Electronic Supplementary Material (ESI) for Chemical Science.

Discovery of Rare Sulfated *N*-Unsubstituted Glucosamine Based Heparan Sulfate Analogs Selectively Activating Chemokines.

Prashant Jain,[b,d] Chethan D. Shanthamurthy,[b,d] Shani Leviatan Ben-Arye,[a] Robert J. Woods,[c] Raghavendra Kikkeri*[b] , Vered Padler-Karavani,*[a]

[a]Department of Cell Research and Immunology, The George S. Wise Faculty of Life Sciences, Tel Aviv University, Tel Aviv, 69978, Israel.

[b]Indian Institute of Science Education and Research, Dr. Homi Bhabha Road, Pune-411008, India.

[c]Complex Carbohydrate Research Center, University of Georgia, Athens 30606, GA, USA

[d]Equal Contribution

Corresponding Email: rkikkeri@iiserpune.ac.in

vkaravani@tauex.tau.ac.il

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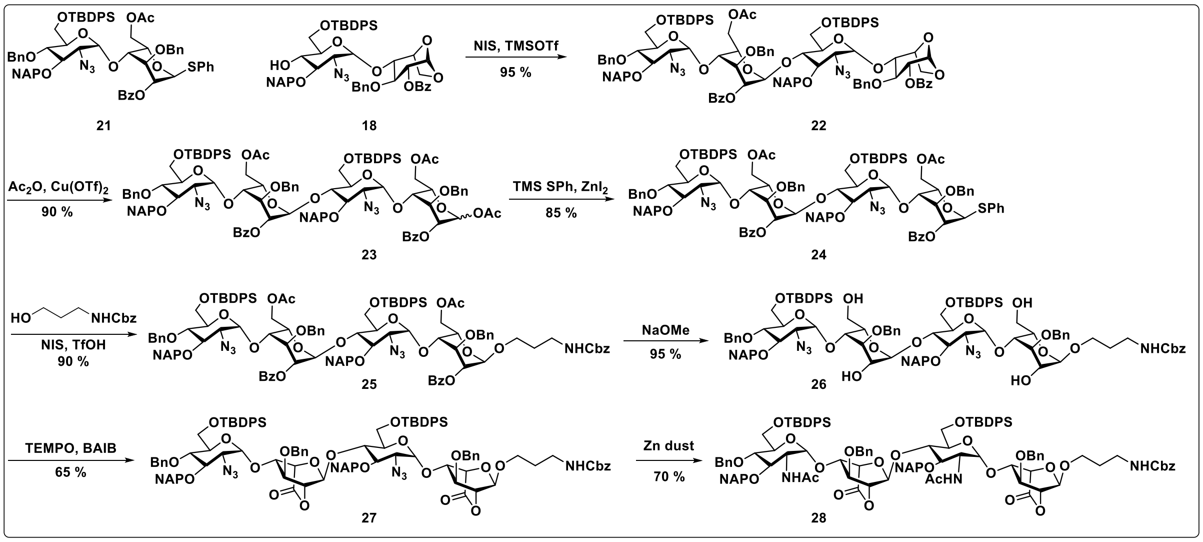
1. General information

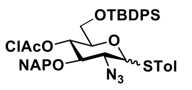
All chemicals were reagent grade and used as supplied except where noted. Analytical thin layer chromatography (TLC) was performed on Merck silica gel 60 F254 plates. Compounds were visualized by UV irradiation or dipping the plate in CAM/ninhydrin solution followed by heating. Column chromatography was carried out using force flow of the indicated solvent on Fluka Kieselgel 60 (230–400 mesh). ^{1}H and ^{13}C NMR spectra of all compounds were recorded on Jeol 400 MHz, and Bruker 600 MHz with cryo probe using residual solvents signals as an internal reference ($CDCl_3$ δH, 7.26 ppm, δC 77.3 ppm, CD_3OD δH 3.31 ppm, δC 49.0 ppm and D_2O δH 4.79 ppm). The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz.

2. Synthesis of HS tetrasaccharide (1-13):

2.1 Synthesis of HS tetrasaccharide precursor:



4-Methylphenyl 2-azido-4-*O*-chloroacetyl-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(2-naphthylmethyl)-2-deoxy-1-thio-*α*/*β*-D-glucopyranoside (16)

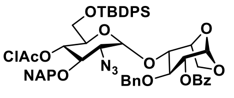


16

To a solution of compound **15** (1.5 g, 2.78 mmol) in CH_2Cl_2 (5 mL) and MeOH (10 mL) was added PTSA (0.95 g, 5.56 mmol) and stirred for 6 h. Upon completion, the reaction mixture was quenched using Et_3N and extracted with ethyl acetate and brine. The organic layer was collected, dried over Na_2SO_4, filtered, concentrated and purified through flash silica gel column chromatography (ethyl acetate/

hexane= 1/1, v/v) Next, the obtained compound (1 g, 2.21 mmol) was dissolved in CH_2Cl_2 (10 mL) and stirred at ice cold temperature under N_2 atmosphere followed by the addition of imidazole (0.45 g, 6.64 mmol) and DMAP (0.10 g, 0.88 mmol). Finally, TBDPS-Cl was added dropwise and reaction mixture was left for stirring. After 12 h, the reaction was quenched using MeOH and extracted with brine. The combined organic layer was collected, dried over Na_2SO_4, filtered, concentrated and purified through silica gel column chromatography (ethyl acetate/ hexane= 1/10, v/v). Further, the solution of 6-*O*-TBDPS compound (1 g, 1.45 mmol) in CH_2Cl_2 (8 mL) and pyridine (2 mL) was stirred at ice cold temperature for 15 minutes under N_2 atmosphere before the addition of chloroacetic anhydride (0.32 g, 1.85 mmol). Reaction completion was monitored by TLC (approx. 20 min). After the completion of reaction, the mixture was washed with 1 N HCl and brine. The organic layer was collected, dried over Na_2SO_4, filtered, concentrated and purified through silica gel column chromatography (ethyl acetate/ hexane= 1/20, v/v) to obtain compound **16** in 95 % yield. ^{1}H NMR (400 MHz, Chloroform-d) **(α anomer)** δ 7.87 – 7.83 (m, 3H), 7.78 (s, 1H), 7.64 – 7.61 (m, 4H), 7.51 – 7.48 (m, 2H), 7.43 – 7.30 (m, 9H), 7.06 (d, *J* = 7.9 Hz, 2H), 5.59 (d, *J* = 5.4 Hz, 1H), 5.28 – 5.23 (m, 1H), 5.07 (d, *J* = 11.6 Hz, 1H), 4.80 (d, *J* = 11.6 Hz, 1H), 4.37 (ddd, *J* = 10.1, 4.2, 2.3 Hz, 1H), 4.03 (dd, *J* = 10.2, 5.4 Hz, 1H), 3.86 – 3.81 (m, 1H), 3.67 (qd, *J* = 11.7, 3.3 Hz, 2H), 3.53 – 3.44 (m, 2H), 2.33 (s, 3H), 1.02 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 165.85, 138.06, 135.81, 135.67, 134.92, 134.89, 133.28, 133.12, 133.11, 132.96, 132.43, 130.01, 129.81, 129.72, 129.65, 128.47, 128.13, 127.79, 127.70, 127.17, 126.40, 126.31, 126.15, 87.46, 79.35, 75.46, 71.68, 71.56, 64.24, 62.35, 40.43, 26.77, 21.24, 19.28. **(β anomer)** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87- 7.85 (m, 3H), 7.78 – 7.74 (m, 3H), 7.70 (dd, *J* = 7.7, 1.4 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.54 – 7.51 (m, 2H), 7.47 – 7.41 (m, 7H), 7.09 (d, *J* = 8.0 Hz, 2H), 5.21 (t, *J* = 6.8 Hz, 1H), 5.03 (d, *J* = 11.5 Hz, 1H), 4.80 (d, *J* = 11.6 Hz, 1H), 4.43 (d, *J* = 10.0 Hz, 1H), 3.80 (dd, *J* = 11.6, 1.9 Hz, 1H), 3.68 – 3.64 (m, 1H), 3.58 (dd, *J* = 13.2, 5.4 Hz, 1H), 3.51 – 3.45 (m, 4H), 2.36 (s, 3H), 1.10 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 165.67, 139.07, 135.79, 135.78, 134.83, 134.54, 133.25, 133.12, 132.99, 132.92, 130.01, 129.90, 129.81, 128.48, 128.08, 127.83, 127.78, 127.25, 126.51, 126.40, 126.33, 126.16, 86.05, 82.60, 78.65, 75.49, 70.67, 64.75, 62.20, 26.80, 21.29, 19.26. HR-ESI-MS *(m/z)*: $[M+Na]^+$ calcd for $C_{42}H_{44}ClN_3O_5SSiNa$, 788.2357; found, 788.2358.

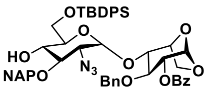
1,6-Anhydro-[2-azido-4-*O*-chloroacetyl-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(2 naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl]-(1→4)-*O*-2-*O*-benzoyl-3-*O*-benzyl-*β*-L- idopyranose (17)



17

A solution of donor **16** (1 g, 1.30 mmol) and acceptor **14** (0.41 g, 1.17 mmol) in CH_2Cl_2 (20 mL) was stirred under N_2 atmosphere in round bottom flask containing freshly dried 4 Å molecular sieves for 2 h. The mixture solution was cooled down to -78 ° C followed by the addition of NIS (0.46 g, 2.08 mmol) and TMSOTf (71 μL, 0.39 mmol). The temperature was gradually increased to -20 ° C and reaction mixture was left for stirring for another 15 minutes. After 15 minutes reaction completion was monitored by TLC and quenched using few drops of Et_3N. Molecular sieves were filtered using celite and organic layer was washed with aqueous $Na_2S_2O_3$ and brine. The collected organic layer was dried over Na_2SO_4, filtered, concentrated and purified through silica gel column chromatography (ethyl acetate/ hexane= 1/12, v/v) to obtain compound **17** in 65 % yield. ^1H NMR (400 MHz, Chloroform-d) δ 8.08 – 8.06 (m, 2H), 7.85 (td, *J* = 7.0, 6.4, 2.9 Hz, 3H), 7.78 (s, 1H), 7.64 (dt, *J* = 8.0, 1.4 Hz, 4H), 7.61 – 7.58 (m, 1H), 7.51 – 7.36 (m, 12H), 7.30 – 7.27 (m, 2H), 7.26 – 7.22 (m, 2H), 5.55 (d, *J* = 1.7 Hz, 1H), 5.36 (d, *J* = 3.8 Hz, 1H), 5.16 – 5.09 (m, 2H), 5.06 (d, *J* = 11.5 Hz, 1H), 4.91 (d, *J* = 10.8 Hz, 1H), 4.80 (dd, *J* = 11.0, 9.5 Hz, 2H), 4.65 (t, *J* = 4.5 Hz, 1H), 4.19 (d, *J* = 7.6 Hz, 1H), 4.12 (t, *J* = 8.0 Hz, 1H), 4.07 (dd, *J* = 8.1, 4.0 Hz, 1H), 4.03 – 3.98 (m, 1H), 3.77 – 3.72 (m, 2H), 3.67 (dd, *J* = 11.4, 5.3 Hz, 1H), 3.62 – 3.59 (m, 1H), 3.57 (d, *J* = 2.1 Hz, 2H), 3.51 (dd, *J* = 10.3, 3.8 Hz, 1H), 1.06 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 165.84, 165.80, 137.92, 135.73, 135.68, 134.87, 133.55, 133.28, 133.14, 132.86, 132.74, 129.97, 129.47, 128.60, 128.52, 128.50, 128.07, 127.93, 127.89, 127.87, 127.82, 127.01, 126.45, 126.34, 125.96, 99.48, 99.37, 79.51, 78.94, 75.07, 74.96, 74.24, 71.75, 71.41, 65.77, 63.36, 62.64, 40.41, 26.82, 19.22. HR-ESI-MS *(m/z)*: $[M+Na]^+$ calcd for $C_{55}H_{56}ClN_3O_{11}SiNa$, 1020.3270; found, 1020.3271.

1,6-Anhydro-[2-azido-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl]-(1→4)-*O*-2-*O*-benzoyl-3-*O*-benzyl-*β*-L-idopyranose (18)

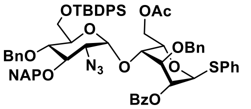


18

To a solution of compound **17** (0.70 g, 0.7 mmol) in MeOH (5 mL) and pyridine (5 mL) was added thiourea (0.10 g, 1.4 mmol) and refluxed at 80 ° C. After 1 h, volatiles were evaporated and residue was extracted with ethyl acetate, 1 N HCl and brine. The collected organic layer was dried over Na_2SO_4, filtered, concentrated and purified through silica gel column chromatography (ethyl acetate/ hexane= 1/8, v/v) to obtain compound **18** in 90 % yield. ^1H NMR (400 MHz, Chloroform-d) δ 8.06 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.86 (dq, *J* = 9.6, 4.2 Hz, 4H), 7.68 (td, *J* = 7.6, 7.0, 1.5 Hz, 4H), 7.62 – 7.55

(m, 2H), 7.53 – 7.38 (m, 11H), 7.26 – 7.20 (m, 4H), 5.54 (d, J = 1.7 Hz, 1H), 5.26 (d, *J* = 3.7 Hz, 1H), 5.12 (d, *J* = 11.3 Hz, 1H), 5.08 – 5.03 (m, 2H), 4.90 (d, *J* = 10.9 Hz, 1H), 4.76 (d, *J* = 10.9 Hz, 1H), 4.56 (t, *J* = 4.6 Hz, 1H), 4.17 (d, *J* = 7.7 Hz, 1H), 4.08 (t, *J* = 8.1 Hz, 1H), 4.00 (dd, *J* = 8.1, 4.1 Hz, 1H), 3.91 – 3.82 (m, 3H), 3.72 (t, *J* = 6.2 Hz, 2H), 3.61 (dt, *J* = 9.4, 4.5 Hz, 1H), 3.37 (dd, *J* = 10.3, 3.7 Hz, 1H), 2.66 (s, 1H), 1.08 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 165.83, 137.98, 135.69, 135.68, 135.45, 133.51, 133.42, 133.22, 132.83, 132.71, 130.14, 130.10, 129.98, 129.48, 128.62, 128.57, 128.47, 128.09, 127.98, 127.96, 127.85, 127.83, 127.07, 126.35, 126.22, 125.98, 99.76, 99.33, 79.50, 79.44, 78.90, 75.33, 75.05, 74.32, 72.61, 71.89, 65.75, 64.36, 62.96, 26.93, 19.27. HR-ESI-MS *(m/z)*: $[M+Na]^+$ calcd for $C_{53}H_{55}N_3O_{10}SiNa$, 944.3555; found, 944.3540.

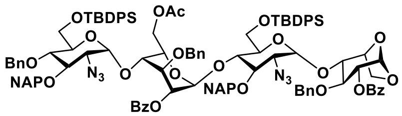
Phenyl-[2-azido-4-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl]-(1→4)-*O*-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-acetyl-1-thio-*α*-L- idopyranoside (21)



21

A solution of compound **20** (1 g, 0.98 mmol) in Ac_2O (10 mL) was stirred at ice cold temperature for 15 minutes before the addition of $Cu(OTf)_2$ (0.035 g, 0.098 mmol). After 16 h, the reaction mixture was concentrated under reduced pressure and the residue was extracted with ethyl acetate, $NaHCO_3$ and washed with brine. The combined organic layer was dried over Na_2SO_4, filtered, concentrated and preceded further without any purification. Next, the as obtained acetylated solution of compound (0.98 g, 0.88 mmol), ZnI_2 (0.59 g, 1.84 mmol) and phenyl trimethylsilyl sulphide (0.50 g, 2.72 mmol) in CH_2Cl_2 (15 mL) was stirred under N_2 atmosphere for 2 h. Upon completion, the reaction mixture was filtered through celite, evaporated and purified through silica gel column chromatography (ethyl acetate/ hexane= 1/5, v/v) to obtain compound **21** in 85 % yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.20 (dd, *J* = 6.8, 2.9 Hz, 2H), 7.87 – 7.77 (m, 3H), 7.72 (s, 1H), 7.71 – 7.68 (m, 2H), 7.68 – 7.66 (m, 1H), 7.61 – 7.58 (m, 3H), 7.54 – 7.48 (m, 4H), 7.44- 7.41 (m, 4H), 7.40 (s, 1H), 7.38 (d, *J* = 2.2 Hz, 4H), 7.37 – 7.35 (m, 4H), 7.34- 7.32 (m, 4H), 7.31- 7.29 (m, 2H), 7.21- 7.19 (m, 2H), 5.64 (s, 1H), 5.42 (s, 1H), 5.01 (d, *J* = 11.6 Hz, 1H), 4.92 (dt, *J* = 6.9, 4.0 Hz, 1H), 4.83 (d, *J* = 10.9 Hz, 1H), 4.78 (d, *J* = 11.7 Hz, 1H), 4.72 (d, *J* = 10.8 Hz, 1H), 4.65 (d, *J* = 3.6 Hz, 1H), 4.57 (d, *J* = 10.6 Hz, 1H), 4.44 (dd, *J* = 11.5, 8.1 Hz, 1H), 4.26 (d, *J* = 10.6 Hz, 1H), 4.20 (dd, *J* = 10.7, 3.6 Hz, 2H), 4.02 (dd, *J* = 11.6, 2.1 Hz, 1H), 3.91 (d, *J* = 11.5 Hz, 1H), 3.81 (s, 1H), 3.79 – 3.76 (m, 1H), 3.73 (d, *J* = 9.8 Hz, 1H), 3.68 (s, 1H), 3.38 (dd, *J* = 9.9, 3.6 Hz, 1H), 1.93 (s, 3H), 1.08 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 170.36, 165.76, 138.04, 137.34, 135.88, 135.61, 135.54, 135.09, 133.48, 133.27, 133.05, 133.03, 131.71, 129.88, 129.70, 129.69, 128.90, 128.61, 128.48, 128.43, 128.24, 128.12, 128.07, 127.98, 127.77, 127.73, 127.67, 127.59, 127.49, 127.00, 126.11, 126.06, 125.98, 98.96, 85.87, 80.76, 77.80, 75.34, 75.12, 75.05, 73.17, 72.83, 71.95, 69.74, 66.42, 64.12, 63.11, 62.18, 26.88, 20.72, 19.36. HR-ESI-MS *(m/z)*: $[M+Na]^+$ calcd for $C_{68}H_{69}N_3O_{11}SSiNa$, 1186.4320; found, 1186.4319

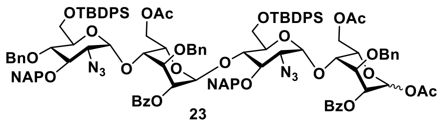
1,6-Anhydro-[(2-azido-4-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(2-*O*-benzoyl-3-*O*-benzyl-6-*O*-acetyl-*α*-L-idopyranosyl)-(1→4)-*O*-(2-azido-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl)]-(1→4)-*O*-2-*O*-benzoyl-3-*O*-benzyl-*β*-L-idopyranose (22)



22

A solution of donor **21** (0.87 g, 0.74 mmol) and acceptor **18** (0.55 g, 0.60 mmol) in CH_2Cl_2 (15 mL) was stirred under N_2 atmosphere in round bottom flask containing freshly dried 4 Å molecular sieves for 2 h. The mixture solution was cooled down to -10 ^{o} C followed by the addition of NIS (0.26 g, 1.18 mmol) and TMSOTf (26 µL, 0.148 mmol). After 15 minutes reaction completion was monitored by TLC and quenched using few drops of Et_3N. Molecular sieves were filtered using celite and organic layer was washed with aqueous $Na_2S_2O_3$ and brine. The collected organic layer was dried over Na_2SO_4, filtered, concentrated and purified through silica gel column chromatography (ethyl acetate/ hexane= 1/6, v/v) to obtain compound **22** in 95 % yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.03 (dd, *J* = 6.5, 1.4 Hz, 4H), 7.83 – 7.81 (m, 1H), 7.78 – 7.75 (m, 1H), 7.71- 7.58 (m, 15H), 7.48 – 7.27 (m, 29H), 7.22-7.19 (m, 9H), 5.51 (d, *J* = 1.7 Hz, 1H), 5.36 (s, 1H), 5.22 (s, 1H), 5.18 (d, J = 3.9 Hz, 1H), 5.13 (d, *J* = 11.3 Hz, 1H), 5.04 (dd, *J* = 8.2, 1.7 Hz, 1H), 4.87 (d, *J* = 11.3 Hz, 1H), 4.83 (d, *J* = 4.2 Hz, 1H), 4.81 – 4.80 (m, 1H), 4.75 (s, 1H), 4.73 – 4.67 (m, 3H), 4.63 (d, J = 10.6 Hz, 1H), 4.50 (dt, J = 6.8, 3.5 Hz, 1H), 4.41-4.38 (m, 1H), 4.36 (d, J = 4.78 Hz, 1H), 4.18 – 4.06 (m, 4H), 4.01 (tt, *J* = 7.0, 3.9 Hz, 2H), 3.93 – 3.86 (m, 4H), 3.83 (dd, *J* = 9.4, 2.9 Hz, 2H), 3.74 (t, *J* = 9.8 Hz, 3H), 3.66 – 3.61 (m, 2H), 3.59 – 3.51 (m, 2H), 3.38 (dd, *J* = 10.4, 3.8 Hz, 1H), 3.31 (dd, *J* = 10.1, 3.5 Hz, 1H), 1.41 (s, 3H), 1.03 (s, 9H), 1.00 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 170.07, 165.75, 138.11, 137.91, 137.44, 135.87, 135.82, 135.66, 135.59, 135.45, 135.21, 133.43, 133.37, 133.29, 133.21, 133.15, 133.03, 132.98, 132.86, 129.89, 129.82, 129.76, 129.72, 129.55, 129.43, 128.66, 128.55, 128.48, 128.44, 128.40, 128.36, 128.21, 128.15, 127.98, 127.84, 127.79, 127.76, 127.71, 127.67, 127.62, 127.53, 127.00, 126.94, 126.30, 126.08, 126.06, 125.97, 125.76, 125.72, 99.35, 99.21, 98.32, 97.35, 80.38, 79.21, 79.04, 78.45, 77.70, 77.25, 76.95, 75.35, 75.30, 75.10, 74.95, 74.13, 73.46, 73.34, 73.00, 72.95, 72.90, 72.83, 68.87, 65.52, 65.34, 64.04, 62.42, 62.36, 61.98, 26.86, 26.80, 20.20, 19.35, 19.33. HR-ESI-MS *(m/z)*: $[M+Na]^+$ calcd for $C_{115}H_{118}N_6O_{21}Si_2Na$, 1997.7787; found, 1997.7722.

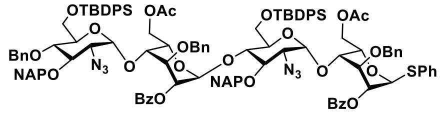
Acetyl-*O*-[(2-azido-4-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(2-*O*-benzoyl-3-*O*-benzyl-6-*O*-acetyl-*α*-L-idopyranosyl)-(1→4)-*O*-(2-azido-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl)]-(1→4)-*O*-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-acetyl-*α/β*-L- idopyranoside (23)



23

A solution of compound **22** (1 g, 0.98 mmol) in Ac_2O (10 mL) was stirred at ice cold temperature for 15 minutes before the addition of $Cu(OTf)_2$ (0.035 g, 0.098 mmol). After 16 h, the reaction mixture was concentrated under reduced pressure and the residue was extracted with ethyl acetate, $NaHCO_3$ and washed with brine. The combined organic layer was dried over Na_2SO_4, filtered, concentrated and purified through silica gel column chromatography (ethyl acetate/ hexane= 1/5, v/v) to obtain compound **23** in 90 % yield.. ^1H NMR (400 MHz, Chloroform-d) δ 8.16 – 8.11 (m, 3H), 8.05 (d, *J* = 7.7 Hz, 3H), 7.86 – 7.77 (m, 4H), 7.64 (ddq, *J* = 22.1, 13.3, 7.6, 6.4 Hz, 21H), 7.56 – 7.29 (m, 50H), 7.28 – 7.14 (m, 17H), 6.24 (d, *J* = 2.3 Hz, 1H), 5.42 (s, 1H), 5.25 – 5.16 (m, 3H), 4.95 – 4.67 (m, 13H), 4.61 (dd, *J* = 7.2, 3.4 Hz, 2H), 4.41 (dq, *J* = 16.1, 6.1, 5.4 Hz, 5H), 4.30 – 4.10 (m, 8H), 4.09 – 4.01 (m, 3H), 3.93 – 3.63 (m, 18H), 3.52 (s, 1H), 3.35 – 3.30 (m, 3H), 2.12 (d, *J* = 3.9 Hz, 2H), 1.97 (s, 2H), 1.90 (s, 3H), 1.28 (s, 2H), 1.25 (s, 3H), 1.05 (s, 15H), 1.00 (s, 13H). ^{13}C NMR (101 MHz, Chloroform-d) δ 170.44, 170.31, 169.98, 169.97, 169.04, 168.91, 166.05, 165.76, 165.71, 138.18, 137.52, 137.51, 137.24, 135.90, 135.87, 135.64, 135.60, 135.49, 135.45, 135.23, 133.46, 133.40, 133.36, 133.34, 133.28, 133.25, 133.22, 133.17, 133.16, 133.02, 132.99, 132.74, 132.71, 129.90, 129.80, 129.76, 129.72, 129.65, 129.63, 129.50, 128.72, 128.69, 128.63, 128.60, 128.52, 128.47, 128.44, 128.36, 128.23, 128.18, 128.15, 128.13, 128.09, 128.05, 128.00, 127.98, 127.84, 127.76, 127.75, 127.71, 127.66, 127.63, 127.53, 127.43, 127.41, 127.37, 126.94, 126.10, 126.04, 126.00, 125.94, 125.88, 125.86, 125.69, 125.67, 125.61, 125.58, 98.52, 98.13, 97.91, 97.00, 96.98, 91.74, 90.56, 80.36, 79.11, 78.91, 77.64, 77.27, 75.31, 75.04, 73.97, 73.88, 73.83, 73.33, 73.29, 73.26, 72.93, 72.80, 72.68, 72.55, 72.46, 71.98, 68.63, 68.54, 67.80, 67.25, 64.65, 64.37, 64.29, 64.06, 62.48, 62.33, 62.26, 61.94, 26.87, 26.79, 21.01, 20.73, 20.66, 20.01, 19.95, 19.44, 19.34. HR-ESI-MS *(m/z)*: $[M+Na]^+$ calcd for $C_{119}H_{124}N_6O_{24}Si_2Na$, 2100.8137; found, 2100.8171.

Phenyl-[(2-azido-4-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(2-*O*-benzoyl-3-*O*-benzyl-6-*O*-acetyl-*α*-L-idopyranosyl)-(1→4)-*O*-(2-azido-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl)]-(1→4)-*O*-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-acetyl-1-thio-*α*-L-idopyranoside (24)

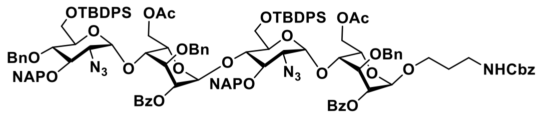


24

A solution of compound **23** (0.98 g, 0.88 mmol), ZnI_2 (0.59 g, 1.84 mmol) and phenyl trimethylsilyl sulphide (0.50 g, 2.72 mmol) in CH_2Cl_2 (15 mL) was stirred under N_2 atmosphere for 2 h. Upon completion, the reaction mixture was filtered through celite, evaporated and purified through silica gel column chromatography (ethyl acetate/ hexane= 1/5, v/v) to obtain compound **24** in 85 % yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.12 (ddd, J = 5.7, 3.0, 1.6 Hz, 2H), 8.03 (s, 1H), 8.01 (d, J = 1.3 Hz, 1H), 7.82 – 7.79 (m, 1H), 7.77 – 7.74 (m, 1H), 7.67 – 7.56 (m, 15H), 7.48 – 7.43 (m, 7H), 7.40 – 7.37 (m, 7H), 7.35 – 7.33 (m, 4H), 7.31 – 7.28 (m, 14H), 7.25- 7.21 (m, 5H), 7.17 (d, *J* = 7.5 Hz, 2H), 7.14 – 7.10 (m, 4H), 5.62 (s, 1H), 5.38 (s, 1H), 5.34 (s, 1H), 5.18 (s, 1H), 4.94 – 4.83 (m, 3H), 4.79 (d, *J* = 10.8 Hz, 1H), 4.75 (d, *J* = 4.0 Hz, 1H), 4.72 (d, *J* = 4.1 Hz, 1H), 4.70 (d, *J* = 2.4 Hz, 1H), 4.67 (d, *J* = 3.2 Hz, 1H), 4.64 (d, *J* = 3.5 Hz, 1H), 4.56 (d, *J* = 10.6 Hz, 1H), 4.47 (d, J = 3.8 Hz, 1H), 4.38 (dd, *J* = 5.5, 3.2 Hz, 1H), 4.36 – 4.32 (m, 2H), 4.14 – 4.08 (m, 2H), 4.05 – 4.02 (m, 3H), 3.99 (t, *J* = 5.4 Hz, 1H), 3.91 (dd, *J* = 5.6, 1.9 Hz, 1H), 3.88 – 3.85 (m, 2H), 3.83 (t, *J* = 3.4 Hz, 1H), 3.79 (d, *J* = 10.2 Hz, 1H), 3.74 (d, *J* = 9.9 Hz, 1H), 3.71 – 3.66 (m, 2H), 3.63 – 3.57 (m, 2H), 3.54 – 3.51 (m, 1H), 3.47 (s, 1H), 3.28 (d, J = 3.5 Hz, 1H), 3.26 (d, J = 3.6 Hz, 1H), 1.86 (s, 3H), 1.20 (s, 3H), 1.02 (s, 9H), 0.97 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 170.26, 169.96, 165.86, 165.70, 138.18, 137.54, 137.31, 135.90, 135.87, 135.65, 135.59, 135.46, 135.45, 135.23, 133.46, 133.39, 133.28, 133.26, 133.21, 133.14, 133.02, 133.00, 132.70, 131.73, 129.90, 129.82, 129.76, 129.71, 129.66, 129.63, 128.91, 128.69, 128.60, 128.47, 128.43, 128.36, 128.25, 128.18, 128.12, 128.09, 127.98, 127.85, 127.82, 127.76, 127.75, 127.70, 127.66, 127.63, 127.52, 127.40, 127.34, 126.93, 126.10, 126.03, 125.99, 125.94, 125.85, 125.69, 125.57, 98.16, 98.03, 96.96, 85.84, 80.36, 79.15, 77.63, 77.25, 75.30, 75.04, 74.97, 74.22, 73.28, 72.91, 72.83, 72.80, 72.59, 72.42, 71.58, 69.80, 68.54, 66.30, 64.62, 64.46, 64.06, 62.89, 62.27, 61.93, 26.87, 26.80, 20.65, 19.95, 19.44, 19.33. HR-ESI-MS *(m/z)*: $[M+Na]^+$ calcd for $C_{123}H_{126}N_6O_{22}SSi_2Na$, 2149.8080; found, 2149.8088.

N-benzyloxycarbonyl-3-aminopropyl-*O*-[(2-azido-4-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(2-*O*-benzoyl-3-*O*-benzyl-6-*O*-acetyl-*α*-L-idopyranosyl)-(1→4)-*O*-(2-azido-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(2-

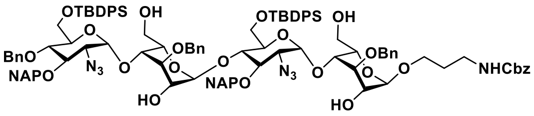
naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl)]-(1→4)-*O*-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-acetyl-*α*-L-idopyranoside (25)



25

A solution of donor **24** (0.90 g, 0.42 mmol) and linker benzyl (3-hydroxypropyl)carbamate (0.097 g, 0.46 mmol) in CH_2Cl_2 (15 mL) was stirred under N_2 atmosphere in round bottom flask containing freshly dried 4 Å molecular sieves for 2 h. Next, NIS (0.15 g, 0.67 mmol) and TfOH (7.4 µL, 0.084 mmol) was added at room temperature and reaction completion was monitored by TLC, quenched using few drops of Et_3N. Molecular sieves were filtered using celite and organic layer was washed with aqueous $Na_2S_2O_3$ and brine. The collected organic layer was dried over Na_2SO_4, filtered, concentrated and purified through silica gel column chromatography (ethyl acetate/ hexane= 1/3, v/v) to obtain compound **25** in 90 % yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.09 (dd, J = 6.4, 3.1 Hz, 2H), 8.01 – 7.99 (m, 1H), 7.82 – 7.78 (m, 1H), 7.76 – 7.74 (m, 1H), 7.67 – 7.54 (m, 14H), 7.49 (s, 1H), 7.47 – 7.45 (m, 2H), 7.43 (s, 1H), 7.40 (s, 1H), 7.39 (s, 2H), 7.37 (s, 2H), 7.34 – 7.27 (m, 24H), 7.24 – 7.20 (m, 6H), 7.17 – 7.11 (m, 6H), 5.63 (s, 1H), 5.37 (s, 1H), 5.18 (s, 1H), 5.08 (s, 2H), 5.03 (s, 1H), 4.96 (s, 1H), 4.88 (dd, *J* = 11.4, 4.5 Hz, 1H), 4.78 (d, *J* = 10.7 Hz, 2H), 4.74 (d, *J* = 11.3 Hz, 2H), 4.68 (d, *J* = 10.8 Hz, 1H), 4.64 (d, *J* = 3.6 Hz, 1H), 4.58 (dd, *J* = 17.4, 11.3 Hz, 2H), 4.39 (dt, *J* = 8.6, 4.4 Hz, 1H), 4.33 (dt, *J* = 11.2, 3.9 Hz, 2H), 4.27 – 4.24 (m, 2H), 4.10 (t, *J* = 9.4 Hz, 2H), 4.03 (d, *J* = 12.5 Hz, 1H), 3.99 – 3.93 (m, 3H), 3.89 (s, 1H), 3.87 – 3.80 (m, 5H), 3.74 (d, J = 11.9 Hz, 1H), 3.68 (t, *J* = 9.7 Hz, 2H), 3.61 (d, *J* = 10.3 Hz, 2H), 3.57 – 3.54 (m, 3H), 3.47 (s, 1H), 3.39 (s, 1H), 3.28 (d, *J* = 3.6 Hz, 1H), 3.25 (d, *J* = 3.3 Hz, 1H), 3.24 – 3.18 (m, 2H), 1.86 (s, 3H), 1.18 (s, 3H), 1.01 (s, 9H), 0.97 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 170.37, 169.91, 165.79, 165.68, 156.55, 138.18, 137.54, 137.50, 136.72, 135.88, 135.86, 135.61, 135.58, 135.47, 135.23, 133.46, 133.42, 133.28, 133.23, 133.19, 133.14, 133.01, 132.70, 129.88, 129.84, 129.74, 129.69, 129.64, 129.63, 129.61, 129.59, 128.70, 128.66, 128.58, 128.54, 128.45, 128.38, 128.34, 128.30, 128.25, 128.17, 128.13, 128.10, 128.01, 127.97, 127.82, 127.74, 127.72, 127.68, 127.64, 127.61, 127.58, 127.51, 127.40, 127.34, 126.91, 126.08, 126.01, 125.95, 125.92, 125.84, 125.65, 125.56, 98.15, 98.11, 97.84, 96.93, 80.36, 79.09, 77.63, 77.24, 75.28, 75.02, 74.97, 73.82, 73.25, 73.16, 72.89, 72.80, 72.56, 72.50, 72.40, 72.38, 71.63, 68.79, 68.56, 67.01, 66.57, 65.12, 64.59, 64.42, 64.07, 63.04, 62.34, 62.21, 61.94, 39.64, 29.41, 26.86, 26.78, 20.63, 19.90, 19.44, 19.32. HR-ESI-MS *(m/z)*: $[M+Na]^+$ calcd for $C_{128}H_{135}N_7O_{25}Si_2Na$, 2248.8944; found, 2248.9016.

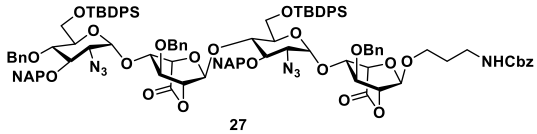
N-benzyloxycarbonyl-3-aminopropyl-*O*-[(2-azido-4-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(3-*O*-benzyl-*α*-L-idopyranosyl)-(1→4)-*O*-(2-azido-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl)]-(1→4)-*O*-3-*O*-benzyl-*α*-L-idopyranoside (26)



26

To a solution of compound **25** (0.84 g, 0.37 mmol) in CH_2Cl_2 (7 mL) and MeOH (7 mL) was added NaOMe (0.06g, 1.11 mmol) and stirred at room temperature. After 12 h, reaction mixture was quenched using Amberlite IR 120H$^+$ resin, filtered, evaporated and purified through silica gel column chromatography (ethyl acetate/ hexane= 1/2.5, v/v) to obtain compound **26** in 95 % yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.81 – 7.68 (m, 13H), 7.57 (d, J = 8.5 Hz, 2H), 7.51 – 7.44 (m, 15H), 7.41 – 7.35 (m, 11H), 7.33 – 7.30 (m, 4H), 7.29 – 7.27 (m, 6H), 7.17 – 7.14 (m, 3H), 5.72 (s, 1H), 5.10 (s, 1H), 5.05 (s, 3H), 5.01 – 4.94 (m, 2H), 4.88 – 4.84 (m, 2H), 4.80 (dd, *J* = 10.6, 4.7 Hz, 2H), 4.73 (d, *J* = 11.3 Hz, 2H), 4.68 (dd, *J* = 10.9, 3.7 Hz, 2H), 4.63 – 4.51 (m, 2H), 4.25 (dt, *J* = 14.0, 6.9 Hz, 2H), 3.99 (t, *J* = 9.5 Hz, 1H), 3.89 – 3.83 (m, 7H), 3.81 – 3.71 (m, 8H), 3.61 – 3.54 (m, 8H), 3.48 (d, J = 11.5 Hz, 1H), 3.36 (d, *J* = 8.3 Hz, 1H), 3.22 (ddt, *J* = 18.0, 13.6, 5.6 Hz, 2H), 2.70 (dt, *J* = 10.7, 5.2 Hz, 1H), 2.16 (s, 1H), 1.85 (s, 2H), 1.10 (s, 9H), 1.05 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 156.68, 138.02, 137.50, 137.48, 136.61, 136.00, 135.84, 135.79, 135.60, 135.10, 134.86, 133.44, 133.32, 133.30, 133.15, 133.14, 133.08, 132.84, 132.64, 129.87, 129.82, 129.79, 129.69, 128.72, 128.51, 128.48, 128.45, 128.43, 128.27, 128.07, 128.04, 128.02, 127.90, 127.84, 127.79, 127.70, 127.67, 127.60, 127.56, 127.52, 127.08, 126.61, 126.32, 126.07, 126.00, 125.59, 100.99, 100.07, 94.79, 94.36, 81.25, 79.86, 77.75, 77.26, 76.02, 75.52, 75.06, 73.64, 72.94, 72.47, 72.32, 72.02, 71.69, 70.87, 70.30, 69.56, 66.99, 66.95, 66.88, 66.86, 66.85, 66.63, 66.51, 66.36, 64.61, 63.99, 62.76, 62.49, 61.79, 61.44, 39.68, 29.72, 26.93, 26.83, 19.46, 19.31. HR-ESI-MS *(m/z)*: [M+Na]$^+$ calcd for $C_{110}H_{123}N_7O_{21}Si_2Na$, 1957.8242; found, 1957.8326.

N-benzyloxycarbonyl-3-aminopropyl-*O*-[(2-azido-4-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(3-*O*-benzyl-*α*-L-idopyranosylurono-6,2-lactone)-(1→4)-*O*-(2-azido-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl)]-(1→4)-*O*-3-*O*-benzyl-*α*-L-idopyranosidurono-6,2-lactone (27)

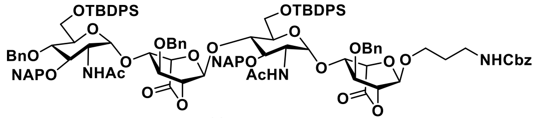


27

To a solution of compound **26** (0.67 g, 0.34 mmol) in CH_2Cl_2 (5 mL) and H_2O (5 mL) was added TEMPO (0.01g, 0.07 mmol), BAIB (0.54 g, 1.70

mmol) and stirred at room temperature. After 16 h, the reaction mixture was extracted using saturated aqueous NH_4Cl. The collected organic layer was dried over Na_2SO_4, filtered, concentrated and purified through silica gel column chromatography (ethyl acetate/ hexane= 1/3, v/v) to obtain compound **27** in 65 % yield. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.89 – 7.78 (m, 7H), 7.71 – 7.68 (m, 4H), 7.65 – 7.61 (m, 4H), 7.51 – 7.29 (m, 36H), 7.22 – 7.17 (m, 3H), 5.84 (s, 1H), 5.47 (s, 1H), 5.25 (d, J = 12.0 Hz, 1H), 5.20 – 5.05 (m, 4H), 4.99 (d, J = 10.7 Hz, 1H), 4.95 (s, 1H), 4.92 (s, 1H), 4.87 (d, J = 11.6 Hz, 1H), 4.82 (d, *J* = 11.5 Hz, 1H), 4.76 (d, *J* = 8.9 Hz, 1H), 4.70 (d, *J* = 20.3 Hz, 1H), 4.65 – 4.62 (m, 1H), 4.49 (d, *J* = 12.4 Hz, 2H), 4.32 (d, *J* = 2.8 Hz, 1H), 4.24 (s, 1H), 4.21 – 4.14 (m, 3H), 4.01 – 3.85 (m, 5H), 3.82 – 3.76 (m, 3H), 3.71 (dt, *J* = 8.0, 3.3 Hz, 3H), 3.65 – 3.59 (m, 3H), 3.53 (dd, *J* = 14.1, 3.7 Hz, 1H), 3.48 – 3.45 (m, 2H), 3.34 (dt, *J* = 13.6, 6.6 Hz, 1H), 2.77 (dd, *J* = 9.4, 4.4 Hz, 1H), 1.89 – 1.87 (m, 2H), 1.07 (s, 18H). ^{13}C NMR (101 MHz, Chloroform-d) δ 167.43, 167.04, 156.60, 138.13, 137.02, 136.86, 136.70, 136.21, 136.00, 135.88, 135.58, 135.56, 135.19, 133.65, 133.34, 133.30, 133.14, 133.01, 132.77, 132.74, 130.02, 129.85, 129.73, 129.70, 129.64, 128.52, 128.49, 128.42, 128.32, 128.23, 128.21, 128.19, 128.11, 128.08, 128.03, 127.93, 127.81, 127.70, 127.65, 127.53, 127.52, 127.19, 126.49, 126.19, 126.09, 126.02, 125.91, 124.87, 124.68, 99.84, 98.98, 96.78, 96.74, 80.99, 80.27, 80.00, 78.32, 78.06, 77.87, 77.77, 77.24, 76.10, 75.82, 74.95, 74.34, 72.65, 72.57, 72.49, 72.35, 72.25, 71.82, 69.42, 69.37, 69.11, 66.64, 63.34, 61.69, 61.47, 39.89, 29.48, 26.91, 19.36, 19.28. HR-ESI-MS *(m/z)*: $[M+Na]^+$ calcd for $C_{110}H_{115}N_7O_{21}Si_2Na$, 1949.7616; found, 1949.7651.

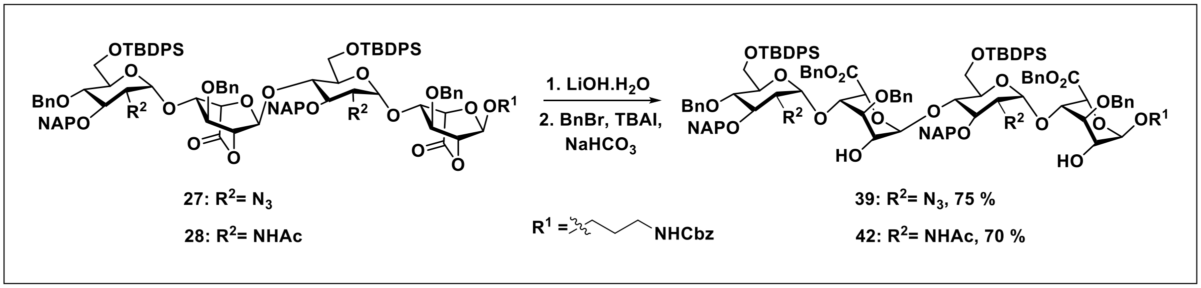
N-benzyloxycarbonyl-3-aminopropyl-*O*-[(2-acetamido-4-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(3-*O*-benzyl-*α*-L-idopyranosylurono-6,2-lactone)-(1→4)-*O*-(2-acetamido-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl)]-(1→4)-*O*-3-*O*-benzyl-*α*-L-idopyranosidurono-6,2-lactone (28)



28

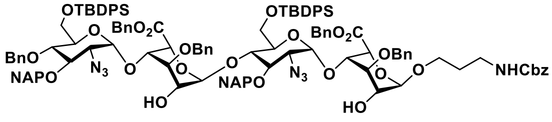
To a solution of compound **27** (0.40 g, 0.20 mmol) in THF (3 mL), AcOH (2 mL) and Ac_2O (2 mL) was added Zn dust (0.52 g, 8 mmol) and stirred for 12 h at room temperature. Upon completion, the reaction mixture was filtered through celite and volatiles were evaporated. The remaining residue was extracted with ethyl acetate, saturated $NaHCO_3$ and washed with brine. The collected organic layer was dried over Na_2SO_4, filtered, concentrated and purified through silica gel column chromatography (ethyl acetate/ hexane= 1/2.5, v/v) to obtain compound **28** in 70 % yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.86 (m, 3H), 7.82- 7.81 (m, 2H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.76 – 7.74 (m, 1H), 7.71- 7.70 (m, 2H), 7.69 – 7.68 (m, 3H), 7.68 – 7.66 (m, 2H), 7.65 (d, *J* = 1.3 Hz, 1H), 7.58 (s, 1H), 7.53 (dt, *J* = 6.1, 2.7 Hz, 2H), 7.51 – 7.49 (m, 1H), 7.48 – 7.46 (m, 2H), 7.45 – 7.42 (m, 3H), 7.41 (s, 2H), 7.39 – 7.38 (m, 2H), 7.38 – 7.37 (m, 1H), 7.35- 7.31 (m, 7H), 7.29 (s, 1H), 7.28 – 7.27 (m, 7H), 7.26 – 7.24 (m, 3H), 7.23 – 7.20 (m, 3H), 7.18 – 7.16 (m, 2H), 7.05 (d, *J* = 7.3 Hz, 2H), 5.50 (s, 1H), 5.42 (t, *J* = 5.2 Hz, 1H), 5.16 (d, *J* = 3.6 Hz, 1H), 5.07 – 5.03 (m, 4H), 5.00 (s, 1H), 4.93 – 4.90 (m, 3H), 4.80 (d, *J* = 3.5 Hz, 1H), 4.77 (d, *J* = 2.1 Hz, 1H), 4.73 (d, *J* = 6.9 Hz, 1H), 4.63 (d, *J* = 12.4 Hz, 1H), 4.48 (s, 1H), 4.42 (d, *J* = 3.4 Hz, 1H), 4.37 (s, 1H), 4.33 (d, *J* = 2.5 Hz, 2H), 4.30 (d, *J* = 5.4 Hz, 1H), 4.27 – 4.21 (m, 1H), 4.09 (qd, *J* = 6.2, 4.2, 3.7 Hz, 3H), 4.02 – 3.89 (m, 7H), 3.86 – 3.70 (m, 2H), 3.68 – 3.59 (m, 5H), 3.53 (q, *J* = 10.8, 9.0 Hz, 2H), 3.36 (dt, *J* = 11.3, 6.0 Hz, 1H), 3.27 (dt, *J* = 13.8, 6.7 Hz, 1H), 1.83 – 1.80 (m, 2H), 1.59 (s, 3H), 1.39 (s, 3H), 1.09 (s, 9H), 1.06 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.88, 169.77, 167.57, 167.18, 156.46, 138.08, 136.62, 136.59, 135.92, 135.89, 135.78, 135.64, 135.57, 133.55, 133.28, 133.20, 133.08, 133.02, 132.94, 132.85, 132.54, 129.96, 129.83, 129.63, 128.64, 128.50, 128.46, 128.33, 128.29, 128.22, 128.09, 128.04, 127.93, 127.90, 127.78, 127.71, 127.66, 127.52, 127.16, 126.58, 126.44, 126.38, 126.34, 126.28, 126.26, 98.94, 98.73, 98.38, 96.61, 79.70, 79.39, 79.08, 79.00, 78.65, 78.28, 78.04, 77.29, 76.88, 75.09, 74.98, 74.79, 72.84, 72.28, 72.22, 72.13, 71.74, 69.35, 68.57, 66.60, 61.94, 61.70, 52.92, 52.80, 39.16, 29.61, 26.94, 26.87, 23.17, 22.87, 19.26, 19.20. HR-ESI-MS *(m/z)*: $[M+H]^+$ calcd for $C_{114}H_{124}N_3O_{23}Si_2$, 1958.8164; found, 1958.8163.

2.2 General procedure for benzyl ester formation:



To a solution of starting material (1 mmol) in THF/ H_2O (1/ 1) was added $LiOH{\cdot}H_2O$ (3 mmol) and stirred at room temperature for 2 h. Upon completion, the reaction mixture was quenched using Amberlite IR 120H$^+$ resin, filtered, evaporated and dried. Next, the residue was dissolved in DMF and added BnBr (4 mmol), TBAI (1.4 mmol), $NaHCO_3$ (5 mmol) and stirred at 60 °C under N_2 atmosphere. After 2 h, the reaction mixture was extracted with ethyl acetate and washed with brine. The collected organic layer was dried over Na_2SO_4, filtered, concentrated and purified through silica gel column chromatography.

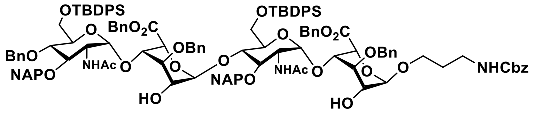
N-benzyloxycarbonyl-3-aminopropyl-*O*-[(benzyl (2-azido-4-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl))-(1→4)-*O*-(3-*O*-benzyl-*α*-L-idopyranosyluronate)-(1→4)-*O*-(benzyl (2-azido-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl))]-(1→4)-*O*-3-*O*-benzyl-*α*-L-idopyranosiduronate (39)



39

^{1}H NMR (400 MHz, Chloroform-d) δ 7.74 – 7.66 (m, 3H), 7.65 – 7.41 (m, 13H), 7.38 – 7.35 (m, 2H), 7.33 – 7.11 (m, 37H), 7.07 (ddd, J = 13.9, 6.6, 2.9 Hz, 4H), 6.94 (ddt, J = 8.6, 3.3, 1.7 Hz, 1H), 6.85 (t, J = 7.5 Hz, 2H), 6.77 (d, J = 7.2 Hz, 2H), 5.44 – 5.36 (m, 2H), 5.04 (d, J = 12.4 Hz, 1H), 4.96 (d, J = 3.6 Hz, 1H), 4.93 – 4.88 (m, 4H), 4.77 – 4.73 (m, 4H), 4.70 – 4.67 (m, 2H), 4.61 (dd, J = 12.2, 6.2 Hz, 2H), 4.56 (d, J = 2.7 Hz, 2H), 4.53 (d, J = 4.4 Hz, 1H), 4.51 – 4.39 (m, 3H), 4.08 (t, J = 9.5 Hz, 1H), 3.95 – 3.93 (m, 2H), 3.85 (t, J = 3.9 Hz, 1H), 3.76 (ddd, J = 22.1, 12.9, 7.5 Hz, 5H), 3.68 (d, J = 4.5 Hz, 1H), 3.64 – 3.57 (m, 4H), 3.53 – 3.47 (m, 3H), 3.43 – 3.30 (m, 5H), 3.19 (d, J = 10.6 Hz, 1H), 3.16 – 3.11 (m, 1H), 1.78 – 1.65 (m, 2H), 0.98 (s, 9H), 0.94 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.02, 168.76, 156.46, 138.24, 137.35, 137.32, 136.57, 135.99, 135.88, 135.86, 135.60, 135.19, 135.18, 134.81, 133.47, 133.34, 133.30, 133.26, 133.15, 133.05, 132.75, 129.74, 129.69, 129.67, 128.68, 128.62, 128.51, 128.41, 128.33, 128.27, 128.24, 128.21, 128.12, 128.01, 127.94, 127.92, 127.81, 127.77, 127.72, 127.65, 127.62, 127.55, 127.53, 127.50, 126.95, 126.30, 126.25, 126.05, 126.02, 125.96, 125.71, 125.51, 101.48, 100.99, 95.43, 80.83, 79.48, 79.46, 77.59, 77.24, 75.79, 75.17, 74.93, 74.29, 73.33, 72.96, 72.55, 72.22, 71.56, 71.39, 71.24, 68.44, 68.22, 68.00, 67.99, 67.21, 67.09, 67.08, 67.00, 66.64, 66.61, 64.15, 63.81, 62.13, 61.68, 39.83, 29.45, 26.94, 26.88. HR-ESI-MS *(m/z)*: [M+Na]$^+$ calcd for $C_{124}H_{131}N_7O_{23}Si_2Na$, 2165.8766; found, 2165.8772.

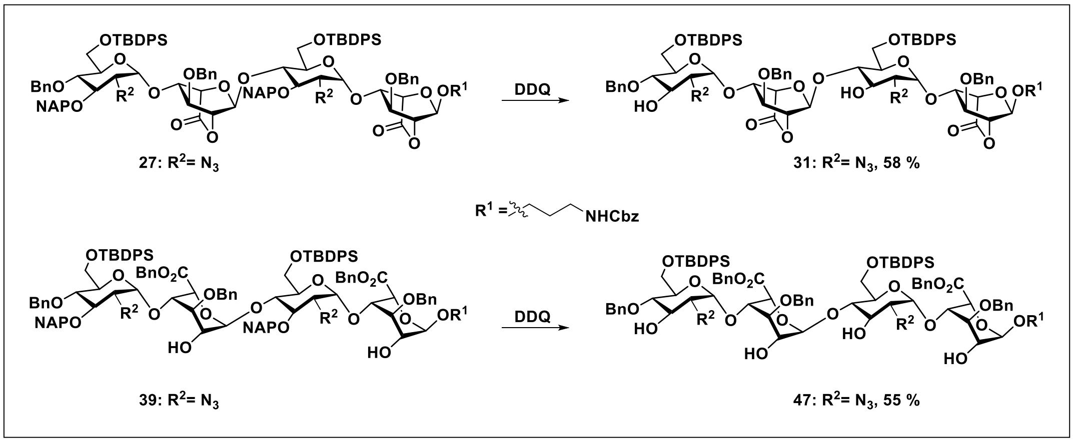
N-benzyloxycarbonyl-3-aminopropyl-*O*-[(benzyl (2-acetamido-4-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl))-(1→4)-*O*-(3-*O*-benzyl-*α*-L-idopyranosyluronate)-(1→4)-*O*-(benzyl (2-acetamido-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl))]-(1→4)-*O*-3-*O*-benzyl-*α*-L-idopyranosiduronate (42)



42

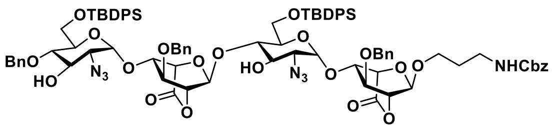
^{1}H NMR (400 MHz, Chloroform-d) δ 7.82- 7.77 (m, 3H), 7.76 – 7.74 (m, 2H), 7.73 – 7.72 (m, 2H), 7.71 (d, J = 1.6 Hz, 1H), 7.70 (d, J = 1.6 Hz, 2H), 7.69 – 7.68 (m, 2H), 7.67 – 7.66 (m, 1H), 7.65 (d, J = 1.3 Hz, 1H), 7.63 (d, J = 1.4 Hz, 1H), 7.55 (s, 1H), 7.45 (dd, J = 6.2, 3.3 Hz, 2H), 7.42 (s, 1H), 7.41 – 7.40 (m, 2H), 7.39 (d, J = 1.5 Hz, 2H), 7.37 (d, J = 2.1 Hz, 2H), 7.36- 7.35 (m, 2H), 7.35 (s, 4H), 7.32 – 7.30 (m, 6H), 7.29 (s, 1H), 7.28 – 7.22 (m, 17H), 7.20- 7.16 (m, 5H), 6.95 (t, J = 7.7 Hz, 2H), 6.86 (d, J = 7.9 Hz, 2H), 5.77 – 5.75 (m, 1H), 5.45 (t, J = 5.3 Hz, 1H), 5.37 (s, 1H), 5.16 (s, 1H), 5.14 – 5.09 (m, 2H), 5.03 – 5.00 (m, 1H), 5.00 – 4.93 (m, 1H), 4.91 (s, 1H), 4.88 (s, 2H), 4.85 (s, 1H), 4.81 (s, 1H), 4.77 – 4.74 (m, 2H), 4.70 (dd, J = 11.7, 3.6 Hz, 2H), 4.62 (d, J = 12.3 Hz, 1H), 4.56 (d, J = 11.4 Hz, 1H), 4.48 (d, J = 5.4 Hz, 1H), 4.46 – 4.42 (m, 2H), 4.30 (td, J = 10.7, 3.0 Hz, 1H), 4.26 – 4.15 (m, 2H), 4.05 (s, 1H), 3.95 (d, J = 9.5 Hz, 1H), 3.92 – 3.84 (m, 3H), 3.84 – 3.81 (m, 1H), 3.78 (d, J = 12.1 Hz, 2H), 3.73 (dd, J = 5.9, 1.8 Hz, 1H), 3.71 – 3.65 (m, 3H), 3.65 – 3.62 (m, 3H), 3.58 – 3.53 (m, 2H), 3.53 – 3.50 (m, 1H), 3.39 (dd, J = 16.5, 7.9 Hz, 2H), 3.30 – 3.21 (m, 1H), 2.90 – 2.86 (m, 1H), 2.74 (s, 1H), 1.80 – 1.79 (m, 2H), 1.67 (s, 3H), 1.29 (s, 3H), 1.07 (s, 9H), 1.04 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.65, 170.42, 169.27, 168.97, 156.50, 138.43, 137.24, 137.15, 136.47, 135.96, 135.89, 135.70, 135.60, 134.57, 134.36, 133.54, 133.43, 133.27, 133.18, 133.09, 132.91, 132.80, 129.82, 129.62, 129.61, 128.66, 128.63, 128.55, 128.44, 128.33, 128.29, 128.18, 128.09, 128.00, 127.93, 127.87, 127.85, 127.79, 127.70, 127.62, 127.55, 126.73, 126.51, 126.17, 126.12, 125.97, 125.93, 101.13, 100.61, 96.80, 94.89, 79.93, 78.26, 77.73, 75.17, 75.13, 74.48, 74.26, 73.00, 72.73, 72.53, 72.45, 72.08, 71.87, 71.55, 69.35, 68.01, 67.60, 67.33, 67.18, 67.15, 67.07, 66.67, 62.15, 62.05, 52.64, 52.41, 39.54, 29.73, 29.48, 26.93, 26.86, 22.83, 22.56, 19.47, 19.29. HR-ESI-MS *(m/z)*: [M+Na]$^+$ calcd for $C_{128}H_{139}N_3O_{25}Si_2Na$, 2196.9134; found, 2196.9077.

2.3 General procedure for selective NAP deprotection:



To a solution of starting material (1 mmol) in CH_2Cl_2 (6 mL) and H_2O (340 μL) was added DDQ (5 mmol) portion wise over the interval of 20 min. After 1 h, the reaction mixture was quenched using $NaHCO_3$, extracted with CH_2Cl_2 and washed with brine. The collected organic layer was dried over Na_2SO_4, filtered, concentrated and purified through silica gel column chromatography.

