Supporting Information

Chemoenzymatic Synthesis of *Campylobacter jejuni* Lipo-oligosaccharide Core Domains to Examine Guillain-Barré Syndrome Serum Antibody Specificities

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Table of Contents

1. General materials and methods

Organic reactions were performed under an atmosphere of argon using anhydrous solvents unless otherwise noted. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on a Varian/Agilent 600 (at 600 MHz). Multiplicities were given as singlet (s), broad signal (br), doublet (d), doublet of doublets (dd), triplet (t) or multiplet (m). Carbon nuclear magnetic resonance (^{13}C) spectra were recorded on Varian/Agilent 600 (at 150 MHz). Spectra were assigned using gCOSY, HSQCAD, HMBCAD, zTOCSY and NOESY experiments. The stereochemistry of glycosidic linkage was confirmed by bsHSQCAD for coupling constant between the anomeric carbon and proton ($J_{\mathrm{C1\text{-}H1}}$), and EXSIDE for coupling constant between the C1 and H3ax of Kdo ($^3J_{C1\text{-}H3ax}$). MALDI spectra were recorded on an AB SCIEX TOF/TOF 5800 system instrument using 2,5-dihydroxybenzoic acid (DHB) as matrix. ESI-MS spectra were recorded on Shimadzu LC-ESI-IT-TOF. LC-MS analysis was recorded on Shimadzu LC-ESI-IT-TOF with XBridge® Amide 5 µm, 4.6 mm x 250 mm column (Waters). Purification was performed by Shimadzu LC-ESI-IT-TOF with XBridge® Amide 5 µm, 10 mm x 250 mm column (Waters). Thin layer chromatography (TLC) was carried out on Merck silica gel 60 F_{254} coated aluminum sheets. TLC plates were detected with UV-absorption (254 nm), and sprayed with 10% sulfuric acid in ethanol (1:9, v/v), followed by heating for visualization. Flash column chromatography was performed on Combi*Flash*®*Rf* (Teledyne Isco) with the pre-packed Redi*Sep*®*Rf* silica normal-phase silica flash columns. Size-exclusion chromatography was performed on Sephadex LH-20, Bio-Gel P-2 or P-4 (45-90 µm) column. Molecular sieves were activated prior to use. Chemical reagents were purchased from Sigma-Aldrich and TCI America.

Cytidine-5′-monophospho-*N*-acetylneuraminic acid (CMP-Neu5Ac) and uridine 5′-diphosphogalactose (UDP-Gal) were purchased from Roche Life Science. Uridine 5′-diphospho-*N*-acetylgalactosamine (UDP-GalNAc) was purchased from Carbosynth Ltd. *Pasteurella multocida* α2,3-sialyltransferase 1 (PmST1), *Campylobacter jejuni* β1,4-*N*-acetylgalactosaminyltransferase (CgtA), *Campylobacter jejuni β*1,3-galactosyltransferase (CgtB), and *Campylobacter jejuni* α2,8-sialyltransferase (CstII) were purchased from Chemily Glycoscience. Calf intestine alkaline phosphatase (CIAP), α2-3,6,8 neuraminidase from *Clostridium perfringens* and α2-3,6,8,9 neuraminidase A from *Arthrobacter ureafaciens* were purchased from BioLabs® Inc*.* α2-3,6,8 Neuraminidase from *Vibrio cholerae* was purchased from Sigma-Aldrich.

2. Chemical synthesis

2.1. Synthesis of a 3,4-branched heptose trisaccharide

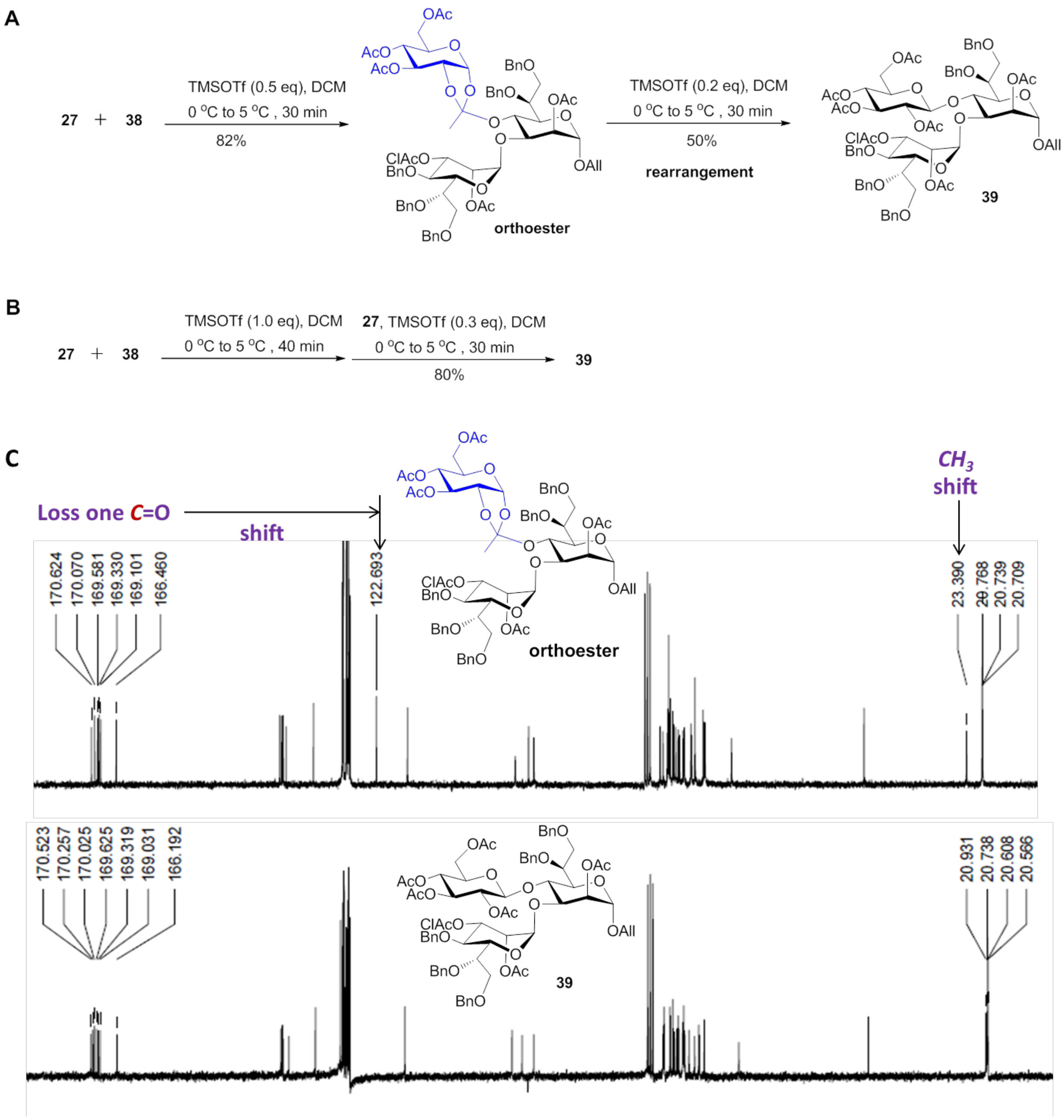


Figure S1. Synthesis of a 3,4-branched heptose trisaccharide.

2,3,4,6-Tetra-acetyl glucosyl donor **27** (1.5 eq) was coupled with disaccharide acceptor **38** (1.0 eq) using TMSOTf (0.5 eq) as the activator to afford an orthoester trisaccharide in 82% yield, which was rearranged in the presence of TMSOTf (0.2 eq) to give the 3,4-branched heptose trisaccharide **39** in 50% yield (Figure S1A). The structural identification of both compounds was established by examining characteristic signals in ^{13}C-NMR spectra. The orthoester trisaccharide showed loss a carbon signal of carbonyl group and shift to 122.69 ppm compared with heptose trisaccharide **39** in ^{13}C-NMR spectra (Figure S1C**)**. However, coupling glucosyl donor **27** (1.5 eq) with disaccharide acceptor **38** (1.0 eq) in the presence of TMSOTf (1.0 eq) for 40 min showed that the major product **39** was generated and acceptor **38** still remained. Subsequently, additional donor **27** (1.0 eq) and TMSOTf (0.3 eq) were added and stirred for 30 min to afford the heptose trisaccharide **39** in 80% yield, which was confirmed by NMR analysis and no orthoester was produced (Figure S1B-C).

2.2. Initial synthesis of Kdo2 acceptor

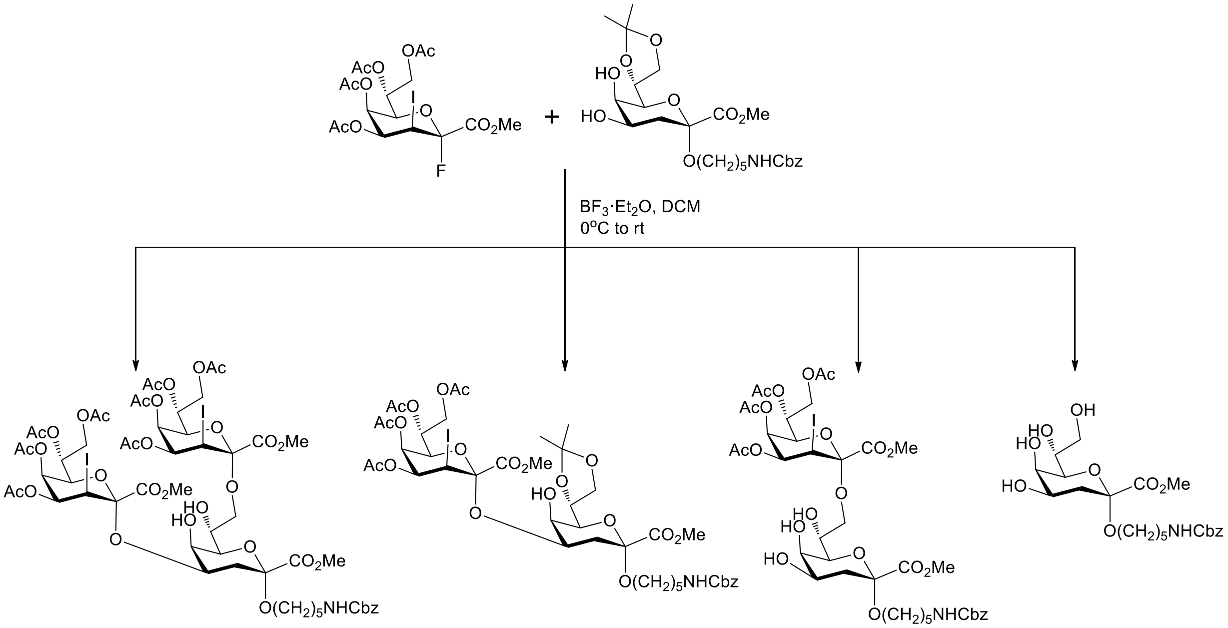


Figure S2. Initial synthesis of Kdo2 acceptor led to complex reaction system.

Based on the activity difference of 4-hydroxyl and 5-hydroxyl of Kdo as glycosyl acceptor and reducing the manipulations of protecting groups at a minimum, we only need to protect 7,8-diol for regioselective glycosylation of 4-hydroxyl without affecting axial 5-hydroxyl due to its low reactivity. Coupling 3-Iodo-Kdo fluoride glycosyl donor with 7,8-*O*-isopropylidene protected Kdo acceptor in the presence of $BF_3{\cdot}Et_2O$ (2 eq) indicated that partial isopropylidene acetal was cleaved, which resulted in complex reaction system, and yielded the mixture of a trisaccharide, two disaccharides and an unprotected Kdo with isopropylidene cleavage.

2.3. Initial strategy for synthesis of fully protected hexasaccharide

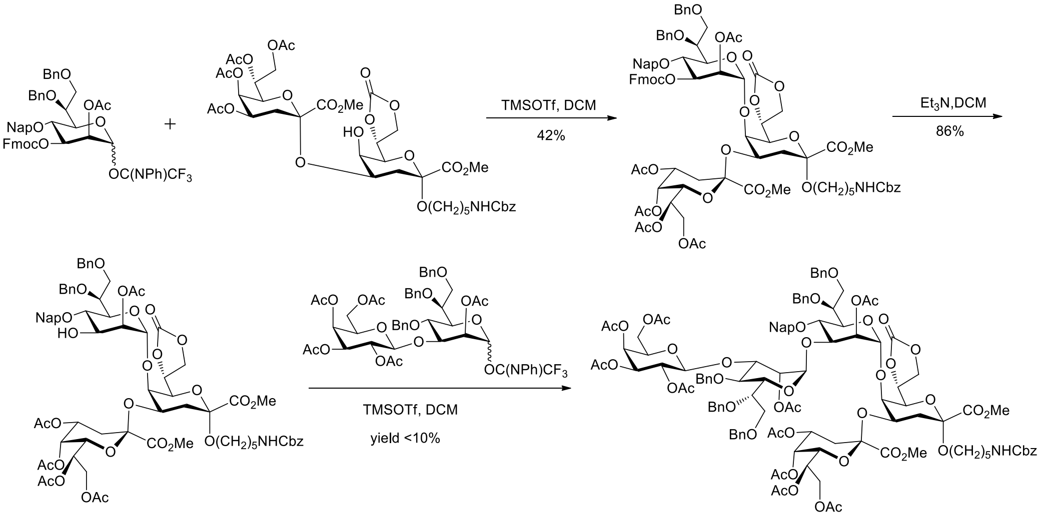


Figure S3. Initial synthesis of fully protected hexasaccharide by a convergent and stereo–controlled [2+3+1] approach.

The challenging α-Hep-(1→5)-Kdo glycosidic bond was firstly constructed to give α-Hep-(1→5)-Kdo-α-(2→4)-Kdo trisaccharide. Subsequently, removal of Fmoc afforded a trisaccharide glycosyl acceptor, which was coupled with β-Gal-(1→3)-Hep disaccharide glycosyl donor to give a protected pentasaccharide for further glucosylation. Unfortunately, although the pentasaccharide was detected by MALDI-MS, it was difficult to purify and the yield was unacceptably low (<10%). Probably, the steric hindrance of the C-3” hydroxy group of α-Hep-(1→5)-Kdo-α-(2→4)-Kdo trisaccharide led to failure of the glycosylation.

2.4. Synthesis of Kdo2 acceptor 29

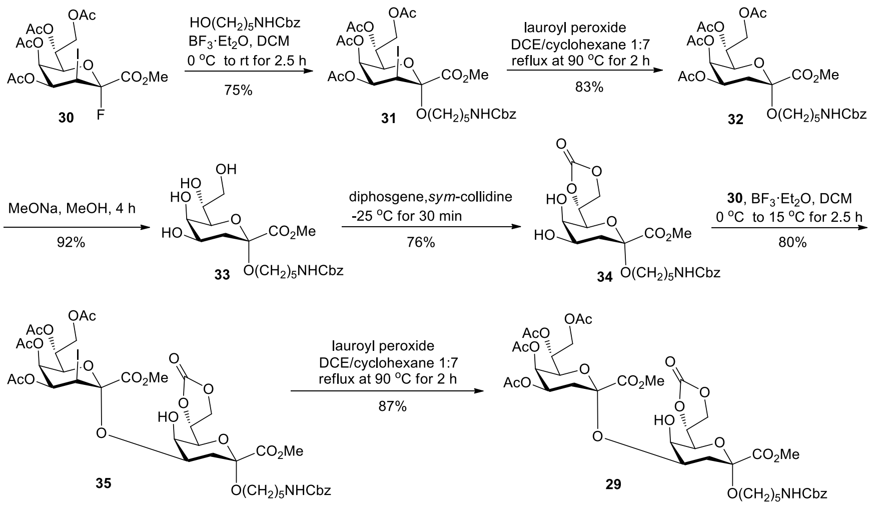
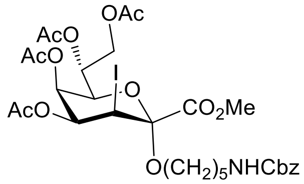


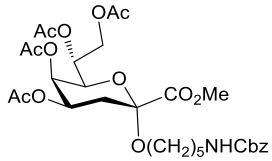
Figure S4. Synthesis of Kdo2 acceptor **29**.



31

Methyl [2-*O*-(5-amino-*N*-benzyloxycarbonylpentyl)-4,5,7,8-tetra-*O*-acetyl-3-deoxy-3-iodo-D-glycero-α-D-talo-oct-2-ulopyranosyl]onate (31)[1,2]

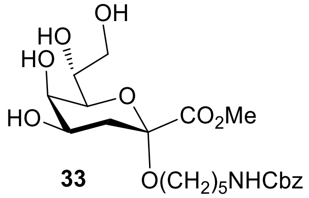
A mixture of 3-Iodo-Kdo fluoride glycosyl donor **30** (130 mg, 0.237 mmol), 5-amino-*N*-benzyloxycarbonylpentanol (67.5 mg, 0.284 mmol) and freshly activated 3 Å molecular sieves in anhydrous CH_2Cl_2 (6 mL) was stirred for 1 h at room temperature (RT) under an atmosphere of argon. The mixture was cooled to 0 °C, and $BF_3{\cdot}Et_2O$ (59 µL, 0.474 mmol) was added dropwise. The reaction mixture was slowly warmed to RT in 2.5 h, TLC analysis showed conversion of compound **30** to a major product **31** (hexane/ethyl acetate 2:1, v/v, R_f = 0.21). The reaction was quenched by the addition of trimethylamine (0.1 mL), and the reaction mixture was filtered by celite. The filtrate was concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (20% ethyl acetate in hexane to 40%) to afford compound **31** (136 mg, 75%) as colorless oil and a glycal (8 mg, 8%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.35-1.40 (m, 2 H, $CH_2CH_2\mathit{CH_2}CH_2CH_2$NHCbz), 1.49-1.61 (m, 4 H, $CH_2\mathit{CH_2}CH_2\mathit{CH_2}CH_2$NHCbz), 1.96 (s, 3 H, $\mathit{CH_3}$CO), 2.03 (s, 3 H, $\mathit{CH_3}$CO), 2.04 (s, 3 H, $\mathit{CH_3}$CO), 2.10 (s, 3 H, $\mathit{CH_3}$CO), 3.14-3.19 (m, 3H, $CH\mathit{H}CH_2CH_2CH_2\mathit{CH_2}$NHCbz), 3.55-3.58 (m, 1 H, $\mathit{CH}HCH_2CH_2CH_2CH_2$NHCbz), 3.83 (s, 3 H, $CO_2\mathit{CH_3}$), 4.17-4.20 (m, 2 H, H-8a, H-6), 4.47 (d, *J* = 4.2 Hz, 1 H, H-3), 4.65 (d, *J* = 12.0 Hz, 1H, H-8b), 4.81 (br, 1 H, *NH*Cbz), 5.02 (t, *J* = 3.6 Hz, 1 H, H-4), 5.07-5.13 (m, 2 H, $O{=}CO\mathit{CH_2}$Ph), 5.34-5.36 (m, 1 H, H-7), 5.40 (s, 1 H, H-5), 7.30-7.34 (m, 4 H, H-Ar); ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.57 ($\mathit{CH_3}$CO), 20.73 ($\mathit{CH_3}$CO), 20.82 ($\mathit{CH_3}$CO), 20.92 ($\mathit{CH_3}$CO), 22.32 (C-3), 23.21 ($CH_2CH_2\mathit{CH_2}CH_2CH_2$NHCbz), 28.96 ($CH_2\mathit{CH_2}CH_2CH_2CH_2$NHCbz), 29.70 ($CH_2CH_2CH_2\mathit{CH_2}CH_2$NHCbz), 40.82 ($CH_2CH_2CH_2CH_2\mathit{CH_2}$NHCbz), 53.00 ($CO_2\mathit{CH_3}$), 61.77 (C-8), 63.23 (C-5), 65.39 (C-4), 65.79 ($\mathit{CH_2}CH_2CH_2CH_2CH_2$NHCbz), 66.61 ($O{=}CO\mathit{CH_2}$Ph), 67.43 (C-7), 67.78 (C-6), 101.66 (C-2), 128.09-136.52 (*C*-Ar), 156.35 (*O*=$COCH_2$Ph), 166.28 (C-1), 169.44 (2x*O*=*C*CH_3), 170.17 (*O*=*C*CH_3), 170.26 (*O*=*C*CH_3); MALDI-TOF-MS: $[M+Na]^+$ calcd for $C_{30}H_{40}INO_{14}Na$, 788.1391; found 788.2600.



32

Methyl [2-*O*-(5-amino-*N*-benzyloxycarbonylpentyl)-4,5,7,8-tetra-*O*-acetyl-3-deoxy-α-D-manno-oct-2-ulopyranosid]onate (32)[3]

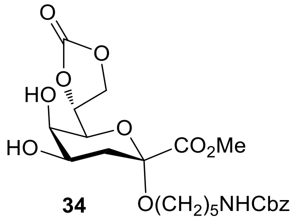
A solution of compound **31** (100 mg, 0.13 mmol) in $ClCH_2CH_2Cl$ (2.5 mL) and cyclohexane (17.5 mL) was degassed with argon, and heated under reflux (90 °C) for 15 min. Lauroyl peroxide (31 mg, 0.078 mmol) was added, and the reflux was continued for 2 h. MALDI-TOF-MS analysis showed complete conversion of **31** into a major product **32**. The reaction mixture was cooled to RT, and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (20% ethyl acetate in hexane to 40%) to give compound **32** (69 mg, 83%) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.30-1.32 (m, 2 H, $CH_2CH_2\mathit{CH_2}CH_2CH_2NHCbz$), 1.43-1.55 (m, 4 H, $CH_2\mathit{CH_2}CH_2\mathit{CH_2}CH_2NHCbz$), 1.89 (s, 3 H, $\mathit{CH_3}CO$), 1.91 (s, 3 H, $\mathit{CH_3}CO$), 1.95-2.00 (m, 7 H, 2x$\mathit{CH_3}CO$, H-3ax), 2.09 (dd, *J* = 4.8, 12.6 Hz, 1 H, H-3eq), 3.10-3.12 (m, 2 H, $CH_2CH_2CH_2CH_2\mathit{CH_2}NHCbz$), 3.21-3.25 (m, 1 H, $CH\mathit{H}CH_2CH_2CH_2CH_2NHCbz$), 3.39-3.41 (m, 1 H, $\mathit{CH}HCH_2CH_2CH_2CH_2NHCbz$), 3.72 (s, 3 H, $CO_2\mathit{CH_3}$), 4.00 (d, *J* = 9.6 Hz, 1 H, H-6), 4.06 (dd, *J* = 3.0, 12.6 Hz, 1 H, H-8a), 4.51 (d, *J* = 12.0 Hz, H-8b), 5.00-5.06 (m, 3 H, *NH*Cbz, $O{=}CO\mathit{CH_2}Ph$), 5.14-5.16 (m, 1 H, H-7), 5.26 (dd, *J* = 3.6, 12.0 Hz, 1 H, H-4), 5.29 (s, 1 H, H-5), 7.22-7.27 (m, 4 H, H-Ar); ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.57 ($\mathit{CH_3}CO$), 20.58 ($\mathit{CH_3}CO$), 20.65 ($\mathit{CH_3}CO$), 20.70 ($\mathit{CH_3}CO$), 23.28 ($CH_2CH_2\mathit{CH_2}CH_2CH_2NHCbz$), 29.00 ($CH_2\mathit{CH_2}CH_2CH_2CH_2NHCbz$), 29.68 ($CH_2CH_2CH_2\mathit{CH_2}CH_2NHCbz$), 32.01 (C-3), 40.80 ($CH_2CH_2CH_2CH_2\mathit{CH_2}NHCbz$), 52.63 ($CO_2\mathit{CH_3}$), 61.95 (C-8), 63.71 ($\mathit{CH_2}CH_2CH_2CH_2CH_2NHCbz$), 64.26 (C-5), 66.33 (C-4), 66.41 ($O{=}CO\mathit{CH_2}Ph$), 67.50 (C-7), 68.04 (C-6), 98.71 (C-2), 127.96-136.61 (*C*-Ar), 156.37 ($\mathit{O{=}C}OCH_2Ph$), 167.75 (C-1), 169.58 ($\mathit{O{=}C}CH_3$), 169.89 ($\mathit{O{=}C}CH_3$), 170.33 ($\mathit{O{=}C}CH_3$), 170.36 ($\mathit{O{=}C}CH_3$); MALDI-TOF-MS: $[M+Na]^+$ calcd for $C_{30}H_{41}NO_{14}Na$, 662.2425; found 662.4012.



33

Methyl [2-*O*-(5-amino-*N*-benzyloxycarbonylpentyl)-3-deoxy-α-D-manno-oct-2-ulopyranosid]onate (33)

A solution of compound **32** (480 mg, 0.75 mmol) in dry CH_2Cl_2 (4 mL) and MeOH (8 mL) was added $NaOCH_3$ (cat.) to adjust pH ~10. The reaction mixture was stirred for 4 h at RT under an atmosphere of argon. MALDI-TOF-MS analysis showed complete conversion of **32** into a major product **33**. The pH of reaction mixture was neutralized to ~7 by Amberlite® IR120 H^+ form resin, and the mixture was filtered. The filtrate was concentrated under reduced pressure to afford **33** (325 mg, 92%) as colorless oil. ^{1}H NMR (600 MHz, CD_3OD): δ 1.37-1.41 (m, 2H, $CH_2CH_2\mathit{CH_2}CH_2CH_2NHCbz$), 1.48-1.52 (m, 2H, $CH_2CH_2CH_2\mathit{CH_2}CH_2NHCbz$), 1.54-1.57 (m, 2 H, $CH_2\mathit{CH_2}CH_2CH_2CH_2NHCbz$), 1.90 (t, *J* = 12.0 Hz, 1 H, H-3ax), 2.01 (dd, *J* = 4.8, 12.0 Hz, 1 H, H-3eq), 3.10 (t, *J* = 7.2 Hz, 2 H, $CH_2CH_2CH_2CH_2\mathit{CH_2}NHCbz$), 3.18-3.22 (m, 1H, $CH\mathit{H}CH_2CH_2CH_2CH_2NHCbz$), 3.52-3.56 (m, 1 H, $\mathit{CH}HCH_2CH_2CH_2CH_2NHCbz$), 3.60 (d, *J* = 8.4 Hz, 1 H, H-6), 3.63 (dd, *J* = 5.4, 11.4 Hz, 1 H, H-8a), 3.76 (s, 3 H, $CO_2\mathit{CH_3}$), 3.81 (dd, *J* = 3.6, 11.4 Hz, 1 H, H-8b), 3.92-3.99 (m, 3 H, H-7, H-4, H-5), 5.06 (s, 2 H, O=CO*CH$_2$*Ph), 7.28-7.34 (m, 4 H, H-Ar); ^{13}C NMR (150 MHz, CD$_3$OD): δ 24.44 (CH$_2$CH$_2$*CH$_2$*CH$_2$CH$_2$NHCbz), 30.18 (CH$_2$*CH$_2$*CH$_2$CH$_2$CH$_2$NHCbz), 30.66 (CH$_2$CH$_2$CH$_2$*CH$_2$*CH$_2$NHCbz), 35.65 (C-3), 41.69 (CH$_2$CH$_2$CH$_2$CH$_2$*CH$_2$*NHCbz), 52.95 (CO$_2$*CH$_3$*), 64.34 (*CH$_2$*CH$_2$CH$_2$CH$_2$CH$_2$NHCbz), 64.50 (C-8), 67.29 (C-4 and O=CO*CH$_2$*Ph), 67.61 (C-5), 70.77 (C-7), 73.35 (C-6), 100.07 (C-2), 128.75-138.45 (*C*-Ar), 158.90 (*O*=*C*OCH$_2$Ph), 170.87 (C-1, $^{3}J_{C1\text{-}H3ax}$ < 1 Hz); EXSIDE NMR was used to calculate coupling constant between the C1 and H3ax of Kdo ($^{3}J_{C1\text{-}H3ax}$); MALDI-TOF-MS: [M+Na]$^+$ calcd for C$_{22}$H$_{33}$NO$_{10}$Na, 494.2002; found 494.2910.

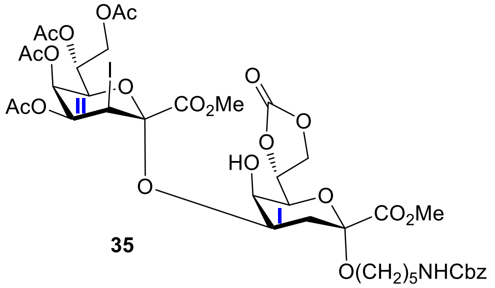


34

Methyl [2-*O*-(5-amino-*N*-benzyloxycarbonylpentyl)-7,8-*O*-carbonyl-3-deoxy-α-D-manno-oct-2-ulopyranosid]onate (34)

A solution of compound **33** (310 mg, 0.66 mmol) in dry THF (15 mL) was added *sym*-collidine (436 µL, 3.30 mmol, 5 eq) under an atmosphere of argon, and the mixture was cooled to -30 °C. A freshly prepared solution of diphosgene (80 µL, 0.66 mmol, 1 eq) in dry THF (1.5 mL) was slowly added at -30 °C to -25 °C, and the reaction mixture was stirred for 30 min at -25 °C. The reaction was quenched by the addition of dry MeOH (0.5 mL) at -25 °C. The reaction mixture was concentrated under reduced pressure. The resulting residue was dissolved in CH$_2$Cl$_2$ (50 mL), and washed with 1 M HCl (20 mL), the aqueous phase was re-extracted with CH$_2$Cl$_2$ three times (3x40 mL). The combined organic phase was dried (Na$_2$SO$_4$), filtered, and the filtrate was concentrated under reduced pressure. The resulting residue was purified by silica gel column (2% MeOH in CH$_2$Cl$_2$ to 5%) to give a syrup, which was further purified by size-exclusion chromatography (Sephadex LH-20) in CH$_2$Cl$_2$/MeOH (1/1, v/v) to afford compound **34** (248 mg, 76%) as colorless oil. ^{1}H NMR (600 MHz, CDCl$_3$): δ 1.34-1.38 (m, 2 H, CH$_2$CH$_2$*CH$_2$*CH$_2$CH$_2$NHCbz), 1.47-1.55 (m, 4 H, CH$_2$*CH$_2$*CH$_2$*CH$_2$*CH$_2$NHCbz), 1.86 (t, *J* = 12.6 Hz, 1 H, H-3ax), 1.95 (br, 1 H, OH), 2.08 (dd, *J* = 4.8, 12.6 Hz, 1 H, H-3eq), 3.09-3.16 (m, 3 H, OH, CH$_2$CH$_2$CH$_2$CH$_2$*CH$_2$*NHCbz), 3.27-3.31 (m, 1 H, CH*H*CH$_2$CH$_2$CH$_2$CH$_2$NHCbz), 3.40-3.44 (m, 1 H, *CH*HCH$_2$CH$_2$CH$_2$CH$_2$NHCbz), 3.76 (s, 3 H, CO$_2$*CH$_3$*), 3.85-3.91 (m, 2 H, H-5, H-6), 4.10-4.12 (m, 1 H, H-4), 4.52 (t, *J* = 8.4 Hz, 1 H, H-8a), 4.73 (t, *J* = 8.4 Hz, 1 H, H-8b), 4.90-4.93 (m, 1 H, H-7), 4.98 (br, 1 H, *NH*Cbz), 5.06-5.11 (m, 2 H, O=CO*CH$_2$*Ph), 7.29-7.35 (m, 4 H, H-Ar); ^{13}C NMR (150 MHz, CDCl$_3$): δ 23.25 (CH$_2$CH$_2$*CH$_2$*CH$_2$CH$_2$NHCbz), 28.83 (CH$_2$*CH$_2$*CH$_2$CH$_2$CH$_2$NHCbz), 29.53 (CH$_2$CH$_2$CH$_2$*CH$_2$*CH$_2$NHCbz), 34.41 (C-3), 40.88 (CH$_2$CH$_2$CH$_2$CH$_2$*CH$_2$*NHCbz), 52.77 (CO$_2$*CH$_3$*), 63.61 (*CH$_2$*CH$_2$CH$_2$CH$_2$CH$_2$NHCbz), 65.06 (C-4), 66.27 (C-8), 66.61 (O=CO*CH$_2$*Ph), 66.96 (C-5), 70.94 (C-6), 76.32 (C-7), 99.01 (C-2), 127.99-138.52 (*C*-Ar), 155.05 (O*C*(=O)O), 156.59

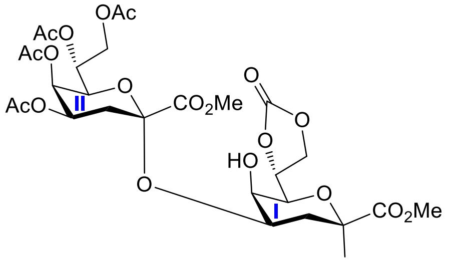
(*O*=*C*OCH$_2$Ph), 168.61 (C-1); MALDI-TOF-MS: [M+Na]$^+$ calcd for $C_{23}H_{31}NO_{11}Na$, 520.1795; found 520.2401.



35

Methyl [4,5,7,8-tetra-*O*-acetyl-3-deoxy-3-iodo-D-glycero-α-D-talo-oct-2-ulopyranosyl]onate)-(2→4)-2-*O*-(5-amino-*N*-benzyloxycarbonylpentyl)-7,8-*O*-carbonyl-3-deoxy-α-D-manno-oct-2-ulopyranosid)onate (35)

A mixture of 3-Iodo-Kdo fluoride glycosyl donor **30** (197 mg, 0.36 mmol), glycosyl acceptor **34** (167 mg, 0.34 mmol), and freshly activated 3 Å molecular sieves in anhydrous CH_2Cl_2 (8 mL) was stirred for 1 h at RT under an atmosphere of argon. The mixture was cooled to 0 °C, and $BF_3{\cdot}Et_2O$ (84 µL, 0.68 mmol) was added dropwise. The reaction mixture was slowly warmed to 15 °C in 2 h. TLC analysis showed conversion of donor **30** to a major product (50 % ethyl acetate in toluene, R_f = 0.31). The reaction was quenched by the addition of triethylamine (0.1 mL) and filtered by celite. The filtrate was concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (30% ethyl acetate in toluene to 70%) to afford compound **35** (280 mg, 80%) as colorless oil and a glycal (8 mg, 6%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.27-1.30 (m, 2 H, CH$_2$CH$_2$*CH$_2$*CH$_2$CH$_2$NHCbz), 1.46-1.52 (m, 4 H, CH$_2$*CH$_2$*CH$_2$*CH$_2$*CH$_2$NHCbz), 1.94 (s, 3 H, *CH$_3$*CO), 2.05-2.14 (m, 11 H, 3x*CH$_3$*CO, H-3ax-Kdo-I, H-3eq-Kdo-I), 2.48 (s, 1 H, OH), 3.13-3.17 (m, 2 H, CH$_2$CH$_2$CH$_2$CH$_2$*CH$_2$*NHCbz), 3.29-3.33 (m, 1 H, CH*H*CH$_2$CH$_2$CH$_2$CH$_2$NHCbz), 3.39-3.43 (m, 1 H, *CH*HCH$_2$CH$_2$CH$_2$CH$_2$NHCbz), 3.59 (s, 1 H, H-5-Kdo-I), 3.77 (s, 3 H, CO$_2$*CH$_3$*-Kdo-I), 3.85-3.87 (m, 4 H, CO$_2$*CH$_3$*-Kdo-II, H-6-Kdo-I), 3.98 (dd, *J* = 4.2, 12.0 Hz, 1 H, H-8a-Kdo-II), 4.14-4.19 (m, 2 H, H-4-Kdo-I, H-6-Kdo-II), 4.49-4.52 (m, 2 H, H-3-Kdo-II, H-8a-Kdo-I), 4.71 (t, *J* = 8.4 Hz, 1 H, H-8b-Kdo-I), 4.76 (d, *J* = 12.0 Hz, 1 H, H-8b-Kdo-II), 4.84-4.87 (m, 1 H, H-7-Kdo-I), 4.90 (t, *J* = 4.2 Hz, 1 H, H-4-Kdo-II), 5.07-5.12 (m, 3 H, O=CO*CH$_2$*Ph, *NH*Cbz), 5.28-5.30 (m, 1 H, H-7-Kdo-II), 5.41 (s, 1 H, H-5-Kdo-II), 7.28-7.35 (m, 4 H, H-Ar); ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.50 (*CH$_3$*CO), 20.69 (*CH$_3$*CO), 20.79 (*CH$_3$*CO), 20.93 (*CH$_3$*CO), 22.02 (C-3-Kdo-II), 23.16 (CH$_2$CH$_2$*CH$_2$*CH$_2$CH$_2$NHCbz), 28.81 (CH$_2$*CH$_2$*CH$_2$CH$_2$CH$_2$NHCbz), 29.43 (CH$_2$CH$_2$CH$_2$*CH$_2$*CH$_2$NHCbz), 32.96 (C-3-Kdo-I), 40.77 (CH$_2$CH$_2$CH$_2$CH$_2$*CH$_2$*NHCbz), 52.78 (CO$_2$*CH$_3$*-Kdo-I), 53.50 (CO$_2$*CH$_3$*-Kdo-II), 61.49 (C-8-Kdo-II), 62.96 (C-5-Kdo-II), 63.76 (*CH$_2$*CH$_2$CH$_2$CH$_2$CH$_2$NHCbz), 64.33 (C-5-Kdo-I), 64.95 (C-4-Kdo-II), 66.00 (C-8-Kdo-I), 66.50 (O=CO*CH$_2$*Ph), 67.42 (C-7-Kdo-II), 69.60 (C-4-Kdo-I), 69.63 (C-6-Kdo-II), 70.20 (C-6-Kdo-I), 76.09 (C-7-Kdo-I), 98.68 (C-2-Kdo-I), 100.81 (C-2-Kdo-II), 127.99-136.66 (*C*-Ar), 154.64 (O*C*(=O)O), 156.47 (*O*=*C*OCH$_2$Ph), 167.06 (C1-Kdo-II), 167.72 (C1-Kdo-I), 169.30 (*O*=*C*CH$_3$), 169.42 ($\mathit{O}{=}\mathit{C}CH_3$), 169.97 ($\mathit{O}{=}\mathit{C}CH_3$), 170.85 ($\mathit{O}{=}\mathit{C}CH_3$); MALDI-TOF-MS: $[M+Na]^+$ calcd for $C_{40}H_{52}INO_{22}Na$, 1048.1923; found 1048.5782.



29

Methyl (methyl 4,5,7,8-tetra-*O*-acetyl-3-deoxy-α-D-manno-oct-2-ulopyranosyl)onate)-(2→4)-2-*O*-(5-amino-*N*-benzyloxycarbonylpentyl)-7,8-*O*-carbonyl-3-deoxy-α-D-manno-oct-2-ulopyranosid)onate (29)

A solution of compound **35** (270 mg, 0.263 mmol) in $ClCH_2CH_2Cl$ (5 mL) and cyclohexane (35 mL) was degassed with argon, and heated under reflux (90 °C) for 15 min. Lauroyl peroxide (63 mg, 0.158 mmol) was added, and the reflux was continued for 2 h. MALDI-TOF-MS analysis showed complete conversion of **35** into a major product **29**. The reaction mixture was cooled to RT, and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (30% ethyl acetate in toluene to 70%) to give compound **29** (205 mg, 87%) as colorless oil. ^1H NMR (600 MHz, $CDCl_3$): δ 1.28-1.32 (m, 2 H, $CH_2CH_2\mathit{CH_2}CH_2CH_2$NHCbz), 1.46-1.52 (m, 4 H, $CH_2\mathit{CH_2}CH_2\mathit{CH_2}CH_2$NHCbz), 1.96 (d, 6 H, 2x$\mathit{CH_3}$CO), 2.01-2.11 (m, 9 H, 2x$\mathit{CH_3}$CO, H-3ax-Kdo-II, H-3ax-Kdo-I, H-3eq-Kdo-I), 2.19 (dd, J = 4.8, 13.2 Hz, 1 H, H-3eq-Kdo-II), 2.53 (s, 1 H, OH), 3.13-3.16 (m, 2 H, $CH_2CH_2CH_2CH_2\mathit{CH_2}$NHCbz), 3.29-3.33 (m, 1 H, $CH\mathit{H}CH_2CH_2CH_2CH_2$NHCbz), 3.40-3.43 (m, 1 H, $\mathit{CH}HCH_2CH_2CH_2CH_2$NHCbz), 3.68 (s, 1 H, H-5-Kdo-I), 3.77 (s, 3 H, $CO_2\mathit{CH_3}$-Kdo-I), 3.82 (s, 3 H, $CO_2\mathit{CH_3}$-Kdo-II), 3.88 (m, 1 H, H-6-Kdo-I), 3.95 (dd, J = 4.2, 12.6 Hz, 1 H, H-8a-Kdo-II), 4.08 (d, J = 9.6 Hz, 1 H, H-6-Kdo-II), 4.21-4.23 (m, 1 H, H-4-Kdo-I), 4.50 (t, J = 9.0 Hz, 1 H, H-8a-Kdo-I), 4.70-4.75 (m, 2 H, H-8b-Kdo-II, H-8b-Kdo-I), 4.85-4.88 (m, 1 H, H-7-Kdo-I), 5.06-5.12 (m, 3 H, $O{=}CO\mathit{CH_2}$Ph, *NH*Cbz), 5.17-5.23 (m, 2 H, H-7-Kdo-II, H-4-Kdo-II), 5.35 (s, 1 H, H-5-Kdo-II), 7.28-7.34 (m, 4 H, H-Ar); ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.60 ($\mathit{CH_3}$CO), 20.65 ($\mathit{CH_3}$CO), 20.71 ($\mathit{CH_3}$CO), 20.74 ($\mathit{CH_3}$CO), 23.21 ($CH_2CH_2\mathit{CH_2}CH_2CH_2$NHCbz), 28.83 ($CH_2\mathit{CH_2}CH_2CH_2CH_2$NHCbz), 29.45 ($CH_2CH_2CH_2\mathit{CH_2}CH_2$NHCbz), 32.24 (C-3-Kdo-II), 33.11 (C-3-Kdo-I), 40.79 ($CH_2CH_2CH_2CH_2\mathit{CH_2}$NHCbz), 52.73 ($CO_2\mathit{CH_3}$-Kdo-I), 53.43 ($CO_2\mathit{CH_3}$-Kdo-II), 61.65 (C-8-Kdo-II), 63.67 ($\mathit{CH_2}CH_2CH_2CH_2CH_2$NHCbz), 64.01 (C-5-Kdo-II), 64.90 (C-5-Kdo-I), 65.84 (C-4-Kdo-II), 66.00 (C-8-Kdo-I), 66.44 ($O{=}CO\mathit{CH_2}$Ph), 67.48 (C-7-Kdo-II), 67.76 (C-4-Kdo-I), 69.65 (C-6-Kdo-II), 70.26 (C-6-Kdo-I), 76.34 (C-7-Kdo-I), 98.20 (C-2-Kdo-II), 98.74 (C-2-Kdo-I), 127.98-136.70 (*C*-Ar), 154.77 (O*C*(=O)O), 156.47 ($\mathit{O}{=}COCH_2$Ph), 167.89 (C-1-Kdo-I), 168.59 (C-1-Kdo-II), 169.55 ($\mathit{O}{=}\mathit{C}CH_3$), 169.95 ($\mathit{O}{=}\mathit{C}CH_3$), 170.26 ($\mathit{O}{=}\mathit{C}CH_3$), 170.94 ($\mathit{O}{=}\mathit{C}CH_3$); MALDI-TOF-MS: $[M+Na]^+$ calcd for $C_{40}H_{53}NO_{22}Na$, 922.2957; found 922.4725.

2.5. Synthesis of L,D-heptoside S6[4]

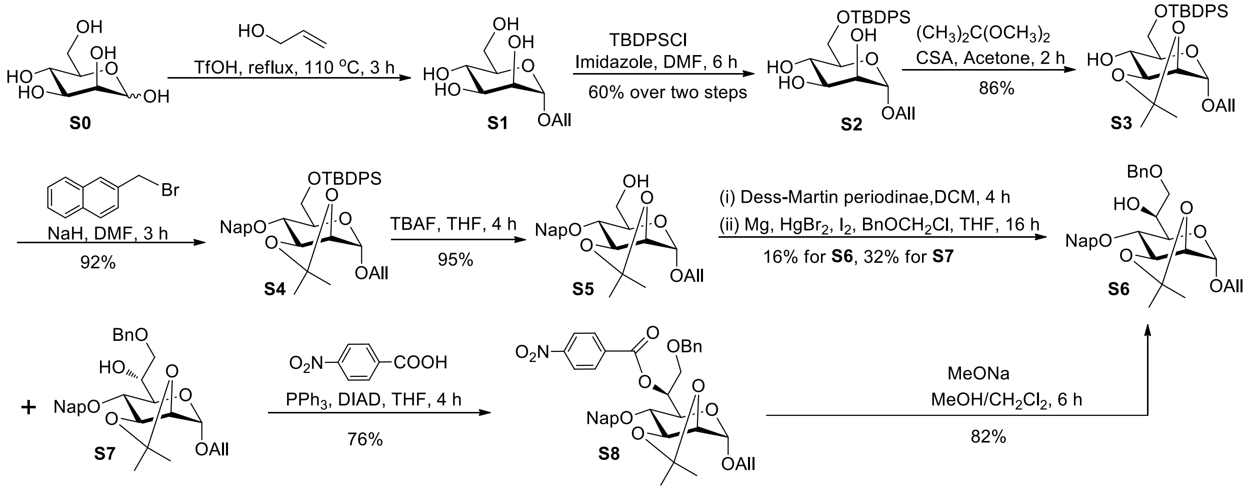
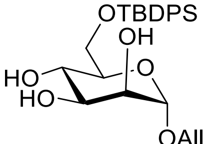


Figure S5. Synthesis of L,D-heptoside **S6**.

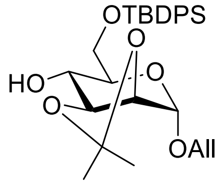


S2

Allyl 6-*O-tert*-butyldiphenylsilyl-α-D-mannopyranoside (S2)

A stirring mixture of D-mannose (13.5 g, 0.075 mol), allyl alcohol (100 mL) and trifluoromethanesulfonic acid (TfOH, 1 mL) was heated under reflux (110 °C) for 3 h. TLC analysis showed conversion of **S0** into a major product **S1** (dichloromethane/methanol 5:1, v/v, R_f = 0.67). The reaction was cooled to RT and neutralized with trimethylamine. The reaction mixture was concentrated under reduced pressure, and the resulting residue was co-evaporated with toluene (3 x 50 mL) *in vacuo* to afford **S1** as yellow oil, which was directly used for next step.

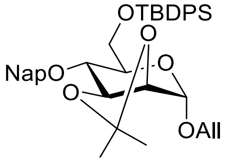
The resulting compound **S1** and imidazole (7.66 g, 0.1125 mol) were dissolved in dry DMF (80 mL) and cooled to 0 °C. *Tert*-butylchlorodiphenylsilane (TBDPSCl, 23.4 mL, 0.09 mol) was added slowly and the reaction mixture was stirred for 6 h at RT. TLC analysis indicated complete conversion of **S1** into a major product **S2** (dichloromethane/methanol 20:1, v/v, R_f = 0.47). The reaction was quenched with water (2 mL), and the reaction mixture was concentrated under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 (300 mL), and the mixture was washed with 1 M HCl (100 mL) and water (100 mL). The organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo.* The resulting residue was purified by silica gel column chromatography (2% methanol in dichloromethane to 3%) to give compound **S2** (20.5 g, 60%, over two steps) as light yellow oil. ^{1}H NMR (600 MHz, CD_3OD): δ 1.03 (s, 9 H, *t*-Bu), 3.53 (t, *J* = 9.6 Hz, 1 H, H-4), 3.67-3.70 (m, 2 H, H-3, H-5), 3.79-3.82 (m, 2 H, H-2, H-6a), 4.01-4.04 (m, 2 H, CH*H*-CH=CH$_2$, H-6b), 4.26 (dd, *J* = 4.8, 7.2 Hz, 1 H, *CH*H-CH=CH$_2$), 4.82 (d, *J* = 1.2 Hz, 1 H, H-1), 5.16 (dd, *J* = 1.8, 10.8 Hz, 1 H, CH$_2$-CH=CH*H*), 5.26 (dd, *J* = 1.8, 17.4 Hz, 1 H, CH$_2$-CH=*CH*H), 5.91-5.98 (m, 1 H, CH$_2$-*CH*=CH$_2$), 7.36-7.42 (m, 6 H, H-Ar), 7.70-7.73 (m, 4 H, H-Ar); ^{13}C NMR (150 MHz, CD$_3$OD): δ 20.11 (*C*-Si), 27.30 (*t*-Bu), 65.40 (C-6), 68.68 (C-4), 68.87 (*CH$_2$*-CH=CH$_2$), 72.09 (C-2), 72.82 (C-3), 75.34 (C-5), 100. 53 (C-1), 117.44 (CH$_2$-CH=*CH$_2$*), 128.69-134.84 (*C*-Ar), 135.53 (CH$_2$-*CH*=CH$_2$), 136.78 (*C*-Ar); MALDI-TOF-MS: [M+Na]$^+$ calcd for $C_{25}H_{34}O_6SiNa$, 481.2022; found 481.3226.



S3

Allyl 6-*O*-*tert*-butyldiphenylsilyl-2,3-*O*-isopropylidene-α-D-mannopyranoside (S3)

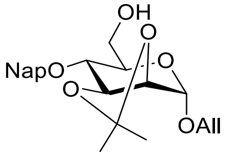
A solution of compound **S2** (11.45 g, 0.025 mol) in dry acetone (50 mL) was added dimethoxypropane (4.6 mL, 0.0375 mol) and camphorsulfonic acid (CSA, 348 mg, 0.0015 mol). The reaction mixture was stirred for 2 h at RT under an atmosphere of argon. TLC analysis showed complete conversion of **S2** to a major product **S3** (dichloromethane/methanol 20:1, v/v, R_f = 0.85). The reaction was quenched with triethylamine (2 mL), and the reaction mixture was concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (10% ethyl acetate in hexane to 18%) to give compound **S3** (10.7 g, 86%) as colorless oil. ^{1}H NMR (600 MHz, CDCl$_3$): δ 1.05 (s, 9 H, *t*-Bu), 1.34 (s, 3 H, CH$_3$), 1.49 (s, 3 H, CH$_3$), 2.73 (d, *J* = 3.6 Hz, 1 H, OH), 3.65-3.68 (m, 1 H, H-5), 3.77-3.80 (m, 1 H, H-4), 3.85-3.91 (m, 2 H, H-6a, H-6b), 3.95 (dd, *J* = 6.0, 12.6 Hz, 1H, CH*H*-CH=CH$_2$), 4.13-4.17 (m, 3 H, H-2, H-3, *CH*H-CH=CH$_2$), 5.03 (s, H-1), 5.18 (dd, *J* = 1.8, 10.8 Hz, 1 H, CH$_2$-CH=CH*H*), 5.25 (dd, *J* = 1.8, 17.4 Hz, 1H, CH$_2$-CH=*CH*H), 5.83-5.89 (m, 1 H, CH$_2$-*CH*=CH$_2$), 7.36-7.44 (m, 6 H, H-Ar), 7.68-7.70 (m, 4 H, H-Ar); ^{13}C NMR (150 MHz, CDCl$_3$): δ 19.19 (*C*-Si), 26.13 (CH$_3$), 26.78 (*t*-Bu), 27.88 (CH$_3$), 64.62 (C-6), 67.85 (*CH$_2$*-CH=CH$_2$), 69.52 (C-5), 70.73 (C-4), 75.36 (C-2), 78.15 (C-3), 96.17 (C-1), 109.48 (*C*Me$_2$), 117.86 (CH$_2$-CH=*CH$_2$*), 127.72-129.81 (*C*-Ar), 135.55 (CH$_2$-*CH*=CH$_2$), 135.63 (*C*-Ar); MALDI-TOF-MS: [M+Na]$^+$ calcd for $C_{28}H_{38}O_6SiNa$, 521.2335; found 521.2610.



S4

Allyl 6-*O*-*tert*-butyldiphenylsilyl-4-*O*-(2-methylnaphthyl)-2,3-*O*-isopropylidene-α-D-mannopyranoside (S4)

A mixture of **S3** (10.7 g, 0.0214 mol) and 2-(bromomethyl)naphthalene (7.12 g, 0,0322 mol) in DMF (80 mL) was cooled to 0 °C. Sodium hydride (60% dispersion in mineral oil, 1.28 g, 0.0321 mmol) was added slowly. The reaction mixture was stirred for 3 h at RT under an atmosphere of argon. TLC analysis showed complete conversion of starting material **S3** to a major product **S4** (hexane/ethyl acetate 8:1, v/v, R_f = 0.53). The reaction was quenched with NH_4Cl (satd. aqueous, 2 mL), and the reaction mixture was concentrated *in vacuo*. The resulting residue was dissolved with CH_2Cl_2 (200 mL), and the mixture was washed with water (100 mL). The organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo.* The resulting residue was purified by silica gel column chromatography (4% ethyl acetate in hexane to 8%) to give compound **S4** (12.62 g, 92%) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.04 (s, 9 H, *t*-Bu), 1.34 (s, 3 H, CH_3), 1.53 (s, 3 H, CH_3), 3.68 (dd, *J* = 7.2, 10.2 Hz, 1 H, H-4), 3.74-3.77 (m, 1 H, H-5), 3.87 (dd, *J* = 4.8, 10.8 Hz, 1 H, H-6a), 3.96 (dd, *J* = 1.2, 10.8 Hz, 1 H, H-6b), 4.00 (dd, *J* = 6.6, 12.6 Hz, 1 H, CH*H*-CH=CH_2), 4.20-4.24 (m, 2 H, *CH*H-CH=CH_2 , H-2), 4.40 (t, *J* = 6.6 Hz, 1 H, H-3), 4.72 (d, *J* = 12.0 Hz, 1 H, CH*H*-Nap), 5.03 (d, *J* = 11.6 Hz, 1 H, *CH*H-Nap), 5.12 (s, 1 H, H-1), 5.18 (dd, *J* = 1.2, 10.2 Hz, 1 H, CH_2-CH=CH*H*), 5.26 (dd, *J* = 1.2, 17.4 Hz, 1H, CH_2-CH=*CH*H), 5.85-5.92 (m, 1 H, CH_2-*CH*=CH_2), 7.31-7.45 (m, 9 H, H-Ar), 7.69-7.80 (m, 8 H, H-Ar); ^{13}C NMR (150 MHz, $CDCl_3$): δ 19.28(*C*-Si), 26.41 (CH_3), 26.75 (*t*-Bu), 27.98 (CH_3), 63.31 (C-6), 67.52 (*CH_2*-CH=CH_2), 69.69 (C-5), 73.00 (*OCH_2*-Nap), 75.64 (C-4), 75.95 (C-2), 79.02 (C-3), 95.95 (C-1), 109.28 (*C*Me_2), 117.82 (CH_2-CH=*CH_2*), 125.73-133.29 (*C*-Ar), 133.61 (CH_2-*CH*=CH_2), 133.70-135.82 (*C*-Ar); MALDI-TOF-MS: $[M+Na]^+$ calcd for $C_{39}H_{46}O_6SiNa$, 661.2961; found 661.4761.

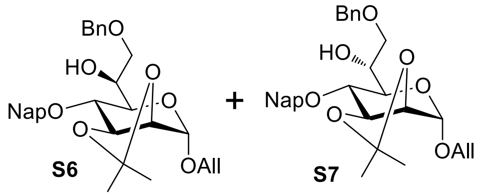


S5

Allyl 4-*O*-(2-methylnaphthyl)-2,3-*O*-isopropylidene-α-D-mannopyranoside (S5)

A solution of compound **S4** (12.6 g, 0.0197 mol) in THF (20 mL) was added 1 M TBAF in THF (39.4 mL, 0.0394 mol). The reaction mixture was stirred for 4 h at RT. TLC analysis (hexane/ethyl acetate 4:1, v/v) showed complete conversion of starting material **S4** to a major product **S5** (R_f = 0.23). The reaction mixture was concentrated *in vacuo*. The resulting residue was dissolved with

CH_2Cl_2 (150 mL), and the mixture was washed with water (50 mL). The organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo.* The resulting residue was purified by silica gel column chromatography (15% ethyl acetate in hexane to 50%) to give compound **S5** (7.5 g, 95%) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.38 (s, 3 H, CH_3), 1.49 (s, 3 H, CH_3), 1.97 (dd, *J* = 6.0, 7.2 Hz, 1 H, OH), 3.58 (dd, *J* = 6.6, 10.2 Hz, 1 H, H-4), 3.69-3.72 (m, 1 H, H-5), 3.74-3.78 (m, 1 H, H-6a), 3.86-3.89 (m, 1 H, H-6b), 3.98 (dd, *J* = 6.6, 12.6 Hz, 1 H, CH*H*-CH=CH_2), 4.17-4.19 (m, 2 H, *CH*H-CH=CH_2, H-2), 4.38 (t, *J* = 6.6 Hz, 1 H, H-3), 4.79 (d, *J* = 11.4 Hz, 1 H, CH*H*-Nap), 5.04 (d, *J* = 11.4 Hz, 1 H, *CH*H-Nap), 5.08 (s, 1 H, H-1), 5.20 (dd, *J* = 1.2, 10.8 Hz, 1 H, CH_2-CH=CH*H*), 5.29 (dd, *J* = 1.2, 17.4 Hz, 1 H, CH_2-CH=*CH*H), 5.86-5.92 (m, 1 H, CH_2-*CH*=CH_2), 7.44-7.47 (m, 3 H, H-Ar), 7.79-7.83 (m, 4 H, H-Ar); ^{13}C NMR (150 MHz, $CDCl_3$): δ 26.32 (CH_3), 27.97 (CH_3), 62.54 (C-6), 68.07 (*CH_2*-CH=CH_2), 68.50 (C-5), 72.87 (*OCH_2*-Nap), 75.83 (C-4), 75.93 (C-2), 78.66 (C-3), 96.27 (C-1), 109.39 (*C*Me_2), 117.97 (CH_2-CH=*CH_2*), 125.88-133.18 (*C*-Ar), 133.37 (CH_2-*CH*=CH_2), 135.43 (*C*-Ar); MALDI-TOF-MS: $[M+Na]^+$ calcd for $C_{23}H_{28}O_6Na$, 423.1784; found 423.1422.



S6 + **S7**

Allyl 7-*O*-benzyl-4-*O*-(2-methylnaphthyl)-2,3-*O*-isopropylidene-L-glycero-α-D-manno-heptopyranoside (S6) and Allyl 7-*O*-benzyl-4-*O*-(2-methylnaphthyl)-2,3-*O*-isopropylidene-D-glycero-α-D-manno-heptopyranoside (S7)[4]

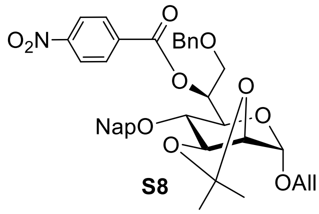
A solution of compound **S5** (2 g, 5 mmol) in CH_2Cl_2 (30 mL) was added Dess-Martin periodinae (2.33 g, 5.5 mol). The reaction mixture was stirred for 4 h at RT under an atmosphere of argon. TLC analysis showed complete conversion of starting material **S5** to a major product (hexane/ethyl acetate 4:1, v/v, R_f=0.14). The reaction mixture was filtered through celite, and the filtrate was concentrated *in vacuo*. The resulting residue was rapidly purified by silica gel column chromatography (15% ethyl acetate in hexane to 40%) to afford the corresponding aldehyde for next step.

Magnesium (850 mg, 35 mmol), I_2 (cat.) and $HgBr_2$ (cat.) were dissolved in dry THF (10 mL) under an atmosphere of argon. Benzyloxymethyl chloride (3.5 mL, 15 mmol, 60%) was measured in a dropping funnel, and a small amount of benzyloxymethyl chloride (0.20 mL) was added dropwise to the magnesium mixture until the exothermic reaction started and the purple-brown colour disappeared. The reaction temperature was kept at 25-28 °C by immediately cooling of the mixture due to initial increase in temperature. The solution of aldehyde in dry THF (10 ml) was added to the dropping funnel containing benzyloxymethyl chloride. The mixture of aldehyde and benzyloxymethyl chloride was added dropwise to the magnesium mixture over 45 min, strictly keeping the reaction temperature at 25-28 °C. After the reaction mixture was stirred for 16 h at RT, Et_2O (100 mL) was added. The mixture was washed with NH_4Cl (satd. aqueous, 100 mL). The organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo.* The resulting residue was purified by silica gel column chromatography (10% ethyl acetate in hexane to 20%) to give compound **S7** (832 mg, 32%), followed by compound **S6** (416 mg, 16%) as colorless oil.

Compound **S6** (L,D-heptoside): R_f =0.26 (hexane/ethyl acetate 4:1, v/v); ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.38 (s, 3 H, CH_3), 1.50 (s, 3 H, CH_3), 2.26 (d, *J* = 8.4 Hz, 1 H, OH), 3.58 (dd, *J* = 6.0, 9.6 Hz, 1 H, H-7a), 3.66 (dd, *J* = 7.2, 9.6 Hz, 1 H, H-7b), 3.74-3.76 (m, 1 H, H-5), 3.84 (dd, *J* = 7.2, 10.2 Hz, 1 H, H-4), 3.92 (dd, *J* = 6.6, 12.6 Hz, 1 H, CH*H*-CH=CH_2), 4.12 (dd, *J* = 5.4, 12.6 Hz, 1H, *CH*H-CH=CH_2), 4.18 (d, *J* = 6.0 Hz, 1 H, H-2), 4.24-4.27 (m, 1 H, H-6), 4.41 (t, *J* = 6.6 Hz, 1 H, H-3), 4.52-4.58 (m, 2 H, *CH_2*Ph), 4.83 (d, *J* = 11.4 Hz, 1 H, CH*H*-Nap), 5.08 (d, *J* = 11.4 Hz, 1 H, *CH*H-Nap), 5.11 (s, 1 H, H-1), 5.17 (dd, *J* = 1.2, 10.8 Hz, 1 H, CH_2-CH=CH*H*), 5.22 (dd, *J* = 1.2, 17.4 Hz, 1H, CH_2-CH=*CH*H), 5.80-5.87 (m, 1 H, CH_2-*CH*=CH_2), 7.26-7.35 (m, 5 H, Ar), 7.45-7.51 (m, 3 H, Ar), 7.82-7.83 (m, 4 H, Ar); ^{13}C NMR (150 MHz, $CDCl_3$): δ 26.40 (*CH_3*), 27.98 (*CH_3*), 67.71 (C-5), 67.86 (C-6), 67.94 (*CH_2*-CH=CH_2), 71.46 (C-7), 73.28 (*CH_2*-Nap), 73.41 (*CH_2*Ph), 75.12 (C-4), 75.70 (C-2), 78.91 (C-3), 96.35 (C-1), 109.39 (*C*Me_2), 117.96 (CH_2-CH=*CH_2*), 125.80-132.98 (*C*-Ar), 133.24 (CH_2-*CH*=CH_2), 135.71 (*C*-Ar), 137.88 (*C*-Ar); MALDI-TOF-MS: $[M+Na]^+$ calcd for $C_{31}H_{36}O_7Na$, 543.2359; found 543.2542.

Compound **S7** (D,D-heptoside): R_f =0.34 (hexane/ethyl acetate 4:1, v/v); ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.38 (s, 3 H, CH_3), 1.52 (s, 3 H, CH_3), 3.15 (s, 1 H, OH), 3.52 (dd, *J* = 2.4, 10.2 Hz, 1 H, H-7a), 3.61 (dd, *J* = 6.6, 10.2 Hz, 1 H, H-7b), 3.66 (dd, *J* = 6.6, 9.6 Hz, 1 H, H-4), 3.79 (dd, *J* = 5.4, 10.2 Hz, 1 H, H-5), 3.94 (dd, *J* = 6.0, 12.6 Hz, 1 H, CH*H*-CH=CH_2), 4.06-4.08 (m, 1 H, H-6), 4.18 (d, *J* = 6.0 Hz, 1 H, H-2), 4.21 (dd, *J* = 6.0, 12.6 Hz, 1H, *CH*H-CH=CH_2), 4.39 (t, *J* = 6.0 Hz, 1 H, H-3), 4.43-4.49 (m, 2 H, *CH_2*Ph), 4.76 (d, *J* = 11.4 Hz, 1 H, CH*H*-Nap), 5.03 (s, 1 H, H-1), 5.08 (d, *J* = 11.4 Hz, 1 H, *CH*H-Nap), 5.16 (dd, *J* = 1.2, 10.2 Hz, 1 H, CH_2-CH=CH*H*), 5.22 (dd, *J* = 1.2, 16.8 Hz, 1H, CH_2-CH=*CH*H), 5.81-5.88 (m, 1 H, CH_2-*CH*=CH_2), 7.24-7.31 (m, 5 H, Ar), 7.44-7.47 (m, 3 H, Ar), 7.78-7.82 (m, 4 H, Ar); ^{13}C NMR (150 MHz, $CDCl_3$): δ 26.25 (*CH_3*), 27.98 (*CH_3*), 67.53 (C-5), 68.01 (*CH_2*-CH=CH_2), 70.65 (C-7), 72.35 (C-6), 72.67 (*CH_2*-Nap), 73.47 (*CH_2*Ph), 75.68 (C-2), 77.80 (C-4), 78.79 (C-3), 96.14 (C-1), 109.44 (*C*Me_2), 117.94 (CH_2-CH=*CH_2*), 125.98-133.17 (*C*-Ar), 133.37 (CH_2-*CH*=CH_2), 134.99 (*C*-Ar), 138.10 (*C*-Ar); MALDI-TOF-MS: $[M+Na]^+$ calcd for $C_{31}H_{36}O_7Na$, 543.2359; found 543.2598.

Compound **S7** (D,D-heptoside) can be converted into compound **S6** (L,D-heptoside) by Mitsunobu reaction for inversion of configuration at the C-6 of **S7** in the presence of diisopropyl azodicarboxylate (DIAD), PPh_3 and *p*-nitrobenzoic acid, followed by treatment with base ($NaOCH_3$) to remove *p*-nitrobenzyl ester of compound **S8**.



S8

Allyl 7-*O*-benzyl-4-*O*-(2-methylnaphthyl)-2,3-*O*-isopropylidene-6-*O*-*p*-nitrobenzoyl-L-glycero-α-D-manno-heptopyranoside (S8)

A solution of compound **S7** (520 mg, 1 mmol) in dry THF (10 mL) was added PPh_3 and *p*-nitrobenzoic acid. Subsequently, diisopropyl azodicarboxylate (DIAD) was added dropwise. The resulting reaction mixture was stirred for 4 h at RT under an atmosphere of argon. TLC analysis showed complete conversion of starting material **S7** to a major product **S8** (hexane/ethyl acetate 4:1, v/v, R_f = 0.50). The reaction mixture was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (8% ethyl acetate in hexane to 20%) to give compound **S8** (509 mg, 76%) as a yellow amorphous solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.43 (s, 3 H, CH_3), 1.53 (s, 3 H, CH_3), 3.57 (dd, *J* = 6.6, 10.2 Hz, 1 H, H-4), 3.74-3.81 (m, 2 H, H-7a, H-7b), 3.93 (dd, *J* = 6.0, 12.6 Hz, 1 H, $CH\mathit{H}$-CH=CH_2), 4.07 (d, *J* = 10.4 Hz, 1 H, H-5), 4.18 (dd, *J* = 5.4, 12.6 Hz, 1 H, CHH-CH=CH_2), 4.22 (d, *J* = 6.0 Hz, 1 H, H-2), 4.47 (t, *J* = 6.0 Hz, 1 H, H-3), 4.51-4.58 (m, 2 H, $\mathit{CH_2}$Ph), 4.72 (d, *J* = 11.4 Hz, 1 H, $CH\mathit{H}$-Nap), 4.86 (d, *J* = 11.4 Hz, 1 H, CHH-Nap), 5.14-5.20 (m, 3 H, H-1, CH_2-CH=$\mathit{CH_2}$), 5.60 (t, *J* = 6.6 Hz, 1H, H-6), 5.78-5.84 (m, 1 H, CH_2-CH=CH_2), 7.25-7.33 (m, 7 H, Ar), 7.37 (d, *J* = 8.4 Hz, 1 H, Ar), 7.46 (d, *J* = 8.4 Hz, 1 H, Ar), 7.52 (d, *J* = 8.4 Hz, 1 H, Ar), 7.62 (d, *J* = 8.4 Hz, 1 H, Ar), 7.70 (s, 1 H, Ar), 7.75-7.77 (m, 2 H, Ar), 7.89-7.90 (m, 2 H, Ar); ^{13}C NMR (150 MHz, $CDCl_3$): δ 26.34 ($\mathit{CH_3}$), 28.16 ($\mathit{CH_3}$), 66.01 (C-5), 66.71 (C-7), 68.04 ($\mathit{CH_2}$-CH=CH_2), 70.72 (C-6), 71.24 ($\mathit{CH_2}$-Nap), 72.50 (C-4), 73.26 ($\mathit{CH_2}$Ph), 75.53 (C-2), 79.20 (C-3), 96.17 (C-1), 109.53 (*C*Me_2), 118.08 (CH_2-CH=$\mathit{CH_2}$), 122.98-132.63 (*C*-Ar), 133.22 (CH_2-CH=CH_2), 134.41-137.65 (*C*-Ar), 150.17 (NO_2-*C*-Ar), 163.57 (*C*=O); MALDI-TOF-MS: $[M+Na]^+$ calcd for $C_{38}H_{39}NO_{10}Na$, 692.2472; found 692.2596.

Synthesis of S6 from S8: a solution of compound **S8** (790 mg, 1.18 mmol) in dry CH_2Cl_2 (4 mL) and MeOH (8 mL) was added $NaOCH_3$ (cat.) to adjust pH ~10, and then stirred for 6 h at RT under an atmosphere of argon. TLC analysis showed complete conversion of starting material **S8** to a major product **S6** (hexane/ethyl acetate 4:1, v/v, R_f = 0.26). The reaction mixture was concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (10% ethyl acetate in hexane to 25%) to give compound **S6** (504 mg, 82%) as colorless oil.

2.6. Synthesis of L,D-heptose donor 36 and acceptor 37

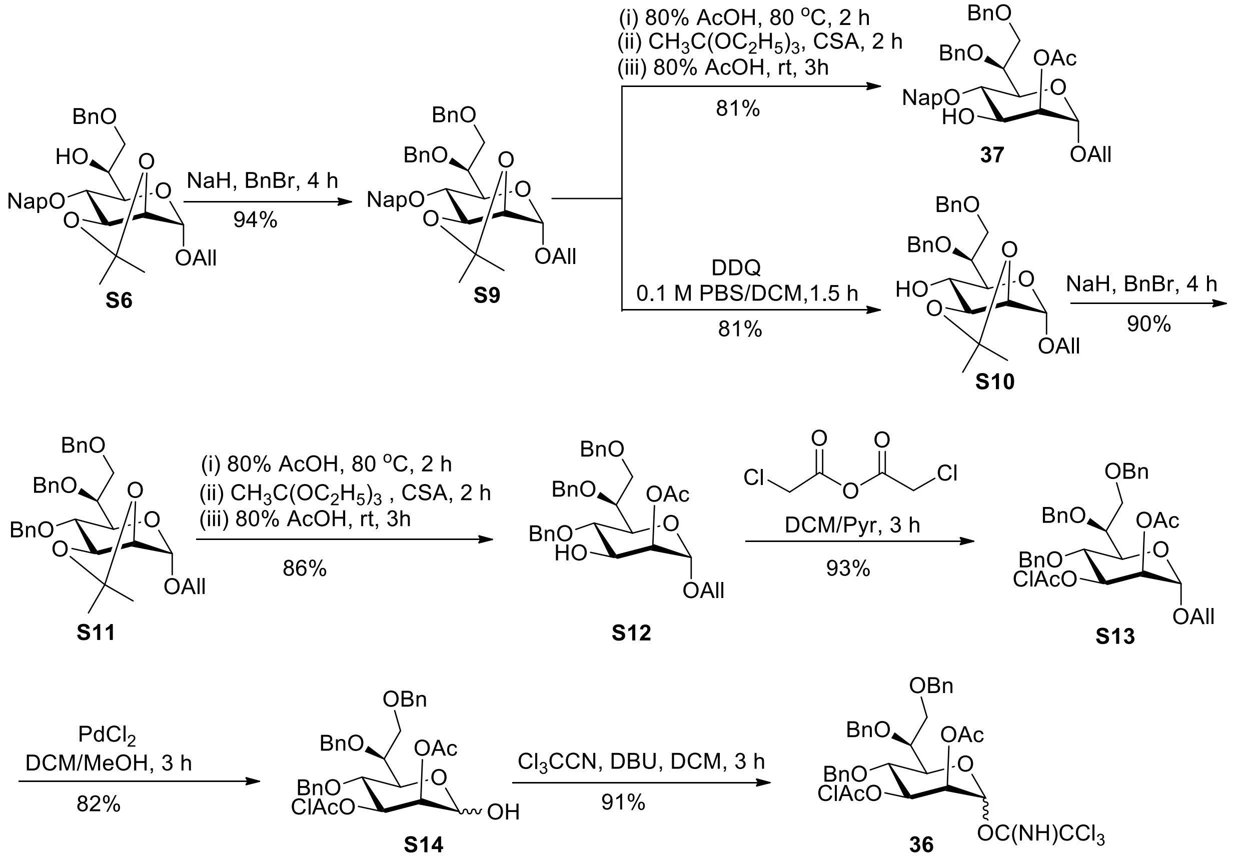
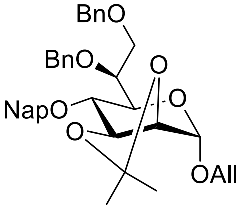


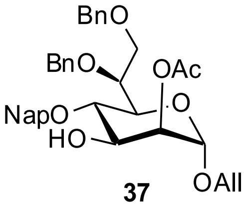
Figure S6. Synthesis of L,D-heptose donor **36** and acceptor **37**.



S9

Allyl 6,7-*O*-dibenzyl-4-*O*-(2-methylnaphthyl)-2,3-*O*-isopropylidene-L-glycero-α-D-manno-heptopyranoside (S9)

A mixture of **S6** (630 mg, 1.21 mmol) and benzyl bromide (216.5 µL, 1.82 mmol) in DMF (15 mL) was cooled to 0 °C. Sodium hydride (60% dispersion in mineral oil, 73 mg, 1.82 mmol) was added slowly. The reaction mixture was stirred for 4 h at RT under an atmosphere of argon. TLC analysis showed complete conversion of starting material **S6** to a major product **S9** (hexane/ethyl acetate 4:1, v/v, R_f = 0.56). The reaction was quenched with MeOH (1 mL), and the reaction mixture was concentrated *in vacuo*. The resulting residue was dissolved with CH_2Cl_2 (50 mL), and the mixture was washed with water (30 mL). The organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo.* The resulting residue was purified by silica gel column chromatography (8% ethyl acetate in hexane to 20%) to give compound **S9** (694 mg, 94%) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.38 (s, 3 H, CH_3), 1.55 (s, 3 H, CH_3), 3.71-3.77 (m, 2 H, H-7a, H-7b), 3.81-3.86 (m, 2 H, H-5, H-4), 3.92 (dd, *J* = 6.6, 12.6 Hz, 1 H, CH*H*-CH=CH_2), 4.10-4.14 (m, 2 H, H-6, *CH*H-CH=CH_2), 4.16 (d, *J* = 6.0 Hz, 1 H, H-2), 4.39-4.46 (m, 3 H, H-3, CH*H*-Nap, CH*H*-Ph), 4.51 (s, 2 H, *CH*$_2$Ph), 4.73 (d, *J* = 11.4 Hz, 1 H, CH*H*-Ph), 5.00 (d, *J* = 11.4 Hz, 1 H, *CH*H-Nap), 5.12-5.14 (m, 2 H, H-1, CH_2-CH=CH*H*), 5.19 (dd, *J* = 1.2, 17.4 Hz, 1H, CH_2-CH=*CH*H), 5.78-5.84 (m, 1 H, CH_2-*CH*=CH_2), 7.18-7.45 (m, 13 H, Ar), 7.70 (s, 1 H, Ar), 7.75-7.79 (m, 3 H, Ar); ^{13}C NMR (150 MHz, $CDCl_3$): δ 26.42 (*CH*$_3$), 27.95 (*CH*$_3$), 67.90 (*CH*$_2$-CH=CH_2), 68.16 (C-5), 70.11 (C-7), 72.23 (*CH*$_2$-Nap), 73.41 (*CH*$_2$Ph), 73.47 (*CH*$_2$Ph), 75.09 (C-4), 75.15 (C-6), 75.69 (C-2), 79.13 (C-3), 96.38 (C-1), 109.39 (*C*Me$_2$), 117.83 (CH_2-CH=*CH*$_2$), 125.72-133.19 (*C*-Ar), 133.43 (CH_2-*CH*=CH_2), 135.84 (*C*-Ar), 138.00 (*C*-Ar), 138.52 (*C*-Ar); MALDI-TOF-MS: $[M+Na]^+$ calcd for $C_{38}H_{42}O_7Na$, 633.2828; found 633.3223.



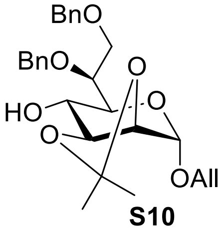
37

Allyl 2-*O*-acetyl-6,7-di-*O*-benzyl-4-*O*-(2-methylnaphthyl)-L-glycero-α-D-manno-heptopyranoside (37)

The compound **S9** (310 mg, 0.507 mmol) was dissolved in AcOH (16 mL) and H_2O (4 mL), and the mixture was heated (80 °C) and stirred for 2 h. The reaction mixture was cooled to RT, and concentrated under reduced pressure. The resulting residue was co-evaporated three times with toluene (3 x10 mL) *in vacuo* to give colorless oil for next step.

The resulting oil was dissolved in DMF (10 mL), and triethyl orthoacetate (466 µL, 2.54 mmol) and camphorsulfonic acid (CSA, 12 mg, 0.0507 mmol) were added. After the reaction mixture was stirred for 2 h at RT under an atmosphere of argon, the reaction was quenched with triethylamine (1 mL). The reaction mixture was concentrated under reduced pressure to afford colorless oil for next step.

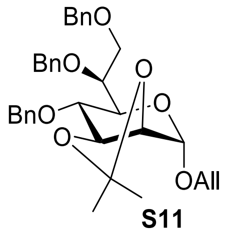
The resulting oil was dissolved in AcOH (16 mL) and H_2O (4 mL), and the mixture was stirred for 3 h at RT. The reaction mixture was concentrated under reduced pressure, followed by co-evaporation three times with toluene (3 x10 mL) *in vacuo*. The resulting residue was purified by silica gel column chromatography (15% ethyl acetate in hexane to 40%) to afford glycosyl acceptor **37** (253 mg, 81% for 3 steps) as colorless oil. Moreover, HMBC NMR revealed a good correlation of the carbonyl carbon (*O*=*C*CH$_3$) with H-2 (170.92 & 5.10), which indicated 2-hydroxyl was selectively acetylated. ^{1}H NMR (600 MHz, CDCl$_3$): δ 2.11 (d, *J* = 4.2 Hz, 1 H, OH), 2.15 (s, 3 H, *CH$_3$*CO), 3.76 (dd, *J* = 6.6, 9.6 Hz, H-7a), 3.82-3.91 (m, 3 H, H-7b, H-5, CH*H*-CH=CH$_2$), 3.97 (t, *J* = 9.6 Hz, H-4), 4.09 (dd, *J* = 4.8, 12.6 Hz, 1H, *CH*H-CH=CH$_2$), 4.16 (t, *J* = 6.0 Hz, 1 H, H-6), 4.24 (d, *J* = 9.0 Hz, 1 H, H-3), 4.53-4.56 (m, 4 H, CH*H*-Nap, CH*H*-Ph, *CH$_2$*-Ph), 4.86-4.92 (m, 3 H, *CH*H-Ph, *CH*H-Nap, H-1), 5.10-5.14 (m, 2 H, H-2, CH$_2$-CH=CH*H*), 5.19 (dd, *J* = 1.2, 16.8 Hz, 1 H, CH$_2$-CH=*CH*H), 5.77-5.83 (m, 1 H, CH$_2$-*CH*=CH$_2$), 7.23-7.46 (m, 13 H, H-Ar), 7.66 (s, 1 H, H-Ar), 7.75-7.81 (m, 3 H, H-Ar); ^{13}C NMR (150 MHz, CDCl$_3$): δ 21.12 (*CH$_3$*), 68.05 (*CH$_2$*-CH=CH$_2$), 69.95 (C-7), 70.90 (C-5, C-3), 72.68 (C-2), 72.78 (*CH$_2$*Ph), 73.50 (*CH$_2$*Ph), 74.54 (*CH$_2$*Nap), 74.91(C-6), 75.64 (C-4), 96.43 (C-1), 117.82 (CH$_2$-CH=*CH$_2$*), 125.55-132.91 (*C*-Ar), 133.20 (CH$_2$-*CH*=CH$_2$),133.24 (*C*-Ar), 135.87 (*C*-Ar), 137.90 (*C*-Ar), 138.46 (C-Ar), 170.92 (*C*=O); MALDI-TOF-MS: [M+Na]$^+$ calcd for C$_{37}$H$_{40}$O$_8$Na, 635.2621; found 635.1024.



S10

Allyl 6,7-di-*O*-benzyl-2,3-*O*-isopropylidene-L-glycero-α-D-manno-heptopyranoside (S10)

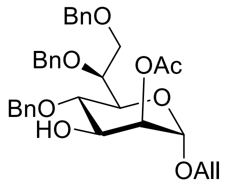
A solution of compound **S9** (380 mg, 0.622 mmol) in CH$_2$Cl$_2$ (5 mL) and PBS buffer (0.1 M, pH 7.4, 0.5 mL) was added DDQ (212 mg, 0.933 mmol), and stirred for 1.5 h at RT in the dark. TLC analysis showed conversion of starting material **S9** to a major product **S10** (hexane/ethyl acetate 4:1, v/v, R_f = 0.25). The reaction mixture was diluted by CH$_2$Cl$_2$ (30 mL), and washed with NaHCO$_3$ (satd. aqueous, 10 mL). The aqueous phase was re-extracted twice with CH$_2$Cl$_2$ (30 mL). The combined organic phase was dried (Na$_2$SO$_4$), filtered, and the filtrate was concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (10% ethyl acetate in hexane to 30%) to give compound **S10** (236 mg, 81%) as colorless oil. ^{1}H NMR (600 MHz, CDCl$_3$): δ 1.32 (s, 3 H, CH$_3$), 1.50 (s, 3 H, CH$_3$), 1.87 (s, 1 H, OH), 3.63 (d, *J* = 10.2 Hz, 1 H, H-5), 3.68-3.77 (m, 3 H, H-4, H-7a, H-7b), 3.89-3.92 (m, 2 H, CH*H*-CH=CH$_2$, H-6), 4.05 (t, *J* = 6.0 Hz, 1 H, H-3), 4.08-4.11 (m, 2 H, *CH*H-CH=CH$_2$, H-2), 4.54 (s, 2 H, *CH$_2$*Ph), 4.59 (d, *J* = 12.0 Hz, 1 H, CH*H*-Ph), 4.80 (d, *J* = 12.0 Hz, 1 H, *CH*H-Ph), 5.07 (s, 1 H, H-1), 5.13 (dd, *J* = 1.2, 10.8 Hz, 1 H, CH$_2$-CH=CH*H*), 5.19 (dd, *J* = 1.2, 17.4 Hz, 1 H, CH$_2$-CH=*CH*H), 5.77-5.84 (m, 1 H, CH$_2$-*CH*=CH$_2$), 7.27-7.37 (m, 10 H, Ar); ^{13}C NMR (150 MHz, CDCl$_3$): δ 26.27 (*CH$_3$*), 28.07 (*CH$_3$*), 67.89 (*CH$_2$*-CH=CH$_2$), 68.68 (C-5), 69.01 (C-4), 69.60 (C-7), 73.07 (*CH$_2$*Ph), 73.43 (*CH$_2$*Ph), 74.27 (C-6), 75.66 (C-2), 78.46 (C-3), 96.44 (C-1), 109.37 (*C*Me$_2$), 117.85 (CH$_2$-CH=*CH$_2$*), 127.55-128.54 (*C*-Ar), 133.40 (CH$_2$-*CH*=CH$_2$), 137.91 (*C*-Ar), 138.23 (*C*-Ar); MALDI-TOF-MS: [M+Na]$^+$ calcd for C$_{27}$H$_{34}$O$_7$Na, 493.2202; found 493.3526.



S11

Allyl 4,6,7-tri-*O*-benzyl-2,3-*O*-isopropylidene-L-glycero-α-D-manno-heptopyranoside (S11)

A mixture of compound **S10** (232 mg, 0.493 mmol) and benzyl bromide (87.3 µL, 0.734 mmol) in DMF (15 mL) was cooled to 0 °C. Sodium hydride (60% dispersion in mineral oil, 29.4 mg, 0.734 mmol) was added slowly. The reaction mixture was stirred for 4 h at RT under an atmosphere of argon. TLC analysis showed complete conversion of starting material **S10** to a major product **S11** (hexane/ethyl acetate 4:1, v/v, R_f = 0.62). The reaction was quenched with MeOH (1 mL) and concentrated *in vacuo*. The resulting residue was dissolved with CH_2Cl_2 (30 mL), and the mixture was washed with water (10 mL). The organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo.* The resulting residue was purified by silica gel column chromatography (8% ethyl acetate in hexane to 20%) to give compound **S11** (248 mg, 90%) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.37 (s, 3 H, CH_3), 1.55 (s, 3 H, CH_3), 3.71-3.77 (m, 2 H, H-7a, H-7b), 3.79-3.83 (m, 2 H, H-5, H-4), 3.92 (dd, *J* = 6.0, 12.6 Hz, CH*H*-CH=CH_2), 4.08-4.16 (m, 3 H, H-6, *C*HH-CH=CH_2, H-2), 4.28 (d, *J* = 11.4 Hz, 1 H, CH*H*-Ph), 4.36 (t, *J* = 5.4 Hz, 1 H, H-3), 4.48 (d, *J* = 12.0 Hz, 1 H, CH*H*-Ph), 4.52 (s, 2 H, *CH_2*Ph), 4.75 (d, *J* = 12.0 Hz, 1 H, *C*HH-Ph), 4.87 (d, *J* = 11.4 Hz, 1 H, *C*HH-Ph), 5.13-5.14 (m, 2 H, H-1, CH_2-CH=CH*H*), 5.19 (dd, *J* = 1.2, 16.8 Hz, 1H, CH_2-CH=*C*HH), 5.78-5.84 (m, 1 H, CH_2-*CH*=CH_2), 7.21-7.36 (m, 15 H, Ar); ^{13}C NMR (150 MHz, $CDCl_3$): δ 26.42 (*CH_3*), 27.95 (*CH_3*), 67.89 (*CH_2*-CH=CH_2), 68.14 (C-5), 70.18 (C-7), 72.18 (*CH_2*Ph), 73.43 (*CH_2*Ph), 73.55 (*CH_2*Ph), 75.11 (C-4), 75.19 (C-6), 75.67 (C-2), 79.11 (C-3), 96.37 (C-1), 109.36 (*C*Me_2), 117.82 (CH_2-CH=*CH_2*), 127.49-128.36 (*C*-Ar), 133.44 (CH_2-*CH*=CH_2), 138.01 (*C*-Ar), 138.41 (*C*-Ar), 138.60 (C-Ar); MALDI-TOF-MS: $[M+Na]^+$ calcd for $C_{34}H_{40}O_7Na$, 583.2672; found 583.2124.



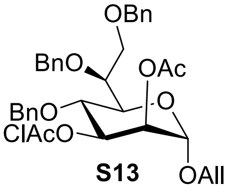
S12

Allyl 2-*O*-acetyl-4,6,7-tri-*O*-benzyl-L-glycero-α-D-manno-heptopyranoside (S12)

The compound **S11** (244 mg, 0.435 mmol) was dissolved in AcOH (16 mL) and H_2O (4 mL), and the mixture was heated (80 °C) and stirred for 2 h. The reaction mixture was cooled to RT, and concentrated under reduced pressure. The resulting residue was co-evaporated three times with toluene (3 x10 mL) *in vacuo* to give colorless oil for next step.

The resulting oil was dissolved in DMF (10 mL), and triethyl orthoacetate (399 μL, 2.18 mmol) and camphorsulfonic acid (CSA, 10 mg, 0.0435 mmol) were added. After the reaction mixture was stirred for 2 h at RT under an atmosphere of argon, the reaction was quenched with triethylamine (1 mL). The mixture was concentrated under reduced pressure to afford colorless oil for next step.

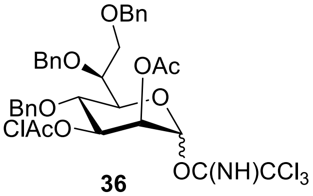
The resulting oil was dissolved in AcOH (16 mL) and H_2O (4 mL), and the mixture was stirred for 3 h at RT. The reaction mixture was concentrated under reduced pressure, followed by co-evaporation three times with toluene (3 x10 mL) *in vacuo*. The resulting residue was purified by silica gel column chromatography (15% ethyl acetate in hexane to 40%) to afford compound **S12** (210 mg, 86% for 3 steps) as colorless oil. Moreover, HMBC NMR revealed a good correlation of the carbonyl carbon (*O*=*C*CH_3) with H-2 (170.93 & 5.09), which indicated 2-hydroxyl was selectively acetylated. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.15 (s, 3 H, *CH_3*CO), 3.74 (dd, *J* = 6.0, 9.6 Hz, H-7a), 3.82-3.84 (m, 2 H, H-7b, H-5), 3.87-3.93 (m, 2 H, CH*H*-CH=CH_2, H-4), 4.07 (dd, *J* = 4.8, 12.6 Hz, 1H, *CH*H-CH=CH_2), 4.12 (t, *J* = 6.0 Hz, 1 H, H-6), 4.21 (d, *J* = 3.0, 9.0 Hz, 1 H, H-3), 4.39 (d, *J* = 11.4 Hz, 1 H, CH*H*-Ph), 4.52-4.56 (m, 3 H, *CH_2*-Ph, CH*H*-Ph), 4.76 (d, *J* = 11.4 Hz, 1 H, *CH*H-Ph), 4.86 (d, *J* = 11.4 Hz, 1 H, *CH*H-Ph), 4.91 (s, 1 H, H-1), 5.09 (t, *J* = 1.8 Hz, 1 H, H-2), 5.13 (dd, *J* = 1.2, 10.2 Hz, 1 H, CH_2-CH=CH*H*), 5.18 (dd, *J* = 1.2, 17.4 Hz, 1 H, CH_2-CH=*CH*H), 5.76-5.82 (m, 1 H, CH_2-*CH*=CH_2), 7.24-7.37 (m, 15 H, H-Ar); ^{13}C NMR (150 MHz, $CDCl_3$): δ 21.12 (*CH_3*), 68.03 (*CH_2*-CH=CH_2), 70.03 (C-7), 70.87 (C-5, C-3), 72.68 (C-2), 72.85 (*CH_2*Ph), 73.52 (*CH_2*Ph), 74.49 (*CH_2*Ph), 74.95 (C-6), 75.56 (C-4), 96.41 (C-1), 117.80 (CH_2-CH=*CH_2*), 127.53-128.43 (*C*-Ar), 133.19 (CH_2-*CH*=CH_2), 137.90 (*C*-Ar), 138.40 (*C*-Ar), 138.47 (*C*-Ar), 170.92 (*C*=O); MALDI-TOF-MS: $[M+Na]^+$ calcd for $C_{33}H_{38}O_8Na$ 585.2464; found 585.3882.



S13

Allyl 2-*O*-acetyl-3-chloroacetyl-4,6,7-tri-*O*-benzyl-L-glycero-α-D-manno-heptopyranoside (S13)

A solution of compound **S12** (250 mg, 0.426 mmol) in CH_2Cl_2 (10 mL) and pyridine (171 μL, 2.13 mmol) was added chloroacetic anhydride (218 mg, 1.278 mmol) and dimethylaminopyridine (DMAP, 5 mg, 0.04 mmol). The mixture was stirred for 3 h at RT under an atmosphere of argon. TLC analysis showed complete conversion of starting material **S12** to a major product **S13** (hexane/ethyl acetate 2:1, v/v, R_f = 0.58). The reaction mixture was diluted by ethyl acetate (50 mL), and washed with 1 M HCl (20 mL), $NaHCO_3$ (satd. aqueous, 20 mL) and brine (20 mL). The organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated *in vacuo.* The resulting residue was purified by silica gel column chromatography (15% ethyl acetate in hexane to 30%) to give compound **S13** (254 mg, 93%) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.13 (s, 3 H, *CH₃*CO), 3.73-3.77 (m, 2 H, H-7a, ClCH*H*CO), 3.82-3.84 (m, 2 H, Cl*CH*HCO, H-7b), 3.88-3.95 (m, 2 H, CH*H*-CH=CH₂, H-5), 4.07-4.11 (m, 3 H, H-4, *CH*H-CH=CH₂, H-6), 4.32 (d, *J* = 11.4 Hz, 1 H, CH*H*-Ph), 4.49-4.55 (m, 4 H, *CH*H-Ph, *CH₂*-Ph, CH*H*-Ph), 4.86-4.88 (m, 2 H, *CH*H-Ph, H-1), 5.14 (dd, *J* = 1.2, 10.2 Hz, 1 H, CH₂-CH=CH*H*), 5.19 (dd, *J* = 1.2, 16.8 Hz, 1 H, CH₂-CH=*CH*H), 5.27 (t, *J* = 1.8, 3.0 Hz, 1 H, H-2), 5.41 (dd, *J* = 3.0, 9.6 Hz, 1 H, H-3), 5.76-5.82 (m, 1 H, CH₂-*CH*=CH₂), 7.14-7.38 (m, 15 H, H-Ar); ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.91 (*CH₃*CO), 40.54 (Cl*CH₂*CO), 68.11 (*CH₂*-CH=CH₂), 69.64 (C-7), 69.75 (C-2), 71.13 (C-5), 72.75 (*CH₂*Ph), 72.85 (C-4), 73.55 (*CH₂*Ph), 74.37 (*CH₂*Ph), 74.46 (C-3), 74.60 (C-6), 96.33 (C-1), 118.15 (CH₂-CH=*CH₂*), 127.19-128.42 (*C*-Ar), 132.96 (CH₂-*CH*=CH₂), 137.81 (*C*-Ar), 138.15 (*C*-Ar), 138.41 (*C*-Ar), 166.17 (ClCH₂*C*=*O*), 170.22 (CH₃*C*=O); MALDI-TOF-MS: $[M+Na]^+$ calcd for $C_{35}H_{39}ClO_9Na$ 661.2180; found 661.3551.



36

2-*O*-acetyl-3-chloroacetyl-4,6,7-tri-*O*-benzyl-L-glycero-α/β-D-manno-heptopyranosyl trichloroacetimidate (36)

A solution of compound **S13** (340 mg, 0.532 mmol) in CH_2Cl_2 (2 mL) and MeOH (10 mL) was added $PdCl_2$ (94 mg, 0.532 mmol), and stirred for 3 h at RT. TLC analysis showed complete conversion of starting material **S13** to a major product **S14** (hexane/ethyl acetate 2:1, v/v, R_f = 0.28). The reaction mixture was filtered by celite, and the filtrate was concentrated *in vacuo.* The resulting residue was purified by silica gel column chromatography (20% ethyl acetate in hexane to 40%) to give a hemiacetal **S14** (260 mg, 82%) as colorless oil for next step. MALDI-TOF-MS: $[M+Na]^+$ calcd for $C_{32}H_{35}ClO_9Na$, 621.1867; found 621.3559.

A mixture of the resulting hemiacetal **S14** (255 mg, 0.426 mmol), CCl_3CN (2 mL) and DBU (50 µL) in anhydrous CH_2Cl_2 (8 mL) was stirred for 3 h at RT. TLC analysis showed complete conversion of starting material to a major product (hexane/ethyl acetate 2:1, v/v, R_f = 0.43). The reaction mixture was concentrated under reduced pressure. The resulting residue was purified by silica gel chromatography (10% ethyl acetate in hexane to 30%) to afford glycosyl donor **36** (288mg, 91%) for next coupling step.

2.7. Synthesis of tetrasaccharide donor 42

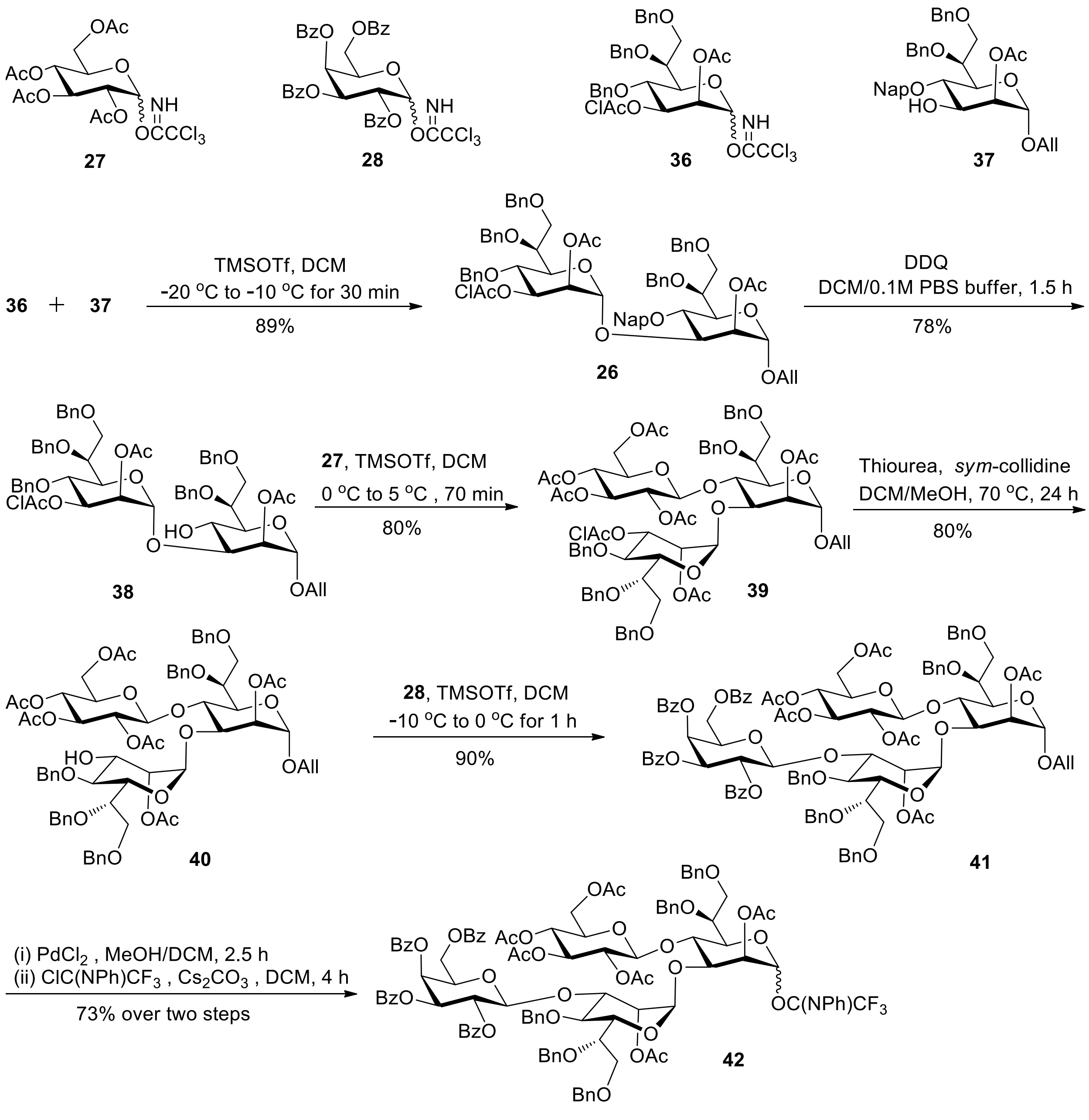
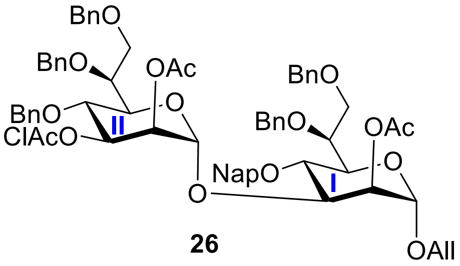


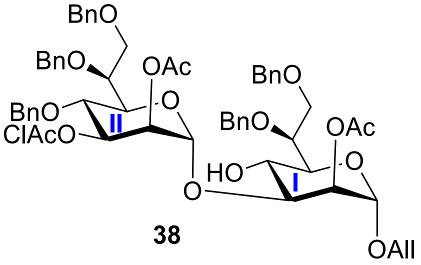
Figure S7. Synthesis of tetrasaccharide donor **42**.



26

Allyl [2-*O*-acetyl-3-chloroacetyl-5,6,7-tri-*O*-benzyl-L-glycero-α-D-manno-heptopyranosyl]-(1→3)-2-*O*-acetyl-6,7-di-*O*-benzyl-4-*O*-(2-methylnaphthyl)-L-glycero-α-D-manno-heptopyranoside (26)

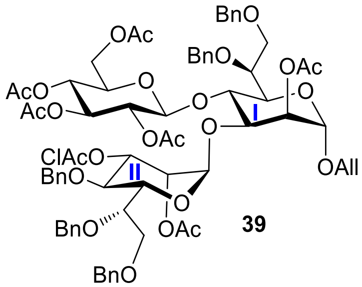
A mixture of donor **36** (250 mg, 0.336 mmol), acceptor **37** (170 mg, 0.277 mmol) and freshly activated 4 Å molecular sieves in anhydrous CH_2Cl_2 (5 mL) was stirred for 30 min at RT under an atmosphere of argon. The mixture was cooled to –20 °C, TMSOTf (15 µL, 0.083 mmol) was added. The reaction mixture was slowly warmed to –10 °C in 30 min, TLC analysis showed complete conversion of acceptor to a major product (hexane/ethyl acetate 2:1, v/v, R_f = 0.57). The reaction was quenched by the addition of trimethylamine (0.1 mL), and the reaction mixture was filtered by celite. The filtrate was concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (12% ethyl acetate in hexane to 25%) to afford disaccharide **26** (294 mg, 89%) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.70 (s, 3 H, *CH*$_3$CO), 2.21 (s, 3 H, *CH*$_3$CO), 3.64 (d, *J* = 15.0 Hz, 1 H, ClCH*H*CO), 3.75-3.78 (m, 3 H, H-7a-Hep-I, H-7a-Hep-II, Cl*CH*HCO), 3.81-3.89 (m, 4 H, CH*H*-CH=CH$_2$, H-7b-Hep-I, H-7b-Hep-II, H-5-Hep-I), 4.00 (t, *J* = 9.6 Hz, 1 H, H-4-Hep-II), 4.07-4.14 (m, 5 H, *CH*H-CH=CH$_2$, H-5-Hep-II, H-4-Hep-I, H-6-Hep-I, H-6-Hep-II), 4.27 (dd, *J* = 3.0, 9.6 Hz, H-3-Hep-I), 4.36 (d, *J* = 12.0 Hz, CH*H*-Ph), 4.43-4.55 (m, 7 H, C*H*H-Ph, CH*H*-Nap, 3xCH*H*-Ph, *CH*$_2$-Ph), 4.63 (d, *J* = 12.0 Hz, *CH*H-Ph), 4.71 (d, *J* = 12.0 Hz, *CH*H-Ph), 4.81 (s, 1 H, H-1-Hep-I), 4.83-4.86 (m, 2 H, *CH*H-Ph, *CH*H-Nap), 5.13 (dd, *J* = 1.2, 10.2 Hz, 1 H, CH$_2$-CH=CH*H*), 5.17 (s, 1 H, H-1-Hep-II), 5.20 (dd, *J* = 1.2, 10.2 Hz, 1 H, CH$_2$-CH=CH*H*), 5.24-5.26 (m, 2 H, H-2-Hep-I, H-2-Hep-II), 5.30 (dd, *J* = 3.0, 9.6 Hz, 1 H, H-3-Hep-II), 5.73-5.79 (m, 1 H, CH$_2$-*CH*=CH$_2$), 7.15-7.43 (m, 32 H, H-Ar); ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.37 (*CH*$_3$C=O), 21.04 (*CH*$_3$C=O), 40.58 (Cl*CH*$_2$CO), 67.86 (*CH*$_2$-CH=CH$_2$), 69.36 (C2-Hep-II), 69.74 (C7-Hep-II), 70.89 (C7-Hep-I), 71.44 (C5-Hep-I), 71.73 (C2-Hep-I), 72.32 (C5-Hep-II), 72.42 (*CH*$_2$Nap), 72.55 (C4-Hep-II), 72.73 (*CH*$_2$Ph), 73.28 (*CH*$_2$Ph), 73.54 (*CH*$_2$Ph), 73.57 (C3-Hep-II), 73.73 (*CH*$_2$Ph), 74.50 (*CH*$_2$Ph), 74.58 (C6-Hep-II), 74.83 (C6-Hep-I), 75.02 (C3-Hep-I), 75.31 (C4-Hep-I), 96.51 (C1-Hep-I, $J_{C1\text{-}H1}$ = 173 Hz), 99.10 (C1-Hep-II, $J_{C1\text{-}H1}$ = 176 Hz), 117.69 (CH$_2$-CH=*CH*$_2$), 125.06-133.12 (*C*-Ar), 133.23 (CH$_2$-*CH*=CH$_2$), 135.38 (*C*-Ar), 137.83 (*C*-Ar), 138.31 (*C*-Ar), 138.45 (C-Ar), 138.56 (C-Ar), 166.42 (ClCH$_2$*C*=*O*), 169.78 (CH$_3$*C*=O), 170.42 (CH$_3$*C*=O); bsHSQCAD NMR was used to calculate coupling constant between the anomeric carbon and proton ($J_{\mathrm{C1\text{-}H1}}$); MALDI-TOF-MS: [M+Na]$^+$ calcd for $C_{69}H_{73}ClO_{16}Na$, 1215.4485; found 1215.6980.



38

Allyl [2-*O*-acetyl-3-chloroacetyl-5,6,7-tri-*O*-benzyl-L-glycero-α-D-manno-heptopyranosyl]-(1→3)-2-*O*-acetyl-6,7-di-*O*-benzyl-L-glycero-α-D-manno-heptopyranoside (38)

A solution of compound **26** (244 mg, 0.204 mmol) in CH_2Cl_2 (4 mL) and PBS buffer (0.1 M, pH 7.4, 0.4 mL) was added DDQ (69 mg, 0.306 mmol), and the mixture was stirred for 1.5 h at RT in the dark. TLC analysis showed conversion of starting material **26** to a major product **38** (hexane/ethyl acetate 2:1, v/v, $R_f = 0.45$). The reaction mixture was diluted by CH_2Cl_2 (30 mL), and washed with $NaHCO_3$ (satd. aqueous, 10 mL). The aqueous phase was re-extracted twice with CH_2Cl_2 (30 mL). The combined organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (10% ethyl acetate in hexane to 30%) to give disaccharide acceptor **38** (168 mg, 78%) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.75 (d, J = 3.0 Hz, 1 H, OH), 2.10 (s, 3 H, $\mathit{CH_3}$CO), 2.16 (s, 3 H, $\mathit{CH_3}$CO), 3.63-3.81 (m, 7 H, H-5-Hep-I, Cl$\mathit{CH_2}$CO, H-7a-Hep-II, H-7b-Hep-II, H-7a-Hep-I, CH*H*-CH=CH_2), 3.84-3.91 (m, 3 H, H-7b-Hep-I, H-4-Hep-I, H-6-Hep-I), 3.96 (dd, J = 3.6, 9.6 Hz, 1 H, H-3-Hep-I), 4.01-4.09 (m, 3 H, CH*H*-CH=CH_2, H-5-Hep-II, H-4-Hep-II), 4.11 (t, J = 6.0 Hz, 1 H, H-6-Hep-II), 4.40 (d, J = 12.0 Hz, CH*H*-Ph), 4.45-4.63 (m, 7 H, C*H*H-Ph, 2xCH*H*-Ph, 2x$\mathit{CH_2}$-Ph), 4.74 (s, 1 H, H-1-Hep-I), 4.82 (dd, J = 12.0 Hz, C*H*H-Ph), 4.86 (dd, J = 12.0 Hz, C*H*H-Ph), 5.10 (dd, J = 1.2, 10.8 Hz, 1 H, CH_2-CH=CH*H*), 5.15-5.19 (m, 3 H, H-1-Hep-II, *CH*H-CH=CH_2, H-2-Hep-I), 5.26-5.27 (m, 2 H, H-2-Hep-II, H-3-Hep-II), 5.69-5.76 (m, 1 H, CH_2-*CH*=CH_2), 7.17-7.40 (m, 25 H, H-Ar); ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.92 ($\mathit{CH_3}$C=O), 20.97 ($\mathit{CH_3}$C=O), 40.58 (Cl$\mathit{CH_2}$CO), 67.80 ($\mathit{CH_2}$-CH=CH_2 and C4-Hep-I), 69.50 (C7-Hep-II), 69.54 (C2-Hep-II), 70.88 (C7-Hep-I), 71.05 (C2-Hep-I), 71.13 (C5-Hep-I), 72.16 (C5-Hep-II), 72.66 (C4-Hep-II and $\mathit{CH_2}$Ph), 73.03 ($\mathit{CH_2}$Ph), 73.34 ($\mathit{CH_2}$Ph), 73.50 ($\mathit{CH_2}$Ph), 73.66 (C3-Hep-II), 73.77 (C6-Hep-I and $\mathit{CH_2}$Ph), 74.73 (C3-Hep-I), 74.88 (C6-Hep-II), 96.71 (C1-Hep-I), 98.84 (C1-Hep-II), 117.67 (CH_2-CH=$\mathit{CH_2}$), 127.14-128.65 (*C*-Ar), 133.21 (CH_2-*CH*=CH_2), 137.91 (*C*-Ar), 138.03 (*C*-Ar), 138.29 (*C*-Ar), 138.50 (C-Ar), 136.65 (C-Ar), 166.43 (ClCH_2*C*=*O*), 170.23 (CH_3*C*=O), 170.37 (CH_3*C*=O); MALDI-TOF-MS: [M+Na]$^+$ calcd for $C_{58}H_{65}ClO_{16}Na$, 1075.3859; found 1075.6085.

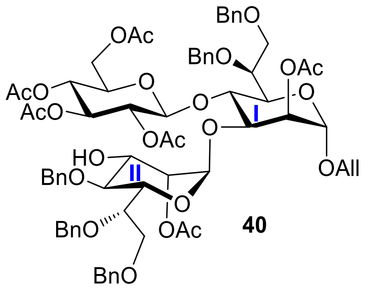


39

Allyl [2-*O*-acetyl-3-chloroacetyl-5,6,7-tri-*O*-benzyl-L-glycero-α-D-manno-heptopyranosyl]-(1→3)-[2,3,4,6-*O*-tetra-acetyl-β-D-glucopyranosyl]-(1→4)-2-*O*-acetyl-6,7-di-*O*-benzyl-L-glycero-α-D-manno-heptopyranoside (39)

A mixture of donor **27** (117 mg, 0.238 mmol), acceptor **38** (168 mg, 0.159 mmol) and freshly activated 4 Å molecular sieves in anhydrous CH_2Cl_2 (4 mL) was stirred for 30 min at RT under an atmosphere of argon. The mixture was cooled to 0 °C, TMSOTf (29 µL, 0.159 mmol) was added. The reaction mixture was slowly warmed to 5 °C in 40 min. TLC analysis showed that a major product (hexane/ethyl acetate 2:1, v/v, R_f = 0.23) was generated and acceptor **38** still remained. The mixture was cooled to 0 °C again, additional donor **27** (78 mg, 0.159 mmol) was added, followed by the addition of TMSOTf (9 µL, 0.0477 mmol). The reaction mixture was slowly warmed to 5 °C in 30 min. TLC analysis (hexane/ethyl acetate 2:1, v/v) showed that the acceptor **38** disappeared. The reaction was quenched by the addition of trimethylamine (0.2 mL), and the reaction mixture was filtered by celite. The filtrate was concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (15% ethyl acetate in hexane to 40%) to afford trisaccharide **39** (175 mg, 80%) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.95 (s, 3 H, CH_3CO), 1.97 (s, 6 H, 2xCH_3CO), 2.07 (s, 3 H, CH_3CO), 2.11 (s, 3 H, CH_3CO), 2.17 (s, 3 H, CH_3CO), 2.73-2.77 (m, 1 H, H-5-Glc), 3.64 (d, *J* = 15.0 Hz,1 H, ClCH*H*CO), 3.73-3.80 (m, 5 H, H-7a-Hep-II, H-7a-Hep-I, H-5-Hep-I Cl*CH*HCO, CH*H*-CH=CH_2), 3.86-3.90 (m, 2 H, H-7b-Hep-II, H-7b-Hep-I), 4.01-4.13 (m, 9 H, H-6a-Glc, H-6b-Glc, H-6-Hep-I, *CH*H-CH=CH_2, H-5-Hep-II, H-4-Hep-II, H-3-Hep-I, H-6-Hep-II, H-1-Glc), 4.20 (t, *J* = 9.6 Hz, 1 H, H-4-Hep-I), 4.40-4.55 (m, 7 H, 3xCH*H*-Ph, 2xCH_2-Ph), 4.61 (d, *J* = 12.0 Hz, 1 H, C*H*H-Ph), 4.70-4.77 (m, 3 H, H-2-Glc, H-4-Glc, H-1-Hep-I), 4.82-4.85 (m, 2 H, H-3-Glc, C*H*H-Ph), 5.01 (d, *J* = 12.6 Hz, 1 H, C*H*H-Ph), 5.12-5.20 (m, 3 H, CH_2-CH=CH_2, H-1-Hep-II), 5.24-5.28 (m, 3 H, H-2-Hep-II, H-2-Hep-I, H-3-Hep-II), 5.68-5.75 (m, 1 H, CH_2-*CH*=CH_2), 7.16-7.44 (m, 25 H, H-Ar); ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.57 (CH_3C=O), 20.61 (3xCH_3C=O), 20.74 (CH_3C=O), 20.93 (CH_3C=O), 40.57 (ClCH_2CO), 62.24 (C6-Glc), 68.01 (CH_2-CH=CH_2), 68.80 (C4-Glc), 68.94 (C7-Hep-I), 69.61 (C2-Hep-II), 70.57 (C7-Hep-II), 71.23 (C2-Glc), 71.34 (C2-Hep-I), 71.46 (C3-Hep-I, CH_2-Ph), 71.58 (C5-Glc), 71.63 (C5-Hep-I), 72.24 (CH_2-Ph), 72.35 (C5-Hep-II), 72.61 (C4-Hep-II), 73.01 (C3-Hep-II), 73.23 (C3-Glc), 73.27 (CH_2-Ph), 73.65 (CH_2-Ph), 73.73 (CH_2-Ph), 74.74 (C4-Hep-I, C6-Hep-I), 74.88 (C6-Hep-II), 96.53 (C1-Hep-I, J_{C1-H1} = 173 Hz), 98.46 (C1-Hep-II, J_{C1-H1} = 178 Hz), 100.16 (C1-Glc, J_{C1-H1} = 161 Hz), 118.07 (CH_2-CH=CH_2), 127.24-128.81 (*C*-Ar), 133.02 (CH_2-*CH*=CH_2), 137.45 (*C*-Ar), 138.39 (*C*-Ar), 138.52 (*C*-Ar), 138.59 (*C*-Ar), 138.80 (*C*-Ar), 166.19 ($ClCH_2C=O$), 169.03

(CH$_3$*C*=O), 169.32 (CH$_3$*C*=O), 169.63 (CH$_3$*C*=O), 170.03 (CH$_3$*C*=O), 170.26 (CH$_3$*C*=O), 170.52 (CH$_3$*C*=O); bsHSQCAD NMR was used to calculate coupling constant between the anomeric carbon and proton ($J_{C1\text{-}H1}$); MALDI-TOF-MS: [M+Na]$^+$ calcd for $C_{72}H_{83}ClO_{25}Na$, 1405.4810; found 1405.5571.

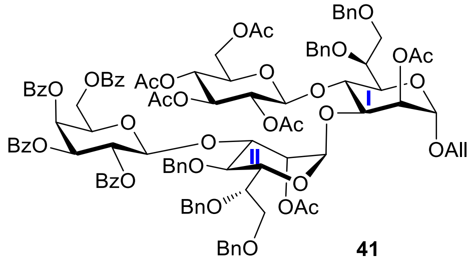


40

Allyl [2-*O*-acetyl-5,6,7-tri-*O*-benzyl-L-glycero-α-D-manno-heptopyranosyl]-(1→3)-[2,3,4,6-*O*-tetra-acetyl-β-D-glucopyranosyl]-(1→4)-2-*O*-acetyl-6,7-di-*O*-benzyl-L-glycero-α-D-manno-hepto-pyranoside (40)

A solution of compound **39** (175 mg, 0.126 mmol) in CH_2Cl_2 (2 mL) and MeOH (3 mL) was added *sym*-collidine (83 µL, 0.63 mmol) and thiourea (48 mg, 0.63 mmol), and the mixture was heated under reflux (70 °C) for 24 h. TLC analysis showed conversion of starting material **39** to a major product **40** (hexane/ethyl acetate 3:2, v/v, R_f = 0.17). The reaction mixture was concentrated under reduced pressure. The resulting residue was dissolved in ethyl acetate (30 mL), and washed with 1 M HCl (10 mL), $NaHCO_3$ (satd. aqueous, 10 mL) and brine (10 mL). The organic phase was dried (Na_2SO_4), filtered, and the filtrate was concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (20% ethyl acetate in hexane to 50%) to give trisaccharide acceptor **40** (140 mg, 85%) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.95 (s, 3 H, *CH$_3$*CO), 1.96 (s, 3 H, *CH$_3$*CO), 1.98 (s, 3 H, *CH$_3$*CO), 2.05 (s, 3 H, 2x*CH$_3$*CO), 2.13 (s, 3 H, *CH$_3$*CO), 2.46 (d, *J* = 4.2 Hz, 1 H, *OH*), 2.82-2.85 (m,1 H, H-5-Glc), 3.71-3.73 (m, 3 H, H-7a-Hep-II, H-7a-Hep-I, H-5-Hep-I), 3.79-3.89 (m, 5 H, CH*H*-CH=CH$_2$, H-6a-Glc, H-5-Hep-II, H-7b-Hep-II, H-7b-Hep-I), 3.93-4.05 (m, 5 H, H-3-Hep-II, H-4-Hep-II, H-6-Hep-I, *CH*H-CH=CH$_2$, H-3-Hep-I), 4.10-4.12 (m, 2 H, H-6-Hep-II, H-1-Glc), 4.17 (t, *J* = 9.6 Hz, 1 H, H-4-Hep-I), 4.42-4.56 (m, 6 H, 2xCH*H*-Ph, 2x*CH$_2$*-Ph), 4.58-4.62 (m, 2 H, H-6b-Glc, CH*H*-Ph), 4.79-4.84 (m, 4 H, H-1-Hep-I, 2x*CH*H-Ph, H-2-Glc), 4.88 (t, *J* = 9.6 Hz, 1 H, H-3-Glc), 4.97-5.01 (m, 2 H, H-4-Glc, *CH*H-Ph), 5.07 (s, 1 H, H-1-Hep-II), 5.11-5.13 (m, 2 H, H-2-Hep-I, CH$_2$-CH=CH*H*), 5.18 (dd, *J* = 1.2, 17.4 Hz, 1 H, CH$_2$-CH=*CH*H), 5.24 (dd, *J* = 1.8, 3.0 Hz, 1 H, H-2-Hep-II), 5.70-5.77 (m, 1 H, CH$_2$-*CH*=CH$_2$), 7.19-7.43 (m, 25 H, H-Ar); ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.58 (2x*CH$_3$*C=O), 20.67 (*CH$_3$*C=O), 20.73 (*CH$_3$*C=O), 20.98 (*CH$_3$*C=O), 21.12 (*CH$_3$*C=O), 62.31 (C6-Glc), 68.06 (*CH$_2$*-CH=CH$_2$), 68.69 (C4-Glc), 68.92 (C7-Hep-I), 70.34 (C7-Hep-II, C4-Hep-II), 70.85 (C2-Glc), 71.33 (C5-Glc), 71.46 (*CH$_2$*-Ph), 71.59 (*CH$_2$*-Ph), 71.90 (C2-Hep-II, C5-Hep-I), 72.48 (C5-Hep-II), 72.59 (C2-Hep-I), 73.04 (C3-Glc), 73.23 (*CH$_2$*-Ph, C3-Hep-I), 73.68 (*CH$_2$*-Ph), 73.88 (C4-Hep-I), 73.95 (*CH$_2$*-Ph), 74.88 (C3-Hep-II), 74.98 (C6-Hep-I), 75.26 (C6-Hep-II), 96.38 (C1-Hep-I), 99.75 (C1-

Hep-II), 100.07 (C1-Glc), 117.80 (CH_2-CH=*CH_2*), 127.18-128.74 (*C*-Ar), 133.03 (CH_2-*CH*=CH_2), 137.49 (*C*-Ar), 138.46 (*C*-Ar), 138.69 (*C*-Ar), 138.83 (*C*-Ar), 138.87 (*C*-Ar), 168.96 (CH_3*C*=O), 169.18 (CH_3*C*=O), 169.71 (CH_3*C*=O), 170.07 (CH_3*C*=O), 170.42 (CH_3*C*=O), 170.93 (CH_3*C*=O). MALDI-TOF-MS: $[M+Na]^+$ calcd for $C_{70}H_{82}O_{24}Na$, 1329.5094; found 1329.7941.

