Supporting Information

Obstacles and Solutions for Chemical Synthesis of Syndecan-3 (53-62) Glycopeptides with Two Heparan Sulfate Chains

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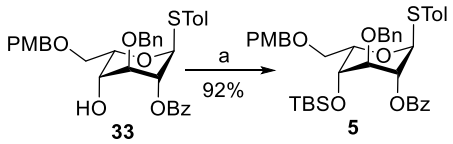
General Experimental Procedures. All reactions were carried out under nitrogen with anhydrous solvents in flame-dried glassware, unless otherwise noted. Glycosylation reactions were performed in the presence of molecular sieves, which were flame–dried right before the reaction under high vaccum. Glycosylation solvents were dried using a solvent purification system and used directly without further drying. Chemicals used were reagent grade as supplied except where noted. Compounds were visualized by UV light (254 nm) and by staining with a yellow solution containing $Ce(NH_4)_2(NO_3)_6$ (0.5 g) and $(NH_4)_6Mo_7O_{24}$ $4H_2O$ (24.0 g) in 6% H_2SO_4 (500mL). Flash column chromatography was performed on silica gel 60 (230-400 Mesh). NMR spectra were referenced using residual $CHCl_3$ (δ ^{1}H-NMR 7.26 ppm) and $CDCl_3$ (δ ^{13}C-NMR 77.0 ppm). Peak and coupling constants assignments are based on ^{1}H-NMR, ^{1}H-^{1}H gCOSY and (or) ^{1}H-^{13}C gHMQC and ^{1}H-^{13}C gHMBC experiments.

Characterization of anomeric stereochemistry. The stereochemistries of the newly formed glycosidic linkages were determined by $^3J_{H1,H1}$ through ^{1}H-NMR and/or $^1J_{C1,H1}$ through gHMQC 2-D NMR (without ^{1}H decoupling). For the glucoside, galactoside and xyloside linkages, smaller coupling constants of $^3J_{H1,H2}$ (around 3 Hz) indicate α linkages and larger coupling constants $^3J_{H1,H1}$ (7.2 Hz or larger) indicate β linkages. For all glycosyl linkages including idosides, $^1J_{C1,H1}$ around 170 Hz suggests α linkages and 160 Hz suggests β linkages.[1]

General procedure for pre-activation based single-step glycosylation. A solution of donor (60 μmol) and freshly activated molecular sieve MS 4 Å (200 mg) in CH_2Cl_2 (DCM) (2 mL) was stirred at room temperature for 30 minutes, and cooled to −78 °C, which was followed by addition of AgOTf (47 mg, 180 μmol) dissolved in Et_2O (1 mL) without touching the wall of the flask. After 5 minutes, orange colored *p*-TolSCl (9.5 μL, 60 μmol) was added to the solution through a microsyringe. Since the reaction temperature was lower than the freezing point of *p*-TolSCl, *p*-TolSCl was added directly into the reaction mixture to prevent it from freezing on the flask wall. The characteristic yellow color of *p*-TolSCl in the reaction solution dissipated rapidly within a few seconds indicating depletion of *p*-TolSCl. After the donor was completely consumed according to TLC analysis (< 5 minutes), a solution of acceptor (54 μmol) in DCM (0.2 mL) was slowly added dropwise via a syringe together with one equivalent of TTBP. The reaction mixture was warmed to 0 °C under stirring in 2 h. Then the mixture was diluted with DCM (20 mL) and filtered over Celite. The Celite was thoroughly washed with DCM until no organic compounds were observed in the filtrate by TLC. All DCM solutions were combined and washed twice with a saturated aqueous solution of $NaHCO_3$

(20 mL) and twice with water (10 mL). The organic layer was collected and dried over Na_2SO_4. After removal of the solvent, the desired oligosaccharide was purified from the reaction mixture via silica gel flash chromatography.

General procedure for deprotection of Lev. The Lev-protected compound (1 equiv.) was dissolved in DCM/MeOH (for 150 mg of compound, 2.4 mL, 1:1) and acetic acid (0.2 mL). The mixture was cooled to 0 °C, followed by addition hydrazine monohydrate (5 equiv. for each Lev). The mixture was stirred at 0 °C for 2h and then quenched by acetone (0.28 mL). The mixture was stirred at room temperature for another 1h and the acetone was evaporated under vaccum. The residue was diluted with EtOAc (50 mL) and washed with saturated $NaHCO_3$, 10% HCl and water and the organic phase was dried over Na_2SO_4. The solvent was concentrated in vacuo and the compound was purified by silica gel column chromatography.

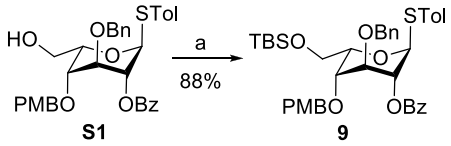


Reagents and conditions: (a) TBSOTf, 2, 6-lutidine, -40 °C-0 °C.

***p*-Tolyl-2-*O*-benzoyl-3-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-6-*O*-*p*-methoxybenzyl-1-thio-α-L-idopyranoside (5)**. Compound **33**[2] (500 mg, 0.83 mmol) in DCM (5 mL) was cooled down to –40 °C, followed by sequential addition of 2, 6-lutidine (203 μL, 1.74 mmol) and TBSOTf (299 μL, 1.3 mmol). The resulting solution was warmed up very slowly to room temperature. The mixture was quenched by Et_3N and then diluted with DCM (100 mL). The organic phase was washed with saturated $NaHCO_3$ and then dried over Na_2SO_4, filtered and the solvents were removed *in vacuo*. Silica gel column chromatography (hexanes–EtOAc) afforded compound **5** (547 mg, 92%). ^{1}H-NMR (600 MHz, $CDCl_3$): δ -0.27 (br, 3 H, Si(CH_3)$_2$), -0.12 (br, 3 H, Si(CH_3)$_2$), 0.69 (s, 9 H, C(CH_3)$_3$), δ 2.28 (s, 3 H, SPhCH_3), 3.67-3.70 (m, 1 H, H-3), 3.76-3.79 (m, 3 H, H-4, H-6a, H-6b), 3.80 (s, 3 H, CH_3OPhCH$_2$O), 4.48 (br, 2 H, CH$_3$OPhCH_2O), 4.66-4.68 (m, 1 H, OCH_2Ph), 4.78-4.82 (m, 1 H), 4.88-4.90 (m, 1 H, OCH_2Ph), 5.36-5.37 (m, 1 H, H-2), 5.52 (d, 1 H, J = 2 Hz, H-1), 6.86-6.88 (m, 2 H), 6.98-7.00 (m, 2 H), 7.24-7.27 (m, 3 H), 7.29-7.32 (m, 2 H), 7.36-7.42 (m, 4 H), 7.45-7.46 (m, 2 H), 7.51-7.54 (m, 1 H), 8.02-8.04 (m, 2 H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ 17.9, 21.0, 25.6, 55.2, 68.7, 69.4, 69.9, 72.4, 72.8, 74.7, 86.1, 113.6, 127.8, 128.1, 128.1, 128.3, 129.2, 129.5, 129.7, 130.0, 130.3, 131.9, 132.3, 133.1, 137.3, 137.5, 159.0, 165.6. HRMS: $C_{41}H_{50}O_7SSi$ $[M+NH_4]^+$ calcd:

732.3390, obsd: 732.3377.

***p*-Tolyl 2-*O*-benzoyl-3-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-6-*O*-*p*-methoxybenzyl-1-thio-α-L-idopyranosyl-(1→4)-6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-β-D-glucopyranoside (7)**. Synthesis of compound **7** from donor **5** and acceptor **6**[2] following the general procedure of single step glycosylation failed. Andydro sugar **8** (60%) and acceptor **6** (63%) were isolated. Compound **7**: ^{1}H-NMR (600 MHz, $CDCl_3$): δ -0.03 (br, 6 H, Si(CH_3)$_2$), 0.89 (s, 9 H, C(CH_3)$_3$), 3.65-3.68 (m, 1 H), 3.76-3.79 (m, 3 H), 4.68-4.71 (m, 1 H, OCH_2Ph), 4.79-4.83 (m, 1 H), 4.87-4.89 (m, 1 H, OCH_2Ph), 5.36-5.37 (m, 1 H, H-2), 5.52 (d, 1 H, J = 4 Hz, H-1), 6.86-6.88 (m, 2 H), 6.98-7.00 (m, 2 H), 7.24-7.27 (m, 3 H), 7.29-7.32 (m, 2 H), 7.36-7.42 (m, 4 H), 7.45-7.46 (m, 2 H), 7.51-7.54 (m, 1 H), 8.02-8.04 (m, 2 H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ -5.2, 17.9, 21.0, 25.6, 55.2, 68.7, 69.4, 69.9, 72.4, 72.8, 74.7, 86.1, 113.6, 127.8, 128.1, 128.1, 128.3, 129.2, 129.5, 129.7, 130.0, 130.3, 131.9, 132.3, 133.1, 137.3, 137.5, 159.0.



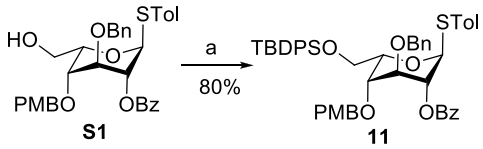
S1 **9**

Reagents and conditions: (a) TBSOTf, 2, 6-lutidine, -40 ºC-r.t., DCM.

***p*-Tolyl 2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*t*-butyldimethylsilyl-4-*O*-*p*-methoxybenzyl-1-thio-α-L-idopyranoside (9)**. Compound **S1**[2] (420 mg, 0.7 mmol) in DCM (5 mL) was cooled down to –40 °C, followed by sequential addition of 2, 6-lutidine (165 µL, 1.4 mmol) and TBSOTf (242 µL, 1.05 mmol). The resulting solution was warmed up very slowly to room temperature. The mixture was quenched by Et_3N and then diluted with DCM (10 mL). The organic phase was washed with saturated $NaHCO_3$ and then dried over Na_2SO_4, filtered and the solvents were removed *in vacuo*. Silica gel column chromatography (hexanes–EtOAc) afforded compound **9** (440 mg, 88%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.06 (s, 3 H, Si(CH_3)$_2$), 0.08 (s, 3 H, Si(CH_3)$_2$), 0.90 (s, 9 H, C(CH_3)$_3$), 2.29 (s, 3 H, SPhCH_3), 3.61 (br, 1 H), 3.76 (s, 3 H, CH_3OPh), 3.86-3.90 (m, 2 H), 3.94-3.98 (m, 1 H), 4.34-4.42 (m, 2 H, PhCH_2), 4.58-4.62 (m, 1 H, PhCH_2), 4.63-4.66 (m, 1 H, PhCH_2), 4.84-4.87 (m, 1 H), 5.39-5.43 (m, 1 H, H-2), 5.53 (br, 1 H, H-1), 6.71-6.73 (m, 2 H), 7.05-7.08 (m, 4 H), 7.27-7.51 (m, 10 H), 7.95-7.97 (m, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ -5.4, -5.3, 18.2, 21.0, 25.9, 55.1, 62.0, 69.4, 70.0, 72.2, 72.5, 73.5, 86.1, 127.7, 127.8, 128.2, 128.3, 129.3, 129.5, 129.7, 129.9, 130.1, 131.8, 132.3, 132.9, 137.1, 137.6, 159.5, 165.8. HRMS: $C_{41}H_{50}O_7SSi$ $[M+NH_4]^+$ calcd: 732.3390, obsd:

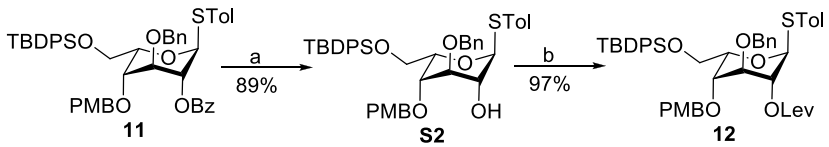
732.3326.

Anhydro sugar (10). ^{1}H-NMR (600 MHz, $CDCl_3$): δ 3.67-3.70 (m, 1 H), 3.78 (s, 3 H, C*H*$_3$OPh), 3.80-3.83 (m, 1 H), 3.93 (t, 1 H, *J* = 7 Hz), 4.15 (t, 1 H, *J* = 6.5 Hz), 4.42 (t, 1 H, *J* = 4 Hz), 4.56-4.58 (m, 1 H, PhC*H*$_2$), 4.65-4.77 (m, 3 H, PhC*H*$_2$), 4.99 (dd, 1 H, *J* = 1.5 Hz, *J* = 7 Hz), 5.48 (d, 1 H, *J* = 1.5 Hz), 6.84-6.86 (m, 2 H), 7.17-7.24 (m, 7 H), 7.39-7.42 (m, 2 H), 7.53-7.55 (m, 1 H), 7.99-8.01 (m, 2 H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ 55.2, 65.5, 72.9, 73.3, 74.8, 79.0, 79.2, 99.2, 113.9, 127.5, 127.7, 128.2, 128.3, 129.4, 129.5, 129.8, 129.9, 133.2, 138.1, 159.4, 165.7. ESI-MS: $C_{28}H_{28}O_7Na$ calcd: 499.18, obsd: 499.19. HRMS: $C_{28}H_{28}O_7$ $[M+NH_4]^+$ calcd: 494.2179, obsd: 494.2161.



Reagents and conditions: (a) TBDPSCl, imidazole, DCM.

***p*-Tolyl 2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-4-*O*-*p*-methoxybenzyl-1-thio-α-L-idopyranoside (11)**. Compound **S1** (1.3 g, 2.16 mmol) was dissolved in DCM (10 mL), followed by addition of imidazole (176 mg, 2.59 mmol) and TBDPSCl (840 μL, 3.24 mmol). The resulting mixture was stirred under room temperature overnight and diluted with DCM. The solution was washed with 10% HCl solution, sat. $NaHCO_3$ solution and dried over Na_2SO_4. After concentration, column purification afforded compound **11** (1.45 g, 80%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.13 (s, 9 H, C(C*H*$_3$)$_3$), 2.31 (s, 3 H, SPhC*H*$_3$), 3.74-3.76 (m, 1 H), 3.79 (s, 3 H, C*H*$_3$OPh), 3.96-4.05 (m, 2 H, H-6a, H-6b), 4.10-4.12 (m, 1 H, H-3), 4.36-4.48 (m, 2 H, PhC*H*$_2$), 4.73-4.76 (m, 2 H, H-5, PhC*H*$_2$), 4.92-4.95 (m, 1 H, PhC*H*$_2$), 5.48-5.49 (m, 1 H, H-2), 5.60 (dd, 1 H, *J* = 2.5 Hz, H-1), 6.72-6.74 (m, 2 H), 7.02-7.05 (m, 4 H), 7.32-7.53 (m, 16 H), 7.72-7.78 (m, 4 H), 8.02-8.04 (m, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 19.1, 21.0, 26.8, 55.1, 63.0, 69.4, 70.1, 72.2, 72.4, 72.6, 73.7, 86.2, 113.5, 127.6, 127.7, 127.7, 128.1, 128.3, 129.3, 129.4, 129.6, 129.7, 129.9, 129.9, 131.8, 132.4, 132.9, 133.1, 133.2, 135.5, 135.6, 137.2, 137.6, 159.0, 165.5. HRMS: $C_{51}H_{54}O_7SSi$ $[M+NH_4]^+$ calcd: 856.3703, obsd: 856.3743.



Reagents and conditions: (a) NaOMe, DCM/MeOH; (b) LevOH, EDC-HCl, DMAP,

DCM.

***p*-Tolyl 3-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-4-*O*-*p*-methoxybenzyl-1-thio-α-L-idopyranoside (S2)**. Compound **11** (2.7 g, 3.22 mmol) was dissolved in DCM/MeOH (1:1, 20 mL) and was added freshly prepared NaOMe in MeOH (5 M) to maintain the pH above 12. After the reaction was complete, the reaction was diluted with 10% HCl solution until the pH was around 6. The solution was washed with 10% HCl solution, sat. $NaHCO_3$ solution and the organic phase was dried over Na_2SO_4. After concentration, column purification afforded compound **S2** (2.1 g, 89%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.11 (s, 9 H, C(C*H*$_3$)$_3$), 2.30 (s, 3 H, SPhC*H*$_3$), 3.71-3.73 (m, 1 H, O*H*), 3.79 (s, 1 H, C*H*$_3$OPh), 3.82-3.84 (m, 1 H), 3.85-3.87 (m, 2 H), 4.03-4.10 (m, 2 H), 4.39-4.42 (m, 1 H), 4.52-4.55 (m, 1 H), 4.57-4.60 (m, 1 H), 4.75-4.81 (m, 2 H), 5.39 (br, 1 H, H-1), 6.80-6.82 (m, 2 H), 7.01-7.03 (m, 2 H), 7.09-7.11 (m, 2 H), 7.34-7.47 (m, 13 H), 7.70-7.73 (m, 4 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 19.1, 20.9, 26.8, 55.1, 62.6, 67.9, 69.4, 71.7, 71.9, 72.6, 73.4, 89.7, 113.8, 127.6, 127.6, 127.7, 128.4, 128.9, 129.4, 129.6, 129.6, 129.7, 131.9, 133.0, 133.1, 133.3, 135.5, 135.5, 136.9, 137.6, 159.4. HRMS: $C_{44}H_{50}O_6SSi$ $[M+NH_4]^+$ calcd: 752.3441, obsd: 752.3485.

***p*-Tolyl-3-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-2-*O*-levulinoyl-4-*O*-*p*-methoxybenzyl-1-thio-α-L-idopyranoside (12)**. Compound **S2** (2.1 g, 2.86 mmol) was dissolved in 10 mL DCM, which was followed by addition of LevOH (347 μL, 3.43 mmol), DMAP (348 mg, 2.86 mmol) and EDC-HCl (657 mg, 3.43 mmol). After stirring under room temperature overnight, the reaction was quenched by 10% HCl solution and diluted with DCM. The organic phase was extracted with sat. $NaHCO_3$ solution and dried over Na_2SO_4. Silica gel column purification afforded compound **14** (2.3 g, 97%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.05 (s, 9 H, C(C*H*$_3$)$_3$), 2.13 (s, 3 H, C*H*$_3$COCH$_2$CH$_2$), 2.27 (s, 3 H, SPhC*H*$_3$), 2.52-2.75 (m, 4 H, CH$_3$COC*H*$_2$C*H*$_2$), 3.59-3.61 (m, 1 H, H-4), 3.77 (s, 1 H, C*H*$_3$OPh), 3.88-3.91 (m, 3 H, H-3, H-6a, H-6b), 4.30-4.32 (m, 1 H), 4.45-4.47 (m, 1 H), 4.61-4.64 (m, 2 H), 4.82-4.85 (m, 1 H), 5.16-5.18 (m, 1 H, H-2), 5.42 (d, 1 H, J = 2.5 Hz, H-1), 6.75-6.77 (m, 2 H), 6.97-6.99 (m, 2 H), 7.05-7.07 (m, 2 H), 7.31-7.43 (m, 13 H), 7.64-7.69 (m, 4 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 14.1, 19.0, 20.9, 20.9, 26.7, 28.0, 29.7, 37.6, 55.1, 60.2, 62.9, 69.3, 70.0, 71.9, 72.5, 73.3, 86.0, 113.6, 127.6, 127.7, 127.8, 128.3, 129.4, 129.4, 129.5, 129.9, 131.8, 132.0, 133.1, 133.2, 135.5, 135.5, 137.1, 137.7, 159.1, 165.4, 171.7, 206.1. HRMS: $C_{49}H_{56}O_8SSi$ $[M+NH_4]^+$ calcd: 850.3809, obsd: 850.3805.

***p*-Tolyl-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-4-*O*-*p*-methoxybenzyl-α-L-idopyranosyl-(1→4)-6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-1-thio-β-D-**

glucopyranoside (13). Compound **13** was synthesized from donor **11** and acceptor **5** in 61% yield following the general procedure of single step glycosylation. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.05 (s, 9 H, C(CH_3)$_3$), 1.86 (s, 3 H, COCH_3), 2.29 (s, 3 H, SPhCH_3), 3.12-3.17 (m, 1 H), 3.35-3.39 (m, 2 H), 3.59-3.63 (m, 1 H), 3.71-3.73 (m, 1 H), 3.76 (s, 3 H, CH_3OPh), 3.77-3.82 (m, 1 H), 3.88-3.92 (m, 1 H), 4.06-4.09 (m, 1 H), 4.12-4.16 (m, 3 H), 4.22 (d, 1 H, J = 10 Hz), 4.30-4.34 (m, 2 H), 4.44-4.47 (m, 1 H, PhCH_2), 4.59-4.62 (m, 1 H, PhCH_2), 4.66 (s, 1 H), 4.91-4.93 (m, 1 H, PhCH_2), 5.15 (t, 1 H, J = 5.5 Hz), 5.21-5.22 (m, 1 H), 6.71-6.74 (m, 2 H), 7.02-7.07 (m, 4 H), 7.16-7.19 (m, 8 H), 7.25-7.44 (m, 12 H), 7.51-7.55 (m, 1 H), 7.62-7.66 (m, 4 H), 7.93-7.95 (m, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 19.0, 20.6, 21.1, 26.9, 55.2, 62.7, 62.9, 64.6, 70.8, 71.5, 72.4, 72.6, 73.5, 75.2, 75.6, 75.8, 83.4, 85.6, 98.6, 113.7, 126.7, 127.5, 127.7, 127.7, 127.7, 127.9, 127.9, 128.1, 128.2, 128.2, 128.3, 128.4, 128.5, 128.5, 129.3, 129.4, 129.4, 129.6, 129.6, 129.7, 129.8, 129.8, 129.9, 129.9, 130.1, 132.8, 132.9, 133.1, 134.3, 135.4, 135.5, 135.6, 135.7, 137.7, 137.8, 138.7, 159.2, 165.3, 170.3. HRMS: $C_{66}H_{71}N_3O_{12}SSi$ $[M+NH_4]^+$ calcd: 1175.4871, obsd: 1175.4918.

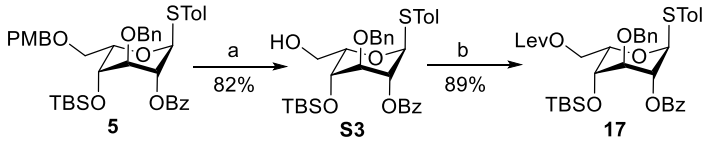
***p*-Tolyl 2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-4-*O*-*p*-methoxybenzyl-β-L-idopyranosyl-(1→4)-6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-1-thio-β-D-glucopyranoside (14)**. Compound **14** was a side product generated during the synthesis of **13**. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.06 (s, 9 H, C(CH_3)$_3$), 1.72 (s, 3 H, COCH_3), 2.31 (s, 3 H, SPhCH_3), 3.16-3.20 (m, 1 H), 3.29-3.34 (m, 1 H), 3.38-3.42 (m, 1 H), 3.53 (s, 1 H), 3.65 (t, 1 H, J = 9.5 Hz), 3.70-3.72 (m, 1 H), 3.72 (s, 3 H, CH_3OPh), 3.93-3.97 (m, 2 H), 4.00-4.05 (m, 1 H), 4.09-4.13 (m, 1 H), 4.22-4.28 (m, 3 H), 4.37-4.40 (m, 1 H), 4.47-4.63 (m, 2 H, PhCH_2), 4.81 (br, 2 H), 5.17 (br, 1 H), 5.25 (br, 1 H), 6.57-6.59 (m, 2 H), 6.88-6.90 (m, 2 H), 7.03-7.05 (m, 2 H), 7.16-7.52 (m, 21 H), 7.63-7.66 (m, 4 H), 7.99-8.02 (m, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 19.1, 20.5, 21.1, 26.8, 55.1, 61.5, 62.8, 64.6, 68.0, 71.2, 72.1, 72.4, 72.8, 74.5, 74.6, 76.1, 84.4, 85.5, 98.1, 113.4, 126.7, 127.7, 127.7, 127.7, 127.9, 128.0, 128.2, 128.4, 128.5, 128.5, 129.3, 129.6, 129.7, 129.7, 129.8, 129.9, 130.0, 132.8, 133.1, 133.3, 134.2, 135.4, 135.5, 137.0, 137.3, 138.6, 158.9, 166.1, 170.2. HRMS: $C_{66}H_{71}N_3O_{12}SSi$ $[M+NH_4]^+$ calcd: 1175.4871, obsd: 1175.4896.

***p*-Tolyl-3-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-2-*O*-levulinoyl-4-*O*-*p*-methoxybenzyl-α-L-idopyranosyl-(1→4)-2-azido-3-O-benzyl-2-deoxy-6-O-levulinoyl -1-thio-β-D-glucopyranoside (15)**. To a solution of compound **13** (60 mg, 0.052 mmol) in DCM (3 mL) was added freshly prepared NaOMe in MeOH (1 M) dropwise. The pH was maintained above 12. After the reaction was complete as indicated by TLC analysis, it was neutralized by 1 M HOAc to pH around 6 and diluted with DCM. The solution was

washed with sat. $NaHCO_3$ solution and dried over Na_2SO_4. After concentration, column purification afforded diol compound (50 mg, 95%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.00 (s, 9 H, C(C*H*$_3$)$_3$), 2.30 (s, 3 H, SPhC*H*$_3$), 2.41 (br, 1 H), 3.15-3.19 (m, 1 H), 3.21 (br, 1 H), 3.29-3.32 (m, 1 H), 3.33-3.37 (m, 1 H), 3.58-3.68 (m, 4 H), 3.75-3.77 (m, 5 H), 3.82-3.88 (m, 2 H), 4.15-4.19 (m, 1 H), 4.30-4.32 (m, 2 H), 4.43-4.45 (m, 1 H), 4.56-4.64 (m, 3 H), 4.84-4.86 (m, 1 H), 5.10 (d, 1 H, *J* = 3 Hz), 5.27 (d, 1 H, *J* = 1 Hz), 6.77-6.77 (m, 2 H), 7.03-7.05 (m, 2 H), 7.08-7.10 (m, 2 H), 7.18-7.19 (m, 3 H), 7.22-7.24 (m, 3 H), 7.27-7.32 (m, 8 H), 7.37-7.41 (m, 3 H), 7.58-7.62 (m, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 14.1, 19.0, 21.1, 26.8, 55.1, 60.3, 62.4, 62.6, 65.1, 69.3, 69.7, 72.6, 73.0, 74.3, 75.0, 75.3, 76.4, 79.6, 83.5, 86.0, 100.9, 113.7, 126.6, 127.5, 127.6, 127.6, 127.9, 128.0, 128.1, 128.2, 128.4, 129.2, 129.6, 129.8, 132.9, 133.0, 134.2, 135.5, 135.6, 137.6, 137.8, 138.8, 159.3. This diol compound (210 mg, 0.207 mmol) was dissolved in dry DCM (5 mL), followed by addition of EDC-HCl (1.1 g, 5.1 mmol), DMAP (160 mg, 0.42 mmol) and LevOH (598 mg, 5.14 mmol). The resulting mixture was stirred under room temperature for overnight. The reaction was diluted with DCM and washed with 10% HCl solution, sat. $NaHCO_3$ solution sequentially. The combined organic phase was dried over Na_2SO_4 and purified by silica gel column (hexanes-EtOAc) to afford compound **15** (151 mg, 60%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.97 (s, 9 H, C(C*H*$_3$)$_3$), 2.10 (s, 3 H, C*H*$_3$COCH$_2$CH$_2$), 2.12 (s, 3 H, C*H*$_3$COCH$_2$CH$_2$), 2.31 (s, 3 H, SPhC*H*$_3$), 2.41-2.79 (m, 8 H, CH$_3$COC*H*$_2$C*H*$_2$), 3.15 (t, 1 H, *J* = 9.5 Hz), 3.35 (t, 1 H, *J* = 9.5 Hz), 3.45-3.50 (m, 1 H), 3.58-3.63 (m, 2 H), 3.73-3.75 (m, 1 H), 3.75 (s, 3 H, C*H*$_3$OPh), 3.84-3.89 (m, 1 H), 3.94 (t, 1 H, *J* = 5.5 Hz), 4.04-4.11 (m, 2 H), 4.24-4.27 (m, 2 H), 4.41-4.43 (m, 1 H), 4.46-4.49 (m, 1 H), 4.55-4.64 (m, 3 H), 4.86-4.89 (m, 2 H), 5.02 (d, 1 H, *J* = 4.5 Hz), 6.73-6.75 (m, 2 H), 7.01-7.03 (m, 2 H), 7.07-7.09 (m, 2 H), 7.18-7.20 (m, 3 H), 7.25-7.31 (m, 12 H), 7.36-7.42 (m, 3 H), 7.56-7.61 (m, 4 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 19.0, 21.1, 26.8, 27.8, 27.8, 29.7, 29.8, 37.6, 37.8, 55.2, 62.6, 62.9, 64.7, 70.4, 71.0, 72.3, 73.5, 74.2, 75.3, 75.6, 75.7, 83.4, 85.6, 98.3, 113.6, 126.7, 127.5, 127.6, 127.7, 128.0, 128.1, 128.3, 128.4, 129.5, 129.7, 129.7, 129.8, 132.9, 133.0, 134.3, 135.6, 135.6, 137.8, 137.9, 138.7, 159.2, 171.8, 172.2, 206.2, 206.3. ESI-MS: $C_{61}H_{77}N_3O_{14}SSi$ $[M+NH_4]^+$ calcd: 1225.49, obsd: 1126.30. HRMS: calcd: 1225.5318, obsd: 1225.6290.

***p*-Tolyl-benzyl-3-*O*-benzyl-2-*O*-levulinoyl-4-*O*-*p*-methoxybenzyl-α-L-idopyranosyluronate-(1→4)-2-azido-3-*O*-benzyl-6-*O*-levulinoyl-β-D-glucopyranoside (16).** Compound **15** (32 mg, 0.0265 mmol) was dissolved in pyridine (2 mL), followed by addition of HF-Pyridine (300 μL) under 0 °C. The resulting mixture was stirred under room temperature overnight. After the reaction was complete, it was

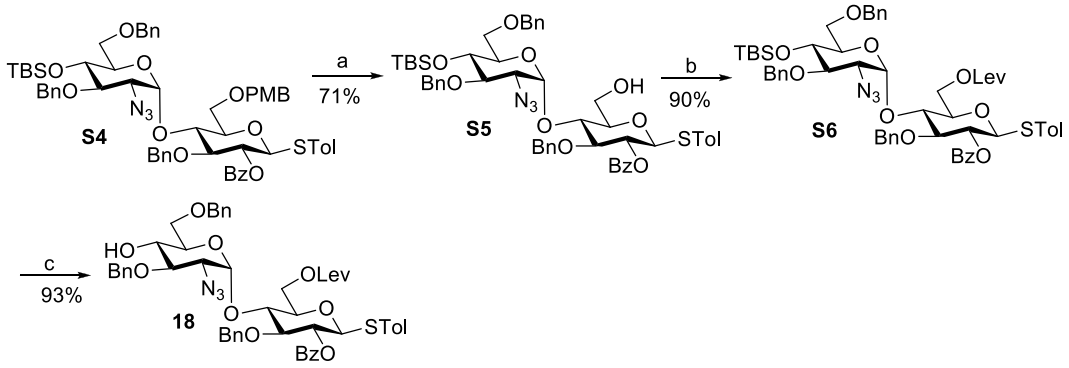
quenched by solid $NaHCO_3$ and diluted with DCM. The solution was extracted with 10% HCl solution and sat. $NaHCO_3$ solution. The combined organic phase was dried over Na_2SO_4. After concentration, it was purified by silica gel column (hexanes-EtOAc, 1:1) to afford the primary hydroxyl compound (25 mg, 63%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.13 (s, 3 H, C*H*$_3$COCH$_2$CH$_2$), 2.16 (s, 3 H, C*H*$_3$COCH$_2$CH$_2$), 2.33 (s, 3 H, SPhC*H*$_3$), 2.44-2.76 (m, 8 H, CH$_3$COC*H*$_2$C*H*$_2$), 3.20-3.28 (m, 2 H), 3.33 (t, 1 H, J = 9.5 Hz), 3.39-3.42 (m, 1 H), 3.47-3.51 (m, 2 H), 3.72-3.83 (m, 5 H), 3.96-3.99 (m, 1 H), 4.13-4.17 (m, 1 H), 4.29-4.31 (m, 2 H), 4.50-4.53 (m, 2 H), 4.59-4.61 (m, 1 H), 4.66-4.72 (m, 3 H), 4.83-4.84 (m, 1 H), 4.88-4.90 (m, 1 H), 6.80-6.83 (m, 2 H), 7.10-7.13 (m, 4 H), 7.28-7.36 (m, 5 H), 7.42-7.44 (m, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 21.1, 27.8, 27.9, 29.7, 29.8, 37.6, 37.8, 55.2, 61.8, 62.4, 65.0, 68.9, 69.7, 72.1, 73.0, 73.2, 74.3, 74.6, 75.7, 83.4, 85.8, 97.5, 113.7, 126.4, 127.8, 127.9, 128.0, 128.3, 128.4, 129.6, 129.6, 129.7, 134.5, 137.5, 137.8, 138.9, 159.4, 171.9, 172.1, 206.6, 206.7. This compound (20 mg, 0.0205 mmol) was dissolved in DCM/*t*BuOH/H_2O (4:4:1, 4.5 mL), followed by addition of TEMPO (2 mg) and BAIB (138 mg). The resulting mixture was stirred under room temperature overnight. After the reaction was complete as indicated by TLC analysis, it was neutralized by 1 M HCl solution to adjust pH around 6. The solution was diluted with DCM, then extracted with H_2O. The combined organic phase was dried over Na_2SO_4. After concentration, the crude product (ESI-MS: $C_{51}H_{56}N_3O_{15}S$ $[M-H]^-$ calcd: 982.34, obsd: 982.10) was dissolved in DCM (1 mL) and was treated with phenyl diazomethane solution in diethyl ether (100 μL). The reaction was stirred under room temperature for 3 h and concentrated to afford compound **16** (15 mg, 63% over two steps) after column purification (hexanes-EtOAc, 1:2). ^{1}H-NMR (600 MHz, $CDCl_3$): δ 2.11 (s, 3 H, C*H*$_3$COCH$_2$CH$_2$), 2.14 (s, 3 H, C*H*$_3$COCH$_2$CH$_2$), 2.32 (s, 3 H, SPhC*H*$_3$), 2.49-2.82 (m, 8 H, CH$_3$COC*H*$_2$C*H*$_2$), 3.20 (t, 2 H, J = 8.5 Hz), 3.38 (t, 1 H, J = 8 Hz), 3.49-3.52 (m, 1 H), 3.74 (s, 3 H, C*H*$_3$OPh), 3.78-3.82 (m, 3 H), 4.15 (dd, 1 H, J = 3.5 Hz, J = 10 Hz), 4.27-4.31 (m, 2 H), 4.38-4.40 (m, 1 H), 4.50 (dd, 1 H, J = 1.5 Hz, J = 10 Hz), 4.59-4.68 (m, 4 H), 4.83-4.87 (m, 2 H), 4.90-4.92 (m, 1 H), 5.24 (d, 1 H, J = 4.5 Hz), 6.71-6.74 (m, 2 H), 7.00-7.02 (m, 2 H), 7.09-7.11 (m, 2 H), 7.18-7.22 (m, 5 H), 7.24-7.31 (m, 10 H), 7.42-7.44 (m, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 21.1, 27.8, 27.9, 29.7, 29.8, 37.6, 37.9, 55.2, 62.5, 64.6, 66.6, 70.9, 71.2, 72.4, 73.2, 75.0, 75.1, 75.1, 75.5, 82.9, 85.7, 97.7, 113.6, 126.6, 127.5, 127.7, 127.8, 128.1, 128.2, 128.3, 128.3, 128.3, 128.4, 129.3, 129.4, 129.7, 134.4, 135.2, 137.7, 137.7, 138.8, 159.3, 169.3, 171.8, 172.2, 206.2, 206.5. HRMS: $C_{58}H_{63}N_3O_{15}S$ $[M+NH_4]^+$ calcd: 1091.4324, obsd: 1091.4363.



Reagents and conditions: (a) DDQ, DCM/H_2O; (b) LevOH, EDC-HCl, DMAP, DCM.

***p*-Tolyl-2-*O*-benzoyl-3-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-1-thio-α-L-idopyranoside (S3)**. Compound **4** (1 g, 1.4 mmol) was dissolved in DCM/H_2O (20 mL, 10:1), followed by addition of DDQ (476 mg). The resulting mixture was stirred under room temperature overnight. After the reaction was complete, it was diluted with DCM, washed with sat. $NaHCO_3$. The combined organic phase was dried over Na_2SO_4 and concentrated. Column purification afforded compound **S3** (682 mg, 82%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ -0.28 (br, 3 H, Si(CH_3)$_2$), -0.10 (br, 3 H, Si(CH_3)$_2$), 0.67 (s, 9 H, C(CH_3)$_3$), 1.82 (dd, 1 H, J = 3 Hz, J = 10 Hz, H-4), 2.30 (s, 3 H, SPhCH_3), 3.67-3.75 (m, 3 H, H-3, H-6a, O*H*), 3.90-3.95 (m, 1 H, H-5), 4.65-4.68 (m, 2 H, H-6b, CH_2Ph), 4.90-4.93 (m, 1 H, CH_2Ph), 5.39-5.41 (m, 1 H, H-2), 5.53 (br, 1 H, H-1), 7.09-7.11 (m, 2 H), 7.26-7.45 (m, 9 H), 7.51-7.54 (m, 1 H), 8.03-8.06 (m, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ -5.48, -4.66, 17.9, 21.0, 25.6, 62.7, 68.9, 69.5, 69.6, 72.3, 74.2, 86.2, 127.9, 128.2, 128.4, 129.6, 129.7, 130.0, 131.5, 132.6, 133.2, 137.4, 137.8, 165.5. HRMS: $C_{33}H_{42}O_6SSi$ $[M+NH_4]^+$ calcd: 612.2815, obsd: 612.2813.

***p*-Tolyl-2-*O*-benzoyl-3-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-6-*O*-levulinoyl-1-thio-α-L-idopyranoside (17)**. Compound **S3** (650 mg, 1.09 mmol) was dissolved in dry DCM (10 mL), followed by addition of EDC-HCl (579 mg, 2.7 mmol), DMAP (26 mg, 0.27 mmol) and LevOH (316 mg, 2.7 mmol). The resulting mixture was stirred under room temperature for overnight. The reaction was diluted with DCM and washed with 10% HCl solution and sat. $NaHCO_3$ solution sequentially. The combined organic phase was dried over Na_2SO_4 and purified by silica gel column (3:1 hexanes-EtOAc) to afford compound **17** (674 mg, 89%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ -0.30 (s, 3 H, Si(CH_3)$_2$), -0.10 (s, 3 H, Si(CH_3)$_2$), 0.68 (s, 9 H, C(CH_3)$_3$), 2.13 (s, 3 H, CH_3COCH$_2$CH$_2$), 2.29 (s, 3 H, SPhCH_3), 2.55-2.71 (m, 4 H, CH$_3$COCH_2CH_2), 3.71-3.76 (m, 2 H, H-3, H-4), 4.22-4.25 (m, 1 H, H-6a), 4.34-4.38 (m, 1 H, H-6b), 4.65-4.68 (m, 1 H, PhCH_2), 4.83-4.86 (m, 1 H, H-5), 4.91-4.94 (m, 1 H, PhCH_2), 5.37-5.39 (m, 1 H, H-2), 5.32 (br, 1 H, H-1), 7.08-7.10 (m, 2 H), 7.25-7.29 (m, 1 H), 7.32-7.38 (m, 4 H), 7.43-7.52 (m, 5 H), 8.03-8.05 (m, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ -5.7, -4.6, 17.8, 20.9, 25.5, 27.6, 29.6, 37.7, 63.9, 66.9, 68.1, 69.2, 72.1, 73.6, 86.0, 127.9, 128.0, 128.1, 128.3, 129.5, 129.9, 132.0, 133.1, 137.2, 137.3, 165.5, 172.3, 206.1.



Reagents and conditions: (a) DDQ, DCM/H_2O; (b) EDC-HCl, LevOH, DMAP, DCM; (c) HF/Pyridine, Pyridine.