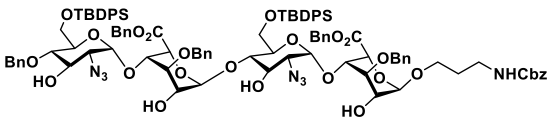
N-benzyloxycarbonyl-3-aminopropyl-*O*-[(2-azido-4-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(3-*O*-benzyl-*α*-L-idopyranosylurono-6,2-lactone)-(1→4)-*O*-(2-azido-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-*α*-D-glucopyranosyl)]-(1→4)-*O*-3-*O*-benzyl-*α*-L-idopyranosidurono-6,2-lactone (31)



31

^{1}H NMR (400 MHz, Chloroform-d) δ 7.72 (t, J = 1.3 Hz, 1H), 7.70 – 7.67 (m, 3H), 7.63 – 7.61 (m, 4H), 7.46 – 7.42 (m, 3H), 7.41 – 7.34 (m, 12H), 7.33 – 7.29 (m, 13H), 7.26 – 7.23 (m, 4H), 5.82 (t, J = 5.4 Hz, 1H), 5.12 – 5.08 (m, 3H), 5.04 (dd, J = 2.3, 1.0 Hz, 1H), 4.99 (d, J = 3.8 Hz, 1H), 4.91 (d, J = 3.6 Hz, 1H), 4.81 – 4.69 (m, 3H), 4.62 (d, J = 12.4 Hz, 1H), 4.54 (d, J = 11.6 Hz, 1H), 4.45 – 4.42 (m, 2H), 4.36 (dd, J = 5.9, 3.3 Hz, 2H), 4.22 – 4.19 (m, 1H), 4.13 – 4.11 (m, 1H), 4.03 (t, J = 2.6 Hz, 1H), 4.00 – 3.92 (m, 5H), 3.90 (dd, J = 12.0, 1.8 Hz, 1H), 3.81 – 3.79 (m, 2H), 3.77 – 3.75 (m, 2H), 3.72 (s, 1H), 3.70 – 3.68 (m, 2H), 3.65 – 3.59 (m, 2H), 3.49 – 3.41 (m, 1H), 3.35 – 3.28 (m, 1H), 3.24 (dd, J = 10.4, 3.7 Hz, 1H), 3.18 (dd, J = 10.5, 3.7 Hz, 1H), 2.46 (s, 1H), 1.86 (s, 1H), 1.09 (s, 9H), 1.06 (s, 9H). 13C NMR (101 MHz, Chloroform-d) δ 167.28, 166.35, 156.61, 137.96, 136.92, 136.69, 136.53, 135.95, 135.79, 135.67, 135.57, 133.42, 133.02, 132.78, 130.02, 129.89, 129.82, 129.76, 128.69, 128.65, 128.54, 128.48, 128.32, 128.23, 128.18, 128.16, 128.10, 128.09, 128.00, 127.93, 127.86, 127.72, 127.70, 127.60, 100.17, 99.91, 97.84, 96.72, 81.04, 80.48, 79.81, 79.06, 78.70, 78.06, 77.23, 74.89, 72.67, 72.55, 72.27, 71.67, 71.17, 71.04, 70.29, 69.61, 69.46, 69.29, 66.63, 62.68, 62.43, 62.26, 61.72, 39.87, 29.44, 26.94. HR-ESI-MS *(m/z)*: [M+Na]$^+$ calcd for $C_{88}H_{99}N_7O_{21}Si_2Na$, 1668.6330; found, 1668.6327.

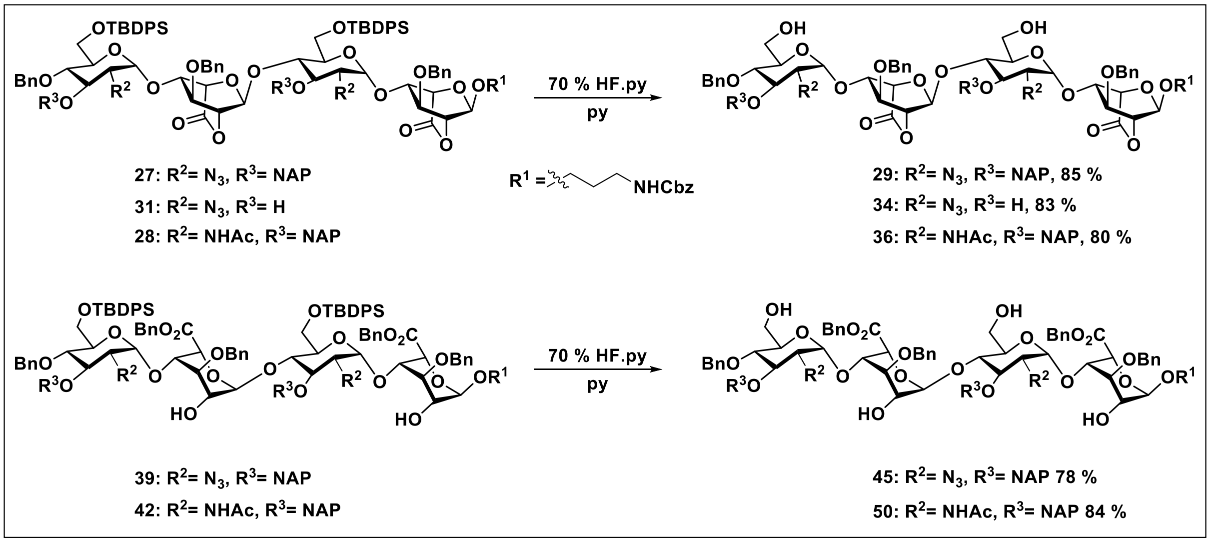
N-benzyloxycarbonyl-3-aminopropyl-*O*-[(benzyl (2-azido-4-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-*α*-D-glucopyranosyl))-(1→4)-*O*-(3-*O*-benzyl-*α*-L-idopyranosyluronate)-(1→4)-*O*-(benzyl (2-azido-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-*α*-D-glucopyranosyl))]-(1→4)-*O*-3-*O*-benzyl-*α*-L-idopyranosiduronate (47)



47

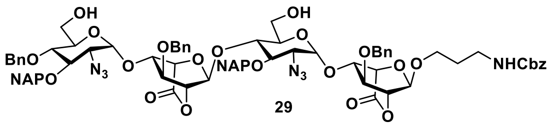
^{1}H NMR (400 MHz, Chloroform-d) δ 7.67 (tdd, J = 8.0, 4.1, 1.8 Hz, 8H), 7.42 – 7.28 (m, 19H), 7.25 – 7.20 (m, 15H), 7.19 – 7.15 (m, 6H), 7.10 (dd, J = 7.2, 2.5 Hz, 2H), 5.52 (t, J = 5.2 Hz, 1H), 5.16 (d, J = 3.5 Hz, 1H), 5.11 (d, J = 12.1 Hz, 1H), 5.04 – 4.94 (m, 6H), 4.81 (d, J = 3.3 Hz, 2H), 4.75 – 4.70 (m, 4H), 4.52 (d, J = 8.7 Hz, 3H), 4.30 (d, J = 2.0 Hz, 1H), 4.10 – 4.08 (m, 1H), 4.03 (s, 1H), 3.88 – 3.70 (m, 11H), 3.65 – 3.56 (m, 3H), 3.55 – 3.46 (m, 4H), 3.40 (td, J = 10.9, 10.4, 4.7 Hz, 2H), 3.34 (dd, J = 10.2, 3.7 Hz, 1H), 3.20 (ddt, J = 12.6, 7.0, 4.5 Hz, 1H), 2.95 (d, J = 9.3 Hz, 1H), 2.32 (d, J = 3.3 Hz, 1H), 1.78 (s, 2H), 1.08 (s, 9H), 1.06 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 169.04, 168.53, 156.46, 138.23, 137.34, 137.30, 136.56, 135.84, 135.79, 135.74, 135.64, 134.78, 134.55, 133.41, 133.27, 133.25, 133.12, 129.83, 129.77, 129.74, 129.70, 128.70, 128.64, 128.62, 128.59, 128.51, 128.50, 128.40, 128.27, 128.11, 128.08, 128.05, 128.00, 127.97, 127.78, 127.75, 127.61, 102.91, 101.42, 96.09, 94.99, 80.84, 77.92, 77.24, 74.96, 74.24, 73.00, 72.65, 72.41, 72.19, 71.94, 71.80, 71.25, 71.09, 69.65, 69.53, 68.00, 67.66, 67.24, 67.13, 66.95, 66.59, 63.27, 63.02, 62.19, 61.96, 39.84, 29.41, 26.93. HR-ESI-MS *(m/z)*: [M+Na]$^+$ calcd for $C_{102}H_{115}N_7O_{23}Si_2Na$, 1885.7514; found, 1885.7581.

2.4 General procedure for desilylation pre *O*- sulfation:



A solution of starting material (1 mmol) in pyridine (1 mL) was stirred at ice cold temperature under N_2 atmosphere. After 15 minutes, 70 % HF.py complex (5 mmol) was added drop wise and reaction mixture was stirred for 12 h. Upon completion, the mixture was extracted with ethyl acetate and washed with 1 N HCl and brine. The combined organic layer was dried over Na_2SO_4, filtered, concentrated and purified through silica gel column chromatography.

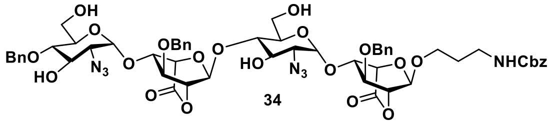
N-benzyloxycarbonyl-3-aminopropyl-*O*-[(2-azido-4-*O*-benzyl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(3-*O*-benzyl-*α*-L-idopyranosylurono-6,2-lactone)-(1→4)-*O*-(2-azido-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl)]-(1→4)-*O*-3-*O*-benzyl-*α*-L-idopyranosidurono-6,2-lactone (29)



29

^{1}H NMR (400 MHz, Chloroform-d) δ 7.92 (s, 1H), 7.89 – 7.76 (m, 6H), 7.72 (s, 1H), 7.53 – 7.50 (m, 2H), 7.49 – 7.45 (m, 3H), 7.44 – 7.40 (m, 2H), 7.38 (s, 2H), 7.37 – 7.31 (m 8H), 7.30 – 7.29 (m, 7H), 7.24 (dd, J = 7.5, 1.9 Hz, 2H), 5.75 (t, J = 5.1 Hz, 1H), 5.35 (s, 1H), 5.16 (d, J = 12.1 Hz, 1H), 5.09 – 5.07 (m, 3H), 5.01 (s, 1H), 4.98 – 4.93 (m, 3H), 4.79 – 4.70 (m, 3H), 4.67 – 4.64 (m, 1H), 4.62 – 4.56 (m, 2H), 4.52 (t, J = 3.4 Hz, 2H), 4.46 (t, J = 2.6 Hz, 1H), 4.30 – 4.28 (m, 2H), 3.95 – 3.85 (m, 5H), 3.82 – 3.76 (m, 2H), 3.73 (td, J = 3.1, 1.5 Hz, 1H), 3.71 – 3.68 (m, 3H), 3.66 – 3.61 (m, 2H), 3.57 (d, J = 3.8 Hz, 1H), 3.51 – 3.27 (m, 6H), 2.83 (dd, J = 10.4, 3.7 Hz, 1H), 2.05 (s, 1H), 1.85 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 167.92, 167.82, 156.62, 137.78, 137.02, 136.76, 136.67, 135.98, 135.15, 133.50, 133.28, 133.06, 132.84, 129.71, 128.57, 128.54, 128.48, 128.46, 128.27, 128.24, 128.22, 128.18, 128.11, 128.09, 128.00, 127.99, 127.84, 127.81, 127.69, 127.68, 127.61, 126.87, 126.22, 126.10, 126.00, 125.94, 125.89, 125.04, 124.64, 99.68, 99.50, 97.00, 96.69, 80.78, 80.67, 79.57, 78.47, 78.22, 77.97, 77.67, 77.23, 76.49, 75.54, 74.97, 73.94, 72.66, 72.63, 72.30, 72.26, 72.08, 72.03, 69.47, 69.23, 69.18, 66.63, 63.23, 63.16, 61.09, 39.76, 29.44. HR-ESI-MS *(m/z)*: [M+Na]$^+$ calcd for $C_{78}H_{79}N_7O_{21}Na$, 1472.5227; found, 1472.5231.

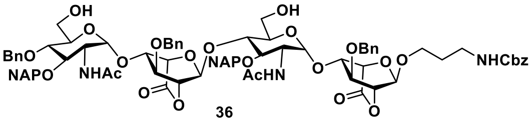
N-benzyloxycarbonyl-3-aminopropyl-*O*-[(2-azido-4-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(3-*O*-benzyl-*α*-L-idopyranosylurono-6,2-lactone)-(1→4)-*O*-(2-azido-2-deoxy-*α*-D-glucopyranosyl)]-(1→4)-*O*-3-*O*-benzyl-*α*-L-idopyranosidurono-6,2-lactone (34)



34

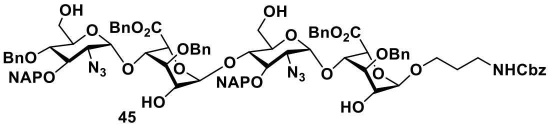
^{1}H NMR (400 MHz, Chloroform-d) δ 7.40 – 7.28 (m, 20H), 5.75 (t, J = 5.2 Hz, 1H), 5.28 (s, 1H), 5.09 (d, J = 3.7 Hz, 1H), 5.06 (s, 3H), 4.94 (d, J = 3.4 Hz, 1H), 4.78 – 4.70 (m, 4H), 4.67 (d, J = 3.3 Hz, 1H), 4.66 – 4.60 (m, 2H), 4.53 (t, J = 2.6 Hz, 1H), 4.50 (d, J = 3.2 Hz, 1H), 4.47 (t, J = 2.6 Hz, 1H), 4.30 – 4.28 (m, 1H), 4.25 – 4.23 (m, 1H), 4.03 – 3.89 (m, 6H), 3.83 – 3.80 (m, 2H), 3.77 – 3.70 (m, 3H), 3.60 (td, J = 9.7, 9.2, 3.9 Hz, 3H), 3.47 – 3.40 (m, 2H), 3.28 (q, J = 5.9 Hz, 1H), 3.24 – 3.19 (m, 2H), 2.73 (s, 1H), 2.21 (s, 2H), 1.83 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 167.99, 167.19, 156.64, 137.73, 136.83, 136.64, 136.50, 128.76, 128.75, 128.55, 128.48, 128.45, 128.27, 128.25, 128.22, 128.18, 128.09, 99.96, 99.64, 97.33, 96.66, 80.70, 80.18, 79.33, 79.20, 78.78, 77.96, 77.24, 75.03, 73.04, 72.60, 72.54, 72.24, 72.20, 71.42, 70.92, 70.26, 69.65, 69.41, 69.11, 66.63, 62.76, 62.32, 61.55, 61.34, 39.73, 29.41. HR-ESI-MS *(m/z)*: [M+Na]$^+$ calcd for $C_{56}H_{63}N_7O_{21}Na$, 1192.3975; found, 1192.3975.

N-benzyloxycarbonyl-3-aminopropyl-*O*-[(2-acetamido-4-*O*-benzyl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(3-*O*-benzyl-*α*-L-idopyranosylurono-6,2-lactone)-(1→4)-*O*-(2-acetamido-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl)]-(1→4)-*O*-3-*O*-benzyl-*α*-L-idopyranosidurono-6,2-lactone (36)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (s, 1H), 7.84 (d, *J* = 10.4 Hz, 5H), 7.77 (s, 1H), 7.67 (s, 1H), 7.51 (dd, *J* = 7.8, 4.9 Hz, 4H), 7.45 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.36 – 7.30 (m, 14H), 7.24 (d, *J* = 8.4 Hz, 3H), 7.20 – 7.17 (m, 2H), 7.08 (d, *J* = 6.7 Hz, 2H), 5.50 (t, *J* = 5.1 Hz, 1H), 5.41 (d, *J* = 0.8 Hz, 1H), 5.11 (d, *J* = 3.7 Hz, 1H), 5.08 – 5.03 (m, 3H), 5.01- 4.88 (m, 4H), 4.85 (d, *J* = 11.0 Hz, 1H), 4.75 – 4.67 (m, 4H), 4.59 (s, 1H), 4.53 – 4.52 (m, 1H), 4.47 (d, *J* = 2.8 Hz, 1H), 4.42 – 4.31 (m, 5H), 4.18 (d, *J* = 3.4 Hz, 1H), 4.13 – 4.07 (m, 2H), 3.95 – 3.87 (m, 3H), 3.78 (dd, *J* = 25.8, 10.9 Hz, 3H), 3.68 – 3.53 (m, 11H), 3.44 – 3.36 (m, 1H), 3.23 (ddd, *J* = 10.4, 9.5, 5.3 Hz, 1H), 1.81 (s, 2H), 1.52 (d, *J* = 9.8 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.00, 169.88, 167.96, 167.82, 156.58, 137.84, 136.61, 136.48, 135.58, 133.28, 133.22, 132.99, 132.95, 128.67, 128.56, 128.51, 128.48, 128.46, 128.39, 128.21, 128.09, 128.04, 128.01, 127.97, 127.74, 127.69, 127.28, 126.70, 126.52, 126.41, 126.35, 126.21, 125.86, 98.80, 98.69, 97.72, 96.52, 79.65, 79.29, 78.94, 78.81, 78.28, 77.97, 77.26, 76.64, 75.08, 74.77, 73.37, 72.48, 72.22, 72.11, 72.02, 71.89, 69.41, 69.34, 68.53, 66.62, 61.28, 61.02, 52.73, 52.32, 39.22, 29.71, 29.52, 23.03, 22.92. HR-ESI-MS *(m/z)*: [M+Na]$^+$ calcd for $C_{82}H_{87}N_3O_{23}Na$, 1504.5628; found, 1504.5608.

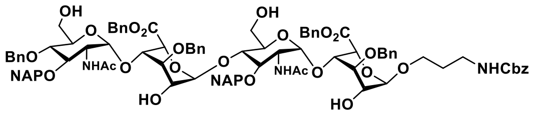
N-benzyloxycarbonyl-3-aminopropyl-*O*-[(benzyl (2-azido-4-*O*-benzyl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl))-(1→4)-*O*-(3-*O*-benzyl-*α*-L-idopyranosyluronate)-(1→4)-*O*-(benzyl (2-azido-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl))]-(1→4)-*O*-3-*O*-benzyl-*α*-L-idopyranosiduronate (45)



^{1}H NMR (400 MHz, Chloroform-d) δ 7.82 – 7.78 (m, 2H), 7.75 (dd, J = 6.1, 3.5 Hz, 1H), 7.71 (s, 4H), 7.67 (d, J = 8.5 Hz, 1H), 7.46 (dd, J = 6.2, 3.3 Hz, 2H), 7.42 (dd, J = 8.5, 1.6 Hz, 1H), 7.38 – 7.29 (m, 21H), 7.25 – 7.16 (m, 8H), 7.14 – 7.10 (m, 2H), 7.04 – 7.02 (m, 2H), 5.54 (t, J = 5.0 Hz, 1H), 5.32 – 5.29 (m, 2H), 5.13 (d, J = 12.4 Hz, 1H), 5.03 (s, 2H), 4.99 (s, 1H), 4.97 (d, J = 3.7 Hz, 1H), 4.90 – 4.87 (m, 3H), 4.84 (t, J = 2.6 Hz, 2H), 4.81 (s, 1H), 4.78 (d, J = 3.2 Hz, 1H), 4.74 (s, 1H), 4.72 – 4.59 (m, 5H), 4.48 (d, J = 12.2 Hz, 1H), 4.08 – 4.06 (m, 1H), 4.04 (s, 1H), 3.93 – 3.85 (m, 3H), 3.81 – 3.69 (m, 7H), 3.62 – 3.57 (m, 2H), 3.47 (ddt, J = 22.2, 15.5, 7.5 Hz, 9H), 3.28 – 3.20 (m, 1H), 2.02 (s, 1H), 1.83 (s, 2H), 1.44

(s, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 169.31, 169.21, 156.48, 137.79, 137.23, 137.18, 136.55, 135.22, 135.07, 134.92, 134.70, 133.27, 133.02, 132.85, 128.74, 128.71, 128.65, 128.52, 128.48, 128.43, 128.41, 128.30, 128.26, 128.24, 128.21, 128.13, 128.08, 128.07, 128.04, 127.98, 127.97, 127.92, 127.85, 127.78, 127.66, 127.60, 126.81, 126.34, 126.09, 125.99, 125.89, 125.85, 125.68, 125.63, 101.63, 101.07, 95.96, 95.53, 80.66, 79.37, 77.24, 75.69, 75.26, 75.05, 74.98, 74.48, 73.15, 72.54, 72.38, 72.30, 72.11, 71.54, 69.45, 69.28, 68.07, 67.31, 67.10, 67.03, 66.96, 66.65, 63.99, 63.64, 61.18, 60.98, 39.90, 29.45. HR-ESI-MS *(m/z)*: $[M+Na]^+$ calcd for $C_{92}H_{95}N_7O_{23}Na$, 1689.6411; found, 1689.6372.

N-benzyloxycarbonyl-3-aminopropyl-*O*-[(benzyl (2-acetamido-4-*O*-benzyl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl))-(1→4)-*O*-(3-*O*-benzyl-*α*-L-idopyranosyluronate)-(1→4)-*O*-(benzyl (2-acetamido-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl))]-(1→4)-*O*-3-*O*-benzyl-*α*-L-idopyranosiduronate (50)

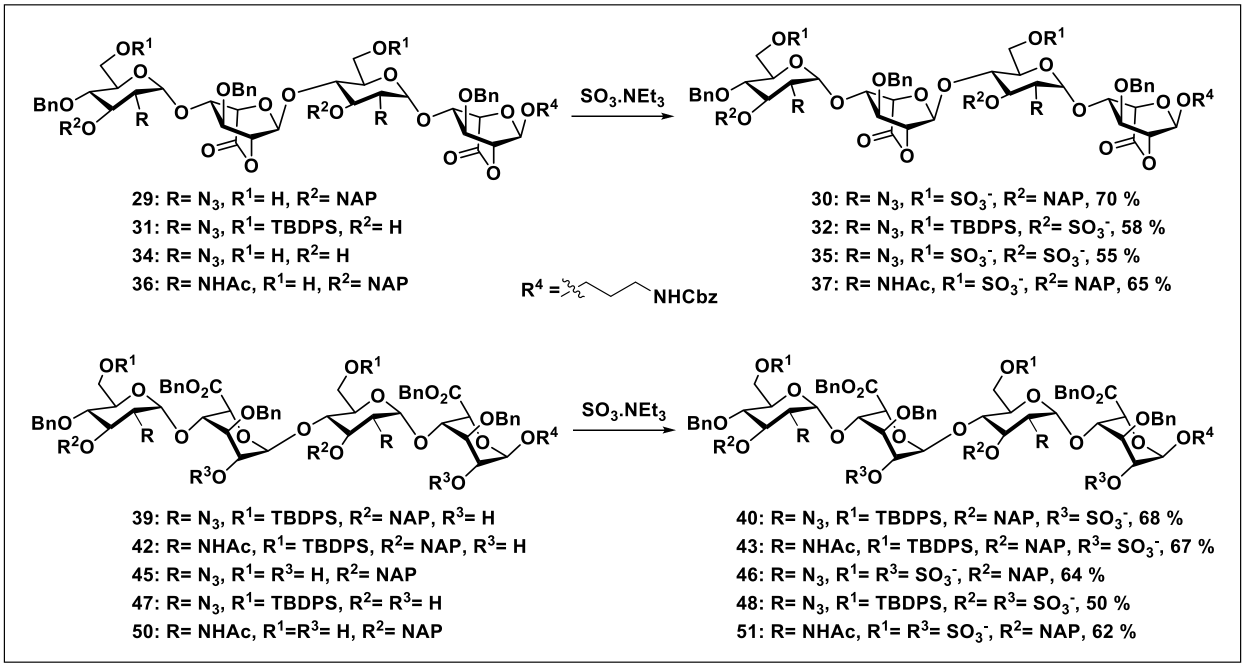


50

^{1}H NMR (400 MHz, Chloroform-d) δ 7.81- 7.75 (m, 4H), 7.75 – 7.70 (m, 2H), 7.66 (d, J = 6.9 Hz, 2H), 7.47 (dd, J = 6.2, 3.3 Hz, 2H), 7.44 – 7.39 (m, 3H), 7.39 – 7.36 (m, 2H), 7.35 – 7.33 (m, 4H), 7.32- 7.29 (m, 9H), 7.27- 7.22 (m, 9H), 7.21 – 7.13 (m, 5H), 7.07 (d, J = 7.5 Hz, 2H), 5.48 (t, J = 5.4 Hz, 1H), 5.31 – 5.25 (m, 2H), 5.06- 5.04 (m, 4H), 4.99 – 4.96 (m, 2H), 4.93 – 4.87 (m, 4H), 4.87 – 4.82 (m, 3H), 4.75 (d, J = 11.7 Hz, 1H), 4.65 (dd, J = 11.3, 8.1 Hz, 2H), 4.58 (d, J = 12.2 Hz, 1H), 4.52 (d, J = 11.6 Hz, 2H), 4.43 (t, J = 12.2 Hz, 1H), 4.23 – 4.15 (m, 2H), 4.11 – 4.09 (m, 1H), 4.01 – 3.94 (m, 2H), 3.88 – 3.84 (m, 2H), 3.79 – 3.62 (m, 9H), 3.61 – 3.48 (m, 6H), 3.42 – 3.37 (m, 1H), 3.31- 3.25 (m, 1H), 3.08 (s, 1H), 2.63 (s, 1H), 1.81 (s, 2H), 1.67 (s, 3H), 1.44 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 170.93, 170.65, 169.45, 169.26, 156.53, 138.08, 137.19, 136.45, 135.79, 135.67, 134.75, 134.58, 133.22, 133.20, 132.90, 132.83, 128.75, 128.72, 128.65, 128.52, 128.46, 128.45, 128.42, 128.34, 128.26, 128.22, 128.18, 128.15, 128.10, 128.01, 127.97, 127.84, 127.62, 126.62, 126.17, 126.04, 125.98, 101.15, 96.81, 96.07, 79.79, 77.92, 77.70, 75.51, 75.07, 74.03, 73.70, 72.84, 72.66, 72.44, 72.35, 71.98, 71.32, 69.22, 68.66, 67.92, 67.48, 67.34, 67.30, 67.11, 66.69, 61.31, 61.10, 52.76, 52.55, 39.55, 29.72, 29.47. HR-ESI-MS *(m/z)*: $[M+H]^+$ calcd for $C_{96}H_{104}N_3O_{25}$, 1698.6959; found, 1698.6862.

2.5 General procedure for *O*-sulfation:

To a solution of starting material (1 mmol) in DMF (2 mL) was added $SO_3.NEt_3$ complex (10 mmol per -OH) under N_2 atmosphere and stirred at 60 ° C for 3 days. Upon completion of reaction, aqueous $NaHCO_3$ (20 mmol) was added to reaction mixture and stirred for another 16 h. Next, the reaction mixture was concentrated under reduced pressure and the resulting residue was filtered with MeOH through wattman filter paper. The filtrate was concentrated and purified using silica column chromatography.



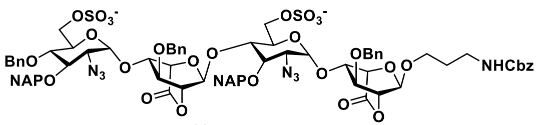
29: R= N_3, R^1= H, R^2= NAP
31: R= N_3, R^1= TBDPS, R^2= H
34: R= N_3, R^1= H, R^2= H
36: R= NHAc, R^1= H, R^2= NAP

30: R= N_3, R^1= SO_3^-, R^2= NAP, 70 %
32: R= N_3, R^1= TBDPS, R^2= SO_3^-, 58 %
35: R= N_3, R^1= SO_3^-, R^2= SO_3^-, 55 %
37: R= NHAc, R^1= SO_3^-, R^2= NAP, 65 %

39: R= N_3, R^1= TBDPS, R^2= NAP, R^3= H
42: R= NHAc, R^1= TBDPS, R^2= NAP, R^3= H
45: R= N_3, R^1= R^3= H, R^2= NAP
47: R= N_3, R^1= TBDPS, R^2= R^3= H
50: R= NHAc, R^1=R^3= H, R^2= NAP

40: R= N_3, R^1= TBDPS, R^2= NAP, R^3= SO_3^-, 68 %
43: R= NHAc, R^1= TBDPS, R^2= NAP, R^3= SO_3^-, 67 %
46: R= N_3, R^1= R^3= SO_3^-, R^2= NAP, 64 %
48: R= N_3, R^1= TBDPS, R^2= R^3= SO_3^-, 50 %
51: R= NHAc, R^1= R^3= SO_3^-, R^2= NAP, 62 %

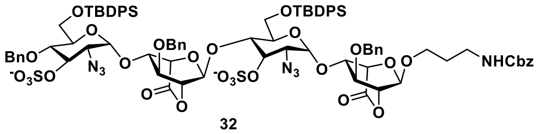
N-benzyloxycarbonyl-3-aminopropyl-*O*-[(2-azido-4-*O*-benzyl-6-*O*-sulfonato-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(3-*O*-benzyl-*α*-L-idopyranosylurono-6,2-lactone)-(1→4)-*O*-(2-azido-6-*O*-sulfonato-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl)]-(1→4)-*O*-3-*O*-benzyl-*α*-L-idopyranosidurono-6,2-lactone (30)



30

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.85 – 7.80 (m, 4H), 7.79 (d, *J* = 2.2 Hz, 1H), 7.76 – 7.74 (m, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.58- 7.54 (m, 2H), 7.52 – 7.50 (m, 1H), 7.49 (d, *J* = 2.1 Hz, 1H), 7.48 – 7.39 (m, 8H), 7.38 – 7.26 (m, 13H), 5.29 (s, 1H), 5.18 (d, *J* = 3.2 Hz, 1H), 5.15 (d, *J* = 3.5 Hz, 1H), 5.07 (s, 2H), 4.99 (d, *J* = 2.9 Hz, 1H), 4.93 (s, 2H), 4.82 (d, *J* = 3.1 Hz, 2H), 4.80 – 4.79 (m, 2H), 4.76- 4.75 (m, 5H), 4.34 – 4.26 (m, 2H), 4.23 (dt, *J* = 4.9, 2.4 Hz, 1H), 4.20 – 4.18 (m, 1H), 4.12 (d, *J* = 9.4 Hz, 1H), 4.04 (t, *J* = 3.8 Hz, 1H), 3.98- 3.93 (m, 3H), 3.91 – 3.84 (m, 3H), 3.78 – 3.68 (m, 4H), 3.67 – 3.58 (m, 3H), 3.55 (dd, *J* = 9.9, 3.5 Hz, 1H), 3.45 (d, *J* = 9.5 Hz, 1H), 3.26 (tt, *J* = 13.0, 6.5 Hz, 2H), 1.86- 1.79 (m, 2H). ^{13}C NMR (101 MHz, Methanol-d_4) δ 170.23, 170.06, 157.43, 138.27, 138.00, 137.89, 136.95, 135.52, 135.13, 133.42, 133.31, 133.05, 133.01, 131.01, 128.47, 128.31, 128.09, 128.04, 128.01, 127.83, 127.76, 127.68, 127.65, 127.60, 127.55, 127.50, 127.48, 127.45, 127.38, 127.30, 127.25, 127.15, 126.35, 126.22, 125.91, 125.65, 125.59, 125.49, 101.46, 100.56, 96.18, 95.58, 80.06, 78.87, 77.24, 74.86, 74.67, 74.40, 74.03, 72.77, 72.58, 72.36, 71.69, 70.72, 70.38, 68.65, 68.51, 68.36, 67.99, 67.71, 66.45, 66.03, 65.64, 65.33, 64.09, 63.48, 51.72, 50.83, 38.77, 38.03, 33.50, 31.67, 30.76, 29.07, 28.70, 23.55, 22.63, 22.34. HR-ESI-MS (m/z): [M-2H]$^{2-}$ calcd for $C_{78}H_{77}N_7O_{27}S_2^{2-}$, 803.7160; found, 803.7170.

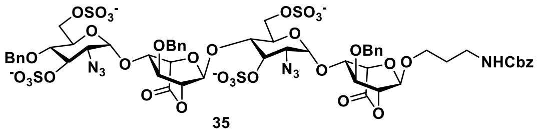
N-benzyloxycarbonyl-3-aminopropyl-*O*-[(2-azido-4-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-sulfonato-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(3-*O*-benzyl-*α*-L-idopyranosylurono-6,2-lactone)-(1→4)-*O*-(2-azido-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-sulfonato-2-deoxy-*α*-D-glucopyranosyl)]-(1→4)-*O*-3-*O*-benzyl-*α*-L-idopyranosidurono-6,2-lactone (32)



32

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.68 – 7.67 (m, 1H), 7.66 (d, J = 2.0 Hz, 1H), 7.65 – 7.61 (m, 4H), 7.60 (s, 1H), 7.58 (d, J = 1.3 Hz, 1H), 7.41 (d, J = 7.4 Hz, 2H), 7.39 – 7.34 (m, 4H), 7.32 – 7.29 (m, 9H), 7.29 – 7.22 (m, 13H), 7.20 – 7.13 (m, 4H), 5.49 (s, 1H), 5.18 (d, J = 10.6 Hz, 1H), 5.13 (d, J = 3.4 Hz, 1H), 5.06 (s, 1H), 5.02- 5.00 (m, 2H), 4.98 – 4.87 (m, 2H), 4.76 – 4.70 (m, 5H), 4.56 (dd, J = 18.2, 11.0 Hz, 2H), 4.43 – 4.42 (m, 1H), 4.41- 4.39 (m, 2H), 4.35 – 4.32 (m, 1H), 4.07 – 3.94 (m, 3H), 3.87- 3.83 (m, 3H), 3.80- 3.65 (m, 5H), 3.55 (dt, J = 9.3, 5.5 Hz, 1H), 3.26 – 3.16 (m, 3H), 1.78 – 1.74 (m, 2H), 0.99 (s, 9H), 0.96 (s, 9H). ^{13}C NMR (101 MHz, Methanol-d_4) δ 168.67, 167.84, 157.33, 138.44, 137.64, 137.34, 136.96, 135.65, 135.56, 135.43, 135.40, 133.36, 133.05, 132.95, 132.75, 129.53, 129.50, 129.39, 128.37, 128.18, 128.13, 128.08, 128.02, 127.98, 127.72, 127.67, 127.62, 127.59, 127.41, 127.38, 127.36, 127.29, 127.07, 100.08, 99.67, 97.02, 94.52, 79.87, 79.56, 79.41, 79.12, 78.50, 78.07, 76.48, 75.53, 74.72, 73.99, 71.92, 71.81, 71.51, 71.32, 69.49, 69.39, 67.63, 66.07, 62.84, 62.52, 62.40, 62.10, 38.36, 29.23, 26.05. HR-ESI-MS (m/z): [M-2H]$^{2-}$ calcd for $C_{88}H_{97}N_7O_{27}S_2Si_2^{2-}$, 901.7711; found 901.7706.

N-benzyloxycarbonyl-3-aminopropyl-*O*-[(2-azido-4-*O*-benzyl-6-*O*-sulfonato-3-*O*-sulfonato-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(3-*O*-benzyl-*α*-L-idopyranosylurono-6,2-lactone)-(1→4)-*O*-(2-azido-6-*O*-sulfonato-3-*O*-sulfonato-2-deoxy-*α*-D-glucopyranosyl)]-(1→4)-*O*-3-*O*-benzyl-*α*-L-idopyranosidurono-6,2-lactone (35)

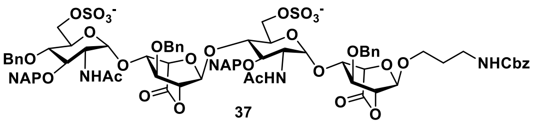


35

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.53 (d, J = 7.0 Hz, 2H), 7.46 (d, J = 7.4 Hz, 2H), 7.42 – 7.22 (m, 16H), 5.33 (s, 1H), 5.21 – 5.14 (m, 4H), 5.08 – 5.02 (m, 3H), 4.83 (d, J = 11.8 Hz, 2H), 4.78 – 4.76 (m, 1H), 4.70 (d, J = 11.7 Hz, 2H), 4.64 (t, J = 9.1 Hz, 2H), 4.58 – 4.52 (m, 1H), 4.32 (td, J = 10.4, 9.7, 3.0 Hz, 1H), 4.27 (d, J = 3.2 Hz, 1H), 4.24 –

4.18 (m, 3H), 4.11 (t, J= 4.6 Hz, 1H), 3.94 – 3.80 (m, 6H), 3.71 – 3.67 (m, 2H), 3.63 – 3.55 (m, 2H), 3.55 – 3.44 (m, 2H), 3.31 – 3.22 (m, 2H), 1.85 – 1.76 (m, 2H). ^{13}C NMR (101 MHz, Methanol-*d₄*) δ 171.28, 170.46, 157.45, 138.41, 138.10, 137.97, 136.94, 128.91, 128.10, 128.08, 128.00, 127.80, 127.69, 127.59, 127.45, 127.37, 127.11, 126.99, 102.93, 101.09, 96.85, 95.66, 78.94, 78.08, 76.76, 76.60, 75.76, 74.57, 73.85, 72.82, 72.31, 72.23, 72.09, 70.61, 70.20, 69.48, 69.24, 69.04, 67.90, 66.56, 66.02, 65.71, 65.54, 63.01, 62.67, 37.93, 29.35. HR-ESI-MS (m/z): $[M-4H]^{4-}$ calcd for $C_{56}H_{59}N_7O_{35}S_4^{4-}$, 371.3015; found, 371.3012.

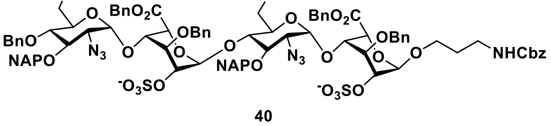
N-benzyloxycarbonyl-3-aminopropyl-*O*-[(2-acetamido-4-*O*-benzyl-6-*O*-sulfonato-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(3-*O*-benzyl-*α*-L-idopyranosylurono-6,2-lactone)-(1→4)-*O*-(2-acetamido-6-*O*-sulfonato-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl)]-(1→4)-*O*-3-*O*-benzyl-*α*-L-idopyranosidurono-6,2-lactone (37)



37

^{1}H NMR (400 MHz, Methanol-*d₄*) δ 7.91 – 7.70 (m, 9H), 7.51 – 7.37 (m, 14H), 7.33 – 7.22 (m, 11H), 5.54 (s, 1H), 5.13 (d, *J* = 7.0 Hz, 2H), 5.09 (s, 1H), 5.06 (s, 2H), 4.81 – 4.52 (m, 9H), 4.46 (d, *J* = 8.9 Hz, 1H), 4.39 (d, *J* = 8.3 Hz, 2H), 4.32 – 4.27 (m, 3H), 4.25 – 4.16 (m, 3H), 4.10 – 3.89 (m, 8H), 3.83 – 3.54 (m, 6H), 3.26 – 3.15 (m, 2H), 1.84 – 1.75 (m, 8H). ^{13}C NMR (101 MHz, Methanol-*d₄*) δ 171.75, 171.66, 168.63, 168.43, 157.34, 138.24, 137.55, 137.08, 136.22, 136.19, 133.39, 133.35, 133.33, 133.02, 132.99, 132.91, 128.29, 128.26, 128.11, 128.03, 127.90, 127.81, 127.64, 127.60, 127.51, 127.46, 127.43, 127.29, 126.00, 125.76, 125.60, 125.51, 125.46, 125.41, 125.28, 125.04, 99.43, 99.29, 98.51, 96.93, 80.13, 80.10, 79.78, 79.62, 78.24, 78.08, 77.74, 77.66, 74.58, 72.13, 72.10, 71.96, 71.92, 71.87, 70.26, 69.65, 69.62, 66.93, 65.94, 65.52, 52.93, 52.82, 37.71, 29.29, 21.50, 21.42. HR-ESI-MS *(m/z)*: $[M-2H]^{2-}$ calcd for $C_{82}H_{85}N_3O_{29}S_2^{2-}$, 819.7361; found, 819.7369.

N-benzyloxycarbonyl-3-aminopropyl-*O*-[(benzyl (2-azido-4-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl))-(1→4)-*O*-(3-*O*-benzyl-2-*O*-sulfonato-*α*-L-idopyranosyluronate)-(1→4)-*O*-(benzyl (2-azido-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl))]-(1→4)-*O*-3-*O*-benzyl-2-*O*-sulfonato-*α*-L-idopyranosiduronate (40)

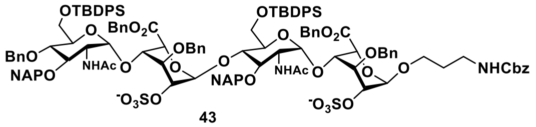


40

^{1}H NMR (400 MHz, Methanol-*d₄*) δ 7.79 – 7.76 (m, 7H), 7.74 – 7.70 (m, 3H), 7.61 – 7.41 (m, 13H), 7.38 – 7.30 (m, 14H), 7.29 – 7.15 (m, 23H), 7.04 (t, J = 6.6 Hz, 2H), 6.96 (t, J = 7.5 Hz, 2H), 6.65 (d, J = 7.7 Hz, 1H), 5.71 (s, 1H), 5.37 (d, J = 12.1

Hz, 1H), 5.22 (d, J = 3.5 Hz, 1H), 5.17 (s, 2H), 5.06 (s, 1H), 5.02 – 4.89 (m, 7H), 4.83 (d, J = 5.6 Hz, 1H), 4.77 – 4.69 (m, 4H), 4.63 – 4.51 (m, 3H), 4.48 (s, 1H), 4.38 (d, J = 11.7 Hz, 1H), 4.33 – 4.26 (m, 2H), 4.22 – 4.19 (m, 2H), 4.04 – 3.98 (m, 3H), 3.86 (d, J = 10.4 Hz, 2H), 3.82 – 3.70 (m, 4H), 3.65 – 3.54 (m, 4H), 3.29 – 3.12 (m, 3H), 1.81 – 1.73 (m, 2H), 0.99 (d, J = 6.8 Hz, 18H). ^{13}C NMR (101 MHz, Methanol-d_4) δ 169.75, 169.00, 157.34, 138.43, 137.89, 137.83, 136.89, 135.91, 135.79, 135.69, 135.41, 134.97, 133.67, 133.35, 133.25, 133.03, 132.78, 129.45, 129.20, 128.45, 128.15, 128.09, 128.04, 127.83, 127.47, 127.38, 127.22, 126.97, 126.45, 125.95, 125.56, 125.41, 125.36, 125.22, 125.07, 99.44, 98.67, 96.01, 94.54, 79.41, 78.57, 77.75, 74.81, 74.28, 74.15, 73.06, 72.48, 72.31, 72.03, 71.88, 71.38, 70.72, 69.27, 67.89, 67.22, 66.95, 66.35, 65.94, 63.89, 63.75, 62.39, 62.06, 37.92, 29.35, 29.16, 26.31, 26.05. HR-ESI-MS (m/z): [M-2H]$^{2-}$ calcd for $C_{124}H_{129}N_7O_{29}S_2Si_2^{2-}$, 1150.3930; found, 1150.3950.

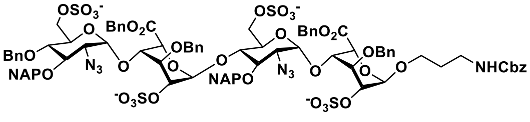
N-benzyloxycarbonyl-3-aminopropyl-*O*-[(benzyl (2-acetamido-4-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl))-(1→4)-*O*-(3-*O*-benzyl-2-*O*-sulfonato-*α*-L-idopyranosyluronate)-(1→4)-*O*-(benzyl (2-acetamido-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl))]-(1→4)-*O*-3-*O*-benzyl-2-*O*-sulfonato-*α*-L-idopyranosiduronate (43)



43

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.83 (s, 1H), 7.82 – 7.80 (m, 2H), 7.79 (s, 2H), 7.76 – 7.73 (m, 3H), 7.71 (s, 1H), 7.68 (d, J = 7.6 Hz, 3H), 7.63 (s, 1H), 7.61 (d, J = 5.1 Hz, 2H), 7.58 (d, J = 6.1 Hz, 3H), 7.48 (dd, J = 16.8, 8.0 Hz, 4H), 7.43- 7.38 (m, 9H), 7.36- 7.30 (m, 16H), 7.25 – 7.20 (m, 7H), 7.19- 7.15 (m, 7H), 6.98 (d, J = 7.4 Hz, 2H), 5.71 (s, 1H), 5.20 (s, 4H), 4.98 (s, 3H), 4.83 (s, 1H), 4.81 – 4.75 (m, 3H), 4.69 (d, J = 12.0 Hz, 2H), 4.57 – 4.50 (m, 5H), 4.41 – 4.34 (m, 5H), 4.24 – 4.03 (m, 5H), 3.90 (d, J = 15.9 Hz, 2H), 3.81- 3.74 (m, 6H), 3.65 – 3.56 (m, 5H), 3.29 – 3.25 (m, 1H), 3.20- 3.13 (m, 1H), 2.01 (s, 3H), 1.84 – 1.75 (m, 5H), 1.07 (s, 9H), 0.98 (s, 9H). ^{13}C NMR (101 MHz, Methanol-d_4) δ 169.56, 169.49, 169.38, 157.31, 137.61, 137.59, 136.82, 136.31, 135.95, 135.79, 135.75, 135.66, 135.38, 135.15, 134.79, 134.55, 134.31, 134.25, 133.42, 133.33, 133.32, 133.29, 133.20, 133.01, 132.93, 132.63, 129.45, 129.28, 129.24, 128.45, 128.33, 128.28, 128.23, 128.21, 128.18, 128.10, 128.05, 127.97, 127.92, 127.83, 127.74, 127.71, 127.67, 127.63, 127.61, 127.57, 127.45, 127.35, 127.28, 127.26, 127.23, 127.21, 127.18, 126.98, 126.38, 125.90, 125.63, 125.58, 125.47, 125.41, 99.99, 99.54, 98.82, 80.73, 79.13, 78.20, 77.87, 77.70, 77.67, 77.55, 75.38, 75.34, 74.51, 73.19, 72.75, 72.48, 72.13, 72.07, 72.03, 70.76, 70.49, 70.36, 67.09, 66.53, 66.31, 66.01, 62.40, 62.09, 53.23, 38.23, 34.06, 31.66, 30.78, 29.33, 26.37, 26.05. HR-ESI-MS (m/z): [M-2H]$^{2-}$ calcd for $C_{128}H_{137}N_3O_{31}S_2Si_2^{2-}$, 1166.4130; found, 1166.4142.

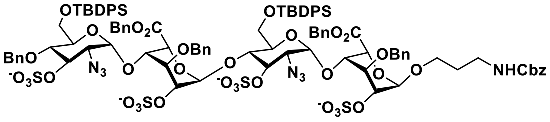
N-benzyloxycarbonyl-3-aminopropyl-*O*-[(benzyl (2-azido-4-*O*-benzyl-6-*O*-sulfonato-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl))-(1→4)-*O*-(3-*O*-benzyl-2-*O*-sulfonato-*α*-L-idopyranosyluronate)-(1→4)-*O*-(benzyl (2-azido-6-*O*-sulfonato-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl))]-(1→4)-*O*-3-*O*-benzyl-2-*O*-sulfonato-*α*-L-idopyranosiduronate (46)



46

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.84 – 7.75 (m, 4H), 7.71- 7.68 (m, 3H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.55 – 7.42 (m, 9H), 7.40 (d, *J* = 8.5 Hz, 5H), 7.36-7.31 (m, 10H), 7.28 – 7.23 (m, 7H), 7.15 – 7.09 (m, 1H), 7.02 (t, *J* = 7.3 Hz, 2H), 6.59 (d, *J* = 7.5 Hz, 2H), 5.53 (s, 1H), 5.44 (d, *J* = 12.1 Hz, 1H), 5.22 – 5.15 (m, 3H), 5.11 (s, 1H), 5.07 – 5.02 (m, 3H), 5.01 – 4.94 (m, 3H), 4.82- 4.74 (m, 4H), 4.72- 4.65 (m, 4H), 4.62 – 4.57 (m, 2H), 4.53-4.50 (m, 2H), 4.40 – 4.34 (m, 4H), 4.17- 4.07 (m, 4H), 4.01 – 3.80 (m, 6H), 3.67- 3.58 (m, 3H), 3.41 – 3.36 (m, 1H), 3.31 – 3.16 (m, 2H), 1.87- 1.75 (m, 2H). ^{13}C NMR (101 MHz, Methanol-d_4) δ 170.01, 169.88, 157.39, 138.37, 137.81, 137.42, 136.92, 135.91, 135.57, 135.31, 134.50, 133.35, 133.33, 133.03, 132.92, 128.59, 128.49, 128.40, 128.36, 128.29, 128.16, 128.15, 128.08, 127.99, 127.83, 127.57, 127.44, 127.34, 127.26, 127.15, 126.22, 125.75, 125.65, 125.63, 125.60, 125.46, 125.35, 99.56, 97.94, 96.62, 80.01, 78.48, 77.41, 74.92, 74.68, 74.57, 72.35, 72.08, 71.84, 70.68, 70.48, 67.73, 67.28, 67.04, 66.95, 66.40, 66.01, 65.38, 64.16, 63.91, 63.89, 38.09, 31.67, 30.77, 29.33, 29.19, 29.06, 28.72. HR-ESI-MS (m/z): [M-4H] $^{4-}$ calcd for $C_{92}H_{91}N_7O_{35}S_4{}^{4-}$, 495.3615; found, 495.3588.

N-benzyloxycarbonyl-3-aminopropyl-*O*-[(benzyl (2-azido-4-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-sulfonato-2-deoxy-*α*-D-glucopyranosyl))-(1→4)-*O*-(3-*O*-benzyl-2-*O*-sulfonato-*α*-L-idopyranosyluronate)-(1→4)-*O*-(benzyl (2-azido-6-*O*-*tert*-butyldiphenylsilyl-3-*O*-sulfonato-2-deoxy-*α*-D-glucopyranosyl))]-(1→4)-*O*-3-*O*-benzyl-2-*O*-sulfonato-*α*-L-idopyranosiduronate (48)

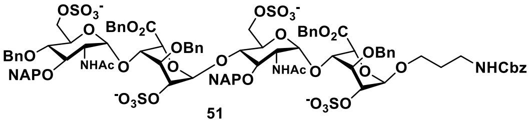


48

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.61 (dd, *J* = 6.4, 3.0 Hz, 3H), 7.58 (dd, *J* = 3.0, 1.4 Hz, 2H), 7.56 (d, *J* = 1.6 Hz, 1H), 7.53 (d, *J* = 1.3 Hz, 1H), 7.51 (d, *J* = 1.4 Hz, 1H), 7.31 (t, *J* = 2.1 Hz, 1H), 7.29 (dd, *J* = 2.6, 1.2 Hz, 1H), 7.27 (s, 2H), 7.25 (s, 2H), 7.24 (s, 2H), 7.22- 7.20 (m, 7H), 7.18 – 7.15 (m, 7H), 7.13 – 7.11 (m, 5H), 7.07 (d, *J* = 1.5 Hz, 2H), 7.05 – 7.03 (m, 6H), 7.02 (s, 4H), 7.01 – 6.99 (m, 3H), 5.35 (s, 2H), 5.09 (d, *J* = 10.1 Hz, 1H), 5.04 (d, *J* = 2.6 Hz, 1H), 5.03- 4.99 (m, 3H), 4.96 (s, 1H), 4.90 (d, *J* = 12.1 Hz, 2H), 4.84 (s, 2H), 4.61 (d, *J* = 9.4 Hz, 2H), 4.55 (d, *J* = 12.3 Hz, 2H), 4.44 (d, *J* = 6.3 Hz, 1H), 4.33 (s, 1H), 4.28 (d, *J* = 12.2 Hz, 2H), 4.16 (d, *J* = 11.7 Hz, 2H), 3.94 (s, 1H), 3.90 (s, 1H), 3.84 (d, *J* =

8.2 Hz, 2H), 3.77 (dd, *J* = 19.4, 9.5 Hz, 3H), 3.71- 3.69 (m, 3H), 3.56- 3.50 (m, 3H), 3.44 – 3.41 (m, 2H), 3.29 (dd, *J* = 10.2, 3.3 Hz, 1H), 3.10 (d, *J* = 6.4 Hz, 1H), 3.05- 3.00 (m, 1H), 2.92 (dd, *J* = 9.7, 3.5 Hz, 1H), 1.66- 1.60 (m, 2H), 0.91 (s, 9H), 0.87 (s, 9H). ^{13}C NMR (151 MHz, Methanol-*d$_4$*) δ 170.11, 169.28, 157.33, 138.09, 137.94, 137.46, 136.89, 135.80, 135.65, 135.62, 135.45, 134.95, 134.76, 133.52, 133.39, 133.16, 132.94, 129.54, 129.50, 129.30, 129.20, 128.54, 128.43, 128.28, 128.11, 128.08, 128.03, 127.80, 127.77, 127.49, 127.43, 127.41, 127.36, 127.31, 127.25, 127.15, 99.53, 99.36, 94.65, 79.20, 76.45, 75.07, 72.15, 72.10, 72.06, 71.95, 71.55, 70.56, 69.92, 69.39, 67.90, 67.23, 67.21, 66.91, 66.21, 65.90, 63.61, 63.16, 62.32, 62.05, 37.89, 29.37, 29.08, 26.26, 26.06. HR-ESI-MS (m/z): [M-4H]$^{4-}$ calcd for $C_{102}H_{111}N_7O_{35}S_4Si_2^{4-}$, 544.6399; found, 544.6364.

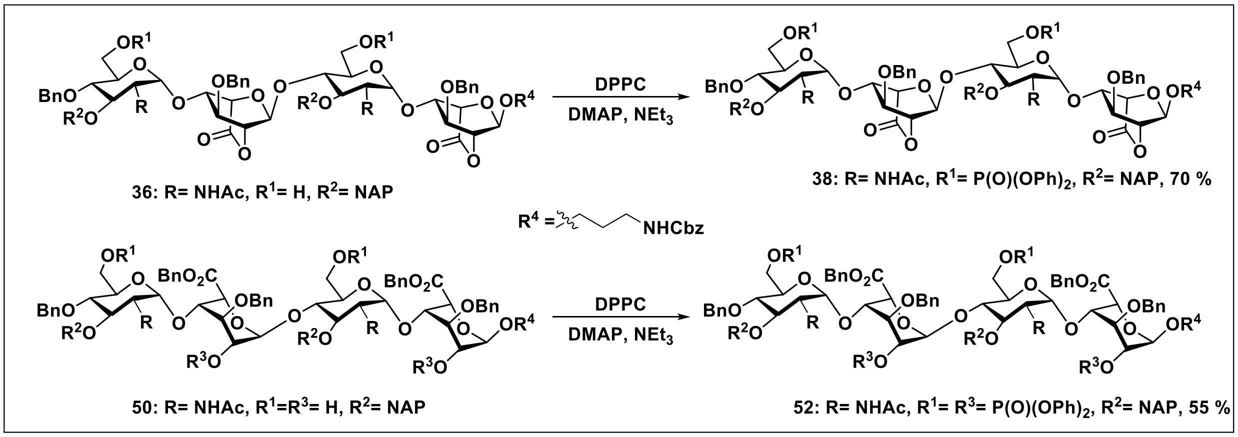
N-benzyloxycarbonyl-3-aminopropyl-*O*-[(benzyl (2-acetamido-4-*O*-benzyl-6-*O*-sulfonato-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl))-(1→4)-*O*-(3-*O*-benzyl-2-*O*-sulfonato-*α*-L-idopyranosyluronate)-(1→4)-*O*-(benzyl (2-acetamido-6-*O*-sulfonato-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl))]-(1→4)-*O*-3-*O*-benzyl-2-*O*-sulfonato-*α*-L-idopyranosiduronate (51)



51

^{1}H NMR (400 MHz, Methanol-*d$_4$*) δ 7.78 – 7.62 (m, 8H), 7.53 (d, J = 8.5 Hz, 1H), 7.43 – 7.25 (m, 20H), 7.25 – 7.13 (m, 11H), 7.11- 7.07 (m, 1H), 6.98 (t, J = 7.6 Hz, 2H), 6.60 (d, J = 7.5 Hz, 1H), 5.47 (s, 1H), 5.35 (d, J = 12.1 Hz, 1H), 5.16 (d, J = 12.9 Hz, 3H), 5.03- 4.94 (m, 4H), 4.83 – 4.76 (m, 2H), 4.74- 4.68 (m, 4H), 4.67 – 4.46 (m, 8H), 4.36 (d, J = 11.0 Hz, 1H), 4.28 (d, J = 14.2 Hz, 2H), 4.23 – 4.17 (m, 2H), 4.13- 4.11 (m, 2H), 4.07- 4.02 (m, 2H), 3.89- 3.87 (m, 2H), 3.83- 3.72 (m, 5H), 3.63 – 3.55 (m, 2H), 3.19- 3.12 (m, 1H), 1.92 (s, 3H), 1.83- 1.74 (m, 2H), 1.69 (s, 3H). ^{13}C NMR (126 MHz, Methanol-*d$_4$*) δ 173.34, 170.81, 170.57, 158.07, 139.19, 138.14, 138.04, 137.53, 137.05, 137.02, 135.96, 135.16, 134.06, 133.67, 133.47, 129.10, 129.07, 129.05, 128.98, 128.81, 128.77, 128.65, 128.55, 128.50, 128.45, 128.32, 128.29, 128.26, 128.24, 128.17, 128.13, 127.94, 127.89, 127.76, 126.73, 126.44, 126.23, 126.03, 125.89, 125.80, 125.73, 100.33, 99.07, 80.98, 79.68, 78.24, 75.91, 75.42, 75.31, 73.50, 72.95, 72.47, 71.73, 71.46, 71.40, 71.31, 71.18, 68.13, 67.81, 67.34, 67.29, 66.78, 66.38, 66.11, 54.01, 53.95, 39.07, 29.98, 29.87. HR-ESI-MS (m/z): [M-4H]$^{4-}$ calcd for $C_{96}H_{99}N_3O_{37}S_4^{4-}$, 503.6224; found, 503.6204.

2.6 General procedure for *O*-phophorylation:



36: R= NHAc, R^1= H, R^2= NAP

38: R= NHAc, R^1= P(O)(OPh)$_2$, R^2= NAP, 70 %

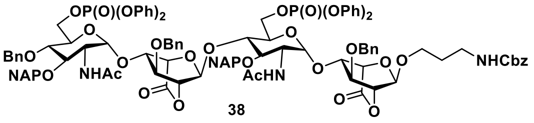
R^4 = NHCbz

50: R= NHAc, R^1=R^3= H, R^2= NAP

52: R= NHAc, R^1= R^3= P(O)(OPh)$_2$, R^2= NAP, 55 %

To a solution of starting material (1 mmol) in CH_2Cl_2 (1 mL) and pyridine (1 mL) was added NEt_3 (10 mmol), DMAP (0.3 mmol) and Diphenyl phosphoryl chloride (5 mmol for **38** and 10 mmol for **52**) at 0 ° C. After 12 h, the reaction mixture was diluted with CH_2Cl_2 and extracted with 1 N HCl and brine. The combined organic layer was dried over Na_2SO_4, filtered, concentrated and purified through silica gel column chromatography.

