deprotected by following the general procedure 2 (Method 1) to afford compound **G2** (0.020 g, 52%) as a white powder. ^{1}H NMR (600 MHz, D_2O): δ 5.10 (d, *J* = 1.3 Hz, 1H, H-1^{d}), 5.09 (d, *J* = 1.5 Hz, 1H, H-1$^{d'}$), 4.78 (s, 1H, overlapped with D_2O, H-1^{c}), 4.59 (d, *J* = 8.4 Hz, 1H, H-1^{a}), 4.49 (d, *J* = 7.8 Hz, 1H, H-1^{b}), 4.25 (s, 1H), 4.01 (d, *J* = 1.5 Hz, 1H), 4.00 (d, *J* = 1.3 Hz, 1H), 3.97-3.77 (m, 8H), 3.75-3.65 (m, 19H), 3.52-3.48 (m, 2H), 2.98 (t, *J* = 11.2 Hz, 2H), 2.06 (s, 3H),2.02 (s, 3H), 1.68-1.65 (m, 2H), 1.60-1.57 (m, 2H), 1.49-1.40 (m, 2H); ^{13}C NMR (150 MHz, D_2O): δ 181.17, 174.69, 174.42, 102.51 (C-1^{d}, $^{1}J_{C,H}$ = 171.5 Hz), 101.34, 101.04, 100.35 (C-1$^{d'}$, $^{1}J_{C,H}$ = 173.5 Hz), 99.60, 80.48, 79.61, 79.30, 74.49, 74.36, 74.16, 73.43, 72.66, 72.37, 71.93, 70.39, 70.31, 70.13, 70.09, 69.98, 69.85, 66.84, 66.76, 65.80, 61.12, 90.93, 60.07, 59.97, 54.97, 54.85, 39.30, 28.03, 26.35, 23.07, 22.17, 22.07; ESI-MS: *m/z* calcd for $C_{39}H_{69}N_3O_{26}$: 995.4067; found 1018.4106 $(M + Na)^{+}$.



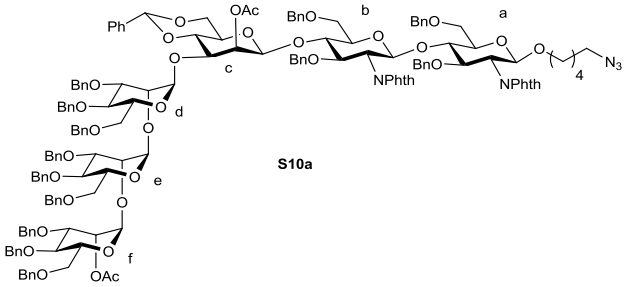
5-Azidopentyl-O-(2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→3)-{2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→3)}-[2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→6)]-2,4-di-O-benzyl-α-D-mannopyranosyl-(1→6)}-2-O-acetyl-β-D-mannopyranosyl-(1→4)-O-(3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-

(1→4)-O-3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S9e): A mixture of Silver triflate (0.127 g, 0.497 mmol), Bis(cyclopentadienyl) hafnium dichloride (0.121 g, 0.319 mmol) and 4 Å activated molecular sieves in dry toluene (10 mL) was stirred at room temperature for 1 h. The reaction mixture was then cooled to -40 ℃, a solution of donor **4** (0.103 g, 0.085 mmol) and acceptor **S9c** (0.125 g, 0.071 mmol) in 5 mL toluene was added. The mixture was stirred for 2 h, quenched with Et_3N, diluted with CH_2Cl_2 and filtered through celite. The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL), and a brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 15% EA in toluene) to afford **S9e** (0.110 g, 52%) as colorless foam. TLC: (acetone: toluene = 2/8, v/v): R_f = 0.36; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.77-7.40 (m, 8H, Ar-H), 7.32-7.07 (m, 65H, Ar-H), 6.99-6.88 (m, 4H, Ar-H), 6.79-6.68 (m, 6H, Ar-H), 5.44 (s, 1H, H-2^d), 5.43 (s, 1H, H-2^e), 5.41 (s, 1H, H-2$^{e'}$), 5.29 (d, *J* = 3.4 Hz, 1H, H-2^c), 5.18 (s, 2H, H-1$^{d,d'}$), 5. 16 (s, 1H, H-1^e), 5.09 (s, 1H, H-1$^{e'}$), 4.92 (s, 1H, H-1^c), 4.91 (d, *J* = 8.5 Hz, 1H, H-1^a), 4.83-4.78 (q, 1H), 4.84-4.73 (m, 6H), 4.65-4.61 (m, 2H), 4.60-4.57 (m, 5H), 4.52-4.35 (m, 17H), 4.27 (d, *J* = 12.3Hz, 1H), 4.20-4.19 (m, 1H), 4.10-3.99 (m, 6H), 3.97-3.70 (m, 13H), 3.69-3.57 (m, 6H), 3.56-3.31 (m, 6H), 3.30 (dd, *J* = 3.2, 9.2 Hz, 1H), 3.30-3.18 (m, 5H), 2.97-2.96 (m, 1H), 2.89-2.79 (m, 2H, -CCH_2C-, linker), 2.12 (s, 3H, -C(O)CH_3), 2.07 (s, 3H, -C(O)CH_3), 2.01 (s, 6H, -C(O)CH_3), 1.33-1.23 (m, 4H, -CCH_2C-, linker), 1.06-0.99 (m, 2H, -CCH_2C-, linker); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.56, 170.42, 170.26, 170.02, 168.45, 168.69, 138.95, 138.93, 138.72, 138.68, 138.58, 138.24, 138.22, 138.07, 133.83, 132.09, 131.76, 128.87, 128.79, 128.67, 128.63, 128.61, 128.58, 128.52, 128.42, 128.13, 128.06, 127.99, 127.92, 127.81, 127.76, 127.74, 127.46, 127.08, 123.71, 123.36, 100.13 (C-1$^{e,e'}$, $^1J_{C,H}$ = 169.2 Hz), 99.39 (C-1^b, $^1J_{C,H}$ = 162.2 Hz), 98.35 (C-1^d, $^1J_{C,H}$ = 171.5 Hz), 98.31 (C-1^a, $^1J_{C,H}$ = 160.2 Hz), 97.16 (C-1$^{d'}$, $^1J_{C,H}$ = 170.5 Hz), 76.20, 76.05, 75.42, 74.97, 74.89, 74.80, 74.70, 74.65, 74.47, 74.28, 73.94,73.68, 73.26, 72.60, 72.25, 72.20, 71.70, 71.50, 69.15, 69.07, 69.04, 68.99, 68.50, 68.45, 67.80, 65.54, 56.73, 55.90, 51.29,31.14, 29.91, 28.87, 28.47, 23.19, 21.33, 21.27, 21.19l; HRMS (MALDI-TOF): *m/z* calcd for $C_{176}H_{185}N5O_{42}$: 3042.2400; found 3065.2210 $(M + Na)^+$.



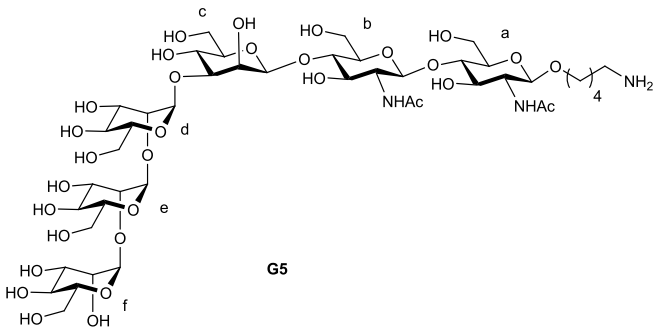
G4

5-Aminopentyl-α-D-mannopyranosyl(1→3),[di-(α-D-mannopyranosyl)-(1→3), (1→6)-α-D-mannopyranosyl](1→6)-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl -(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (G4):- Heptasaccharide **S9e** (0.140 g, 0.024 mmol), was deprotected by following the general procedure 2 (Method 1) to obtain title compound **G4** (0.039 g, 29%) as a white solid. ^{1}H NMR (600 MHz, D_2O): δ 5.09 (s, 1H, H-1^{d}), 4.89 (s, 1H, H-1d$^{'}$), 4.86 (d, *J* = 1.5 Hz, 1H, H-1^{e}), 4.75 (d, *J* = 1.5 Hz, 1H, H-1$^{e'}$), 4.76 (s, 1H, overlapped with D_2O, H-1^{c}), 4.50 (d, *J* = 7.8 Hz, 1H, H-1^{a}), 4.35 (d, *J* = 7.9 Hz, 1H, H-1^{b}), 4.17 (d, *J* = 1.7 Hz, 1H), 4.07 – 4.05 (m, 1H), 4.00-3.97 (m, 2H), 3.94-3.37 (m, 40H), 2.90-2.85 (m, 2H, -CH_2NH_2, linker), 1.98 (s, 3H, -C(O)CH_3), 1.94 (s, 3H, -C(O)CH_3), 1.61-1.46 (m, 4H, -CCH_2C-, linker), 1.35-1.26 (m, 2H, -CCH_2C-, linker); ^{13}C NMR (150 MHz, D_2O): δ 177.2, 172.3, 102.44, 101.44, 101.01, 100.37, 99.85, 99.25, 80.54, 79.49, 79.28, 78.58, 74.45, 74.43,72.50, 71.93, 70.64, 70.24, 70.15, 70.04, 70.01, 69.87, 69.46, 69.39, 66.69, 66.66, 65.94,65.91, 65.56, 65.13, 65.12, 60.93, 60.91, 60.43, 60.13, 60.04, 59.97, 54.90, 54.86, 39.28,27.98, 26.48, 22.08, 22.02, 21.99; ESI-MS: *m/z* calcd for $C_{51}H_{89}N_3O_{36}$: 1319.5123; found 1342.5165 $(M + Na)^{+}$.

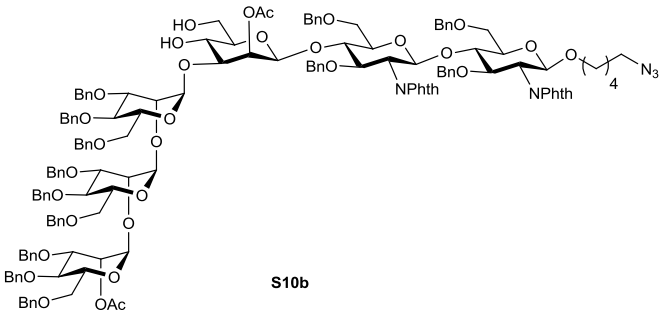


S10a

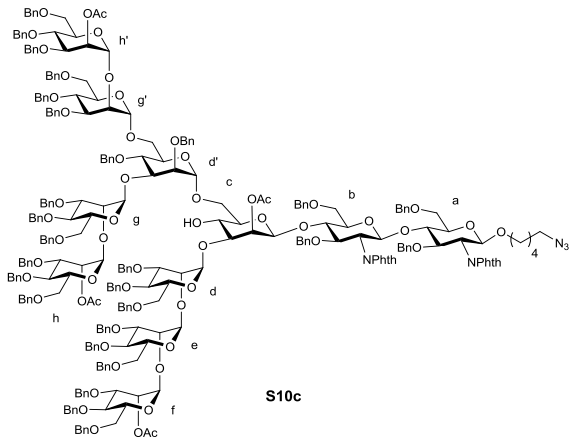
5-Azidopentyl-O-(2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→3)-2-O-acetyl-4,6-O-benzylidene-β-D-mannopyranosyl-(1→4)-O-(3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-O-3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S10a): A mixture of Silver triflate (0.328 g, 1.28 mmol), Bis(cyclopentadienyl) hafnium dichloride (0.340 g, 0.897 mmol) and 4 Å activated molecular sieves in dry toluene (10 mL) was stirred at rt for 1 h. The reaction mixture was then cooled to -40 ℃, a solution of donor **2** (0.383 g, 0.282 mmol) and acceptor **14** (0.350 g, 0.256 mmol) in 5 mL toluene was added. The mixture was stirred for 2 h, quenched with Et_3N, diluted with CH_2Cl_2 and filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL), and a brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 15% EA in toluene) to afford **S10a** (0.405 g, 58%) as colorless foam. TLC: (ethyl acetate: toluene = 2/8, v/v): R_f = 0.46; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.89-7.35 (m, 8H, Ar-H), 7.38-7.12 (m, 56H, Ar-H), 7.12-7.08 (m, 3H, Ar-H), 7.03-6.88 (m, 7H, Ar-H), 6.78-6.69 (m, 4H, Ar-H), 5.50 (s, 1H, H-1^f), 5.37 (d, *J* = 1.4 Hz, 1H, H-2^c), 5.25 (s, 1H, Ph-C<u>H</u>-, benzylidene), 5.23-5.17 (m, 3H, overlapped, H-1^{d,e,f}), 4.98 (s, 1H, H-1^c), 4.95 (d, *J* = 7.5 Hz, 1H, H-1^a), 4.91-4.53 (m, 5H), 4.69-4.58 (m, 3H), 4.55-4.28 (m, 16H), 4.25-4.00 (m, 13H), 3.95-3.91 (m, 1H), 3.91-3.60 (m, 10H), 3.58 (d, *J* = 12 Hz, 1H), 3.51-3.45 (m, 4H), 3.42-3.38 (m, 3H), 3.29-3.10 (m, 3H), 2.98-2.78 (m, 3H), 2.08 (s, 3H, -C(O)CH_3), 1.99 (s, 3H, -C(O)CH_3), 1.35-1.23 (m, 4H, -CCH_2C-, linker), 1.07-1.00 (m, 2H, -CCH_2C-, linker); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.38, 169.81, 168.76, 168.26, 139.06, 138.95, 138.92, 138.87, 138.60, 137.36, 128.85, 128.66, 128.64, 128.58, 128.55, 128.48, 128.43, 128.39, 128.35, 128.26, 128.10, 128.02, 127.82, 127.71, 101.48, 100.08, 99.75, 99.39, 98.36, 97.27, 77.80, 78.75, 76.10, 75.38, 74.93, 74.82, 74.70, 73.58, 73.28, 73.21, 73.06, 72.79, 72.65, 72.57, 72.17, 71.01, 69.60, 69.10, 68.96, 68.63, 66.74, 56.85, 55.97, 51.37, 28.95, 28.54, 23.27, 21.43, 21.09; ESI-MS: *m/z* calcd for $C_{159}H_{163}N_5O_{35}$: 2703.1054; found 2726.1214 $(M + Na)^+$.



5-Aminopentyl-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→2)-α-D-manno-pyranosyl-(1→3)-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (G5): Hexasaccharide **S10a** (0.140 g, 0.051 mmol), was deprotected by following general procedure 2 (Method 1) to obtain the title compound **G5** (0.025 g, 42%) as white solid. ^{1}H NMR (600 MHz, D_2O): δ 5.32 (s, 1H, H-1^{d}), 5.27 (s, 1H, H-1^{e}), 5.01 (s, 1H, H-1^{f}), 4.74 (s, 1H, H-1^{c}), 4.56 (d, *J* = 7.8 Hz, 1H, H-1^{a}), 4.63 (d, *J* = 7.8 Hz, 1H, H-1^{b}),4.18 (d, *J* = 3.3 Hz, 1H), 4.07 (s, 1H), 4.04 (d, *J* = 3.2 Hz, 1H), 4.03 (d, *J* = 3.1 Hz, 1H), 3.32-3.33 (m, 35H), 2.05 (t, *J* = 11.2 Hz, 2H, -CH_2NH_2, linker), 2.03 (s, 3H, -C(O)CH_3), 2.00 (s, 3H, -C(O)CH_3), 1.64 (m, 2H, -CCH_2C-, linker), 1.50 (m, 2H, -CCH_2C-, linker), 1.36 (m, 2H, -CCH_2C-, linker); ^{13}C NMR (150 MHz, D_2O): δ 174.54, 174.38, 102.17 (C-1^{e}, $^{1}J_{C,H}$ = 170.2 Hz), 101.34 (C-1^{b}, $^{1}J_{C,H}$ = 161.2 Hz), 101.014 (C-1^{d}, $^{1}J_{C,H}$ = 169.8 Hz), 100.70 (C-1^{f}, $^{1}J_{C,H}$ = 172.2 Hz), 100.56 (C-1^{a}, $^{1}J_{C,H}$ = 160.2 Hz), 99.85, 80.50, 79.25, 78.66, 78.55, 78.47, 76.12, 74.48, 73.37, 73.13, 72.33, 71.88, 70.24, 70.17, 70.05, 69.95, 69.89, 66.95, 66.81,66.71, 65.81, 61.01, 60.97, 60.88, 60.76, 60.02, 59.92, 54.92, 39.25, 27.99, 26.32, 23.19, 22.06, 22.04; ESI-MS: *m/z* calcd for $C_{45}H_{79}N_3O_{31}$: 1157.4590; found 1180.4591 $(M + Na)^{+}$.

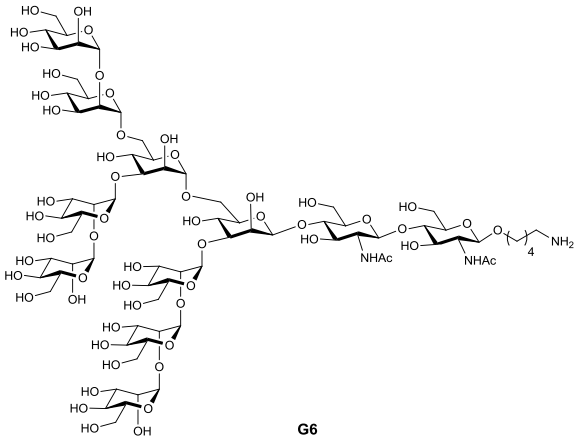


5-Azidopentyl-O-(2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→3)-2-O-acetyl-β-D-mannopyranosyl-(1→4)-O-(3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-O-3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S10b):- To a solution of **S10a** (0.205 g, 0.075 mmol) in 10 mL acetonitrile was added *p*-toluene sulfonic acid monohydrate (0.020 g, 0.113 mmol), stirred at room temperature for 9 h. The reaction was quenched with Et_3N and concentrated in *vacuo.* The residue was purified by flash column chromatography (0% → 20% EA in toluene) to give diol **S10b** (0.120 g, 60%). TLC: (acetone: toluene = 2/8, v/v): R_f = 0.26; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.83-7.62 (m, 8H, Ar-H), 7.41-7.06 (m, 57H, Ar-H), 6.95-6.89 (m, 6H, Ar-H), 6.73-6.71 (m, 2H, Ar-H), 5.50 (d, *J* = 4.8 Hz, 1H, H-2^f), 5.23 (d, *J* = 1.8 Hz, 1H, H-1^d), 5.22 (d, *J* = 3.8 Hz, 1H, H-1^c), 5.19 (d, *J* = 3.2 Hz, 1H, H-1^e), 5.18 (s, 1H, H-1^f), 5.03 (d, *J* = 7.8 Hz, 1H, H-1^a), 4.88 (t, *J* = 7.8 Hz, 1H), 4.82-4.74 (m, 5H), 4.68-4.38 (m, 21H), 4.33 (d, *J* = 7.8 Hz, 1H), 4.29 (d, *J* = 7.9 Hz, 1H), 4.20-4.00 (m, 7H), 3.95-3.71 (m, 9H), 3.69-3.53 (m, 6H), 3.52-3.33 (m, 8H), 3.29-3.15 (m, 5H), 2.90-2.79 (m, 2H), 2.08 (s, 3H, -C(O)CH_3), 1.92 (s, 3H, -C(O)CH_3), 1.35-1.20 (m, 4H, -CCH_2C-, linker), 1.08-1.01 (m, 2H, -CCH_2C-, linker); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.40, 169.88, 168.68, 138.20, 138.94, 138.78, 138.71, 138.56, 138.48, 138.38, 138.21, 138.02, 134.30, 133.84, 132.02, 128.78, 128.65, 128.63, 128.43, 128.40, 128.38, 128.25, 128.15, 128.06, 127.94, 127.88, 127.84, 127.77, 127.69, 127.65, 127.56, 127.10, 123.90, 123.41, 100.98, 99.83, 98.34, 97.32, 78.31, 78.17, 78.11, 78.00, 76.22, 75.52, 75.28, 75.05, 74.82, 74.40, 73.98, 73.67, 73.58, 73.36, 73.06, 72.59, 72.48, 72.42, 72.09, 71.32, 70.52, 69.46, 69.09, 68.83, 68.72, 68.42, 68.20, 67..61, 62.57, 56.77, 55.98, 51.37, 29.99, 29.65, 28.94, 28.54, 23.27, 21.44, 21.13, 14.41; ESI-MS: *m/z* calcd for $C_{152}H_{159}N_5O_{35}$: 1615.0741; found 2638.0754 $(M + Na)^+$.



5-Azidopentyl-O-(2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→3)-{2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-manno-pyranosyl-(1→3)-[2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→6)]-2,4-di-O-benzyl-α-D-mannopyranosyl-(1→6)}-2-O-acetyl-β-D-mannopyranosyl-(1→4)-O-(3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-gluco-pyranosyl)-(1→4)-O-3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D -glucopyranoside (S10c): A mixture of hexasaccharide acceptor **S10a** (0.1 g, 0.038 mmol), thiomannoside donor **5** (0.104 g, 0.045 mmol) and activated 4 Å molecular sieves in CH_3CN (10 mL) was stirred at rt for 1 h. The resulting mixture was cooled to -10 ℃, tris(4-bromophenyl)aminium hexachloroantimonate (0.096 g, 0.114 mmol) was added and stirred at rt for 6 h. TLC (ethyl acetate: toluene, 2/8) indicated formation of product with consumption of starting material, reaction was quenched by Et_3N. The reaction mixture was diluted with CH_2Cl_2 and filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL), and a brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 10% EA in toluene) to afford **S10c** (0.095 g, 52%) as colorless foam. TLC: (acetone: toluene = 2/8, v/v): R_f = 0.41; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.77-7.50 (m, 8H, Ar-H), 7.29-6.98 (m, 126H, Ar-H), 6.95-6.89 (m, 4H, Ar-H), 6.74-6.64 (m, 5H, Ar-H), 5.56 (s, 1H, H-2^f), 5.53 (s, 1H, H-2^h), 5.51 (s, 1H$^{h'}$), 5.34 (s, 1H, H-2^c), 5.32 (d, *J* = 12.2 Hz, 2H), 5.18 (d,

J = 7.8 Hz, 1H), 5.12 (s, 1H), 5.08 (s, 1H), 5.04 (s, 2H), 4.59-3.75 (m, 116H), 3.26-3.16 (m, 4H), 3.08-3.02 (m, 2H), 2.93-2.83 (m, 2H), 2.12 (s, 3H), 2.06 (s, 3H), 2.06 (s, 3H), 1.97 (s, 3H), 1.39-1.26 (m, 4H), 1.07-1.05 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.12, 170.03, 169.76, 168.14, 167.36, 138.64, 138.54, 138.45, 138.41, 138.27, 138.07, 133.68, 133.57, 131.74, 129.05, 128.62, 128.57, 128.51, 128.33, 128.23, 128.14, 128.06, 127.99, 127.94, 127.81, 127.78, 127.73, 127.45, 101.24, 99.81, 99.59, 99.48, 99.34, 99.24, 99.05, 98.02, 96.95, 79.82, 79.23, 78.33, 78.24, 78.14, 75.86, 75.22, 75.12, 75.02, 74.93, 74.77, 74.57, 74.47, 74.38, 74.30, 74.17, 73.29, 73.11, 72.50, 72.20, 71.94, 71.35, 71.25, 69.13, 69.03, 68.79, 68.53, 68.48, 68.35, 68.17, 67.40, 56.56, 55.69, 51.09, 28.66, 28.26, 22.99, 21.17, 21.12; HRMS (MALDI-TOF): *m/z* calcd for $C_{284}H_{297}N_5O_{62}$: 4772.0232; found 4794.9783 $(M + Na)^+$.



G6

5-Aminopentyl-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→2)-α-D-manno-pyranosyl-(1→3)-{α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→3)-[α-D-manno-pyranosyl-(1→2)-α-D-mannopyranosyl-(1→6)]-α-D-mannopyranosyl-(1→6)}-β-D-manno-pyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (G6): Compound **S10c** (0.120 g, 0.024 mmol) was deprotected by following general procedure 2 (Method 1) to get $Man_9GlcNAc_2$ **G6** (0.012 g, 26%) as a white solid. ^{1}H NMR (600 MHz, D_2O): δ 5.40 (s, 1H, H-1^d), 5.33 (s, 1H, H-1$^{d'}$), 5.30 (s, 1H, H-1^e), 5.14 (s, 1H, H-1), 5.05 (s, 1H, H-1), 5.03 (d, *J* =2.4 Hz, 2H, H-1), 4.86 (s, 1H, H-1), 4.58 (d, *J* = 7.8 Hz, 1H,

H-1[a]), 4.48 (d, *J* = 7.8 Hz, 1H, H-1b), 4.22 (d, *J* = 2.4 Hz, 1H), 4.14 (s, 1H), 4.14-3.95 (m, 12H), 3.94-3.59 (m, 54H), 3.50-3.48 (m, 1H), 3.02 (t, *J* = 9.2 Hz, 2H), 2.06 (s, 3H, -C(O)CH_3), 2.02 (s, 3H, -C(O)CH_3), 1.68-1.63 (m, 2H, -CCH_2C-, linker), 1.59-1.56 (m, 2H, -CCH_2C-, linker), 1.41-1.37 (m, 2H, -CCH_2C-, linker); ^{13}C NMR (150 MHz, D2O): δ 174.47, 171.01, 102.24 (C-1[d], $^1J_{C,H}$ = 171.8 Hz), 102.21 (C-1[d'], $^1J_{C,H}$ = 169.0 Hz), 102.19 (C-1[e], $^1J_{C,H}$ = 173.8 Hz), 101.43, 101.03, 100.82, 100.59 (C-1[a], $^1J_{C,H}$ = 162.8 Hz), 100.21, 99.61, 97.97 (C-1[b], $^1J_{C,H}$ = 159.8 Hz), 81.86, 79.32, 78.88, 78.63, 78.45, 74.50, 74.48, 74.14, 73.39, 73.27, 73.20, 73.17, 72.69, 72.36, 71.90, 71.61, 70.21, 70.03, 69.93, 69.37, 67.01, 66.94, 66.90, 66.85, 66.81, 66.76, 65.42, 65.40, 65.07, 64.90, 61.11, 61.06, 61.01, 60.91, 60.06, 59.94, 54.95, 39.29, 38.61, 28.02, 26.34, 22.16, 22.10, 22.06; ESI-MS: *m/z* calcd for $C_{75}H_{129}N_3O_{56}$: 1967.7231; found 1990.7279 $(M + Na)^+$.

vi. Synthesis of hybrid type oligosaccharides (G7-G14).

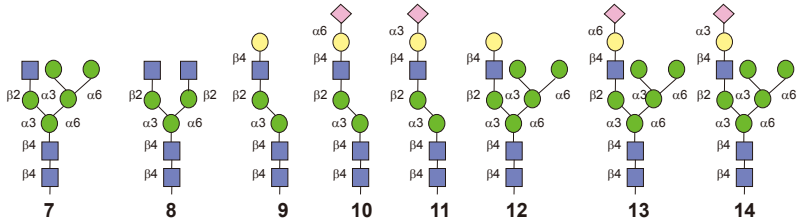
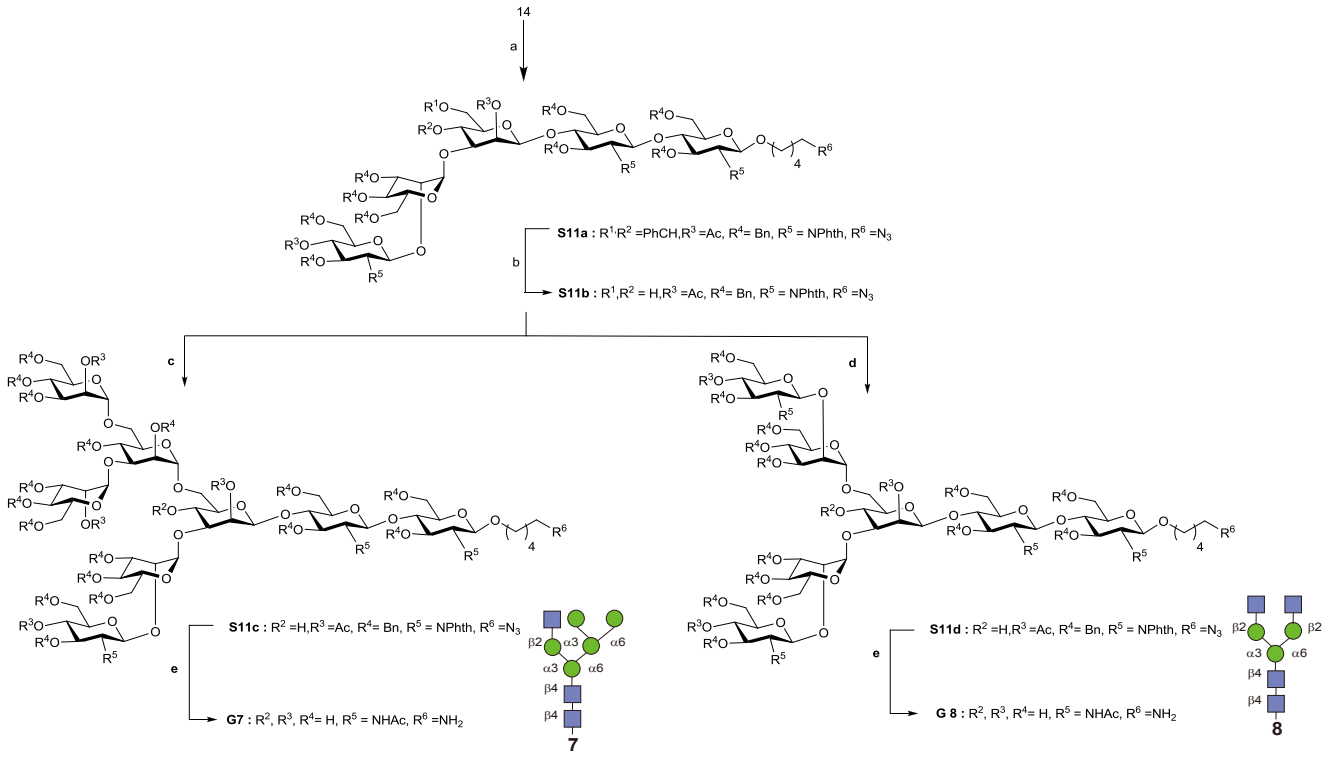
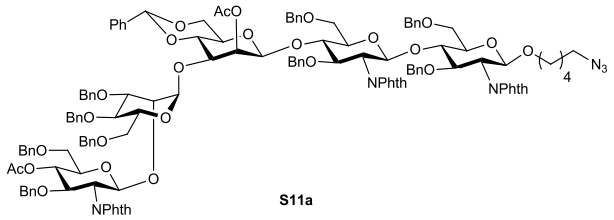


Figure S2 | Structures of hybrid type glycans and their fragments

Synthesis of hybrid type sugars commenced with condensation of **14** with **6** catalyzed by AgOTf/CP_2HfCl_2 to give pentasaccharide **S11a** in 63% yield (Scheme S11). The benzilidine opening resulted in diol **S11b,** which was further glycosylated at 6"-O with trimannosyl thioglycoside **3** to afford **S11c** in 55% yield. Cp_2HfCl_2 /AgOTf mediated condensation of acceptor **S11b** with **6** resulted in the formation of **S11d** in 58% yield.

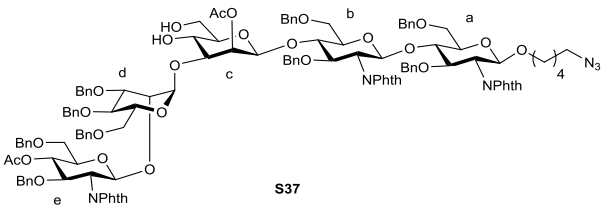


Scheme S11 | Preparation of octasaccharide G7 and heptasaccharide G8. **a**, **6**, AgOTf, Cp_2HfCl_2, Toluene, 4 Å MS, -40 °C, 4 h, 63%; **b**, *p*TsOH, CH_3CN, 5 h, 78%; **c**, **3**, $(BrC_6H_4)_3NSbCl_6$, CH_3CN, 4 Å MS, -10 ^oC to RT, 4 h, 55%; **d**, **6**, AgOTf, Cp_2HfCl_2, Toluene, 4 Å MS, -40 °C, 4 h, 58%; **e**, (1) $NH_2CH_2CH_2NH_2$, *n*BuOH, 90 ^oC, overnight; (2) Ac_2O, pyridine, overnight; (3) NaOMe, MeOH, overnight; (4) $Pd(OH)_2$, MeOH: H_2O: HCOOH (5:3:2), H_2; **G7**:26; **G8**:32%.



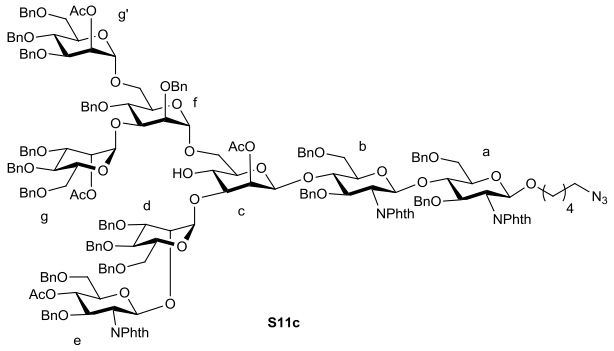
5-Azidopentyl-O-2-O-acetyl-3,6-O-di-benzyl-2-deoxy-2-phthalimido-β-D-gluco-pyranosyl-(1→2)-O-(3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→3)-2-O-acetyl-4,6-O-benzylidine-β-D-mannopyranosyl-(1→4)-O-(3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)

-(1→4)-O-3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S11a): A mixture of Silver triflate (0.080 g, 0.315 mmol), Bis(cyclopentadienyl)hafnium dichloride (0.084 g, 0.220 mmol) and 4 Å activated molecular sieves in dry toluene (10 mL) was stirred at rt for 1 h. The reaction mixture was then cooled to -40 ℃, a solution of donor **6** (0.341 g, 0.308 mmol), chitobiose acceptor **14** (0.350 g, 0.256 mmol) in 5 mL toluene was added. The mixture was stirred for 4 h, quenched with Et_3N, diluted with CH_2Cl_2 and filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL), and a brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*The residue was purified by flash column chromatography (0% → 10% EA in toluene) to afford **S11a** (0.360 g, 63%) as white foam. TLC: (ethyl acetate: toluene = 2/8, v/v): R_f = 0.56; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.84-7.55 (m, 12H, Ar-H), 7.45-7.10 (m, 28H, Ar-H), 7.06-6.90 (m, 18H, Ar-H), 6.75-6.71 (m, 4H, Ar-H), 5.37 (d, *J* = 8.4 Hz, 1H, H-1), 5.21 (d, *J* = 8.4 Hz, 1H, H-1), 5.19 (s, 1H, Ph-C<u>H</u>, benzylidene), 5.09 (t, *J* = 9.0 Hz, 1H), 4.93-4.76 (m, 6H), 4.57 (s, 1H), 4.54 (d, *J* = 12.0 Hz, 1H), 4.45-4.07 (m, 20H), 3.69-3.15 (m, 22H), 3.02-3.00 (m, 1H), 2.86-2.81 (m, 2H, linker), 2.25 (s, 3H, -C(O)CH_3), 1.84 (s, 3H, -C(O)CH_3), 1.35-1.23 (m, 4H, -CCH_2C-, linker), 1.07-1.02 (m, 2H, -CCH_2C-, linker); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.68, 170.05, 167.88, 138.98, 138.89, 138.85, 138.71, 138.63, 138.14, 138.07, 137.78, 134.08, 133.90, 133.46, 132.06, 131.81, 129.32, 128.90, 128.83, 128.67, 128.55, 128.50, 128.34, 128.27, 127.95, 127.79, 127.70, 127.60, 101.00, 99.41, 98.38, 97.91, 97.29, 80.38, 79.02, 76.82, 76.76, 76.52, 76.14, 75.25, 74.90, 74.83, 74.67, 74.51, 74.44, 73.68, 73.52, 73.38, 73.06, 73.02, 72.93, 71.46, 70.65, 70.40, 70.03, 69.66, 69.14, 68.52, 67.56, 56.83, 55.98, 55.85, 51.37, 29.99, 28.95, 28.55, 23.28, 21.67, 21.19; ESI-MS: *m/z* calcd for $C_{133}H_{132}N_6O_{31}$: 2309.8862; found 2332.8861 $(M + Na)^+$.



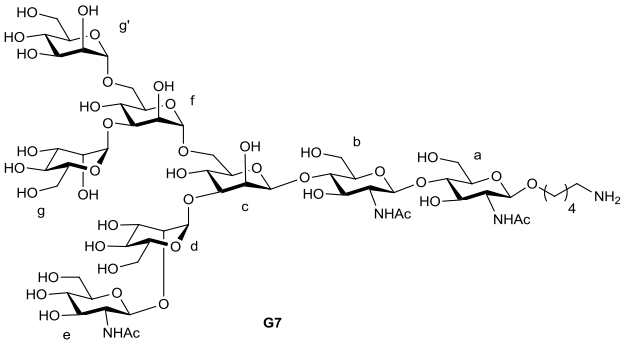
S37

5-Azidopentyl-O-2-O-acetyl-3,6-O-di-benzyl-2-deoxy-2-phthalimido-β-D-gluco-pyranosyl-(1→2)-O-(3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→3)-2-O-acetyl-β-D-mannopyranosyl-(1→4)-O-(3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-O-3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S11b): *p*-Toluene sulfonic acid monohydrate (0.020 g, 0.143 mmol) was added to a solution of **S11a** (0.220 g, 0.095 mmol) in acetonitrile (20 mL) and the resulting reaction mixture was stirred at rt for 5 h. The reaction was quenched by adding Et_3N and concentrated in *vacuo.* The residue was purified by flash column chromatography (0% → 15% EA in toluene) to give diol **S11b** (0.165 g, 78%). TLC: (ethyl acetate: toluene = 2/8, v/v): R_f = 0.32; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.89-7.43 (m, 12H, Ar-H), 7.35-7.16 (m, 28H, Ar-H), 7.09-7.05 (m, 5H, Ar-H), 7.03-6.89 (m, 9H, Ar-H), 6.75-6.72 (m, 3H, Ar-H), 5.30 (d, *J* = 8.4 Hz, 1H, H-1^a), 5.23 (d, *J* = 8.4 Hz, 1H, H-1^b), 5.12 (d, *J* = 9.0 Hz, 1H), 5.09 (t, *J* = 9.8 Hz, 1H), 4.95 (d, *J* = 12.0 Hz, 1H), 4.90 (d, *J* = 8.4 Hz, 1H, H-1^e), 4.87-4.80 (m, 2H), 4.58-4.55 (m, 2H), 4.50-4.41 (m, 10H, overlapped, H-1^d), 4.37-4.34 (m, 3H), 4.27-4.24 (m, 2H), 4.18-4.15 (m, 2H), 4.10-3.92 (m, 5H), 3.73-3.70 (m, 2H), 3.65-3.61 (m, 2H), 3.59-3.51 (m, 6H), 3.47-3.38 (m, 6H), 3.23-3.17 (m, 4H), 3.04 (dd, *J* = 3.6, 9.0 Hz, 1H), 3.01-3.98 (m, 1H), 2.83-2.78 (m, 3H), 2.38 (s, 3H, -C(O)CH_3), 1.90 (s, 3H, -C(O)CH_3), 1.36-1.22 (m, 4H, -CCH_2C-, linker), 1.06-1.01 (m, 2H, -CCH_2C-, linker); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.93, 170.05, 168.77, 167.86, 167.69, 138.90, 138.83, 138.65, 138.47, 138.23, 138.14, 138.07, 138.04, 134.35, 134.13, 133.91, 132.04, 131.84, 131.72, 128.81, 128.65, 128.64, 128.62, 128.54, 128.53, 128.48, 128.46, 128.36, 128.17, 128.09, 128.02, 127.99, 127.97, 127.92, 127.91, 127.83, 127.77, 127.74, 127.63, 127.13, 124.73, 123.97, 123.43, 123.08, 118.73, 100.25 (C-1^e), 98.37 (C-1^d), 98.21 (C-1^c), 97.86 (C-1^b), 97.30 (C-1^a), 82.86, 80.05, 78.38, 76.92, 76.15, 75.72, 75.60, 75.45, 74.86, 74.83, 74.70, 74.42, 74.24, 73.75, 73.42, 73.38, 72.82, 70.81, 70.60, 70.27, 69.99, 69.50, 69.15, 69.13, 68.53, 67.88, 66.28, 62.98, 56.78, 55.99, 55.88, 51.37, 32.21, 29.98, 28.94, 28.54, 23.27, 21.69, 21.18; ESI-MS: *m/z* calcd for $C_{126}H_{128}N_6O_{31}$: 2221.8549; found 2244.8529 $(M+Na)^+$.



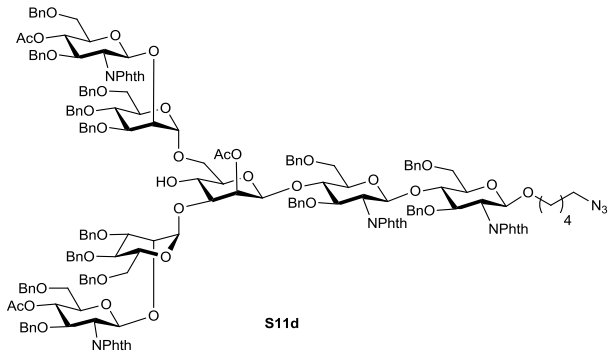
5-Azidopentyl-O-{4-O-acetyl-3,6-O-di-benzyl-2-deoxy-2-phthalimido-β-D-gluco-pyranosyl-(1→2)}-O-{3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→3)-{2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→3)}-[2-O-acetyl-3,4,6-tri-O-benzyl-α-D-manno-pyranosyl-(1→6)]-2,4-di-O-benzyl-α-D-mannopyranosyl-(1→6)}-2-O-acetyl-β-D-manno-pyranosyl-(1→4)-O-(3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-O-3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S11c): A mixture of pentasaccharide acceptor **S11b** (0.150 g, 0.067 mmol), thiomannoside donor **3** (0.110 g, 0.080 mmol) and activated 4 Å molecular sieves in CH_3CN (10 mL) was stirred at rt for 1 h. The resulting mixture was cooled to -10 ℃, tris (4-bromophenyl) aminium hexachloroantimonate (0.170 g, 0.201 mmol) was added and resulting reaction was stirred at room temperature for 4 h. TLC (ethyl acetate: toluene, 2/8) indicated formation of product with consumption of starting material, the reaction was quenched by Et_3N. The reaction mixture was diluted with CH_2Cl_2 and filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL), and a brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 10% EA in toluene) to afford **S11c** (0.130 g, 55%) as colorless foam. TLC: (ethyl acetate: toluene= 1/9, v/v): R_f = 0.42; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.71-7.30 (m, 12H, Ar-H), 7.28-7.10 (m, 70H, Ar-H), 7.97-6.86 (m, 12H, Ar-H), 6.69 (m, 3H, Ar-H), 5.47 (d, *J* = 8.4 Hz, 2H), 5.44 (s, 1H), 5.32 (d, *J* = 8.4 Hz, 1H, H-1^a), 5.15 (d, *J* = 8.4 Hz, 1H, H-1^b), 5.13-5.10 (m, 2H), 5.00 (s, 1H, H-1^d), 4.95 (s, 1H, H-1^f), 4.91 (s, 2H, H-1^g, H-1$^{g'}$), 4.87-4.73 (m, 8H), 4.62 (d, *J* = 8.7 Hz, 1H), 4.57-4.28 (m, 26H), 4.15-3.70 (m, 20H), 3.68-

3.40 (m, 13H), 3.38-3.25 (m, 6H), 3.24-3.09 (m, 5H), 2.98 (dd, *J* = 2.3, 7.8Hz, 1H), 2.89-2.79 (m, 2H), 2.73-2.71 (m, 1H), 2.27 (s, 3H, -C(O)CH_3), 2.05 (s, 3H, -C(O)CH_3), 1.99 (s, 3H, -C(O)CH_3), 1.88 (s, 3H, -C(O)CH_3), 1.32-1.28 (m, 4H, -CCH_2C-, linker), 1.07-0.98 (m, 2H, -CCH_2C-, linker); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.26, 168.89, 138.38, 128.47, 128.37, 128.32, 128.30, 128.26, 128.24, 128.19, 128.08, 128.04, 127.91, 127.86, 127.73, 127.56, 127.49, 127.39, 127.26, 100.35, 100.23, 99.89, 99.56, 99.23, 98.54, 98.33, 98.23, 78.43, 76.09, 75.37, 75.07, 74.08, 74.44, 74.04, 73.47, 73.31, 72.63, 68.81, 51.08, 29.71, 29.37, 28.66, 28.25, 22.98; HRMS (MALDI-TOF): *m/z* calcd for $C_{204}H_{210}N_6O_{48}$; 3513.4134 found 3536.4050 $(M+Na)^+$.



5-Aminopentyl-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranosyl-(1→3),[di-(α-D-mannopyranosyl)-(1→3),(1→6)-α-D-mannopyranosyl](1→6)-β-D-manno-pyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (G7): Compound **S11c** (0.105 g, 0.030 mmol) was deprotected by following general procedure 2 (Method 1) to get the title compound **G7** (0.012 g, 26%) as a white solid. ^{1}H NMR (600 MHz, D_2O): δ 5.09 (d, *J* = 1.2 Hz, 1H, H-1^d), 5.02 (d, *J* = 8.4 Hz, 1H, H-1^a), 4.95 (s, 1H, H-1^f), 4.91 (s, 1H, H-1^g), 4.85 (s, 1H, H-1$^{g'}$), 4.78 (S, 1H, H-1^c), 4.61 (d, *J* = 7.8 Hz, 1H, H-1e), 4.51 (d, *J* = 7.8 Hz, 1H, H-1^b), 4.22 (t, *J* = 10.2 Hz, 2H), 4.18 (dd, *J* = 1.8, 3.0 Hz, 1H), 4.00 (dd, *J* = 1.8, 3.1 Hz, 1H), 4.08-3.38 (m, 46H), 3.03 (t, *J* = 8.2 Hz, 2H, -NCH_2-, linker), 2.09 (s, 3H, -C(O)CH_3), 2.08 (s, 3H, -C(O)CH_3), 2.01 (s, 3H, -C(O)CH_3), 1.71-1.66 (m, 2H, -CCH_2C-, linker), 1.62-1.59 (m, 2H, -CCH_2C-, linker), 1.44-1.40 (m, 2H, -CCH_2C-, linker); ^{13}C NMR (150 MHz, D_2O): δ 174.91, 174.42, 171.02, 110.64 (C-1^d, $^1J_{C,H}$ =174 Hz), 102.32, 101.48, 100.51

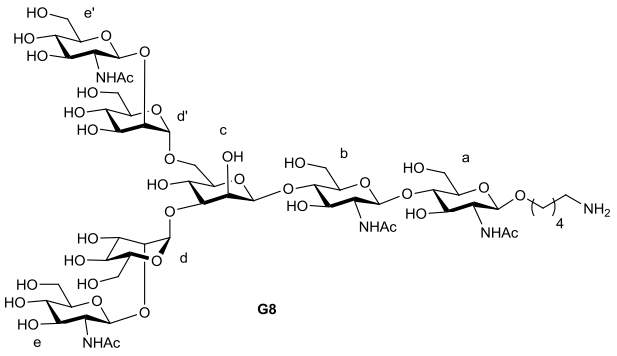
(C-1[a], $^{1}J_{C,H}$ = 161 Hz), 100.44, 100.15, 99.26, 97.58 (C-1[g], $^{1}J_{C,H}$ =169.6 Hz), 79.48, 78.86, 78.72, 76.64, 76.04, 75.72, 74.65, 74.51, 74.42, 73.31, 72.69, 72.35, 72.09, 71.96, 70.86, 70.57, 70.34, 70.12, 70.09, 69.94, 69.42, 67.39, 66.70, 66.36, 65.54, 65.14, 61.68, 61.02, 60.93, 39.31, 38.62, 28,03, 26.39, 22.58, 22.20, 22.11, 22.08, 21.82; ESI-MS: *m/z* calcd for $C_{59}H_{102}N_4O_{41}$; 1522.6092 found 1523.6148 $(M+H)^+$.



S11d

5-Azidopentyl-O-di-[{4-O-acetyl-3,6-O-di-benzyl-2-deoxy-2-phthalimido-β-D-gluco-pyranosy-(1→2)}-O-{3,4,6-tri-O-benzyl-α-D-mannopyranosyl}]-(1→3),(1→6)-2-O-acetyl-β-D-mannopyranosyl-(1→4)-O-(3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl) -(1→4)-O-3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S11d):- A mixture of Silver triflate (0.080 g, 0.315 mmol), Bis(cyclopentadienyl)hafnium dichloride (0.084 g, 0.220 mmol) and 4 Å activated molecular sieves in dry toluene (10 mL) was stirred at rt for 1 h. The reaction mixture was then cooled to -40 ℃, a solution of donor **6** (0.091 g, 0.094 mmol) and acceptor **S11b** (0.140 g, 0.063 mmol) in 5 mL toluene was added. The mixture was stirred for 4 h, quenched with Et_3N, diluted with CH_2Cl_2 and filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL), and a brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 15% EA in toluene) to afford **S11d** (0.110 g, 58%) as colorless foam. TLC: (acetone: toluene =2/8, v/v): R_f = 0.39; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.62-7.32 (m, 16H, Ar-H), 7.27-6.87 (m, 41H, Ar-H), 6.85-6.59 (m, 29H, Ar-H), 5.27 (d, *J* = 8.4 Hz, 1H), 5.16 (s,

1H), 5.14 (d, *J* = 3.6 Hz, 1H), 5.10 (d, *J* = 1.8 Hz, 1H), 4.98 (d, *J* = 3.6 Hz, 1H), 4.89-4.68 (m, 10H), 4.59-4.21 (m, 21H), 4.19-3.87 (m, 7H), 3.80 (dd, *J* = 3.2, 1.8 Hz, 1H), 3.70-3.52 (m, 7H), 3.51-3.28 (m, 8H), 3.27-3.18 (m, 5H), 3.15-3.03 (m, 3H), 3.01 (dd, *J* = 3.2, 1.8 Hz, 1H), 2.91-2.75 (m, 5H), 2.73-2.69 (m, 1H), 2.27 (s, 3H), 1.98 (s, 3H), 1.86 (s, 3H), 1.32-1.23 (m, 4H), 1.03-0.99 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.09, 171.04, 170094, 167.91, 167.57, 139.19, 138.86, 138.63, 138.54, 138.42, 138.31, 138.21, 138.14, 137.93, 133.84, 133.71, 132.04, 131.80, 131.69, 128.80, 128.64, 128.39, 128.32, 128.13, 128.08, 127.79, 127.70, 127.60, 100.18, 100.00, 98.36, 97.88, 97.61, 97.30, 97.22, 80.14, 79.97, 79.31, 75.85, 75.56, 75.39, 75.30, 75.04, 74.71, 74.59, 73.95, 73.64, 73.24, 72.86, 72.14, 71.55, 71.37, 71.04, 70.53, 70.40, 70.15, 69.71, 69.12, 68.12, 65.40, 63.29, 56.34, 55.92, 51.45, 51.37, 51.27, 28.95, 28.54, 23.26, 21.13, 21.02; HRMS (MALDI-TOF): *m/z* calcd for $C_{183}H_{183}N_7O_{43}$; 3168.2306 found 3191.2375 $(M+Na)^+$.

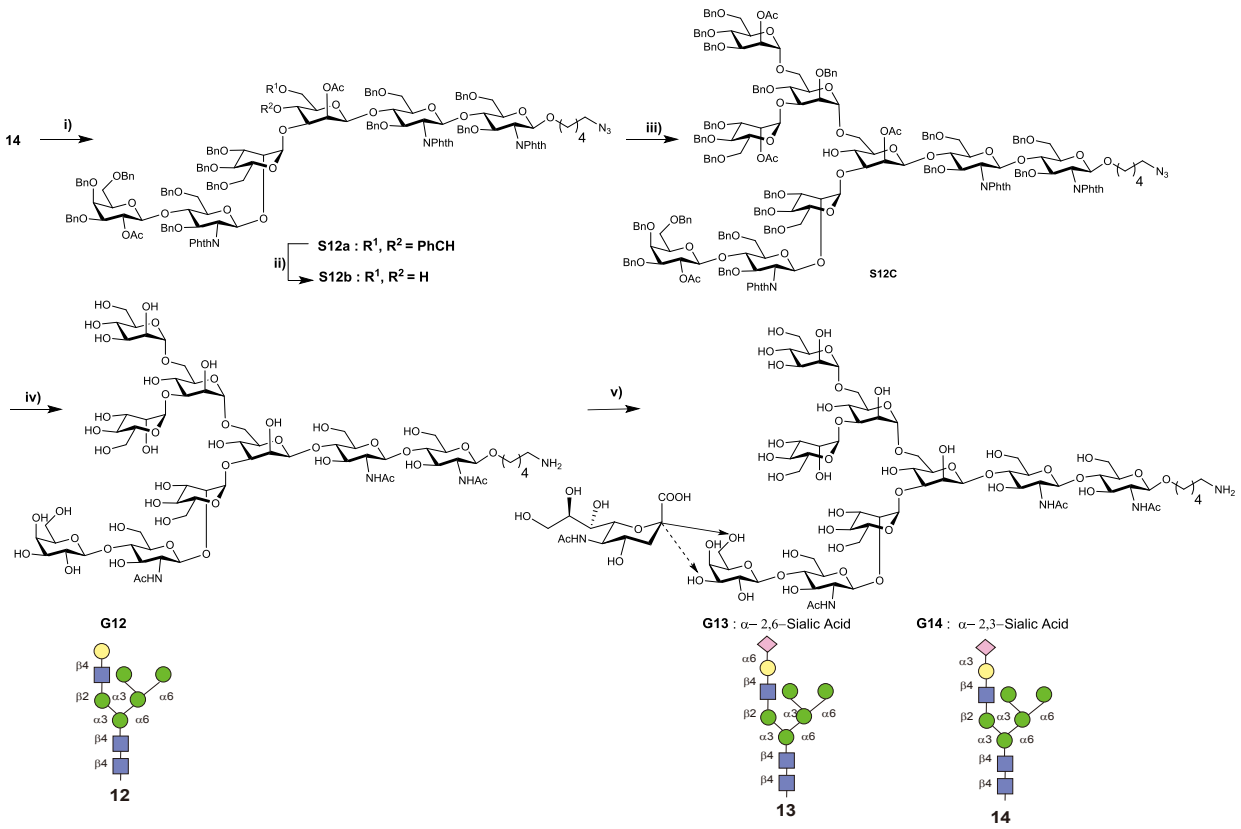


5-Aminopentyl-di-[2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranosyl] -(1→3),(1→6)-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (G8): Compound **S11d** (0.130 g, 0.041 mmol) was deprotected by following general procedure 2 (Method 1) to get the desired heptasaccharide **G8** (0.015 g, 32%) as a white solid. ^{1}H NMR (600 MHz, D_2O): δ 5.99 (d, *J* = 8.5Hz, 1H, H-1^a), 4.93 (s, 1H, H-1^d), 4.83 (s, 1H, H-1$^{d'}$), 4.76 (s, 1H, H-1^c), 4.60 (d, *J* = 7.8 Hz, 1H, H-1^b), 4.56 (d, *J* = 7.9 Hz, 1H, H-1e), 4.49 (d, *J* = 7.9 Hz, 1H, H-1$^{e'}$), 4.27 (s, 2H), 4.11 (d, *J* = 1.8 Hz, 1H), 3.96-3.41 (m, 41H), 2.98 (t, *J* = 8.9 Hz, 2H, -NCH_2-, linker), 2.13 (s, 3H, -

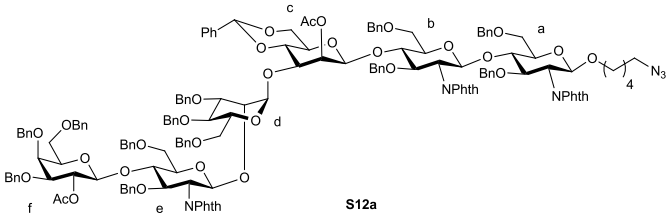
$C(O)CH_3$), 2.09 (s, 3H, -$C(O)CH_3$), 2.06 (s, 3H, -$C(O)CH_3$), 2.01 (s, 3H, -$C(O)CH_3$), 1.69-1.64 (m, 2H, -CCH_2C-, linker), 1.60-1.57 (m, 2H, -CCH_2C-, linker), 1.42-1.38 (m, 2H, -CCH_2C-, linker); ^{13}C NMR (150 MHz, D_2O): δ 174.88, 174.78, 174.65, 174.42, 171.0, 101.39, 101.05, 100.61 (C-1^c), 100.39 (C-1^a), 99.55 (C-$1^{e'}$), 97.60 (C-$1^{d'}$), 97.20 (C-1^d), 79.41, 79.28, 78.92, 76.63, 76.25, 75.79, 74.50, 73.64, 72.84, 71.95, 70.09, 69.89, 69.48, 67.39, 67.35, 66.20, 65.39, 61.66, 61.61, 60.75, 60.61, 59.96, 55.68, 54.98, 54.94, 39.30, 28.04, 26.35, 22.55, 22.31, 22.21, 22.12, 22.08; ESI-MS: *m/z* calcd for $C_{55}H_{95}N_5O_{36}$; 1402.5830; found 1403.5862 $(M + H)^+$ **.**

Preparation of glycans G12-G14

Stereoselective installation of trisaccharide antenna **7** at the 3-O position of the core trisaccharide acceptor **14** was performed under the promotion of Cp_2HfCl_2/AgOTf to afford hexasaccharide **S12a**. The *p*-toluene sulfonic acid-mediated ring opening of **S12a** provided diol **S12b.** Considering the higher reactivity of the primary hydroxyl**, S12b** was further glycosylated at the 6-O position with trimannosyl thioglycoside **3** and, then, activated by the stable radical cation tris(4-bromophenyl) ammoniumyl hexachloroantimonate in a one electron transfer reaction to afford nonasaccharide **S12c**. With compound **S12c** in hand, a series of functional group transformations were carried out to afford the desired fully deprotected glycan **G12**. The precursor oligosaccharide G**12**, is an appropriate starting material for sialylation by α-2,6 or 2,3 sialyltransferase derived from marine bacteria, known for their broader acceptor specificity and no intrinsic sialidase activity. Sialyl transferase (SiaT)-mediated enzymatic terminal sialylation[1-4] of G**12** efficiently permitted access to α-2,6 and α-2,3 sialylated glycans G**13** and G**14,** respectively (Scheme S12).

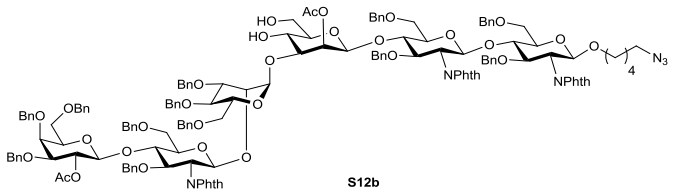


Scheme S12 | Preparation of G12-G14. i) **7**, Cp_2HfCl_2, AgOTf, 4 Å MS, -40 ^oC, 2 h, 63%; ii) *p*-TsOH, CH_3CN, 5 h, 78%; iii) **3**, $(BrC_6H_4)_3NSbCl_6$, CH_3CN, 4 Å MS, -10 ^oC to RT, 4 h, 55%; iv) (1) $NH_2CH_2CH_2NH_2$, n-BuOH, 90 ^oC, overnight; (2) Ac_2O, pyridine, overnight; (3) NaOMe, MeOH, overnight; (4) $Pd(OH)_2$, MeOH: H_2O : HCOOH (5:3:2), H_2; 62%; v) CMP-β-D-Sialic acid, α-2,6- or 2,3-sialyltransferase, G13: 60%; G14: 56%; Cp_2HfCl_2: Bis(cyclopentadienyl) hafnium dichloride; AgOTf: Silver trifluromethanesulfonate; $(BrC_6H_4)_3NSbCl_6$: Tris (4-bromophenyl) ammoniumyl hexachloroantimonate.



5-Azidopentyl-O-2-O-acetyl-3,4,6-O-tri-benzyl-β-D-galactopyranosyl-(1→4)-O-3,6-O-di-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→2)-O-(3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→3)-2-O-acetyl-4,6-O-benzylidine-β-D-mannopyranosyl-(1→4)-O-(3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-O-3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S12a): A mixture of silver triflate (0.327 g, 1.28 mmol), bis (cyclopentadienyl) hafnium dichloride (0.339 g, 0.896 mmol) and 4 Å activated molecular sieves in dry toluene (10 mL) was stirred at rt for 1 h. The reaction mixture was then cooled to -40 ℃, a solution of donor **7** (0.430 g, 0.307 mmol) and acceptor chitobiose trisaccharide **14** (0.35 g, 0.256 mmol) in 5 mL toluene was added. The mixture was stirred for 2 h, quenched with Et_3N, diluted with EtOAc and filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL), and a brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 15% EA in toluene) to afford **S12a** (0.500 g, 71%) as white foam. TLC: (ethyl acetate: toluene = 2/8, v/v): R_f = 0.62; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.85-7.49 (m, 12H, Ar-H), 7.02-7.39 (m, 45H, Ar-H), 7.19-7.02 (m, 10H, Ar-H), 6.99-6.90 (m, 6H, Ar-H), 6.83-6.78 (m, 4H, Ar-H), 5.310 (t, *J* = 7.5 Hz, 1H, H-2^f), 5.27 (d, *J* = 8.1 Hz, 1H, H-1^a), 5.25 (d, *J* = 8.4 Hz, 1H, H-1^e), 5.15 (d, *J* = 2.3 Hz, 1H), 5.01 (s, 1H, Ph-C<u>H</u>, benzylidene), 4.90-4.80 (m, 7H), 4.62 (d, *J* = 8.5Hz, 1H), 4.58-4.53 (m, 3H), 4.52-4.38 (m, 10H), 4.32-4.13 (m, 10H), 4.12-4.05 (m, 5H), 4.02 (m, 1H), 3.89 (d, *J* = 3.2 Hz, 1H), 3.75-3.73 (m, 2H), 3.72-3.49 (m, 8H), 3.48-3.37 (m, 5H), 3.34-3.29 (m, 4H), 3.29-3.18 (m, 4H), 2.98 (m, 1H), 2.89-2.79 (m, 2H, linker), 2.29 (s, 3H, -C(O)CH_3), 1.99 (s, 3H, -C(O)CH_3), 1.49-1.30 (m, 4H, -CCH_2C-), 1.10-1.00 (m, 2H, -CCH_2C-); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.8, 169.4, 168.7, 167.7, 139.1, 139.9, 138.9, 138.8, 138.8, 138.5, 138.2, 138.2, 138.1, 137.9, 137.6, 134.2, 133.8, 133.1, 131.9, 131.8, 131.6, 129.1, 128.8, 128.6, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.7, 127.7, 127.5, 127.5, 127.4, 127.3, 127.0, 126.7, 126.1, 123.8, 123.3, 122.8, 100.88, 100.83, 99.94, 99.38, 98.43, 98.30, 97.26, 80.31, 79.00, 78.05, 77.61, 76.42, 76.31, 76.1,. 75.1, 74.8, 74.7, 74.6, 74.6, 74.4, 74.4, 74.2, 73.6, 73.4, 73.3, 72.9, 72.8, 72.2, 71.8, 71.7, 70.4, 70.0, 69.8, 69.0,

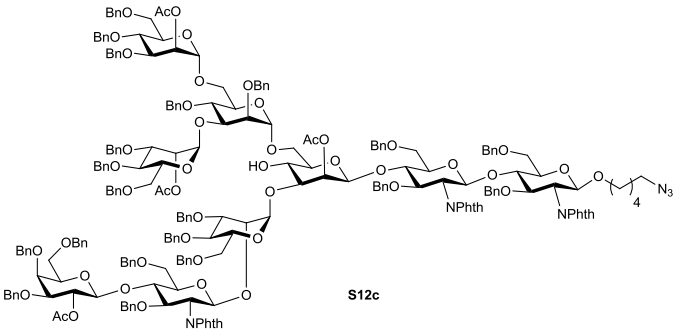
68.8, 68.4, 68.2, 67.7, 67.6, 56.7 56.0, 55.9, 51.3, 28.8, 28.4, 23.2, 21.7, 21.2; ESI-MS: *m/z* calcd for $C_{160}H_{160}N_6O_{36}$; 2742.0799 found 2765.0952 $(M+Na)^+$.



S12b

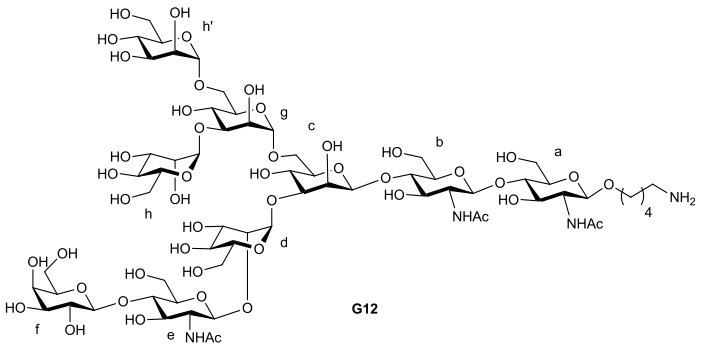
5-Azidopentyl-O-2-O-acetyl-3,4,6-O-tri-benzyl-β-D-galactopyranosyl-(1→4)-O-3,6-O-di-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→2)-O-(3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→3)-2-O-acetyl-β-D-mannopyranosyl-(1→4)-O-(3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-O-3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S12b): To a solution of **S12a** (0.601 g, 0.219 mmol) in acetonitrile (10 mL) was added *p*-toluene sulfonic acid monohydrate (0.046 g, 0.328 mmol), stirred at rt for 5 h. The reaction was quenched with Et_3N and concentrated in *vacuo.* The residue was purified by flash column chromatography (0% → 15% EA in toluene) to afford diol **S12b** (0.460 g, 78%). TLC: (acetone: toluene = 2/8, v/v): R_f = 0.32; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.91-7.42 (m, 12H, Ar-H), 7.39-7.12 (m, 41H, Ar-H), 7.10-6.93 (m, 13H, Ar-H), 6.85-6.81 (m, 3H, Ar-H), 6.78-6.73 (m, 3H, Ar-H), 5.33 (t, *J* = 7.8 Hz, 1H, H-2^f), 5.23 (t, *J* = 8.4 Hz, 2H, H-1), 5.08 (d, *J* = 6.2 Hz, 1H), 4.97 (d, *J* = 8.9 Hz, 1H, H-1), 4.94-4.80 (m, 5H), 4.64-4.60 (m, 2H), 4.49-4.21 (m, 21H), 4.19-4.15 (m, 2H), 4.15-3.89 (m, 8H), 3.89 (d, *J* = 6.2 Hz, 1H), 3.78 (d, *J* = 5.8 Hz, 1H), 3.69 (dd, *J* = 6.3, 12.1 Hz, 1H), 3.65-3.64 (m, 1H), 3.56-3.32 (m, 14H), 3.29 (dd, *J* = 6.6, 12.5 Hz, 1H), 3.29-3.23 (m, 3H), 3.00-2.99 (m, 2H), 2.87-2.82 (m, 2H), 2.74 (t, *J* = 9.5Hz, 1H), 2.28 (s, 3H, -C(O)CH_3), 1.98 (s, 3H, -C(O)CH_3), 1.37-1.22 (m, 4H, -CCH_2C-), 1.07-1.00 (m, 2H, -CCH_2C-); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.29, 169.57, 168.78, 168.58, 168.03, 167.90, 139.01, 138.92, 138.84, 138.68, 138.45, 138.39, 138.36, 138.22, 138.14, 137.98, 134.35, 134.15, 134.02, 133.89, 132.04, 131.95, 131.68, 130.10, 129.54, 129.46, 128.80, 128.70, 128.66, 128.62, 128.60, 128.52, 128.47, 128.46, 128.39, 128.30, 128.15, 128.07, 128.01, 127.98, 127.94, 127.91,

127.83, 127.72, 127.60, 127.39, 127.20, 126.96, 123.90, 123.46, 122.88, 101.11, 100.87, 98.87, 98.33, 83.75, 80.57, 80.14, 78.58, 78.29, 76.15, 75.78, 75.45, 74.11, 74.96, 74.83, 74.70, 74.61, 74.44, 74.10, 73.77, 73.73, 73.59, 73.43, 73.38, 73.03, 72.30, 71.97, 70.61, 70.29, 69.82, 69.14, 69.08, 68.54, 68.38, 67.94, 66.94, 66.47, 63.21, 56.80, 56.09, 56.01, 51.37, 31.71, 31.21, 30.97, 30.59, 29.99, 29.65, 28.55, 27.87, 27.29, 26.96, 26.24, 25.59, 25.36, 24.26, 23.27, 22.98, 21.86, 21.32, 20.80, 20.49, 18.94, 16.76, 15.95, 15.44, 15.10, 14.40, 14.07, 13.67, 13.47; ESI-MS: *m/z* calcd for $C_{153}H_{156}N_6O_{36}$; 1327.0189; found 1350.0207 $(M+Na)^+$.

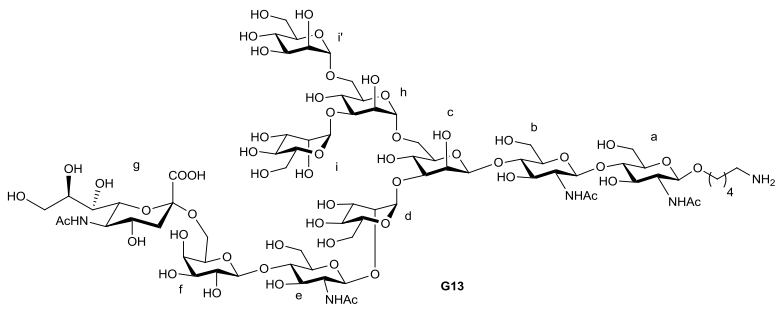


5-Azidopentyl-O-{2-O-acetyl-3,4,6-O-tri-benzyl-β-D-galactopyranosyl-(1→4)}-O-{3,6-O-di-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→2)}-O-{3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→3)-{2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→3)}-[2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→6)]-2,4-di-O-benzyl-α-D-manno-pyranosyl-(1→6)}-2-O-acetyl-β-D-mannopyranosyl-(1→4)-O-(3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-O-3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S12c): A mixture of hexasaccharide acceptor **S12b** (0.40 g, 0.15 mmol), thiomannoside donor **3** (0.229 g, 0.226 mmol) and activated 4 Å molecular sieves in CH_3CN (10 mL) was stirred at rt for 1 h. The resulting mixture was cooled to -10 ℃, tris (4-bromophenyl)aminium hexachloroantimonate (0.254 g, 0.30 mmol) was added and stirred at rt for 4 h. TLC indicated formation of product with consumption of starting material, the reaction was then quenched by Et_3N. The reaction mixture was diluted with CH_2Cl_2 and filtered through celite. The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL), and a brine (50 mL) solution.

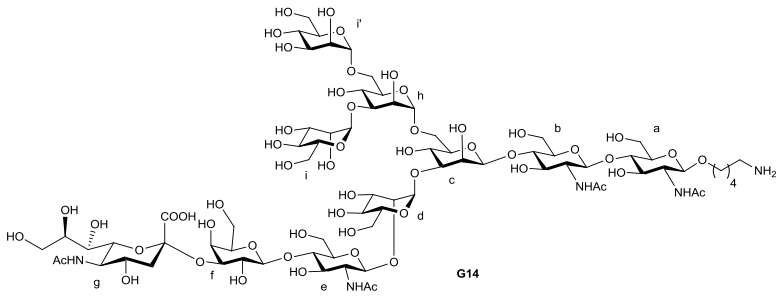
The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 10% EA in toluene) to afford **S12c** (0.335 g, 55%) as colorless foam and acceptor 9 (0.103 g). TLC: (ethyl acetate: toluene = 1/9, v/v): R_f = 0.46; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.72-7.45 (m, 12H, Ar-H), 7.37-7.28 (m, 5H, Ar-H), 7.28-7.12 (m, 67H, Ar-H), 7.09-7.02 (m, 11H, Ar-H), 6.94-6.90 (m, 7H, Ar-H), 6.80-6.78 (m, 4H, Ar-H), 6.69-6.68 (m, 3H, Ar-H), 6.62-6.61 (m, 3H, Ar-H), 5.49 (s, 1H), 5.48 (s, 1H), 5.35 (t, *J* = 8.4 Hz, 1H), 5.28 (d, *J* = 8.4 Hz, 1H, H-1), 5.17 (d, *J* = 8.4 Hz, 1H, H-1), 5.09 (d, *J* = 6.2 Hz, 1H), 5.00 (s, 1H, H-1), 4.92 (d, *J* = 3.1 Hz, 1H), 4.90-4.72 (m, 12H), 4.69-4.72 (m, 23H), 4.26-4.17 (m, 5H), 4.13-3.97 (m, 12H), 3.89-3.82 (m, 12H), 3.72 (t, 1H), 3.68-3.62 (m, 1H), 3.65-3.55 (m, 7H), 3.54-3.45 (m, 4H), 3.43-3.40 (m, 4H), 3.40-3.29 (m, 9H), 3.23-3.19 (m, 3H), 3.17-3.09 (m, 2H), 2.91-2.79 (m, 3H), 2.68 (s, 1H), 2.28 (s, 3H, -C(O)CH_3), 2.05 (s, 3H, -C(O)CH_3), 2.01 (s, 3H, -C(O)CH_3), 1.99 (s, 3H, -C(O)CH_3), 1.34-1.22 (m, 4H, linker), 1.06-1.00 (m, 2H, linker); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.37, 170.38, 170.29, 169.54, 168.49, 168.23, 167.97, 167.53, 139.28, 139.11, 139.03, 138.97, 138.94, 138.67, 138.63, 138.58, 138.53, 138.41, 138.38, 138.25, 138.10, 128.74, 128.70, 128.67, 128.63, 128.58, 128.55, 128.53, 128.51, 128.48, 128.44, 128.40, 128.37, 128.34, 128.30, 128.15, 128.03, 128.00, 127.95, 127.92, 127.84, 127.77, 127.75, 127.70, 127.64, 127.61, 101.17, 100.92, 98.84, 98.28, 97.71, 97.45, 75.49, 75.36, 75.26, 75.17, 75.06, 74.96, 74.82, 74.75, 74.65, 74.60, 74.38, 74.30, 73.99, 73.77, 73.73, 73.59, 73.25, 73.25, 73.06, 72.99, 72.91, 72.26, 72.18, 71.98, 71.82, 71.57, 71.45, 70.52, 70.03, 69.92, 69.56, 69.10, 68.90, 68.85, 68.57, 68.48, 68.37, 66.64, 66.06, 56.75, 56.09, 55.99, 51.37, 34.25, 29.99, 28.94, 28.54, 25.90, 23.27, 21.86, 21.42, 21.33; HRMS (MALDI-TOF): *m/z* calcd for $C_{231}H_{238}N_6O_{53}$; 3945.6071; found 3968.6006 $(M + Na)^+$.



5-Aminopentyl-β-D-galactopyranosyl-(1→4)-[2-acetamido-2-deoxy-β-D-gluco-pyranosyl-(1→2)-α-D-mannopyranosyl-(1→3),[di-(α-D-mannopyranosyl)-(1→3),(1→6)-α-D-manno-pyranosyl](1→6)-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-gluco-pyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (G12): Compound **S12c** (0.16 g, 0.048 mmol) was deprotected by following general procedure 2 (Method 1) to afford desired the nonasaccharide **G12** (0.052 g, 62%). ^{1}H NMR (600 MHz, D_2O): δ 5.10 (s, 1H, H-1^{d}), 5.07 (d, *J* = 9.5 Hz, 1H, H-1^{a}), 4.91 (s, 2H, H-1$^{h,h'}$), 4.84 (s, 1H, H-1^{f}), 4.61(s, 1H, H-1^{c}), 4.50 (d, *J* = 9.2 Hz, 1H, H-1^{b}), 4.49 (d, *J* = 8.1 Hz, 1H, H-1^{e}), 4.31 (s, 2H), 4.19 (bs, 1H), 4.07 (bs, 1H), 4.02-3.51 (m, 53H), 3.40-3.30 (m, 2H) 2.99 (t, *J* = 11.2 Hz, 2H, -NCH_2-, linker), 2.08 (s, 3H, -C(O)CH_3), 2.07 (s, 3H, -C(O)CH_3), 2.04 (s, 3H, -C(O)CH_3), 1.70–1.65 (m, 2H, -CCH_2C-, linker), 1.62-1.58 (m, 2H, -CCH_2C-, linker), 1.48–1.38 (m, 2H, -CCH_2C-, linker); ^{13}C NMR (150 MHz, D_2O): δ 177.60, 177.17, 105.68 (C-1^{b}), 105.05 (C-1^{d}), 104.23, 104.04, 103.79, 103.37, 103.18, 102.88, 102.23 (C-1$^{h'}$), 102.03 (C-1^{h}), 100.24 (C-1^{g}), 82.20, 82.06, 82.01, 81.58, 81.51, 81.40, 79.38, 78.70, 78.08, 77.43, 77.37, 77.18, 77.03, 76.07, 75.66, 75.43, 75.23, 75.11, 75.06, 74.96, 74.83, 74.71, 73.72, 73.65, 73.33, 73.20, 73.11, 72.95, 72.89, 72.84, 72.69, 72.18, 71.28, 70.15, 68.50, 69.46, 69.36, 69.01, 68.31, 67.90, 67.86, 64.45, 63.75, 63.69, 63.61, 62.87, 62.82, 62.75, 57.94, 57.72, 42.06, 30.78, 29.10, 25.35, 25.30, 24.96, 24.87, 24.83; ESI-MS: *m/z* calcd for $C_{65}H_{112}N_4O_{46}$; 1684.6620 found 1685.6968 $(M + H)^{+}$.



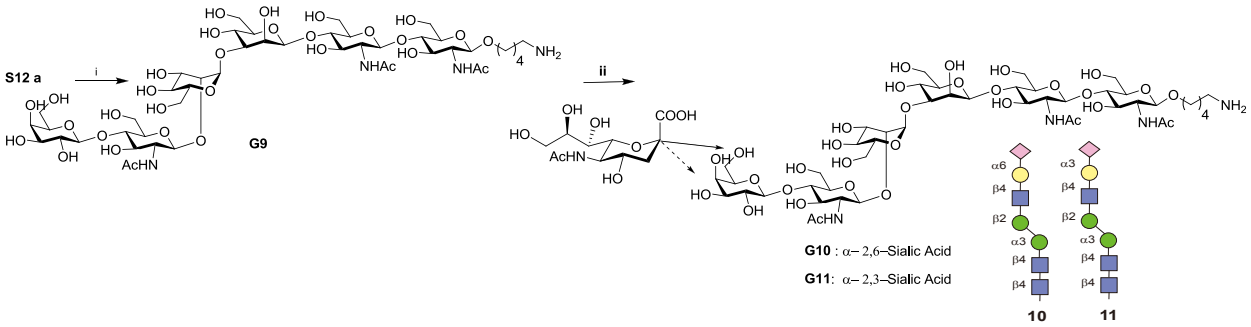
5-Aminopentyl-5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyrano-sylonate-(2→6)-β-D-galactopyranosyl-(1→4)-[2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranosyl-(1→3),[di-(α-D-mannopyranosyl)-(1→3),(1→6)-α-D-manno-pyranosyl] (1→6)-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (G13): Compound G**12** (5 mg, 0.0029 mmol) was sialylated with α-2,6-sialyltransferase for 2 days by following general procedure 3 to get the desired title compound **G13** (3.5 mg, 60%) as white solid. ^{1}H NMR (600 MHz, D_2O): δ 5.07 (s, 1H, H-1^{d}), 5.06 (d, *J* = 8.5 Hz, 1H, H-1^{a}), 4.92 (s, 1H, H-1^{h}), 4.90 (s, 1H^{i}), 4.89 (s, 1H, H-1$^{i'}$), 4.78 (s, 1H, H-1^{c}), 4.58 (d, *J* = 7.2 Hz, 1H, H-1^{f}), 4.46 (d, *J* = 7.8 Hz, 1H, H-1^{b}), 4.41 (d, *J* = 8.4 Hz, 1H, H-1^{e}), 4.25-4.24 (m, 2H), 4.12 (s, 1H), 4.04 (d, *J* = 4.7 Hz, 1H), 4.04-3.42 (m, 55H), 3.40 (t, *J* = 10.8 Hz, 1H), 3.39-3.35 (m, 1H), 2.95 (t, *J* = 10.9 Hz, 2H), 2.64 (dd, *J* = 4.2, 12.2 Hz, 1H, H-3$^{equi.\ g}$), 2.04 (s, 3H, -C(O)CH_3), 2.04 (s, 3H, -C(O)CH_3), 2.00 (s, 3H, -C(O)CH_3), 2.00 (s, 3H, -C(O)CH_3), 1.71-1.61 (m, 3H, -CCH_2C-, linker and H-3$^{axial\ g}$), 1.58-1.54 (m, 2H, -CCH_2C-, linker), 1.39-1.35 (m, 2H, -CCH_2C-, linker); ^{13}C NMR (150 MHz, D_2O): δ 174.90, 174.79, 174.38, 173.47, 103.42, 102.29 (C-1^{d}, $^{1}J_{C,H}$ = 170.9 Hz), 101.48, 101.01, 100.41, 100.18 (C-1^{a}, $^{1}J_{C,H}$ = 162.9 Hz), 100.15, 99.24 ((C-1^{h}, $^{1}J_{C,H}$ = 171.3 Hz)), 97.87, 97.27, 80.78, 79.59, 79.20, 78.72, 78.36, 76.61, 75.81, 74.79, 74.48, 74.36, 73.63, 73.28, 72.63, 72.52, 72.35, 72.30, 72.09, 71.94, 71.65, 70.82, 70.69, 70.53, 70.31, 70.12, 70.05, 69.89, 69.41, 68.33, 68.17, 67.32, 67.17, 66.66, 65.47, 65.09, 63.30, 62.62, 61.66, 60.98, 60.89, 60.32, 60.02, 59.94, 57.95, 54.91, 51.81, 40.01, 39.27, 28.00, 26.37, 23.62, 23.19, 22.59, 22.17, 22.05, 22.00; ESI-MS (negative mode): *m/z* calcd for $C_{76}H_{129}N_5O_{54}$; 1975.7418 found 1974.7600 (*M* -H)$^{-}$.



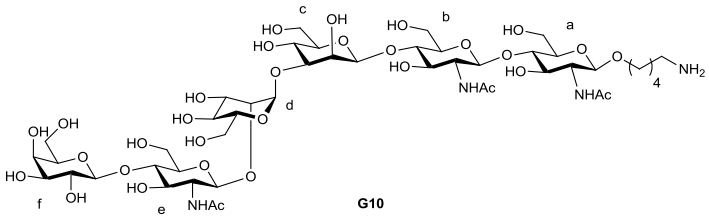
5-Aminopentyl-5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyrano-sylonate-(2→3)-β-D-galactopyranosyl-(1→4)-[2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranosyl-(1→3),[di-(α-D-mannopyranosyl)-(1→3),(1→6)-α-D-manno-pyranosyl] (1→6)-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (G14): Compound G**12** (5 mg, 0.0029 mmol) was sialylated with α-2,3-sialyltransferase for 3 d by following general procedure 3 to get the desired title compound **G14** (3.1 mg, 56%) as white solid. ^{1}H NMR (600 MHz, D_2O): δ 5.01 (s, 1H, H-1^{d}), 4.97 (dd, *J* = 3.2, 7.2 Hz, 1H, H-1^{a}), 4.84 (s, 1H, H-1^{h}), 4.81 (s, 1H, H-1^{i}), 4.75 (s, 1H, H-1$^{i'}$), 4.62 (s, 1H, H-1^{c}), 4.52 (d, *J* = 7.8 Hz, 1H, H-1^{f}), 4.97 (d, *J* = 9.2 Hz, 1H, H-1^{b}), 4.42 (d, *J* = 8.3 Hz, 1H, H-1^{e}), 4.39 (d, *J* = 8.3 Hz, 1H), 4.22 (t, *J* = 7.8 Hz, 2H), 4.09 (s, 1H), 4.06 (d, *J* = 7.4 Hz, 1H), 4.03 (d, *J* = 7.3 Hz, 1H), 4.00 (d, *J* = 3.2 Hz, 1H), 3.96-3.85 (m, 16H), 3.85-3.71 (m, 19H), 3.72-3.52 (m, 26H), 3.51-3.48 (m, 2H,), 3.38-3.370 (m, 2H), 2.90 (t, *J* = 7.9 Hz, 2H, -NCH$_2$-, linker), 2.68 (dd, *J* = 4.8, 12.0 Hz, 1H, H-3 $^{equi.\ g}$), 2.01 (s, 3H, -C(O)CH$_3$), 1.99 (s, 3H, -C(O)CH$_3$), 1.96 (s, 3H, -C(O)CH$_3$), 1.95 (s, 3H, -C(O)CH$_3$), 1.73 (t, *J* = 8.6 Hz, 1H, H-3 $^{axial\ g}$), 1.61-1.56 (m, 2H, -CCH$_2$C-, linker), 1.54-1.46 (m, 2H, -CCH$_2$C-, linker), 1.34-1.33 (m, 2H, -CCH$_2$C-, linker); ^{13}C NMR (150 MHz, D_2O): δ 171.94, 171.81, 171.37, 170.80, 113.44, 99.86, 99.53, 99.27, 98.42, 97.99, 97.38, 97.08, 96.74, 96.21, 75.74, 75.66, 75.52, 73.56, 72.85, 72.41, 72.10, 71.62, 71.45, 71.36, 70.27, 69.81, 69.62, 69.28, 69.14, 69.02, 68.90, 68.69, 67.91, 67.82, 67.50, 67.20, 67.08, 66.87, 66.36, 65.46, 65.29, 65.01, 64.39, 64.32, 63.68, 62.47, 62.09, 61.02, 59.50, 59.39, 58.64, 57.96, 57.87, 57.10, 56.91, 52.12, 51.91, 48.60, 42.85, 40.32, 36.54, 36.25,

35.04, 25.27, 24.98, 23.34, 20.60, 19.53, 19.13, 19.03, 18.95, 13.70; ESI-MS (negative mode): *m/z* calcd for $C_{76}H_{129}N_5O_{54}$; 1975.7418 found 1974.7671 $(M - H)^-$.

Preparation of glycans G9-G11

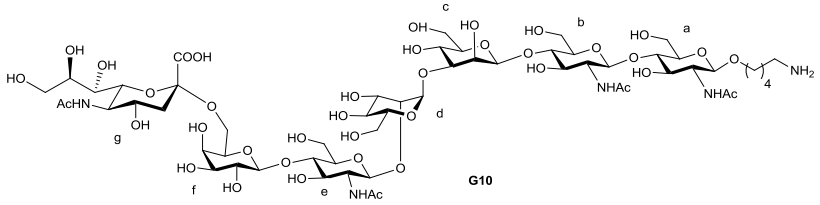


Scheme S13 | Preparation of G9-G11. i) (1) $NH_2CH_2CH_2NH_2$, n-BuOH, 90 ^oC, overnight; (2) Ac_2O, pyridine, overnight; (3) NaOMe, MeOH, overnight; (4) $Pd(OH)_2$, MeOH: H_2O: HCOOH (5:3:2), H_2; 51%; ii) CMP- β-D-Sialic acid, α-2,6/2,3- sialyltransferase,**G10**: 77%;**G11**: 52%



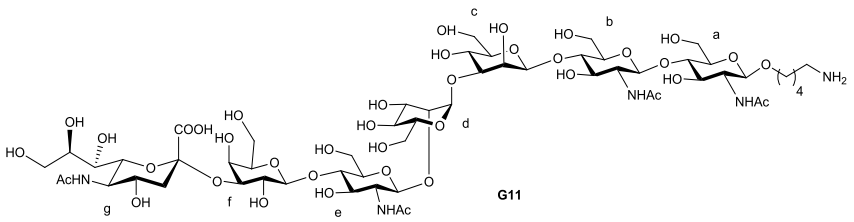
5-Aminopentyl-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl -(1→2)-α-D-mannopyranosyl]-(1→3)-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (G10): Hexasaccharide **S12a** (0.110 g, 0.041 mmol) was deprotected following general procedure 2 (Method 1) to get the desired compound **G10** (0.025 g, 51%) as white solid. ^1H NMR (600 MHz, D_2O): δ 5.04 (d, J = 8.4 Hz, 1H, H-1^a), 4.84 (s, 1H, H-1^d), 4.78 (s, 1H, H-1^c), 4.60 (d, J = 8.2 Hz, 1H, H-1^e), 4.51 (d, J = 8.1 Hz, 1H, H-1^b), 4.46 (d, J = 7.8 Hz, 1H, H-1^f), 4.28 (d, J = 3.3 Hz, 1H), 4.26 (d, J = 3.6 Hz, 1H), 4.10-3.82 (m, 9H), 3.82-3.56 (m, 22H), 3.52-3.38 (m, 5H), 2.97 (t, J = 7.8 Hz, 2H, -NCH_2-, linker), 2.07 (s, 3H, -C(O)CH_3), 2.05 (s, 3H, -C(O)CH_3), 2.03 (s, 3H, -C(O)CH_3), 1.70-

1.65 (m, 2H, -CCH_2C-, linker), 1.62-1.58 (m, 2H, -CCH_2C-, linker), 1.48-1.41 (m, 2H, -CCH_2C-, linker); ^{13}C NMR (150 MHz, D_2O): δ 177.64, 177.32, 177.17, 173.74, 105.65, 104.13, 103.80, 103.18, 102.70, 100.08, 82.05, 81.50, 81.37, 79.38, 79.04, 78.85, 78.09, 77.42, 77.28, 77.24, 75.23, 75.13, 75.06, 74.80, 74.67, 73.69, 72.84, 71.27, 70.14, 70.07, 68.12, 64.43, 63.74, 63.61, 62.85, 62.82, 62.75, 57.91, 57.78, 57.73, 42.05, 30.78, 29.10, 25.27, 24.87, 24.85, 24.83; ESI-MS: *m/z* calcd for $C_{47}H_{82}N_4O_3$; 1198.4855 found 1221.5223 $(M + Na)^+$.



5-Aminopentyl-[5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyrano-sylonate-(2→6)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranosyl]-(1→3)-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-gluco-pyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (G10): Compound **G9** (10 mg, 0.0083 mmol) was sialylated with α-2,6-sialyltransferase for 2 days by following general procedure 3 to get the desired title compound **G10** (9.5 mg, 77%) as white solid. ^{1}H NMR (600 MHz, D_2O): δ 5.06 (d, *J* = 7.8 Hz, 1H, H-1^a), 4.80 (s, 1H, H-1^d), 4.78 (s, 1H, H-1^c), 4.60 (d, *J* = 7.8 Hz, 1H, H-1^e), 4.49 (d, *J* = 7.8 Hz, 1H, H-1^b), 4.43 (d, *J* = 7.8 Hz, 1H, H-1^f), 4.27 (d, *J* = 3.6 Hz, 1H), 4.25 (d, *J* = 3.6 Hz, 1H), 4.08-3.38 (m, 42H), 2.98 (t, *J* =11.2 Hz, 2H, -NCH_2-, linker), 2.60 (dd, *J* = 4.8, 12.0 Hz, 1H, H-3 $^{equi.\ g}$), 2.08 (s, 6H, -C(O)CH_3) 2.05 (s, 3H, -C(O)CH_3), 2.03 (s, 3H, -C(O)CH_3, 1.71 (t, *J* = 7.8Hz, 1H, H-3 $^{axial\ g}$), 1.69-1.69 (m, 2H, -CCH_2C-, linker), 1.61-1.56 (m, 2H, -CCH_2C-, linker), 1.41-1.37 (m, 2H, -CCH_2C-, linker); ^{13}C NMR (150 MHz, D_2O): δ 174.94, 174.83, 174.56, 174.40, 103.50, 101,37, 101.03, 100.31, 100.12, 99.92, 97.31, 80.99, 79.28, 78.63, 78.59, 76.61, 76.32, 76.07, 74.51, 74.48, 74.38, 73.67, 72.52, 72.38, 72.36, 72.08, 71.90, 71.66, 70.70, 70.06, 68.37, 68.34, 67.33, 63.35, 62.63, 61.67, 60.88, 60.09, 59.98, 54.99,

54.87, 51.85, 40.02, 39.30, 28.01, 26.36, 22.56, 22.10, 22.08, 21.99; ESI-MS (negative mode): *m/z* calcd for $C_{58}H_{99}N_5O_{39}$; 1489.5833 found 1488.5949 $(M - H)^-$.



5-Aminopentyl-[5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyrano-sylonate-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranosyl]-(1→3)-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-gluco-pyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (G11): Compound **G9** (7 mg, 0.0058 mmol) was sialylated with α-2,3-sialyltransferase for 3 days by following general procedure 3 to get desired the title compound **G11** (4.6 mg, 52%) as white solid. ^{1}H NMR (600 MHz, D_2O): δ 5.06 (d, *J* = 8.4 Hz, 1H, H-1^a), 4.79 (s, 1H, H-1^d), 4.75 (s, 1H, H-1^c), 4.62 (d, *J* = 6.6 Hz, 1H, H-1^e), 4.56 (d, *J* = 7.8 Hz, 1H, H-1^b), 4.51 (d, *J* = 7.8 Hz, 1H, H-1^f), 4.28 (d, *J* = 8.4 Hz, 2H), 4.13 (d, *J* = 9.6 Hz, 1H), 3.99-3.83 (m, 12H), 3.82-3.57 (m, 25H), 3.53-3.39 (m, 4H), 2.99 (t, *J* = 7.8 Hz, 2H), 2.77 (dd, *J* = 4.8, 2.0 Hz, 1H, H-3 $^{equi.\ g}$), 2.12 (s, 3H, -C(O)CH_3) 2.09 (s, 3H, -C(O)CH_3), 2.05 (s, 3H, -C(O)CH_3), 2.03 (s, 3H, -C(O)CH_3), 1.80 (t, *J* = 7.8 Hz, 1H, H-3 $^{axial\ g}$), 1.71-1.66 (m, 2H, -CCH_2C-, linker), 1.62-1.59 (m, 2H, -CCH_2C-, linker), 1.44-1.41 (m, 2H, -CCH_2C-, linker); ^{13}C NMR (150 MHz, D_2O): δ 174.88, 174.53, 174.46, 174.40, 102.50, 102,37, 101.65, 101.31, 100.12, 99.86, 98.31, 80.32, 79.67, 78.78, 78.56, 76.66, 75.32, 75.07, 74.51, 74.48, 74.38, 73.67, 72.52, 72.38, 72.36, 72.08, 71.90, 71.66, 70.70, 70.06, 68.37, 68.34, 67.33, 63.35, 62.63, 61.67, 60.88, 60.09, 59.98, 54.99, 54.87, 51.85, 40.02, 39.30, 28.01, 26.36, 22.56, 22.10, 22.08, 21.27 20.27; ESI-MS (negative mode): *m/z* calcd for $C_{58}H_{99}N_5O_{39}$; 1489.5833 found 1488.5944$(M - H)^-$.

vii. Synthesis of complex type oligosaccharides

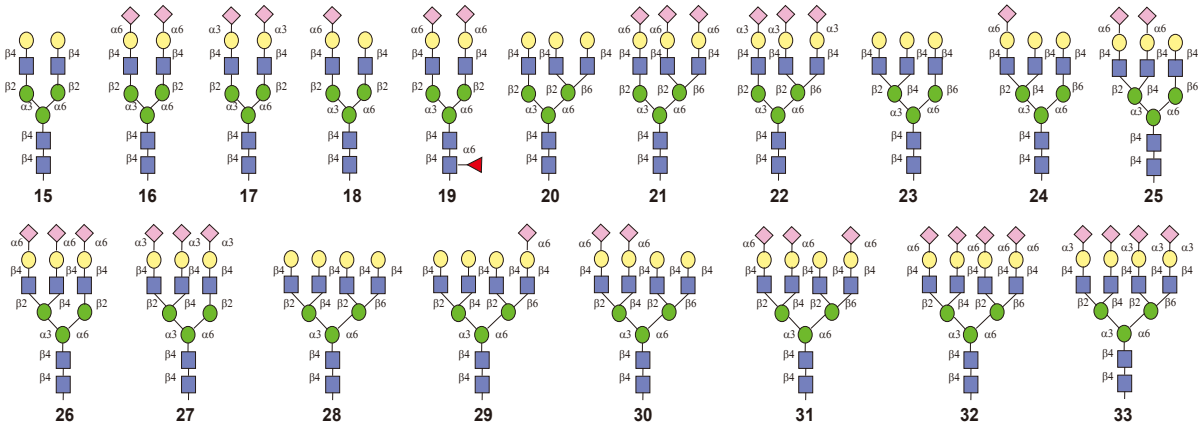
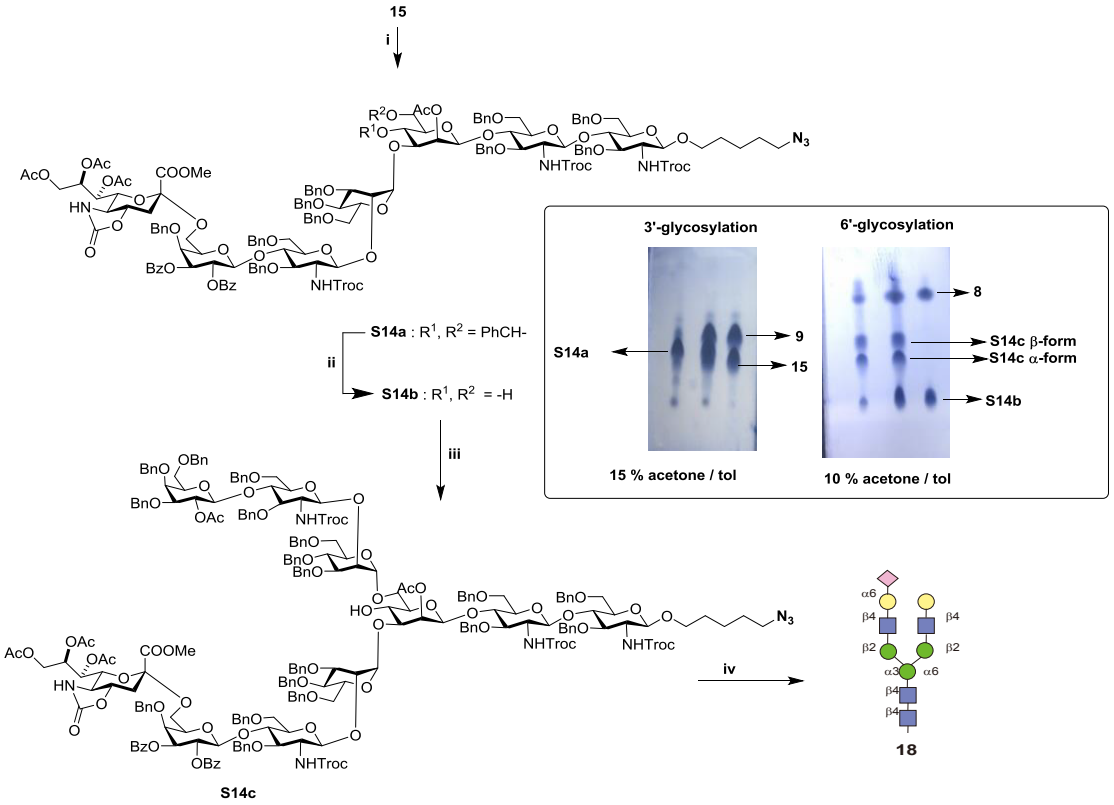


Figure S3 | Structures of complex type glycans.

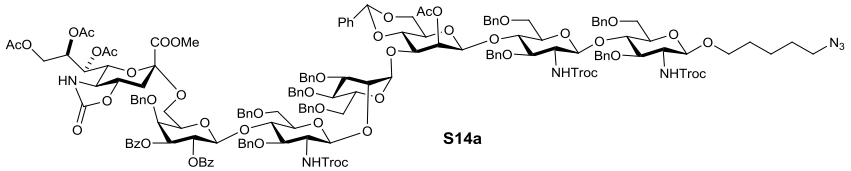
Previously, we have developed a efficient chemo-enzymatic strategy for the rapid production of bi-(G15, G16, and G17), tri- (G20-G23, G26, and G27) and tetraantennary (G28, G32, and G33) complex type *N*-glycans, with and without terminal *N*-acetylneuraminic acid residues connected via the α-2,6 or α-2,3 linkages. In addition, we have developed a total chemical synthesis strategy which utilized a modular set of glycosyl donors (1-13) for stereo- and region-selective glycosylation to core trisaccharide **15**. However, the synthesis of assymetrically sialylated glycans by enzyme is complicated by their specificity. For this reason, we demonstrated the utility of glycosyl fluoride to prepare assymetric complex type glycans. Intitially, we started with pthallamide protections at C2-amine of all glucosamine residues of both antennae and core trisaccharides (**14**), however, in presence of preinstalled sialic acid, the process of global deprotection was found to be complicated. To overcome this difficulty, the pthallamide protections at C2-amine of all glucosamine residues were replaced with trichloroethyl carbonate (troc).

Synthesis of glycan G18.

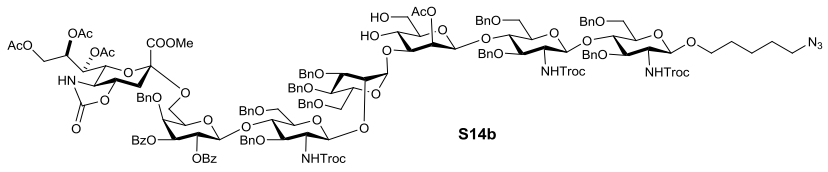
Glycosylation of sialylated antenne **9** with core **15** at 3-O site provided desired heptasaccharide **S14a** in 63% yield. Benzylidene was removed in the presence of *p*-TSA to get 4,6-diol **S14b**, which was further alpha glycosylated at 6-O position with 8 to afford desired S14c as mixture of α and β forms (7/3 isolated yield). The major α isomer was isolated by column chromatography and finally deprotected to get G18 as a white solid.



Scheme S14 | Preparation of G18. i, **9**, AgOTf, Cp_2HfCl_2, toluene, -20 ^oC to O ^oC, 63%; ii, *p*TSA, acetonitrile, 59%; iii, **8**, AgOTf, Cp_2HfCl_2, toluene, -40 ^oC to -20 ^oC, 58%; iv, (1) LiOH, 1, 4-dioxane: H_2O, 90 ^oC, (2) Ac_2O, pyridine, (3) NaOMe, MeOH, (4) Pd $(OH)_2$, MeOH: H_2O, H_2, 25%.

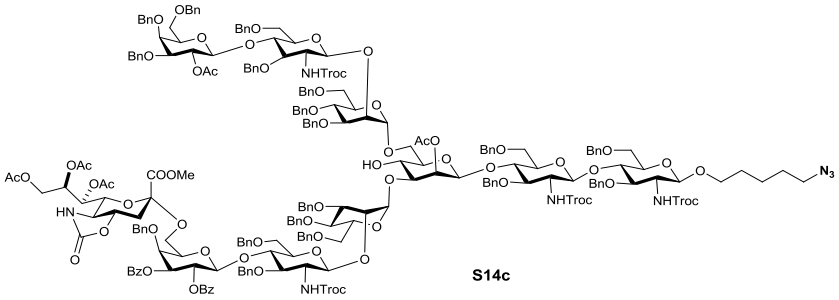


Compound S14a: A mixture of silver triflate (0.087 g, 0.34 mmol), bis (cyclopentadienyl) hafnium dichloride (0.090 g, 0.23 mmol) and 4 Å activated molecular sieves in dry toluene (10 mL) was stirred at rt for 1 h. The reaction mixture was then cooled to -20 ℃, a solution of donor **9** (0.153 g, 0.082 mmol) and acceptor chitobiose trisaccharide **15** (0.100 g, 0.068 mmol) in 5 mL toluene was added. The mixture was stirred for 2 h at 0 ^{o}C, quenched with Et_3N, diluted with EtOAc and filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL), and a brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 10% acetone in toluene) to afford **S14a** (0.140 g, 63%) as white foam. TLC: (acetone: toluene = 1.5/8.5, v/v): R_f = 0.52; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.89 (d, *J* = 7.8 Hz, 4H), 7.49-7.46 (m, 2H), 7.37-7.06 (m, 59H), 5.77 (t, *J* = 10.8 Hz, 1H), 5.35-5.37 (m, 2H), 5.26 (s, 1H), 5.18 (dd, *J* = 3.8 & 7.7 Hz, 1H), 5.08 (d, *J* = 3.2 Hz, 1H), 5.07 (dd, *J* = 3.2 & 8.4 Hz, 1H), 4.97 (d, *J* = 8.4 Hz, 1H), 4.91 (d, *J* = 9.1 Hz, 1H), 4.86 (d, *J* = 8.7 Hz, 3H), 4.73-4.13 (m, 32H), 4.02-3.30 (m, 30H), 3.20 (t, *J* = 10.8 Hz, 2H), 3.10 (d, *J* = 8.7 Hz, 1H), 2.98 (t, *J* = 9.2 Hz, 1H), 2.87-2.85 (m, 1H), 2.80 (dd, *J* = 3.2 & 7.8 Hz, 1H), 2.10 (s, 6H), 2.08 (t, *J* = 9.3 Hz, 1H), 2.00 (s, 6H), 1.40-1.17 (m, 4H), 0.87-0.82 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.9, 170.8, 170.2, 170.0, 167.9, 166.1, 165.5, 159.5, 154.5, 154.3, 154.1, 138.2, 130.1, 129.8, 129.6, 129.4, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.6, 127.0, 100.8, 100.5, 98.0, 95.8, 76.8, 76.7, 75.5, 74.8, 74.6, 74.4, 74.3, 74.1, 73.8, 73.7, 73.4, 73.2, 69.9, 69.7, 69.5, 68.7, 67.5, 66.7, 61.9, 58.9, 57.6, 53.4, 37.4, 29.9, 29.2, 28.8, 23.4, 21.3, 21.2, 21.0, 20.9, 14.3; ESI-MS: *m/z* calcd for $C_{160}H_{172}Cl_9N_7O_{48}$; 3278.8343 found 3278.8127.



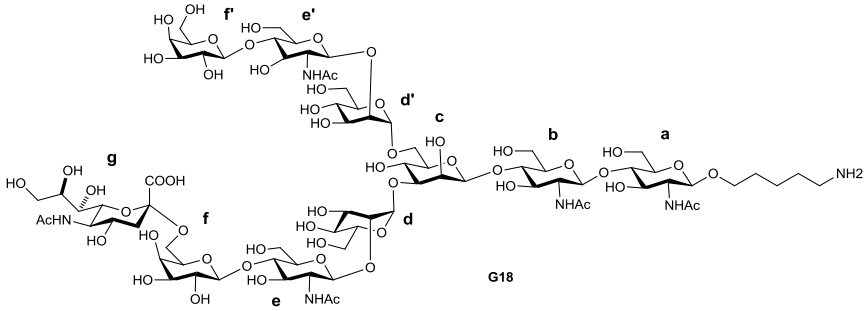
S14b

Compound S14b: *p*-Toluene sulfonic acid monohydrate (0.004 g, 0.022 mmol) was added to a solution of **S14a** (0.150 g, 0.045 mmol) in acetonitrile (5 mL) and the resulting reaction mixture was stirred at room temperature for 5h. The reaction was quenched by adding Et_3N and concentrated in *vacuo.* The residue was purified by flash column chromatography (0% → 15% EA in toluene) to give diol **S14b** (0.085 g, 58%). TLC: (acetone: toluene = 2/8, v/v): R_f = 0.32; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.89-7.86 (m, 4H), 7.49-7.37 (m, 2H), 7.30-7.09 (m, 54H), 5.78 (t, *J* = 10.2 Hz, 1H), 5.51 (d, *J* = 7.8 Hz, 1H), 5.37 (dt, *J* = 2.4 & 7.2 Hz, 1H), 5.26 (s, 1H), 5.19 (dd, *J* = 2.4 & 10.8 Hz, 1H), 5.12 (d, *J* = 3.6 Hz, 1H), 4.95-4.85 (m, 5H), 4.75-4.12 (m, 25H), 4.08-4.03 (m, 3H), 3.96-3.89 (m, 7H), 3.74-3.67 (m, 8H), 3.63-3.30 (m, 20H), 3.20 (t, *J* = 10.2 Hz, 2H), 3.10 (d, *J* = 8.9 Hz, 2H), 2,89 (s, 1H), 2.76 (dd, *J* = 3.6 & 7.9 Hz, 1H), 2.08 (s, 3H), 2.05 (s, 3H), 1.99 (s, 3H), 1.95 (s, 3H), 1.41-1.31 (m, 4H), 1.27-1.17 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 172.4, 172.3, 171.3, 171.2, 170.7, 170.3, 170.0, 168.4, 168.3, 166.1, 165.5, 154.5, 154.3, 154.1, 153.9, 138.5, 138.4, 138.1, 138.0, 133.7, 133.3, 130.1, 129.8, 129.7, 129.5, 129.3, 128.9, 128.8, 128.7, 128.6, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 101.1, 100.8, 100.6, 100.4, 99.7, 99.2, 96.0, 95.8, 76.3, 76.1, 75.7, 75.5, 74.9, 74.8, 74.5, 74.3, 74.0, 73.7, 73.4, 73.3, 73.2, 73.1, 73.0, 72.6, 72.3, 72.1, 71.3, 71.0, 69.9, 69.6, 69.4, 69.3, 68.4, 67.8, 66.1, 66.2, 62.8, 62.2, 59.2, 57.7, 53.4, 51.5, 36.9, 29.9, 29.2, 28.8, 25.0, 23.4, 21.4, 21.3, 21.2, 21.1, 15.5, 14.4; ESI-MS (negative mode): *m/z* calcd for $C_{153}H_{168}Cl_9N_7O_{48}$; 3191.8105 found 3236.8033 (*M* + 2Na).



S14c

Compound S14c: A mixture of silver triflate (0.067 g, 0.27 mmol), bis (cyclopentadienyl) hafnium dichloride (0.071 g, 0.18 mmol) and 4 Å activated molecular sieves in dry toluene (10 mL) was stirred at rt for 1 h. The reaction mixture was then cooled to -40 ℃, a solution of donor **8** (0.097 g, 0.068 mmol) and acceptor **S14b** (0.175 g, 0.054 mmol) in 5 mL toluene was added. The mixture was stirred for 2 h at -20 ^{o}C, quenched with Et_3N, diluted with EtOAc and filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL), and a brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 10% acetone in toluene) to separate mixture of α and β isomers to afford **S14c** (0.149 g, 58%) as white foam. TLC: (acetone: toluene = 1.5/8.5, v/v): R_f = 0.52; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.2 Hz, 2H), 7.83 (d, *J* = 7.8 Hz, 2H), 7.51-7.41 (m, 4H), 7.34-7.06 (m, 92H), 5.83 (t, *J* = 10.2 Hz, 1H), 5.48-5.03 (m, 3H), 5.00-4.75 (m, 13H), 4.60-4.08 (m, 41H), 3.99-3.07 (m, 53H), 2.96 (t, *J* = 10.2 Hz, 2H), 2.80 (dd, *J* = 3.8 & 7.9 Hz, 1H), 2.15 (s, 3H), 2.10 (s, 3H), 2.07 (s, 3H), 2.00 (s, 3H), 1.93 (s, 3H), 1.40-1.17 (m, 5H), 0.91-0.81 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.9, 170.6, 170.4, 169.9, 169.4, 166.5, 159.5, 154.7, 154.4, 139.8, 138.8, 138.7, 138.6, 138.4, 138.2, 133.7, 130.9, 130.7, 129.7, 129.6, 129.4, 129.2, 129.0, 128.7, 128.6, 128.6, 128.4, 128.3, 128.2, 127.9, 127.6, 127.3, 100.4, 100.2, 99.8, 99.4, 74.9, 74.7, 74.5, 73.3, 73.2, 66.1, 60.6, 51.5, 32.1, 29.8, 29.7, 29.6, 29.3, 28.7, 23.7, 22.8, 22.4, 22.0, 21.6, 21.4, 21.2, 20.9, 15.4, 14.3, 14.2, 14.0, 11.3, 10.2; ESI-MS: *m/z* calcd for $C_{232}H_{250}Cl_{12}N_8O_{65}$; 4607.2765 found 2330.6261 $(M + Na)^{2+}$.



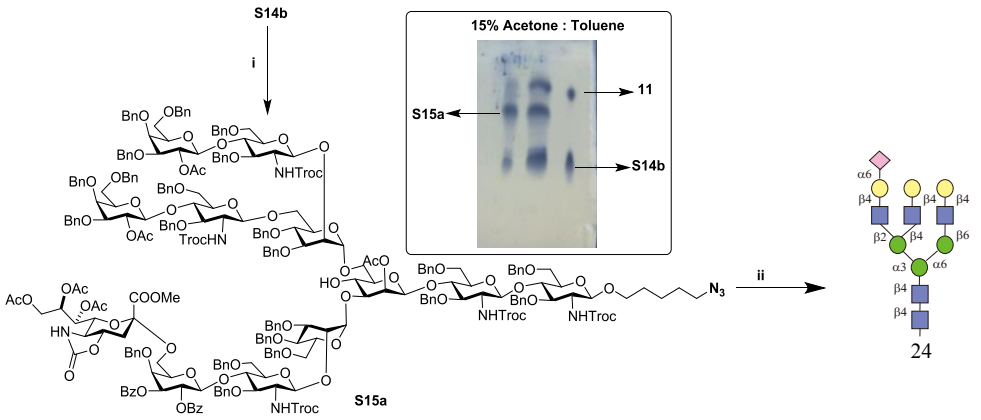
5-Aminopentyl-[5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyrano-sylonate-(2→6)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-

mannopyranosyl]-(1→3),-[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-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside

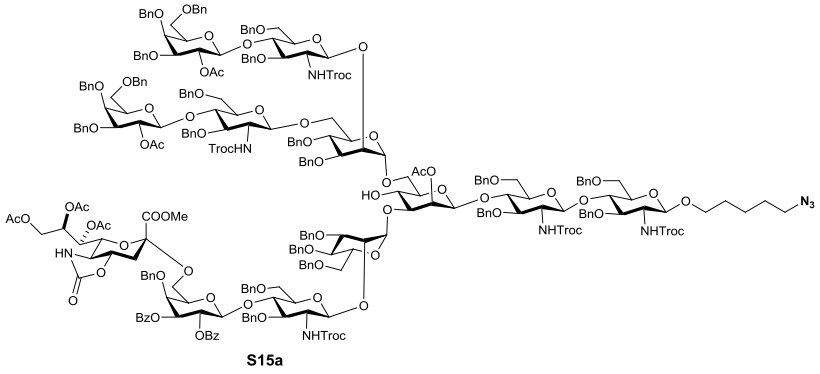
G18: Compound **S14c** (0.135 g, 0.029 mmol) was deprotected by following general procedure 2 (method 2) to afford the desired glycan **G18** (0.015 g, 25%). ^{1}H NMR (600 MHz, D_2O): δ 5.11 (s, 1H, H-1^{d}), 4.89 (s, 1H, H-1$^{d'}$), 4.73 (s, 1H, H-1^{c}), 4.57 (dt, *J* = 10.2 Hz, 2H, H-1$^{f,f'}$), 4.47 (d, *J* = 7.8 Hz, 2H, H-1^{a,b}), 4.47 (d, *J* = 8.4 Hz, 2H, H-1$^{e,e'}$), 4.23 (s, 1H), 4.17 (s, 1H), 4.09 (d, *J* = 1.3 Hz, 1H), 4.03-3.48 (m, 59H), 2.98 (t, *J* = 10.2 Hz, 2H, -CH_2- linker), 2.65 (dd, *J* = 4.8 & 12.6 Hz, 1H, H-3$^{equi.\ g}$), 2.10 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H), 2.02 (s, 6H), 1.72-1.64 (m, 3H, H-3$^{axial\ g}$, linker -CH_2-), 1.63-1.54 (m, 2H), 1.39-1.35 (m, 2H); ^{13}C NMR (150 MHz, D_2O): δ 177.7, 177.5, 177.4, 177.1, 176.2, 176.1, 106.2, 106.1, 104.1, 103.7, 103.5, 103.1, 102.9, 102.9, 99.5, 83.6, 83.1, 82.2, 82.1, 81.7, 79.4, 79.1, 78.9, 77.3, 77.2, 76.8, 76.4, 75.3, 75.1, 74.8, 74.5, 73.5, 73.4, 72.8, 71.2, 70.9, 70.0, 67.6, 66.0, 65.6, 65.4, 64.5, 62.8, 57.7, 57.3, 55.0, 54.6, 54.0, 42.8, 42.3, 42.0, 41.78, 30.7, 30.5; ESI-MS (negative mode): *m/z* calcd for $C_{78}H_{132}N_6O_{54}$ 2016.7767; found 1007.3799 $(M - H)^{2-}$.

Synthesis of glycan G24.

Compound **S14b** acts as common acceptor for both **G18** and **G24**. Glycosylation of **S14b** at 6-O site provided the desired **S15a** with 10% acceptor recovery. At last, global deprotection yielded the desired glycan **G24**.

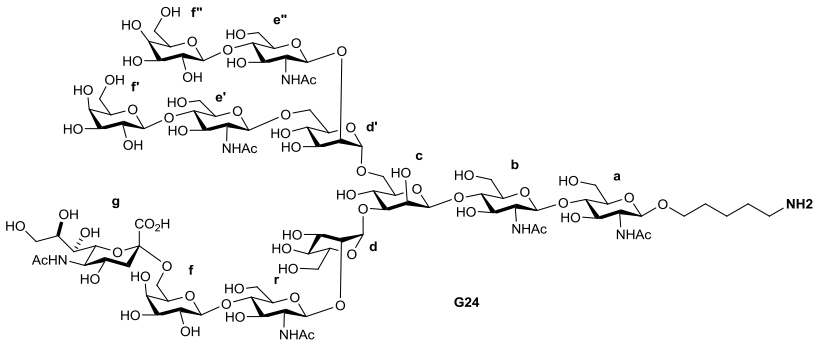


Scheme S15 | Preparation of G24. i, **11**, AgOTf, Cp_2HfCl_2, toluene, -40 ^oC, 63%; ii, (1) LiOH, 1, 4-dioxane, 90 ^oC, (2) Ac_2O, pyridine, (3) NaOMe, MeOH, (4) $Pd(OH)_2$, MeOH: H_2O, H_2, 42%.