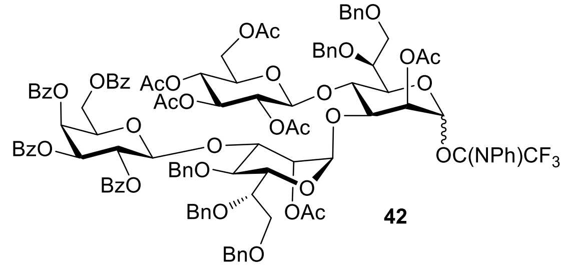


41

Allyl [2,3,4,6-*O*-tetra-benzyol-β-D-galactopyranosyl-(1→3)-2-*O*-acetyl-5,6,7-tri-*O*-benzyl-L-glycero-α-D-manno-heptopyranosyl]-(1→3)-[2,3,4,6-*O*-tetra-acetyl-β-D-glucopyranosyl]-(1→4)-2-*O*-acetyl-6,7-di-*O*-benzyl-L-glycero-α-D-manno-heptopyranoside (41)

A mixture of donor **28** (111 mg, 0.15 mmol), acceptor **40** (130 mg, 0.10 mmol) and freshly activated 4 Å molecular sieves in anhydrous CH_2Cl_2 (3 mL) was stirred for 30 min at RT under an atmosphere of argon. The mixture was cooled to -10 °C, TMSOTf (5.4 µL, 0.03 mmol) was added. The reaction mixture was slowly warmed to -5 °C in 40 min, TLC analysis showed that a major product **41** (hexane/ethyl acetate 2:3, v/v, R_f = 0.46) was generated and a little acceptor **40** still remained. The additional donor **28** (37 mg, 0.05 mmol) was added, the reaction mixture was slowly warmed to 0 °C in 20 min. TLC analysis (hexane/ethyl acetate 2:3, v/v) showed that the acceptor **40** disappeared. The reaction was quenched by the addition of trimethylamine (0.1 mL), and the reaction mixture was filtered by celite. The filtrate was concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (20% ethyl acetate in hexane to 40%) to afford tetrasaccharide **41** (169 mg, 90%) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.24 (s, 3 H, *CH_3*CO), 1.96 (s, 3 H, *CH_3*CO), 2.00 (s, 3 H, *CH_3*CO), 2.07 (s, 3 H, *CH_3*CO), 2.12 (s, 3 H, *CH_3*CO), 2.16 (s, 3 H, *CH_3*CO), 3.08-3.12 (m,1 H, H-5-Glc), 3.69-3.75 (m, 3 H, H-7a-Hep-II, H-7a-Hep-I, H-5-Hep-I), 3.79-3.81 (m, 2 H, H-7b-Hep-II, CH*H*-CH=CH_2), 3.90-3.95 (m, 2 H, H-7b-Hep-I, H-5-Hep-II), 3.98-4.07 (m, 4 H, H-6-Hep-I, H-6a-Glc, *CH*H-CH=CH_2 H-4-Hep-II), 4.10-4.16 (m, 2 H, H-3-Hep-I, H-6-Hep-II), 4.20-4.26 (m, 3 H, H-6a-Gal, H-1-Glc, H-4-Hep-I), 4.40-4.44 (m, 3 H, 2xCH*H*-Ph, H-3-Hep-II), 4.50-4.60 (m, 6 H, H-5-Gal, 2x*CH*H-Ph, 3xCH*H*-Ph), 4.71 (t, *J* = 9.6 Hz, 1 H, H-2-Glc), 4.77-4.82 (m, 4 H, H-6b-Glc, *CH*H-Ph, H-6b-Gal, H-1-Hep-I), 4.95 (t, *J* = 9.6 Hz, 1 H, H-3-Glc), 4.98 (t, *J* = 12.6 Hz, 1 H, *CH*H-Ph), 5.10-5.20 (m, 5 H, CH_2-CH=CH*H*, H-2-Hep-I, H-1-Hep-II, H-4-Glc, CH_2-CH=*CH*H), 5.25-5.27 (m, 2 H, *CH*H-Ph, H-1-Gal), 5.34 (dd, *J* = 1.2, 3.0 Hz, 1 H, H-2-Hep-II), 5.69-5.76 (m, 2 H, CH_2-*CH*=CH_2, H-3-Gal), 5.82 (t, *J* = 9.6 Hz, 1 H, H-2-Gal), 6.02 (s, 1 H, H-4-Gal), 7.17-7.54 (m, 37 H, H-Ar), 7.75-7.76 (m, 2 H, H-Bz), 7.90-7.91 (m, 2 H, H-Bz), 7.97-8.01 (m, 4 H, H-Bz); ^{13}C NMR (150 MHz, $CDCl_3$): δ 19.84 (*CH_3*C=O), 20.57 (*CH_3*C=O), 20.72 (*CH_3*C=O), 20.74 (*CH_3*C=O), 20.89 (*CH_3*C=O), 20.95 (*CH_3*C=O), 60.95 (C6-Gal), 63.69 (C6-Glc), 67.88 (C2-Hep-II), 67.96 (*CH_2*-CH=CH_2), 68.02

(C4-Gal), 69.00 (C7-Hep-I), 69.44 (C2-Hep-I), 69.90 (C2-Gal), 70.13 (C5-Gal), 70.90 (C7-Hep-II), 71.41 (C2-Glc), 71.50 (C3-Hep-I, CH_2-Ph), 71.54 (C5-Glc), 71.65 (C5-Hep-I), 71.83 (C5-Hep-II), 72.04 (C3-Gal), 72.17 (C4-Hep-II), 72.26 (C4-Glc), 73.07 (C3-Glc), 73.11 (CH_2-Ph), 73.13 (CH_2-Ph), 73.61 (CH_2-Ph, C4-Hep-I), 73.95 (CH_2-Ph), 74.58 (C6-Hep-I), 74.98 (C6-Hep-II), 75.22 (C3-Hep-II), 96.49 (C1-Hep-I), 97.24 (C1-Gal), 99.04 (C1-Hep-II), 99.60 (C1-Glc), 117.88 (CH_2-CH=CH_2), 127.21-130.08 (*C*-Ar), 133.01 (*C*-Bz), 133.06 (CH_2-*CH*=CH_2), 133.25 (2x*C*-Bz), 133.29 (*C*-Bz), 137.52 (*C*-Bn), 138.39 (*C*-Bn), 138.51 (*C*-Bn), 138.75 (*C*-Bn), 139.19 (*C*-Bn), 165.25 (Ph*C*=O), 165.46 (Ph*C*=O), 165.51 (Ph*C*=O), 165.91 (Ph*C*=O), 168.88 (Ph*C*=O), 169.22 (CH_3*C*=O), 169.29 (CH_3*C*=O), 169.72 (CH_3*C*=O), 170.41 (CH_3*C*=O), 170.43 (CH_3*C*=O); MALDI-TOF-MS: $[M+Na]^+$ calcd for $C_{104}H_{108}O_{33}Na$, 1907.6671; found 1907.7678.



42

[2,3,4,6-*O*-tetra-benzyol-β-D-galactopyranosyl-(1→3)-2-*O*-acetyl-5,6,7-tri-*O*-benzyl-L-glycero-α-D-manno-heptopyranosyl]-(1→3)-[2,3,4,6-*O*-tetra-acetyl-β-D-glucopyranosyl]-(1→4)-2-*O*-acetyl-6,7-di-*O*-benzyl-L-glycero-α/β-D-manno-heptopyranosyl *N*-phenyl-trifluoroacetimidate (42)

A solution of compound **41** (168 mg, 0.089 mmol) in CH_2Cl_2 (1 mL) and MeOH (5 mL) was added $PdCl_2$ (16 mg, 0.089 mmol), and the mixture was stirred for 2.5 h at RT. TLC analysis showed conversion of starting material **41** to a major product (hexane/ethyl acetate 3:2, v/v, $R_f = 0.27$). The reaction mixture was filtered by celite, and the filtrate was concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (20% ethyl acetate in hexane to 50%) to give a hemiacetal (142 mg, 86%) as colorless oil for next step. MALDI-TOF-MS: $[M+Na]^+$ calcd for $C_{101}H_{104}O_3Na$,1867.6358; found 1867.9351.

A mixture of the resulting hemiacetal (140 mg, 0.076 mmol), *N*-phenyltrifluoroacetimidoyl chloride (25 µL, 0.152 mmol) and Cs_2CO_3 (50 mg, 0.152 mmol) in anhydrous CH_2Cl_2 (5 mL) was stirred for 4 h at RT. TLC analysis showed conversion of the hemiacetal to a major product **42** (hexane/ethyl acetate 3:2, v/v, $R_f = 0.50$). The reaction mixture was concentrated under reduced pressure. The resulting residue was purified by silica gel chromatography (20% ethyl acetate in hexane to 40%) to afford glycosyl donor **42** (130 mg, 85%) for next coupling step. ESI-MS: $[M+NH_4]^+$ calcd for $C_{109}H_{112}F_3N_2O_{33}$, 2033.7099; found 2034.0613.

2.8. Synthesis of inner core hexasaccharide 1

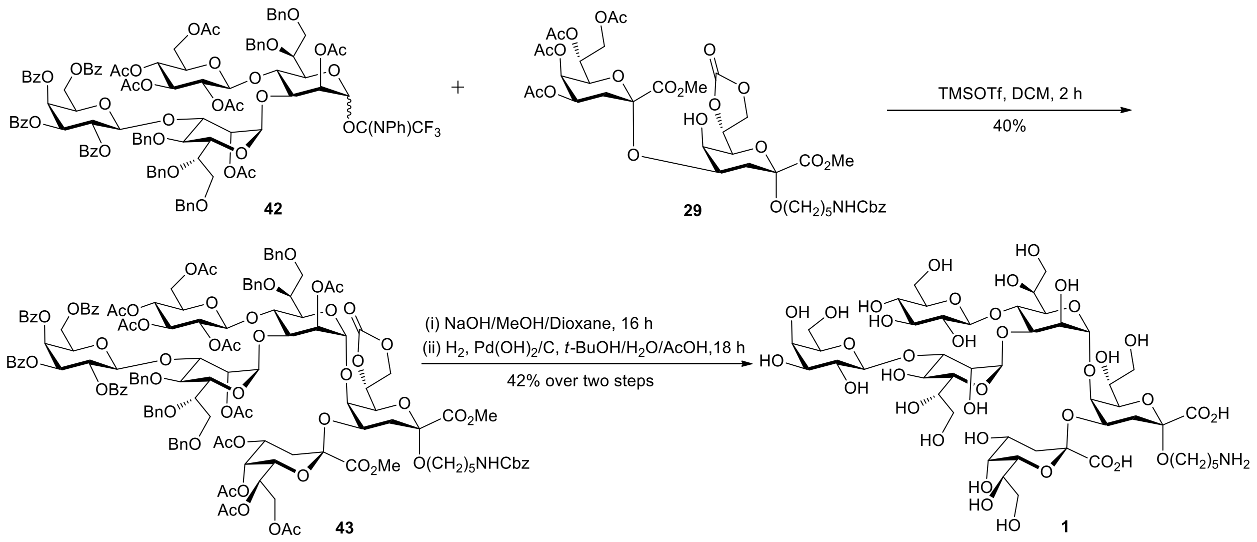
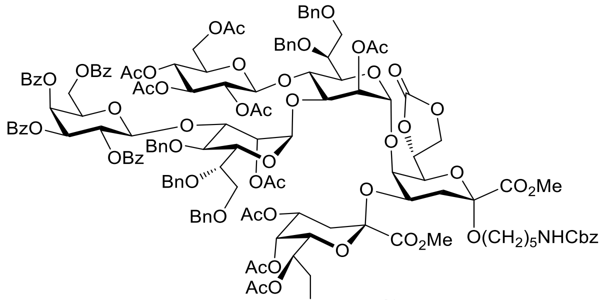


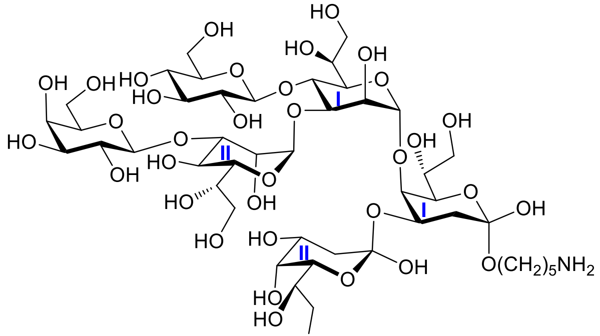
Figure S8. Synthesis of inner core hexasaccharide **1**.



43

Methyl (methyl 4,5,7,8-tetra-*O*-acetyl-3-deoxy-α-D-manno-oct-2-ulopyranosyl)onate)-(2→4)-[[2,3,4,6-*O*-tetra-benzyol-β-D-galactopyranosyl-(1→3)-2-*O*-acetyl-5,6,7-tri-*O*-benzyl-L-glycero-α-D-manno-heptopyranosyl]-(1→3)-[2,3,4,6-*O*-tetra-acetyl-β-D-glucopyranosyl]-(1→4)-2-*O*-acetyl-6,7-di-*O*-benzyl-L-glycero-α-D-manno-heptopyranosyl-(1→5)]-2-*O*-(5-amino-*N*-benzyloxycarbonylpentyl)-7,8-*O*-carbonyl-3-deoxy-α-D-manno-oct-2-ulo-pyranosid)onate (43)

A solution of glycosyl acceptor **29** (36 mg, 0.04 mmol) and freshly activated 5 Å molecular sieves in anhydrous CH_2Cl_2 (0.5 mL) was stirred for 1 h at RT under an atmosphere of argon. TMSOTf (1 µL, 0.006 mmol) was added and stirred for 10 min. A solution of glycosyl donor **42** (121 mg, 0.06 mmol) in anhydrous CH_2Cl_2 (0.5 mL) was added dropwise to the mixture in 1.5 h. Subsequently, TMSOTf (0.7 µL, 0.004 mmol) was added, and the reaction mixture was stirred for 30 min at RT under an atmosphere of argon. TLC analysis showed that the donor disappeared and a major product was generated (20% acetone in toluene, v/v, $R_f = 0.29$). The reaction was quenched by the addition of trimethylamine (5 µL), and the mixture was filtered by celite. The filtrate was concentrated under reduced pressure. The resulting residue was purified by size-exclusion chromatography (Sephadex LH-20) in DCM/MeOH (1/1, v/v) to afford hexasaccharide **43** (44 mg, 40%) as colorless oil, which was directly deprotected in next step for further purification. MALDI-TOF-MS: $[M+Na]^+$ calcd for $C_{141}H_{155}NO_{54}Na$, 2748.9311; found 2748.9470.



1

[3-deoxy-α-D-manno-oct-2-ulopyranosid-(2→4)]-[[β-D-galactopyranosyl-(1→3)-L-glycero-α-D-manno-heptopyranosyl-(1→3)]-[(β-D-glucopyranosyl)-(1→4)]-L-glycero-α-D-manno-heptopyranosyl-(1→5)]-2-*O*-(5-aminopentyl)-3-deoxy-α-D-manno-oct-2-ulopyranosidonic acid (1)

A solution of compound **43** (44 mg) in dioxane (1.2 mL), MeOH (0.4 mL) and NaOH (1 M, 0.4 mL) was stirred at RT for 16 h. ESI-MS analysis showed complete conversion of starting material to a major product (ESI-MS: $[M-2H]^{2-}$ $C_{90}H_{115}NO_{39}$, calcd for 916.8528, found 916.6277). Subsequently, MeOH (2 mL) was added, and the pH of mixture was neutralized to ~7 by Amberlite® IR120 hydrogen form resin. The reaction mixture was filtered, and the filtrate was concentrated under reduced pressure to afford a residue for next step.

A solution of the resulting residue in *t*-BuOH (3 mL), H_2O (2 mL) and AcOH (20 µL) was added $Pd(OH)_2/C$ (20 mg), and stirred for 18 h under an atmosphere of H_2. ESI-MS analysis showed that complete conversion of starting material to a major product **1**. The reaction mixture was filtered by celite, and the pH of filtrate was adjusted to ~7. The mixture was concentrated under reduced pressure to give a crude product, which was purified by size-exclusion chromatography (BioGel P-2, 45-90 µm, eluent: 0.1 M NH_4HCO_3). The product containing fractions were lyophilized to afford inner core hexasaccharide **1** as a white amorphous solid (8.1 mg, 42% for two steps). ESI-MS: m/z calcd $C_{47}H_{80}NO_{37}$ $[M-H]^-$ 1250.4487, found 1250.1510.

Table S1. ^{1}H NMR (600 MHz, D_2O) of **1**.

1	H1	H2	H3	H4	H5	H6	H7	H8
Kdo-I	-	-	1.820, 2.031	3.984	4.086	3.436	NA	NA
Kdo-II	-	-	1.654, 1.957	3.910	3.892	3.497	NA	NA
Hep-I	5.061	3.944	3.930	4.118	4.088	NA	NA	-
Hep-II	5.142	4.206	3.952	3.827	3.542	NA	NA	-
Glc	4.384	3.146	3.340	3.138	3.318	3.557, 3.816	-	-
Gal	4.394	3.470	3.461	3.763	3.524	NA	-	-
R	3.140, 3.231	1.456	1.131	1.550	2.854	-	-	-

^{13}C NMR (150 MHz, D_2O): δ 20.91 ($CH_2CH_2\mathit{CH_2}CH_2CH_2NH_2$), 26.74 ($CH_2CH_2CH_2\mathit{CH_2}CH_2NH_2$), 27.91 ($CH_2\mathit{CH_2}CH_2CH_2CH_2NH_2$), 34.32 (C3-Kdo-I), 34.59 (C3-Kdo-II), 39.37 ($CH_2CH_2CH_2CH_2\mathit{CH_2}NH_2$), 61.02, 61.56, 62.95 ($\mathit{CH_2}CH_2CH_2CH_2CH_2NH_2$), 62.98, 63.00, 63.10, 63.75, 64.26, 66.06 (C5-Kdo-II), 66.25, 67.24 (C2-Hep-II), 68.09 (C5-Kdo-I), 68.60 (C4-Gal), 68.62 (C4-Kdo-II), 68.65, 68.99, 70.17 (C4-Glc), 70.31 (C2-Hep-I), 70.34 (C4-Hep-II), 70.57, 70.87 (C4-Kdo-I), 71.65, 71.67, 71.76 (C5-Hep-II), 72.09 (C5-Hep-I), 72.61, 73.11 (C4-Hep-I), 73.32 (C2-Glc), 73.82 (C3-Hep-I), 75.13 (C3-Glc), 76.52 (C5-Glc), 78.27 (C3-Hep-II), 98.59 (C1-Hep-I, $J_{C1\text{-}H1}$ = 173 Hz), 99.34 (C2-Kdo-I), 100.80 (C1-Gal, $J_{C1\text{-}H1}$ = 160 Hz), 101.26 (C2-Kdo-II), 101.29 (C1-Hep-II, $J_{C1\text{-}H1}$ = 176 Hz), 102.19 (C1-Glc, $J_{C1\text{-}H1}$ = 162 Hz), 174.11 (C1-Kdo-II, $^{3}J_{C1\text{-}H3ax}$ < 1 Hz), 174.29 (C1-Kdo-I, $^{3}J_{C1\text{-}H3ax}$ < 1 Hz); bsHSQCAD NMR was used to calculate coupling constant between the anomeric carbon and proton ($J_{C1\text{-}H1}$); EXSIDE NMR was used to calculate coupling constant between the C1 and H3ax of Kdo ($^{3}J_{C1\text{-}H3ax}$).

3. Enzymatic synthesis

3.1. NMR nomenclature

Glycan assignments were made by numbering each monosaccharide starting from the reducing terminus and continuing in sequential order.

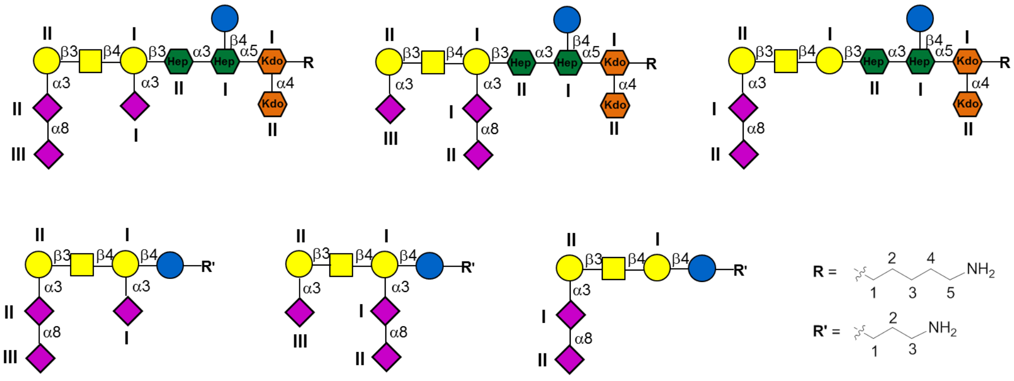


Figure S9. Oligosaccharide residues labels.

3.2 General analysis and semi-preparative procedures of LC-MS

A. Analysis procedure was performed on Shimadzu LC-ESI-IT-TOF with XBridge® Amide 5 µm, 4.6 mm x 250 mm column (Waters) at a flow rate of 0.8 mL/min using ESI-MS for compound detection. Mobile phase A consisted of 100 mM ammonium formate adjusted to pH 3.6 using formic acid; mobile phase B consisted of 100% acetonitrile. The following gradient was used.

Time (min)	A%
0	35
35	50
40	60
50	35
60	35

B. Purification by semi-preparative HPLC was performed on Shimadzu LC-ESI-IT-TOF using XBrigde® Amide 5 µm, 10 mm x 250 mm column (Waters) at a flow rate of 3.8 mL/min, and 1% of the flow was diverted to ESI-MS detector using a splitter. Mobile phase A consisted of 100mM ammonium formate adjusted to pH 3.6 using formic acid; mobile phase B consisted of 100% acetonitrile. The following gradient was used.

Time (min)	A%
0	35
35	50
40	60
50	35
60	35

3.3. Enzymatic synthesis of ganglioside mimics

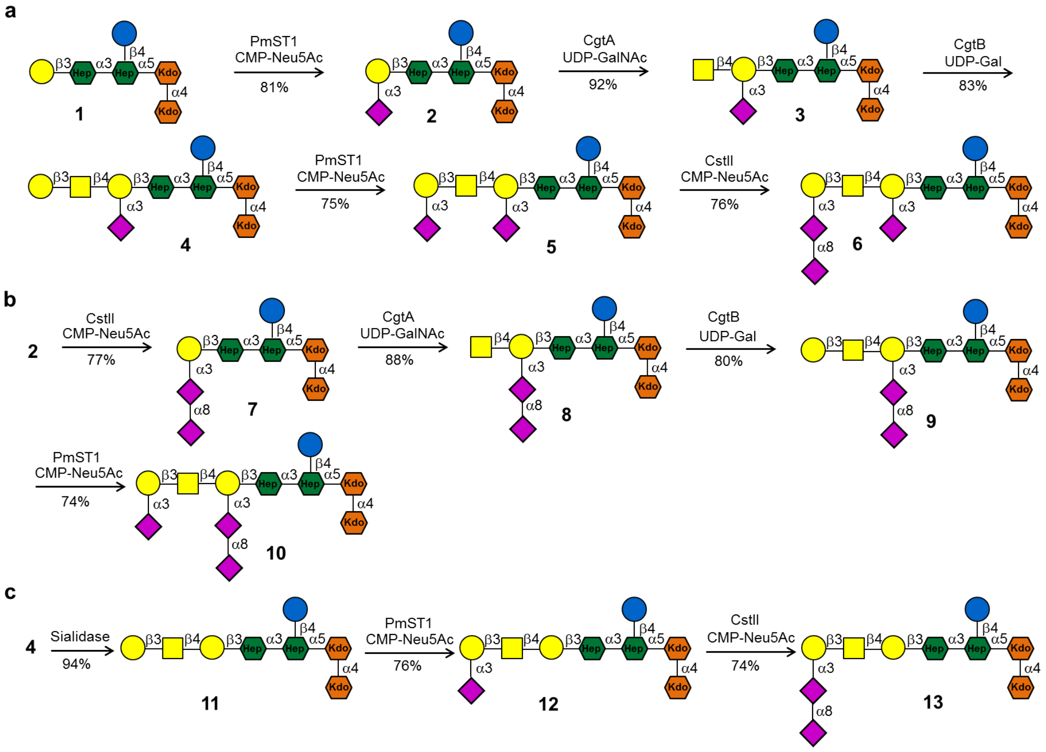


Figure S10. Enzymatic synthesis of ganglioside mimics.

3.4. Chemoenzymatic synthesis of normal ganglioside glycans

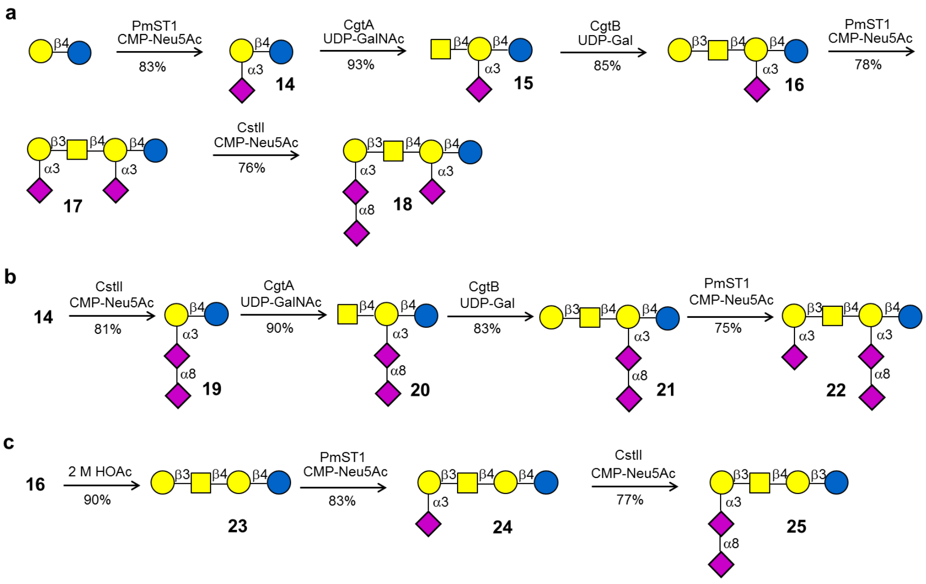


Figure S11. Chemoenzymatic synthesis of normal ganglioside glycans.

3.5. General procedures for enzymatic synthesis[5]

General procedure for the installation of α2,3-Neu5Ac by PmST1

A solution of glycans (2-10 mM), CMP-Neu5Ac (4-20 mM, 2 eq) in Tris-HCl buffer (100 mM, pH 8.0) was added PmST1 (5 μg/mL), and the mixture was incubated at 37 °C for 20 min. Subsequently, ESI-MS analysis was performed to monitor the reaction every 10 min until an optimal yield was achieved. The reaction mixture was centrifuged, and the resulting supernatant was loaded on Bio-Gel P4 column (1.0 × 120 cm, eluent: 0.1 NH_4HCO_3). Product containing fractions were combined and lyophilized to give the target glycans as a white amorphous solid. The product containing impure side fractions were combined and lyophilized for further purification by HPLC.

General procedure for the installation of α2,8-Neu5Ac by CstII for GD3

A solution of glycans (3-10 mM), CMP-Neu5Ac (4.5-15 mM, 1.5 eq) in Tris-HCl buffer (100 mM, pH 8.0) was added CstII (0.1 mg /mL), and the mixture was incubated at 37 °C for 2 h. Subsequently, ESI-MS analysis was performed to monitor the reaction every 30 min until an optimal yield was achieved. The reaction mixture was centrifuged, and the resulting supernatant was loaded on Bio-Gel P4 column (1.0 × 120 cm, eluent: 0.1 NH_4HCO_3). Product containing fractions were combined and lyophilized to give the target glycans as a white amorphous solid. The product containing impure side fractions were combined and lyophilized for further purification by HPLC.

General procedure for the installation of α2,8-Neu5Ac by CstII for GT3 and GD1c

A solution of glycans (4-10 mM), CMP-Neu5Ac (6-15 mM, 1.5 eq) in Tris-HCl buffer (100 mM, pH 8.0) was added calf intestine alkaline phosphatase (CIAP, 1 U /μL) and CstII (0.1 mg /mL), and the mixture was incubated at 37 °C for 3 h. Subsequently, ESI-MS analysis was performed to monitor the reaction every 30 min until an optimal yield was achieved. The reaction mixture was centrifuged, and the resulting supernatant was loaded on Bio-Gel P4 column (1.0 × 120 cm, eluent: 0.1 NH_4HCO_3). Product containing fractions were combined and lyophilized to give the target glycans as a white amorphous solid. Product containing impure side fractions were combined and lyophilized for further purification by HPLC.

General procedure for the installation of β1,4-GalNAc by CgtA

A solution of glycans (5-10 mM), UDP-GalNAc (7.5-15 mM, 1.5 eq), $MgCl_2$ (10 mM) in Tris-HCl buffer (50 mM, pH 7.5) was added CgtA (0.2 mg /mL), and the mixture was incubated at 37 °C for 4 h. Subsequently, ESI-MS analysis was performed to monitor the reaction every 1 h until no starting material was detected. The reaction mixture was centrifuged, and the resulting supernatant was loaded on Bio-Gel P4 column (1.0 × 120 cm, eluent: 0.1 NH_4HCO_3). Product containing fractions were combined and lyophilized to give the target glycans as a white amorphous solid.

General procedure for the installation of β1,3-Gal by CgtB

A solution of glycans (5-10 mM), UDP-Gal (5-10 mM, 1 eq), $MgCl_2$ (10 mM) in Tris-HCl buffer (50 mM, pH 7.5) was added CgtB (0.2 mg /mL), and the mixture was incubated at 37 ^{o}C for 2 h. Subsequently, ESI-MS analysis was performed to monitor the reaction every 30 min until an optimal yield was achieved. The reaction mixture was centrifuged, and the resulting supernatant was loaded on Bio-Gel P4 column (1.0 × 120 cm, eluent: 0.1 NH_4HCO_3). Product containing fractions were combined and lyophilized to give the target glycans as a white amorphous solid. Product containing impure side fractions were combined and lyophilized for further purification by HPLC.

Procedure for removal of internal Neu5Ac of GM1a mimic 3 by neuraminidase

A solution of GM1a mimic **4** (5-10 mM) in sodium acetate buffer (50 mM, pH 5.5) containing $CaCl_2$ (5 mM) was added α2-3,6,8,9 neuraminidase A (10000 U/mL, P0722L, NEW ENGLAND BioLabs®Inc.), and the mixture was incubated at 37 ^{o}C for 2 days. ESI-MS analysis was performed to monitor the reaction every day and additional α2-3,6,8,9 neuraminidase A was added until no starting material was detected. Once the reaction was finished, α2-3,6,8,9 neuraminidase A was inactivated at 65 ^{o}C for 10 min. The reaction mixture was centrifuged, and the resulting supernatant was loaded on Bio-Gel P4 column (1.0 × 120 cm, eluent: 0.1 NH_4HCO_3). Product containing fractions were combined and lyophilized to give GA1 mimic **11** as a white amorphous solid.

3.6. General procedure for removal of Neu5Ac by acid hydrolysis

GM1a **16** (5-10 mM) was dissolved in an aqueous solution of acetic acid (2 M). The reaction mixture was incubated at 80 ^{o}C for 2 h. Subsequently, ESI-MS analysis was performed to monitor the reaction every 30 min until an optimal yield was achieved. The reaction was quenched with saturated ammonium bicarbonate, and the mixture was loaded on Bio-Gel P4 column (1.0 × 120 cm, eluent: 0.1 NH_4HCO_3). Product containing fractions were combined and lyophilized to give GA1 **23**. Product containing impure side fractions were combined and lyophilized for further purification by HPLC.

4. Serology serum samples

Demographic characteristics of Dutch GBS patients seropositive for *C. jejuni* (n=17; from previous studies[6-8] coordinated by Erasmus MC) and healthy controls (n=10) are shown in Table S2. All samples were collected after approval of the Institutional Review Board of the Erasmus MC and all patients gave written informed consent. Controls consisted of healthy Dutch blood bank donors. Sera were aliquoted and stored at -80 °C. Evidence for an additional recent infection was found in three patients, two with hepatitis E (S017 and S024) and one with cytomegalovirus (S019). No evidence was found for a recent infection with *Mycoplasma pneumoniae*. *C. jejuni* was cultured from the stool of two patients (S012 and S020). Preceding diarrhea was present in all GBS patients except for S017, S019, and S024. Samples were assayed by ELISA[9] for IgG and IgM antibodies against gangliosides (GM1, GM2, GD1a, and GD1b) and purified LOS from *C. jejuni* strains GB2 wt (GM1/GD1a mimics), GB2 CstII ko (GA1/GA2 mimics), GB19 wt (GD1c/possibly GA1 mimics), GB25 (GM1b/GD1c/GA1 mimics), BD067 (GD3 mimics), and 11168 (GM1a/GM2 mimics).[10-12]

Table S2. Demographic characteristics of GBS patients seropositive for *C. jejuni* (n=17) and healthy controls (n=10).

				Clinical diagnosis	
SS#	Code	Gender	Age	GBS / *C. jejuni*	Max GBS disability score*
S002	Q132A	M	50	+ / +	3
S005	F263A	M	50	+ / +	4
S007	Q184A	F	32	+ / +	3
S010	Q136A	M	69	+ / +	2
S012	Q217A	F	79	+ / +	3
S014	Q128A	M	66	+ / +	4
S020	F320A	M	57	+ / +	5
S023	F241A	M	69	+ / +	4
S027	Q127A	M	67	+ / +	4
S035	Q246A	M	61	+ / +	3
S038	F325A	M	60	+ / +	4
S039	Q230A	M	65	+ / +	4
S017	F283A	F	61	+ / +	3
S019	F280A	F	61	+ / +	5
S024	F289A	M	69	+ / +	3
S033	Q224A	F	45	+ / +	3
S037	F291A	M	67	+ / +	3
S003	BCN052	F	70	- / -	-
S004	BCN053	F	68	- / -	-
S006	BCN054	M	36	- / -	-
S008	BCN045	F	42	- / -	-
S009	BCN055	M	34	- / -	-

S013	BCN047	M	49	- / -	-
S015	BCN048	M	34	- / -	-
S016	BCN049	M	49	- / -	-
S018	BCN024	M	44	- / -	-
S028	BCN017	F	55	- / -	-

*GBS disability score:[13] 0, normal; 1, Minor symptoms and capable of running; 2, Able to walk 10 min or more without assistance but unable to run; 3, Able to walk 10 min across an open space with help; 4, Bedridden or chairbound; 5, Requiring assisted ventilation for at least part of the day; 6, Dead.

Table S3. Ganglioside IgG and IgM Ab titer* of all serum samples determined by ELISA.

	GM1		GM2		GD1a		GD1b	
SS#	IgG	IgM	IgG	IgM	IgG	IgM	IgG	IgM
S002	0	100	0	0	400	0	1600	0
S005	6400	0	0	0	0	0	0	0
S007	0	0	0	0	100	0	200	0
S010	12800	3200	0	100	0	0	0	400
S012	25600	1600	0	0	0	0	0	0
S014	102400	400	0	0	0	0	0	0
S020	100	0	0	0	6400	0	0	0
S023	6400	800	0	0	12800	0	0	0
S027	0	0	0	0	6400	0	0	0
S035	3200	200	0	100	0	0	0	0
S038	0	0	0	1600	0	0	0	0
S039	400	400	200	400	100	0	0	0
S017	0	0	0	0	0	0	0	0
S019	0	0	0	0	0	0	0	0
S024	0	0	0	0	0	0	0	0
S033	0	0	0	0	0	0	0	0
S037	0	0	0	0	0	0	0	0
S003	0	0	0	0	0	0	0	0
S004	0	0	0	0	0	0	0	0
S006	0	0	0	0	0	0	0	0
S008	0	0	0	0	0	0	0	0
S009	0	0	0	0	0	0	0	0
S013	0	0	0	0	0	0	0	0
S015	0	0	0	0	0	0	0	0
S016	0	0	0	0	0	0	0	0
S018	0	0	0	0	0	0	0	0
S028	0	0	0	0	0	0	0	0

*Titers were determined using two-fold dilutions starting at 1:100. Zero indicates a titer <100. Colored entries are considered positive, blue for IgG and green for IgM.

Table S4. LOS serology IgG and IgM (ELISA dOD values) of the *C. jejuni* positive GBS patient serum samples.

	GB2 wt		GB2 ko		GB19 wt		GB25		BD067		11168	
SS#	IgG	IgM	IgG	IgM	IgG	IgM	IgG	IgM	IgG	IgM	IgG	IgM
S002	0,704	0,370	0,067	0,177	1,207	0,803	0,115	0,081	0,019	0,100	0,041	0,321
S005	1,286	0,136	-0,003	0,065	0,036	0,067	-0,015	0,049	0,003	0,077	1,416	0,305
S007	0,659	0,371	0,082	0,307	0,960	0,616	0,123	0,128	0,071	0,308	0,045	0,115
S010	0,476	1,047	0,034	0,429	0,150	0,667	0,007	0,063	0,012	0,122	1,083	0,818
S012	0,472	0,655	0,037	0,205	0,031	0,602	0,018	0,025	0,054	0,122	0,539	0,411
S014	1,479	1,389	0,346	0,245	0,301	0,185	0,280	0,161	0,237	0,229	0,250	0,173
S020	1,230	1,077	0,169	0,152	0,209	0,258	0,076	-0,048	0,128	0,190	0,531	0,278
S023	1,357	1,210	0,212	0,123	0,240	0,181	0,122	0,087	0,174	0,051	0,095	0,020
S027	0,547	0,200	0,084	0,070	0,609	0,091	0,073	0,035	0,095	0,140	0,092	0,060
S035	0,641	0,287	0,214	0,131	0,214	0,108	0,177	0,357*	0,167	0,088	1,278	0,869
S038	0,043	0,102	0,039	0,170	0,052	0,307	0,024	0,068	0,044	0,174	0,025	0,988
S039	0,663	0,593	0,463	0,477	0,225	0,200	0,396	0,281	0,494	0,243	0,983	1,010
S017	0,015	-0,112	0,019	0,171	0,032	0,317	0,005	0,070	0,019	0,297	0,010	0,092
S019	0,001	0,228	0,008	0,415	0,009	0,337	0,013	0,201	0,026	0,450	0,009	0,275
S024	0,009	0,117	0,007	0,053	0,026	0,144	0,053	0,021	0,089	0,062	-0,004	0,167
S033	0,001	0,110	0,018	0,044	0,000	0,087	0,010	0,003	0,022	0,087	0,021	0,089
S037	0,025	0,121	0,012	0,175	0,058	0,205	0,031	0,048	0,040	0,149	0,017	0,076

Colored entries are considered positive, blue for IgG and green for IgM (cut-off values differ between LOS structures).
*In repeat assay found negative.

5. Microarray

5.1 Glycan array printing

The synthetic glycans (100 µM in sodium phosphate (250 mM), pH 8.5 buffer) were printed as replicates of 6 on activated glass slides (Nexterion Slide H, Schott Inc) by piezoelectric non-contact printing (sciFLEXARRAYER S3, Scienion Inc) with a drop volume of ~400 pL and 1 drop per spot at 50 % relative humidity. Each slide contained 24 subarrays (3x8). The slides were incubated overnight in a saturated NaCl chamber (providing a 75% relative humidity environment), after which the remaining activated esters were quenched with ethanolamine (50 mM) in TRIS (100 mM), pH 9.0. Slides were rinsed with DI water, dried by centrifugation, and stored in a desiccator at RT.

5.2 Microarray validation and serum sample screening

Sub-arrays were incubated with biotinylated lectins (*Maackia amurensis* leukagglutinin (MAL-II), *Ricinus communis* agglutinin I (RCA I), Soybean agglutinin (SBA) and Wheat Germ agglutinin

(WGA); from Vector Labs) at the indicated concentrations premixed with Streptavidin-AlexaFluor635 (5 µg/mL; ThermoFisher Scientific, S32364) in TSM binding buffer (20 mM Tris Cl, pH 7.4, 150 mM NaCl, 2 mM $CaCl_2$, 2 mM $MgCl_2$, 0.05% Tween, 1% BSA) for 1 h followed by washing. Wash steps involved 4 successive washes of the whole slides with TSM wash buffer (20 mM Tris Cl, pH 7.4, 150 mM NaCl, 2 mM $CaCl_2$, 2 mM $MgCl_2$, 0.05% Tween-20) - TSM buffer (20 mM Tris Cl, pH 7.4, 150 mM NaCl, 2 mM $CaCl_2$, 2 mM $MgCl_2$) - 2x deionized H_2O with 5 min soak times.

Biotinylated ganglioside GM1 rabbit polyclonal antibody (2 µg/mL; Bioss, bs-2367R-Biotin) in TSM binding buffer at 2 µg/mL was incubated for 1 h followed by washing as described above. Next the subarrays were incubated with Streptavidin-AlexaFluor635 (5 µg/mL) for 1 h followed by washing. Anti-ganglioside GD1a mouse monoclonal antibody, clone GD1a-1 (2 µg/mL; Sigma-Aldrich MAB5606Z) and anti-human ganglioside GD2 mouse monoclonal antibody, clone 14.G2a (2 µg/mL; Abcam ab68456) in TSM binding buffer were incubated for 1 h followed by step-wise incubation with biotinylated goat anti-mouse IgG (5 µg/mL; Sigma-Aldrich B7264) and Streptavidin-AlexaFluor635 (5 µg/mL) for 1 h with washes in between as described above.

Human serum samples (see Section 4) were provided randomly numbered and were blindly assayed on the microarray similarly as described above. Sub-arrays were incubated with human serum samples (1:50, 1:100, 1:500) in TSM binding buffer for 1 h. After washing steps the sub-array were incubated with a mixture of Cy3-labeled goat anti-human IgG (1.5 µg/mL; Jackson Immuno Research, 109-165-098) and AlexaFluor647-labeled goat anti-human IgM (1.5 µg/mL; Jackson Immuno Research, 109-165-129) for 1 h. Other conditions were also investigated: with blocking of the microarray (TSM 1X+1%BSA 1 h), absence of Tween, absence of Ca^{2+}/Mg^{2+}, first step incubation longer (1 h *vs* overnight) and at lower temp (RT *vs* 4 °C), and longer detection incubation time.

In the event of neuraminidase treatment, subarrays were first incubated with α2-3,6,8,9 Neuraminidase A (BioLabs, P0722, 20 U/50 µL in 1X GlycoBuffer) for 3 h at 37 °C. Neuraminidase A (N-A) is a broad specificity sialidase, that catalyzes the hydrolysis of α2,3-, α2,6-, and α2,8-linked sialic acid residues from glycoproteins, glycopeptides, and oligosaccharides. See Table S5 for the expected compound formation after N-A treatment.

Unless stated otherwise, all incubation and wash steps were performed at RT. Washed arrays were dried by centrifugation and immediately scanned for fluorescence on a GenePix 4000 B microarray scanner (Molecular Devices). The detection gain was adjusted to avoid saturation of the signal, whereby the same settings were used for each experiment to allow comparison between patient and control samples. The data were processed with GenePix Pro 7 software and further analyzed using our home written Microsoft Excel macro. After removal of the lowest and highest value of the six replicates, the mean fluorescent intensities (corrected for mean background) and standard deviations (SD) were calculated (n=4). Data were fitted using Prism software Version 8.3.0 (GraphPad Software, Inc). Bar graphs represent the mean ± SD for each compound. The highest possible protein concentration / serum dilution was employed at which good responsiveness was observed to achieve an appropriate dynamic range.

Table S5. Compound structure formation after neuraminidase N-A treatment.

Cmpd	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
+ N-A	1	3	4	4	4	1	3	4	4	11	11	11	L	15	16	16	16	L	15	16	16	23	23	23

L = lactose

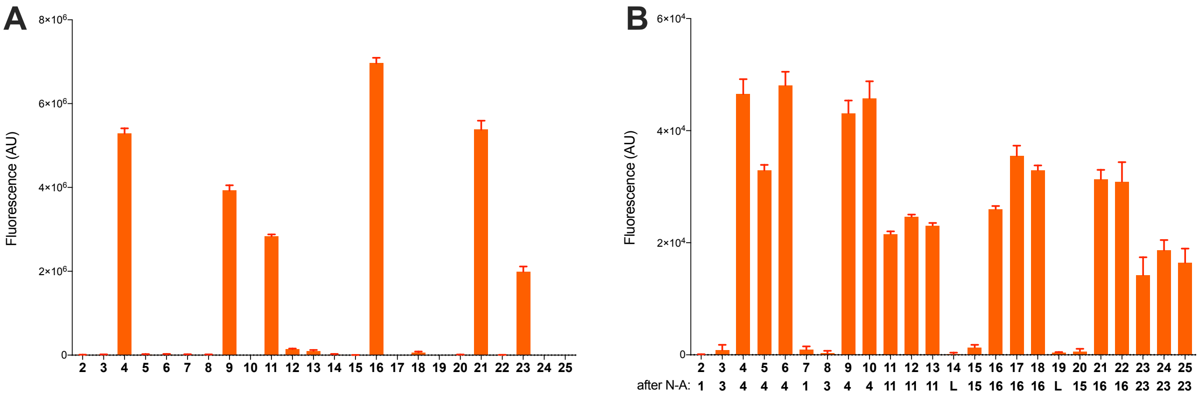
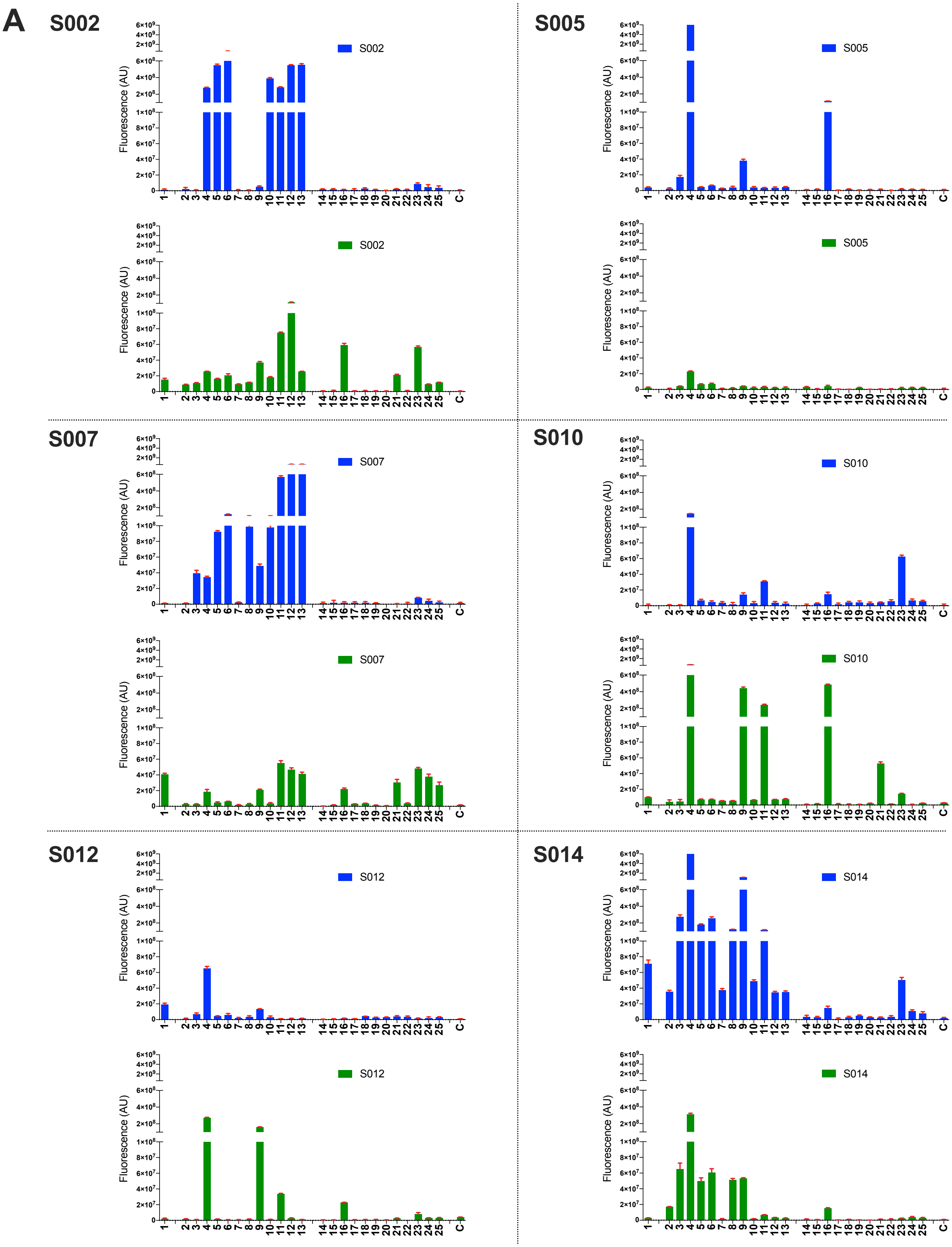


Figure S12. Microarray results of the synthetic ganglioside library at 100 μM with (A) polyclonal GM1 antibody (2 μg/mL) and (B) polyclonal GM1 antibody (2 μg/mL) after N-A treatment. Bars represent the mean ± SD. L = lactose.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S005
S007
S010
S012
S014
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4×10⁹
2×10⁹
6×10⁸
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2×10⁸
1×10⁸
8×10⁷
6×10⁷
4×10⁷
2×10⁷
0
1
2
3
4
5
6
7
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23
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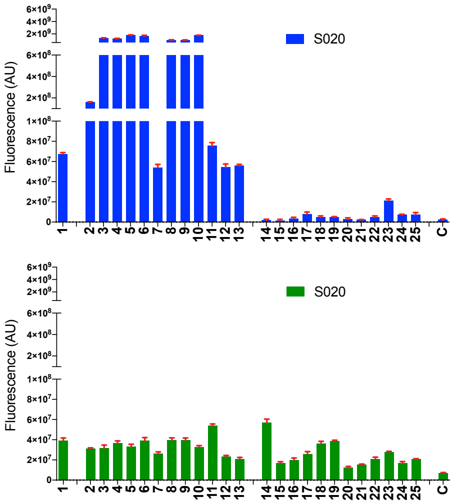
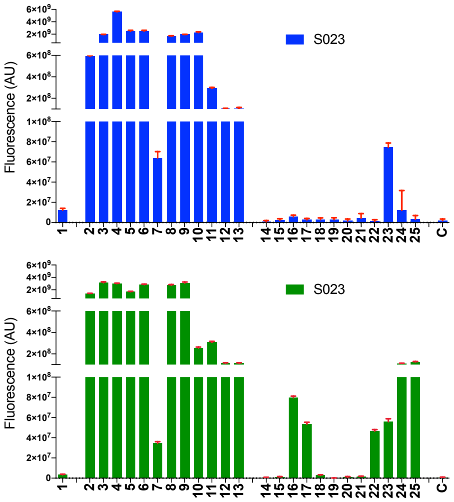
25
C-

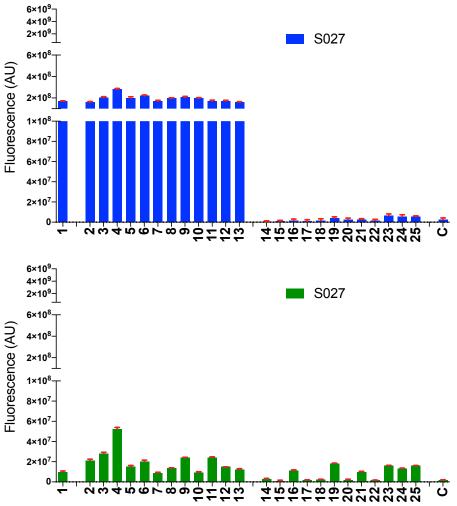
S020



S023



S027



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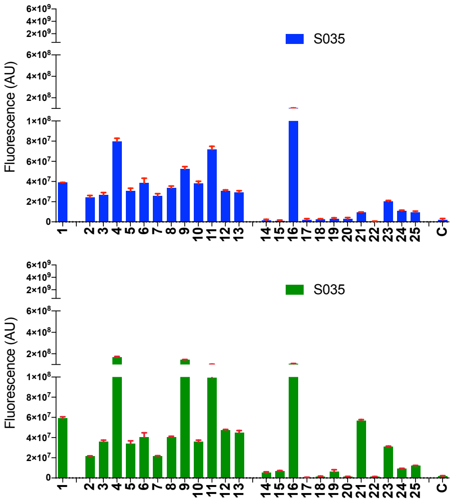

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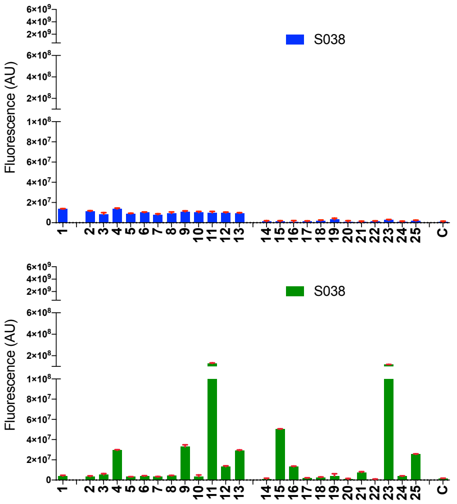

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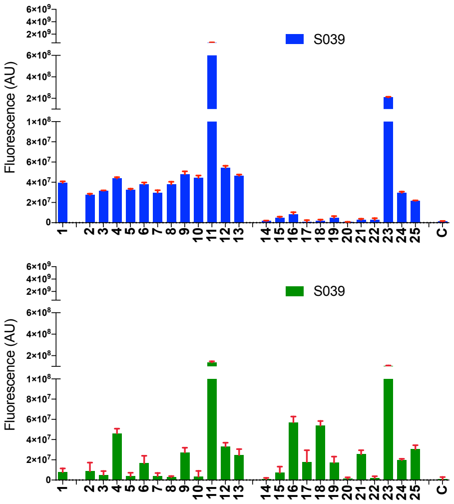

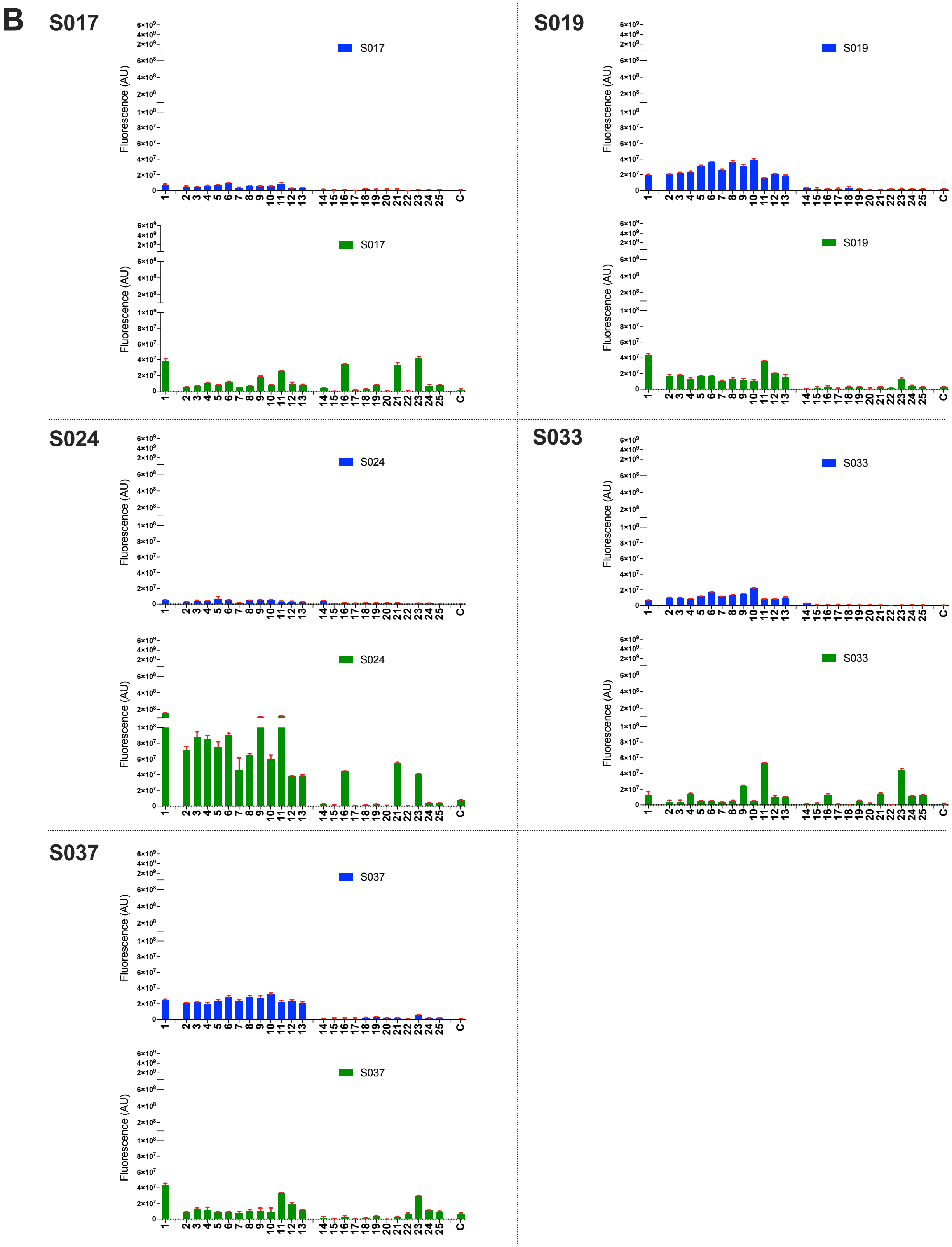
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S019
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S037
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2×10⁹
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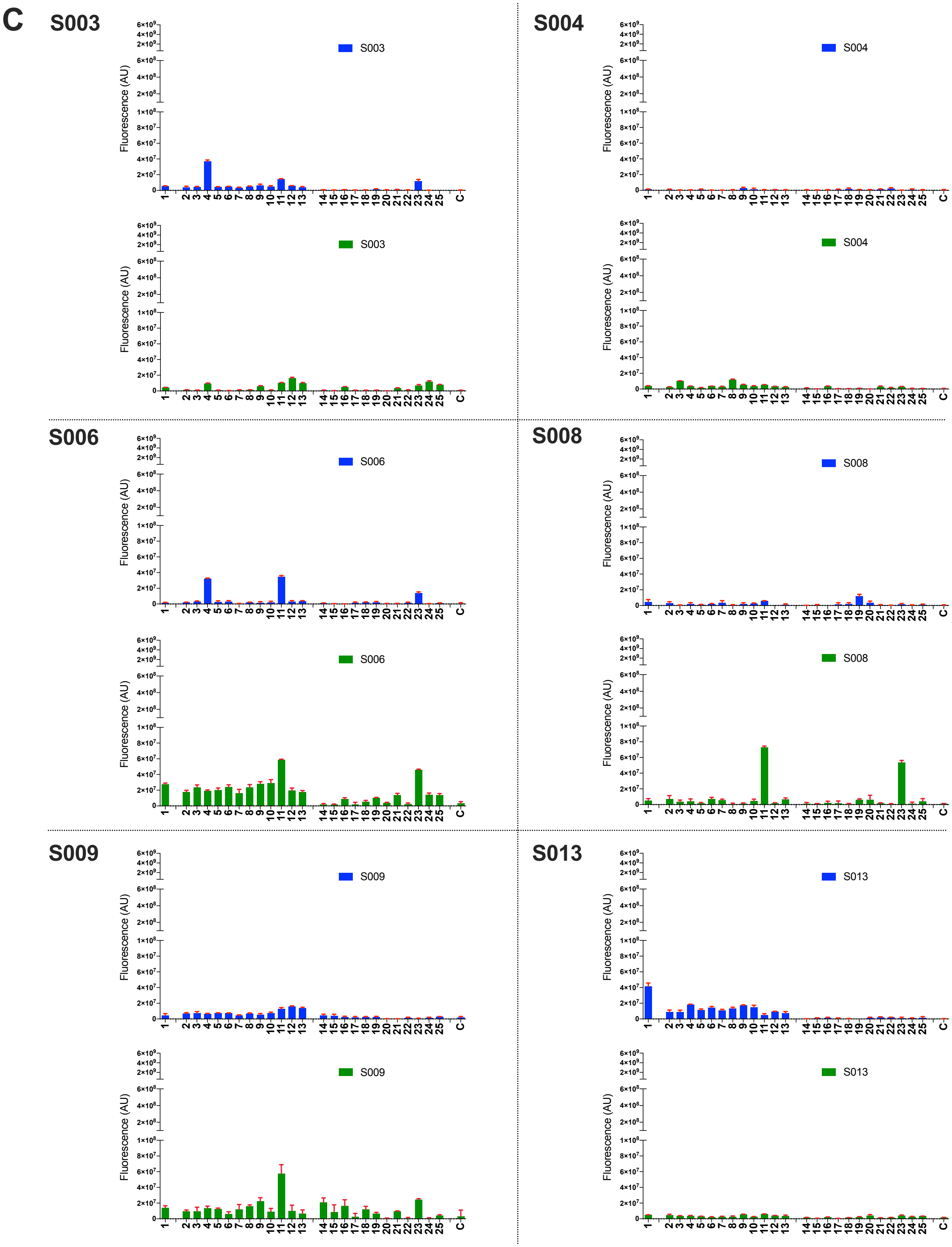
C-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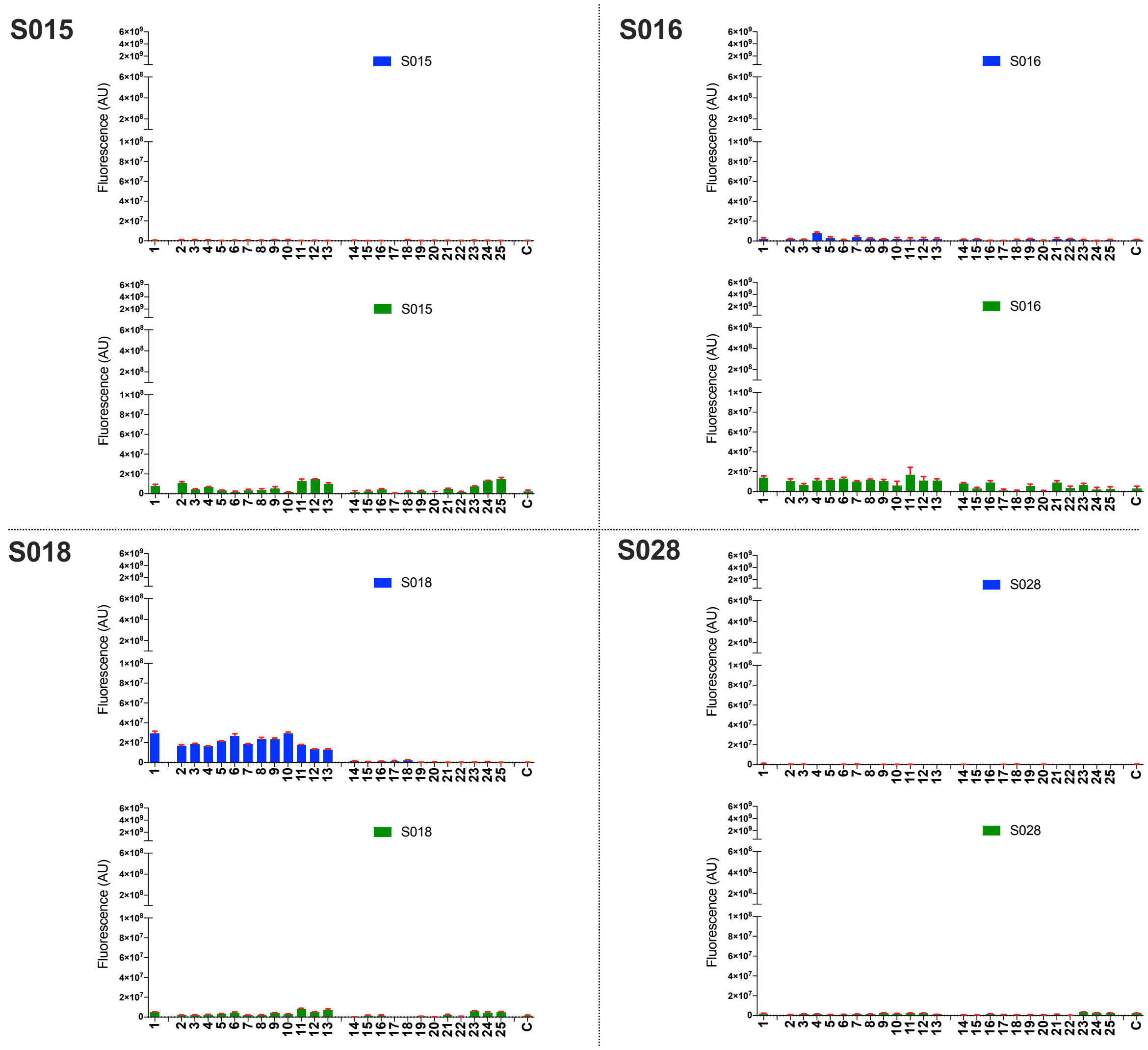


Figure S13. Microarray results of the synthetic ganglioside library at 100 µM with serum samples (1:500) of (A) *C. jejuni* positive GBS and positive serology by ELISA patients; (B) *C. jejuni* positive GBS and negative serology by ELISA patients; and (C) controls. For each sample, the graph at the top shows in blue IgG responses and the graph at the bottom in green IgM responses. Bars represent the mean ± SD. C indicates blank control. Assays are performed in the same session and results are depicted at the same scale. C = blank control.

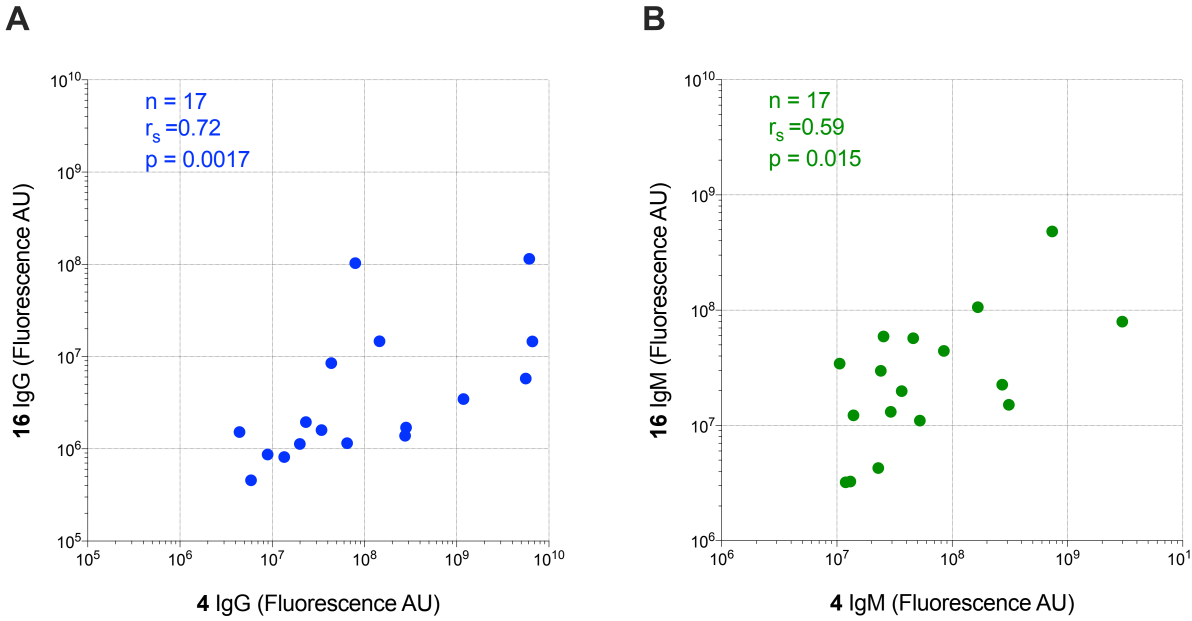


Figure S14. Correlation of microarray data of *C. jejuni* positive GBS patients of GM1a (**16**) *vs* GM1a mimic (**4**) for (A) IgG and (B) IgM. Spearman p values for A and B are 0.0017 and 0.015, respectively.

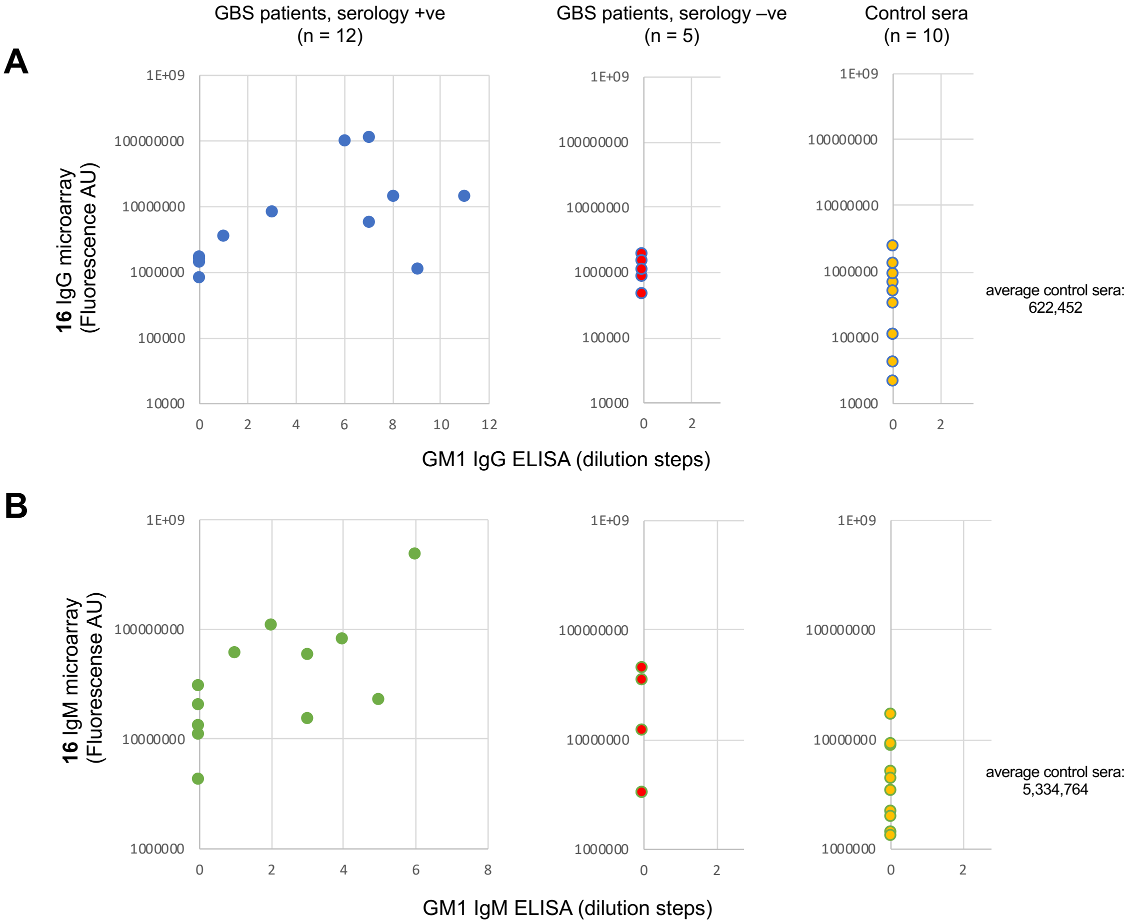
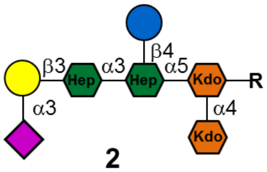


Figure S15. Correlation of GM1a (**16**) microarray *vs* GM1 ELISA data for (A) IgG and (B) IgM. ELISA titers determined by two-fold dilutions starting at 1:100 are plotted as dilution steps with zero indicating a titer <100.

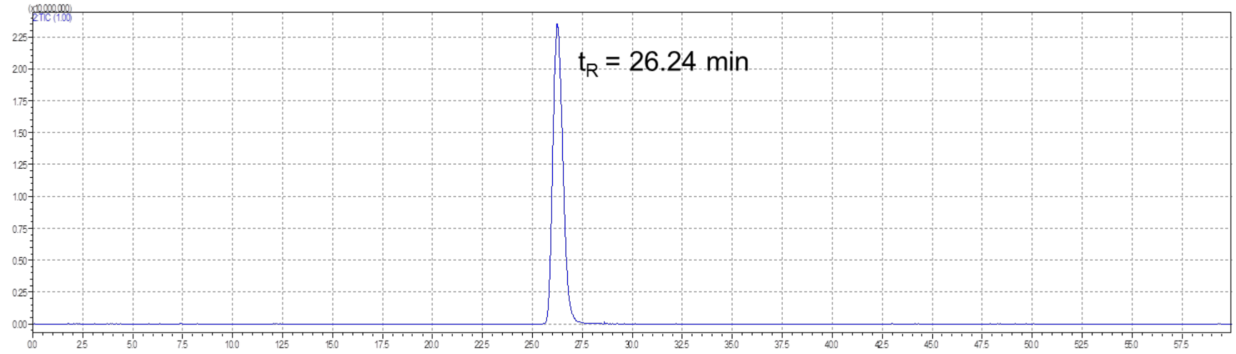
6. NMR assignments and LC-MS spectra

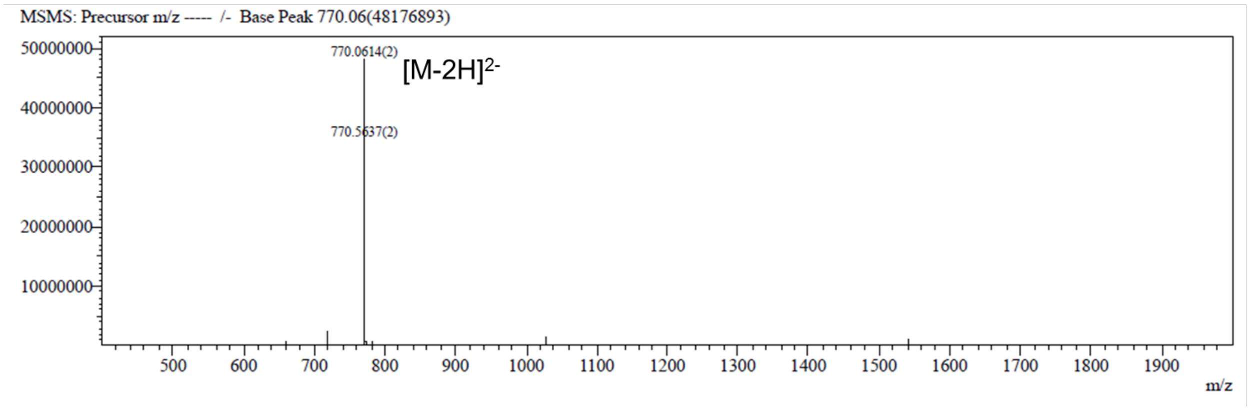


2

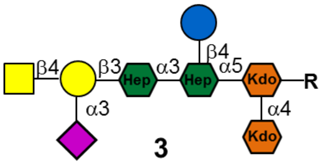
Table S6. ^{1}H NMR (600 MHz, D_2O) of **2**.

Compound 2	**H1**	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**
Kdo-I	-	-	1.840, 2.043	3.984	4.093	NA	NA	NA
Kdo-II	-	-	1.673, 1.959	3.920	3.898	NA	3.687	NA
Hep-I	5.056	3.942	3.936	4.115	4.086	NA	NA	-
Hep-II	5.135	4.246	3.969	3.828	3.541	NA	NA	-
Glc	4.383	3.148	3.343	3.137	3.321	3.547, 3.861	-	-
Gal	4.470	3.494	3.948	3.812	3.498	NA	-	-
Neu5Ac	-	-	1.652, 2.617	3.539	3.693	3.484	3.457	3.714
R	3.147, 3.249	1.458	1.309	1.551	2.854	-	-	-





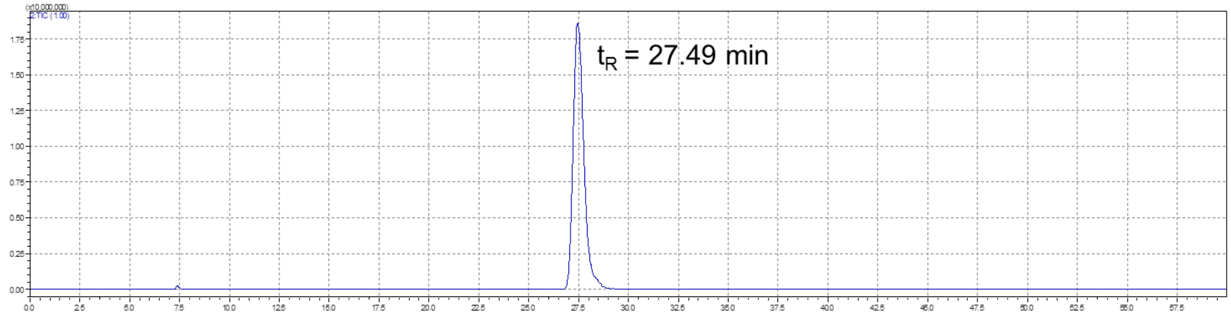
ESI-MS: m/z calcd $C_{58}H_{96}N_2O_{45}^{2-}$ $[M-2H]^{2-}$ 770.2648, found 770.0614.

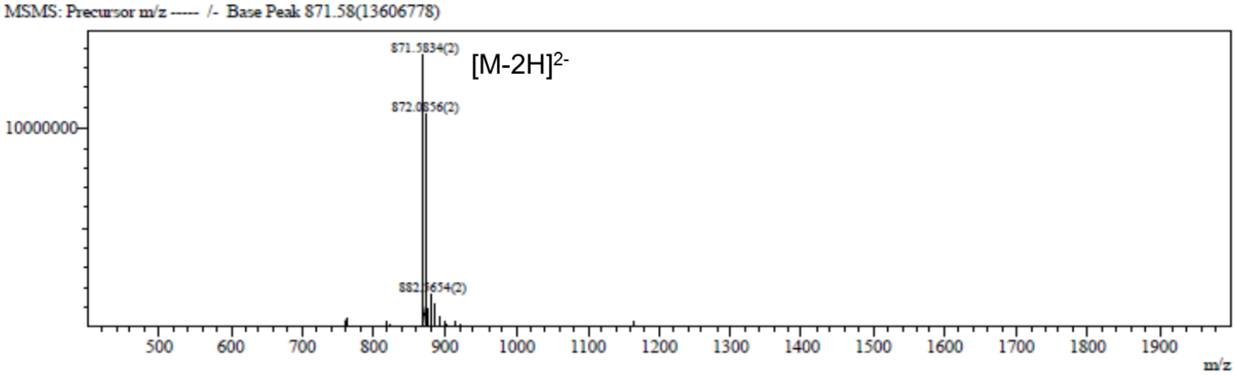


3

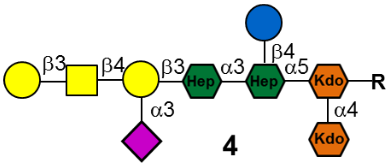
Table S7. ^{1}H NMR (600 MHz, D_2O) of **3**.

Compound 3	**H1**	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**
Kdo-I	-	-	1.822, 2.035	3.978	4.088	NA	NA	NA
Kdo-II	-	-	1.653, 1.957	3.914	3.895	NA	NA	NA
Hep-I	5.061	3.948	3.932	4.121	4.097	NA	NA	-
Hep-II	5.153	4.209	3.924	3.826	3.531	NA	NA	-
Glc	4.386	3.151	3.344	3.146	3.325	3.583, 3.867	-	-
Gal	4.472	3.293	3.994	3.970	3.581	NA	-	-
GalNAc	4.575	3.754	3.530	3.756	3.551	NA		
Neu5Ac	-	-	1.781, 2.532	3.621	3.667	3.342	3.443	3.588
R	3.143, 3.231	1.459	1.311	1.553	2.856	-	-	-





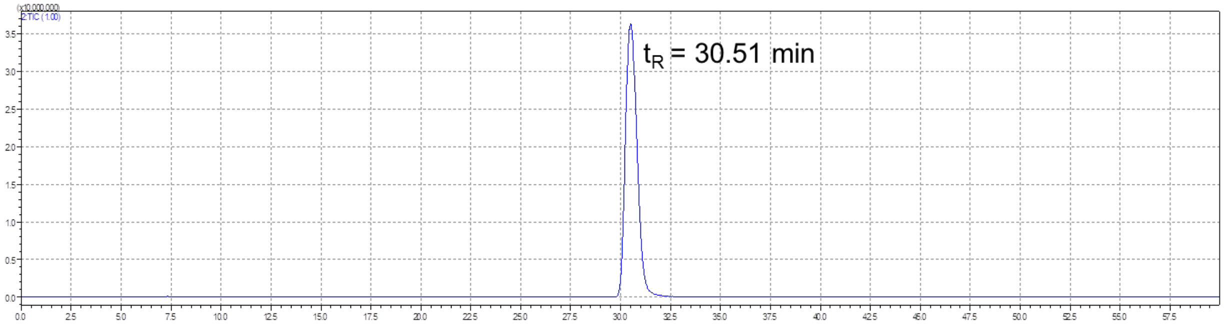
ESI-MS: m/z calcd $C_{66}H_{109}N_3O_{50}^{2-}$ $[M-2H]^{2-}$ 871.8045, found 871.5834.

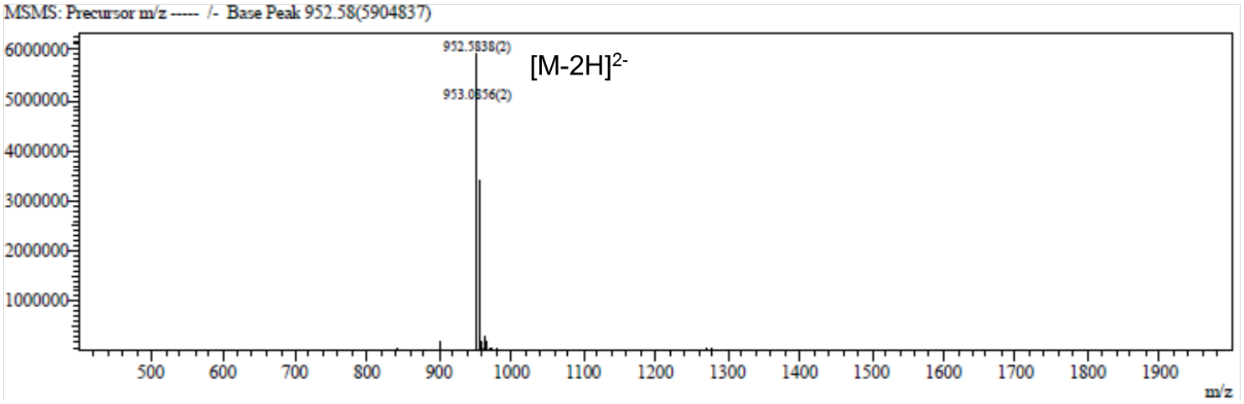


4

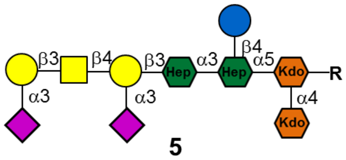
Table S8. ^{1}H NMR (600 MHz, D_2O) of **4**.

Compound 4	**H1**	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**
Kdo-I	-	-	1.843, 2.043	3.980	4.093	NA	NA	NA
Kdo-II	-	-	1.667, 1.960	3.916	3.901	NA	NA	NA
Hep-I	5.057	3.948	3.933	4.120	4.087	NA	NA	-
Hep-II	5.158	4.208	3.923	3.825	3.531	NA	NA	-
Glc	4.390	3.153	3.343	3.146	3.327	3.584, 3.868	-	-
Gal-I	4.476	3.294	3.995	3.983	NA	NA	-	-
GalNAc	4.618	3.884	3.666	4.003	3.565	NA		
Gal-II	4.382	3.366	3.478	3.755	3.527	NA		
Neu5Ac	-	-	1.789, 2.532	3.625	3.664	3.356	3.455	3.591
R	3.150, 3.246	1.458	1.311	1.552	2.856	-	-	-





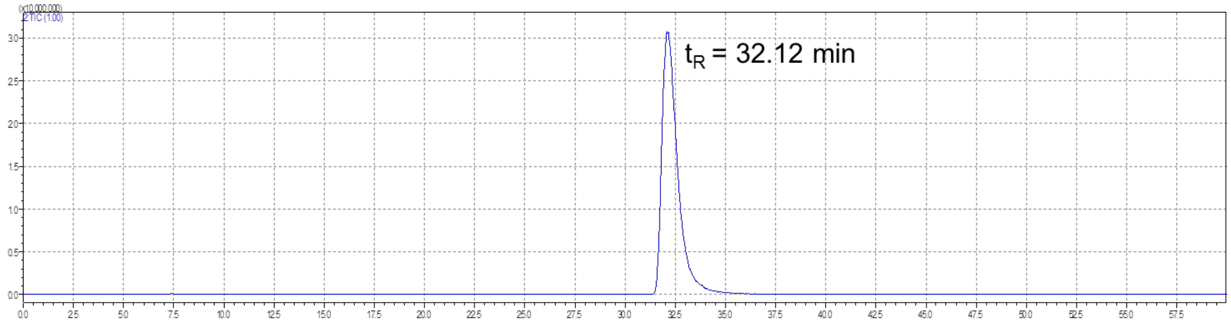
ESI-MS: m/z calcd $C_{72}H_{119}N_3O_{55}^{2-}$ [M-2H]$^{2-}$ 952.8309, found 952.5838.

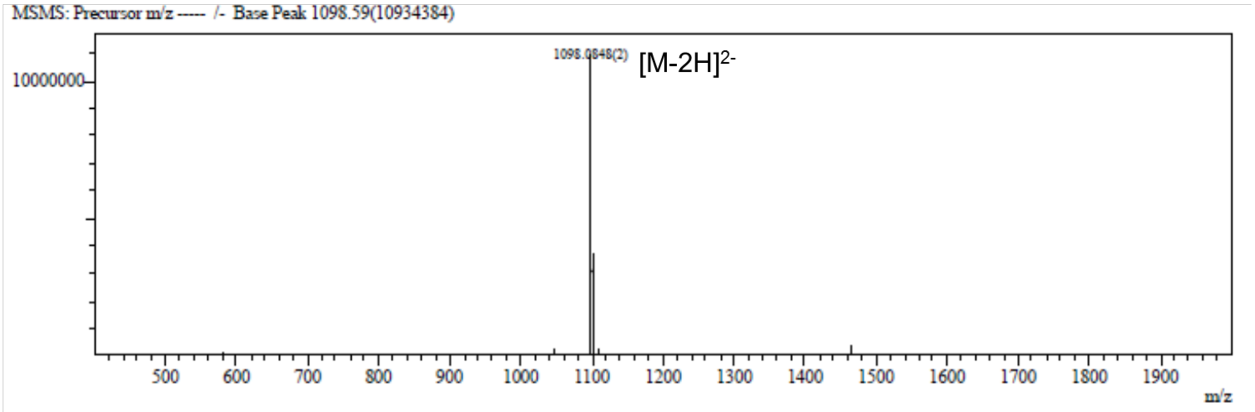


5

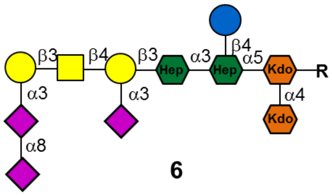
Table S9. ^{1}H NMR (600 MHz, D_2O) of **5**.

Compound 5	**H1**	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**
Kdo-I	-	-	1.868, 2.051	3.980	4.102	NA	NA	NA
Kdo-II	-	-	1.685, 1.959	3.919	3.909	NA	NA	NA
Hep-I	5.049	3.946	3.932	4.125	4.081	NA	NA	-
Hep-II	5.163	4.209	3.924	3.828	3.528	NA	NA	-
Glc	4.390	3.152	3.342	3.146	3.324	3.582, 3.867	-	-
Gal-I	4.470	3.306	3.995	3.972	NA	NA	-	-
GalNAc	4.610	3.880	3.676	4.009	NA	NA		
Gal-II	4.450	3.385	3.938	3.789	3.511	NA		
Neu5Ac-I	-	-	1.775, 2.548	3.622	3.677	3.374	3.440	3.606
Neu5Ac-II	-	-	1.651, 2.589	3.528	3.694	3.475	3.432	3.732
R	3.159, 3.269	1.466	1.313	1.549	2.855	-	-	-





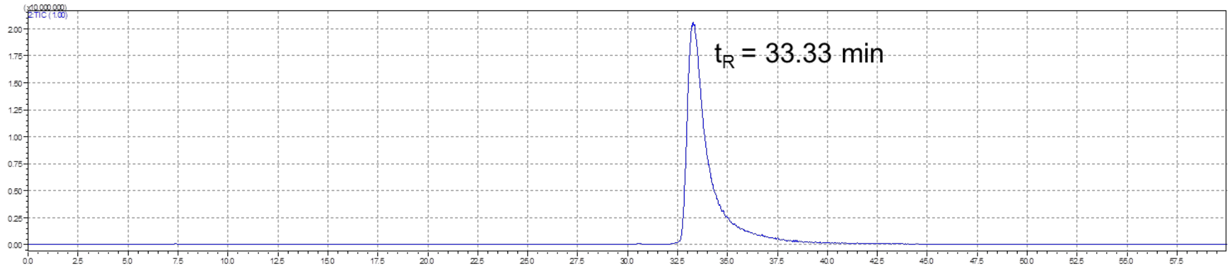
ESI-MS: m/z calcd $C_{83}H_{136}N_4O_{63}^{2-}$ $[M-2H]^{2-}$ 1098.3786, found 1098.0848.

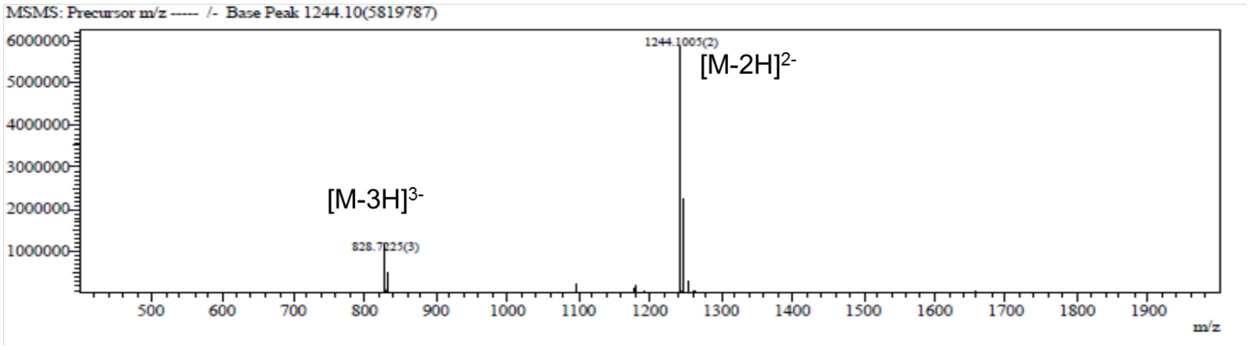


6

Table S10. ^{1}H NMR (600 MHz, D_2O) of **6**.

Compound 6	**H1**	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**
Kdo-I	-	-	1.786, 2.020	3.982	4.080	NA	NA	NA
Kdo-II	-	-	1.630, 1.958	3.921	3.893	NA	NA	NA
Hep-I	5.074	3.954	3.926	4.123	4.098	NA	NA	-
Hep-II	5.143	4.219	3.922	3.830	3.530	NA	NA	-
Glc	4.387	3.156	3.341	3.148	3.324	3.583, 3.868	-	-
Gal-I	4.471	3.319	3.989	3.963	NA	NA	-	-
GalNAc	4.597	3.869	3.702	4.008	NA	NA		
Gal-II	4.458	3.387	3.929	3.818	NA	NA		
Neu5Ac-I	-	-	1.761, 2.570	3.617	3.673	3.376	3.437	3.615
Neu5Ac-II	-	-	1.600, 2.502	3.448	3.652	3.457	3.704	4.016
Neu5Ac-III	-	-	1.580, 2.613	3.512	3.678	3.452	NA	3.766
R	3.128, 3.204	1.454	1.316	1.559	2.860	-	-	-





ESI-MS: m/z calcd $C_{94}H_{153}N_5O_{71}^{2-}$ $[M-2H]^{2-}$ 1243.9263, found 1244.1005.

^{1}H NMR analysis of **6** showed that an obvious downfield shift of the H-8 from 3.732 to 4.016 compared with terminal α(2,3)-Neu5Ac-II of **5**, and NOESY spectrum of **6** revealed a good correlation between the H-3ax (δ =1.580) of terminal α(2,8)-Neu5Ac-III and H-8 (δ =4.016) of α(2,3)-Neu5Ac-II.[6] These data well demonstrated that α(2, 8)-Neu5Ac was added to terminal α(2,3)-Neu5Ac of **5** to give GT1a mimic **6**.

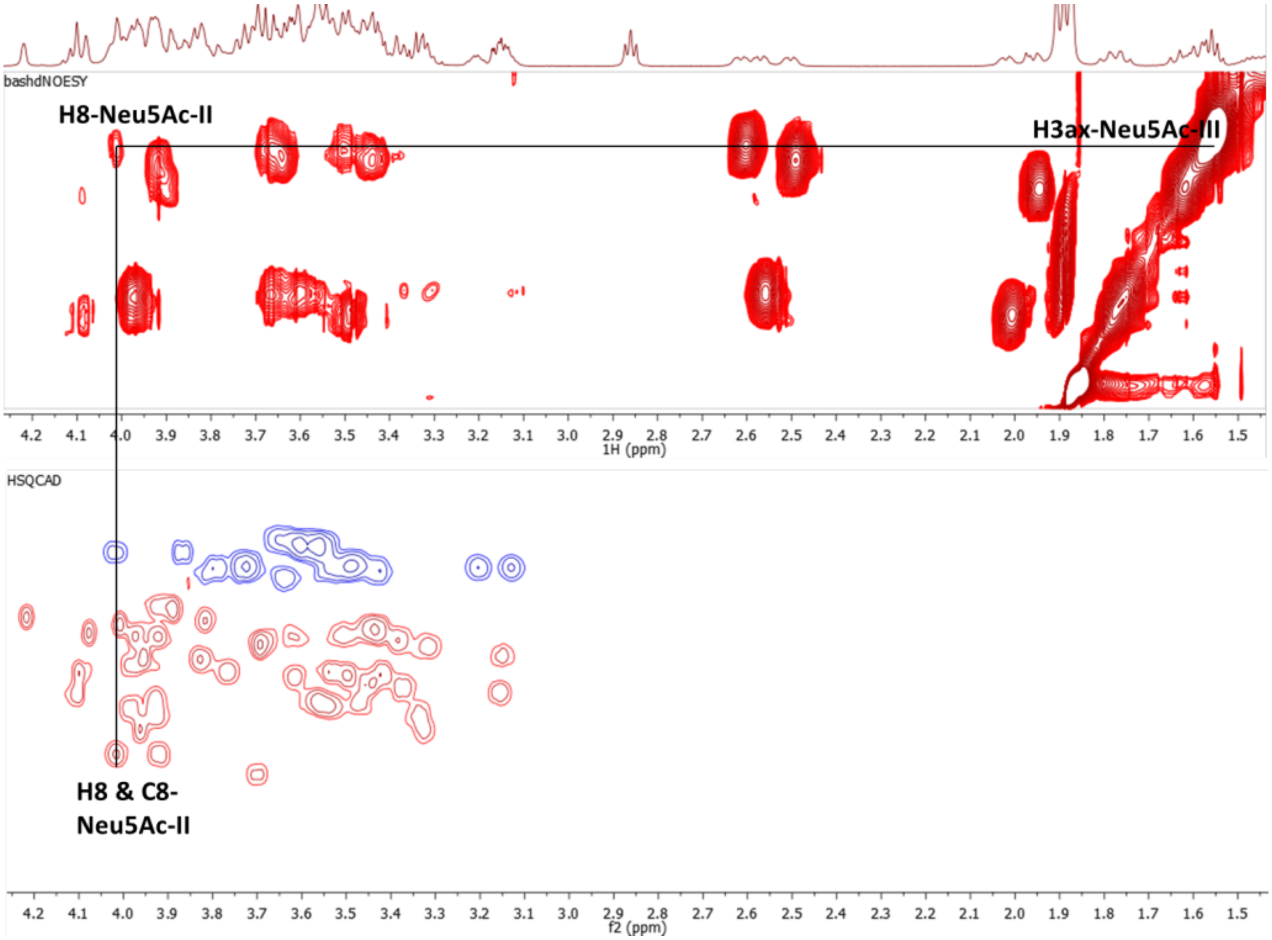
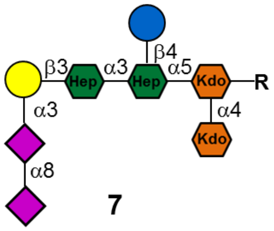


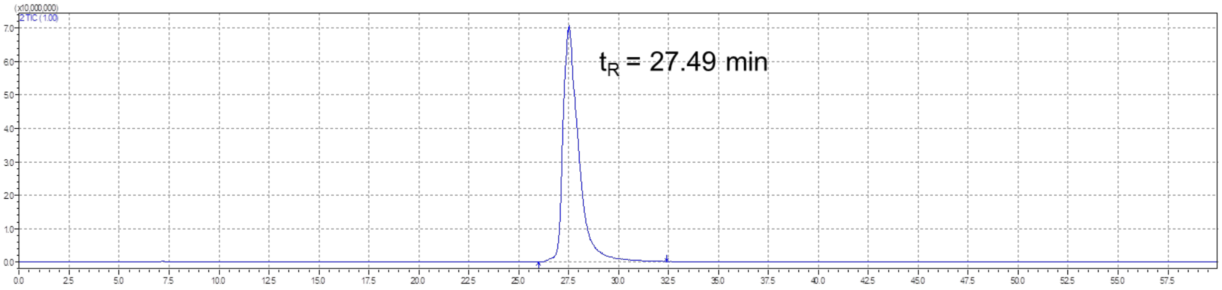
Figure S16. HSQCAD and NOESY spectra of **6**.

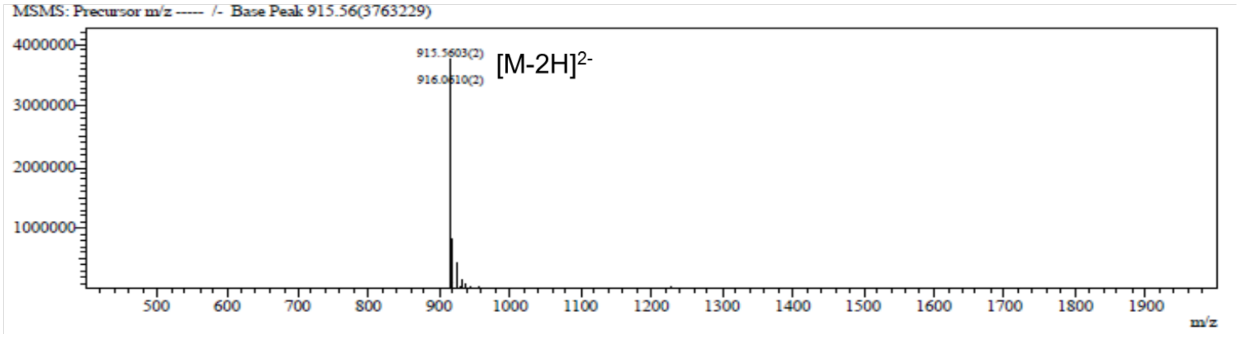


7

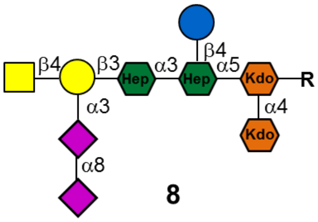
Table S11. ^{1}H NMR (600 MHz, D_2O) of **7**.

Compound 7	**H1**	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**
Kdo-I	-	-	1.789, 2.032	3.975	4.078	3.424	NA	NA
Kdo-II	-	-	1.632, 1.951	3.919	3.895	NA	NA	NA
Hep-I	5.066	3.949	3.928	4.118	NA	NA	NA	-
Hep-II	5.157	4.235	3.987	3.829	3.543	NA	NA	-
Glc	4.384	3.151	3.344	3.157	3.321	3.558, 3.888	-	-
Gal-I	4.474	3.490	3.945	3.834	NA	NA	-	-
Neu5Ac-I	-	-	1.620, 2.528	3.468	3.663	3.479	3.699	3.978
Neu5Ac-II	-	-	1.572, 2.606	3.499	3.673	3.454	3.429	3.747
R	3.131, 3.202	1.454	1.313	1.558	2.859	-	-	-





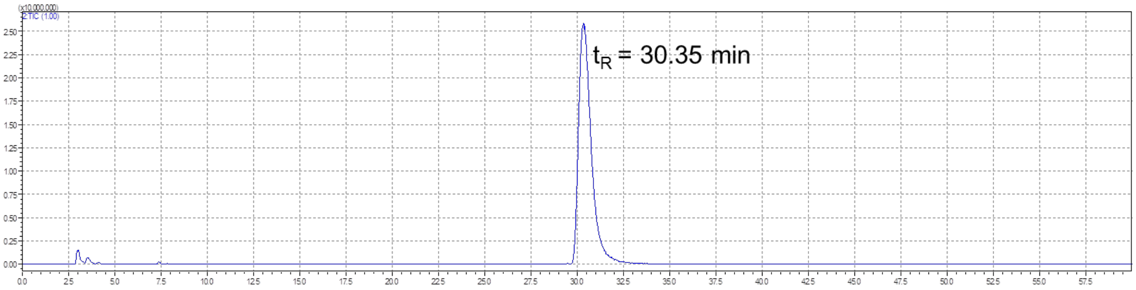
ESI-MS: m/z calcd $C_{69}H_{113}N_3O_{53}^{2-}$ [M-2H]$^{2-}$ 915.8125, found 915.5603.

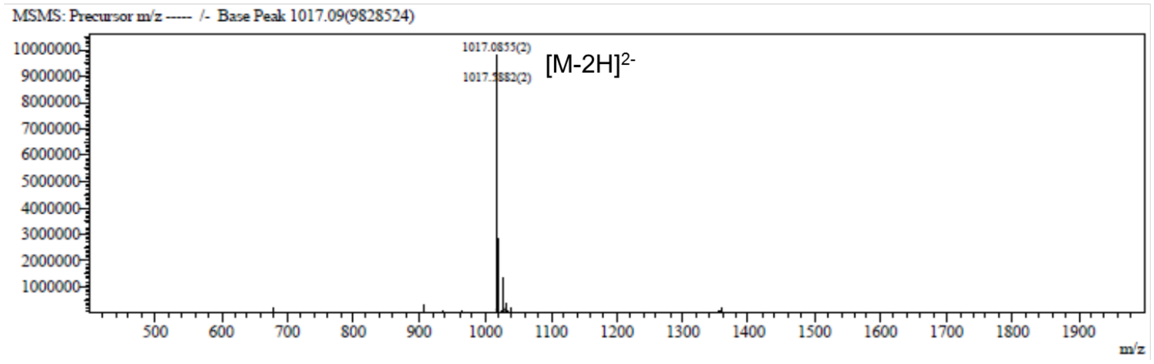


8

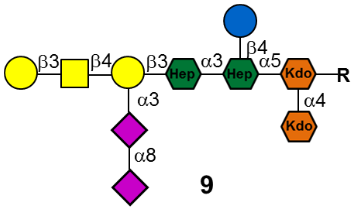
Table S12. ^{1}H NMR (600 MHz, D_2O) of **8**.

Compound 8	**H1**	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**
Kdo-I	-	-	1.850, 2.050	3.975	4.095	NA	NA	NA
Kdo-II	-	-	1.671, 1.958	3.922	3.905	NA	NA	NA
Hep-I	5.053	3.946	3.926	4.125	4.095	NA	NA	-
Hep-II	5.171	4.214	3.932	3.827	3.525	NA	NA	-
Glc	4.388	3.147	3.342	3.153	3.316	3.560, 3.869	-	-
Gal-I	4.463	3.333	4.032	3.903	NA	NA	-	-
GalNAc	4.539	3.728	3.627	3.756	NA	NA		
Neu5Ac-I	-	-	1.692, 2.550	3.562	3.685	3.433	3.684	3.905
Neu5Ac-II	-	-	1.596, 2.620	3.518	3.681	3.523	3.417	3.720
R	3.151, 3.248	1.457	1.311	1.553	2.857	-	-	-





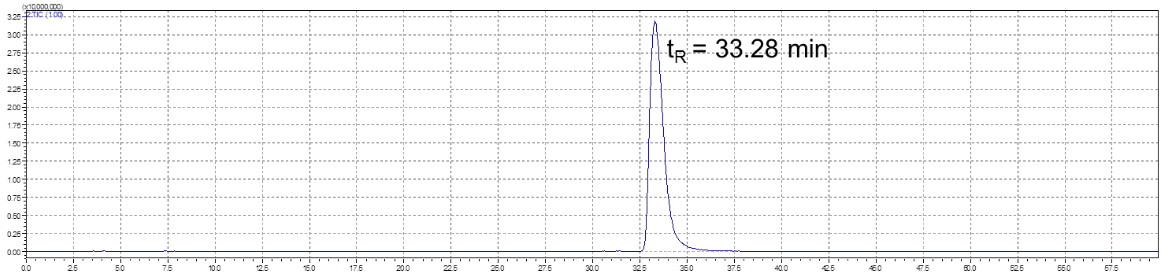
ESI-MS: m/z calcd $C_{77}H_{126}N_4O_{58}^{2-}$ $[M-2H]^{2-}$ 1017.3522, found 1017.0855.

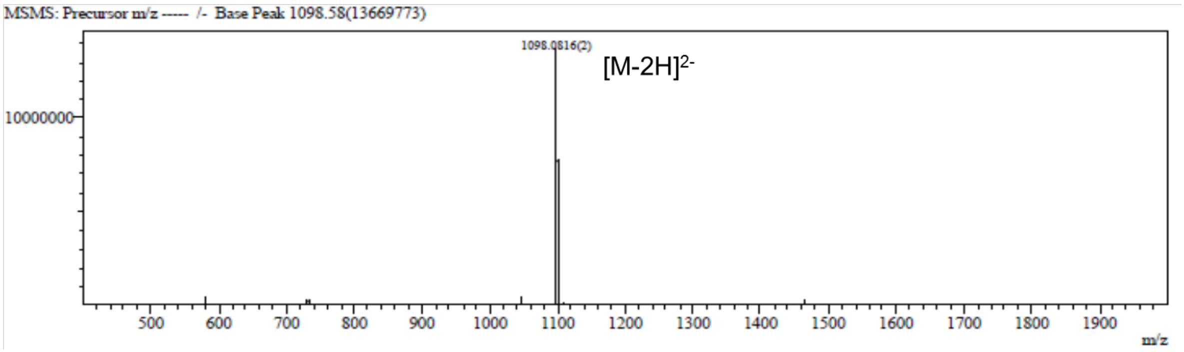


9

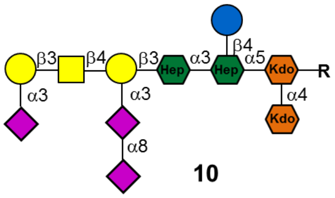
Table S13. ^{1}H NMR (600 MHz, D_2O) of **9**.

Compound 9	**H1**	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**
Kdo-I	-	-	1.796, 2.036	3.980	4.085	NA	NA	NA
Kdo-II	-	-	1.639, 1.958	3.926	3.897	NA	NA	NA
Hep-I	5.074	3.959	3.929	4.128	4.118	NA	NA	-
Hep-II	5.164	4.219	3.942	3.834	3.536	NA	NA	-
Glc	4.392	3.157	3.345	3.163	3.320	3.576, 3.895	-	-
Gal-I	4.468	3.324	4.011	3.926	NA	NA	-	-
GalNAc	4.623	3.867	3.758	4.012	NA	NA	-	-
Gal-II	4.374	3.373	3.488	3.762	NA	NA	-	-
Neu5Ac-I	-	-	1.687, 2.516	3.552	3.665	3.397	3.703	3.946
Neu5Ac-II	-	-	1.577, 2.606	3.508	3.668	3.452	3.429	3.755
R	3.137, 3.205	1.458	1.316	1.562	2.866	-	-	-





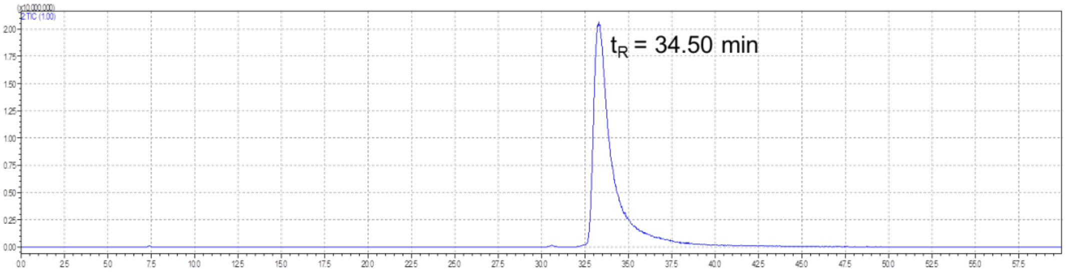
ESI-MS: m/z calcd $C_{83}H_{136}N_4O_{63}{}^{2-}$ $[M-2H]^{2-}$ 1098.3786, found 1098.0816.

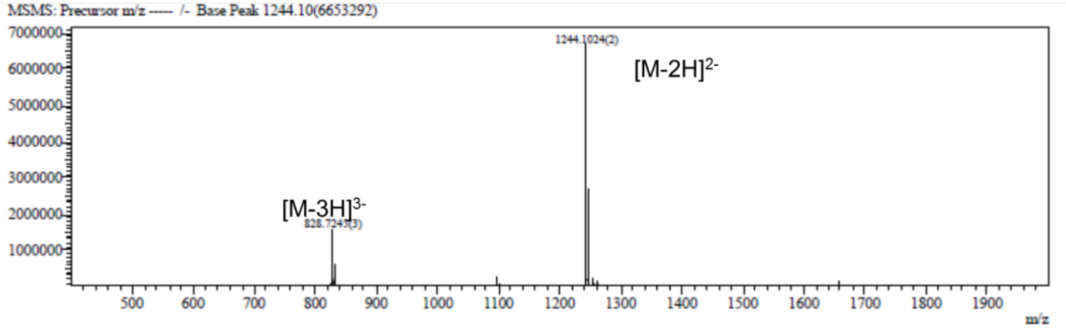


10

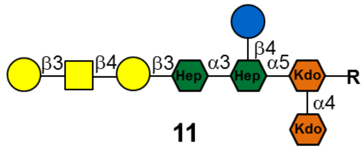
Table S14. ^{1}H NMR (600 MHz, D_2O) of **10**.

Compound 10	H1	H2	H3	H4	H5	H6	H7	H8
Kdo-I	-	-	1.797, 2.036	3.981	4.085	NA	NA	NA
Kdo-II	-	-	1.640, 1.958	3.928	3.899	NA	NA	NA
Hep-I	5.074	3.958	3.929	4.132	4.120	NA	NA	-
Hep-II	5.167	4.222	3.943	3.835	3.534	NA	NA	-
Glc	4.391	3.158	3.348	3.164	3.322	3.568, 3.896	-	-
Gal-I	4.459	3.336	4.007	3.918	NA	NA	-	-
GalNAc	4.612	3.864	3.773	4.020	NA	NA		
Gal-II	4.446	3.398	3.942	3.794	3.534	NA		
Neu5Ac-I	-	-	1.660, 2.555	3.520	3.670	3.407	3.701	3.951
Neu5Ac-II	-	-	1.577, 2.605	3.506	3.679	3.461	3.433	3.748
Neu5Ac-III	-	-	1.648, 2.597	3.524	3.689	3.465	NA	3.687
R	3.137, 3.205	1.458	1.315	1.562	2.866	-	-	-





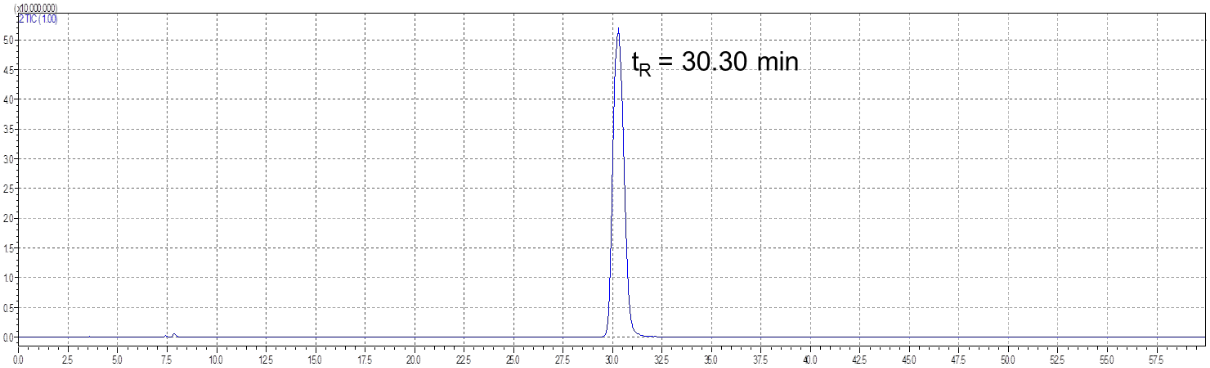
ESI-MS: m/z calcd $C_{94}H_{153}N_5O_{71}^{2-}$ $[M-2H]^{2-}$ 1243.9263, found 1244.1024.

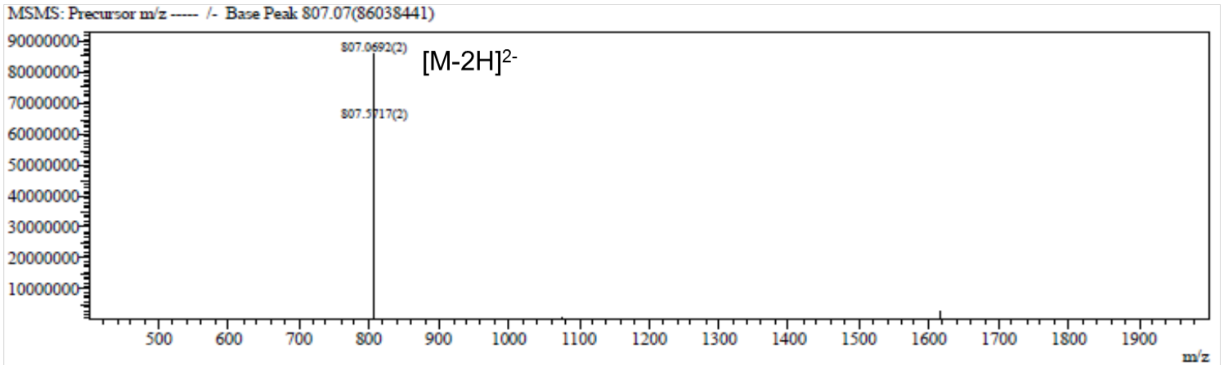


11

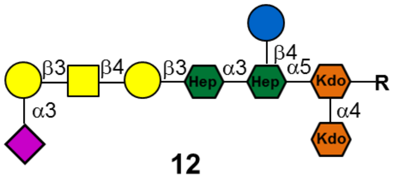
Table S15. ^{1}H NMR (600 MHz, D_2O) of **11**.

Compound 11	**H1**	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**
Kdo-I	-	-	1.791, 2.021	3.989	4.082	NA	NA	NA
Kdo-II	-	-	1.636, 1.967	3.919	3.892	NA	NA	NA
Hep-I	5.078	3.959	3.936	4.123	4.100	NA	NA	-
Hep-II	5.141	4.194	3.921	3.835	3.534	NA	NA	-
Glc	4.390	3.155	3.348	3.147	3.322	3.560, 3.816	-	-
Gal-I	4.390	3.338	3.634	3.955	3.554	NA	-	-
GalNAc	4.556	3.863	3.749	4.005	NA	NA		
Gal-II	4.296	3.387	3.467	3.753	NA	NA		
R	3.209, 3.134	1.458	1.318	1.563	2.865	-	-	-





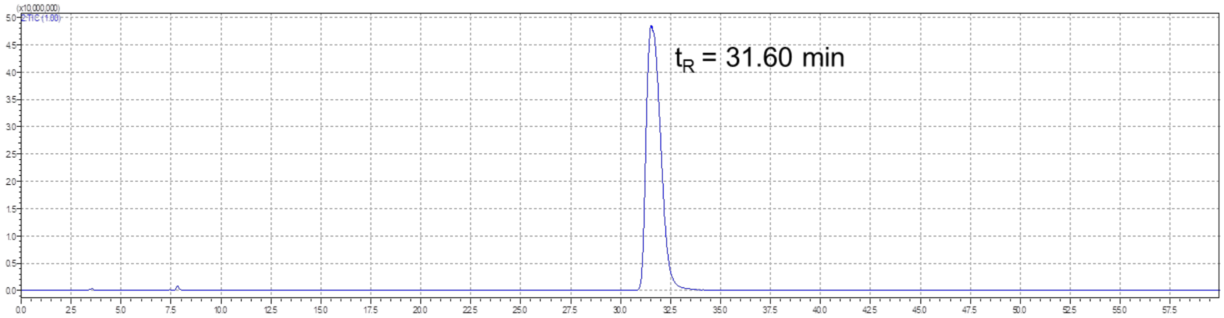
ESI-MS: m/z calcd $C_{61}H_{102}N_2O_{47}^{2-}$ [M-2H]$^{2-}$ 807.2832, found 807.0692.

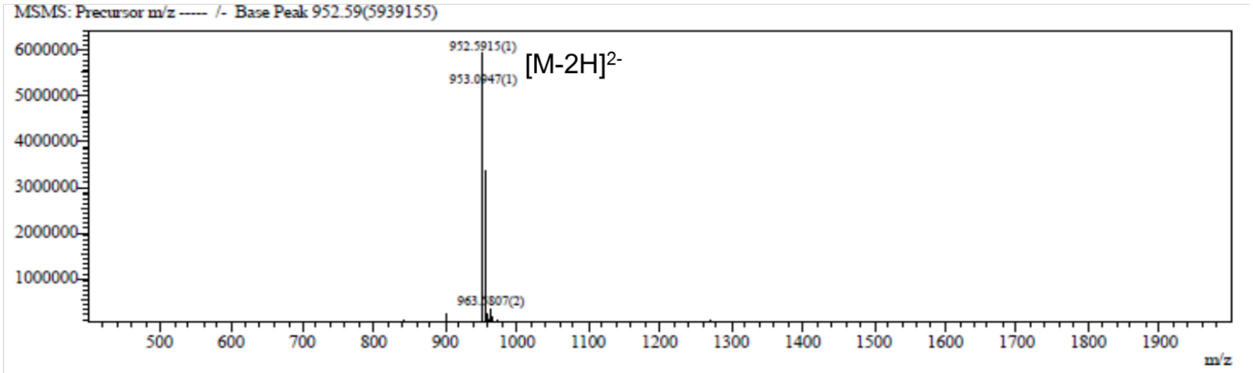


12

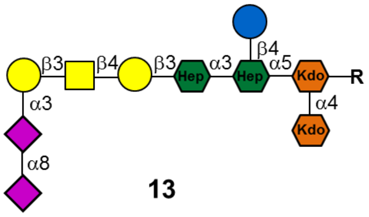
Table S16. ^{1}H NMR (600 MHz, D_2O) of **12**.

Compound 12	**H1**	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**
Kdo-I	-	-	1.790, 2.021	3.989	4.080	NA	NA	NA
Kdo-II	-	-	1.635, 1.965	3.918	3.891	NA	NA	NA
Hep-I	5.079	3.959	3.938	4.123	4.100	NA	NA	-
Hep-II	5.140	4.195	3.918	3.836	3.540	NA	NA	-
Glc	4.389	3.156	3.348	3.147	3.322	3.559, 3.817	-	-
Gal-I	4.386	3.341	3.633	3.956	3.552	NA	-	-
GalNAc	4.554	3.871	3.743	4.001	NA	NA		
Gal-II	4.367	3.398	3.917	3.781	NA	NA		
Neu5Ac	-	-	1.634, 2.599	3.524	3.690	3.462	3.440	3.726
R	3.208, 3.134	1.458	1.318	1.562	2.864	-	-	-





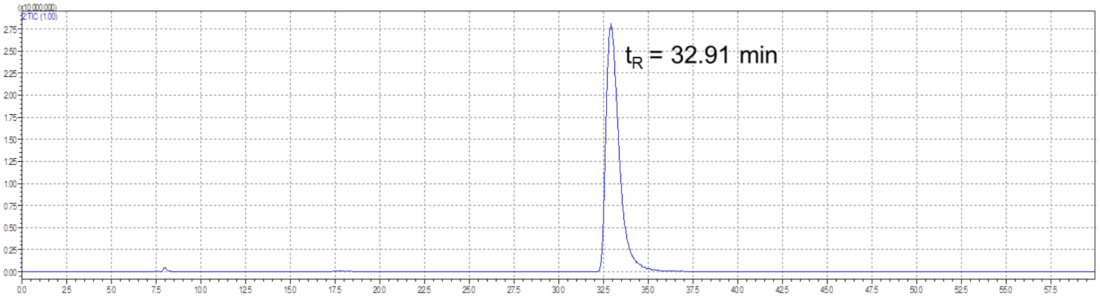
ESI-MS: m/z calcd $C_{72}H_{119}N_3O_{55}^{2-}$ $[M-2H]^{2-}$ 952.8309, found 952.5915.

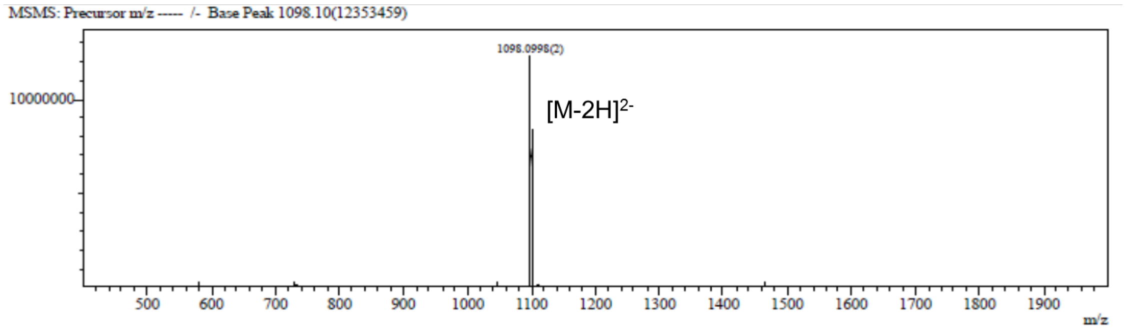


13

Table S17. ^{1}H NMR (600 MHz, D_2O) of **13**.

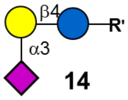
Compound 13	**H1**	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**
Kdo-I	-	-	1.792, 2.020	3.900	4.080	NA	NA	NA
Kdo-II	-	-	1.636, 1.967	3.920	3.895	NA	NA	NA
Hep-I	5.080	3.960	3.937	4.123	4.099	NA	NA	-
Hep-II	5.142	4.198	3.916	3.837	3.540	NA	NA	-
Glc	4.389	3.157	3.348	3.149	3.323	3.561, 3.819	-	-
Gal-I	4.386	3.341	3.633	3.956	3.552	NA	-	-
GalNAc	4.546	3.878	3.741	4.001	NA	NA		
Gal-II	4.357	3.396	3.915	3.795	NA	NA		
Neu5Ac-I	-	-	1.576, 2.523	3.435	3.662	3.495	3.694	3.997
Neu5Ac-II	-	-	1.573, 2.619	3.516	3.676	3.451	3.441	3.760
R	3.207, 3.133	1.456	1.318	1.561	2.865	-	-	-





ESI-MS: m/z calcd $C_{83}H_{136}N_4O_{63}^{2-}$ [M-2H]$^{2-}$ 1098.3786, found 1098.0998.