***p*-Tolyl-2-azido-3,6-di-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-2-deoxy-β-D-glucopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-1-thio-β-D-glucopyranoside (S5)**. Compound **S4**[2] (300 mg, 0.277 mmol) was dissolved in DCM/H_2O (10:1, 5 mL), followed by addition of DDQ (95 mg, 0.42 mmol). The resulting mixture was stirred under room temperature overnight. After the reaction was complete, it was diluted with DCM, washed with sat. $NaHCO_3$ and dried over Na_2SO_4. Silica gel column purification afforded compound **S5** (189 mg, 71%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ -0.10 (s, 3 H, Si(CH_3)$_2$), -0.08 (s, 3 H, Si(CH_3)$_2$), 0.78 (s, 9 H, C(CH_3)$_3$), 2.30 (s, 3 H, SPhCH_3), 3.04 (d, 1 H, J = 6 Hz), 3.15 (dd, 1 H, J = 5.5 Hz, J = 8.5 Hz), 3.40 (dd, 1 H, J = 5.5 Hz, J = 8.5 Hz), 3.46-3.52 (m, 2 H), 3.61-3.65 (m, 2 H), 3.70-3.72 (m, 1 H), 3.88-3.94 (m, 2 H), 4.02 (t, 1 H, J = 7.5 Hz), 4.11 (t, 1 H, J = 7.5 Hz), 4.45-4.47 (m, 1 H), 4.62-4.81 (m, 6 H), 5.31 (t, 1 H, J = 8 Hz), 5.61 (d, 1 H, J = 3.5 Hz), 7.06-7.08 (m, 2 H), 7.11-7.18 (m, 5 H), 7.23-7.35 (m, 12 H), 7.54-7.57 (m, 1 H), 8.05-8.07 (m, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ -4.8, -3.9, 14.0, 17.8, 21.0, 21.0, 25.7, 60.2, 61.3, 63.2, 68.5, 71.3, 72.6, 73.0, 73.1, 73.3, 74.4, 74.8, 79.1, 80.2, 84.9, 86.5, 97.9, 114.2, 127.1, 127.3, 127.4, 127.5, 127.7, 127.8, 128.1, 128.1, 128.3, 128.3, 128.8, 129.5, 129.6, 129.7, 133.1, 133.1, 137.2, 137.3, 137.7, 138.0, 164.9. HRMS: $C_{53}H_{63}N_3O_{10}SSi$ $[M+NH_4]^+$ calcd: 979.4347, obsd: 979.4371.

***p*-Tolyl-2-azido-3,6-di-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-2-deoxy-β-D-glucopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-levulinoyl-1-thio-β-D-glucopyranoside (S6)**. Compound **S5** (189 mg, 0.197 mmol) was dissolved in dry DCM (100 mL), followed by addition of EDC-HCl (105 mg, 0.49 mmol), DMAP (15 mg, 0.04 mmol) and LevOH (57 mg, 0.49 mmol). The resulting mixture was stirred under room temperature for overnight. The reaction was diluted with DCM and washed with 10%

HCl solution, sat. $NaHCO_3$ solution sequentially. The combined organic phase was dried over Na_2SO_4 and purified by silica gel column (3:1 hexanes-EtOAc) to afford compound **S6** (187 mg, 90%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ -0.01 (s, 3 H, Si(CH_3)$_2$), 0.02 (s, 3 H, Si(CH_3)$_2$), 0.87 (s, 9 H, C(CH_3)$_3$), 2.19 (s, 3 H, CH_3COCH$_2$CH$_2$), 2.33 (s, 3 H, SPhCH_3), 2.54-2.73 (m, 4 H, CH$_3$COCH_2CH_2), 3.27 (dd, 1 H, J = 4 Hz, J = 10.5 Hz), 3.58-3.77 (m, 6 H), 3.94-3.98 (m, 2 H), 4.04-4.08 (m, 1 H), 4.24-4.28 (m, 1 H), 4.47-4.50 (m, 1 H), 4.60-4.64 (m, 2 H), 4.70-4.72 (m, 1 H), 4.77-4.88 (m, 4 H), 5.30-5.34 (m, 1 H), 5.62 (d, 1 H, J = 4 Hz), 7.09-7.11 (m, 2 H), 7.15-7.21 (m, 5 H), 7.25-7.29 (m, 2 H), 7.32-7.39 (m, 10 H), 7.45-7.48 (m, 2 H), 7.56-7.61 (m, 1 H), 8.09-8.12 (m, 2 H). HRMS: $C_{58}H_{69}N_3O_{12}SSi$ $[M+NH_4]^+$ calcd: 1077.4715, obsd: 1077.4690.

***p*-Tolyl-2-azido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-levulinoyl-1-thio-β-D-glucopyranoside (18)**. Compound **S6** (187 mg, 0.177 mmol) was dissolved in pyridine (2 mL) in a plastic flask followed by addition of 65-70% HF-pyridine solution (2 mL) under 0 °C. The solution was stirred overnight until complete disappearance of starting material as judged by TLC analysis. The reaction mixture was quenched by solid $NaHCO_3$ and diluted with DCM. The aqueous phase was extracted with DCM twice. The combined organic phase was further washed with sat. $NaHCO_3$ and dried over Na_2SO_4. Column purification afforded compound **18** (155 mg, 93%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.16 (s, 3 H, CH_3COCH$_2$CH$_2$), 2.32 (s, 3 H, SPhCH_3), 2.56-2.72 (m, 4 H, CH$_3$COCH_2CH_2), 2.82 (d, 1 H, J = 3 Hz), 3.23 (dd, 1 H, J = 4 Hz, J = 10 Hz), 3.60-3.62 (m, 1 H), 3.68-3.80 (m, 5 H), 3.90 (t, 1 H, J = 9.5 Hz), 4.02 (t, 1 H, J = 9 Hz), 4.18 (dd, 1 H, J = 5.5 Hz, J = 12 Hz), 4.52-4.59 (m, 3 H), 4.68-4.70 (m, 1 H), 4.75-4.79 (m, 2 H), 4.85-4.91 (m, 2 H, CH_2Ph), 5.30 (t, 1 H, J = 4.5 Hz), 5.57 (t, 1 H, J = 4 Hz), 7.08-7.10 (m, 2 H), 7.14-7.24 (m, 5 H), 7.26-7.48 (m, 14 H), 7.57-7.60 (m, 1 H), 8.09-8.11 (m, 2 H).

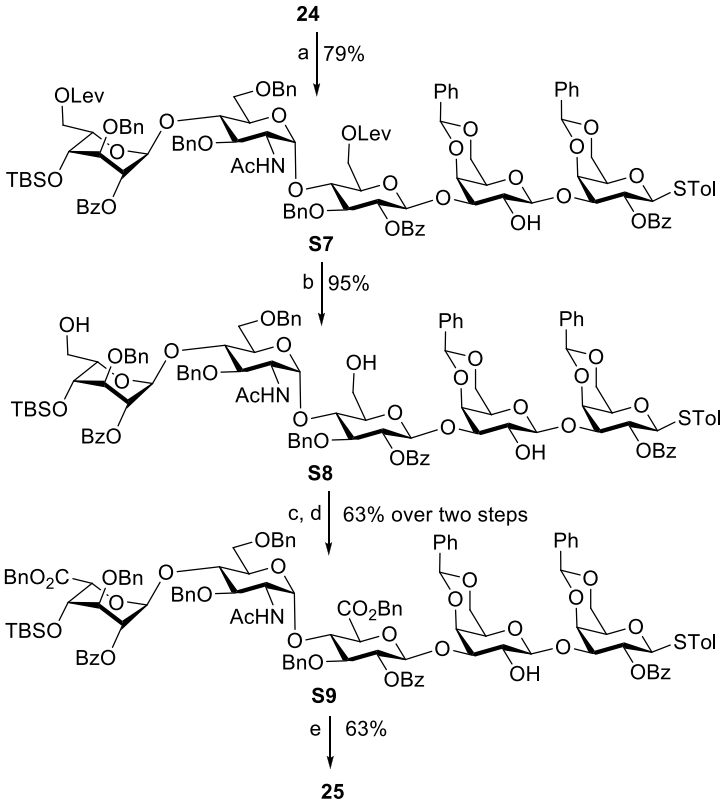
***p*-Tolyl-2-*O*-benzoyl-3-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-6-*O*-levulinoyl-α-L-idopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-levulinoyl-1-thio-β-D-glucopyranoside (19)**. Compound **19** was synthesized from donor **17** and acceptor **18** in 85% yield following the general procedure of single step glycosylation. ^{1}H-NMR (600 MHz, $CDCl_3$): δ -0.19 (s, 3 H, Si(CH_3)$_2$), -0.07 (s, 3 H, Si(CH_3)$_2$), 0.76 (s, 9 H, C(CH_3)$_3$), 2.08 (s, 3 H, CH_3COCH$_2$CH$_2$), 2.13 (s, 3 H, CH_3COCH$_2$CH$_2$), 2.30 (s, 3 H, SPhCH_3), 2.38-2.64 (m, 8 H, CH$_3$COCH_2CH_2), 3.26 (dd, 1 H, J = 3 Hz, J = 8.5 Hz), 3.46-3.48 (m, 1 H), 3.64-3.72 (m, 5 H), 3.76-3.79 (m, 1 H), 3.82-3.85 (m, 1 H), 3.95-4.01 (m, 3 H), 4.06-4.11 (m, 1 H),

4.18-4.22 (m, 1 H), 4.28-4.32 (m, 1 H), 4.40-4.48 (m, 3 H), 4.63-4.78 (m, 6 H), 5.00 (d, 1 H, J = 8.5 Hz), 5.11-5.15 (m, 2 H), 5.22-5.26 (m, 1 H), 5.51 (d, 1 H, J = 3.5 Hz), 7.05-7.29 (m, 19 H), 7.32-7.38 (m, 7 H), 7.43-7.46 (m, 2 H), 7.51-7.58 (m, 2 H), 7.92-7.94 (m, 2H), 8.06-8.08 (m, 2 H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ -5.2, -4.6, 17.9, 21.1, 25.7, 27.7, 27.7, 29.7, 29.8, 37.7, 37.8, 62.5, 63.2, 63.3, 67.7, 68.1, 68.9, 70.3, 71.9, 72.7, 72.9, 73.3, 74.2, 74.5, 74.6, 75.0, 76.2, 78.3, 84.5, 86.0, 97.0, 97.9, 127.4, 127.5, 127.6, 127.6, 127.7, 127.8, 128.0, 128.2, 128.2, 128.3, 128.3, 128.4, 128.5, 129.5, 129.5, 129.6, 129.8, 133.2, 133.3, 133.4, 137.2, 137.6, 137.7, 138.1, 138.2, 165.1, 165.5, 171.9, 172.2, 206.1, 206.3. MALDI-MS: $C_{83}H_{95}N_3O_{20}SSi$ $[M+Na]^+$ calcd: 1537.8, obsd: 1537.2.

***p*-Tolyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-1-thio-β-D-galactopyranoside (20)**. Compound **20** was synthesized from compound **23**[3] in 89% yield following the general procedure of Lev deprotection. ^{1}H-NMR (500 MHz, $(CD_3)_2CO$): δ2.31 (s, 3 H, SPhCH_3), 3.32-3.37 (m, 1 H), 3.45-3.54 (m, 3 H), 3.68-3.70 (m, 1 H), 3.82 (br, 1 H), 4.09-4.30 (m, 6 H), 4.46 (d, 1 H, J = 8 Hz), 4.59 (d, 1 H, J = 3 Hz), 5.00 (d, 1 H, J = 10 Hz), 5.05 (t, 1 H, J = 9.5 Hz), 5.56 (s, 1 H, PhCH), 5.64 (s, 1 H, PhCH), 7.07-7.09 (m, 2 H), 7.29-7.36 (m, 6 H), 7.44-7.51 (m, 8 H), 7.60-7.63 (m, 1 H), 8.02-8.04 (m, 2 H). ^{13}C-NMR (150 MHz, $(CD_3)_2CO$): δ 21.1, 67.5, 69.6, 69.7, 70.2, 70.9, 71.5, 73.1, 76.7, 77.2, 79.9, 86.1, 101.2, 101.5, 106.0, 127.2, 127.6, 128.6, 129.1, 129.2, 129.4, 129.8, 130.2, 130.4, 131.5, 133.7, 133.7, 138.3, 139.7, 139.7, 166.0. HRMS: $C_{40}H_{40}O_{11}S$ $[M+NH_4]^+$ calcd: 746.2635, obsd: 746.2517.

***p*-Tolyl-4,6-*O*-benzylidene-2,3-di-*O*-levulinoyl-β-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4,6-O-benzylidene-1-thio-β-D-galactopyranoside (23)**. Compound **23** was synthesized from donor **21** and acceptor **22** in 85% yield following the general procedure of single step glycosylation. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.95 (s, 3 H, CH_3COCH$_2$CH$_2$), 2.00 (s, 3 H, CH_3COCH$_2$CH$_2$), 2.28 (s, 3 H, SPhCH_3), 2.10-2.69 (m, 8 H, CH$_3$COCH_2CH_2), 3.35 (br, 1 H), 3.52 (br, 1 H), 3.95-4.03 (m, 2 H), 4.13-4.19 (m, 3 H), 4.33-4.36 (m, 1 H), 4.43 (d, 1 H, J = 3 Hz), 4.65-4.68 (m, 2 H), 4.72 (d, 1 H, J = 9.5 Hz), 5.24-5.28 (m, 1 H), 5.42 (s, 1 H, PhCH), 5.48-5.53 (m, 1 H), 5.54 (s, 1 H, PhCH), 6.98-7.00 (m, 2 H), 7.29-7.34 (m, 6 H), 7.41-7.48 (m, 8 H), 7.57-7.61 (m, 1 H), 8.01-8.04 (m, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 21.1, 27.5, 28.1, 29.5, 29.5, 37.7, 37.7, 66.4, 68.2, 68.7, 69.0, 69.4, 70.3, 71.7, 73.1, 75.9, 86.1, 100.7, 100.8, 100.9, 126.3, 126.5, 127.9, 128.1, 128.2, 128.5, 128.7, 129.0, 129.4, 129.6, 130.0, 133.2, 133.7, 137.4, 137.8, 137.9, 164.7, 171.2, 172.1, 206.5, 206.6.

***p*-Tolyl-2-*O*-benzoyl-3-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-6-*O*-levulinoyl-α-L-idopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-levulinoyl-β-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-1-thio-β-D-galactopyranoside (24)**. Compound **24** was synthesized from donor **19** and acceptor **20** in 65% yield following the general procedure of single step glycosylation. ^{1}H-NMR (500 MHz, $CDCl_3$): δ -0.17 (s, 3 *H*, $Si(CH_3)_2$), -0.04 (s, 3 H, $Si(CH_3)_2$), 0.78 (s, 9 H, $C(CH_3)_3$), 1.99 (s, 3 H, $CH_3COCH_2CH_2$), 2.09 (s, 3 H, $CH_3COCH_2CH_2$), 2.33 (s, 3 H, $SPhCH_3$), 2.25-2.60 (m, 8 H, $CH_3COCH_2CH_2$), 3.25-3.29 (m, 2 H), 3.37-3.40 (m, 1 H), 3.45-3.53 (m, 3 H), 3.64-3.76 (m, 5 H), 3.78-3.83 (m, 2 H), 3.87-3.92 (m, 1 H), 3.94-4.02 (m, 7 H), 4.15-4.35 (m, 6 H), 4.40-4.48 (m, 3 H), 4.62-4.82 (m, 6 H), 4.98 (d, 1 H, J = 8 Hz), 5.04 (d, 1 H, J = 10.5 Hz), 5.06-5.14 (m, 2 H), 5.21-5.25 (m, 1 H), 5.39 (s, 1 H), 5.44-5.48 (m, 2 H), 5.55-5.57 (m, 1 H), 7.04-7.06 (m, 2 H), 7.11-7.62 (m, 41 H), 7.91-7.96 (m, 4 H), 8.01-8.04 (m, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ -5.4, -4.6, 14.1, 17.8, 20.9, 21.1, 25.6, 27.6, 29.5, 29.7, 37.6, 37.6, 60.2, 62.4, 63.1, 66.6, 68.0, 68.7, 68.9, 69.0, 69.1, 70.1, 71.8, 72.3, 72.8, 73.2, 73.7, 74.3, 74.4, 74.9, 75.6, 76.0, 76.0, 77.9, 78.2, 78.4, 83.0, 85.0, 96.9, 97.7, 100.0, 100.1, 101.0, 104.3, 125.8, 126.6, 127.1, 127.3, 127.4, 127.5, 127.6, 127.8, 127.9, 127.9, 127.9, 127.9, 128.1, 128.1, 128.2, 128.2, 128.3, 128.5, 128.9, 129.3, 129.4, 129.5, 129.6, 129.6, 129.7, 130.3, 132.8, 133.1, 134.3, 137.2, 137.5, 137.6, 137.7, 138.1, 138.1, 165.0, 165.2, 165.4, 172.1, 172.1, 206.3, 206.6. MALDI-MS: $C_{116}H_{127}N_3O_{31}SSi$ $[M+Na]^+$ calcd: 2144.4, obsd: 2144.4



Reagents and conditions: (a) HSAc, pyridine; (b) NH_2NH_2-H_2O, HOAc, DCM/MeOH; (c) TEMPO, BAIB, *t*BuOH/H_2O/DCM; (d) $PhCHN_2$, DCM; (e) HF/pyridine.

***p*-Tolyl-2-*O*-benzoyl-3-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-6-*O*-levulinoyl-α-L-idopyranosyl-(1→4)-2-*N*-acetyl-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-levulinoyl-β-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-1-thio-β-D-galactopyranoside (S7)**. Compound **24** (17 mg, 0.008 mmol) was dissolved in thioacetic acid (HSAc) and pyridine (1:1, 2 mL). The resulting reaction was left under room temperature overnight. After the reaction was complete, it was diluted with DCM and washed with 10% HCl and sat. $NaHCO_3$ sequentially. After drying over Na_2SO_4, it was concentrated and purified by column (hexanes–EtOAc, 1:3) to afford compound **S7** (13 mg, 79%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ -0.16 (s, 3 H, Si(CH_3)$_2$), -0.05 (s, 3 H, Si(CH_3)$_2$), 0.77 (s, 9 H, C(CH_3)$_3$), 1.36 (3s, 3 H, NHCOCH_3), 2.00 (s, 3 H, CH_3COCH$_2$CH$_2$), 2.09 (s, 3 H, CH_3COCH$_2$CH$_2$), 2.31 (s, 3 H, SPhCH_3), 2.40-2.66 (m, 8 H, CH$_3$COCH_2CH_2), 3.25 (br, 2 H), 3.34-3.38 (m, 1 H), 3.52 (s, 1 H), 3.55-3.68 (m, 6 H), 3.71-3.75 (m, 1H), 3.77-3.81 (m, 1 H), 3.84-3.88 (m, 1 H), 3.91-4.16 (m, 10 H), 4.22-4.54 (m, 11 H), 4.60-4.63 (m, 1 H), 4.68-4.77 (m, 4 H), 4.89-4.91 (m, 2 H), 5.10-5.12 (m, 1 H), 5.17-5.23 (m, 2 H), 5.37 (s, 1 H), 5.42-5.46 (m. 2 H), 6.23 (d, 1

H, J = 9.5 Hz), 6.99-7.09 (m, 7 H), 7.14-7.55 (m, 36 H), 7.86-7.88 (m, 2 H), 7.96-7.99 (m, 4 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ -5.3, -4.6, 14.1, 17.8, 20.9, 21.2, 22.3, 25.6, 27.7, 27.8, 29.6, 29.7, 37.7, 60.3, 62.1, 66.6, 68.1, 68.8, 68.9, 69.2, 69.3, 70.1, 70.7, 73.0, 73.1, 73.2, 73.6, 74.5, 75.0, 75.5, 76.0, 76.5, 78.4, 78.5, 81.6, 85.1, 97.3, 100.0, 100.2, 101.1, 104.3, 125.8, 126.7, 127.1, 127.2, 127.4, 127.5, 127.6, 127.7, 127.9, 127.9, 128.0, 128.0, 128.1, 128.2, 128.2, 128.2, 128.3, 128.4, 128.5, 128.9, 129.4, 129.4, 129.5, 129.5, 129.6, 129.8, 130.3, 132.9, 133.0, 133.2, 134.3, 136.4, 137.5, 137.6, 137.7, 137.9, 138.2, 138.4, 165.1, 165.3, 165.5, 170.1, 171.0, 172.2, 172.4, 206.8, 206.8. MALDI-MS: $C_{118}H_{131}NO_{32}SSi$ $[M+Na]^+$ calcd: 2158.4, obsd: 2158.7.

***p*-Tolyl-2-*O*-benzoyl-3-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-α-L-idopyranosyl-(1→4)-2-*N*-acetyl-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-β-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-1-thio-β-D-galactopyranoside (S8)**. Compound **S7** was synthesized from compound **S8** in 95% yield following the general procedure of Lev deprotection. ^{1}H-NMR (500 MHz, $CDCl_3$): δ -0.14 (s, 3 H, $Si(CH_3)_2$), -0.04 (s, 3 H, $Si(CH_3)_2$), 0.77 (s, 9 H, $C(CH_3)_3$), 1.24 (s, 3 H, $NHCOCH_3$), 2.32 (s, 3 H, $SPhCH_3$), 2.41-2.44 (m, 2 H), 2.57-2.61 (m, 1 H), 3.16-3.20 (m, 1 H), 3.23 (s, 1 H), 3.44-3.59 (m, 4 H), 3.63-3.86 (m, 10 H), 3.93-4.04 (m, 6 H), 4.14-4.16 (m, 1 H), 4.21 (s, 1 H, J = 8 Hz), 4.32-4.44 (m, 6 H), 4.54-4.81 (m, 6 H), 4.99-5.06 (m, 3 H), 5.17-5.24 (m, 2 H), 5.39-5.47 (m, 3 H), 6.34 (d, 1 H, J = 9.5 Hz), 5.17-5.23 (m, 2 H), 5.37 (s, 1 H), 5.42-5.46 (m. 2 H), 6.23 (d, 1 H, J = 9.5 Hz), 7.03-7.06 (m, 4 H), 7.12-7.47 (m, 37 H), 7.52-7.59 (m, 2 H), 7.93-7.95 (m, 2 H), 8.00-8.04 (m, 4 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ -5.2, -4.4, 14.2, 17.8, 20.9, 21.2, 22.3, 25.6, 27.7, 27.9, 29.6, 29.7, 37.8, 61.0, 61.4, 66.8, 67.9, 68.7, 68.9, 69.3, 70.1, 70.1, 70.4, 70.5, 72.9, 73.1, 73.3, 73.8, 73.9, 74.8, 75.2, 75.4, 75.9, 76.0, 78.1, 78.5, 81.7, 85.0, 98.0, 100.0, 100.1, 101.0, 104.2, 125.2, 125.8, 126.7, 126.9, 127.6, 127.7, 127.7, 127.8, 127.9, 127.9, 128.0, 128.1, 128.1, 128.2, 128.3, 128.3, 128.4, 128.5, 128.9, 128.9, 129.4, 129.4, 129.5, 129.6, 129.7, 129.8, 130.2, 132.9, 133.0, 133.3, 134.4, 136.7, 137.5, 137.5, 137.6, 137.6, 137.8, 137.8, 138.3, 152.8, 165.2, 165.5, 165.6, 167.0, 170.3. MALDI-MS: $C_{108}H_{119}NO_{28}SSi$ $[M+Na]^+$ calcd: 1963.2, obsd: 1963.3.

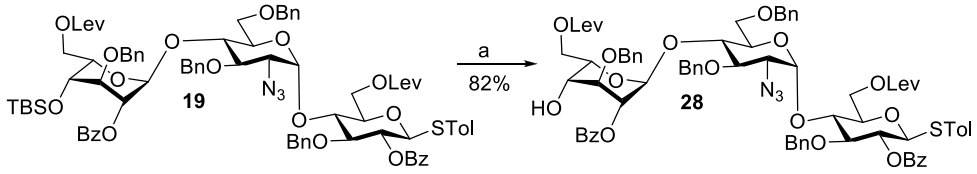
***p*-Tolyl-benzyl-2-*O*-benzoyl-3-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-α-L-idopyranosyluronate-(1→4)-2-*N*-acetyl-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-benzyl-2-*O*-benzoyl-3-*O*-benzyl-β-D-glucopyranosyluronate-(1→3)-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-1-thio-β-D-galactopyranoside (S9)**. Compound **S8**

(132 mg, 0.07 mmol) was dissolved in DCM/*t*BuOH/H_2O (4:4:1, 4.5 mL), followed by addition of TEMPO (6 mg) and BAIB (350 mg). The resulting mixture was stirred under room temperature overnight. After the reaction was complete indicated by TLC analysis, it was neutralized by 1 M HCl solution to adjust pH around 6. The solution was first diluted with DCM, then extracted with H_2O. The combined organic phase was dried over Na_2SO_4. After concentration, the crude product was confirmed by ESI-MS analysis. ESI-MS: $C_{108}H_{114}NO_{30}SSi$ calcd: $[M-H]^-$ calcd: 1964.68, obsd: 1966.40, $[M-2\ H]^{2-}$ calcd: 981.84, obsd: 982.30. The crude compound was dissolved in DCM (1 mL) and was treated with phenyl diazomethane[4] solution in diethyl ether (500 μL). The reaction was stirred under room temperature for 3 h and concentrated to afford compound **S9** (106 mg, 63% over two steps). ^{1}H-NMR (500 MHz, $CDCl_3$): δ -0.18 (s, 3 H, Si(C*H*$_3$)$_2$), -0.12 (s, 3 H, Si(C*H*$_3$)$_2$), 0.72 (s, 9 H, C(C*H*$_3$)$_3$), 1.30 (s, 3 H, NHCOC*H*$_3$), 2.31 (s, 3 H, SPhC*H*$_3$), 2.61 (s, 1 H), 3.11 (s, 1 H), 3.29-3.33 (m, 1 H), 3.39-3.43 (m, 1 H), 3.52-3.68 (m, 6 H), 3.72-3.76 (m, 3 H), 3.82-3.86 (m, 2 H), 3.92-4.15 (m, 9 H), 4.18-4.26 (m, 2 H), 4.30-4.36 (m, 2 H), 4.42-4.48 (m, 4 H), 4.58-4.63 (m, 2 H), 4.67 (s, 2H), 4.71-4.98 (m, 7 H), 5.16-5.19 (m, 1 H), 5.23-5.27 (m, 1 H), 5.30 (s, 1 H), 5.37-5.43 (m, 2 H), 5.58-5.65 (m, 2 H), 7.01-7.54 (m, 55 H), 7.88-7.97 (m, 4 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ -5.8, -4.8, 14.4, 17.8, 20.9, 21.2, 22.3, 25.6, 27.7, 27.9, 29.6, 29.7, 31.2, 32.3, 34.2, 51.6, 63.9, 66.7, 66.8, 67.2, 67.5, 68.6, 68.9, 69.1, 69.3, 70.0, 70.2, 71.8, 72.2, 72.4, 72.6, 73.2, 73.2, 73.6, 74.3, 75.0, 75.0, 75.3, 75.9, 76.5, 77.7, 78.3, 81.2, 85.0, 98.3, 98.9, 100.0, 100.9, 101.0, 104.0, 114.0, 117.0, 125.2, 125.8, 125.9, 126.3, 126.7, 126.7, 126.9, 127.0, 127.3, 127.4, 127.4, 127.5, 127.6, 127.9, 127.9, 127.9, 128.0, 128.0, 128.1, 128.1, 128.1, 128.2, 128.2, 128.3, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.9, 128.9, 129.0, 129.4, 129.5, 129.6, 129.7, 129.8, 130.2, 132.9, 133.0, 133.1, 133.1, 134.4, 135.0, 135.0, 136.6, 137.6, 137.6, 137.7, 137.8, 138.1, 138.3, 138.8, 164.9, 165.4, 165.6, 167.5, 169.2, 169.7. ESI-MS: $C_{122}H_{127}NO_{30}SSi$ $[M+NH_4]^+$ calcd: 2163.79, obsd: 2165.10, $[M+H+NH_4]^{2+}$ calcd: 1082.39, obsd: 1083.10. MALDI-MS: $[M+Na]^+$ calcd: 2171.5, obsd: 2171.8.

***p*-Tolyl-benzyl-2-*O*-benzoyl-3-*O*-benzyl-α-L-idopyranosyluronate-(1→4)-2-*N*-acetyl-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-benzyl-2-*O*-benzoyl-3-*O*-benzyl-β-D-glucopyranosyluronate-(1→3)-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-1-thio-β-D-galactopyranoside (25).** Compound **S9** (31 mg, 0.0144 mmol) was dissolved in pyridine (2 mL), which was followed by addition of HF-Pyridine (115 μL) under 0 °C. The resulting mixture was stirred under room temperature overnight. After the reaction was complete, it was quenched by solid $NaHCO_3$ and diluted with DCM. The solution

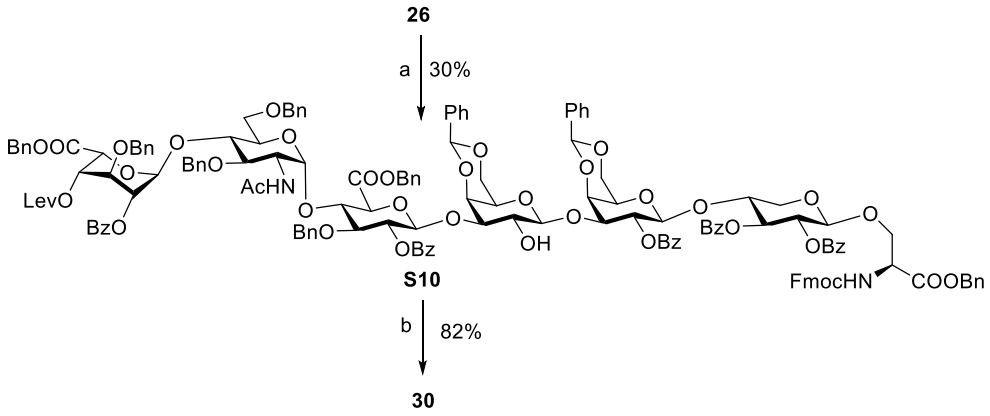
was extracted with 10% HCl solution and sat. $NaHCO_3$ solution. The combined organic phase was dried over Na_2SO_4. After concentration, it was purified by silica gel column (toluene-acetone, 2:3) to afford compound **25** (25 mg, 63%). ^{1}H-NMR (600 MHz, $CDCl_3$): δ 1.25 (s, 3 H, NHCOCH_3), 2.31 (s, 3 H, SPhCH_3), 2.70-2.72 (m, 1 H), 3.12 (s, 1 H), 3.35-3.39 (m, 1 H), 3.52-3.56 (m, 1 H), 3.61-3.66 (m, 1 H), 3.71-3.88 (m, 4 H), 3.96-3.98 (m, 2 H), 4.03-4.17 (m, 4 H), 4.30-4.47 (m, 5 H), 4.57-4.66 (m, 3 H), 4.72-4.80 (m, 2 H), 4.89-5.07 (m, 5 H), 5.20 (br, 1 H), 5.28-5.44 (m, 4 H), 5.67-5.69 (m, 1 H), 7.01-7.58 (m, 55 H), 7.92-8.00 (m, 4 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 21.0, 21.2, 22.3, 51.5, 66.6, 66.7, 67.4, 67.7, 68.1, 68.3, 68.5, 68,7, 69.0, 69.4, 70.2, 70.3, 71.8, 72.4, 72.5, 73.1, 73.2, 74.3, 74.5, 75.0, 75.3, 76.0, 78.1, 78.3, 81.1, 85.0, 98.1, 99.5, 100.1, 100.9, 101.1, 104.0, 114.7, 125.9, 126.7, 126.9, 127.0, 127.1, 127.4, 127.6, 127.9, 127.9, 127.9, 128.0, 128.1, 128.1, 128.2, 128.2, 128.3, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.6, 128.9, 129.4, 129.5, 129.6, 129.7, 129.7, 130.2, 133.1, 133.2, 133.7, 134.4, 134.9, 135.4, 136.5, 137.5, 137.6, 137.6, 137.9, 138.3, 138.3, 164.9, 165.0, 165.6, 167.4, 169.0, 169.7. MALDI-MS: $C_{116}H_{113}NO_{30}SSi$ $[M+Na]^+$ calcd: 2056.2, obsd: 2056.4.

***p*-Tolyl-benzyl-2-*O*-benzoyl-3-*O*-benzyl-4-*O*-levulinoyl-α-L-idopyranosyluronate-(1→4)-2-*N*-acetyl-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-benzyl-2-*O*-benzoyl-3-*O*-benzyl-β-D-glucopyranosyluronate-(1→3)-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-1-thio-β-D-galactopyranoside (26)**. Compound **25** (18 mg, 0.00886 mmol), EDC-HCl (16 mg, 0.0177 mmol), DMAP (10 mg, 0.0177 mmol) and LevOH (2 μL, 0.0177 mmol) were dissolved in DCM (2 mL). The resulting mixture was stirred under room temperature overnight. After the reaction was complete, it was diluted with DCM and washed with 10% HCl and sat. $NaHCO_3$ sequentially. After drying over Na_2SO_4, it was concentrated and purified by column (toluene–acetone, 4:1) to afford compound **26** (14 mg, 76%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.19 (s, 3 H, NHCOCH_3), 2.31 (s, 3 H, CH_3COCH$_2$CH$_2$), 2.01-2.08 (m, 1 H), 2.33 (s, 3 H, SPhCH_3), 2.26-2.46 (m, 4 H, CH$_3$COCH_2CH_2), 2.86-2.93 (m, 1 H), 3.12 (s, 1 H), 3.34-3.37 (m, 1 H), 3.51-3.56 (m, 2 H), 3.61 (t, 2 H, J = 10 Hz), 3.70-3.89 (m, 6 H), 3.93-3.97 (m, 3 H), 4.05-4.16 (m, 4 H), 4.32-4.48 (m, 8 H), 4.56-4.59 (m, 1 H), 4.64-4.66 (m, 1 H), 4.70-4.78 (m, 3 H), 4.86-4.92 (m, 2 H), 4.96-5.04 (m, 3 H), 5.10-5.17 (m, 3 H), 5.28 (m, 2 H), 5.38-5.44 (m, 3 H), 5.70 (d, 1 H, J = 9.5 Hz), 7.01-7.03 (m, 2 H), 7.07-7.56 (m, 51 H), 7.93-8.04 (m, 6 H). ESI-MS: $C_{121}H_{119}NO_{32}S$ $[M+Na]^+$ calcd: 2154.7, obsd: 2154.8.



Reagents and conditions: (a) HF/Pyridine, 50 °C.

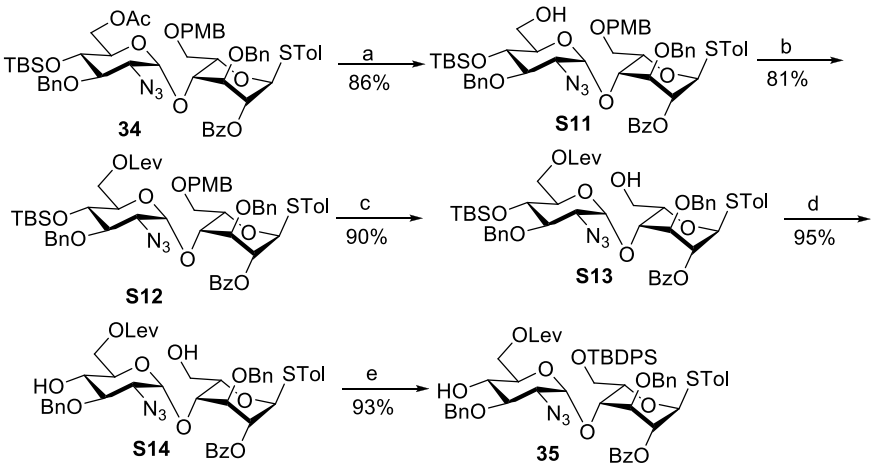
***p*-Tolyl-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-levulinoyl-α-L-idopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-levulinoyl-1-thio-β-D-glucopyranoside (28)**. Compound **19** (51 mg, 0.0337 mmol) was dissolved in pyridine (2 mL), which was followed by addition of HF-Pyridine (400 μL) at 0 °C. The resulting mixture was stirred under 50 °C overnight. After the reaction was complete, it was quenched by solid $NaHCO_3$ and diluted with DCM. The solution was extracted with 10% HCl solution and sat. $NaHCO_3$ solution. The combined organic phase was dried over Na_2SO_4. After concentration, it was purified by silica gel column (hexanes-EtOAc, 2:1) to afford compound **28** (38 mg, 82%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.09 (s, 3 H, C*H*$_3$COCH$_2$CH$_2$), 2.14 (s, 3 H, C*H*$_3$COCH$_2$CH$_2$), 2.34 (s, 3 H, SPhC*H*$_3$), 2.37-2.68 (m, 8 H, CH$_3$COC*H*$_2$C*H*$_2$), 3.28 (dd, 1 H, J = 4.5 Hz, J = 10.5 Hz), 3.56-3.63 (m, 2 H), 3.69-3.95 (m, 8 H), 3.99-4.05 (m, 2 H), 4.11-4.14 (m, 1 H), 4.45-4.47 (m, 3 H), 4.57-4.67 (m, 4 H), 4.72-4.83 (m, 4 H), 5.13 (s, 1 H), 5.20 (br, 1 H), 5.25-5.29 (m, 1 H), 5.59 (d, 1 H, J = 4 Hz), 7.06-7.47 (m, 28 H), 7.55-7.59 (m, 2 H), 7.93-7.95 (m, 2 H), 8.07-8.09 (m, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 21.1, 21.1, 27.7, 27.8, 29.7, 29.8, 29.8, 37.8, 37.8, 63.0, 63.2, 63.6, 65.2, 66.8, 67.6, 68.0, 72.1, 72.2, 72.7, 73.0, 73.3, 73.7, 74.6, 74.9, 75.0, 78.6, 84.6, 86.0, 97.0, 97.9, 127.4, 127.4, 127.5, 127.7, 127.7, 128.0, 128.2, 128.3, 128.3, 128.4, 128.5, 128.6, 129.0, 129.5, 129.6, 129.7, 129.8, 133.4, 133.6, 137.1, 137.4, 137.6, 137.8, 138.2, 165.1, 165.1, 172.1, 172.2, 206.1, 206.5. HRMS: $C_{77}H_{81}N_3O_{20}S$ $[M+NH_4]^+$ calcd: 1417.5478, obsd: 1417.5514.



Reagents and conditions: (a) AgOTf, *p*-TolSCl, DCM, -78 °C, then **29**, TTBP, -78 °C-0 °C; (b) NH_2NH_2-H_2O, HOAc, DCM, MeOH.

***N*-Fluorenylmethyloxycarbonyl-*O*-[benzyl-2-*O*-benzoyl-3-*O*-benzyl-4-*O*-levulinoyl-α-L-idopyranosyluronate-(1→4)-2-*N*-acetyl-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-benzyl-2-*O*-benzoyl-3-*O*-benzyl-β-D-glucopyranosyluronate-(1→3)-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzoyl-β-D-xylopyranosyl]-L-serine benzyl ester (S10)**. Compound **S10** was synthesized from donor **26** and acceptor **29** in 30% yield following the general procedure of single step glycosylation. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 1.20 (s, 3 H, NHCOCH_3), 2.14 (s, 3 H, CH_3COCH_2CH_2), 2.28-2.45 (m, 4 H, CH_3COCH_2CH_2), 2.61 (s, 1 H), 3.20 (s, 1 H), 3.40-3.65 (m, 6 H), 3.72-3.91 (m, 8 H), 3.96-4.02 (m, 3 H), 4.06-4.24 (m, 8 H), 4.26-4.35 (m, 4 H), 4.38-4.53 (m, 6 H), 4.56-4.63 (m, 3 H), 4.70-4.76 (m, 2 H, PhCH_2), 4.91-4.99 (m, 4 H), 5.04-5.17 (m, 6 H), 5.26-5.30 (m, 1 H), 5.34-5.50 (m, 5 H), 5.52-5.60 (m, 2 H), 5.67 (d, 1 H, J = 8 Hz), 7.05-7.46 (m, 64 H), 7.50-7.57 (m, 4 H), 7.66-7.68 (m, 2 H), 7.73-7.76 (m, 2 H), 7.85-7.87 (m, 4 H), 7.98-8.00 (m, 2 H). MALDI-MS: $C_{158}H_{150}N_2O_{43}$ $[M+Na]^+$ calcd: 2790.9, obsd: 2790.6.