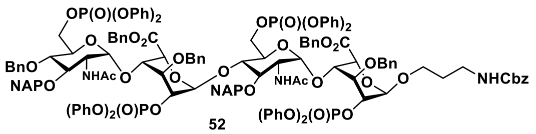
N-benzyloxycarbonyl-3-aminopropyl-*O*-[(2-acetamido-4-*O*-benzyl-6-*O*-diphenylphosphoryl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(3-*O*-benzyl-*α*-L-idopyranosylurono-6,2-lactone)-(1→4)-*O*-(2-acetamido-6-*O*-diphenylphosphoryl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl)]-(1→4)-*O*-3-*O*-benzyl-*α*-L-idopyranosidurono-6,2-lactone (38)



38

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (dd, *J* = 12.9, 8.5 Hz, 6H), 7.73 (d, *J* = 20.7 Hz, 2H), 7.54 – 7.46 (m, 4H), 7.44 – 7.31 (m, 16H), 7.28 – 7.21 (m, 19H), 7.19 – 7.08 (m, 7H), 5.35 – 5.29 (m, 2H), 5.05 (s, 3H), 5.01 – 4.97 (m, 3H), 4.89 (d, *J* = 11.6 Hz, 2H), 4.78 – 4.69 (m, 3H), 4.63 (t, *J* = 2.6 Hz, 1H), 4.56 (dd, *J* = 15.6, 7.7 Hz, 3H), 4.52 – 4.42 (m, 4H), 4.41 – 4.33 (m, 4H), 4.31 – 4.27 (m, 2H), 4.21 (dd, *J* = 4.9, 3.3 Hz, 1H), 4.11 – 4.07 (m, 1H), 4.06 – 3.88 (m, 3H), 3.76 – 3.69 (m, 2H), 3.66 – 3.52 (m, 7H), 3.39 – 3.30 (m, 1H), 3.23 (dt, *J* = 12.9, 5.5 Hz, 1H), 1.81 (s, 2H), 1.51 (s, 3H), 1.42 (s, 3H). 13C NMR (101 MHz, Chloroform-*d*) δ 169.99, 169.79, 167.70, 167.68, 156.42, 150.55, 150.49, 150.43, 150.36, 150.21, 150.14, 137.59, 136.71, 136.63, 136.45, 135.57, 135.34, 133.21, 133.00, 132.96, 130.06, 129.92, 129.84, 129.81, 128.68, 128.51, 128.46, 128.40, 128.33, 128.29, 128.16, 128.07, 128.02, 127.95, 127.85, 127.70, 127.28, 127.00, 126.59, 126.46, 126.41, 126.25, 126.22, 125.93, 125.62, 125.54, 125.48, 120.34, 120.29, 120.09, 120.07, 120.05, 120.03, 99.12, 98.65, 98.28, 96.58, 80.09, 79.95, 79.02, 78.28, 77.92, 77.70, 77.24, 75.06, 74.82, 73.61, 72.65, 72.25, 72.20, 71.59, 70.70, 70.62, 69.99, 69.92, 69.48, 69.26, 68.38, 66.56, 52.50, 52.21, 39.01, 29.59, 23.02, 22.73. ^{31}P NMR (162 MHz, Chloroform-*d*) δ -10.59, -11.46. HR-ESI-MS *(m/z)*: [M+H]$^+$ calcd for $C_{106}H_{106}N_3O_{29}P_2$, 1947.6421; found, 1947.5958.

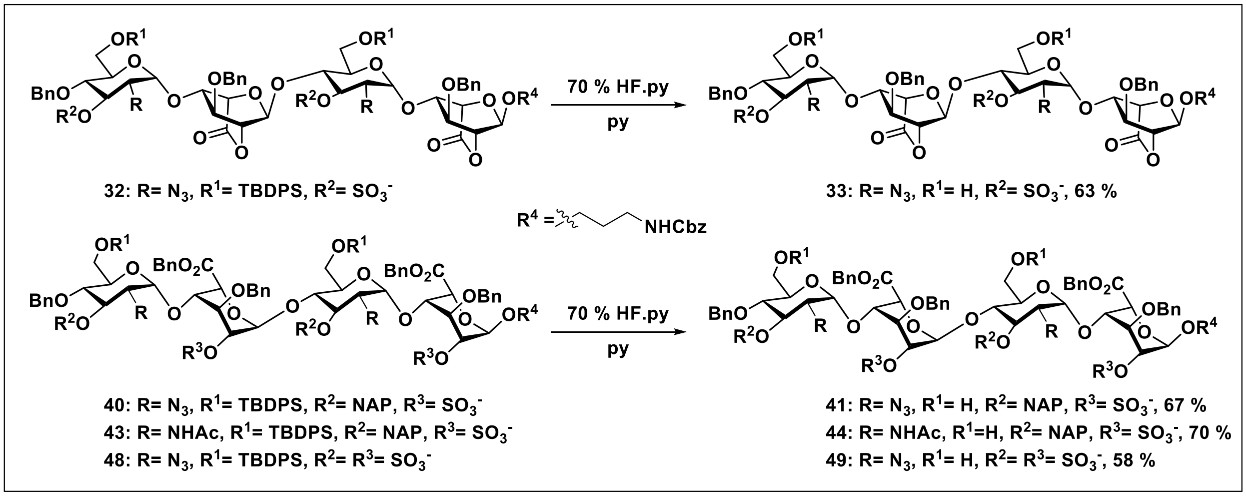
N-benzyloxycarbonyl-3-aminopropyl-*O*-[(benzyl (2-acetamido-4-*O*-benzyl-6-*O*-diphenylphosphoryl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl))-(1→4)-*O*-(3-*O*-benzyl-2-*O*-diphenylphosphoryl-*α*-L-idopyranosyluronate)-(1→4)-*O*-(benzyl (2-acetamido-6-*O*-diphenylphosphoryl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl))]-(1→4)-*O*-3-*O*-benzyl-2-*O*-diphenylphosphoryl-*α*-L-idopyranosiduronate (52)



52

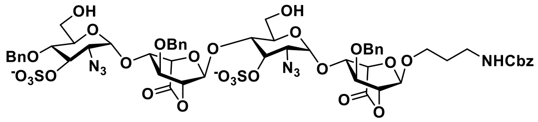
^{1}H NMR (400 MHz, Chloroform-d) δ 7.78 – 7.74 (m, 1H), 7.67 (t, J = 7.7 Hz, 3H), 7.65 – 7.60 (m, 4H), 7.51 (s, 1H), 7.43 – 7.39 (m, 2H), 7.36 (s, 1H), 7.35 – 7.34 (m, 1H), 7.33 – 7.32 (m, 3H), 7.31 (dd, J = 3.2, 1.1 Hz, 2H), 7.29 (d, J = 1.9 Hz, 1H), 7.27 (s, 2H), 7.26- 7.25 (m, 2H), 7.23 (t, J = 2.3 Hz, 3H), 7.22- 7.21 (m, 3H), 7.20 (d, J = 2.1 Hz, 2H), 7.19 (s, 6H), 7.17 – 7.16 (m, 5H), 7.15- 7.14 (m, 10H), 7.13 (s, 5H), 7.12 (s, 6H), 7.10 (d, J = 4.1 Hz, 3H), 7.08 (s, 3H), 7.05 (s, 3H), 7.04 (s, 2H), 7.02 (s, 1H), 7.00- 6.95 (m, 3H), 6.91- 6.87 (m, 4H), 6.80 (d, J = 7.3 Hz, 2H), 5.49 (t, J = 5.4 Hz, 1H), 5.46 (s, 1H), 5.27 (d, J = 12.0 Hz, 1H), 5.06 (d, J = 12.0 Hz, 1H), 4.99 (s, 2H), 4.92 (s, 2H), 4.84 (dd, J = 23.1, 11.8 Hz, 3H), 4.78 – 4.74 (m, 1H), 4.71 (s, 1H), 4.69 – 4.64 (m, 2H), 4.64 – 4.61 (m, 2H), 4.61 – 4.57 (m, 4H), 4.56- 4.49 (m, 4H), 4.44 (s, 2H), 4.41- 4.40 (m, 3H), 4.37 (d, J = 2.0 Hz, 1H), 4.24 – 4.13 (m, 4H), 4.01 (d, J = 8.8 Hz, 1H), 3.94 – 3.81 (m, 6H), 3.78 – 3.71 (m, 1H), 3.59 (d, J = 9.5 Hz, 1H), 3.56 – 3.50 (m, 1H), 3.46- 3.40 (m, 1H), 3.25 – 3.17 (m, 1H), 1.80 (m, 2H), 1.75 (s, 3H), 1.68 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 171.23, 170.89, 168.76, 168.18, 156.40, 150.52, 150.52, 150.45, 150.44, 150.42, 150.34, 150.26, 150.24, 150.20, 150.17, 150.03, 149.95, 138.27, 136.47, 136.39, 136.35, 136.32, 136.28, 134.92, 134.82, 133.29, 133.22, 132.77, 132.74, 130.10, 130.07, 130.02, 129.80, 129.77, 129.72, 128.97, 128.70, 128.65, 128.60, 128.42, 128.37, 128.31, 128.20, 128.10, 128.07, 127.99, 127.92, 127.90, 127.78, 127.72, 127.60, 127.57, 127.49, 127.43, 126.14, 125.99, 125.83, 125.77, 125.64, 125.58, 125.54, 125.44, 125.38, 125.35, 125.32, 102.44, 100.52, 99.12, 98.97, 98.77, 98.64, 80.34, 78.62, 74.77, 74.72, 73.43, 72.75, 72.64, 72.54, 72.42, 72.29, 72.22, 72.16, 70.67, 70.65, 70.61, 70.57, 68.21, 67.98, 67.13, 66.96, 66.73, 66.55, 53.12, 52.41, 39.83, 29.38, 22.65. ^{31}P NMR (162 MHz, Chloroform-d) δ -10.81, -11.15, -14.13, -14.74. HR-ESI-MS *(m/z)*: [M+Na]$^+$ calcd for $C_{144}H_{139}N_3O_{37}P_4Na$, 2649.7969; found, 2649.4785.

2.7 General procedure for desilylation post *O*- sulfation:



To a solution of starting material (1 mmol) in pyridine (1 mL) was added HF.py (5 mmol) at ice cold temperature. After stirring for 12 h the volatiles were evaporated and the residue was purified using Sephadex LH 20 column using MeOH as an eluent.

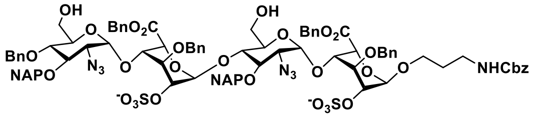
N-benzyloxycarbonyl-3-aminopropyl-*O*-[(2-azido-4-*O*-benzyl-3-*O*-sulfonato-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(3-*O*-benzyl-*α*-L-idopyranosylurono-6,2-lactone)-(1→4)-*O*-(2-azido-3-*O*-sulfonato-2-deoxy-*α*-D-glucopyranosyl)]-(1→4)-*O*-3-*O*-benzyl-*α*-L-idopyranosidurono-6,2-lactone (33)



33

1H NMR (400 MHz, Methanol-*d$_4$*) δ 7.50 – 7.41 (m, 7H), 7.38- 7.37 (m, 3H), 7.34 – 7.25 (m, 10H), 5.40 (dd, J = 7.5, 2.8 Hz, 2H), 5.24 – 5.13 (m, 4H), 5.07 (s, 2H), 4.94 (dd, J = 5.1, 3.0 Hz, 1H), 4.83 – 4.78 (m, 3H), 4.76 (d, J = 3.7 Hz, 4H), 4.61 (d, J = 3.0 Hz, 1H), 4.57 (d, J = 10.5 Hz, 1H), 4.50 (d, J = 3.2 Hz, 1H), 4.41 – 4.37 (m, 1H), 3.95 – 3.88 (m, 3H), 3.88 – 3.83 (m, 4H), 3.83 – 3.57 (m, 2H), 3.26 (dt, J = 12.8, 6.1 Hz, 2H), 1.82 – 1.79 (m, 2H). 13C NMR (101 MHz, Methanol-*d$_4$*) δ 169.02, 168.19, 157.38, 138.44, 137.74, 137.37, 137.00, 128.48, 128.29, 128.10, 128.06, 128.01, 127.73, 127.63, 127.57, 127.53, 127.39, 127.19, 100.09, 100.02, 97.04, 96.02, 80.05, 79.93, 79.30, 78.82, 78.46, 78.07, 76.40, 76.10, 75.34, 74.56, 72.12, 72.08, 71.82, 71.77, 71.57, 69.71, 69.54, 67.44, 66.02, 62.71, 62.32, 60.35, 60.02, 38.16.HR-ESI-MS (m/z): [M-2H]$^{2-}$ calcd for $C_{56}H_{61}N_7O_{27}S_2^{2-}$, 663.6534; found 663.6534.

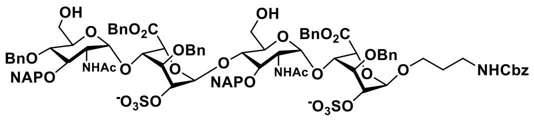
N-benzyloxycarbonyl-3-aminopropyl-*O*-[(benzyl (2-azido-4-*O*-benzyl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl))-(1→4)-*O*-(3-*O*-benzyl-2-*O*-sulfonato-*α*-L-idopyranosyluronate)-(1→4)-*O*-(benzyl (2-azido-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl))]-(1→4)-*O*-3-*O*-benzyl-2-*O*-sulfonato-*α*-L-idopyranosiduronate (41)



41

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.82 – 7.78 (m, 1H), 7.76- 7.74 (m, 2H), 7.72- 7.70 (m, 2H), 7.63 (dd, *J* = 16.5, 8.2 Hz, 2H), 7.47- 7.39 (m, 10H), 7.36- 7.34 (m, 5H), 7.32- 7.27 (m, 10H), 7.26 – 7.24 (m, 5H), 7.17 – 7.10 (m, 3H), 7.02 (t, *J* = 7.5 Hz, 2H), 6.62 (d, *J* = 7.5 Hz, 2H), 5.51 (s, 1H), 5.41 (d, *J* = 12.1 Hz, 1H), 5.27 – 5.26 (m, 1H), 5.20 (s, 1H), 5.15 (d, *J* = 3.0 Hz, 1H), 5.09 – 5.06 (m, 2H), 5.02 – 4.97 (m, 4H), 4.94 – 4.89 (m, 2H), 4.79 – 4.69 (m, 3H), 4.64 – 4.62 (m, 1H), 4.62 – 4.50 (m, 4H), 4.39- 4.35 (m, 3H), 4.18 – 4.14 (m, 1H), 4.12 – 4.03 (m, 2H), 3.99 – 3.73 (m, 7H), 3.61- 3.51 (m, 3H), 3.48 – 3.38 (m, 3H), 3.31 – 3.13 (m, 4H), 1.84- 1.76 (m, 2H). ^{13}C NMR (101 MHz, Methanol-d_4) δ 174.15, 169.81, 157.39, 138.37, 137.87, 137.71, 136.94, 135.77, 135.69, 135.07, 134.51, 133.33, 133.31, 133.04, 132.85, 128.51, 128.41, 128.27, 128.25, 128.20, 128.13, 128.06, 127.95, 127.89, 127.82, 127.75, 127.68, 127.60, 127.58, 127.55, 127.54, 127.39, 127.37, 127.31, 127.24, 127.18, 126.39, 125.86, 125.62, 125.49, 125.45, 125.22, 125.09, 99.55, 98.87, 95.46, 95.27, 79.55, 78.42, 77.42, 74.73, 74.36, 74.06, 73.69, 72.81, 72.32, 72.19, 72.08, 71.28, 71.25, 70.76, 70.26, 69.98, 69.74, 68.03, 67.49, 67.26, 66.50, 66.39, 65.96, 65.07, 63.71, 62.66, 59.83, 59.72, 37.99, 33.56, 31.67, 29.37, 29.35, 29.31, 29.20, 29.07, 29.01, 28.81, 24.60, 22.34, 13.07, 7.89. HR-ESI-MS (m/z): [M-2H]$^{2-}$ calcd for $C_{92}H_{93}N_7O_{29}S_2^{2-}$, 911.7735; found, 911.7748.

N-benzyloxycarbonyl-3-aminopropyl-*O*-[(benzyl (2-acetamido-4-*O*-benzyl-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl))-(1→4)-*O*-(3-*O*-benzyl-2-*O*-sulfonato-*α*-L-idopyranosyluronate)-(1→4)-*O*-(benzyl (2-acetamido-3-*O*-(2-naphthylmethyl)-2-deoxy-*α*-D-glucopyranosyl))]-(1→4)-*O*-3-*O*-benzyl-2-*O*-sulfonato-*α*-L-idopyranosiduronate (44)

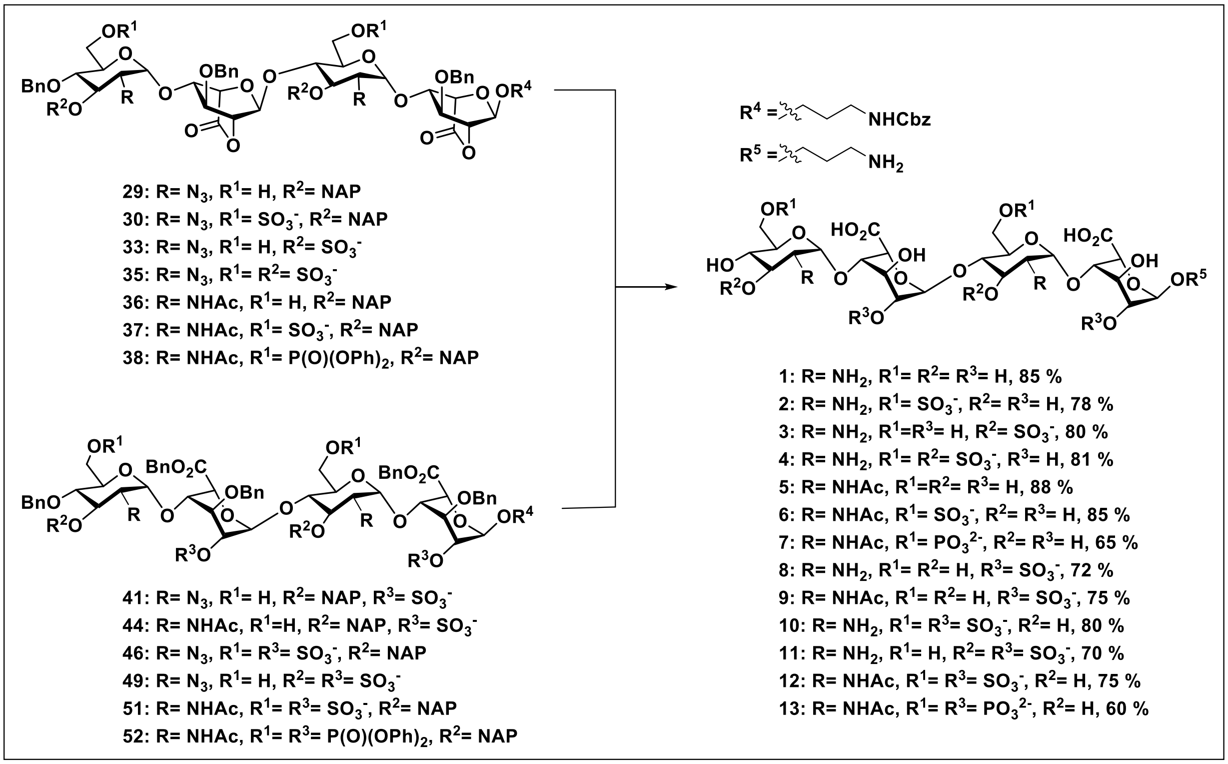


44

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.68 – 7.65 (m, 2H), 7.63- 7.60 (m, 3H), 7.53 – 7.45 (m, 4H), 7.34 (d, *J* = 3.3 Hz, 2H), 7.32 – 7.31 (m, 4H), 7.28- 7.25 (m, 7H), 7.20- 7.18 (m, 7H), 7.16 – 7.12 (m, 5H), 7.08 (dd, *J* = 5.0, 1.9 Hz, 3H), 7.05 (dd, *J* = 8.5, 1.5 Hz, 2H), 6.99 (dd, *J* = 6.6, 3.1 Hz, 2H), 6.95 (d, *J* = 7.4 Hz, 1H), 6.81 (t, *J* = 7.7 Hz, 2H), 5.43 (s, 1H), 5.21 (d, *J* = 12.0 Hz, 1H), 5.07 (d, *J* = 9.6 Hz, 2H), 4.97- 4.94 (m, 2H), 4.87 (d, *J* = 2.9 Hz, 1H), 4.68 – 4.66 (m, 2H), 4.61 (dd, *J* = 11.1, 4.7

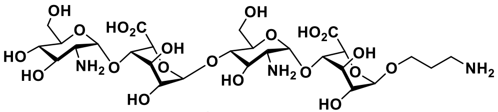
Hz, 3H), 4.48 (d, *J* = 5.3 Hz, 3H), 4.44 (dd, *J* = 9.1, 3.0 Hz, 3H), 4.39 (d, *J* = 9.3 Hz, 2H), 4.16 (s, 3H), 4.04 – 3.98 (m, 4H), 3.85 (t, *J* = 12.0 Hz, 4H), 3.67- 3.60 (m, 4H), 3.55 – 3.41 (m, 5H), 3.30- 3.26 (m, 2H), 3.11 – 3.05 (m, 2H), 1.93 (s, 3H), 1.74 – 1.68 (m, 2H), 1.61 (s, 3H). ^{13}C NMR (151 MHz, Methanol-*d₄*) δ 169.82, 169.70, 157.37, 138.45, 137.52, 137.49, 136.90, 136.37, 136.00, 134.89, 134.19, 133.34, 133.01, 132.71, 128.57, 128.46, 128.33, 128.08, 128.06, 128.04, 127.83, 127.75, 127.70, 127.61, 127.55, 127.54, 127.48, 127.45, 127.36, 127.29, 127.28, 127.21, 127.10, 126.34, 126.13, 125.89, 125.59, 125.51, 125.43, 125.10, 124.47, 99.56, 98.88, 80.32, 78.98, 77.33, 75.18, 74.47, 73.33, 72.75, 72.09, 71.64, 70.55, 70.13, 67.37, 66.78, 66.68, 66.51, 66.00, 59.78, 59.45, 53.23, 53.14, 38.22, 29.19, 22.04, 21.76. HR-ESI-MS (m/z): $[M-2H]^{2-}$ calcd for $C_{96}H_{101}N_3O_{31}S_2^{2-}$, 928.2952; found, 928.2969.

2.8 Global Deprotection:



To a solution of starting material (1 mmol for **1-7**) in THF (1 mL) and H_2O (1 mL) was added LiOH.H_2O (10 mmol) and stirred at room temperature for 2 h. Upon completion, the reaction mixture was diluted with MeOH and quenched using Dowex 50WX8 H^+ resin. The mixture was filtered, concentrated and eluted through Bond Elute C-18 column (H_2O/ ACN= 1/5, v/v). The combined fraction was concentrated under reduced pressure and dissolved in MeOH for hydrogenolysis. The reaction mixture along with $Pd(OH)_2$ was stirred under H_2 atm. After 36 h, the mixture was filtered, concentrated and eluted through Bond Elute C-18 column using H_2O as eluent. The combined H_2O fraction were pooled and lyophilized to yield fully deprotected *O*-sulfated tetrasaccharides. For **7 & 13** after $Pd(OH)_2$ hydrogenolysis the as obtained product was again kept for hydrogenolysis using PtO_2 as a catalyst under H_2 atm for 24 h. Finally, the reaction mixture was filtered, concentrated under reduced pressure and eluted through Bond Elute C-18 column using H_2O as eluent. The combined H_2O fraction were pooled and lyophilized to yield fully deprotected 6-*O*- phosphorylated tetrasaccharides **7 & 13.** For **8-12** hydrogenation was carried out by the above described method.

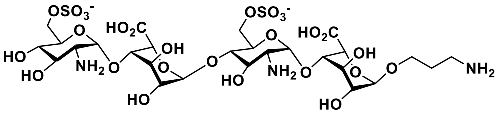
3-aminopropyl-*O*-[(2-amino-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(*α*-L-idopyranosyluronate)-(1→4)-*O*-(2-amino-2-deoxy-*α*-D-glucopyranosyl)]-(1→4)-*O*-*α*-L-idopyranosiduronate (1)



1

^{1}H NMR (400 MHz, Deuterium Oxide) δ 5.37 (d, J = 3.6 Hz, 1H), 5.29 (d, J = 3.7 Hz, 1H), 4.72 (d, J = 4.2 Hz, 1H), 4.59 (d, J = 3.2 Hz, 1H), 4.36 (d, J = 2.7 Hz, 1H), 4.03 – 4.01 (m, 1H), 3.96 (t, J = 3.1 Hz, 1H), 3.91 – 3.88 (m, 1H), 3.79 (dd, J = 7.0, 3.8 Hz, 1H), 3.76- 3.72 (m, 2H), 3.70 (s, 3H), 3.68- 3.66 (m, 3H), 3.65 – 3.63 (m, 1H), 3.61 (d, J = 9.4 Hz, 1H), 3.57- 3.56 (m, 1H), 3.55- 3.51 (m, 3H), 3.32 (t, J = 9.4 Hz, 1H), 3.19 (ddd, J = 12.6, 10.6, 3.6 Hz, 2H), 2.97 (t, J = 6.7 Hz, 2H), 1.87- 1.78 (m, 2H). ^{13}C NMR (101 MHz, Deuterium Oxide) δ 174.73, 174.51, 101.85, 100.65, 92.25, 92.22, 75.58, 74.41, 73.27, 72.32, 71.49, 70.12, 70.10, 69.42, 69.23, 68.69, 68.41, 68.12, 67.59, 66.35, 59.88, 59.30, 54.23, 53.97, 38.03, 26.36. HR-ESI-MS (m/z): $[M+H]^+$ calcd for $C_{27}H_{47}N_3O_{21}^+$, 750.2775; found, 750.2780.

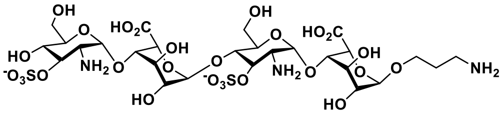
3-aminopropyl-*O*-[(2-amino-6-*O*-sulfonato-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(*α*-L-idopyranosyluronate)-(1→4)-*O*-(2-amino-6-*O*-sulfonato-2-deoxy-*α*-D-glucopyranosyl)]-(1→4)-*O*-*α*-L-idopyranosiduronate (2)



2

^{1}H NMR (600 MHz, Deuterium Oxide) δ 5.41 (d, J = 3.7 Hz, 1H), 5.39 (d, J = 3.6 Hz, 1H), 5.04 – 5.03 (m, 3H), 4.15 – 4.11 (m, 1H), 4.07 – 3.97 (m, 1H), 3.85 – 3.81 (m, 2H), 3.80- 3.72 (m, 5H), 3.70 – 3.59 (m, 5H), 3.50 – 3.39 (m, 2H), 3.30 (td, J = 10.7, 10.0, 3.6 Hz, 1H), 3.08- 3.05 (m, 2H), 2.76 (d, J = 5.2 Hz, 1H), 1.96- 1.88 (m, 2H). ^{13}C NMR (151 MHz, Deuterium Oxide) δ 171.27, 101.97, 100.86, 93.16, 92.70, 76.71, 73.37, 73.00, 72.55, 71.93, 69.35, 69.02, 68.46, 68.01, 67.80, 67.35, 66.81, 65.95, 60.01, 59.35, 54.03, 53.83, 38.01, 26.26. HR-ESI-MS (m/z): [M-2H] $^{2-}$ calcd for $C_{27}H_{45}N_3O_{27}S_2^{2-}$, 453.5846; found, 453.5981.

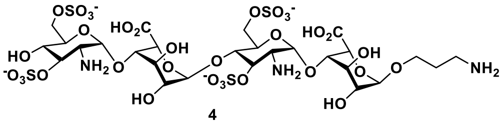
3-aminopropyl-*O*-[(2-amino-3-*O*-sulfonato-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(*α*-L-idopyranosyluronate)-(1→4)-*O*-(2-amino-3-*O*-sulfonato-2-deoxy-*α*-D-glucopyranosyl)]-(1→4)-*O*-*α*-L-idopyranosiduronate (3)



3

^{1}H NMR (600 MHz, Deuterium Oxide) δ 5.51 (d, J = 3.5 Hz, 1H), 5.41 – 5.39 (m, 1H), 4.95 (d, J = 2.8 Hz, 1H), 4.87 (d, J = 4.0 Hz, 1H), 4.56 – 4.50 (m, 1H), 4.48 – 4.42 (m, 2H), 4.19 (t, J = 3.6 Hz, 1H), 4.08 – 4.05 (m, 1H), 3.99 (t, J = 3.8 Hz, 1H), 3.93 (t, J = 9.6 Hz, 1H), 3.89 (s, 1H), 3.88 – 3.84 (m, 2H), 3.82 – 3.77 (m, 6H), 3.69- 3.67 (m, 1H), 3.64 – 3.59 (m, 4H), 3.55 (dd, J = 10.4, 3.6 Hz, 1H), 3.06 – 3.04 (m, 2H), 1.96 – 1.87 (m, 2H). ^{13}C NMR (151 MHz, Deuterium Oxide) δ 174.57, 100.92, 100.59, 92.63, 92.42, 77.31, 74.86, 74.78, 73.72, 72.07, 71.46, 71.42, 69.98, 69.80, 69.50, 68.57, 68.15, 67.39, 67.29, 66.43, 59.78, 59.17, 53.63, 53.12, 38.06. HR-ESI-MS (m/z): [M-2H] $^{2-}$ calcd for $C_{27}H_{45}N_3O_{27}S_2^{2-}$, 453.5846; found, 453.5826.

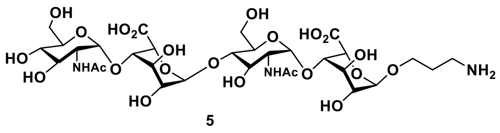
3-aminopropyl-*O*-[(2-amino-6-*O*-sulfonato-3-*O*-sulfonato-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(*α*-L-idopyranosyluronate)-(1→4)-*O*-(2-amino-6-*O*-sulfonato-3-*O*-sulfonato-2-deoxy-*α*-D-glucopyranosyl)]-(1→4)-*O*-*α*-L-idopyranosiduronate (4)



4

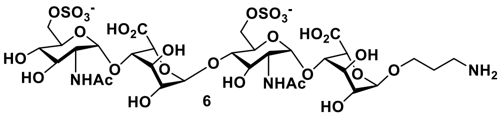
^{1}H NMR (600 MHz, Deuterium Oxide) δ 5.26 (d, J = 3.2 Hz, 1H), 5.09 (d, J = 3.5 Hz, 1H), 4.87 (d, J = 4.2 Hz, 1H), 4.80- 4.78 (m, 2H), 4.42 (d, J = 2.7 Hz, 1H), 4.31 – 4.24 (m, 4H), 4.20 – 4.17 (m, 1H), 4.13 – 4.08 (m, 2H), 4.02 – 3.99 (m, 3H), 3.96 – 3.95 (m, 2H), 3.88 (t, J = 9.7 Hz, 1H), 3.84- 3.79 (m, 2H), 3.67 – 3.55 (m, 4H), 3.08- 3.04 (m, 4H), 2.99 (dd, J = 10.2, 3.5 Hz, 1H), 1.94- 1.87 (m, 2H). ^{13}C NMR (151 MHz, Deuterium Oxide) δ 174.98, 171.04, 100.49, 100.43, 96.66, 95.49, 79.53, 75.67, 74.77, 71.37, 70.91, 70.40, 70.14, 70.03, 69.95, 68.98, 68.79, 68.40, 67.47, 66.48, 66.29, 66.13, 54.46, 53.86, 38.14, 26.39. HR-ESI-MS (m/z): $[M+H]^+$ calcd for $C_{27}H_{48}N_3O_{33}S_4^+$, 1070.1048; found, 1070.1050.

3-aminopropyl-*O*-[(2-acetamido-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(*α*-L-idopyranosyluronate)-(1→4)-*O*-(2-acetamido-2-deoxy-*α*-D-glucopyranosyl)]-(1→4)-*O*-*α*-L-idopyranosiduronate (5)


5

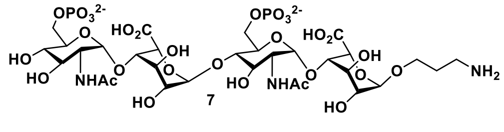
^{1}H NMR (400 MHz, Deuterium Oxide) δ 5.08 (d, J = 3.7 Hz, 1H), 5.05 (d, J = 3.8 Hz, 1H), 5.00 (d, J = 2.7 Hz, 1H), 4.90 (d, J = 2.7 Hz, 1H), 4.84 (d, J = 1.8 Hz, 1H), 4.67 (d, J = 2.4 Hz, 1H), 4.02 (t, J = 3.1 Hz, 1H), 3.99 (t, J = 2.6 Hz, 1H), 3.94 (t, J = 3.6 Hz, 1H), 3.91 – 3.79 (m, 4H), 3.75- 3.71 (m, 4H), 3.67 – 3.65 (m, 3H), 3.64 – 3.58 (m, 3H), 3.58 – 3.52 (m, 2H), 3.45 (d, J = 9.3 Hz, 1H), 3.06 (t, J = 6.6 Hz, 2H), 1.95 – 1.88 (m, 8H). ^{13}C NMR (101 MHz, Deuterium Oxide) δ 174.43, 174.40, 173.41, 173.02, 101.63, 100.57, 95.15, 95.00, 76.85, 73.76, 73.26, 72.45, 71.49, 71.08, 69.77, 69.29, 69.03, 68.07, 68.04, 67.96, 67.16, 66.63, 60.03, 59.55, 53.64, 53.39, 38.13, 26.24, 21.93. HR-ESI-MS (m/z): [M-H]$^-$ calcd for $C_{31}H_{50}N_3O_{23}^-$, 832.2840; found, 832.2835.

3-aminopropyl-*O*-[(2-acetamido-6-*O*-sulfonato-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(*α*-L-idopyranosyluronate)-(1→4)-*O*-(2-acetamido-6-*O*-sulfonato-2-deoxy-*α*-D-glucopyranosyl)]-(1→4)-*O*-*α*-L-idopyranosiduronate (6)


6

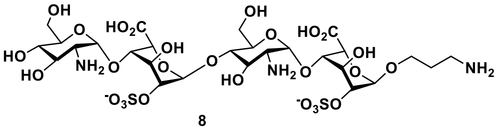
^{1}H NMR (400 MHz, Deuterium Oxide) δ 4.99 (t, *J* = 4.2 Hz, 2H), 4.95 (d, *J* = 2.4 Hz, 1H), 4.87 (s, 1H), 4.77 (s, 1H), 4.60 (d, *J* = 1.9 Hz, 1H), 4.16 (ddd, *J* = 11.0, 8.0, 3.3 Hz, 2H), 4.06 (ddd, *J* = 10.9, 6.7, 1.8 Hz, 2H), 3.94 (dt, *J* = 4.8, 2.8 Hz, 2H), 3.89 – 3.72 (m, 6H), 3.64- 3.62 (m, 2H), 3.60 – 3.53 (m, 4H), 3.50 (d, *J* = 10.4 Hz, 1H), 3.42 (d, *J* = 9.7 Hz, 1H), 2.99 (t, *J* = 6.6 Hz, 2H), 1.88- 1.80 (m, 8H). ^{13}C NMR (101 MHz, Deuterium Oxide) δ 174.43, 174.33, 173.41, 101.86, 100.50, 95.24, 94.96, 77.25, 73.66, 73.34, 71.03, 70.60, 69.91, 69.54, 68.99, 68.58, 68.06, 67.55, 67.42, 67.15, 66.67, 66.58, 66.53, 66.13, 53.49, 53.22, 38.18, 26.21, 21.96. HR-ESI-MS *(m/z)*: [M-2H]$^{2-}$ calcd for $C_{31}H_{49}N_3O_{29}S_2^{2-}$, 495.5952; found, 495.5974.

3-aminopropyl-*O*-[(2-acetamido-6-*O*-phosphonato-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(*α*-L-idopyranosyluronate)-(1→4)-*O*-(2-acetamido-6-*O*-phosphonato-2-deoxy-*α*-D-glucopyranosyl)]-(1→4)-*O*-*α*-L-idopyranosiduronate (7)


7

^{1}H NMR (400 MHz, Deuterium Oxide) δ 4.98 (d, *J* = 3.1 Hz, 2H), 4.89 (s, 1H), 4.78 (s, 1H), 3.99- 3.70 (m, 6H), 3.85 (ddd, *J* = 14.1, 8.1, 3.2 Hz, 4H), 3.80 – 3.73 (m, 1H), 3.69 – 3.49 (m, 9H), 3.48 – 3.40 (m, 1H), 2.99 (t, *J* = 6.4 Hz, 2H), 1.92- 1.82 (m, 8H). ^{13}C NMR (151 MHz, Deuterium Oxide) δ 174.65, 174.46, 174.34, 101.85, 100.44, 95.06, 94.58, 81.76, 77.10, 74.05, 73.37, 71.07, 70.33, 70.28, 69.87, 69.15, 68.97, 68.52, 68.46, 68.13, 67.97, 67.11, 63.64, 63.30, 53.64, 53.43, 38.24, 26.31, 21.97. ^{31}P NMR (162 MHz, D_2O) δ 1.35, 0.85. HR-ESI-MS *(m/z)*: $[M-2H]^{2-}$ calcd for $C_{31}H_{53}N_3O_{29}P_2^{2-}$, 495.6047; found, 495.6060.

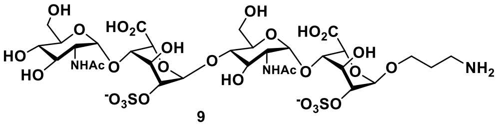
3-aminopropyl-*O*-[(2-amino-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(2-*O*-sulfonato-*α*-L-idopyranosyluronate)-(1→4)-*O*-(2-amino-2-deoxy-*α*-D-glucopyranosyl)]-(1→4)-*O*-2-*O*-sulfonato-*α*-L-idopyranosiduronate (8)



8

^{1}H NMR (600 MHz, Deuterium Oxide) δ 5.33 (s, 1H), 5.15 (s, 1H), 5.05 (s, 1H), 4.84 (s, 1H), 4.46 (s, 1H), 4.28 – 4.25 (m, 3H), 4.17 (s, 1H), 4.06 (d, *J* = 14.2 Hz, 2H), 3.88 (t, *J* = 9.9 Hz, 1H), 3.81 – 3.77 (m, 5H), 3.73 (s, 2H), 3.68- 3.67 (m, 2H), 3.64 – 3.62 (m, 1H), 3.40 (t, *J* = 9.6 Hz, 1H), 3.29 (d, *J* = 10.7 Hz, 1H), 3.26 – 3.24 (m, 1H), 3.09- 3.05 (m, 2H), 1.96- 1.87 (m, 2H). ^{13}C NMR (151 MHz, Deuterium Oxide) δ 175.38, 174.85, 98.74, 97.78, 91.06, 90.96, 76.07, 72.53, 72.42, 72.01, 71.44, 70.06, 69.95, 69.33, 69.06, 67.99, 66.87, 66.59, 66.43, 62.40, 62.37, 59.71, 59.27, 54.50, 54.14, 38.32, 26.06. HR-ESI-MS (m/z): $[M-2H]^{2-}$ calcd for $C_{27}H_{45}N_3O_{27}S_2^{2-}$, 453.5846; found, 453.5911.

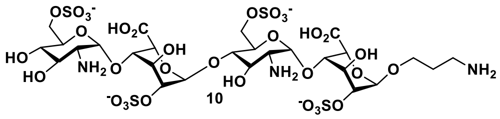
3-aminopropyl-*O*-[(2-acetamido-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(2-*O*-sulfonato-*α*-L-idopyranosyluronate)-(1→4)-*O*-(2-acetamido-2-deoxy-*α*-D-glucopyranosyl)]-(1→4)-*O*-2-*O*-sulfonato-*α*-L-idopyranosiduronate (9)



9

^{1}H NMR (600 MHz, Deuterium Oxide) δ 5.12 (s, 2H), 5.06 (s, 1H), 5.03 (d, *J* = 3.4 Hz, 1H), 5.01 (d, *J* = 3.4 Hz, 1H), 4.76 (d, *J* = 1.8 Hz, 1H), 4.21 (d, *J* = 6.5 Hz, 2H), 4.17 (d, *J* = 13.4 Hz, 2H), 3.97 (d, *J* = 11.1 Hz, 2H), 3.90 (ddd, *J* = 18.5, 10.5, 3.4 Hz, 2H), 3.85 – 3.81 (m, 1H), 3.76 (s, 2H), 3.71 (d, *J* = 2.8 Hz, 2H), 3.65 – 3.59 (m, 4H), 3.56 – 3.50 (m, 2H), 3.42 (d, *J* = 9.2 Hz, 1H), 3.06 (t, *J* = 6.3 Hz, 2H), 1.98 (s, 3H), 1.96 (s, 3H), 1.93 – 1.88 (m, 2H). ^{13}C NMR (151 MHz, Deuterium Oxide) δ 174.80, 173.03, 172.79, 99.17, 98.34, 94.86, 94.32, 76.95, 73.19, 73.15, 72.36, 71.60, 71.36, 71.05, 70.94, 69.70, 69.34, 66.72, 66.19, 63.97, 63.42, 60.02, 59.47, 53.51, 53.22, 38.15, 26.02, 22.14. HR-ESI-MS *(m/z)*: $[M-2H]^{2-}$ calcd for $C_{31}H_{49}N_3O_{29}S_2^{2-}$, 495.5952; found, 495.5922.

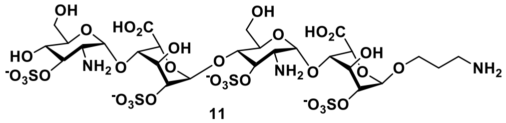
3-aminopropyl-*O*-[(2-amino-6-*O*-sulfonato-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(2-*O*-sulfonato-*α*-L-idopyranosyluronate)-(1→4)-*O*-(2-amino-6-*O*-sulfonato-2-deoxy-*α*-D-glucopyranosyl)]-(1→4)-*O*-2-*O*-sulfonato-*α*-L-idopyranosiduronate (10)



10

^{1}H NMR (400 MHz, Deuterium Oxide) δ 5.29 (dd, *J* = 7.0, 3.7 Hz, 2H), 5.10 (s, 1H), 5.01 (s, 1H), 4.83 (s, 1H), 4.47 (s, 1H), 4.25 – 4.23 (m, 2H), 4.22 (d, *J* = 2.0 Hz, 1H), 4.19 (d, *J* = 3.0 Hz, 1H), 4.17 – 4.14 (m, 2H), 4.13 – 4.11 (m, 1H), 4.09 (s, 1H), 4.06 (s, 1H), 4.04 (s, 1H), 3.87 (d, *J* = 9.6 Hz, 1H), 3.82 (d, *J* = 10.4 Hz, 1H), 3.80 – 3.75 (m, 2H), 3.74 – 3.69 (m, 1H), 3.66 (d, *J* = 9.7 Hz, 1H), 3.61- 3.55 (m, 1H), 3.43 (t, *J* = 9.7 Hz, 1H), 3.31 – 3.22 (m, 2H), 3.02 (q, *J* = 6.7, 5.6 Hz, 2H), 1.91- 1.82 (m, 2H). ^{13}C NMR (151 MHz, Deuterium Oxide) δ 174.95, 98.71, 97.82, 91.30, 90.92, 75.55, 72.67, 72.48, 70.32, 70.14, 69.59, 69.23, 68.64, 68.10, 67.05, 66.76, 66.38, 66.13, 62.72, 62.30, 54.27, 53.99, 38.43, 26.08. HR-ESI-MS (m/z): [M+H]$^{+}$ calcd for $C_{27}H_{48}N_{3}O_{33}S_{4}^{+}$, 1070.1048; found, 1070.1051.

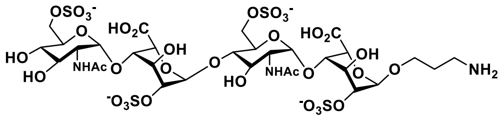
3-aminopropyl-*O*-[(2-amino-3-*O*-sulfonato-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(2-*O*-sulfonato-*α*-L-idopyranosyluronate)-(1→4)-*O*-(2-amino-3-*O*-sulfonato-2-deoxy-*α*-D-glucopyranosyl)]-(1→4)-*O*-2-*O*-sulfonato-*α*-L-idopyranosiduronate (11)



11

^{1}H NMR (600 MHz, Deuterium Oxide) δ 5.44 (d, J = 3.6 Hz, 1H), 5.37 (d, J = 3.7 Hz, 1H), 4.83 (d, J = 3.7 Hz, 1H), 4.80 (d, J = 2.4 Hz, 1H), 4.77 (d, J = 3.1 Hz, 1H), 4.52 (d, J = 2.6 Hz, 1H), 4.12 – 4.11 (m, 1H), 4.06 – 4.05 (m, 1H), 4.00 – 3.97 (m, 1H), 3.90 (dd, J = 6.8, 4.1 Hz, 1H), 3.85- 3.81 (m, 2H), 3.77- 3.72 (m, 6H), 3.70 – 3.67 (m, 2H), 3.66 – 3.62 (m, 3H), 3.41 (t, J = 9.6 Hz, 1H), 3.31 – 3.26 (m, 2H), 3.07 – 3.05 (m, 2H), 1.94 – 1.87 (m, 2H). ^{13}C NMR (151 MHz, Deuterium Oxide) δ 174.23, 173.94, 101.86, 100.69, 92.45, 92.34, 75.87, 74.15, 73.16, 72.48, 69.81, 69.45, 69.40, 69.17, 68.49, 68.09, 68.03, 67.22, 66.45, 59.90, 59.32, 54.23, 53.96, 38.06, 26.35 HR-ESI-MS (m/z): [M+H]$^{+}$ calcd for $C_{27}H_{48}N_{3}O_{33}S_{4}^{+}$, 1070.1048; found, 1070.1052.

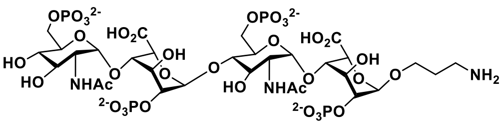
3-aminopropyl-*O*-[(2-acetamido-6-*O*-sulfonato-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(2-*O*-sulfonato-*α*-L-idopyranosyluronate)-(1→4)-*O*-(2-acetamido-6-*O*-sulfonato-2-deoxy-*α*-D-glucopyranosyl)]-(1→4)-*O*-2-*O*-sulfonato-*α*-L-idopyranosiduronate (12)



12

1H NMR (400 MHz, Deuterium Oxide) δ 5.14 (s, 1H), 5.10 (d, J = 1.7 Hz, 1H), 5.07 (d, J = 3.7 Hz, 3H), 4.76 (d, J = 2.0 Hz, 1H), 4.28 – 4.13 (m, 8H), 4.04 – 4.03 (m, 2H), 3.96 (ddd, J = 16.3, 10.3, 3.5 Hz, 2H), 3.91- 3.83 (m, 2H), 3.77 – 3.62 (m, 4H), 3.61 – 3.55 (m, 1H), 3.50 (d, J = 9.6 Hz, 1H), 3.09 (t, J = 6.4 Hz, 2H), 2.00 (s, 3H), 1.98 (s, 3H), 1.96- 1.91 (m, 2H). ^{13}C NMR (101 MHz, Deuterium Oxide) δ 174.82, 173.03, 99.15, 98.35, 95.05, 93.90, 76.67, 73.68, 73.24, 72.06, 70.91, 70.83, 70.52, 69.88, 69.62, 69.12, 66.82, 66.56, 66.50, 64.65, 63.24, 53.30, 53.15, 38.30, 26.05, 22.19. HR-ESI-MS (m/z): $[M-3H]^{3-}$ calcd for $C31H_{48}N_3O_{35}S_4^{3-}$, 383.3656; found, 383.3639.

3-aminopropyl-*O*-[(2-acetamido-6-*O*-phosphonato-2-deoxy-*α*-D-glucopyranosyl)-(1→4)-*O*-(2-*O*-phosphonato-*α*-L-idopyranosyluronate)-(1→4)-*O*-(2-acetamido-6-*O*-phosphonato-2-deoxy-*α*-D-glucopyranosyl)]-(1→4)-*O*-2-*O*-phosphonato-*α*-L-idopyranosiduronate (13)



13

^{1}H NMR (400 MHz, Deuterium Oxide) δ 5.13 (d, J = 10.1 Hz, 1H), 5.05 (dd, J = 10.2, 6.5 Hz, 2H), 4.79 (s, 1H), 4.15 – 4.02 (m, 10H), 3.94 (td, J = 10.5, 3.4 Hz, 2H), 3.88 – 3.75 (m, 4H), 3.72 – 3.62 (m, 4H), 3.59 – 3.57 (m, 1H), 3.51 (d, J = 9.2 Hz, 1H), 3.08 (t, J = 6.4 Hz, 1H), 2.02 – 1.90 (m, 8H). ^{13}C NMR (151 MHz, Deuterium Oxide) δ 174.81, 172.75, 172.64, 100.08, 99.35, 95.88, 95.61, 77.05, 73.30, 73.24, 71.62, 71.33, 70.66, 69.65, 69.12, 66.86, 66.79, 66.61, 63.79, 53.58, 53.34, 38.27, 26.07, 22.21, 22.15. ^{31}P NMR (162 MHz, Deuterium Oxide) δ 0.75, 0.15, -0.10, -0.27. HR-ESI-MS *(m/z)*: $[M-2H]^{2-}$ calcd for $C_{31}H_{53}N_3O_{35}P_4^2$, 575.5710; found, 575.5759.

3. Glycan microarray

Materials. PBSx10 was purchased from Hy-labs, ethanolamine from Fisher, ovalbumin (Grade V), sodium phosphate monobasic monohydrate, sodium phosphate dibasic heptahydrate, Tween-20 and Tris/HCl were purchased from Sigma-Aldrich. Antibodies were purchased from Peprotech: Human SD1α CXCL12, human IL8 CXCL8 72 aa, human exodus-2 CCL21, human MCP-3 CCL7, human MCP-4 CCL13, human IP-10 CXCL10, human MEC CCL28, human RANTES CCL5, human MCP-1/MCAF CCL2, biotinylated antigen affinity-purified goat-anti-murine SDF-1α, biotinylated-rabbit-anti-human IL8 CXCL8, biotinylated-rabbit-anti-human Exodus-2 CCL21, biotinylated goat-anti-human MCP-3, biotinylated anti-H-MCP-4, biotinylated rabbit-anti-human IP-10, biotinylated anti-human MEC, biotinylated-rabbit-anti-human MCAF/MCP-1. Biotinylated anti-Rantes was purchased from R&D. Cy3-sterptavidin (Cy3-SA) was purchased from Jackson ImmunoResearch. IVIG GammaGard 10% (Baxter, USA) were a kind gift from Adriana Tremolot, Childrens hospital UCSD.

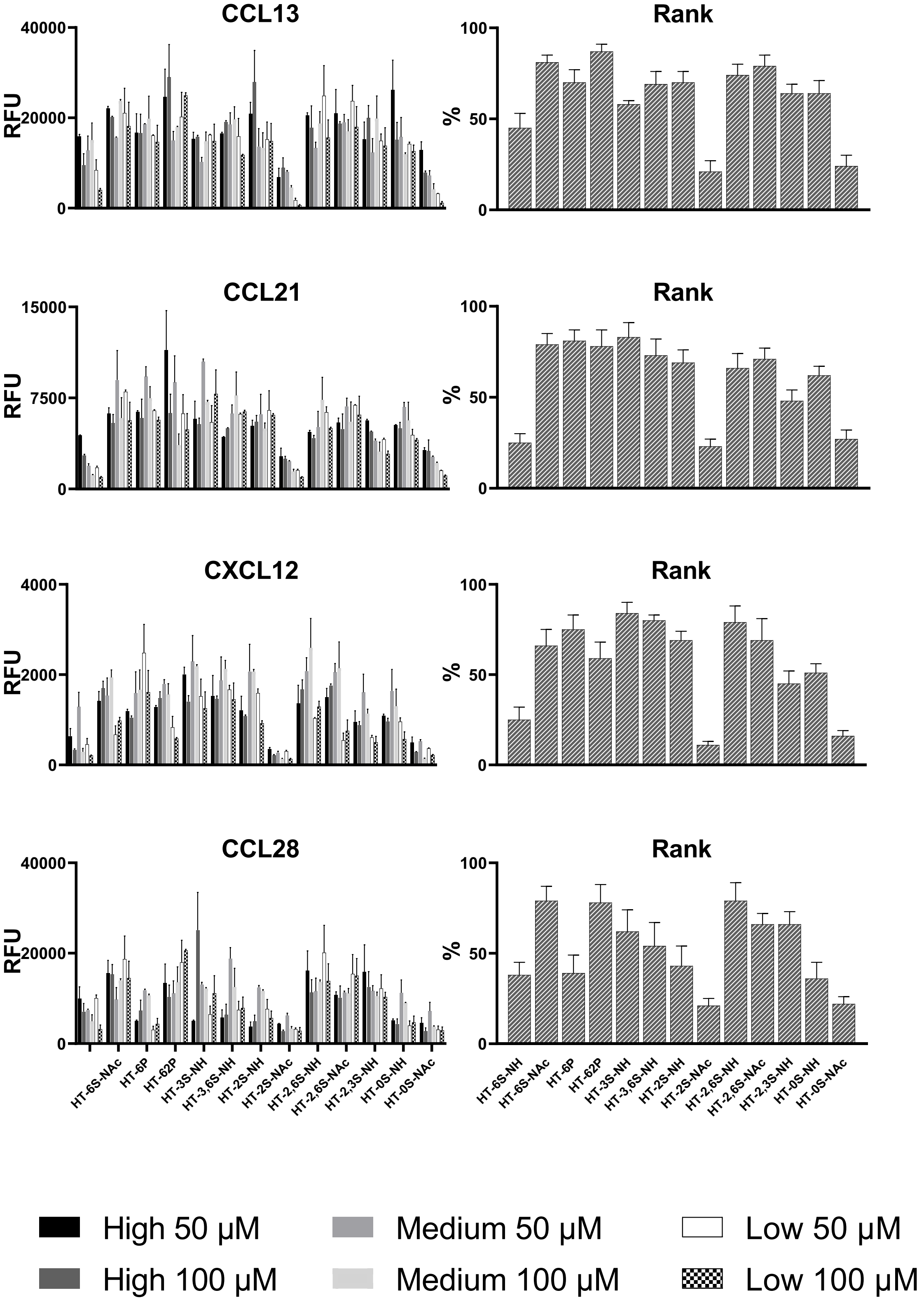
Heparin tetrasaccharide microarray fabrication. Arrays were fabricated with NanoPrint LM-60 Microarray Printer (Arrayit) on epoxide-derivatized slides (PolyAn 2D) with 16 sub-array blocks on each slide. Glycoconjugates were distributed into 384-well source plates using 4 replicate wells per sample and 7 µl per well. Each glycoconjugate diluted into 50 and 100 µM in an optimized printing buffer (300 mM phosphate buffer, pH 8.4 Version VrHI.01. To monitor printing Alexaflour-555-hydraside (Invitrogen, at 1 ng/µl in 178 mM phosphate buffer, pH 5.5) was used for each printing run. The arrays were printed with four 946MP3 pins (5 µm tip, 0.25 µl sample channel, ~100 µm spot diameter; Arrayit). The humidity level in the arraying chamber was maintained at about 70% during printing. Printed slides were left on arrayer deck over-night, allowing humidity to drop to ambient levels (40-45%). Next, slides were packed, vacuum-sealed and stored at room temperature (RT) until used.

HS tetrasaccharide microarray binding assay. Slides were developed and analyzed as previously described[1] with some modifications. Slides were rehydrated with dH_2O and incubated for 30 min in a staining dish with 50°C pre-warmed ethanolamine (0.05 M) in Tris-HCl (0.1 M, pH 9.0) to block the remaining reactive epoxy groups on the slide surface, then washed with 50 °C pre-warmed dH_2O. Slides were centrifuged at 200×*g* for three min then fitted with ProPlate™ Multi-Array 16-well slide module (Grace Bio-lab P37001) to divide into the sub-arrays (blocks). Slides were washed with PBST (0.1% Tween 20), aspirated and blocked with 200 µl/sub-array of blocking buffer (PBS pH 7.3 + 1% w/v ovalbumin) for 1 hour at RT with gentle shaking. Next, the blocking solution was aspirated and 100 µl/block of primary detection proteins (for each detection, 3 serially decreasing concentrations were used, see Table S1) diluted in PBS pH 7.3 + 1% w/v ovalbumin, were incubated with gentle shaking for 2 hours at RT. Slides were washed 4 times with PBST, then with PBS (without Tween-20) for 2 min. Bound antibodies were detected by incubating with biotinylated secondary detections (1 ng/µl, see Table S1) diluted in PBS, 200 µl/block at RT for 1 hour. Slides were washed 4 times with PBST, then with PBS (without Tween-20) for 2 min and biotinylated antibodies were detected with Cy3-SA (1.2µg/ml). Slides were washed 4 times with PBST, then with PBS for 10 min followed by removal from ProPlate™ Multi-Array slide module and immediately dipping in a staining dish with dH_2O for 10 min with shaking. Slide then were centrifuged at 200×*g* for 3 min. and the dry slides immediately scanned.

Array slide processing. Processed slides were scanned and analyzed as described at 10 µm resolution with a Genepix 4000B microarray scanner (Molecular Devices) using 350 gain. Image analysis was carried out with Genepix Pro 4.0 analysis software (Molecular Devices). Spots were defined as circular features with a variable radius as determined by the Genepix scanning software. Local background subtraction was performed. RFU from each spot was calculated and Ranking (per printed glycan per concentration, per each chemokine dilution, per printed block) was used to compare the data between detections; since each glycans was printed at 2 concentration, 100% binding was set separately for each concentration. Then, binding to all the other glycans at the same concentration was ranked in comparison to the maximal binding, and the average rank binding and SEM for each glycan across the two glycan concentrations and three examined dilutions of each chemokine was calculated (n=6, 2 glycan concentrations across 3 chemokine dilutions).[1]

Table S1. Primary detection concentrations used on the array and Secondary Biotinylated antibodies.