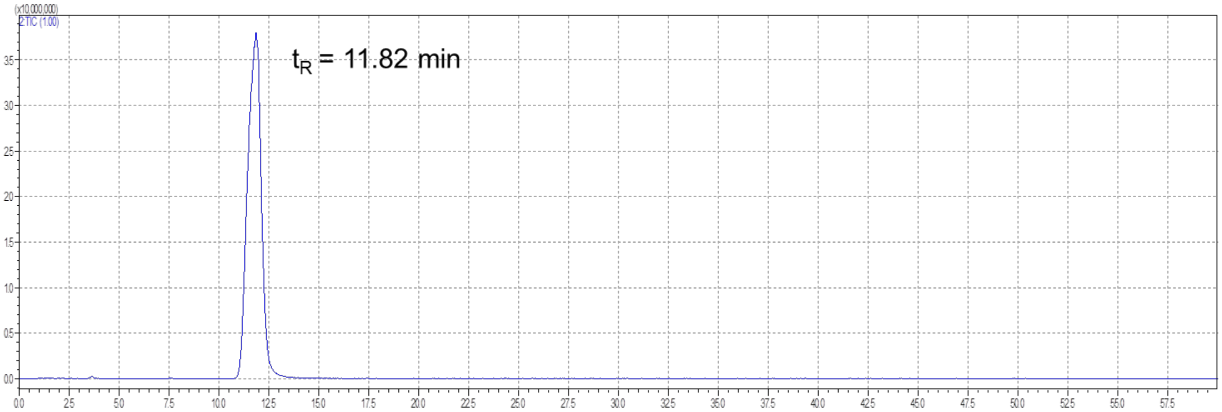
Normal gangliosides

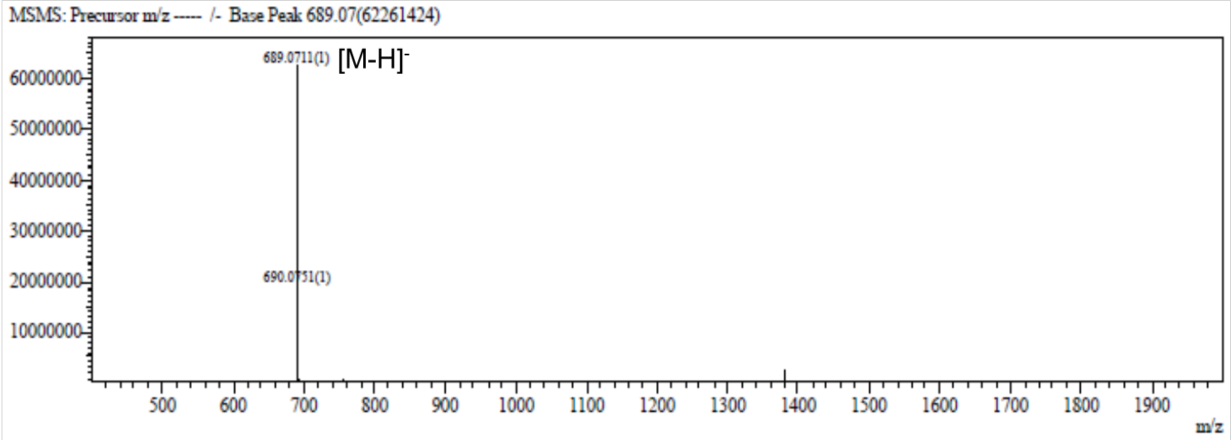


14

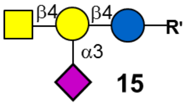
Table S18. ^1H NMR (600 MHz, D_2O) of **14**.

Compound 14	**H1**	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**
Glc	4.355	3.177	3.501	3.505	3.456	3.672, 3.844	-	-
Gal	4.372	3.418	3.955	3.800	3.556	3.584	-	-
Neu5Ac	-	-	1.641, 2.605	3.535	3.692	3.486	3.439	3.733
R′	3.664, 3.896	1.852	3.004	-	-	-	-	-





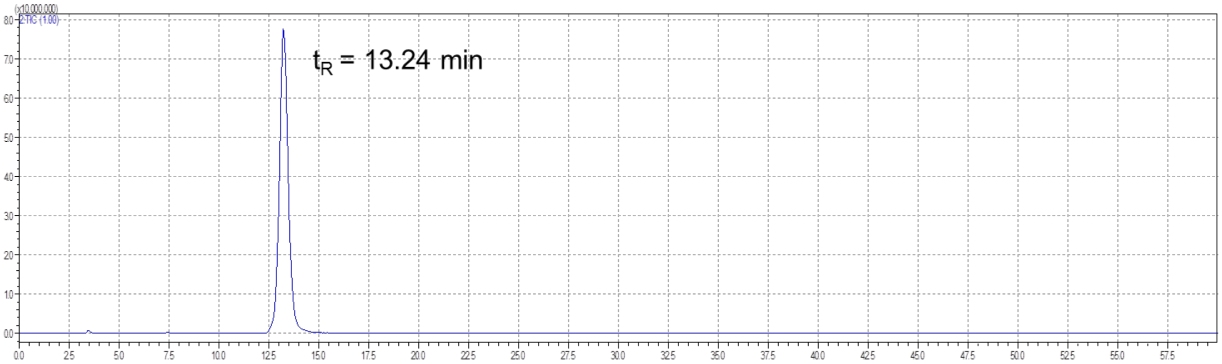
ESI-MS: m/z calcd $C_{26}H_{45}N_2O_{19}^-$ $[M-H]^-$ 689.2622, found 689.0711.

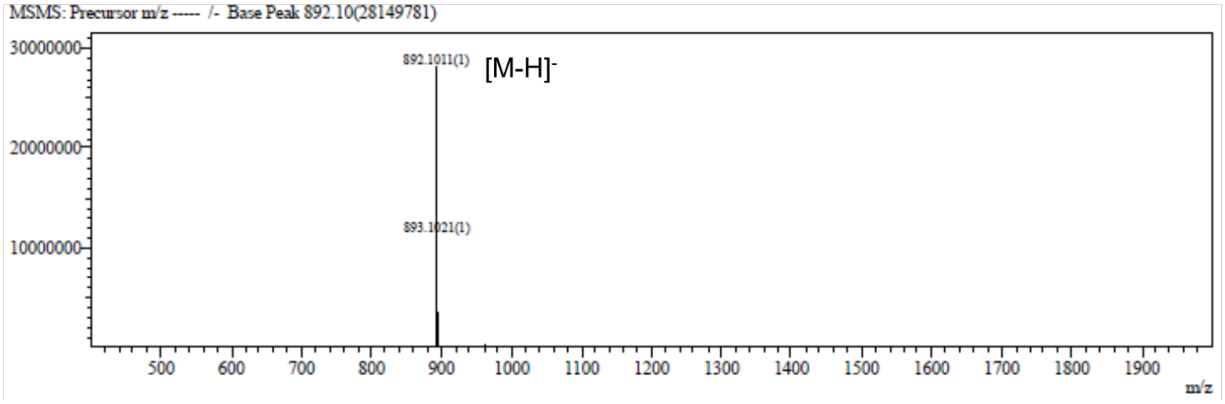


15

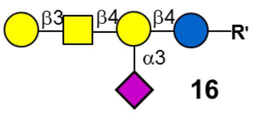
Table S19. ^{1}H NMR (600 MHz, D_2O) of **15**.

Compound 15	**H1**	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**
Glc	4.360	3.169	3.509	3.458	3.455	3.650, 3.841	-	-
Gal	4.371	3.214	3.993	3.960	3.605	3.611, 3.664	-	-
GalNAc	4.578	3.756	3.528	3.765	NA	3.566, 3.643	-	-
Neu5Ac	-	-	1.766, 2.508	3.618	3.668	3.333	3.441	3.592
R′	3.666, 3.898	1.854	3.006	-	-	-	-	-





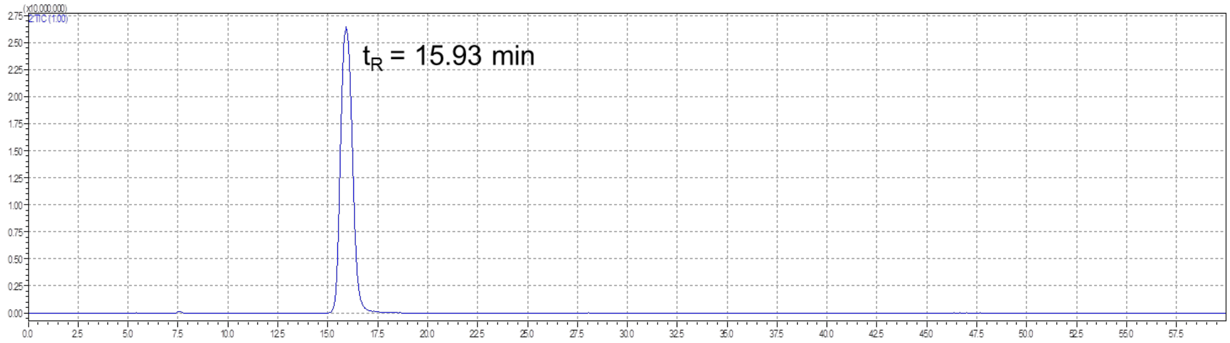
ESI-MS: m/z calcd $C_{34}H_{58}N_3O_{24}^-$ [M-H]$^-$ 892.3416, found 892.1011.

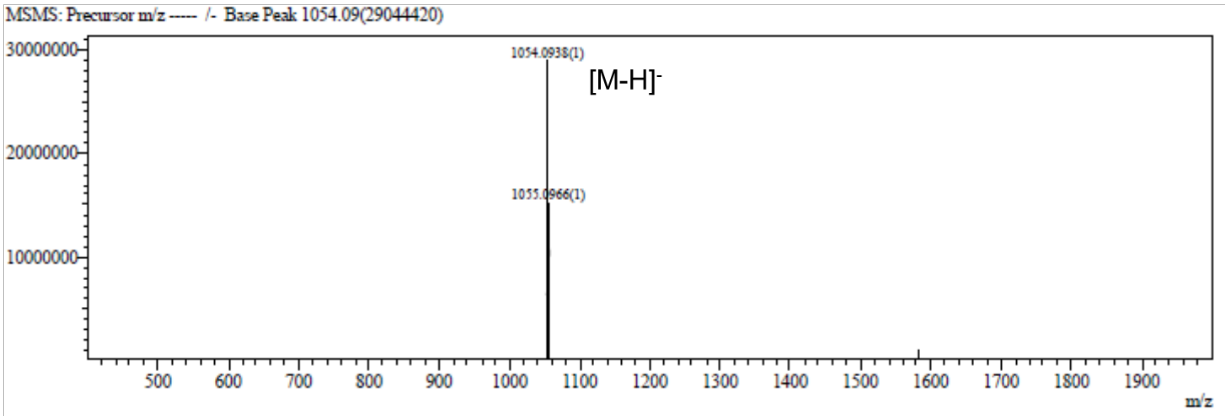


16

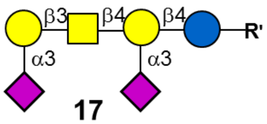
Table S20. ^{1}H NMR (600 MHz, D$_2$O) of **16**.

Compound 16	**H1**	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**
Glc	4.361	3.170	3.512	3.459	3.457	3.651, 3.842	-	-
Gal-I	4.375	3.209	3.997	3.974	3.608	NA	-	-
GalNAc	4.622	3.884	3.657	4.011	NA	NA	-	-
Gal-II	4.388	3.370	3.483	3.763	3.537	NA	-	-
Neu5Ac	-	-	1.773, 2.508	3.622	3.669	3.344	3.444	3.594
R′	3.664, 3.896	1.849	2.999	-	-	-	-	-





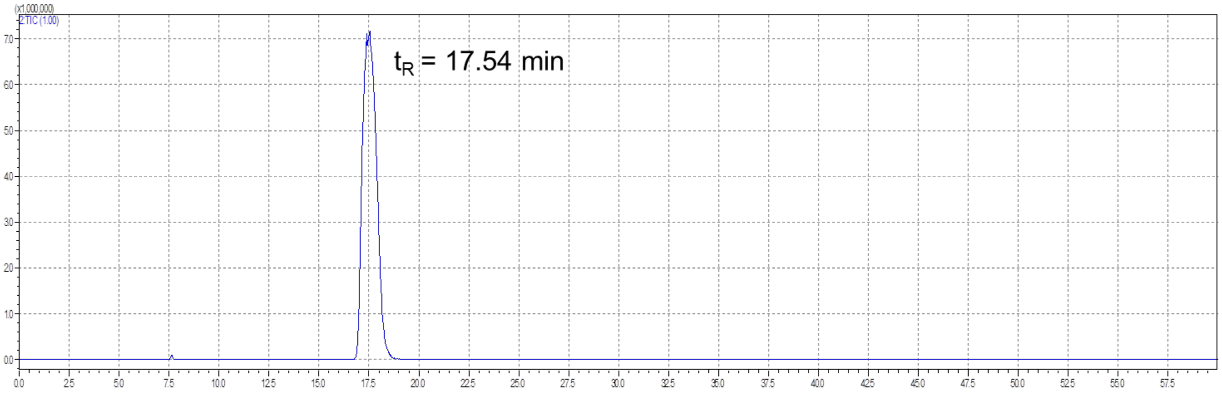
ESI-MS: m/z calcd $C_{40}H_{68}N_3O_{29}^-$ [M-H]$^-$ 1054.3944, found 1054.0938.

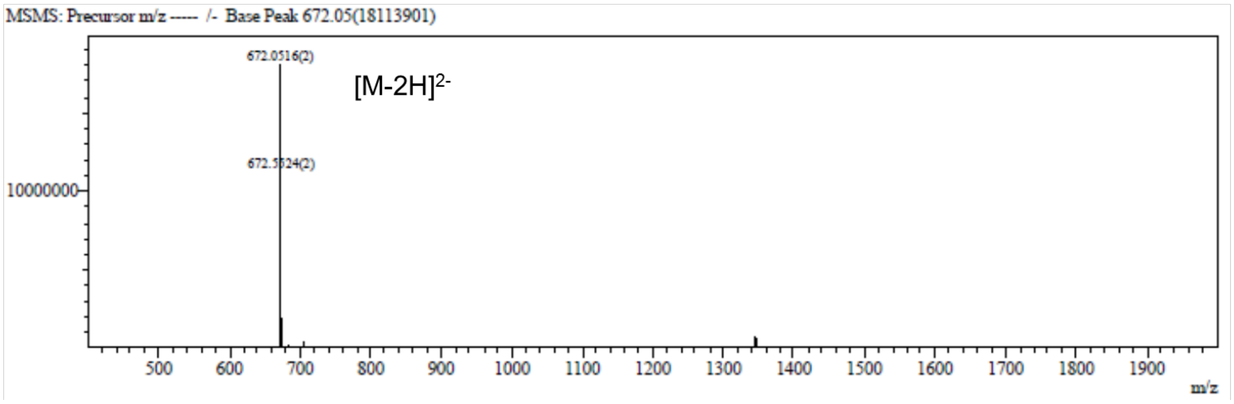


17

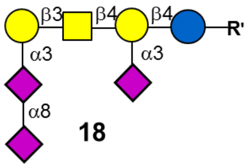
Table S21. ^{1}H NMR (600 MHz, D_2O) of **17**.

Compound 17	**H1**	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**
Glc	4.367	3.169	3.513	3.458	3.454	3.651, 3.841	-	-
Gal-I	4.374	3.226	3.994	3.965	3.603	NA	-	-
GalNAc	4.617	3.882	3.669	4.012	NA	NA	-	-
Gal-II	4.456	3.387	3.938	3.798	NA	NA		
Neu5Ac-I	-	-	1.757, 2.528	3.616	3.676	3.356	3.442	3.607
Neu5Ac-II	-	-	1.645,2.601	3.525	3.696	3.464	3.432	3.740
R′	3.669, 3.899	1.853	3.010	-	-	-	-	-





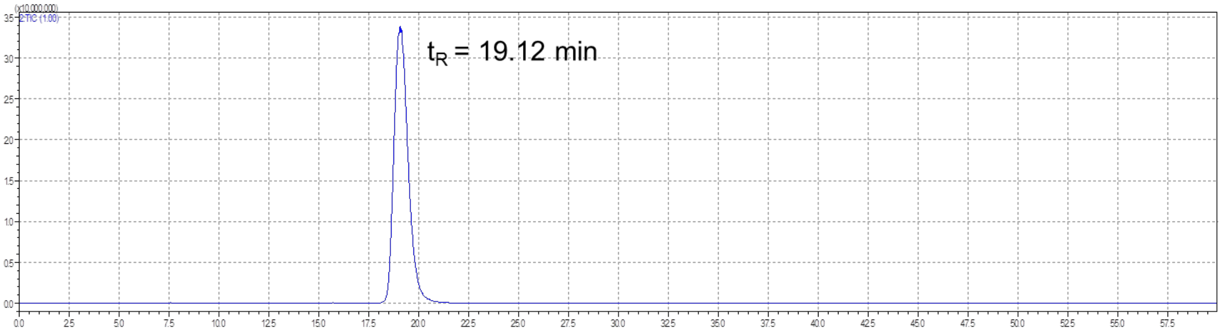
ESI-MS: m/z calcd $C_{51}H_{84}N_4O_{37}^{2-}$ $[M-2H]^{2-}$ 672.2412, found 672.0516.

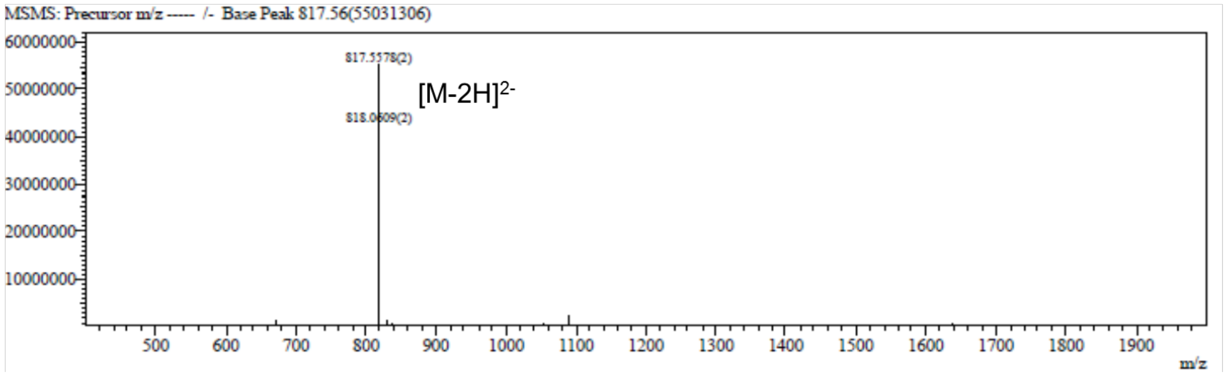


18

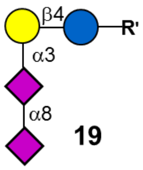
Table S22. ^{1}H NMR (600 MHz, D_2O) of **18**.

Compound 18	**H1**	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**
Glc	4.367	3.167	3.514	3.458	3.455	3.652, 3.842	-	-
Gal-I	4.371	3.324	3.993	3.963	3.604	NA	-	-
GalNAc	4.608	3.873	3.688	4.014	NA	NA	-	-
Gal-II	4.462	3.384	3.942	3.829	NA	NA	-	-
Neu5Ac-I	-	-	1.754, 2.540	3.617	3.678	3.367	3.443	3.612
Neu5Ac-II	-	-	1.663, 2.500	3.553	3.684	3.468	3.692	3.877
Neu5Ac-III	-	-	1.595, 2.644	3.519	3.690	3.532	3.433	3.728
R′	3.669, 3.900	1.855	3.010	-	-	-	-	-





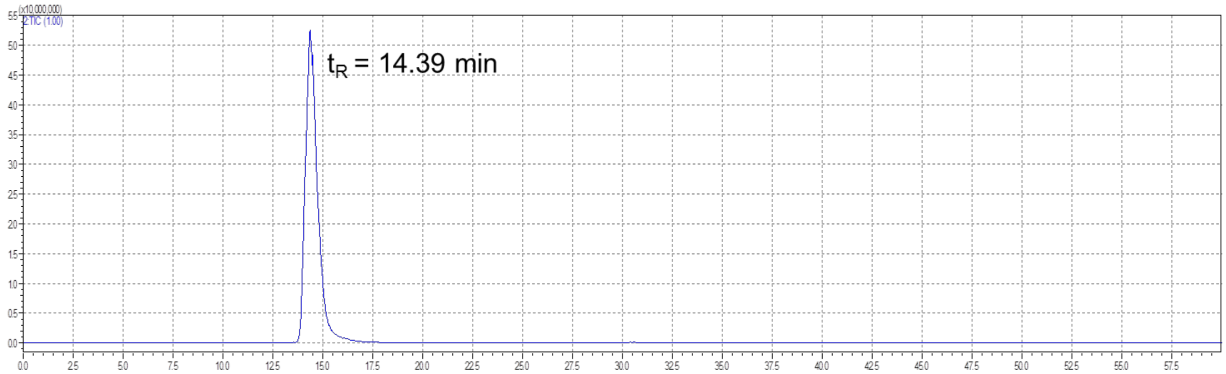
ESI-MS: m/z calcd $C_{62}H_{101}N_5O_{45}^{2-}$ [M-2H]$^{2-}$ 817.7890, found 817.5578.

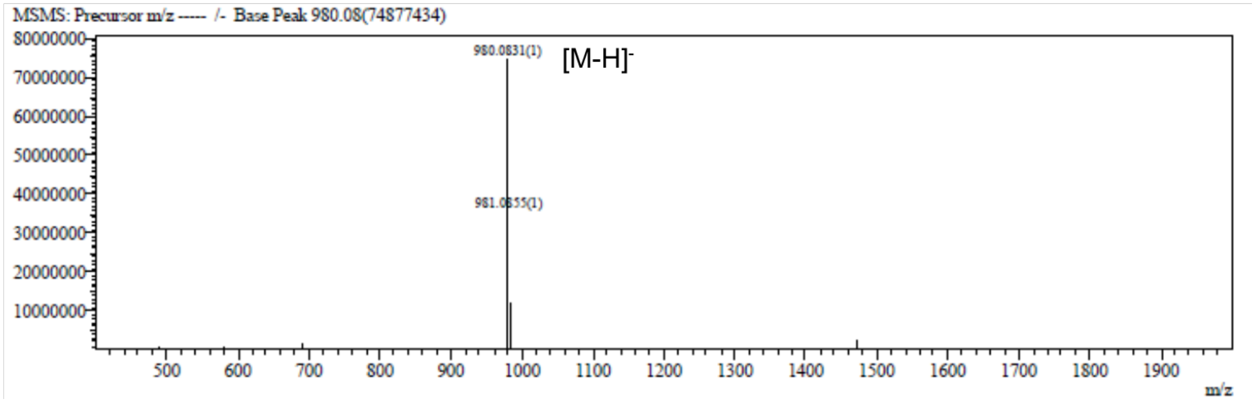


19

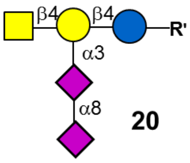
Table S23. ^{1}H NMR (600 MHz, D_2O) of **19**.

Compound 19	**H1**	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**
Glc	4.356	3.182	3.495	3.523	3.466	3.703, 3.860	-	-
Gal	4.386	3.413	3.933	3.806	3.564	3.586	-	-
Neu5Ac-I	-	-	1.576, 2.532	3.444	3.671	3.552	3.709	3.981
Neu5Ac-II	-	-	1.587, 2.630	3.518	3.679	3.455	3.436	3.745
R′	3.675, 3.894	1.856	3.011	-	-	-	-	-





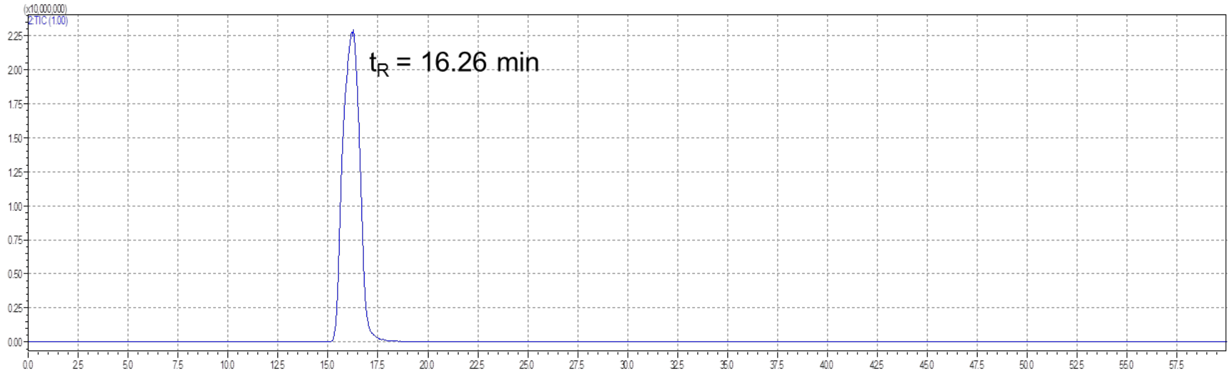
ESI-MS: m/z calcd $C_{37}H_{62}N_3O_{27}^-$ $[M-H]^-$ 980.3576, found 980.0831.

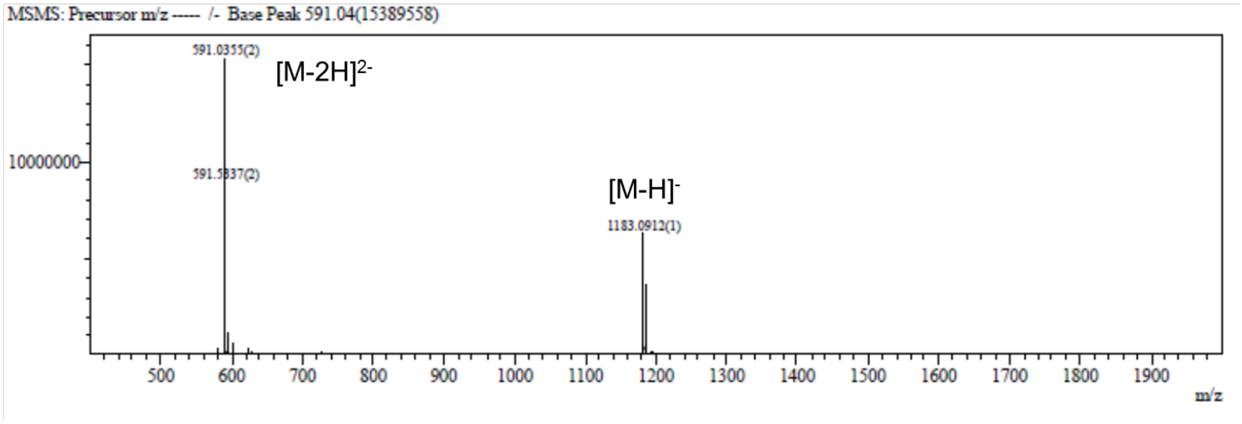


20

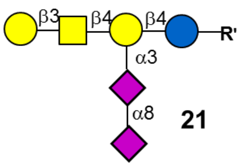
Table S24. ^{1}H NMR (600 MHz, D_2O) of **20**.

Compound 20	**H1**	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**
Glc	4.359	3.171	3.510	3.486	3.463	3.688, 3.855	-	-
Gal	4.348	3.252	4.006	3.883	NA	NA	-	-
GalNAc	4.540	3.726	3.613	3.764	NA	NA	-	-
Neu5Ac-I	-	-	1.612, 2.542	3.498	3.667	3.435	3.707	3.958
Neu5Ac-II	-	-	1.580, 2.641	3.516	3.674	3.452	3.747	3.438
R′	3.674, 3.894	1.855	3.011	-	-	-	-	-





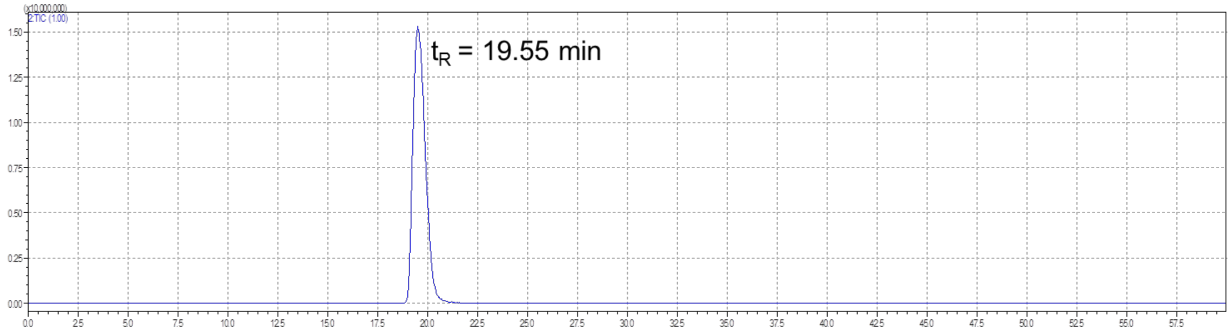
ESI-MS: m/z calcd $C_{45}H_{74}N_4O_{32}^{2-}$ [M-2H]$^{2-}$ 591.2148, found 591.0355.

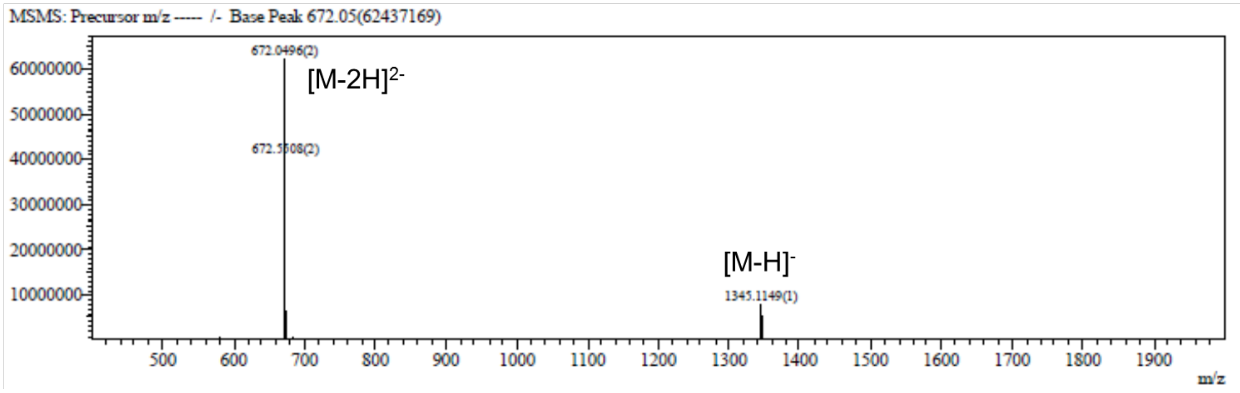


21

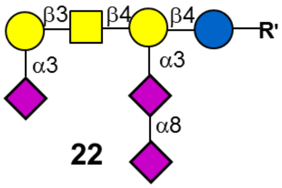
Table S25. ^{1}H NMR (600 MHz, D_2O) of **21**.

Compound 21	**H1**	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**
Glc	4.359	3.172	3.514	3.477	3.461	3.685, 3.852	-	-
Gal-I	4.352	3.250	4.000	3.904	3.560	NA	-	-
GalNAc	4.595	3.855	3.758	4.017	NA	NA	-	-
Gal-II	4.372	3.371	3.487	3.763	3.461	NA		
Neu5Ac-I	-	-	1.626, 2.539	3.506	3.669	3.444	3.708	3.959
Neu5Ac-II	-	-	1.581, 2.616	3.516	3.676	3.451	3.437	3.750
R′	3.673, 3.893	1.854	3.011	-	-	-	-	-





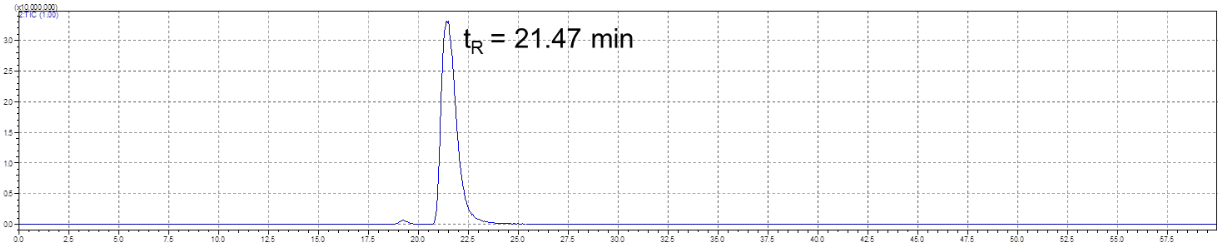
ESI-MS: m/z calcd $C_{51}H_{84}N_4O_{37}^{2-}$ $[M-2H]^{2-}$ 672.2412, found 672.0496.

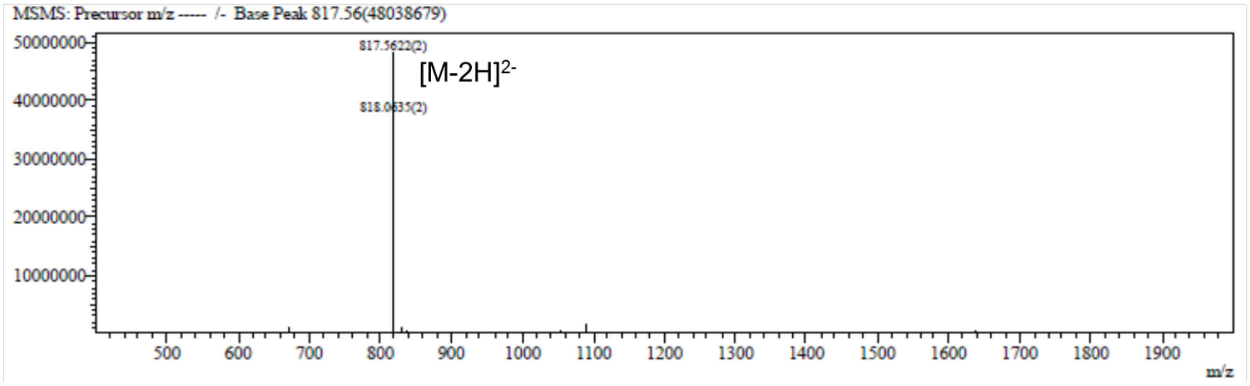


22

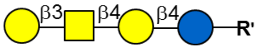
Table S26. ^{1}H NMR (600 MHz, D_2O) of **22**.

Compound 22	**H1**	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**
Glc	4.363	3.171	3.513	3.480	3.464	3.692, 3.856	-	-
Gal-I	4.346	3.266	4.004	3.896	NA	NA	-	-
GalNAc	4.587	3.852	3.765	4.021	NA	NA	-	-
Gal-II	4.445	3.399	3.937	3.791	NA	NA	-	-
Neu5Ac-I	-	-	1.602, 2.575	3.495	3.668	3.449	3.707	3.967
Neu5Ac-II	-	-	1.583, 2.619	3.513	3.676	3.456	3.439	3.746
Neu5Ac-III	-	-	1.641, 2.600	3.522	3.687	3.458	NA	3.735
R′	3.678, 3.895	1.855	3.013	-	-	-	-	-





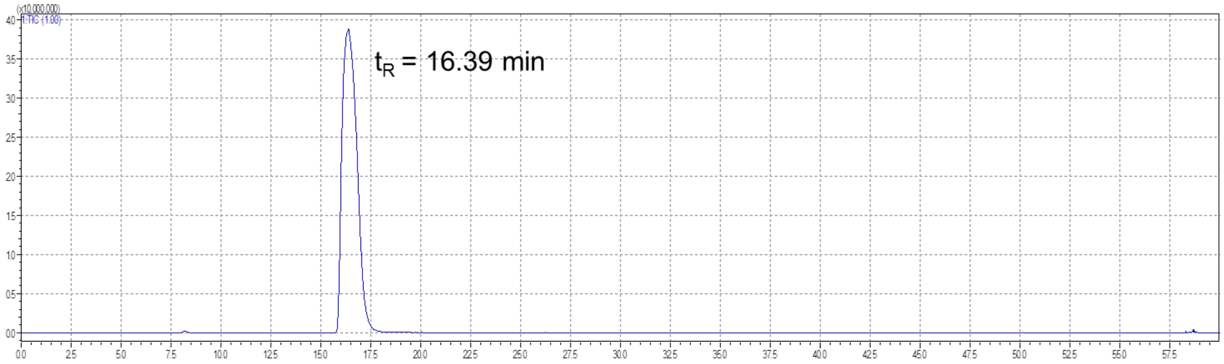
ESI-MS: m/z calcd $C_{62}H_{101}N_5O_{45}^{2-}$ [M-2H]$^{2-}$ 817.7890, found 817.5578.

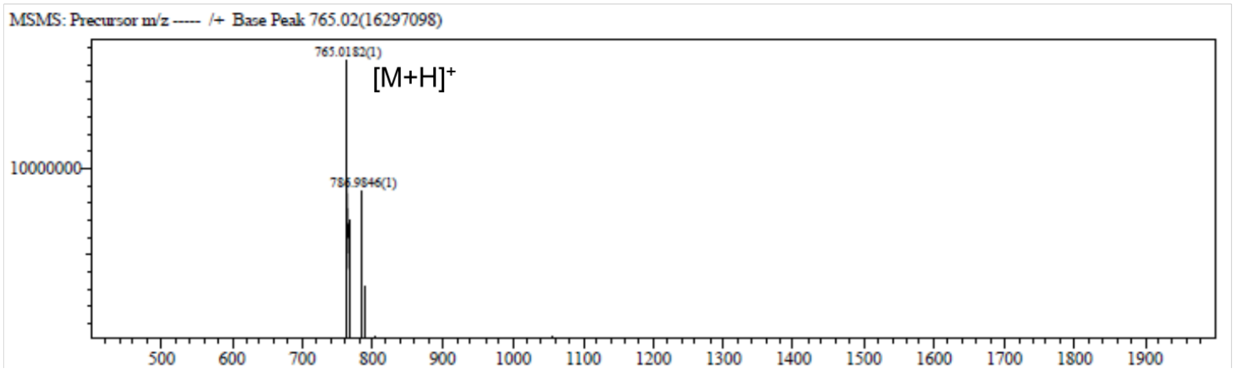


23

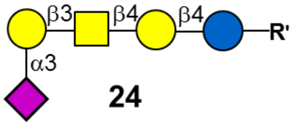
Table S27. ^{1}H NMR (600 MHz, D_2O) of **23.**

Compound 23	**H1**	**H2**	**H3**	**H4**	**H5**	**H6**
Glc	4.359	3.166	3.511	3.449	3.445	3.644, 3.828
Gal-I	4.285	3.255	3.614	3.954	3.657	NA
GalNAc	4.535	3.865	3.730	4.006	3.512	NA
Gal-II	4.296	3.376	3.465	3.754	3.501	NA
R′	3.655, 3.898	1.845	2.987	-	-	-





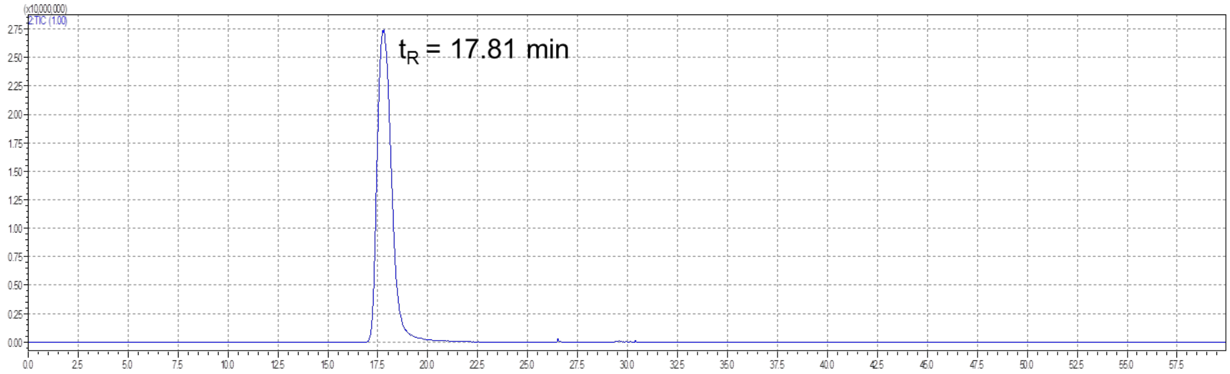
ESI-MS: m/z calcd $C_{29}H_{53}N_2O_{21}^+$ $[M+H]^+$ 765.3135, found 765.0182.

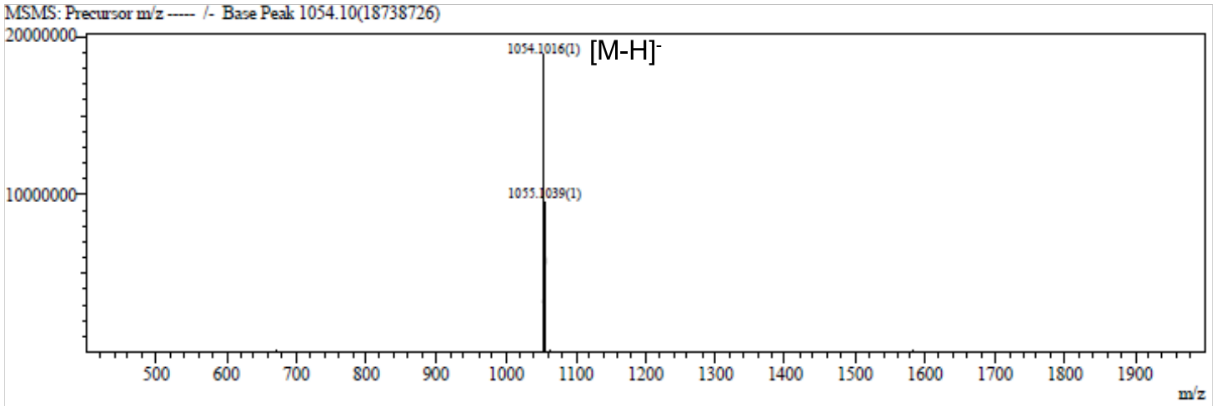


24

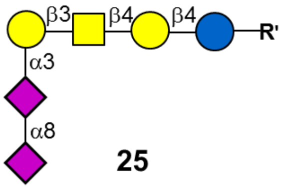
Table S28. ^{1}H NMR (600 MHz, D_2O) of **24**.

Compound 24	**H1**	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**
Glc	4.363	3.165	3.512	3.447	3.446	3.643, 3.827	-	-
Gal-I	4.282	3.264	3.609	3.955	3.566	NA	-	-
GalNAc	4.540	3.871	3.725	4.001	3.513	NA	-	-
Gal-II	4.365	3.395	3.917	3.782	3.493	NA	-	-
Neu5Ac	-	-	1.633, 2.600	3.526	3.690	3.463	3.450	3.724
R′	3.659, 3.899	1.852	3.006	-	-	-	-	-





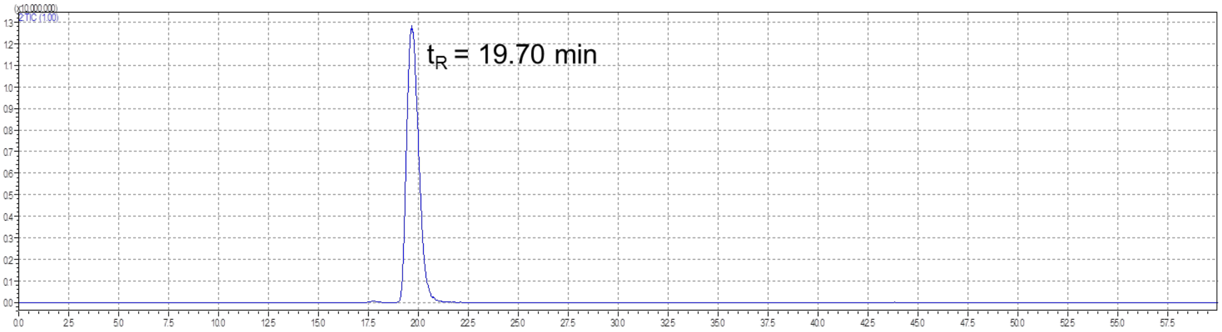
ESI-MS: m/z calcd $C_{40}H_{68}N_3O_{29}^-$ $[M-H]^-$ 1054.3944, found 1054.1016.

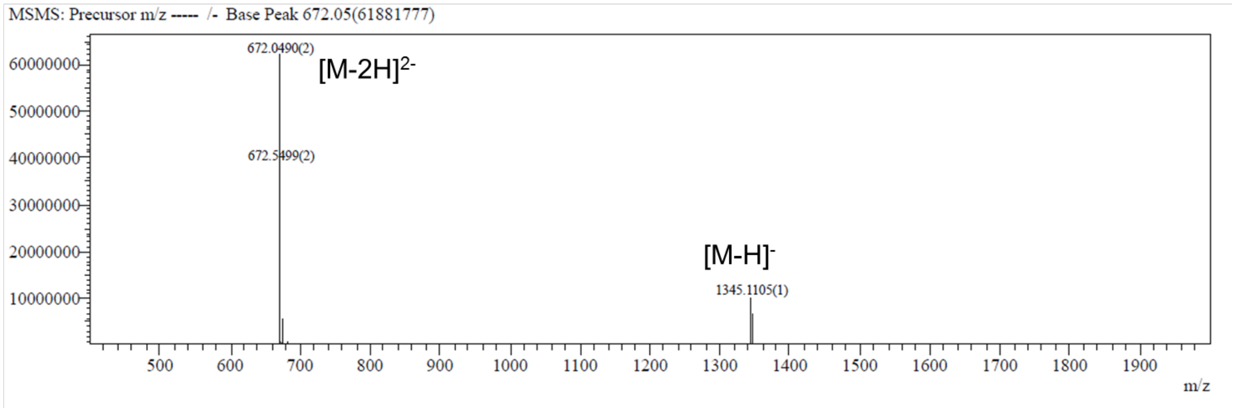


25

Table S29. ^{1}H NMR (600 MHz, D_2O) of **25**.

Compound 25	**H1**	**H2**	**H3**	**H4**	**H5**	**H6**	**H7**	**H8**
Glc	4.368	3.165	3.518	3.447	3.446	3.646, 3.833	-	-
Gal-I	4.283	3.272	3.607	3.957	3.565	NA	-	-
GalNAc	4.543	3.874	3.730	3.996	NA	NA	-	-
Gal-II	4.350	3.389	3.910	3.789	NA	NA	-	-
Neu5Ac-I	-	-	1.567, 2.532	3.429	3.662	3.499	3.694	3.994
Neu5Ac-II	-	-	1.573, 2.617	3.519	3.676	3.452	3.440	3.758
R′	3.661, 3.900	1.853	3.008	-	-	-	-	-





ESI-MS: m/z calcd $C_{51}H_{84}N_4O_{37}^{2-}$ $[M-2H]^{2-}$ 672.2412, found 672.0490.

7. References

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(3) Pokorny, B.; Kosma, P. Synthesis of 5-O-oligoglucosyl extended alpha-(2→4)-Kdo disaccharides corresponding to inner core fragments of Moraxellaceae lipopolysaccharides. *Carbohydr. Res.* **2016**, *422*, 5-12.

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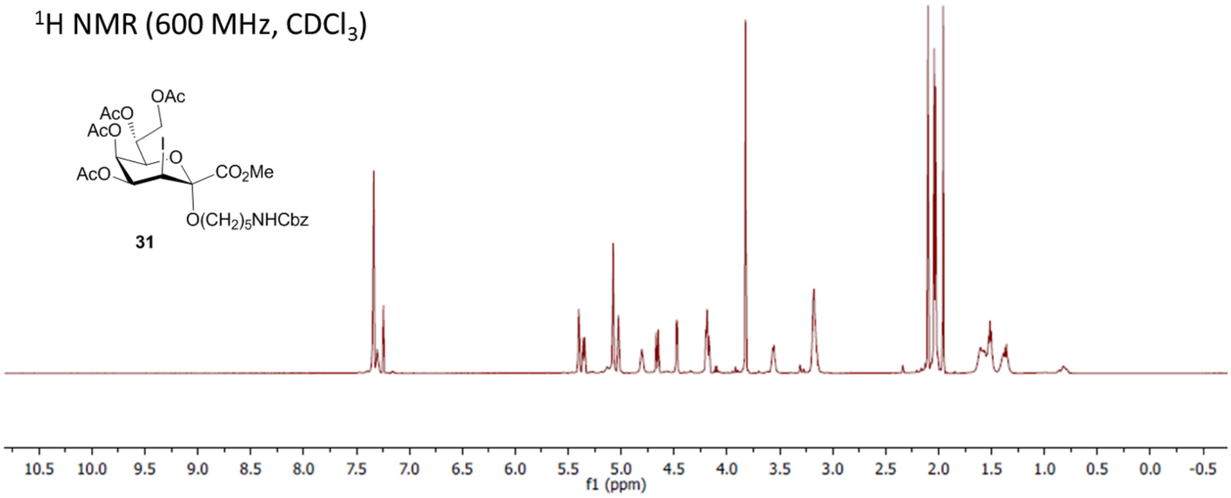
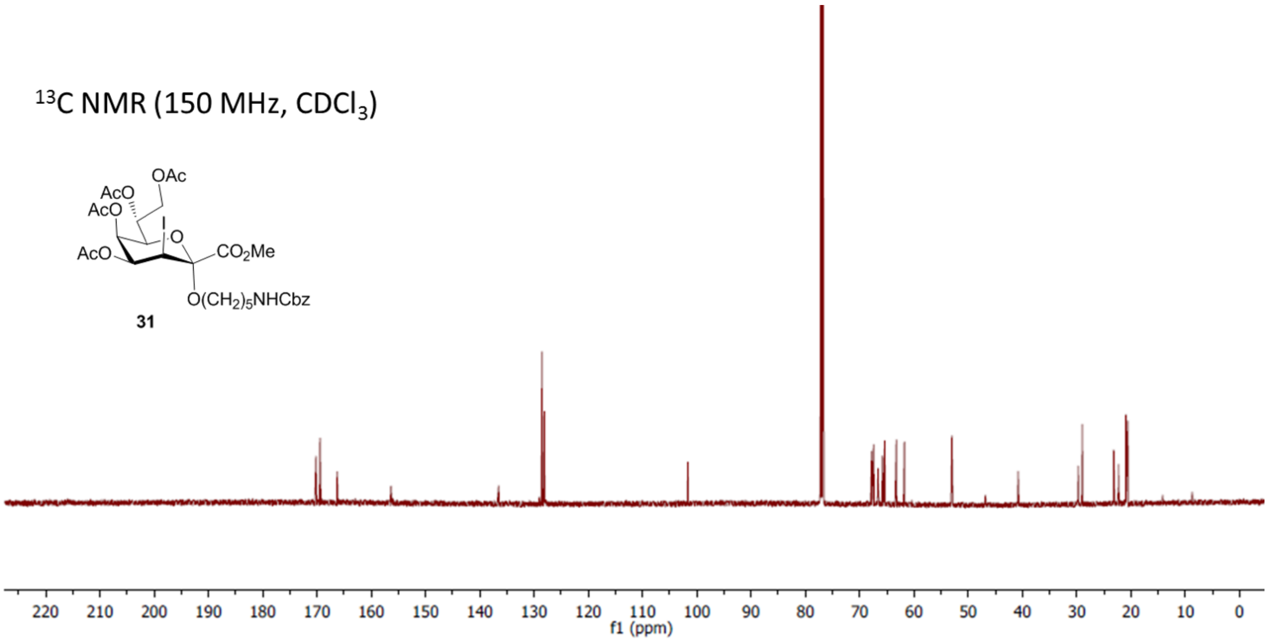
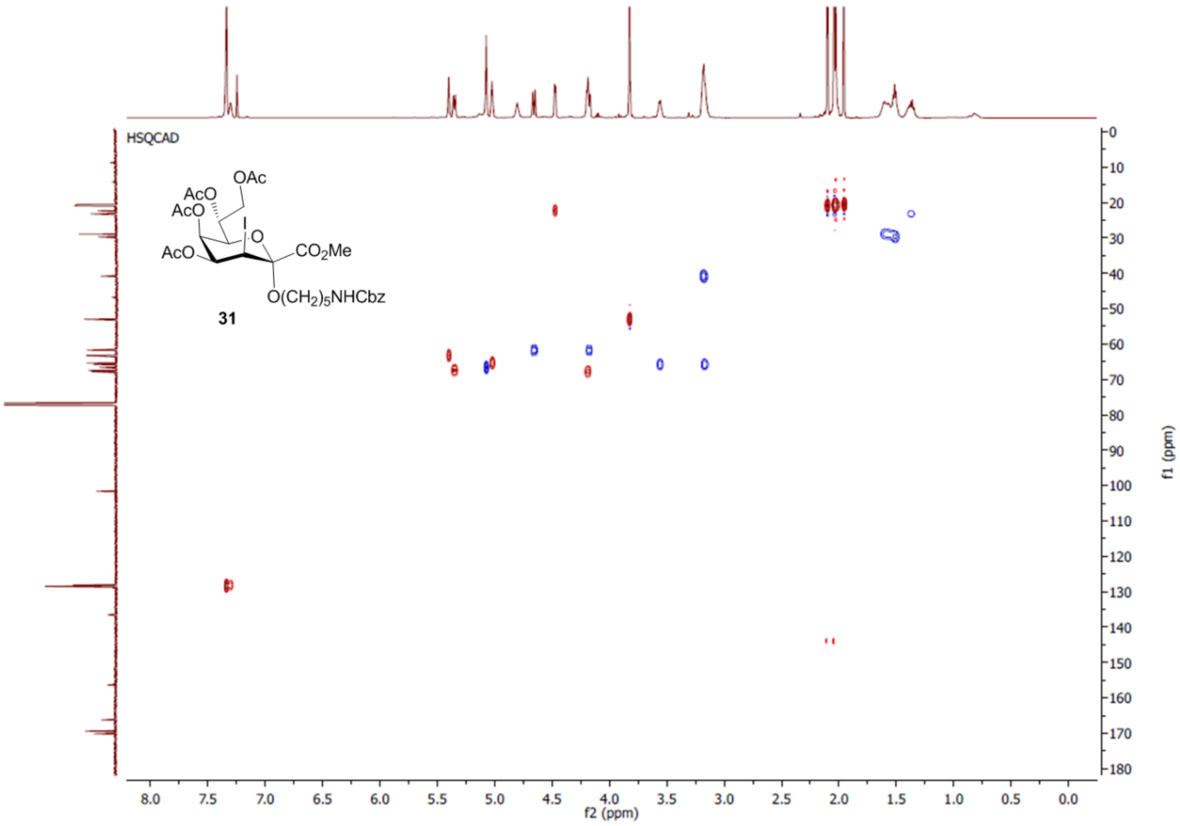
8. NMR spectra


^{1}H NMR (600 MHz, $CDCl_3$)

31


^{13}C NMR (150 MHz, $CDCl_3$)

31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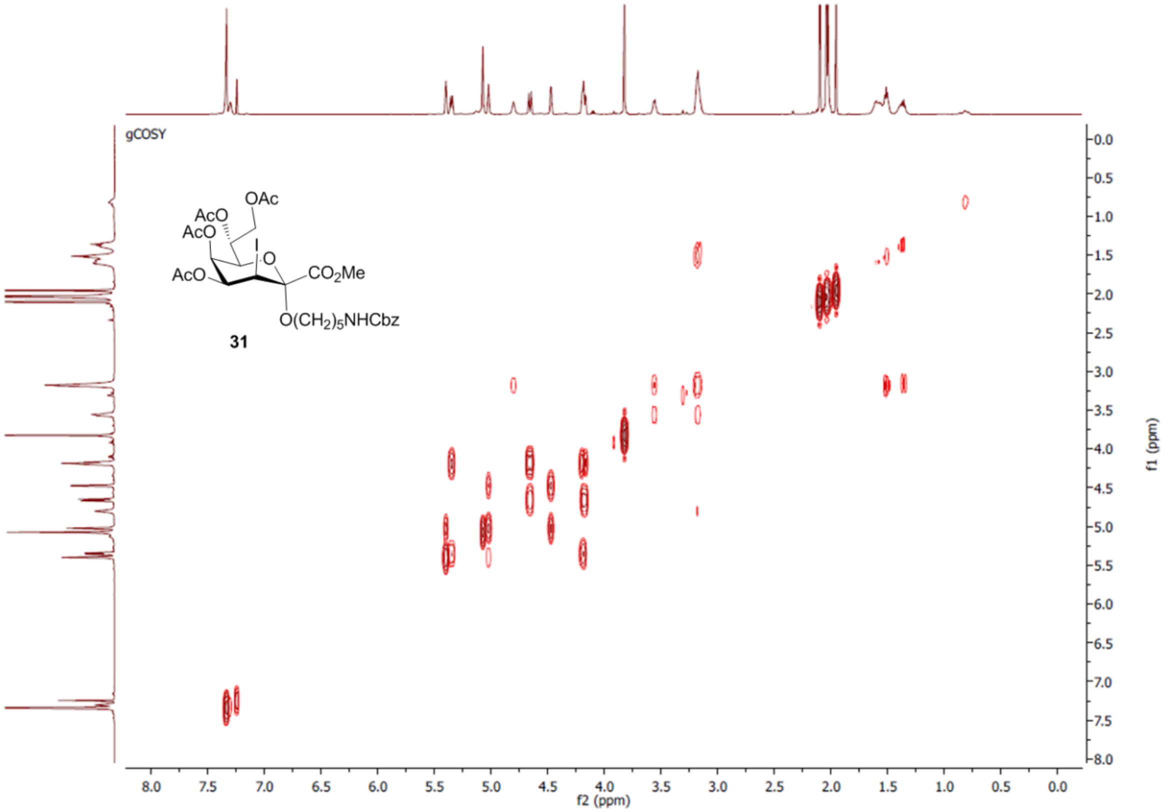
AcO
AcO
I
O
CO$_2$Me
AcO
O(CH$_2$)$_5$NHCbz
31
f2 (ppm)
f1 (ppm)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180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AcO
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I
O
CO$_2$Me
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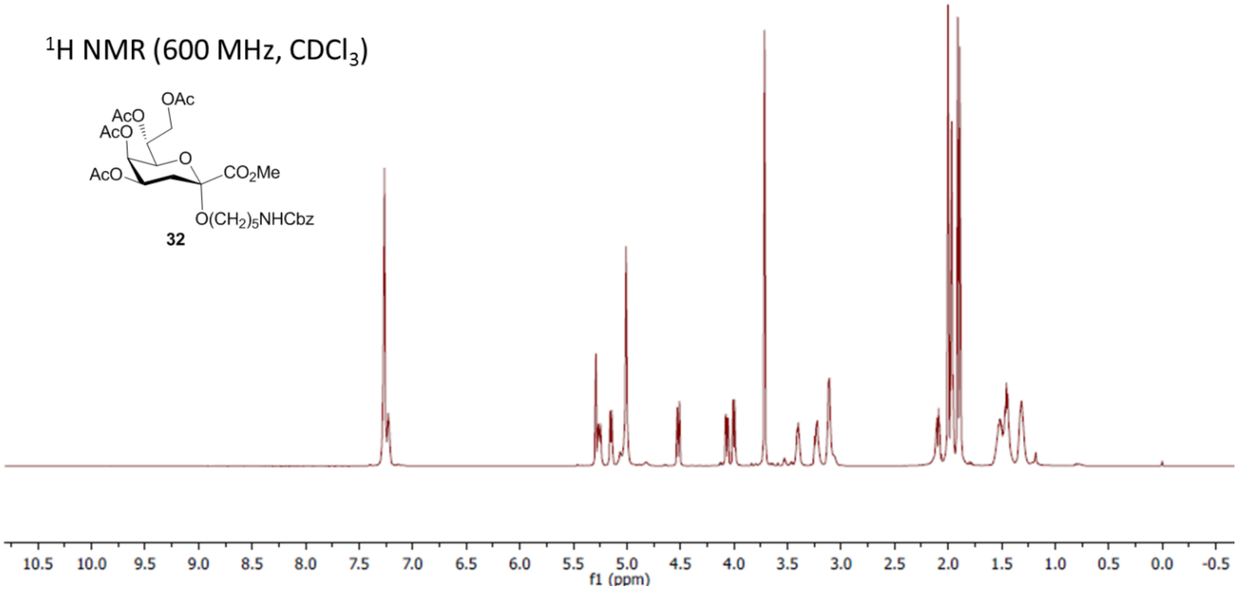
O(CH$_2$)$_5$NHCbz
31
f2 (ppm)
f1 (ppm)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0

^1H NMR (600 MHz, $CDCl_3$)



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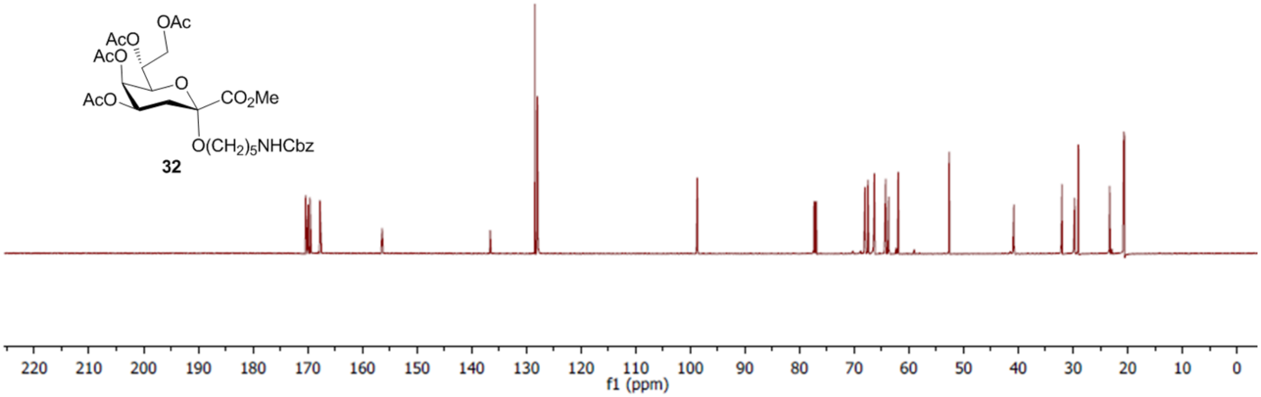

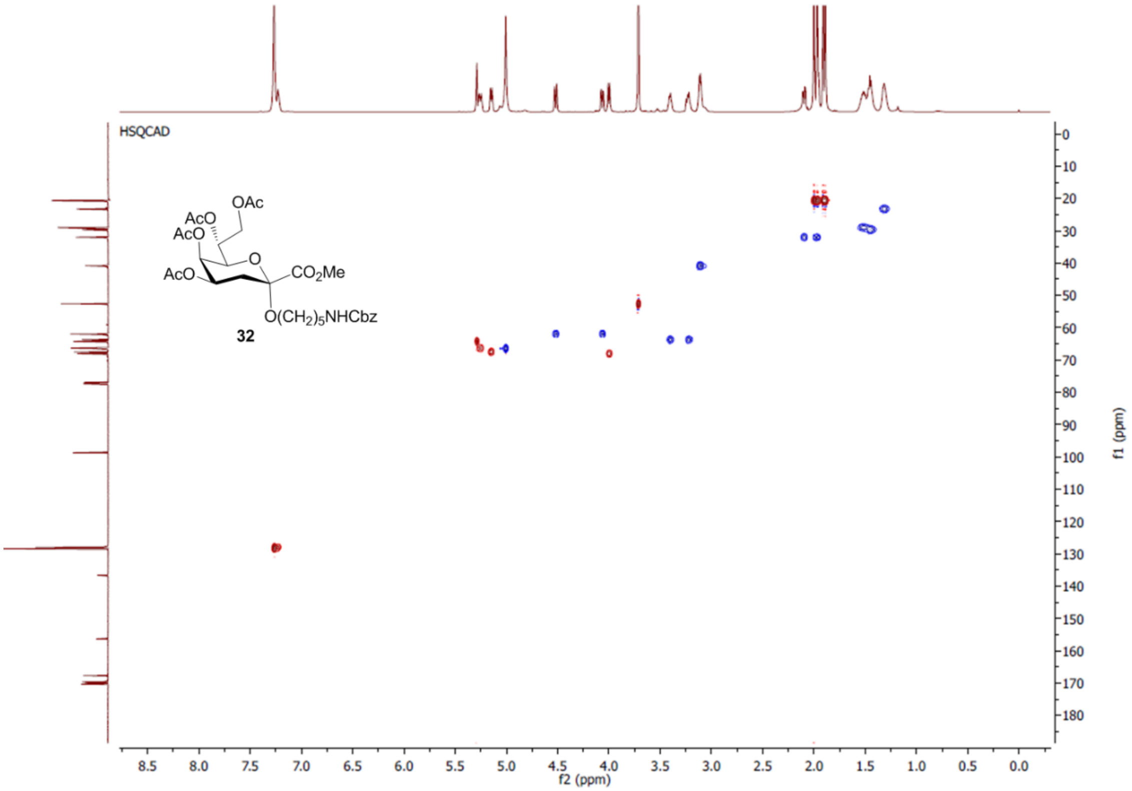
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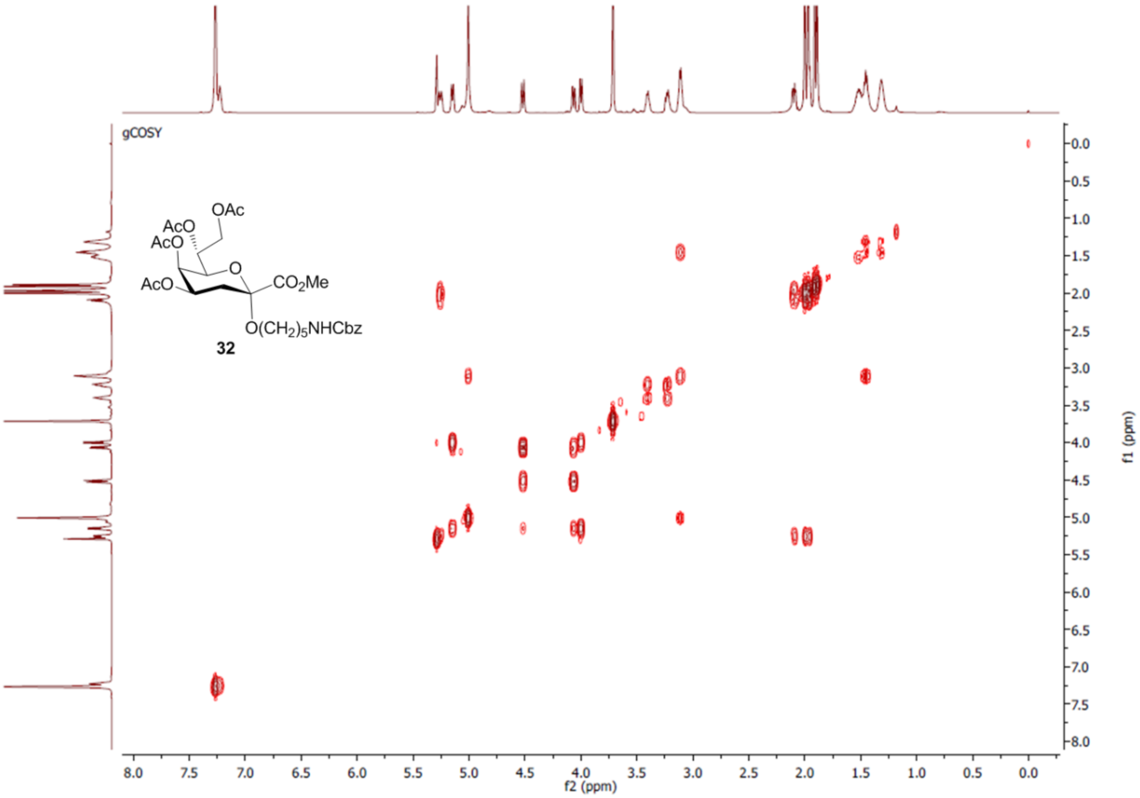
OAc
AcO
AcO
O
AcO
CO2Me
O(CH2)5NHCbz
32
f2 (ppm)
f1 (ppm)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180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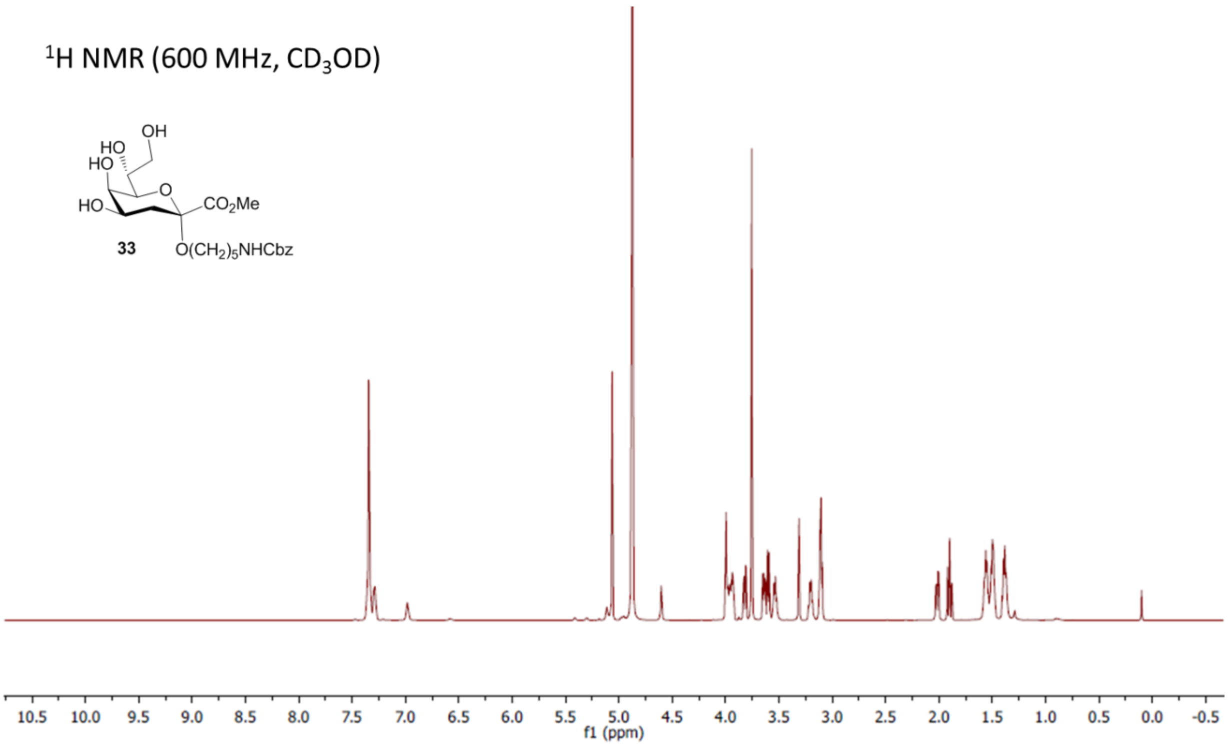
f2 (ppm)
f1 (ppm)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0

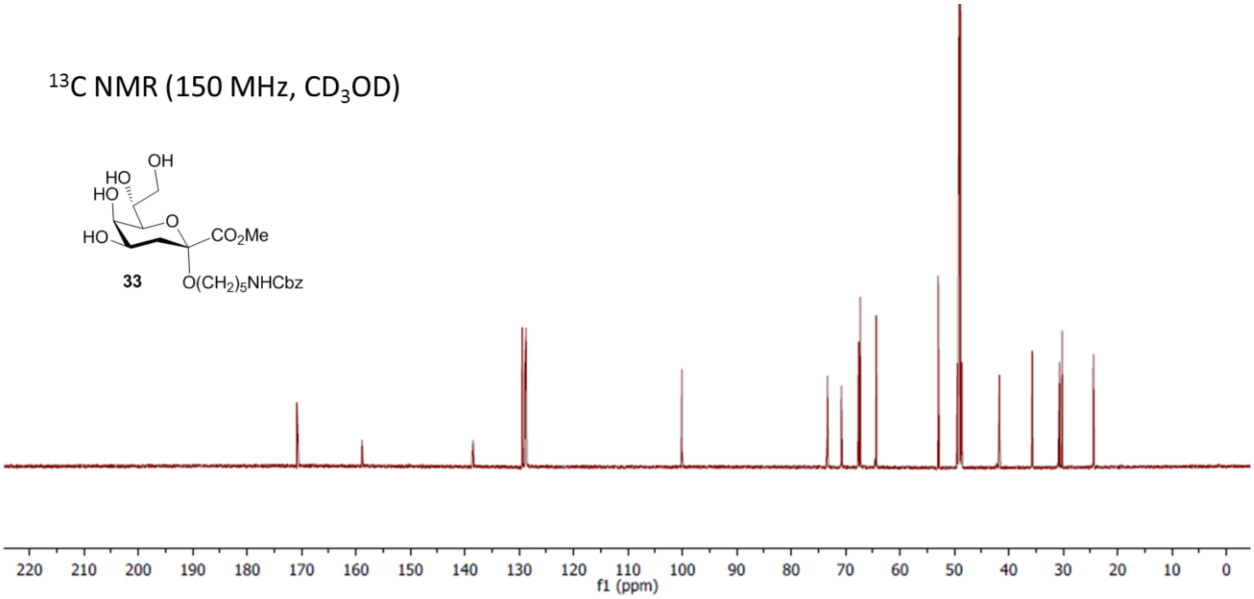
^{1}H NMR (600 MHz, CD_3OD)

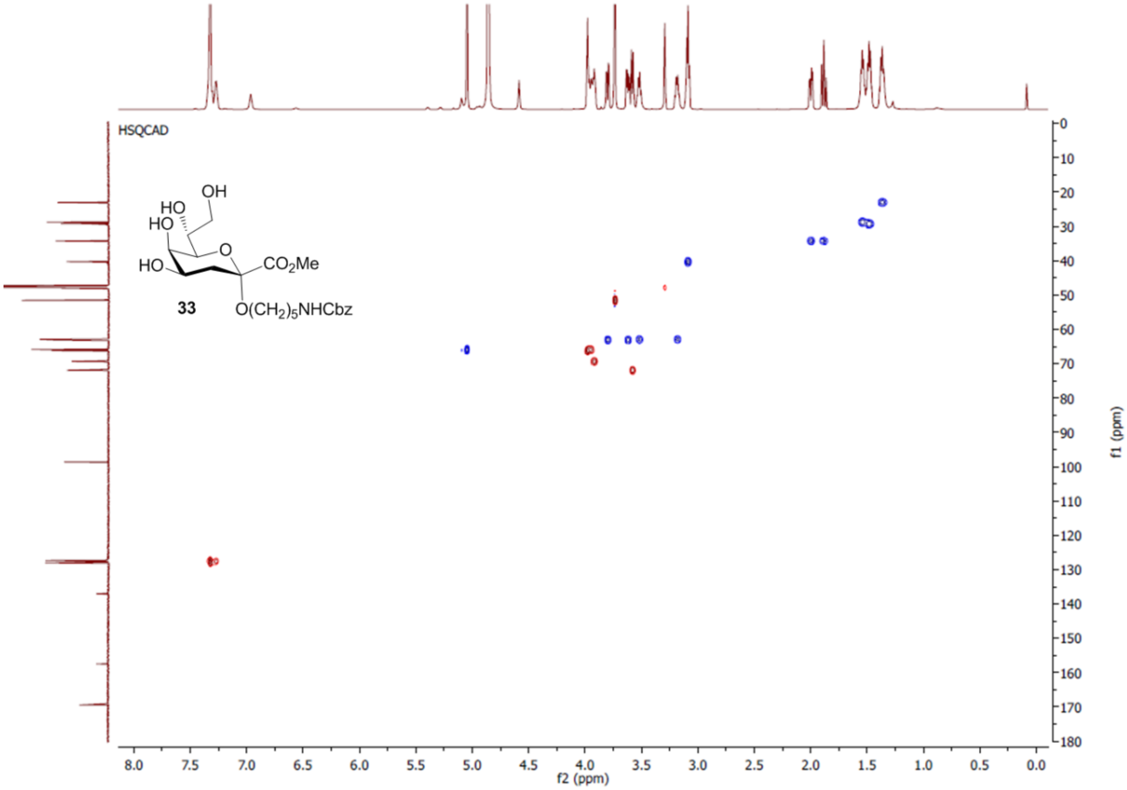
33



^{13}C NMR (150 MHz, CD_3OD)

33

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HO
HO
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f1 (ppm)
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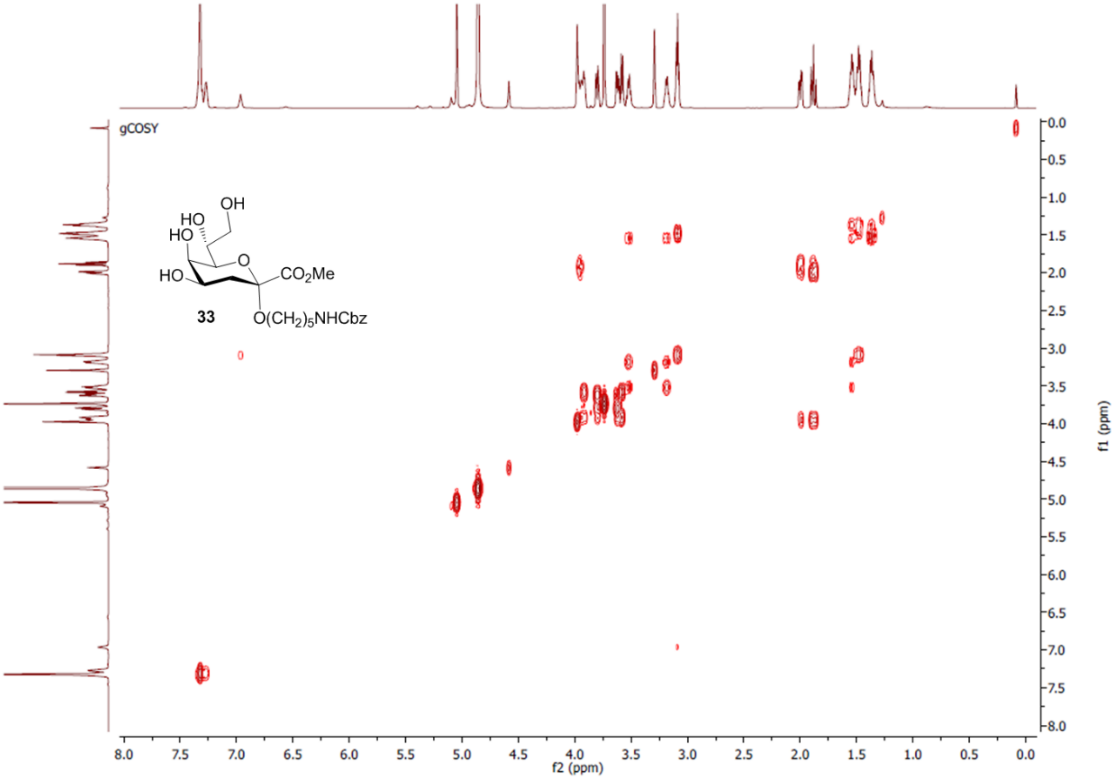
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180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f2 (ppm)
f1 (ppm)
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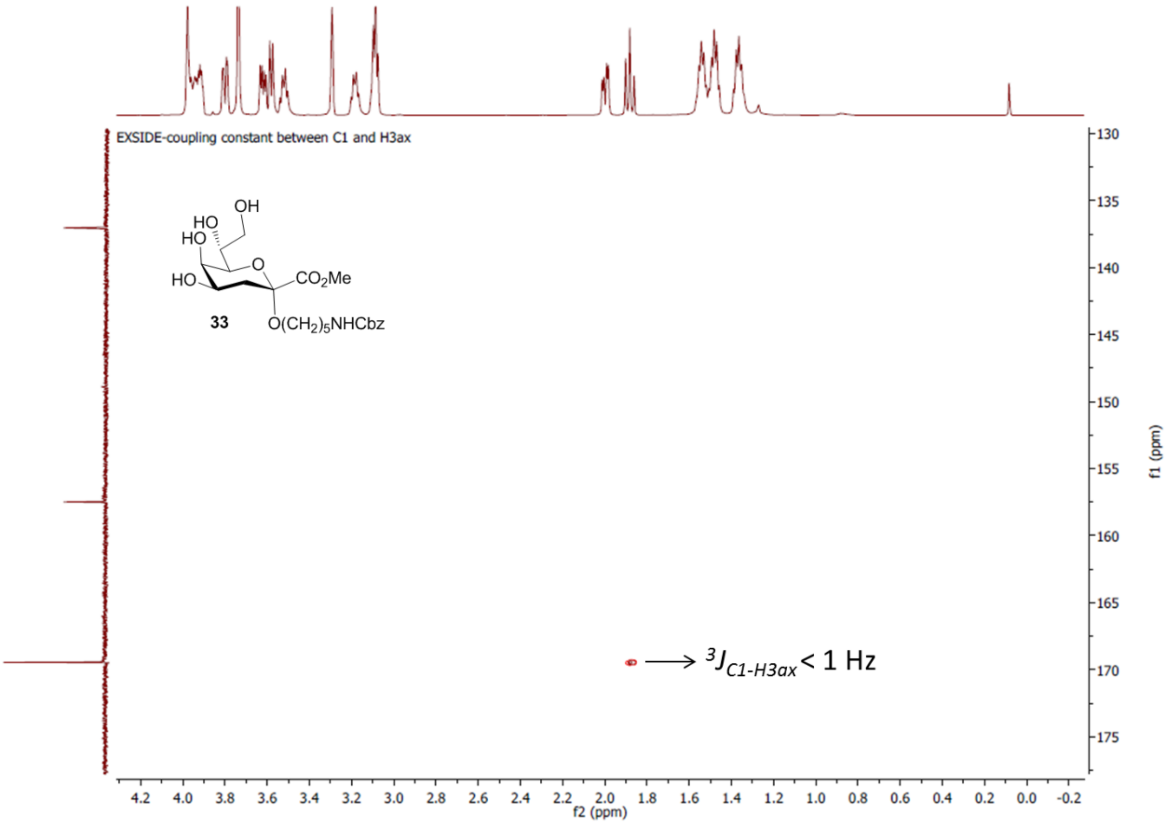
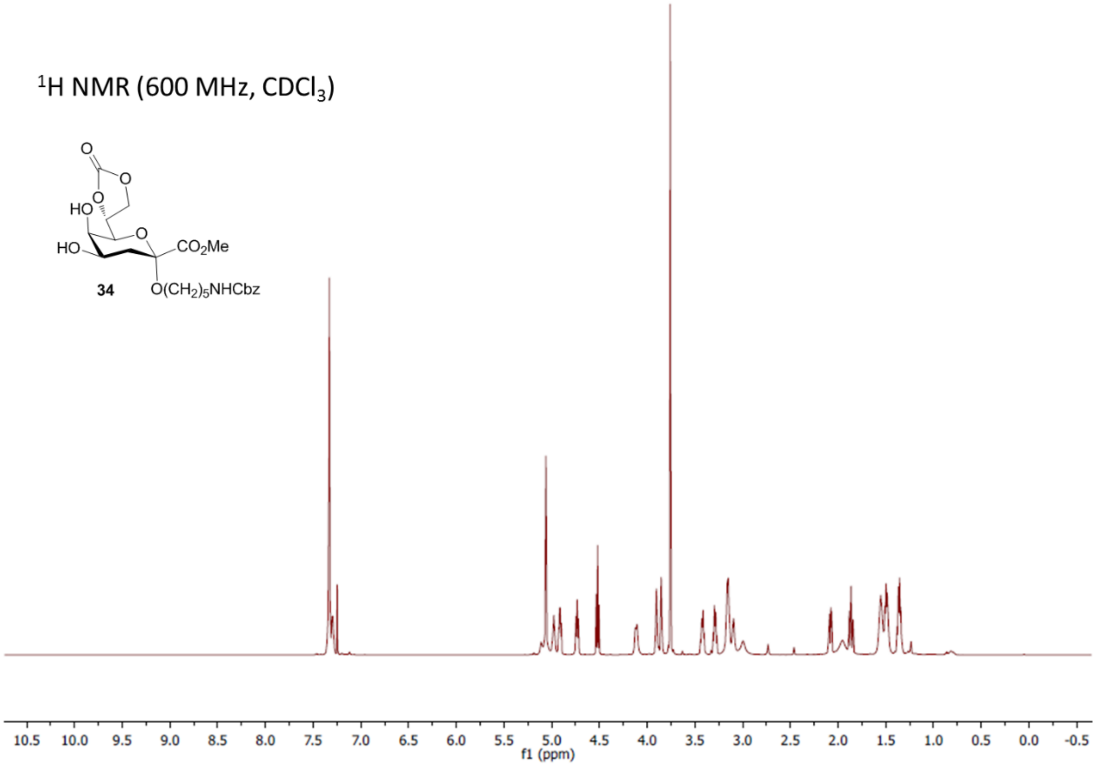
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0



$\longrightarrow {}^{3}J_{C1\text{-}H3ax} < 1$ Hz

^{1}H NMR (600 MHz, CDCl$_3$)



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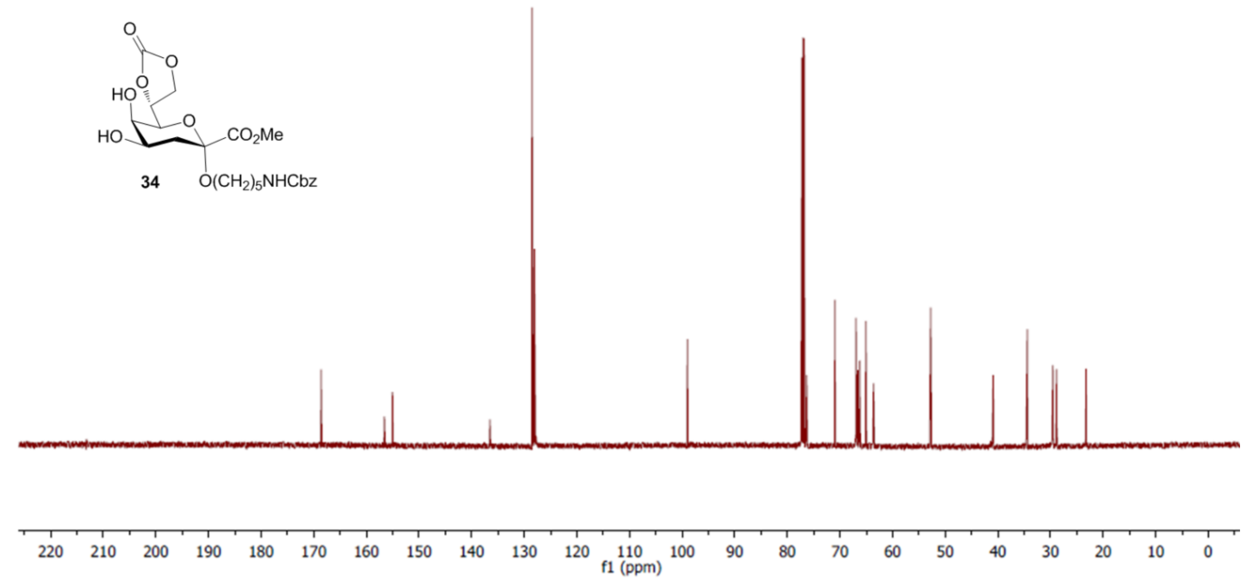

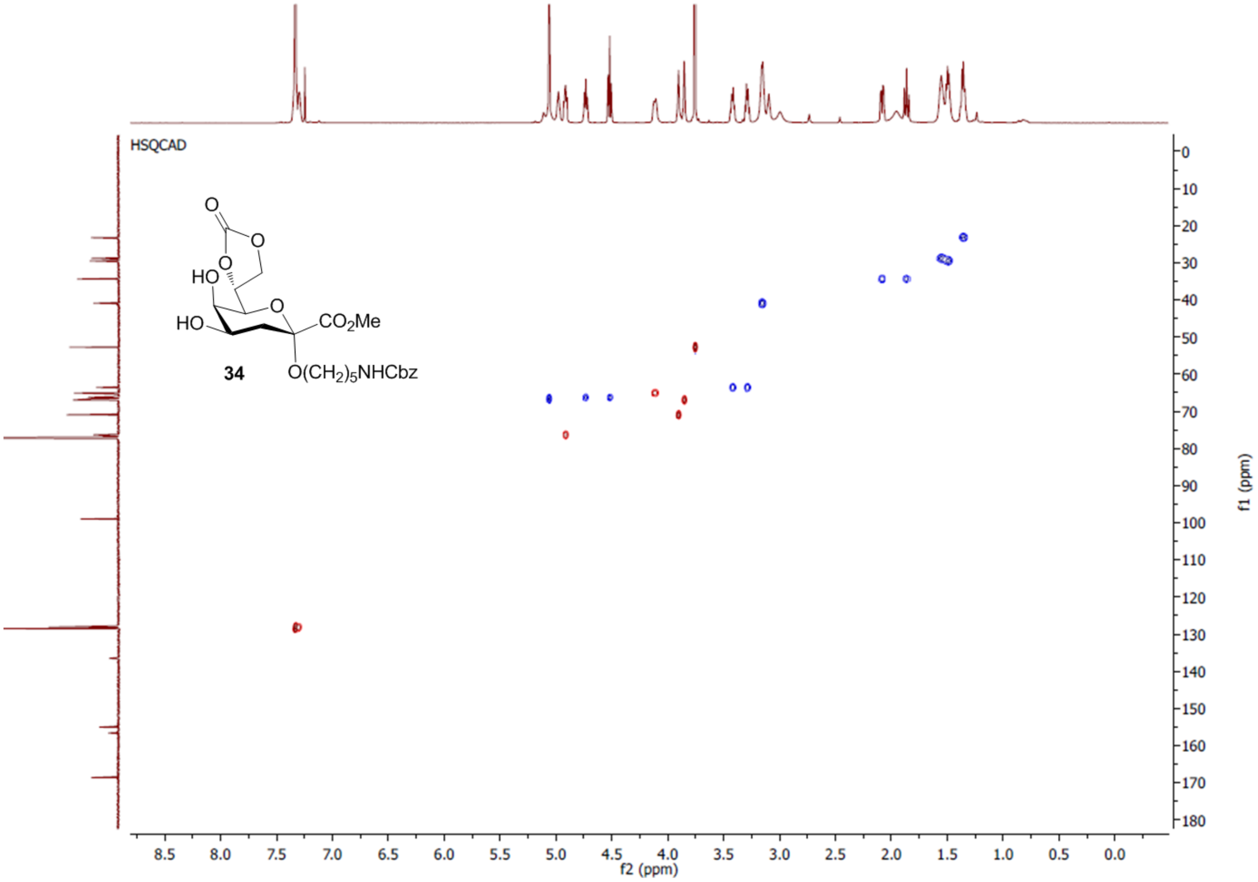

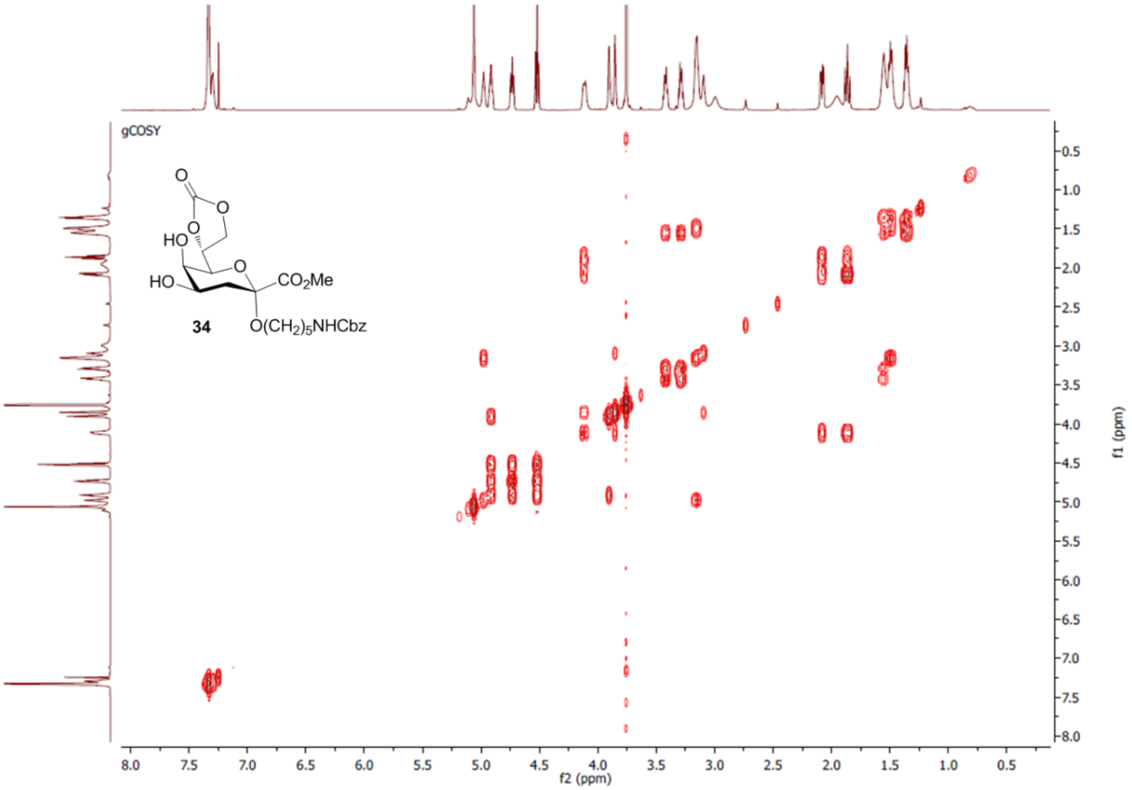

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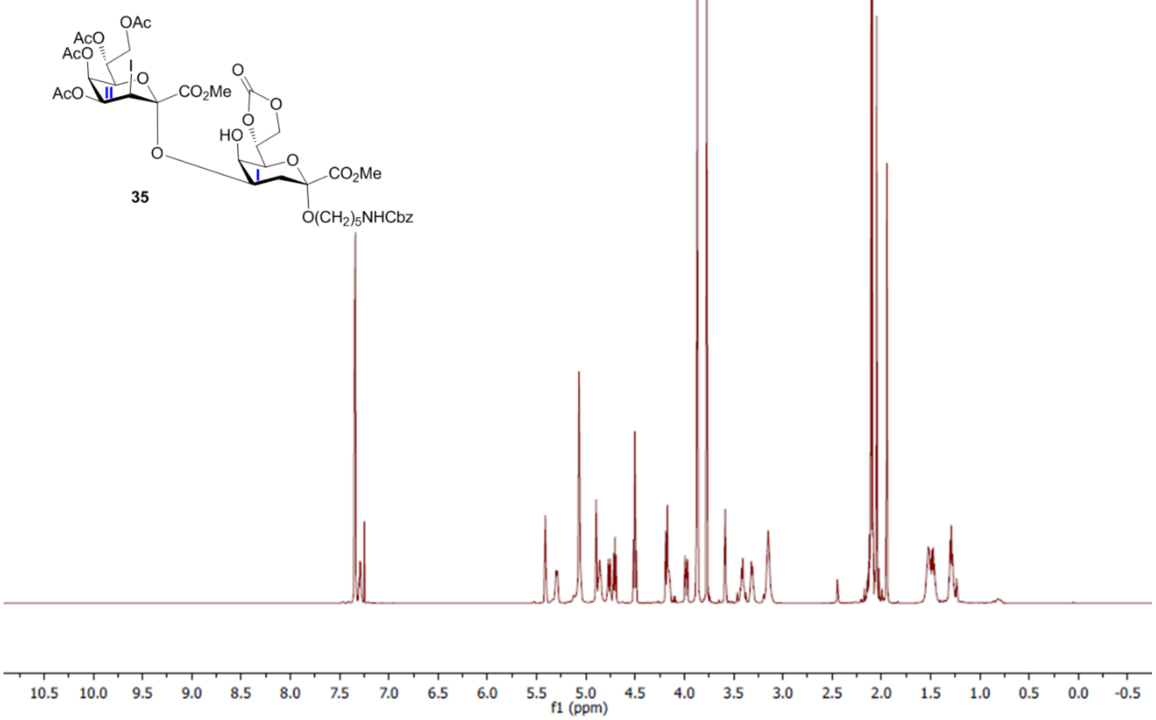

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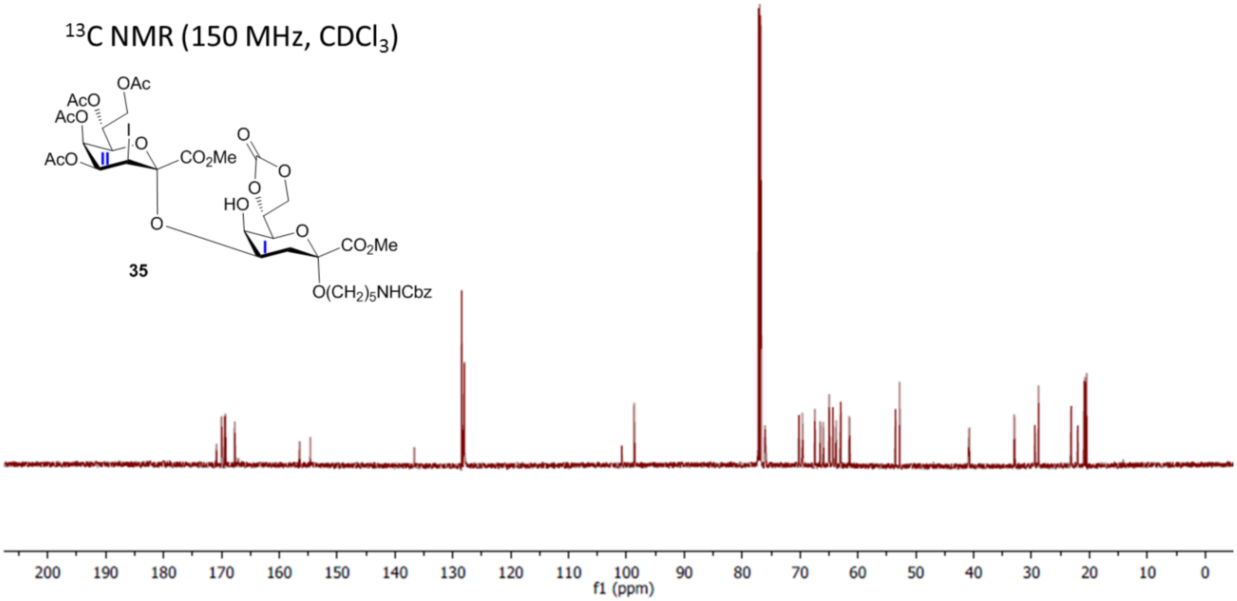

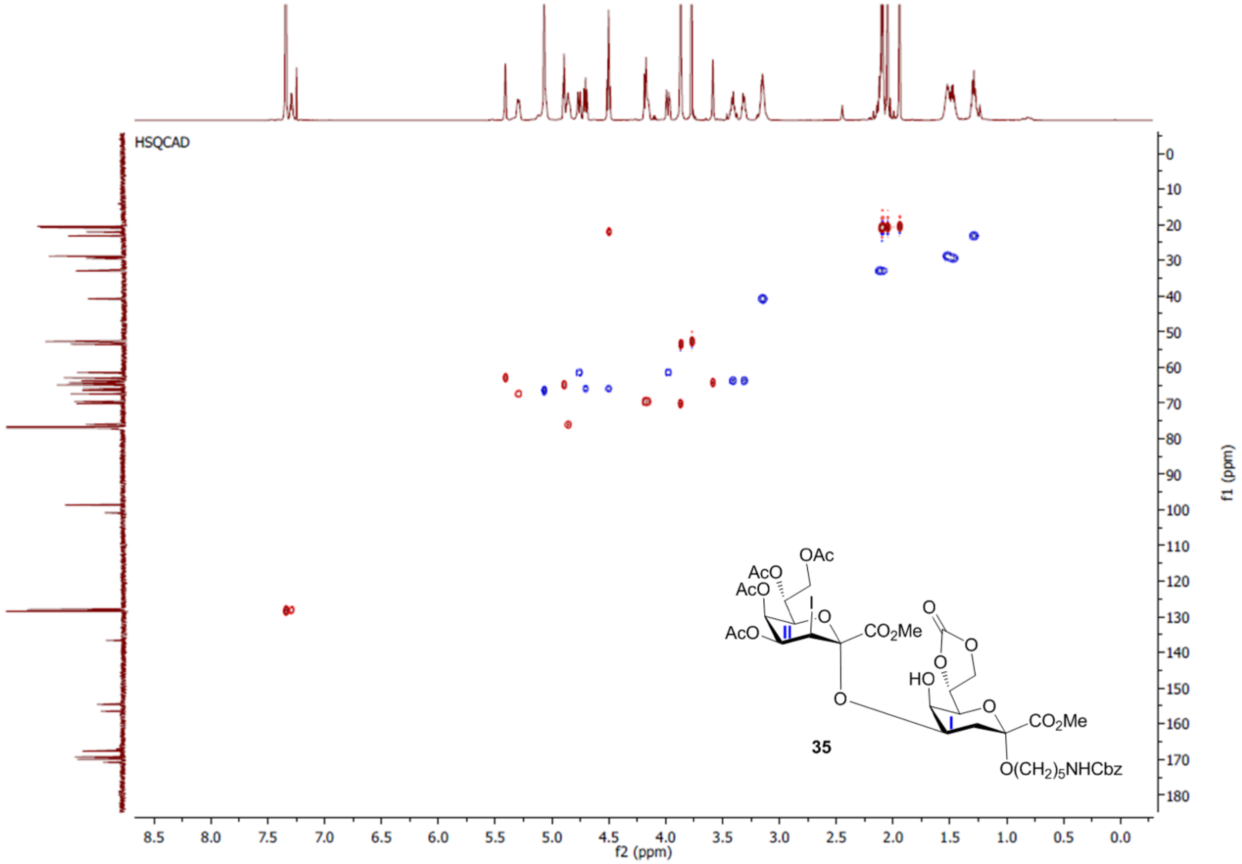

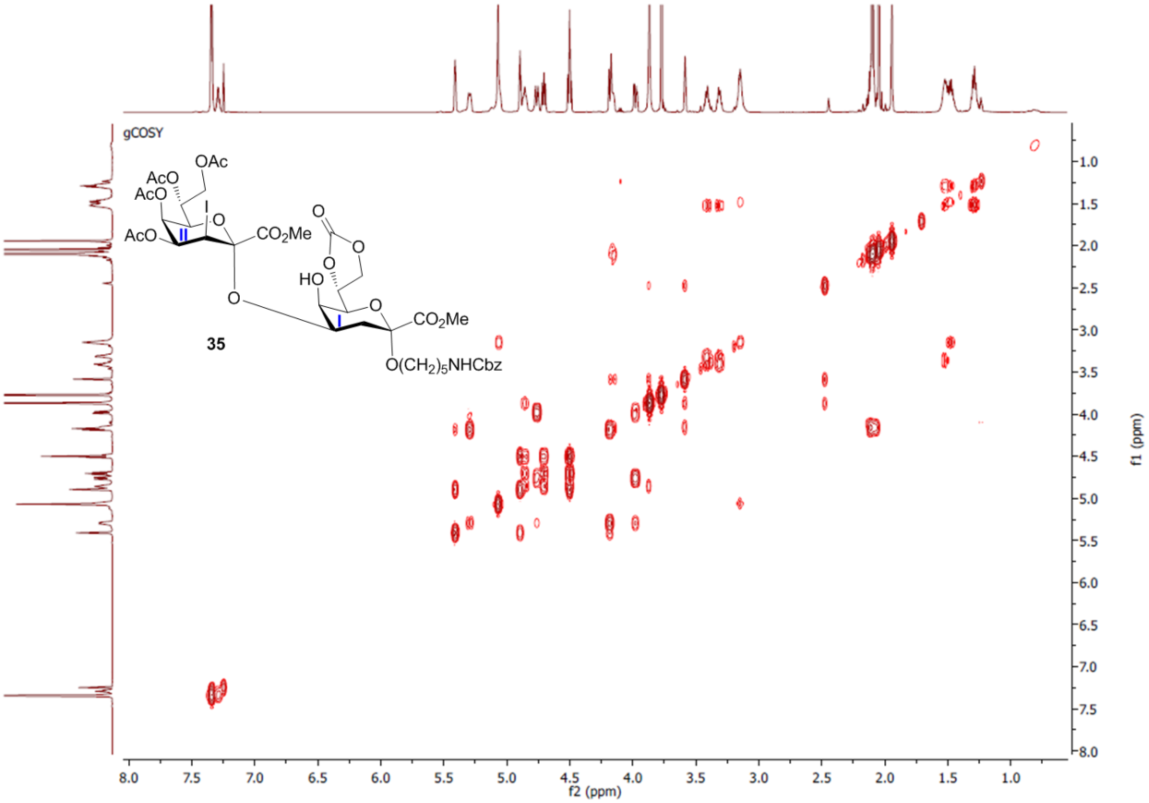
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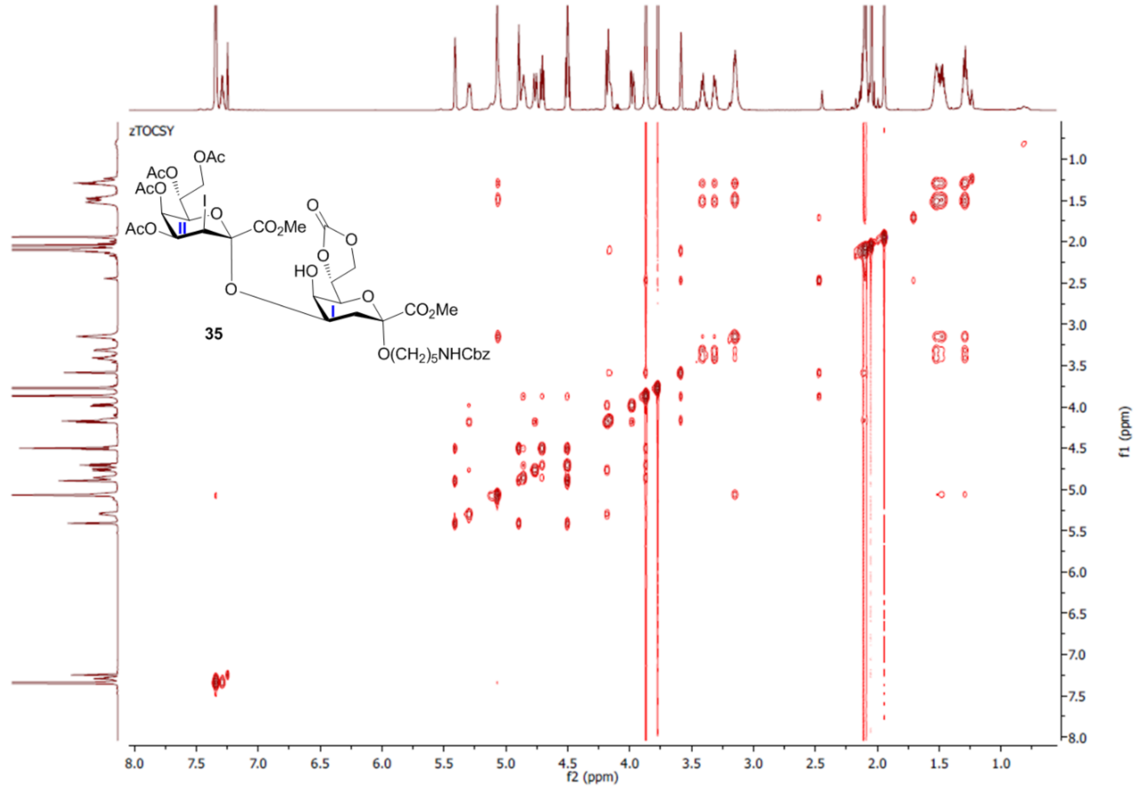
f2 (ppm)
f1 (ppm)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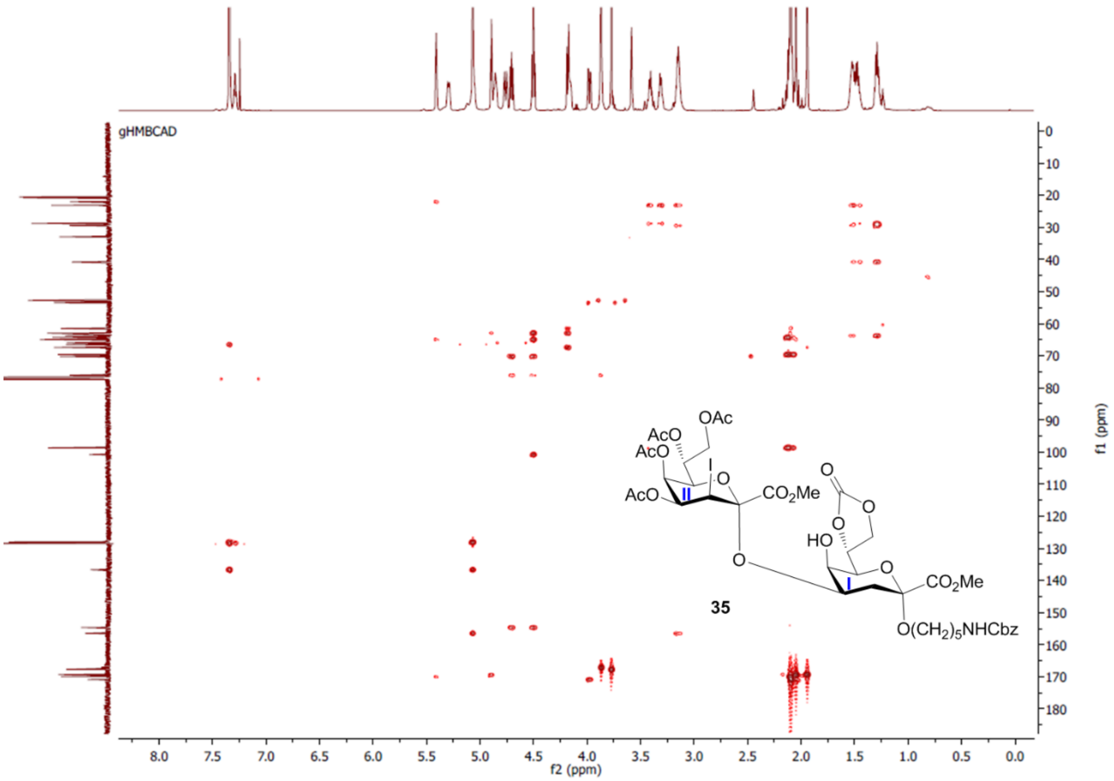
f1 (ppm)



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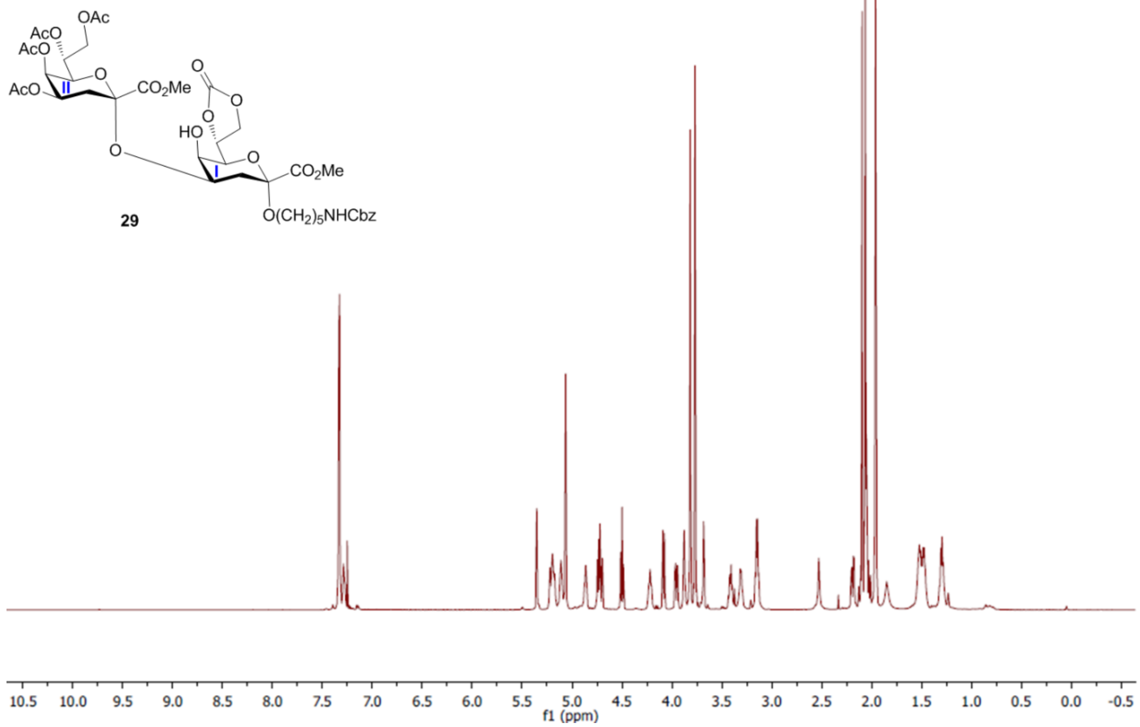

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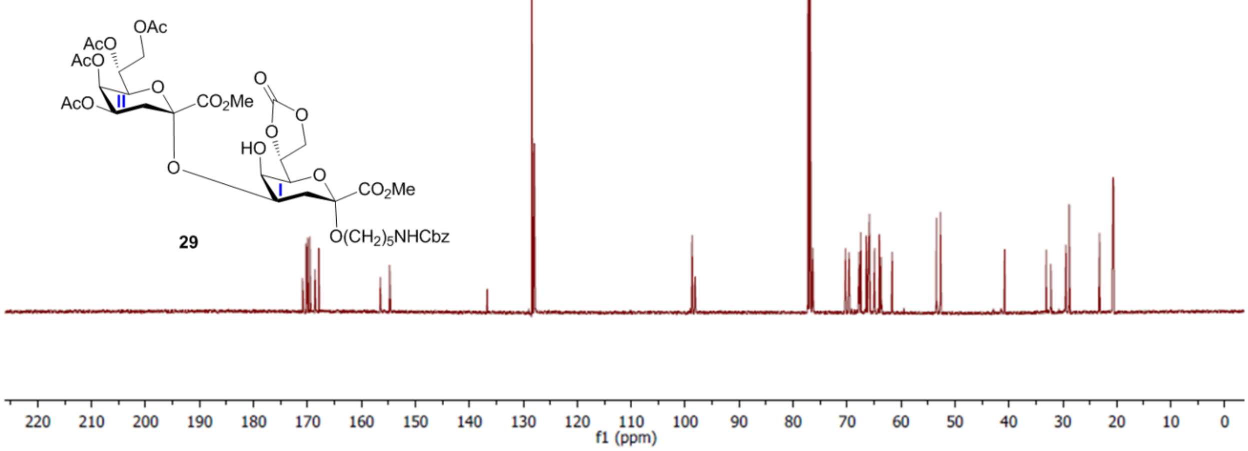
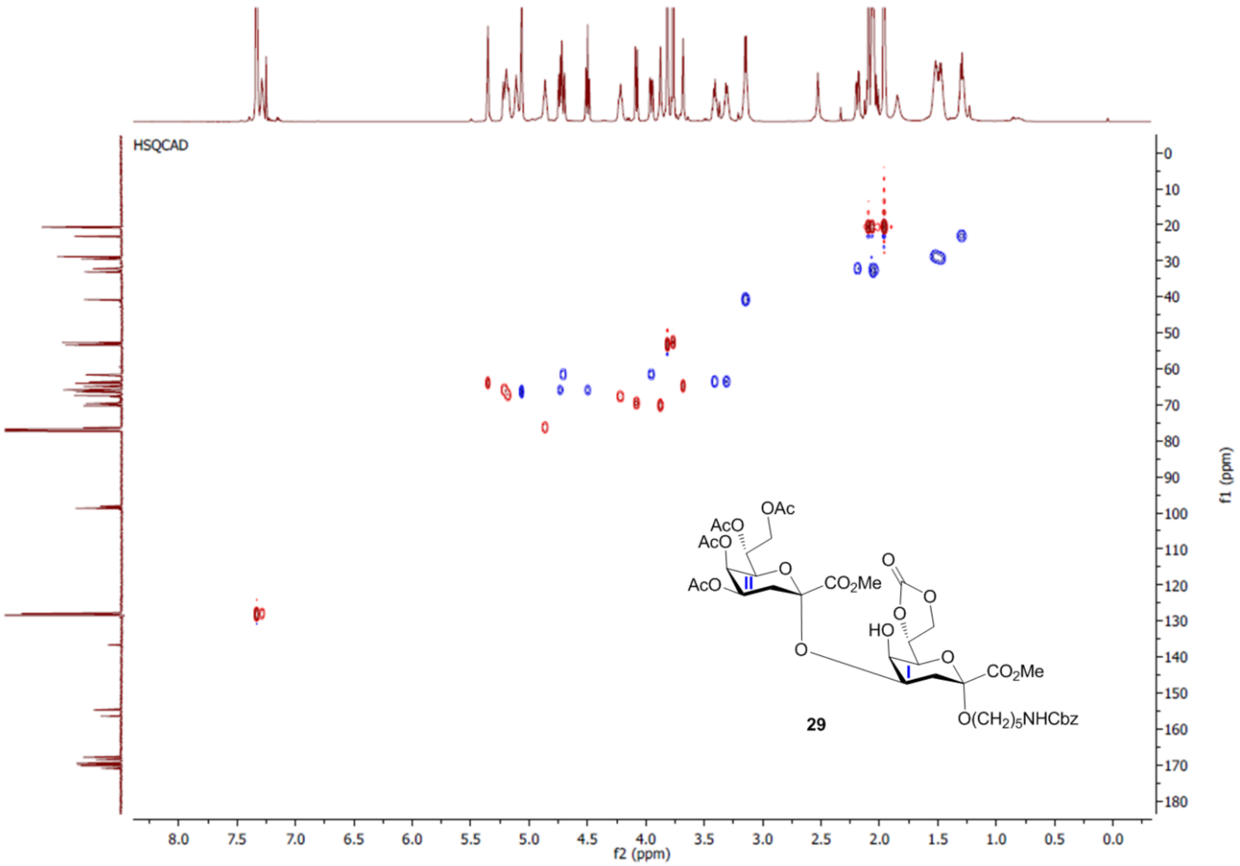
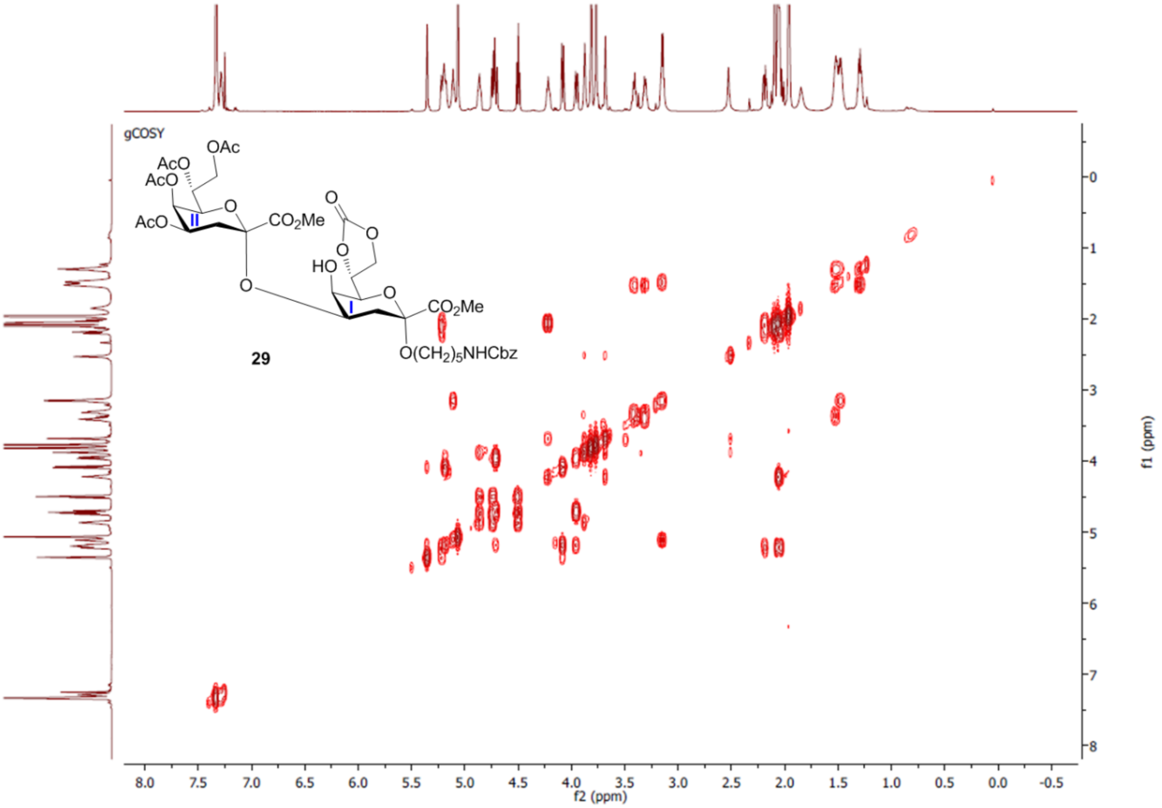
^{13}C NMR (150 MHz, CDCl$_3$)