***N*-Fluorenylmethyloxycarbonyl-*O*-[benzyl-2-*O*-benzoyl-3-*O*-benzyl-α-L-idopyranosyluronate-(1→4)-2-*N*-acetyl-3,6-di-O-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-benzyl-2-*O*-benzoyl-3-O-benzyl-β-D-glucopyranosyluronate-(1→3)-4,6-O-benzylidene-β-D-galactopyranosyl-(1→3)-2-O-benzoyl-4,6-O-benzylidene-β-D-galactopyranosyl-(1→4)-2,3-di-O-benzoyl-β-D-xylopyranosyl]-L-serine benzyl ester (30)**. Compound **30** was synthesized from compound **S10** in 82% yield following the general procedure of Lev deprotection. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.10 (s, 3 H, NHCOCH_3), 2.71 (d, 1 H, J = 11 Hz), 3.21 (s, 1 H), 3.39-3.49 (m, 3 H), 3.55-3.64 (m, 4 H), 3.71-3.93 (m, 9 H), 3.99-4.36 (m, 16 H), 4.39-4.56 (m, 7 H), 4.60-4.66 (m, 4 H), 4.74-4.77 (m, 1 H), 4.91-4.94 (m, 3 H), 5.02-5.07 (m, 3 H), 5.09-5.20 (m, 4 H), 5.26-5.30 (m, 3 H), 5.35 (s, 2 H), 5.40-5.46 (m, 2 H), 5.49 (s, 1 H), 5.42-5.60 (m, 2 H), 5.67 (d, 1 H, J = 10 Hz), 7.07-7.46 (m, 65 H), 7.50-7.59 (m, 4 H), 7.65-7.67 (m, 2 H), 7.85-7.87 (m, 3 H), 7.91-7.93 (m, 2 H).



Reagents and conditions: (a) $Mg(OMe)_2$, DCM, -20 ºC-0 ºC; (b) LevOH, EDC-HCl, DMAP, DCM; (c) DDQ, DCM/H_2O; (d) HF/Pyridine; (e) TBDPSCl, imidazole, DCM.

***p*-Tolyl-2-azido-3-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*p*-methoxybenzyl-1-thio-α-L-idopyranoside (S11)**. Compound **34**[5] (2.2 g, 2.13 mmol) was dissolved in dry DCM (50 mL) and cooled down to -20 ºC. Fresh methanolic $Mg(OMe)_2$ solution (8%) (21 mL) was added to the reaction mixture. The resulting mixture was left under N_2 and monitored by TLC. After the reaction was complete, it was neutralized by 1 M HOAc to pH 5 and diluted with DCM. After washing with sat. $NaHCO_3$ solution and drying over Na_2SO_4, the solution was concentrated and purified by silica gel column to afford compound **S11** (1.81 g, 86%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ -0.14 (s, 3 H, Si(CH_3)$_2$), -0.01 (s, 3 H, Si(CH_3)$_2$), 0.85 (s, 9 H, C(CH_3)$_3$), 1.70-1.73 (m, 1 H), 2.28 (s, 3 H, SPhCH_3), 3.18 (m, 1 H, J = 3.5 Hz, J = 10 Hz), 3.31-3.35 (m, 1 H), 3.44-3.48 (m, 1 H), 3.53-3.66 (m, 4 H), 3.73-3.75 (m, 2 H), 3.79 (s, 3 H, CH_3OPh), 3.99-4.02 (m, 1 H, CH_2Ph), 4.12-4.14 (m, 1 H), 4.24-4.27 (m, 1 H), 4.49 (s, 2 H), 4.58 (d, 1 H, J = 4.0 Hz), 4.70-4.73 (m, 1 H, CH_2Ph), 4.88-4.91 (m, 1 H), 4.92-4.94 (m, 1 H, CH_2Ph), 5.31-5.33 (m, 1 H), 5.53 (br, 1 H), 6.85-6.87 (m, 2 H), 7.00-7.02 (m, 2 H), 7.08-7.10 (m, 2 H), 7.20-7.29 (m, 7 H), 7.32-7.36 (m, 4 H), 7.38-7.45 (m, 4 H), 8.08-8.10 (m, 2 H). HRMS: $C_{54}H_{65}N_3O_{11}SSi$ $[M+NH_4]^+$ calcd: 1009.4453, obsd: 1009.4430.

***p*-Tolyl-2-azido-3-O-benzyl-4-*O*-*t*-butyldimethylsilyl-2-deoxy-6-*O*-levulinoyl-α-D-glucopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*p*-methoxybenzyl-1-thio-α-L-idopyranoside (S12)**. Compound **S12** was synthesized from compound **S11** in 81% yield by dissolving 1.81 g **S12** and LevOH (2 equiv.), EDC-HCl (2 equiv) and DMAP (2 equiv.) in 100 mL. After overnight stirring under room temperature and extraction with sat.

$NaHCO_3$ solution,the organic layer was concentrated and purified by column chromatography. ^{1}H-NMR (500 MHz, $CDCl_3$): δ -0.09 (s, 3 H, Si(CH_3)$_2$), -0.01 (s, 3 H, Si(CH_3)$_2$), 0.88 (s, 9 H, C(CH_3)$_3$), 2.14 (s, 3 H, $CH_3COCH_2CH_2$), 2.31 (s, 3 H, SPhCH_3), 2.55-2.76 (m, 4 H, $CH_3COCH_2CH_2$), 3.27-3.29 (m, 1 H), 3.35-3.39 (m, 1 H), 3.50-3.54 (m, 1 H), 3.73-3.86 (m, 7 H), 4.02-4.15 (m, 2 H), 4.17 (br, 1 H), 4.24-4.27 (m, 1 H), 4.31-4.34 (m, 1 H), 4.50-4.56 (m, 2 H), 4.68-4.69 (m, 1 H), 4.75-4.77 (m, 1 H), 4.94-4.97 (m, 2 H), 5.37 (br, 1 H), 5.58 (br, 1 H), 6.88-6.90 (m, 2 H), 7.03-7.05 (m, 2 H), 7.14-7.16 (m, 2 H), 7.24-7.30 (m, 6 H), 7.34-7.39 (m, 4 H), 7.43-7.49 (m, 5 H), 8.12-8.14 (m, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ -4.9, -3.9, 14.1, 17.8, 21.0, 25.8, 27.6, 29.7, 37.6, 55.1, 60.2, 62.9, 64.4, 67.1, 69.1, 70.0, 70.8, 71.2, 71.7, 72.5, 72.8, 74.4, 74.7, 80.4, 86.3, 98.2, 113.6, 126.9, 127.2, 127.8, 127.9, 128.0, 128.3, 128.3, 129.1, 129.5, 129.7, 129.8, 130.0, 131.7, 132.2, 133.1, 137.3, 137.4, 137.6, 159.0, 165.5, 172.3, 206.0. HRMS: $C_{59}H_{71}N_3O_{13}SSi$ $[M+NH_4]^+$ calcd: 1107.4821, obsd: 1107.4768.

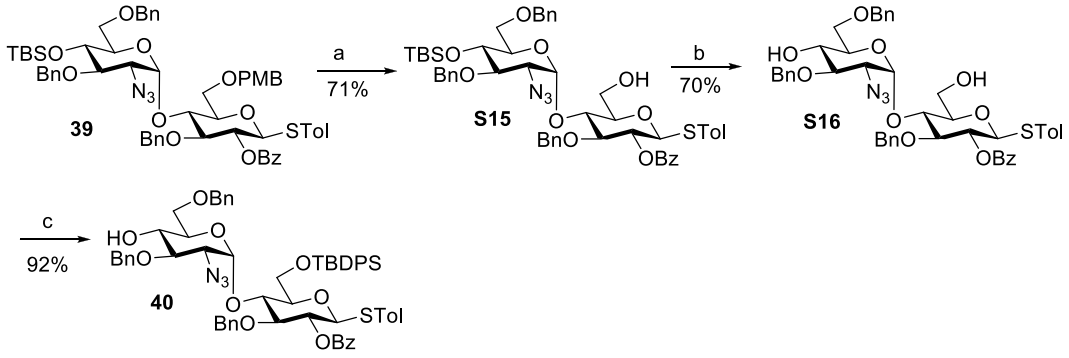
***p*-Tolyl-2-azido-3-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-2-deoxy-6-*O*-levulinoyl-α-D-glucopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-1-thio-α-L-idopyranoside (S13)**. Compound **S12** (1.6 g, 1.48 mmol) was dissolved in DCM/H_2O (10:1, 30 mL), followed by addition of DDQ (500 mg, 2.25 mmol). The resulting mixture was stirred under room temperature overnight. After the reaction was complete, it was diluted with DCM, washed with sat. $NaHCO_3$ solution, dried over Na_2SO_4. Silica gel column purification afforded compound **S13** (1.29 g, 90%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ -0.17 (s, 3 H, Si(CH_3)$_2$), -0.03 (s, 3 H, Si(CH_3)$_2$), 0.84 (s, 9 H, C(CH_3)$_3$), 2.14 (s, 3 H, $CH_3COCH_2CH_2$), 2.31 (s, 3 H, SPhCH_3), 2.57-2.72 (m, 4 H, $CH_3COCH_2CH_2$), 3.22-3.25 (m, 2 H), 3.35-3.39 (m, 1 H), 3.68 (br, 1 H), 3.76-3.98 (m, 6 H), 4.06-4.10 (m, 1 H), 4.15 (br, 1 H), 4.40 (br, 1 H, J = 10.5 Hz), 4.52 (s, 1 H), 4.73-4.75 (m, 1 H, CH_2Ph), 4.82-4.85 (m, 1 H), 4.95-4.97 (m, 1 H, CH_2Ph), 5.36 (s, 1 H), 5.56 (s, 1 H), 7.03-7.10 (m, 4 H), 7.18-7.48 (m, 13 H), 8.10-8.12 (m, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ -4.8, -3.9, 14.0, 17.8, 21.0, 25.7, 27.5, 29.7, 37.6, 61.3, 63.3, 64.4, 67.8, 69.7, 71.0, 71.1, 71.6, 72.3, 74.2, 75.9, 80.3, 86.3, 99.2, 126.7, 127.1, 127.9, 128.1, 128.2, 128.4, 129.6, 129.6, 129.9, 131.6, 132.2, 133.1, 137.2, 137.5, 137.6, 165.4, 172.3, 206.4. HRMS: $C_{51}H_{63}N_3O_{12}SSi$ $[M+NH_4]^+$ calcd: 987.4245, obsd: 987.4199.

***p*-Tolyl-2-azido-3-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-1-thio-α-L-idopyranoside (S14)**. Compound **S13** (1.29 g, 1.33 mmol) was dissolved in pyridine (10 mL) in a plastic flask followed by addition of 65-70% HF-pyridine solution (15 mL) under 0 ºC. The solution was stirred overnight

until complete disappearance of starting material as judged by TLC analysis. The reaction mixture was quenched by solid $NaHCO_3$ and diluted with DCM. The aqueous phase was extracted with DCM twice. The combined organic phase was further washed with sat. $NaHCO_3$ and dried over Na_2SO_4. Column purification afforded compound **S14** (1.08 g, 95%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.13 (s, 3 H, C*H*$_3$COCH$_2$CH$_2$), 2.26-2.29 (m, 1 H), 2.31 (s, 3 H, SPhC*H*$_3$), 2.54-2.72 (m, 4 H, CH$_3$COC*H*$_2$C*H*$_2$), 2.92 (br, 1 H), 3.21 (dd, 1 H, *J* = 3.5 Hz, *J* = 10 Hz), 3.31-3.35 (m, 1 H), 3.39-3.44 (m, 1 H), 3.69-3.71 (m, 1 H), 3.75-3.79 (m, 1 H), 3.85-3.90 (m, 2 H), 4.04-4.07 (m, 1 H, C*H*$_2$Ph), 4.12-4.14 (m, 1 H), 4.21 (dd, 1 H, *J* = 2 Hz, *J* = 12 Hz), 4.26-4.28 (m, 1 H, C*H*$_2$Ph), 4.35 (dd, 1 H, *J* = 5.5 Hz, *J* = 12 Hz), 4.55 (d, 1 H, *J* = 4 Hz), 4.73-4.76 (m, 1 H, C*H*$_2$Ph), 4.80-4.83 (m, 1 H), 4.95-4.98 (m, 1 H, C*H*$_2$Ph), 5.38 (s, 1 H), 5.55 (s, 1 H), 7.10-7.16 (m, 4 H), 7.24-7.30 (m, 4 H), 7.34-7.47 (m, 9 H), 8.13-8.15 (m, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 14.1, 20.9, 21.0, 27.6, 29.7, 37.7, 60.3, 61.4, 63.2, 63.3, 68.0, 69.7, 70.5, 71.1, 71.2, 72.4, 74.8, 74.9, 80.2, 86.3, 98.6, 127.8, 127.9, 128.1, 128.3, 128.3, 128.4, 129.7, 129.9, 131.6, 132.4, 133.1, 137.2, 137.6, 137.7, 165.6, 173.1, 206.8. HRMS: $C_{45}H_{49}N_3O_{12}S$ $[M+NH_4]^+$ calcd: 873.3381, obsd: 873.3345.

***p*-Tolyl-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-levulinoyl-α-D-glucopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-1-thio-α-L-idopyranoside (35)**. Compound **S14** (1.08 g, 1.26 mmol) was dissolved in DCM (10 mL), followed by addition of imidazole (102 mg, 1.5 mmol) and TBDPSCl (487 μL, 1.88 mmol). The resulting mixture was stirred under room temperature overnight and diluted with DCM. The solution was washed with 10% HCl solution, sat. $NaHCO_3$ solution and dried over Na_2SO_4. After concentration, column purification afforded compound **35** (1.28 g, 93%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.08 (s, 9 H, C(C*H*$_3$)$_3$), 2.13 (s, 3 H, C*H*$_3$COCH$_2$CH$_2$), 2.29 (s, 3 H, SPhC*H*$_3$), 2.47-2.69 (m, 4 H, CH$_3$COC*H*$_2$C*H*$_2$), 2.76 (d, 1 H, *J* = 4.5 Hz), 3.24 (dd, 1 H, *J* = 3.5 Hz, *J* = 10 Hz), 3.31-3.36 (m, 1 H), 3.41-3.45 (m, 1 H), 3.56-3.61 (m, 2 H), 3.75 (br, 1 H), 3.89-3.97 (m, 2 H), 4.14-4.17 (m, 1 H, C*H*$_2$Ph), 4.22-4.23 (m, 1 H), 4.33-4.36 (m, 1 H), 4.40-4.43 (m, 1 H, C*H*$_2$Ph), 4.68 (d, 1 H, *J* = 3.5 Hz), 4.75-4.81 (m, 2 H), 4.95-4.97 (m, 1 H, C*H*$_2$Ph), 5.39-5.41 (m, 1 H), 5.58-5.59 (m, 1 H), 6.99-7.01 (m, 2 H), 7.18-7.20 (m, 2 H), 7.26-7.50 (m, 19 H), 7.69-7.76 (m, 4 H), 8.12-8.15 (m, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 14.1, 19.1, 21.0, 26.8, 27.6, 29.6, 37.8, 60.3, 62.5, 63.3, 63.5, 69.3, 69.4, 70.2, 70.3, 70.9, 72.5, 72.7, 74.9, 75.0, 79.9, 86.7, 98.5, 127.7, 127.7, 127.8, 127.9, 127.9, 128.3, 128.3, 128.4, 129.5, 129.7, 129.8, 129.9, 131.6, 132.7, 132.8, 132.9, 133.1, 135.5, 135.6, 137.5, 137.5, 137.8, 165.6, 173.4, 206.4. HRMS: $C_{61}H_{67}N_3O_{12}SSi$ $[M+NH_4]^+$ calcd: 1111.4558, obsd: 1111.4517.

***p*-Tolyl-3-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-2-*O*-levulinoyl-4-*O*-*p*-methoxybenzyl-α-L-idopyranosyl-(1→4)-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-levulinoyl-α-D-glucopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-1-thio-α-L-idopyranoside (36)**. Compound **36** was synthesized from donor **12** and acceptor **35** in 52% yield following the general procedure of single step glycosylation. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.03 (s, 9 H, C(C*H*$_3$)$_3$), 1.06 (s, 9 H, C(C*H*$_3$)$_3$), 2.01 (s, 3 H, C*H*$_3$COCH$_2$CH$_2$), 2.02 (s, 3 H, C*H*$_3$COCH$_2$CH$_2$), 2.27 (s, 3 H, SPhC*H*$_3$), 2.31-2.68 (m, 8 H, CH$_3$COC*H*$_2$C*H*$_2$), 3.23 (dd, 1 H, *J* = 4 Hz, *J* = 10.5 Hz), 3.41 (t, 1 H, *J* = 9 Hz), 3.53-3.55 (m, 1 H), 3.66-3.71 (m, 2 H), 3.77 (s, 1 H, C*H*$_3$OPh), 3.82-3.95 (m, 7 H), 3.98-4.02 (m, 3 H), 4.15-4.17 (m, 1 H), 4.23 (d, 1 H, *J* = 10.5 Hz), 4.29-4.31 (m, 1 H), 4.33-4.36 (m, 1 H), 4.58-4.62 (m, 4 H), 4.78-4.83 (m, 2 H), 4.87-4.89 (m, 2 H), 4.93-4.95 (m, 1 H), 5.37 (t, 1 H, *J* = 4.5 Hz), 5.58 (d, 1 H, *J* = 3.5 Hz), 6.73-6.75 (m, 2 H), 6.96-6.99 (m, 4 H), 7.12-7.17 (m, 6 H), 7.22-7.40 (m, 23 H), 7.45-7.49 (m, 1 H), 7.56-7.61 (m, 4 H), 7.65-7.67 (m, 2 H), 7.72 (m 2 H), 8.06-8.08 (m, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 14.1, 19.1, 19.1, 21.0, 26.8, 26.9, 27.7, 27.9, 29.5, 29.6, 29.6, 34.6, 37.6, 55.2, 60.3, 62.9, 63.9, 64.0, 70.1, 70.4, 70.8, 71.4, 72.2, 73.0, 73.6, 74.3, 74.9, 75.2, 75.4, 75.6, 75.9, 78.9, 86.4, 97.9, 98.7, 113.6, 113.9, 127.1, 127.6, 127.6, 127.7, 127.7, 127.7, 127.8, 127.8, 128.0, 128.1, 128.2, 128.3, 128.6, 129.4, 129.4, 129.5, 129.6, 129.7, 129.7, 129.8, 129.8, 129.9, 131.3, 132.0, 132.8, 132.9, 133.1, 133.3, 135.6, 135.6, 135.6, 135.6, 137.5, 137.7, 137.9, 138.1, 159.2, 165.3, 171.7, 172.1, 206.0, 206.2. MALDI-MS: $C_{103}H_{115}N_3O_{20}SSi_2$ $[M+Na]^+$ calcd: 1826.3, obsd: 1826.3.



Reagents and conditions: (a) DDQ, DCM/H_2O; (b) HF/Pyridine; (c) TBDPSCl, imidazole, DCM.

***p*-Tolyl-2-azido-3,6-di-O-benzyl-4-*O*-*t*-butyldimethylsilyl-2-deoxy-β-D-glucopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-1-thio-β-D-glucopyranoside (S15)**.

Compound **39** (300 mg, 0.277 mmol) was dissolved in DCM/H_2O (10:1, 5 mL), which was followed by addition of DDQ (95 mg, 0.42 mmol). The resulting mixture was stirred under room temperature overnight. After the reaction was complete, it was diluted with DCM, washed with sat. $NaHCO_3$ and dried over Na_2SO_4. Silica gel column purification afforded compound **S15** (189 mg, 71%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ -0.10 (s, 3 H, Si(CH_3)$_2$), -0.08 (s, 3 H, Si(CH_3)$_2$), 0.78 (s, 9 H, C(CH_3)$_3$), 2.30 (s, 3 H, SPhCH_3), 3.04 (d, 1 H, J = 6 Hz), 3.15 (dd, 1 H, J = 5.5 Hz, J = 8.5 Hz), 3.40 (dd, 1 H, J = 5.5 Hz, J = 8.5 Hz), 3.46-3.52 (m, 2 H), 3.61-3.65 (m, 2 H), 3.70-3.72 (m, 1 H), 3.88-3.94 (m, 2 H), 4.02 (t, 1 H, J = 7.5 Hz), 4.11 (t, 1 H, J = 7.5 Hz), 4.45-4.47 (m, 1 H), 4.62-4.81 (m, 6 H), 5.31 (t, 1 H, J = 8 Hz), 5.61 (d, 1 H, J = 3.5 Hz), 7.06-7.08 (m, 2 H), 7.11-7.18 (m, 5 H), 7.23-7.35 (m, 12 H), 7.54-7.57 (m, 1 H), 8.05-8.07 (m, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ -4.8, -3.9, 14.0, 17.8, 21.0, 21.0, 25.7, 60.2, 61.3, 63.2, 68.5, 71.3, 72.6, 73.0, 73.1, 73.3, 74.4, 74.8, 79.1, 80.2, 84.9, 86.5, 97.9, 114.2, 127.1, 127.3, 127.4, 127.5, 127.7, 127.8, 128.1, 128.1, 128.3, 128.3, 128.8, 129.5, 129.6, 129.7, 133.1, 133.1, 137.2, 137.3, 137.7, 138.0, 164.9. HRMS: $C_{53}H_{63}N_3O_{10}SSi$ $[M+NH_4]^+$ calcd: 979.4347, obsd: 979.4371.

***p*-Tolyl-2-azido-3,6-di-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-2-deoxy-α-D-glucopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-1-thio-β-D-glucopyranoside (S16)**. Compound **S15** (1.3 g, 1.35 mmol) was dissolved in pyridine (10 mL) in a plastic flask followed by addition of 65-70% HF-pyridine solution (15 mL) under 0 °C. The solution was stirred overnight until complete disappearance of starting material as judged by TLC analysis. The reaction mixture was quenched by solid $NaHCO_3$ and diluted with DCM. The aqueous phase was extracted with DCM twice. The combined organic phase was further washed with sat. $NaHCO_3$ and dried over Na_2SO_4. Column purification afforded compound **S16** (800 mg, 70%). ^{1}H-NMR (600 MHz, $CDCl_3$): δ 2.31 (s, 3 H, SPhCH_3), 2.43-2.46 (m, 1 H), 2.51-2.53 (m, 1 H), 3.16-3.19 (m, 1 H), 3.50-3.53 (m, 1 H), 3.58-3.66 (m, 3 H), 3.72-3.77 (m, 2 H), 3.79-3.83 (m, 1 H), 3.90-3.94 (m, 1 H), 4.00-4.06 (m, 2 H), 4.50-4.58 (m, 2 H, CH_2Ph), 4.67-4.69 (m, 1 H, CH_2Ph), 4.74-4.81 (m, 3 H), 4.88-4.90 (m, 1 H), 5.30 (t, 1 H, J = 7.5 Hz), 5.58-5.59 (m, 1 H), 7.07-7.09 (m, 2 H), 7.12-7.20 (m, 5 H), 7.26-7.39 (m, 12 H), 7.43-7.47 (m, 2 H), 7.56-7.59 (m, 1 H), 8.07-8.09 (m, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 21.1, 21.1, 60.3, 61.7, 62.4, 69.4, 71.0, 72.0, 72.3, 73.0, 73.6, 74.6, 75.0, 78.9, 79.6, 84.9, 86.5, 97.8, 113.7, 127.6, 127.7, 127.8, 127.8, 128.0, 128.2, 128.4, 128.5, 128.6, 128.7, 129.6, 129.8, 133.1, 133.3, 137.3, 137.3, 137.9, 138.3, 165.1, 171.7, 172.1, 206.0, 206.2. HRMS: $C_{47}H_{49}N_3O_{10}S$ $[M+NH_4]^+$ calcd: 865.3482, obsd: 865.3478.

***p*-Tolyl-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-1-thio-β-D-glucopyranoside (40)**. Compound **S16** (800 mg, 0.945 mmol) was dissolved in DCM (10 mL), followed by addition of imidazole (102 mg, 1.5 mmol) and TBDPSCl (487 μL, 1.88 mmol). The resulting mixture was stirred under room temperature overnight and diluted with DCM. The solution was washed with 10% HCl solution, sat. $NaHCO_3$ solution and dried over Na_2SO_4. After concentration, column purification afforded compound **8** (930 mg, 92%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.09 (s, 9 H, C(C*H*$_3$)$_3$), 2.28 (s, 3 H, SPhC*H*$_3$), 2.31-2.32 (m, 1 H), 3.13-3.19 (m, 2 H), 3.25-3.28 (m, 1 H), 3.43-3.47 (m, 1 H), 3.60-3.67 (m, 3 H), 3.92-3.97 (m, 2 H), 4.00-4.04 (m, 2 H), 4.20-4.35 (m, 2 H, C*H*$_2$Ph), 4.68-4.76 (m, 2 H, C*H*$_2$Ph), 4.82-4.87 (m, 3 H), 5.34-5.38 (m, 1 H), 5.59 (d, 1 H, J = 3.5 Hz), 6.98-7.00 (m, 2 H), 7.12-7.20 (m, 7 H), 7.27-7.41 (m, 16 H), 7.44-7.47 (m, 2 H), 7.56-7.59 (m, 1 H), 7.70-7.72 (m, 4 H), 8.08-8.10 (m, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 19.3, 21.0, 26.9, 62.4, 63.8, 69.0, 70.8, 72.0, 72.9, 73.1, 73.5, 74.4, 74.9, 79.2, 79.6, 85.0, 87.3, 97.6, 127.6, 127.7, 127.7, 127.8, 127.9, 127.9, 128.2, 128.3, 128.4, 128.5, 129.6, 129.6, 129.7, 129.8, 130.4, 131.9, 133.1, 133.3, 133.6,235.5, 135.8, 137.3, 137.5, 137.5, 138.0, 165.2. HRMS: $C_{63}H_{67}N_3O_{10}SSi$ $[M+NH_4]^+$ calcd: 1103.4660, obsd: 1103.4486.

***N*-Fluorenylmethyloxycarbonyl-*O*-[2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-levulinoyl-β-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzoyl-β-D-xylopyranosyl]-L-serine benzyl ester (42)**. Compound **42** was synthesized from donor **41** and acceptor **29** in 81% yield following the general procedure of single step glycosylation. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.87 (s, 3 H, C*H*$_3$COCH$_2$CH$_2$), 2.41-2.61 (m, 4 H, CH$_3$COC*H*$_2$C*H*$_2$), 3.23-3.31 (m, 2 H), 3.71-3.83 (m, 4 H), 3.90-3.95 (m, 1 H), 4.09-4.13 (m, 1 H), 4.20-4.24 (m, 3 H), 4.29-4.33 (m, 1 H), 4.45-4.51 (m, 1 H), 4.55 (d, 1 H, J = 6 Hz), 4.76 (d, 1 H, J = 8 Hz), 5.00-5.17 (m, 4 H), 5.35 (s, 1 H, PhC*H*), 5.53-5.62 (m, 3 H), 7.20-7.48 (m, 21 H), 7.51-7.56 (m, 3 H), 7.74-7.76 (m, 2 H), 7.94-7.98 (m, 6 H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ 28.4, 29.6, 37.9, 38.1, 47.3, 54.5, 62.5, 66.9, 67.4, 67.5, 68.5, 69.2, 69.3, 69.6, 71.0, 72.0, 72.1, 73.4, 76.2, 91.5, 100.8, 101.2, 102.3, 120.2, 125.4, 126.5, 126.7, 127.3, 127.3, 127.9, 127.9, 128.2, 128.3, 128.4, 128.5, 128.5, 128.6, 128.6, 128.7, 128.8, 129.1, 129.3, 129.6, 129.7, 129.8, 130.0, 130.1, 130.1, 133.3, 133.6, 135.3, 137.7, 141.4, 143.9, 144.0, 156.1, 165.1, 165.3, 165.7, 169.6, 172.3, 206.3. HRMS: $C_{69}H_{63}NO_{19}$ $[M+NH_4]^+$ calcd: 1227.4338, obsd: 1227.3872.

***N*-Fluorenylmethyloxycarbonyl-*O*-[2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→4)-2,3-di-O-benzoyl-β-D-xylopyranosyl]-L-serine benzyl ester**

(43). Compound **43** was synthesized from compound **42** in 90% yield following the general procedure of Lev deprotection. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 2.60 (d, 1 H, J = 9.5 Hz, O*H*), 3.26-3.34 (m, 2 H), 3.74-3.86 (m, 5 H), 3.93-3.97 (m, 1 H), 4.09-4.13 (m, 2 H), 4.21-4.33 (m, 2 H), 4.48-4.50 (m, 1 H), 4.57 (d, 1 H, *J* = 5 Hz), 4.71 (d, 1 H, *J* = 7 Hz), 5.02-5.10 (m, 2 H, COOC*H*$_2$Ph), 5.16-5.19 (m, 1 H), 5.27-5.30 (m, 1 H), 5.40 (s, 1 H, PhC*H*), 5.56 (d, 1 H, *J* = 7.5 Hz), 5.61 (t, 1 H, *J* = 6 Hz), 7.21-7.47 (m, 23 H), 7.52-7.54 (m, 3 H), 7.74-7.76 (m, 2 H), 7.95-8.01 (m, 5 H). ^{13}C-NMR (150 MHz, $CDCl_3$): δ 47.0, 54.2, 62.2, 66.8, 67.2, 67.3, 68.3, 69.0, 70.7, 71.6, 71.8, 73.0, 75.3, 75.7, 100.5, 101.4, 101.7, 119.9, 125.1, 126.2, 126.5, 127.0, 127.7, 127.7, 127.9, 128.1, 128.2, 128.3, 128.3, 128.4, 128.4, 128.4, 128.5, 129.1, 129.1, 129.5, 129.6, 129.8, 129.9, 133.1, 133.2, 135.1, 137.2, 141.2, 143.7, 143.8, 155.9, 165.1, 165.5, 165.9, 169.4. HRMS: $C_{64}H_{57}NO_{17}$ $[M+NH_4]^+$ calcd: 1129.3970, obsd: 1129.3920.

***N*-Fluorenylmethyloxycarbonyl-*O*-[4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→4)-2,3-di-O-benzoyl-β-D-xylopyranosyl]-L-serine benzyl ester (44)**. Donor **21** was coupled to acceptor **43** in 80% yield following the general procedure of single step glycosylation to afford the trisaccharide intermediate. This compound was converted to compound **44** in 89% yield following the general procedure for Lev deprotection. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.53-2.55 (m, 1 H), 2.77 (s, 1 H), 3.25-3.36 (m, 4 H), 3.64-3.68 (m, 1 H), 3.73-3.76 (m, 2 H), 3.80-3.84 (m, 2 H), 3.95-4.06 (m, 4 H), 4.10-4.14 (m, 1 H), 4.17-4.34 (m, 6 H), 4.48-4.50 (m, 1 H), 4.56 (d, 1 H, *J* = 5.5 Hz), 4.78 (d, 1 H, *J* = 8 Hz), 5.01-5.09 (m, 2 H, C*H*$_2$Ph), 5.15-5.18 (m, 1 H), 5.44-5.47 (m, 2 H), 5.54-5.63 (m, 3 H), 7.20-7.54 (m, 29 H), 7.73-7.76 (m, 2 H), 7.94-7.97 (m, 6 H), 8.33-8.37 (m 1 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 47.0, 54.2, 62.2, 66.7, 67.0, 67.2, 67.3, 68.3, 69.0, 70.7, 71.0, 71.3, 71.5, 72.0, 75.0, 75.5, 75.9, 77.9, 100.4, 101.1, 101.2, 101.9, 104.1, 119.9, 125.1, 126.2, 126.6, 127.0, 127.0, 127.6, 127.7, 128.0, 128.2, 128.2, 128.3, 128.3, 128.4, 128.4, 128.5, 128.7, 128.8, 129.1, 129.2, 129.5, 129.5, 129.6, 129.8, 129.9, 130.8, 133.1, 133.1, 133.2, 135.1, 137.4, 137.6, 141.2, 141.2, 143.6, 143.8, 155.9, 165.1, 165.5, 165.6, 169.4. MALDI-MS: $C_{77}H_{71}NO_{22}$ $[M+Na]^+$ calcd: 1385.4, obsd: 1385.6.

***p*-Tolyl-3-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-2-*O*-levulinoyl-4-*O*-*p*-methoxybenzyl-α-L-idopyranosyl-(1→4)-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-levulinoyl-α-D-glucopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-α-L-idopyranosyl-(1→4)-2-azido-3,6-di-O-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-1-thio-β-D-glucopyranoside (45)**.

Compound **45** was synthesized from donor **36** and acceptor **40** in 93% yield following the general procedure of single step glycosylation. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 0.99 (s, 9 H, C(CH_3)$_3$), 1.00 (s, 9 H, C(CH_3)$_3$), 1.04 (s, 9 H, C(CH_3)$_3$), 2.00 (s, 3 H, CH_3COCH$_2$CH$_2$), 2.01 (s, 3 H, CH_3COCH$_2$CH$_2$), 2.25 (s, 3 H, SPhCH_3), 2.30-2.65 (m, 8 H, CH_3COCH$_2$CH$_2$), 3.05-3.10 (m, 1 H), 3.13-3.15 (m, 2 H), 3.18-3.20 (m, 1 H), 3.40-3.44 (m, 2 H), 3.47-3.59 (m, 3 H), 3.64-3.69 (m, 2 H), 3.72-3.76 (m, 6 H), 3.82-4.03 (m, 10 H), 4.08-4.20 (m, 6 H), 4.28-4.31 (m, 2 H), 4.53-4.57 (m, 2 H), 4.60-4.64 (m, 2 H), 4.69-4.79 (m, 6 H), 4.84-4.89 (m, 2 H), 4.97 (d, 1 H, J = 9.5 Hz), 5.16-5.19 (m, 2 H), 5.27-5.31 (m, 1 H), 5.46-5.48 (m, 1 H), 6.71-6.73 (m, 2 H), 6.93-6.97 (m, 4 H), 7.02-7.38 (m, 52 H), 7.42-7.49 (m, 4 H), 7.53-7.76 (m, 12 H), 8.03-8.06 (m 4 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 19.2, 19.2, 19.2, 21.0, 26.8, 26.9, 27.0, 27.7, 27.9, 29.6, 29.6, 37.6, 55.2, 62.2, 62.6, 63.0, 63.0, 63.7, 63.9, 68.1, 69.6, 69.9, 70.6, 70.9, 71.9, 72.0, 72.9, 73.2, 73.2, 74.2, 74.3, 74.5, 74.6, 74.7, 74.9, 74.9, 75.0, 78.4, 78.9, 79.7, 84.6, 87.0, 97.7, 97.7, 98.3, 113.6, 127.1, 127.3, 127.4, 127.5, 127.6, 127.6, 127.7, 127.7, 127.8, 127.8, 127.9, 128.0, 128.0, 128.1, 128.2, 128.2, 128.3, 128.3, 128.4, 128.6, 129.4, 129.6, 129.6, 129.6, 129.7, 129.7, 129.8, 129.8, 129.9, 130.3, 132.0, 132.9, 133.2, 133.3, 133.5, 135.6, 135.6, 135.6, 135.6, 135.7, 137.4, 137.5, 137.5, 137.8, 137.8, 138.1, 138.2, 159.2, 165.2, 165.3, 171.7, 172.1, 206.1, 206.1. MALDI-MS: $C_{159}H_{174}N_6O_{30}SSi_3$ $[M+Na]^+$ calcd: 2790.4, obsd: 2790.9.

_N_-Fluorenylmethyloxycarbonyl-_O_-[3-_O_-benzyl-6-_O_-_t_-butyldiphenylsilyl-2-_O_-levulinoyl-4-_O_-_p_-methoxybenzyl-α-L-idopyranosyl-(1→4)-2-azido-3-_O_-benzyl-2-deoxy-6-_O_-levulinoyl-α-D-glucopyranosyl-(1→4)-2-_O_-benzoyl-3-_O_-benzyl-6-_O_-_t_-butyldiphenylsilyl-α-L-idopyranosyl-(1→4)-2-azido-3,6-di-_O_-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-2-_O_-benzoyl-3-_O_-benzyl-6-_O_-_t_-butyldiphenylsilyl-β-D-glucopyranosyl-(1→4)-4,6-_O_-benzylidene-β-D-galactopyranosyl-(1→3)-2-_O_-benzoyl-4,6-_O_-benzylidene-β-D-galactopyranosyl-(1→4)-2,3-di-_O_-benzoyl-β-D-xylopyranosyl]-L-serine benzyl ester (46). Compound **46** was synthesized from donor **45** and acceptor **44** in 83% yield following the general procedure of single step glycosylation. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 0.92 (s, 9 H, C(CH_3)$_3$), 1.00 (s, 9 H, C(CH_3)$_3$), 1.03 (s, 9 H, C(CH_3)$_3$), 1.99 (s, 3 H, CH_3COCH$_2$CH$_2$), 2.00 (s, 3 H, CH_3COCH$_2$CH$_2$), 2.20 (s, 1 H), 2.27-2.66 (m, 8 H, CH_3COCH$_2$CH$_2$), 3.02-3.06 (m, 2 H), 3.09-3.15 (m, 2 H), 3.18-3.22 (m, 2 H), 3.30-3.46 (m, 5 H), 3.47-3.49 (m, 1 H), 3.53-3.57 (m, 1 H), 3.64-3.87 (m, 19 H), 3.94-4.33 (m, 18 H), 4.48-4.77 (m, 12 H), 4.84-4.88 (m, 2 H), 4.96-5.03 (m, 3 H), 5.14-5.18 (m, 3 H), 5.22-5.27 (m, 1 H), 5.31 (s, 2 H), 5.42-5.44 (m, 1 H), 5.47-5.51 (m, 1 H), 5.53-5.55 (m, 1 H), 5.58-5.62 (m, 1 H), 6.71-6.73 (m, 2 H),

6.94-6.96 (m, 4 H), 7.01-7.03 (m, 2 H), 7.04-7.07 (m, 3 H), 7.11-7.38 (m, 78 H), 7.43-7.64 (m, 18 H), 7.42-7.46 (m, 2 H), 7.94-8.02 (m 10 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 19.2, 19.2, 19.3, 26.7, 26.7, 26.9, 27.0, 27.6, 27.9, 29.6, 29.6, 29.6, 37.6, 47.0, 54.2, 55.2, 62.2, 62.3, 62.6, 62.9, 62.9, 63.7, 64.2, 66.8, 67.0, 67.2, 67.3, 68.0, 68.2, 69.0, 69.5, 68.7, 69.9, 70.6, 70.7, 71.3, 71.5, 71.8, 72.0, 73.2, 73.2, 73.3, 73.9, 74.1, 74.2, 74.3, 74.4, 74.7, 74.8, 74.9, 75.0, 75.0, 75.2, 75.5, 75.5, 75.8, 76.5, 78.1, 78.4, 78.9, 83.3, 97.6, 97.7, 98.3, 100.1, 100.5, 101.0, 101.4, 102.0, 104.0, 113.6, 119.9, 125.1, 126.0, 126.6, 127.0, 127.1, 127.3, 127.4, 127.5, 127.6, 127.7, 127.8, 127.8, 127.8, 127.9, 127.9, 127.9, 128.0, 128.0, 128.1, 128.2, 128.2, 128.3, 128.3, 128.3, 128.4, 128.5, 128.6, 128.7, 129.1, 129.4, 129.5, 129.6, 129.6, 129.7, 129.7, 129.9, 130.0, 132.9, 133.1, 133.1, 133.1, 133.2, 133.2, 133.3, 133.5, 135.1, 135.4, 135.4, 135.6, 135.6, 135.6, 137.5, 137.5, 137.6, 137.7, 138.1, 138.2, 141.2, 143.6, 143.8, 155.9, 159.1, 165.1, 165.2, 165.3, 165.3, 165.5, 169.4, 171.7, 172.1, 206.1, 206.2. MALDI-MS: $C_{229}H_{237}N_7O_{52}Si_3$: $[M+Na]^+$ calcd: 4024.5, obsd: 4024.6.