Primary Detection	**Concentrations used (ng/µl)**	**Secondary Detection**
Human SD1α (CXCL12)	20, 10, 5	Biotinylated antigen affinity-purified goat-anti-murine SDF-1α
Human IL8 (CXCL8) 72 aa	20, 10, 5	Biotinylated-rabbit-anti-human IL8 (CXCL8)
Human Exodus-2 (CCL21)	20, 10, 5	Biotinylated-rabbit-anti-human Exodus-2 (CCL21)
Human MCP-3 (CCL7)	20, 10, 5	Biotinylated-goat-anti-human MCP-3
Human MCP-4 (CCL13)	20, 10, 5	Biotinylated anti-human MCP-4
Human IP-10 (CXCL10)	10, 5, 2.5	Biotinylated-rabbit-anti-human IP-10
Human BCA-1 (CXCL13)	10, 5, 2.5	Biotinylated-rabbit-anti-human BCA-1
Human MEC (CCL28)	10, 5, 2.5	Biotinylated-anti-human MEC
Human RANTES (CCL5)	2, 1, 0.5	Biotinylated anti-Rantes
Human MCP-1/MCAF (CCL2)	2, 1, 0.5	Biotinylated-rabbit-anti-human MCAF/MCP-1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%
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HT-6P
HT-62P
HT-3S-NH
HT-3,6S-NH
HT-2S-NH
HT-2S-NAc
HT-2,6S-NH
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HT-0S-NH
HT-0S-NAc
Rank
%
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HT-2,6S-NAc
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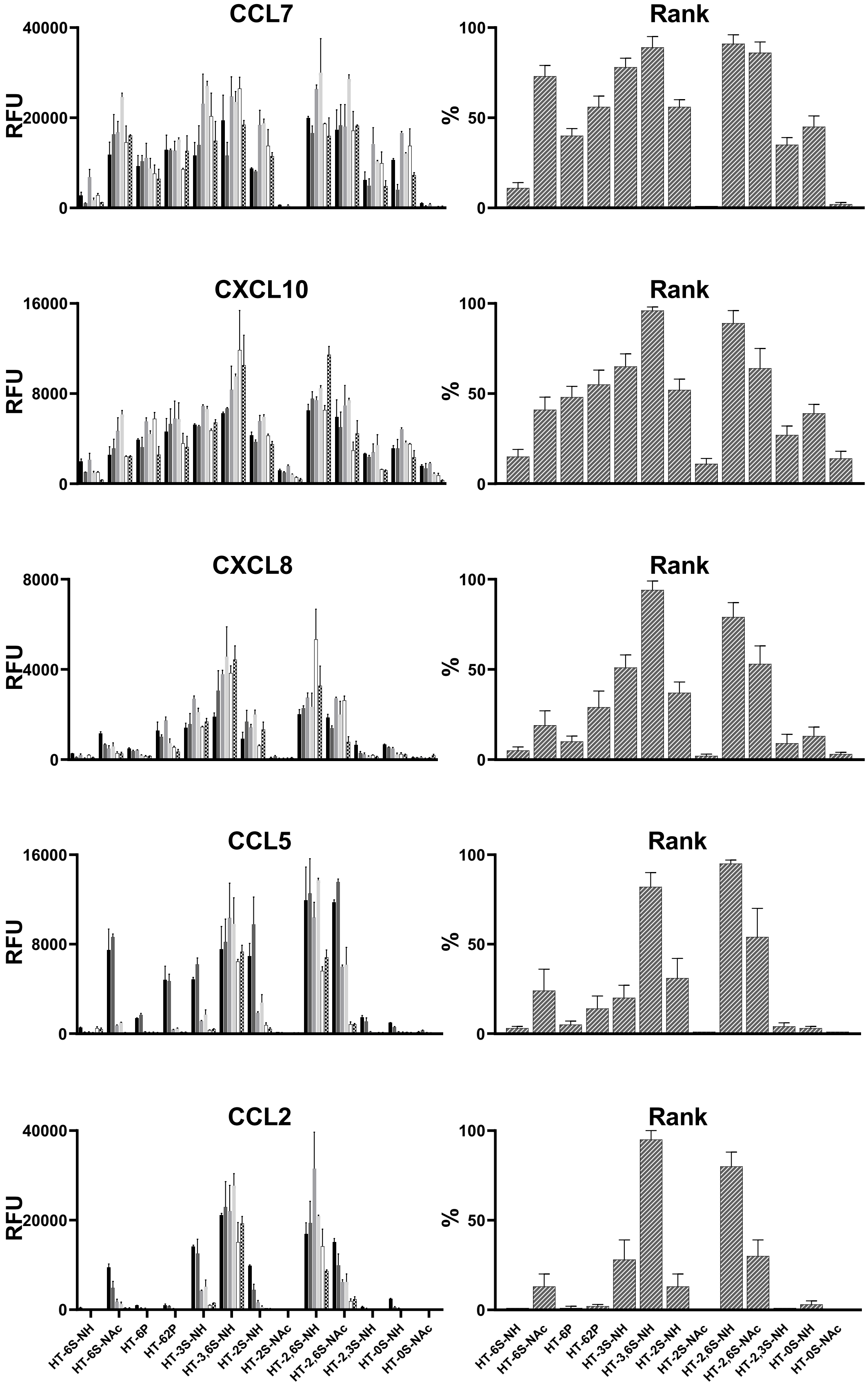
High 100 μM
Medium 50 μM
Medium 100 μM
Low 50 μM
Low 100 μM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HT-2S-NH
HT-2S-NAc
HT-2,6S-NH
HT-2,6S-NAc
HT-2,3S-NH
HT-0S-NH
HT-0S-NAc

Figure S1. Chemokine glycan microarray binding assay. Binding was tested at 3 serial dilutions across 2 glycan concentrations (High, medium and low chemokine concentration at 50μM and 100μM glycan concentration on the array), then detected with the relevant biotinylated secondary antibody (1 μg/ml) followed by Cy3-Strepavidin (1.5 μg/ml) (**Table S1**). Arrays were scanned, relative fluorescent units (RFU) obtained, and maximum RFU determined and set as 100% binding. Then rank binding (per printed glycan per concentration, per each chemokine dilution, per printed block) was determined. Since each glycans was printed at 2 concentration, 100% binding was set separately for each concentration. Then, binding to all the other glycans at the same concentration was ranked in comparison to the maximal binding, and the average rank binding and SEM for each glycan across the two glycan concentrations and three examined dilutions of each chemokine was calculated (n=6, 2 glycan concentrations across 3 chemokine dilutions). This analysis allowed to compare the glycan binding profiles of the different chemokines and dissect their binding preferences. The mean rank is shown as a heatmap of all the examined binding assays together (red highest, blue lowest and white 50th percentile of ranking).

4. Surface Plasmon Resonance binding kinetics.

HS tetrasaccharides (**HT-2,6S-NH** or **HT-3,6S-NH**) were immobilized on CM5 sensor surface using a coupling reaction. Briefly, CM5 chip was activated with N-hydroxysuccimide (0.05 mM) and EDC (0.1mM) in water before injecting 0.05 mM of HS oligosaccharides at a flow rate of 100 μl/min until 500 RU is achieved. Next, remaining active esters were quenched with ethanolamine (0.1 mM) in HBS-EP buffer. Similarly, the control flow cell was active with NHS and EDC and neutralized with ethanolamine. A known concentration of chemokines was injected in HBS-EP buffer at a flow rate of 50 μl/min at 25 º C for 200 sec followed by running buffer (HBS-EP without chemokine) was then flowed for another 100 sec to enable dissociation. The CM5 chip was regenerated by washing with 0.1% SDS and 0.085% H_3PO_4 injected for 3 min at a flow rate of 100 μL/min. Kinetic analysis was executed using the BIAevaluation software for T100. K_{off} and K_{on} phase was globally fitted to a simple 1:1 interaction model.

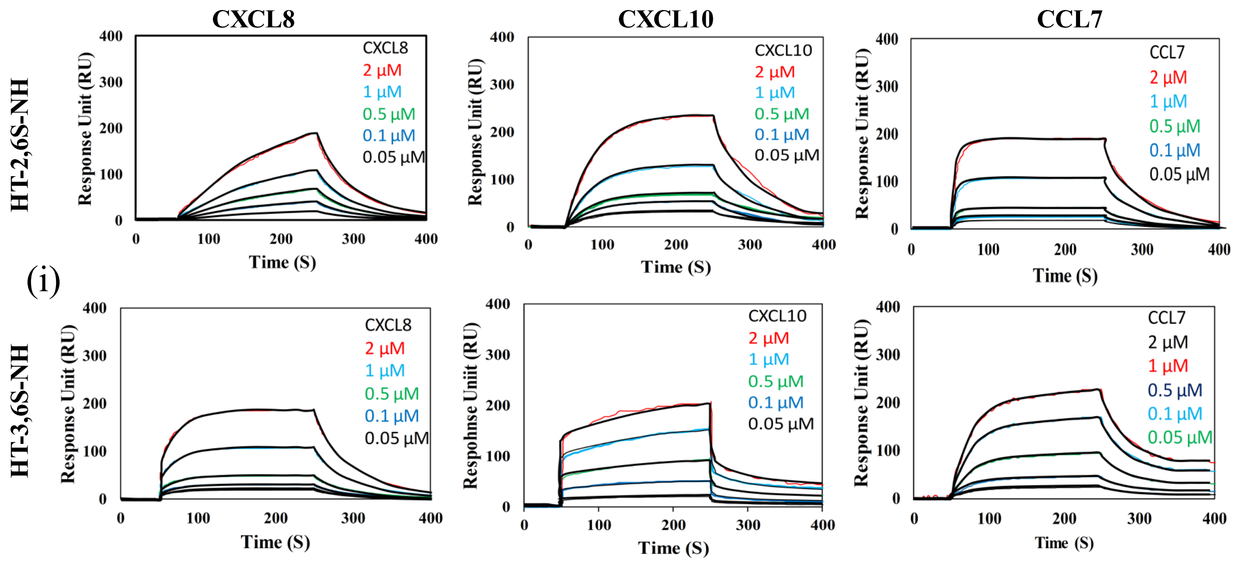


Figure S2. SPR analysis of chemokine binding profile on sensor chip having HT-2,6S-NH and HT-3,6S-NH ligands: (a) (b) & (c) SPR binding analysis of the interaction between HT-2,6S-NH with CXCL8, CXCL10 and CCL7 respectively. Concentrations of chemokine were 0.05–2 µM. A global fit according to a 1:1 binding model was applied (black curves); (d), (e) & (f) SPR binding analysis of the interaction between HT-3,6S-NH with CXCL8, CXCL10 and CCL7 respectively.

Table S2: SPR analysis of kinetic rate constants and equilibrium affinities for HS ligands binding to chemokines from Fig S2 and Fig 3.

Substrate	Chemokines	K_D (µM)	K_{on} ($M^{-1}S^{-1}$)	K_{off} (s^{-1})
HT-2,6S-NH	**CXCL8**	**15.93 ± 0.23**	**$1.23 \pm 0.17 \times 10^4$**	**$1.96 \pm 0.29 \times 10^{-1}$**
	CXCL10	**10.7 ± 0.37**	**$2.07 \pm 0.26 \times 10^4$**	**$2.24 \pm 0.35 \times 10^{-1}$**
	CCL7	**11.51 ± 0.17**	**$1.96 \pm 0.22 \times 10^4$**	**$2.25 \pm 0.29 \times 10^{-1}$**
	CCL5	**2.34 ± 0.44**	**$9.15 \pm 0.34 \times 10^4$**	**$2.14 \pm 0.48 \times 10^{-1}$**
	CCL2	**9.82 ± 0.18**	**$2.07 \pm 0.13 \times 10^4$**	**$2.03 \pm 0.17 \times 10^{-1}$**
HT-3,6S-NH	**CXCL8**	**11.67 ± 0.17**	**$1.87 \pm 0.22 \times 10^4$**	**$2.18 \pm 0.28 \times 10^{-1}$**
	CXCL10	**11.02 ± 0.37**	**$1.53 \pm 0.26 \times 10^4$**	**$1{,}69 \pm 0.33 \times 10^{-1}$**
	CCL7	**11.3 ± 0.18**	**$2.53 \pm 0.15 \times 10^4$**	**$2.86 \pm 0.21 \times 10^{-1}$**
	CCL5	**6.81 ± 0.33**	**$4.37 \pm 0.31 \times 10^4$**	**$2.98 \pm 0.31 \times 10^{-1}$**
	CCL2	**1.89 ± 0.24**	**$11.17 \pm 0.32 \times 10^4$**	**$2.11 \pm 0.34 \times 10^{-1}$**

5. CCR2 expression level.

MCF-7 cells were seeded on 6 well plate in RPMI-1640 medium in 1% FBS. Approximately 10^4 cells were transferred to FACS tubes and incubated with primary murine Anti-CCR2 antibody (2 µl) for half hour, followed by FITC tagged secondary antibody. The fluorescent channel FL-2 was used to quantify CCR2 expression level on MCF-7 cells.

6. Cell proliferation assay

Approximately 10^4 MCF-7 were feeded on 96-well plates in a RPMI-1640 medium in 1% FBS. Then, HS tetrasaccharide (**HT-3,6S-NH**, 10 or 50 µg/ml) and native heparin (10 or 50 µg/ml) were mixed with CCL2 (50 ng) and added to the cells. After 72 h of incubation, cell were fixed with paraformaldehyde and stained with 4% sulforhodamine B in 1% acetic acid for 30 min. Cell proliferation was quantified with 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-(2,4-disulfophenyl)- 2H-tetrazolium monosodium salt at 450 nm.

7. Cell-division cycle analysis

Chemokines and **HT-3,6S-NH** treated MCF-7 cells were harvested and fixed with 70 % ethanol at -20 °C for 12 h. The fixed cells were incubated with propidium iodide (5 µg/mL) and RNase (10 µg/mL) for 30 min at RT. Using flow cytometer stained cells were quantified. The DNA content in the cell phases was quantified by using ModFitLT version 3.0 software.

8. Wound healing assay

MCF-7 cells were seeded on 24-well plat and cell monolayer was generated, Then, by using 1000 µl pipette tip wound was created. Cells were treated with native heparin and **HT-3,6S-NH** (50 µg/ml) with CCL2 (50 ng). It was observed that CCL2 treated monolayer showed complete wound healing after 8 h. At that point, percentage of cell migration distance of **HT-3,6S-NH,** heparin and control cells were quantified.

9. Cell invasion assay.

Boyden chamber cell invasion assay was performed in as reported in the protocol. Briefly, the upper chamber of transwell inserts were coated with Matrigel and the bottom chamber contained RPMI-1640 medium supplemented with 1 % FBS and CCL2 (50 ng/ml) with **HT-3,6S-NH** (50 µg/ml) and heparin. MCF-7 cells were feeded to the upper chamber. After 24 h of incubation, non-invading cells were removed and lower chamber cells were fixed and stained with 0.5 % crystal violet for 30 min and cell invasion was quantified by bright field imaging

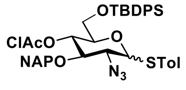
10. Western Blot Analysis

MCF-7 cells were seeded on Petri dishes and CCL2 (50 ng) was added with or without **HT-3,6S-NH** (50 µg./ml) for half hr. The cells were transferred into folcon tube and pelleted. Then cell pellet was treasted with lysis buffer containing 150 mM NaCl, 1% NP-40, 0.25% sodium dodecyl sulfate (SDS), 1 mM ethylenediamine tetraacetic acid (EDTA) and protease inhibitor, and 1 mM phenylmethane sulfonyl fluoride (PMSF) in 50 mM Tris-Cl (pH 7.4). After 1 h, mixture was centrifuge and supernatant was collected. Using Brandford method, the protein concentration was determined. Approximately 35 µg of protein was loaded on SDS-polyacrylamide gel electrophoresis (10%) and transferred onto a polyvinylidene fluoride (PVDF) membrane. Using specific antibodies corresponding to MAPK blot was developed. Finally, The membrane was incubated with horse radish peroxidase (HRP)-conjugated secondary antibody and visualization by using an Immobilon Western Chemiluminescent HRP substrate kit (Millipore Corporation, MA, USA) with GAPDH as internal standard.

11. References:

1. a) V. Padler-Karavani, X. Song, H. Yu, N. Hurtado-Ziola, S. Huang, S. Muthana, H. A. Chokhawala, J. Cheng, A. Verhagen and M. A. Langereis, *J. Biol. Chem.*, 2012, **287**, 22593-22608; b) S. L. Ben-Arye, H. Yu, X. Chen and V. Padler-Karavani, *J. Vis. Exp.*, 2017, e56094.

12. NMR Spectra



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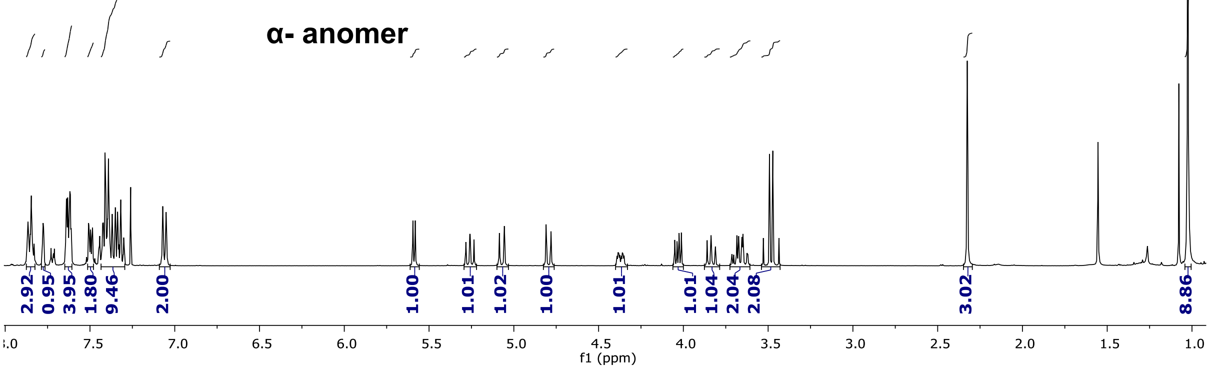

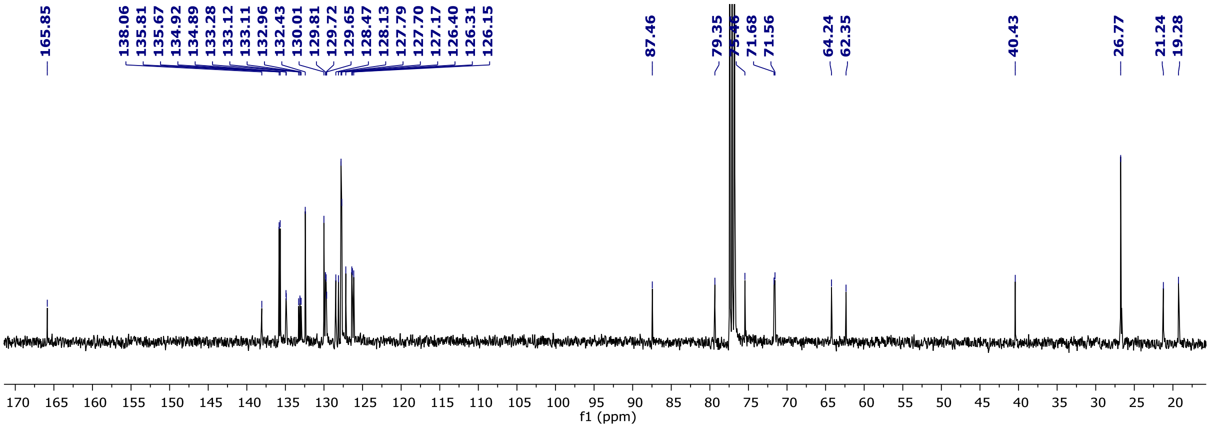

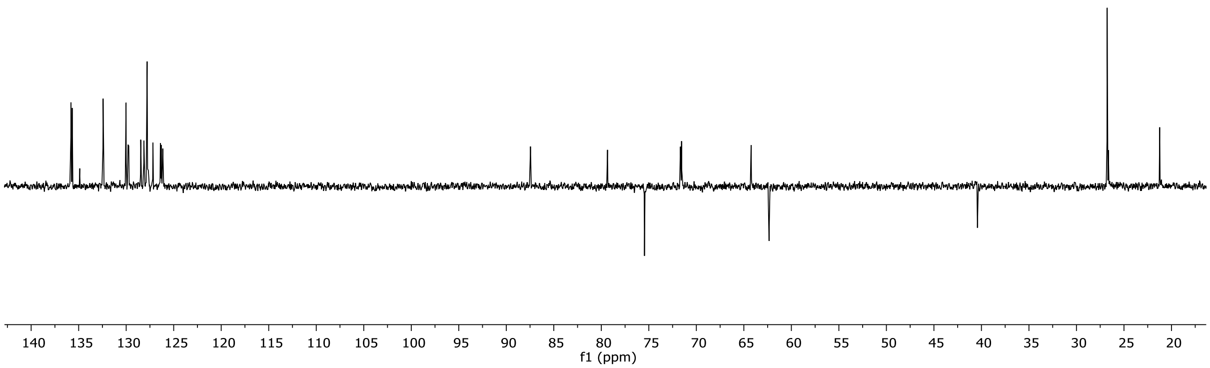
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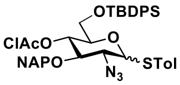
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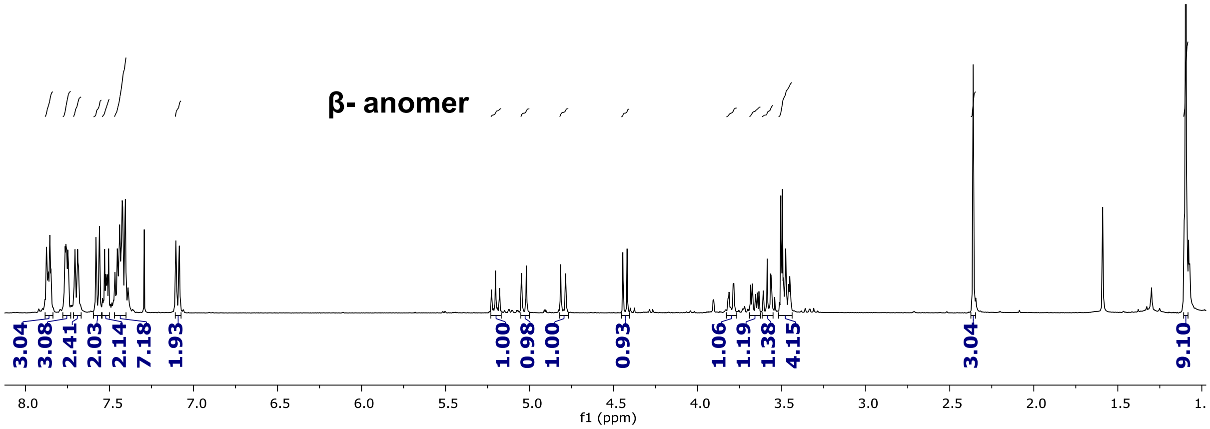
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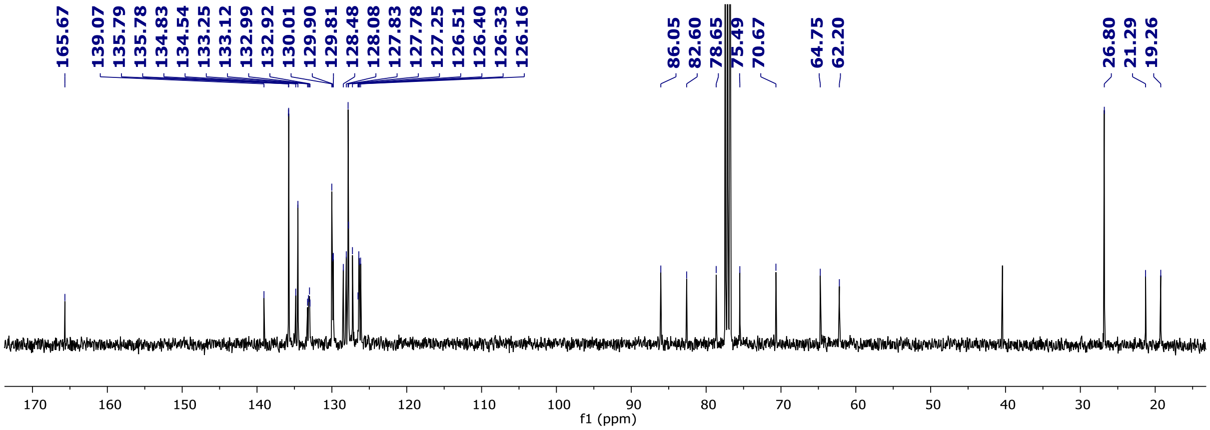
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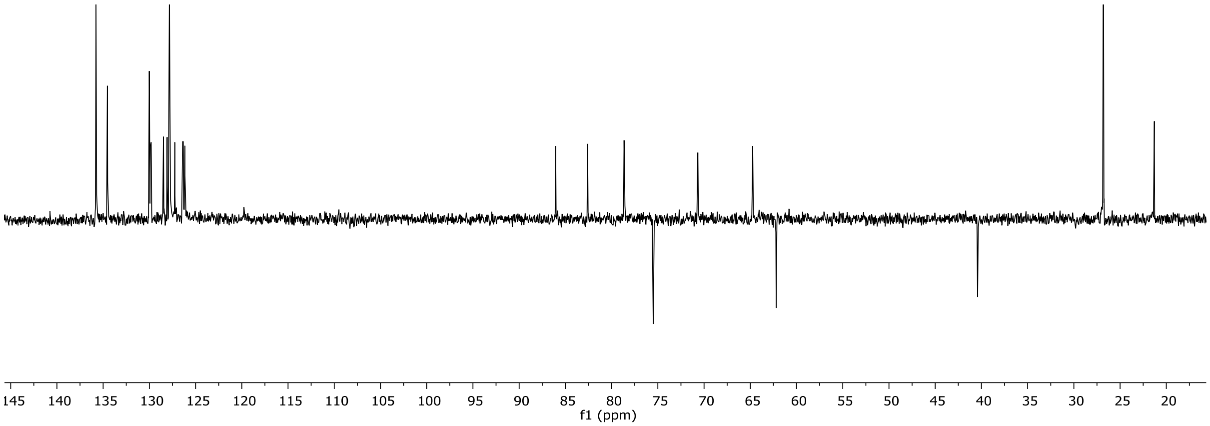
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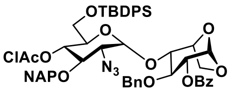
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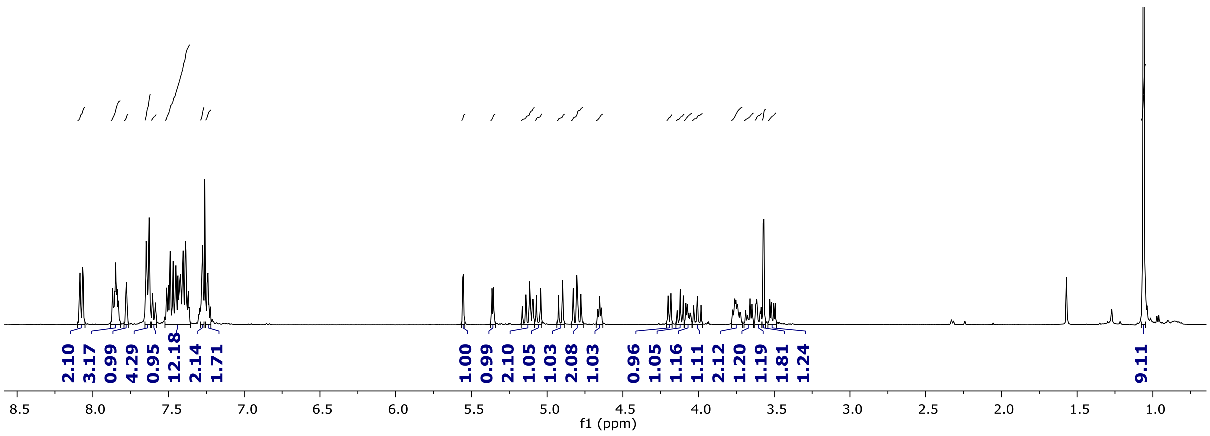
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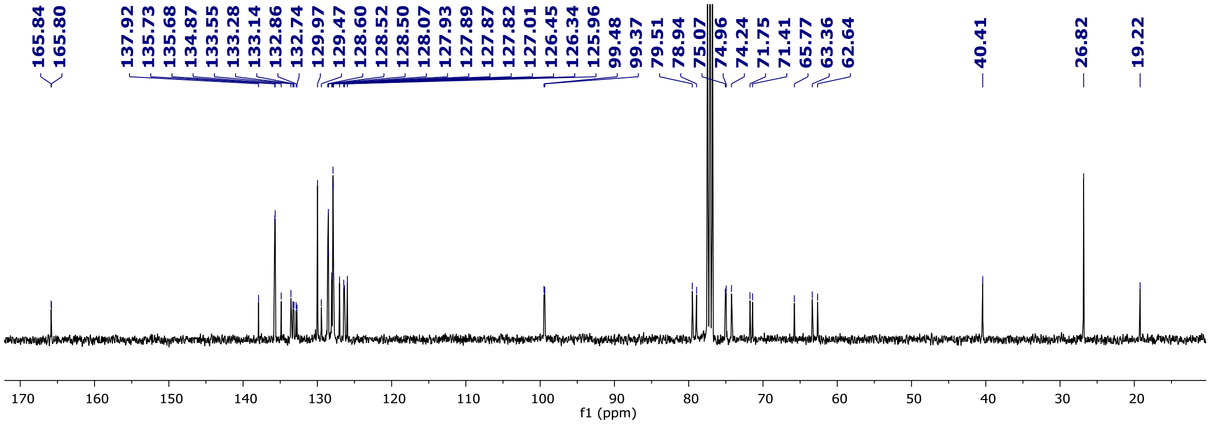
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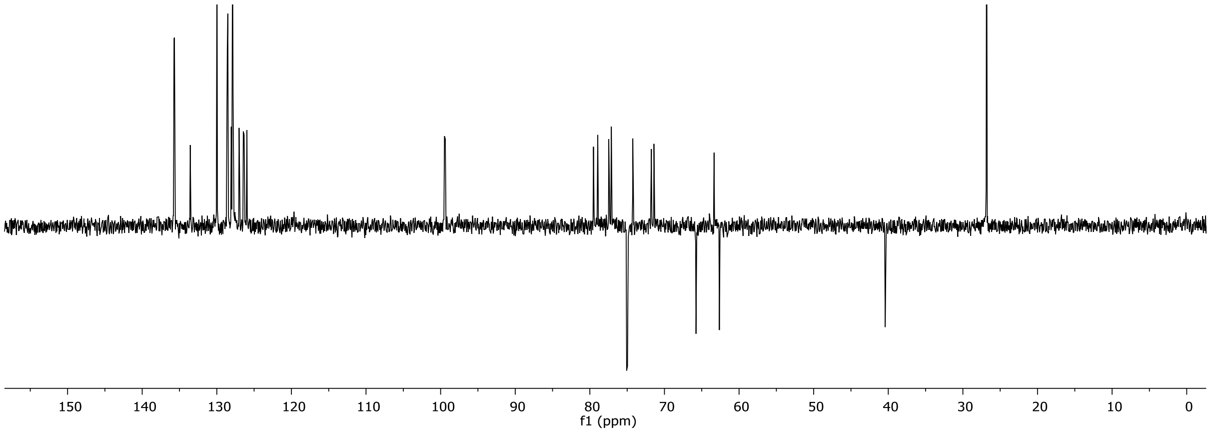
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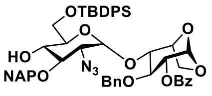
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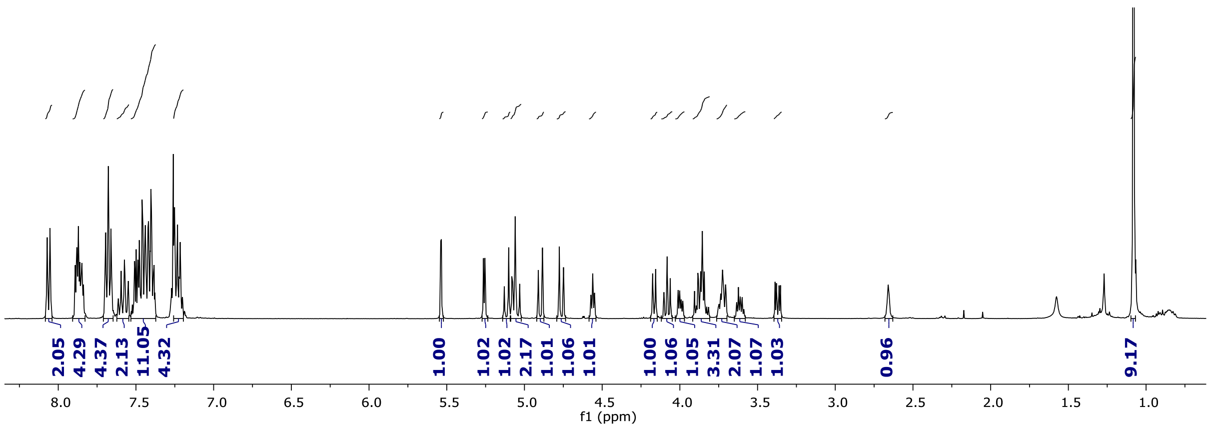
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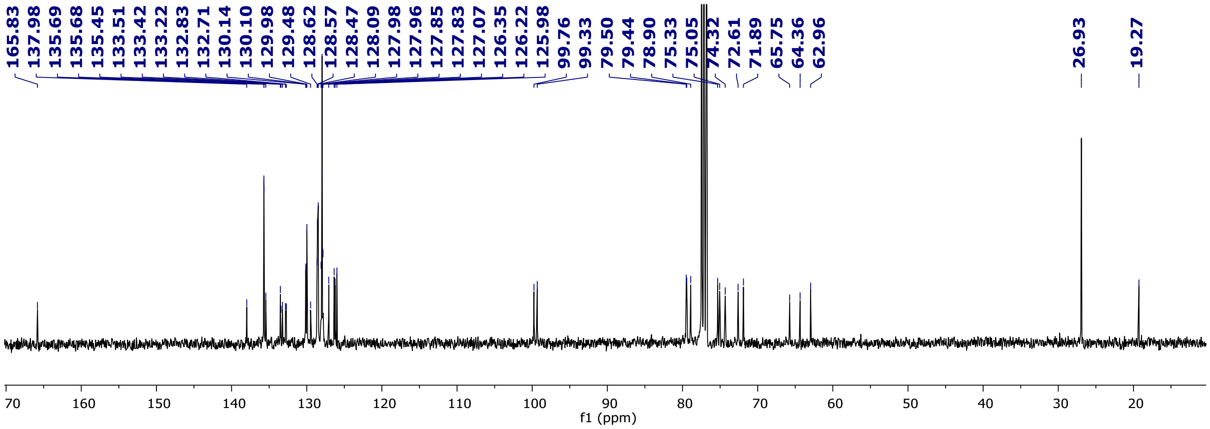
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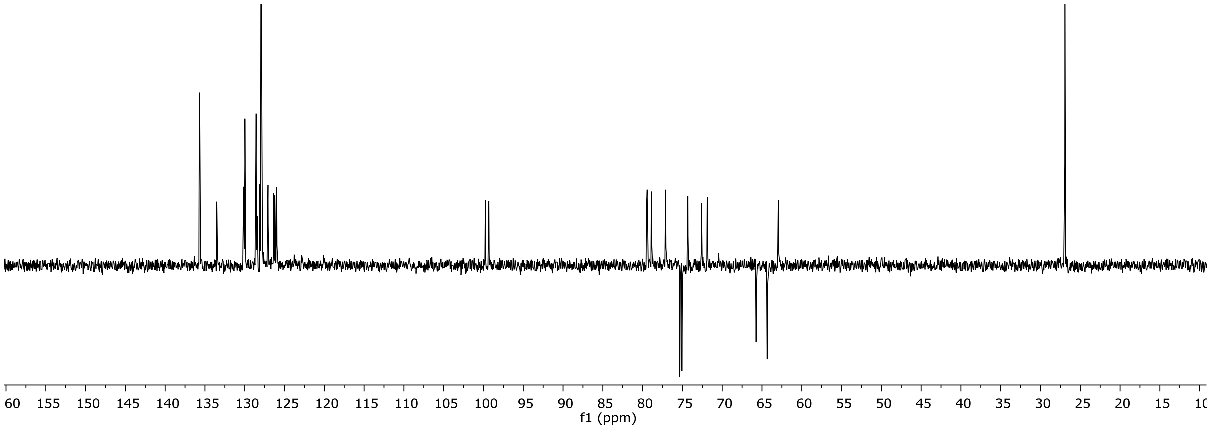
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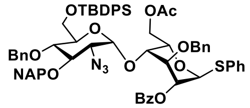
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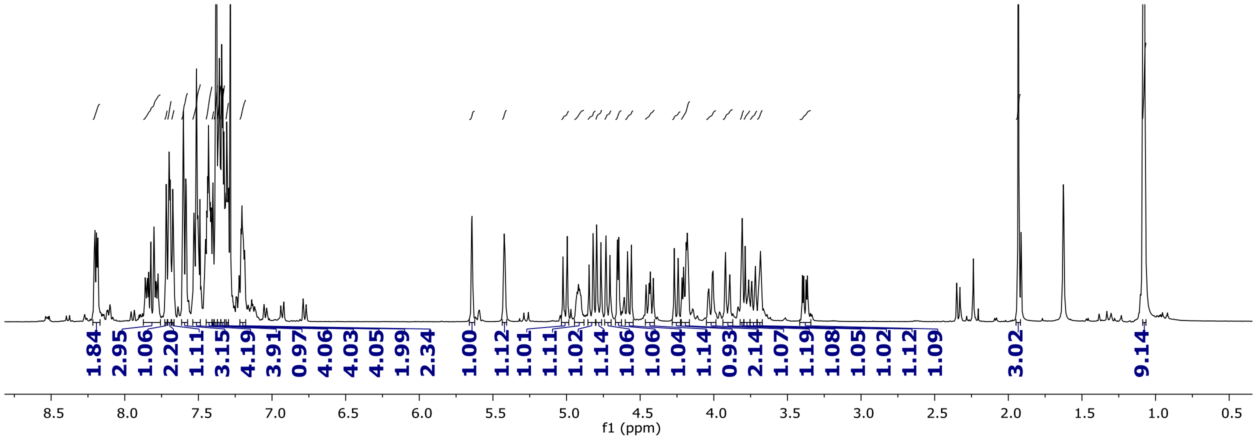
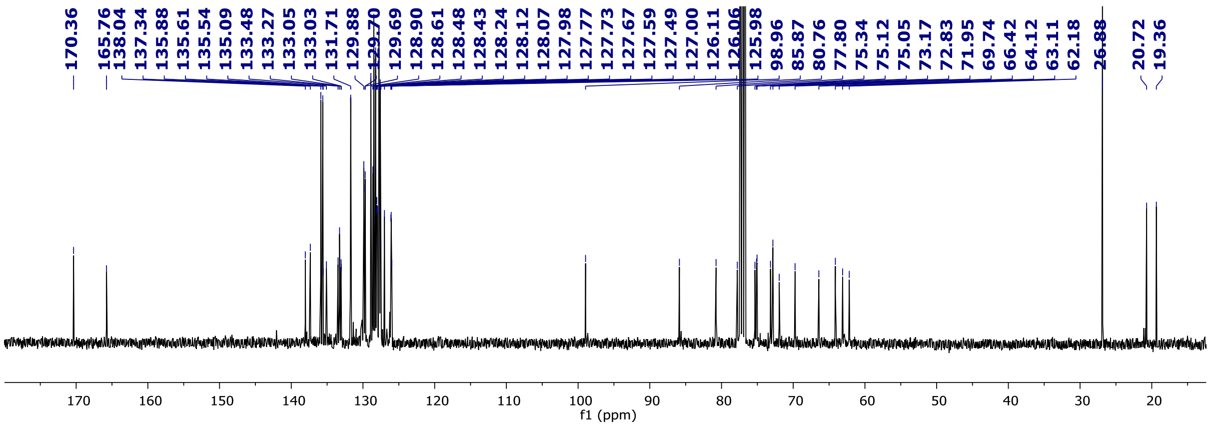
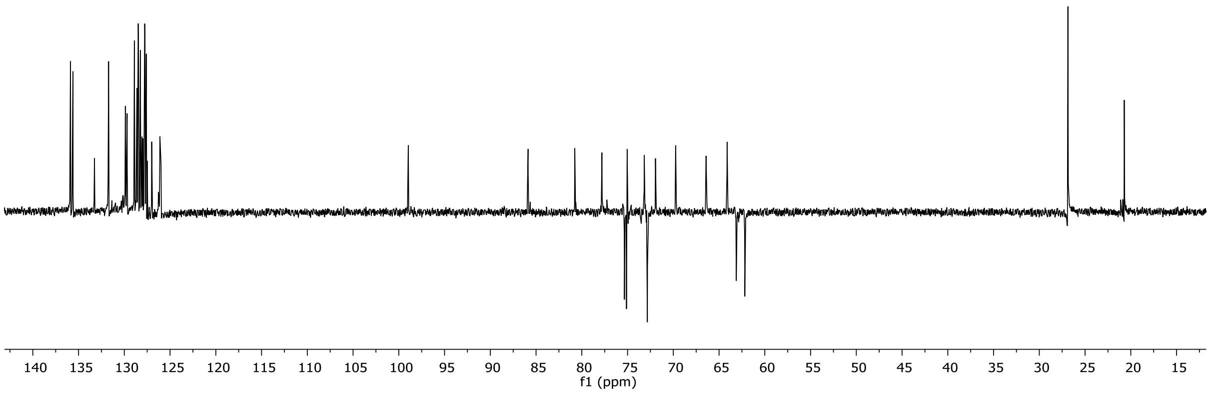
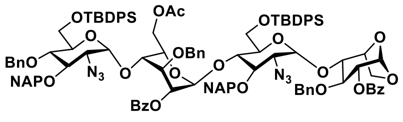
21

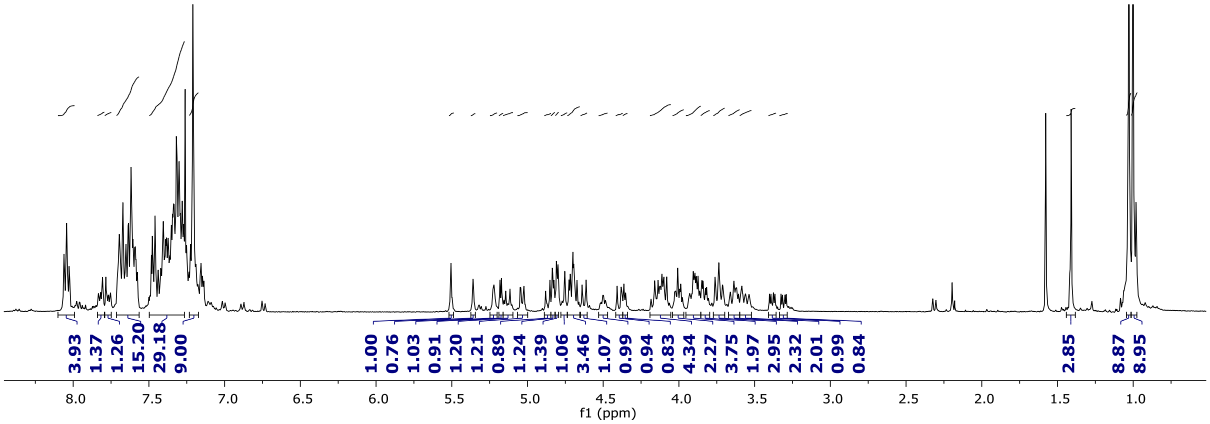

1.84
2.95
1.06
2.20
1.11
3.15
4.19
3.91
0.97
4.06
4.03
4.05
1.99
2.34
1.00
1.12
1.01
1.11
1.02
1.14
1.06
1.06
1.04
1.14
0.93
2.14
1.07
1.19
1.08
1.05
1.02
1.12
1.09
3.02
9.14
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

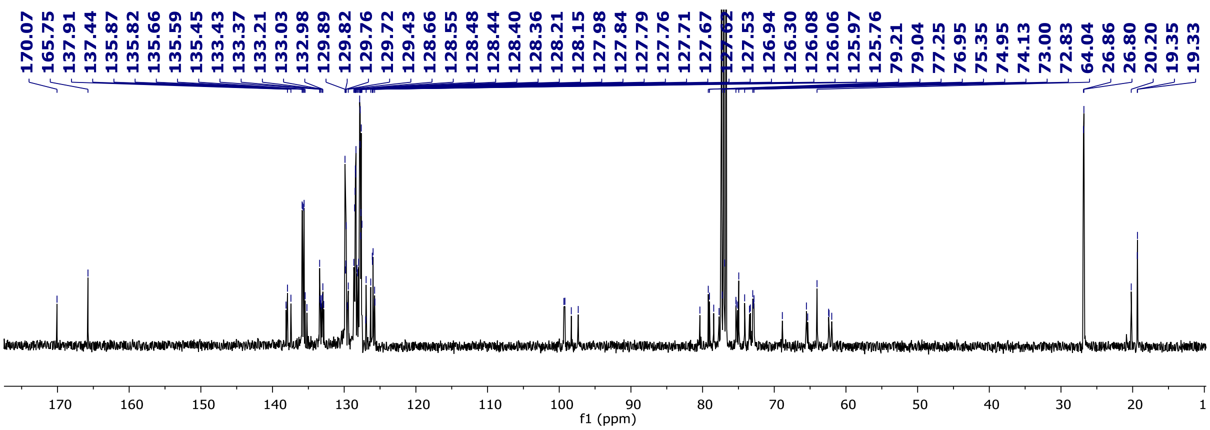

170.36
165.76
138.04
137.34
135.88
135.61
135.54
135.09
133.48
133.27
133.05
133.03
131.71
129.88
129.70
129.69
128.90
128.61
128.48
128.43
128.24
128.12
128.07
127.98
127.77
127.73
127.67
127.59
127.49
127.00
126.11
126.06
125.98
98.96
85.87
80.76
77.80
75.34
75.12
75.05
73.17
72.83
71.95
69.74
66.42
64.12
63.11
62.18
26.88
20.72
19.36
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

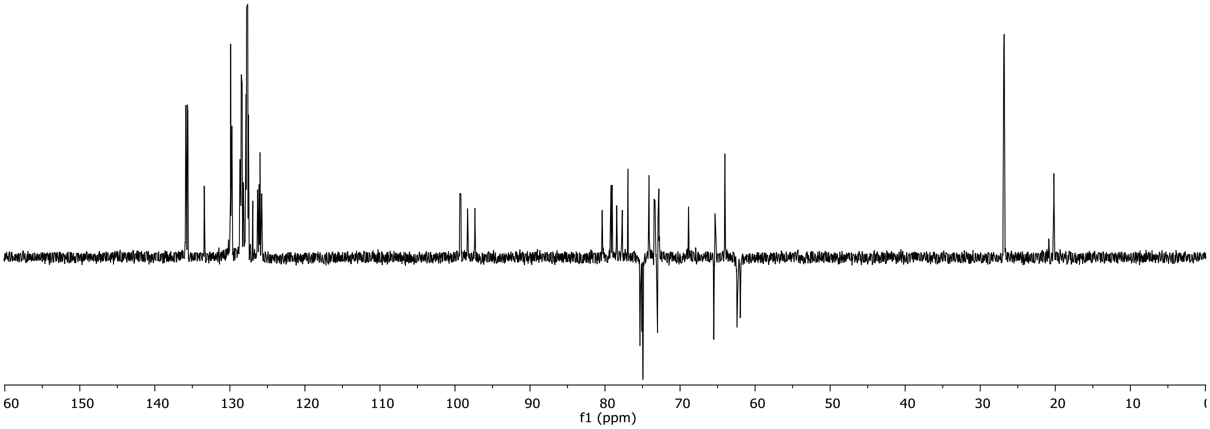

140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
f1 (ppm)


OTBDPS
OAc
OTBDPS
BnO
OBn
O
NAPO
N3
O
O
O
O
BzO
NAPO
N3
BnO
OBz
O

22


3.93
1.37
1.26
15.20
29.18
9.00
1.00
0.76
1.03
0.91
1.20
1.21
0.89
1.24
1.39
1.06
3.46
1.07
0.99
0.94
0.83
4.34
2.27
3.75
1.97
2.95
2.32
2.01
0.99
0.84
2.85
8.87
8.95
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
f1 (ppm)


170.07
165.75
137.91
137.44
135.87
135.82
135.66
135.59
135.45
133.43
133.37
133.21
133.03
132.98
129.89
129.82
129.76
129.72
129.43
128.66
128.55
128.48
128.44
128.40
128.36
128.21
128.15
127.98
127.84
127.79
127.76
127.71
127.67
127.62
127.53
126.94
126.30
126.08
126.06
125.97
125.76
79.21
79.04
77.25
76.95
75.35
74.95
74.13
73.00
72.83
64.04
26.86
26.80
20.20
19.35
19.33
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
1
f1 (ppm)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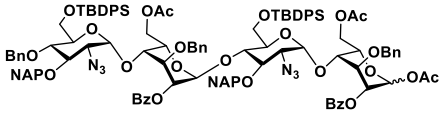
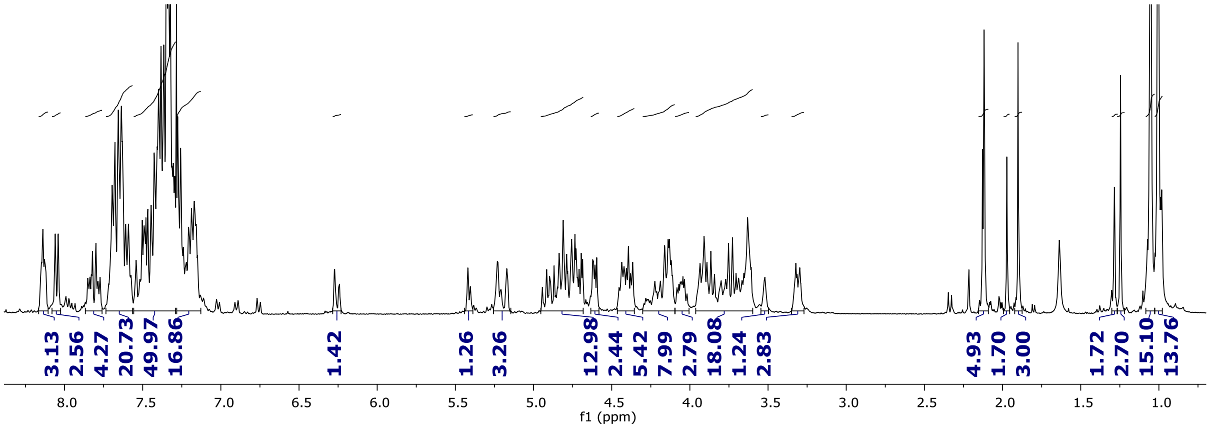
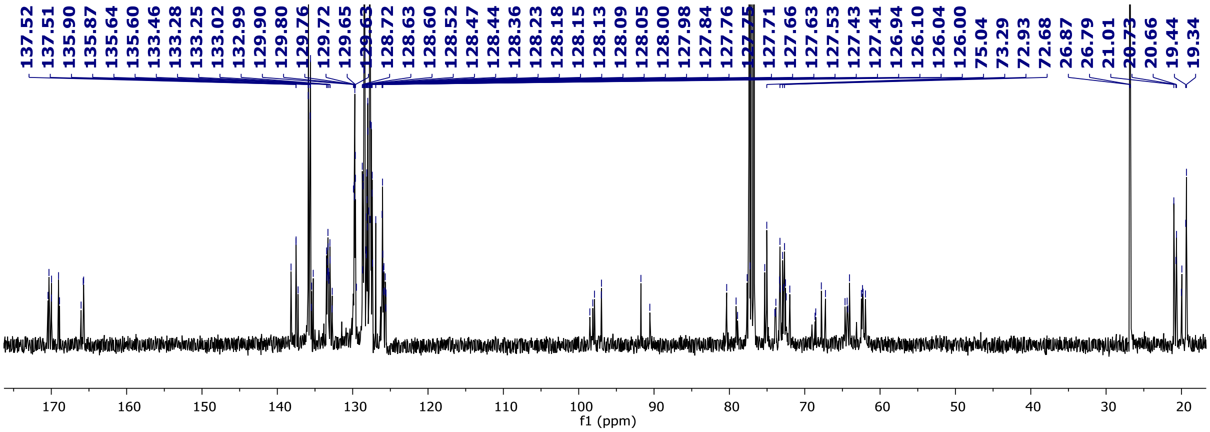
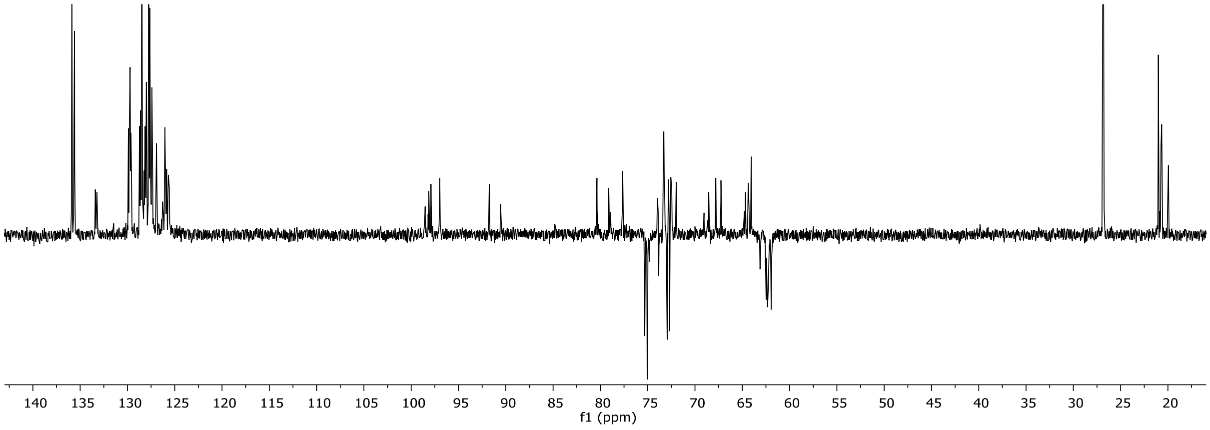
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

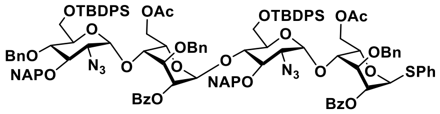

OTBDPS
OAc
OBn
BnO
NAPO
N3
O
BzO
OTBDPS
OAc
OBn
OAc
NAPO
N3
BzO

23

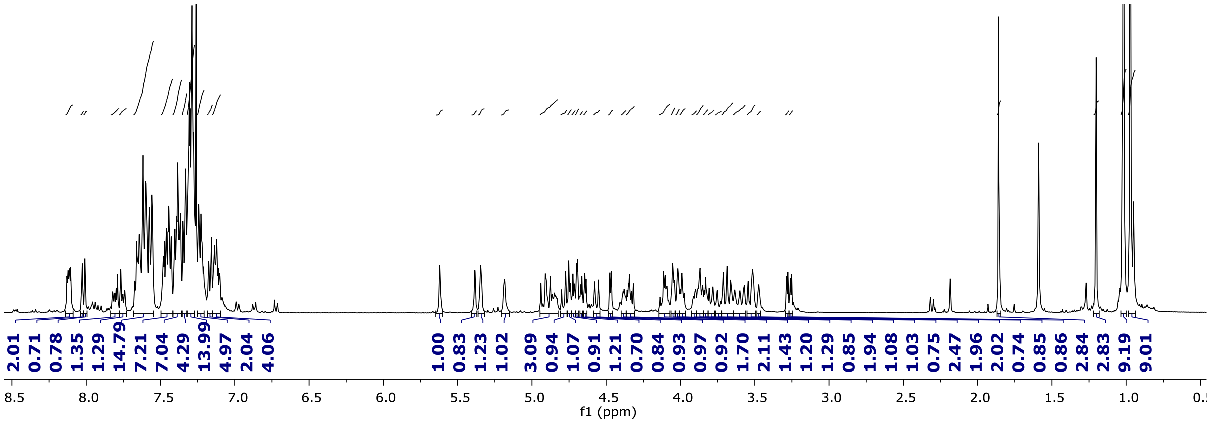

3.13
2.56
4.27
20.73
49.97
16.86
1.42
1.26
3.26
12.98
2.44
5.42
7.99
2.79
18.08
1.24
2.83
4.93
1.70
3.00
1.72
2.70
15.10
13.76
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

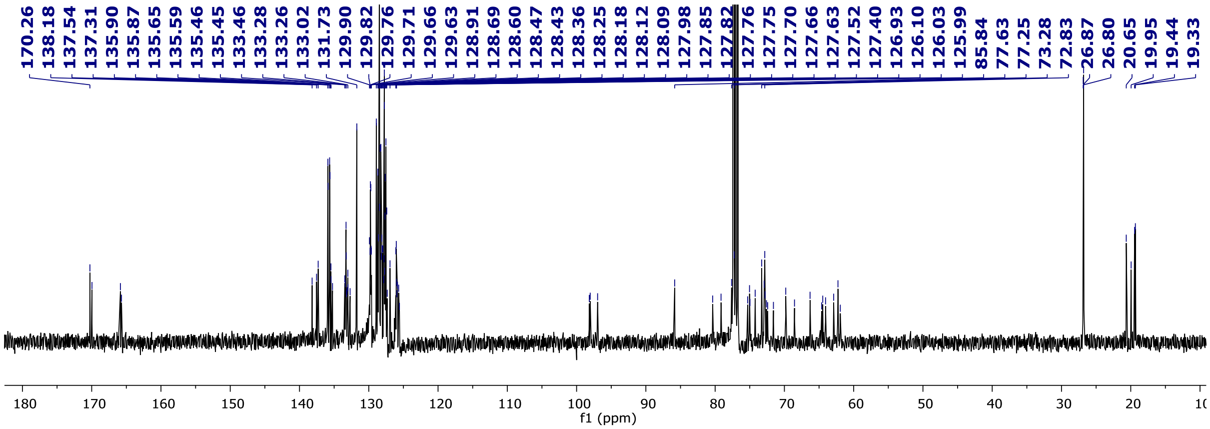

137.52
137.51
135.90
135.87
135.64
135.60
133.46
133.28
133.25
133.02
132.99
129.90
129.80
129.76
129.72
129.65
129.63
128.72
128.63
128.60
128.52
128.47
128.44
128.36
128.23
128.18
128.15
128.13
128.09
128.05
128.00
127.98
127.84
127.76
127.75
127.71
127.66
127.63
127.53
127.43
127.41
126.94
126.10
126.04
126.00
75.04
73.29
72.93
72.68
26.87
26.79
21.01
20.73
20.66
19.44
19.34
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

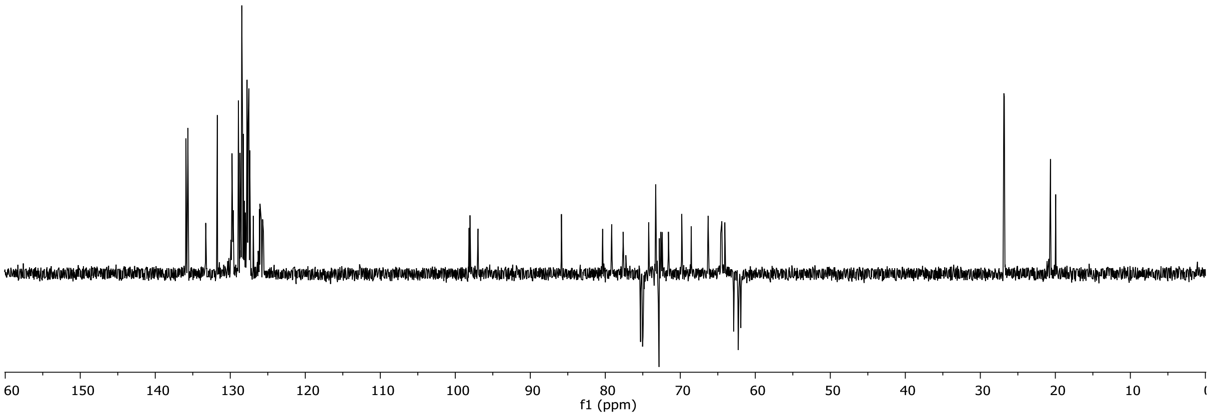

140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
f1 (ppm)


OTBDPS
OAc
OBn
BnO
NAPO
N_3
O
BzO
O
OTBDPS
OAc
OBn
NAPO
N_3
O
BzO
SPh

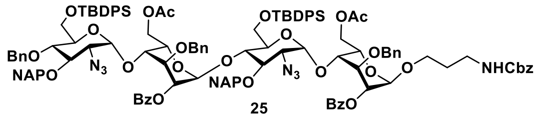
24


2.01
0.71
0.78
1.35
1.29
14.79
7.21
7.04
4.29
13.99
4.97
2.04
4.06
1.00
0.83
1.23
1.02
3.09
0.94
1.07
0.91
1.21
0.70
0.84
0.93
0.97
0.92
1.70
2.11
1.43
1.20
1.29
0.85
1.94
1.08
1.03
0.75
2.47
1.96
2.02
0.74
0.85
0.86
2.84
2.83
9.19
9.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


170.26
138.18
137.54
137.31
135.90
135.87
135.65
135.59
135.46
135.45
133.46
133.28
133.26
133.02
131.73
129.90
129.82
129.76
129.71
129.66
129.63
128.91
128.69
128.60
128.47
128.43
128.36
128.25
128.18
128.12
128.09
127.98
127.85
127.82
127.76
127.75
127.70
127.66
127.63
127.52
127.40
126.93
126.10
126.03
125.99
85.84
77.63
77.25
73.28
72.83
26.87
26.80
20.65
19.95
19.44
19.33
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