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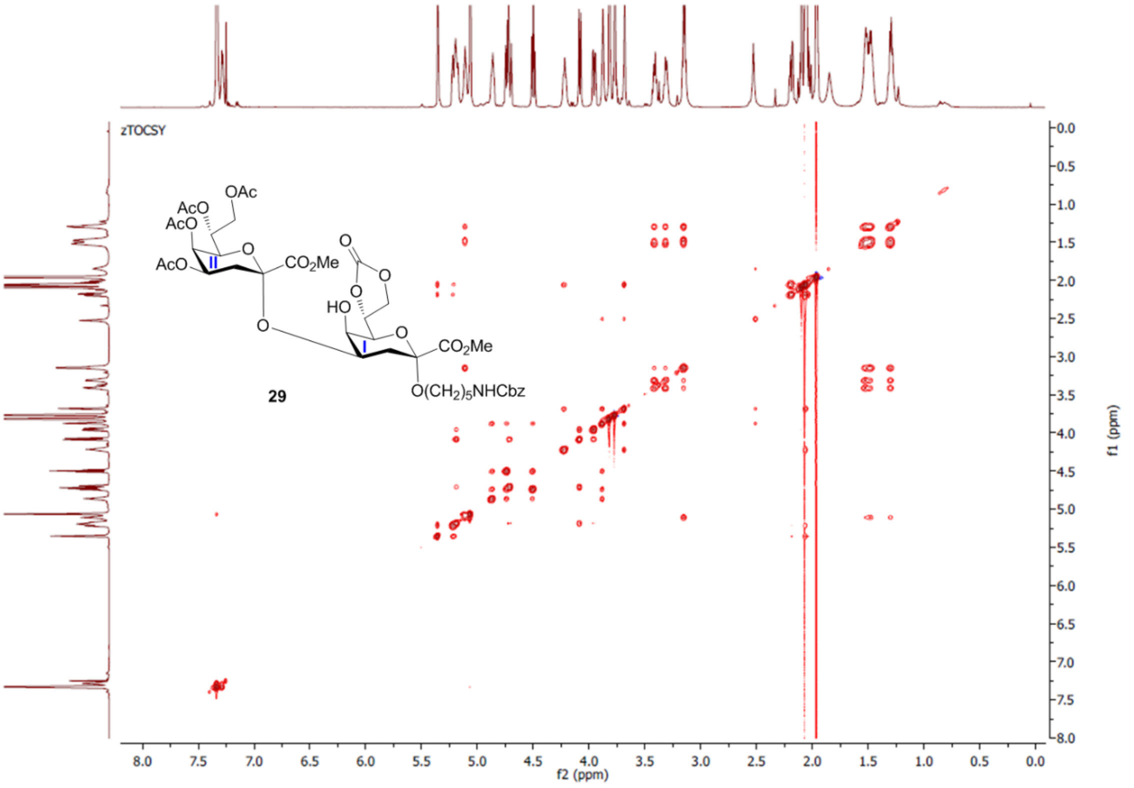
29
f2 (ppm)
f1 (ppm)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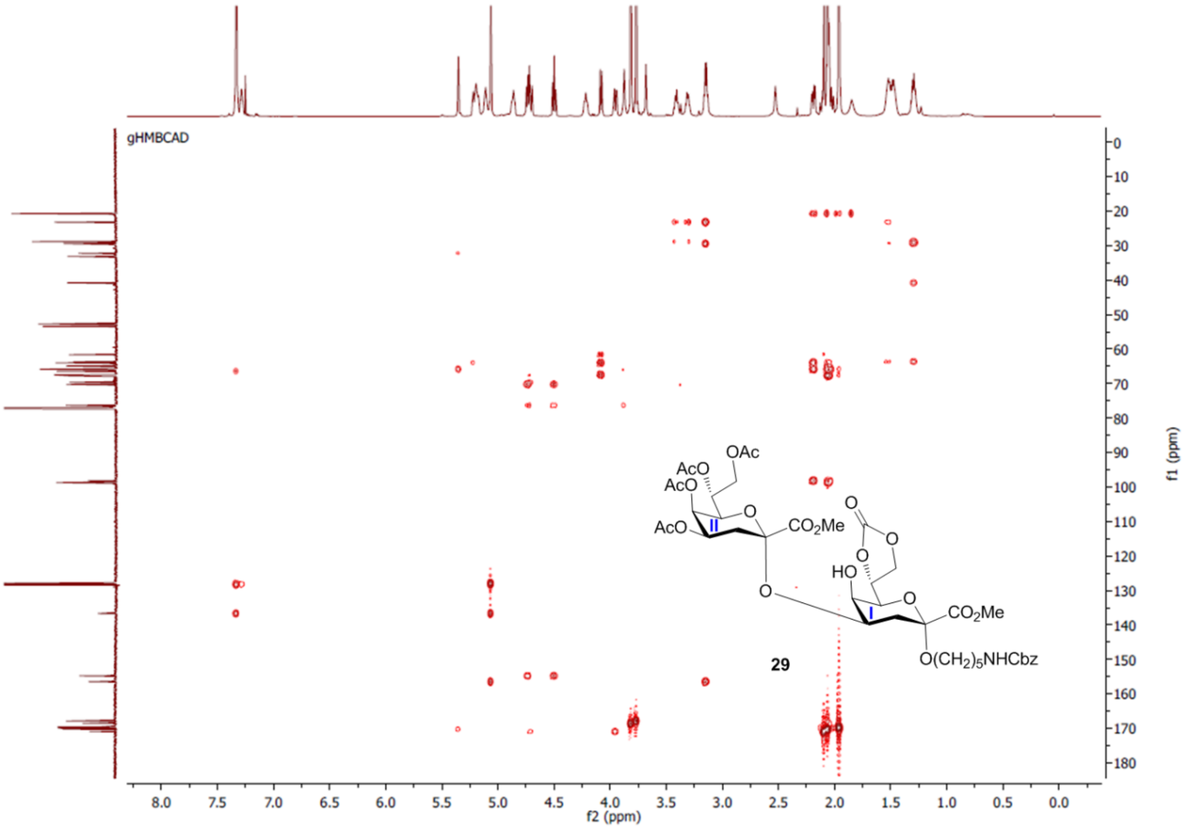
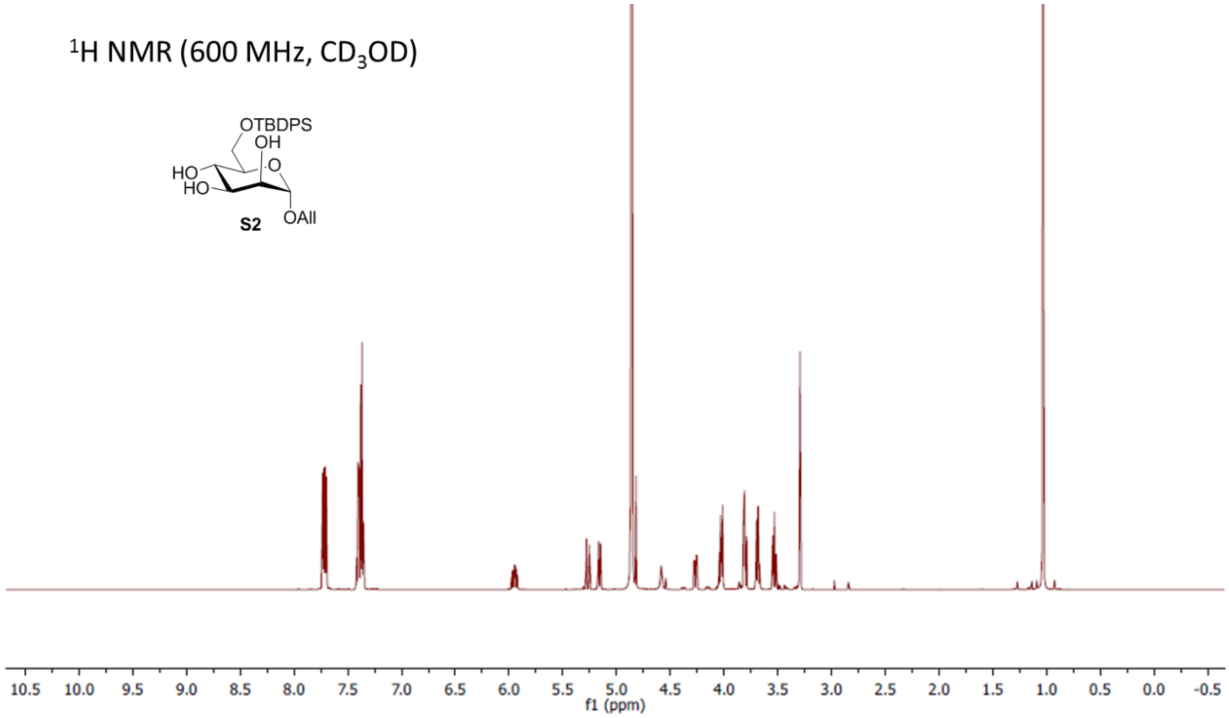
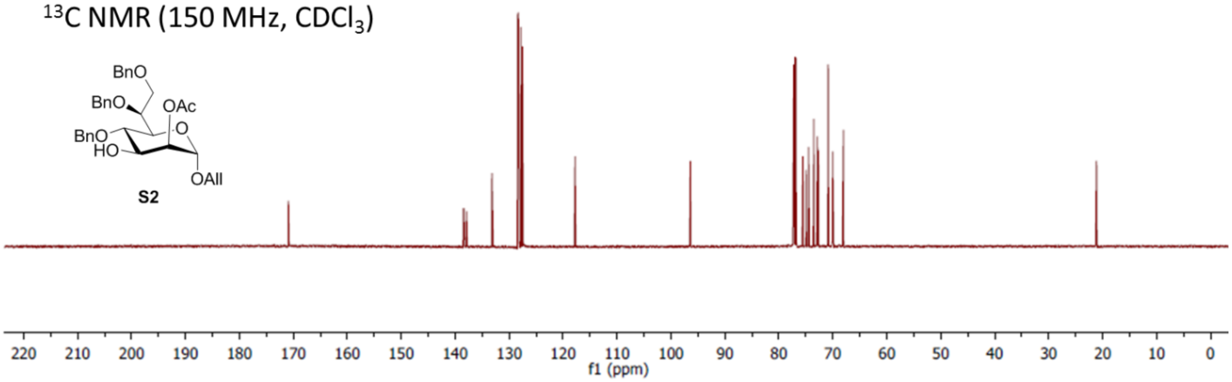
f2 (ppm)
f1 (ppm)

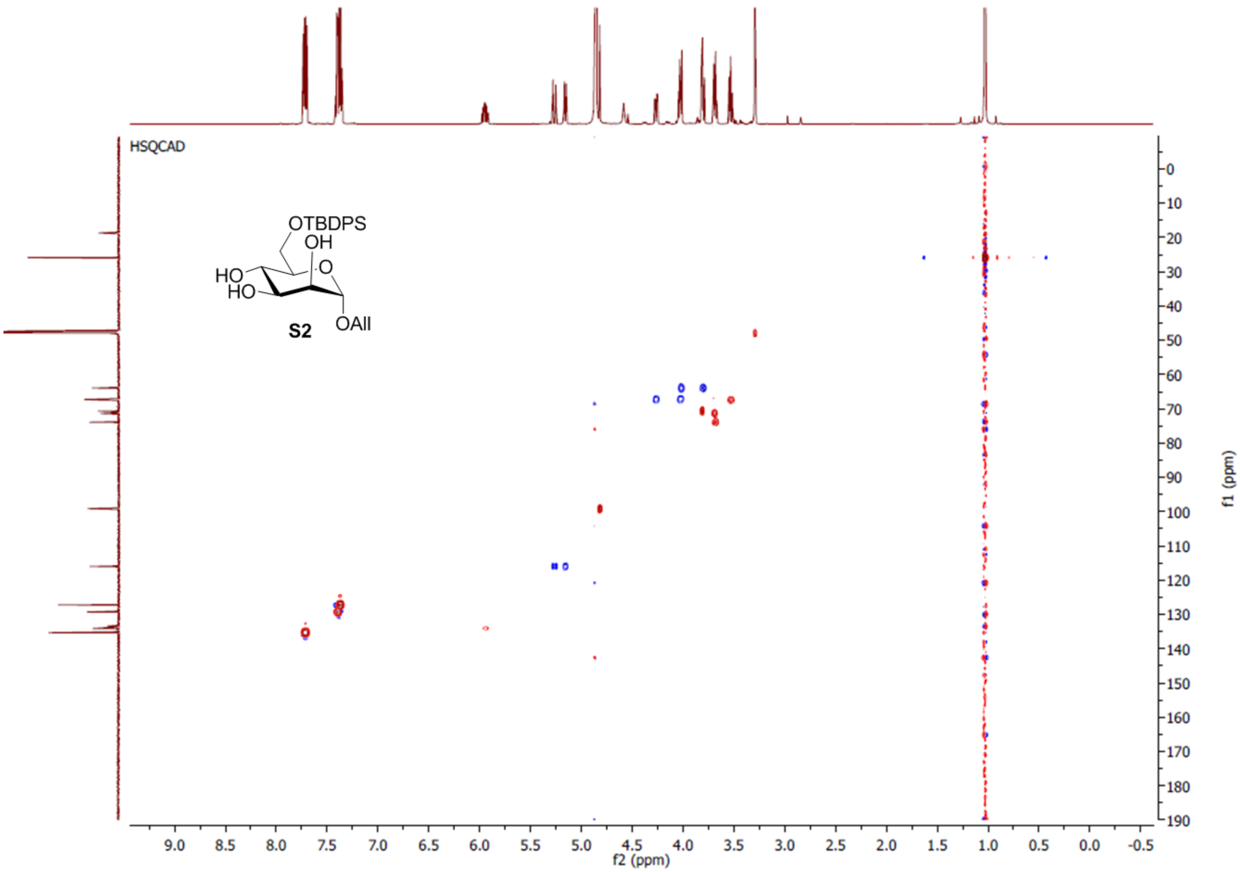


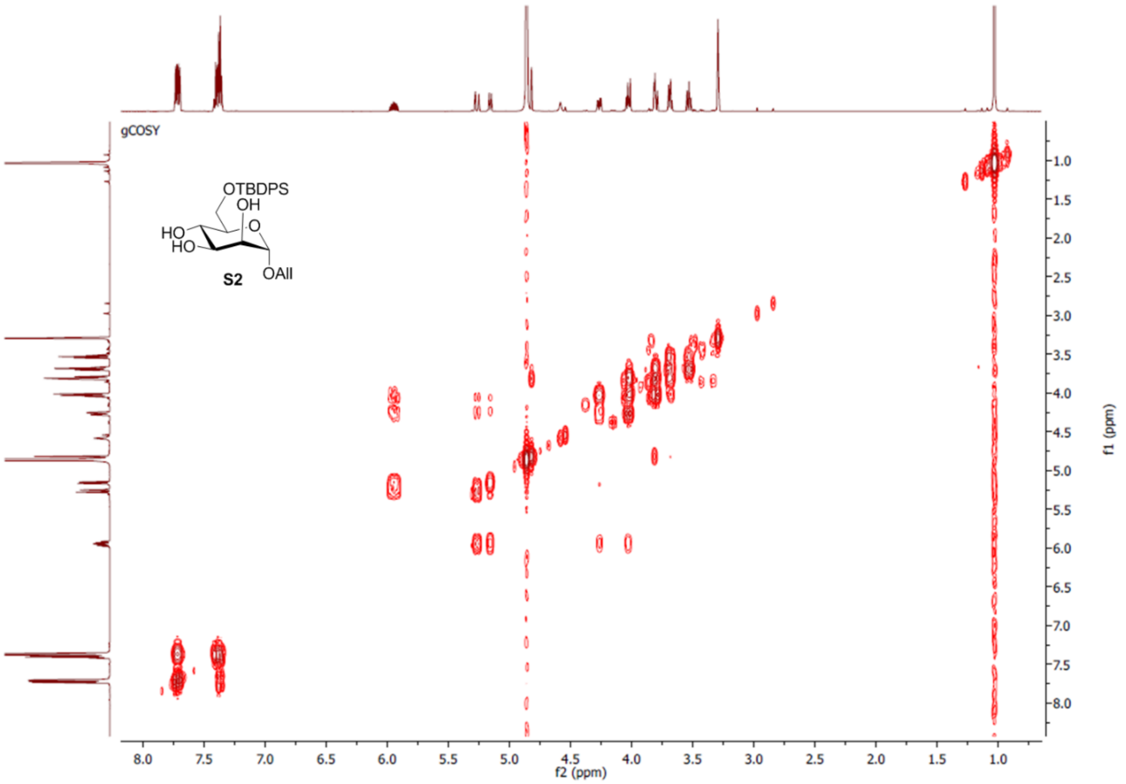
¹H NMR (600 MHz, CD_3OD)



^{13}C NMR (150 MHz, CDCl$_3$)







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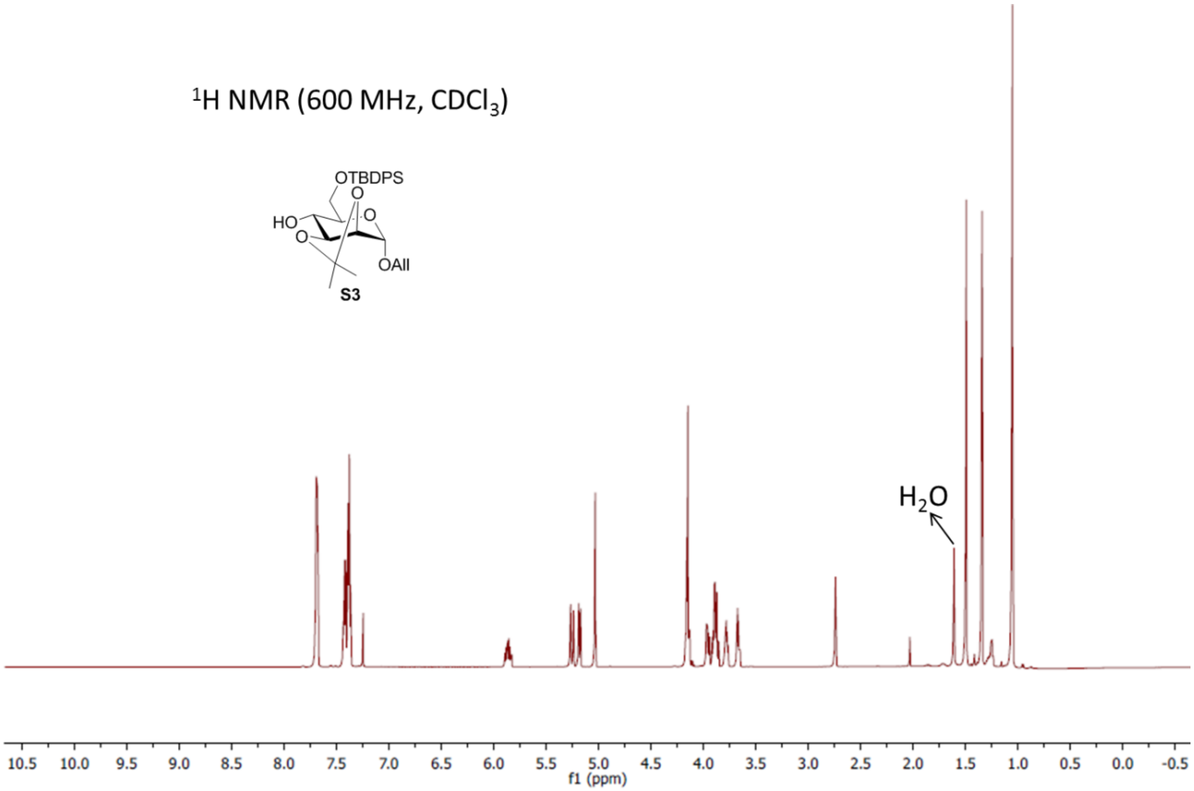
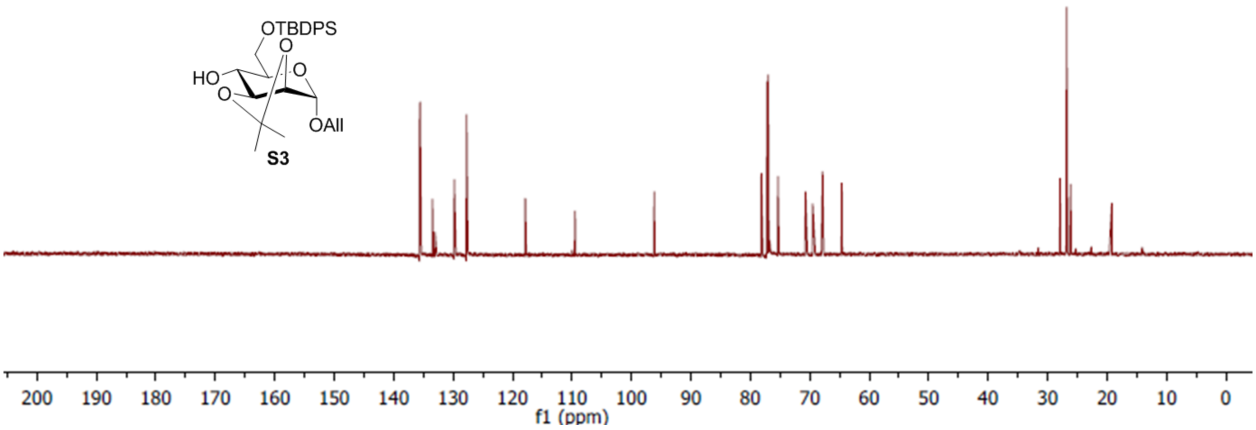
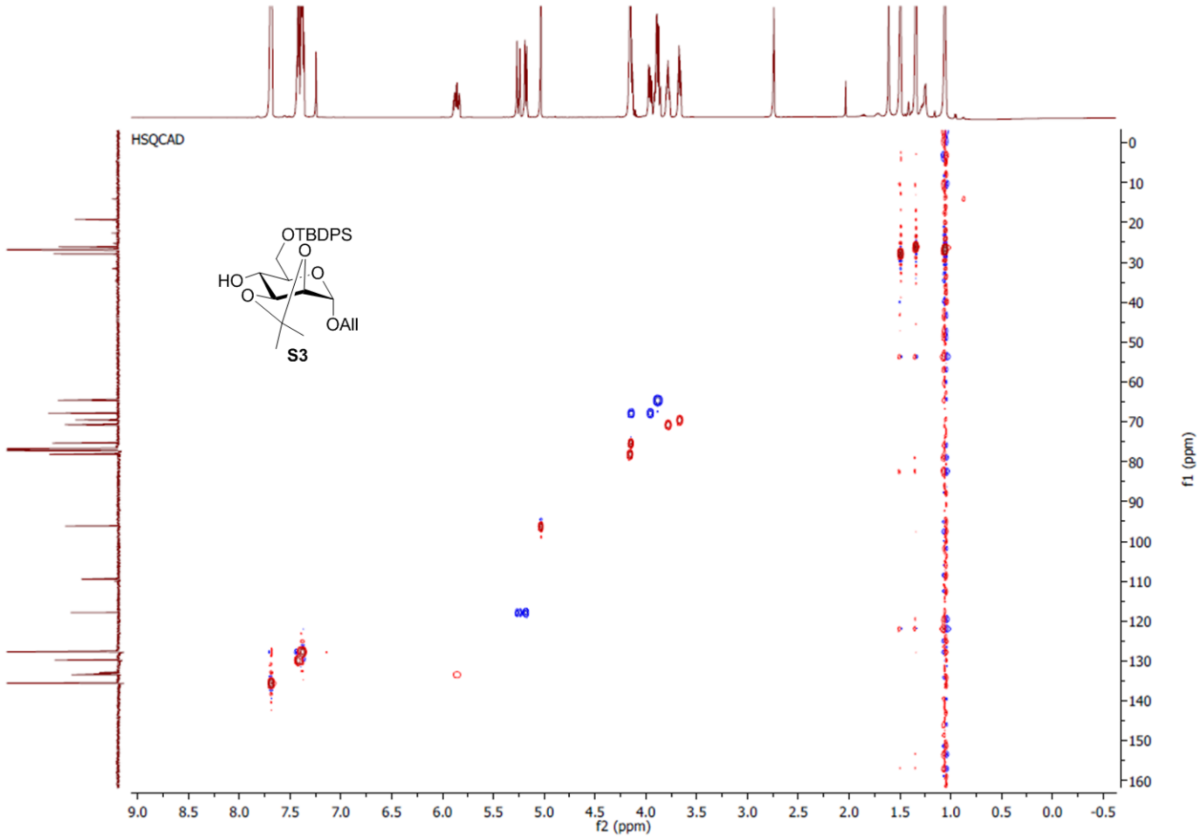
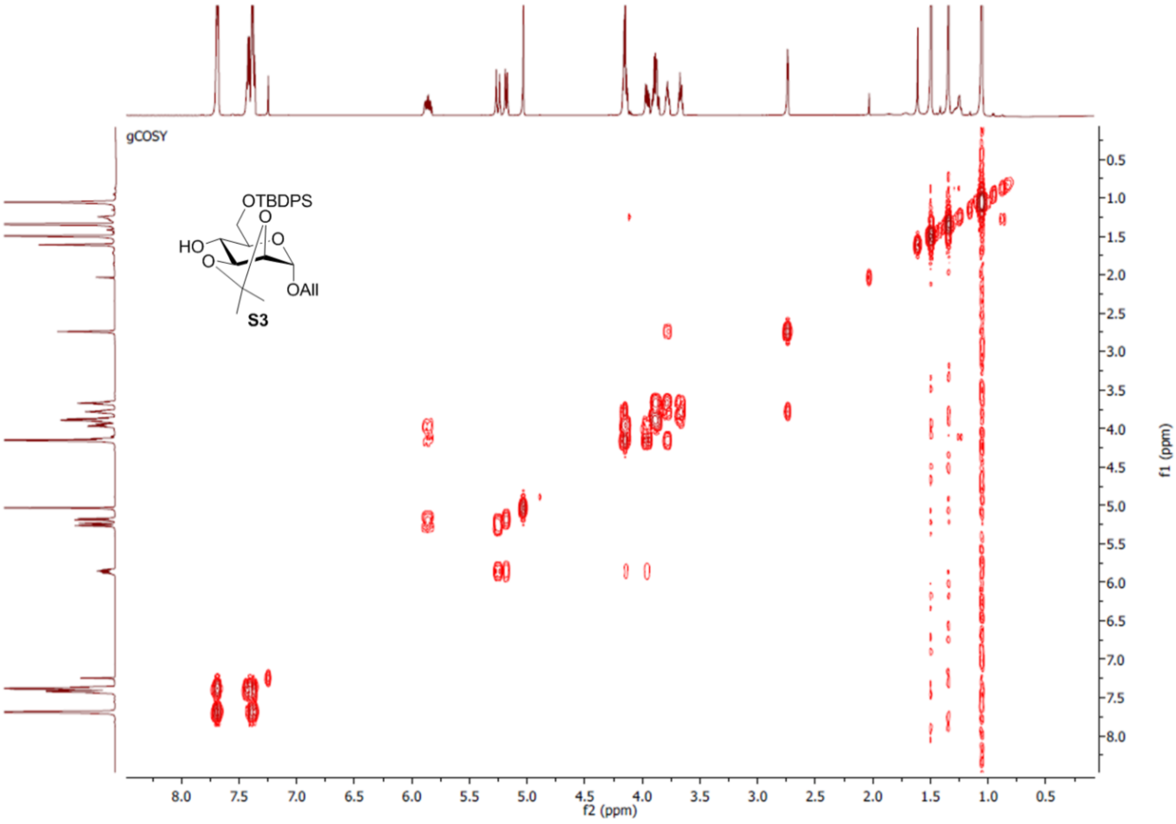


^{13}H NMR (150 MHz, CDCl$_3$)

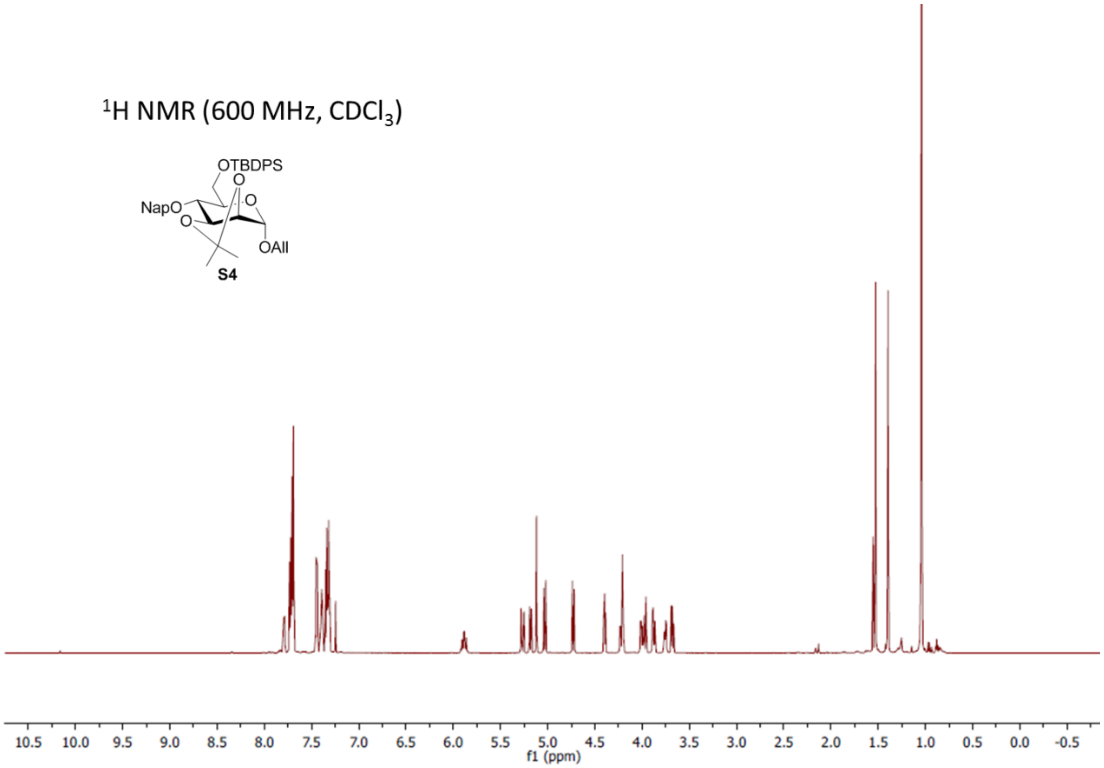






S3

¹H NMR (600 MHz, $CDCl_3$)



S4

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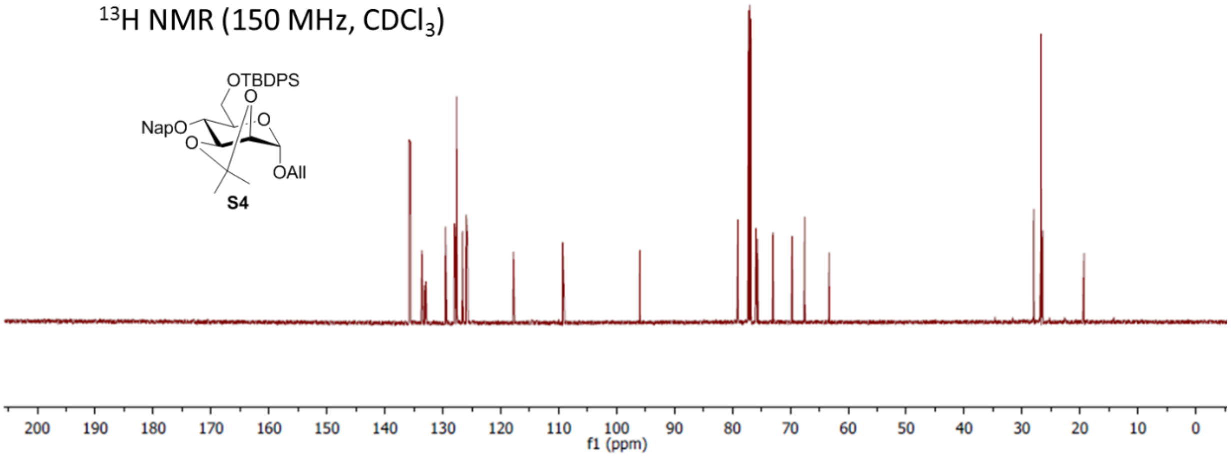
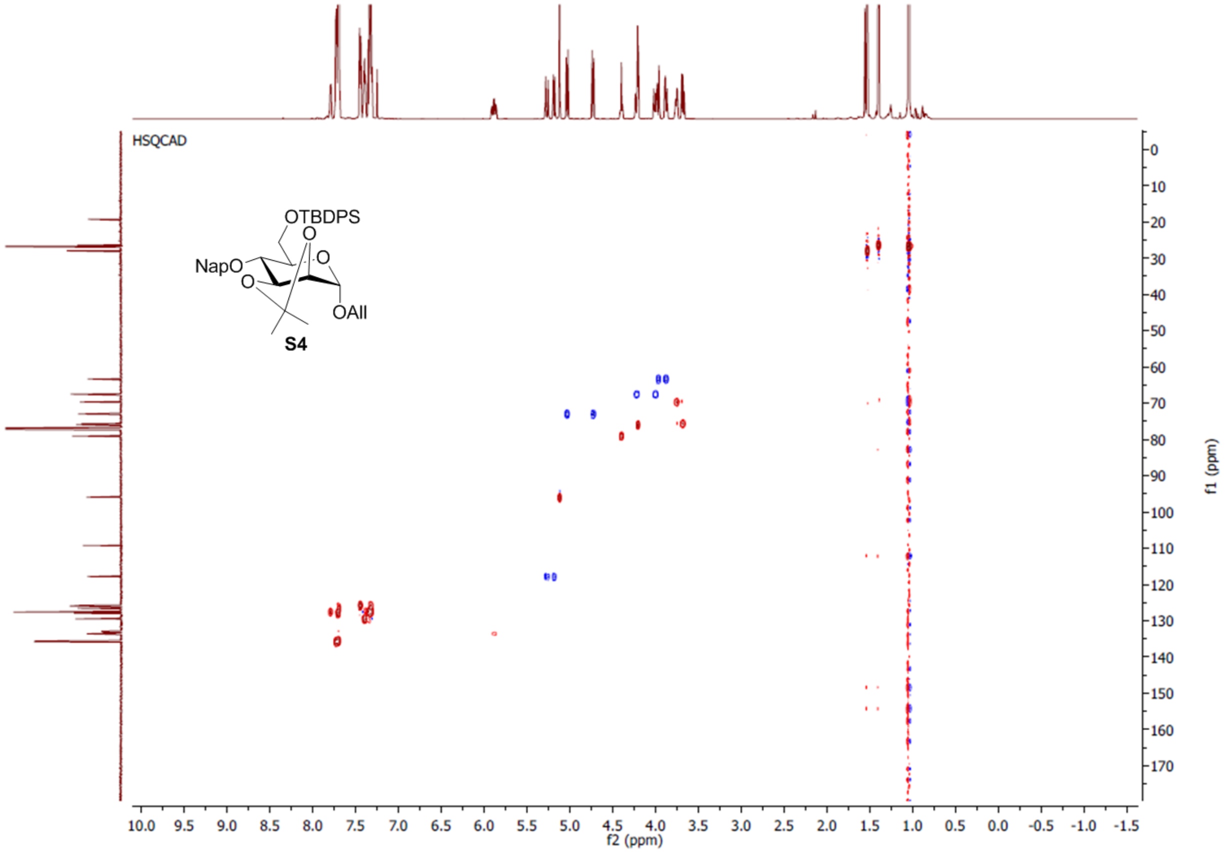
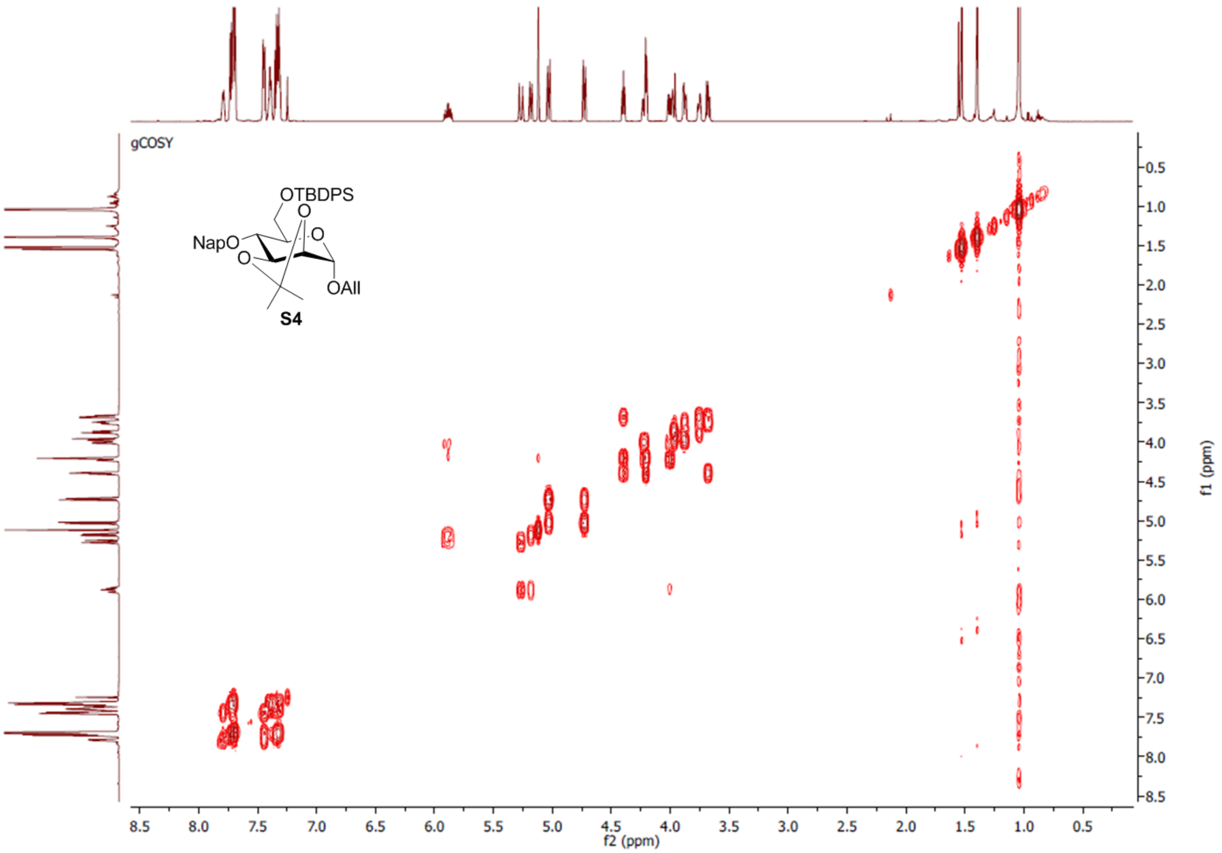
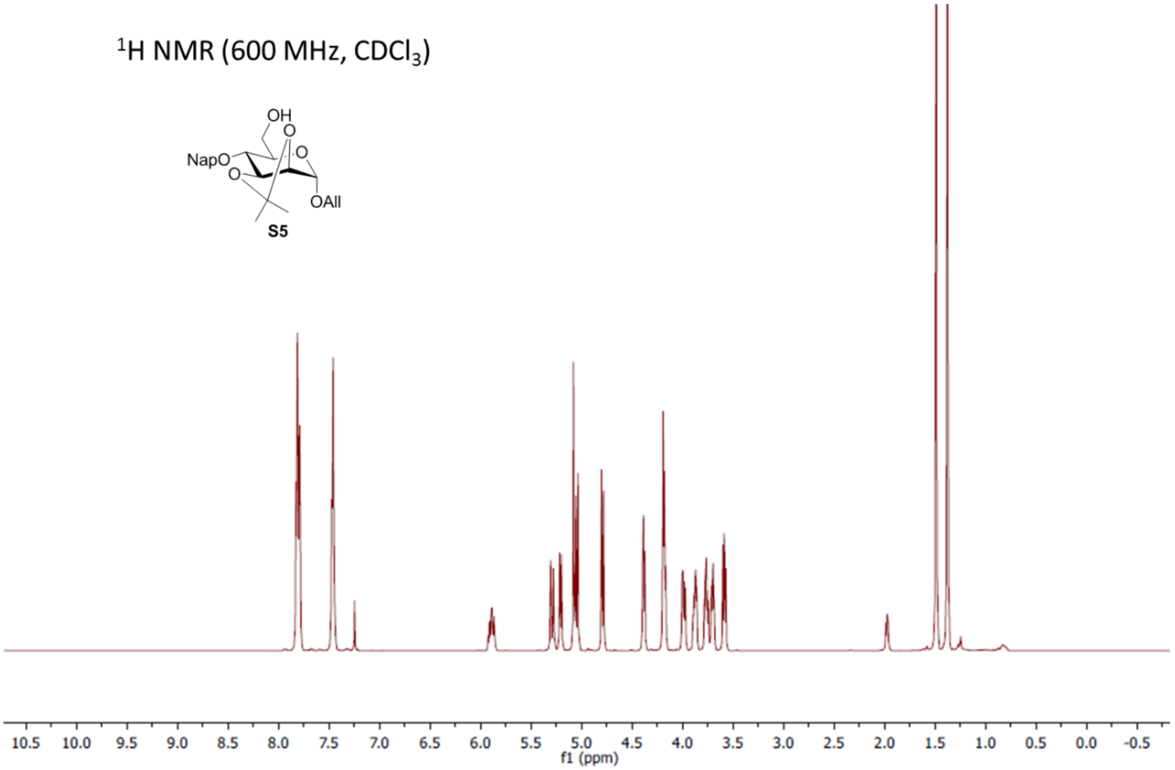






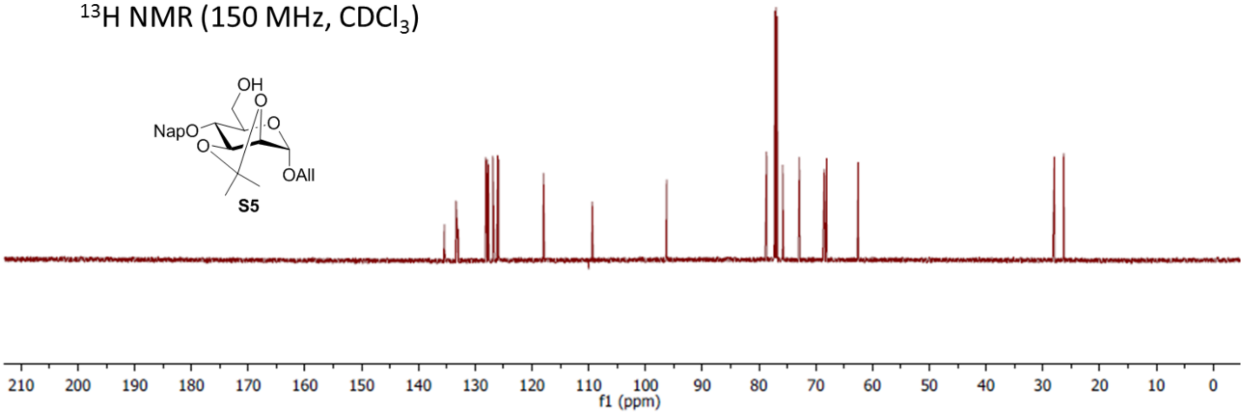
S4

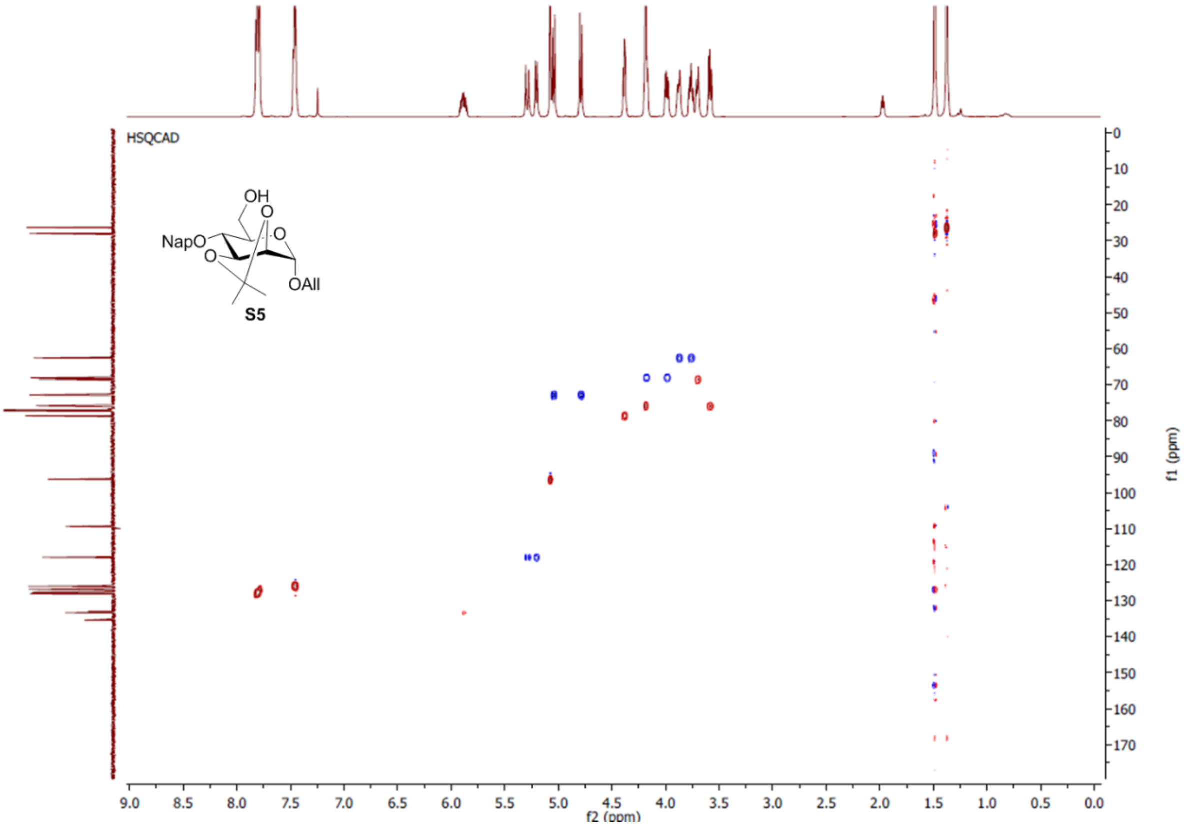
^{1}H NMR (600 MHz, CDCl$_3$)

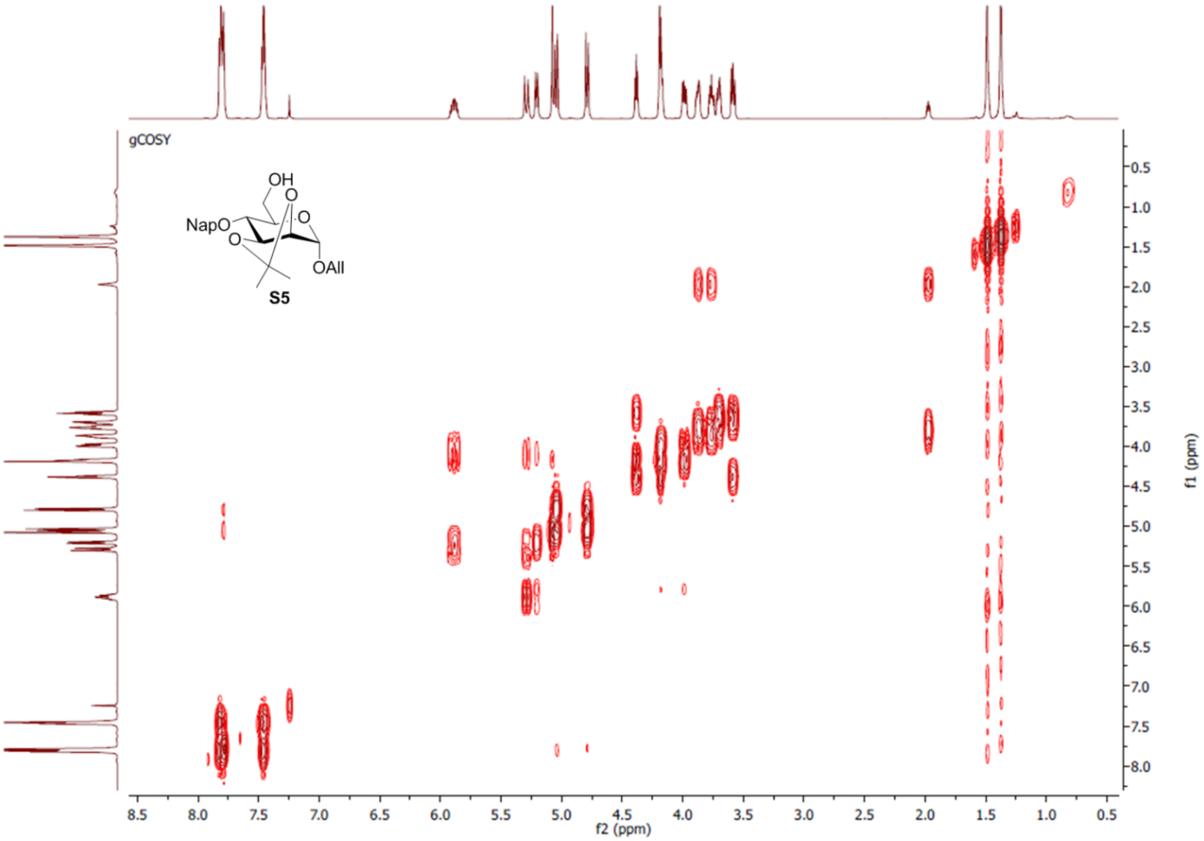


S5

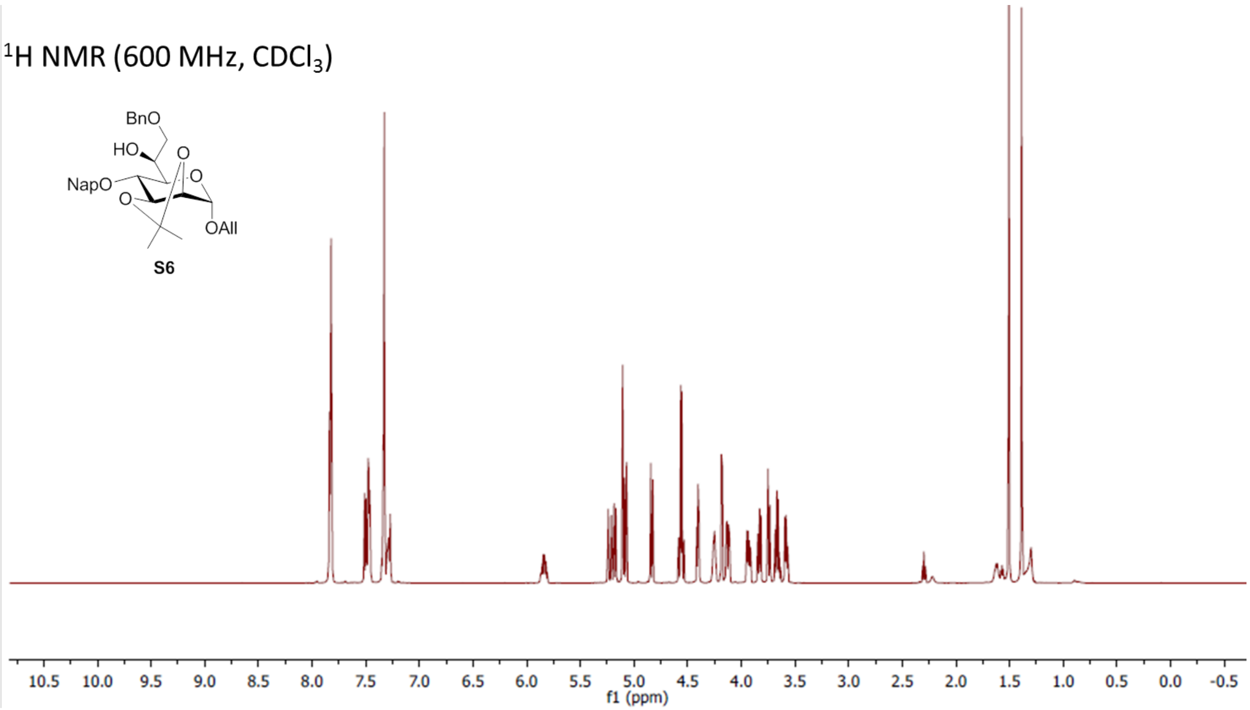
^{13}H NMR (150 MHz, CDCl$_3$)



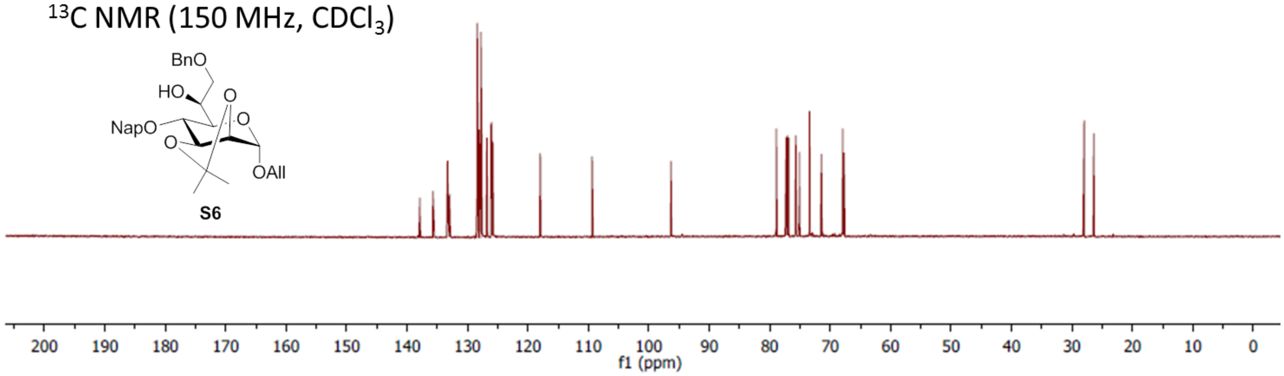


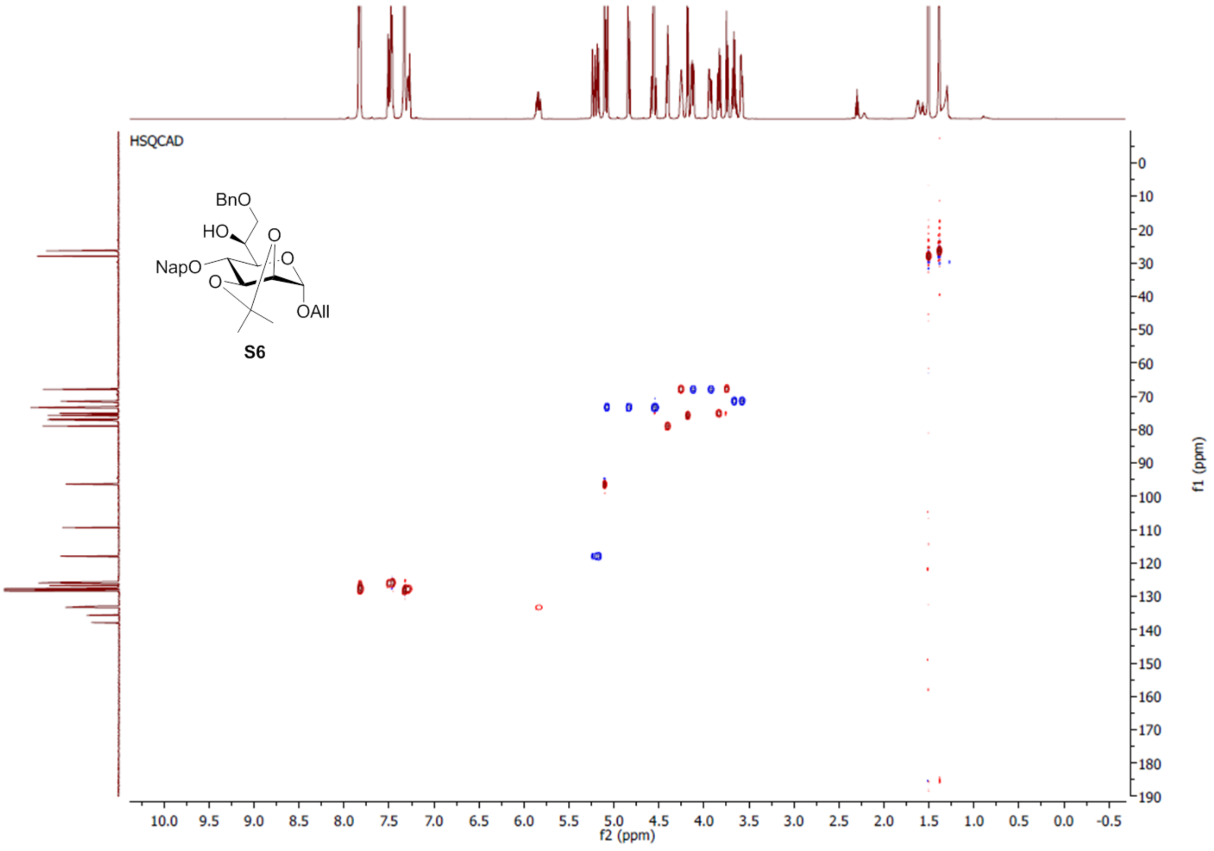


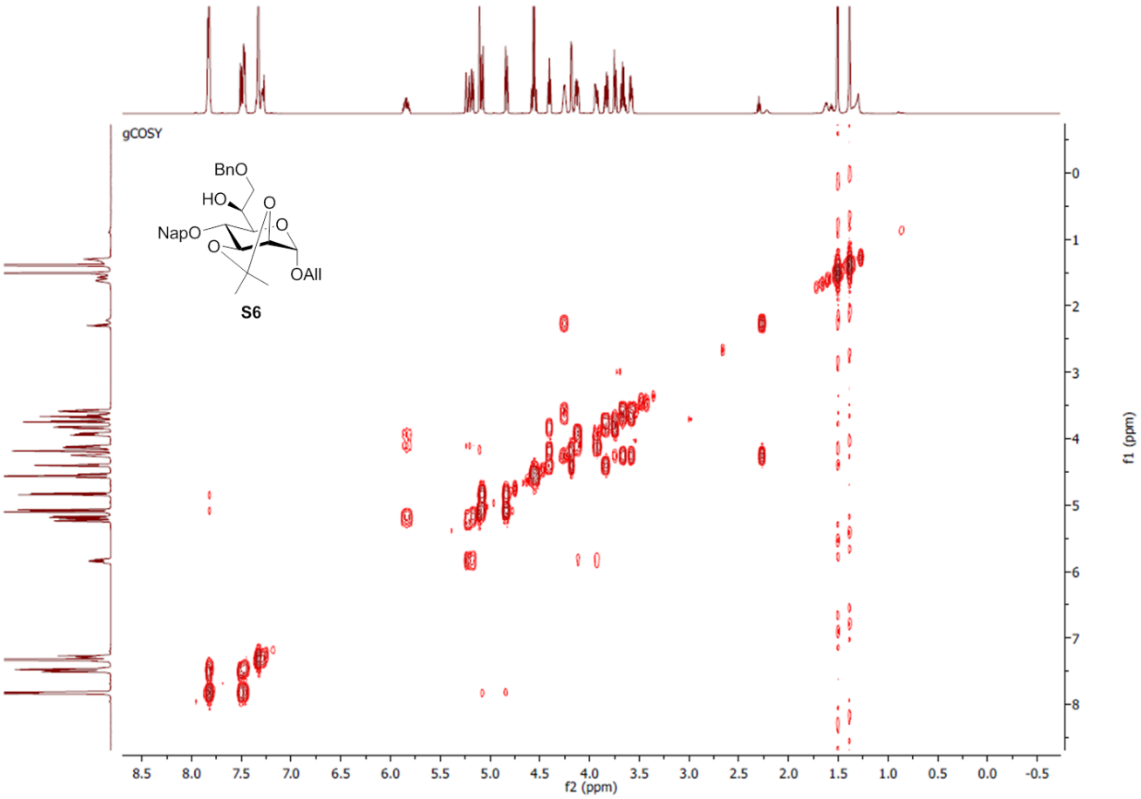
^{1}H NMR (600 MHz, $CDCl_3$)



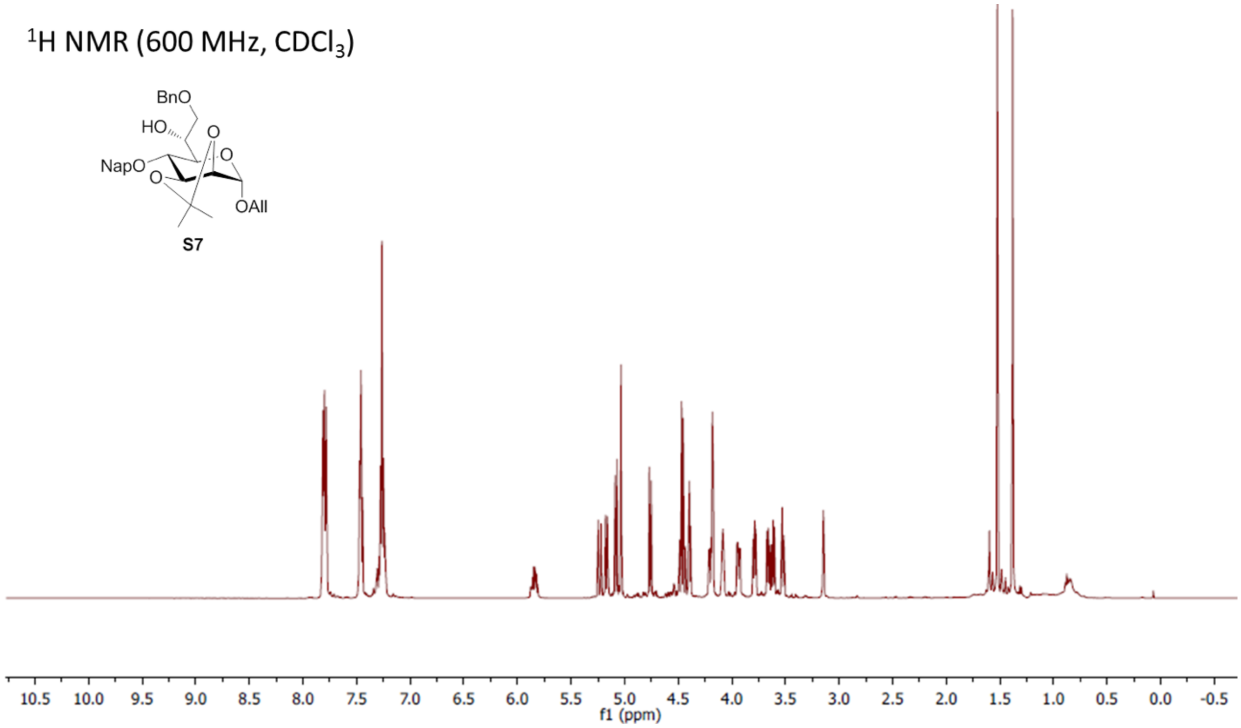
^{13}C NMR (150 MHz, CDCl$_3$)



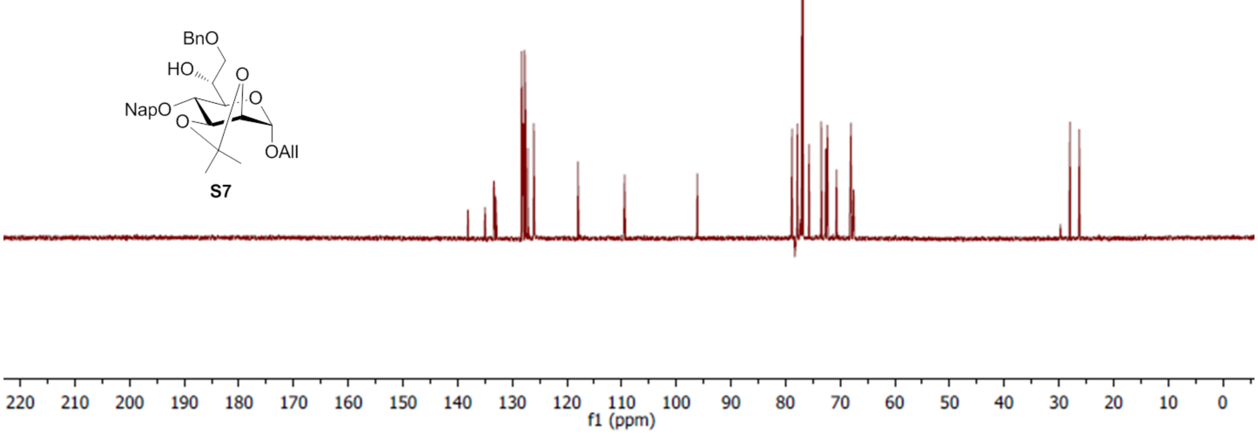


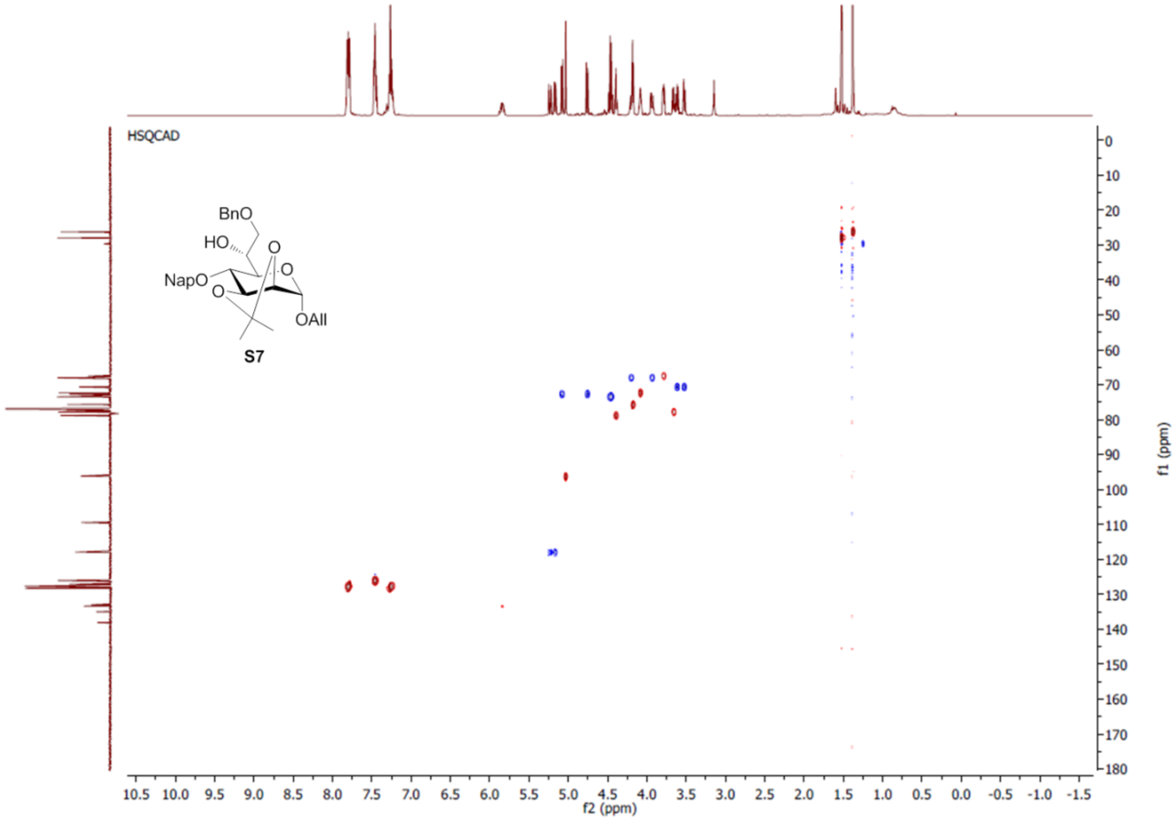


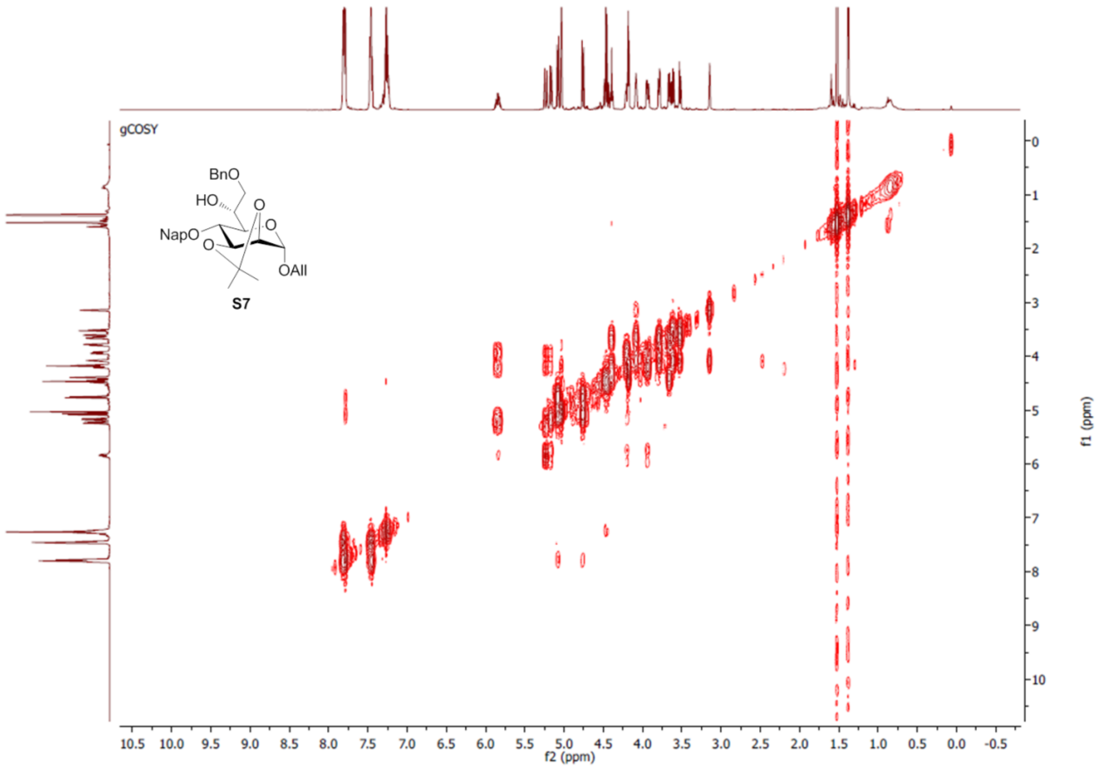
^{1}H NMR (600 MHz, CDCl$_3$)

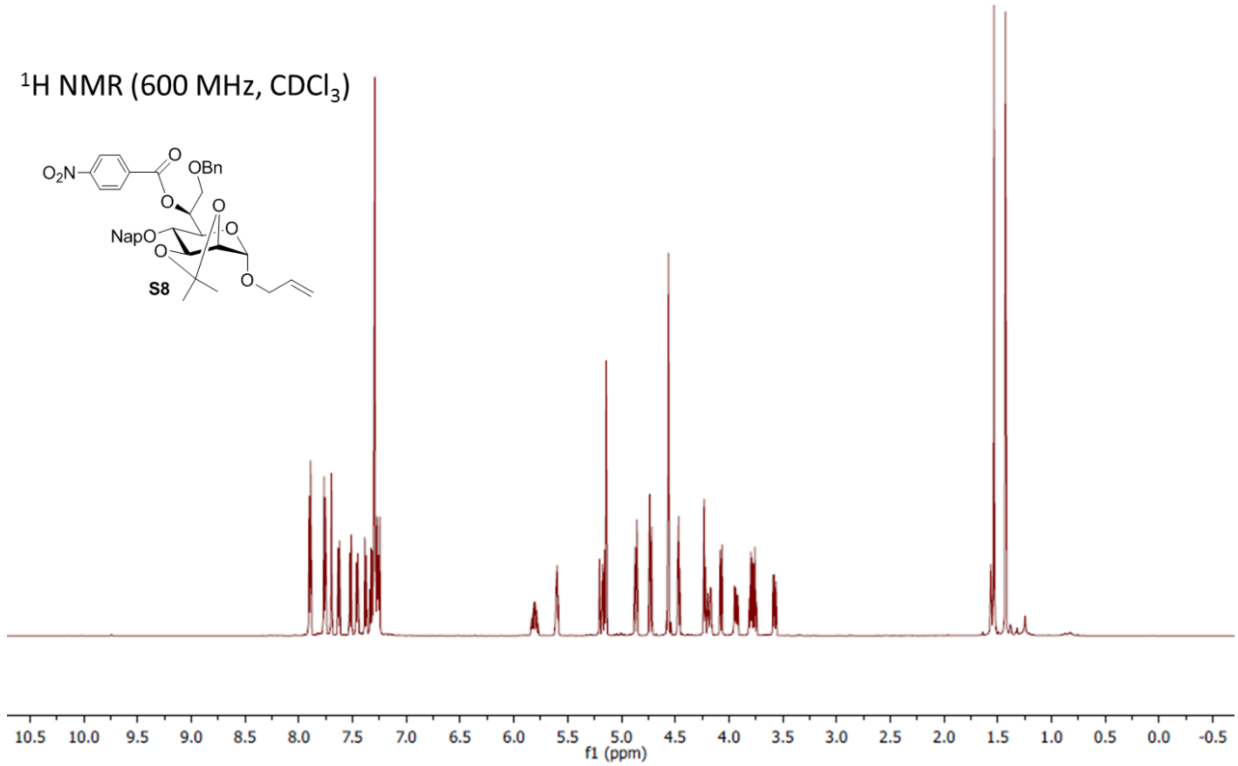


^{13}C NMR (150 MHz, CDCl$_3$)

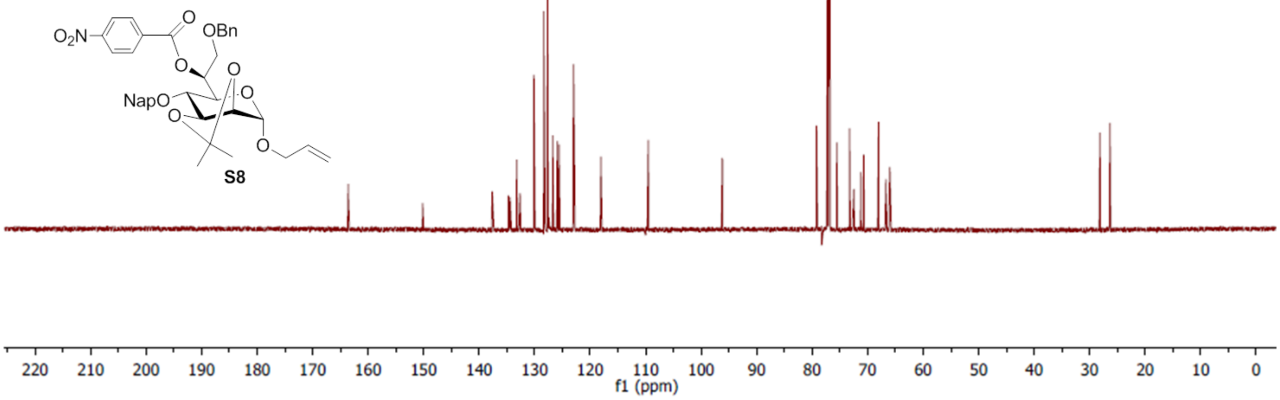


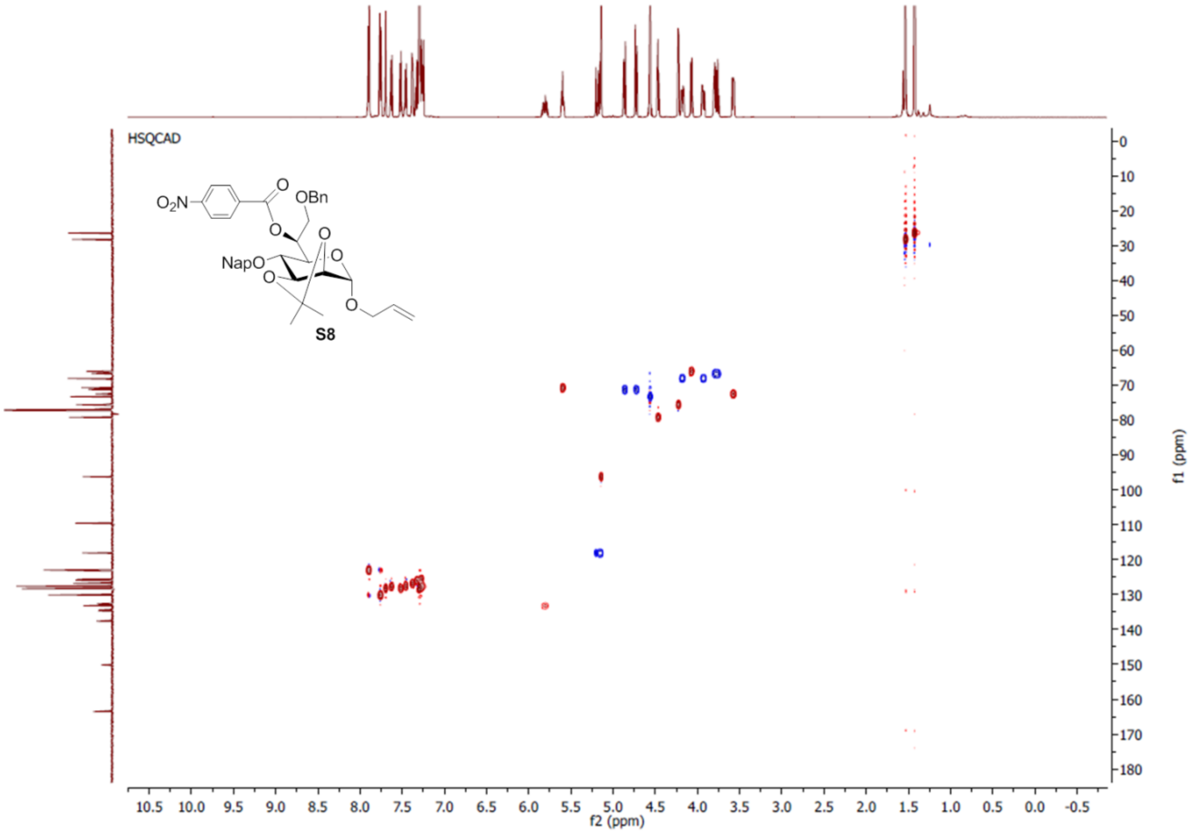


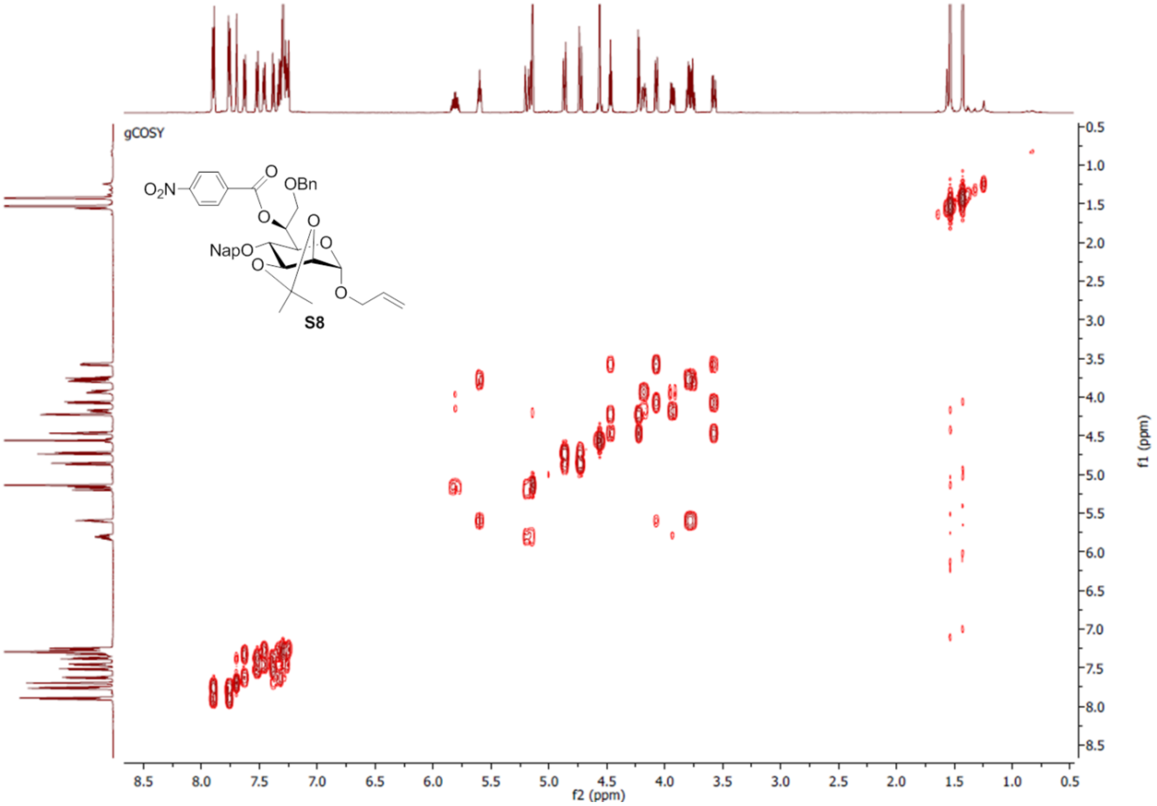

gCOSY
BnO
HO
NapO
O
O
O
OAll
S7
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f2 (ppm)
0 1 2 3 4 5 6 7 8 9 10
f1 (ppm)


^{1}H NMR (600 MHz, CDCl$_3$)
O$_2$N
O
OBn
O
O
NapO
O
O
O
S8
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

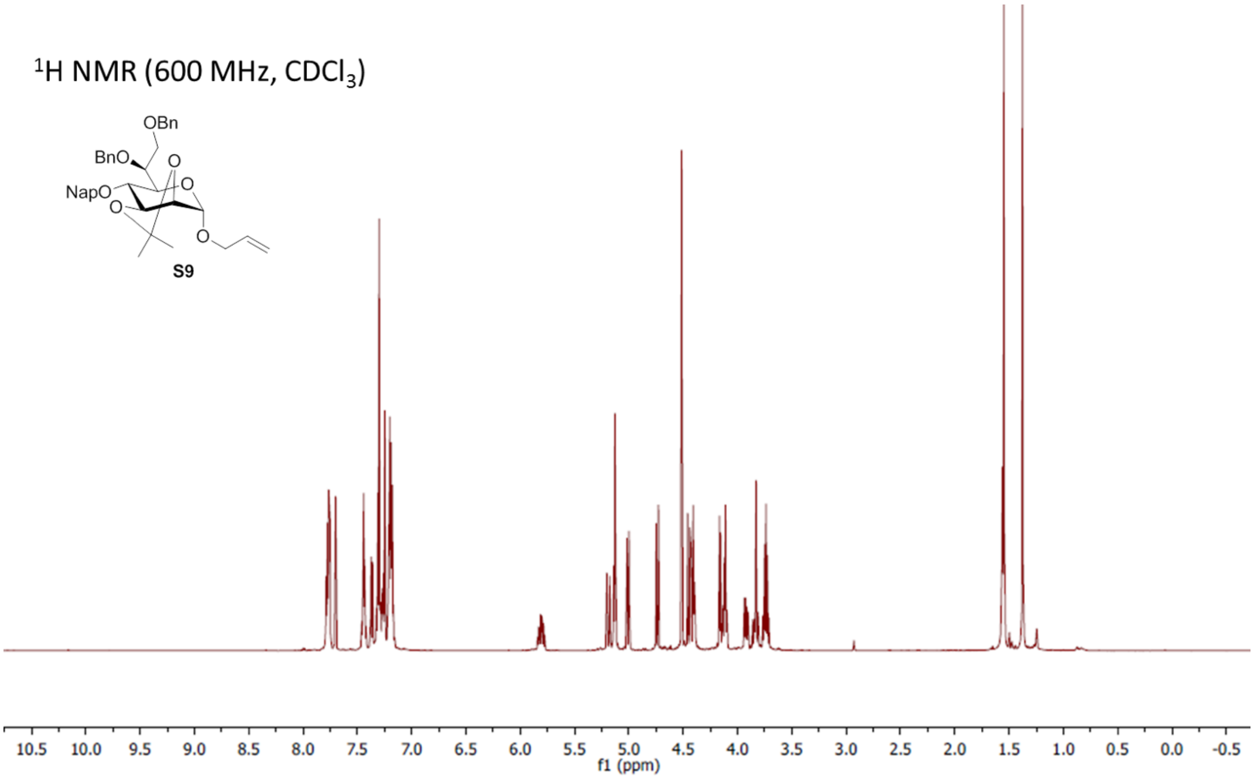
^{13}C NMR (150 MHz, CDCl$_3$)







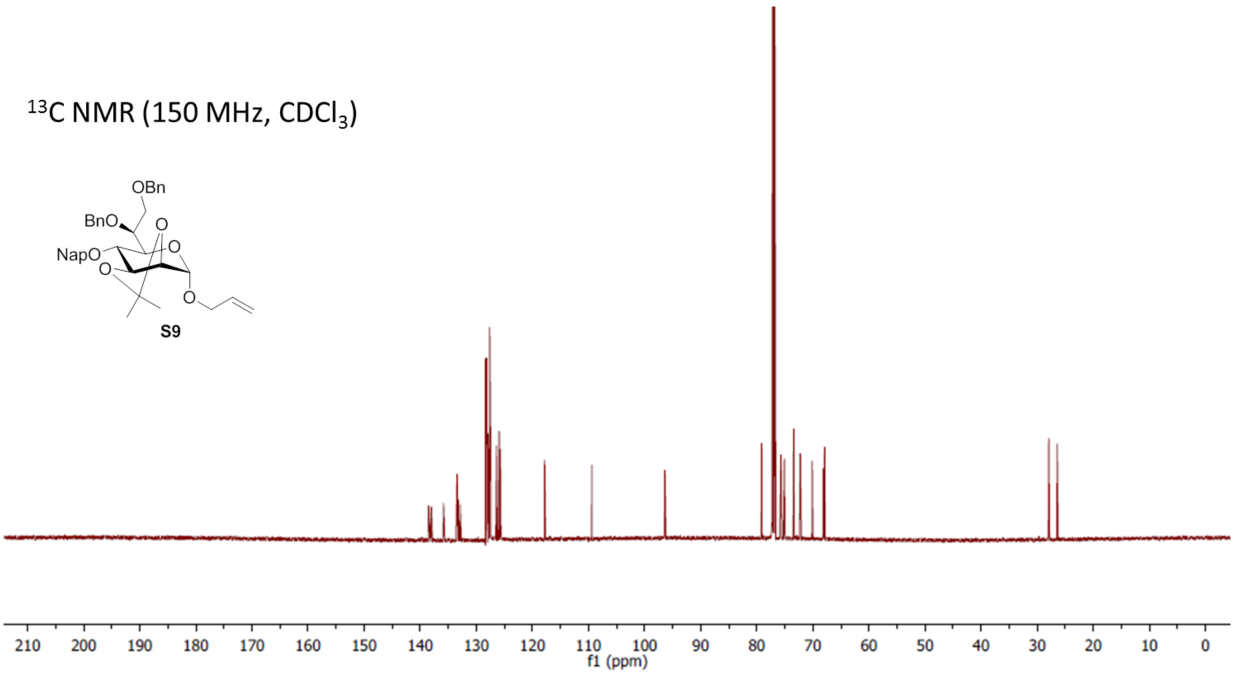
S8

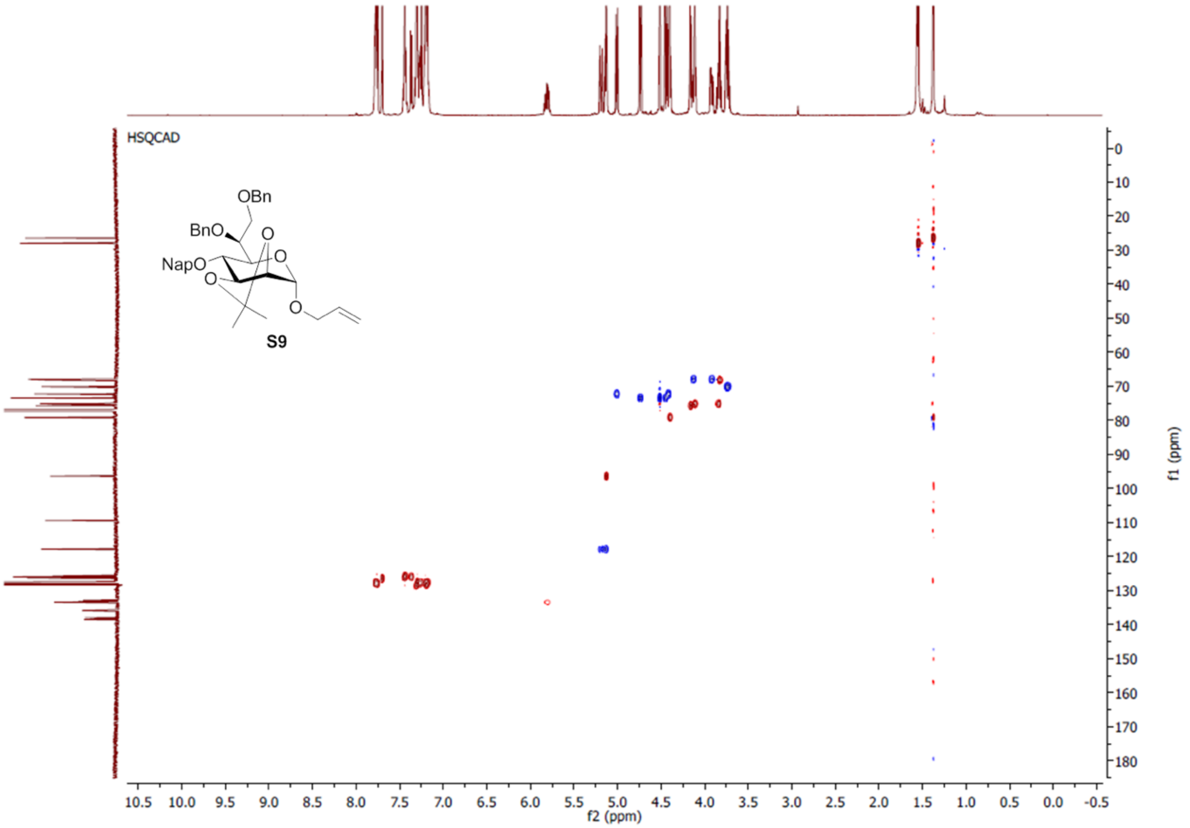


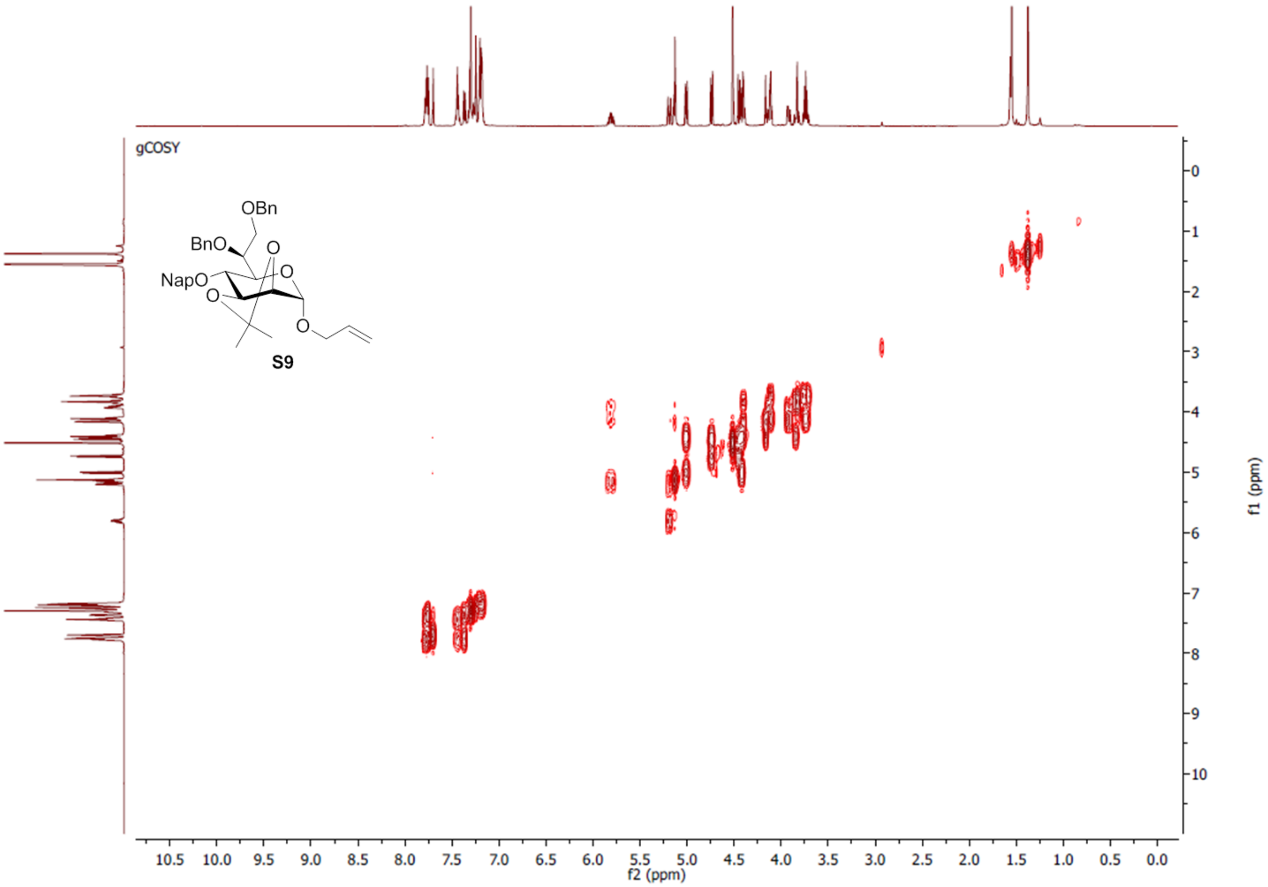
^{1}H NMR (600 MHz, $CDCl_3$)

S9

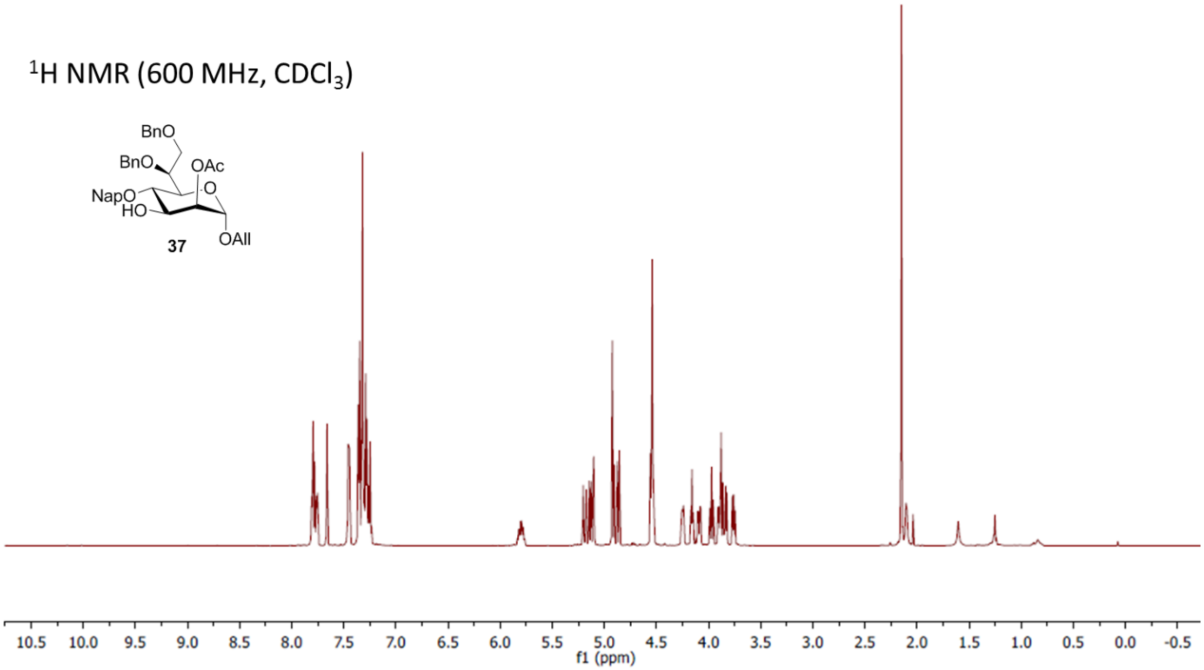
^{13}C NMR (150 MHz, CDCl$_3$)



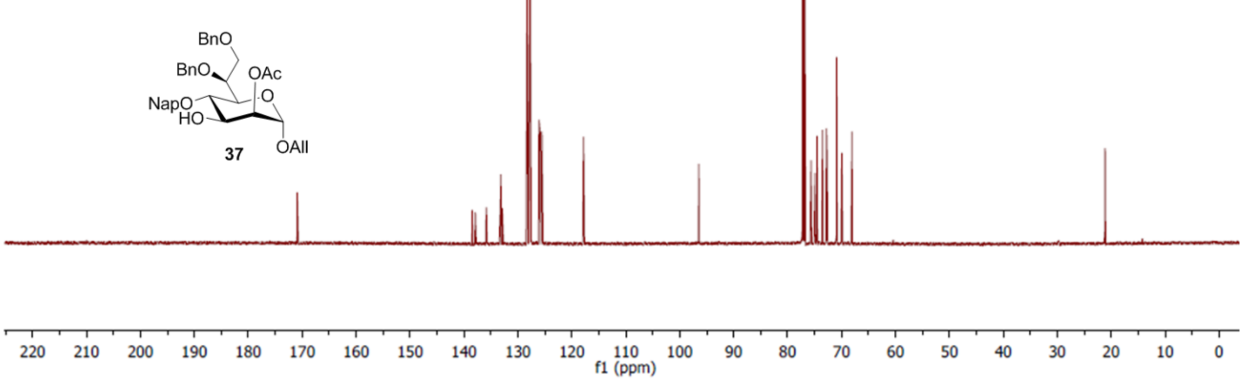


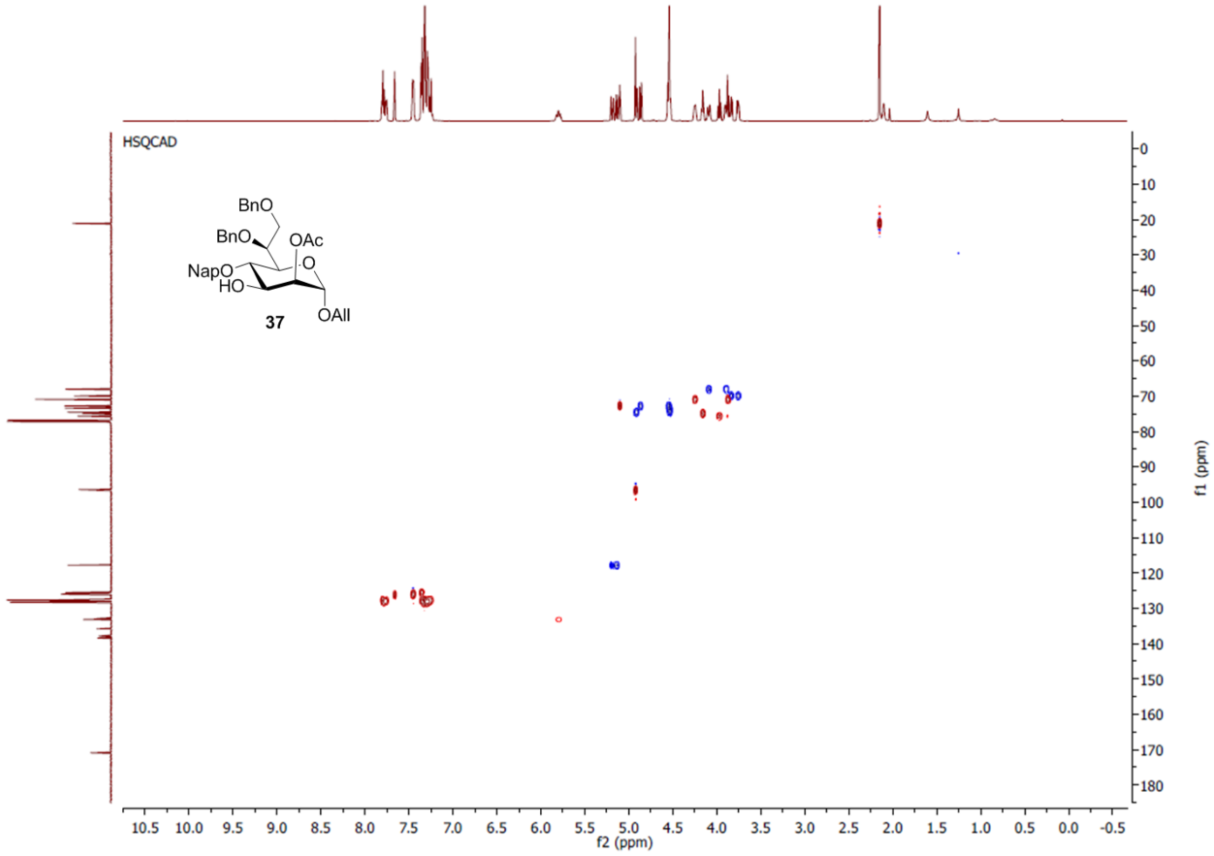


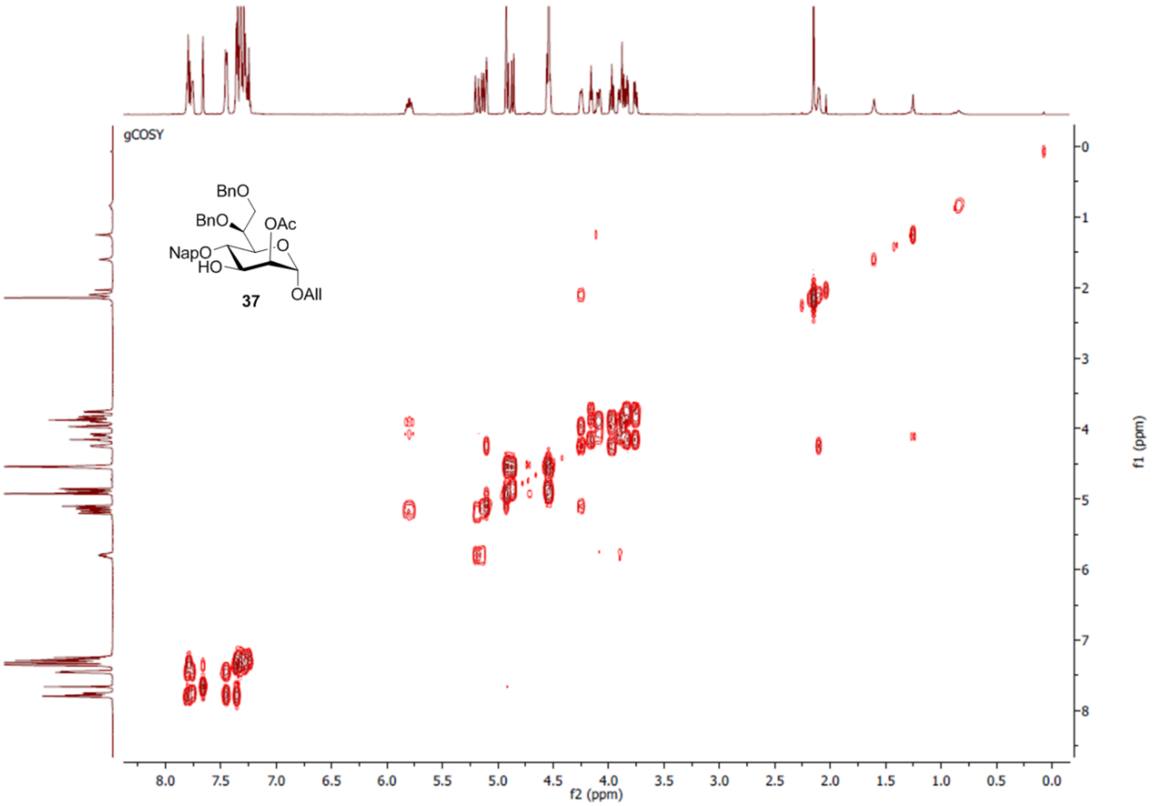
^{1}H NMR (600 MHz, CDCl$_3$)

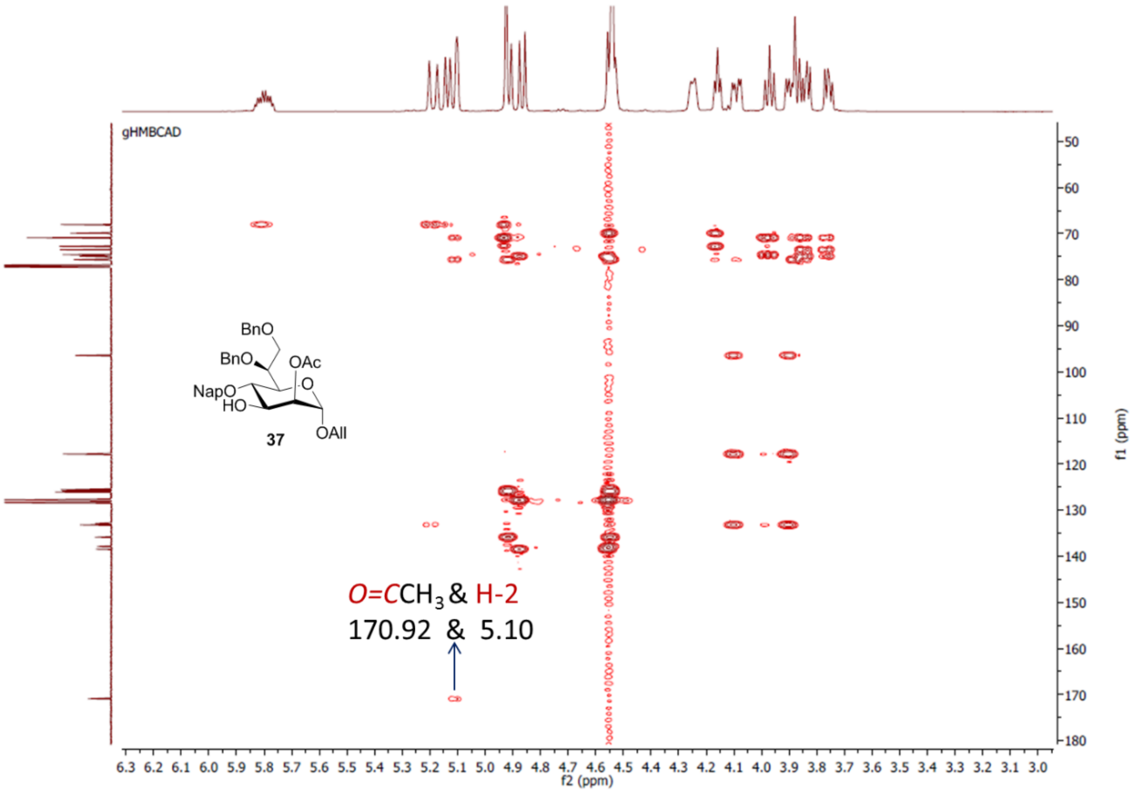


^{13}C NMR (150 MHz, CDCl$_3$)



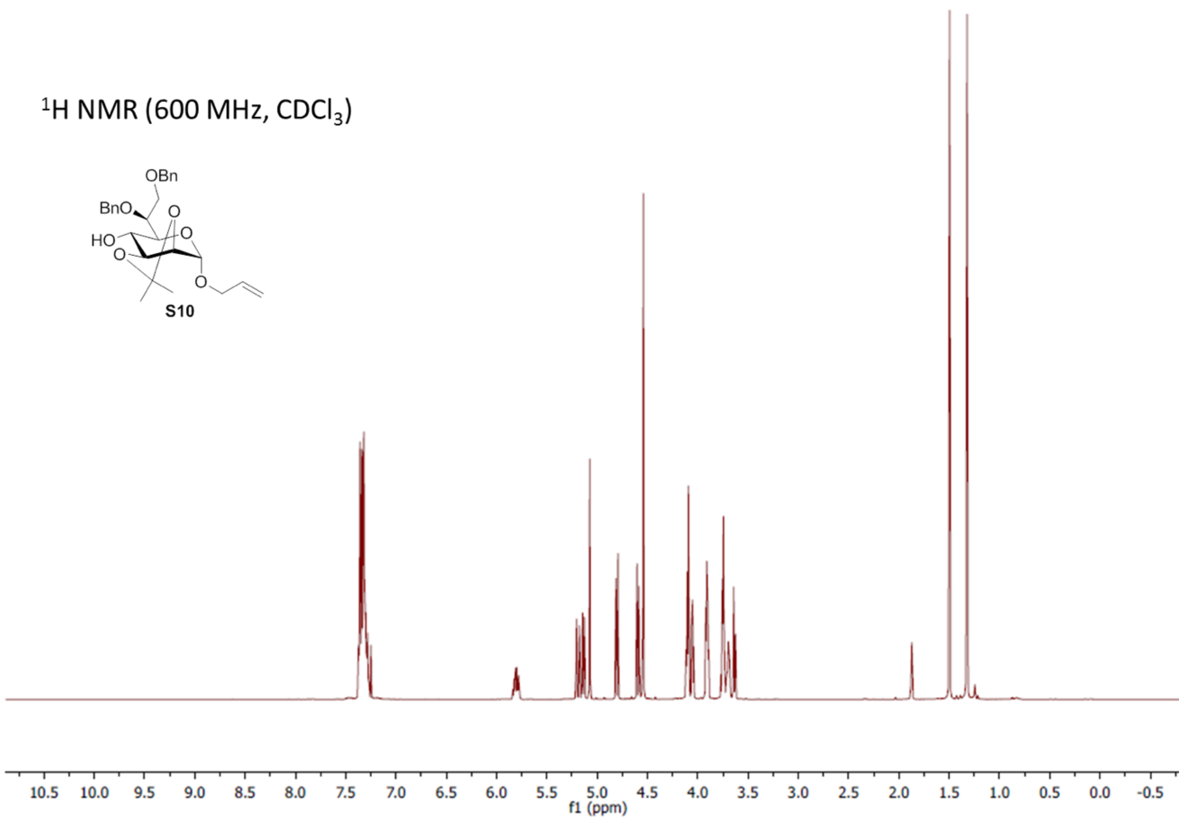






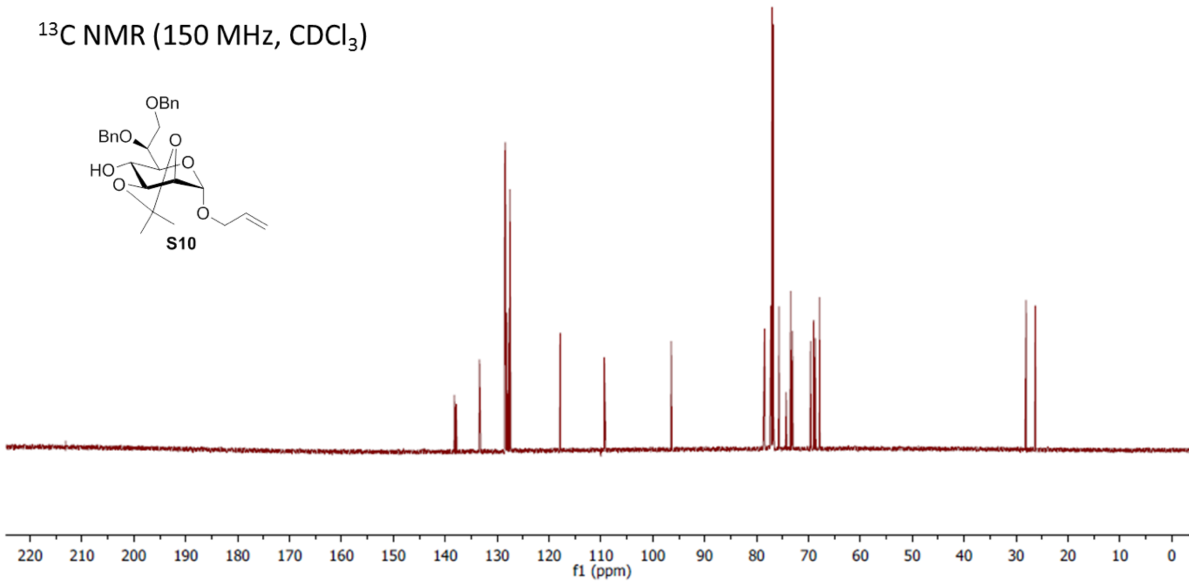
O=CCH_3 & H-2
170.92 & 5.10

^{1}H NMR (600 MHz, CDCl$_3$)

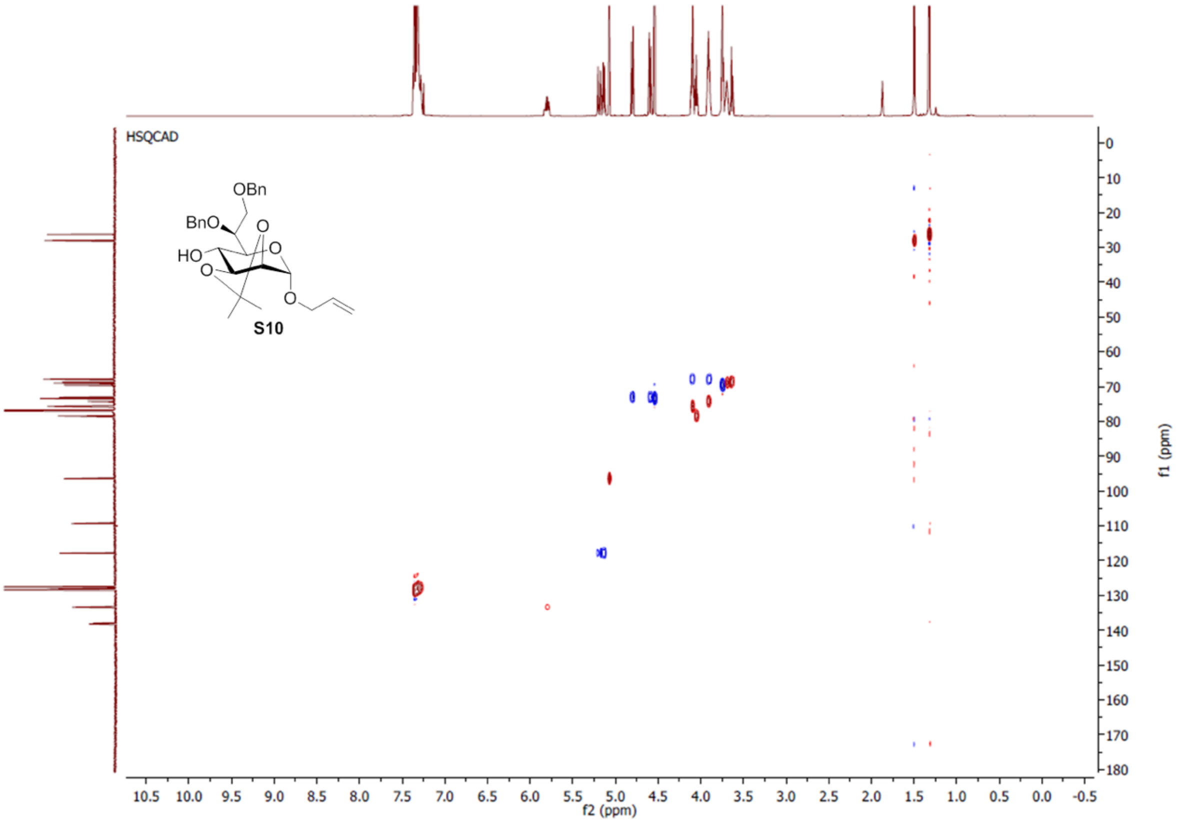


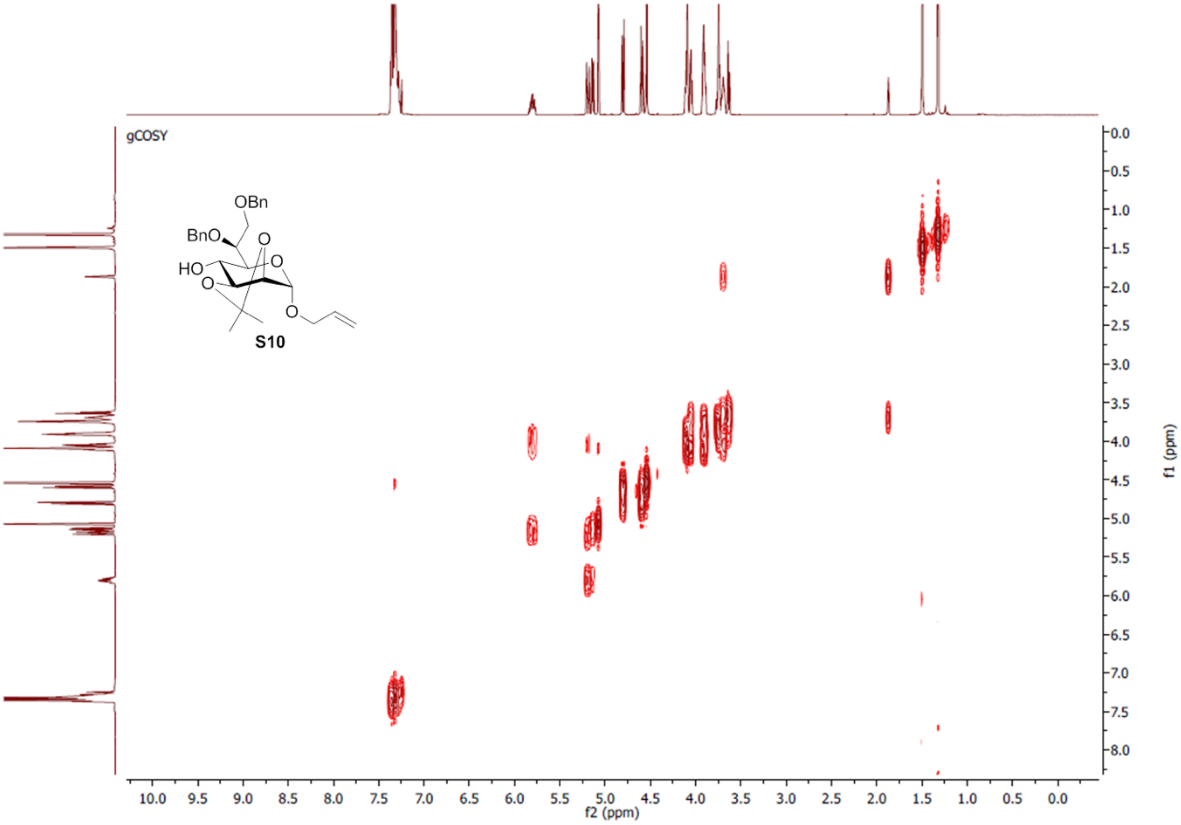
S10

^{13}C NMR (150 MHz, CDCl$_3$)

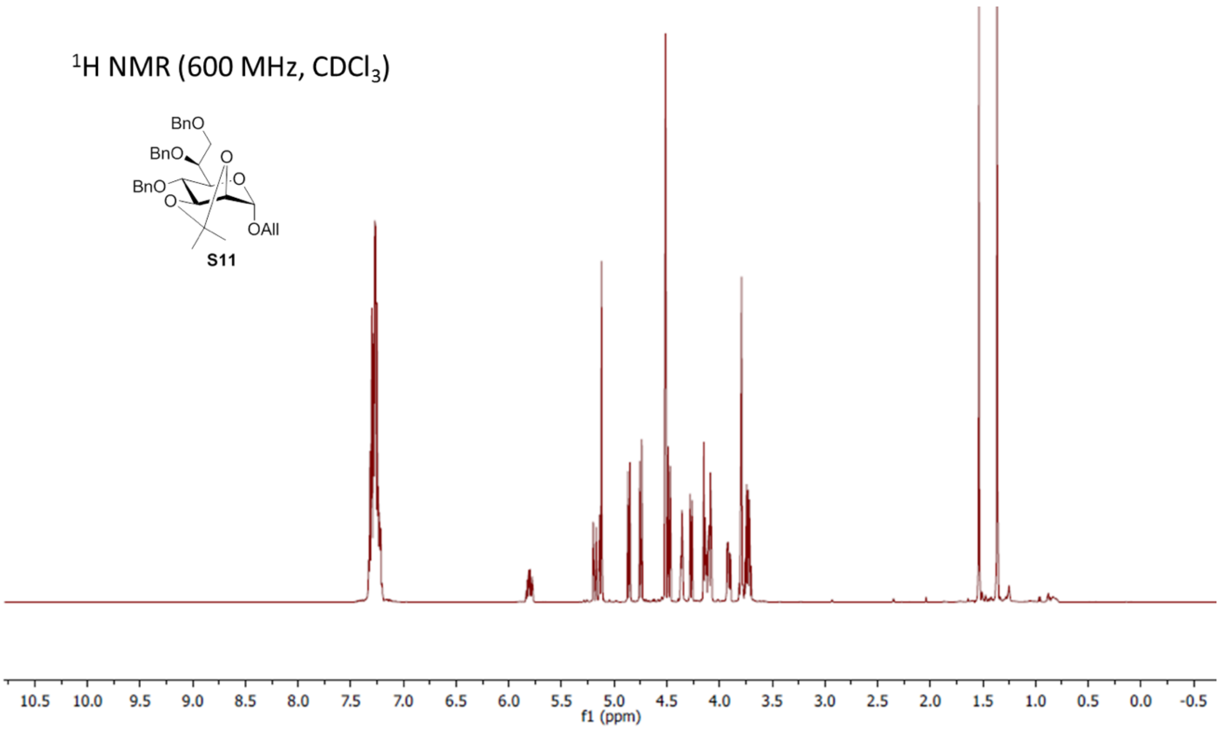


S10

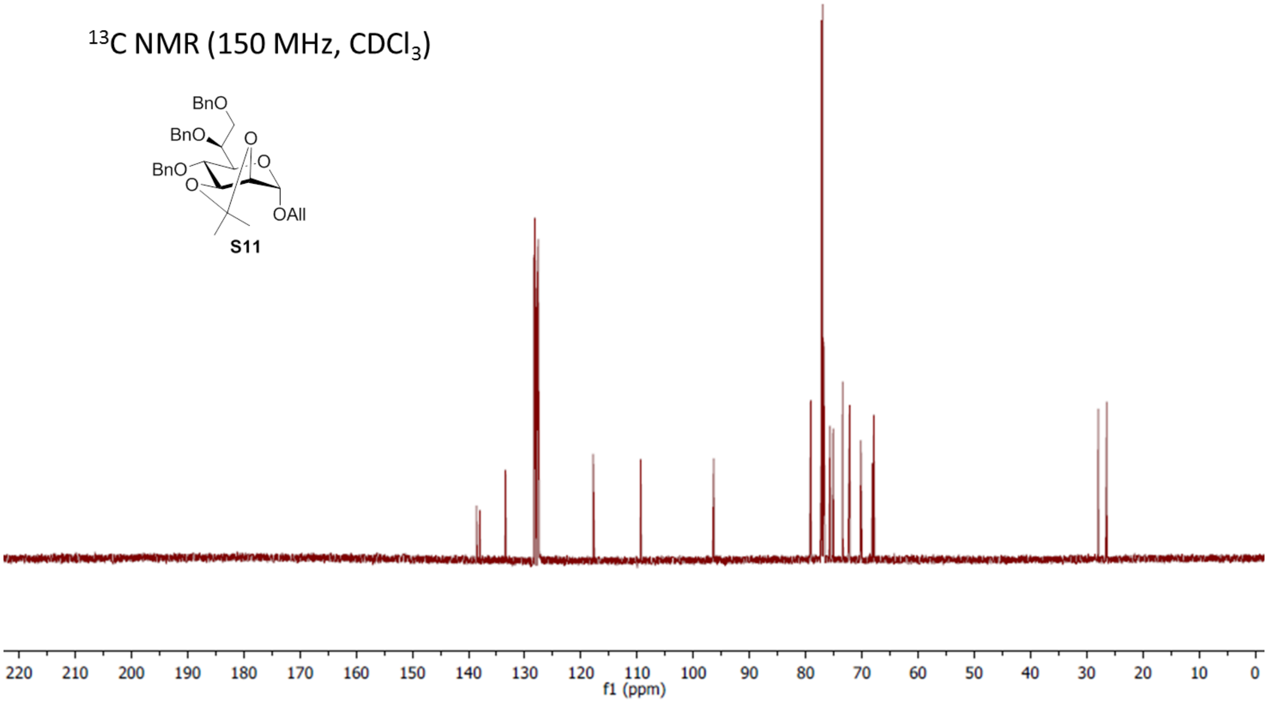

HSQCAD
OBn
BnO
O
HO
O
O
O
S10
f2 (ppm)
f1 (ppm)
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180

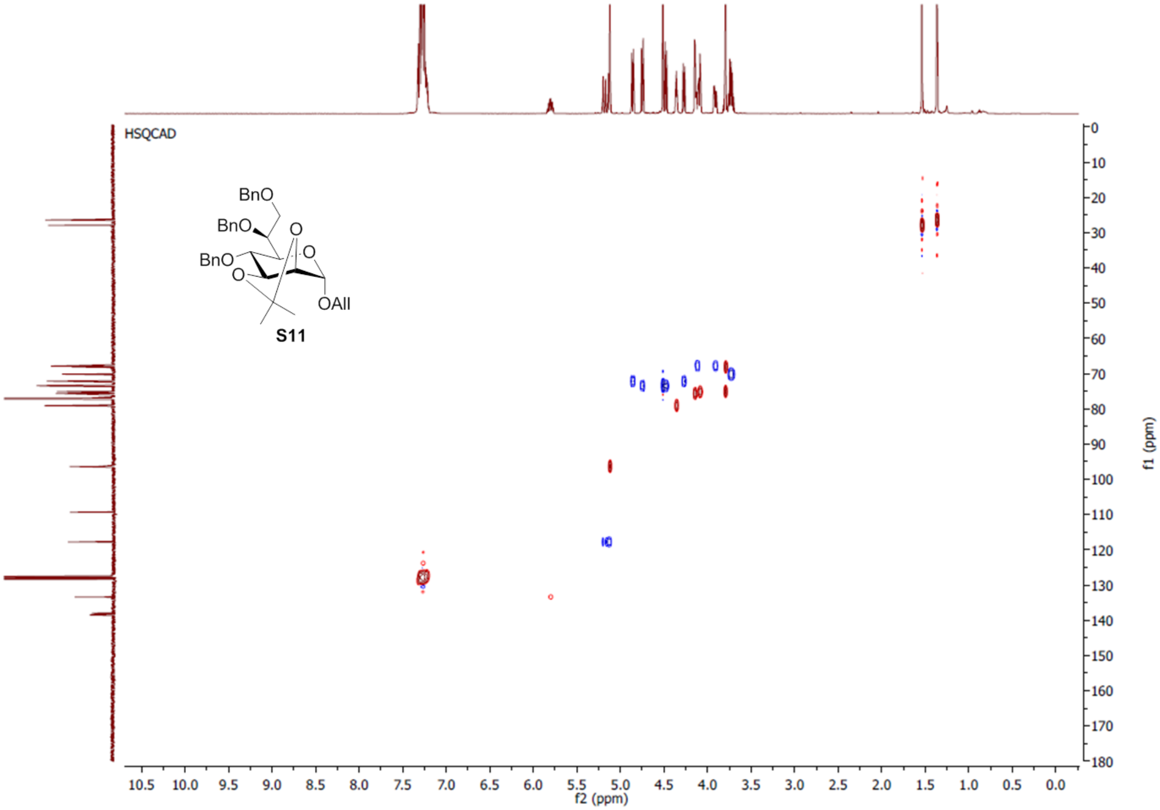

gCOSY
OBn
BnO
O
HO
O
O
O
S10
f2 (ppm)
f1 (ppm)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0