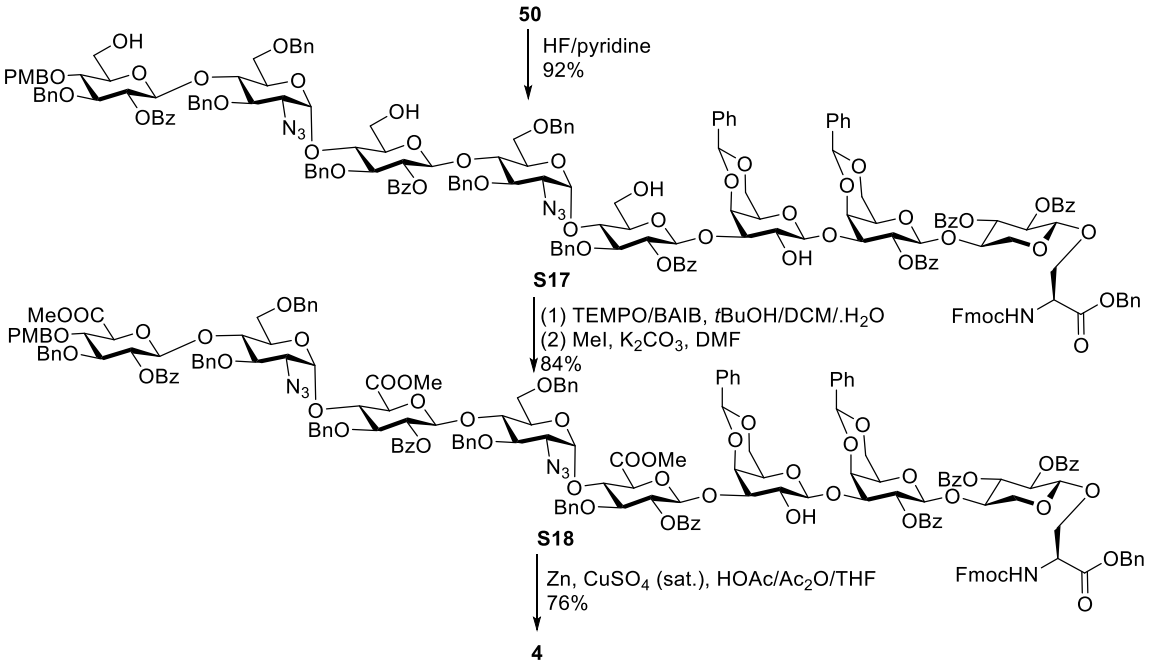
***p*-Tolyl-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-4-*O*-*p*-methoxybenzyl-β-D-glucopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-1-thio-β-D-glucopyranoside** (**48**). Compound **48** was synthesized from donor **47** and acceptor **40** in 85% yield following the general procedure of single step glycosylation. ^{1}H-NMR (500 MHz, $CDCl_3$), 0.98 (s, 9 H), 1.07 (s, 9 H), 2.30 (s, 3 H), 3.15-3.25 (m, 2 H), 3.28-3.35 (m, 1 H), 3.42-3.50 (m, 2 H), 3.52-3.59 (m, 2 H), 3.65-3.75 (m, 3 H), 3.84 (s, 3 H), 3.85-4.02 (m, 6 H), 4.06-4.15 (m, 2 H), 4.48 (d, 1 H, J = 12.5 Hz), 4.58-4.70 (m, 3 H), 4.74-4.84 (m, 6 H), 5.05 (d, 1 H, J = 12.5 Hz), 5.32-5.38 (m, 2 H), 5.05 (d, 1 H, J = 4 Hz), 6.83 (d, 2 H, J = 8.5 Hz), 6.96 (d, 2 H, J = 8.5 Hz), 7.08 (d, 1 H, J = 8.5 Hz), 7.12-7.52 (m, 38 H), 7.58-7.68 (m, 6 H), 7.71 (d, 2 H, J = 7.5 Hz), 7.77 (d, 2 H, J = 7.5 Hz), 8.01 (d, 2 H, J = 7.0 Hz), 8.12 (d, 2 H, J = 7.0 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$), 19.1, 19.2, 21.0, 55.2, 62.4, 63.0, 63.9, 67.5, 71.2, 72.9, 73.5, 74.3, 74.4, 74.4, 74.5, 75.0, 75.2, 75.4, 79.5, 83.1, 84.4, 86.9, 98.1, 99.7, 113.8, 127.1, 127.5, 127.6, 127.7, 127.7, 127.7, 127.7, 127.8, 128.0, 128.0, 128.2,128.2, 128.4, 128.5, 129.5, 129.5, 129.6, 129.6, 129.7, 129.8, 129.8, 129.9, 130.1, 130.1, 130.3, 133.1, 133.2, 133.3, 133.5, 135.6, 135.7, 135.8, 137.4, 137.5, 137.6, 137.7, 138.5, 159.2, 165.0, 165.1. MALDI-MS: $C_{107}H_{113}N_3O_{17}SSi_2$ $[M+Na]^+$ calcd: 1824.2, obsd: 1824.2.

***p*-Tolyl-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-4-*O*-*p*-methoxybenzyl-β-D-glucopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-1-thio-β-D-glucopyranosyl-**

(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-1-thio-β-D-glucopyranoside (**49**). Compound **49** was synthesized from donor **48** and acceptor **40** in 80% yield following the general procedure of single step glycosylation. ^{1}H-NMR (500 MHz, $CDCl_3$), 0.82 (s, 9 H), 0.93 (s, 9 H), 1.02 (s, 9 H), 2.27 (s, 3 H), 2.97 (dd, 1 H, *J* = 10.5, 4.0 Hz), 3.10-3.20 (m, 4 H), 3.28-3.50 (m, 7 H), 3.54-3.70 (m, 7 H), 3.78 (t, 3 H *J* = 9.0 Hz), 3.81 (s, 3 H), 3.83-3.96 (m, 6 H), 4.06-4.10 (m, 2 H), 4.21(d, 1 H, *J* = 12.0 Hz), 4.44-4.82 (m, 15 H), 4.89 (d, 1 H, *J* = 12.0 Hz), 5.04 (d, 1 H, *J* = 12.0 Hz), 5.19 (t, 1 H, *J* = 8.0 Hz), 5.25-5.35 (m, 3 H), 5.44 (d, 1 H, *J* = 4.0 Hz), 6.78 (d, 2 H, *J* = 8.5 Hz), 6.92 (d, 2 H, *J* = 8.5 Hz), 7.12-7.52 (m, 67 H), 7.54-7.63 (m, 7 H), 7.65 (d, 2 H, *J* = 7.5 Hz), 7.71 (d, 2 H, *J* = 7.5 Hz), 7.90-8.00 (m, 4 H), 8.12 (d, 2 H, *J* = 7 Hz), ^{13}C-NMR (125 MHz, $CDCl_3$), 19.1, 19.2, 19.3, 21.0, 55.2, 62.6, 62.9, 63.2, 63.9, 64.0, 67.4, 71.2, 71.4, 72.9, 73.6, 73.6, 74.3, 74.4, 74.4, 74.7, 75.2, 75.4, 75.8, 76.1, 77.4, 77.6, 79.5, 83.1, 83.2, 84.4, 86.9, 98.0, 98.0, 99.2, 99.7, 113.8, 126.9, 127.2, 127.5, 127.5, 127.6, 127.6, 127.7, 127.7, 127.7, 127.8, 127.8, 127.9, 127.9, 127.9, 128.0, 128.0, 128.1, 128.2, 128.2, 128.3, 128.4, 128.5, 128.6, 128.6, 129.5, 129.6, 129.6, 129.6, 129.7, 129.7, 129.8, 129.8, 129.9, 130.1, 130.4, 131.9, 133.1, 133.2, 133.3, 133.3, 133.6, 135.4, 135.5, 135.6, 135.7, 135.8, 137.4, 137.5, 137.7, 137.7, 137.7, 138.5, 159.3, 164.8, 164.9, 165.2, MALDI-MS: $C_{163}H_{172}N_6O_{27}SSi_3$ $[M+Na]^+$ calcd: 2786.4, obsd: 2786.4.

***N*-Fluorenylmethyloxycarbonyl-*O*-[2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-4-*O*-*p*-methoxybenzyl-β-D-glucopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-β-D-glucopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-β-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzoyl-β-D-xylopyranosyl]-L-serine benzyl ester** (**50**). Compound **50** was synthesized from donor **49** and acceptor **44** in 87% yield following the general step of single step glycosylation. ^{1}H-NMR (500MHz, $CDCl_3$), 0.93 (brd, 1H, *J* = 11.5, 4.0Hz), 1.18 (brs, 1H), 3.22-3.52 (m, 18H), 3.54-3.68 (m, 6H), 3.69-4.02 (m, 18H), 3.84 (s, 3H), 4.08 (d, 1H, *J* = 2.5Hz), 4.10-4.20 (m, 3H), 4.22-4.32 (m, 5H), 4.34-4.42 (m, 2H), 4.46 (d, 2H, *J* = 7.5Hz), 4.50-4.68 (m, 6H), 4.70-4.90 (m, 10H), 5.00-5.02 (m, 2H), 5.04-5.18 (m, 3H), 5.20-5.28 (m, 4H), 5.40-5.42 (m, 2H), 5.50-5.70 (m, 5H), 6.91 (d, 2H, *J* = 8.5Hz), 7.02 (d, 2H, *J* = 8.5Hz), 7.04-7.60 (m, 67H), 7.54-7.63 (m, 6H), 7.75 (d, 2H, *J* = 7.5Hz), 7.79-7.84 (m, 2H), 7.89 (d, 2H, *J* = 7.0Hz), 7.95 (d, 2H, *J* = 8.5Hz), 7.98-8.07(m, 8H), ^{13}C-NMR

(125MHz, $CDCl_3$), 26.3, 29.9, 47.4, 54.3, 55.2, 62.8, 63.1, 63.9, 64.0, 66.8, 67.1, 67.3, 67.5, 67.6, 68.5, 69.1, 69.4, 71.6, 72.9, 73.6, 73.7, 73.8, 74.2, 74.3, 74.7, 75.1, 75.2, 75.3, 75.4, 75.6, 75.8, 76.1, 76.6, 77.6, 83.1, 83.2, 97.9, 98.0, 99.4, 99.7, 100.1, 100.5, 101.0, 101.1, 102.0, 104.0, 113.8, 120.0, 125.2, 126.0, 126.6, 126.9, 127.1, 127.2, 127.4, 127.5, 127.7, 127.7, 127.7, 127.8, 127.9, 127.9, 128.0, 128.0, 128.1, 128.2, 128.2, 128.2, 128.3, 128.3, 128.4, 128.5, 128.5, 128.8, 129.1, 129.5, 129.6, 129.7, 129.8, 129.9, 130.0, 130.1, 133.1, 133.1, 133.2, 133.2, 133.3, 133.4, 133.5, 133.8, 135.1, 135.4, 135.4, 135.5, 135.7, 135.8, 137.5, 137.6, 137.6, 137.7, 137.8, 138.5, 138.8, 141.2, 143.7, 143.8, 155.9, 159.2, 164.8, 164.9, 165.2, 165.2, 165.4, 165.5, 169.5. MALDI-MS: $C_{233}H_{235}N_7O_{49}Si_3$ $[M+Na]^+$ calcd: 4024.6, obsd: 4024.3.



***N*-Fluorenylmethyloxycarbonyl-*O*-[2-*O*-benzoyl-3-*O*-benzyl-4-*O*-*p*-methoxybenzyl-β-D-glucopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-1-thio-β-D-glucopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-1-thio-β-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzoyl-β-D-xylopyranosyl]-L-serine benzyl ester** (**S17**). Compound **50** (132 mg, 0.040 mmol) was dissolved in pyridine (3.5 mL) in a plastic flask followed by addition of 65-70% HF-pyridine solution (1 mL) under 0 °C. The solution was stirred overnight until complete disappearance of starting material as judged by TLC analysis. The reaction mixture was

quenched by solid $NaHCO_3$ and diluted with DCM. The aqueous phase was extracted with DCM twice. The combined organic phase was further washed with sat. $NaHCO_3$ and dried over Na_2SO_4. Column purification afforded compound **S17** (100 mg, 92%). ^{1}H-NMR (500 MHz, $CDCl_3$), 2.40 (s, 1 H), 2.93 (dd, 1 H, *J* = 10.5, 4.0 Hz), 2.97 (s, 1 H), 3.30-3.25 (m, 6 H), 3.30-3.45 (m, 10 H), 3.56-3.92 (m, 25 H), 3.81 (s, 3 H), 3.93-4.12 (m, 4 H), 4.14-4.30 (m, 6 H), 4.36 (m, 1 H), 4.44 (d, 2 H, *J* = 11.5 Hz), 4.50-4.82 (m, 18 H), 4.89 (d, 1H, *J* = 11.5 Hz), 5.04 (d, 1 H, *J* = 12.0 Hz), 5.07 (d, 1 H, *J* = 12.0 Hz), 5.12 (d, 1 H, *J* = 12.0 Hz), 5.19-5.35 (m, 7 H), 5.44 (d, 1 H, *J* = 4.0 Hz), 5.51 (t, 2 H, *J* = 7.0 Hz), 5.58-5.66 (m, 2 H), 6.78 (d, 2 H, *J* = 8.5 Hz), 7.02 (d, 2 H, *J* = 8.5 Hz), 7.04-7.60 (m, 67 H), 7.54-7.63 (m, 7 H), 7.66 (d, 2 H, *J* = 7.5 Hz), 7.72 (d, 2 H, *J* = 7.5 Hz), 7.79 (dd, 2 H, *J* = 7.0, 3.5 Hz), 7.94 (m, 4 H), 7.99 (m, 8 H). ^{13}C-NMR (125 MHz, $CDCl_3$), 19.2, 19.2, 19.3, 26.7, 26.8, 47.1, 54.3, 55.2, 62.8, 63.1, 63.9, 64.0, 66.8, 67.0, 67.2, 67.3, 68.2, 69.1, 69.4, 70.1, 71.0, 71.2, 71.6, 72.5, 73.5, 74.0, 74.2, 74.4, 74.7, 74.9, 75.1, 75.2, 75.3, 75.5, 75.6, 75.7, 75.8, 76.0, 76.4, 76.7, 76.8, 78.0, 78.1, 82.9, 83.6, 97.5, 97.7, 100.3, 100.5, 100.5, 100.8, 101.3, 102.2, 104.2, 114.2, 120.3, 125.5, 125.6, 126.2, 127.0, 127.4, 127.4, 127.4, 127.6, 127.8, 127.9, 128.0, 128.0, 128.1, 128.2, 128.3, 128.3, 128.5, 128.5, 128.6, 128.6, 128.7, 128.8, 128.8, 128.9, 129.0, 129.1, 129.3, 129.4, 129.6, 129.8, 129.9, 129.9, 130.0, 130.1, 130.1, 130.2, 130.2, 130.5, 133.5, 133.5, 133.6, 133.6, 133.9, 134.7, 135.4, 137.6, 137.7, 137.8, 137.8, 137.9, 138.0, 138.0, 138.1, 138.7, 138.7, 141.5, 144.0, 144.1, 156.2, 159.7, 162.5, 165.2, 165.4, 165.4, 165.5, 165.7, 165.8, 169.8. MALDI-MS: $C_{185}H_{181}N_7O_{49}$ $[M+Na]^+$ calcd: 3310.4, obsd: 3310.6.

***N*-Fluorenylmethyloxycarbonyl-*O*-[methyl-2-*O*-benzoyl-3-*O*-benzyl-4-*O*-*p*-methoxybenzyl-β-D-glucopyranosyluronate-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl-2-*O*-benzoyl-3-*O*-benzyl-1-thio-β-D-glucopyranosyluronate-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl-2-*O*-benzoyl-3-*O*-benzyl-1-thio-β-D-glucopyranosyluronate-(1→3)-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzoyl-β-D-xylopyranosyl]-L-serine benzyl ester** (**S18**). Compound **S17** (56 mg, 0.017 mmol) was dissolved in DCM/*t*BuOH/H2O (4:4:1, 4.5 mL), followed by addition of TEMPO (5 mg) and BAIB (55 mg). The resulting mixture was stirred under room temperature overnight. After the reaction was complete indicated by TLC analysis, it was neutralized by 1 M HCl solution to adjust pH around 6. The solution was first diluted with DCM, then extracted with H_2O. The combined organic phase was dried over Na_2SO_4. MALDI-MS: $C_{185}H_{175}N_7O_{52}$ $[M+Na]^+$ calcd: 3351.4, obsd: 3352.3. After concentration, the crude

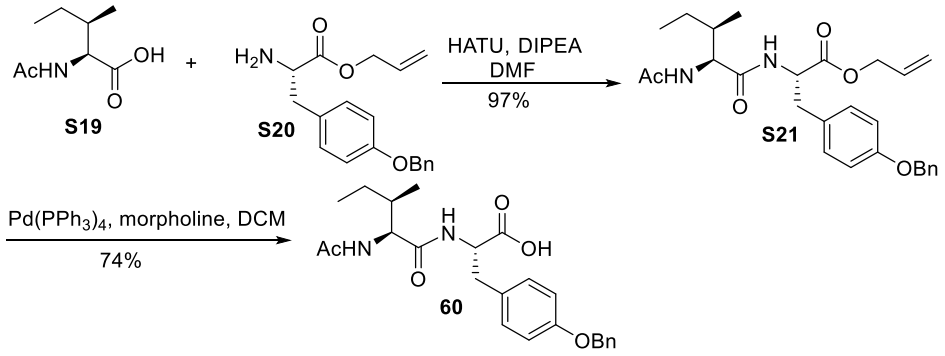
compound was dissolved in dry DMF (5 mL), to which was added MeI (11 μL, 0.177 mmol) and K_2CO_3 (46 mg, 0.333 mmol). The resulting mixture was stirred under room temperature overnight. The reaction mixture was diluted with DCM and H_2O. The aqueous phase was extracted with DCM twice. The combined organic phase was further washed with sat. $NaHCO_3$ and dried over Na_2SO_4. Column purification afforded compound **S18** (48 mg, 2 steps 84%). ^{1}H-NMR (500MHz, $CDCl_3$), 2.83 (s, 3 H), 2.99 (s, 3 H), 3.03 (d, 1H, *J* = 10.5 Hz), 3.05-3.15 (m, 2 H), 3.20 (s, 2 H), 3.24-3.38 (m, 4 H), 3.40 (d, 1 H, *J* = 9.5 Hz), 3.50-4.00 (m, 29 H), 4.01-4.16 (m, 6 H), 4.18-4.28 (m, 5 H), 4.30-4.42 (m, 3 H), 4.46-4.84 (m, 18 H), 4.89 (d, 1 H, *J* = 8.5 Hz), 5.01 (d, 1 H, *J* = 10.5 Hz), 5.04 (d, 1 H, *J* = 12.5 Hz), 5.10 (d, 1 H, *J* = 12.5 Hz), 5.15-5.28 (m, 5 H), 5.34 (s, 1 H), 5.37 (s, 1 H), 5.40 (d, 1 H, *J* = 4.0 Hz), 5.42 (d, 1 H, *J* = 4.0 Hz), 5.50-5.64 (m, 3 H), 6.85 (d, 2 H, *J* = 8.5 Hz), 6.90-7.12 (m, 2 H), 7.04-7.60 (m, 71 H), 7.52-7.63 (m, 5 H), 7.70-7.84 (m, 6 H), 7.93-8.00 (m, 8 H). ^{13}C-NMR (125 MHz, $CDCl_3$), 21.4, 47.0, 51.6, 51.7, 52.4, 54.2, 55.2, 62.2, 62.2, 62.4, 66.4, 66.5, 66.8, 67.0, 67.1, 67.2, 68.2, 68.7, 69.1, 70.1, 70.2, 70.4, 70.7, 71.3, 71.5, 73.2, 73.3, 73.5, 73.5, 73.7, 73.8, 73.9, 74.4, 74.4, 74.6, 75.0, 75.3, 75.6, 76.0, 76.5, 76.6, 79.4, 81.8, 82.6, 82.7, 97.0, 97.2, 99.9, 100.0, 100.0, 100.5, 100.7, 101.0, 101.9, 103.8, 113.8, 119.9, 125.1, 125.2, 125.8, 126.6, 127.1, 127.1, 127.4, 127.5, 127.7, 127.7, 127.8, 127.9, 128.2, 128.2, 128.2, 128.2, 128.3, 128.4, 128.4, 128.5, 128.5, 128.6, 128.7, 128.8, 129.0, 129.0, 129.1, 129.1, 129.2, 129.4, 129.5, 129.6, 129.8, 129.8, 129.9, 133.1, 133.3, 133.4, 133.6, 135.1, 137.0, 137.1, 137.5, 137.6, 137.7, 137.8, 137.8, 138.0, 138.2, 141.2, 141.2, 143.6, 143.8, 155.8, 159.3, 164.4, 164.5, 164.9, 165.2, 165.4, 165.5, 167.6, 168.2, 168.8, 169.5. MALDI-MS: $C_{188}H_{181}N_7NaO_{52}$ $[M+Na]^+$ calcd: 3393.4, obsd: 3393.4.

***N*-Fluorenylmethyloxycarbonyl-*O*-[methyl-2-*O*-benzoyl-3-*O*-benzyl-4-*O*-*p*-methoxybenzyl-β-D-glucopyranosyluronate-(1→4)-2-*N*-acetyl-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl-2-*O*-benzoyl-3-*O*-benzyl-1-thio-β-D-glucopyranosyluronate-(1→4)-2-*N*-acetyl-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl-2-*O*-benzoyl-3-*O*-benzyl-1-thio-β-D-glucopyranosyluronate-(1→3)-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzoyl-β-D-xylopyranosyl]-L-serine benzyl ester** (**4**). Compound **S18** (44 mg, 0.013 mmol) was dissolved in THF/Ac_2O/HOAc (3:2:1, 7.5 mL), followed by addition of Zn (720 mg), $CuSO_4$ (saturated solution, 47 μL). The resulting mixture was stirred under room temperature for 30min. After filtration, the mixture was diluted with DCM and washed with sat. $NaHCO_3$. The combined organic phase was dried over Na_2SO_4 and purified by

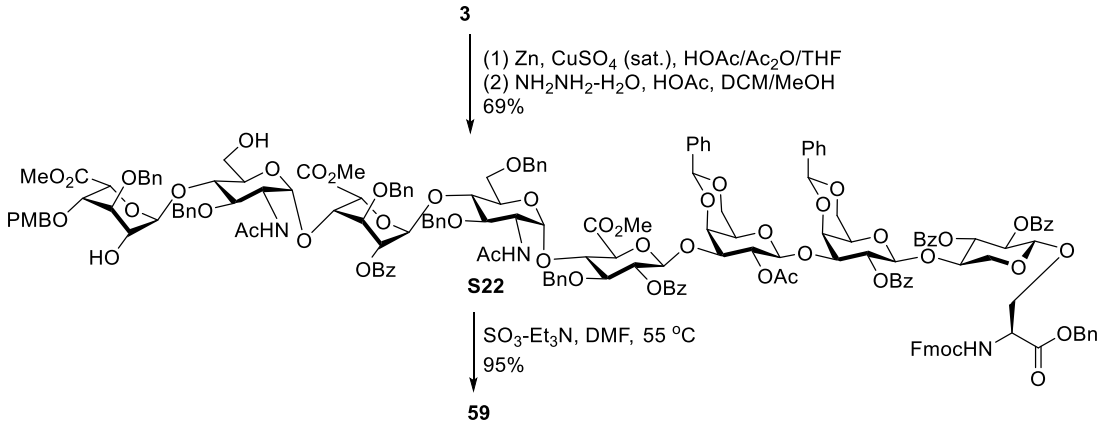
silica gel column to afford compound **4** (34 mg, 76%). ^{1}H-NMR (500 MHz, $CDCl_3$), 1.43 (s, 3 H), 1.44 (s, 3 H), 3.18 (s, 3 H), 3.22-3.40 (m, 10 H), 3.42-3.50 (m, 2 H), 3.54 (s, 3 H), 3.55-3.71 (m, 7 H), 3.74-3.86 (m, 7 H), 3.88-3.96 (m, 6 H), 4.02 (s, 1 H), 4.04-4.15 (m, 4 H), 4.18-4.26 (m, 5 H), 4.30-4.44 (m, 6 H), 4.48-4.60 (m, 6 H), 4.61-4.82 (m, 7 H), 4.90-5.01 (m, 2 H), 5.02-5.06 (m, 2 H), 5.16-5.42 (m, 8 H), 5.45-5.62 (m, 3 H), 6.83 (d, 2 H, J = 8.5 Hz), 6.90-7.00 (m, 2 H), 7.04-7.60 (m, 69 H), 7.48-7.63 (m, 5 H), 7.70-7.84 (m, 2 H), 7.82-7.85 (m, 2 H), 7.86-7.92 (m, 3 H), 7.93-8.00 (m, 6 H). ^{13}C-NMR (125MHz, $CDCl_3$), 22.8, 22.8, 47.1, 51.6, 51.7, 51.8, 52.3, 52.4, 52.5, 54.3, 55.3, 55.4, 62.2, 62.2, 62.3, 66.9, 67.1, 67.3, 67.4, 67.5, 68.8, 68.8, 69.2, 70.4, 70.8, 70.9, 71.6, 71.6, 71.7, 73.2, 73.3, 73.6, 73.7, 73.7, 73.8, 73.9, 74.5, 74.7, 74.7, 75.2, 75.3, 75.6, 75.8, 76.0, 76.5, 76.6, 79.5, 81.5, 81.9, 98.4, 98.5, 100.1, 100.2, 100.5, 100.5, 100.6, 100.6, 100.7, 101.1, 101.1, 101.9, 103.7, 103.8, 105.1, 113.8, 120.1, 125.3, 125.4, 125.9, 126.7, 127.2, 127.2, 127.4, 127.5, 128.0, 128.3, 128.3, 128.3, 128.5, 128.6, 129.1, 129.1, 129.2, 129.3, 129.6, 129.7, 129.7, 129.9, 129.9, 130.0, 133.2, 133.6, 133.7, 135.2, 136.5, 136.6, 137.6, 137.6, 137.7, 137.8, 137.9, 138.1, 138.2, 139.1, 139.2, 141.3, 141.3, 143.8, 143.9, 156.0, 159.4, 164.7, 164.9, 165.0, 165.3, 165.5, 165.6, 167.4, 168.4, 168.5, 169.5, 169.8, 169.9. MALDI-MS: $C_{192}H_{189}N_3NaO_{54}$ $[M+Na]^+$ calcd: 3427.5, obsd: 3427.7.

Glycopeptide 52. Compound **4** was dissolved in DMF, to which was added 20 μL piperidine. The resulting mixture was stirred for 20min and concentrated and the residue was purified by preparative TLC (PTLC) to give free amine compound (15.4 mg), which was mixed with compound **51** (2 mg, 0.0170 mmol) and dissolved in 0.6 mL dry DMF, followed by addition of 4 mg HATU, 4 μL. The resulting mixture was stirred under room temperature overnight and diluted with DCM. The solution was washed with a 1M HCl and a saturated aqueous $NaHCO_3$ solution. The combined organic phase was dried over Na_2SO_4 and concentrated, purified by PTLC to afford intermediate glycopeptide (13.5 mg, 73%). MALDI-MS: $C_{181}H_{184}N_4O_{54}$ $[M+Na]^+$ calcd: 3302.4, obsd: 3302.4. This compound was dissolved in DCM-MeOH (1:1, 2 mL), followed by addition of Pd/C (50 mg). The resulting mixture was stirred under H_2 atmosphere overnight. The reaction was diluted with MeOH and filtered. After concentration, the residue was purified by LH-20 column to afford compound **52** (9 mg, quanti.). MALDI-MS: $C_{103}H_{120}N_4O_{53}$ $[M+Na]^+$ calcd: 2308.0, obsd: 2308.2.

Glycopeptide **55**. ESI-MS: $C_{106}H_{131}N_{13}O_{49}S_2$ calcd: 2431.75, $[M-4H]^{4-}$ obsd: 607.65; $[M-3H]^{3-}$ obsd: 810.51; $[M-2H]^{2-}$ obsd: 1219.38;.



Dipeptide 60. Amino acid **S19** (67 mg, 0.386 mmol) and **S20** (100 mg, 0.322 mmol) were dissolved in dry DMF (0.6 mL), followed by addition of HATU (146 mg) and DIPEA (112μL). The resulting mixture was stirred under room temperature overnight and diluted with EtOAc. The solution was washed with 1M HCl and a saturated aqueous $NaHCO_3$ solution. The combined organic phase was dried over Na_2SO_4 and concentrated, purified by silica gel column to afford compound **S21** (145 mg, 97%). ^{1}H-NMR (500 MHz, CD_3OD), 0.82-0.93 (m, 6 H), 1.06-1.16 (m, H), 1.42-1.56 (m, 1 H), 1.76-1.82 (m, 1 H), 2.00 (s, 3 H), 3.02-3.12 (m, 2 H), 4.29 (t, 1 H, J = 7.5 Hz), 4.58-4.62 (m, 2 H), 4.84 (q, 1 H, J = 8.0 Hz), 5.03 (s, 2 H), 5.20-5.35 (m, 2 H), 5.82-5.92 (m, 1 H), 6.17 (d, 1 H, J = 9.0 Hz), 6.38 (d, 1 H, J = 7.5 Hz), 6.87 (d, 2 H, J = 8.5 Hz), 7.04 (d, 1 H, J = 8.5 Hz), 7.30-7.45 (m, 5 H). ^{13}C-NMR (125MHz, CD_3OD), 11.3, 15.2, 23.2, 25.0, 37.0, 37.4, 53.2, 57.5, 66.1, 69.9, 115.0, 119.1, 127.4, 127.7, 127.9, 128.6, 130.3, 131.3, 136.9, 158.0, 169.8, 169.8, 170.8. ESI-MS: $C_{24}H_{30}N_2O_5$ $[M+H]^+$ calcd: 467.25, obsd: 467.25. Dipeptide **S15** (100 mg, 0.2141 mmol) was dissolved in DCM (10 mL), followed by addition of $Pd(PPh_3)_4$ (2.5 mg) and morpholine (24μL). The resulting mixture was stirred under room temperature for 1hr and diluted with DCM. The solution was washed with 1M citric acid and a saturated aqueous NaCl solution. The combined organic phase was dried over Na_2SO_4 and concentrated, purified by silica gel column to afford compound **60** (68 mg, 74%). ^{1}H-NMR (500 MHz, CD_3OD), 0.82-0.90 (m, 9 H), 1.06-1.16 (m, 2 H,), 1.22-1.45 (m, 3 H), 1.78 (brs, 1 H), 1.97 (s, 3 H), 2.93 (m, 1 H), 3.15 (m, 1H), 4.12 (d, 1 H, J = 8.0 Hz), 4.47 (brs, 1 H), 5.03 (s, 2 H), 6.86 (d, 2 H, J = 8.0 Hz), 7.12 (d, 2 H, J = 8.0 Hz), 7.29 (d, 1 H, J = 7.0 Hz), 7.36 (d, 2 H, J = 7.0 Hz), 7.41 (d, 2 H, J = 8.0 Hz). ^{13}C-NMR (125MHz, CD_3OD), 10.7, 14.8, 22.2, 24.4, 35.8, 35.9, 55.4, 59.1, 69.8, 114.4, 127.1, 127.7, 128.3, 130.0, 130.2, 136.8, 137.7, 157.2, 162.0, 164.1, 178.2. ESI-MS: $C_{24}H_{31}N_2O_5$ $[M+H]^+$ calcd: 427.22, obsd: 427.22.



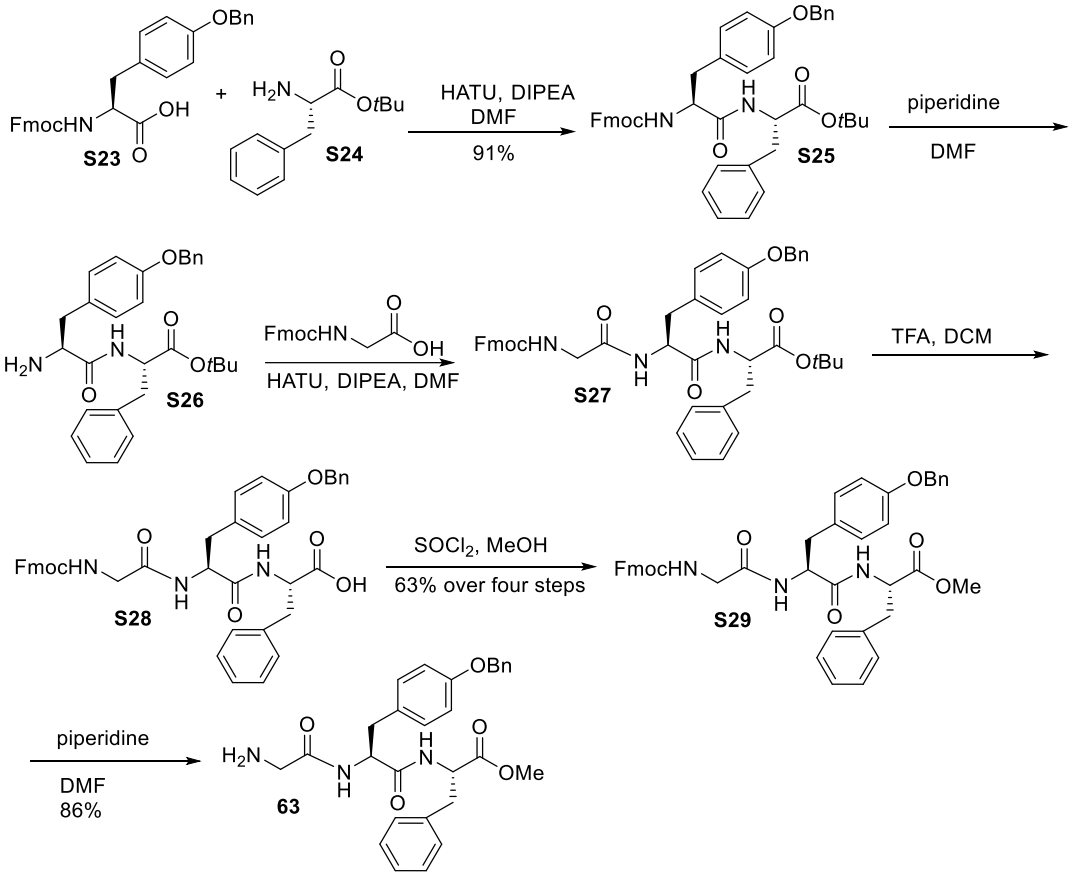
Glycopeptide 61. Compound **3**[3] (9 mg, 0.0018 mmol) was dissolved in THF/Ac_2O/HOAc (3:2:1, 1.5 mL), followed by addition of Zn (100 mg), $CuSO_4$ (saturated solution, 10 μL). The resulting mixture was stirred under room temperature overnight. After filtration, the mixture was diluted with DCM and washed with sat. $NaHCO_3$. The combined organic phase was dried over Na_2SO_4 and purified by silica gel column to afford the intermediate compound (7 mg, 72%). This compound (7 mg, 0.002 mmol) was dissolved in DCM/MeOH (1:1, 2 mL) followed by addition of HOAc (0.2 mL) and NH_2NH_2-H_2O (0.05 mL). The resulting mixture was stirred under room temperature overnight. The reaction was quenched by acetone and extracted by saturated $NaHCO_3$ solution. The organic layer was dried over Na_2SO_4 and purified by prep TLC to afford compound **S22** (6 mg, 90%). Compound **S22** (6.0 mg, 0.00185 mmol) was dissolved in dry DMF (0.5 mL), followed by addition of SO_3-NEt_3 (5 mg). The resulting mixture was stirred under 50 °C overnight. After cooling back to room temperature, it was diluted with DCM-MeOH and LH-Column purification afforded compound **59** (6.0 mg, 95%). ESI-MS: $C_{180}H_{179}N_3O_{60}S_2^{2-}$ $[M]^{2-}$ calcd: 1703.2, obsd: 1703.0. This compound (6.0 mg, 0.00176 mmol) was dissolved in 0.4 mL DMF, followed by addition of 20 μL piperidine. The resulting mixture was stirred under room temperature for 20 min and the product was purified by prep TLC to afford 5 mg free amine compound (ESI-MS: $C_{165}H_{169}N_3O58S_2^{2-}$ $[M\text{-}2H]^{2-}$ calcd: 1593.1, obsd: 1593.1). Dipeptide **60** (1 mg, 0.011 mmol) and the free amine compound (5 mg, 0.00157 mmol) were dissolved in dry DMF (0.6 mL), to which were added HATU (2.2 mg) and collidine (1 μL). The resulting mixture was stirred under room temperature 3hrs and the solution was purified by LH-20 and silica gel column to afford compound **61** (5.0 mg, 89%). ^{1}H-NMR (500 MHz, $CDCl_3$), 0.70-0.78 (s, 3 H), 1.12 (s, 3 H), 1.29 (s, 3 H), 1.30 (s, 3 H), 1.90 (s, 3 H), 2.60-2.75 (m, 14 H), 2.90-3.08 (m, 7 H), 3.10-3.22 (m, 10 H), 3.28 (s, 3 H), 3.34 (s, 3 H), 3.44 (s, 3 H), 3.48-3.72 (m, 20 H), 3.75-4.30 (m, 37 H), 4.35-4.82 (m, 30 H), 4.84-5.10 (m, 14 H), 5.15-5.40 (m, 7 H), 5.57 (d, 1 H, J = 4.5 Hz), 6.65-6.75 (m, 6 H), 6.80-6.90 (m, 3 H), 6.92-

7.44 (m, 87 H), 7.48-7.66 (m, 4 H), 7.72-7.96 (m, 14 H). ESI-MS: $C_{189}H_{197}N_5O_{62}S_2^{2-}$ $[M]^{2-}$ calcd: 1797.4, obsd: 1797.2.

Glycopeptide 57. Compound **61** (5 mg, 0.00157 mmol) was dissolved in DCM/MeOH (1:1, 2 mL) followed by addition of Pd/C (15 mg) and NH_4OAc (1 mg). The resulting mixture was stirred under H_2 atmosphere and the reaction was carefully monitored. When the reaction was complete, the reaction mixture was filtered and purified by LH-20 to afford compound **57** (3.5 mg, 71%). ESI-MS: $C_{182}H_{191}N_5O_{62}S_2^{2-}$ $[M]^{2-}$ calcd: 1751.1, obsd: 1751.6.

***N*-Fluorenylmethyloxycarbonyl-*O*-[methyl-2-*O*-benzoyl-3-*O*-benzyl-4-*O*-*p*-methoxybenzyl-β-D-glucopyranosyluronate-(1→4)-2-*N*-acetyl-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl-2-*O*-benzoyl-3-*O*-benzyl-1-thio-β-D-glucopyranosyluronate-(1→4)-2-*N*-acetyl-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl-2-*O*-benzoyl-3-*O*-benzyl-1-thio-β-D-glucopyranosyluronate-(1→3)-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzoyl-β-D-xylopyranosyl]-L-serine (62)**. Compound **4** (29 mg, 0.008 mmol) was dissolved in DCM/MeOH (1:1, 2 mL), followed by addition of Pd/C (20 mg) and NH_4OAc (20 mg, 0.259 mmol). The resulting mixture was stirred under H_2 atmosphere. The reaction was carefully monitored. After the complete disappearance of starting material, the reaction was diluted with DCM and filtered. After concentration, the residue was purified by silica gel column to afford compound **62** (21 mg, 72%). ^{1}H-NMR (500 MHz, $CDCl_3$), 1.41 (s, 3 H), 1.42 (s, 3 H), 3.17 (s, 3 H), 3.22-3.40 (m, 10 H), 3.42-3.50 (m, 2 H), 3.53 (s, 3 H), 3.55-3.71 (m, 7 H), 3.74-3.96 (m, 10 H), 4.04-4.26 (m, 7 H), 4.28-4.44 (m, 5 H), 4.48-4.60 (m, 5 H), 4.61-4.75 (m, 4 H), 4.75-4.84 (m, 1 H), 4.88-5.06 (m, 4 H), 5.16-5.42 (m, 7 H), 6.83 (d, 2 H, J = 8.5 Hz), 6.90-7.00 (m, 2 H), 7.04-7.60 (m, 64 H), 7.48-7.63 (m, 2 H), 7.70-7.78 (m, 1 H), 7.80-7.96 (m, 7 H), ^{13}C-NMR (125 MHz, $CDCl_3$), 22.7, 22.8, 51.7, 51.8, 52.3, 52.4, 52.4, 55.3, 66.9, 67.1, 67.3, 67.4, 67.5, 68.8, 68.8, 70.3, 71.2, 71.6, 71.7, 73.2, 73.5, 73.6, 73.7, 73.8, 73.8, 73.9, 74.4, 74.6, 74.7, 75.1, 75.3, 75.6, 75.8, 76.1, 76.5, 76.6, 79.4, 81.5, 81.9, 98.4, 98.5, 100.1, 100.2, 100.4, 100.5, 100.6, 100.6, 100.7, 101.1, 101.1, 101.9, 103.7, 103.8, 105.8, 113.8, 120.0, 125.3, 125.4, 125.9, 126.7, 127.3, 127.7, 127.8, 127.8, 127.9, 128.0, 128.1, 128.2, 128.2, 128.5, 128.6, 128.7, 128.8, 129.0, 129.2, 129.6, 129.7, 129.8, 133.2, 133.2, 133.5, 133.7, 136.4, 136.5, 137.6, 137.6, 137.7, 137.8, 137.9, 138.0, 138.1, 139.0, 139.1, 141.2, 141.2, 159.4, 164.7, 164.9, 165.0, 165.3, 165.5, 167.4, 168.3, 168.4, 169.8, 169.8, 169.9. MALDI-MS: $C_{185}H_{183}N_3O_{54}$ $[M+Na]^+$

calcd: 3337.4, obsd: 3337.5.

