Supporting Information

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NMR spectra **See NMR spectra file**

Animal study ethics statement

All animal care procedures and experimental protocols have been approved by the Institutional Animal Care and Use Committee (IACUC) of Michigan State University (**protocol number:** 202200444).

General experimental procedures

All chemical reactions were carried out under nitrogen with anhydrous solvents in flame-dried glassware, unless otherwise noted. Glycosylation reactions were performed in the presence of molecular sieves, which were flame–dried right before the reaction under high vacuum. Glycosylation solvents were dried using a solvent purification system and used directly without further drying. Chemicals used were reagent grade as supplied except where noted. Analytical thin-layer chromatography was performed using silica gel 60 F254 glass plates. Compounds were visualized by UV light (254 nm) and by staining with a yellow solution containing $Ce(NH_4)_2(NO_3)_6$ (0.5 g) and $(NH_4)_6Mo_7O_{24}\bullet 4H_2O$ (24.0 g) in 6% H_2SO_4 (500 mL). Flash column chromatography was performed on silica gel 60 (230-400 Mesh). Optical rotations were recorded on a Perkin Elemer 341 Polarimeter (λ= 589 nm, 1 dm cell). No unexpected or unusually high safety hazards were encountered during this work.

Mass spectrometry (MS) analysis

ESI-MS measurements were performed according to the published procedures[1] on a Q-TOF Ultima API LC-MS instrument with Waters 2795 Separation Module (Waters Corporation, Milford, MA). MALDI mass spectra were recorded on a Shimadzu Axima-CFR plus MALDI-TOF. The matrix used was 2,5-dihydroxy-benzoic acid (DHB) as the calibration compound.

Nuclear magnetic resonance analysis

Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on an Agilent-500MHz spectrometer at ambient temperature with $CDCl_3$ as the solvent unless otherwise stated. Chemical shifts are reported in parts per million (ppm) relative to residual protic solvent internal standard $CDCl_3$: ^{1}H NMR at δ 7.26 ppm, ^{13}C NMR at δ 77.36 ppm. All ^{13}C NMR spectra were recorded with complete proton decoupling. Peak and coupling constants assignments are based on ^{1}H-NMR, ^{13}C-NMR, ^{1}H-^{1}H gCOSY and (or) ^{1}H-^{13}C gHSQC and ^{1}H-^{13}C gHMBC experiments.

Characterization of anomeric stereochemistry

The stereochemistry of the newly formed glycosidic linkages in the oligosaccharides and intermediates are determined by $^3J_{(H1, H2)}$ through ^{1}H-NMR and/or $^1J_{(C1, H1)}$ through gHSQC 2-D NMR (without ^{1}H decoupling). For galactosyl and glucosyl building blocks, the smaller coupling constants of $^3J_{(H1, H2)}$ (around 3 Hz) indicate α linkages and larger coupling constants $^3J_{(H1, H2)}$ (7.5 Hz or larger) indicate β linkages. For all glycosyl linkages, the stereochemistry can be further

confirmed as larger $^{1}J_{(C1,\ H1)}$ (around 170 Hz) suggests α linkages and smaller $^{1}J_{(C1,\ H1)}$ (around 160 Hz) for β linkages.[2]

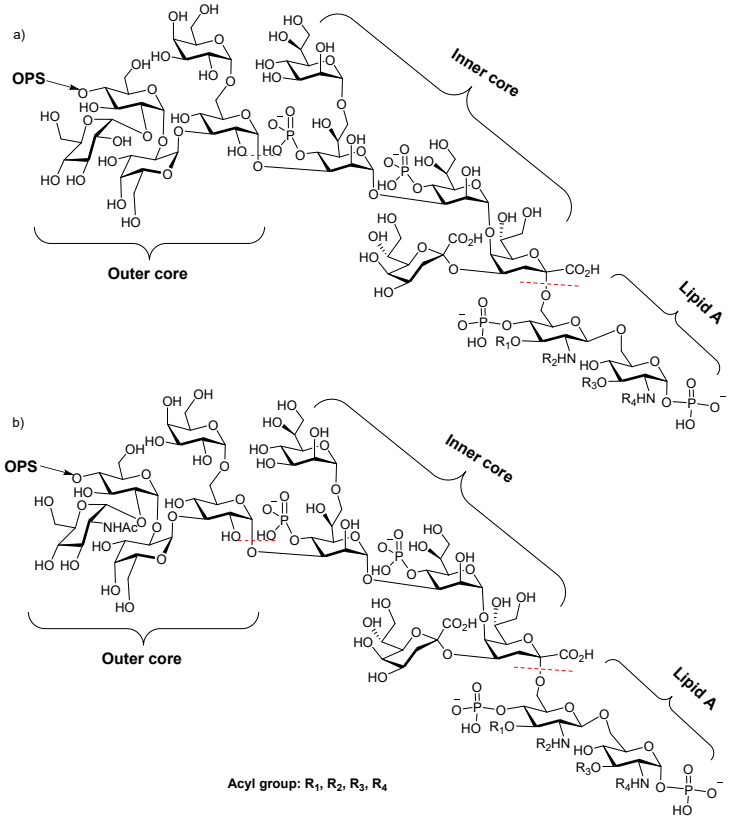
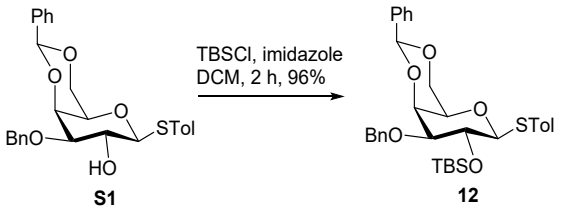


Figure S1. Chemical structures of *Salmonella* LPS including: a) *S. enterica* subsp. IIIa (R1) and b) *S. enterica* subsp. I (R2).

Experimental procedures and characterization data:

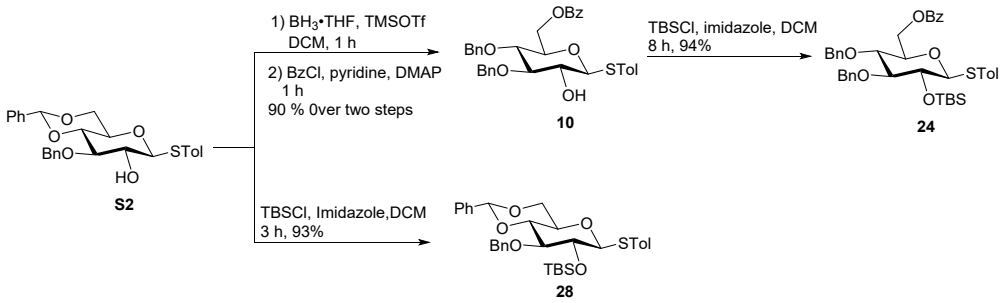


Scheme S1. Synthesis of monosaccharide donor **12**

***p*-Tolyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-tert-butyldimethylsilyl-1-thio-β-D-galactopyranoside (12)**

To a solution of compound **S1**[3] (2 g, 3.5 mmol) in CH_2Cl_2 (DCM) (35 mL), imidazole (0.6 g, 8.8 mmol) and TBSCl (0.8 g, 5.3 mmol) were added. The reaction was stirred at room temperature for

2 hours, then quenched with MeOH. The mixture was extracted with DCM and washed with water and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (10:1, hexanes/ethyl acetate), yielding compound **12** (2.4 g, 96% yield). $[\alpha]_D^{20}$ -65.7 (*c* 0.21, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55-7.53 (m, 2H), 7.50-7.49 (m, 2H), 7.45-7.35 (m, 5H), 7.33-7.25 (m, 3H), 7.01 (d, *J* = 7.7 Hz, 2H), 5.36 (s, 1H), 4.67 (d, *J* = 12.1 Hz, 1H), 4.63 (d, *J* = 12.1 Hz, 1H), 4.52 (d, *J* = 9.0 Hz, 1H), 4.32 (dd, *J* = 12.3, 1.6 Hz, 1H), 4.08 (dd, *J* = 3.5, 1.1 Hz, 1H), 4.02 (t, *J* = 9.0 Hz, 1H), 3.93 (dd, *J* = 12.3, 1.8 Hz, 1H), 3.42 (dd, *J* = 9.0, 3.5 Hz, 1H), 3.37-3.35 (m, 1H), 2.31 (s, 3H), 0.94 (s, 9H), 0.08 (s, 3H), 0.03 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.52, 138.17, 136.99, 132.09, 130.65, 129.56, 129.00, 128.34, 128.23, 127.97, 127.75, 126.60, 101.18, 89.52, 82.43, 73.01, 71.25, 69.77, 69.57, 69.21, 26.30, 21.26, 18.58, -3.54, -4.42. HRMS (ESI): *m*/*z* calcd for $C_{33}H_{42}O_{5S}Si[M+NH_4]^+$: 596.2866, found: 596.2881.



Scheme S2. Synthesis of monosaccharide donors **24** and **28**

***p*-Tolyl 3,4-di-*O*-benzyl-6-*O*-benzoyl-1-thio-β-D-glucopyranoside (10)**

To a solution of compound **S2** (4.7 g, 10.1 mmol) in DCM (100 mL) was added BH_3·THF (53.3 mL, 53.3 mmol) and TMSOTf (0.3 mL, 1.5 mmol) at 0 °C. The mixture was stirred at room temperature for 3 h until TLC showed complete conversion of the starting material. The mixture was cooled down to 0 °C and quenched with MeOH. Organic layer was washed with saturated $NaHCO_3$, dried over Na_2SO_4 and concentrated. The crude mixture was purified by silica gel flash chromatography (3:1, hexanes/ethyl acetate) to give colorless syrup. The obtained compound was dissolved in pyridine (50 mL), cooled to 0 °C and BzCl (0.8 mL, 10.2 mmol) was added dropwise. After 1 h, the solution was diluted with DCM and washed with 1 M HCl, dried over Na_2SO_4, and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by flash chromatography (5:1, hexanes/ethyl acetate) to afford **10** (5.2 g, 90% over two steps) as a white solid. $[\alpha]_D^{20}$ +24.1 (*c* 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02-8.0 (m, 2H), 7.62-7.57 (m, 1H), 7.47-7.42 (m, 2H), 7.41-7.35 (m, 4H), 7.34-7.30 (m, 2H), 7.30-7.20 (m, 6H), 6.90 (d, *J* = 7.9 Hz, 2H), 4.96 (d, *J* = 11.0 Hz, 1H), 4.87 (d, *J* = 11.0 Hz, 1H), 4.84 (d, *J* = 11.0 Hz, 1H), 4.69 (dd, *J* = 11.9, 2.1 Hz, 1H), 4.59 (d, *J* = 11.0 Hz, 1H), 4.46 (d, *J* = 9.3 Hz, 1H), 4.44 (dd, *J* = 11.9, 4.5 Hz), 3.69-3.63 (m, 2H), 3.59-3.55 (m, 1H), 3.43 (t, *J* = 9.3 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.16, 138.67, 138.34, 137.65, 134.14, 133.21, 130.04, 129.90, 129.76, 128.67,

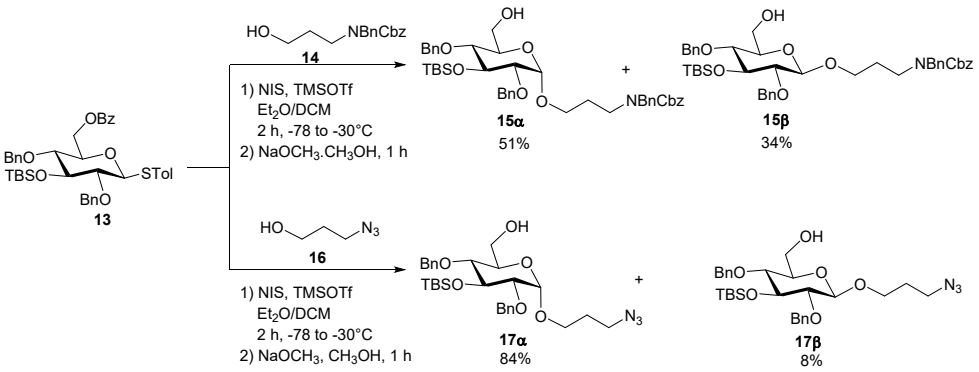
128.62, 128.47, 128.26, 128.24, 128.12, 128.04, 126.84, 87.75, 85.96, 77.31, 76.99, 75.63, 75.33, 72.44, 63.35, 21.26. HRMS (ESI): *m*/*z* calcd for $C_{34}H_{34}O_6S[M+NH_4]^+$: 588.2420, found: 588.2431.

_p_-Tolyl 3,4-di-*O*-benzyl-6-*O*-benzoyl-2-*O*-tert-butyldimethylsilyl-1-thio-β-D-glucopyranoside (24)

To a solution of compound **10** (3 g, 5.3 mmol) in DCM (50 mL), imidazole (0.9 g, 13.2 mmol) and TBSCl (1.2 g, 8 mmol) were added. The reaction was stirred at room temperature for 8 hours, then quenched with MeOH. The mixture was extracted with DCM and washed with water and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (10:1, hexanes/ethyl acetate), yielding compound **24** (3.5 g, 94% yield). $[\alpha]_D^{20}$ -61.4 (*c* 0.05, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.0 Hz, 2H), 7.63-7.59 (m, 1H), 7.51-7.37 (m, 4H), 7.37-7.31 (m, 4H), 7.29-7.26 (m, 1H), 7.25-7.21 (m, 3H), 7.15 (d, *J* = 7.9, 2H), 6.92 (d, *J* = 7.9 Hz, 2H), 4.98 (d, *J* = 11.7 Hz, 1H), 4.89 (d, *J* = 11.7 Hz, 1H), 4.76 (d, *J* = 10.7 Hz, 1H), 4.63 (dd, *J* = 11.8, 2.0 Hz, 1H), 4.55 (dd, *J* = 10.0, 5.7 Hz, 2H), 4.38 (dd, *J* = 11.8, 6.6 Hz, 1H), 3.70-3.68 (m, 2H), 3.62 (t, *J* = 9.2 Hz, 1H), 3.56 (t, *J* = 8.5 Hz, 1H), 2.26 (s, 3H), 0.94 (s, 9H), 0.25 (s, 3H), 0.04 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.36, 138.66, 137.52, 137.48, 133.21, 132.14, 131.06, 130.12, 129.96, 129.70, 128.63, 128.51, 128.40, 128.20, 128.16, 127.39, 126.87, 90.38, 87.32, 78.89, 77.21, 75.43, 75.26, 73.88, 64.17, 26.31, 21.26, 18.39, -3.22, -3.60. HRMS (ESI): *m*/*z* calcd for $C_{40}H_{48}O_6SSi[M+NH_4]^+$: 702.3285, found: 702.3291.

_p_-Tolyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-tert-butyldimethylsilyl-1-thio-β-D-glucopyranoside (28)

To a solution of compound **S2**[4] (1 g, 2.2 mmol) in DCM (22 mL), imidazole (0.4 g, 5.5 mmol) and TBSCl (0.5 g, 2.6 mmol) were added. The reaction was stirred at room temperature for 2 hours, then quenched with MeOH. The mixture was extracted with DCM and washed with water and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (10:1, hexanes/ethyl acetate), yielding compound **28** (1.2 g, 93% yield). $[\alpha]_D^{20}$ -81.1 (*c* 0.34, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46-7.40 (m, 4H), 7.40-7.25 (m, 8H), 7.15 (d, *J* = 7.9 Hz, 2H), 5.56 (s, 1H), 5.03 (d, *J* = 11.1 Hz, 1H), 4.72 (d, *J* = 11.1 Hz, 1H), 4.69-4.65 (m, 1H), 4.37 (dd, *J* = 10.5, 5.0 Hz, 1H), 3.81 (t, *J* = 10.5 Hz, 1H), 3.78-3.73 (m, 1H), 3.71-3.64 (m, 2H), 3.54-3.45 (m, 1H), 2.36 (s, 3H), 0.96 (s, 9H), 0.21 (s, 3H), 0.09 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.64, 137.78, 137.36, 132.14, 130.63, 129.83, 129.07, 128.35, 128.29, 127.96, 127.53, 126.10, 126.09, 101.31, 90.96, 83.38, 82.20, 74.62, 73.87, 69.95, 68.90, 26.30, 21.27, 18.49, -3.43, -4.09. HRMS (ESI): *m*/*z* calcd for $C_{33}H_{42}O_5SSi[M+NH_4]^+$: 596.2866, found:596.2879.



Scheme S3. Synthesis of monosaccharide acceptors **15** and **17**.

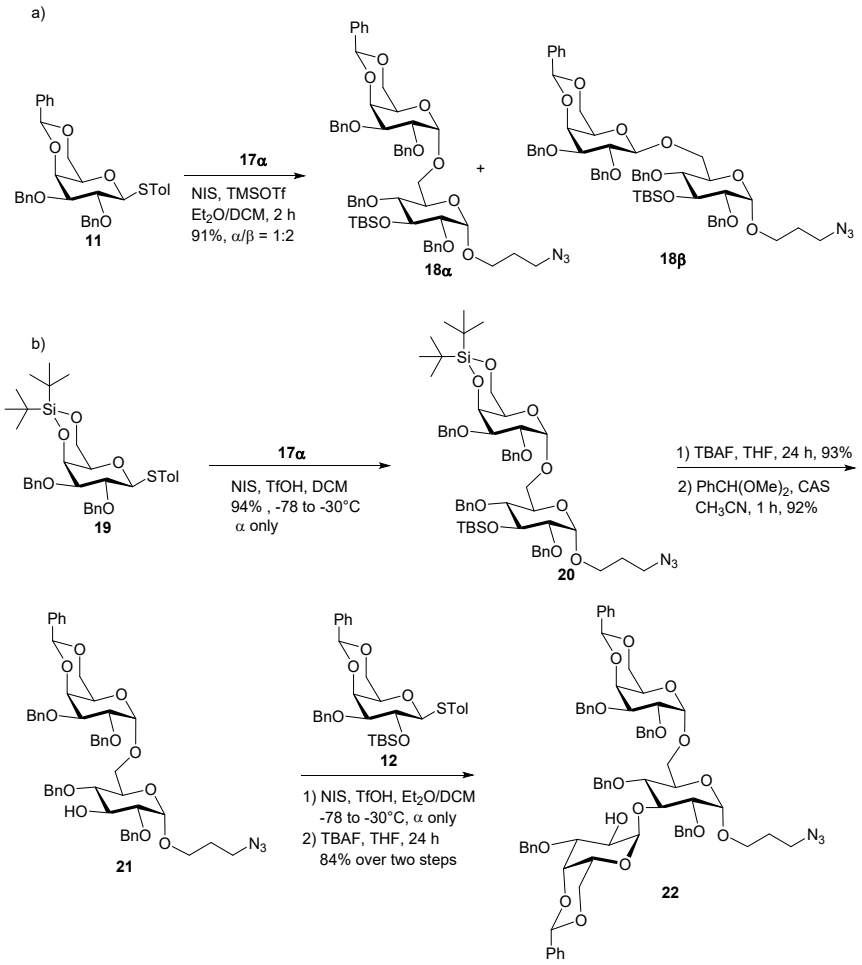
***N*-(Benzyl)benzyloxycarbonyl-3-aminopropyl 2,4-di-*O*-benzyl-3-*O*-tert-butyldimethylsilyl-α/β-D-glucopyranoside (15α/β)**

A mixture of galactose donor **13**[5] (680 mg, 1 mmol), acceptor protected 3-amino-1-propanol **14** (359 mg, 1.2 mmol), and freshly activated 4 Å molecular sieves in CH_2Cl_2/Et_2O (v/v = 1:1, 2 mL) were stirred for 15 minutes at room temperature. The suspension was cooled to -78 °C and then NIS (338 mg, 1.5 mmol) and TfOH (9 µL, 0.1 mmol) were added. The reaction mixture was gradually warmed to -30 °C and stirred for 1 h at the same temperature. Then, the mixture was quenched with triethylamine, diluted with CH_2Cl_2 and filtered. The filtrate was concentrated *in vacuo*. The obtained residue was dissolved in MeOH (5 mL). The solution was cooled to 0 °C and NaOMe (32 mg, 0.5 mmol) was added. After stirring 1 h at room temperature, the mixture was neutralized with DOWEX-H^+ ion exchange resins, filtered and concentrated. The residue was purified by flash chromatography (3:1, hexanes/ethyl acetate) to afford **15β** and **15α** (638 mg, 85% over two steps). **15β:** $[\alpha]_D^{20}$ -34.1 (*c* 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.06 (m, 20H), 5.18-5.10 (m, 2H), 4.85 (d, *J* = 11.4 Hz, 1H), 4.89-4.74 (m, 1H), 4.61 (d, *J* = 11.4 Hz, 1H), 4.69-4.54 (m, 1H), 4.50-4.39 (m, 2H), 4.38-4.25 (m, 1H), 3.88-3.74 (m, 2H), 3.71-3.64 (m, 2H), 3.57-3.44 (m, 1H), 3.40 (t, *J* = 9.3 Hz, 2H), 3.31-3.09 (m, 3H), 1.91-1.69 (m, 2H), 0.91 (s, 9H), 0.04 (s, 3H), -0.00 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.84, 156.29, 138.82, 138.19, 137.83, 136.68, 128.69, 128.65, 128.55, 128.53, 128.48, 128.33, 128.25, 128.08, 127.96, 127.87, 127.77, 127.63, 127.42, 127.31, 127.24, 104.10, 103.71, 82.58, 82.48, 78.80, 78.63, 76.59, 75.19, 75.03, 74.61, 68.17, 67.35, 62.00, 50.54, 44.80, 43.50, 28.43, 26.14, 18.15, -3.88, -4.06. HRMS (ESI): *m*/*z* calcd for $C_{44}H_{57}NO_8Si[M+NH_4]^+$: 773.4197, found: 773. 4215.

15α: $[\alpha]_D^{20}$ +50.3 (*c* 0.18, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51-7.15 (m, 20H), 5.15 (d, *J* = 12.9 Hz, 2H), 4.86 (d, *J* = 11.4 Hz, 1H), 4.67 (d, *J* = 12.2 Hz, 1H), 4.58 (d, *J* = 11.4 Hz, 1H), 4.55-4.39 (m, 4H), 4.00 (t, *J* = 9.0 Hz, 1H), 3.71-3.46 (m, 4H), 3.37-3.10 (m, 5H), 1.84-1.70 (m, 2H), 0.92 (s, 9H), 0.07 (s, 3H), 0.05 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.57, 138.34, 137.98, 128.70, 128.51, 128.46, 128.18, 128.07, 127.90, 127.86, 127.51, 97.21, 80.61, 78.93, 75.12, 73.91, 73.41, 71.00, 67.33, 65.41, 62.02, 51.05, 44.77, 28.46, 26.22, 18.27, -3.77, -4.11. HRMS (ESI): *m*/*z* calcd for $C_{44}H_{57}NO_8Si[M+NH_4]^+$: 773.4197, found: 773. 4226.

3-Azidopropyl 2,4-di-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-α-D-glucopyranoside (17α)

A mixture of galactose donor **11** (960 mg, 1.4 mmol), acceptor 3-azidopropan-1-ol **16** (170 mg, 1.7 mmol), and freshly activated 4 Å molecular sieves in CH_2Cl_2/Et_2O (v/v = 1:1, 2 mL) were stirred for 15 minutes at room temperature. The suspension was cooled to -78 °C and then NIS (473 mg, 0.66 mmol) and TfOH (51 μL, 0.28 mmol) were added. The reaction mixture was gradually warmed to -30 °C and stirred for 1 h at the same temperature. Then, the mixture was quenched with triethylamine, diluted with CH_2Cl_2 and filtered. The filtrate was concentrated *in vacuo*. The obtained residue was dissolved in MeOH (2 mL), the solution was cooled to 0 °C and NaOMe (112 mg, 1.6 mmol) was added. After stirring 1 h at room temperature, the mixture was neutralized with DOWEX-H^+ ion exchange resins, filtered and concentrated. The residue was purified by flash chromatography (3:1, hexanes/ethyl acetate) to afford **17α** (790 mg, 84%) as white solid. $[\alpha]_D^{20}$ +48.4 (*c* 0.14, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.20 (m, 10H), 4.89 (d, *J* = 11.5 Hz, 1H), 4.73 (d, *J* = 12.1 Hz, 1H), 4.61 (d, *J* = 11.5 Hz, 1H), 4.56 (d, *J* = 3.7 Hz, 1H, H-1), 4.49 (d, *J* = 12.1 Hz, 1H), 4.03 (t, *J* = 9.0 Hz, 1H), 3.71 (dd, *J* = 11.8, 2.8 Hz, 1H), 3.68-3.61 (m, 2H), 3.60-3.56 (m, 1H), 3.43-3.36 (m, 3H), 3.34-3.30 (m, 1H), 3.28 (dd, *J* = 9.3, 3.5 Hz, 1H), 1.91-1.78 (m, 2H), 0.94 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.64, 138.32, 128.56, 128.52, 128.15, 127.96, 127.92, 127.87, 97.34, 80.72, 78.75, 77.42, 77.17, 76.91, 75.17, 73.93, 73.50, 71.11, 64.71, 61.96, 48.46, 28.97, 26.24, 18.29, -3.77, -4.10. HRMS (ESI): *m*/*z* calcd for $C_{29}H_{43}N_3O_6Si$ $[M+NH_4]^+$: 575.3265, found: 575.3275.



Scheme S4. Synthesis of trisaccharide acceptor **22**.

3-Azidopropyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α/β-D-galactopyranosyl-(1→6)-2,4-di-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-α-D-glucopyranoside (18)

A mixture of galactose donor **11**[6] (244 mg, 0.44 mmol), acceptor **17α** (206 mg, 0.37 mmol), and freshly activated 4 Å molecular sieves in CH_2Cl_2/Et_2O (v/v = 1:1, 7 mL) were stirred for 15 minutes at room temperature. The suspension was cooled to -78 °C and then NIS (149 mg, 0.66 mmol) and TfOH (4 μL, 44 μmol) were added. The reaction mixture was gradually warmed to -30 °C and stirred for 1 h at the same temperature. Then, the mixture was quenched with triethylamine, diluted with CH_2Cl_2 and filtered. The filtrate was concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (10:1, hexanes/ethyl acetate) to afford **18** (294 mg, 91%) as colorless syrups. **18β**: $[\alpha]_D^{20}$ -14.1 (*c* 0.14, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54-7.53 (m, 2H), 7.40-7.17 (m, 23H), 5.47 (s, 1H), 4.96 (d, *J* = 11.7 Hz, 1H), 4.82 (d, *J* = 11.0 Hz, 1H), 4.75 (d, *J* = 2.5 Hz, 2H), 4.71 (d, *J* = 12.2 Hz, 2H), 4.64 (d, *J* = 3.5 Hz, 1H), 4.53 (d, *J* = 11.7 Hz, 1H), 4.48 (d, *J* = 12.2 Hz, 1H), 4.27-4.23 (m, 2H), 4.16 (dd, *J* = 11.0, 2.2 Hz, 1H), 4.07 (dd, *J* = 3.7, 1.0 Hz, 1H), 4.01 (t, *J* = 9.0 Hz, 1H), 3.97 (dd, *J* = 12.3, 1.8 Hz, 1H), 3.90-3.88 (m, 1H), 3.78-3.76 (m, 1H), 3.70-3.60 (m, 2H), 3.51 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.40 (dd, *J* = 10.1, 8.7 Hz, 1H), 3.34-

3.24 (m, 4H), 3.20 (s, 1H), 1.77 (p, *J* = 6.5 Hz, 2H), 0.92 (s, 9H), 0.08 (s, 3H), 0.01 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.03, 138.77, 138.65, 138.50, 137.97, 129.05, 128.49, 128.47, 128.43, 128.40, 128.31, 128.25, 128.12, 127.93, 127.90, 127.88, 127.84, 127.59, 127.39, 127.36, 126.59, 104.12, 101.32, 97.08, 80.60, 79.47, 79.44, 78.24, 75.38, 74.83, 73.97, 73.87, 73.38, 72.03, 70.19, 69.20, 68.56, 66.53, 64.62, 48.46, 28.84, 26.25, 18.27, -3.78, -4.16; **18α**: $[\alpha]_D^{20}$ +34.1 (*c* 0.15, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51-7.49 (m, 2H), 7.41-7.20 (m, 23H), 5.44 (s, 1H), 5.11 (d, *J* = 3.5 Hz, 1H), 4.89 (d, *J* = 11.8 Hz, 1H), 4.77 (d, *J* = 5.0 Hz, 2H), 4.74 (s, 2H), 4.60 (d, *J* = 12.1 Hz, 1H), 4.55-4.50 (m, 2H), 4.35 (d, *J* = 12.1 Hz, 1H), 3.98 (t, *J* = 9.1 Hz, 1H), 3.92 (dd, *J* = 10.1, 3.5 Hz, 1H), 3.84 (dd, *J* = 12.5, 1.8 Hz, 1H), 3.77-3.64 (m, 3H), 3.61-3.59 (m, 1H), 3.47 (t, *J* = 9.3 Hz, 1H), 3.40 (d, *J* = 1.6 Hz, 1H), 3.36-3.33 (m, 2H), 3.27-3.25 (m, 1H), 3.15 (dd, *J* = 9.3, 3.6 Hz, 1H), 1.82-1.70 (m, 2H), 0.95 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.07, 138.81, 138.80, 138.70, 137.96, 129.02, 128.48, 128.44, 128.42, 128.25, 127.97, 127.92, 127.83, 127.72, 127.57, 127.52, 127.50, 127.29, 126.51, 101.21, 98.43, 97.12, 80.89, 79.51, 75.81, 75.04, 74.89, 74.86, 74.05, 73.33, 72.60, 71.90, 70.75, 69.48, 66.31, 64.57, 62.70, 48.47, 28.91, 26.25, 18.31, -3.80, -4.14. HRMS (ESI): *m*/*z* calcd for: $C_{56}H_{69}N_3O_{11}Si[M+NH_4]^+$: 1005.5045, found: 1005.5081.

3-Azidopropyl 2,3-di-*O*-benzyl-4,6-*O*-di-*tert*-butylsilanediyl-α-D-galactopyranosyl-(1→6)-2,4-di-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-α-D-glucopyranoside (20)

A mixture of galactose donor **19**[7] (264 mg, 0.44 mmol), acceptor **17α** (218 mg, 0.39 mmol), and freshly activated 4 Å molecular sieves in CH_2Cl_2/Et_2O (v/v = 1:1, 4 mL) were stirred for 15 minutes at room temperature. The suspension was cooled to -78 °C and then NIS (148 mg, 0.66 mmol) and TfOH (5 μL, 44 μmol) were added. The reaction mixture was gradually warmed to -30 °C and stirred for 1 h at the same temperature. Then, the mixture was quenched with triethylamine, diluted with CH_2Cl_2 and filtered. The filtrate was concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (10:1, hexanes/ethyl acetate) to afford **20** (385 mg, 94%) as colorless syrups. $[\alpha]_D^{20}$ +51.3 (*c* 0.3, $CHCl_3$);^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.38 (m, 4H), 7.33-7.27 (m, 13H), 7.25-7.20 (m, 3H), 4.96 (d, *J* = 3.6 Hz, 1H), 4.89 (d, *J* = 12.2 Hz, 1H), 4.81-4.75 (m, 1H), 4.74 (d, *J* = 8.1 Hz, 2H), 4.69 (d, *J* = 12.2 Hz, 1H), 4.62 (d, *J* = 12.2 Hz, 1H), 4.52 (dd, *J* = 7.7, 4.0 Hz, 2H), 4.42 (dd, *J* = 3.0, 1.1 Hz, 1H), 4.37 (d, *J* = 12.2 Hz, 1H), 4.07-3.95 (m, 4H), 3.76 (dd, *J* = 10.0, 3.1 Hz, 1H), 3.72 (dd, *J* = 11.3, 4.1 Hz, 1H), 3.70-3.66 (m, 2H), 3.63-3.59 (m, 1H), 3.47 (t, *J* = 9.4 Hz, 1H), 3.43 (s, 1H), 3.37-3.31 (m, 2H), 3.30-3.22 (m, 1H), 3.16 (dd, *J* = 9.3, 3.6 Hz, 1H), 1.84-1.72 (m, 2H), 1.04 (s, 9H), 0.99 (s, 9H), 0.94 (s, 9H), 0.07 (s, 3H), 0.05 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.03, 139.01, 138.78, 138.73, 128.43, 128.40, 128.36, 128.34, 127.97, 127.95, 127.81, 127.78, 127.77, 127.75, 127.65, 127.62, 127.59, 127.54, 127.48, 127.23, 98.27, 97.14, 80.84, 79.56, 76.74, 75.02, 74.49, 74.04, 73.34, 72.62, 71.20, 70.74, 70.67, 67.28, 67.24, 66.19, 64.57, 48.48, 28.93, 27.79, 27.44, 26.24, 23.53, 20.78, 18.29, -3.81, -4.16; HRMS (ESI): *m*/*z* calcd for $C_{57}H_{81}N_4O_{11}Si_2[M+NH_4]^+$: 1057.5753, found: 1057.5785.

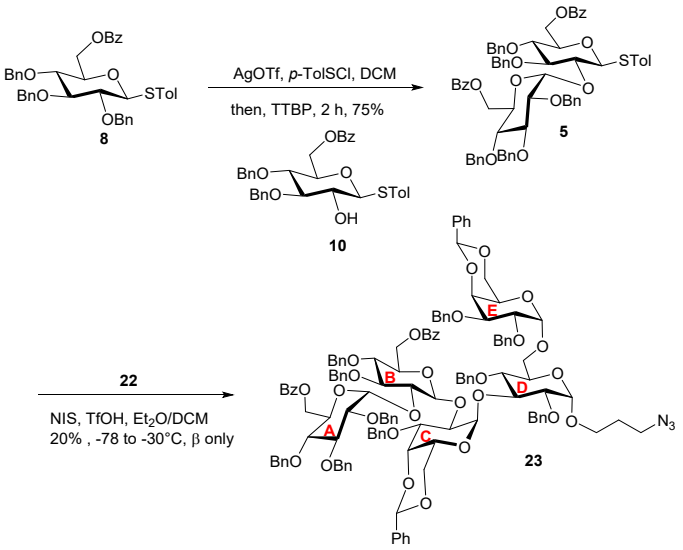
3-Azidopropyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranosyl-(1→6)-2,4-di-*O*-benzyl-α-D-glucopyranoside (21)

To a solution of **20** (220 mg, 0.21 mmol) in pyridine (2 ml) and HF·pyridine (70% HF in pyridine, 0.2 mL), and the solution was stirred for 3 h at room temperature. The reaction mixture was diluted with DCM, washed with saturated aqueous $NaHCO_3$, dried over Na_2SO_4, and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by flash chromatography (DCM/MeOH, 40:1). The obtained product was dissolved in CH_3CN and camphorsulfonic acid (CSA) (24 mg, 0.1 mmol) and $PhCH(OMe)_2$ (63 μL, 0.42 mmol) were added. After stirring for 1 hour at room temperature, the reaction mixture was diluted with DCM, washed with saturated aqueous $NaHCO_3$, dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (3:1, hexanes/ethyl acetate) to yield compound **21** as a white solid (157 mg, 83% yield over two steps). $[\alpha]_D^{20}$ +26.7 (*c* 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53-7.51 (m, 2H), 7.42-7.26 (m, 23H), 5.46 (s, 1H), 5.10 (d, *J* = 3.4 Hz, 1H), 4.93 (d, *J* = 12.0 Hz, 1H), 4.82 (dd, *J* = 12.0, 2.3 Hz, 2H), 4.76 (d, *J* = 12.0 Hz, 1H), 4.71 (d, *J* = 12.0 Hz, 1H), 4.69 (d, *J* = 3.5 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 2H), 4.54 (d, *J* = 12.0 Hz, 1H), 4.16-4.03 (m, 4H), 3.96 (dd, *J* = 10.1, 3.4 Hz, 1H), 3.86 (dd, *J* = 12.5, 1.8 Hz, 1H), 3.82 (dd, *J* = 11.4, 4.4 Hz, 1H), 3.77-3.65 (m, 3H), 3.58 (t, *J* = 9.3 Hz, 1H), 3.51 (d, *J* = 1.5 Hz, 1H), 3.42-3.30 (m, 3H), 3.26 (dd, *J* = 9.6, 3.5 Hz, 1H), 1.83-1.76 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.07, 138.84, 138.72, 138.11, 137.96, 129.01, 128.71, 128.57, 128.45, 128.43, 128.24, 128.22, 128.05, 127.82, 127.80, 127.70, 127.59, 126.49, 101.20, 98.53, 96.50, 80.05, 77.68, 75.79, 75.35, 74.86, 74.50, 73.50, 73.04, 72.96, 72.00, 70.27, 69.48, 66.46, 64.64, 62.74, 48.35, 28.93. HRMS (ESI): *m*/*z* calcd for $C_{50}H_{55}N_3O_{11}[M+NH_4]^+$: 891.4180, found:891.4190.

3-Azidopropyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranosyl)-α-D-glucopyranoside (22)

A mixture of galactose donor **12** (460 mg, 0.8 mmol), acceptor **21** (628 mg, 0.7 mmol), and freshly activated 4 Å molecular sieves in CH_2Cl_2/Et_2O (v/v = 1:1, 1.5 mL) were stirred for 15 minutes at room temperature. The suspension was cooled to -78 °C and then NIS (270 mg, 1.2 mmol) and TfOH (7 μL, 0.08 mmol) were added. The reaction mixture was gradually warmed to -30 °C and stirred for 1 h at the same temperature. Then, the mixture was quenched with triethylamine, diluted with CH_2Cl_2 and filtered. The filtrate was concentrated *in vacuo*. The obtained residue was dissolved in THF (2 mL). The solution was cooled to 0 °C and TBAF (0.2 mL) was added. After stirring 1 h at room temperature, the mixture was concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (5:1, hexanes/ethyl acetate) to afford **22** (815 mg, 84% over two steps) as colorless syrups. $[\alpha]_D^{20}$ +71.2 (*c* 0.25, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63-7.04 (m, 35H), 5.60 (d, *J* = 3.8 Hz, 1H), 5.49 (s, 1H), 5.27 (s, 1H), 5.19 (d, *J* = 3.5 Hz, 1H), 5.03 (d, *J* = 10.8 Hz, 1H), 4.87-4.81 (m, 2H), 4.83 (d, *J* = 3.6 Hz, 1H), 4.81-4.75 (m, 3H), 4.73 (d, *J* = 11.9 Hz, 1H), 4.57 (d, *J* = 10.8 Hz, 1H), 4.51 (d, *J* = 10.7 Hz, 1H), 4.26 (d, *J* = 10.7 Hz, 1H), 4.24-4.15 (m, 4H), 4.11 (dd, *J* = 10.0, 3.5 Hz, 1H), 3.98 (dd, *J* = 10.0, 3.5 Hz, 1H), 3.96-3.91 (m,

2H), 3.90-3.83 (m, 3H), 3.80-3.71 (m, 5H), 3.54 (s, 1H), 3.49-3.35 (m, 3H), 3.33-3.25 (m, 2H), 2.36 (d, J = 6.2 Hz, 1H), 1.84 (p, J = 6.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.23, 138.76, 138.49, 138.20, 138.04, 138.01, 137.92, 129.00, 128.83, 128.63, 128.58, 128.51, 128.48, 128.45, 128.42, 128.23, 128.20, 128.15, 128.14, 127.96, 127.88, 127.78, 127.77, 127.75, 127.48, 127.42, 126.47, 126.27, 101.19, 100.73, 98.79, 98.77, 96.38, 79.34, 78.93, 76.62, 75.83, 75.20, 74.79, 74.42, 73.39, 72.66, 72.59, 72.02, 71.12, 70.87, 69.49, 69.45, 67.99, 66.23, 64.53, 62.87, 62.38, 48.29, 28.89. HRMS (ESI): *m/z* calcd for $C_{70}H_{75}N_3O_{16}[M+NH_4]^+$: 1231.5491, found:1231.5533.



Scheme S5. Synthesis of pentasaccharide **23.**

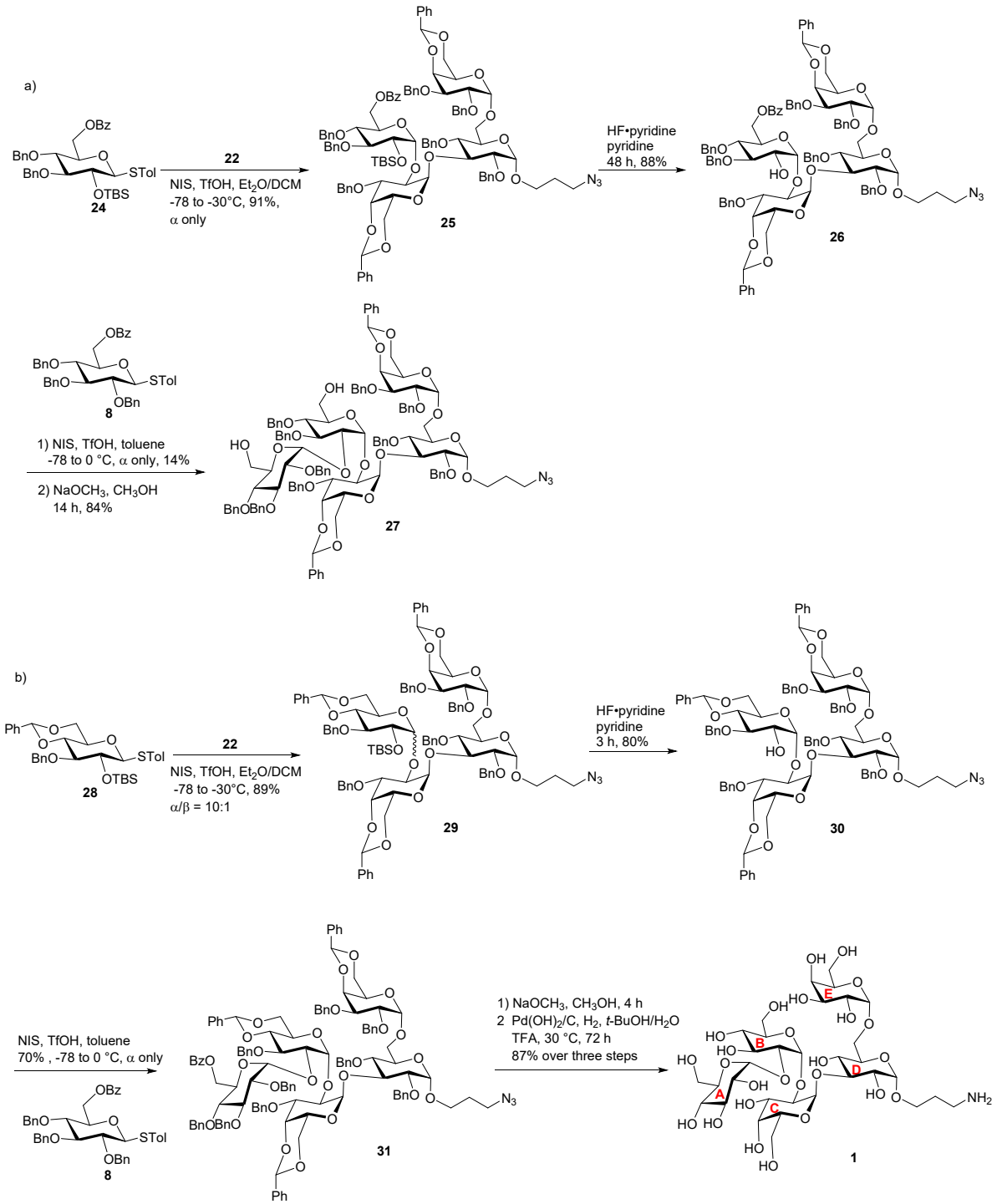
4-Tolyl 6-*O*-benzoyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl-(1→2)- 6-*O*-benzoyl-3,4-di-*O*-benzyl-1-thio-β-D-galactopyranoside (5)

A solution of donor **8**[8] (55.3 mg, 83 μmol) and freshly activated molecular sieve MS 4Å (200 mg) in DCM (2 mL) was stirred for 5 minutes at room temperature, and then cooled to -78 °C. A solution of AgOTf (65 mg, 249 μmol) in anhydrous Et_2O/DCM (0.8 mL/0.2 mL) was added to reaction solution. After 5 min, orange colored *p*-TolSCl (13 μL, 83 μmol) was added to the reaction mixture through a microsyringe. The characteristic orange color of *p*-TolSCl in the reaction solution disappeared rapidly in a few seconds indicating depletion of *p*-TolSCl. After the donor was completely activated according to TLC analysis (about 5 minutes), a solution of acceptor **10** (43 mg, 75 μmol) with one equivalent of TTBP in DCM (1.2 mL) was slowly added via a syringe along the flask wall. The reaction was warmed up to -20 °C under stirring in 2 h. Upon reaction completion, the reaction mixture was quenched by Et_3N and filtered over Celite. The Celite was washed with DCM. After removal of the solvent, the desired oligosaccharide was purified by silica gel flash chromatography (5:1, hexanes/ethyl acetate) to afford **5** (62 mg, 75%) as colorless syrups. $[\alpha]_D^{20}$ +107 (c 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07-8.05 (m, 2H), 8.04-8.02 (m, 2H), 7.66-7.63 (m, 1H), 7.58-7.47 (m, 3H), 7.45-7.24 (m, 23H), 7.23-7.18 (m, 3H), 7.16-7.05 (m, 4H), 6.88 (d, J = 8.2 Hz, 2H), 6.05 (d, J = 3.8 Hz, 1H), 5.06 (d, J = 11.1, 1H), 5.05 (d, J = 11.6 Hz, 1H), 5.00 (d, J = 11.6 Hz, 1H), 4.92 (d, J = 11.0 Hz, 1H), 4.89-4.84 (m, 3H), 4.82 (d, J = 9.4 Hz, 1H),

4.80-4.74 (m, 1H), 4.70 (dd, *J* = 12.0, 2.1 Hz, 1H), 4.61 (d, *J* = 10.6 Hz, 1H), 4.52 (d, *J* = 11.0 Hz, 1H), 4.46 (dd, *J* = 12.0, 5.2 Hz, 1H), 4.38-4.36 (m, 1H), 4.31 (dd, *J* = 12.1, 2.1 Hz, 1H), 4.07 (t, *J* = 9.3 Hz, 1H), 3.95 (t, *J* = 9.2 Hz, 1H), 3.91 (dd, *J* = 12.1, 3.9 Hz, 1H), 3.85 (t, *J* = 8.9 Hz, 1H), 3.75-3.71 (m, 1H), 3.71-3.65 (m, 2H), 3.65-3.59 (m, 1H), 2.23 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.25, 166.20, 138.61, 138.26, 138.07, 138.04, 137.90, 137.57, 137.29, 133.25, 133.03, 132.81, 130.24, 130.01, 129.95, 129.80, 129.76, 129.74, 128.67, 128.63, 128.62, 128.60, 128.55, 128.54, 128.53, 128.50, 128.43, 128.40, 128.36, 128.31, 128.28, 128.27, 128.22, 128.21, 128.19, 127.94, 127.92, 127.85, 127.70, 127.68, 127.53, 127.48, 95.29, 86.97, 84.88, 81.88, 80.04, 78.80, 77.80, 76.91, 76.04, 75.99, 75.39, 75.16, 74.28, 73.28, 68.96, 63.51, 63.26, 21.20. HRMS (ESI): *m*/*z* calcd for $C_{68}H_{66}O_{12}S$ $[M+NH_4]^+$: 1124.4619, found:1124.4634.

3-Azidopropyl 6-*O*-benzoyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl-(1→2)-6-*O*-benzoyl-3,4-di-*O*-benzyl-β-D-glucopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranosyl)-α-D-glucopyranoside (23)

A solution of donor **5** (55.3 mg, 50 μmol), acceptor **22** (51 mg, 42 μmol) and freshly activated molecular sieve MS 4Å (200 mg) in CH_2Cl_2 (DCM) (2 mL) was stirred for 5 minutes at room temperature, and then the suspension was cooled to -78 °C and then NIS (34 mg, 0.15 mmol) and TfOH (1.3 μL, 15 μmol) were added. The reaction mixture was gradually warmed to -10 °C and stirred for 3 h at the same temperature. Then, the mixture was quenched with triethylamine, diluted with CH_2Cl_2 and filtered. The filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography (2:1, hexanes/ethyl acetate) to afford **23** (19 mg, 20%) as colorless syrups. $[\alpha]_D^{20}$ +83.9 (*c* 0.26, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98-7.93 (m, 4H), 7.53-7.50 (m, 3H), 7.36-7.25 (m, 29H), 7.24-7.08 (m, 32H), 7.00 (t, *J* = 7.6 Hz, 2H), 6.17 (d, *J* = 3.5 Hz, 1H), 5.80 (d, *J* = 3.6 Hz, 1H), 5.45 (s, 1H), 5.31 (s, 1H), 5.13 (d, *J* = 10.9 Hz, 1H), 5.01 (d, *J* = 7.8 Hz, 1H), 4.95-4.92 (m, 1H), 4.89 (d, *J* = 4.0 Hz, 1H), 4.86-4.82 (m, 2H), 4.81-4.72 (m, 6H), 4.72-4.62 (m, 5H), 4.52-4.48 (m, 2H), 4.46-4.38 (m, 6H), 4.38-4.34 (m, 2H), 4.33-4.30 (m, 1H), 4.19 (dd, *J* = 9.2, 3.5 Hz, 2H), 4.13 (d, *J* = 3.5 Hz, 1H), 4.11-4.06 (m, 2H), 4.05-4.01 (m, 3H), 3.96 (d, *J* = 3.7 Hz, 2H), 3.92 (dd, *J* = 10.1, 3.4 Hz, 1H), 3.86 (dd, *J* = 12.5, 1.8 Hz, 1H), 3.83-3.78 (m, 1H), 3.71-3.61 (m, 3H), 3.57-3.49 (m, 5H), 3.47-3.38 (m, 5H), 3.28-3.19 (m, 3H), 1.66-1.62 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.24, 139.03, 138.96, 138.66, 138.50, 138.26, 138.38, 138.36, 138.2, 138.02, 137.96, 137.74, 137.61, 133.08, 129.96, 129.74, 128.61, 128.55, 128.51, 128.46, 128.45, 128.43, 128.40, 128.37, 128.35, 128.28, 128.26, 128.24, 128.17, 128.01, 127.99, 127.92, 127.90, 127.64, 127.63, 127.60, 126.49, 126.24, 107.11, 103.53, 101.16, 101.0, 98.43, 98.14, 96.22, 95.85, 94.44, 83.53, 81.73, 80.88, 80.33, 79.89, 79.27, 78.81, 77.36, 75.79, 75.67, 75.13, 73.10, 72.38, 71.80, 70.83, 70.19, 69.52, 64.50, 48.34, 28.65. HRMS (ESI): *m/z* calcd for $C_{131}H_{133}N_3O_{28}$[M+NH_4]+: 2213.9419, found: 2213.9460.



Scheme S6. Synthesis of pentasaccharide **1**.

3-Azidopropyl 6-*O*-benzoyl-3,4-di-*O*-benzyl-2-*O*-tert-butyldimethylsilyl-α-D-glucopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranosyl)-α-D-glucopyranoside (25)

A mixture of galactose donor **24** (273.6 mg, 0.4 mmol), acceptor **22** (400 mg, 0.33 mmol), and freshly activated 4 Å molecular sieves in CH_2Cl_2/Et_2O (v/v = 1:1, 6 mL) were stirred for 15 minutes at room temperature. The suspension was cooled to -78 °C and then NIS (135 mg, 0.6 mmol) and TfOH (4 μL, 0.04 mmol) were added. The reaction mixture was gradually warmed to -30 °C and stirred for 1 h at the same temperature. Then, the mixture was quenched with triethylamine, diluted with CH_2Cl_2 and filtered. The obtained residue was purified by silica gel column chromatography (5:1, hexanes/ethyl acetate) to afford **25** (532 mg, 91%) as colorless syrups. $[\alpha]_D^{20}$ +24.9 (*c* 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 2H), 7.52-7.47 (m, 5H), 7.41-7.34 (m, 12H), 7.33-7.27 (m, 14H), 7.25-7.20 (m, 10H), 7.19-7.12 (m, 7H), 5.85 (d, *J* = 3.3 Hz, 1H), 5.44 (s, 1H), 5.35 (s, 1H), 5.31 (d, *J* = 3.5 Hz, 1H), 5.13 (d, *J* = 11.5 Hz, 1H), 4.92 (d, *J* = 3.5 Hz, 1H), 4.79 (dd, *J* = 12.1, 4.1 Hz, 3H), 4.75 (d, *J* = 3.6 Hz, 1H), 4.71 (d, *J* = 3.7 Hz, 1H), 4.70 (d, *J* = 12.1 Hz, 1H), 4.66 (d, *J* = 12.1 Hz, 2H), 4.62-4.48 (m, 4H), 4.45 (d, *J* = 8.9 Hz, 3H), 4.39-4.30 (m, 5H), 4.15-4.09 (m, 3H), 4.08-4.00 (m, 4H), 3.91 (dd, *J* = 10.0, 3.5 Hz, 2H), 3.88-3.80 (m, 3H), 3.69 (dd, *J* = 9.5, 3.3 Hz, 1H), 3.65-3.60 (m, 2H), 3.58-3.53 (m, 3H), 3.43 (s, 1H), 3.39 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.34-3.29 (m, 1H), 3.28-3.22 (m, 1H), 1.69 (s, 2H), 0.87 (s, 9H), 0.08 (s, 3H), 0.03 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.44, 139.06, 138.93, 138.84, 138.31, 138.17, 138.12, 137.94, 130.08, 129.81, 129.00, 128.60, 128.59, 128.50, 128.41, 128.39, 128.32, 128.29, 128.24, 128.10, 128.08, 127.98, 127.93, 127.80, 127.77, 127.63, 127.60, 127.35, 126.50, 126.44, 101.13, 100.92, 98.83, 98.46, 97.53, 96.36, 82.68, 79.93, 79.43, 78.18, 75.82, 75.60, 75.35, 74.98, 74.73, 74.46, 73.29, 73.01, 72.06, 71.82, 69.97, 69.62, 64.53, 63.80, 62.61, 48.30, 28.81, 26.20, 18.25, -4.08, -4.45; HRMS (ESI): *m*/*z* calcd for $C_{103}H_{115}N_3O_{22}Si[M+ NH_4]^+$: 1791.8085, found: 1791.8093.

3-Azidopropyl 6-*O*-benzoyl-3,4-di-*O*-benzyl-α-D-glucopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranosyl)-α-D-glucopyranoside (26)

To a solution of **25** (550 mg, 0.31 mmol) in pyridine (3 mL), HF·pyridine (70% HF in pyridine, 0.3 mL) was added, and the solution was stirred for 48 h at room temperature. The reaction mixture was diluted with DCM, washed with saturated aqueous $NaHCO_3$, dried over Na_2SO_4, and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by flash chromatography (4:1, hexanes/ethyl acetate) to afford **26** (453 mg, 88%) as a white solid. $[\alpha]_D^{20}$ +92.6 (*c* 0.34, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01-7.95 (m, 2H), 7.60-7.48 (m, 5H), 7.43-7.17 (m, 49H), 5.84 (d, *J* = 3.2 Hz, 1H), 5.46 (s, 1H), 5.45 (s, 1H), 5.07 (d, *J* = 11.1 Hz, 1H), 5.03 (d, *J* = 3.2 Hz, 1H), 5.02 (d, *J* = 3.1 Hz, 1H), 4.86-4.80 (m, 2H), 4.80-4.76 (m, 2H), 4.75 (d, *J* = 3.6 Hz, 1H), 4.74-4.68 (m, 5H), 4.67-4.48 (m, 8H), 4.39 (dt, *J* = 10.1, 2.7 Hz, 1H), 4.33 (dd, *J* = 9.4, 3.3 Hz, 1H), 4.29 (dd, *J* = 12.2, 2.1 Hz, 1H), 4.26-4.20 (m, 2H), 4.17-4.06 (m, 7H), 3.96-3.94 (m, 2H), 3.90 (dd, *J* = 12.2, 1.7 Hz, 1H), 3.79 (d, *J* = 12.3 Hz, 1H), 3.74-3.58 (m, 5H), 3.56-3.45 (m, 3H), 3.35-3.33 (m, 1H), 3.29-3.24 (m, 1H), 3.21-3.19 (m, 1H), 1.68 (p, *J* = 6.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.29, 139.09, 138.90, 138.71, 138.42, 138.37, 138.36, 138.27, 138.21, 138.09, 137.92, 132.94,

130.08, 129.75, 128.98, 128.91, 128.67, 128.63, 128.55, 128.48, 128.47, 128.44, 128.38, 128.36, 128.34, 128.24, 128.22, 128.15, 128.11, 128.07, 128.04, 128.01, 127.94, 127.79, 127.77, 127.74, 127.68, 127.61, 127.57, 127.53, 126.43, 126.34, 101.11, 100.86, 98.40, 96.80, 96.59, 96.38, 82.26, 80.28, 79.33, 78.76, 77.72, 75.81, 75.65, 75.60, 75.11, 74.98, 74.80, 74.69, 74.26, 73.82, 73.26, 73.02, 72.78, 72.54, 71.85, 71.38, 69.60, 69.47, 69.23, 69.00, 66.67, 64.59, 63.40, 62.77, 62.63, 48.19, 28.75. HRMS (ESI): *m*/*z* calcd for $C_{97}H_{101}N_3O_{22}[M+NH_4]^+$: 1677.7220, found:1677.7235.

3-Azidopropyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl-(1→2)-3,4-di-*O*-benzyl-α-D-glucopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranosyl)-α-D-glucopyranoside (27)

A mixture of galactose donor **8** (33 mg, 0.05 mmol), acceptor **26** (33 mg, 0.02 mmol), and freshly activated 4 Å molecular sieves in toluene (8 mL) was stirred for 15 minutes at room temperature. The suspension was cooled to -78 °C and then NIS (34 mg, 0.15 mmol) and TfOH (1.3 μL, 15 μmol) were added. The reaction mixture was gradually warmed to room temperature and stirred for 5 h at the same temperature. Then, the mixture was quenched with triethylamine, diluted with CH_2Cl_2 and filtered. The filtrate was concentrated *in vacuo*. The obtained residue was dissolved in MeOH/CH_2Cl_2 (v/v = 1:1, 2 mL). The solution was cooled to 0 °C and NaOMe (14 mg, 0.2 mmol) was added. After stirring overnight at room temperature, the mixture was neutralized with DOWEX-H^+ ion exchange resins, filtered and concentrated. The residue was purified by flash chromatography (2:1, hexanes/ethyl acetate) to afford **27** (5 mg, 12% over two steps) as colorless syrups. $[\alpha]_D^{20}$ +63.1 (*c* 0.26, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51-7.49 (m, 2H), 7.45-7.00 (m, 58H), 5.79 (d, *J* = 3.4 Hz, 1H), 5.45 (s, 1H), 5.42 (d, *J* = 3.5 Hz, 1H), 5.26 (s, 1H), 4.98 (d, *J* = 12.1 Hz, 1H), 4.94 (d, *J* = 3.5 Hz, 1H), 4.88 (d, *J* = 11.4 Hz, 1H), 4.85-4.81 (m, 3H), 4.79-4.74 (m, 2H), 4.71 (dd, *J* = 8.5, 5.0 Hz, 2H), 4.69-4.64 (m, 3H), 4.61-4.54 (m, 4H), 4.52 (d, *J* = 4.8 Hz, 1H), 4.48 (d, *J* = 15.8 Hz, 1H), 4.45-4.39 (m, 2H), 4.35 (dd, *J* = 10.4, 3.3 Hz, 1H), 4.23 (d, *J* = 10.7 Hz, 1H), 4.18-4.12 (m, 2H), 4.09-3.99 (m, 5H), 3.98-3.88 (m, 4H), 3.84 (t, *J* = 9.9 Hz, 2H), 3.77 (s, 1H), 3.71-3.52 (m, 11H), 3.49 (t, *J* = 9.5 Hz, 1H), 3.43-3.23 (m, 6H), 1.73-1.71 (m, 2H). ^{13}C NMR (200 MHz, $CDCl_3$) δ 139.06, 138.96, 138.84, 138.75, 138.66, 138.62, 138.37, 138.35, 137.93, 137.86, 137.29, 129.00, 128.74, 128.68, 128.65, 128.64, 128.61, 128.54, 128.51, 128.46, 128.44, 128.42, 128.39, 128.33, 128.27, 128.25, 128.18, 128.11, 128.08, 128.00, 127.94, 127.88, 127.81, 127.78, 127.71, 127.69, 127.65, 127.63, 127.60, 127.51, 127.22, 126.49, 126.45, 126.20, 126.15, 101.14, 100.69, 98.53, 96.43, 96.09, 93.56, 81.93, 81.82, 80.93, 79.93, 79.65, 77.86, 75.92, 75.75, 75.69, 75.53, 75.22, 74.89, 74.87, 74.70, 73.86, 73.27, 72.80, 72.74, 71.97, 71.71, 71.51, 71.49, 71.25, 69.57, 69.54, 69.31, 66.88, 64.57, 62.70, 62.19, 61.76, 61.71, 61.61, 52.11, 48.29, 28.77. HRMS (ESI): *m*/*z* calcd for $C_{117}H_{125}N_3O_{26}[M+NH_4]^+$: 2005.8895, found: 2005.8868.

3-Azidopropyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-tert-butyldimethylsilyl-α-D-glucopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranosyl-(1→3)-2,4-di-

***O*-benzyl-6-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranosyl)-α/β-D-glucopyranoside (29)**

A solution of donor **28** (125 mg, 0.22 mmol), acceptor **22** (218.4 mg, 0.18 mmol) and freshly activated molecular sieve MS 4Å (400 mg) in CH_2Cl_2 (DCM) (4 mL) was stirred for 5 minutes at room temperature. The suspension was cooled to -78 °C and then NIS (74 mg, 0. 33 mmol) and TfOH (2 μL, 22 μmol) were added. The reaction mixture was gradually warmed to -10 °C and stirred for 2 h at the same temperature. Then, the mixture was quenched with triethylamine, diluted with CH_2Cl_2 and filtered. The filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography (2:1, hexanes/ethyl acetate) to afford **29** (267 mg, 89%) as α/β mixture. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 2H), 7.52-7.47 (m, 5H), 7.41-7.34 (m, 12H), 7.33-7.27 (m, 14H), 7.25-7.20 (m, 10H), 7.19-7.12 (m, 7H), 5.85 (d, *J* = 3.3 Hz, 1H), 5.44 (s, 1H), 5.35 (s, 1H), 5.31 (d, *J* = 3.5 Hz, 1H), 5.13 (d, *J* = 11.5 Hz, 1H), 4.92 (d, *J* = 3.5 Hz, 1H), 4.79 (dd, *J* = 12.2, 4.1 Hz, 3H), 4.75 (d, *J* = 3.6 Hz, 1H), 4.72-4.68 (m, 2H), 4.66 (d, *J* = 12.2 Hz, 2H), 4.62-4.48 (m, 4H), 4.45 (d, *J* = 8.9 Hz, 3H), 4.39-4.30 (m, 5H), 4.15-4.09 (m, 3H), 4.08-4.00 (m, 4H), 3.91 (dd, *J* = 10.0, 3.5 Hz, 2H), 3.88-3.80 (m, 3H), 3.69 (dd, *J* = 9.5, 3.3 Hz, 1H), 3.65-3.60 (m, 2H), 3.58-3.53 (m, 3H), 3.43 (s, 1H), 3.39 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.34-3.29 (m, 1H), 3.28-3.22 (m, 1H), 1.69 (s, 2H), 0.87 (s, 9H), 0.08 (s, 3H), 0.03 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.44, 139.06, 138.93, 138.84, 138.31, 138.17, 138.12, 137.94, 130.08, 129.81, 129.00, 128.60, 128.59, 128.50, 128.41, 128.39, 128.32, 128.29, 128.24, 128.10, 128.08, 127.98, 127.93, 127.80, 127.77, 127.63, 127.60, 127.35, 126.50, 126.44, 101.13, 100.92, 98.46, 97.53, 96.36, 82.68, 79.93, 79.43, 78.18, 75.82, 75.60, 75.35, 74.98, 74.73, 74.46, 73.29, 73.01, 72.06, 71.82, 69.97, 69.62, 64.53, 63.80, 62.61, 48.30, 28.81, 26.20, 18.25, -4.08, -4.45. HRMS (ESI): *m*/*z* calcd for $C_{96}H_{109}N_3O_{21}Si[M+NH_4]^+$: 1685.7667, found: 1685.7706.

3-Azidopropyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl (1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranosyl)-α-D-glucopyranoside (30)

To a solution of **29** (217 mg, 0.13 mmol) in pyridine (1.5 mL), HF·pyridine (70% HF in pyridine, 0.2 mL) was added. The solution was stirred for 3 h at room temperature. The reaction mixture was diluted with DCM, washed with saturated aqueous $NaHCO_3$, dried over Na_2SO_4, and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by flash chromatography (4:1, hexanes/ethyl acetate) to afford **30** (162 mg, 80%) as a white solid. $[\alpha]_D^{20}$ +95.9 (*c* 0.18, $CHCl_3$); ^{1}H NMR (500 MHz, CDCl3) δ 7.63-7.58 (m, 4H), 7.53-7.47 (m, 8H), 7.45-7.35 (m, 21H), 7.35-7.26 (m, 11H), 7.23 (t, *J* = 7.3 Hz, 1H), 5.67 (d, *J* = 3.4 Hz, 1H), 5.55-5.48 (m, 3H), 5.22 (d, *J* = 3.4 Hz, 1H), 5.07 (d, *J* = 11.7 Hz, 1H), 4.92 (d, *J* = 3.9 Hz, 1H), 4.89-4.79 (m, 5H), 4.75 (d, *J* = 2.3 Hz, 1H), 4.75-4.69 (m, 3H), 4.62 (d, *J* = 11.7 Hz, 1H), 4.57 (d, *J* = 11.1 Hz, 1H), 4.46 (d, *J* = 11.1 Hz, 1H), 4.43-4.39 (m, 1H), 4.39-4.34 (m, 2H), 4.28-4.14 (m, 6H), 4.10-4.02 (m, 3H), 3.98 (d, *J* = 12.2 Hz, 1H), 3.90-3.73 (m, 6H), 3.71-3.59 (m, 4H), 3.54 (s, 1H), 3.48-3.41 (m, 3H), 3.36 (dd, *J* = 9.5, 3.7 Hz, 1H), 3.24 (d, *J* = 10.3 Hz, 1H), 1.94-1.84 (m, 2H).^{13}C NMR (125 MHz,

$CDCl_3$) δ 139.21, 138.98, 138.78, 138.09, 137.98, 137.88, 137.86, 137.80, 128.87, 128.82, 128.72, 128.61, 128.54, 128.49, 128.31, 128.29, 128.20, 128.16, 128.11, 128.02, 127.81, 127.72, 127.62, 127.54, 127.33, 127.21, 126.37, 126.23, 126.20, 101.05, 101.00, 100.69, 98.42, 96.80, 96.64, 96.27, 81.56, 80.12, 79.94, 78.66,76.43(C-3A), 75.76 (C-2B), 75.12, 74.72, 74.55, 74.03, 73.77, 73.27, 72.73, 72.53, 71.95, 71.80, 70.71, 70.07, 69.40, 69.37, 68.77, 66.00, 64.41, 62.66, 62.15, 48.17, 28.65. HRMS (ESI): *m*/*z* calcd for $C_{90}H_{95}N_3O_{21}[M+NH_4]^+$: 1571.6802, found:1571.6835.