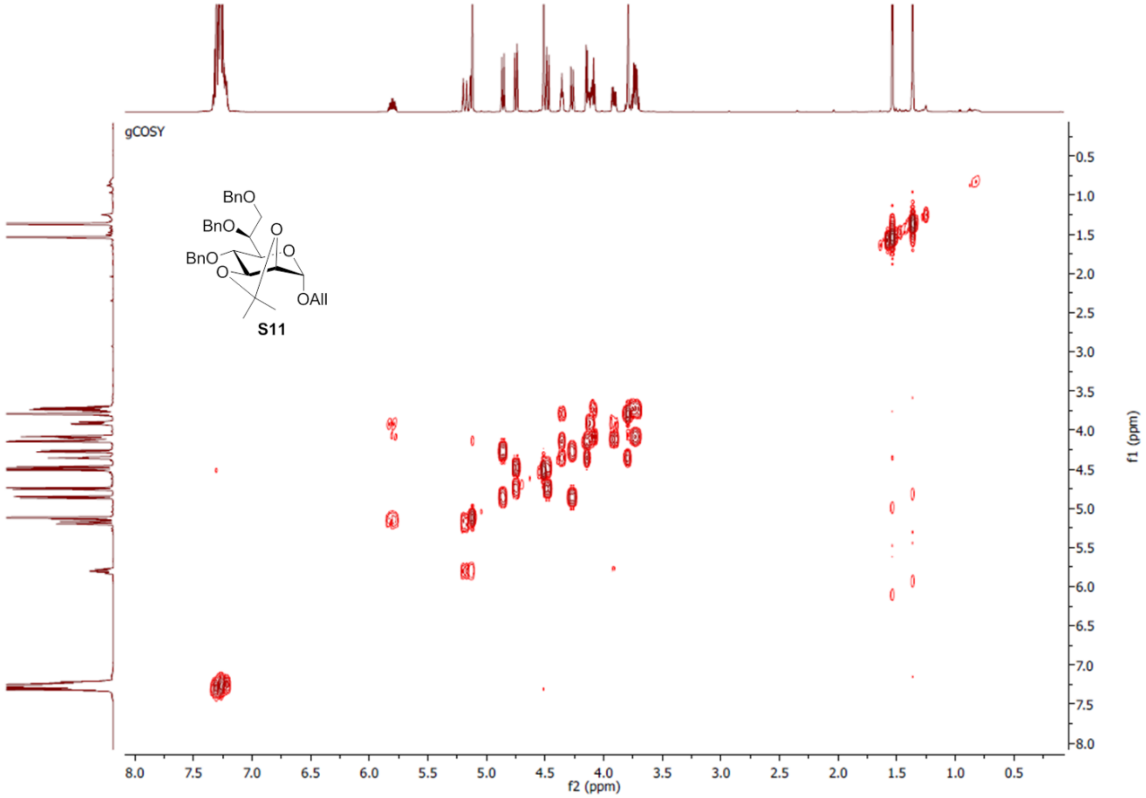
^{1}H NMR (600 MHz, CDCl$_3$)



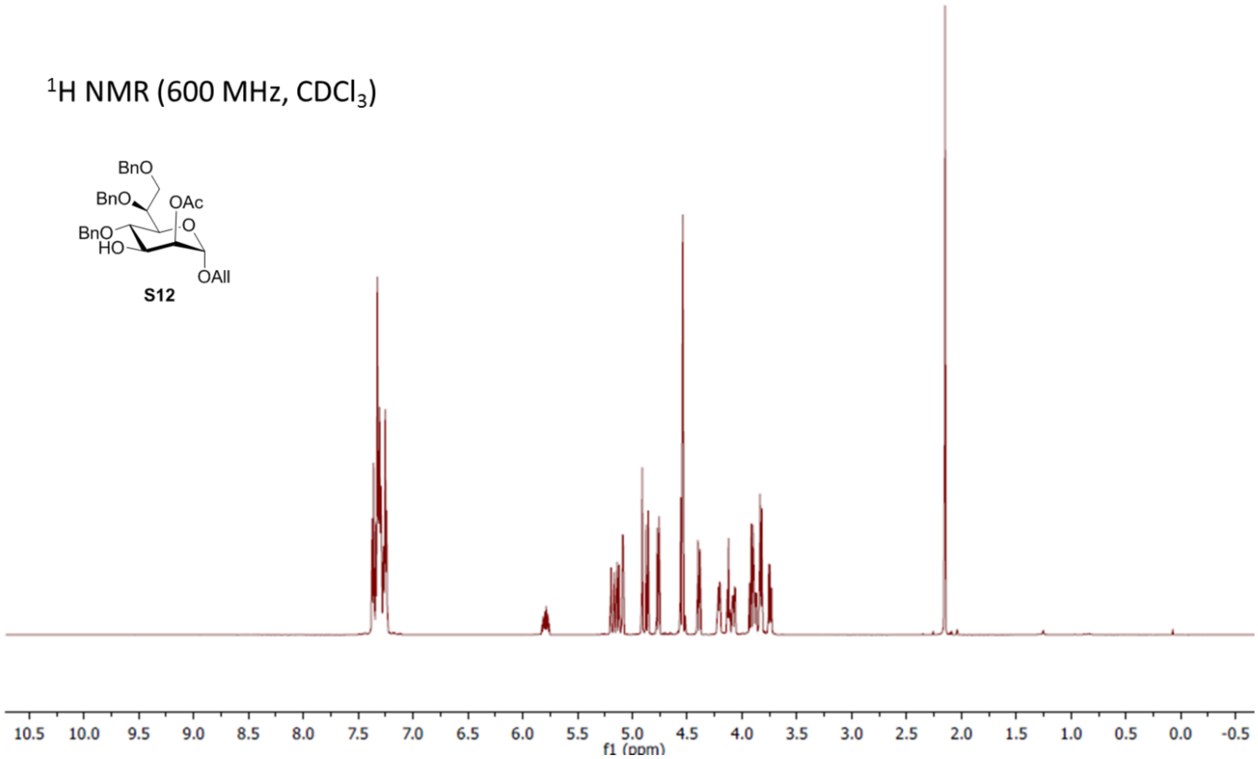
^{13}C NMR (150 MHz, CDCl$_3$)



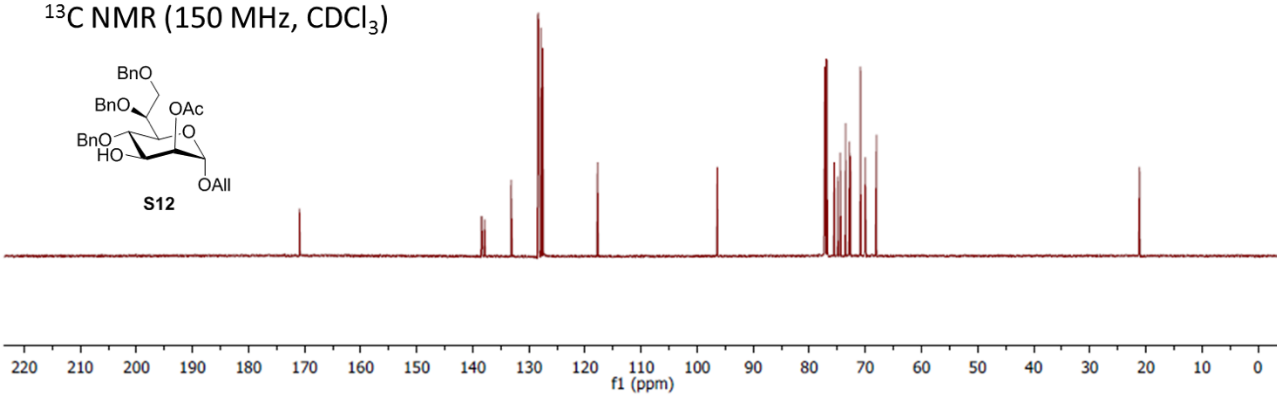

HSQCAD
BnO
BnO
BnO
O
O
O
OAll
S11
f2 (ppm)
f1 (ppm)
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180

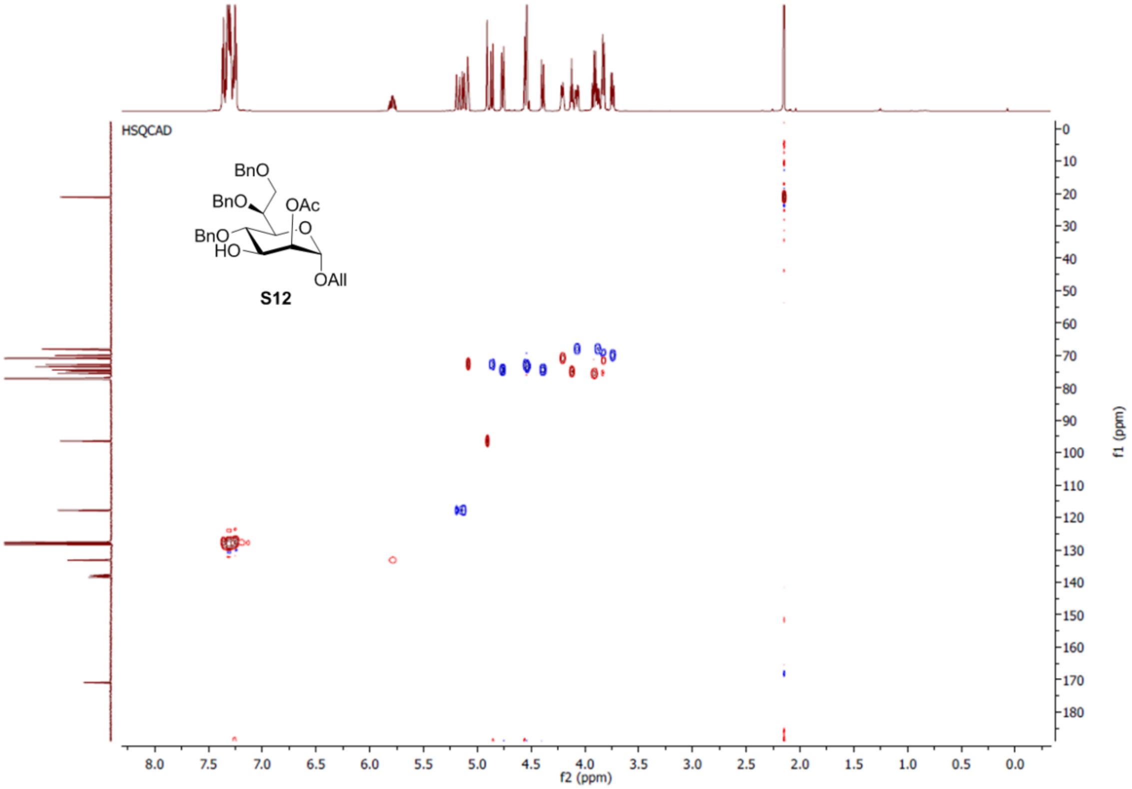

gCOSY
BnO
BnO
BnO
O
O
O
OAll
S11
f2 (ppm)
f1 (ppm)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0

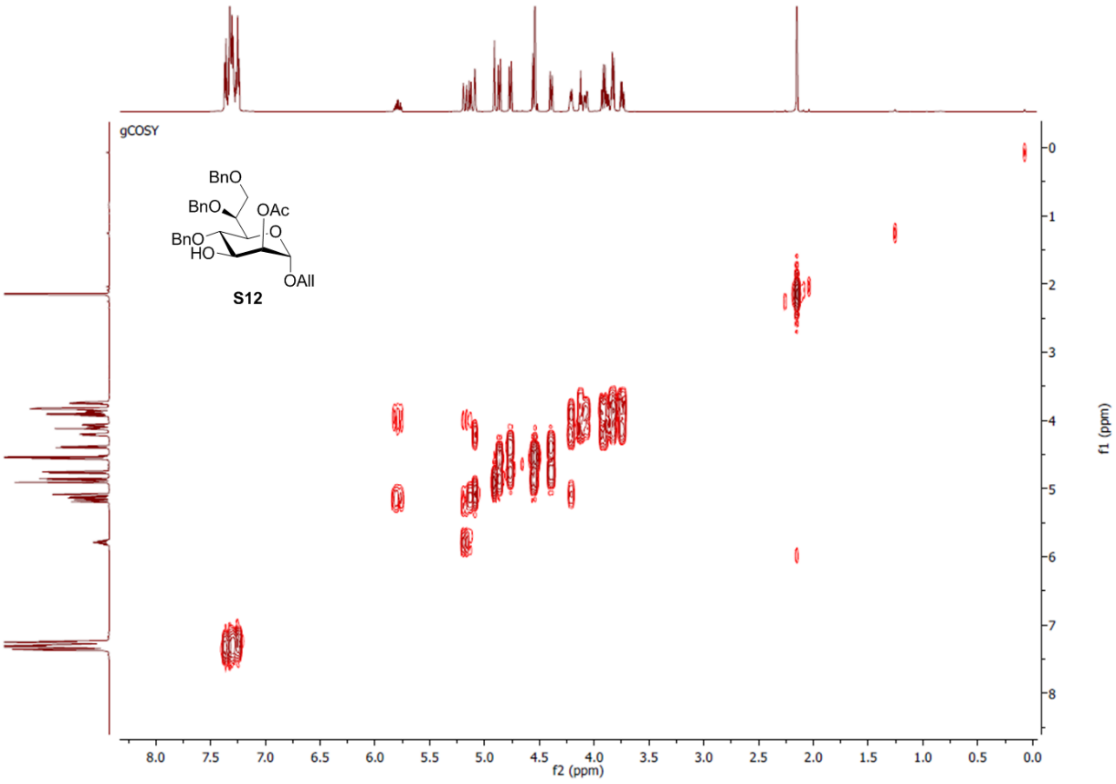
^{1}H NMR (600 MHz, CDCl$_3$)



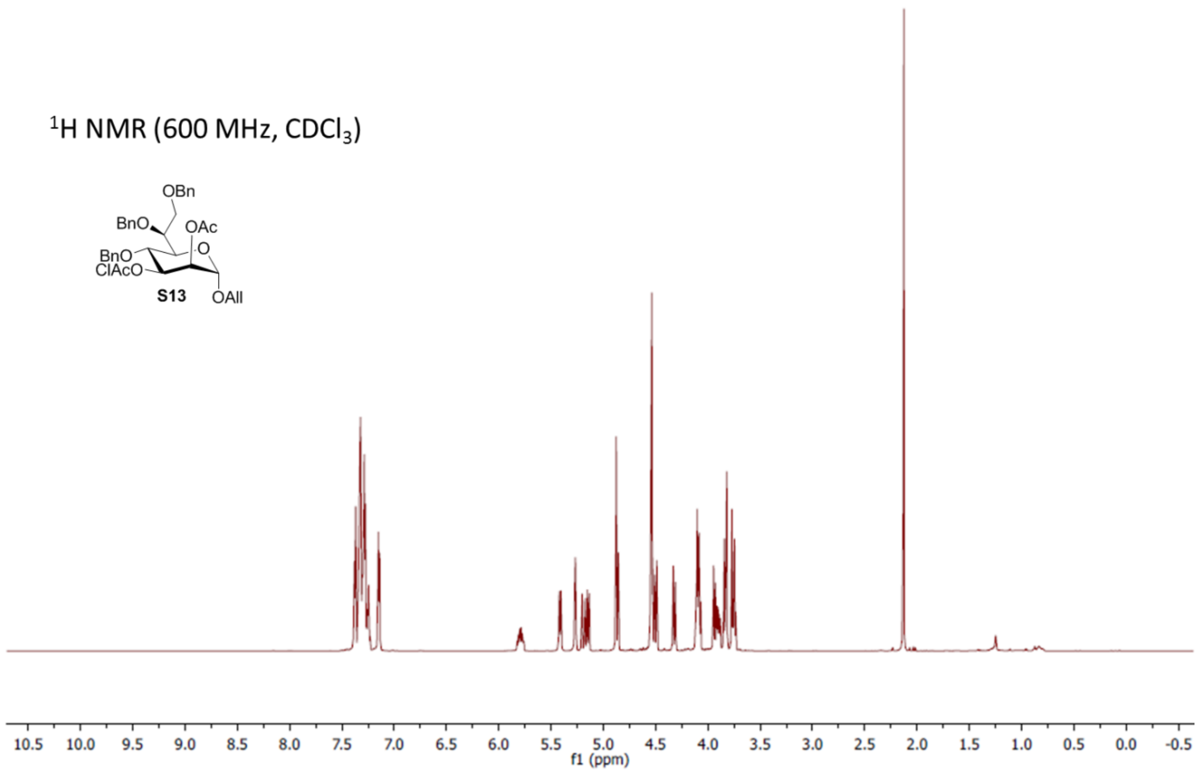
^{13}C NMR (150 MHz, CDCl$_3$)



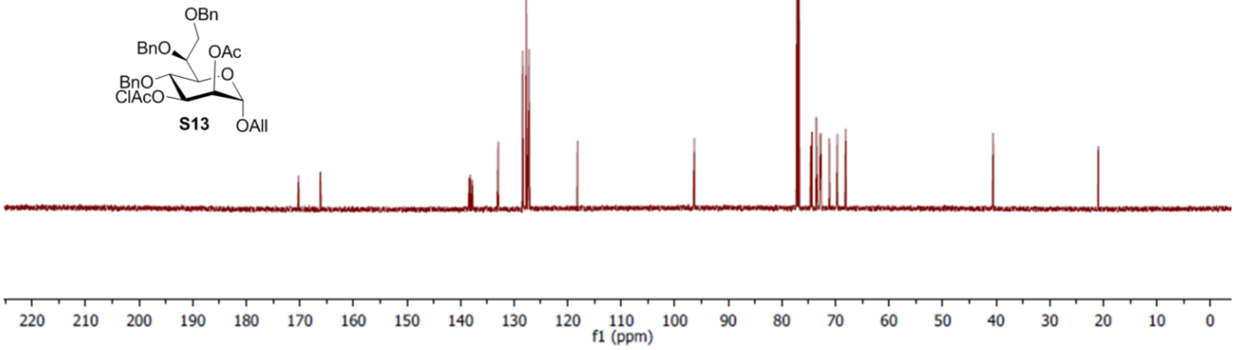

HSQCAD
BnO
BnO
OAc
O
BnO
HO
OAll
S12
f2 (ppm)
f1 (ppm)

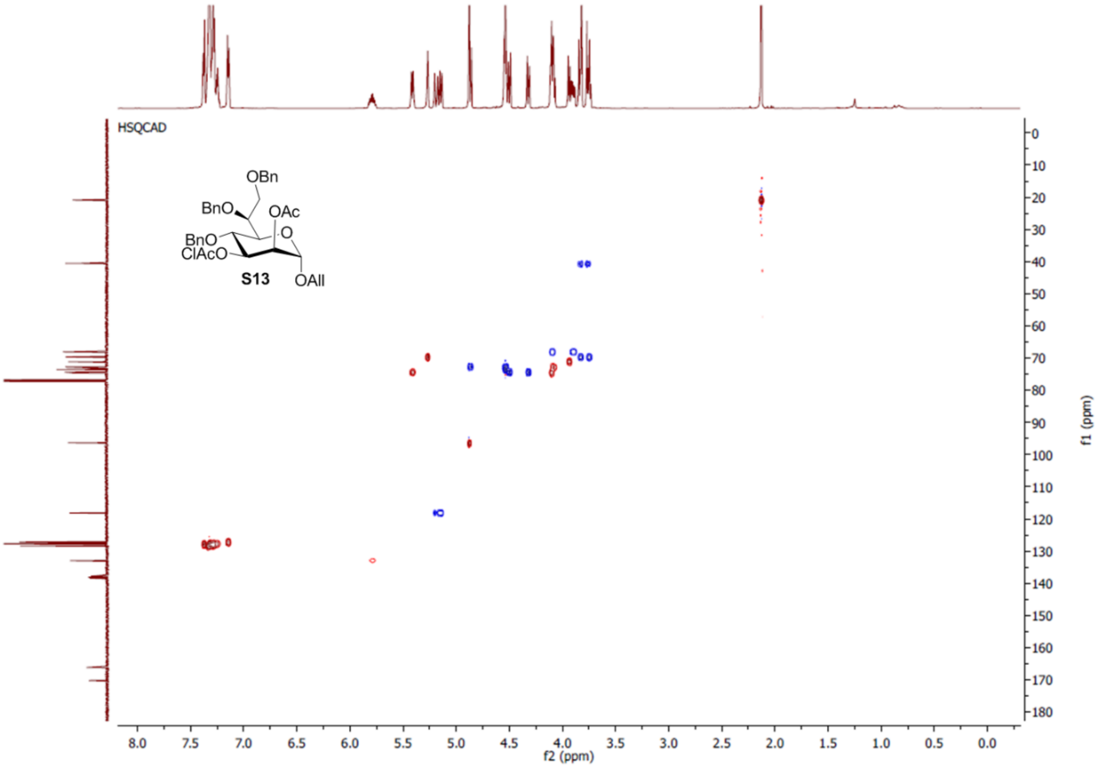

gCOSY
BnO
BnO
OAc
O
BnO
HO
OAll
S12
f2 (ppm)
f1 (ppm)

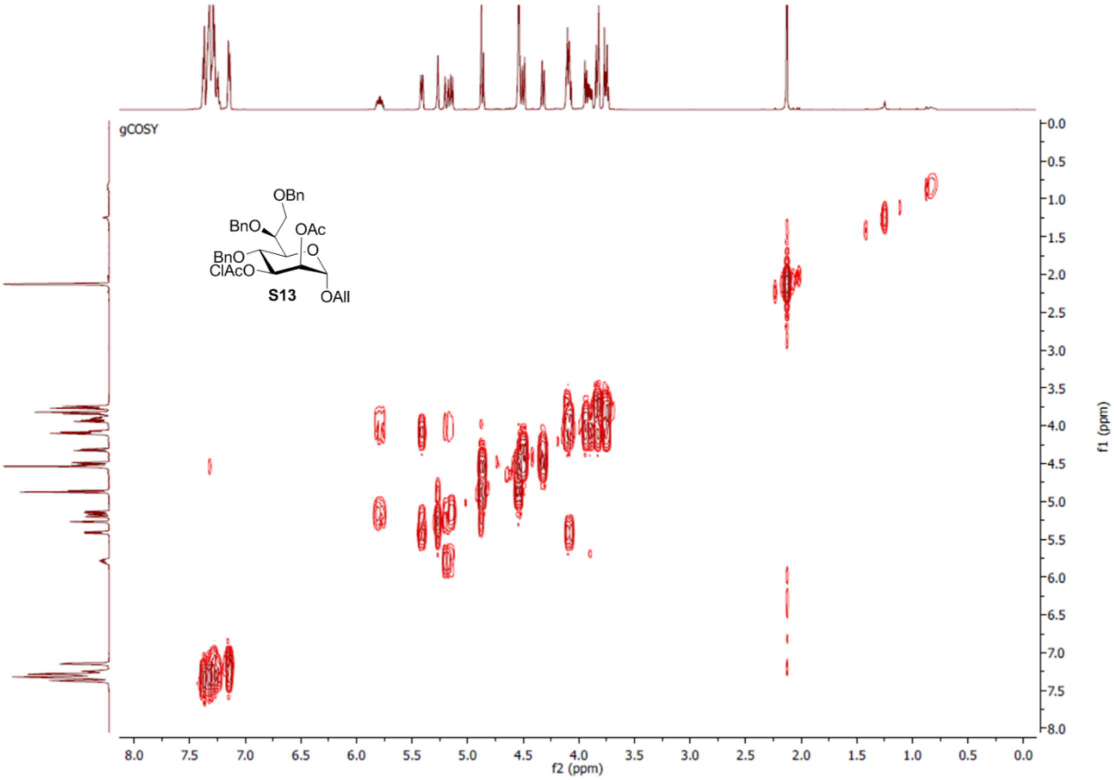
^{1}H NMR (600 MHz, $CDCl_3$)



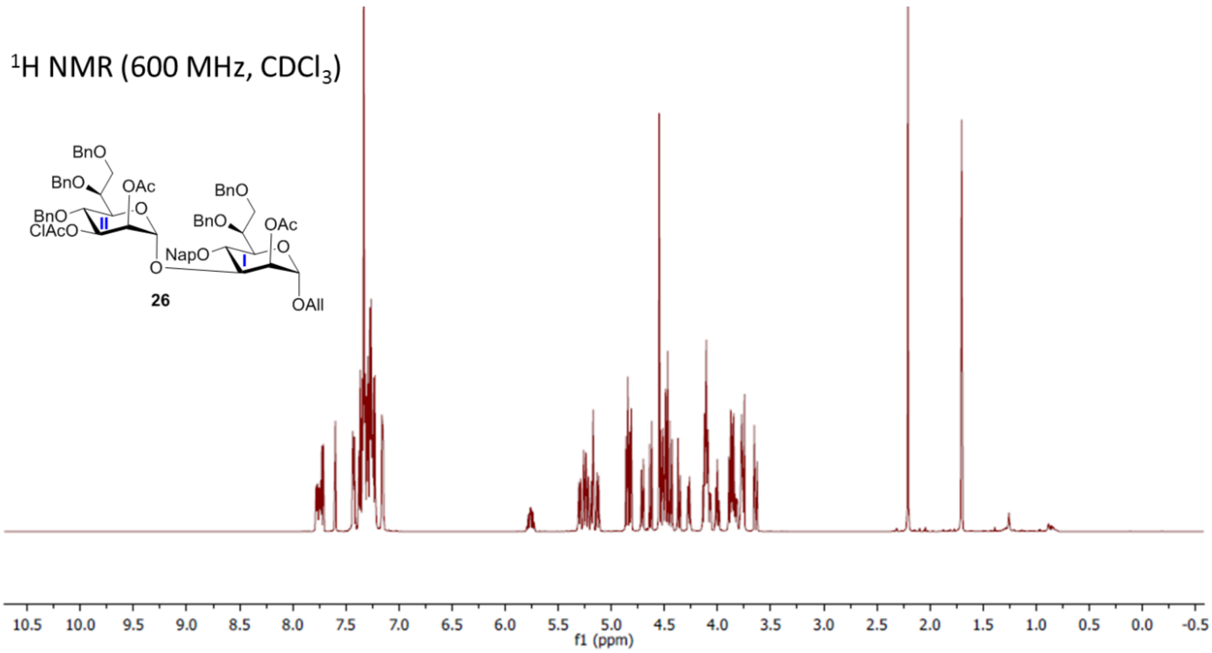
^{13}C NMR (150 MHz, $CDCl_3$)




HSQCAD
OBn
BnO
OAc
O
BnO
ClAcO
S13
OAll
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
f1 (ppm)

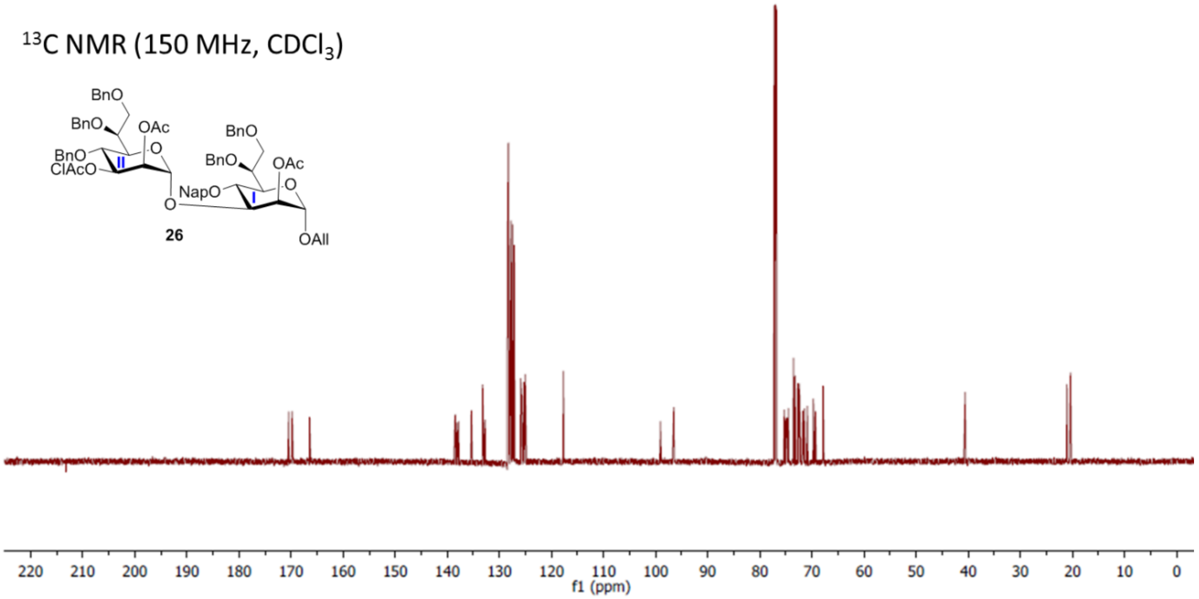

gCOSY
OBn
BnO
OAc
O
BnO
ClAcO
S13
OAll
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)

^{1}H NMR (600 MHz, CDCl$_3$)

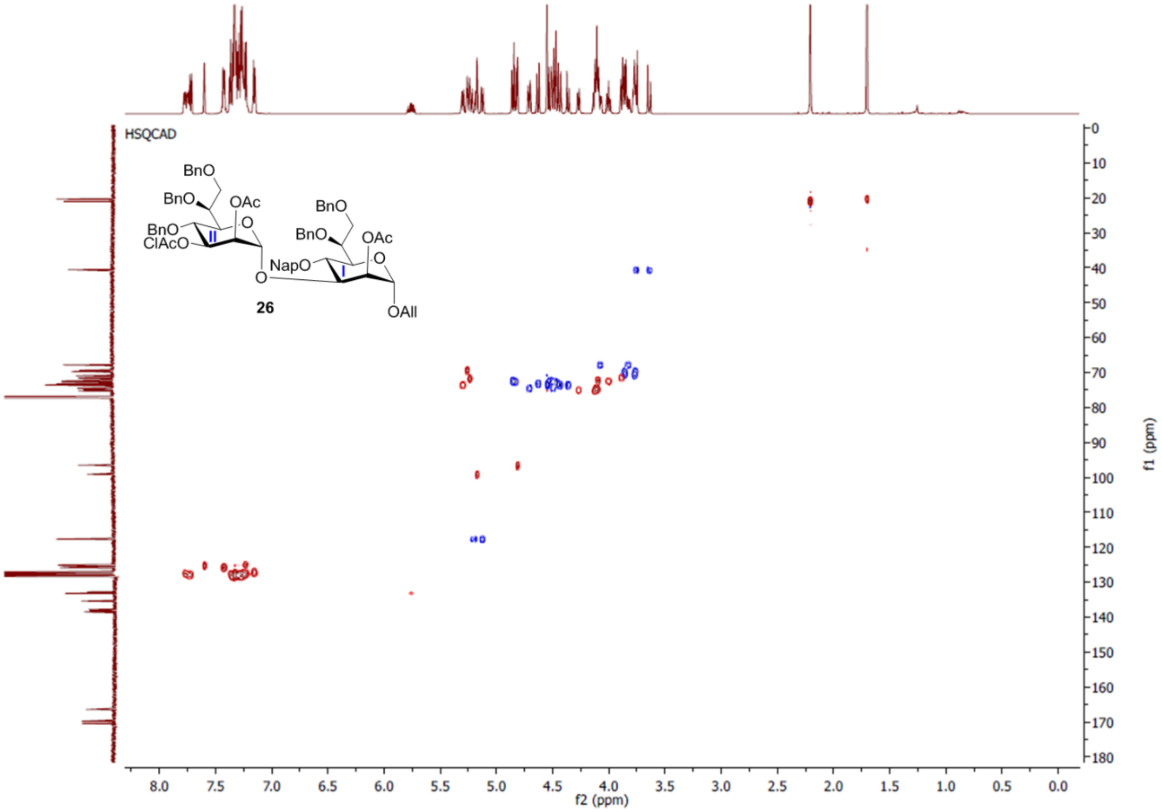


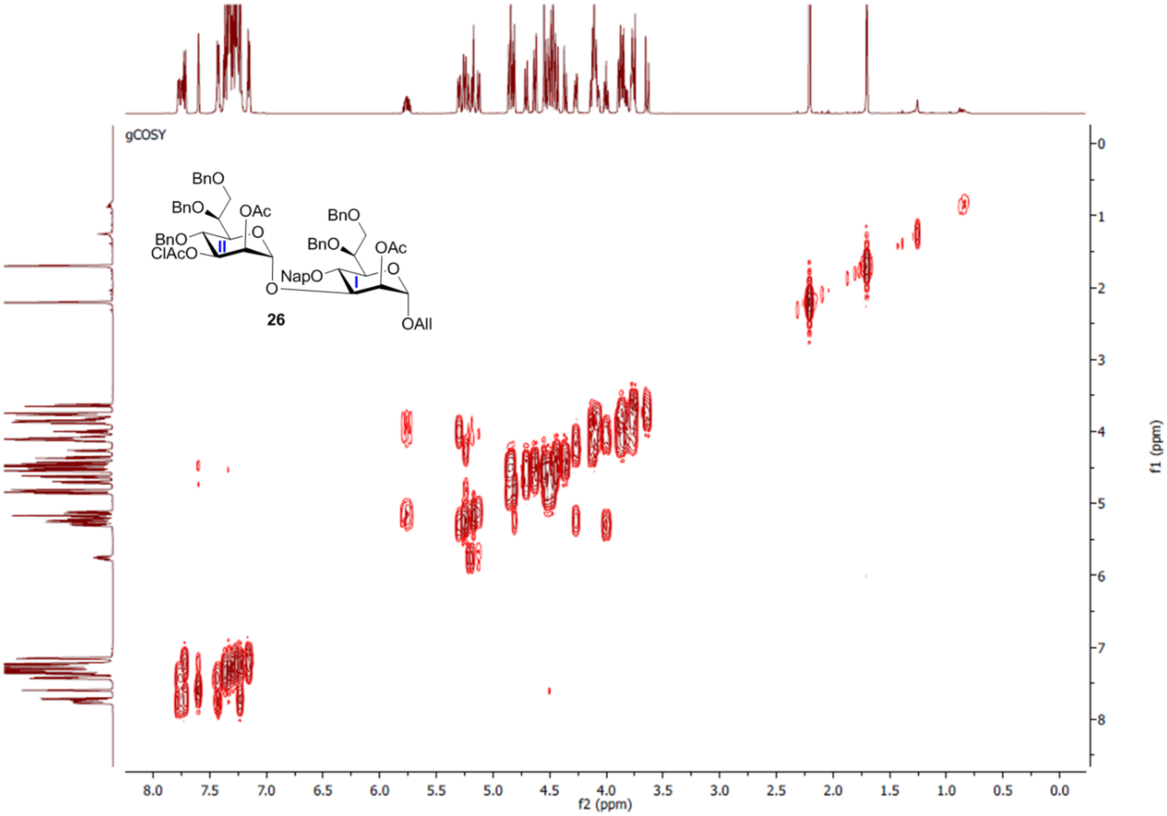
26

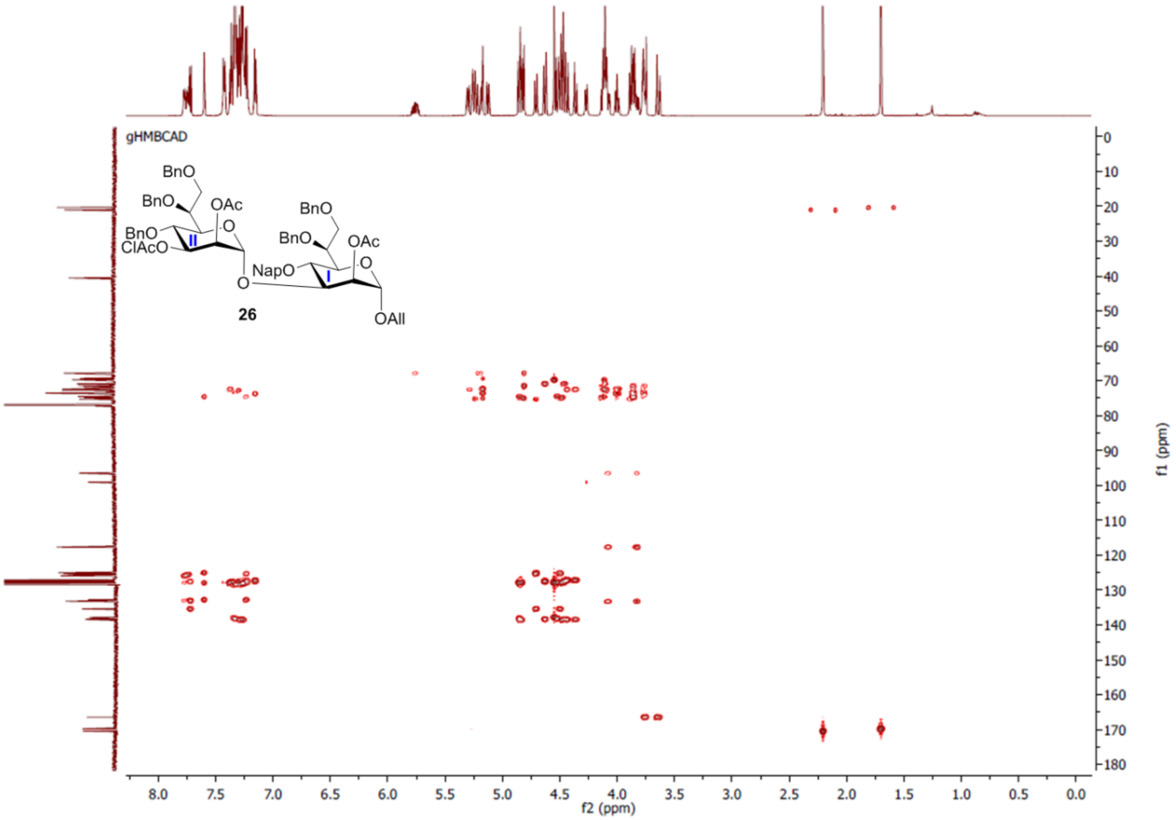
^{13}C NMR (150 MHz, CDCl$_3$)

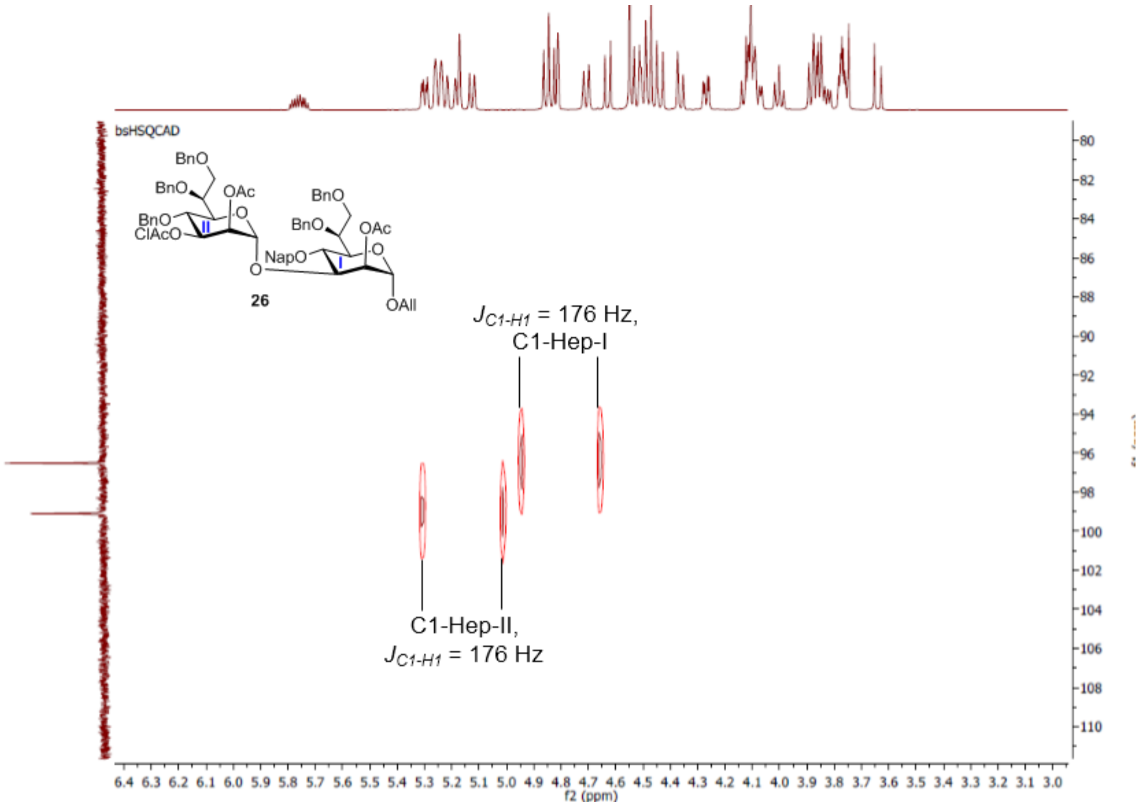


26


HSQCAD
BnO
BnO
OAc
O
BnO
ClAcO
II
O
BnO
BnO
OAc
NapO
I
O
OAll
26
f2 (ppm)
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180


gCOSY
BnO
BnO
OAc
O
BnO
ClAcO
II
O
BnO
BnO
OAc
NapO
I
O
OAll
26
f2 (ppm)
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
1
2
3
4
5
6
7
8

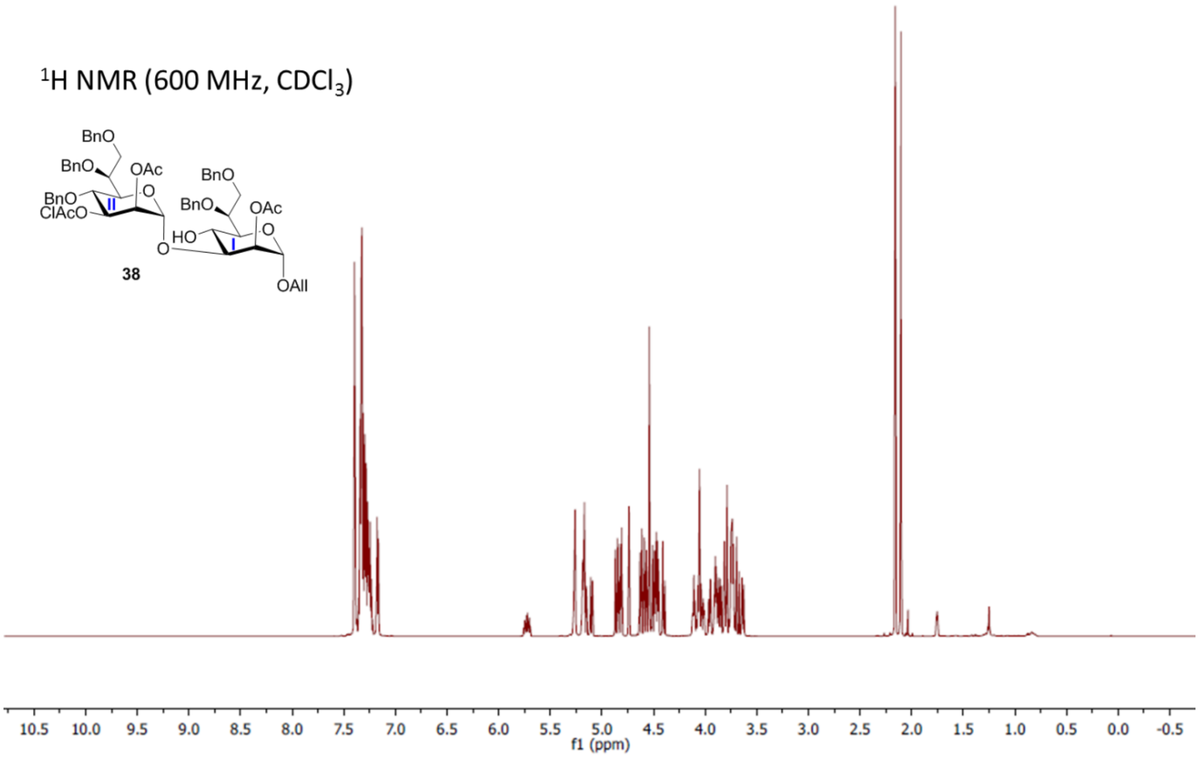




$J_{C1\text{-}H1}$ = 176 Hz,
C1-Hep-I

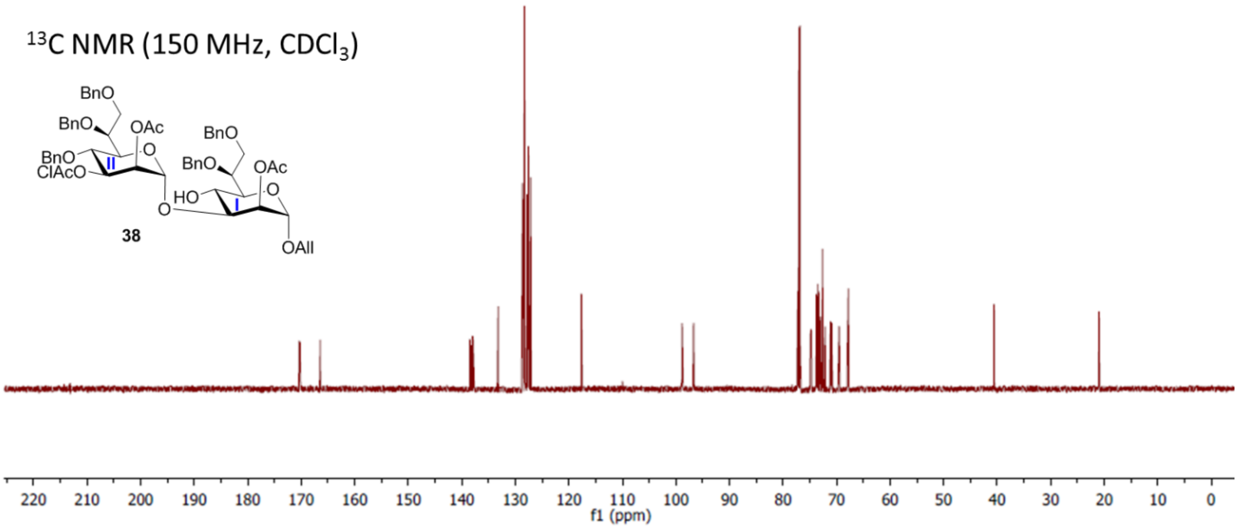
C1-Hep-II,
$J_{C1\text{-}H1}$ = 176 Hz

^{1}H NMR (600 MHz, CDCl$_3$)

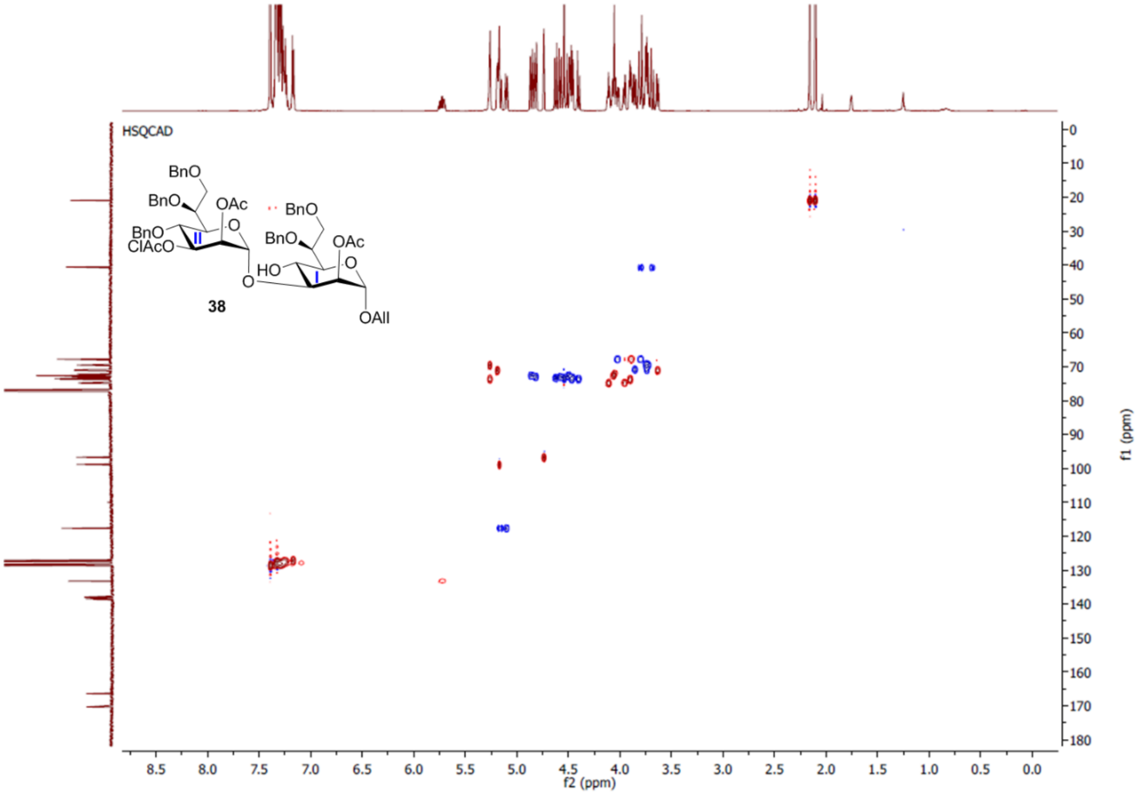


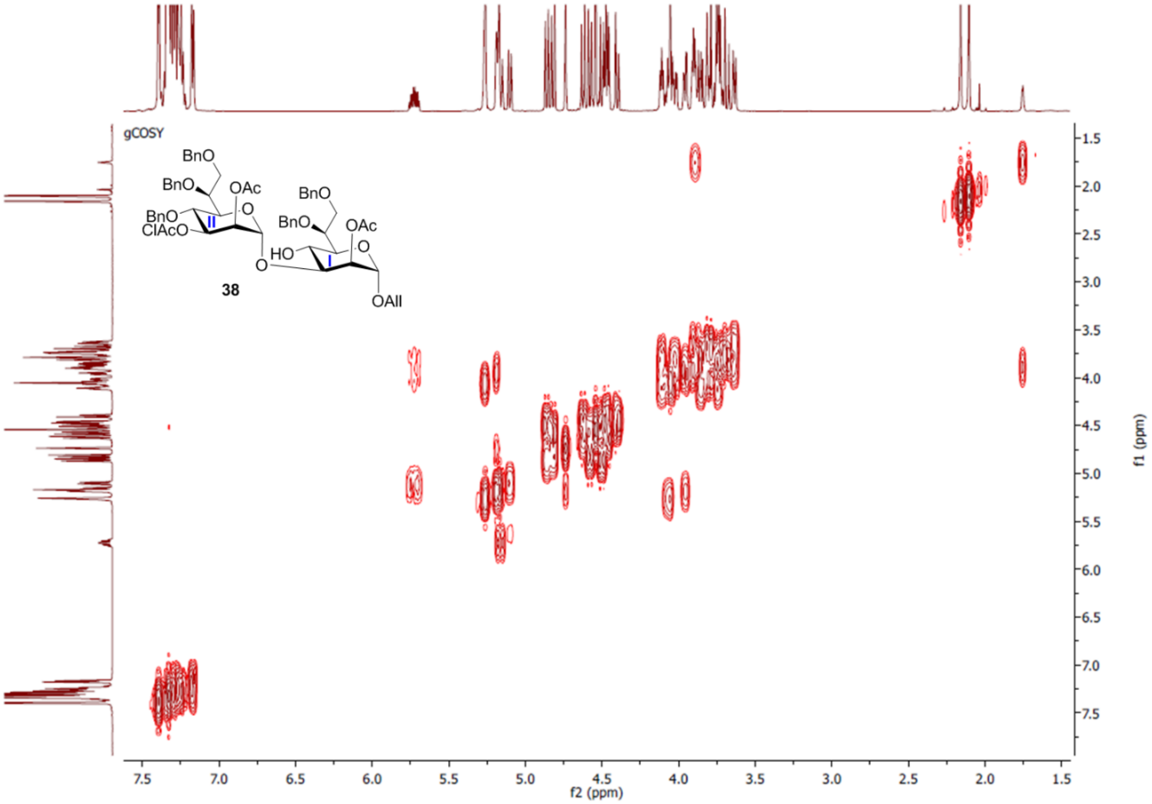
38

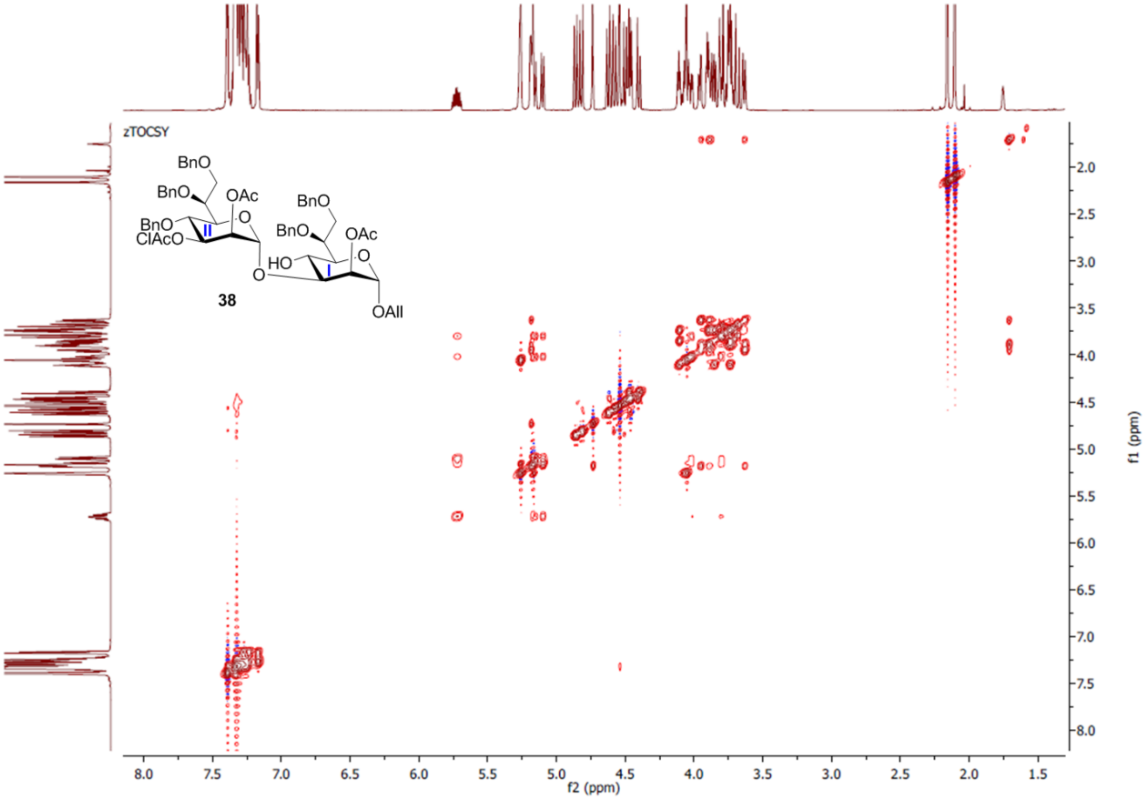
^{13}C NMR (150 MHz, CDCl$_3$)



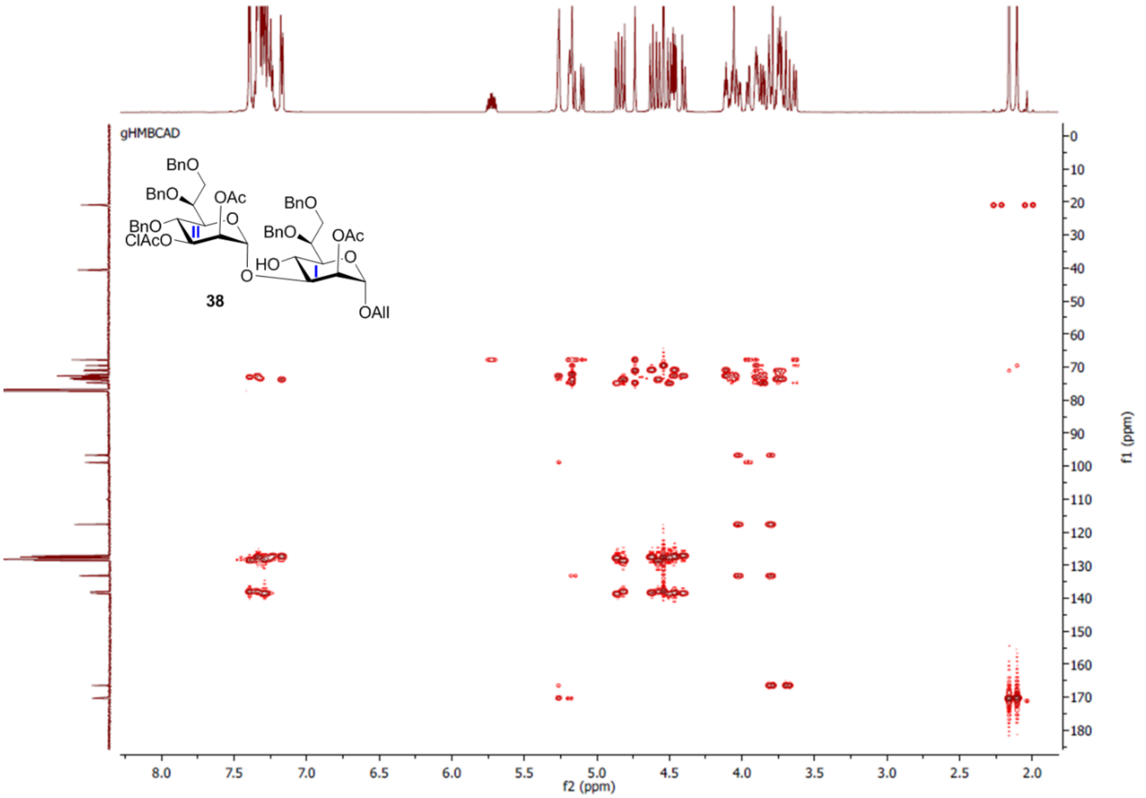
38


HSQCAD
BnO
BnO
OAc
BnO
ClAcO
II
O
BnO
BnO
OAc
HO
I
O
O
OAll
38
f2 (ppm)
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180


gCOSY
BnO
BnO
OAc
BnO
ClAcO
II
O
BnO
BnO
OAc
HO
I
O
O
OAll
38
f2 (ppm)
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5

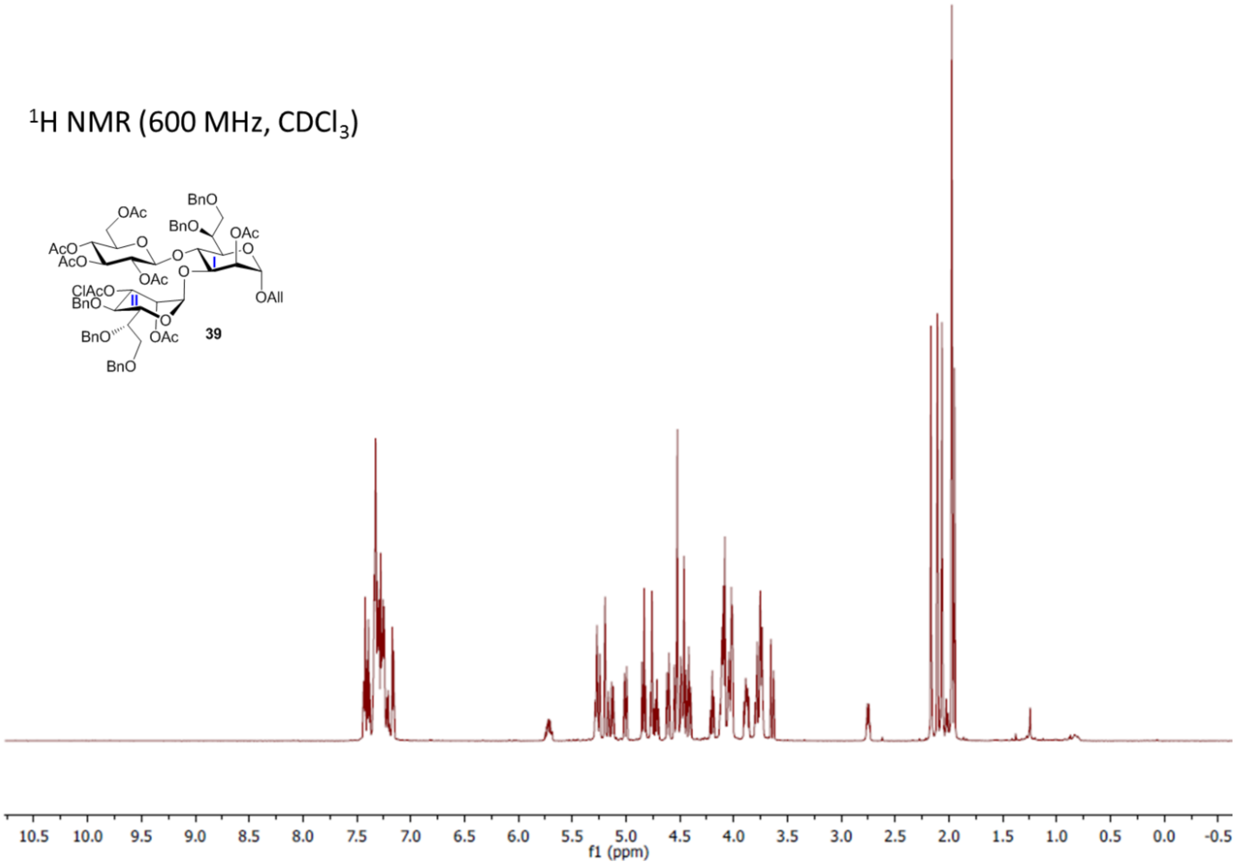


zTOCSY
BnO
BnO
OAc
BnO
ClAcO
II
O
BnO
BnO
OAc
HO
I
O
O
OAll
38
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)

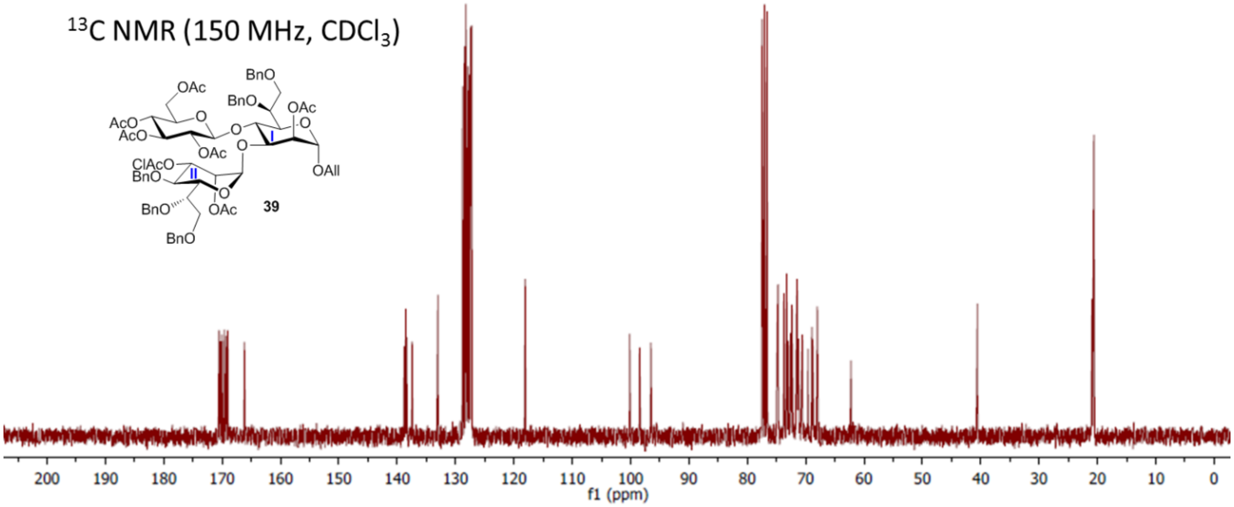


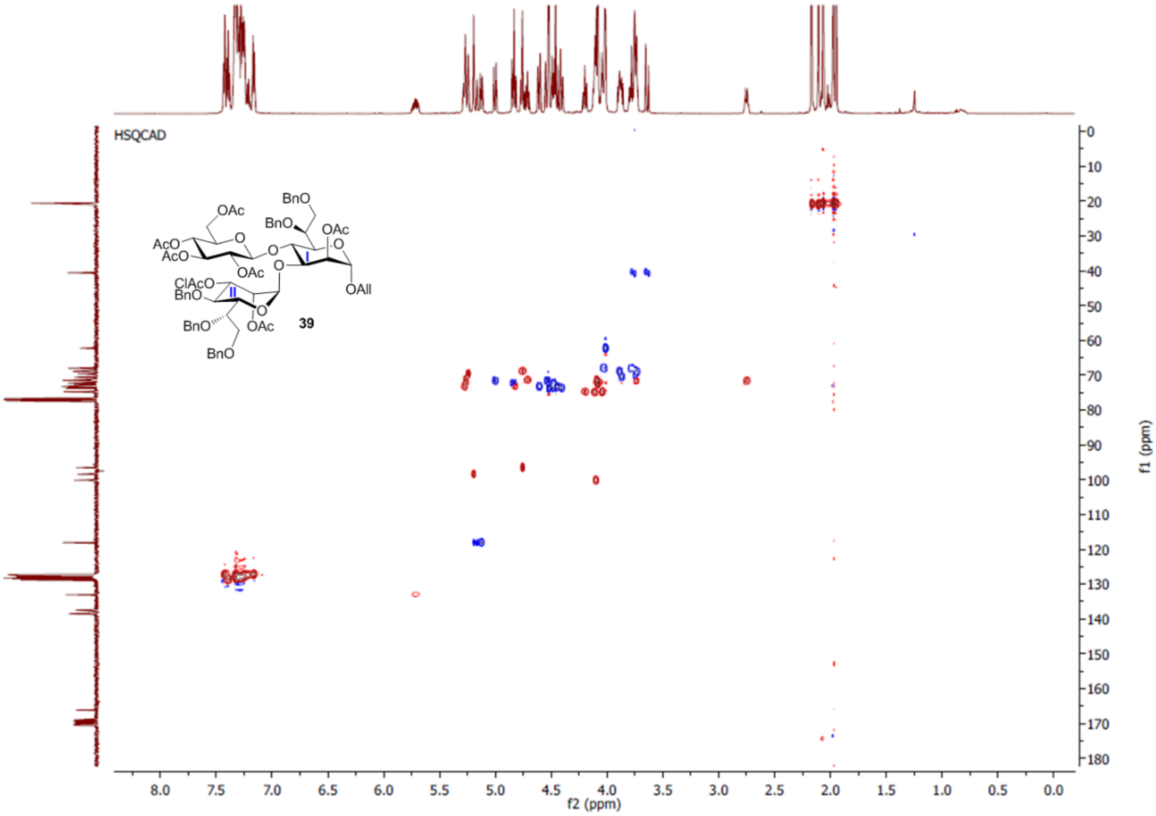
gHMBCAD
BnO
BnO
OAc
BnO
ClAcO
II
O
BnO
BnO
OAc
HO
I
O
O
OAll
38
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
f1 (ppm)

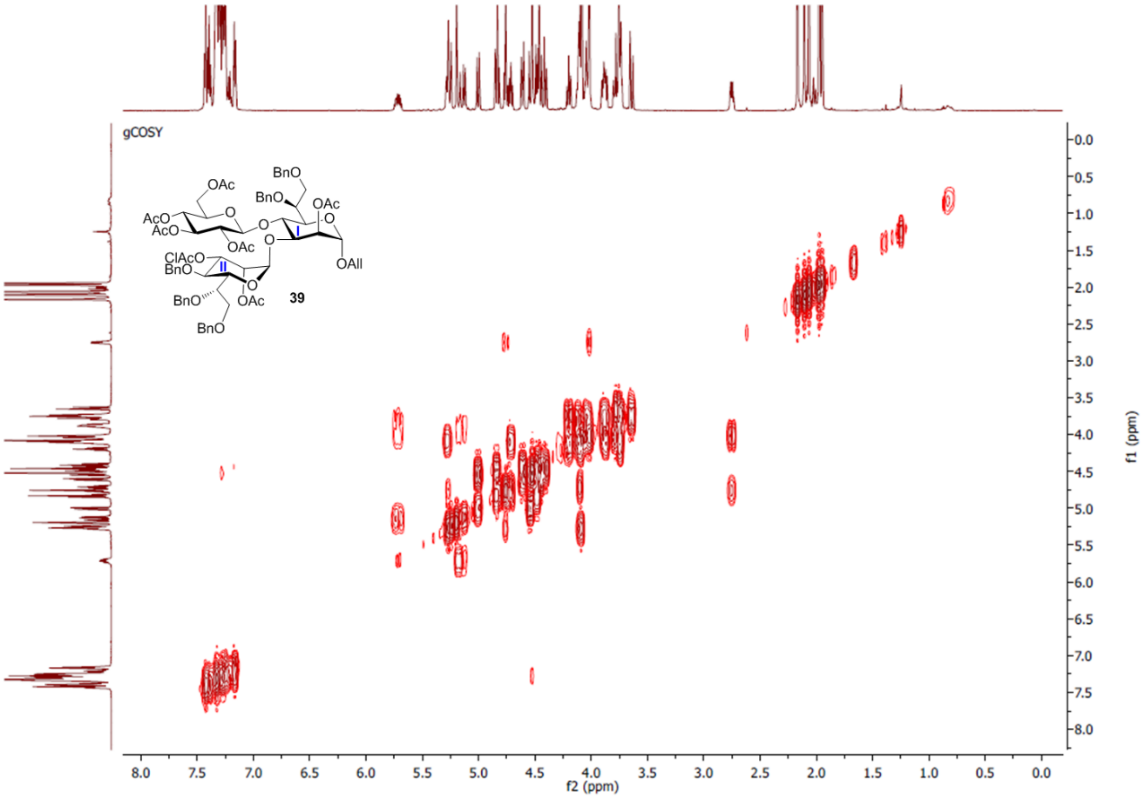
^{1}H NMR (600 MHz, CDCl$_3$)

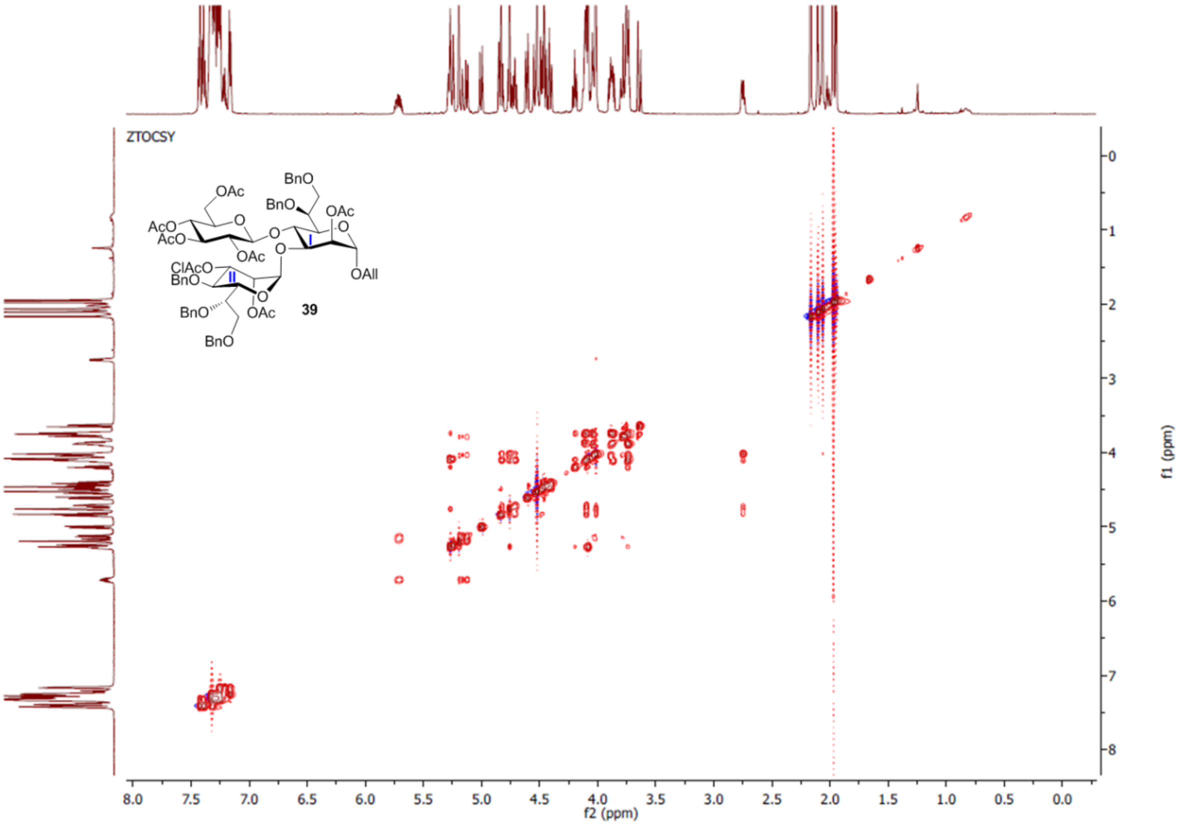


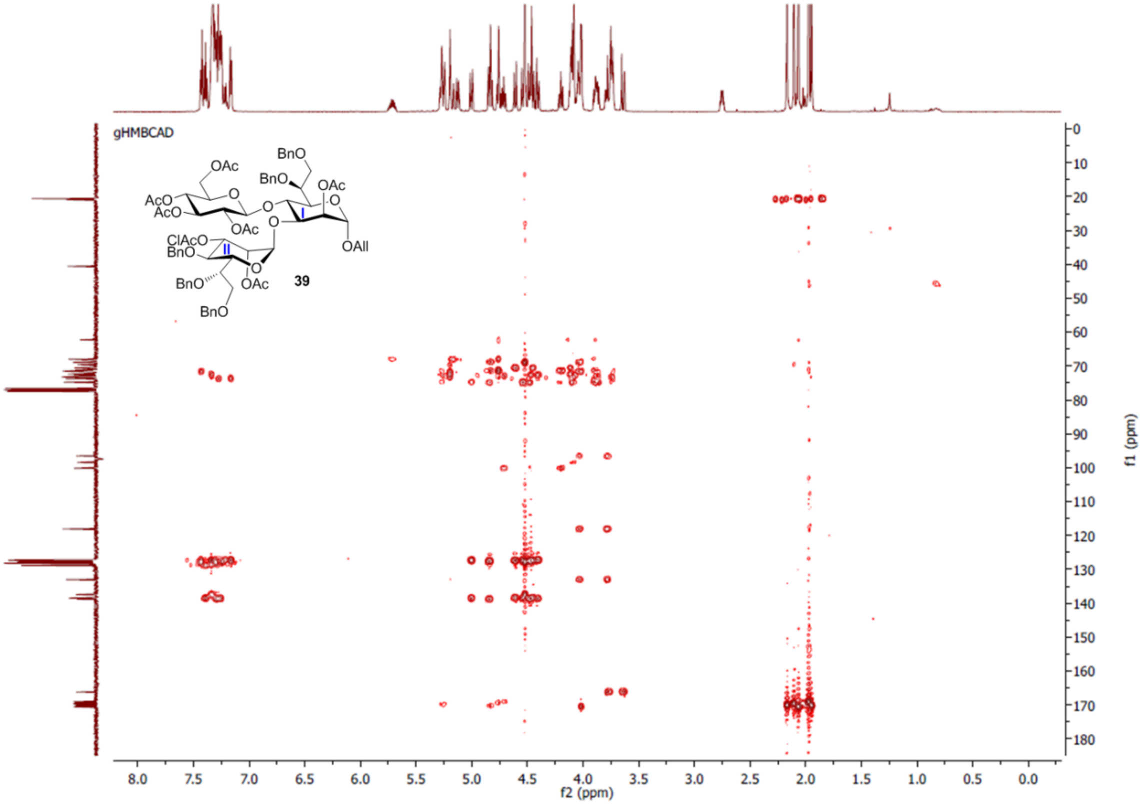
^{13}C NMR (150 MHz, CDCl$_3$)

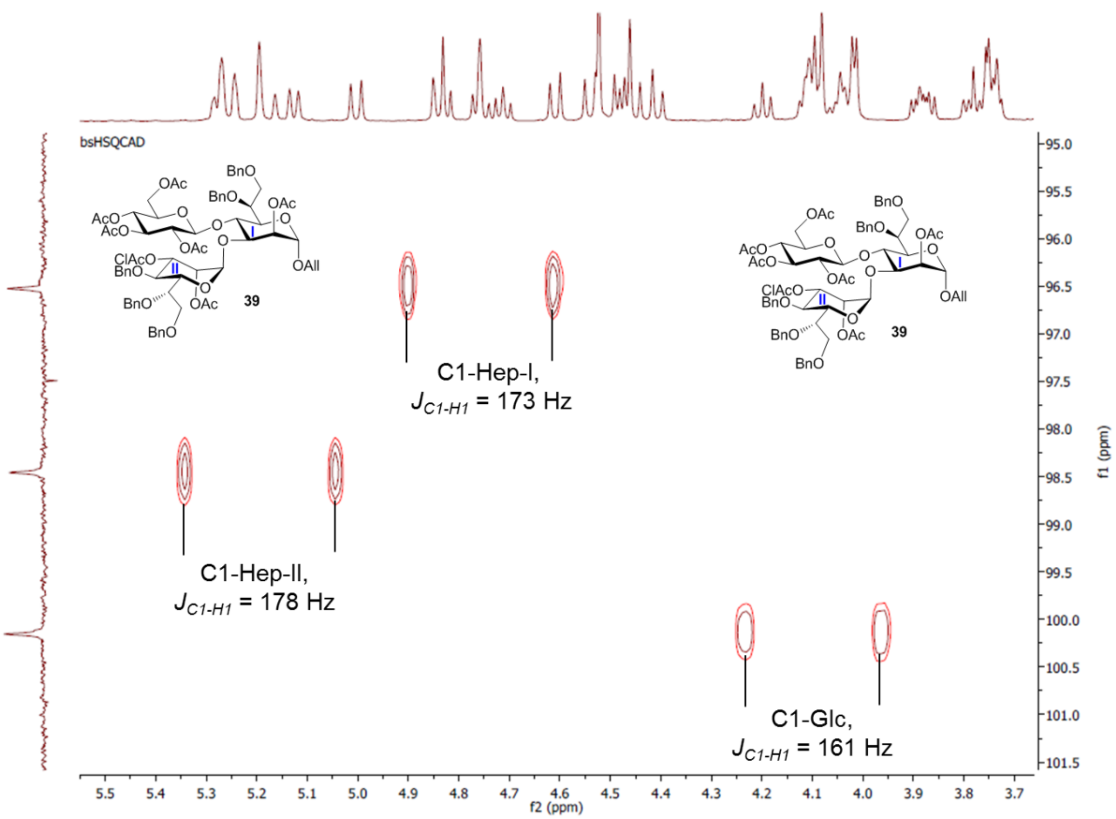



HSQCAD
OAc
AcO
AcO
OAc
BnO
BnO
OAc
O
OAll
I
ClAcO
BnO
II
BnO
OAc
BnO
39
f2 (ppm)
f1 (ppm)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180


gCOSY
OAc
AcO
AcO
OAc
BnO
BnO
OAc
O
OAll
I
ClAcO
BnO
II
BnO
OAc
BnO
39
f2 (ppm)
f1 (ppm)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0


ZTOCSY
OAc
BnO
BnO
OAc
AcO
AcO
O
O
OAc
I
O
OAll
ClAcO
BnO
II
O
BnO
OAc
BnO
39
f2 (ppm)
f1 (ppm)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
0 1 2 3 4 5 6 7 8


gHMBCAD
OAc
BnO
BnO
OAc
AcO
AcO
O
O
OAc
I
O
OAll
ClAcO
BnO
II
O
BnO
OAc
BnO
39
f2 (ppm)
f1 (ppm)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180

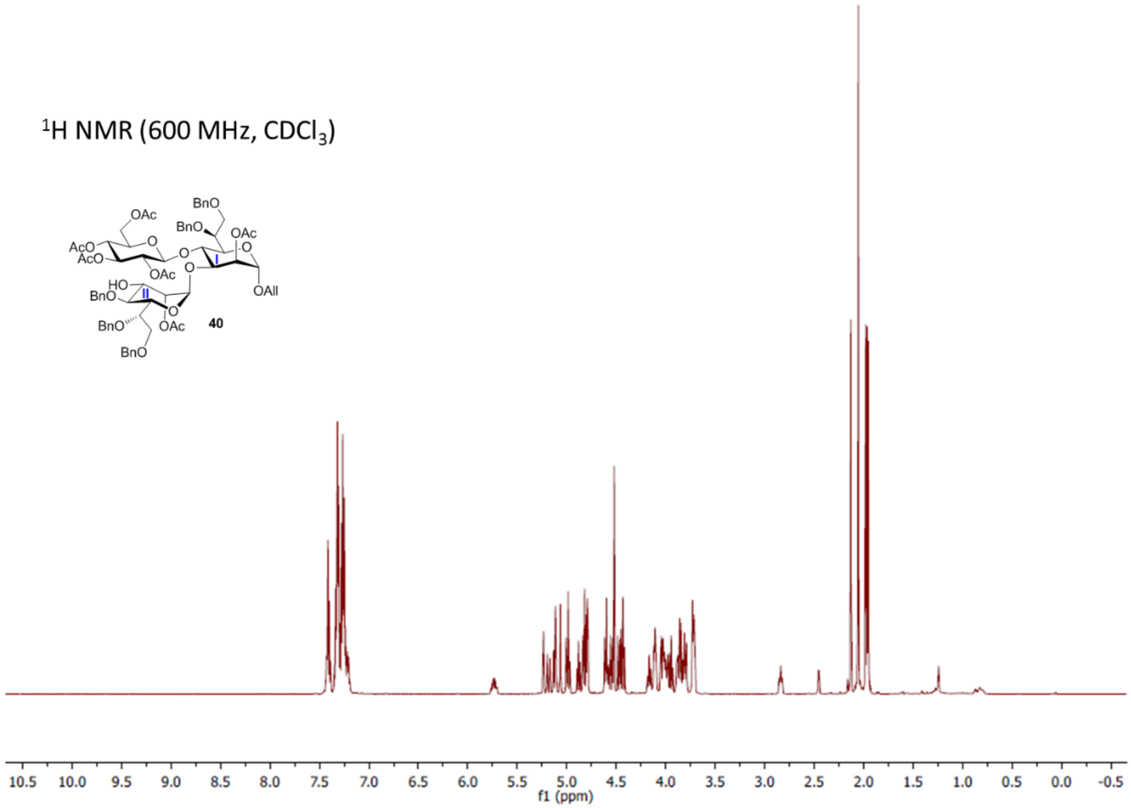


39

C1-Hep-I, $J_{C1\text{-}H1}$ = 173 Hz

C1-Hep-II, $J_{C1\text{-}H1}$ = 178 Hz

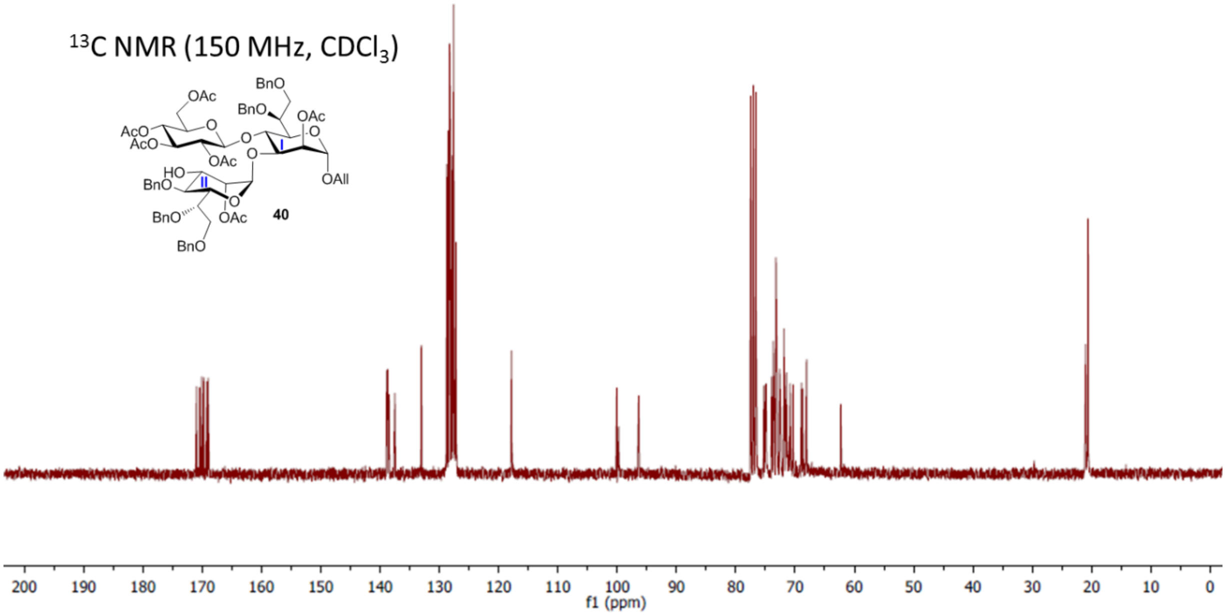
C1-Glc, $J_{C1\text{-}H1}$ = 161 Hz

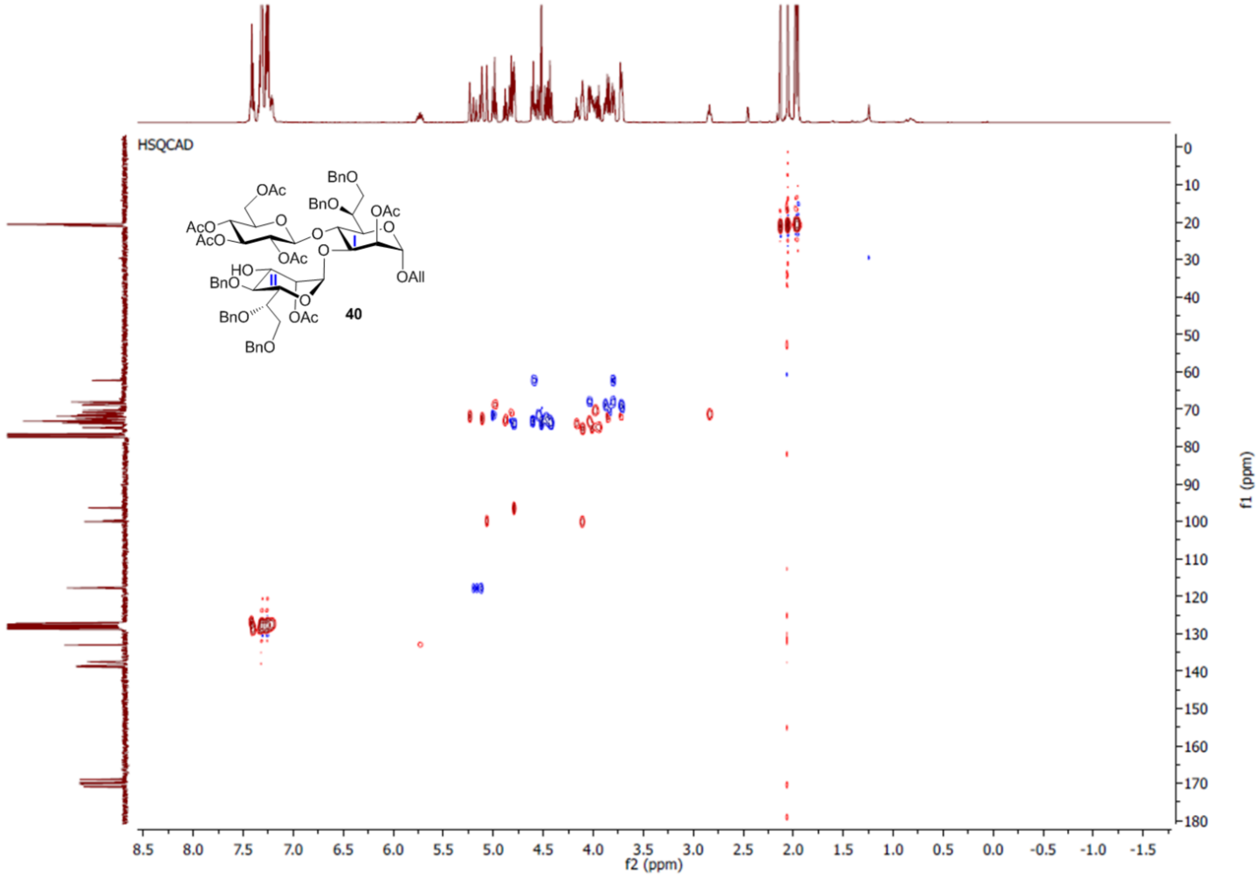


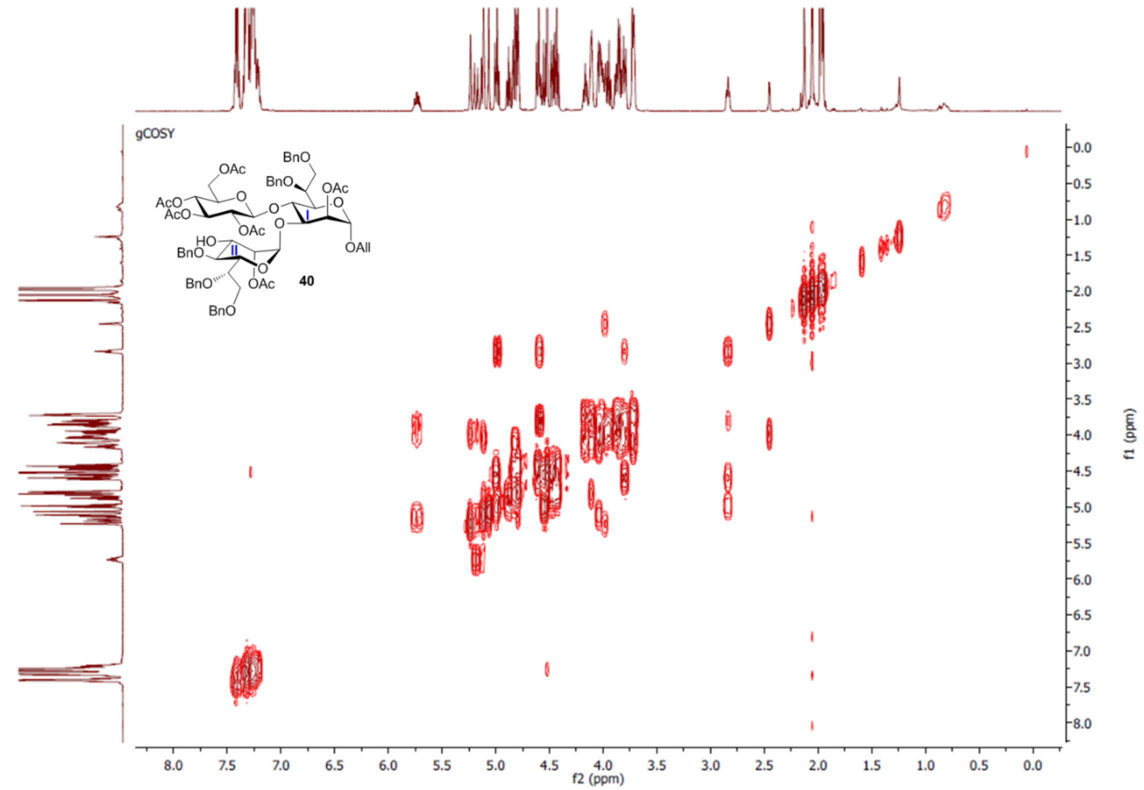
^{1}H NMR (600 MHz, CDCl$_3$)

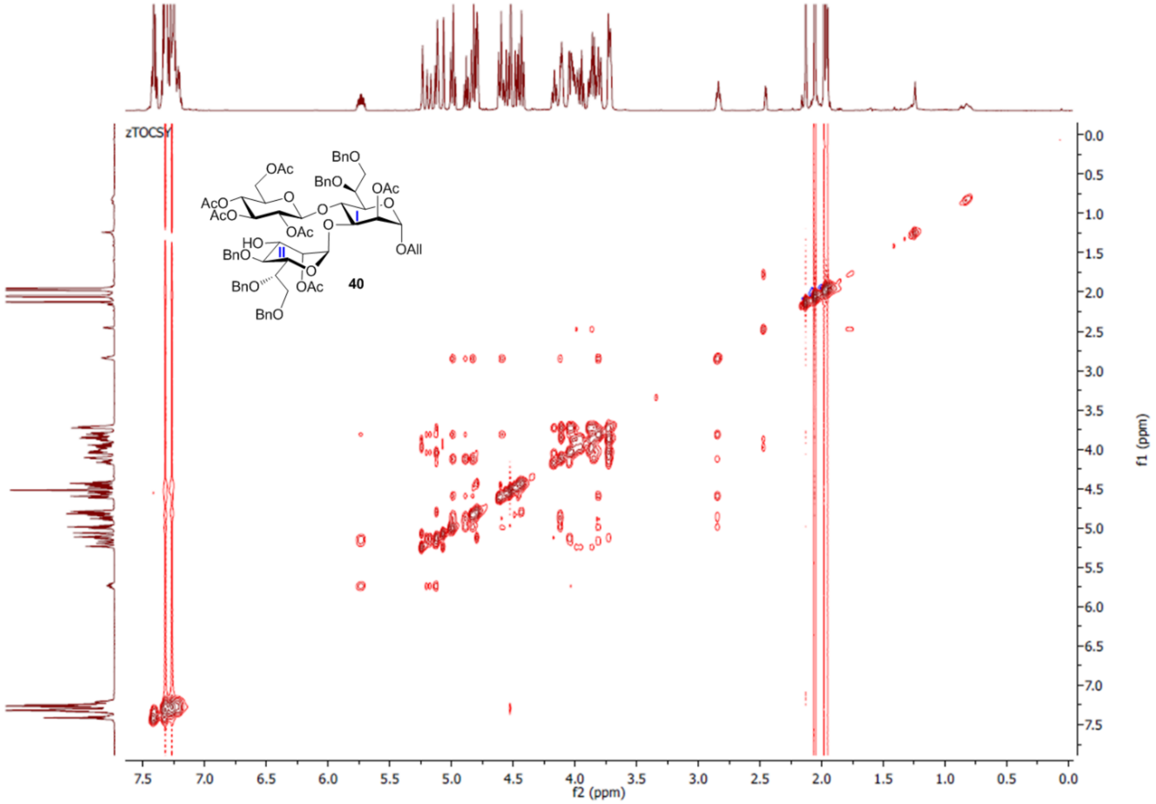
40

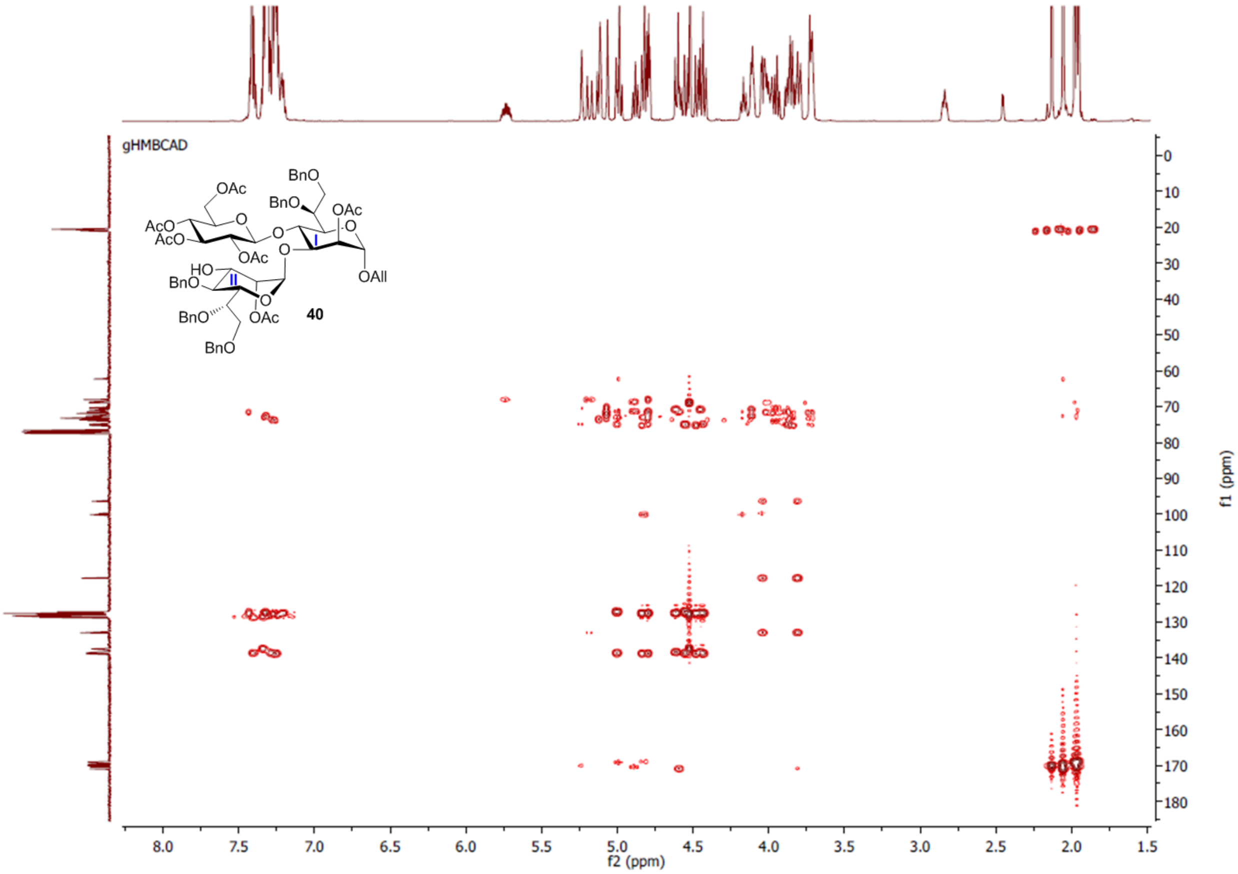
^{13}C NMR (150 MHz, CDCl$_3$)



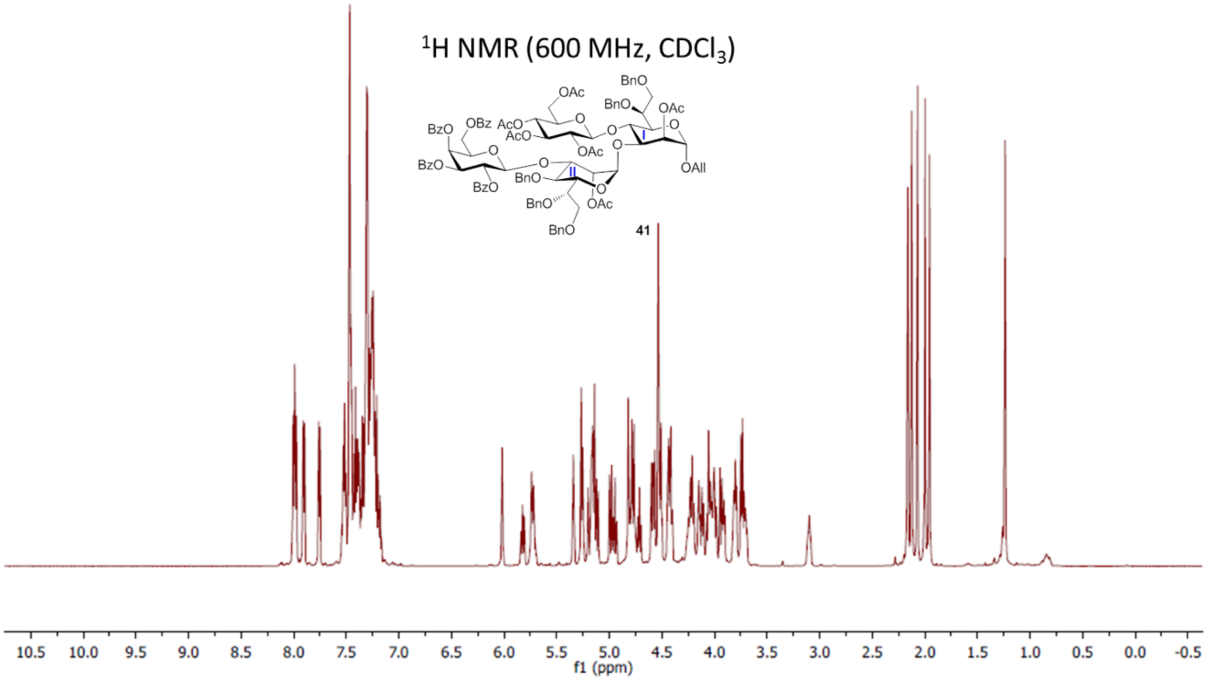


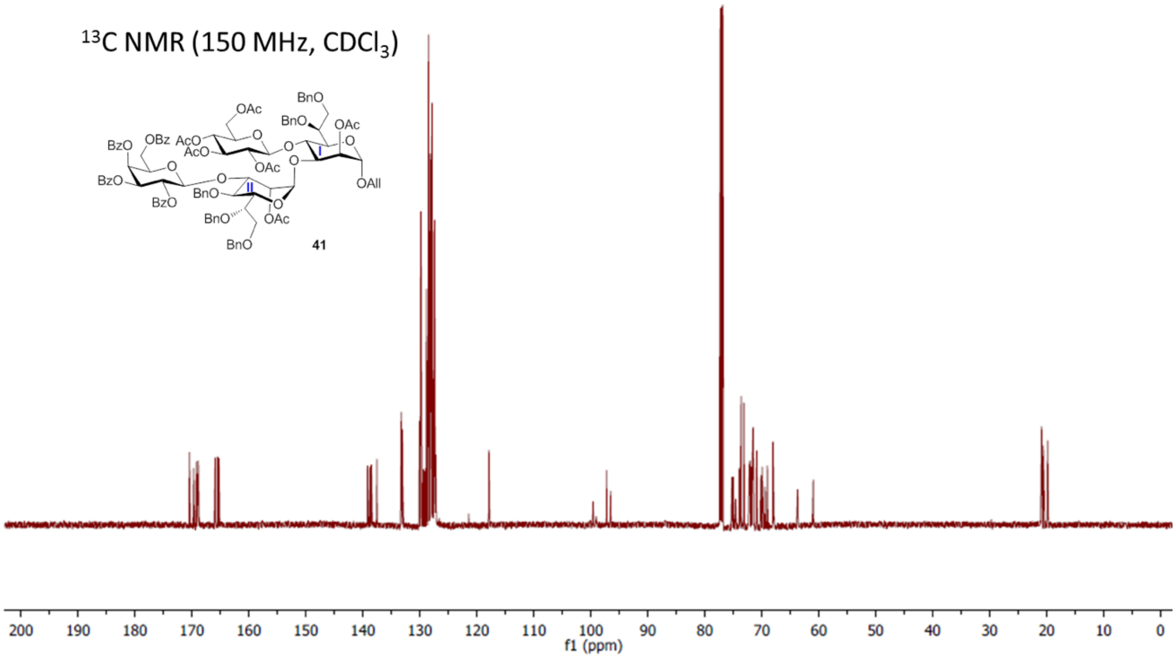

gCOSY
OAc
BnO
BnO
OAc
AcO
AcO
O
O
O
OAc
I
O
O
OAll
HO
BnO
II
O
BnO
OAc
BnO
40
f1 (ppm)
f2 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

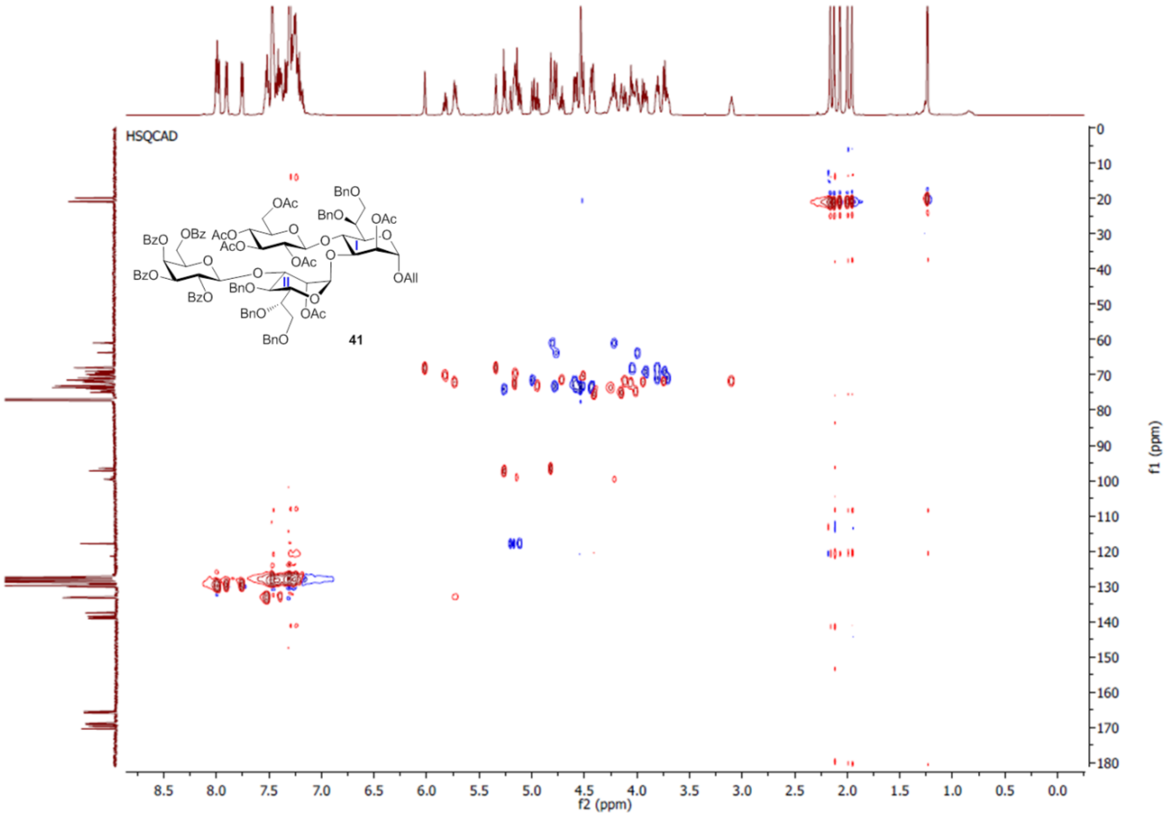

zTOCSY
OAc
BnO
BnO
OAc
AcO
AcO
O
O
O
OAc
I
O
O
OAll
HO
BnO
II
O
BnO
OAc
BnO
40
f1 (ppm)
f2 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

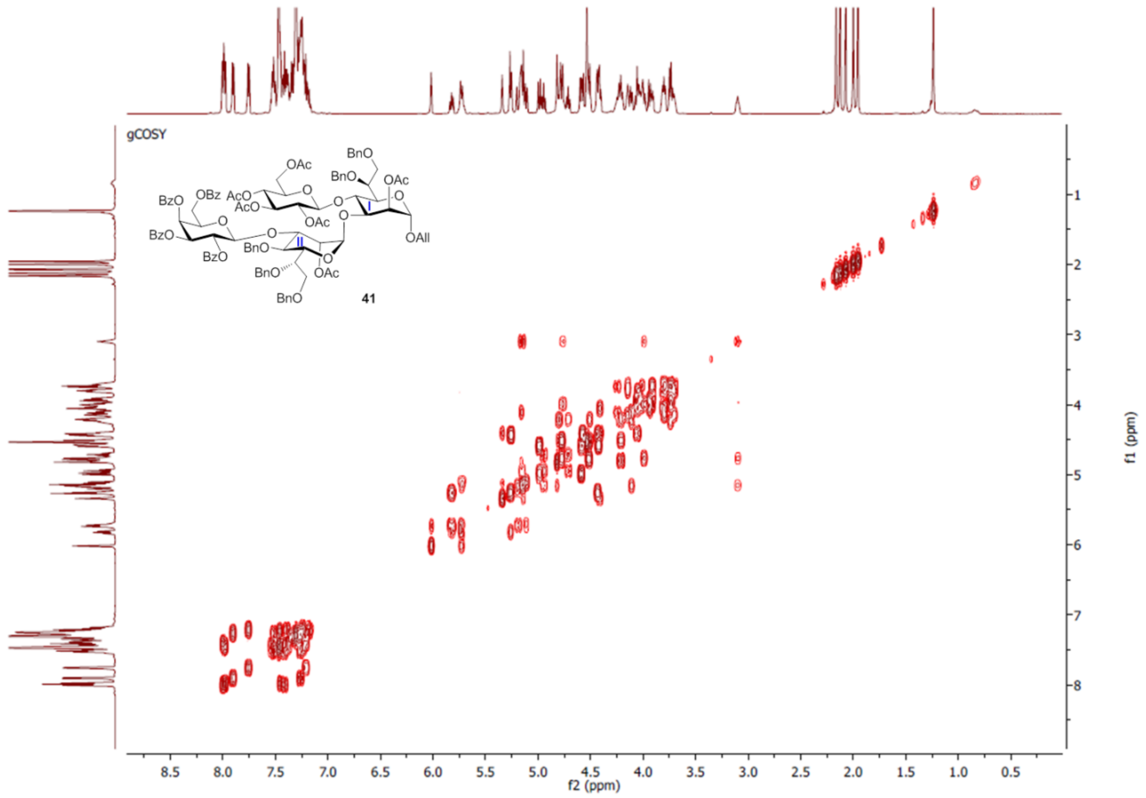


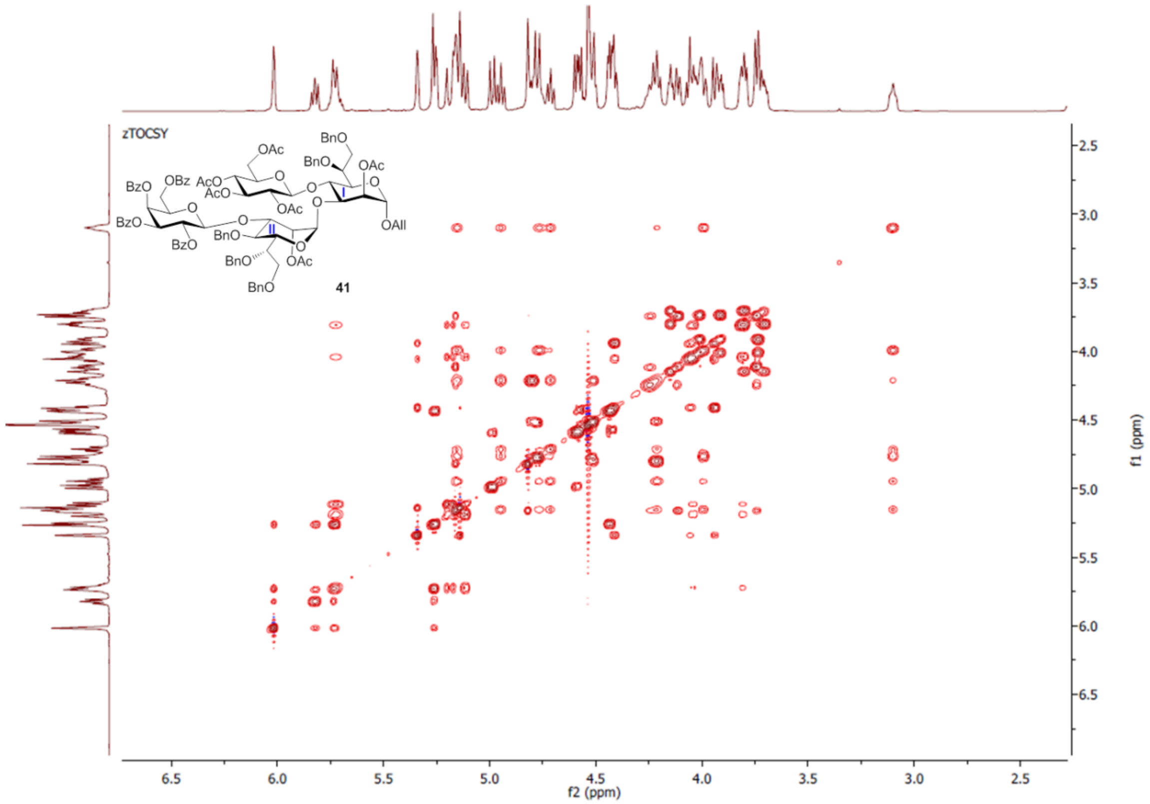
^{1}H NMR (600 MHz, CDCl$_3$)

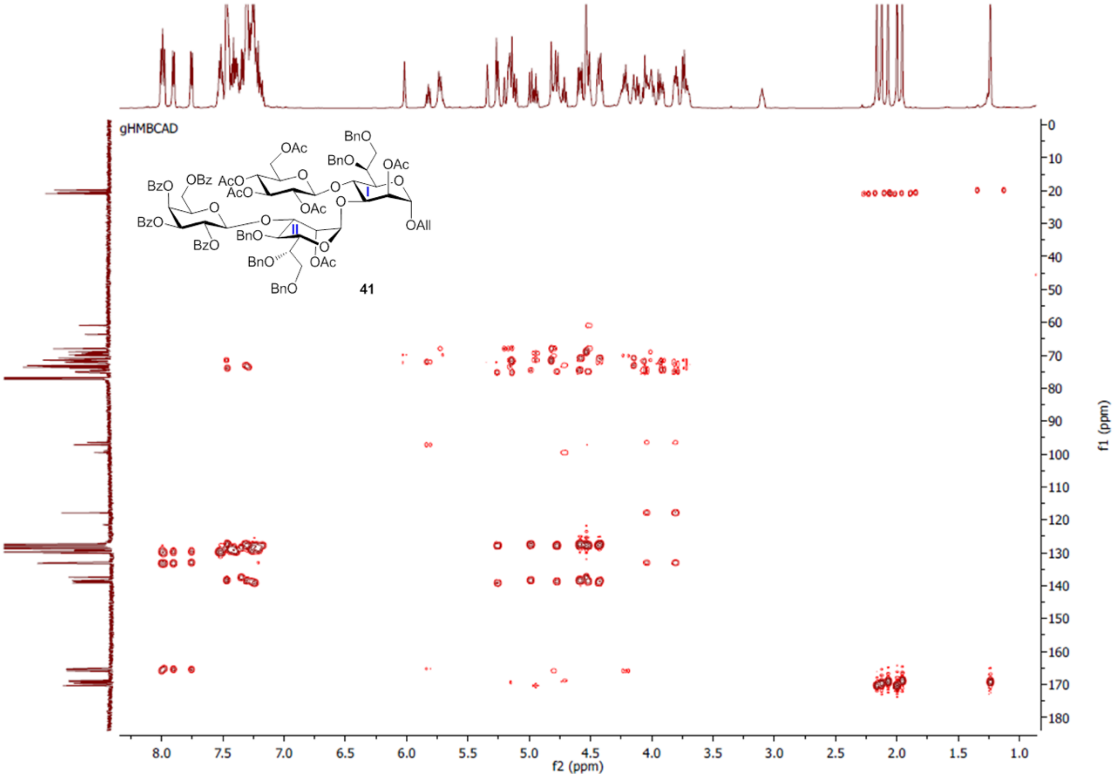


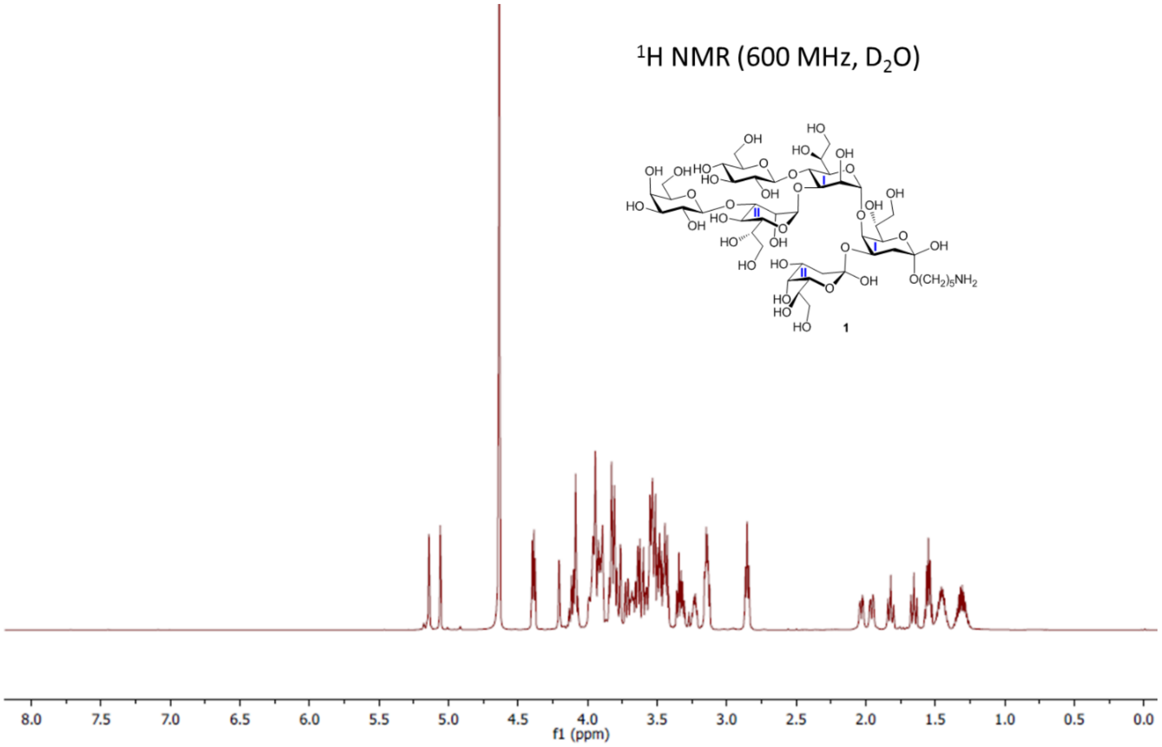

^{13}C NMR (150 MHz, $CDCl_3$)




gCOSY
BnO
OAc
BnO
OAc
BzO
OBz
AcO
AcO
O
O
OAc
O
OAll
I
BzO
O
O
BnO
II
O
BzO
BnO
OAc
BnO
41
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
1
2
3
4
5
6
7
8
f1 (ppm)

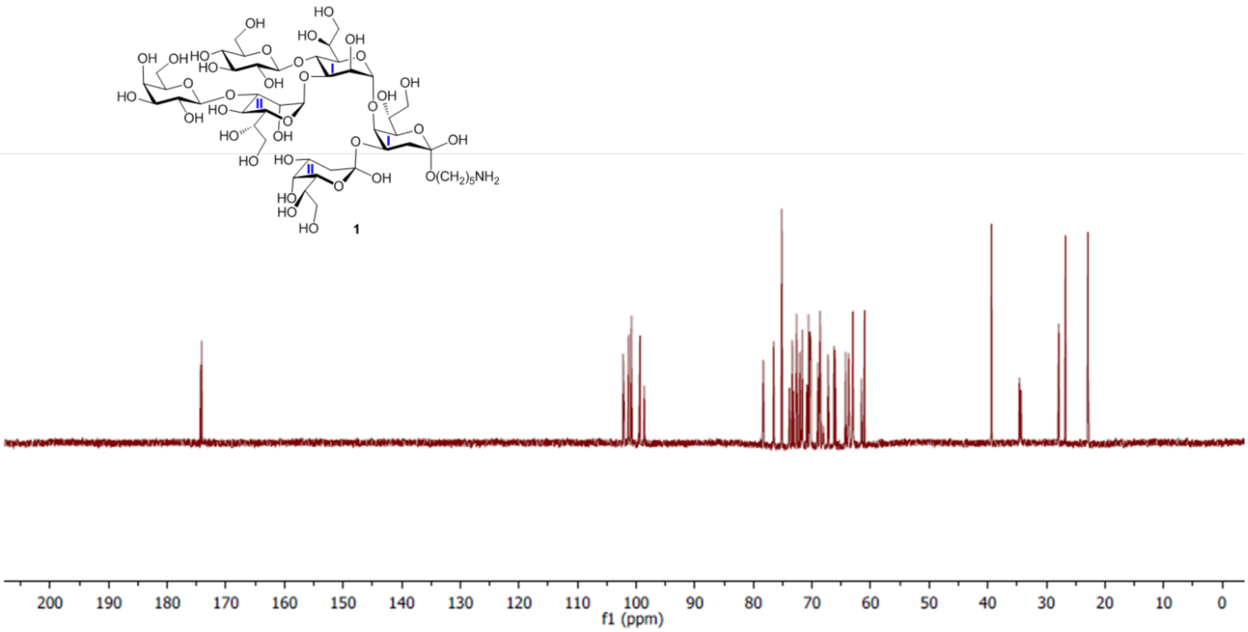

zTOCSY
BnO
OAc
BnO
OAc
BzO
OBz
AcO
AcO
O
O
OAc
O
OAll
I
BzO
O
O
BnO
II
O
BzO
BnO
OAc
BnO
41
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f2 (ppm)
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
f1 (ppm)