Compound S15a: A mixture of silver triflate (0.058 g, 0.23 mmol), bis (cyclopentadienyl) hafnium dichloride (0.061 g, 0.23 mmol) and 4 Å activated molecular sieves in dry toluene (10 mL) was stirred at rt for 1 h. The reaction mixture was then cooled to -40 °C, a solution of donor **11** (0.135 g, 0.056 mmol) and acceptor **S14b** (0.150 g, 0.046 mmol) in 5 mL toluene was added. The mixture was stirred for 2 h at -20 ^oC, quenched with Et_3N, diluted with EtOAc and filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL), and a brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 10% acetone in toluene) to afford **S15a** (0.165 g, 63%) as white foam. TLC: (acetone: toluene = 1.5/8.5, v/v): R_f = 0.58; ^1H NMR (600 MHz,

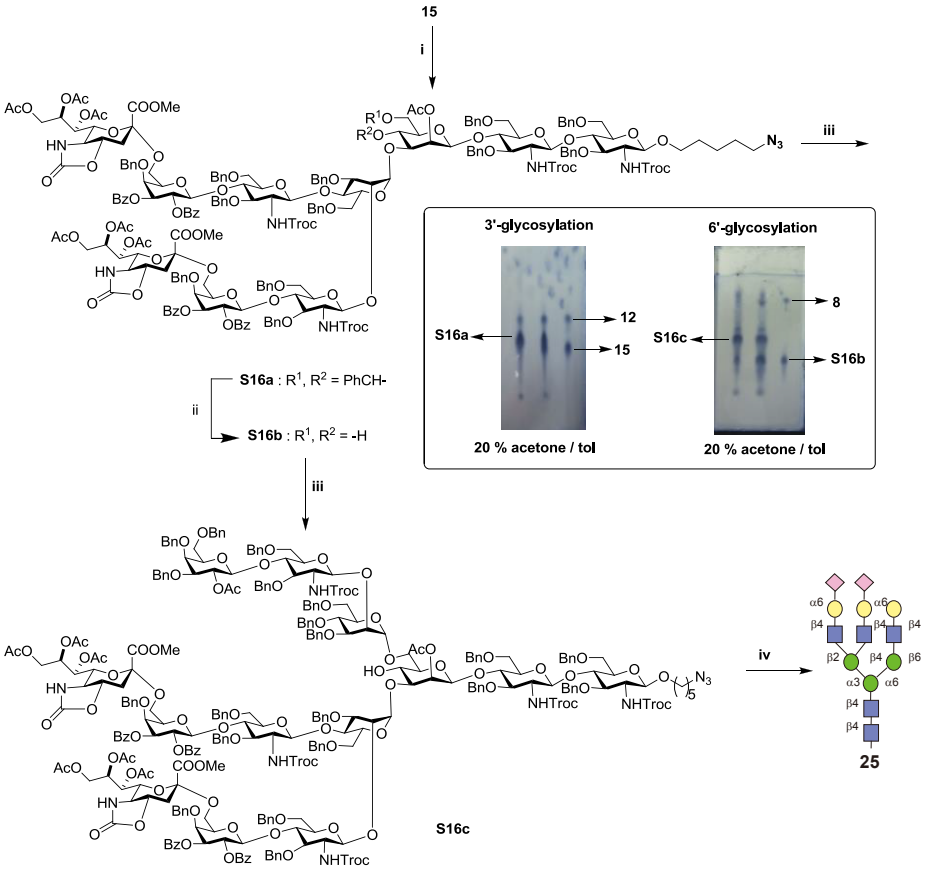
$CDCl_3$): δ 8.00-7.80 (m, 4H), 7.50-6.80 (m, 116H), 5.80 (t, *J* = 10.2 Hz, 1H), 5.40-5.30 (m, 7H), 5.10-4.08 (m, 65H), 4.00-3.05 (m, 65H), 2.98 (dd, *J* = 3.2 & 8.5 Hz, 1H), 2.15 (s, 6H), 2.10 (s, 6H), 2.00 (s, 6H), 1.37-1.17 (m, 5H), 0.87-0.84 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.8, 167.9 154.1, 139.1, 139.0, 138.9, 138.8, 138.6, 138.3, 138.1, 138.0, 129.8, 129.6, 129.3, 128.9, 128.8, 128.7, 128.7, 128.6, 128.5, 128.4, 128.2, 128.0, 127.7, 127.4, 127.3, 127.2, 127.1, 127.0, 100.8, 100.0, 74.9, 74.8, 74.5, 74.4, 73.6, 73.3, 72.6, 53.5, 29.9, 29.2, 23.4, 21.3, 21.2, 21.0, 20.9, 15.5, 14.4; ESI-MS (negative mode): *m/z* calcd for $C_{277}H_{298}Cl_{15}N_9O_{77}$; 5517.1670 found 2803.7442 $(M + 2Na)^{2+}$.



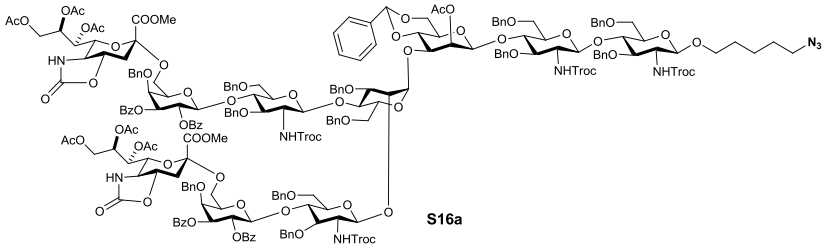
5-Aminopentyl-[5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyrano-sylonate-(2→6)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranosyl]-(1→3),-[β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2), (1→6)-α-D-mannopyranosyl]-(1→6)-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside G24: Compound **S15a** (0.090 g, 0.016 mmol) was deprotected by following general procedure 2 (method 2) to afford desired glycan **G24** (0.016 g, 42%) as a white solid. ^{1}H NMR (600 MHz, D_2O): δ 5.14 (s, 1H, H-1^{d}), 4.88 (s, 1H, H-$1^{d'}$), 4.60 (t, *J* = 10.2 Hz, 3H, H-$1^{e,f,e'}$), 4.55 (d, *J* = 8.4 Hz, 1H), 4.48 (dd, *J* = 3.2 & 8.6 Hz, 4H), 4.45 (d, *J* = 7.8 Hz, 1H), 4.26 (s, 1H), 4.20 (s, 1H), 4.09 (s, 1H), 4.01-3.50 (m, 71H), 2.97 (t, *J* = 10.2 Hz, 2H, linker -CH_2-), 2.68 (dd, *J* = 3.8 & 8.3 Hz, 1H, H-$3^{equi.\ g}$), 2.08 (s, 3H, -C(O)CH_3), 2.07 (s, 3H, -C(O)CH_3), 2.04 (s,

3H, -C(O)CH_3), 2.03 (s, 6H, -C(O)CH_3), 1.72 (t, J = 10.2 Hz, 1H, H-3$^{axial\ g}$), 1.67-1.65 (m, 2H), 1.60-1.56 (m, 2H, linker -CH_2-), 1.40-1.39 (m, 2H, linker -CH_2-); ^{13}C NMR (150 MHz, D_2O): δ 174.9, 174.7, 174.6, 174.5, 174.4, 174.1, 173.5, 103.6, 103.5, 102.9, 102.8, 101.5, 101.4, 101.0, 100.3, 100.1, 99.5, 99.3, 80.7, 80.4, 79.5, 79.3, 79.2, 78.5, 76.5, 75.4, 75.2, 74.7, 74.5, 74.4, 74.3, 73.7, 73.4, 72.5, 72.4, 72.3, 72.1, 71.9, 71.6, 71.3, 70.9, 70.8, 70.5, 70.3, 69.5, 69.4, 68.5, 68.3, 68.2, 67.5, 67.3, 65.4, 63.3, 62.5, 61.7, 61.0, 60.2, 60.1, 59.8, 55.08, 54.9, 54.8, 54.6, 51.0, 40.9, 39.4, 28.0, 26.7, 22.5, 22.4, 22.3, 22.2, 22.1, 22.0, 21.09 ; ESI-MS (negative mode): *m/z* calcd for $C_{92}H_{155}N_7O_{64}$; 2383.2370 found 1213.4483 $(M + Na)^{2-}$.

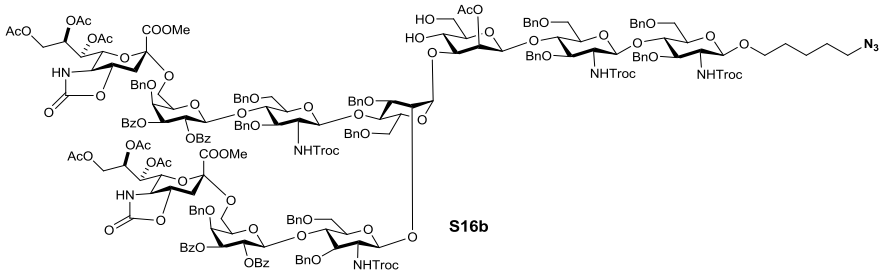
Synthesis of glycan G25.



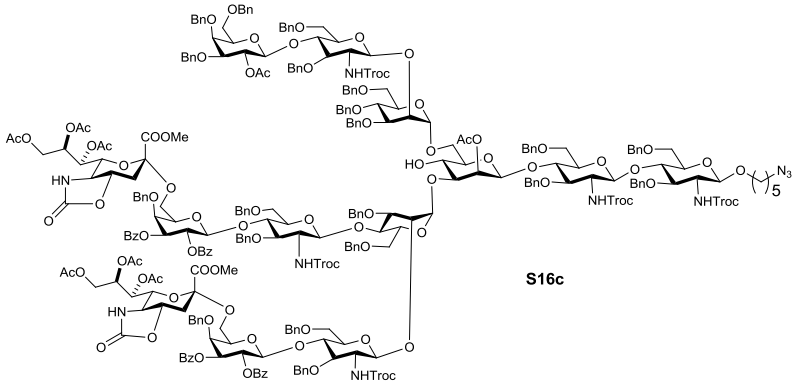
Scheme S16 | Preparation of G25. i, **12**, AgOTf, Cp_2HfCl_2, toluene, -40 ^oC, 64%; ii, *p*TSA, acetonitrile, 56%; iii, **8**, AgOTf, Cp_2HfCl_2, toluene, -78 ^oC, 49%; iv, (1) LiOH, 1,4-dioxane, 90 ^oC, (2) Ac_2O, pyridine, (3) NaOMe, MeOH, (4) $Pd(OH)_2$, MeOH: H_2O, H_2, 38%.



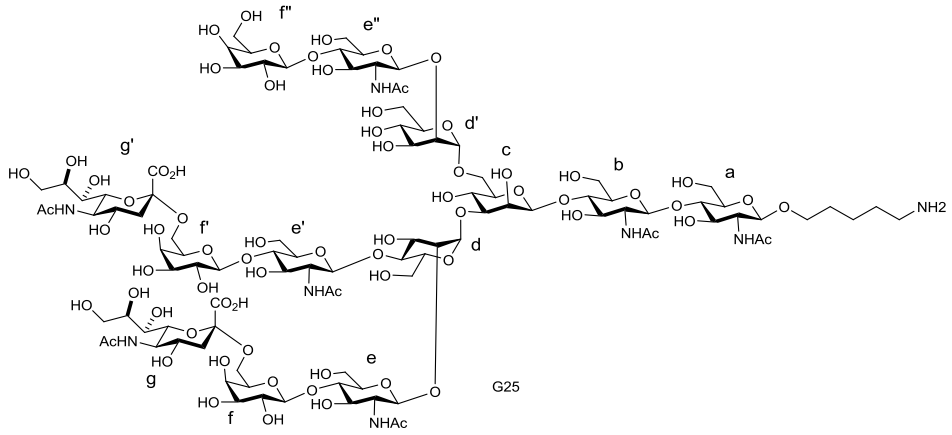
Compound 16a: A mixture of silver triflate (0.087 g, 0.34 mmol), bis (cyclopentadienyl) hafnium dichloride (0.090 g, 0.23 mmol) and 4 Å activated molecular sieves in dry toluene (10 mL) was stirred at rt for 1 h. The reaction mixture was then cooled to -40 ℃, a solution of donor **12** (0.259 g, 0.082 mmol) and acceptor **15** (0.100 g, 0.068 mmol) in 5 mL toluene was added. The mixture was stirred for 3 h at -10 ^{o}C, quenched with Et_3N, diluted with EtOAc and filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL), and a brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 20% acetone in toluene) to afford **S16a** (0.201 g, 64%) as white foam. TLC: (acetone: toluene = 2.5/7.5, v/v): R_f = 0.50; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.92-7.83 (m, 9H), 7.69-7.67 (m, 2H), 7.52-7.44 (m, 6H), 7.37-6.96 (m, 68H), 5.34-5.32 (m, 2H), 5.26-5.24 (m, 4H), 5.20-5.10 (m, 3H), 5.08 (d, *J* = 9.8 Hz, 3H), 4.59-4.40 (m, 16H), 4.75-4.50 (m, 28H), 4.49-4.00 (m, 20H), 3.98-3.60 (m, 16H), 3.48-3.06 (m, 16H), 2.98 (t, *J* = 10.7 Hz, 2H), 2.76 (dd, *J* = 3.8 & 7.8 Hz, 2H), 2.08 (s, 3H), 2.07 (s, 3H), 2.06 (s, 6H), 1.99 (s, 9H), 1.37-1.17 (m, 6H), 0.89-0.84 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.8, 171.7, 171.6, 169.8, 169.4, 168.0, 167.6, 166.6, 166.4, 166.2, 165.4, 165.3, 159.7, 159.4, 154.3, 154.2, 139.8, 139.7, 139.6, 139.4, 139.2, 138.7, 138.6, 138.5, 138.4, 138.3, 138.2, 133.9, 132.7, 131.9, 131.2, 130.6, 129.8, 129.6, 129.4, 129.3, 129.2, 129.0, 128.8, 128.7, 128.6, 128.6, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 127.2, 127.0, 102.7, 102.4, 101.9, 101.8, 100.8, 100.7, 100.4, 100.2, 100.0, 99.2, 99.4, 98.4, 96.5, 95.9, 74.3, 74.1, 74.0, 73.8, 73.7, 73.5, 73.4, 73.2, 73.1, 72.7, 72.5, 72.1, 71.3, 70.9, 70.4, 69.5, 69.4, 68.5, 68.4, 68.3, 68.1, 67.9, 67.4, 53.4, 51.6, 37.5, 33.9, 32.2, 31.8, 29.9, 28.8, 26.5, 23.4, 22.9, 21.2, 21.0, 20.0, 14.6, 14.3; ESI-MS: *m/z* calcd for $C_{220}H_{235}Cl_{12}N_9O_{72}$; 4582.6910 found 915.6684 $(M + H)^{5+}$.



Compound 16b: *p*-Toluene sulfonic acid monohydrate (0.002 g, 0.008 mmol) was added to a solution of **S14a** (0.200 g, 0.043 mmol) in acetonitrile (10 mL) and resulting reaction mixture was stirred at rt for overnight. Reaction was quenched by adding Et_3N and concentrated in *vacuo.* The residue was purified by flash column chromatography (0% → 20% acetone in toluene) to give diol **S16b** (0.110 g, 56%). TLC: (acetone: toluene = 2.5/7.5, v/v): R_f = 0.32; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.90-7.80 (m, 8H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.69-7.46 (m, 5H), 7.41-7.04 (m, 65H), 5.78 (t, *J* = 10.1 Hz, 1H), 5.73 (t, *J* = 10.7 Hz, 1H), 5.35-5.25 (m, 7H), 5.20 (dd, *J* = 3.2 & 7.9 Hz, 1H), 5.15 (dd, *J* = 3.8 & 8.4 Hz, 1H), 5.08 (t, *J* = 10.8 Hz, 2H), 4.90-4.80 (m, 5H), 4.79-4.50 (m, 15H), 4.48-4.30 (m, 18H), 4.20-4.10 (m, 25H), 3.92-3.20 (m, 35H), 3.2 (t, *J* = 8.8 Hz, 2H), 3.18-3.05 (m, 3H), 3.0-2.95 (m, 3H), 2.81-2.70 (m, 3H), 2.08 (s, 6H), 2.07 (s, 6H), 2.03 (s, 6H), 1.92 (s, 6H), 1.32-1.17 (m, 6H), 0.89-0.83 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.8, 170.7, 168.0, 166.1, 159.6, 138.1, 133.7, 132.7, 131.1, 130.1, 129.9, 129.7, 129.4, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2, 127.8, 127.7, 127.6, 74.9, 74.7, 74.6, 73.9, 68.8, 66.1, 53.4, 51.6, 37.3, 32.4, 31.4, 29.9, 29.8, 29.7, 28.7, 28.4, 23.4, 22.3, 20.9, 20.7, 20.4, 15.5, 14.6, 14.2 ; ESI-MS: *m/z* calcd for $C_{213}H_{231}Cl_{12}N_9O_{72}$; 4494.5820 found 681.2953 $(M + K)^{7+}$.



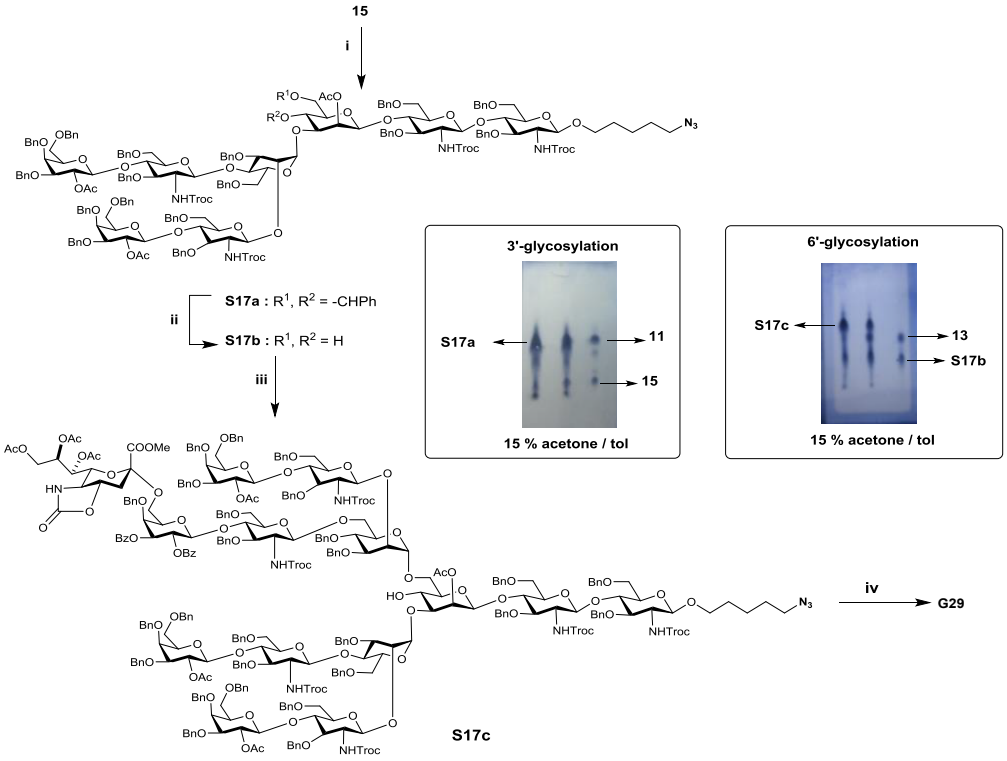
Compound 16c: A mixture of silver triflate (0.068 g, 0.34 mmol), bis (cyclopentadienyl) hafnium dichloride (0.065 g, 0.17 mmol) and 4 Å activated molecular sieves in dry toluene (10 mL) was stirred at rt for 1 h. The reaction mixture was then cooled to -78 °C, a solution of donor **8** (0.109 g, 0.076 mmol) and acceptor **16b** (0.230 g, 0.051 mmol) in 5 mL toluene was added. The mixture was stirred for 3 h at -20 ^{o}C, quenched with Et_3N, diluted with EtOAc and filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL), and a brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 20% acetone in toluene) to afford **S16c** (0.148 g, 49%) as white foam. TLC: (acetone: toluene = 2.5/7.5, v/v): R_f = 0.50; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.90 (m, 10H), 7.52-6.80 (m, 110H), 5.79 (t, *J* = 10.2 Hz, 2H), 5.48 (dd, *J* = 4.2 & 8.7 Hz, 2H), 5.34-5.14 (m, 10H), 4.98-3.10 (m, 123H), 2.85 (t, *J* = 10.2 Hz, 2H), 2.30 (dd, *J* = 3.4 & 8.2 Hz, 2H), 2.01 (s, 3H), 2.00 (s, 6H), 1.95 (s, 6H), 1.94 (s, 6H), 1.91 (s, 3H), 1.39-1.29 (m, 6H), 1.26-1.91 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 172.1, 170.8, 170.3, 170.1, 170.0, 169.3, 169.2, 168.0, 167.3, 166.5, 165.8, 165.1, 165.0, 154.0, 153.8, 153.7, 153.7, 139.0, 138.9, 138.8, 138.7, 138.6, 138.3, 138.2, 138.1, 137.9, 137.4, 133.4, 133.2, 132.0, 130.3, 129.8, 129.7, 129.4, 129.3, 129.2, 129.1, 128.9, 128.8, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 100.4, 100.2, 99.3, 75.8, 75.6, 75.4, 75.3, 75.2, 75.1, 74.8, 74.7, 74.6, 74.5, 74.4, 74.3, 74.2, 74.2, 74.1, 73.5, 73.4, 73.3, 73.2, 73.1, 73.0, 72.9, 72.6, 72.2, 71.9, 71.7, 71.6, 71.3, 71.1, 70.1, 69.9, 69.8, 68.5, 68.3, 68.2, 63.4, 58.8, 58.3, 58.0, 53.4, 51.3, 31.9, 30.3, 30.0, 29.8, 29.7, 29.5, 28.7, 28.5, 28.3, 27.1, 24.5, 24.1, 23.8, 22.7, 22.1, 21.7, 20.9, 20.7, 20.6, 14.1, 14.0, 10.9 ; ESI-MS: *m/z* calcd for $C_{292}H_{313}Cl_{15}N_{10}O_{89}$; 5918.4470 found 1486.4746 $(M + 6H)^{4+}$.



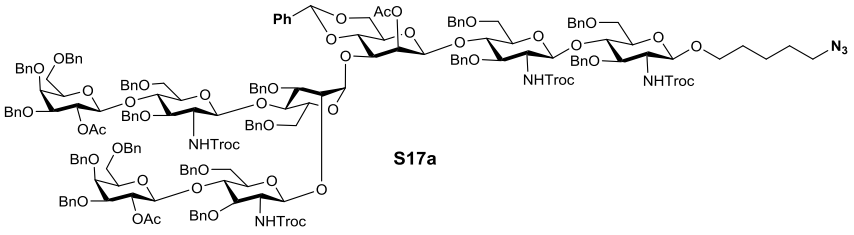
5-Aminopentyl-di-[5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyrano-sylonate-(2→6)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2),(1→4)-α-D-mannopyranosyl]-(1→3),-[β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranosyl]-(1→6)-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside G25: Compound **S16c** (0.115 g, 0.019 mmol) was deprotected by following general procedure 2 (method 2) to afford the desired glycan **G25** (0.020 g, 38%).^{1}H NMR (600 MHz, D_2O): δ 5.15 (d, 1H, H-1^{d}), 4.94 (s, 1H, H-1$^{d'}$), 4.63 (d, *J* = 8.4 Hz, 2H, H-1^{a,b}), 4.58 (d, *J* = 7.8 Hz, 2H, H-1$^{e,e'}$), 4.52 (d, *J* = 7.8 Hz, 2H, H-1$^{e'',f'}$), 4.50 (s, 1H, H-1^{c}), 4.42 (dd, *J* = 3.2 & 10.2 Hz, 2H, H-1$^{f,f''}$), 4.23 (s, 2H), 4.08 (s, 1H), 3.92 (dd, *J* = 3.2 & 7.8 Hz, 2H), 3.90-3.45 (m, 75H), 3.01 (t, *J* = 10.2 Hz, 2H, linker CH_2), 2.69 (dd, *J* = 3.6 & 12.1 Hz, 2H, H-3$_{equi.}^{g,g'}$), 2.12 (s, 3H), 2.10 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H), 2.05 (s, 9H), 1.77-1.66 (m, 4H, H-3$_{axial.}^{g,g'}$ and linker CH_2), 1.62-1.60 (m, 2H), 1.42-1.40 (m, 2H) ; ^{13}C NMR (150 MHz, D_2O): δ 177.6, 177.4, 177.3, 177.1, 176.1, 106.3, 105.6, 104.2, 104.1, 103.7, 103.1, 102.8, 102.1, 101.8, 99.8, 78.7, 78.0, 77.4, 77.2, 77.1 76.4, 75.5, 75.2, 75.1, 75.0, 74.8, 74.4, 74.0, 73.7, 73.4, 73.0, 72.8, 72.1, 71.5, 70.9, 70.8, 70.0, 68.4, 66.0, 65.4, 64.3, 64.0, 63.7, 63.1, 63.8, 62.6, 57.7, 57.6, 57.5, 57.3, 54.6, 42.7, 42.0, 30.7, 29.0, 25.3, 25.0, 24.9, 24.8, 24.7; ESI-MS (negative mode): *m/z* calcd for $C_{103}H_{172}N_8O_{72}$; 2674.4930 found 1335.9948 $(M - 2H)^{2-}$.

Synthesis of glycan G29.

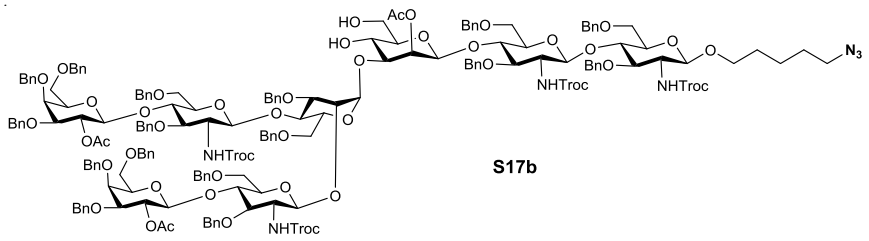
Glycan **G29** is mono sialylated tetraantennary complex type structure. The synthesis began with construction of D1 arm by glycosylation of donot **11** at 3-O position of **15** to afford compound **S17a.** The reaction was progress was checked by TLC as shown in Scheme S17. Removal benzyledene followed by 6-O glycosylation afforded desired tetra-decasaccharide **S17c**. Finally global deprotection provided desired glycan **G29**.



Scheme S17 | Preparation of G29. i, **11**, AgOTf, Cp_2HfCl_2, toluene, -40 ^oC, 77%; ii, *p*TSA, acetonitrile, 73%; iii, **13**, AgOTf, Cp_2HfCl_2, toluene, -40 ^oC, 57%; iv, (1) LiOH, 1,4-dioxane, 90 ^oC, (2) Ac_2O, pyridine, (3) NaOMe, MeOH, (4) $Pd(OH)_2$, MeOH:H_2O, H_2, 34%.



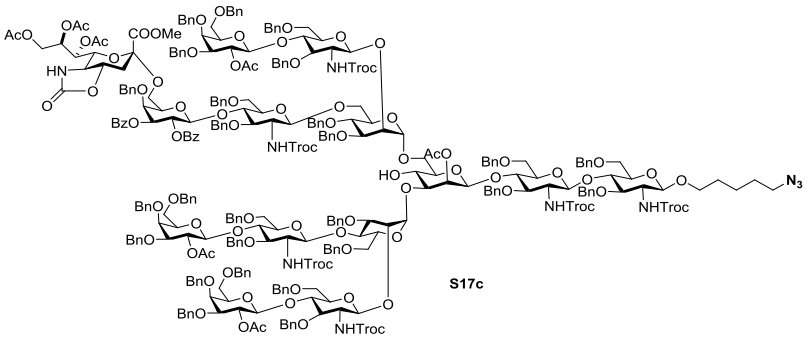
Compoind S17a: A mixture of silver triflate (0.173 g, 0.675 mmol), bis (cyclopentadienyl) hafnium dichloride (0.177 g, 0.469 mmol) and 4 Å activated molecular sieves in dry toluene (10 mL) was stirred at room temperature for 1 h. The reaction mixture was then cooled to -40 ℃, a solution of donor **11** (0.345 g, 0.470 mmol) and acceptor **15** (0.195 g, 0.134 mmol) in 5 mL toluene was added. The mixture was stirred for 2 h at -10 ^{o}C, quenched with Et_3N, diluted with EtOAc and filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL), and a brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 10% acetone in toluene) to afford **S17a** (0.380 g, 77%) as white foam. TLC: (acetone: toluene = 1/9, v/v): R_f = 0.60; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30-7.12 (m, 60H), 7.08-6.72 (m, 25H), 5.39 (t, *J* = 10.2 Hz, 1H), 5.29 (t, *J* = 10.3 Hz, 1H$^{'}$), 5.16 (d, *J* = 4.2 Hz, 1H), 5.09 (d, *J* = 8.4 Hz, 1H), 4.91-4.72 (m, 18H, overlapped), 4.63-4.56 (m, 5H), 4.01-4.80 (m, 30H), 3.80-3.95 (m, 10H), 3.60-3.75 (m, 4H), 3.52-3.48 (m, 6H), 3.41-3.15 (m, 20H), 2.98 (d, *J* = 9.6Hz, 1H), 2.90-2.76 (m, 3H), 2.66-2.62 (m, 1H), 1.95 (s, 3H), 1.93 (s, 3H), 1.87 (s, 3H), 1.38-1.23 (m, 4H, -CCH_2C-), 1.08-1.01 (m, 2H, -CCH_2C-); ^{13}C NMR (150 MHz, $CDCl_3$): δ 172.1, 171.9, 170.5, 156.7, 156.6, 142.0, 141.8, 141.6, 141.5, 141.4, 141.3, 141.3, 141.1, 140.8, 140.6, 140.5, 139.8, 135.2, 133.6, 133.2, 131.8, 131.5, 131.3, 131.1, 130.6, 130.5, 130.2, 130.1, 129.8, 129.0, 127.3, 104.8, 104.8, 103.2, 102.9, 77.7,7 7.5,77.3, 77.2, 77.1, 76.9, 76.2, 76.1, 76.0, 75.9, 75.5, 75.4, 74.8,, 74.6, 74.5, 74.4, 74.3, 71.0, 70.8, 70.6, 54.0, 31.7, 31.3, 25.9, 23.9, 23.8, 23.7, 23.6, 17.2, 17.1, 16.8, 16.7, 13.7, 13.6; HRMS: *m/z* calcd for $C_{190}H_{205}Cl_{12}N_7O_{48}$; 3778.9981 found 3824.9969 (*M* + 2Na).



S17b

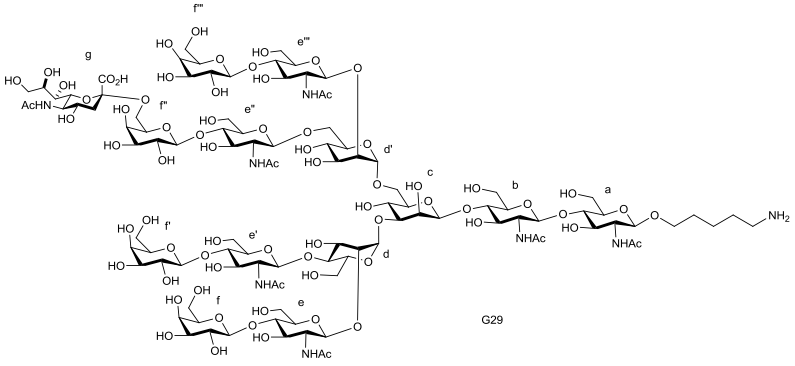
Compoind S17b: *p*-Toluene sulfonic acid monohydrate (0.004 g, 0.02 mmol) was added to a solution of **S17a** (0.377 g, 0.102 mmol) in acetonitrile (10 mL) and the resulting reaction mixture

was stirred at rt for overnight. The reaction was quenched by adding Et_3N and concentrated in *vacuo.* The residue was purified by flash column chromatography (0% → 10% acetone in toluene) to give diol **S17b** (0.270 g, 73%). TLC: (acetone: toluene = 1.5/8.5, v/v): R_f = 0.32; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34-7.11 (m, 80H), 5.37 (s, 1H), 5.29 (t, *J* = 10.2 Hz, 1H), 5.22 (t, *J* = 9.8 Hz, 1H), 5.02 (d, *J* = 3.6 Hz, 2H), 4.92-4.74 (m, 7H), 4.70-4.21 (m, 34H), 3.93-3.51 (m, 17H), 3.65-3.20 (m, 34H), 3.20 (t, *J* = 10.2 Hz, 4H), 2.98 (d, *J* = 3.8 Hz, 2H), 2.89 (s, 1H), 2.11 (s, 3H), 1.94 (s, 3H), 1.90 (s, 3H), 1.40-1.17 (m, 4H), 091-0.84 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.1, 170.0, 169.6, 168.0, 154.3, 154.1, 139.6, 139.1, 139.0, 138.9, 138.7, 138.5, 138.3, 138.1, 138.0, 132.7, 131.1, 129.6, 129.4, 129.3, 129.0, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.6, 127.5, 127.3, 127.1, 127.0, 100.9, 100.6, 100.5, 98.6, 95.9, 95.8, 76.75, 76.3, 75.6, 74.8, 74.6, 74.5, 74.3, 74.2, 73.8, 73.7, 73.5, 73.2, 72.8, 72.5, 72.1, 69.6, 68.8, 68.5, 68.4, 68.2, 68.1, 62.8, 62.1, 57.6, 39.0, 37.3, 33.7, 32.5, 31.4, 30.6, 29.9, 29.2, 28.8, 26.6, 24.0, 23.4, 23.2, 22.9, 21.5, 21.3, 20.1, 15.5, 14.6, 14.4, 14.3, 11.2; HRMS: *m/z* calcd for $C_{183}H_{201}Cl_{12}N_7O_{48}$; 3692.0222 found 3737.9645 (*M* + 2Na).



Compoind S17c: A mixture of silver triflate (0.046 g, 0.180 mmol), bis (cyclopentadienyl) hafnium dichloride (0.048 g, 0.126 mmol) and 4 Å activated molecular sieves in dry toluene (5 mL) was stirred at rt for 1 h. The reaction mixture was then cooled to -40 ℃, a solution of donor **13** (0.100 g, 0.36 mmol) and acceptor **S17b** (0.118 g, 0.032 mmol) in 5 mL toluene was added. The mixture was stirred for 3 h at -10 ^{o}C, quenched with Et_3N, diluted with EtOAc and filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL), and a brine (50 mL)

solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 10% actone in toluene) to afford **S17c** (0.120 g, 57%) as white foam. TLC: (acetone: toluene = 1/9, v/v): R_f = 0.60; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.58-7.54 (m, 6H), 7.50-6.98 (m, 134H), 5.57 (t, *J* = 10.3 Hz, 4H), 5.42-5.30 (m, 24H), 5.01-4.70 (m, 35H), 4.65-4.10 (m, 50H), 4.0-2.90 (m, 54H), 2.80 (d, *J* = 9.8 Hz, 2H), 2.15 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H), 1.96 (s, 3H), 1.93 (s, 3H), 1.88 (s, 3H), 1.86 (s, 3H), 1.34-1.17 (m, 5H), 0.89-0.81 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 139.1, 139.0, 138.3, 138.2, 138.1, 130.1, 129.9, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.6, 127.4, 74.8, 74.6, 73.7, 73.6, 71.9 ; HRMS: *m/z* calcd for $C_{322}H_{346}Cl_{18}N_{10}O_{89}$; 6418.3910 found 3253.3555 $(M + 2Na)^{2+}$.

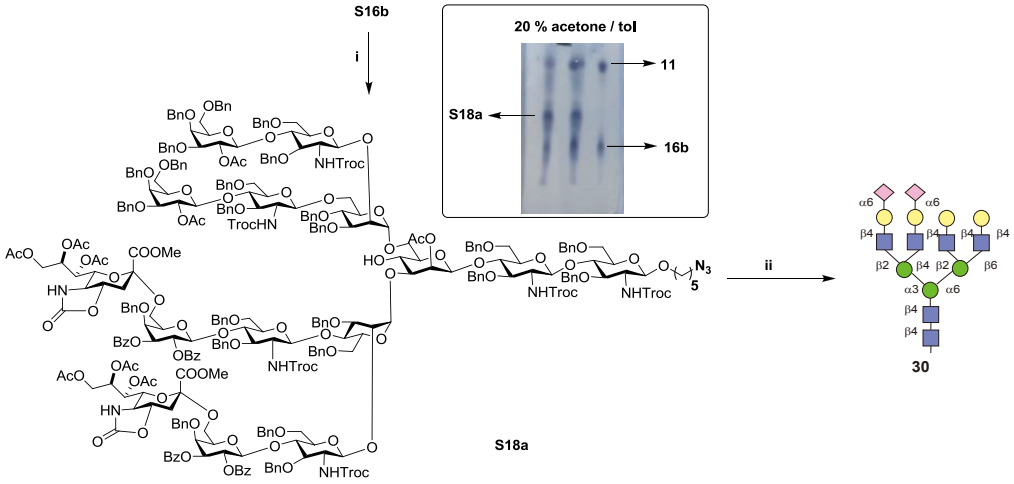


5-Aminopentyl-di-[β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2),(1→4)-α-D-mannopyranosyl]-(1→3),-[5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyrano-sylonate-(2→6)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranosyl]-(1→6)-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside G29: Compound **S17c** (0.095 g, 0.015 mmol) was deprotected by following general procedure 2 (method 2) to afford desired glycan **G29** (0.014 g, 34%) as a white powder. ^{1}H NMR (600 MHz, D_2O): δ 4.99 (s, 1H, H-1^{d}), 4.75 (s, 1H, H-1$^{d'}$), 4.72 (d, *J* = 8.4 Hz, 1H, H-1^{e}), 4.62 (d, 1H, *J* = 7.8 Hz, 1H, H-1$^{e'}$), 4.63 (s, 1H, H-1^{c}), 4.45 (dd, *J* = 3.6 & 7.8 Hz, 4H, H-1$^{e'',e''',f,f'}$), 4.36-4.31 (m,

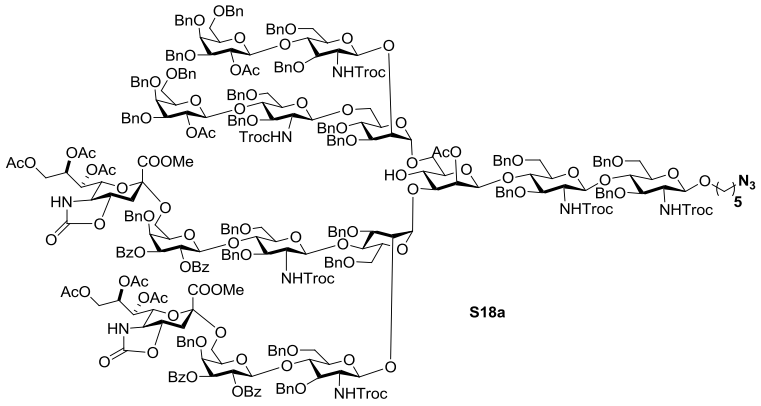
4H), 4.09 (s, 3H), 3.98-3.04 (m, 82H), 2.83 (t, J = 10.2 Hz, 2H, linker), 2.56 (dd, J = 3.2 & 8.4 Hz, 1H, H-$3^{equi.\ g'}$), 1.95 (s, 3H, -C(O)CH_3), 1.94 (s, 3H, -C(O)CH_3), 1.93 (s, 3H, -C(O)CH_3), 1.92 (s, 3H, -C(O)CH_3), 1.92 (s, 3H, -C(O)CH_3), 1.90 (s, 3H, -C(O)CH_3), 1.89 (s, 3H, -C(O)CH_3), 1.61-1.42 (m, 5H, H-$3^{axial\ g'}$ and linker CH_2), 1.30-1.24 (m, 2H, linker); ^{13}C NMR (150 MHz, D_2O): δ 186.6, 174.7, 174.3, 174.2, 103.3, 102.7, 101.8, 100.8, 99.9, 98.5, 97.3, 78.9, 78.1, 77.8, 75.1, 74.4, 74.2, 74.1, 72.2, 71.7, 71.5, 70.7, 69.8, 68.3, 68.1, 63.1, 62.4, 60.8, 60.2, 59.7, 54.9, 54.6, 51.6, 39.9, 39.1, 27.8, 26.1, 22.2, 21.8, 17.6; ESI-MS (negative mode): *m/z* calcd for $C_{106}H_{178}N_8O_{74}$; 2747.0411 found 1396.0177 $(M + Na)^{2-}$.

Synthesis of glycan G30.

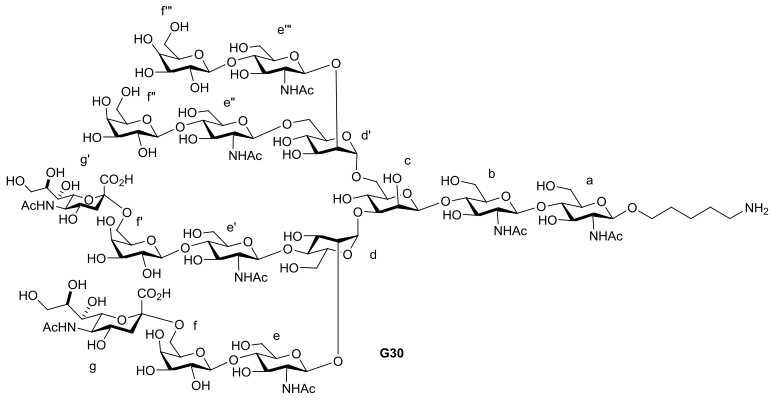
Depicted in Scheme S18, precussor S16b from scheme S16 was used as acceptor for 6-O glycosylation with donor **11** under the promotion of silver triflate and hafnocene dichloride to obtain the desired **S18a**. The final deprotection provided the disialylated tetra-antennary complex glycan G30.



Scheme S18 | Preparation of G30. i, **11**, AgOTf, Cp_2HfCl_2, toluene, -40 ^oC, 37%; ii, (1) LiOH, 1, 4-dioxane, 90 ^oC, (2) Ac_2O, pyridine, (3) NaOMe, MeOH, (4) $Pd(OH)_2$, MeOH:H_2O, H_2, 45%



Compound S18a: A mixture of silver triflate (0.051 g, 0.200 mmol), bis (cyclopentadienyl) hafnium dichloride (0.053 g, 0.140 mmol) and 4 Å activated molecular sieves in dry toluene (5 mL) was stirred at room temperature for 1 h. The reaction mixture was then cooled to -50 ℃, a solution of donor **11** (0.144 g, 0.060 mmol) and acceptor **S16b** (0.180 g, 0.040 mmol) in 5 mL toluene was added. The mixture was stirred for 3 h at -10 ^{o}C, quenched with Et_3N, diluted with EtOAc and filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL), and a brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 10% acetone in toluene) to afford **S18a** (0.103 g, 37%) as white foam. TLC: (acetone: toluene = 2/8, v/v): R_f = 0.53; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.69-7.52 (m, 20H), 7.33-7.06 (m, 120H), 5.60 (m, 17H), 4.80-4.30 (m, 40H), 4.20-4.00 (m, 50H), 3.99-3.02 (m, 68H), 2.08 (s, 9H), 2.07 (s, 6H), 2.05 (s, 6H), 2.02 (s, 6H), 1.78-1.74 (m, 6H), 0.91-0.84 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.9, 170.4, 170.2, 169.8, 169.4, 169.3, 132.7, 131.1, 129.0, 128.7, 128.4, 128.3, 128.2, 128.0, 127.8, 127.7, 127.6, 127.5, 68.8, 68.4, 39.0, 37.3, 33.7, 31.4, 30.6, 29.9, 29.2, 26.6, 26.0, 24.0, 23.2, 22.9, 20.1, 14.6, 14.2, 11.40; ESI-MS: *m/z* calcd for $C_{337}H_{361}Cl_{18}N_{11}O_{101}$; 6806.6710 found 723.5969 $(M + K)^{10+}$.

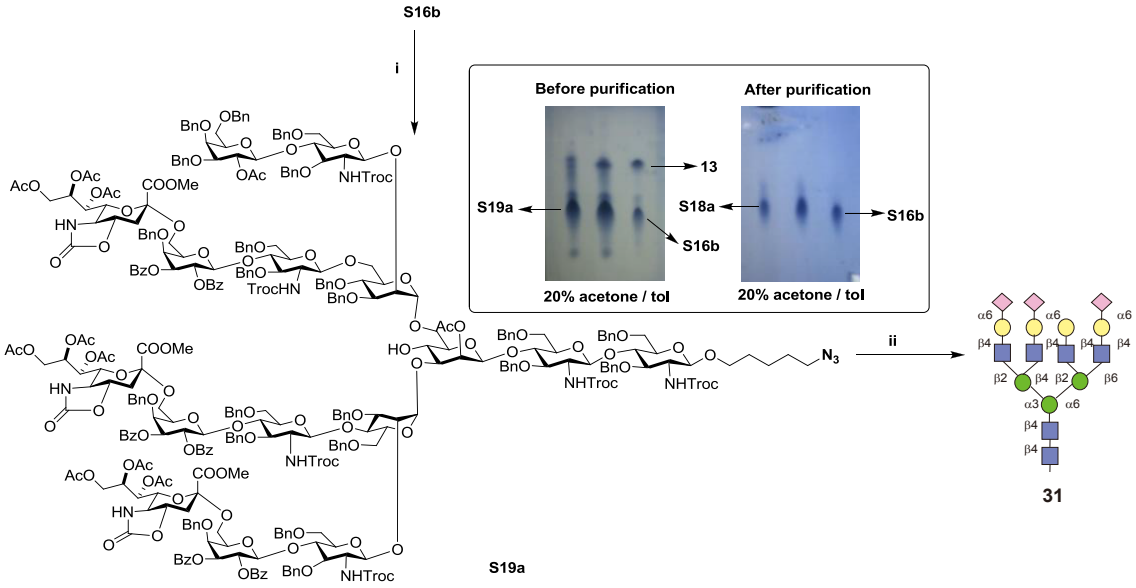


5-Aminopentyl-di-[5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyrano-sylonate-(2→6)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2),(1→4)-α-D-mannopyranosyl]-(1→3),-di-[-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6),(1→2)-α-D-mannopyranosyl]-(1→6)-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside G30: Compound **S18a** (0.075 g, 0.010 mmol) was deprotected by following general procedure 2 (method 2) to afford desired glycan **G30** (0.015 mg, 45%). ^{1}H NMR (600 MHz, D_2O): δ 5.12 (s, 1H, H-1^{d}), 4.86-4.74 (m, 3H, H-1$^{d', c, b}$, overlapped with D_2O), 4.59-4.55 (m, 5H, H-1$^{e,e',e'',e''',a}$), 1.48-4.42 (m, 4H, H-1$^{f,f',f'',f'''}$), 4.21-4.06 (m, 5H), 3.98-3.3.20 (m, 86H), 2.98 (t, *J* = 10.7 Hz, 2H, linker CH_2), 2.66 (dd, *J* = 3.7 & 10.1 Hz, 2H, 2 x H-3$_{equi.}^{g,g'}$), 2.12 (s, 3H, -C(O)CH_3), 2.09 (s, 3H, -C(O)CH_3), 2.06 (s, 3H, -C(O)CH_3), 2.05 (s, 3H, -C(O)CH_3), 2.03 (s, 12H, -C(O)CH_3), 1.75-1.54 (m, 6H, 2 x H-3$_{axial.}^{g,g'}$ and linker CH_2), 1.42-1.36 (m, 2H, linker); ^{13}C NMR (150 MHz, D_2O): δ 174.7, 174.2, 174.1, 103.4, 102.7, 101.3, 101.2, 101.0, 100.8, 100.6, 99.9, 98.9, 97.9, 78.1, 75.1, 74.3, 73.4, 72.3, 72.1, 71.7, 70.7, 70.4, 69.8, 68.3, 68.0, 59.9, 59.7, 54.7, 51.6, 39.9, 27.8, 22.7, 22.0, 21.9, 21.8; ESI-MS (negative mode): *m/z* calcd for $C_{117}H_{195}N_9O_{82}$; 3039.8280 found 1518.5585 $(M - H)^{2-}$.

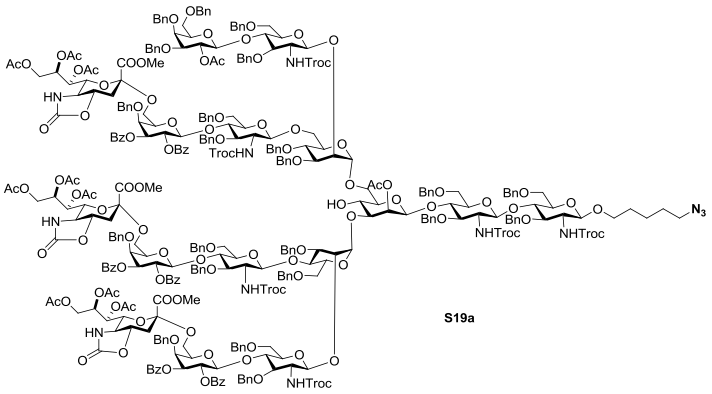
Synthesis of glycan G31.

Intermidiate **S16b** derived from scheme S16 was used for α-selective glycosylation using donor **13** in presence of AgOTf/Cp_2HfCl_2 to get **S19a** in 74% yield. However, the newly formed

product was overlaped with acceptor on TLC (Scheme S19). S19a was then further deprotected to furnish glycan **G31**.

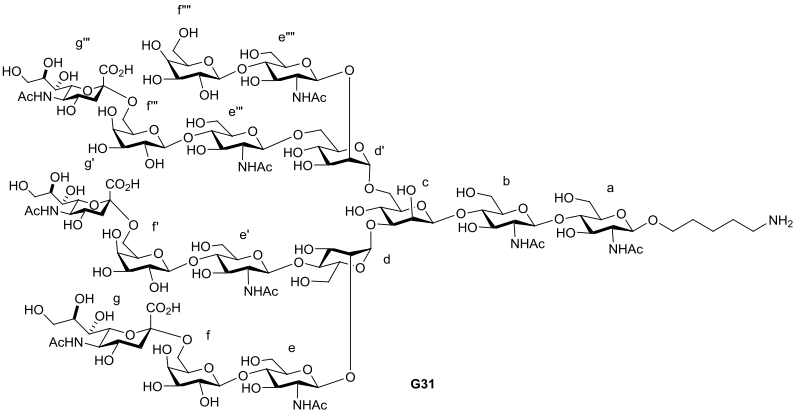


Scheme S19 | Preparation of G31. i, **13**, AgOTf, Cp_2HfCl_2, toluene, -50 ^oC, 74%; ii, (1) LiOH, 1,4-dioxane, 90 ^oC, (2) Ac_2O, pyridine, (3) NaOMe, MeOH, (4) $Pd(OH)_2$, MeOH: H_2O, H_2, 47%.



Compound S19a: A mixture of silver triflate (0.042 g, 0.165 mmol), bis (cyclopentadienyl) hafnium dichloride (0.043 g, 0.115 mmol) and 4 Å activated molecular sieves in dry toluene (5 mL) was stirred at rt for 1 h. The reaction mixture was then cooled to -50 °C, a solution of donor **13** (0.100 g, 0.036 mmol) and acceptor **S16b** (0.150 g, 0.033 mmol) in 5 mL toluene was added. The reaction mixture was stirred for 2 h at -20 ^oC, quenched with Et_3N, diluted with EtOAc and

filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL), and a brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 15% acetone in toluene) to afford **S19a** (0.183 g, 74%) as white foam. TLC: (acetone: toluene = 2/8, v/v): R_f = 0.50; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.90-7.83 (m, 9H), 7.69-7.67 (m, 3H), 7.57-7.50 (m, 3H), 7.38-7.04 (m, 125H), 5.77 (t, *J* = 10.2 Hz, 4H), 5.54-5.40 (m, 20H), 5.39 (t, *J* = 8.4 Hz, 4H), 5.08 (t, *J* = 7.8 Hz, 4H), 4.98-4.60 (m, 25H), 4.53-4.10 (m, 30H), 4.00-3.80 (m, 42H), 3.21-3.18 (m, 44H), 2.93-2.78 (m, 4H), 2.08 (s, 6H), 2.07 (s, 6H), 2.05 (s, 3H), 2.02 (s, 3H), 1.98 (s, 6H), 1.94 (s, 6H), 1.74-1.18 (m, 7H), 0.91-0.84 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.8, 171.7, 170.8, 169.9, 169.8, 168.5, 168.0, 166.1, 165.4, 159.5, 132.7, 131.7, 130.1, 129.9, 129.2, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 100.7, 100.6, 100.4, 95.8, 74.9, 74.6, 74.2, 73.9, 73.7, 73.6, 73.2, 72.9, 72.2, 71.9, 71.0, 70.5, 69.3, 68.5, 68.3, 68.0, 67.3, 66.1, 65.3, 62.3, 61.2, 53.4, 51.5, 39.0, 37.3, 33.7, 32.4, 32.2, 30.6, 29.9, 29.6, 29.4, 29.3, 28.8, 26.6, 24.0, 23.9, 23.5, 23.4, 23.1, 21.2, 20.1, 15.5, 14.6, 14.4, 14.3, 11.2; HRMS: *m/z* calcd for $C_{352}H_{376}Cl_{18}N_{12}O_{113}$; 7220.9510 found 3654.9220 $(M + 2Na)^{2+}$.



5-Aminopentyl-di-[5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyrano-sylonate-(2→6)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2),(1→4)-α-D-mannopyranosyl]-(1→3),-[5-Acetamido-3,5-dideoxy-D-glycero-α-D-

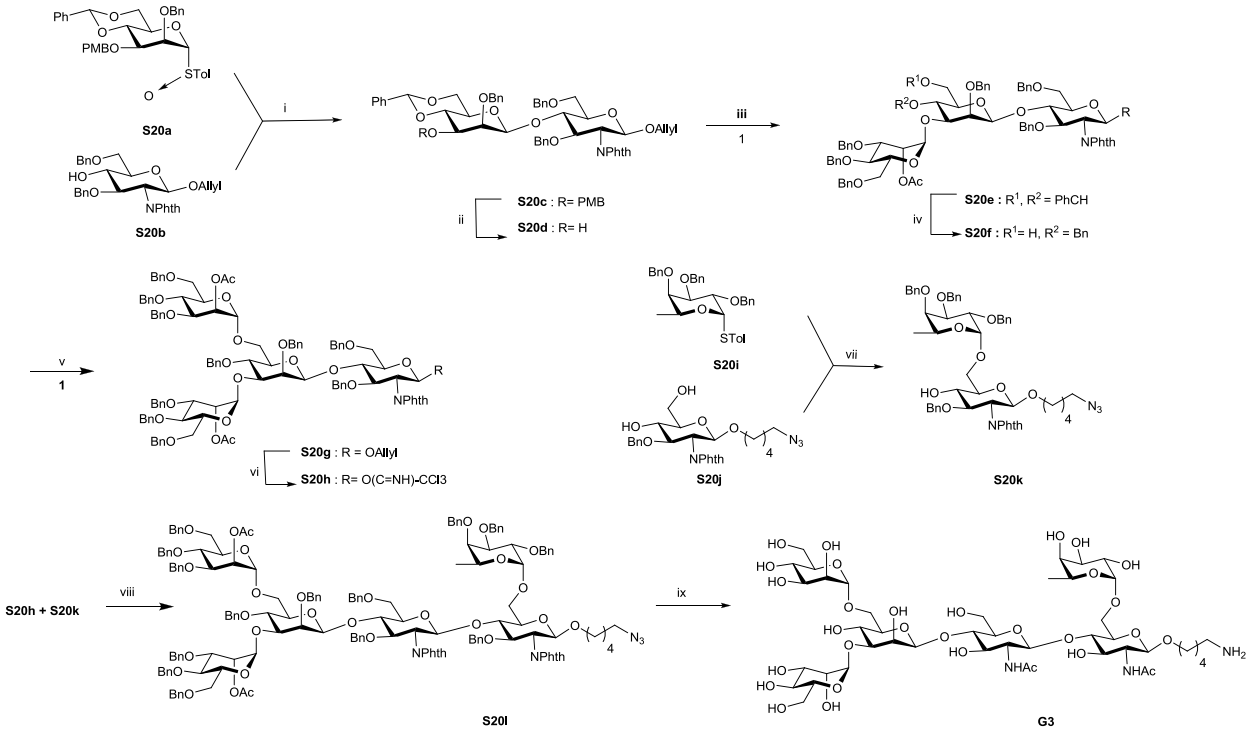
galacto-2-nonulopyrano-sylonate-(2→6)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)- β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranosyl]-(1→6)-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside

G31: Compound **S19a** (0.180 g, 0.024 mmol) was deprotected by following general procedure 2 (method 2) to afford desired glycan **G31** (0.039 g, 47%). ^{1}H NMR (600 MHz, D_2O): δ 5.12 (s, 1H, H-1^{d}), 4.87 (s, 2H, H-$1^{d',c}$), 4.75 (d, *J* = 8.4 Hz, 2H, H-$1^{b,\ e}$), 5.59-4.55 (m, 5H, overlapped H-$^{1a,\ e',\ e''',\ e'''',\ f}$), 4.49-4.42 (m, 5H, overlapped H-$1^{f'-f''''}$), 4.21-4.19 (m, 4H), 4.06-3.54 (m, 83H), 2.97 (t, *J* = 10.2 Hz, 2H, linker -CH_2), 2.66 (dd, *J* = 3.2 & 7.8 Hz, 3H, H-$3^{g,g',g'''equi}$), 2.09 (s, 3H), 2.06 (s, 9H), 2.04 (s, 3H), 2.02 (s, 12H), 1.74 (m, 2H, linker), 1.64 (t, *J* = 10.2 Hz, 3H, H-$3^{g,g',g'''axial}$), 1.59-1.57 (m, 2H, linker), 1.39-1.37 (m, 2H, linker); ^{13}C NMR (150 MHz, D_2O): δ 174.8, 174.7, 174.5, 174.4, 174.3, 174.1, 173.3, 103.5, 102.9, 101.7, 101.4, 101.2, 100.2, 100.0, 99.8, 99.6, 99.3, 80.8, 80.6, 80.3, 79.3, 78.4, 78.3, 76.7, 75.3, 74.3, 74.2, 74.1, 74.0, 73.8, 72.9, 72.8, 72.6, 72.4, 72.3, 72.2, 72.1, 72.0, 71.9, 71.7, 71.3, 70.8, 70.4, 70.3, 70.2, 68.4, 68.4, 63.4, 62.9, 60.4, 60.3, 60.2, 59.8, 54.8, 54.3, 54.2, 51.8, 51.0, 43.7, 43.3, 39.8, 39.5, 34.4, 27.5, 26.3, 22.6, 22.4, 22.4, 22.2, 22.0, 21.9 ; ESI-MS (negative mode): *m/z* calcd for $C_{128}H_{212}N_{10}O_{90}$; 3331.0840 found 1664.1108 $(M - H)^{2-}$.

viii. Synthesis of core fucosylated glycans G3 and G19

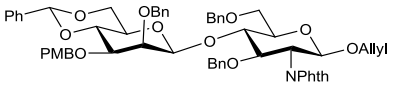
The pauci mannose type structure bearing core fucose **G3**[12] was assembled from the reducing end disaccharide **S20k** through fucosylation of diol acceptor **S20j** by donor **S20i** (Scheme S20). The *α*-selectivity was enhanced by in situ anomarization protocol ($CuBr_2$, tetrabutyl ammonium bromide), which was first developed by Lemieux and co-workers[14], to get disaccharide **S20k** in 67% yield with its regio- and stereo-chemistry confirmed by NMR analysis. The formation of the key *β*-mannosyl linkage using sulfoxide donor **S20a**[13] and acceptor **S20b** was performed using DTBP and Tf_2O to get disaccharide **S20c** in 67% yield with α/β ratio of 1:7. The *p*-methoxy benzyl ether protection at 3" was removed by using DDQ to afford 3"-OH **S20d**, which was further subjected to 3"-O α-mannosylation by using imidate **1** under the promotion of $BF_3.OEt_2$

to obtained trisaccharide **S20e**. Selective benzylidene opening of **S20e** produced **S20f**, which further underwent α-mannosylation at 6''-O position to get tetrasaccharide **S20g**. Compound **S20g** was then converted into glycosyl imidate **S20h** by treatment with $PdCl_2$ and then trichloroacetimidate and DBU. Finally the condensation of imidate **S20h** and disaccharide **S20k**[12] in the presence of $BF_3.OEt_2$ provided desired hexasaccharide **S20i**. The global deprotection afforded the paucimannose type oligosaccharide **G3**.



Scheme S20 | Preparation of glycan G3. i, DTBP, Tf_2O, CH_2Cl_2, -60 ^oC, 3 h, 67% (α/β 1:7); ii, DDQ, CH_2Cl_2 : H_20 = 10/1, 3 h, 70%; iii, **1,** $BF_3.OEt_2$, CH_2Cl_2, 4 Å MS, -40 ^oC, 1 h, 81%; iv, Triethyl sillane, $PhBCl_2$, CH_2Cl_2, 1 h, 73%; v, $BF_3.OEt_2$, CH_2Cl_2, 4 Å MS, -20°C, 2 h, 65%; vi, (i) $PdCl_2$, MeOH:CH_2Cl_2, RT, 6 h, (ii) DBU, trichloroacetonitrile, CH_2Cl_2, 63% over 2 steps; vii, Cu(II)Br, TBAB, DMF:CH_2Cl_2, 4 Å MS,0°C to RT, overnight, 76%; viii, $BF_3.OEt_2$, CH_2Cl_2, 4 Å MS,-70 ^oC, 2 h, 45%; ix, (i) $NH_2CH_2CH_2NH_2$, *n*BuOH, 100 ^oC; (ii) Ac_2O, pyridine, 0 ^oC to RT;

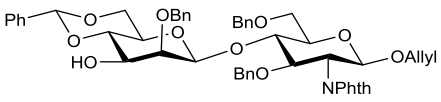
(iii) NaOMe, MeOH; (iv) $Pd(OH)_2$, MeOH: H_2O: HCOOH (5:3:2), H_2, 22% over 4 steps. TBAB = Tetrabutyl ammonium bromide.



S20c

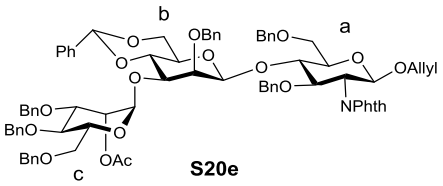
Allyl-O-2-O-benzyl-3-O-*p*-methoxy-benzyl-4,6-O-benzylidine-β-D-mannopyranosyl-(1→4)-O-(3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S20c): A mixture of donor **S20a** (0.272 g, 0.483 mmol) and activated 4 Å molecular sieves in CH_2Cl_2 (10 mL) was stirred at rt for 1 h. The reaction mixture was cooled to -60 ^oC, 2,6-di-ter-butyl pyridine (268 µL, 1.24 mmol) followed by Tf_2O (79 µL, 0.483 mmol) was added and stirred for 40 minutes. A solution of acceptor **S20b** (0.2 g, 0.378 mmol) in CH_2Cl_2 (5 mL) was added slowly and the resulting reaction mixture was stirred for 1 h until TLC (ethyl acetate: toluene, 1/9) indicated formation of a product with consumption of the starting material. The reaction mixture was quenched with Et_3N, diluted with CH_2Cl_2, filtered through Celite and concentrated in *vacuo.* The residue was purified by flash column chromatography (0% → 10% EA in toluene) to afford **S20c** (0.230 g, 67%) as white solid. TLC: (ethyl acetate: toluene = 1/9, v/v): R_f = 0.52; ^1H NMR (600 MHz, $CDCl_3$): δ 7.65-7.45 (m, 4H, Ar-H), 7.35-7.21 (m, 13H, Ar-H), 6.91-6.90 (m, 2H, Ar-H), 6.90-6.81 (m, 10H, Ar-H), 5.67-5.65 (m, 1H, allyl), 5.49 (s, 1H, Ph-C<u>H</u>, benzylidene), 5.13 (d, *J* = 8.4 Hz, 1H, H-1^a), 5.07 (d, *J* = 8.8 Hz, 1H), 4.99 (d, *J* = 10.4 Hz, 1H), 4.87-4.82 (m, 3H), 4.65 (d, *J* = 5.4 Hz, 1H), 4.63 (d, *J* = 5.4 Hz, 1H), 4.53 (s, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 4.41 (d, *J* = 6.0 Hz, 1H), 4.39 (d, *J* = 6.0 Hz, 1H), 4.24-4.21 (m, 2H), 4.05-3.96 (m, 3H), 3.81 (s, 3H, OMe of PMB), 3.71 (d, *J* = 3.0 Hz, 1H), 3.64 (d, *J* = 10.8 Hz, 1H), 3.56-3.52 (m, 2H), 3.45-3.47 (d, *J* = 10.0 Hz, 1H), 3.40 (dd, *J* = 3.0, 6.6 Hz, 1H), 3.13-3.12 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 159.46, 139.08, 138.99, 138.12, 138.00, 134.05, 130.93, 129.37, 129.22, 128.84, 128.60, 128.54, 128.47, 128.45, 128.26, 128.12, 128.09, 128.07, 127.83, 127.21, 126.41, 117.60, 114.04, 102.28,

101.63, 97.70, 79.85, 78.99, 78.33, 77.44, 75.29, 75.03, 74.95, 73.86, 72.61, 69.99, 68.86, 68.84, 67.66, 55.96, 55.58; ESI-MS: *m/z* calcd for $C_{59}H_{59}NO_{13}$: 989.3879; found 1012.3888 $(M + Na)^+$.



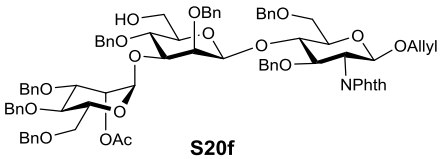
S20d

Allyl-O-2-O-benzyl-4,6-O-benzylidine-β-D-mannopyranosyl-(1→4)-O-(3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S20d): To a solution of **S20c** (0.5 g, 0.505 mmol) in 10 mL CH_2Cl_2 : H_2O (10:1) was added DDQ (0.219g, 1.01 mmol) at 0 ℃ and the resulting reaction mixture was stirred for 3 h. The reaction mixture was then filtered, organic layer washed with H_2O (2 x 30 mL). The aqueous layer was further extracted with CH_2Cl_2 (2 x 50 mL). The combined organic layers were washed with brine solution (40 mL), dried over Na_2SO_4 and concentrated in *vacuo.* The residue was purified by flash column chromatography (0% → 10% EA in toluene) to afford **S20d** (0.308 g, 70%) as colorless foam. TLC: (ethyl acetate: toluene = 2/8, v/v): R_f = 0.42; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.65-7.44 (m, 4H, Ar-H), 7.43-7.28 (m, 13H, Ar-H), 6.92-6.90 (m, 2H, Ar-H), 6.83-6.81 (m, 5H, Ar-H), 5.68-5.64 (m, 1H, Allyl), 5.42 (s, 1H, Ph-C<u>H</u>, benzylidene), 5.14 (d, *J* = 8.4 Hz, 1H, H-1^a), 5.08 (d, *J* = 12.8 Hz, 1H), 5.01-4.98 (m, 2H), 4.85 (d, *J* = 12.6 Hz, 1H), 4.74 (d, *J* = 12.0 Hz, 1H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.62 (s, 1H, H-1^b), 4.84 (d, *J* = 12.0 Hz, 1H), 4.40 (d, *J* = 12.0 Hz, 1H), 4.25-4.16 (t, *J* = 9.6 Hz, 1H), 3.99 (dd, *J* = 13.0 & 6.3 Hz, 1H), 3.73-3.65 (m, 4H), 3.54-3.47 (m, 3H), 3.13-3.09 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): 138.97, 138.44, 137.93, 137.56, 133.98, 129.37, 128.92, 128.79, 128.53, 128.43, 128.35, 128.26, 128.21, 128.10, 127.99, 127.27, 126.58, 117.64, 102.33, 102.25, 97.66, 79.91, 79.42, 79.15, 77.43, 76.00, 75.03, 74.89, 74.01, 71.24, 69.99, 68.78, 68.67, 67.17, 55.90; ESI-MS: *m/z* calcd for $C_{51}H_{51}NO_{12}$: 869.3303; found 892.3314 $(M + Na)^+$.



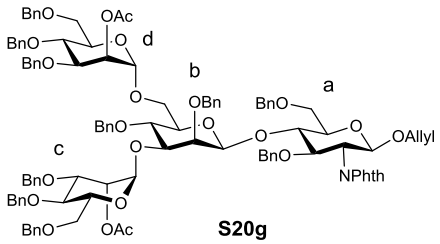
S20e

Ally-O-(2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→3)-2-O-benzyl-4,6-O-benzylidine-β-D-mannopyranosyl-(1→4)-O-(3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S20e):- A mixture of donor **1** (0.537 g, 0.863 mmol), acceptor **S20d** (0.50 g, 0.574 mmol) and activated 4 Å molecular sieves in dry CH_2Cl_2 (10 mL) was stirred at rt for 30 minutes. The reaction was cooled to -40 ^oC, boron trifluoride ethyl etherate (32 μL, 0.288 mmol) was then added slowly and the resulting reaction mixture was stirred for 1 h. The reaction was quenched by adding Et_3N, diluted with CH_2Cl_2, filtered through Celite and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 20% EA in hexane) to afford **S20e** (0.630 g, 81%) as colorless oil. TLC: (ethyl acetate: hexane = 3/7, v/v): R_f = 0.62; ^1H NMR (600 MHz, $CDCl_3$): δ 7.41-7.39 (m, 4H, Ar-H), 7.39-7.25 (m, 30H, Ar-H), 7.16-6.82 (m, 5H, Ar-H), 5.57-5.57 (m, 1H, Allyl), 5.59 (d, *J* = 3.0 Hz, 1H), 5.47 (s, 1H, Ph-CH, benzylidene), 5.29 (d, *J* = 2.1 Hz, 1H, H-1^c), 5.13 (d, *J* = 8.4 Hz, 1H, H-1^a), 5.08 (dd, *J* = 6.0 & 12.2 Hz, 1H), 5.00 (dd, *J* = 6.0, 10.2 Hz, 1H), 4.87-4.82 (m, 2H), 4.79-4.78 (m, 2H), 4.66-4.59 (m, 3H), 4.54 (s, 1H, H-1^b), 4.46-4.44 (m, 3H), 4.22-4.20 (m, 2H), 4.17-4.14 (m, 2H), 4.03-3.93 (m, 4H), 3.82-3.71 (m, 5H), 3.64-3.62 (m, 2H), 3.60-3.52 (m, 2H), 3.50 (d, *J* = 8.2Hz, 1H), 3.19 (m, 1H), 2.34 (s, 3H, -C(O)CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.26, 163.58, 162.83, 138.98, 138.77, 138.60, 138.40, 138.09, 138.04, 137.58, 133.97, 131.97, 129.01, 128.79, 128.71, 128.64, 128.62, 128.56, 128.52, 128.38, 128.32, 128.24, 128.12, 128.05, 127.97, 127.94, 127.84, 127.18, 126.26, 123.57, 117.58, 101.76, 101.35, 98.96, 97.63, 79.24, 78.91, 78.56, 78.22, 75.76, 75.62, 75.03, 74.77, 74.44, 73.75, 72.55, 71.83, 69.94, 69.32, 68.64, 68.54, 68.39, 67.16, 55.88, 36.75, 31.70, 21.27; ESI-MS: *m/z* calcd for $C_{80}H_{81}NO_{18}$: 1343.5346; found 1366.5369 $(M + Na)^+$.



S20f

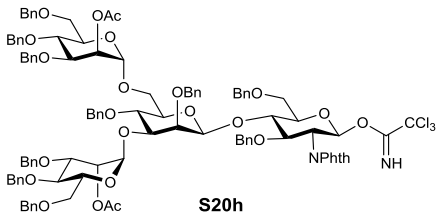
Ally-O-(2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→3)-2,4-O-di-benzyl-β-D-mannopyranosyl-(1→4)-O-(3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S20f): A mixture of compound **S20e** (0.630 g, 0.468 mmol) and activated 4 Å molecular sieves in 20 mL CH_2Cl_2 was stirred for 1 h at rt. The reaction mixture was cooled to -78 ^oC, triethyl silane (148 µL, 0.946 mmol) followed by dichlorophenyl borane (146 µL, 1.18mmol) was added and stirred for 1 h. The reaction was quenched by Et_3N, methanol, filtered through Celite and concentrated in *vacuo.* The residue was co-distilled with methanol 2-3 times before being purified by flash column chromatography (0% → 10% EA in toluene) to give alcohol **S20f** (0.460 g, 73%)**.** TLC: (ethyl acetate: toluene = 2/8, v/v): R_f= 0.42; ^1H NMR (600 MHz, $CDCl_3$): δ 7.73-7.57 (m, 4H, Ar-H), 7.50-7.08 (m, 31H, Ar-H), 6.83-6.81 (m, 4H, Ar-H), 5.76-5.69 (m, 1H, Allyl), 5.44 (t, *J* = 3.0 Hz, 1H), 5.13 (s, 1H, H-1^c), 5.12 (s, 1H), 5.08 (d, *J* = 7.8Hz, 1H, H-1^a), 5.01 (d, *J* = 11Hz, 1H), 4.93 (d, *J* = 11.0 Hz, 1H), 4.87 (d, *J* = 8.6 Hz, 1H), 4.83 (d, *J* = 8.0 Hz, 1H), 4.76 (d, *J* = 12.0 Hz, 1H*)*, 4.69 (d, *J* = 11.0 Hz, 1H*)*, 4.62 (t, *J* = 8.6 Hz, 1H), 4.57 (t, *J* = 7.8 Hz, 2H), 4.50 (d, *J* = 10.8 Hz, 1H), 4.44 (d, *J* = 2.5 Hz, 1H), 4.42 (s, 1H), 4.40 (d, *J* = 8.0 Hz, 1H), 4.35 (d, *J* = 12.0 Hz, 1H), 4.22-4.181 (m, 3H), 4.00-3.99 (m, 2H), 4.90-3.91 (s, 1H), 3.83-3.82 (m, 1H), 3.83 (d, *J* = 2.4 Hz, 1H), 3.77-3.78 (m, 2H), 3.64-3.54 (m, 6H), 3.41-3.39 (m, 2H), 3.19-3.18 (m, 1H), 2.08 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ170.34, 138.90, 138.77, 138.73, 138.36, 138.14, 138.07, 138.03, 135.91, 134.50, 134.03, 133.86, 132.97, 131.94, 131.40, 129.31, 128.86, 128.68, 128.66, 128.61, 128.57, 128.50, 128.45, 128.38, 128.26, 128.20, 128.12, 128.11, 128.03, 127.97, 127.94, 127.79, 127.76, 127.72, 127.47, 127.35, 123.50, 117.59, 101.04, 99.89, 97.61, 80.92, 78.64, 78.48, 78.41, 78.21, 75.93, 75.26, 75.20, 75.19, 75.16, 74.82, 74.59, 74.52, 73.78, 73.75, 72.61, 72.11, 69.91, 69.50, 68.99, 68.43, 62.25, 55.86, 21.29; ESI-MS: *m/z* calcd for $C_{80}H_{83}NO_{18}$: 1345.5502; found 1368.5527 $(M + Na)^+$.



S20g

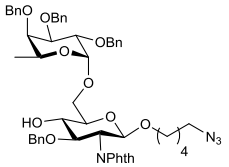
Allyl-O-di-(2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→3),(1→6)-2,4-O-di-benzyl-β-D-mannopyranosyl-(1→4)-O-(3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S20g): A mixture of donor **1** (0.429 g, 0.690 mmol), acceptor **S20f** (0.460 g, 0.345 mmol) and activated 4 Å molecular sieves in dry CH_2Cl_2 (10 mL) was stirred at rt for 30 minutes. The reaction was cooled to -20 ^oC, boron trifluoride ethyl etherate (19 μL, 0.173 mmol) was then added slowly and the resulting reaction mixture was stirred for 2 h. The reaction was quenched by adding Et_3N, diluted with CH_2Cl_2, filtered through Celite and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 20% EA in hexane) to afford **S57** (0.380 g, 65%) as colorless foam. TLC: (ethyl acetate: hexane = 3/7, v/v): R_f = 0.56; ^1H NMR (600 MHz, $CDCl_3$): δ 7.60-7.29 (m, 4H, Ar-H), 7.28-7.08 (m, 37H, AR-H), 7.07-7.08 (m, 8H, Ar-H), 7.07-6.93 (d, *J* = 8.0 Hz, 1H, Ar-H), 6.82-6.59 (m, 4H, Ar-H), 5.61-5.59 (m, 1H, Allyl), 5.43 (d, *J* = 6.0 Hz, 1H, H-2^c), 5.31 (d, *J* = 6.0 Hz, 1H, H-2^d), 5.10 (d, *J* = 3.0 Hz, 1H, H-1^c), 5.06 (d, *J* = 8.0 Hz, 1H, H-1^a), 4.99 (d, *J* = 10.0 Hz, 1H), 4.85 (d, *J* = 8.0 Hz, 1H), 4.83 (s, 1H, H-1^d), 4.67 (d, *J* = 8.0 Hz, 1H), 4.64-4.62 (q, 4H), 4.56 (d, *J* = 3.0 Hz, 1H, H-1^b), 4.55-4.45 (m, 8H), 4.45-4.39 (m, 9H), 4.38 (d, *J* = 10.0 Hz, 1H), 4.21 (d, *J* = 9.0 Hz, 1H), 4.19-4.10 (m, 2H), 4.08-3.70 (m, 10H), 3.69-3.49 (m, 7H), 3.39 (d, *J* = 9.1 Hz, 1H), 3.19 (d, *J* = 9.1 Hz, 1H), 2.07 (s, 3H, -C(O)CH_3), 1.82 (s, 3H, -C(O)CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.31, 170.11, 163.43, 139.07, 138.93, 138.83, 138.80, 138.65, 138.35, 138.32, 138.21, 138.09, 134.08, 133.77, 132.00, 128.87, 128.76, 128.66, 128.56, 128.43, 128.37, 128.16, 127.99, 127.91, 127.82, 127.73, 127.13, 123.46, 117.45, 102.07, 99.92, 99.74, 98.62, 97.55, 81.40, 79.81, 78.31, 78.23, 76.84,

75.87, 75.77, 75.66, 74.87, 74.65, 74.44, 74.38, 31.21, 21.29, 21.23; ESI-MS: *m/z* calcd for $C_{109}H_{113}NO_{24}$: 1820.7578; found 1843.7676 $(M + Na)^+$.



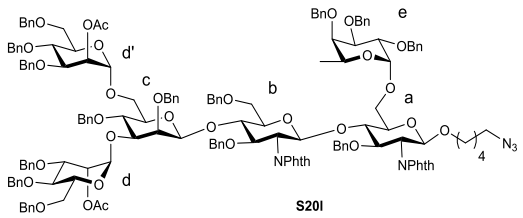
S20h

Di-(2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→3),(1→6)-2,4-O-di-benzyl-β-D-mannopyranosyl-(1→4)-O-(3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-gluco-pyranosyl trichloroacetimidate (S20h): To a solution of **S20g** (0.2 g, 0.109 mmol) in 10 mL CH_2Cl_2:MeOH (1/1) was added $PdCl_2$ (20 mg) and stirred at room temperature for 6 h until TLC (ethyl acetate: toluene, 2/8) indicated formation of a product with consumption of the starting material. The reaction mixture was then concentrated in *vacuo.* The residue was purified by flash column chromatography (0% → 10% EA in toluene) to afford alcohol (0.140 g, 60%) as colorless foam. To a solution of alcohol (0.150 g, 0.084 mmol) in CH_2Cl_2 (10 mL) was added trichloroacetamidate (33 µL, 0.336 mmol) followed by DBU (12 µL, 0.033 mmol) at 0 ^oC and stirred at rt for 8 h. The reaction was quenched with Et_3N and concentrated in *vacuo.* The residue was purified by flash column chromatography (0% → 10% EA in toluene) to afford **S20h** (0.121 g, 67%) as colorless oil. TLC: (ethyl acetate: toluene = 2/8, v/v): R_f = 0.47; ^1H NMR (600 MHz, $CDCl_3$): δ 8.51 (s, 1H, C=N<u>H</u>), 7.53-7.42 (m, 4H, Ar-H), 7.40-7.00 (m, 48H, Ar-H), 6.58 (d, *J* = 6.6 Hz, 2H, Ar-H), 6.52-6.50 (m, 3H, Ar-H), 5.43 (s, 1H, H-1^a), 5.32 (s, 1H, H-1^c), 5.03 (s, 1H), 5.01 (t, *J* = 7.8 Hz, 1H), 4.90-4.78 (m, 6H), 4.67-4.45 (m, 7H), 4.43-4.30 (m, 9H), 4.28-4.20 (m, 2H), 4.10 (t, *J* = 7.8 Hz, 1H), 3.39-3.42 (m, 18H), 3.19 (d, *J* = 9.3 Hz, 1H), 2.09 (s, 3H, -C(O)CH_3), 1.83 (s, 3H, -C(O)CH_3).



S20k

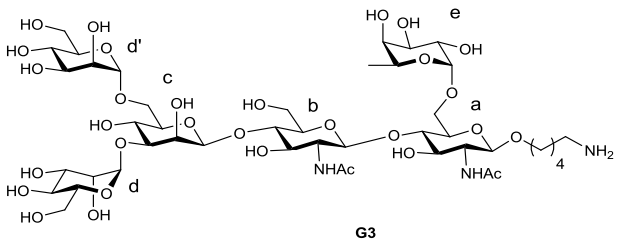
5-Azidopentyl-O-2,3,4-tri-O-benzyl-α-L-fucopyranosyl-(1→6)-3-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S20k): A mixture of $CuBr_2$ (0.450 g, 2.01 mmol), Bu_4NBr (0.655 g, 2.03 mmol) and activated 4 Å molecular sieves in 10 mL of CH_2Cl_2 : DMF (2/1) was stirred and cooled over an ice water bath. A solution of donor **S20i** (0.5 g, 0.925 mmol) and acceptor **S20j** (0.450 g, 0.882 mmol) in CH_2Cl_2 (10 mL) was added drop wise and the resulting reaction mixture was stirred at rt for overnight. TLC (ethyl acetate: hexane, 4/6) indicated formation of a product with consumption of the starting material. The reaction was quenched with aq. $NaHCO_3$, diluted with ethyl acetate (50 mL) and filtered through Celite. The filtrate was washed with aq.$NaHCO_3$, brine (50 mL), dried over sodium sulfate. The organic layer was concentrated in *vacuo.* The residue was purified by flash column chromatography (0% → 30% EA in hexane) to afford **S20k** (0.604 g, 76%) as colorless oil. TLC: (ethyl acetate: hexane = 4/6, v/v): R_f = 0.47; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.80-7.64 (m, 4H, Ar-H), 7.41-7.23 (m, 15H, Ar-H), 7.00-6.98 (m, 2H, Ar-H), 6.90-6.87 (m, 3H, Ar-H), 5.06 (d, *J* = 8.4 Hz, 1H, H-1^a), 4.96 (d, *J* = 11.4 Hz, 1H), 4.86 (d, *J* = 11.4 Hz, 1H), 4.82-4.72 (m, 4H), 4.67 (d, *J* = 12.0 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.48 (d, *J* = 12.6 Hz, 1H), 4.16-4.13 (m, 1H), 4.08-4.05 (m, 2H), 3.39-3.95 (m, 2H), 3.90-3.83 (m, 3H), 3.78 (m, 1H), 3.73-3.69 (m, 2H), 3.56-3.53 (m, 1H), 3.35-3.21 (m, 1H), 2.00-2.03 (m, 2H, -CCH_2C-, linker), 1.38-1.30 (m, 4H, -CCH_2C-, linker), 1.12 (d, *J* = 8.4 Hz, 3H, Me of Fucose), 1.00-0.96 (m, 2H, -CCH_2C-, linker); ^{13}C NMR (150, MHz, $CDCl_3$): δ 138.83, 138.77, 138.36, 134.13, 128.90, 128.77, 128.67, 128.60, 128.52, 128.31, 128.26, 128.17, 127.93, 127.88, 127.52, 123.64, 98.81, 98.59, 79.60, 78.07, 77.77, 76.67, 75.22, 74.54, 74.51, 74.24, 73.35, 73.20, 69.37, 68.79, 67.15, 55.88, 51.39, 29.00, 28.58, 23.30, 16.89; ESI-MS: *m/z* calcd for $C_{53}H_{58}N_4O_{11}$: 926.3994; found 949.3998 $(M + Na)^+$.



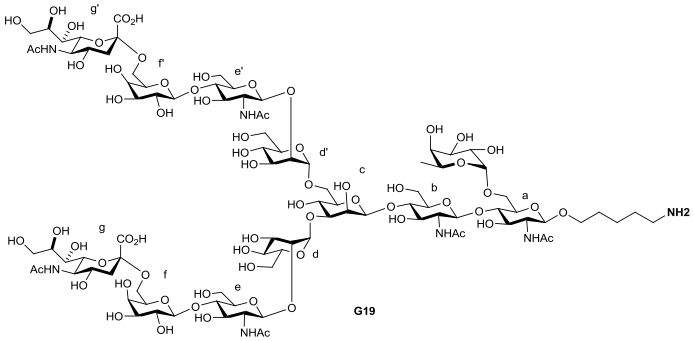
S20l

5-Azidopentyl-O-2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→6)-(2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl-(1→3))-2,4-di-O-benzyl-β-mannopyranosyl-(1→4)-O-3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-(2,3,4-tri-O-benzyl-α-L-fuco pyranosyl-(1→6))-3-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S20l): A mixture of donor **S20h** (0.050 g, 0.025 mmol), acceptor **S20k** (0.028 g, 0.031 mmol) and activated 4 Å molecular sieves in dry CH_2Cl_2 (10 mL) was stirred at rt for 30 minutes. The reaction was cooled to -70 ^oC, boron trifluoride ethyl etherate (0.725 μL, 0.0062 mmol) was then added slowly and the resulting reaction mixture was stirred for 2 h. The reaction was quenched by adding Et_3N, diluted with CH_2Cl_2, filtered through Celite and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 20% EA in hexane) to afford **S20l** (0.027 g, 45%) as a white foam. TLC: (ethyl acetate : hexane = 3/7, v/v): R_f = 0.50; ^1H NMR (600 MHz, $CDCl_3$): δ 7.83-7.62 (m, 8H, Ar-H), 7.49-7.30 (m, 8H, Ar-H), 7.30-7.10 (m, 47H, Ar-H), 7.09-7.03 (m, 10H, AR-H), 7.03-6.99 (m, 5H, Ar-H), 6.55 (t, *J* = 7.8 Hz, 2H, H-$2^{d,d'}$), 5.40 (s, 1H, H-1^{d}), 5.29-5.29 (m, 1H), 5.09 (d, *J* = 1.3 Hz, 1H, $H^{1d'}$), 4.88-4.76 (m, 13H), 4.67-4.65 (m, 2H), 4.58-5.48 (m, 9H), 4.42-4.40 (m, 3H), 4.36-4.30 (m, 5H), 4.20-4.10 (m, 5H), 4.05-4.00 (m, 2H), 3.92-3.80 (m, 7H), 3.79-3.60 (m, 7H), 3.62-3.41 (m, 10H), 3.25(dd, *J* = 3.2, 8.2 Hz, 1H), 3.18-3.17 (m, 2H), 2.85-2.79 (m, 2H), 2.06 (s, 3H, -C(O)CH_3), 1.76 (s, 3H, -C(O)CH_3, 1.42-1.34 (m, 4H, -CCH_2C-, linker), 1.03-0.99 (m, 5H, -CCH_2C-, linker and CH_3 of Fucose); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.30, 169.91, 168.15, 167.76, 139.16, 138.99, 138.88, 138.82, 138.77, 138.54, 138.28, 138.21, 138.10, 138.08, 138.05, 133.86, 132.02, 131.72, 128.80, 128.62, 128.60, 128.57, 128.55, 128.33, 128.23, 128.40, 127.98, 127.92, 127.70, 127.55, 127.26, 127.06, 123.33, 101.97, 99.62, 98.41, 97.95, 97.09, 97.05, 81.42, 79.71, 78.36, 74.98, 74.75, 74.68, 73.65, 72.57,

72.51, 72.03, 71.38, 68.93, 68.86, 68.12, 66.63, 66.12, 56.76, 56.01, 51.26, 28.82, 28.56, 23.20, 21.23, 20.91; ESI-MS: *m/z* calcd for $C_{159}H_{165}N_5O_{34}$: 2689.1261; found 2712.1338 $(M + Na)^+$.



5-Aminopentyl-di-(α-D-mannopyranosyl)-(1→3),(1→6)-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-(α-L-fucopyranosyl-(1→6)-2-acetamido-2-deoxy-β-D-glucopyranoside (G3): Compound **S20h** (0.030 g, 0.011 mmol) was deprotected by following general procedure 2 (method 1) to obtain the title compound **G3** (0.007 g, 22%) as a white powder. ^{1}H NMR (600 MHz, D_2O): δ 5.09 (s, 1H, H-1^d), 4.91 (s, 1H, H-1d$^'$), 4.89 (d, *J* = 3.2 Hz, 1H, H-1^e), 4.78 (s, 1H, H-1^c), 4.65 (d, *J* = 7.8 HZ, 1H, H-1^a), 4.49 (d, *J* = 7.8 Hz, 1H, H-1^b), 4.25 (s, 1H), 4.15-4.10 (m, 1H), 4.05 (s, 1H), 3.95 (s, 1H), 3.95-3.80 (m, 8H), 3.80-3.50 (m, 23H), 3.00 (m, 2H), 2.10 (s, 3H, -C(O)CH_3), 2.09 (s, 3H, -C(O)CH_3, 1.67-1.60 (m, 2H, -CCH_2C-), 1.60-1.57 (m, 2H, -CCH_2C-), 1.41-1.37 (m, 2H, -CCH_2C-), 1.25 (d, *J* = 7.8 Hz, 3H, -CH_3 of Fucose); ^{13}C NMR (150 MHz, D_2O): δ 174.67, 174.39, 170.97, 102.51, 101.10, 101.04, 100.38, 99.60, 99.39, 80.46, 79.72, 78.60, 74.33, 74.15, 73.42, 72.65, 72.30, 71.95, 71.85, 70.29, 70.12, 70.00, 69.97, 69.85, 69.45, 68.15, 66.77, 66.14, 65.85, 65.80, 61.11, 60.92, 59.97, 55.05, 54.86, 46.66, 39.28, 38.61, 28.05, 26.36, 22.27, 22.15, 21.08, 21.50, 15.37, 15.34; ESI-MS: *m/z* calcd for $C_{45}H_{80}N_3O_{30}$; 1141.4821; found 1142.4827 $(M + H)^+$.

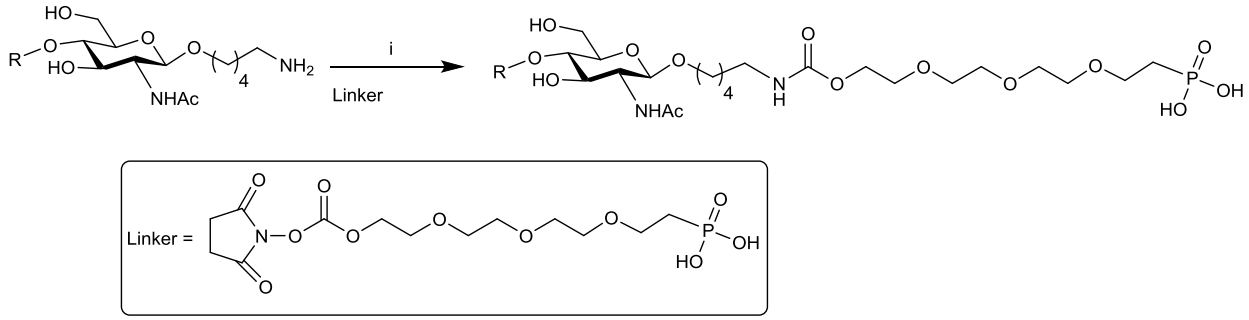


5-Aminopentyl-di-[5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyrano-sylonate-(2→6)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranosyl]-(1→3),(1→6)-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-(α-L-fucopyranosyl-(1→6)-2-acetamido-2-deoxy-β-D-glucopyranoside (G19): Sialylated biantennary with core fucose glycan **G19** was prepared by using reported procedure[11,12]**.** ^{1}H NMR (600 MHz, D_2O): δ 4.90 (s, 1H, H-1^{d}), 4.72 (s, 1H, H-1$^{d'}$), 4.66 (d, *J* = 3.6 Hz, 1H, H-1^{c}), 4.56 (s, 1H), 4.43 (d, *J* = 7.2 Hz, 1H, H-1^{b}), 4.37 (d, *J* = 7.2 Hz, 2H, H-1$^{e,e'}$), 4.25 (d, *J* = 7.8 Hz, 1H, H-1^{a}), 4.21 (d, *J* = 7.8 Hz, 2H, H-1^{f}), 4.04 (s, 1H), 3.97 (s, 1H), 3.90 (t, *J* = 10.1 Hz, 2H), 3.76-3.25 (m, 65H), 2.74 (t, *J* = 7.8 Hz, 2H, linker), 2.43 (dd, *J* = 3.8 & 7.2 Hz, 1H, H-3$^{equi.\ g,\ g'}$), 1.87 (s, 3H), 1.84 (s, 3H, -C(O)CH_3), 1.83 (s, 3H, -C(O)CH_3), 1.80 (s, 6H, -C(O)CH_3), 1.51 (t, *J* = 12 H, 2H, H-3$^{axial\ g,g'}$), 1.46-1.41 (m, 2H), 1.37-1.34 (m, 2H), 1.18-1.15 (m, 2H), 1.00 (d, *J* = 6.6 Hz, 3H, -CH_3 of Fucose); ^{13}C NMR (150 MHz, D_2O): δ 174.5, 174.3, 174.1, 173.3, 103.3, 100.9, 100.7, 100.2, 99.7, 99.6, 99.3, 99.1, 98.9, 96.5, 80.2, 79.5, 77.8, 75.9, 75.6, 74.0, 73.3, 73.2, 73.1, 72.4, 72.2, 71.8, 71.7, 71.3, 70.3, 69.9, 69.7, 69.3, 69.1, 68.0, 67.9, 67.0, 66.9, 66.5, 65.7, 65.4, 63.0, 62.2, 61.4, 61.3, 59.8, 59.4, 54.7, 54.4, 54.2, 51.5, 39.7, 38.9, 27.7, 26.1, 22.1, 22.0, 22.0, 21.8, 21.7, 15.1 ; ESI-MS: *m/z* calcd for $C_{95}H_{159}N_7O_{66}$; 2451.9121; found 1226.4513 $(M - H)^{2-}$.

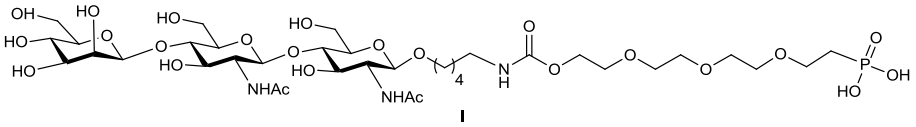
ix. Synthesis of glycans with phosphonic acid tails.

General procedure: To a solution of sugars with amine tail (3-5 µmol) in DMF (400 µL) was added linker [2(2(2(bis(benzyloxy)phosphoryl)ethoxyethoxy)ethyl(2,5-dioxopyrrolidin-1-yl)carbonate] (15-25 µmol), and the resulting reaction mixture was stirred at rt for 5 h. DMF was removed by using high vacuum and the product was purified by using Bio-Gel P-2 chromatography (eluent H_2O). The solid was dissolved in 2 mL of H_2O, added $Pd(OH)_2$ (50% by weight) and hydrogenated for overnight. The reaction mixture was filtered through Celite and

concentrated in *vacuo*. The residue was purified by Bio-Gel P-2 (BIO-RAD) column chromatography using water as eluent. The product was the lypholysed to obtain the desired sugar with phosphonic acid tail as white color powder.

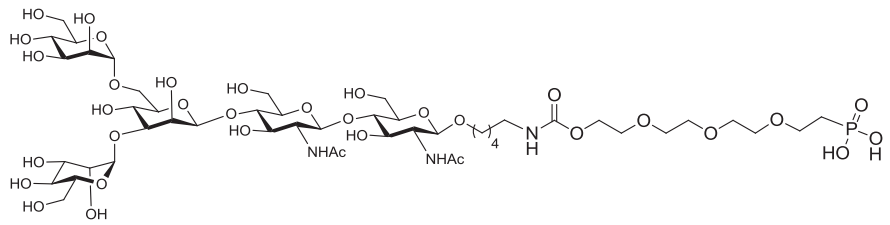


Scheme S21 | Preparation of sugars with phosphonic acid linker. i, (1) Linker, DMF, RT, 5 h; (2) $Pd(OH)_2$, H_2O, H_2, RT, overnight.



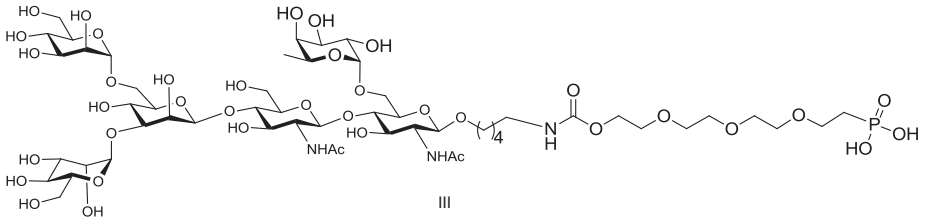
I

(Phosphonate-tetra-(ethyleneglycol)-carbonyl-amino)-pentyl-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (I): Compound **G1** (3.5 mg, 5.4 μmol) was modified by above general procedure to afford compound **I** (2.2 mg, 61%), as white solid. TLC (MeOH: EA:AcOH: H_2O, 7/1/1/1, v/v). ^{1}H NMR (600 MHz, D_2O): δ 4.60 (d, *J* = 8.4 Hz, 1H), 4.48 (d, *J* = 7.8 Hz, 1H), 4.19 (s, 2H), 4.05 (d, *J* = 3.2 Hz, 1H), 3.93-3.49 (m, 33H), 1.75 (t, *J* = 7.8 Hz, 2H), 2.06 (s, 3H), 1.95 (s, 3H), 1.95-1.92 (m, 2H), 1.58-1.54 (m, 2H), 1.50-1.47 (m, 2H), 1.33-1.30 (m, 2H). HRMS (MALDI-TOF): *m/z* calcd for $C_{36}H_{66}N_3O_{24}P$; 955.8887 found 954.3099 (*M* -H).



II

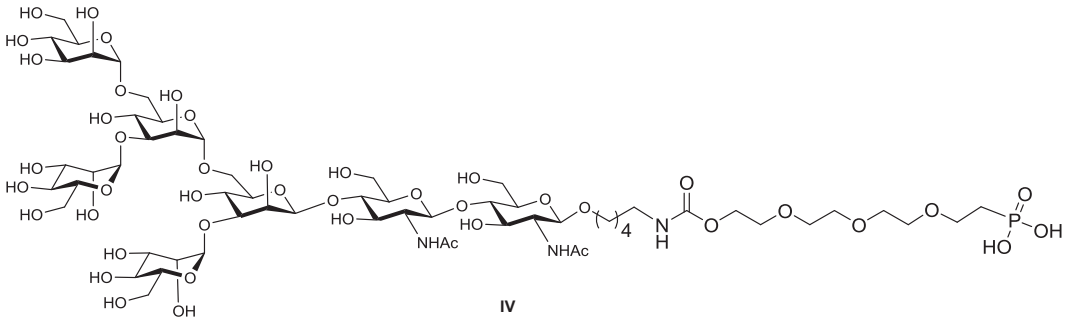
(Phosphonate-tetra-(ethyleneglycol)-carbonyl-amino)-pentyl-α-D-manno-pyranosyl(1→3)-α-D-mannopyranosyl]-(1→6)-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (II): Glycan G2 (4 mg, 2.3 μmol) was modified by above general procedure to afford compound II (3.2 mg, 71%), as white solid. TLC (MeOH: EA: AcOH: H_2O, 7/1/1/1, v/v). ^{1}H NMR (600 MHz, D_2O): δ 5.01 (s, 1H), 4.83 (s, 1H), 4.51 (d, *J* = 6.1 Hz, 1H), 4.40 (d, *J* = 6.2 Hz, 1H), 4.17 (s, 1H), 4.11 (s, 2H), 3.98 (s, 1H), 3.88-3.39 (m, 42H), 3.03 (t, *J* = 7.8 Hz, 2H), 1.99 (s, 3H), 1.95 (s, 3H), 1.95-1.91 (m, 2H), 1.50-1.45 (m, 2H), 1.42-1.38 (m, 2H), 1.26-1.22 (m, 2H). HRMS (MALDI-TOF) Negative mode: *m/z* calcd for $C_{48}H_{86}N_3O_{34}P$; 1279.4830 found 1278.5001 (*M* - H).



III

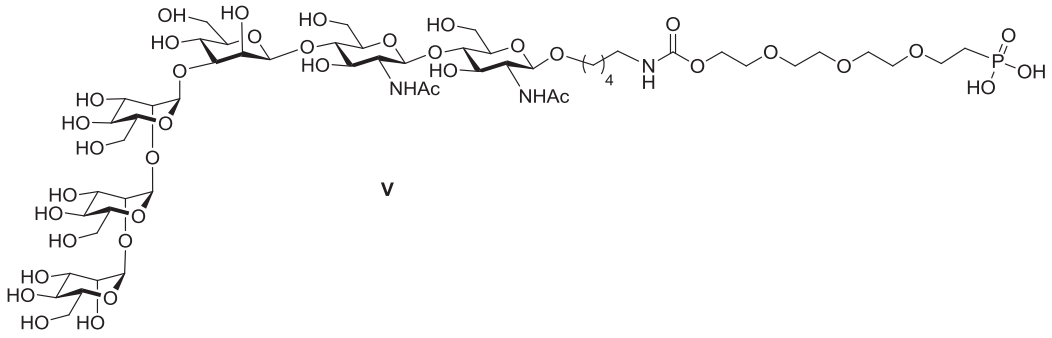
(Phosphonate-tri-(ethyleneglycol)-carbonyl-amino)-pentyl-α-D-manno-pyranosyl(1→3)-α-D-mannopyranosyl]-(1→6)-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-)-(α-L-fucopyranosyl-(1→6)-2-acetamido-2-deoxy-β-D-glucopyranoside) (III): Glycan **G3** (1.2 mg, 1.0 μmol) was modified by above general procedure to afford compound **III** (1.0 mg, 91%), as white solid. TLC (MeOH: EA: AcOH: H_2O, 7/1/1/1, v/v). ^{1}H NMR (600 MHz, D_2O): δ 5.09 (s, 1H), 4.90 (s, 1H), 4.88 (d, *J* = 7.4 Hz, 1H), 4.66 (d, *J* = 7.5 Hz, 1H), 4.48 (d, *J* = 7.2 Hz, 1H), 4.25 (s, 1H), 4.19 (s, 2H), 4.12-4.10 (m, 1H), 4.06 (s, 1H), 3.95 (s, 1H), 3.92-3.84 (m, 14H), 3.79-3.69 (m, 31H), 3.11-3.09 (m, 2H), 2.08 (s,

3H), 2.02 (s, 3H), 1.99-1.93 (m, 2H), 1.58-1.53 (m, 2H), 1.49-1.47 (m, 2H), 1.34-1.30 (m, 2H), 1.22 (d, 3H). HRMS (MALDI-TOF): *m/z* calcd for $C_{54}H_{96}N_3O_{38}P$; 1427.6754 found 1450.5709 (*M* + Na).



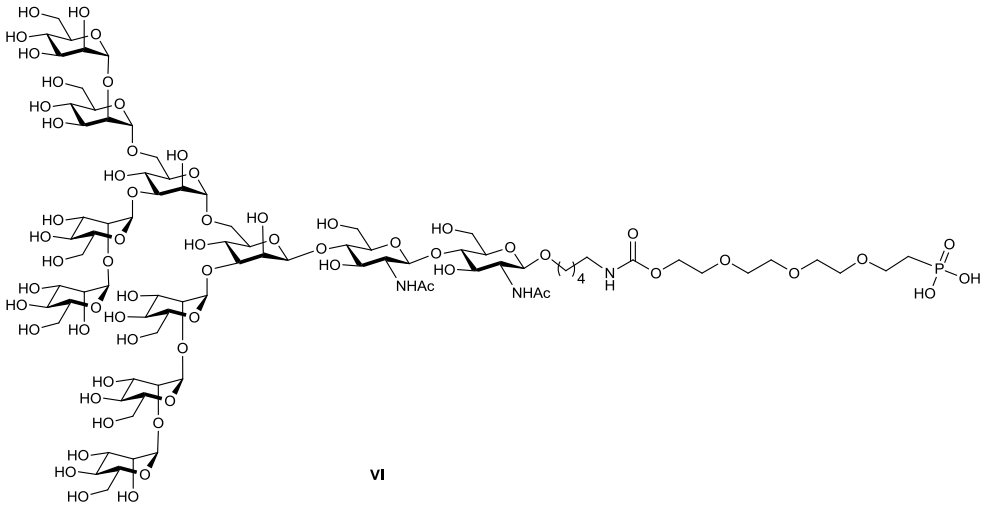
IV

(Phosphonate-tetra-(ethyleneglycol)-carbonyl-amino)-pentyl-α-D-manno-pyranosyl(1→3),[di-(α-D-mannopyranosyl)-(1→3),(1→6)-α-D-mannopyranosyl]-(1→6)-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (IV): Glycan **G4** (4 mg, 3.1 μmol) was modified by above general procedure to afford compound **IV** (3.7 mg, 78%), as white solid. TLC (MeOH: EA: AcOH: H_2O, 7/1/1/1, v/v). ^{1}H NMR (600 MHz, D_2O): δ 5.10 (d, *J* = 9.6 Hz, 2H), 4.93 (s, 1H), 4.70 (s, 1H), 4.57 (d, *J* = 7.2 Hz, 1H), 4.48 (d, *J* = 7.8 Hz, 1H), 4.24 (d, *J* = 3.2 Hz, 2H), 4.19-4.13 (m, 4H), 4.06-4.04 (m, 3H), 3.95-3.40 (m, 49H), 3.38-3.37 (m, 1H), 2.10 (t, *J* = 7.8 Hz, 2H), 2.07 (s, 6H), 2.02 (s, 6H), 1.98-1.93 (m, 2H), 1.58-1.47 (m, 2H), 1.34-1.29 (m, 2H), 1.27-1.25 (m, 2H); HRMS (MALDI-TOF): *m/z* calcd for $C_{60}H_{106}N_3O_{44}P$; 1604.5411 found 1607.0452 (*M* + 3H).



V

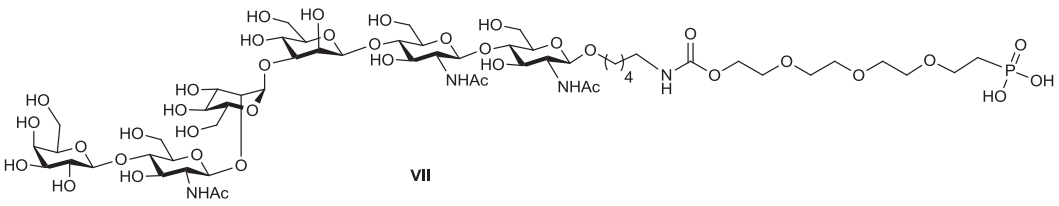
(Phosphonate-tetra-(ethylene glycol)-carbonyl-amino)-pentyl-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→2)-α-D-manno- pyranosyl-(1→3)-β-D-manno- pyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (V): Glycan **G5** (5 mg, 4.4 µmol) was modified by above general procedure to afford compound **V** (3.5 mg, 58%), as white solid. TLC (MeOH: EA: AcOH: H_2O, 7/1/1/1, v/v). ^{1}H NMR (600 MHz, D_2O): δ 5.34 (s, 1H), 5.29 (s, 1H), 5.03 (s, 1H), 4.58 (d, *J* = 7.8 Hz, 1H), 4.47 (d, *J* = 7.8 Hz, 1H), 4.20 (bs, 3H), 4.09-4.05 (m, 3H), 3.90-3.20 (m, 47H), 3.10 (t, J = 7.8 Hz, 2H), 2.05 (s, 3H), 2.01 (s, 3H), 2.00-1.92 (m, 2H), 1.56-1.53 (m, 2H), 1.49-1.46 (m, 2H), 1.33-1.30 (m, 2H); HRMS (MALDI-TOF): *m/z* calcd for $C_{54}H_{96}N_3O_{39}P$; 1442.3105 found 1444.5470 (*M* + 2H).



VI

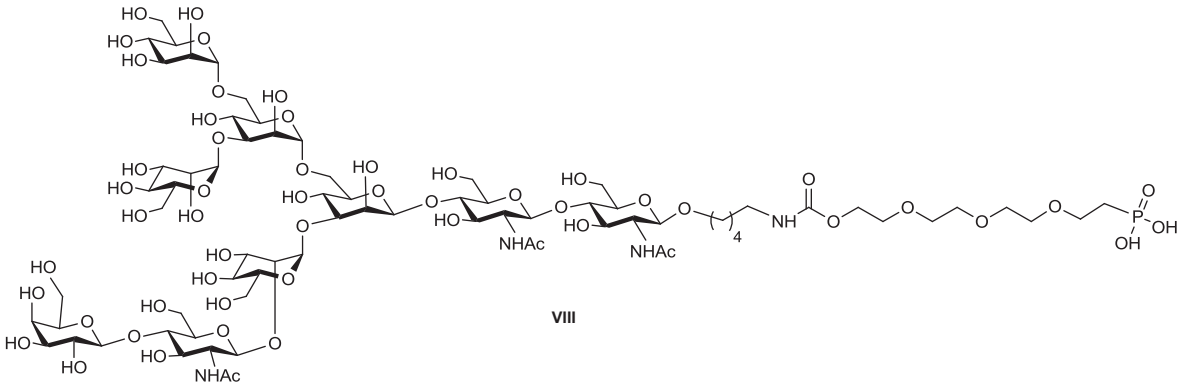
(Phosphonate-tetra-(ethyleneglycol)-carbonyl-amino)-pentyl-α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→2)-α-D-manno- pyranosyl-(1→3)-{α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→3)-[α-D-manno- pyranosyl-(1→2)-α-D-mannopyranosyl-(1→6)]-α-D-mannopyranosyl-(1→6)}-β-D-manno- pyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (VI): Glycan G6 (4 mg, 2.0 µmol) was modified by above general procesure to afford compound **VI** (3.7 mg, 66%), as white solid. TLC (MeOH: EA: AcOH: H_2O, 7/1/1/1, v/v). ^{1}H NMR (600 MHz, D_2O): δ 5.53 (s,

1H), 5.39 (d, *J* = 10.2 Hz, 1H), 5.26 (d, *J* = 9.8 Hz, 1H), 5.23 (s, 1H), 5.16 (d, *J* = 4.8 Hz, 1H), 5.08-5.05 (m, 5H), 4.60-3.20 (m, 83H), 2.08 (s, 3H), 2.02 (s, 3H), 1.38-1.03 (m, 2H), 1.58-1.56 (m, 2H), 1.52-1.48 (m, 2H), 1.35-1.32 (m, 2H); HRMS (MALDI-TOF): *m/z* calcd for $C_{84}H_{146}N_3O_{64}P$; 2253.0310 found 2257.0812 (*M* + 4H).



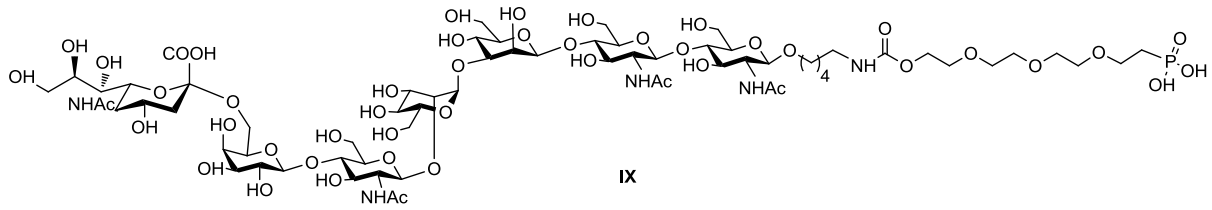
VII

(Phosphonate-tetr-(ethyleneglycol)-carbonyl-amino)-pentyl-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl -(1→2)-α-D-mannopyranosyl]-(1→3)-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (VII): Glycan **G9** (6.0 mg, 5.1 μmol) was modified by above general procedure to afford compound **VII** (3.5 mg, 50%), as white solid. TLC (MeOH: EA: AcOH: H_2O, 7/1/1/1, v/v). ^{1}H NMR (600 MHz, D_2O): δ 5.03 (d, *J* = 8.4 Hz, 2H), 4.58 (d, *J* = 7.2 Hz, 1H), 4.48 (d, *J* = 7.2 Hz, 1H), 4.45 (d, *J* = 7.8 Hz, 1H), 4.26 (dd, *J* = 3.0 & 9.2 Hz, 2H), 4.19 (bs, 2H), 4.00-3.38 (m, 49H), 3.11 (t, *J* = 7.8 Hz, 2H), 2.06 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 1.99-1.93 (m, 2H), 1.56-1.54 (m, 2H), 1.50-1.48 (m, 2H), 1.31-1.27 (m, 2H); HRMS (MALDI-TOF): *m/z* calcd for $C_{56}H_{99}N_4O_{39}P$; 1482.5624 found 1481.5069 (*M* -H).



VIII

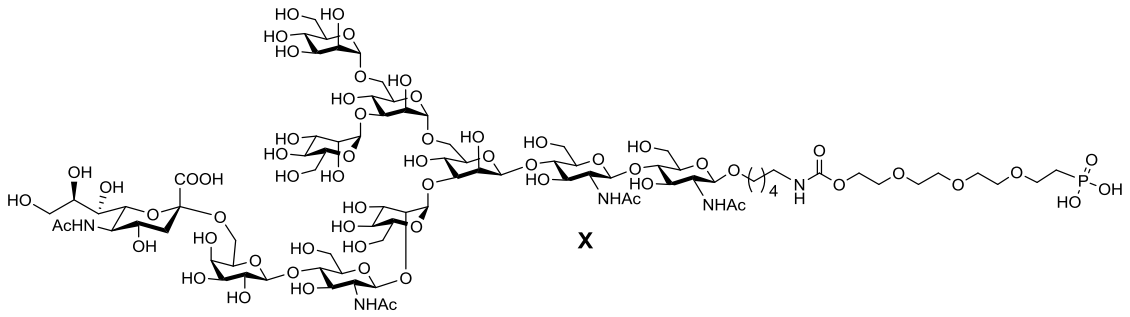
(Phosphonate-tetra-(ethyleneglycol)-carbonyl-amino)-pentyl-β-D-galactopyranosyl-(1→4)-[2-acetamido-2-deoxy-β-D-gluco-pyranosyl-(1→2)-α-D-mannopyranosyl-(1→3),[di-(α-D-mannopyranosyl)-(1→3),(1→6)-α-D-manno-pyranosyl](1→6)-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-gluco-pyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (VIII): Glycan **G12** (5.0 mg, 3.0 μmol) was modified by above general procedure to afford compound **VIII** (3.1 mg, 54%), as white solid. TLC (MeOH: EA: AcOH: H_2O, 7/1/1/1, v/v). ^{1}H NMR (600 MHz, D_2O): δ 5.11 (s, 2H), 5.02 (d, *J* = 7.8Hz, 2H), 4.68 (d, *J* = 3.2 Hz, 2H), 4.48 (d, *J* = 7.2 Hz, 1H), 4.45 (d, *J* = 7.2 Hz, 1H), 4.27 (s, 2H), 4.22 (s, 2H), 4.15 (s, 1H), 4.08 (s, 2H), 4.00-3.30 (m, 64H), 3.10 (t, *J* = 7.8 Hz, 2H), 2.08 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 1.93-1.87 (m, 2H), 1.56-1.54 (m, 2H), 1.51-1.47 (m, 2H), 1.33-1.30 (m, 2H); HRMS (MALDI-TOF): *m/z* calcd for $C_{74}H_{129}N_4O_{54}P$; 1968.6502 found 1967.6622 (*M* - H).



IX

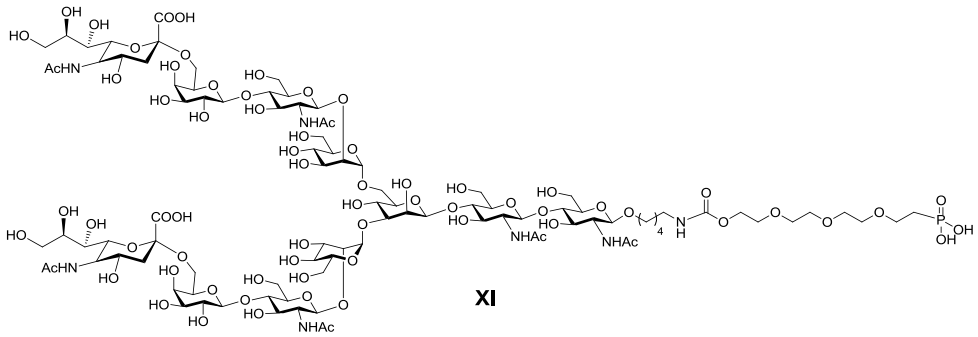
Phosphonate-tetra-(ethyleneglycol)-carbonyl-amino)-pentyl-[5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyrano-sylonate-(2→6)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranosyl]-(1→3)-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-gluco-pyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (IX): Glycan **G10** (5.0 mg, 2.5 μmol) was modified by above general procedure to afford compound **IX** (3.8 mg, 63%), as white solid. TLC (MeOH: EA: AcOH: H_2O, 7/1/1/1, v/v). ^{1}H NMR (600 MHz, D_2O): δ 5.08 (d, *J* = 8.4 Hz, 2H), 4.93 (s, 1H), 4.62 (d, *J* = 7.2 Hz, 1H), 4.51 (d, *J* = 7.8 Hz, 1H), 4.45 (d, *J* = 7.8 Hz, 1H), 4.30 (d, *J* = 3.2 Hz, 1H), 4.28 (s, 1H), 4.22 (s, 2H), 4.02-3.30 (m, 54H), 3.13 (t, *J* = 7.8 Hz, 2H), 2.68 (dd, *J* = 3.2, 7.8 Hz, 1H), 2.09 (s, 6H), 2.05 (s, 6H), 2.01-1.93 (m, 2H), 1.74 (t, *J* = 12.1 Hz, 1H), 1.60-1.57

(m, 2H), 1.54-1.51 (m, 2H), 1.35-1.32 (m, 2H); HRMS (MALDI-TOF): *m/z* calcd for $C_{67}H_{116}N_5O_{47}P$; 1773.5871 found 1772.5817 (*M* -H).



X

(Phosphonate-tetra-(ethyleneglycol)-carbonyl-amino)-pentyl-5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyrano-sylonate-(2→6)-β-D-galactopyranosyl-(1→4)-[2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranosyl-(1→3),[di-(α-D-mannopyranosyl)-(1→3),(1→6)-α-D-manno-pyranosyl](1→6)-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (X): Glycan **G13** (4.0 mg, 2.3 µmol) was modified by above general procedure to afford compound **X** (3.2 mg, 71%), as white solid. TLC (MeOH: EA: AcOH: H_2O, 7/1/1/1, v/v). ^{1}H NMR (600 MHz, D_2O): δ 5.08 (d, *J* = 10.2 Hz, 1H), 5.03 (s, 1H), 4.94 (s, 2H), 4.91 (s, 1H), 4.62 (s, 1H), 4.51 (d, *J* = 6.6 Hz, 1H), 4.46 (d, *J* = 7.8 Hz, 1H), 4.30 (s, 2H), 4.25 (s, 2H), 4.17 (s, 1H), 4.06 (s, 1H), 4.00-3.20 (m, 73H), 2.70 (dd, *J* = 3.2, 7.8 Hz, 1H), 2.11 (s, 6H), 2.05 (s, 6H), 2.03-1.97 (m, 2H), 1.14 (t, *J* = 12.6 Hz, 1H), 1.58-1.51 (m, 4H), 1.36-1.31 (m, 2H). HRMS (MALDI-TOF): *m/z* calcd for $C_{85}H_{146}N_5O_{62}P$; 2259.8163 found 1152.2946 $(M + Na)^{2+}$.