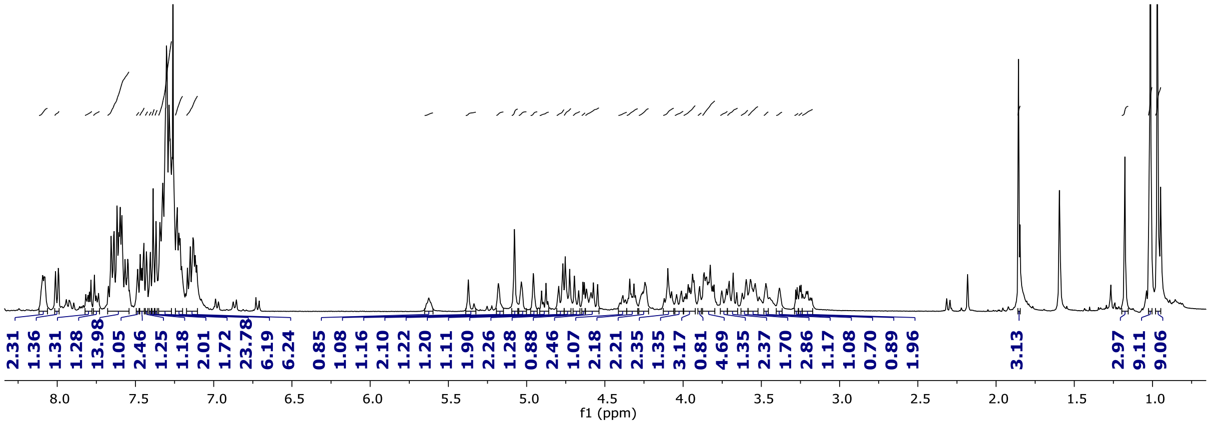


60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

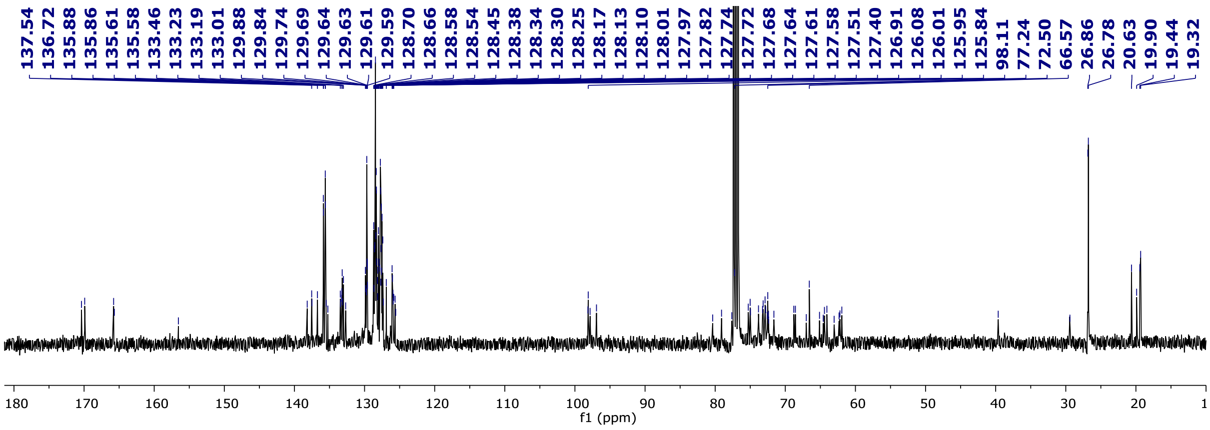


OTBDPS
OAc
BnO
NAPO
N3
O
OBn
BzO
NAPO
OTBDPS
OAc
N3
O
OBn
BzO
NHCbz

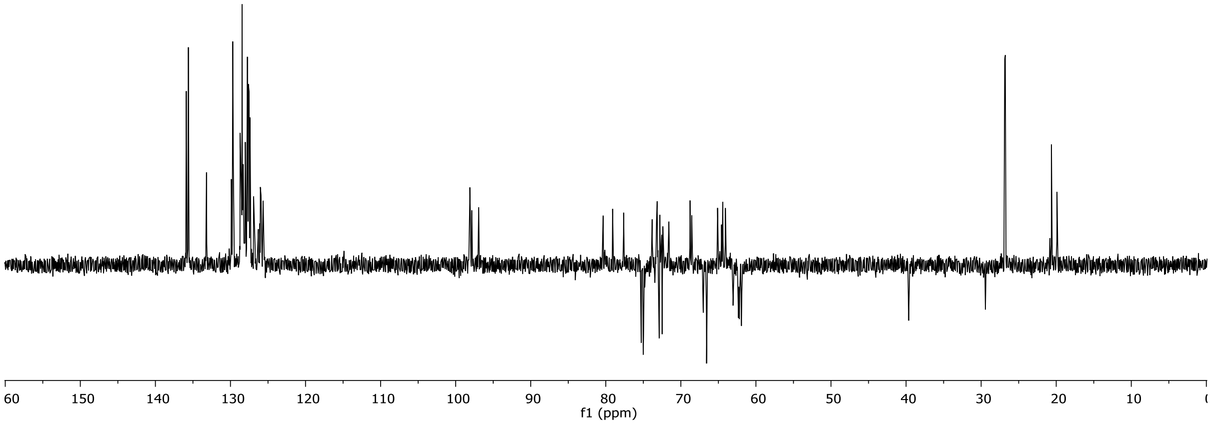
25



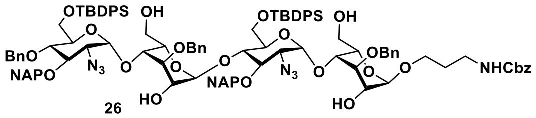
2.31
1.36
1.31
1.28
13.98
1.05
2.46
1.25
1.18
2.01
1.72
23.78
6.19
6.24
0.85
1.08
1.16
2.10
1.22
1.20
1.11
1.90
2.26
1.28
0.88
2.46
1.07
2.18
2.21
2.35
1.35
3.17
0.81
4.69
1.35
2.37
1.70
2.86
1.17
1.08
0.70
0.89
1.96
3.13
2.97
9.11
9.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)



137.54
136.72
135.88
135.86
135.61
135.58
133.46
133.23
133.19
133.01
129.88
129.84
129.74
129.69
129.64
129.63
129.61
129.59
128.70
128.66
128.58
128.54
128.45
128.38
128.34
128.30
128.25
128.17
128.13
128.10
128.01
127.97
127.82
127.74
127.72
127.68
127.64
127.61
127.58
127.51
127.40
126.91
126.08
126.01
125.95
125.84
98.11
77.24
72.50
66.57
26.86
26.78
20.63
19.90
19.44
19.32
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

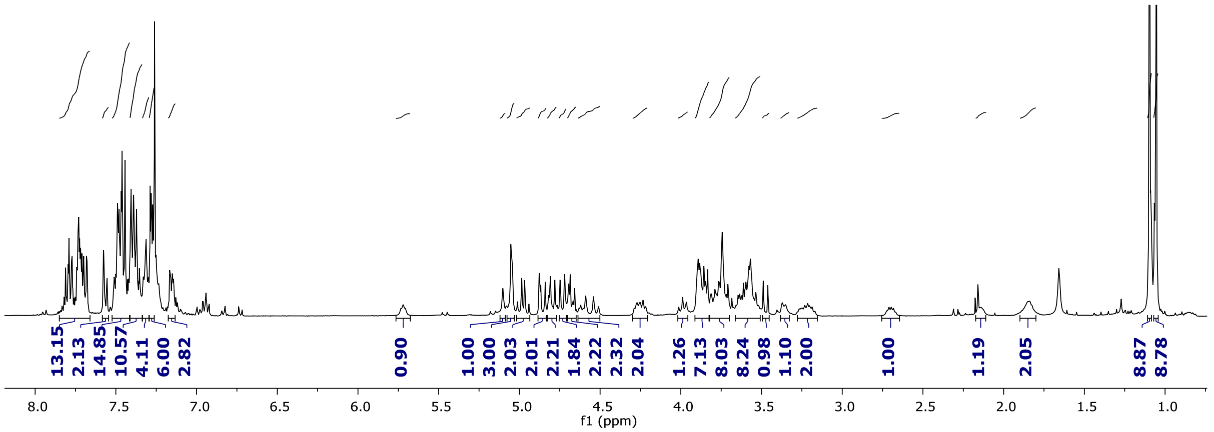


60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

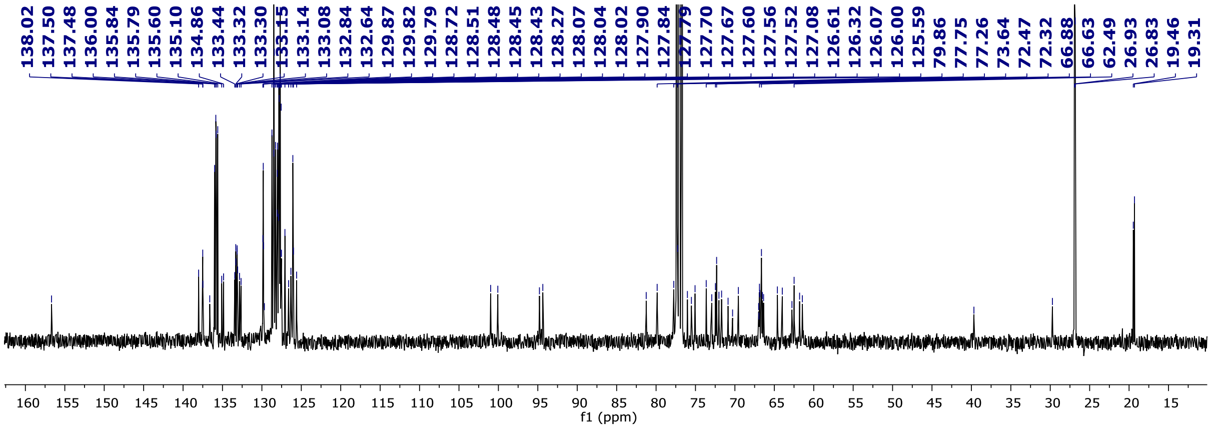


OTBDPS
OH
BnO
NAPO
N3
O
OBn
HO
OTBDPS
OH
NAPO
N3
OBn
HO
NHCbz

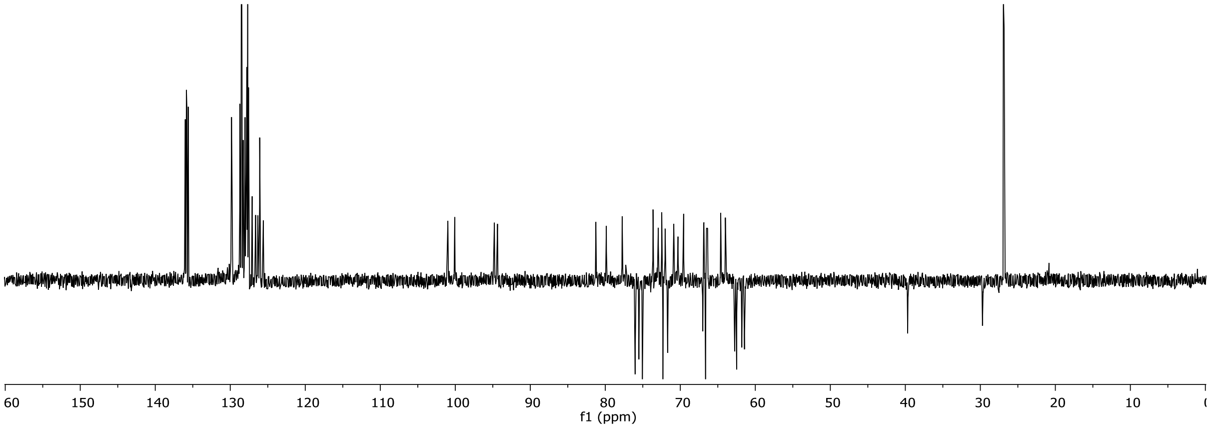
26



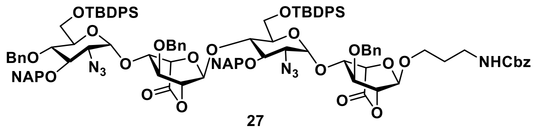
13.15
2.13
14.85
10.57
4.11
6.00
2.82
0.90
1.00
3.00
2.03
2.01
2.21
1.84
2.22
2.32
2.04
1.26
7.13
8.03
8.24
0.98
1.10
2.00
1.00
1.19
2.05
8.87
8.78
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)



138.02
137.50
137.48
136.00
135.84
135.79
135.60
135.10
134.86
133.44
133.32
133.30
133.15
133.14
133.08
132.84
132.64
129.87
129.82
129.79
128.72
128.51
128.48
128.45
128.43
128.27
128.07
128.04
128.02
127.90
127.84
127.79
127.70
127.67
127.60
127.56
127.52
127.08
126.61
126.32
126.07
126.00
125.59
79.86
77.75
77.26
73.64
72.47
72.32
66.88
66.63
62.49
26.93
26.83
19.46
19.31
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
f1 (ppm)

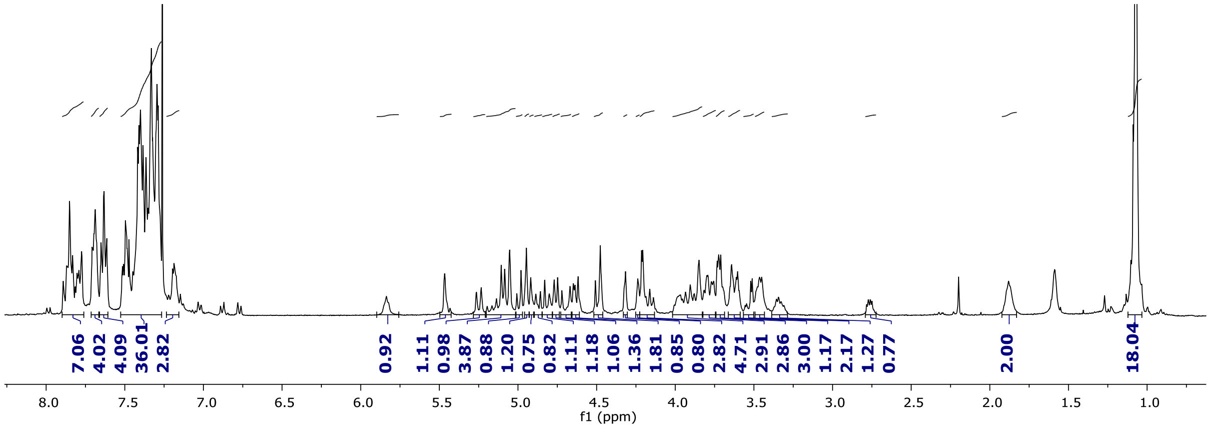


60
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

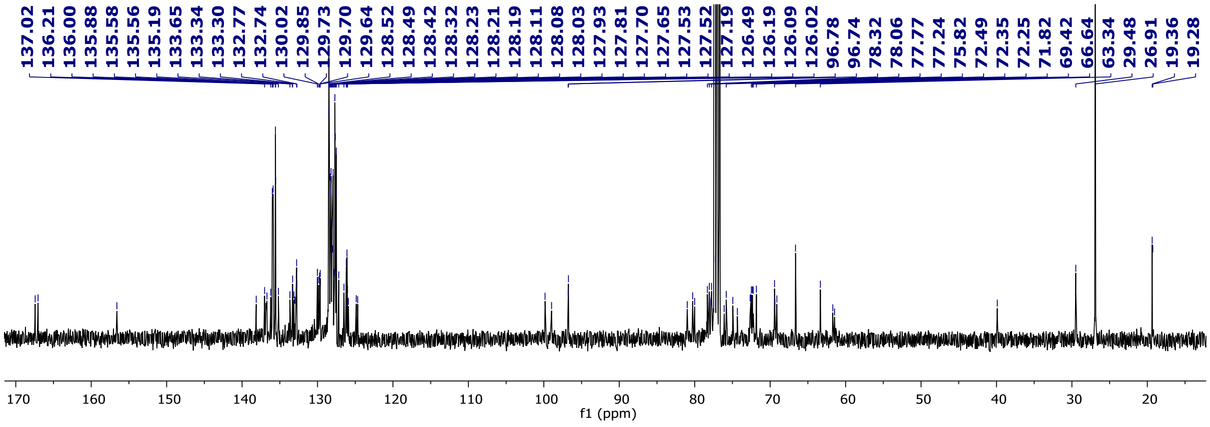


OTBDPS
BnO
NAPO
N3
OBn
O
NAPO
OTBDPS
N3
OBn
NHCbz

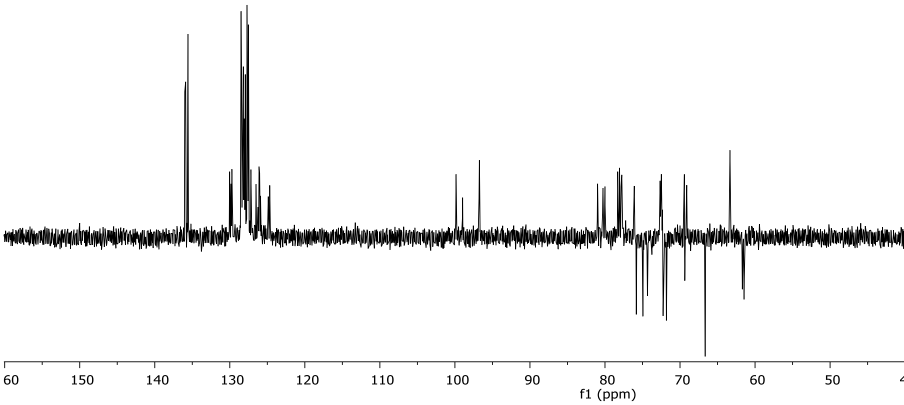
27

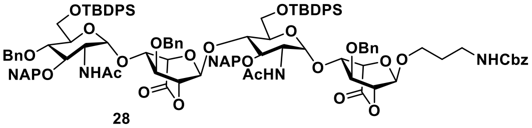


7.06
4.02
4.09
36.01
2.82
0.92
1.11
0.98
3.87
0.88
1.20
0.75
0.82
1.11
1.18
1.06
1.36
1.81
0.85
0.80
2.82
4.71
2.91
2.86
3.00
1.17
2.17
1.27
0.77
2.00
18.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

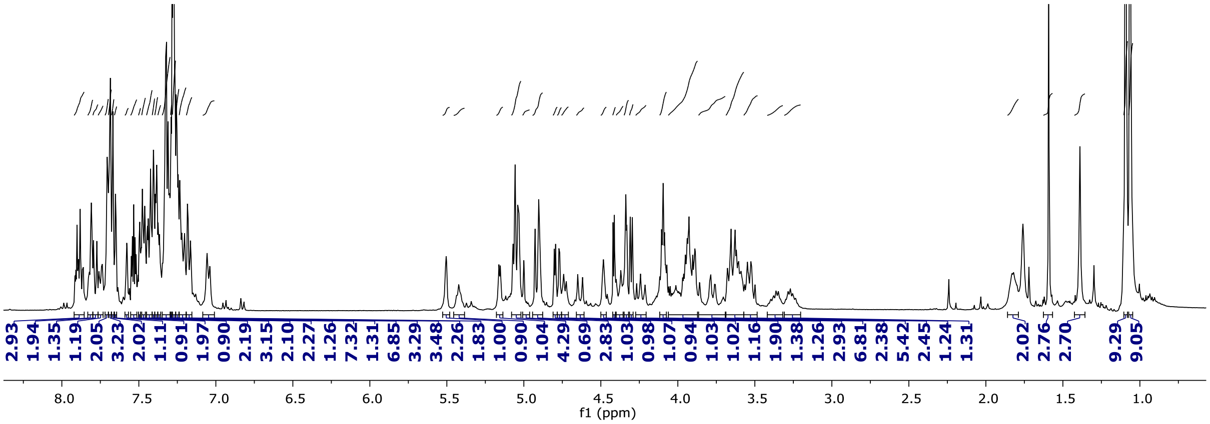


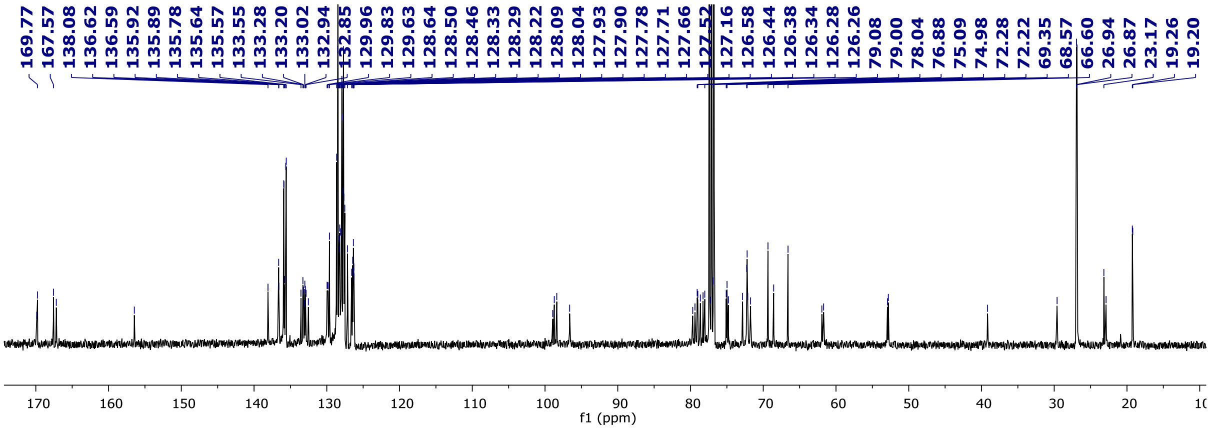
137.02
136.21
136.00
135.88
135.58
135.56
135.19
133.65
133.34
133.30
132.77
132.74
130.02
129.85
129.73
129.70
129.64
128.52
128.49
128.42
128.32
128.23
128.21
128.19
128.11
128.08
128.03
127.93
127.81
127.70
127.65
127.53
127.52
127.19
126.49
126.19
126.09
126.02
96.78
96.74
78.32
78.06
77.77
77.24
75.82
72.49
72.35
72.25
71.82
69.42
66.64
63.34
29.48
26.91
19.36
19.28
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

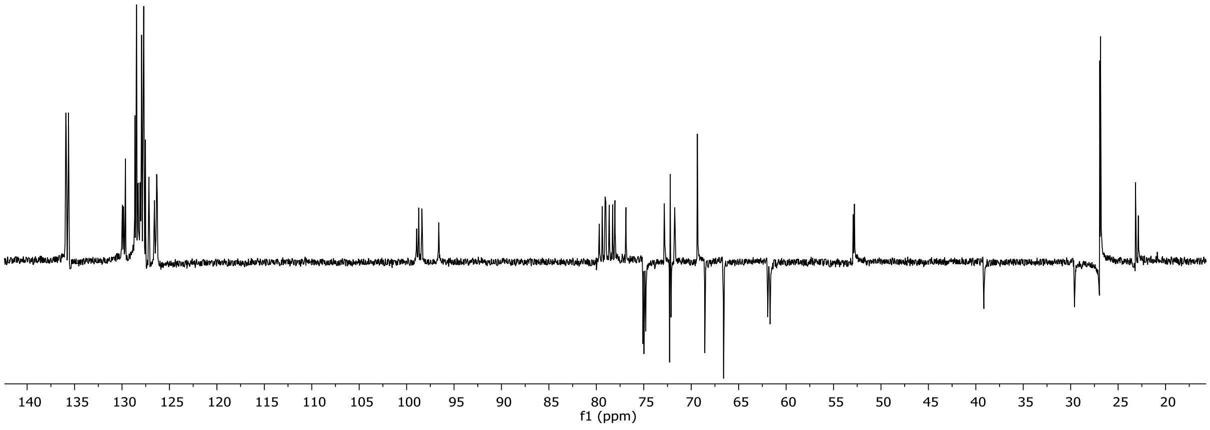

60
150
140
130
120
110
100
90
80
70
60
50
f1 (ppm)

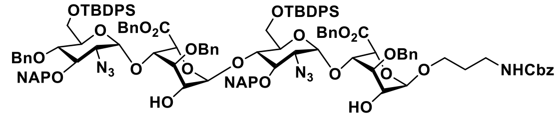

OTBDPS
BnO
NAPO
NHAc
O
OBn
O
O
O
O
NAPO
OTBDPS
O
AcHN
O
OBn
O
O
O
O
NHCbz

28

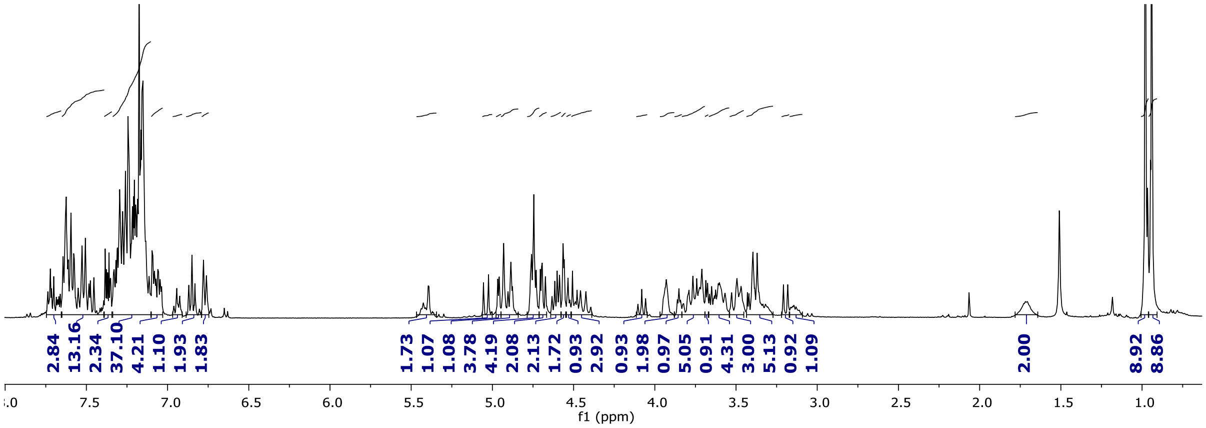

2.93
1.94
1.35
1.19
2.05
3.23
2.02
1.11
0.91
1.97
0.90
2.19
3.15
2.10
2.27
1.26
7.32
1.31
6.85
3.29
3.48
2.26
1.83
1.00
0.90
1.04
4.29
0.69
2.83
1.03
0.98
1.07
0.94
1.03
1.02
1.16
1.90
1.38
1.26
2.93
6.81
2.38
5.42
2.45
1.24
1.31
2.02
2.76
2.70
9.29
9.05
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

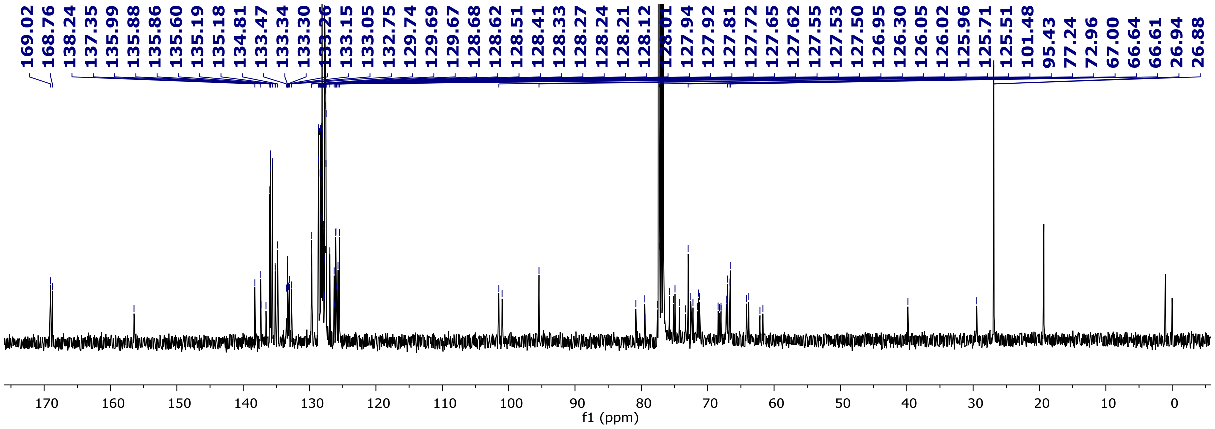

169.77
167.57
138.08
136.62
136.59
135.92
135.89
135.78
135.64
135.57
133.55
133.28
133.20
133.02
132.94
132.85
129.96
129.83
129.63
128.64
128.50
128.46
128.33
128.29
128.22
128.09
128.04
127.93
127.90
127.78
127.71
127.66
127.52
127.16
126.58
126.44
126.38
126.34
126.28
126.26
79.08
79.00
78.04
76.88
75.09
74.98
72.28
72.22
69.35
68.57
66.60
26.94
26.87
23.17
19.26
19.20
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
1(
f1 (ppm)

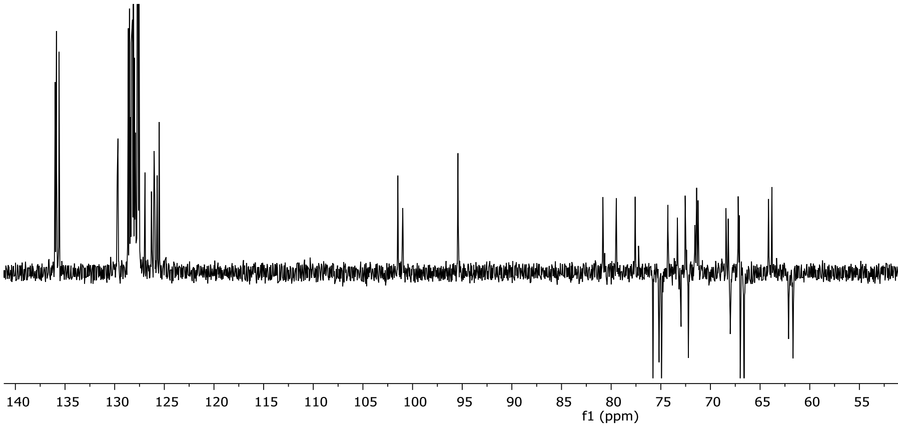

140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
f1 (ppm)


OTBDPS
O
BnO$_2$C
OBn
BnO
NAPO
N$_3$
O
O
HO
O
OTBDPS
O
BnO$_2$C
OBn
NAPO
N$_3$
O
O
HO
O
NHCbz

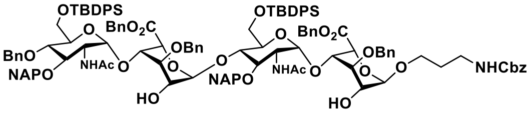
39


2.84
13.16
2.34
37.10
4.21
1.10
1.93
1.83
1.73
1.07
1.08
3.78
4.19
2.08
2.13
1.72
0.93
2.92
0.93
1.98
0.97
5.05
0.91
4.31
3.00
5.13
0.92
1.09
2.00
8.92
8.86
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
f1 (ppm)


169.02
168.76
138.24
137.35
135.99
135.88
135.86
135.60
135.19
135.18
134.81
133.47
133.34
133.30
133.26
133.15
133.05
132.75
129.74
129.69
129.67
128.68
128.62
128.51
128.41
128.33
128.27
128.24
128.21
128.12
128.01
127.94
127.92
127.81
127.72
127.65
127.62
127.55
127.53
127.50
126.95
126.30
126.05
126.02
125.96
125.71
125.51
101.48
95.43
77.24
72.96
67.00
66.64
66.61
26.94
26.88
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

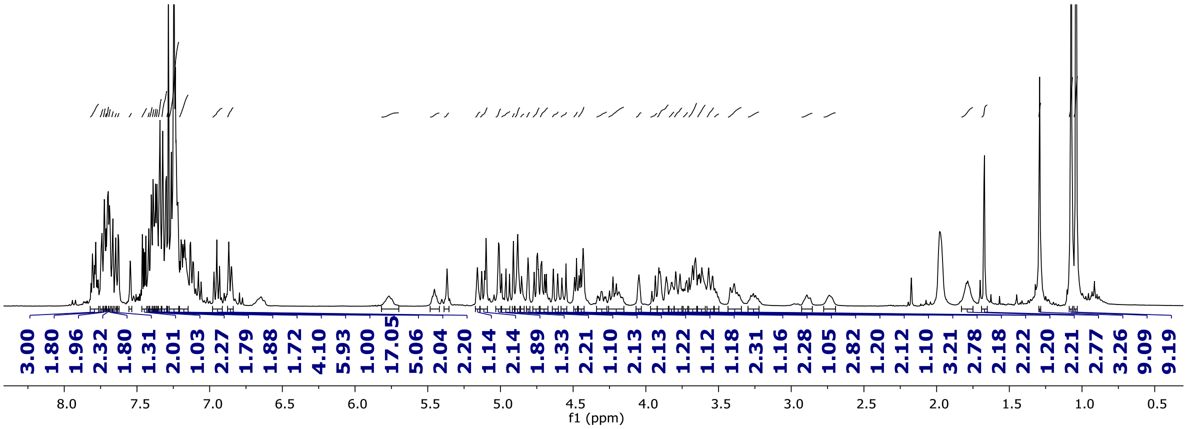


140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
f1 (ppm)

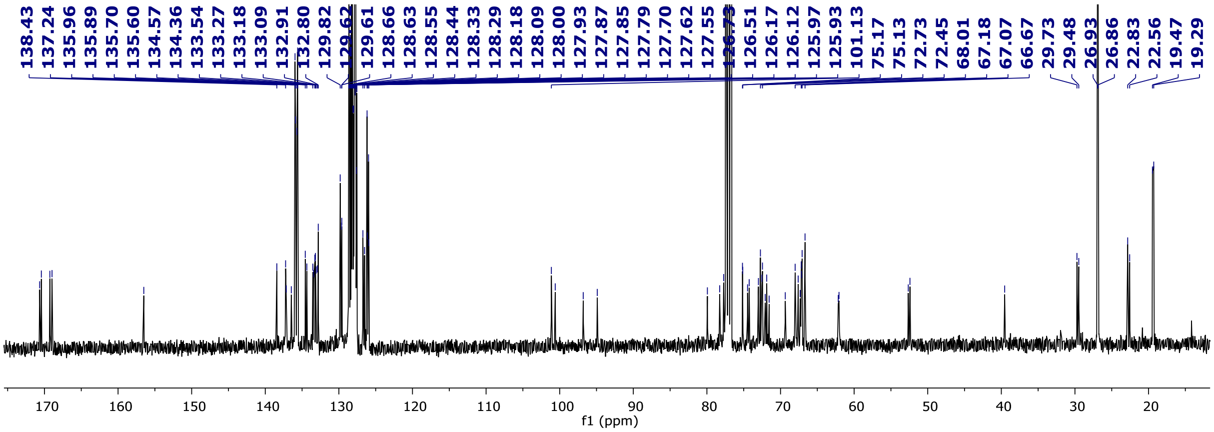


OTBDPS
BnO$_2$C
OBn
BnO
NAPO
NHAc
O
HO
OTBDPS
BnO$_2$C
OBn
NAPO
NHAc
O
HO
NHCbz

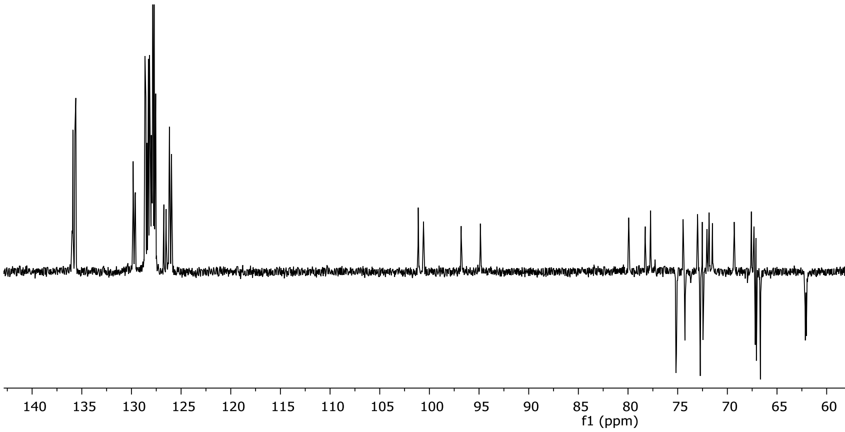
42

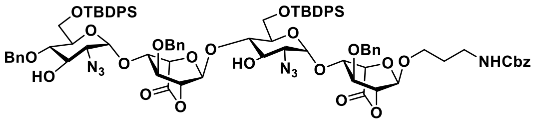


3.00
1.80
1.96
2.32
1.80
1.31
2.01
1.03
2.27
1.79
1.88
1.72
4.10
5.93
1.00
17.05
5.06
2.04
2.20
1.14
2.14
1.89
1.33
2.21
1.10
2.13
2.13
1.22
1.12
1.18
2.31
1.16
2.28
1.05
2.82
1.20
2.12
1.10
3.21
2.78
2.18
2.22
1.20
2.21
2.77
3.26
9.09
9.19
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

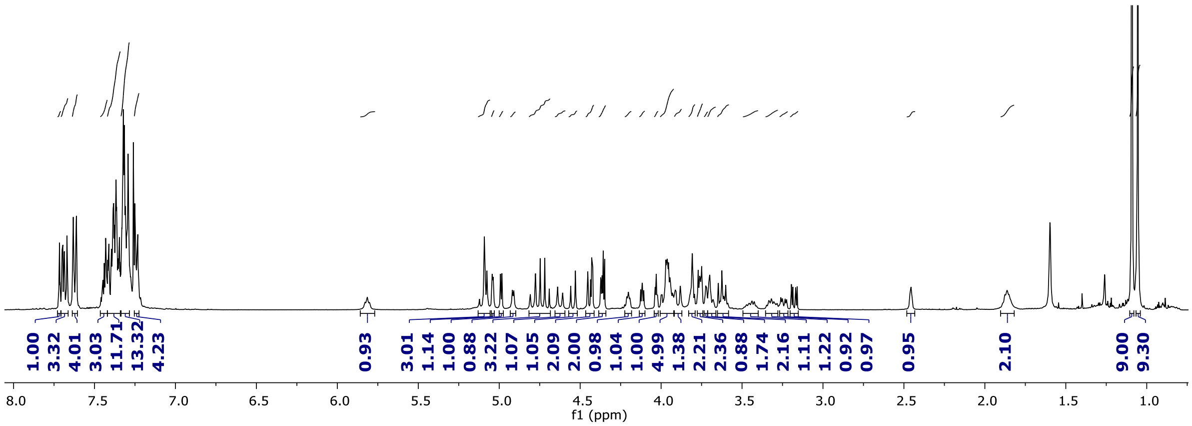


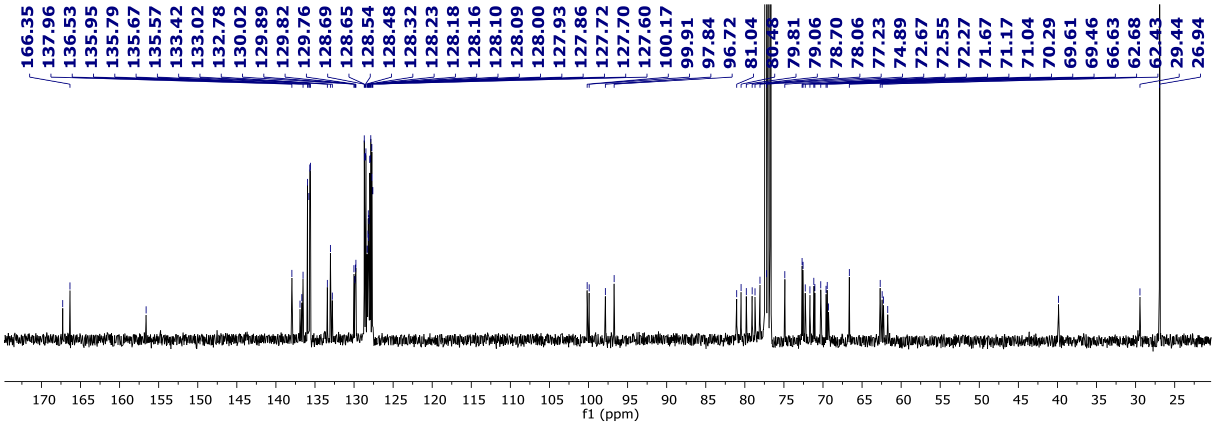
138.43
137.24
135.96
135.89
135.70
135.60
134.57
134.36
133.54
133.27
133.18
133.09
132.91
132.80
129.82
129.62
129.61
128.66
128.63
128.55
128.44
128.33
128.29
128.18
128.09
128.00
127.93
127.87
127.85
127.79
127.70
127.62
127.55
126.73
126.51
126.17
126.12
125.97
125.93
101.13
75.17
75.13
72.73
72.45
68.01
67.18
67.07
66.67
29.73
29.48
26.93
26.86
22.83
22.56
19.47
19.29
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

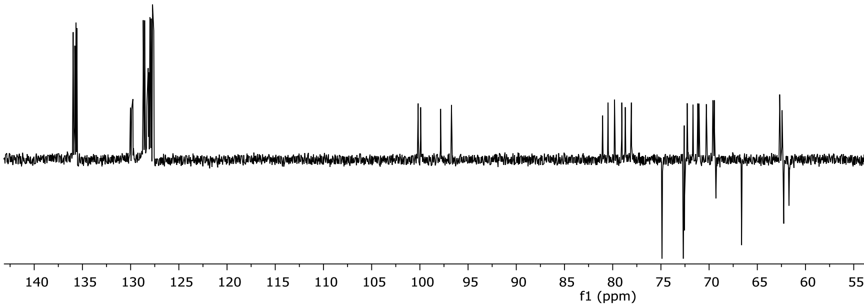

140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
f1 (ppm)

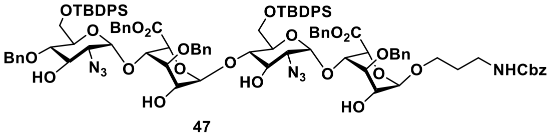

OTBDPS
O
BnO
HO
N$_3$
O
OBn
O
O
O
O
OTBDPS
O
HO
N$_3$
O
OBn
O
O
O
O
NHCbz

31

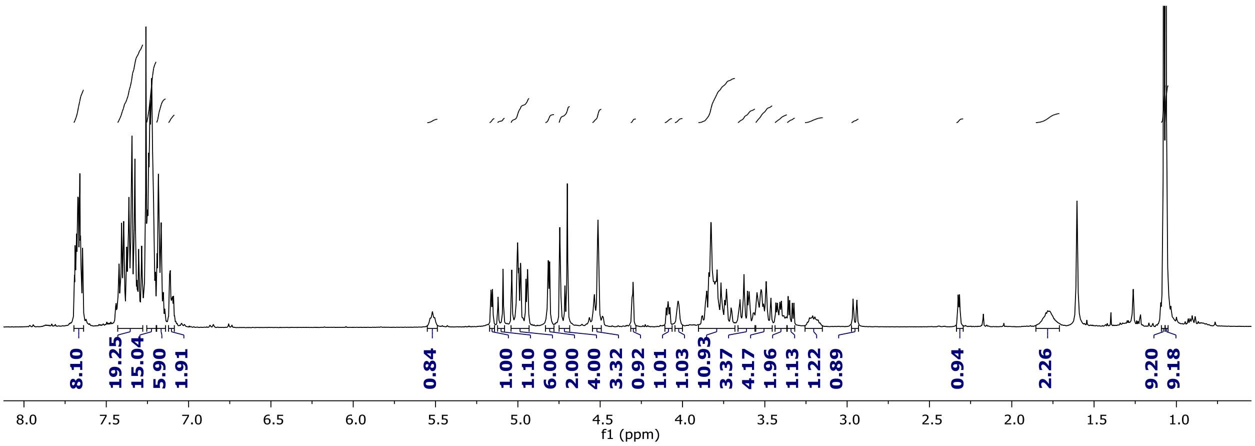

1.00
3.32
4.01
3.03
11.71
13.32
4.23
0.93
3.01
1.14
1.00
0.88
3.22
1.07
1.05
2.09
2.00
0.98
1.04
1.00
4.99
1.38
2.21
2.36
0.88
1.74
2.16
1.11
1.22
0.92
0.97
0.95
2.10
9.00
9.30
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

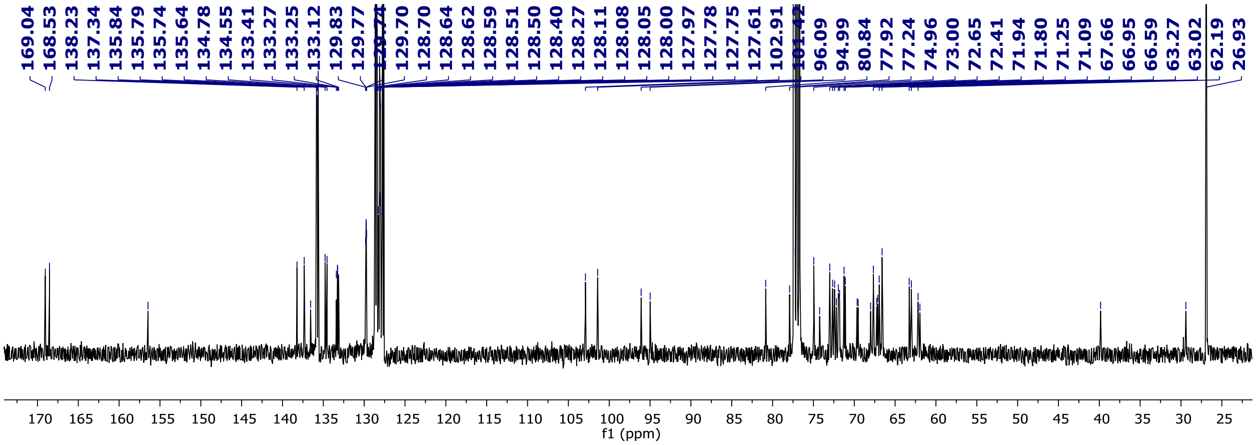

166.35
137.96
136.53
135.95
135.79
135.67
135.57
133.42
133.02
132.78
130.02
129.89
129.82
129.76
128.69
128.65
128.54
128.48
128.32
128.23
128.18
128.16
128.10
128.09
128.00
127.93
127.86
127.72
127.70
127.60
100.17
99.91
97.84
96.72
81.04
80.48
79.81
79.06
78.70
78.06
77.23
74.89
72.67
72.55
72.27
71.67
71.17
71.04
70.29
69.61
69.46
66.63
62.68
62.43
29.44
26.94
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
f1 (ppm)

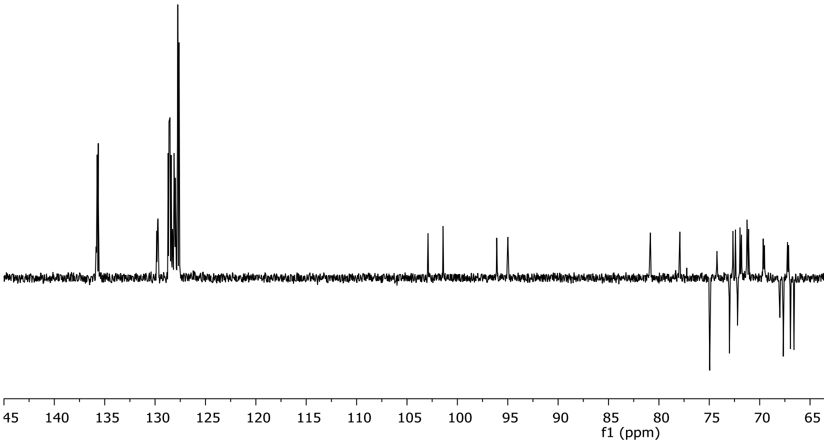

140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
f1 (ppm)

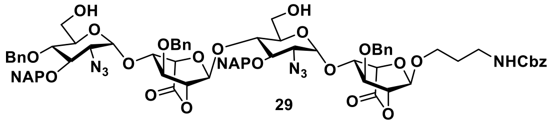

OTBDPS
BnO
O
HO
N3
BnO2C
O
OBn
O
HO
O
OTBDPS
O
HO
N3
BnO2C
O
OBn
O
HO
O
NHCbz

47

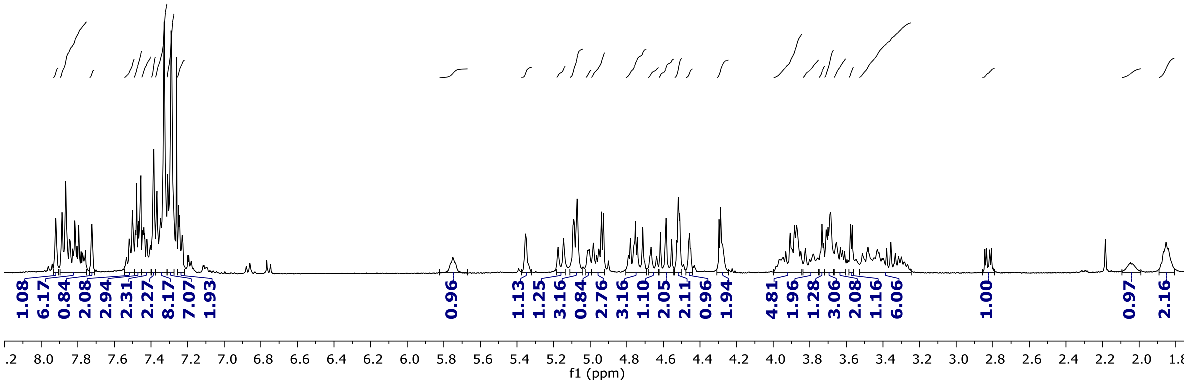

8.10
19.25
15.04
5.90
1.91
0.84
1.00
1.10
6.00
2.00
4.00
3.32
0.92
1.01
1.03
10.93
3.37
4.17
1.96
1.13
1.22
0.89
0.94
2.26
9.20
9.18
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

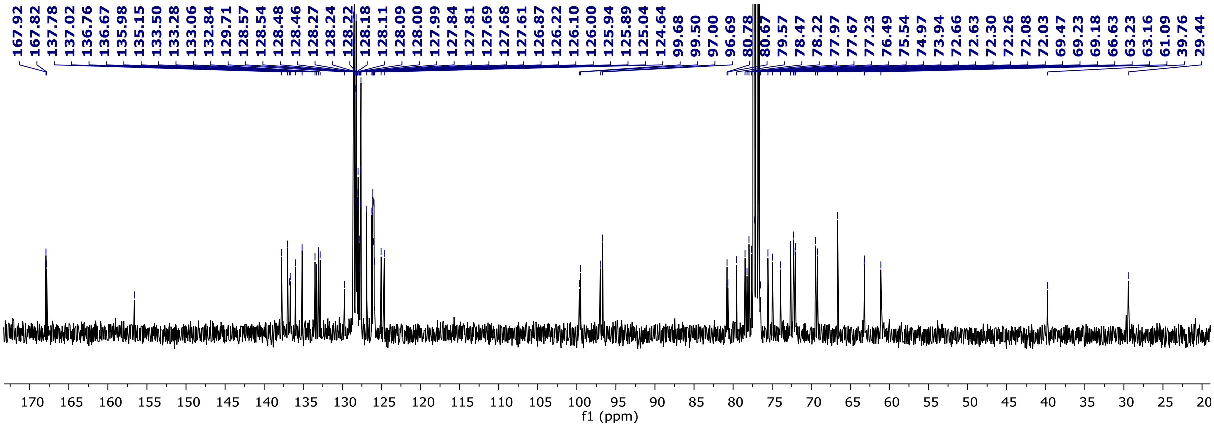

169.04
168.53
138.23
137.34
135.84
135.79
135.74
135.64
134.78
134.55
133.41
133.27
133.25
133.12
129.83
129.77
129.74
129.70
128.70
128.64
128.62
128.59
128.51
128.50
128.40
128.27
128.11
128.08
128.05
128.00
127.97
127.78
127.75
127.61
102.91
101.42
96.09
94.99
80.84
77.92
77.24
74.96
73.00
72.65
72.41
71.94
71.80
71.25
71.09
67.66
66.95
66.59
63.27
63.02
62.19
26.93
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
f1 (ppm)

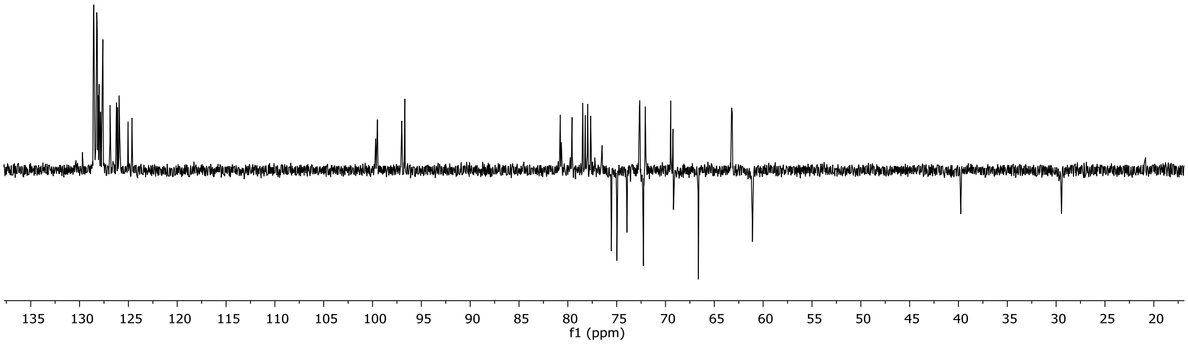

45
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
f1 (ppm)

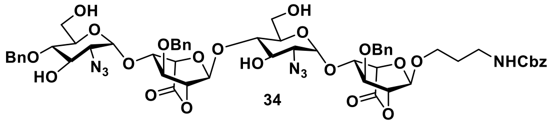

OH
BnO
NAPO
N3
O
OBn
O
NAPO
O
O
O
OH
N3
O
OBn
O
O
NHCbz
O
O

29

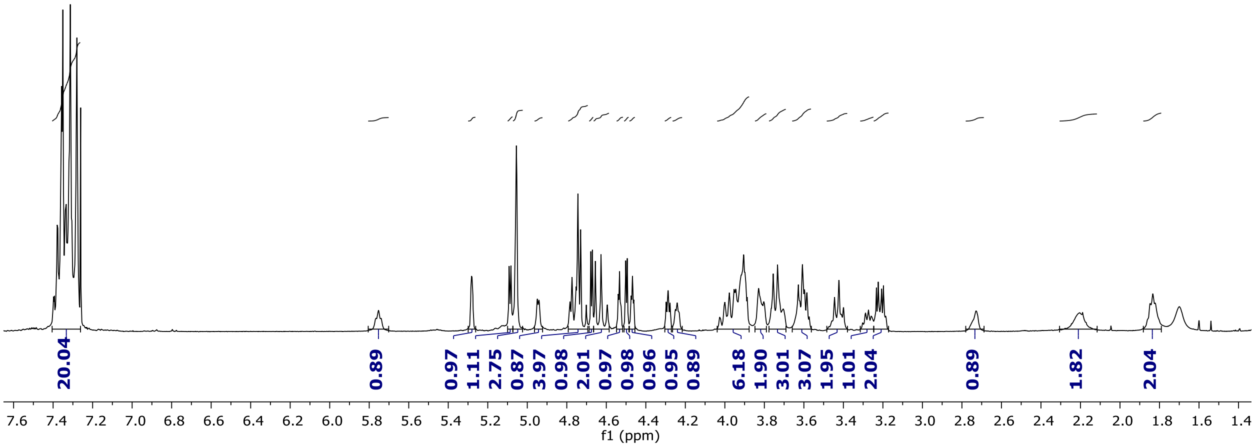

1.08
6.17
0.84
2.08
2.94
2.31
2.27
8.17
7.07
1.93
0.96
1.13
1.25
3.16
0.84
2.76
3.16
1.10
2.05
2.11
0.96
1.94
4.81
1.96
1.28
3.06
2.08
1.16
6.06
1.00
0.97
2.16
.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
f1 (ppm)

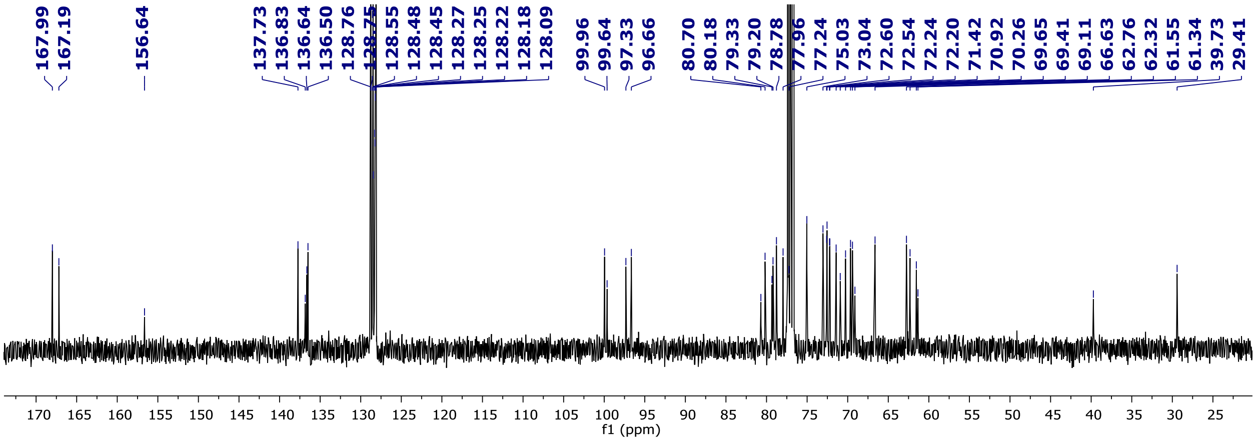

167.92
167.82
137.78
137.02
136.76
136.67
135.98
135.15
133.50
133.28
133.06
132.84
129.71
128.57
128.54
128.48
128.46
128.27
128.24
128.22
128.18
128.11
128.09
128.00
127.99
127.84
127.81
127.69
127.68
127.61
126.87
126.22
126.10
126.00
125.94
125.89
125.04
124.64
99.68
99.50
97.00
96.69
80.78
80.67
79.57
78.47
78.22
77.97
77.67
77.23
76.49
75.54
74.97
73.94
72.66
72.63
72.30
72.26
72.08
72.03
69.47
69.23
69.18
66.63
63.23
63.16
61.09
39.76
29.44
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
f1 (ppm)

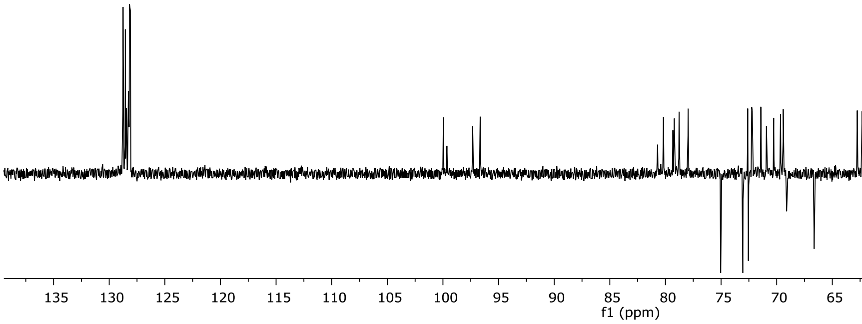

135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
f1 (ppm)

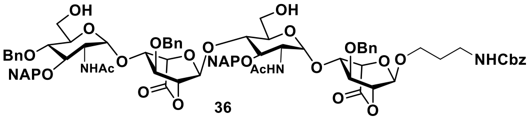

OH
BnO
HO
N3
O
OBn
O=
OH
HO
N3
OBn
NHCbz

34

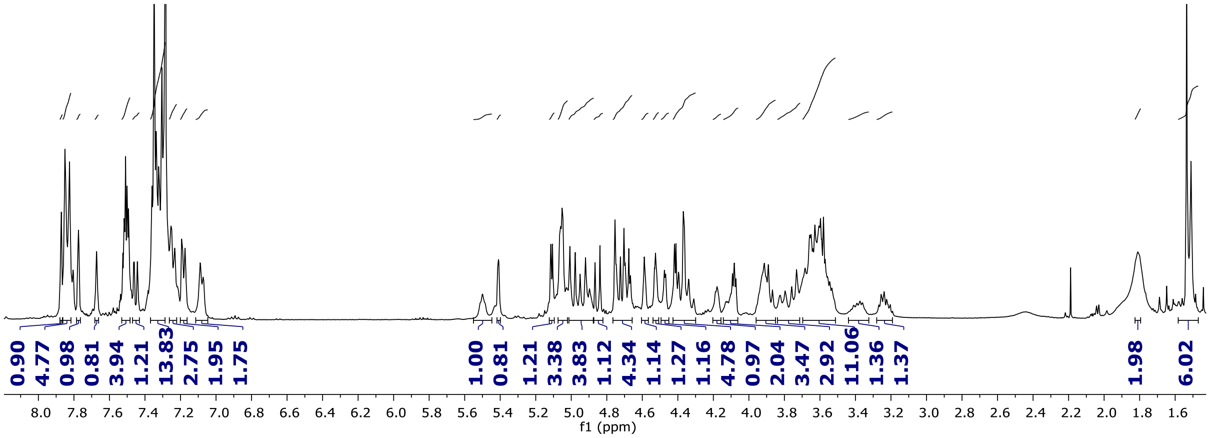

20.04
0.89
0.97
1.11
2.75
0.87
3.97
0.98
2.01
0.97
0.98
0.96
0.95
0.89
6.18
1.90
3.01
3.07
1.95
1.01
2.04
0.89
1.82
2.04
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
f1 (ppm)