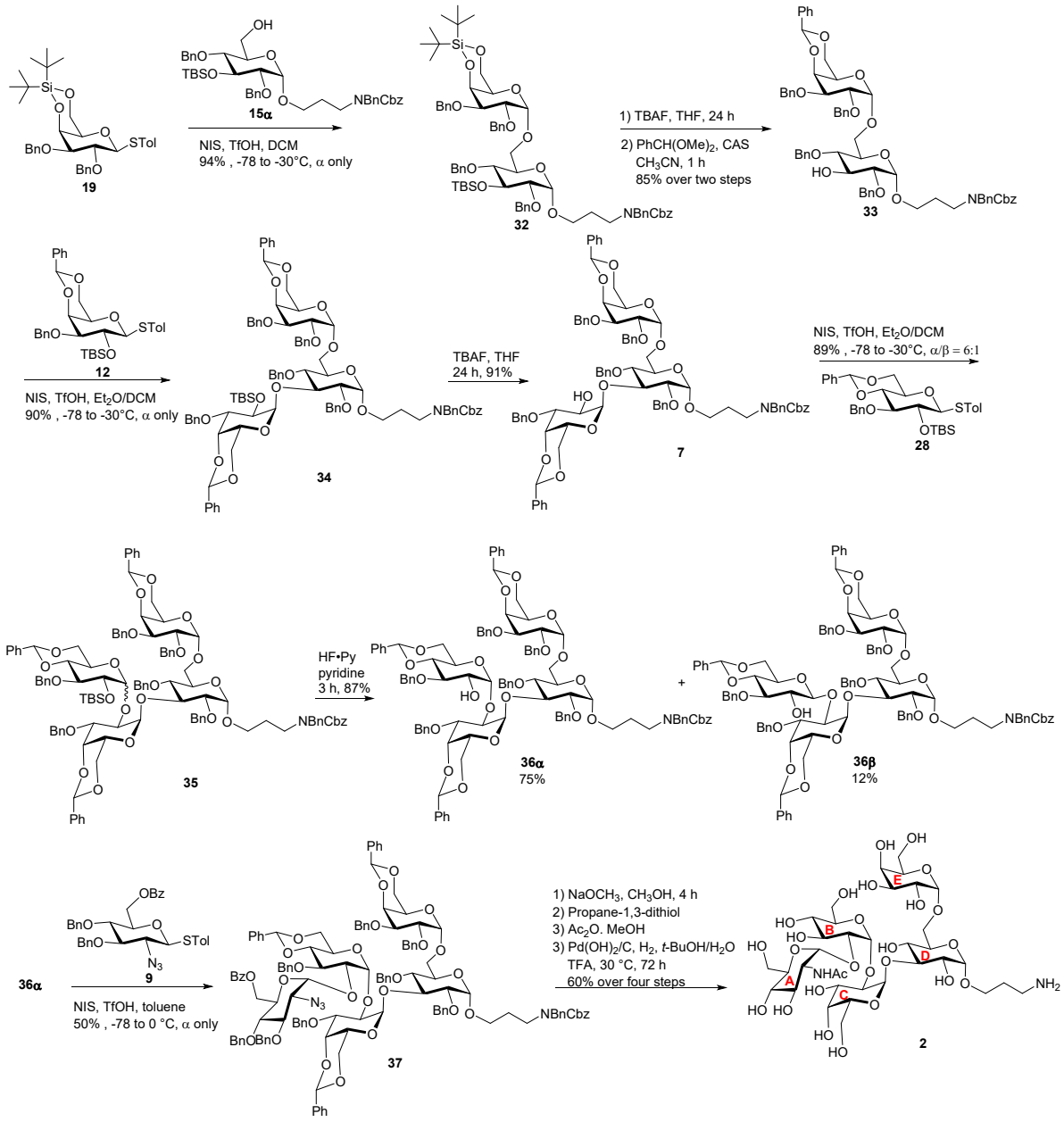
3-Azidopropyl 6-*O*-benzoyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranosyl)-α-D-glucopyranoside (31)

A mixture of galactose donor **8** (40 mg, 0.14 mmol), acceptor **30** (73 mg, 47 μmol), and freshly activated 4 Å molecular sieves in toluene (2 mL) were stirred for 15 minutes at room temperature. The suspension was cooled to -78 °C and then NIS (94.5 mg, 0.42 mmol) and TfOH (4 μL, 42 μmol) were added. The reaction mixture was gradually warmed to room temperature and stirred for 3 h at the same temperature. Then, the mixture was quenched with triethylamine, diluted with CH_2Cl_2 and filtered. The filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography (3:1, hexanes/ethyl acetate) to afford **31** (68 mg, 70%) as colorless syrups. $[\alpha]_D^{20}$ +80.1 (*c* 0.12, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.7 Hz, 2H), 7.56-7.52 (m, 3H), 7.47-7.45 (m, 4H), 7.41-7.23 (m, 40H), 7.22-7.09 (m, 14H), 7.07-7.05 (m, 2H), 5.86 (d, *J* = 3.3 Hz, 1H), 5.55 (s, 1H), 5.53 (d, *J* = 3.6 Hz, 1H), 5.46 (s, 1H), 5.27 (s, 1H), 5.09 (d, *J* = 11.4 Hz, 2H), 4.93-4.77 (m, 6H), 4.7-4.63 (m, 6H), 4.62-4.55 (m, 3H), 4.55-4.46 (m, 3H), 4.41-4.33 (m, 3H), 4.29-4.21 (m, 4H), 4.19-4.01 (m, 8H), 4.00-3.87 (m, 4H), 3.84-3.75 (m, 2H), 3.74-3.65 (m, 2H), 3.56-3.54 (m, 6H), 3.49-3.22 (m, 6H), 1.77-1.64 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.13, 139.02, 138.96, 138.82, 138.70, 138.36, 138.24, 138.14, 138.01, 137.93, 137.77, 137.70, 133.03, 130.13, 129.79, 129.03, 128.97, 128.70, 128.65, 128.62, 128.57, 128.48, 128.41, 128.32, 128.28, 128.23, 128.17, 128.10, 128.04, 127.98, 127.77, 127.72, 127.62, 127.59, 126.47, 126.25, 126.07, 101.43, 101.12, 100.61, 98.36, 96.86, 96.04, 95.53, 94.67, 82.79, 82.16, 80.48, 79.37, 78.84, 77.75, 76.76, 75.89, 75.86, 75.73, 75.56, 75.05, 74.88, 74.79, 73.75, 73.24, 72.70, 72.27, 71.83, 71.57, 69.85, 69.53, 69.31, 69.28, 69.08, 67.16, 64.45, 63.43, 62.90, 62.67, 62.04, 48.31, 28.79. HRMS (ESI): *m*/*z* calcd for $C_{124}H_{127}N_3O_{27}[M+NH_4]^+$: 2107.9001, found:2107.8940.

3-Aminopropyl α-D-glucopyranosyl-(1→2)-α-D-glucopyranosyl-(1→2)-α-D-galactopyranosyl-(1→3)-3-*O*-(α-D-galactopyranosyl)-α-D-glucopyranoside (1)

To a solution of **31** (50 mg, 24 μmol) in MeOH/DCM (5 mL, v/v = 1:1) was added NaOMe (13 mg, 0.19 mmol) at 0 °C, and the resulting mixture was warmed gradually to room temperature. The mixture was stirred for 12 h at the same temperature, at the end of which time TLC indicated the reaction was finished. The reaction was quenched with Amberlite IR120 H+ resin. After

filtration, the resulting mixture was concentrated to dryness. The obtained residue was purified by silica gel column chromatography (3:1, hexanes/ethyl acetate) to afford a white solid. To a solution of the obtained solid in *t*-BuOH/H_2O/TFA (5 mL, v/v/v = 4:1:0.04) was added 20% $Pd(OH)_2/C$ (100 mg), and the reaction mixture was stirred under a hydrogen atmosphere at 30 °C. The mixture was stirred for 72 h. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. The obtained residue was purified by Sephadex G-10 column (H_2O) to afford **1** (18 mg, 87% over two steps) as a white solid. $[\alpha]_D^{20}$ +11.6 (*c* 0.1, H_2O); ^{1}H NMR (800 MHz, D_2O) δ 5.69 (d, *J* = 3.8 Hz, 1H), 5.39 (d, *J* = 3.5 Hz, 1H), 5.10 (d, *J* = 3.8 Hz, 1H), 4.94 (d, *J* = 2.2 Hz, 1H), 4.92 (d, *J* = 3.8 Hz, 1H), 4.23 (t, *J* = 6.4 Hz, 1H), 4.03 (dd, *J* = 10.3, 3.5 Hz, 1H), 3.99 (d, *J* = 3.3 Hz, 1H), 3.97-3.78 (m, 14H), 3.77-3.67 (m, 11H), 3.61-3.56 (m, 1H), 3.51 (dd, *J* = 9.9, 3.7 Hz, 1H), 3.47 (t, *J* = 9.5 Hz, 1H), 3.41 (t, *J* = 9.7 Hz, 1H), 3.15 (dt, *J* = 13.5, 6.8 Hz, 1H), 3.10 (dt, *J* = 12.9, 7.2 Hz, 1H), 2.02-1.94 (m, 2H). ^{13}C NMR (200 MHz, D_2O) δ 98.31, 98.16, 95.81, 95.19, 92.80, 77.14, 74.61, 72.81, 72.50, 71.81, 71.43, 71.02, 71.00, 70.58, 70.37, 70.34, 69.42, 69.35, 69.33, 69.18, 69.11, 68.19, 67.58, 65.94, 65.76, 61.12, 61.02, 60.28, 60.16, 37.79, 26.43; HRMS (ESI): *m*/*z* calcd for $C_{33}H_{59}NO_{26}[M+H]^+$: 886.3404, found:886.3397.



Scheme S7. Synthesis of pentasaccharide **2**.

N-(Benzyl)benzyloxycarbonyl-3-aminopropyl 2,3-di-*O*-benzyl-4,6-*O*-di-tert-butylsilanediyl-α-D-galactopyranosyl-(1→6)-2,4-di-*O*-benzyl-3-*O*-tert-butyldimethylsilyl-α-D-glucopyranoside (32)

A mixture of galactose donor **19** (300 mg, 0.49 mmol), acceptor **15α** (336 mg, 0.45 mmol), and freshly activated 4 Å molecular sieves in CH_2Cl_2 (4 mL) were stirred for 15 minutes at room temperature. The suspension was cooled to -78 °C and then NIS (165 mg, 0.74 mmol) and TfOH (5 μL, 49 μmol) were added. The reaction mixture was gradually warmed to -30 °C and stirred for 1 h at the same temperature. Then, the mixture was quenched with triethylamine, diluted with

CH_2Cl_2 and filtered. The filtrate was concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (8:1, hexanes/ethyl acetate) to afford **32** (529 mg, 94%) as colorless syrups. $[\alpha]_D^{20}$ +64 (*c* 0.25, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.18 (m, 30H), 5.20 (d, *J* = 10.7 Hz, 2H), 5.00 (d, *J* = 3.5 Hz, 1H), 4.92 (d, *J* = 11.8 Hz, 1H), 4.74 (d, *J* = 13.7 Hz, 4H), 4.60 (d, *J* = 11.8 Hz, 1H), 4.56 (d, *J* = 11.8 Hz, 2H), 4.53-4.47 (m, 2H), 4.44 (s, 1H), 4.39-4.32 (m, 1H), 4.07-3.97 (m, 4H), 3.81-3.71 (m, 2H), 3.71-3.63 (m, 2H), 3.62-3.50 (m, 2H), 3.43 (s, 1H), 3.39-3.11 (m, 4H), 1.87-1.73 (m, 2H), 1.07 (s, 9H), 1.01 (s, 9H), 0.97 (s, 9H), 0.11-0.08 (m, 3H), 0.06 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.76, 156.20, 138.99, 138.89, 138.65, 138.03, 136.98, 128.67, 128.63, 128.54, 128.40, 128.38, 128.36, 128.35, 128.14, 128.04, 127.97, 127.77, 127.72, 127.55, 127.52, 127.48, 127.39, 127.12, 98.22, 97.02, 80.78, 79.47, 77.16, 76.61, 74.95, 74.42, 74.03, 73.33, 72.44, 71.18, 70.75, 70.63, 67.25, 67.21, 66.05, 65.90, 65.37, 65.18, 51.07, 50.75, 44.79, 43.86, 28.46, 27.89, 27.77, 27.43, 26.22, 23.50, 20.76, 18.27, -3.82, -4.16; (28.46 and 27.89 are from the same carbon atoms due to rotamers; 44.79 and 43.86 are from the same carbon atoms due to rotamers; 51.07 and 50.75 are from the same carbon atoms due to rotamers; 65.37 and 65.18 are from the same carbon atoms due to rotamers; 66.05 and 65.90 are from the same carbon atoms due to rotamers; 156.76 and 156.20 are from the same carbon atoms due to rotamers); HRMS (ESI): *m*/*z* calcd for $C_{72}H_{95}NO_{13}Si_2[M+NH_4]^+$: 1255.6686, found:1255.6725.

_N_-(Benzyl)benzyloxycarbonyl-3-aminopropyl 2,3-di-_O_-benzyl-4,6-_O_-benzylidene-α-D-galactopyranosyl-(1→6)-2,4-di-_O_-benzyl-α-D-glucopyranoside (33)

A solution of **32** (260 mg, 0.21 mmol) in pyridine (2 mL) and HF·pyridine (70% HF in pyridine, 0.2 mL) was stirred for 3 h at room temperature. The reaction mixture was diluted with DCM, washed with saturated aqueous $NaHCO_3$, dried over Na_2SO_4, and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by flash chromatography (DCM/MeOH, 40:1). The obtained product was dissolved in CH_3CN and camphorsulfonic acid (CSA) (24 mg, 0.1 mmol) and $PhCH(OMe)_2$ (63 μL, 0.42 mmol) were added. After stirring for 1 hour at room temperature, the reaction mixture was diluted with DCM, washed with saturated aqueous $NaHCO_3$, dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (3:1, hexanes/ethyl acetate) to yield compound **33** as a white solid (191 mg, 85% yield over two steps). $[\alpha]_D^{20}$ +37.1 (*c* 0.19, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55-7.49 (m, 2H), 7.47-7.08 (m, 33H), 5.45 (s, 1H), 5.18 (d, *J* = 10.5 Hz, 2H), 5.10 (d, *J* = 3.6 Hz, 1H), 4.93 (d, *J* = 11.7 Hz, 1H), 4.80 (d, *J* = 12.2 Hz, 1H), 4.79 (d, *J* = 12.2 Hz, 1H), 4.75 (d, *J* = 12.2 Hz, 1H), 4.70 (d, *J* = 12.2 Hz, 1H), 4.59 (d, *J* = 11.7 Hz, 1H), 4.63-4.42 (m, 5H), 4.16-4.00 (m, 4H), 3.96 (dd, *J* = 10.1, 3.4 Hz, 1H), 3.84-3.80 (m, 2H), 3.78-3.65 (m, 2H), 3.65-3.52 (m, 2H), 3.48 (d, *J* = 10.1 Hz, 1H), 3.35-3.33 (m, 2H), 3.23 (t, *J* = 11.4 Hz, 2H), 2.35 (s, 1H), 1.90-1.68 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.10, 138.86, 138.18, 137.98, 128.97, 128.67, 128.62, 128.52, 128.43, 128.40, 128.22, 128.08, 128.00, 127.93, 127.83, 127.71, 127.67, 127.52, 127.38, 126.48, 101.16, 98.50, 96.27, 80.01, 77.67, 75.77, 75.31, 74.87, 74.33, 73.43, 72.83, 72.02, 70.22, 69.46, 67.31, 66.42, 65.56, 62.72, 50.99, 50.68, 44.78, 43.85, 28.44, 27.93. (28.44 and 27.93

are from the same carbon atoms due to rotamers; 44.78 and 43.85are from the same carbon atoms due to rotamers; 50.99 and 50.68 are from the same carbon atoms due to rotamers); HRMS (ESI): *m*/*z* calcd for $C_{65}H_{69}NO_{13}[M+NH_4]^+$: 1089.5113, found: 1089.5146.

_N_-(Benzyl)benzyloxycarbonyl-3-aminopropyl 2-_O_-tert-butyldimethylsilyl-3-_O_-benzyl-4,6-_O_-benzylidene-α-D-galactopyranosyl-(1→3)-2,4-di-_O_-benzyl-6-_O_-(2,3-di-_O_-benzyl-4,6-_O_-benzylidene-α-D-galactopyranosyl)-α-D-glucopyranoside (34)

A mixture of galactose donor **12** (200 mg, 0.35 mmol), acceptor **33** (334 mg, 0.32 mmol), and freshly activated 4 Å molecular sieves in CH_2Cl_2 (3 mL) were stirred for 15 minutes at room temperature. The suspension was cooled to -78 °C and then NIS (165 mg, 0.74 mmol) and TfOH (5 μL, 49 μmol) were added. The reaction mixture was gradually warmed to -30 °C and stirred for 1 h at the same temperature. Then, the mixture was quenched with triethylamine, diluted with CH_2Cl_2 and filtered. The filtrate was concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (5:1, hexanes/ethyl acetate) to afford **34** (433 mg, 90%) as white solid. $[\alpha]_D^{20}$ = +88.9 (*c* 0.31, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59-7.52 (m, 4H), 7.46-7.44 (m, 6H), 7.42-7.36 (m, 9H), 7.36-7.30 (m, 14H), 7.29-7.24 (m, 9H), 7.20-7.11 (m, 3H), 5.54 (d, *J* = 3.3 Hz, 1H), 5.49 (s, 1H), 5.30 (s, 1H), 5.21 (d, *J* = 12.1 Hz, 2H), 5.12 (s, 1H), 5.09-5.03 (m, 1H), 4.90-4.80 (m, 2H), 4.76 (dd, *J* = 12.4, 3.8 Hz, 2H), 4.73-4.59 (m, 5H), 4.58-4.40 (m, 3H), 4.36-4.24 (m, 4H), 4.16 (dt, *J* = 7.3, 3.0 Hz, 1H), 4.12-4.08 (m, 2H), 4.07-3.96 (m, 3H), 3.94-3.79 (m, 5H), 3.78-3.71 (m, 2H), 3.69-3.55 (m, 2H), 3.48 (t, *J* = 11.4 Hz, 2H), 3.44-3.24 (m, 4H), 1.89-1.75 (m, 2H), 0.91 (s, 9H), 0.04 (s, 3H), 0.00 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.67, 156.19, 139.22, 139.01, 138.52, 138.32, 138.19, 137.94, 136.78, 128.94, 128.71, 128.64, 128.53, 128.48, 128.44, 128.38, 128.27, 128.18, 128.15, 128.07, 127.94, 127.73, 127.67, 127.60, 127.53, 127.45, 127.40, 127.32, 127.27, 126.96, 126.44, 126.21, 101.11, 100.38, 99.14, 98.49, 96.18, 79.49, 79.13, 75.80, 75.78, 75.65, 74.94, 74.04, 73.75, 72.93, 72.64, 72.26, 71.32, 69.82, 69.53, 69.42, 67.27, 66.02, 65.43, 62.65, 62.45, 51.19, 50.78, 44.93, 44.04, 28.42, 27.90, 26.15,18.47, -4.14, -4.39. (28.42 and 27.90 are from the same carbon atoms due to rotamers; 44.93 and 44.04 are from the same carbon atoms due to rotamers; 51.19 and 50.78 are from the same carbon atoms due to rotamers; 156.67 and 156.19 are from the same carbon atoms due to rotamers); HRMS (ESI): *m*/*z* calcd for $C_{91}H_{103}NO_{18}Si[M+NH_4]^+$: 1543.7288, found: 1543.7324.

_N_-(Benzyl)benzyloxycarbonyl-3-aminopropyl 3-_O_-benzyl-4,6-_O_-benzylidene-α-D-galactopyranosyl-(1→3)-2,4-di-_O_-benzyl-6-_O_-(2,3-di-_O_-benzyl-4,6-_O_-benzylidene-α-D-galactopyranosyl)-α-D-glucopyranoside (7)

A solution of **34** (287 mg, 0.19 mmol) in THF (2 mL) and TBAF (0.2 mL) was added. After stirring 2 h at room temperature, the mixture was concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (2:1, hexanes/ethyl acetate) to afford **7** (244 mg, 91%) as colorless syrups. $[\alpha]_D^{20}$ = +79.6 (*c* 0.61, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68-6.92 (m, 45H), 5.58 (d, *J* = 3.8 Hz, 1H), 5.47 (s, 1H), 5.25 (s, 1H), 5.19-5.15 (m, 3H), 5.01 (d, *J* = 10.8 Hz,

1H), 4.82-4.71 (m, 7H), 4.57 (d, *J* = 10.8 Hz, 1H), 4.54- 4.36 (m, 3H), 4.17 (td, *J* = 13.0, 5.9 Hz, 5H), 4.08 (dd, *J* = 10.1, 3.5 Hz, 1H), 3.96 (dd, *J* = 10.1, 3.5 Hz, 1H), 3.92 (d, *J* = 12.3 Hz, 1H), 3.89-3.80 (m, 4H), 3.78-3.69 (m, 3H), 3.66 (q, *J* = 6.4 Hz, 2H), 3.52 (s, 1H), 3.37-3.18 (m, 4H), 2.33 (s, 1H), 1.79-1.61 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.73, 156.26, 139.29, 138.79, 138.55, 138.30, 138.09, 137.96, 136.82, 129.00, 128.82, 128.76, 128.65, 128.59, 128.56, 128.51, 128.49, 128.45, 128.42, 128.24, 128.21, 128.16, 128.14, 127.98, 127.96, 127.92, 127.89, 127.80, 127.75, 127.45, 127.39, 126.49, 126.29, 101.20, 100.69, 98.78, 96.11, 79.35, 78.98, 76.66, 75.85, 75.27, 75.18, 74.83, 74.36, 73.45, 72.56, 72.06, 71.13, 70.77, 69.51, 69.45, 68.04, 67.32, 66.19, 65.52, 65.38, 62.90, 62.40, 51.23, 50.84, 44.96, 44.03, 28.48, 27.94. (28.48 and 27.94 are from the same carbon atoms due to rotamers; 44.96 and 44.03 are from the same carbon atoms due to rotamers; 51.23 and 50.84 are from the same carbon atoms due to rotamers; 156.73 and 156.26 are from the same carbon atoms due to rotamers); HRMS (ESI): *m*/*z* calcd for $C_{85}H_{89}NO_{18}[M+NH_4]^+$: 1429.6423, found: 1429.6450.

_N_-(Benzyl)benzyloxycarbonyl-3-aminopropyl 2-_O_-tert-butyldimethylsilyl-3-_O_-benzyl-4,6-_O_-benzylidene-α/β-D-glucopyranosyl-3-_O_-benzyl-4,6-_O_-benzylidene-α-D-galactopyranosyl-(1→3)-2,4-di-_O_-benzyl-6-_O_-(2,3-di-_O_-benzyl-4,6-_O_-benzylidene-α-D-galactopyranosyl)-α-D-glucopyranoside (35)

A mixture of galactose donor **28** (480 mg, 0.81 mmol), acceptor **7** (1.03 g, 0.73 mmol), and freshly activated 4 Å molecular sieves in CH_2Cl_2 (13 mL) were stirred for 15 minutes at room temperature. The suspension was cooled to -78 °C and then NIS (273 mg, 1.22 mmol) and TfOH (8 µL, 81 µmol) were added. The reaction mixture was gradually warmed to -20 °C and stirred for 2 h at the same temperature. Then, the mixture was quenched with triethylamine, diluted with CH_2Cl_2 and filtered. The filtrate was concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (3:1, hexanes/ethyl acetate) to afford an inseparable mixture of α/β isomers **35** (1.2 g, α/β = 6:1, 89%) as colorless syrup. Selected analytical data for α-isomer of **35**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.81 (d, *J* = 3.3 Hz, 1H), 5.53 (s, 1H), 5.43 (s, 1H), 5.36 (d, *J* = 3.7 Hz, 1H), 5.30 (s, 1H), 0.86 (s, 9H), 0.04 (s, 3H), -0.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 101.22, 101.04, 100.78, 98.47, 51.18, 50.77, 44.99, 44.08, 28.40, 27.88, 26.11, 18.27, -4.37, -4.49. (28.40 and 27.88 are from the same carbon atoms due to rotamers; 44.99 and 44.08 are from the same carbon atoms due to rotamers; 51.18 and 50.77 are from the same carbon atoms due to rotamers are from the same carbon atoms due to rotamers); Selected analytical data for β-isomer of **35**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.62 (s, 1H), 5.47 (s, 1H), 5.29 (s, 1H), 0.96 (s, 9H), 0.33 (s, 3H), 0.18 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.29, 18.51, -3.21, -4.09; HRMS (ESI): *m*/*z* calcd for $C_{111}H_{123}NO_{23}Si[M+NH_4]^+$: 1883.8599, found: 1883.8611.

_N_-(Benzyl)benzyloxycarbonyl-3-aminopropyl 3-_O_-benzyl-4,6-_O_-benzylidene-α-D-glucopyranosyl-3-_O_-benzyl-4,6-_O_-benzylidene-α-D-galactopyranosyl-(1→3)-2,4-di-_O_-

benzyl-6-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranosyl)-α-D-glucopyranoside (36α)

A solution of **35** (392 mg, 0.21 mmol) in pyridine (2 mL) and HF·pyridine (70% HF in pyridine, 0.2 mL) was stirred for 3 h at room temperature. The reaction mixture was diluted with DCM, washed with saturated aqueous $NaHCO_3$ solution, dried over Na_2SO_4, and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by flash chromatography (DCM/MeOH, 40:1) to afford **36α** (274 mg, 75%) as white solid. $[\alpha]_D^{20}$ +104 (*c* 0.04, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59-7.56 (m, 4H), 7.52-6.99 (m, 51H), 5.64 (d, *J* = 3.3 Hz, 1H), 5.52 (s, 1H), 5.48 (s, 1H), 5.46 (s, 1H), 5.28-5.16 (m, 3H), 5.04 (d, *J* = 12.0 Hz, 1H), 4.88-4.77 (m, 6H), 4.71 (dd, *J* = 12.0, 4.3 Hz, 3H), 4.66-4.45 (m, 5H), 4.38-4.30 (m, 3H), 4.21-4.12 (m, 6H), 4.03 (dt, *J* = 10.4, 5.2 Hz, 3H), 3.95 (dd, *J* = 12.5, 1.8 Hz, 1H), 3.89-3.79 (m, 3H), 3.78-3.50 (m, 8H), 3.48-3.27 (m, 4H), 3.16 (d, *J* = 8.3 Hz, 1H), 1.92-1.78 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.19, 139.31, 139.04, 138.88, 138.21, 138.15, 138.07, 137.94, 137.86, 128.91, 128.85, 128.76, 128.68, 128.64, 128.60, 128.54, 128.53, 128.34, 128.21, 128.16, 128.07, 127.91, 127.82, 127.79, 127.75, 127.65, 127.56, 127.37, 127.36, 127.27, 127.18, 126.42, 126.28, 126.24, 101.12, 101.05, 100.69, 98.48, 96.64, 96.09, 81.65, 79.99, 78.79, 75.82, 75.18, 74.81, 74.60, 73.87, 73.38, 73.10, 72.75, 72.52, 71.88, 70.80, 69.98, 69.44, 68.84, 67.25, 66.10, 65.51, 62.73, 62.65, 62.19, 50.67, 44.84, 28.38. HRMS (ESI): *m*/*z* calcd for $C_{105}H_{109}NO_{23}[M+NH_4]^+$: 1769.7734, found:1769.7737.

***N*-(Benzyl)benzyloxycarbonyl-3-aminopropyl 3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranosyl)-α-D-glucopyranoside (36β)**

A solution of **35** (392 mg, 0.21 mmol) in pyridine (2 mL) and HF·pyridine (70% HF in pyridine, 0.2 mL) was stirred for 3 h at room temperature. The reaction mixture was diluted with DCM, washed with saturated aqueous $NaHCO_3$ solution, dried over Na_2SO_4, and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by flash chromatography (DCM/MeOH, 40:1) to afford **36β** (46 mg, 12%) as white solid. $[\alpha]_D^{20}$ +33.3 (*c* 0.12, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55-7.47 (m, 6H), 7.46-7.32 (m, 28H), 7.32-7.26 (m, 12H), 7.26-7.11 (m, 9H), 5.61 (s, 1H), 5.46 (s, 1H), 5.33-5.07 (m, 6H), 4.92-4.68 (m, 10H), 4.58-4.43 (m, 4H), 4.28 (d, *J* = 10.6 Hz, 1H), 4.24-4.13 (m, 3H), 4.12-4.01 (m, 4H), 3.96 (dd, *J* = 10.1, 3.4 Hz, 1H), 3.91-3.83 (m, 3H), 3.82-3.61 (m, 6H), 3.62-3.54 (m, 3H), 3.44-3.29 (m, 4H), 3.27-3.20 (m, 2H), 3.12 (d, *J* = 12.7 Hz, 1H), 2.93 (s, 1H), 2.78 (t, *J* = 9.9 Hz, 1H), 1.85-1.80 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.25, 138.67, 138.20, 137.94, 137.44, 128.98, 128.89, 128.75, 128.63, 128.60, 128.52, 128.48, 128.46, 128.40, 128.29, 128.22, 128.18, 128.17, 128.09, 128.07, 127.98, 127.81, 127.74, 127.71, 127.54, 127.41, 127.10, 126.47, 126.33, 126.31, 126.08, 104.65, 101.17, 100.86, 100.83, 98.83, 98.74, 96.00, 80.86, 80.47, 79.05, 75.78, 75.57, 75.42, 75.16, 74.79, 74.60, 74.20, 73.88, 72.71, 72.04, 71.38, 69.43, 68.05, 67.30, 65.98, 62.69, 62.00, 51.26, 45.11, 27.93. HRMS (ESI): *m*/*z* calcd for $C_{105}H_{109}NO_{23}[M+NH_4]^+$: 1769.7734, found: 1769.7749.

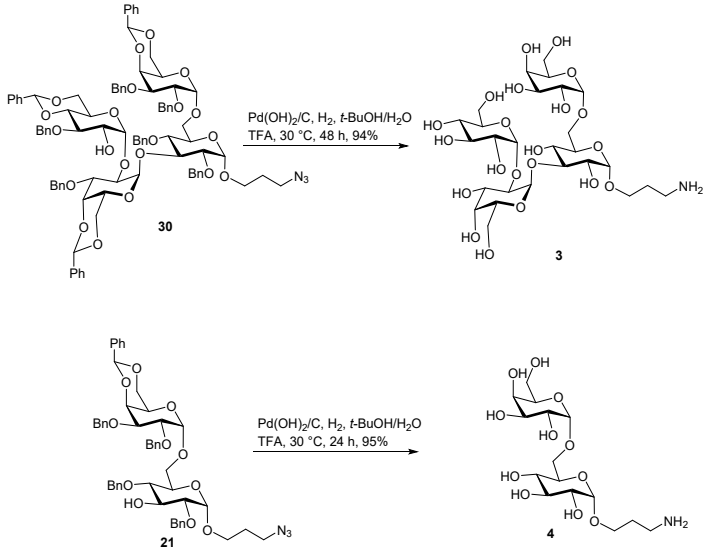
***N*-(Benzyl)benzyloxycarbonyl-3-aminopropyl 2-azido-6-*O*-benzoyl-3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranosyl-(1→3)-2,4-di-*O*-benzyl-6-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranosyl)-α-D-glucopyranoside (37)**

A mixture of donor **9**[9] (100 mg, 0.17 mmol), acceptor **36α** (59 mg, 33 μmol), and freshly activated 4 Å molecular sieves in toluene (3 mL) was stirred for 15 minutes at room temperature. The suspension was cooled to -78 °C and then NIS (191 mg, 0.85 mmol) and TfOH (8 μL, 85 μmol) were added. The reaction mixture was gradually warmed to room temperature and stirred for 5 h at the same temperature. Then, the mixture was quenched with triethylamine, diluted with CH_2Cl_2 and filtered. The filtrate was concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (2:1, hexanes/ethyl acetate) to afford **37** (37 mg, 50%) as white solid. $[\alpha]_D^{20}$ +37.6 (*c* 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.1 Hz, 2H), 7.56-7.48 (m, 5H), 7.48-7.42 (m, 4H), 7.42-7.26 (m, 37H), 7.26-7.13 (m, 20H), 7.09 (t, *J* = 7.2 Hz, 2H), 5.73 (s, 1H), 5.49 (s, 1H), 5.44 (s, 1H), 5.32-5.29 (m, 1H), 5.28 (d, *J* = 3.5 Hz, 1H), 5.23 (d, *J* = 3.7 Hz, 1H), 5.18 (d, *J* = 10.6 Hz, 2H), 4.90-4.84 (m, 3H), 4.82-4.76 (m, 4H), 4.75-4.46 (m, 12H), 4.45-4.30 (m, 5H), 4.25-4.09 (m, 5H), 4.09-3.82 (m, 10H), 3.77 (d, *J* = 9.4 Hz, 1H), 3.71 (d, *J* = 3.7 Hz, 1H), 3.69-3.56 (m, 6H), 3.53 (d, *J* = 9.2 Hz, 1H), 3.47 (t, *J* = 9.4 Hz, 1H), 3.41-3.26 (m, 4H), 3.22 (dd, *J* = 10.4, 3.4 Hz, 1H), 1.83-1.70 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.14, 139.23, 138.88, 138.15, 138.04, 137.88, 137.64, 133.19, 130.09, 129.81, 129.01, 128.96, 128.77, 128.66, 128.53, 128.51, 128.48, 128.42, 128.38, 128.30, 128.22, 128.18, 128.16, 128.09, 127.98, 127.95, 127.82, 127.63, 127.59, 127.55, 127.49, 127.24, 126.44, 126.30, 126.27, 101.38, 101.06, 100.66, 98.39, 95.02, 95.90, 92.09, 82.75, 79.68, 79.21, 78.74, 76.14, 75.53, 75.16, 75.11, 74.81, 74.70, 74.38, 73.16, 72.52, 71.78, 69.45, 69.05, 67.35, 65.32, 63.23, 62.85, 62.75, 62.30, 62.19, 51.14, 44.96, 27.84; HRMS (ESI): *m*/*z* calcd for $C_{132}H_{134}N_4O_{28}[M+NH_4]^+$: 2240.9528, found: 2240.9553.

3-Aminopropyl 2-acetamino-2-deoxy-α-D-glucopyranosyl-(1→2)-α-D-glucopyranosyl-(1→2)-α-D-galactopyranosyl-(1→3)-3-*O*-(α-D-galactopyranosyl)-α-D-glucopyranoside (2)

To a solution of **37** (55 mg, 25 μmol) in MeOH/DCM (5 mL, v/v = 1:1) was added NaOMe (14 mg, 0.2 mmol) at 0 °C, and the resulting mixture was warmed gradually to room temperature. The mixture was stirred for 12 h at the same temperature, at the end of which time TLC indicated the reaction was finished. The reaction was quenched with Amberlite IR120 H+ resin. After filtration, the resulting mixture was concentrated to dryness. The obtained residue was purified by silica gel column chromatography (3:1, hexanes/ethyl acetate) to afford a white solid. 1,3-Propanedithiol was added to a solution of the obtained solid in pyridine/H_2O. The mixture was stirred at 50 °C for 2 days. Afterward, the solvent was evaporated without purification. The residue was dissolved in MeOH, followed by the addition of Ac_2O, and stirred at room temperature overnight. The solvent was then evaporated to dryness, and the product was purified by silica gel column chromatography

to yield a white solid. To a solution of the obtained solid in *t*-BuOH/H_2O/TFA (5 mL, v/v/v = 4:1:0.04) was added 20% $Pd(OH)_2$/C (50 mg), and the reaction mixture was stirred under a hydrogen atmosphere at 30 °C. The mixture was stirred for 72 h. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. The obtained residue was purified by Sephadex G-10 column (H_2O) to afford **2** (14 mg, 60% over four steps) as a white solid. $[\alpha]_D^{20}$ -2.9 (*c* 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, D_2O) δ 5.59 (d, *J* = 3.6 Hz, 1H), 5.53 (d, *J* = 3.7 Hz, 1H), 5.04 (d, *J* = 3.7 Hz, 1H), 4.90 (d, *J* = 3.7 Hz, 1H), 4.86 (d, *J* = 3.9 Hz, 1H), 4.33 (t, *J* = 6.4 Hz, 1H), 3.96-3.73 (m, 15H), 3.73-3.52 (m, 12H), 3.47-3.31 (m, 4H), 3.13-3.02 (m, 2H), 2.00 (s, 3H), 1.94 (p, *J* = 6.1 Hz, 2H). ^{13}C NMR (125 MHz, D_2O) δ 173.54, 98.35, 98.28, 94.96, 93.02, 90.16, 76.23, 72.89, 72.08, 71.83, 71.41, 71.09, 70.95, 70.90, 70.38, 70.10, 69.89, 69.69, 69.46, 69.37, 69.11, 68.85, 68.78, 68.27, 67.91, 66.18, 65.80, 61.08, 60.89, 60.64, 60.11, 53.15, 37.72, 26.41, 22.16; HRMS (ESI): *m*/*z* calcd for $C_{35}H_{62}N_2O_{26}[M+H]^+$: 927.3669, found:927.3645.



Scheme S8. Synthesis of fragments of the pentasaccharides **3** and **4**.

3-Aminopropyl α-D-glucopyranosyl-(1→2)-α-D-galactopyranosyl-(1→3)-3-*O*-(α-D-galactopyranosyl)-α-D-glucopyranoside (3)

To a solution of **30** (100 mg, 0.06 mmol) in *t*-BuOH/H_2O/TFA (5 mL, v/v/v = 4:1:0.04) was added 20% $Pd(OH)_2$/C (100 mg), and the reaction mixture was stirred under a hydrogen atmosphere at 30 °C. The mixture was stirred for 48 h. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. The obtained residue was purified by Sephadex G-10 column (H_2O) to afford **3** (36 mg, 94%) as a white solid. $[\alpha]_D^{20}$ +10.1 (*c* 0.09, H_2O); ^{1}H NMR (500 MHz, D_2O) δ 5.46 (d, *J* = 3.3 Hz, 1H), 5.12 (d, *J* = 3.9 Hz, 1H), 4.92 (d, *J* = 3.7 Hz, 1H), 4.91 (d, *J* = 3.8 Hz, 1H), 4.28-4.22 (m, 1H), 4.00 (dd, *J* = 3.0, 1.3 Hz, 1H), 3.99-3.94 (m, 4H), 3.91 (tt, *J* = 5.9, 2.2 Hz, 2H), 3.88-3.76 (m, 7H), 3.75-3.72 (m, 2H), 3.71-3.65 (m, 6H), 3.64-3.63 (m, 1H), 3.58 (td, *J* = 5.3, 2.4 Hz, 1H), 3.54 (dd, *J* = 9.8, 3.9 Hz, 1H), 3.39 (dd, *J* = 10.1, 9.2 Hz, 1H), 3.08-2.95 (m, 2H),

1.97-1.87 (m, 2H). ^{13}C NMR (125 MHz, D_2O) δ 98.50, 97.99, 96.75, 95.71, 80.31, 72.79, 72.47, 71.65, 71.26, 70.91, 70.50, 70.06, 69.50, 69.30, 69.19, 69.10, 69.05, 68.29, 67.39, 65.94, 65.08, 61.00, 60.66, 60.28, 37.72, 26.38; HRMS (ESI): *m/z* calcd for $C_{27}H_{49}NO_{21}[M+H]^+$: 724.2875, found:724.2860.

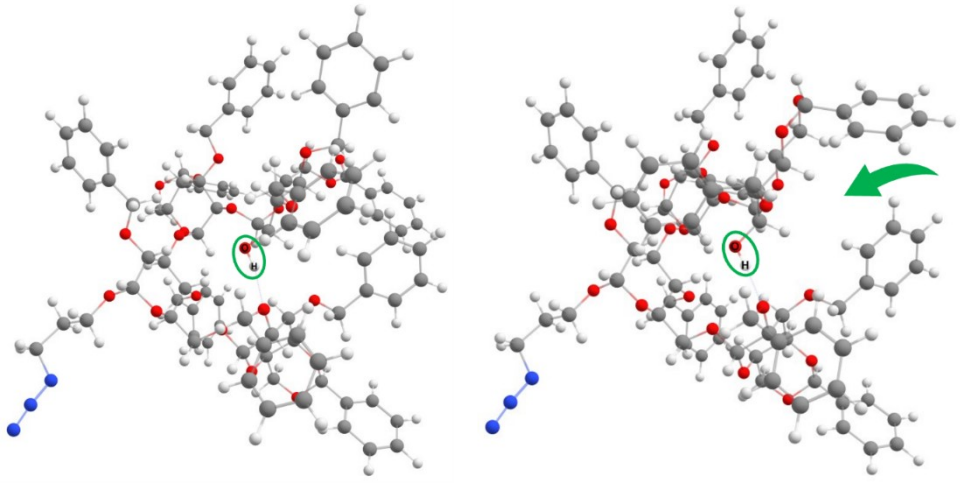
3-Aminopropyl α-D-galactopyranosyl-(1→6)-α-D-glucopyranoside (4)

To a solution of **21** (50 mg, 57 μmol) in *t*-BuOH/H_2O/TFA (5 mL, v/v/v = 4:1:0.04) was added 20% $Pd(OH)_2$/C (50 mg), and the reaction mixture was stirred under a hydrogen atmosphere at 30 °C. The mixture was stirred for 24 h. The reaction mixture was filtered and the filtrate was concentrated *in vacuo*. The obtained residue was purified by Sephadex G-10 column (H_2O) to afford **4** (22 mg, 95%) as a white solid. $[\alpha]_D^{20}$ +22.2 (*c* 0.05, H_2O); ^{1}H NMR (500 MHz, D_2O) δ 4.93 (d, *J* = 3.6 Hz, 1H), 4.90 (d, *J* = 3.8 Hz, 1H), 3.98-3.90 (m, 3H), 3.87 (dt, *J* = 10.8, 5.6 Hz, 1H), 3.82 (dd, *J* = 10.3, 3.1 Hz, 1H), 3.80-3.76 (m, 2H), 3.73-3.67 (m, 3H), 3.64 (t, *J* = 9.4 Hz, 1H), 3.61-3.56 (m, 1H), 3.55 (dd, *J* = 9.9, 3.4 Hz, 1H), 3.48 (t, *J* = 9.8 Hz, 1H), 3.18-3.03 (m, 2H), 1.97 (p, *J* = 6.2 Hz, 2H). ^{13}C NMR (125 MHz, D_2O) δ 98.26, 97.95, 73.09, 70.89, 70.85, 70.30, 69.34, 69.22, 69.07, 68.25, 65.80, 65.42, 60.97, 37.65, 26.38; HRMS (ESI): *m/z* calcd for $C_{15}H_{29}NO_{11}[M+H]^+$: 400.1819, found: 400.1818.

Computational Methods and Results

All computational results were obtained from the Gaussian 16 program.[10] Chemcraft 1.6 and Chimera were used to visualize structures and molecular orbitals. Calculations were performed adopting the B3LYP functional,[11, 12] and the 6-31+G(d) basis set for structure optimizations, single point geometries calculations, and free energy calculations. Calculations were conducted on closed-shell singlet. Geometry optimizations were also performed without symmetry constraints at 298.15 K and 1 atmosphere with unscaled vibrational frequencies.

a)



26 **30**

b)

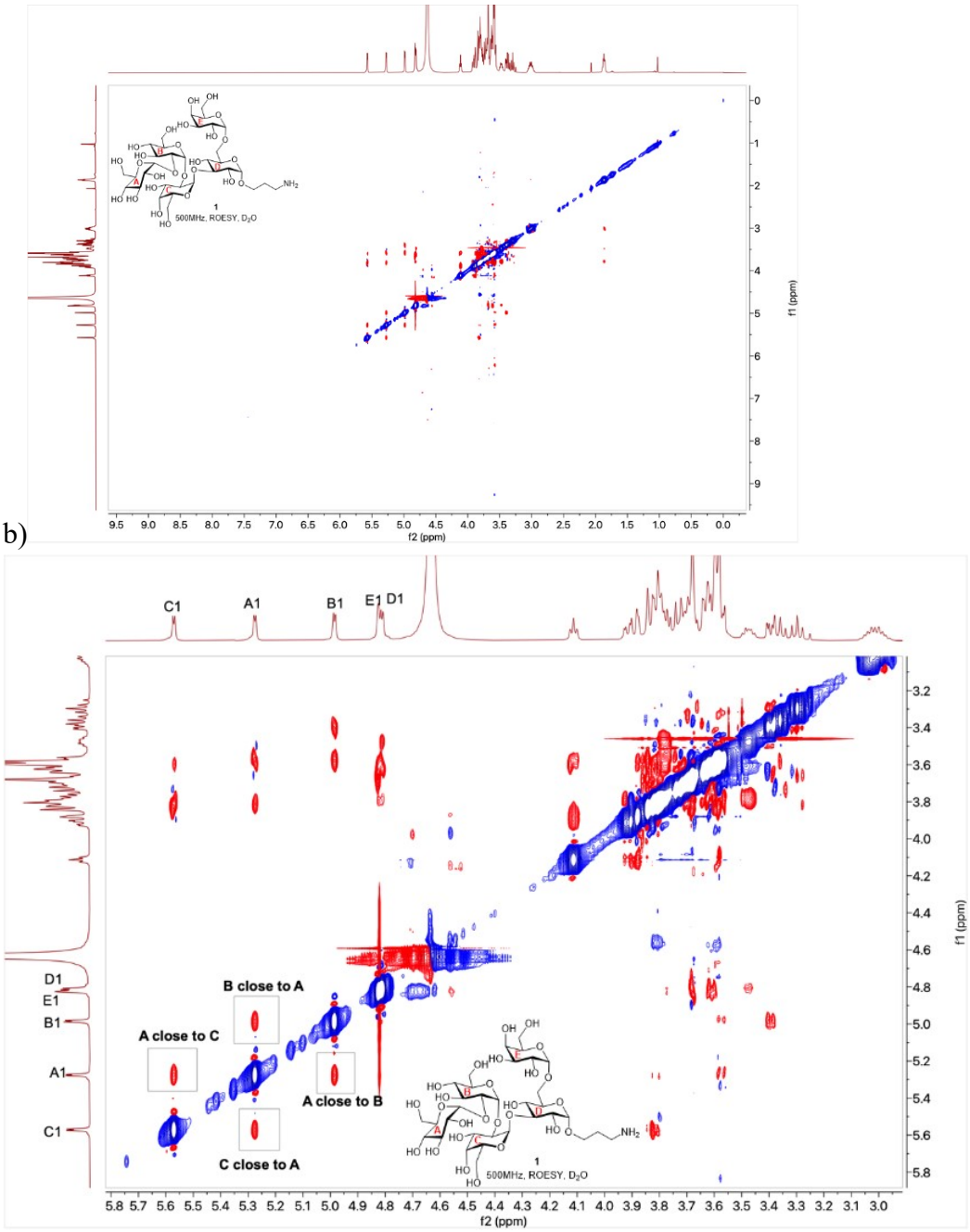
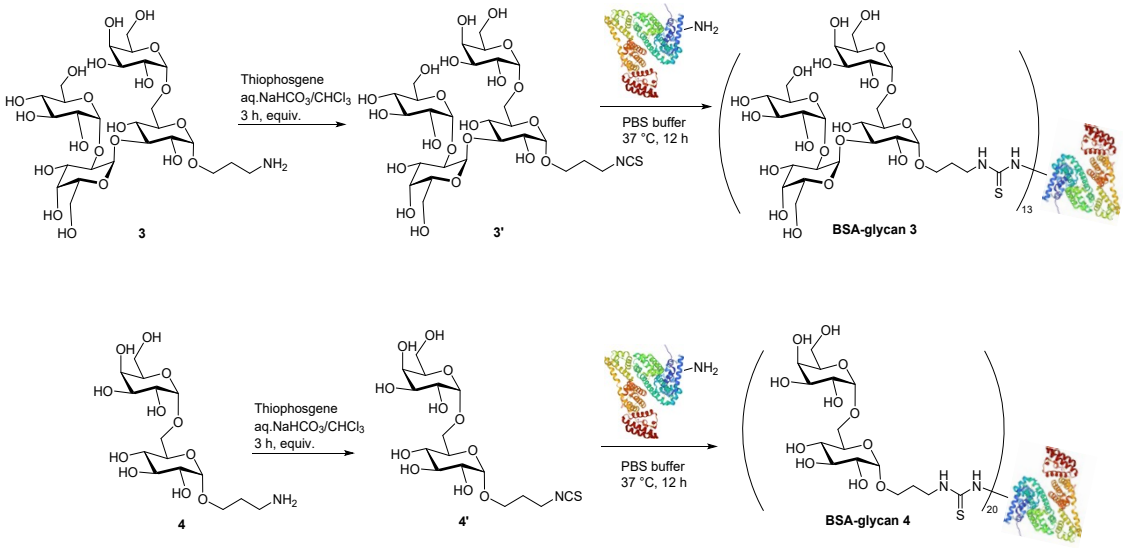


Figure S2. a) Geometry optimized structure of pentasaccharides **26** and **30** with charge = 0, multiplicity = 1. The OH in the compound **26** is deeply embedded within the center of molecule. Red atom: oxygen; white atom: hydrogen; grey atom: carbon; blue atom: nitrogen. b) ROESY-NMR spectrum and expansion of the ROESY-NMR spectrum of pentasaccharide **1**. Correlations

were observed between the anomeric protons of residues A, B and C suggesting these residues are close to each other in space confirming the sterically congested nature of pentasaccharide **1**.

Synthesis of BSA-glycan conjugates

An aqueous solution of compound **1** (5 mg, 5.6 μmol) in $NaHCO_3$ was prepared (500 μL, 10 mg/mL), then chloroform (750 μL) containing thiophosgene (1.67 μL, 21.8 μmol) was added. The reaction mixture was stirred vigorously at room temperature until complete consumption of starting material **1**, as monitored by ESI-HRMS. Upon completion, the reaction mixture was diluted with 2 mL of water, and the aqueous layer was extracted twice with 1 mL chloroform to remove excess thiophosgene. The aqueous layer was collected and lyophilized to afford compound **1'**. To a solution of 10 mg/ml BSA in PBS (100 mM, pH=8.0), **1'** (90 equiv to per BSA molecule) was added. The solution was gently mixed and nutated under 37 °C overnight. The protein was recovered with a 0.5 ml Amicon filter (MWCO = 30 kDa) under 13,000 g and washed with Milli-Q water four times, then lyophilized and stored in -20 °C. Conjugation reactions of BSA with **2', 3', 4'** were conducted in similar manners. The final conjugates were analyzed by matrix assisted laser desorption ionization mass spectrometry (MALDI-MS) (**Figure S2**).



Scheme S9: Syntheses of BSA-glycan **3** and BSA-glycan **4** conjugates.

Synthesis of mQβ-glycan conjugates

To a solution of mQβ particle (Qβ A38K/A40C/D102C, 5 mg/ml) in PBS (100 mM, pH=7.4), **1'** (30 equiv to mQβ subunits) was added. The solution was gently mixed and nutated under 37 °C overnight. The protein was recovered with a 0.5 ml Amicon filter (MWCO= 50 kDa) under 13,000 g and washed with PBS (100 mM, pH=7.4) four times. Conjugation of mQβ with **2'** was conducted in similar manners. The final conjugates were analyzed by electrospray high resolution mass spectrometry (ESI-HRMS) (**Figure S3**).

Procedure for mouse immunization.

Pathogen-free C57BL6 female mice aged 6 weeks were purchased from Charles River and maintained in the University Laboratory Animal Resources facility of Michigan State University. All animal experiments were performed in accordance with the guidelines of the Institutional Animal Care and Use Committee (IACUC) of Michigan State University. C57BL6 mice were injected subcutaneously under the scruff with 0.2 mL vaccine constructs. Immunization procedures were performed on days 0, 14 and 28. Blood samples were collected on days 0, 7, 21 and 35.

Procedure for rabbit immunization.

Rabbit immunization studies were performed by ProSci Inc (Poway, CA). Each dose of the vaccine construct (with an equivalent glycan amount of 15 nmol glycan for group I and 5 nmol for all other groups) was injected subcutaneously. The vaccination was adjuvanted with Alum in group F, G, I. In Group J, the vaccination was adjuvanted with MPLA. Immunization procedures were performed on day 0, 14, 28 and 42. Blood samples were collected on days 0, 7, 21 and 35. The terminal bleeding was performed on day 49.

Evaluation of antibody titters and subtypes by ELISA

Immulon 4 HBX 384 well plates (Thermo Fisher 8755) were coated with a solution of BSA-glycan conjugates or COPS (10 μg/mL, 50 μL/well) in PBS buffer and incubated at 4 °C overnight. The plate was washed with PBST (4 × 100 μL) and blocked with 1% BSA/PBS (100 μL/well) for 1 h at room temperature. The liquid was discarded. The plates were washed with PBST (4 × 100 μL), and incubated with serial dilutions of anti-sera from immunized mice or rabbits in 0.1% BSA/PBS (50 μL/well, 3 wells for each dilution). The plates were incubated for 2 h and then liquid was discarded. The plates were washed with PBST (4 × 100 μL). A 1:2000 dilution of HRP-conjugated goat anti-mouse IgG (Cat # 115-035-003, Jackson Immuno Research Laboratory) or a 1:5000 dilution of HRP-conjugated goat anti-rabbit IgG (Cat # 111-035-003, Jackson Immuno Research Laboratory) in 0.1% BSA/PBS (50 μL) was added to each well and incubated for 1 h. The liquid was discarded, and the plates were washed with PBST (4 × 100 μL). Then, the substrate solution (75 μL) was added to each well, and the reaction was incubated for 15 minutes. To stop the reaction, 0.5 M H_2SO_4 (50 μL) was added. OD450 nm was immediately recorded and fitted into 4PL nonlinear logistic model via GraphPad Prism 6 with least squares algorism. The near-background (endpoint) titer was determined through regression analysis, where the log10 dilution was plotted against optical density. It was reported as the highest dilution fold (ELISA units) that yielded an optical absorbance at the threshold level. The threshold should be 3 times standard deviation above the blank wells on the plate.

Bacterial strains and growth conditions

All the subtypes of *Salmonella* have been described previously (*S.* Enteritidis R11[13], *S.* Enteritidis R11 Δ*invA* Δ*rfaL*[14], *S.* Typhimurium I77[13], *S.* Paratyphi A ATCC 9150[15], *S.* Newport Chile 361, *S.* Newport Chile 361 Δ*rfaL* [16]) and was maintained in Hy-Soy media (Teknova, CA) as described.[17]

Procedure for flow cytometry

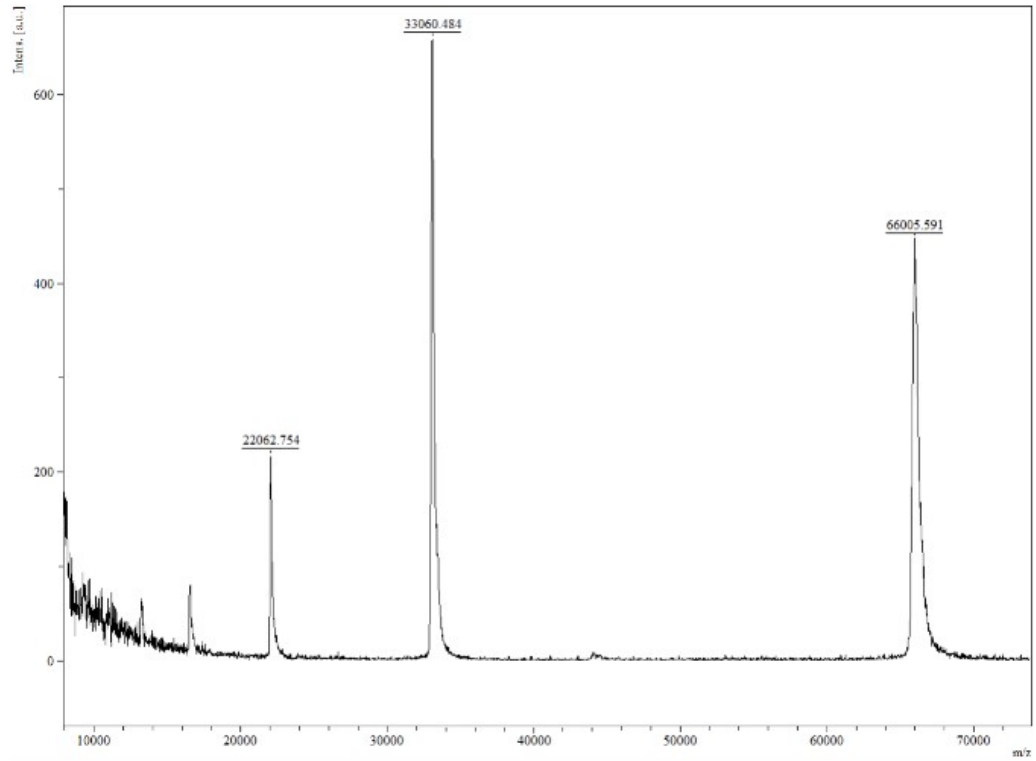
A single colony of *S.* Paratyphi A ATCC 9150 was grown in HS broth overnight at 37°C with shaking at 220 rpm. The following day, bacteria were adjusted to an OD600 of 0.4 and placed on ice. For samples requiring thanatin treatment, the overnight culture (10 mL) was inoculated into fresh HS broth (10 mL) in a 50 mL tube. Thanatin (HY-P5601, MedChemExpress, NJ) was then added to achieve a final concentration of 0.1 μM. The cells were incubated at 37°C for 6 hours. After incubation, the bacterial culture was adjusted to an OD600 of 0.4 and placed on ice. The bacterium suspension (250 μL) was washed once with flow buffer (1% heat-inactivated FBS in PBS) and incubated with various dilutions of pooled rabbit sera (heat-inactivated for 30 min at 56 °C) for 1 h at 4°C. Rabbit sera tested included both the pre-immune and the post-immune (D49) sera. Bacteria were then washed two times with flow buffer, followed by incubation with FITC-conjugated donkey anti-rabbit IgG (Cat # 406403, Biolegend, CA, 1 μg/mL) diluted in flow buffer for 1 h at 4 °C. Bacteria were then washed twice with PBS, fixed with 2% formaldehyde, and read using BD Accuri C6 with 1×10^4 events recorded. As a negative control, bacteria were incubated with the secondary antibody alone. Flow cytometry analysis of the other strains was conducted in similar manners.

Serum bactericidal antibody assay

Bacteria were prepared as follows: a single colony of *S.* Typhimurium I77 was used to inoculate an overnight HS broth culture incubated at 37 °C with shaking at 220 rpm. On the following day, log-phase cultures were prepared by diluting the overnight culture 1:50 in fresh HS broth (37 °C, 220 rpm) with thanatin added to the broth (final concentration of thanatin was 0.5 μM). Bacteria were harvested when the OD600 value reached 0.4. Heat-inactivated serum (56 °C for 30 minutes) was diluted 1:50 in Hanks' Balanced Salt Solution (HBSS) and mixed with *S.* Typhimurium I77 (250 CFU). The sera and bacteria were incubated at 4 °C overnight. After incubation, the mixture was supplemented with 15% (final concentration) baby rabbit complement (31061-1, Pel-Freez Biologicals). Negative controls included *S.* Typhimurium I77 only and *S.* Typhimurium I77 with complement alone. To confirm that the serum was free of active complement following heat inactivation, a subset of samples containing *S.* Typhimurium I77 and serum (without exogenous complement) was tested for bactericidal activity. The mixtures were then incubated for 1 hour at 37 °C, plated on HS agar plates, and incubated overnight at 37 °C. The bactericidal percentage was calculated as the number of bacteria that survived divided by the number of bacteria in the bacteria-plus-complement control group × 100%. All samples were assayed in duplicate, and the average results were reported. The same procedure was followed for *S.* Enteritidis R11, *S.* Newport Chile 361, and *S.* Paratyphi A ATCC 9150, with the following modifications: (1) for *S.*

Newport Chile 361, the final complement concentration used was 10%; (2) for *S.* Paratyphi A ATCC 9150, 1,000 CFU were used instead of 250 CFU.

a)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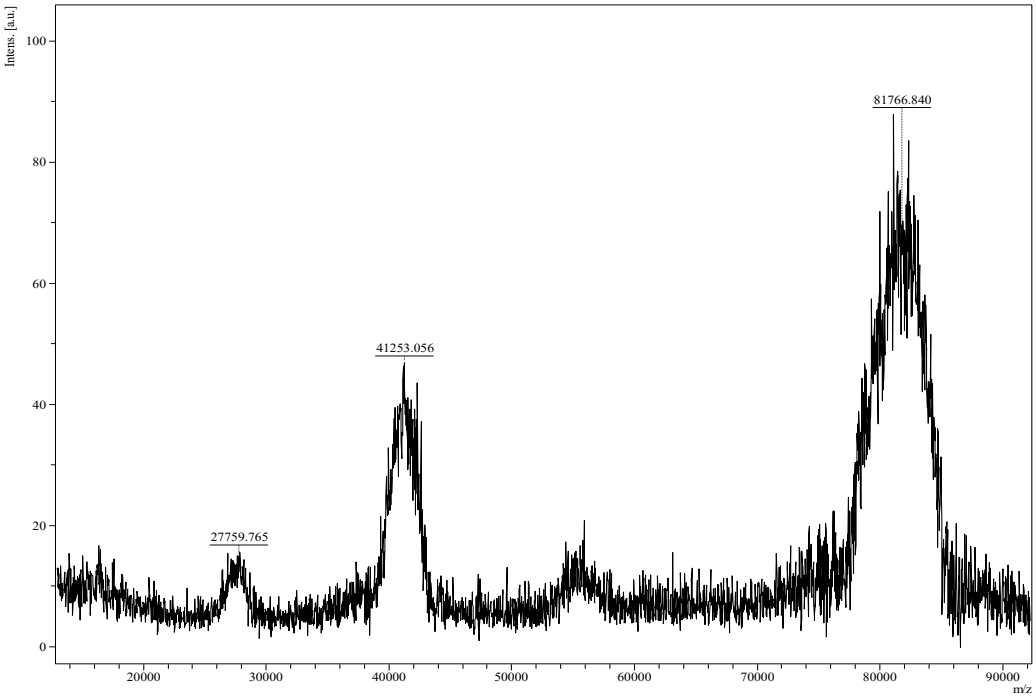
60000
70000
m/z

b)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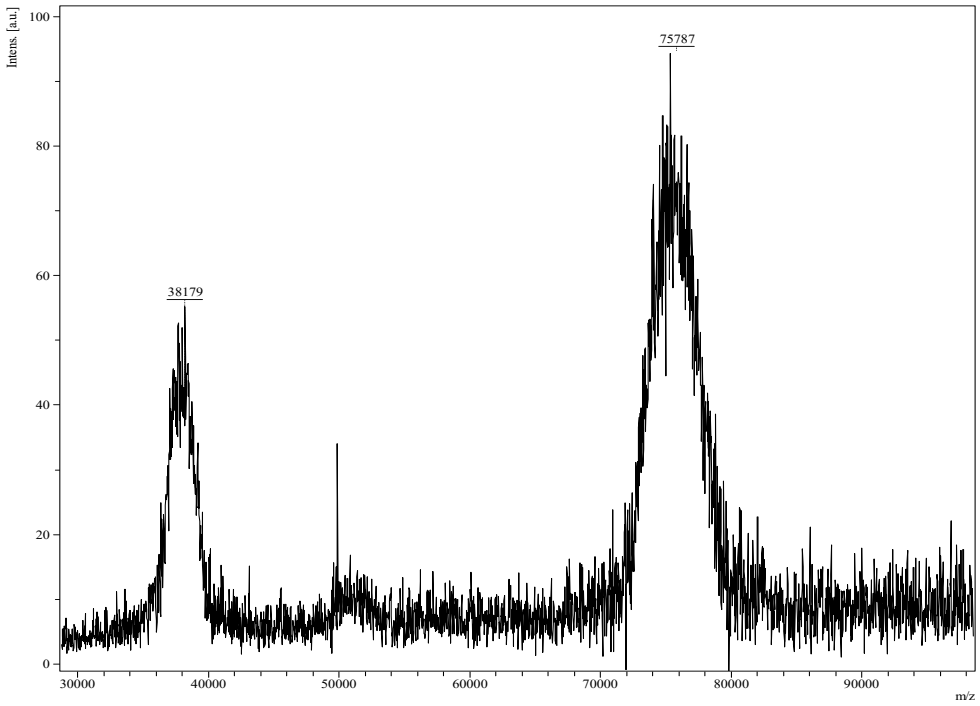
60000
70000
80000
90000
m/z

c)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70000
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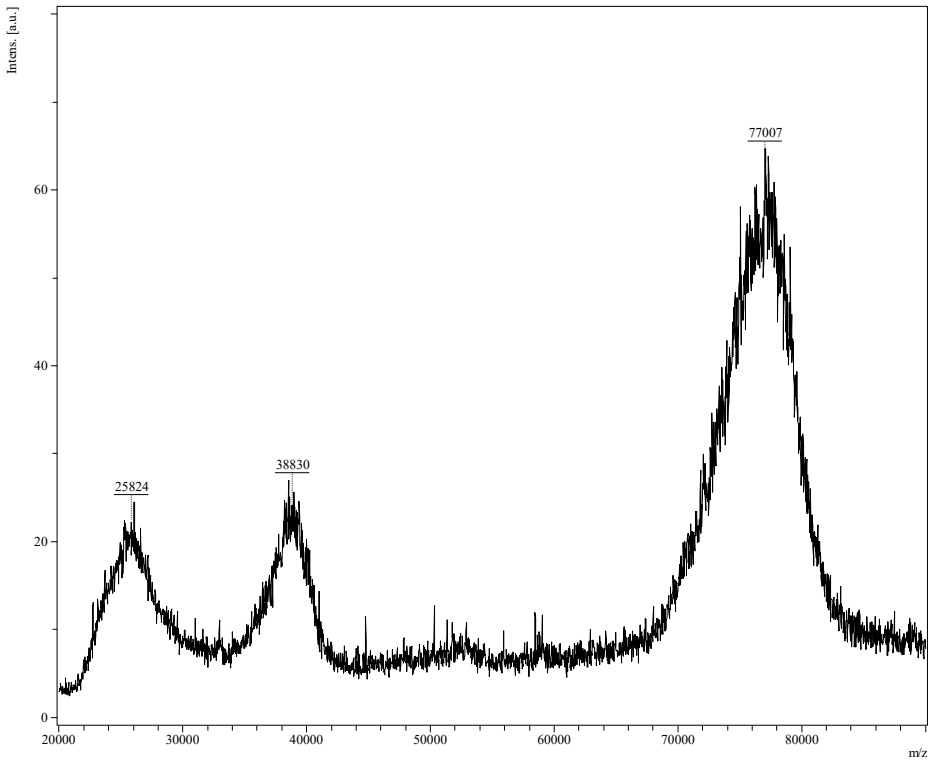
90000
m/z

d)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e)

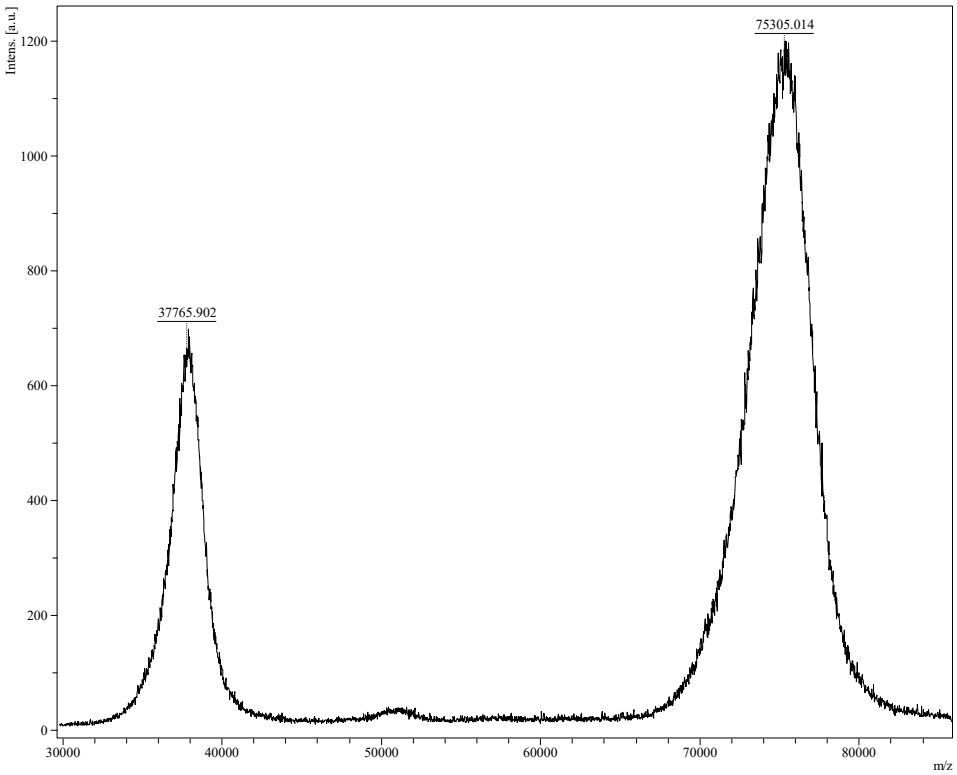
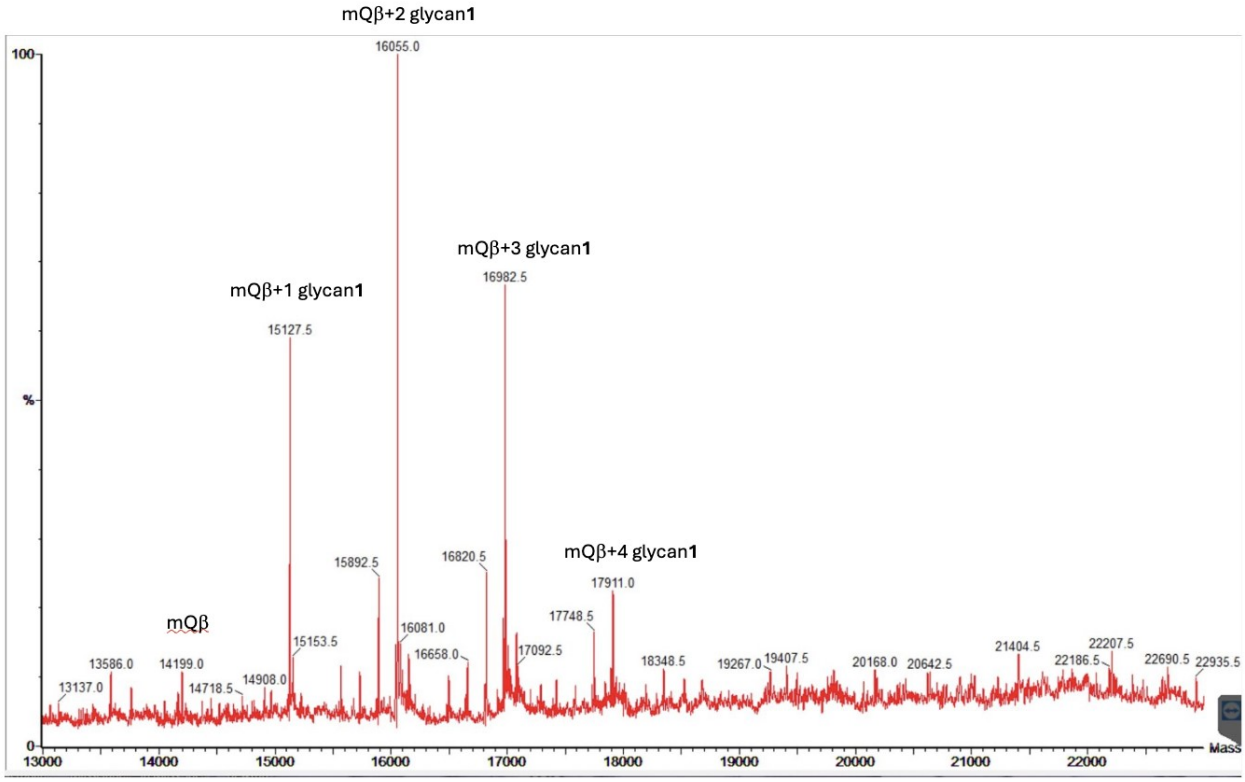


Figure S3. MALDI-TOF MS characterization of BSA-glycans. a) BSA protein only; b) BSA-glycan **1**. The molecular weight of BSA shifted from 66,005 Da to 81,766 Da after conjugation, indicating an average of 17 glycan **1** units per BSA molecule; c) BSA-glycan **2**. The molecular weight of BSA shifted from 66,005 Da to 75,787 Da after conjugation, indicating an average of 10 glycan **2** units per BSA molecule; d) BSA-glycan **3**. The molecular weight of BSA shifted from 66,005 Da to 77,007 Da after conjugation, indicating an average of 13 glycan **3** units per BSA molecule; e) BSA-glycan **4**. The molecular weight of BSA shifted from 66,005 Da to 75,305 Da after conjugation, indicating an average of 20 glycan **4** units per BSA molecule. The difference of MW before and after conjugation divided by the MW of glycans (glycan **1**: 927; glycan **2**: 969; glycan **3**: 754; glycan **4**: 461) gave the average loading copies of glycans per BSA molecule.

a)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mQβ+3 glycan1
16982.5
mQβ+1 glycan1
15127.5
mQβ+4 glycan1
17911.0
mQβ
15892.5
16820.5
17748.5
16081.0
15153.5
16658.0
17092.5
13586.0
14199.0
14908.0
13137.0
14718.5
18348.5
19267.0
19407.5
20168.0
20642.5
21404.5
22207.5
22186.5
22690.5
22935.5
100
%
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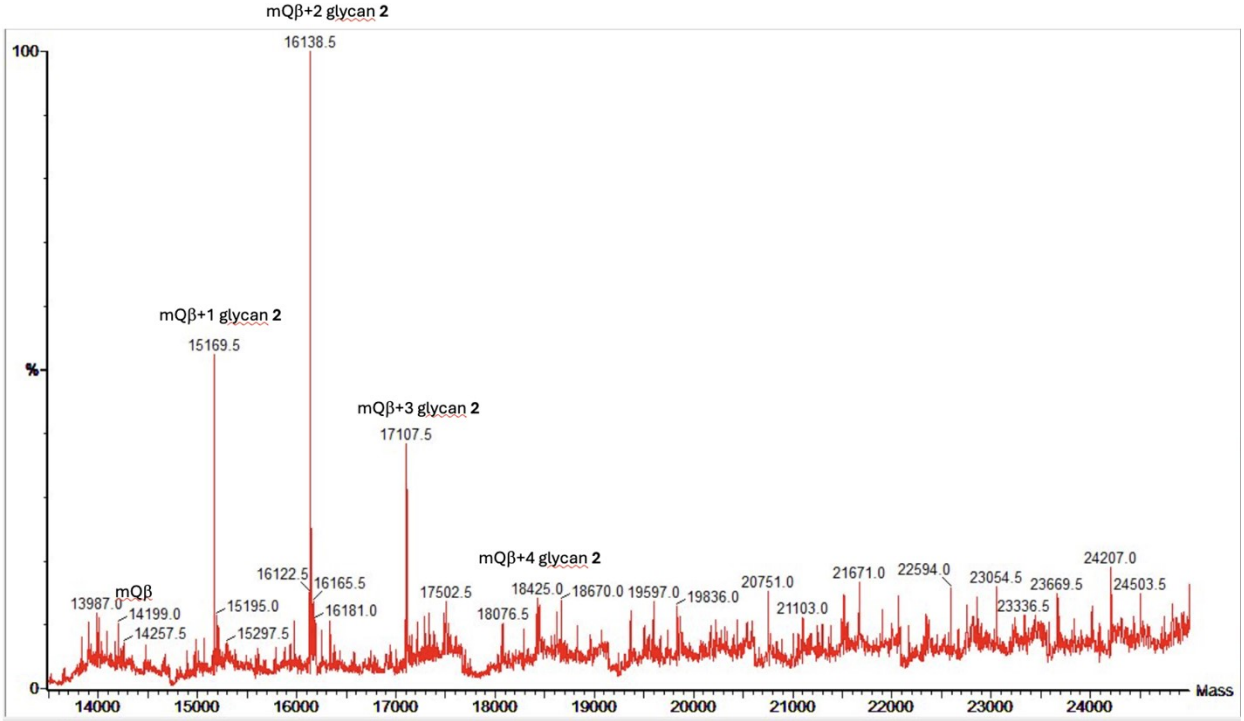
14000
15000
16000
17000
18000
19000
20000
21000
22000
Mass

b)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mQβ
16122.5
16165.5
13987.0
14199.0
15195.0
16181.0
14257.5
15297.5
17502.5
18425.0
18670.0
19597.0
18076.5
19836.0
20751.0
21103.0
21671.0
22594.0
23054.5
23669.5
23336.5
24207.0
24503.5
100
%
0
14000
15000
16000
17000
18000
19000
20000
21000
22000
23000
24000
Mass

Figure S4. ESI-TOF HRMS spectra of mQβ-glycan **1** and mQβ-glycan **2** conjugates. a) Mass spectrometry analysis of the mQβ-glycan **1** conjugate showed an average loading of 378 pentasaccharides on each capsid. The peaks observed showed a sequential mass shift of ~928 corresponding to the addition of one unit of glycan **1**. b) Mass spectrometry analysis of mQβ-glycan **2** conjugate showed an average loading of 350 pentasaccharides on each capsid. The peaks observed showed a sequential mass shift of ~969 corresponding to the addition of one unit of glycan **2**. The average loading was calculated using the following formula: (sum of the intensities of peaks of mQβ conjugate multiplied by the number of glycan attached for the peak) / (sum of the intensities of peaks of mQβ conjugate and that of the unmodified mQβ).