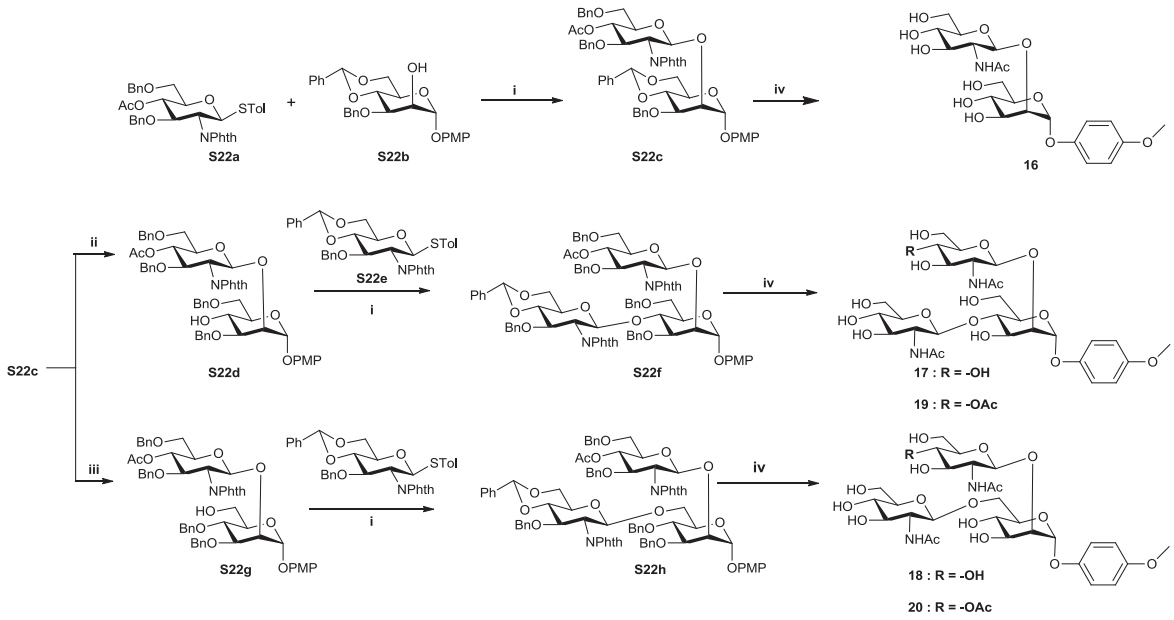


XI

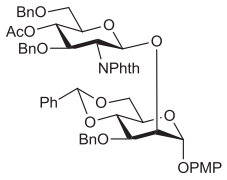
Phosphonate-tetra-(ethyleneglycol)-carbonyl-amino)-pentyl-di-[5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyrano-sylonate-(2→6)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranosyl]-(1→3),(1→6)-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (XI): Glycan **G16** (3.5 mg, 1.5 µmol) was modified by above general procedure to afford compound **XI** (2.6 mg, 69%) as a white solid. TLC (MeOH: AcOH: H_2O, 8/1/1, v/v). ^{1}H NMR (600 MHz, D_2O): δ 5.05 (d, *J* = 8.4 Hz, 1H), 4.63 (d, *J* = 6.6 Hz, 1H), 4.51 (s, 1H), 4.46 (t, *J* = 7.8 Hz, 2H), 4.32 (s, 1H), 4.29 (s, 2H), 4.22 (s, 2H), 4.09-3.48 (m, 83H), 3.13 (t, *J* = 7.8 Hz, 2H), 2.74-2.68 (m, 2H), 2.10 (s, 9H), 2.05 (s, 9H), 2.12-2.00 (m, 2H), 1.76-1.73 (m, 2H), 1.58-1.55 (m, 2H), 1.51-1.50 (m, 2H), 1.35-1.29 (m, 2H); HRMS (MALDI-TOF negative mode): *m/z* calcd for $C_{98}H_{166}N_7O_{70}P$; 2592.9383 found 1294.9685 $(M - 2H)^{2-}$.

x. Chemo-enzymatic synthesis of D1 and D2/D3 arm modules.

Our chemo-enzymatic strategy commensed with preparation of acceptor substrates **16-20.** As depicted in scheme S22, mannosyl acceptor **S22b** was glycosylated with donor **S22a** in the presence of NIS/TfOH to afford the disaccharide **S22c** in 60% yield. Benzyledine ring of **S22c** was opened both at 4-OH, **S22d** or 6-OH, **S22g** under diffirent reaction conditions. Donor **S22e** was installed separately at 4-O and 6-O positions of **S22d** and **S22g** respectively. Finally, global deprotection of intermidiates **S22c**, **S22f** and **S22h** was performed. In case of compounds **S22j** and **S22l**, the GlcNAc residues at Man 4 and 6-O positions were diffirenciated from 2-O GlcNAc through acetylation of 4-OH, for preparation of assymetric modules.

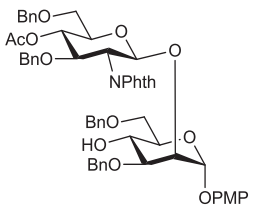


Scheme S22 | Preparation of acceptor substrates. i, NIS, TfOH, CH_2Cl_2, -50 ^oC; **ii**, Triethyl silane, TFA, 4 Å MS,CH_2Cl_2, 0 ^oC, 2 h, 58%; **iii**, BH_3.THF, Bu_2BOTf, CH_2Cl_2, 4 Å MS, 0 ^oC, 3 h, 71%; **iv**, (1) $NH_2CH_2CH_2NH_2$, *n*-BuOH, 100 ^oC; (2) Ac_2O, pyridine, 0 ^oC to RT; (3) $Pd(OH)_2$, MeOH: H_2O: HCOOH (5:3:2), H_2;



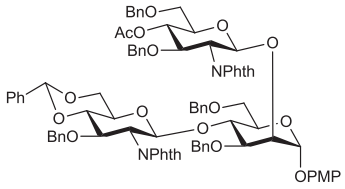
S22c

p-methoxyphenyl-O-[4-O-acetyl-3,6-O-di-benzyl-2-deoxy-2-phthalimido-β-D-gluco-pyranosyl-(1→2)-O-4,6-O-benzylidene-3-O-benzyl-α-D-mannopyranoside (S22c): Activated 4Å molecular sieves were added to a solution of acceptor **S22b** (0.250 g, 0.536 mmol) and donor **S22a** (0.410 g, 0.643 mmol) in anhydrous CH_2Cl_2 (10 mL). The reaction mixture was stirred for 1 h at rt then cooled to -50 ^oC. NIS (0.241 g, 1.07 mmol) and TfOH (11.8 μL, 0.134 mmol) were added slowly, and the resulting reaction mixture was stirred for 1 h. When TLC (ethyl acetate: toluene, 2/8) indicated formation of product with consumption of starting material, the reaction was quenched by adding Et_3N then filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL), aqueous $Na_2S_2O_3$ (2 x 50 mL), and brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 10% EA in toluene) to afford **S22c** (0.403 g, 76%) as a white foam. TLC (ethyl acetate: toluene = 2/8, v/v); R_f = 0.49; ^1H NMR (400 MHz, $CDCl_3$): δ 7.69-3.56 (m, 4H), 7. 36-7.22 (m, 15H), 7. 20-6.96 (m, 5H), 6.53 (d, J = 8.4 Hz, 2H), 6.50 (d, J = 8.2 Hz, 2H), 5.41 (s, 1H), 5.24 (d, J = 7.8 Hz, 1H), 5.10 (t, 1H), 4.93 (s, 1H), 4.73-4.43 (m, 10H), 4.00-3.20 (m, 5H), 1.98 (s, 3H) ; ^{13}C NMR (150 MHz, $CHCl_3$): δ 169.2, 152.3, 135.1, 134.9, 133.9, 128.7, 128.6, 128.4, 128.1, 128.1, 128.0, 127.7, 127.6, 127.5, 117.8, 114.7, 97.1, 96.3,74.0, 73.9, 73.1, 72.9, 72.8, 72.8, 72.5, 72.2, 71.4, 65.7, 55.4, 54.2, 22.5; ESI-MS: *m/z* calcd for $C_{57}H_{55}NO_{14}$; 977.3623 found 1000.3490 $(M + Na)^+$.



S22d

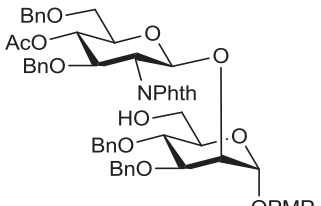
p-methoxyphenyl-O-[4-O-acetyl-3,6-O-di-benzyl-2-deoxy-2-phthalimido-β-D-gluco-pyranosyl-(1→2)-O-3,6-O-dibenzyl-α-D-mannopyranoside (S22d): To a solution of **S22c** (1.01 g, 1.02 mmol) in anhydrous CH_2Cl_2 (10 mL) was added triethyl silane (1.63 mL, 10.2 mmol) followed by trifluroacetic acid (0.758 mL, 10.2 mmol) at 0 ^oC. The resulting reaction mixture was stirred for 2 h. After 2 h, TLC (ethyl acetate: toluene, 1.5/8.5 v/v) indicated product formation with consumption of starting material. The reaction mixture was washed with sat. $NaHCO_3$ (2 x 50 mL). The aqueous layer was further extracted with CH_2Cl_2 (3 x 30 mL), and the combined organic layer were washed with brine solution (100 mL), dried over $MgSO_4$, filtered and concentrated in *vacuo.* The residue was purified by flash column chromatography (0% 10% EA in toluene) to afford **S22d** (0.580 g, 58%) as clear oil. TLC (ethyl acetate: toluene = 1.5/8.5, v/v): R_f = 0.35; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63-7.35 (m, 4H), 7. 30-7.10 (m, 14H), 7.02-6.97 (m, 3H), 6.93-6.86 (m, 3H), 6.72-6.66 (m, 4H), 5.27 (d, *J* = 8.4 Hz, 1H), 5.11 (t, *J* = 10.2 Hz, 1H), 5.02 (d,*J* = 2.8 Hz, 1H), 4.88 (s, 2H), 4.80 (s, 1H), 4.60 (d, *J* = 10.2 Hz, 2H), 4.58-4.24 (m, 6H), 4.01 (s, 2H), 3.79-3.74 (m, 2H), 3.72 (s, 3H), 3.64-3.56 (m, 3H), 3.35 (dd, *J* = 2.8 & 8 Hz, 1H), 2.93 (dd, *J* = 2.3 & 7.8 Hz, 1H), 1.94 (s, 3H); ^{13}C NMR (150 MHz, $CHCl_3$): δ 150.33, 138.18, 137.98, 133.96, 128.70, 128.65, 128.42, 128.18, 128.12, 128.02, 127.76, 127.62, 127.52, 117.89, 114.71, 97.19, 96.33,74.08, 73.96, 73.10, 72.95, 72.80, 71.86, 70.96, 70.75, 70.48, 67.72, 55.89, 55.69, 21.21; ESI-MS: *m/z* calcd for $C_{57}H_{57}NO_{14}$; 979.3779 found 1002.3660 $(M + Na)^+$.



S22f

p-methoxyphenyl-O-4-O-acetyl-3,6-O-di-benzyl-2-deoxy-2-phthalimido-β-D-gluco pyranosyl-(1→2)-[-O-4,6-O-benzylidene-3-O-benzyl-2-deoxy-2-phthalimido-β-D-gluco pyranosyl-(1→4)]-3,6-O-di-benzyl-α-D-mannopyranoside (S33f): Activated 4 Å molecular sieves were added to a solution of acceptor **S22d** (0.580 g, 0.590 mmol) and donor **S22e** (0.525 g,

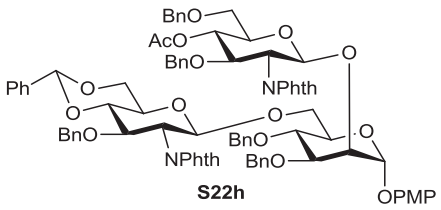
0.880 mmol) in anhydrous CH_2Cl_2 (10 mL). The reaction mixture was stirred for 1 h at rt then cooled to -50 ^oC. NIS (0.265 g, 1.14 mmol) and TfOH (13 µL, 0.147 mmol) were added slowly, and the resulting reaction mixture was stirred for 2 h. When TLC (ethyl acetate: toluene, 1.5/8.5) indicated formation of product with consumption of starting material, the reaction was quenched by adding Et_3N then filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL), aqueous $Na_2S_2O_3$ (2 x 50 mL), and brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 10% EA in toluene) to afford **S22f** (0.730 g, 85%) as a pale yellow solid. TLC (ethyl acetate: toluene = 1.5/8.5, v/v): R_f=0.60; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69- 6.67 (m, 8H), 7.59-7.18 (m, 20H), 6.96-6.75 (m, 10H), 6.57-6.52 (m, 4H), 5.44 (s, 1H), 5.27 (d, *J* = 8.4 Hz, 1H), 5.21 (d, *J* = 8.8 Hz, 1H), 5.11 (t, *J* = 10.7 Hz, 1H), 3.29-3.24 (m, 1H), 4.94 (d,*J* = 8.4 Hz, 1H), 4.76-4.69 (m, 2H), 4.57 (d, *J* = 7.8 Hz, 1H), 4.53 (d, *J* = 7.2 Hz, 1H), 4.45-4.19 (m, 9H), 4.10-4.06 (m, 2H), 3.99-3.94 (m, 2H), 3.63 (s, 3H), 3.56 -3.48 (m, 8H), 3.00 (dd, *J* = 2.3 and 7.8 Hz, 2H), 1.99 (s, 3H); ^{13}C NMR (150 MHz, $CHCl_3$): δ 169.98, 168.04, 138.94, 138.46, 138.14, 137.96, 133.90, 131.78, 129.24, 128.69, 128.52, 128.34, 128.25, 128.18, 128.08, 127.72, 127.33, 126.38, 123.56, 117.90, 114.47, 101.43. 99.38, 83.11, 78.85, 74.79, 74.27, 73.94, 73.76, 72.80, 72.34, 71.43, 70.26, 69.23, 68.90, 66.00, 56.49, 55.85, 55.70, 21.70; ESI-MS: *m/z* calcd for $C_{85}H_{80}N_2O_{20}$; 1448.5153 found 1471.5156 $(M + Na)^+$.



S22g

p-methoxyphenyl-O-[4-O-acetyl-3,6-O-di-benzyl-2-deoxy-2-phthalimido-β-D-gluco-pyranosyl-(1→2)-O-3,4-O-dibenzyl-α-D-mannopyranoside (S22g): To a mixture of compound **S22c** (0.800 g, 0.816 mmol) and activated molecular sieves in anhydrous CH_2Cl_2 (10 mL) was added borane.THF complex (0.781 mL of a 1M solution in THF, 8.15 mmol) and

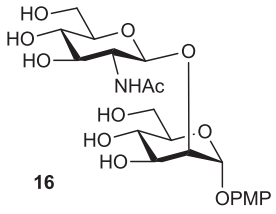
Bu_2BOTf (0.351 mL of a 1M solution in CH_2Cl_2, 1.63 mmol) were added at 0°C. The reaction mixture was allowed to stired at room temperature for 3 h. TLC (acetone: toluene, 1/9) indicated formation of a product with consumption of the starting material. Triethyl amine was added to the reaction mixture followed by slow addition of methanol at 0 °C. When no more hydrogen was produced, the reaction mixture was filtered through Celite, The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL), and brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% →10% EA in toluene) to afford **S22g** (0.500 g, 71%) as clear foam. TLC (acetone: toluene = 2/8, v/v): R_f = 0.41; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84-7.55 (m, 4H), 7. 40-6.90 (m, 10H), 6.87-6.80 (m, 7H), 6.93-6.86 (m, 3H), 6.72-6.66 (m, 4H), 5.27 (d, *J* = 8.4 Hz, 1H), 5.11 (t, *J* = 10.2 Hz, 1H), 5.02 (d,*J* = 2.8 Hz, 1H), 4.88 (s, 2H), 4.80 (s, 1H), 4.60 (d, *J* = 10.2 Hz, 2H), 4.58-4.24 (m, 6H), 4.01 (s, 2H), 3.79-3.74 (m, 2H), 3.72 (s, 3H), 3.64-3.56 (m, 3H), 3.35 (dd, *J* = 2.8 & 8 Hz, 1H), 2.93 (dd, *J* = 2.3 & 7.8 Hz, 1H), 1.94 (s, 3H); ^{13}C NMR (150 MHz, $CHCl_3$): δ 154.2, 138.6, 136.5, 133.5, 128. 0, 127.5 127.4, 128.18, 127.1, 127.0, 126.7, 126.6, 126.5, 117.89, 114.71, 97.19, 96.33,74.08, 73.96, 73.10, 72.9, 72.8, 72.5, 72.6, 71.9, 71.4, 65.7, 56.8, 56.6, 21.9; ESI-MS: *m/z* calcd for $C_{57}H_{57}NO_{14}$; 979.2640; found 979.2012.



S22h

p-methoxyphenyl-O-4-O-acetyl-3,6-O-di-benzyl-2-deoxy-2-phthalimido-β-D-gluco pyranosyl-(1→2)-[-O-4,6-O-benzylidene-3-O-benzyl-2-deoxy-2-phthalimido-β-D-gluco pyranosyl-(1→6)]-3,6-O-di-benzyl-α-D-mannopyranoside (S22h): Activated 4 Å molecular sieves were added to a solution of acceptor **S22g** (0.500 g, 0.509 mmol) and donor **S22e** (0.452 g, 0.763 mmol) in anhydrous CH_2Cl_2 (10 mL). The reaction mixture was stirred for 1 h at room temperature then cooled to -50 ^{o}C. NIS (0.229 g, 1.01 mmol) and TfOH (22 µL, 0.250 mmol)

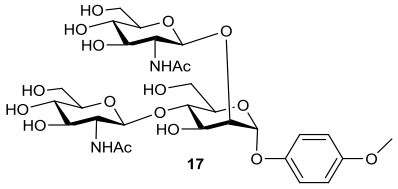
were added slowly, and the resulting reaction mixture was stirred for 1 h. When TLC (ethyl acetate: toluene, 1/9) indicated formation of product with consumption of starting material, the reaction was quenched by adding Et_3N then filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ (2 x 50 mL), aqueous $Na_2S_2O_3$ (2 x 50 mL), and brine (50 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 10% EA in toluene) to afford **S22h** (0.610 g, 82%) as a pale yellow solid. TLC (ethyl acetate: toluene = 1/9, v/v): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.50 (m, 8H), 7.47-7.05 (m, 20H), 7.02-6.82 (m, 10H), 6.66 (d, *J* = 8.5 Hz, 2H), 6.48 (d, *J* = 8.6 Hz, 2H), 5.38 (s, 1H), 5.17 (d, *J* = 8.4 Hz, 1H), 5.21 (t, *J* = 10.3 Hz, 1H), 4.85 (d, *J* = 8.6 Hz, 1H), 3.29-3.24 (m, 1H), 4.94 (d, *J* = 8.4 Hz, 1H), 4.76-4.69 (m, 2H), 4.57 (d, *J* = 7.8 Hz, 1H), 4.53 (d, *J* = 7.2 Hz, 1H), 4.45-4.19 (m, 9H), 4.10-4.06 (m, 2H), 3.99-3.94 (m, 2H), 3.63 (s, 3H), 3.56 - 3.55 (m, 6H), 3.44-3.25 (m, 2H), 3.00 (t, *J* = 10.3 Hz, 2H), 1.99 (s, 3H); ^{13}C NMR (150 MHz, $CHCl_3$): δ 170.0, 154.9, 150.7, 146.8, 138.6, 137.9, 137.4, 137.1, 136.9, 133.9, 132.7, 129.24, 128.69, 128.52, 128.34, 128.25, 127.9, 127.72, 127.33, 126.38, 123.56, 117.90, 114.47, 101.43. 99.38, 83.11, 78.85, 74.79, 74.27, 73.94, 73.76, 72.80, 72.34, 71.43, 70.26, 69.23, 68.90, 66.00, 58.49, 56.8, 56.7, 55.90, 55.8, 21.8; ESI-MS: *m/z* calcd for $C_{85}H_{80}N_2O_{20}$; 1448.5153 found 1449.5678 $(M + H)^+$.



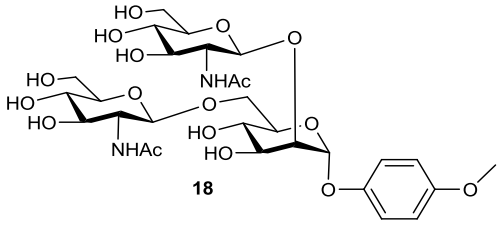
16

p-methoxyphenyl-O-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (16): Compound **S22c** (0.105 g, 0.107 mmole) was deprotected by following general procedure 2 (method 1) to get the title compound **16** (0.035 g, 66%) as a white solid. ^{1}H NMR (400 MHz, D_2O): δ 7. 08 (d, *J* = 9.6 Hz, 2H), 6.92 (d, *J* = 9.1 Hz, 2H), 5.43 (s, 1H), 4.60 (d, *J* = 8.4 Hz, 1H), 4.25 (t, *J* = 2.3 Hz, 1H), 4.01 (dd, *J* = 3.2 & 10.1 Hz, 1H), 3.87 (dd, *J* = 3.1 & 12.2 Hz, 1H), 3.80 (dd, *J* = 3.0 & 12.8 Hz, 1H), 3.78 (s, 3H), 3.72- 3.67 (m, 3H), 3.61-3.52 (m,

3H), 3.46- 3.40 (m, 2H), 1.99 (s, 3H), ^{13}C NMR (150 MHz, D_2O): δ 174.64, 170.85, 154.46, 149.57, 118.60, 114.83, 99.57, 96.50, 76.24, 75.67, 73.35, 73.10, 69.67, 69.28, 66.90, 61.14, 60.40, 55.55, 55.20; ESI-MS: *m/z* calcd for $C_{21}H_{31}NO_1$; 489.1738 found 512.1715 $(M + Na)^+$.

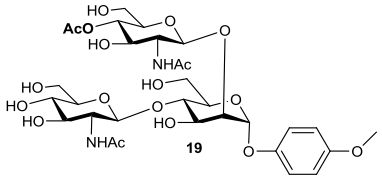


***p*-methoxyphenyl-O-di-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2),(1→4)-α-D-mannopyranoside (17):** Compound **S22f** (0.125 g, 0.086 mmol) was deprotected by following general procedure 2 (method 1) to get the title compound **17** (0.42 g, 66%) as a white solid. 1H NMR (400 MHz, D_2O): δ 7. 10 (d, *J* = 8.8 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 5.39 (s, 1H), 4.53 (d, *J* = 8.2 Hz, 1H), 4.50 (d, *J* = 7.8 Hz, 1H), 4.25 (s, 1H), 4.20 (d, *J* = 7.8 Hz, 1H), 4.00 (dd, *J* = 3.2 and 7.2 Hz, 1H), 3.71 (s, 3H), 3.67-3.74 (m, 15H), 2.02 (s, 3H), 1.91 (s, 3H); 13C NMR (150 MHz, D_2O): δ 174.48, 147.04, 154.49, 149.86, 118.53, 114.97, 100.80, 99.64, 96.55, 76.40, 75.71, 75.66, 73.74, 73.01, 72.63, 69.74, 69.27, 69.19, 67.32, 60.72, 60.60, 60.45, 59.05, 55.62, 55.34, 55.22, 22.24, 22.01; ESI-MS: *m/z* calcd for $C_{29}H_{44}N_2O_{17}$; 693.2713 found 693.2688 $(M + H)^+$.

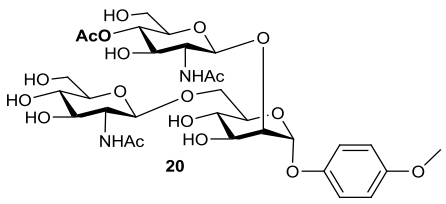


***p*-methoxyphenyl-O-di-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2),(1→6)-α-D-mannopyranoside (18)**: Compound **S22h** (0.200 g, 0.138 mmol) was deprotected by following general procedure 2 (method 1) to get the title compound **18** (0.60 g, 63%) as a white solid. ^{1}H NMR (400 MHz, D_2O): δ 7.10 (d, *J* = 8.8Hz, 2H), 6.96 (d, *J* = 8.2 Hz, 2H), 5.44 (s, 1H), 4.60 (d,

J = 7.5Hz, 1H), 4.52 (d, *J* = 7.3Hz, 1H), 4.31 (s, 1H), 4.18 (d, *J* = 2.8 Hz, 1H), 3.90 (t, *J* = 10.7 Hz, 2H), 3.80 (s, 3H), 3.77-3.70 (m, 6H), 3.56-3.44 (m, 8H), 2.02 (s, 6H); ^{13}C NMR (150 MHz, $CHCl_3$): δ 172.7, 171.9, 157.9, 150.3, 118.5, 114.9, 100.2, 99.4, 99.0, 75.74, 74.2, 73.9, 72.1, 70.3, 68.7, 68.3, 68.2, 55.9, 55.6, 55.1, 20.1; ESI-MS: m/z calcd for $C_{29}H_{44}N_2O_{17}$; 692.2532 found 715.2518 (*M* + Na)+.



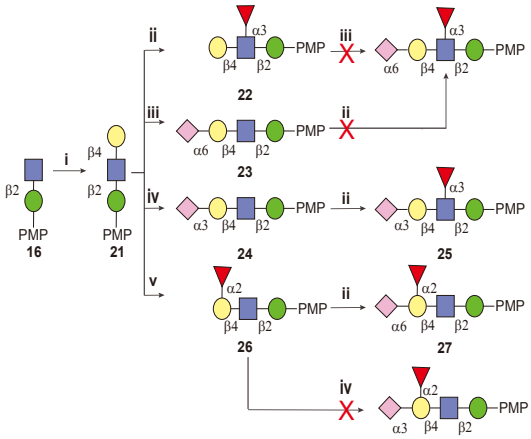
***p*-methoxyphenyl-O-(4-O-acetyl-2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-O-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→4)-α-D-mannopyranoside (19)**: A mixture of **S22f** (0.610 g, 0.421 mmol) and 10 mL of ethylene diamine: *n*-BuOH (1:4) was stirred at 90 ^{o}C for overnight. Volatiles were then evaporated and the crude product was reacted with 10 mL Ac_2O/pyridine (1:2) for overnight. The solvents were removed using high vacuum and product was purified by flash column chromatography (acetone: toluene, 2/8, v/v). The product was dissolved in 10 mL MeOH: H_2O: HCOOH (6:3:1), $Pd(OH)_2$ (50% by weight) was added and the reaction mixture was hydrogenated for overnight. The reaction mixture was filtered through Celite and concentrated in *vacuo.* The residue was purified by Bio-Gel P-2 (BIO-RAD) column chromatography using water as eluent, and the product was the lyophilized to get **19** (0.210 g, 67%) as a white color powder. ^{1}H NMR (400 MHz, D_2O): δ 7. 01 (d, *J* = 9.2 Hz, 2H), 6.90 (d, *J* = 9.8 Hz, 2H), 5.40 (s, 1H), 4.61 (d, *J* = 8.0 Hz, 1H), 4.52 (d, *J* = 8.4 Hz, 1H), 4.25 (d, *J* = 2.1 Hz, 1H), 4.73 (dd, *J* = 1.2 & 7.2 Hz, 1H), 3.92 (d, *J* = 12.3 Hz, 1H), 3.74 (s, 3H), 3.72-3.67 (m, 8H), 3.60-3.41 (m, 7H), 2.12 (s, 3H), 2.03 (s, 6H); ^{13}C NMR (150 MHz, D_2O): δ 174.67, 174 17, 172.91, 154.43, 149.58, 118.53, 118.37, 114.81, 101.48, 99.70, 96.04,77.51, 76.00, 75.75, 73.50, 73.39, 71.74, 71.06, 70.93, 69.57, 69.34, 68.04, 60.58, 60.47, 60.00, 55.55, 55.39, 55.13, 22.24, 21.95, 20.17, 20.03; ESI-MS: *m/z* calcd for $C_{31}H_{46}N_2O_{18}$; 735.2818 found 735.2780 $(M + H)^+$.



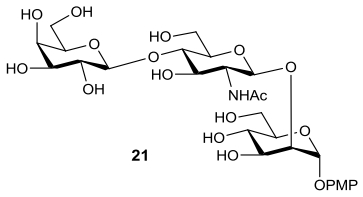
***p*-methoxyphenyl-O-(4-O-acetyl-2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-O-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→6)-α-D-mannopyranoside (20)**: A mixture of **S22h** (0.350 g, 0.241 mmol) and 10 mL of ethylene diamine: *n*BuOH (1:4) was stirred at 90 ^{o}C for overnight. Volatiles were then evaporated and the crude product was reacted with 10 mL Ac_2O/pyridine (1:2) for overnight. The solvents were removed using high vacuum and product was purified by flash column chromatography (acetone: toluene, 2/8, v/v). The product was dissolved in 10 mL MeOH: H_2O: HCOOH (6:3:1), Pd $(OH)_2$ (50% by weight) was added and the reaction mixture was hydrogenated for overnight. The reaction mixture was filtered through Celite and concentrated in *vacuo.* The residue was purified by Bio-Gel P-2 (BIO-RAD) column chromatography using water as eluent, and the product was the lyophilized to get **20** (0.120 g, 70%) as a white color powder. ^{1}H NMR (400 MHz, D_2O): δ 7. 08 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.2 Hz, 2H), 5.38 (s, 1H), 4.66 (d, *J* = 8.0 Hz, 1H), 4.48 (d, *J* = 8.2 Hz, 1H), 4.38-4.27 (m, 2H), 4.19 (t, *J* = 2.8 Hz, 1H), 4.09 (d, *J* = 12.2 Hz, 1H), 3.98 (dd, *J* = 2.8 and 7.8 Hz, 1H), 3.84 (d, *J* = 12.3 Hz, 2H), 3.75 (s, 3H), 3.67-3.33 (m, 11H), 1.93 (s, 3H), 1.91 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (150 MHz, D_2O): δ 174.41, 173.93, 173.75, 154.47, 149.86, 118.53, 118.48, 114.93, 100.84, 99.71, 96.50, 76.76, 75.66, 73.75, 73.27, 72.74, 72.60, 69.76, 69.47, 69.24, 69.12, 67.28,62.94, 60.62, 55.60, 55.32, 55.22, 22.30, 22.06, 20.03; ESI-MS: *m/z* calcd for $C_{31}H_{46}N_2O_{18}$; 735.2818 found 735.2769 $(M + H)^{+}$.

Preparation of linear module. As depicted in scheme S23, **t**he preparation of linear modules was commensed with enzymatic β-1,4-galctosylation of GlcNAc residue of acceptor **16** to form LacNAc moiety **21**. Modules **21** was then underwent action of α-1,3- fucosyltransferase, α-2,6-sialyltransferase, α-2,3- sialyltransferase, and α-1,3- fucosyltransferase to obtain modules **22**, **23**, **24,** and **25** respectively. Presnece of α-1,3 fucose residue on GlcNAc restrict addition of sialic

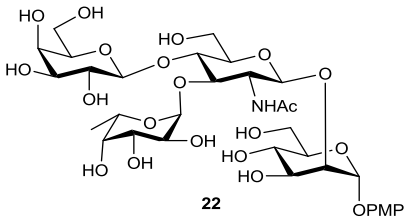
acid on adjacent galactose at both 3 and 6 positions. Interstingly, α-2,3-sialylated LacNAc **24** was found to be the substarte of α-1,3- fucosyltransferase to get **25**, but not the α-2,6-sialylated LacNAc **23**. More striking to us was the α-1,2- fucosylated LacNAc **26** was the substarte of α-2,6- sialyltransferase, but not of α-2,3- sialyltransferase. Unique substrate specificities of FucTs and SiaTs allowed us to establish a rapid access to more diverse type of modules for *N*-glycan synthesis.



Scheme S23 | Preparation of linear modules. i, UDP-galactose, β 1, 4-GalT; **ii**, GDP-fucose, α 1, 3-FucT; **iii**, CMP-Neu5Ac, α 2, 6-SiaT; **iv**, CMP-Neu5Ac, α 2, 3-SiaT; **v**, GDP-fucose, α 1, 2-FucT.

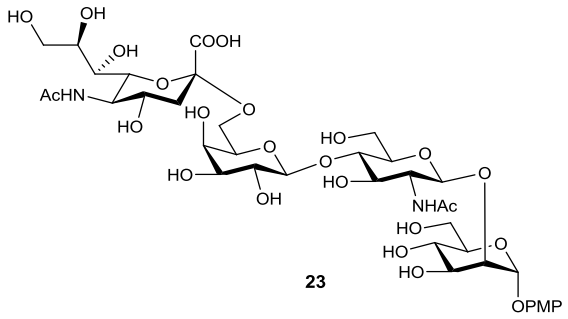


***p*-methoxyphenyl-O-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (21):** Compound **16** (100 mg, 0.204 mmol) was galactosylated by using general procedure **4** to get **21** (115 mg, 86 %) as amorphous white solids. ^{1}H NMR (400 MHz, D_2O): δ 7.10 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 8.1 Hz, 2H), 5.44 (s, 1H), 4.59 (d, J = 8.4 Hz, 1H), 4.49 (d, J = 8.2 Hz, 1H), 4.45 (s, 1H), 4.00-3.75 (m, 17H), 3.60 (s, 3H), 2.01 (s, 3H); ESI-MS: *m/z* calcd for $C_{27}H_{41}NO_{17}$; 652.2447 found 674.2262 $(M + H)^+$.



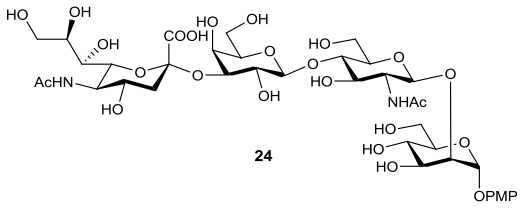
22

***p*-methoxyphenyl-O-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranosyl]-(1→2)-α-D-mannopyranoside (22):** Compound **21** (80 mg, 0.122 mmol) was fucosylated by using general procedure **5** to afford **22** (82 mg, 84%) as white solid after lyophilization. ^{1}H NMR (400 MHz, D_2O): δ 7.15 (d, *J* = 9.2 Hz, 2H), 7.00 (d, *J* = 9.1 Hz, 2H), 5.45 (s, 1H), 5.12 (d, *J* = 4.1 Hz, 1H), 4.67 (d, *J* = 7.8 Hz, 2H), 4.44 (d, *J* = 8.4 Hz, 1H), 4.05 (s, 1H), 4.01 (dd, *J* = 3.2 and 7.8 Hz, 1H), 3.98 (t, *J* = 10.2 Hz, 2H), 3.80-3.70 (m, 6H), 3.79 (s, 3H), 3.70-3.40 (m, 11H), 2.06 (s, 3H), 1.18 (d, *J* = 6.4 Hz, 3H); ESI-MS: *m/z* calcd for $C_{33}H_{51}NO_{21}$; 797.7570 found 820.2837 $(M + Na)^+$.



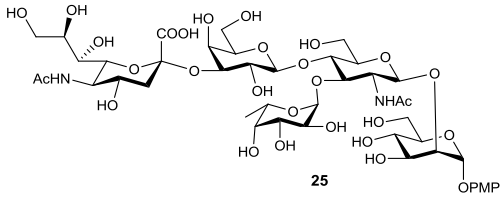
23

***p*-methoxyphenyl-O-[5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyrano-sylonate-(2→6)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (23):** Compound **21** (150 mg, 0.184 mmol) was **α** 2,6-sialylated by using general procedure **3** to afford **23** (169 mg, 90%) as white solid after lyophilization. ^{1}H NMR (400 MHz, D_2O): δ 7. 10 (d, *J* = 9.2 Hz, 2H), 7.08 (d, *J* = 9.1 Hz, 2H), 5.49 (s, 1H), 4.64 (d, *J* = 8.1 Hz, 1H), 4.40 (d, *J* = 8.2 Hz, 1H), 4.26 (t, *J* = 2.1 Hz, 1H), 4.01-3.80 (m, 7H), 3.74 (s, 3H), 3.66-3.58 (m, 17H), 2.63(dd, *J* = 4.4 and 12.8 Hz, 1H), 2.07 (s, 3H), 1.97 (s, 3H), 1.68 (t, 1H); ESI-MS: *m/z* calcd for $C_{38}H_{58}N_2O_{25}$; 942.3245 found 941.3269 $(M - H)^-$.



24

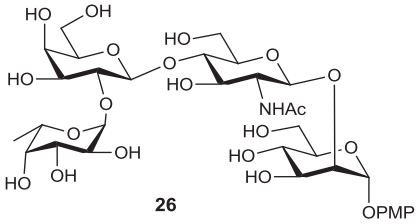
***p*-methoxyphenyl-O-[5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyrano-sylonate-(2→3)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranoside (24):** Compound **21** (10 mg, 15.3 µmol) was **α** 2,3-sialylated by using general procedure **3** to afford **24** (11.5 mg, 80%) as white solid after lyophilization. ^{1}H NMR (400 MHz, D_2O): δ 7. 16 (d, *J* = 9.2 Hz, 2H), 7.03 (d, *J* = 9.5 Hz, 2H), 5.49 (s, 1H), 4.67 (d, *J* = 8.4 Hz, 1H), 4.56 (d, *J* = 8.4 Hz, 1H), 4.32 (t, *J* = 2.1 Hz, 1H), 4.15 (dd, *J* = 3.2 & 7.5 Hz, 1H), 4.10-3.98 (m, 4H), 3.95-3.85 (m, 6H), 3.84 (s, 3H), 3.80-3.50 (m, 13H), 2.79 (dd, *J* = 4.8 and 12.1 Hz, 1H), 2.09 (s, 3H), 2.07 (s, 3H), 1.85 (t, 1H) ; ESI-MS: *m/z* calcd for $C_{38}H_{58}N_2O_{25}$; 942.3245 found 941.3312 $(M\text{-}H)^-$.



25

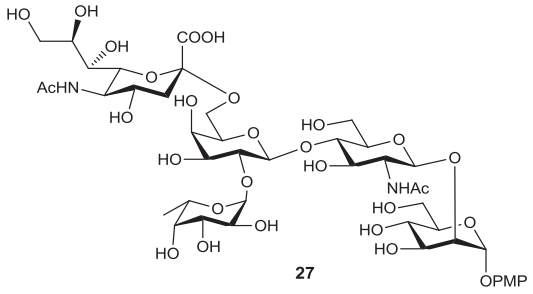
***p*-methoxyphenyl-O-[5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyrano-sylonate-(2→3)-β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranosyl]-(1→2)-α-D-mannopyranoside (25):** Compound **24** (8 mg, 8.5 µmol) was fucosylated by using general procedure **5** to afford **25** (6.5 mg, 70%) as white solid after lyophilization. ^{1}H NMR (400 MHz, D_2O): δ 7. 14 (d, *J* = 6.8 Hz, 2H), 6.98 (d, *J* = 7.2 Hz, 2H), 5.46 (s, 1H), 5.12 (d, *J* = 4.2 Hz, 1H), 4.67 (d, *J* = 8.4 Hz, 1H), 4.30 (t, *J* = 2.3 Hz, 1H), 4.10 (dd, *J* = 3.0 & 7.8 Hz, 1H), 4.00-3.80 (m, 14H), 3.79 (s, 3H), 3.75-3.50 (m, 13H), 2.75 (dd,

J = 4.0 and 12.0 Hz, 1H), 2.03 (s, 3H), 2.01(s, 3H), 1.76 (t, 1H), 1.17 (d, 3H, Fuc-Me); ESI-MS: *m/z* calcd for $C_{44}H_{68}N_2O_{29}$; 1088.3857 found 1087.3850 $(M - H)^-$.



26

p-methoxyphenyl-O-[α-L-fucopyranosyl-(1→2)-β-D-galactopyranosyl]-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl]-(1→2)-α-D-mannopyranoside (26): Compound **21** (3 mg, 4.6 μmol) was fucosylated by using general procedure **5** to afford **26** (2.1 mg, 53%) as white solid after lyophilization. ^{1}H NMR (400 MHz, D_2O): δ 7.17 (d, *J* = 7.2 Hz, 2H), 7.01 (d, *J* = 10.1 Hz, 2H), 5.49 (s, 1H), 5.33 (s, 1H), 4.67 (d, *J* = 8.2 Hz, 1H), 4.56 (d, *J* = 8.2 Hz, 1H), 4.33 (m, 1H), 4.25 (q, 1H), 3.98 (dd, *J* = 3.1 and 7.2 Hz, 1H), 3.96 (dd, *J* = 1.8 and 7.2 Hz, 1H), 3.85-3.50 (m, 20H), 3.40 (m, 1H), 1.97 (s, 3H), 1.14 (d, *J* = 6.4 Hz, 3H) ; ESI-MS: *m/z* calcd for $C_{33}H_{51}NO_{21}$; 797.2954 found 820.2922 $(M + Na)^+$.

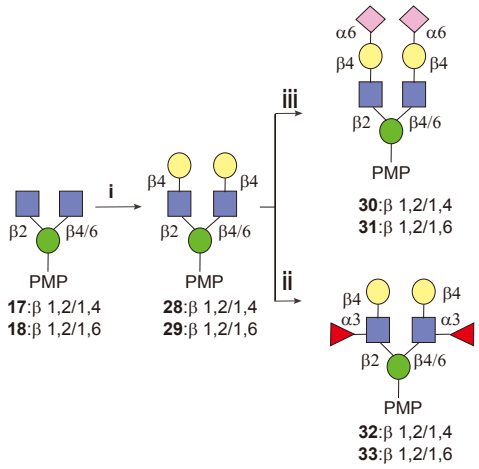


27

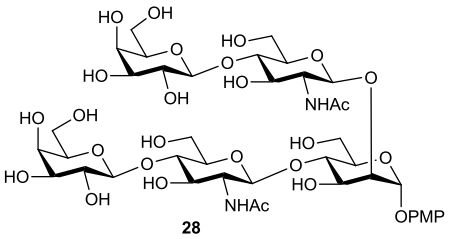
p-methoxyphenyl-O-[5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyrano-sylonate-(2→6)-[α-L-fucopyranosyl-(1→2)-β-D-galactopyranosyl]-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl]-(1→2)-α-D-mannopyranoside (27): Compound **26** (2.0 mg, 2.7 μmol) was α 2,6-sialylated by using general procedure **3** to afford **27** (1.8 mg, 66%) as white solid after lyophilization. ^{1}H NMR (400 MHz, D_2O): δ 7.08 (d, *J* = 9.5 Hz, 2H), 6.91 (d, *J* = 9.2 Hz, 2H), 5.49 (s, 1H), 5.27 (s, 1H), 4.59 (d, *J* = 8.2 Hz, 1H), 4.47 (d, *J* = 8.1 Hz, 1H), 4.22 (bs, 1H), 4.12 (d, *J* = 6.8 Hz, 1H), 4.00-3.49 (m, 30H), 2.63 (dd, *J* = 3.2 and 12.0 Hz, 1H), 2.01(s,

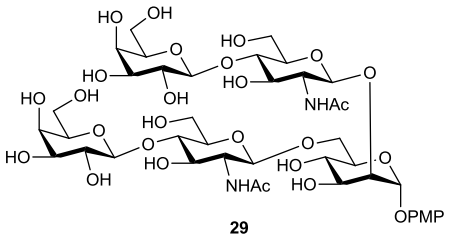
3H), 1.97 (s, 3H), 1.67 (t, 1H), 1.19 (d, 3H, Fuc-Me) ; ESI-MS: *m/z* calcd for $C_{44}H_{68}N_2O_{29}$; 1088.3857 found 1087.3814 $(M - H)^-$.

Preparation of symmetrically branched modules.



Scheme S24 | Preparation of symmetrically branched modules. i, β-1, 4 GalT, UDP-Gal; ii, α1,3- fucosyltransferase, GDP-fucose; iii, α 2,6- sialyltransferase, CMP-β-D-Sialic acid; .



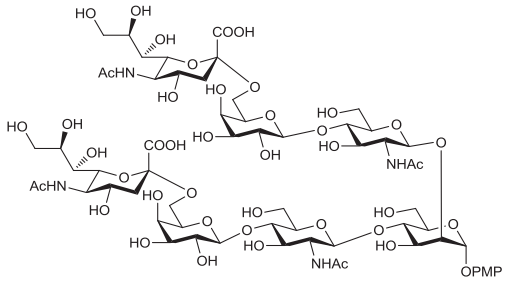


Compound 28 and 29: Compound **17** (10 mg, 14.3 µmol) and **18** (10 mg, 14.3 µmol) were galactosylated by using general procedure 4 to get **28** (10 mg, 71%) and **29** (9 mg, 61%) as amorphous white solids.

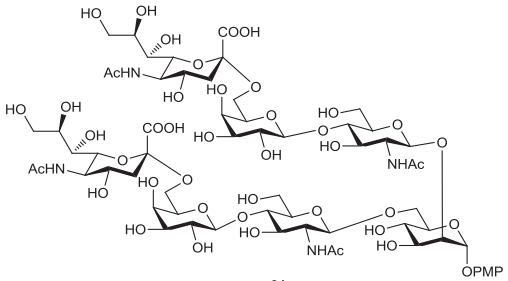
p-methoxyphenyl-O-di-[β-D-galactopyranosyl-(1→4) -2-acetamido-2-deoxy-β-D-glucopyranosyl]-(1→2), (1→4) -α-D-mannopyranoside (28): ^{1}H NMR (400 MHz, D_2O): δ 7.11 (d, *J* = 9.2 Hz, 2H), 6.95 (d, *J* = 8.5 Hz, 2H), 5.44 (s, 1H), 4.65 (d, *J* = 8.9 Hz, 1H), 4.58 (d, *J* = 9.2 Hz, 1H), 4.45 (dd, *J* = 3.8 & 9.2 Hz, 2H), 4.30 (t, *J* = 2.1 & 6.5 Hz, 1H), 4.18 (dd, *J* = 3.2

& 7.8 Hz, 1H), 4.00 (t, *J* = 10.8 Hz, 2H), 3.90 (d, *J* = 8.2 Hz, 2H), 3.78 (s, 3H), 3.75-3.64 (m, 20H), 3.58-3.49 (m, 4H), 2.02 (s, 3H), 2.01 (s, 3H); ESI-MS: *m/z* calcd for $C_{41}H_{64}N_2O_{27}$; 1016.9564 found 1039.3607 $(M + Na)^+$.

p-methoxyphenyl-O-di-[β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl]-(1→2), (1→6)-α-D-mannopyranoside (29): ^{1}H NMR (400 MHz, D_2O): δ 7.02 (d, *J* = 9.0 Hz, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 5.32 (s, 1H), 4.55 (d, *J* = 4.3 Hz, 1H), 4.41 (d, *J* = 8.2 Hz, 1H), 4.34 (dd, *J* = 13.1, 7.9 Hz, 2H), 4.16 (s, 1H), 4.00 (d, *J* = 11.0 Hz, 1H), 3.84-3.95 (m, 2H), 3.70-3.81 (m, 9H), 3.49-3.68 (m, 16H), 3.37-3.44 (m, 4H), 1.94 (s, 3H), 1.82 (s, 3H); ESI-MS: m/z calcd for $C_{41}H_{64}N_2NaO_{27}$; 1039.3594 found 1039.3551.



30

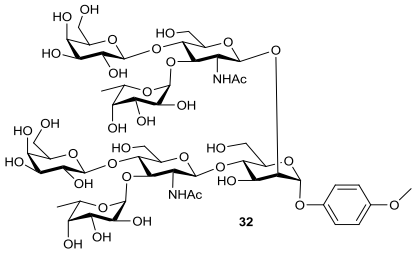


31

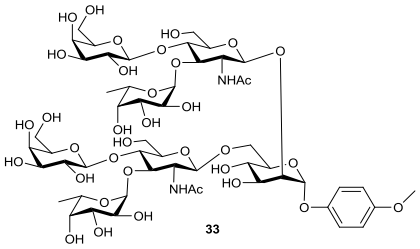
Compound 30 and 31: Compound **28 (**8 mg, 7.3 μmol**)** and **29** (8 mg, 7.3 μmol) were sialylated by using general procedure 3 to afford **30** (9 mg, 78%) and **31** (7.5 mg, 65%) as a white solid after lyophilization.

p-methoxyphenyl-O-di-[5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosylonate-(2→6)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl]-(1→2), (1→4)-α-D-mannopyranoside (30): ^{1}H NMR (400 MHz, D_2O): δ 7.12 (d, *J* = 9.8 Hz, 2H), 6.98 (d, *J* = 9.3 Hz, 2H), 5.46 (s, 1H), 4.63 (d, *J* = 8.4 Hz, 1H), 4.58 (d, *J* = 8.2 Hz, 1H), 4.42 (d, *J* = 7.8 Hz, 2H), 4.32 (t, *J* = 3.2 Hz, 1H), 4.20 (dd, *J* = 3.2 & 7.2 Hz, 1H), 4.03-3.85 (m, 4H), 3.82-3.40 (m, 41H), 2.58 (dd, *J* = 3.2 & 10.3 Hz, 2H), 2.05 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.53 (m, 2H) ; ESI-MS: *m/z* calcd for $C_{63}H_{98}N_4O_{43}$; 1599.4620 found 798.2775 $(M - H)^{2-}$.

***p*-methoxyphenyl-O-di-[5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyrano-sylonate-(2→6)-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl]-(1→2), (1→6)-α-D-mannopyranoside (31):** ^{1}H NMR (600 MHz, D_2O): δ 7.05 (d, *J* = 9.2 Hz, 2H), 6.95 (d, *J* = 9.2 Hz, 2H), 5.36 (d, *J* = 1.6 Hz, 1H), 4.59 (d, *J* = 8.2 Hz, 1H), 4.46 (d, *J* = 8.1 Hz, 1H), 4.36 (d, *J* = 7.9 Hz, 1H), 4.32 (d, *J* = 7.9 Hz, 1H), 4.20 (dd, *J* = 3.4, 1.8 Hz, 1H), 4.06 (d, *J* = 10.3 Hz, 1H), 3.86-3.98 (m, 4H), 3.64-3.86 (m, 19H), 3.53-3.62 (m, 13H), 3.37-3.50 (m, 9H), 2.58 (ddd, *J* = 12.0, 4.4, 2.1 Hz, 2H), 1.98 (s, 3H), 1.94 (s, 3H), 1.94 (s, 3H), 1.87 (s, 3H), 1.63 (td, *J* = 12.2, 8.6 Hz, 2H); ESI-MS : m/z calcd for $C_{63}H_{98}N_4NaO_{43}$; 1621.5479 found 1621.5473.

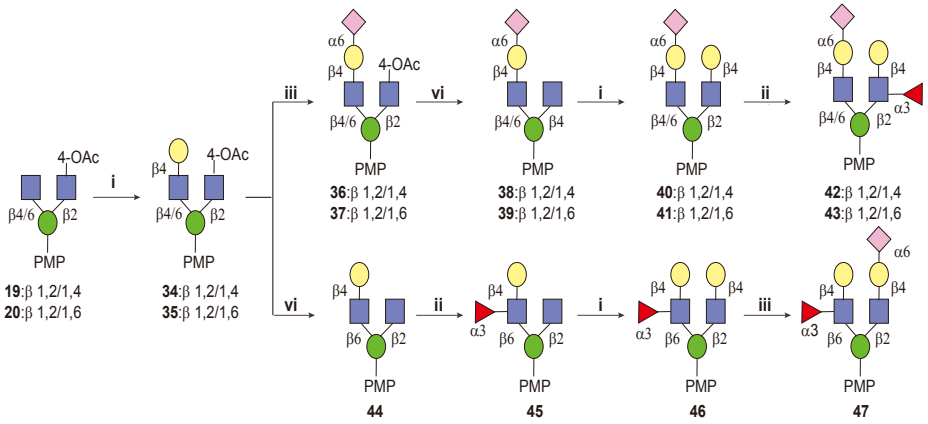


***p*-methoxyphenyl-O-di-{β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranosyl]}-(1→2),(1→4)-α-D-mannopyranoside (32):** Compound **28** (15 mg, 14.7 µmol) was fucosylated by using general procedure 5 to get **32** (14 mg, 73%) as amorphous white solids. ^{1}H NMR (400 MHz, D_2O): δ 7.13 (d, *J* = 9.2 Hz, 2H), 6.99 (d, *J* = 9.0 Hz, 2H), 5.44 (d, *J* = 3.2 Hz, 1H), 5.12 (d, *J* = 4.1 Hz, 1H), 5.10 (d, *J* = 4.0 Hz, 1H), 4.81 (d, *J* = 8.4 Hz, 2H), 4.68 (d, *J* = 7.4 Hz, 1H), 4.58 (d, *J* = 7.2 Hz, 1H), 4.45 (dd, *J* = 3.2 & 8.4 Hz, 2H), 4.31 (t, *J* = 3.2 Hz, 1H), 4.20 (dd, *J* = 3.2 & 8.4 Hz, 1H), 4.09-3.84 (m, 20H), 3.82 (s, 3H), 3.80-3.40 (m, 14H), 2.06 (s, 6H), 1.17 (d, *J* = 6.4 Hz, 6H); ESI-MS: m/z calcd for $C_{53}H_{84}N_2O_{35}$; 1308.4855 found 1309.4911 $(M + H)^+$.

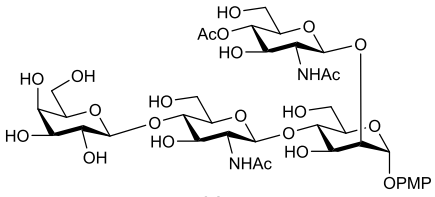


***p*-methoxyphenyl-O-di-{β-D-galactopyranosyl-(1→4)-[α-L-fucopyranosyl-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranosyl]}-(1→2),(1→6)-α-D-mannopyranoside (33):** Compound **29** (15 mg, 14.7 µmol) was fucosylated by using general procedure 5 to get **33** (15.5 mg, 81%) as amorphous white solids. ^{1}H NMR (400 MHz, D_2O): δ 7.17 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 5.42 (s, 1H), 5.14 (d, *J* = 4.0 Hz, 1H), 5.09 (d, *J* = 4.0 Hz, 1H), 4.87-4.85 (m, 2H), 4.60 (d, *J* = 7.2 Hz, 1H), 4.56 (q, 2H), 4.30 (m, 1H), 4.15 (d, *J* = 12.2 Hz, 1H), 4.06 (dd, *J* = 3.2 & 7.8 Hz, 1H), 4.00-3.45 (m, 37), 2.06 (s, 3H), 1.95 (s, 3H), 1.19 (d, *J* = 6.5 Hz, 6H) ; ESI-MS : m/z calcd for $C_{53}H_{84}N_2O_{35}$; 1308.4855 found 1331.3561 $(M + Na)^+$.

Preparation of asymmetrically branched module.

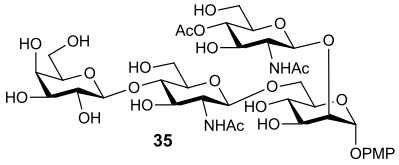


Scheme S25 | Preparation of assymetric module. UDP-galactose, β 1, 4-GalT; **ii**, GDP-fucose α1, 3-FucT; **iii**, CMP-Neu5Ac, α2, 6-SiaT; **vi**, NaOH.



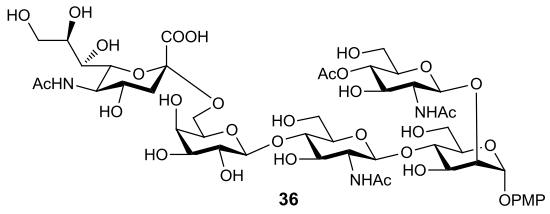
34

p-methoxyphenyl-O-(4-O-acetyl-2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-O-(β-D-galactopyranosyl-(1→4)-O-2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→4)-α-D-mannopyranoside (34): Compound **19** (15 mg, 20.4 µmol) was galactosyalated using general procedure 4 to afford the **34** (12.5 mg, 68%) as amorphous white solids. ^{1}H NMR (600 MHz, D_2O): δ 7.01 (d, *J* = 9.2 Hz, 2H), 6.88 (d, *J* = 9.2 Hz, 2H), 5.34 (d, *J* = 1.8 Hz, 1H), 4.56 (d, *J* = 8.5 Hz, 1H), 4.45 (d, *J* = 8.1 Hz, 1H), 4.37 (d, *J* = 7.7 Hz, 1H), 4.20-4.33 (m, 2H), 4.16-4.20 (m, 1H), 4.07 (dd, *J* = 8.7, 3.0 Hz, 1H), 3.86-3.94 (m, 1H), 3.81 (d, *J* = 3.4 Hz, 1H), 3.31-3.78 (m, 21H), 2.03 (s, 3H), 1.93 (s, 3H), 1.92 (s, 3H); ESI-MS: m/z calcd for $C_{37}H_{56}N_2NaO_{23}$; 919.9166 found 919.3156.



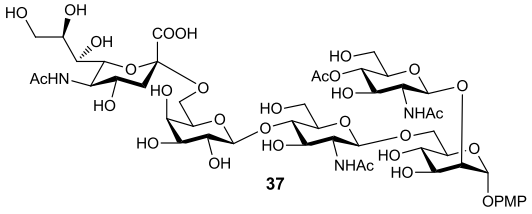
35

p-methoxyphenyl-O-(4-O-acetyl-2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-O-(β-D-galactopyranosyl-(1→4)-O-2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→6)-α-D-mannopyranoside (S27a): Compound **20** (8 mg, 10.9 µmol) was galactosylated by using general procedure 4 to give the **35** (5 mg, 75 %) as amorphous white solids. ^{1}H NMR (600 MHz, D_2O): δ 7.12 (d, *J* = 9.1 Hz, 2H), 7.01 (d, *J* = 9.8 Hz, 2H), 5.40 (s, 1H), 4.67 (d, *J* = 8.4 Hz, 1H), 4.49 (d, *J* = 8.4 Hz, 1H), 4.40 (d, *J* = 8.3 Hz, 2H), 4.31 (dd, *J* = 3.1 & 7.8 Hz, 1H), 4.21 (t, *J* = 3.1 Hz, 1H), 4.08 (d, *J* = 12.3 Hz, 2H), 4.00 (dd, *J* = 3.2 & 8.1 Hz, 1H), 3.90-3.48 (m, 3H), 3.80 (s, 3H), 3.75-3.47 (m, 15H), 2.15 (s, 3H), 2.0 (s, 3H), 1.98 (s, 3H); ESI-MS: *m/z* calcd for $C_{37}H_{56}N_2O_{23}$; 896.3162 found 919.3164 $(M+Na)^+$.



36

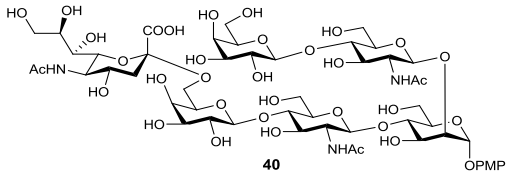
***p*-methoxyphenyl-O-(4-O-acetyl-2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-O-(5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyrano-sylonate-(2→6)-β-D-galactopyranosyl-(1→4)-O-2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→4)-α-D-mannopyranoside (36)**: Compound **34** (10 mg, 11.1 µmol) was α 2,6-sialylated by using general procedure 3 to afford **36** (11.2 mg, 84%) as white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O): δ 7.02 (d, *J* = 9.2 Hz, 2H), 6.89 (d, *J* = 9.2 Hz, 2H), 5.35 (d, *J* = 2.0 Hz, 1H), 4.55 (dd, *J* = 18.4, 8.4 Hz, 1H), 4.48 (d, *J* = 7.9 Hz, 1H), 4.17-4.37 (m, 4H), 4.05-4.12 (m, 1H), 3.29-3.97 (m, 30H), 2.56 (dd, *J* = 12.4, 4.7 Hz, 1H), 2.04 (s, 3H), 1.96 (s, 3H), 1.92 (s, 3H), 1.92 (s, 3H), 1.60 (t, *J* = 12.2 Hz, 1H); ESI-MS: *m/z* calcd for $C_{48}H_{72}N_3O_{31}$; 1186.4155 found 1186.4175.



37

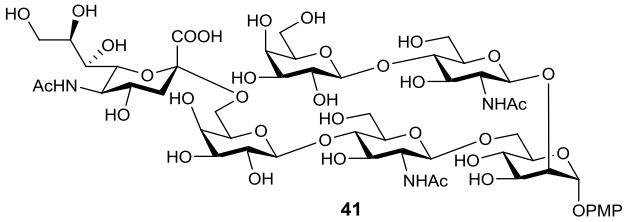
***p*-methoxyphenyl-O-(4-O-acetyl-2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-O-(5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyrano-sylonate-(2→6)-β-D-galactopyranosyl-(1→4)-O-2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→6)-α-D-mannopyranoside (37)**: Compound **35** was α2,6-sialylated by using general procedure 3 to afford **37** (5.1 mg, 77%) as white solid after lyophilization. ^{1}H NMR (600 MHz, D_2O): δ 7.11 (d, *J* = 9.1 Hz, 2H), 7.00 (d, *J* = 9.2 Hz, 2H), 5.38 (s, 1H), 4.50 (d, *J* = 8.4 Hz, 1H), 4.36 (d, *J* = 8.2 Hz, 1H), 4.22 (t, *J* = 2.1 Hz, 1H), 4.10 (dd, *J* = 3.1 & 7.8 Hz, 1H), 3.97-3. 85 (m, 4H), 3.77 (s, 3H), 3.73-3.46 (m, 26H), 2.63 (dd, *J* = 3.2 and 7.8 Hz, 1H), 2.09 (s, 3H), 2.01 (s, 3H), 1.99 (s,

3H), 1.94 (s, 3H), 1.65 (t, 1H); ESI-MS: *m/z* calcd for $C_{48}H_{73}N_3O_{31}$; 1187.4144 found 1186.4133 $(M-H)^-$.



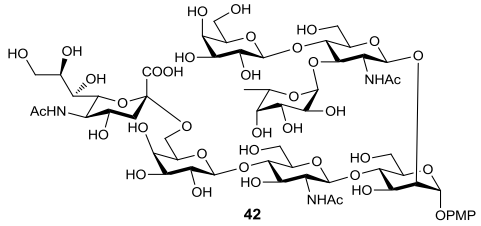
40

***p*-methoxyphenyl-O-(β-D-galactopyranosyl-(1→4)-O-2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-O-(5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyrano-sylonate-(2→6)-β-D-galactopyranosyl-(1→4)-O-2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→4)-α-D-mannopyranoside (40)**: To a solution of compound **36** (7 mg, 5.8 µmol) in 0.5 mL H_2O was added NaOH (9.4 mg, 23.6 µmol) and stirred for 4 h. Reaction was neutralized and product was putified by Bio-Gel P-2 chromatography (eluent H_2O) to afford **38** (6.1 mg, 89%) as white solid after lyophilization. Compound **38** (6 mg, 5.3 µmol) and UDP galactose (6.4 mg, 10.6 µmol) were dissolved in Tris buffer (25 mM, pH 7.5) and MnCl2 (20 mM). GalT-1 (150 units) were added to achieve a final concentration of glycan to 5 mM. The resulting reaction mixture was incubated at 37 ^oC for 48 h. The reaction mixture was centrifuged and the supernatant subjected to gel filtration over P2-Biogel (eluent water). Fractions containing the product were combined and lyophilized to give the **40** (5 mg, 73%) as amorphous white solids. ^1H NMR (400 MHz, D_2O) δ 7.02 (d, *J* = 9.2 Hz, 2H), 6.88 (d, *J* = 9.2 Hz, 2H), 5.35 (d, *J* = 1.8 Hz, 1H), 4.56 (d, *J* = 7.9 Hz, 1H), 4.48 (d, *J* = 7.9 Hz, 1H), 4.35 (dd, *J* = 9.6, 7.7 Hz, 2H), 4.27-4.30 (m, 2H), 4.21-4.24 (m, 1H), 4.02-4.20 (m, 6H), 3.87-3.92 (m, 3H), 3.39-3.85 (m, 28H), 2.56 (dd, *J* = 12.4, 4.6 Hz, 1H), 1.96 (s, 3H), 1.93 (s, 3H), 1.92 (s, 3H), 1.60 (t, *J* = 12.2 Hz, 1H); ESI-MS: *m/z* calcd for $C_{52}H_{80}N_3O_{35}$; 1306.4578 found 1306.4617.



41

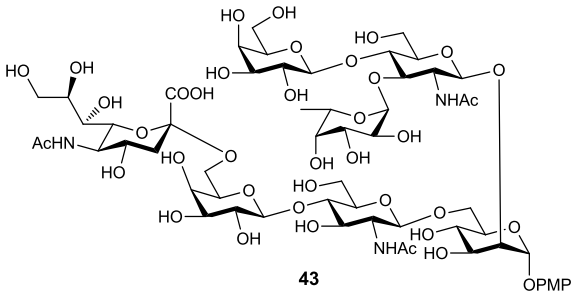
***p*-methoxyphenyl-O-(β-D-galactopyranosyl-(1→4)-O-2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-O-(5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyrano-sylonate-(2→6)-β-D-galactopyranosyl-(1→6)-O-2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→4)-α-D-mannopyranoside (41)**: To a solution of compound **37** (5 mg, 4.2 µmol) in 0.5 mL H_2O was added NaOH (6.7 mg, 16.8 µmol) and stirred for 4 h. Reaction was neutralized and product was putified by Bio-Gel P-2 chromatography (eluent H_2O) to afford **39** (3.8 mg, 79%) as white solid after lyophilization. Compound **39** (3.5 mg, 3.0 µmol) and UDP galactose (3.9 mg, 6.1 µmol) were dissolved in Tris buffer (25 mM, pH 7.5) and MnCl2 (20 mM). GalT-1 (150 units) were added to achieve a final concentration of glycan to 5 mM. The resulting reaction mixture was incubated at 37 ^{o}C for 48 h. The reaction mixture was centrifuged and the supernatant subjected to gel filtration over P2-Biogel (eluent water). Fractions containing the product were combined and lyophilized to give the **41** (3.3 mg, 75%) as amorphous white solids. ^{1}H NMR (400 MHz, D_2O): δ 7.11 (d, *J* = 9.1 Hz, 2H), 7.00 (d, *J* = 9.2 Hz, 2H), 5.38 (s, 1H), 4.64 (d, *J* = 8.1 Hz, 1H), 4.50 (d, *J* = 8.2 Hz, 1H), 4.23 (d, *J* = 8.3 Hz, 1H), 4.38 (d, *J* = 8.0 Hz, 1H), 4.22 (t, *J* = 2.1 Hz, 1H), 4.10 (d, *J* = 12.2 Hz, 1H), 4.01-3. 95 (m, 4H), 3.87-3. 63 (m, 26H), 3.52-3.45 (m, 7H), 2.63 (dd, *J* = 2.1 and 7.8 Hz, 1H), 2.63 (dd, *J* = 3.2 and 7.8 Hz, 1H), 2.01 (s, 3H), 1.99 (s, 3H), 1.93 (s, 3H), 1.67 (t, 1H); ESI-MS: *m/z* calcd for $C_{52}H_{81}N_3O_{35}$; 1307.4567 found 1306.4609 $(M-H)^-$.



42

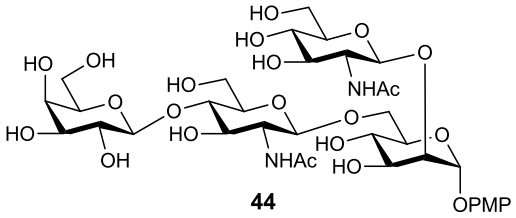
***p*-methoxyphenyl-O-(β-D-galactopyranosyl-(1→4)-O-[α-L-fucopyranosyl-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranosyl]-(1→2)-O-(5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyrano-sylonate-(2→6)-β-D-galactopyranosyl-(1→4)-O-2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→4)-α-D-mannopyranoside (42)**: Compound **40** (2 mg, 1.52

μmol) was α1,3-fucosylated by using general procedure 5 to get **42** (2 mg, 85%) as amorphous white solids. ^{1}H NMR (400 MHz, D_2O): δ 7.16 (d, *J* = 8.8 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 5.45 (s, 1H), 5.08 (d, *J* = 4.1 Hz, 1H), 4.60 (d, *J* = 4.2 Hz, 1H), 4.44 (dd, *J* = 3.5 & 7.9 Hz, 2H), 4.30 (bs, 1H), 4.15 (d, *J* = 8.4 Hz, 1H), 4.09-3.40 (m, 43H), 2.70 (d, *J* = 11.2 Hz, 1H), 2.08 (s, 3H), 2.05 (s, 3H), 1.93 (s, 3H), 1.74 (t, 1H), 1.20 (d, *J* = 6.4 Hz, 3H); ESI-MS: *m/z* calcd for $C_{58}H_{91}N_3O_{39}$; 1453.5245 found 1452.5157 $(M-H)^-$.



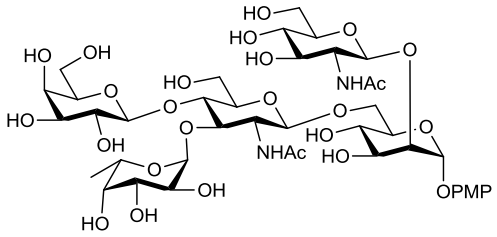
43

***p*-methoxyphenyl-O-(β-D-galactopyranosyl-(1→4)-O-[*α*-L-fucopyranosyl-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranosyl]-(1→2)-O-(5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyrano-sylonate-(2→6)-β-D-galactopyranosyl-(1→4)-O-2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→6)-α-D-mannopyranoside (43):** Compound **41** (4 mg, 3.05 μmol) was α 1,3-fucosylated by using general procedure 5 to get **43** (3.2 mg, 72%) as amorphous white solids. ^{1}H NMR (400 MHz, D_2O): δ 7.21 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 5.74 (s, 1H), 5.72 (d, *J* = 8.1 Hz, 2H), 5.52 (dd, *J* = 3.1 & 7.2 Hz, 1H), 5.40 (s, 1H), 5.01 (d, *J* = 4.2 Hz, 1H), 4.50-3.25 (m, 44H), 2.50 (dd, *J* = 3.1 & 7.2 Hz, 1H), 2.01 (s, 3H), 1.99 (s, 6H), 1.56 (t, 1H), 1.05 (d, 3H, Fuc-Me); ESI-MS: *m/z* calcd for $C_{58}H_{91}N_3O_{39}$; 1453.5245 found 1452.5445 $(M-H)^-$.



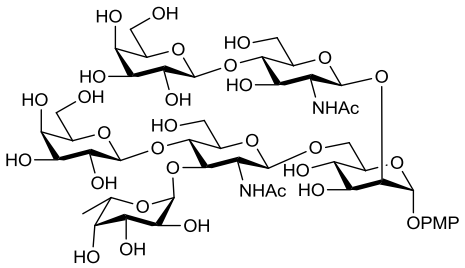
44

***p*-methoxyphenyl-O-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-O-(β-D-galactopyranosyl-(1→4)-O-2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→6)-α-D-mannopyranoside (44)**: To a solution of compound **35** (20 mg, 22.3 µmol) in 0.5 mL H_2O was added NaOH (3.57 mg, 89.2 µmol) and stirred for 4 h. Reaction was neutralized and product was putified by Bio-Gel P-2 chromatography (eluent H_2O) to afford **44** (15.3 mg, 80%) as white solid after lyophilization. ^{1}H NMR (400 MHz, D_2O): δ 7.15 (d, *J* = 9.2 Hz, 2H), 7.06 (d, *J* = 9.8 Hz, 2H), 5.42 (s, 1H), 4.67 (d, *J* = 8.2 Hz, 1H), 4.54 (d, *J* = 8.0 Hz, 1H), 4.47(d, *J* = 8.2 Hz, 1H), 4.32 (t, *J* = 2.1 Hz, 1H), 4.10 (d, *J* = 12.2 Hz, 1H), 4.09 (dd, *J* = 3.2 & 8.2 Hz, 1H), 4.01-3.91(m, 4H), 3.85 (s, 3H), 3.80-3. 40 (m, 17H), 2.03 (s, 3H), 1.98 (s, 3H); ESI-MS: *m/z* calcd for $C_{35}H_{54}N_2O_{22}$; 854.3125 found 877.3062 $(M + Na)^+$.



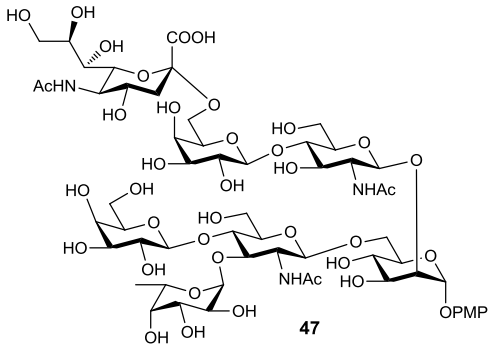
45

***p*-methoxyphenyl-O-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-O-(β-D-galactopyranosyl-(1→4)-O-[α-L-fucopyranosyl-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranosyl]-(1→6)-α-D-mannopyranoside (45)**: Compound **44** (8 mg, 9.3 µmol) was α 1,3-fucosylated by using general procedure **5** to afford **45** (6 mg, 66%) as w hite solid after lyophilization. ^{1}H NMR (400 MHz, D_2O): δ 7.14 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 8.1 Hz, 2H), 5.41 (s, 1H), 5.07 (d, *J* = 4.0 Hz, 1H), 4.64 (d, *J* = 8.2 Hz, 2H), 4.58 (d, *J* = 7.4 Hz, 1H), 4.44 (d, *J* = 8.5 Hz, 1H), 4.28 (t, *J* = 2.1 Hz, 1H), 4.10 (d, *J* = 12.2 Hz, 1H), 4.05 (dd, *J* = 3.1 & 7.2 Hz, 1H), 3.95-3.85 (m, 8H), 3.82 (s, 3H), 3.80-3.33 (m, 16H), 2.04 (s, 3H), 1.93 (s, 3H), 1.17 (d, *J* = 6.8 Hz, 3H); ESI-MS: *m/z* calcd for $C_{41}H_{64}N_2O_{26}$; 1000.2356 found 1023.3599 $(M + Na)^+$.



46

***p*-methoxyphenyl-O-(β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-O-(β-D-galactopyranosyl-(1→4)-O-[α-L-fucopyranosyl-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranosyl]-(1→6)-α-D-mannopyranoside (46)**: Compound **45** (7 mg, 7.2 µmol) was β 1,4-galactosylated by using general procedure 4 to give the **46** (6.5 mg, 80 %) as amorphous white solids. ^{1}H NMR (400 MHz, D_2O): δ 7.16 (d, *J* = 9.4 Hz, 2H), 7.05 (d, *J* = 9.3 Hz, 2H), 5.43 (s, 1H), 5.09 (d, *J* = 4.2 Hz, 1H), 4.83 (d, *J* = 7.5 Hz, 1H), 4.78 (d, *J* = 7.2 Hz, 1H), 4.58 (d, *J* = 8.2 Hz, 1H), 4.48 (d, *J* = 9.5 Hz, 1H), 4.42 (d, *J* = 8.5 Hz, 1H), 4.30 (dd, *J* = 2.1 & 3.4 Hz, 1H), 4.14 (s, 1H), 4.09-3.92 (m, 14H), 3.85 (s, 3H), 3.84-3.50 (m, 17H), 2.06 (s, 3H), 1.95 (s, 3H), 1.20 (d, *J* = 6.5 Hz. 3H); ESI-MS: *m/z* calcd for $C_{47}H_{74}N_2O_{31}$; 1162.4309 found 1185.4076 $(M+Na)^+$.

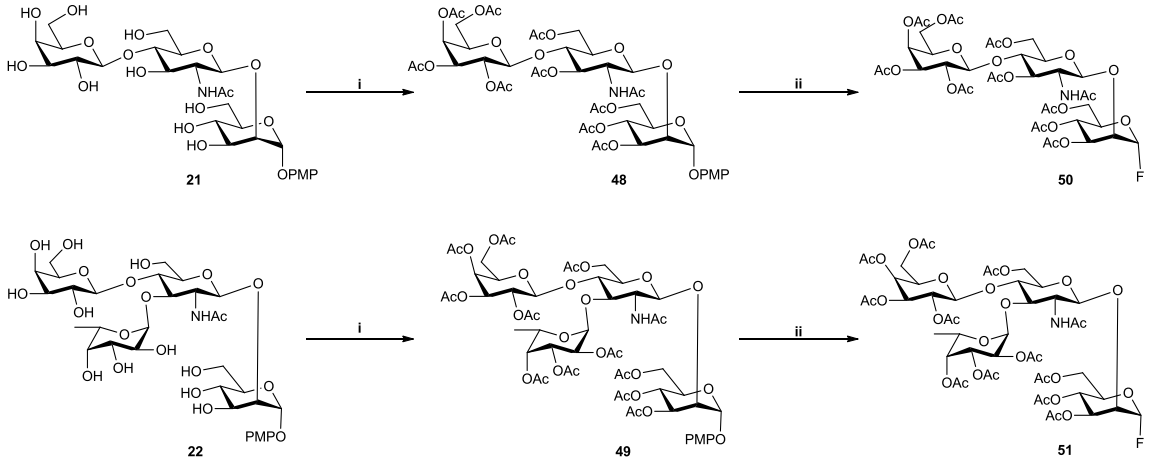


47

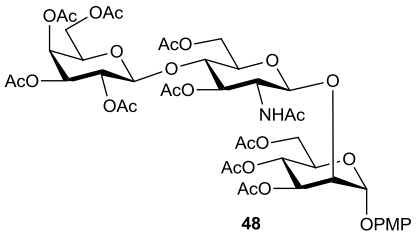
***p*-methoxyphenyl-O-(β-D-galactopyranosyl-(1→4)-O-[α-L-fucopyranosyl-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranosyl]-(1→6)-O-(5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyrano-sylonate-(2→6)-β-D-galactopyranosyl-(1→4)-O-2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-α-D-mannopyranoside (47)**: Compound **46** (5 mg, 4.31 µmol) was α2,6-sialylated by using general procedure 3 to get **47** (5.2 mg, 83%) as amorphous

white solids. ^{1}H NMR (400 MHz, D_2O): δ 7.08 (d, *J* = 8.1 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 5.48 (s, 1H), 5.10 (d, *J* = 5.1 Hz, 1H), 4.50 (d, *J* = 7.2 Hz, 1H), 4.43 (dd, *J* = 3.1 & 8.2 Hz, 2H), 4.32 (bs, 1H), 4.08 (d, *J* = 8.1 Hz, 1H), 4.09-3.40 (m, 43H), 2.60 (dd, *J* = 3.2 & 9.2 Hz, 1H), 1.97 (s, 3H), 1.95 (s, 3H), 1.90 (s, 3H), 1.54 (t, 1H), 1.18 (d, *J* = 6.4 Hz, 3H); ESI-MS: *m/z* calcd for $C_{58}H_{91}N_3O_{39}$; 1453.5245 found 1452.5101 (*M* -H)$^-$.

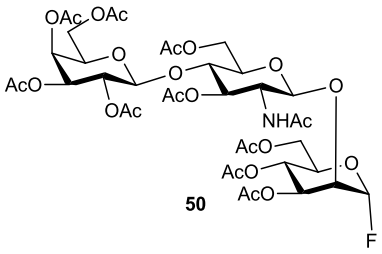
Chemical derivatization of chemo-enzymatically prepared modules. The modules **21** and **22** generated by chemo-enzymatic way were then peracetylated in presence of Ac_2O/pyridine. The reducing end *p*-methoxy phenyl ether protection was then cleaved using cerium ammonium nitrate and free hydroxyl was changed to fluoride to obtained donors **50** and **51** (Scheme S26).



Scheme S26 | Reagents and conditions. i, Ac_2O, pyridine, RT, overnight; ii, (1) CAN, ACN: toluene: H_2O, (2) DAST, CH_2Cl_2, -30 ^oC. CAN: Cerium ammonium nitrate; DAST: Diethylaminosulfur trifluoride.



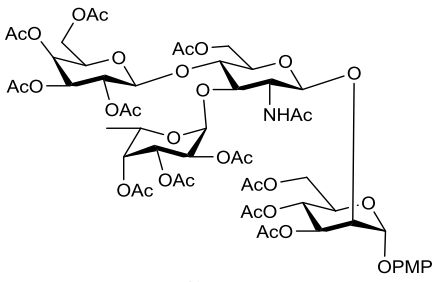
***p*-methoxyphenyl-O-[2,3,4,6-O-tetraacetyl-β-D-galactopyranosyl]-(1→4)-[3,6-O-diacetyl-2-acetamido-2-deoxy-β-D-glucopyranosyl]-(1→2)-3,4,6-O-triacetyl-α-D-mannopyranoside (48):** To a solution of **21** (0.230 g, 0.360 mmol) in 10 mL pyridine at 0 ^{o}C was added acetic anhydride (6 mL) and stirred at rt for overnight. Reaction mixture was then concentrated, diluted with 50 mL of CH_2Cl_2 and extracted with sat. $NaHCO_3$. Combined organic layers were evaporated and product was purified by silica gel column chromatography (0% → 20% acetone in toluene) to afford desired **48** (0.260 g, 72 %). TLC (acetone : toluene =3/7, v/v), R_f = 0.34; ^{1}H NMR (400 MHz, $CHCl_3$): δ 7.00 (d, *J* = 9.1 Hz, 2H), 6.82 (d, *J* = 9.1 Hz, 2H), 5.74 (d, *J* = 8.7 Hz, 1H), 5.33-5.35 (m, 2H), 5.27-5.30 (m, 2H), 5.22 (dd, *J* = 9.6, 8.2 Hz, 1H), 5.10 (dd, *J* = 10.5, 7.9 Hz, 1H), 4.96 (dd, *J* = 10.5, 3.4 Hz, 1H), 4.72 (d, *J* = 7.5 Hz, 1H), 4.47 (d, *J* = 7.9 Hz, 1H), 4.41 (dd, *J* = 11.8, 2.7 Hz, 1H), 4.31 (t, *J* = 2.2 Hz, 1H), 3.98-4.21 (m, 6H), 3.81-3.91 (m, 2H), 3.72-3.79 (m, 4H), 3.63 (ddd, *J* = 8.6, 5.6, 2.7 Hz, 1H), 2.14 (s, 3H), 2.11 (s, 3H), 2.08 (s, 3H), 2.06 (s, 2H), 2.03 (s, 3H), 2.03 (s, 6H), 2.02 (s, 3H), 1.96 (s, 6H); ESI-MS: *m/z* calcd for $C_{45}H_{59}NO_{26}$; 1029.9480 found 1030.4587 $(M + H)^+$.



50

[2,3,4,6-O-tetraacetyl-β-D-galactopyranosyl]-(1→4)-[3,6-O-diacetyl-2-acetamido-2-deoxy-β-D-glucopyranosyl]-(1→2)-3,4,6-O-triacetyl-α-D-mannopyranosyl fluoride (50): Cerium ammonium nitrate (0.2 g, 0.554 mmol) was added to a solution of compound **48** (0.200 g, 0.203 mmol) in 10 mL of acetonitrile: toluene: H_2O (4:2:1). The resulting reaction mixture was stirred at RT for 3 h. The reaction was diluted with EtOAc (50 mL) and washed with H_2O (30 x 2 mL) and brine (30 mL). The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The product was purified by flash column chromatography (0% → 25% acetone in toluene) to afford

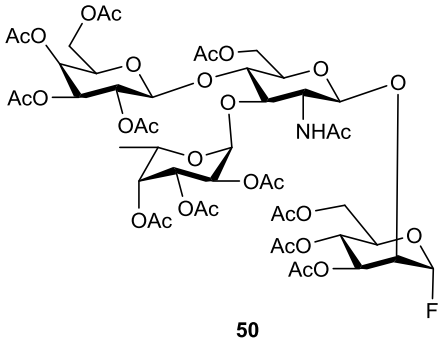
-OH compound (0.120 g) as a foam. The residue (0.120 g, 0.130 mmol) was dissolved in CH_2Cl_2 (10 mL) at -30 ^oC. Then, DAST (34 μL, 0.260 mmol) was added slowly, and the resulting reaction mixture was stirred for 1 h. When TLC (acetone: toluene, 3/7) indicated formation of product with consumption of starting material, the reaction was quenched with aq. $NaHCO_3$. The filtrate was washed with aqueous $NaHCO_3$ (2 x 30 mL) and brine (20 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (0% → 20% acetone in toluene) to afford **50** (0.080 g, 51% over 2 steps) as white solid. TLC (acetone: toluene =3/7, v/v), R_f = 0.34; ^1H NMR (600 MHz, $CHCl_3$): δ 5.50 (d, *J* = 49.6 Hz, 1H), 5.30 (d, *J* = 3.8 Hz, 1H), 2.26 (t, *J* = 7.8 Hz, 1H), 5.05-4.89 (m, 4H), 4.55 (d, *J* = 8.4 Hz, 1H), 4.40 (d, *J* = 8.2 Hz, 1H), 4.32 (s, 2H), 4.18 (dd, *J* = 3.2 and 7.8 Hz, 1H), 4.05-4.01 (m, 6H), 3.81 (t, *J* =7.8 Hz, 1H), 3.71 (t, *J* =7.1 Hz, 1H), 3.50 (t, *J* = 3.1 Hz, 1H), 2.29 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H), 1.96 (s, 3H), 1.91 (s, 3H), 1.82 (s, 3H), ^{13}C NMR (150 MHz, $CHCl_3$): 171.29, 171.10, 170.66, 170.56, 170.35, 170.30, 169.50, 129.21, 128.40, 125.47, 106.54, 104.31, 101.05, 100.31, 76.07, 72.82, 72.64, 72.36, 71.16, 70.95,70.71, 69.41, 69.28, 66.86, 64.92, 62.38, 62.13, 61.04, 53.12, 23.13, 21.64, 21.22, 20.95, 20.87, 20.77, 20.68, 20.62; ESI-MS: *m/z* calcd for $C_{38}H_{52}FNO_{24}$; 925.8145 found 925.8354 $(M+H)^+$.



49

***p*-methoxyphenyl-O-[2,3,4,6-O-tetraacetyl-β-D-galactopyranosyl]-(1→4)-[2,3,4-O-triacetyl-α-L-fucopyranosyl-(1→3)-3,6-O-diacetyl-2-acetamido-2-deoxy-β-D-glucopyranosyl]-(1→2)-3,4,6-O-triacetyl-α-D-mannopyranoside (49):** To a solution of **22** (0.100 g, 0.125 mmol) in 6 mL pyridine at 0 ^oC was added acetic anhydride (4 mL) and stirred at rt for overnight. Reaction

mixture was then concentrated, diluted with 50 mL of CH_2Cl_2 and extracted with sat. $NaHCO_3$. Combined organic layers were evaporated and product was purified by silica gel column chromatography (0% → 10% acetone in CH_2Cl_2) to afford desired **49** (0.135 g, 85 %). TLC (acetone: CH_2Cl_2 =1/9, v/v), R_f = 0.31; ^{1}H NMR (400 MHz, $CHCl_3$): δ 7.00 (d, *J* = 6.8 Hz, 2H), 6.83 (d, *J* = 6.8 Hz, 2H), 5.43 (d, *J* = 3.2 Hz, 1H), 4.42 (d, *J* = 3.2 Hz, 1H), 3.98 (d, *J* = 2.1 Hz, 2H), 5.25 (dd, *J* = 3.2 & 8.2 Hz, 2H), 5.19 (dd, *J* = 3.8 & 8.5 Hz, 2H), 5.10 (t, *J* = 9.8 Hz, 2H), 4.89 (d, *J* = 6.3 Hz, 1H), 4.85 (d, *J* = 2.2 Hz, 1H), 4.70 (d, *J* = 9.8 Hz, 2H), 4.61 (d, *J* = 1.2 Hz, 1H), 4.40 (dd, *J* = 3.2 & 7.2 Hz, 1H), 4.31 (m, 3H), 4.22-3.89 (m, 6H), 3.80 (m, 2H), 3.78 (s, 3H), 3.60 (m, 1H), 2.10 (s, 3H), 2.08 (s, 3H), 2.08 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H), 1.96 (s, 3H), 1.93 (s, 3H), 1.90 (s, 3H), 1.89 (s, 3H), 1.88 (s, 3H), 1.11 (d, 3H); ESI-MS: *m/z* calcd for $C_{55}H_{73}NO_{32}$; 1259.4116 found 1282.3974 $(M+Na)^+$.

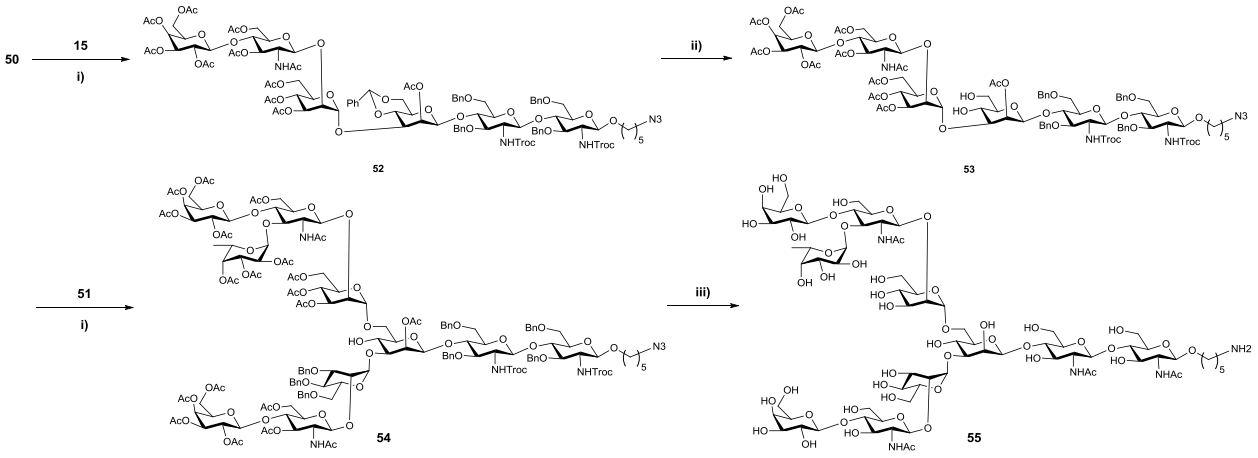


50

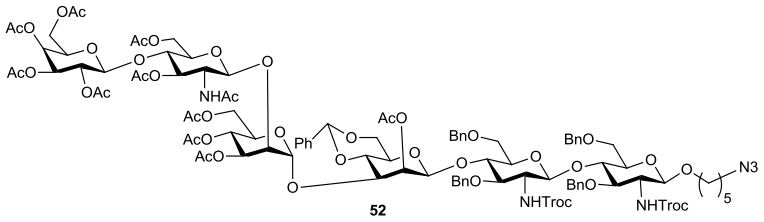
[2,3,4,6-O-tetraacetyl-β-D-galactopyranosyl]-(1→4)-[2,3,4-O-triacetyl-α-L-fucopyranosyl-(1→3)-3,6-O-diacetyl-2-acetamido-2-deoxy-β-D-glucopyranosyl]-(1→2)-3,4,6-O-triacetyl-α-D-mannopyranosyl fluoride (50): Cerium ammonium nitrate (0.121 g, 0.142 mmol) was added to a solution of compound **49** (0.090 g, 0.071 mmol) in 7 mL of acetonitrile: toluene: H_2O (4:2:1). The resulting reaction mixture was stirred at rt for 3 h. The reaction was diluted with EtOAc (40 mL) and washed with H_2O (10 x 2 mL) and brine (10 mL). The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The product was purified by flash column chromatography (0% → 15% acetone in CH_2Cl_2) to afford **-OH** compound (0.065 g) as a foam. The residue (0.060 g,

0.052 mmol) was dissolved in CH_2Cl_2 (5 mL) at -30 ^oC. Then, DAST (11.6 μL, 0.104 mmol) was added slowly, and the resulting reaction mixture was stirred for 1 h. When TLC (acetone: CH_2Cl_2, 1/9) indicated formation of product with consumption of starting material, the reaction was quenched with aq. $NaHCO_3$. The filtrate was washed with aqueous $NaHCO_3$ (2 x 10 mL) and brine (10 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by silica gel column chromatography (0% → 10% acetone in CH_2Cl_2) to afford **51** (0.055 g, 67% over 2 steps) as white solid. TLC (acetone: CH_2Cl_2 =1/9, v/v), R_f = 0.44; ^1H NMR (400 MHz, $CHCl_3$): δ 5.55 (d, *J* = 52.1 Hz, 1H), 5.40 (dt, *J* = 3.2 & 7.8 Hz, 3H), 5.21 (dd, *J* = 2.1 & 8.2 Hz, 2H), 5.18-5.04 (m, 3H), 5.0 (bs, 1H), 4.60 (s, 2H), 4.40 (dd, *J* = 5.6 & 8.5 Hz, 1H), 4.38-4.00 (m, 7H), 3.80 (m, 2H), 3.60 (m, 1H), 2.16 (s, 3H), 2.14 (s, 3H), 2.13 (s, 3H), 2.10 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.00 (s, 3H), 1.95 (s, 3H), 1.94 (s, 3H), 1.17 (d, *J* = 6.4 Hz, 3H) ; ESI-MS: *m/z* calcd for $C_{48}H_{66}FNO_{30}$; 1155.0314 found 1178.3491 $(M+Na)^+$.

Chemical glycosylation to core trisaccharide: At this stage we are in position to investigate the coupling efficiency of fluoride donors **50** and **51** to core trisaccharide **15**. Depicted in Scheme S27**,** stereoselctive conjugation of **50** to 3-O position of core in presence of $AgOTf/Cp_2HfCl_2$ provided expected hexasaccharide **52** in 56% yield. The cleavage of benzylidine ring using catalytic *p*-toluene sulfonic acid provided 4, 6-diol **53**. Taking advantage of its reactivity, primary hydroxyl group of **53** was then selectively glcycosylated with **51** to afford fully protected decasaccharide **54** in moderate yield. At last, the global deprotection afforded the desired selectively fucosylated bi-antennary complex type glycan **55**.

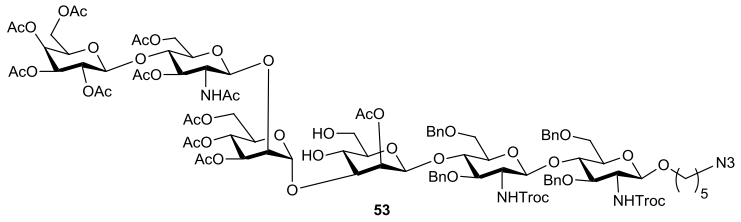


Scheme S27 | Reagents and conditions. i, AgOTf, Cp_2HfCl_2, toluene, 4 Å MS, 0 ^oC to rt; ii, *p*-TSA, acetonitrile, rt; iii, (1) LiOH, 1,4-dioxane: H_2O; 90 ^oC, overnight; (2) Ac_2O, pyridine, overnight; (3) NaOMe, MeOH, overnight; (4) $Pd(OH)_2$, MeOH: H_2O: HCOOH (5:3:2), H_2. AgOTf: Silver trifluromethanesulfonate**;** Cp_2HfCl_2**:** Bis(cyclopentadienyl)hafnium dichloride, MS: molecular sieves.



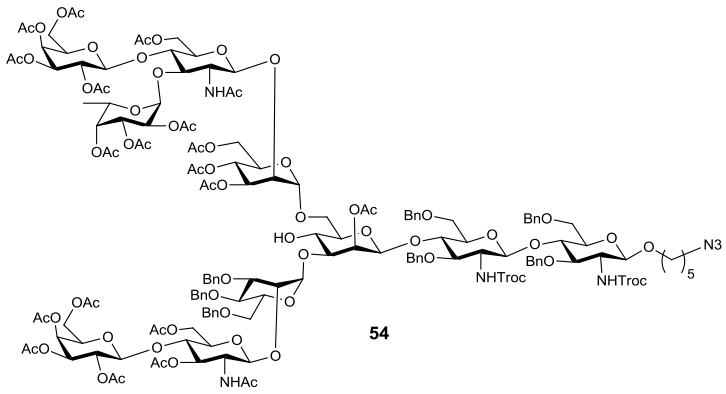
5-Azidopentyl-O-{[2,3,4,6-O-tetraacetyl-β-D-galactopyranosyl]-(1→4)-[3,6-O-diacetyl-2-acetamido-2-deoxy-β-D-glucopyranosyl]-(1→2)-[3,4,6-O-triacetyl-*α*-D-mannopyranosyl]}-(1→3)-[2-O-acetyl-4,6-O-benzylidine-β-D-mannopyranosyl-(1→4)-O-(3,6-di-O-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranosyl)-(1→4)-O-3,6-di-O-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranoside (52). A mixture of Silver triflate (0.039 g, 0.155 mmol), Bis (cyclopentadienyl) hafnium dichloride (0.041 g, 0.108 mmol) and 4 Å activated molecular sieves in dry toluene (3 mL) was stirred at rt

for 1 h. The reaction mixture was then cooled to 0 ℃, a solution of donor **50** (0.043 g, 0.046 mmol) and acceptor **15** (0.045 g, 0.031 mmol) in 3 mL toluene was added. The mixture was stirred at RT for 3 h, quenched with Et_3N, diluted with CH_2Cl_2 and filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ (2 x 20 mL), and a brine (20 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 10% acetone in CH_2Cl_2) to afford **52** (0.051 g, 70%) as colorless foam. TLC: (acetone: CH_2Cl_2 = 1.5/8.5, v/v): R_f = 0.46; ^{1}H NMR (400 MHz, $CHCl_3$): δ 7.46-7.16 (m, 25H), 5.41 (s, 1H), 5.32 (d, *J* = 9.8 Hz, 1H), 5.29 (d, *J* = 7.2 Hz, 1H), 5.20 (t, *J* = 10.2 Hz, 1H), 5.09 (t, *J* = 10.3 Hz, 1H), 4.93-4.87 (m, 5H), 4.82-4.57 (m, 5H), 4.50 (d, *J* = 12.2 Hz, 2H), 4.41-4.22 (m, 4H), 4.13-3.56 (m, 8H), 3.43-3.36 (m, 4H), 3.20 (t, *J* = 10.3 Hz, 4H), 3.19 (t, *J* = 10.2 Hz, 1H), 2.20 (s, 3H), 2.18 (s, 3H), 2.13 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H), 1.96 (s, 3H), 1.90 (s, 3H), 1.81 (s, 3H), 1.58-1.51 (m, 4H), 1.40-1.34 (m, 2H); ^{13}C NMR (150 MHz, $CHCl_3$): δ 171.28, 170.80, 170.69, 170.49, 170.43, 170.36, 169.97, 169.68, 169.41, 154.30, 154.13, 138.83, 138.18, 137.44, 131.28, 129.25, 129.11, 128.91, 128.63, 128.54, 128.37, 128.18, 128.10, 128.00, 127.79, 127.71, 126.47, 102.55, 101.37, 100.84, 100.44, 98.60, 95.82, 76.07, 74.7474.61, 74.51, 74.19, 73.83, 73.59, 72.35, 71.24, 70.95, 70.79, 70.03, 69.62, 69.52, 69.37, 68.66, 68.42, 66.92, 66.41, 65.51, 62.42, 62.02, 61.15, 57.88, 57.23, 53.60, 51.58, 29.27, 28.82, 23.46, 23.29, 21.10, 20.96, 20.82; ESI-MS: *m/z* calcd for $C_{104}H_{126}Cl_6N_6O_{41}$; 2360.8510 found 2361.6131 $(M+H)^+$.



53

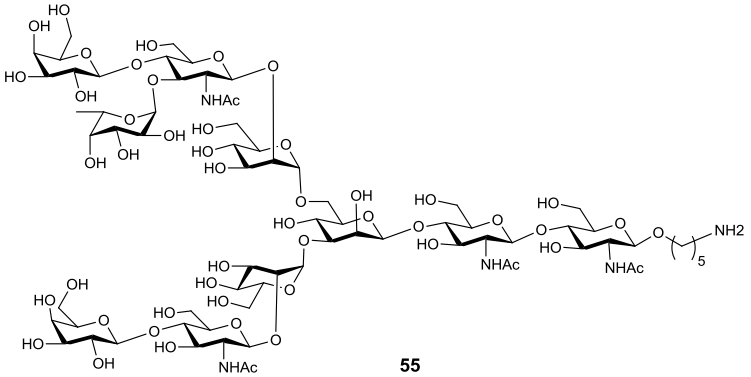
5-Azidopentyl-O-{[2,3,4,6-O-tetraacetyl-β-D-galactopyranosyl]-(1→4)-[3,6-O-diacetyl-2-acetamido-2-deoxy-β-D-glucopyranosyl]-(1→2)-[3,4,6-O-triacetyl-α-D-mannopyranosyl]}-(1→3)-[2-O-acetyl-β-D-mannopyranosyl-(1→4)-O-(3,6-di-O-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranosyl)-(1→4)-O-3,6-di-O-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranoside (53): *p*-Toluene sulfonic acid monohydrate (0.001 g, 0.008 mmol) was added to a solution of **52** (0.040 g, 0.016 mmol) in acetonitrile: MeOH 2/1 (3 mL) and the resulting reaction mixture was stirred at RT for 5 h. The reaction was quenched by adding Et_3N and concentrated in *vacuo.* The residue was purified by flash column chromatography (0% → 15% acetone in CH_2Cl_2) to give diol **53** (0.022 g, 57%). TLC: (acetone: CH_2Cl_2 = 1.5/8.5, v/v): R_f = 0.32; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.17 (m, 20H), 5.33 (d, *J* = 3.2 Hz, 1H), 5.25 (d, *J* = 3.2 Hz, 1H), 5.19-5.04 (m, 4H), 4.98 (d, *J* = 3.2 Hz, 1H), 4.95 (d, *J* = 3.1 Hz, 1H), 4.94-4.89 (m, 2H), 4.72-4.55 (m, 8H), 4.50-4.28 (m, 9H), 4.20-3.30 (m, 30H), 3.20 (t, 5H), 2.15 (s, 3H), 2.14 (s, 3H), 2.12 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.95 (s, 3H), 1.94 (s, 3H), 1.56-1.51 (m, 4H), 1.40-1.34 (m, 2H); ESI-MS: *m/z* calcd for $C_{97}H_{122}Cl_6N_6O_{43}$; 2272.7420 found 2295.5522 $(M+Na)^+$.



54

5-Azidopentyl-O-{[2,3,4,6-O-tetraacetyl-β-D-galactopyranosyl]-(1→4)-[3,6-O-diacetyl-2-acetamido-2-deoxy-β-D-glucopyranosyl]-(1→2)-[3,4,6-O-triacetyl-α-D-mannopyranosyl]}-(1→3)-{2,3,4,6-O-tetraacetyl-β-D-galactopyranosyl]-(1→4)-[2,3,4-O-triacetyl-α-L-

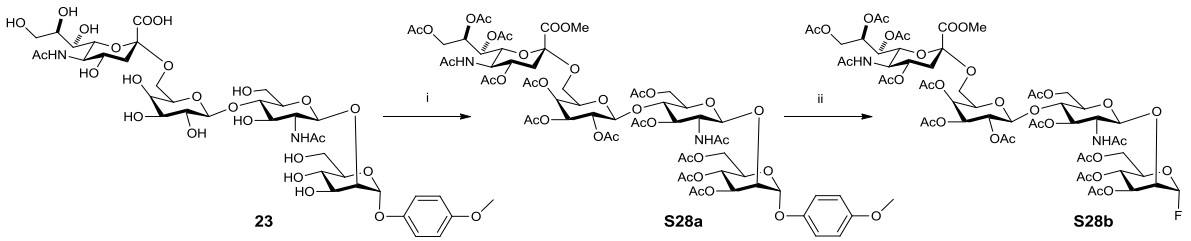
fucopyranosyl-(1→3)-3,6-O-diacetyl-2-acetamido-2-deoxy-β-D-glucopyranosyl]-(1→2)-3,4,6-O-triacetyl-α-D-mannopyranosyl}-(1→6)-[2-O-acetyl-β-D-mannopyranosyl-(1→4)-O-(3,6-di-O-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranosyl)-(1→4)-O-3,6-di-O-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranoside (53): A mixture of Silver triflate (0.011 g, 44.1 μmol), Bis(cyclopentadienyl) hafnium dichloride (0.012 g, 30.8 μmol) and 4 Å activated molecular sieves in dry toluene (3 mL) was stirred at rt for 1 h. The reaction mixture was then cooled to 0 ℃, a solution of donor **50** (0.015 g, 13.2 μmol) and acceptor **15** (0.020 g, 8.80 μmol) in 2 mL toluene was added. The mixture was stirred at RT for 5 h, quenched with Et_3N, diluted with CH_2Cl_2 and filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ (2 x 10 mL), and a brine (20 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by flash column chromatography (0% → 15% acetone in CH_2Cl_2) to afford **52** (0.010 g, 34%) as colorless foam. TLC: (acetone: CH_2Cl_2 = 1.5/8.5, v/v): R_f = 0.41; ^{1}H NMR (400 MHz, $CHCl_3$): δ 7.48-7.20 (m, 20H), 5.40-4.51 (m, 24H), 4.50-4.00 (m, 10H), 3.98-3.50 (m, 30H), 3.49-3.10 (m, 20H), 2.18 (s, 3H), 2.16 (s, 3H), 2.15 (s, 3H), 2.14 (s, 3H), 2.13 (s, 3H), 2.12 (s, 3H), 2.11 (s, 3H), 2.10 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H), 1.97 (s, 3H), 1.95 (s, 3H), 1.94 (s, 3H), 1.93 (s, 3H), 1.33-1.23 (m, 4H), 1.20-1.15 (m, 2H); ESI-MS: *m/z* calcd for $C_{145}H_{187}Cl_6N_7O_{73}$; 3408.7670 found 1176.3855 $(M+K)^{3+}$.



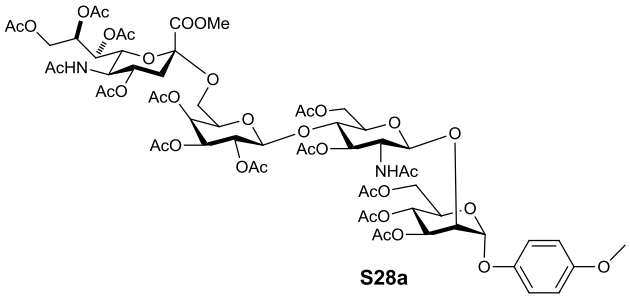
55

5-Aminopentyl-β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→2)-α-D-mannopyranosyl]-(1→3),-[β-D-galactopyranosyl-(1→4)-(α-L-fucopyranosyl-(1→3)-2-2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-α-D-mannopyranosyl]-(1→6)-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (55): A mixture of **54** (0.010 g, 2.9 μmol) and lithium hydroxide (0.005 g, 50% by wt) in 2 mL of 1, 4 dioxane: H_2O (4:1) was stirred at 90 ^oC for overnight. Volatiles were then evaporated and the crude product was reacted with 3 mL Ac_2O: pyridine (1:2) for overnight. The solvents were removed using high vacuum and product was purified by C18 gel column chromatography (MeOH: H_2O as an eluent). The product was de-acetylated using sodium methoxide in MeOH (3 mL) for overnight. The reaction mixture was neutralized by using IR-120, filtered and concentrated in *vacuo.* The residue was purified by C18 gel column chromatography (MeOH: H_2O as an eluent). The product was dissolved in 3 mL MeOH: H_2O: HCOOH (6:3:1), $Pd(OH)_2$ (50% by weight) was added and the mixture was hydrogenated for overnight. The reaction mixture was filtered through Celite and concentrated in *vacuo.* The residue was purified by Bio-Gel P-2 (BIO-RAD) column chromatography using water as eluent. The product was the lyophilized to get desired oligosaccharides **55** (0.002 g, 36%) as a white color powder. TLC: (n-BuOH: AcOH: H_2O = 1/1/1, v/v): R_f = 0.32; ^1H NMR (400 MHz, D_2O): δ 5.15 (d, *J* = 4.2 Hz, 1H), 4.94 (s, 1H), 4.60 (m, 3H), 4.45 (q, 3H), 4.30 (s, 1H), 4.21 (d, *J* = 2.1 Hz, 1H), 4.13 (d, *J* = 2.0 Hz, 1H), 4.05-3.40 (m, 58H), 3.01 (t, 2H, linker), 2.10 (s, 3H, -Ac), 2.07 (s, 3H, -Ac), 2.06 (s, 3H, -Ac), 2.05 (s, 3H, -Ac), 1.76-1.58 (m, 4H, liner), 1.45-1.36 (m, 2H, linker), 1.21 (d, *J* = 6.5 Hz, 3H, Fuc-Me); ^{13}C NMR (100 MHz, $CHCl_3$): δ 174.6, 174.4, 102.9, 101.8, 101.0, 99.4, 99.1, 98.5, 96.8, 80.3, 79.6, 79.3, 78.4, 76.4, 75.3, 75.2, 74.7, 74.6, 74.5, 74.3, 73.5, 72.8, 72.4, 71.9, 71.0, 70.9, 70.0, 69.5, 69.4, 69.1, 68.5, 68.3, 67.7, 67.2, 66.7, 65.8, 61.4, 60.9, 59.6, 59.5, 55.6, 54.9, 54.8, 39.3, 28.0, 26.3, 22.3, 22.2, 22.0, 15.3; ESI-MS: *m/z* calcd for $C_{73}H_{125}N_5O_{50}$; 1871.7545 found 1872.7477 $(M+H)^+$.

Chemical derivatization of sialylated module. Preparation of sialylated antennae is of particular importance due to the complexity associated with sialic acid chemistry. Having established the synthetic protocol for non-sialylated modules (Scheme S28), we turned our attention to sialylated module **22**. The carboxylic acid functionality was esterified in presence of trimethylsilyl diazomethane without affecting free hydroxyl groups. Next, the peracetylation was performed using acetic anhydride and pyridine to afford **S30a**. The peracetylation step allows for purification of the oligosaccharide material before the removal of anomeric groups. At last, reducing end transformation was done to form anomeric fluoride donor **S30b**.



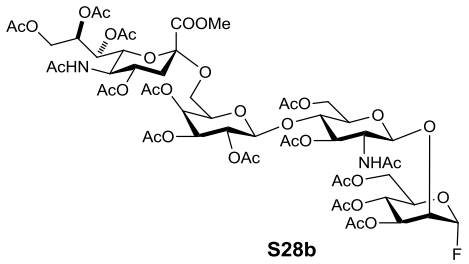
Scheme S28 | Reagents and Conditions. i, (1) Trimethylsilyl diazomethane, MeOH; (2) Ac_2O, pyridine, RT, overnight; ii, (1) CAN, ACN: toluene: H_2O, (2) DAST, CH_2Cl_2, -30 ^oC, 34% over 2 steps.



***p*-methoxyphenyl-O-[3,7,8,9-O-tetraacetyl-5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyrano-sylonate]-(2→6)-O-[2,3,4,6-O-tetraacetyl-β-D-galactopyranosyl]-(1→4)-[3,6-O-diacetyl-2-acetamido-2-deoxy-β-D-glucopyranosyl]-(1→2)-3,4,6-O-triacetyl-α-D-mannopyranoside (S28a):** To a solution of compound **23** (30 mg, 0.031 mmol) in MeOH (3 mL) was added trimethylsilyl diazomethane (1M solution in hexane, 0.046 mL, 0.31 mmol).

The resulting reaction mixture was stirred at RT for overnight. Complete consumption of starting material was confirmed by NMR and mass. The reaction mixture was concentrated to dryness and purified by C18 (eluent MeOH: H_2O). TLC: (n-butanol: H_2O: acetic acid = 2/1/1, v/v): R_f = 0.45; ^{1}H NMR (400 MHz, MeOD): δ 7.14 (d, *J* = 9.5 Hz, 2H), 6.97 (d, *J* = 9.8 Hz, 2H), 5.50 (s, 1H), 4.68 (d, *J* = 8.5 Hz), 1H, 4.45 (d, *J* = 8.0 Hz, 1H), 4.36 (s, 1H), 4.20-3.90 (m, 10H), 3.84 (s, 3H), 3.76-3.58 (m, 17H), 3.51 (s, 3H), 2.66 (dd, *J* = 3.8 and 11.5 Hz, 1H), 2.00 (s, 3H), 1.96 (s, 3H), 1.60 (t, 1H); ESI-MS: m/z calcd for $C_{39}H_{60}N_2O_{25}$; 942.3245 found 987.3033 $(M + Na)^+$.

A solution of methyl ester (0.025 g, 0.025 mmol) in pyridine (2 mL) and acetic anhydride (1.5 mL) was srirred at rt for overnight. Reaction was then concentrated to dryness, dissolved in dicloromethane, extracted with sat. $NaHCO_3$ solution, dried and concentrated. Product was purified by C18 column (MeOH: water eluent) to afford **S28a** (0.030 g, 74%) as a white solid. TLC: (acetone: CH_2Cl_2 4/6, v/v): R_f = 0.42; ^{1}H NMR (400 MHz, MeOD): δ 7.07 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.9 Hz, 2H), 5.45 (s, 1H), 5.40 (d, *J* = 7.2 Hz, 1H), 5.36 (t, *J* = 10.3 Hz, 1H), 5.30 (d, *J* = 7.5 Hz, 1H), 5.28 (d, *J* = 7.0 Hz, 1H), 5.26 (s, 1H), 5.23 (s, 1H), 5.19 (d, *J* = 8.6 Hz, 1H), 5.17 (t, *J* = 10.3 Hz, 1H), 5.11-5.07 (m, 5H), 5.00-4.95 (m, 3H), 4.70 (dd, *J* = 4.2 & 7.8 Hz, 2H), 4.46-4.35 (m, 4H), 4.30-4.13 (m, 3H), 4.08-3.97 (m, 8H), 3.76 (s, 3H), 3.75 (s, 3H), 3.60-3.56 (m, 3H), 2.58 (dd, *J* = 4.2 & 8.5 Hz, 1H), 2.13 (s, 3H), 2.12 (s, 3H), 2.11 (s, 3H), 2.10 (s, 6H), 2.07 (s, 3H), 2.05 (s, 6H), 2.02 (s, 6H), 1.99 (s, 3H), 1.98 (s, 3H), 1.91 (s, 6H), 1.84 (t, *J* = 10.2 Hz, 1H); ESI-MS: *m/z* calcd for $C_{63}H_{84}N_2O_{37}$; 1461.3420 found 1486.4864 $(M + 2H + Na)^+$.



S28b

***p*-methoxyphenyl-O-[3,7,8,9-O-tetraacetyl-5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyrano-sylonate]-(2→6)-O-[2,3,4,6-O-tetraacetyl-β-D-galactopyranosyl]-**

(1→4)-[3,6-O-diacetyl-2-acetamido-2-deoxy-β-D-glucopyranosyl]-(1→2)-3,4,6-O-triacetyl-α-D-mannopyranosyl fluoride (S28b): Cerium ammonium nitrate (0.037 g, 0.065 mmol) was added to a solution of compound **S28a** (0.020 g, 0.013 mmol) in 2 mL of acetonitrile: toluene: H_2O (4:2:1). The resulting reaction mixture was stirred at RT for 3 h. The reaction was diluted with EtOAc (10 mL) and washed with H_2O (10 x 2 mL) and brine (10 mL). The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The product was purified by C18 column chromatography (MeOH: H_2O eluent) to afford 1-**OH** compound (11 mg). The residue (10 mg, 0.007 mmol) was dissolved in CH_2Cl_2 (5 mL) at -30 ^oC. Then, DAST (3 μL, 0.021 mmol) was added slowly, and the resulting reaction mixture was stirred for 1 h. When TLC (acetone: CH_2Cl_2, 4/6) indicated formation of product with consumption of starting material, the reaction was quenched with aq. $NaHCO_3$. The filtrate was washed with aqueous $NaHCO_3$ (2 x 5 mL) and brine (5 mL) solution. The organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The residue was purified by C18 column chromatography (MeOH: H_2O eluent) to afford **S30b** (0.007 g, 38% over 2 steps). TLC (acetone: CH_2Cl_2 = 6/6, v/v), R_f = 0.24; ^1H NMR (400 MHz, $CHCl_3$): δ 5.99 (d, J = 10.2 Hz, 1H), 5.50 (d, J = 52.2 Hz, 1H), 5.39 (d, J = 10.3 Hz, 1H), 5.33-5.17 (m, 7H), 4.87-4.81 (m, 2H), 4.61 (d, J = 10.2 Hz, 1H), 4.52 (d, J = 10.3 Hz, 1H), 4.40-4026 (m, 5H), 4.21-3.83 (m, 4H), 3.70 (s, 3H), 3.49-3.47 (m, 2H), 2.54 (dd, *J* = 3.8 & 8.1 Hz, 1H), 2.19 (s, 6H), 2.17 (s, 6H), 2.14 (s, 6H), 2.10 (s, 3H), 2.05 (s, 6H), 2.02 (s, 6H), 1.98 (s, 3H), 1.97 (s, 6H), 1.23 (t, *J* = 10.1Hz, 1H); ESI-MS: *m/z* calcd for $C_{56}H_{77}FN_2O_{35}$; 1357.2094 found 1339.3978 $(M + Na)^+$.

2. Glycan Array Analysis

i. Microarray Fabrication

a) Fabrication of *N*-hydroxy succinimide-coated glass slide: All monovalent glycans (G1-33) were prepared in 10 mM concentration individually and served as mother solutions which are to be diluted with printing buffer to prepare a working solution. Microarrays were printed (BioDot Cartesian Technologies) by robotic pin (SMP3: TeleChem International) deposition of ~ 0.6 nL of 100 µM concentration of amine-containing glycans in printing buffer from a 384 well plate onto NHS-coated glass slides. The printed slides were allowed to react in an atmosphere of 80% humidity for an hour followed by desiccation overnight. These slides were designed for 16 grids in one slide, and stored at room temperature in a desiccator prior to use. Before the binding assay, these slides were blocked with blocking solution for 3 h. The slides were then washed with PBST-BSA buffer prior to use. Unless otherwise stated, reagents were obtained from commercial suppliers and used without purification. All aqueous solutions were prepared from distilled de-ionized water filtered with a Milli-Q purification system and sterile filtered through a 0.2 µm filter. Buffers used in the experiment include the printing buffer (pH 8.5, 300 mM phosphate buffer containing 0.05% (v/v) Tween-20), the blocking buffer (superblock blocking buffer in PBS, Pierce), the washing buffer (PBST buffer; PBS and 0.05% Tween-20) and the binding buffer (PBST-BSA Buffer; PBST buffer and 3% BSA). Printing buffer, blocking buffer, and binding buffer were prepared freshly before use.

b) Fabrication of aluminium oxide coated glass slide. The aluminum oxide glass substrate provides advantages for being able to be assessed by both mass spectrometry and fluorescence scanning. In addition, the fluorescence intensity of sugar-protein binding on the substrates was found to be more sensitive than that on transparent glass slide[15]. There are many reprots describing the surface of micron to nano pore structures of anodized aluminum oxide. However, only a few articles have mentioned the initial planar layer of aluminum oxide[16] during the treatment of surface anodization. In the development of AAO glass substrate, a computer

experimental design program (Design Expert 8.0) has been used to optimize the planar layer of surface anodized aluminum oxide to be best used in glycan microarray[17].