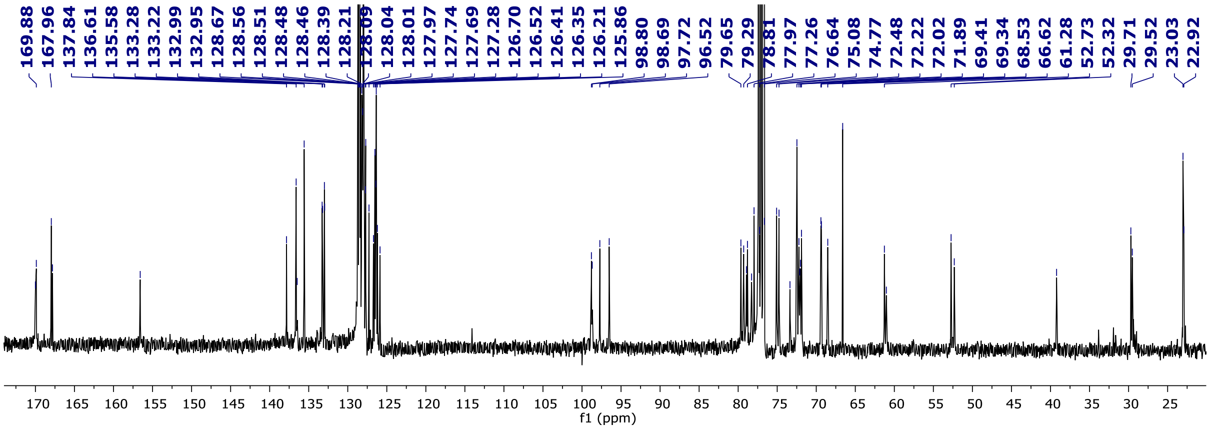

167.99
167.19
156.64
137.73
136.83
136.64
136.50
128.76
128.75
128.55
128.48
128.45
128.27
128.25
128.22
128.18
128.09
99.96
99.64
97.33
96.66
80.70
80.18
79.33
79.20
78.78
77.96
77.24
75.03
73.04
72.60
72.54
72.24
72.20
71.42
70.92
70.26
69.65
69.41
69.11
66.63
62.76
62.32
61.55
61.34
39.73
29.41
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
f1 (ppm)

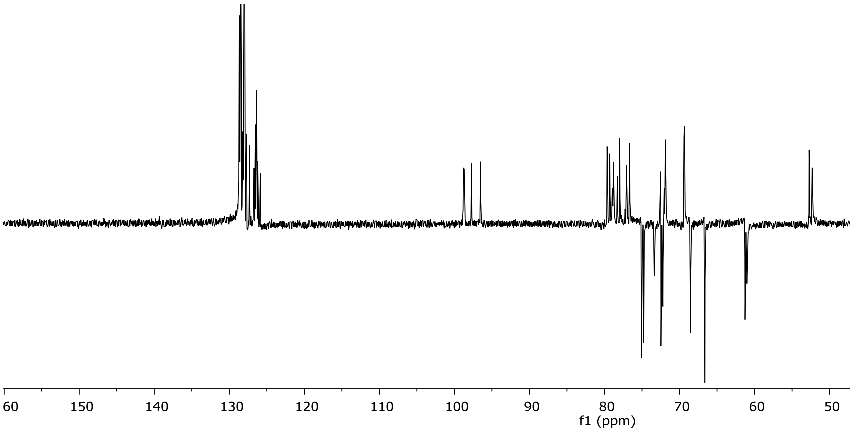

135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
f1 (ppm)

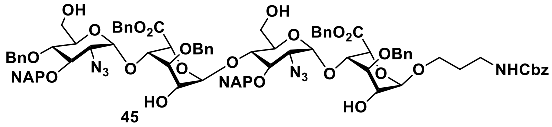

OH
BnO
NAPO
NHAc
O
OBn
O
NAPO
AcHN
OH
O
O
OBn
O
NHCbz
O
O
O
O

36

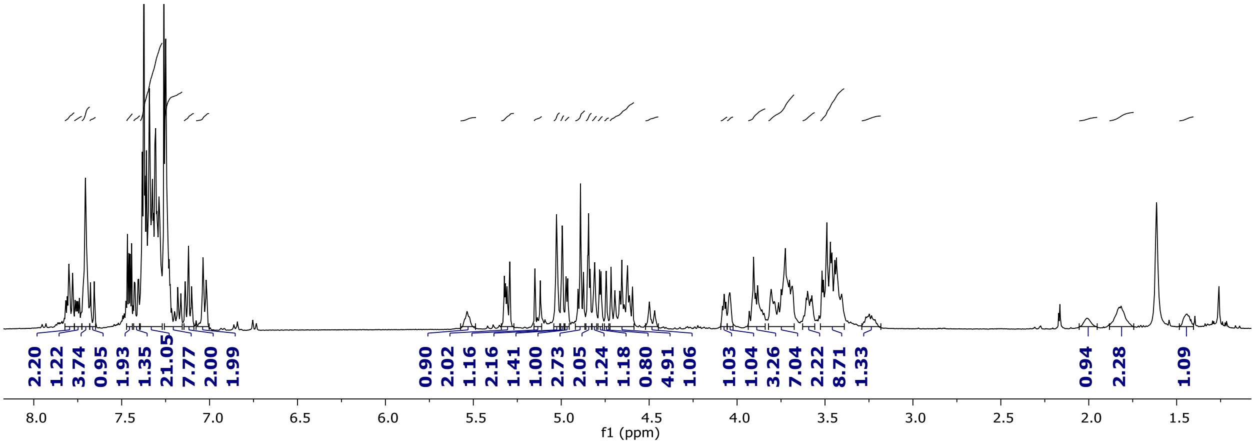

0.90
4.77
0.98
0.81
3.94
1.21
13.83
2.75
1.95
1.75
1.00
0.81
1.21
3.38
3.83
1.12
4.34
1.14
1.27
1.16
4.78
0.97
2.04
3.47
2.92
11.06
1.36
1.37
1.98
6.02
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f1 (ppm)

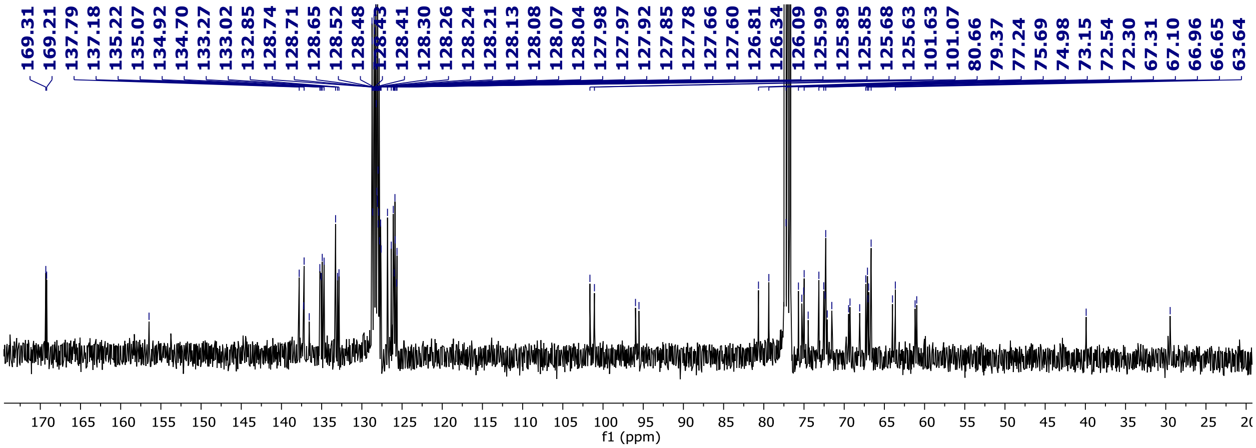

169.88
167.96
137.84
136.61
135.58
133.28
133.22
132.99
132.95
128.67
128.56
128.51
128.48
128.46
128.39
128.21
128.09
128.04
128.01
127.97
127.74
127.69
127.28
126.70
126.52
126.41
126.35
126.21
125.86
98.80
98.69
97.72
96.52
79.65
79.29
78.81
77.97
77.26
76.64
75.08
74.77
72.48
72.22
72.02
71.89
69.41
69.34
68.53
66.62
61.28
52.73
52.32
29.71
29.52
23.03
22.92
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
f1 (ppm)

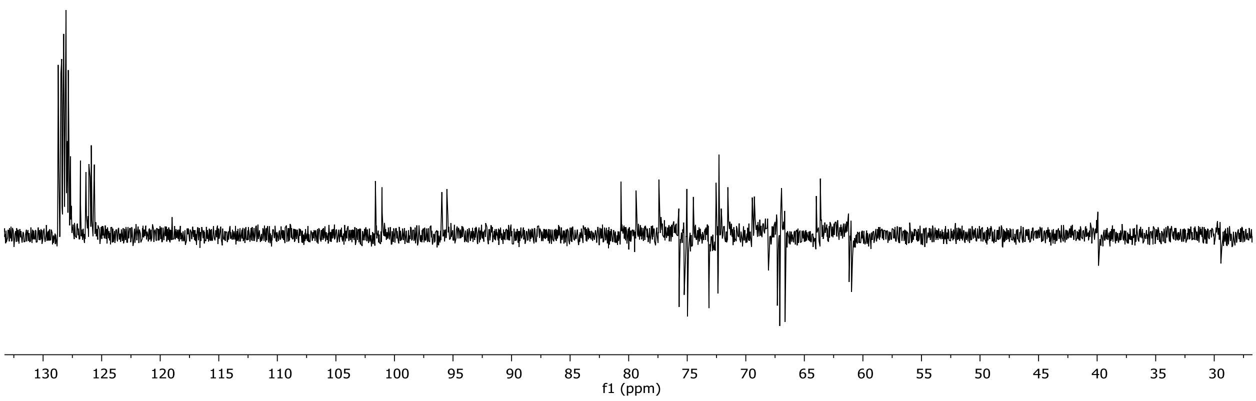

160
150
140
130
120
110
100
90
80
70
60
50
f1 (ppm)

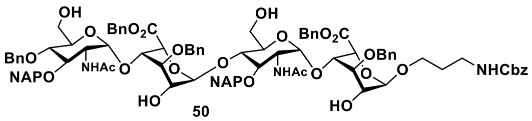

OH
BnO2C
OBn
BnO
NAPO
N3
O
HO
NHCbz

45

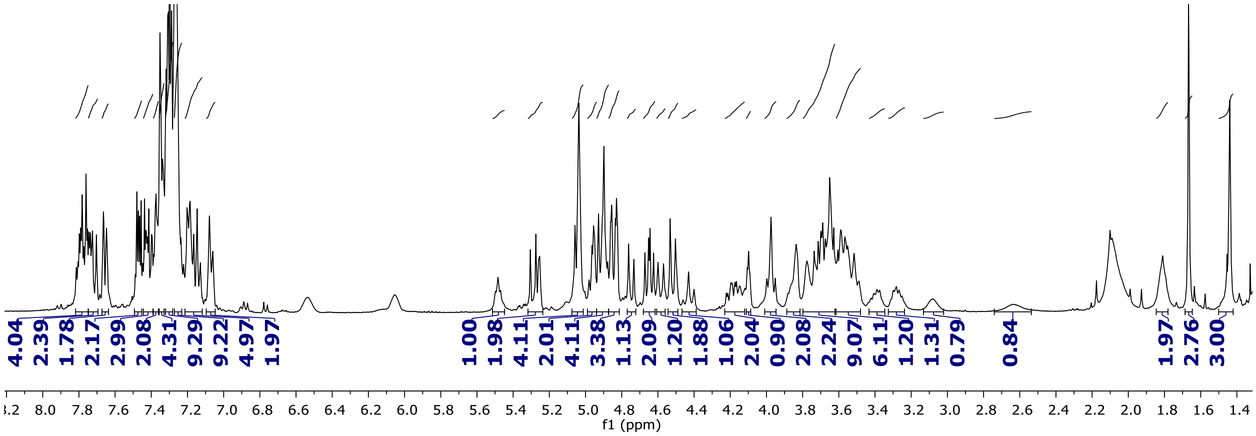

2.20
1.22
3.74
0.95
1.93
1.35
21.05
7.77
2.00
1.99
0.90
2.02
1.16
2.16
1.41
1.00
2.73
2.05
1.24
1.18
0.80
4.91
1.06
1.03
1.04
3.26
7.04
2.22
8.71
1.33
0.94
2.28
1.09
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

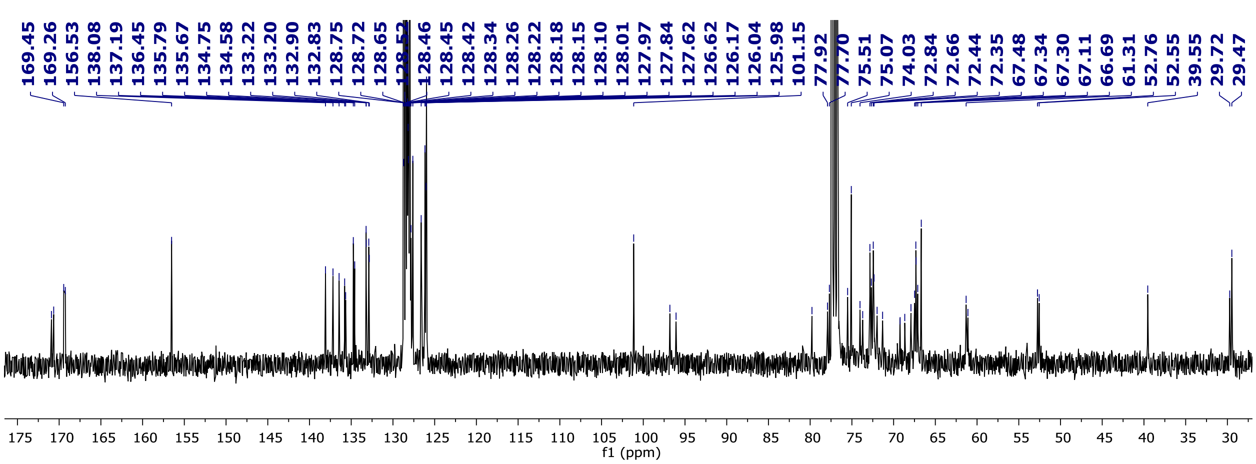

169.31
169.21
137.79
137.18
135.22
135.07
134.92
134.70
133.27
133.02
132.85
128.74
128.71
128.65
128.52
128.48
128.43
128.41
128.30
128.26
128.24
128.21
128.13
128.08
128.07
128.04
127.98
127.97
127.92
127.85
127.78
127.66
127.60
126.81
126.34
126.09
125.99
125.89
125.85
125.68
125.63
101.63
101.07
80.66
79.37
77.24
75.69
74.98
73.15
72.54
72.30
67.31
67.10
66.96
66.65
63.64
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
f1 (ppm)

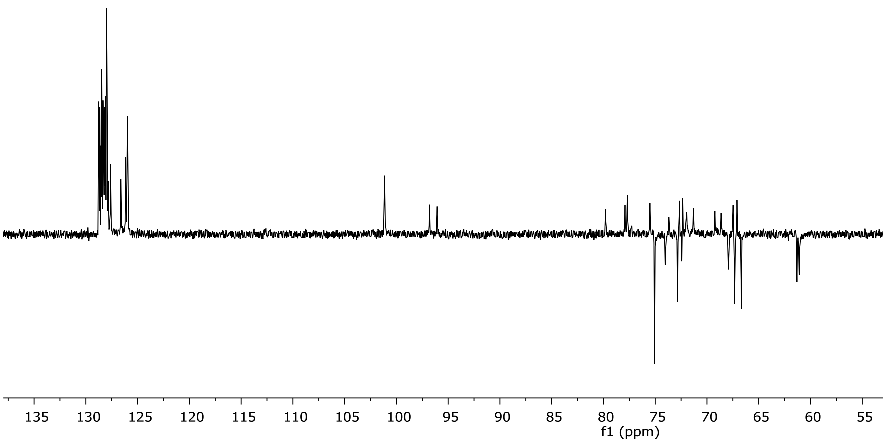

130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
f1 (ppm)

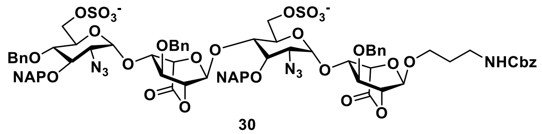

OH
BnO2C
OBn
BnO
NAPO
NHAc
O
HO
OH
BnO2C
OBn
NAPO
NHAc
HO
NHCbz

50

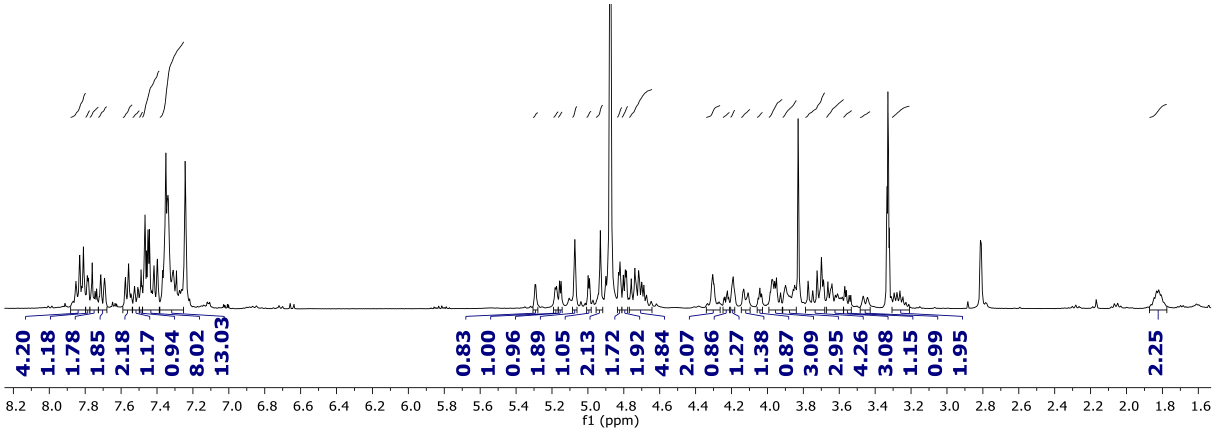

4.04
2.39
1.78
2.17
2.99
2.08
4.31
9.29
9.22
4.97
1.97
1.00
1.98
4.11
2.01
4.11
3.38
1.13
2.09
1.20
1.88
1.06
2.04
0.90
2.08
2.24
9.07
6.11
1.20
1.31
0.79
0.84
1.97
2.76
3.00
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
f1 (ppm)

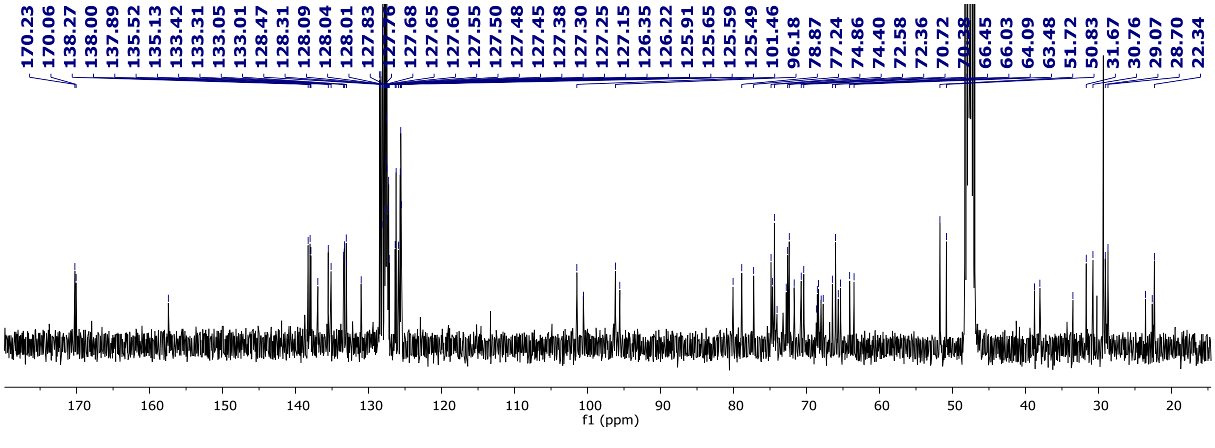

169.45
169.26
156.53
138.08
137.19
136.45
135.79
135.67
134.75
134.58
133.22
133.20
132.90
132.83
128.75
128.72
128.65
128.52
128.46
128.45
128.42
128.34
128.26
128.22
128.18
128.15
128.10
128.01
127.97
127.84
127.62
126.62
126.17
126.04
125.98
101.15
77.92
77.70
75.51
75.07
74.03
72.84
72.66
72.44
72.35
67.48
67.34
67.30
67.11
66.69
61.31
52.76
52.55
39.55
29.72
29.47
175
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
f1 (ppm)

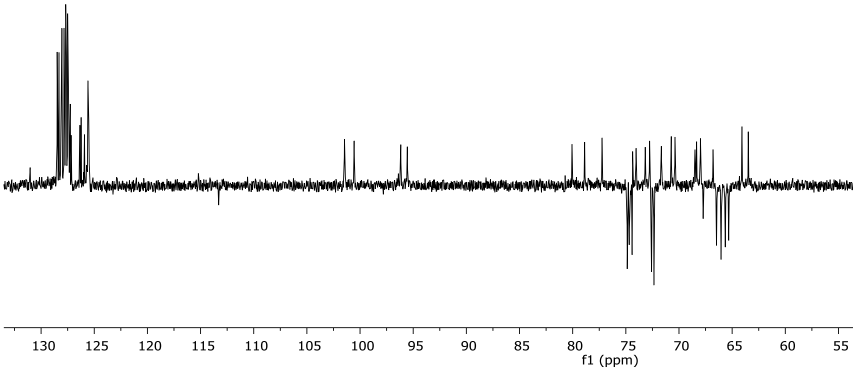

135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
f1 (ppm)


OSO3-
BnO
NAPO
N3
O
OBn
OSO3-
NAPO
N3
OBn
NHCbz
O

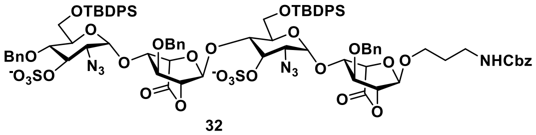
30


4.20
1.18
1.78
1.85
2.18
1.17
0.94
8.02
13.03
0.83
1.00
0.96
1.89
1.05
2.13
1.72
1.92
4.84
2.07
0.86
1.27
1.38
0.87
3.09
2.95
4.26
3.08
1.15
0.99
1.95
2.25
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
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
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f1 (ppm)


170.23
170.06
138.27
138.00
137.89
135.52
135.13
133.42
133.31
133.05
133.01
128.47
128.31
128.09
128.04
128.01
127.83
127.76
127.68
127.65
127.60
127.55
127.50
127.48
127.45
127.38
127.30
127.25
127.15
126.35
126.22
125.91
125.65
125.59
125.49
101.46
96.18
78.87
77.24
74.86
74.40
72.58
72.36
70.72
70.38
66.45
66.03
64.09
63.48
51.72
50.83
31.67
30.76
29.07
28.70
22.34
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

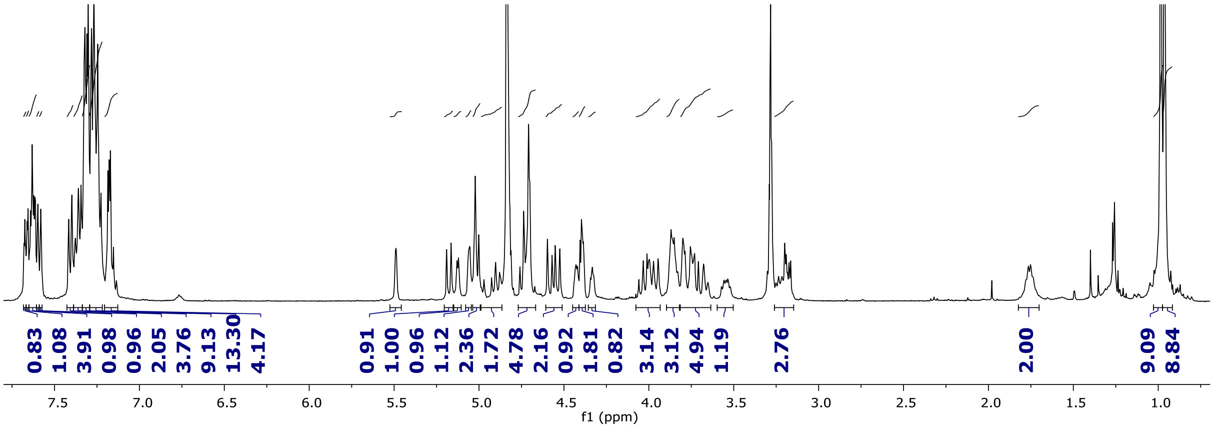


130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
f1 (ppm)

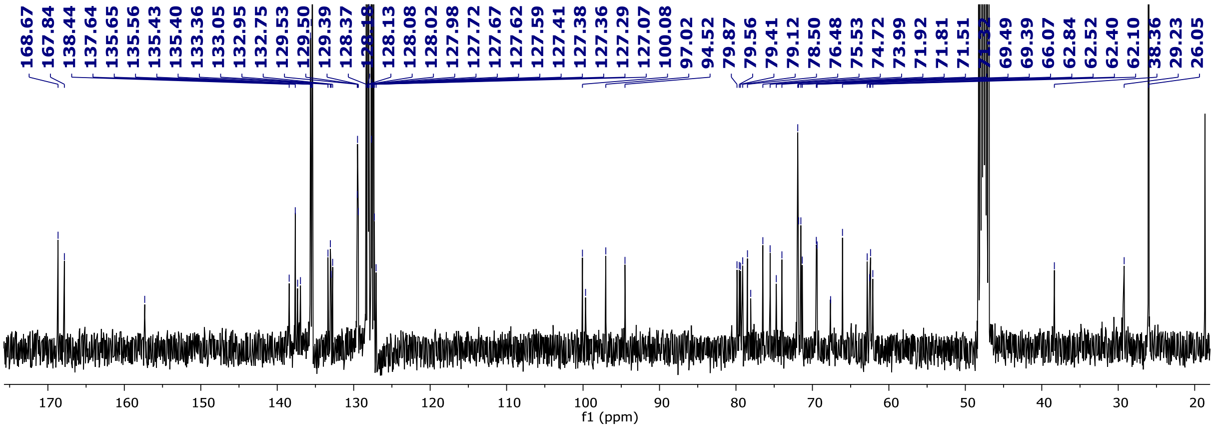


OTBDPS
BnO
-O3SO
N3
OBn
O
OTBDPS
-O3SO
N3
OBn
NHCbz

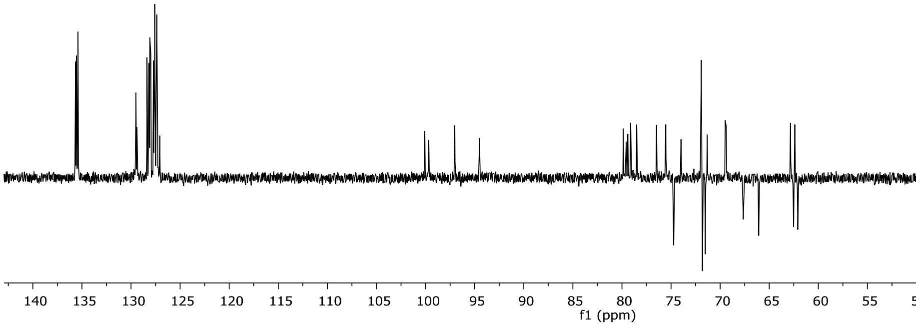
32

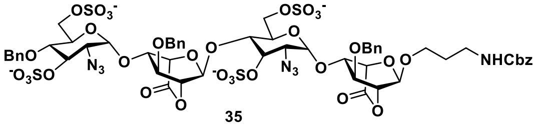


0.83
1.08
3.91
0.98
0.96
2.05
3.76
9.13
13.30
4.17
0.91
1.00
0.96
1.12
2.36
1.72
4.78
2.16
0.92
1.81
0.82
3.14
3.12
4.94
1.19
2.76
2.00
9.09
8.84
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

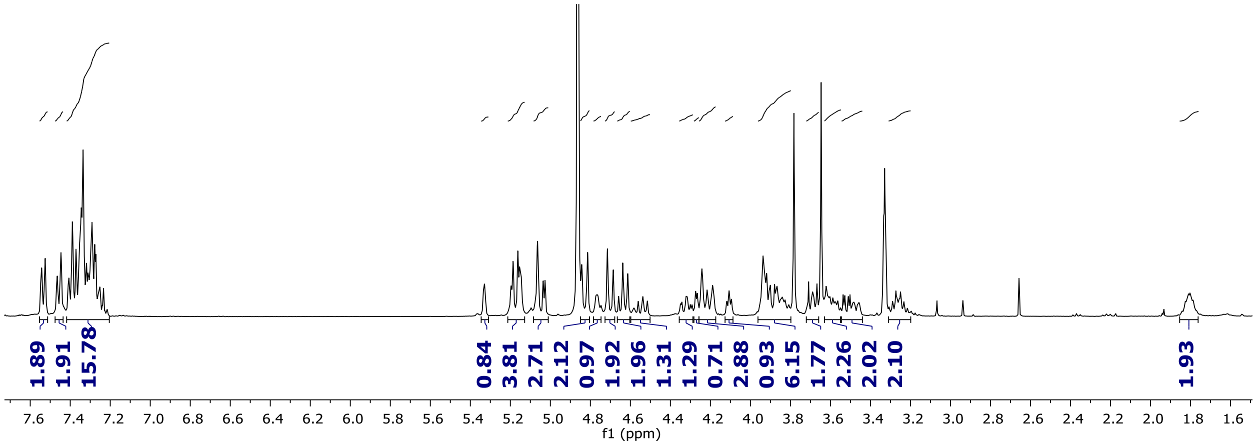


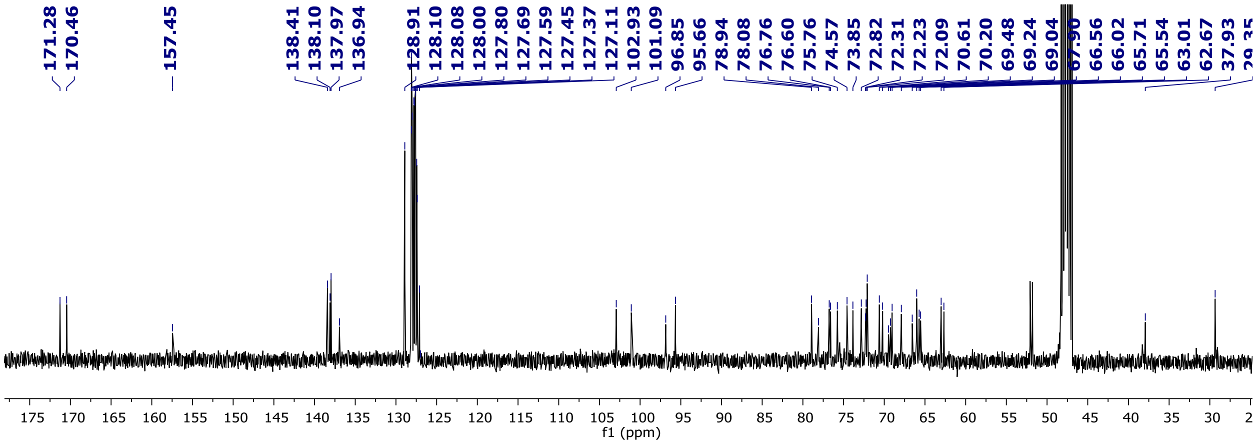
168.67
167.84
138.44
137.64
135.65
135.56
135.43
135.40
133.36
133.05
132.95
132.75
129.53
129.50
129.39
128.37
128.18
128.13
128.08
128.02
127.98
127.72
127.67
127.62
127.59
127.41
127.38
127.36
127.29
127.07
100.08
97.02
94.52
79.87
79.56
79.41
79.12
78.50
76.48
75.53
74.72
73.99
71.92
71.81
71.51
71.32
69.49
69.39
66.07
62.84
62.52
62.40
62.10
38.36
29.23
26.05
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

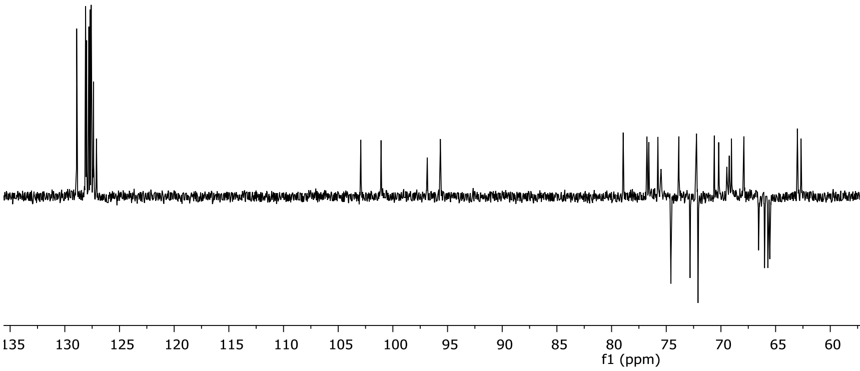

140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
f1 (ppm)

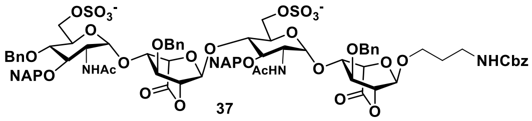

OSO3-
BnO
-O3SO
N3
OBn
O
-O3SO
OSO3-
N3
OBn
NHCbz

35

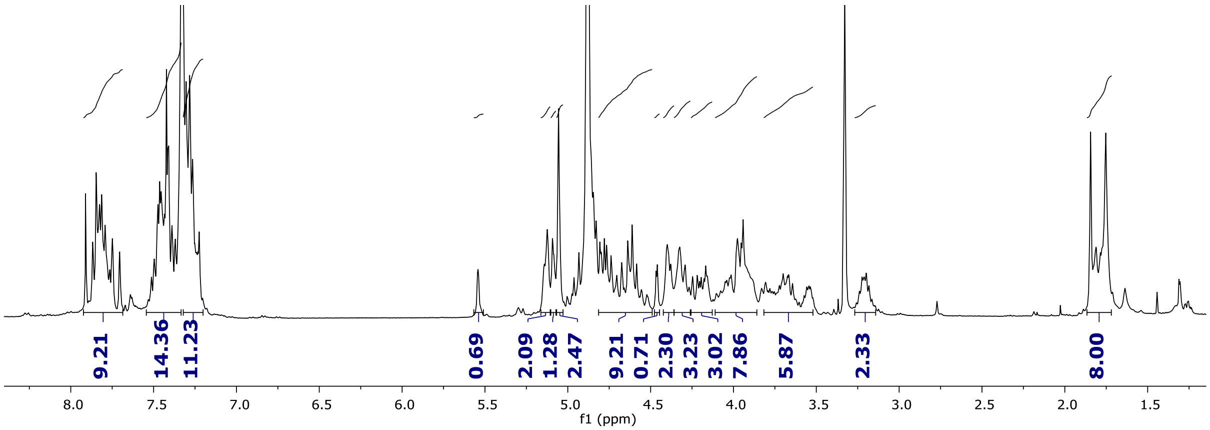

1.89
1.91
15.78
0.84
3.81
2.71
2.12
0.97
1.92
1.96
1.31
1.29
0.71
2.88
0.93
6.15
1.77
2.26
2.02
2.10
1.93
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f1 (ppm)

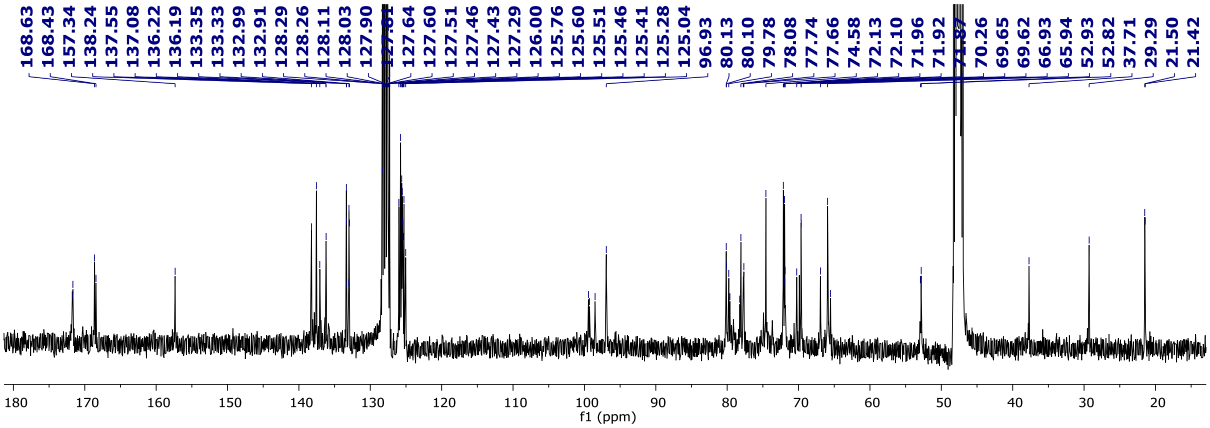

171.28
170.46
157.45
138.41
138.10
137.97
136.94
128.91
128.10
128.08
128.00
127.80
127.69
127.59
127.45
127.37
127.11
102.93
101.09
96.85
95.66
78.94
78.08
76.76
76.60
75.76
74.57
73.85
72.82
72.31
72.23
72.09
70.61
70.20
69.48
69.24
69.04
67.90
66.56
66.02
65.71
65.54
63.01
62.67
37.93
175
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
f1 (ppm)

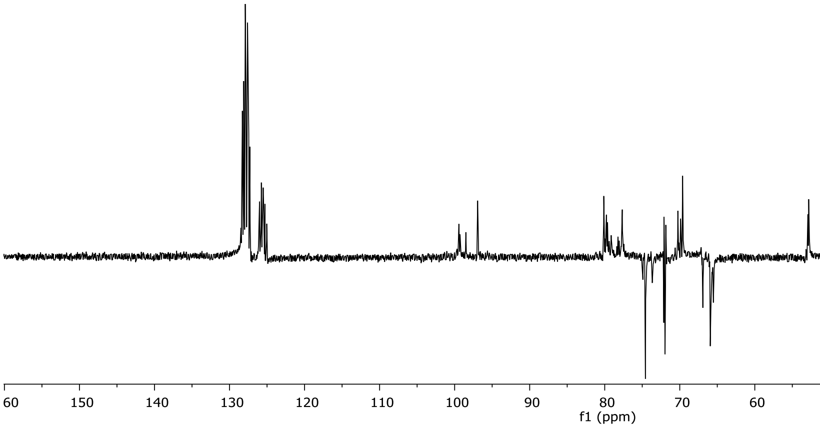

135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
f1 (ppm)


OSO3-
BnO
NAPO
NHAc
O
OBn
O
NAPO
AcHN
OSO3-
OBn
O
NHCbz

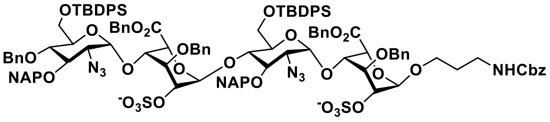
37


9.21
14.36
11.23
0.69
2.09
1.28
2.47
9.21
0.71
2.30
3.23
3.02
7.86
5.87
2.33
8.00
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
f1 (ppm)


168.63
168.43
157.34
138.24
137.55
137.08
136.22
136.19
133.35
133.33
132.99
132.91
128.29
128.26
128.11
128.03
127.90
127.81
127.64
127.60
127.51
127.46
127.43
127.29
126.00
125.76
125.60
125.51
125.46
125.41
125.28
125.04
96.93
80.13
80.10
79.78
78.08
77.74
77.66
74.58
72.13
72.10
71.96
71.92
71.87
70.26
69.65
69.62
66.93
65.94
52.93
52.82
37.71
29.29
21.50
21.42
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

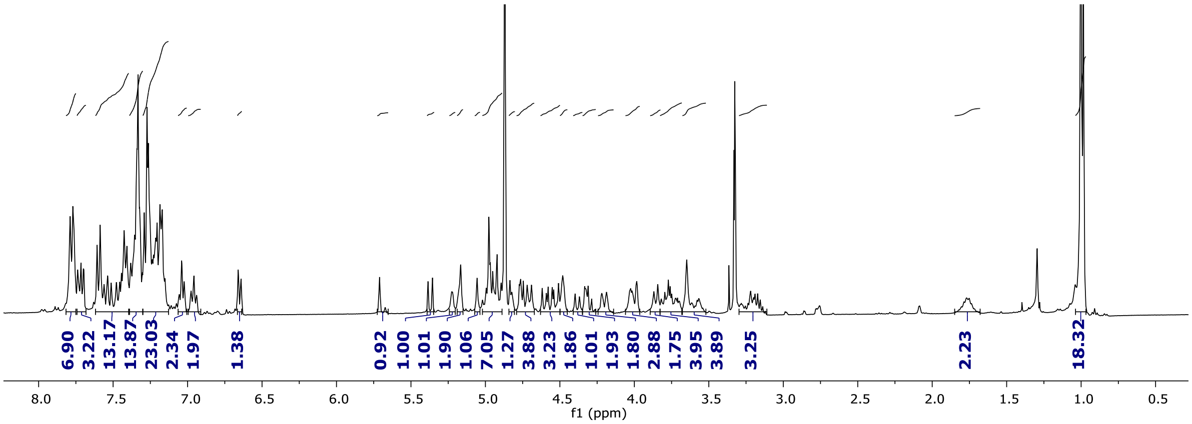


60
150
140
130
120
110
100
90
80
70
60
f1 (ppm)

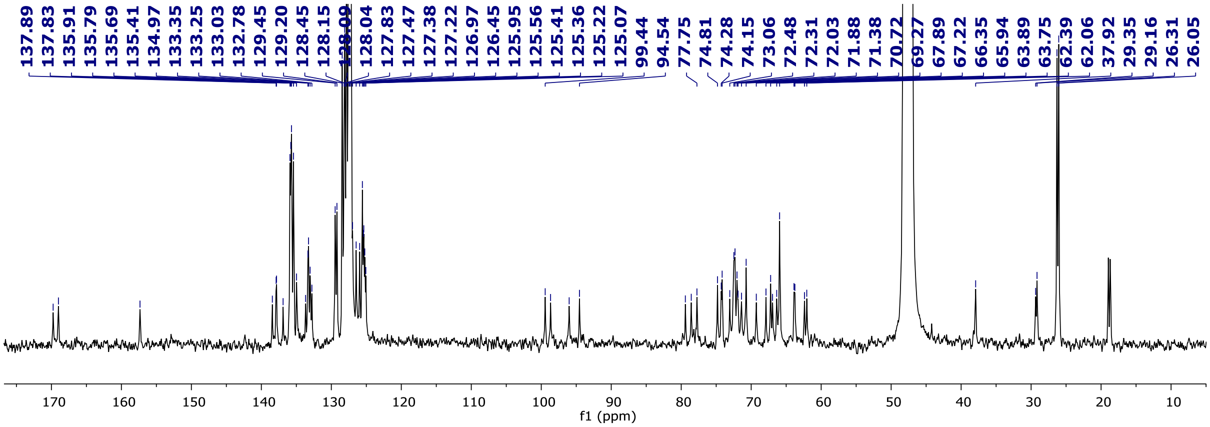


OTBDPS
BnO
NAPO
N3
BnO2C
OBn
-O3SO
OTBDPS
NAPO
N3
BnO2C
OBn
-O3SO
NHCbz

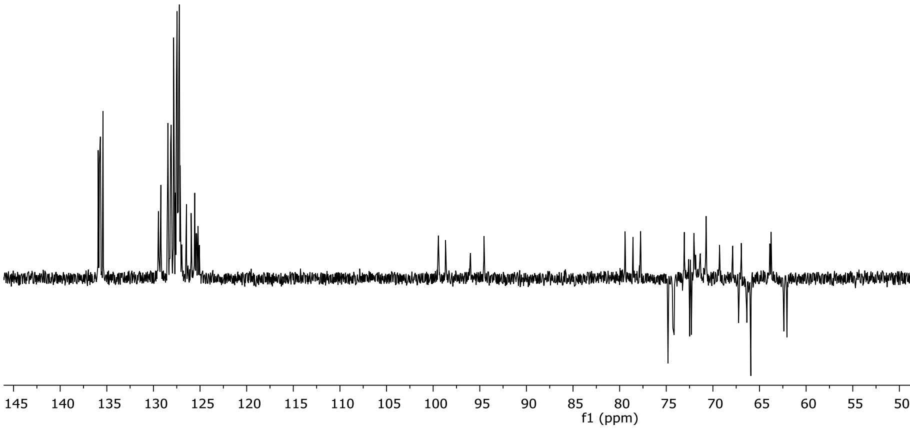
40

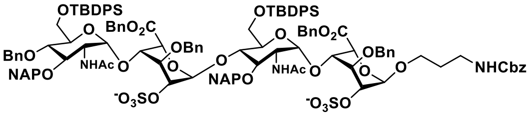


6.90
3.22
13.17
13.87
23.03
2.34
1.97
1.38
0.92
1.00
1.01
1.90
1.06
7.05
1.27
3.88
3.23
1.86
1.01
1.93
1.80
2.88
1.75
3.95
3.89
3.25
2.23
18.32
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

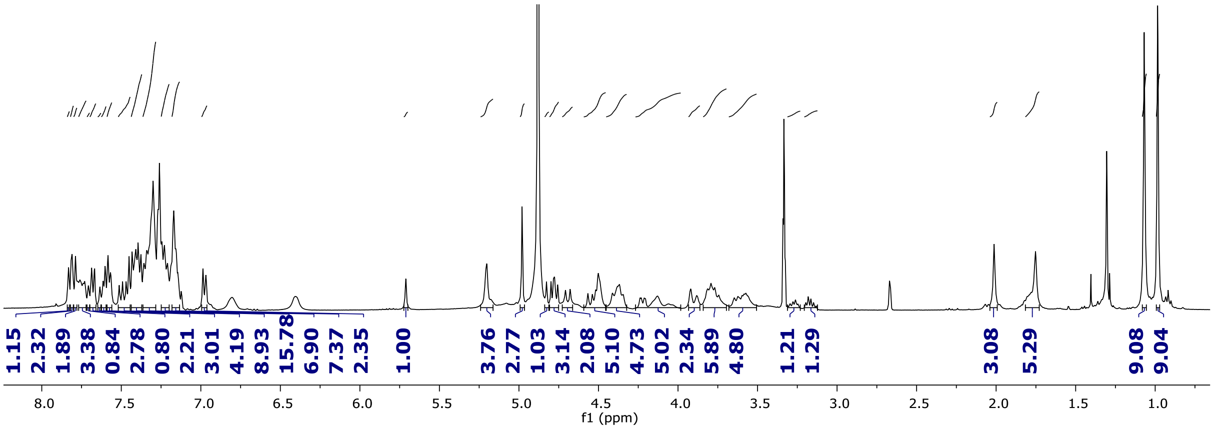


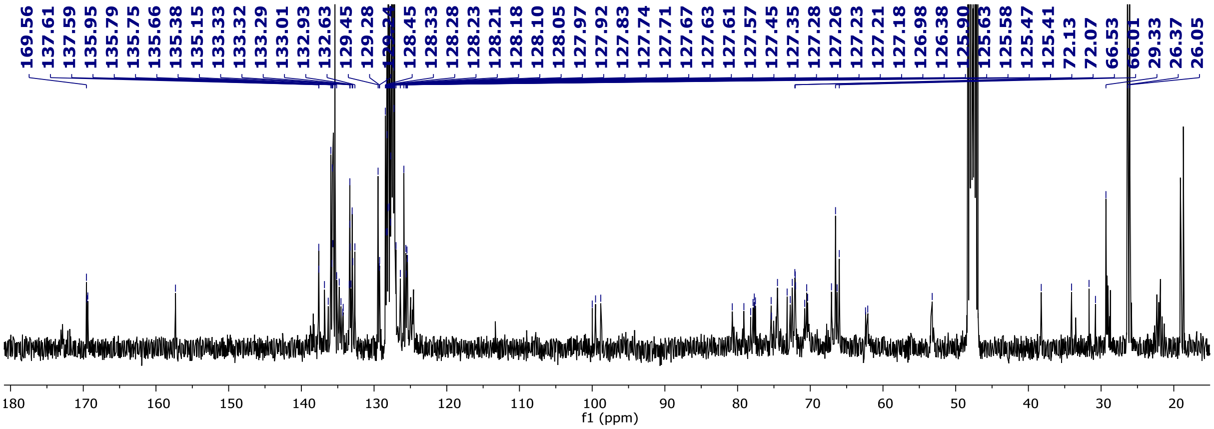
137.89
137.83
135.91
135.79
135.69
135.41
134.97
133.35
133.25
133.03
132.78
129.45
129.20
128.45
128.15
128.09
128.04
127.83
127.47
127.38
127.22
126.97
126.45
125.95
125.56
125.41
125.36
125.22
125.07
99.44
94.54
77.75
74.81
74.28
74.15
73.06
72.48
72.31
72.03
71.88
71.38
70.72
69.27
67.89
67.22
66.35
65.94
63.89
63.75
62.39
62.06
37.92
29.35
29.16
26.31
26.05
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

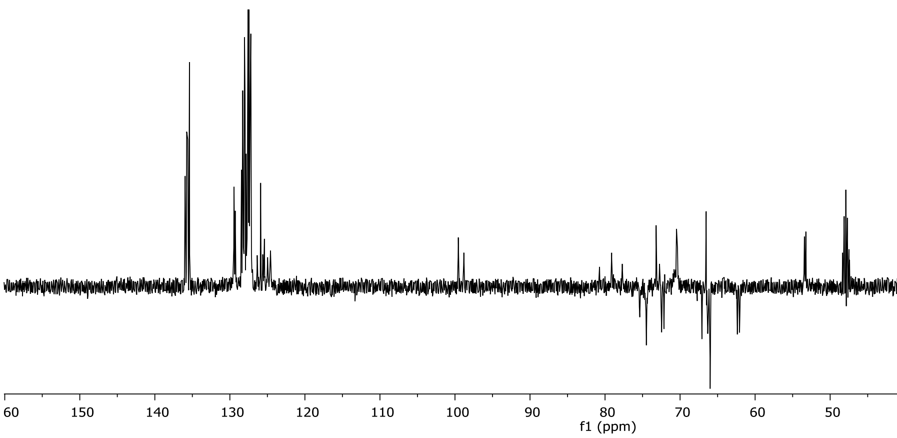

145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
f1 (ppm)


OTBDPS
BnO₂C
OBn
BnO
NAPO
NHAc
O
⁻O₃SO
NAPO
NHAc
OTBDPS
BnO₂C
OBn
⁻O₃SO
NHCbz

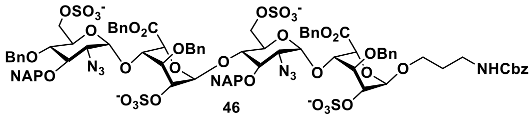
43


1.15
2.32
1.89
3.38
0.84
2.78
0.80
2.21
3.01
4.19
8.93
15.78
6.90
7.37
2.35
1.00
3.76
2.77
1.03
3.14
2.08
5.10
4.73
5.02
2.34
5.89
4.80
1.21
1.29
3.08
5.29
9.08
9.04
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
f1 (ppm)


169.56
137.61
137.59
135.95
135.79
135.75
135.66
135.38
135.15
133.33
133.32
133.29
133.01
132.93
132.63
129.45
129.28
129.24
128.45
128.33
128.28
128.23
128.21
128.18
128.10
128.05
127.97
127.92
127.83
127.74
127.71
127.67
127.63
127.61
127.57
127.45
127.35
127.28
127.26
127.23
127.21
127.18
126.98
126.38
125.90
125.63
125.58
125.47
125.41
72.13
72.07
66.53
66.01
29.33
26.37
26.05
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

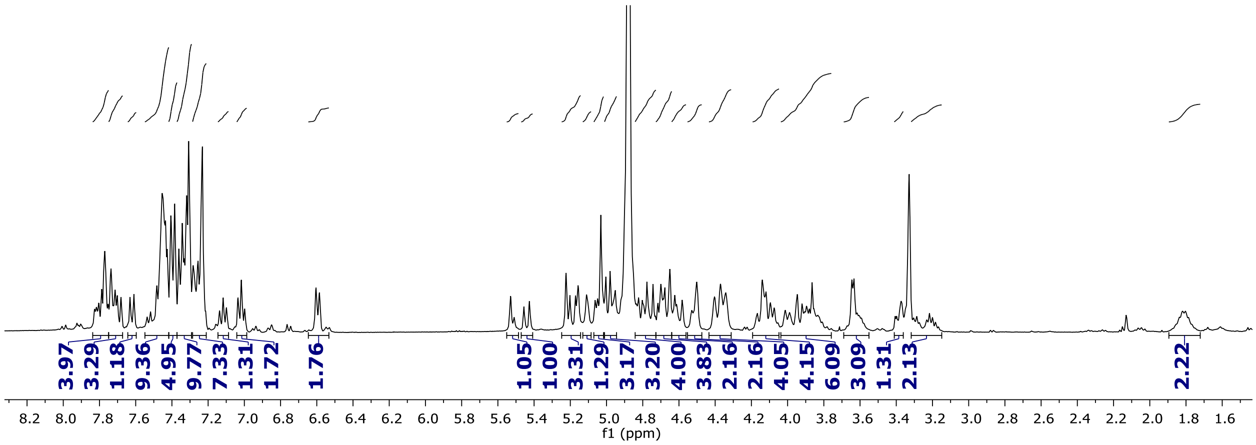


60
150
140
130
120
110
100
90
80
70
60
50
f1 (ppm)

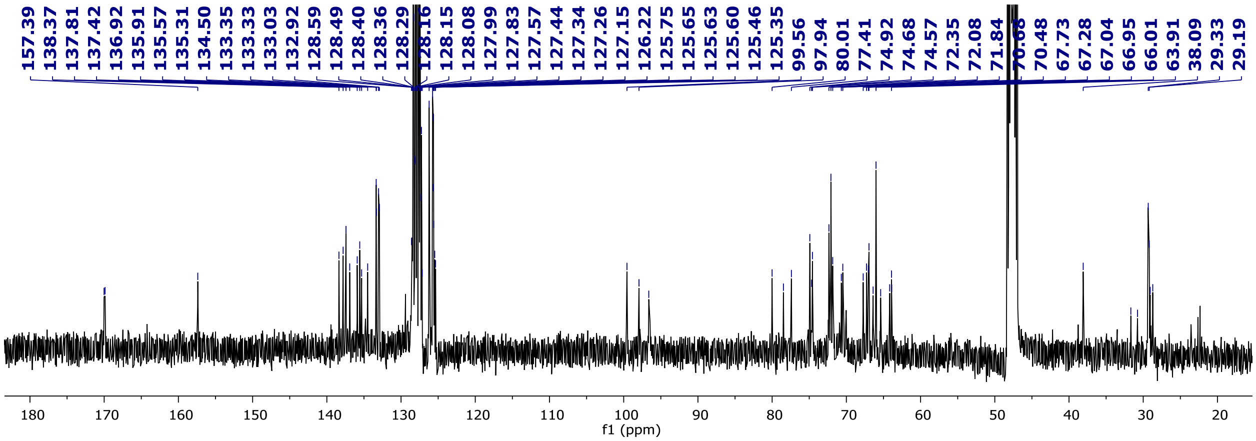


OSO$_3^-$
BnO$_2$C
OBn
BnO
NAPO
N$_3$
O
$^-$O$_3$SO
OSO$_3^-$
BnO$_2$C
OBn
NAPO
N$_3$
$^-$O$_3$SO
NHCbz

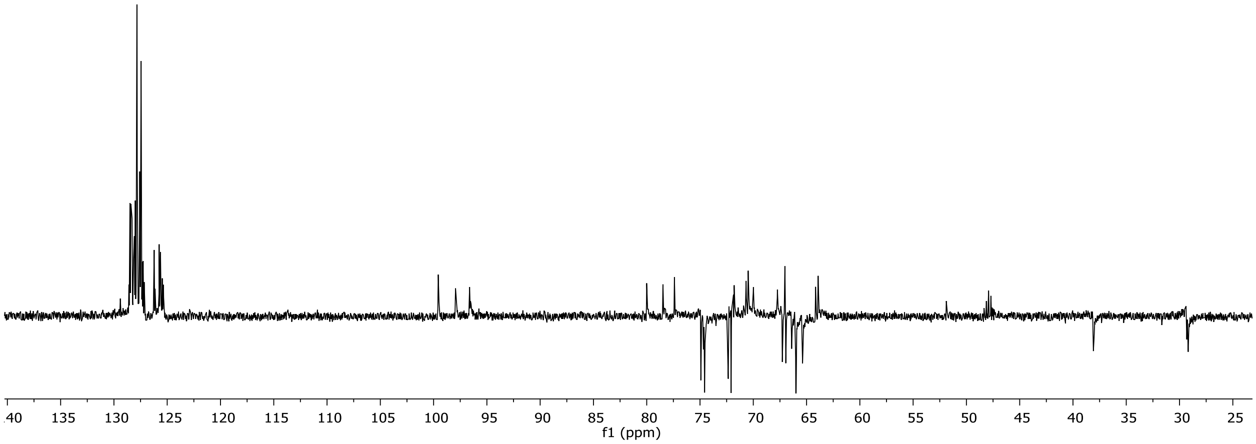
46

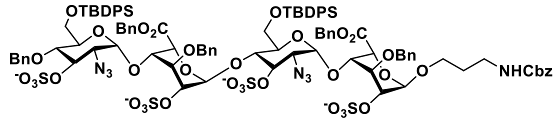


3.97
3.29
1.18
9.36
4.95
9.77
7.33
1.31
1.72
1.76
1.05
1.00
3.31
1.29
3.17
3.20
4.00
3.83
2.16
4.05
4.15
6.09
3.09
1.31
2.13
2.22
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f1 (ppm)