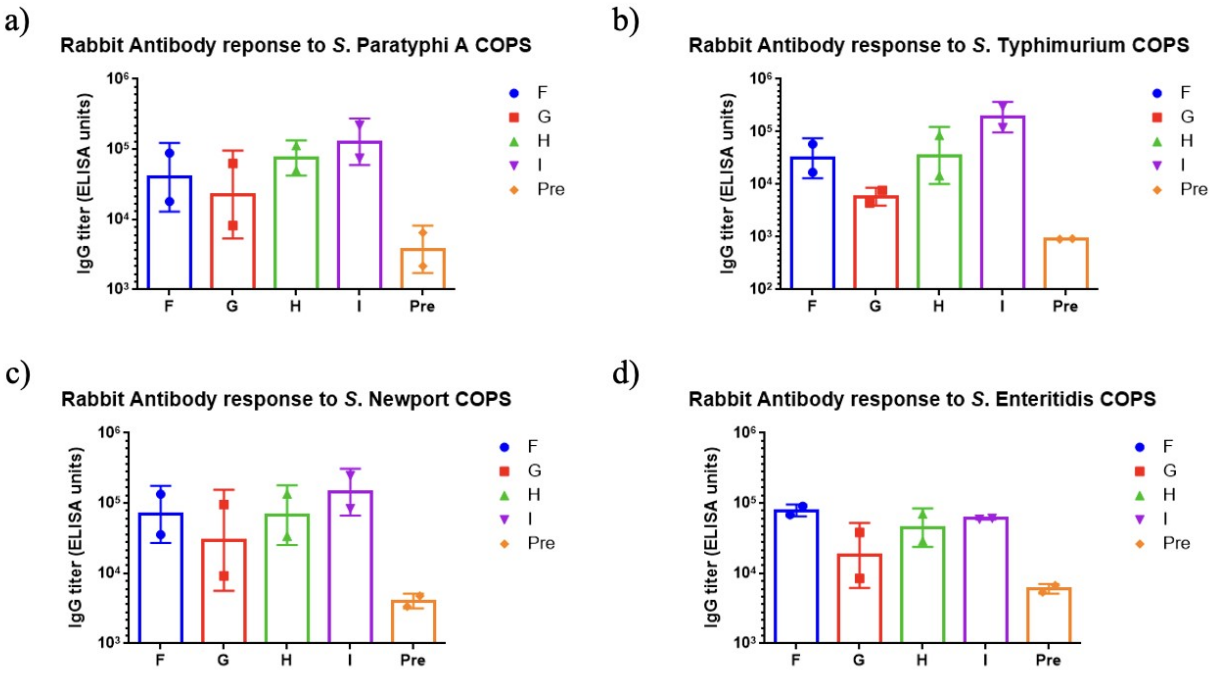


Figure S5. ELISA analysis for antibody binding to native *Salmonella* COPS. Individual anti-sera from rabbits immunized with mQβ-glycan **1** and mQβ-glycan **2** were assessed for COPS binding by ELISA as indicated. Each symbol represents one rabbit. Data are presented as geometric mean values ± standard deviation. X-axis labels: Pre (pre-immunized sera from rabbits); F (F group: day 49 sera from rabbits immunized with mQβ-glycan **1** (5 μg glycan **1** with Alum)); G (G group: day 49 sera from selected two rabbits immunized with mQβ-glycan **1** (15 μg glycan **1** with Alum)); H (H group: day 49 sera from selected two rabbits immunized with mQβ-glycan **2** (5 μg glycan **1** with Alum)); I (I group: day 49 sera from selected two rabbits immunized with mQβ-glycan **2** (5 μg glycan **1** with MPLA)).

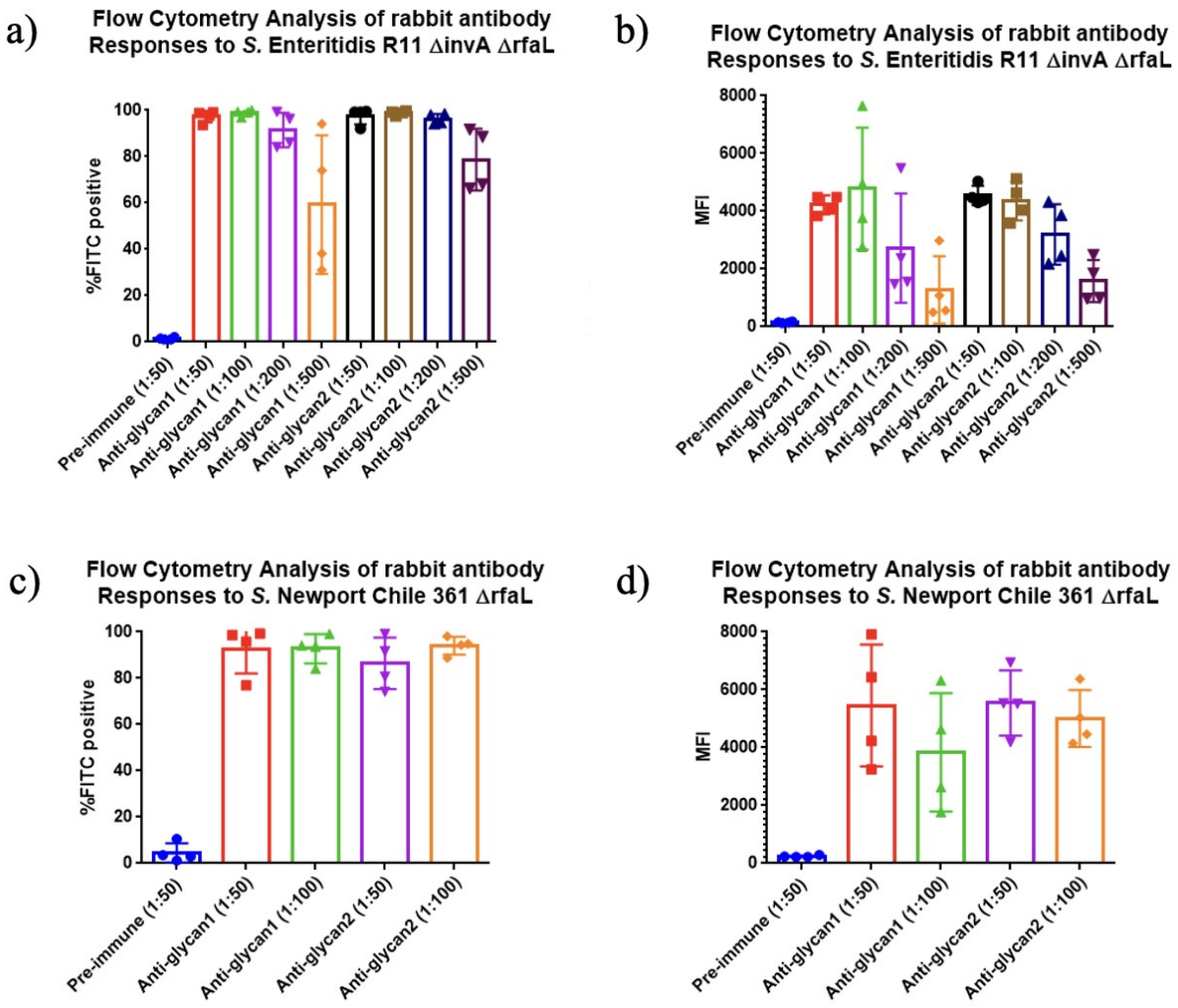


Figure S6. mQβ-glycan **1** and mQβ-glycan **2** induced rabbit antibodies bind *Salmonella* bacteria. Each symbol corresponds to an individual animal. a) percentages of positive *S.* Enteritidis R11 *ΔinvA ΔrfaL* cells stained by various dilutions of sera as quantified by flow cytometry; b) Mean fluorescence intensities (MFI) of *S.* Enteritidis R11 *ΔinvA ΔrfaL* cells; c) percentages of positive *S.* Newport Chile 361 *ΔrfaL* cells stained by various dilutions of sera as quantified by flow cytometry; d) Mean fluorescence intensities (MFI) of *S.* Newport Chile 361 *ΔrfaL* cells. FTIC-conjugated anti rabbit IgG was used as the secondary antibody for detection.

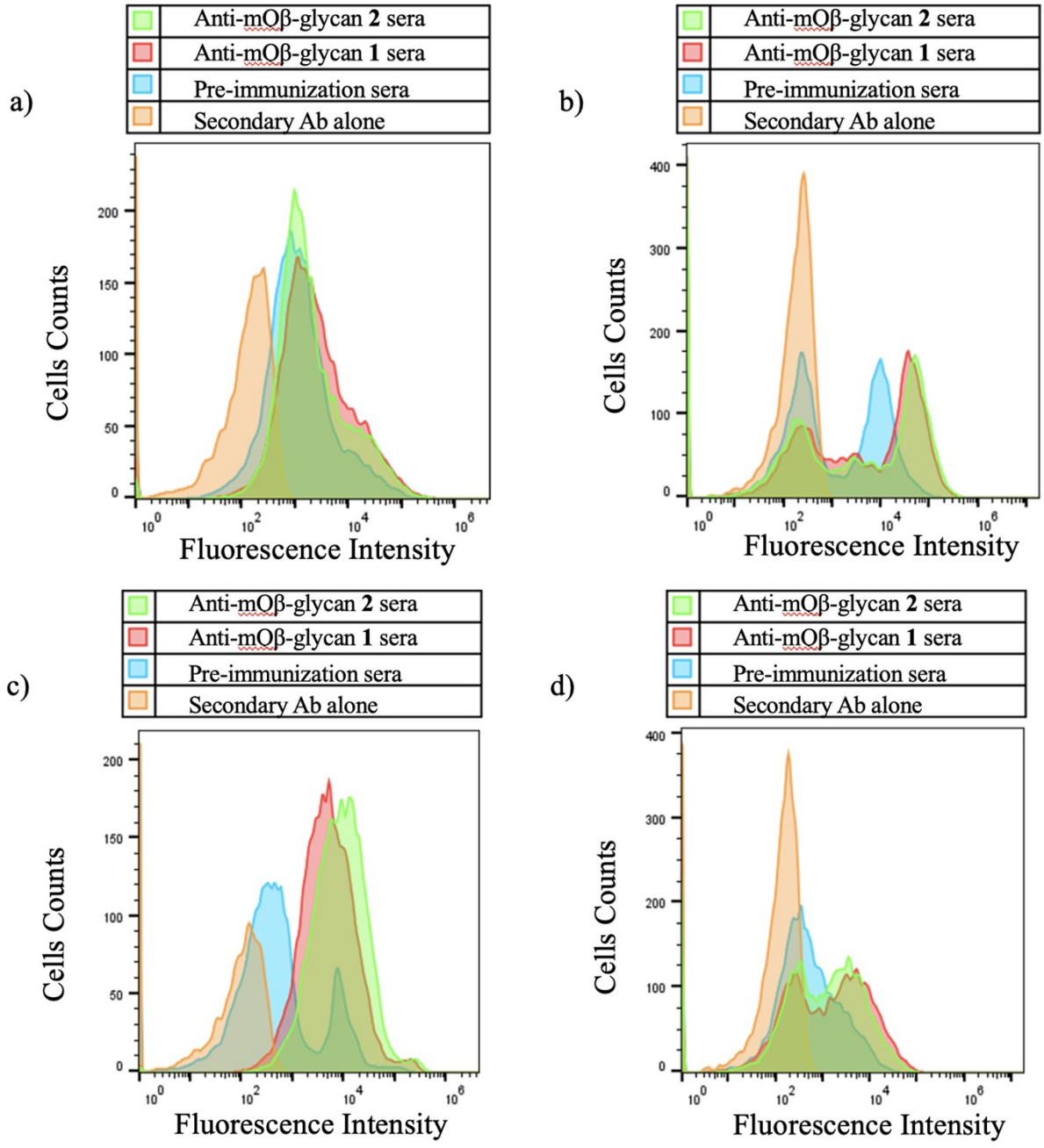
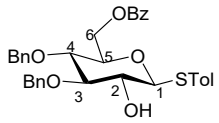


Figure S7. mQβ-glycan **1** and mQβ-glycan **2** induced rabbit antibodies bound thanatin treated *Salmonella* strains. a) Flow cytometry graphs of post-immunization sera (1:50 dilution) binding with *S*. Enteritidis R11 strain treated with thanatin at a final concentration of 0.5 μM, as compared to anti-rabbit IgG secondary antibody alone or pre-immunization rabbit sera (1:50 dilution). b) Flow cytometry graphs of post-immunization sera (1:50 dilution) binding with 0.5 μM thanatin treated *S*. Typhimurium I77 strain, as compared to anti-rabbit IgG secondary antibody alone or pre-immunization rabbit sera (1:50 dilution). c) Flow cytometry graphs of post-immunization sera (1:50 dilution) binding with 0.5 μM thanatin treated *S*. Paratyphi A ATCC 9150 strain, as

compared to anti-rabbit IgG secondary antibody alone or pre-immunization rabbit sera (1:50 dilution). d) Flow cytometry graphs of post-immunization sera (1:50 dilution) binding with 0.2 μM thanatin treated *S.* Newport Chile 361 strain, as compared to anti-rabbit IgG secondary antibody alone or pre-immunization rabbit sera (1:50 dilution).

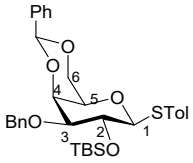
Table S1. NMR data of compound **10**



10

Position	^{1}H (ppm)	^{13}C (ppm)	^{1}H-^{1}H COSY	HMBC (H→C)
1	4.46 (d, *J* = 9.3 Hz, 1H)	87.75	H-2	C-2, C-3
2	3.43 (t, *J* = 9.3 Hz, 1H)	72.44	H-1, H-3	C-1, C-3
3	3.68-3.62 (m, 1H)	85.96	H-2, H-4	C-2, C-4
4	3.59-3.55 (m, 1H)	76.99	H-3, H-5	C-5, C-6
5	3.68-3.66 (m, 1H)	77.31	H-4, H-6	C-4
6	4.69 (dd, *J* = 11.9, 2.1 Hz, H-6a, 1H) 4.44 (dd, *J* = 11.9, 4.5 Hz, H-6b, 1H)	63.35	H-5	C-5

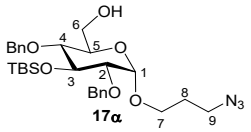
Table S2. NMR data of compound **12**



12

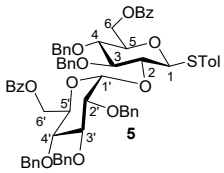
Position	^{1}H (ppm)	^{13}C (ppm)	^{1}H-^{1}H COSY	HMBC(H→C)
1	4.52 (d, *J* = 9.0 Hz, 1H)	89.52	H-2	C-2, C-3
2	4.02 (t, *J* = 9.0 Hz, 1H)	69.21	H-1, H-3	C-1, C-3
3	3.42 (dd, *J* = 9.0, 3.5 Hz, 1H)	82.43	H-2, H-4	C-2, C-4
4	4.08 (dd, *J* = 3.5, 1.1 Hz, 1H)	73.01	H-3, H-5	C-3, C-5
5	3.37-3.35 (m, 1H)	69.77	H-4, H-6	C-1, C-6
6	4.32 (dd, *J* = 12.3, 1.8 Hz, H-6a, 1H) 3.93 (dd, *J* = 12.3, 1.8 Hz, H-6b, 1H)	69.57	H-5	C-4, C-5

Table S3. NMR data of compound **17α**



Position	^{1}H (ppm)	^{13}C (ppm)	^{1}H-^{1}H COSY	HMBC (H→C)
1	4.56 (d, *J* = 3.7 Hz, 1H)	97.34	H-2	C-3, C-5, C-7
2	3.28 (dd, *J* = 9.3, 3.7 Hz, 1H)	80.72	H-1, H-3	C-3
3	4.03 (t, *J* = 9.3 Hz, 1H)	73.93	H-2, H-4	C-2, C-4
4	3.43-3.36 (m, 1H)	78.75	H-3, H-5	C-3, C-5
5	3.63-3.53 (m, 1H)	71.11	H-4, H-6	C-6
6	3.71 (dd, *J* = 11.8, 2.8 Hz, H-6a, 1H); 3.71-3.63 (m, H-6b, 1H)	61.96	H-5	C-4, C-5
7	3.68-3.60 (m, H-7a, 1H); 3.35-3.27 (m, H-7b, 1H)	64.71	H-1, H-8	C-1, C-8, C-9
8	1.89-1.81 (m, 2H)	28.97	H-7, H-9	C-7, C-9
9	3.43-3.35 (m, 2H)	48.46	H-8	C-7, C-8

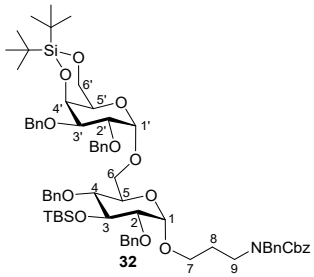
Table S4. NMR data of compound **5**



Position	^{1}H (ppm)	^{13}C (ppm)	^{1}H-^{1}H COSY	HMBC (H→C)
1	4.83 (d, *J* = 9.4 Hz, 1H)	86.97	H-2	C-2, C-3, C-5
2	3.95 (t, *J* = 9.4 Hz, 1H)	74.28	H-1, H-3	C-1, C-3, C-1'
3	3.85 (t, *J* = 8.9 Hz, 1H)	84.88	H-2, H-4	C-2, C-4
4	3.72-3.65 (m ,1H)	78.80	H-3, H-5	C-3, C-5, C-6
5	3.77-3.69 (m, 1H)	77.02	H-4, H-6	C-4
6	4.70 (dd, *J* = 12.0, 2.1 Hz, H-6a, 1H) 4.46 (dd, *J* = 12.0, 2.1 Hz, H-6b, 1H)	63.51	H-5	C-4, C-5
1'	6.05 (d, *J* = 3.8 Hz, 1H)	95.29	H-2'	C-2, C-2', C-3', C-5'
2'	3.72-3.64 (m, 1H)	80.04	H-1', H-3'	C-3'
3'	4.07 (t, *J* = 9.3 Hz, 1H)	81.88	H-2', H-4'	C-2', C-4'

4'	3.66-3.58 (m, 1H)	77.80	H-3', H-5'	C-3', C-5', C-6'
5'	4.39-4.34 (m, 1H)	68.96	H-4', H-6'	C-4'
6'	4.31 (d, *J* = 12.1, 2.1 Hz, H-6a', 1H) 3.91 (dd, *J* = 12.1, 3.6 Hz, H-6b', 1H)	63.26	H-5'	C-5'

Table S5. NMR data of compound **32**

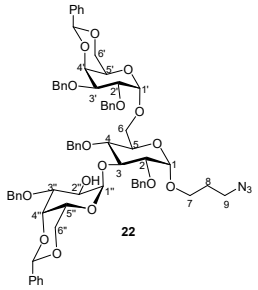


32

Position	^{1}H (ppm)	^{13}C(ppm)	^{1}H-^{1}H COSY	HMBC(H→C)
1	4.52 (1H)	97.02	H-2	
2	3.22-3.14 (m,1H)	80.78	H-1, H-3	
3	4.05-3.98 (m, 1H)	74.42	H-2, H-4	C-2, C-4
4	3.58-3.50 (m, 1H)	79.47	H-3, H-5	C-3, C-5, C-6
5	3.71-3.64 (m, 1H)	70.63	H-4, H-6	C-4
6	3.70-3.63 (m, H-6a, 1H) 3.72-3.67 (m, H-6b, 1H)	66.05	H-5	C-4, C-5, C-1'
7	3.62-3.53 (m, H-7a, 1H) 3.25-3.18 (m, H-7b, 1H)	65.37, 65.18	H-1, H-8	C-1, C-8, C-9
8	1.84-1.78 (m, 2H)	28.46, 27.77	H-7, H-9	C-7, C-9
9	3.41-3.31 (m, 2H)	51.11, 50.75	H-8	C-7, C-8
1'	5.00 (d, *J* = 3.5 Hz, 1H)	98.22	H-2'	C-6, C-3', C-5'
2'	4.03-3.96 (m, 1H)	74.03	H-1', H-3'	C-3'
3'	3.79 (dd, *J* = 10.1, 2.9 Hz, 1H)	77.16	H-2', H-4'	C-2', C-4'
4'	4.48-4.40 (m, 1H)	71.18	H-3', H-5'	C-2', C-3', C-5'
5'	3.47-3.39 (m, 1H)	67.25	H-4', H-6'	C-1', C-4', C-6'
6'	4.07-3.99 (m, 2H)	67.25	H-5'	C-5'

Table S6. NMR data of compound **22**

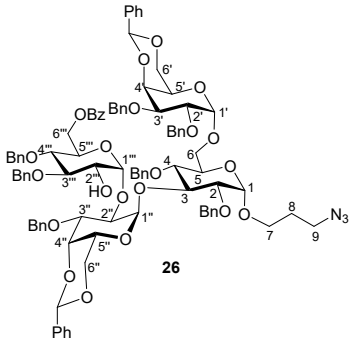
Position	1H (ppm)	13C(ppm)	1H-1H COSY	HMBC(H-C)
1	4.83 (d, *J* = 9.4 Hz, 1H)	86.97	H-2	C-2, C-3, C-5
2	3.95 (t, *J* = 9.2 Hz, 1H)	74.28	H-1, H-3	C-1. C-3. C-1'
3	3.85 (t, *J* = 8.9 Hz, 1H)	84.88	H-2, H-4	C-2, C-4
4	3.68 (m ,1H)	78.8	H-3, H-5	C-3, C-5, C-6
5	3.73 (m, 1H)	77.02	H-4, H-6	C-4
6	4.70 (dd, *J* = 12.0, 2.1 Hz, H-6a); 4.46 (dd, *J* = 12.0, 2.1 Hz, H-6b)	63.51	H-5	C-4, C-5
1'	6.05 (d, *J* = 3.8 Hz, 1H)	95.29	H-2'	C-2, C-2', C-3', C-5'
2'	3.68 (m, 1H)	80.04	H-1', H-3'	C-3'
3'	4.07 (t, *J* = 9.3 Hz, 1H)	801.88	H-2', H-4'	C-2', C-4'
4'	3.62 (m, 1H)	77.8	H-3', H-5'	C-3'. C-5', C-6'
5'	4.37 (ddd, *J* = 10.3, 3.6, 2.1 Hz, 1H)	68.96	H-4', H-6'	C-4'
6'	4.31 (d, *J* = 12.1, 2.1 Hz, H-6a'); 3.91 (dd, *J* = 12.1, 3.9 Hz, H-6b')	63.26	H-5'	C-5'



Position	^{1}H (ppm)	^{13}C(ppm)	^{1}H-^{1}H COSY	HMBC (H→C)
1	4.83 (1H)	96.38	H-2	C-3, C-5, C-7
2	3.34-3.28 (m, 1H)	78.93	H-1, H-3	C-3
3	4.26-4.19 (m, 1H)	75.20	H-2, H-4	C-2, C-1"
4	3.72-3.68 (m ,1H)	79.34	H-3, H-5	C-2, C-3
5	3.78-3.70 (m, 1H)	70.87	H-4, H-6	C-6
6	3.90-3.82 (m, H-6a, 1H); 3.91-3.73 (m, H-6b, 1H)	66.23	H-5	C-4, C-5, C-1'
7	3.78-3.71 (m, H-7a, 1H); 3.70-3.65 (m, H-7b, 1H)	64.53	H-1, H-8	C-1, C-8, C-9
8	1.88-1.79 (m, 2H)	28.89	H-7, H-9	C-7, C-9
9	3.43-3.35 (m, 2H)	48.29	H-8	C-8
1'	5.19 (d, *J* = 3.5 Hz, 1H)	98.79	H-2'	C-3', C-5', C-6

2'	4.11 (dd, *J* = 10.0, 3.5 Hz, 1H)	75.83	H-1', H-3'	C-3', C-4'
3'	3.80-3.72 (m, 1H)	75.20	H-2', H-4'	C-2'
4'	3.91-3.74 (m, 1H)	74.79	H-3', H-5'	C-3'
5'	3.54 (s, 1H)	62.87	H-4', H-6'	C-4'
6'	4.21-4.14 (m, H-6a', 1H); 3.98-3.90 (m, H-6b', 1H)	69.49	H-5'	C-4', C-5'
1"	5.60 (d, *J* = 3.8 Hz, 1H)	98.77	H-2"	C-2", C-3, C-3", C-5"
2"	4.21-4.14 (m, 1H)	67.99	H-1", H-3"	C-3", C-5"
3"	3.80-3.72 (m, 1H)	76.62	H-2", H-4"	C-1", C-4"
4"	3.93-3.84 (m, 1H)	74.76	H-3", H-5"	C-2", C-3"
5"	3.90-3.83 (m, 1H)	62.38	H-4", H-6"	C-1", C-4"
6"	3.98-3.90 (m, H-6a", 1H); 3.30-3.24 (m, H-6b", 1H)	69.45	H-5"	C-5"

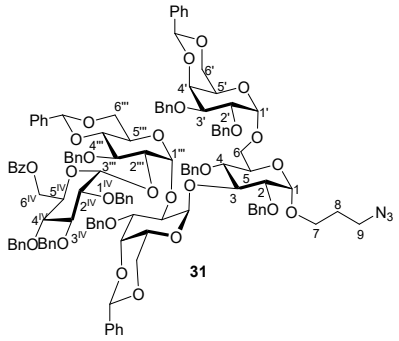
Table S7. NMR data of compound **26**



Position	^{1}H (ppm)	^{13}C (ppm)	^{1}H-^{1}H COSY	HMBC (H→C)
1	4.74 (1H)	96.27	H-2	C-3, C-5, C-7
2	3.36 (dd, *J* = 9.5, 3.7 Hz, 1H)	80.12	H-1, H-3	C-3
3	4.41-4.37 (m, 1H)	76.91	H-2, H-4	C-2, C-4, C-1"
4	3.91-3.86 (m, 1H)	78.66	H-3, H-5	C-3, C-5
5	3.92-3.83 (m, 1H)	70.07	H-4, H-6	C-3, C-4, C-6
6	3.89-3.81 (m, H-6a, 1H); 3.85-3.77 (m, H-6b, 1H)	66.00	H-5	C-5, C-1'
7	3.79-3.70 (m, H-7a, 1H); 3.47-3.39 (m, H-7b, 1H)	64.41	H-1, H-8	C-1, C-8
8	1.93-1.83 (m, 2H)	28.65	H-7, H-9	C-7, C-8
9	3.50-3.40 (m, 2H)	48.17	H-8	C-8
1'	5.22 (d, *J* = 3.4 Hz,1H)	98.42	H-2'	C-6, C-3', C-5'
2'	4.21-4.12 (m, 1H)	76.43	H-1', H-3'	C-3'
3'	4.08-4.00 (m, 1H)	75.76	H-2', H-4'	C-2'
4'	4.24-4.18 (m, 1H)	75.12	H-3', H-5'	C-3', C-5'
5'	3.54 (s, 1H)	62.66	H-4', H-6'	C-4'
6'	3.98 (d, *J* = 12.2 Hz, H-6a', 1H); 3.86-3.78 (m, H-6b', 1H)	69.40	H-5'	C-5'
1"	5.67 (d, *J* = 3.4 Hz, 1H)	96.80	H-2"	C-3, C-3", C-5"
2"	4.41 (dd, *J* = 10.2, 3.4 Hz, 1H)	71.95	H-1", H-3"	C-3", C-1'"
3"	4.09-4.03 (m, 1H)	73.77	H-2", H-4"	C-1", C-4"
4"	4.22-4.15 (m, 1H)	73.27	H-3", H-5"	C-3", C-5"
5"	4.09-4.01 (m, 1H)	62.66	H-4", H-6"	C-4"
6"	4.29-4.21 (m, H-6a", 1H); 4.26-4.18 (m, H-6b", 1H)	69.37	H-5"	C-5"
1'"	4.92 (d, *J* = 3.9 Hz, 1H)	96.64	H-2'"	C-2", C-3'", C-5'"
2'"	3.71-3.63 (m, 1H)	72.73	H-1'", H-3'"	C-3'"

3'''	3.66-3.58 (m, 1H)	79.94	H-2''', H-4'''	C-2''', C-4'''
4'''	3.65-3.56 (m, 1H)	81.56	H-3''', H-5'''	C-3''', C-5'''
5'''	4.40-3.32 (m, 1H)	62.15	H-4''', H-6'''	C-3''', C-6'''
6'''	4.23-4.16 (m, H-6a''', 1H); 3.69-3.61 (m, H-6b''', 1H)	68.77	H-5'''	C-4''', C-5'''

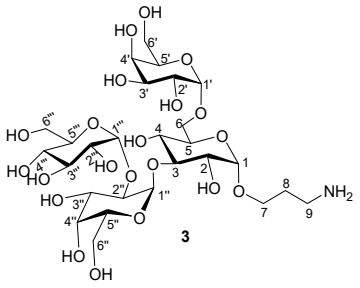
Table S8. NMR data of compound **31**



Position	^{1}H (ppm)	^{13}C (ppm)	^{1}H-^{1}H COSY	HMBC (H→C)
1	4.78 (d, *J* = 3.3 Hz, 1H)	96.04	H-2	C-3, C-5, C-7
2	3.47-3.39 (m, 1H)	79.44	H-1, H-3	C-3
3	4.44-4.37 (m, 1H）	73.53	H-2, H-4	C-2, C-4, C-1"
4	3.58-3.51 (m, 1H)	80.50	H-3, H-5	C-3, C-5
5	3.96-3.88 (m, 1H)	69.89	H-4, H-6	C-4, C-6
6	3.56-3.48 (m, 1H); 3.51-3.43 (m, 1H）	67.18	H-5	C-5, C-1'
7	3.72-3.64 (m, 1H); 3.40-3.32 (m, 1H)	64.47	H-1, H-8	C-1, C-8
8	1.77-1.67 (m, 2H)	28.83	H-7, H-9	C-7, C-8
9	3.33-3.23 (m, 2H)	48.29	H-8	C-7, C-8
1'	4.85 (d, *J* = 3.3 Hz, 1H)	98.38	H-2'	C-6, C-2'
2'	4.08-4.00 (m, 1H)	82.18	H-1', H-3'	C-3', C-4'
3'	3.98-3.90 (m, 1H)	75.86	H-2', H-4'	C-2'
4'	3.97-3.89 (m, 1H)		H-3', H-5'	C-3', C-5'
5'	3.55-3.48 (m, 1H）	62.69	H-4', H-6'	C-4', C-6'
6'	3.97-3.89 (m, H-6a, 1H) 4.16-4.08 (m, H-6b, 1H)	69.11	H-5'	C-5'
1"	5.86 (d, *J* = 3.3 Hz, 1H)	96.83	H-2"	C-3, C-5"
2"	4.55-4.47 (m, 1H)		H-1", H-3"	C-3", C-1'"
3"	4.02-3.94 (m, 1H)		H-2", H-4"	C-1", C-4"
4"	3.84-3.76 (m, 1H)	73.76	H-3", H-5"	C-3", C-5"

5"	4.20-4.12 (m, 1H）	62.05	H-4", H-6"	C-4"
6"	3.44-3.36 (m, H-6"a, 1H); 3.74-3.66 (m, H-6"b, 1H)	69.31	H-5"	C-5"
1‴	5.53 (d, *J* = 3.6 Hz, 1H)	95.51	H-2‴	C-2", C-5‴
2‴	3.82-3.74 (m, 1H)	74.80	H-1‴, H-3‴	C-3‴
3‴	4.10-4.02 (m, 1H)	75.90	H-2‴, H-4‴	C-2‴, C-4‴
4‴	3.62-3.54 (m, 1H)	82.80	H-3‴, H-5‴	C-3‴, C-5‴
5‴	4.41-3.33 (m, 1H)	62.90	H-4‴, H-6‴	C-3‴, C-6‴
6‴	4.27-4.19 (m, H-6a, 1H); 4.14-4.06 (m, H-6b, 1H)	63.43	H-5‴	C-4‴, C-5‴
1^{IV}	5.10 (1H）	94.65		
2^{IV}				
3^{IV}				
4^{V}				
5^{IV}	4.26-4.18 (m, 1H）	69.28	$H\text{-}6^{IV}$	$C\text{-}6^{IV}$
6^{IV}	4.33-4.23 (m, H-6a, H-6b, 2H)	69.53	$H\text{-}5^{IV}$	$C\text{-}5^{IV}$

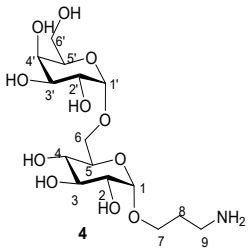
Table S9. NMR data of compound **3**



Position	^{1}H (ppm)	^{13}C (ppm)	$^{1}H\text{-}^{1}H$ COSY	HMBC (H→C)
1	4.91 (d, *J* = 3.8 Hz, 1H)	98.50	H-2	C-2, C-3, C-7
2	3.68-3.60 (m, 1H)	69.30	H-1, H-3	C-1, C-3
3	3.83-3.75 (m, 1H)	80.32	H-2, H-4	C-2, C-4, C-5, C-1"
4	3.86-3.79 (m ,1H)	69.19	H-3, H-5	C-3, C-5
5	3.81-3.73 (m, 1H)	68.30	H-4, H-6	C-3, C-4
6	4.01-3.93 (m, 1H); 3.67-3.59 (m, 1H)	65.08	H-5	C-5, C-1'
7	3.94-3.86 (m, 1H); 3.62-3.54 (m, 1H)	65.93	H-1, H-8	C-1, C-8
8	1.97-1.87 (m, 2H)	26.40	H-7, H-9	C-7, C-8

9	3.07-2.97 (m, 2H)	37.72	H-8	C-8
1'	4.97-4.87 (d, *J* = 3.7 Hz, 1H)	97.99	H-2'	C-6, C-3', C-5'
2'	3.82-3.74 (m, 1H)	70.06	H-1', H-3'	C-3'
3'	3.70-3.62 (m ,1H)	69.50	H-2', H-4'	C-4'
4'	3.76-3.68 (m, 1H)	69.06	H-3', H-5'	C-3'. C-5'
5'	3.95-3.88 (m ,1H)	70.91	H-4', H-6'	C-4'
6'	3.74-3.66 (m, 2H)	61.01	H-5'	C-5'
1"	5.46 (d, *J* = 3.3 Hz, 1H)	96.75	H-2"	C-3, C-3", C-5"
2"	3.98-3.90 (m ,1H)	72.47	H-1", H-3"	C-3", C-4", C-1'"
3"	3.99-3.91 (m, 1H)	67.39	H-2", H-4"	C-1", C-2", C-4"
4"	4.00 (dd, *J* = 3.0, 1.3 Hz, 1H)	69.10	H-3", H-5"	C-3", C-5"
5"	4.29-4.21 (m, 1H)	70.51	H-4"	C-4", C-6"
6"	3.79-3.71 (m, 2H)	60.67	H-5"	C-4", C-5"
1'"	5.12 (d, *J* = 3.9 Hz, 1H)	95.70	H-2'"	C-2", C-3'", C-5'"
2'"	3.54 (dd, *J* = 9.8, 3.9 Hz, 1H)	71.26	H-1'", H-3'"	C-3'"
3'"	3.76-3.69 (m, 1H)	72.79	H-2'", H-4'"	C-2'", C-4'"
4'"	3.35 (dd, *J* =10.1, 9.2 Hz, 1H)	69.29	H-3'", H-5'"	C-3'", C-5'"
5'"	3.89-3.81 (m, 1H)	71.65	H-4'", H-6'"	C-3'", C-6'"
6'"	3.83-3.75 (m, 2H)	60.28	H-5'"	C-4'", C-5'"

Table S10. NMR data of compound **4**

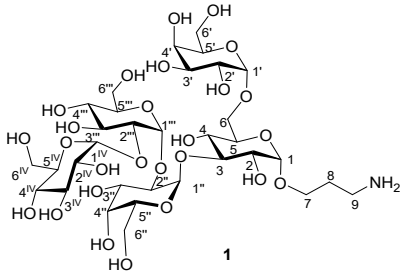


4

Position	^{1}H (ppm)	^{13}C (ppm)	^{1}H-^{1}H COSY	HMBC (H→C)
1	4.90 (d, *J* = 3.8 Hz, 1H)	98.26	H-2	C-3, C-5, C-7
2	3.60-3.52 (m, 1H)	70.89	H-1, H-3	C-3, C-4, C-6
3	3.64 (t, *J* = 9.4 Hz, 1H)	73.09	H-2, H-4	C-2, C-4
4	3.48 (t, *J* = 9.8 Hz, 1H)	69.22	H-3, H-5	C-3, C-5, C-6
5	3.82-3.74 (m, 1H)	70.30	H-4, H-6	C-6
6	3.98-3.90 (m, H-6a); 3.73-3.64 (m, H-6b)	65.42	H-5	C-4, C-5, C-1'
7	3.91-3.83 (m, H-7a); 3.61-3.53 (m, H-7b)	65.80	H-1, H-8	C-1, C-8, C-9
8	2.02-1.92 (m, 2H)	26.38	H-7, H-9	C-7, C-9

9	3.16-3.06 (m, 2H)	37.65	H-8	C-7, C-8
1'	4.93 (d, *J* = 3.6 Hz, 1H)	97.95	H-2'	C-3', C-4', C-6
2'	3.83-3.75 (m, 1H)	68.25	H-1', H-3'	C-3', C-4'
3'	3.85-3.77 (m, 1H)	69.34	H-2', H-4'	C-2', C-4'
4'	3.96-3.88 (m, 1H)	70.85	H-3', H-5'	C-1', C-3', C-5'
5'	3.98-3.90 (m, 1H)	69.07	H-4', H-6'	C-3', C-6'
6'	3.73-3.65 (m, 2H)	60.97	H-5'	C-4', C-5'

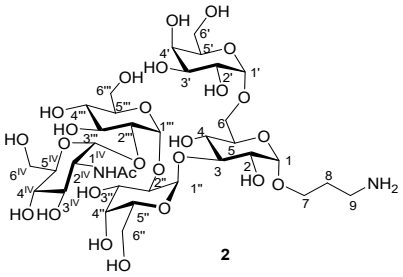
Table S11. NMR data of compound **1**



Position	^{1}H (ppm)	^{13}C (ppm)	^{1}H-^{1}H COSY	HMBC (H→C)
1	4.92 (d, *J* = 3.8 Hz, 1H)	98.32	H-2	C-3, C-5, C-7
2	3.76-3.68 (m ,1H)	69.36	H-1, H-3	C-3
3	3.98-3.90 (m, 1H)	77.15	H-2, H-4	C-1, C-2
4	3.88-3.80 (m, 1H)	70.34	H-3, H-5	C-6
5	3.73-3.65 (m, 1H)	70.37	H-4, H-6	C-1, C-6
6	3.76-3.68 (m, 2H)	65.77	H-5	C-5
7	3.94-3.86 (m, H-7a); 3.63-3.55 (m, H-7b)	65.94	H-8	C-1, C-7, C-8
8	2.03-1.93 (m, 2H)	26.43	H-7, H-9	C-7, C-9
9	3.18-3.10 (m, H-8a); 3.14-3.06 (m, H-8b)	37.79	H-8	C-7, C-8
1'	4.94 (d, *J* = 2.2 Hz, 1H)	98.16	H-2'	C-6, C-2', C-5'
2'	3.83-3.75 (m, 1H)	68.23	H-1', H-3'	C-1', C-3'
3'	3.50-3.43 (t, *J* = 9.5 Hz, 1H)	69.18	H-2', H-4'	C-2'
4'	3.88-3.80 (m, 1H)	69.36	H-3', H-5'	C-5'
5'	3.95-3.87 (m, 1H)	71.03	H-4', H-6'	C-1', C-6'
6'	3.78-3.70 (m, 2H)	60.17	H-5'	C-4', C-5'
1"	5.69 (d, *J* = 3.8 Hz, 1H)	95.20	H-2"	C-3, C-2", C-3", C-5"
2"	3.97-3.89 (m, 1H)	72.52	H-1", H-3"	C-3"

3"	4.03 (dd, *J* = 9.3, 3.3 Hz, 1H)	67.59	H-2", H-4"	C-2", C-4"
4"	3.99 (d, *J* = 3.3 Hz, 1H)	69.10	H-3", H-5"	C-3", C-4"
5"	4.23 (t, *J* = 6.4 Hz, 1H)	70.56	H-4", H-6"	C1", C-4", C-6"
6"	3.74-3.66 (m, 2H)	61.04	H-5"	C-4", C-5"
1'"	5.10 (d, *J* = 3.8 Hz, 1H)	95.82	H-2'"	C-2", C-3'", C-5'"
2'"	3.51 (dd, *J* = 9.9, 3.8 Hz, 1H)	71.43	H-1'", H-3'"	C-3'", C-4'", C-1^{IV}
3'"	3.80-3.72 (m, 1H)	72.81	H-2'", H-4'"	C-2", C-4", C-5"
4'"	3.45-3.67 (t, *J* = 9.7 Hz, 1H)	69.34	H-3'", H-5'"	C-3'", C-5'", C-6'"
5'"	3.96-3.88 (m, 1H)	71.82	H-4'", H-6'"	C-1", C-4", C-6"
6'"	3.85-3.77 (m, 2H)	60.29	H-5'"	C-4", C-5"
1^{IV}	5.39 (d, *J* = 3.5 Hz, 1H)	92.80	H-2^{IV}	C-2'", C-5^{IV}
2^{IV}	3.73-3.65 (m, 1H)	74.61	H-1^{IV}, H-3^{IV}	C-3^{IV}
3^{IV}	3.89-3.81 (m, 1H)	71.00	H-2^{IV}, H-4^{IV}	C-2^{IV}, C-4^{IV}
4^{IV}	3.99-3.91 (m, 1H)	69.10	H-3^{IV}, H-5^{IV}	C-3^{IV}
5^{IV}	3.96-3.88 (m, 1H)	71.81	H-4^{IV}, H-6^{IV}	C-4^{IV}, C-6^{IV}
6^{IV}	3.75-3.68 (m, 2H)	61.13	H-5^{IV}	C-4^{IV}, C-5^{IV}

Table S12. NMR data of compound **2**



2

Position	^{1}H (ppm)	^{13}C (ppm)	^{1}H-^{1}H COSY	HMBC (H→C)
1	4.86 (d, *J* = 3.9 Hz, 1H)	98.35	H-2	C-3, C-5, C-7
2	3.65-3.58 (m, 1H)	69.36	H-1, H-3	C-1, C-3
3	3.91-3.83 (m, 1H)	76.23	H-2, H-4	C-1", C-2, C-4
4	3.40-3.32 (m, 1H)	71.10	H-3, H-5	C-3, C-5
5	3.81-3.73 (m, 1H)	70.36	H-4, H-6	C-4
6	3.87-3.79 (m, H-6a); 3.75-3.67 (m, H-6b)	66.18	H-5	C-5, C-1'
7	3.88-3.80 (m, H-7b); 3.59-3.51 (m, H-7a)	65.80	H-8	C-1, C-7, C-8
8	1.99-1.89 (m, 2H)	26.41	H-7, H-9	C-7, C-9
9	3.14-3.04 (m, 2H)	37.72	H-8	C-7, C-8
1'	4.90 (d, *J* = 3.9 Hz)	98.28	H-2'	C-6, C-2', C-3'
2'	3.79-3.71 (m, 1H)	70.90	H-1', H-3'	C-3'
3'	3.70-3.63 (m, 1H)	69.47	H-2', H-4'	C-2'
4'	3.96-3.88 (m, 1H)	68.86	H-3', H-5'	C-2', C-3'
5'	3.93-3.85 (m, 1H)	68.27	H-4', H-6'	C-1', C-6'
6'	3.70-3.62 (m, 2H)	61.09	H-5'	C-5'
1"	5.59 (d, *J* = 3.6 Hz, 1H)	94.96	H-2"	C-3", C-5"
2"	3.89-3.81 (m, 1H)	71.84	H-1", H-3"	C-3"
3"	3.85-3.78 (m, 1H)	67.91	H-2", H-4"	C-4"
4"	3.99-3.91 (m, 1H)	68.77	H-3", H-5"	C-3"
5"	4.33 (t, *J* = 6.4 Hz, 1H)	70.11	H-4", H-6"	C1", C-4", C-6"
6"	3.69-3.61 (m, 2H)	60.89	H-5"	C-5"
1'"	5.53(d, *J* = 3.7 Hz, 1H)	90.16	H-2'"	C-2"
2'"	3.69-3.61 (m, 1H)	72.90	H-1'", H-3'"	C-1v
3'"	3.87-3.79 (m, 1H)	71.40	H-2'", H-4'"	C-5"
4'"	3.48-3.40 (m, 1H)	69.11	H-3'", H-5'"	C-3'", C-6'"
5'"	3.70-3.62 (m, 1H)	68.77	H-4'", H-6'"	C-3", C-4", C-6"
6'"	3.83-3.75 (m, H-6'"a);	60.12	H-5'"	C-4", C-5"

	3.74-3.66 (m, H-6'"b)			
1^{IV}	5.04 (d, *J* = 3.7 Hz, 1H)	93.03	H-2^{IV}	C-2'", C-5^{IV}
2^{IV}	3.93-3.85 (m, 1H)	70.96	H-1^{IV}, H-3^{IV}	C-3^{IV}
3^{IV}	3.76-3.68 (m,1H)	72.09	H-2^{IV}, H-4^{IV}	C-2^{IV}
4^{IV}	3.39-3.31 (m ,1H)	69.68	H-3^{IV}, H-5^{IV}	
5^{IV}	3.84-3,76 (m, 1H)	69.88	H-4^{IV}, H-6^{IV}	C-4^{IV}, C-6^{IV}
6^{IV}	3.87-3.79 (m, 2H)	60.65	H-5^{IV}	C-5^{IV}

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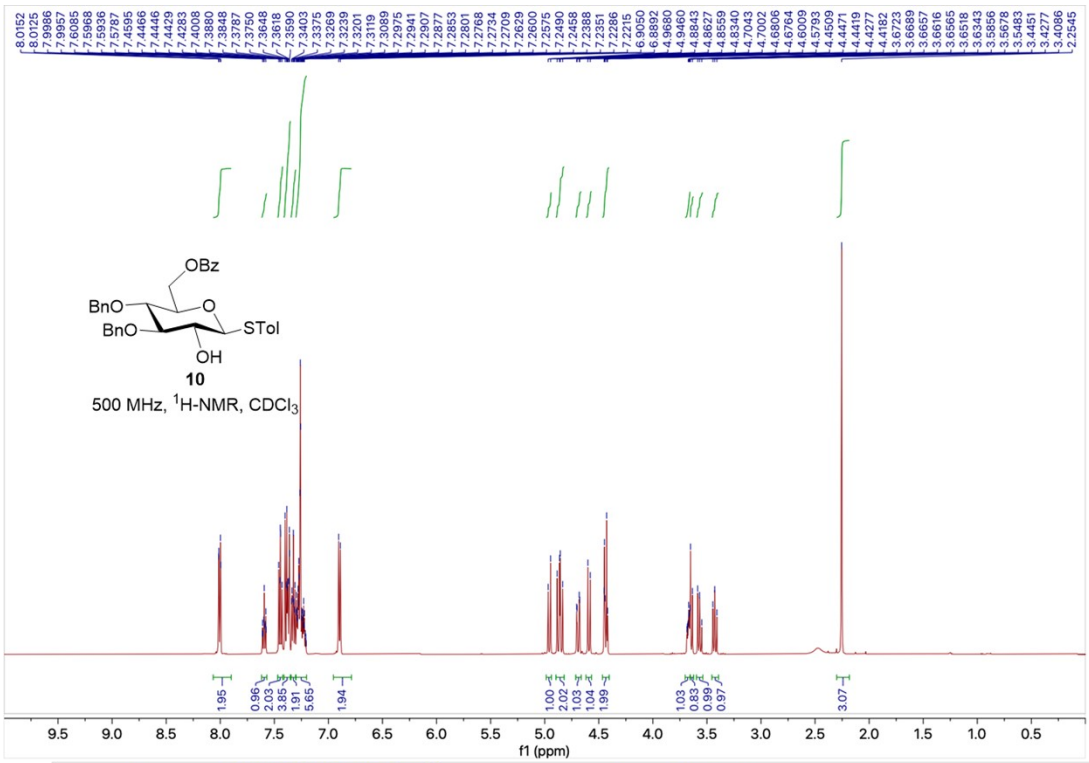
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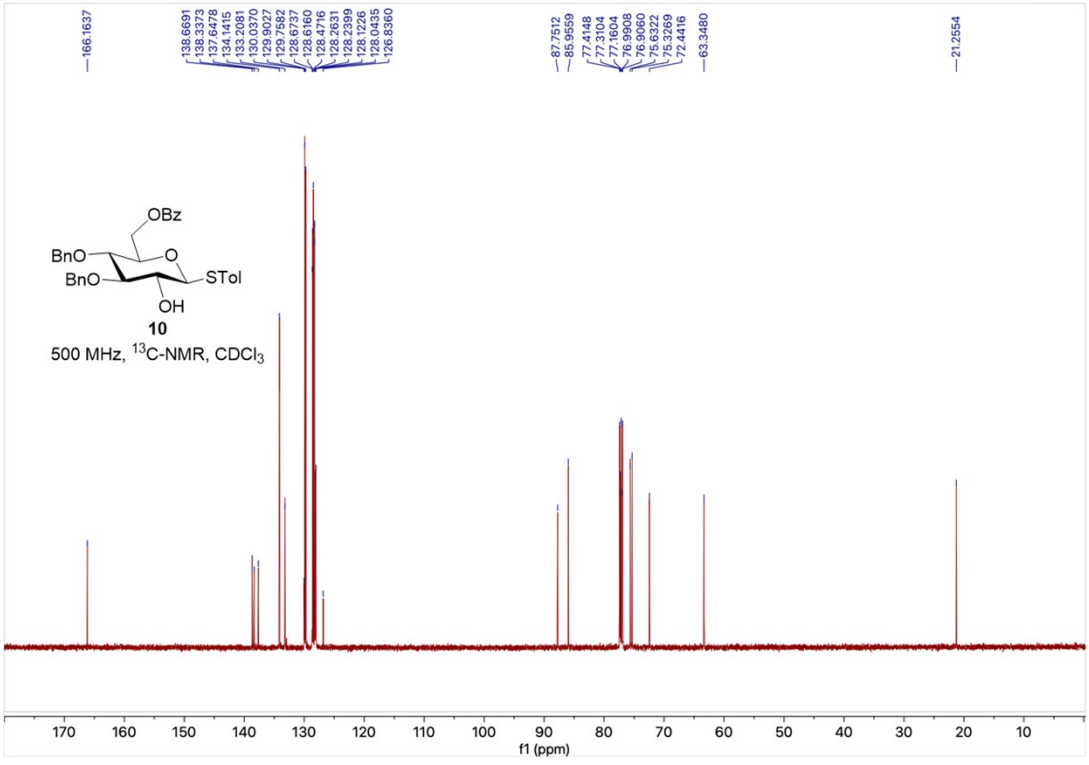
f1 (ppm)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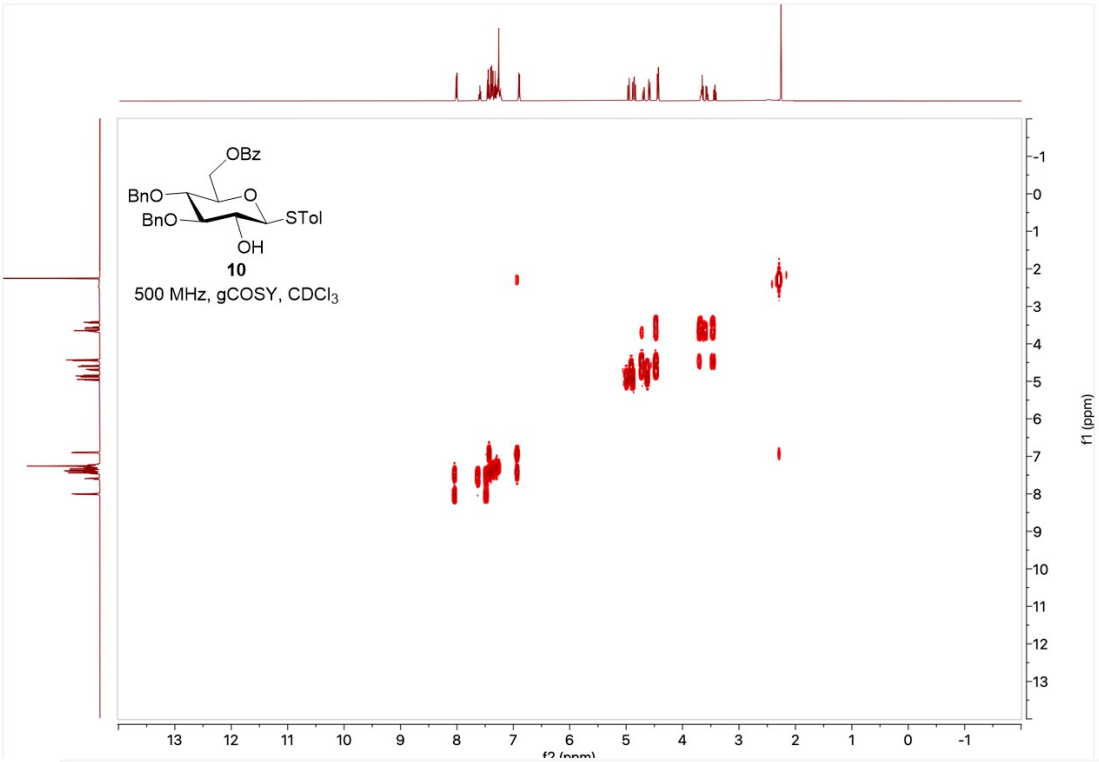
f1 (ppm)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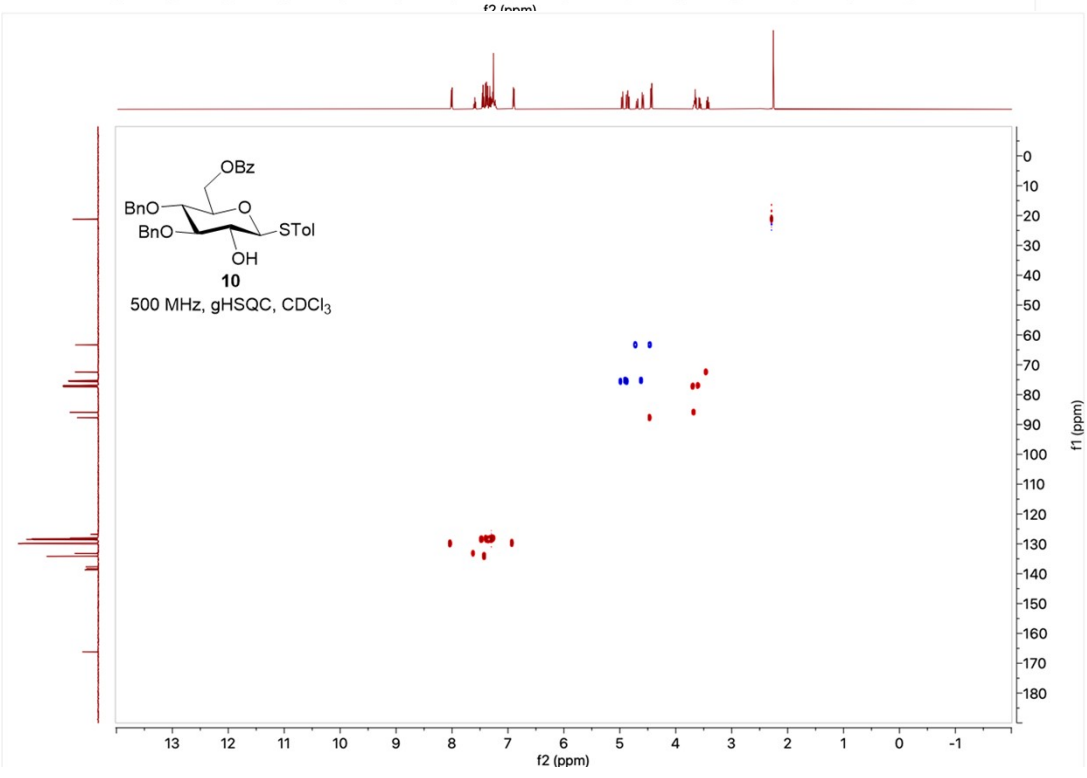
f1 (ppm)
f2 (ppm)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OH
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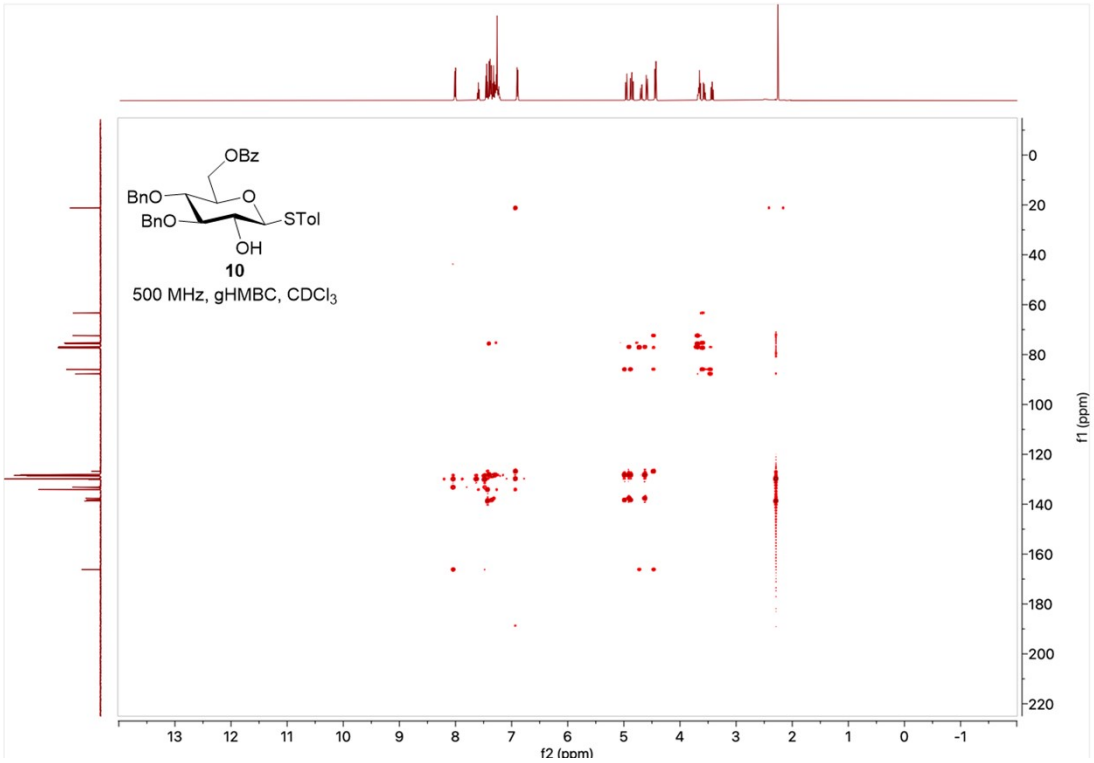
f1 (ppm)
f2 (ppm)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OH
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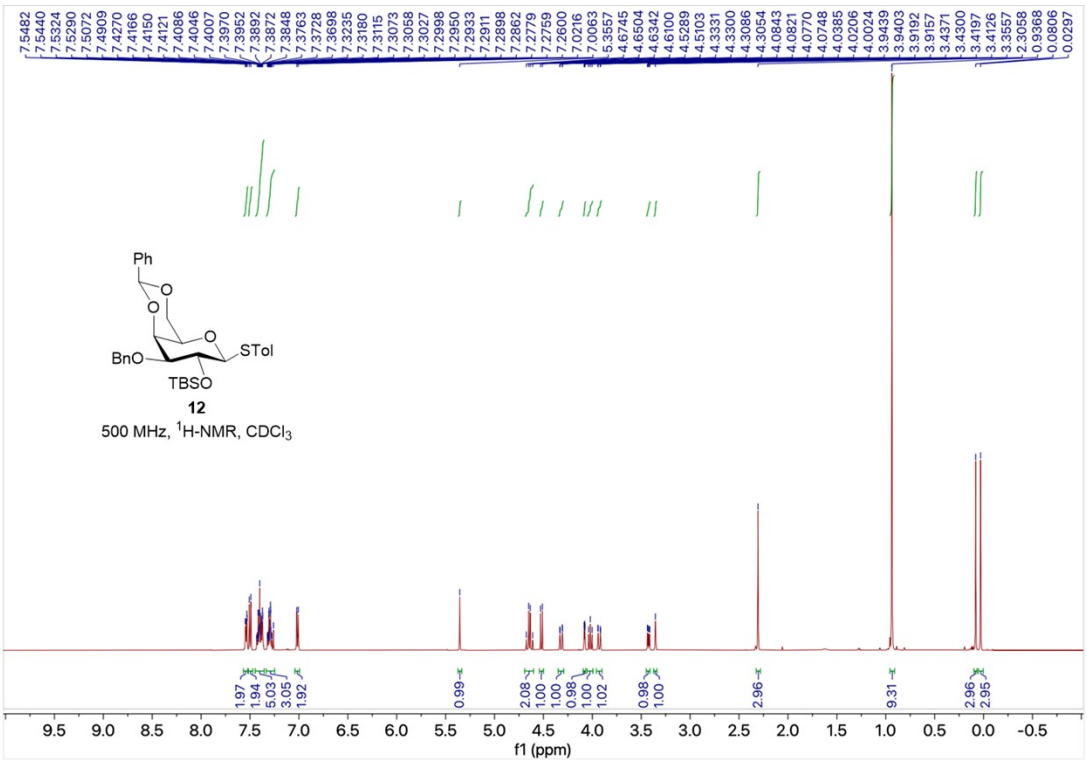
f1 (ppm)
f2 (ppm)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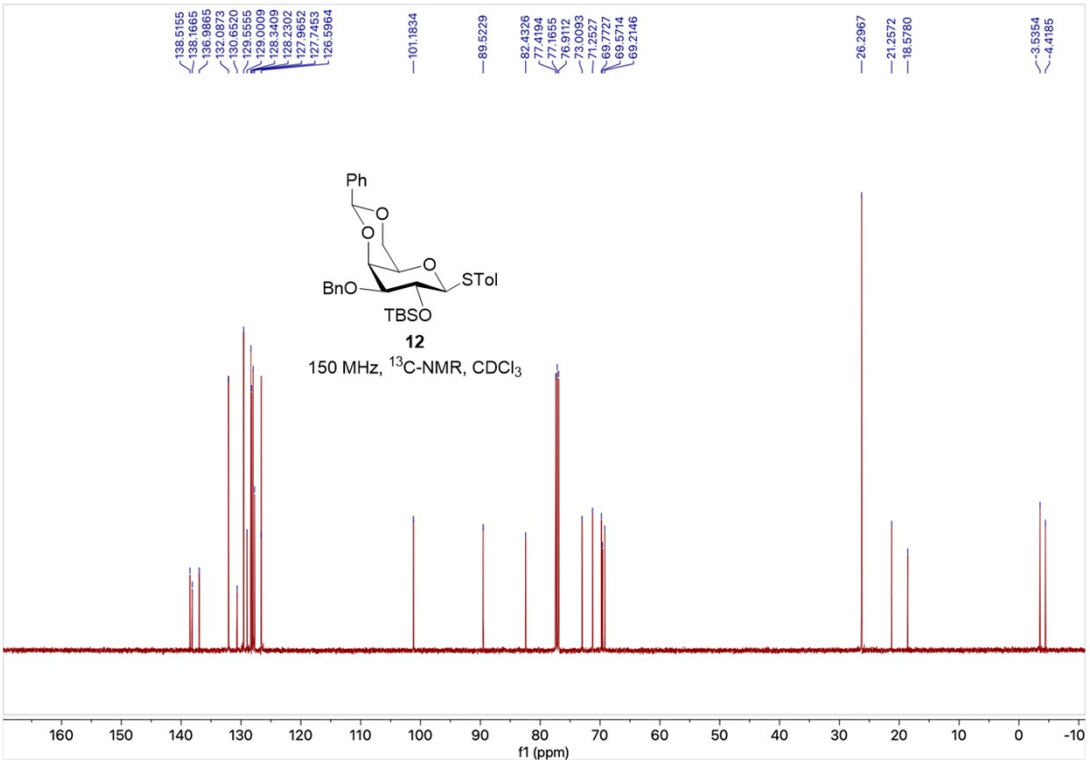
f1 (ppm)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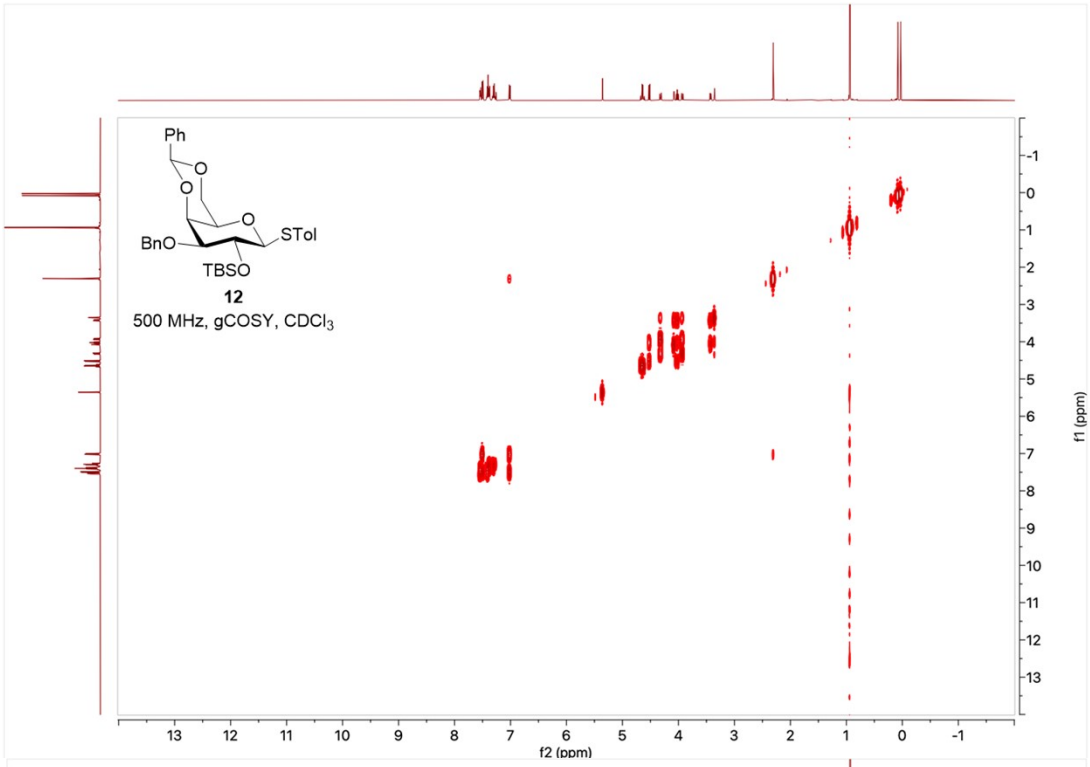
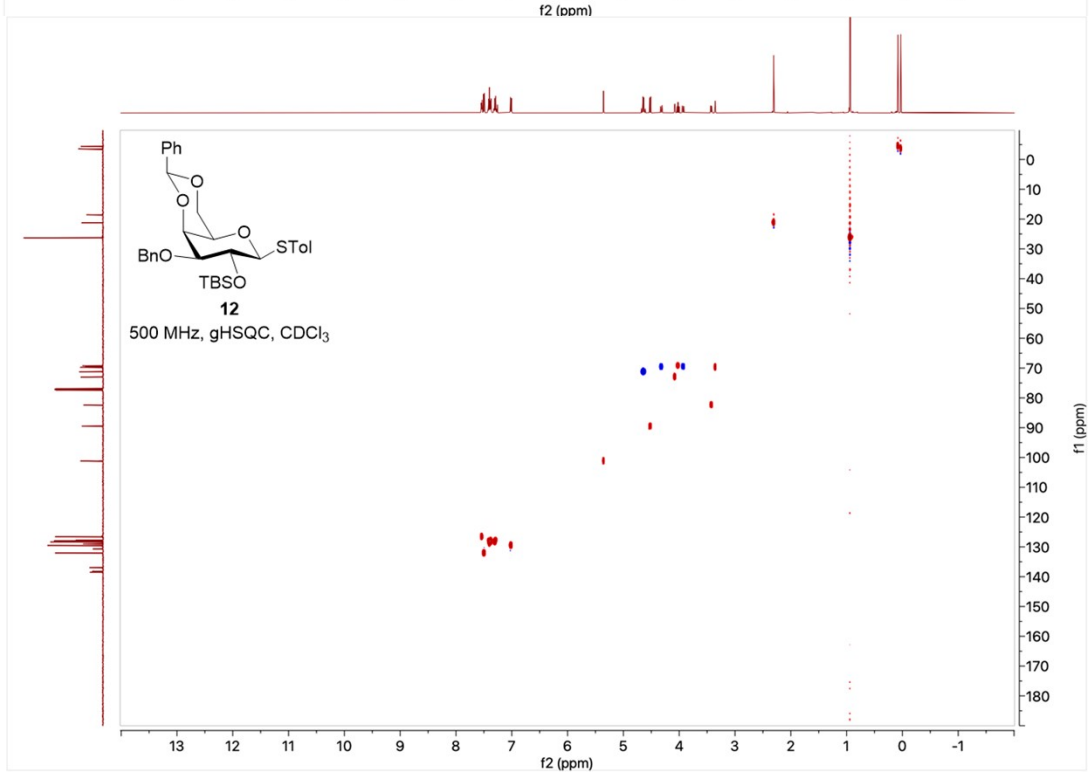
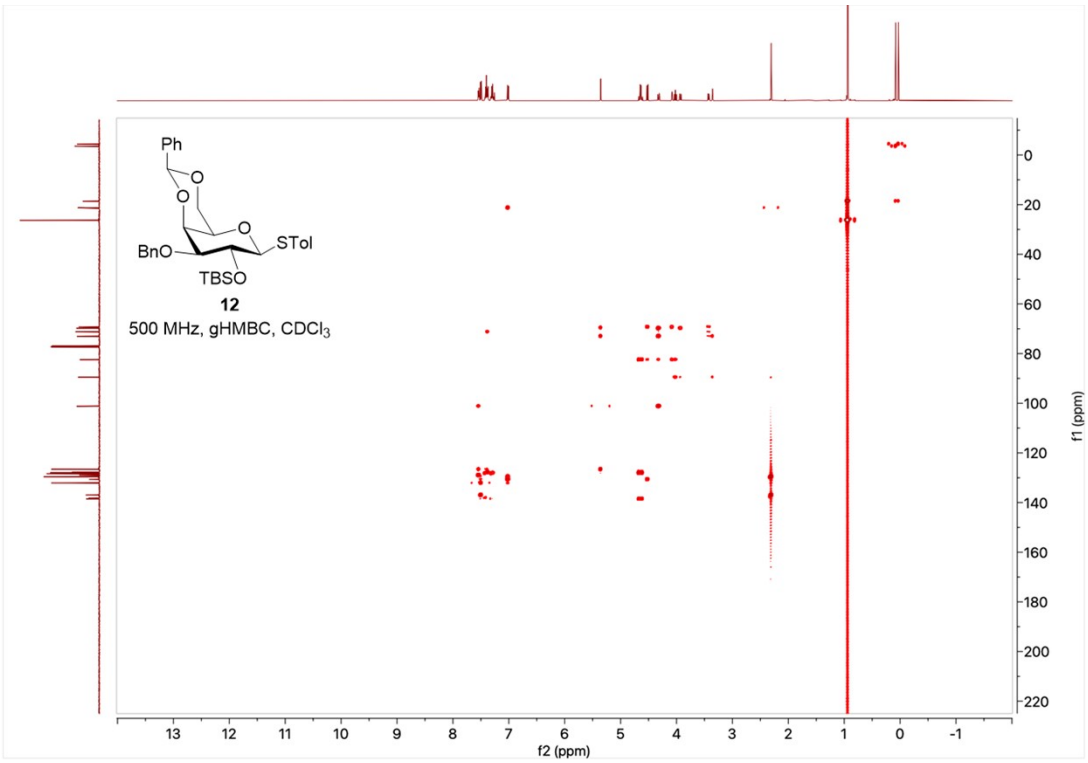
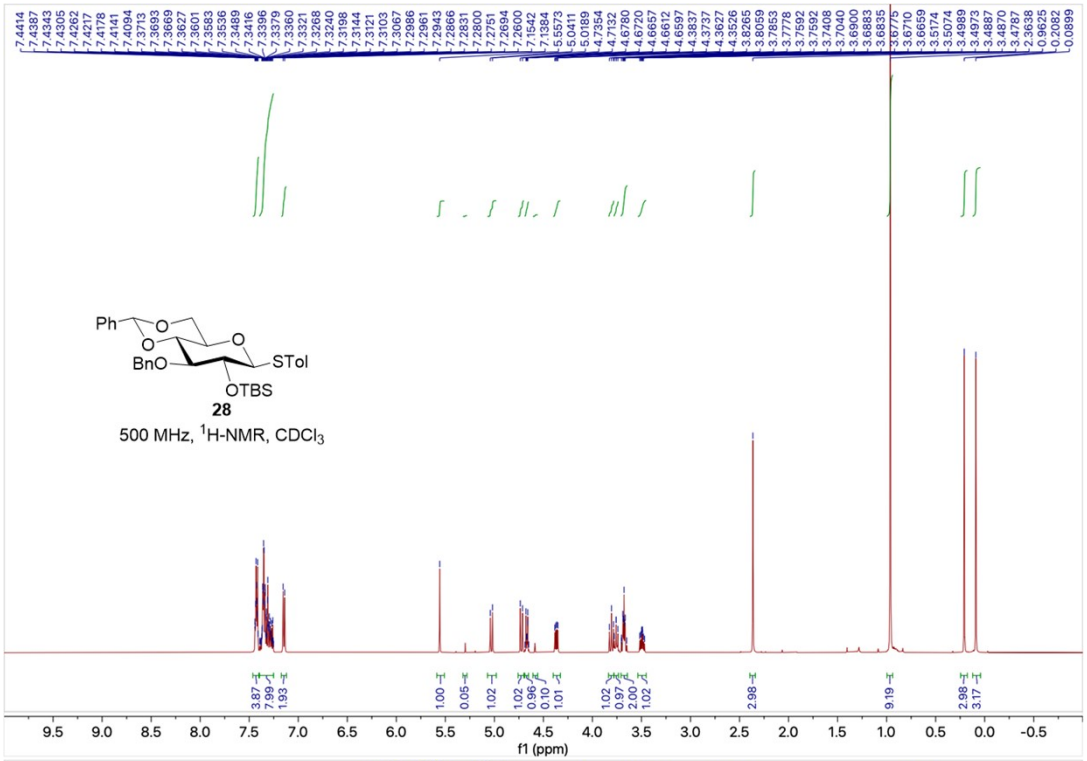
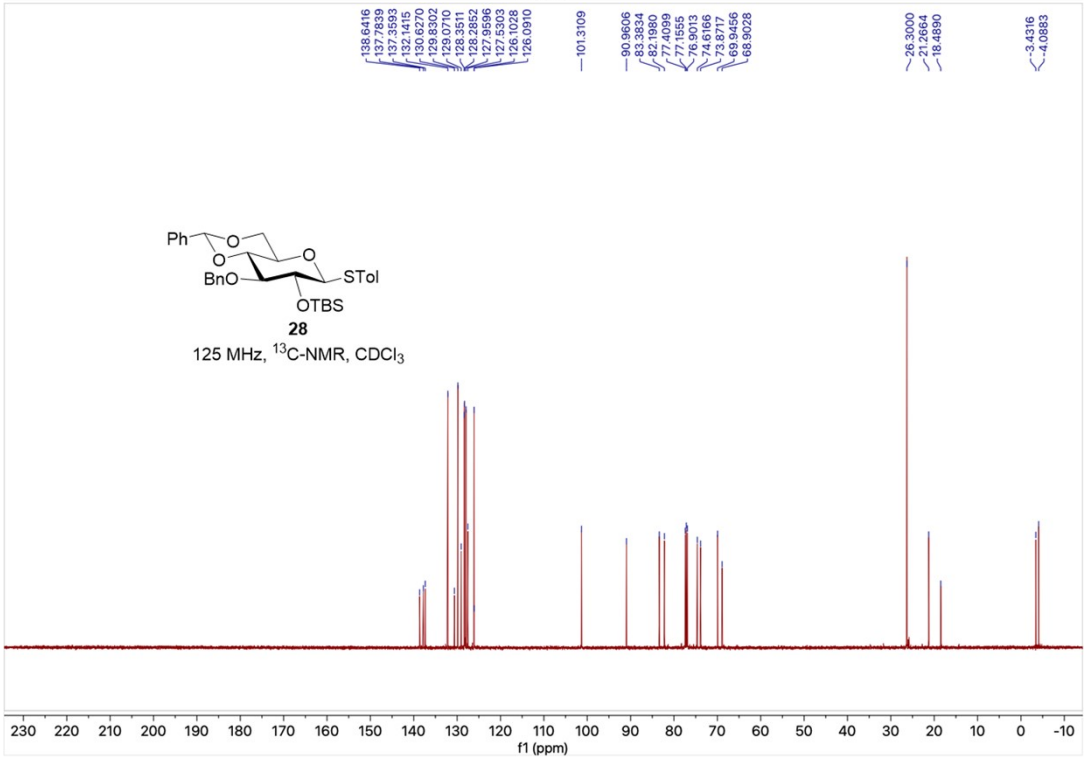
150 MHz, ^{13}C-NMR, CDCl$_3$
f1 (ppm)