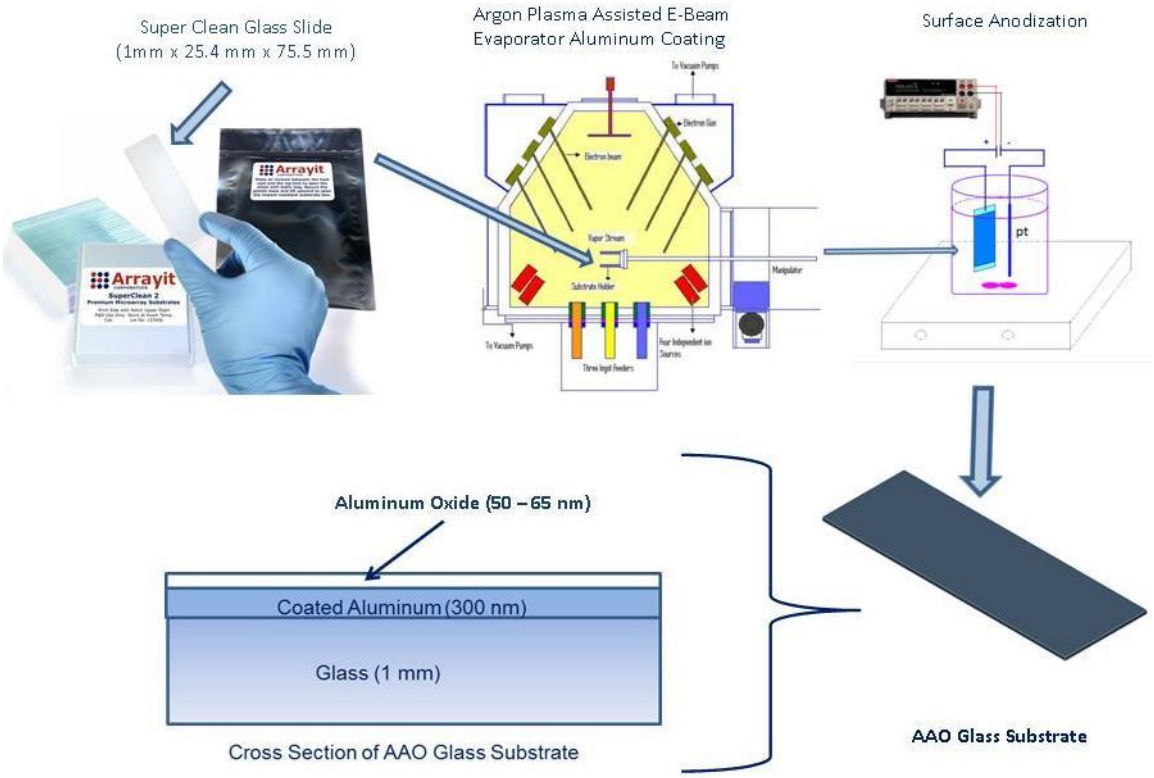


Figure S4 | Schematic drawing of the fabrication of anodized aluminum oxide (AAO) glass substrate.

As shown in Figure S4, approximately a larger of 300 nm aluminum coated on glass slide (1 x 75.5 x 24.5 mm) was fabricated using E-Beam VDP coater by The Thin Film Technology Division, Instrument Technology Research Center at National Applied Research Laboratories, (Hsinchu Science Park, Hsinchu, Taiwan, R.O.C.). The slide after Al-coating was immediately packed (one slide per container) and vacuum sealed in air-tight laminated foil pouches until the moment for surface anodization. Surface anodization of the aluminum coated glass slide has been conducted in-house via electrochemical reaction in a 0.3 M oxalic acid aqueous solution in a 4 ^{o}C chamber. The anodization reaction was controlled by voltage and reaction time. Under proper reaction conditions, a layer of approximately 50 to 65 nm (in thickness) of smooth

anodized aluminum oxide (AAO) can be grown consistently on top of aluminum coated glass slide. Unlike the conventional anodic aluminum oxide surface with pores, as the AFM picture shown in Figure S5A, we have developed a smooth AAO glass substrate with Rsm surface roughness (2.3 nm) similar to the surface of glass slide (< 3 nm). The cross section picture of a typical AAO glass substrate is shown in Figure S5B. To obtain the optimized AAO glass substrate with its physical properties shown in Figure S5, the detail experiment using computer program generated factorial design and response surface methodology has been conducted and will be reported in a separate article.

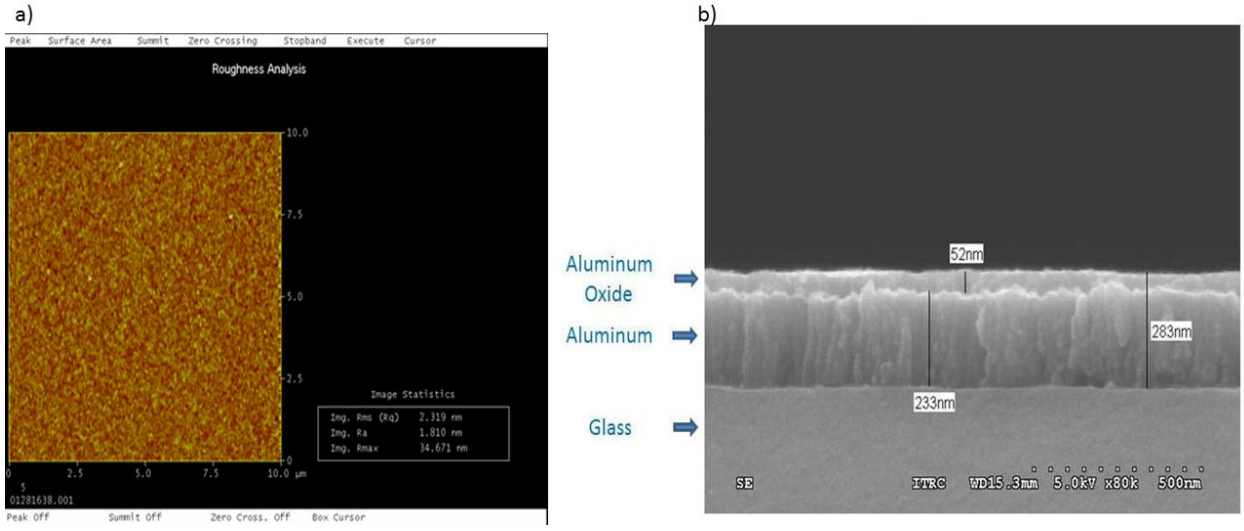


Figure S5 | (A) AFM picture – Roughness Analysis of the surface. Img. Rms (Rq) 2.319 nm and (B) Cross Section SEM picture of the AAO Glass Substrate.

ii. Surface Comparison of AAO Glass Substrate vs. NHS-Activated Glass Slide

NHS-glass slide has been widely used for glycan microarray in our and other groups. The amide formation of the NHS functional group with the amine of sugar derivative was taken place on the surface. Its first chemical reaction was to covalently bond to the carboxyl group of the functionalized glass surface. The AAO glass substrate contains a layer of stable polymer network of amorphous aluminum oxide on the surface which is ready for the chemical reaction with the phosphonic acid tail of glycan derivative to form a phosphonate. Interface reaction of phosphonic

acid on metal oxides, either aluminum oxide or titanium oxide, is spontaneous and the resulting array is more homogeneous, and density and distribution can be easily controlled compared to the reactions on NHS slide. To identify the reactive site available for interface covalent bonding, Cy5-phosphonic acid and Cy5-amine have been used for microarray on the surfaces directly. These dyes (Figure S6) have been synthesized in-house starting from Cy5-NHS ester (Lumiprobe Corp. Item No. 63020).

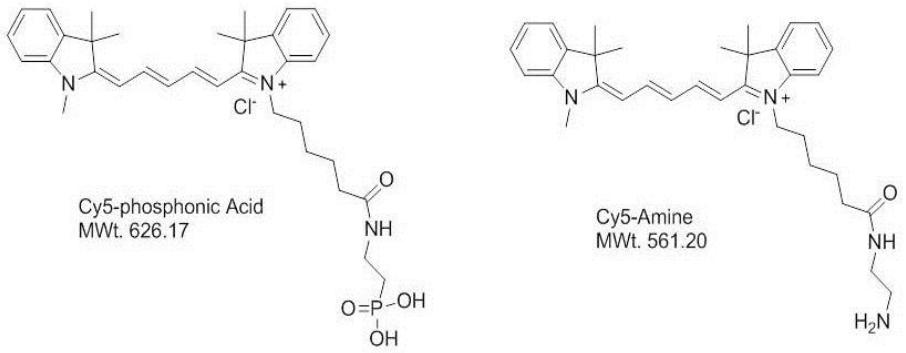


Figure S6 | Structures of Cy5-phosphonic acid linker and Cy5-amine linker

The dyes, Cy5-phosphonic acid and Cy5-amine, were dissolved in a 7:3 ratio of ethylene glycol/water mixtures (1 mM) with pH adjustment to 6 and 8.5 respectively. The arrayed slides were washed thoroughly with a mixture of 5% methanol in water, spin-dried before subjecting for GenePix (4300A) Scanning. Figure S7 shows the microarray pictures of Cy5-phosphonic acid on AAO glass substrate (Figure S7A), Cy5-amine on NHS-glass slide (Figure S7B) and their 20 spots average fluorescence intensity (Figure S7C). The representative confocal microscope pictures of these arrayed spots are given in Figure S8. Higher loading capacity and more uniformly distributed Cy5-molecules have been observed similarly to those which have been seen usually in the glycan microarray and sugar/protein binding.

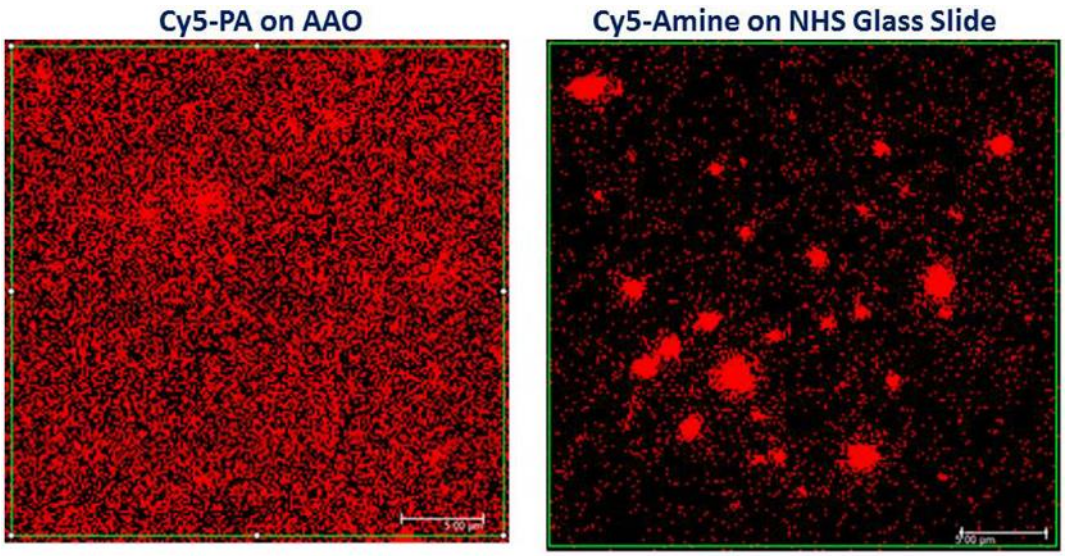


Figure S7 | GenePix Scanning (at PMT 450) of 1 mM of (A) Cy5-phosphonic Acid on AAO glass substrate (B) Cy5-Amine on NHS glass slide, and (C) their averaged 20 spots fluorescence intensity.

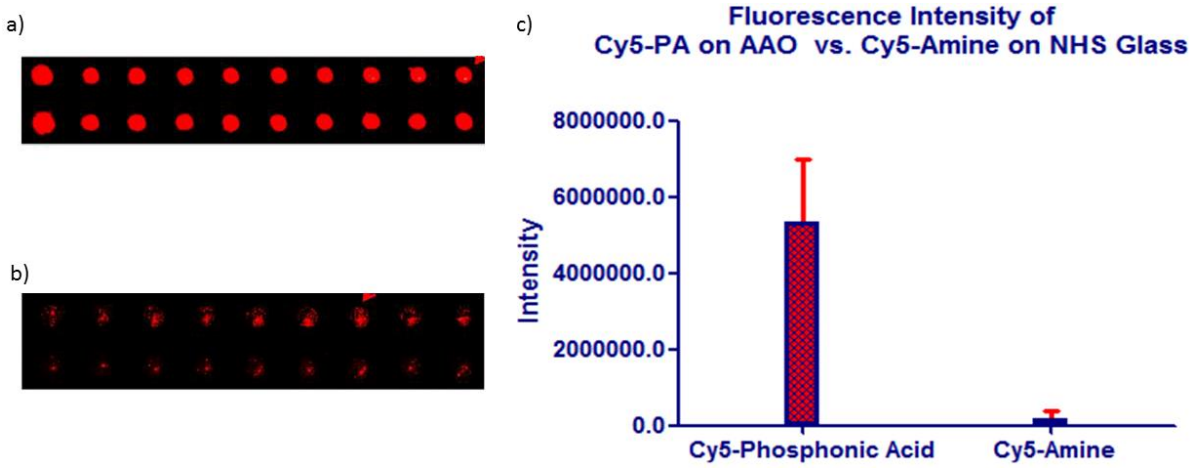


Figure S8 | Representative Confocal Microscopes pictures Cy5-phosphonic Acid, and Cy5-Amine on AAO glass substrate and NHS glass slide. Selective 900 μm^2 area within the spots.

iii. Surface uniformity comparison of ACG and NHS slide using confocal microscope.

To evaluate the density and uniformity of glycan array on ACG and NHS activated glass slide, we used the mannose monosaccharide formed glycan array as a model. A mannose solution of 100 μM was used in arraying, and a solution of ConA488 of 50 μg/mL was used in sugar/protein binding. The images of ConA488/mannose binding observed from confocal microscope further confirmed that the AAO glass substrate has denser and more uniformly distributed covalently bonded sugars. Figure S9 shows the images observed from Confocal Microscope (Leica SP5) of ConA488/mannose binding on AAO Glass Substrate vs. NHS Glass Slide.

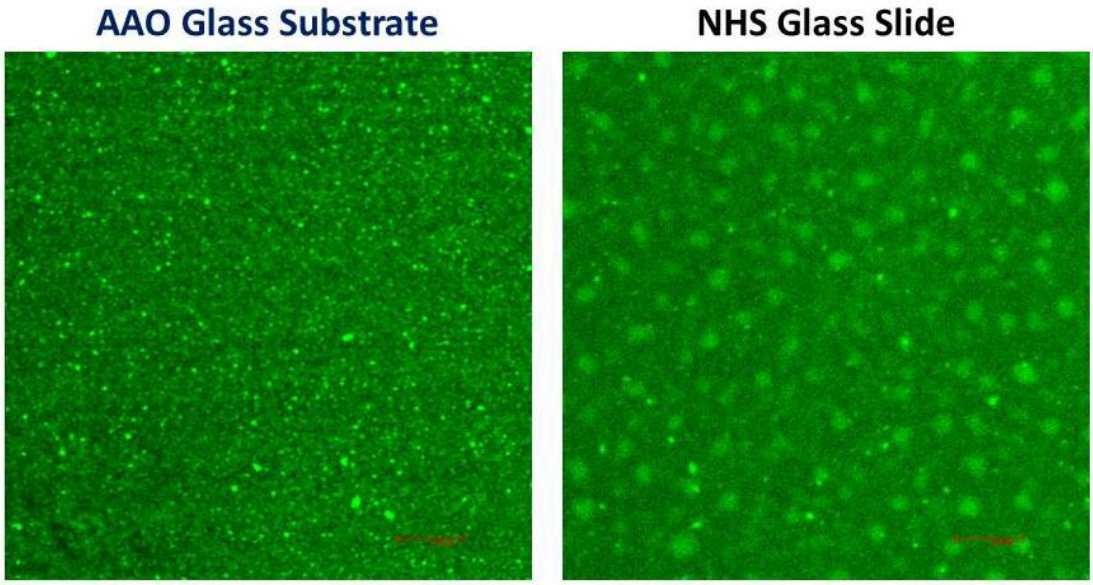


Figure S9 | Confocal Microscope of ConA488/Mannose binding on AAO glass Substrate vs. NHS-Glass Slide.

Atomic force microscopy image of sugar distribution on aluminium-oxide coated glass slide, and NHS coated glass slide suggest that the AAO glass substrate (Figure S10a) provides more uniform distribution of covalently bonded sugars than that of NHS glass slide (Figure S10a). Particle counts of these images were obtained by counting the particles over the height of one half width distribution of the maximum numbers of particle height. Mannose derivatives can

only covalently bond on the slides where the activated functional groups were available on the surface. Regardless of differences in Rms of the glass base materials, the AAO glass substrate provides more homogeneou distribution than that of NHS glass slide.

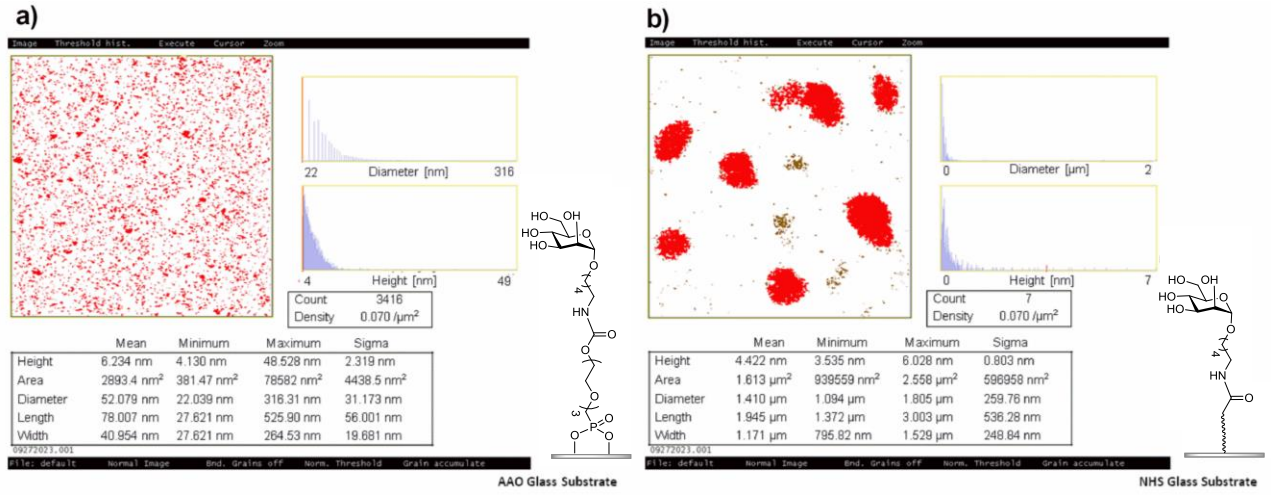


Figure S10 | Atomic force microscopy image showing sugar distribution on **a)** aluminium-oxide coated glass slide, and **b)** NHS coated glass slide.

iv. Antibody binding assay: Antibodies PG9, PG16 and PGTs 141-145 were diluted by binding buffer to 100 µg/mL prior to use. DyLight649-conjugated Donkey Anti-Human IgG antibody was then pre-complexed with primary antibodies. The final concentration of the precomplexed solution was adjusted to 50 µg/mL with binding buffer. The printed glass slide was assembled into FAST® frame slide holder (Whatman®), 80 µL of precomplexed antibody solution were then applied to each well accordingly. The antibodies binding process was maintained in 4 ^{o}C with gentle shaking and then antibody solutions were carefully pipetted out after 6 hours incubation. The glass slide was gently washed by 100 µL PBST washing buffer and then spin-dried for 3 minutes.

v. Image processing and data analysis: The slide was scanned at 635 nm with a microarray fluorescence chip reader (GenePix® 4300A, Molecular Devices Corporation). Scanned images were analyzed with GenePix Pro 6.0 analysis software (Molecular Devices Corporation,). The image resolution was set to 5 µm per pixel. Spots were defined as circular features with defined

diameter of 100 µm. The values of total intensity were chosen for data processing, performed with Graphpad Prism® 6.0. The intensities was calculated and averaged. Error bars represent the standard deviation for all data points reported.

vi. Analyzing glycan binding specificity of HIV-1 bNAbs on NHS-coated glass slide. The slide for the study of PG9, PG16 and PGTs141-145 was prepared by printing glycans **G1-33** (Figure S11) on the N-hydroxysuccinimide coated surface through covalent bond formation. Slide images obtained by fluorescent scan after secondary antibody incubation.

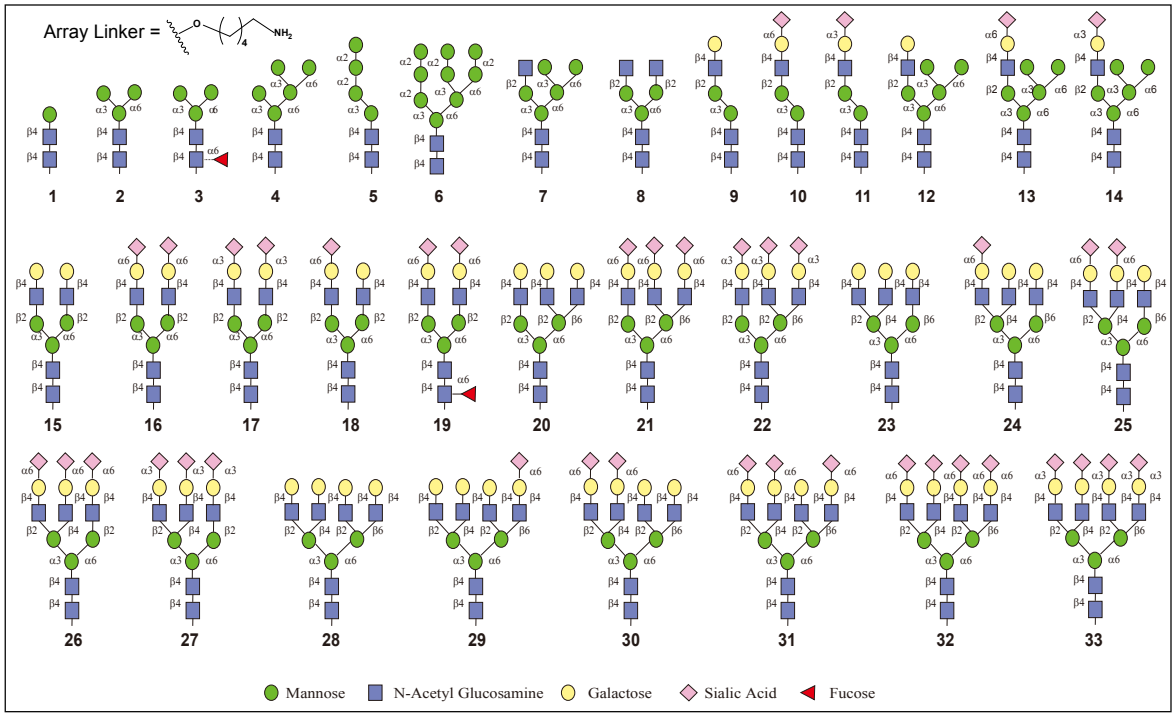


Figure S11 | Schematic representation of *N*-glycans printed on NHS coated glass slide.

Having incorporated diverse HIV-1 gp120 related *N*-glycans in our array, we next proceed to investigate binding behavior of PG16 to those glycans. Our results are consistent with our previously reported data, where, the PG16 binding is proportional to α 2,6-Neu5Ac count at the termini (Figure S12). A short conclusion from our study is presence of di-sialylated antennae in defined orientation is critical for binding in PG16 binding pocket. However, it demand deep investigation to prove the phenomenon.

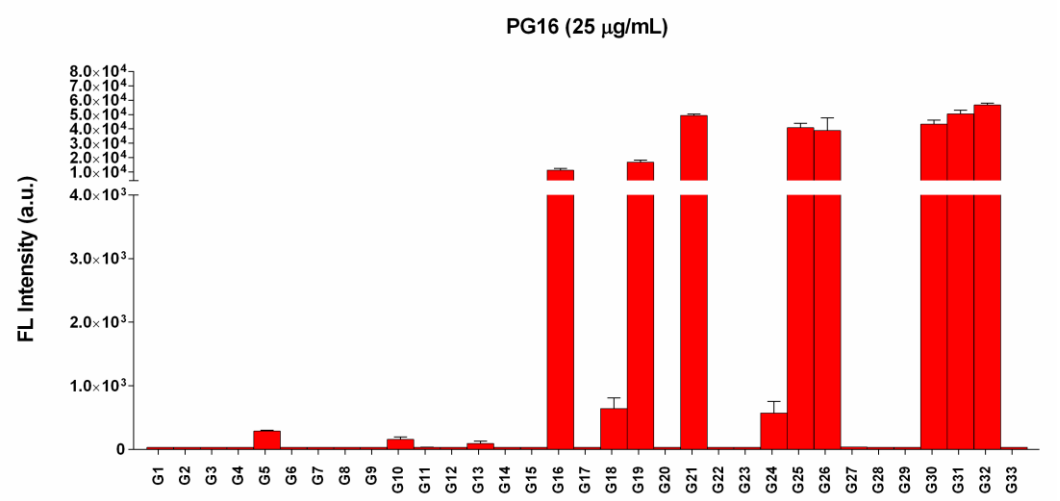


Figure S12. Binding behavior of PG16 using NHS-coated glass slide. Bindings of PG16 to panel of *N*-glycans represented in bar chart.

To our knowledge, there is no any array based study reported before, that showed defined set of glycans binds to antibodies PG9 and PGTs141-45. To get into the details, we sceened PG9 and PGTs141-145 on our NHS-coated glass slide array.

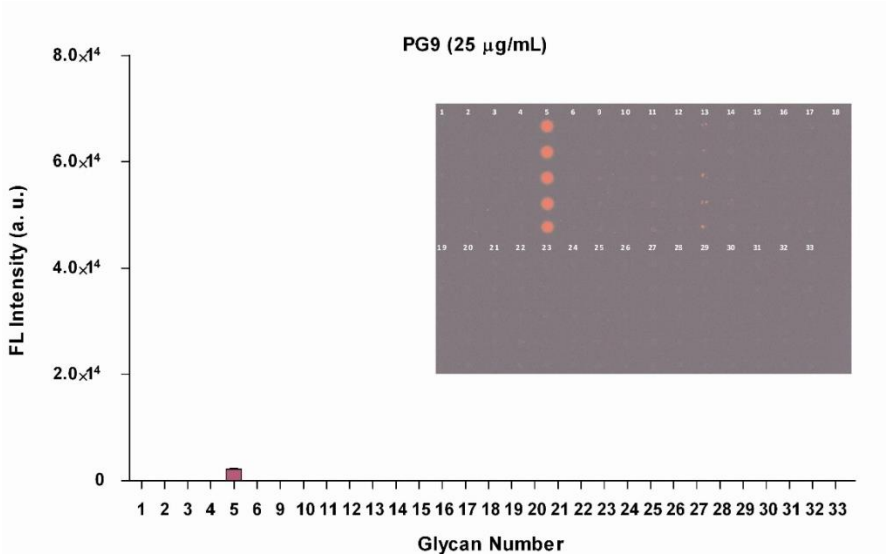


Figure S13. Binding behavior of PG9 using NHS-coated glass slide.

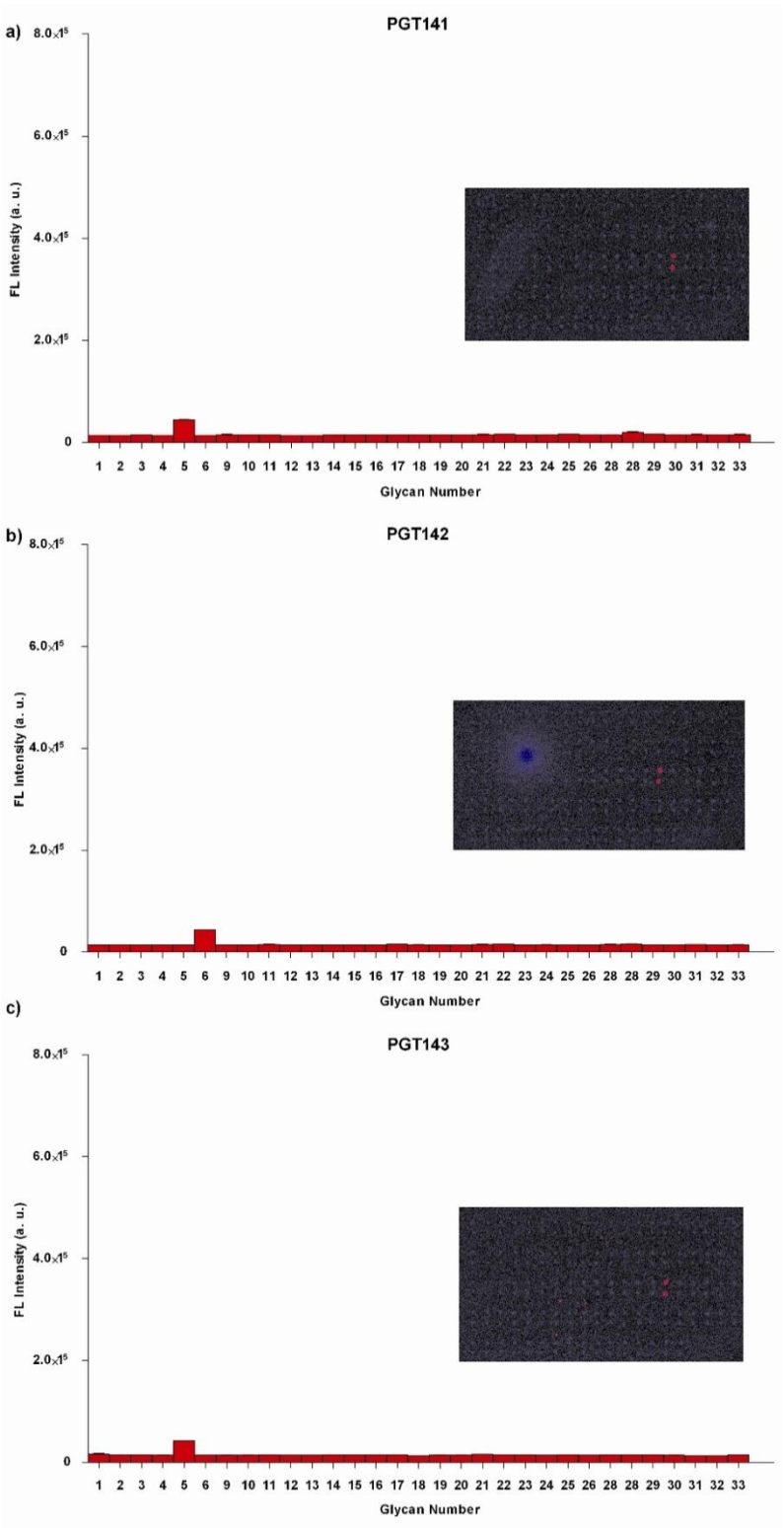


Figure S14. Binding behavior of PGTs 141-143 using NHS-coated glass slide. Antibody concentrations used here are 25 μg/mL

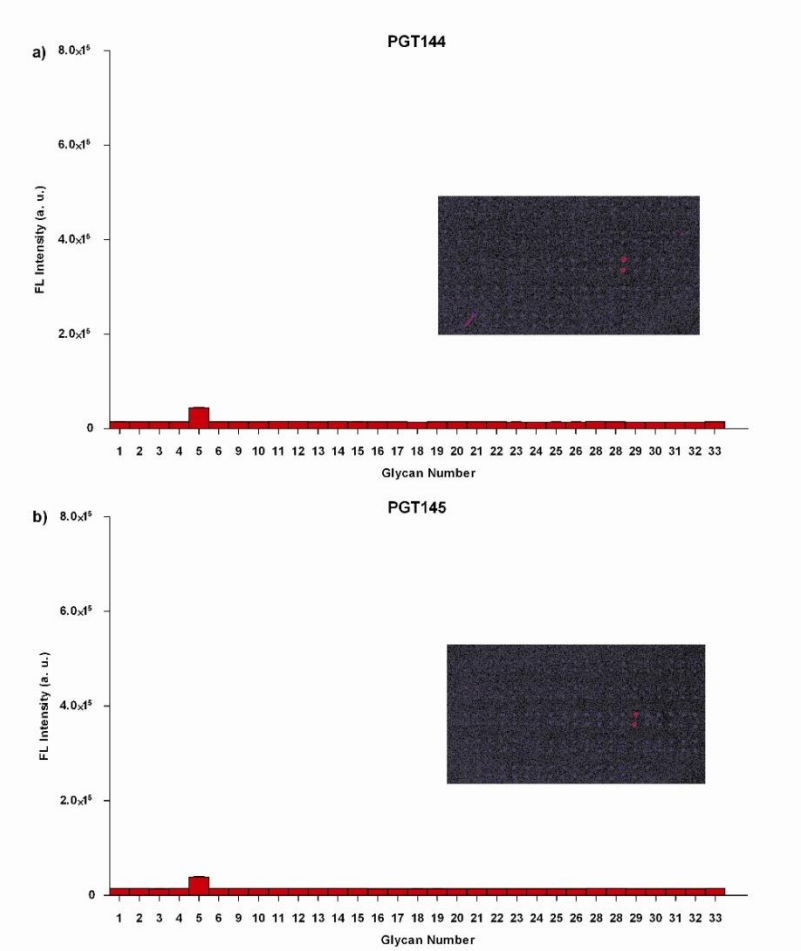


Figure S15. Binding behavior of PGTs14-145 using NHS-coated glass slide. Antibody concentrations used here are 25 μg/mL

In our binding experiment, we could not observed a detectable binding for antibodies PG9 (Figure. S13) and PGTs 141-145 (Figure. S14-15) towards any of the glycans printed on array.The possible explainations are 1) the exremly weak binding abilities of these antibodies to peptide/protein free glycans, 2) the glycan density on NHS-coated array may not be sufficient enough for detectable binding, and 3) the hydrolyzing tendancy of N-hydroxy succinimide activation of carboxylic acid groups on array might affect the efficient immobilization of glycans on array. However, throughout our experiments (Figure S13-15), we observed a strong signal for glycan **5** ($Man_4GlcNAc_2$). In order to confirm whether it's come from non-specific binding between secondary antibody and glycan **5**, we performed a control experiment where the

secondary antibody was applied directly on array without pre-complexed with primary antibody.Indeed, in absence of primary antibody we observed the fluorescent signal for glycan **5** (Figure S16)**.** Although the reason is unknown but it confirmed that secondary antibody showed non-specific binding to glycan **5**.

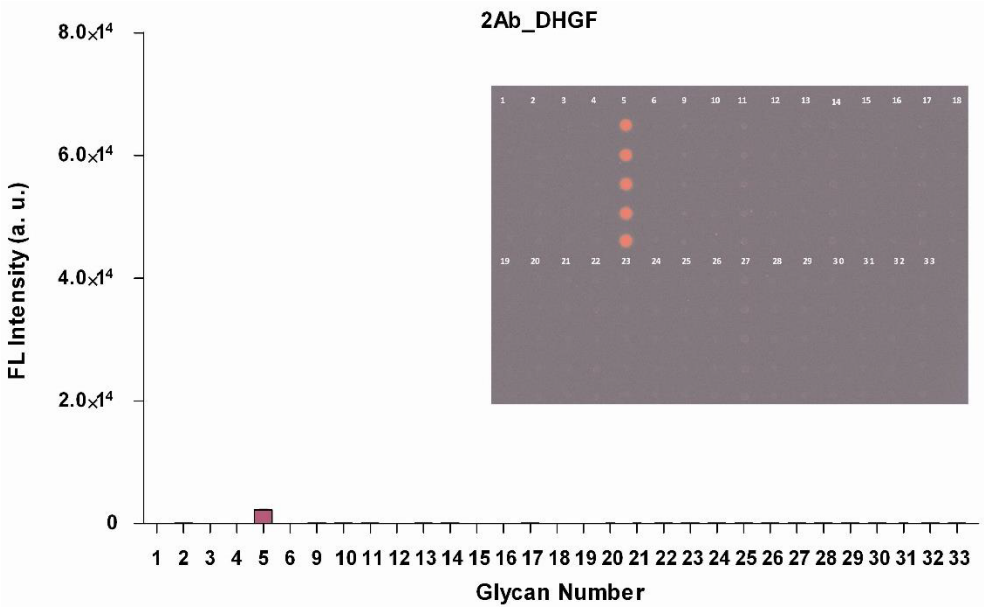


Figure S16. Experimental proof of secondary antibody binding to glycan 5.

vii. Analyzing glycan binding specificity of HIV-1 bNAbs onACG slide. Having demonstrated the applicability of ACG slide over NHS-coated slide in terms of glycan density and inhancement in signal intensity, we printed glycan glycans **I-XI** on ACG array using phosphonate chemistry (Figure S17). The binding specificities of PGTs141-144 are shown bellow.

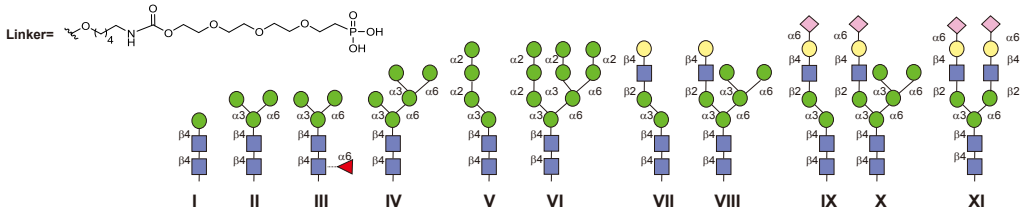


Figure S17. Cartoon represents glycans printed on ACG array. The structure of linker is shown on the upper left corner.

The binding specificities of PGTs141-144 are shown in Figure S18. However, we could not find the binding for PGT145 on ACG array, most probably because of its weak glycan binding affinity.

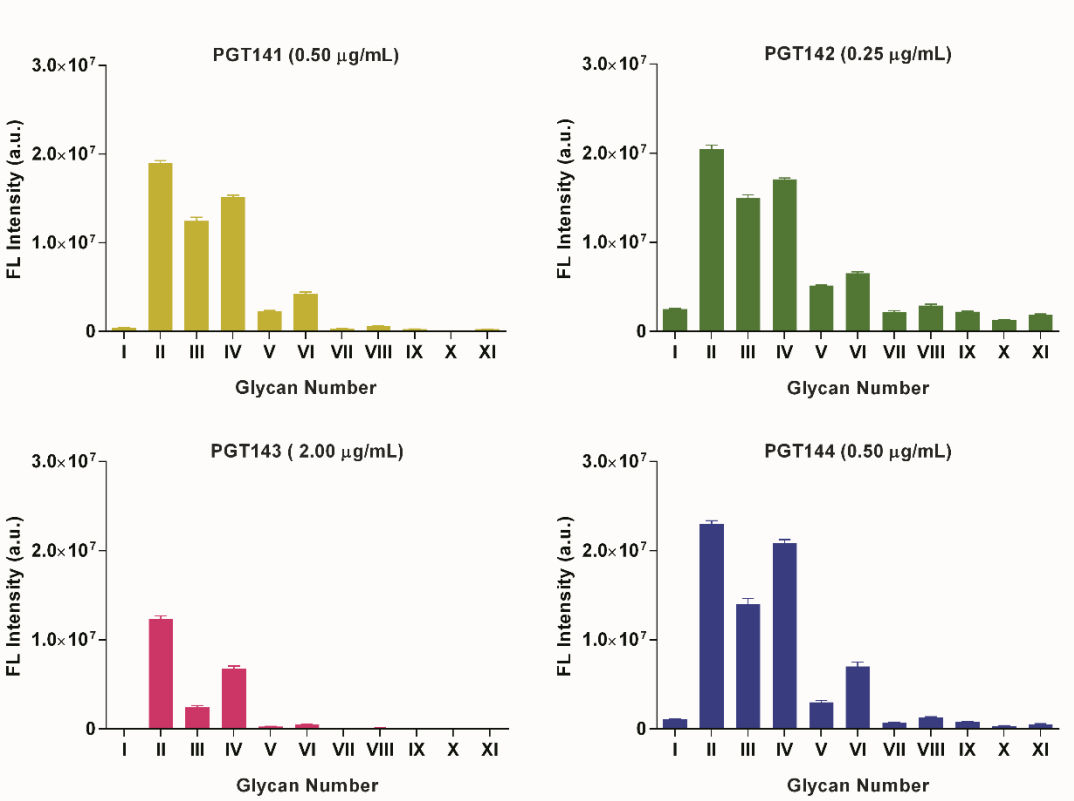


Figure S18. Bindings of PGTs 141-144 towards panel of N-glycans on ACG array is shown in bar chart.

viii. Determination of surface dissociation constants ($K_{D.surf}$) on ACG slide: The aluminium oxide coated glass slides for the determination of dissociation constants were spotted with 100 and 50 µM concentrations of glycans $Man_5GlcNAc_2$ (V), hybrid type (XI), bi-antennary complex type (XII), V+XI (1:1 mole ratio), V+XII, and XI+XII. Antibody PG16 was serially diluted to 3.32, 1.66, 0.833, 0.415, 0.207, 0.103, 0.051 and 0.025 µM with 3% BSA-PBST buffer. DyLight649-conjugated Donkey Anti-Human IgG antibody was pre-complexed with primary antibody PG16 (1:1 by weight). The pre-complexed solution (100 µL) was applied to each well

and incubated at 4 ℃ for 6 h in the dark. Finally, slides were washed with PBST, spin dried and scanned at 450 nm with a microarray fluorescence chip reader. Scanned images were analyzed with GenePix Pro 6.0 analysis software. The signal intensities for binding of PG16 to $Man_5GlcNAc_2$ (V) and mixture of V+XI (1:1 mole ratio) were too weak to determine the K_D. The binding curves for the rest of samples printed on array are shown in Figure S19 and K_D values are summarized in Table S2.

In the case of PG9, because of its very weak glycan binding affinity, we were not able to achieve the signal saturation to measure the binding constants, however, increasing PG9 concentration to 700 µg/mL resulted in a precipitation on array surface.

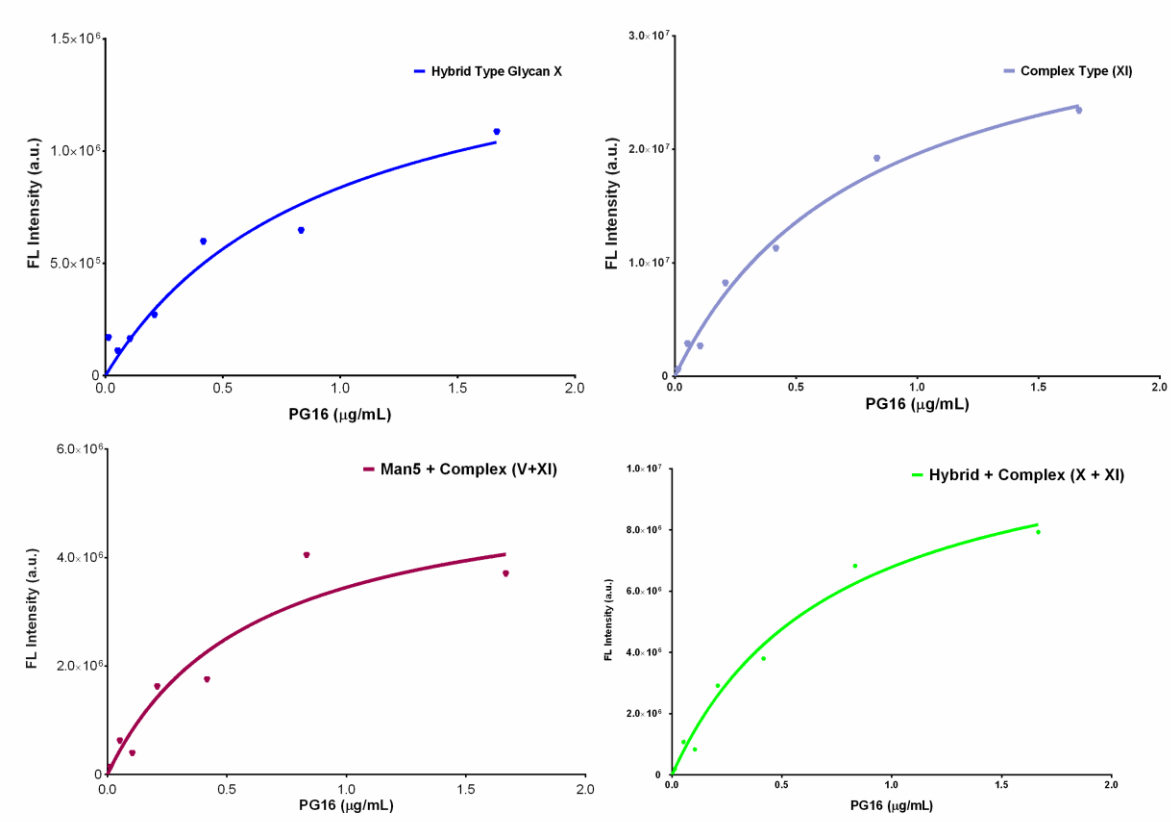


Figure S19. Antibody PG16 binding curves observed for glycans **X, XI** and mixtures **V+XI** and **X+XII** at 100 µM concentration. The curves were obtained by using DyLight649-conjugated donkey anti-Human IgG secondary antibody.

Table S1. $K_{D,surf}$ (μM) values of antibody PG16 and glycans X, XI and mixtures V+XI and X+XI.

Glycan no.	$K_{D,surf}$ (μM) ± SD (μM)
X	0.935 ± 0.026 μM
XI	0.320 ± 0.125 μM
V + XI	0.827 ± 0.200 μM
X + XI	0.988 ± 0.223 μM

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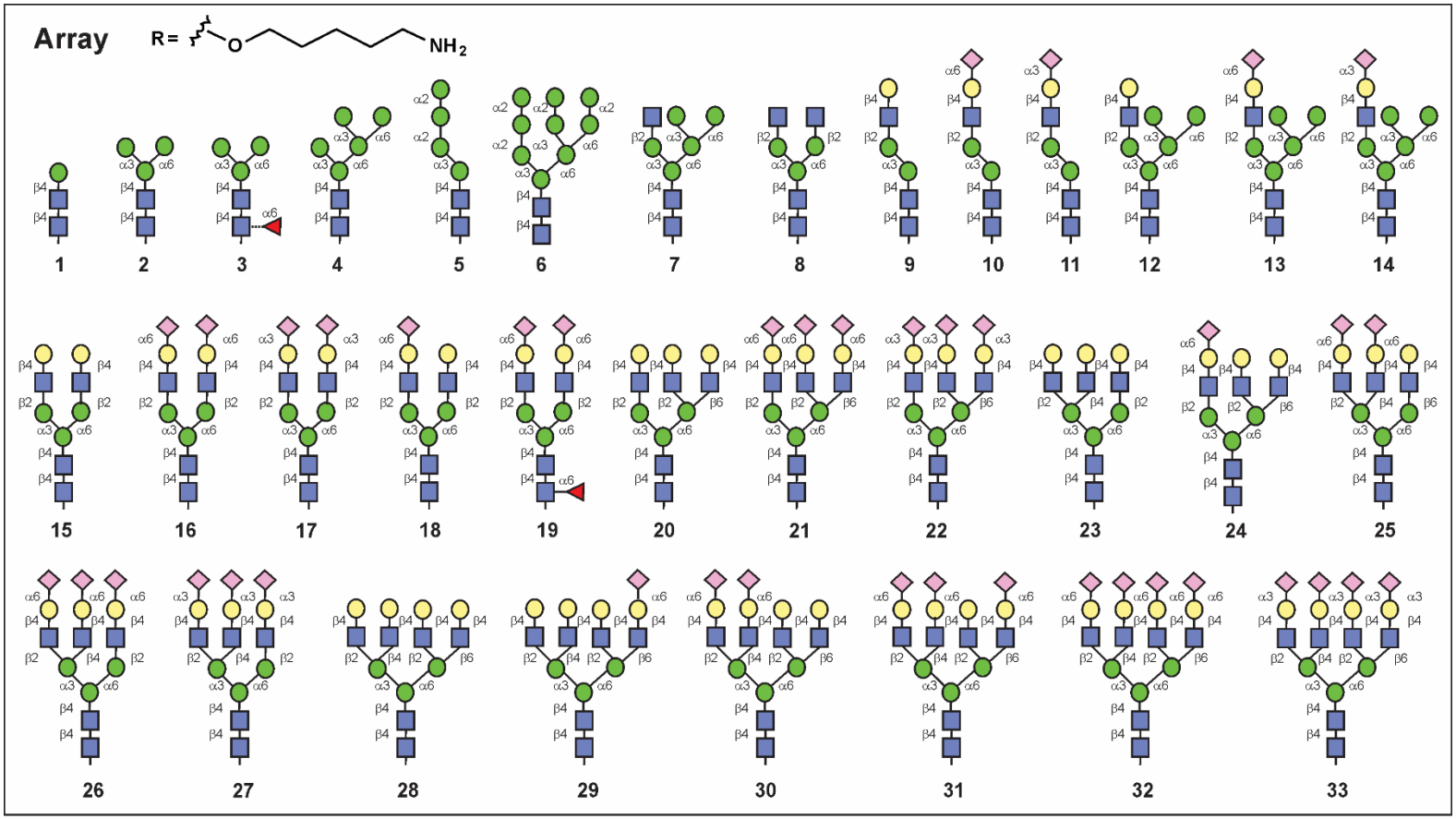
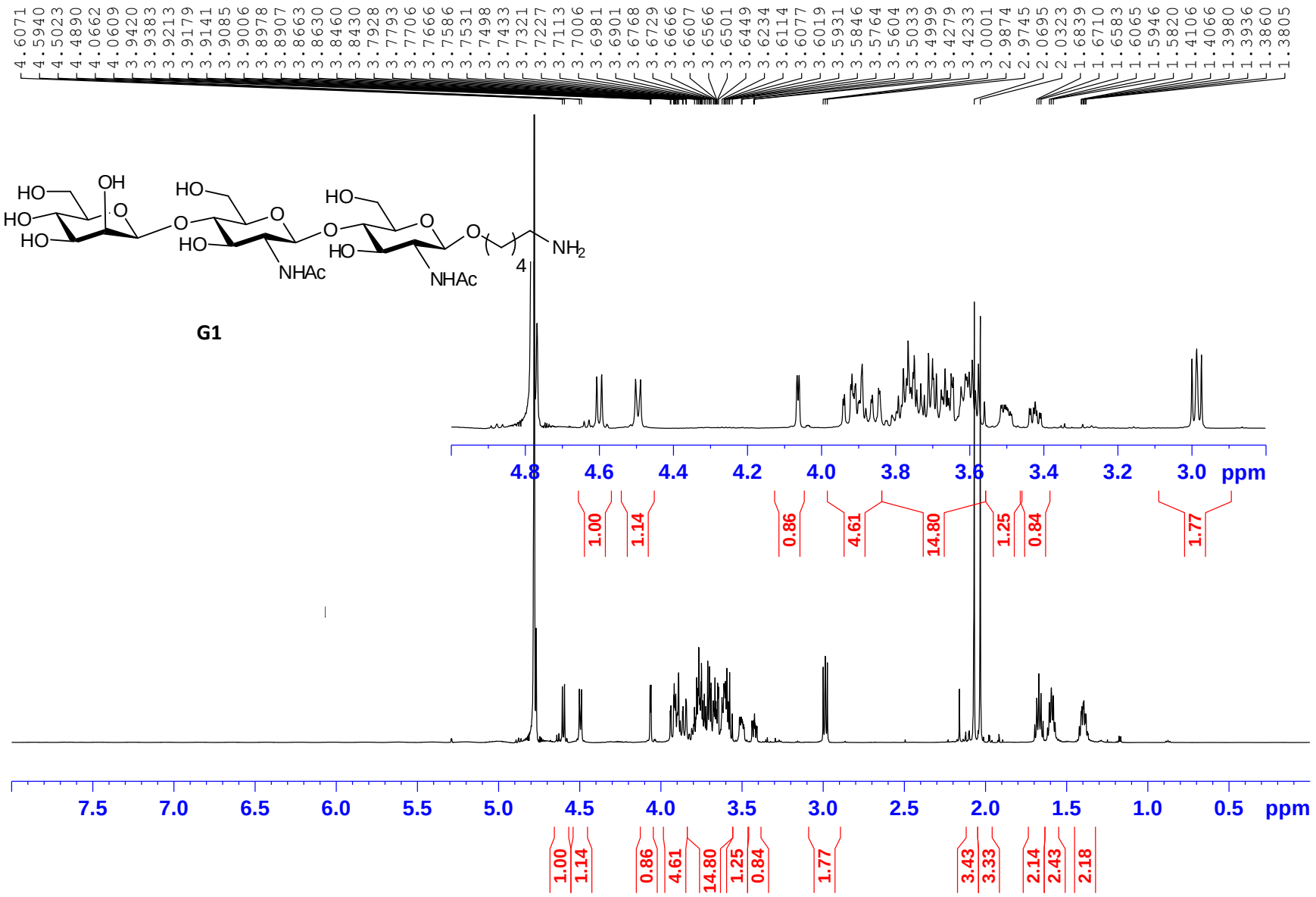
17 K. Rana, G. Kucukayan-Dogu, E. Bengu "Growth of vertically aligned carbon nanotubes over self-ordered nano-proous alumina films and their surface properties" *Applied Surface Science*, 2012, 258 7112-7117.

Spectral Data



Characterization data of structures G15-17, G20-23, G26-28 and G32-33 was reported in *J. Am. Chem. Soc*. **135**(41), 15382-15391, (2013). The data for remaining structures is listed bellow.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HO
OH
O
HO
HO
HO
O
HO
O
HO
NHAc
O
HO
O
HO
NHAc
O
4
NH2
G1
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
ppm
1.00
1.14
0.86
4.61
14.80
1.25
0.84
1.77
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
1.00
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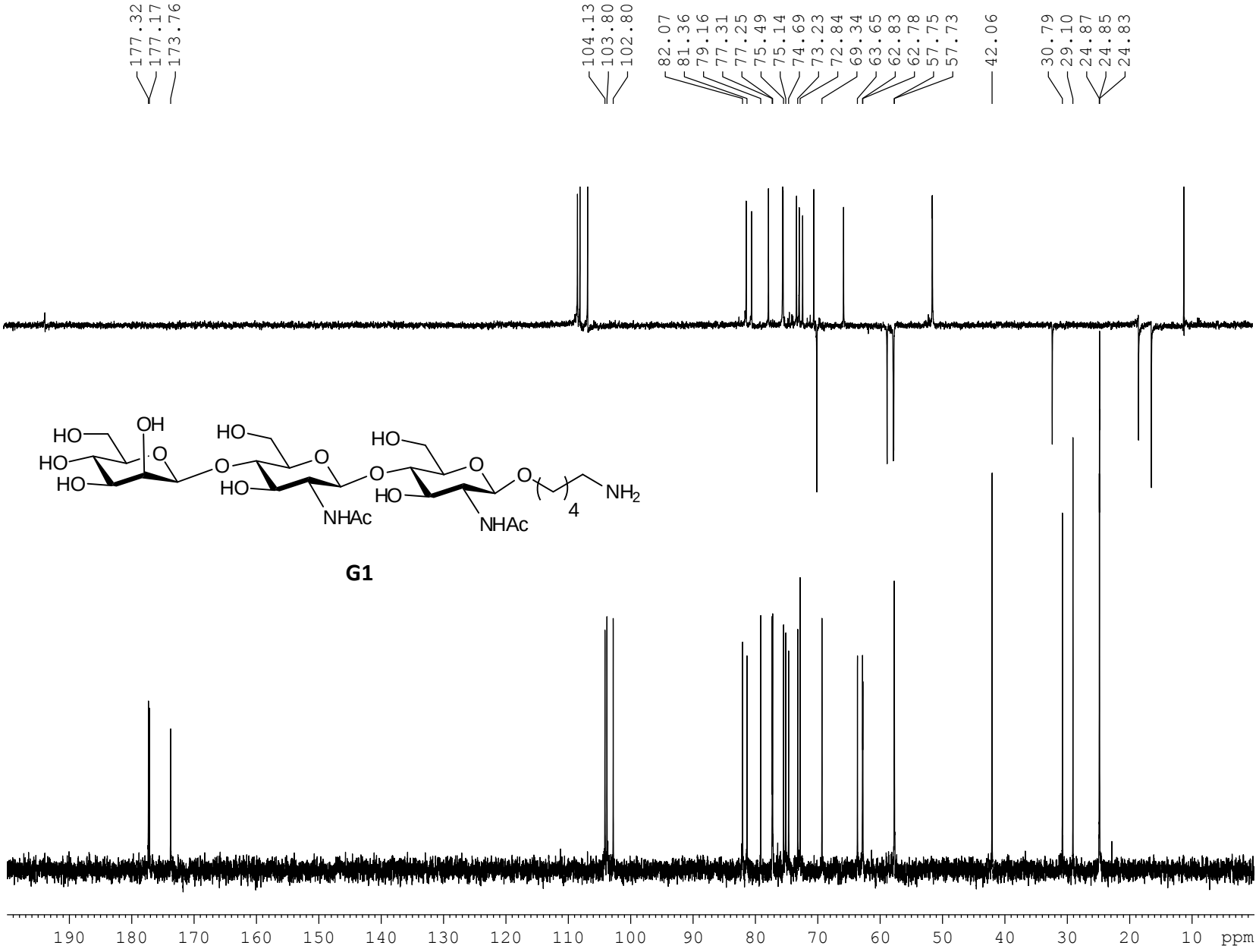
0.84
1.77
3.43
3.33
2.14
2.43
2.18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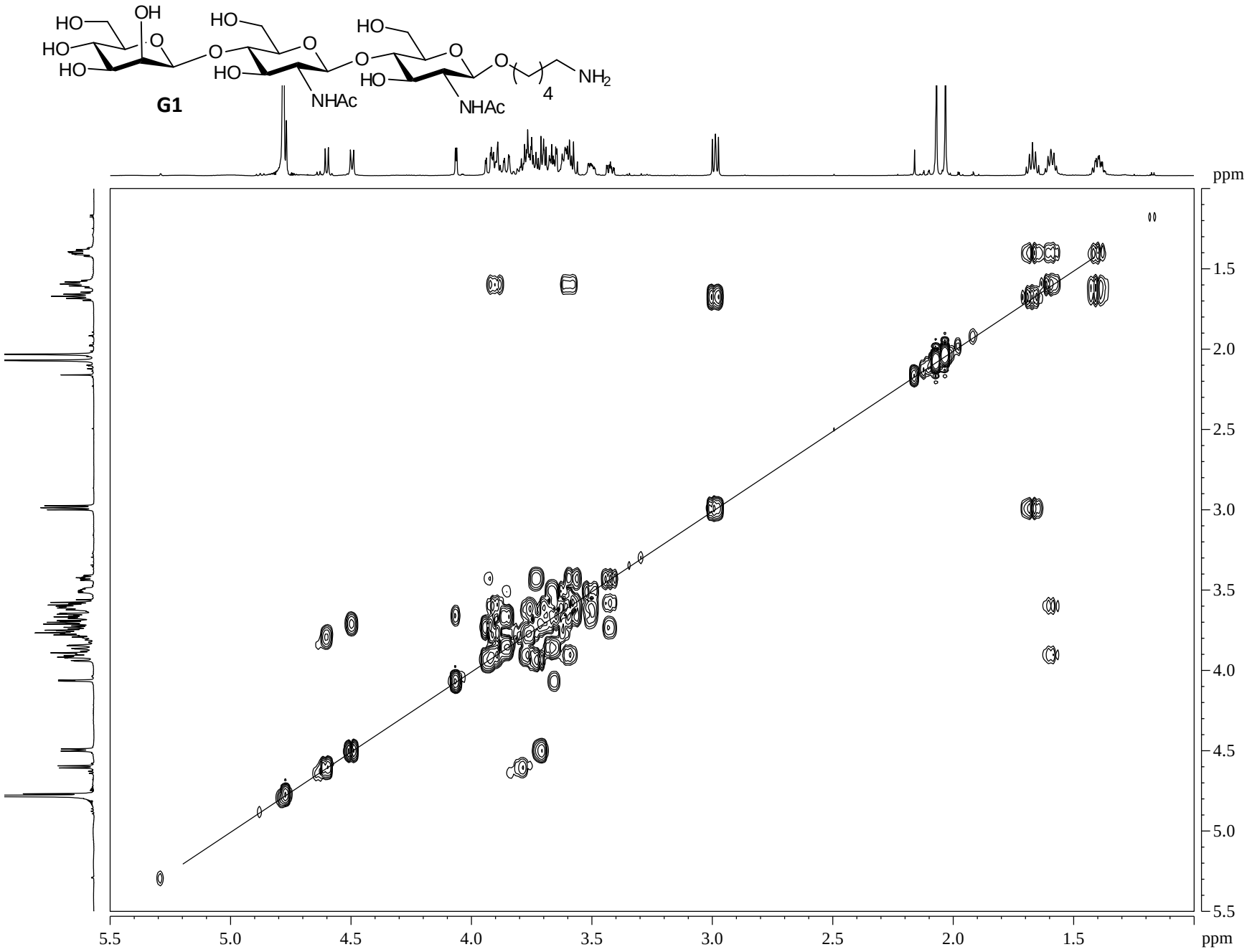
177.17
173.76
104.13
103.80
102.80
82.07
81.36
79.16
77.31
77.25
75.49
75.14
74.69
73.23
72.84
69.34
63.65
62.83
62.78
57.75
57.73
42.06
30.79
29.10
24.87
24.85
24.83
HO
OH
O
NHAc
NH2
4
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

G1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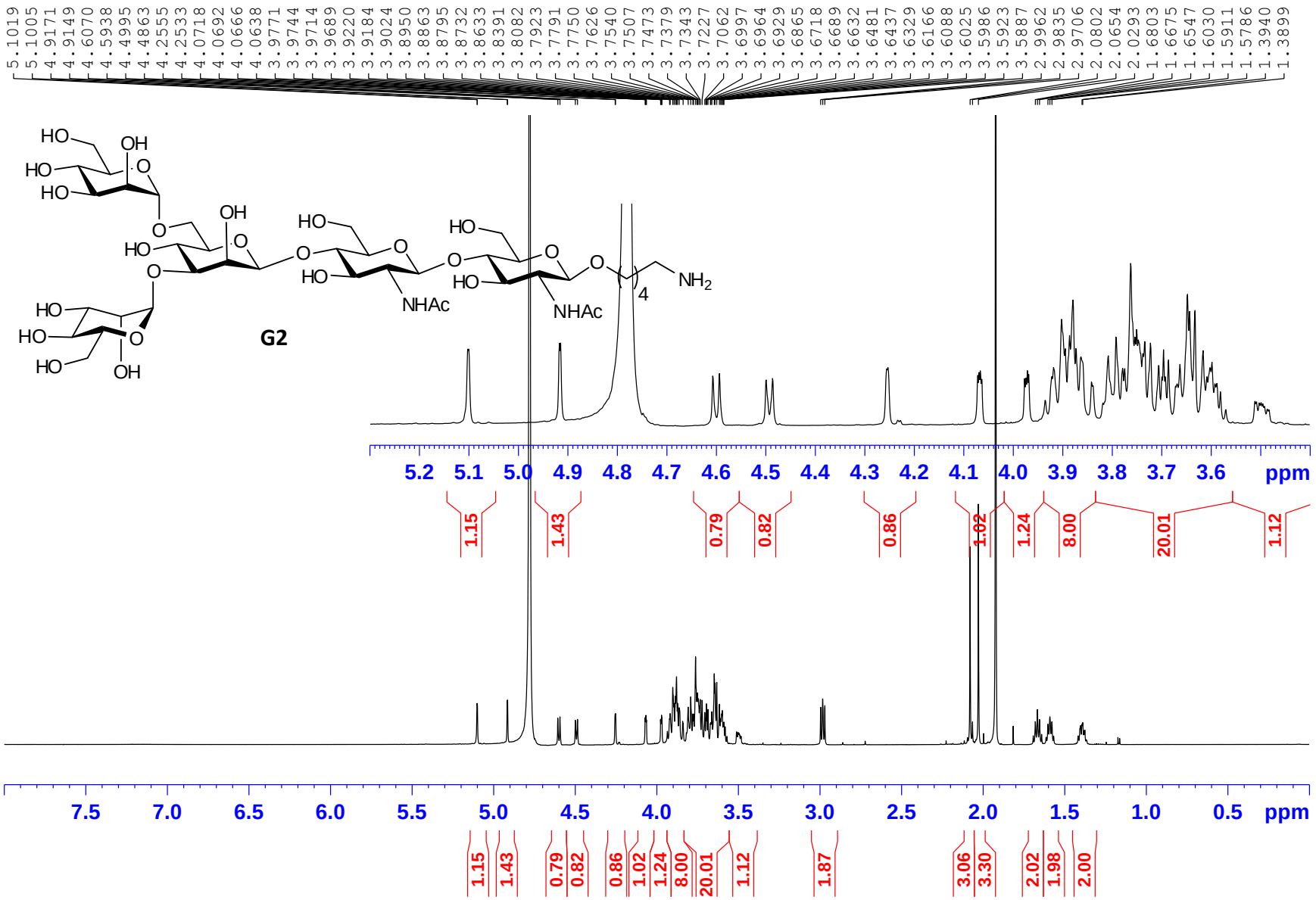
OH
HO
HO
O
O
HO
HO
O
NHAc
O
HO
HO
O
NHAc
O
O
4
NH2
G1
ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm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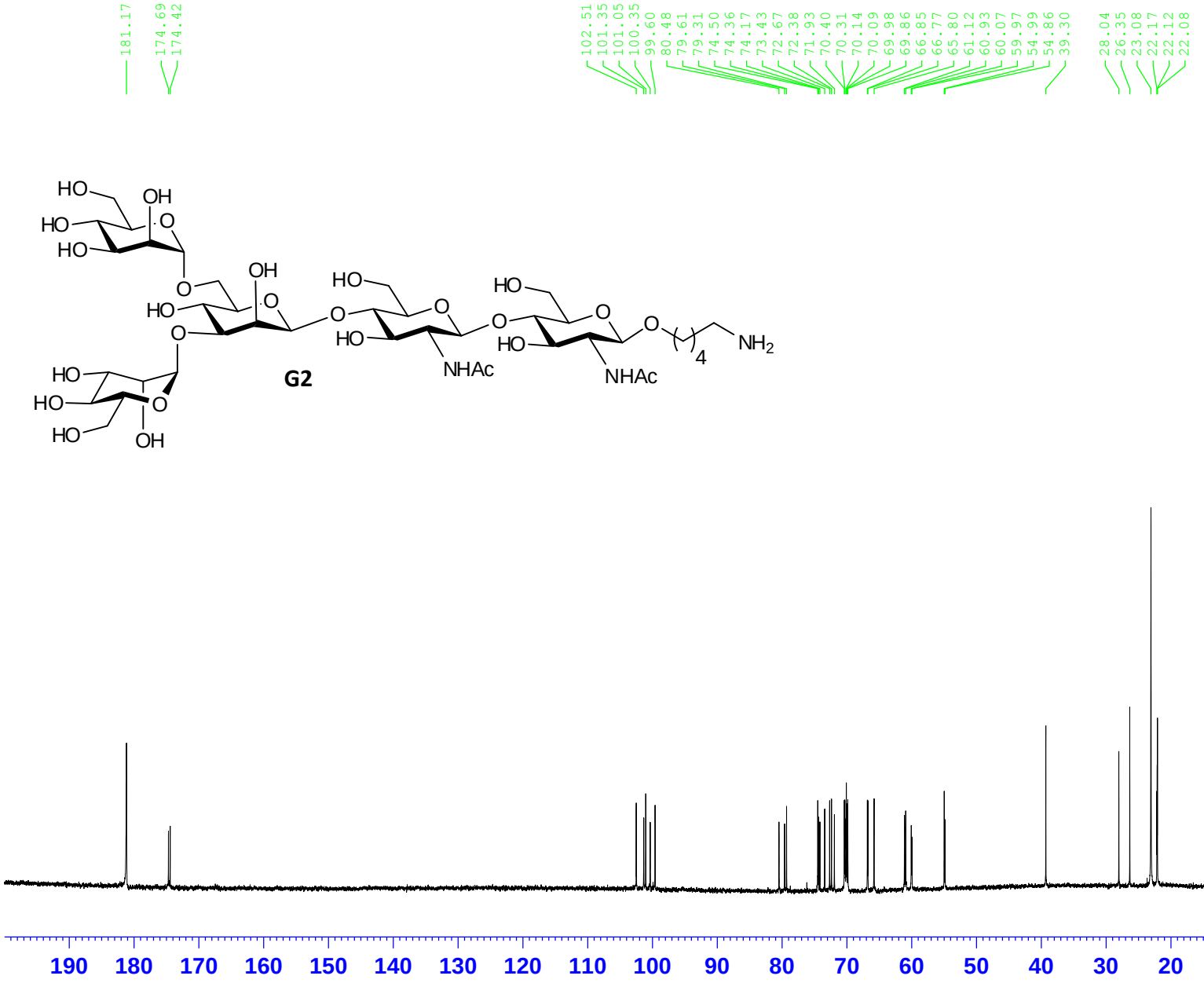
5.1005
4.9171
4.9149
4.6070
4.5938
4.4995
4.4863
4.2555
4.2533
4.0718
4.0692
4.0666
4.0638
3.9771
3.9744
3.9714
3.9689
3.9220
3.9184
3.9024
3.8950
3.8863
3.8795
3.8732
3.8633
3.8391
3.8082
3.7923
3.7791
3.7750
3.7626
3.7540
3.7507
3.7473
3.7379
3.7343
3.7227
3.7062
3.6997
3.6964
3.6929
3.6865
3.6718
3.6689
3.6632
3.6481
3.6437
3.6329
3.6166
3.6088
3.6025
3.5986
3.5923
3.5887
2.9962
2.9835
2.9706
2.0802
2.0654
2.0293
1.6803
1.6675
1.6547
1.6030
1.5911
1.5786
1.3940
1.3899
HO
OH
O
NHAc
NH2
4
G2
5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 ppm
1.15
1.43
0.79
0.82
0.86
1.02
1.24
8.00
20.01
1.12
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
1.15
1.43
0.79
0.82
0.86
1.02
1.24
8.00
20.01
1.12
1.87
3.06
3.30
2.02
1.98
2.00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101.05
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79.31
74.50
74.36
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73.43
72.67
72.38
71.93
70.40
70.31
70.14
70.09
69.98
69.86
66.85
66.77
65.80
61.12
60.93
60.07
59.97
54.99
54.86
39.30
28.04
26.35
23.08
22.17
22.12
22.08
HO
OH
O
NHAc
NH2
4
G2
190
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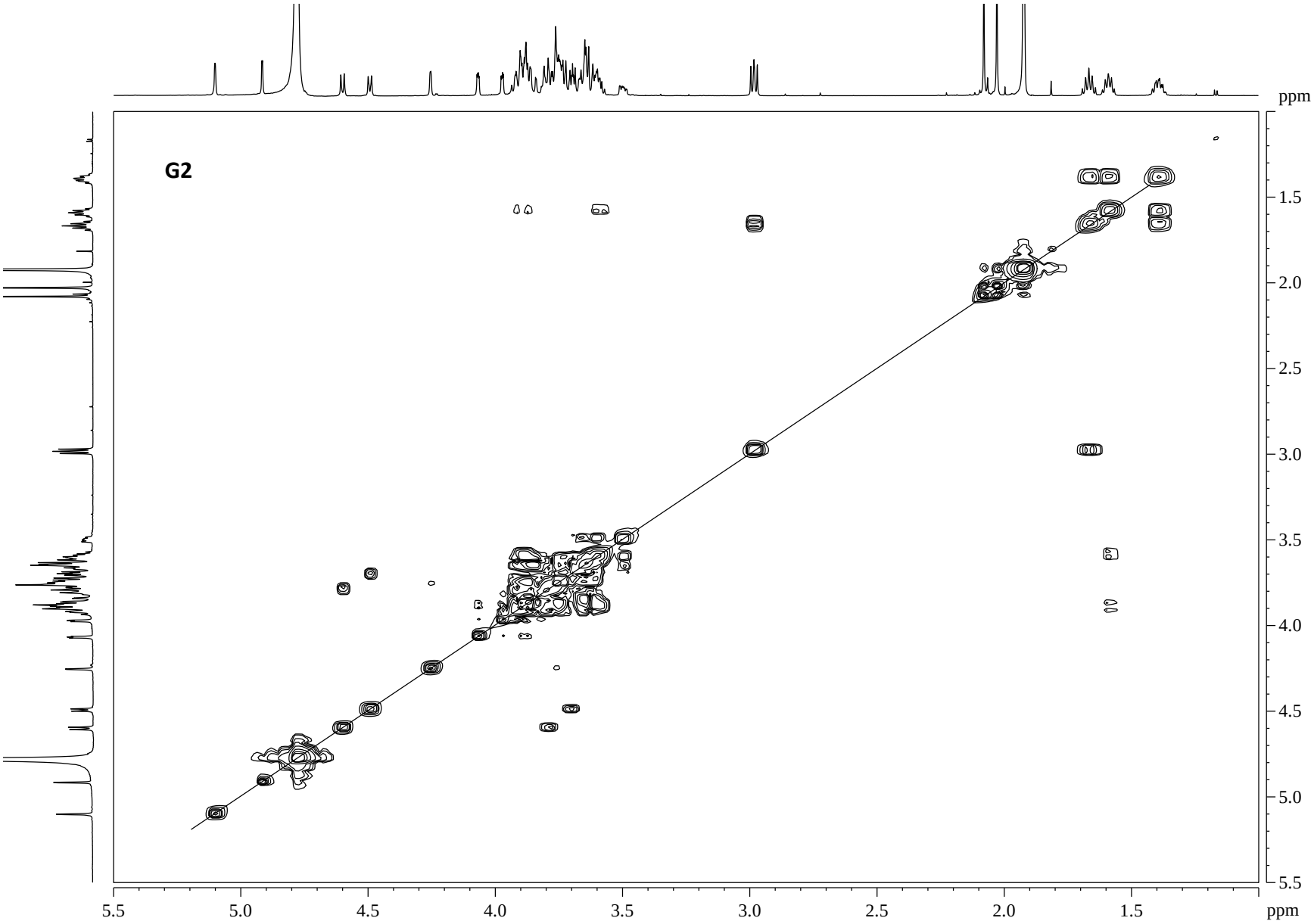
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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ppm
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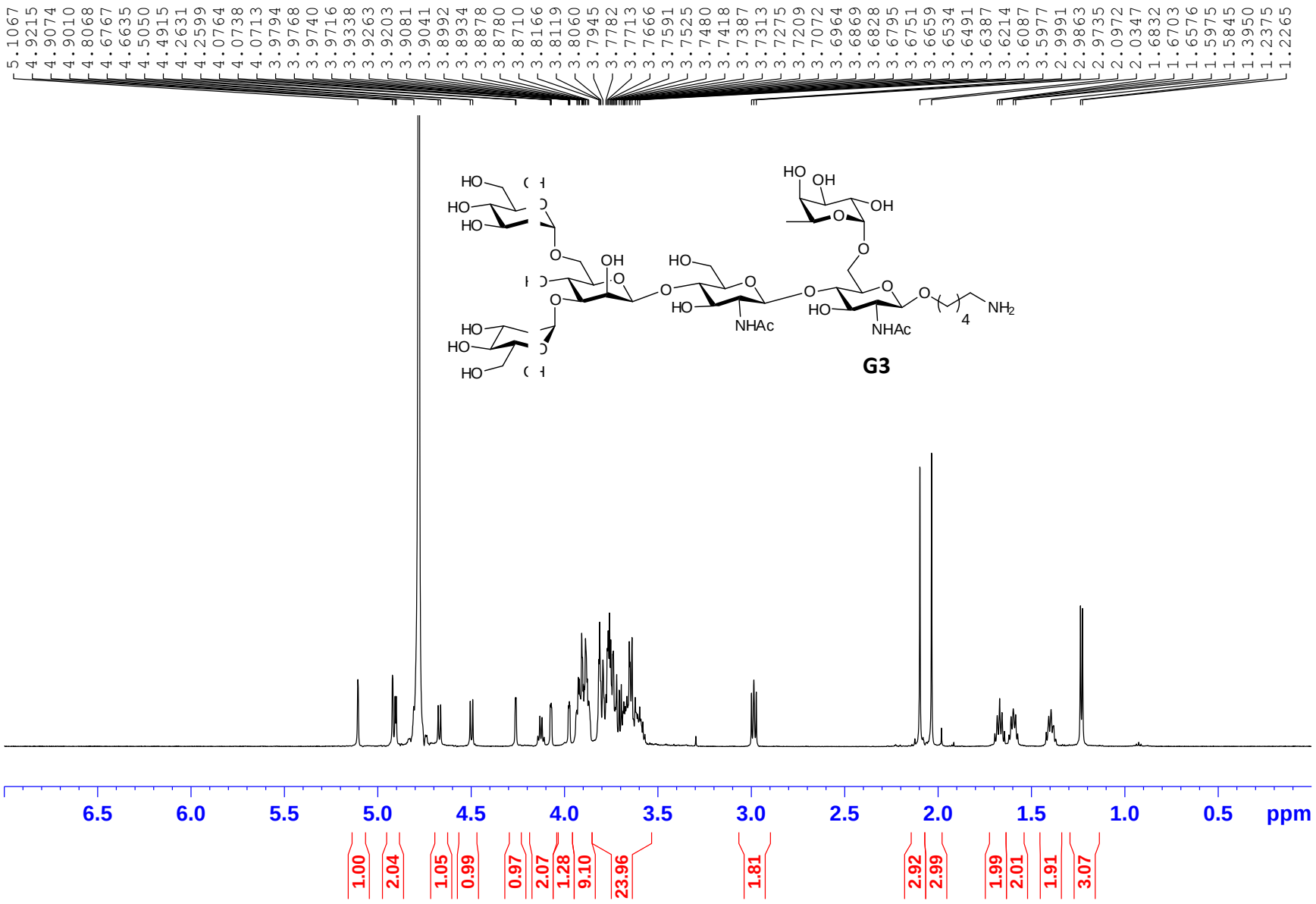
2.5
3.0
3.5
4.0
4.5
5.0
5.5
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm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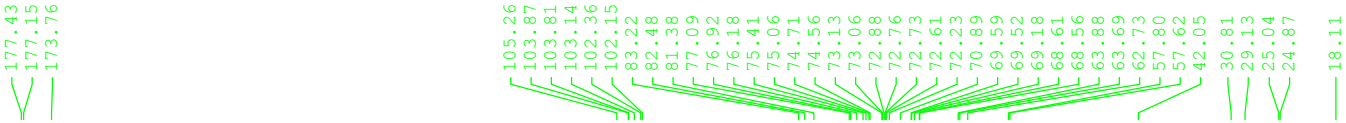
4.9215
4.9074
4.9010
4.8068
4.6767
4.6635
4.5050
4.4915
4.2631
4.2599
4.0764
4.0738
4.0713
3.9794
3.9768
3.9740
3.9716
3.9338
3.9263
3.9203
3.9081
3.9041
3.8992
3.8934
3.8878
3.8780
3.8710
3.8166
3.8119
3.8060
3.7945
3.7782
3.7713
3.7666
3.7591
3.7525
3.7480
3.7418
3.7387
3.7313
3.7275
3.7209
3.7072
3.6964
3.6869
3.6828
3.6795
3.6751
3.6659
3.6534
3.6491
3.6387
3.6214
3.6087
3.5977
2.9991
2.9863
2.9735
2.0972
2.0347
1.6832
1.6703
1.6576
1.5975
1.5845
1.3950
1.2375
1.2265
G3
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
1.00
2.04
1.05
0.99
0.97
2.07
1.28
9.10
23.96
1.81
2.92
2.99
1.99
2.01
1.91
3.07


177.43
177.15
173.76
105.26
103.87
103.81
103.14
102.36
102.15
83.22
82.48
81.38
77.09
76.92
76.18
75.41
75.06
74.71
74.56
73.13
73.06
72.88
72.76
72.73
72.61
72.23
70.89
69.59
69.52
69.18
68.61
68.56
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62.73
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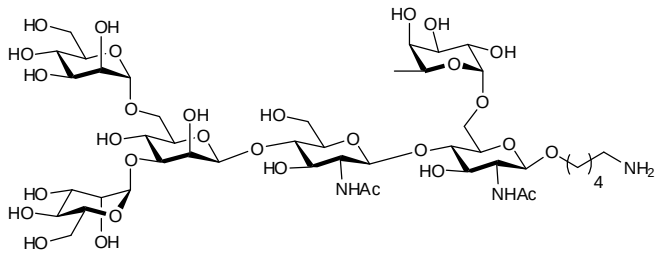
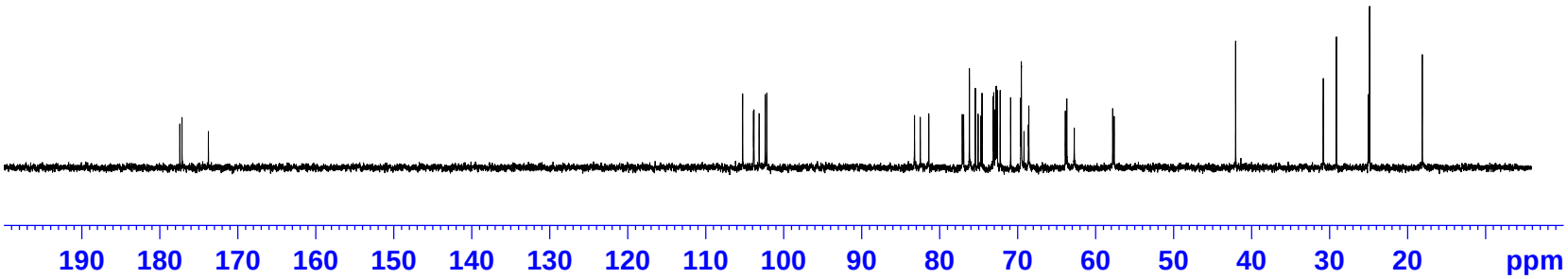
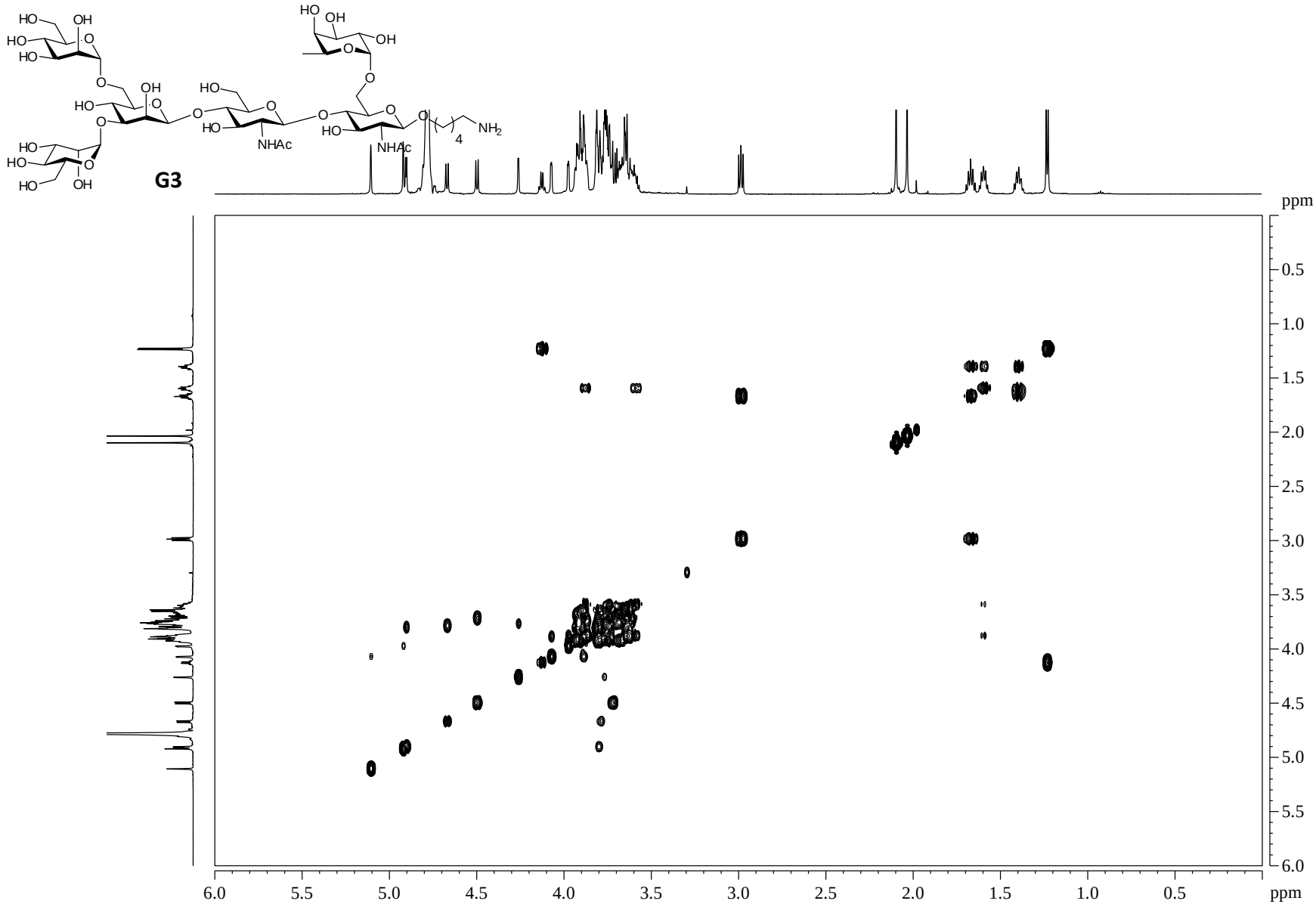
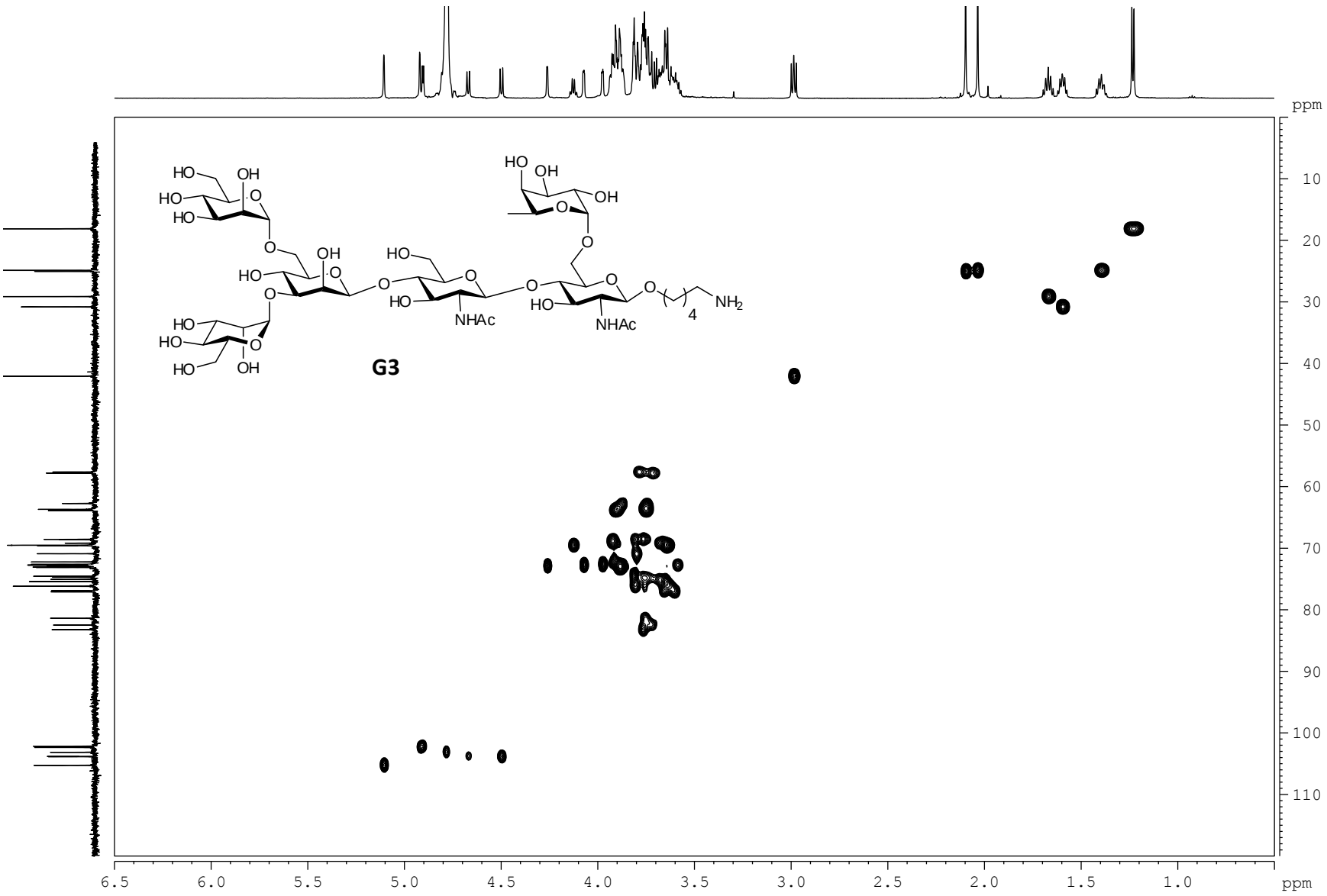
57.62
42.05
30.81
29.13
25.04
24.87
18.11

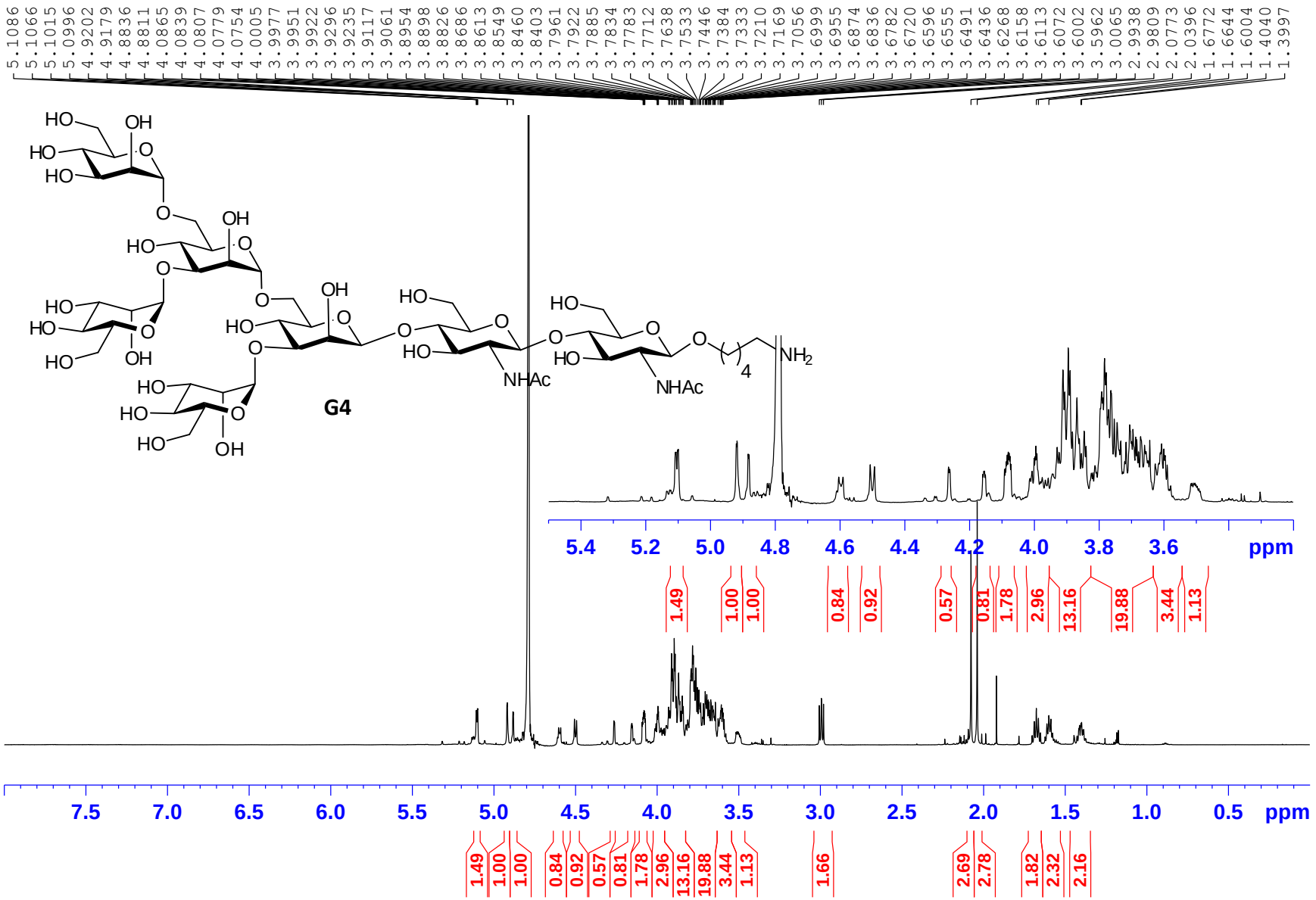

HO
OH
HO
HO
O
OH
HO
O
HO
O
HO
HO
O
HO
NHAc
O
HO
O
HO
NHAc
O
4
NH2

G3


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


G3
NHAc
NHAc
NH2
4
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
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


G3
NHAc
NHAc
NH2
4
ppm
10
20
30
40
50
60
70
80
90
100
110
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm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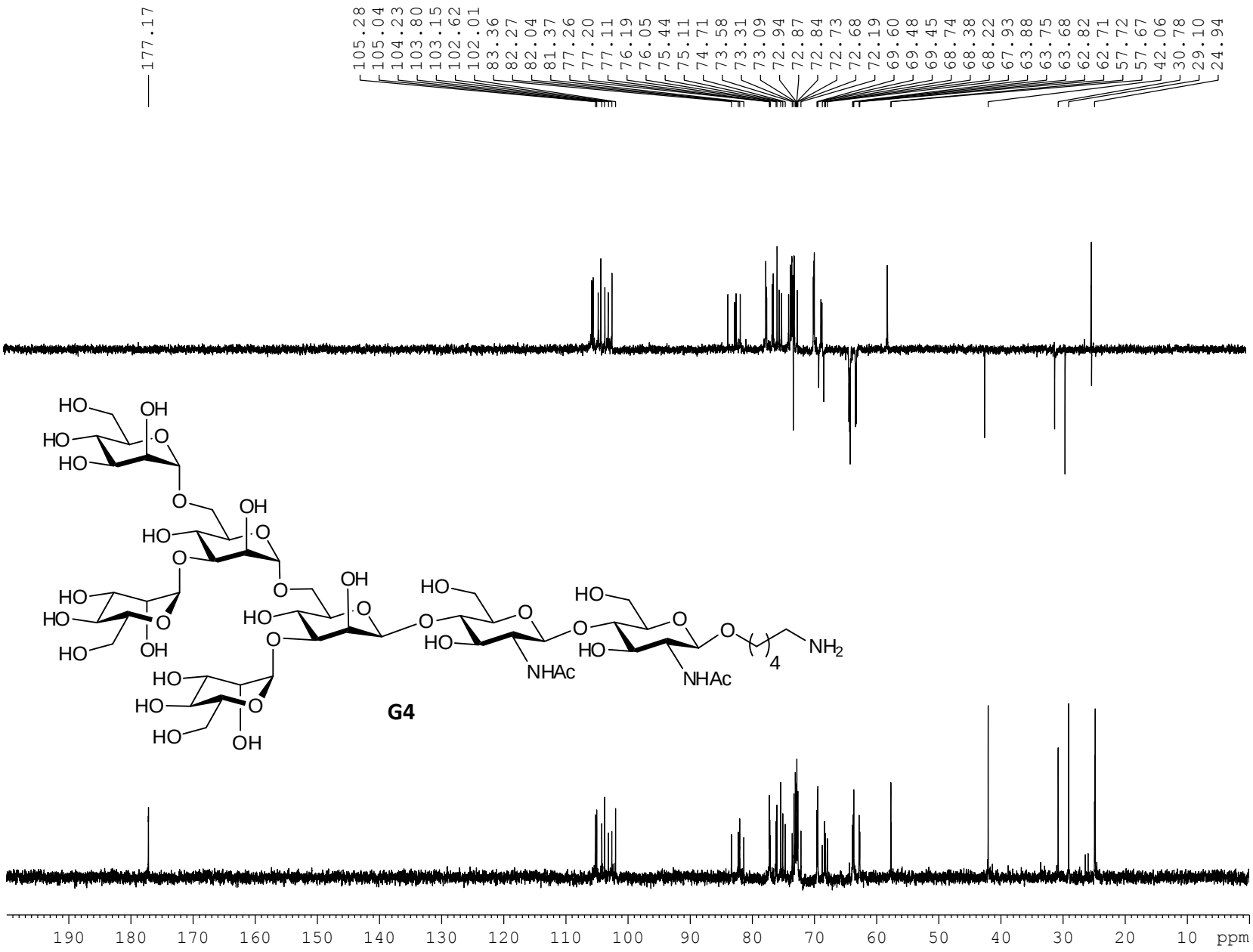
G4
NHAc
NHAc
NH2
4
5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 ppm
1.49 1.00 1.00 0.84 0.92 0.57 0.81 1.78 2.96 13.16 19.88 3.44 1.13
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.49 1.00 1.00 0.84 0.92 0.57 0.81 1.78 2.96 13.16 19.88 3.44 1.13 1.66 2.69 2.78 1.82 2.32 2.16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104.23
103.80
103.15
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102.01
83.36
82.27
82.04
81.37
77.26
77.20
77.11
76.19
76.05
75.44
75.11
74.71
73.58
73.31
73.09
72.94
72.87
72.84
72.73
72.68
72.19
69.60
69.48
69.45
68.74
68.38
68.22
67.93
63.88
63.75
63.68
62.82
62.71
57.72
57.67
42.06
30.78
29.10
24.94
HO
OH
O
NHAc
NH2
4
G4
190
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170
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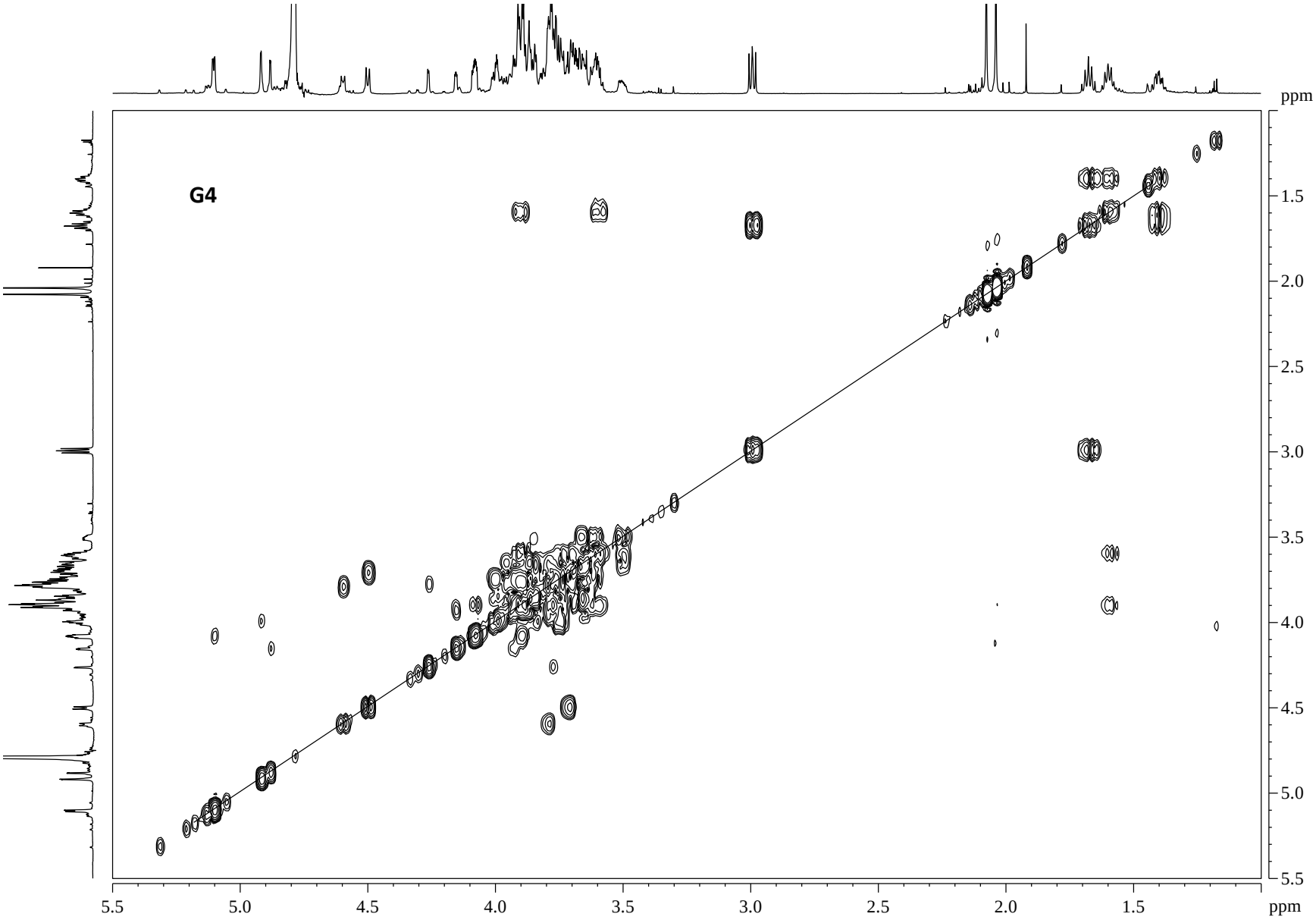
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


G4
ppm
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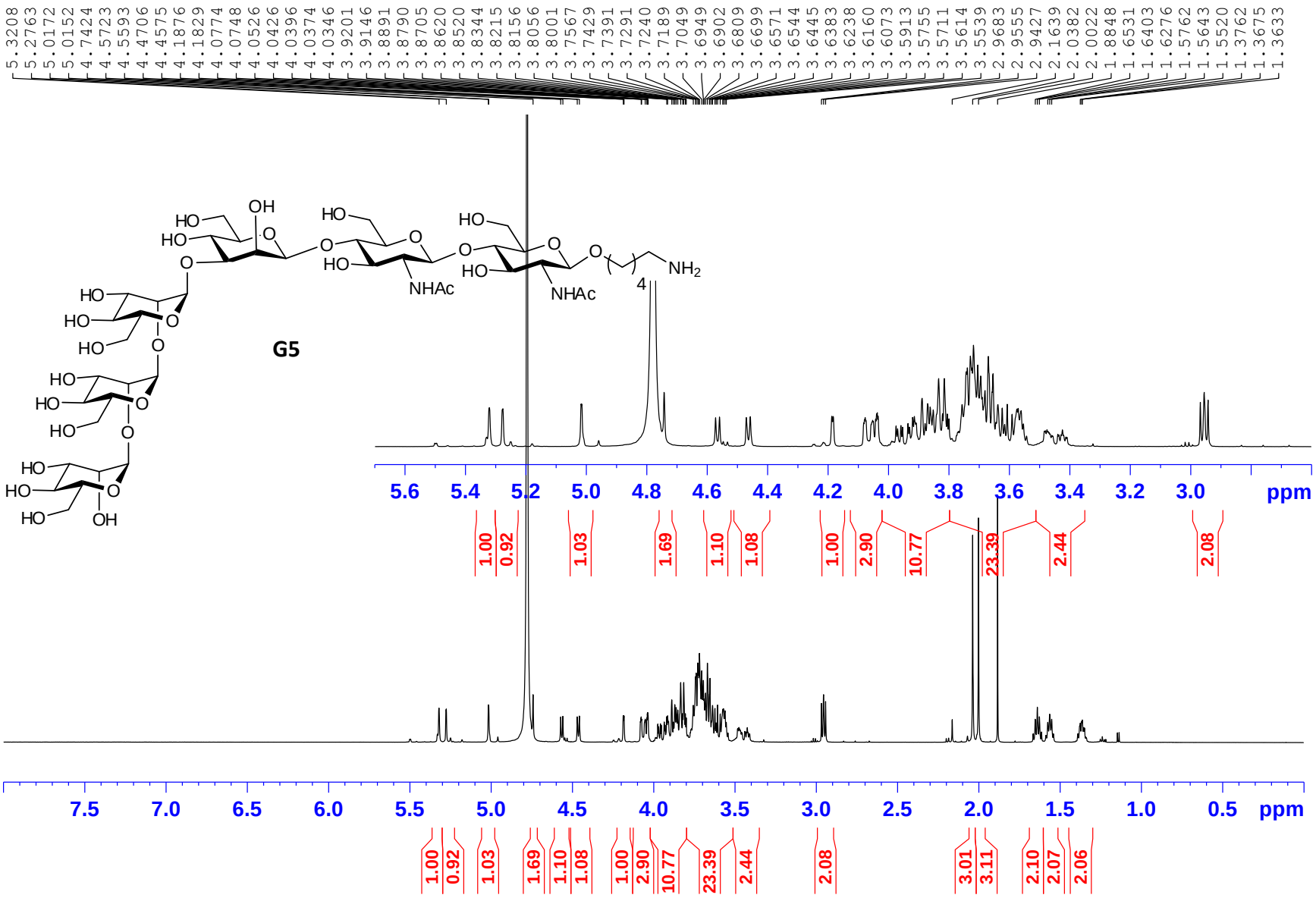
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm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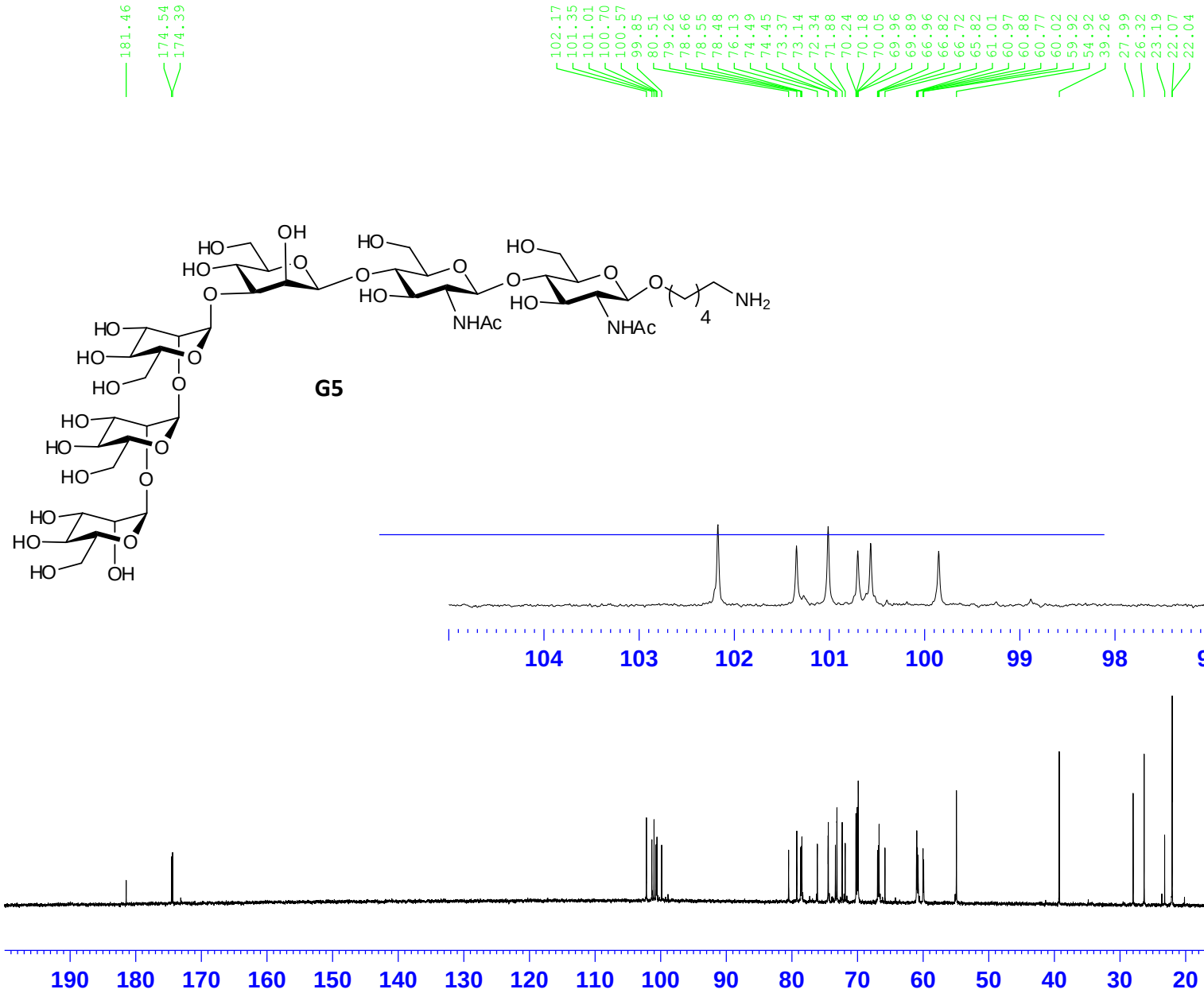
5.2763
5.0172
5.0152
4.7424
4.5723
4.5593
4.4706
4.4575
4.1876
4.1829
4.0774
4.0748
4.0526
4.0426
4.0396
4.0374
4.0346
3.9201
3.9146
3.8891
3.8790
3.8705
3.8620
3.8520
3.8344
3.8215
3.8156
3.8056
3.8001
3.7567
3.7429
3.7391
3.7291
3.7240
3.7189
3.7049
3.6949
3.6902
3.6809
3.6699
3.6571
3.6544
3.6445
3.6383
3.6238
3.6160
3.6073
3.5913
3.5755
3.5711
3.5614
3.5539
2.9683
2.9555
2.9427
2.1639
2.0382
2.0022
1.8848
1.6531
1.6403
1.6276
1.5762
1.5643
1.5520
1.3762
1.3675
1.3633
G5
NHAc
NHAc
NH2
4
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
3.0
ppm
1.00
0.92
1.03
1.69
1.10
1.08
1.00
2.90
10.77
23.39
2.44
2.08
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
1.00
0.92
1.03
1.69
1.10
1.08
1.00
2.90
10.77
23.39
2.44
2.08
3.01
3.11
2.10
2.07
2.06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101.35
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100.57
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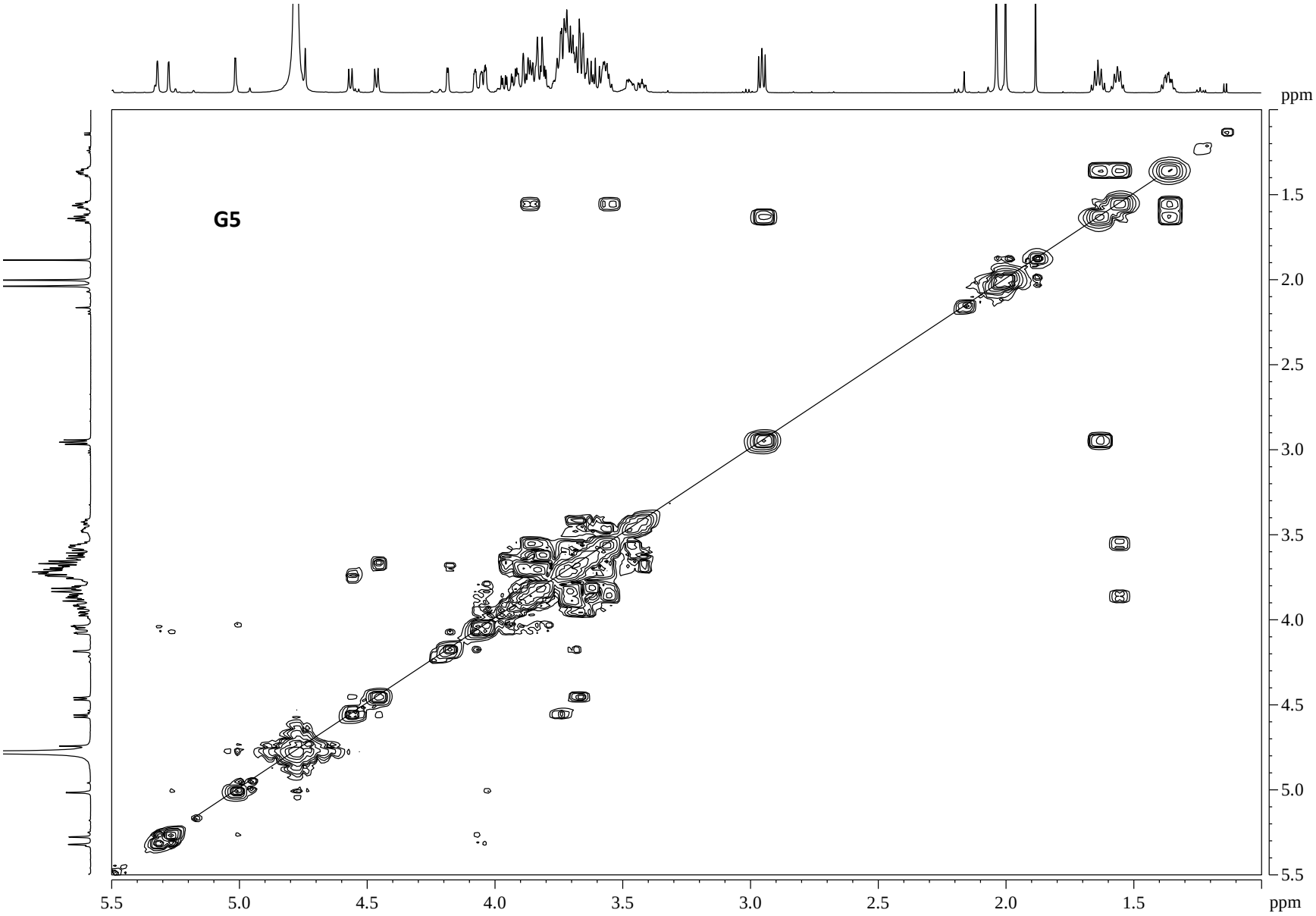
80.51
79.26
78.66
78.55
78.48
76.13
74.49
74.45
73.37
73.14
72.34
71.88
70.24
70.18
70.05
69.96
69.89
66.96
66.82
66.72
65.82
61.01
60.97
60.88
60.77
60.02
59.92
54.92
39.26
27.99
26.32
23.19
22.07
22.04
G5
NHAc
NHAc
NH2
4
104
103
102
101
100
99
98
97
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


G5
ppm
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2.0
2.5
3.0
3.5
4.0
4.5
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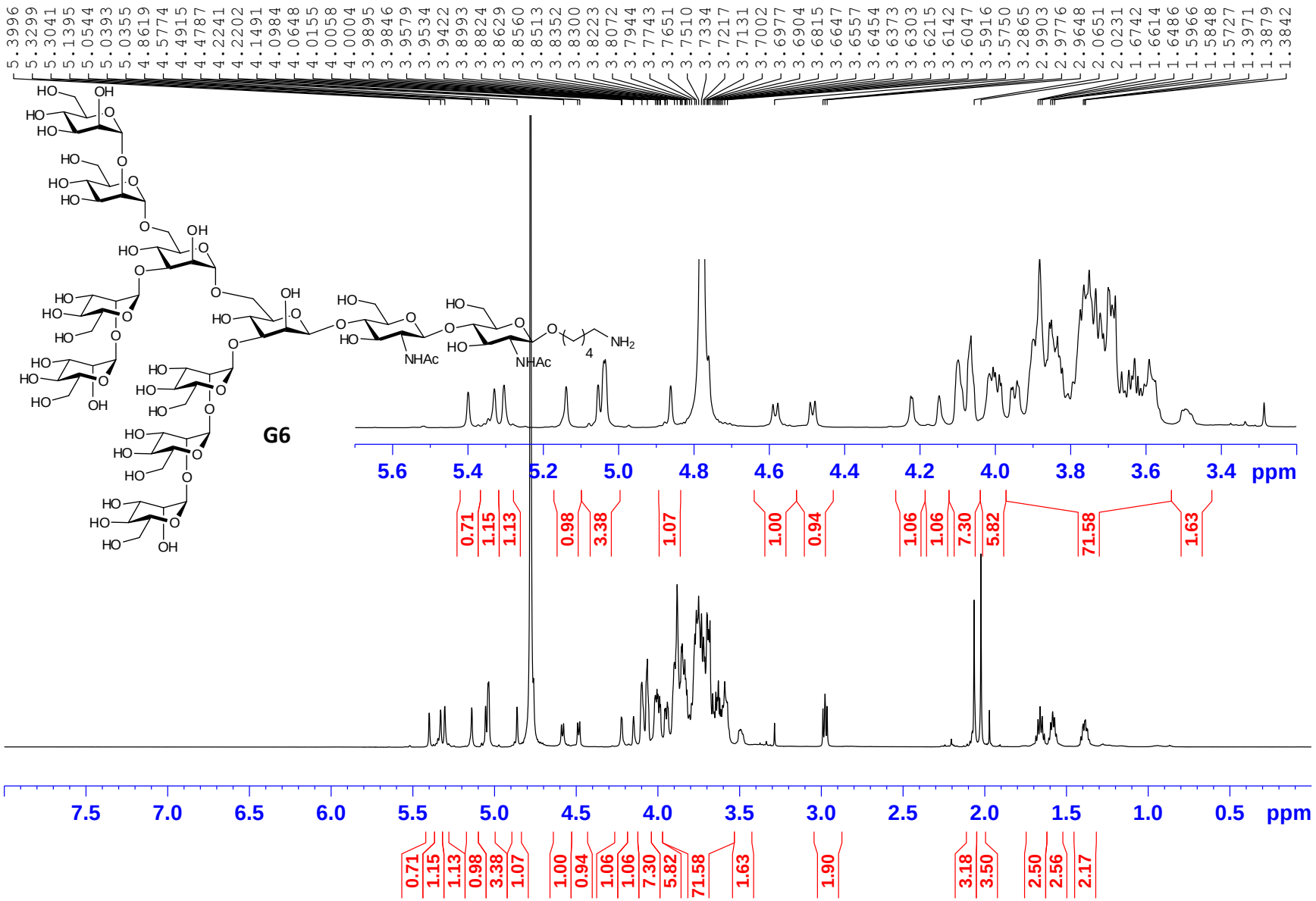
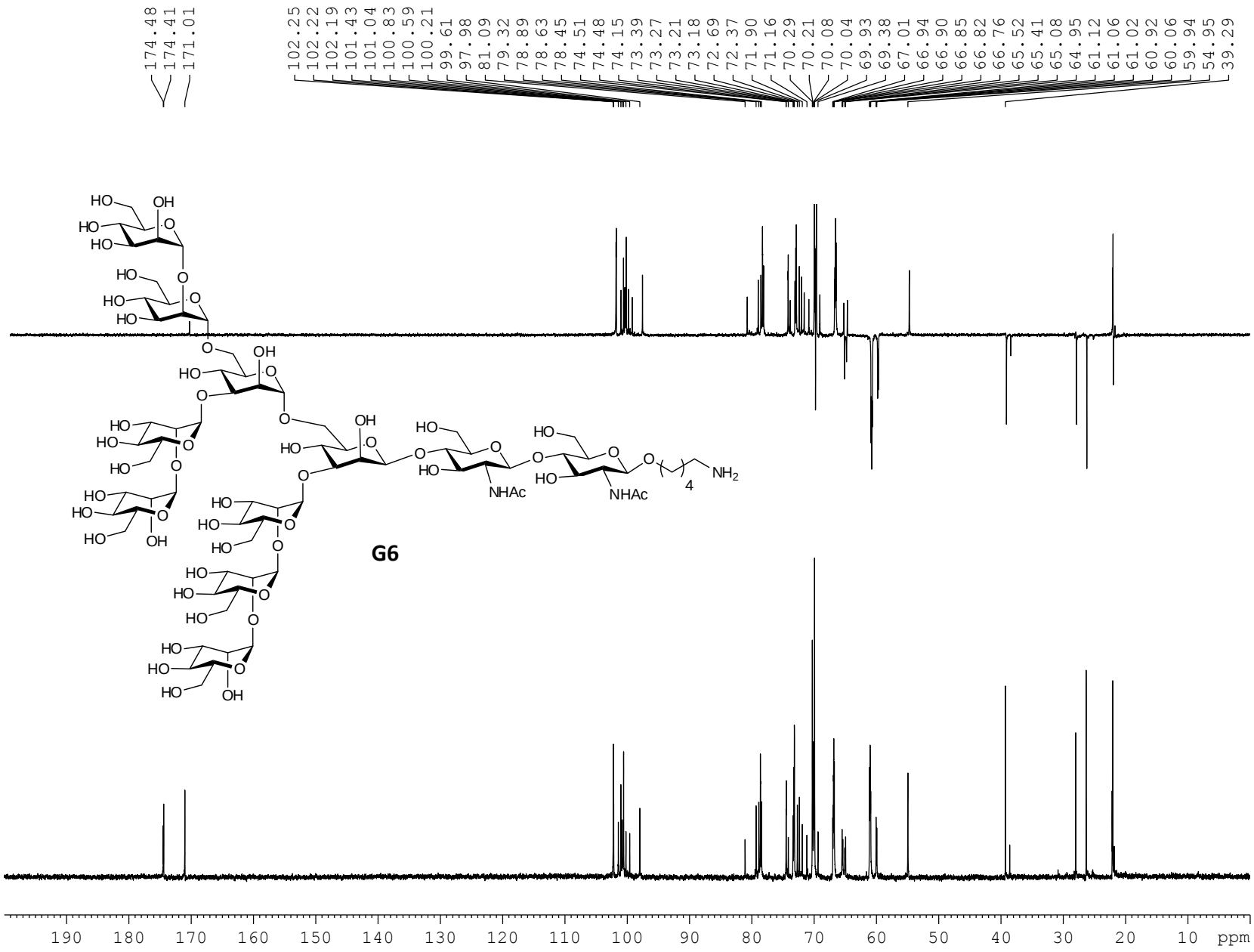
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm