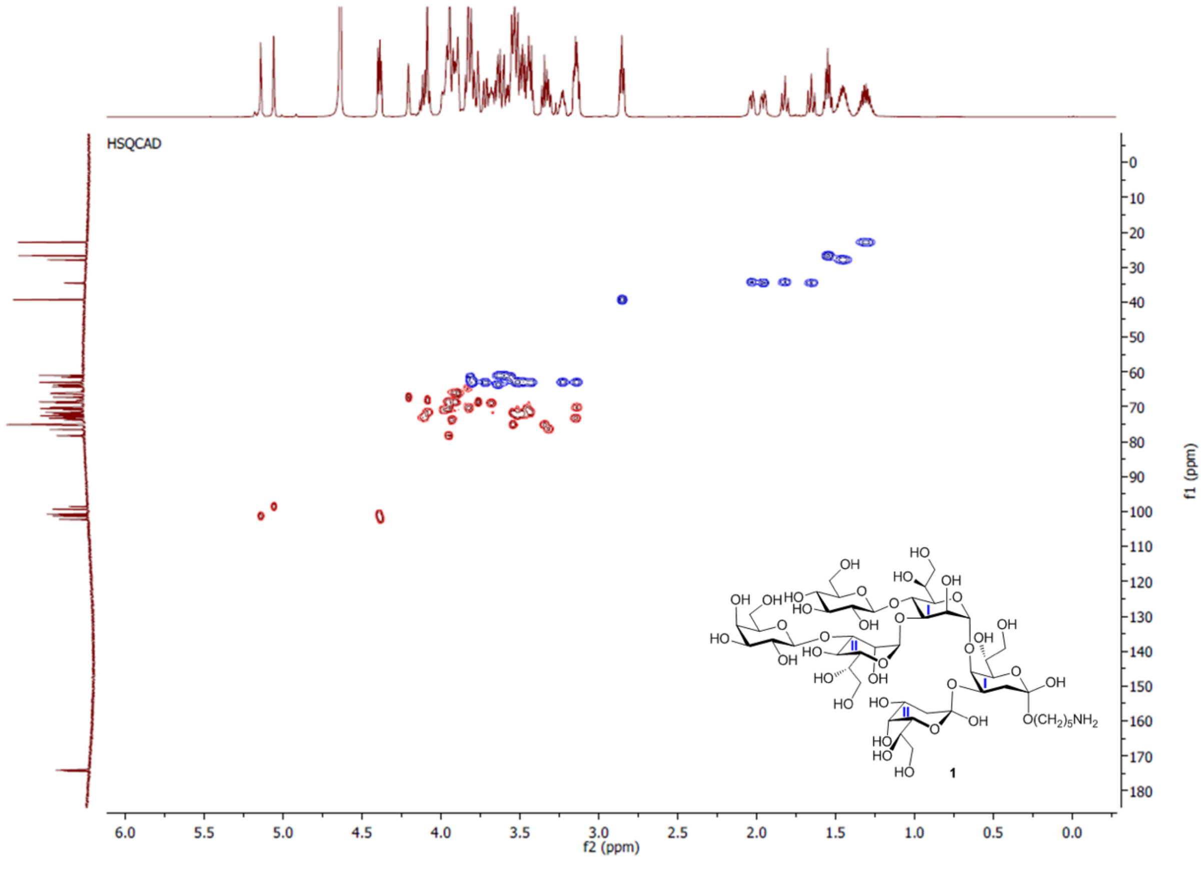


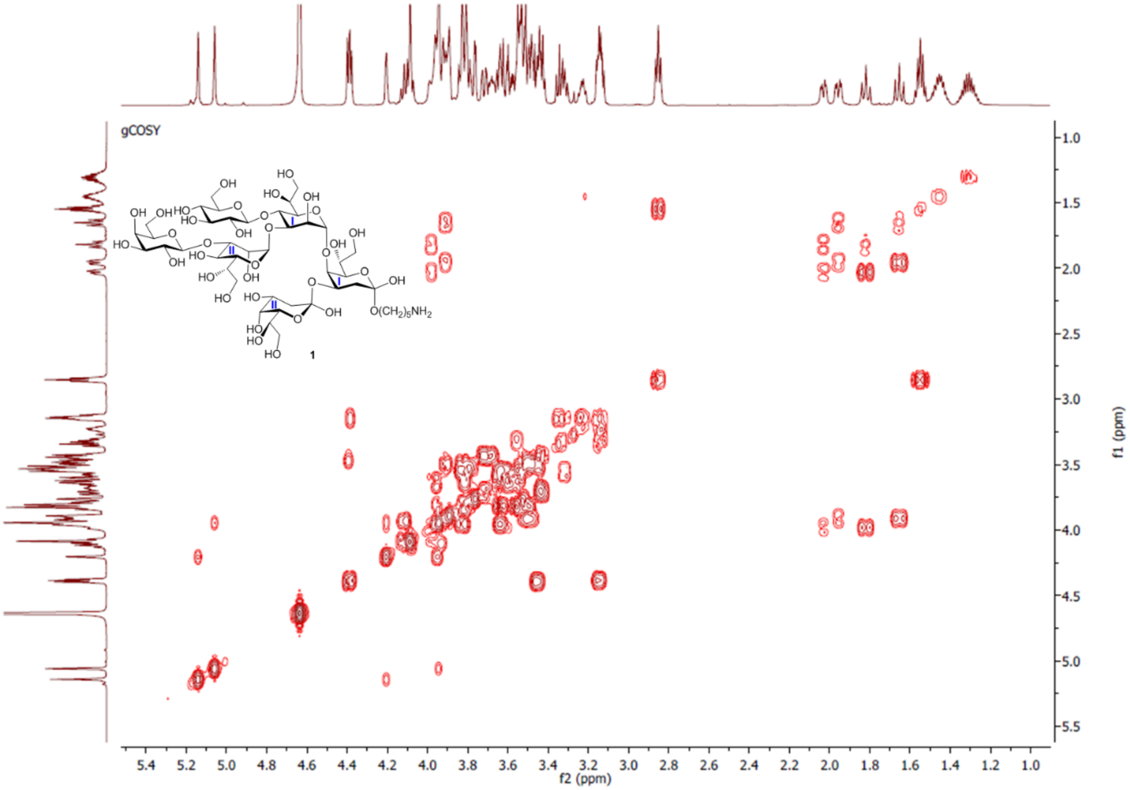


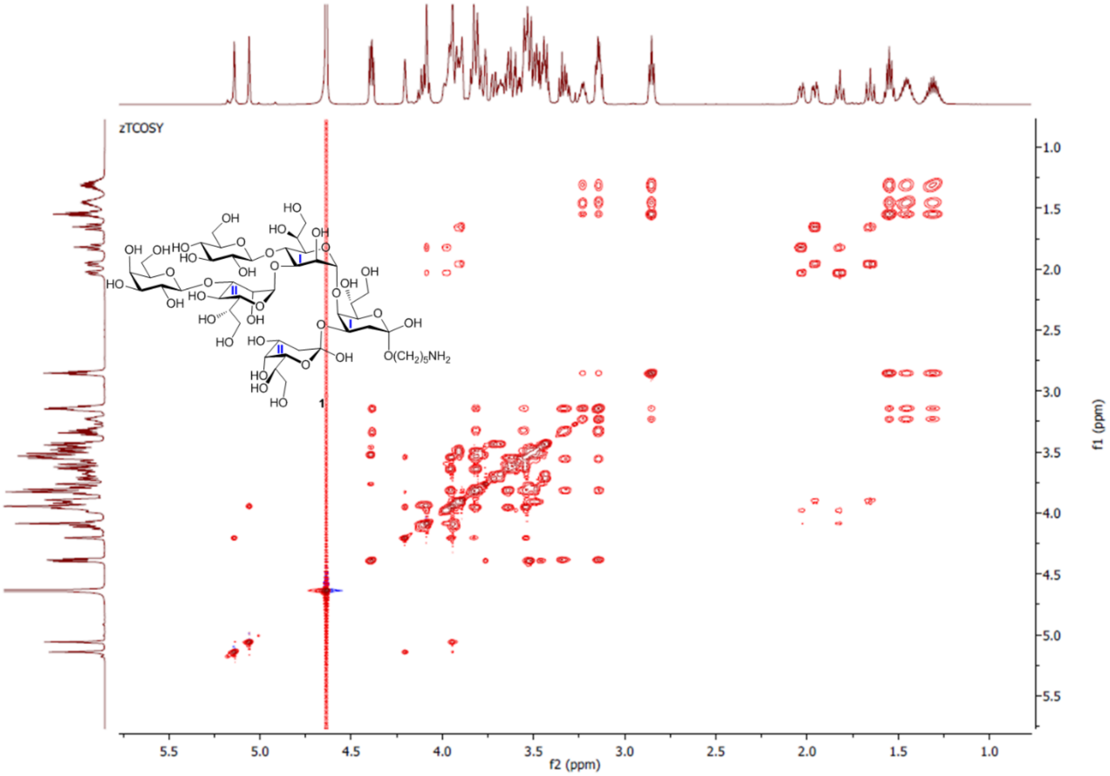
^{1}H NMR (600 MHz, D$_2$O)

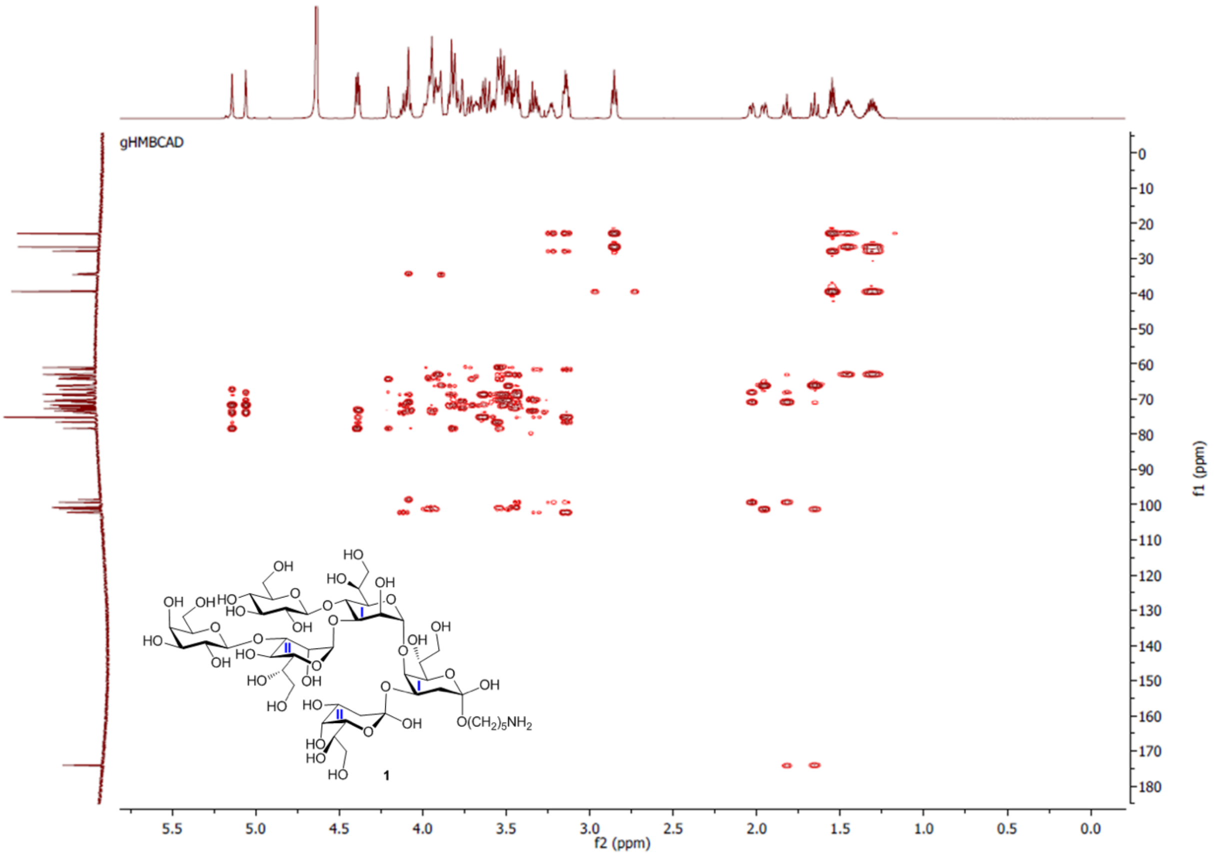
^{13}C NMR (150 MHz, D_2O)

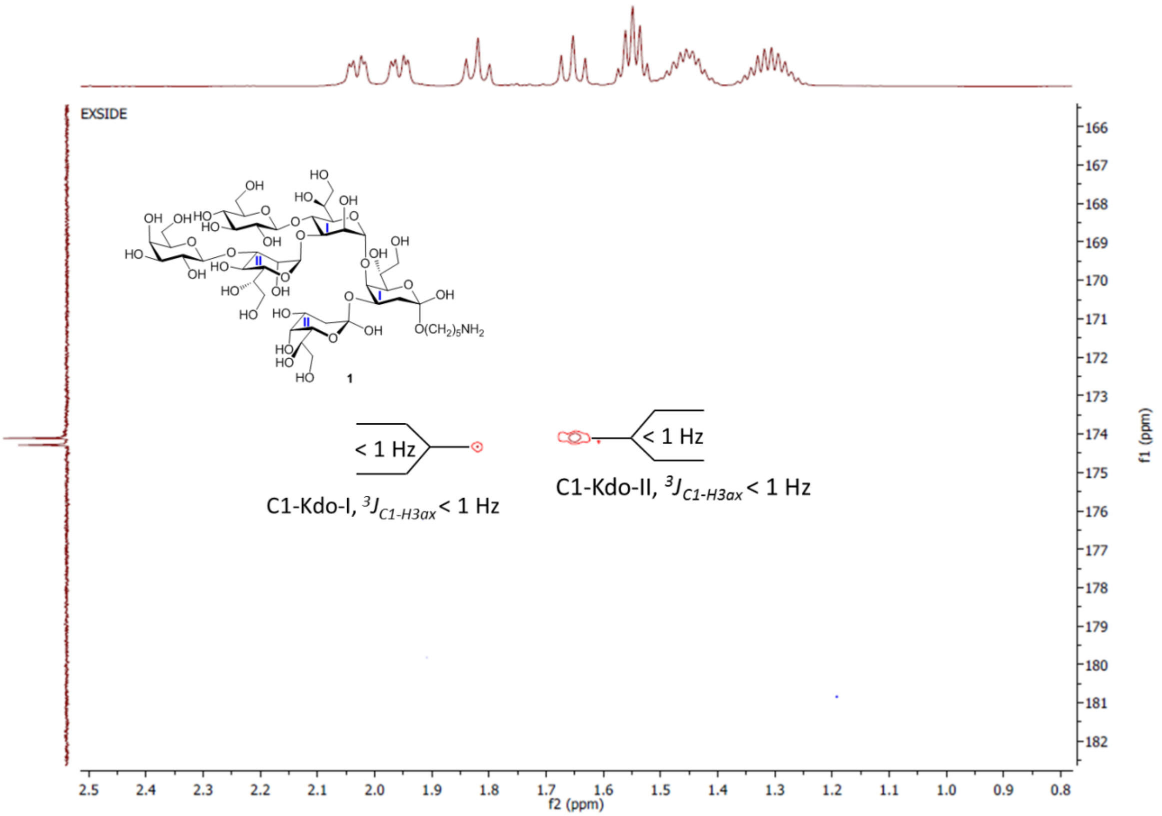





gCOSY
1
O(CH2)5NH2
f2 (ppm)
f1 (ppm)

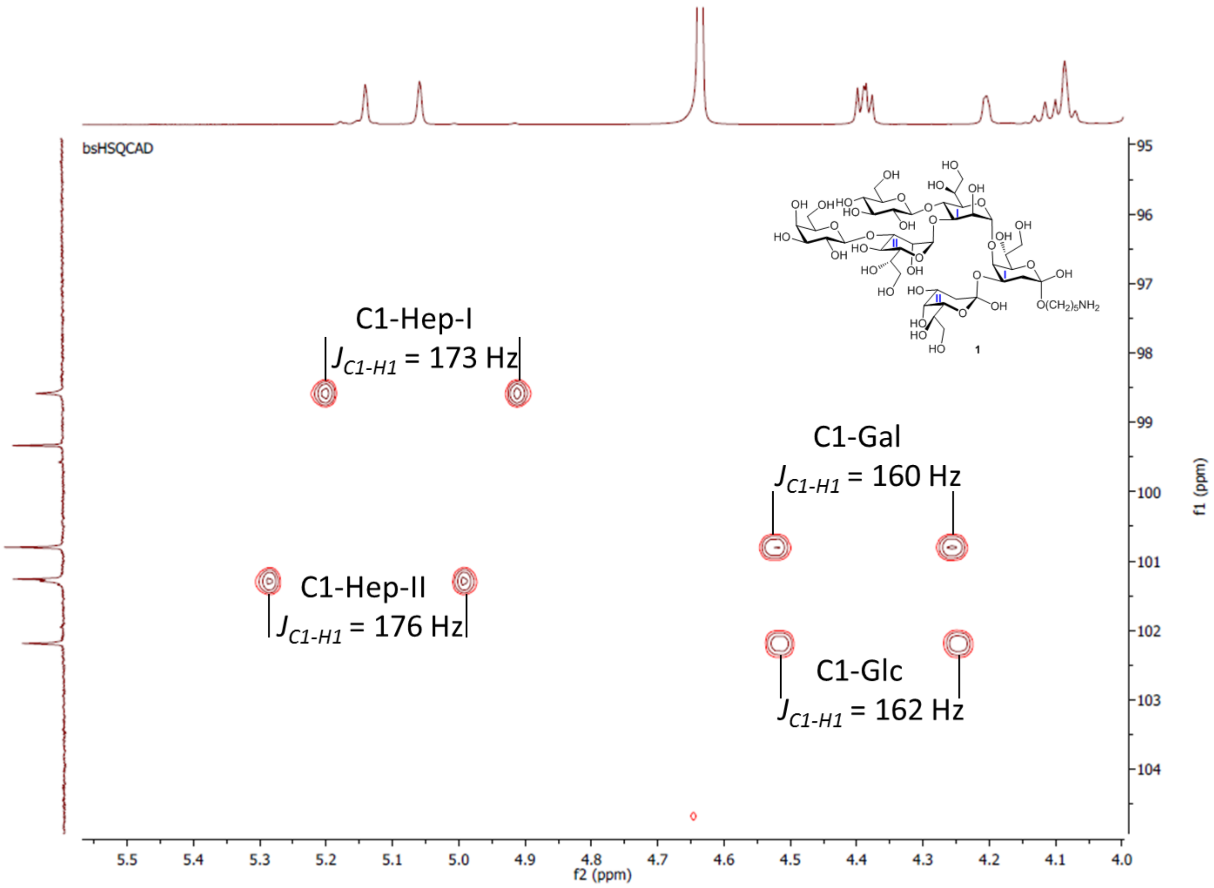

zTCOSY
1
O(CH2)5NH2
f2 (ppm)
f1 (ppm)

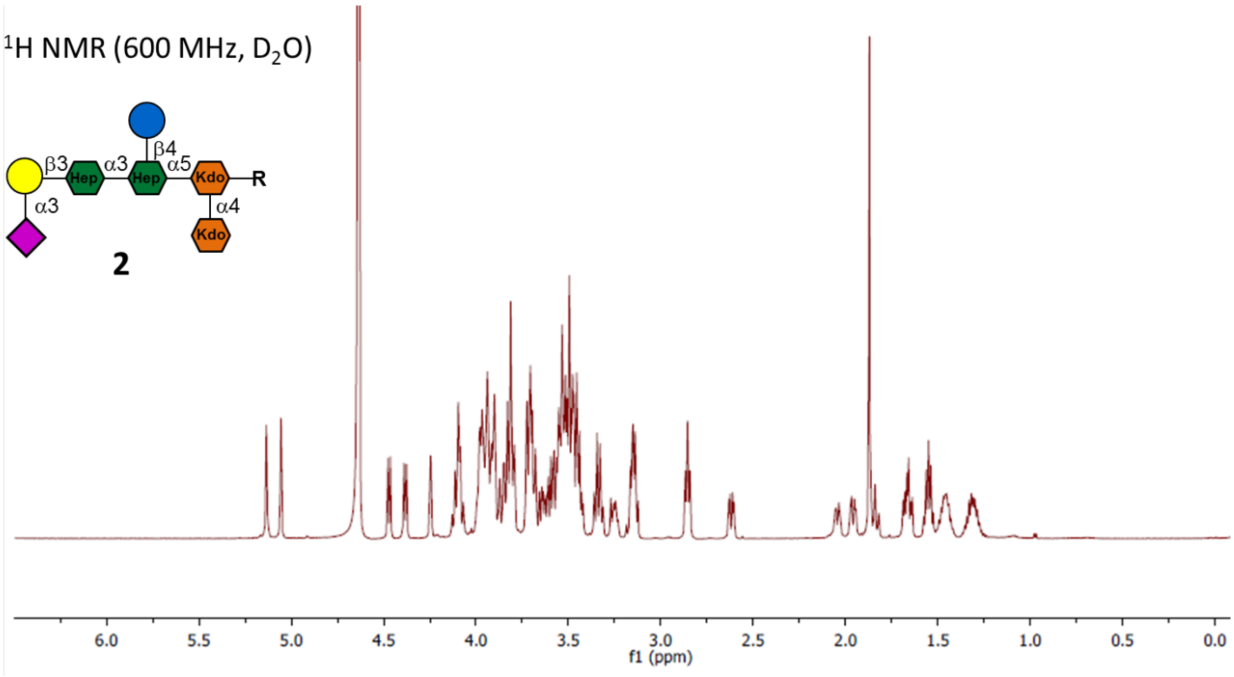


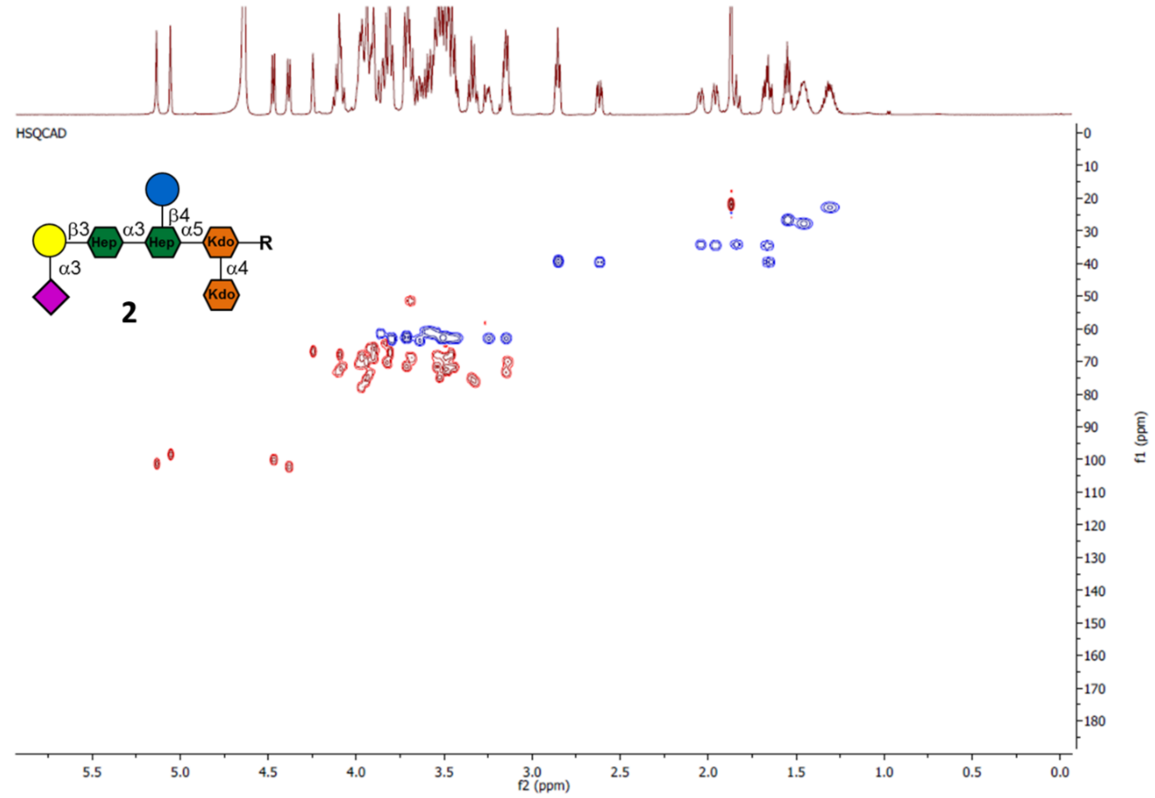


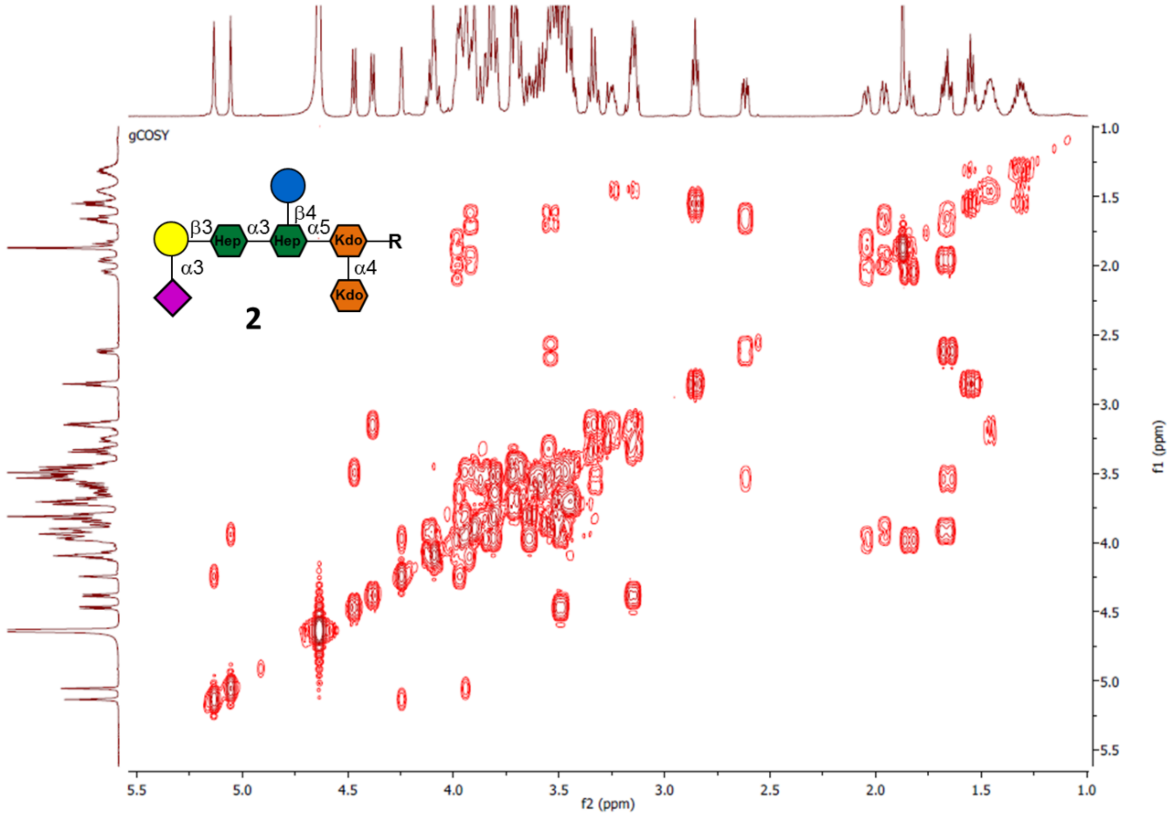
C1-Kdo-I, $^3J_{C1\text{-}H3ax}$ < 1 Hz

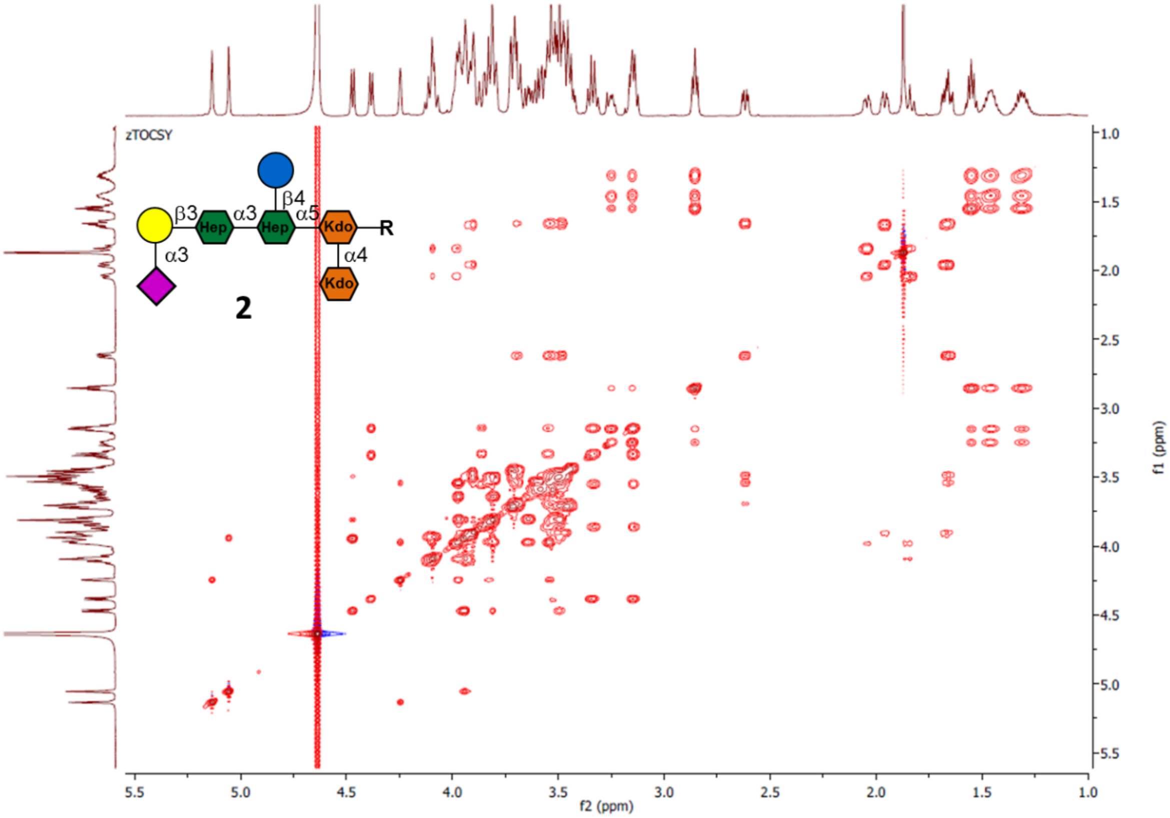
C1-Kdo-II, $^3J_{C1\text{-}H3ax}$ < 1 Hz

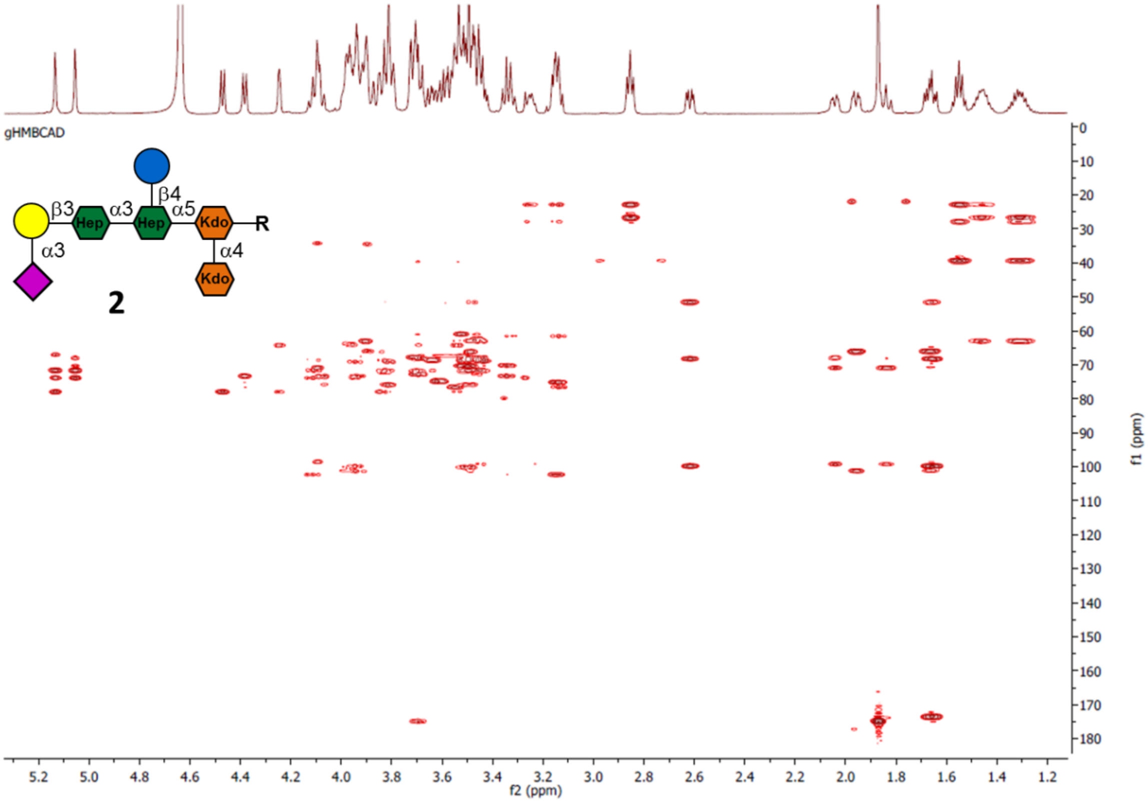

bsHSQCAD
C1-Hep-I
J_{C1-H1} = 173 Hz
C1-Gal
J_{C1-H1} = 160 Hz
C1-Hep-II
J_{C1-H1} = 176 Hz
C1-Glc
J_{C1-H1} = 162 Hz
O(CH2)5NH2
1
95
96
97
98
99
100
101
102
103
104
f1 (ppm)
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
f2 (ppm)

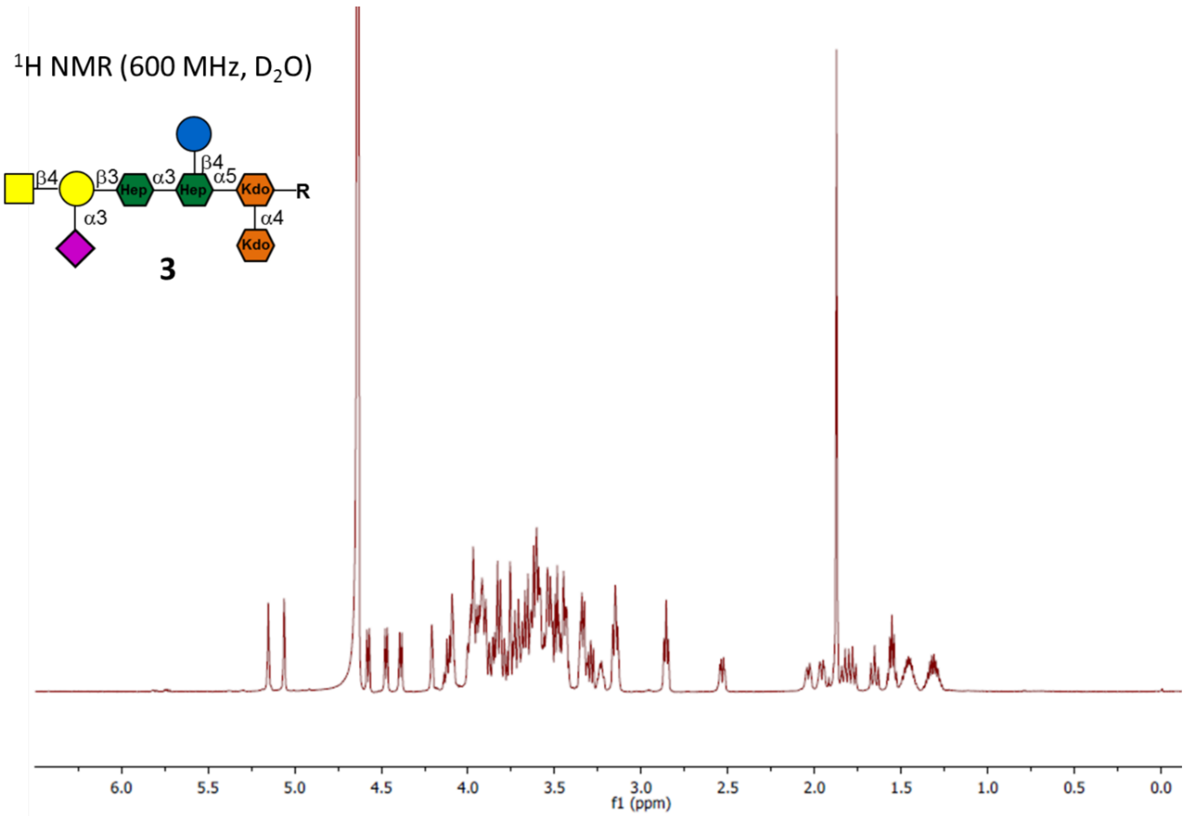

^{1}H NMR (600 MHz, D$_2$O)
β3
α3
Hep
Hep
β4
α5
Kdo
R
α3
α4
Kdo
2
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


HSQCAD
β3
Hep
α3
Hep
β4
α5
Kdo
R
α3
α4
Kdo
2
f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
f2 (ppm)
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

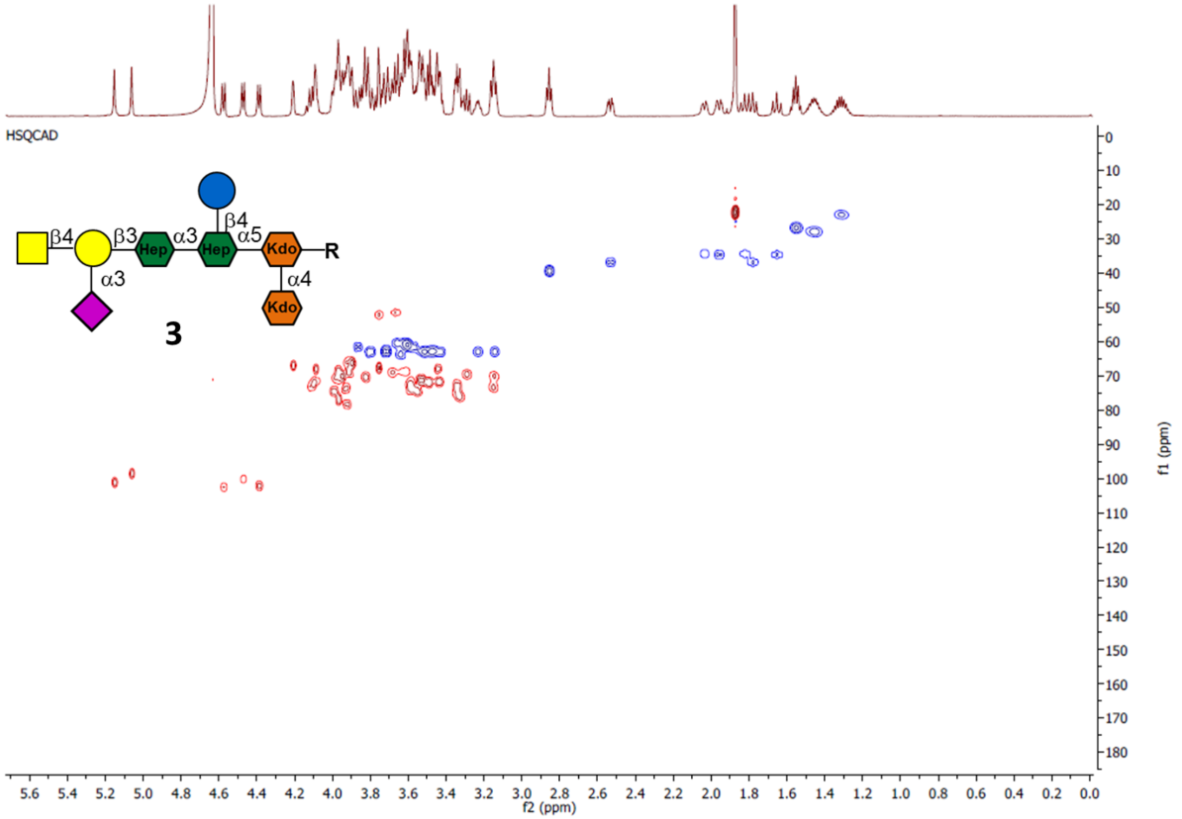

gCOSY
β3
Hep
α3
Hep
β4
α5
Kdo
R
α3
α4
Kdo
2
f1 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
f2 (ppm)
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0


zTOCSY
β3
α3
β4
α5
Hep
Hep
Kdo
R
α3
α4
Kdo
2
f2 (ppm)
f1 (ppm)
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

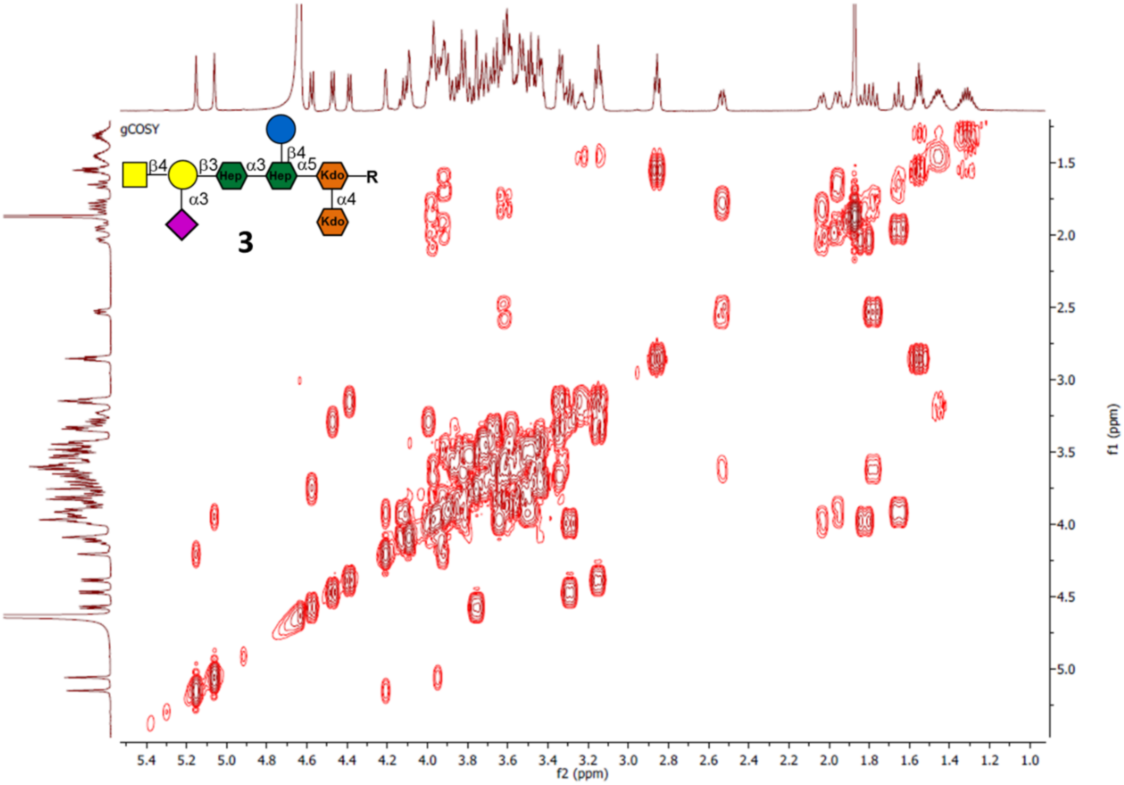

gHMBCAD
β3
α3
β4
α5
Hep
Hep
Kdo
R
α3
α4
Kdo
2
f2 (ppm)
f1 (ppm)
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180

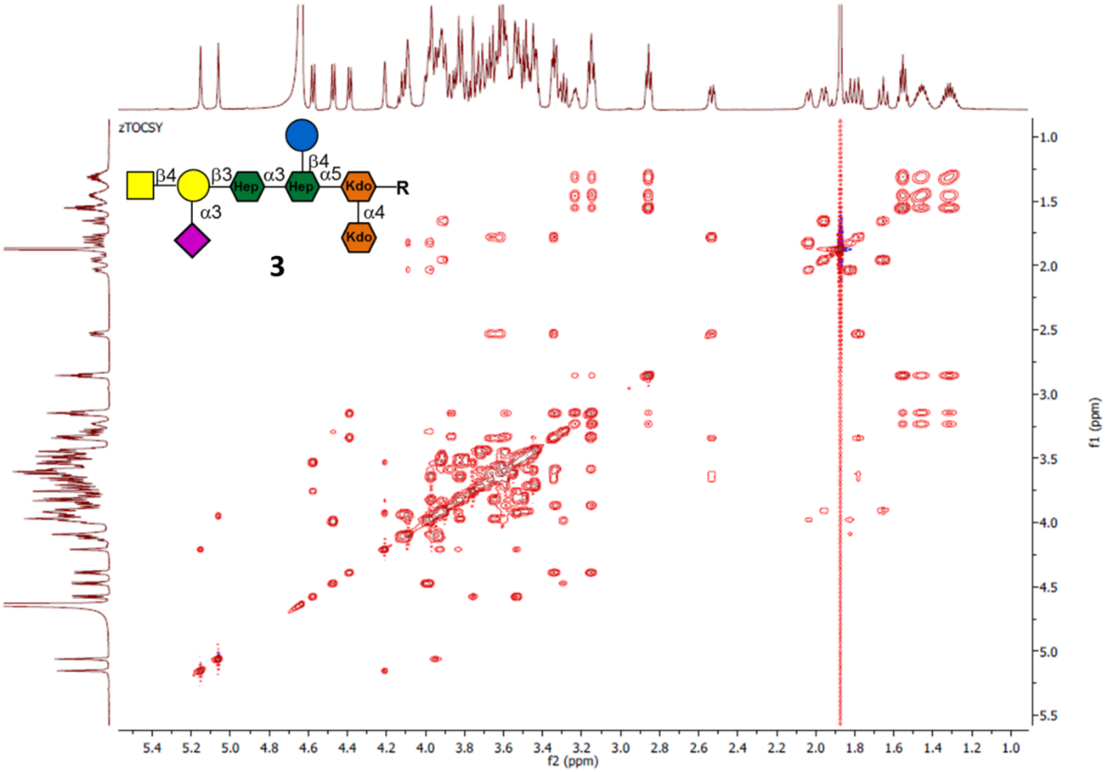

^{1}H NMR (600 MHz, D_2O)

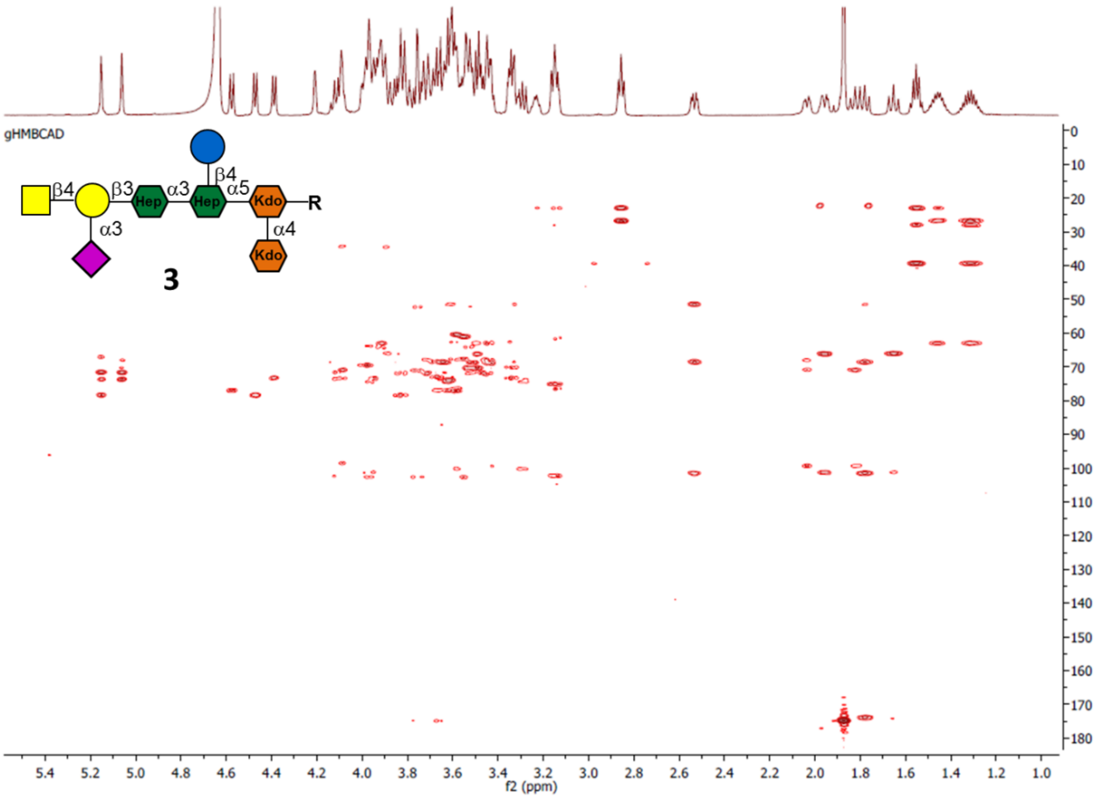
3


HSQCAD

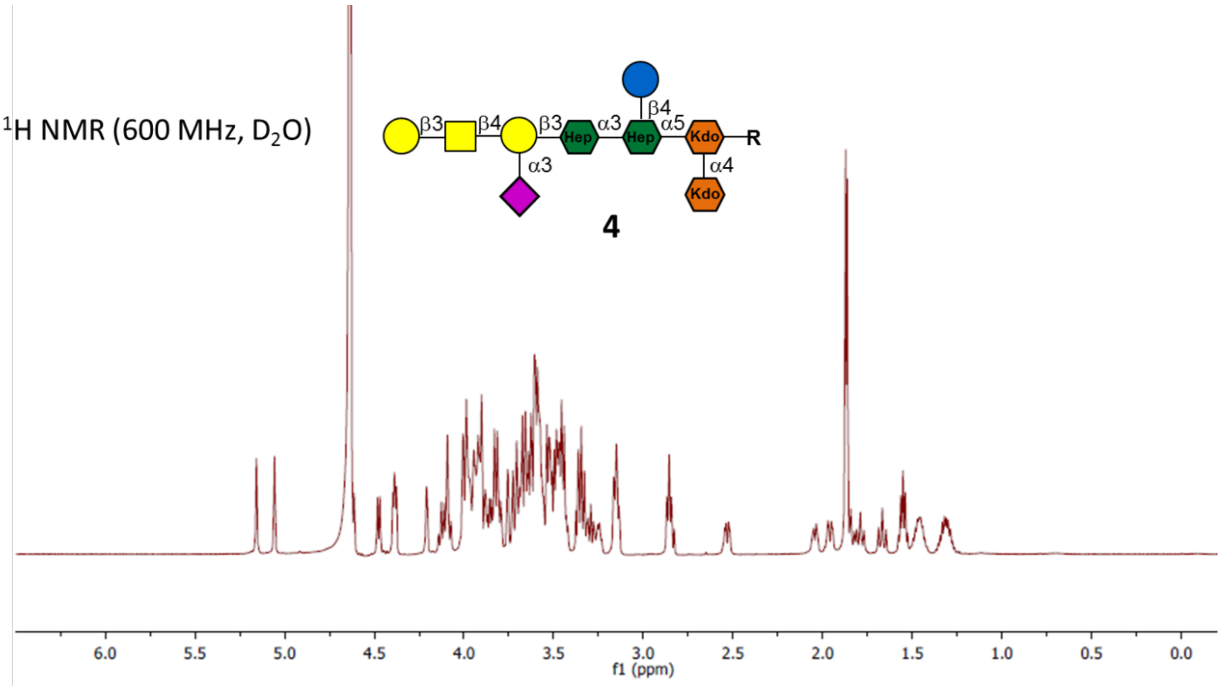
3


gCOSY
β4
β3
α3
β4
α5
α3
α4
Hep
Hep
Kdo
Kdo
R
3
f2 (ppm)
f1 (ppm)


zTOCSY
β4
β3
α3
β4
α5
α3
α4
Hep
Hep
Kdo
Kdo
R
3
f2 (ppm)
f1 (ppm)

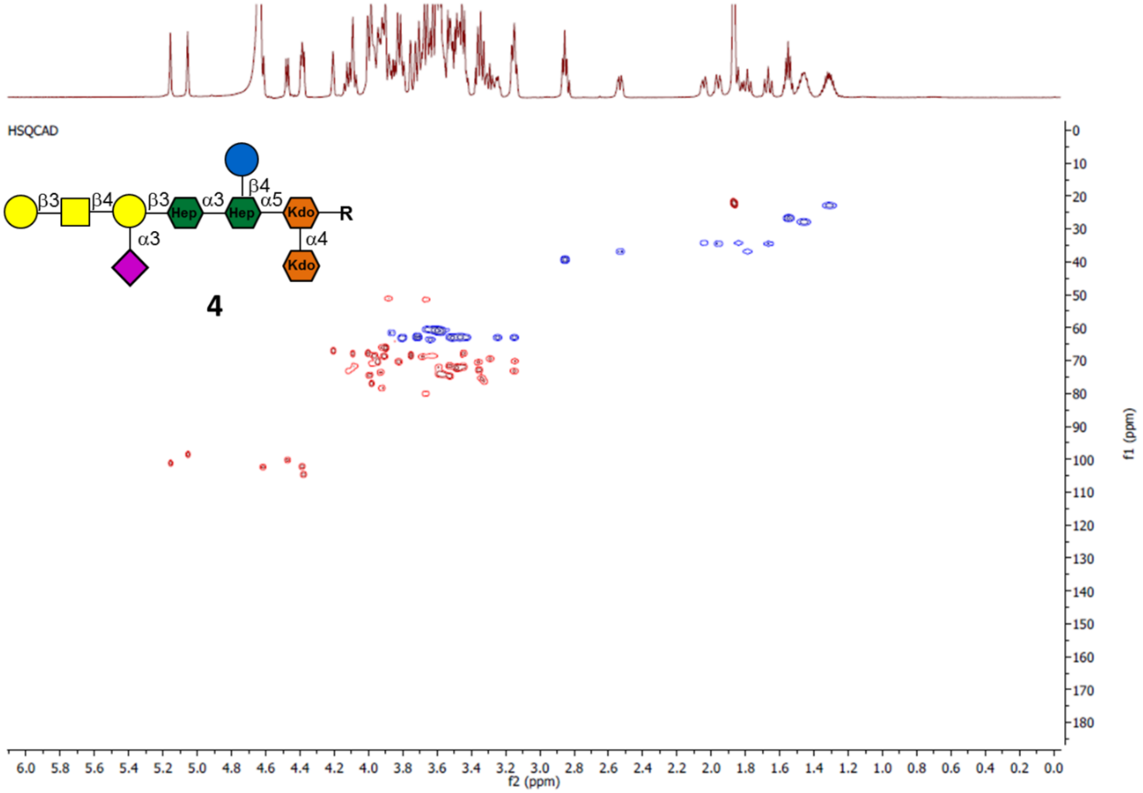


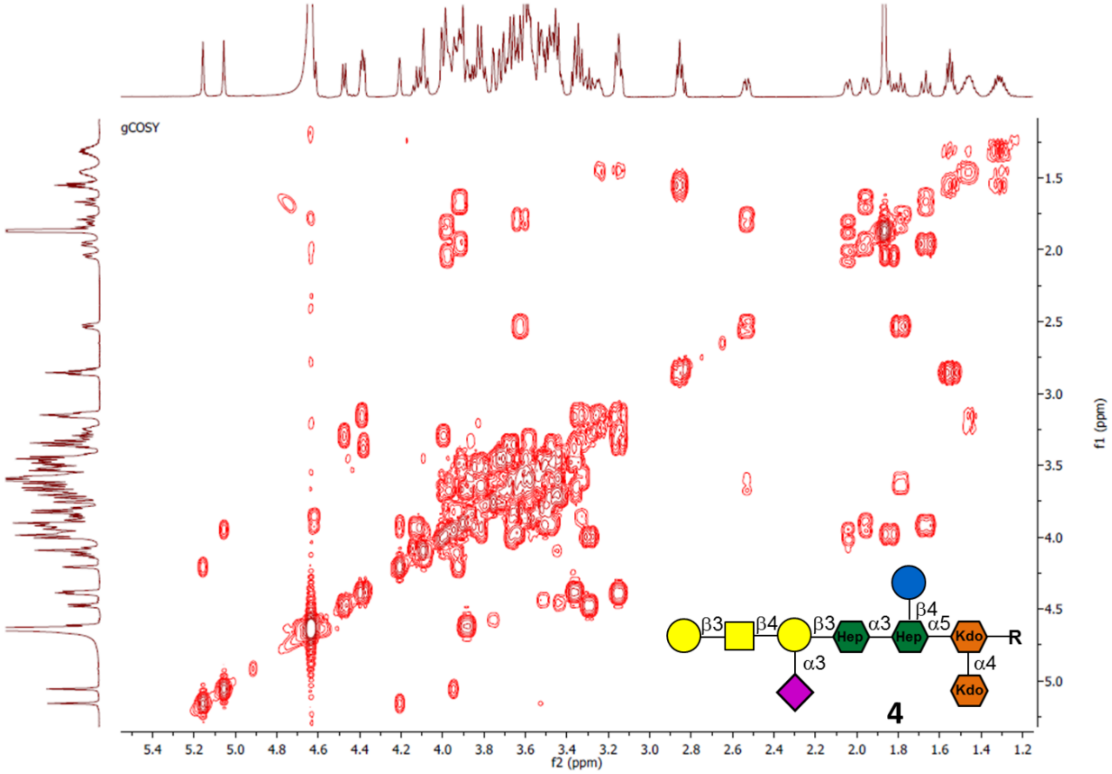
3

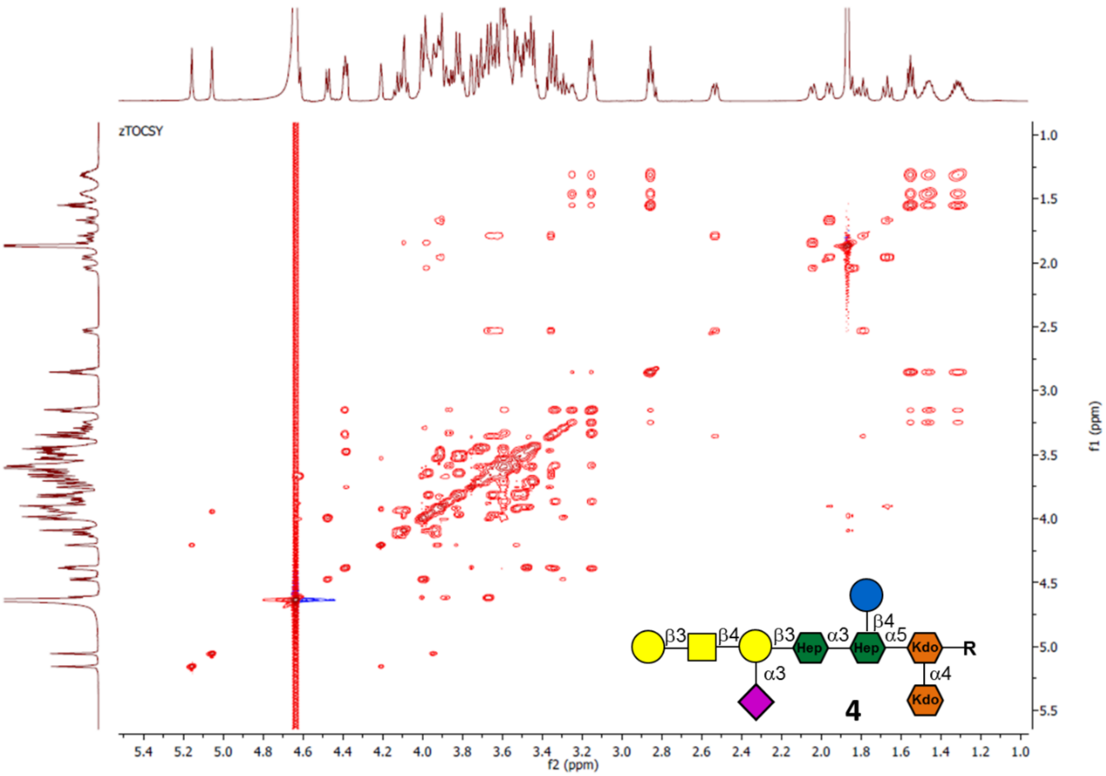


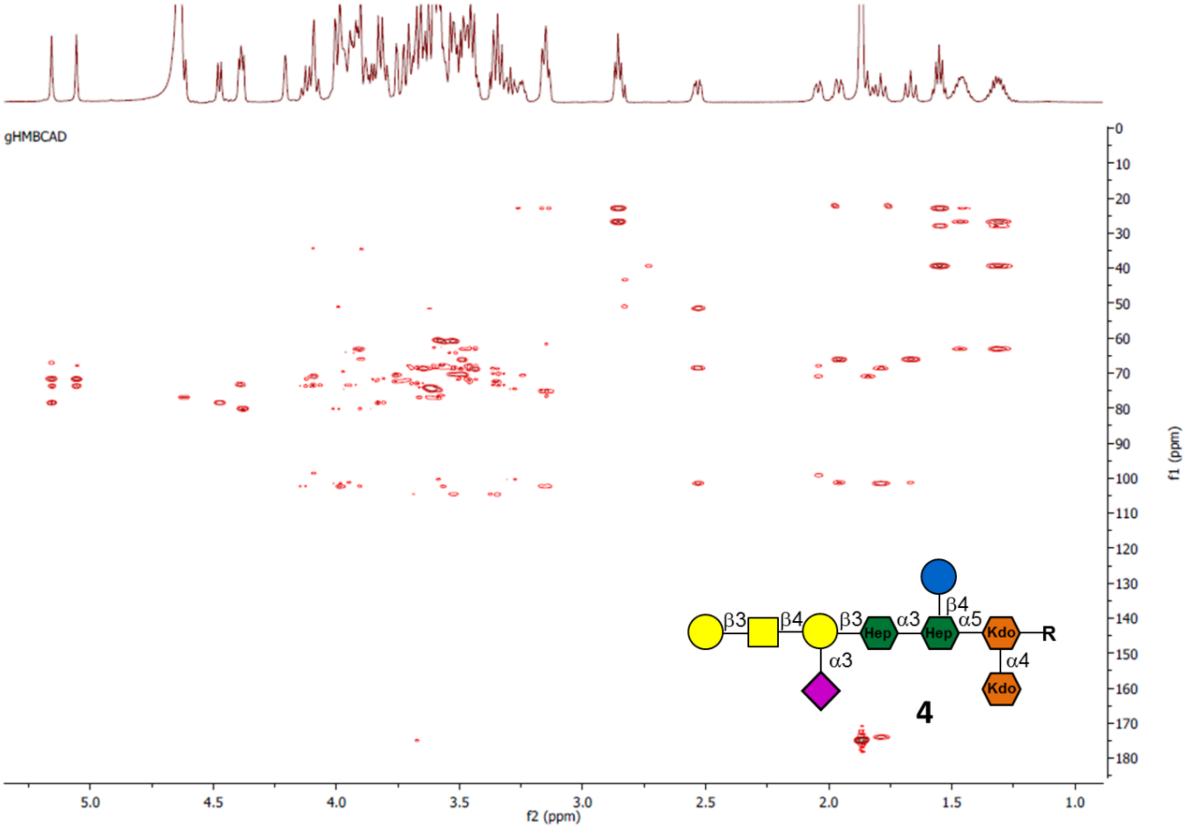
^{1}H NMR (600 MHz, D$_2$O)

4

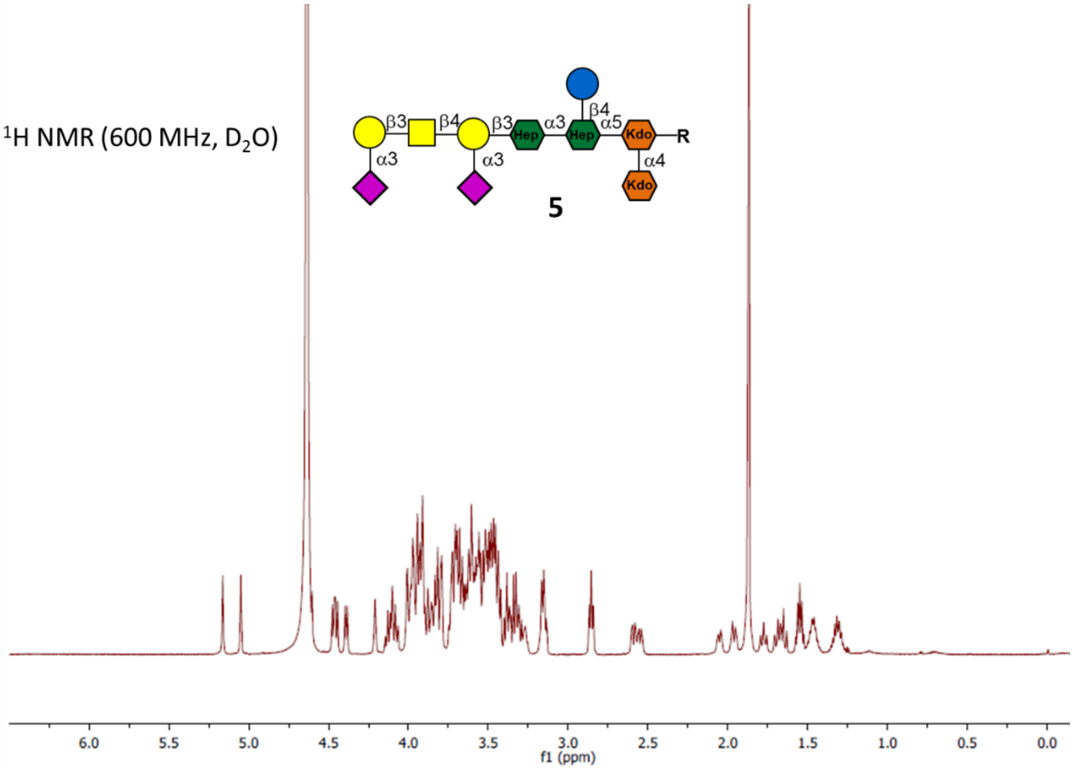

HSQCAD
β3
β4
β3
Hep
α3
Hep
β4
α5
Kdo
R
α3
α4
Kdo
4
f1 (ppm)
f2 (ppm)
6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180


gCOSY
β3
β4
β3
Hep
α3
Hep
β4
α5
Kdo
R
α3
α4
Kdo
4
f1 (ppm)
f2 (ppm)
5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2
1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0


zTOCSY
β3
β4
β3
α3
β4
α5
α3
α4
Hep
Hep
Kdo
Kdo
R
4
f2 (ppm)
f1 (ppm)


gHMBCAD
β3
β4
β3
α3
β4
α5
α3
α4
Hep
Hep
Kdo
Kdo
R
4
f2 (ppm)
f1 (ppm)

^1H NMR (600 MHz, D_2O)



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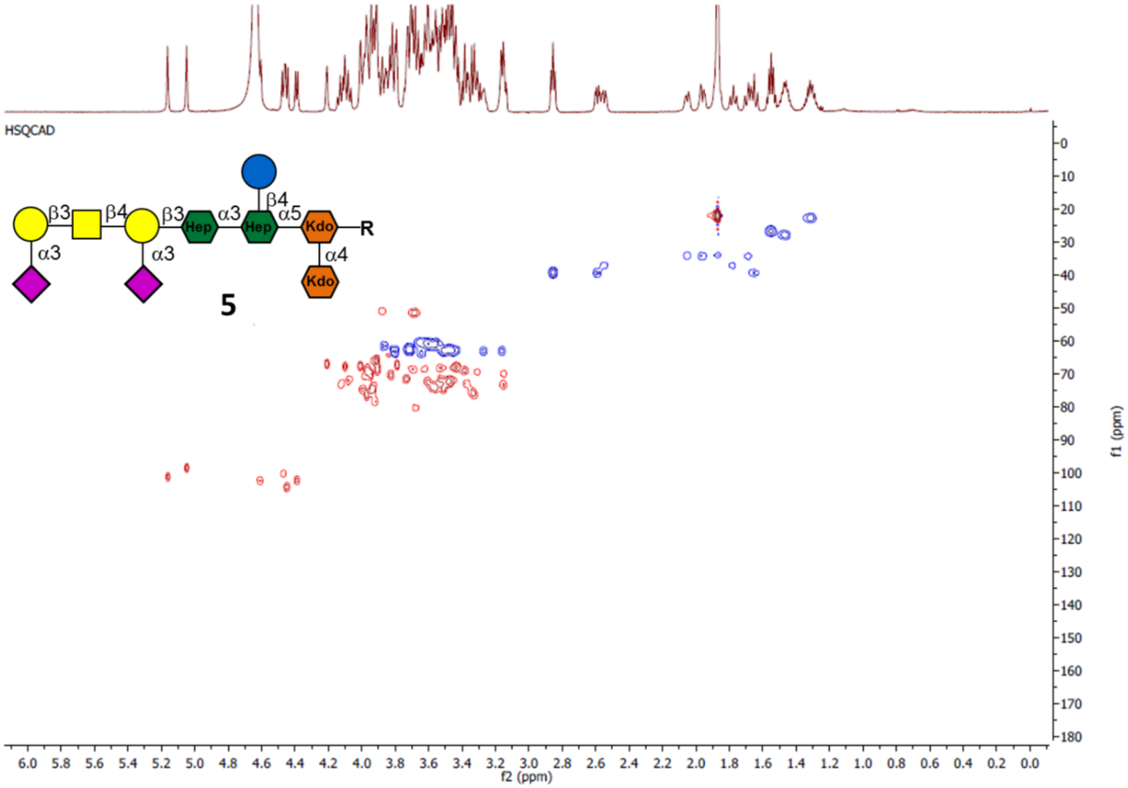

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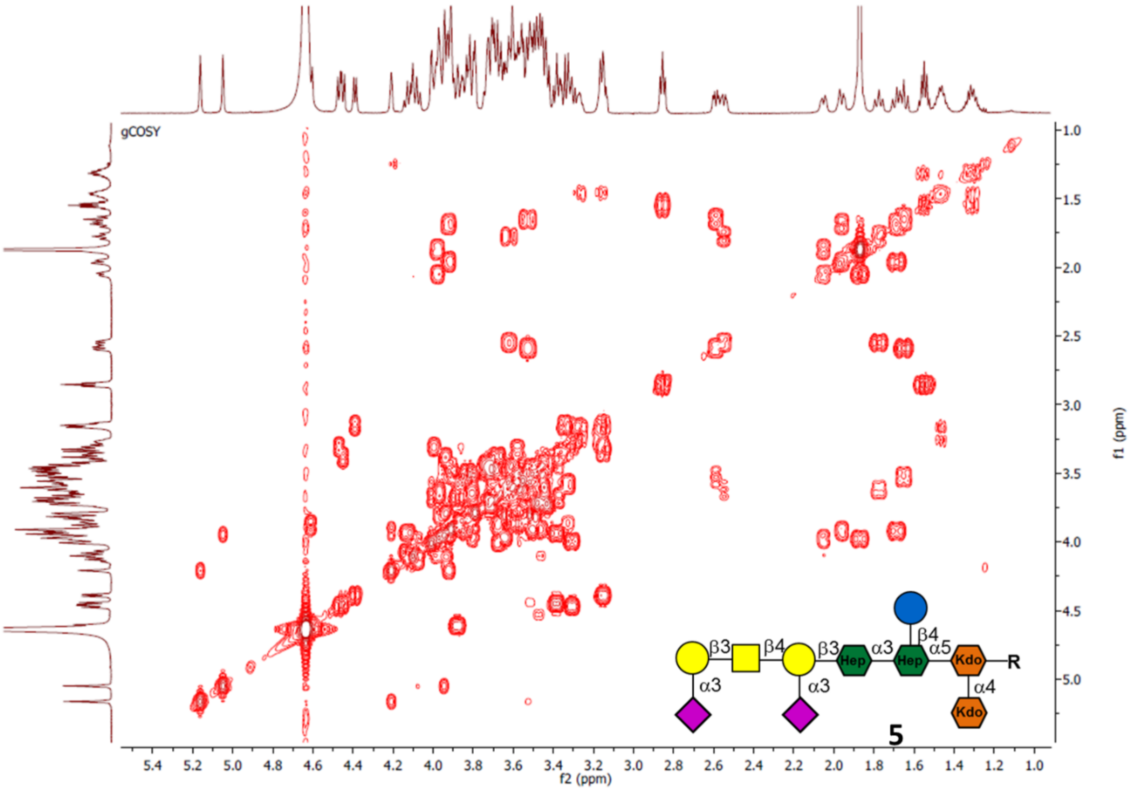
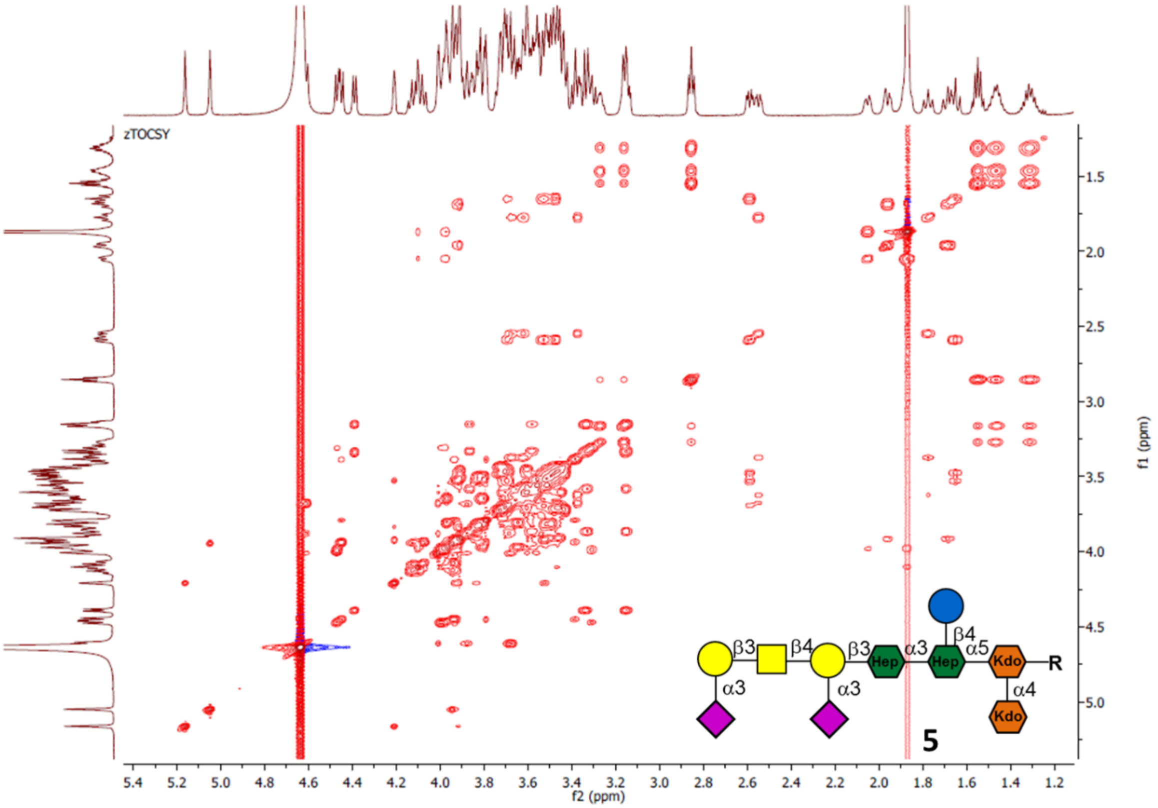
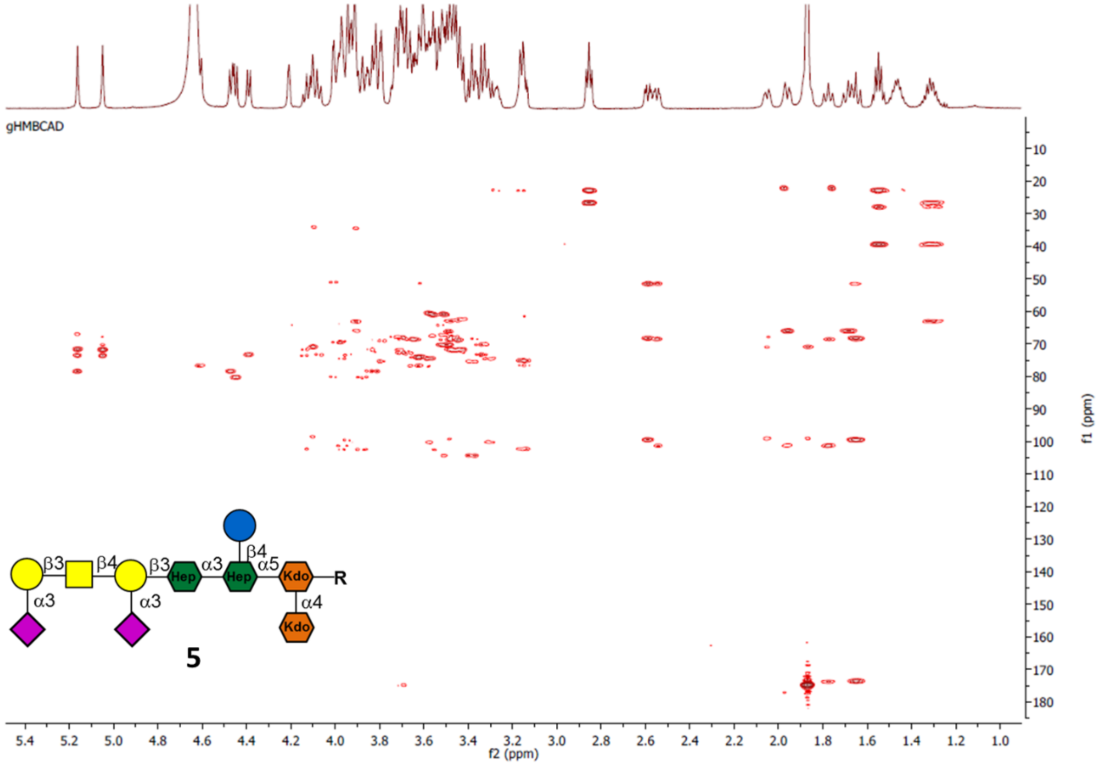
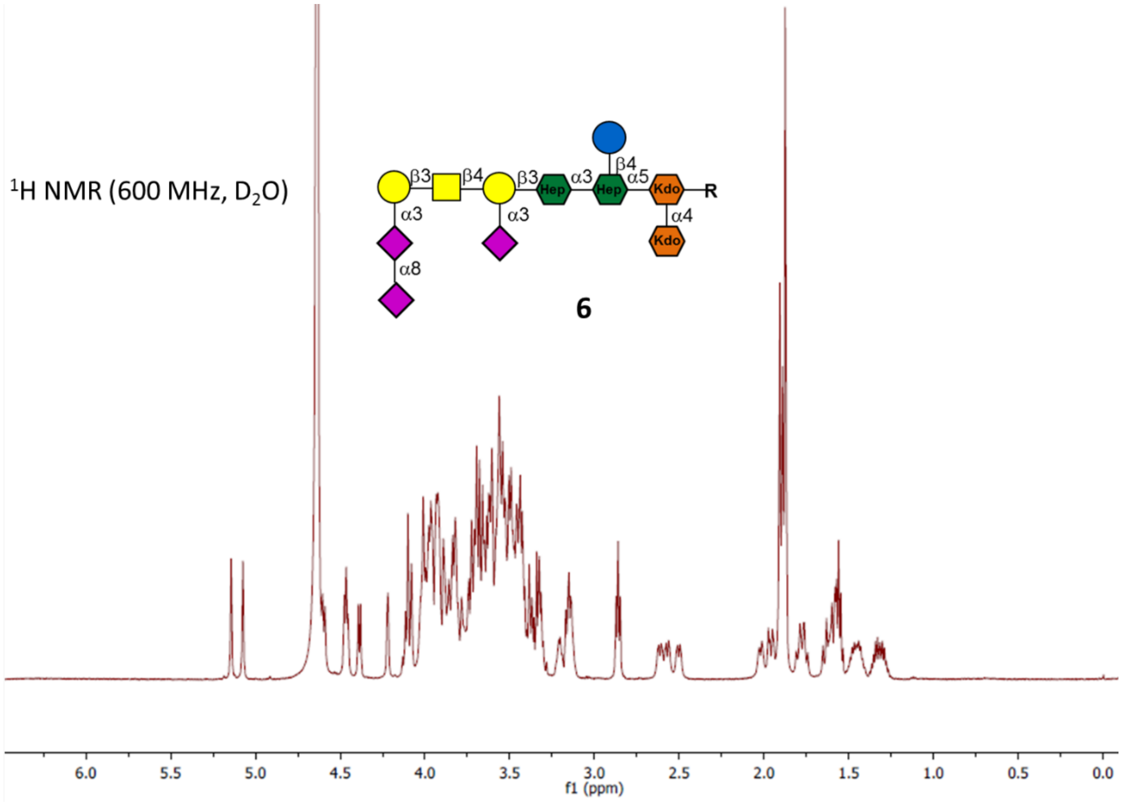

gCOSY
f2 (ppm)
f1 (ppm)
5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0
1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0
β3 β4 β3 α3 β4 α5
α3 α3 α4
Hep Hep Kdo Kdo
R
5


zTOCSY
f2 (ppm)
f1 (ppm)
5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2
1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0
β3 β4 β3 α3 β4 α5
α3 α3 α4
Hep Hep Kdo Kdo
R
5

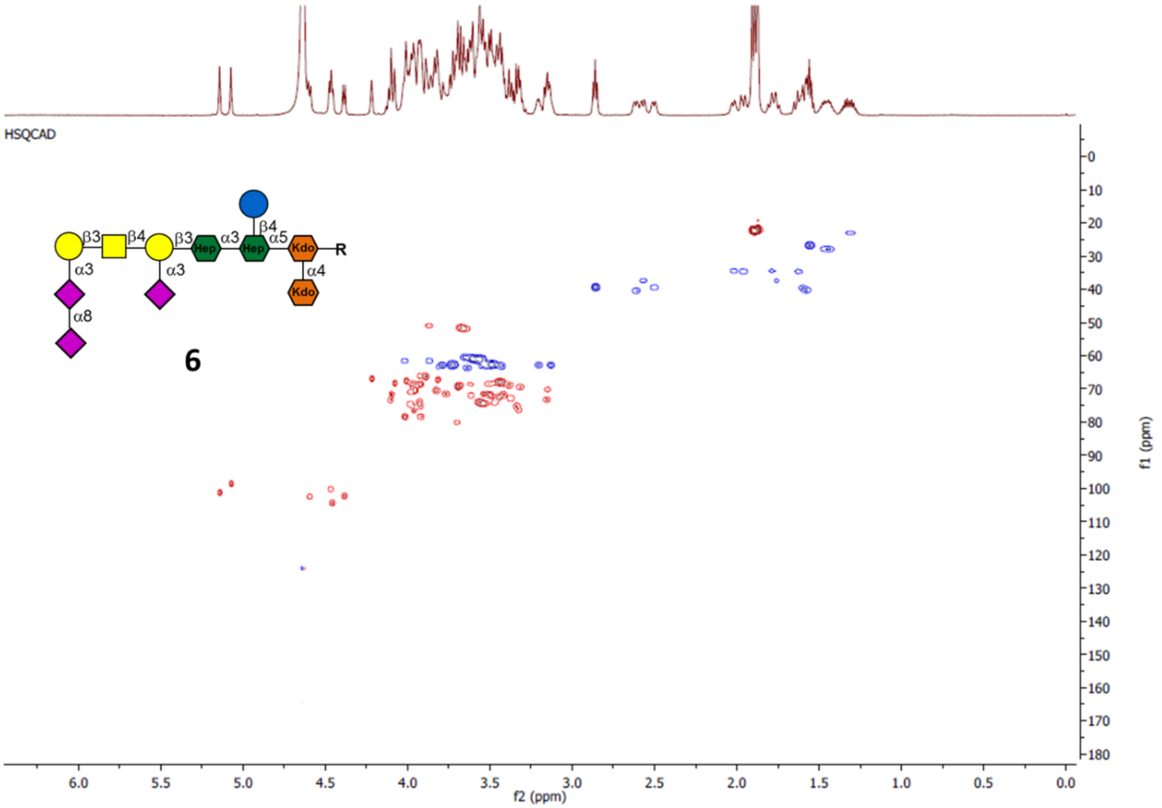


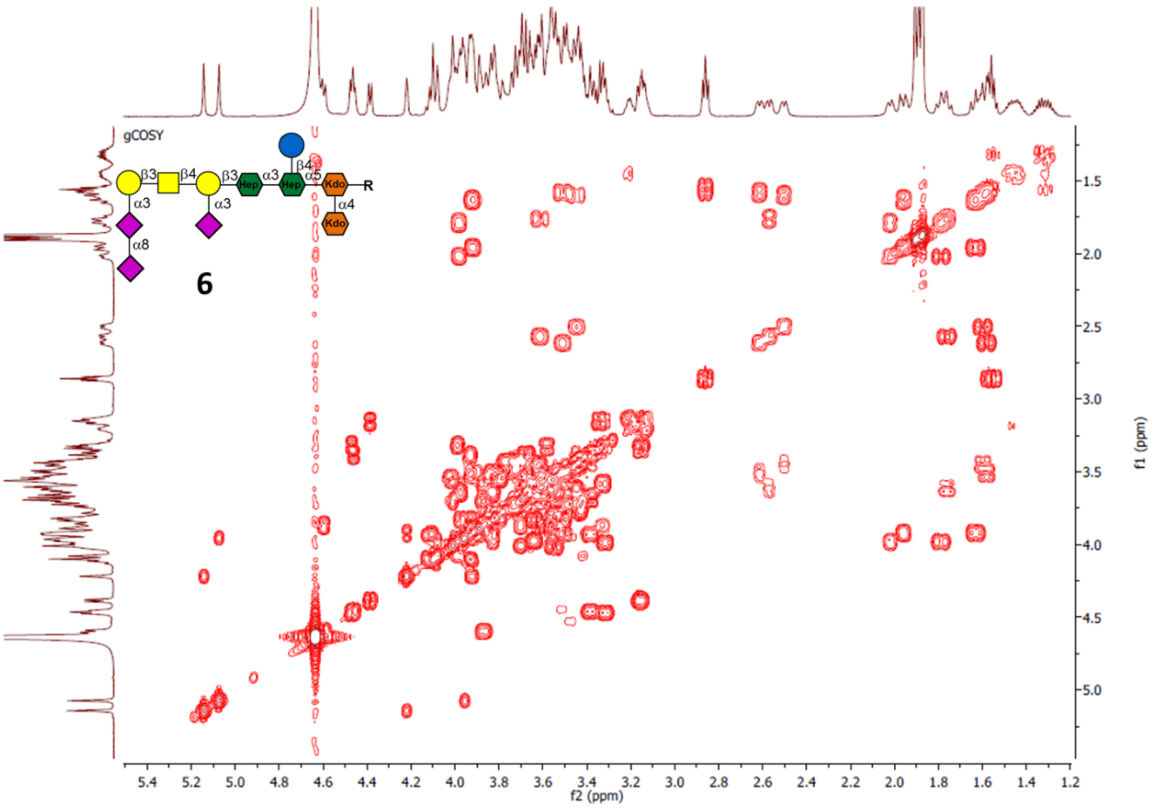
5

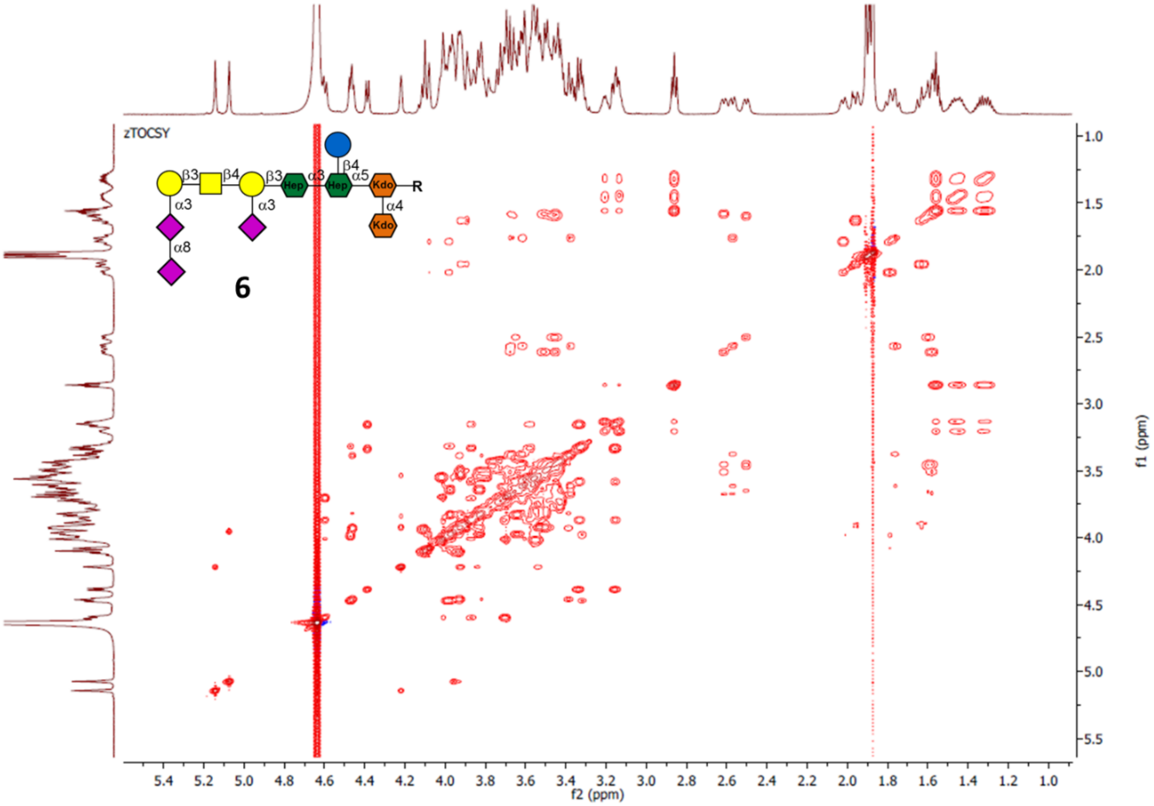


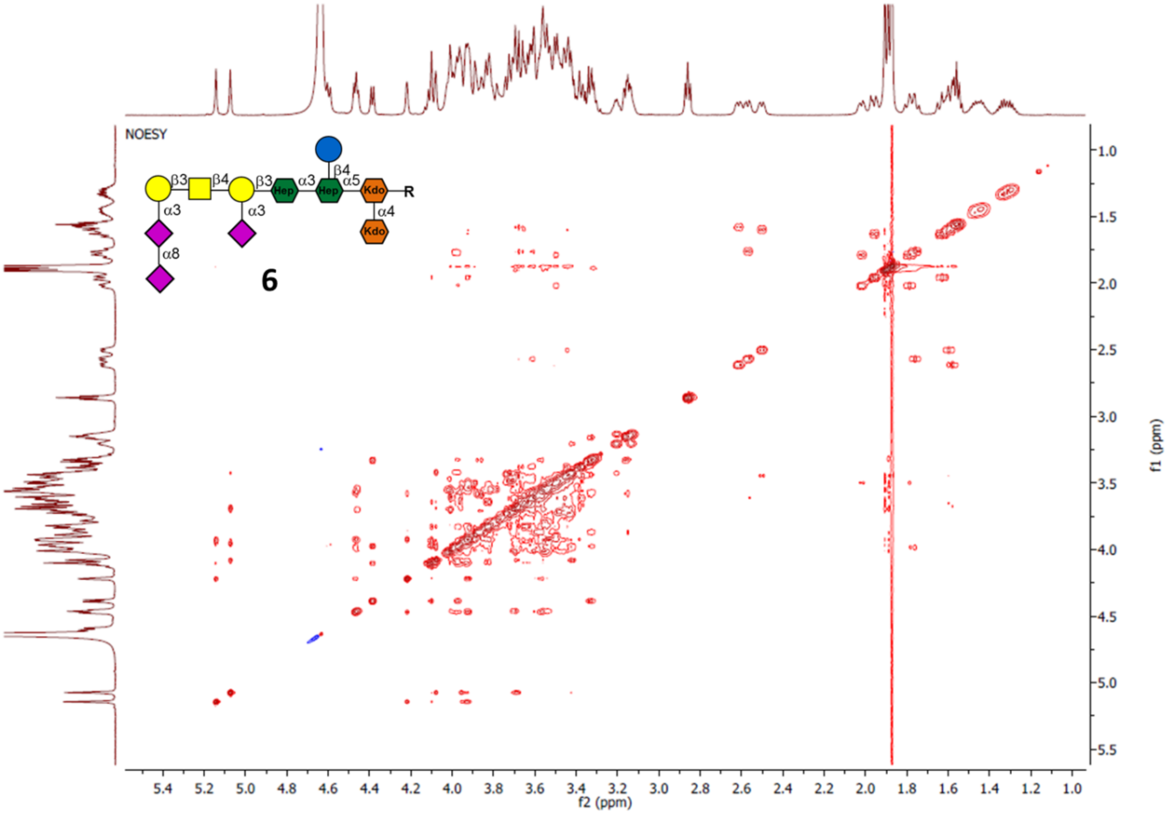
^{1}H NMR (600 MHz, D_2O)

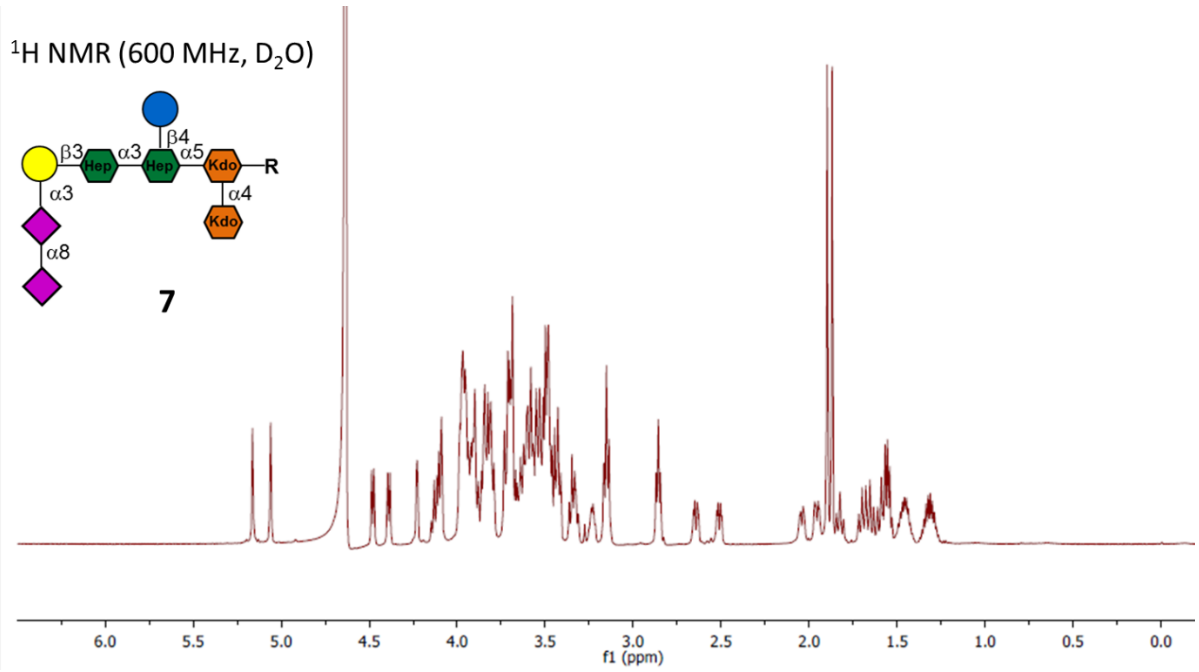
6

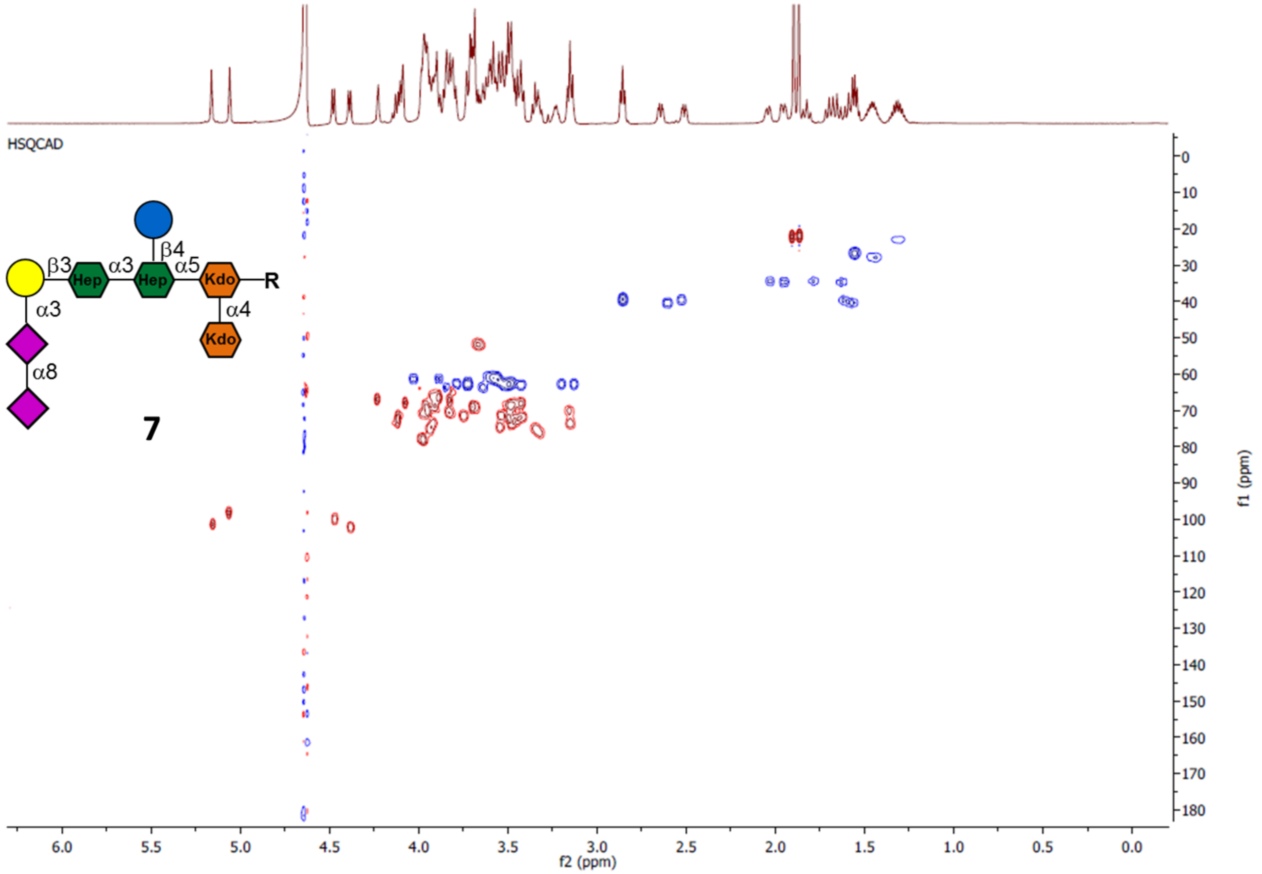

HSQCAD
β3
β4
β3
β3
α3
β4
α5
Hep
Hep
Kdo
R
α3
α3
α4
Kdo
α8
6
f1 (ppm)
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

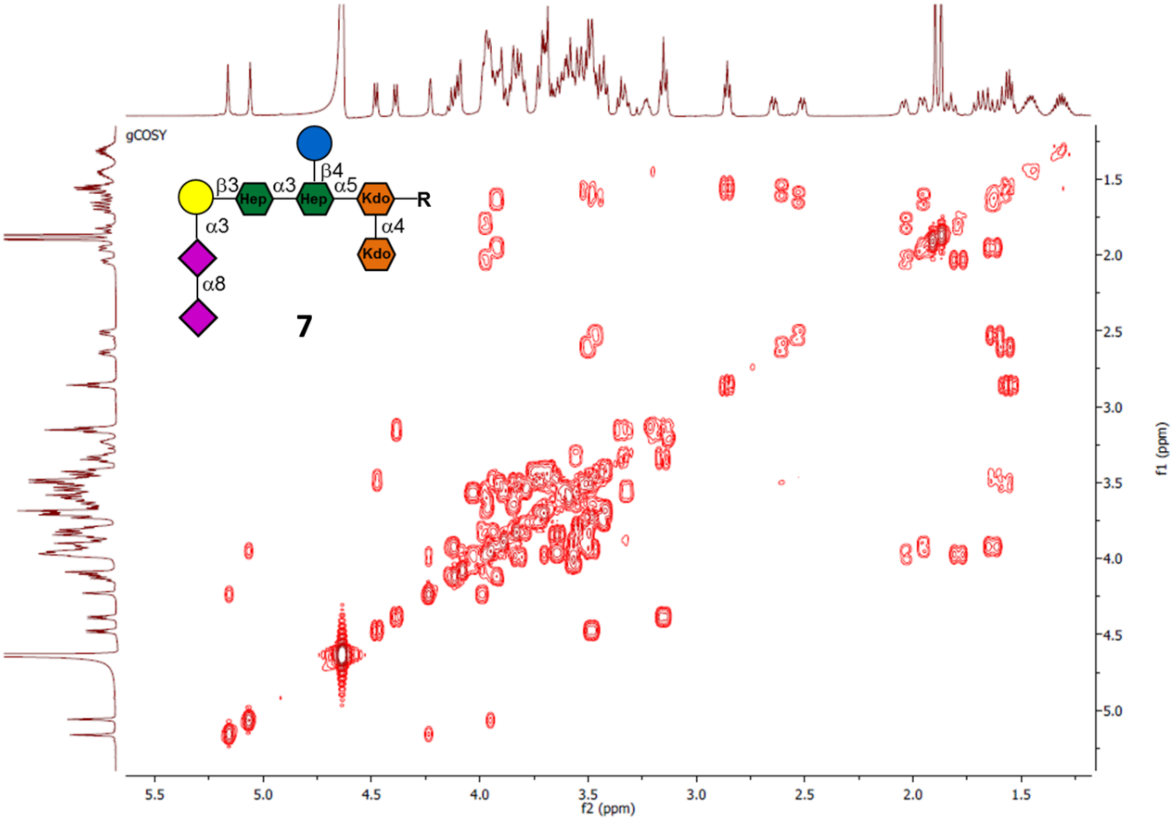

gCOSY
β3
β4
β3
α3
β4
α5
Hep
Hep
Kdo
R
α3
α3
α4
Kdo
α8
6
f1 (ppm)
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2

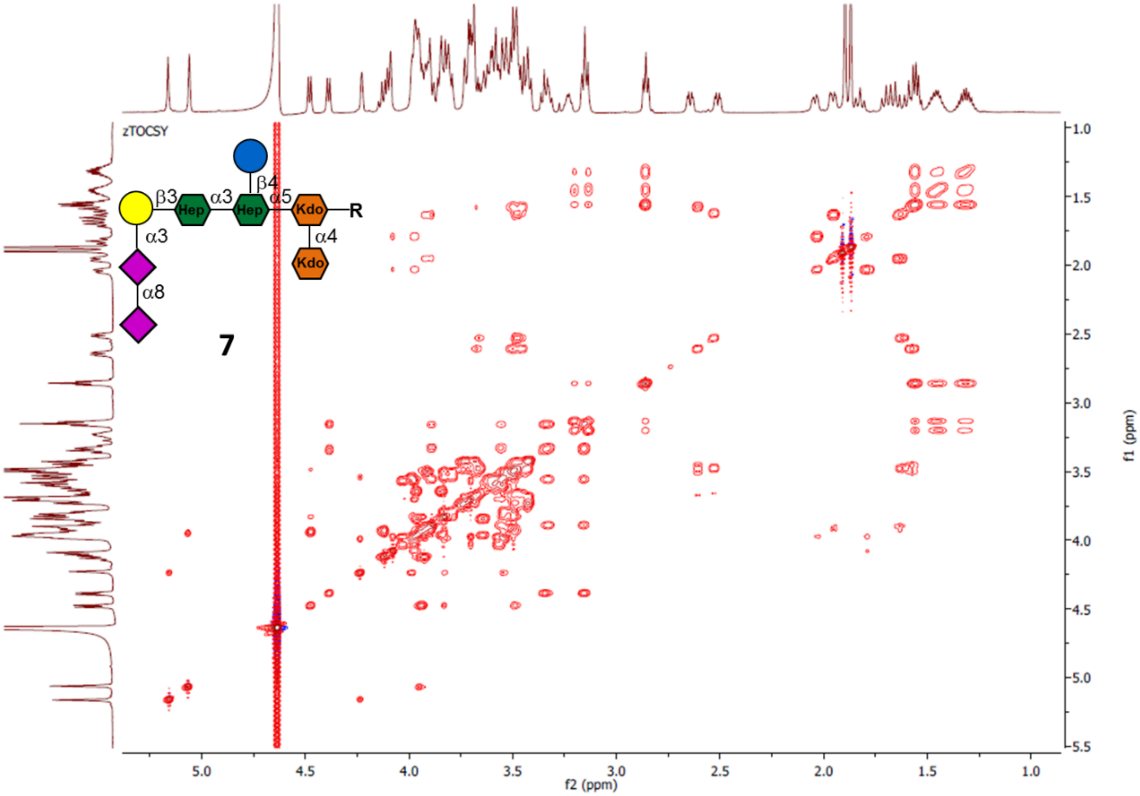

zTOCSY
β3
β4
β3
α3
β4
α5
α3
α3
α8
α4
Hep
Hep
Kdo
Kdo
R
6
f2 (ppm)
f1 (ppm)
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5

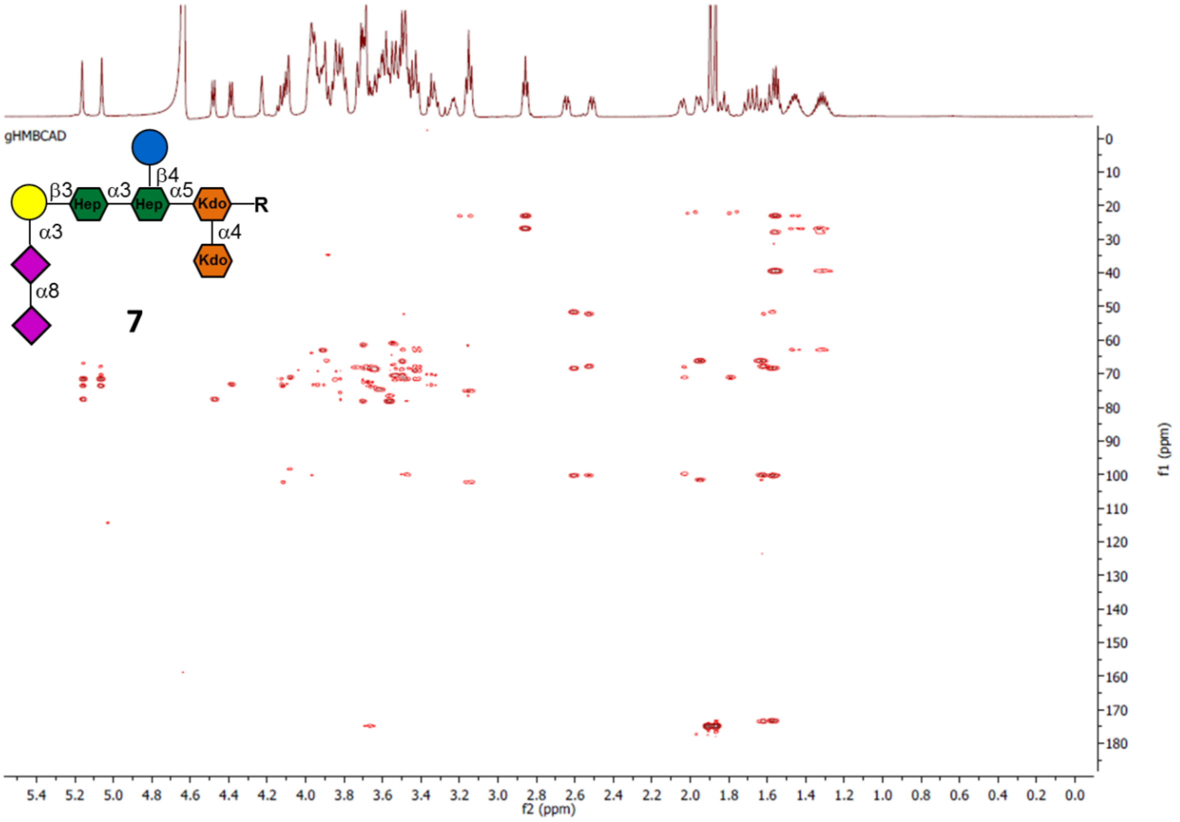

NOESY
β3
β4
β3
α3
β4
α5
α3
α3
α8
α4
Hep
Hep
Kdo
Kdo
R
6
f2 (ppm)
f1 (ppm)
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5


^{1}H NMR (600 MHz, D$_2$O)



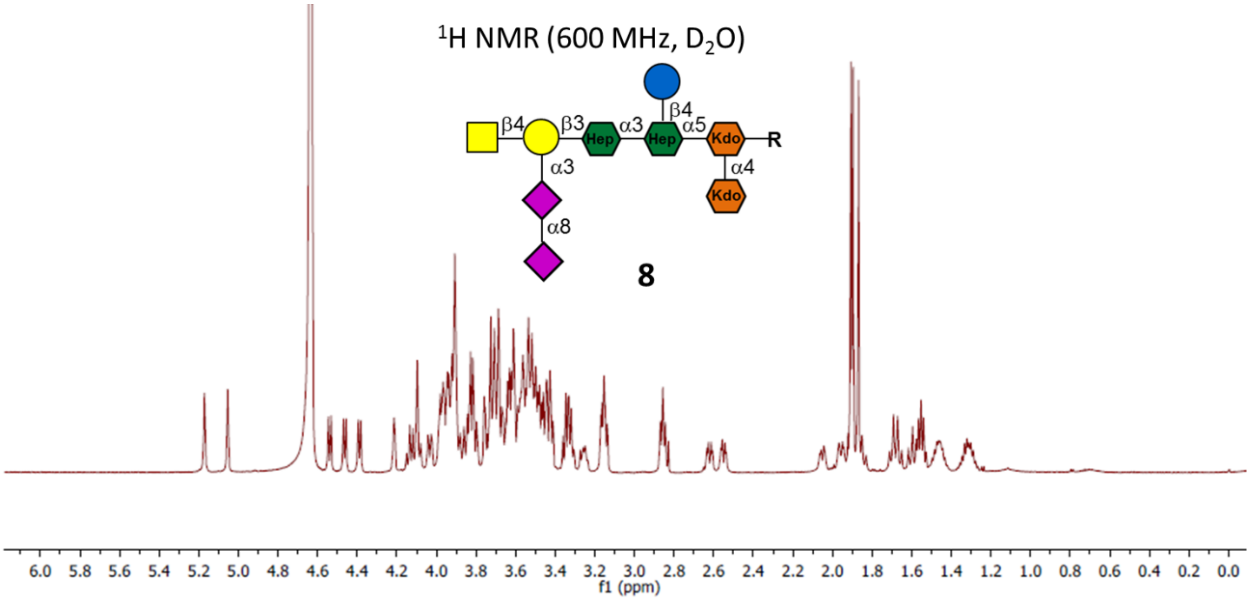

gCOSY
β3
Hep
α3
Hep
β4
α5
Kdo
R
α3
α4
Kdo
α8
7
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
f1 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0


zTOCSY
β3
Hep
α3
Hep
β4
α5
Kdo
R
α3
α4
Kdo
α8
7
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
f1 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5

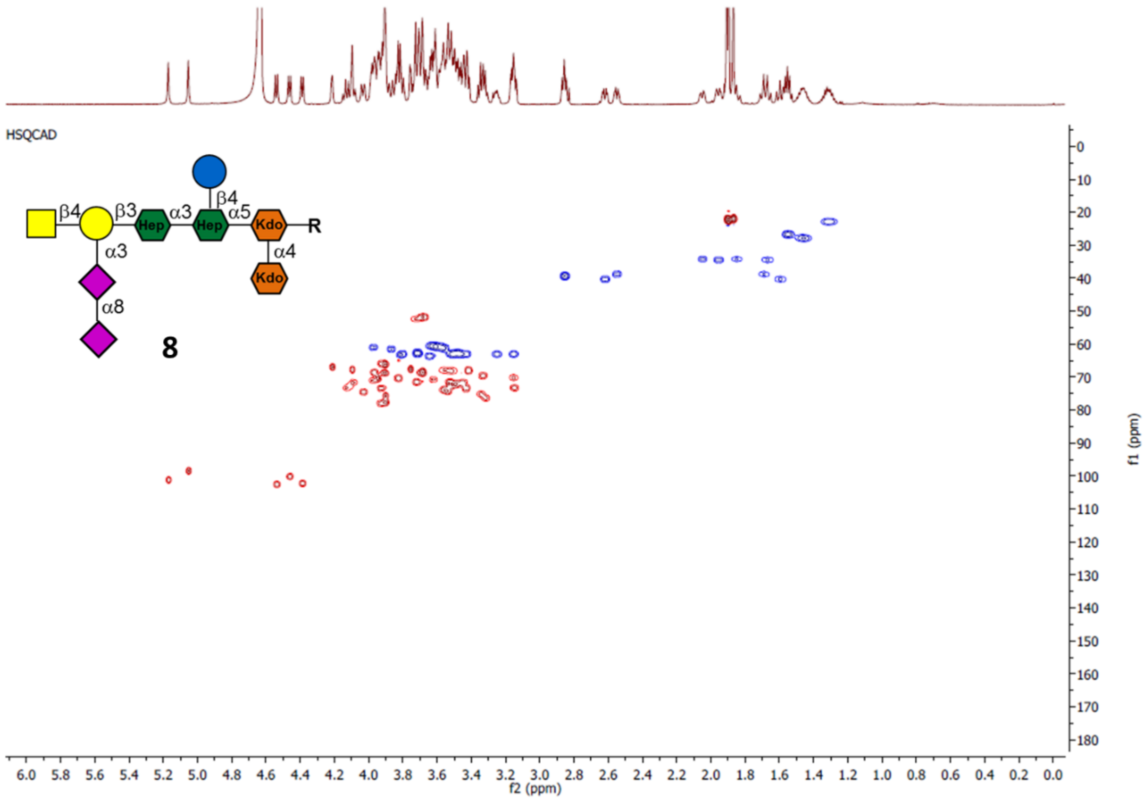


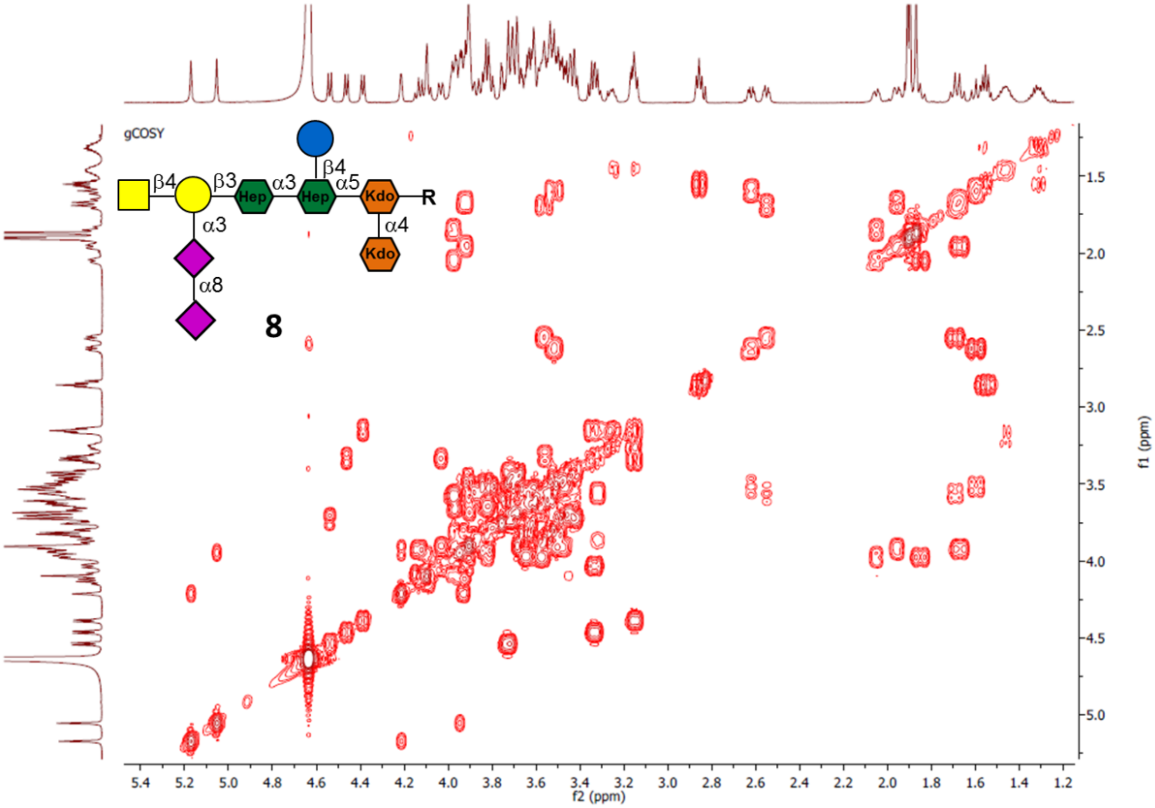
7

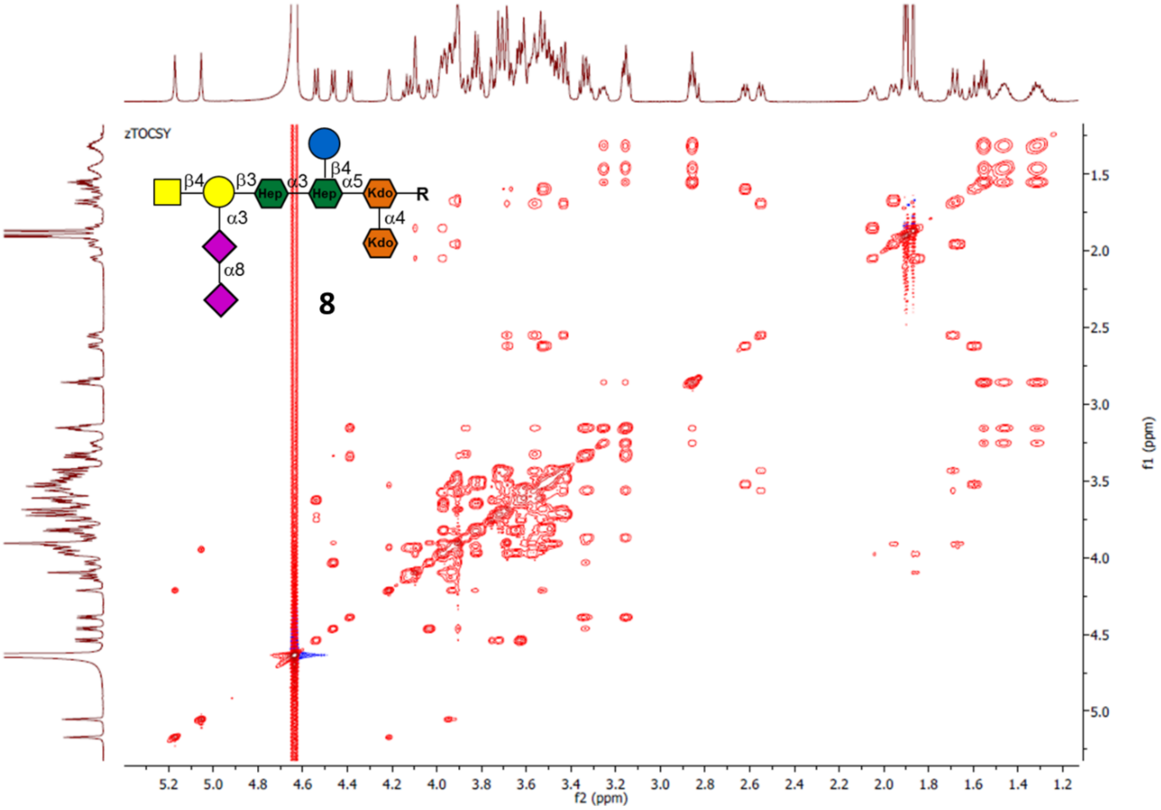
^{1}H NMR (600 MHz, D$_2$O)



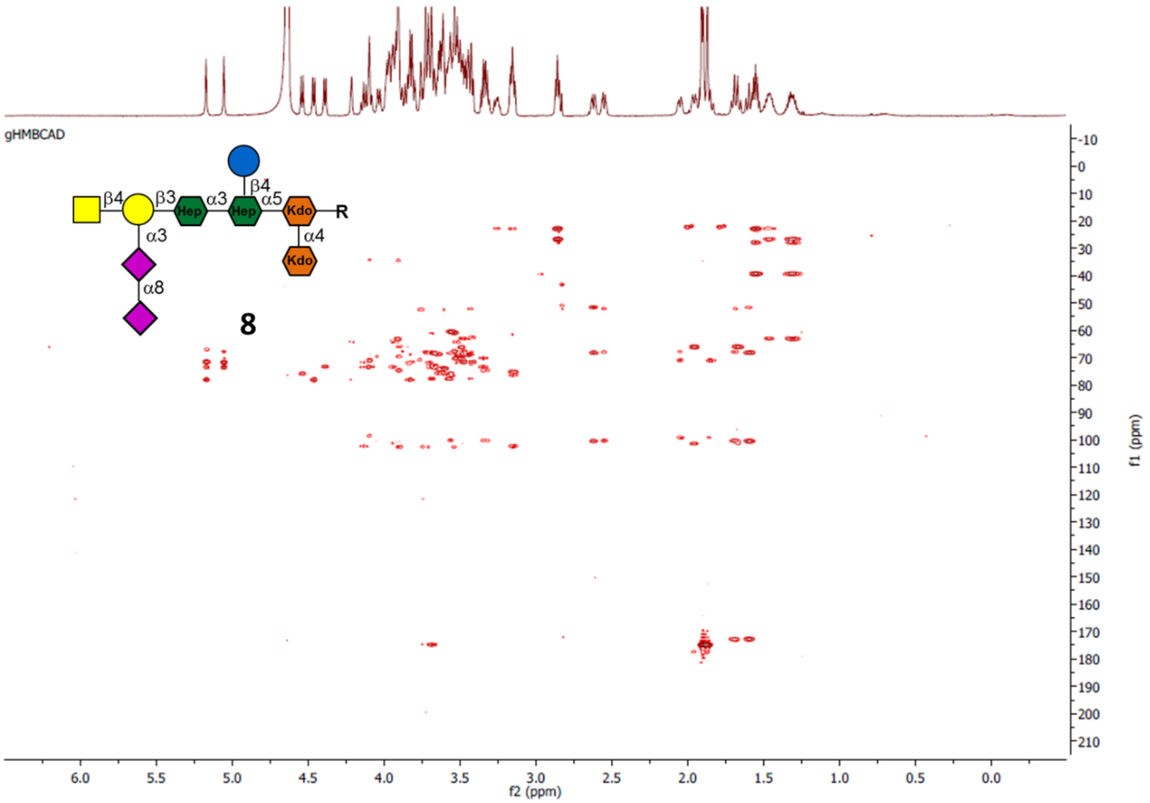
8


HSQCAD
β4
β3
α3
β4
α5
Hep
Hep
Kdo
R
α3
α4
Kdo
α8
8
f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0
f2 (ppm)