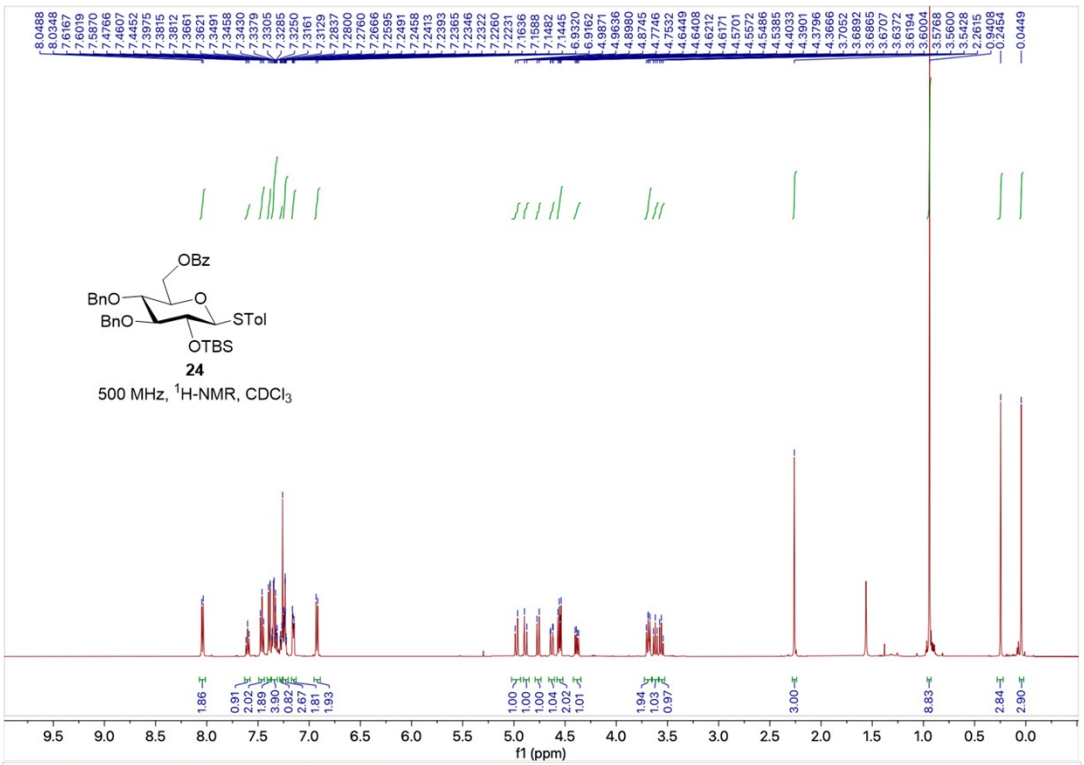

Ph
O
O
O
BnO
STol
TBSO
12
500 MHz, gCOSY, CDCl3
f2 (ppm)
f1 (ppm)

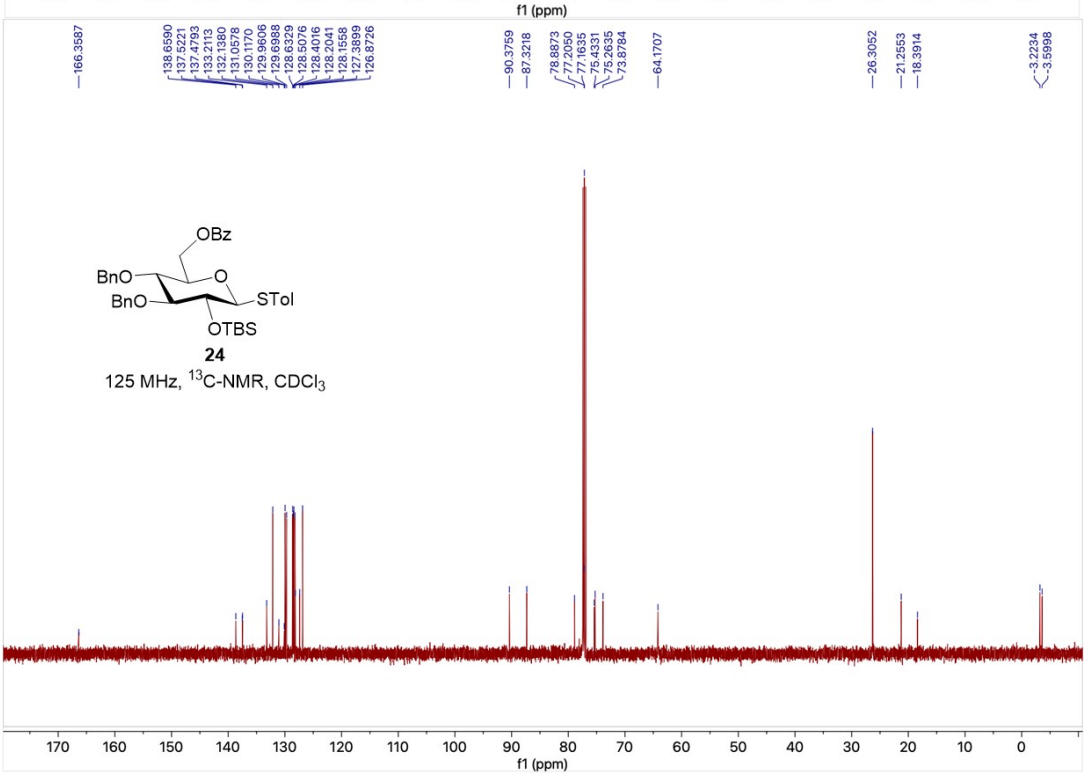

Ph
O
O
O
BnO
STol
TBSO
12
500 MHz, gHSQC, CDCl3
f2 (ppm)
f1 (ppm)

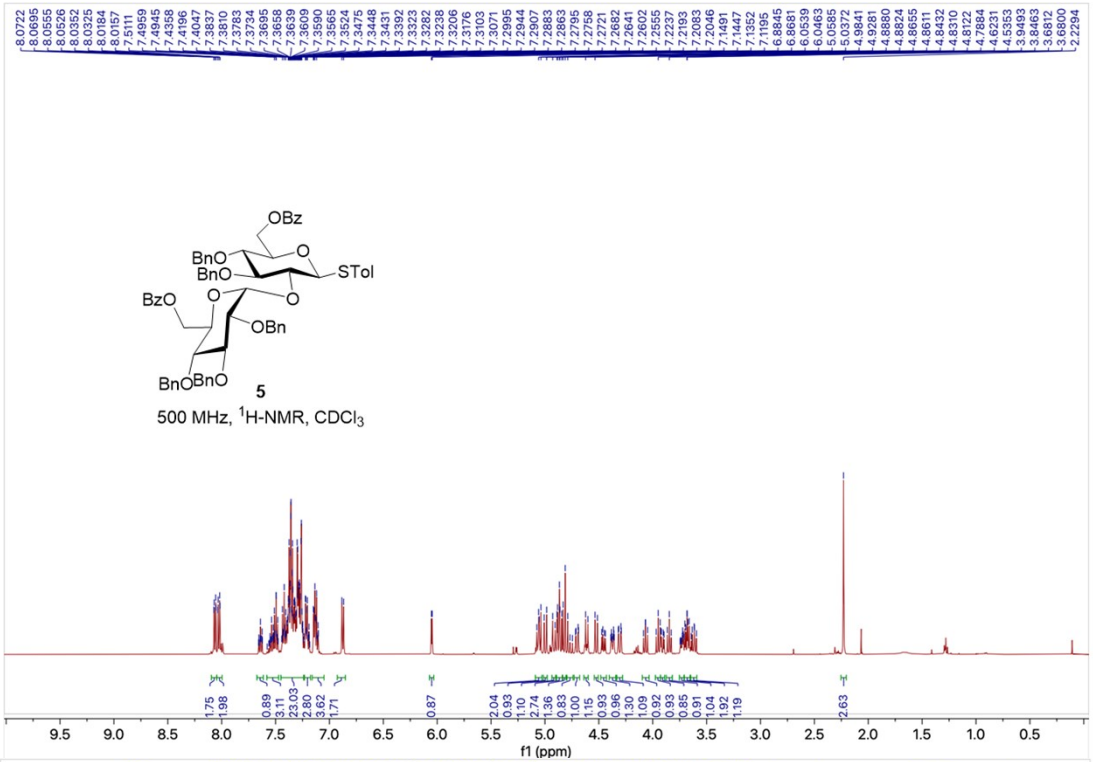

Ph
O
O
O
BnO
STol
TBSO
12
500 MHz, gHMBC, CDCl3
f2 (ppm)
f1 (ppm)

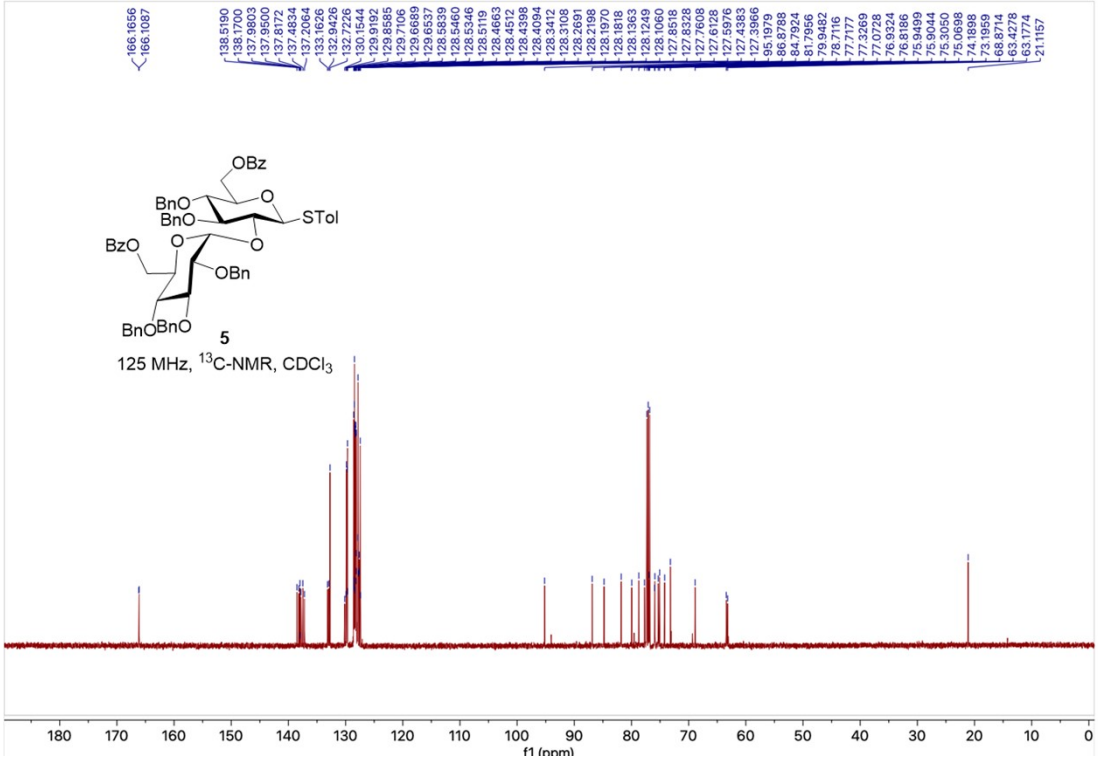

Ph
O
O
O
BnO
STol
OTBS
28
500 MHz, ^{1}H-NMR, CDCl$_3$
f1 (ppm)

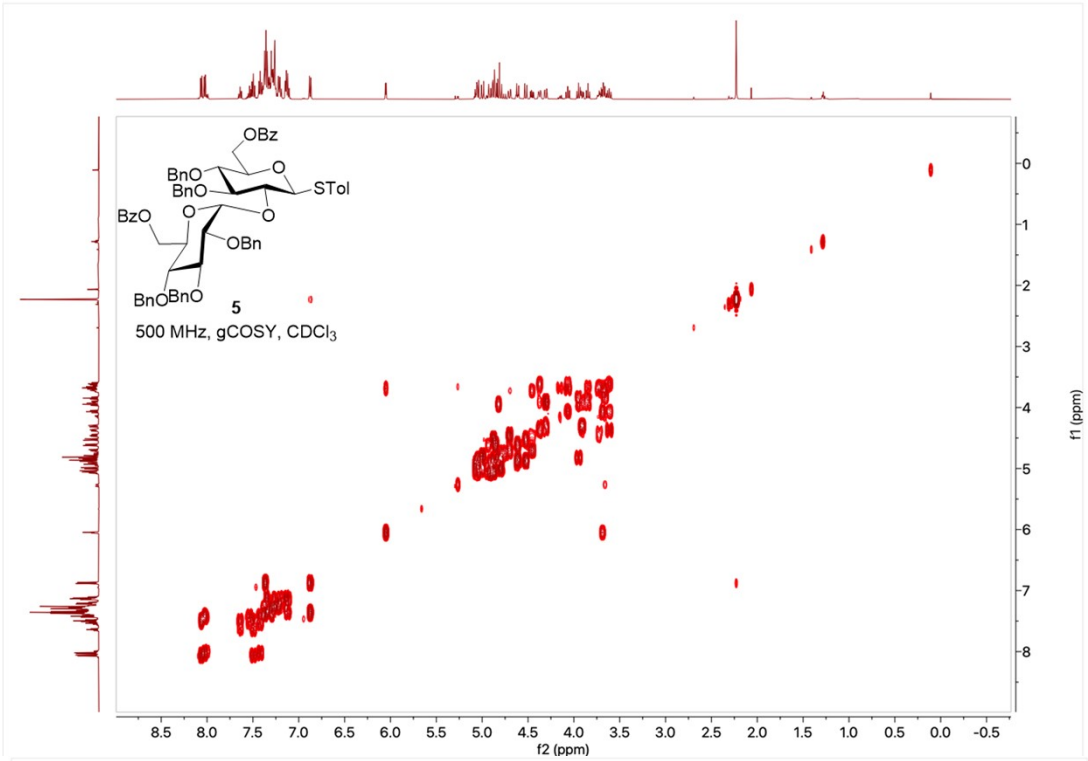

Ph
O
O
O
BnO
STol
OTBS
28
125 MHz, ^{13}C-NMR, CDCl$_3$
f1 (ppm)

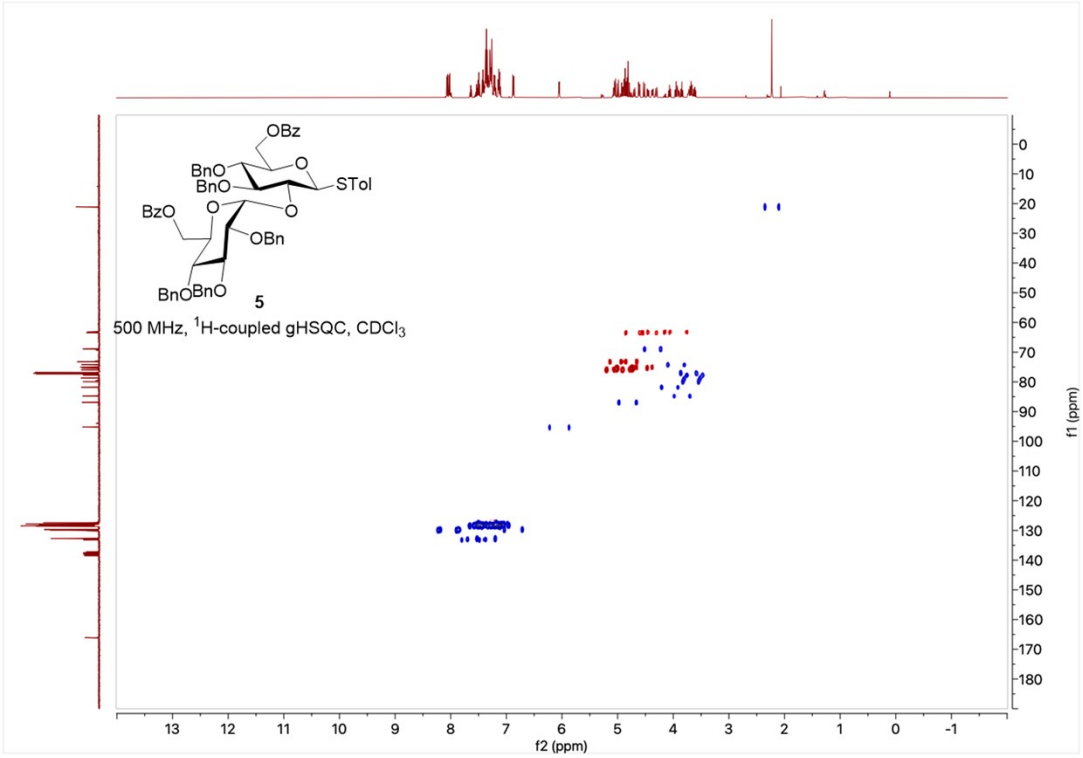

OBz
BnO
O
STol
BnO
OTBS
24
500 MHz, ^{1}H-NMR, CDCl$_3$
f1 (ppm)

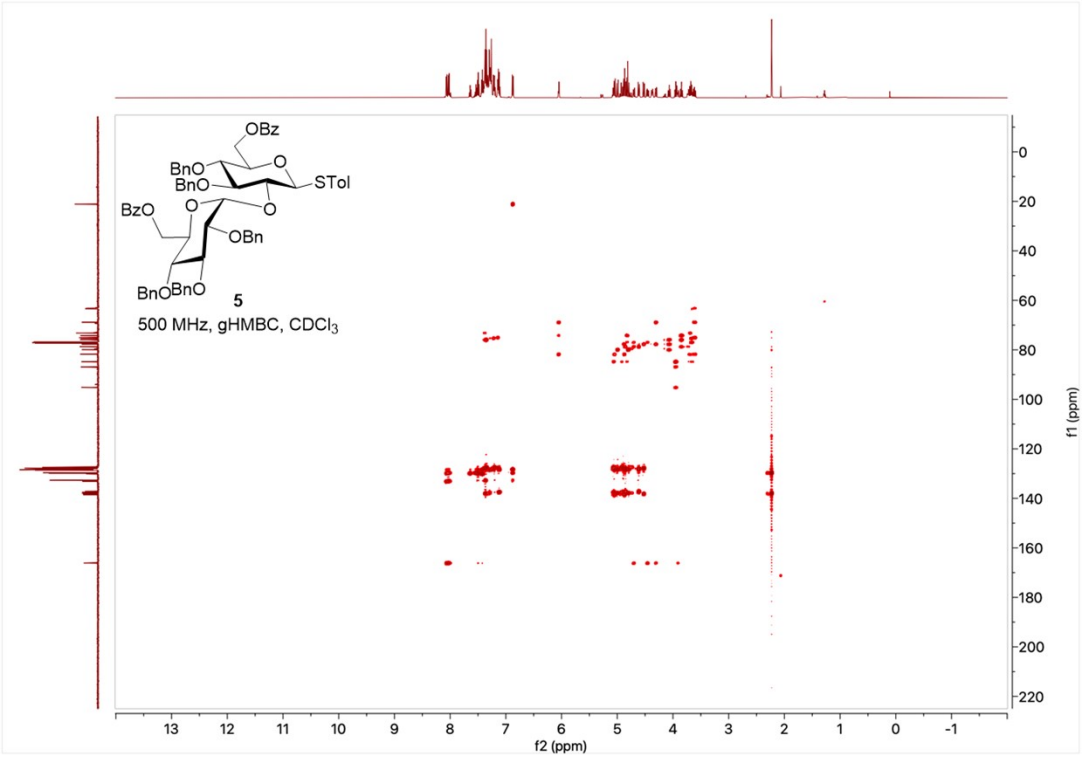

OBz
BnO
O
STol
BnO
OTBS
24
125 MHz, ^{13}C-NMR, CDCl$_3$
f1 (ppm)

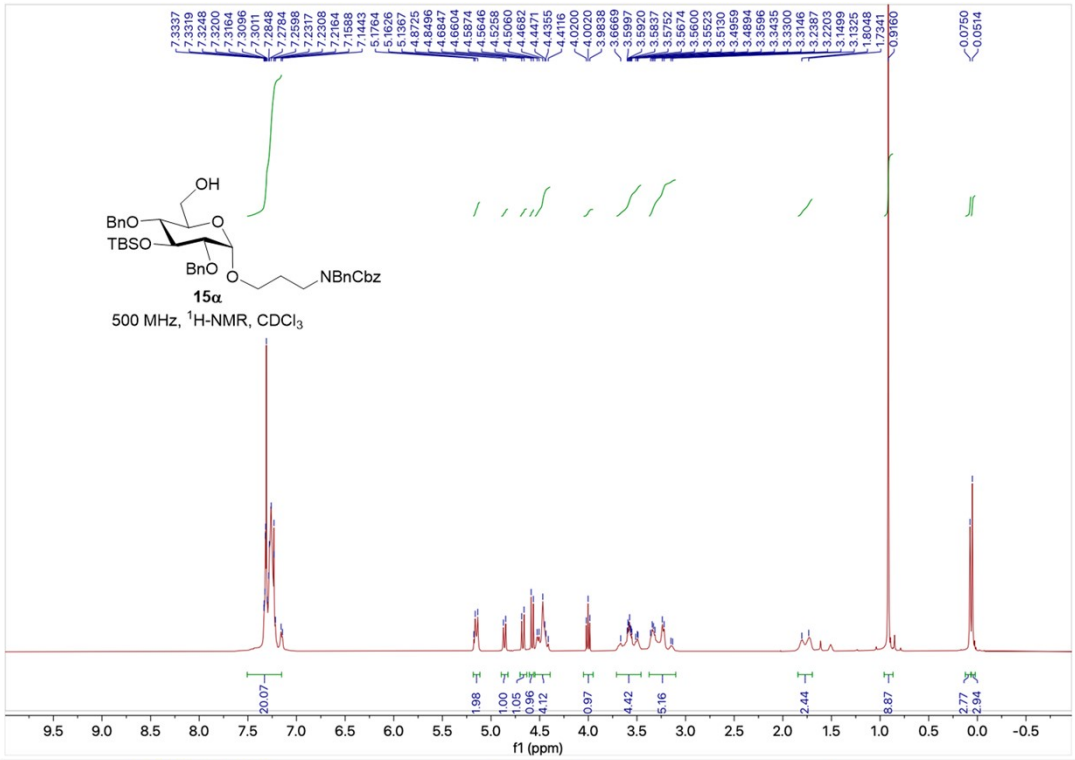

OBz
BnO
BnO
STol
BzO
OBn
BnOBnO
5
500 MHz, ^{1}H-NMR, CDCl$_3$
f1 (ppm)

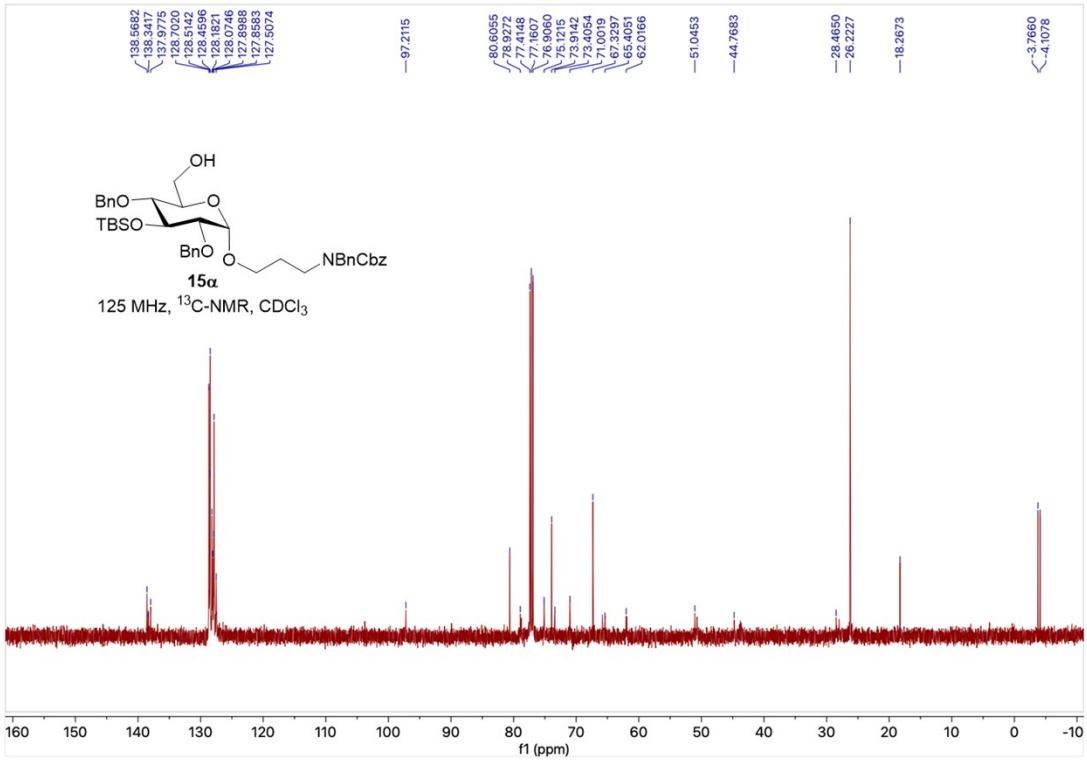

OBz
BnO
BnO
STol
BzO
OBn
BnOBnO
5
125 MHz, ^{13}C-NMR, CDCl$_3$
f1 (ppm)

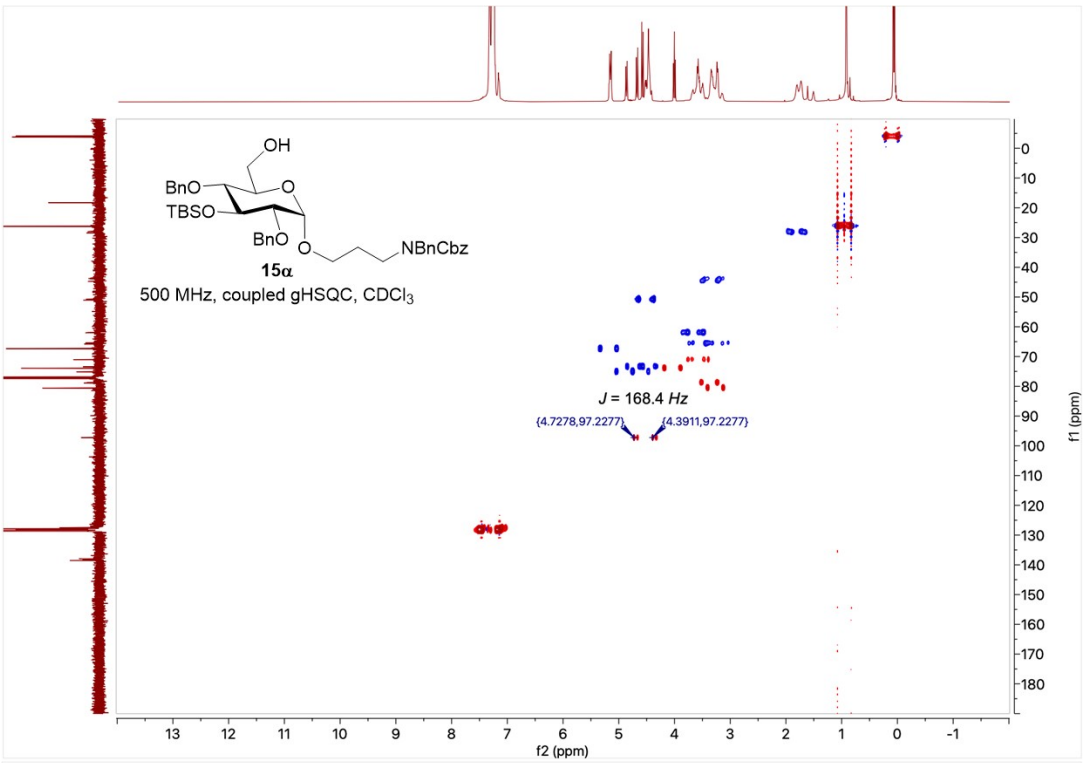

OBz
BnO
BnO
O
STol
BzO
O
O
OBn
BnO
BnO
5
500 MHz, gCOSY, CDCl3
f1 (ppm)
f2 (ppm)

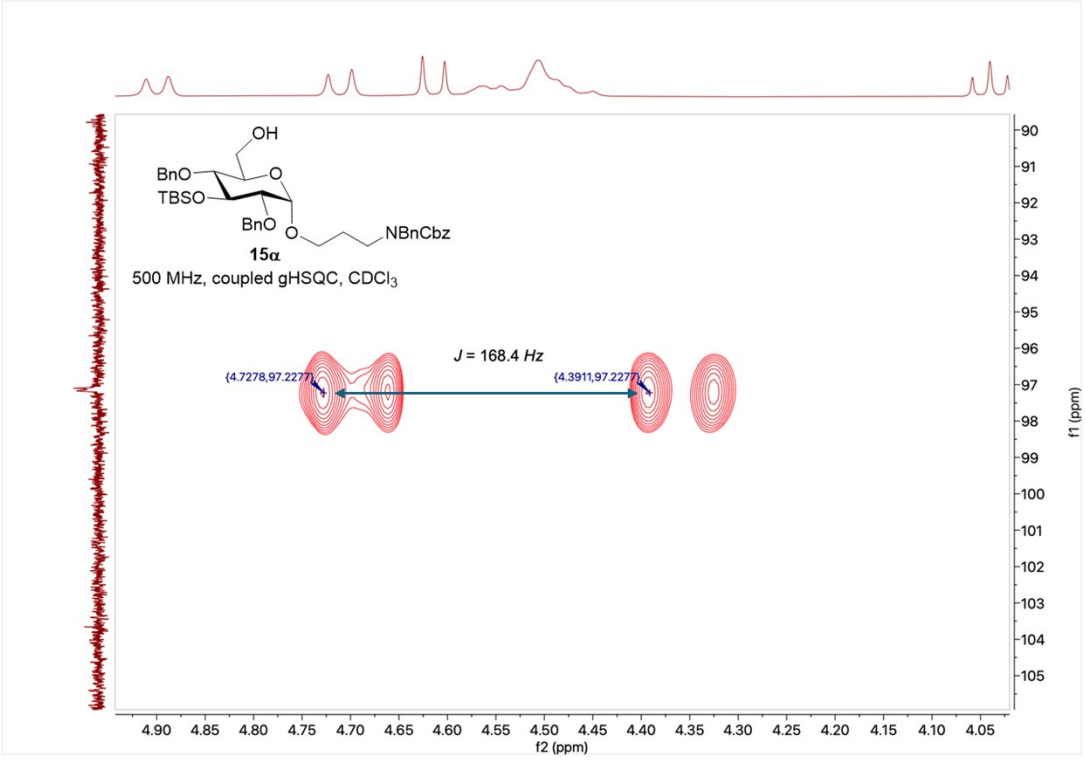

OBz
BnO
BnO
O
STol
BzO
O
O
OBn
BnO
BnO
5
500 MHz, 1H-coupled gHSQC, CDCl3
f1 (ppm)
f2 (ppm)

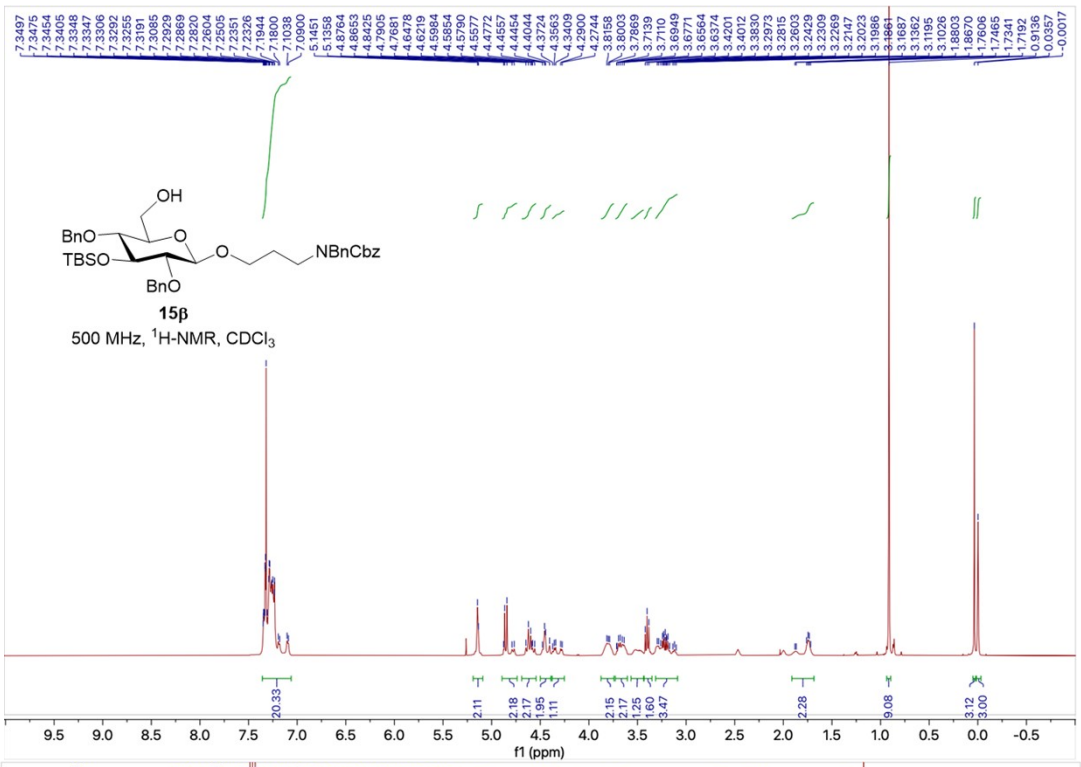

OBz
BnO
BnO
STol
BzO
OBn
BnOBnO
5
500 MHz, gHMBC, CDCl3
f2 (ppm)
f1 (ppm)

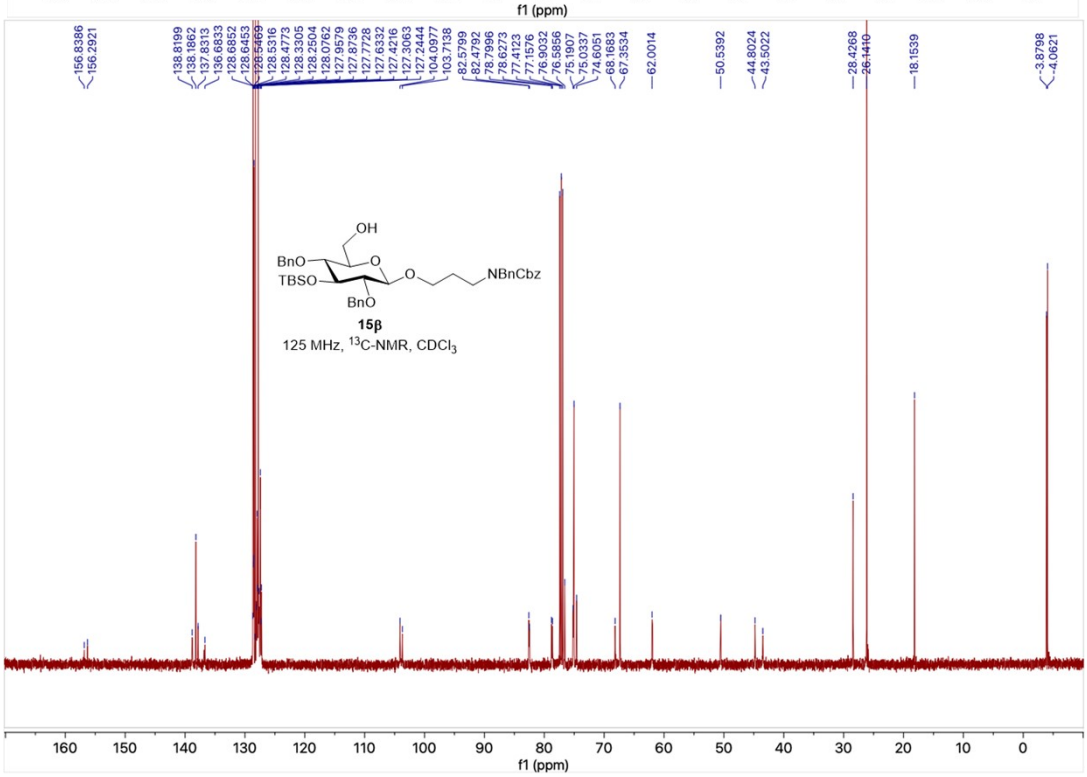

OH
BnO
TBSO
BnO
O
NBnCbz
15α
500 MHz, ^{1}H-NMR, CDCl$_3$
f1 (ppm)

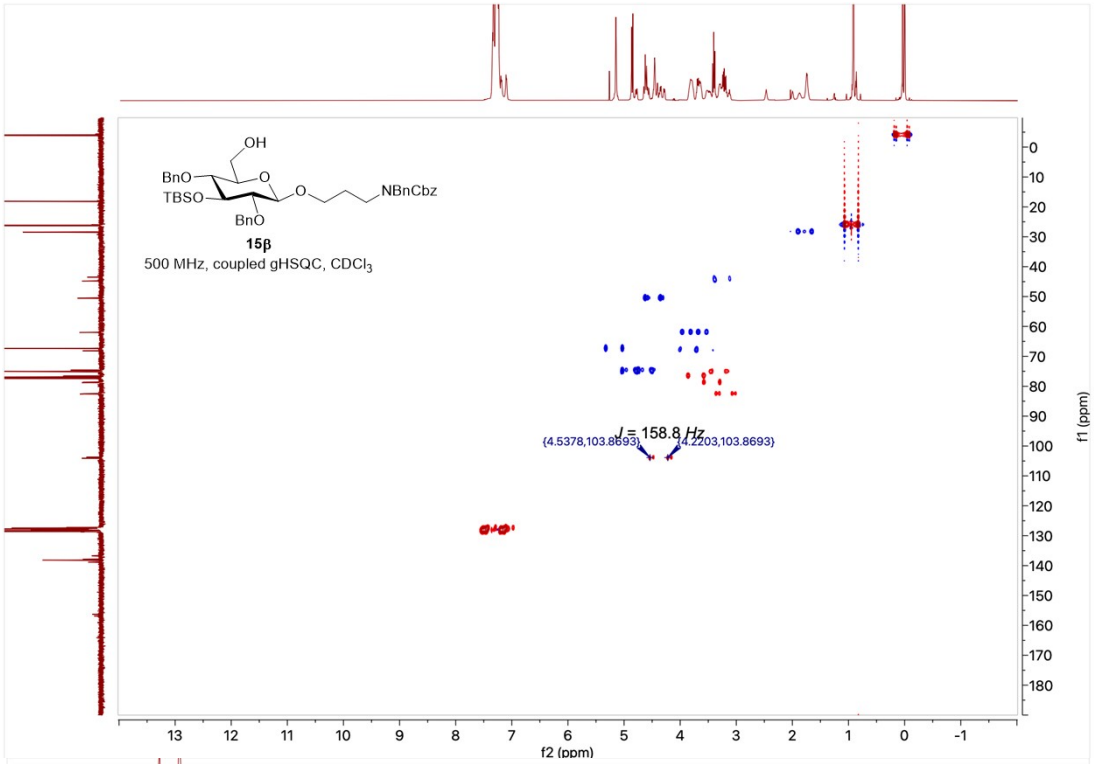

OH
BnO
TBSO
BnO
O
NBnCbz
15α
125 MHz, ^{13}C-NMR, CDCl$_3$
f1 (ppm)

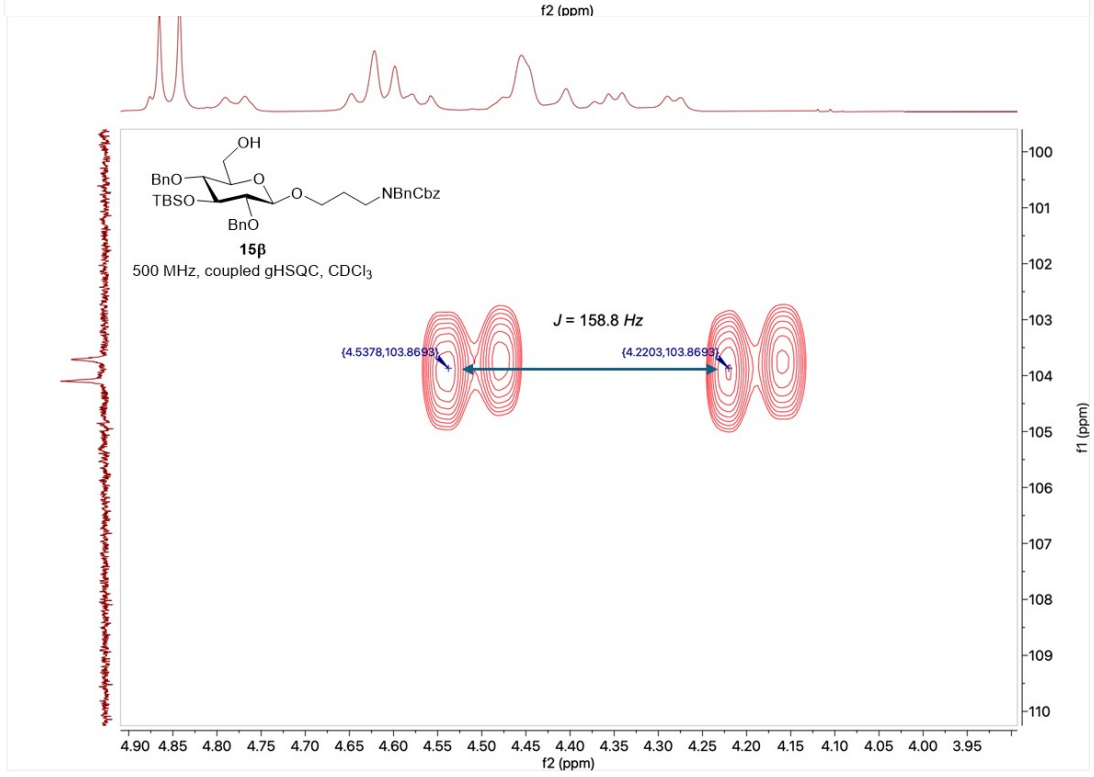

OH
BnO
TBSO
BnO
O
NBnCbz
15α
500 MHz, coupled gHSQC, CDCl3
J = 168.4 Hz
{4.7278,97.2277}
{4.3911,97.2277}
f2 (ppm)
f1 (ppm)

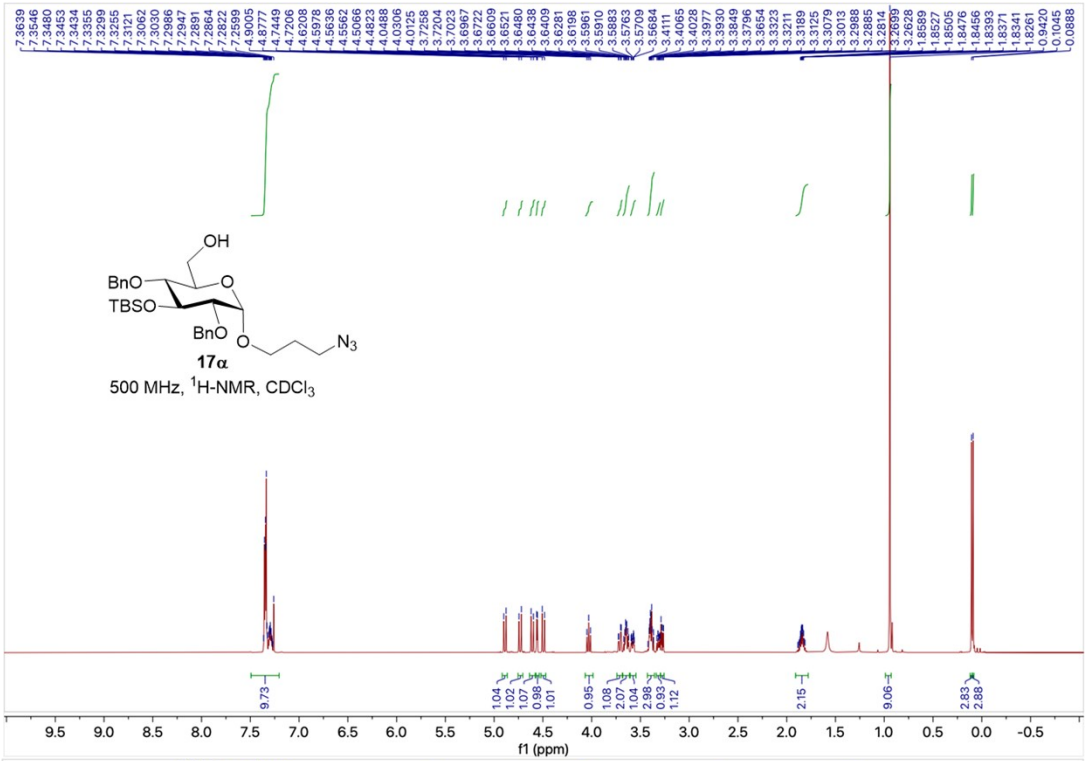

OH
BnO
TBSO
BnO
O
NBnCbz
15α
500 MHz, coupled gHSQC, CDCl3
J = 168.4 Hz
{4.7278,97.2277}
{4.3911,97.2277}
f2 (ppm)
f1 (ppm)

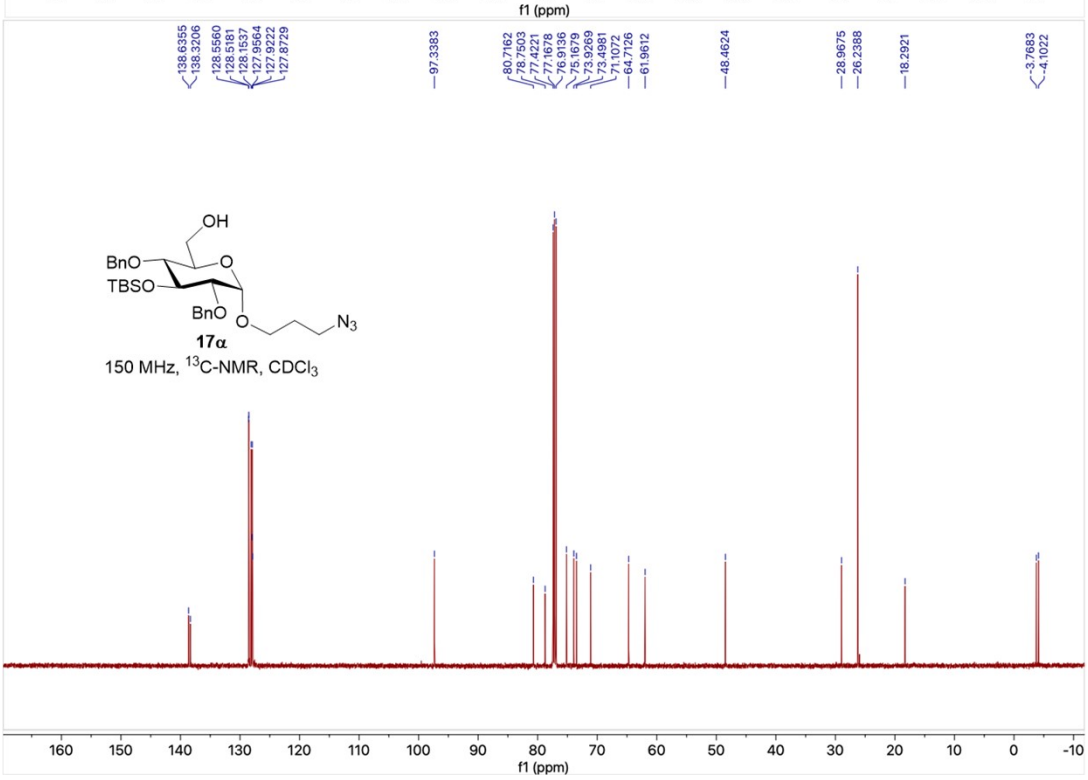

OH
BnO
TBSO
BnO
O
O
NBnCbz
15β
500 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

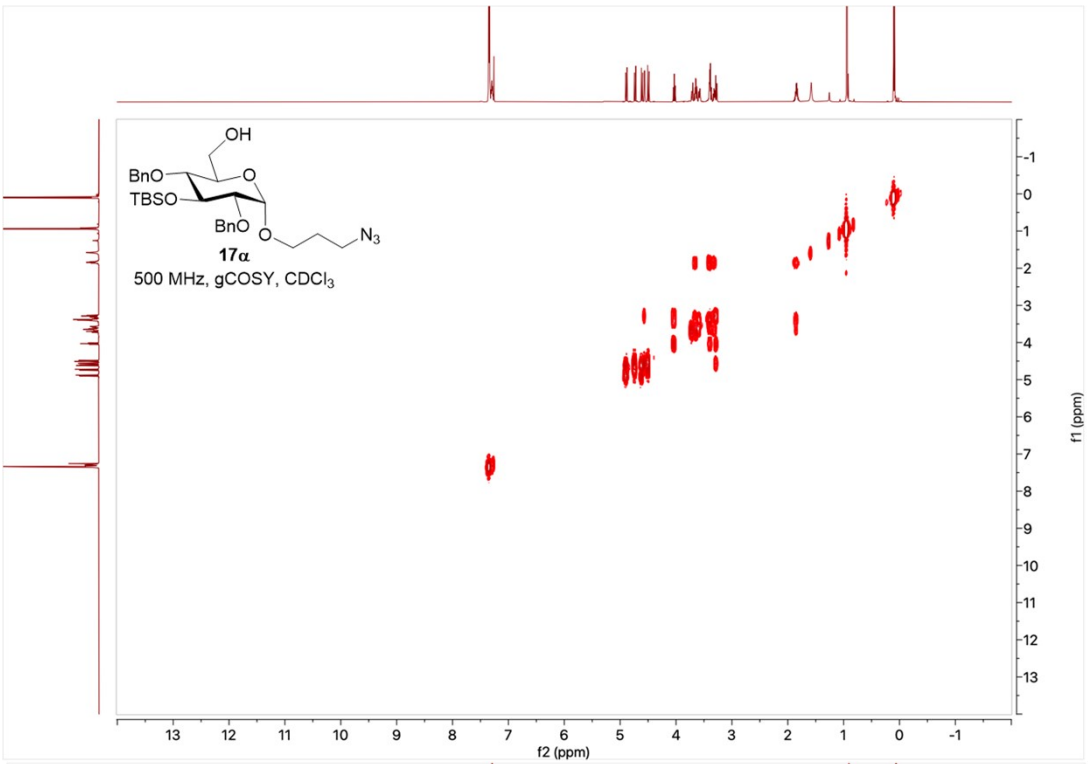

OH
BnO
TBSO
BnO
O
O
NBnCbz
15β
125 MHz, ^{13}C-NMR, $CDCl_3$
f1 (ppm)

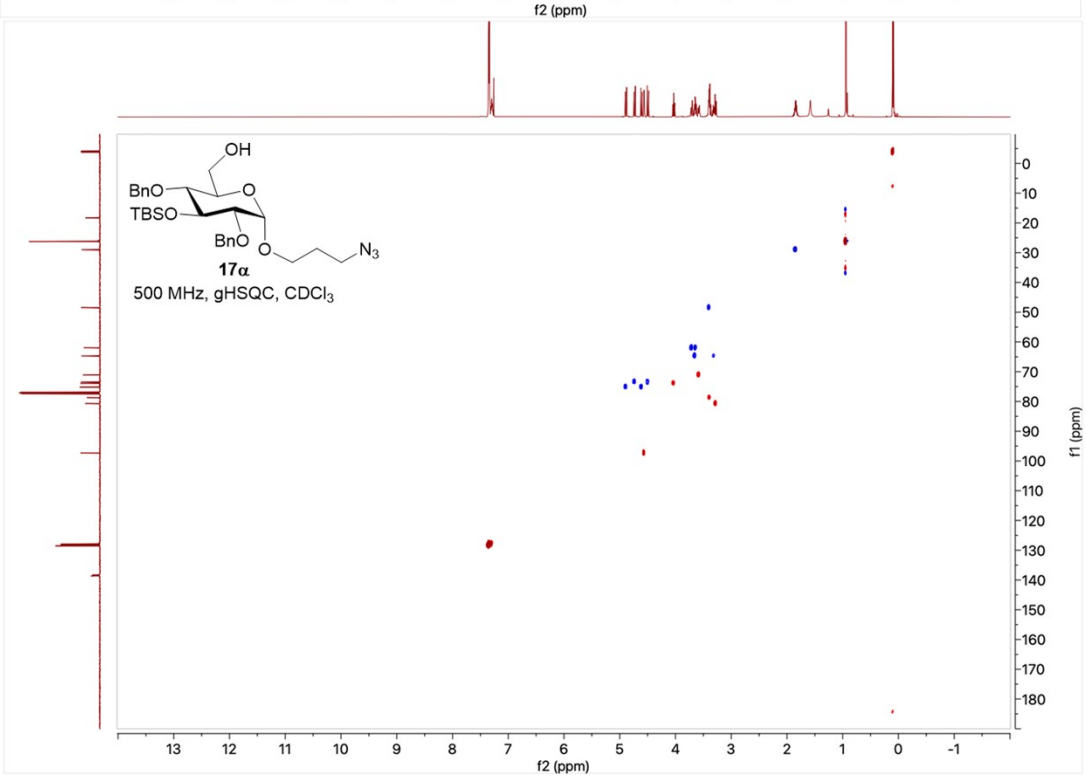

OH
BnO
TBSO
BnO
O
O
NBnCbz
15β
500 MHz, coupled gHSQC, CDCl3
J = 158.8 Hz
{4.5378,103.8693}
{4.2203,103.8693}
f2 (ppm)
f1 (ppm)

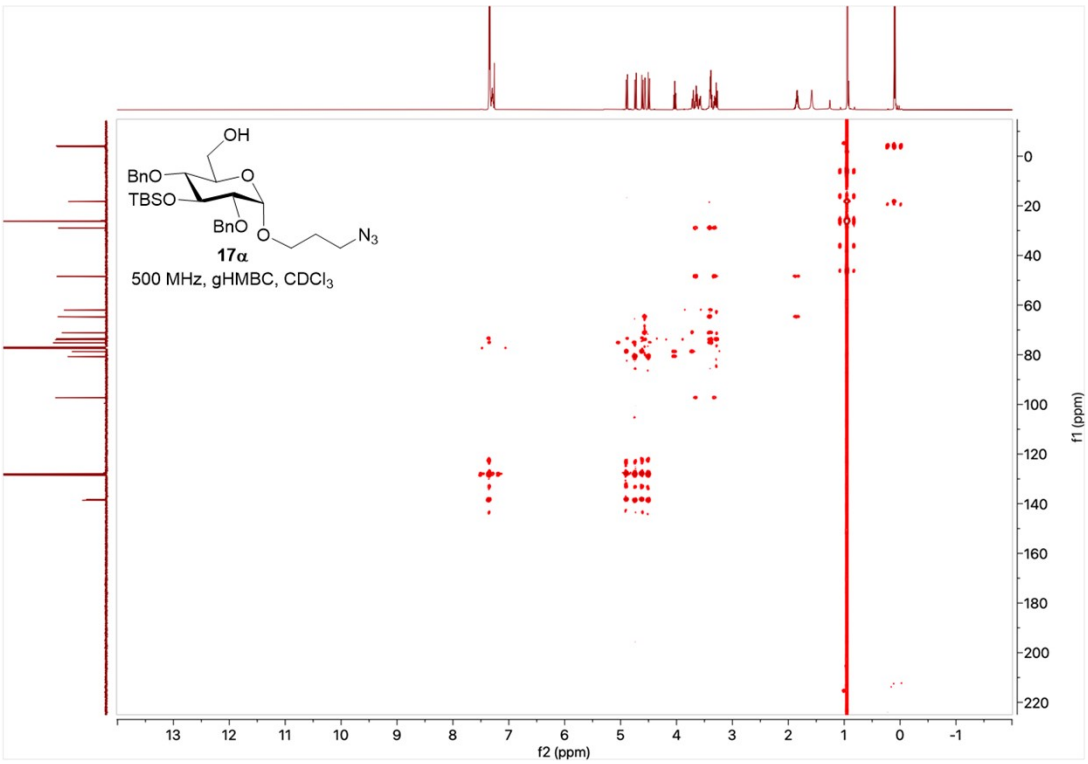

OH
BnO
TBSO
BnO
O
O
NBnCbz
15β
500 MHz, coupled gHSQC, CDCl3
J = 158.8 Hz
{4.5378,103.8693}
{4.2203,103.8693}
f2 (ppm)
f1 (ppm)