5.3996 5.3299 5.3041 5.1395 5.0544 5.0393 5.0355 4.8619 4.5774 4.4915 4.4787 4.2241 4.2202 4.1491 4.0984 4.0648 4.0155 4.0058 4.0004 3.9895 3.9846 3.9579 3.9534 3.9422 3.8993 3.8824 3.8629 3.8560 3.8513 3.8352 3.8300 3.8223 3.8072 3.7944 3.7743 3.7651 3.7510 3.7334 3.7217 3.7131 3.7002 3.6977 3.6904 3.6815 3.6647 3.6557 3.6454 3.6373 3.6303 3.6215 3.6142 3.6047 3.5916 3.5750 3.2865 2.9903 2.9776 2.9648 2.0651 2.0231 1.6742 1.6614 1.6486 1.5966 1.5848 1.5727 1.3971 1.3879 1.3842
G6
NHAc
NHAc
NH2
4
5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 ppm
0.71 1.15 1.13 0.98 3.38 1.07 1.00 0.94 1.06 1.06 7.30 5.82 71.58 1.63
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
0.71 1.15 1.13 0.98 3.38 1.07 1.00 0.94 1.06 1.06 7.30 5.82 71.58 1.63 1.90 3.18 3.50 2.50 2.56 2.17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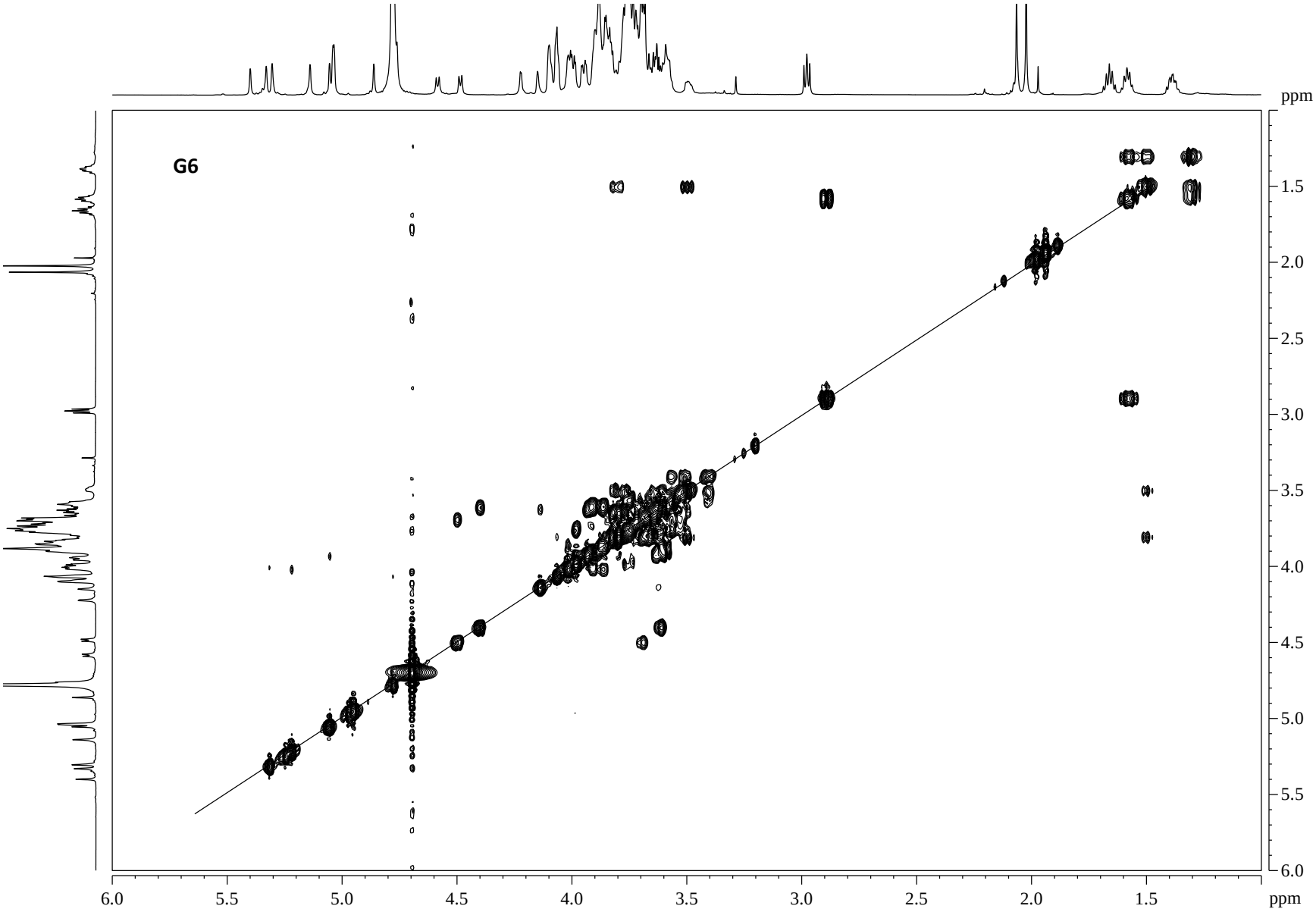
174.41
171.01
102.25
102.22
102.19
101.43
101.04
100.83
100.59
100.21
99.61
97.98
81.09
79.32
78.89
78.63
78.45
74.51
74.48
74.15
73.39
73.27
73.21
73.18
72.69
72.37
71.90
71.16
70.29
70.21
70.08
70.04
69.93
69.38
67.01
66.94
66.90
66.85
66.82
66.76
65.52
65.41
65.08
64.95
61.12
61.06
61.02
60.92
60.06
59.94
54.95
39.29
G6
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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ppm
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2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
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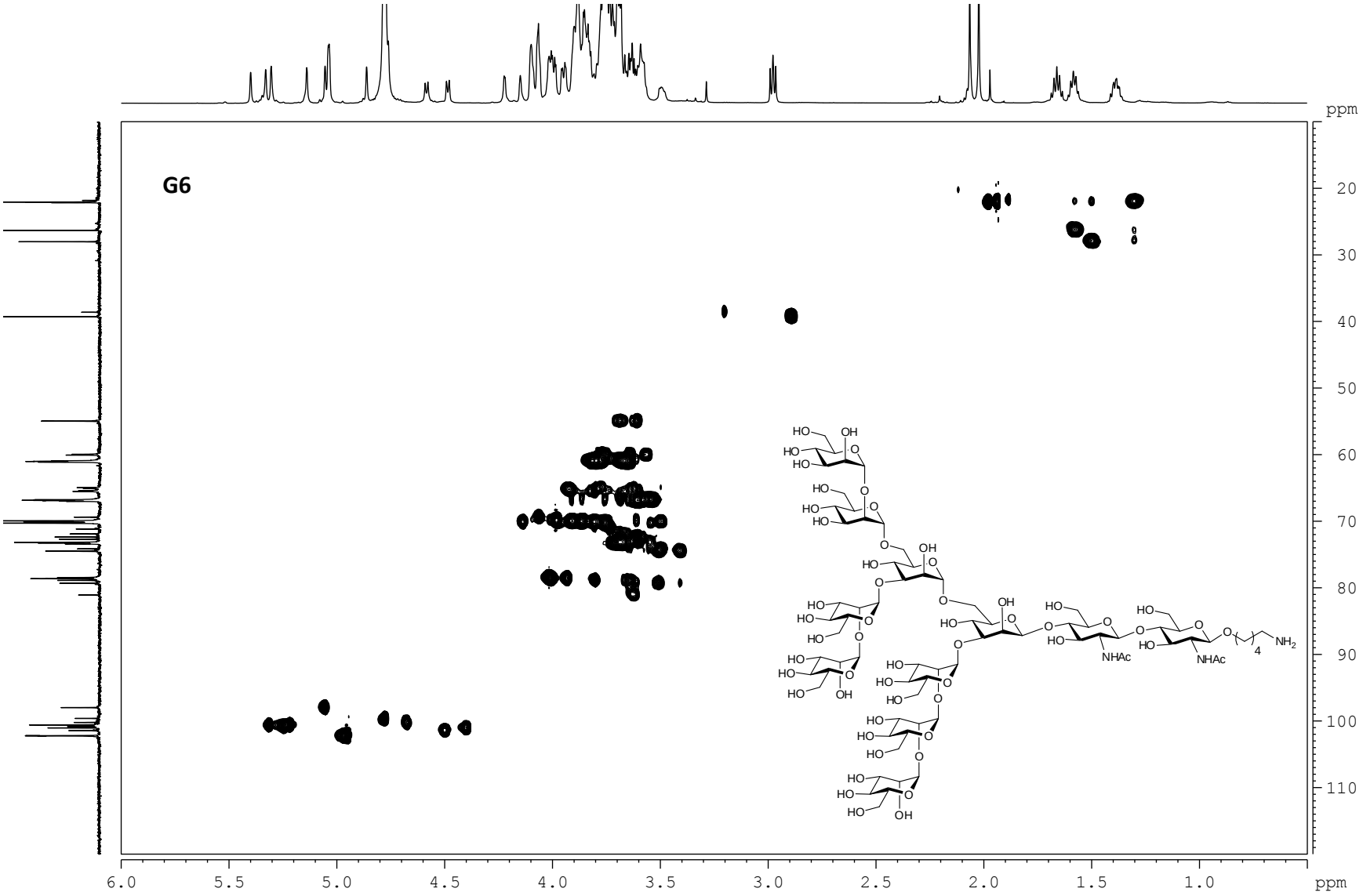
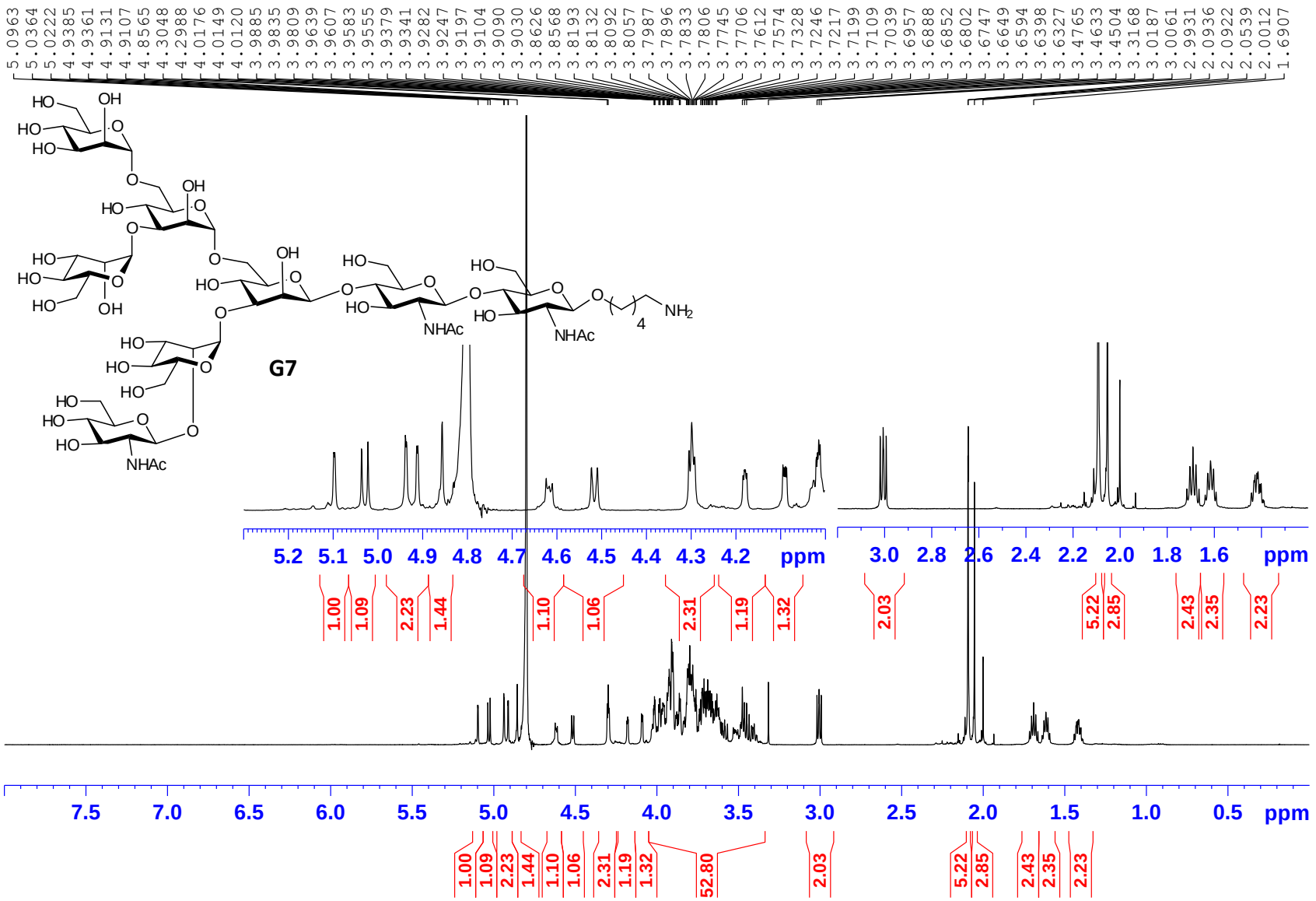
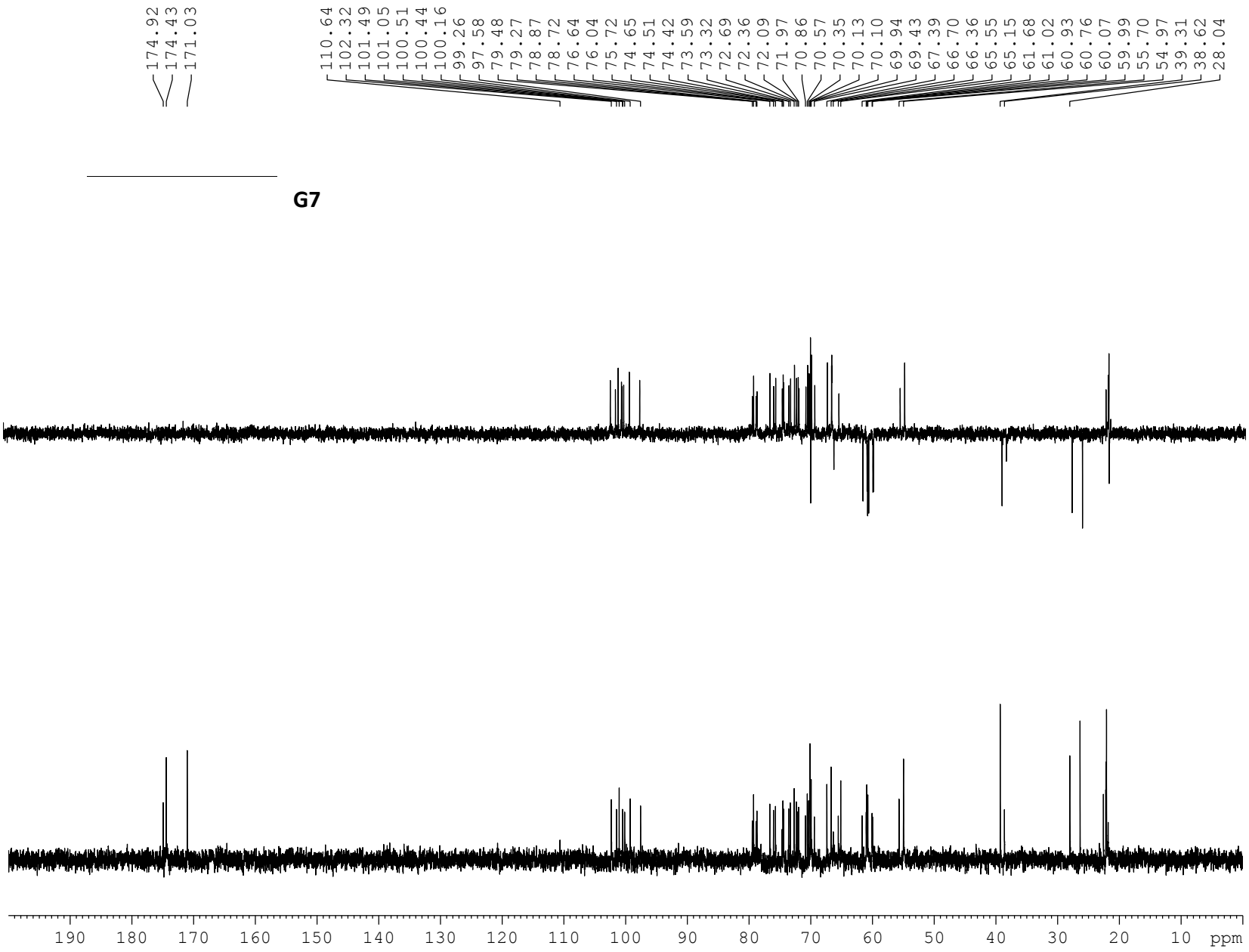
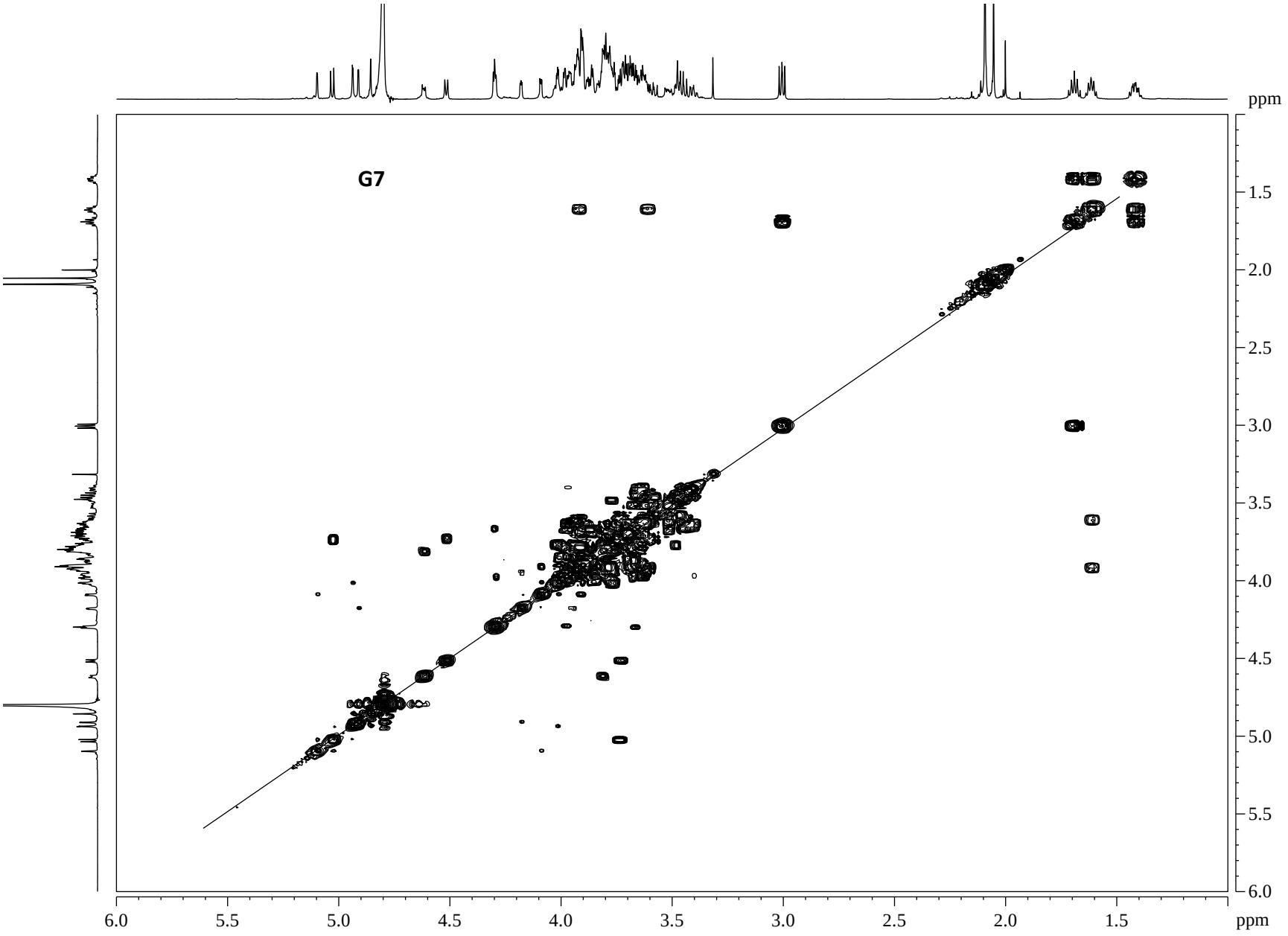
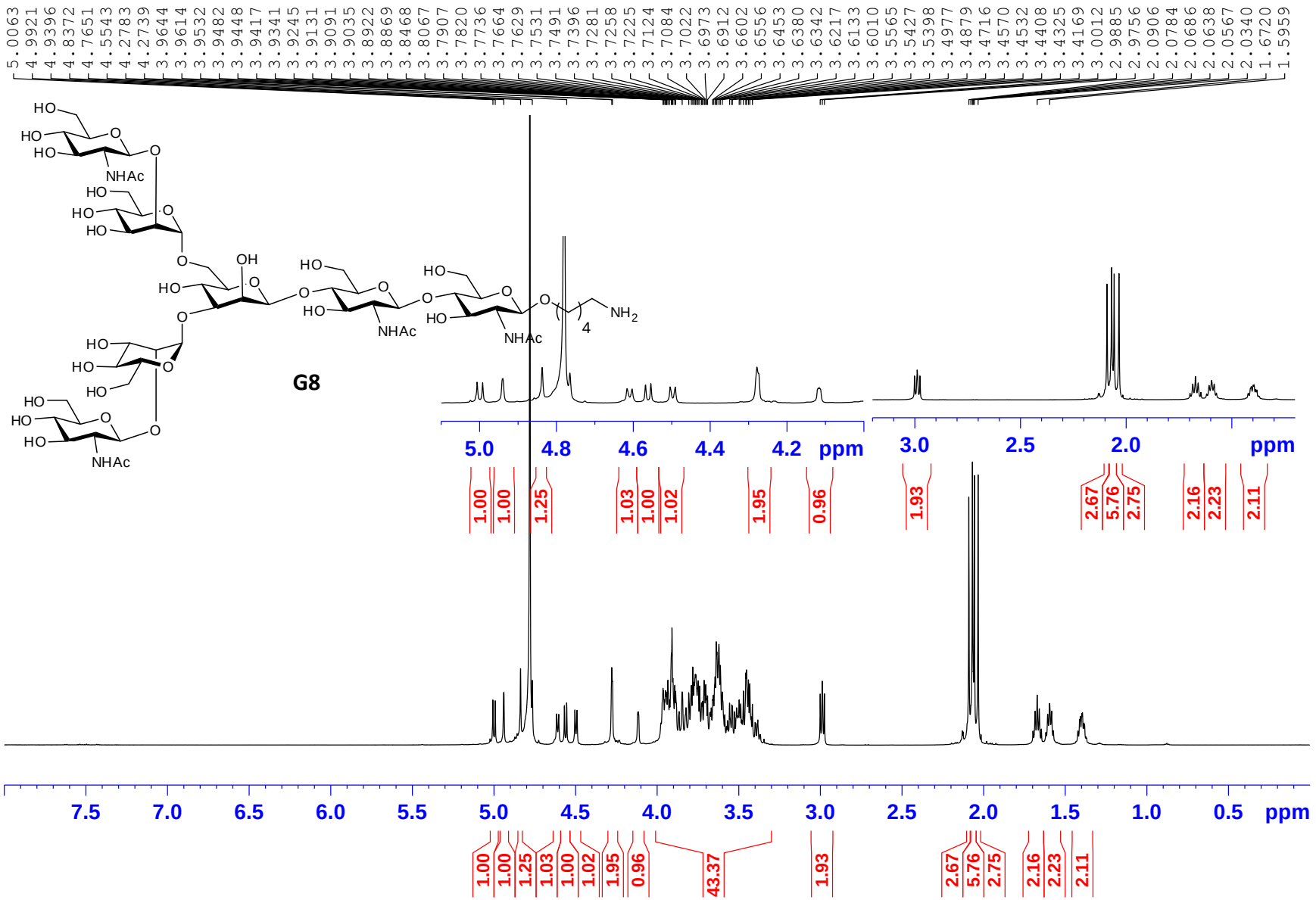
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

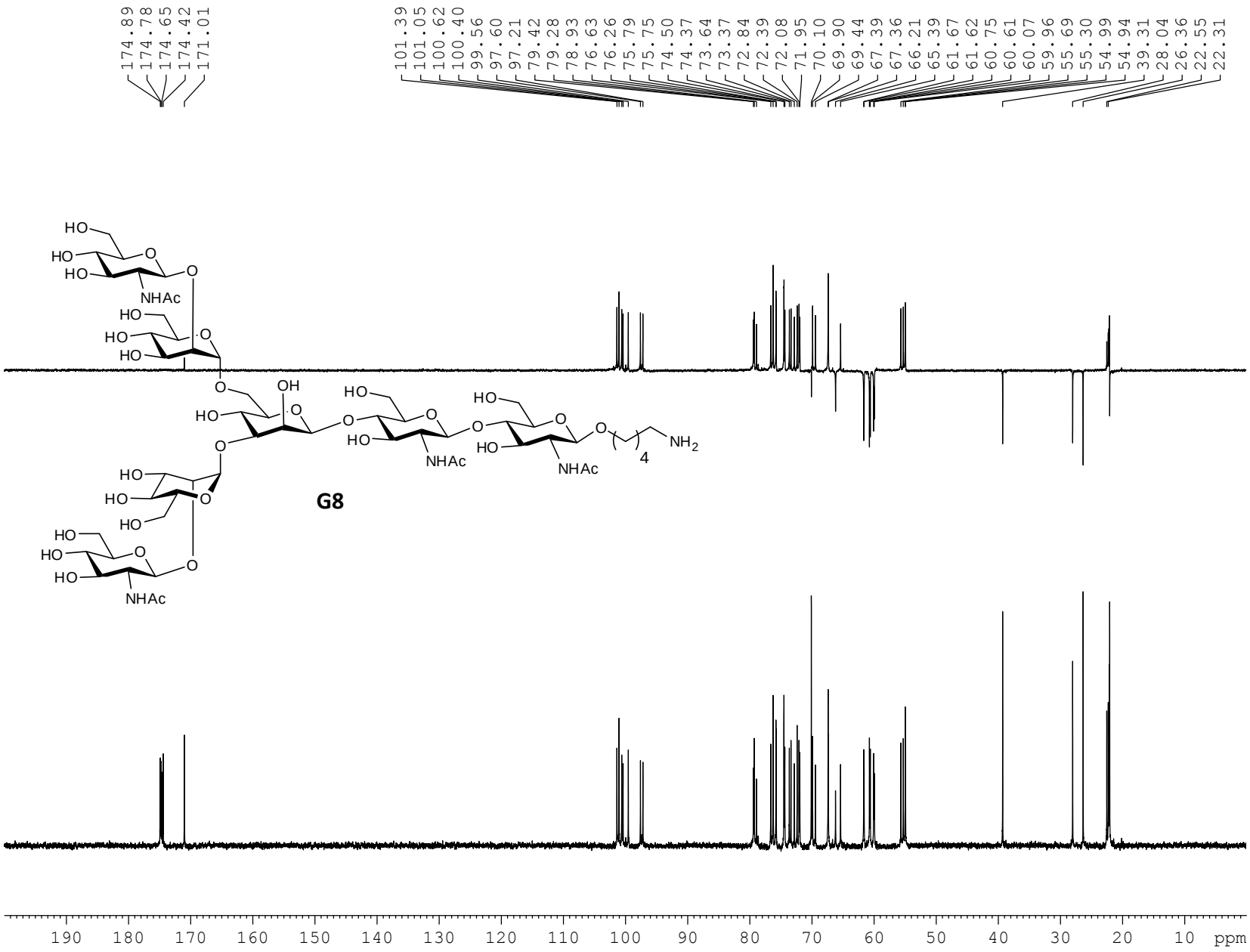

G6
ppm
20
30
40
50
60
70
80
90
100
110
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


G7
NHAc
NHAc
NHAc
NH2
4
5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 ppm
3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 ppm
1.00 1.09 2.23 1.44 1.10 1.06 2.31 1.19 1.32 2.03 5.22 2.85 2.43 2.35 2.23
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
1.00 1.09 2.23 1.44 1.10 1.06 2.31 1.19 1.32 52.80 2.03 5.22 2.85 2.43 2.35 2.23


174.92
174.43
171.03
110.64
102.32
101.49
101.05
100.51
100.44
100.16
99.26
97.58
79.48
79.27
78.87
78.72
76.64
76.04
75.72
74.65
74.51
74.42
73.59
73.32
72.69
72.36
72.09
71.97
70.86
70.57
70.35
70.13
70.10
69.94
69.43
67.39
66.70
66.36
65.55
65.15
61.68
61.02
60.93
60.76
60.07
59.99
55.70
54.97
39.31
38.62
28.04
G7
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


G7
ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm


5.0063
4.9921
4.9396
4.8372
4.7651
4.5543
4.2783
4.2739
3.9644
3.9614
3.9532
3.9482
3.9448
3.9417
3.9341
3.9245
3.9131
3.9091
3.9035
3.8922
3.8869
3.8468
3.8067
3.7907
3.7820
3.7736
3.7664
3.7629
3.7531
3.7491
3.7396
3.7281
3.7258
3.7225
3.7124
3.7084
3.7022
3.6973
3.6912
3.6602
3.6556
3.6453
3.6380
3.6342
3.6217
3.6133
3.6010
3.5565
3.5427
3.5398
3.4977
3.4879
3.4716
3.4570
3.4532
3.4408
3.4325
3.4169
3.0012
2.9885
2.9756
2.0906
2.0784
2.0686
2.0638
2.0567
2.0340
1.6720
1.5959
G8
NHAc
NHAc
NHAc
NH2
4
5.0
4.8
4.6
4.4
4.2
ppm
3.0
2.5
2.0
ppm
1.00
1.00
1.25
1.03
1.00
1.02
1.95
0.96
1.93
2.67
5.76
2.75
2.16
2.23
2.11
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
1.00
1.00
1.25
1.03
1.00
1.02
1.95
0.96
43.37
1.93
2.67
5.76
2.75
2.16
2.23
2.11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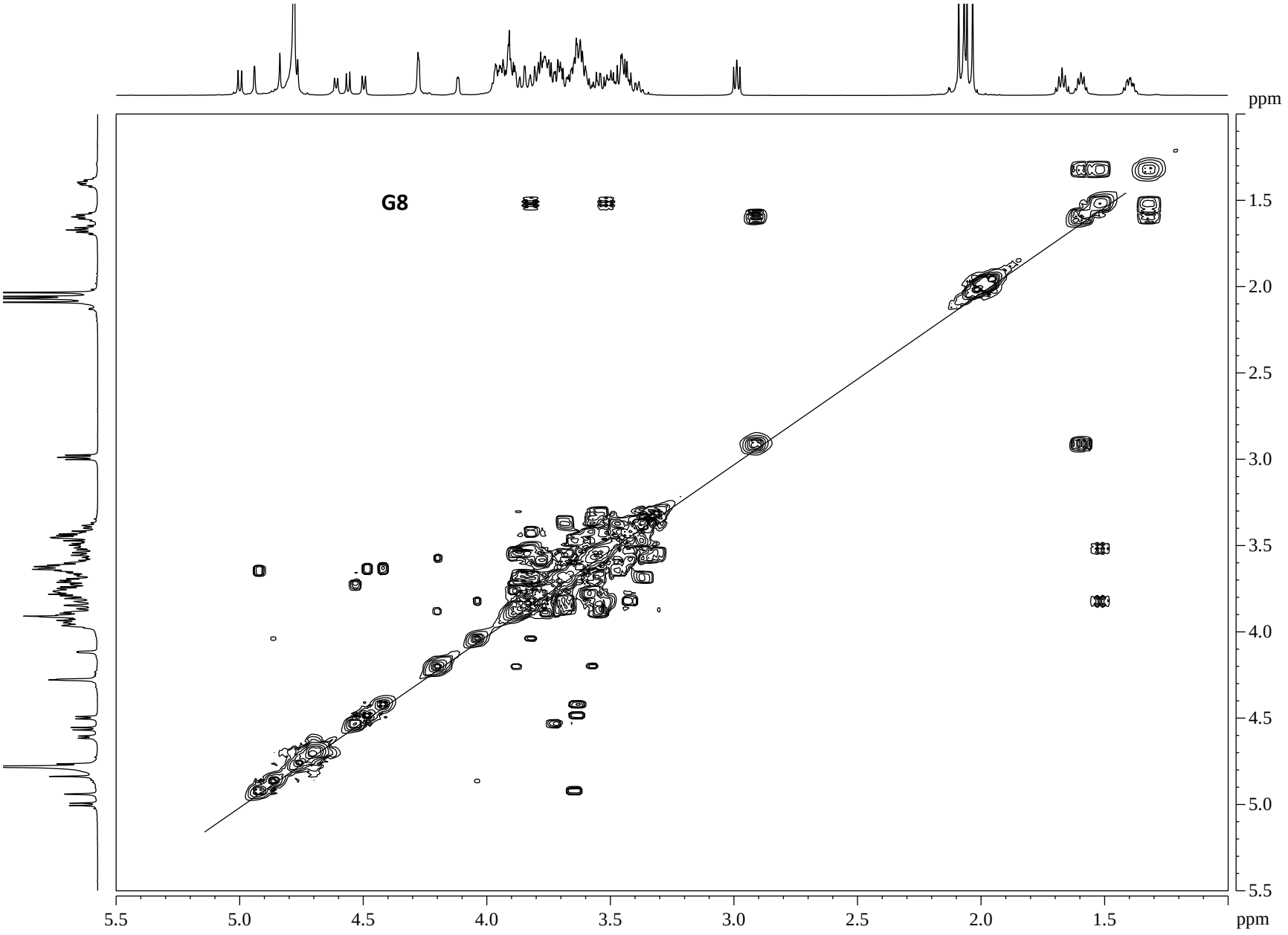
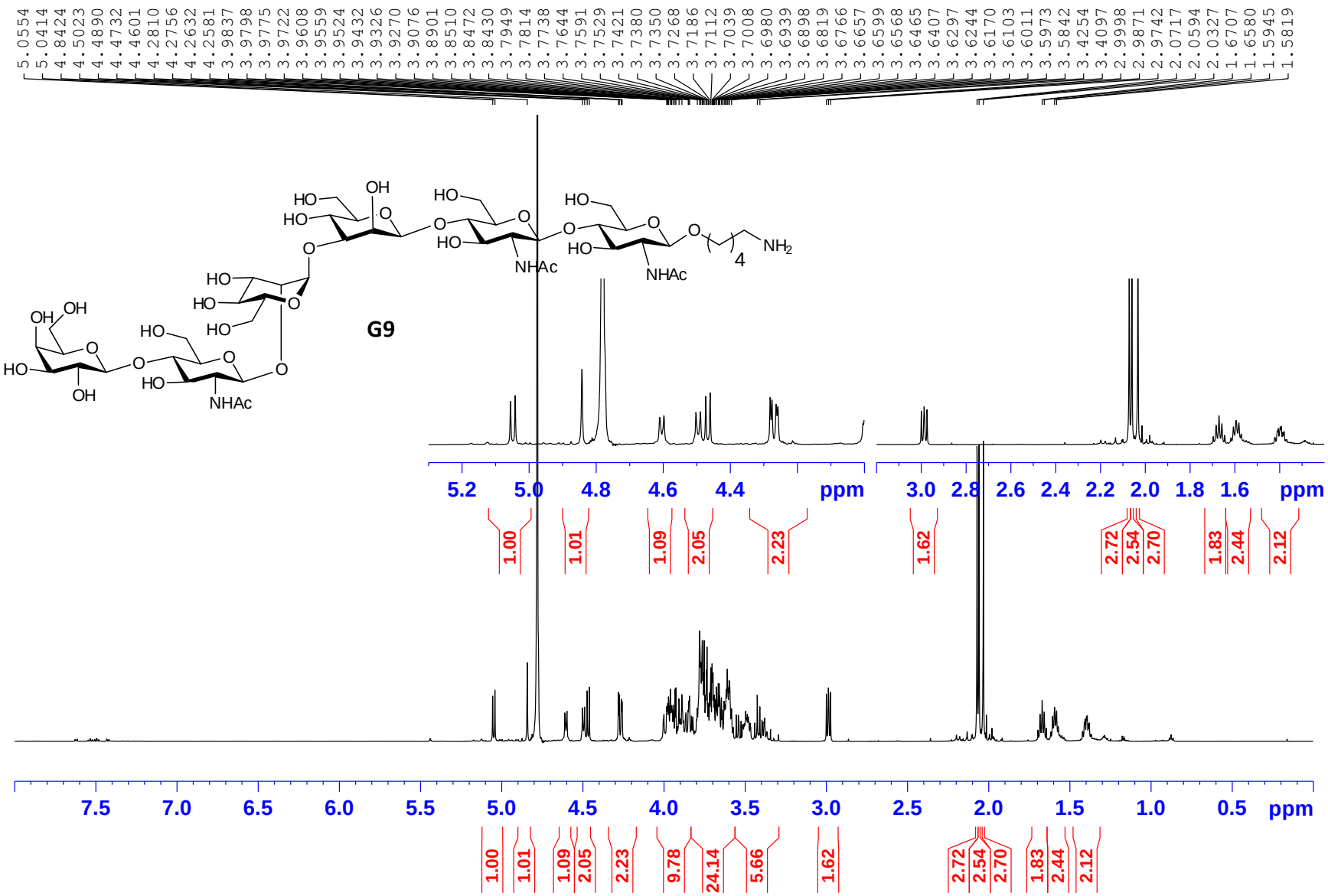
174.78
174.65
174.42
171.01
101.39
101.05
100.62
100.40
99.56
97.60
97.21
79.42
79.28
78.93
76.63
76.26
75.79
75.75
74.50
74.37
73.64
73.37
72.84
72.39
72.08
71.95
70.10
69.90
69.44
67.39
67.36
66.21
65.39
61.67
61.62
60.75
60.61
60.07
59.96
55.69
55.30
54.99
54.94
39.31
28.04
26.36
22.55
22.31
G8
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


G8
ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm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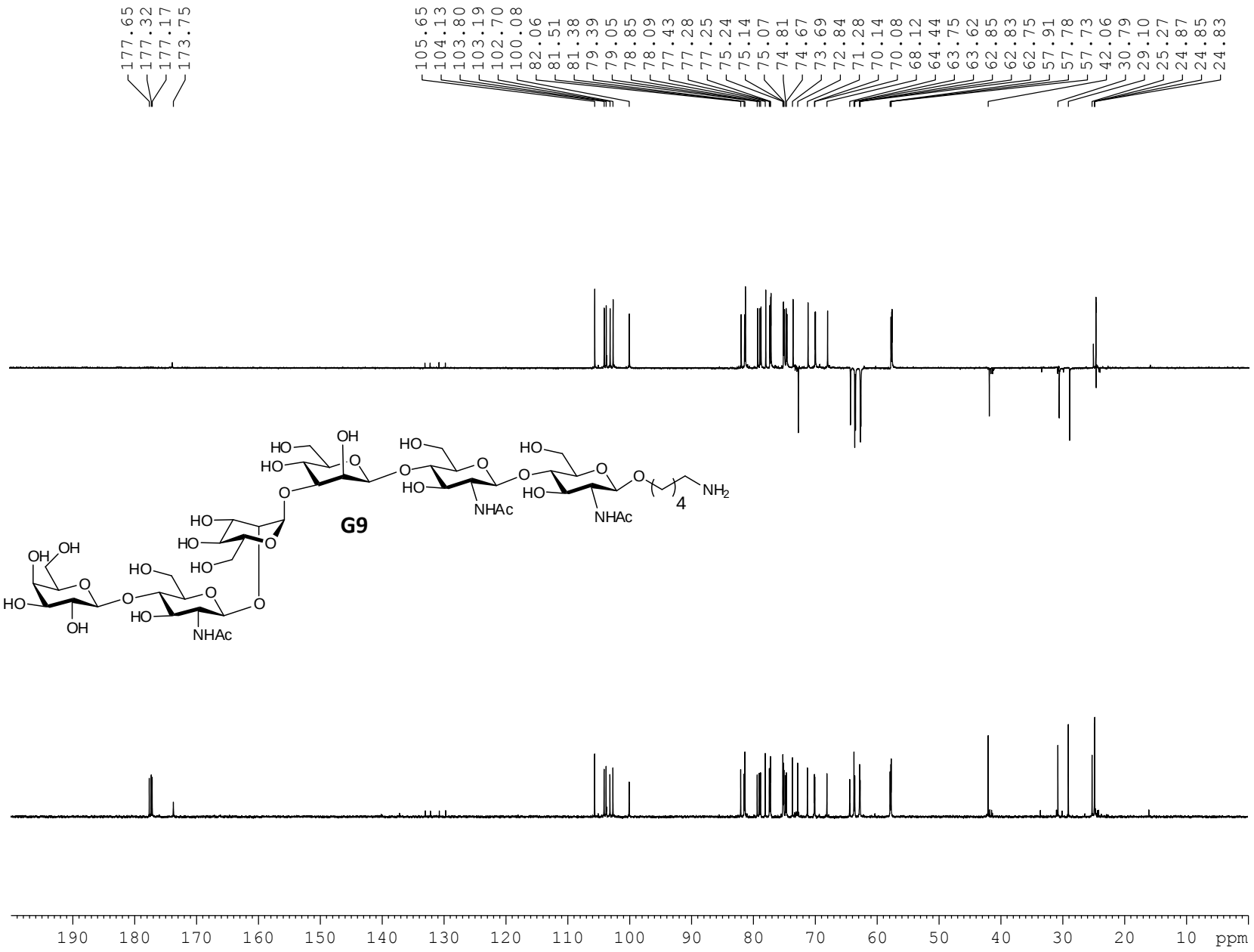
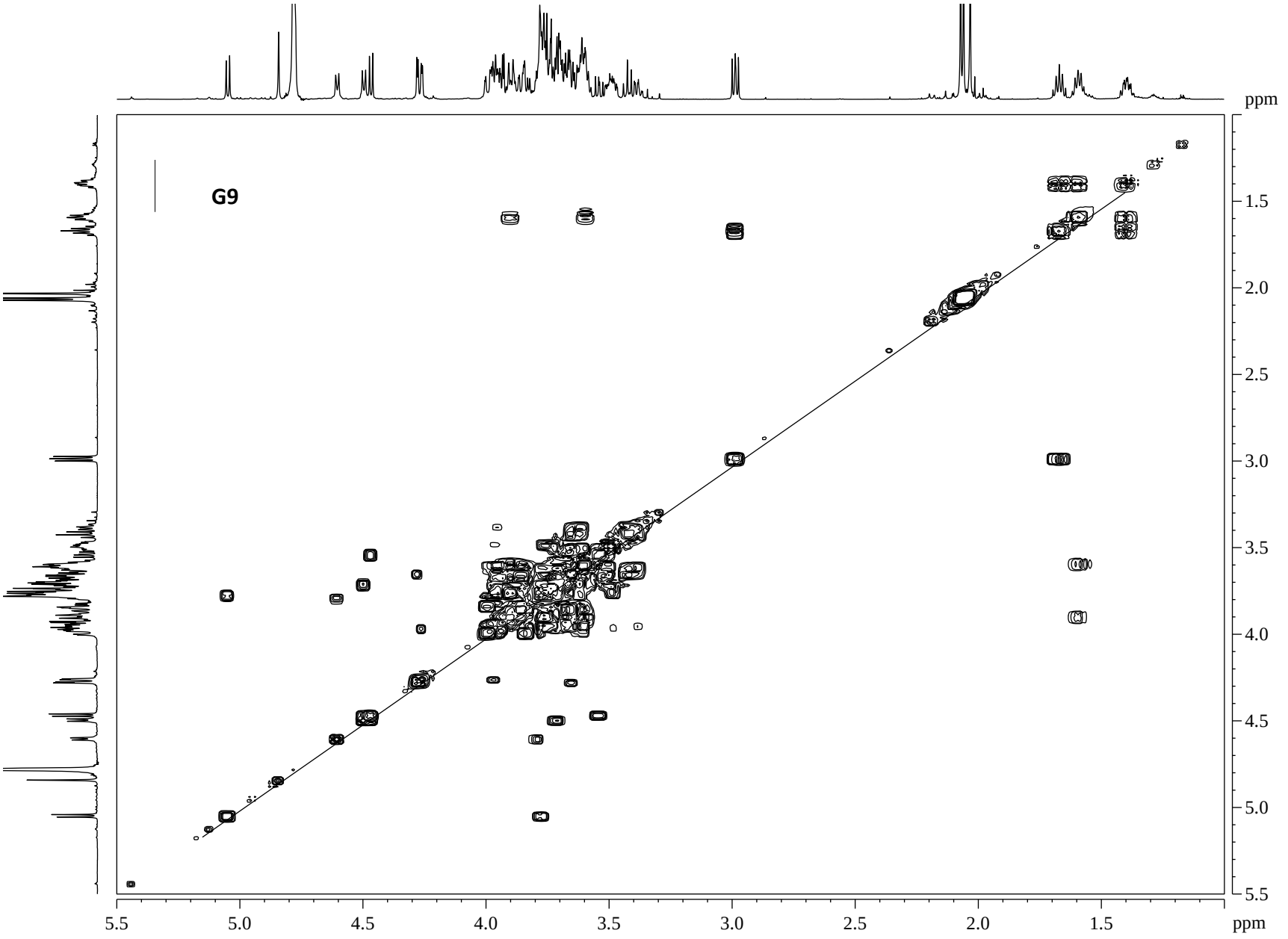
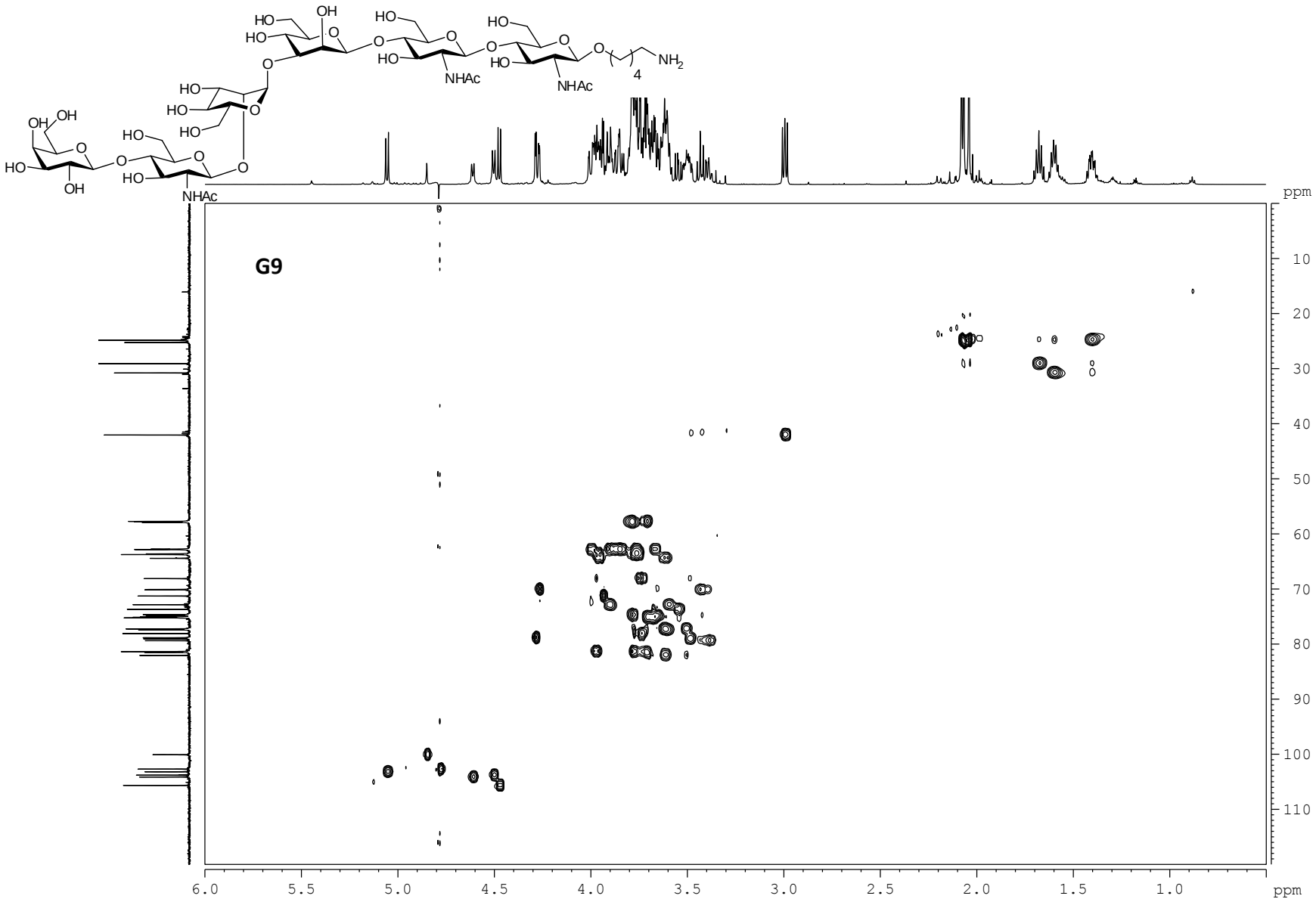
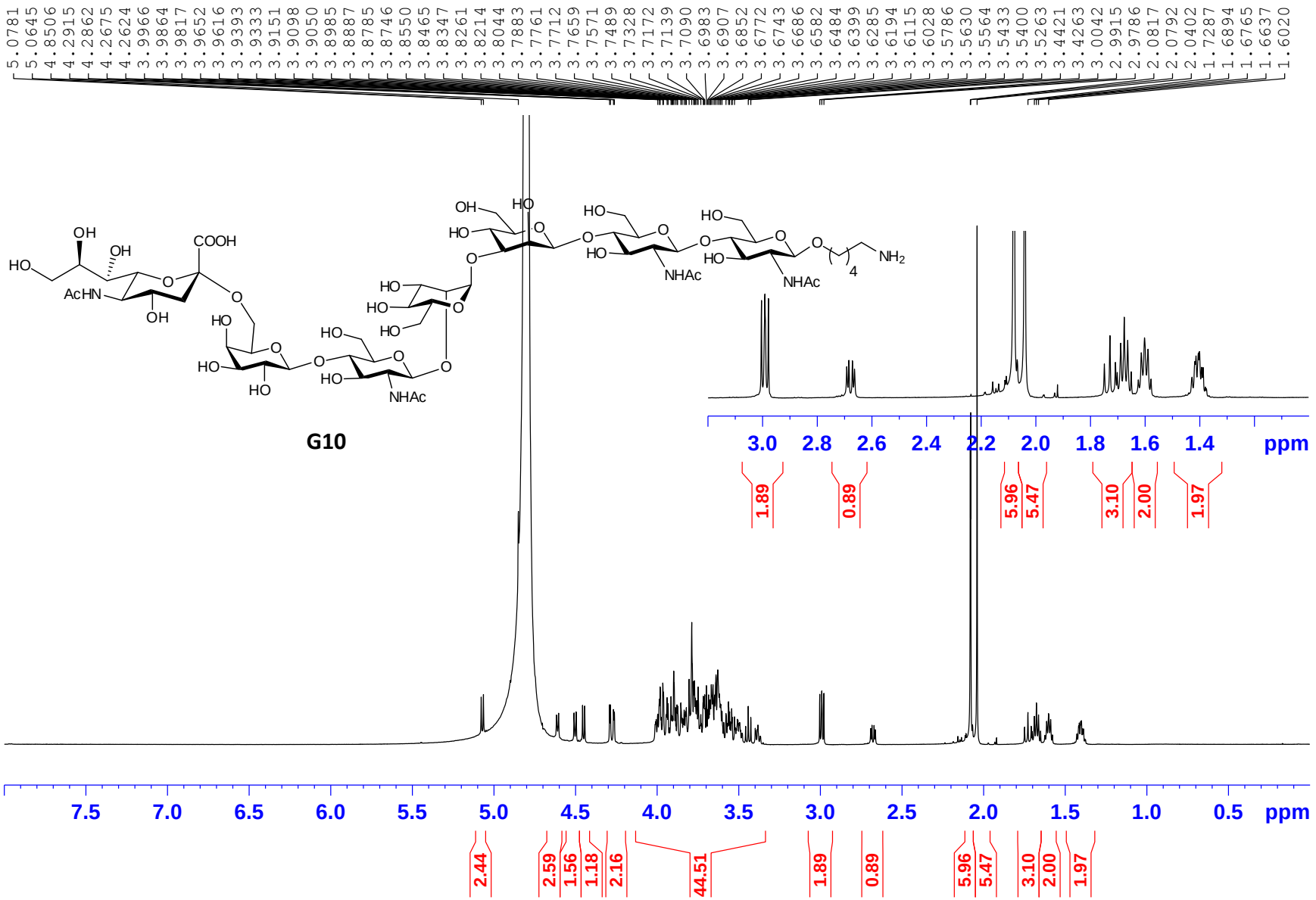
5.0414
4.8424
4.5023
4.4890
4.4732
4.4601
4.2810
4.2756
4.2632
4.2581
3.9837
3.9798
3.9775
3.9722
3.9608
3.9559
3.9524
3.9432
3.9326
3.9270
3.9076
3.8901
3.8510
3.8472
3.8430
3.7949
3.7814
3.7738
3.7644
3.7591
3.7529
3.7421
3.7380
3.7350
3.7268
3.7186
3.7112
3.7039
3.7008
3.6980
3.6939
3.6898
3.6819
3.6766
3.6657
3.6599
3.6568
3.6465
3.6407
3.6297
3.6244
3.6170
3.6103
3.6011
3.5973
3.5842
3.4254
3.4097
2.9998
2.9871
2.9742
2.0717
2.0594
2.0327
1.6707
1.6580
1.5945
1.5819
G9
5.2 5.0 4.8 4.6 4.4 ppm
3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 ppm
1.00 1.01 1.09 2.05 2.23 1.62 2.72 2.54 2.70 1.83 2.44 2.12
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
1.00 1.01 1.09 2.05 2.23 9.78 24.14 5.66 1.62 2.72 2.54 2.70 1.83 2.44 2.12


177.65
177.32
177.17
173.75
105.65
104.13
103.80
103.19
102.70
100.08
82.06
81.51
81.38
79.39
79.05
78.85
78.09
77.43
77.28
77.25
75.24
75.14
75.07
74.81
74.67
73.69
72.84
71.28
70.14
70.08
68.12
64.44
63.75
63.62
62.85
62.83
62.75
57.91
57.78
57.73
42.06
30.79
29.10
25.27
24.87
24.85
24.83
G9
NHAc
NHAc
NHAc
NH2
4
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


G9
ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm


G9
ppm
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
10
20
30
40
50
60
70
80
90
100
110
NHAc
NHAc
NHAc
NH2
4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5.0645
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4.2862
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4.2624
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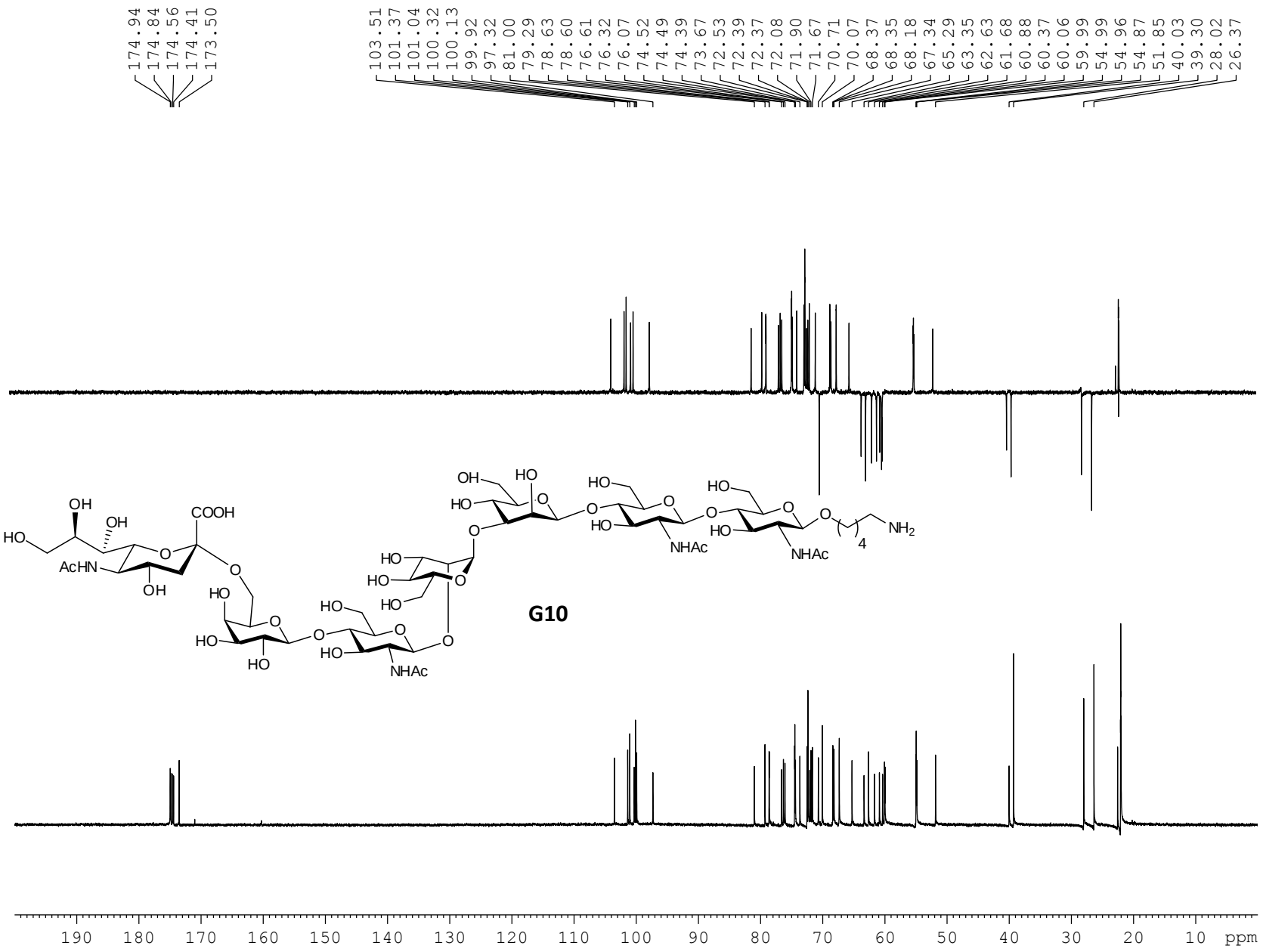
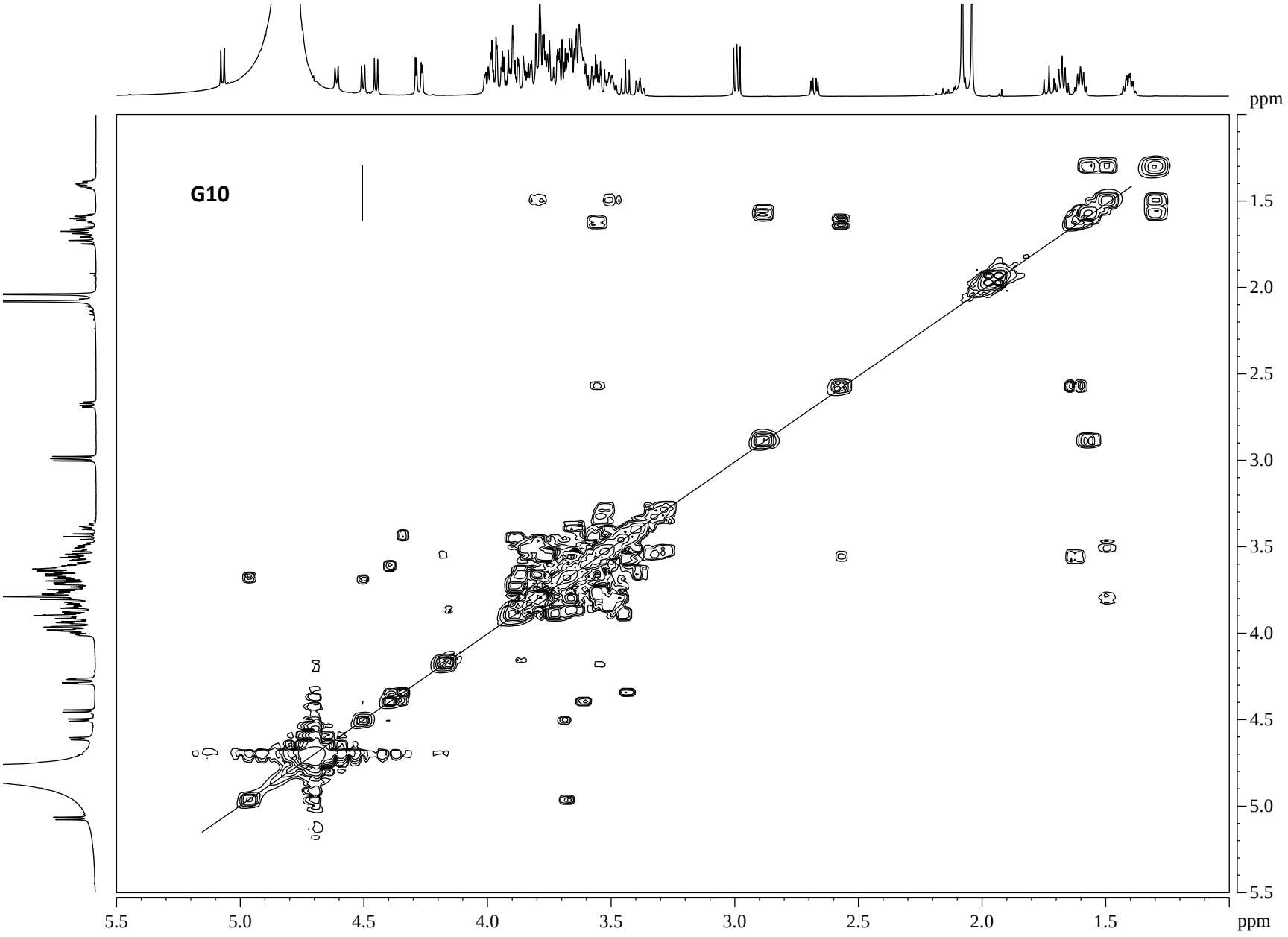
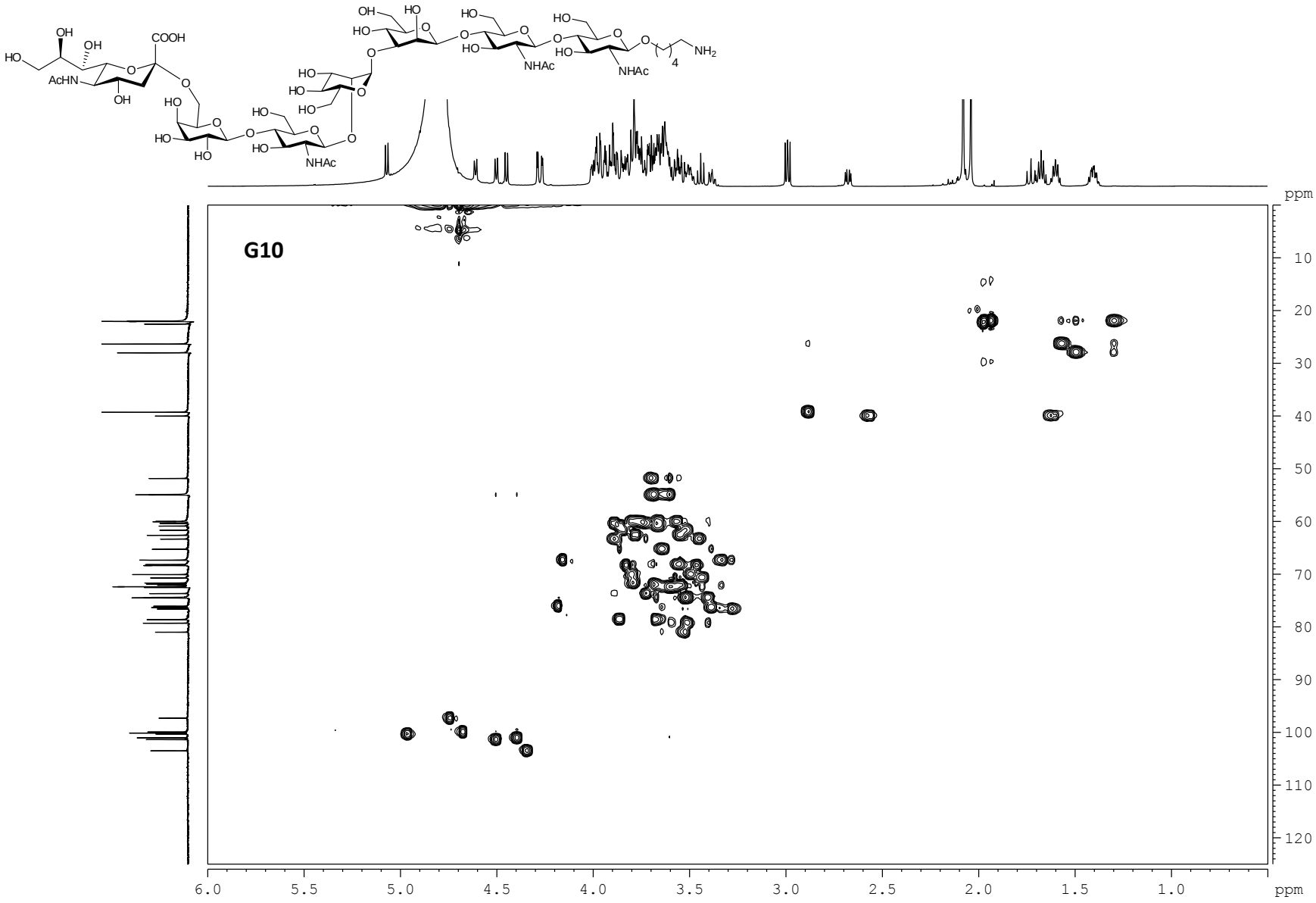
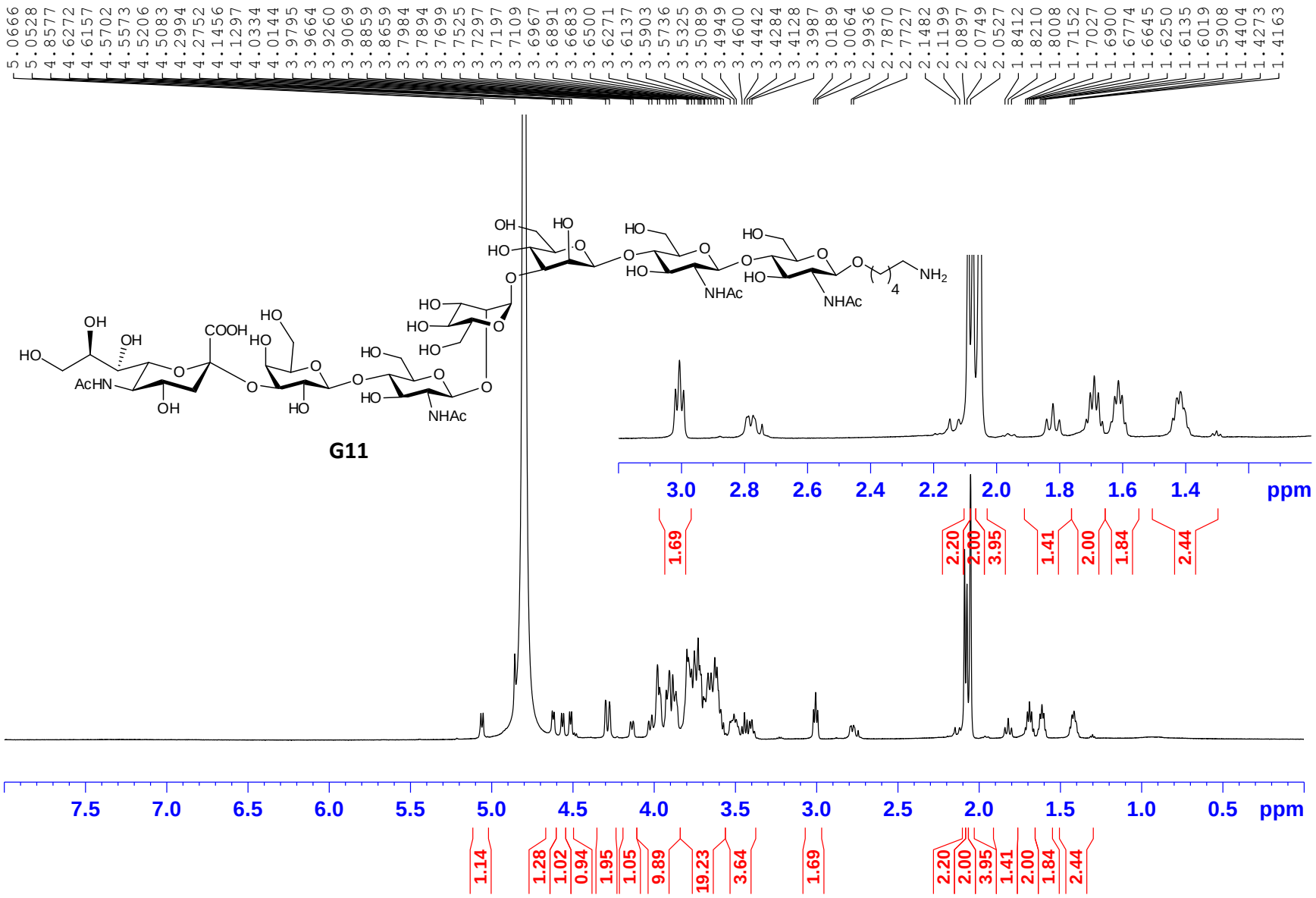
3.9864
3.9817
3.9652
3.9616
3.9393
3.9333
3.9151
3.9098
3.9050
3.8985
3.8887
3.8785
3.8746
3.8550
3.8465
3.8347
3.8261
3.8214
3.8044
3.7883
3.7761
3.7712
3.7659
3.7571
3.7489
3.7328
3.7172
3.7139
3.7090
3.6983
3.6907
3.6852
3.6772
3.6743
3.6686
3.6582
3.6484
3.6399
3.6285
3.6194
3.6115
3.6028
3.5786
3.5630
3.5564
3.5433
3.5400
3.5263
3.4421
3.4263
3.0042
2.9915
2.9786
2.0817
2.0792
2.0402
1.7287
1.6894
1.6765
1.6637
1.6020
G10
3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 ppm
1.89 0.89 5.96 5.47 3.10 2.00 1.97
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
2.44 2.59 1.56 1.18 2.16 44.51 1.89 0.89 5.96 5.47 3.10 2.00 1.97


174.94
174.84
174.56
174.41
173.50
103.51
101.37
101.04
100.32
100.13
99.92
97.32
81.00
79.29
78.63
78.60
76.61
76.32
76.07
74.52
74.49
74.39
73.67
72.53
72.39
72.37
72.08
71.90
71.67
70.71
70.07
68.37
68.35
68.18
67.34
65.29
63.35
62.63
61.68
60.88
60.37
60.06
59.99
54.99
54.96
54.87
51.85
40.03
39.30
28.02
26.37
G10
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


G10
ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm


G10
ppm
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
10
20
30
40
50
60
70
80
90
100
110
120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4.5083
4.2994
4.2752
4.1456
4.1297
4.0334
4.0144
3.9795
3.9664
3.9260
3.9069
3.8859
3.8659
3.7984
3.7894
3.7699
3.7525
3.7297
3.7197
3.7109
3.6967
3.6891
3.6683
3.6500
3.6271
3.6137
3.5903
3.5736
3.5325
3.5089
3.4949
3.4600
3.4442
3.4284
3.4128
3.3987
3.0189
3.0064
2.9936
2.7870
2.7727
2.1482
2.1199
2.0897
2.0749
2.0527
1.8412
1.8210
1.8008
1.7152
1.7027
1.6900
1.6774
1.6645
1.6250
1.6135
1.6019
1.5908
1.4404
1.4273
1.4163
G11
3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 ppm
1.69 2.20 2.00 3.95 1.41 2.00 1.84 2.44
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
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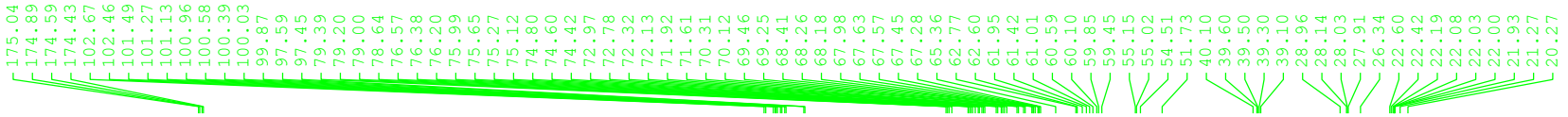
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174.89
174.59
174.43
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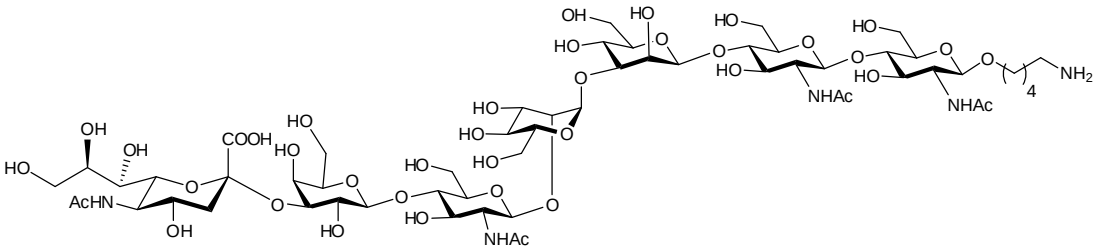
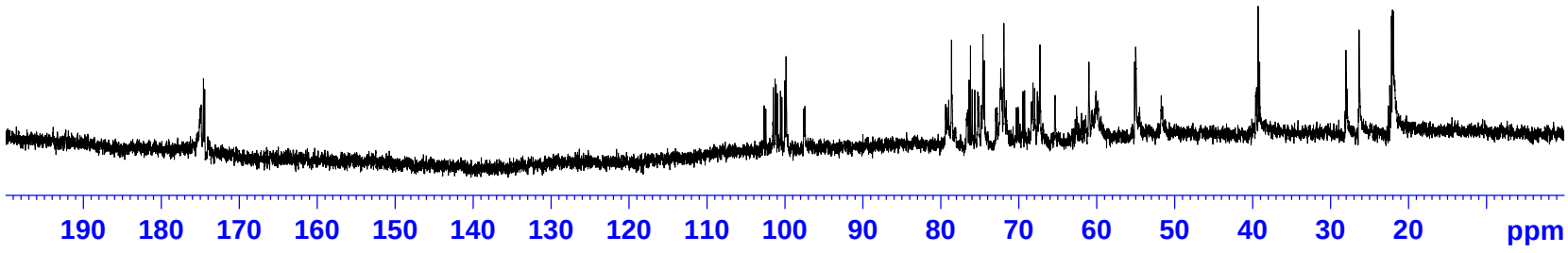
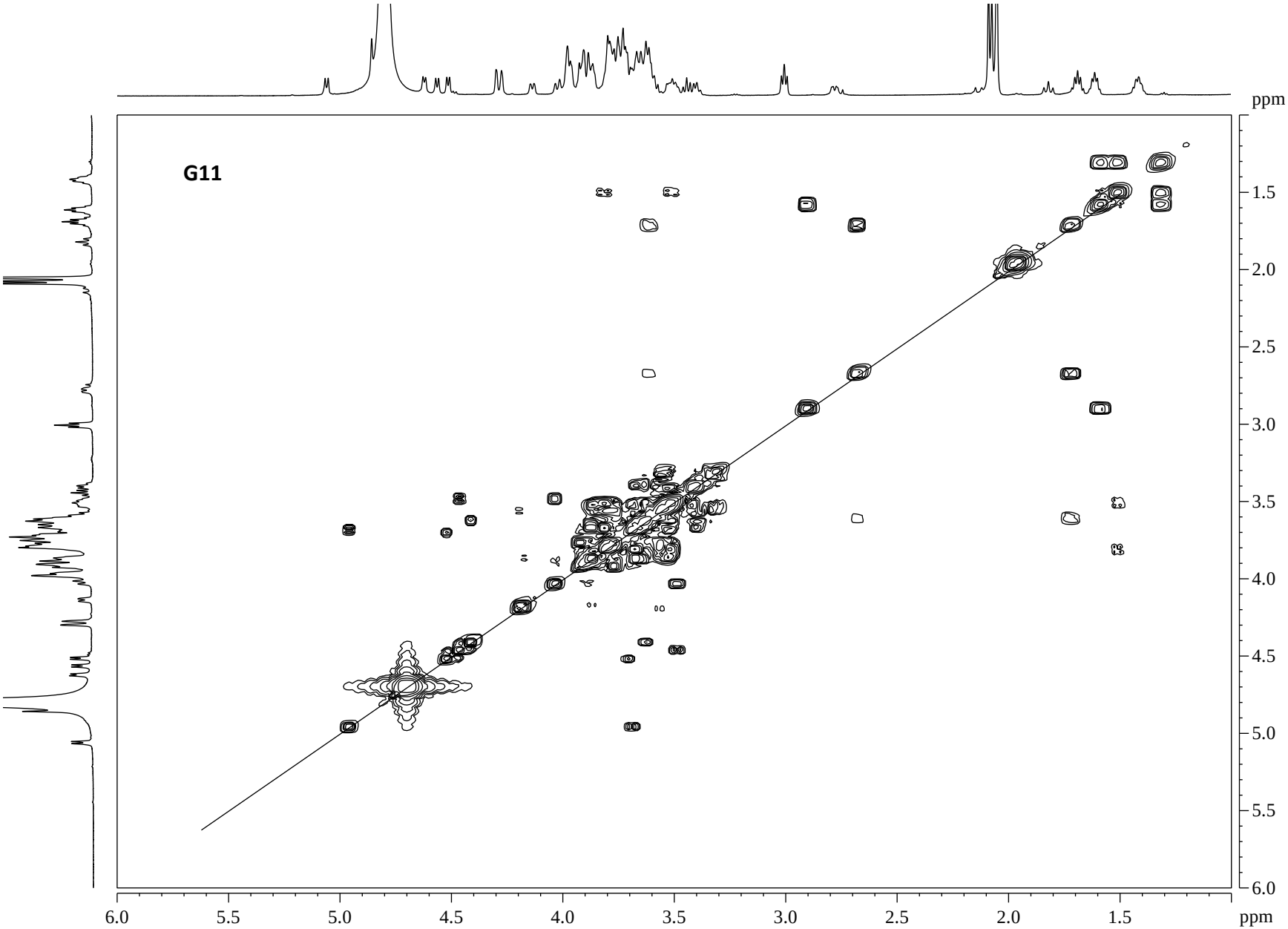
101.49
101.27
101.13
100.96
100.58
100.39
100.03
99.87
97.59
97.45
79.39
79.20
79.00
78.64
76.57
76.38
76.20
75.99
75.65
75.27
75.12
74.80
74.60
74.42
72.97
72.78
72.32
72.13
71.92
71.61
70.31
70.12
69.46
69.25
68.41
68.26
68.18
67.98
67.63
67.57
67.45
67.28
65.36
62.77
62.60
61.95
61.42
61.01
60.59
60.10
59.85
59.45
55.15
55.02
54.51
51.73
40.10
39.60
39.50
39.30
39.10
28.96
28.14
28.03
27.91
26.34
22.60
22.42
22.19
22.08
22.03
22.00
21.93
21.27
20.27


OH
HO
HO
O
HO
O
HO
O
HO
O
HO
O
HO
NHAc
HO
O
HO
NHAc
O
4
NH2
HO
HO
HO
HO
O
HO
HO
O
HO
O
HO
O
HO
NHAc
O
HO
OH
HO
OH
AcHN
O
OH
COOH
HO
O
HO

G11


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


G11
ppm
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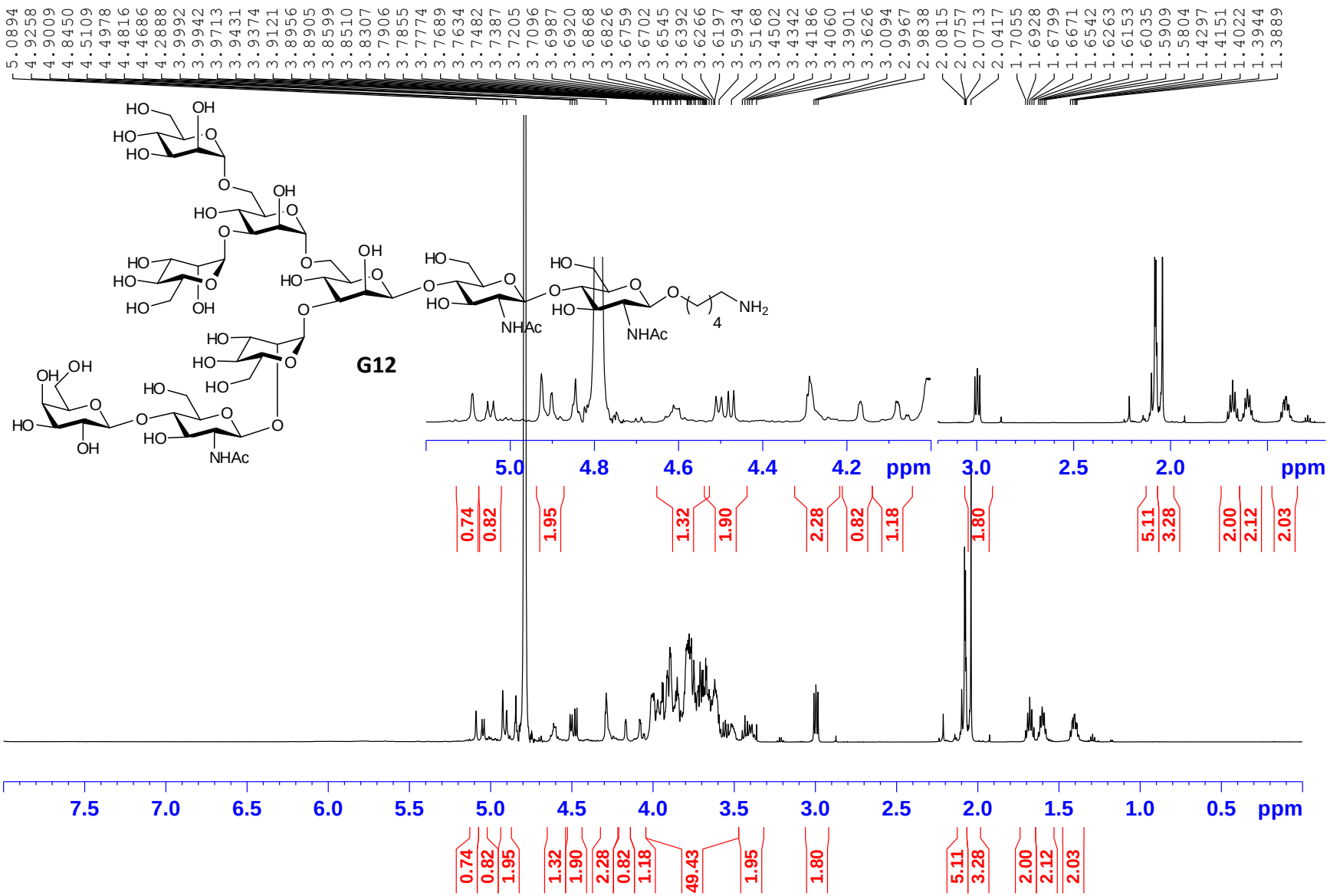
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm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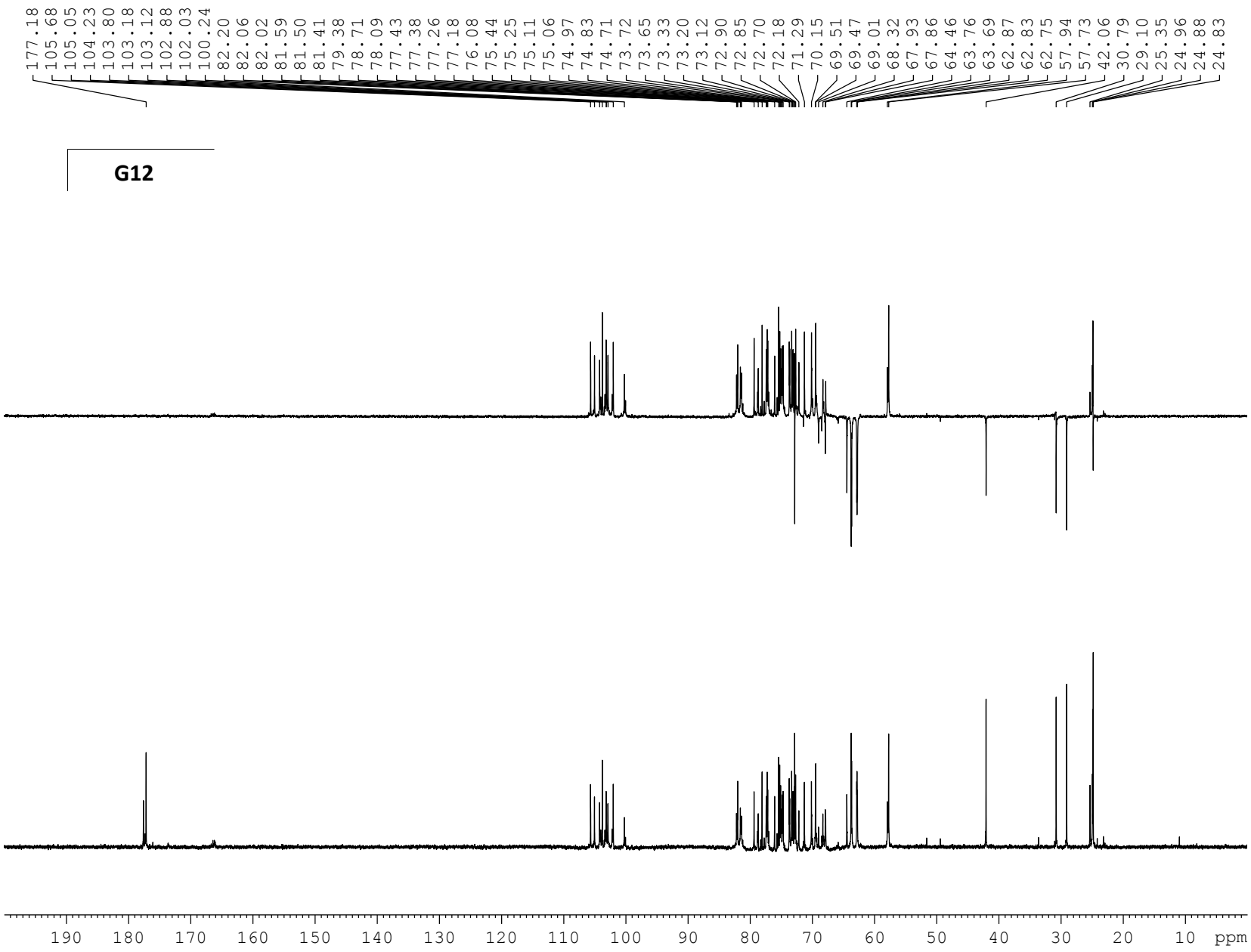
4.9258
4.9009
4.8450
4.5109
4.4978
4.4816
4.4686
4.2888
3.9992
3.9942
3.9713
3.9431
3.9374
3.9121
3.8956
3.8905
3.8599
3.8510
3.8307
3.7906
3.7855
3.7774
3.7689
3.7634
3.7482
3.7387
3.7205
3.7096
3.6987
3.6920
3.6868
3.6826
3.6759
3.6702
3.6545
3.6392
3.6266
3.6197
3.5934
3.5168
3.4502
3.4342
3.4186
3.4060
3.3901
3.3626
3.0094
2.9967
2.9838
2.0815
2.0757
2.0713
2.0417
1.7055
1.6928
1.6799
1.6671
1.6542
1.6263
1.6153
1.6035
1.5909
1.5804
1.4297
1.4151
1.4022
1.3944
1.3889
G12
NHAc
NHAc
NH2
4
5.0
4.8
4.6
4.4
4.2
ppm
3.0
2.5
2.0
ppm
0.74
0.82
1.95
1.32
1.90
2.28
0.82
1.18
1.80
5.11
3.28
2.00
2.12
2.03
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
0.74
0.82
1.95
1.32
1.90
2.28
0.82
1.18
49.43
1.95
1.80
5.11
3.28
2.00
2.12
2.03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105.68
105.05
104.23
103.80
103.18
103.12
102.88
102.03
100.24
82.20
82.06
82.02
81.59
81.50
81.41
79.38
78.71
78.09
77.43
77.38
77.26
77.18
76.08
75.44
75.25
75.11
75.06
74.97
74.83
74.71
73.72
73.65
73.33
73.20
73.12
72.90
72.85
72.70
72.18
71.29
70.15
69.51
69.47
69.01
68.32
67.93
67.86
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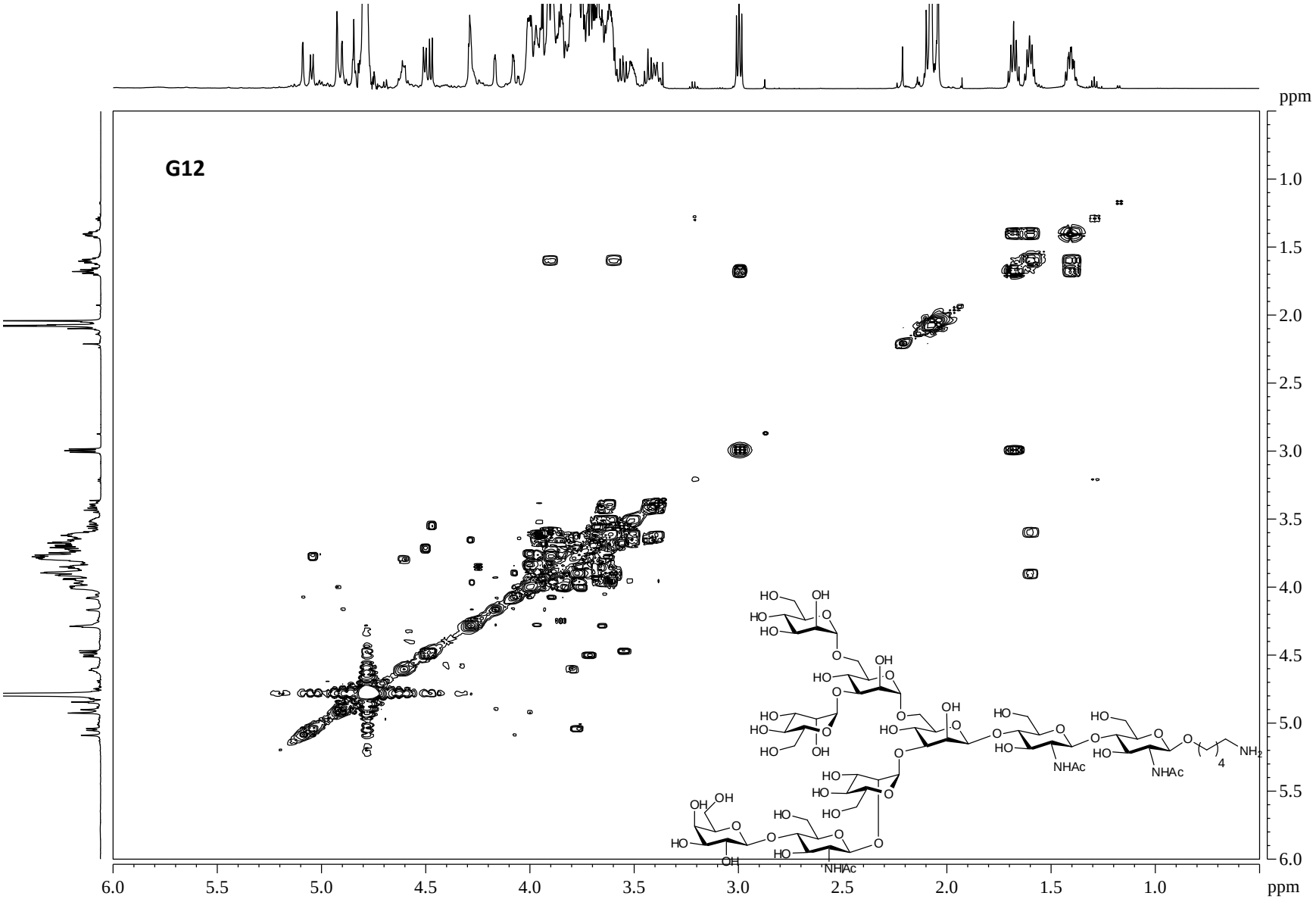
63.76
63.69
62.87
62.83
62.75
57.94
57.73
42.06
30.79
29.10
25.35
24.96
24.88
24.83
G12
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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ppm
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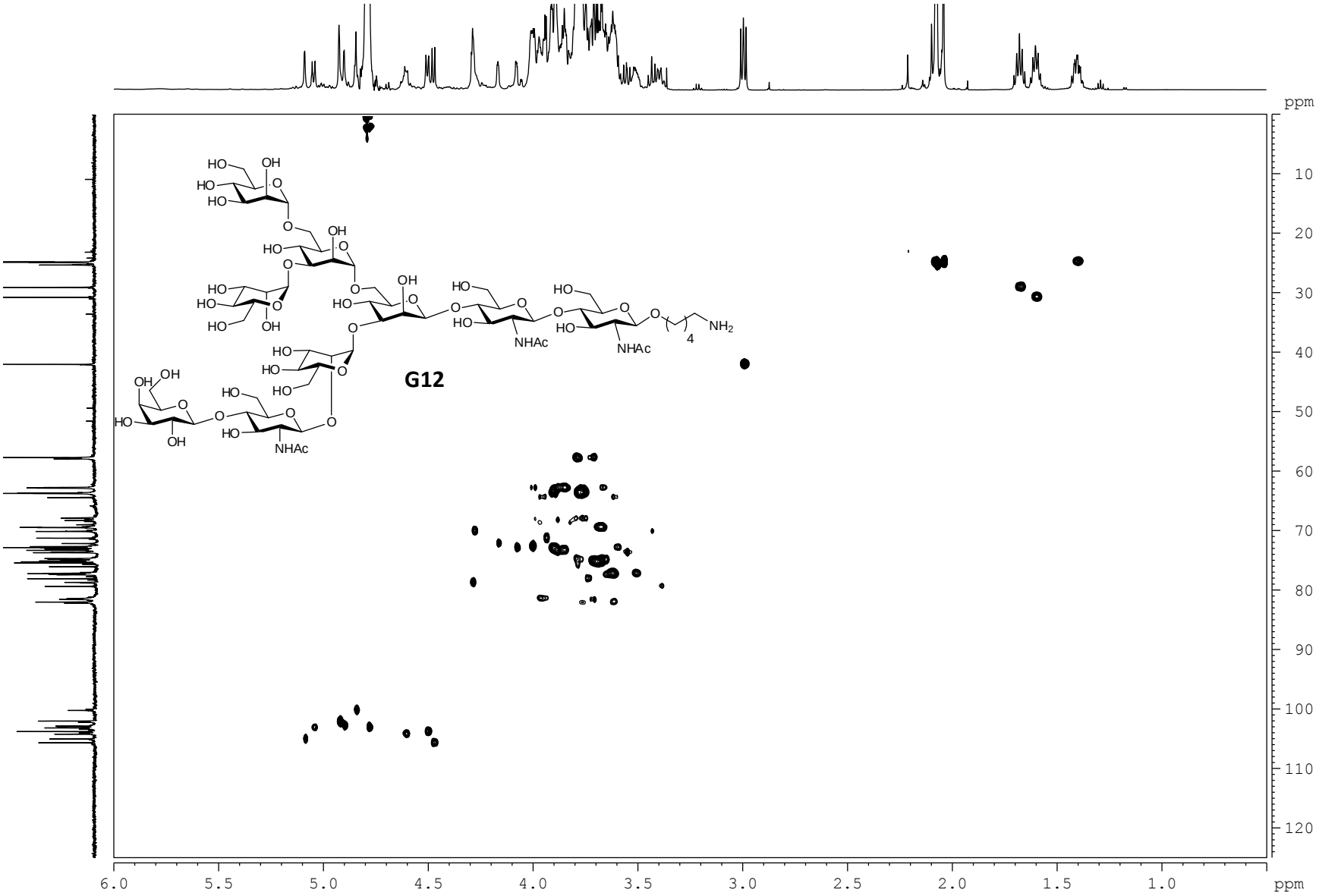
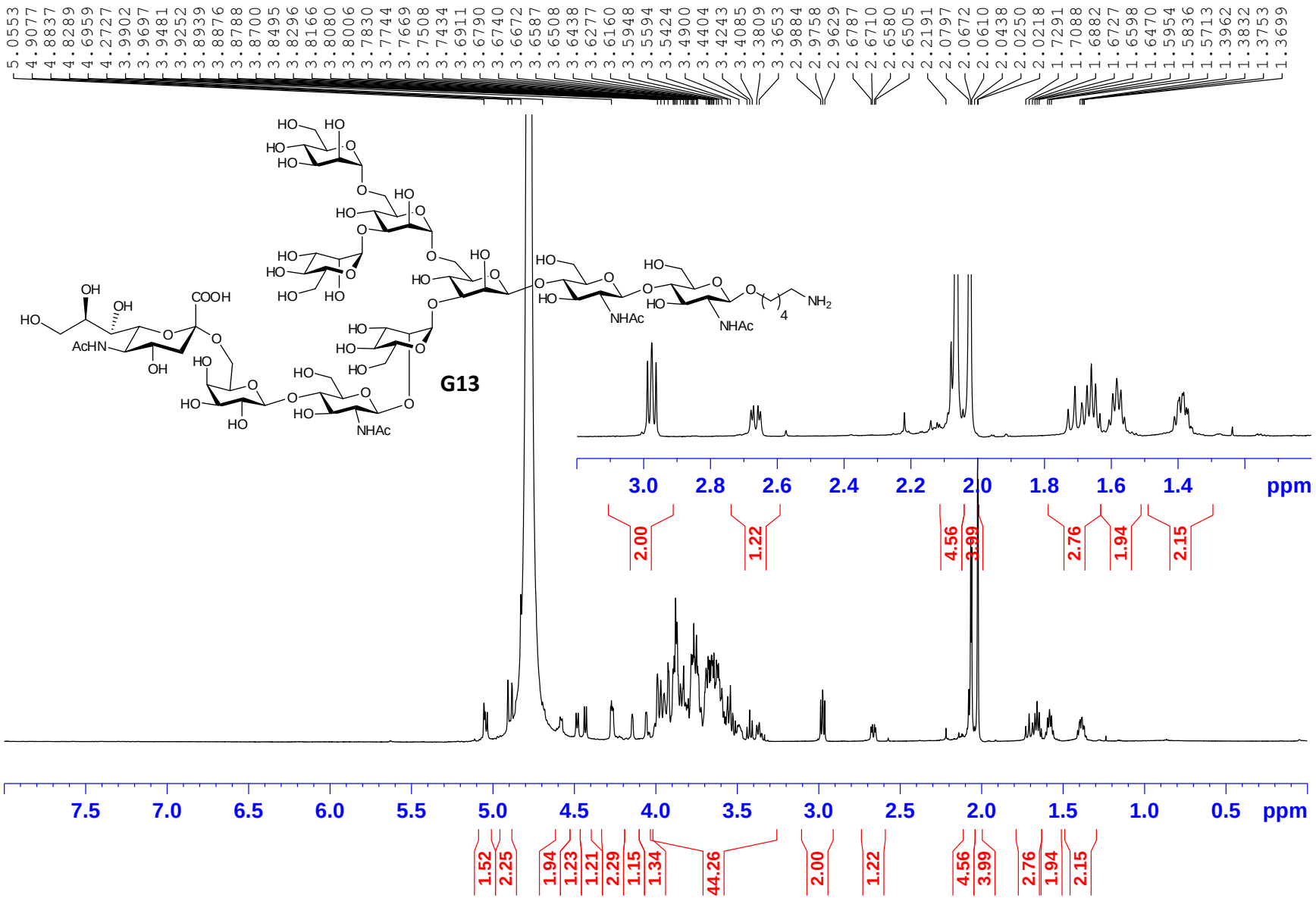
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


G12
ppm
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
10
20
30
40
50
60
70
80
90
100
110
120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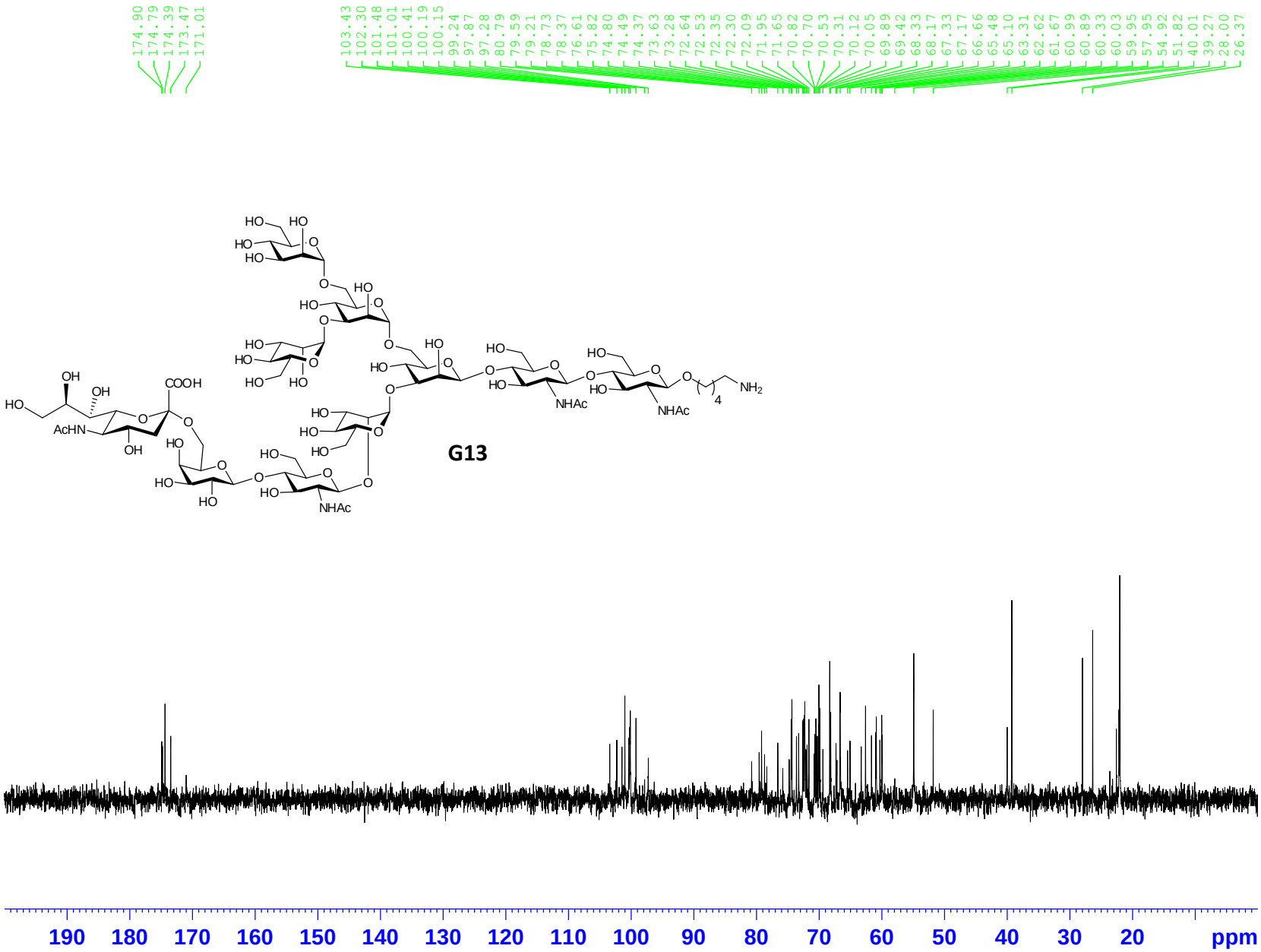
4.9077
4.8837
4.8289
4.6959
4.2727
3.9902
3.9697
3.9481
3.9252
3.8939
3.8876
3.8788
3.8700
3.8495
3.8296
3.8166
3.8080
3.8006
3.7830
3.7744
3.7669
3.7508
3.7434
3.6911
3.6790
3.6740
3.6672
3.6587
3.6508
3.6438
3.6277
3.6160
3.5948
3.5594
3.5424
3.4900
3.4404
3.4243
3.4085
3.3809
3.3653
2.9884
2.9758
2.9629
2.6787
2.6710
2.6580
2.6505
2.2191
2.0797
2.0672
2.0610
2.0438
2.0250
2.0218
1.7291
1.7088
1.6882
1.6727
1.6598
1.6470
1.5954
1.5836
1.5713
1.3962
1.3832
1.3753
1.3699
G13
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
ppm
2.00
1.22
4.56
3.99
2.76
1.94
2.15
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
1.52
2.25
1.94
1.23
1.21
2.29
1.15
1.34
44.26
2.00
1.22
4.56
3.99
2.76
1.94
2.15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174.39
173.47
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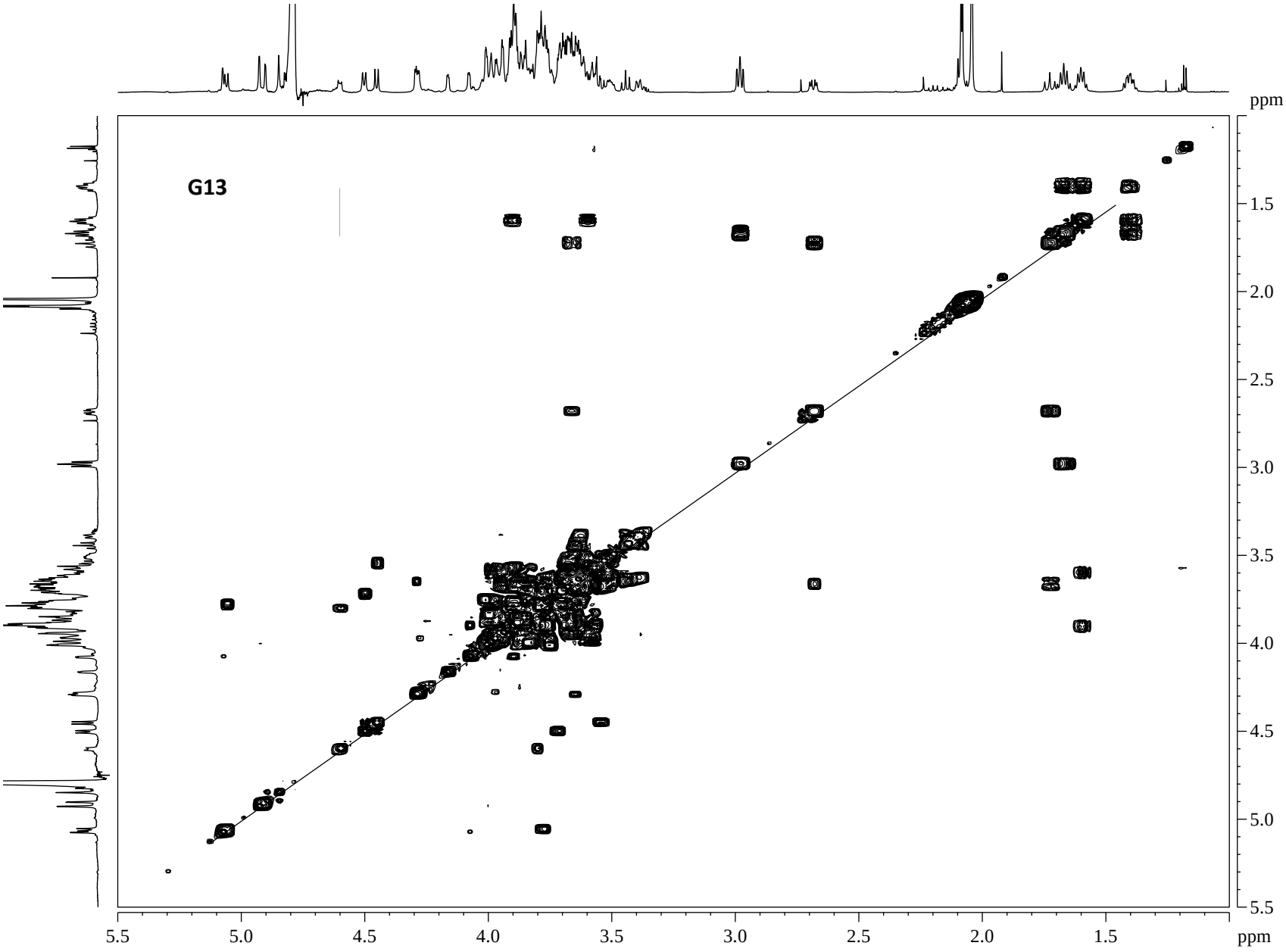
103.43
102.30
101.48
101.01
100.41
100.19
100.15
99.24
97.87
97.28
80.79
79.59
79.21
78.73
78.37
76.61
75.82
74.80
74.49
74.37
73.63
73.28
72.64
72.53
72.35
72.30
72.09
71.95
71.65
70.82
70.70
70.53
70.31
70.12
70.05
69.89
69.42
68.33
68.17
67.33
67.17
66.66
65.48
65.10
63.31
62.62
61.67
60.99
60.89
60.33
60.03
59.95
57.95
54.92
51.82
40.01
39.27
28.00
26.37
G13
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