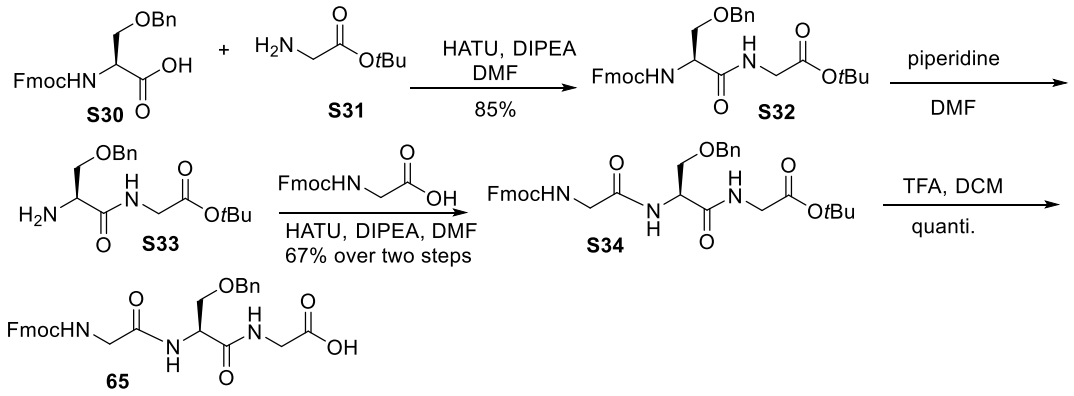


Amino acid **S23** (202 mg, 0.41 mmol) and **S24** (70 mg, 0.27 mmol) were dissolved in dry DMF (3.0 mL), which was followed by addition of HATU (156mg, 0.41mmol) and DIPEA (123μL, 0.71mmol). The resulting mixture was stirred under room temperature overnight and diluted with EtOAc. The solution was washed with 1M HCl and a saturated aqueous $NaHCO_3$ solution. The combined organic phase was dried over Na_2SO_4 and concentrated, purified by silica gel column to afford compound **S25** (172 mg, 91%). ^{1}H-NMR (500 MHz, CD_3OD), 1.41 (s, 9 H), 3.00-3.14 (m, 4 H), 4.22 (t, 1 H, J = 7.0 Hz), 4.31 (brt, 1 H), 4.42-4.52 (m, 2 H), 4.66-4.74 (m, 1 H), 4.98-5.08 (m, 2 H), 5.39 (m, 1 H), 6.38 (d, 1 H, J = 6.0 Hz), 6.90 (d, 2 H, J = 8.0 Hz), 7.00-7.18 (m, 4 H), 7.18-7.26 (m, 3 H), 7.30-7.48 (m, 9 H), 7.52-7.64 (m, 2 H), 7.79 (d, 2 H, J = 7.0 Hz). ^{13}C-NMR (125 MHz, CD_3OD), 27.8, 37.5, 38.0, 47.1, 53.6, 56.0, 67.0, 69.9, 82.4, 114.9, 114.9, 119.9, 120.0, 125.0, 125.1, 126.9, 127.0, 127.4, 127.4, 127.4, 127.7, 127.9, 128.3, 128.5, 128.5, 129.4, 130.3, 130.4, 135.8, 136.9, 141.2, 143.7, 157.9, 169.9, 170.1 HRESI-MS: $C_{44}H_{45}N_2O_6$ $[M+H]^+$ calcd: 697.33, obsd: 697.33. Compound **S25** was dissolved in DMF

(1.0 mL), followed by addition of piperidine (0.2 mL). The resulting mixture was stirred under room temperature for 20 min and the product was purified by silica gel column to afford **S26**. FmocGly-OH 1.2eq and **S26** 1.0eq were dissolved in dry DMF, followed by addition of 1.2eq HATU, 2eq DIPEA. The resulting mixture was stirred under room temperature overnight and diluted with EtOAc. The solution was washed with 1M HCl and a saturated aqueous $NaHCO_3$ solution. The combined organic phase was dried over Na_2SO_4 and concentrated, purified by silica gel column to afford **S27**. Compound **S27** was dissolved in DCM:TFA (1 : 1) mixture. The resulting mixture was stirred under room temperature for 4 hrs and concentrated to give compound **S28**. HRESI-MS: $C_{42}H_{40}N_3O_7$ $[M+H]^+$ calcd: 698.29, obsd: 698.29. Compound **S28** was dissolved in MeOH, followed by addition of 2eq $SOCl_2$ under 0°C. The resulting mixture was stirred under room temperature for 5 hrs and diluted with EtOAc. The solution was washed with a saturated aqueous $NaHCO_3$ solution. The combined organic phase was dried over Na_2SO_4 and concentrated, purified by silica gel column to afford compound **S29** (14.2 mg, 4 steps 63%). ^{1}H-NMR (500 MHz, CD_3OD), 1.56 (s, 2 H), 2.90-3.00 (m, 3 H), 3.05 (dd, 1 H, *J* = 14.0, 6.0Hz), 3.65 (s, 3 H), 3.76-3.80 (m, 2 H), 4.20 (t, 1 H, *J* = 7.0 Hz), 4.40 (d, 2 H, *J* = 7.0 Hz), 4.55 (q, 1 H, *J* = 7.0 Hz), 4.73 (q, 1 H, *J* = 7.0 Hz), 4.95 (s, 2 H), 5.27 (s, 1 H), 6.18 (s, 1 H), 6.43 (d, 1 H, *J* = 8.0 Hz), 6.81 (d, 2 H, *J* = 8.5 Hz), 6.96 (d, 1 H, *J* = 6.5 Hz), 7.04 (d, 2 H, *J* = 8.5 Hz), 7.14-7.22 (m, 3 H), 7.26-7.40 (m, 9 H), 7.58 (d, 2 H, *J* = 8.5 Hz), 7.74 (d, 2 H, *J* = 7.5 Hz). ^{13}C-NMR (125 MHz, CD_3OD), 37.2, 37.8, 44.4, 47.0, 52.3, 53.3, 54.3, 67.2, 69.9, 115.0, 120.0, 125.0, 127.1, 127.4, 127.8, 127.9, 128.3, 128.5, 129.2, 130.3, 135.6, 136.8, 141.3, 143.7, 156.5, 157.9, 168.7, 170.1, 171.3. HRESI-MS: $C_{43}H_{42}N_3O_7$ $[M+H]^+$ calcd: 712.30, obsd: 712.30. Compound **S29** was dissolved in DMF (1.0 mL), which was followed by addition of piperidine (0.2 mL). The resulting mixture was stirred under room temperature for 20 min and the product was purified by silica gel column to afford **63**. HRESI-MS: $C_{28}H_{32}N_3O_5$ $[M+H]^+$ calcd: 490.23, obsd: 490.23.

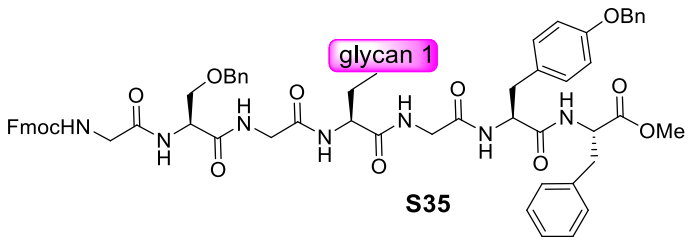
Glycopeptide 64. Compound **63** (3 mg, 0.00604 mmol) and octasaccharide **62** (9.5 mg, 0.00302 mmol) were dissolved in dry DMF (0.6 mL), followed by addition of HATU (2.3 mg) and collidine (1.2 μL). The resulting mixture was stirred under room temperature overnight and diluted with DCM. The solution was washed with a 1M HCl and a saturated aqueous $NaHCO_3$ solution. The combined organic phase was dried over Na_2SO_4 and concentrated, purified by PTLC to afford compound **64** (9.1 mg, 84%). ^{1}H-NMR (500 MHz, $CDCl_3$), 1.41 (s, 3 H), 1.42 (s, 3 H), 1.94-2.20 (m, 4 H), 2.78-3.00 (m, 5 H), 3.02-3.08 (m, 1 H), 3.11 (s, 1 H), 3.17 (s, 3 H), 3.18-3.25 (m, 2 H), 3.26-3.40 (m, 9 H), 3.42-3.50 (m, 4 H), 3.53 (s, 3 H), 3.54-3.80 (m, 20 H), 3.82-4.20 (m, 17 H), 4.22-4.34 (m, 5

H), 4.34-4.42 (m, 4 H), 4.48-4.58 (m, 6 H), 4.60-4.82 (m, 9 H), 4.84-4.96 (m, 4 H), 5.02-5.06 (m, 2 H), 5.16-5.42 (m, 10 H), 5.63 (t, 1 H, J = 9.0 Hz), 5.70 (s, 1 H), 6.75-6.88 (m, 5 H), 6.94-7.13 (m, 20 H), 7.15-7.46 (m, 56 H), 7.47-7.56 (m, 6 H), 7.70-7.75 (m, 2 H), 7.80-7.85 (m, 2 H), 7.84-7.95 (m, 10 H), 8.00 (s, 1 H). MALDI-MS: $C_{213}H_{212}N_6O_{58}$ $[M+Na]^+$ calcd: 3808.0, obsd: 3808.0.



Tripeptide 65. Amino acid **S30** (27 mg, 0.065 mmol) and **S31** (10 mg, 0.0599 mmol) were dissolved in 0.6 mL dry DMF, followed by addition of HATU (30mg, 0.077mmol), DIPEA (25μL, 0.1797 mmol). The resulting mixture was stirred under room temperature overnight and diluted with EtOAc. The solution was washed with 1M HCl and a saturated aqueous $NaHCO_3$ solution. The combined organic phase was dried over Na_2SO_4 and concentrated, purified by silica gel column to afford compound **S32** (27 mg, 85%). ^{1}H-NMR (500 MHz, CD_3OD), 1.43 (s, 9 H), 3.55 (t, 1 H, J = 7.5 Hz), 3.85-4.00 (m, 5 H), 4.19 (t, 1 H, J = 7.0 Hz), 4.35-4.39 (m, 2 H), 4.51 (d, 1 H, J = 12.0 Hz), 4.56 (d, 1 H, J = 12.0 Hz), 4.61 (s, 1 H), 5.49 (s, 1 H), 6.63 (d, 1 H, J = 6.5 Hz), 7.02 (s, 1 H), 7.24-7.32 (m, 6 H), 7.37 (d, 2 H, J = 7.0 Hz), 7.56 (d, 2 H, J = 7.5 Hz), 7.74 (d, 2 H, J = 7.5 Hz). ^{13}C-NMR (125 MHz, CD_3OD), 28.0, 42.2, 44.5, 47.0, 52.4, 67.3, 69.0, 73.5, 82.3, 120.0, 125.1, 127.1, 127.7, 127.8, 127.9, 128.0, 128.5, 137.2, 141.3, 143.7, 143.7, 156.6, 168.4, 169.0, 169.6. HRESI-MS: $C_{31}H_{35}N_2O_6$ $[M+H]^+$ calcd: 531.25, obsd: 531.25. Compound **S32** (70 mg) was dissolved in DMF (0.5 mL), which was followed by addition of piperidine (0.1 mL). The resulting mixture was stirred under room temperature for 20 min and the product was purified by prep TLC to afford the amine compound **S33**. FmocGly-OH (13 mg, 0.011 mmol) and **S33** (41 mg, 0.00385 mmol) were dissolved in anhydrous DMF (0.6 mL), to which HATU (65 mg) and DIPEA (36 μL) were added. The resulting mixture was stirred under room temperature overnight and diluted with EtOAc. The solution was washed with 1M HCl and a saturated aqueous $NaHCO_3$ solution. The combined organic phase was dried over Na_2SO_4 and concentrated, purified by silica gel

column to afford compound **S34** (52 mg, 67%). ^{1}H-NMR (500 MHz, CD_3OD), 1.43 (s, 9 H), 3.55 (t, 1 H, J = 7.5 Hz), 3.85-4.00 (m, 5 H), 4.19 (t, 1 H, J = 7.0 Hz), 4.35-4.39 (m, 2 H), 4.51 (d, 1 H, J = 12.0 Hz), 4.56 (d, 1 H, J = 12.0 Hz), 4.61 (s, 1 H), 5.49 (s, 1 H), 6.63 (d, 1 H, J = 6.5 Hz), 7.02 (s, 1 H), 7.24-7.32 (m, 6 H), 7.37 (d, 2 H, J = 7.0 Hz), 7.56 (d, 2 H, J = 7.5 Hz), 7.74 (d, 2 H, J = 7.5 Hz). ^{13}C-NMR (125 MHz, CD_3OD), 28.0, 42.2, 44.5, 47.0, 52.4, 67.3, 69.0, 73.5, 82.3, 120.0, 125.1, 127.1, 127.7, 127.8, 127.9, 128.0, 128.5, 137.2, 141.3, 143.7, 143.7, 156.6, 168.4, 169.0, 169.6. ESI-MS: $C_{33}H_{38}N_3O_7$ $[M+H]^+$ calcd: 588.27, obsd: 588.27. Compound **S34** was dissolved in DCM : TFA (1 : 1) mixture. The resulting mixture was stirred under room temperature for 4 hrs and concentrated to afford compound **65**. ^{1}H-NMR (500 MHz, CD_3OD), 3.71 (dd, 1 H, J = 10.0, 4.5 Hz), 3.76-3.90 (m, 4 H), 3.97 (d, 1 H, J = 13.0 Hz), 4.18 (t, 1 H, J = 7.0 Hz), 4.34 (d, 1 H, J = 7.0 Hz), 4.50 (s, 1 H), 4.66 (t, 1 H, J = 5.0 Hz), 7.24-7.32 (m, 6 H), 7.36 (d, 2 H, J = 7.0 Hz), 7.60 (d, 2 H, J = 7.5 Hz), 7.74 (d, 2 H, J = 7.5 Hz). ^{13}C-NMR (125 MHz, CD_3OD), 29.6, 41.4, 44.3, 47.0, 52.3, 53.4, 67.3, 69.0, 73.4, 119.9, 125.0, 127.1, 127.7, 127.8, 127.9, 128.4, 137.2, 141.2, 143.7. ESI-MS: $C_{29}H_{30}N_3O_7$ $[M+H]^+$ calcd: 532.21, obsd: 532.21.

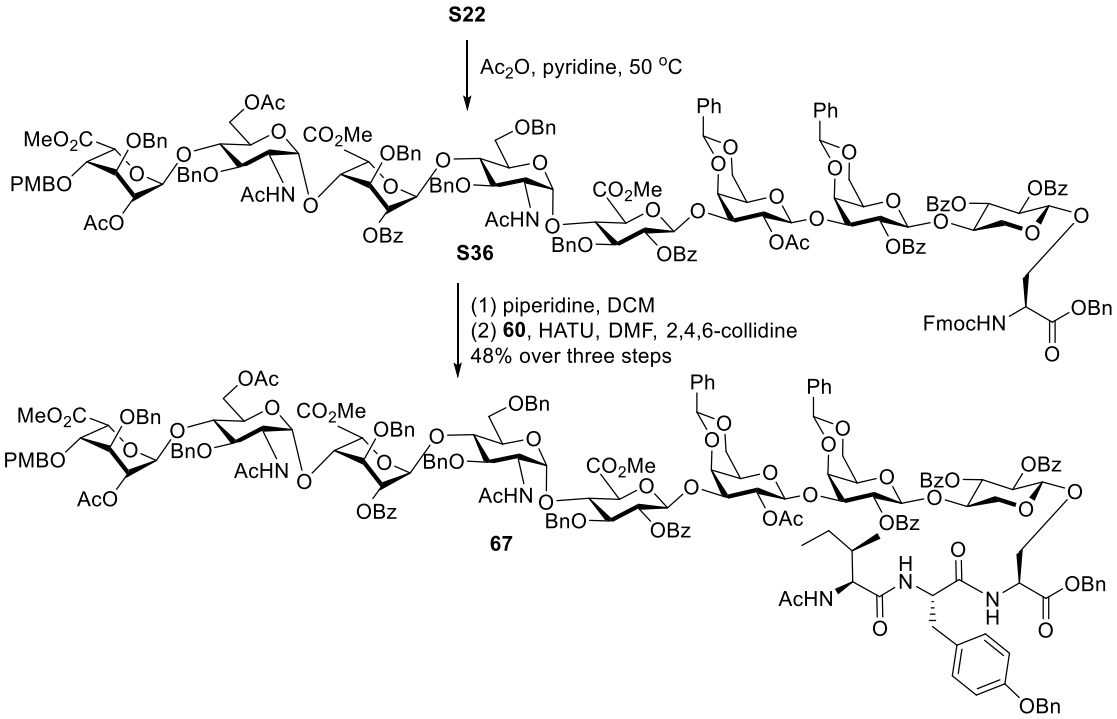


S35

Glycopeptide 58. Compound **64** (9.1mg) was dissolved in DMF (0.4 mL), which was followed by addition of piperidine (16 μL). The resulting mixture was stirred under room temperature for 20 min and concentrated. The product was purified by prep TLC. MALDI-MS: $C_{198}H_{202}N_6O_{56}$ $[M+Na]^+$ calcd: 3584.7, obsd: 3586.6. Tripeptide **65** (2 mg, 0.00332 mmol) and the Fmoc removed glycopeptide (7.4 mg, 0.001955 mmol) were dissolved in dry DMF (0.4 mL), followed by addition of HATU (1.2 mg) and collidine (0.7 μL). The resulting mixture was stirred under room temperature overnight and diluted with DCM. The solution was washed with 1 N HCl and a saturated aqueous $NaHCO_3$ solution. The combined organic phase was dried over Na_2SO_4 and concentrated, purified by silica gel column to afford compound **S35** (7.2 mg, 73%, 2 steps). ^{1}H-NMR (500 MHz, $CDCl_3$), 1.42 (s, 3 H), 1.44 (s, 3 H), 2.60-3.20 (m, 3 H), 3.20-3.70 (m, 17 H), 3.75-3.80 (m, 4 H), 3.80-4.20 (m, 9 H), 4.22-4.50 (m, 5 H), 4.50-4.82 (m, 8 H), 4.90-5.10 (m, 3 H), 5.19-5.50 (m, 6 H), 6.75-6.86 (m, 6 H), 6.95 (d, 2 H, J=7.0 Hz), 6.98-7.56 (m, 20 H), 7.15-7.46 (m, 77 H), 7.75 (d, 1 H, J=7.0 Hz), 7.84-7.95 (m, 14 H). MALDI-MS:

$C_{227}H_{229}N_9O_{62}$ $[M+Na]^+$ calcd: 4099.0, obsd: 4098.7. Compound **S35** (2 mg) was dissolved in DMF (0.3 mL), which was followed by addition of piperidine (30 μL). The resulting mixture was stirred under room temperature for 20 min and concentrated. The product was purified by PTLC to afford compound **58**. MALDI-MS: $C_{198}H_{202}N_6O_{56}$ $[M+Na]^+$ calcd: 3585.7, obsd: 3586.6.

Glycopeptide 66. Compound **57** (3 mg) and compound **58** (3 mg) were dissolved in DMF (0.6 mL) followed by addition of HATU (2 mg) and 2,4,6-collidine (0.5 μL). The resulting mixture was stirred under room temperature for 5 hrs and the solution was purified by LH-20 column and silica gel column to afford compound **66**. MALDI-MS: $C_{394}H_{408}N_{14}O_{123}S_2^{2-}$ $[M+2H+Na]^+$ calcd: 7366.4, obsd: 7370.1. $[M-SO_3+2H+Na]^+$ calcd: 7287.7, obsd: 7291.2, $[M-2SO_3+2H+Na]^+$ calcd: 7208.2, obsd: 7211.6.



***N*-Fluorenylmethyloxycarbonyl-*O*-[methyl-2-*O*-acetyl-3-*O*-benzyl-4-*O*-*p*-methoxybenzyl-β-D-iodopyranosyluronate-(1→4)-2-*N*-acetyl-6-*O*-acetyl-3-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-methyl-2-*O*-benzoyl-3-*O*-benzyl-β-D-glucopyranosyluronate-(1→4)-2-*N*-acetyl-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-β-D-glucopyranosyluronate-(1→3)-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzoyl-β-D-xylopyranosyl]-L-serine benzyl ester** (**67**). Compound **S22** (10.0 mg, 0.00308 mmol) was dissolved in 2 mL pyridine,

followed by addition of 1 mL Ac_2O. The resulting mixture was stirred under 50 °C overnight. After cooling back to room temperature, it was diluted with DCM, washed with 10% HCl, sat. $NaHCO_3$. The combined organic phase was dried over Na_2SO_4. Column purification afforded compound **S36** (9.0 mg, 88%). ^{1}H-NMR (500 MHz, $CDCl_3$), 1.28 (s, 3 H), 1.29 (s, 3 H), 1.41 (s, 3 H), 2.00 (s, 3 H), 2.03 (s, 3 H), 3.11 (s, 1 H), 3.18-3.30 (m, 3 H), 3.31-3.44 (m, 7 H), 3.46-3.60 (m, 7 H), 3.64-3.78 (m, 12 H), 3.80 (d, 1 H, *J* = 9.5 Hz), 3.84-4.00 (m, 5 H), 4.01-4.24 (m, 14 H), 4.25-4.50 (m, 10 H), 4.51-4.58 (m, 3 H), 4.59-4.70 (m, 8 H), 4.75-4.86 (m, 3 H), 4.90-4.95 (m, 2 H), 4.96-5.08 (m, 2 H), 5.09-5.24 (m, 5 H), 5.26-5.40 (d, 4 H), 5.42-5.64 (m, 4 H), 6.76-6.82 (m, 2 H), 7.02-7.48 (m, 67 H), 7.48-7.66 (m, 5 H), 7.72-7.80 (m, 3 H), 7.84-8.02 (m, 10 H). ^{13}C-NMR (125 MHz, $CDCl_3$), 20.1, 20.8, 22.4, 22.7, 46.4, 47.1, 51.8, 51.8, 51.9, 52.5, 54.2, 55.3, 66.6, 66.7, 67.1, 67.2, 67.3, 69.1, 70.1, 70.2, 70.4, 70.8, 71.4, 71.7, 72.3, 72.5, 73.3, 73.5, 73.4, 73.7, 73.8, 73.9, 74.3, 74.8, 74.9, 75.1, 75.8, 76.3, 77.9, 78.0, 81.5, 98.1, 99.0, 100.5, 100.6, 102.3, 104.2, 113.7, 120.0, 125.2, 126.1, 126.4, 127.1, 127.2, 127.6, 127.7, 127.8, 127.8, 127.9, 128.1, 128.1, 128.2, 128.3, 128.4, 128.5, 128.6, 129.0, 129.1, 129.6, 129.7, 129.9, 133.1, 133.5, 133.8, 135.1, 136.2, 137.0, 137.5, 137.7, 137.9, 138.4, 141.2, 143.7, 143.7, 143.8, 155.9, 159.4, 164.5, 164.7, 165.1, 165.6, 169.0, 169.5, 169.8, 170.0, 170.1, 170.7, 168.8, 169.5. MALDI-MS: $C_{184}H_{185}N_3O_{56}$ $[M+Na]^+$ calcd: 3358.4, obsd: 3358.9. Compound **S36** (9.0 mg, 0.0027mmol) was dissolved in DMF (0.4 mL), followed by addition of piperidine (20 μL). The resulting mixture was stirred under room temperature for 20 min and the product was purified by prep TLC to afford 7 mg free compound (MALDI-MS: $C_{169}H_{175}N_3O_{54}$ $[M+Na]^+$ calcd: 3135.2, obsd: 3135.1. Peptide **60** (13 mg, 0.011 mmol) and the free amine compound (7 mg, 0.00225 mmol) were dissolved in dry DMF (0.6 mL), to which were added HATU and collidine. The resulting mixture was stirred under room temperature 3hrs and the solution was purified by LH-20 and silica gel column to afford compound **67** (6.0 mg, 60%). ^{1}H-NMR (500 MHz, $CDCl_3$), 1.25 (s, 3 H), 1.30 (s, 3 H), 1.32 (s, 3 H), 1.96(s, 3 H), 1.98 (s, 3 H), 2.60-2.75 (m, 14 H), 2.90-3.08 (m, 7 H), 3.10-3.22 (m, 10 H), 3.25 (s, 3 H), 3.34 (s, 3 H), 3.44 (s, 3 H), 3.48-3.72 (m, 20 H), 3.75-4.30 (m, 37 H), 4.35-4.82 (m, 30 H), 4.84-5.10 (m, 14 H), 5.15-5.40 (m, 7 H), 5.57 (d, 1 H, *J* = 4.5 Hz), 6.65-6.75 (m, 5 H), 6.76-6.90 (m, 3 H), 6.92-7.44 (m, 87 H), 7.48-7.66 (m, 4 H), 7.72-7.96 (m, 14 H). MALDI-MS: $C_{193}H_{203}N_5O_{58}$ $[M+Na]^+$ calcd: 3545.7, obsd: 3545.4.

Glycopeptide 68. Compound **67** (6.0 mg, 0.0017 mmol) was dissolved in DCM/MeOH (1:1, 2 mL) in the presence of acetic acid (pH 5.5), which was followed by addition of $Pd(OH)_2/C$ (20 mg). The resulting mixture was stirred under H_2 atmosphere. After the

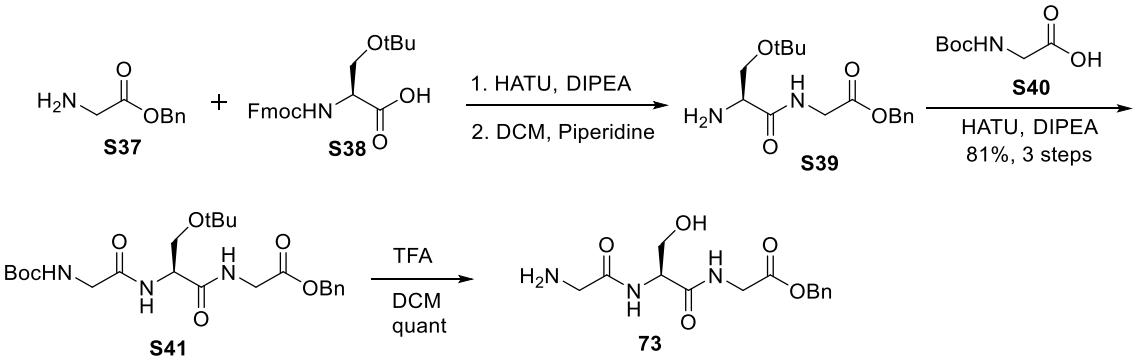
complete disappearance of starting material, the reaction was diluted with MeOH and filtered. After concentration, the residue was purified by LH-20 column to afford compound **68** (4.0 mg, quanti.). MALDI-MS: $C_{115}H_{139}N_5O_{57}$ $[M+Na]^+$ calcd: 2526.3, obsd: 2525.9.

Glycopeptide 69. Compound **61** (5 mg, 0.009 mmol) was dissolved in DCM/MeOH (1:1, 2 mL), followed by addition of $Pd(OH)_2/C$ (25 mg) and HOAc was added to maintain pH around 5.5. The resulting mixture was stirred under H_2 atmosphere. The reaction was carefully monitored by MALDI-MS. The reaction mixture was diluted with MeOH-toluene and filtered. After concentration, the residue was purified by LH-20 column to afford compound **69** (2.9 mg, 86%). ^{1}H-NMR (500 MHz, CD_3OD), 1.77 (s, 3 H), 1.79 (s, 3 H), 1.94 (s, 3 H), 2.35-2.35 (m, 1 H), 2.70 (s, 1 H), 2.91-2.97 (m, 1 H), 3.10-3.15 (m, 4 H), 3.45-4.25 (m, 46 H), 4.31-4.38 (m, 3 H), 4.49 (d, 1 H, *J* = 8.0 Hz), 4.62-4.72 (m, 3 H), 5.04-5.10 (m, 3 H), 5.19-5.36 (m, 6 H), 5.42-5.47 (m, 1 H), 6.61-6.65 (m, 2 H), 6.85 (d, 1 H, J = 8.0 Hz), 6.92 (d, 1 H, J = 7.5 Hz), 7.33-7.53 (m, 12 H), 7.60-7.68 (m, 3 H), 7.93-7.99 (m, 8 H), 8.06-8.07 (m, 2 H) ESI-MS: $C_{111}H_{133}N_5O_{61}S_2^{2-}$ $[M]^{2-}$ calcd: 1287.9, obsd: 1288.1.

Glycopeptide 70. Compound **58** (5.1 mg, 0.00177 mmol) was dissolved in DCM/MeOH (1:1, 2 mL) in the presence of acetic acid (pH 5.5), followed by addition of $Pd(OH)_2/C$ (20 mg). The resulting mixture was stirred under H_2 atmosphere. After the complete disappearance of starting material, the reaction was diluted with MeOH and filtered. After concentration, the residue was purified by LH-20 column to afford compound **70** (2.9 mg, 80%). MALDI-MS: $C_{127}H_{149}N_9O_{59}$ $[M+Na]^+$ calcd: 2768.56, obsd: 2769.3.

Glycopeptide 2. Glycopeptide **68** (2.5 mg, 0.0010 mmol) and glycopeptide **70** (4.0 mg, 0.0015 mmol) were dissolved in dry DMF (0.3 mL), followed by addition of HATU (1.1 mg) and collidine (0.5 μL). The resulting mixture was stirred under room temperature for 3 hrs. The solution was purified by LH-20 column without extraction to afford compound **71** (2.6 mg, 46%). MALDI-MS: $C_{241}H_{284}N_{14}O_{115}$ $[M+Na]^+$ calcd: 5259.7, obsd: 5259.4. Glycopeptide **71** (2.5 mg, 0.000475 mmol) were dissolved in 0.7 mL THF- H_2O (5 : 1), to which 0.25M LiOH was added to maintain pH around 9.5 under 0°C. The mixture was stirred under 0 °C for 1.5 hr and it was neutralized by 1 M HOAc solution to adjust pH around 7. The solution was loaded onto LH-20 column directly to remove the Li salt. Glycopeptide containing fractions were combined and concentrated to afford the methyl ester cleaved compound. This compound was dissolved in MeOH (2 mL), to which was

added hydrazine hydrate (0.2 mL). The resulting mixture was stirred under room temperature overnight and it was neutralized by acetone under 0 °C for 30min. The solution was concentrated and loaded onto G-15 column to afford compound **2** (1.4 mg, 72%). ESI-MS: $C_{152}H_{215}N_{14}O_{101}^{7-}$ $[M+4H]^{3-}$ calcd: 1285.4, obsd: 1284.4, $[M+3H]^{4-}$ calcd: 963.80, obsd: 963.76. ESI-HRMS: $[M+4H]^{3-}$ calcd: 1285.4156, obsd: 1285.4224.



Tripeptide 73. Amino acid **S37** (40 mg, 0.2 mmol) and **S38** (76 mg, 0.2 mmol) were dissolved in 1 mL dry DMF, followed by addition of HATU (76mg, 0.2mmol), DIPEA (87μL, 0.5 mmol). The resulting mixture was stirred under room temperature for 1h and diluted with EtOAc. The solution was washed with 10%M HCl and a saturated aqueous $NaHCO_3$ solution. The combined organic phase was dried over Na_2SO_4 and concentrated. The resulting dipeptide was dissolved in 2.5 ml DCM/Piperidine (4:1) and stirred for 20 min. The solution was washed with water twice and the organic phase was concentrated. The crude product was purified by flash column to yield **S39**. Amino acid **S39** and **S40** (35 mg, 0.2 mmol) were dissolved in 1 mL dry DMF, followed by addition of HATU (76mg, 0.2mmol), DIPEA (70μL, 0.4 mmol). The resulting mixture was stirred under room temperature for 1h and diluted with EtOAc. The solution was washed with 10%M HCl and a saturated aqueous $NaHCO_3$ solution. The combined organic phase was dried over Na_2SO_4 and concentrated. Column purification afforded compound **S41**(75 mg, 81%). ^{1}H-NMR (500 MHz, $CDCl_3$), 1.21 (s, 9 H), 1.45 (s, 9 H), 3.36 (t, 1 H, J = 8.0 Hz), 3.78-3.87 (m, 3 H), 4.09 (d, 2 H, J = 5.0 Hz), 4.49-4.52 (m, 1 H), 5.19 (s, 2 H), 5.19-2.29 (m, 1 H), 6.97 (d, 1 H, J = 7.0), 7.32-7.45 (m, 6 H). Compound **S41** was dissolved in DCM : TFA (1 : 1) mixture. The resulting mixture was stirred under room temperature for 4 hrs and concentrated to afford compound **73** without further purification. ^{1}H-NMR (500 MHz, CD_3OD), 3.77-3.81 (m, 4 H), 4.01-4.02 (m, 2 H), 4.54 (t, 1 H, J = 5.5 Hz), 5.16 (s, 2 H), 7.31-7.36 (m, 5 H). ^{13}C-NMR (125 MHz, CD_3OD): 40.2, 40.7, 55.4, 61.6,

66.6, 127.9 (2 C), 128.2, 135.7, 166.3, 169.7, 171.2. HRMS: $C_{14}H_{20}N_3O_5$ $[M+H]^+$ calcd: 310.1403, obsd: 310.1436.

Glycopeptide 75. Compound **69** (5 mg, 0.002 mmol) and tripeptide 73 (3 mg, 0.01 mmol) were dissolved in dry DMF (0.5 mL), followed by addition of HATU (1 mg) and DIPEA (2.5 μL). The resulting mixture was stirred under room temperature for 1.5 hrs. The solution was purified by LH-20 column to afford compound **74** which was dissolved in DCM/MeOH (1:1, 2 mL), followed by addition of $Pd(OH)_2/C$ (10 mg). The resulting mixture was stirred under H_2 atmosphere for 20 min to afford **75** (4.9 mg, 91%). HRMS: $C_{118}H_{144}N_8O_{65}S_2$ $[M]^{2-}$ calcd: 1388.3830, obsd: 1388.3862. $[M-H]^{3-}$ calcd: 925.2529, obsd: 925.2529.

Glycopeptide 77. Compound **64** (5 mg, 0.0013 mmol) was dissolved in 20% piperidine in DCM (1 ml). The resulting mixture was stirred under room temperature for 20 min and purified by LH-20 column to afford free amine. The free amine was dissolved in DCM/MeOH (1:1, 2 mL), followed by addition of $Pd(OH)_2/C$ (20 mg). The resulting mixture was stirred under H_2 atmosphere for 1 h (pH ~ 6, adjusted by CCl_3COOH). After filtration and concentration, the residue was purified by LH-20 column to afford compound **76** (3 mg, 89%). MALDI-MS: $C_{120}H_{138}N_6O_{55}$ $[M+Na]^+$ calcd: 2565.8, obsd: 2565.6.

Glycopeptide 56. Glycopeptide **75** (1.3 mg, 0.00050 mmol) and glycopeptide **77** (1.8 mg, 0.000700 mmol) were dissolved in dry DMF (0.3 mL), which was followed by addition of HATU (1.1 mg) and DIPEA (1 μL). The resulting mixture was stirred at room temperature for 3 hrs. The solution was loaded onto a LH-20 column to afford compound **56** (1.5 mg, 58%). MALDI-MS: $C_{238}H_{280}N_{14}O_{119}S_2^{2-}$ $[M-SO_3+H+2Na]^+$ calcd: 5268.6, obsd: 5267.2.

Glycopeptide 1. Compound **56** (2.6 mg, 0.5 μmol) were dissolved in THF- H_2O (0.4 mL), to which 0.25 M LiOH was added to maintain pH around 9.0 under 0°C. When MS analysis showed the complete disappearance of the starting material (1 hour at 0°C), the mixture was neutralized by 1 M HOAc solution to adjust pH to around 7. The solution was loaded onto a LH-20 column directly to remove the Li salt. Glycopeptide containing fractions were combined and concentrated. The collected compound was dissolved in MeOH (0.4 mL), followed by addition of hydrazine hydrate (0.1 mL). The resulting mixture was stirred under room temperature overnight and it was neutralized by acetone

under 0°C for 30 min. The solution was concentrated and loaded onto a Sephadex G-15 column to afford compound **1** (1.6 mg, 81%). HRMS: $C_{152}H_{213}N_{14}O_{107}S_2^{9-}$ $[M+3H]^{6-}$ calcd: 668.8564, obsd: 668.8572. $[M+4H]^{5-}$ calcd: 802.8292, obsd: 802.8292. $[M+5H]^{4-}$ calcd: 1003.7885, obsd: 1003.7856. $[M+6H]^{3-}$ calcd: 1338.7206, obsd: 1338.7169.

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[1] K. Bock, C. Pedersen, *J. Chem. Soc., Perkin Trans. 2* **1974**, 293.

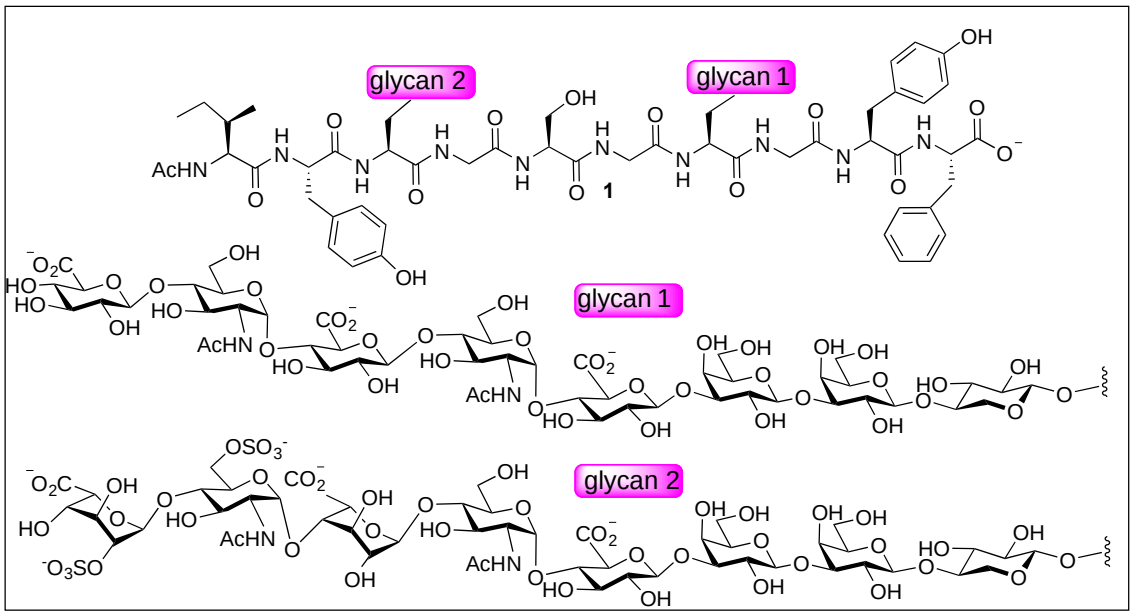
[2] Z. Wang, Y. Xu, B. Yang, G. Tiruchinapally, B. Sun, R. Liu, S. Dulaney, J. Liu, X. Huang, *Chem. Eur. J.* **2010**, *16*, 8365.

[3] B. Yang, K. Yoshida, Z, Yin, H. Dai, H. Kavunja, M. H. El-Dakdouki, S. Sungsuwan, S. B. Dulaney, X. Huang, *Angew. Chem. Int. Ed.* **2012**, 51, 10185.

[4] X. Creary, *Org. Synth.* **1986**, *64*, 207.

[5] G. Tiruchinapally, Z. Yin, M. El-Dakdouki, Z. Wang, X. Huang, *Chem. Eur. J.* **2011**, *17*, 10106.