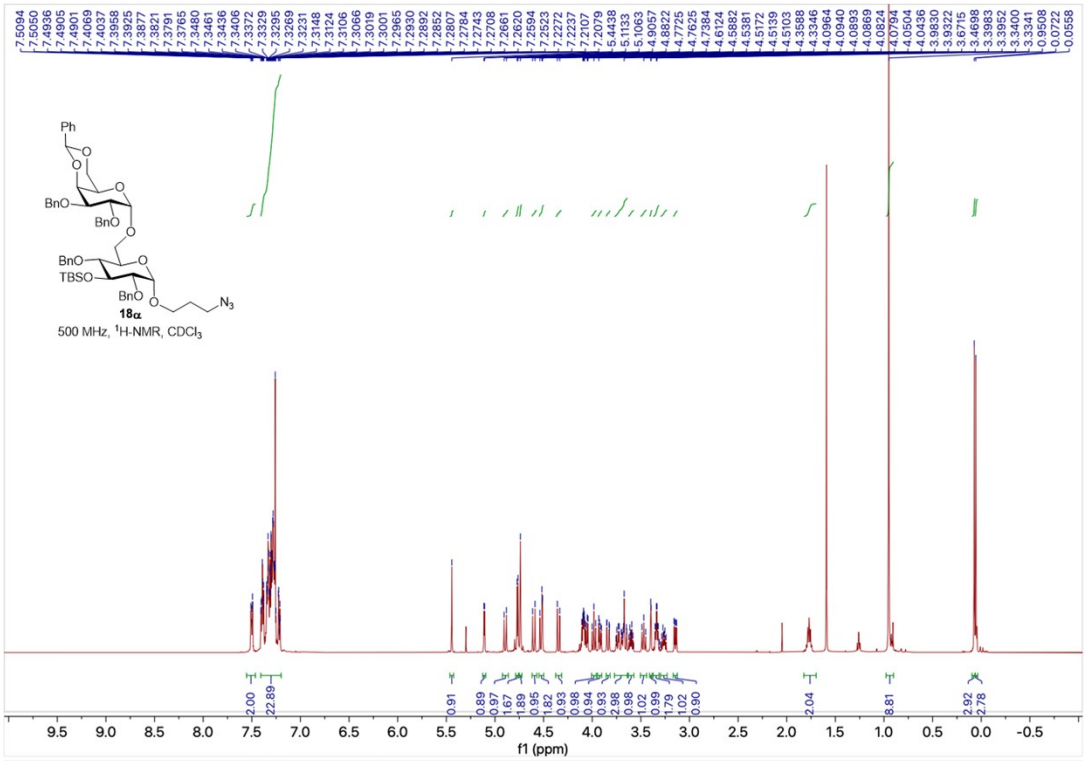

OH
BnO
TBSO
BnO
O
N3
17α
500 MHz, 1H-NMR, CDCl3
f1 (ppm)

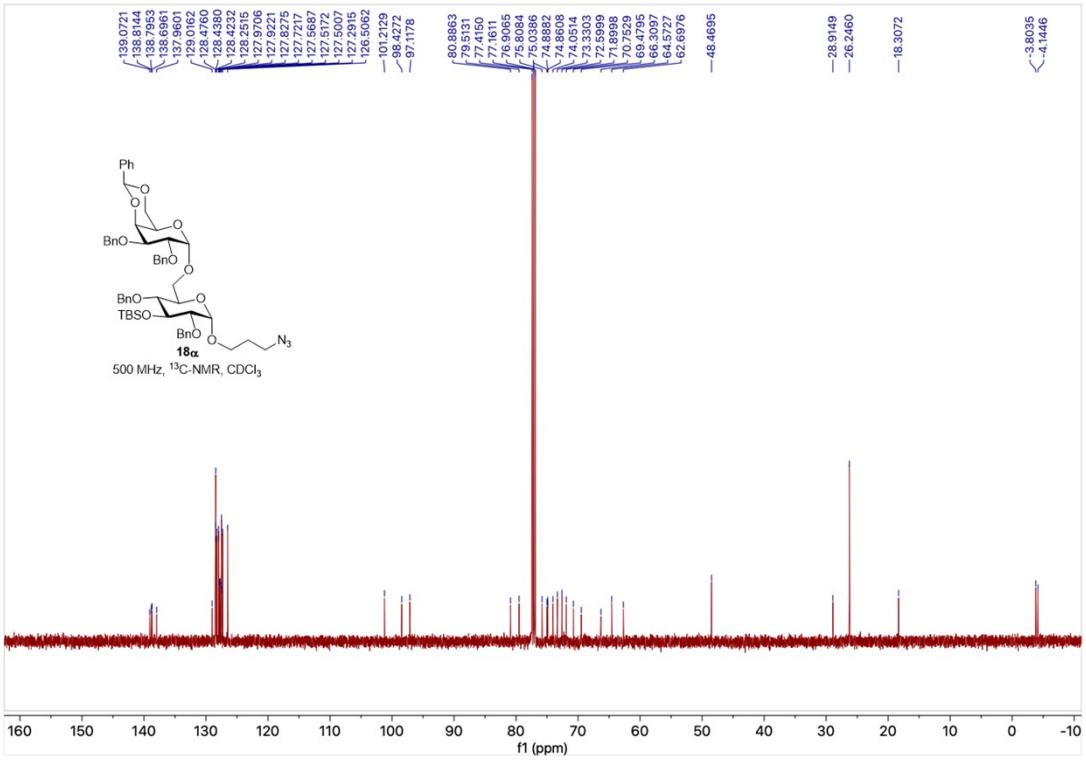

OH
BnO
TBSO
BnO
O
N3
17α
150 MHz, 13C-NMR, CDCl3
f1 (ppm)

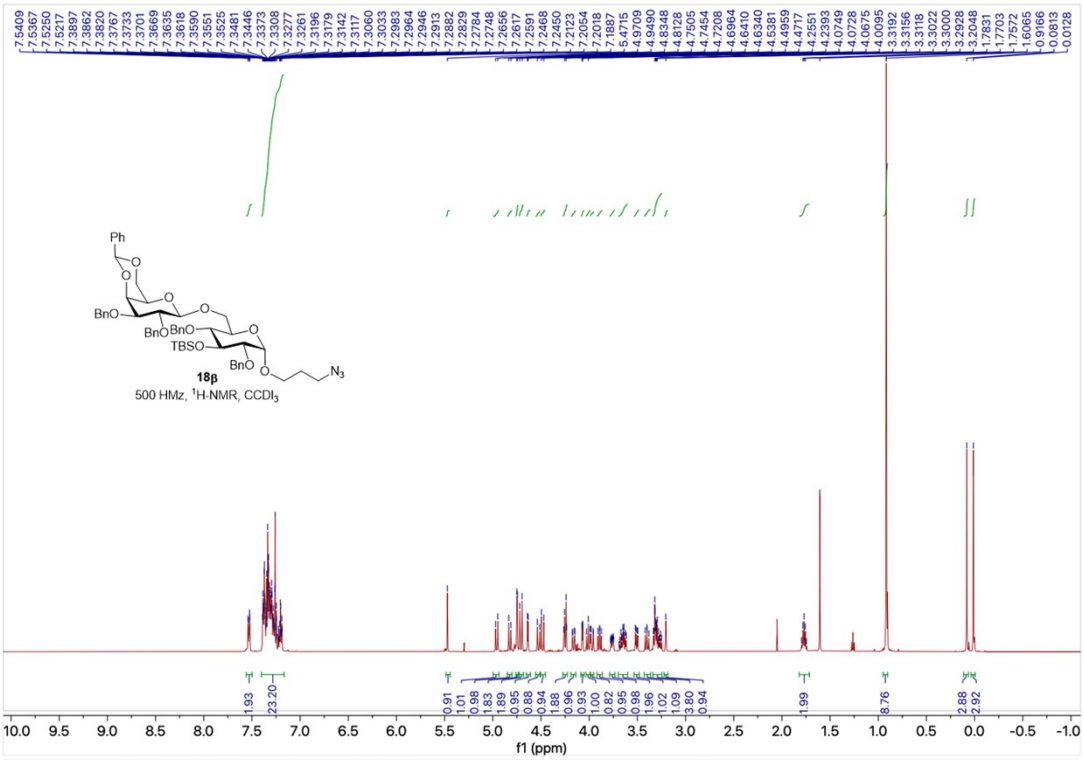

OH
BnO
TBSO
BnO
O
O
N3
17α
500 MHz, gCOSY, CDCl3
f2 (ppm)
f1 (ppm)

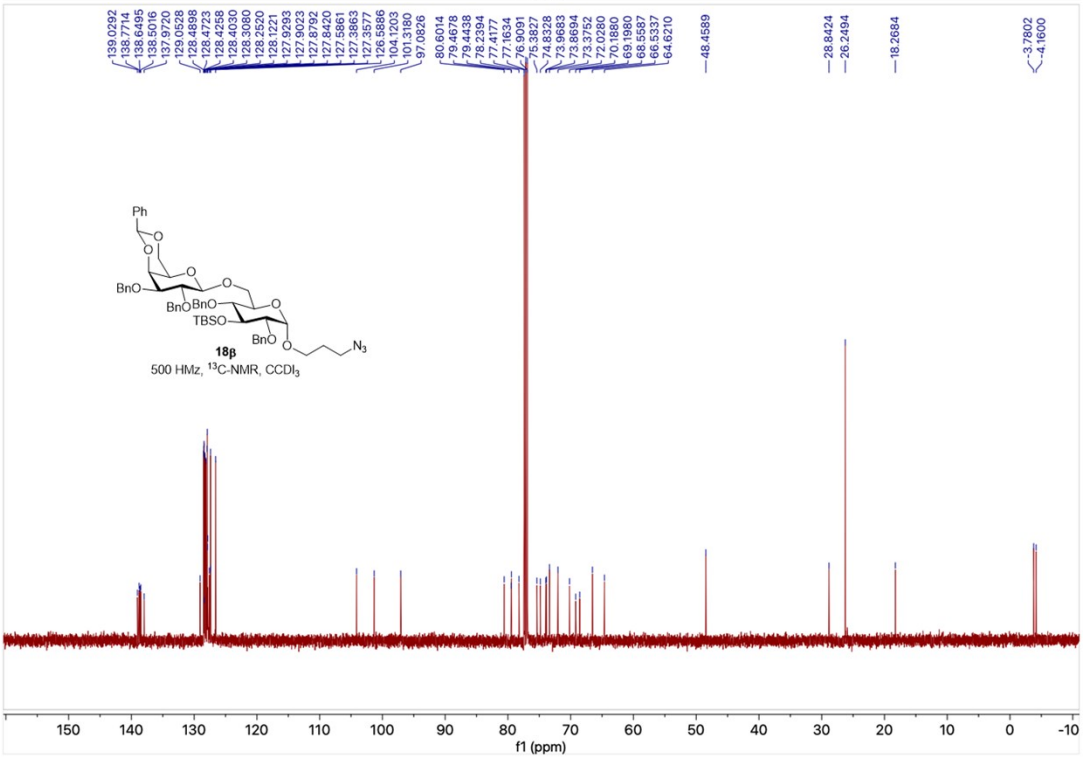

OH
BnO
TBSO
BnO
O
O
N3
17α
500 MHz, gHSQC, CDCl3
f2 (ppm)
f1 (ppm)

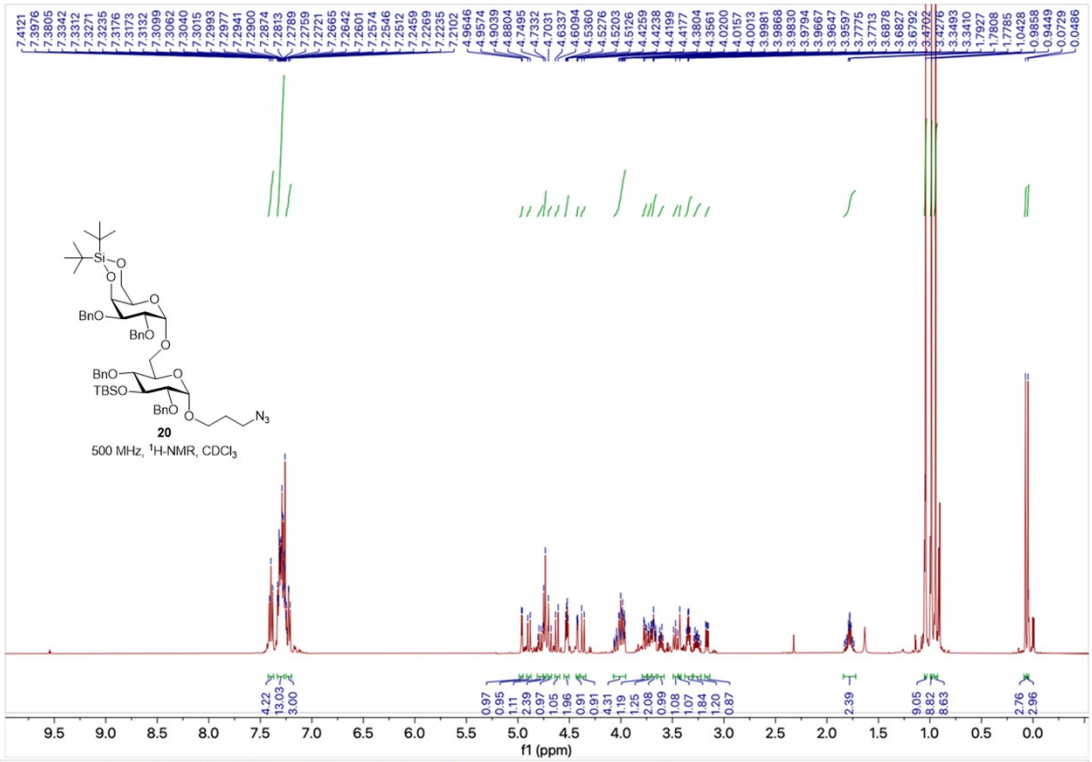

OH
BnO
O
TBSO
BnO
O
N3
17α
500 MHz, gHMBC, CDCl3
f2 (ppm)
f1 (ppm)

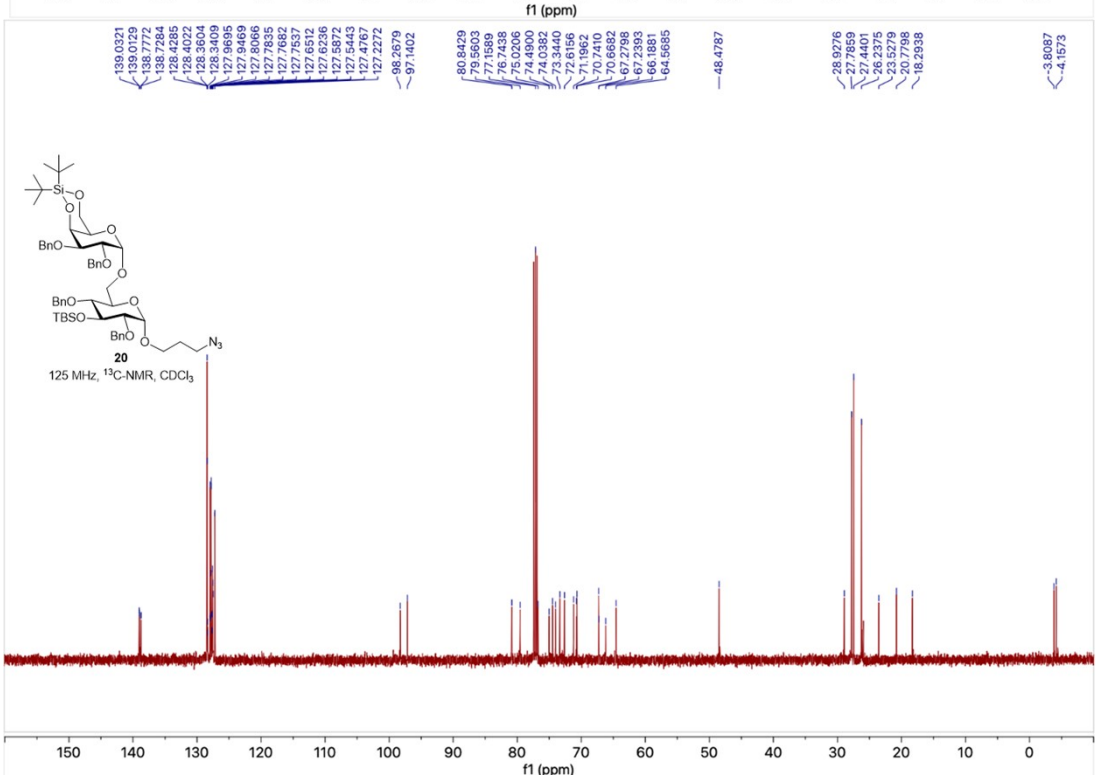

18α
500 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

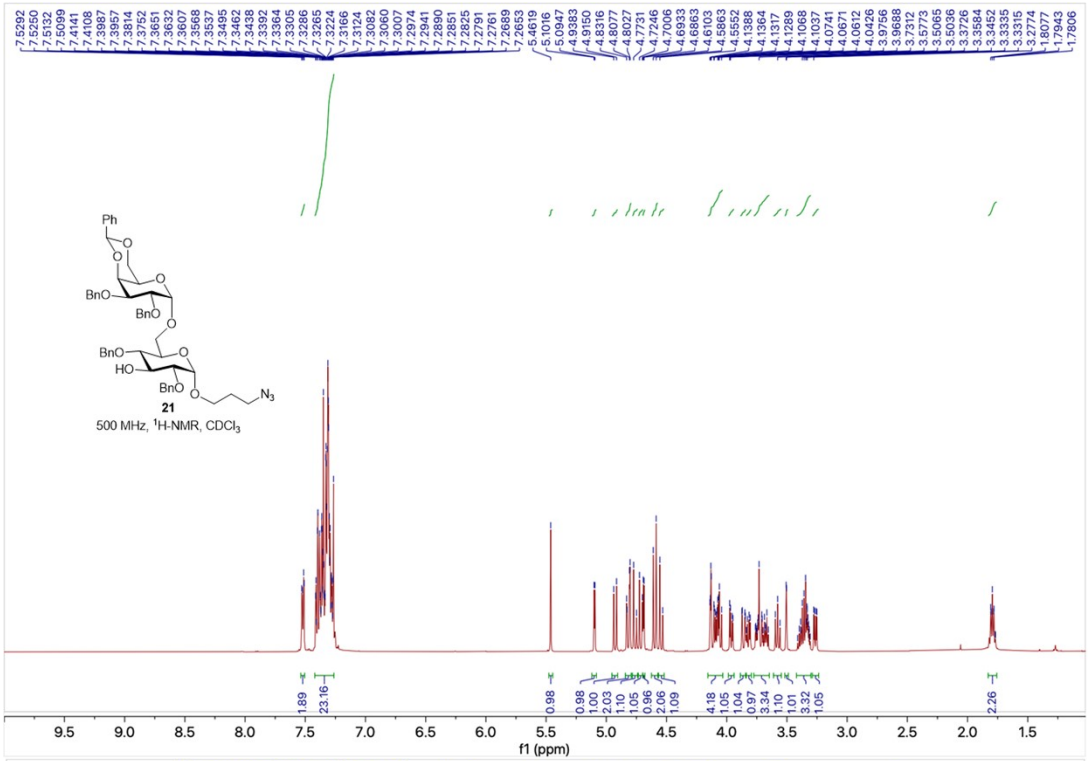

18α
500 MHz, ^{13}C-NMR, $CDCl_3$
f1 (ppm)

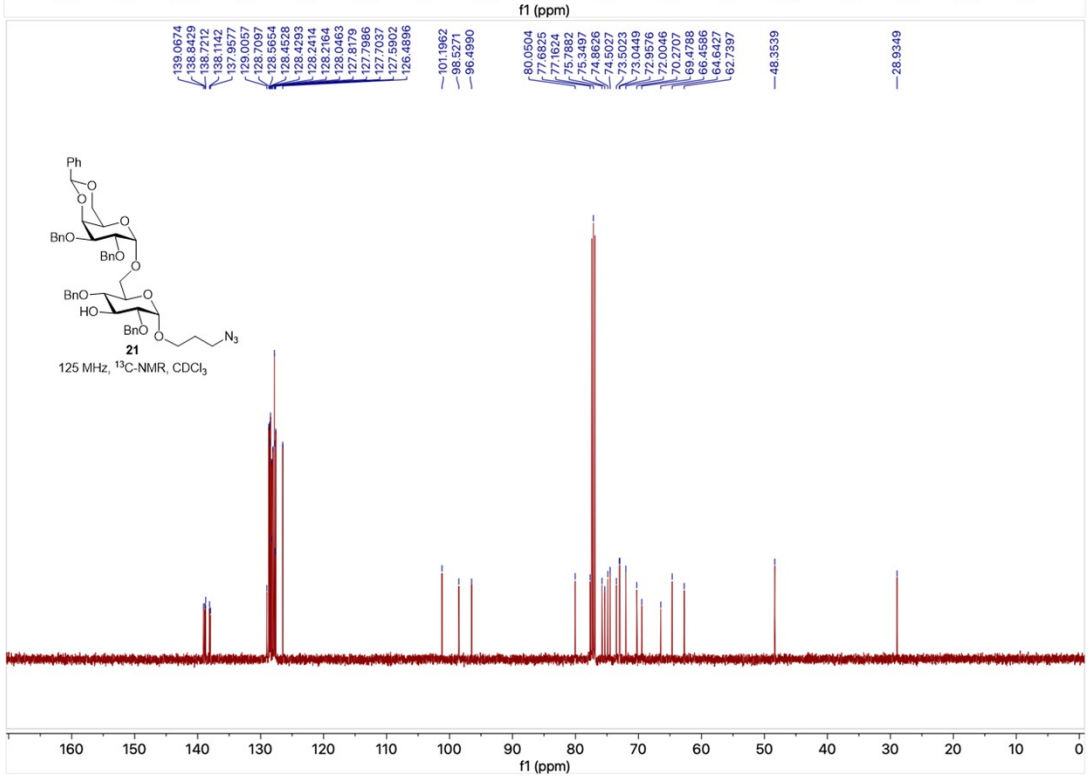

18β
500 HMz, ¹H-NMR, CCDl3
f1 (ppm)

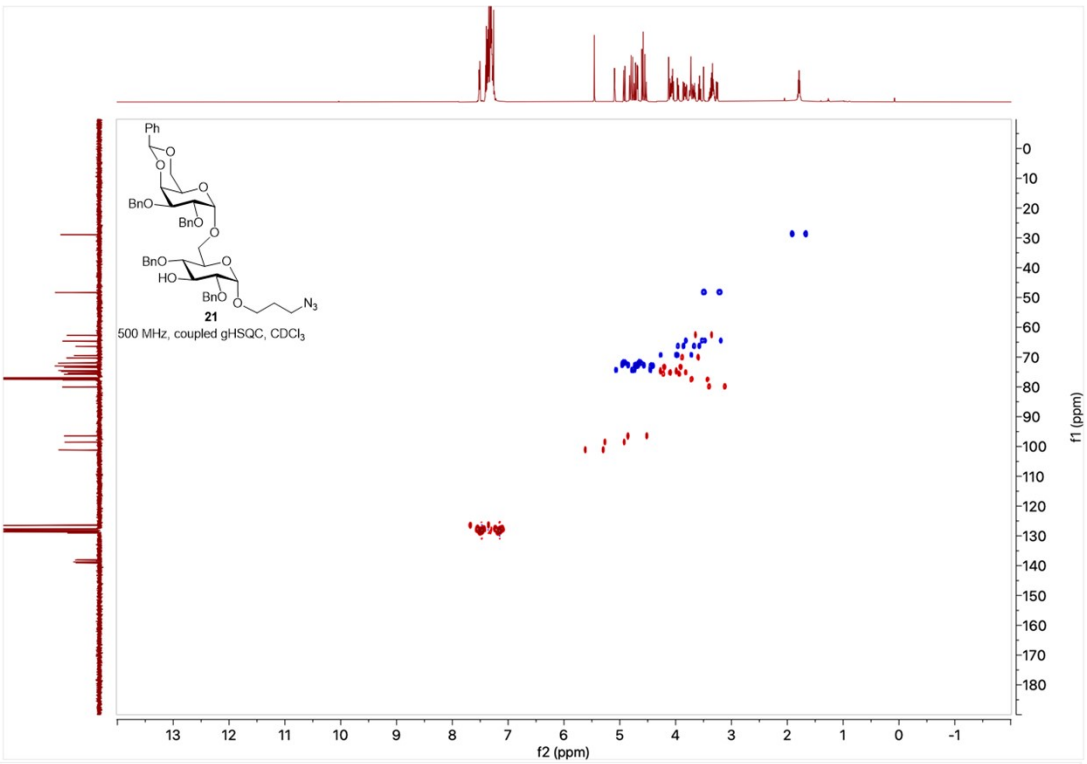

18β
500 HMz, ¹³C-NMR, CCDl3
f1 (ppm)

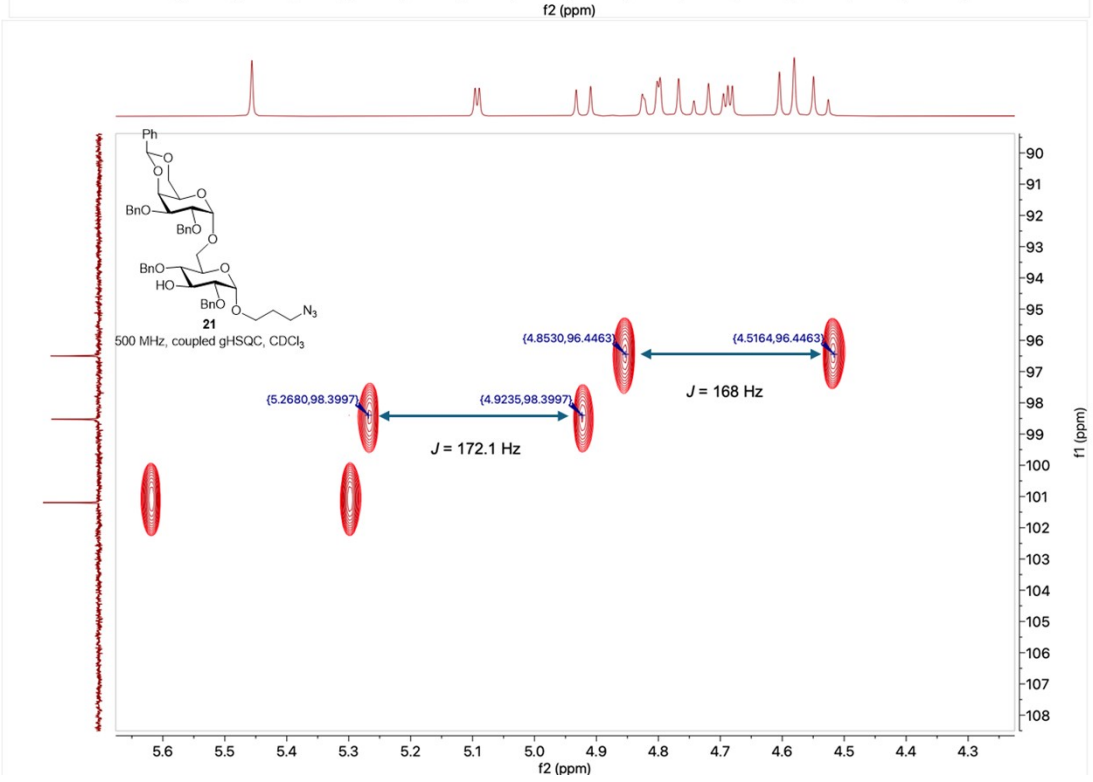

20
500 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

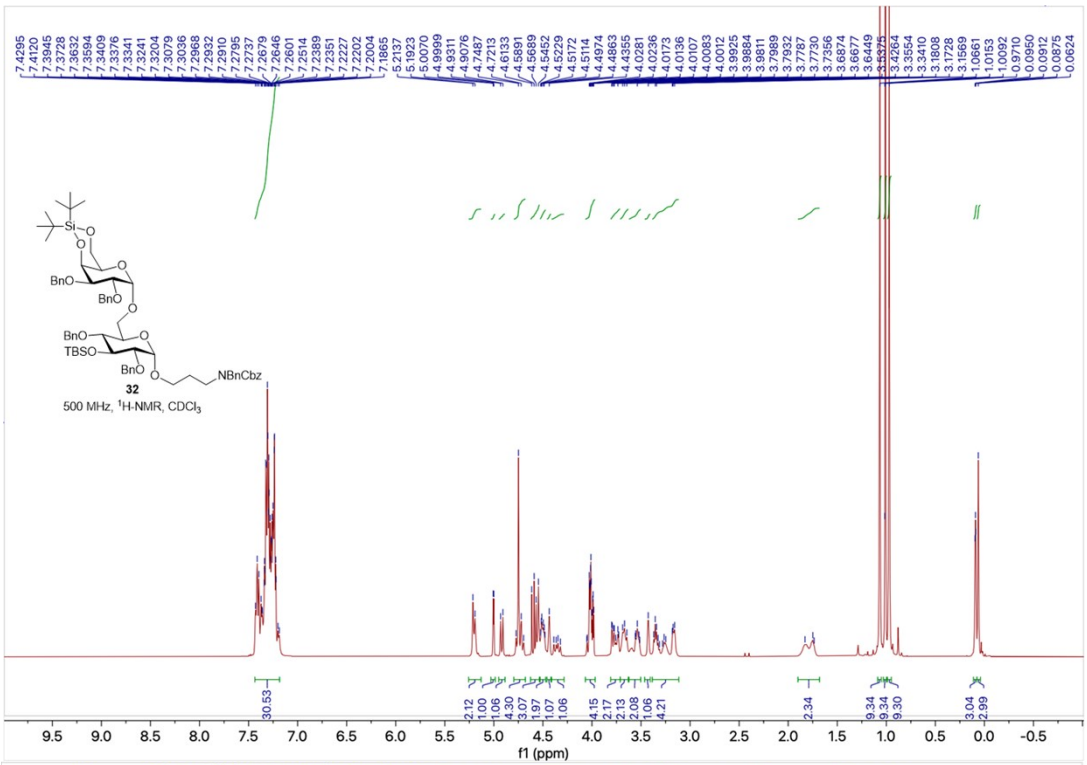

20
125 MHz, ^{13}C-NMR, $CDCl_3$
f1 (ppm)

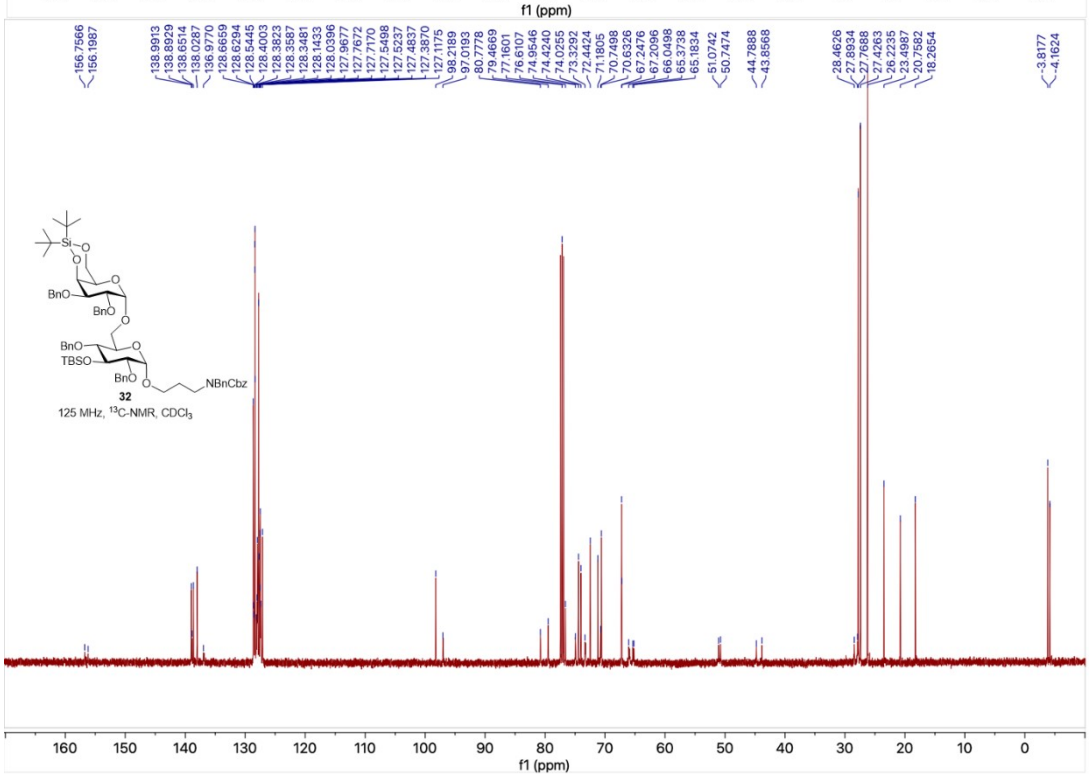

Ph
BnO
BnO
BnO
HO
BnO
N3
21
500 MHz, 1H-NMR, CDCl3
f1 (ppm)

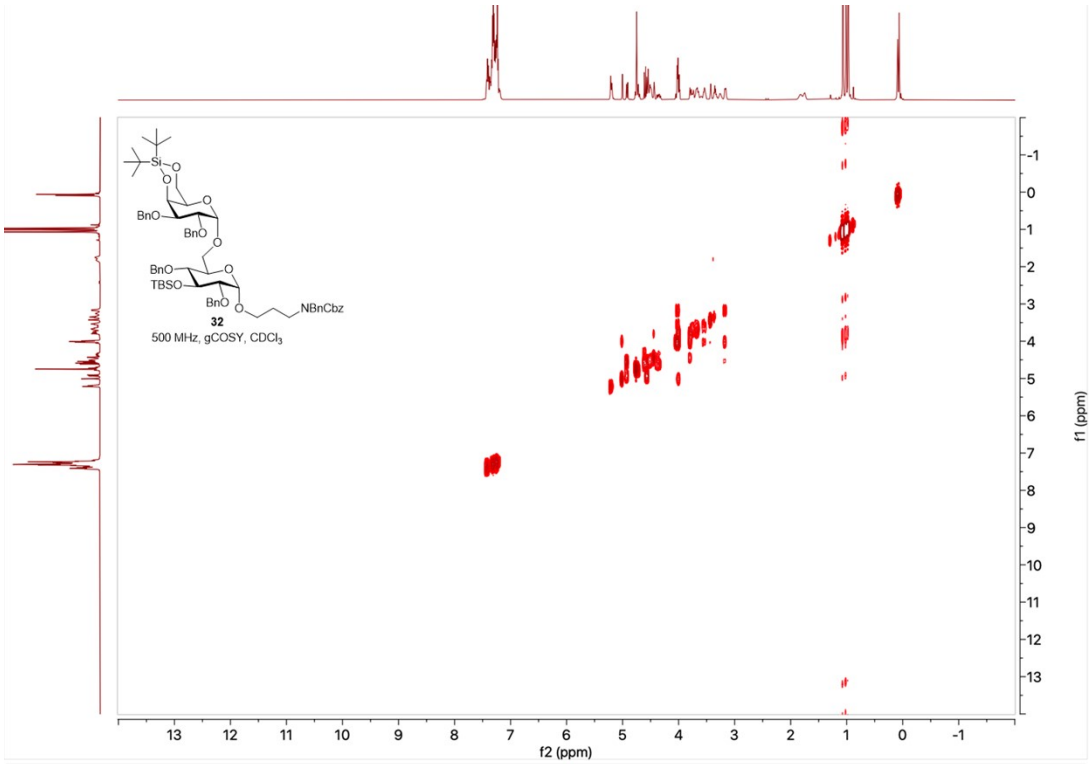

Ph
BnO
BnO
BnO
HO
BnO
N3
21
125 MHz, 13C-NMR, CDCl3
f1 (ppm)

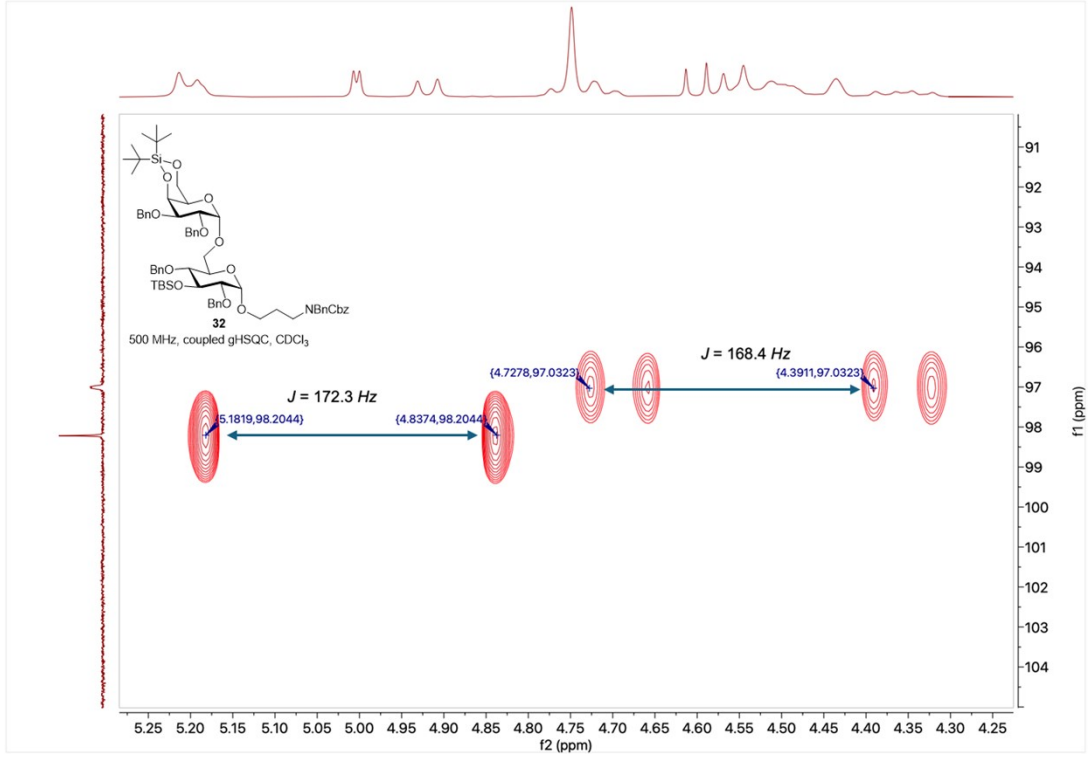

Ph
BnO
BnO
BnO
HO
BnO
N3
21
500 MHz, coupled gHSQC, CDCl3
f2 (ppm)
f1 (ppm)

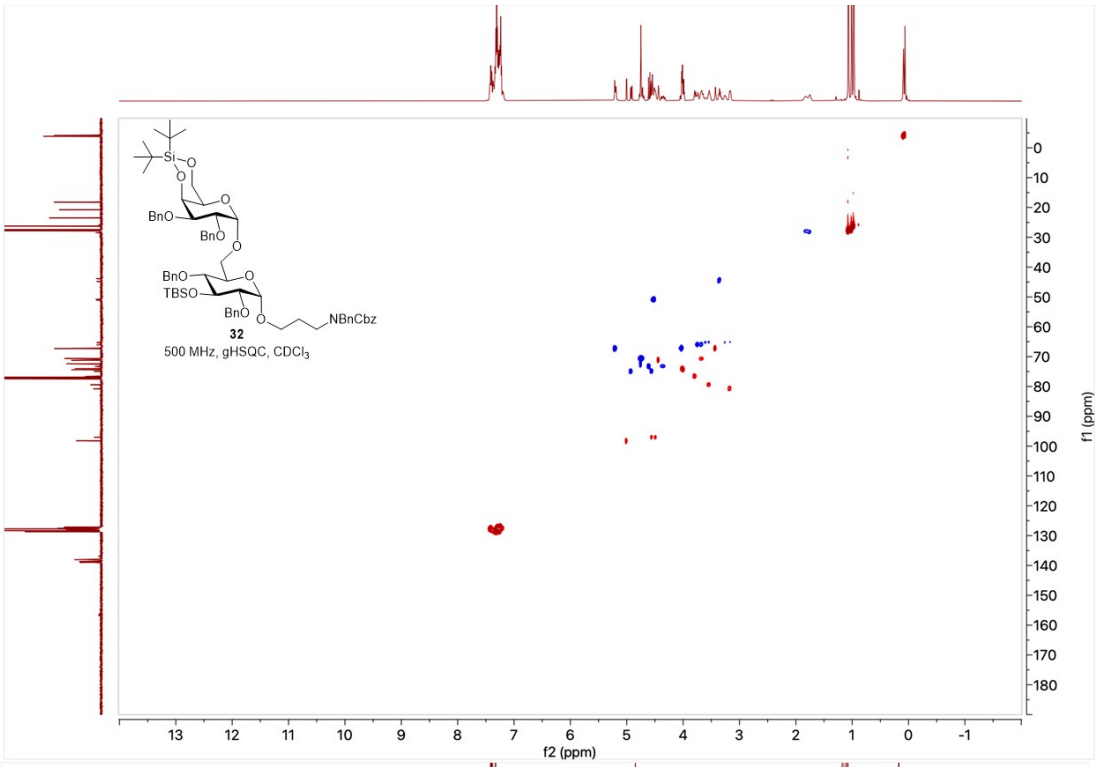

Ph
BnO
BnO
BnO
HO
BnO
N3
21
500 MHz, coupled gHSQC, CDCl3
{4.8530,96.4463}
{4.5164,96.4463}
J = 168 Hz
{5.2680,98.3997}
{4.9235,98.3997}
J = 172.1 Hz
f2 (ppm)
f1 (ppm)

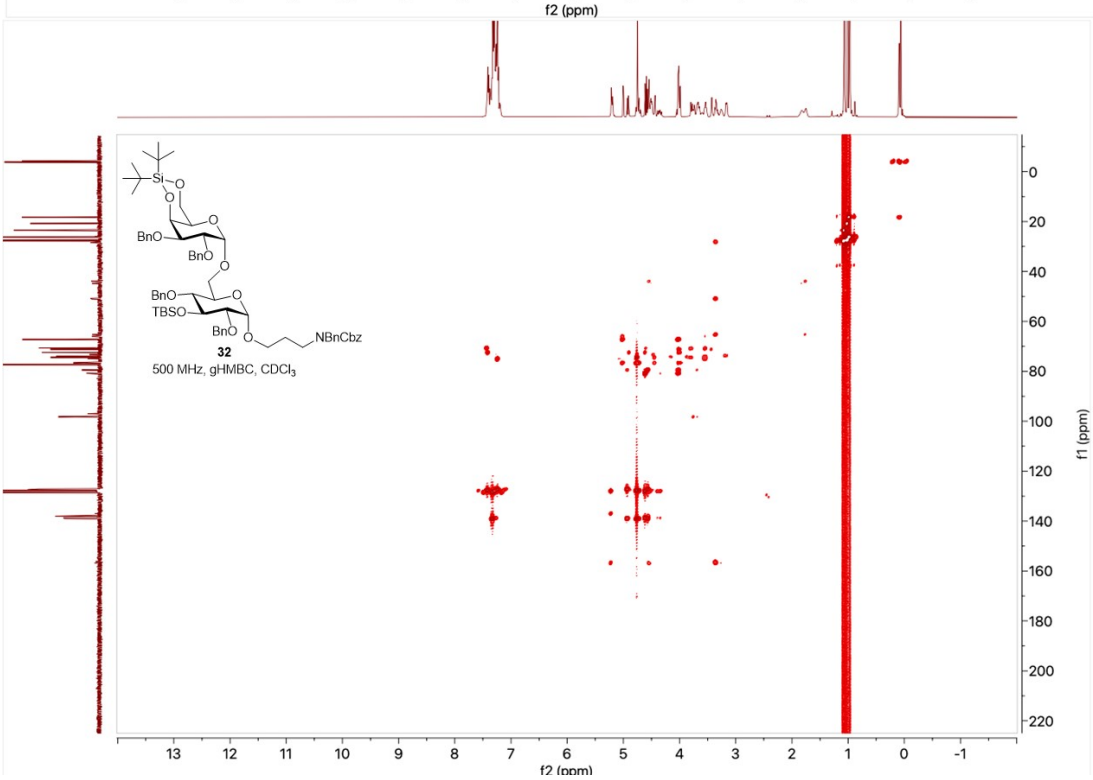

BnO
BnO
BnO
TBSO
BnO
NBnCbz
32
500 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

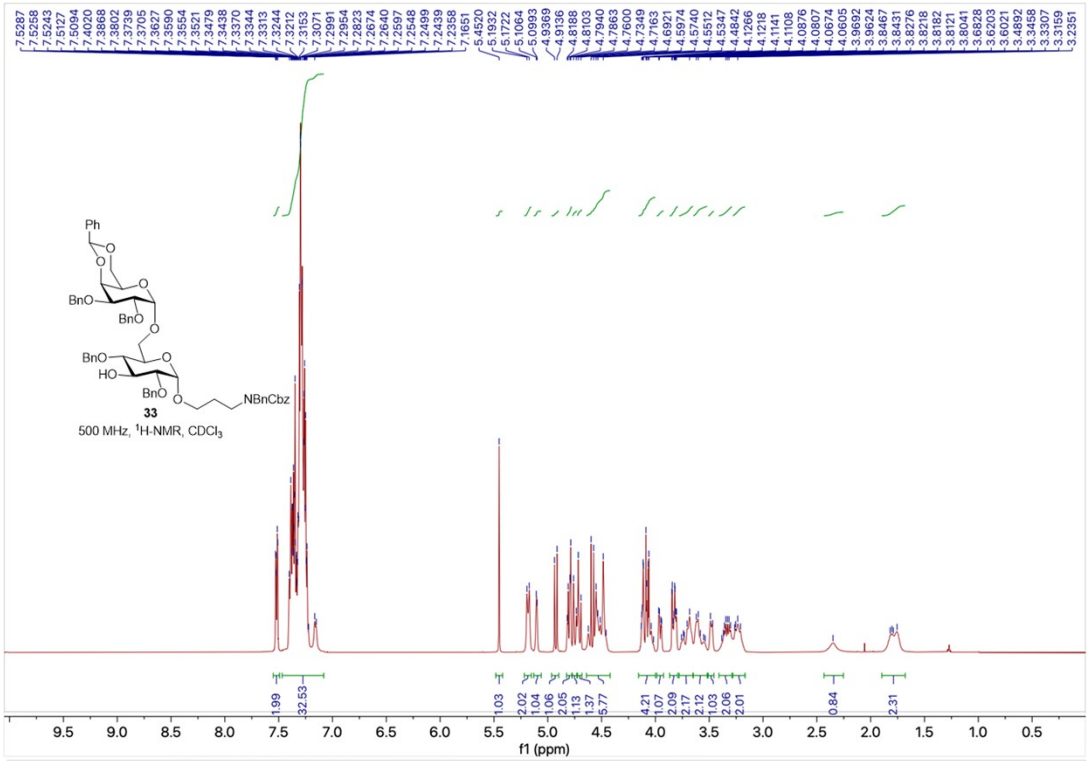

BnO
BnO
BnO
TBSO
BnO
NBnCbz
32
125 MHz, ^{13}C-NMR, $CDCl_3$
f1 (ppm)

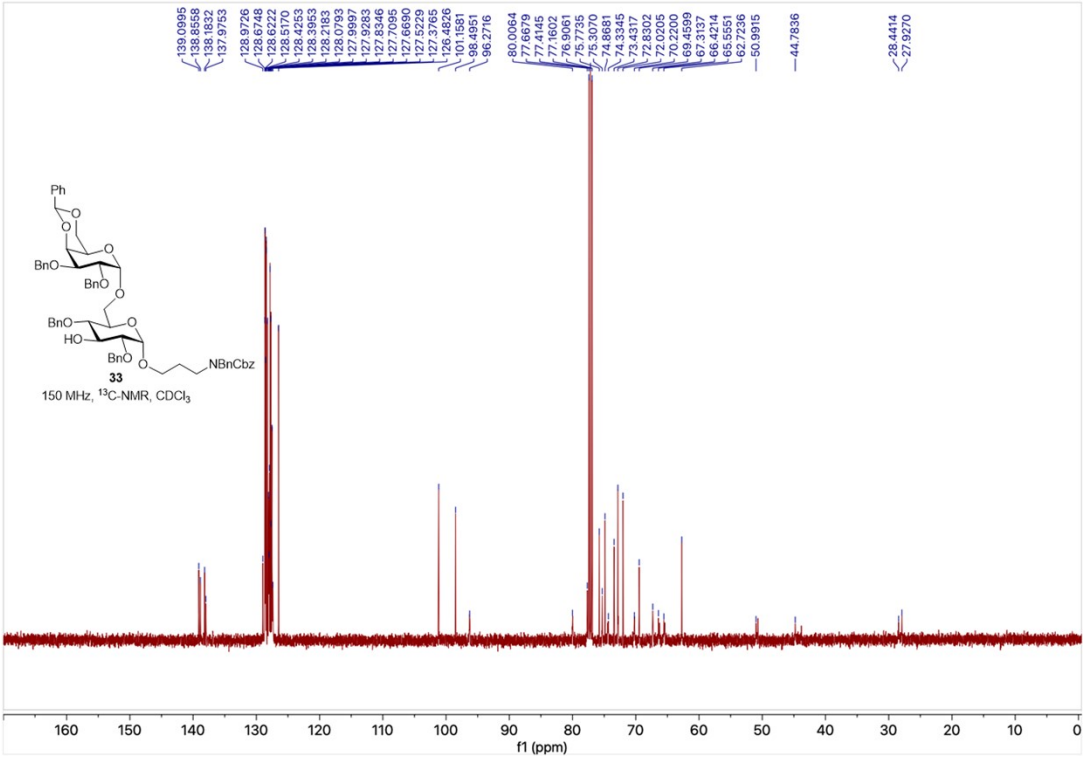

BnO
BnO
BnO
TBSO
BnO
NBnCbz
32
500 MHz, gCOSY, CDCl3
f2 (ppm)
f1 (ppm)

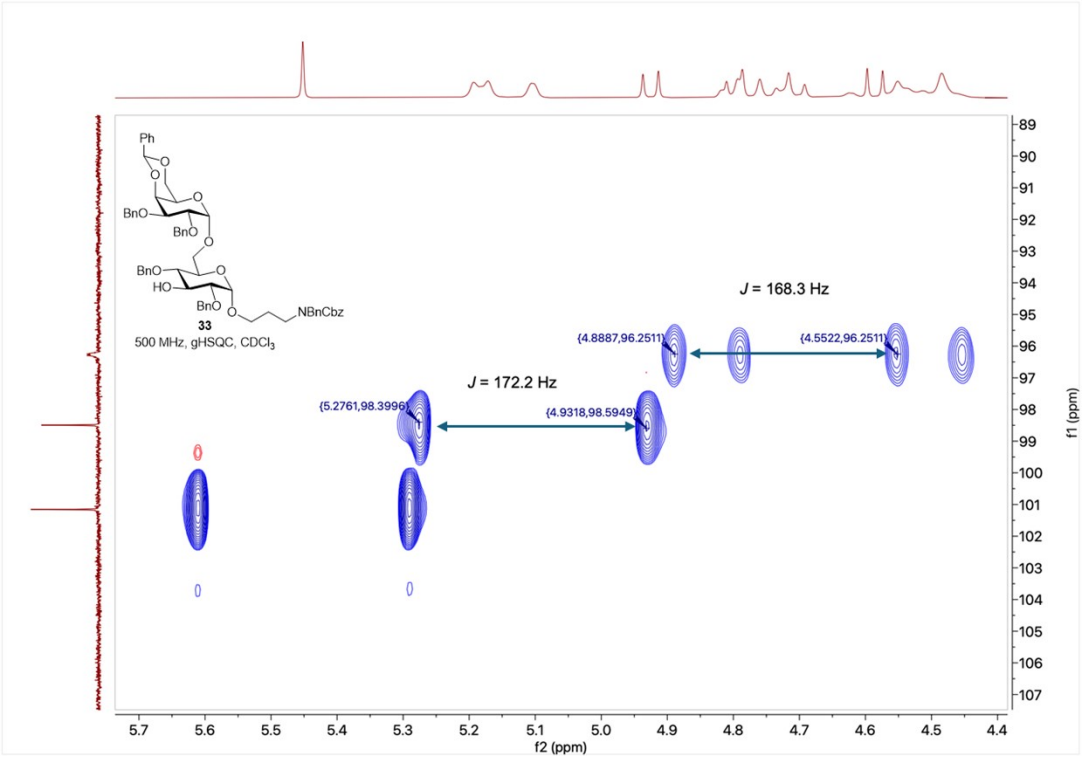

BnO
BnO
BnO
TBSO
BnO
NBnCbz
32
500 MHz, coupled gHSQC, CDCl3
J = 172.3 Hz
{5.1819,98.2044}
{4.8374,98.2044}
J = 168.4 Hz
{4.7278,97.0323}
{4.3911,97.0323}
f2 (ppm)
f1 (ppm)

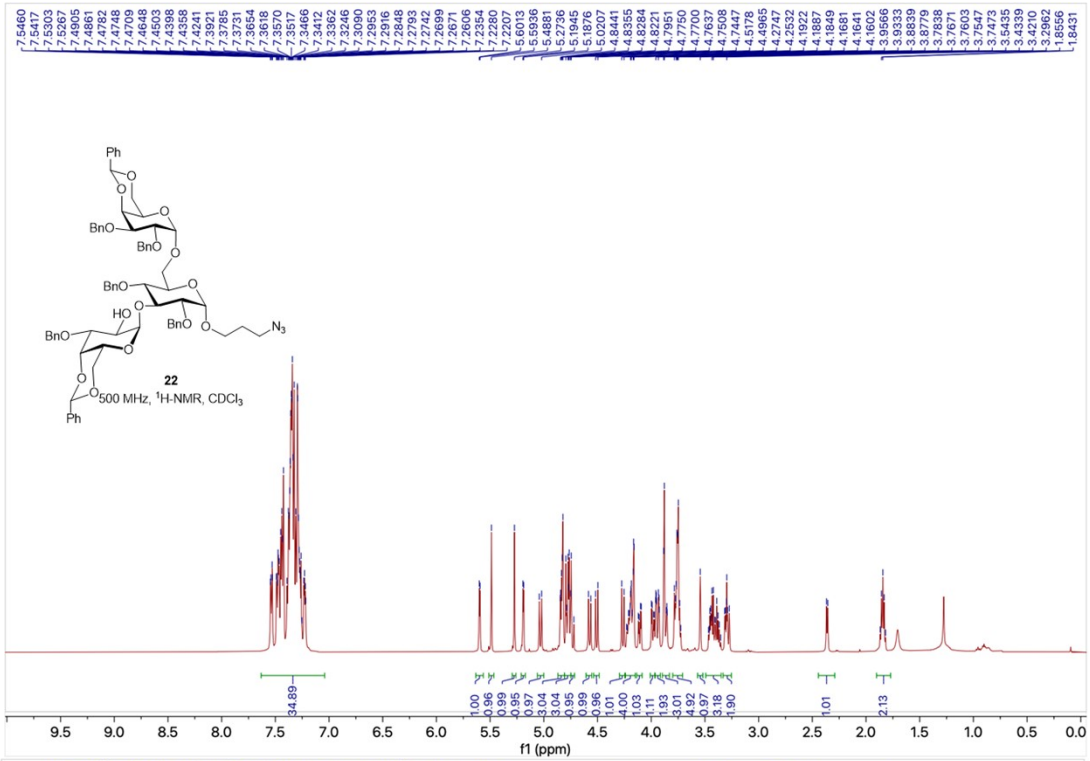

BnO
BnO
BnO
TBSO
BnO
NBnCbz
32
500 MHz, gHSQC, CDCl3
f2 (ppm)
f1 (ppm)

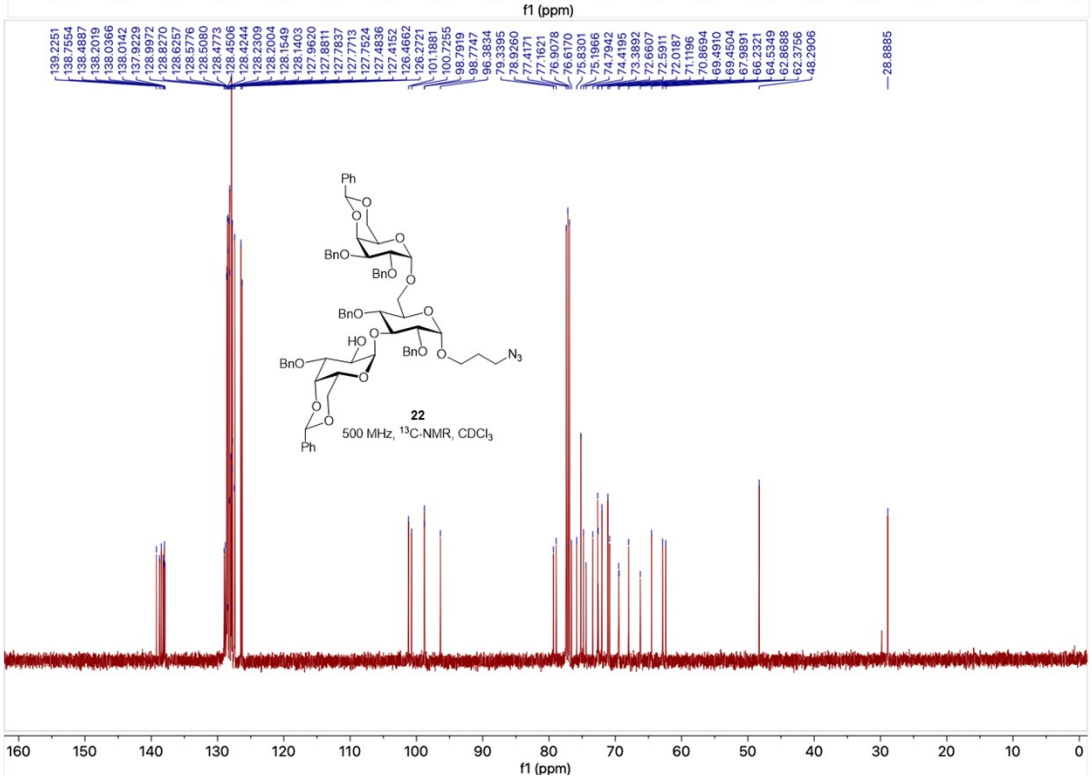

BnO
BnO
BnO
TBSO
BnO
NBnCbz
32
500 MHz, gHMBC, CDCl3
f2 (ppm)
f1 (ppm)

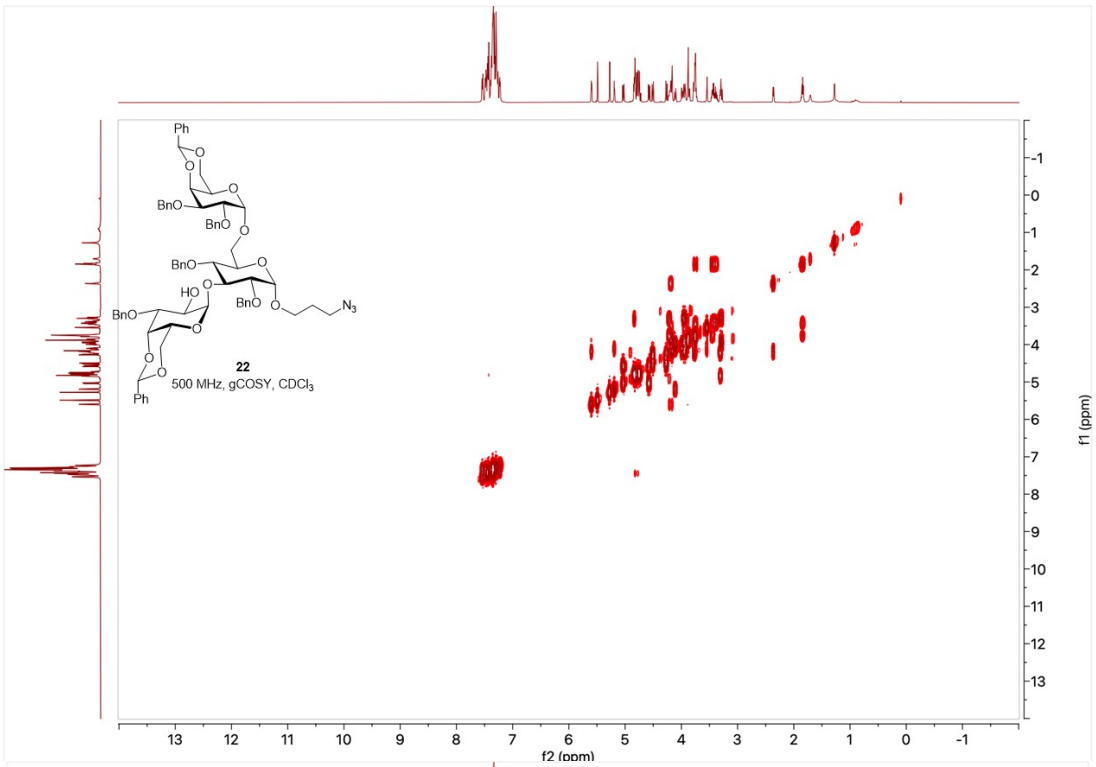

Ph
BnO
BnO
BnO
HO
BnO
NBnCbz
33
500 MHz, ^{1}H-NMR, CDCl$_3$
f1 (ppm)

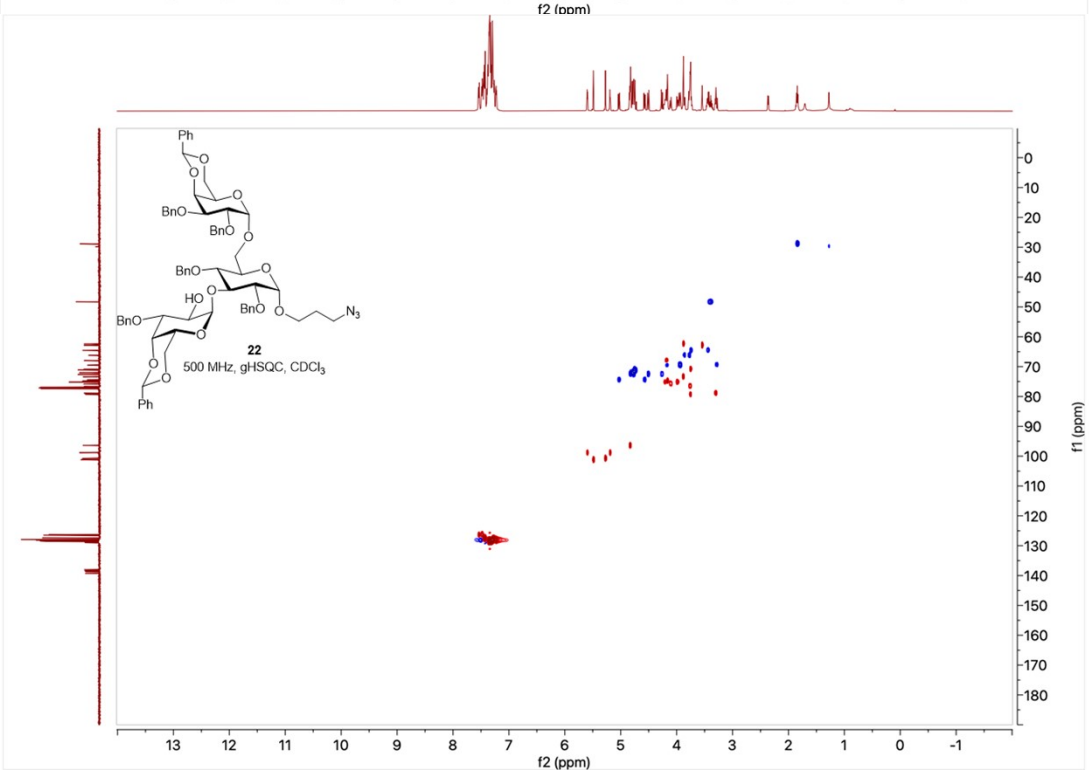

Ph
BnO
BnO
BnO
HO
BnO
NBnCbz
33
150 MHz, ^{13}C-NMR, CDCl$_3$
f1 (ppm)

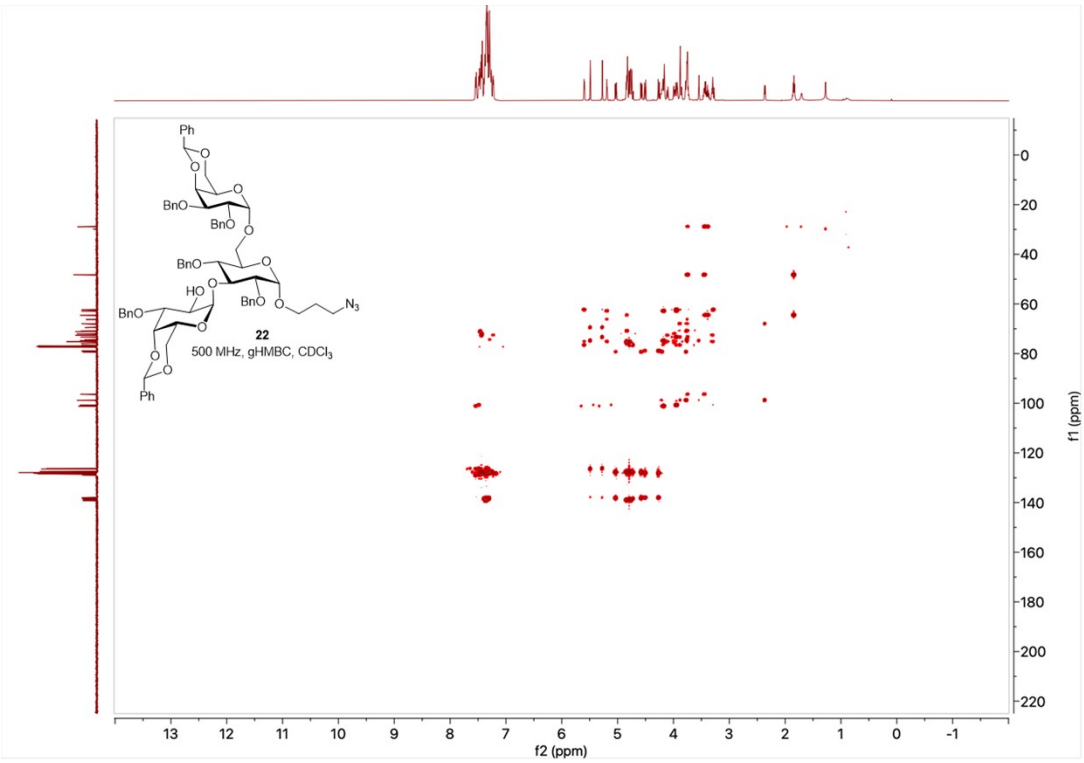

Ph
BnO
BnO
BnO
HO
BnO
NBnCbz
33
500 MHz, gHSQC, CDCl3
J = 168.3 Hz
{4.8887,96.2511}
{4.5522,96.2511}
J = 172.2 Hz
{5.2761,98.3996}
{4.9318,98.5949}
f2 (ppm)
f1 (ppm)

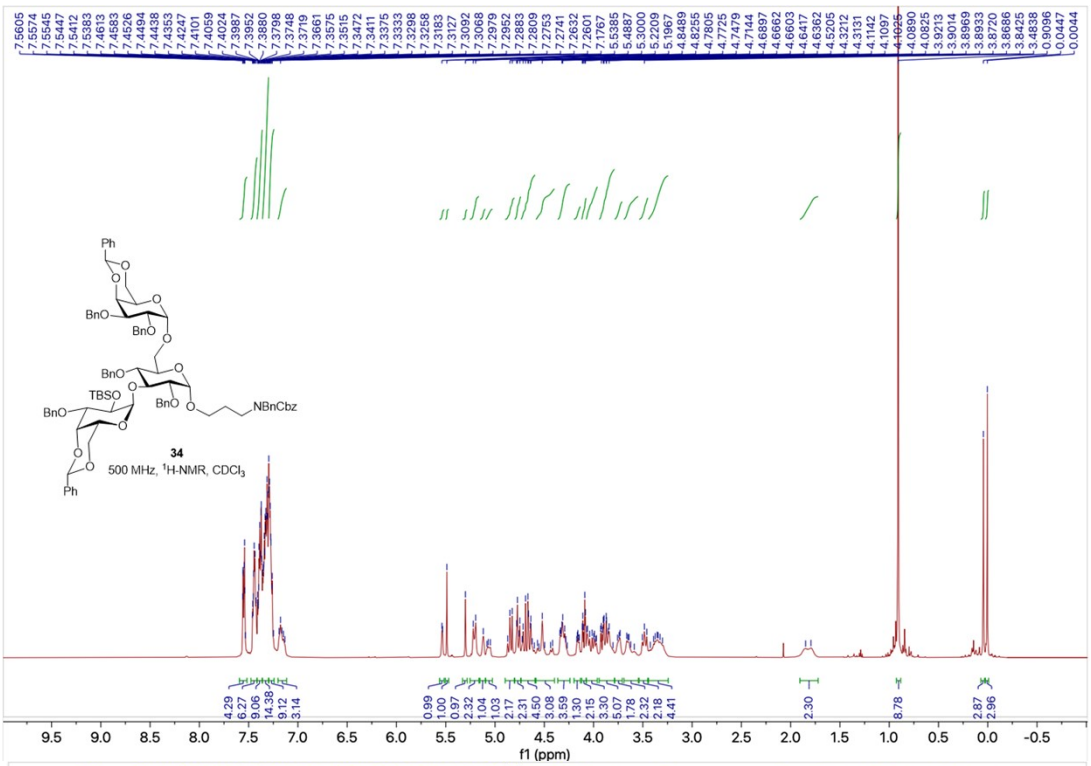

22
500 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

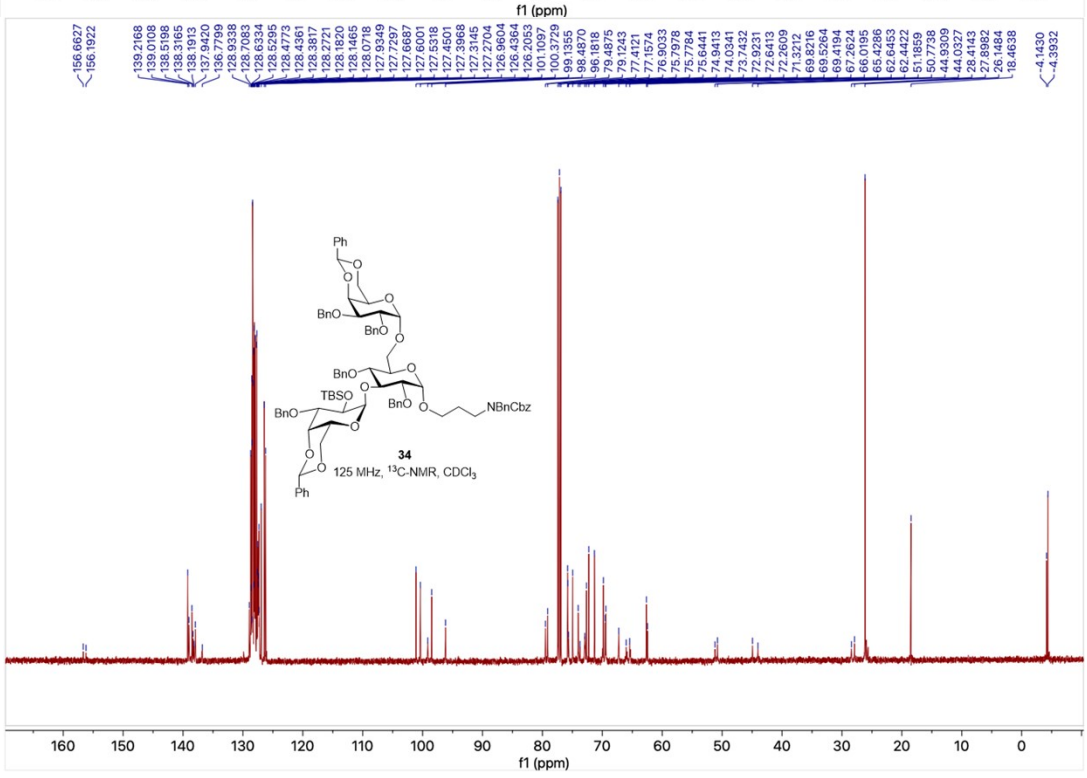

22
500 MHz, ^{13}C-NMR, $CDCl_3$
f1 (ppm)