G13
ppm
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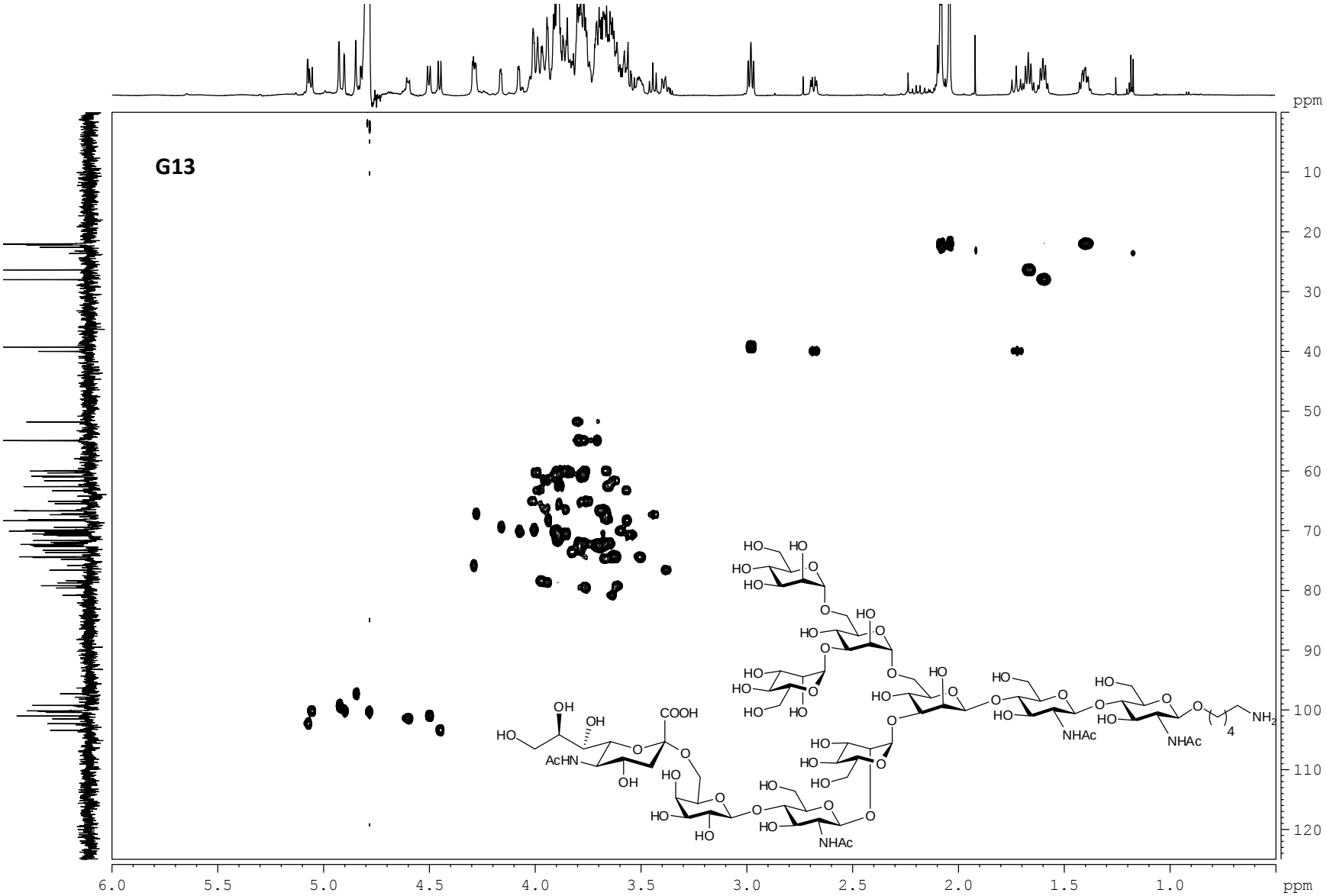
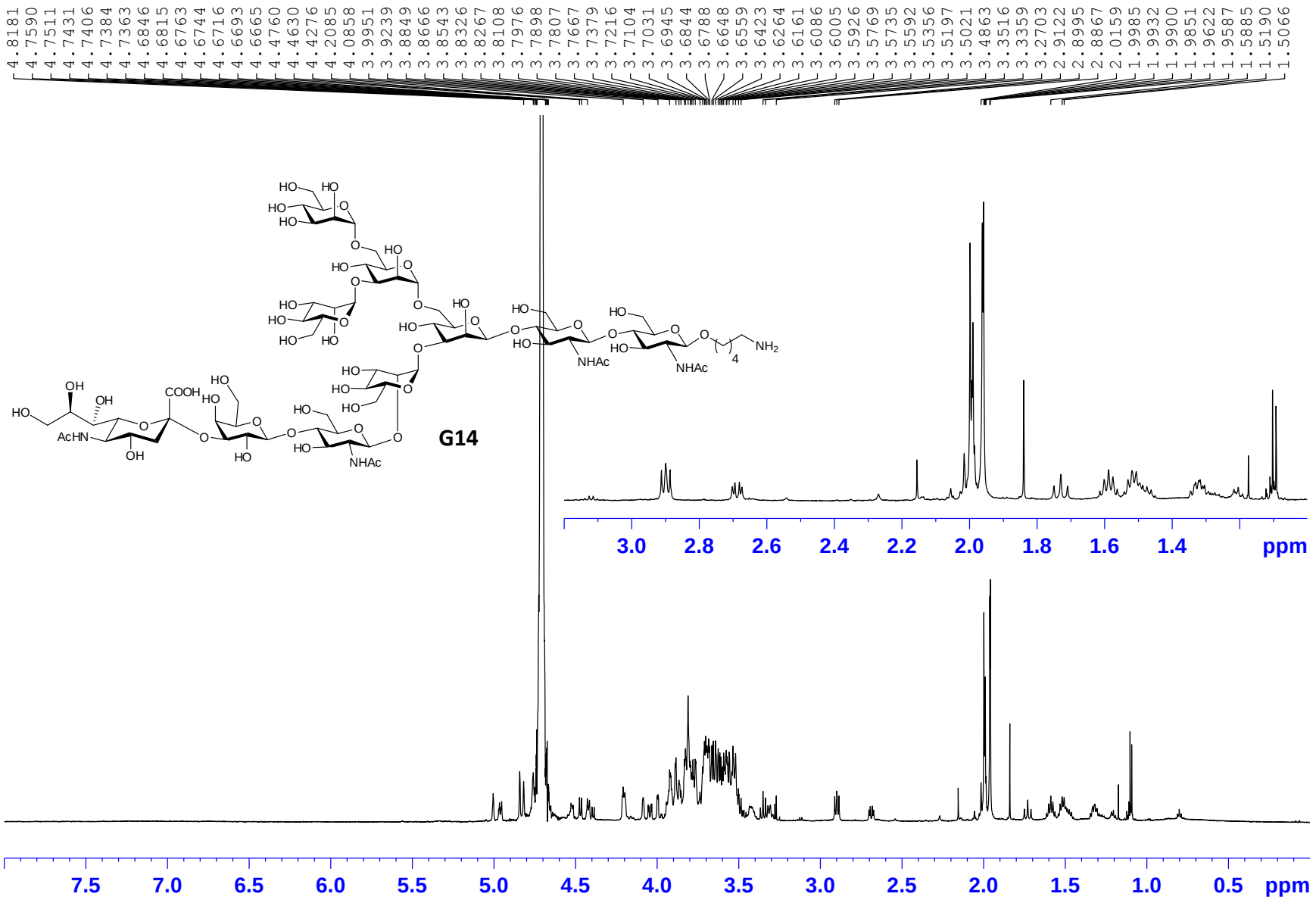
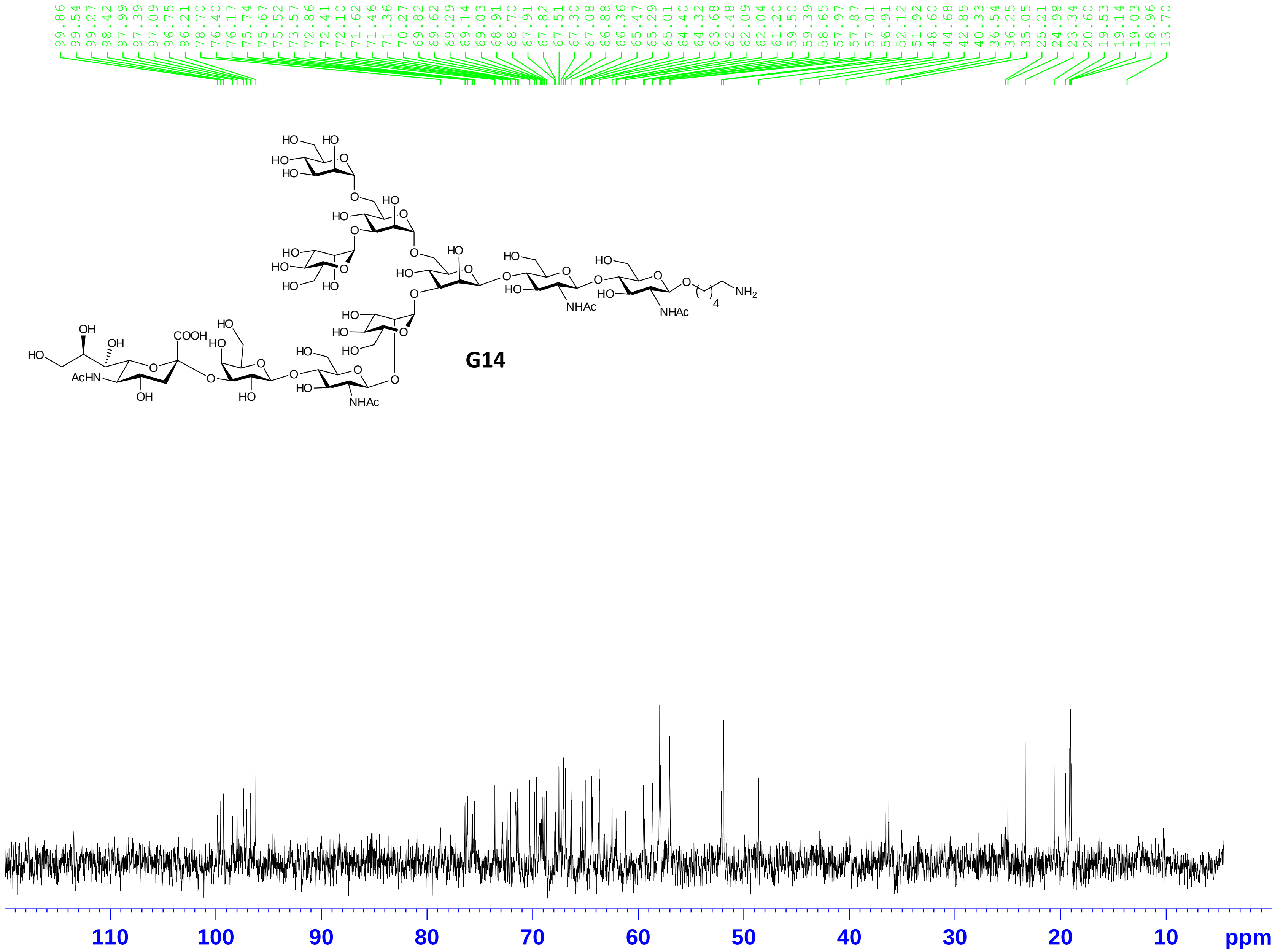
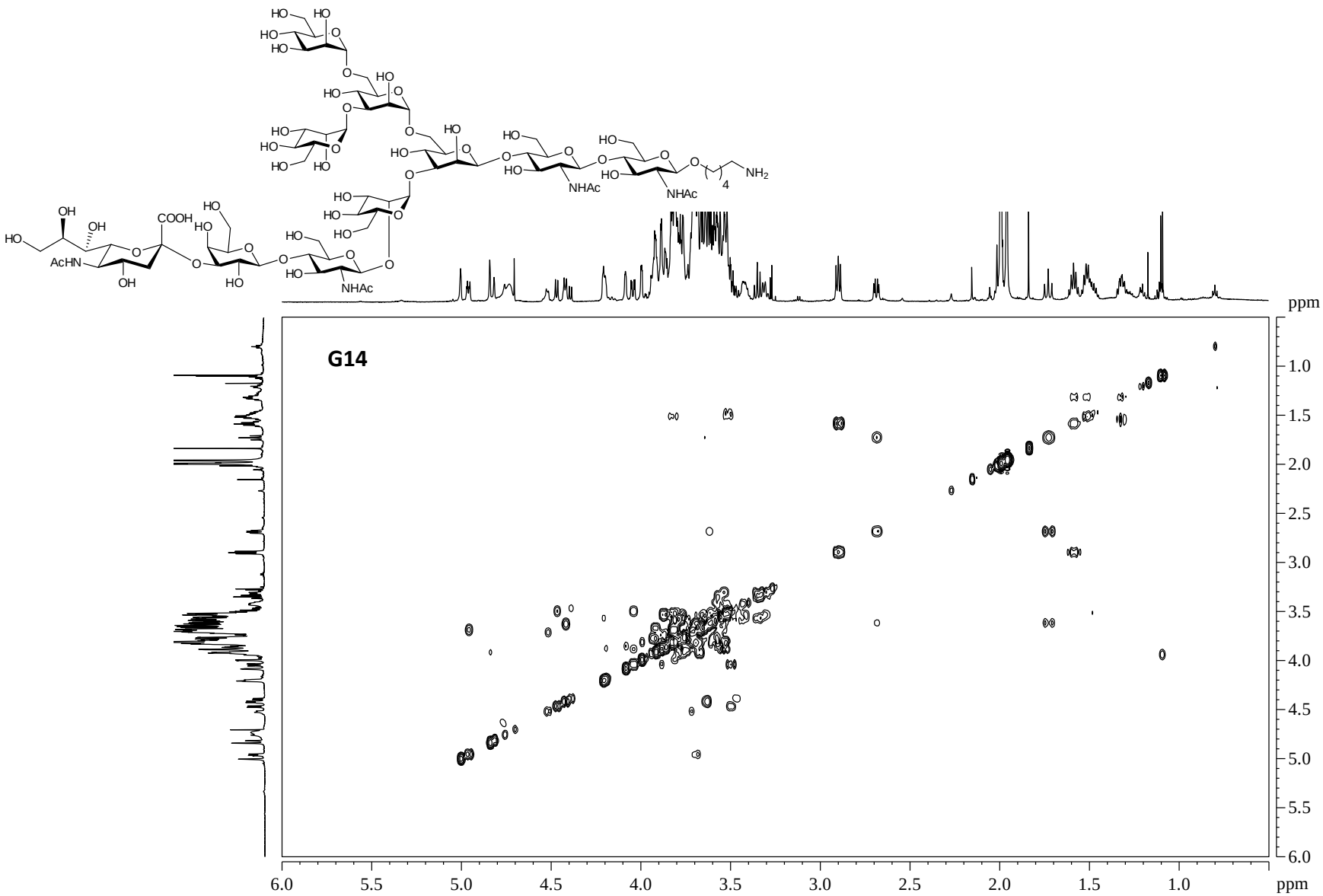
2.5
3.0
3.5
4.0
4.5
5.0
5.5
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm


G13
ppm
10
20
30
40
50
60
70
80
90
100
110
120
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
HO
OH
COOH
AcHN
NHAc
NH2
4


4.8181 4.7590 4.7511 4.7431 4.7406 4.7384 4.7363 4.6846 4.6815 4.6763 4.6744 4.6716 4.6693 4.6665 4.4760 4.4630 4.4276 4.2085 4.0858 3.9951 3.9239 3.8849 3.8666 3.8543 3.8326 3.8267 3.8108 3.7976 3.7898 3.7807 3.7667 3.7379 3.7216 3.7104 3.7031 3.6945 3.6844 3.6788 3.6648 3.6559 3.6423 3.6264 3.6161 3.6086 3.6005 3.5926 3.5769 3.5735 3.5592 3.5356 3.5197 3.5021 3.4863 3.3516 3.3359 3.2703 2.9122 2.8995 2.8867 2.0159 1.9985 1.9932 1.9900 1.9851 1.9622 1.9587 1.5885 1.5190 1.5066
G14
3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 ppm
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


99.86 99.54 99.27 98.42 97.99 97.39 97.09 96.75 96.21 78.70 76.40 76.17 75.74 75.67 75.52 73.57 72.86 72.41 72.10 71.62 71.46 71.36 70.27 69.82 69.62 69.29 69.14 69.03 68.91 68.70 67.91 67.82 67.51 67.30 67.08 66.88 66.36 65.47 65.29 65.01 64.40 64.32 63.68 62.48 62.09 62.04 61.20 59.50 59.39 58.65 57.97 57.87 57.01 56.91 52.12 51.92 48.60 44.68 42.85 40.33 36.54 36.25 35.05 25.21 24.98 23.34 20.60 19.53 19.14 19.03 18.96 13.70
HO
OH
COOH
AcHN
NHAc
NH_2
4
110
100
90
80
70
60
50
40
30
20
10
ppm

G14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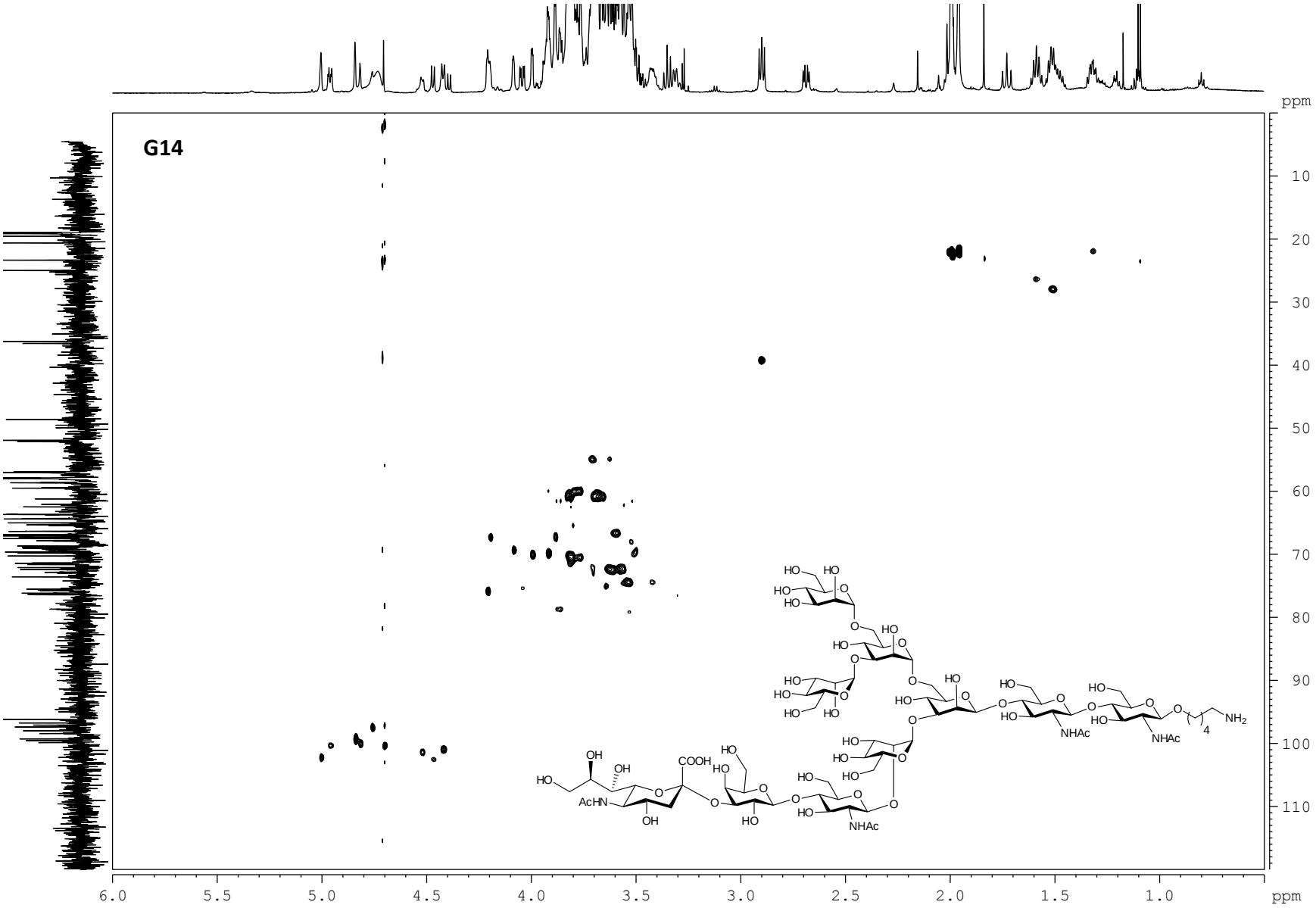
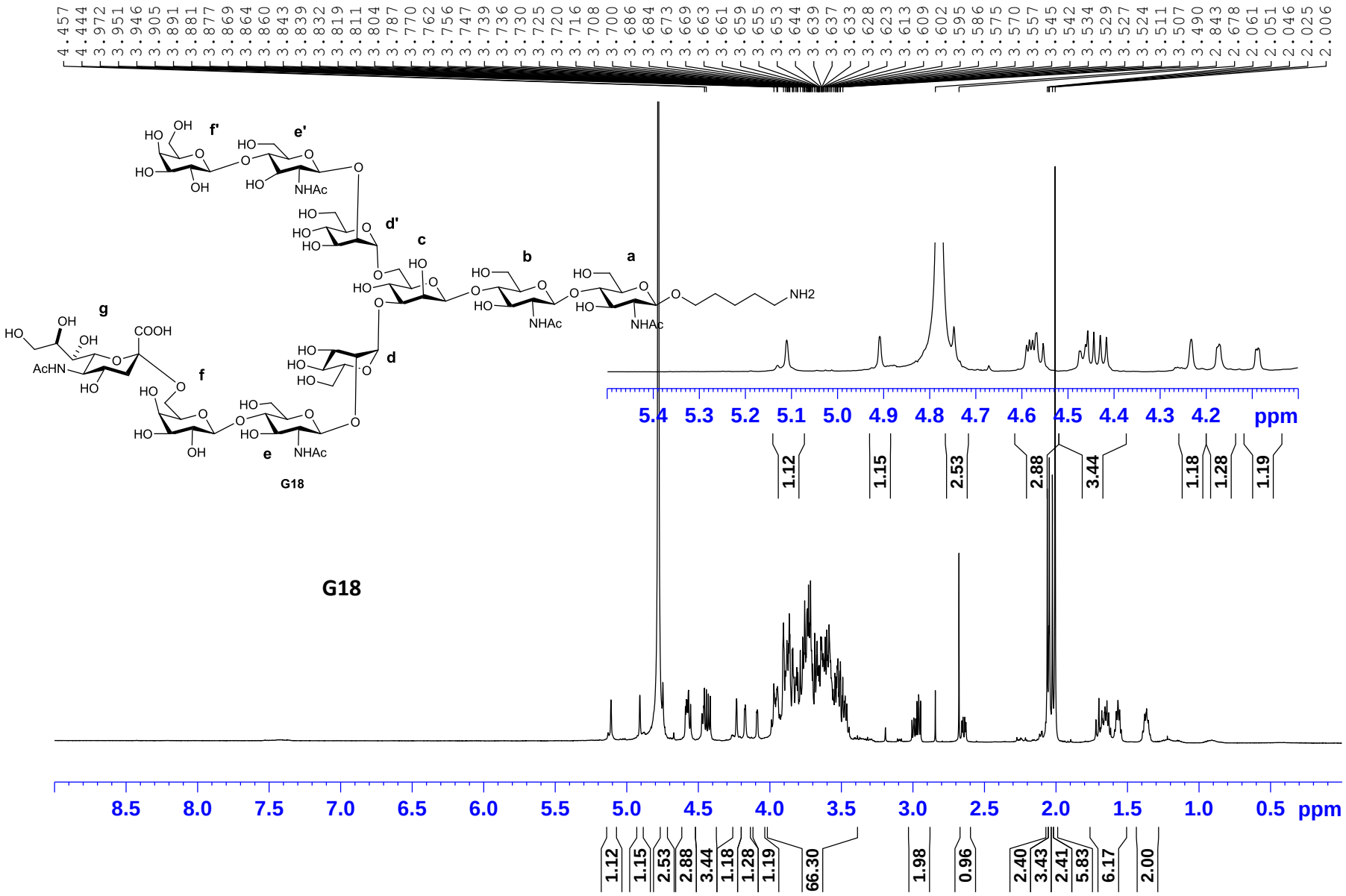
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


G14
ppm
10
20
30
40
50
60
70
80
90
100
110
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


4.457 4.444 3.972 3.951 3.946 3.905 3.891 3.881 3.877 3.869 3.864 3.860 3.843 3.839 3.832 3.819 3.811 3.804 3.787 3.770 3.762 3.756 3.747 3.739 3.736 3.730 3.725 3.720 3.716 3.708 3.700 3.686 3.684 3.673 3.669 3.663 3.661 3.659 3.655 3.653 3.644 3.639 3.637 3.633 3.628 3.623 3.613 3.609 3.602 3.595 3.586 3.575 3.570 3.557 3.545 3.542 3.534 3.529 3.527 3.524 3.511 3.507 3.490 2.843 2.678 2.061 2.051 2.046 2.025 2.006
f'
e'
d'
c
b
a
g
f
d
e
NHAc
NH2
COOH
AcHN
G18
5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 ppm
1.12 1.15 2.53 2.88 3.44 1.18 1.28 1.19
G18
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
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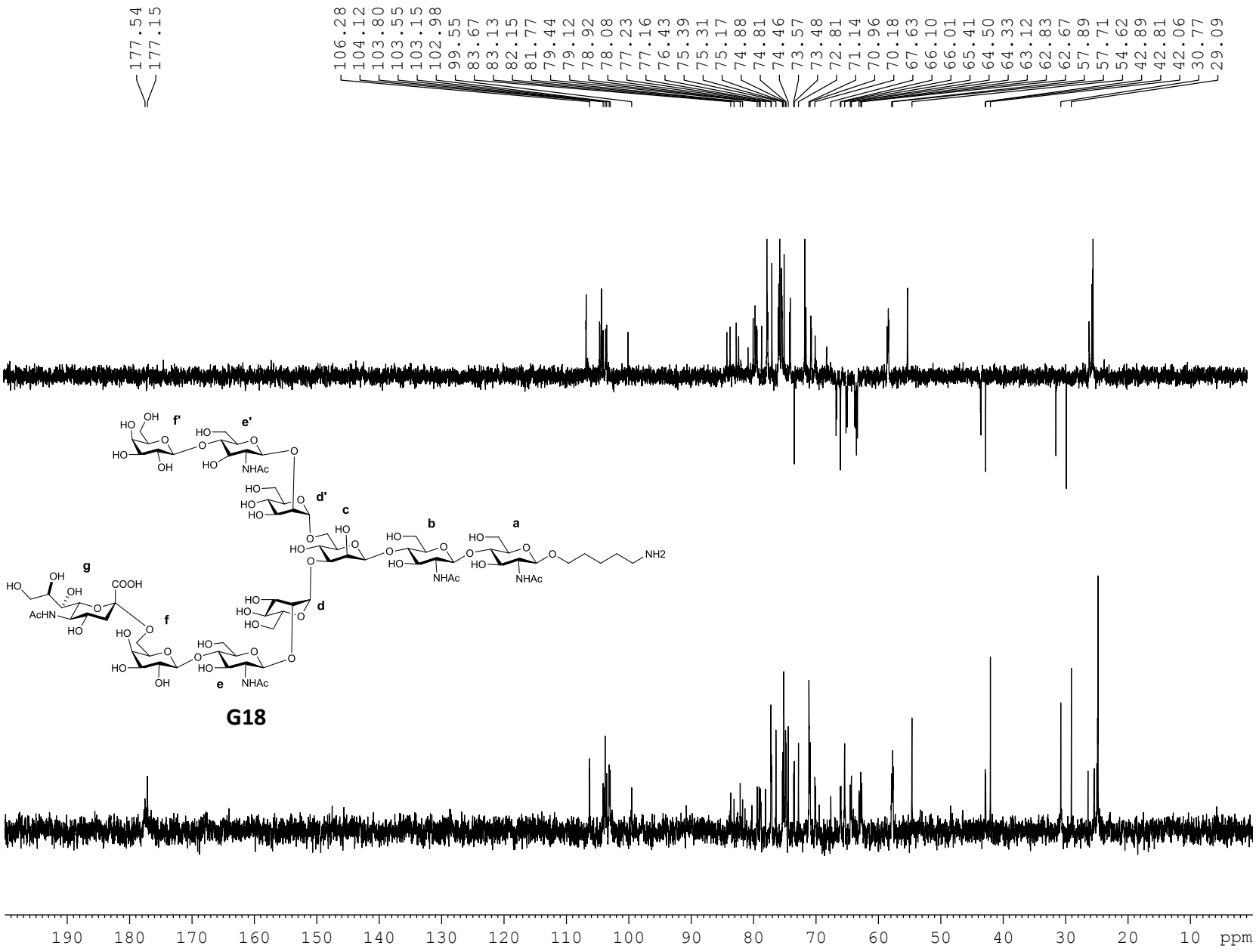
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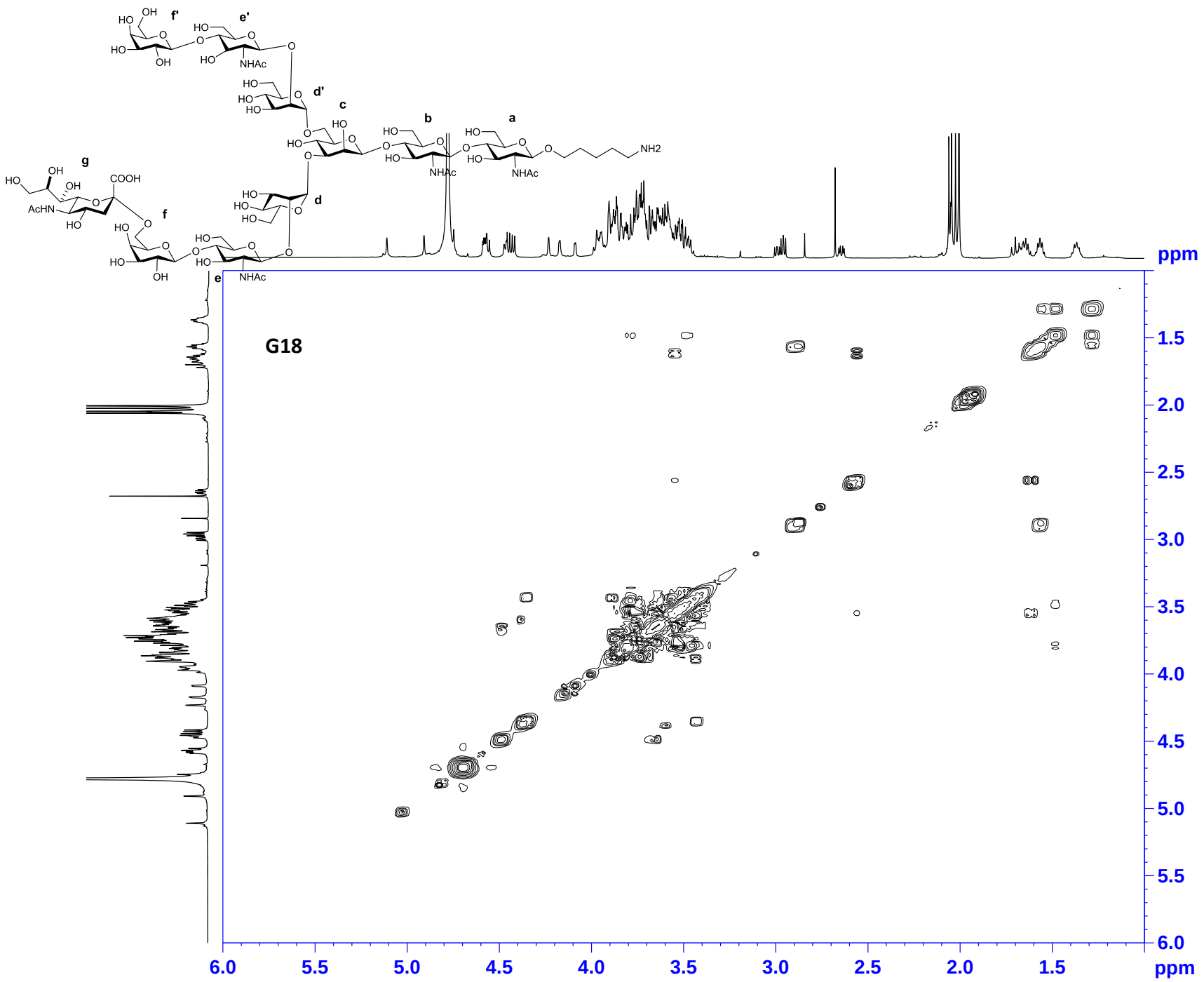
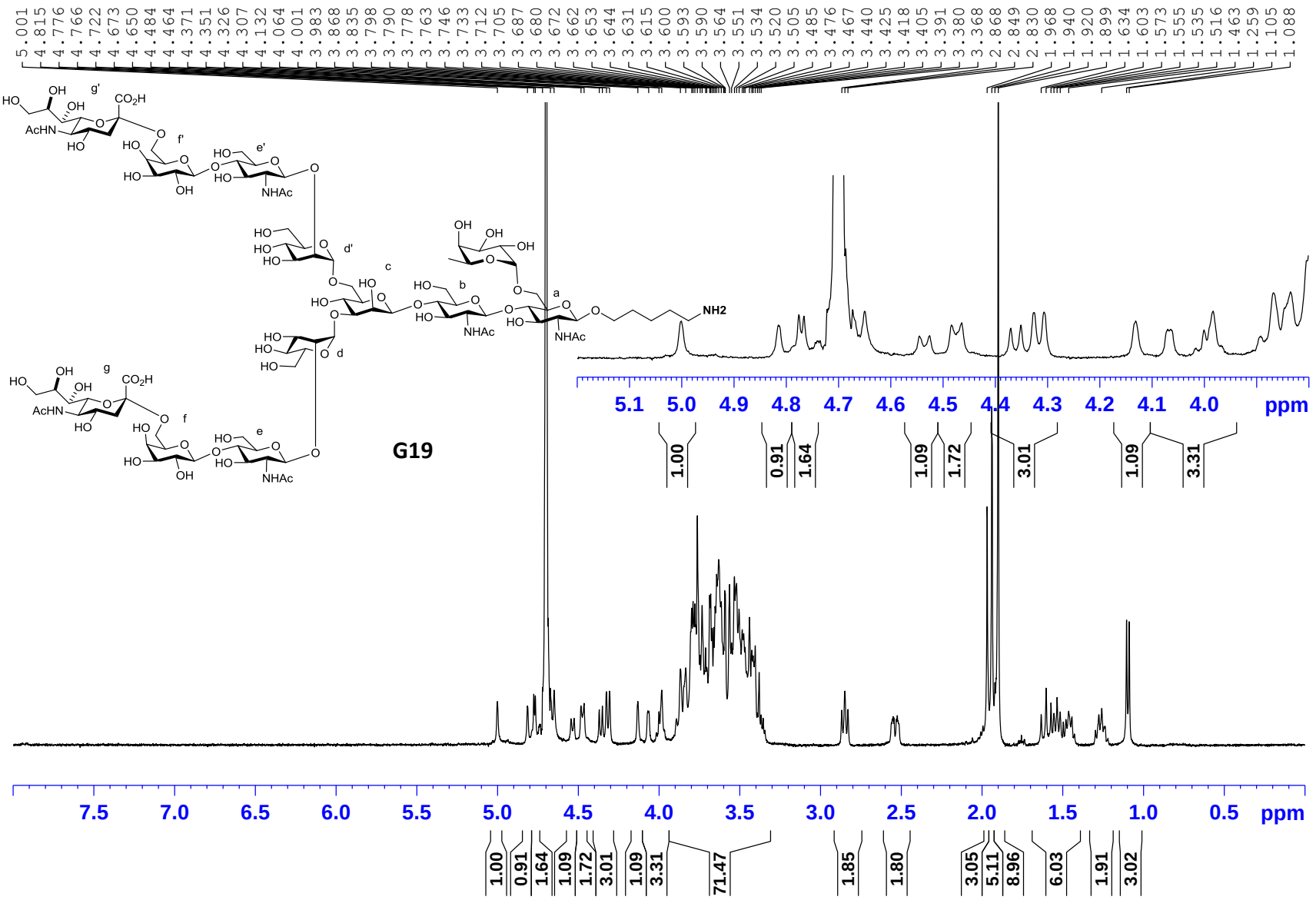
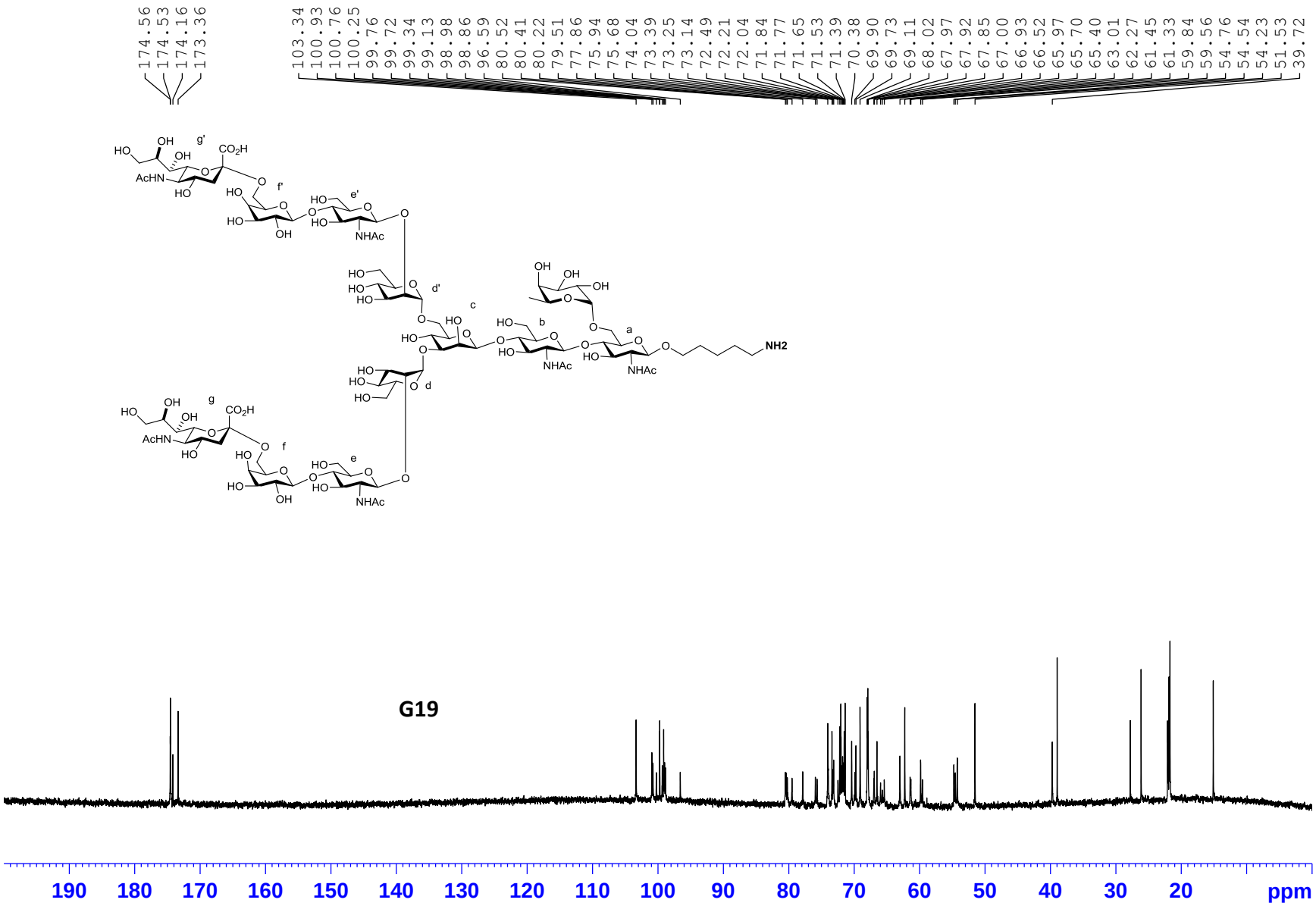
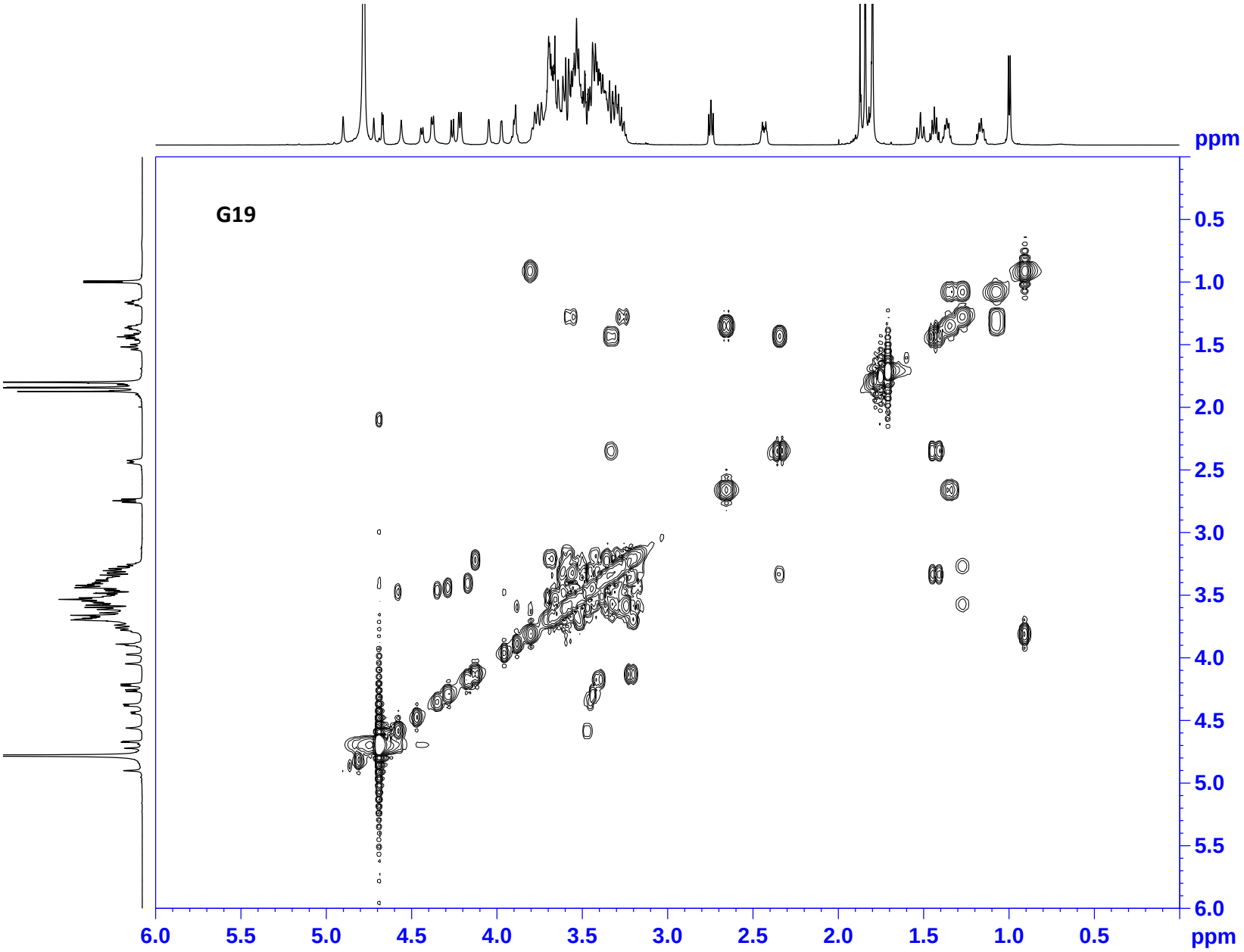
177.15
106.28
104.12
103.80
103.55
103.15
102.98
99.55
83.67
83.13
82.15
81.77
79.44
79.12
78.92
78.08
77.23
77.16
76.43
75.39
75.31
75.17
74.88
74.81
74.46
73.57
73.48
72.81
71.14
70.96
70.18
67.63
66.10
66.01
65.41
64.50
64.33
63.12
62.83
62.67
57.89
57.71
54.62
42.89
42.81
42.06
30.77
29.09
f'
e'
d'
c
b
a
NH2
g
f
d
e
NHAc
COOH
AcHN
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

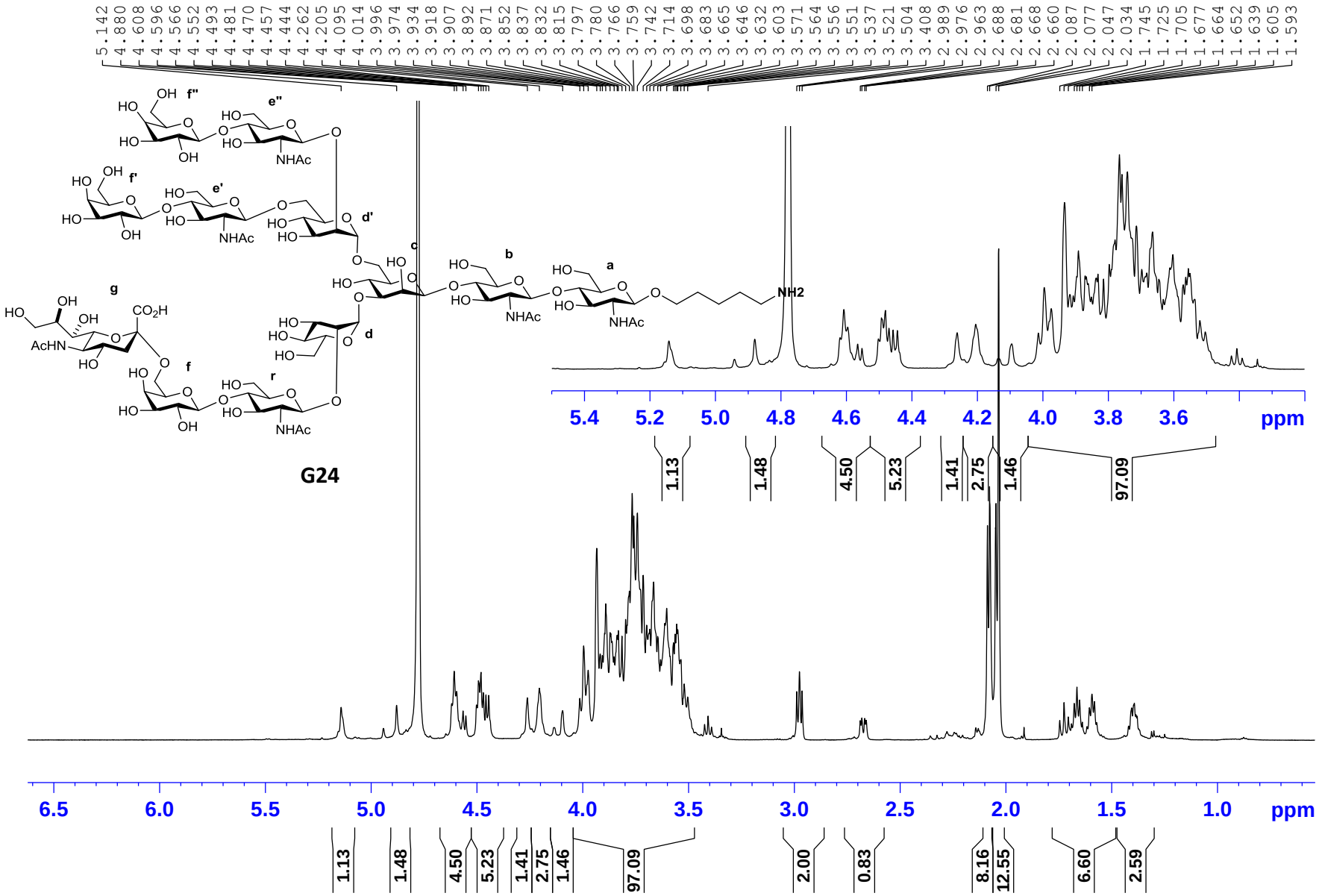
G18

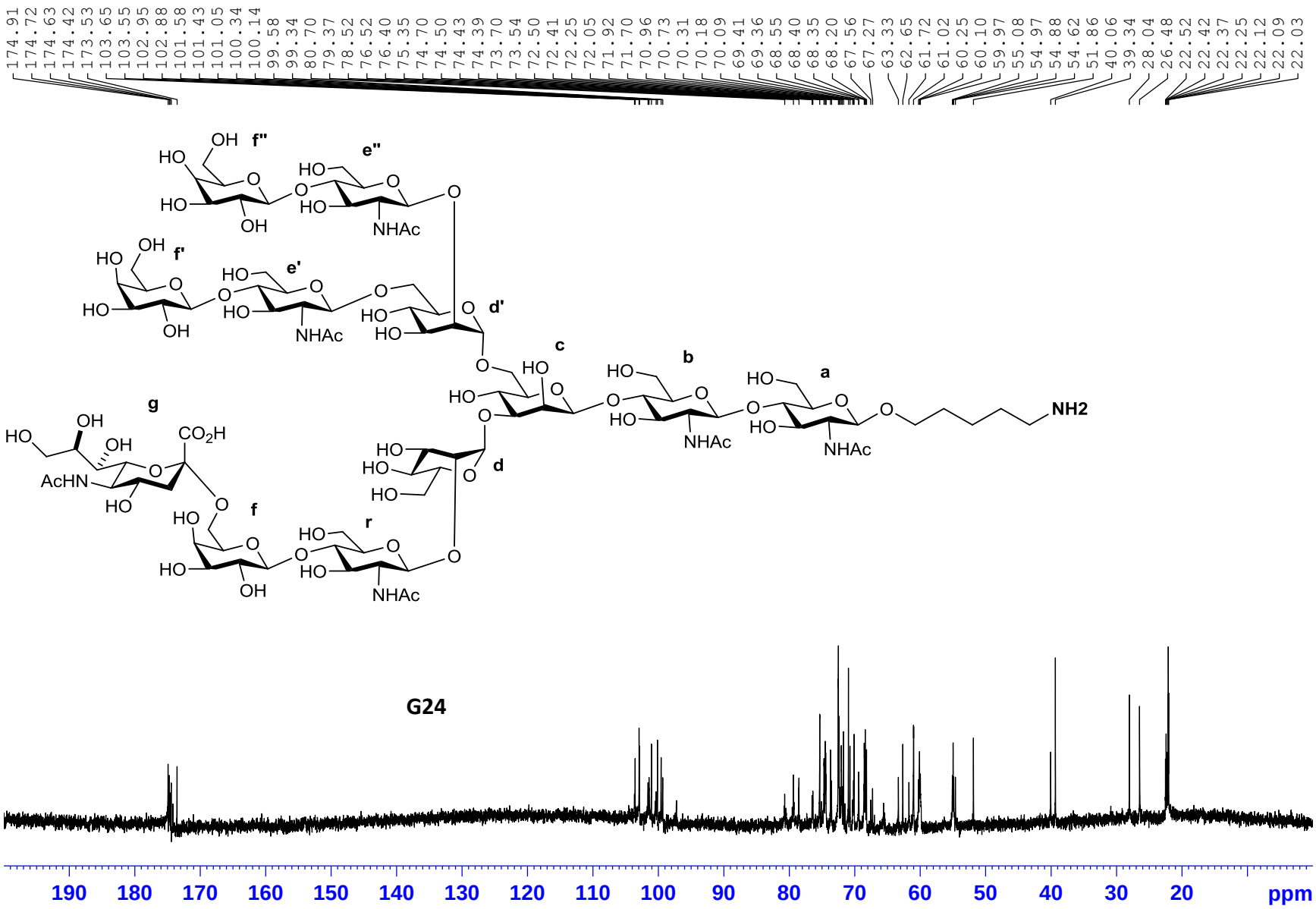

G18
ppm
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5

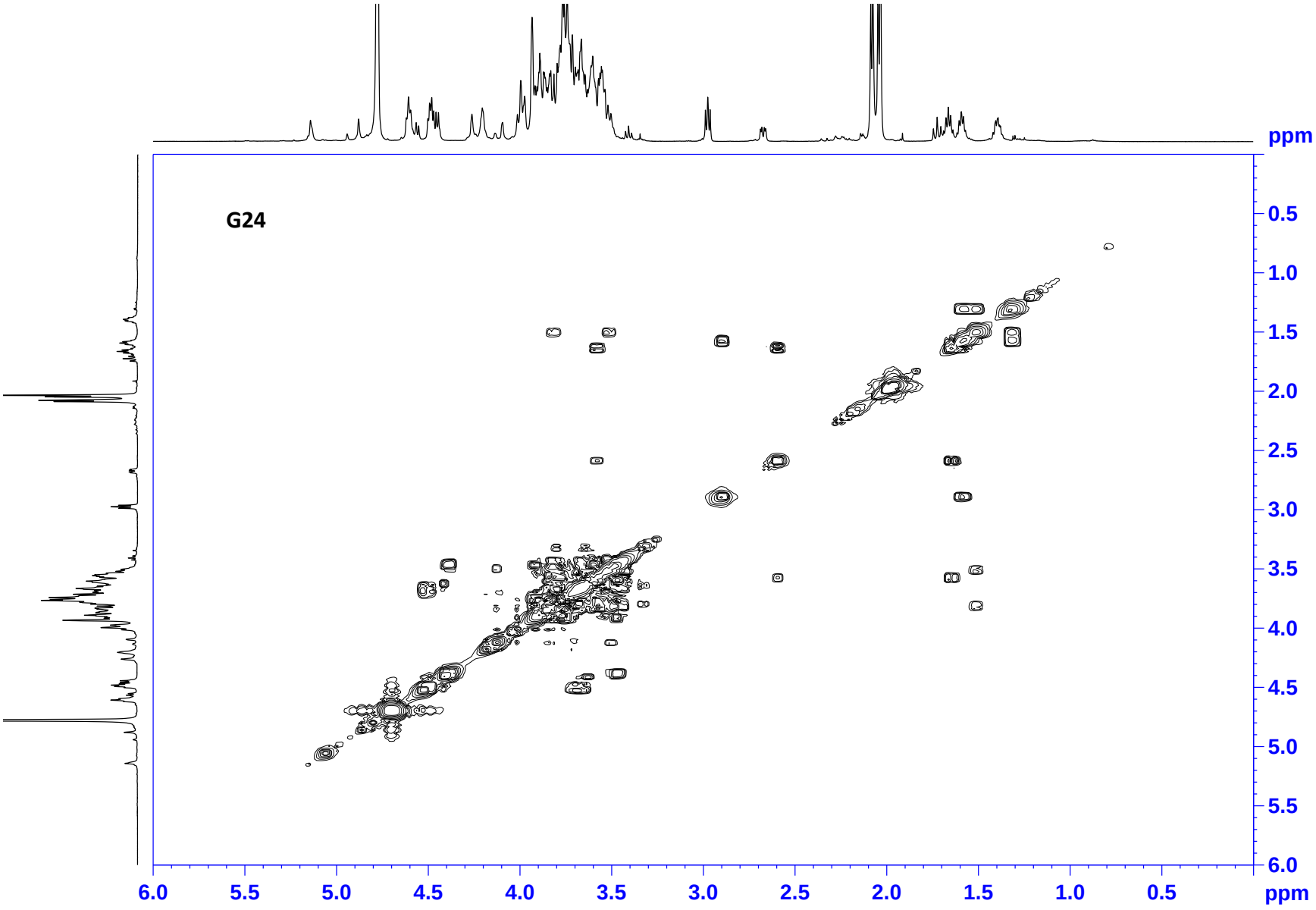

5.001
4.815
4.776
4.766
4.722
4.673
4.650
4.484
4.464
4.371
4.351
4.326
4.307
4.132
4.064
4.001
3.983
3.868
3.835
3.798
3.790
3.778
3.763
3.746
3.733
3.712
3.705
3.687
3.680
3.672
3.662
3.653
3.644
3.631
3.615
3.600
3.593
3.590
3.564
3.551
3.534
3.520
3.505
3.485
3.476
3.467
3.440
3.425
3.418
3.405
3.391
3.380
3.368
2.868
2.849
2.830
1.968
1.940
1.920
1.899
1.634
1.603
1.573
1.555
1.535
1.516
1.463
1.259
1.105
1.088
G19
NH2
NHAc
AcHN
CO2H
5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 ppm
1.00 0.91 1.64 1.09 1.72 3.01 1.09 3.31
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
1.00 0.91 1.64 1.09 1.72 3.01 1.09 3.31 71.47 1.85 1.80 3.05 5.11 8.96 6.03 1.91 3.02

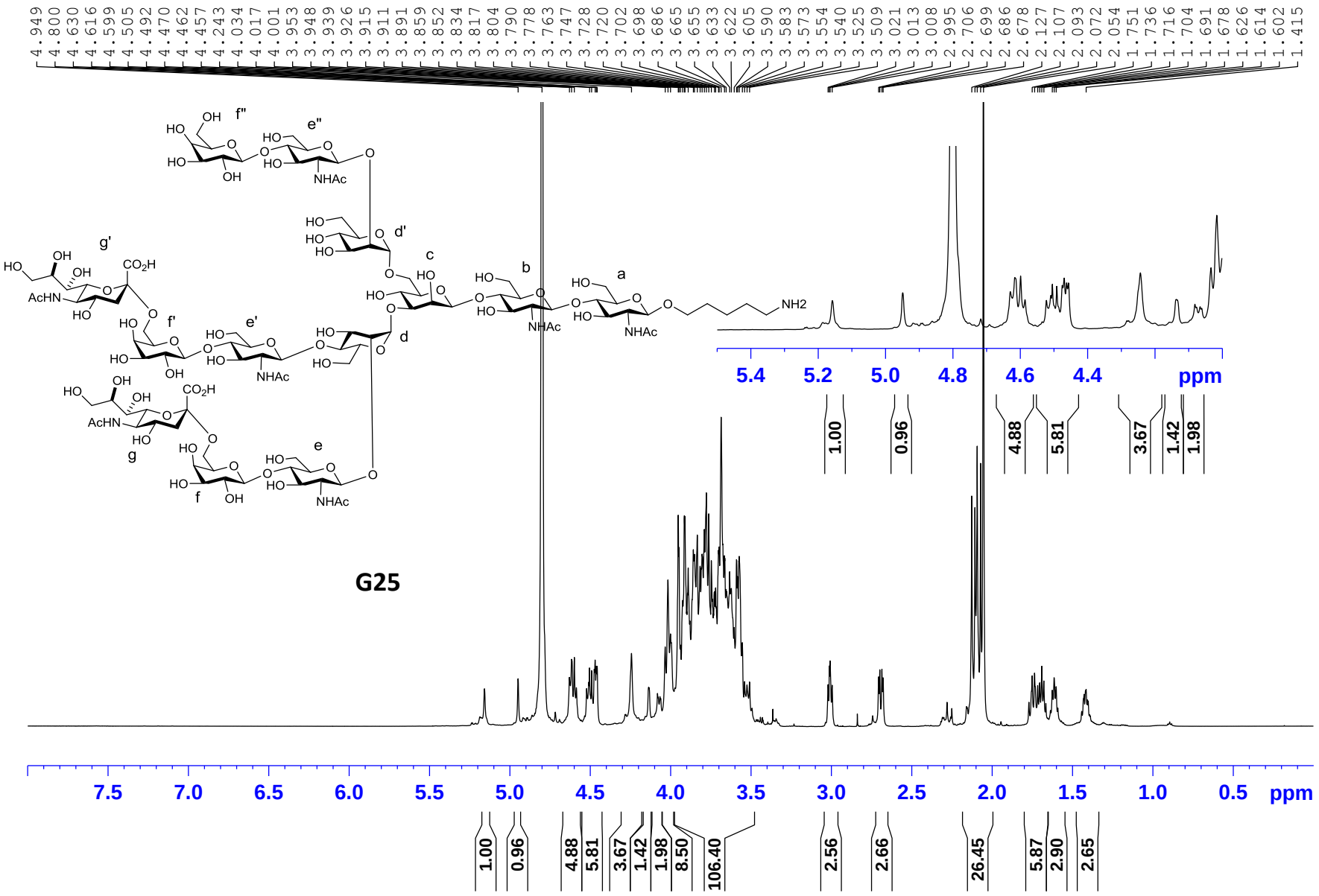

174.56
174.53
174.16
173.36
103.34
100.93
100.76
100.25
99.76
99.72
99.34
99.13
98.98
98.86
96.59
80.52
80.41
80.22
79.51
77.86
75.94
75.68
74.04
73.39
73.25
73.14
72.49
72.21
72.04
71.84
71.77
71.65
71.53
71.39
70.38
69.90
69.73
69.11
68.02
67.97
67.92
67.85
67.00
66.93
66.52
65.97
65.70
65.40
63.01
62.27
61.45
61.33
59.84
59.56
54.76
54.54
54.23
51.53
39.72
NH2
G19
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

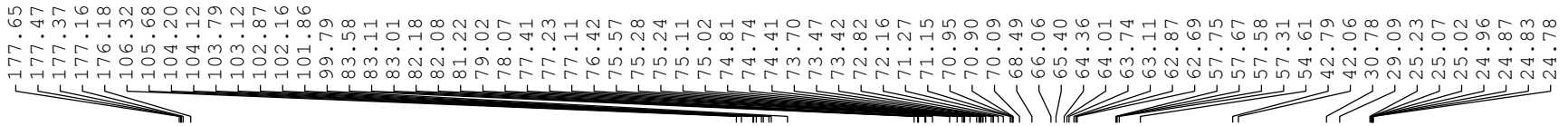

G19
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

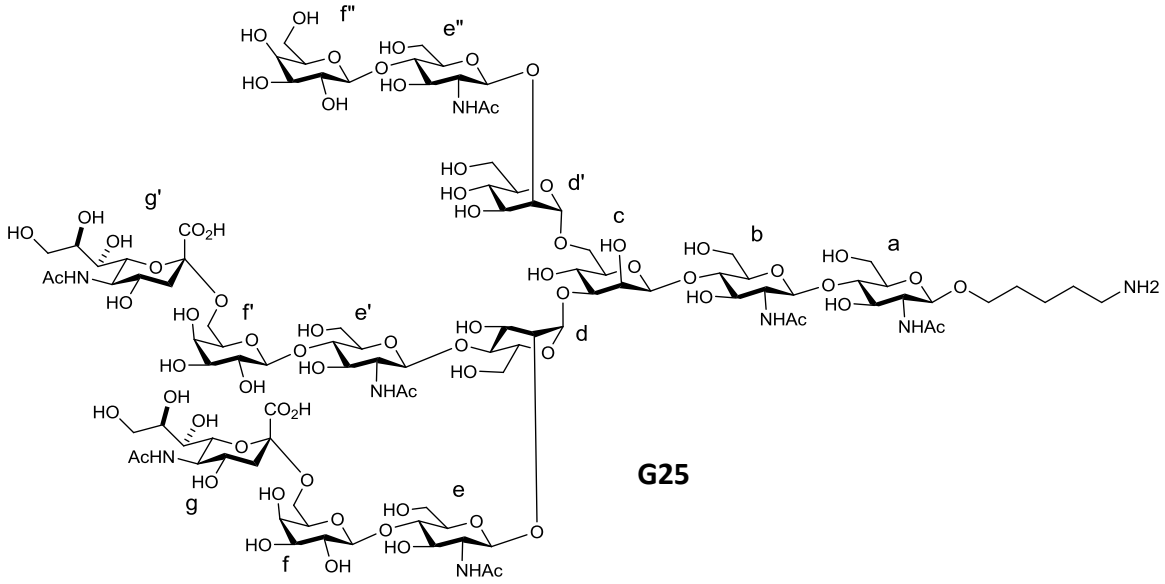

5.142
4.880
4.608
4.596
4.566
4.552
4.493
4.481
4.470
4.457
4.444
4.262
4.205
4.095
4.014
3.996
3.974
3.934
3.918
3.907
3.892
3.871
3.852
3.837
3.832
3.815
3.797
3.780
3.766
3.759
3.742
3.714
3.698
3.683
3.665
3.646
3.632
3.603
3.571
3.564
3.556
3.551
3.537
3.521
3.504
3.408
2.989
2.976
2.963
2.688
2.681
2.668
2.660
2.087
2.077
2.047
2.034
1.745
1.725
1.705
1.677
1.664
1.652
1.639
1.605
1.593
G24
5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 ppm
1.13 1.48 4.50 5.23 1.41 2.75 1.46 97.09
6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.13 1.48 4.50 5.23 1.41 2.75 1.46 97.09 2.00 0.83 8.16 12.55 6.60 2.59


174.91 174.72 174.63 174.42 173.53 103.65 103.55 102.95 102.88 101.58 101.43 101.05 100.34 100.14 99.58 99.34 80.70 79.37 78.52 76.52 76.40 75.35 74.70 74.50 74.43 74.39 73.70 73.54 72.50 72.41 72.25 72.05 71.92 71.70 70.96 70.73 70.31 70.18 70.09 69.41 69.36 68.55 68.40 68.35 68.20 67.56 67.27 63.33 62.65 61.72 61.02 60.25 60.10 59.97 55.08 54.97 54.88 54.62 51.86 40.06 39.34 28.04 26.48 22.52 22.42 22.37 22.25 22.12 22.09 22.03
f''
e''
f'
e'
d'
c
b
a
NH2
g
d
f
r
NHAc
AcHN
CO2H
G24
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

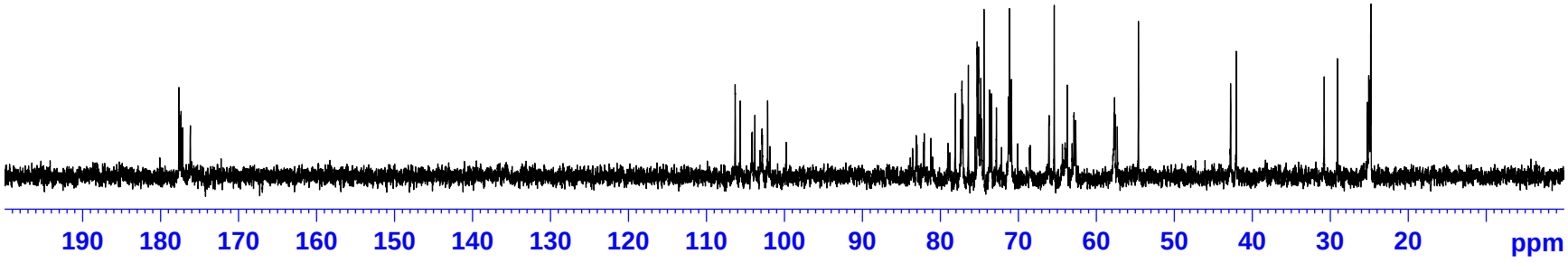

G24
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

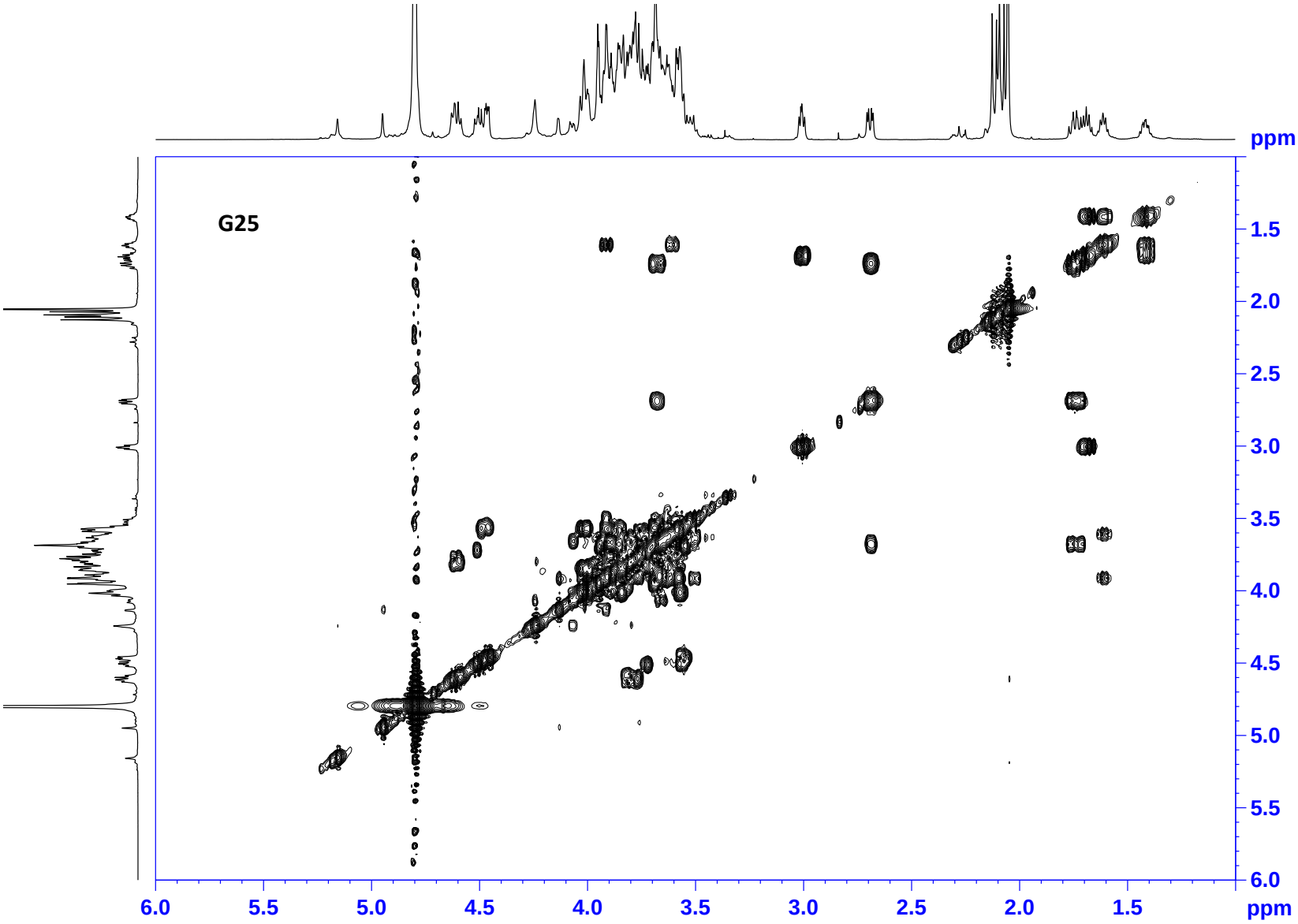

4.949 4.800 4.630 4.616 4.599 4.505 4.492 4.470 4.462 4.457 4.243 4.034 4.017 4.001 3.953 3.948 3.939 3.926 3.915 3.911 3.891 3.859 3.852 3.834 3.817 3.804 3.790 3.778 3.763 3.747 3.728 3.720 3.702 3.698 3.686 3.665 3.655 3.633 3.622 3.605 3.590 3.583 3.573 3.554 3.540 3.525 3.509 3.021 3.013 3.008 2.995 2.706 2.699 2.686 2.678 2.127 2.107 2.093 2.072 2.054 1.751 1.736 1.716 1.704 1.691 1.678 1.626 1.614 1.602 1.415
G25
5.4 5.2 5.0 4.8 4.6 4.4 ppm
1.00 0.96 4.88 5.81 3.67 1.42 1.98
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
1.00 0.96 4.88 5.81 3.67 1.42 1.98 8.50 106.40 2.56 2.66 26.45 5.87 2.90 2.65

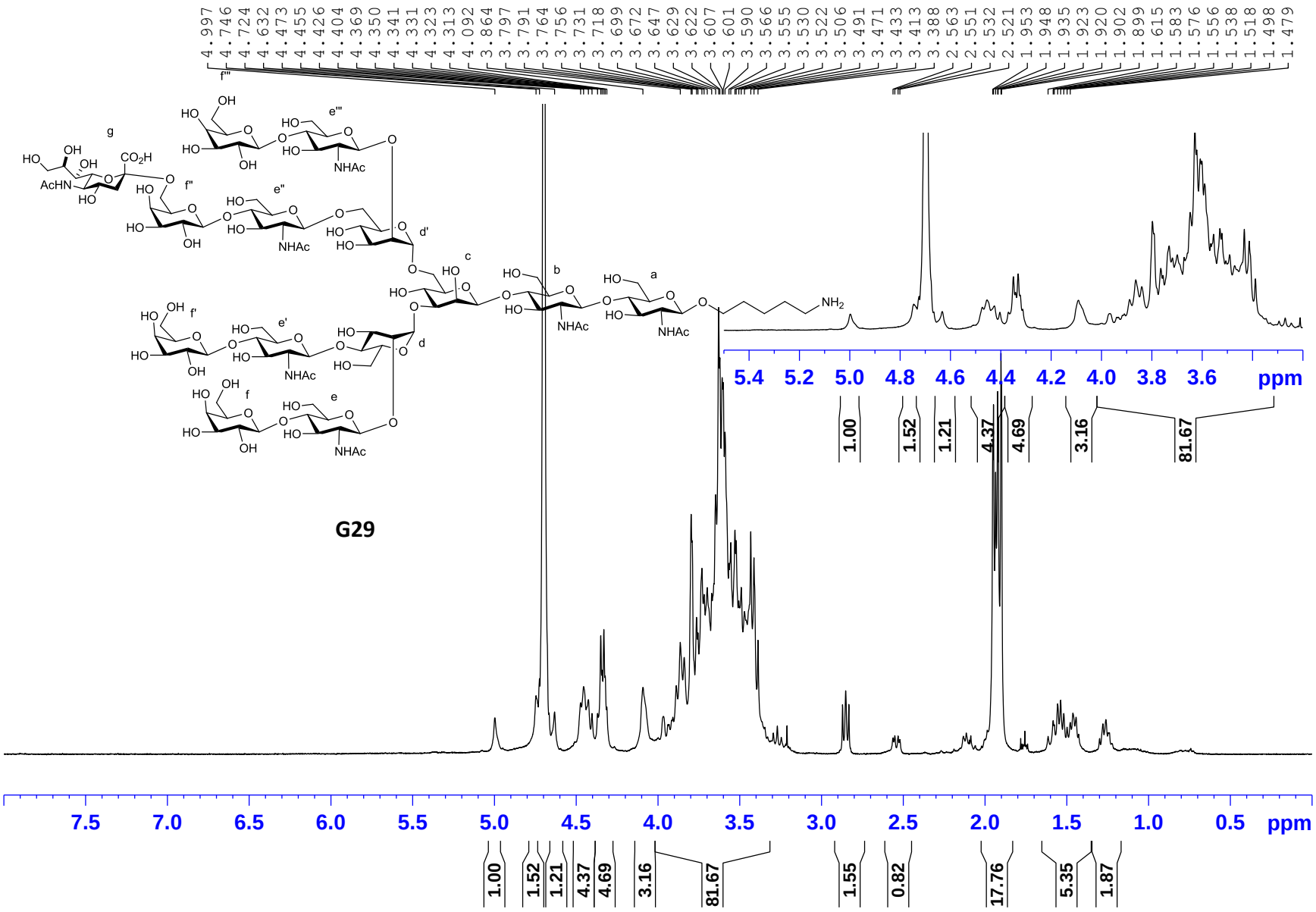

177.65
177.47
177.37
177.16
176.18
106.32
105.68
104.20
104.12
103.79
103.12
102.87
102.16
101.86
99.79
83.58
83.11
83.01
82.18
82.08
81.22
79.02
78.07
77.41
77.23
77.11
76.42
75.57
75.28
75.24
75.11
75.02
74.81
74.74
74.41
73.70
73.47
73.42
72.82
72.16
71.27
71.15
70.95
70.90
70.09
68.49
66.06
65.40
64.36
64.01
63.74
63.11
62.87
62.69
57.75
57.67
57.58
57.31
54.61
42.79
42.06
30.78
29.09
25.23
25.07
25.02
24.96
24.87
24.83
24.78

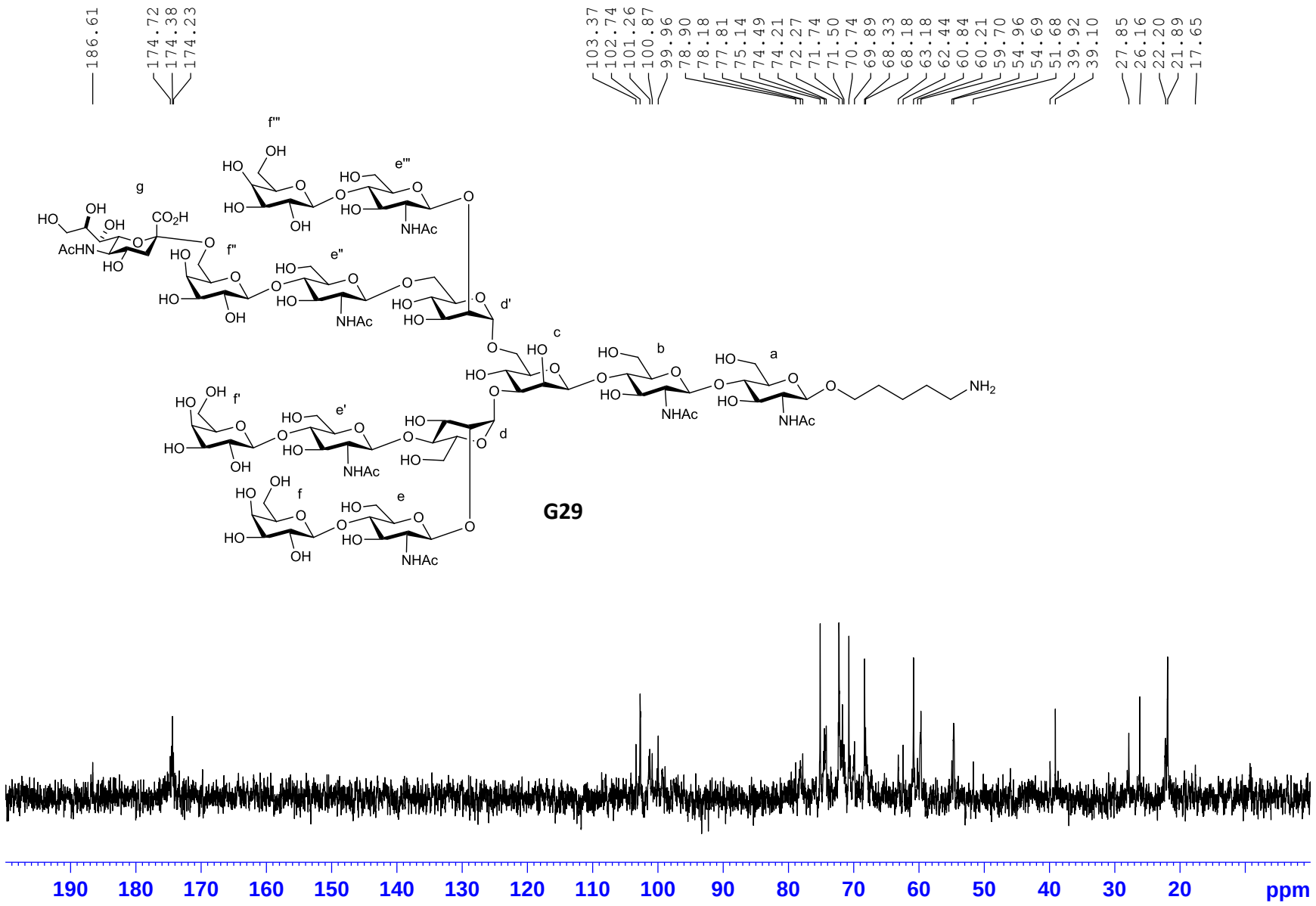

f"
e"
d'
g'
c
b
a
NH2
f'
e'
d
g
e
f

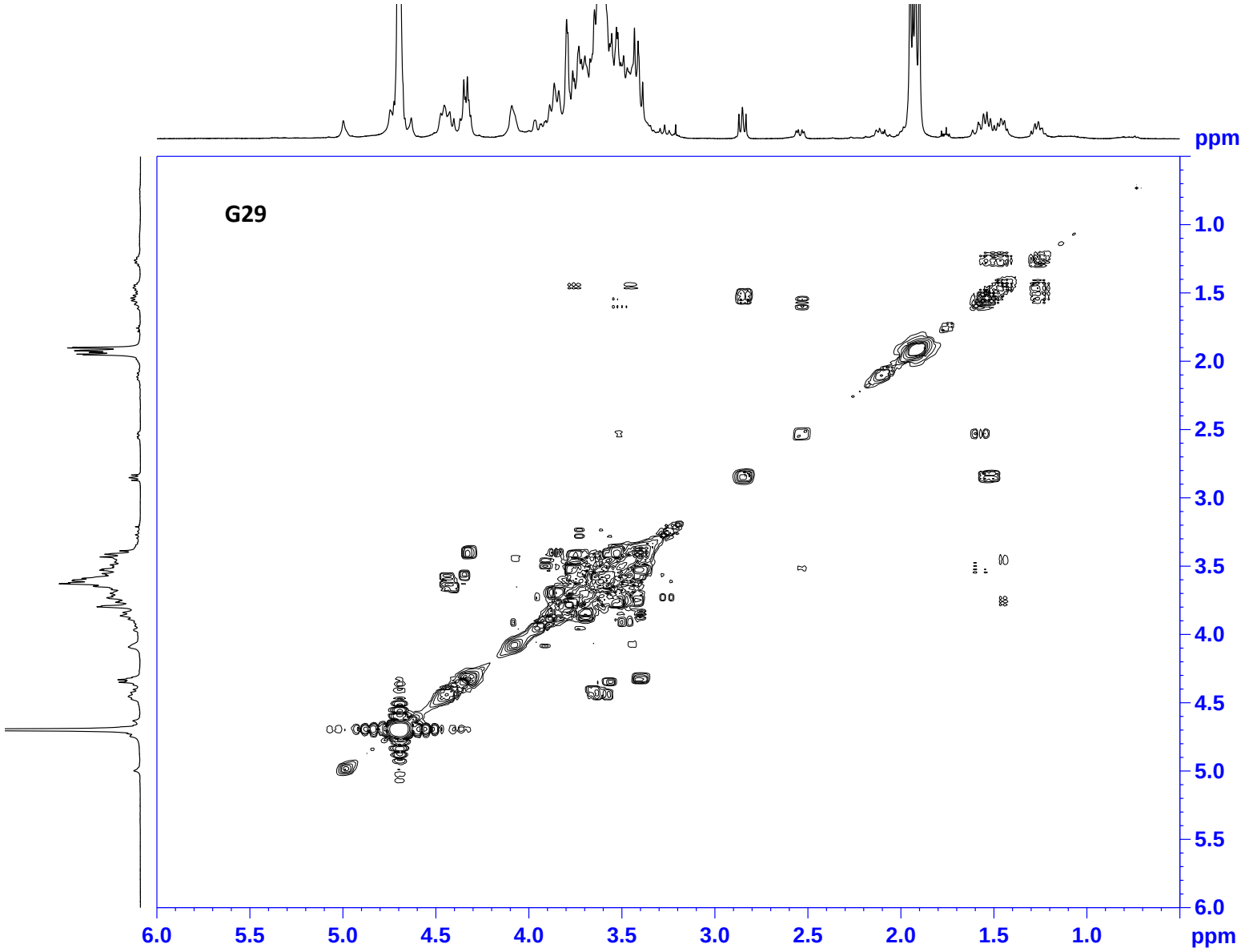
G25

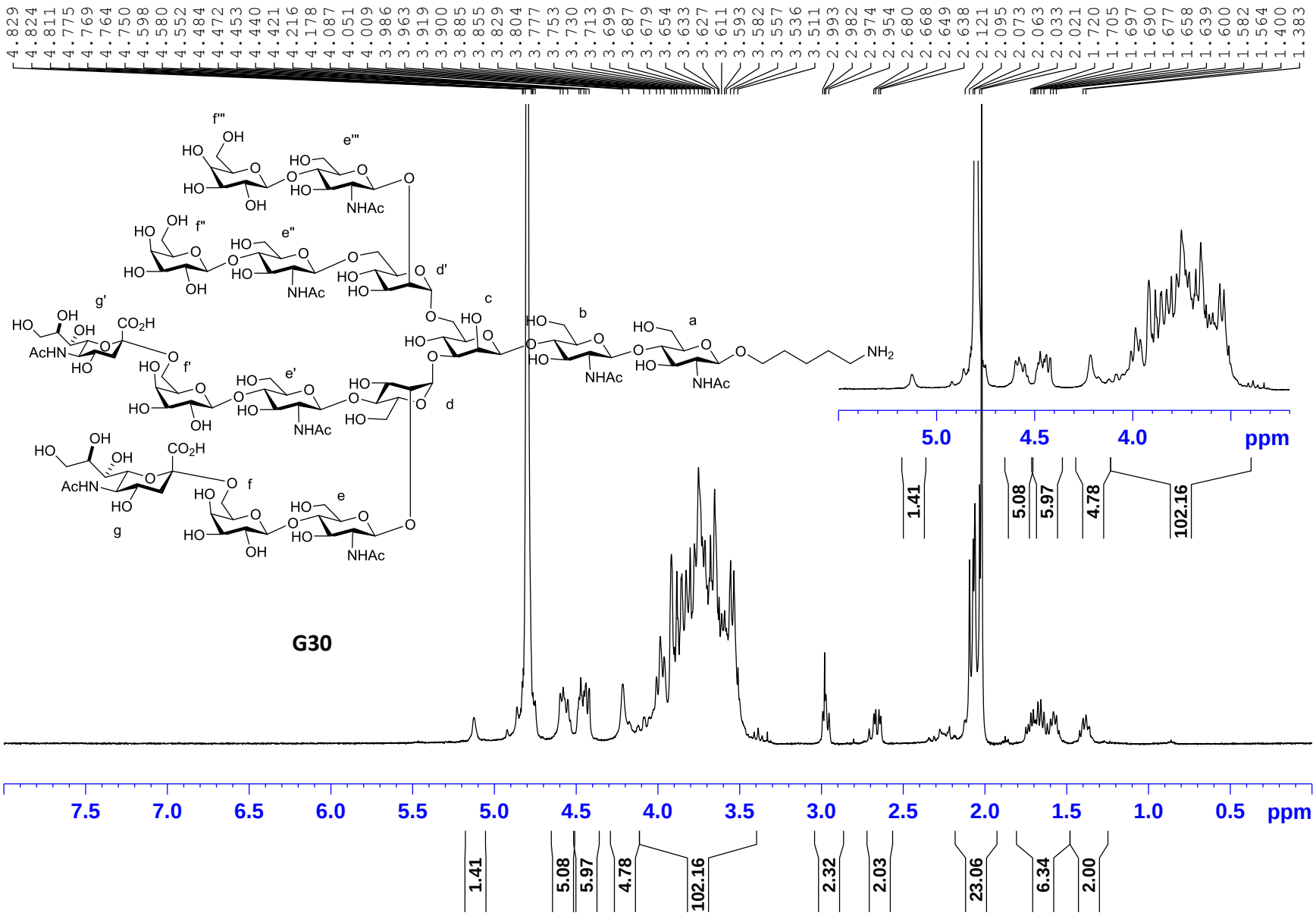

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

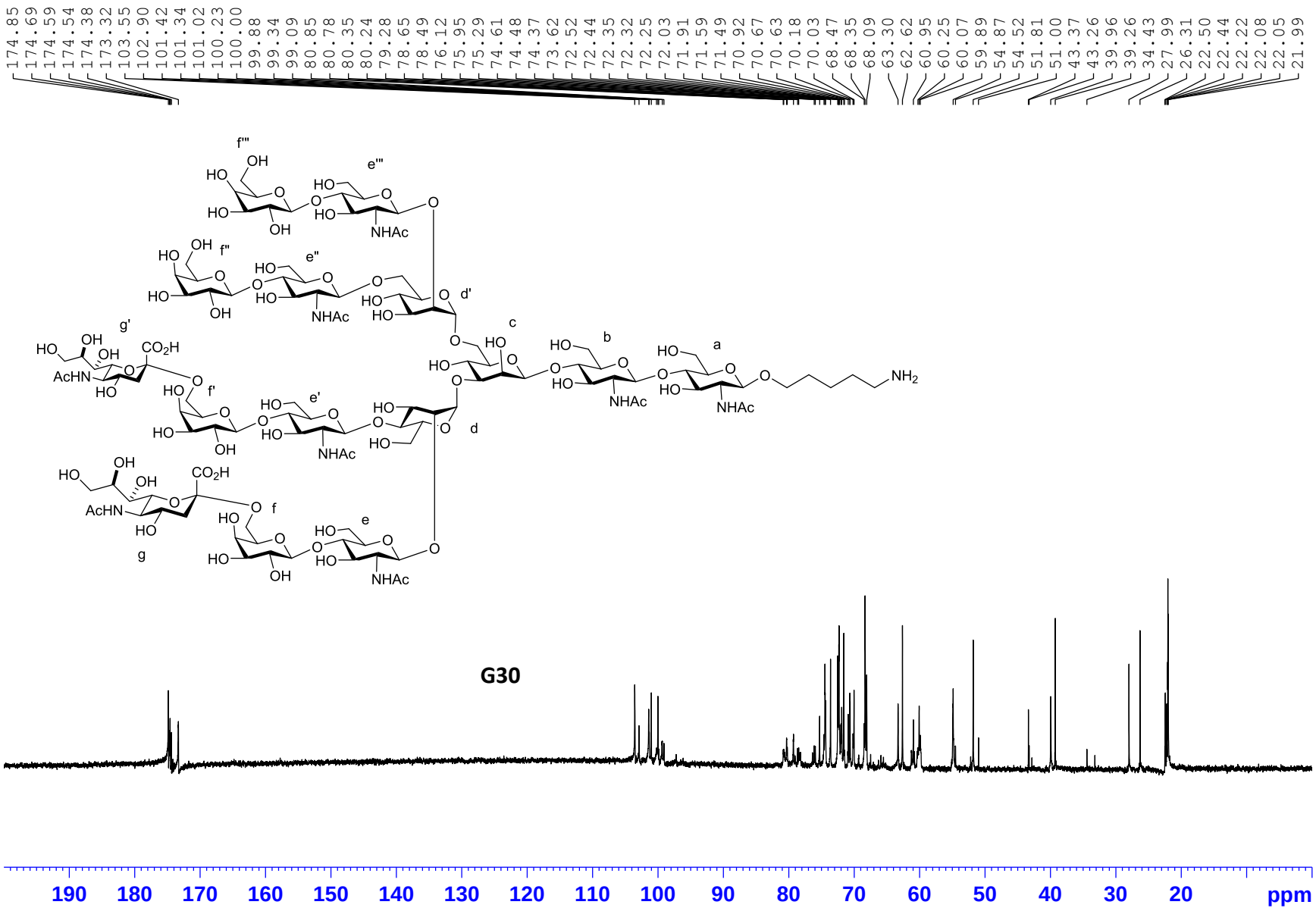

G25
ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

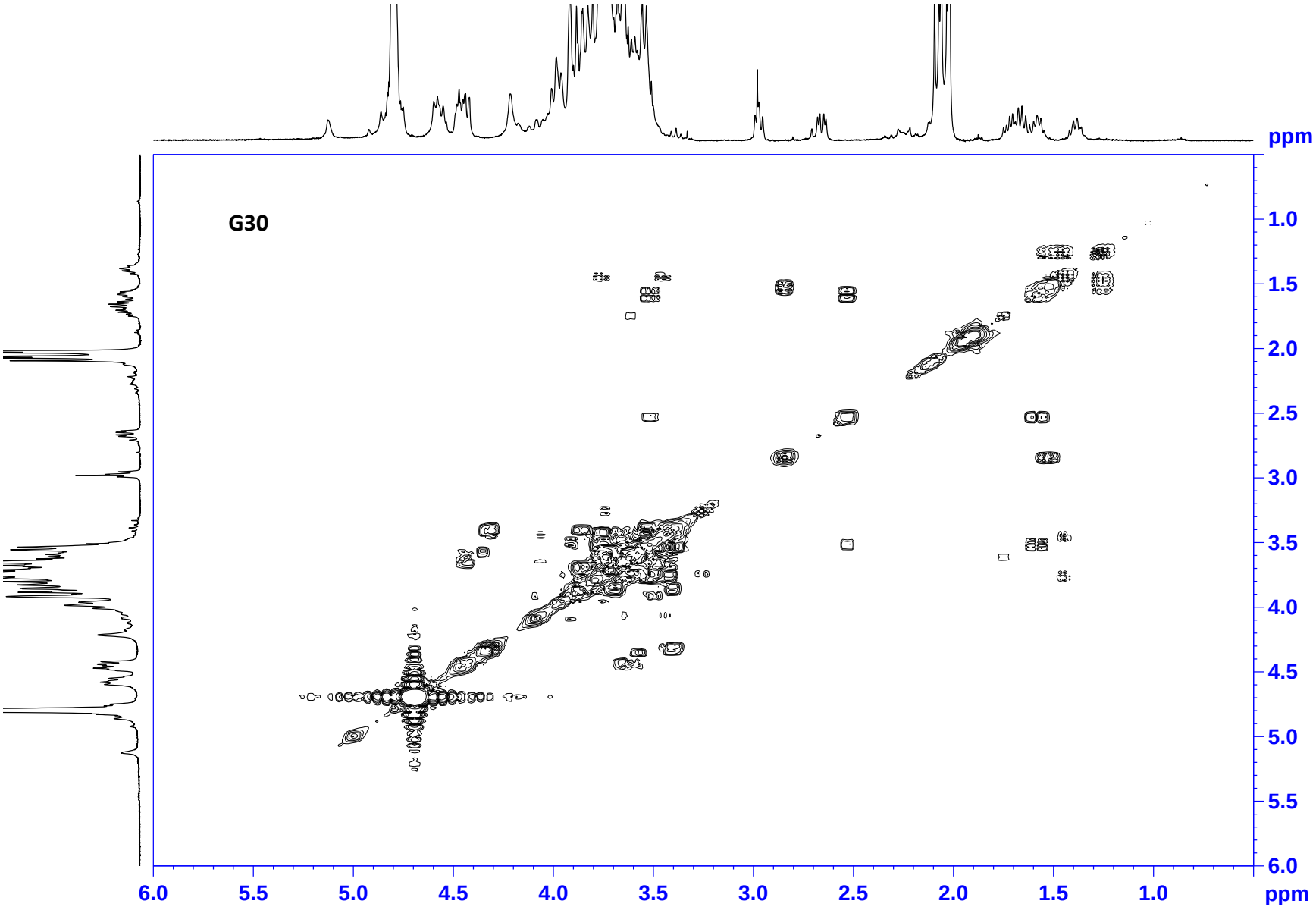

4.997
4.746
4.724
4.632
4.473
4.455
4.426
4.404
4.369
4.350
4.341
4.331
4.323
4.313
4.092
3.864
3.797
3.791
3.764
3.756
3.731
3.718
3.699
3.672
3.647
3.629
3.622
3.607
3.601
3.590
3.566
3.555
3.530
3.522
3.506
3.491
3.471
3.433
3.413
3.388
2.563
2.551
2.532
2.521
1.953
1.948
1.935
1.923
1.920
1.902
1.899
1.615
1.583
1.576
1.556
1.538
1.518
1.498
1.479
G29
5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 ppm
1.00 1.52 1.21 4.37 4.69 3.16 81.67
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
1.00 1.52 1.21 4.37 4.69 3.16 81.67 1.55 0.82 17.76 5.35 1.87

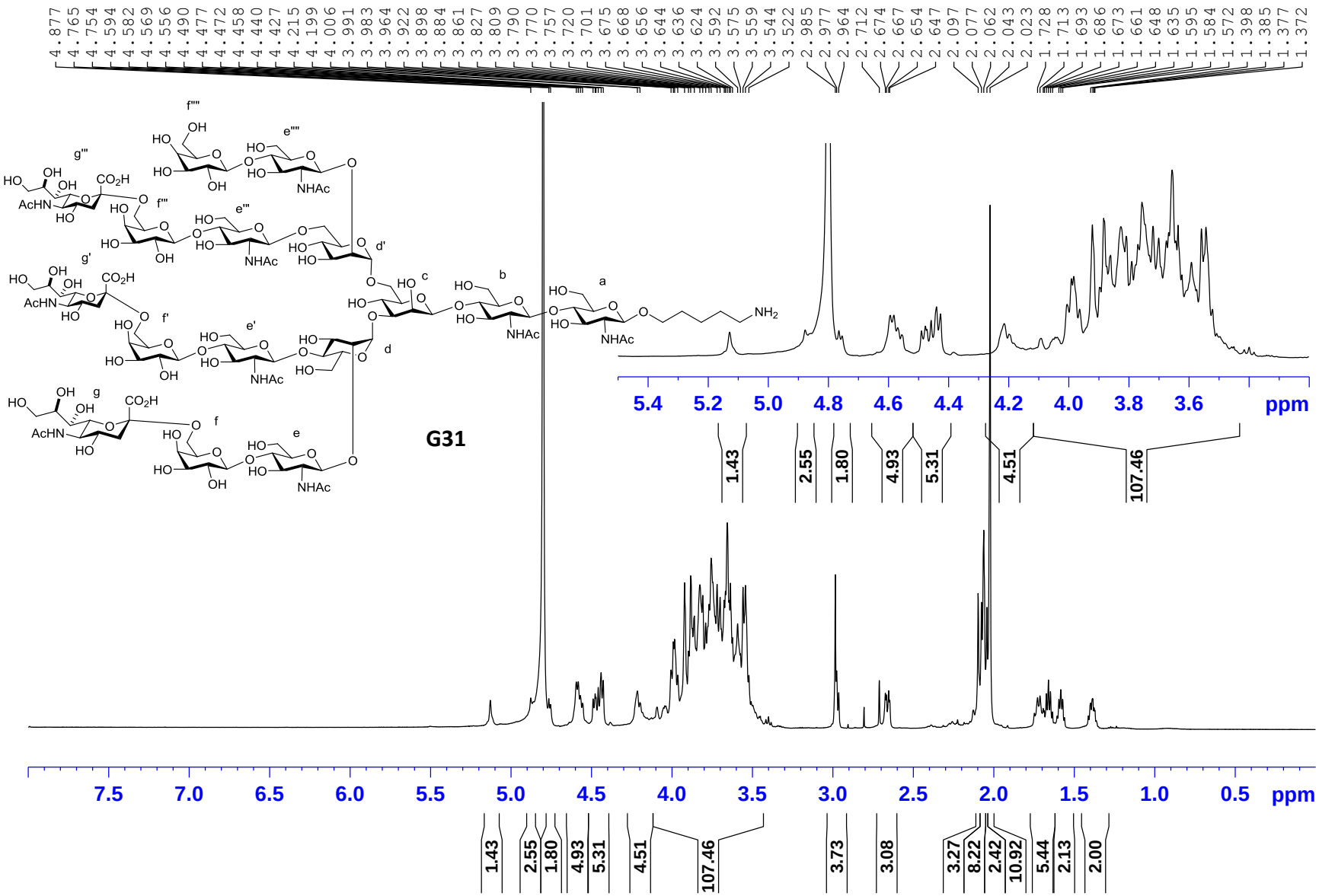

186.61
174.72
174.38
174.23
103.37
102.74
101.26
100.87
99.96
78.90
78.18
77.81
75.14
74.49
74.21
72.27
71.74
71.50
70.74
69.89
68.33
68.18
63.18
62.44
60.84
60.21
59.70
54.96
54.69
51.68
39.92
39.10
27.85
26.16
22.20
21.89
17.65
G29
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

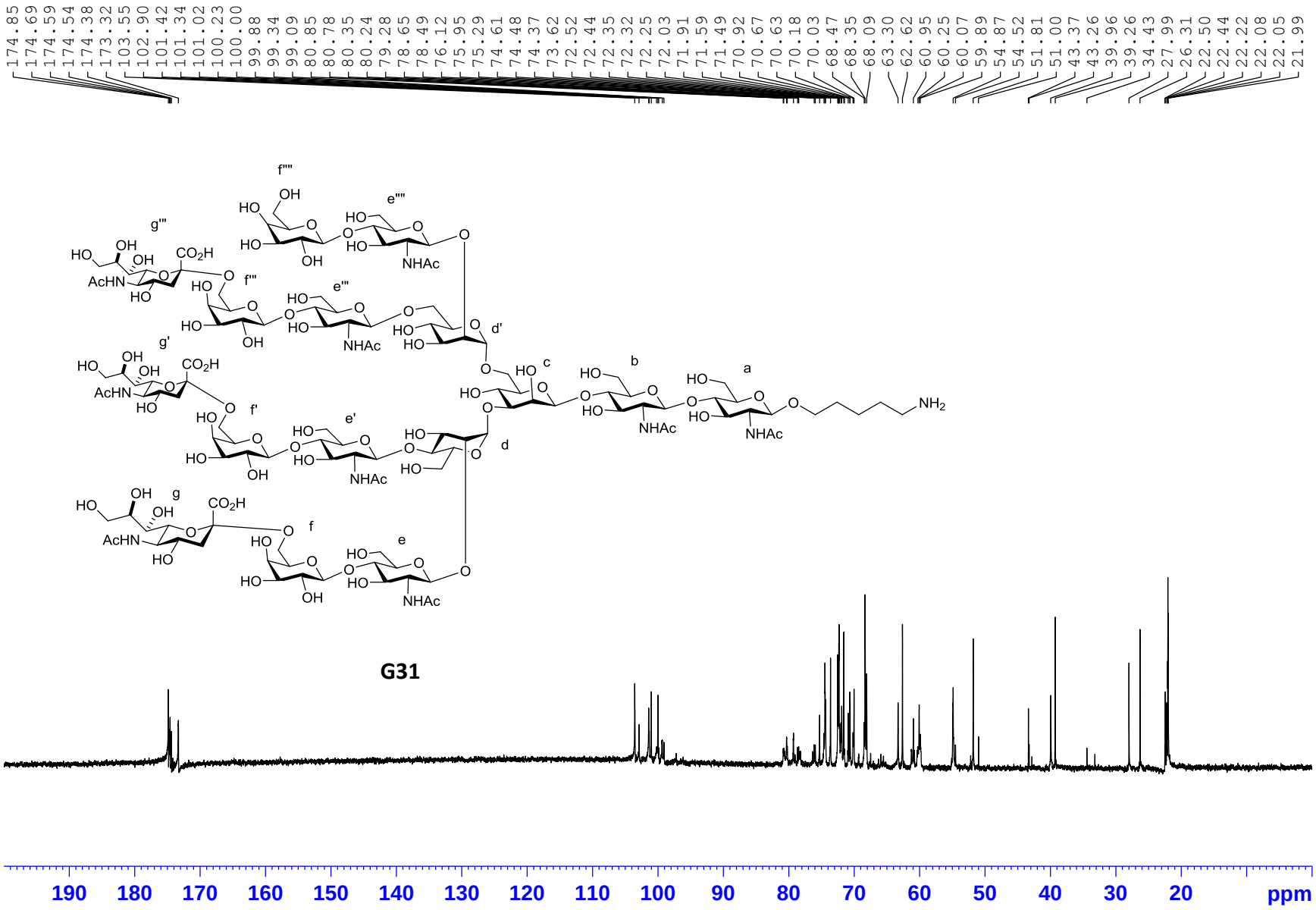

G29
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


4.829 4.824 4.811 4.775 4.769 4.764 4.750 4.598 4.580 4.552 4.484 4.472 4.453 4.440 4.421 4.216 4.178 4.087 4.051 4.009 3.986 3.963 3.919 3.900 3.885 3.855 3.829 3.804 3.777 3.753 3.730 3.713 3.699 3.687 3.679 3.654 3.633 3.627 3.611 3.593 3.582 3.557 3.536 3.511 2.993 2.982 2.974 2.954 2.680 2.668 2.649 2.638 2.121 2.095 2.073 2.063 2.033 2.021 1.720 1.705 1.697 1.690 1.677 1.658 1.639 1.600 1.582 1.564 1.400 1.383
G30
5.0 4.5 4.0 ppm
1.41 5.08 5.97 4.78 102.16
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
1.41 5.08 5.97 4.78 102.16 2.32 2.03 23.06 6.34 2.00


174.85
174.69
174.59
174.54
174.38
173.32
103.55
102.90
101.42
101.34
101.02
100.23
100.00
99.88
99.34
99.09
80.85
80.78
80.35
80.24
79.28
78.65
78.49
76.12
75.95
75.29
74.61
74.48
74.37
73.62
72.52
72.44
72.35
72.32
72.25
72.03
71.91
71.59
71.49
70.92
70.67
70.63
70.18
70.03
68.47
68.35
68.09
63.30
62.62
60.95
60.25
60.07
59.89
54.87
54.52
51.81
51.00
43.37
43.26
39.96
39.26
34.43
27.99
26.31
22.50
22.44
22.22
22.08
22.05
21.99
G30
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


G30
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


4.877 4.765 4.754 4.594 4.582 4.569 4.556 4.490 4.477 4.472 4.458 4.440 4.427 4.215 4.199 4.006 3.991 3.983 3.964 3.922 3.898 3.884 3.861 3.827 3.809 3.790 3.770 3.757 3.720 3.701 3.675 3.668 3.656 3.644 3.636 3.624 3.592 3.575 3.559 3.544 3.522 2.985 2.977 2.964 2.712 2.674 2.667 2.654 2.647 2.097 2.077 2.062 2.043 2.023 1.728 1.713 1.693 1.686 1.673 1.661 1.648 1.635 1.595 1.584 1.572 1.398 1.385 1.377 1.372
G31
5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 ppm
1.43 2.55 1.80 4.93 5.31 4.51 107.46
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
1.43 2.55 1.80 4.93 5.31 4.51 107.46 3.73 3.08 3.27 8.22 2.42 10.92 5.44 2.13 2.00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101.34
101.02
100.23
100.00
99.88
99.34
99.09
80.85
80.78
80.35
80.24
79.28
78.65
78.49
76.12
75.95
75.29
74.61
74.48
74.37
73.62
72.52
72.44
72.35
72.32
72.25
72.03
71.91
71.59
71.49
70.92
70.67
70.63
70.18
70.03
68.47
68.35
68.09
63.30
62.62
60.95
60.25
60.07
59.89
54.87
54.52
51.81
51.00
43.37
43.26
39.96
39.26
34.43
27.99
26.31
22.50
22.44
22.22
22.08
22.05
21.99
G31
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160
150
140
130
120
110
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80
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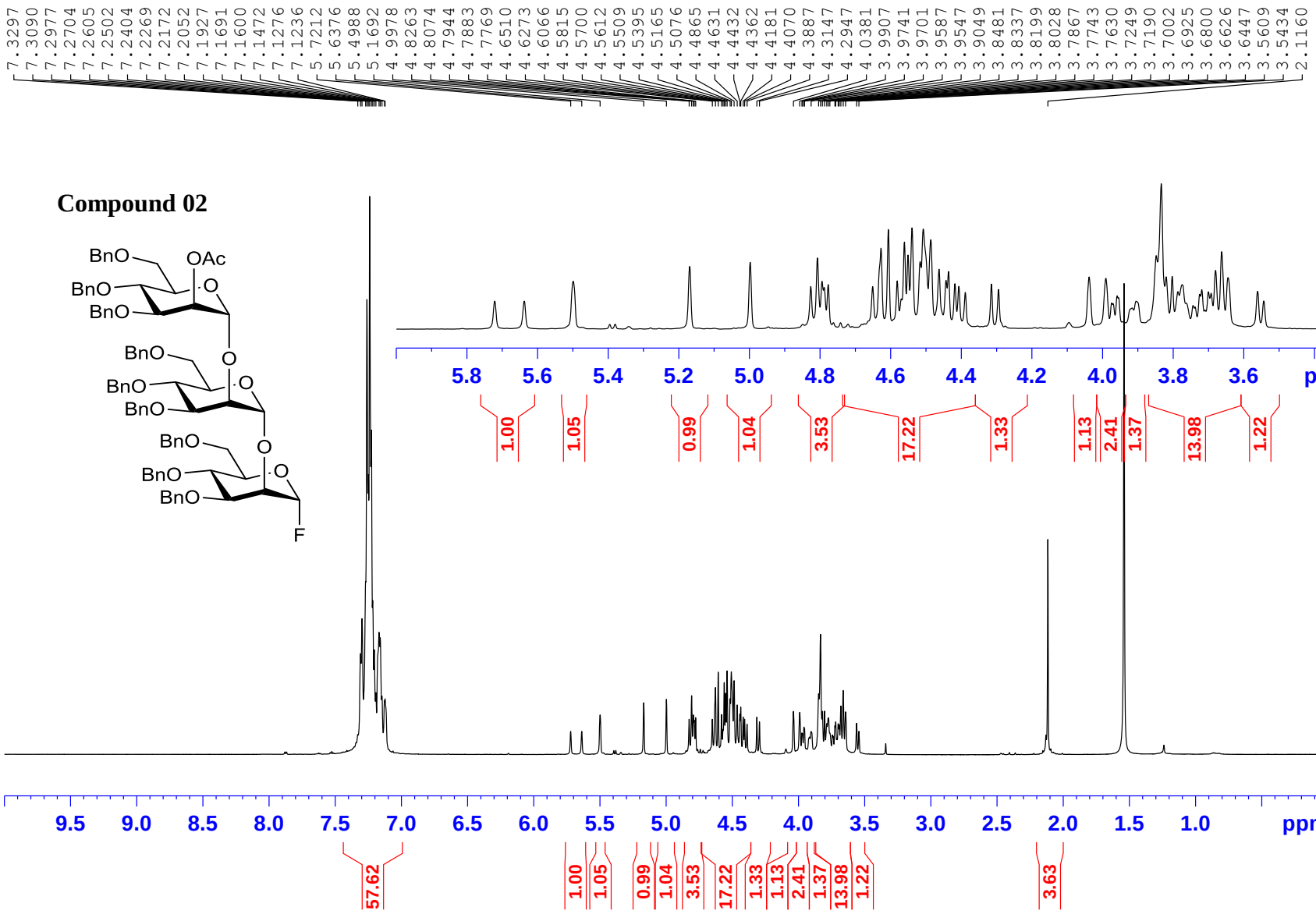
50
40
30
20
ppm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7.2404
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7.1927
7.1691
7.1600
7.1472
7.1276
7.1236
5.7212
5.6376
5.4988
5.1692
4.9978
4.8263
4.8074
4.7944
4.7883
4.7769
4.6510
4.6273
4.6066
4.5815
4.5700
4.5612
4.5509
4.5395
4.5165
4.5076
4.4865
4.4631
4.4432
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4.4181
4.4070
4.3887
4.3147
4.2947
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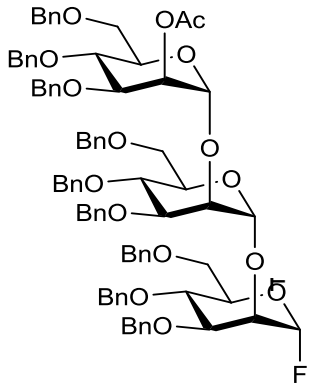
3.9907
3.9741
3.9701
3.9587
3.9547
3.9049
3.8481
3.8337
3.8199
3.8028
3.7867
3.7743
3.7630
3.7249
3.7190
3.7002
3.6925
3.6800
3.6626
3.6447
3.5609
3.5434
2.1160
Compound 02
BnO
OAc
BnO
BnO
O
BnO
BnO
BnO
O
BnO
BnO
BnO
O
F
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
ppm
1.00
1.05
0.99
1.04
3.53
17.22
1.33
1.13
2.41
1.37
13.98
1.22
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
ppm
57.62
1.00
1.05
0.99
1.04
3.53
17.22
1.33
1.13
2.41
1.37
13.98
1.22
3.63

Compound 02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OAc
BnO
O
BnO
BnO
O
BnO
BnO
BnO
O
BnO
BnO
BnO
O
F

170.44
138.78
138.65
138.60
138.55
138.46
138.41
138.28
128.77
128.64
128.61
128.54
128.45
128.32
128.20
128.13
128.09
128.04
128.01
127.95
127.91
127.87
127.84
127.80
127.73
107.66
106.19
101.05
99.73
78.56
78.37
75.46
75.42
75.31
74.87
74.59
74.31
74.11
73.86
73.69
73.65
73.58
72.70
72.49
72.39
72.17
69.51
69.32
69.02
68.95
21.45
105
100
95
ppm
190
180
170
160
150
140
130
120
110
100
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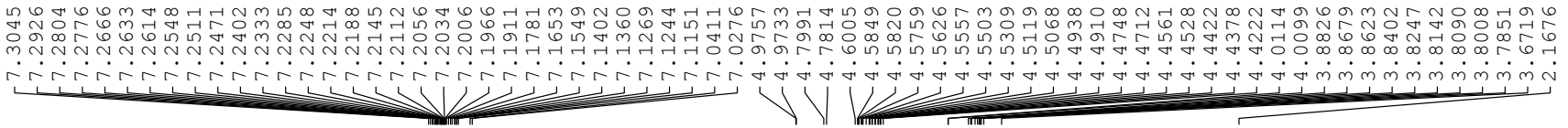
80
70
60
50
40
30
20
ppm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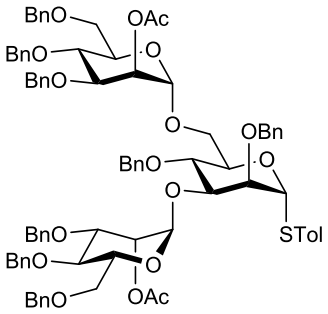
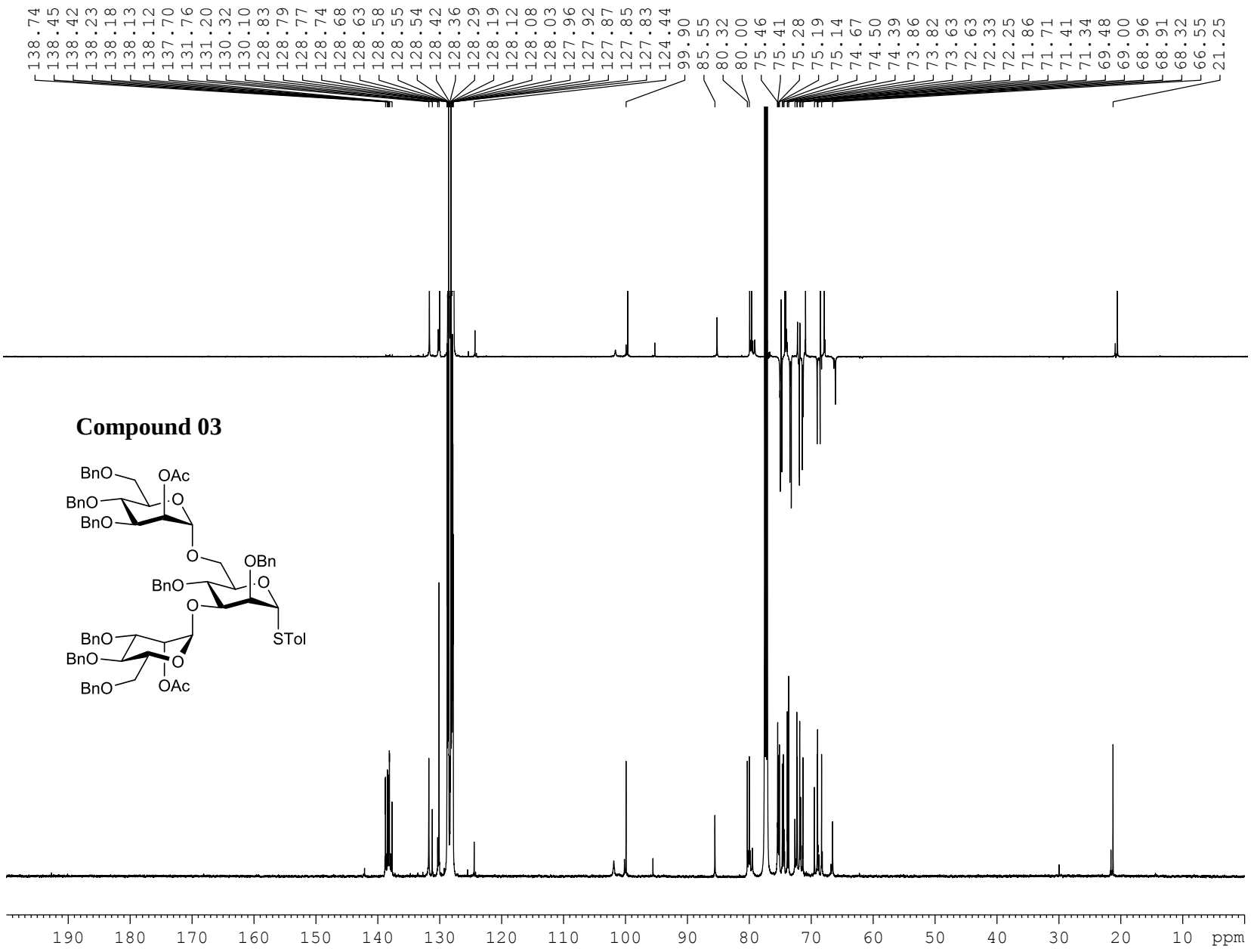
7.2633
7.2614
7.2548
7.2511
7.2471
7.2402
7.2333
7.2285
7.2248
7.2214
7.2188
7.2145
7.2112
7.2056
7.2034
7.2006
7.1966
7.1911
7.1781
7.1653
7.1549
7.1402
7.1360
7.1269
7.1244
7.1151
7.0411
7.0276
4.9757
4.9733
4.7991
4.7814
4.6005
4.5849
4.5820
4.5759
4.5626
4.5557
4.5503
4.5309
4.5119
4.5068
4.4938
4.4910
4.4748
4.4712
4.4561
4.4528
4.4422
4.4378
4.4222
4.0114
4.0099
3.8826
3.8679
3.8623
3.8402
3.8247
3.8142
3.8090
3.8008
3.7851
3.6719
2.1676

Compound 03


BnO
OAc
BnO
BnO
O
O
OBn
BnO
O
O
STol
BnO
BnO
O
BnO
OAc

5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
ppm
1.00
0.99
1.09
2.60
1.57
19.94
1.38
1.27
4.52
12.38
8.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
63.23
3.36
1.00
0.99
1.09
2.60
1.57
19.94
1.38
1.27
4.52
12.38
8.00
3.50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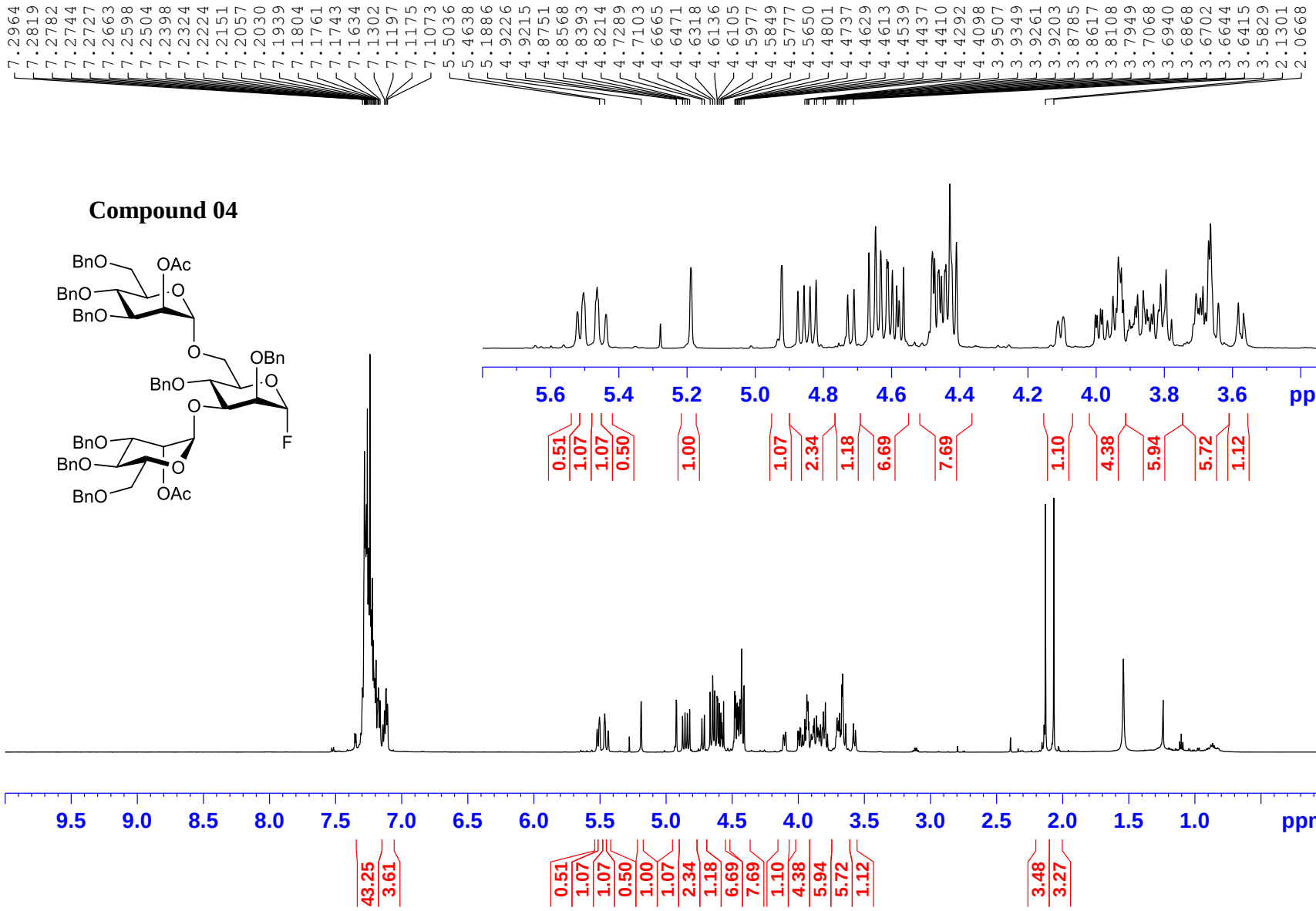
130.32
130.10
128.83
128.79
128.77
128.74
128.68
128.63
128.58
128.55
128.54
128.42
128.36
128.29
128.19
128.12
128.08
128.03
127.96
127.92
127.87
127.85
127.83
124.44
99.90
85.55
80.32
80.00
75.46
75.41
75.28
75.19
75.14
74.67
74.50
74.39
73.86
73.82
73.63
72.63
72.33
72.25
71.86
71.71
71.41
71.34
69.48
69.00
68.96
68.91
68.32
66.55
21.25
Compound 03
BnO
OAc
BnO
BnO
O
O
OBn
BnO
O
STol
BnO
BnO
O
BnO
OAc
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.2598
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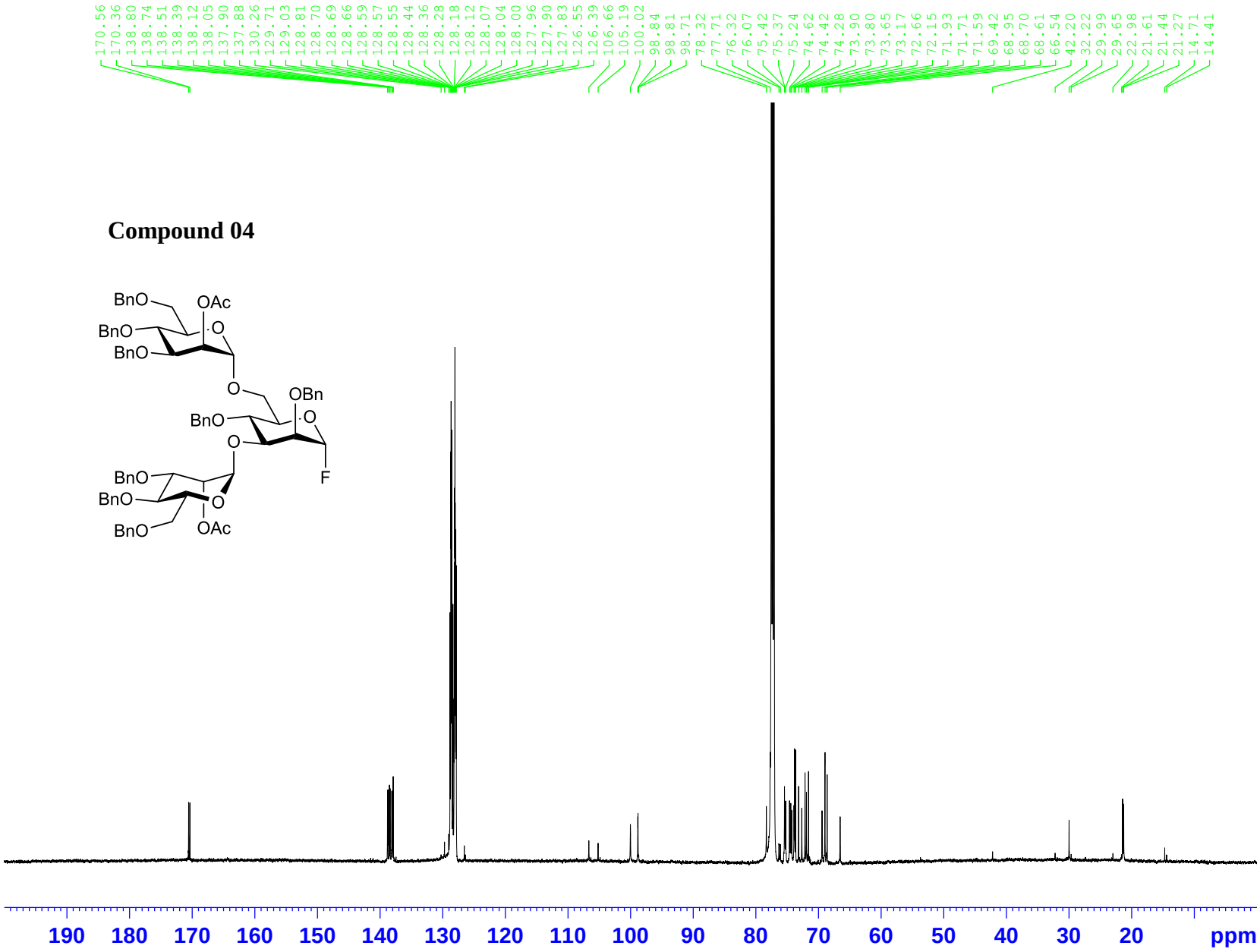
7.2398
7.2324
7.2224
7.2151
7.2057
7.2030
7.1939
7.1804
7.1761
7.1743
7.1634
7.1302
7.1197
7.1175
7.1073
5.5036
5.4638
5.1886
4.9226
4.9215
4.8751
4.8568
4.8393
4.8214
4.7289
4.7103
4.6665
4.6471
4.6318
4.6136
4.6105
4.5977
4.5849
4.5777
4.5650
4.4801
4.4737
4.4629
4.4613
4.4539
4.4437
4.4410
4.4292
4.4098
3.9507
3.9349
3.9261
3.9203
3.8785
3.8617
3.8108
3.7949
3.7068
3.6940
3.6868
3.6702
3.6644
3.6415
3.5829
2.1301
2.0668
Compound 04
BnO
OAc
BnO
BnO
O
OBn
BnO
O
O
F
BnO
BnO
O
BnO
OAc
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
ppm
0.51
1.07
1.07
0.50
1.00
1.07
2.34
1.18
6.69
7.69
1.10
4.38
5.94
5.72
1.12
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
ppm
43.25
3.61
0.51
1.07
1.07
0.50
1.00
1.07
2.34
1.18
6.69
7.69
1.10
4.38
5.94
5.72
1.12
3.48
3.27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137.88
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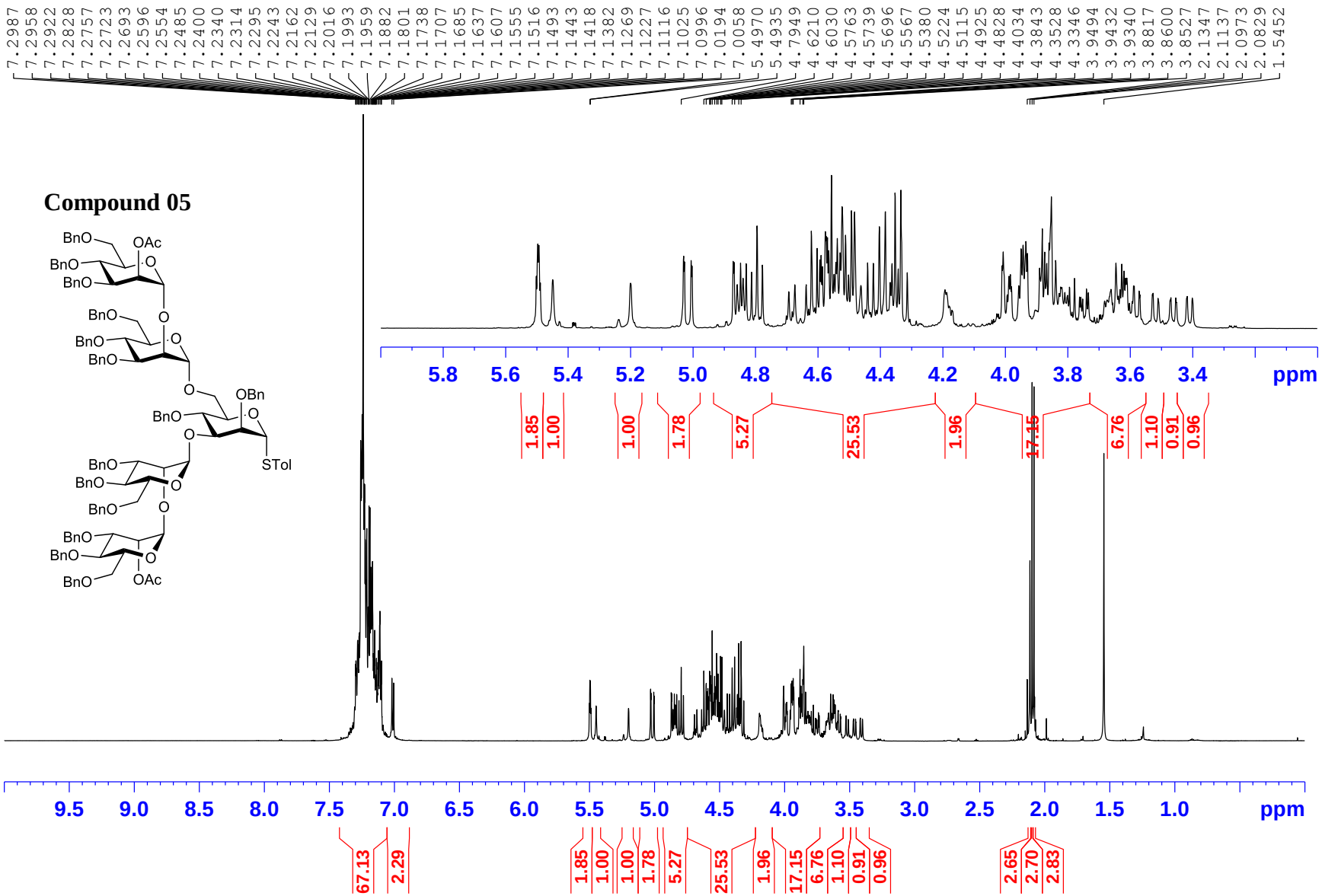
129.71
129.03
128.81
128.70
128.69
128.66
128.59
128.57
128.55
128.44
128.36
128.28
128.18
128.12
128.07
128.04
128.00
127.96
127.90
127.83
126.55
126.39
106.66
105.19
100.02
98.84
98.81
98.71
78.32
77.71
76.32
76.07
75.42
75.37
75.24
74.62
74.42
74.28
73.90
73.80
73.65
73.17
72.66
72.15
71.93
71.71
71.59
69.42
68.95
68.70
68.61
66.54
42.20
32.22
29.99
29.65
22.98
21.61
21.44
21.27
14.71
14.41
Compound 04
BnO
OAc
O
BnO
BnO
O
OBn
BnO
O
O
F
BnO
BnO
O
BnO
OAc
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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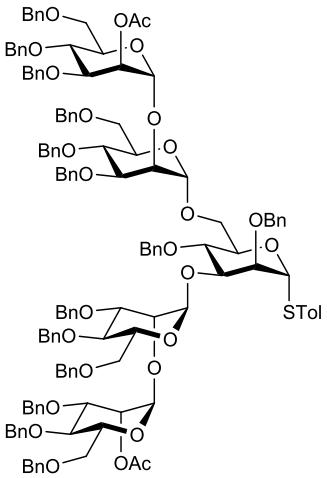
7.2400
7.2340
7.2314
7.2295
7.2243
7.2162
7.2129
7.2016
7.1993
7.1959
7.1882
7.1801
7.1738
7.1707
7.1685
7.1637
7.1607
7.1555
7.1516
7.1493
7.1443
7.1418
7.1382
7.1269
7.1227
7.1116
7.1025
7.0996
7.0194
7.0058
5.4970
5.4935
4.7949
4.6210
4.6030
4.5763
4.5739
4.5696
4.5567
4.5380
4.5224
4.5115
4.4925
4.4828
4.4034
4.3843
4.3528
4.3346
3.9494
3.9432
3.9340
3.8817
3.8600
3.8527
2.1347
2.1137
2.0973
2.0829
1.5452
Compound 05
BnO
OAc
O
BnO
BnO
BnO
O
BnO
O
BnO
O
OBn
BnO
O
STol
BnO
BnO
O
BnO
O
BnO
BnO
O
BnO
OAc
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
ppm
1.85
1.00
1.00
1.78
5.27
25.53
1.96
17.15
6.76
1.10
0.91
0.96
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
ppm
67.13
2.29
1.85
1.00
1.00
1.78
5.27
25.53
1.96
17.15
6.76
1.10
0.91
0.96
2.65
2.70
2.83