ESI-MS of **1**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glycan 1
glycan 2
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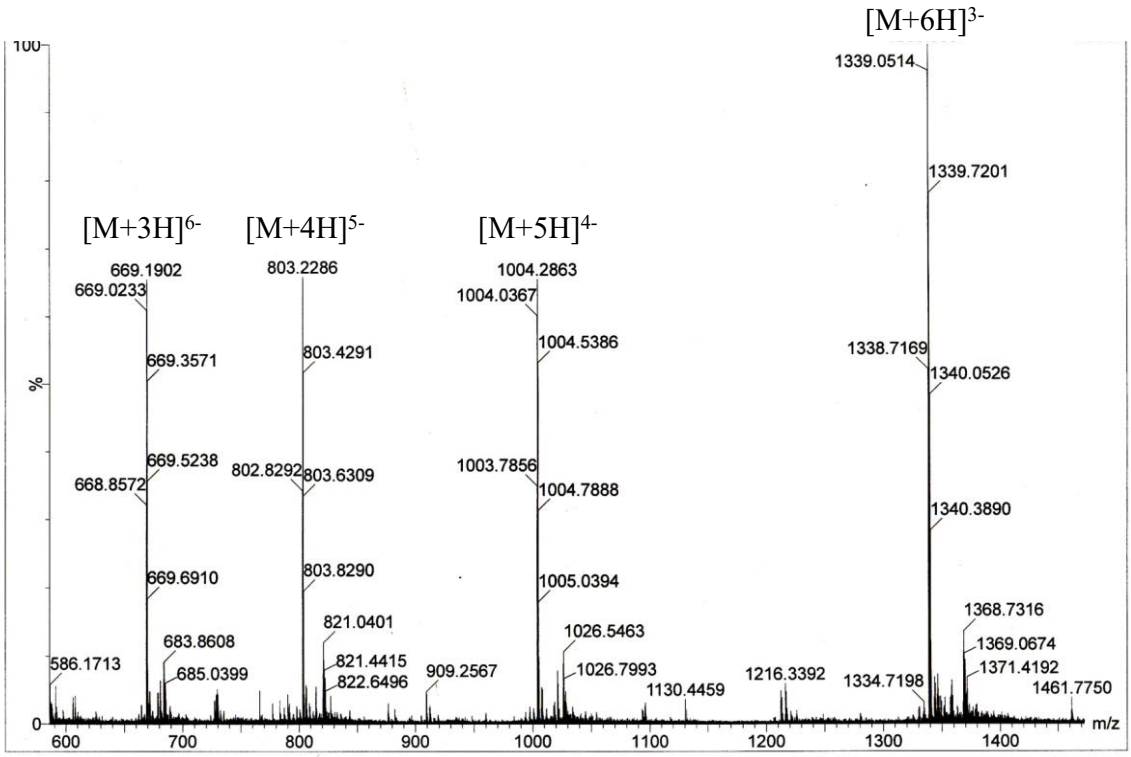
1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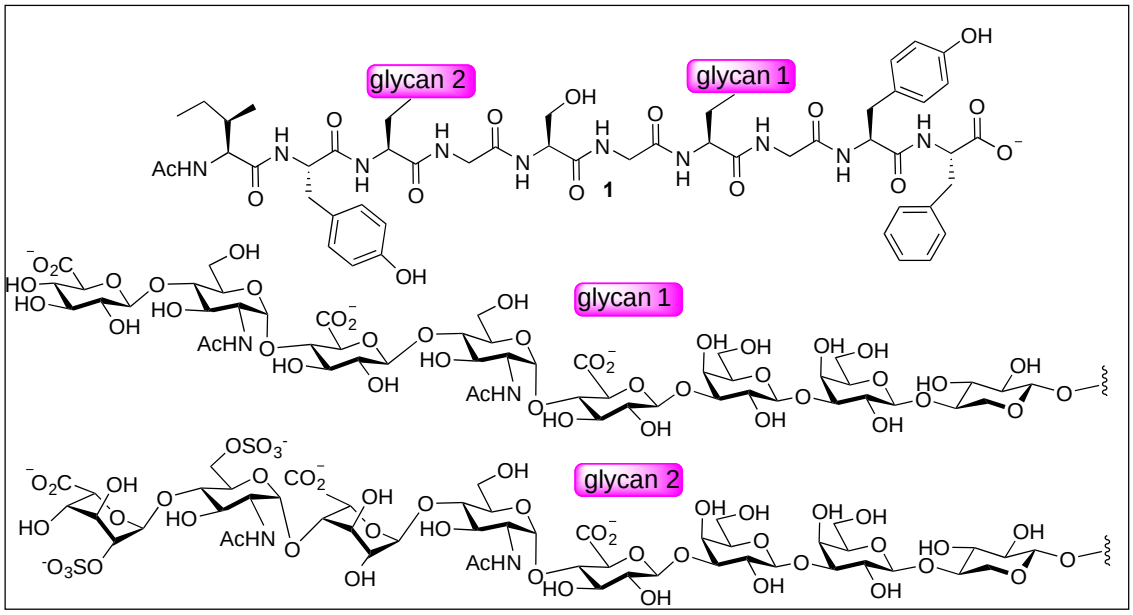
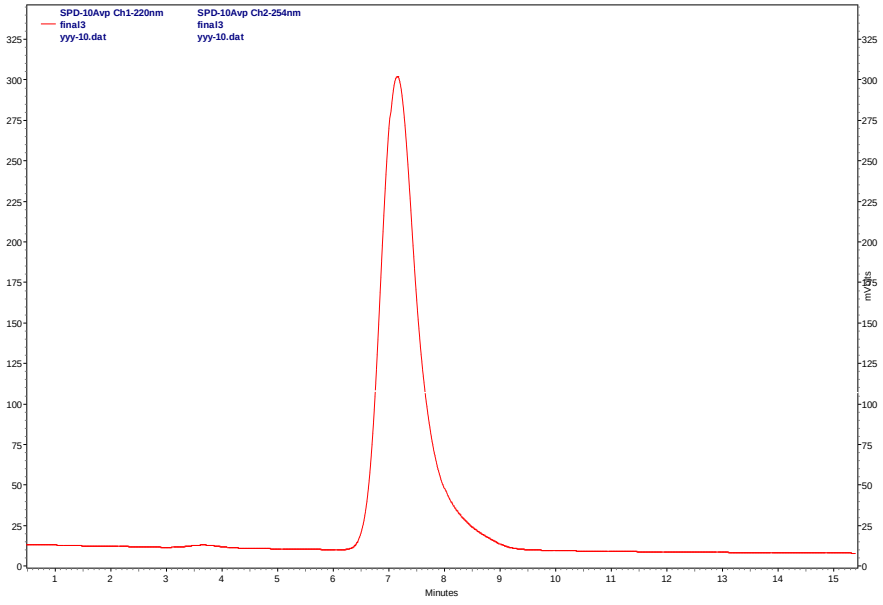
1461.7750
%
m/z
100
0
600
700
800
900
1000
1100
1200
1300
1400

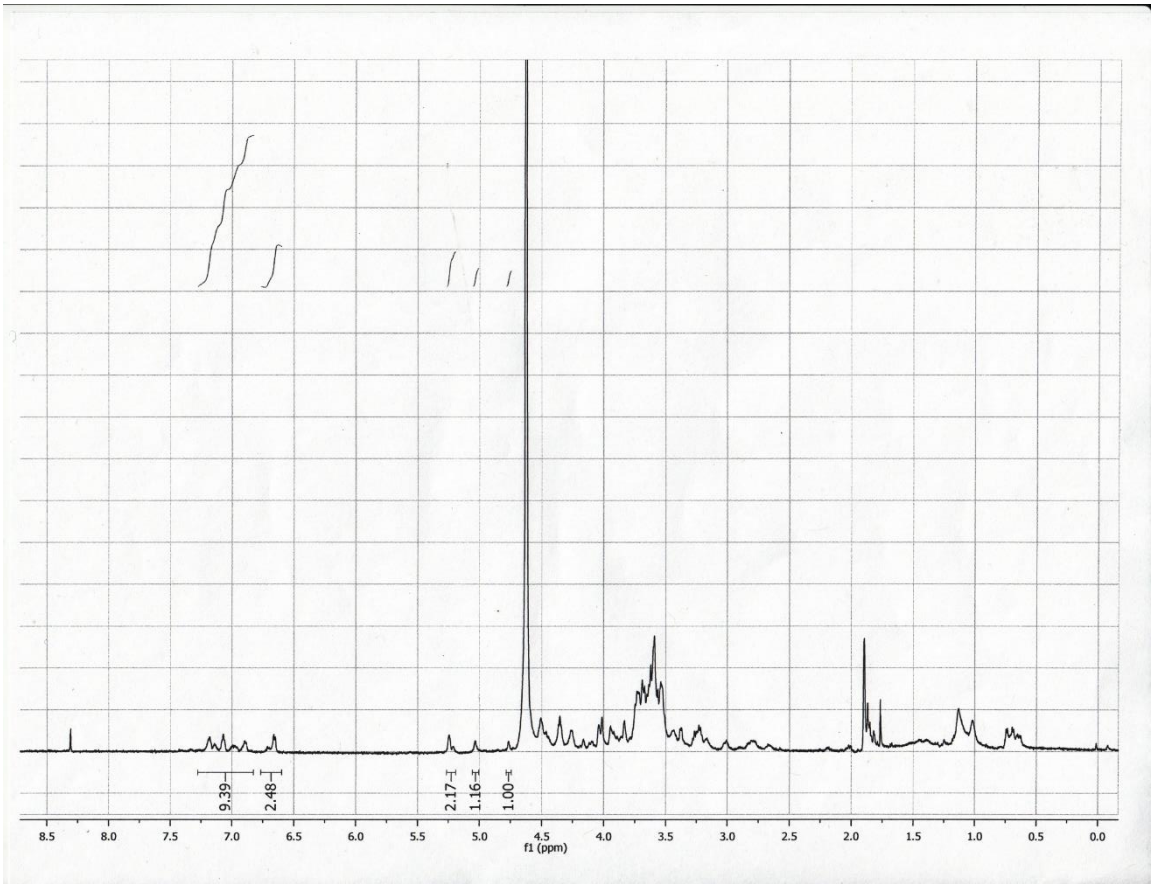
HPLC of **1**

HPLC mobile phase: 30% B in A over 15 min (solvent A: H_2O; solvent B: isopropanol). Flow rate: 1 mL/min. Detection wavelength: 220 nm. HPLC column: SupelCOSIL LC-18, 25 cm X 4.6 mm, 5 μm particle size.

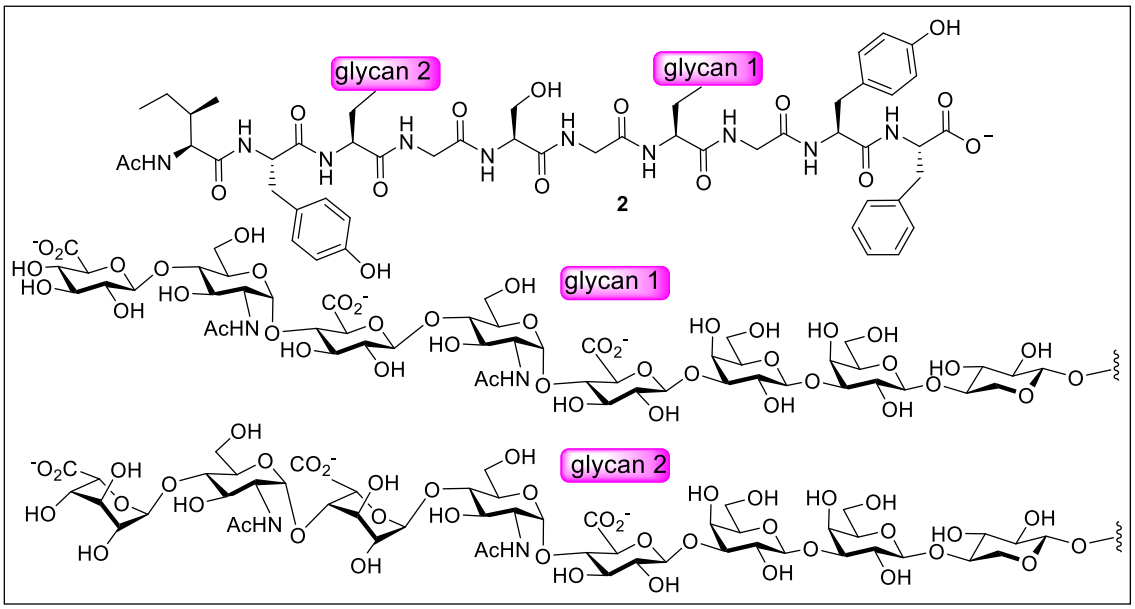




^{1}H-NMR ($CDCl_3$, 600 MHz) of **1**



ESI-MS of **2**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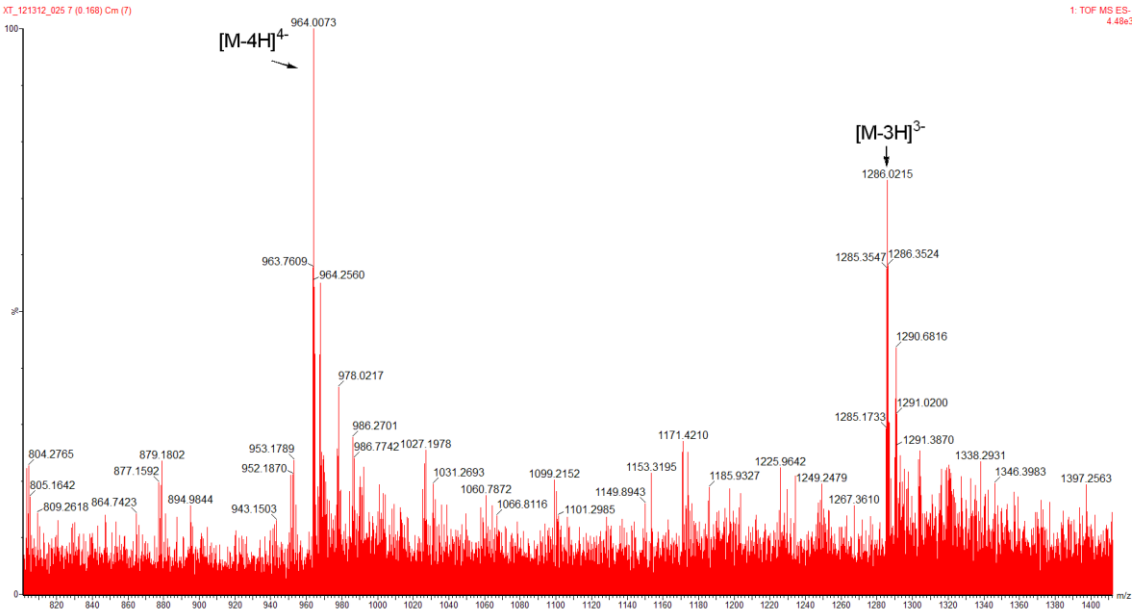
glycan 1
glycan 2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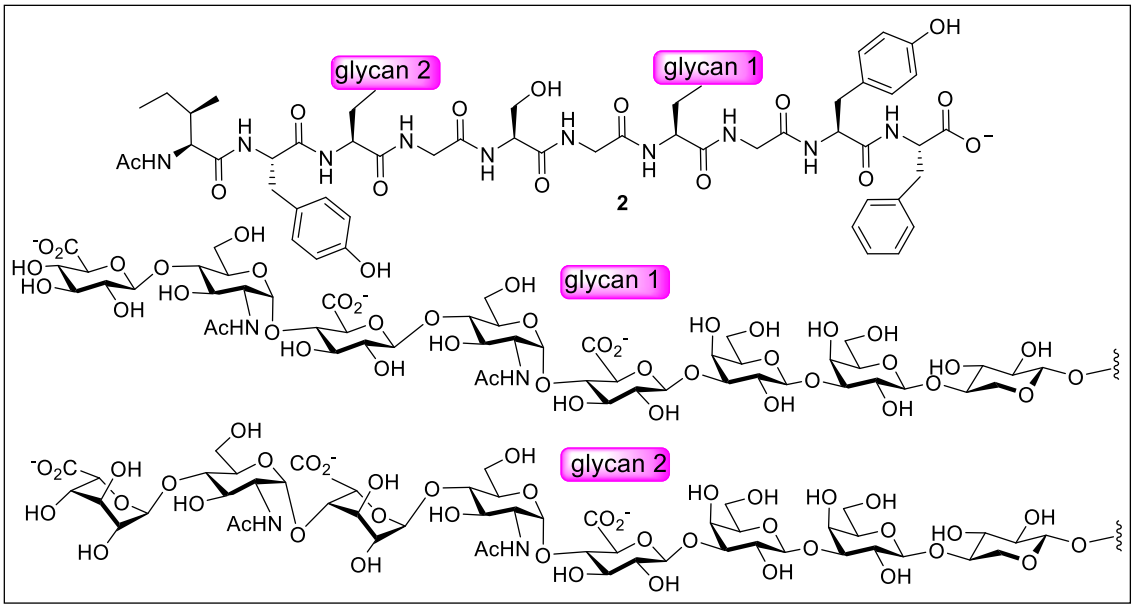
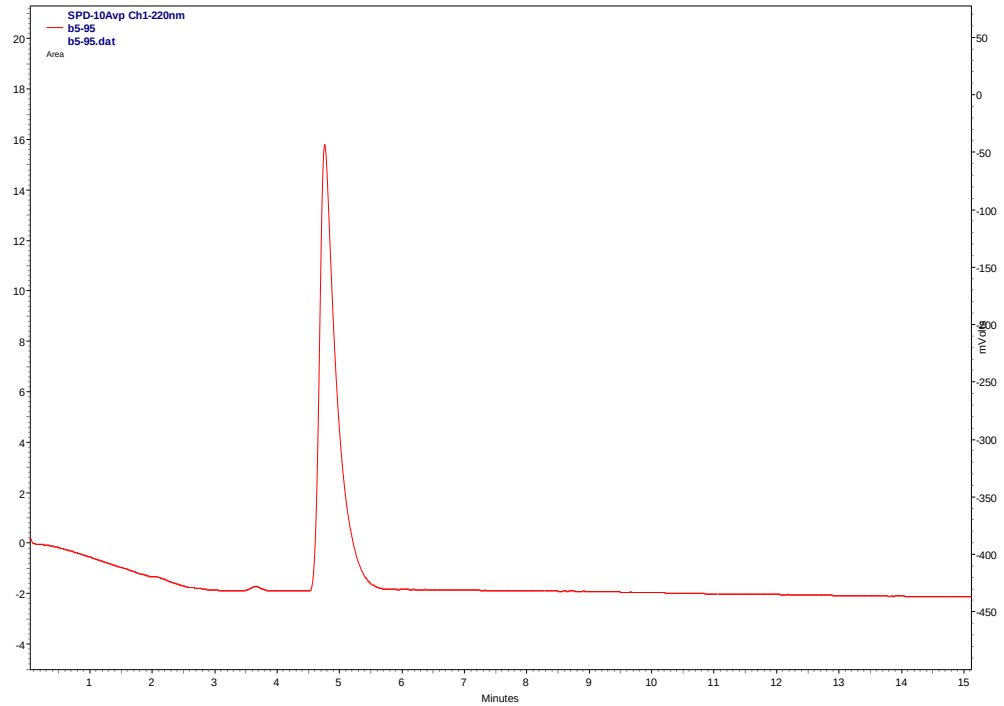
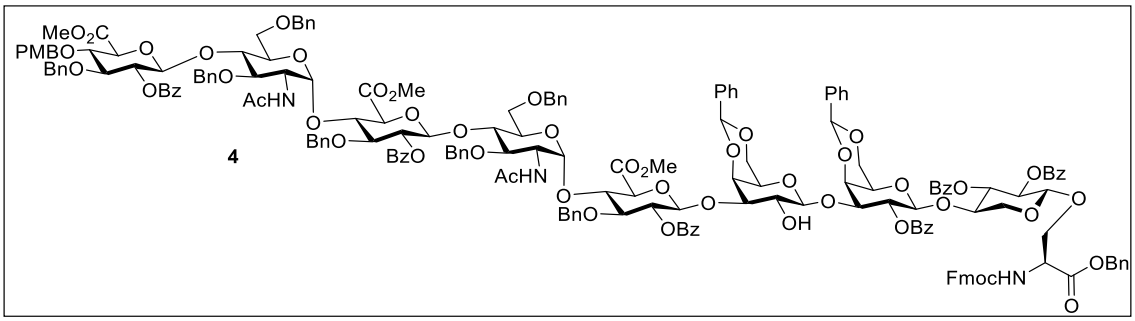
HPLC of **2**

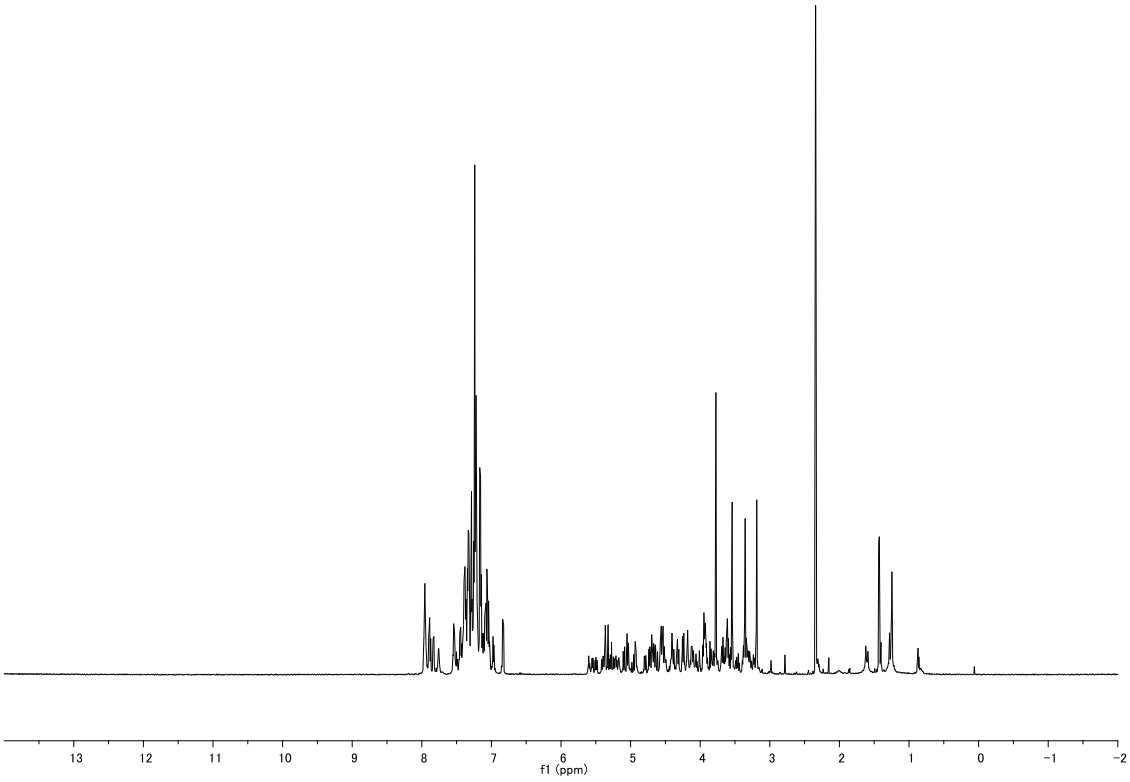
HPLC mobile phase: 40% B in A over 30 min (solvent A: H_2O; solvent B: isopropanol). Flow rate: 1 mL/min. Detection wavelength: 220 nm. HPLC column: SupelCOSIL LC-18, 25 cm X 4.6 mm, 5 μm particle size.



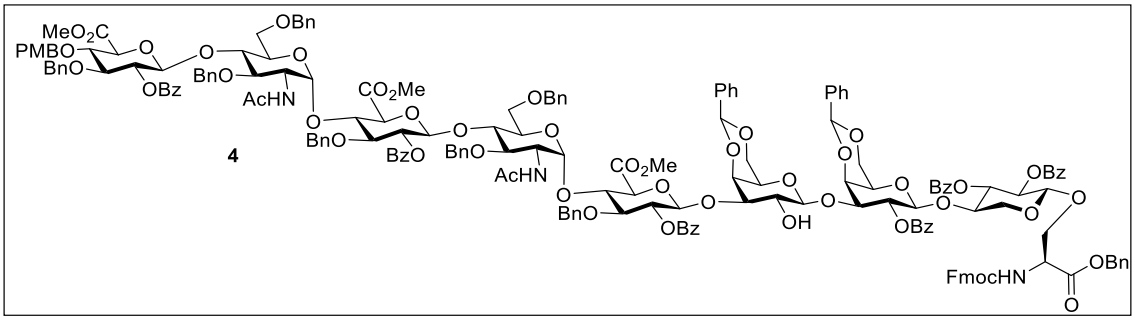


^{1}H-NMR (500 MHz) of **4**





^{13}C-NMR (125 MHz) of **4**



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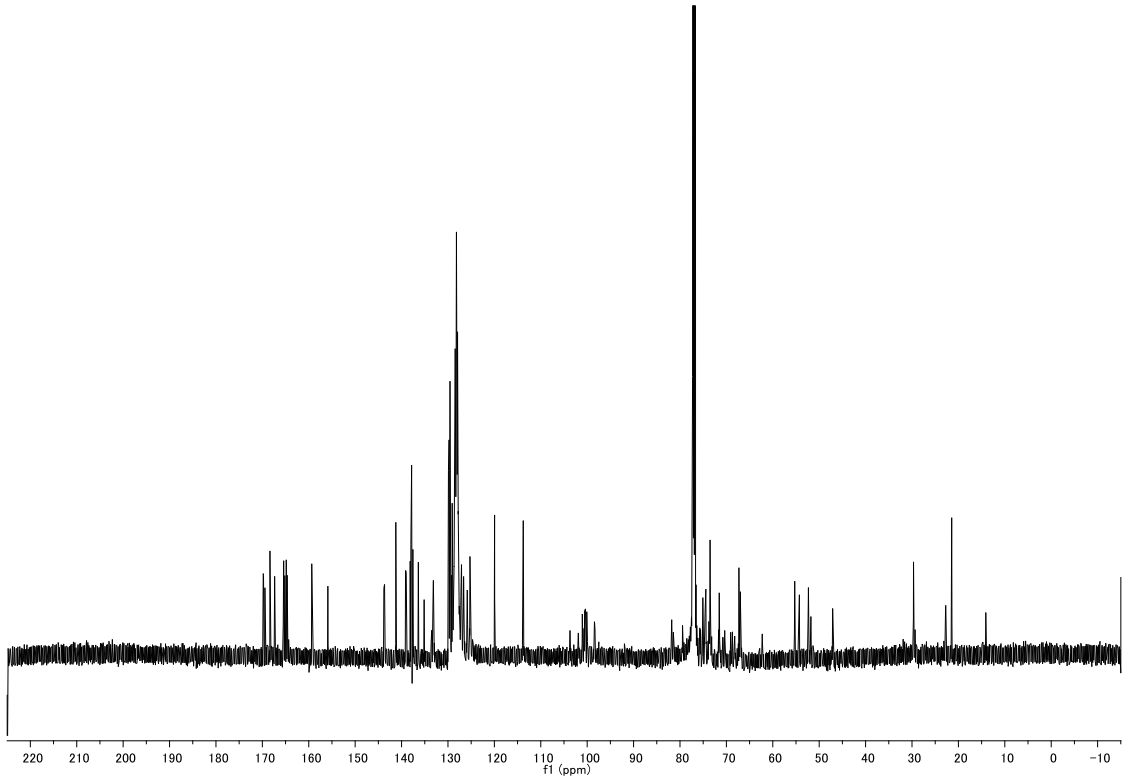
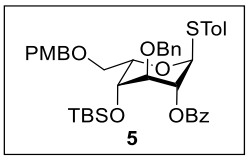
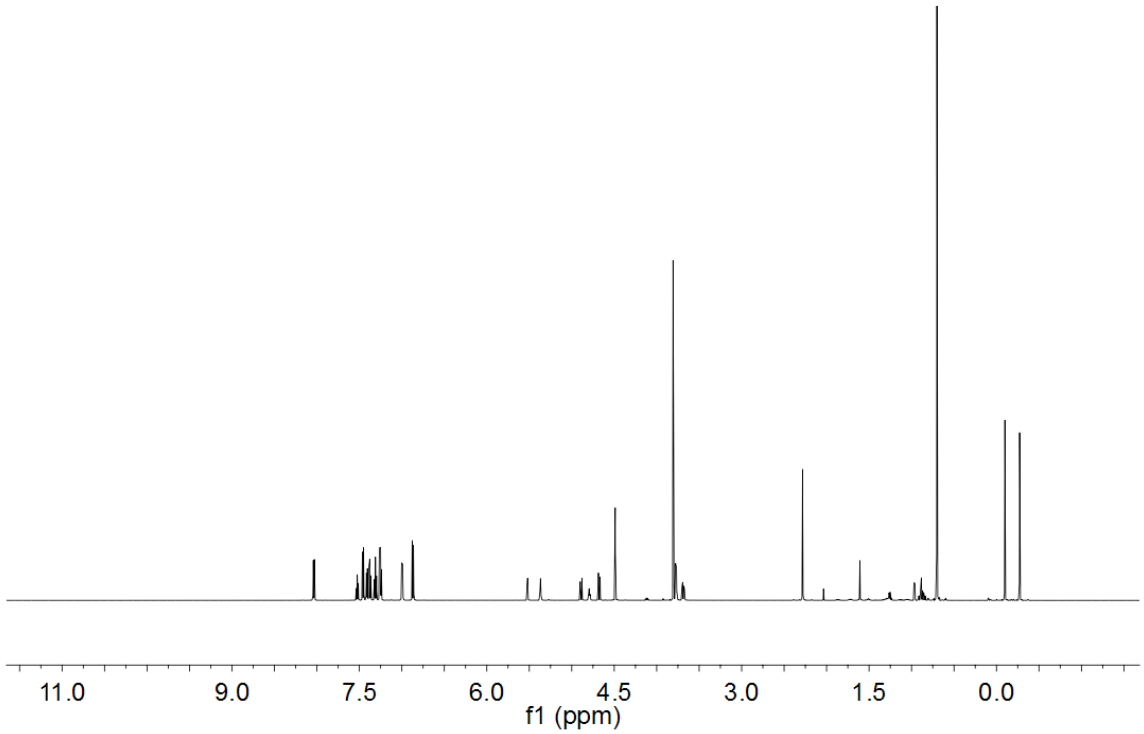


^{1}H-NMR ($CDCl_3$, 600 MHz) of **5**





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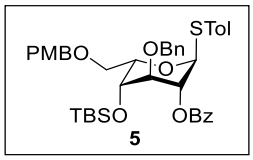

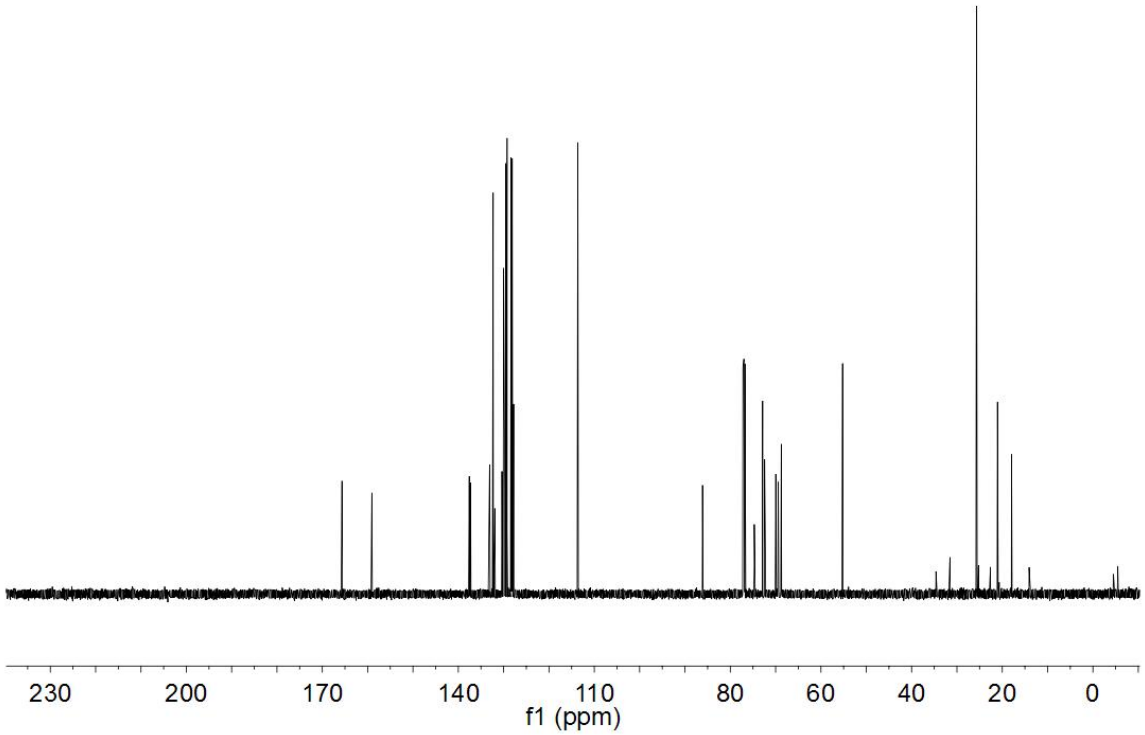

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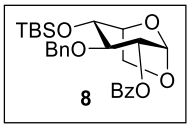
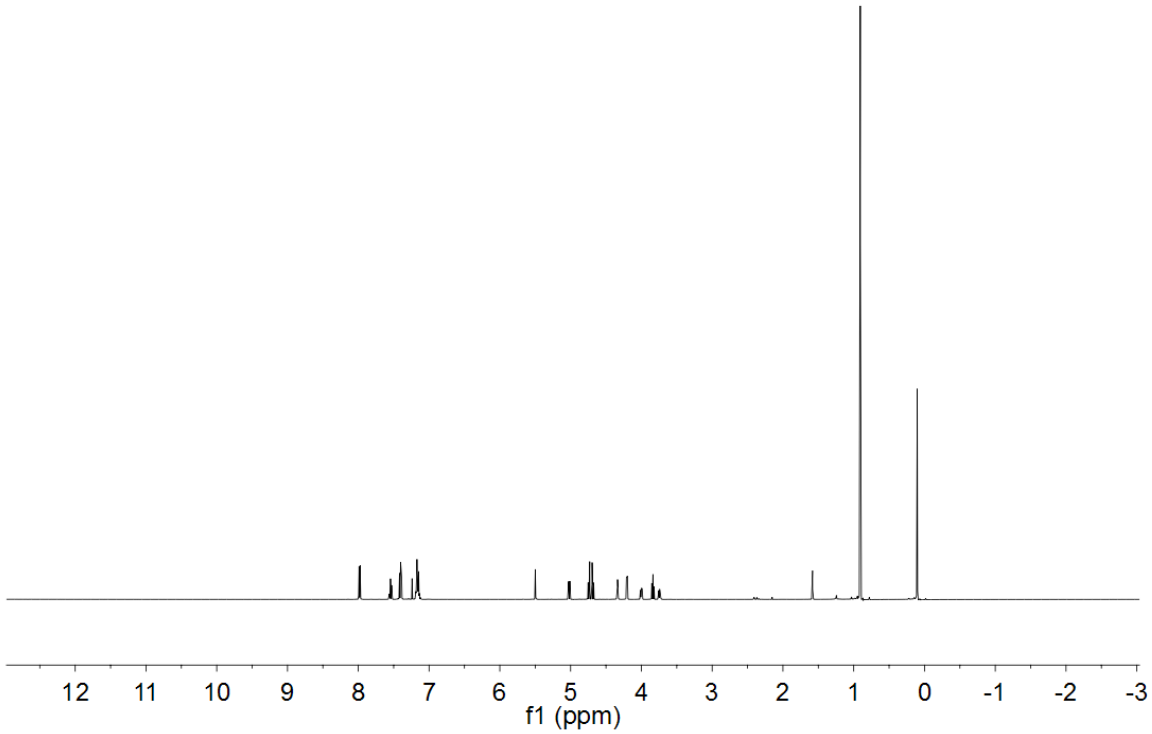
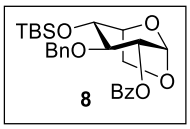
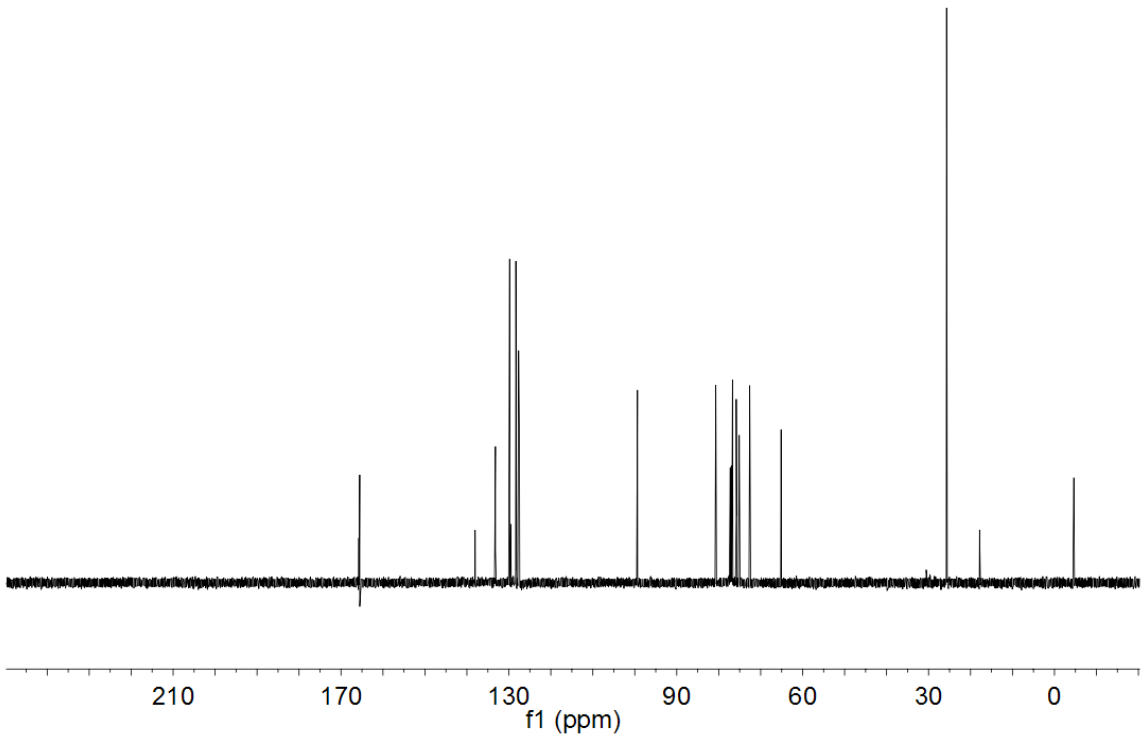


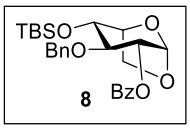


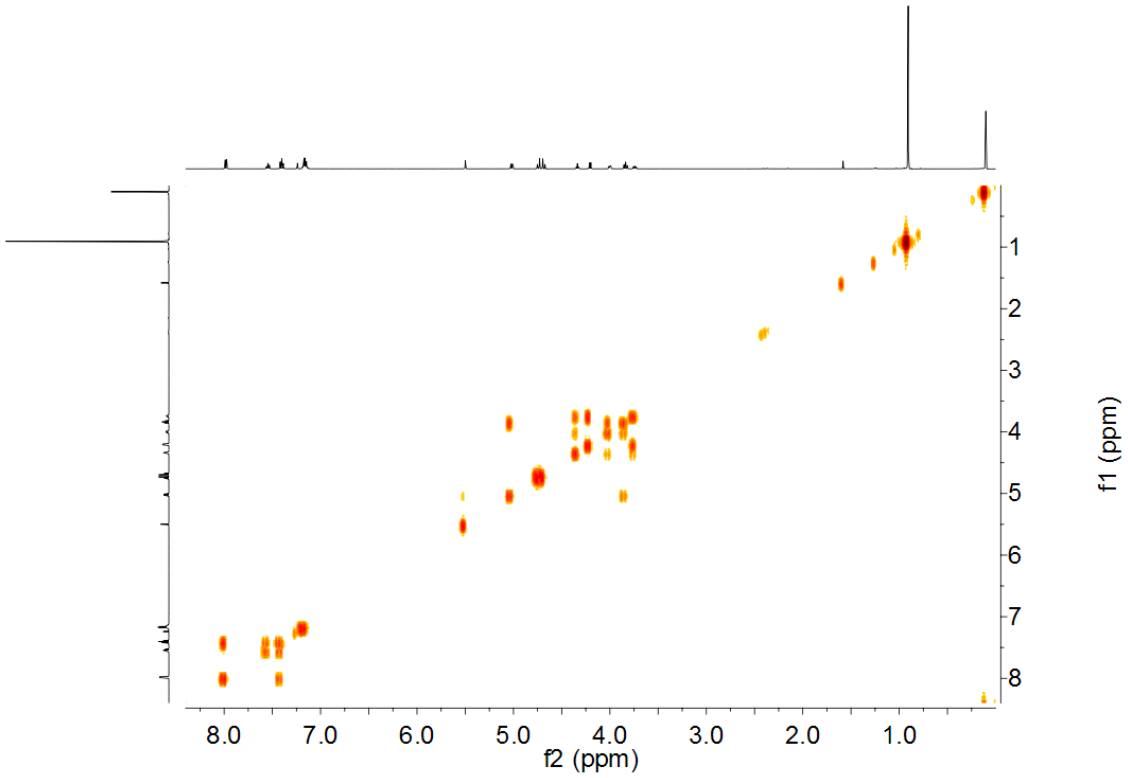
^{13}C-NMR ($CDCl_3$, 125 MHz) of **8**





gCOSY ($CDCl_3$, 500 MHz) of **8**





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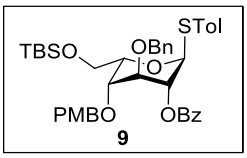