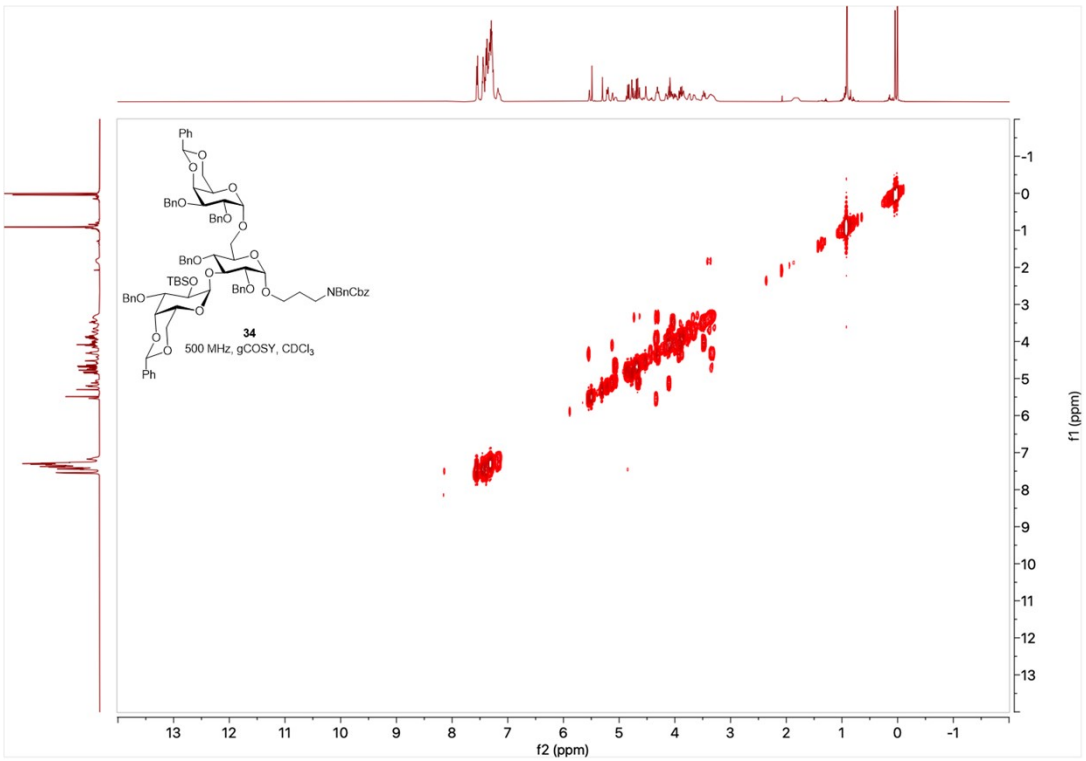

Ph
BnO
BnO
BnO
HO
BnO
BnO
N3
Ph
22
500 MHz, gCOSY, CDCl3
f2 (ppm)
f1 (ppm)

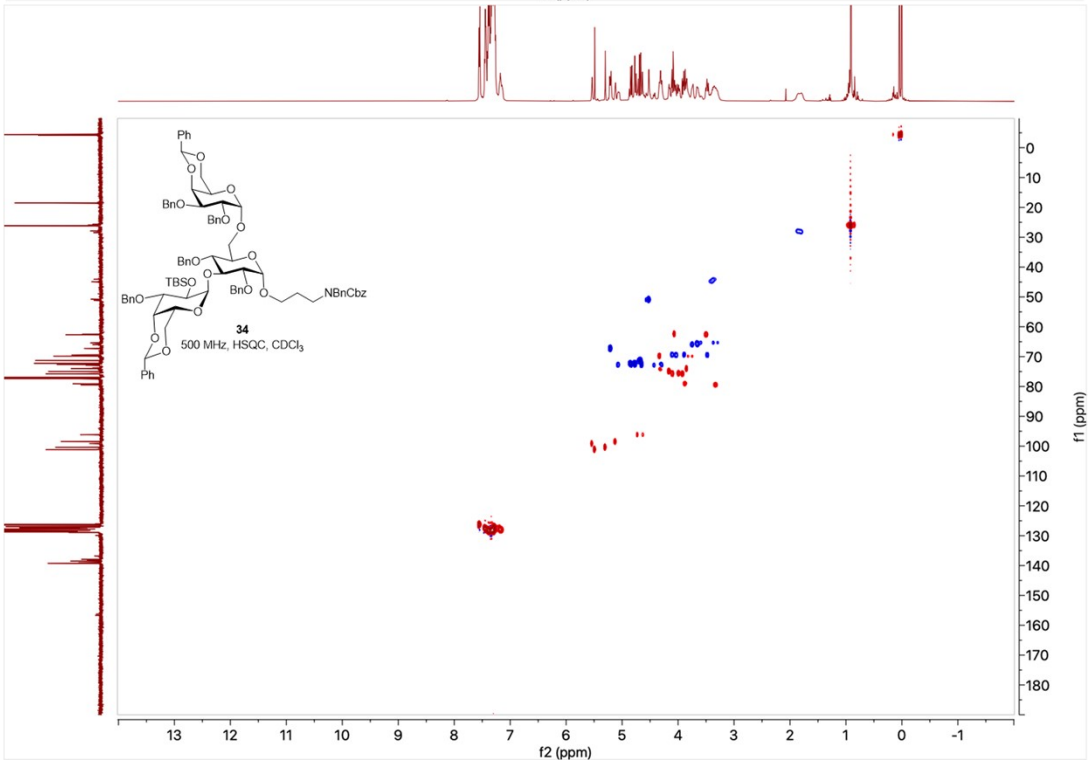

Ph
BnO
BnO
BnO
HO
BnO
BnO
N3
Ph
22
500 MHz, gHSQC, CDCl3
f2 (ppm)
f1 (ppm)

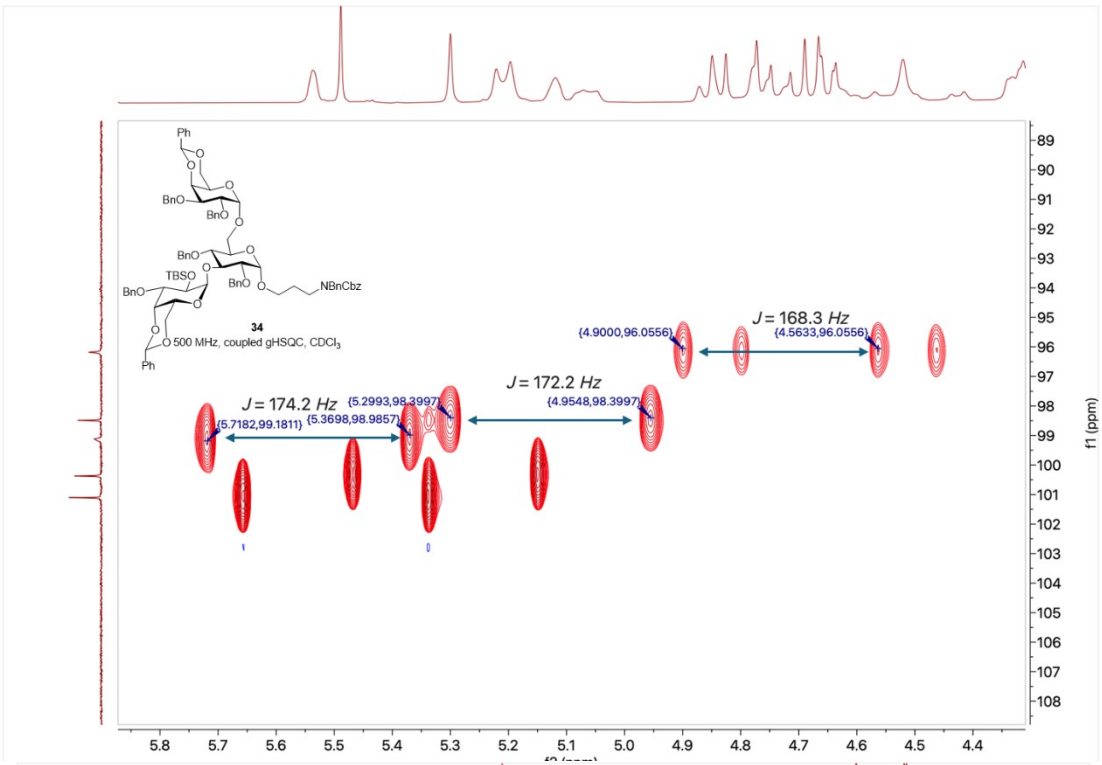

Ph
BnO
BnO
BnO
HO
BnO
BnO
N3
Ph
22
500 MHz, gHMBC, CDCl3
f1 (ppm)
f2 (ppm)

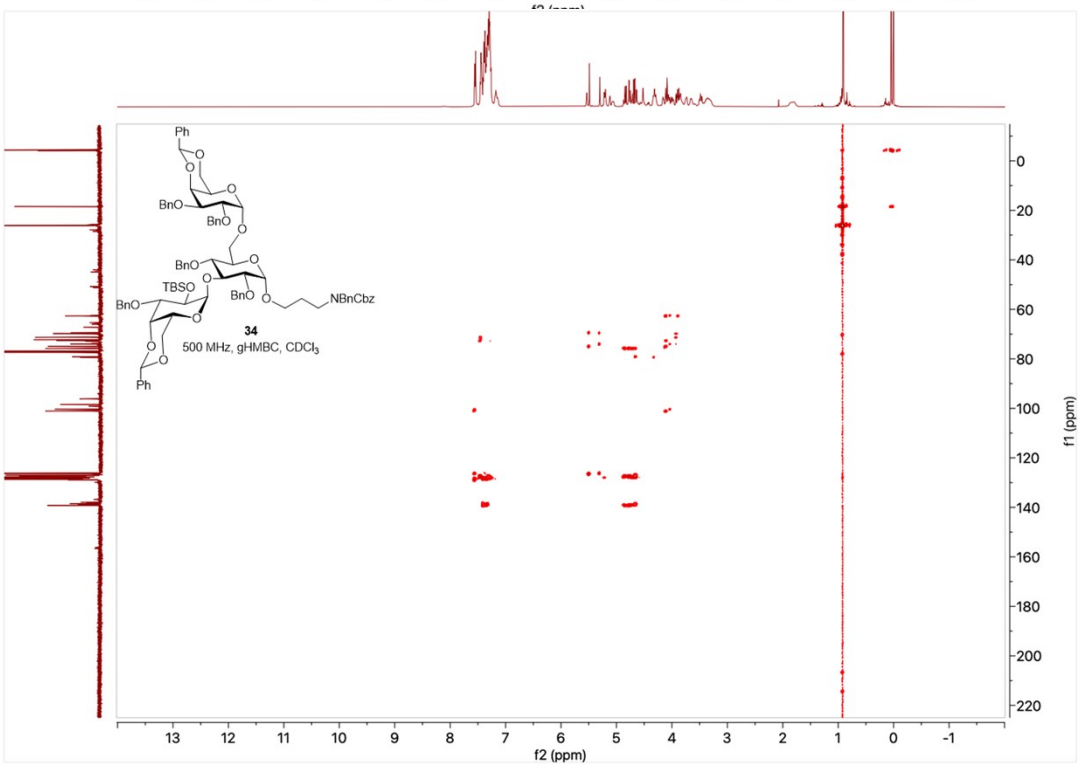

34
500 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

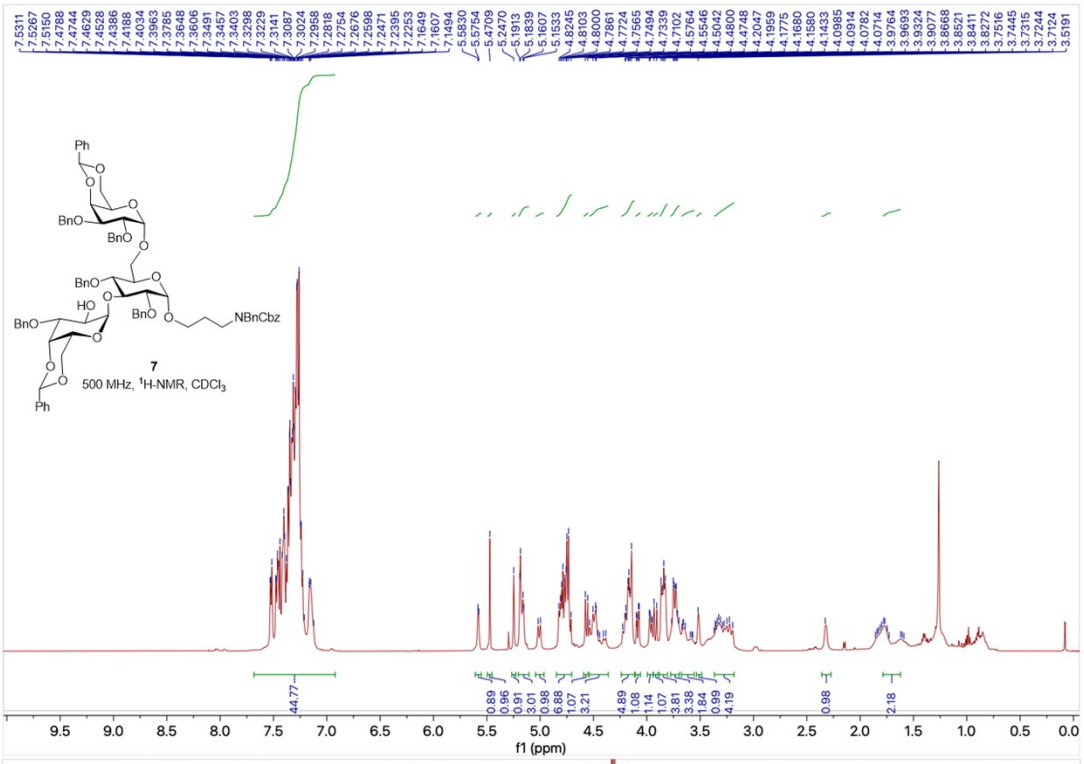

34
125 MHz, ^{13}C-NMR, $CDCl_3$
f1 (ppm)

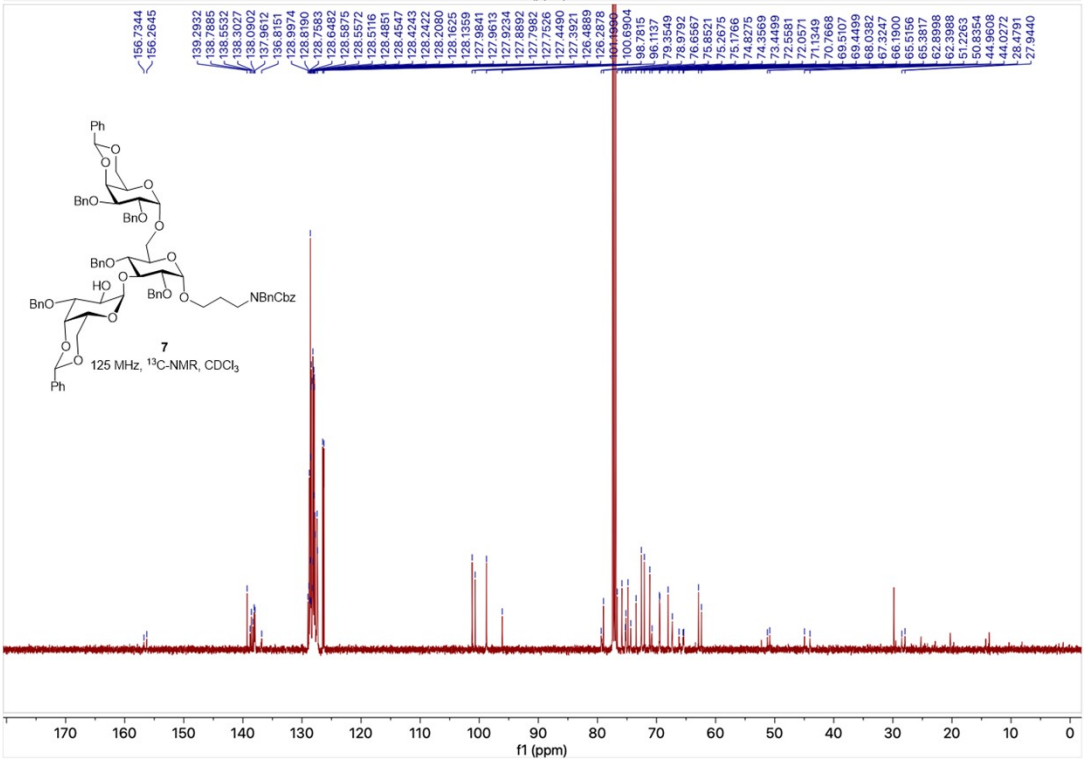

Ph
BnO
BnO
BnO
TBSO
BnO
BnO
NBnCbz
Ph
34
500 MHz, gCOSY, CDCl3
f2 (ppm)
f1 (ppm)

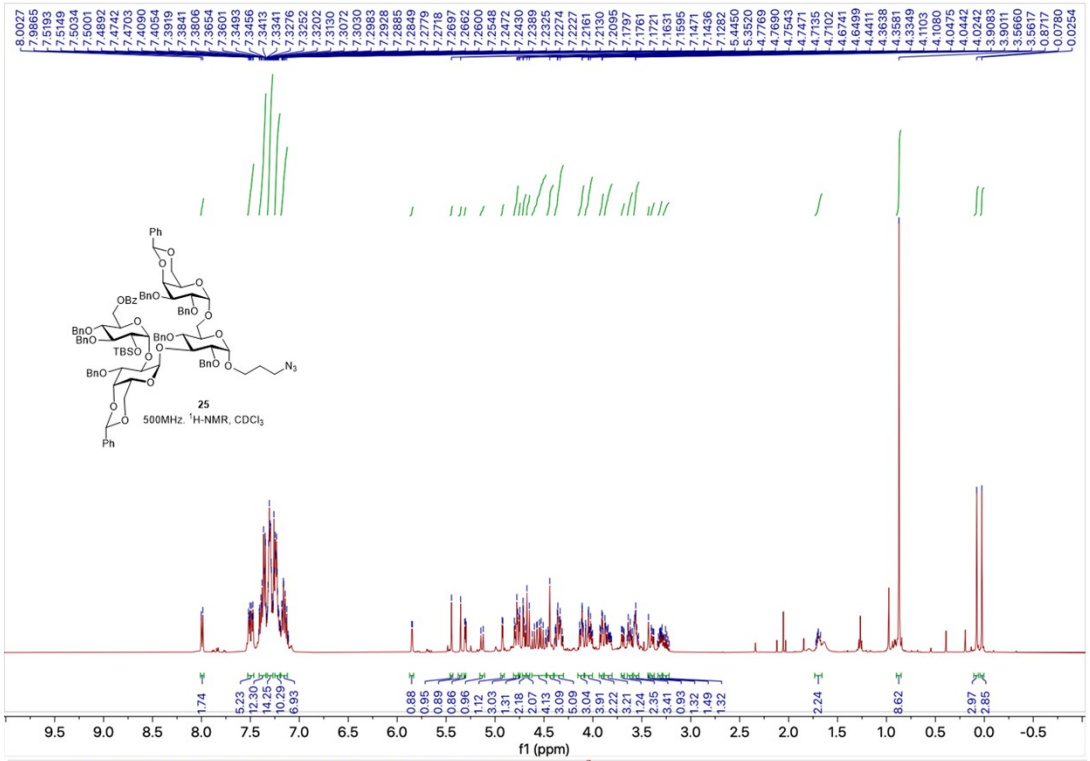

Ph
BnO
BnO
BnO
TBSO
BnO
BnO
NBnCbz
Ph
34
500 MHz, HSQC, CDCl3
f2 (ppm)
f1 (ppm)

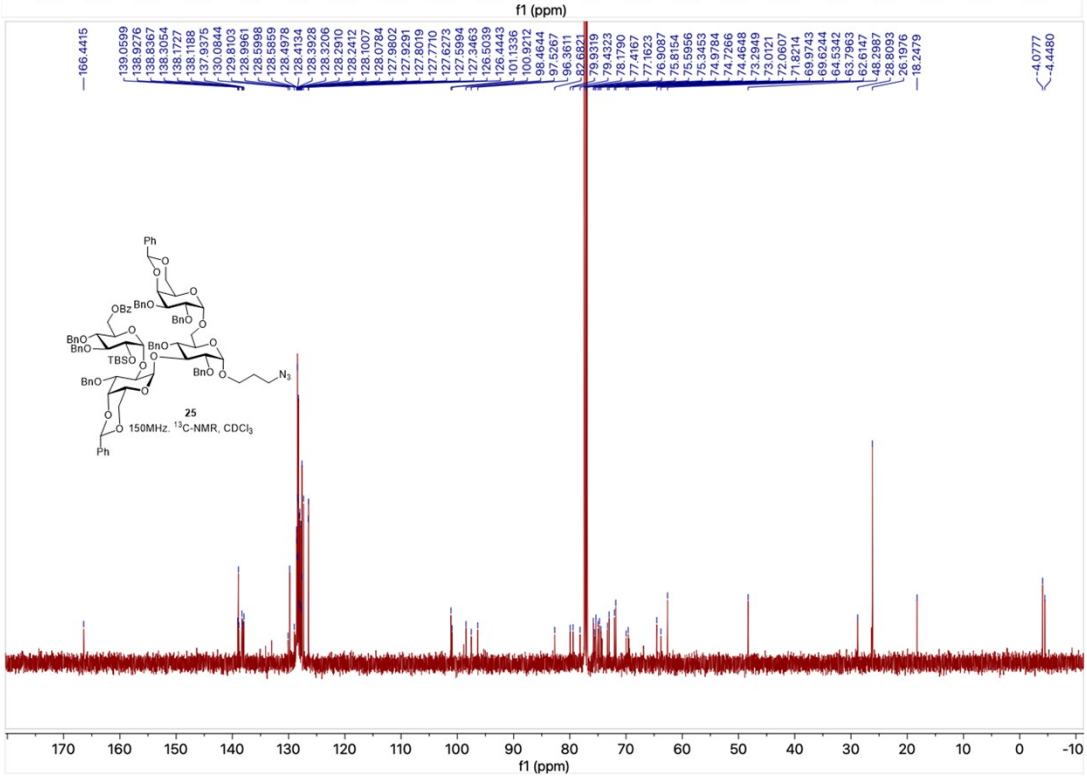

Ph
BnO
BnO
BnO
BnO
TBSO
BnO
BnO
NBnCbz
O
Ph
34
500 MHz, coupled gHSQC, CDCl3
J = 174.2 Hz
{5.7182,99.1811}
{5.3698,98.9857}
{5.2993,98.3997}
J = 172.2 Hz
{4.9548,98.3997}
J = 168.3 Hz
{4.9000,96.0556}
{4.5633,96.0556}
f1 (ppm)
f2 (ppm)

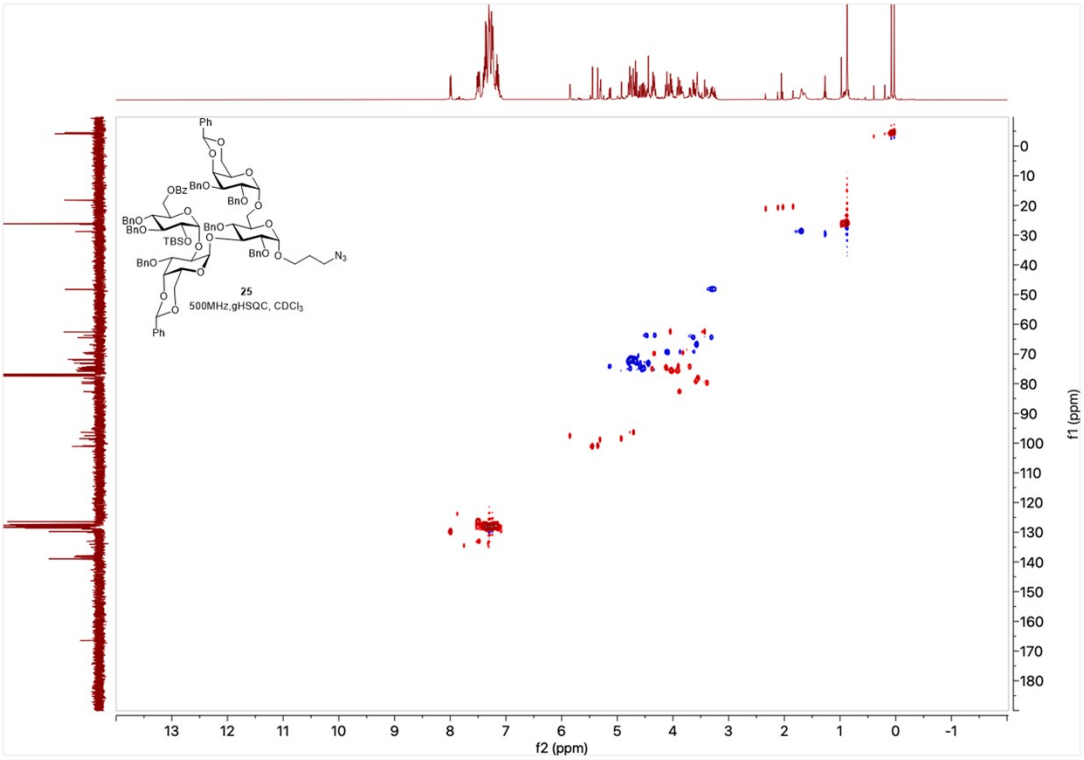

Ph
BnO
BnO
BnO
BnO
TBSO
BnO
BnO
NBnCbz
O
Ph
34
500 MHz, gHMBC, CDCl3
f1 (ppm)
f2 (ppm)

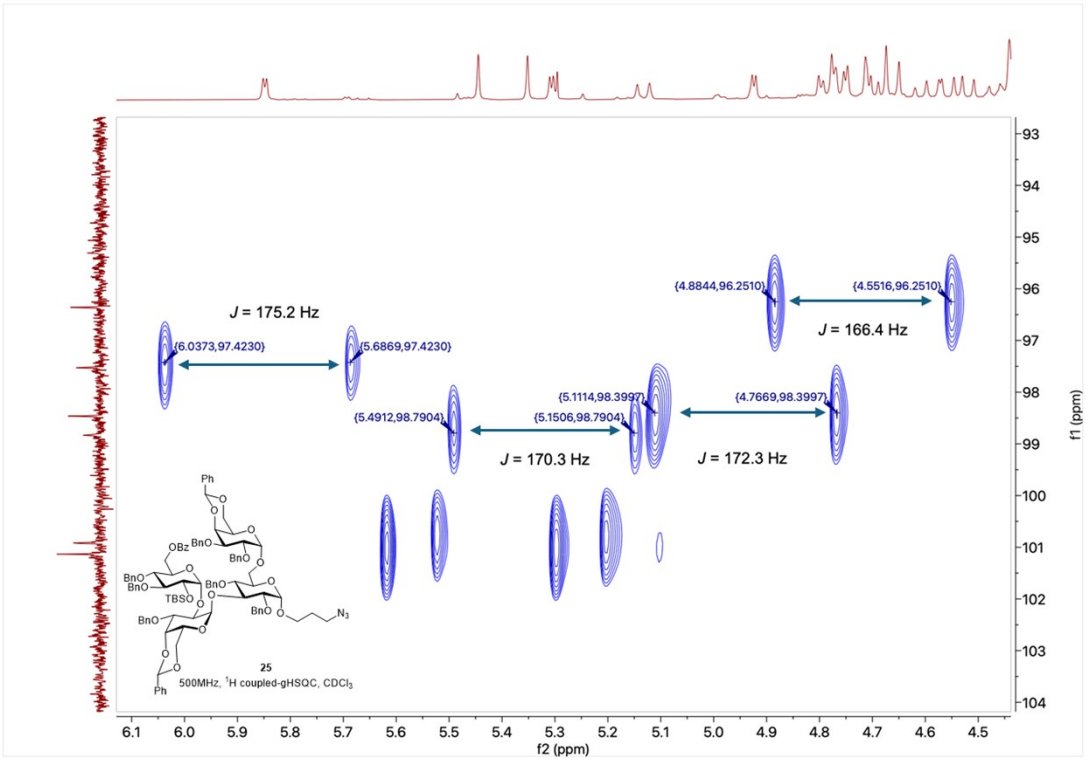

7
500 MHz, ^{1}H-NMR, CDCl$_3$
NBnCbz
f1 (ppm)

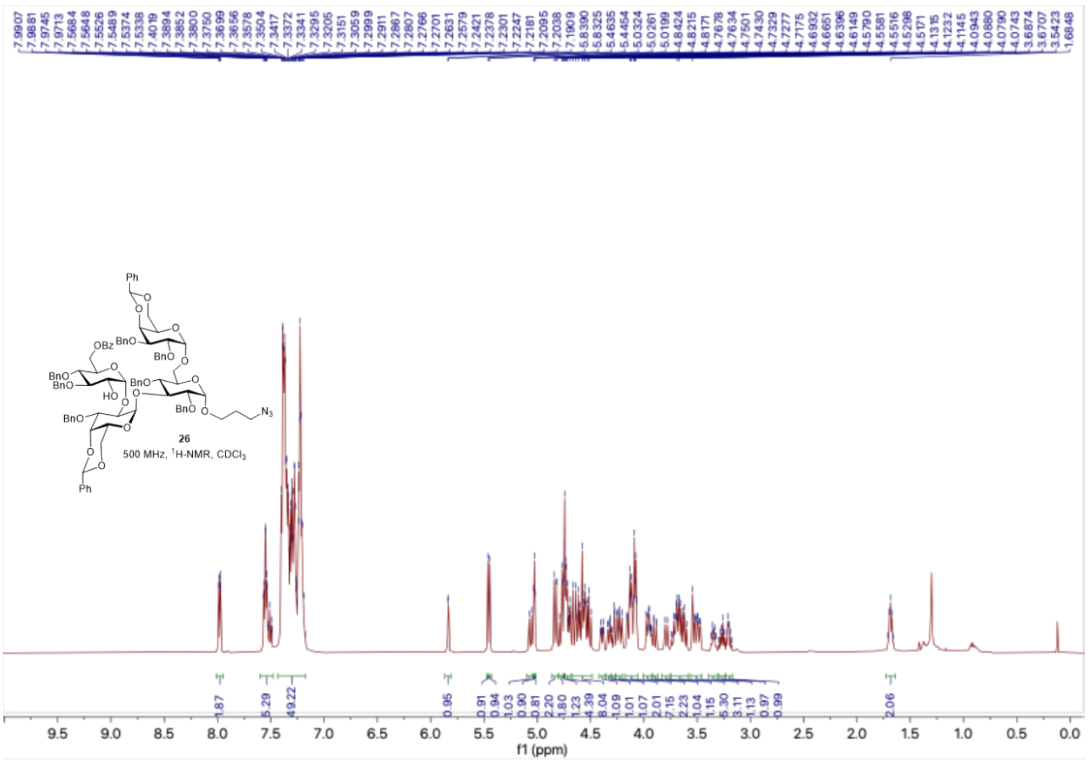

7
125 MHz, ^{13}C-NMR, CDCl$_3$
NBnCbz
f1 (ppm)

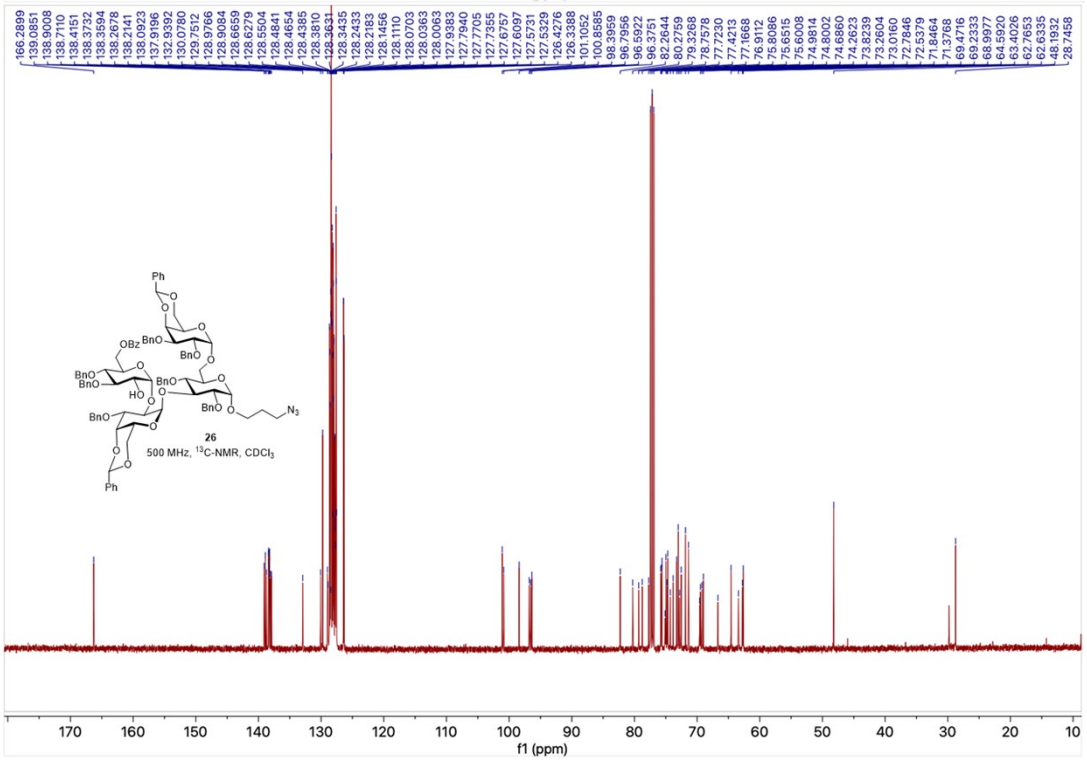

25
500MHz. ^{1}H-NMR, $CDCl_3$
f1 (ppm)

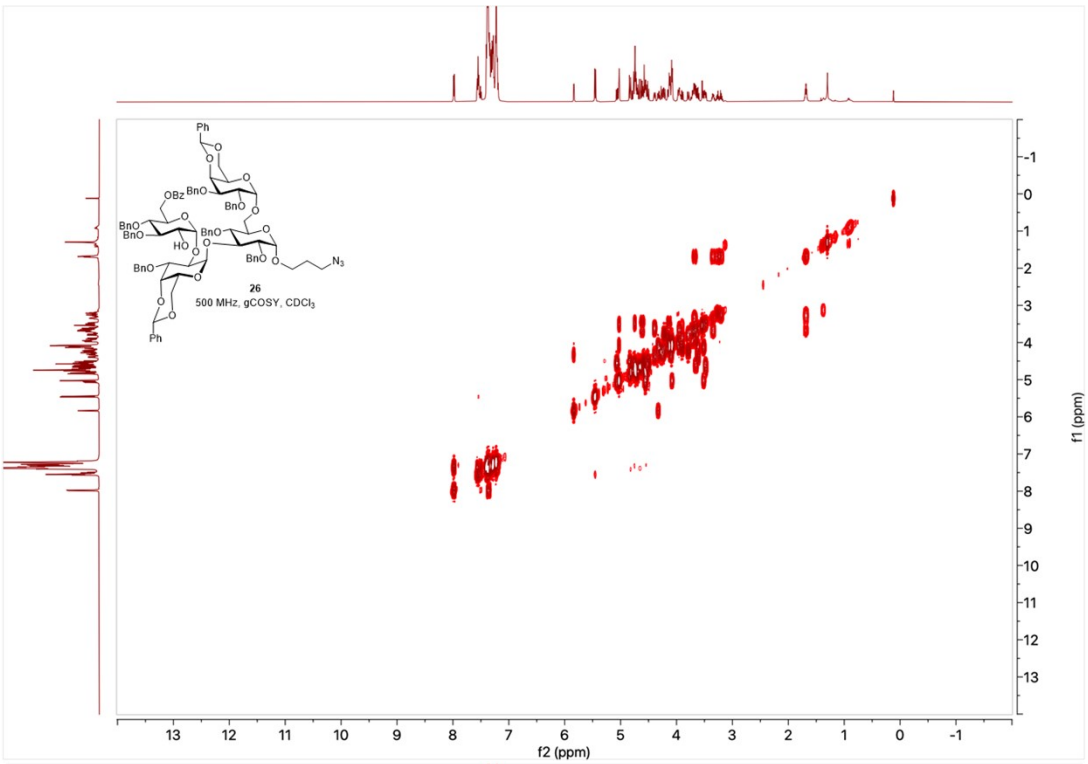

25
150MHz. ^{13}C-NMR, $CDCl_3$
f1 (ppm)

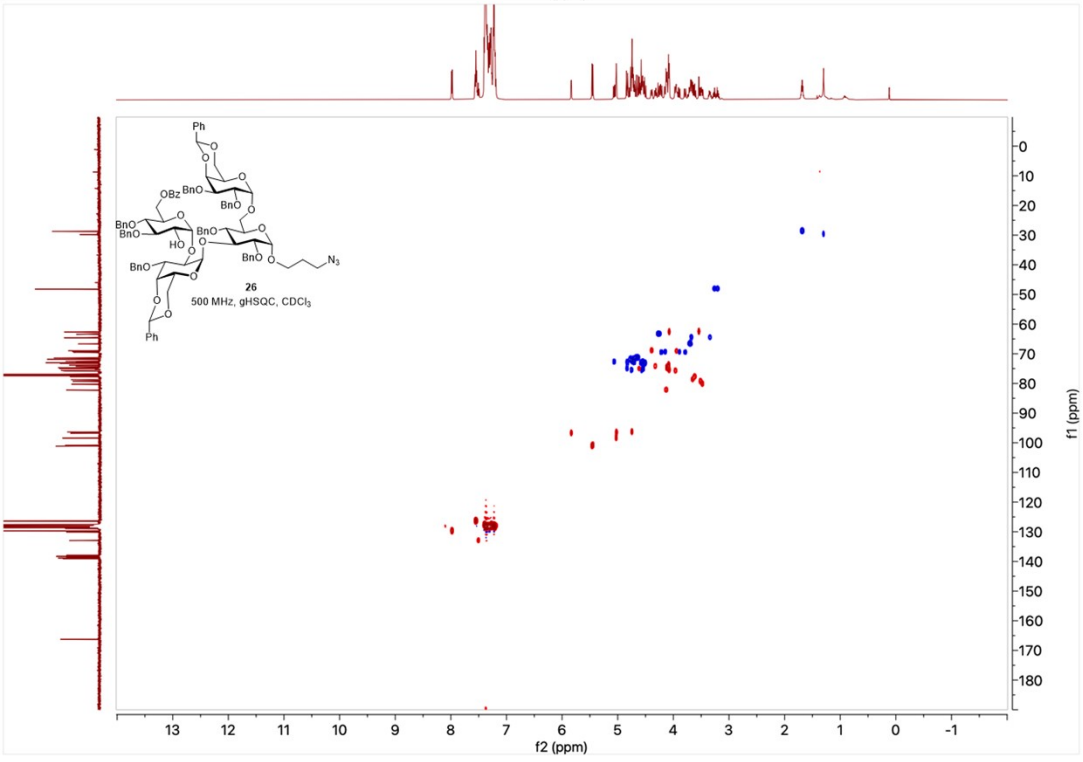

25
500MHz,gHSQC, CDCl3
f2 (ppm)
f1 (ppm)

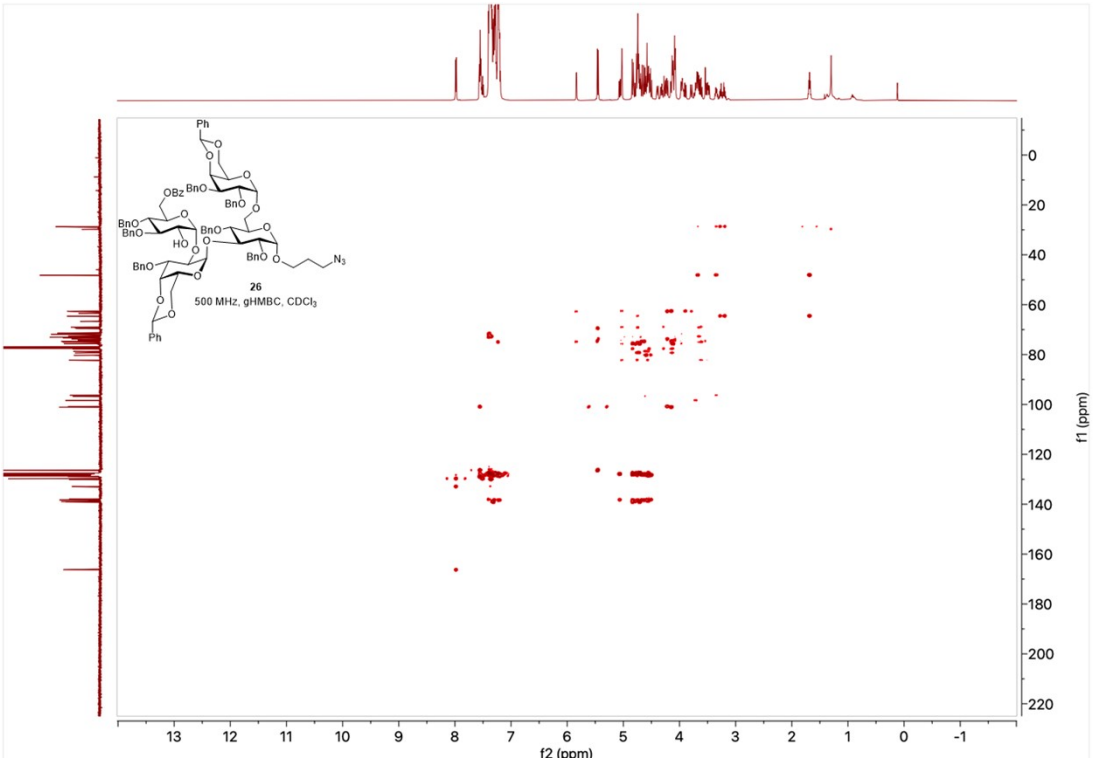

J = 175.2 Hz
{6.0373,97.4230}
{5.6869,97.4230}
{4.8844,96.2510}
{4.5516,96.2510}
J = 166.4 Hz
{5.4912,98.7904}
{5.1506,98.7904}
J = 170.3 Hz
{5.1114,98.3997}
{4.7669,98.3997}
J = 172.3 Hz
25
500MHz, 1H coupled-gHSQC, CDCl3
f2 (ppm)
f1 (ppm)

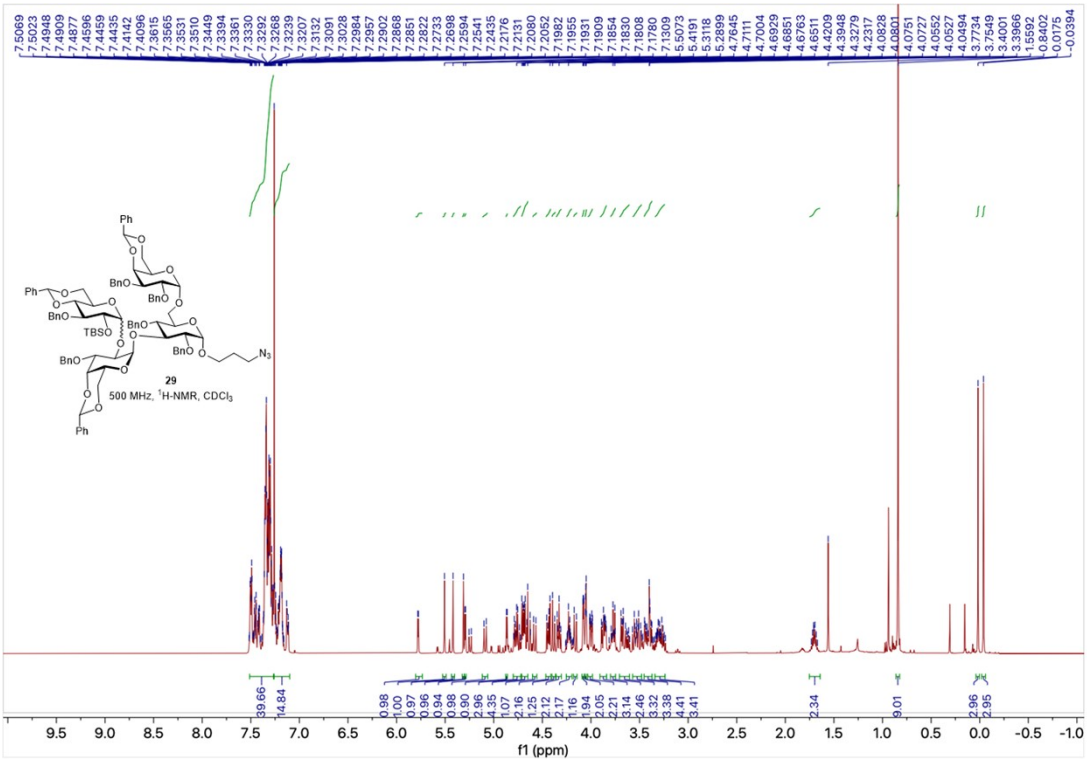

26
500 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

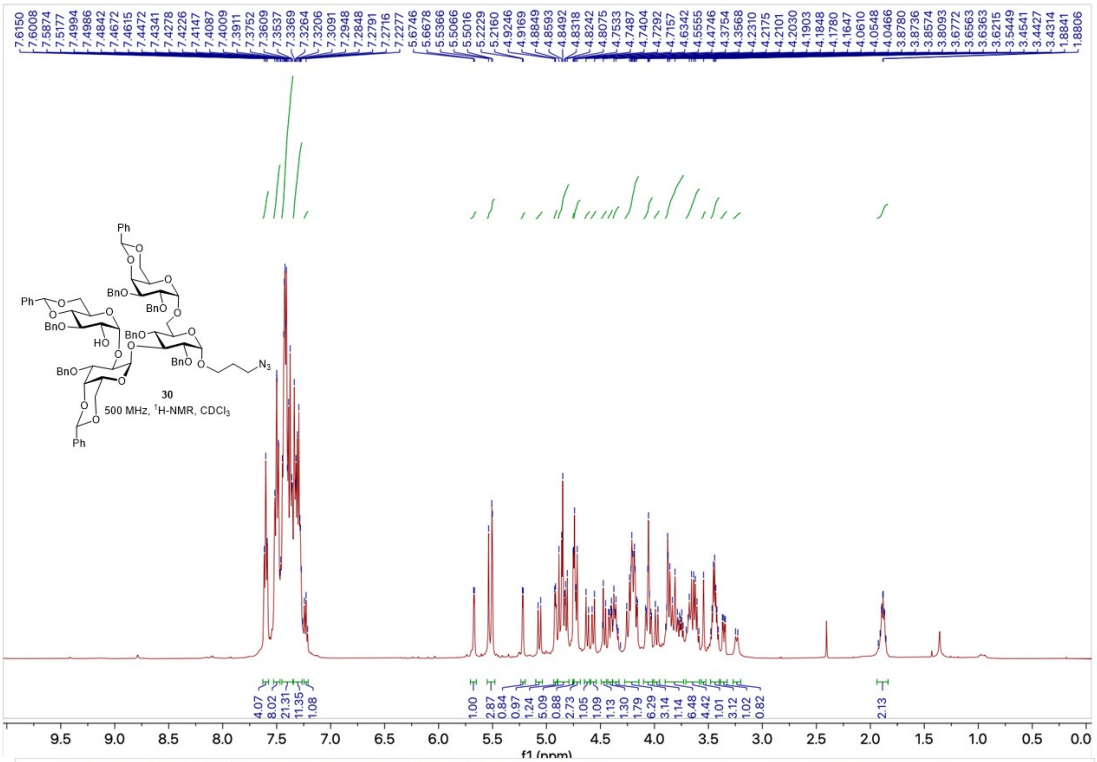

26
500 MHz, ^{13}C-NMR, $CDCl_3$
f1 (ppm)

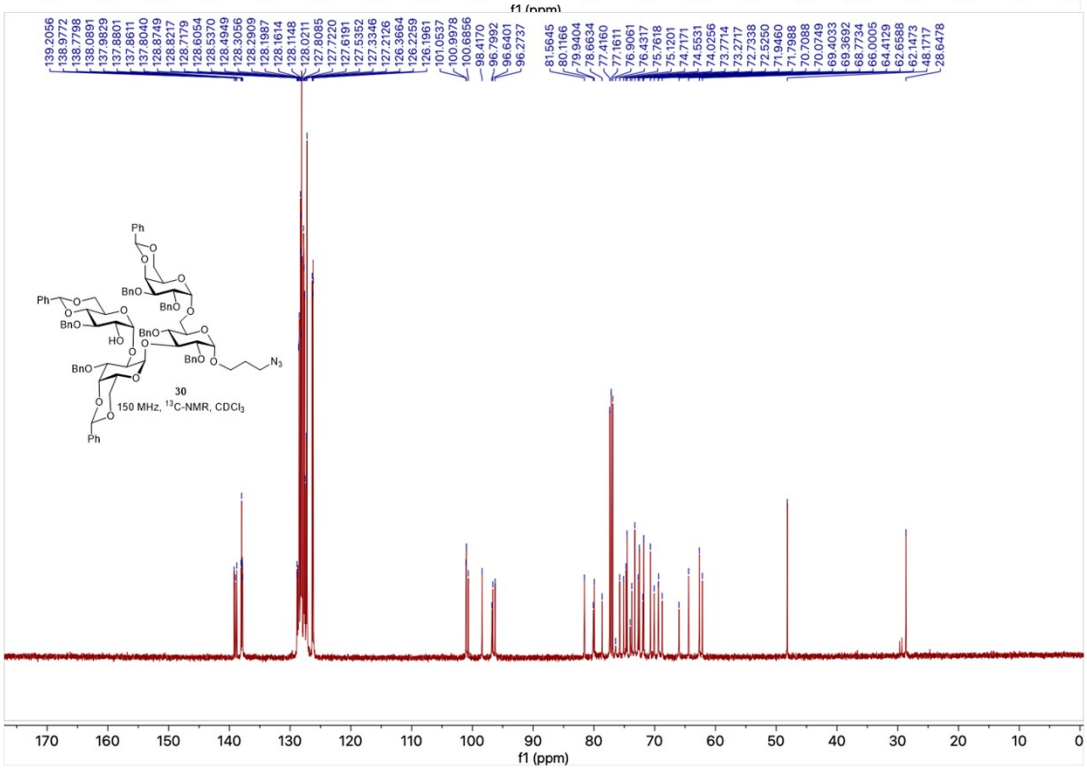

26
500 MHz, gCOSY, CDCl3
f2 (ppm)
f1 (ppm)

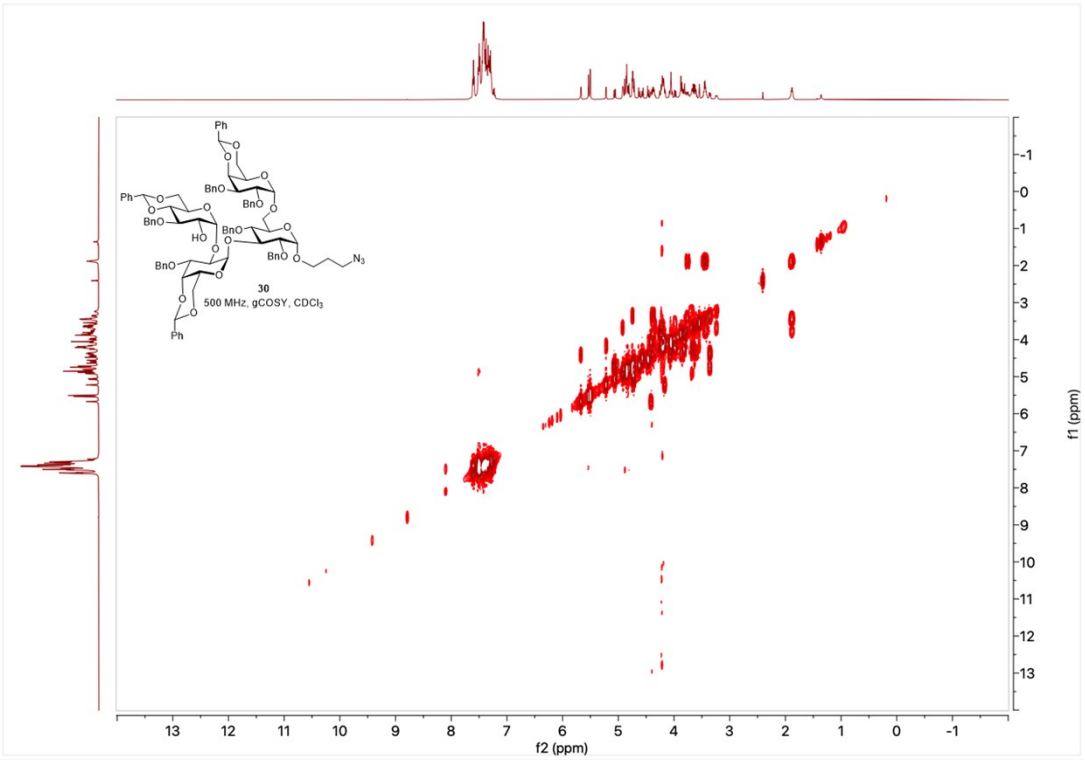

26
500 MHz, gHSQC, CDCl3
f2 (ppm)
f1 (ppm)

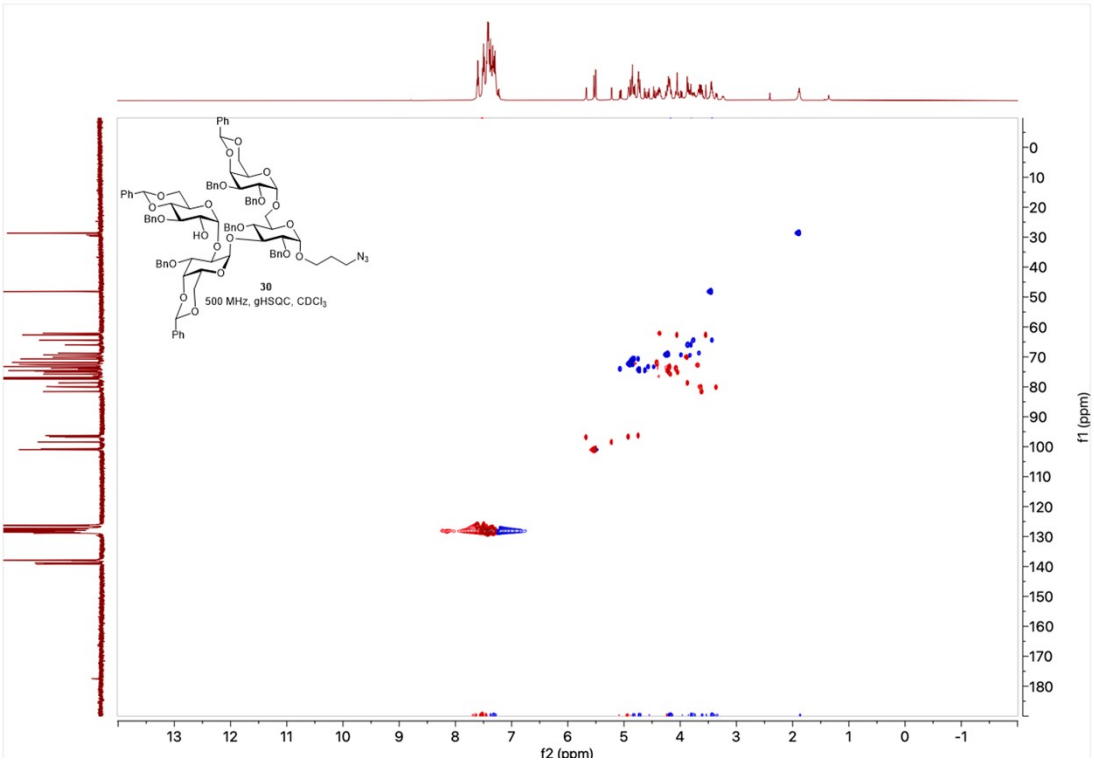

26
500 MHz, gHMBC, CDCl3
f2 (ppm)
f1 (ppm)

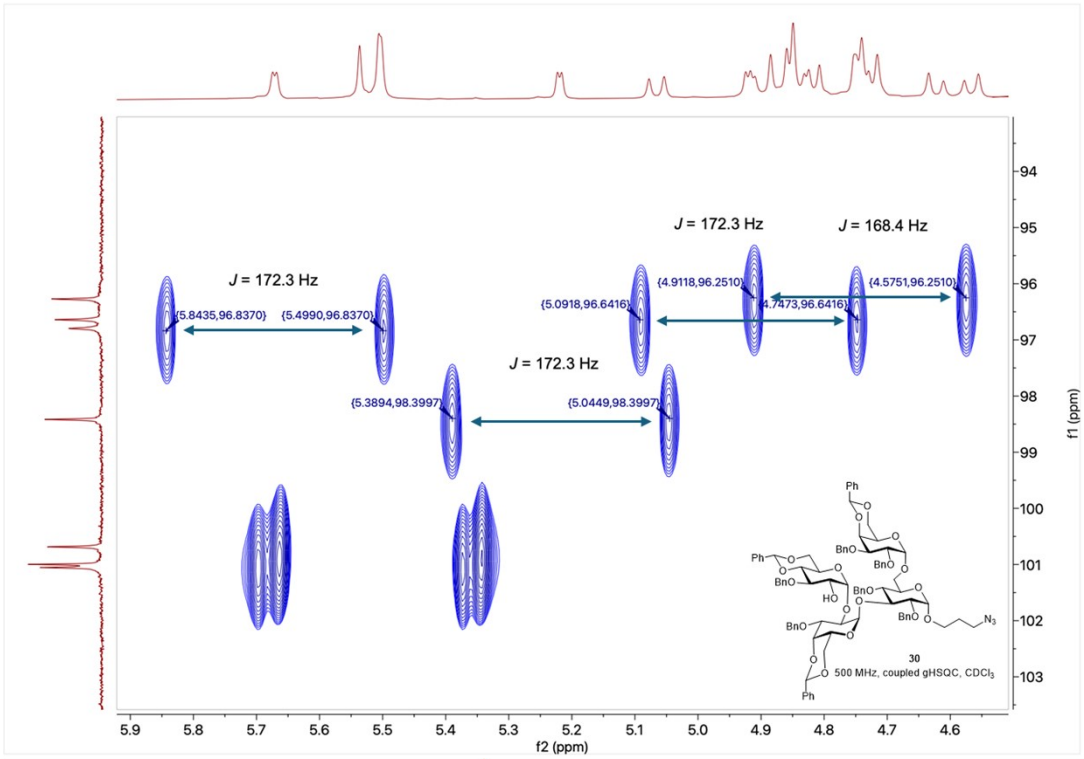

29
500 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

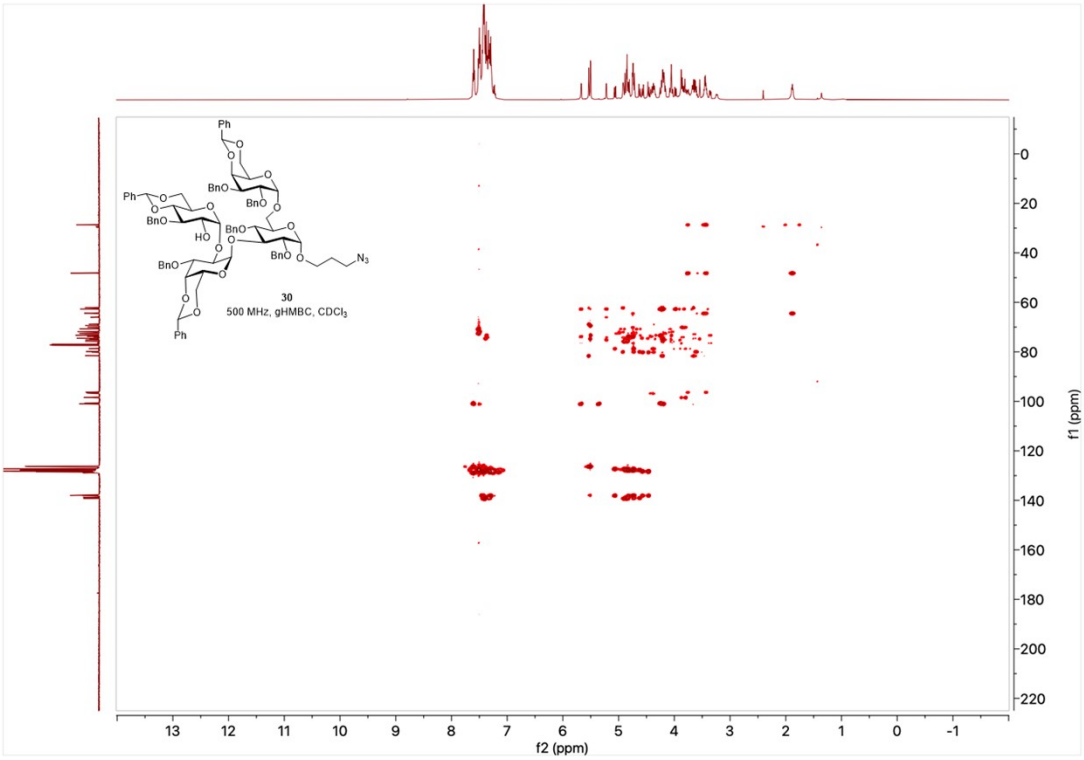

30
500 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

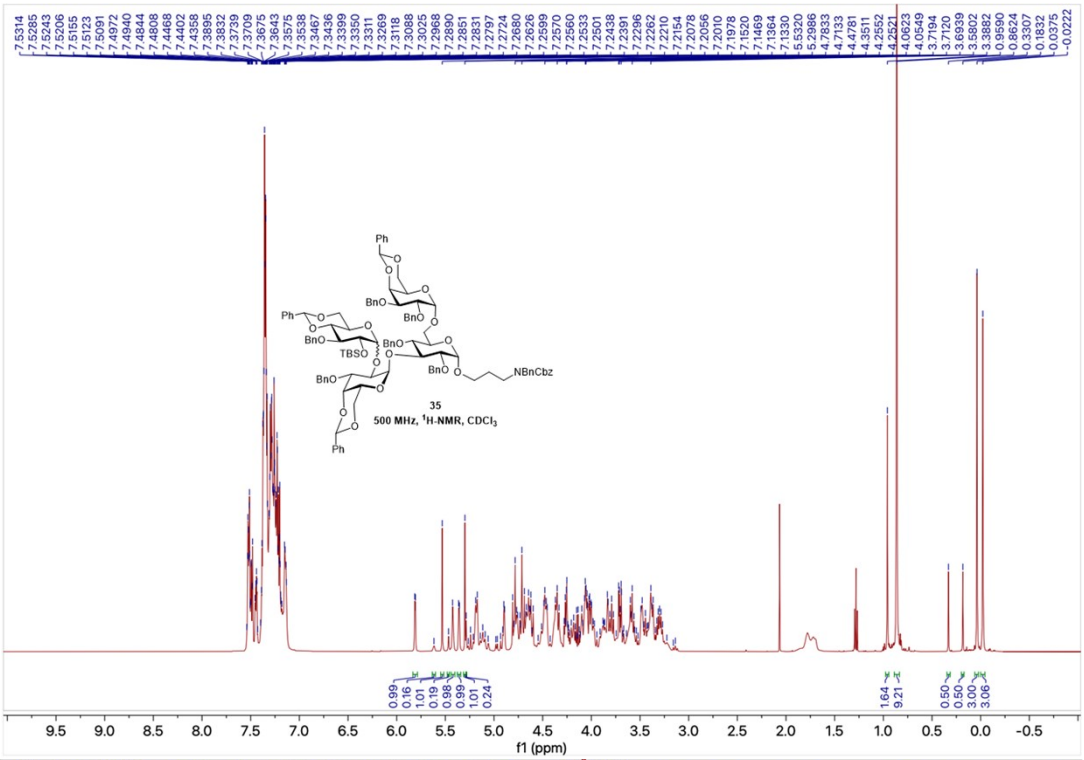

30
150 MHz, ^{13}C-NMR, $CDCl_3$
f1 (ppm)

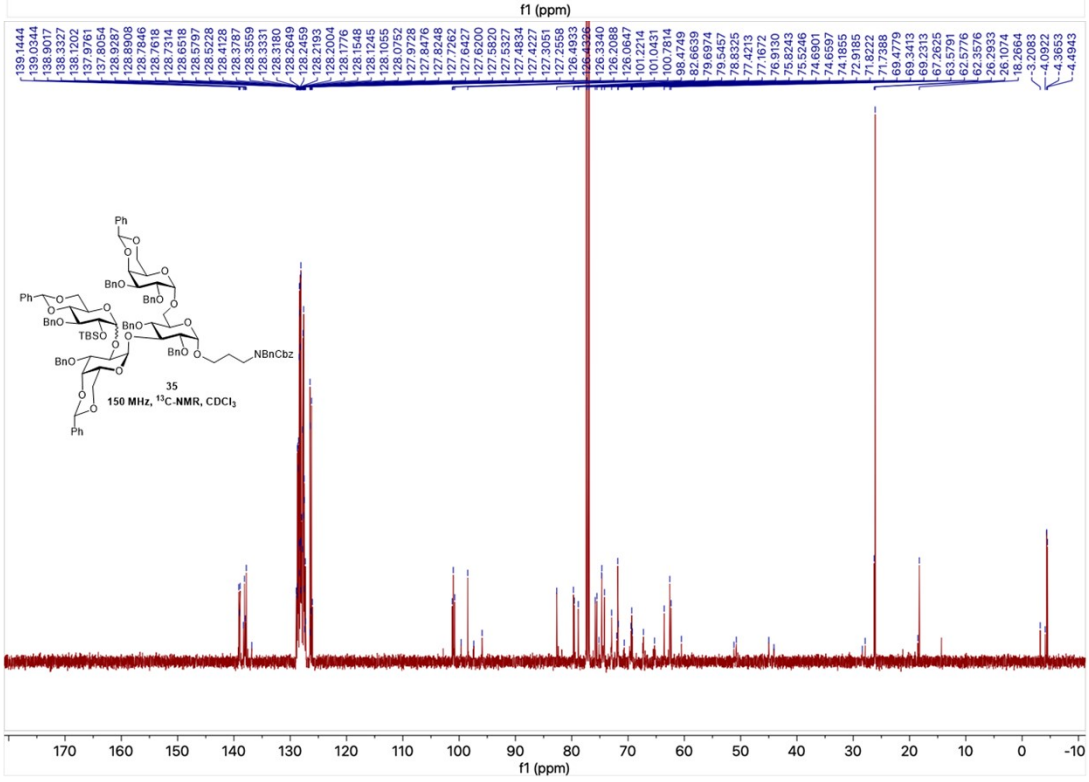

30
500 MHz, gCOSY, CDCl3
f2 (ppm)
f1 (ppm)

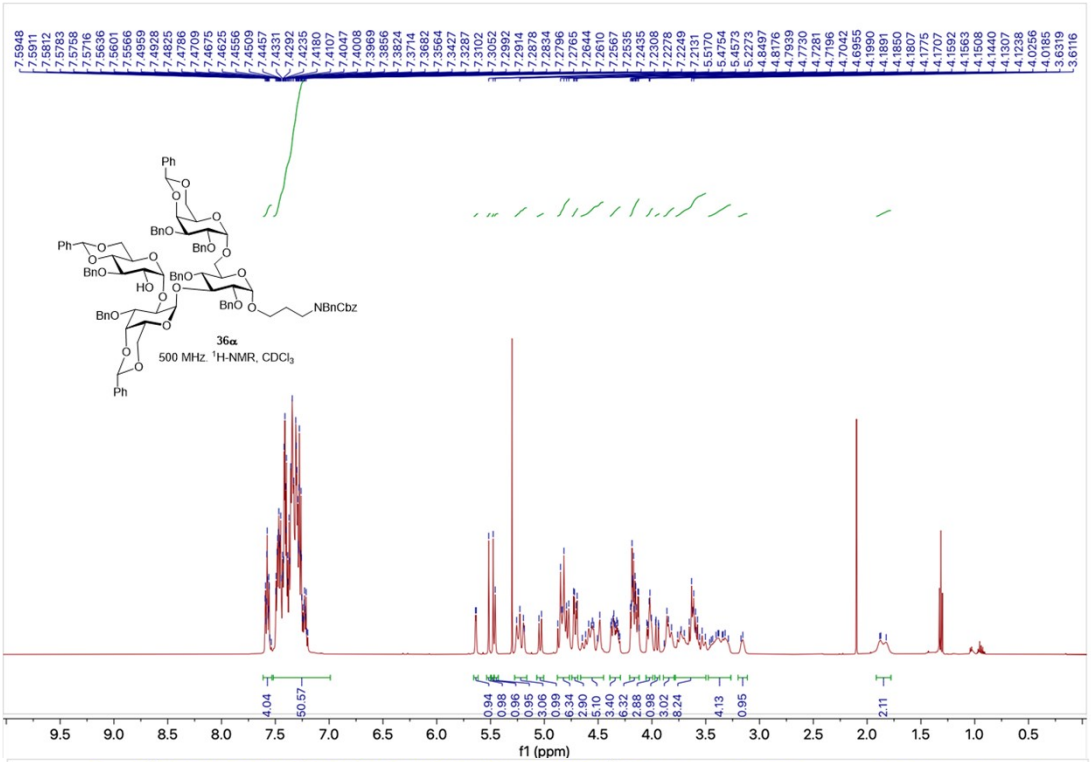

30
500 MHz, gHSQC, CDCl3
f2 (ppm)
f1 (ppm)