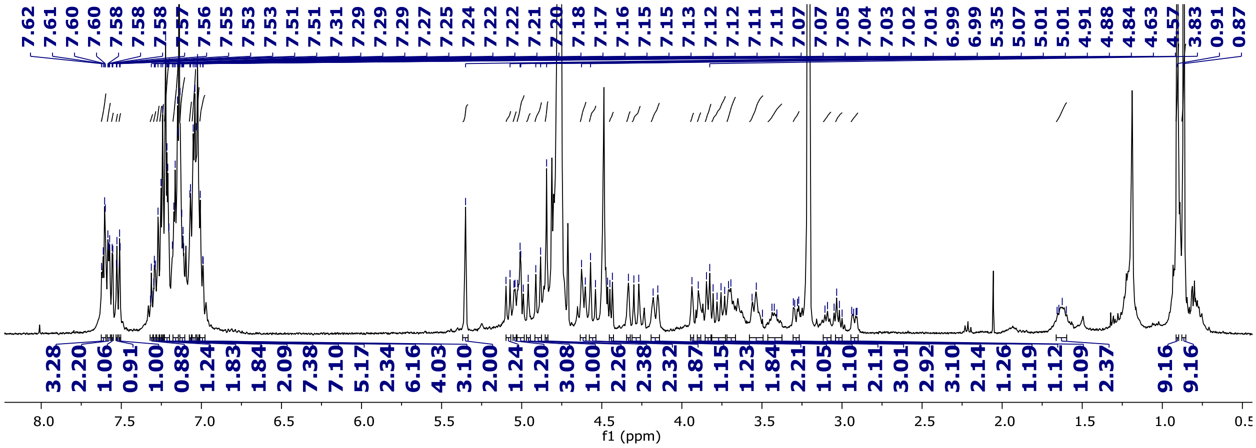


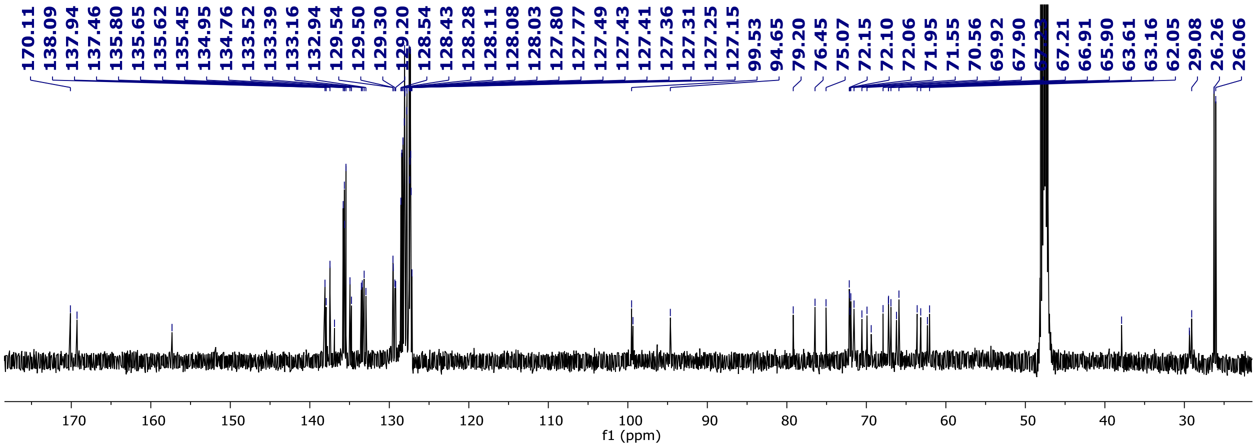
157.39
138.37
137.81
137.42
136.92
135.91
135.57
135.31
134.50
133.35
133.33
133.03
132.92
128.59
128.49
128.40
128.36
128.29
128.16
128.15
128.08
127.99
127.83
127.57
127.44
127.34
127.26
127.15
126.22
125.75
125.65
125.63
125.60
125.46
125.35
99.56
97.94
80.01
77.41
74.92
74.68
74.57
72.35
72.08
71.84
70.68
70.48
67.73
67.28
67.04
66.95
66.01
63.91
38.09
29.33
29.19
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

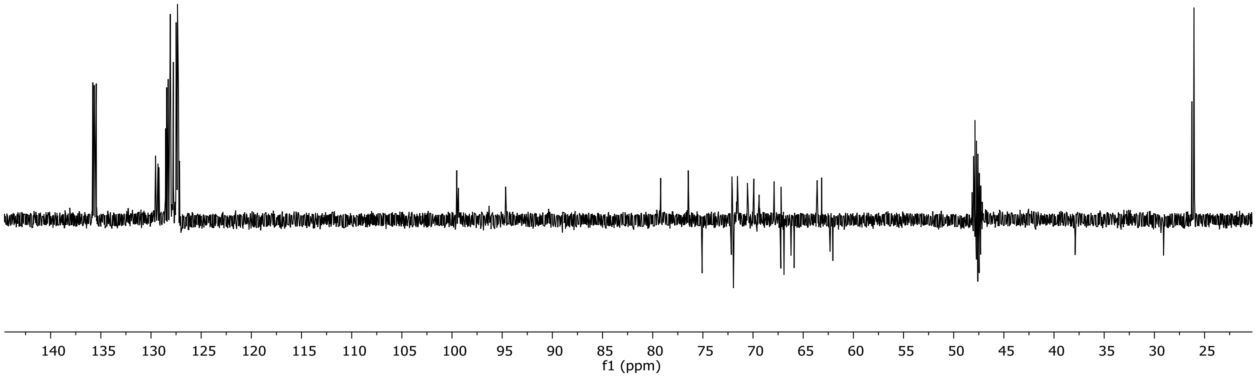

140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
f1 (ppm)

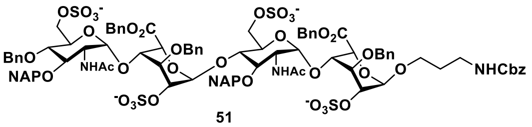

OTBDPS
BnO₂C
OBn
BnO
-O₃SO
N₃
O
-O₃SO
OTBDPS
BnO₂C
OBn
-O₃SO
N₃
-O₃SO
NHCbz

48

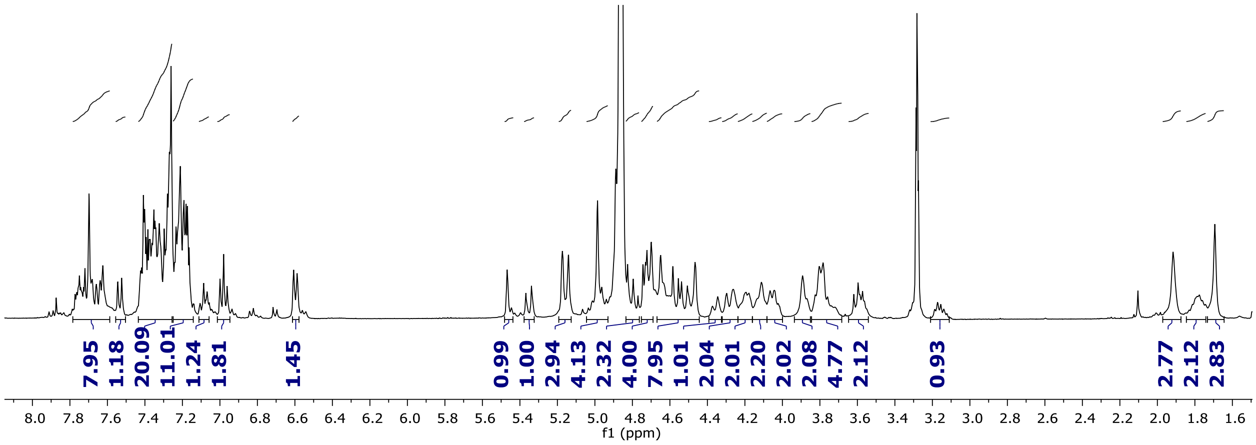

7.62
7.61
7.60
7.60
7.58
7.58
7.57
7.56
7.55
7.53
7.53
7.51
7.51
7.31
7.29
7.29
7.27
7.25
7.24
7.22
7.21
7.21
7.20
7.18
7.17
7.16
7.15
7.15
7.13
7.12
7.12
7.11
7.11
7.07
7.07
7.05
7.04
7.03
7.02
7.01
6.99
6.99
5.35
5.07
5.01
5.01
4.91
4.88
4.84
4.63
4.57
3.83
0.91
0.87
3.28
2.20
1.06
0.91
1.00
0.88
1.24
1.83
1.84
2.09
7.38
7.10
5.17
2.34
6.16
4.03
3.10
2.00
1.24
1.20
3.08
1.00
2.26
2.38
2.32
1.87
1.15
1.23
1.84
2.21
1.05
1.10
2.11
3.01
2.92
3.10
2.14
1.26
1.19
1.12
1.09
2.37
9.16
9.16
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
f1 (ppm)

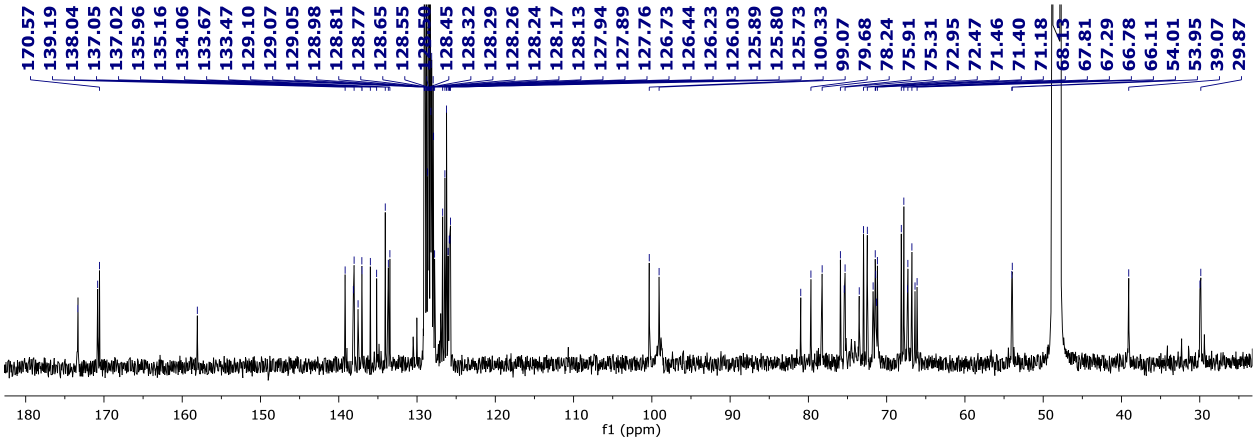

170.11
138.09
137.94
137.46
135.80
135.65
135.62
135.45
134.95
134.76
133.52
133.39
133.16
132.94
129.54
129.50
129.30
129.20
128.54
128.43
128.28
128.11
128.08
128.03
127.80
127.77
127.49
127.43
127.41
127.36
127.31
127.25
127.15
99.53
94.65
79.20
76.45
75.07
72.15
72.10
72.06
71.95
71.55
70.56
69.92
67.90
67.23
67.21
66.91
65.90
63.61
63.16
62.05
29.08
26.26
26.06
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)


140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
f1 (ppm)

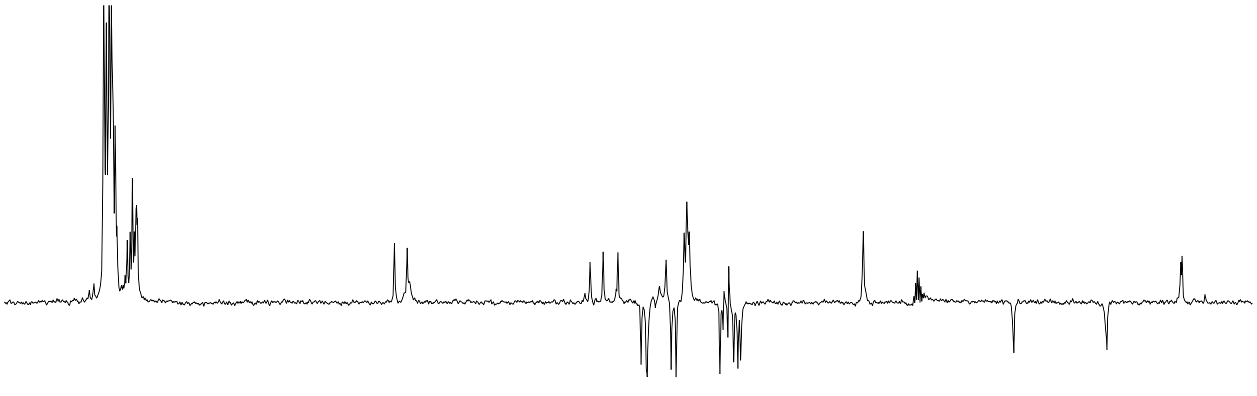

OSO$_3^-$
BnO$_2$C
OBn
BnO
NAPO
NHAc
$^-$O$_3$SO
NAPO
NHAc
NHCbz

51

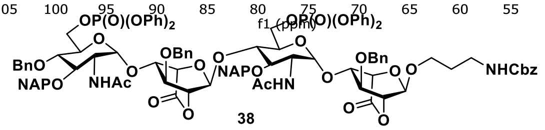

7.95
1.18
20.09
11.01
1.24
1.81
1.45
0.99
1.00
2.94
4.13
2.32
4.00
7.95
1.01
2.04
2.01
2.20
2.02
2.08
4.77
2.12
0.93
2.77
2.12
2.83
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f1 (ppm)



170.57
139.19
138.04
137.05
137.02
135.96
135.16
134.06
133.67
133.47
129.10
129.07
129.05
128.98
128.81
128.77
128.65
128.55
128.45
128.32
128.29
128.26
128.24
128.17
128.13
127.94
127.89
127.76
126.73
126.44
126.23
126.03
125.89
125.80
125.73
100.33
99.07
79.68
78.24
75.91
75.31
72.95
72.47
71.46
71.40
71.18
68.13
67.81
67.29
66.78
66.11
54.01
53.95
39.07
29.87
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)

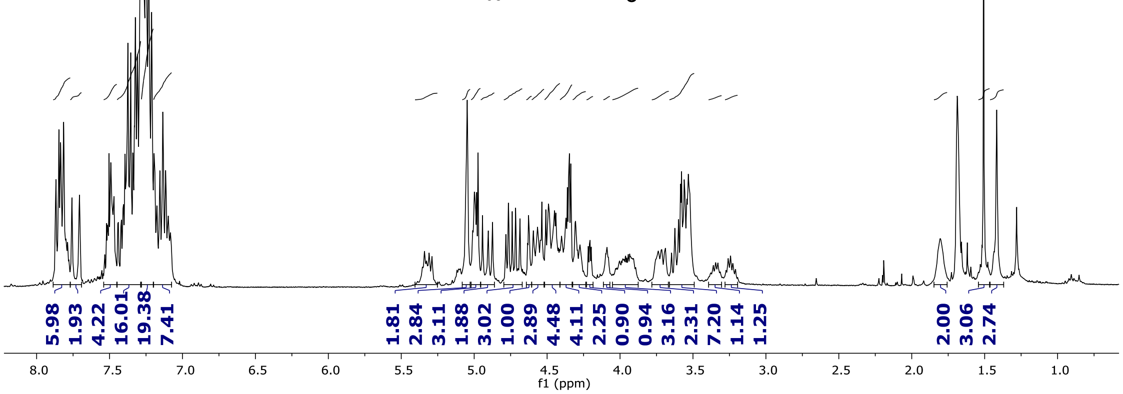


135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
f1 (ppm)

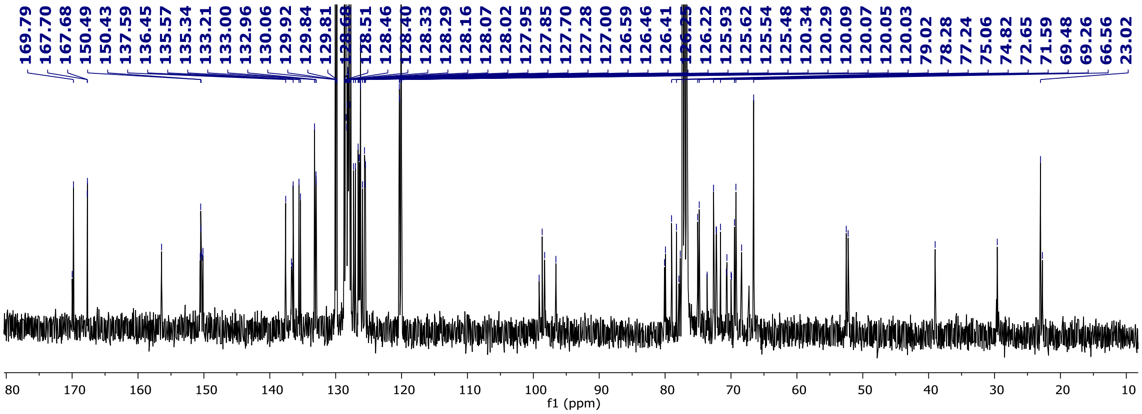


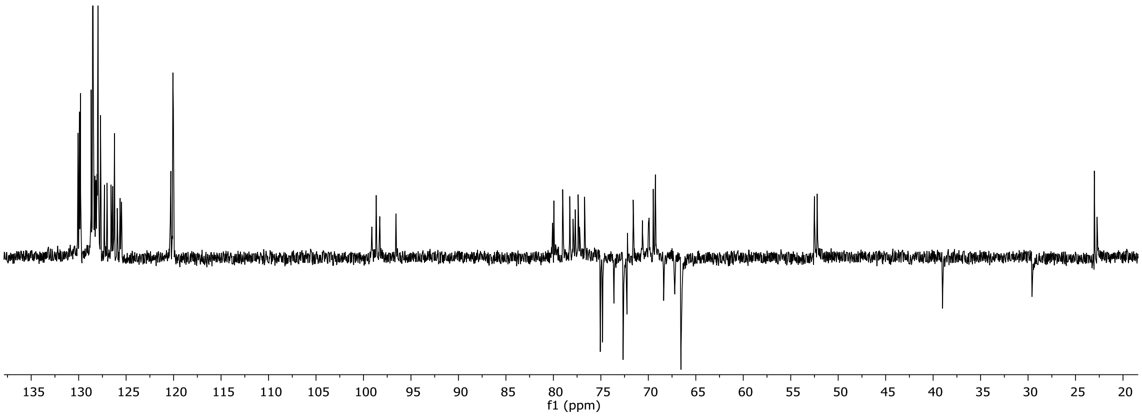
OP(O)(OPh)2
BnO
NAPO
NHAc
OBn
O
NAPO
AcHN
OP(O)(OPh)2
OBn
NHCbz

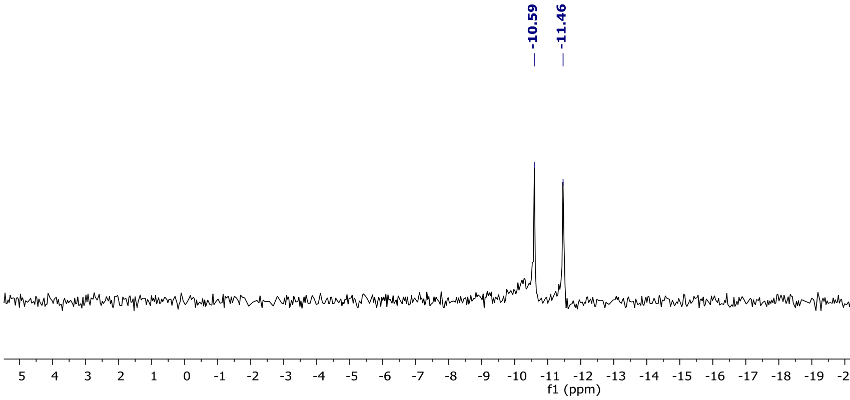
38

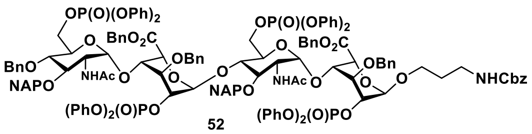


5.98
1.93
4.22
16.01
19.38
7.41
1.81
2.84
3.11
1.88
3.02
1.00
2.89
4.48
4.11
2.25
0.90
0.94
3.16
2.31
7.20
1.14
1.25
2.00
3.06
2.74
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

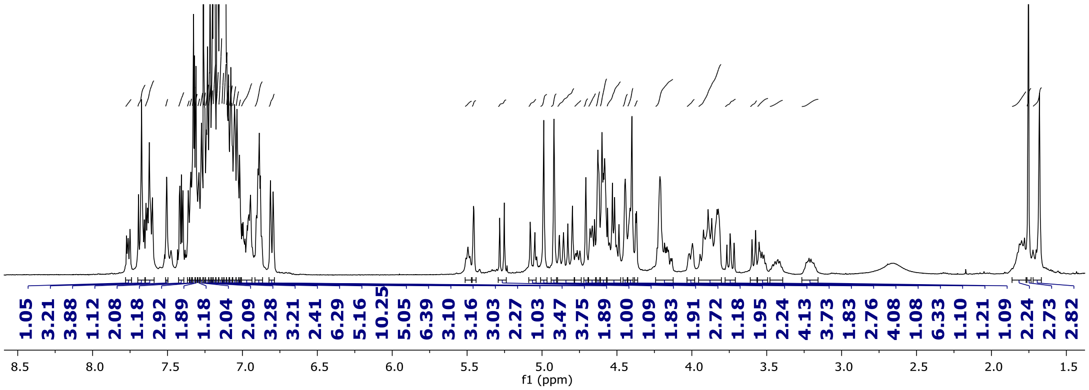

169.79
167.70
167.68
150.49
150.43
137.59
136.45
135.57
135.34
133.21
133.00
132.96
130.06
129.92
129.84
129.81
128.68
128.51
128.46
128.40
128.33
128.29
128.16
128.07
128.02
127.95
127.85
127.70
127.28
127.00
126.59
126.46
126.41
126.25
126.22
125.93
125.62
125.54
125.48
120.34
120.29
120.09
120.07
120.05
120.03
79.02
78.28
77.24
75.06
74.82
72.65
71.59
69.48
69.26
66.56
23.02
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

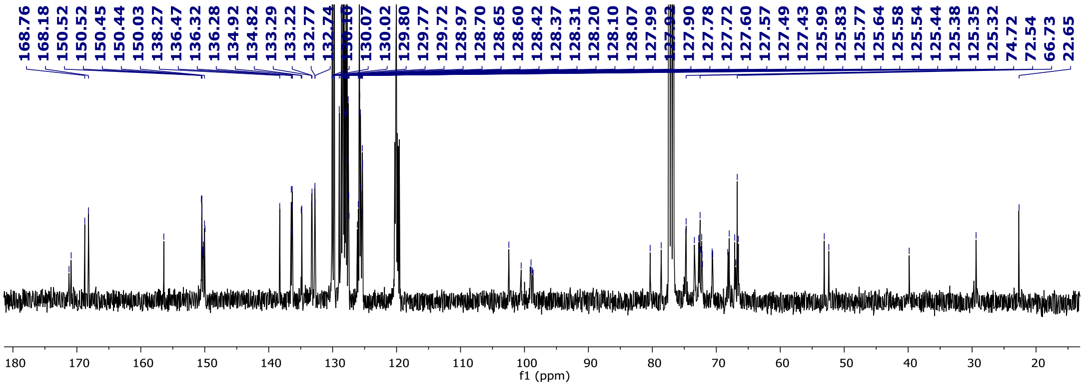

135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)

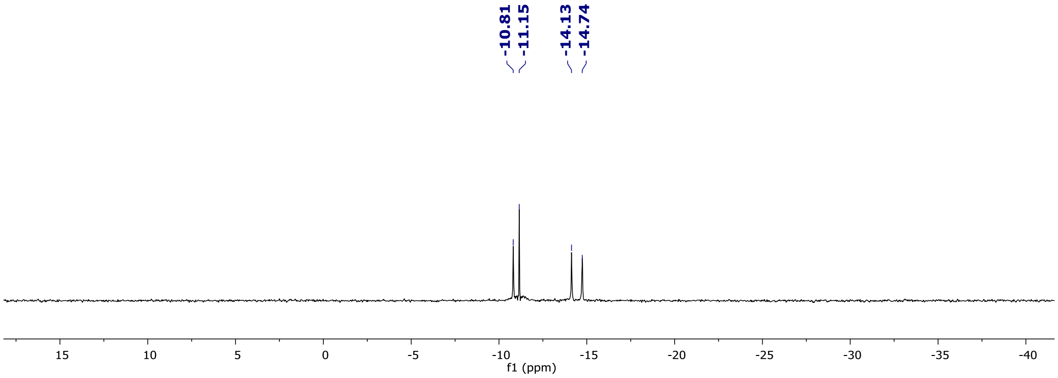

-10.59
-11.46
5 4 3 2 1 0 -1 -2 -3 -4 -5 -6 -7 -8 -9 -10 -11 -12 -13 -14 -15 -16 -17 -18 -19 -2
f1 (ppm)

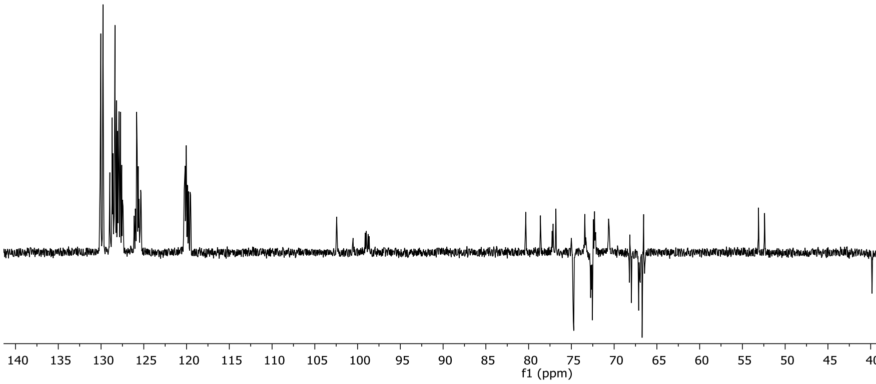

OP(O)(OPh)2
BnO2C
OBn
BnO
NAPO
NHAc
O
(PhO)2(O)PO
NHCbz

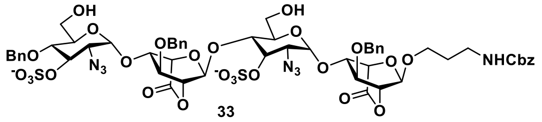
52


1.05
3.21
3.88
1.12
2.08
1.18
2.92
1.89
1.18
2.04
2.09
3.28
3.21
2.41
6.29
5.16
10.25
5.05
6.39
3.10
3.16
3.03
2.27
1.03
3.47
3.75
1.89
1.00
1.09
1.83
1.91
2.72
1.18
1.95
2.24
4.13
3.73
1.83
2.76
4.08
1.08
6.33
1.10
1.21
1.09
2.24
2.73
2.82
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
f1 (ppm)

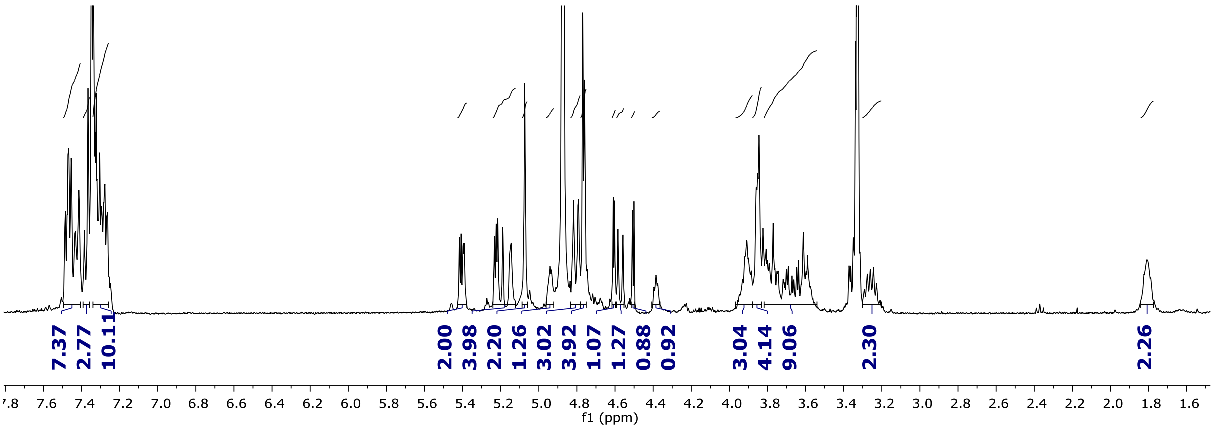

168.76
168.18
150.52
150.52
150.45
150.44
150.03
138.27
136.47
136.32
136.28
134.92
134.82
133.29
133.22
132.77
132.74
130.10
130.07
130.02
129.80
129.77
129.72
128.97
128.70
128.65
128.60
128.42
128.37
128.31
128.20
128.10
128.07
127.99
127.93
127.90
127.78
127.72
127.60
127.57
127.49
127.43
125.99
125.83
125.77
125.64
125.58
125.54
125.44
125.38
125.35
125.32
74.72
72.54
66.73
22.65
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

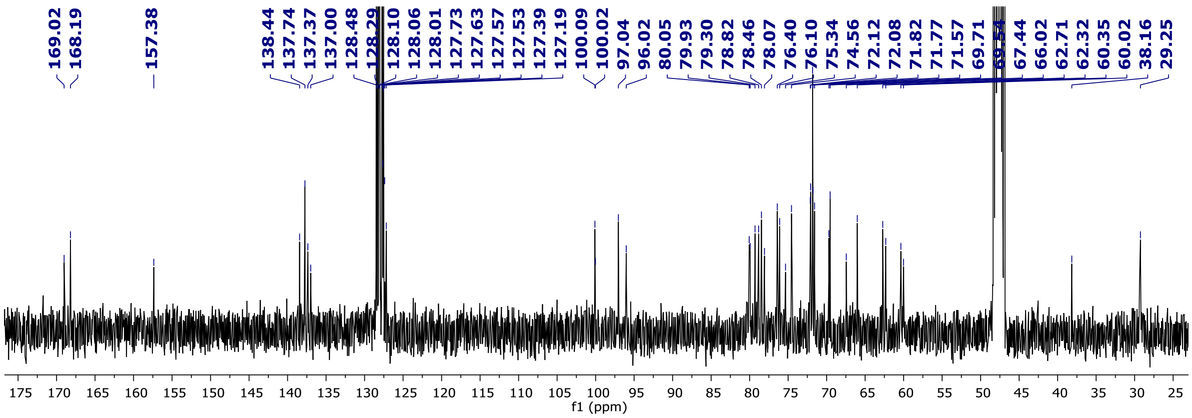

-10.81
-11.15
-14.13
-14.74
15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40
f1 (ppm)

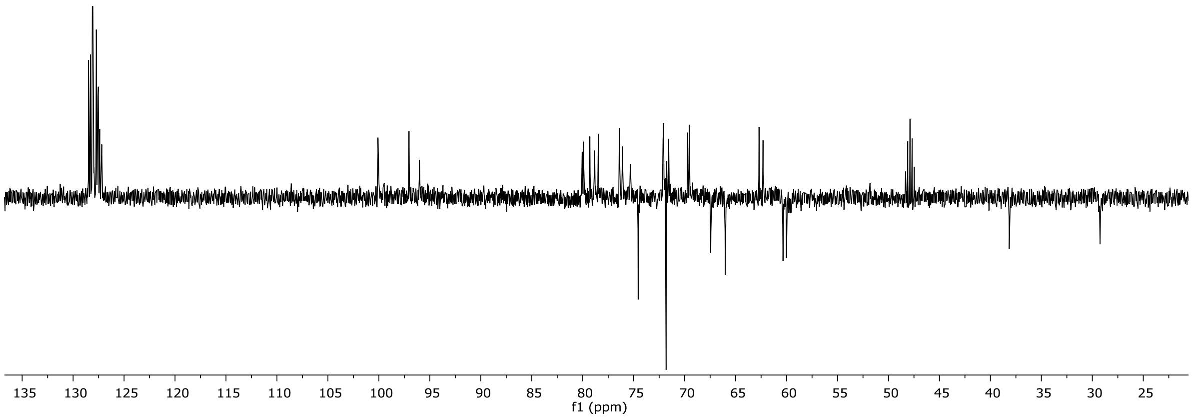

140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40
f1 (ppm)

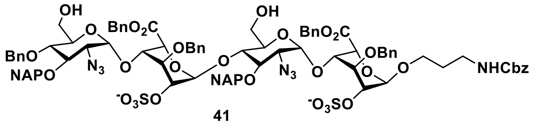

OH
BnO
$^{-}O_3SO$
N_3
OBn
O
OH
$^{-}O_3SO$
N_3
OBn
NHCbz

33

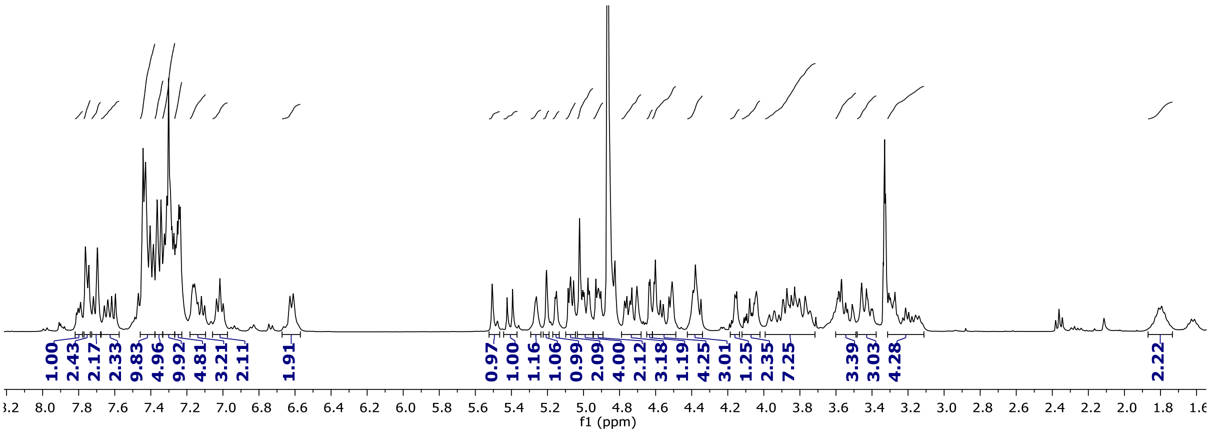

7.37
2.77
10.11
2.00
3.98
2.20
1.26
3.02
3.92
1.07
1.27
0.88
0.92
3.04
4.14
9.06
2.30
2.26
7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6
f1 (ppm)

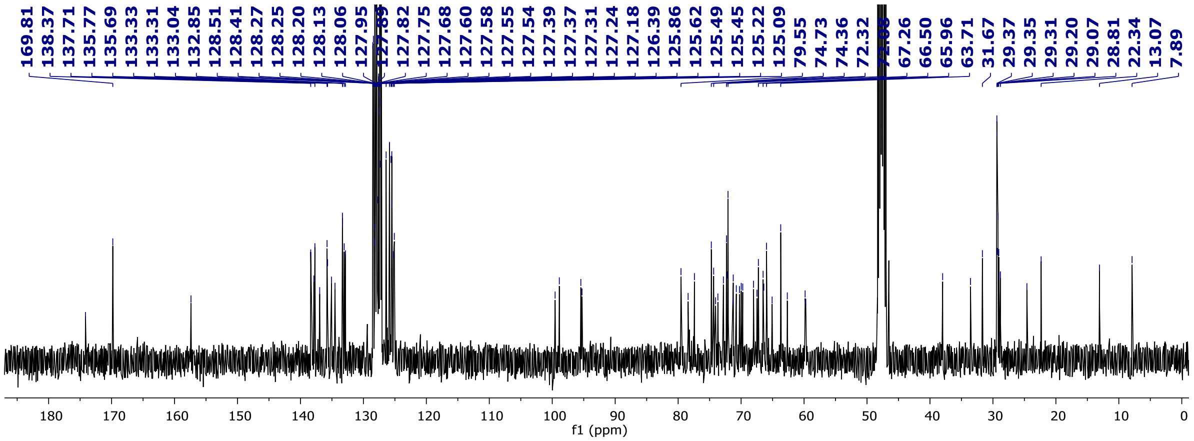

169.02
168.19
157.38
138.44
137.74
137.37
137.00
128.48
128.29
128.10
128.06
128.01
127.73
127.63
127.57
127.53
127.39
127.19
100.09
100.02
97.04
96.02
80.05
79.93
79.30
78.82
78.46
78.07
76.40
76.10
75.34
74.56
72.12
72.08
71.82
71.77
71.57
69.71
69.54
67.44
66.02
62.71
62.32
60.35
60.02
38.16
29.25
175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25
f1 (ppm)

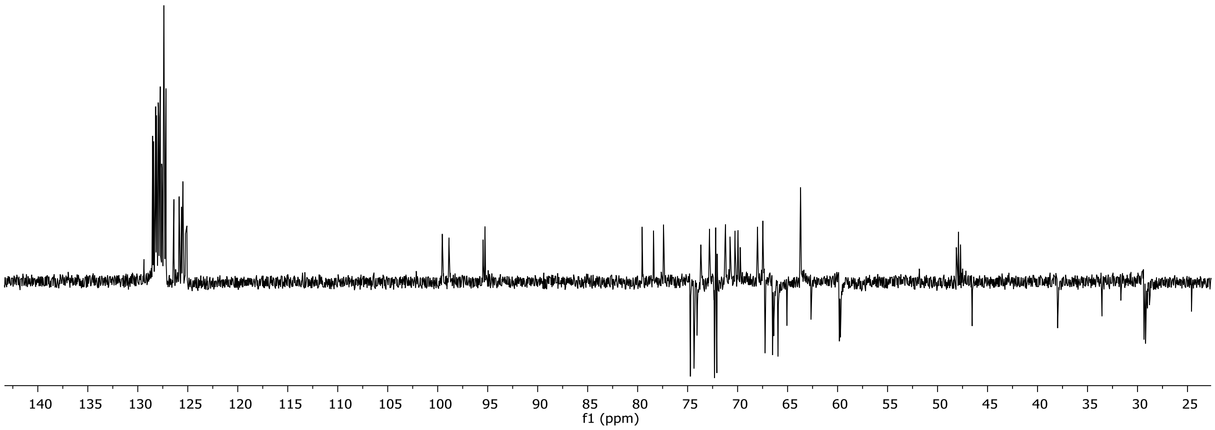

135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25
f1 (ppm)

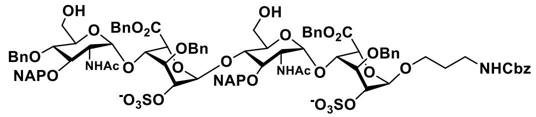

OH
BnO
NAPO
N3
O
BnO2C
OBn
-O3SO
NHCbz

41

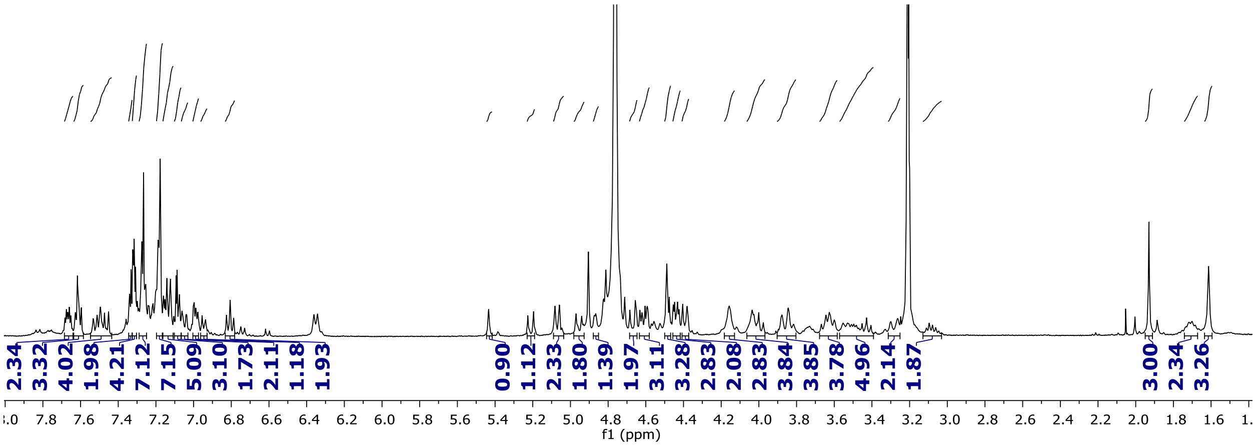

1.00
2.43
2.17
2.33
9.83
4.96
9.92
4.81
3.21
2.11
1.91
0.97
1.00
1.16
1.06
0.99
2.09
4.00
2.12
3.18
1.19
4.25
3.01
1.25
2.35
7.25
3.39
3.03
4.28
2.22
8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6
f1 (ppm)

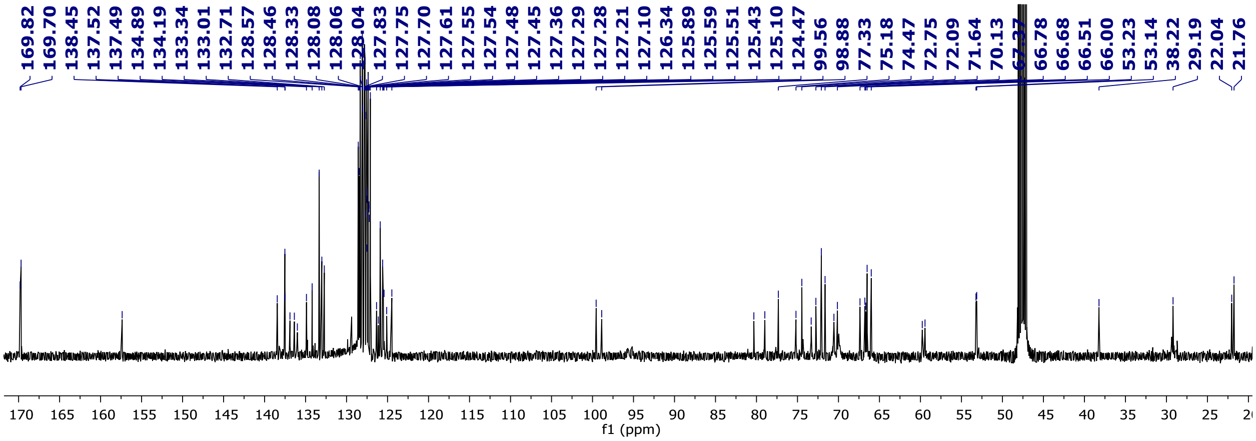

169.81
138.37
137.71
135.77
135.69
133.33
133.31
133.04
132.85
128.51
128.41
128.27
128.25
128.20
128.13
128.06
127.95
127.89
127.82
127.75
127.68
127.60
127.58
127.55
127.54
127.39
127.37
127.31
127.24
127.18
126.39
125.86
125.62
125.49
125.45
125.22
125.09
79.55
74.73
74.36
72.32
67.26
66.50
65.96
63.71
31.67
29.37
29.35
29.31
29.20
29.07
28.81
22.34
13.07
7.89
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

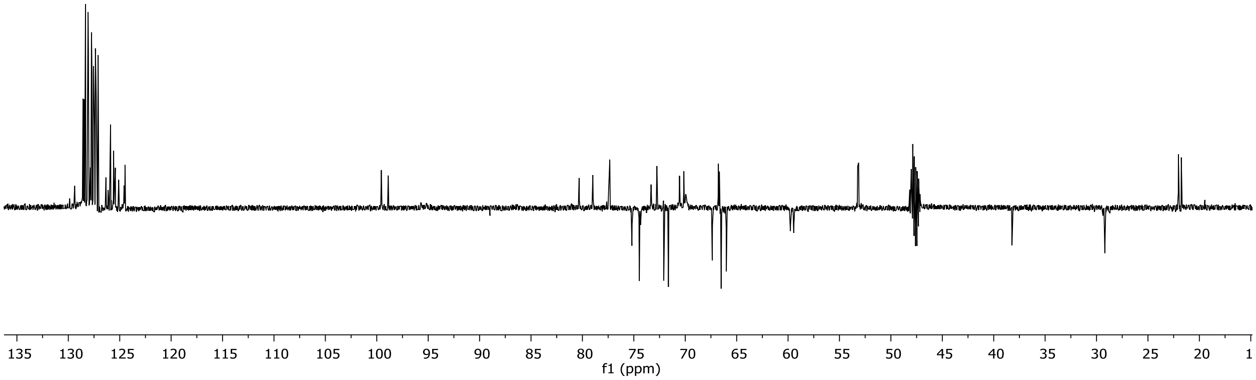

140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
f1 (ppm)

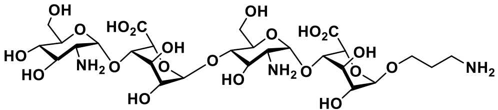

OH
O
BnO
NAPO
NHAc
O
BnO2C
OBn
O
-O3SO
O
OH
O
NAPO
NHAc
O
BnO2C
OBn
O
-O3SO
O
NHCbz

44

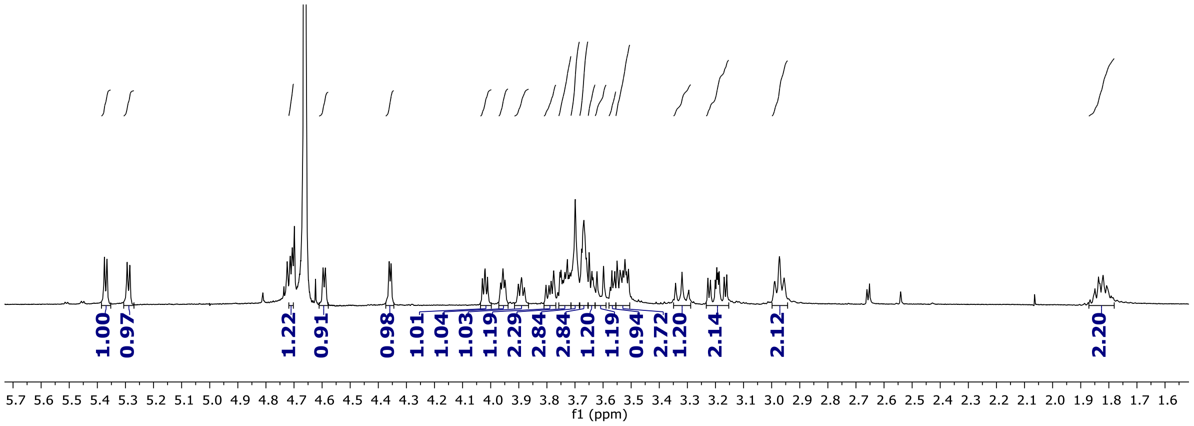

2.34
3.32
4.02
1.98
4.21
7.12
7.15
5.09
3.10
1.73
2.11
1.18
1.93
0.90
1.12
2.33
1.80
1.39
1.97
3.11
3.28
2.83
2.08
2.83
3.84
3.85
3.78
4.96
2.14
1.87
3.00
2.34
3.26
7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6
f1 (ppm)

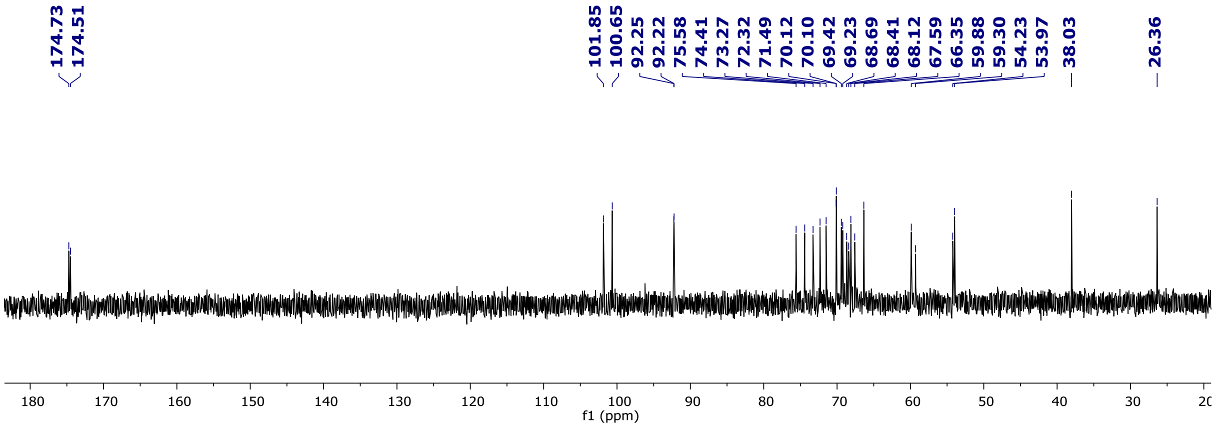

169.82
169.70
138.45
137.52
137.49
134.89
134.19
133.34
133.01
132.71
128.57
128.46
128.33
128.08
128.06
128.04
127.83
127.75
127.70
127.61
127.55
127.54
127.48
127.45
127.36
127.29
127.28
127.21
127.10
126.34
125.89
125.59
125.51
125.43
125.10
124.47
99.56
98.88
77.33
75.18
74.47
72.75
72.09
71.64
70.13
67.37
66.78
66.68
66.51
66.00
53.23
53.14
38.22
29.19
22.04
21.76
170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25
f1 (ppm)

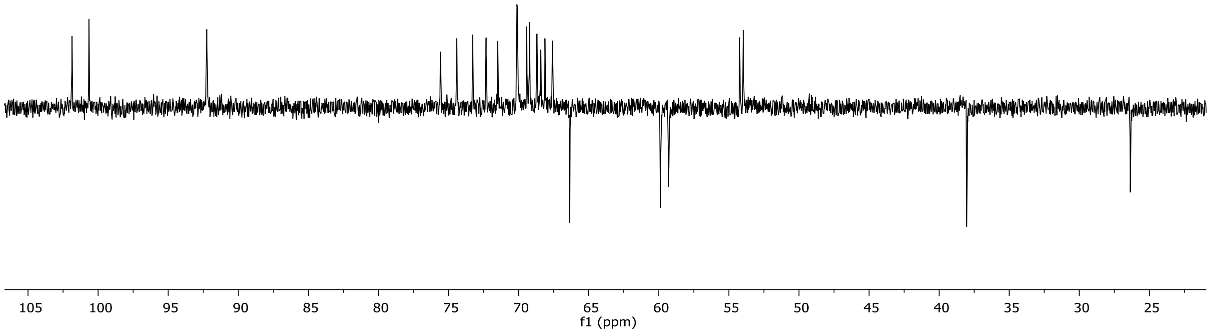

135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)

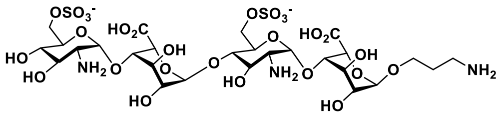


1

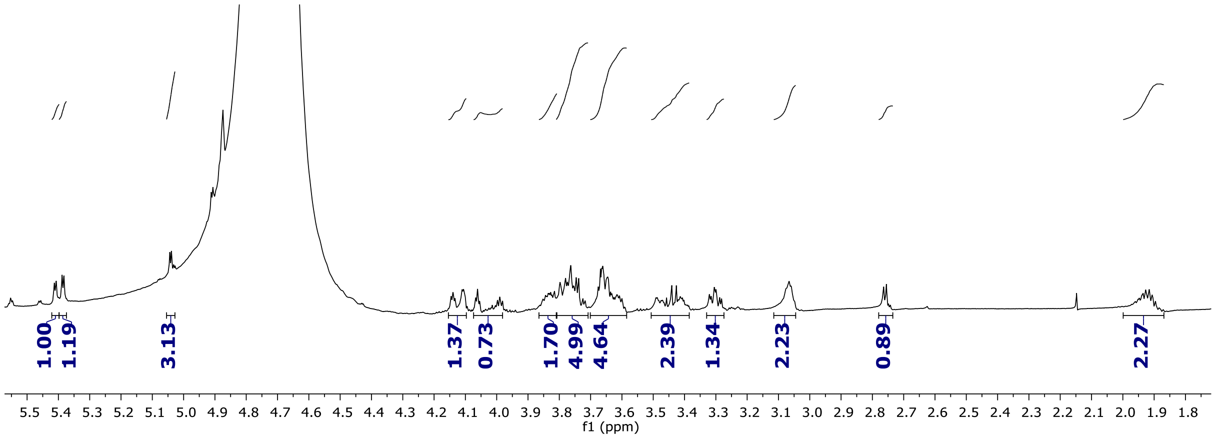

1.00
0.97
1.22
0.91
0.98
1.01
1.04
1.03
1.19
2.29
2.84
2.84
1.20
1.19
0.94
2.72
1.20
2.14
2.12
2.20
5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6
f1 (ppm)

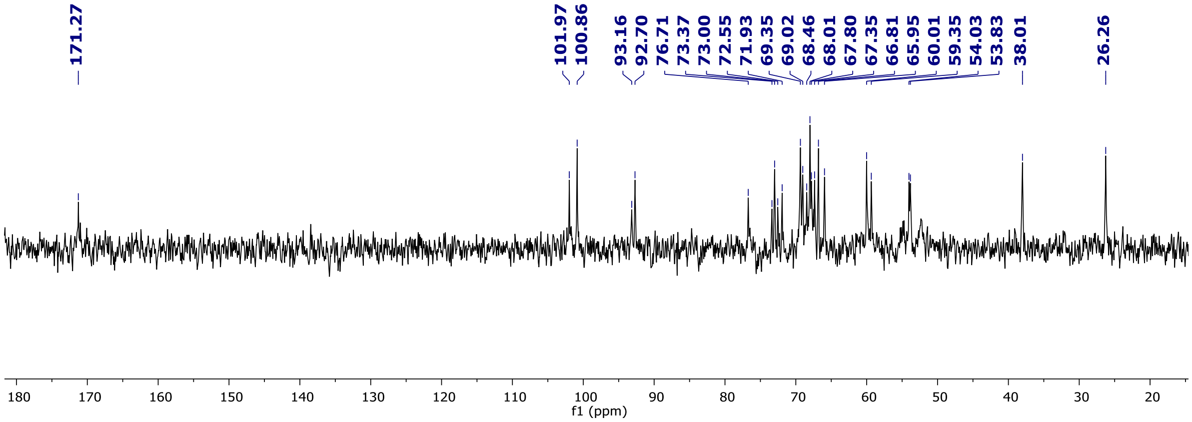

174.73
174.51
101.85
100.65
92.25
92.22
75.58
74.41
73.27
72.32
71.49
70.12
70.10
69.42
69.23
68.69
68.41
68.12
67.59
66.35
59.88
59.30
54.23
53.97
38.03
26.36
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 2
f1 (ppm)

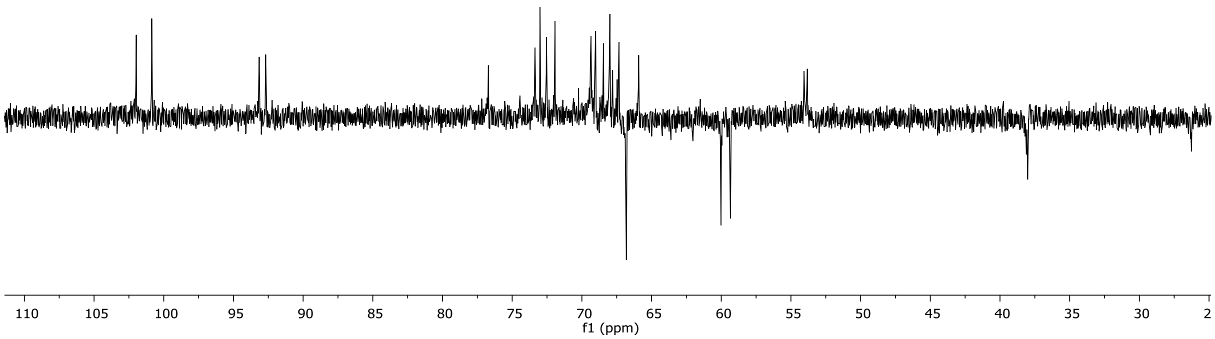

105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25
f1 (ppm)

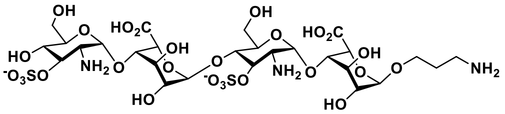

OSO3-
HO2C
OH
HO
HO
NH2
O
HO
OSO3-
HO2C
OH
HO
NH2
O
HO
NH2

2

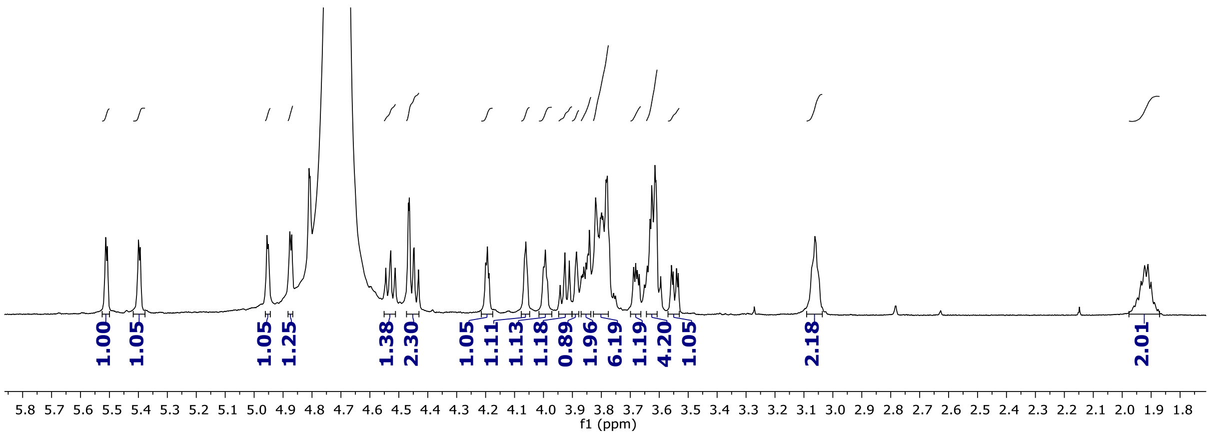

1.00
1.19
3.13
1.37
0.73
1.70
4.99
4.64
2.39
1.34
2.23
0.89
2.27
5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8
f1 (ppm)

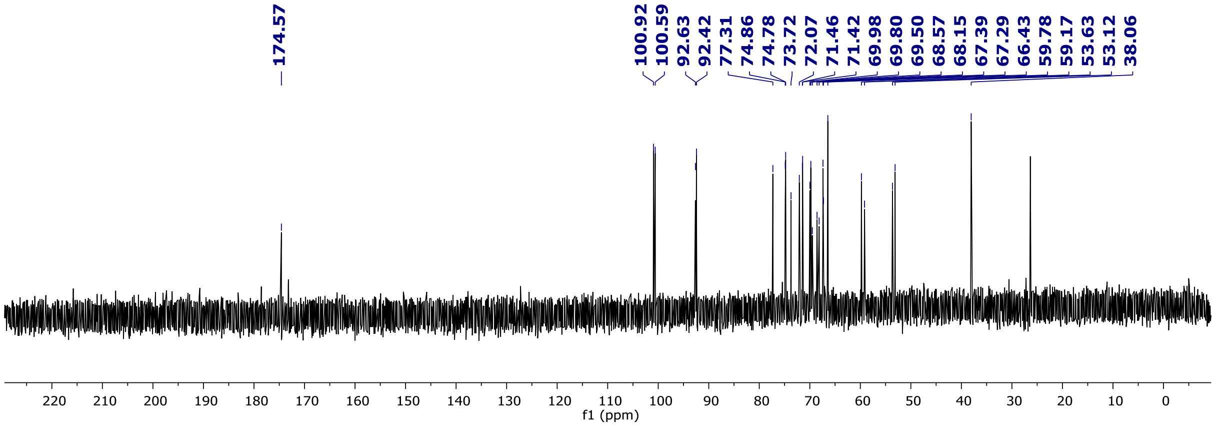

171.27
101.97
100.86
93.16
92.70
76.71
73.37
73.00
72.55
71.93
69.35
69.02
68.46
68.01
67.80
67.35
66.81
65.95
60.01
59.35
54.03
53.83
38.01
26.26
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

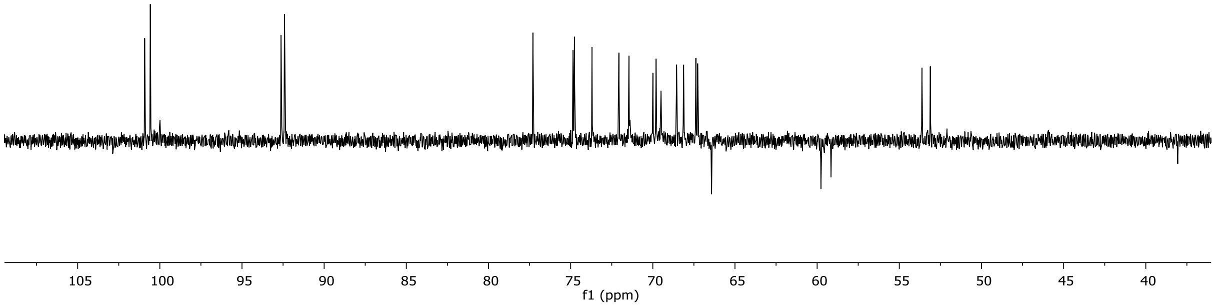

110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 2
f1 (ppm)