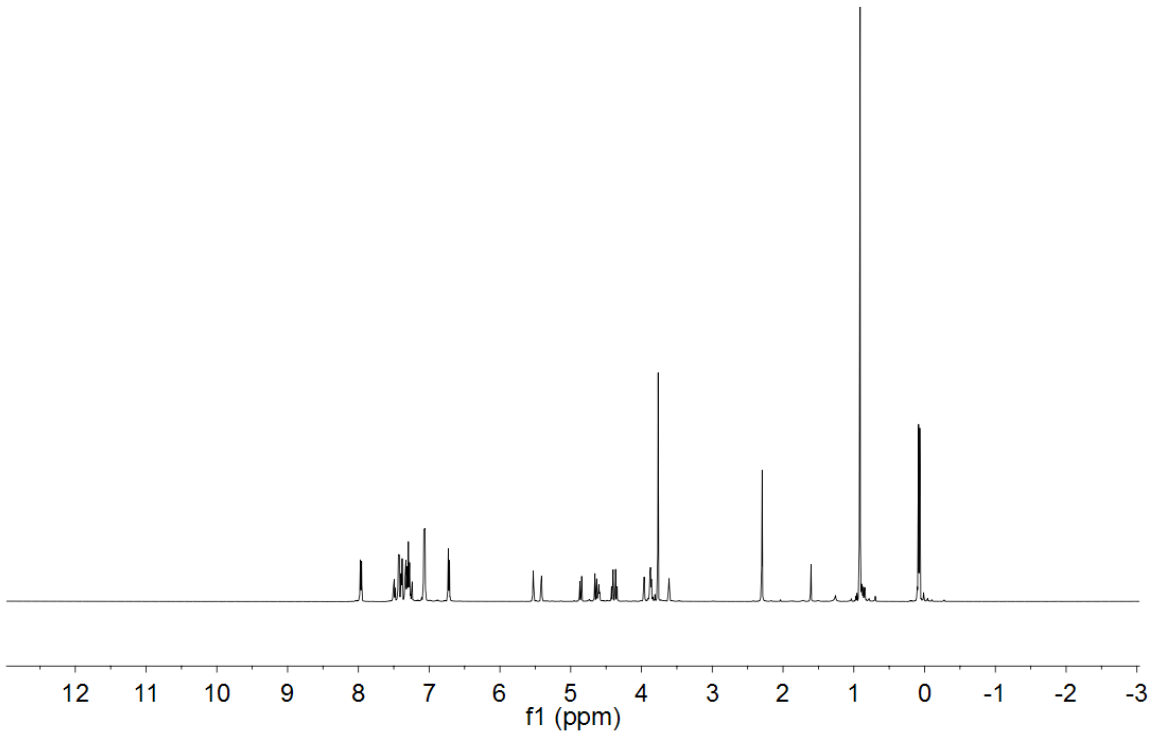

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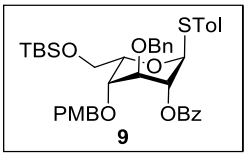

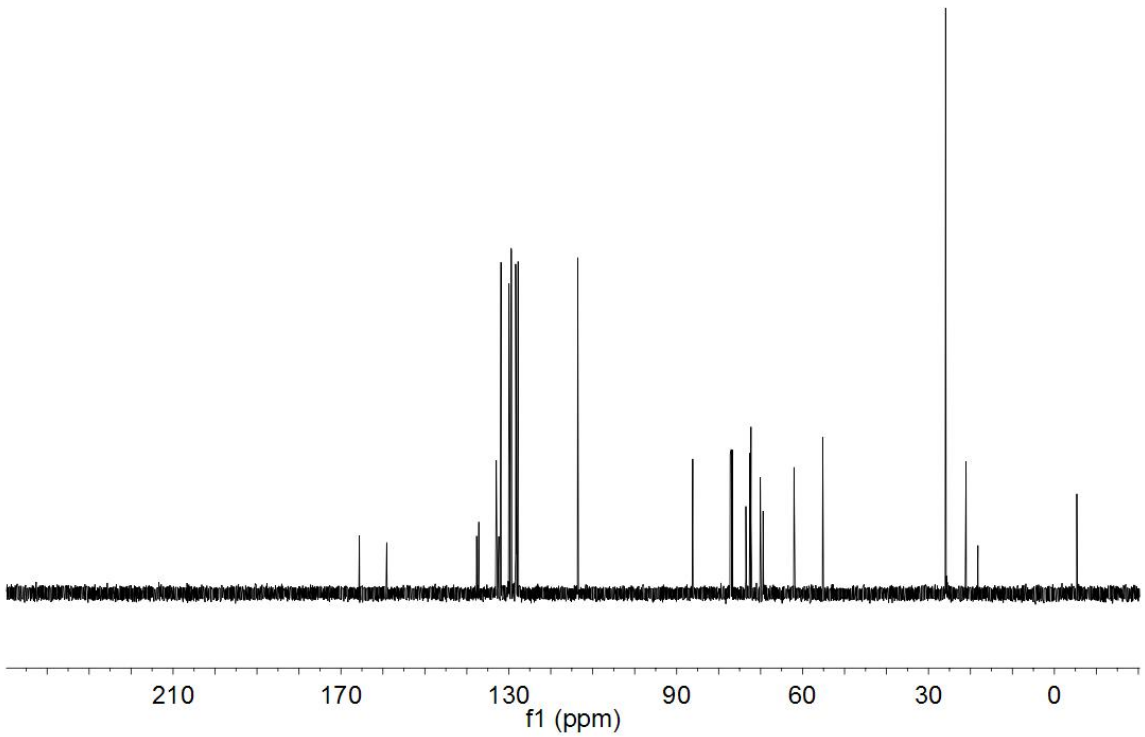

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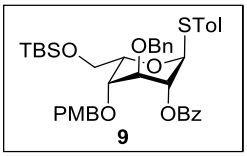
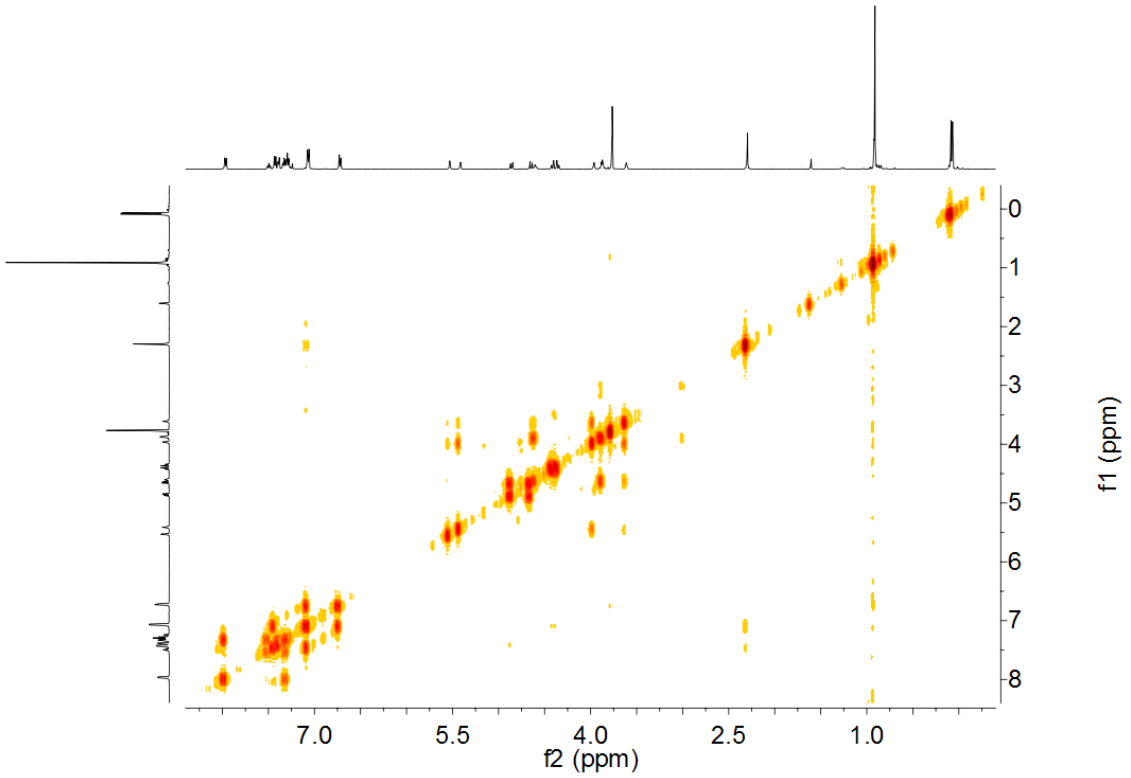
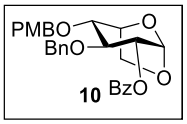
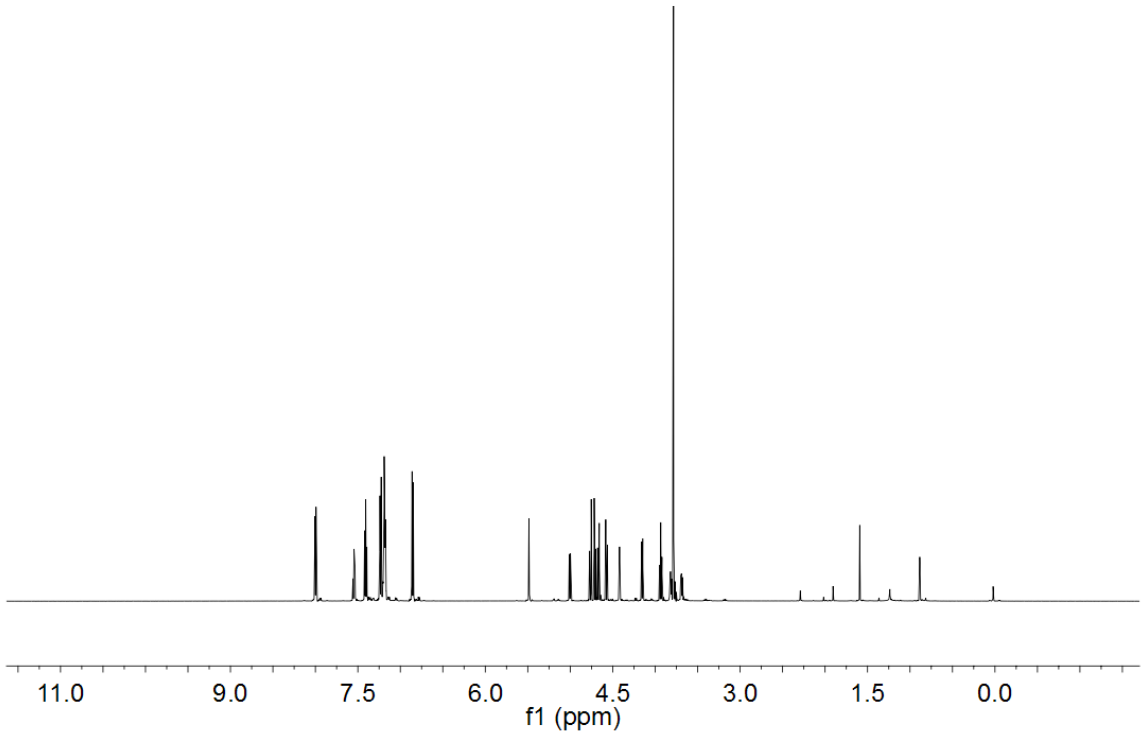


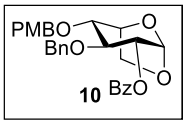


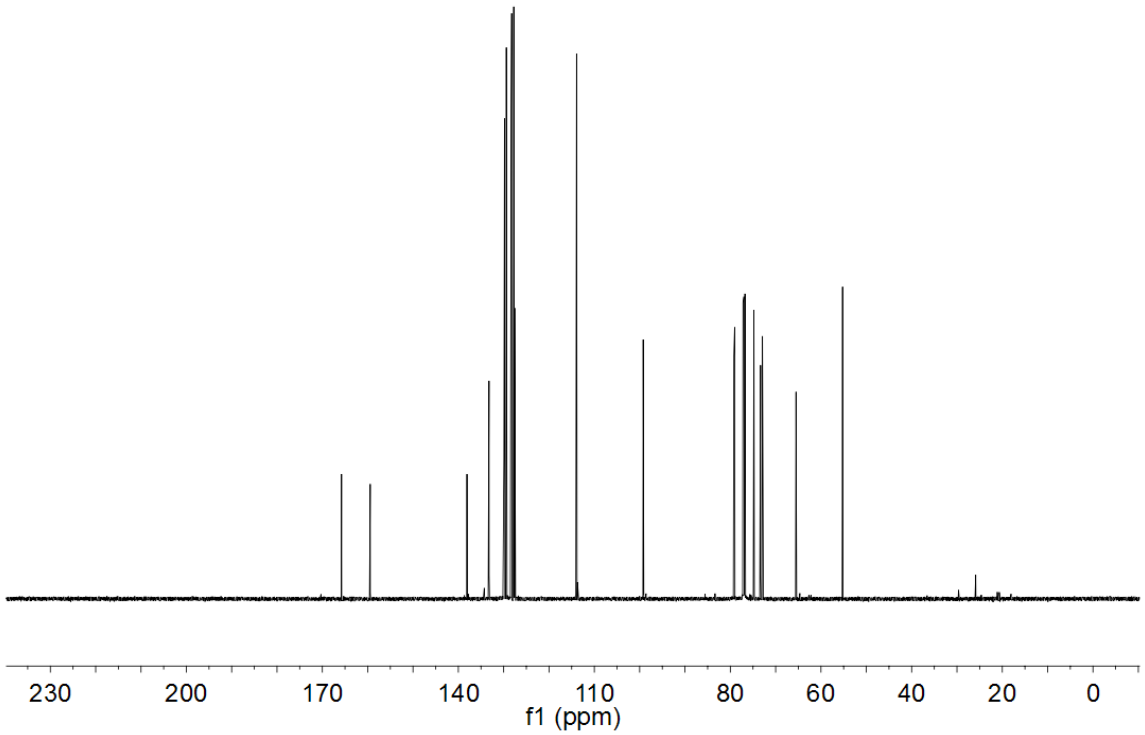
^{1}H-NMR ($CDCl_3$, 600 MHz) of **10**



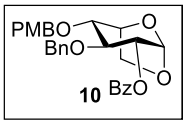


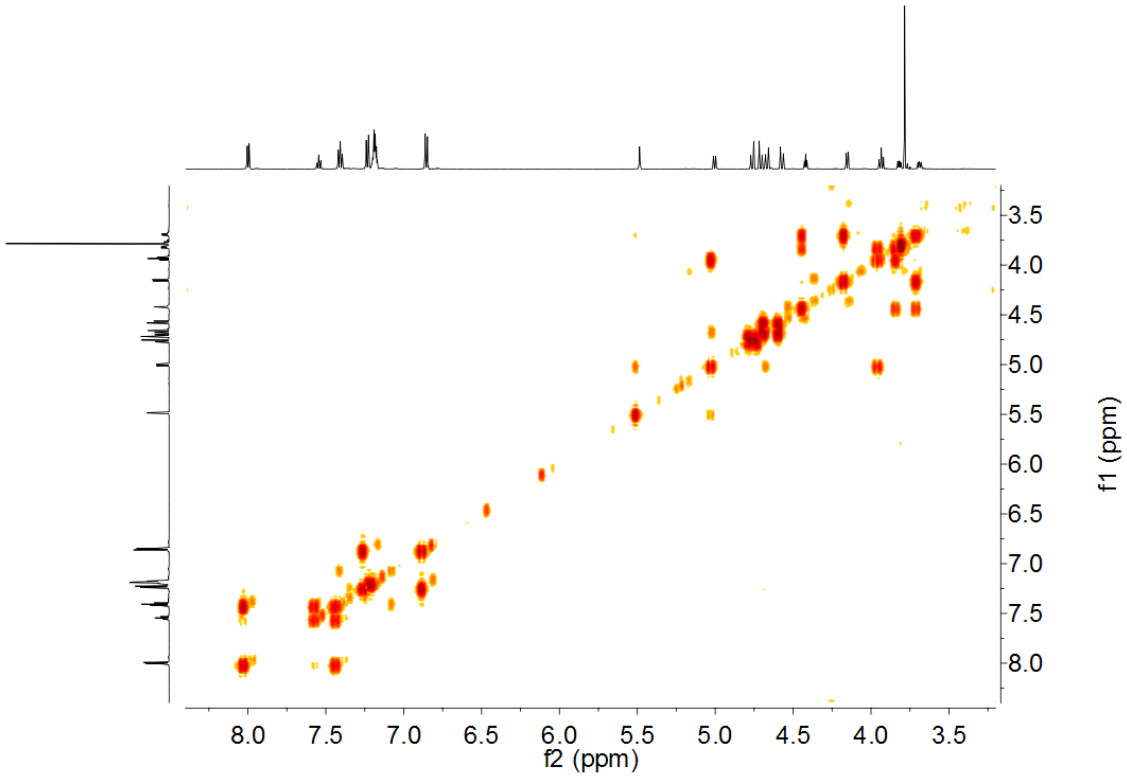
^{13}C-NMR ($CDCl_3$, 150 MHz) of **10**



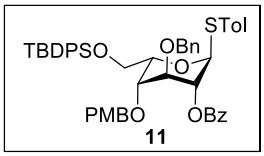


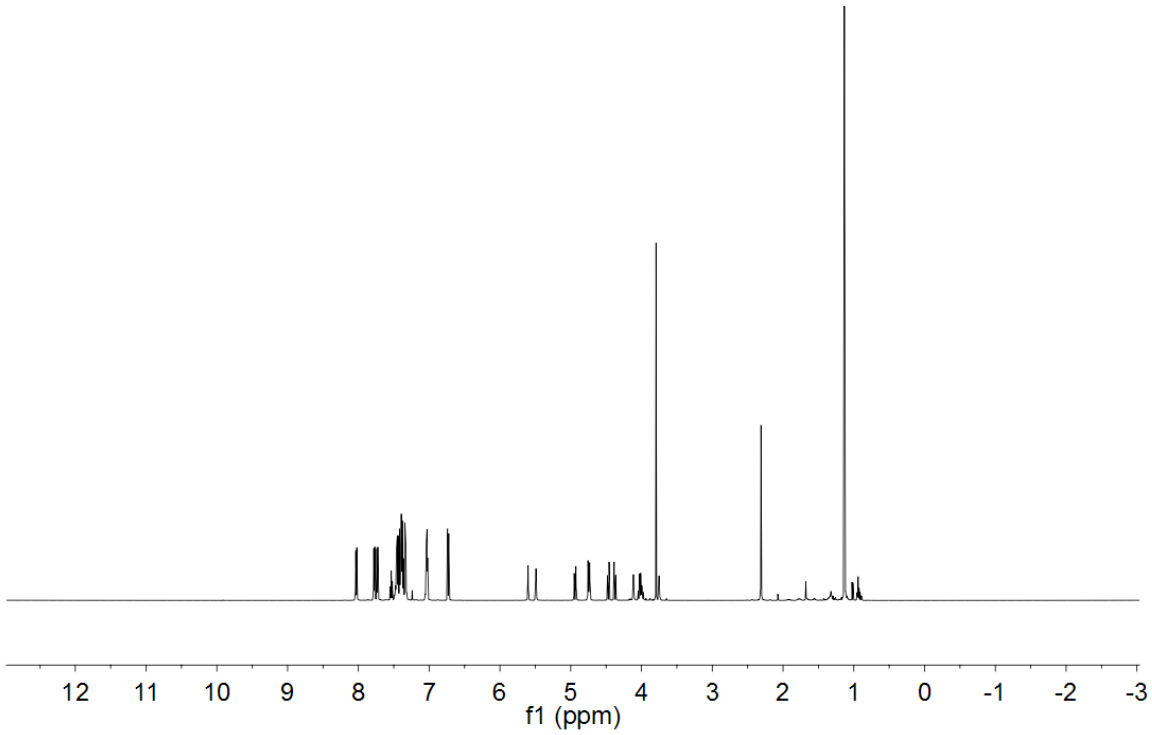
gCOSY ($CDCl_3$, 600 MHz) of **10**



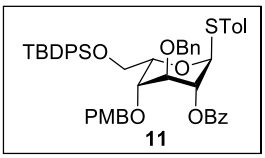


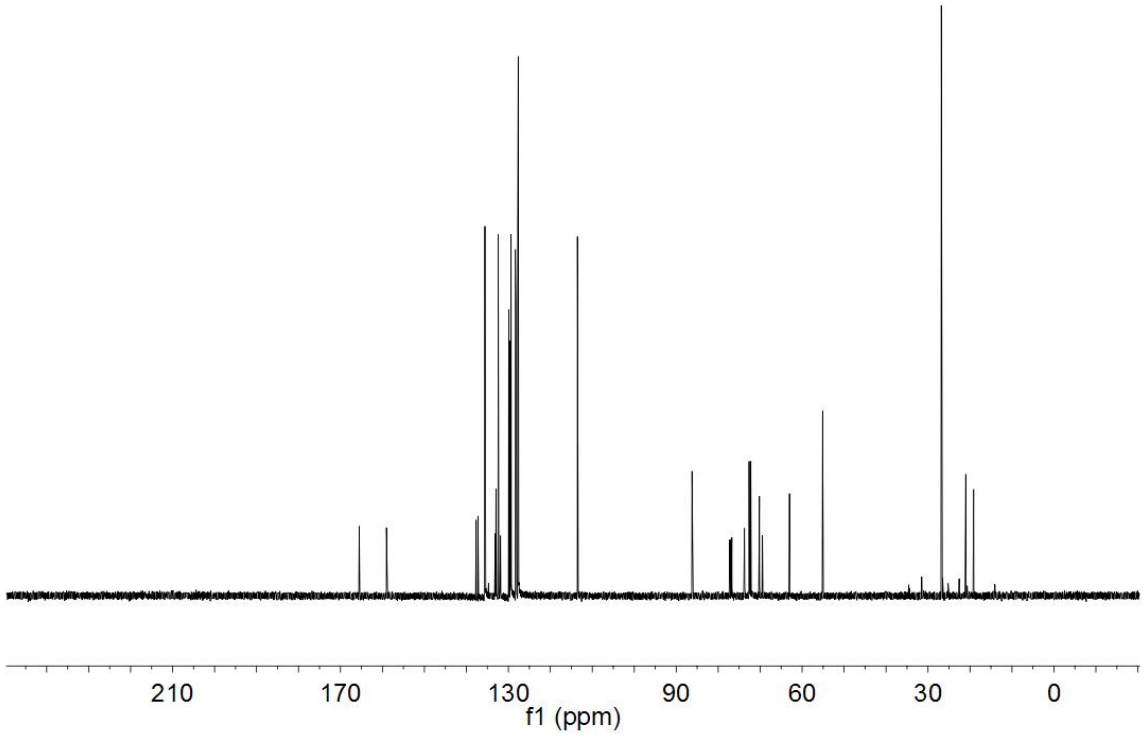
^{1}H-NMR ($CDCl_3$, 500 MHz) of **11**



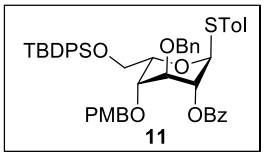


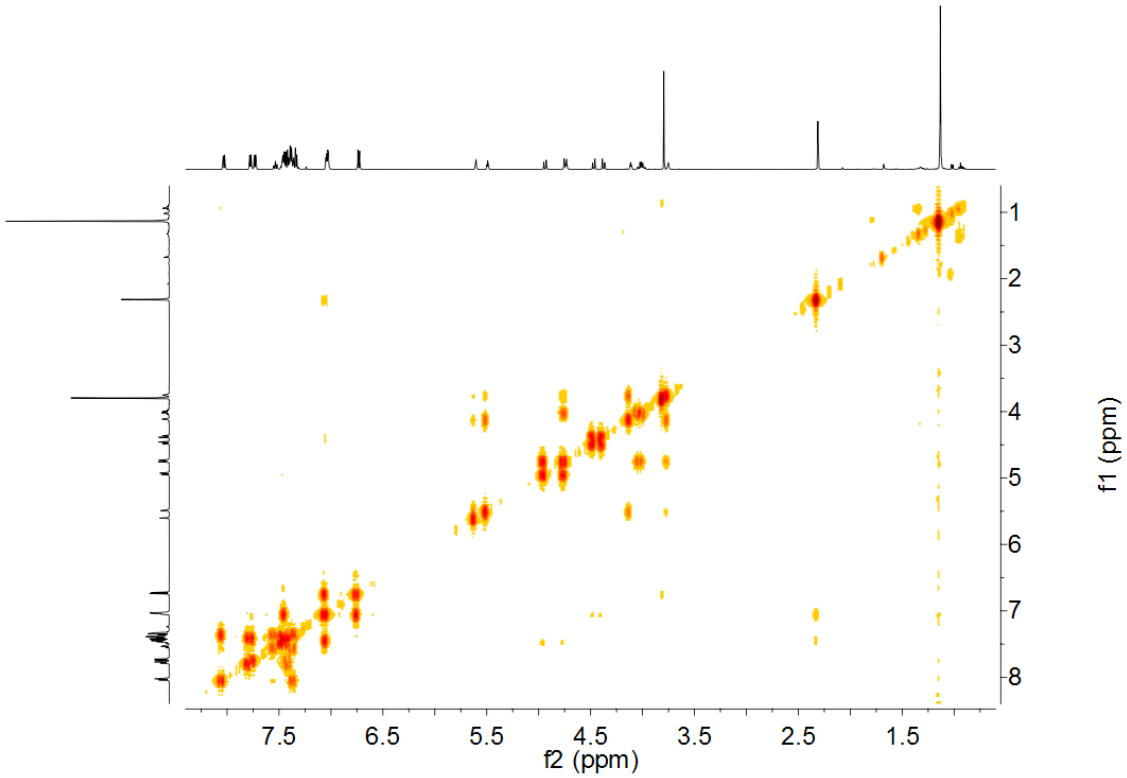
^{13}C-NMR ($CDCl_3$, 125 MHz) of **11**



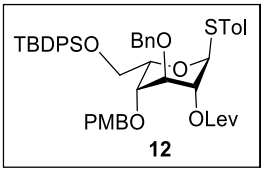


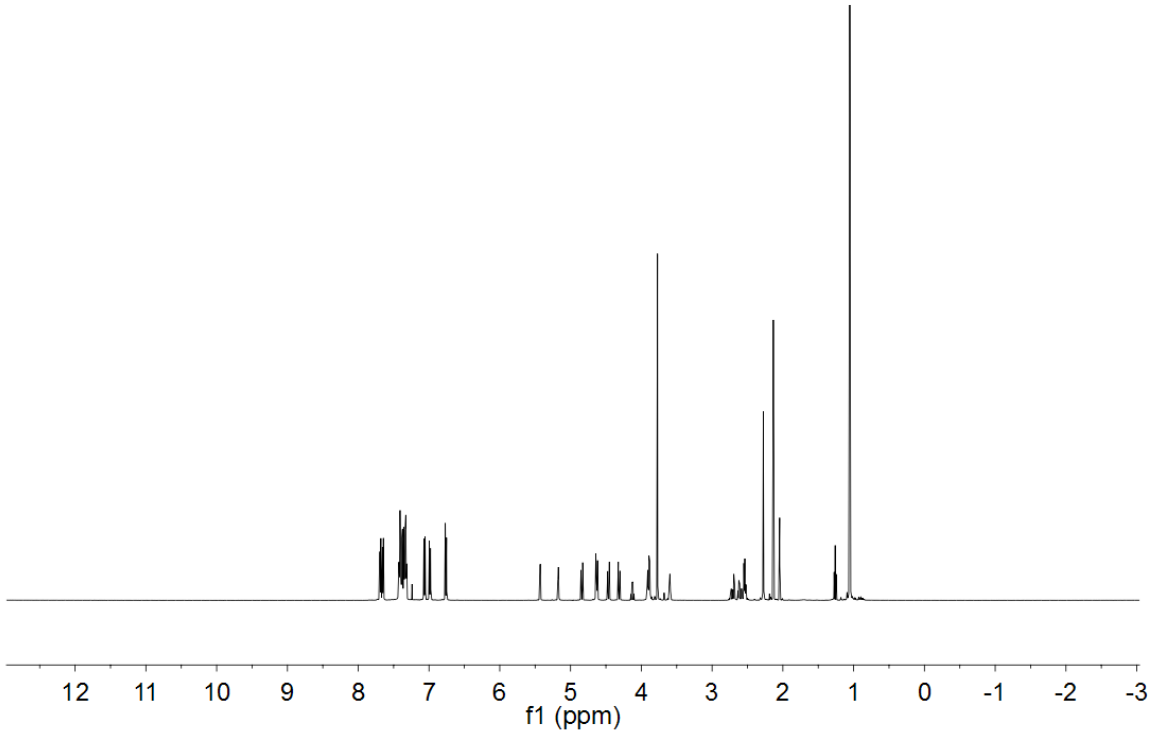
gCOSY ($CDCl_3$, 500 MHz) of **11**



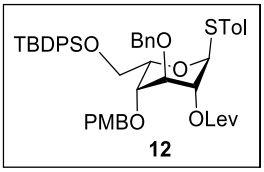


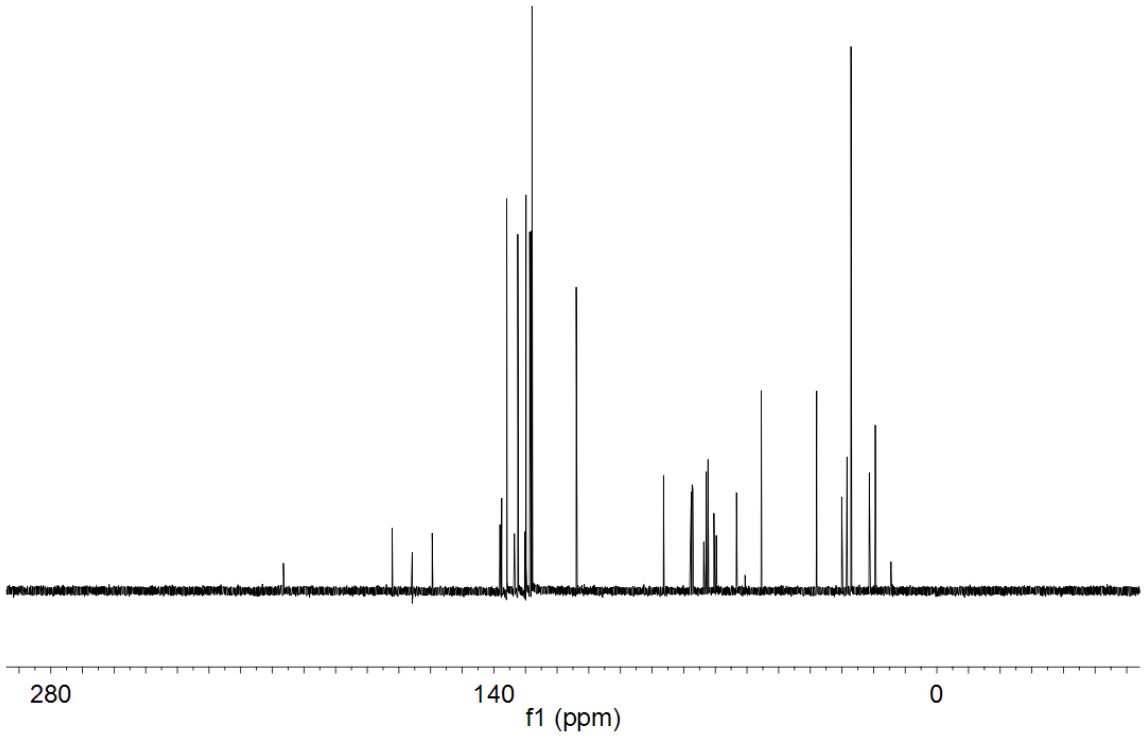
^{1}H-NMR ($CDCl_3$, 500 MHz) of **12**



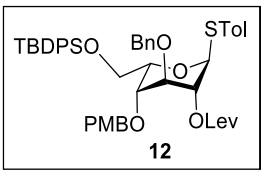


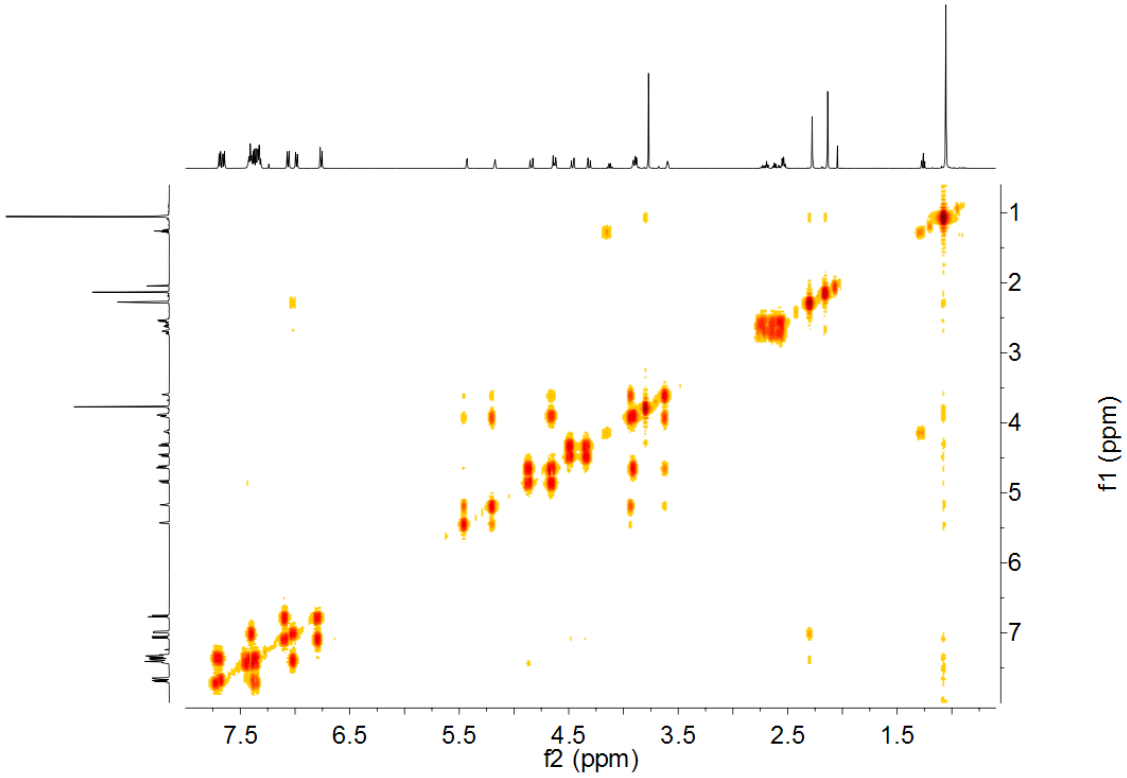
^{13}C-NMR ($CDCl_3$, 125 MHz) of **12**



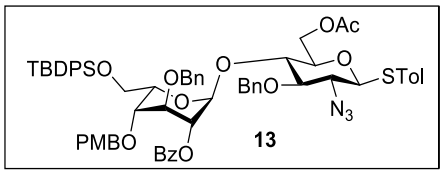


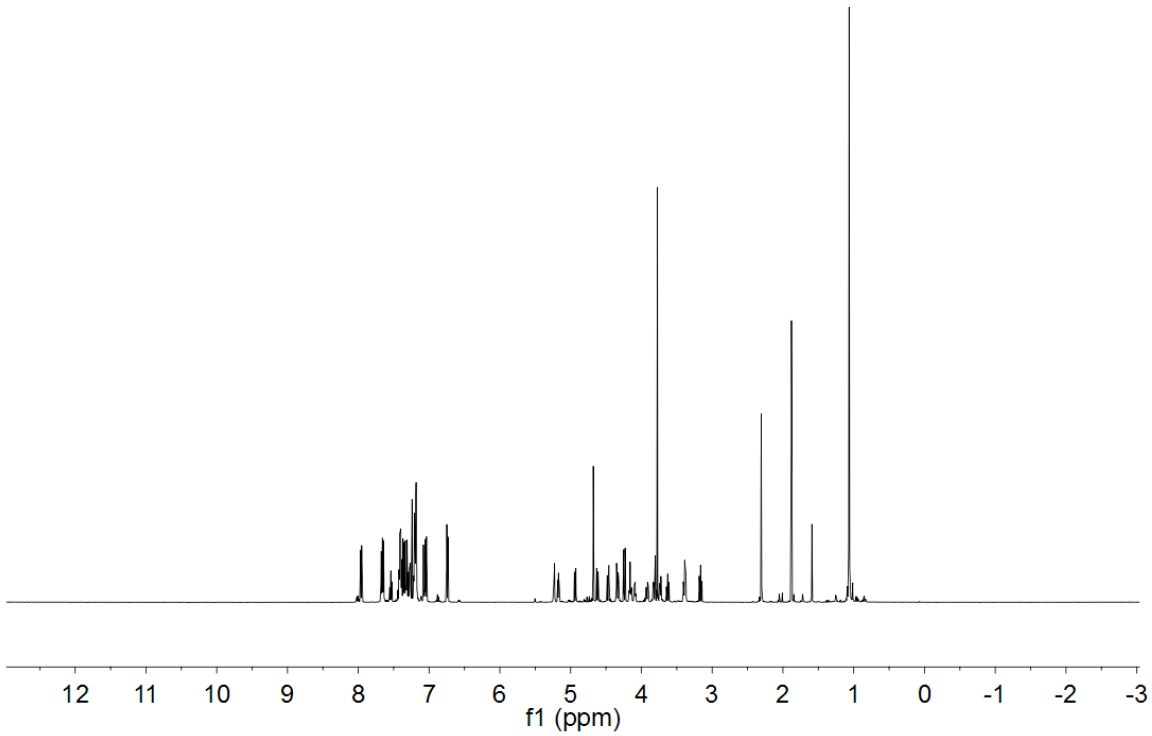
gCOSY ($CDCl_3$, 500 MHz) of **12**



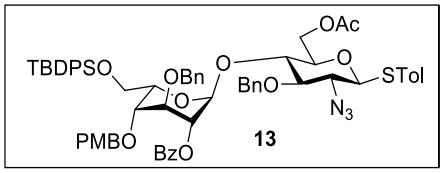


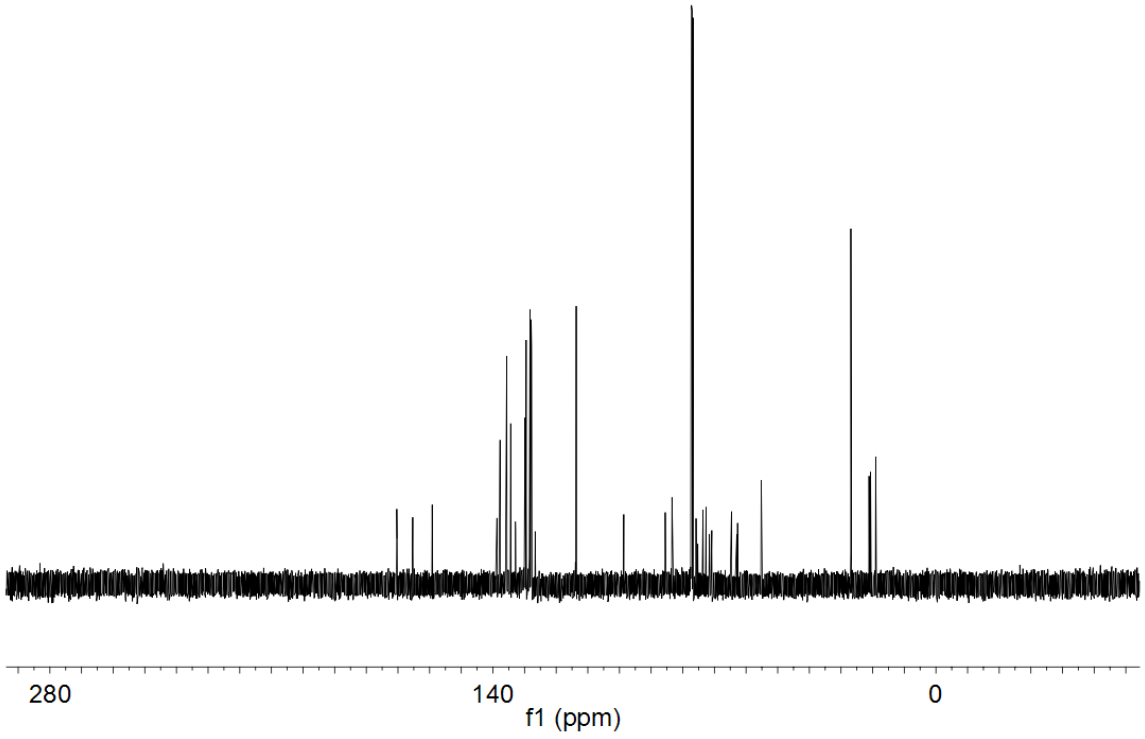
^{1}H-NMR ($CDCl_3$, 500 MHz) of **13**



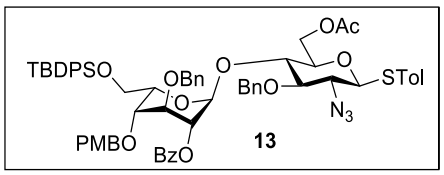


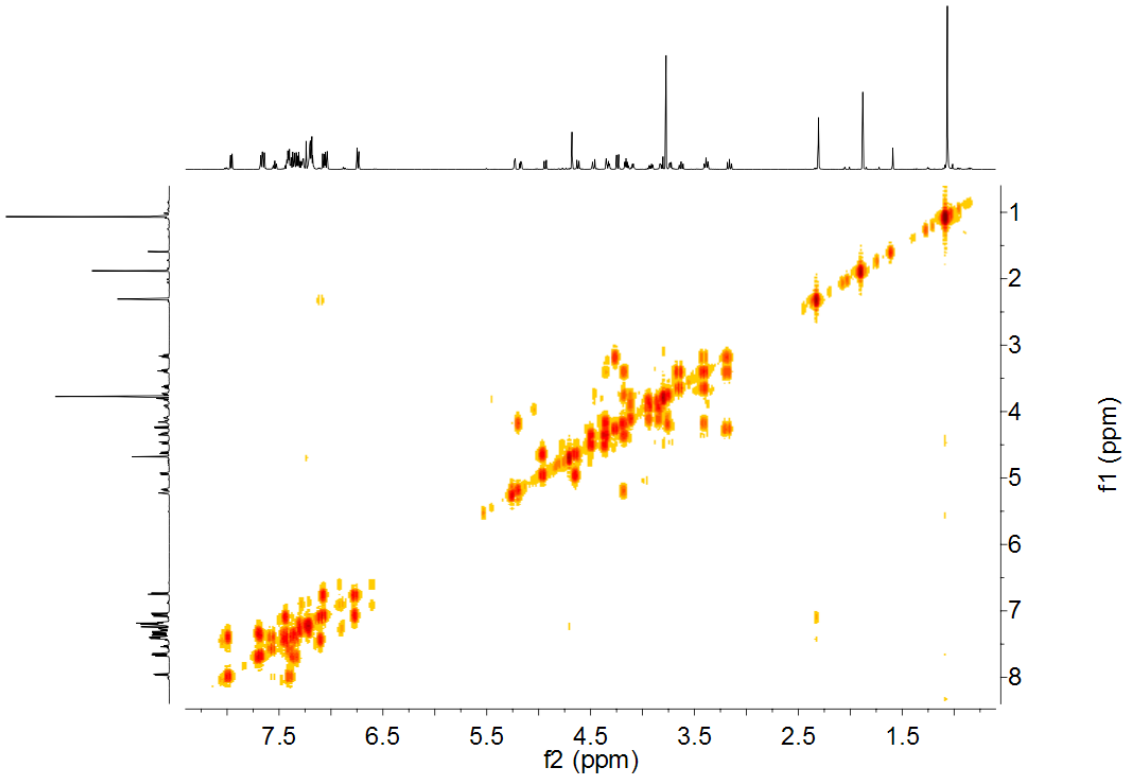
^{13}C-NMR ($CDCl_3$, 125 MHz) of **13**