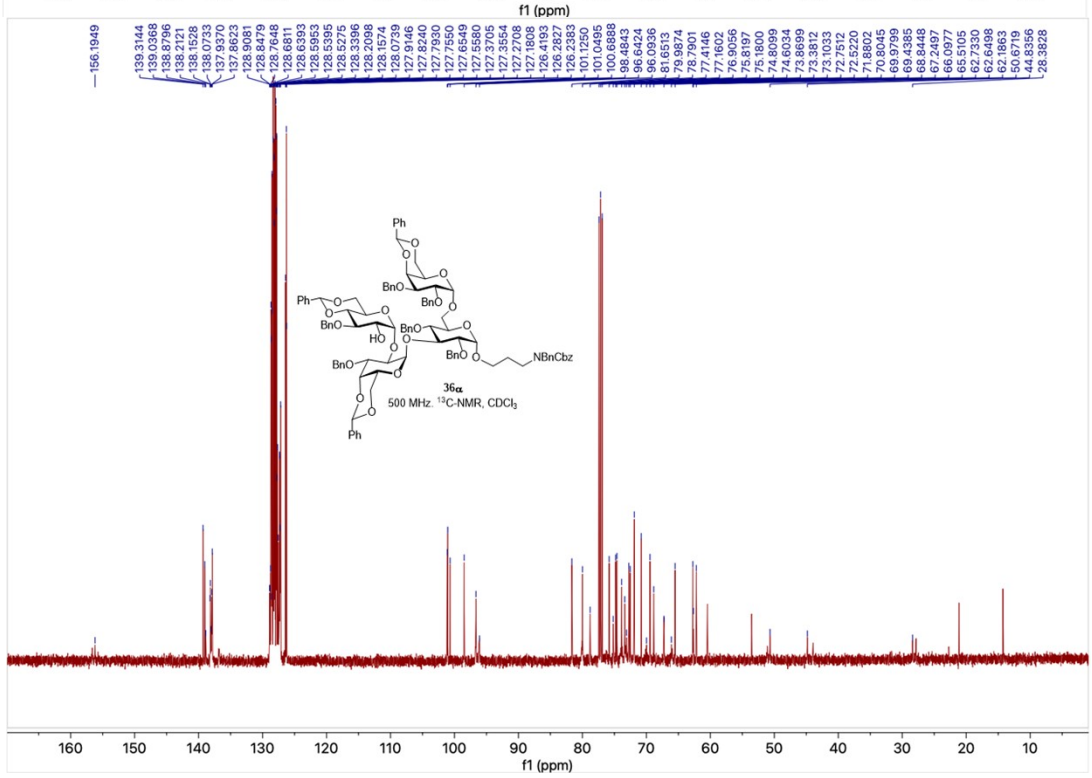

J = 172.3 Hz
{5.8435,96.8370}
{5.4990,96.8370}
J = 172.3 Hz
{5.3894,98.3997}
{5.0449,98.3997}
J = 172.3 Hz
J = 168.4 Hz
{5.0918,96.6416}
{4.9118,96.2510}
{4.7473,96.6416}
{4.5751,96.2510}
30
500 MHz, coupled gHSQC, CDCl3
f2 (ppm)
f1 (ppm)

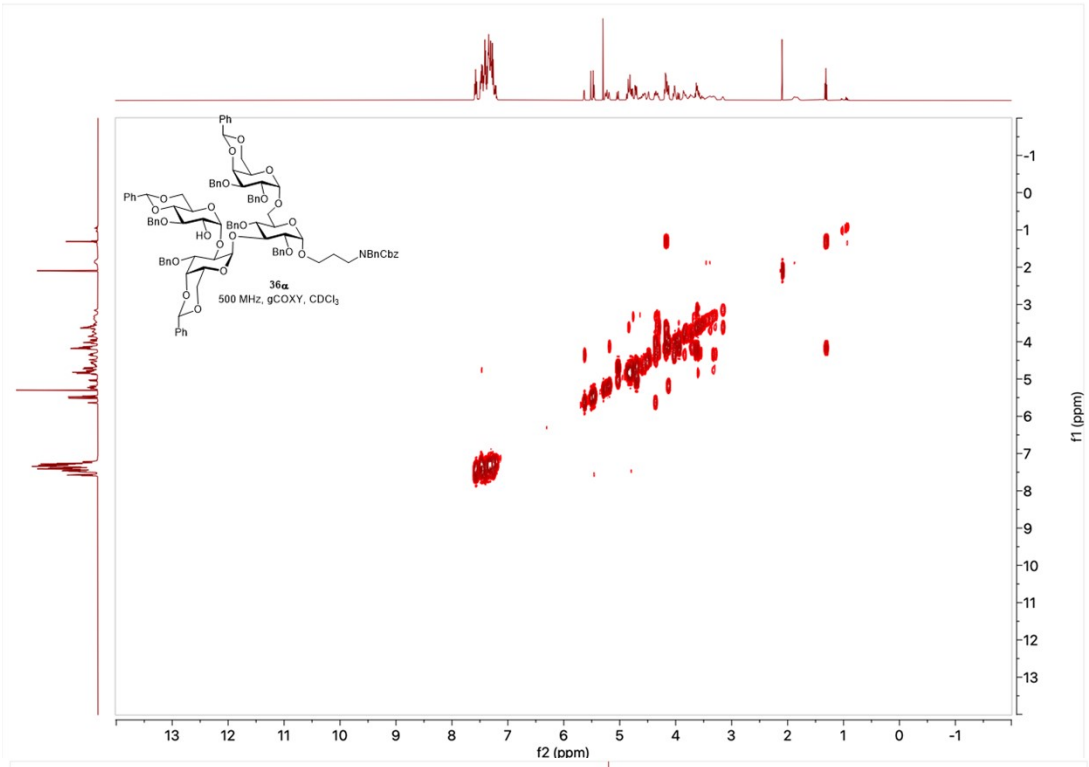

30
500 MHz, gHMBC, CDCl3
f2 (ppm)
f1 (ppm)

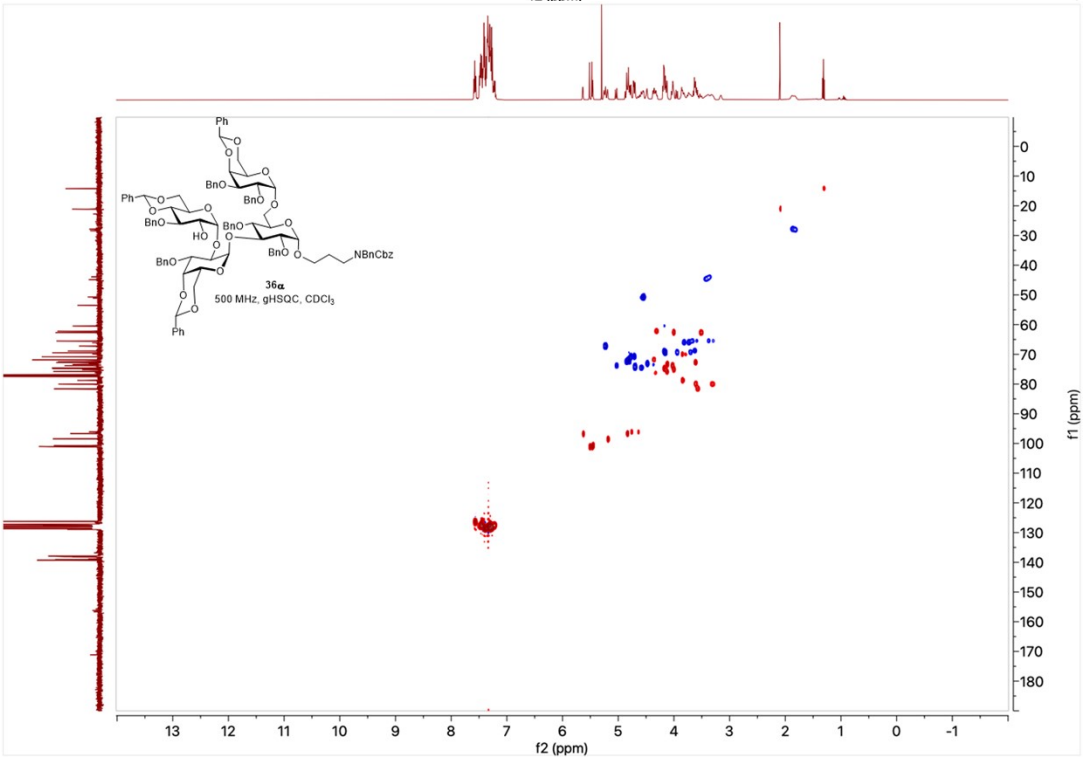

35
500 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

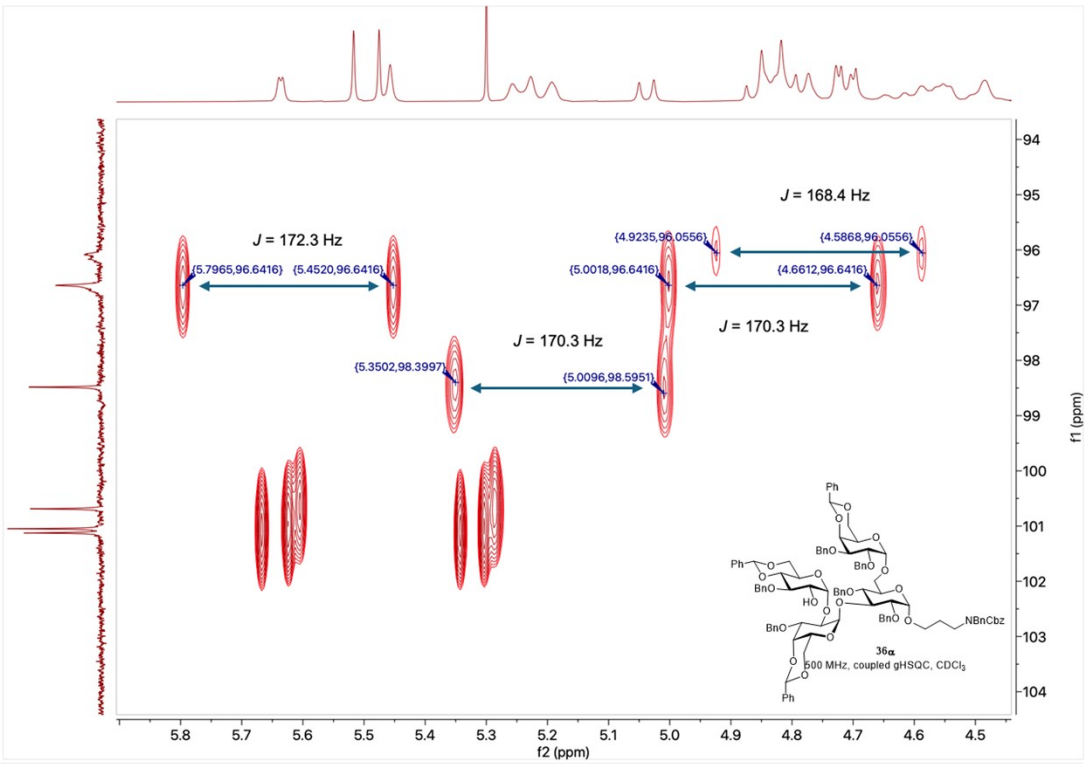

35
150 MHz, ^{13}C-NMR, $CDCl_3$
f1 (ppm)

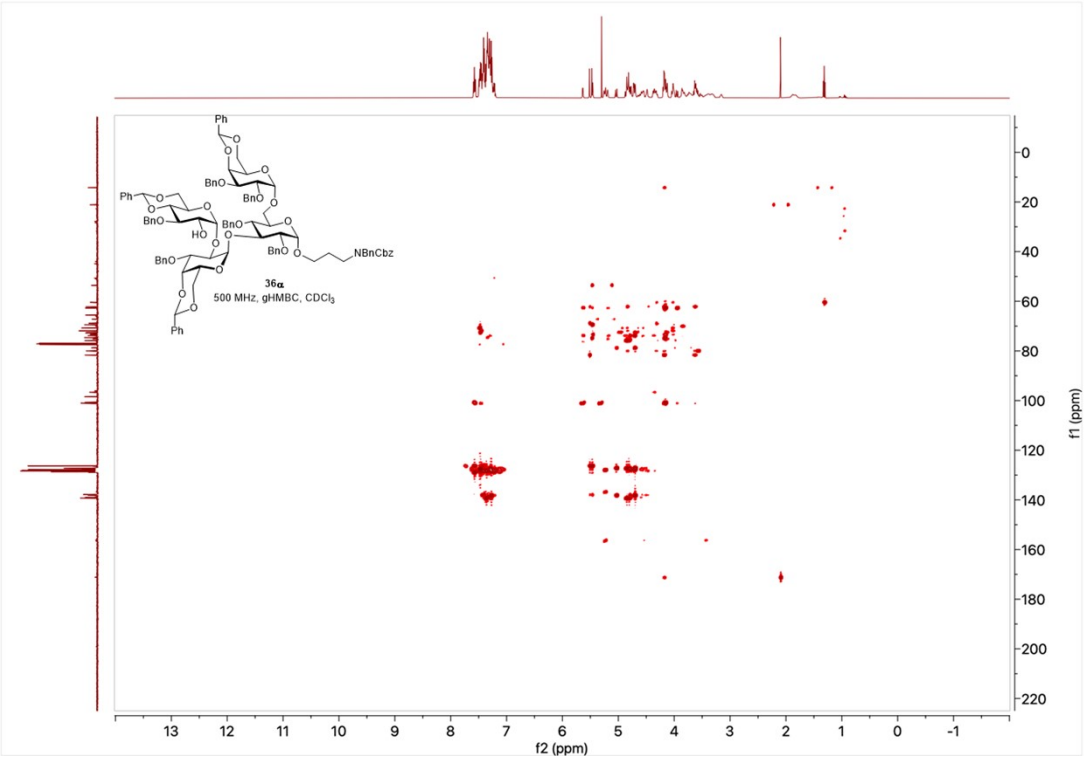

36α
500 MHz. ^{1}H-NMR, $CDCl_3$
f1 (ppm)

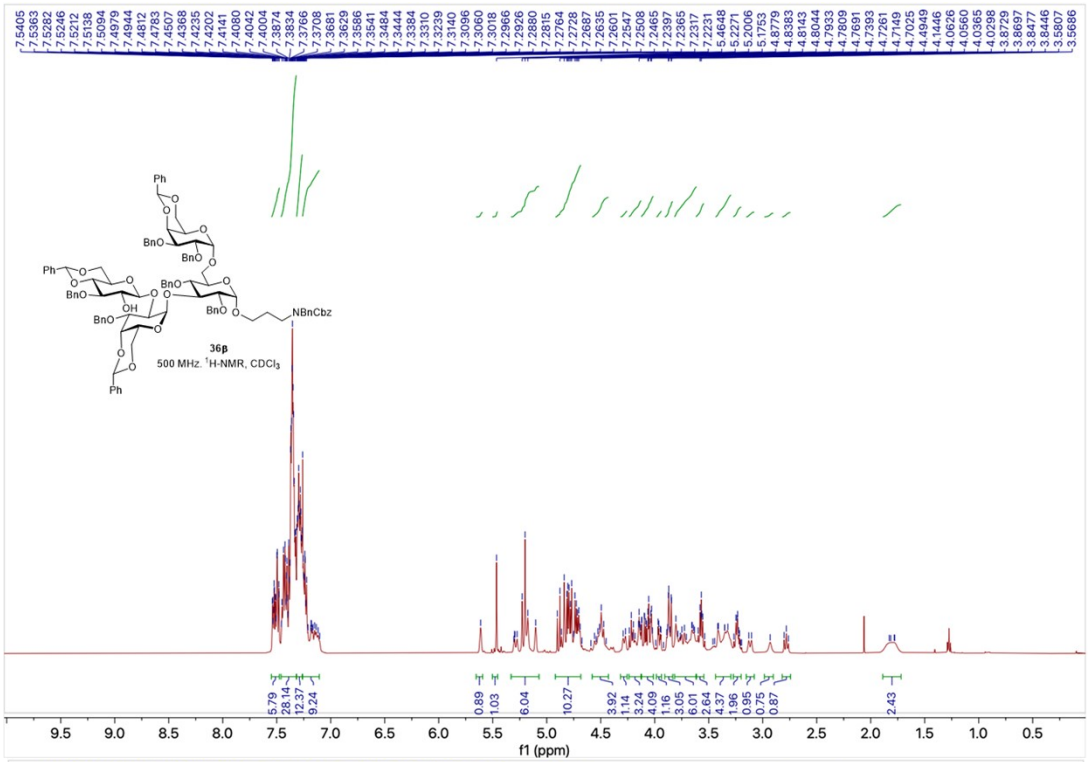

36α
500 MHz. ^{13}C-NMR, $CDCl_3$
f1 (ppm)

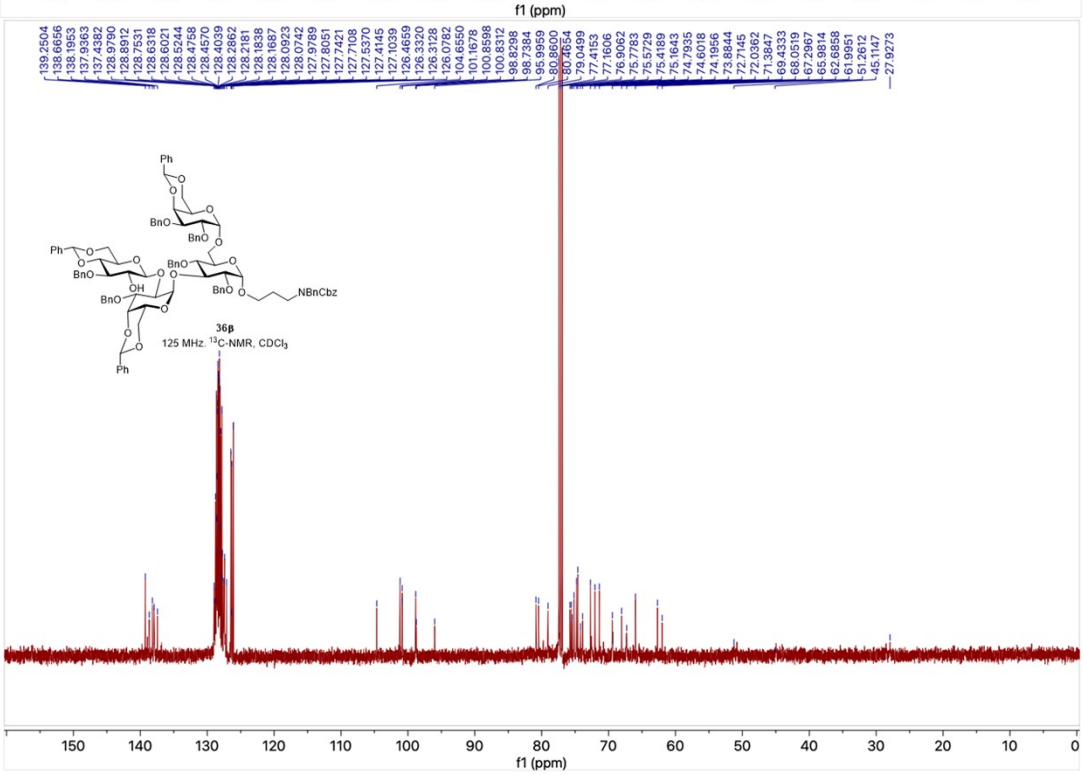

Ph
BnO
BnO
Ph
BnO
BnO
HO
BnO
BnO
NBnCbz
BnO
Ph
36α
500 MHz, gCOXY, CDCl3
f2 (ppm)
f1 (ppm)

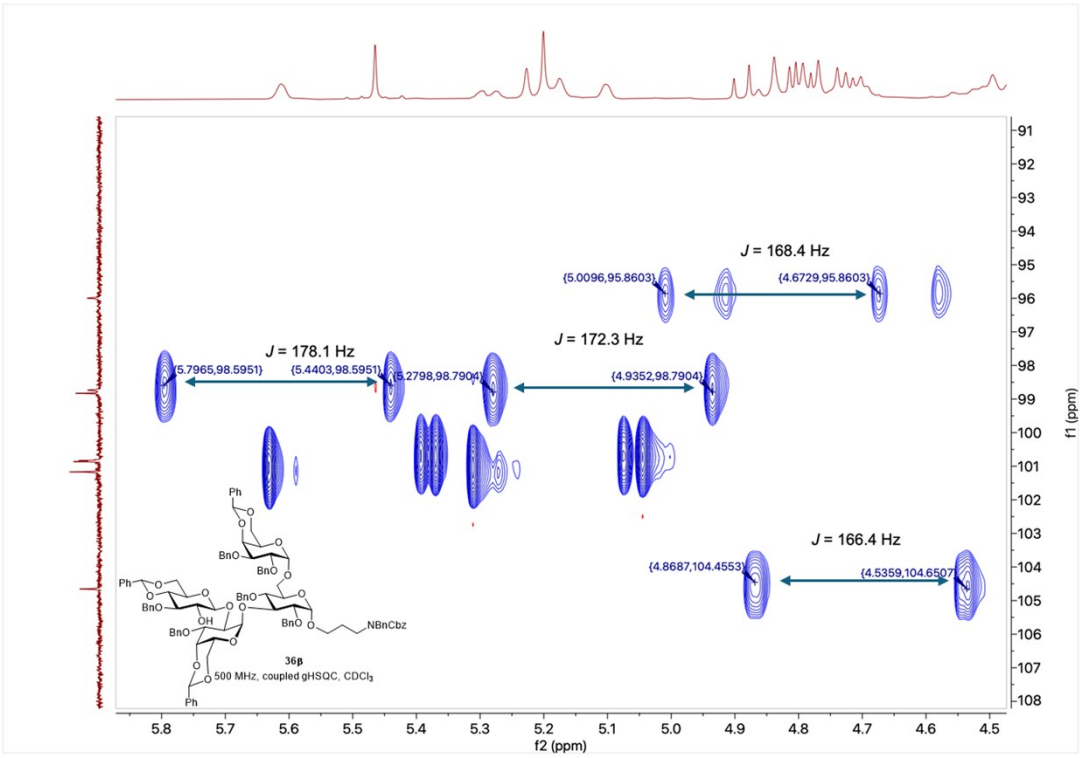

Ph
BnO
BnO
Ph
BnO
BnO
HO
BnO
BnO
NBnCbz
BnO
Ph
36α
500 MHz, gHSQC, CDCl3
f2 (ppm)
f1 (ppm)

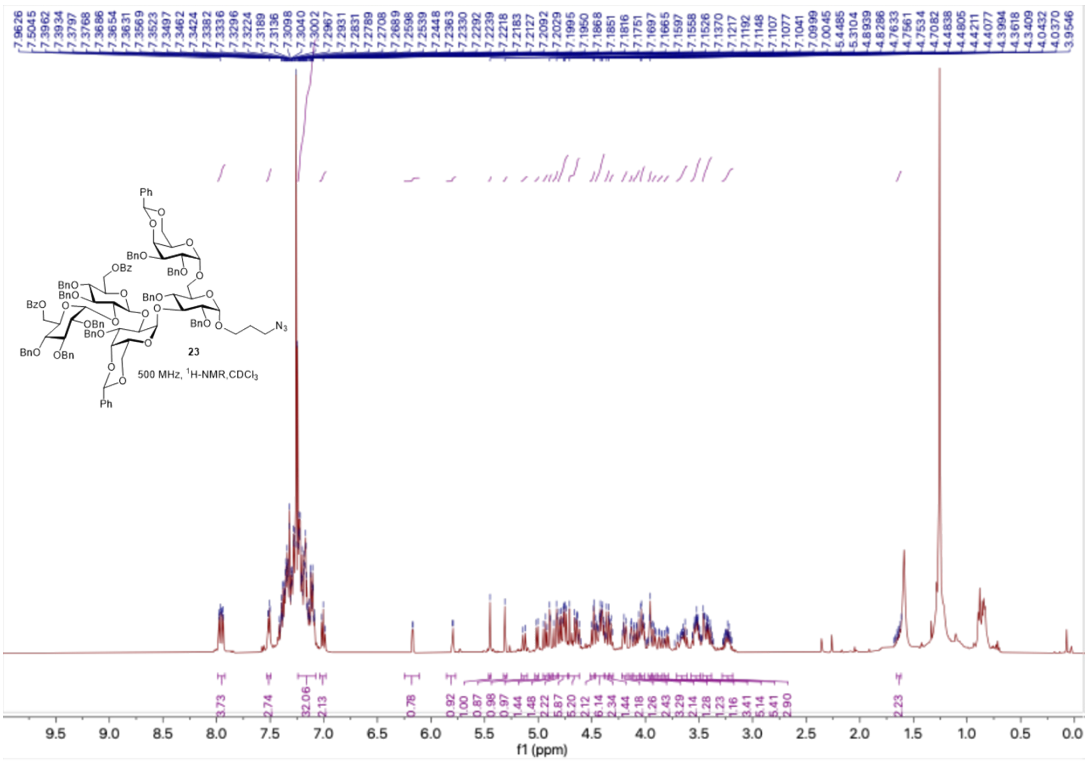

J = 172.3 Hz
{5.7965,96.6416}
{5.4520,96.6416}
J = 170.3 Hz
{5.3502,98.3997}
{5.0096,98.5951}
J = 168.4 Hz
{4.9235,96.0556}
{4.5868,96.0556}
{5.0018,96.6416}
{4.6612,96.6416}
J = 170.3 Hz
36α
500 MHz, coupled gHSQC, CDCl3
f2 (ppm)
f1 (ppm)

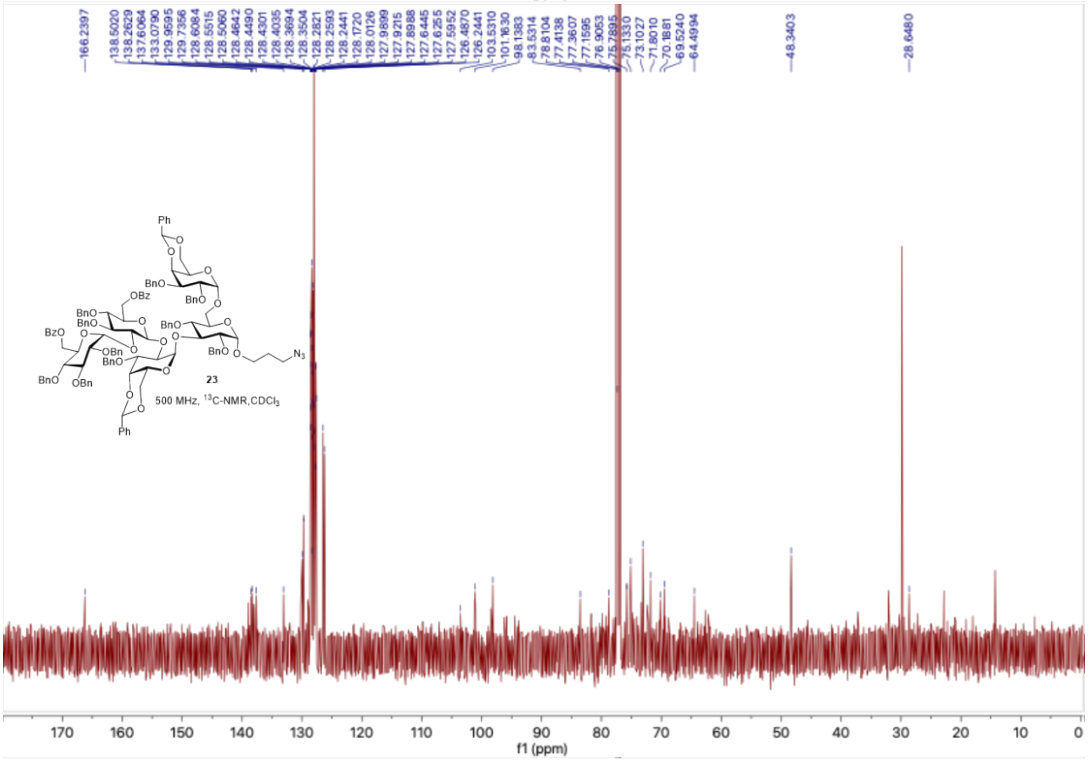

36α
500 MHz, gHMBC, CDCl3
f2 (ppm)
f1 (ppm)

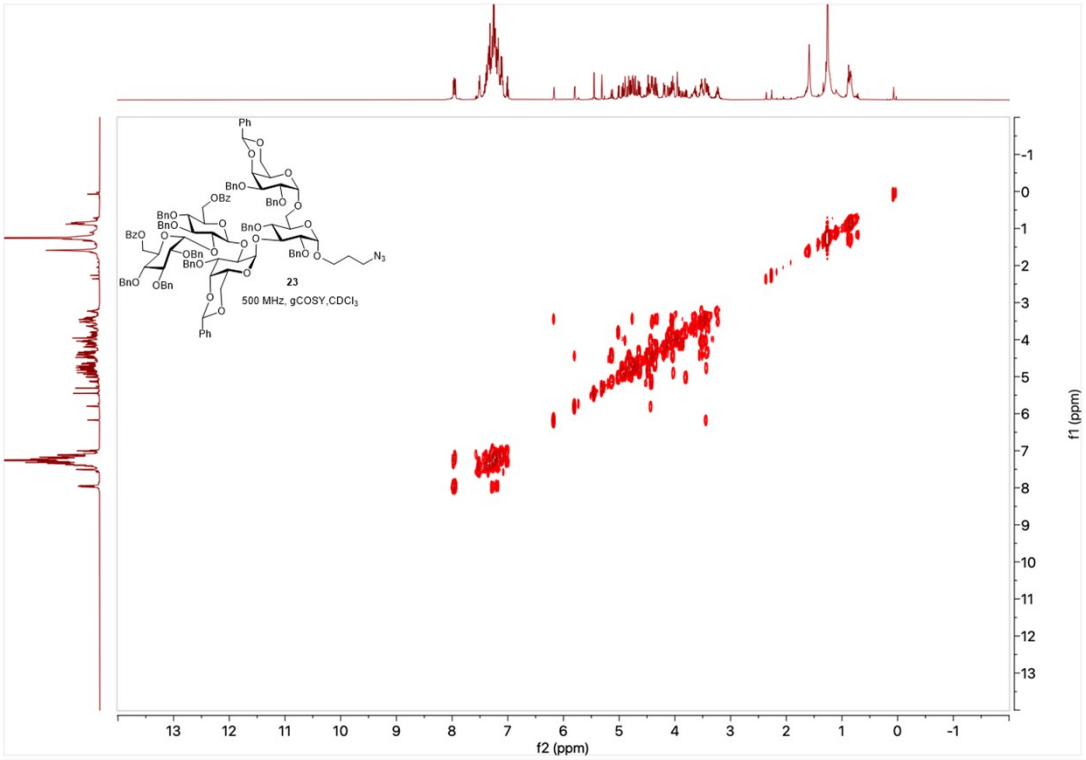

36β
500 MHz. ^{1}H-NMR, CDCl$_3$
NBnCbz
f1 (ppm)

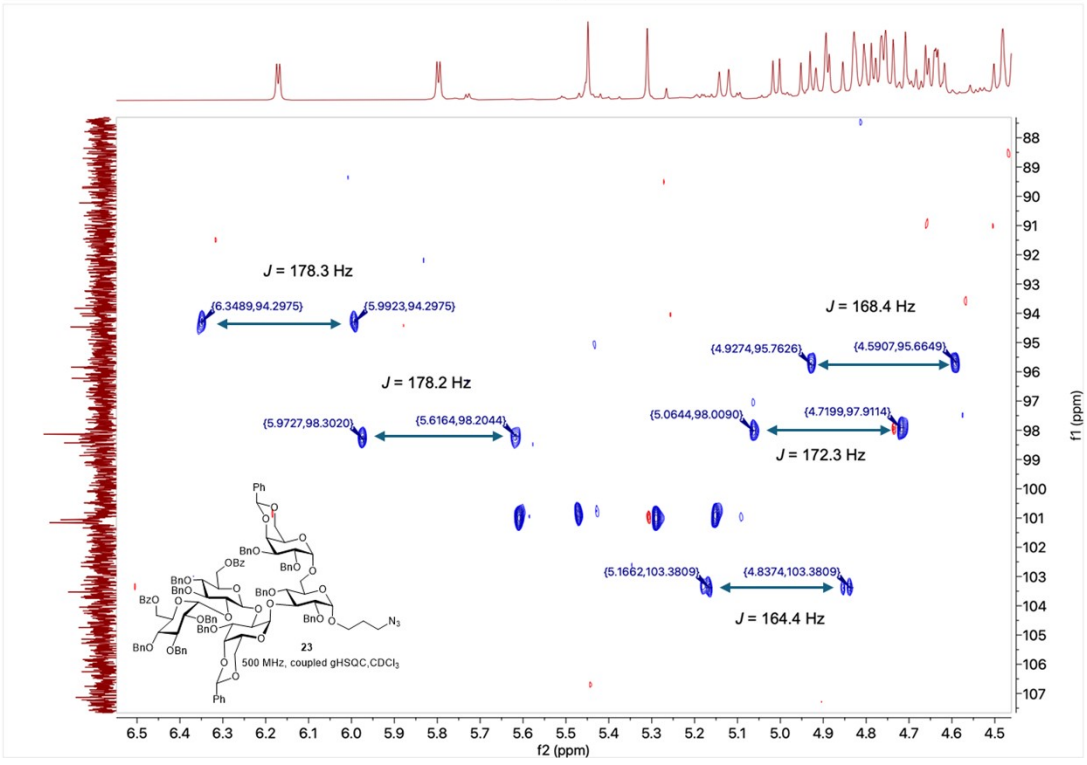

36β
125 MHz. ^{13}C-NMR, CDCl$_3$
NBnCbz
f1 (ppm)

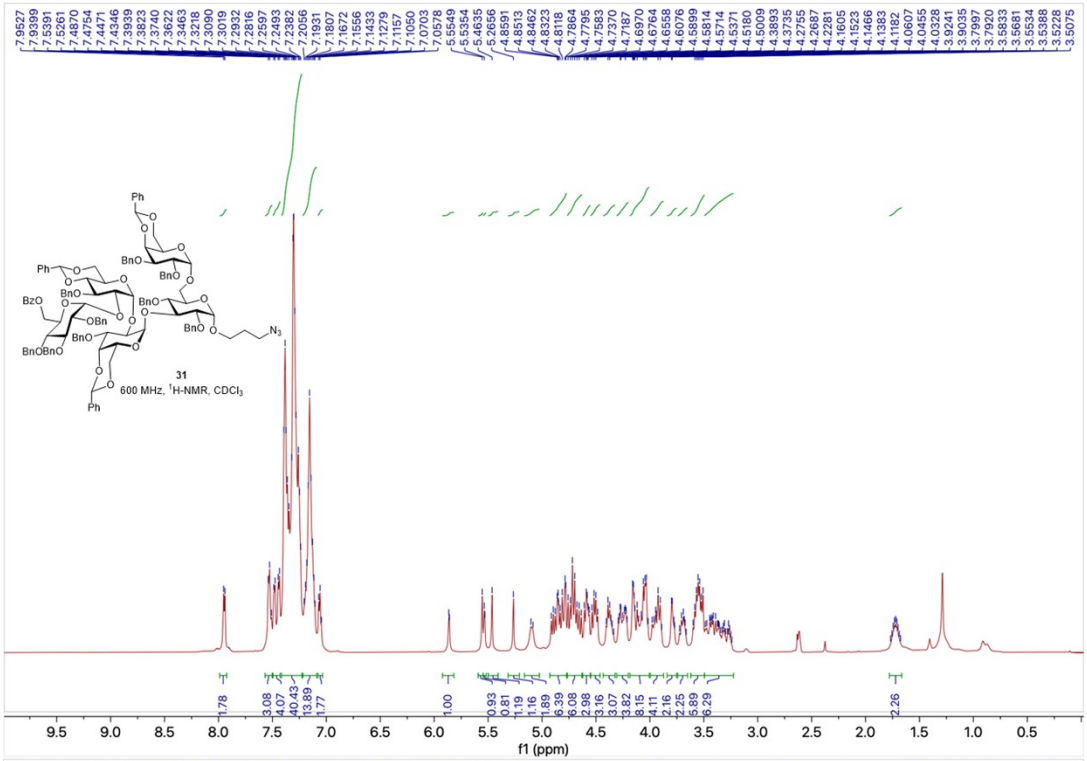

J = 168.4 Hz
{5.0096,95.8603}
{4.6729,95.8603}
J = 178.1 Hz
{5.7965,98.5951}
{5.4403,98.5951}
J = 172.3 Hz
{5.2798,98.7904}
{4.9352,98.7904}
J = 166.4 Hz
{4.8687,104.4553}
{4.5359,104.6507}
36β
500 MHz, coupled gHSQC, CDCl3
f2 (ppm)
f1 (ppm)

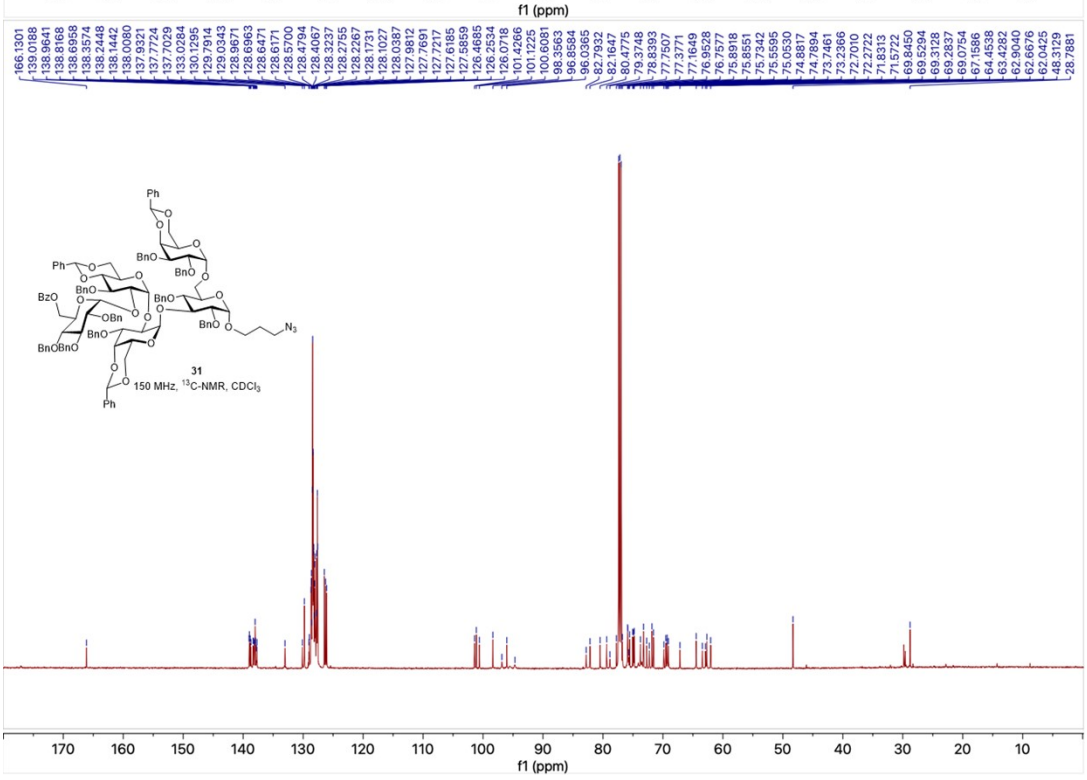

23
500 MHz, ^{1}H-NMR,CDCl$_3$
f1 (ppm)

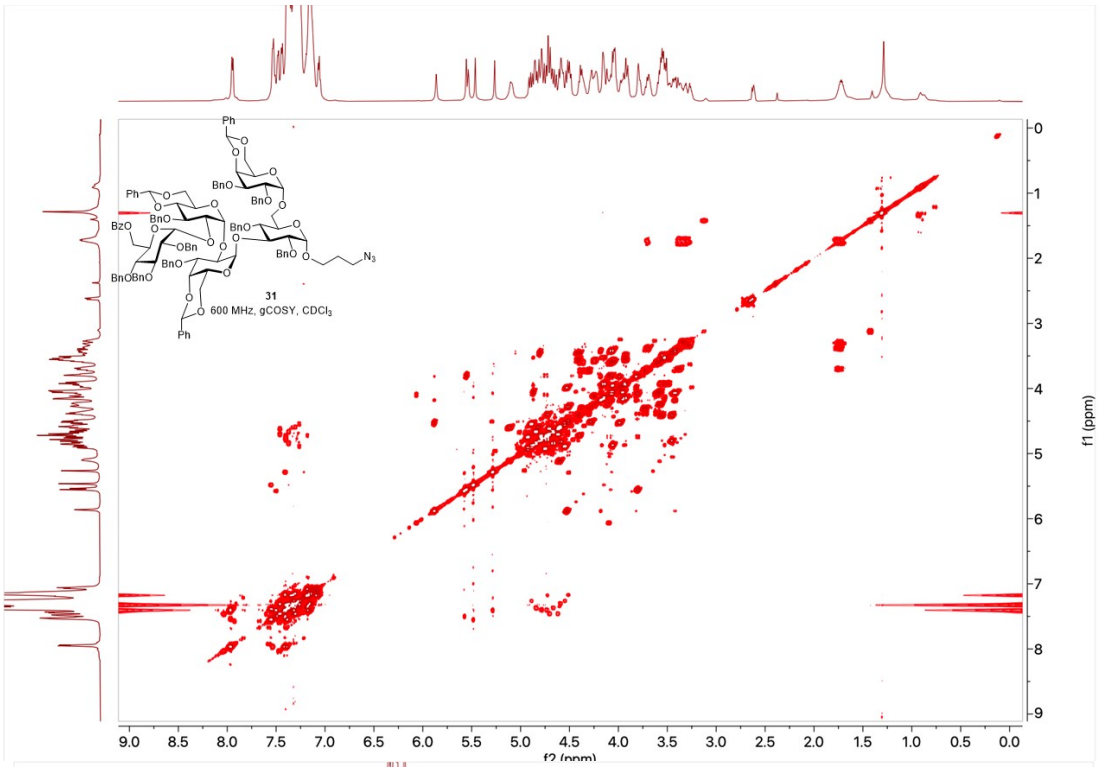

23
500 MHz, ^{13}C-NMR,CDCl$_3$
f1 (ppm)

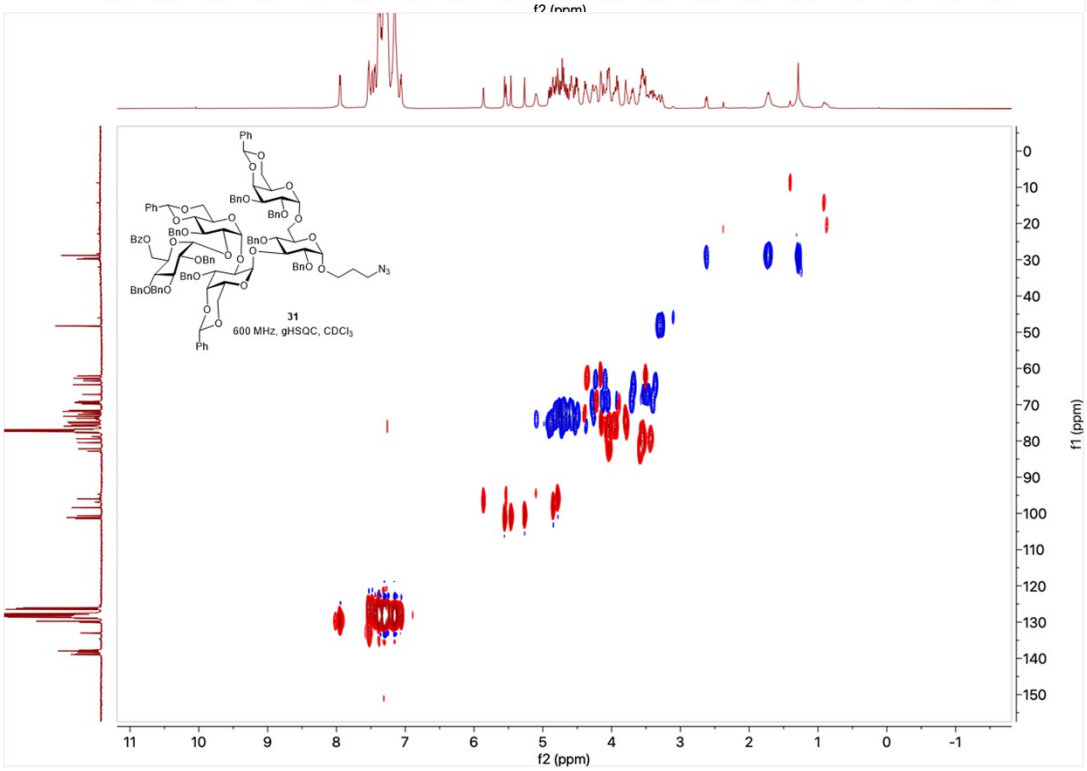

23
500 MHz, gCOSY,CDCl3
f2 (ppm)
f1 (ppm)

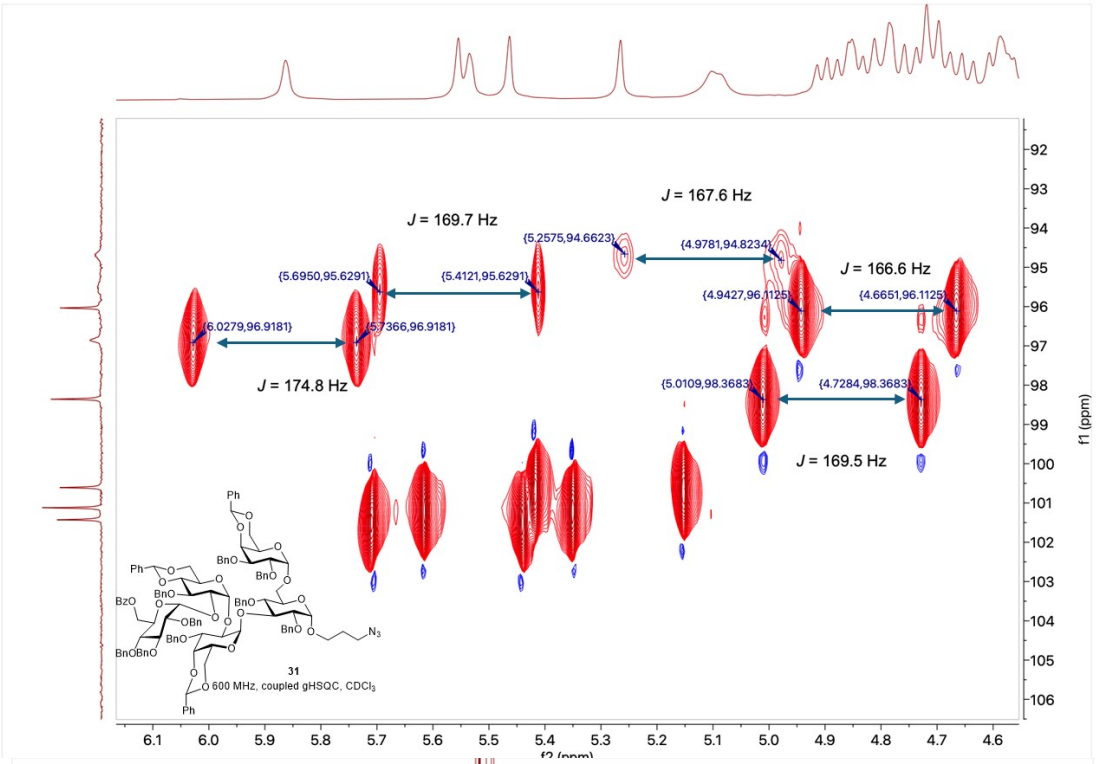

J = 178.3 Hz
{6.3489,94.2975}
{5.9923,94.2975}
J = 178.2 Hz
{5.9727,98.3020}
{5.6164,98.2044}
J = 168.4 Hz
{4.9274,95.7626}
{4.5907,95.6649}
{5.0644,98.0090}
{4.7199,97.9114}
J = 172.3 Hz
{5.1662,103.3809}
{4.8374,103.3809}
J = 164.4 Hz
23
500 MHz, coupled gHSQC,CDCl3
f2 (ppm)
f1 (ppm)

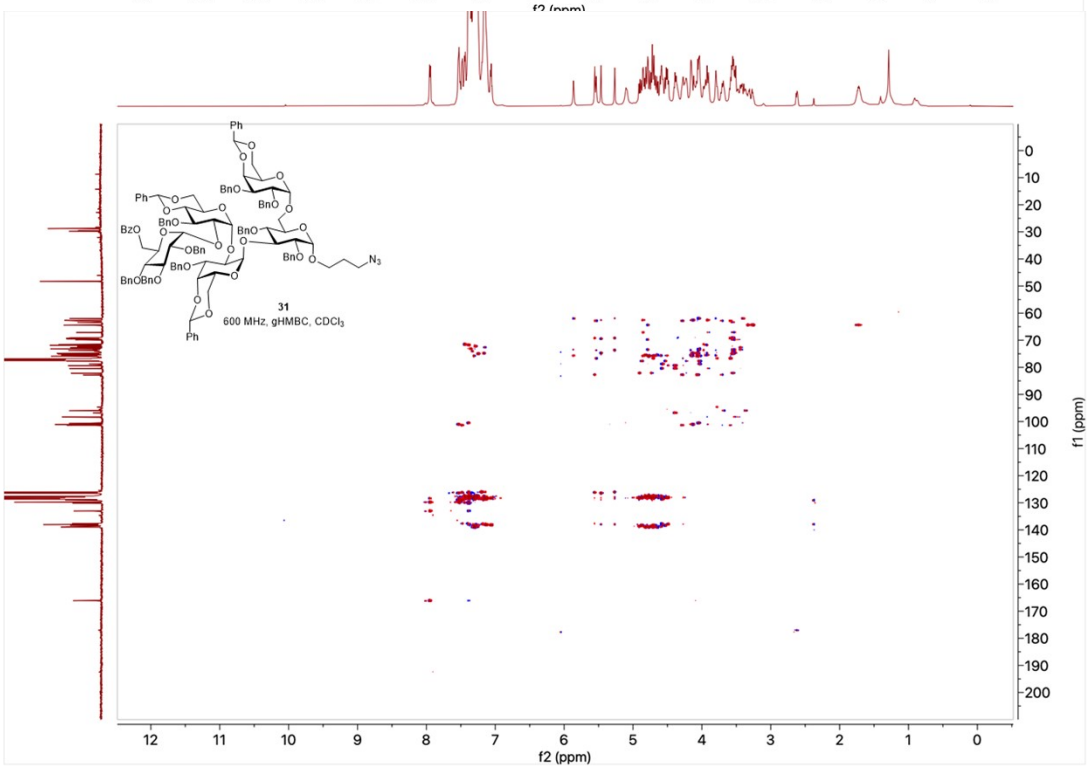

31
600 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

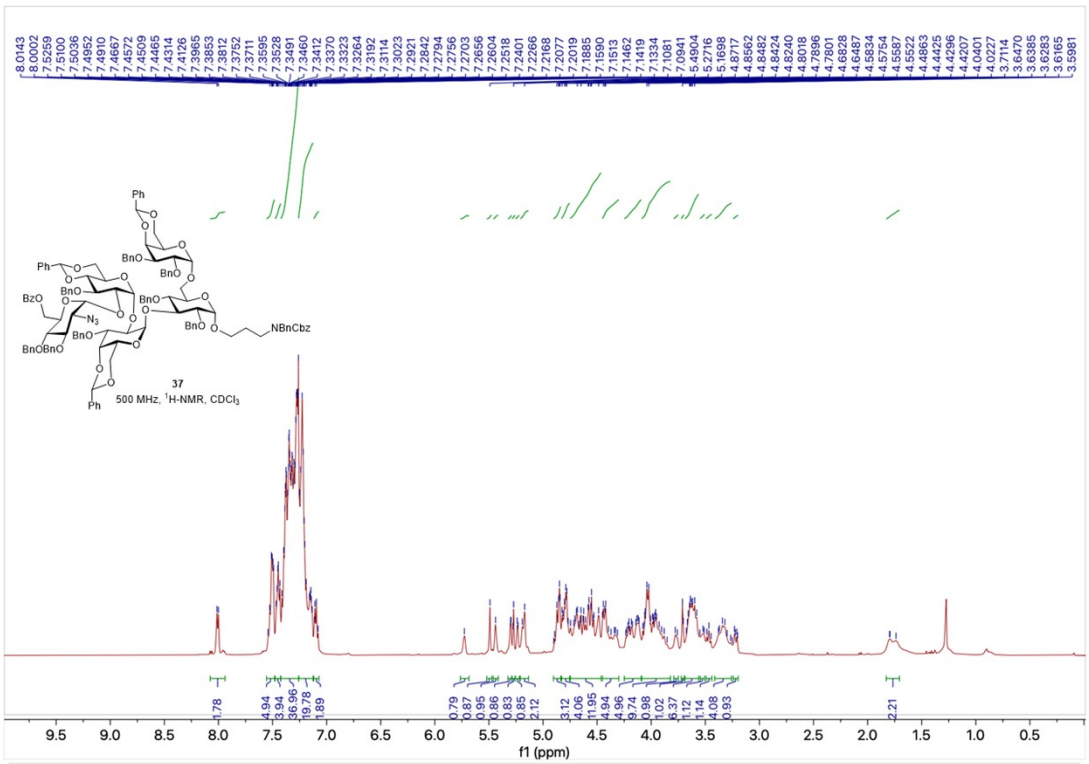

31
150 MHz, ^{13}C-NMR, $CDCl_3$
f1 (ppm)

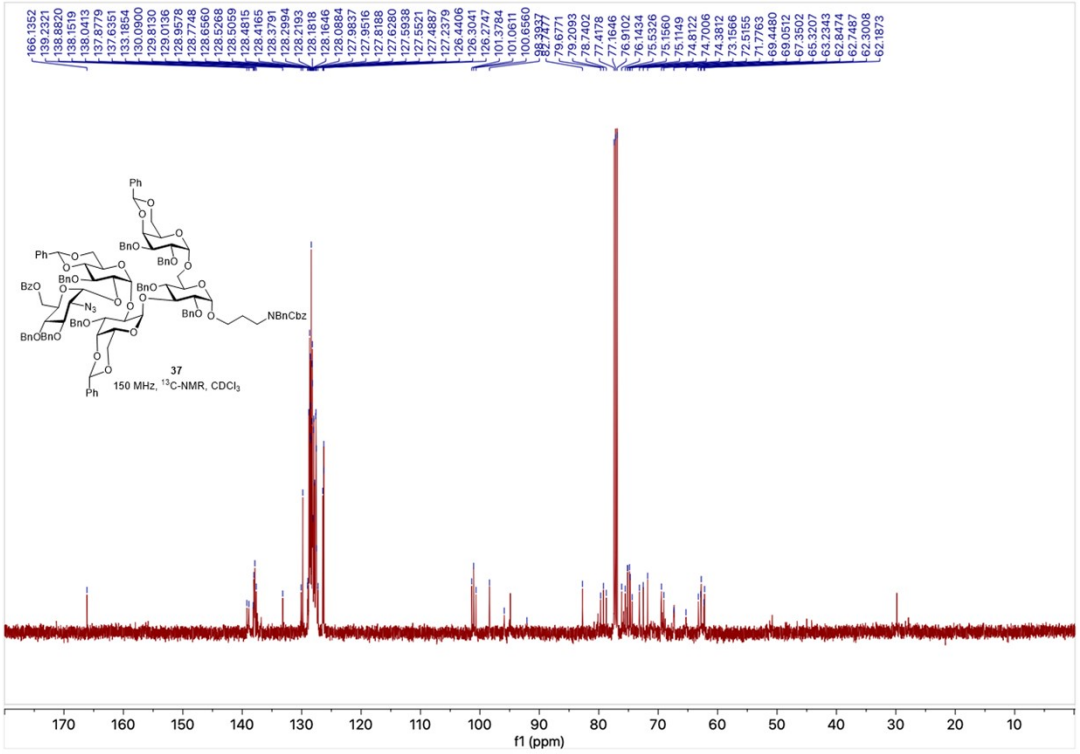

31
600 MHz, gCOSY, CDCl3
f2 (ppm)
f1 (ppm)

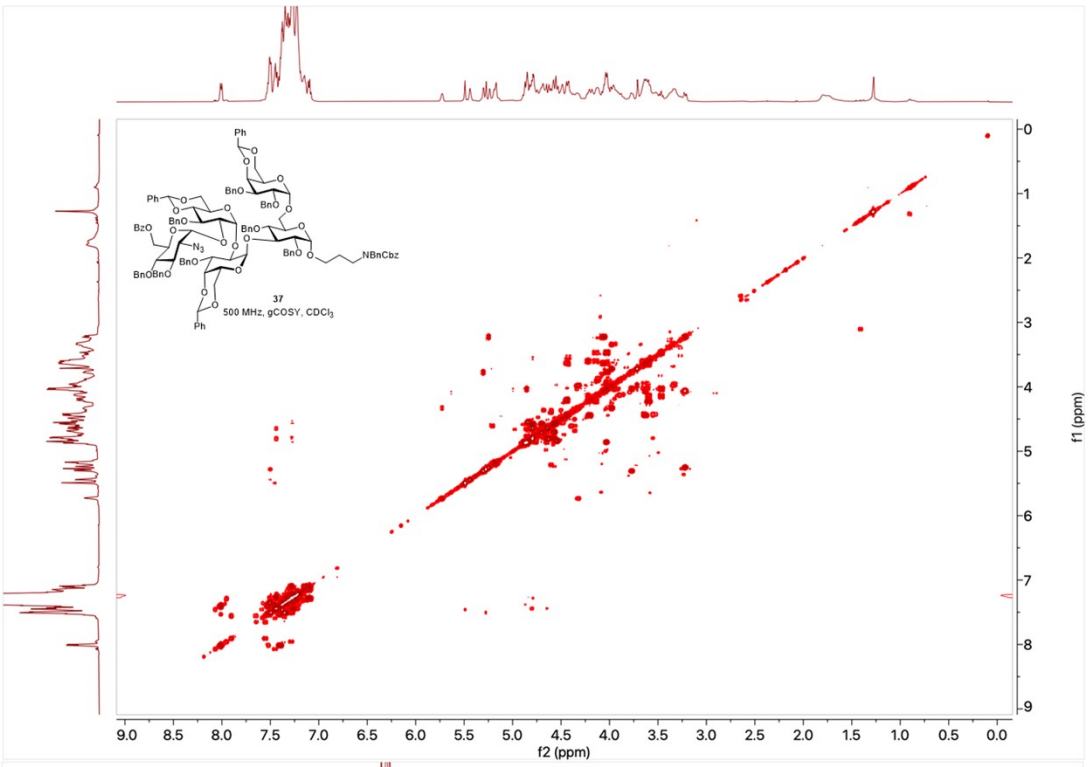

31
600 MHz, gHSQC, CDCl3
f2 (ppm)
f1 (ppm)

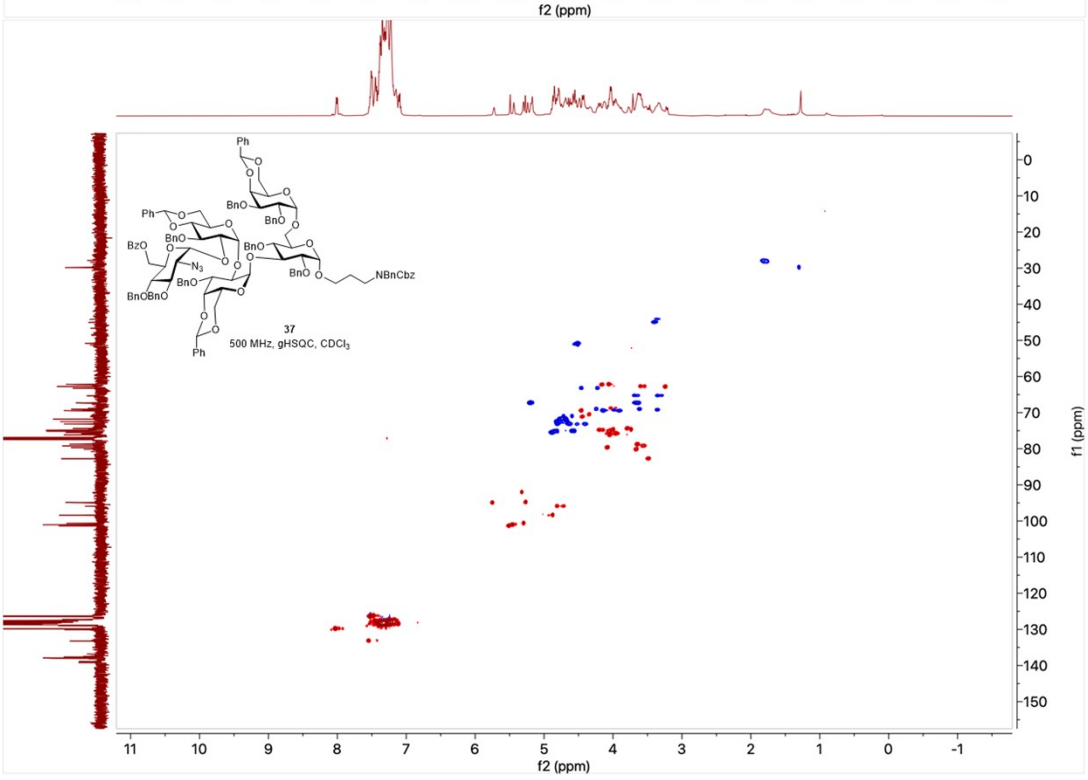

J = 169.7 Hz
J = 167.6 Hz
J = 166.6 Hz
J = 174.8 Hz
J = 169.5 Hz
{6.0279,96.9181}
{5.7366,96.9181}
{5.6950,95.6291}
{5.4121,95.6291}
{5.2575,94.6623}
{4.9781,94.8234}
{4.9427,96.1125}
{4.6651,96.1125}
{5.0109,98.3683}
{4.7284,98.3683}
31
600 MHz, coupled gHSQC, CDCl3
f2 (ppm)
f1 (ppm)

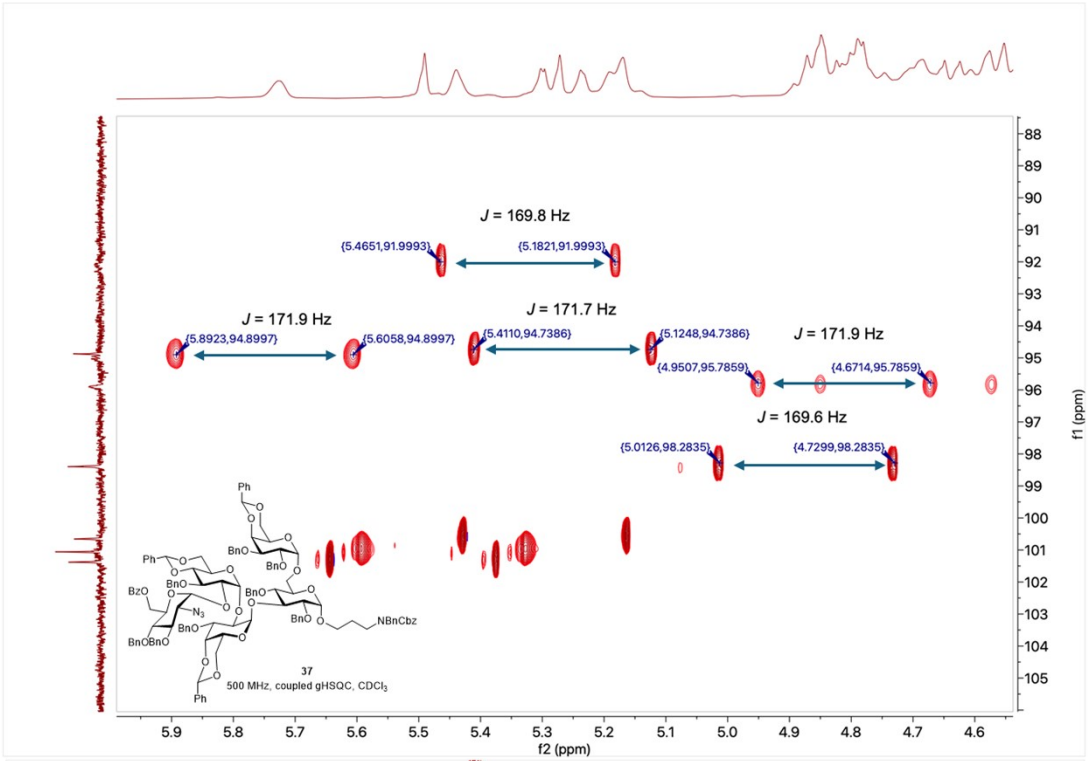

31
600 MHz, gHMBC, CDCl3
f2 (ppm)
f1 (ppm)

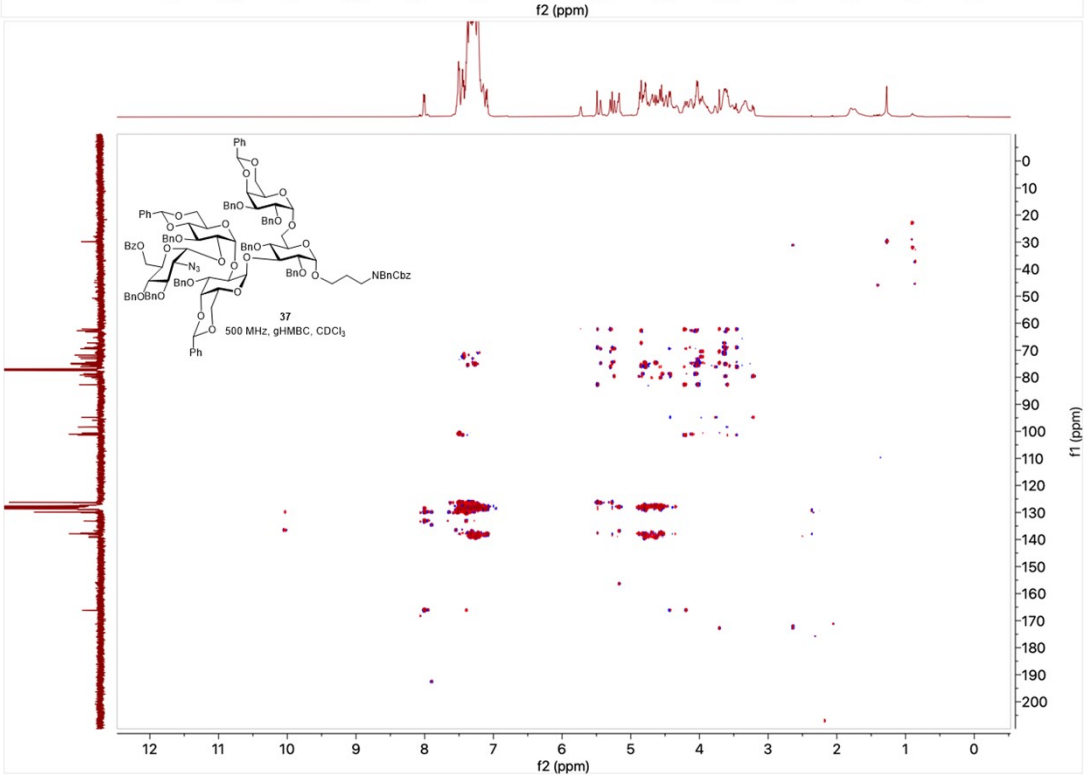

37
500 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

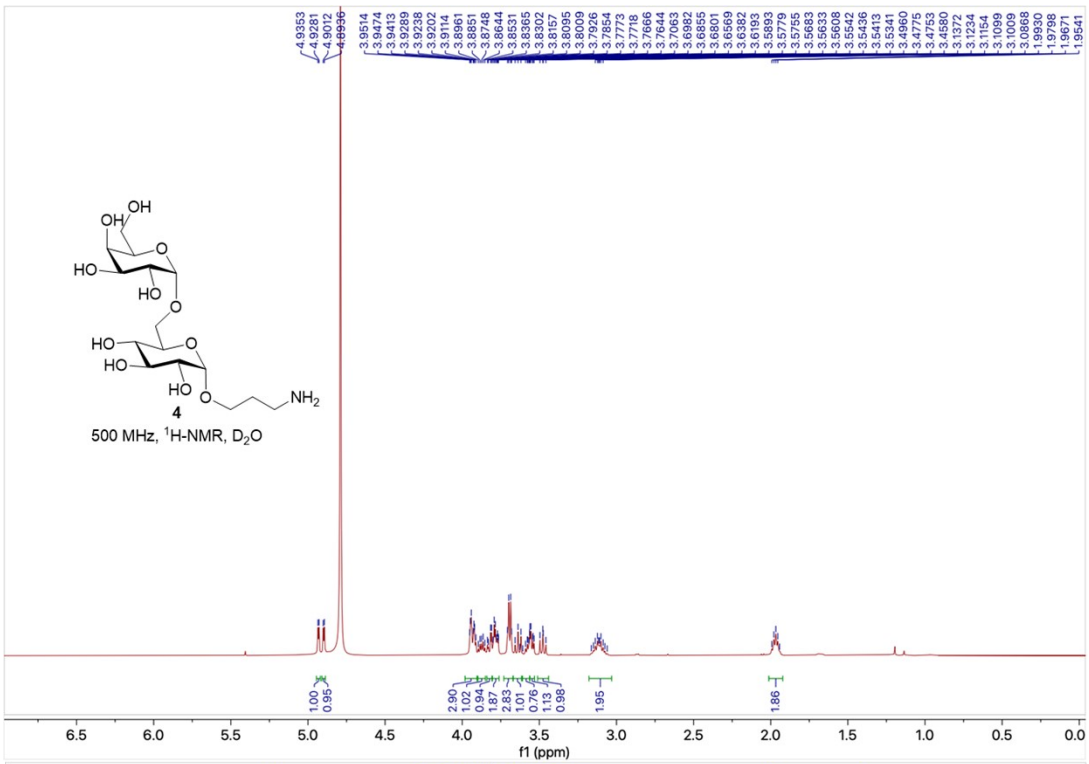

37
150 MHz, ^{13}C-NMR, $CDCl_3$
f1 (ppm)