Compound 05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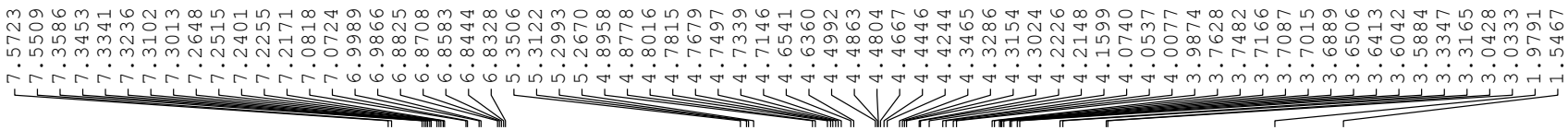
OAc
O
BnO
BnO
BnO
O
BnO
O
BnO
O
OBn
BnO
O
STol
BnO
BnO
O
BnO
O
BnO
BnO
O
BnO
OAc

170.34
138.85
138.83
138.79
138.69
138.64
138.52
138.49
138.44
138.40
138.27
138.20
137.54
131.54
131.45
130.06
128.69
128.63
128.55
128.54
128.51
128.49
128.46
128.43
128.38
128.31
128.27
128.22
128.16
128.10
127.99
127.95
127.91
127.87
127.85
127.81
127.80
127.74
127.72
127.66
127.59
127.55
127.32
99.72
99.63
99.26
85.44
79.53
78.37
78.31
77.81
75.44
75.23
75.14
75.01
74.96
74.90
74.85
74.73
74.42
74.32
73.70
73.52
73.33
72.98
72.29
72.22
72.12
72.10
72.05
71.98
71.81
71.40
69.83
69.15
69.01
68.96
68.91
68.62
21.37
21.13
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.3236
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7.2648
7.2515
7.2401
7.2255
7.2171
7.0818
7.0724
6.9989
6.9866
6.8825
6.8708
6.8583
6.8444
6.8328
5.3506
5.3122
5.2993
5.2670
4.8958
4.8778
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4.7815
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4.7497
4.7339
4.7146
4.6541
4.6360
4.4992
4.4863
4.4804
4.4667
4.4446
4.4244
4.3465
4.3286
4.3154
4.3024
4.2226
4.2148
4.1599
4.0740
4.0537
4.0077
3.9874
3.7628
3.7482
3.7166
3.7087
3.7015
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3.6506
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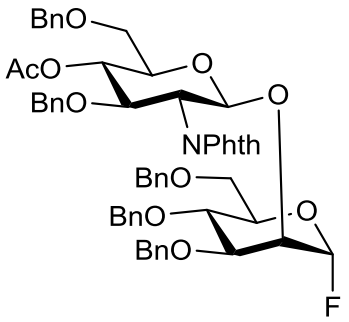
3.0428
3.0333
1.9791
1.5467

Compound 06


BnO
AcO
BnO
O
O
NPhth
BnO
BnO
BnO
O
F

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5.0
4.5
4.0
3.5
3.0
ppm
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0.90
0.50
0.92
2.85
0.97
1.82
1.02
2.88
0.97
0.92
0.95
0.94
3.81
0.95
0.91
0.89
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
1.5
1.0
ppm
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16.63
3.86
1.94
2.83
0.48
0.90
0.50
0.92
2.85
0.97
1.82
1.02
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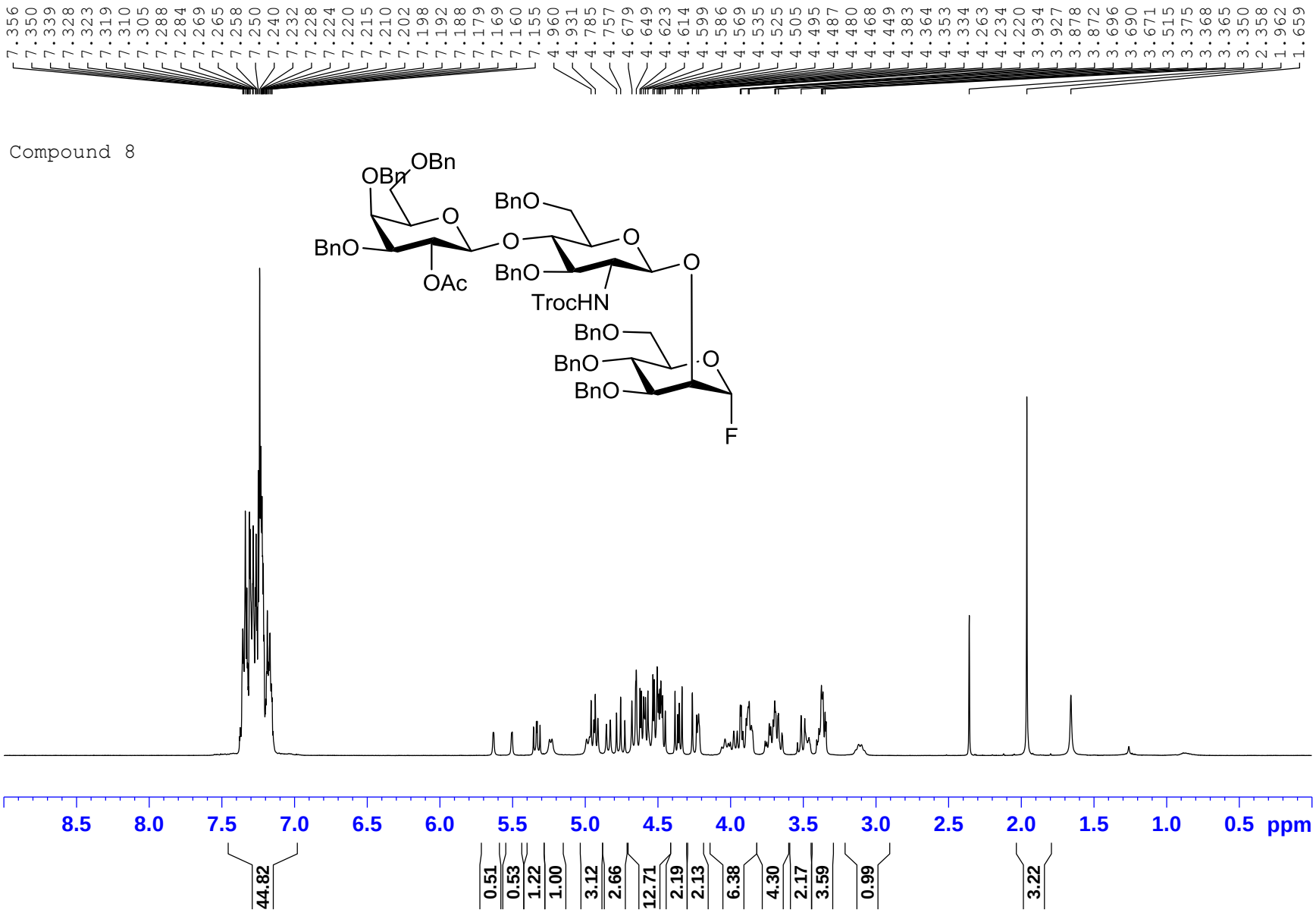
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7.188
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7.155
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4.614
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3.927
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3.872
3.696
3.690
3.671
3.515
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3.368
3.365
3.350
2.358
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1.659
Compound 8
OBn
OBn
O
BnO
O
OAc
BnO
O
BnO
O
BnO
TrocHN
BnO
O
BnO
BnO
F
8.5
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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
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0.53
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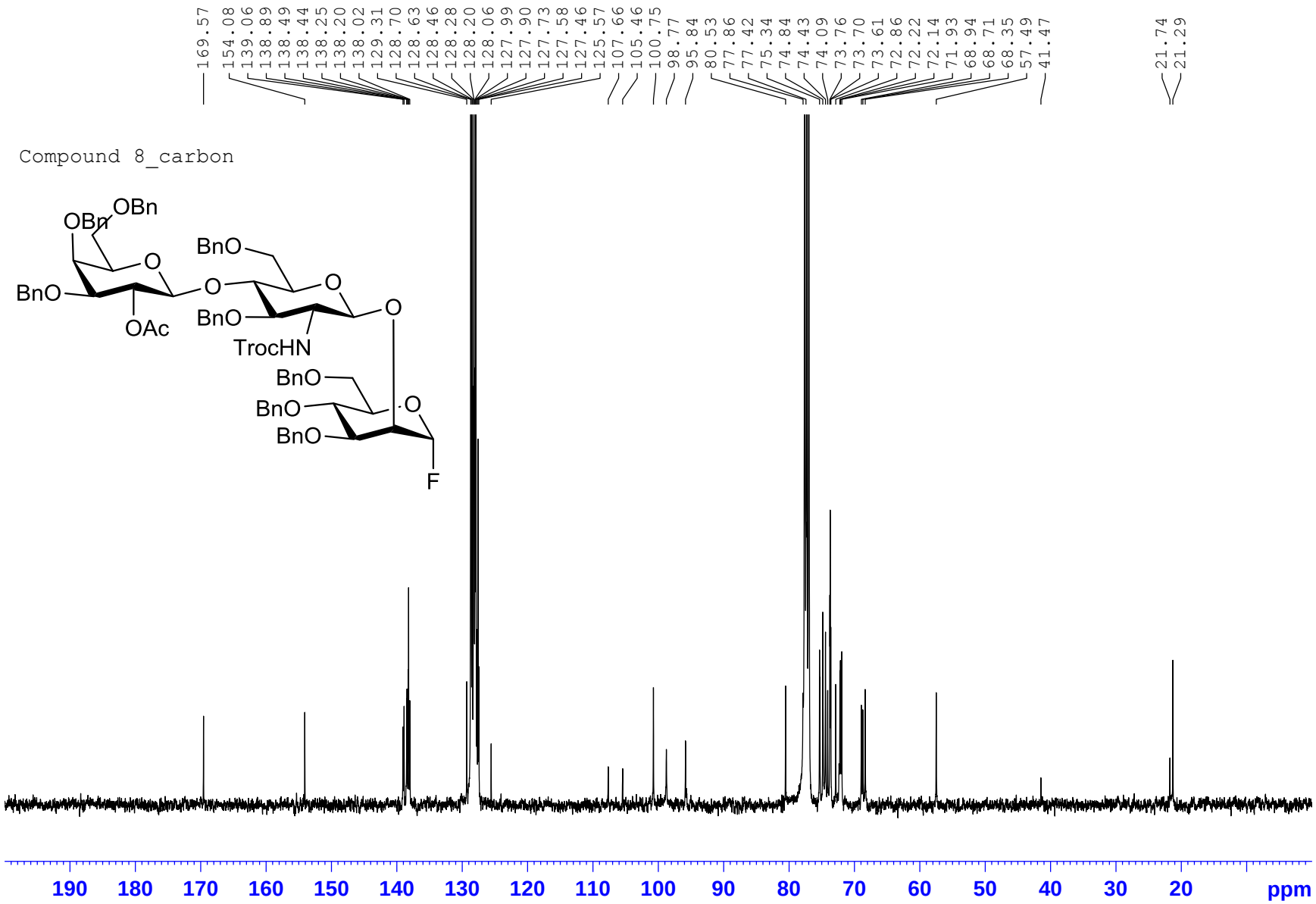
3.22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127.58
127.46
125.57
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105.46
100.75
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80.53
77.86
77.42
75.34
74.84
74.43
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73.70
73.61
72.86
72.22
72.14
71.93
68.94
68.71
68.35
57.49
41.47
21.74
21.29
Compound 8_carbon
OBn
OBn
BnO
O
O
BnO
OAc
BnO
O
O
BnO
TrocHN
O
BnO
BnO
O
BnO
F
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160
150
140
130
120
110
100
90
80
70
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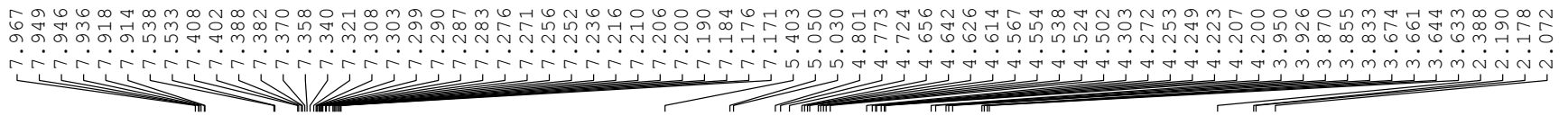
30
20
ppm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7.283
7.276
7.271
7.256
7.252
7.236
7.216
7.210
7.206
7.200
7.190
7.184
7.176
7.171
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5.050
5.030
4.801
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4.724
4.656
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4.626
4.614
4.567
4.554
4.538
4.524
4.502
4.303
4.272
4.253
4.249
4.223
4.207
4.200
3.950
3.926
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3.833
3.674
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3.633
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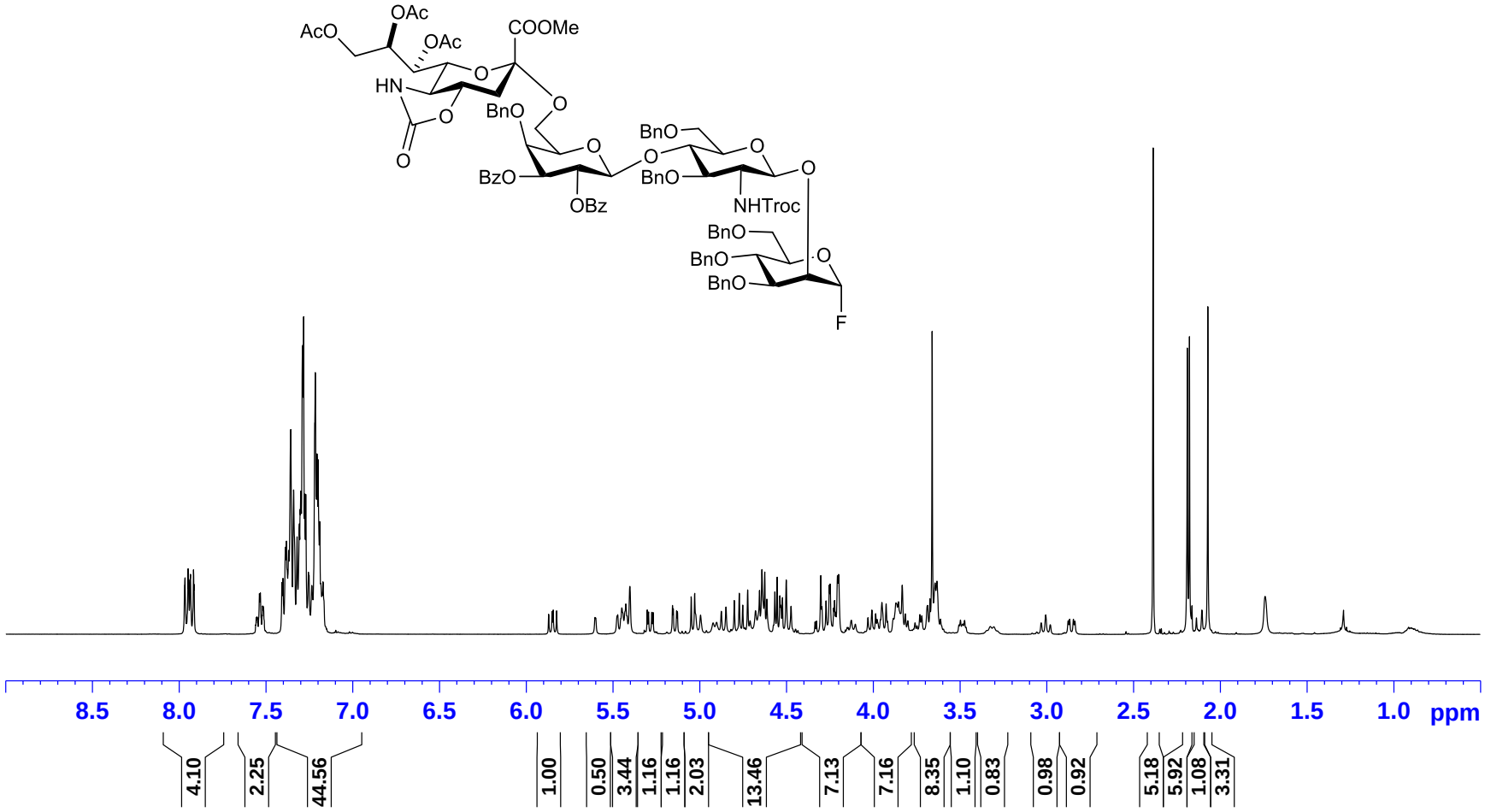
2.190
2.178
2.072

Compound 9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OAc
OAc
COOMe
HN
O
BnO
BzO
OBz
NHTroc
F
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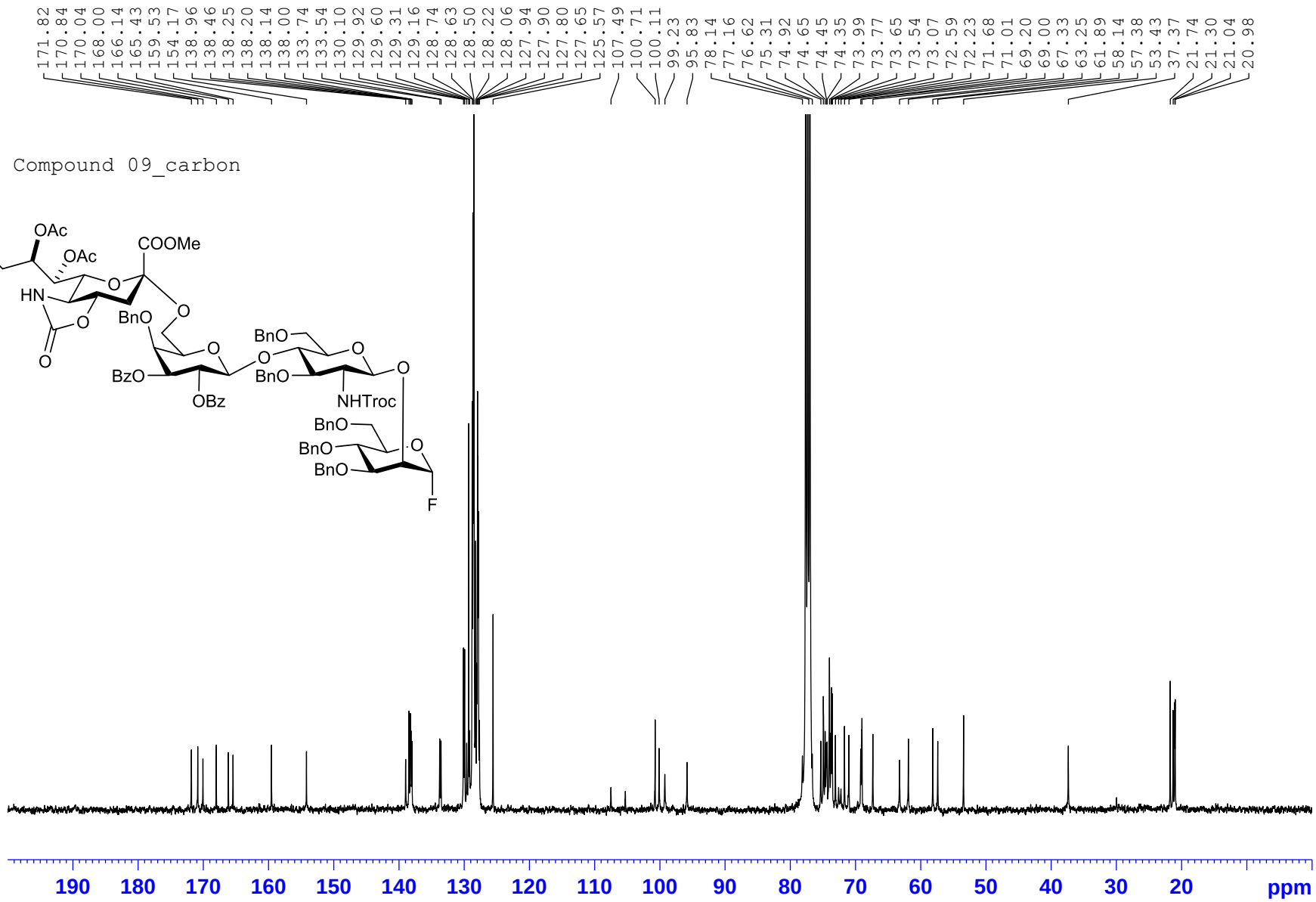
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
4.10
2.25
44.56
1.00
0.50
3.44
1.16
1.16
2.03
13.46
7.13
7.16
8.35
1.10
0.83
0.98
0.92
5.18
5.92
1.08
3.31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133.54
130.10
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129.60
129.31
129.16
128.74
128.63
128.50
128.22
128.06
127.94
127.90
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127.65
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95.83
78.14
77.16
76.62
75.31
74.92
74.65
74.45
74.35
73.99
73.77
73.65
73.54
73.07
72.59
72.23
71.68
71.01
69.20
69.00
67.33
63.25
61.89
58.14
57.38
53.43
37.37
21.74
21.30
21.04
20.98
Compound 09_carbon
AcO
OAc
OAc
COOMe
HN
O
BnO
BzO
OBz
NHTroc
F
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180
170
160
150
140
130
120
110
100
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80
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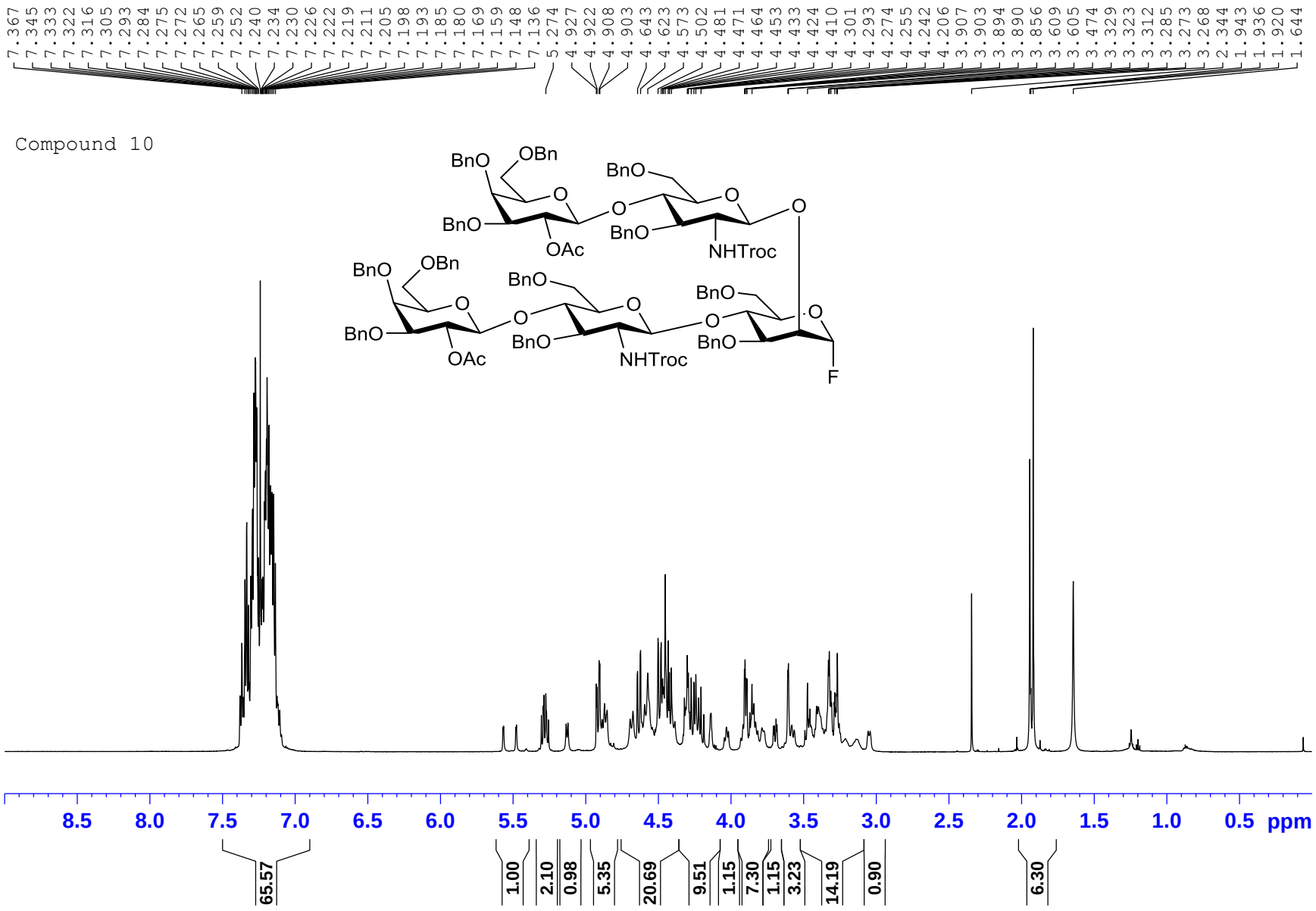
50
40
30
20
ppm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7.259
7.252
7.240
7.234
7.230
7.226
7.222
7.219
7.211
7.205
7.198
7.193
7.185
7.180
7.169
7.159
7.148
7.136
5.274
4.927
4.922
4.908
4.903
4.643
4.623
4.573
4.502
4.481
4.471
4.464
4.453
4.433
4.424
4.410
4.301
4.293
4.274
4.255
4.242
4.206
3.907
3.903
3.894
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3.605
3.474
3.329
3.323
3.312
3.285
3.273
3.268
2.344
1.943
1.936
1.920
1.644
Compound 10
BnO
OBn
O
BnO
OAc
BnO
O
BnO
O
NHTroc
O
BnO
OBn
O
BnO
OAc
BnO
O
BnO
NHTroc
BnO
O
BnO
O
F
8.5
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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
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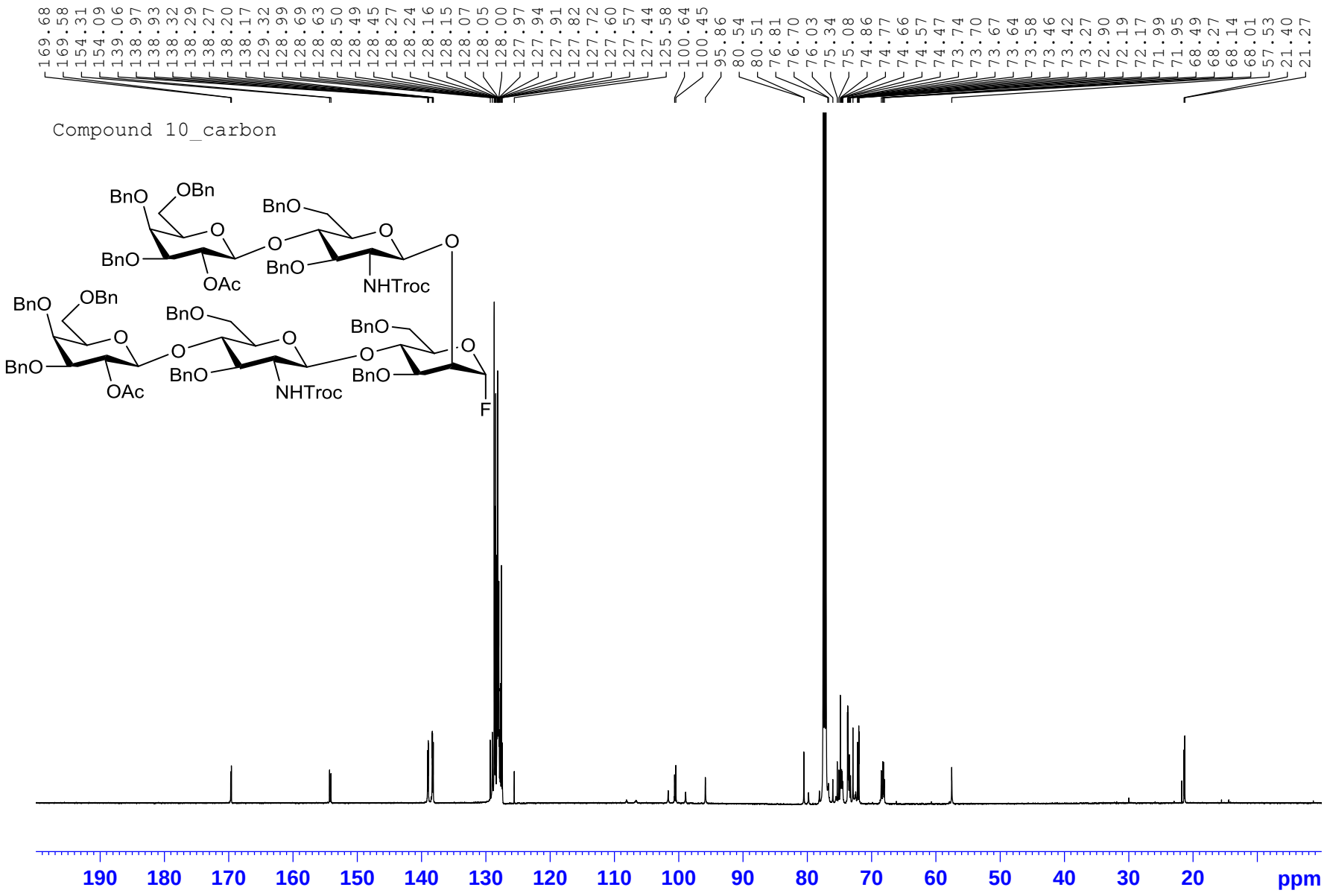
6.30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128.07
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127.94
127.91
127.82
127.72
127.60
127.57
127.44
125.58
100.64
100.45
95.86
80.54
80.51
76.81
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76.03
75.34
75.08
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74.57
74.47
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72.90
72.19
72.17
71.99
71.95
68.49
68.27
68.14
68.01
57.53
21.40
21.27
Compound 10_carbon
BnO
OBn
O
BnO
OAc
O
BnO
O
BnO
NHTroc
O
F
190
180
170
160
150
140
130
120
110
100
90
80
70
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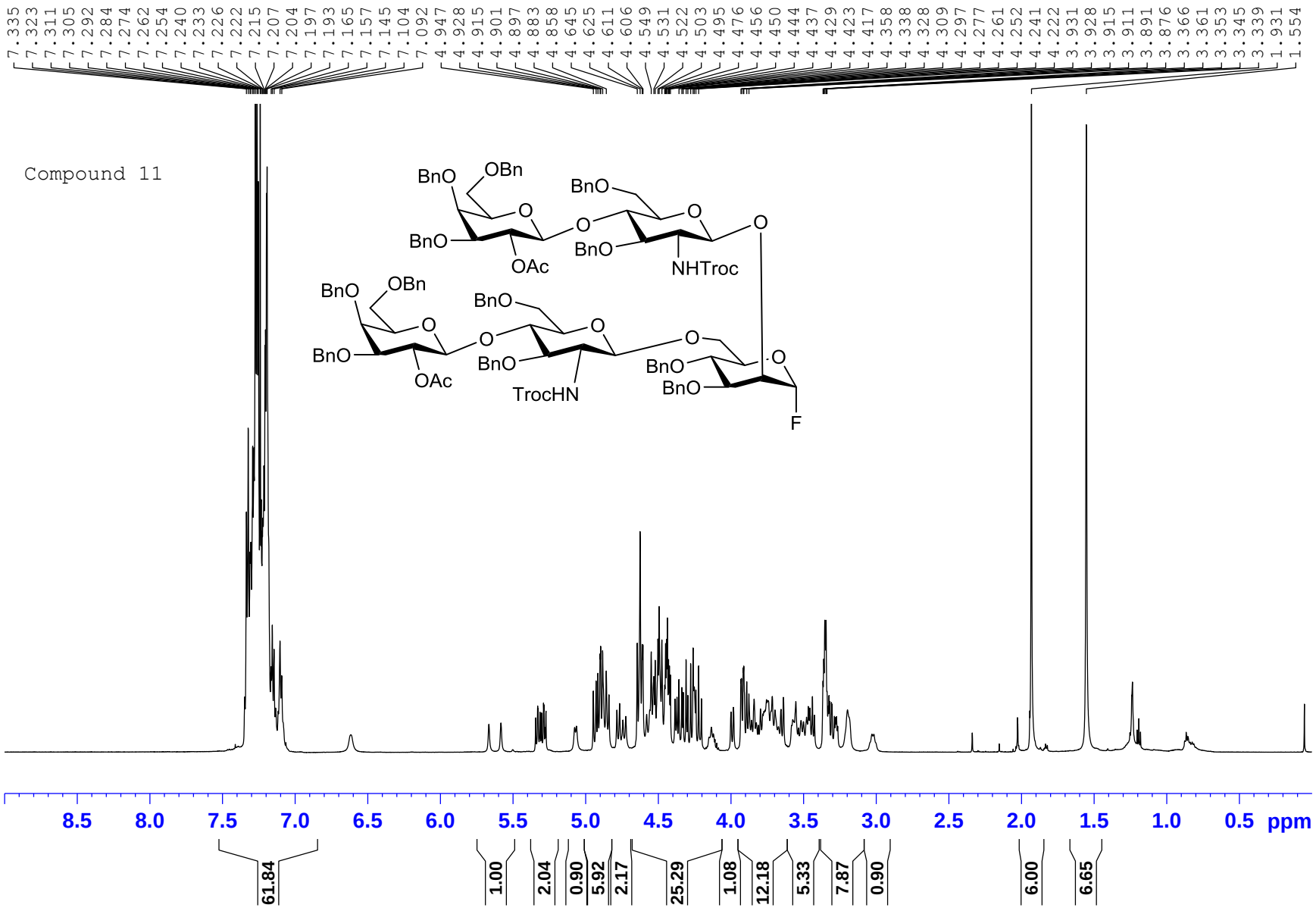
50
40
30
20
ppm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7.215
7.207
7.204
7.197
7.193
7.165
7.157
7.145
7.104
7.092
4.947
4.928
4.915
4.901
4.897
4.883
4.858
4.645
4.625
4.611
4.606
4.549
4.531
4.522
4.503
4.495
4.476
4.456
4.450
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4.423
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4.261
4.252
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4.222
3.931
3.928
3.915
3.911
3.891
3.876
3.366
3.361
3.353
3.345
3.339
1.931
1.554
Compound 11
BnO
OBn
O
BnO
OAc
BnO
O
O
BnO
O
BnO
NHTroc
O
BnO
OBn
O
BnO
OAc
BnO
O
O
BnO
TrocHN
O
BnO
O
BnO
BnO
O
F
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
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2.17
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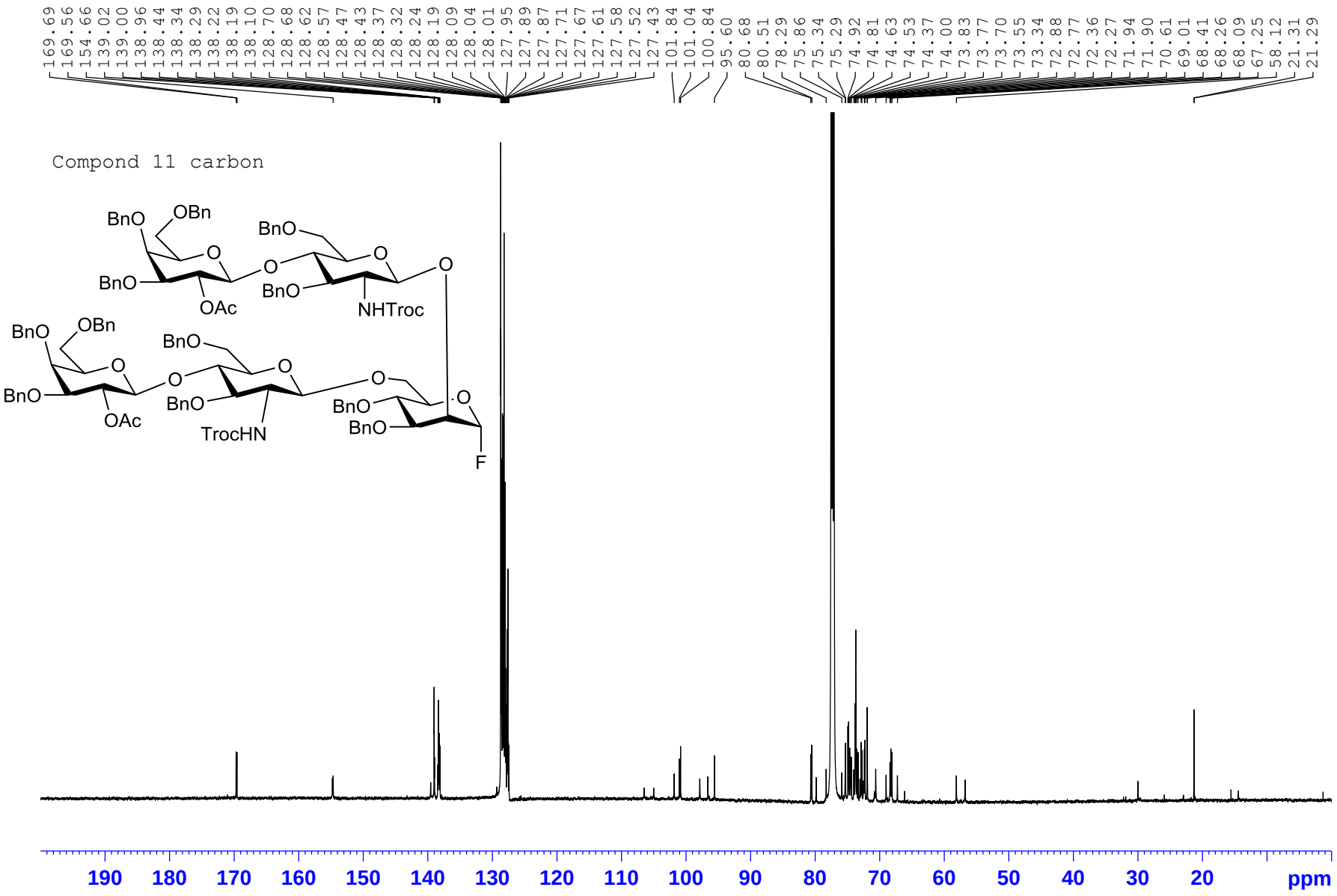
6.65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74.00
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73.70
73.55
73.34
72.88
72.77
72.36
72.27
71.94
71.90
70.61
69.01
68.41
68.26
68.09
67.25
58.12
21.31
21.29
Compond 11 carbon
BnO
OBn
O
BnO
OAc
O
BnO
BnO
O
BnO
NHTroc
O
BnO
OBn
O
BnO
OAc
O
BnO
BnO
TrocHN
O
O
BnO
BnO
O
F
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160
150
140
130
120
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80
70
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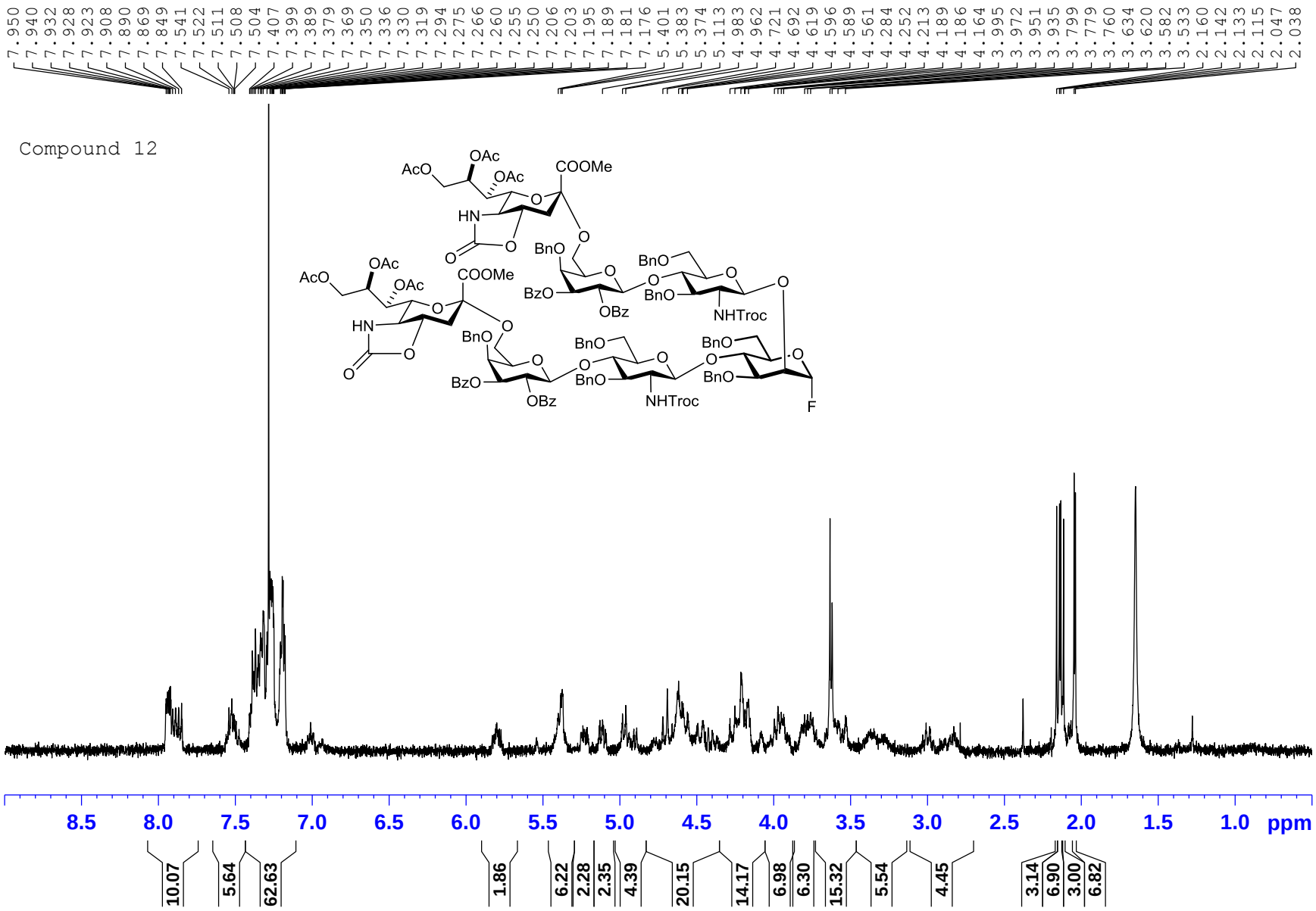
50
40
30
20
ppm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3.799
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2.047
2.038
Compound 12
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OAc
OAc
COOMe
HN
O
BnO
BzO
OBz
NHTroc
F
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8.0
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
ppm
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1.86
6.22
2.28
2.35
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15.32
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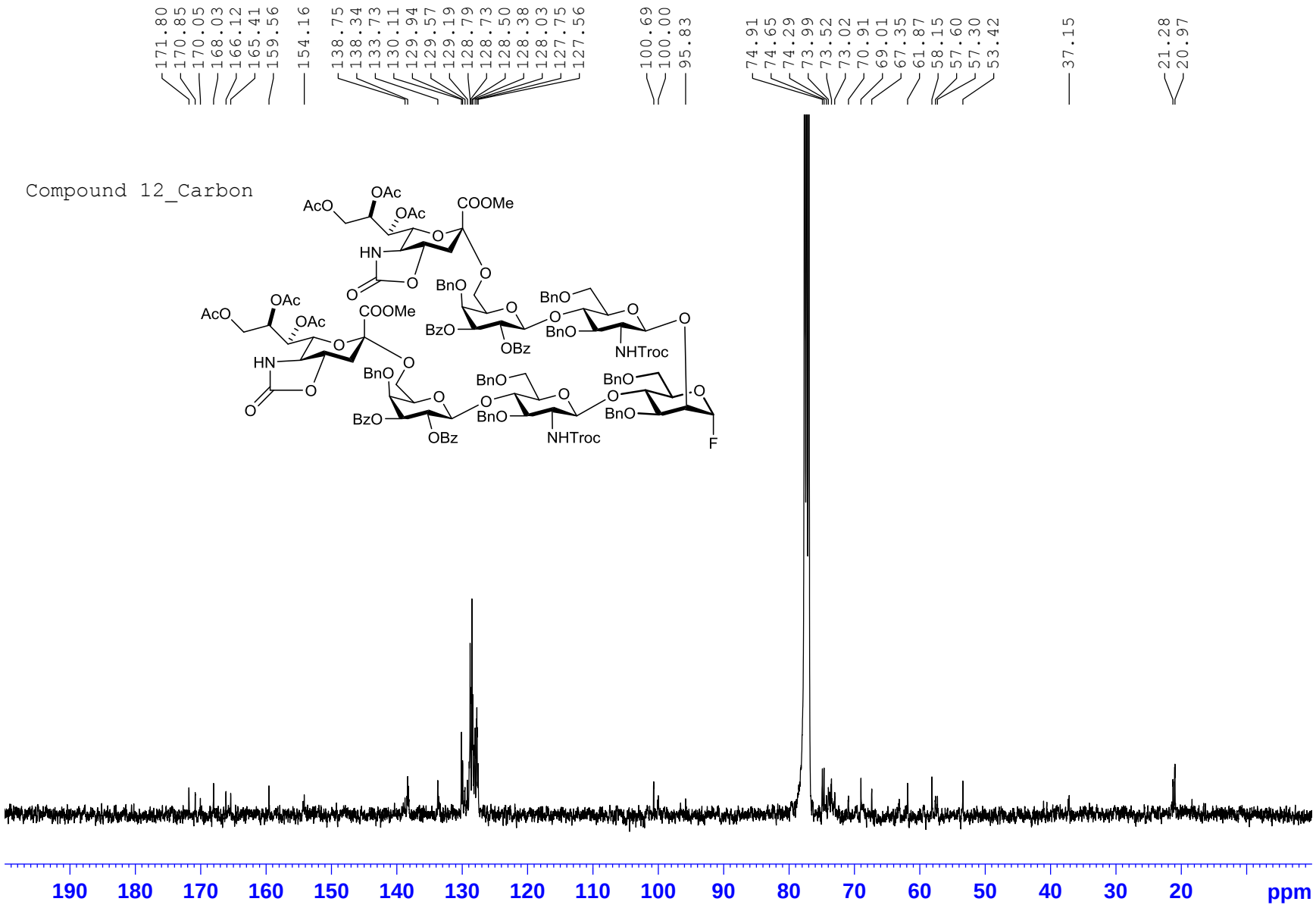
6.82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129.57
129.19
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128.38
128.03
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127.56
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100.00
95.83
74.91
74.65
74.29
73.99
73.52
73.02
70.91
69.01
67.35
61.87
58.15
57.60
57.30
53.42
37.15
21.28
20.97
Compound 12_Carbon
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180
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160
150
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130
120
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80
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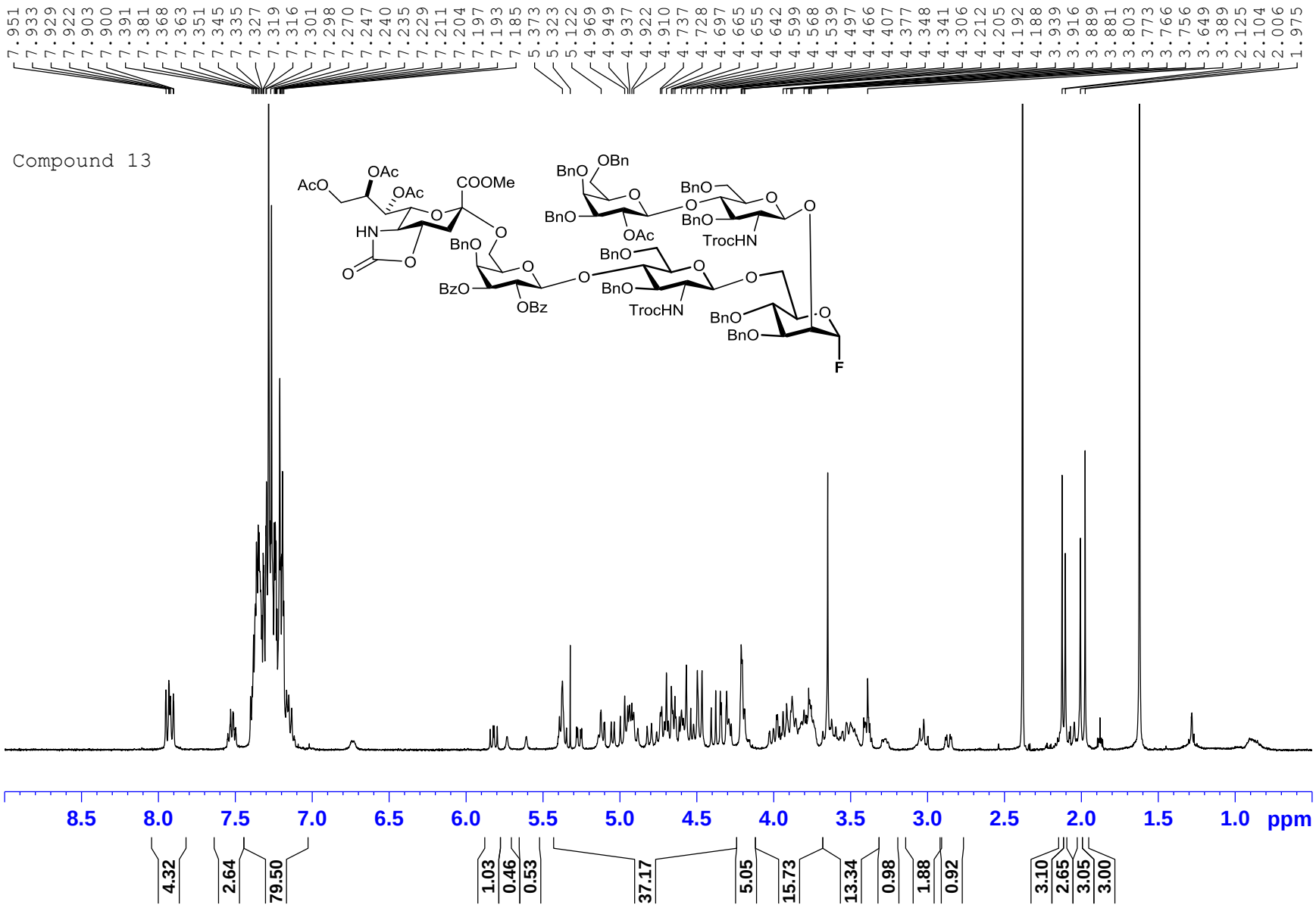
40
30
20
ppm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7.335
7.327
7.319
7.316
7.301
7.298
7.270
7.247
7.240
7.235
7.229
7.211
7.204
7.197
7.193
7.185
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5.122
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4.568
4.539
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4.466
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Compound 13
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OAc
OAc
COOMe
HN
BnO
BzO
OBz
BnO
OBn
BnO
OAc
BnO
BnO
TrocHN
BnO
BnO
TrocHN
BnO
BnO
F
8.5
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7.5
7.0
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6.0
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5.0
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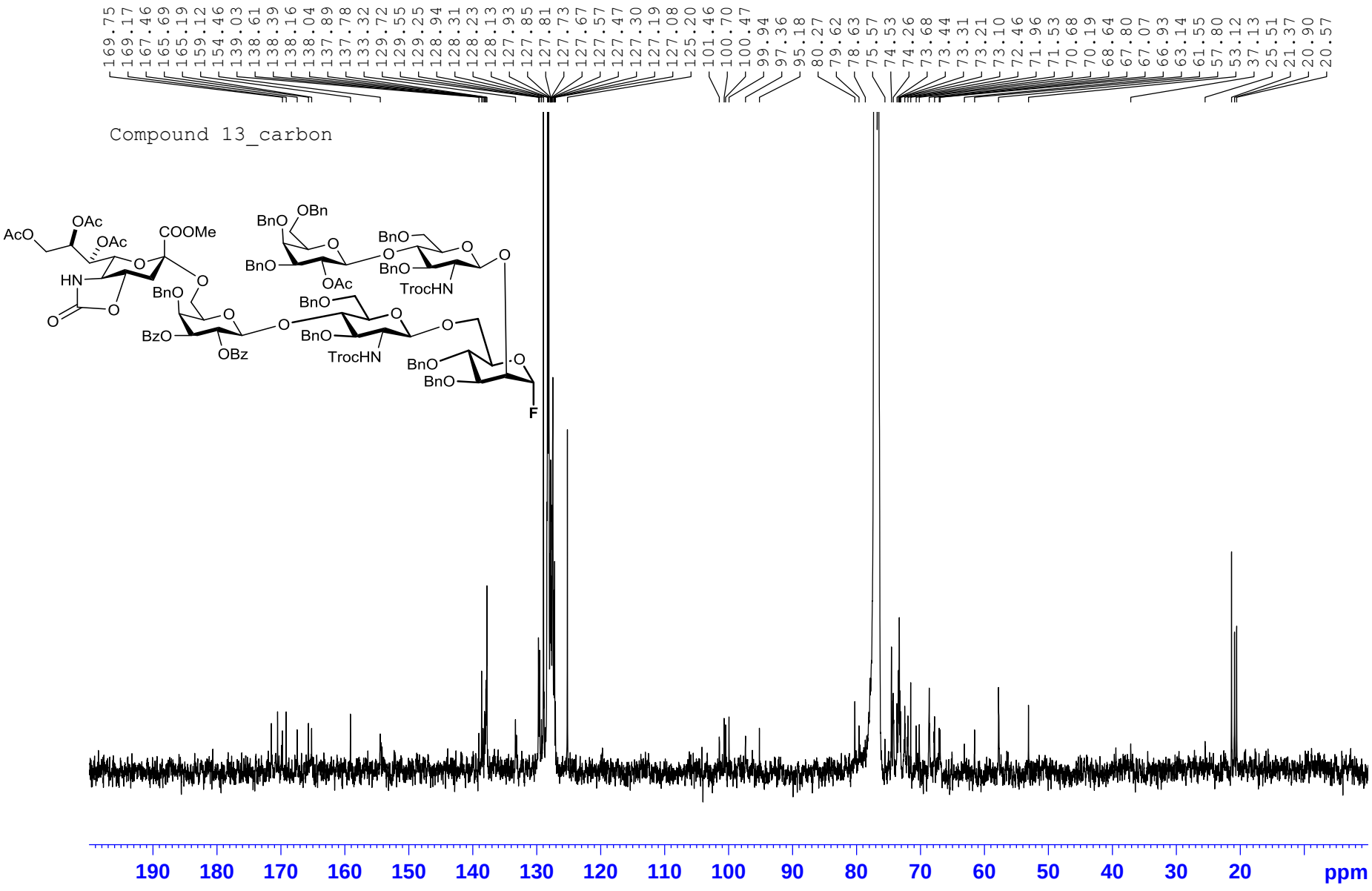
3.00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137.78
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127.81
127.73
127.67
127.57
127.47
127.30
127.19
127.08
125.20
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100.47
99.94
97.36
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80.27
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78.63
75.57
74.53
74.26
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53.12
37.13
25.51
21.37
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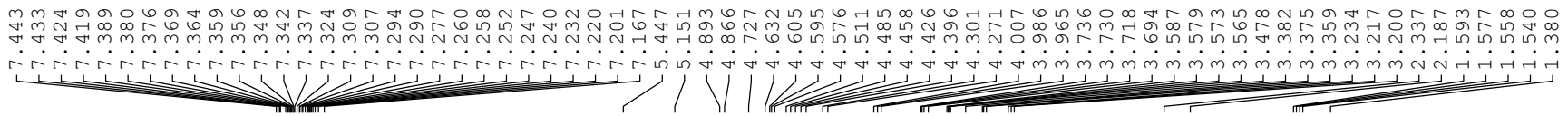
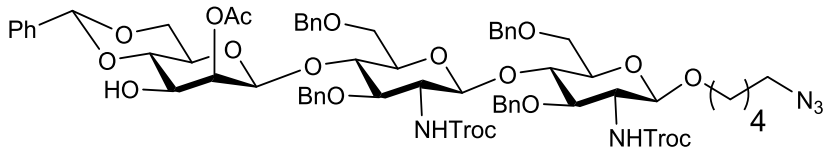
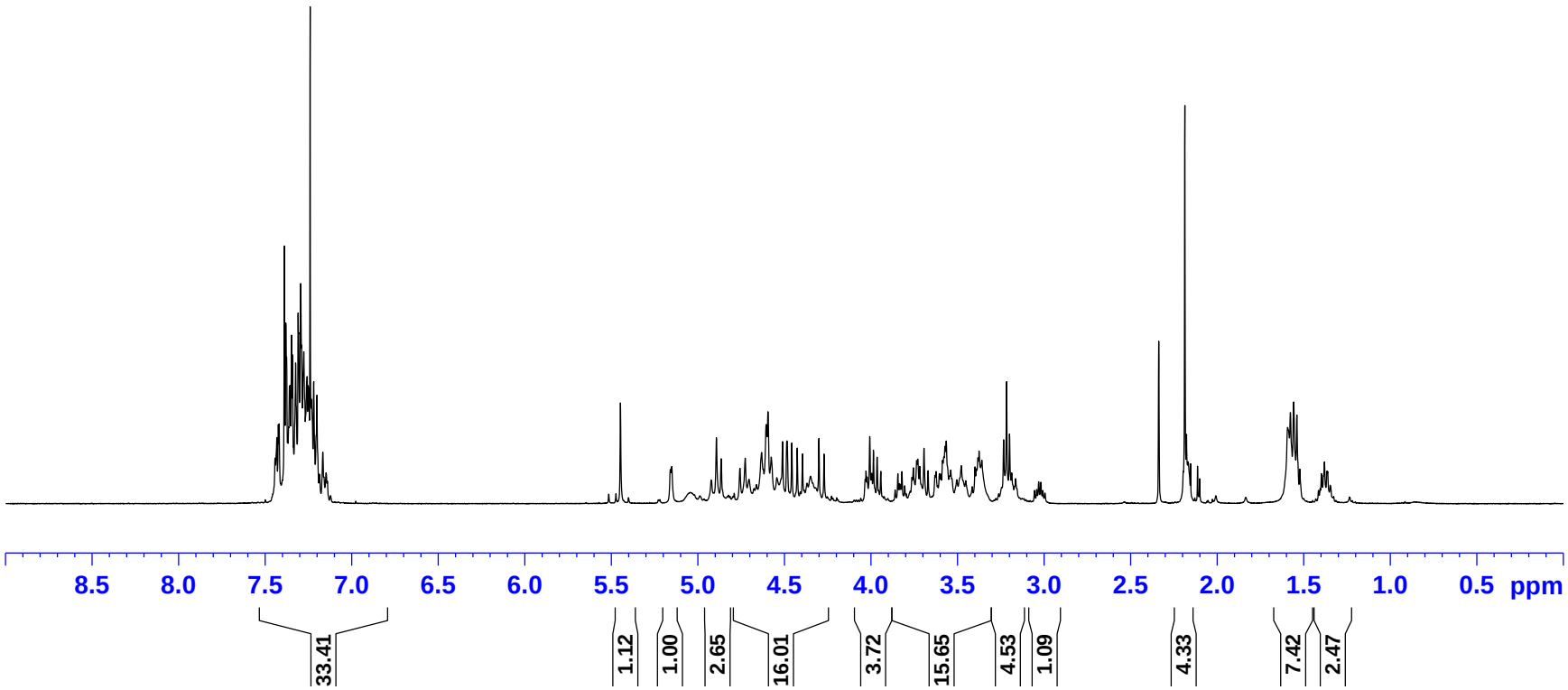
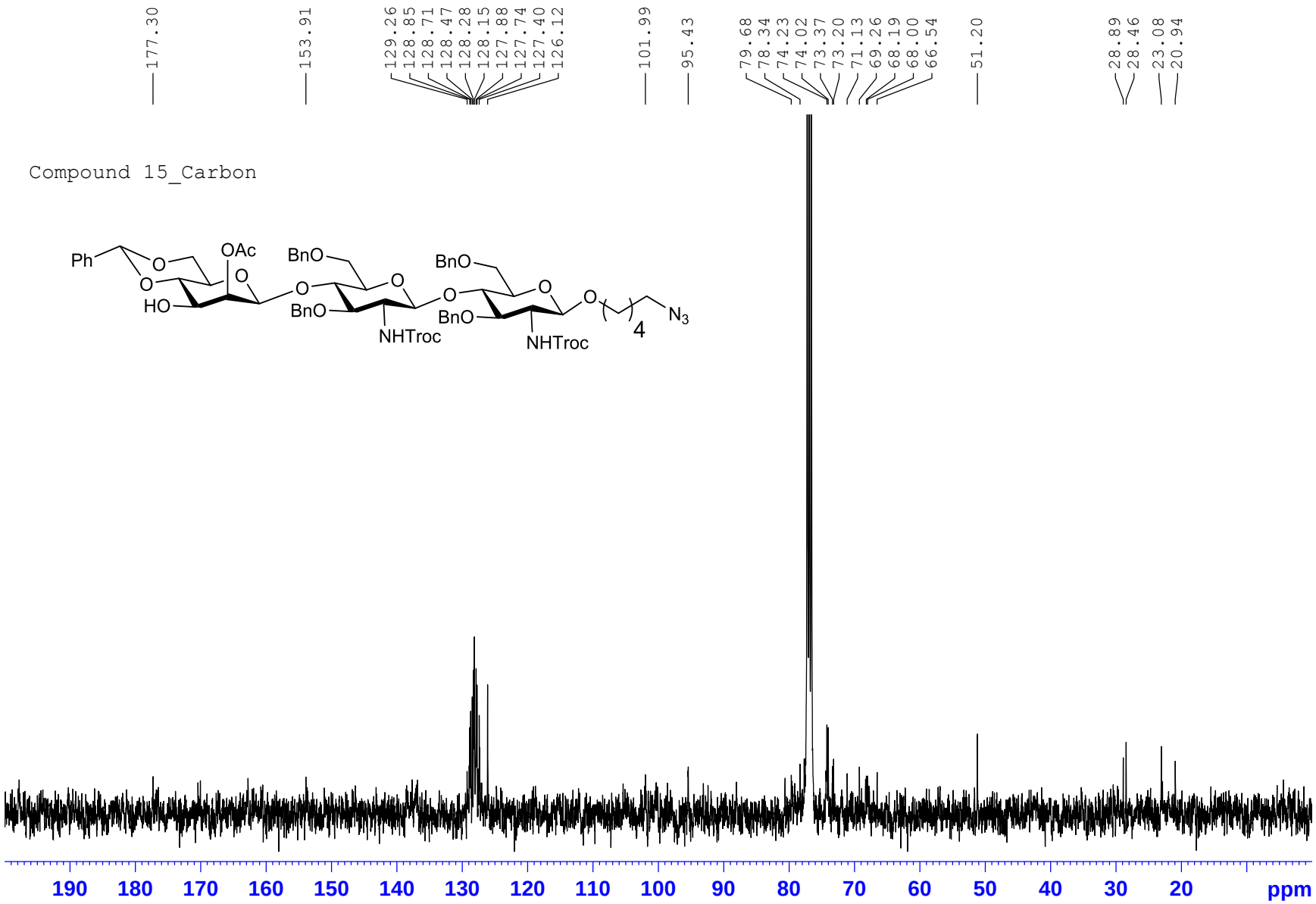
20.57
Compound 13_carbon
AcO
OAc
OAc
COOMe
HN
O
O
O
BnO
O
BzO
OBz
O
BnO
OBn
BnO
O
OAc
BnO
O
BnO
TrocHN
O
BnO
O
BnO
TrocHN
O
BnO
BnO
O
F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

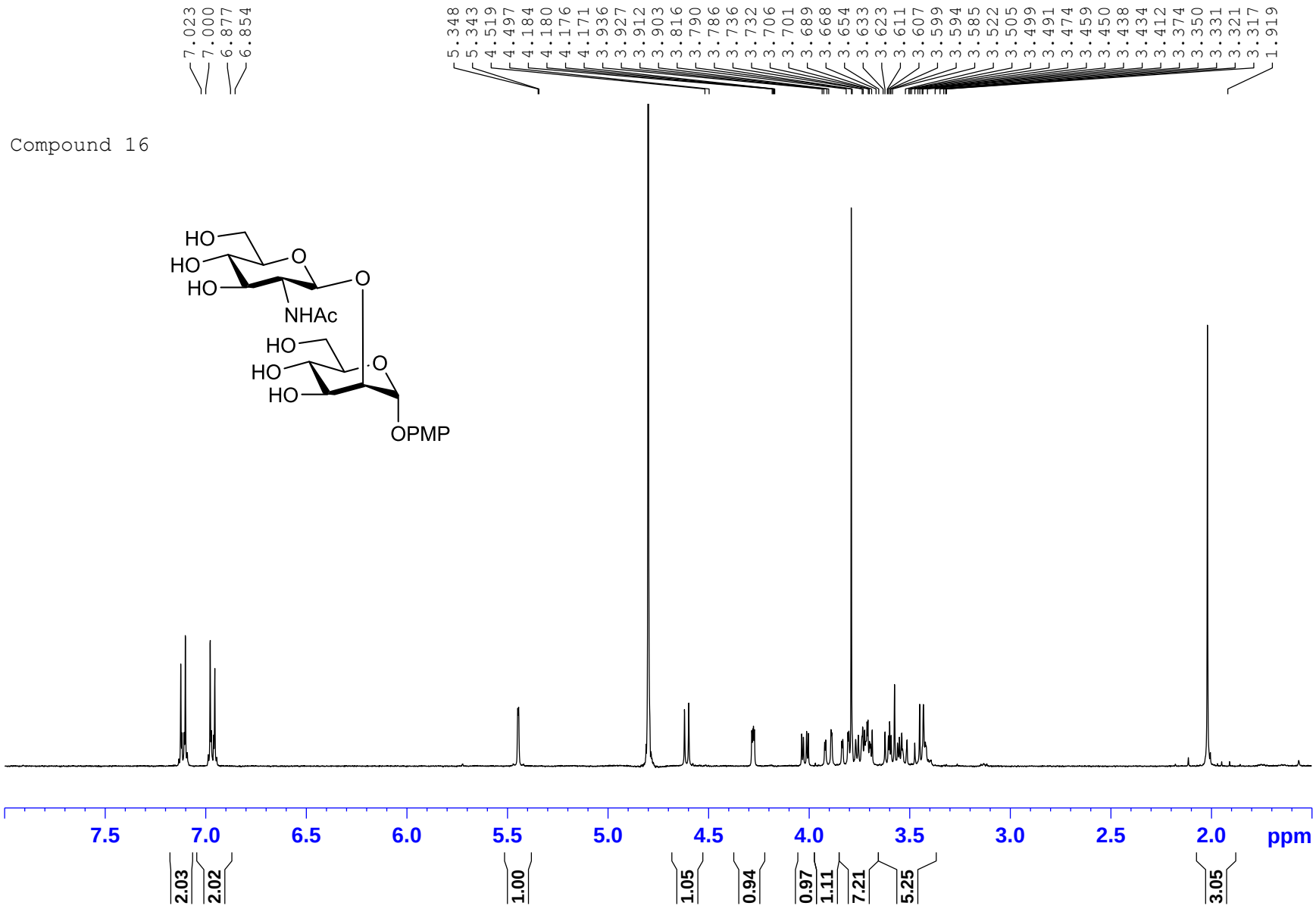

7.443
7.433
7.424
7.419
7.389
7.380
7.376
7.369
7.364
7.359
7.356
7.348
7.342
7.337
7.324
7.309
7.307
7.294
7.290
7.277
7.260
7.258
7.252
7.247
7.240
7.232
7.220
7.201
7.167
5.447
5.151
4.893
4.866
4.727
4.632
4.605
4.595
4.576
4.511
4.485
4.458
4.426
4.396
4.301
4.271
4.007
3.986
3.965
3.736
3.730
3.718
3.694
3.587
3.579
3.573
3.565
3.478
3.382
3.375
3.359
3.234
3.217
3.200
2.337
2.187
1.593
1.577
1.558
1.540
1.380

Compound 15


Ph
OAc
BnO
BnO
HO
BnO
BnO
BnO
NHTroc
NHTroc
N3
4


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
33.41
1.12
1.00
2.65
16.01
3.72
15.65
4.53
1.09
4.33
7.42
2.47


177.30
153.91
129.26
128.85
128.71
128.47
128.28
128.15
127.88
127.74
127.40
126.12
101.99
95.43
79.68
78.34
74.23
74.02
73.37
73.20
71.13
69.26
68.19
68.00
66.54
51.20
28.89
28.46
23.08
20.94
Compound 15_Carbon
Ph
OAc
BnO
HO
NHTroc
N3
4
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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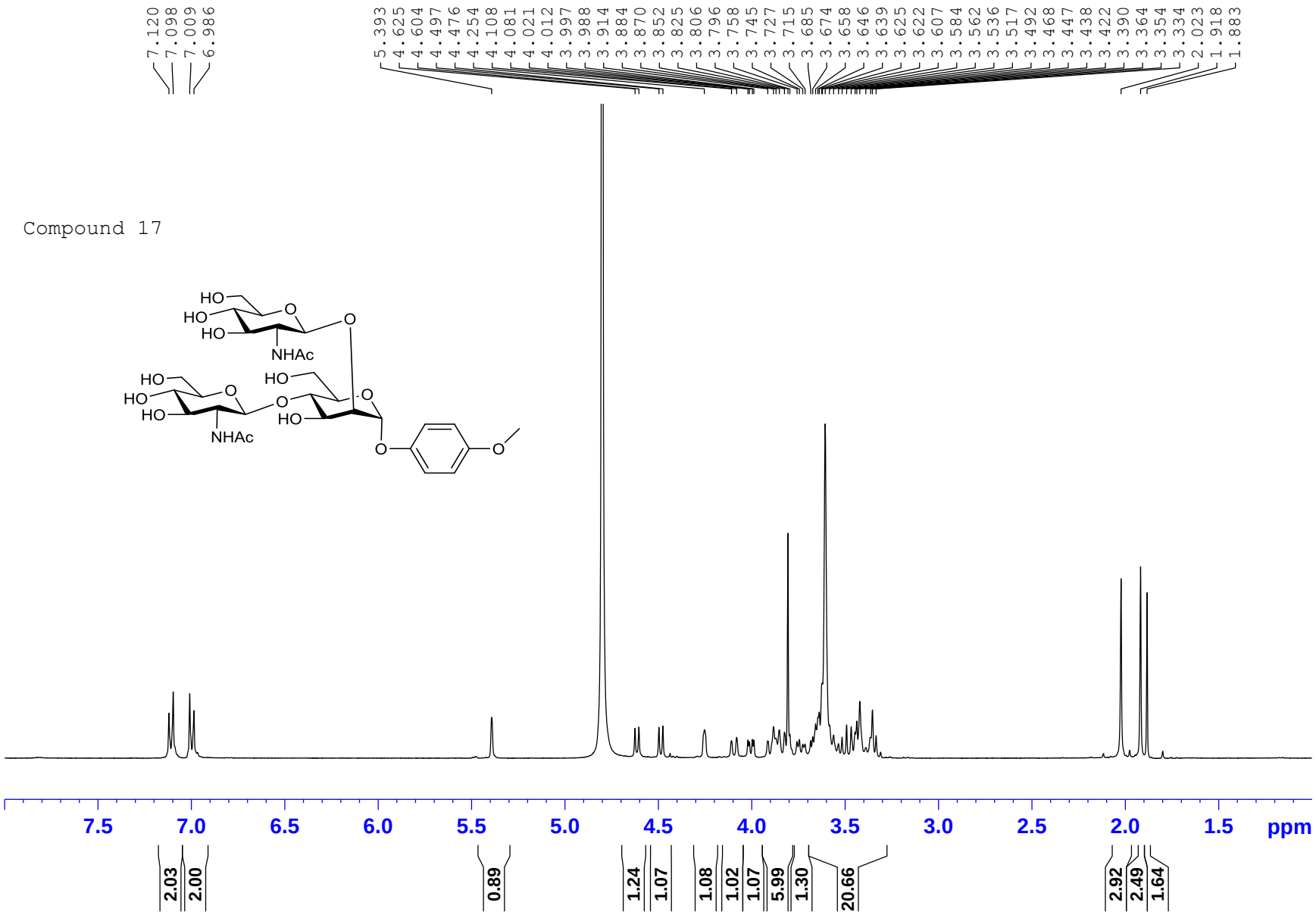
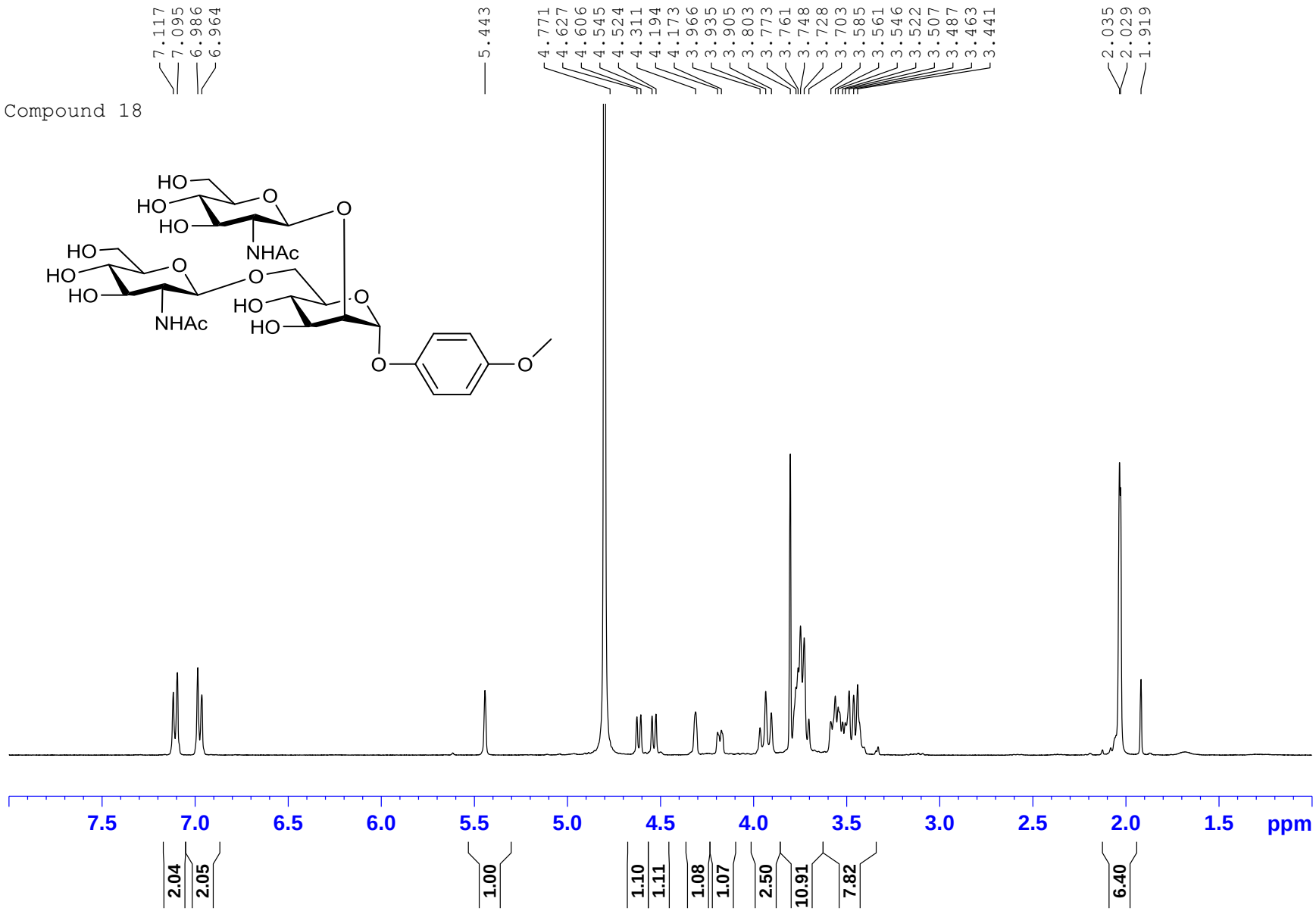
7.000
6.877
6.854
5.348
5.343
4.519
4.497
4.184
4.180
4.176
4.171
3.936
3.927
3.912
3.903
3.816
3.790
3.786
3.736
3.732
3.706
3.701
3.689
3.668
3.654
3.633
3.623
3.611
3.607
3.599
3.594
3.585
3.522
3.505
3.499
3.491
3.474
3.459
3.450
3.438
3.434
3.412
3.374
3.350
3.331
3.321
3.317
1.919
Compound 16
HO
HO
HO
O
O
NHAc
HO
HO
HO
O
OPMP
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
2.03
2.02
1.00
1.05
0.94
0.97
1.11
7.21
5.25
3.05