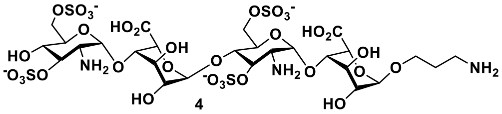

OH
HO₂C
OH
HO
⁻O₃SO
NH₂
O
HO
⁻O₃SO
NH₂
NH₂

3

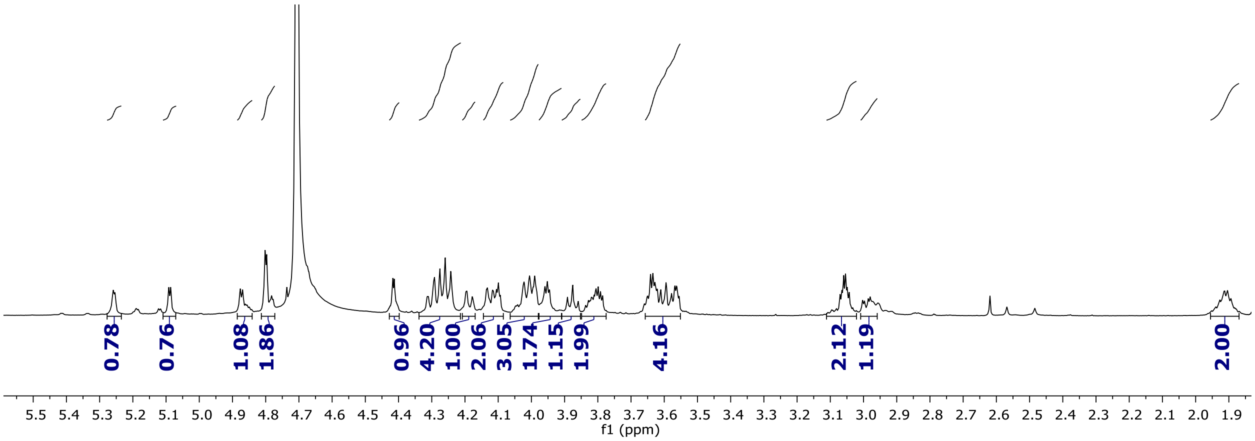

1.00
1.05
1.05
1.25
1.38
2.30
1.05
1.11
1.13
1.18
0.89
1.96
6.19
1.19
4.20
1.05
2.18
2.01
5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8
f1 (ppm)

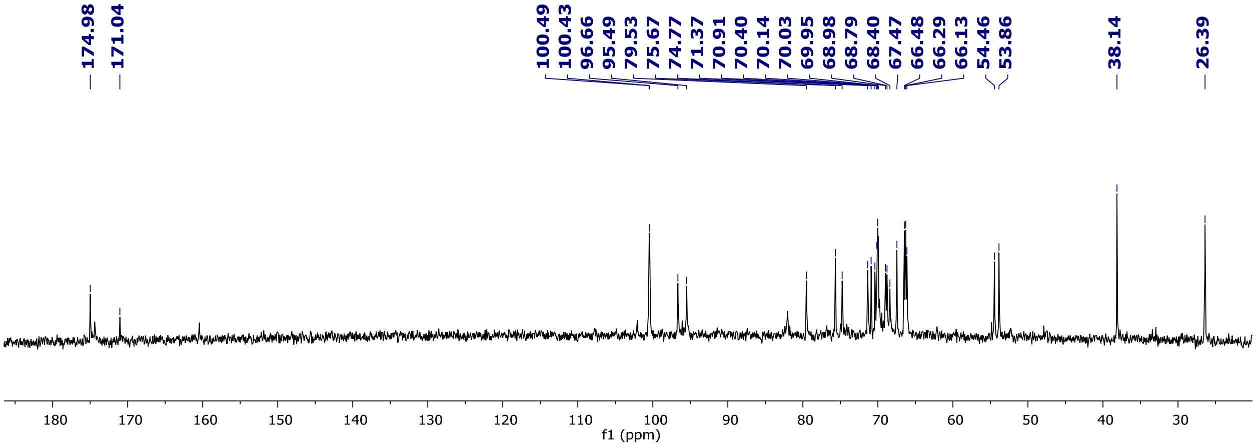

174.57
100.92
100.59
92.63
92.42
77.31
74.86
74.78
73.72
72.07
71.46
71.42
69.98
69.80
69.50
68.57
68.15
67.39
67.29
66.43
59.78
59.17
53.63
53.12
38.06
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

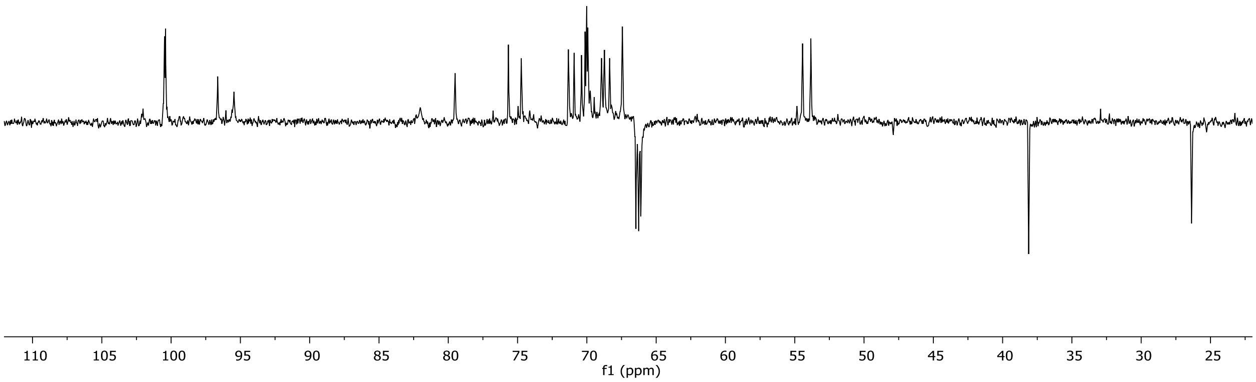

105 100 95 90 85 80 75 70 65 60 55 50 45 40
f1 (ppm)

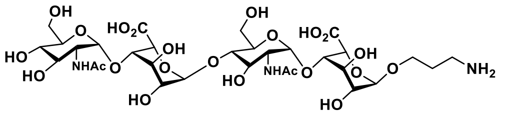

OSO3-
HO2C
OSO3-
HO2C
HO
-O3SO
NH2
O
OH
-O3SO
NH2
OH
HO
HO
NH2

4

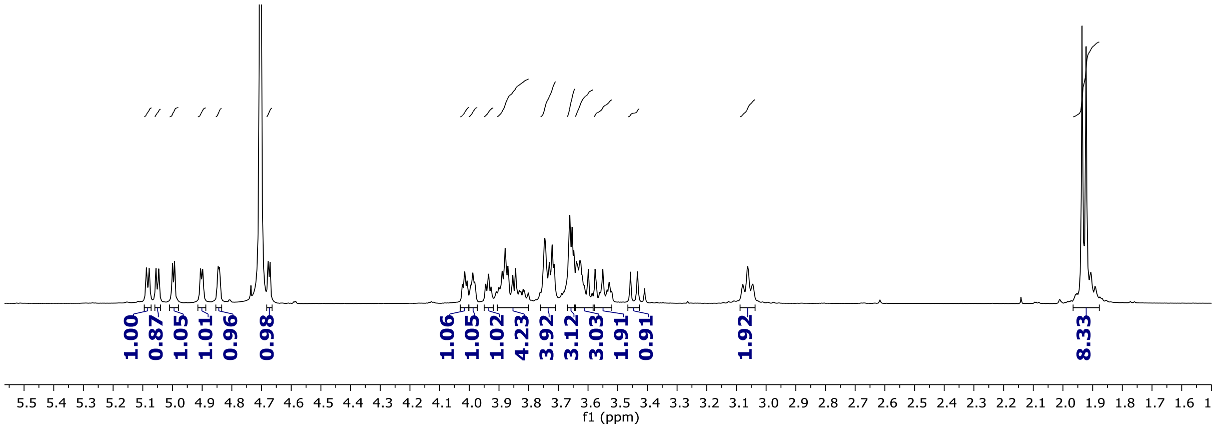

0.78
0.76
1.08
1.86
0.96
4.20
1.00
2.06
3.05
1.74
1.15
1.99
4.16
2.12
1.19
2.00
5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9
f1 (ppm)

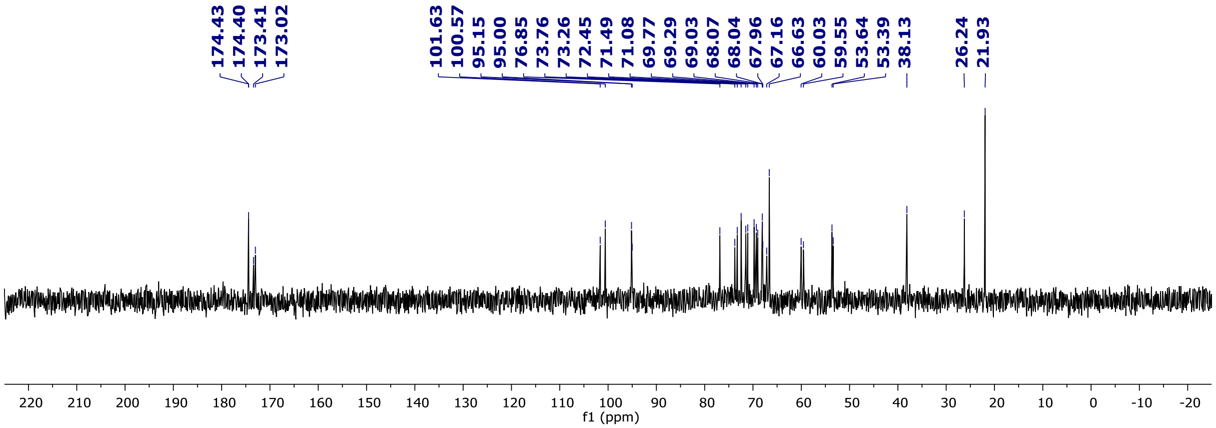

174.98
171.04
100.49
100.43
96.66
95.49
79.53
75.67
74.77
71.37
70.91
70.40
70.14
70.03
69.95
68.98
68.79
68.40
67.47
66.48
66.29
66.13
54.46
53.86
38.14
26.39
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30
f1 (ppm)

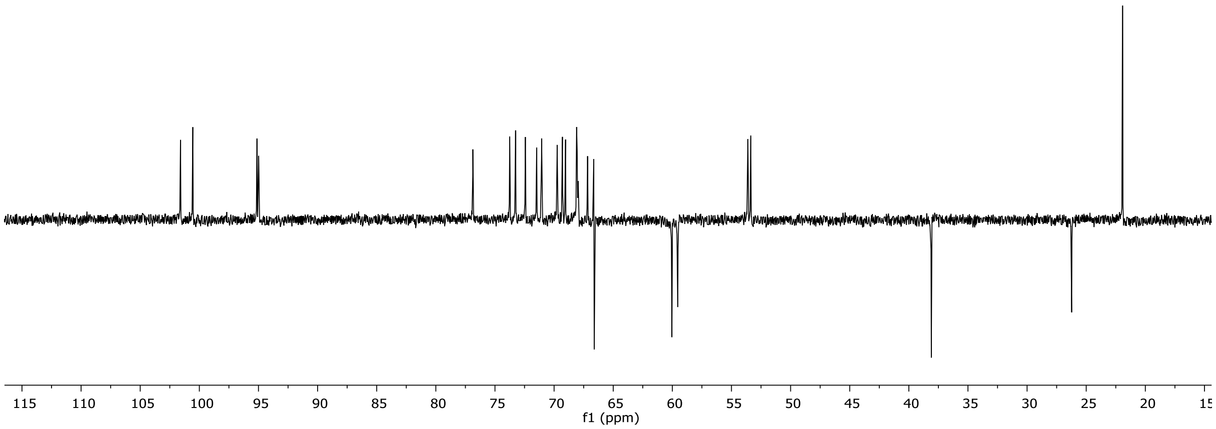

110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25
f1 (ppm)

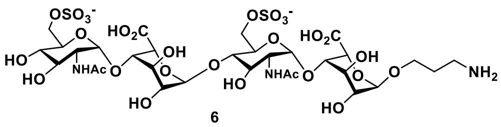

OH
HO₂C
OH
HO
NHAc
O
HO
NH₂

5

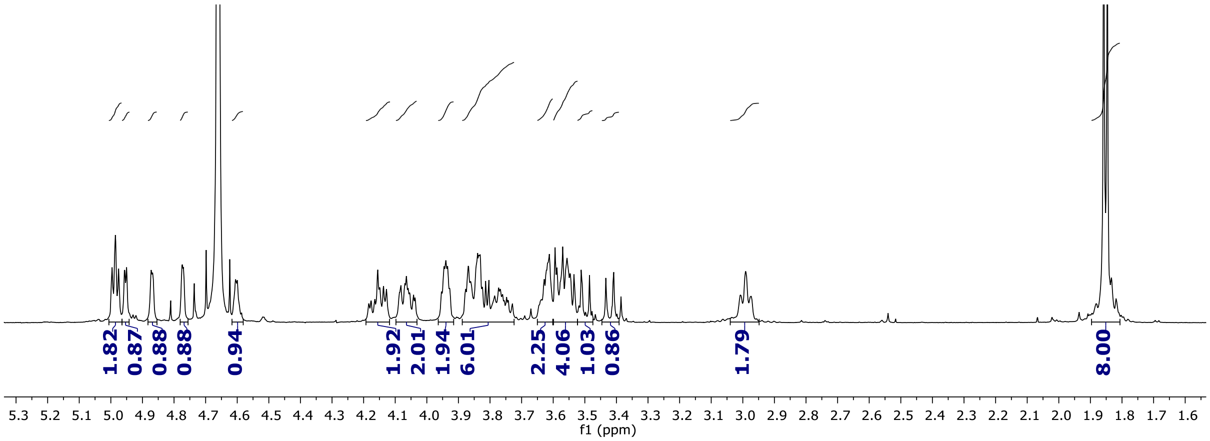

1.00
0.87
1.05
1.01
0.96
0.98
1.06
1.05
1.02
4.23
3.92
3.12
3.03
1.91
0.91
1.92
8.33
5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1
f1 (ppm)

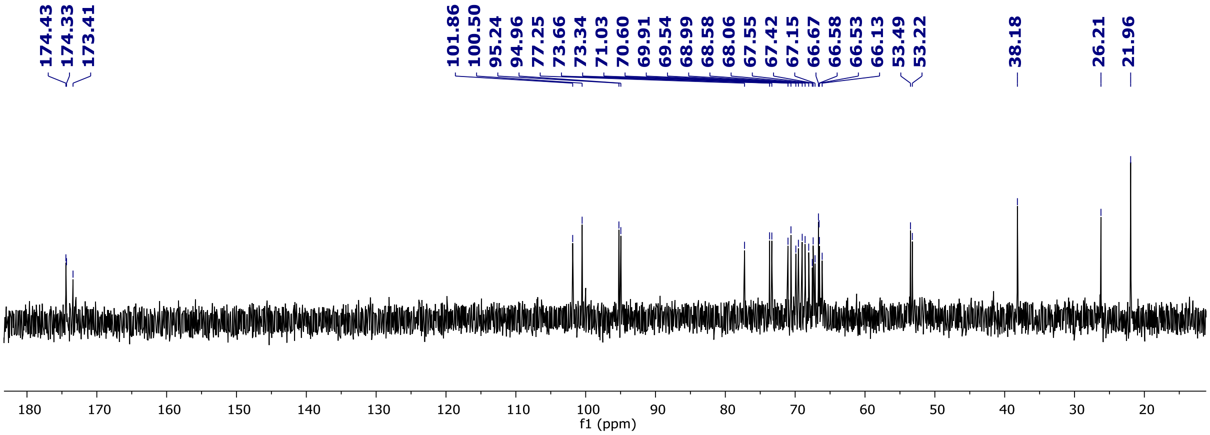

174.43
174.40
173.41
173.02
101.63
100.57
95.15
95.00
76.85
73.76
73.26
72.45
71.49
71.08
69.77
69.29
69.03
68.07
68.04
67.96
67.16
66.63
60.03
59.55
53.64
53.39
38.13
26.24
21.93
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

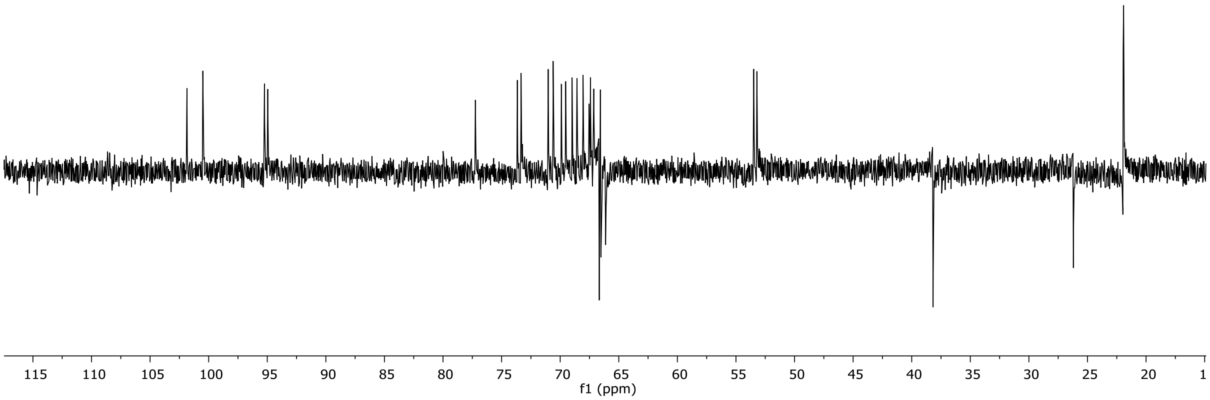

115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
f1 (ppm)

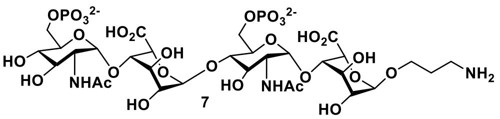

OSO3-
HO2C
OH
HO
NHAc
O
HO
OSO3-
HO2C
OH
HO
NHAc
O
HO
NH2

6


1.82
0.87
0.88
0.88
0.94
1.92
2.01
1.94
6.01
2.25
4.06
1.03
0.86
1.79
8.00
5.3 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 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6
f1 (ppm)

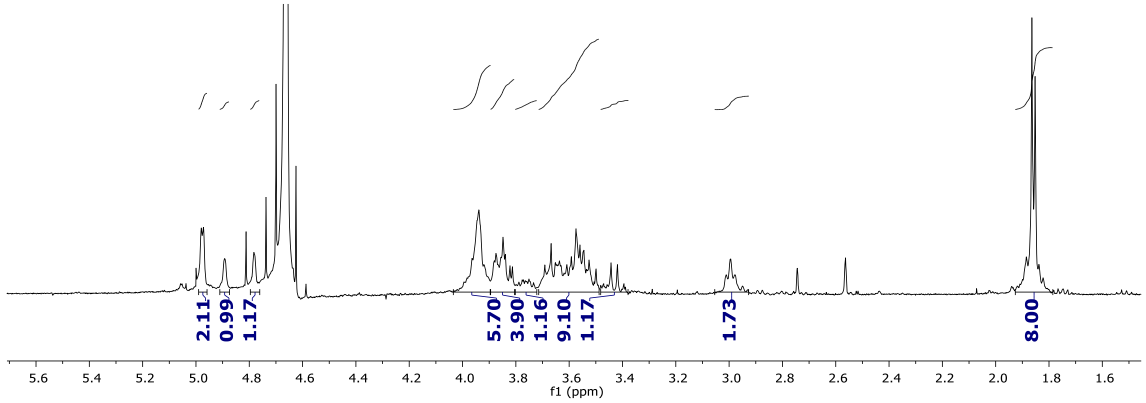

174.43
174.33
173.41
101.86
100.50
95.24
94.96
77.25
73.66
73.34
71.03
70.60
69.91
69.54
68.99
68.58
68.06
67.55
67.42
67.15
66.67
66.58
66.53
66.13
53.49
53.22
38.18
26.21
21.96
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)


115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 1
f1 (ppm)

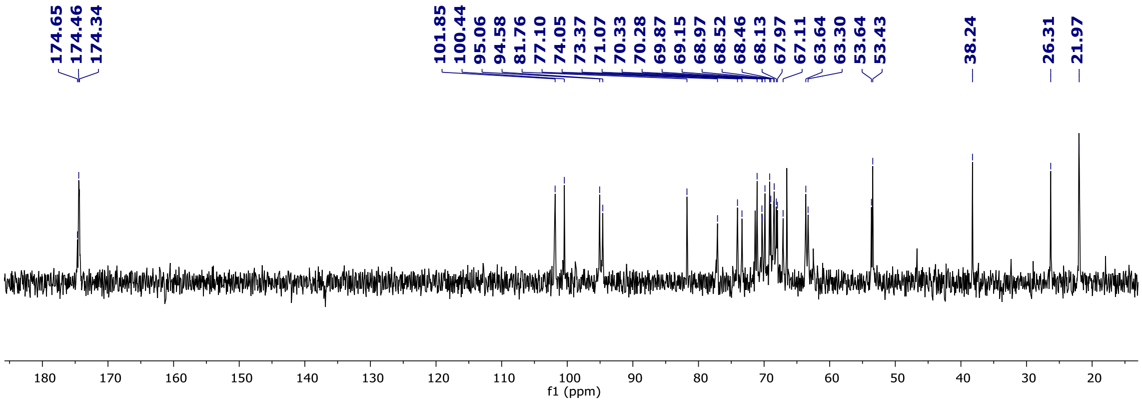


OPO3 2-
HO2C
OH
HO
NHAc
O
NH2

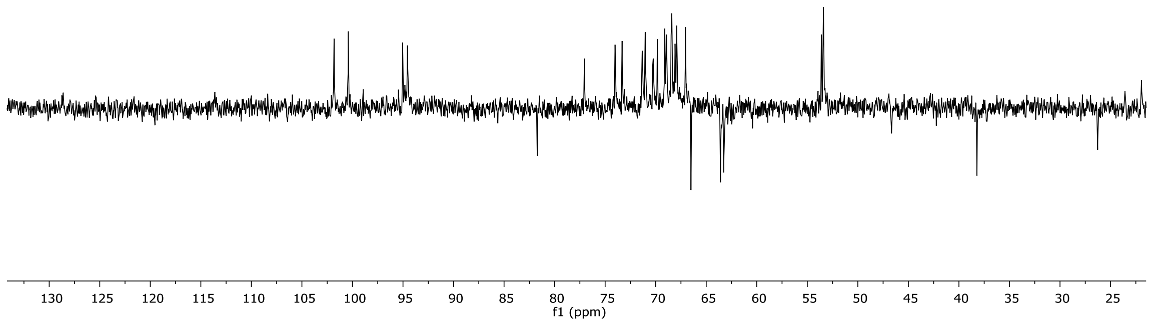
7



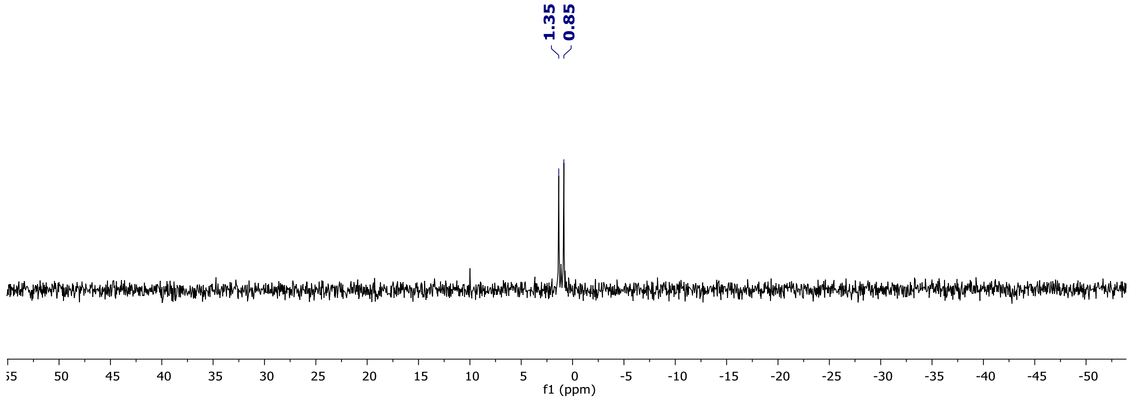
2.11
0.99
1.17
5.70
3.90
1.16
9.10
1.17
1.73
8.00
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f1 (ppm)



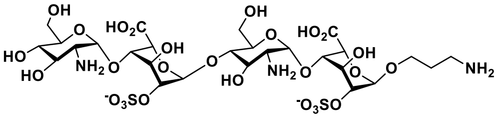
174.65
174.46
174.34
101.85
100.44
95.06
94.58
81.76
77.10
74.05
73.37
71.07
70.33
70.28
69.87
69.15
68.97
68.52
68.46
68.13
67.97
67.11
63.64
63.30
53.64
53.43
38.24
26.31
21.97
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)



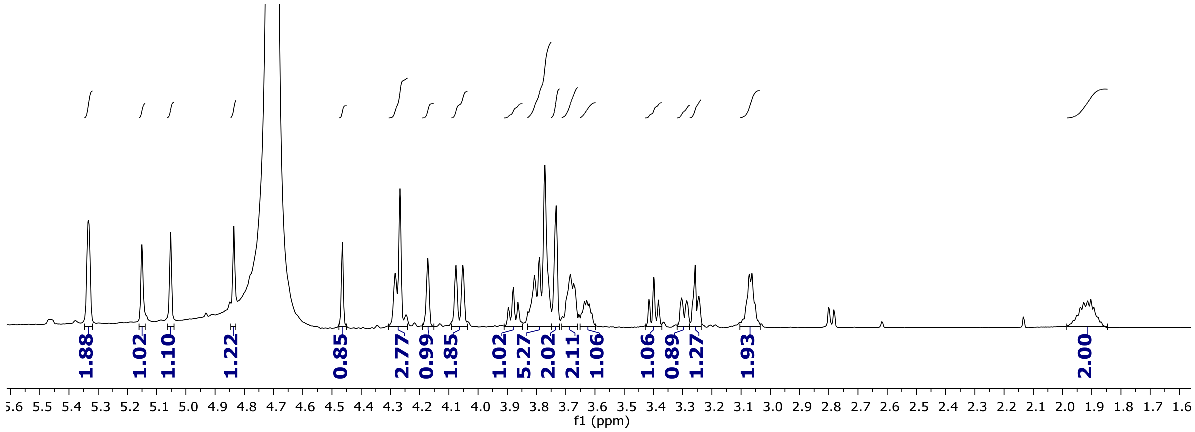
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
f1 (ppm)

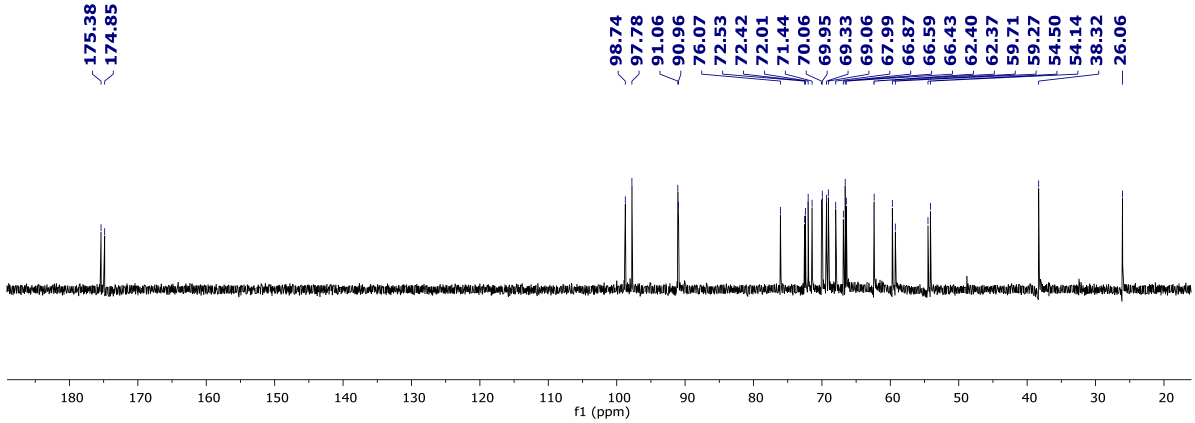


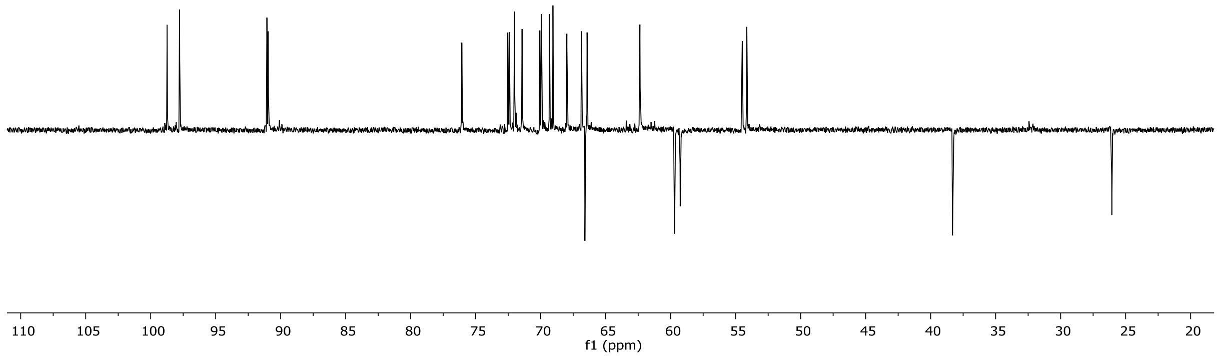
1.35
0.85
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
f1 (ppm)

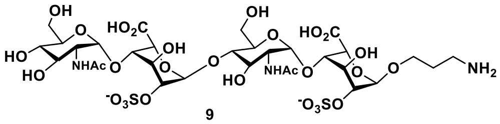

OH
HO₂C
OH
O
HO
HO
NH₂
O
⁻O₃SO
OH
HO₂C
OH
O
HO
NH₂
O
⁻O₃SO
O
NH₂

8

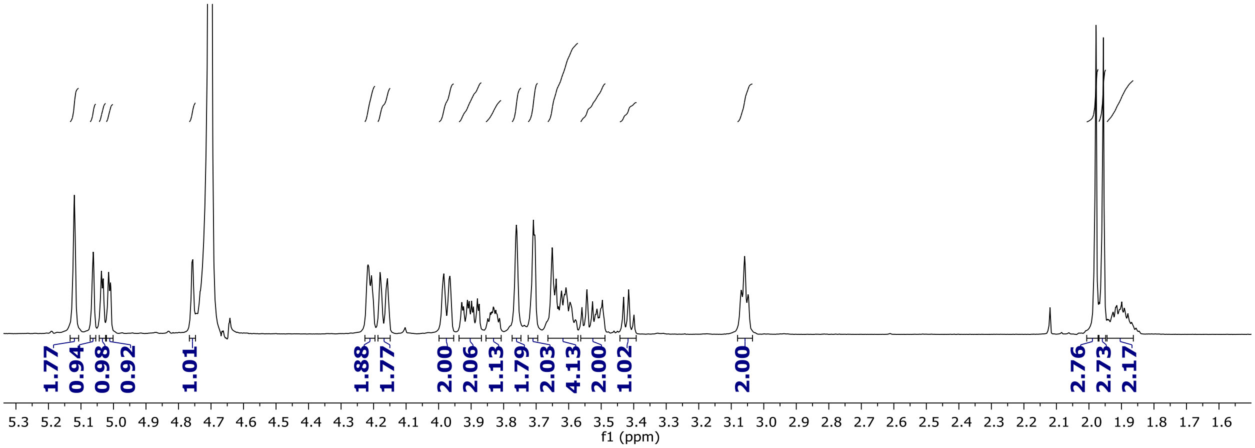

1.88
1.02
1.10
1.22
0.85
2.77
0.99
1.85
1.02
5.27
2.02
2.11
1.06
1.06
0.89
1.27
1.93
2.00
5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6
f1 (ppm)

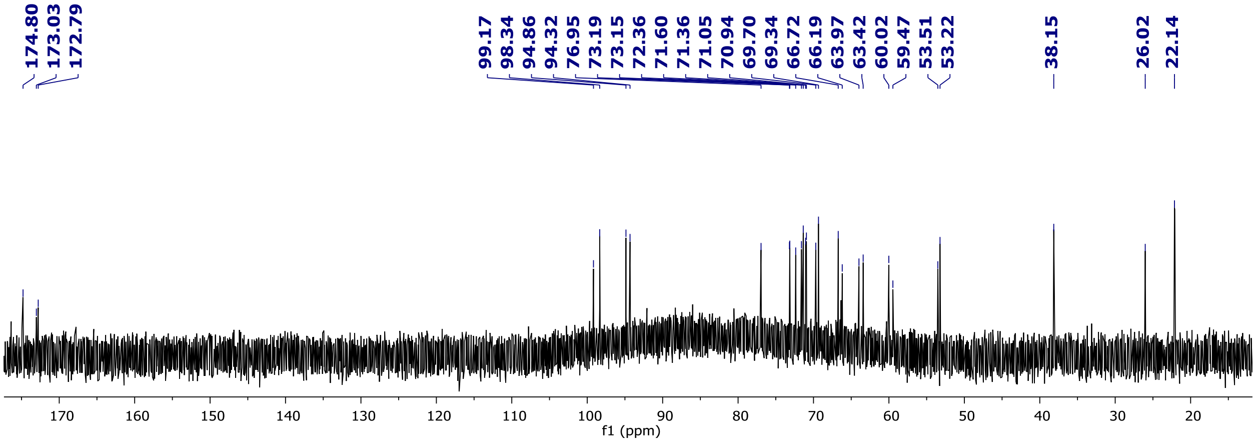

175.38
174.85
98.74
97.78
91.06
90.96
76.07
72.53
72.42
72.01
71.44
70.06
69.95
69.33
69.06
67.99
66.87
66.59
66.43
62.40
62.37
59.71
59.27
54.50
54.14
38.32
26.06
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

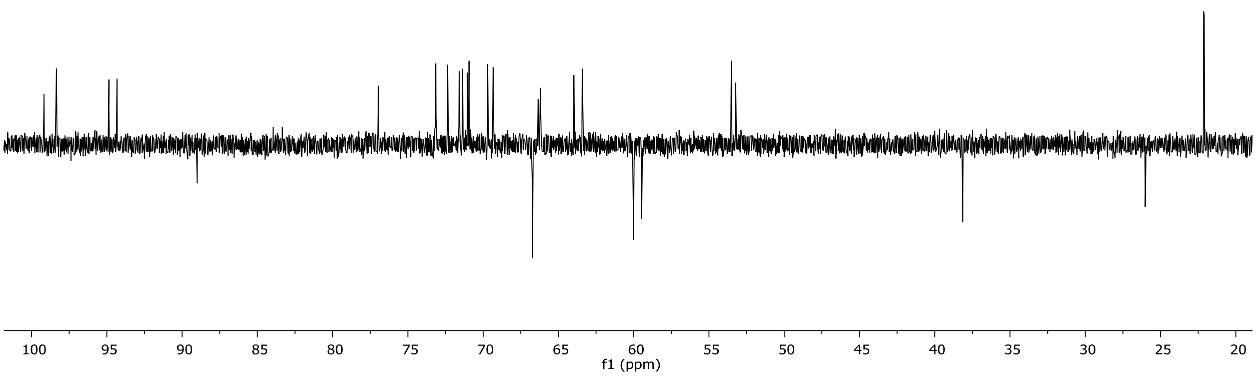

110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)

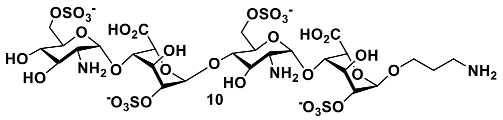

OH
HO₂C
OH
HO₂C
HO
NHAc
OH
O
HO
NHAc
OH
NH₂
HO
⁻O₃SO
⁻O₃SO

9

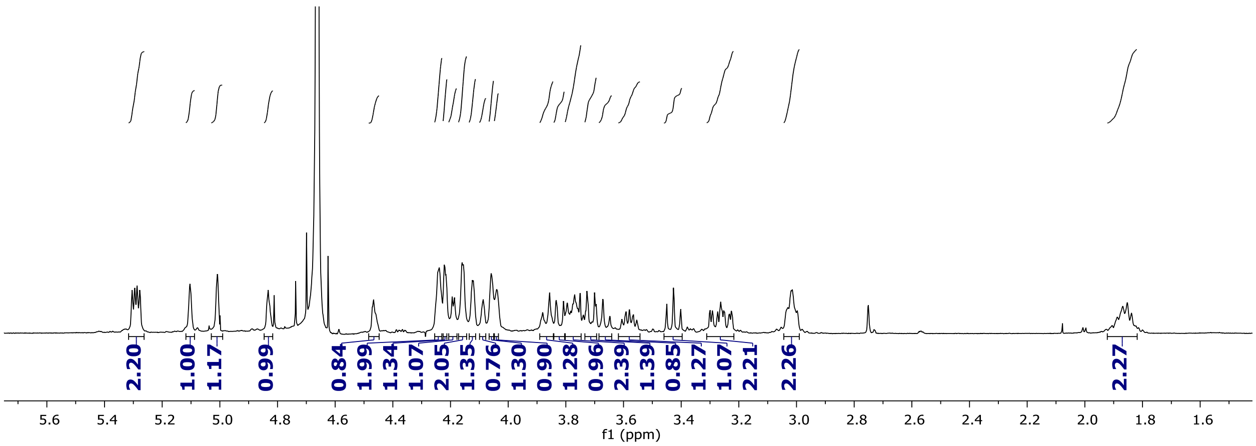

1.77
0.94
0.98
0.92
1.01
1.88
1.77
2.00
2.06
1.13
1.79
2.03
4.13
2.00
1.02
2.00
2.76
2.73
2.17
5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6
f1 (ppm)

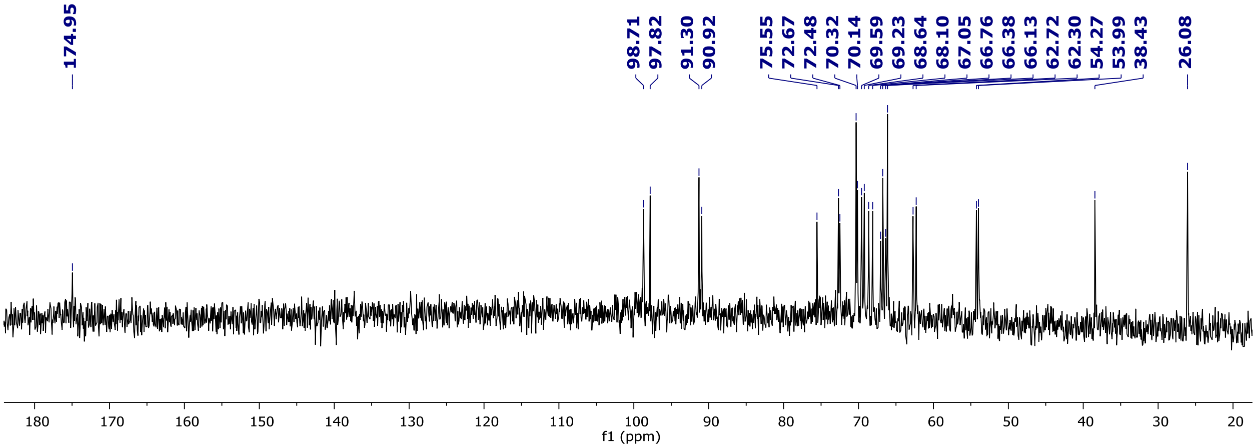

174.80
173.03
172.79
99.17
98.34
94.86
94.32
76.95
73.19
73.15
72.36
71.60
71.36
71.05
70.94
69.70
69.34
66.72
66.19
63.97
63.42
60.02
59.47
53.51
53.22
38.15
26.02
22.14
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

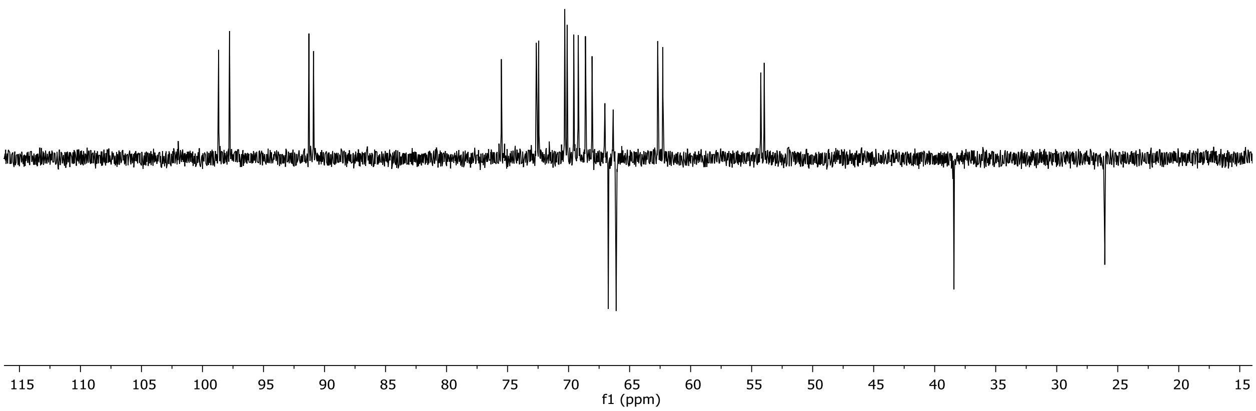

100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)

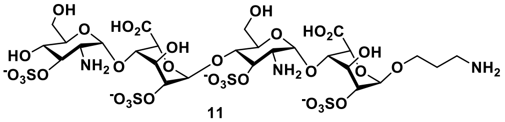

OSO3-
HO
HO
NH2
HO2C
OH
-O3SO
OSO3-
HO
NH2
HO2C
OH
-O3SO
NH2

10

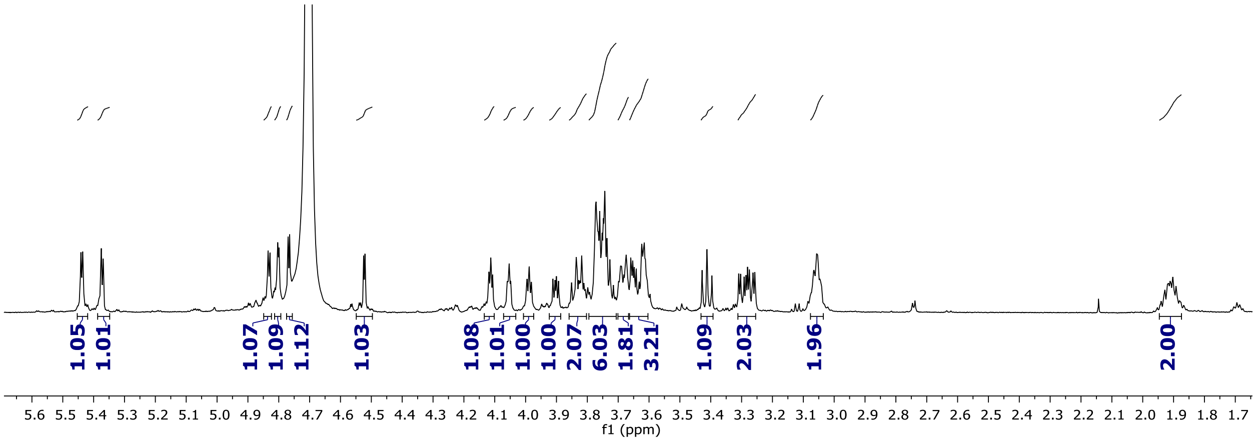

2.20
1.00
1.17
0.99
0.84
1.99
1.34
1.07
2.05
1.35
0.76
1.30
0.90
1.28
0.96
2.39
1.39
0.85
1.27
1.07
2.21
2.26
2.27
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f1 (ppm)

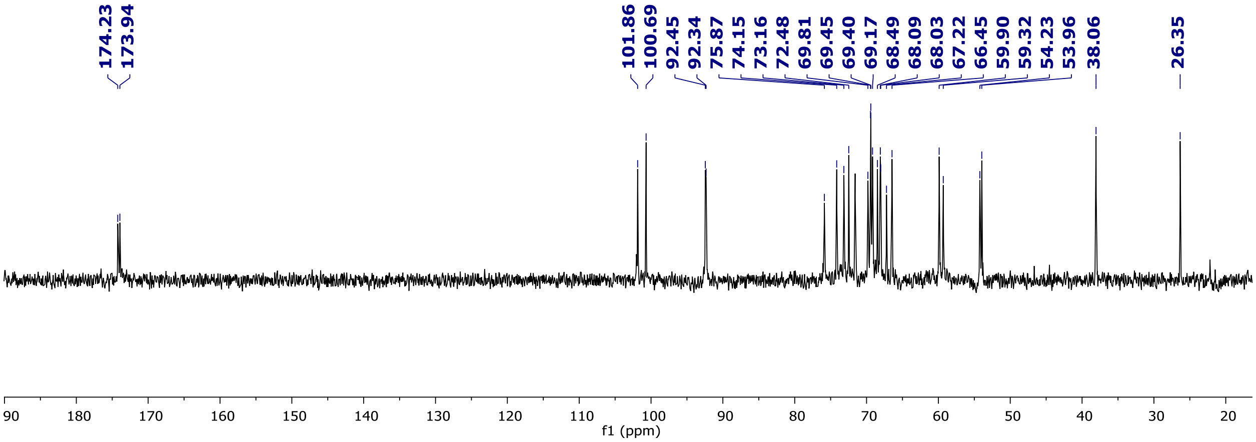

174.95
98.71
97.82
91.30
90.92
75.55
72.67
72.48
70.32
70.14
69.59
69.23
68.64
68.10
67.05
66.76
66.38
66.13
62.72
62.30
54.27
53.99
38.43
26.08
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

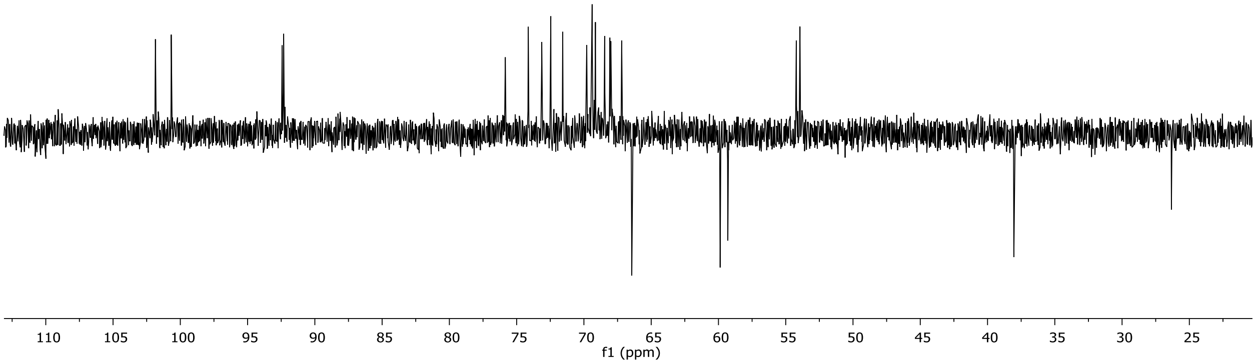

115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
f1 (ppm)

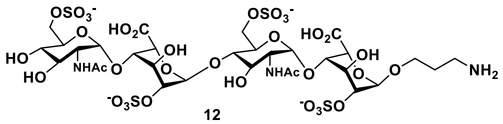


11

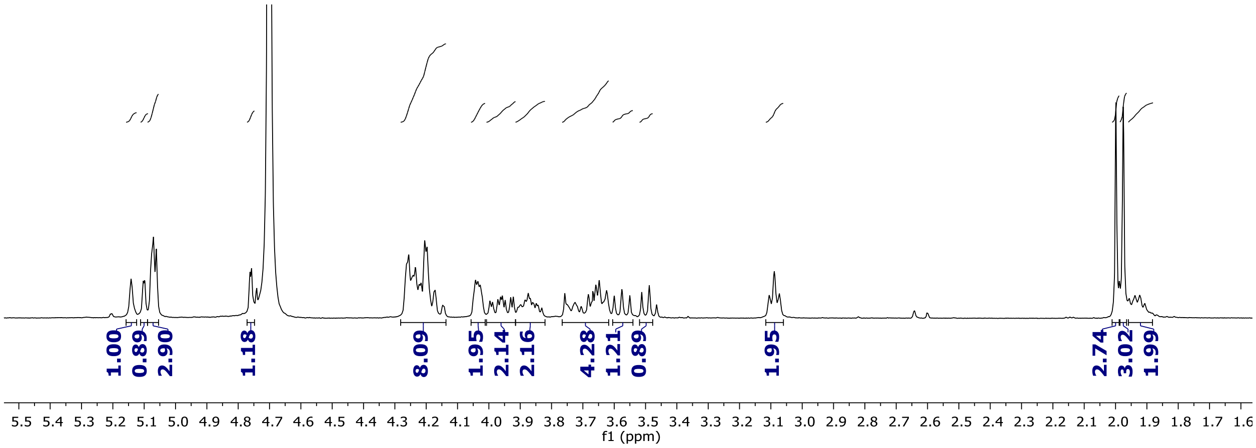

1.05
1.01
1.07
1.09
1.12
1.03
1.08
1.01
1.00
1.00
2.07
6.03
1.81
3.21
1.09
2.03
1.96
2.00
5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7
f1 (ppm)

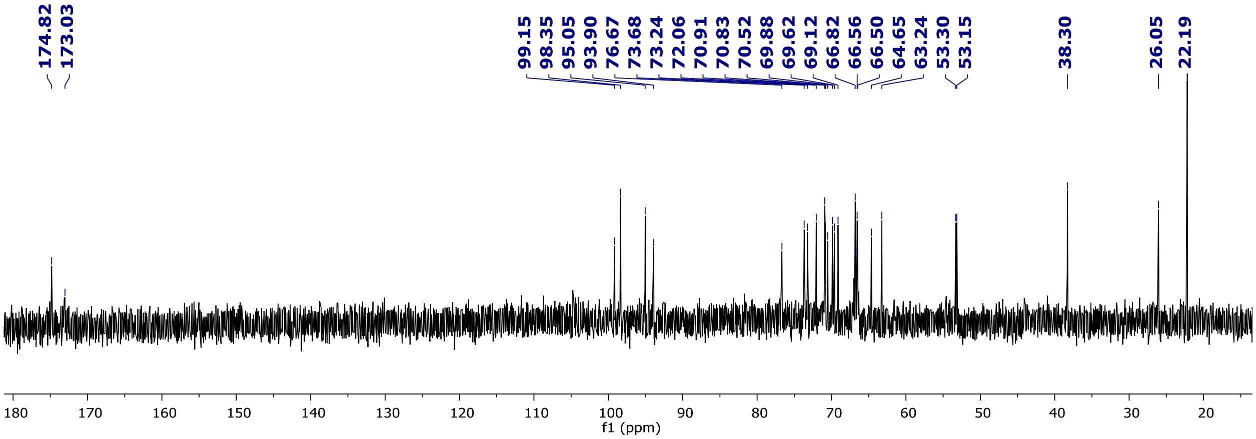

174.23
173.94
101.86
100.69
92.45
92.34
75.87
74.15
73.16
72.48
69.81
69.45
69.40
69.17
68.49
68.09
68.03
67.22
66.45
59.90
59.32
54.23
53.96
38.06
26.35
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

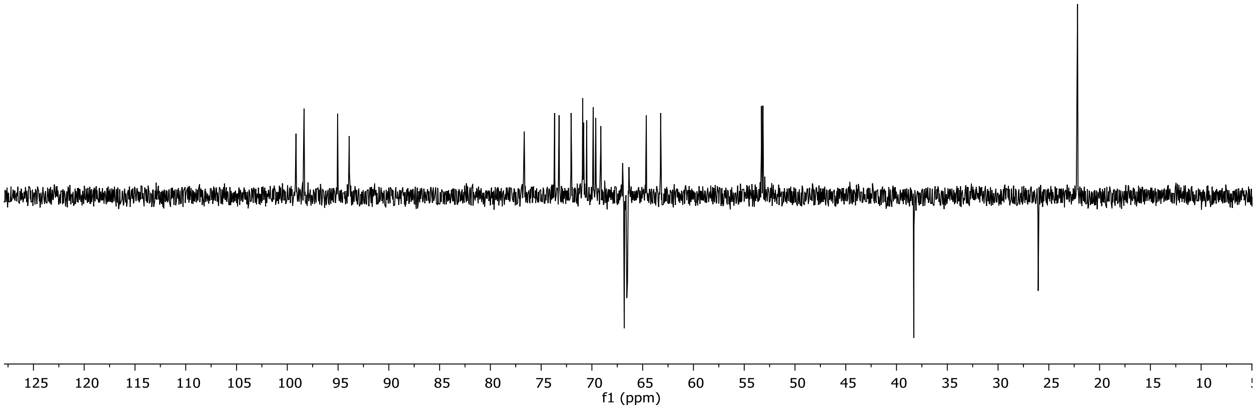

110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25
f1 (ppm)

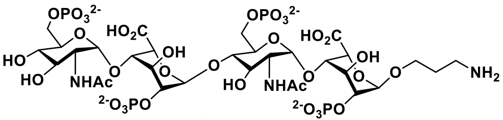

OSO3-
HO2C
OH
HO
NHAc
O
-O3SO
HO
NH2

12


1.00
0.89
2.90
1.18
8.09
1.95
2.14
2.16
4.28
1.21
0.89
1.95
2.74
3.02
1.99
5.5 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 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6
f1 (ppm)

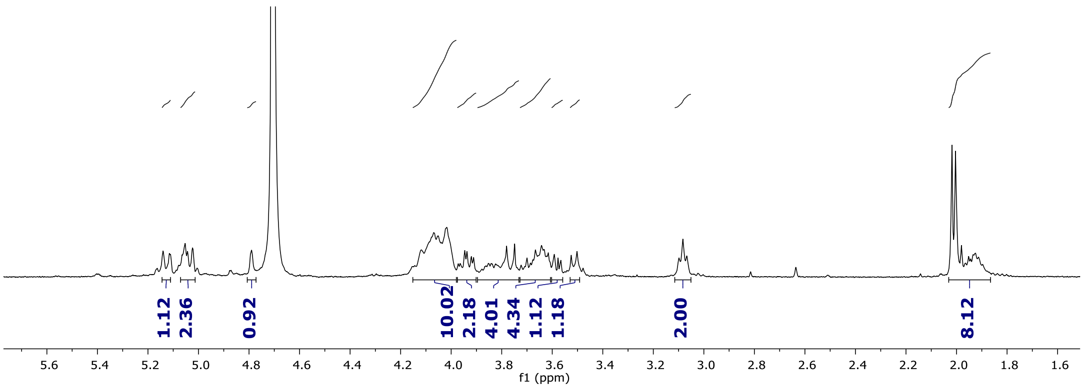

174.82
173.03
99.15
98.35
95.05
93.90
76.67
73.68
73.24
72.06
70.91
70.83
70.52
69.88
69.62
69.12
66.82
66.56
66.50
64.65
63.24
53.30
53.15
38.30
26.05
22.19
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)


125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

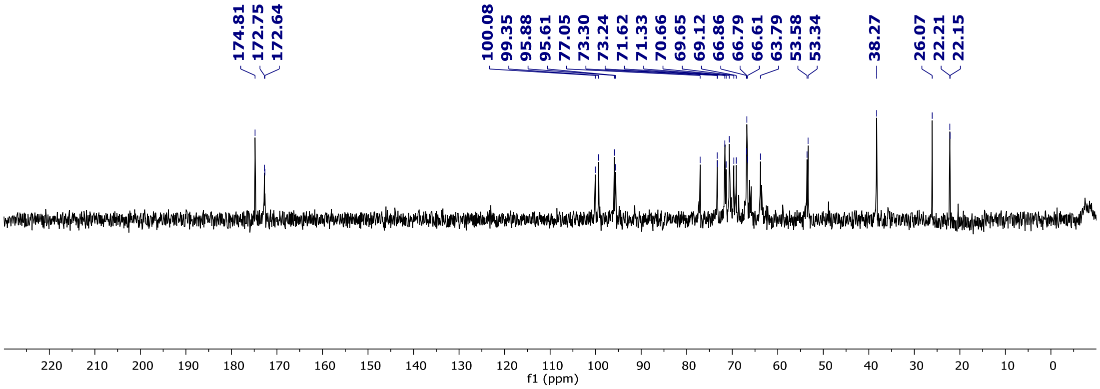


OPO$_3^{2-}$
HO$_2$C
OH
HO
HO
NHAc
O
$^{2-}$O$_3$PO
OPO$_3^{2-}$
HO$_2$C
OH
HO
NHAc
$^{2-}$O$_3$PO
NH$_2$

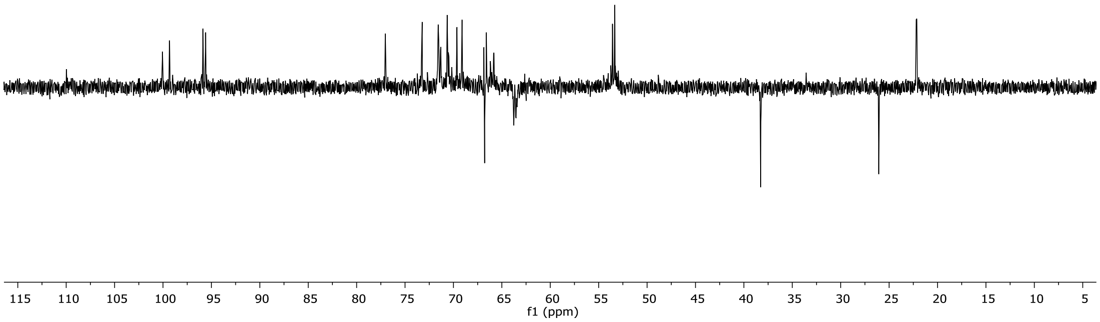
13



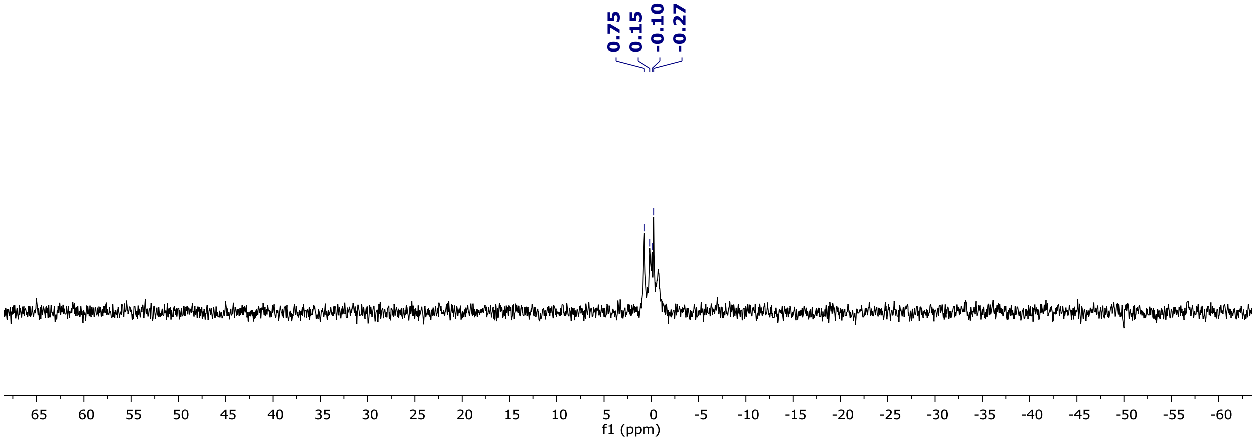
1.12
2.36
0.92
10.02
2.18
4.01
4.34
1.12
1.18
2.00
8.12
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f1 (ppm)



174.81
172.75
172.64
100.08
99.35
95.88
95.61
77.05
73.30
73.24
71.62
71.33
70.66
69.65
69.12
66.86
66.79
66.61
63.79
53.58
53.34
38.27
26.07
22.21
22.15
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)


0.75
0.15
-0.10
-0.27
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
f1 (ppm)