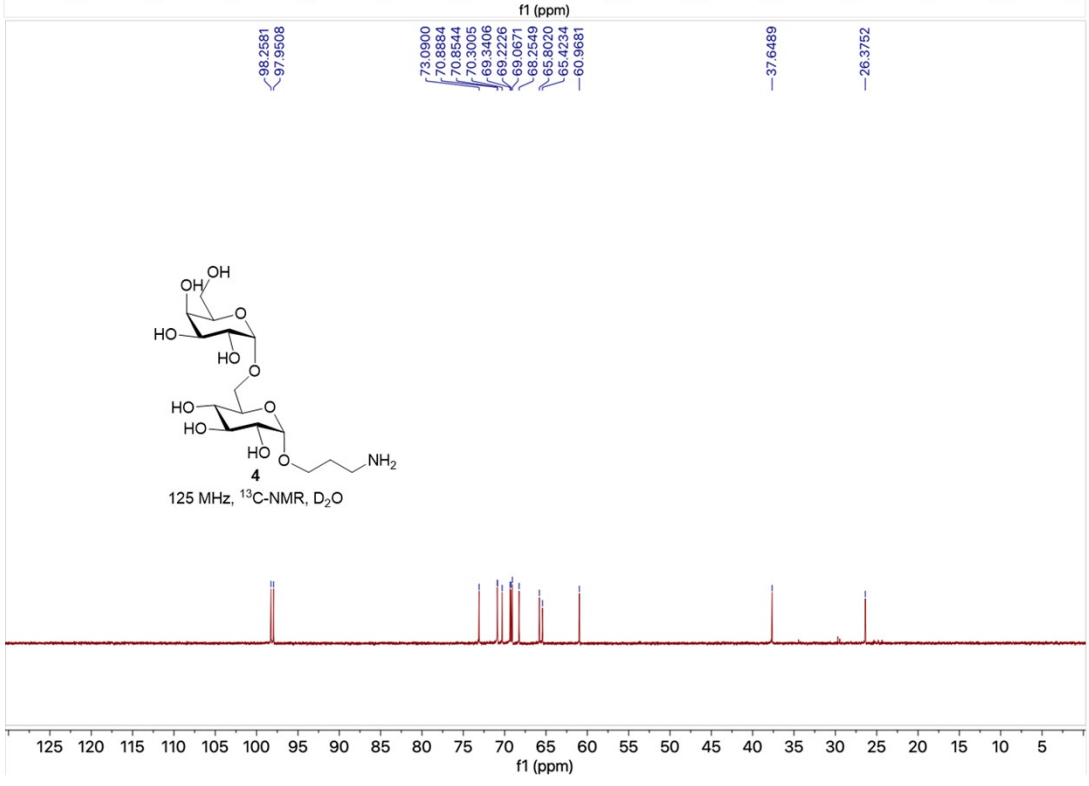

37
500 MHz, gCOSY, CDCl3
f2 (ppm)
f1 (ppm)

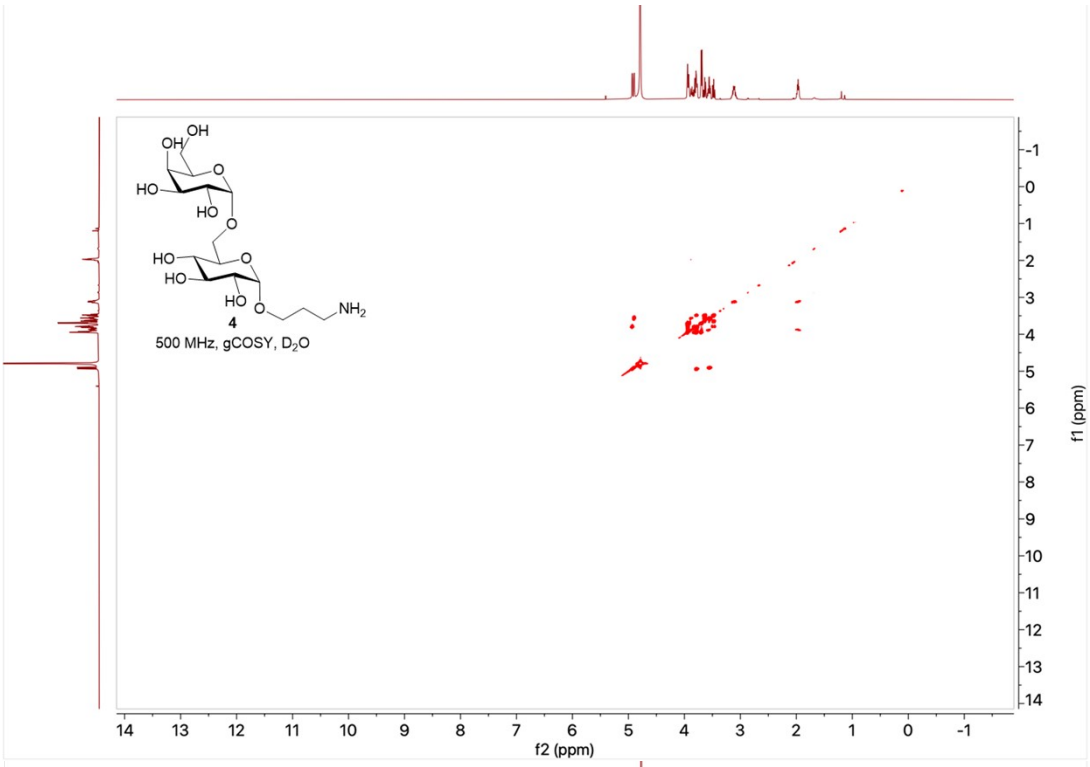

37
500 MHz, gHSQC, CDCl3
f2 (ppm)
f1 (ppm)

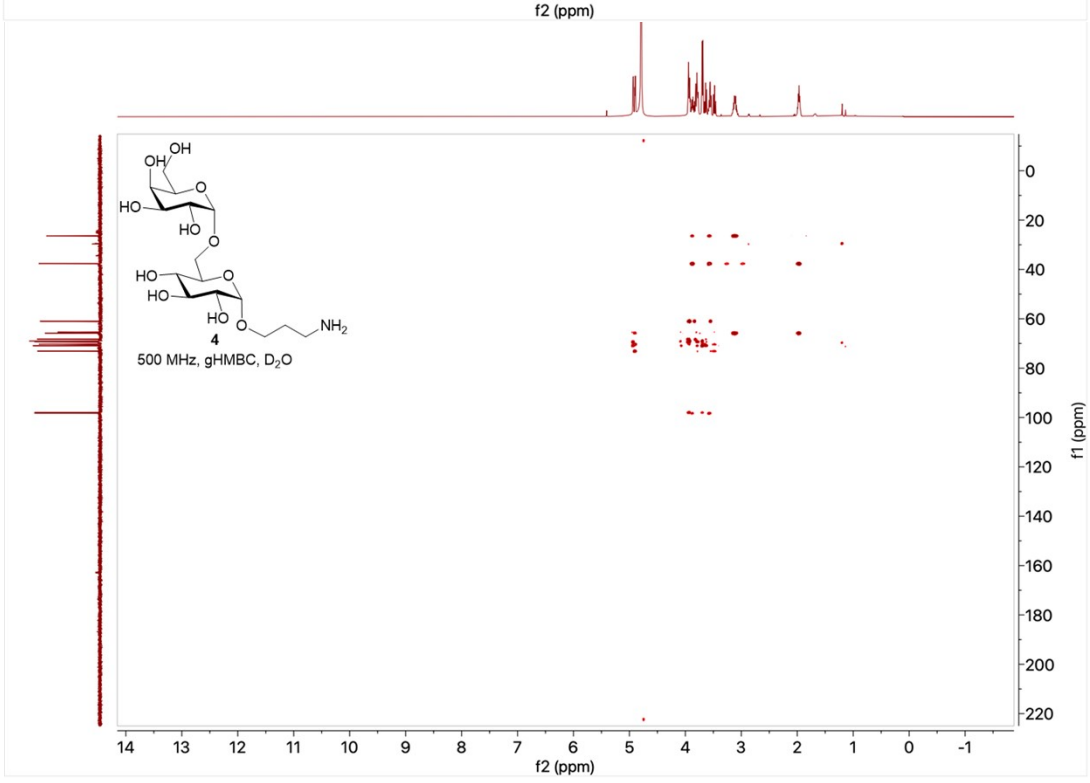

J = 169.8 Hz
{5.4651,91.9993}
{5.1821,91.9993}
J = 171.9 Hz
{5.8923,94.8997}
{5.6058,94.8997}
J = 171.7 Hz
{5.4110,94.7386}
{5.1248,94.7386}
J = 171.9 Hz
{4.9507,95.7859}
{4.6714,95.7859}
J = 169.6 Hz
{5.0126,98.2835}
{4.7299,98.2835}
37
500 MHz, coupled gHSQC, CDCl3
f2 (ppm)
f1 (ppm)

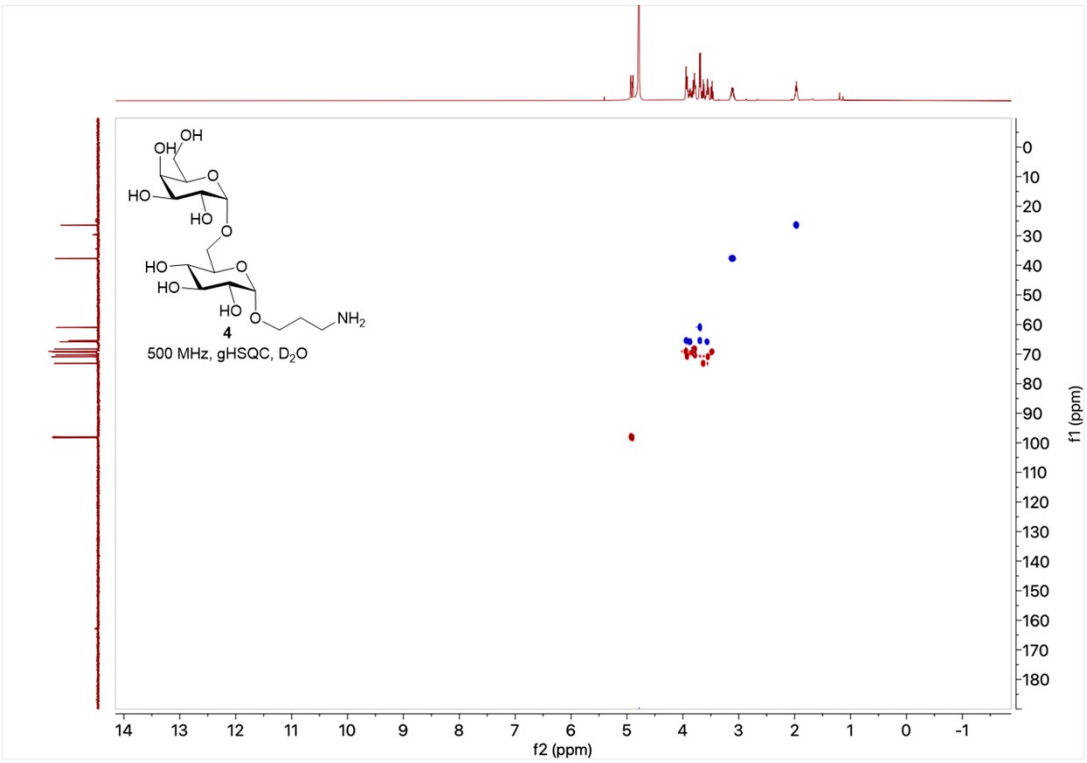

37
500 MHz, gHMBC, CDCl3
f2 (ppm)
f1 (ppm)

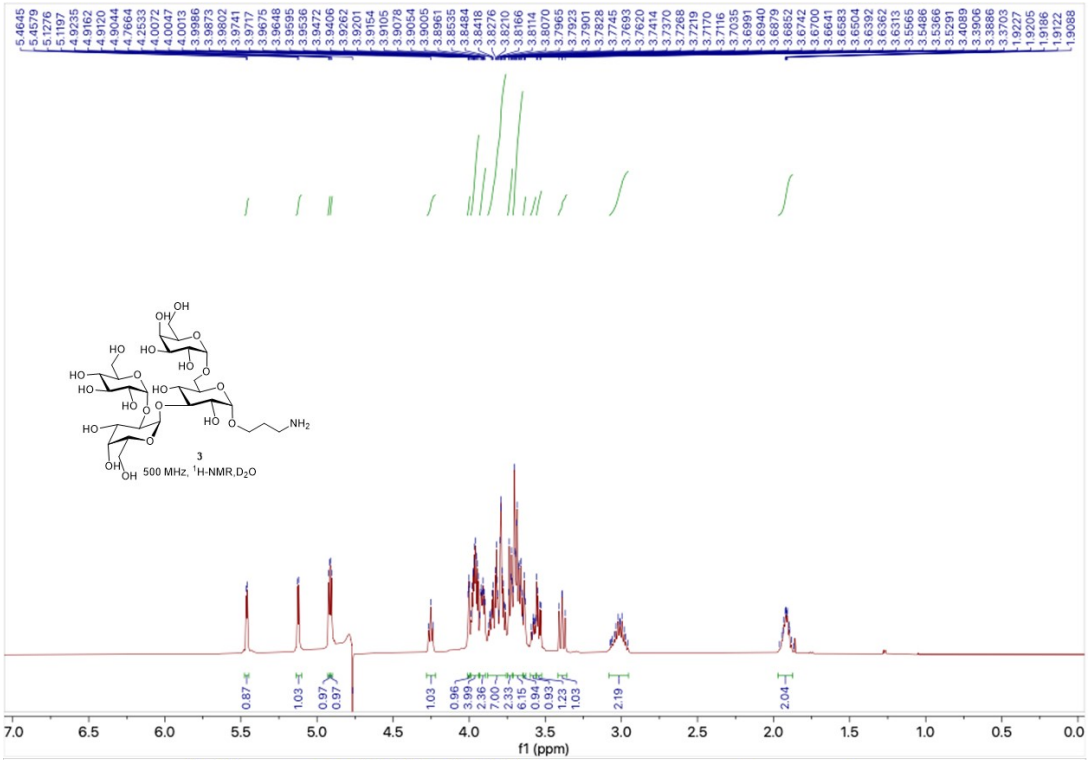

4.9353
4.9281
4.9012
4.8936
3.9514
3.9474
3.9413
3.9289
3.9238
3.9202
3.9114
3.8961
3.8855
3.8748
3.8644
3.8531
3.8365
3.8302
3.8157
3.8095
3.8009
3.7926
3.7854
3.7773
3.7718
3.7666
3.7644
3.7063
3.6982
3.6855
3.6801
3.6569
3.6382
3.6193
3.5893
3.5779
3.5755
3.5683
3.5633
3.5609
3.5542
3.5436
3.5413
3.5341
3.4960
3.4775
3.4753
3.4580
3.1372
3.1234
3.1154
3.1099
3.1009
3.0868
1.9930
1.9798
1.9671
1.9541
1.00
0.95
2.90
1.02
0.94
1.87
2.83
1.01
0.76
1.13
0.98
1.95
1.86
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
0.0
f1 (ppm)
OH
OH
O
HO
HO
O
HO
HO
O
HO
O
NH2
4
500 MHz, 1H-NMR, D2O

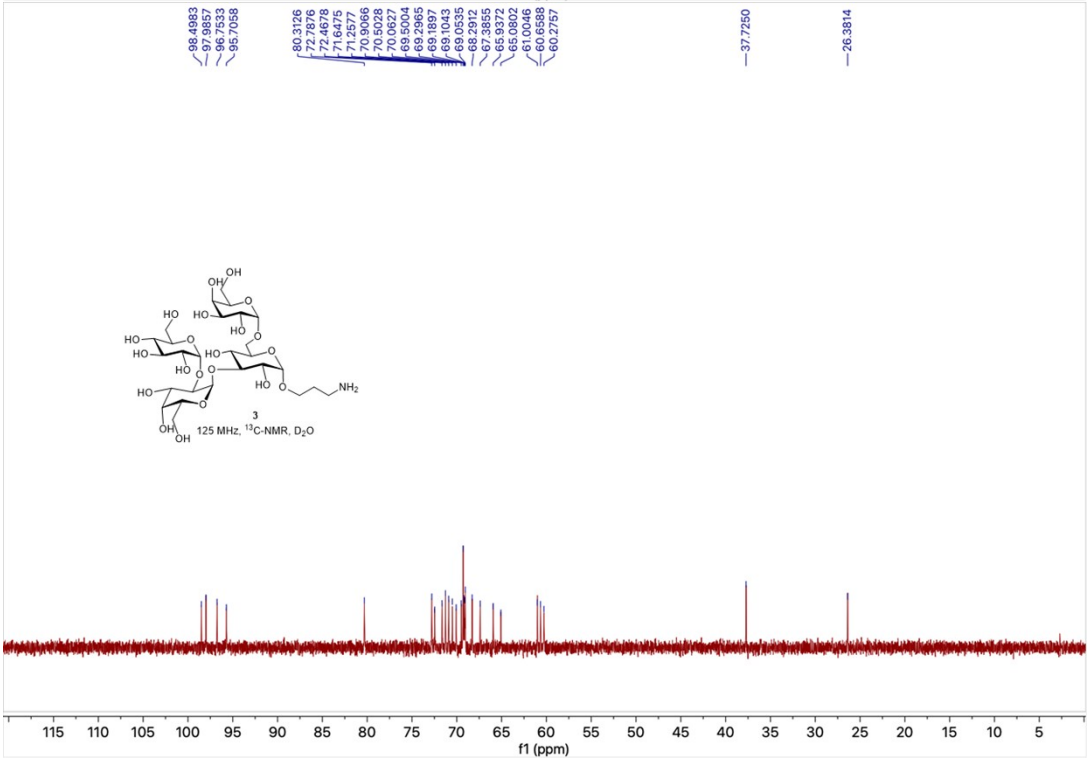

98.2581
97.9508
73.0900
70.8884
70.8544
70.3005
69.3406
69.2226
69.0671
68.2549
65.8020
65.4234
60.9681
37.6489
26.3752
OH
OH
O
HO
HO
O
HO
HO
O
HO
O
NH2
4
125 MHz, 13C-NMR, D2O
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)

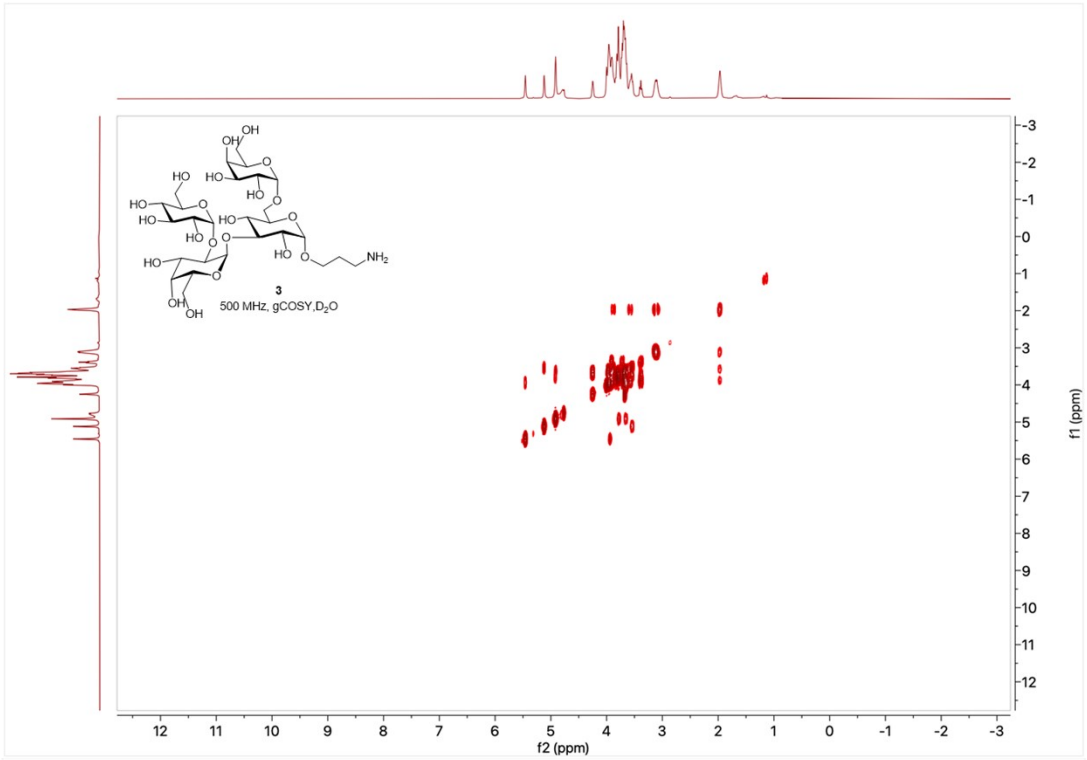

4
500 MHz, gCOSY, D2O
f2 (ppm)
f1 (ppm)

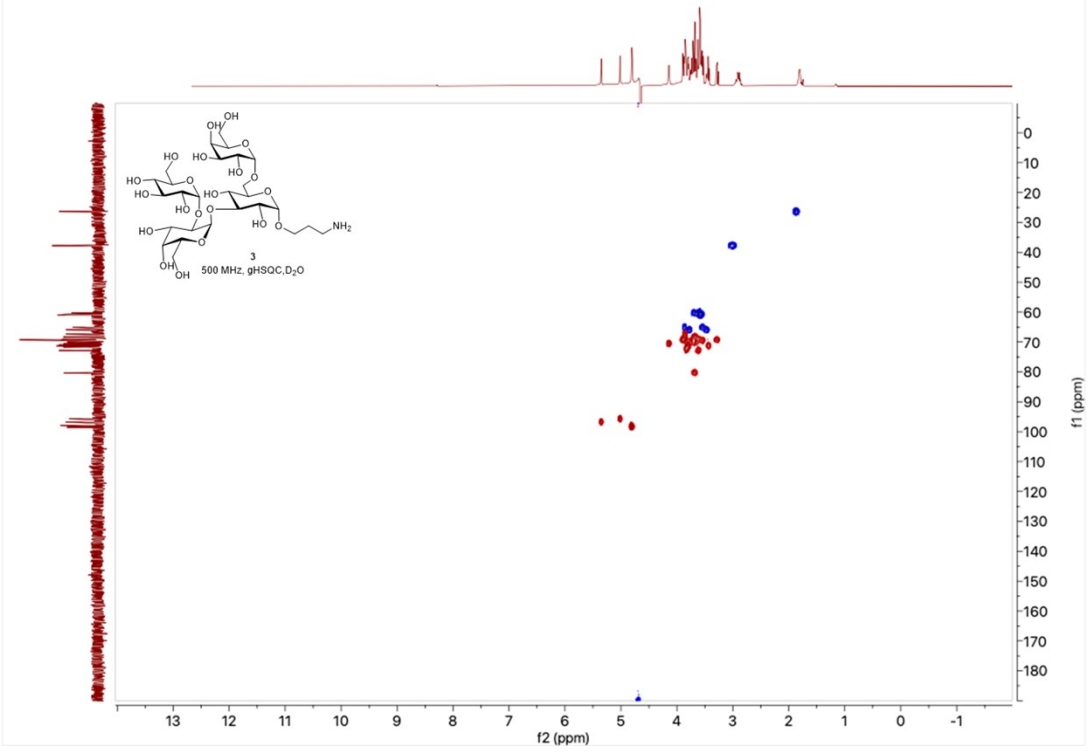

4
500 MHz, gHMBC, D2O
f2 (ppm)
f1 (ppm)

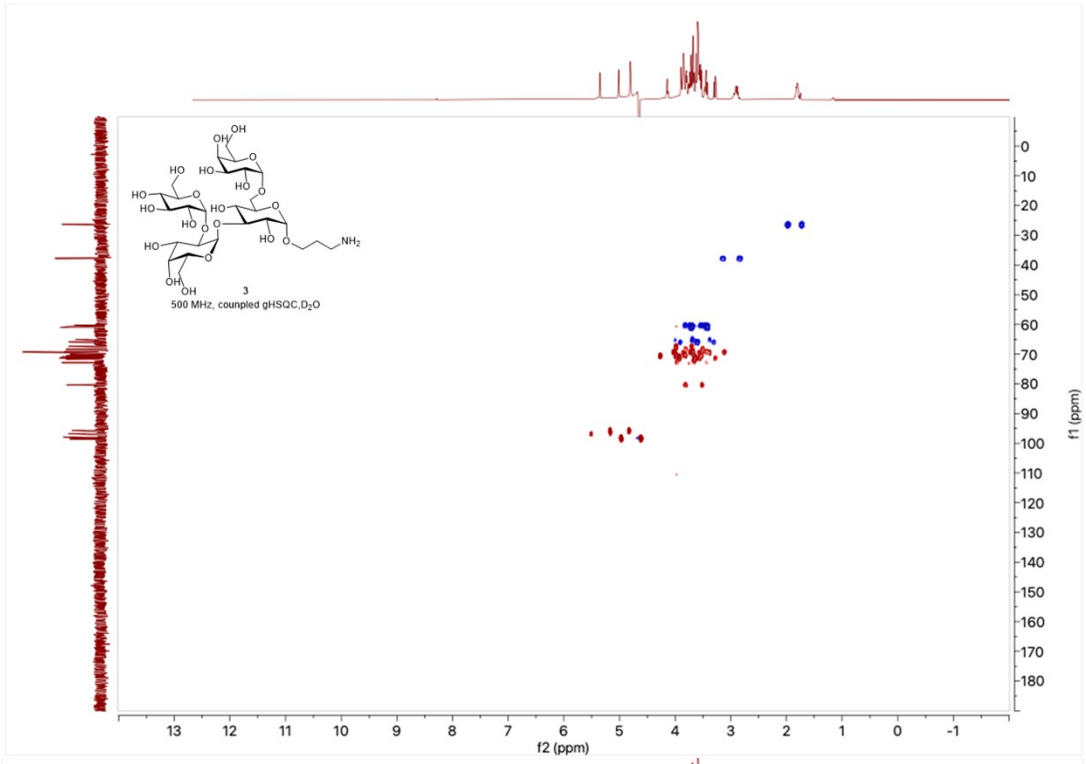

4
500 MHz, gHSQC, D2O
f2 (ppm)
f1 (ppm)

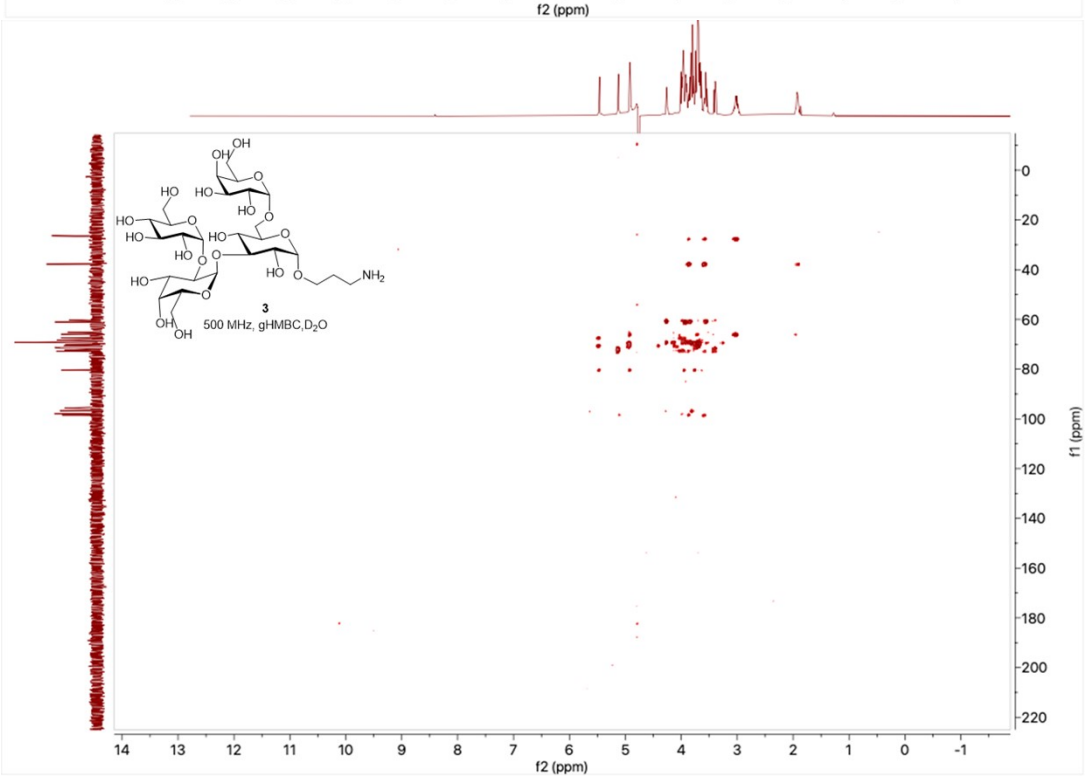

3
500 MHz, ^{1}H-NMR,D_2O
f1 (ppm)

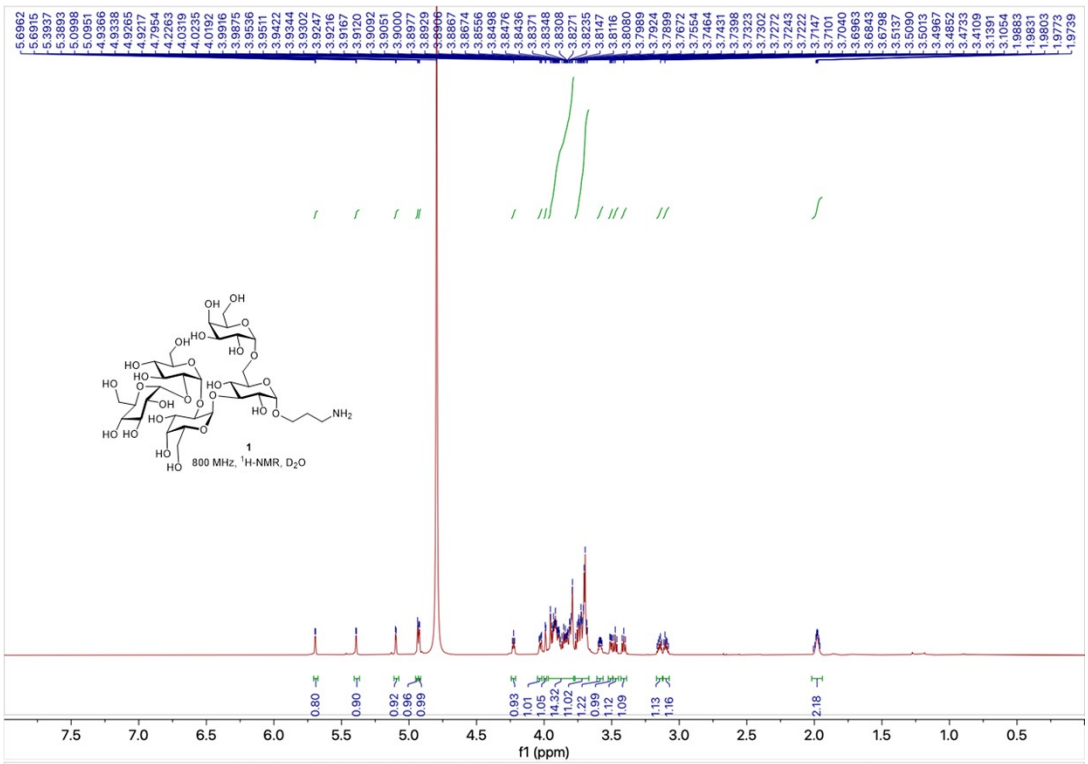

3
125 MHz, ^{13}C-NMR, D_2O
f1 (ppm)

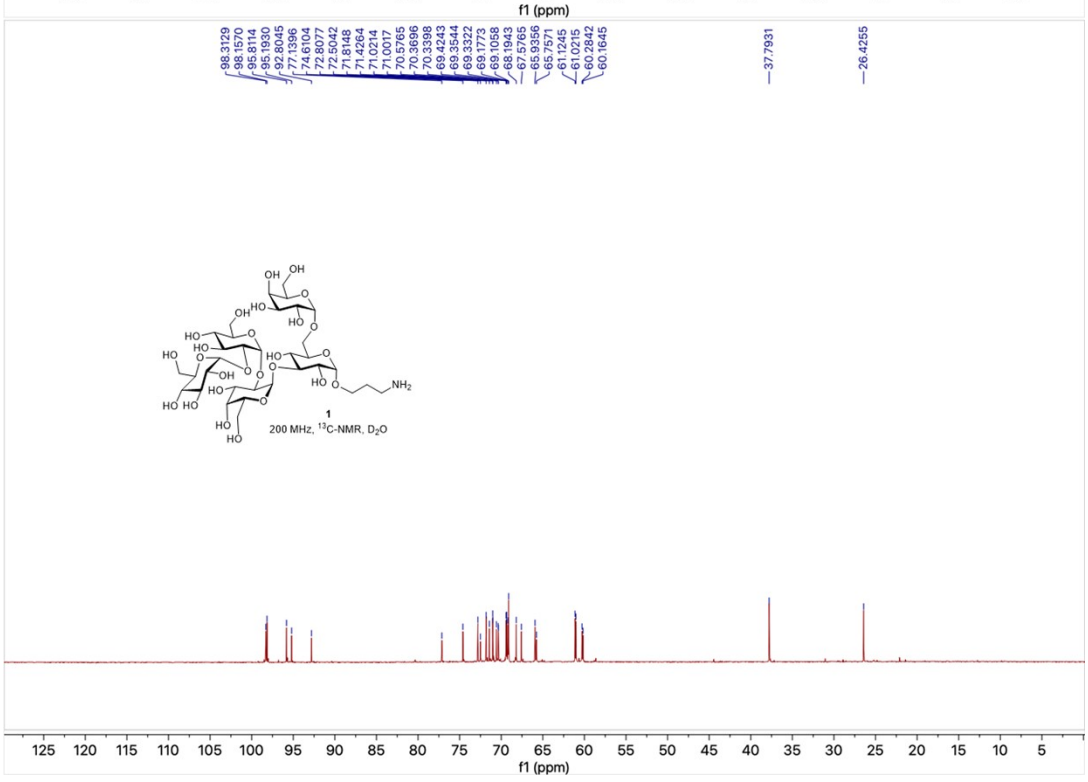

3
500 MHz, gCOSY,D2O
f2 (ppm)
f1 (ppm)

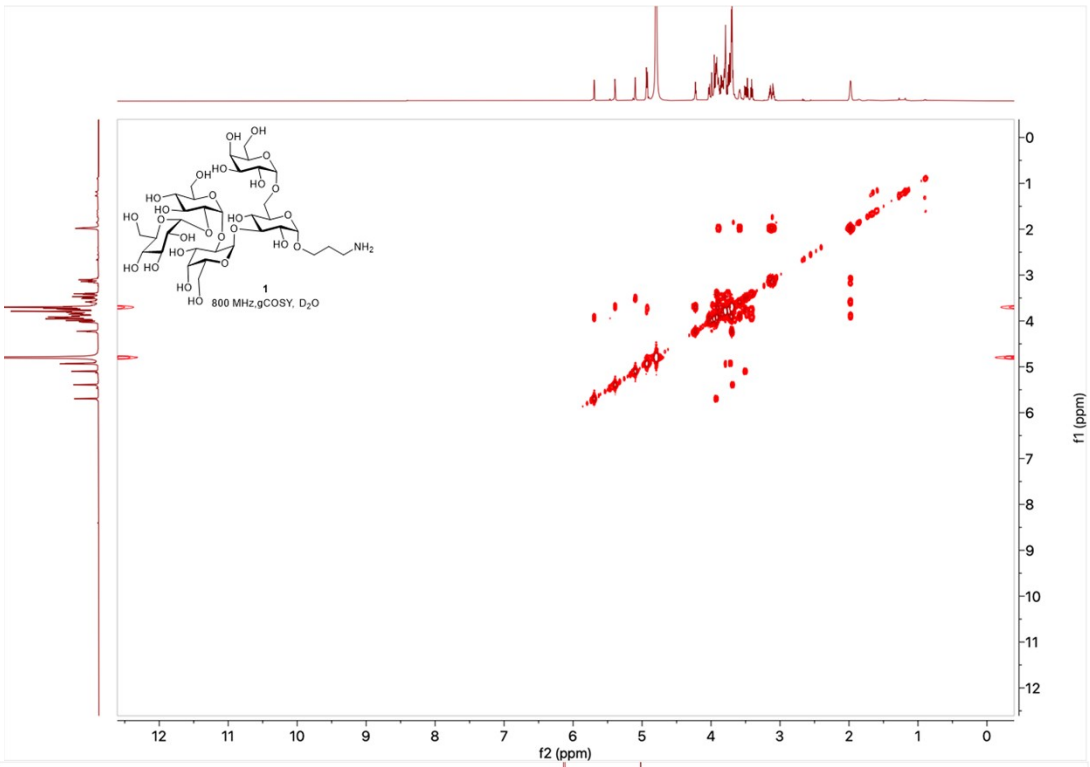

3
500 MHz, gHSQC,D2O
f2 (ppm)
f1 (ppm)

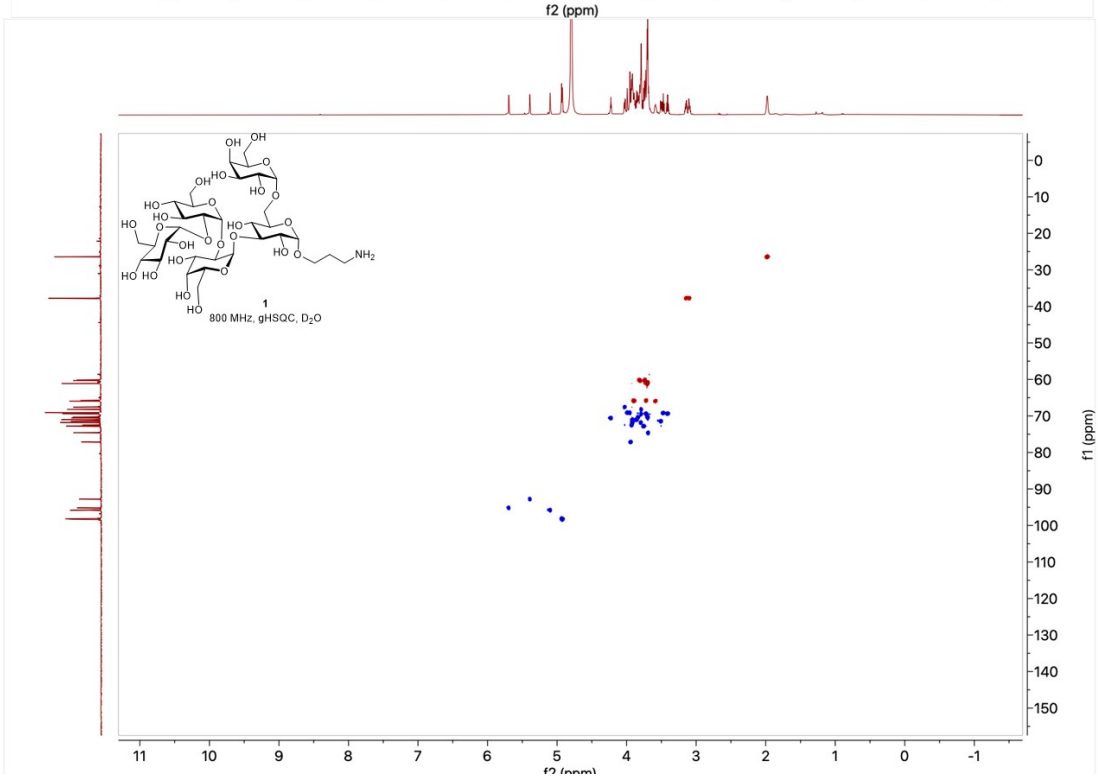

3
500 MHz, counpled gHSQC,D2O
f2 (ppm)
f1 (ppm)

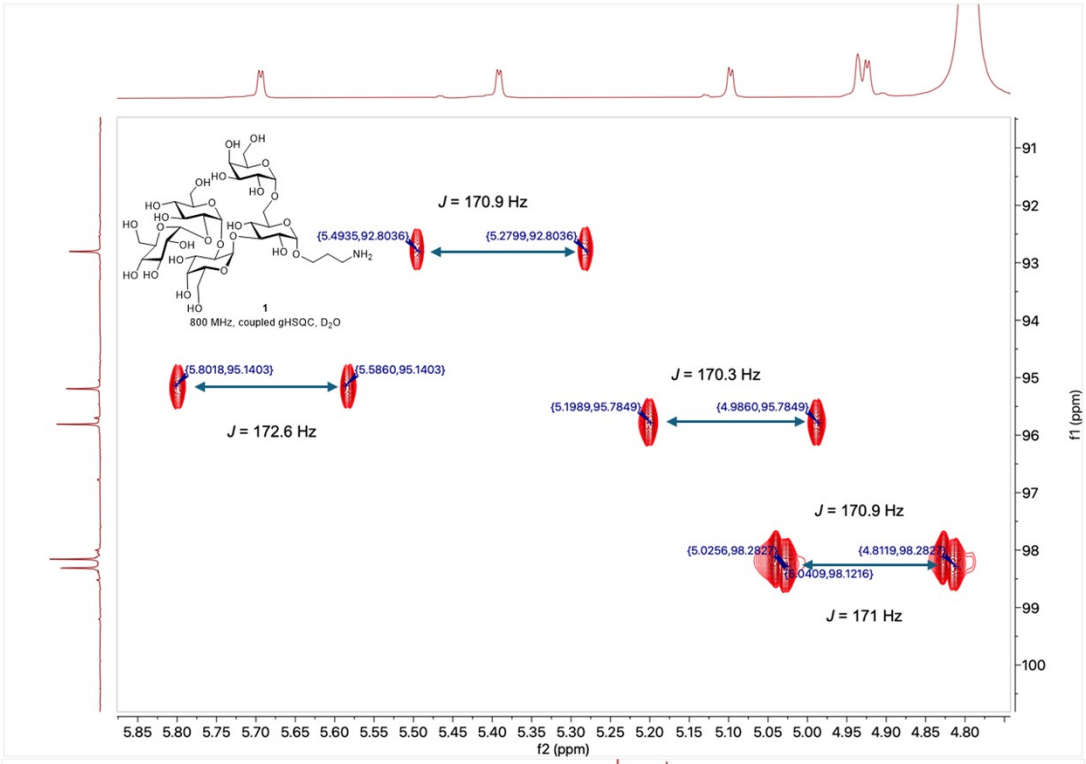

3
500 MHz, gHMBC,D2O
f2 (ppm)
f1 (ppm)

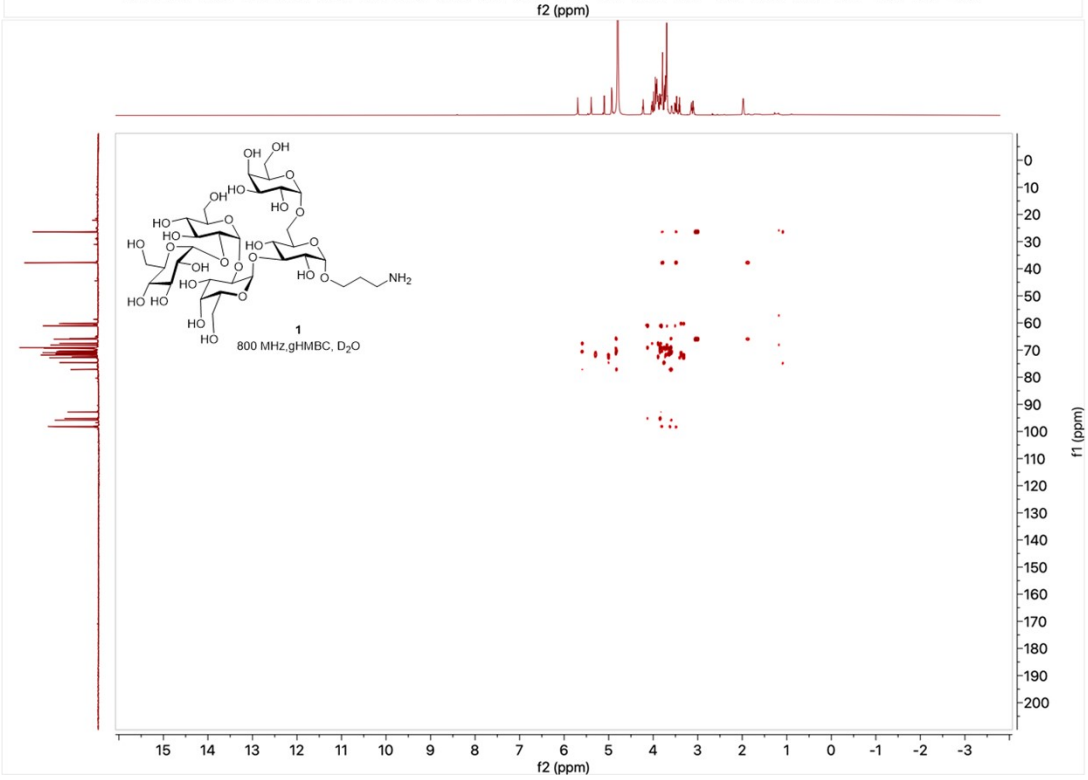

1
800 MHz, ^{1}H-NMR, D_2O
f1 (ppm)

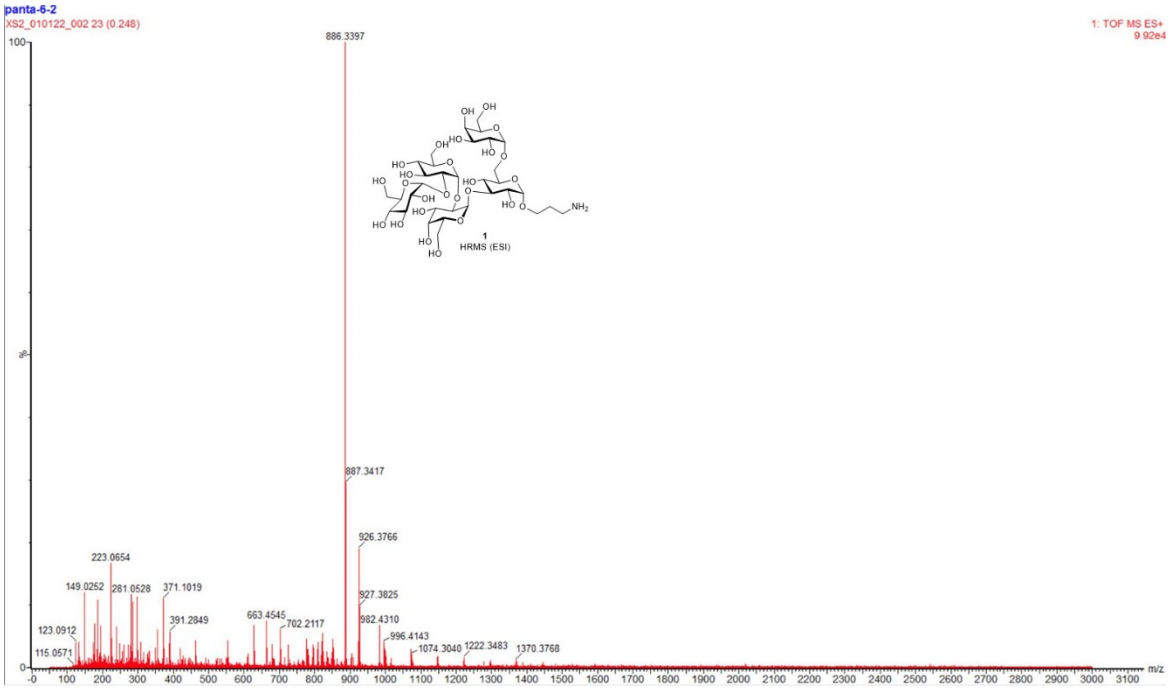

1
200 MHz, ^{13}C-NMR, D_2O
f1 (ppm)

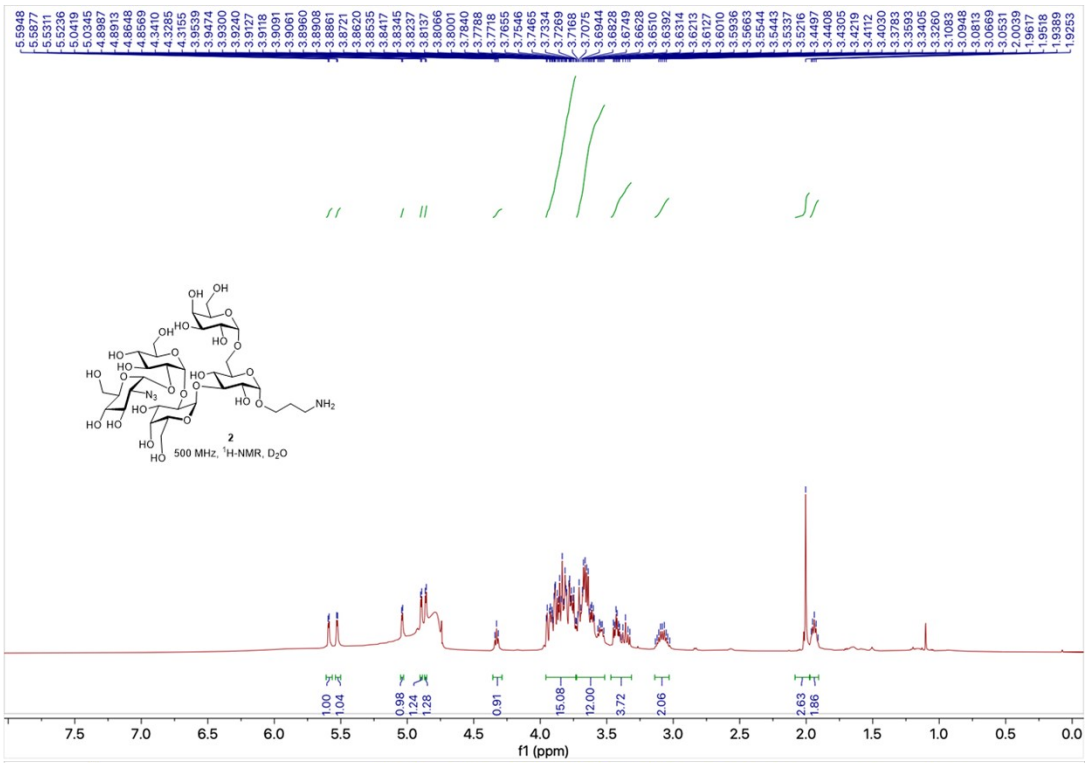

1
800 MHz,gCOSY, D2O
f2 (ppm)
f1 (ppm)

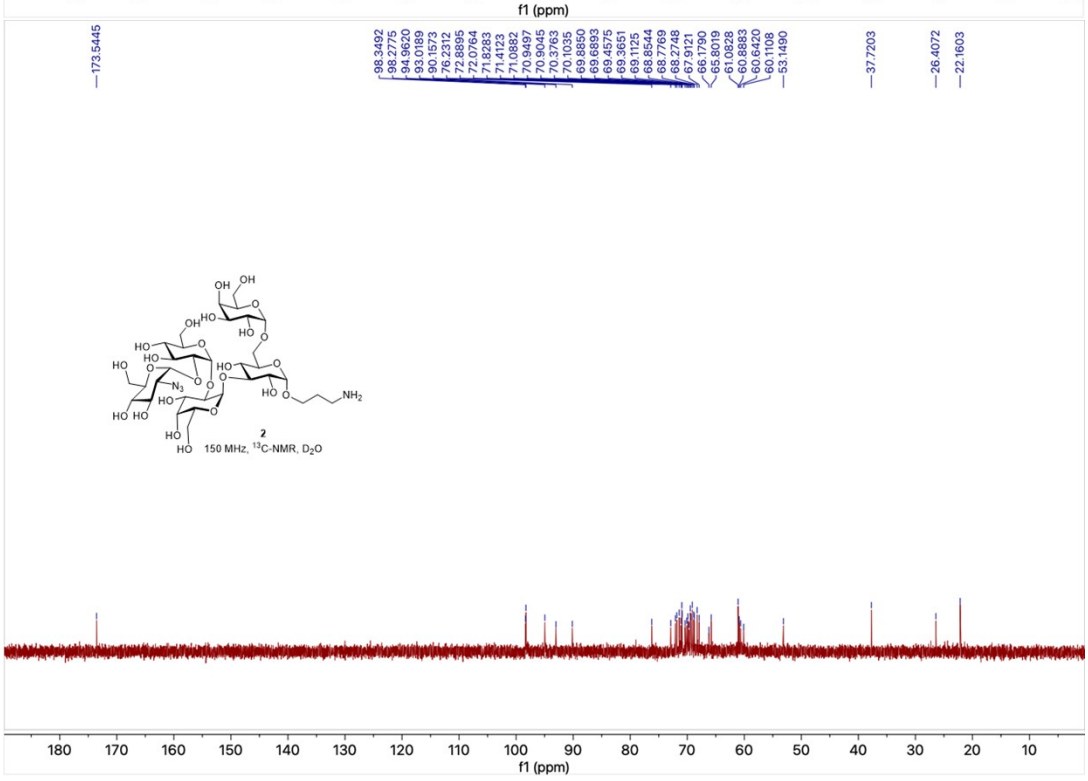

1
800 MHz, gHSQC, D2O
f2 (ppm)
f1 (ppm)

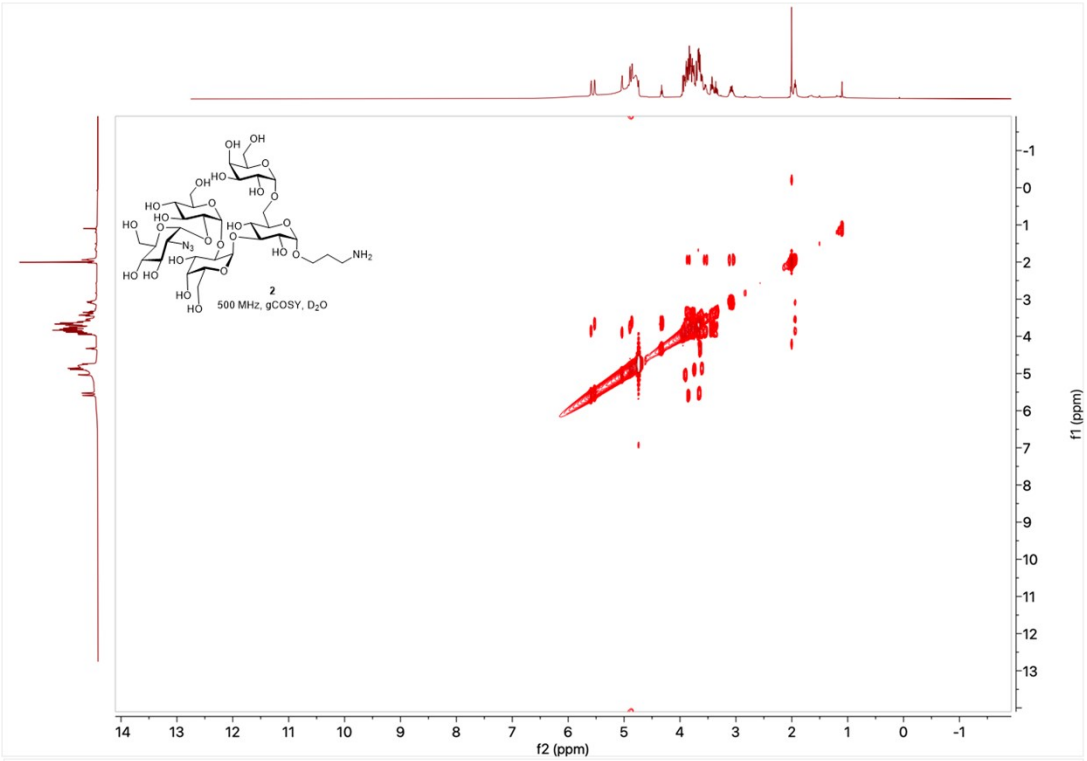

1
800 MHz, coupled gHSQC, D2O
J = 170.9 Hz
{5.4935,92.8036}
{5.2799,92.8036}
{5.8018,95.1403}
{5.5860,95.1403}
J = 172.6 Hz
J = 170.3 Hz
{5.1989,95.7849}
{4.9860,95.7849}
J = 170.9 Hz
{5.0256,98.2821}
{4.8119,98.2821}
{5.0409,98.1216}
J = 171 Hz
f1 (ppm)
f2 (ppm)

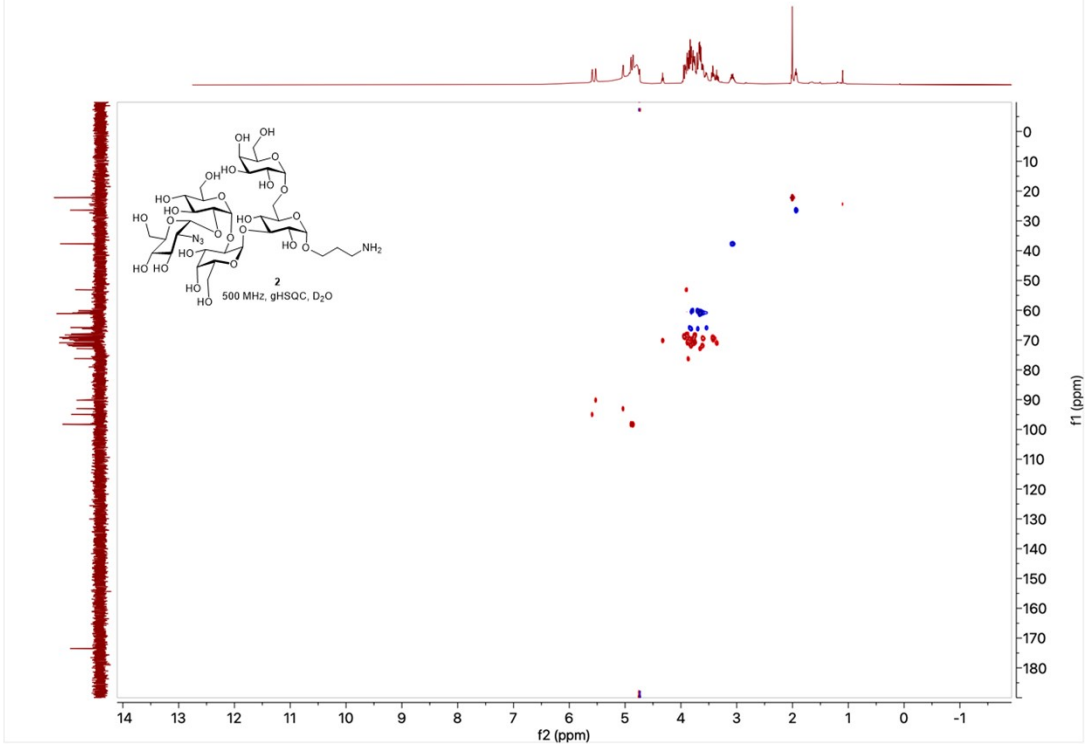

1
800 MHz,gHMBC, D2O
f1 (ppm)
f2 (ppm)

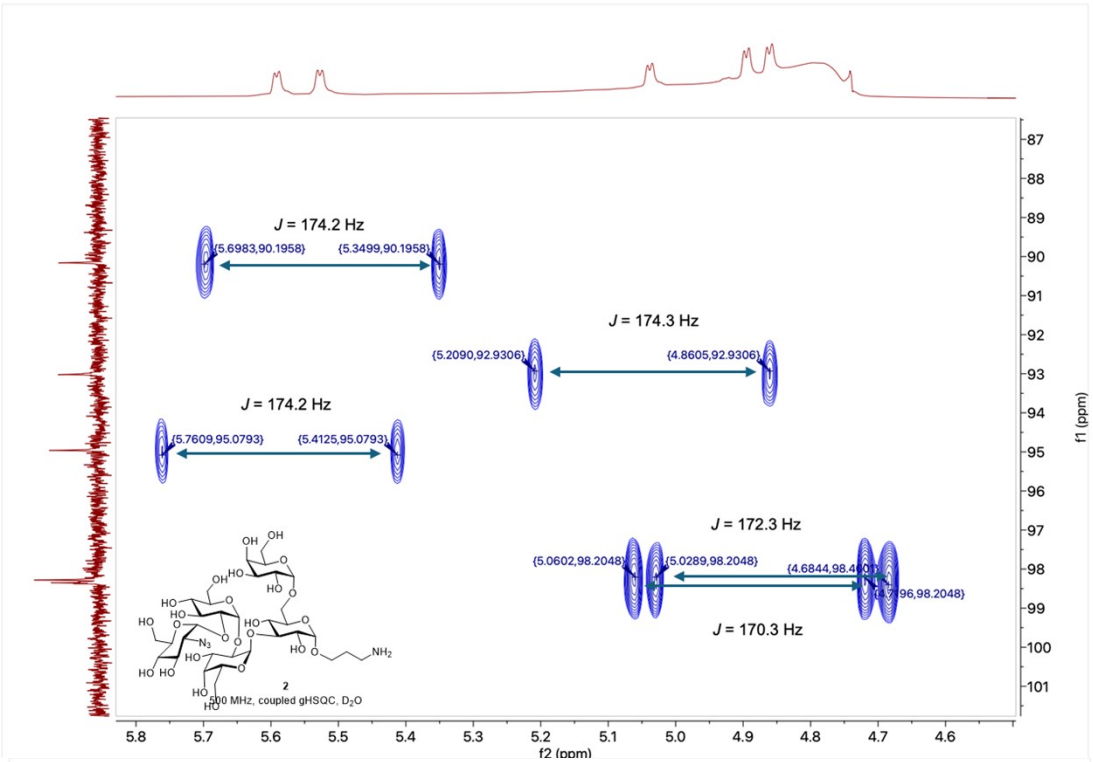

panta-6-2
XS2_010122_002 23 (0.248)
1: TOF MS ES+
9.92e4
100
%
0
886.3397
887.3417
926.3766
927.3825
982.4310
996.4143
1074.3040
1222.3483
1370.3768
223.0654
149.0252
261.0528
371.1019
391.2849
663.4545
702.2117
123.0912
115.0571
1
HRMS (ESI)
m/z
-0 100 200 300 400 500 600 700 800 900 1000 1100 1200 1300 1400 1500 1600 1700 1800 1900 2000 2100 2200 2300 2400 2500 2600 2700 2800 2900 3000 3100

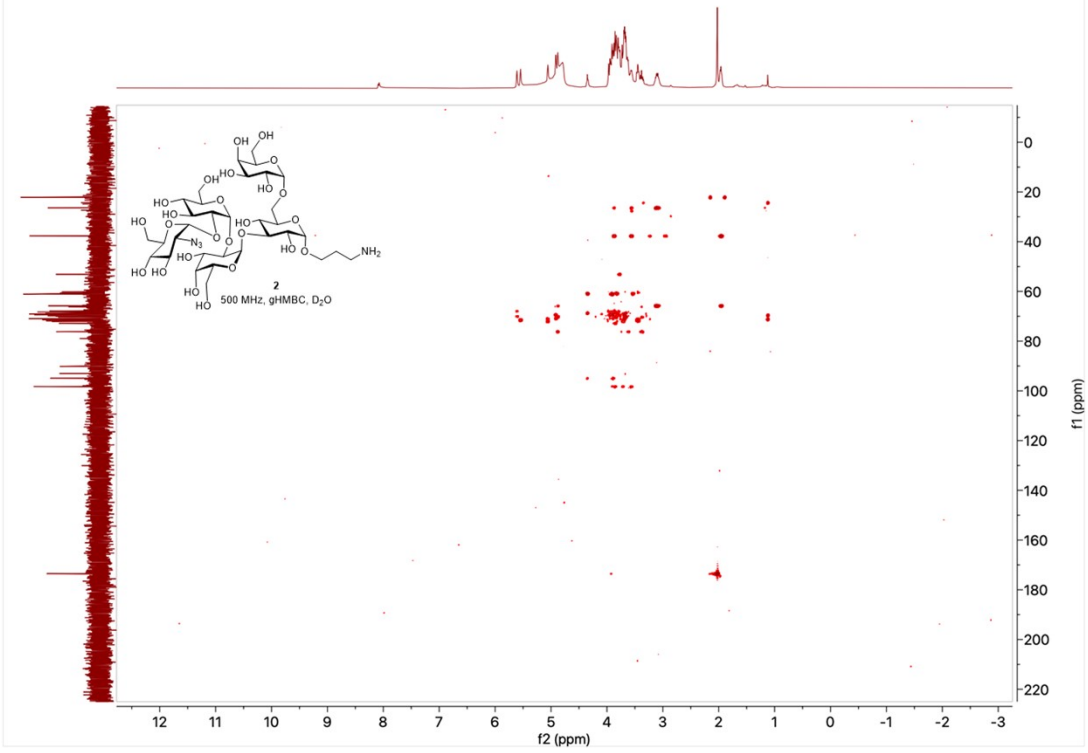

2
500 MHz, ^{1}H-NMR, D_2O
f1 (ppm)

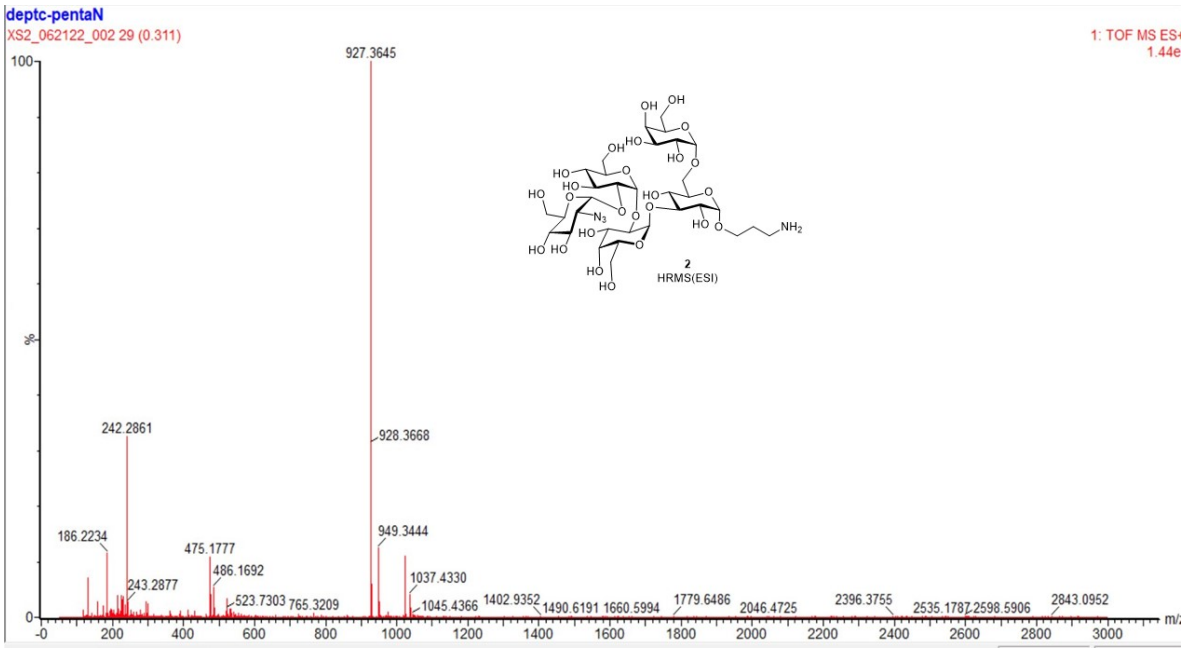

2
150 MHz, ^{13}C-NMR, D_2O
f1 (ppm)


2
500 MHz, gCOSY, D2O
f2 (ppm)
f1 (ppm)


2
500 MHz, gHSQC, D2O
f2 (ppm)
f1 (ppm)


J = 174.2 Hz
{5.6983,90.1958}
{5.3499,90.1958}
J = 174.3 Hz
{5.2090,92.9306}
{4.8605,92.9306}
J = 174.2 Hz
{5.7609,95.0793}
{5.4125,95.0793}
J = 172.3 Hz
{5.0602,98.2048}
{5.0289,98.2048}
J = 170.3 Hz
2
500 MHz, coupled gHSQC, D2O
f2 (ppm)
f1 (ppm)


2
500 MHz, gHMBC, D2O
f2 (ppm)
f1 (ppm)


deptc-pentaN
XS2_062122_002 29 (0.311)
1: TOF MS ES
1.44e
100
%
0
927.3645
928.3668
242.2861
949.3444
186.2234
475.1777
486.1692
243.2877
1037.4330
523.7303
765.3209
1045.4366
1402.9352
1490.6191
1660.5994
1779.6486
2046.4725
2396.3755
2535.1787
2598.5906
2843.0952
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