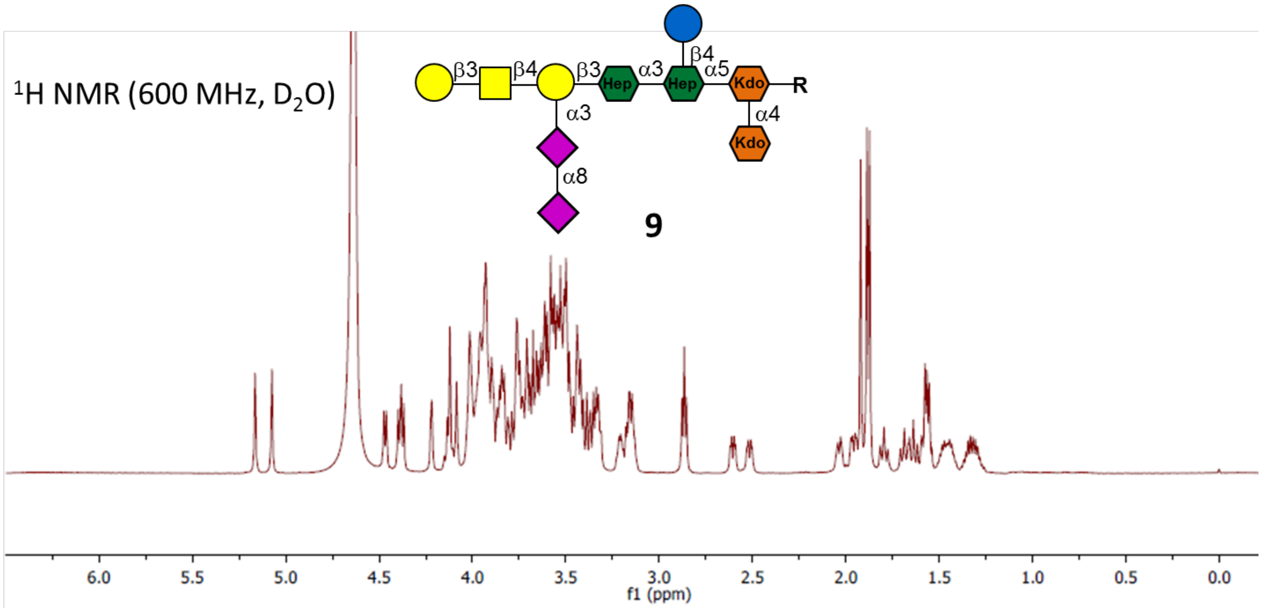

gCOSY
β4
β3
α3
β4
α5
Hep
Hep
Kdo
R
α3
α4
Kdo
α8
8
f1 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2
f2 (ppm)


zTOCSY
β4
β3
α3
β4
α5
Hep
Hep
Kdo
R
α3
α4
Kdo
α8
f2 (ppm)
f1 (ppm)
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0

8

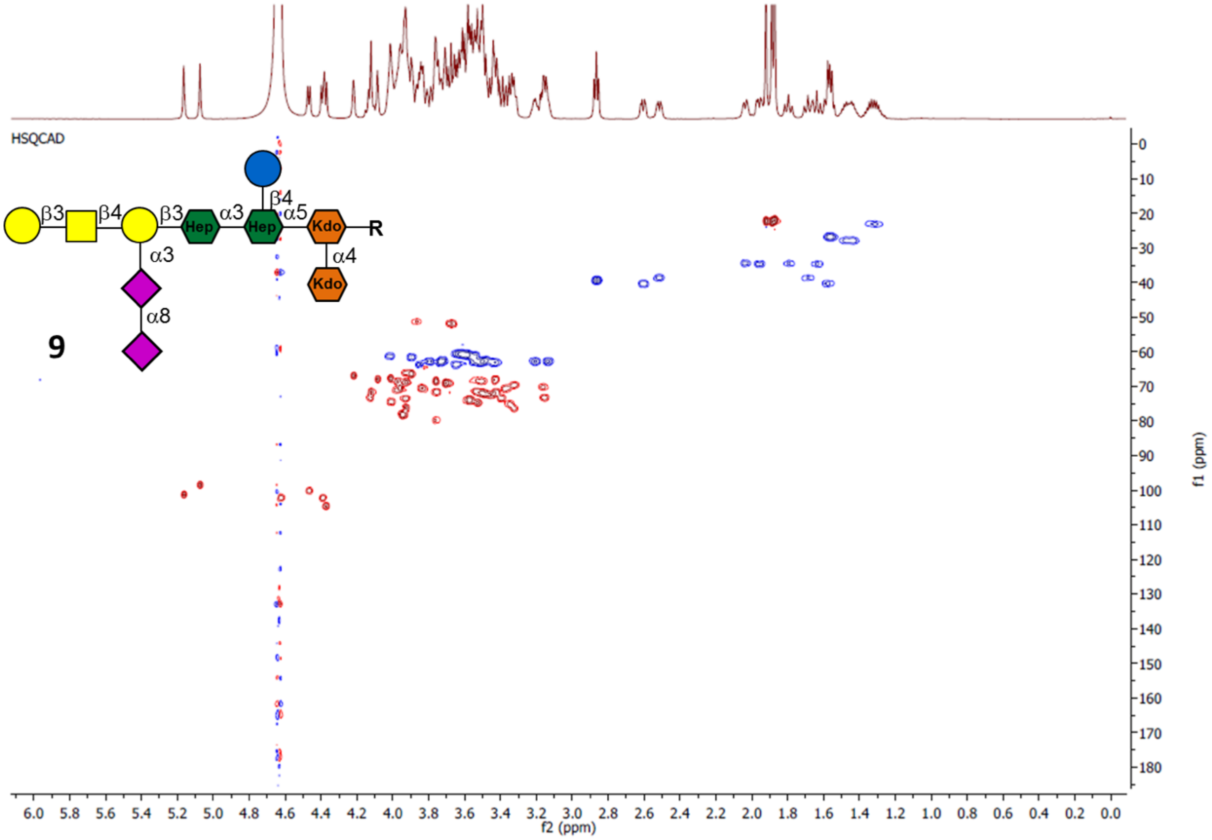

gHMBCAD
β4
β3
α3
β4
α5
Hep
Hep
Kdo
R
α3
α4
Kdo
α8
f2 (ppm)
f1 (ppm)
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210

8



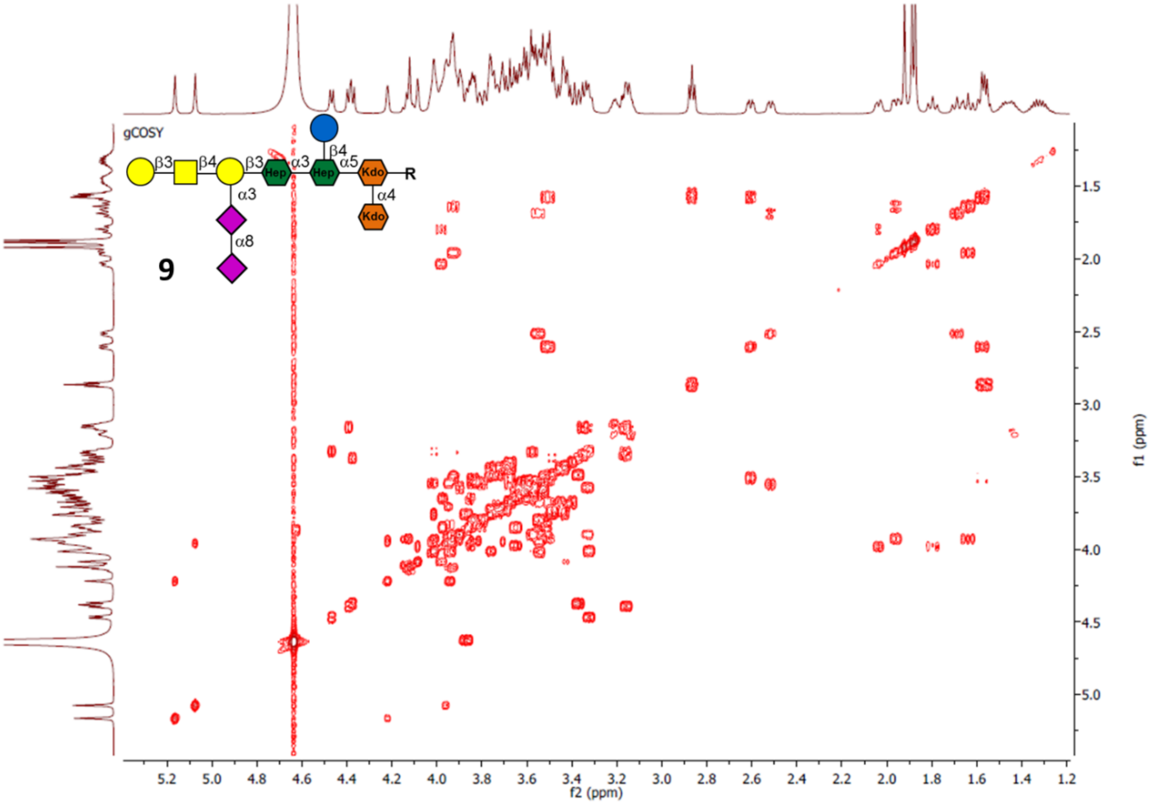
^{1}H NMR (600 MHz, D$_2$O)

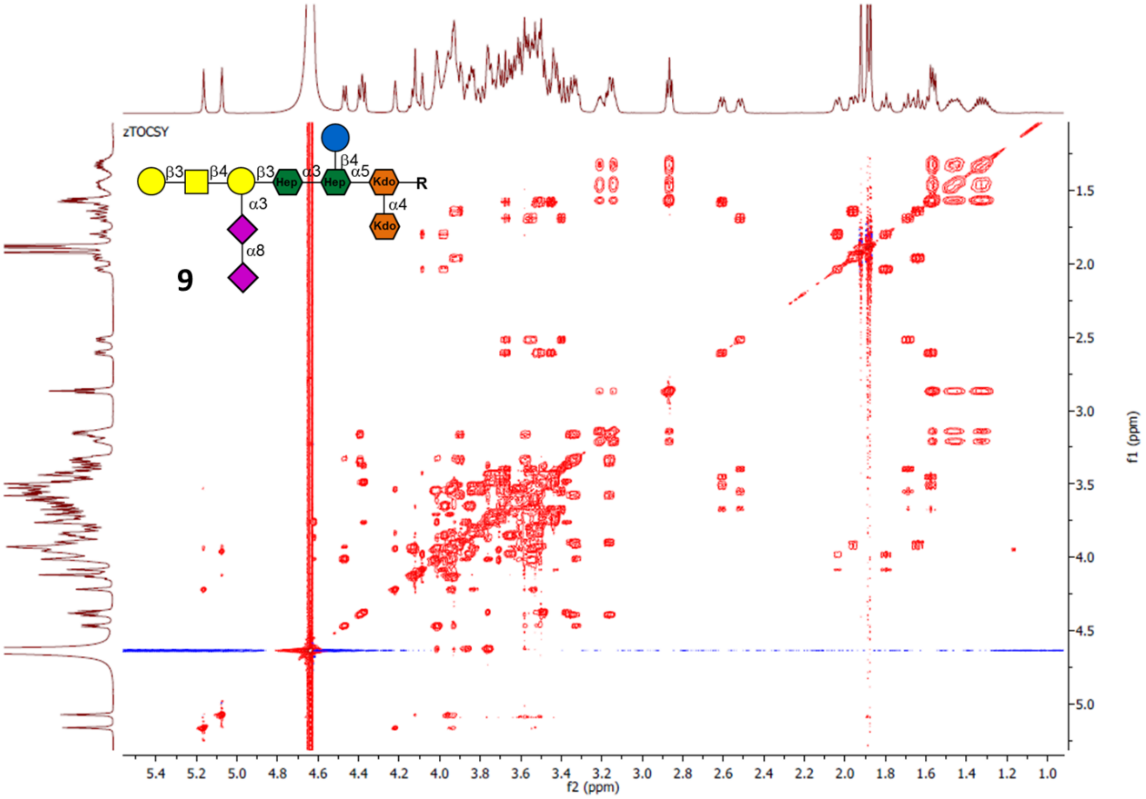
9

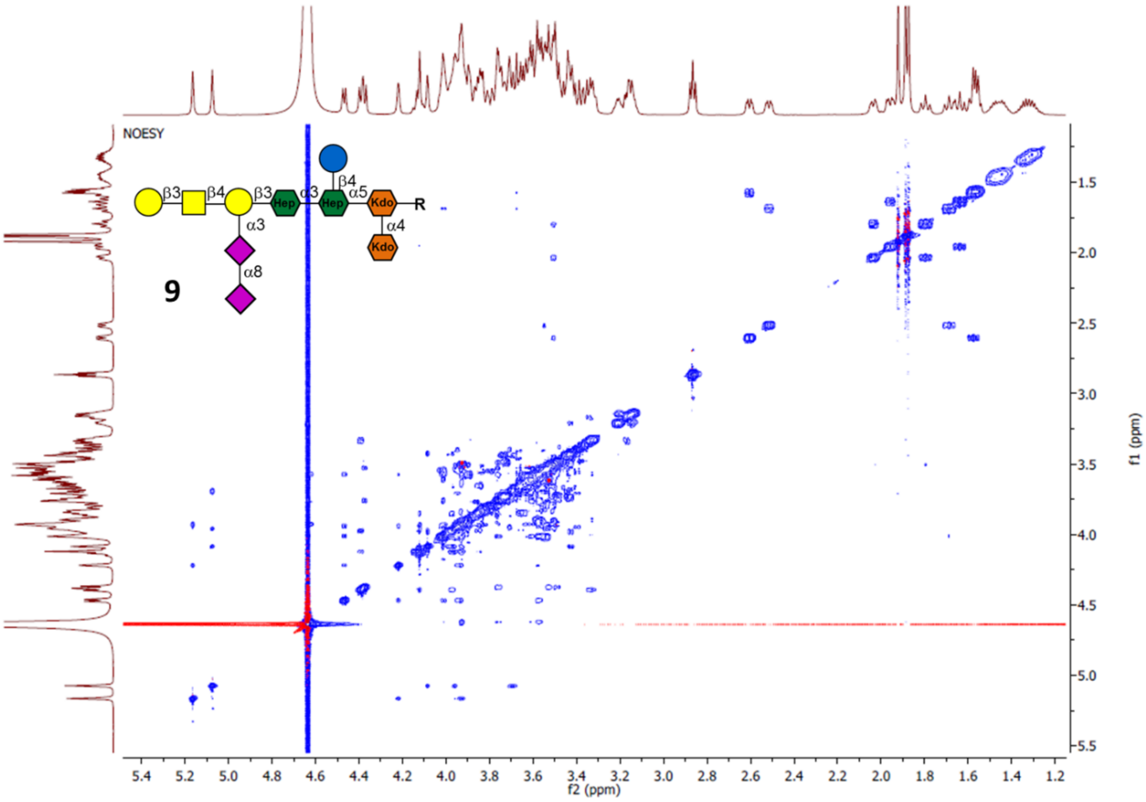


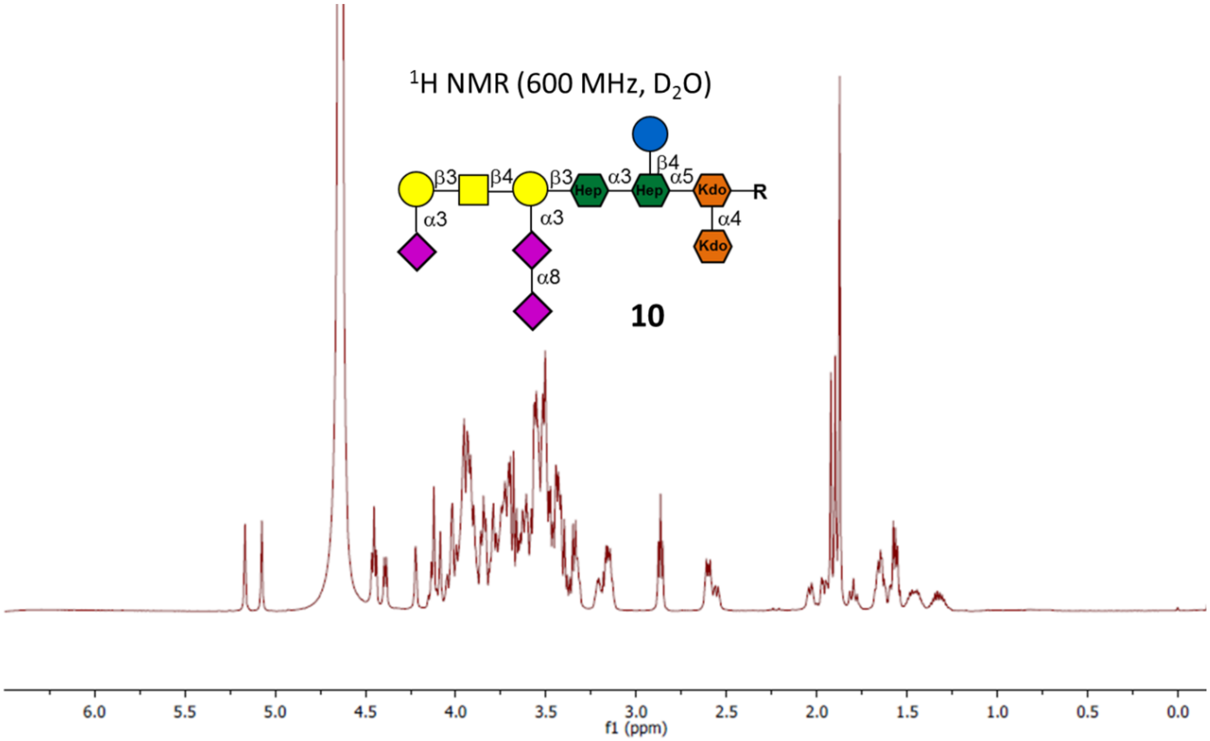
HSQCAD

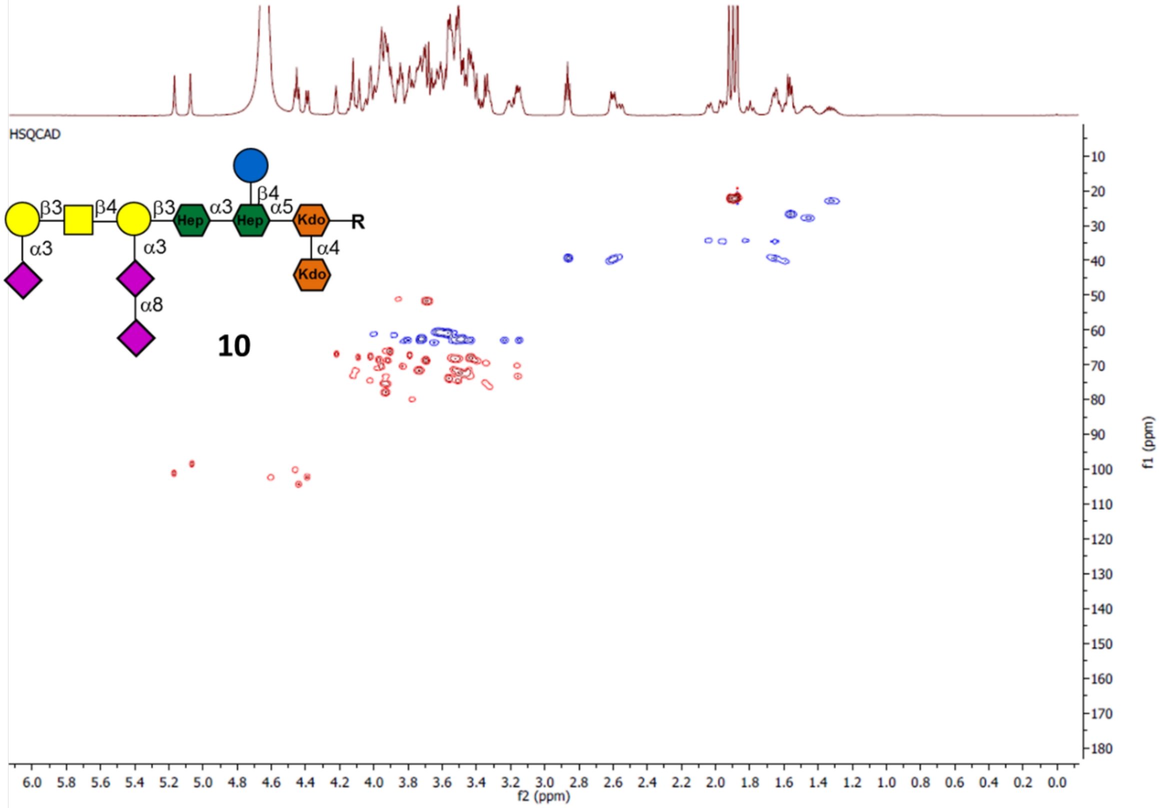
9

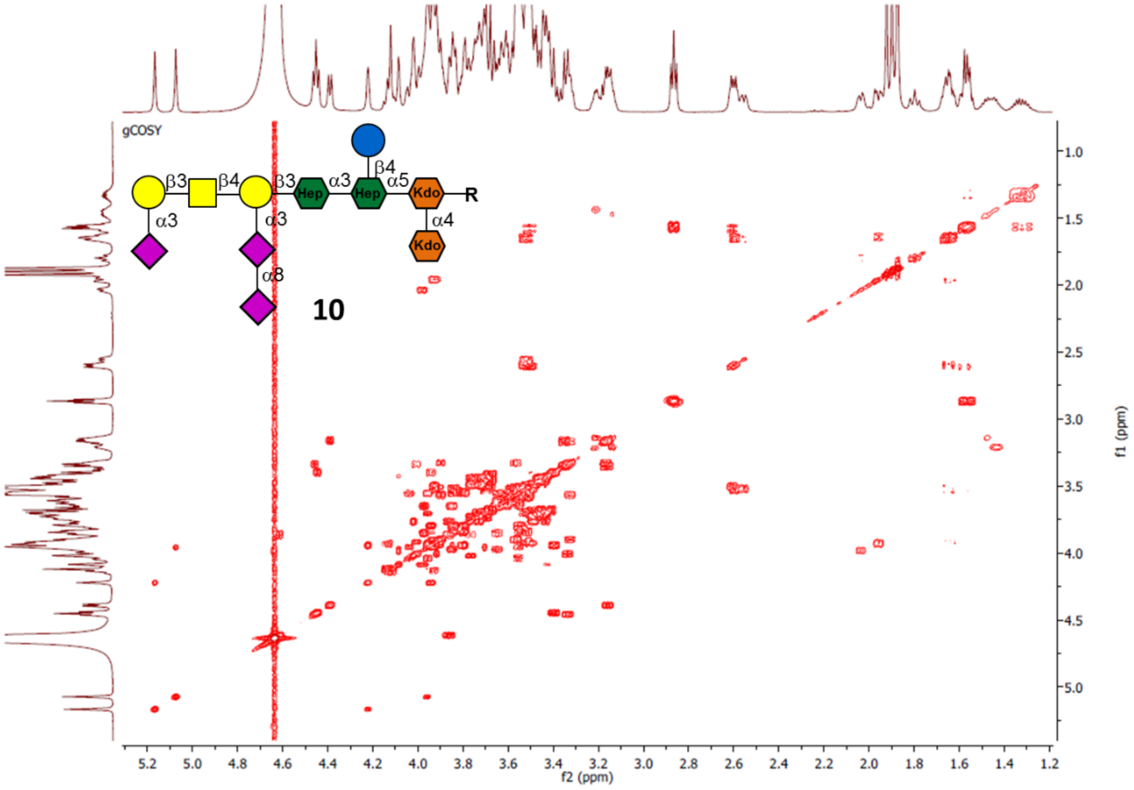

gCOSY
β3
β4
β3
Hep
α3
Hep
β4
α5
Kdo
R
α3
α4
Kdo
α8
9
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)

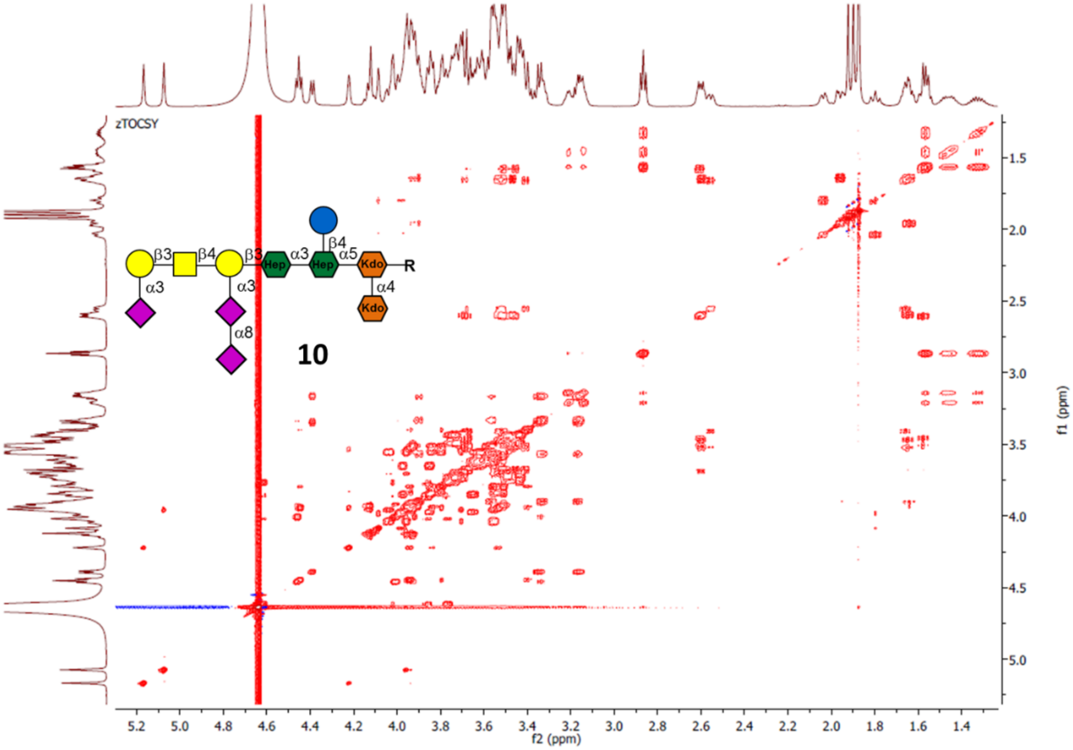

zTOCSY
β3
β4
β3
Hep
α3
Hep
β4
α5
Kdo
R
α3
α4
Kdo
α8
9
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)


NOESY
β3
β4
β3
α3
β4
α5
Hep
Hep
Kdo
R
α3
α4
Kdo
α8
9
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
f1 (ppm)

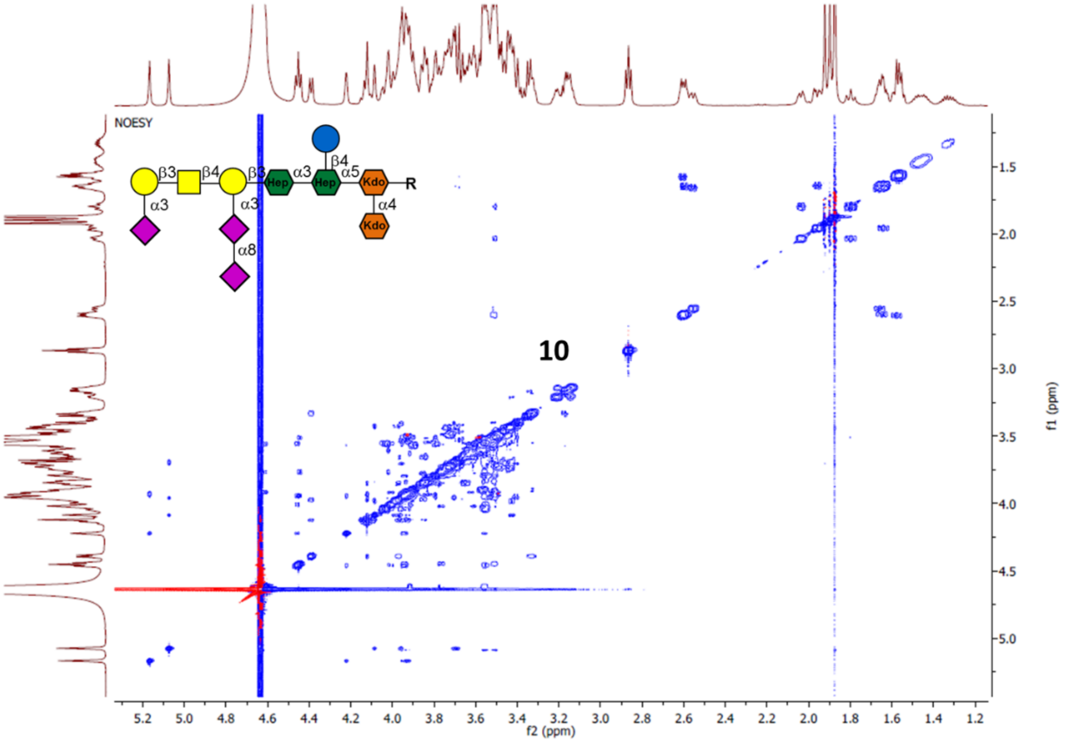

^{1}H NMR (600 MHz, D_2O)
β3
β4
β3
α3
β4
α5
Hep
Hep
Kdo
R
α3
α3
α4
Kdo
α8
10
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


HSQCAD
β3
β4
β3
α3
β4
α5
Hep
Hep
Kdo
R
α3
α3
α4
Kdo
α8
10
f2 (ppm)
f1 (ppm)

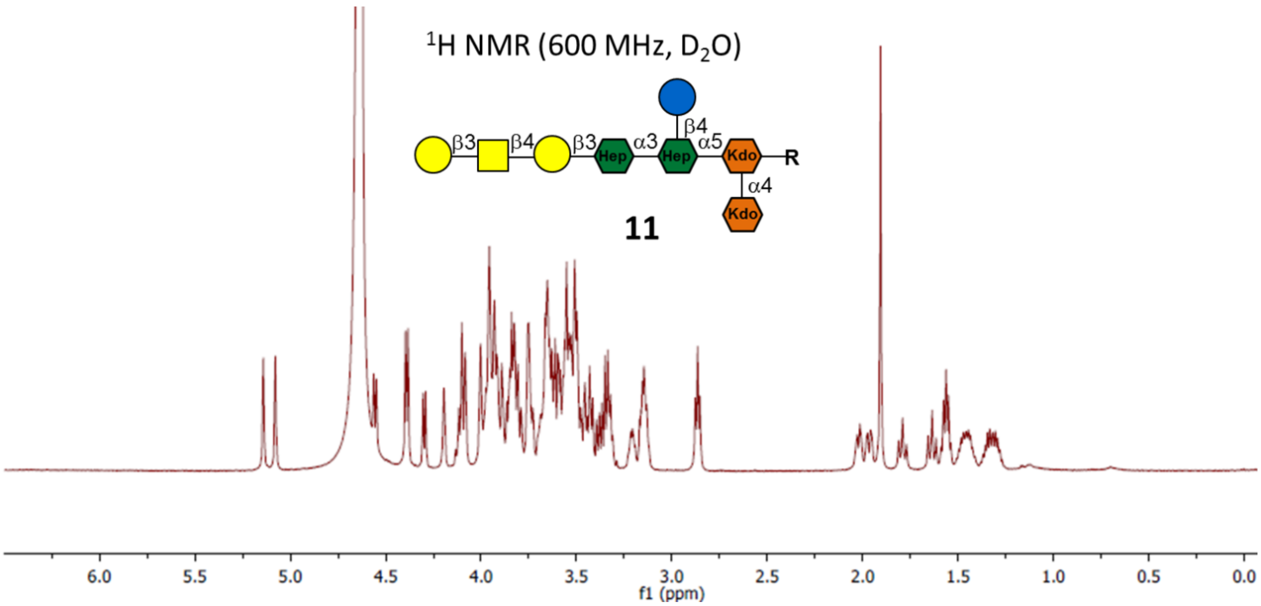

gCOSY
β3
β4
β3
α3
β4
α5
Hep
Hep
Kdo
R
α3
α3
α4
Kdo
α8
10
f2 (ppm)
f1 (ppm)


zTOCSY
β3
β4
β3
α3
β4
α5
α3
α3
α4
α8
Hep
Hep
Kdo
Kdo
R
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)

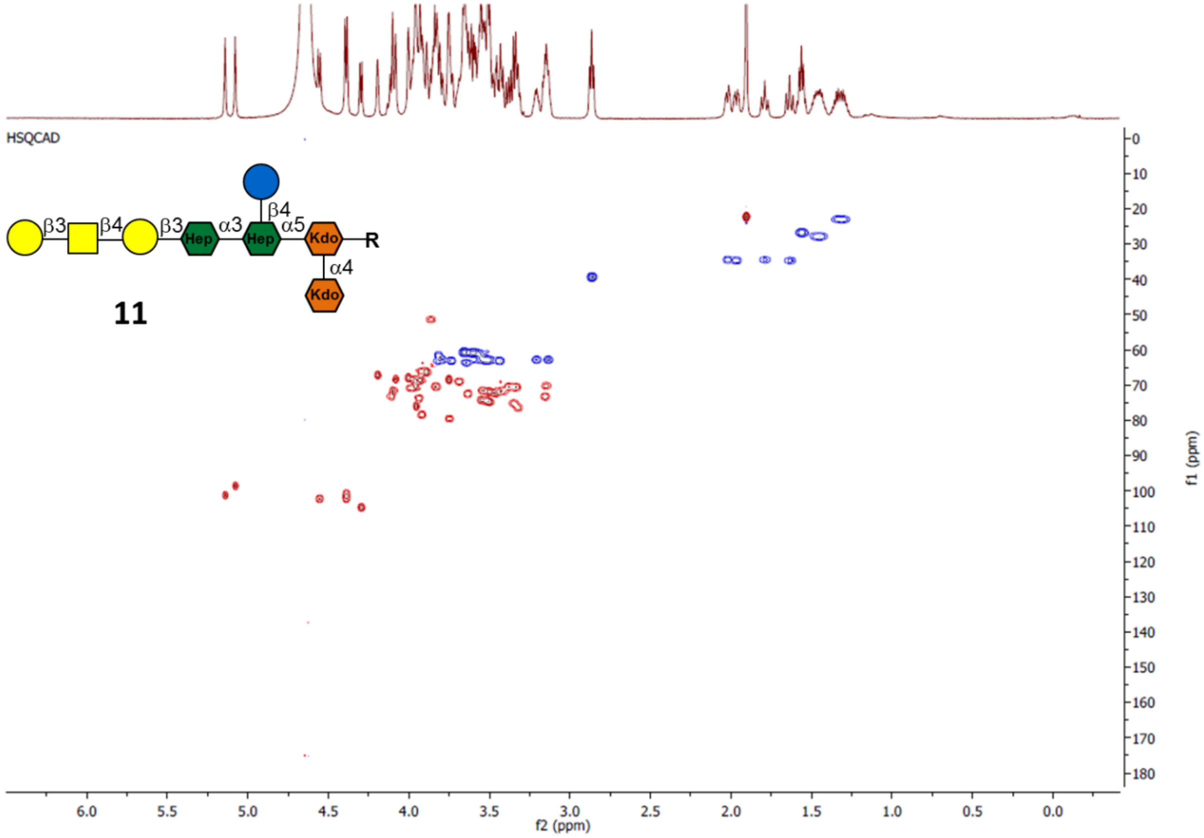
10


NOESY
β3
β4
β3
α3
β4
α5
α3
α3
α4
α8
Hep
Hep
Kdo
Kdo
R
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)

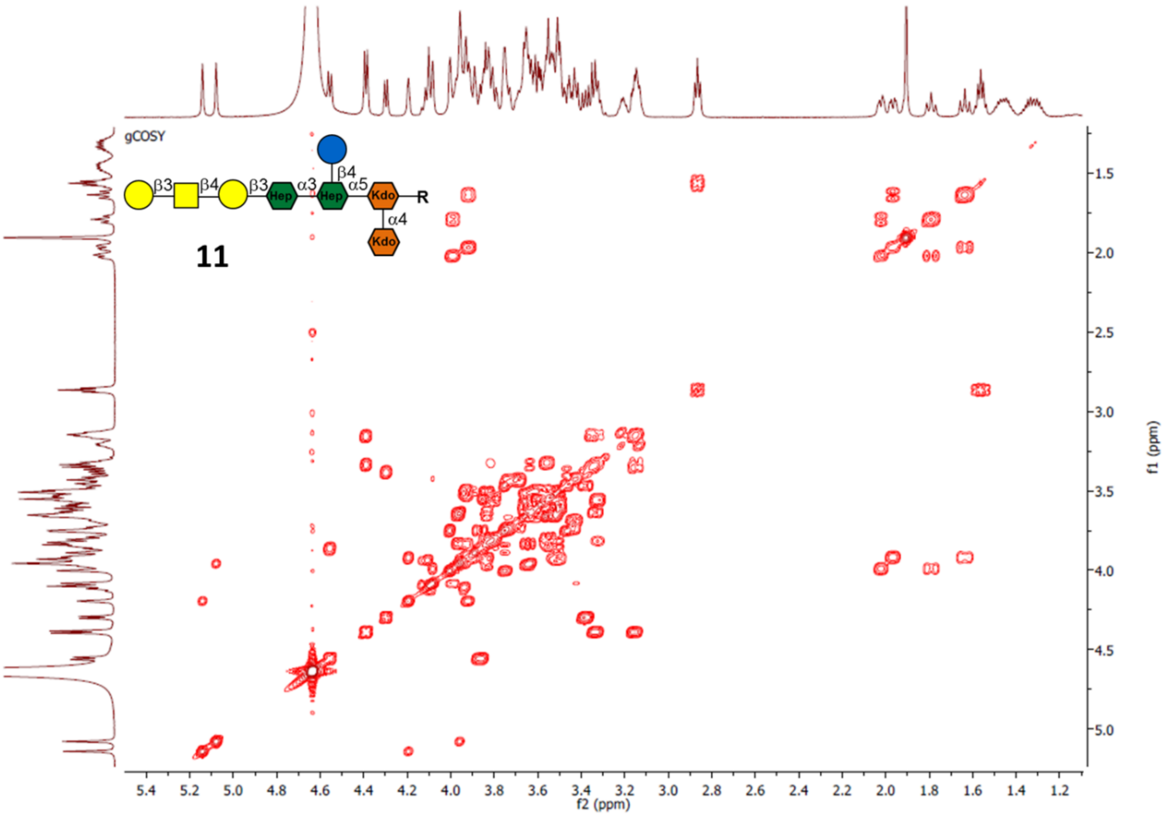
10

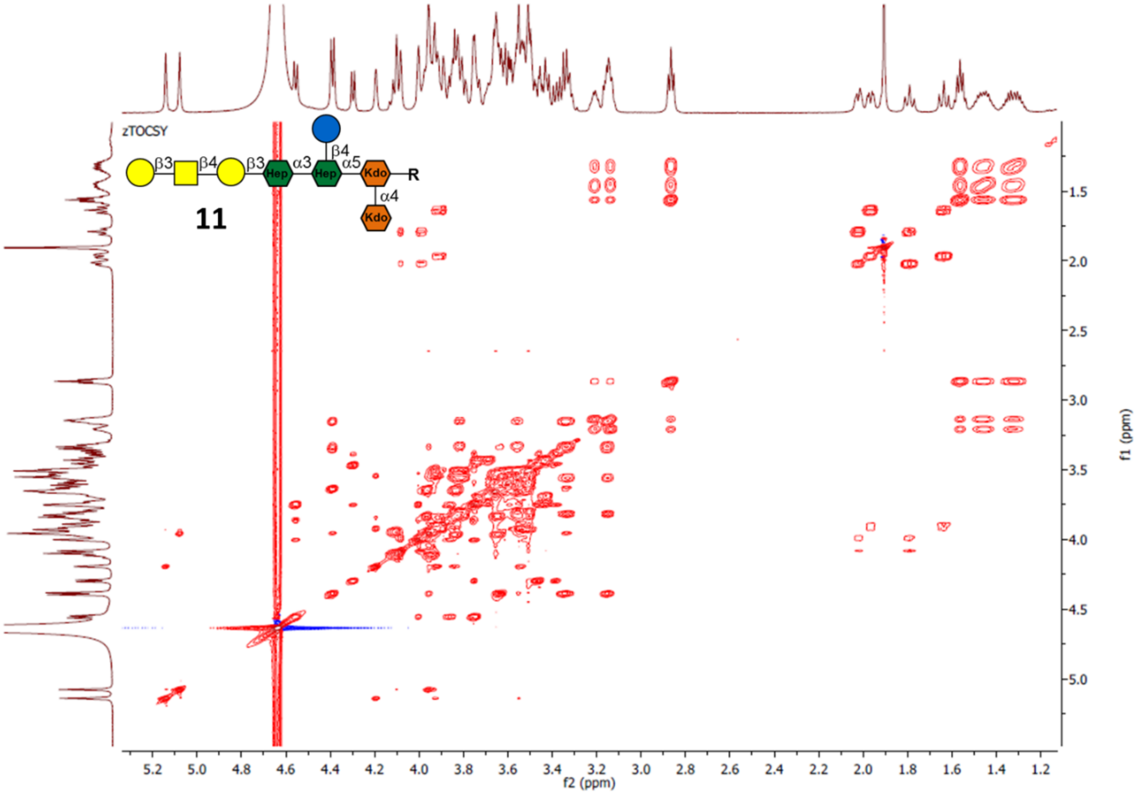


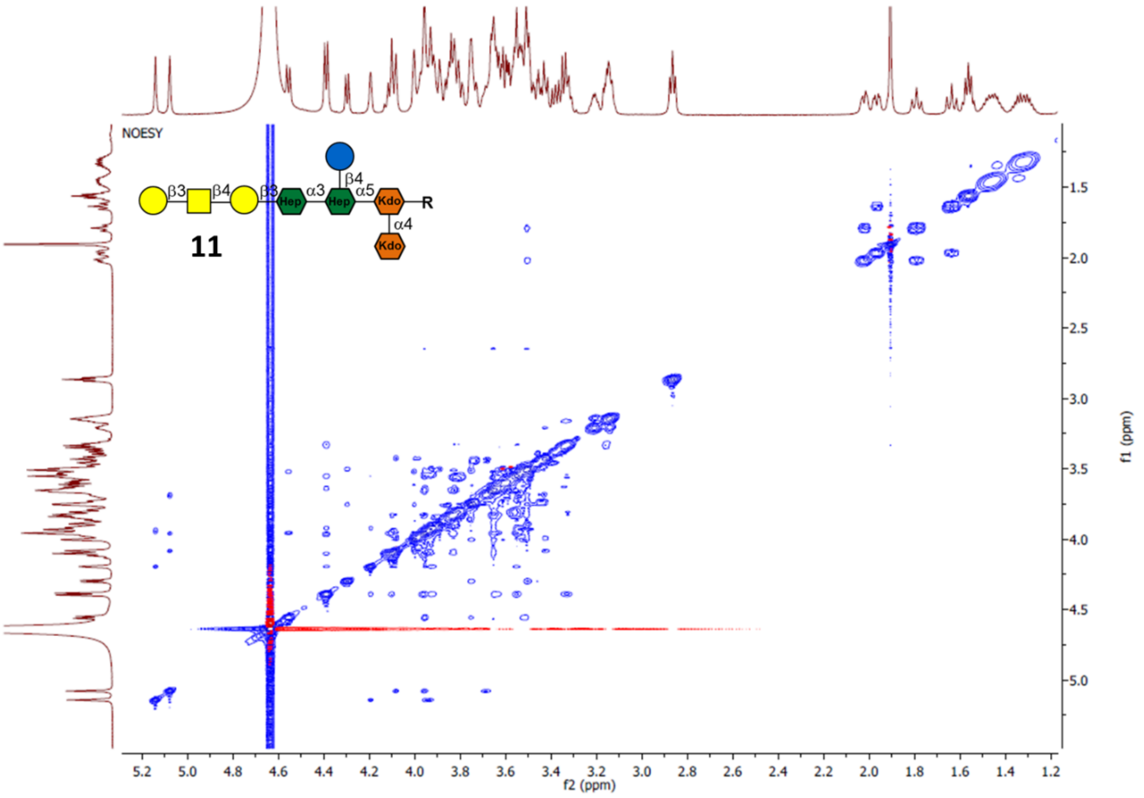
^{1}H NMR (600 MHz, D_2O)
β3
β4
β3
α3
β4
α5
α4
Hep
Hep
Kdo
Kdo
R
11
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



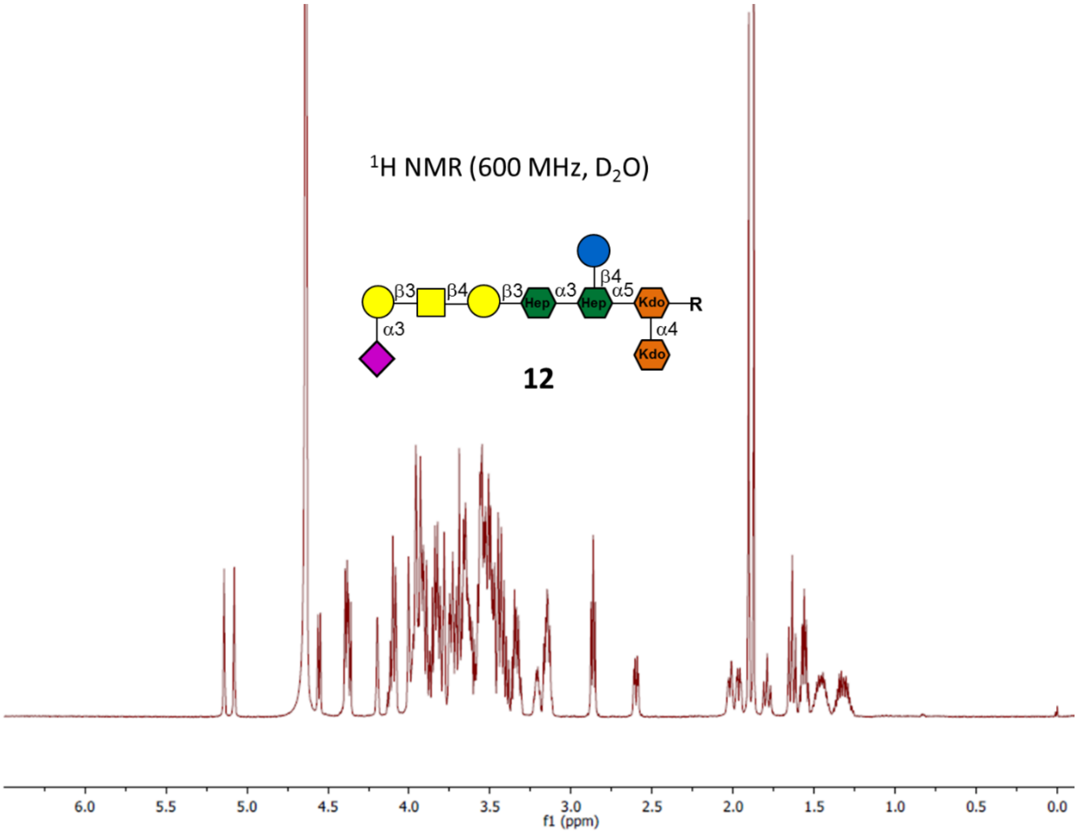
HSQCAD
β3
β4
β3
α3
β4
α5
α4
Hep
Hep
Kdo
Kdo
R
11
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
f1 (ppm)


gCOSY
β3
β4
β3
α3
β4
α5
α4
Hep
Hep
Kdo
Kdo
R
11
5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2
f2 (ppm)
1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0
f1 (ppm)

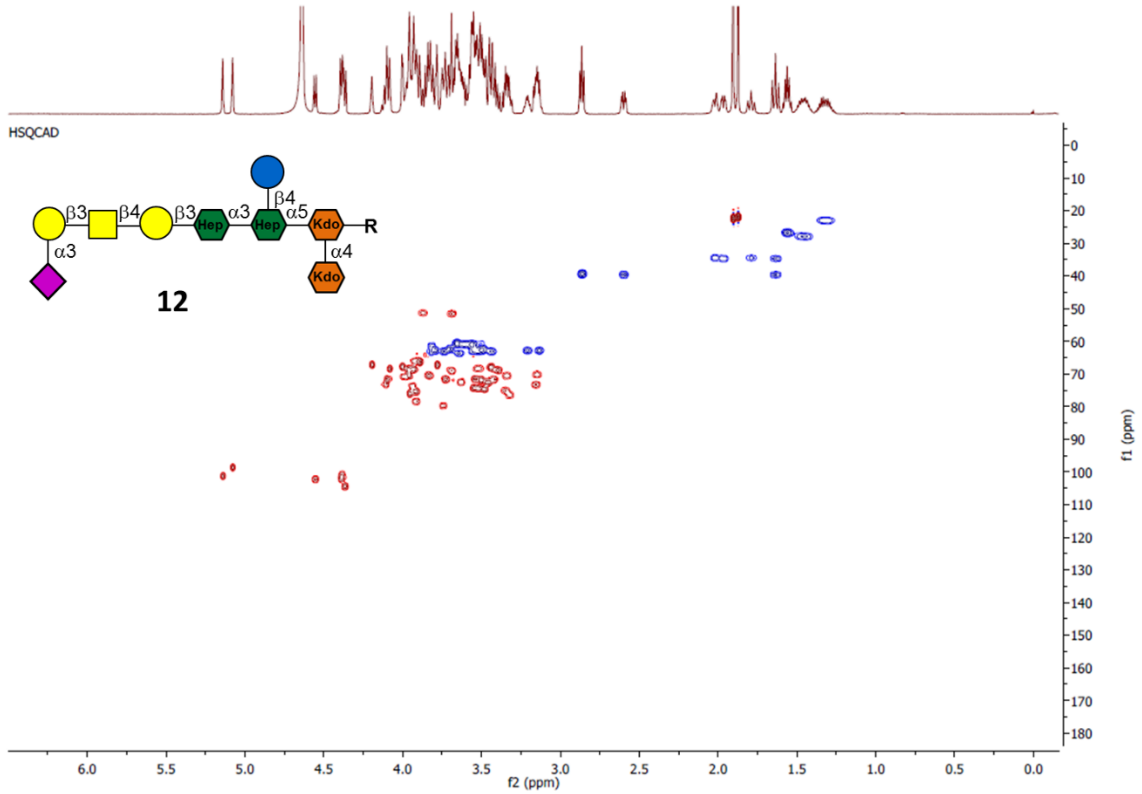

zTOCSY
β3
β4
β3
α3
β4
α5
α4
Hep
Hep
Kdo
Kdo
R
11
5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2
f2 (ppm)
1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0
f1 (ppm)

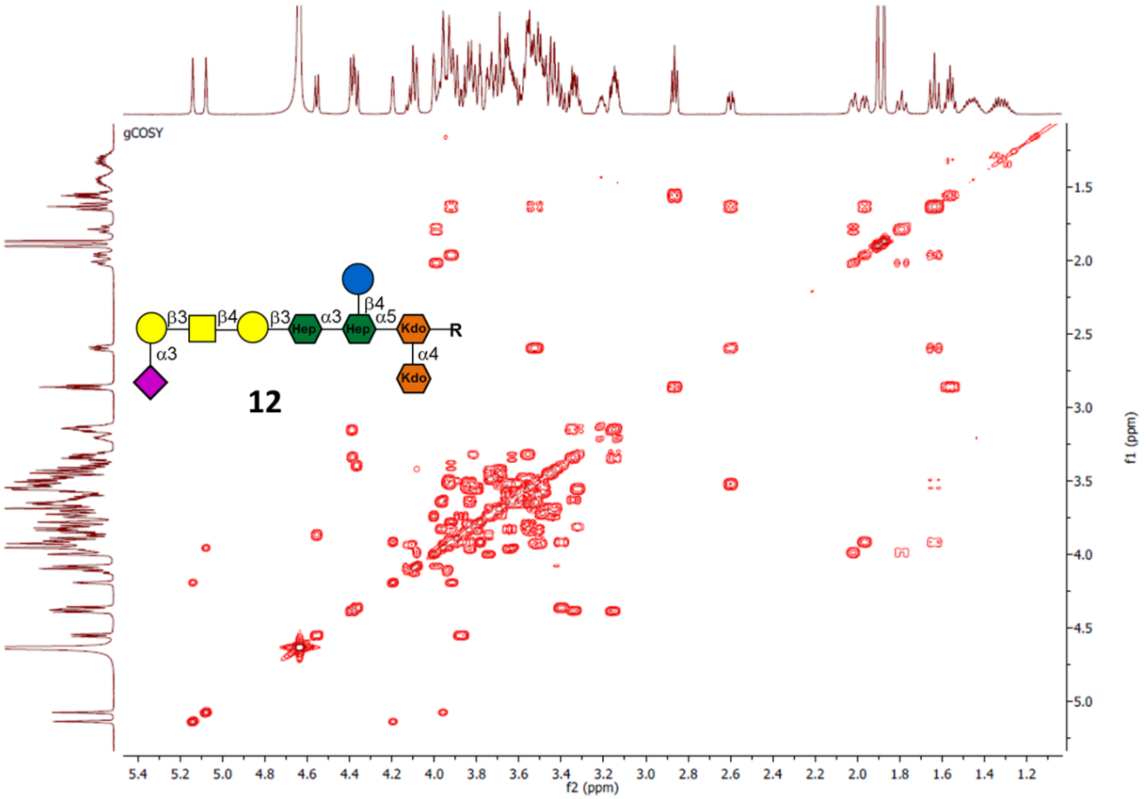

NOESY
β3
β4
β3
α3
β4
α5
Hep
Hep
Kdo
R
α4
Kdo
5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2
f2 (ppm)
1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0
f1 (ppm)

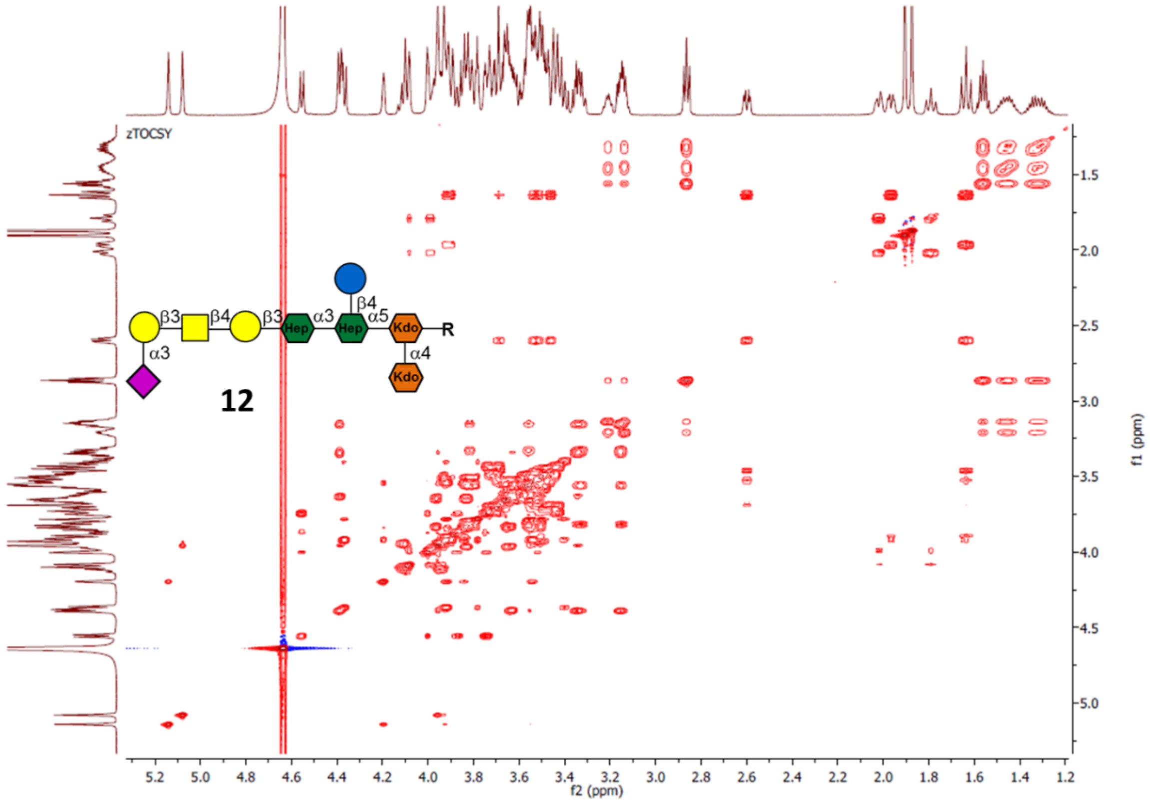
11

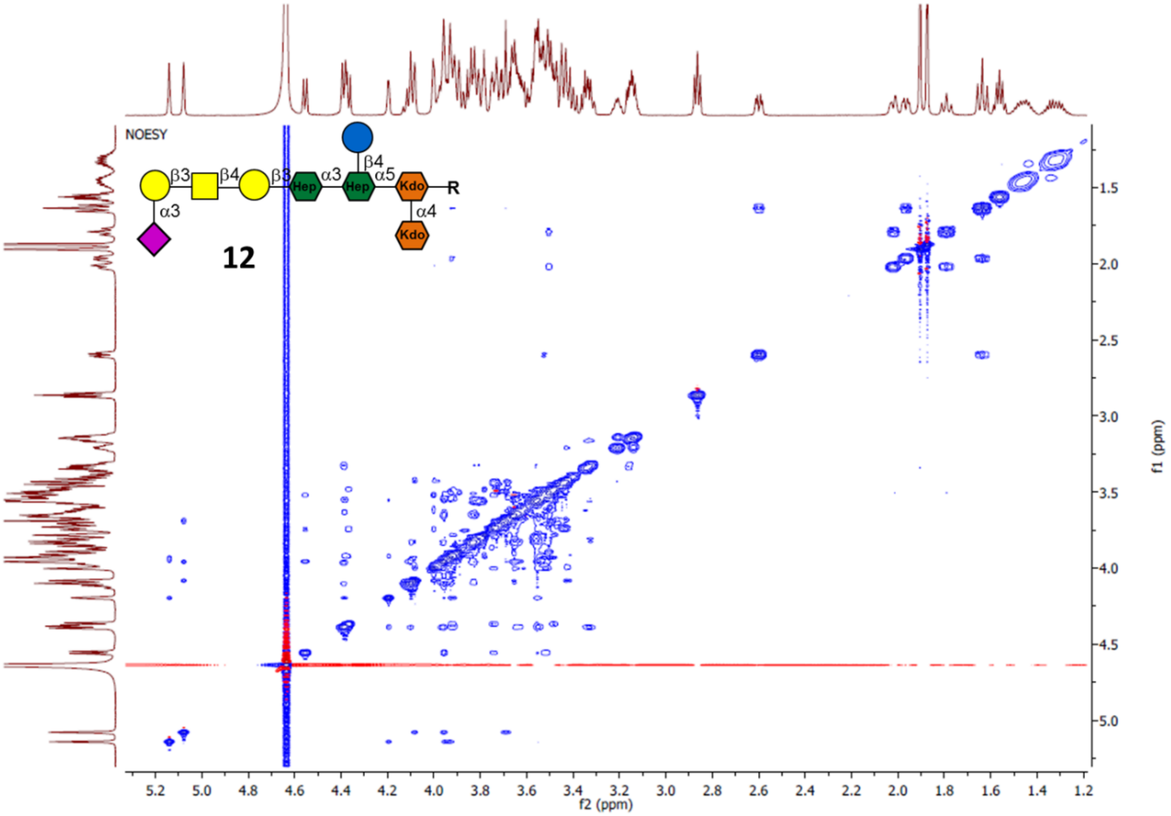

^{1}H NMR (600 MHz, D$_2$O)
β3
β4
β3
α3
β4
α5
α3
Hep
Hep
Kdo
R
α4
Kdo
6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

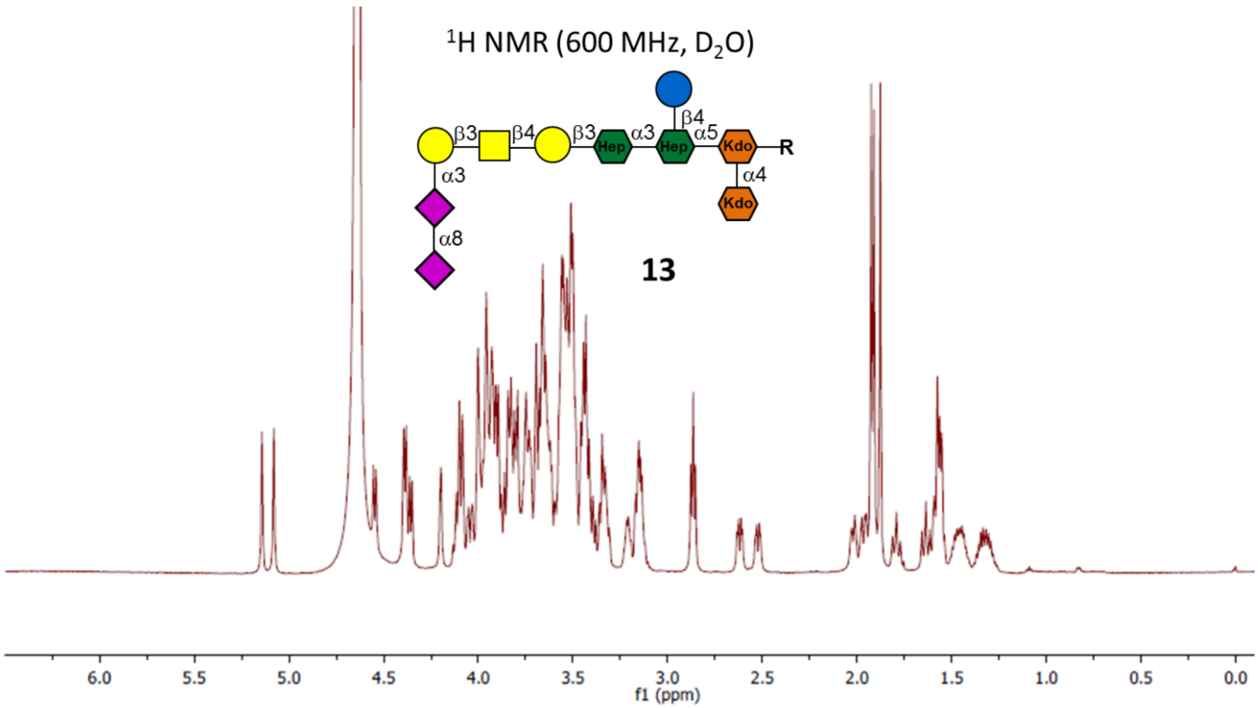
12

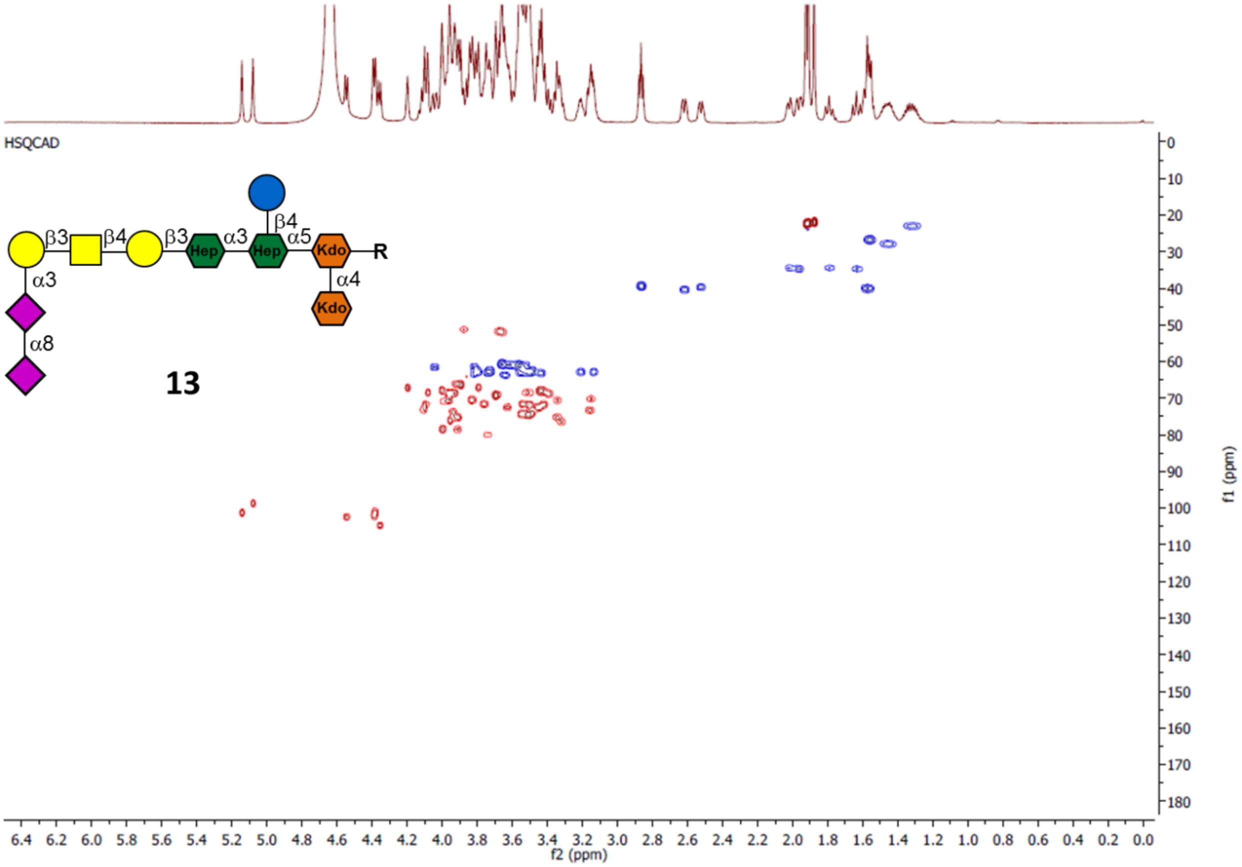

HSQCAD
β3
β4
β3
α3
β4
α5
α3
α4
Hep
Hep
Kdo
Kdo
R
12
f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
f2 (ppm)
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

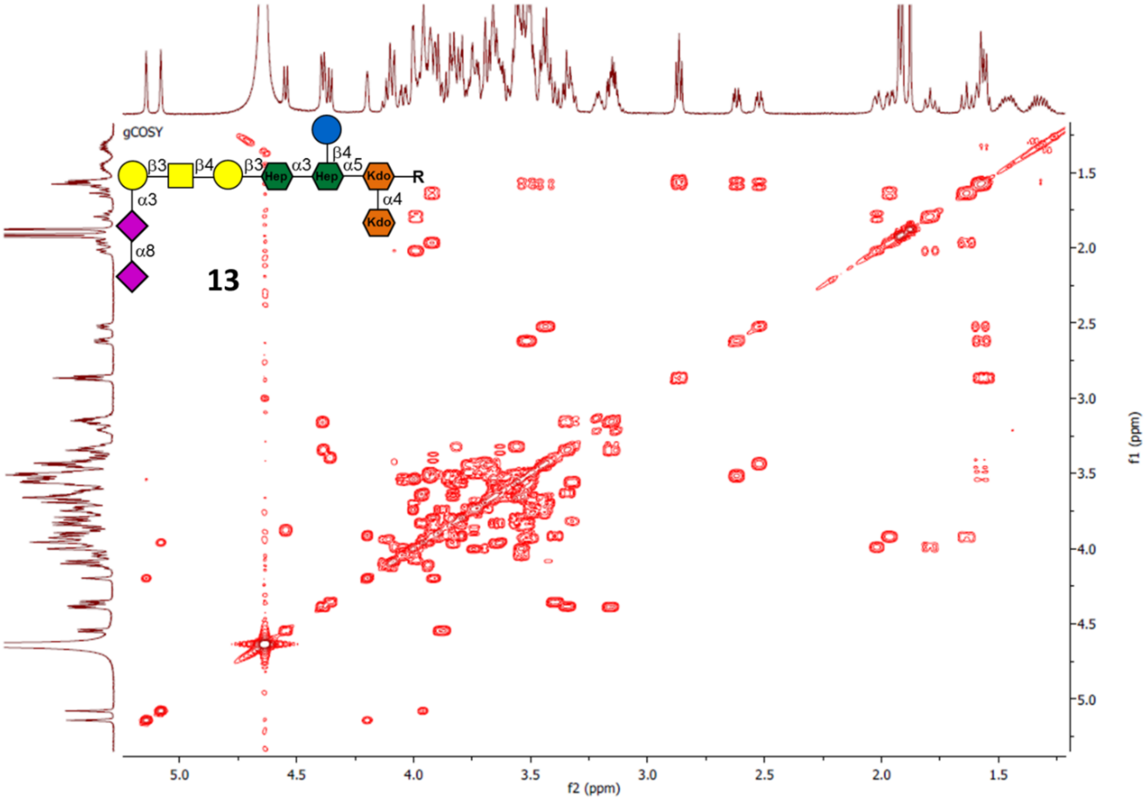

gCOSY
β3
β4
β3
α3
β4
α5
α3
α4
Hep
Hep
Kdo
Kdo
R
12
f1 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f2 (ppm)
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2

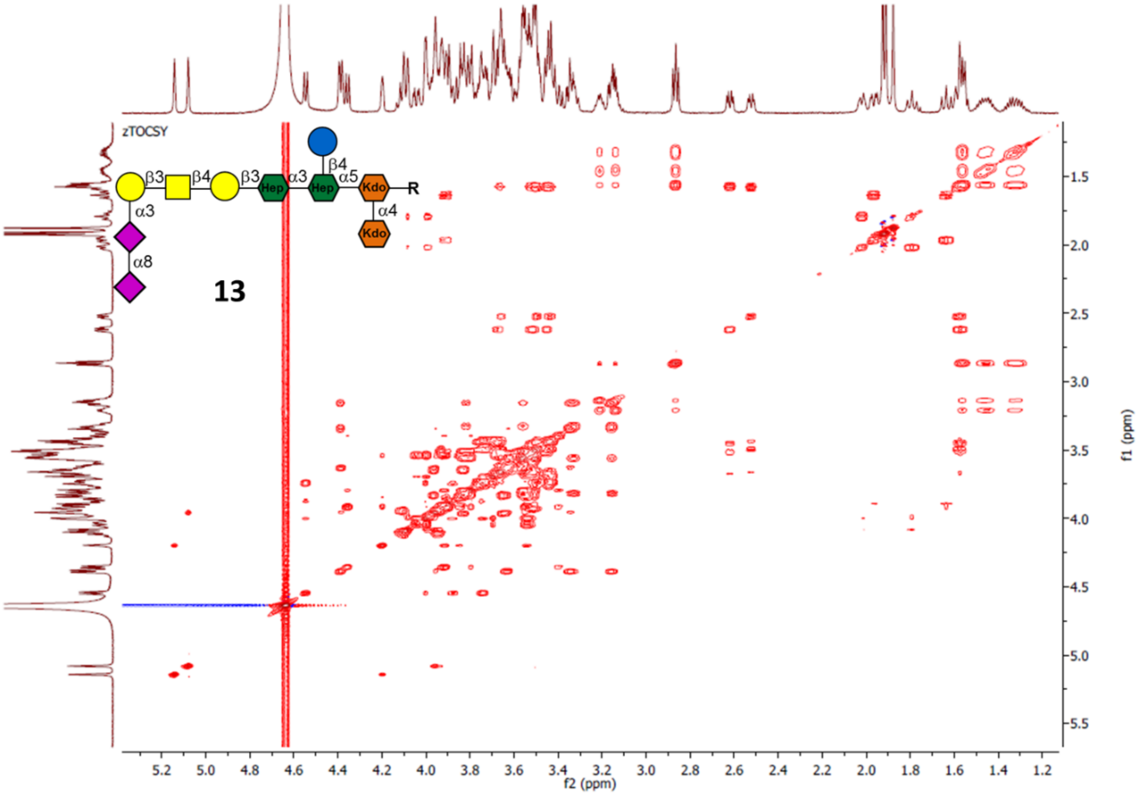

zTOCSY
β3
β4
β3
α3
β4
α5
Hep
Hep
Kdo
R
α3
α4
Kdo
12
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)

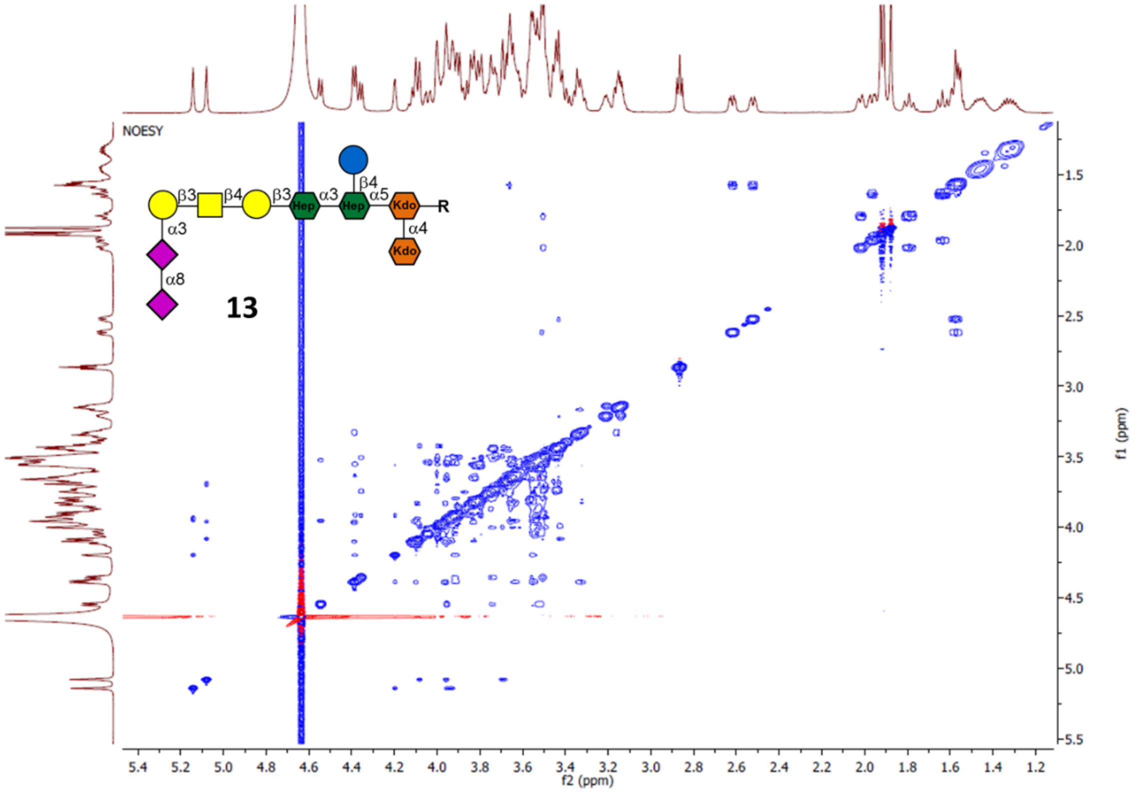

NOESY
β3
β4
β3
α3
β4
α5
Hep
Hep
Kdo
R
α3
α4
Kdo
12
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)


^{1}H NMR (600 MHz, D_2O)
β3
β4
β3
α3
β4
α5
α3
α8
α4
Hep
Hep
Kdo
Kdo
R
13
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)

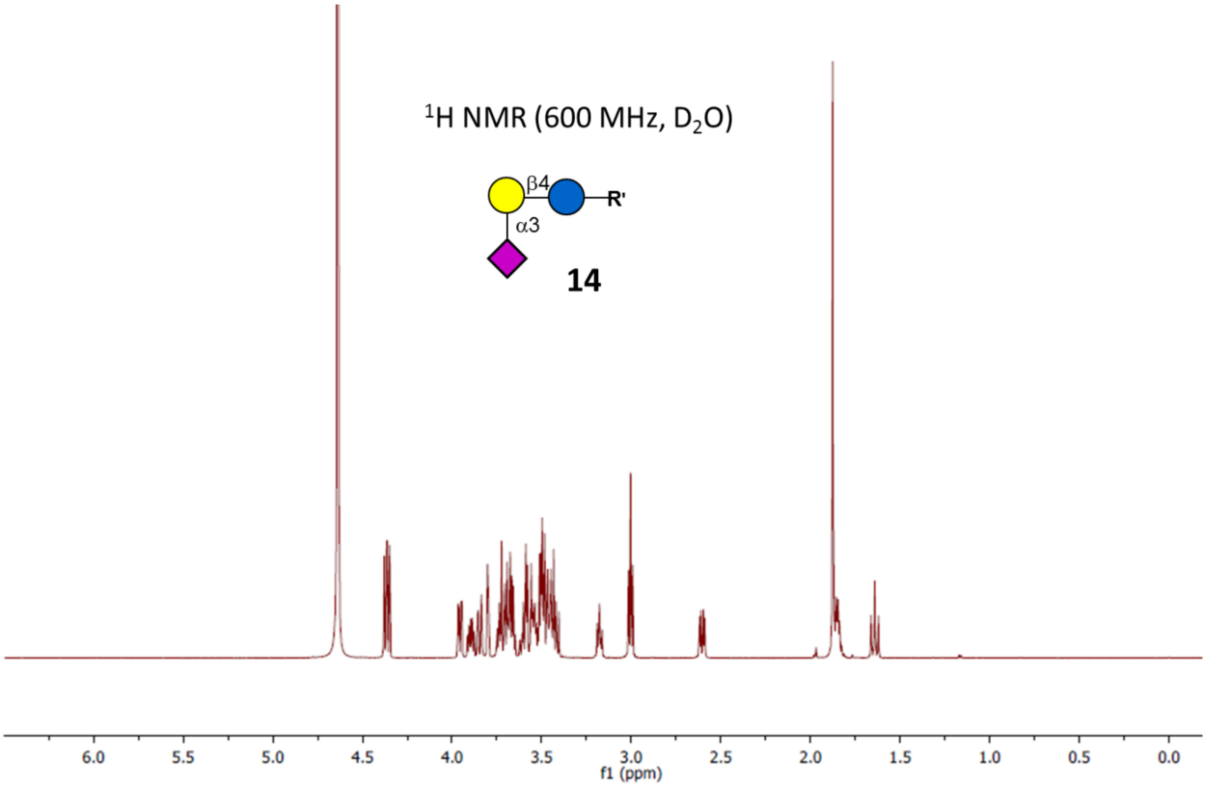

HSQCAD
β3
β4
β3
α3
β4
α5
α3
α8
α4
Hep
Hep
Kdo
Kdo
R
13
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
f1 (ppm)


gCOSY
β3
β4
β3
α3
β4
α5
Hep
Hep
Kdo
R
α3
α4
Kdo
α8
13
f2 (ppm)
f1 (ppm)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5


zTOCSY
β3
β4
β3
α3
β4
α5
Hep
Hep
Kdo
R
α3
α4
Kdo
α8
13
f2 (ppm)
f1 (ppm)
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5

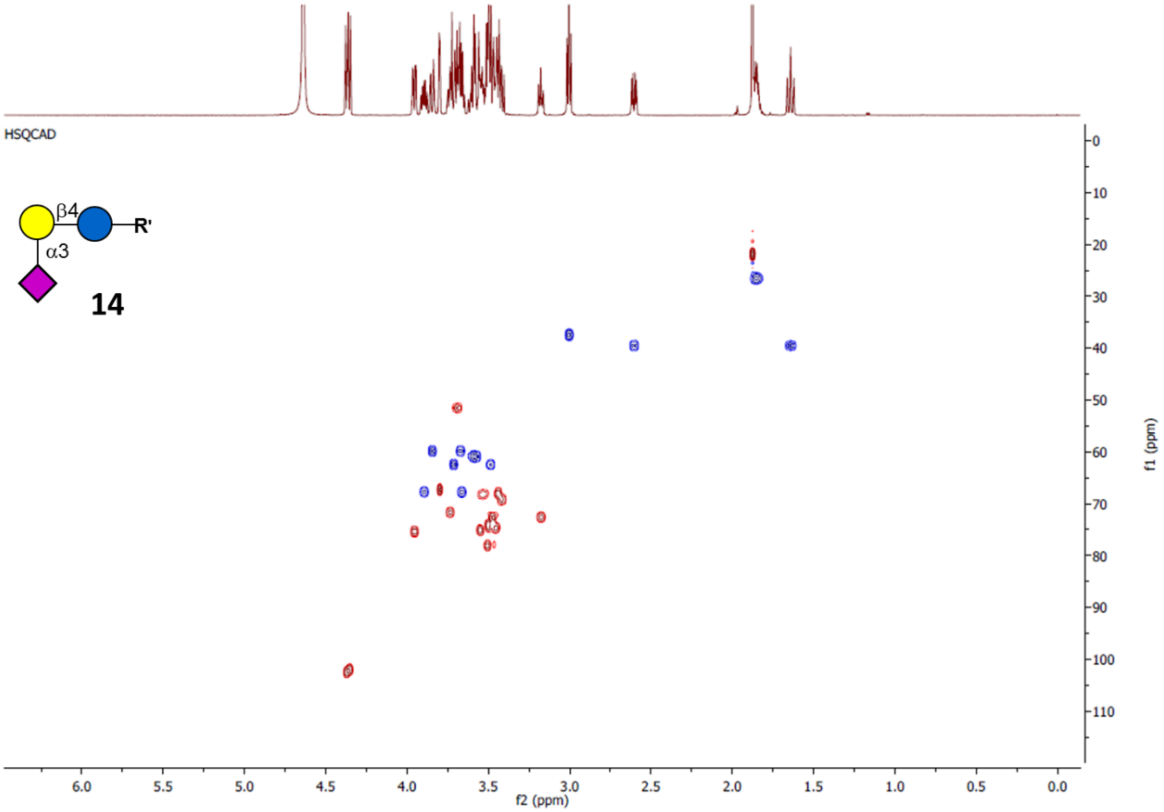


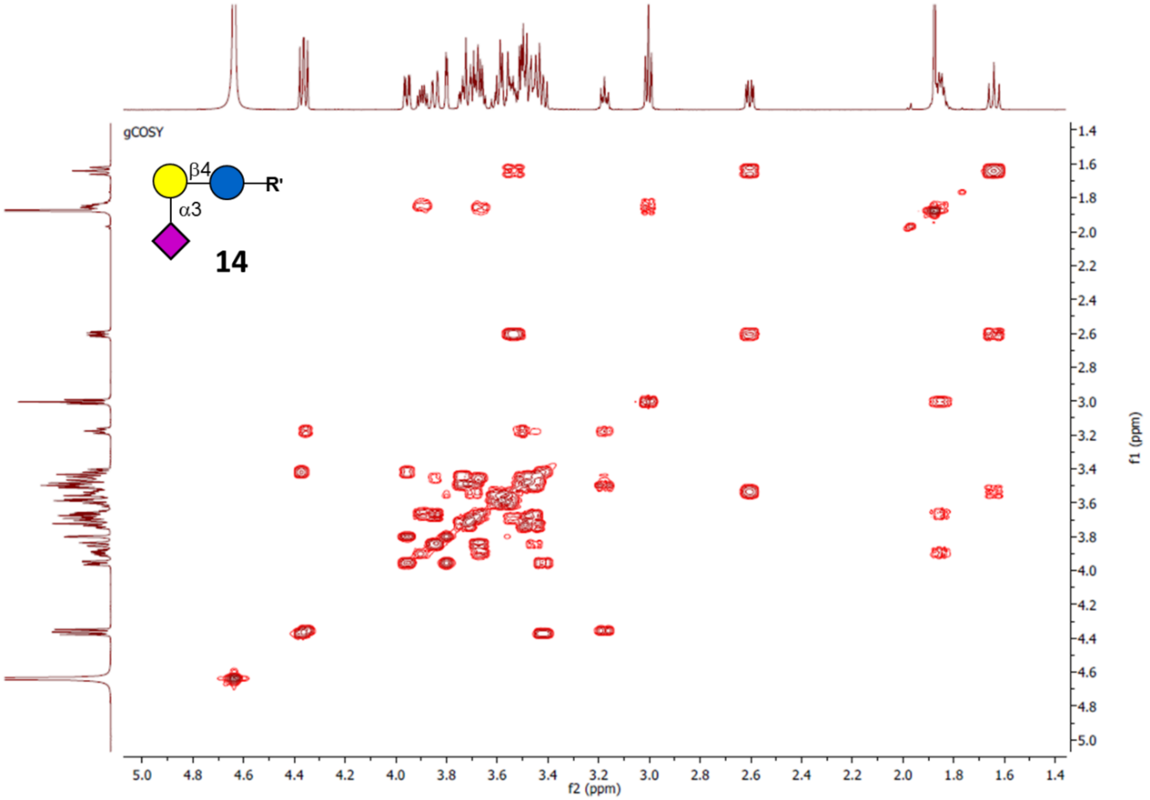
13

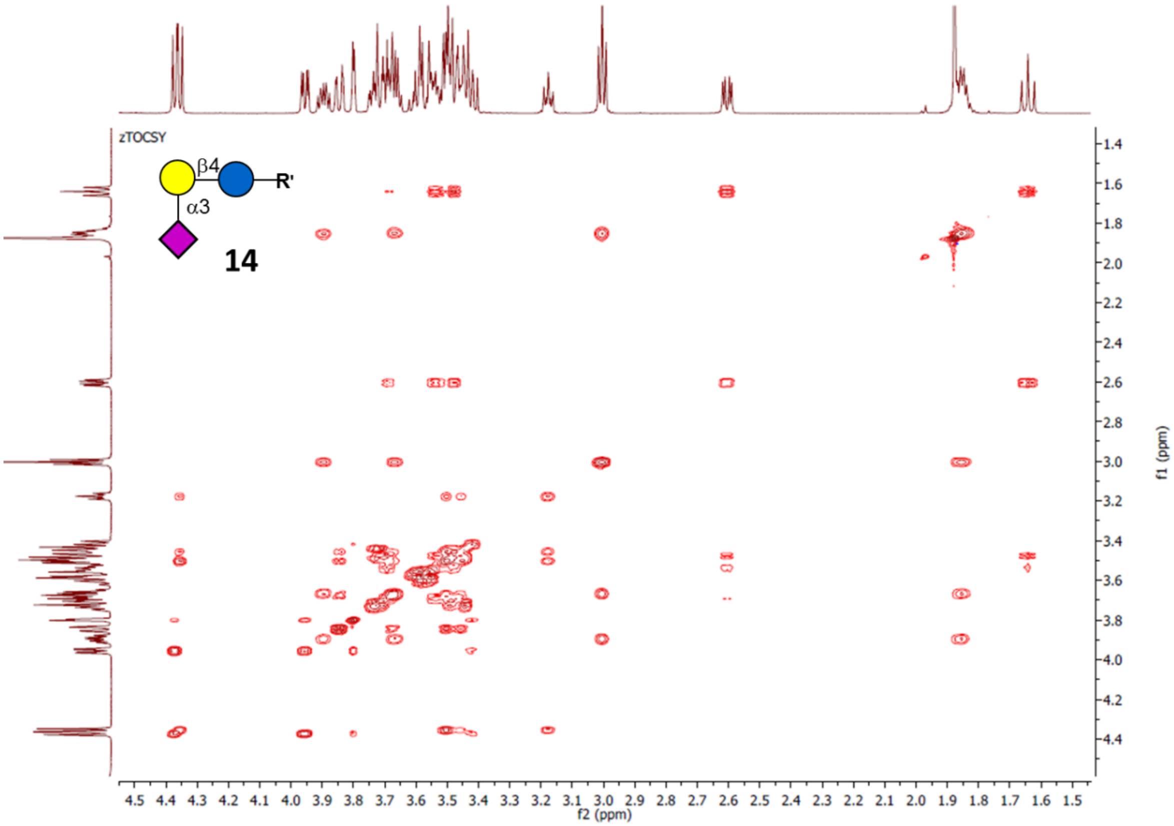


^{1}H NMR (600 MHz, D_2O)

14

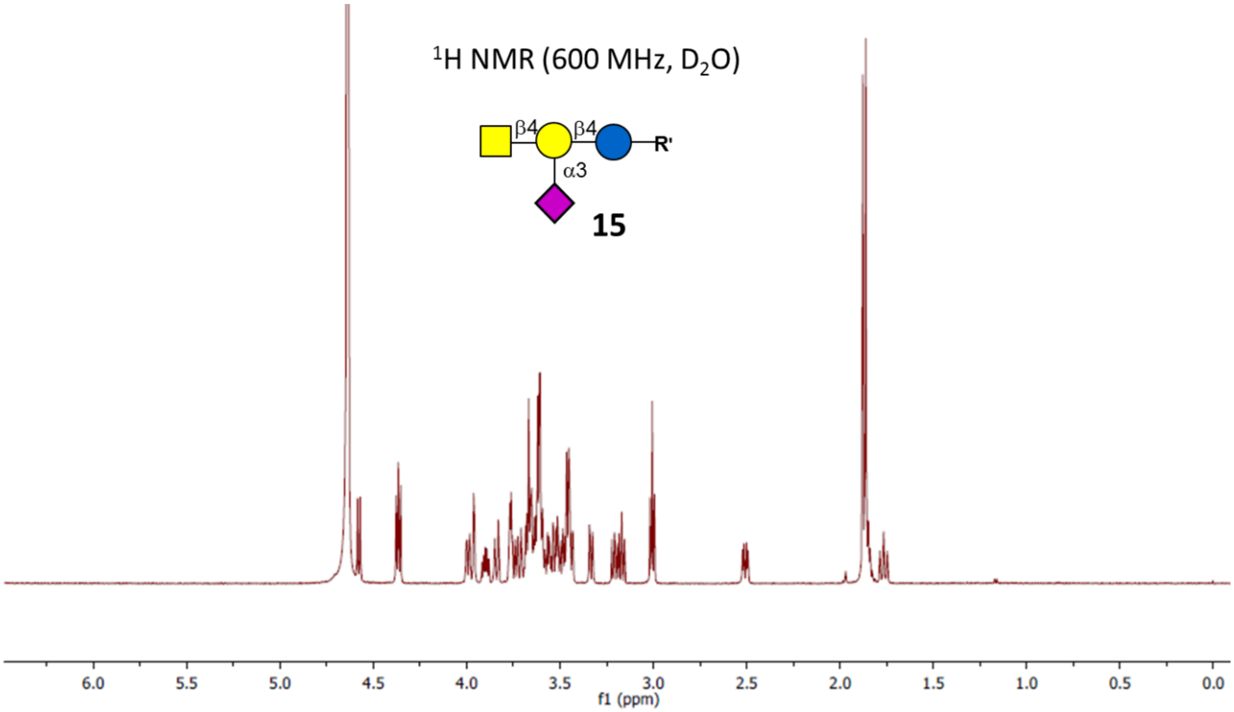

HSQCAD
β4
R'
α3
14
0
10
20
30
40
50
60
70
80
90
100
110
f1 (ppm)
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)


gCOSY
β4
R'
α3
14
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
f1 (ppm)
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
f2 (ppm)

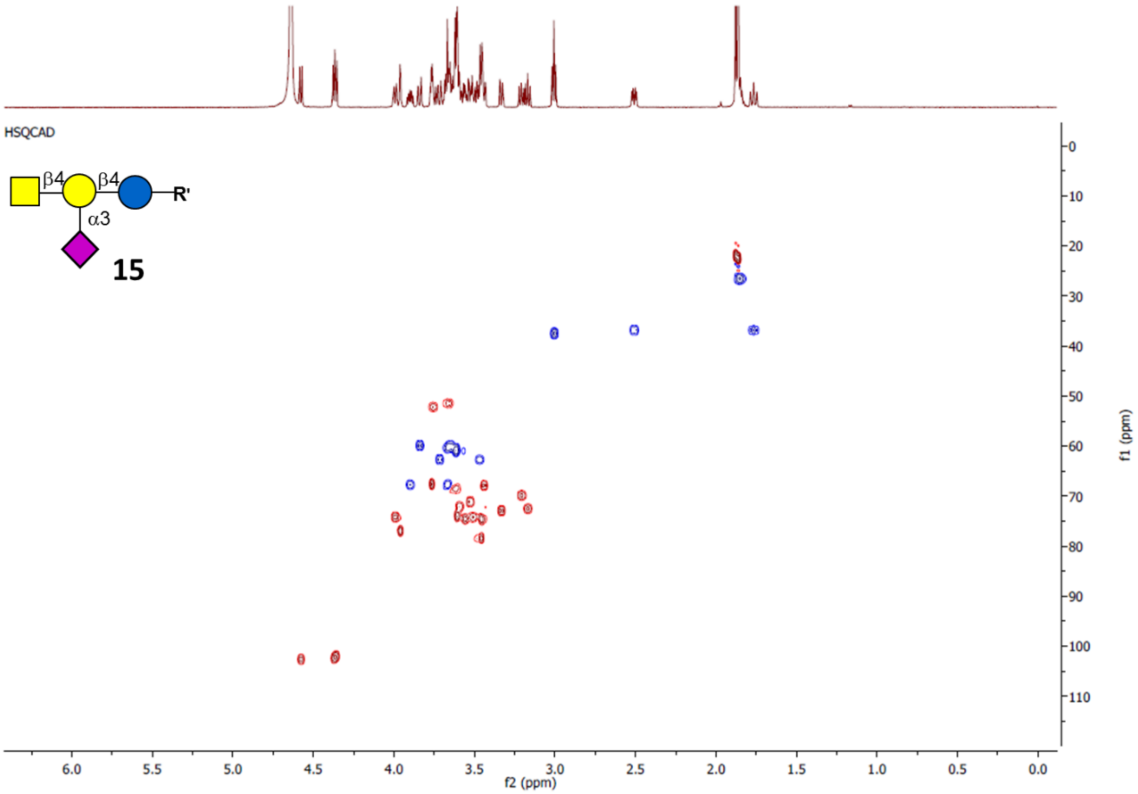


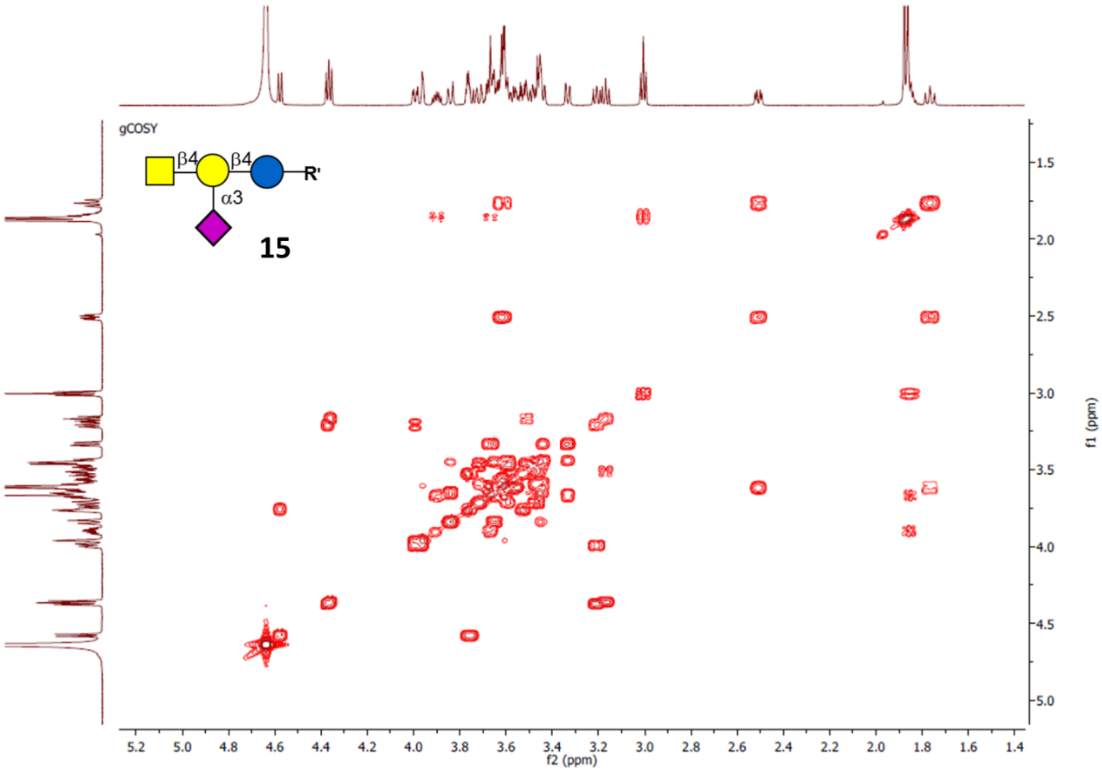
14

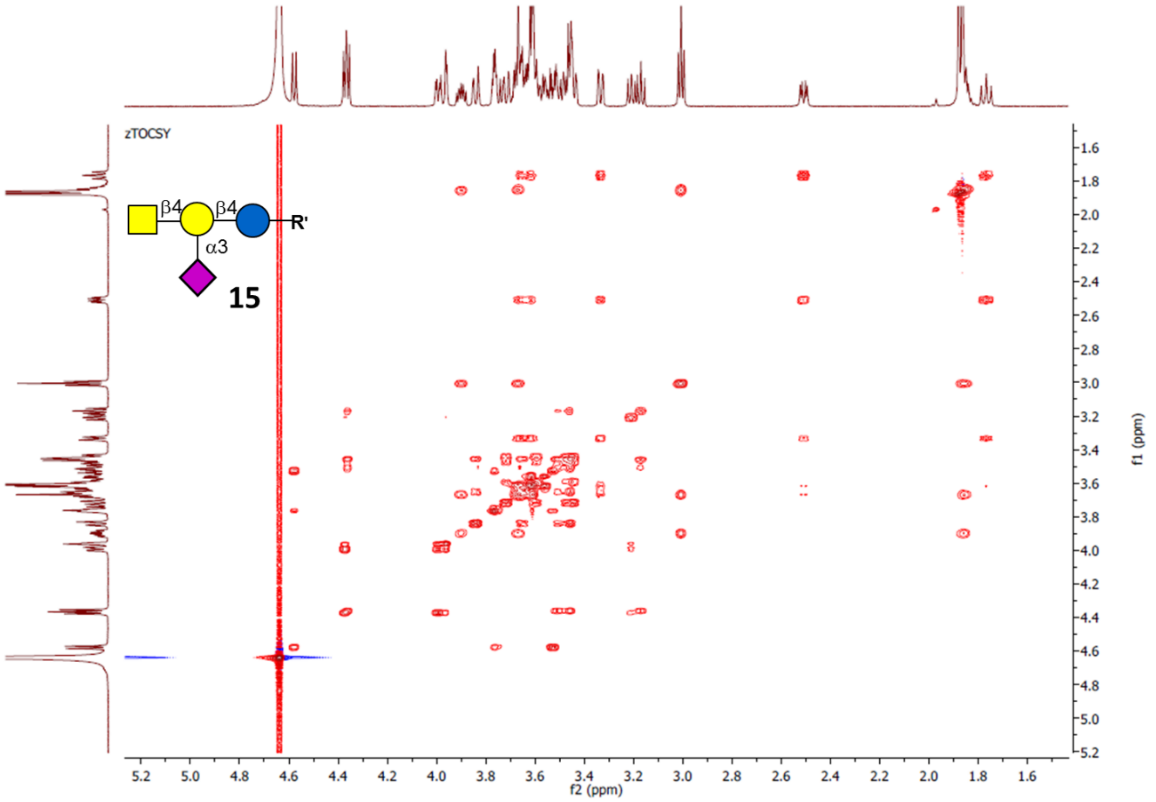
^{1}H NMR (600 MHz, D_2O)



15

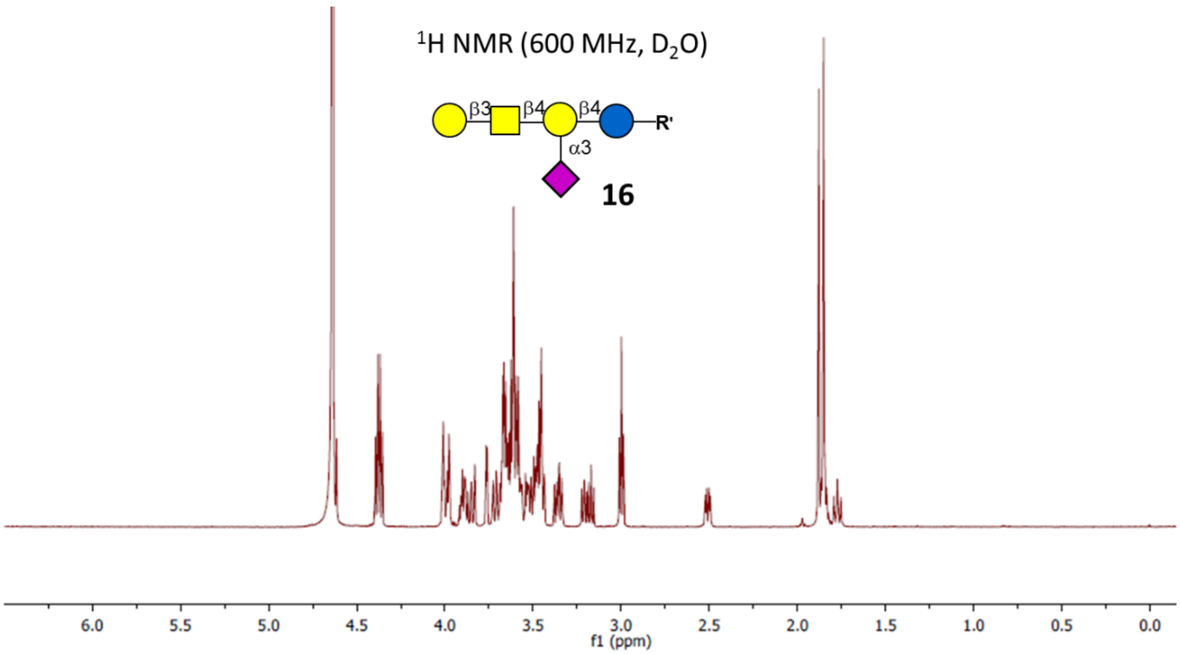

HSQCAD
β4
β4
α3
R'
15
f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)


gCOSY
β4
β4
α3
R'
15
f1 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
f2 (ppm)

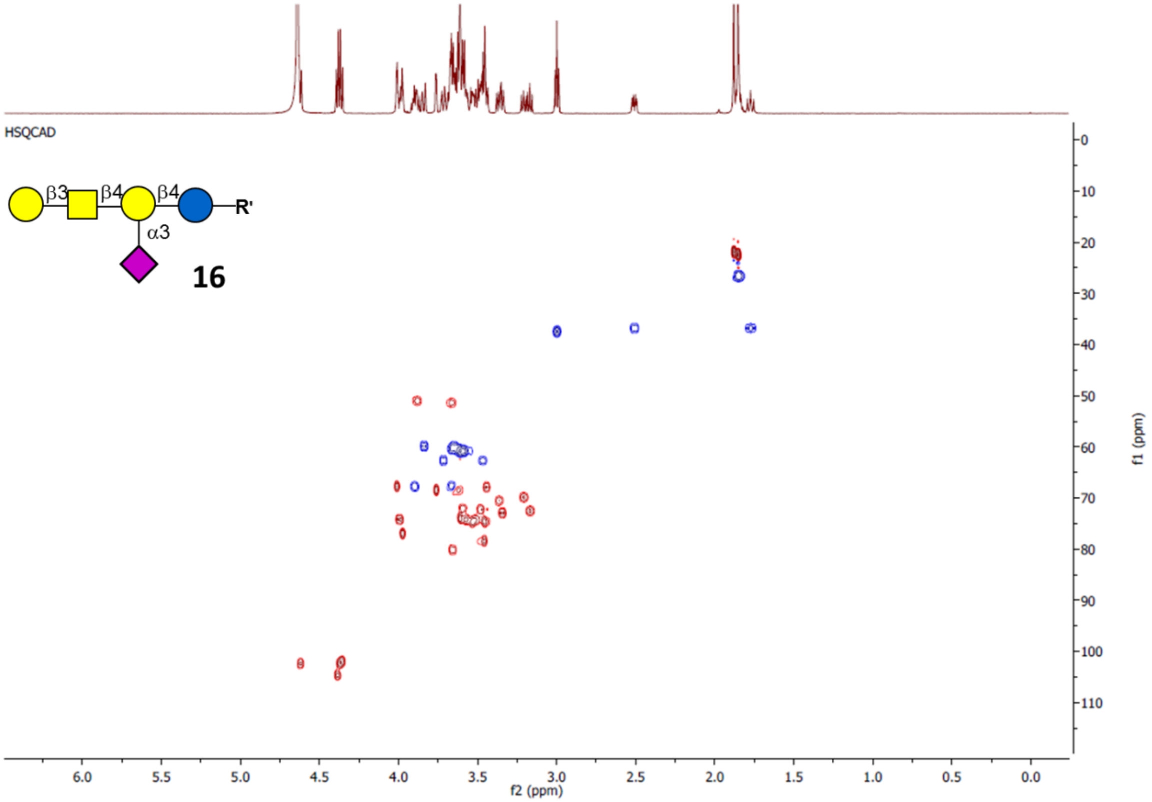


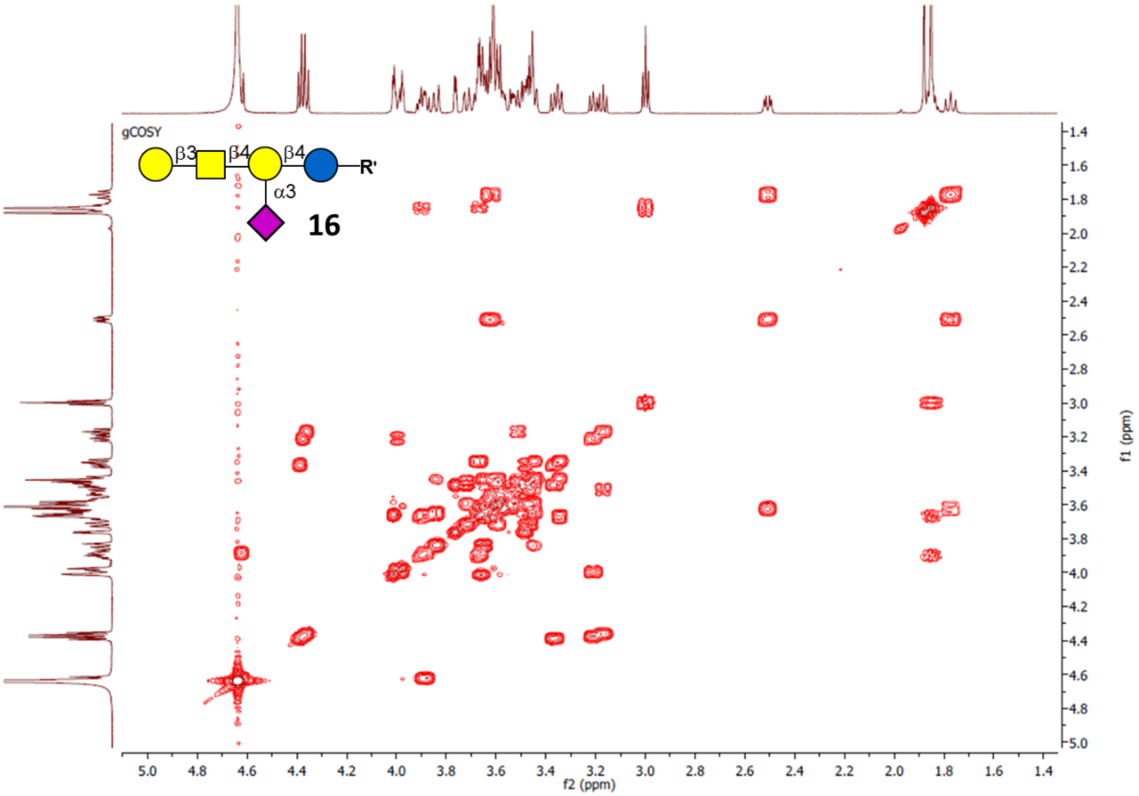
15

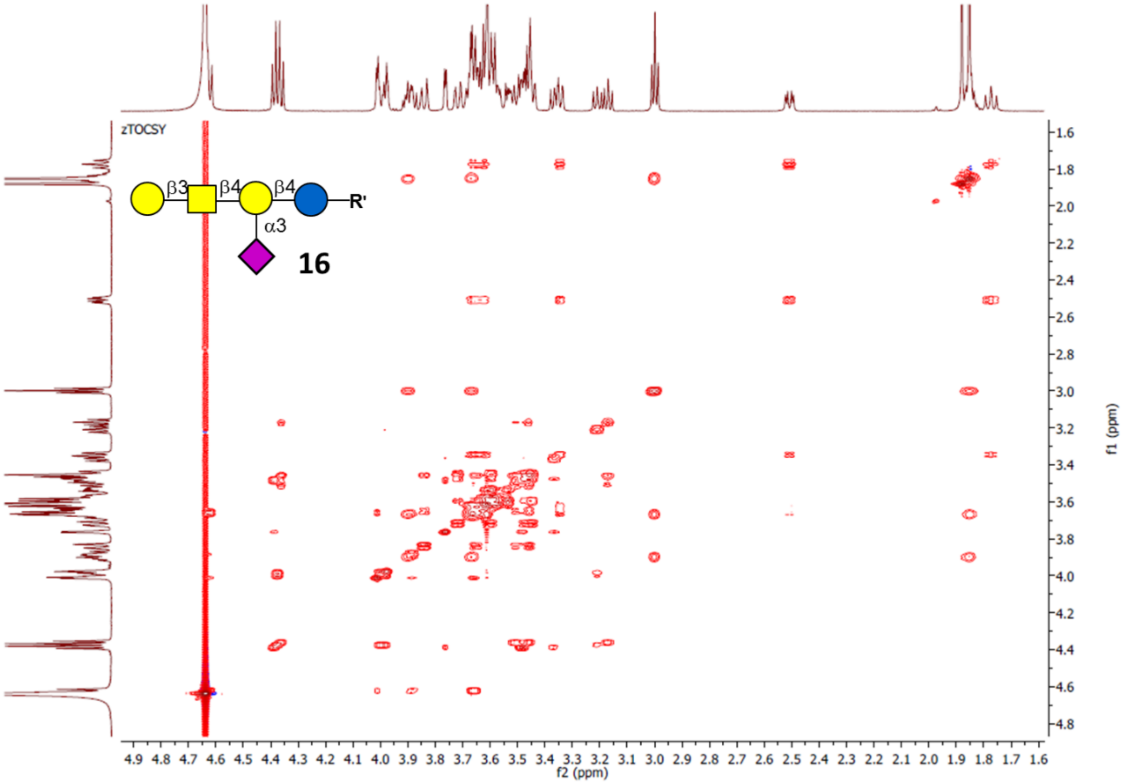
^{1}H NMR (600 MHz, D_2O)

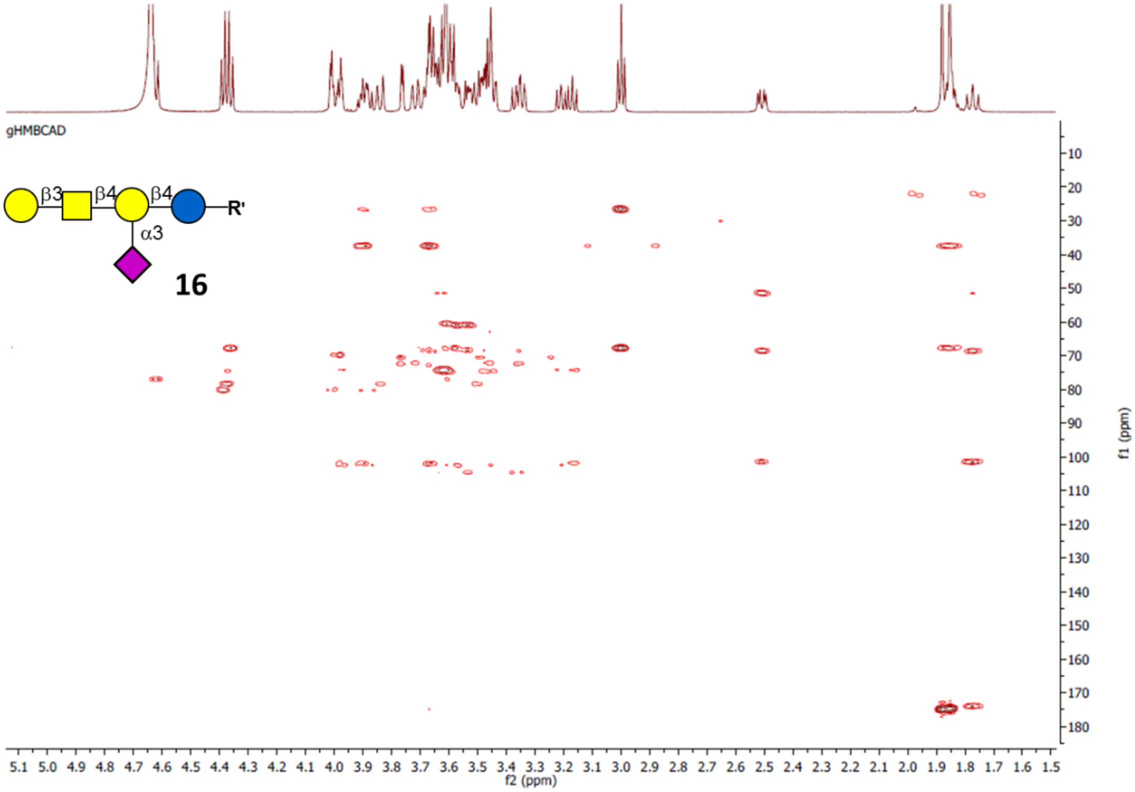


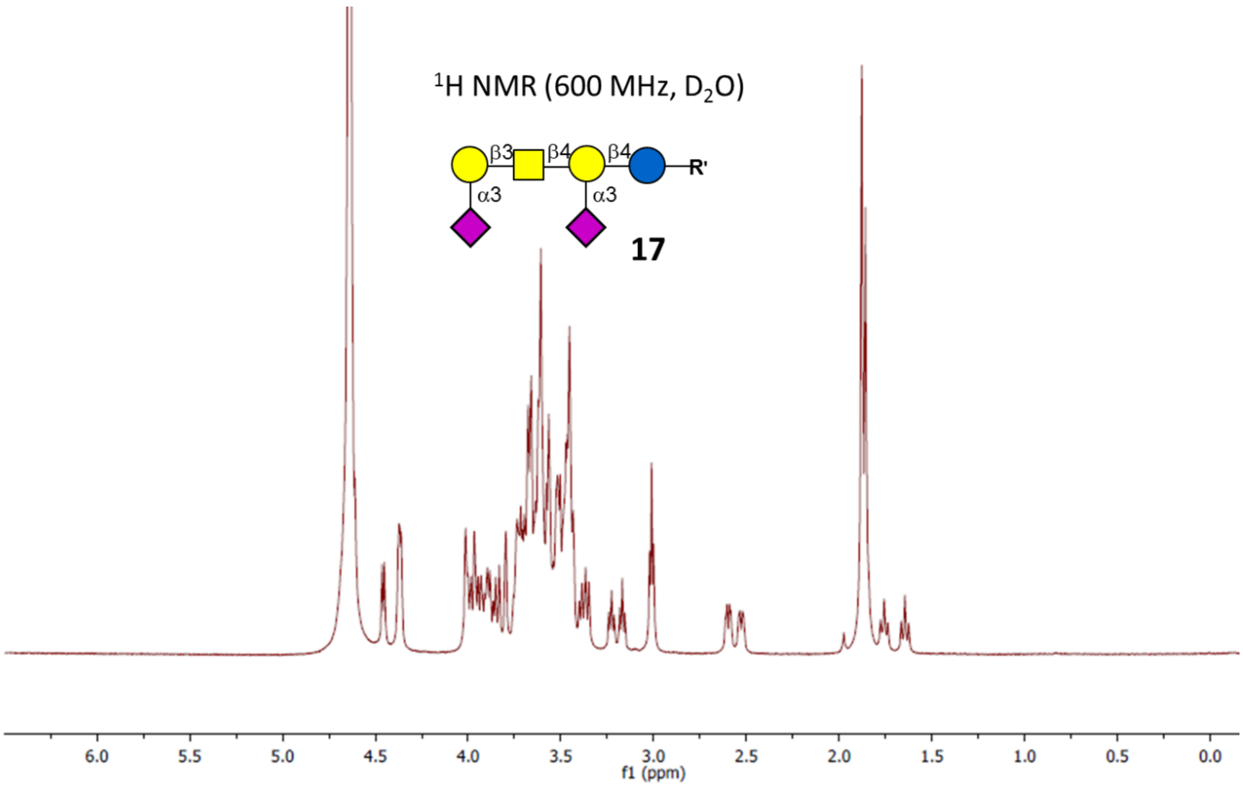
16


HSQCAD
β3
β4
β4
α3
R'
16
f2 (ppm)
f1 (ppm)
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
0
10
20
30
40
50
60
70
80
90
100
110


gCOSY
β3
β4
β4
α3
R'
16
f2 (ppm)
f1 (ppm)
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4

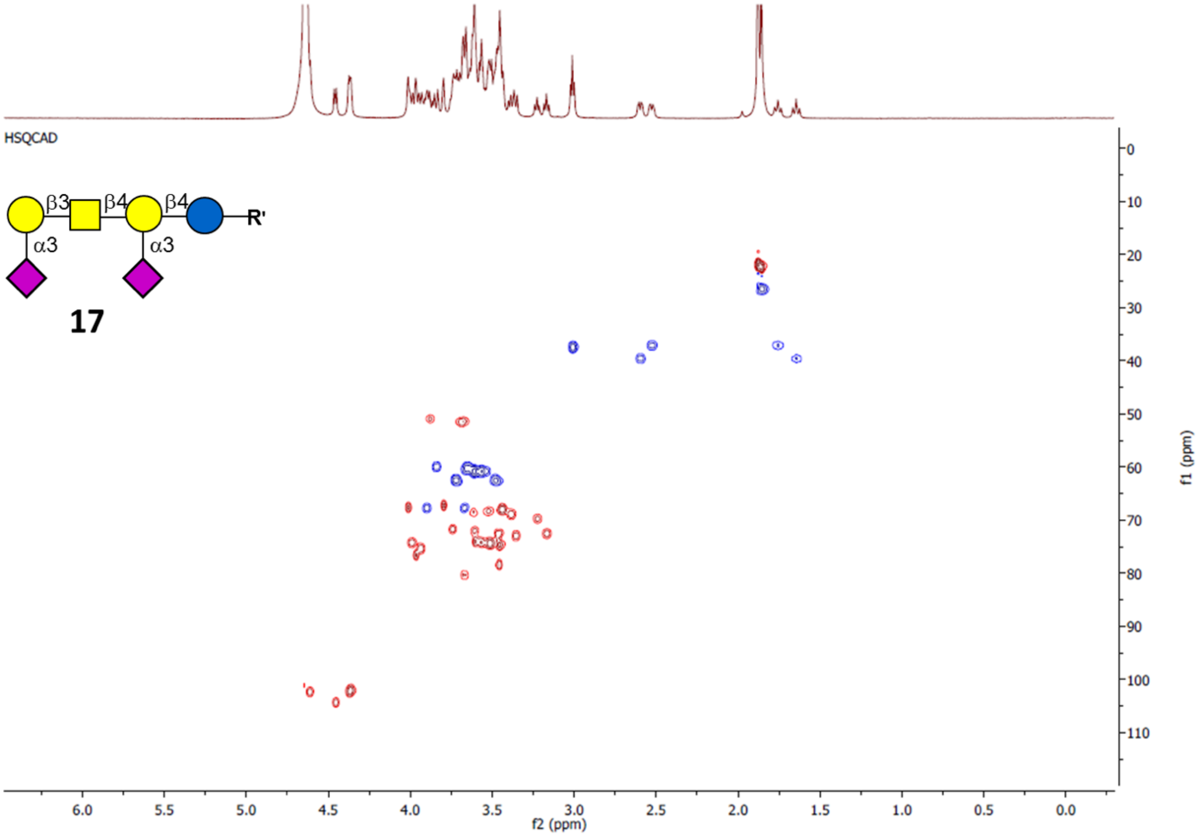

zTOCSY
β3
β4
β4
R'
α3
16
f2 (ppm)
f1 (ppm)
4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6
1.6 1.8 2.0 2.2 2.4 2.6 2.8 3.0 3.2 3.4 3.6 3.8 4.0 4.2 4.4 4.6 4.8


gHMBCAD
β3
β4
β4
R'
α3
16
f2 (ppm)
f1 (ppm)
5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5
10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180

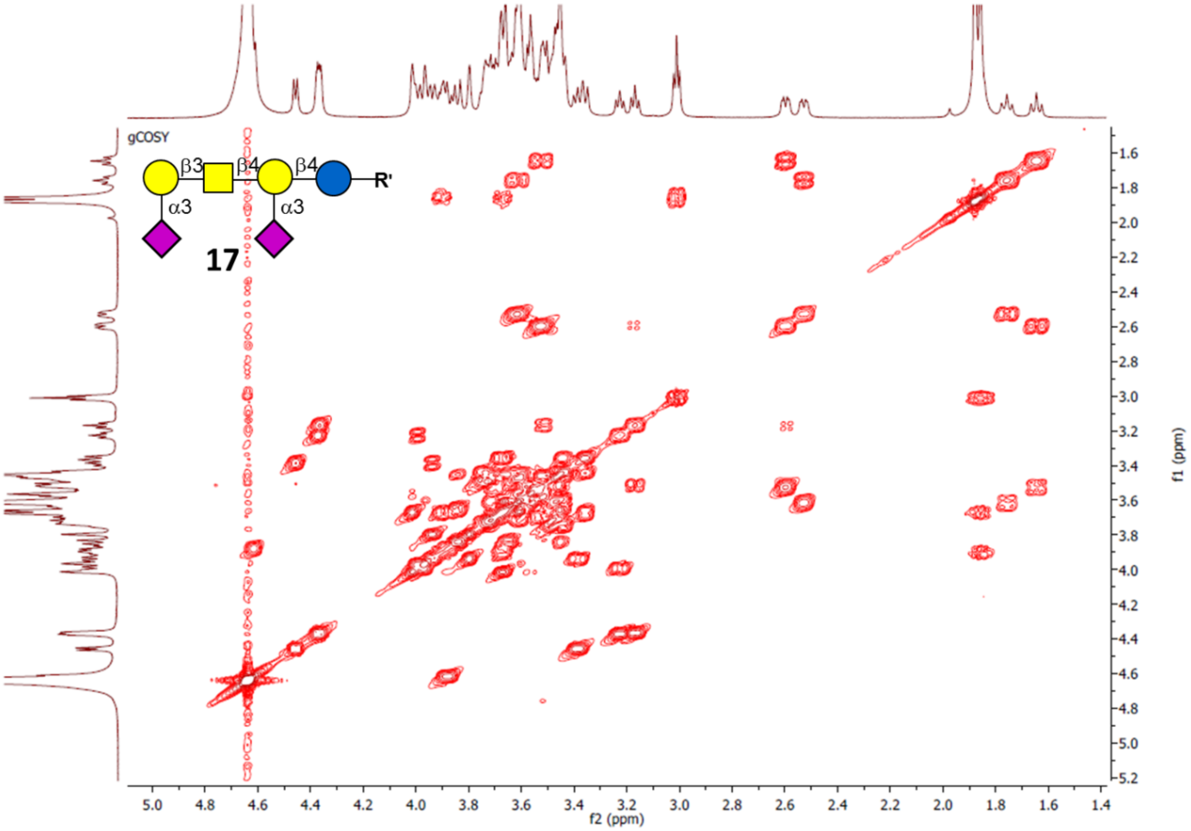


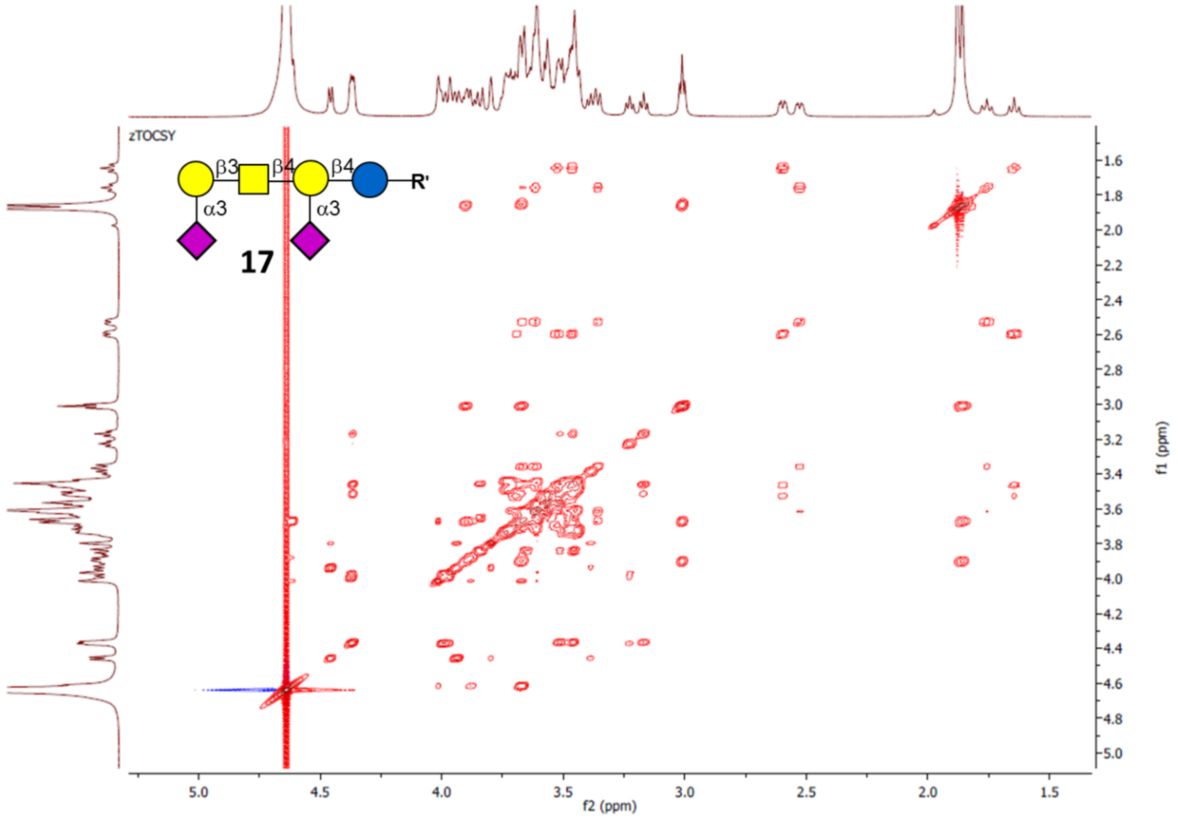
^{1}H NMR (600 MHz, D_2O)