7.120
7.098
7.009
6.986
5.393
4.625
4.604
4.497
4.476
4.254
4.108
4.081
4.021
4.012
3.997
3.988
3.914
3.884
3.870
3.852
3.825
3.806
3.796
3.758
3.745
3.727
3.715
3.685
3.674
3.658
3.646
3.639
3.625
3.622
3.607
3.584
3.562
3.536
3.517
3.492
3.468
3.447
3.438
3.422
3.390
3.364
3.354
3.334
2.023
1.918
1.883
Compound 17
HO
HO
HO
O
O
NHAc
HO
HO
HO
O
NHAc
HO
HO
O
O
HO
O
O
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
ppm
2.03
2.00
0.89
1.24
1.07
1.08
1.02
1.07
5.99
1.30
20.66
2.92
2.49
1.64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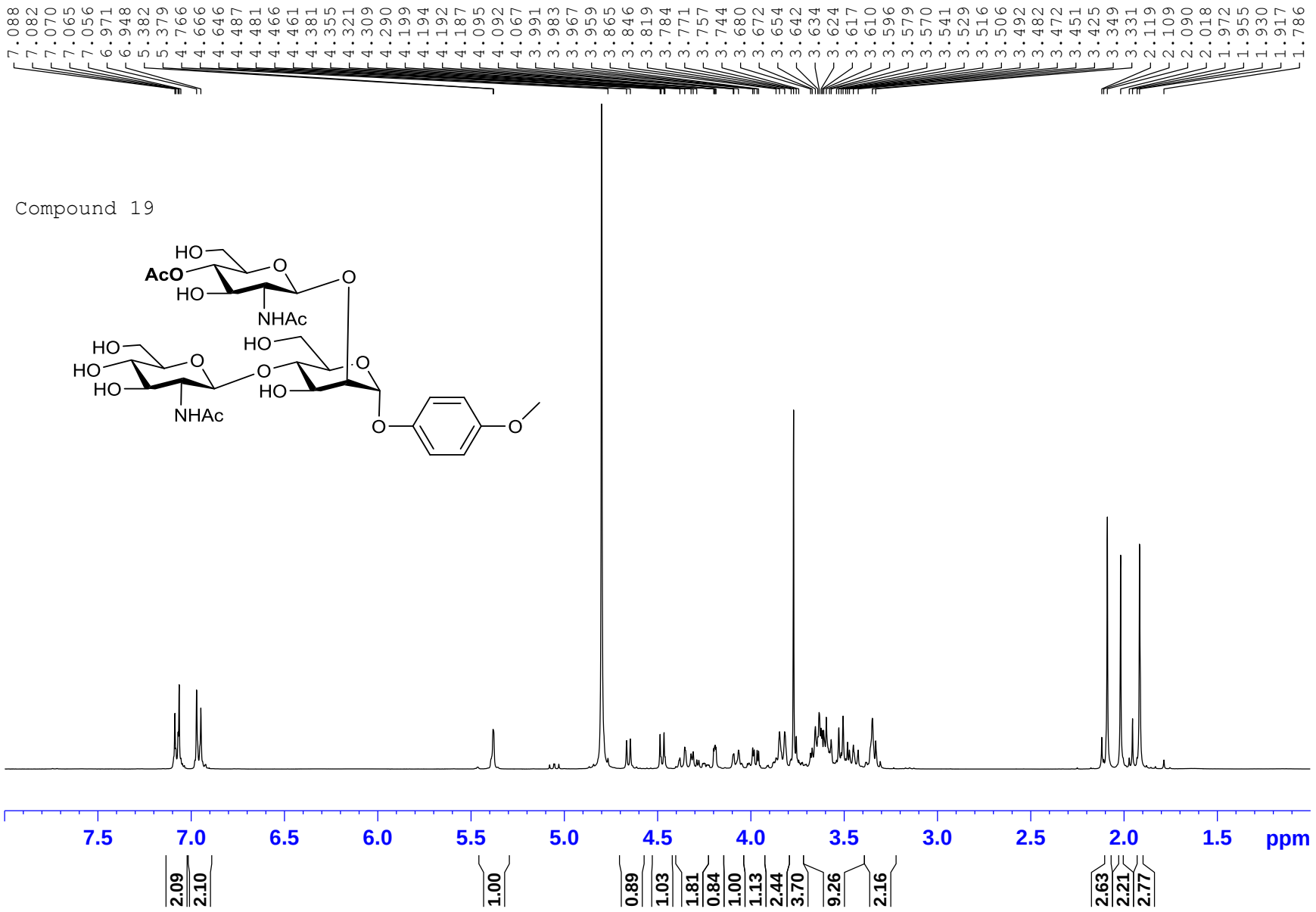
7.095
6.986
6.964
5.443
4.771
4.627
4.606
4.545
4.524
4.311
4.194
4.173
3.966
3.935
3.905
3.803
3.773
3.761
3.748
3.728
3.703
3.585
3.561
3.546
3.522
3.507
3.487
3.463
3.441
2.035
2.029
1.919
Compound 18
HO
HO
HO
O
O
NHAc
HO
HO
HO
O
NHAc
O
HO
HO
O
O
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
2.04
2.05
1.00
1.10
1.11
1.08
1.07
2.50
10.91
7.82
6.40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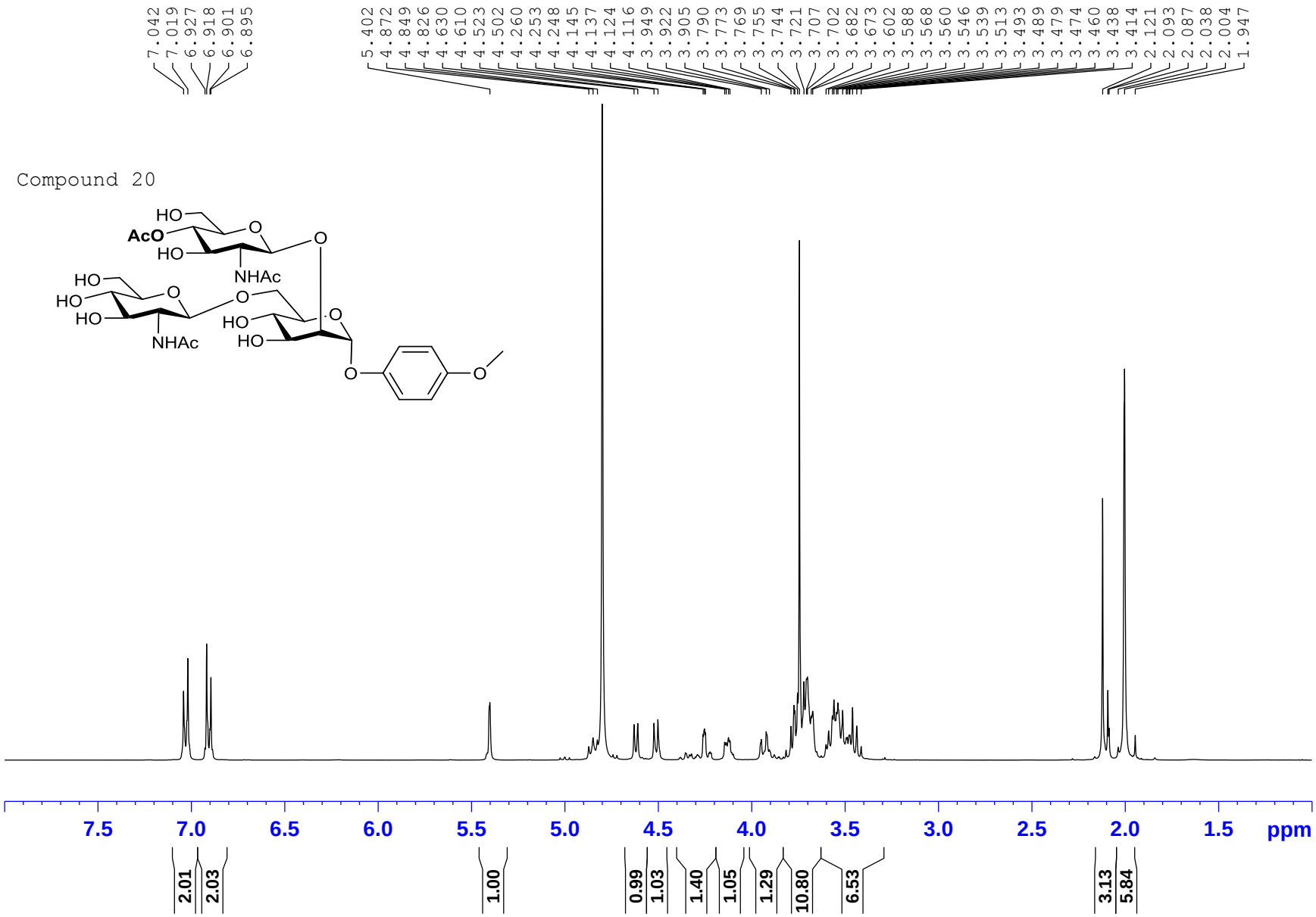
7.082
7.070
7.065
7.056
6.971
6.948
5.382
5.379
4.766
4.666
4.646
4.487
4.481
4.466
4.461
4.381
4.355
4.321
4.309
4.290
4.199
4.194
4.192
4.187
4.095
4.092
4.067
3.991
3.983
3.967
3.959
3.865
3.846
3.819
3.784
3.771
3.757
3.744
3.680
3.672
3.654
3.642
3.634
3.624
3.617
3.610
3.596
3.579
3.570
3.541
3.529
3.516
3.506
3.492
3.482
3.472
3.451
3.425
3.349
3.331
2.119
2.109
2.090
2.018
1.972
1.955
1.930
1.917
1.786
Compound 19
HO
AcO
HO
NHAc
HO
HO
HO
NHAc
HO
HO
O
O
O
O
O
O
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
ppm
2.09
2.10
1.00
0.89
1.03
1.81
0.84
1.00
1.13
2.44
3.70
9.26
2.16
2.63
2.21
2.77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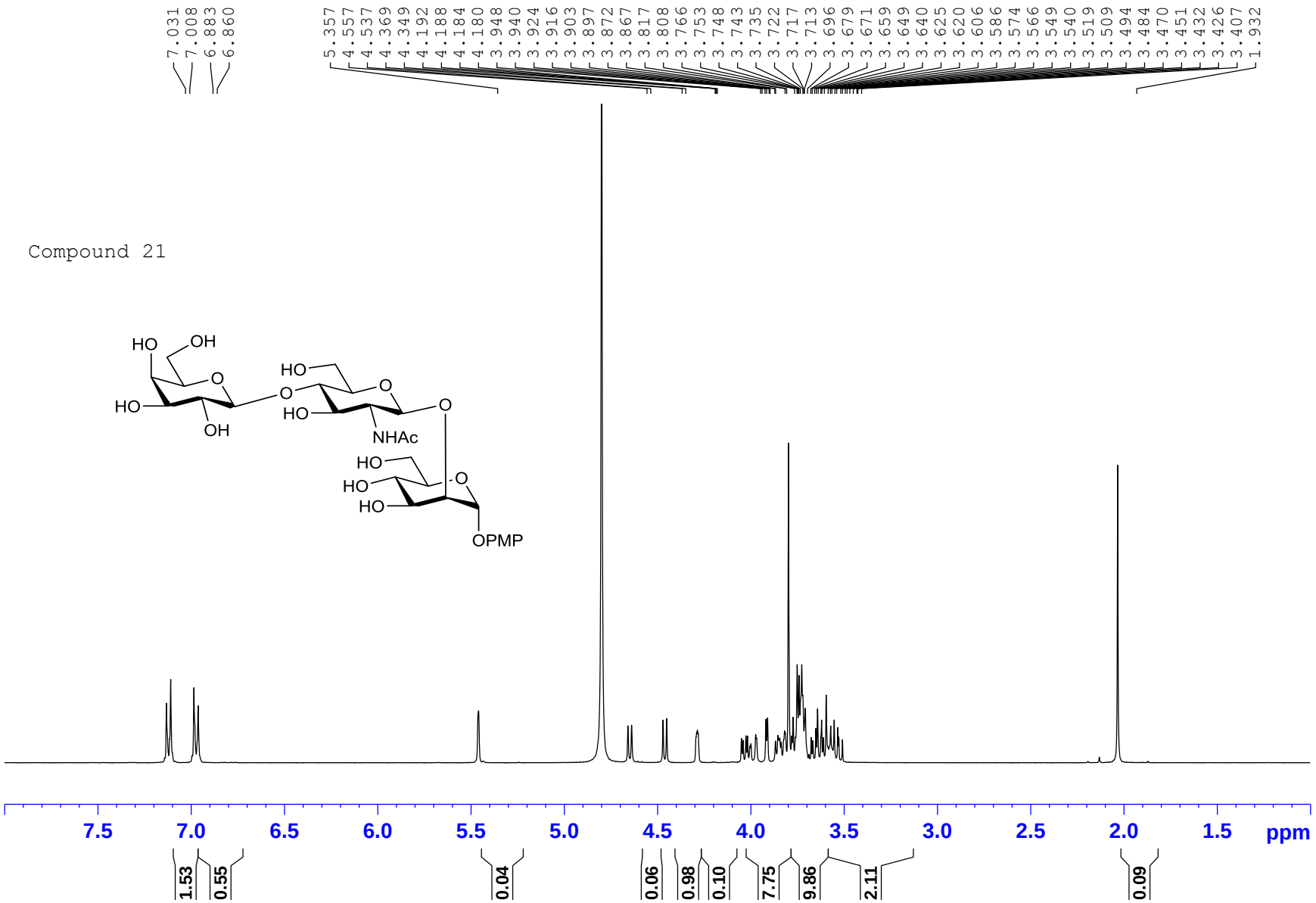
7.019
6.927
6.918
6.901
6.895
5.402
4.872
4.849
4.826
4.630
4.610
4.523
4.502
4.260
4.253
4.248
4.145
4.137
4.124
4.116
3.949
3.922
3.905
3.790
3.773
3.769
3.755
3.744
3.721
3.707
3.702
3.682
3.673
3.602
3.588
3.568
3.560
3.546
3.539
3.513
3.493
3.489
3.479
3.474
3.460
3.438
3.414
2.121
2.093
2.087
2.038
2.004
1.947
Compound 20
HO
AcO
HO
O
O
NHAc
HO
HO
HO
O
O
NHAc
HO
HO
O
O
O
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
ppm
2.01
2.03
1.00
0.99
1.03
1.40
1.05
1.29
10.80
6.53
3.13
5.84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7.008
6.883
6.860
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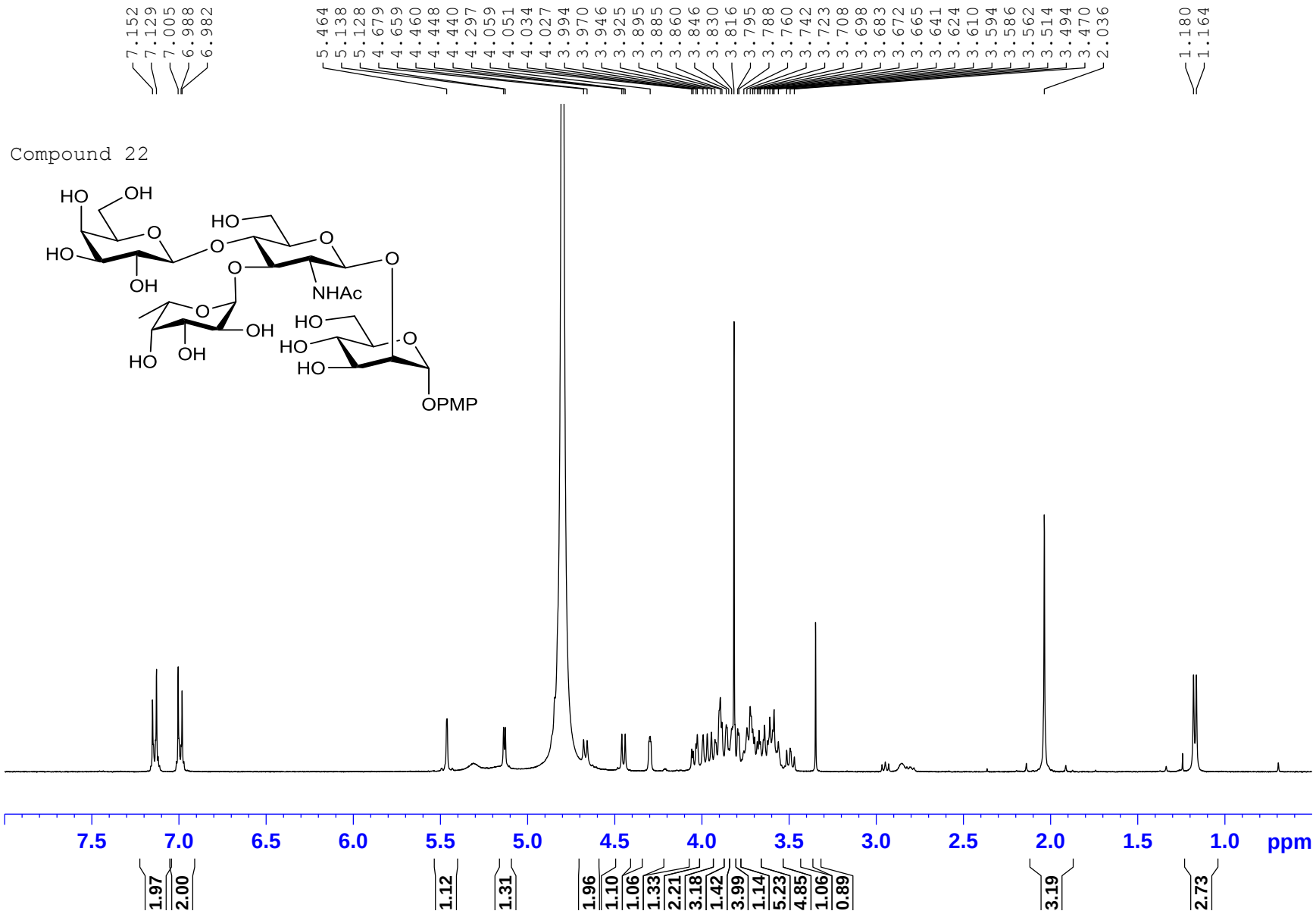
4.557
4.537
4.369
4.349
4.192
4.188
4.184
4.180
3.948
3.940
3.924
3.916
3.903
3.897
3.872
3.867
3.817
3.808
3.766
3.753
3.748
3.743
3.735
3.722
3.717
3.713
3.696
3.679
3.671
3.659
3.649
3.640
3.625
3.620
3.606
3.586
3.574
3.566
3.549
3.540
3.519
3.509
3.494
3.484
3.470
3.451
3.432
3.426
3.407
1.932
Compound 21
HO
OH
O
HO
OH
O
HO
HO
O
NHAc
O
HO
HO
HO
O
OPMP
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
ppm
1.53
0.55
0.04
0.06
0.98
0.10
7.75
9.86
2.11
0.09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7.129
7.005
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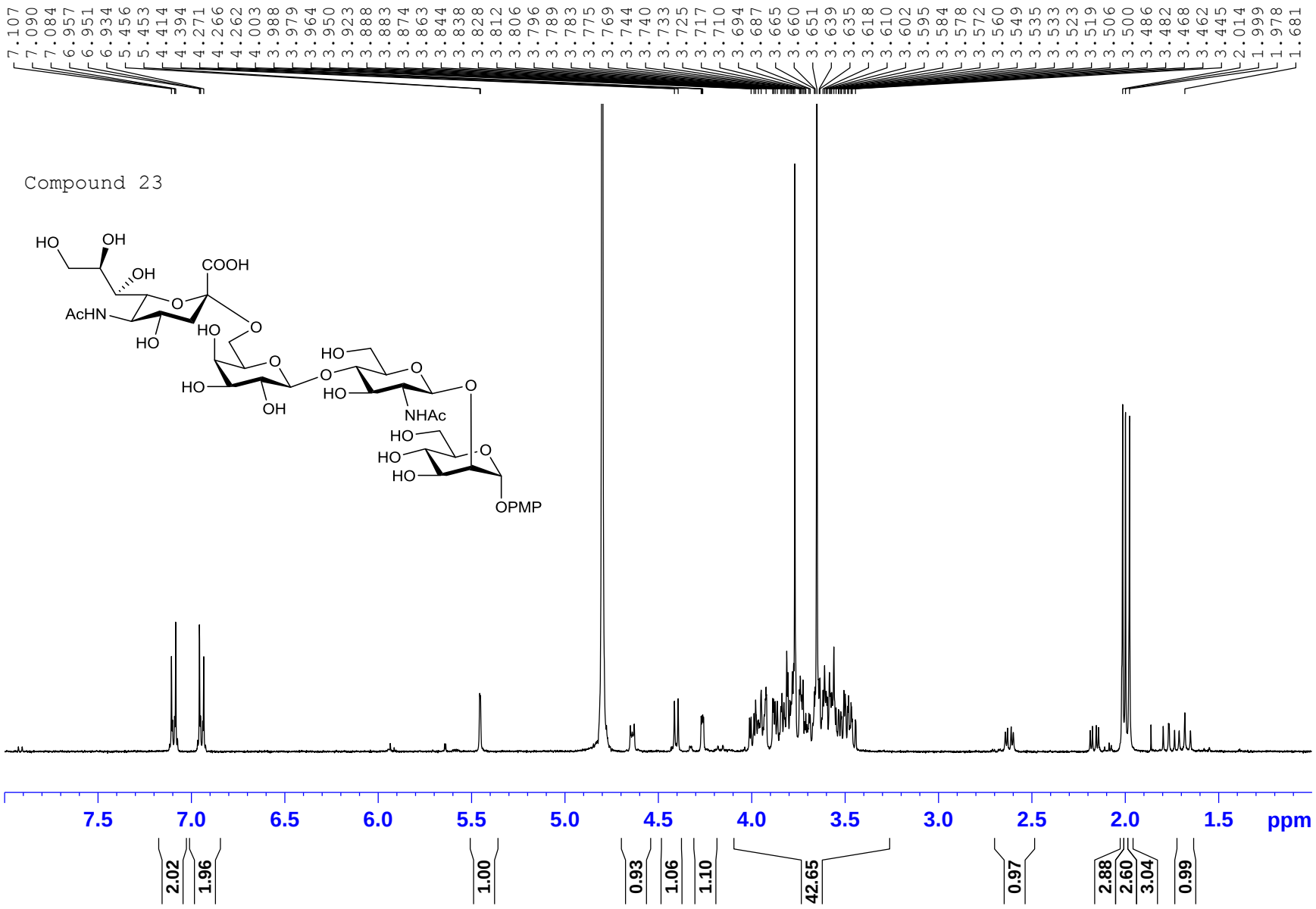
6.982
5.464
5.138
5.128
4.679
4.659
4.460
4.448
4.440
4.297
4.059
4.051
4.034
4.027
3.994
3.970
3.946
3.925
3.895
3.885
3.860
3.846
3.830
3.816
3.795
3.788
3.760
3.742
3.723
3.708
3.698
3.683
3.672
3.665
3.641
3.624
3.610
3.594
3.586
3.562
3.514
3.494
3.470
2.036
1.180
1.164
Compound 22
HO
OH
HO
O
O
HO
O
O
NHAc
OH
O
OH
HO
OH
HO
HO
HO
O
OPMP
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
ppm
1.97
2.00
1.12
1.31
1.96
1.10
1.06
1.33
2.21
3.18
1.42
3.99
1.14
5.23
4.85
1.06
0.89
3.19
2.73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7.090
7.084
6.957
6.951
6.934
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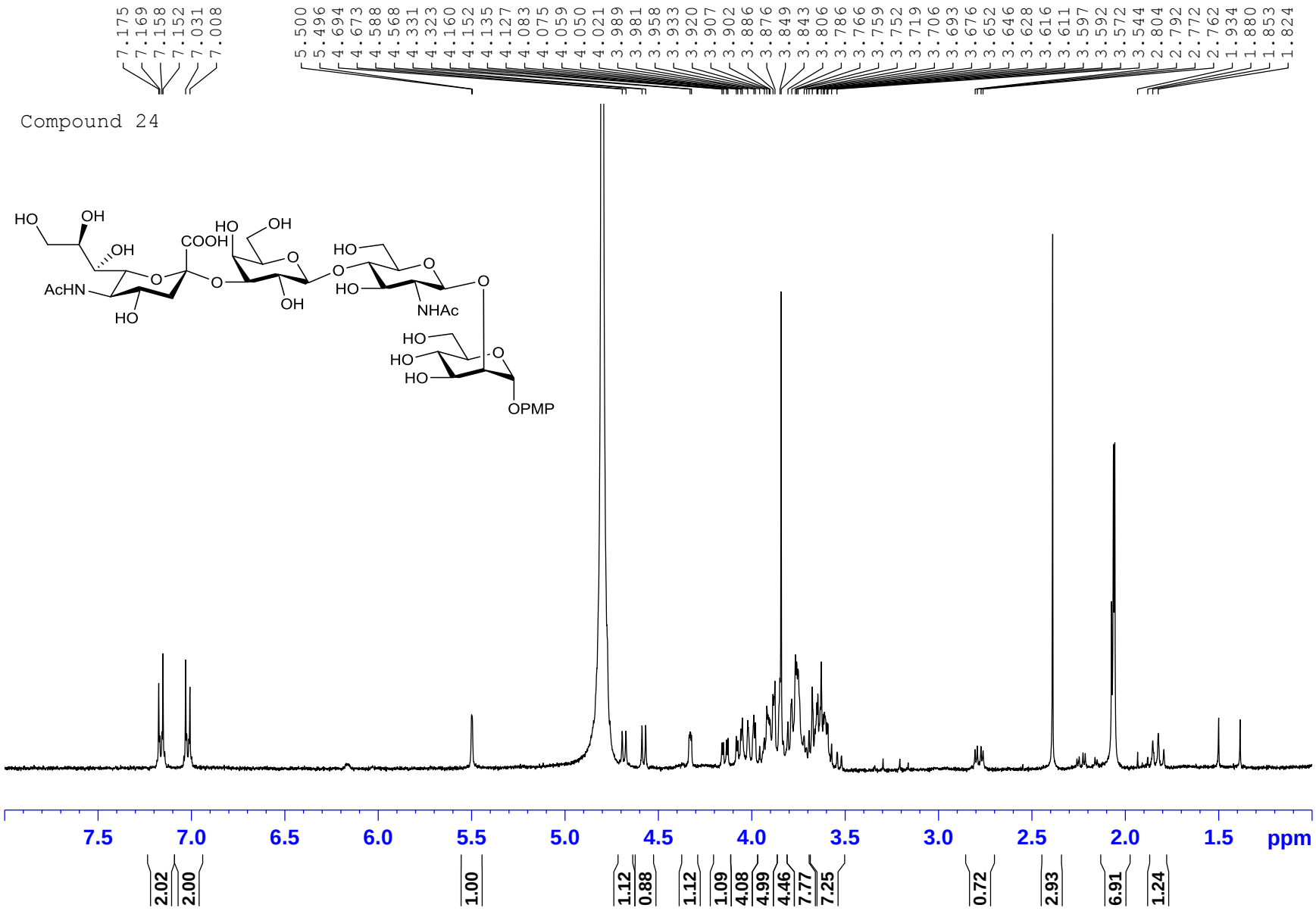
5.453
4.414
4.394
4.271
4.266
4.262
4.003
3.988
3.979
3.964
3.950
3.923
3.888
3.883
3.874
3.863
3.844
3.838
3.828
3.812
3.806
3.796
3.789
3.783
3.775
3.769
3.744
3.740
3.733
3.725
3.717
3.710
3.694
3.687
3.665
3.660
3.651
3.639
3.635
3.618
3.610
3.602
3.595
3.584
3.578
3.572
3.560
3.549
3.535
3.533
3.523
3.519
3.506
3.500
3.486
3.482
3.468
3.462
3.445
2.014
1.999
1.978
1.681
Compound 23
HO
OH
OH
COOH
AcHN
HO
HO
O
HO
O
HO
OH
O
HO
HO
O
HO
NHAc
HO
HO
HO
O
OPMP
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
ppm
2.02
1.96
1.00
0.93
1.06
1.10
42.65
0.97
2.88
2.60
3.04
0.99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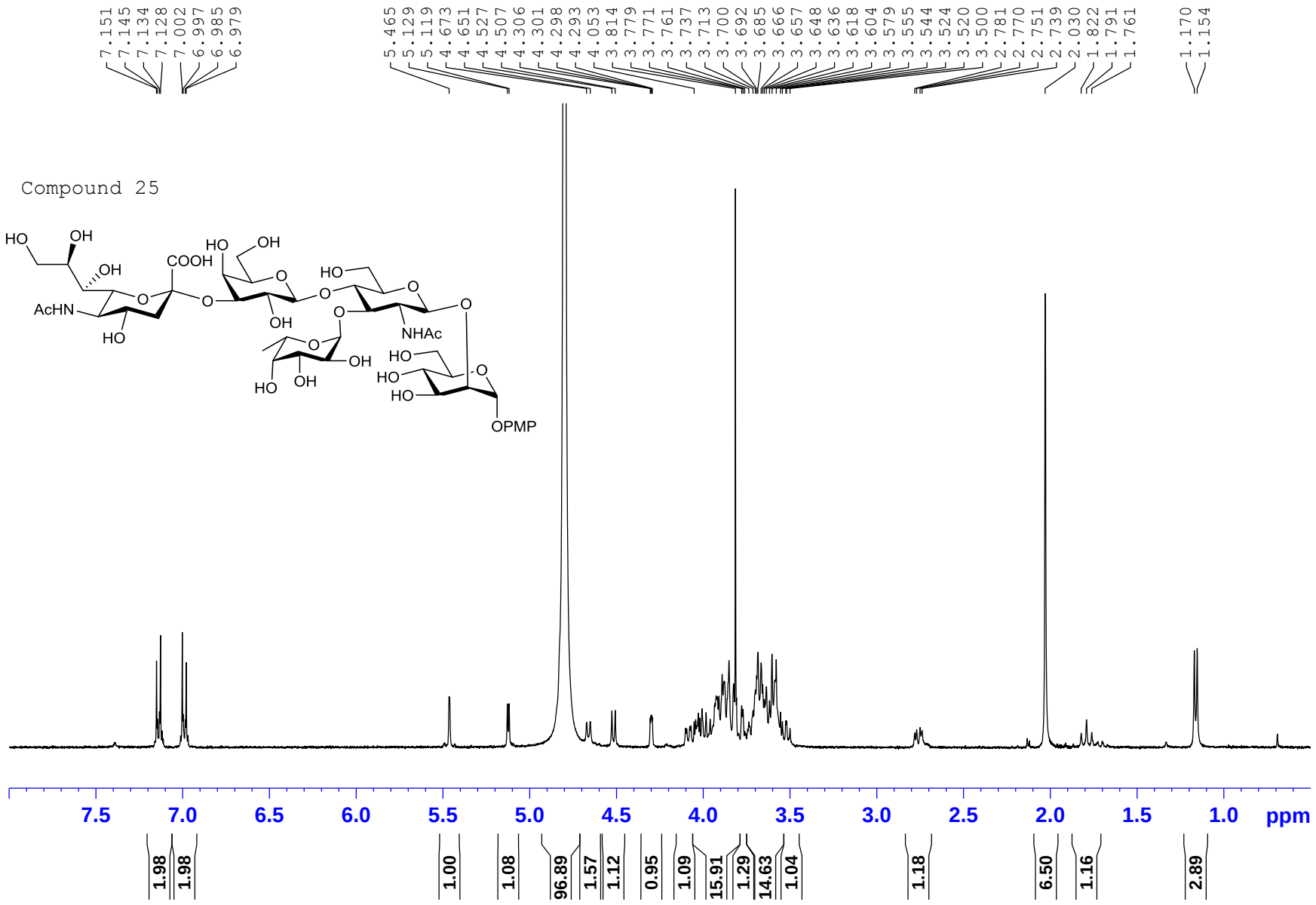
7.169
7.158
7.152
7.031
7.008
5.500
5.496
4.694
4.673
4.588
4.568
4.331
4.323
4.160
4.152
4.135
4.127
4.083
4.075
4.059
4.050
4.021
3.989
3.981
3.958
3.933
3.920
3.907
3.902
3.886
3.876
3.849
3.843
3.806
3.786
3.766
3.759
3.752
3.719
3.706
3.693
3.676
3.652
3.646
3.628
3.616
3.611
3.597
3.592
3.572
3.544
2.804
2.792
2.772
2.762
1.934
1.880
1.853
1.824
Compound 24
HO
OH
OH
COOH
AcHN
HO
O
HO
OH
O
O
OH
HO
O
HO
NHAc
O
HO
HO
HO
O
OPMP
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
ppm
2.02
2.00
1.00
1.12
0.88
1.12
1.09
4.08
4.99
4.46
7.77
7.25
0.72
2.93
6.91
1.24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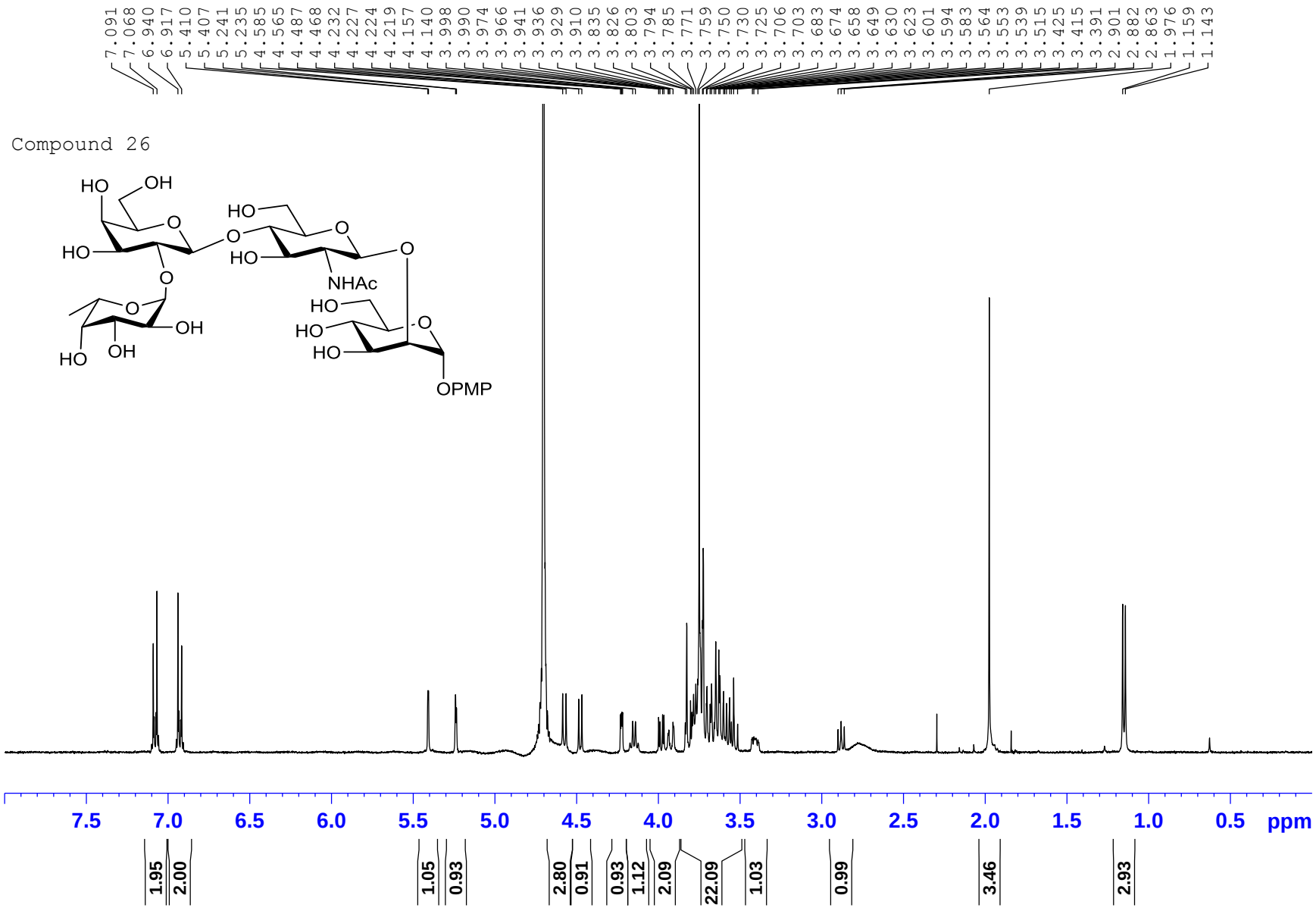
7.145
7.134
7.128
7.002
6.997
6.985
6.979
5.465
5.129
5.119
4.673
4.651
4.527
4.507
4.306
4.301
4.298
4.293
4.053
3.814
3.779
3.771
3.761
3.737
3.713
3.700
3.692
3.685
3.666
3.657
3.648
3.636
3.618
3.604
3.579
3.555
3.544
3.524
3.520
3.500
2.781
2.770
2.751
2.739
2.030
1.822
1.791
1.761
1.170
1.154
Compound 25
HO
OH
OH
COOH
AcHN
HO
O
HO
OH
HO
O
O
O
OH
HO
OH
O
HO
O
NHAc
O
HO
OH
HO
HO
HO
O
OPMP
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
ppm
1.98
1.98
1.00
1.08
96.89
1.57
1.12
0.95
1.09
15.91
1.29
14.63
1.04
1.18
6.50
1.16
2.89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7.068
6.940
6.917
5.410
5.407
5.241
5.235
4.585
4.565
4.487
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4.224
4.219
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4.140
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3.623
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3.553
3.539
3.515
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3.391
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2.882
2.863
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1.159
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Compound 26
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OH
O
HO
O
HO
O
HO
O
NHAc
HO
HO
HO
O
OH
HO
OH
OPMP
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
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22.09
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0.99
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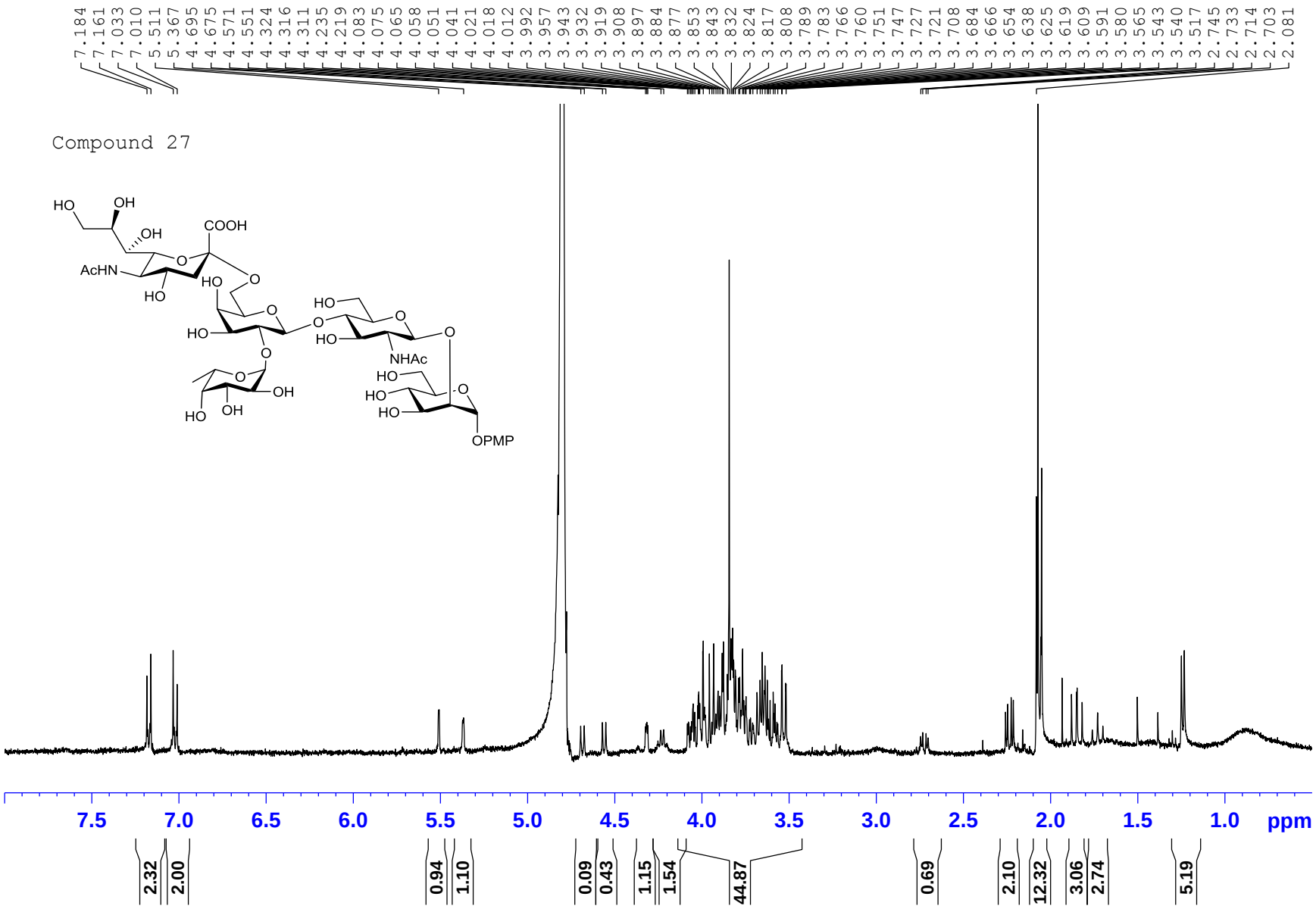
2.93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Compound 27
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OH
OH
COOH
AcHN
HO
HO
O
HO
O
HO
O
HO
O
HO
NHAc
HO
HO
HO
O
OH
HO
OH
O
HO
HO
HO
OPMP
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5.0
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
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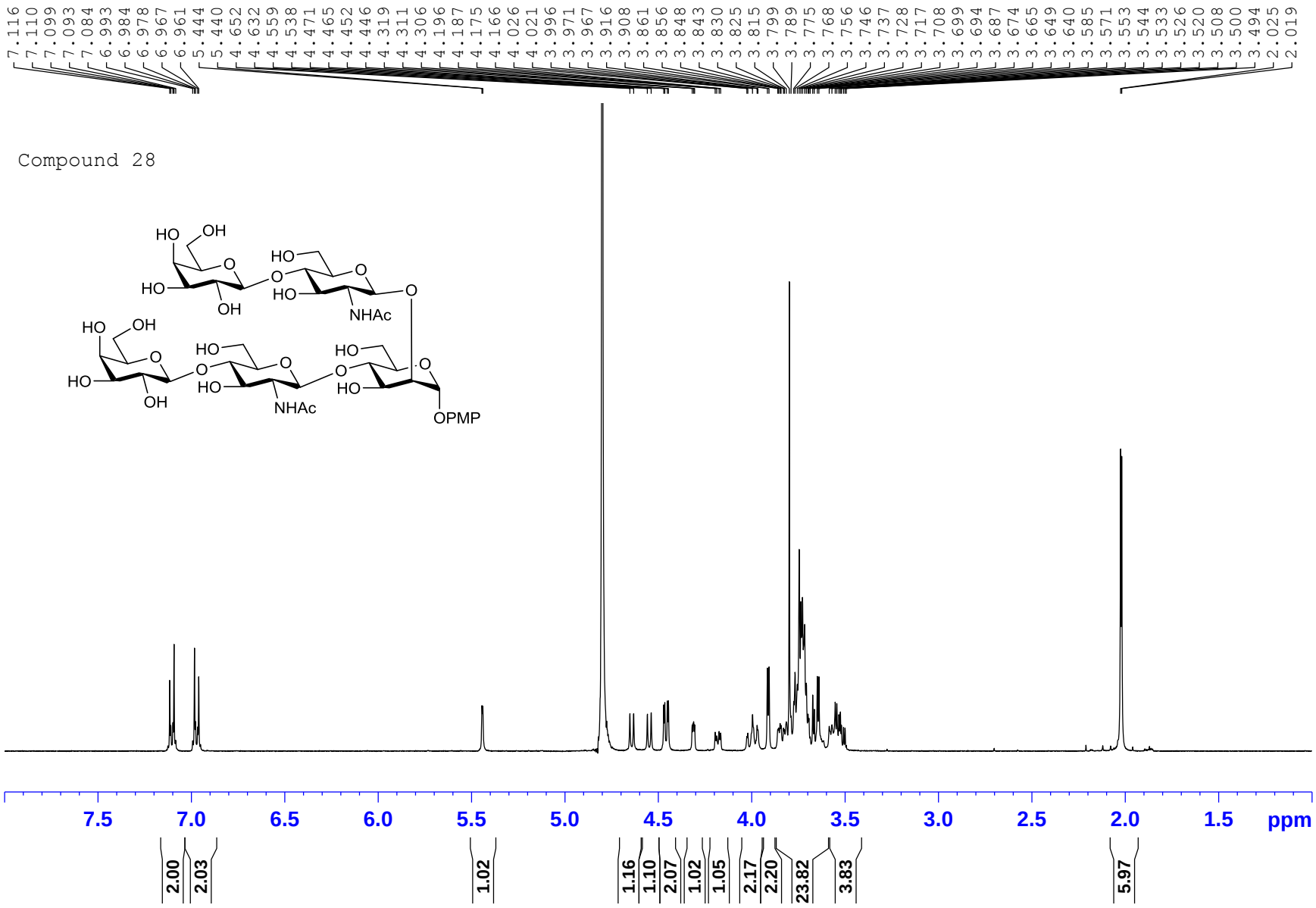
5.19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3.746
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3.649
3.640
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3.544
3.533
3.526
3.520
3.508
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3.494
2.025
2.019
Compound 28
HO
OH
O
HO
OH
HO
O
HO
O
HO
NHAc
O
HO
OH
O
HO
OH
HO
O
HO
O
HO
NHAc
HO
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OPMP
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6.5
6.0
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4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
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2.17
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23.82
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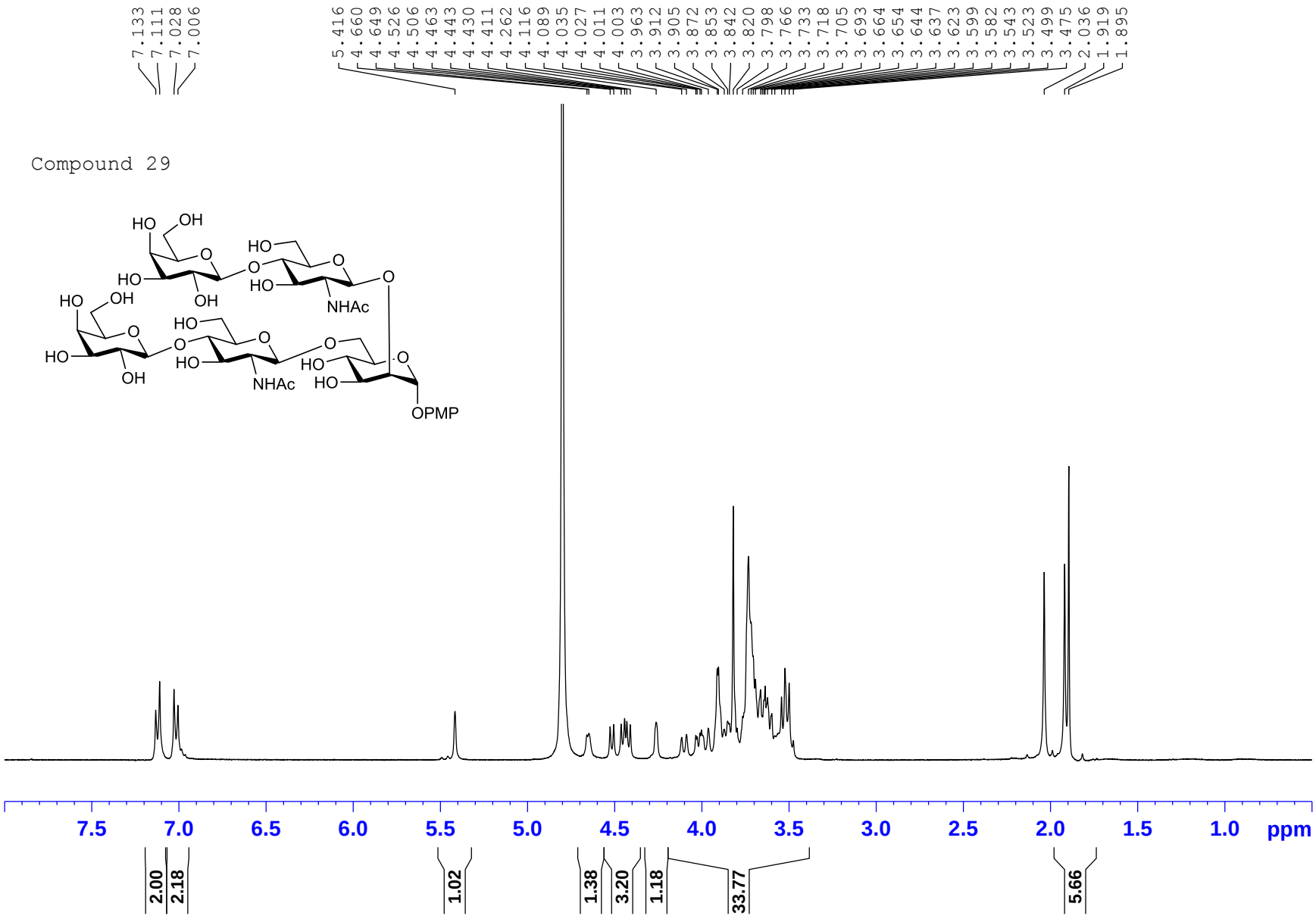
5.97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3.912
3.905
3.872
3.853
3.842
3.820
3.798
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3.733
3.718
3.705
3.693
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3.654
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3.637
3.623
3.599
3.582
3.543
3.523
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1.919
1.895
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OH
O
HO
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O
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OH
HO
O
O
HO
NHAc
O
HO
HO
O
OPMP
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4.0
3.5
3.0
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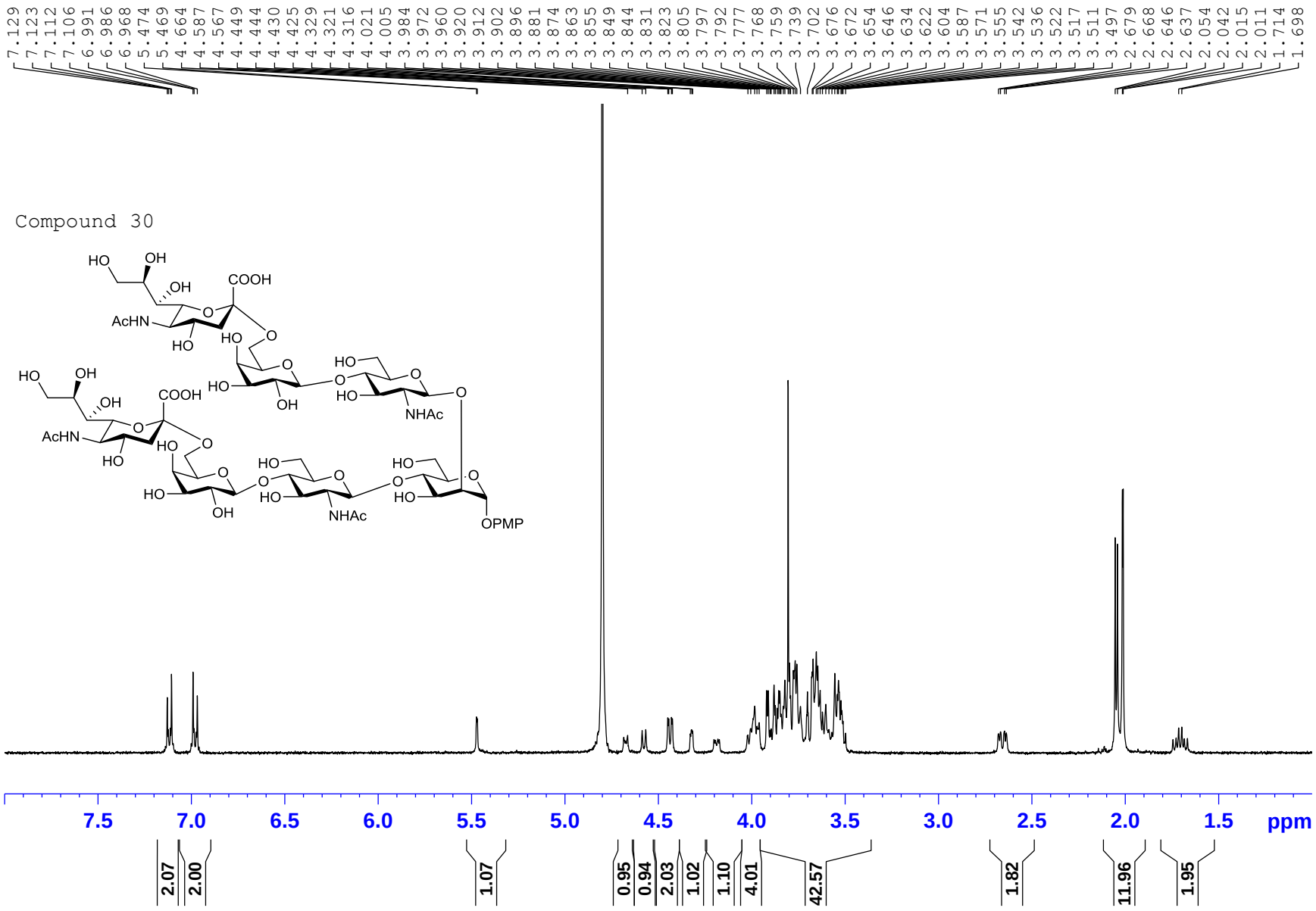
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4.664
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4.567
4.449
4.444
4.430
4.425
4.329
4.321
4.316
4.021
4.005
3.984
3.972
3.960
3.920
3.912
3.902
3.896
3.881
3.874
3.863
3.855
3.849
3.844
3.831
3.823
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3.797
3.792
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3.768
3.759
3.739
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3.654
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3.622
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3.587
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3.555
3.542
3.536
3.522
3.517
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2.054
2.042
2.015
2.011
1.714
1.698
Compound 30
HO
OH
OH
COOH
AcHN
HO
HO
O
HO
O
HO
OH
HO
O
HO
NHAc
HO
OH
OH
COOH
AcHN
HO
HO
O
HO
O
HO
OH
HO
O
HO
NHAc
HO
O
HO
OPMP
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
ppm
2.07
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0.94
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1.02
1.10
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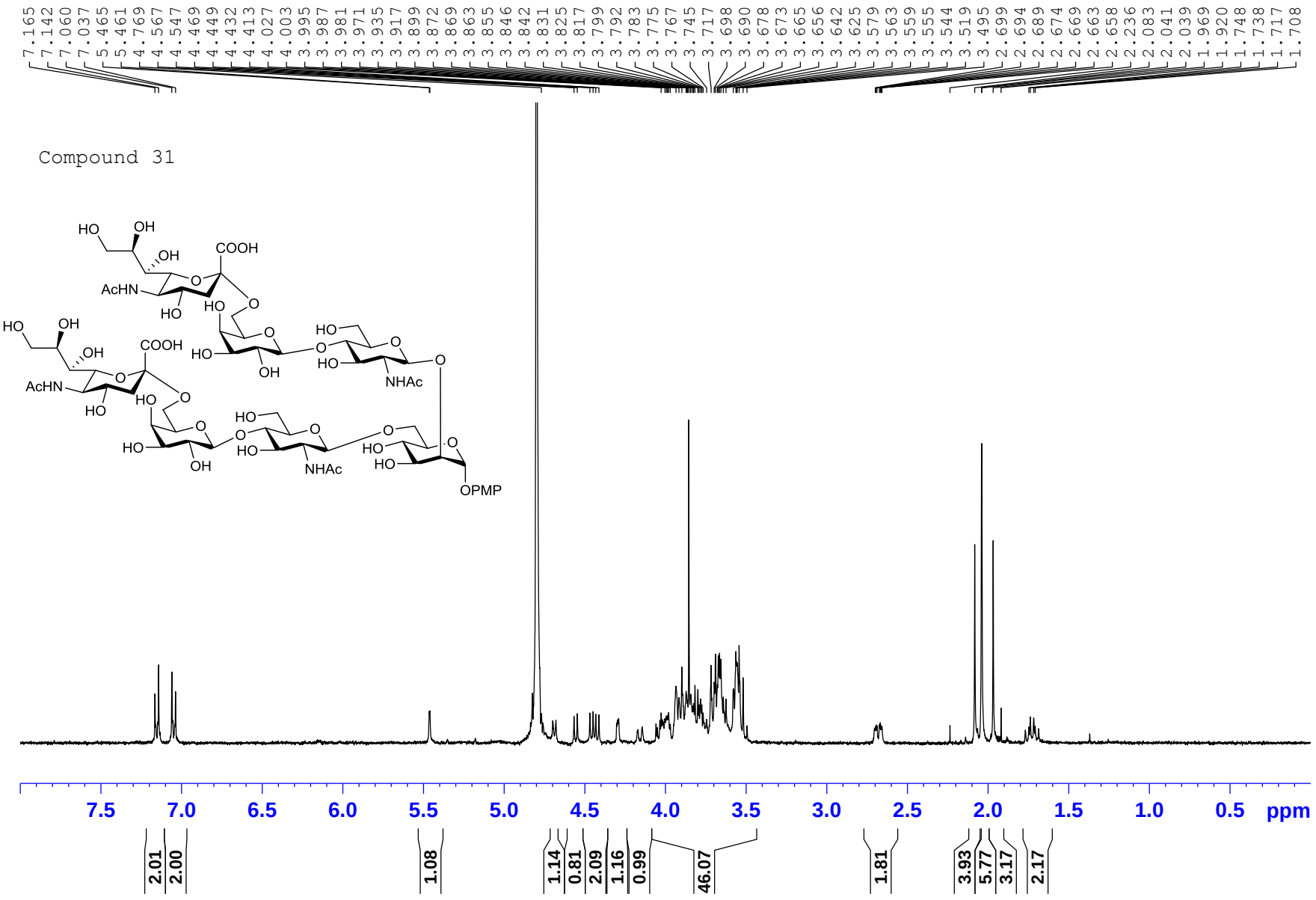
1.95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3.792
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3.665
3.656
3.642
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3.555
3.544
3.519
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1.738
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1.708
Compound 31
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OH
OH
COOH
AcHN
HO
HO
O
HO
O
HO
O
HO
O
HO
NHAc
OH
HO
OH
OH
COOH
AcHN
HO
HO
O
HO
O
HO
O
HO
O
HO
NHAc
HO
O
HO
HO
OPMP
7.5
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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
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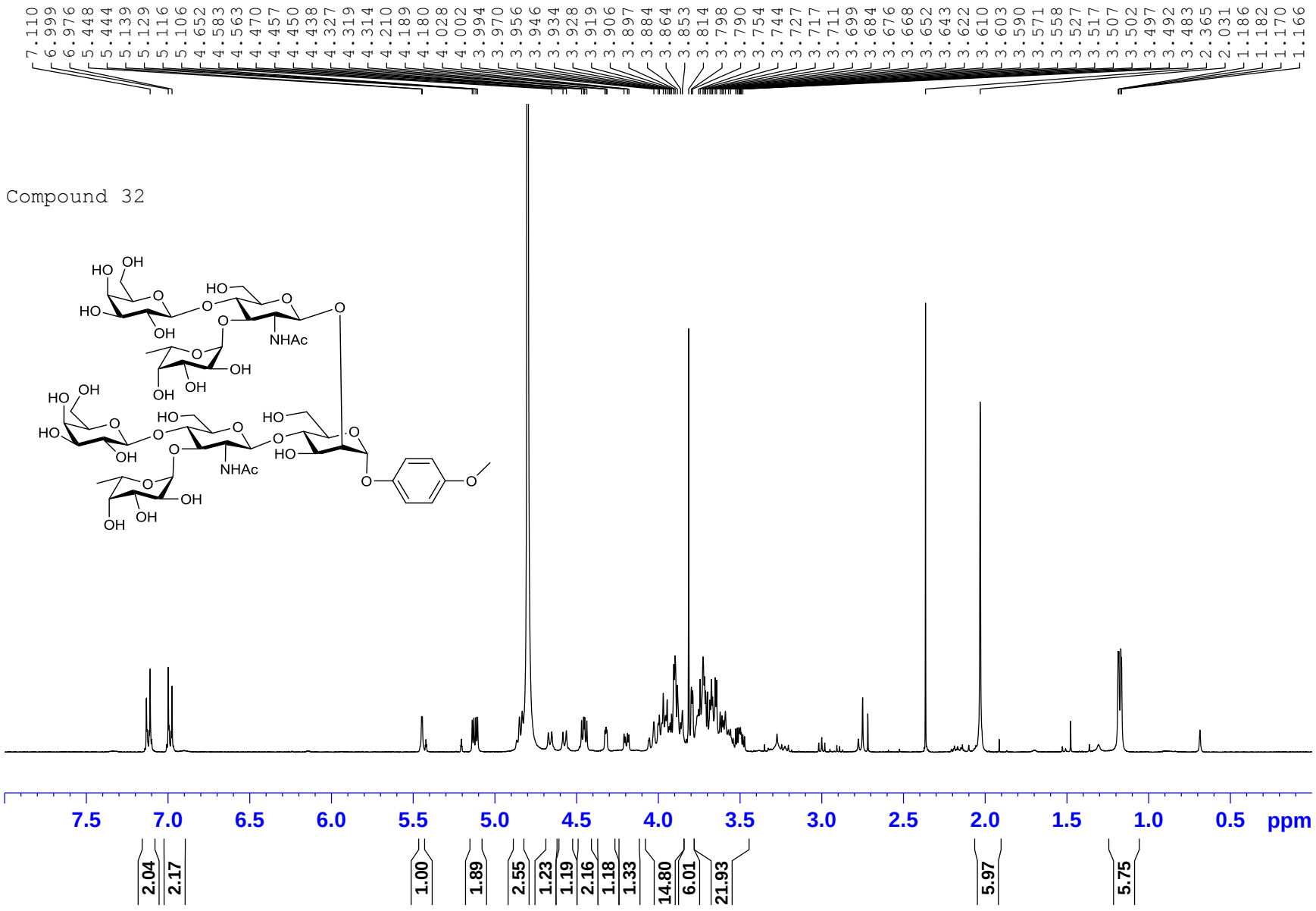
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3.946
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3.928
3.919
3.906
3.897
3.884
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3.853
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3.798
3.790
3.754
3.744
3.727
3.717
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1.182
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Compound 32
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6.0
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5.0
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4.0
3.5
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1.5
1.0
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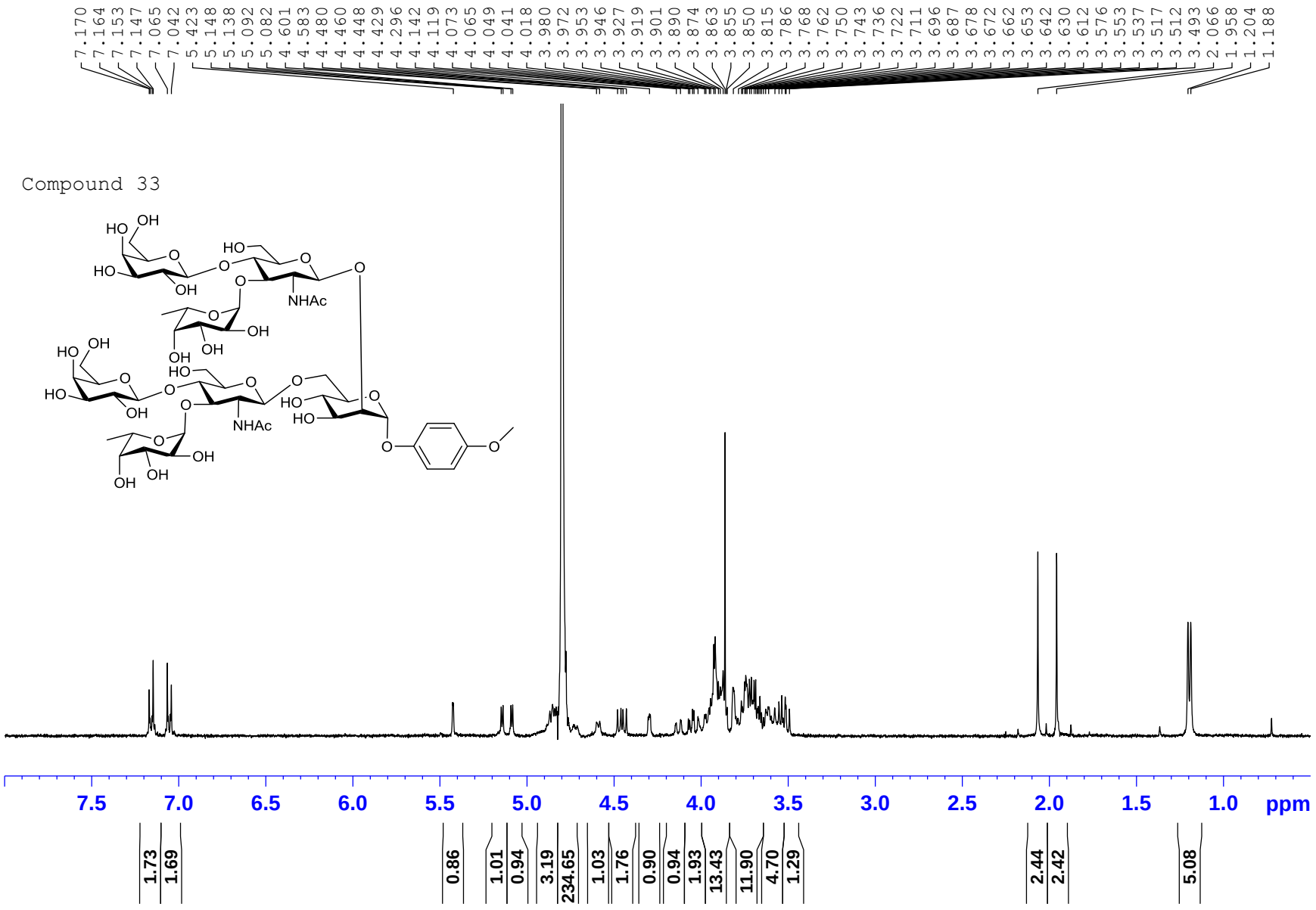
5.75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3.855
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3.815
3.786
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3.750
3.743
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3.722
3.711
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3.630
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3.537
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6.0
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5.0
4.5
4.0
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0.94
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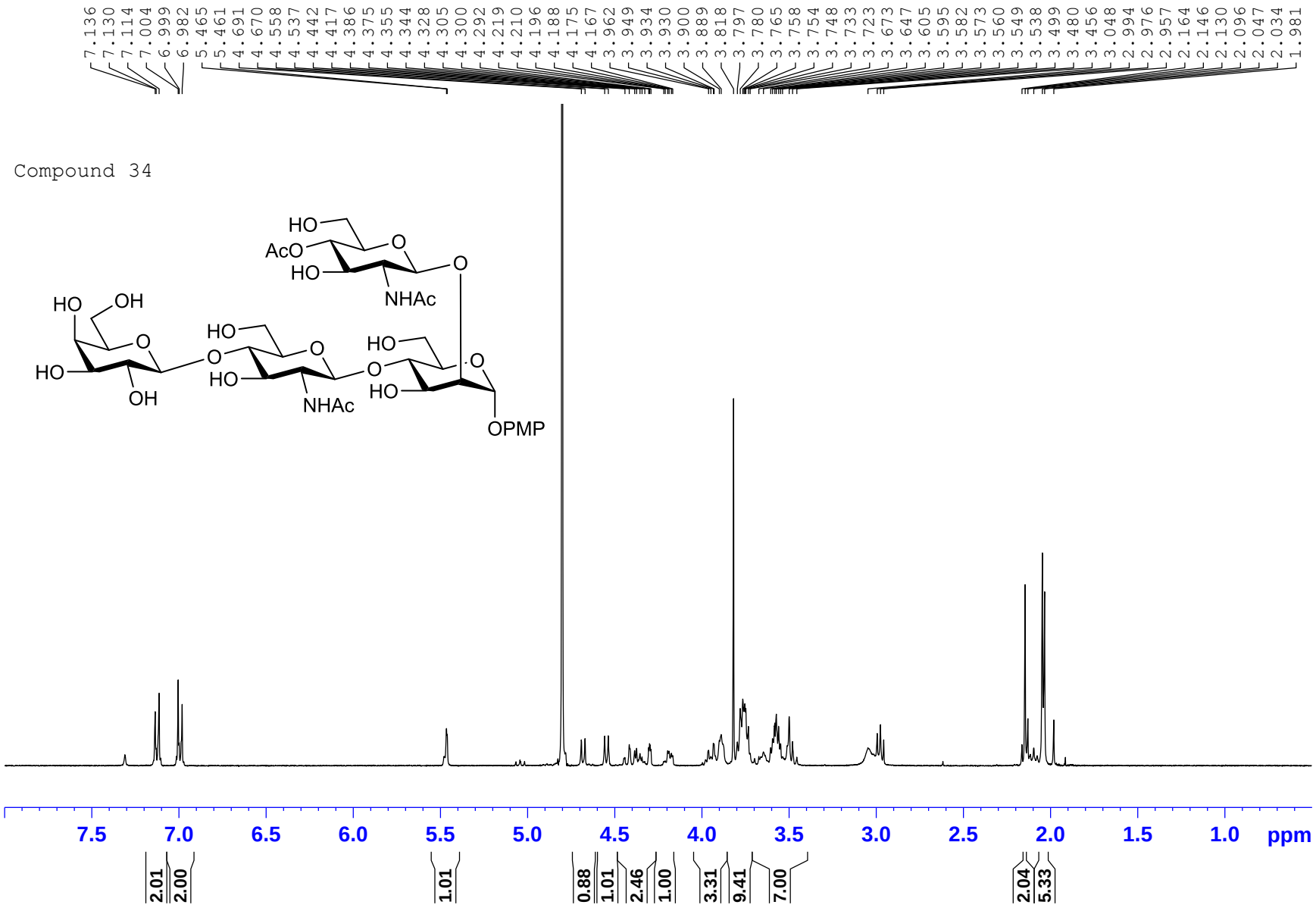
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4.196
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3.754
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3.733
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3.582
3.573
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3.538
3.499
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2.976
2.957
2.164
2.146
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2.047
2.034
1.981
Compound 34
HO
AcO
HO
O
O
NHAc
HO
OH
O
HO
OH
HO
O
O
HO
NHAc
HO
O
HO
O
HO
OPMP
7.5
7.0
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5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.01
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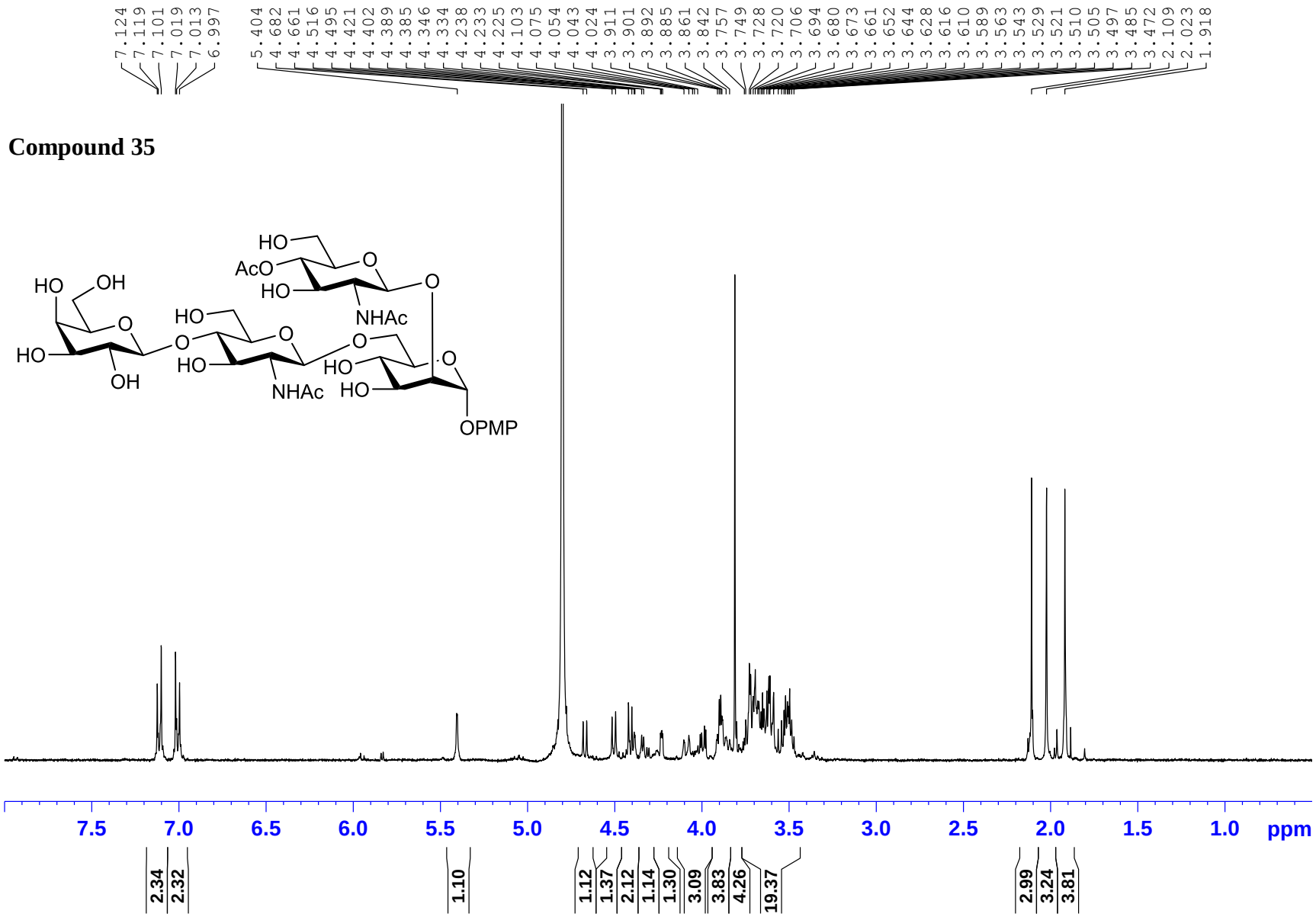
5.33

Compound 35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4.024
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3.529
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3.510
3.505
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2.109
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1.918
HO
OH
HO
O
HO
OH
HO
AcO
HO
O
O
NHAc
HO
O
O
HO
NHAc
HO
O
HO
HO
O
OPMP
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6.5
6.0
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5.0
4.5
4.0
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3.0
2.5
2.0
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ppm
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1.10
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1.14
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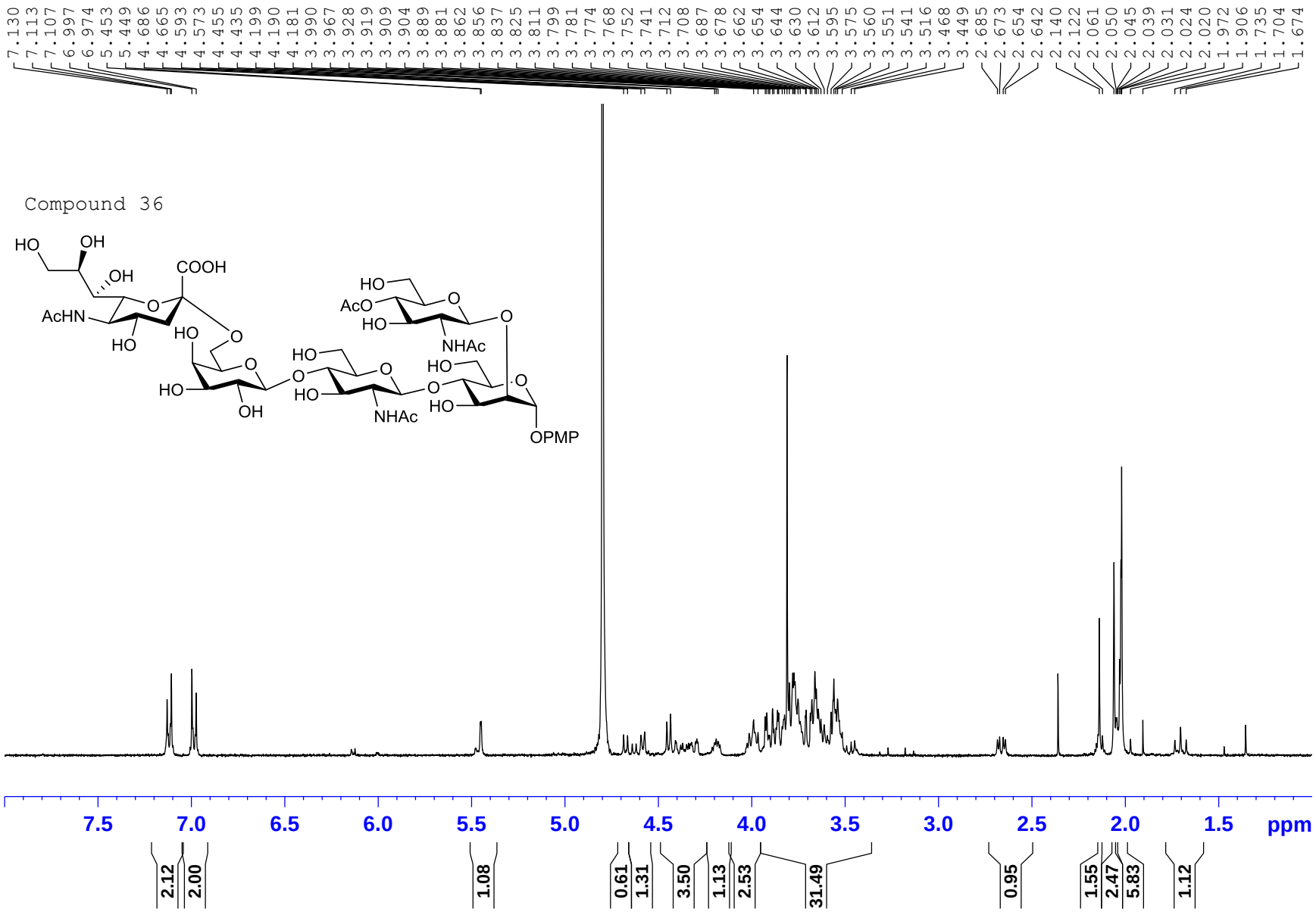
3.81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3.630
3.612
3.595
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3.560
3.551
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3.468
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2.685
2.673
2.654
2.642
2.140
2.122
2.061
2.050
2.045
2.039
2.031
2.024
2.020
1.972
1.906
1.735
1.704
1.674
Compound 36
HO
OH
OH
COOH
AcHN
HO
HO
O
HO
O
HO
OH
O
HO
HO
O
HO
NHAc
O
HO
AcO
HO
O
NHAc
HO
O
HO
OPMP
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
ppm
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2.00
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0.95
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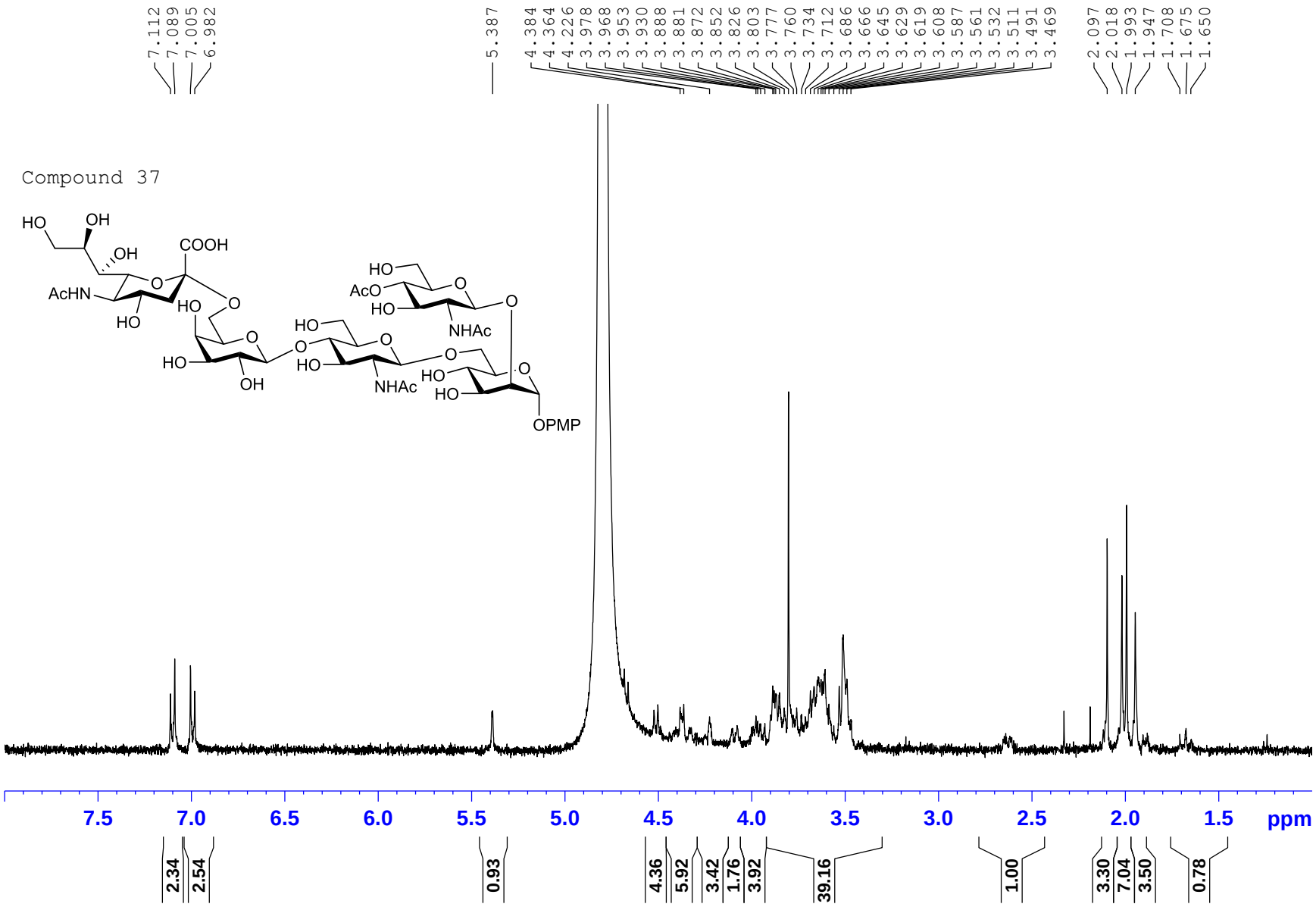
5.83
1.12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3.666
3.645
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3.561
3.532
3.511
3.491
3.469
2.097
2.018
1.993
1.947
1.708
1.675
1.650
Compound 37
HO
OH
OH
COOH
AcHN
HO
HO
O
HO
O
HO
OH
HO
O
HO
NHAc
HO
AcO
HO
O
NHAc
O
HO
HO
O
OPMP
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5.5
5.0
4.5
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3.0
2.5
2.0
1.5
ppm
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5.92
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1.76
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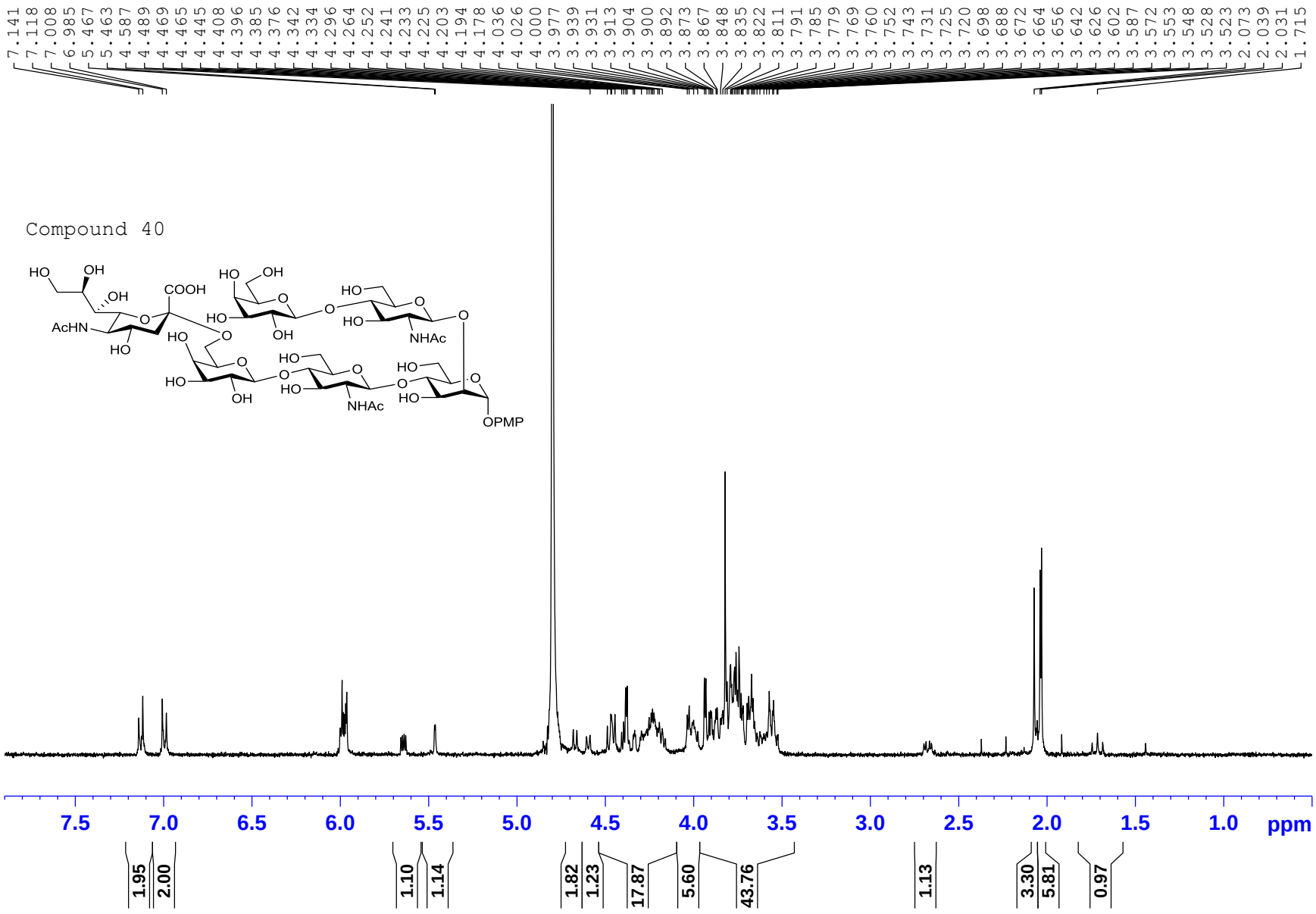
1.00
3.30
7.04
3.50
0.78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4.408
4.396
4.385
4.376
4.342
4.334
4.296
4.264
4.252
4.241
4.233
4.225
4.203
4.194
4.178
4.036
4.026
4.000
3.977
3.939
3.931
3.913
3.904
3.900
3.892
3.873
3.867
3.848
3.835
3.822
3.811
3.791
3.785
3.779
3.769
3.760
3.752
3.743
3.731
3.725
3.720
3.698
3.688
3.672
3.664
3.656
3.642
3.626
3.602
3.587
3.572
3.553
3.548
3.528
3.523
2.073
2.039
2.031
1.715
Compound 40
HO
OH
OH
COOH
AcHN
HO
O
HO
OH
HO
O
HO
OH
HO
O
HO
NHAc
HO
O
HO
O
HO
HO
O
HO
NHAc
HO
O
HO
OPMP
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
ppm
1.95
2.00
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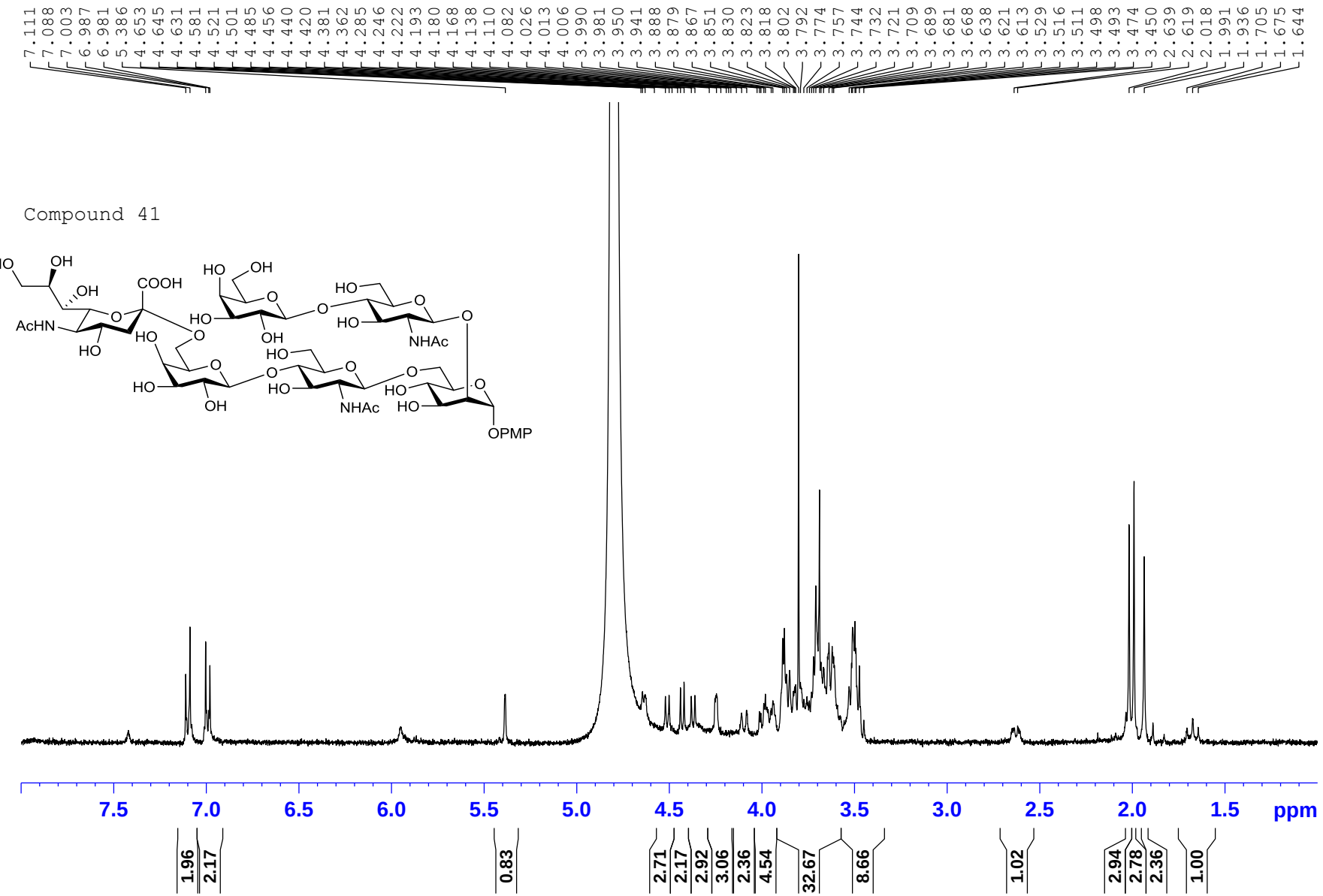
1.82
1.23
17.87
5.60
43.76
1.13
3.30
5.81
0.97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7.003
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4.581
4.521
4.501
4.485
4.456
4.440
4.420
4.381
4.362
4.285
4.246
4.222
4.193
4.180
4.168
4.138
4.110
4.082
4.026
4.013
4.006
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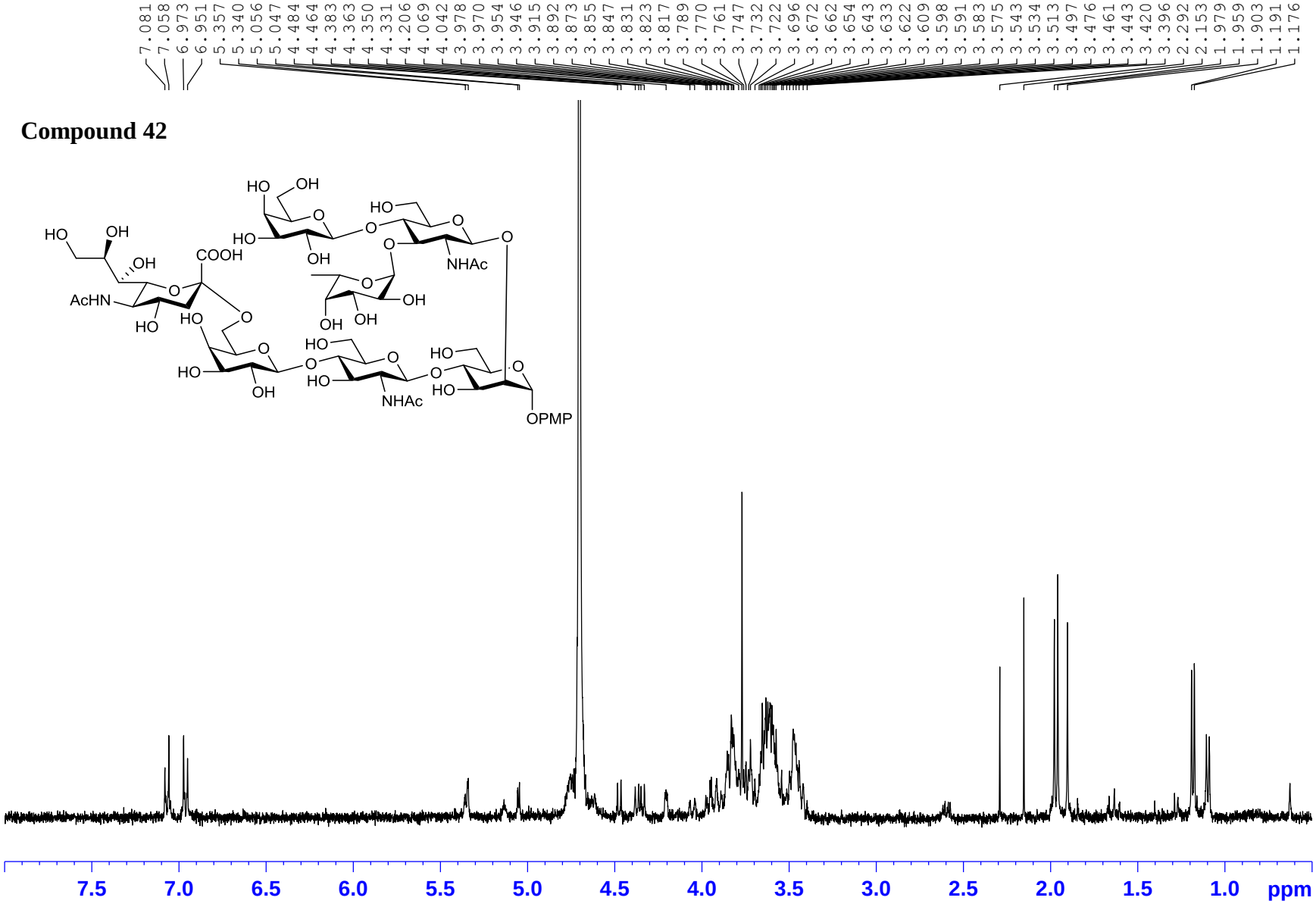
3.981
3.950
3.941
3.888
3.879
3.867
3.851
3.830
3.823
3.818
3.802
3.792
3.774
3.757
3.744
3.732
3.721
3.709
3.689
3.681
3.668
3.638
3.621
3.613
3.529
3.516
3.511
3.498
3.493
3.474
3.450
2.639
2.619
2.018
1.991
1.936
1.705
1.675
1.644
Compound 41
HO
OH
OH
COOH
AcHN
HO
O
HO
HO
OH
HO
OH
HO
O
HO
O
HO
NHAc
HO
O
HO
HO
OH
HO
O
HO
O
HO
NHAc
HO
O
HO
OPMP
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
ppm
1.96
2.17
0.83
2.71
2.17
2.92
3.06
2.36
4.54
32.67
8.66
1.02
2.94
2.78
2.36
1.00

Compound 42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4.331
4.206
4.069
4.042
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3.970
3.954
3.946
3.915
3.892
3.873
3.855
3.847
3.831
3.823
3.817
3.789
3.770
3.761
3.747
3.732
3.722
3.696
3.672
3.662
3.654
3.643
3.633
3.622
3.609
3.598
3.591
3.583
3.575
3.543
3.534
3.513
3.497
3.476
3.461
3.443
3.420
3.396
2.292
2.153
1.979
1.959
1.903
1.191
1.176
HO
OH
HO
OH
COOH
AcHN
HO
HO
O
HO
OH
HO
O
HO
O
HO
NHAc
O
O
OH
OH
OH
HO
HO
O
HO
OH
HO
O
HO
NHAc
HO
O
HO
O
OPMP
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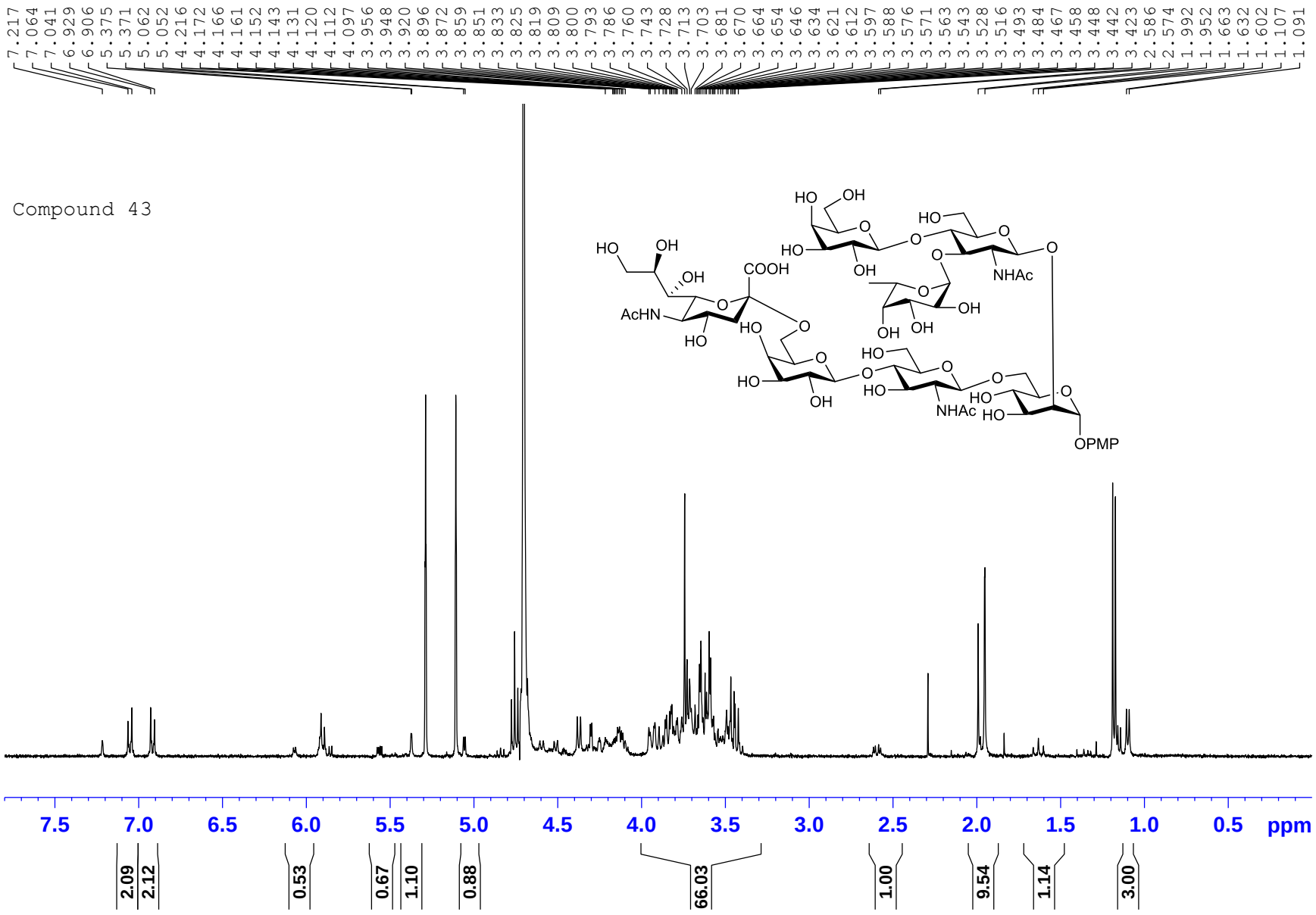
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm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6.906
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5.371
5.062
5.052
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4.172
4.166
4.161
4.152
4.143
4.131
4.120
4.112
4.097
3.956
3.948
3.920
3.896
3.872
3.859
3.851
3.833
3.825
3.819
3.809
3.800
3.793
3.786
3.760
3.743
3.728
3.713
3.703
3.681
3.670
3.664
3.654
3.646
3.634
3.621
3.612
3.597
3.588
3.576
3.571
3.563
3.543
3.528
3.516
3.493
3.484
3.467
3.458
3.448
3.442
3.423
2.586
2.574
1.992
1.952
1.663
1.632
1.602
1.107
1.091
Compound 43
HO
OH
COOH
AcHN
NHAc
OPMP
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
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2.12
0.53
0.67
1.10
0.88
66.03
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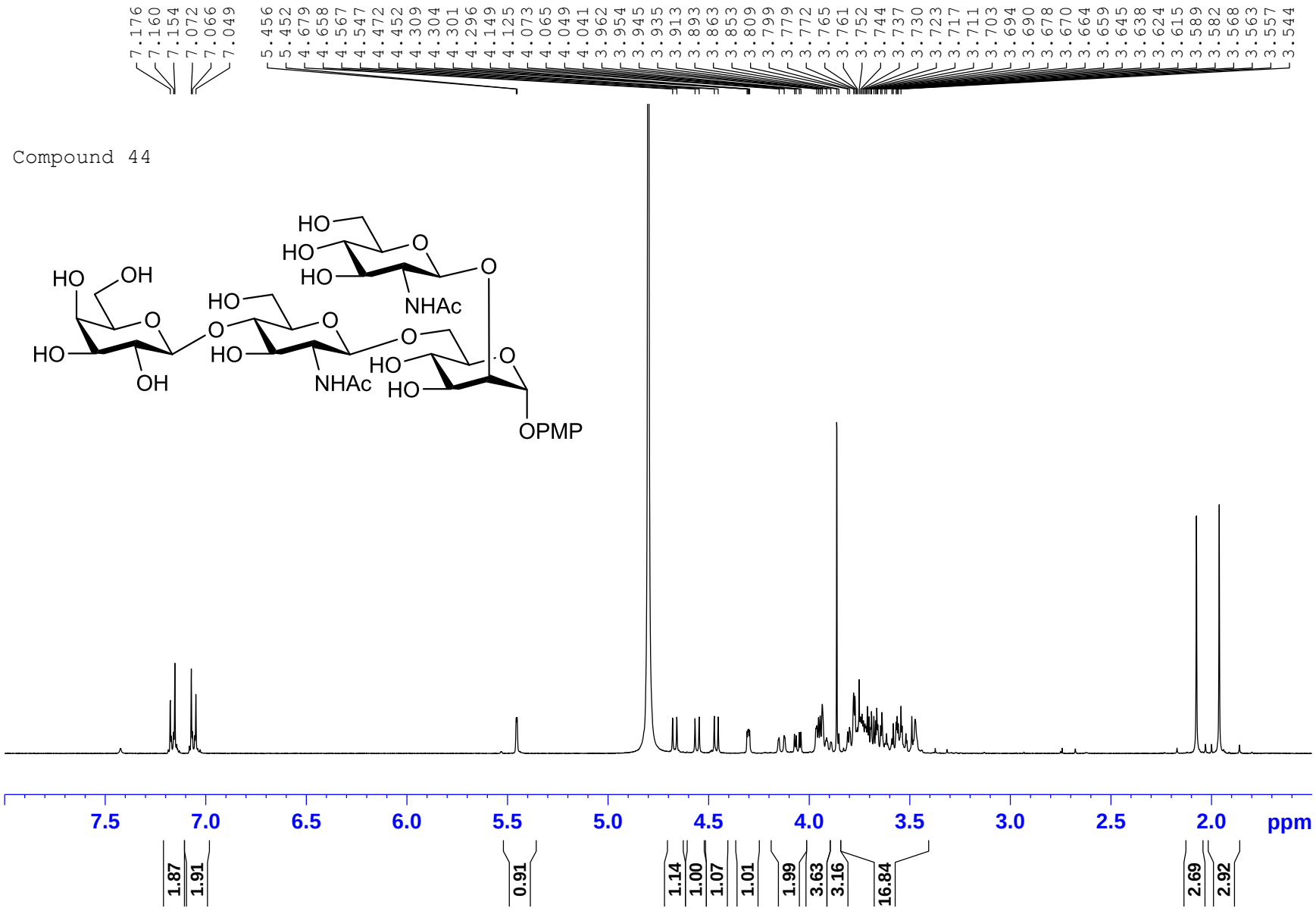
1.14
3.00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5.452
4.679
4.658
4.567
4.547
4.472
4.452
4.309
4.304
4.301
4.296
4.149
4.125
4.073
4.065
4.049
4.041
3.962
3.954
3.945
3.935
3.913
3.893
3.863
3.853
3.809
3.799
3.779
3.772
3.765
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3.752
3.744
3.737
3.730
3.723
3.717
3.711
3.703
3.694
3.690
3.678
3.670
3.664
3.659
3.645
3.638
3.624
3.615
3.589
3.582
3.568
3.563
3.557
3.544
Compound 44
HO
OH
HO
O
OH
O
HO
HO
HO
O
NHAc
HO
HO
O
O
HO
NHAc
HO
O
HO
HO
OPMP
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
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0.91
1.14
1.00
1.07
1.01
1.99
3.63
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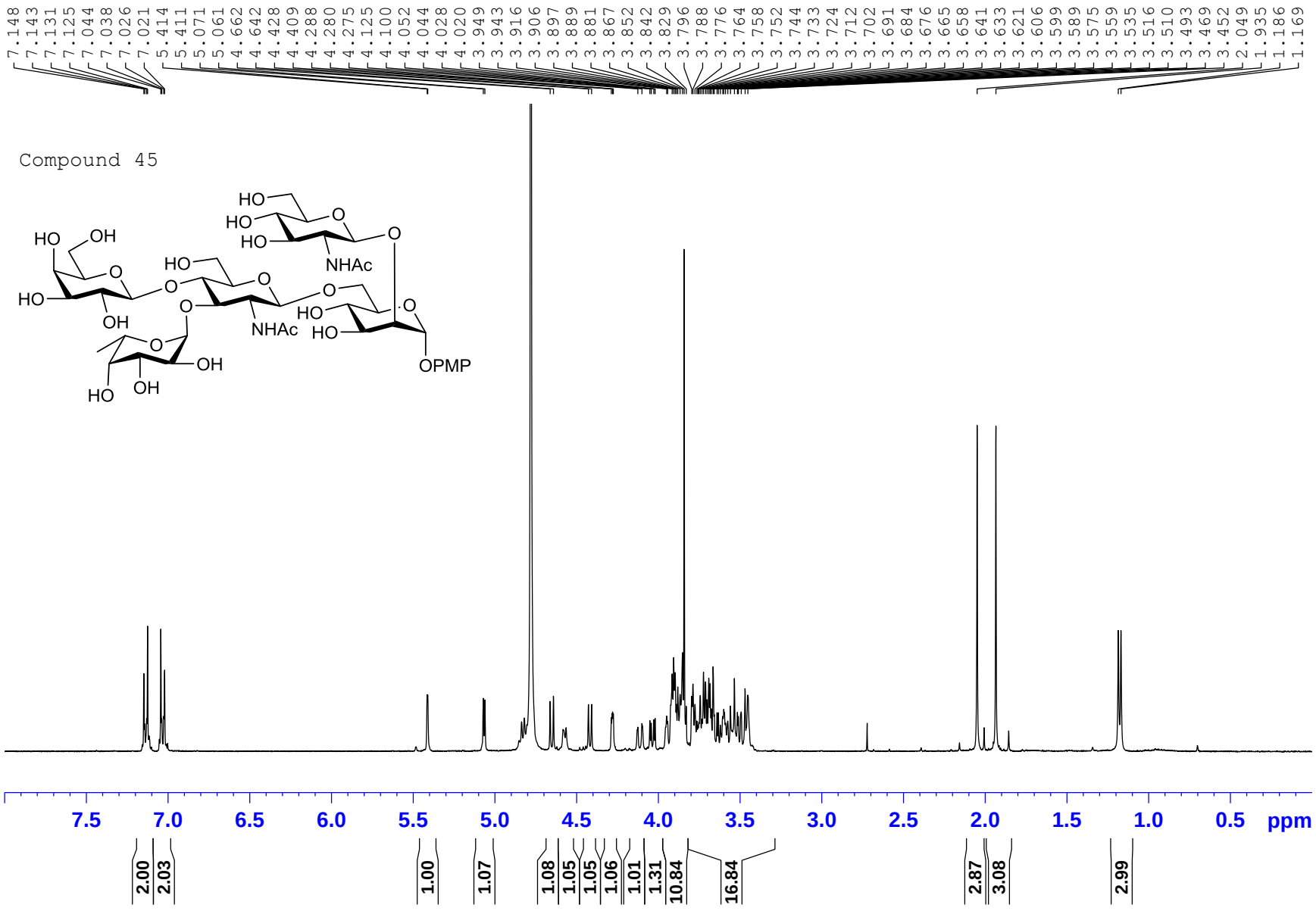
16.84
2.69
2.92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5.071
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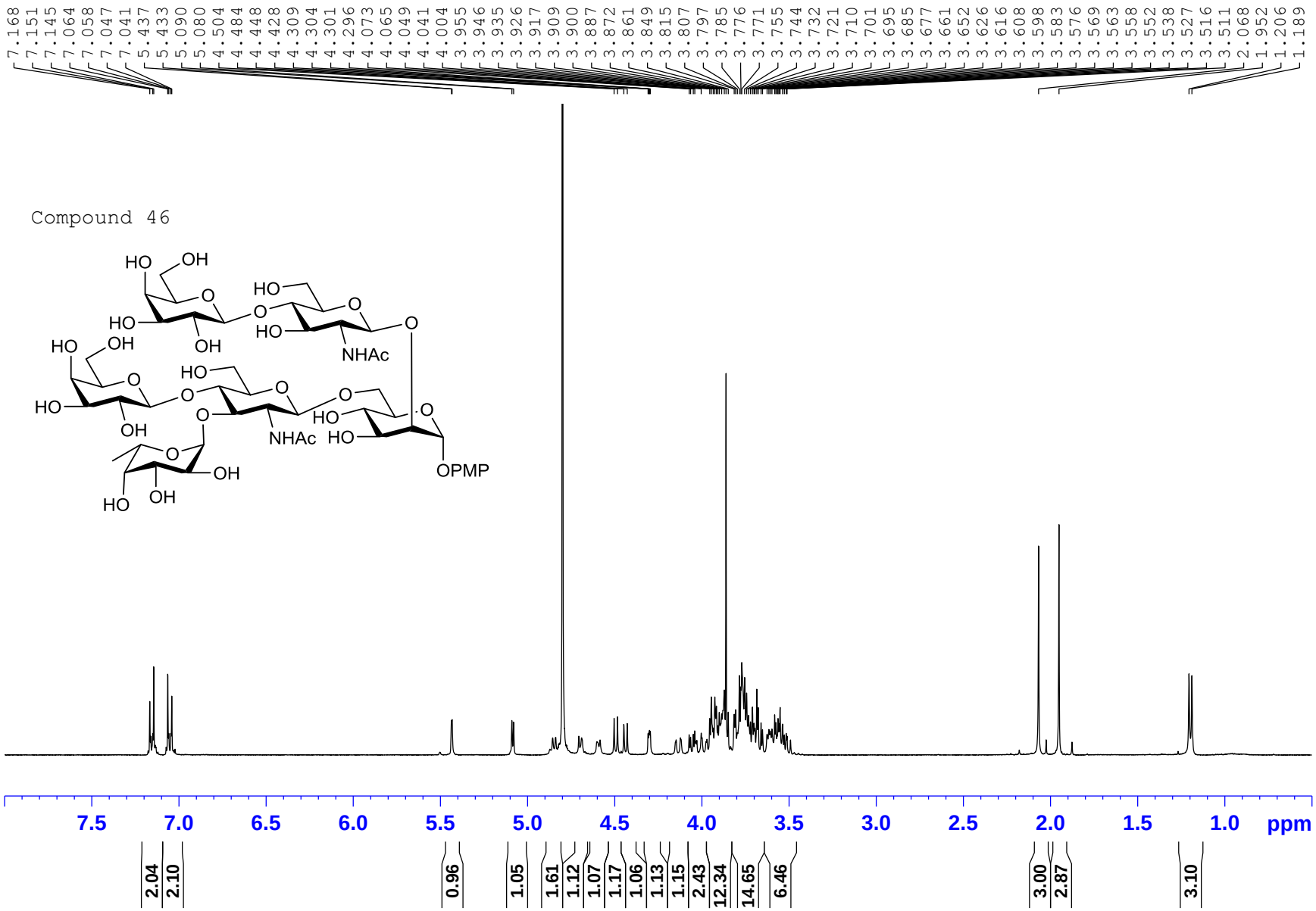
4.642
4.428
4.409
4.288
4.280
4.275
4.125
4.100
4.052
4.044
4.028
4.020
3.949
3.943
3.916
3.906
3.897
3.889
3.881
3.867
3.852
3.842
3.829
3.796
3.788
3.776
3.764
3.758
3.752
3.744
3.733
3.724
3.712
3.702
3.691
3.684
3.676
3.665
3.658
3.641
3.633
3.621
3.606
3.599
3.589
3.575
3.559
3.535
3.516
3.510
3.493
3.469
3.452
2.049
1.935
1.186
1.169
Compound 45
HO
HO
HO
O
NHAc
HO
OH
O
HO
HO
O
O
O
HO
NHAc
O
HO
HO
OPMP
OH
O
OH
HO
OH
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
2.00
2.03
1.00
1.07
1.08
1.05
1.05
1.06
1.01
1.31
10.84
16.84
2.87
3.08
2.99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4.484
4.448
4.428
4.309
4.304
4.301
4.296
4.073
4.065
4.049
4.041
4.004
3.955
3.946
3.935
3.926
3.917
3.909
3.900
3.887
3.872
3.861
3.849
3.815
3.807
3.797
3.785
3.776
3.771
3.755
3.744
3.732
3.721
3.710
3.701
3.695
3.685
3.677
3.661
3.652
3.626
3.616
3.608
3.598
3.583
3.576
3.569
3.563
3.558
3.552
3.538
3.527
3.516
3.511
2.068
1.952
1.206
1.189
Compound 46
HO
OH
O
HO
NHAc
OPMP
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
ppm
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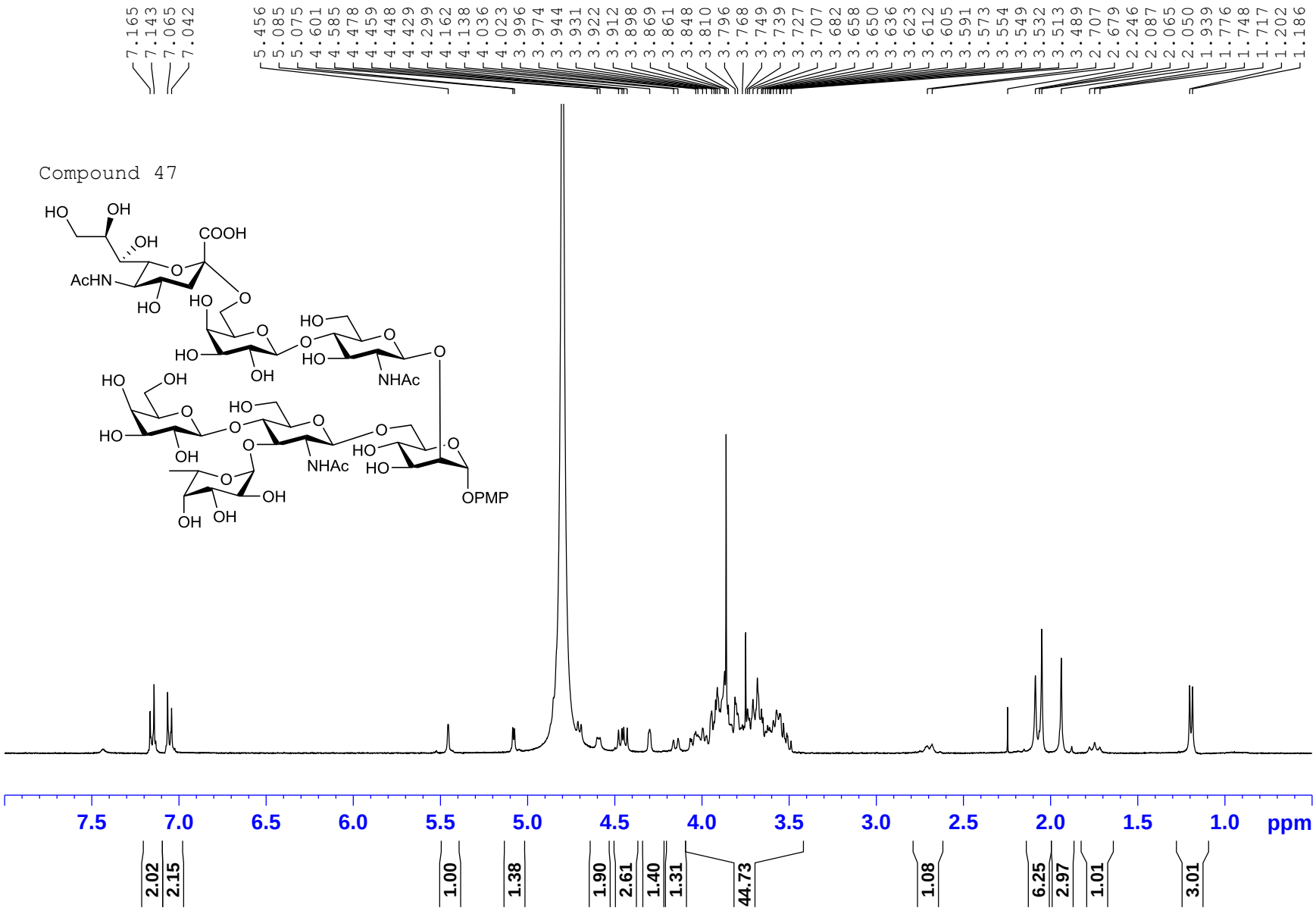
2.10
0.96
1.05
1.61
1.12
1.07
1.17
1.06
1.13
1.15
2.43
12.34
14.65
6.46
3.00
2.87
3.10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4.138
4.036
4.023
3.996
3.974
3.944
3.931
3.922
3.912
3.898
3.869
3.861
3.848
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3.796
3.768
3.749
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3.682
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3.650
3.636
3.623
3.612
3.605
3.591
3.573
3.554
3.549
3.532
3.513
3.489
2.707
2.679
2.246
2.087
2.065
2.050
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1.776
1.748
1.717
1.202
1.186
Compound 47
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OH
OH
COOH
AcHN
HO
HO
O
HO
O
HO
O
HO
O
HO
NHAc
HO
OH
HO
O
HO
O
HO
O
O
HO
HO
NHAc
OH
O
HO
OPMP
OH
OH
OH
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
ppm
2.02
2.15
1.00
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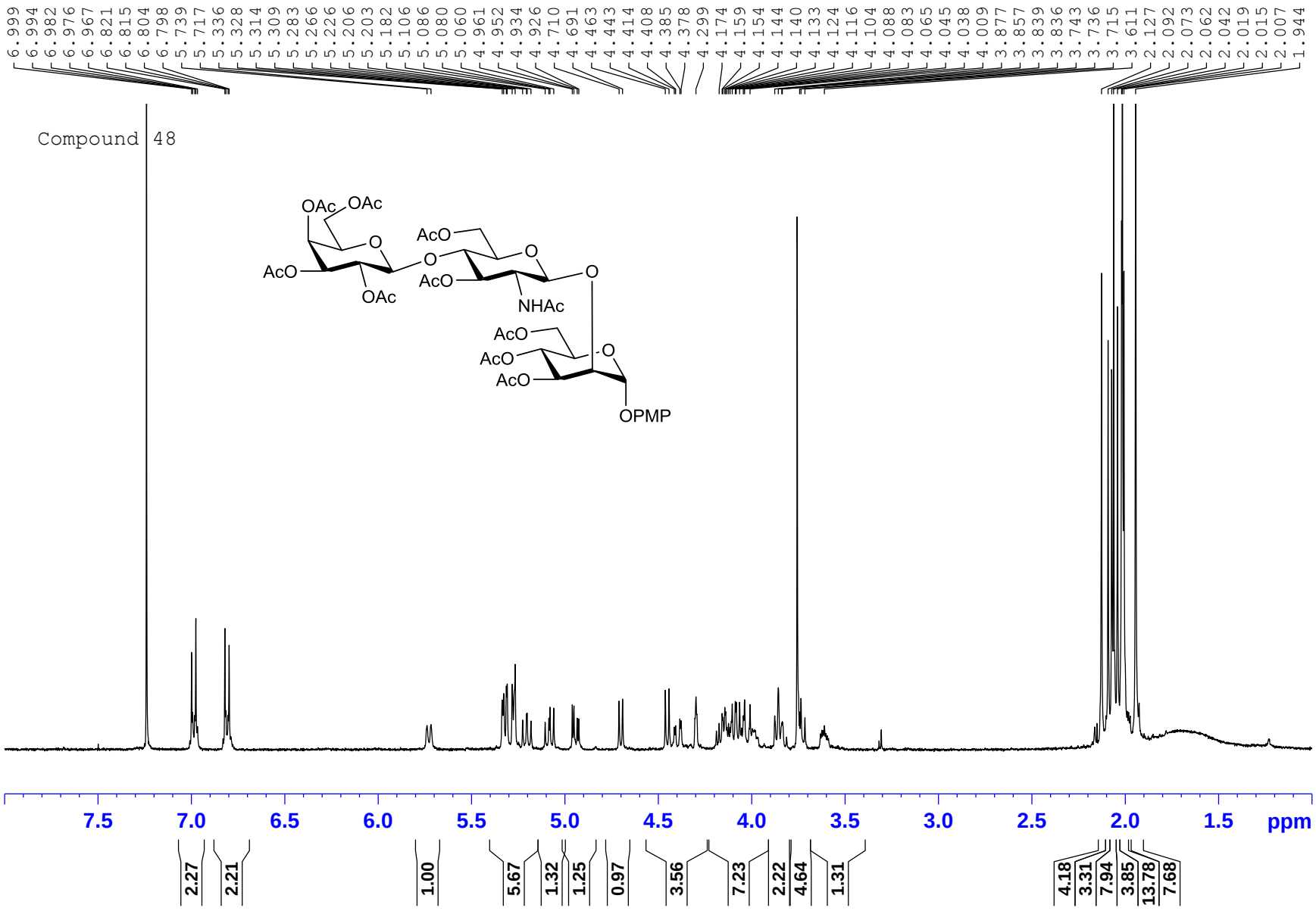
1.40
1.31
44.73
1.08
6.25
2.97
1.01
3.01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5.328
5.314
5.309
5.283
5.266
5.226
5.206
5.203
5.182
5.106
5.086
5.080
5.060
4.961
4.952
4.934
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4.408
4.385
4.378
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4.174
4.159
4.154
4.144
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4.133
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4.116
4.104
4.088
4.083
4.065
4.045
4.038
4.009
3.877
3.857
3.839
3.836
3.743
3.736
3.715
3.611
2.127
2.092
2.073
2.062
2.042
2.019
2.015
2.007
1.944
Compound 48
OAc
OAc
AcO
OAc
O
AcO
O
AcO
O
NHAc
O
AcO
AcO
AcO
O
OPMP
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
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1.00
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1.32
1.25
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2.22
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1.31
4.18
3.31
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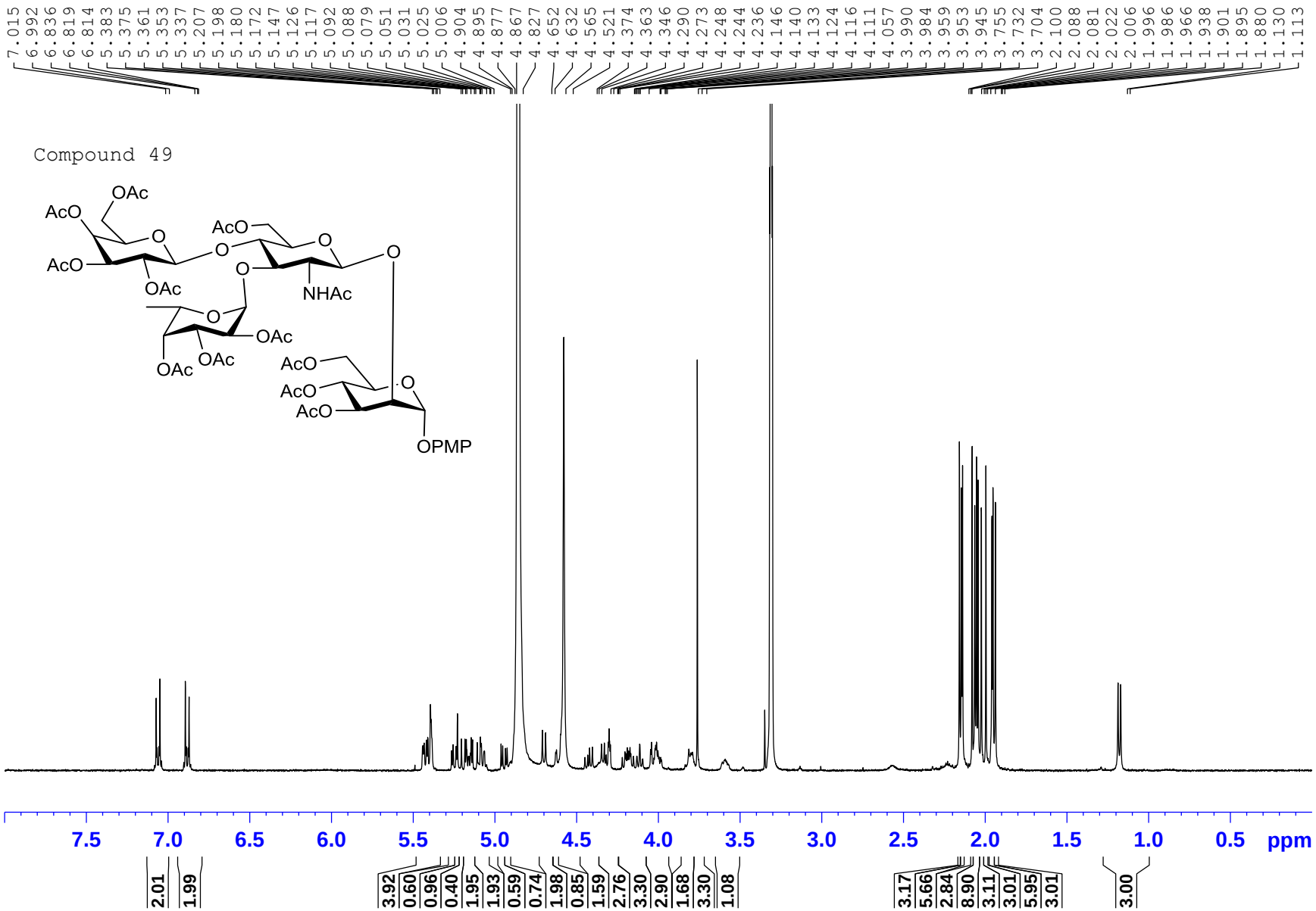
3.85
13.78
7.68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5.180
5.172
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5.006
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4.632
4.565
4.521
4.374
4.363
4.346
4.290
4.273
4.248
4.244
4.236
4.146
4.140
4.133
4.124
4.116
4.111
4.057
3.990
3.984
3.959
3.953
3.945
3.755
3.732
3.704
2.100
2.088
2.081
2.022
2.006
1.996
1.986
1.966
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1.901
1.895
1.880
1.130
1.113
Compound 49
OAc
AcO
AcO
OAc
O
AcO
O
O
NHAc
O
OAc
OAc
OAc
AcO
AcO
AcO
O
OPMP
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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
2.01
1.99
3.92
0.60
0.96
0.40
1.95
1.93
0.59
0.74
1.98
0.85
1.59
2.76
3.30
2.90
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3.17
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3.11
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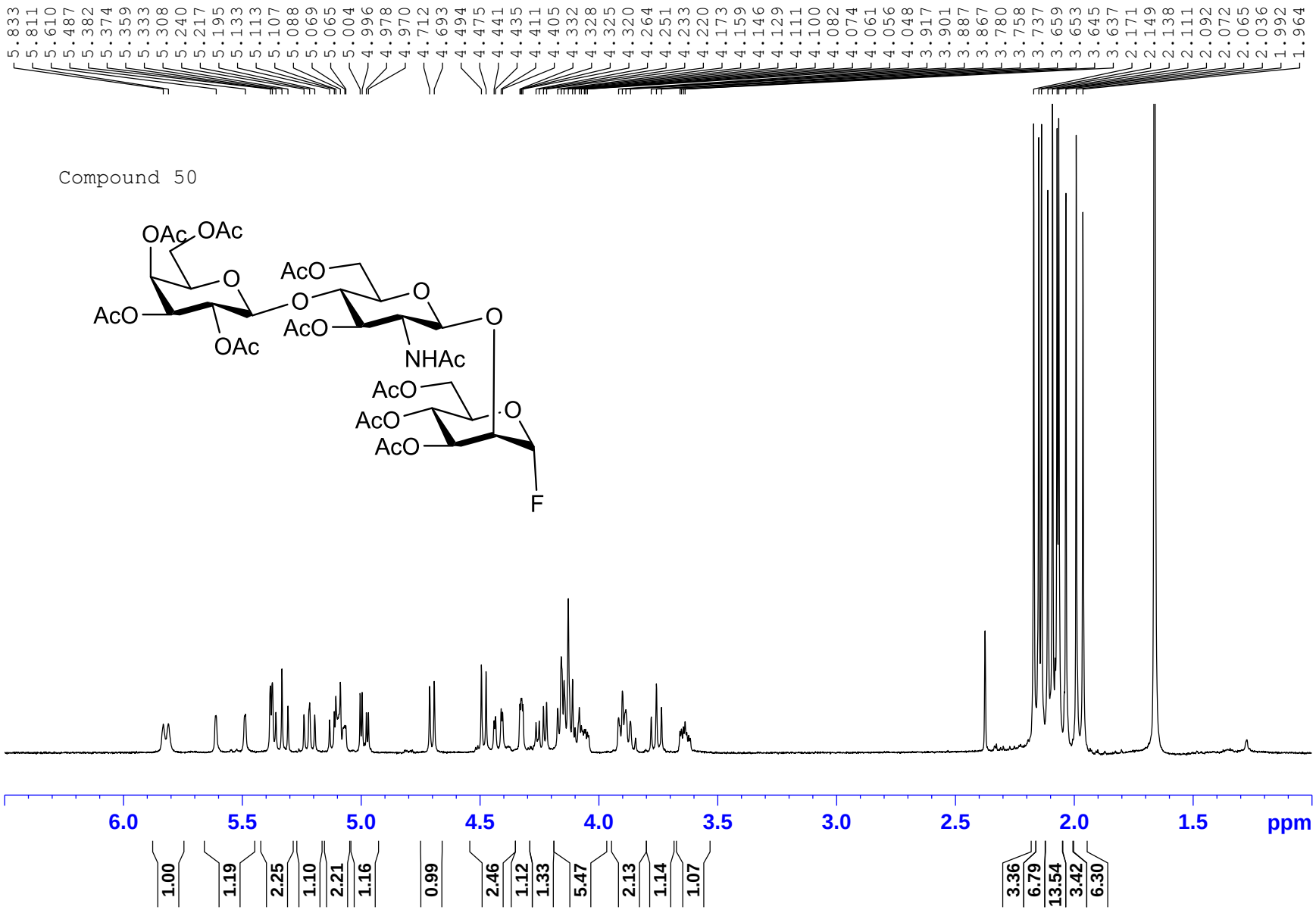
5.95
3.01
3.00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5.088
5.069
5.065
5.004
4.996
4.978
4.970
4.712
4.693
4.494
4.475
4.441
4.435
4.411
4.405
4.332
4.328
4.325
4.320
4.264
4.251
4.233
4.220
4.173
4.159
4.146
4.129
4.111
4.100
4.082
4.074
4.061
4.056
4.048
3.917
3.901
3.887
3.867
3.780
3.758
3.737
3.659
3.653
3.645
3.637
2.171
2.149
2.138
2.111
2.092
2.072
2.065
2.036
1.992
1.964
Compound 50
OAc
OAc
O
AcO
OAc
AcO
O
AcO
O
O
NHAc
AcO
AcO
AcO
O
F
6.0
5.5
5.0
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4.0
3.5
3.0
2.5
2.0
1.5
ppm
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2.21
1.16
0.99
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5.47
2.13
1.14
1.07
3.36
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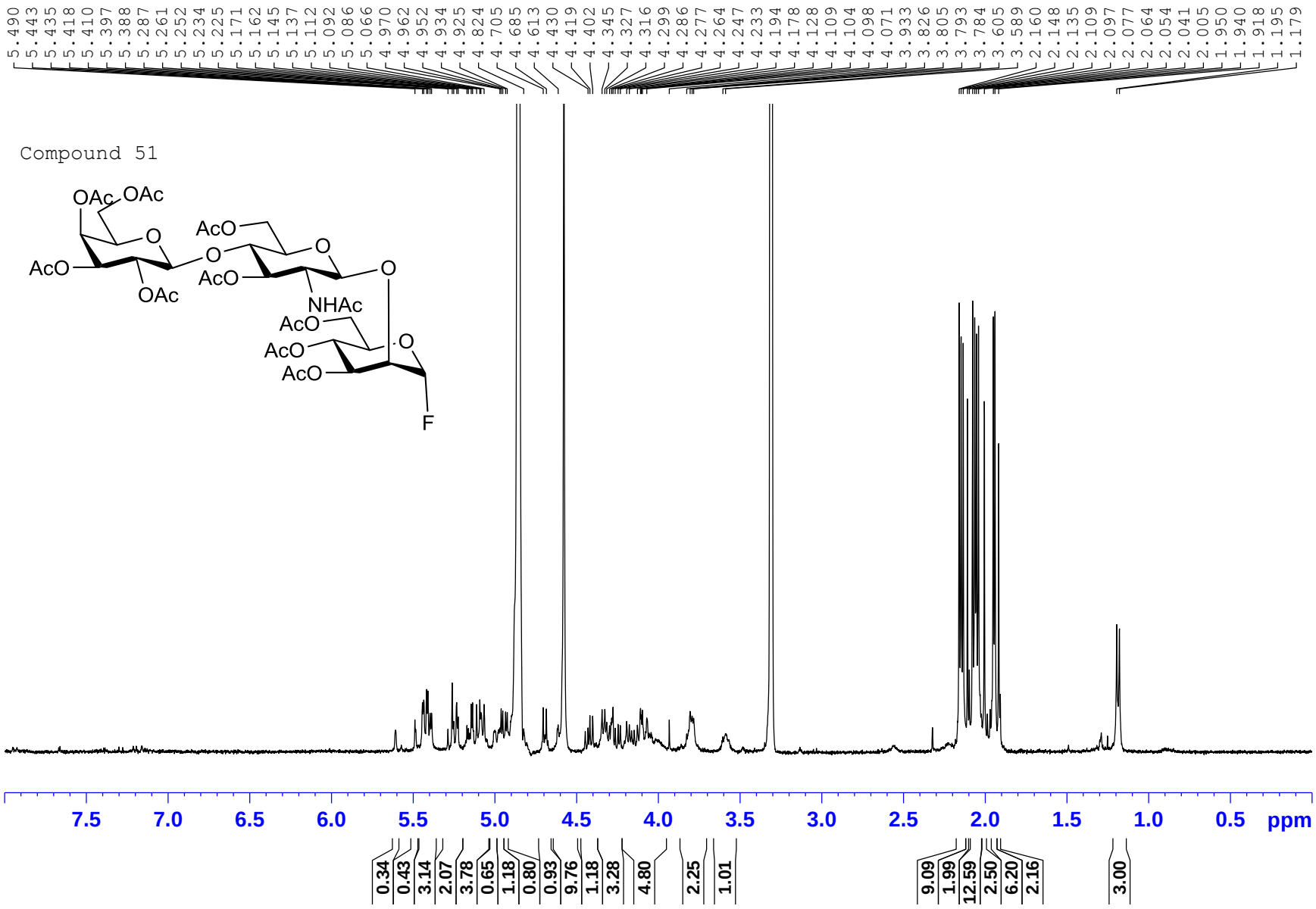
3.42
6.30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5.418
5.410
5.397
5.388
5.287
5.261
5.252
5.234
5.225
5.171
5.162
5.145
5.137
5.112
5.092
5.086
5.066
4.970
4.962
4.952
4.934
4.925
4.824
4.705
4.685
4.613
4.430
4.419
4.402
4.345
4.327
4.316
4.299
4.286
4.277
4.264
4.247
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4.194
4.178
4.128
4.109
4.104
4.098
4.071
3.933
3.826
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3.793
3.784
3.605
3.589
2.160
2.148
2.135
2.109
2.097
2.077
2.064
2.054
2.041
2.005
1.950
1.940
1.918
1.195
1.179
Compound 51
OAc
OAc
AcO
OAc
AcO
AcO
NHAc
AcO
AcO
AcO
F
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
0.34
0.43
3.14
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3.78
0.65
1.18
0.80
0.93
9.76
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9.09
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6.20
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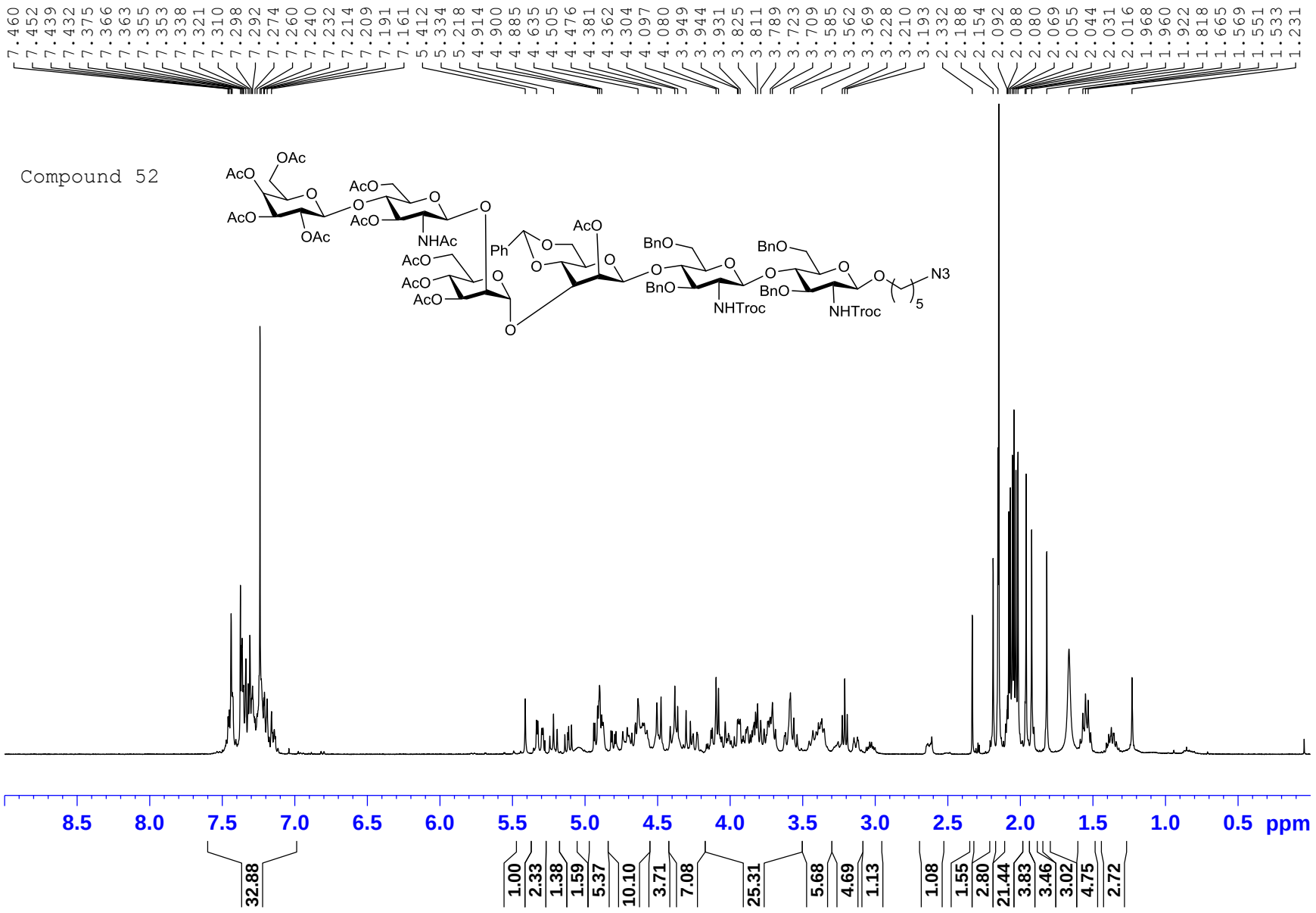
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7.298
7.292
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5.218
4.914
4.900
4.885
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4.505
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3.944
3.931
3.825
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3.789
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2.031
2.016
1.968
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1.231
Compound 52
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
32.88
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1.59
5.37
10.10
3.71
7.08
25.31
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1.08
1.55
2.80
21.44
3.83
3.46
3.02
4.75
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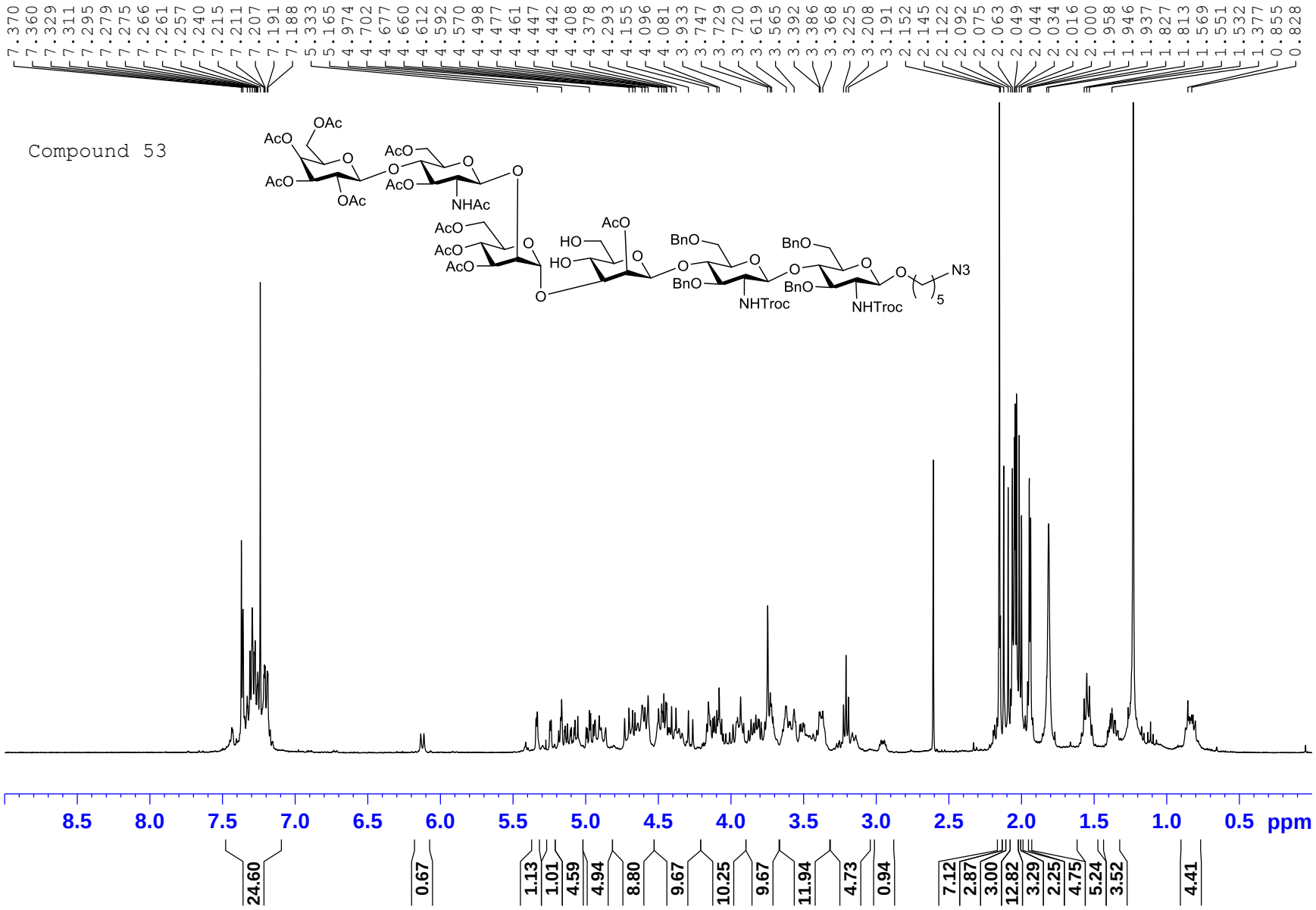
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7.207
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4.677
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2.000
1.958
1.946
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1.377
0.855
0.828
Compound 53
OAc
AcO
AcO
OAc
AcO
AcO
NHAc
AcO
AcO
AcO
HO
HO
AcO
BnO
BnO
NHTroc
BnO
BnO
NHTroc
N3
5
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
24.60
0.67
1.13
1.01
4.59
4.94
8.80
9.67
10.25
9.67
11.94
4.73
0.94
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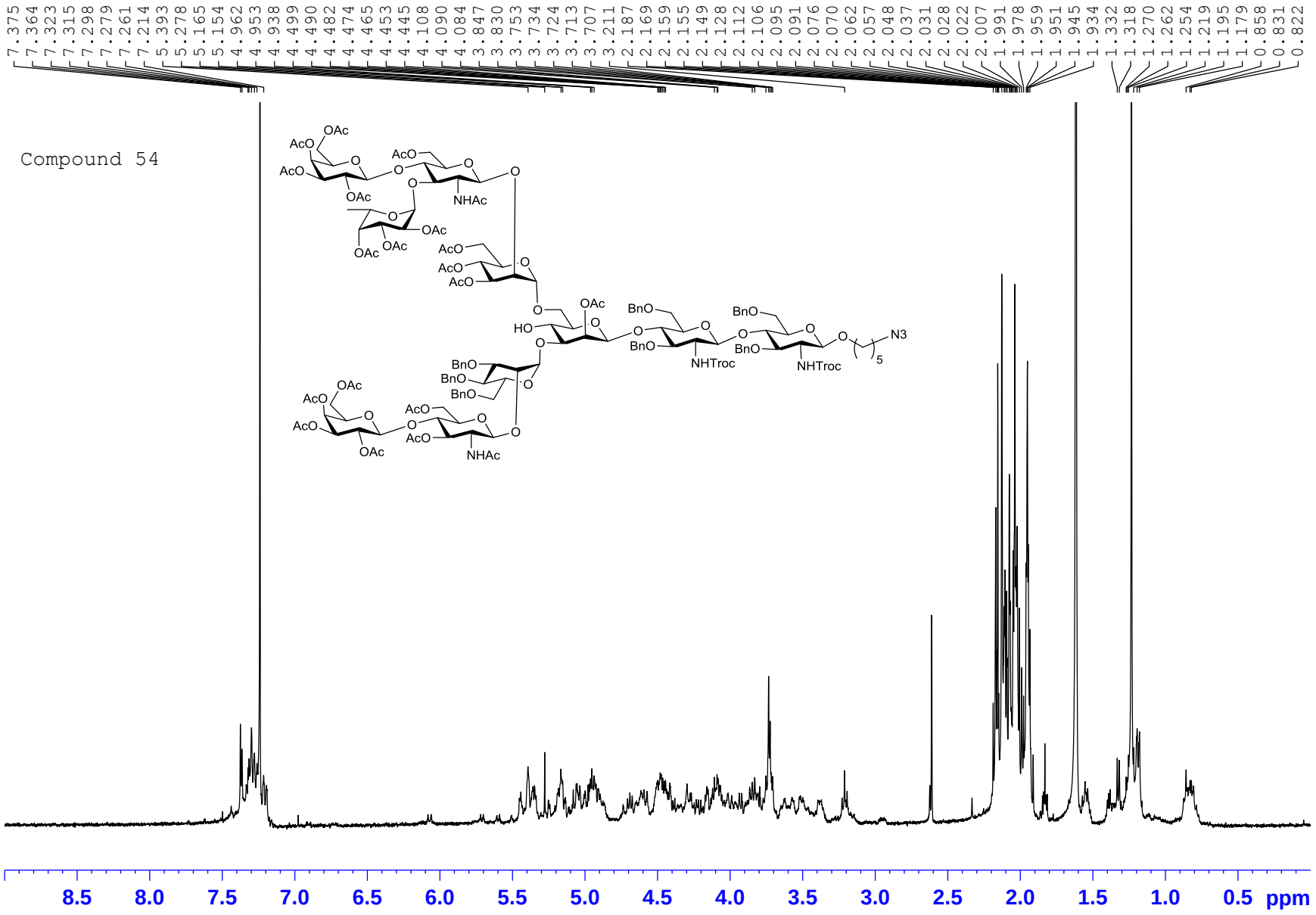
2.87
3.00
12.82
3.29
2.25
4.75
5.24
3.52
4.41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7.261
7.214
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4.953
4.938
4.499
4.490
4.482
4.474
4.465
4.453
4.445
4.108
4.090
4.084
3.847
3.830
3.753
3.734
3.724
3.713
3.707
3.211
2.187
2.169
2.159
2.155
2.149
2.128
2.112
2.106
2.095
2.091
2.076
2.070
2.062
2.057
2.048
2.037
2.031
2.028
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2.007
1.991
1.978
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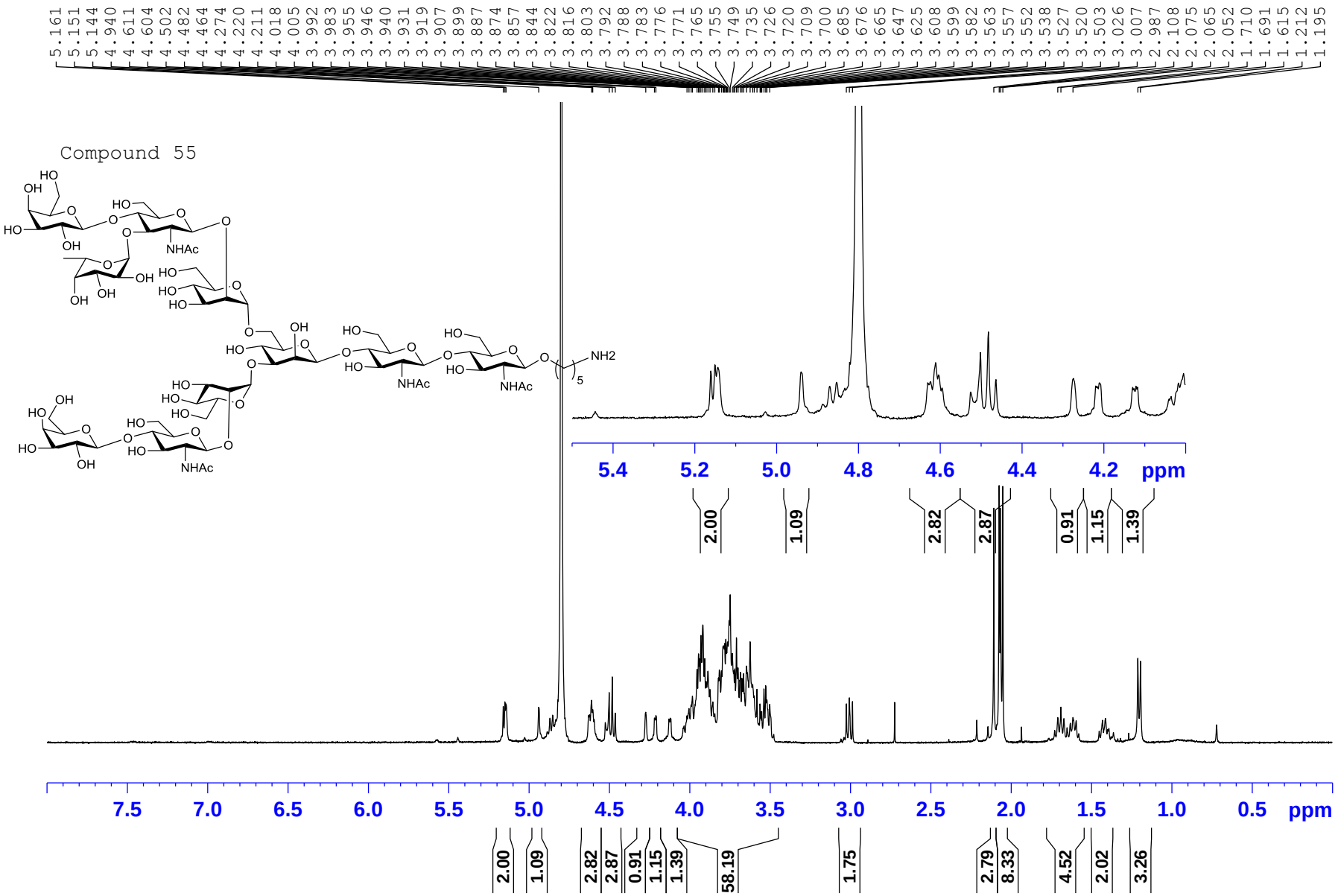
1.934
1.332
1.318
1.270
1.262
1.254
1.219
1.195
1.179
0.858
0.831
0.822
Compound 54
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm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5.144
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4.611
4.604
4.502
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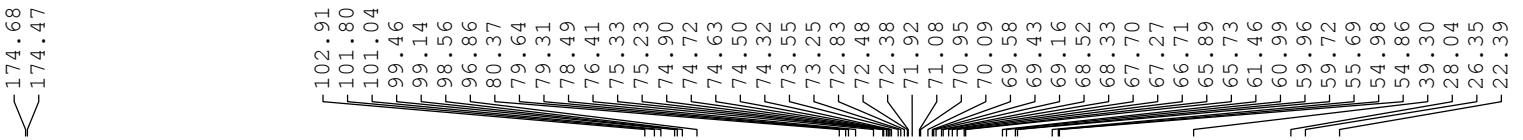
4.464
4.274
4.220
4.211
4.018
4.005
3.992
3.983
3.955
3.946
3.940
3.931
3.919
3.907
3.899
3.887
3.874
3.857
3.844
3.822
3.816
3.803
3.792
3.788
3.783
3.776
3.771
3.765
3.755
3.749
3.735
3.726
3.720
3.709
3.700
3.685
3.676
3.665
3.647
3.625
3.608
3.599
3.582
3.563
3.557
3.552
3.538
3.527
3.520
3.503
3.026
3.007
2.987
2.108
2.075
2.065
2.052
1.710
1.691
1.615
1.212
1.195
Compound 55
NHAc
NH2
5.4
5.2
5.0
4.8
4.6
4.4
4.2
ppm
2.00
1.09
2.82
2.87
0.91
1.15
1.39
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
2.00
1.09
2.82
2.87
0.91
1.15
1.39
58.19
1.75
2.79
8.33
4.52
2.02
3.26



COmpound 55_carbon