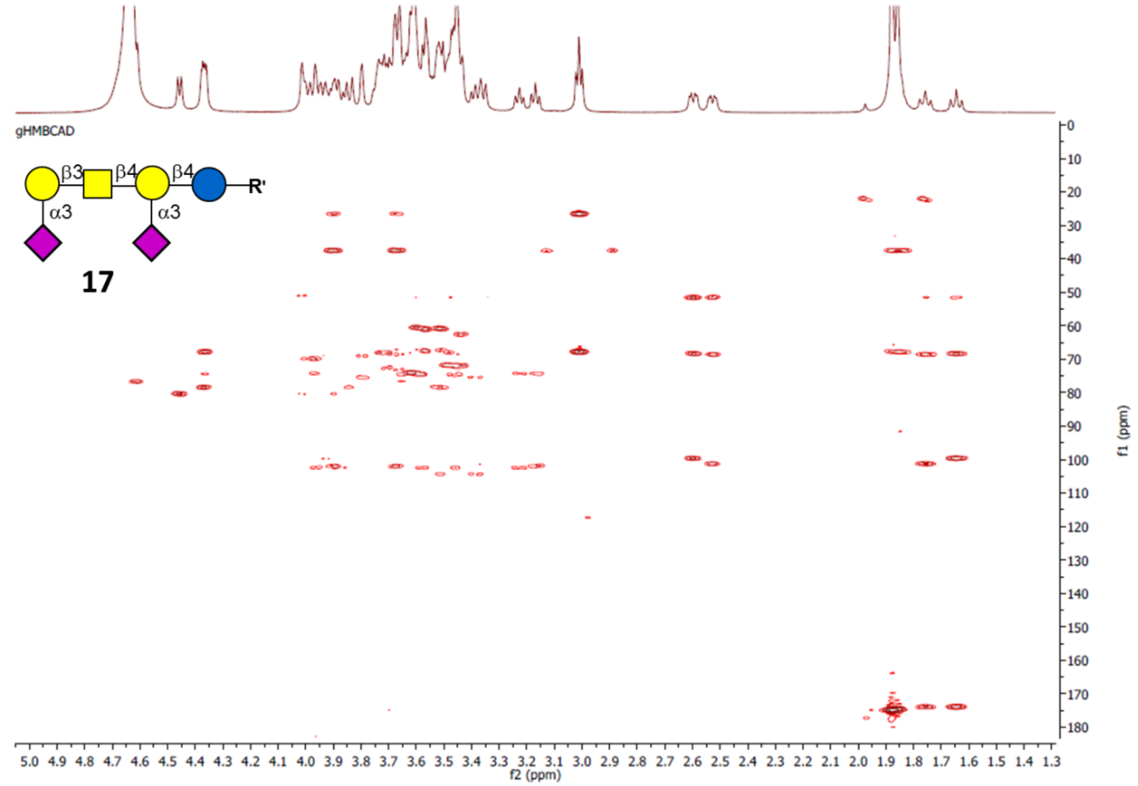
17



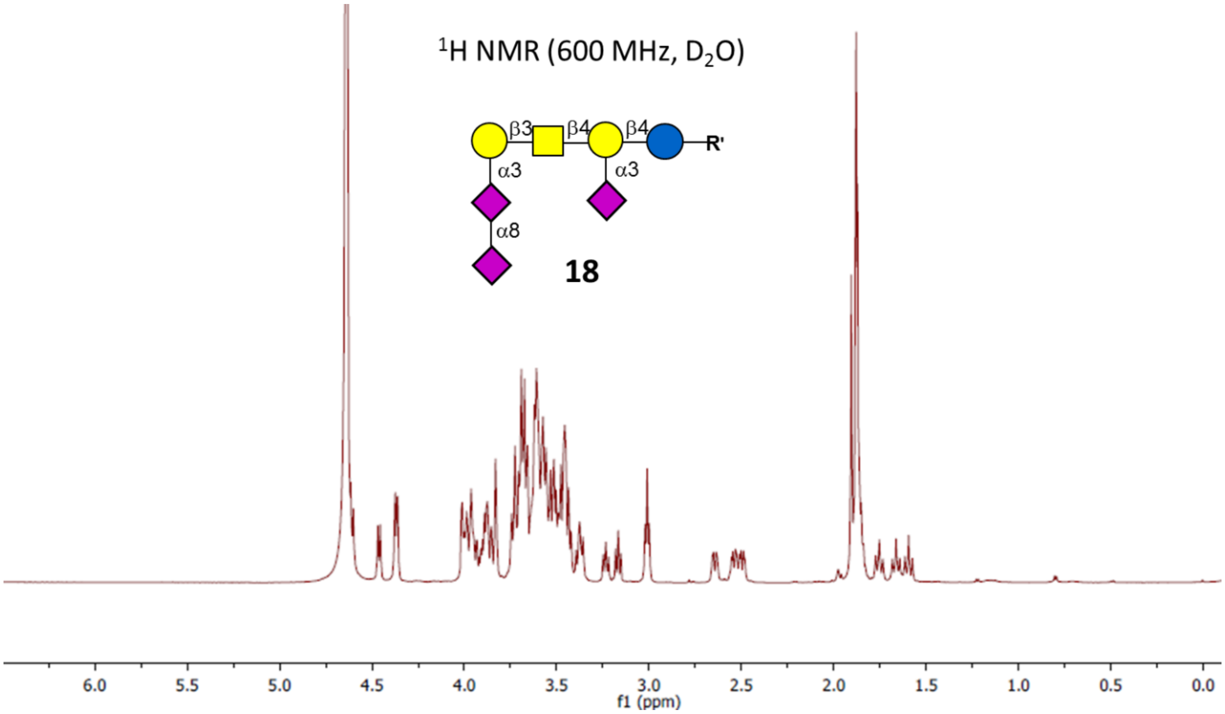
17


gCOSY
β3
β4
β4
α3
α3
R'
17
5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4
f2 (ppm)
1.6 1.8 2.0 2.2 2.4 2.6 2.8 3.0 3.2 3.4 3.6 3.8 4.0 4.2 4.4 4.6 4.8 5.0 5.2
f1 (ppm)


zTOCSY
β3
β4
β4
α3
α3
R'
17
5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
f2 (ppm)
1.6 1.8 2.0 2.2 2.4 2.6 2.8 3.0 3.2 3.4 3.6 3.8 4.0 4.2 4.4 4.6 4.8 5.0
f1 (ppm)

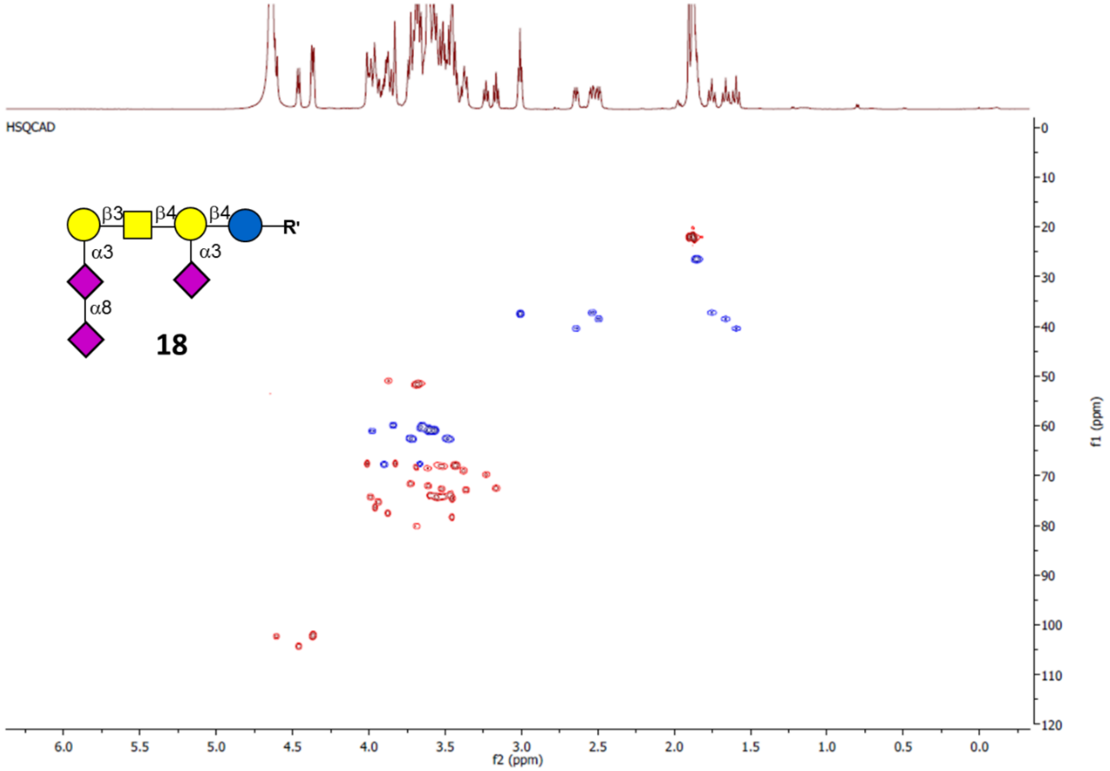


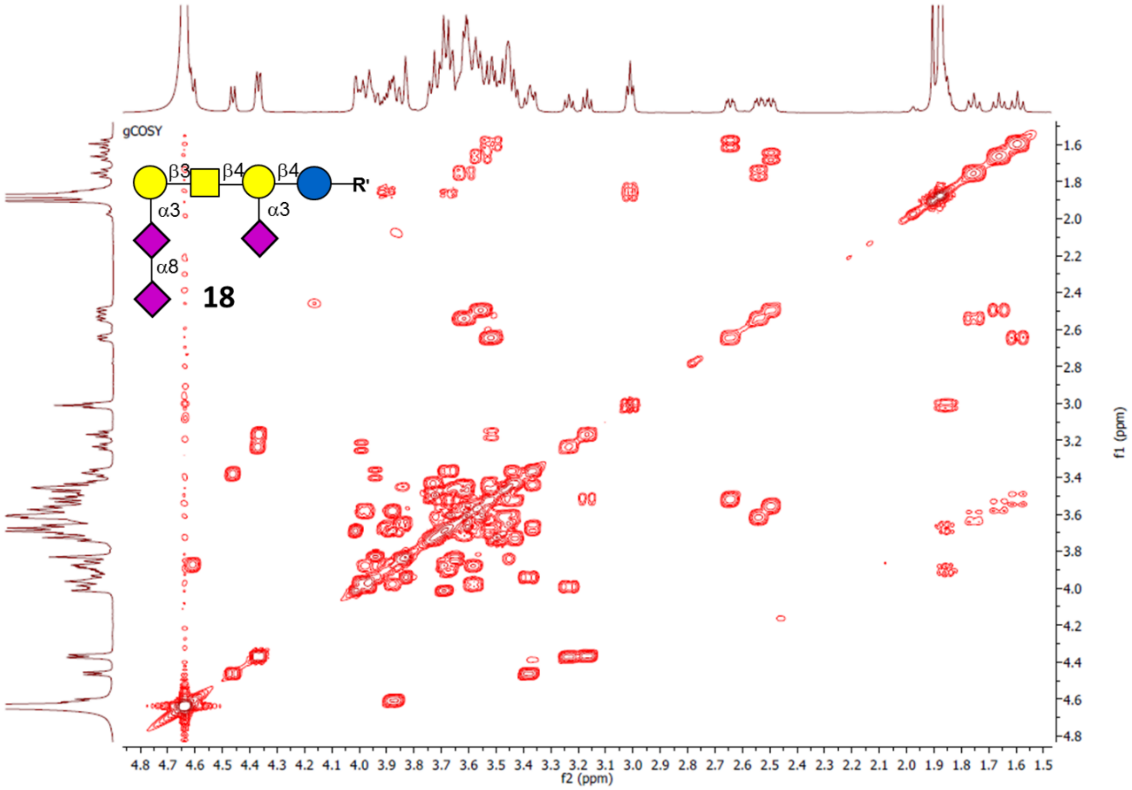
17

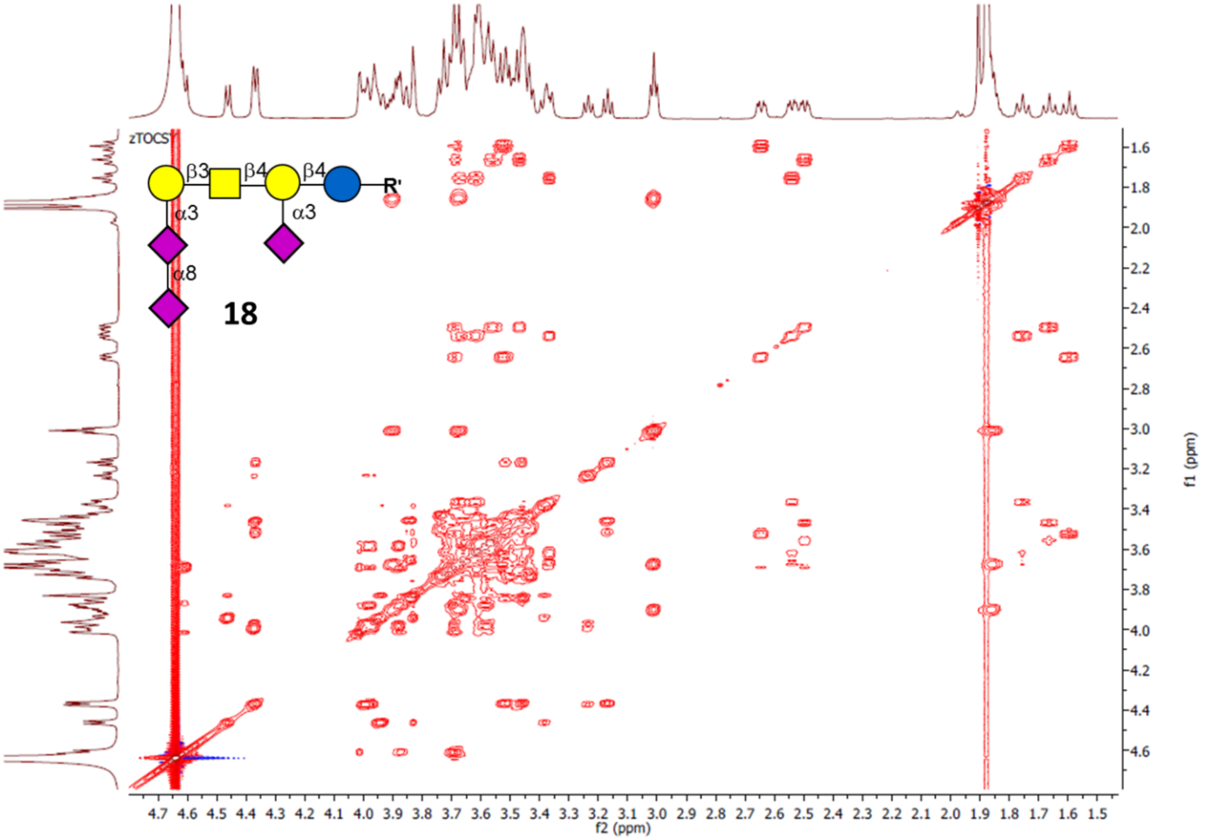


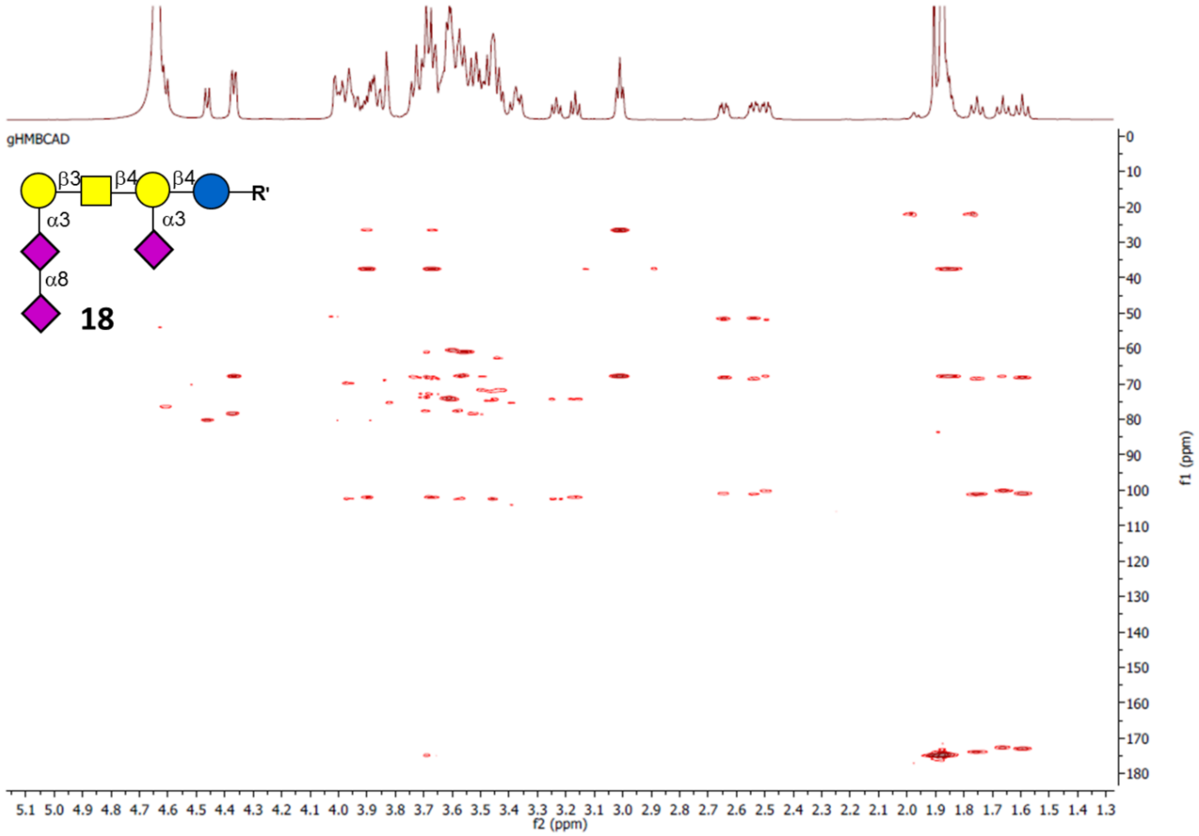
^{1}H NMR (600 MHz, D_2O)

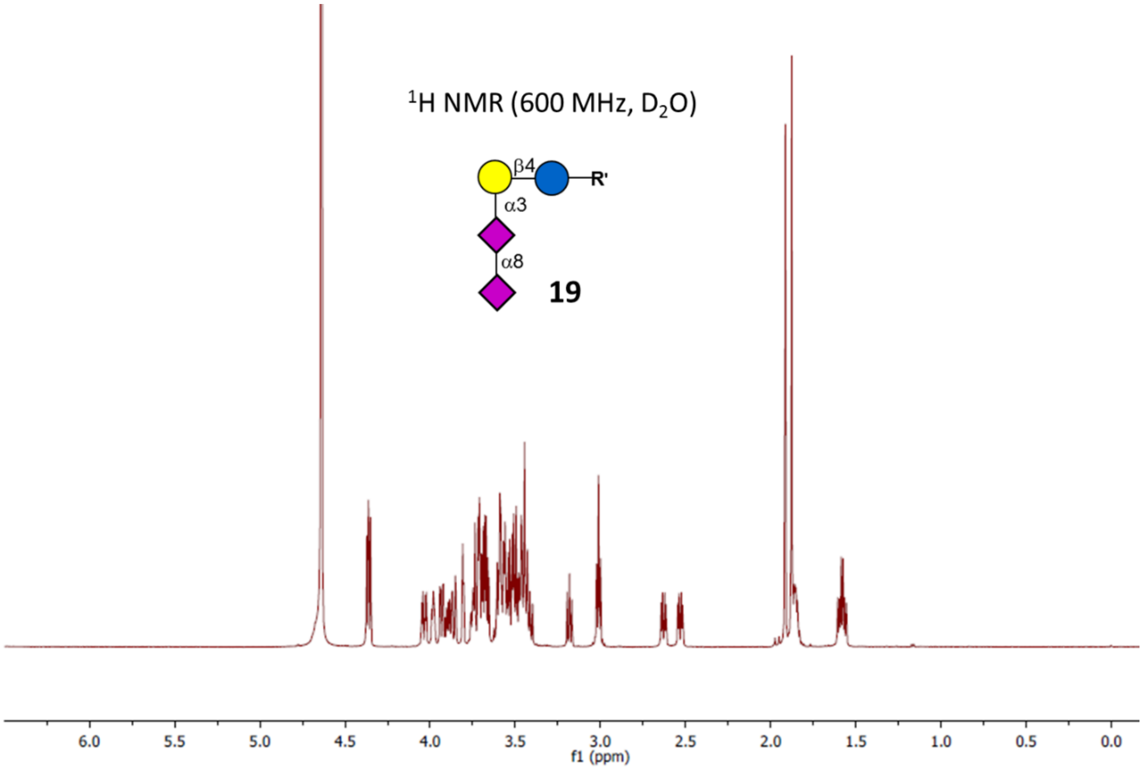
18

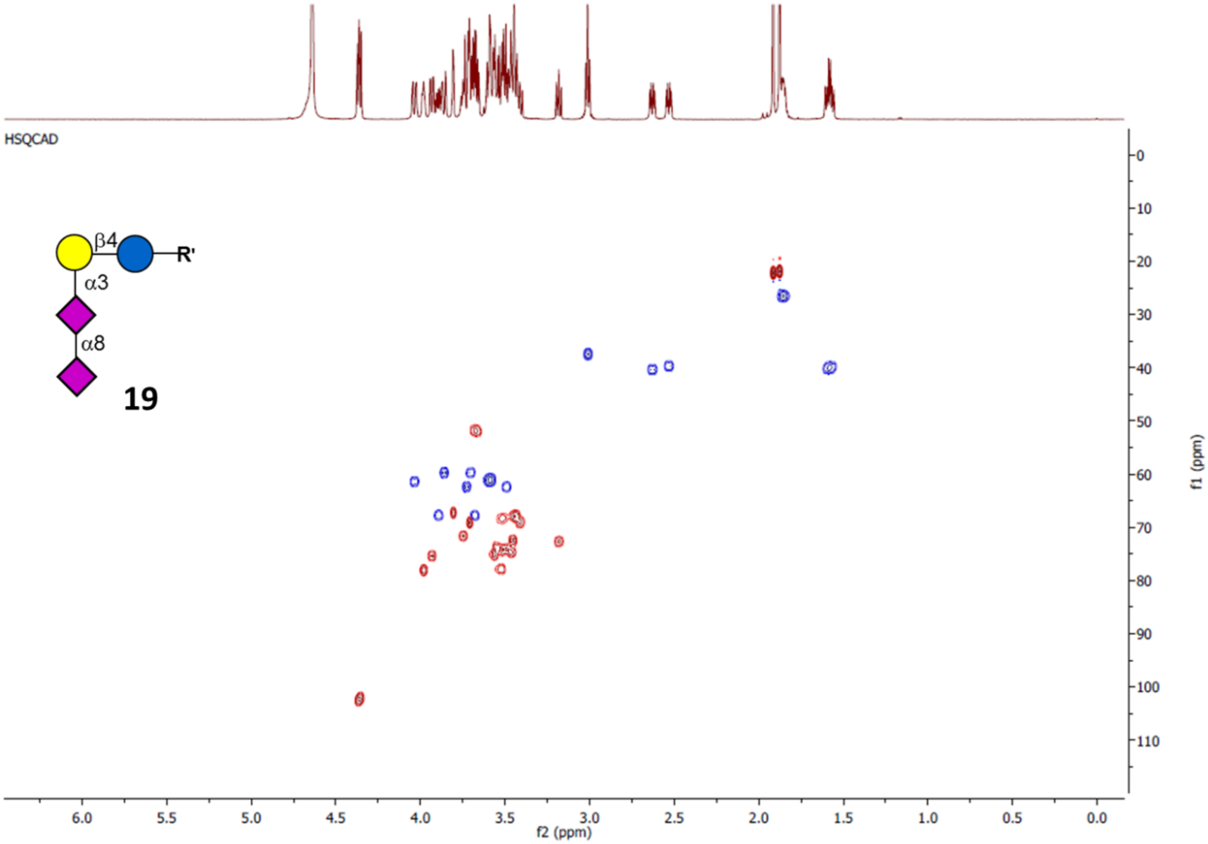

HSQCAD
β3
β4
β4
R'
α3
α3
α8
18
f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

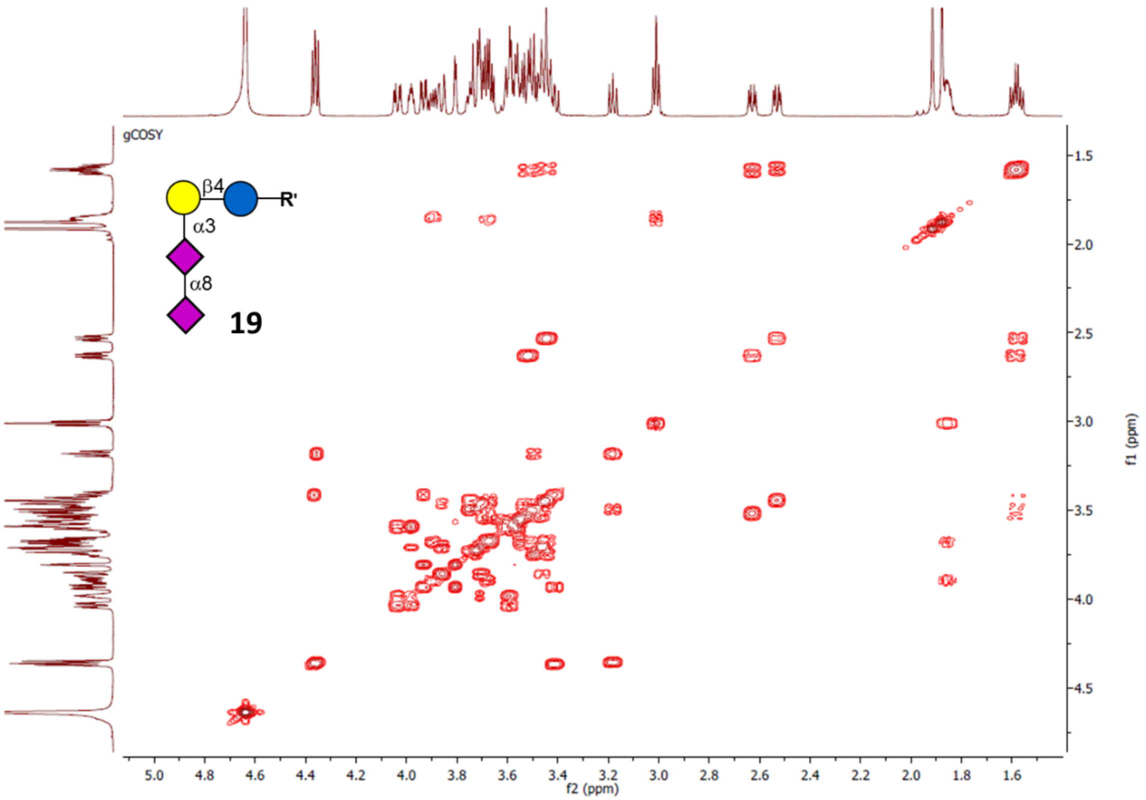

gCOSY
β3
β4
β4
R'
α3
α3
α8
18
f1 (ppm)
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5
f2 (ppm)


zTOCSY
β3
β4
β4
R'
α3
α3
α8
18
f2 (ppm)
4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5
f1 (ppm)
1.6 1.8 2.0 2.2 2.4 2.6 2.8 3.0 3.2 3.4 3.6 3.8 4.0 4.2 4.4 4.6

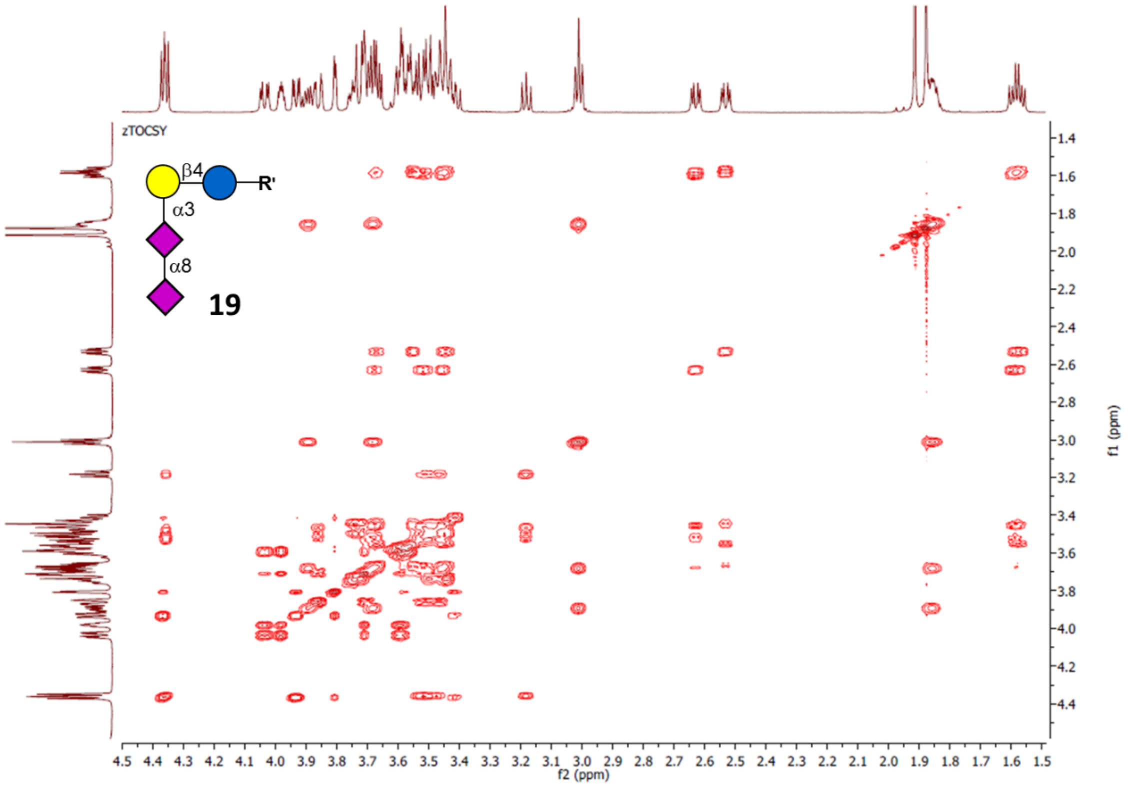

gHMBCAD
β3
β4
β4
R'
α3
α3
α8
18
f2 (ppm)
5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3
f1 (ppm)
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180


^{1}H NMR (600 MHz, D$_2$O)
β4
R'
α3
α8
19
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)

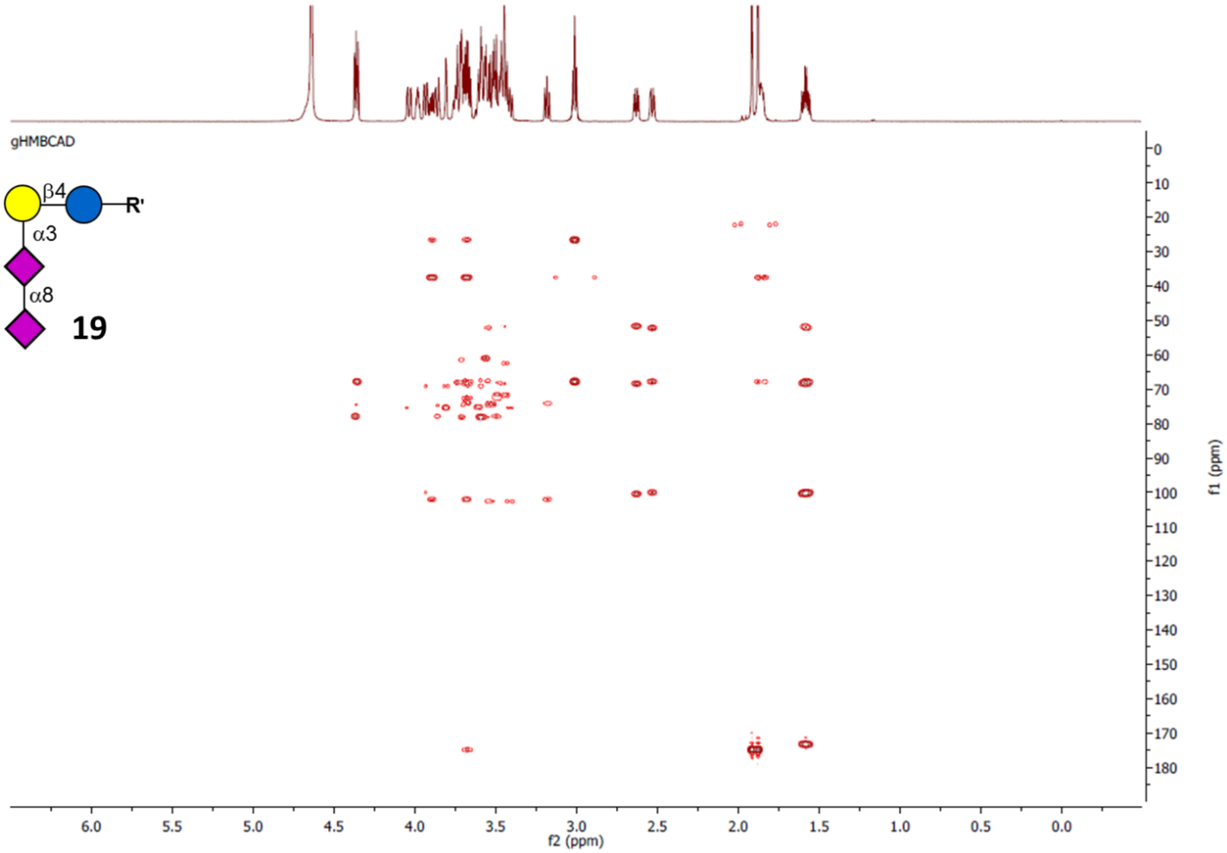

HSQCAD
β4
R'
α3
α8
19
0
10
20
30
40
50
60
70
80
90
100
110
f1 (ppm)
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)


gCOSY
β4
R'
α3
α8
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
f1 (ppm)

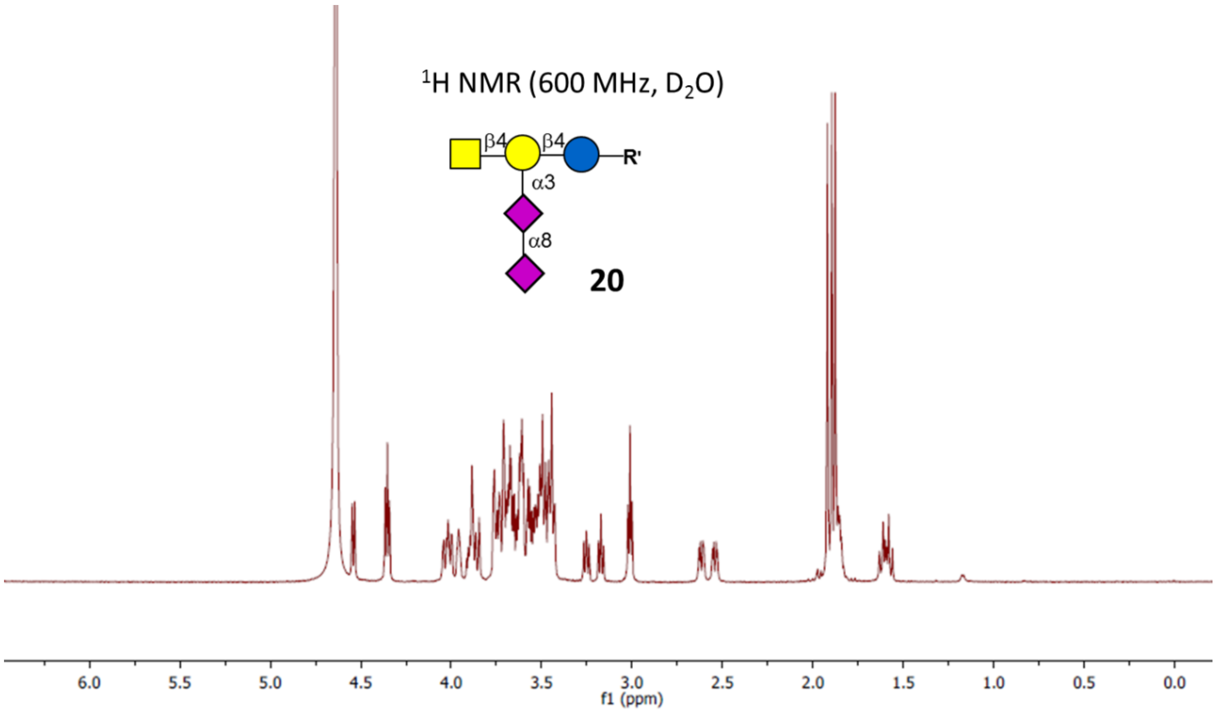
19


zTOCSY
β4
R'
α3
α8
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
3.0
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
f2 (ppm)
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
f1 (ppm)

19

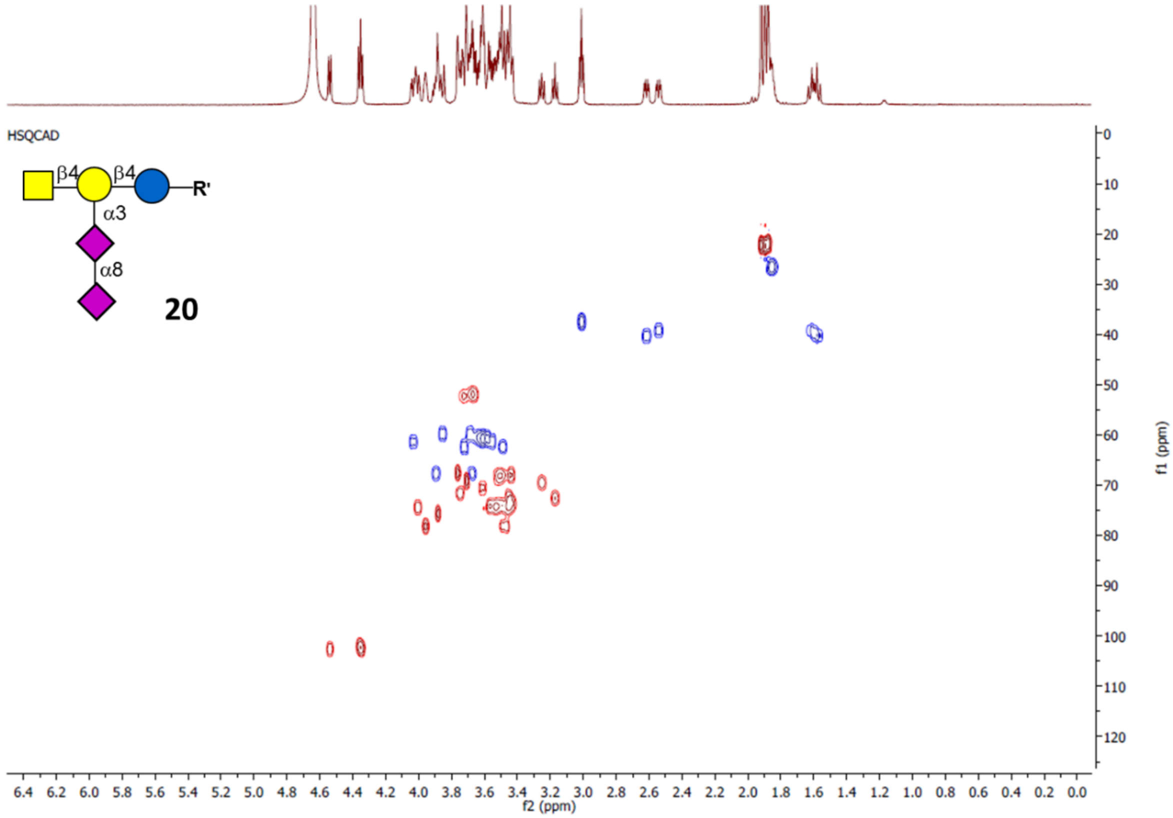


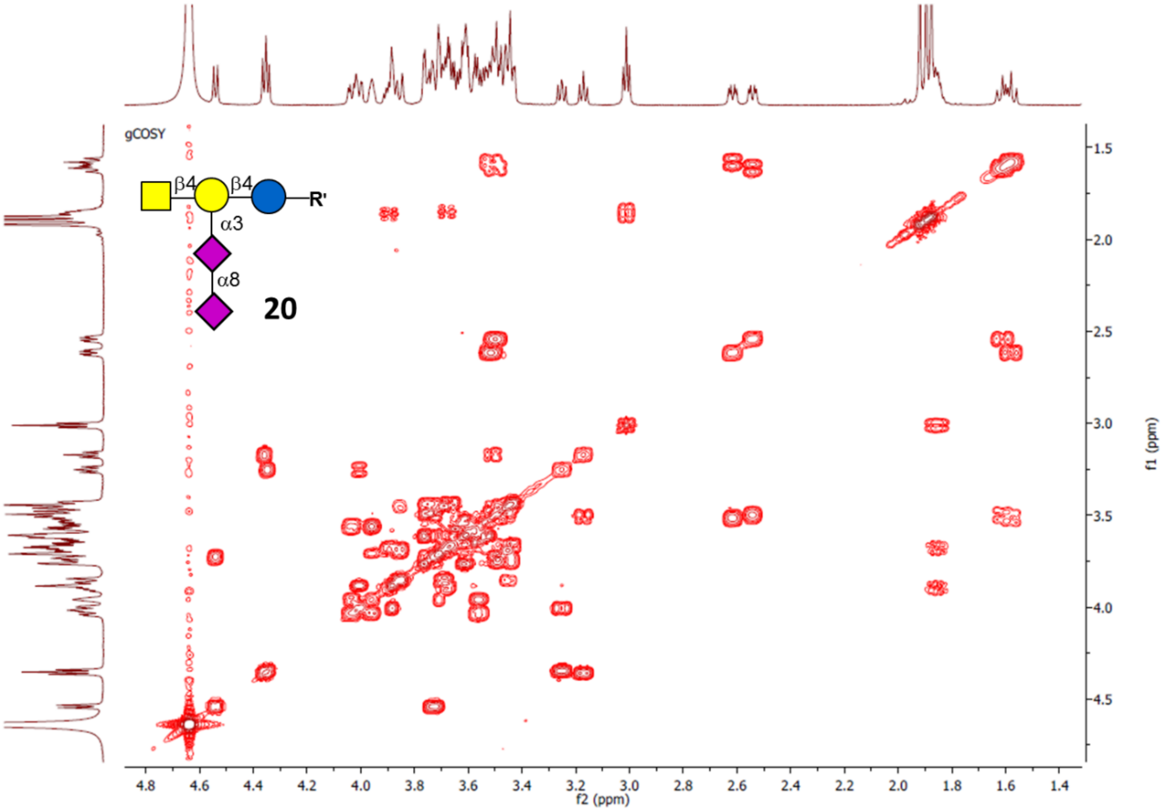
19

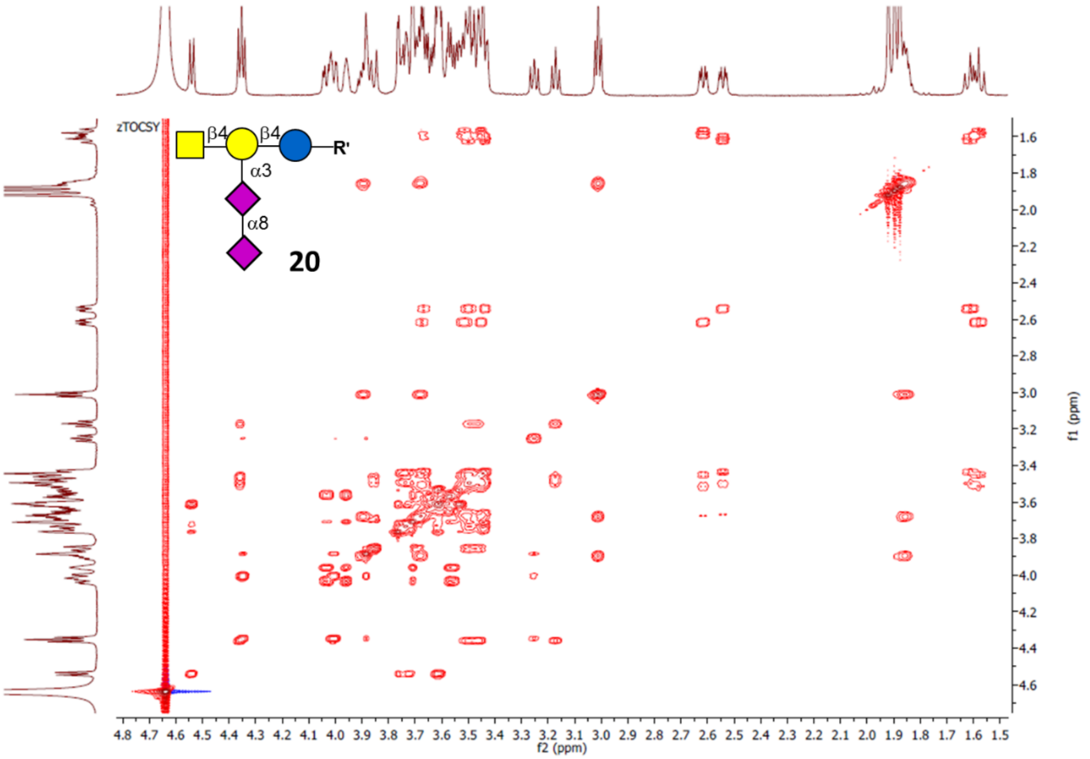


^{1}H NMR (600 MHz, D_2O)

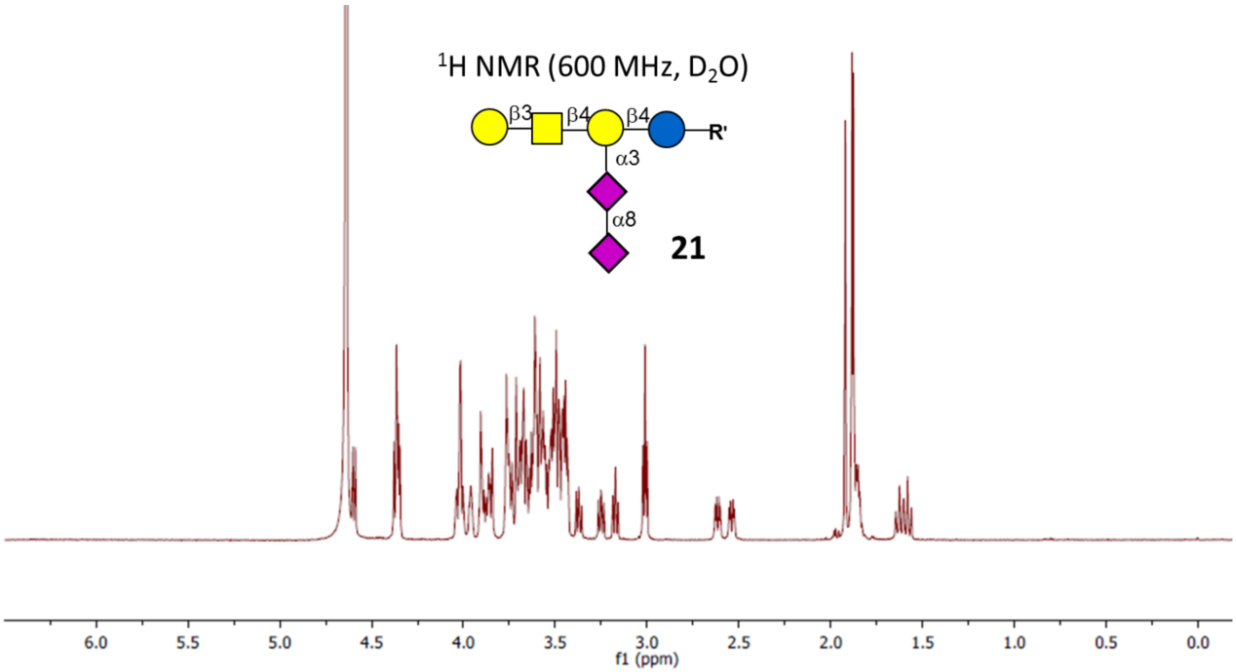
20


HSQCAD
β4
β4
R'
α3
α8
20
f1 (ppm)
f2 (ppm)
6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0
0 10 20 30 40 50 60 70 80 90 100 110 120

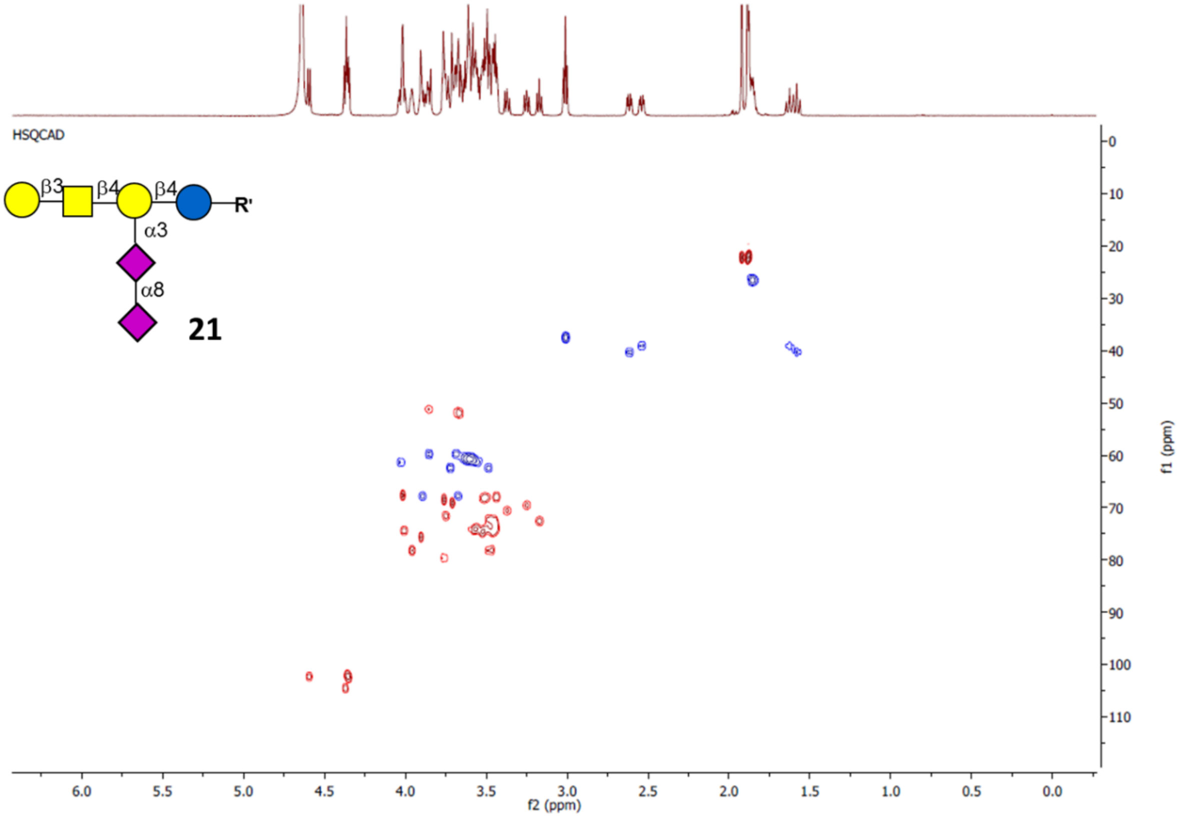

gCOSY
β4
β4
R'
α3
α8
20
f1 (ppm)
f2 (ppm)
4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4
1.5 2.0 2.5 3.0 3.5 4.0 4.5

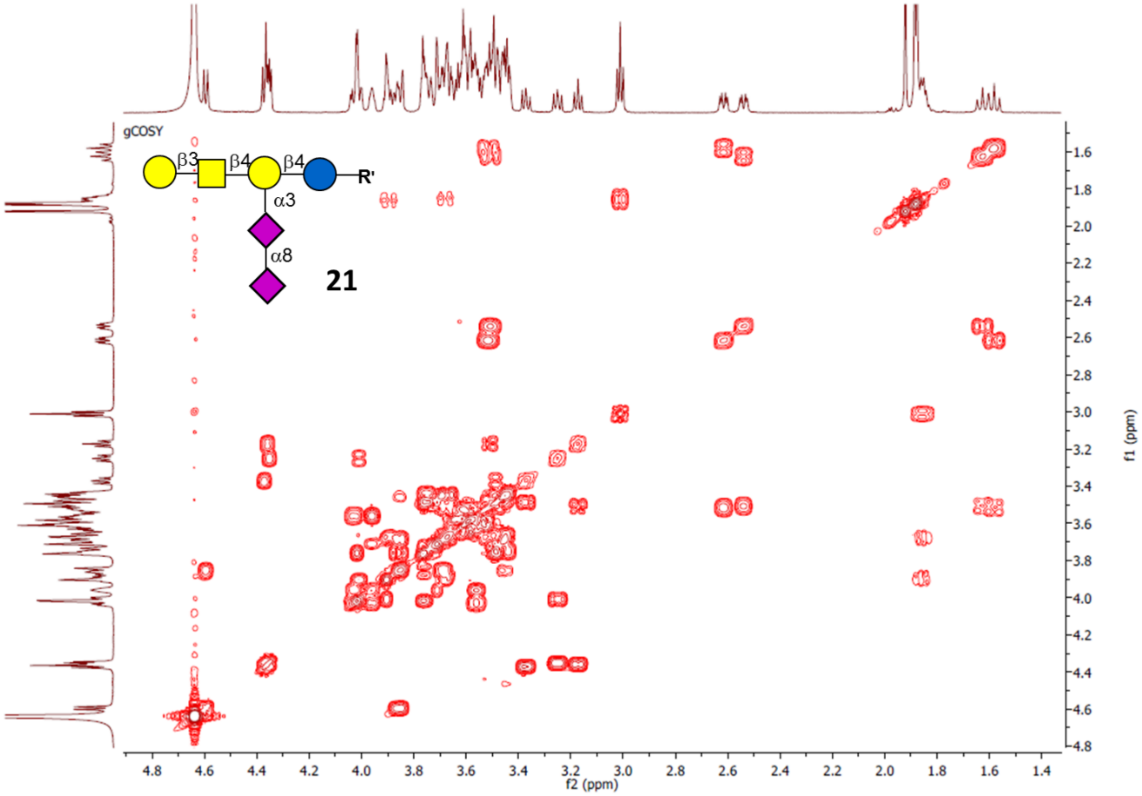


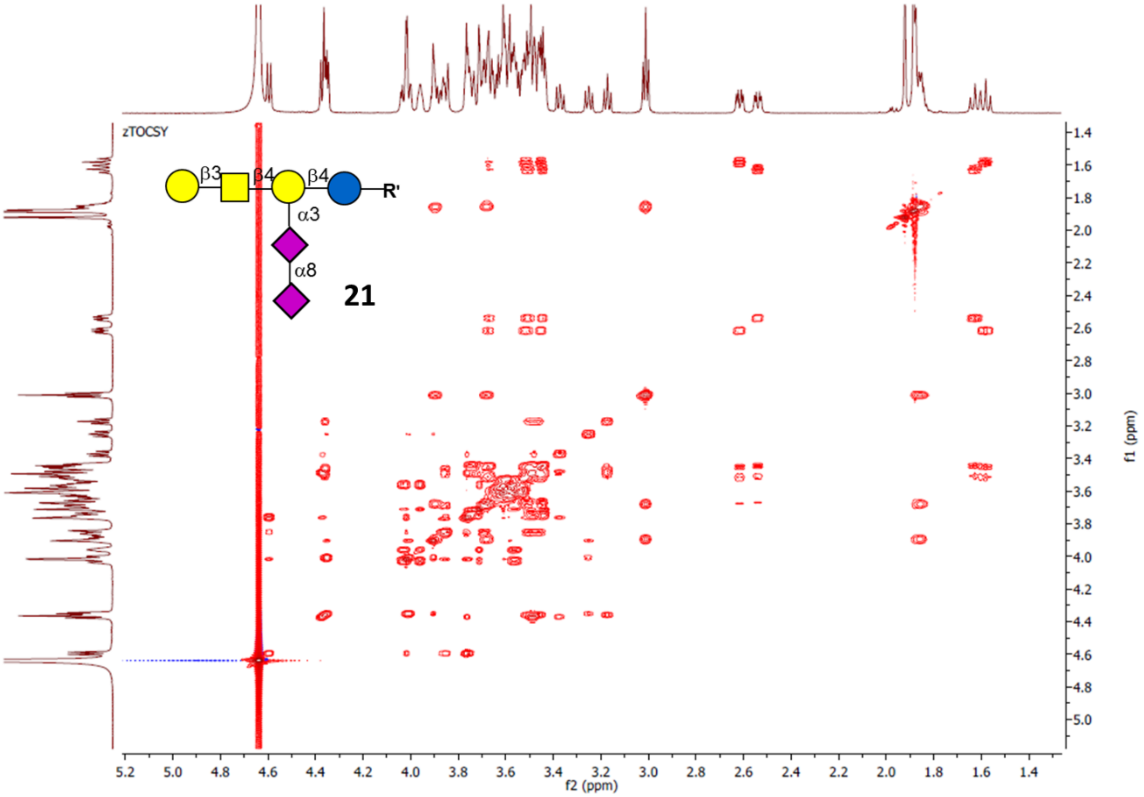
20

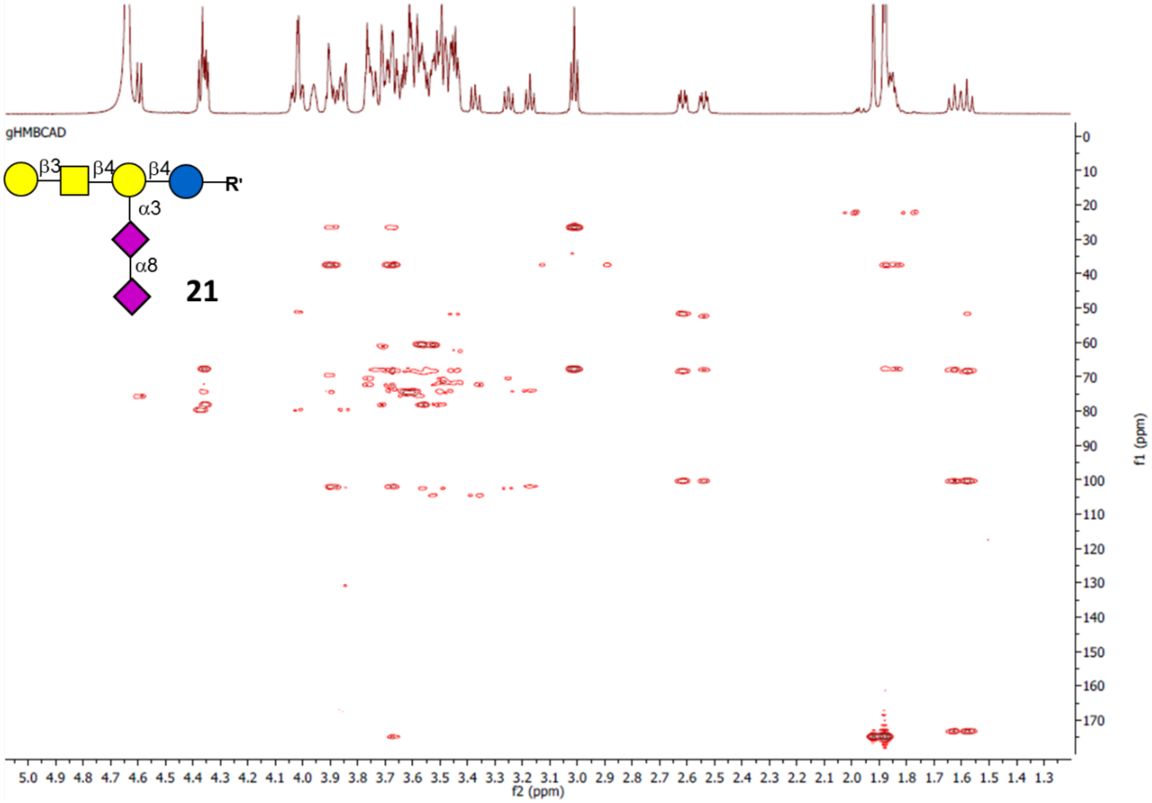

^{1}H NMR (600 MHz, D_2O)

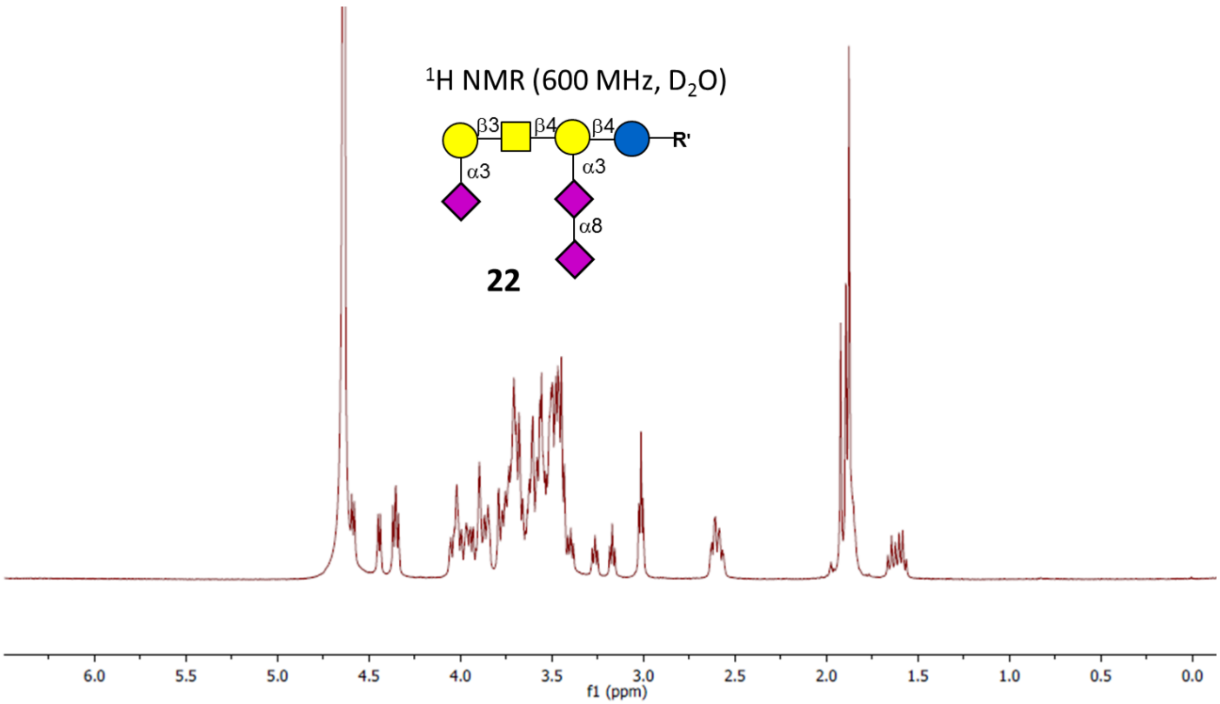
21


HSQCAD
β3
β4
β4
R'
α3
α8
21
f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

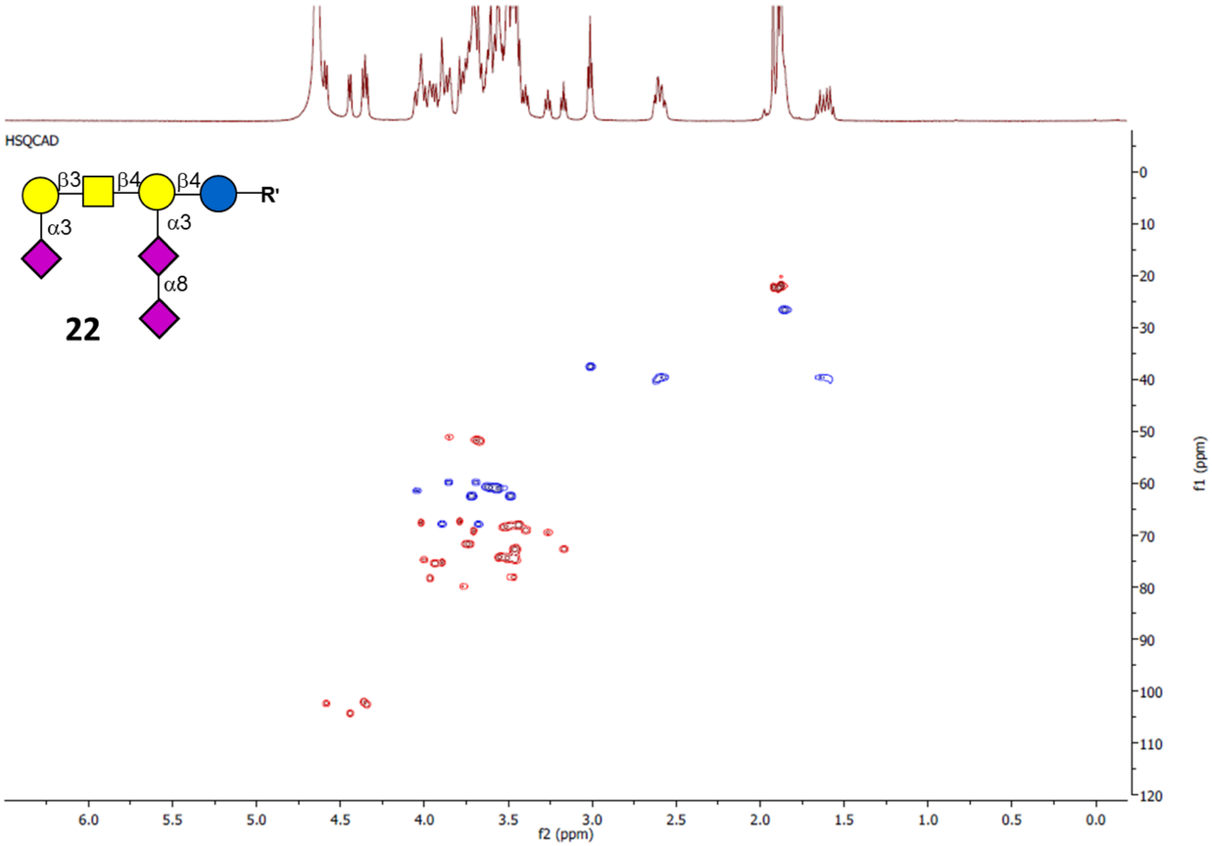

gCOSY
β3
β4
β4
R'
α3
α8
21
f1 (ppm)
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
f2 (ppm)


zTOCSY
β3
β4
β4
R'
α3
α8
21
f2 (ppm)
f1 (ppm)
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4

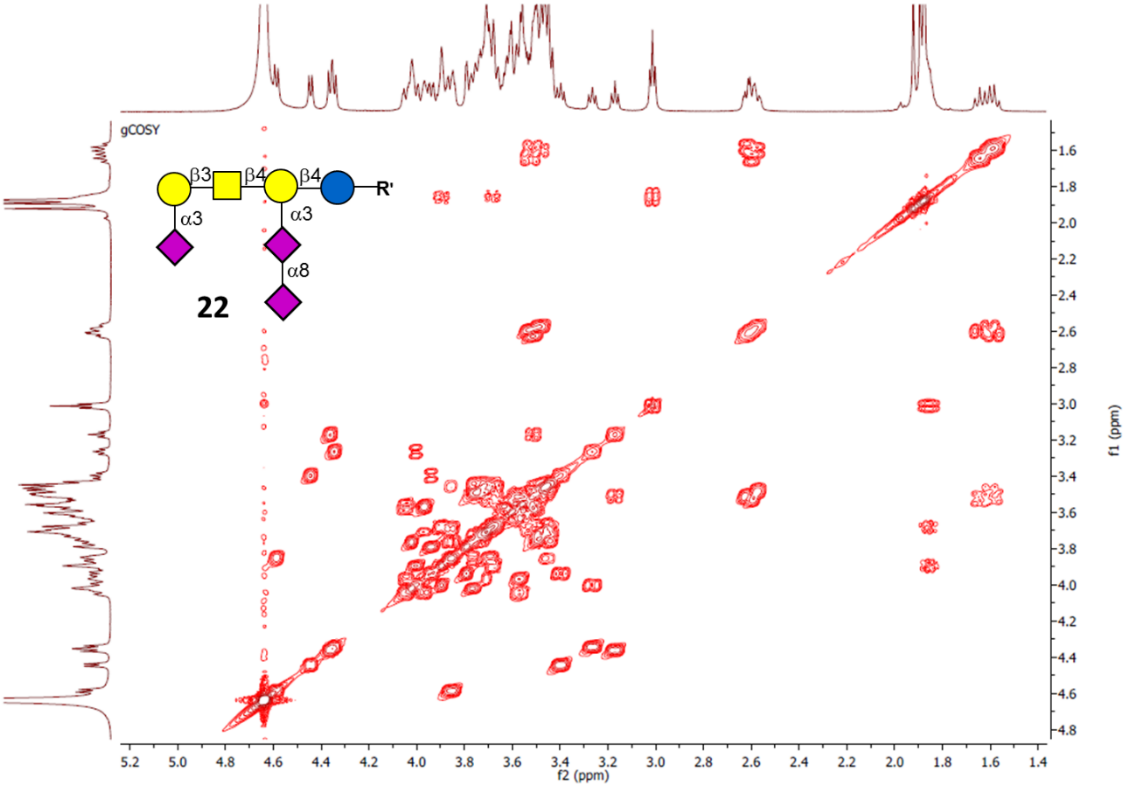

gHMBCAD
β3
β4
β4
R'
α3
α8
21
f2 (ppm)
f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170

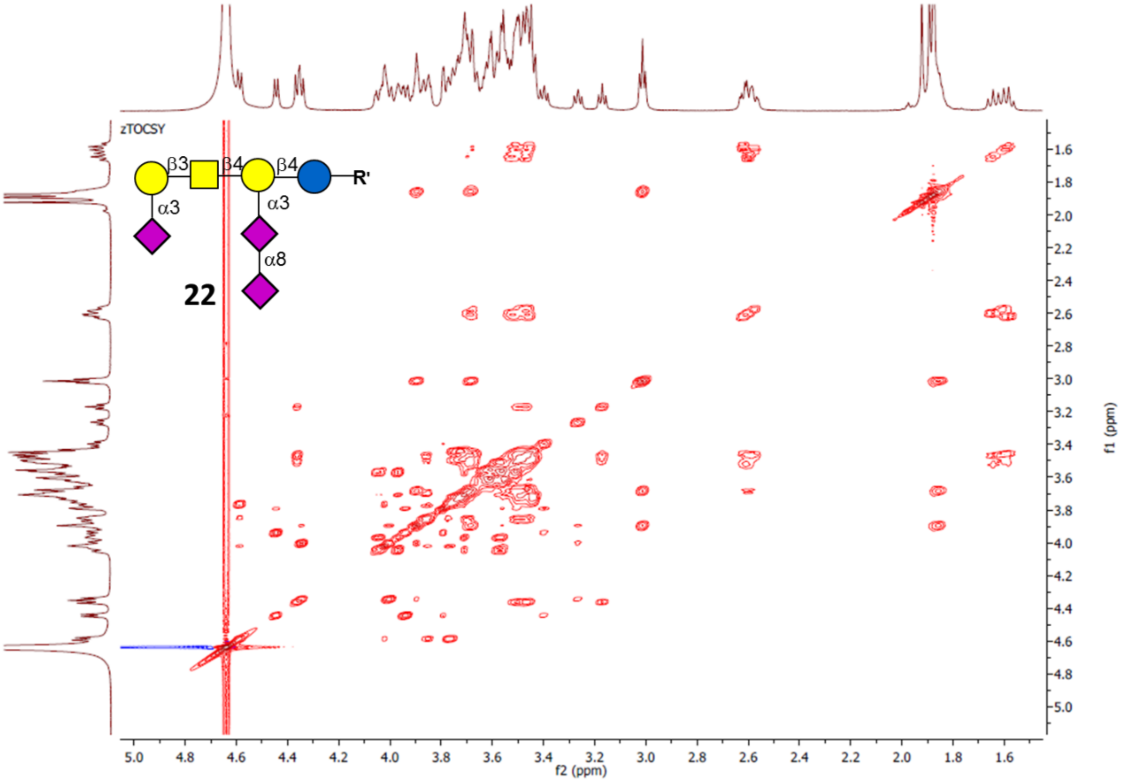

^{1}H NMR (600 MHz, D$_2$O)
β3
β4
β4
R'
α3
α3
α8
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

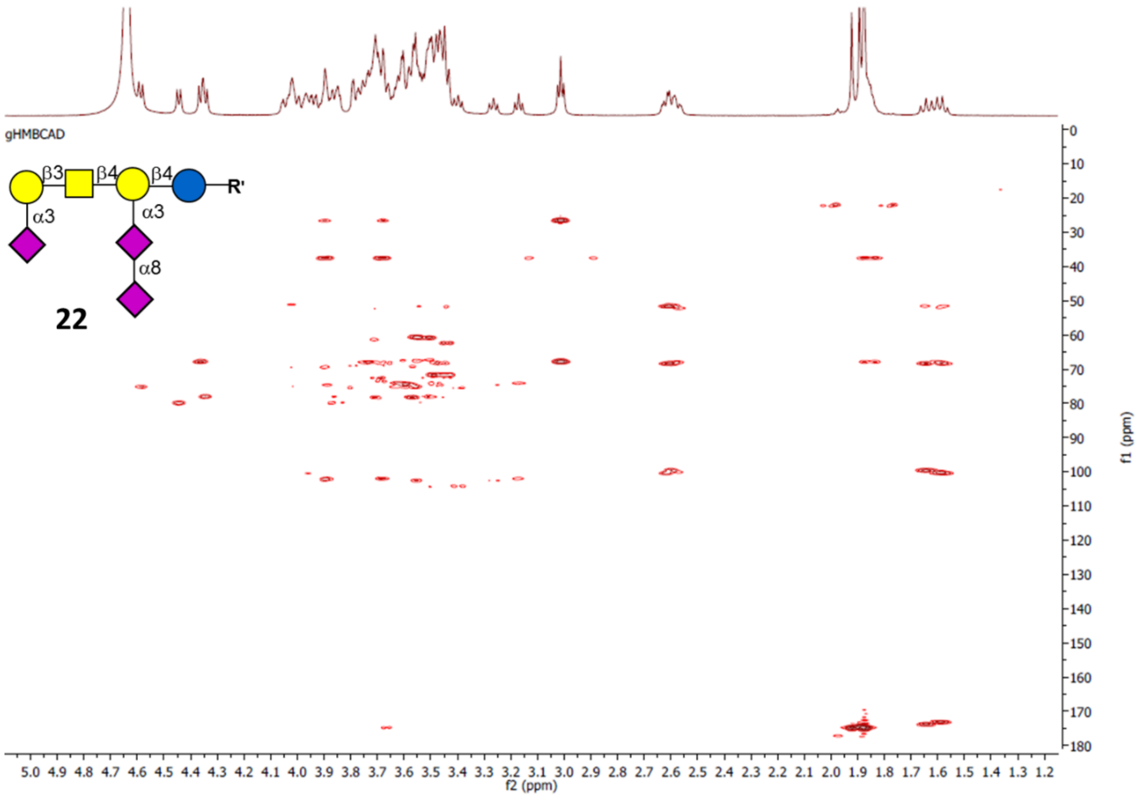
22


HSQCAD
β3
β4
β4
R'
α3
α3
α8
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
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
f1 (ppm)

22

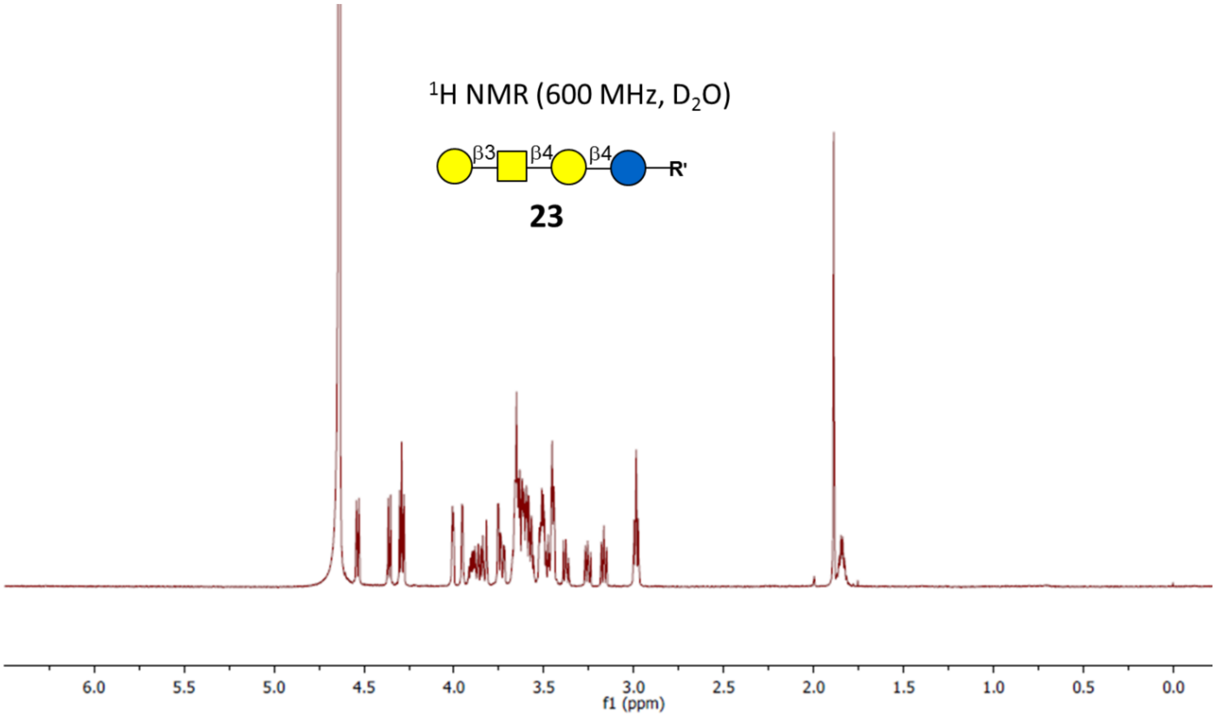

gCOSY
β3
β4
β4
R'
α3
α3
α8
22
f2 (ppm)
f1 (ppm)
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4


zTOCSY
β3
β4
β4
R'
α3
α3
α8
22
f2 (ppm)
f1 (ppm)
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6

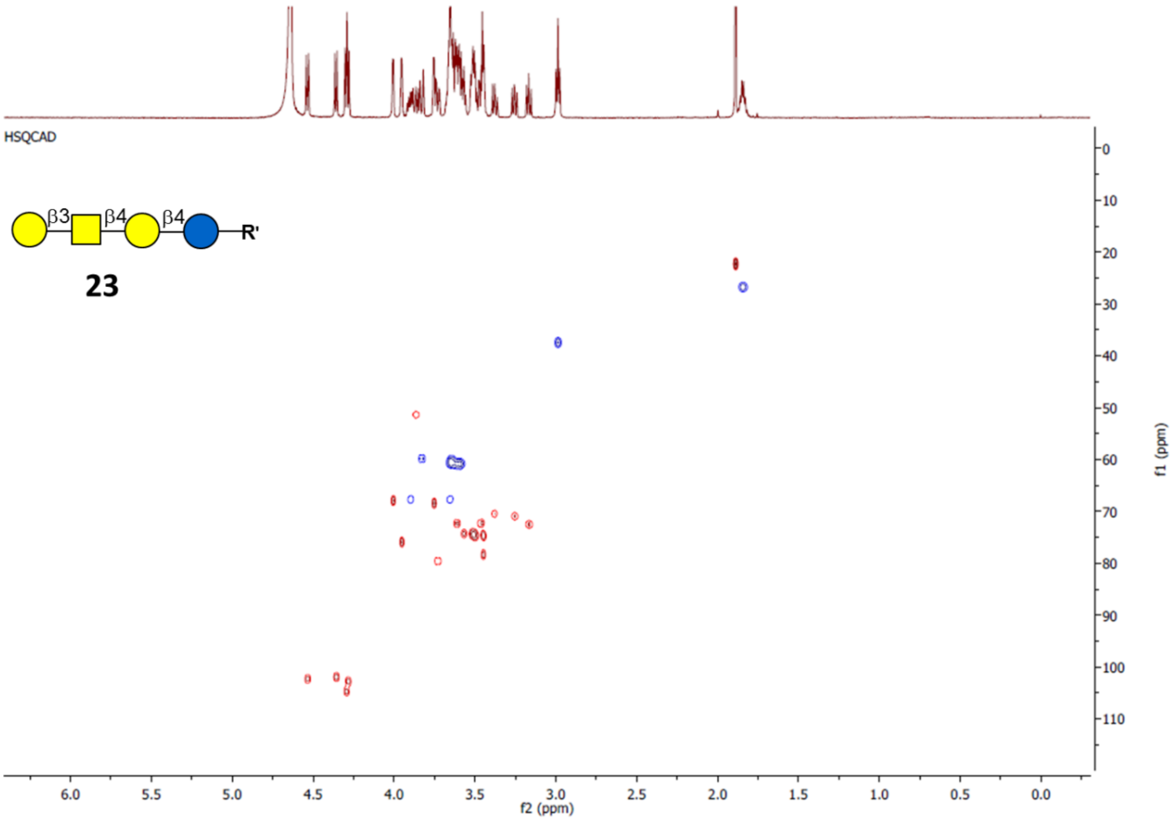


22

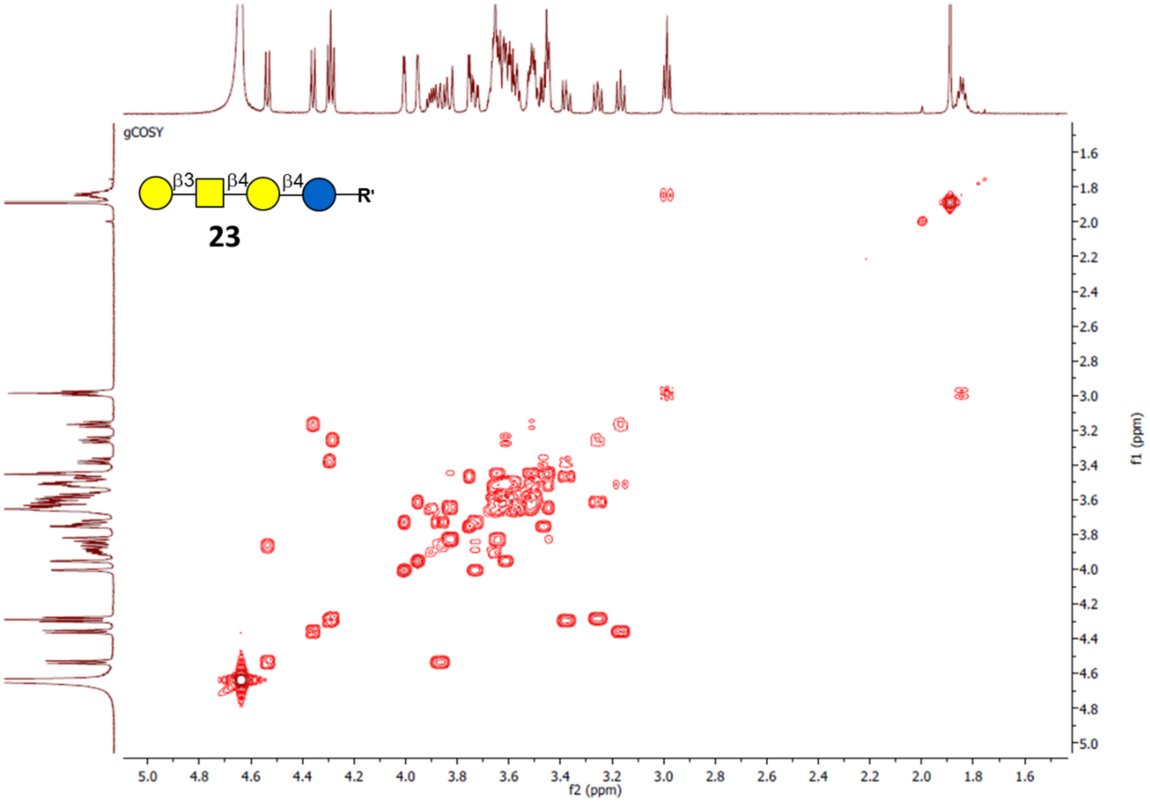
^{1}H NMR (600 MHz, D_2O)



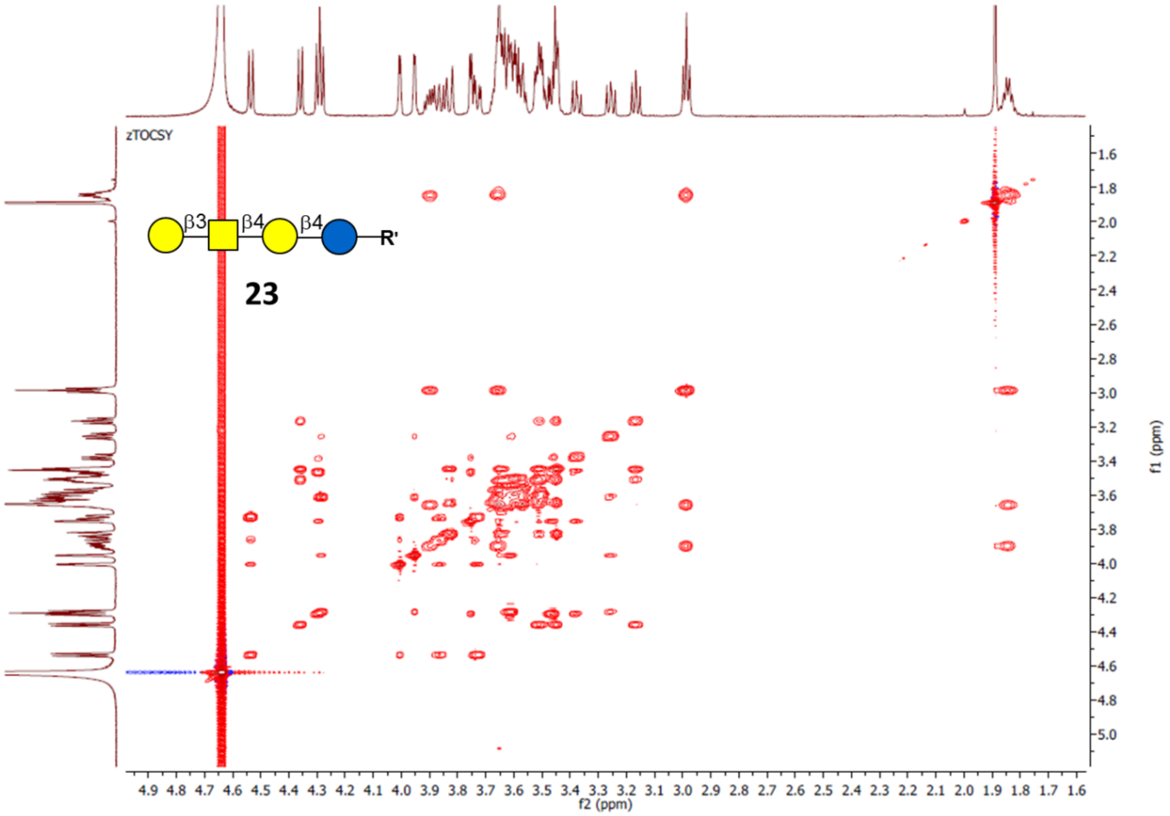
23

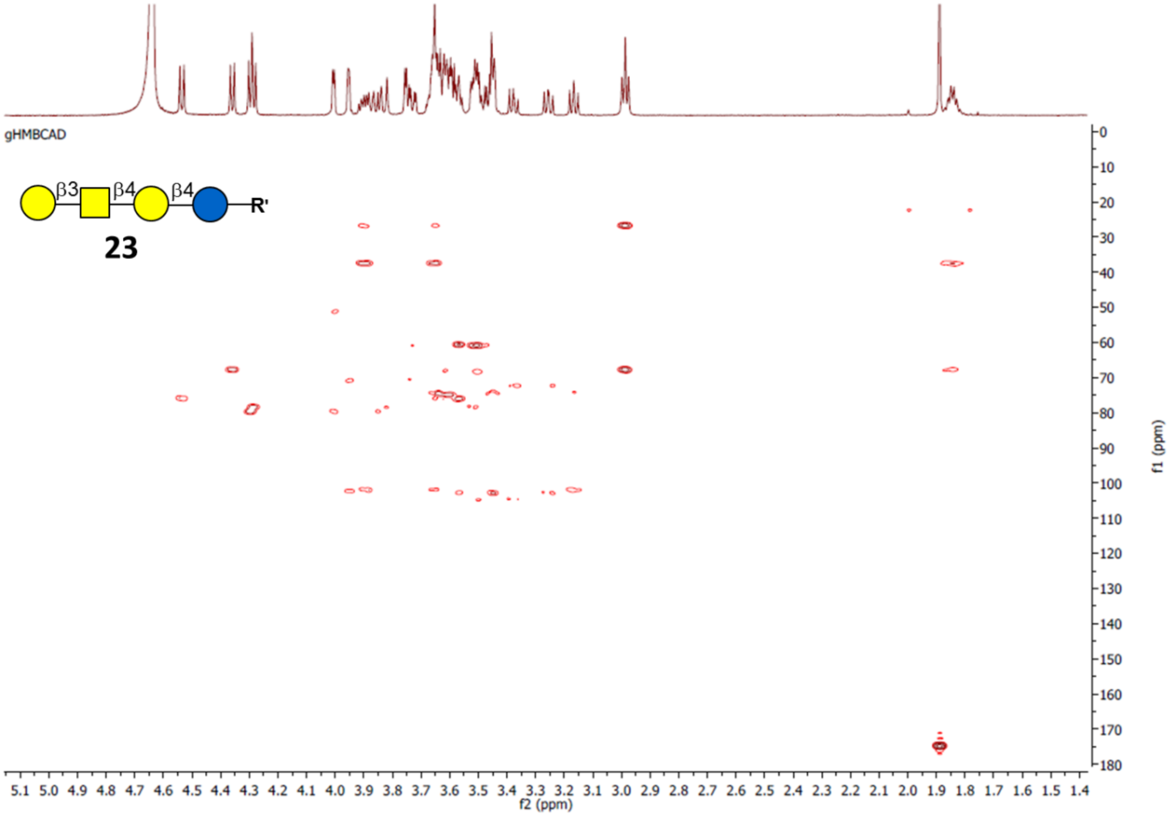

HSQCAD
β3
β4
β4
R'
f1 (ppm)
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

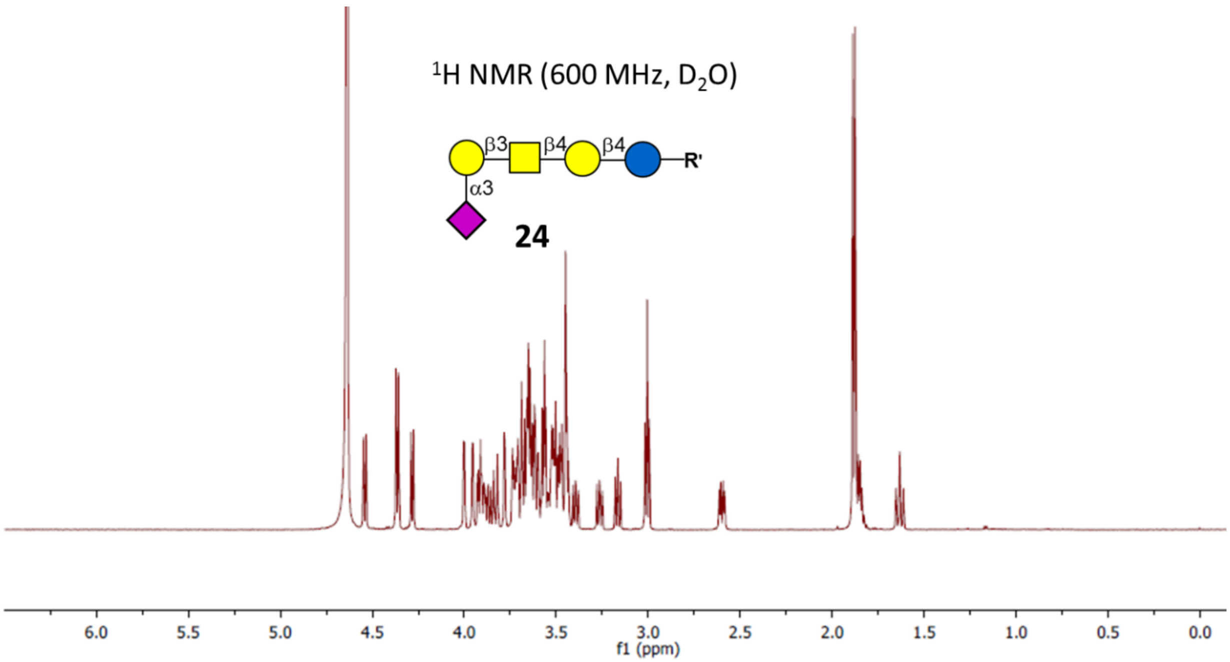
23


gCOSY
β3
β4
β4
R'
f1 (ppm)
f2 (ppm)
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6

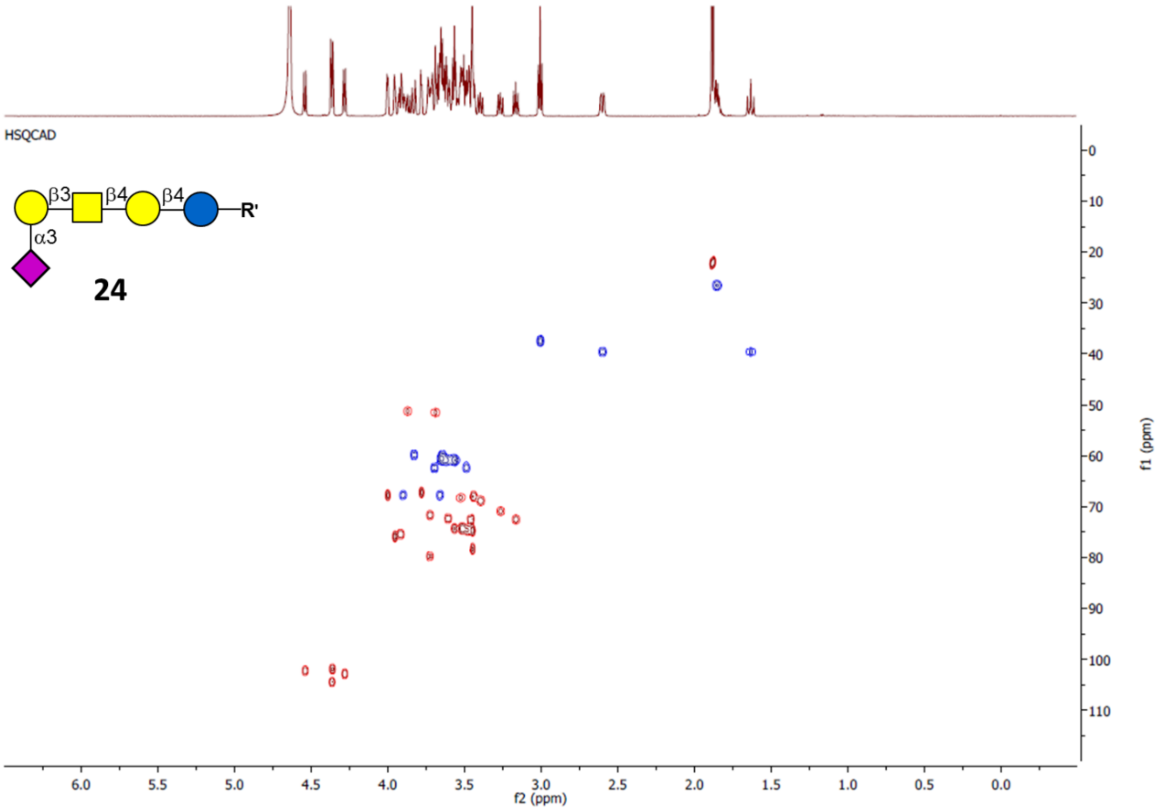
23


zTOCSY
β3
β4
β4
R'
23
f2 (ppm)
4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6
f1 (ppm)
1.6 1.8 2.0 2.2 2.4 2.6 2.8 3.0 3.2 3.4 3.6 3.8 4.0 4.2 4.4 4.6 4.8 5.0

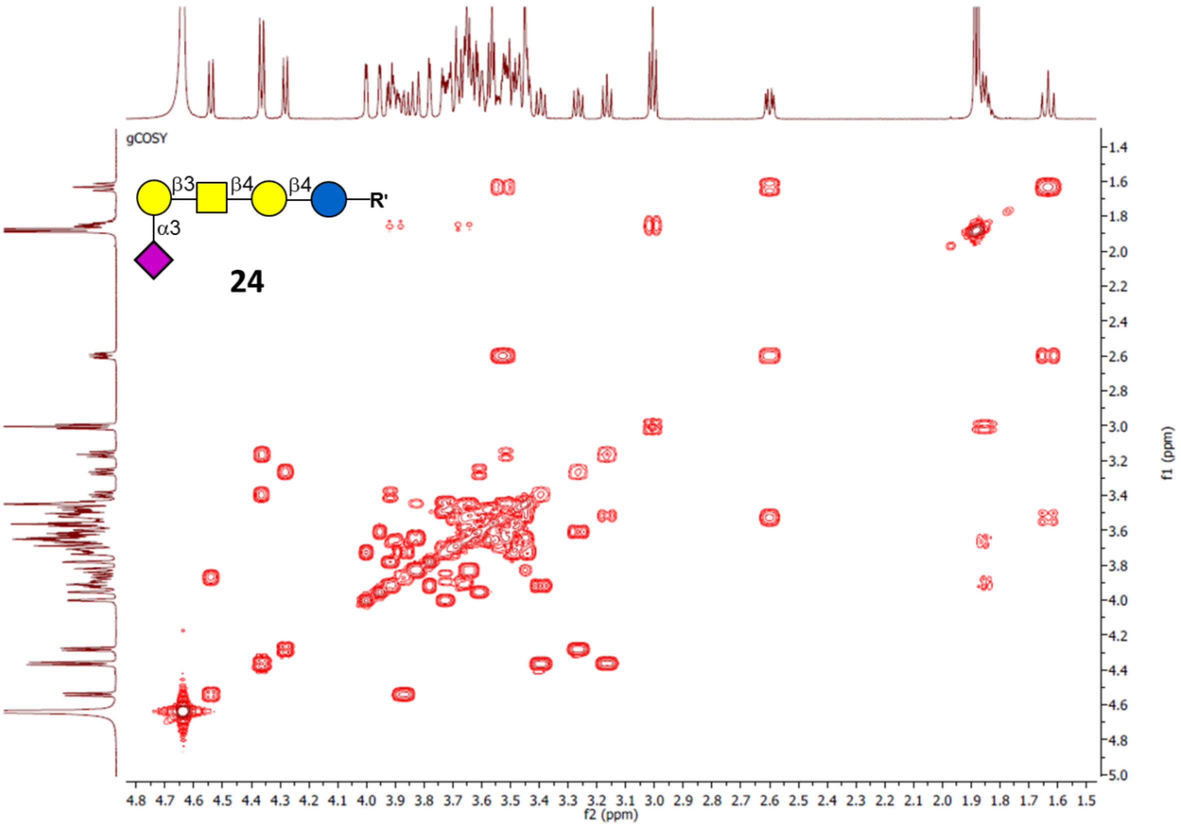

gHMBCAD
β3
β4
β4
R'
23
f2 (ppm)
5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4
f1 (ppm)
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180

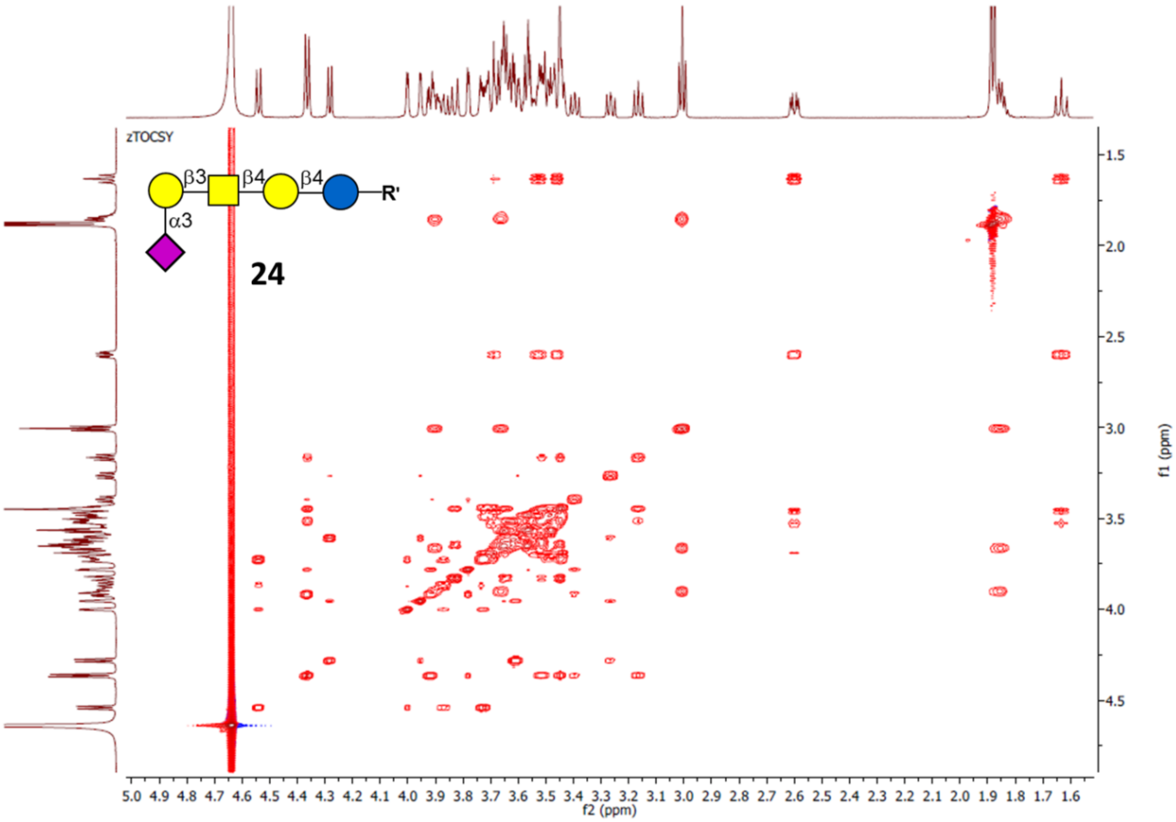


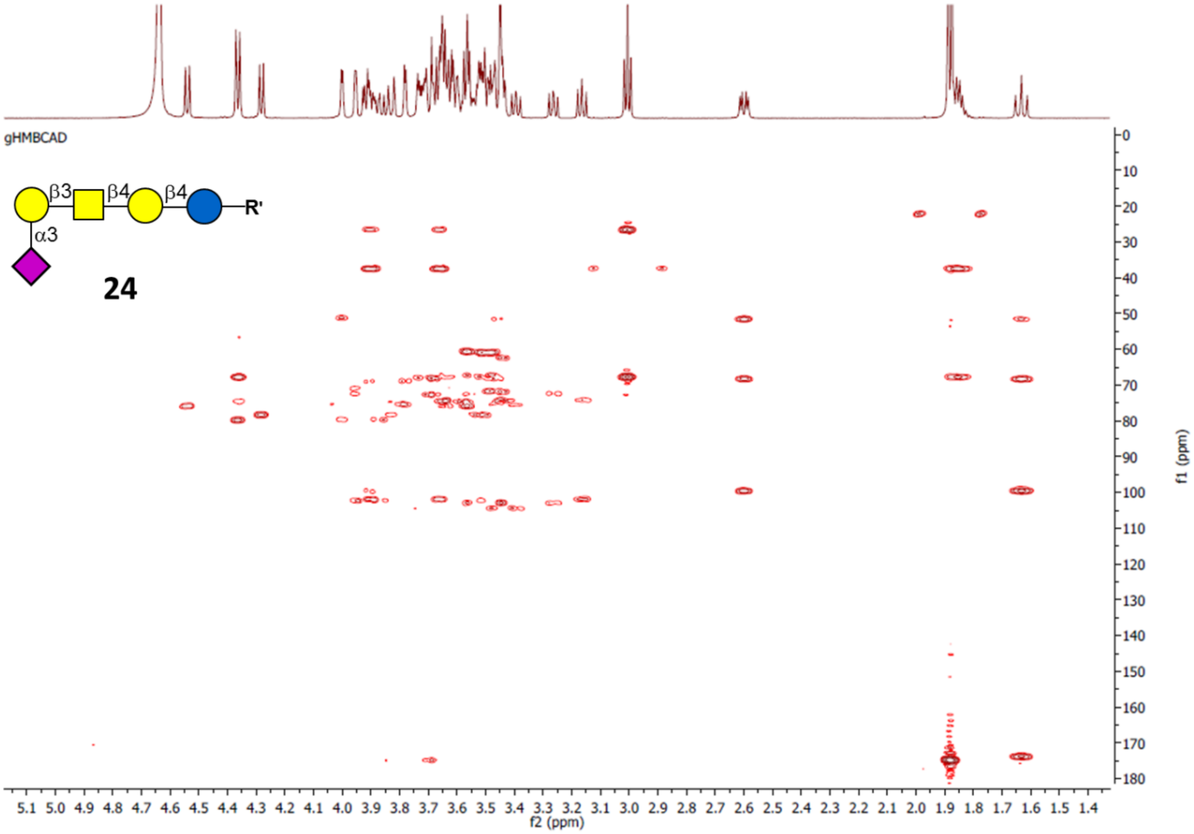
^{1}H NMR (600 MHz, D_2O)
β3
β4
β4
R'
α3
24
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



HSQCAD
β3
β4
β4
R'
α3
24
0
10
20
30
40
50
60
70
80
90
100
110
f1 (ppm)
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
f2 (ppm)

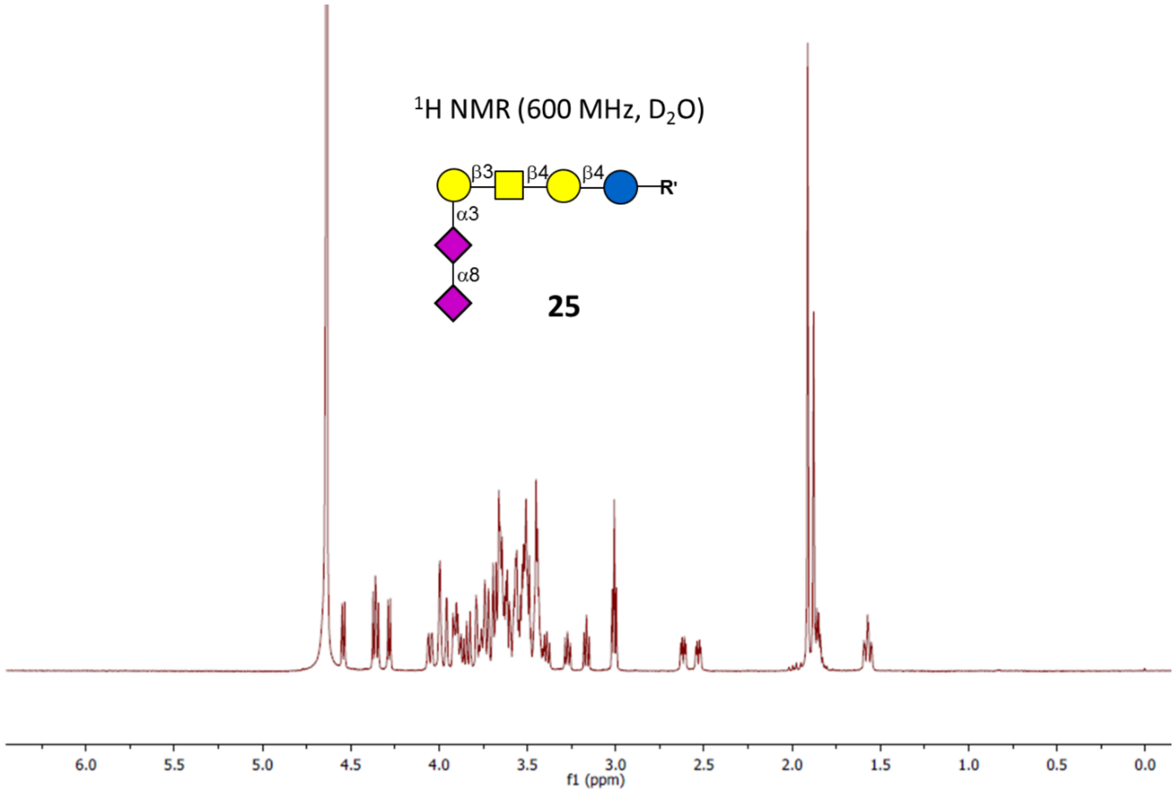

gCOSY
β3
β4
β4
R'
α3
24
4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5
f2 (ppm)
1.4 1.6 1.8 2.0 2.2 2.4 2.6 2.8 3.0 3.2 3.4 3.6 3.8 4.0 4.2 4.4 4.6 4.8 5.0
f1 (ppm)


zTOCSY
β3
β4
β4
R'
α3
24
5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6
f2 (ppm)
1.5 2.0 2.5 3.0 3.5 4.0 4.5
f1 (ppm)

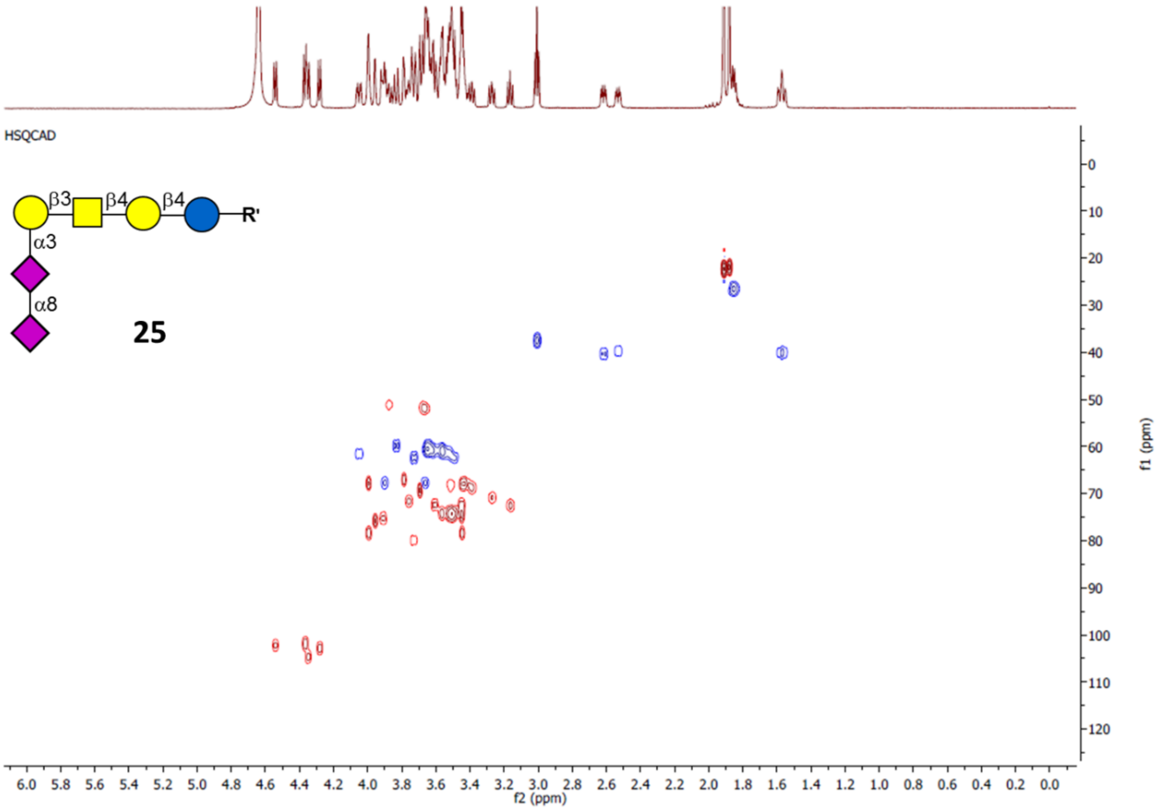


24

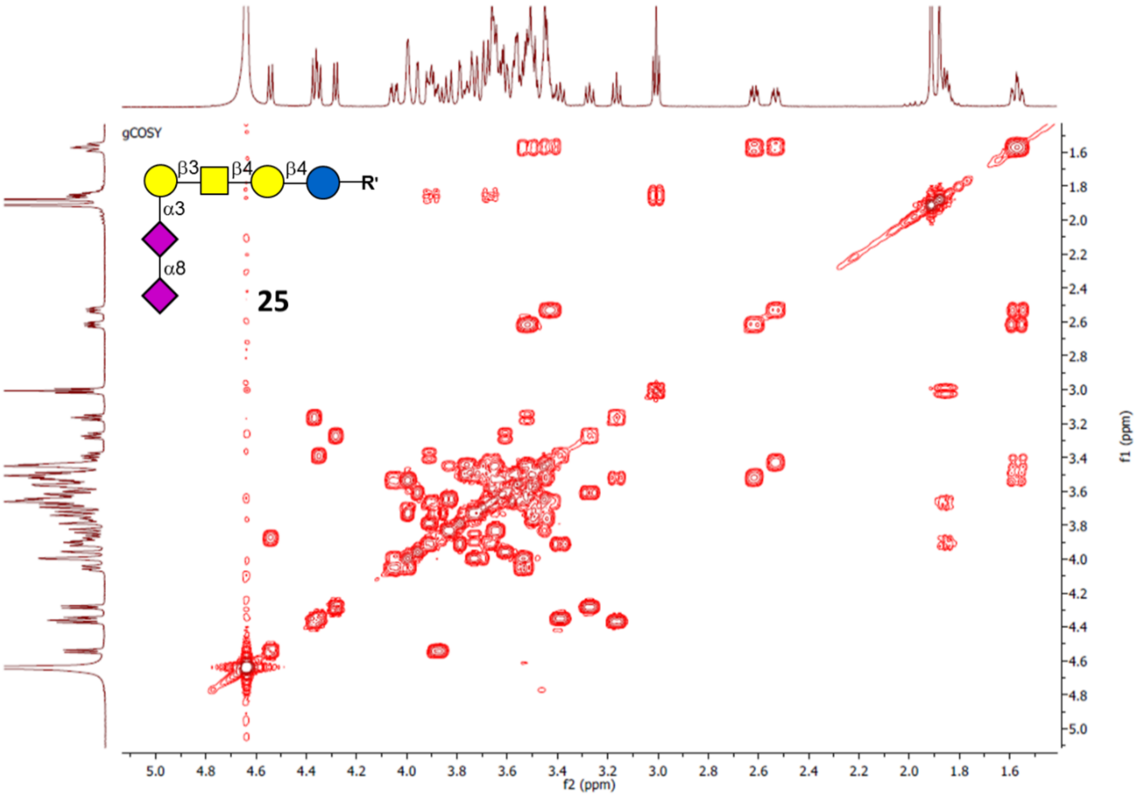
^{1}H NMR (600 MHz, D_2O)



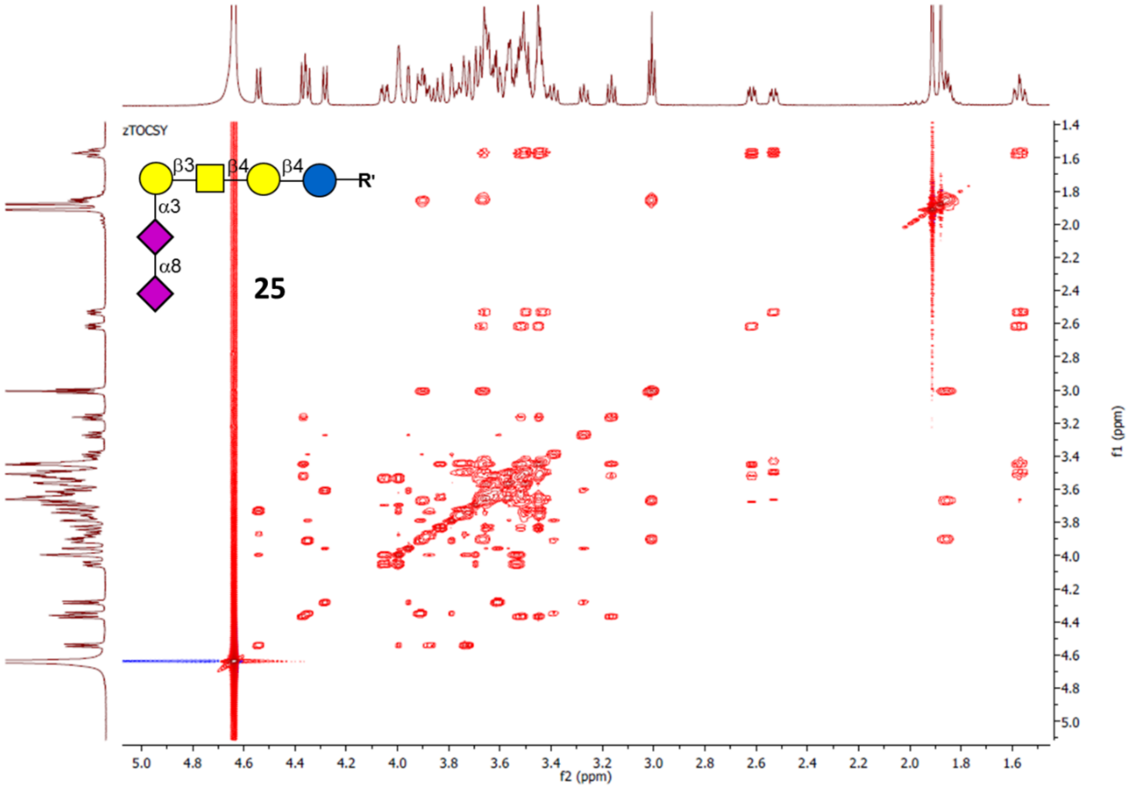
25

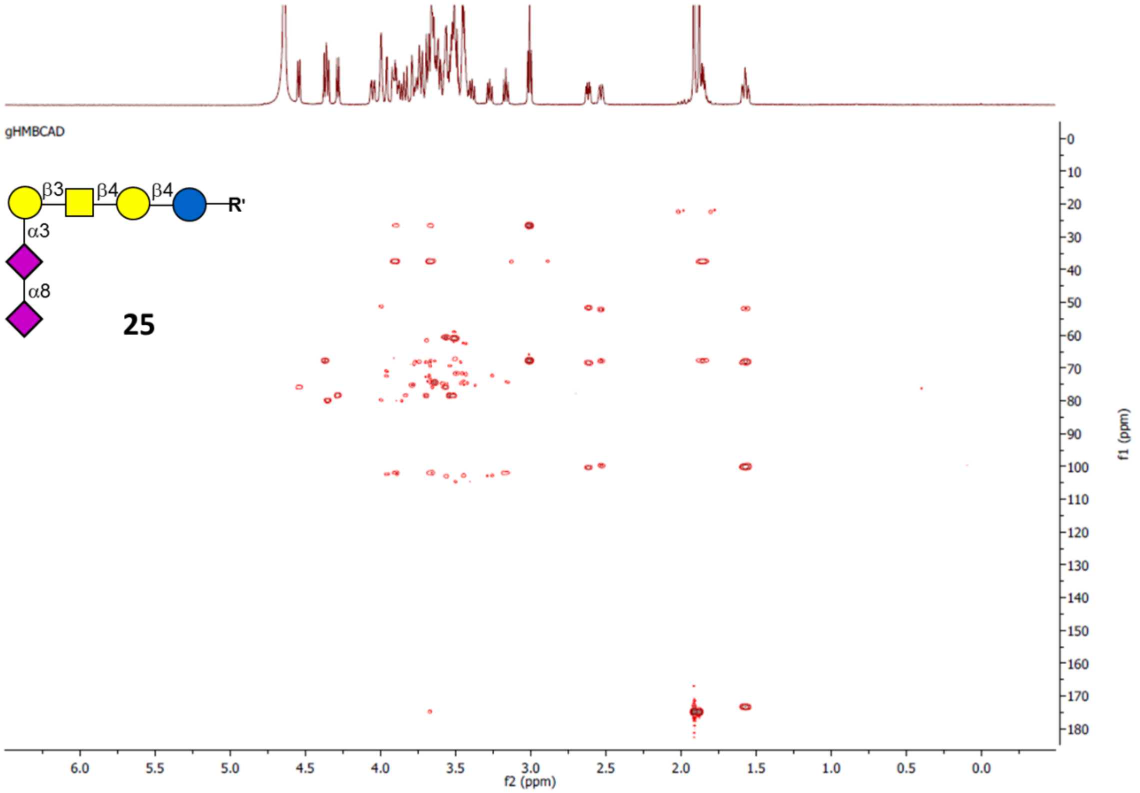

HSQCAD
β3
β4
β4
R'
α3
α8
f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0
f2 (ppm)

25


gCOSY
β3
β4
β4
R'
α3
α8
f1 (ppm)
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6
f2 (ppm)

25


zTOCSY
β3
β4
β4
R'
α3
α8
25
f1 (ppm)
f2 (ppm)
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4


gHMBCAD
β3
β4
β4
R'
α3
α8
25
f1 (ppm)
f2 (ppm)
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
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180