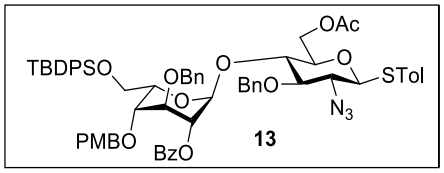


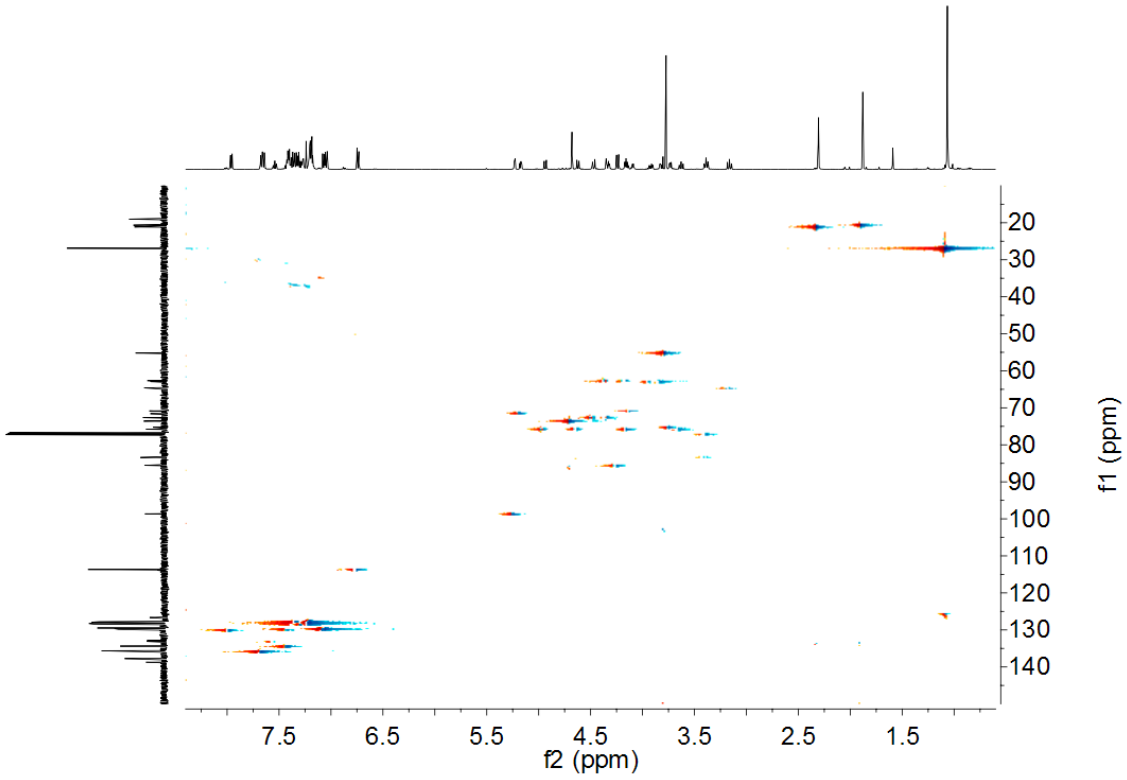
gCOSY ($CDCl_3$, 500 MHz) of **13**



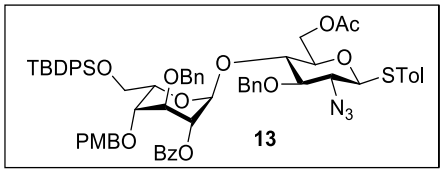


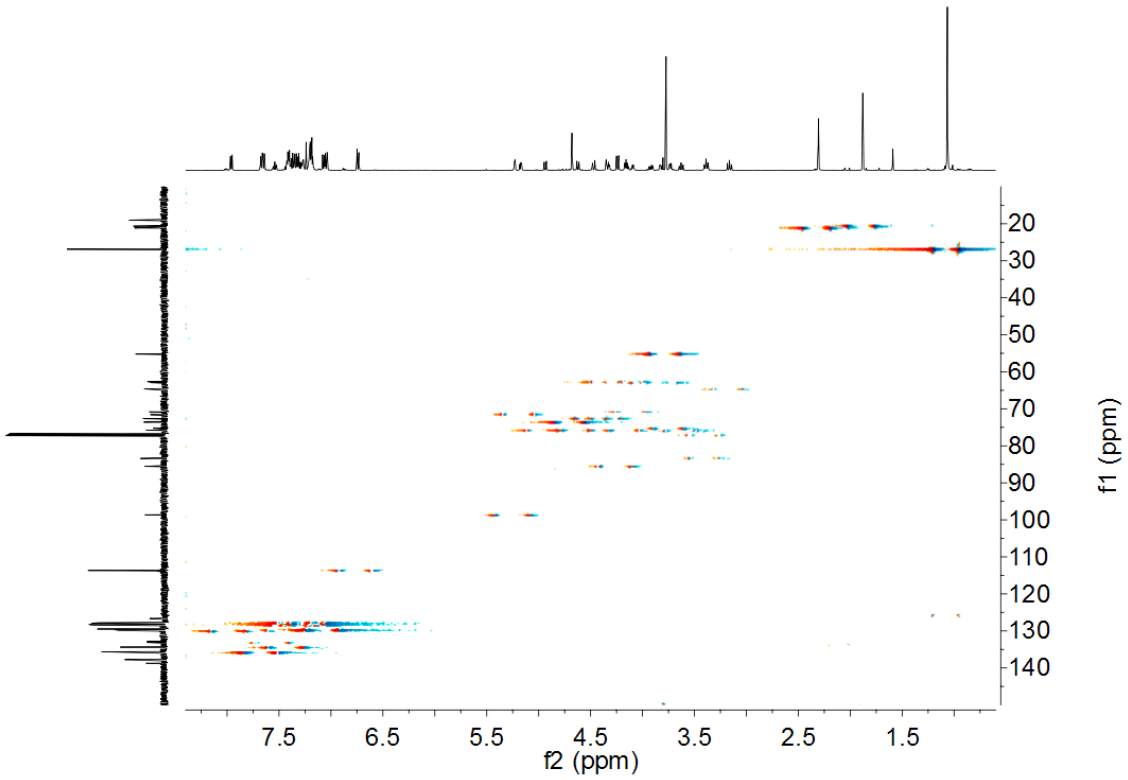
gHMQC ($CDCl_3$, 500 MHz) of **13**



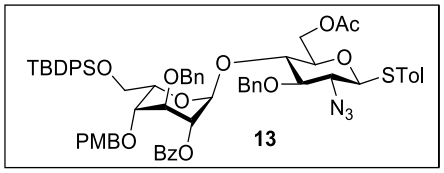


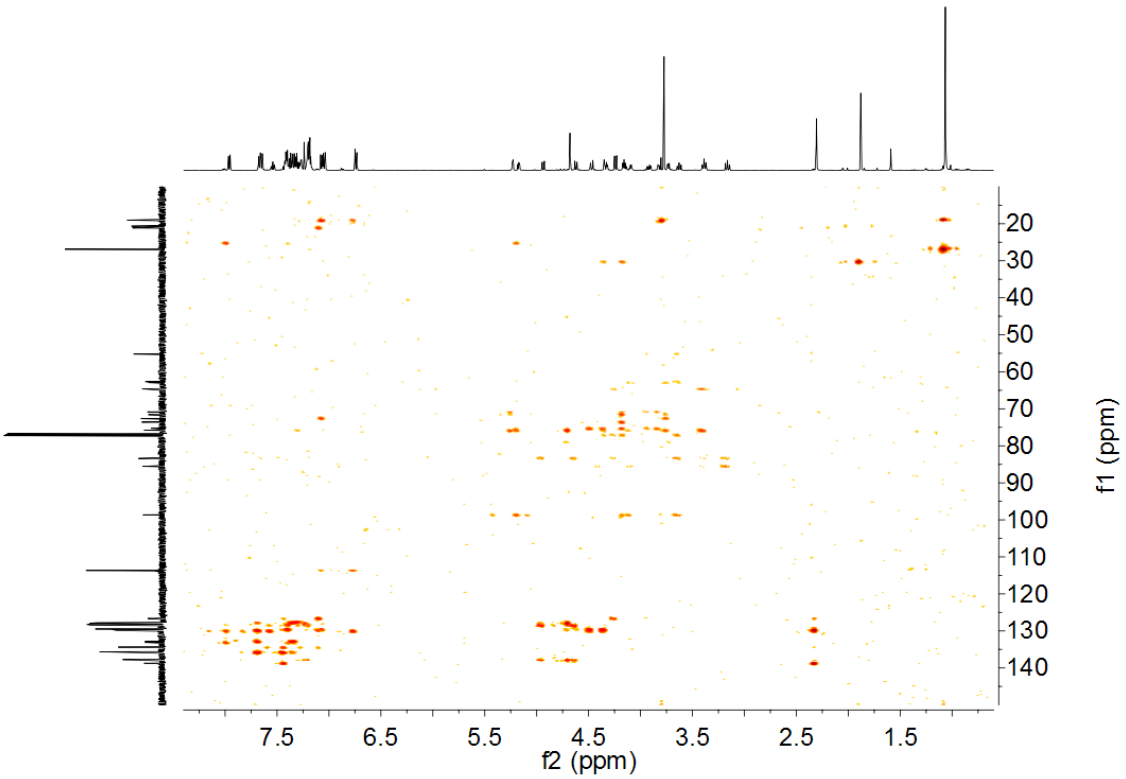
gHMQC (without ^{1}H decoupling) ($CDCl_3$, 500 MHz) of **13**



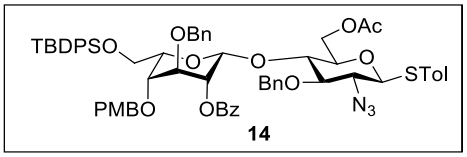


gHMBC ($CDCl_3$, 500 MHz) of **13**





^{1}H-NMR ($CDCl_3$, 500 MHz) of **14**



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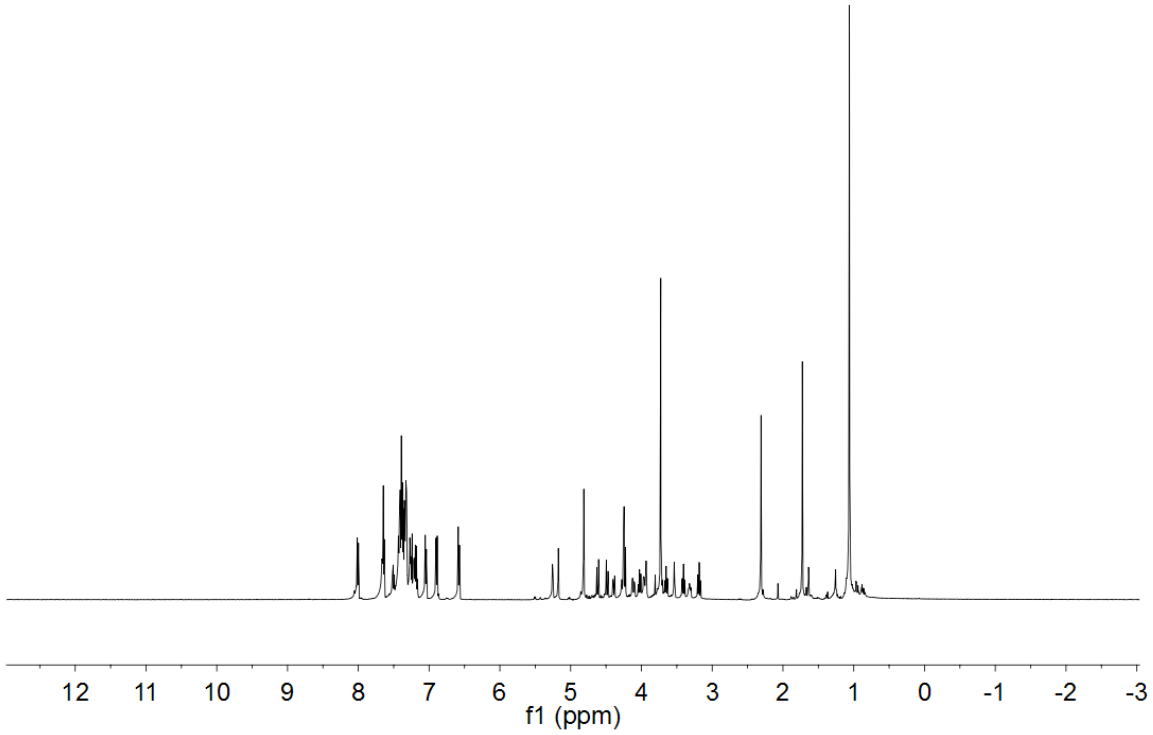
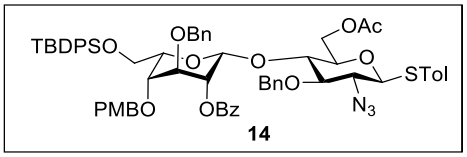


^{13}C-NMR ($CDCl_3$, 125 MHz) of **14**



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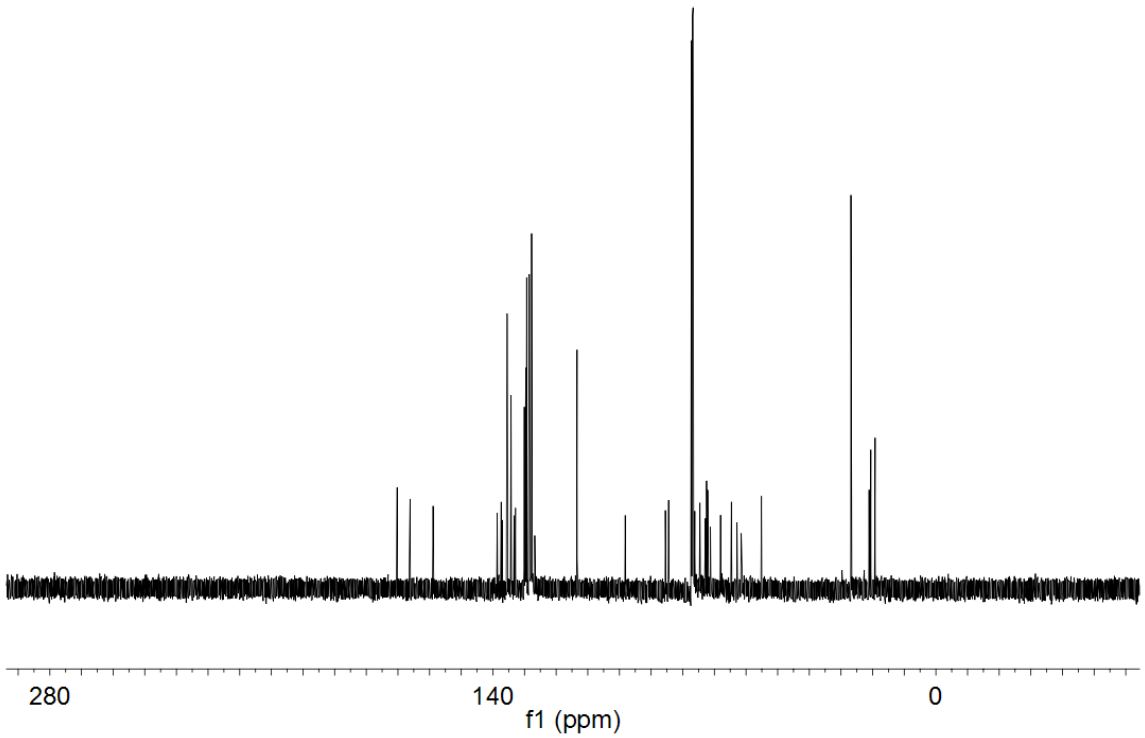
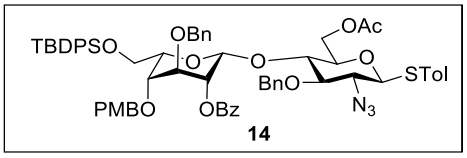


gCOSY ($CDCl_3$, 500 MHz) of **14**



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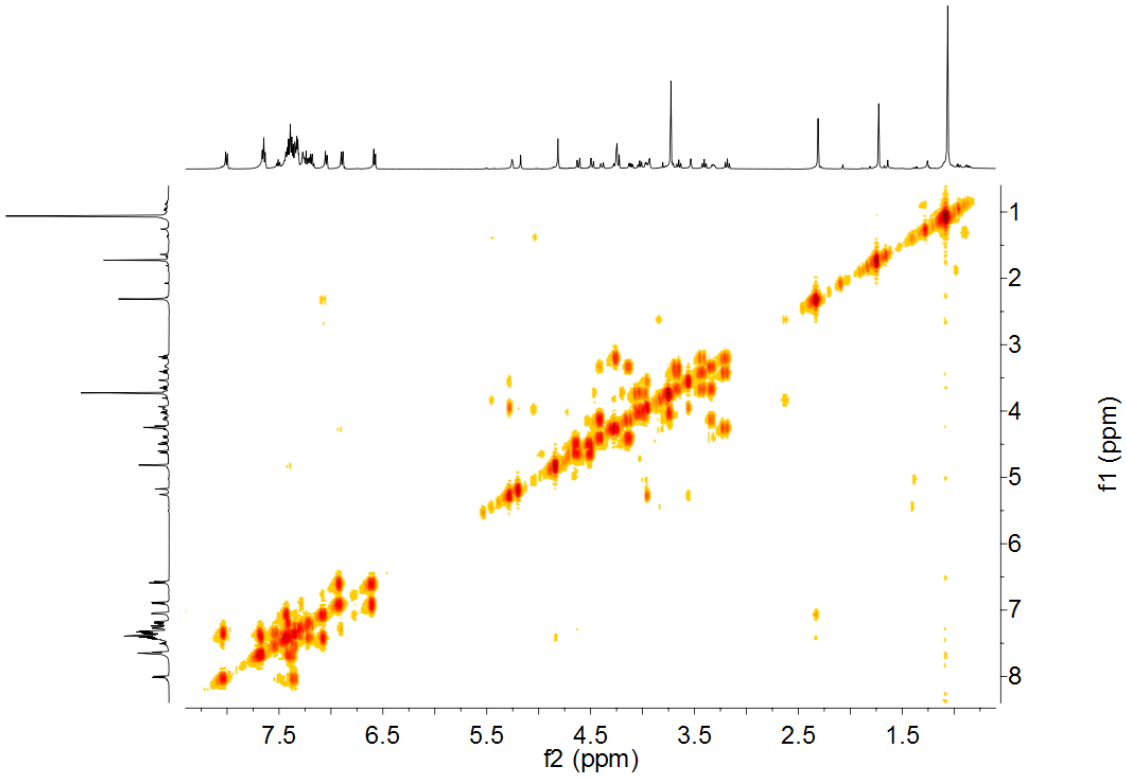
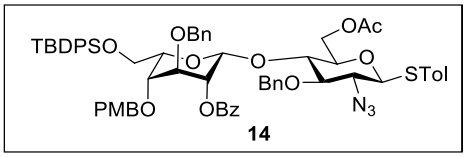
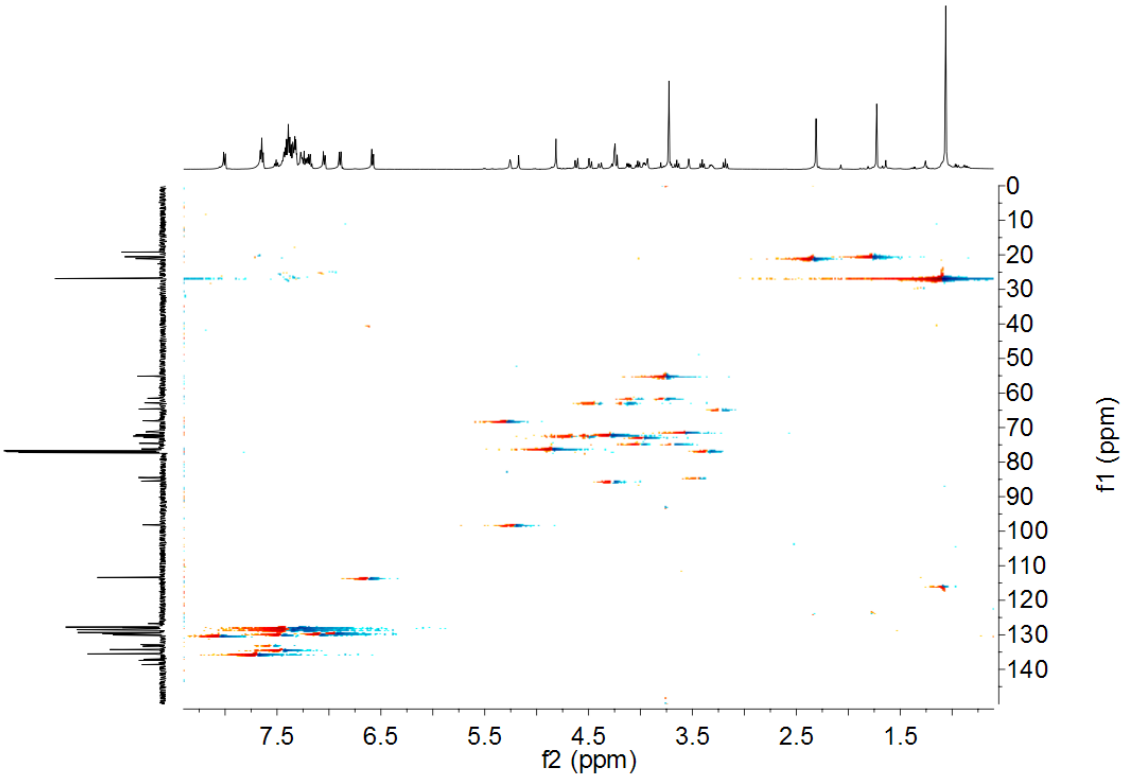


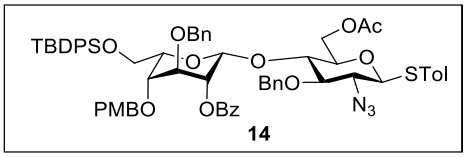
gHMQC ($CDCl_3$, 500 MHz) of **14**



14



gHMQC (without ^{1}H decoupling) ($CDCl_3$, 500 MHz) of **14**



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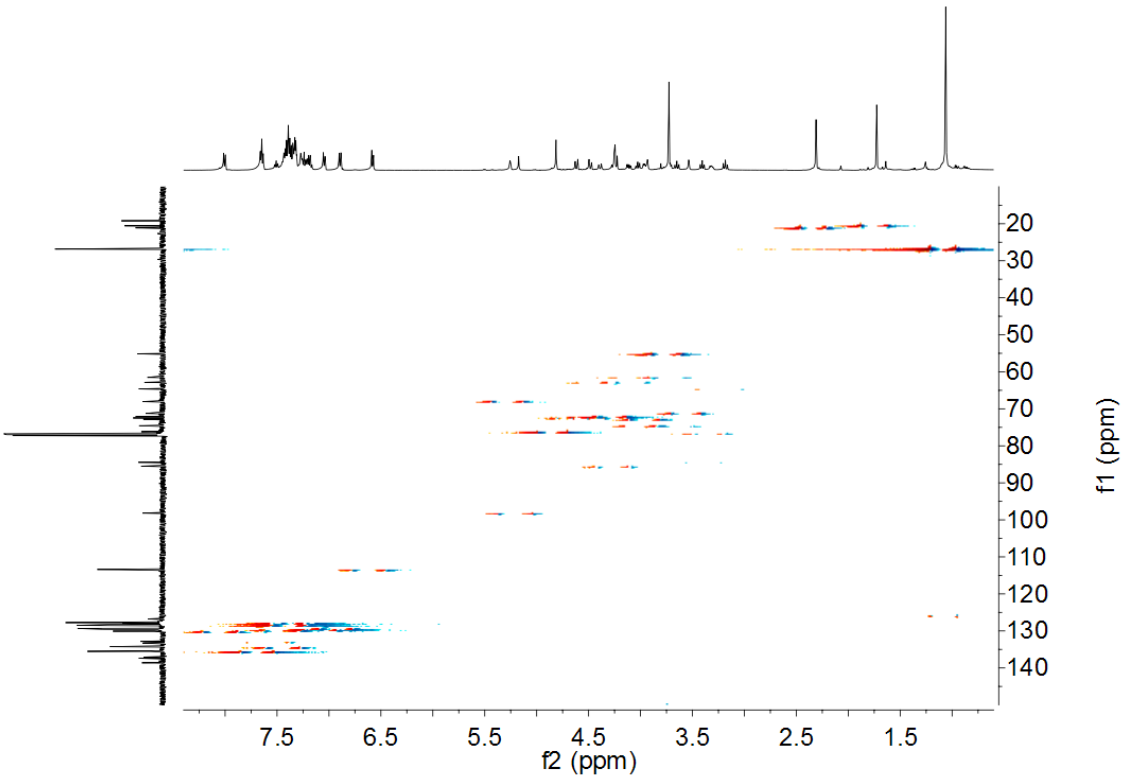
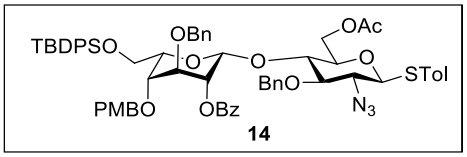


gHMBC ($CDCl_3$, 500 MHz) of **14**



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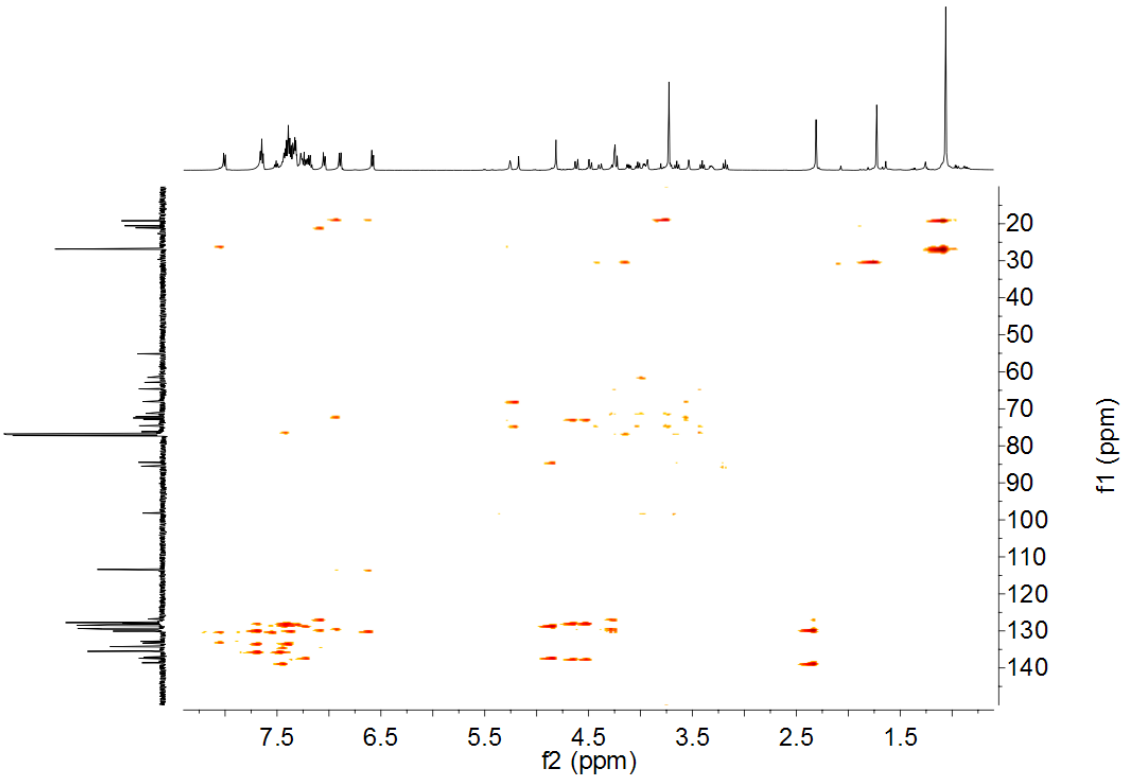
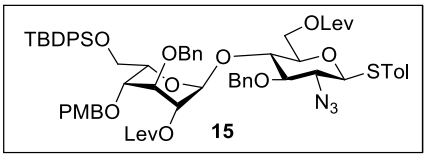
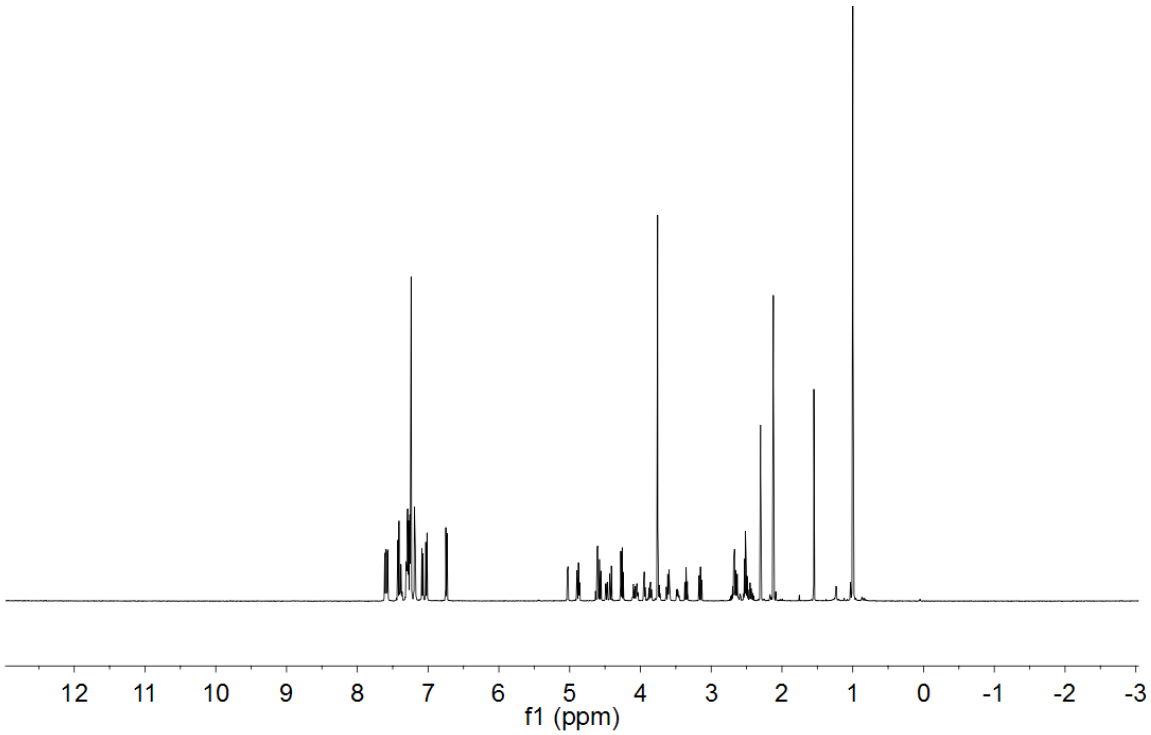
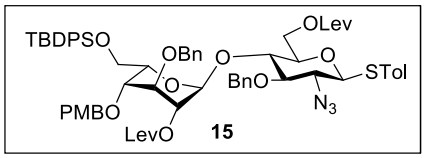


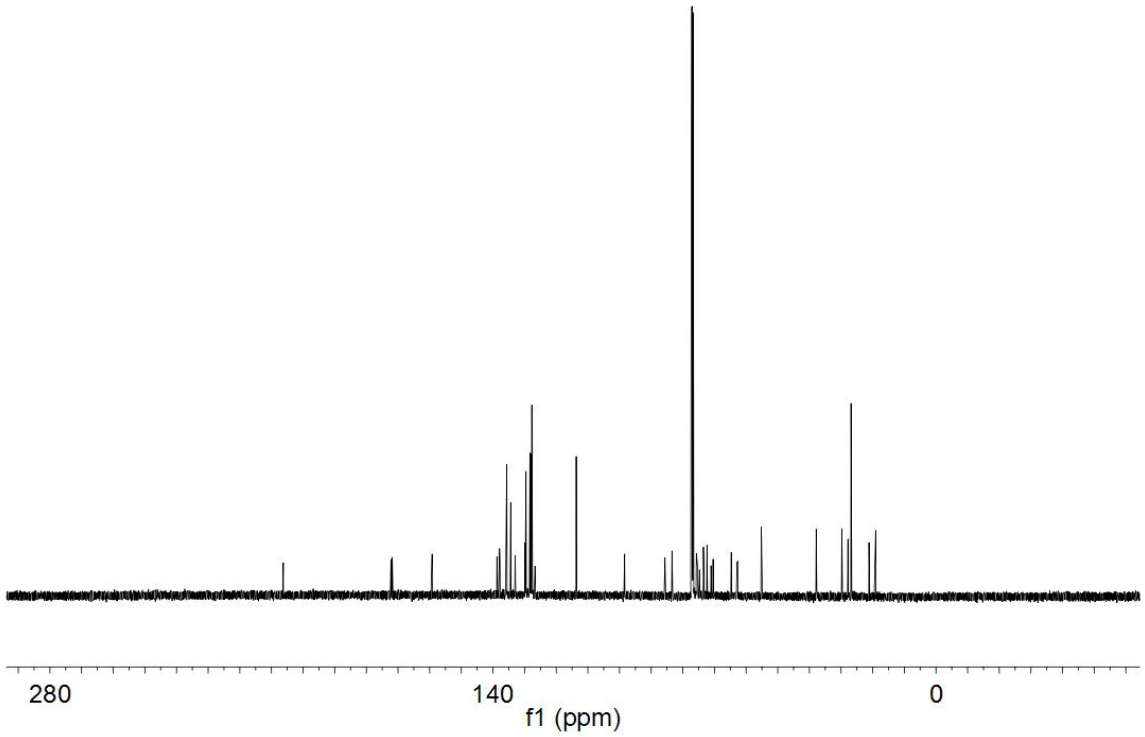
^{1}H-NMR ($CDCl_3$, 500 MHz) of **15**



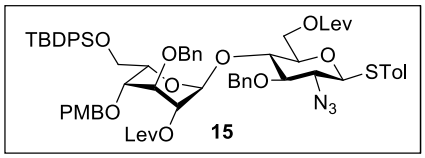


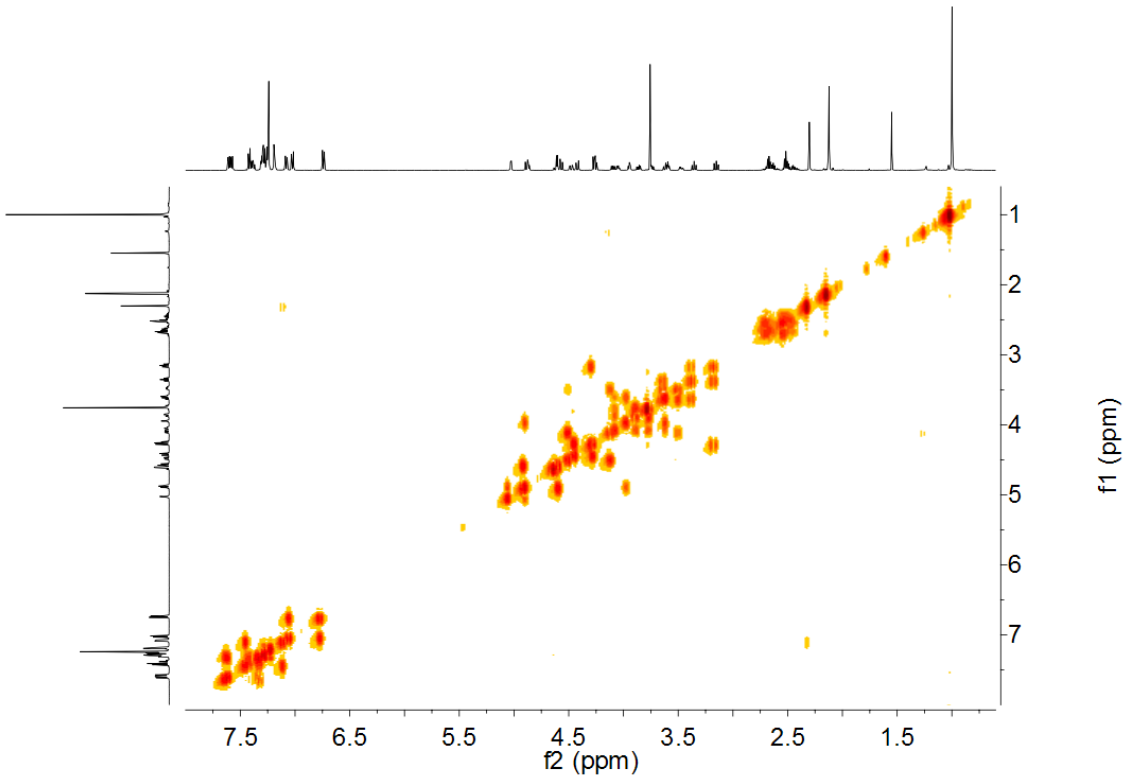
^{13}C-NMR ($CDCl_3$, 125 MHz) of **15**



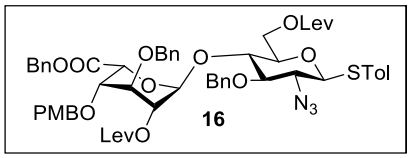


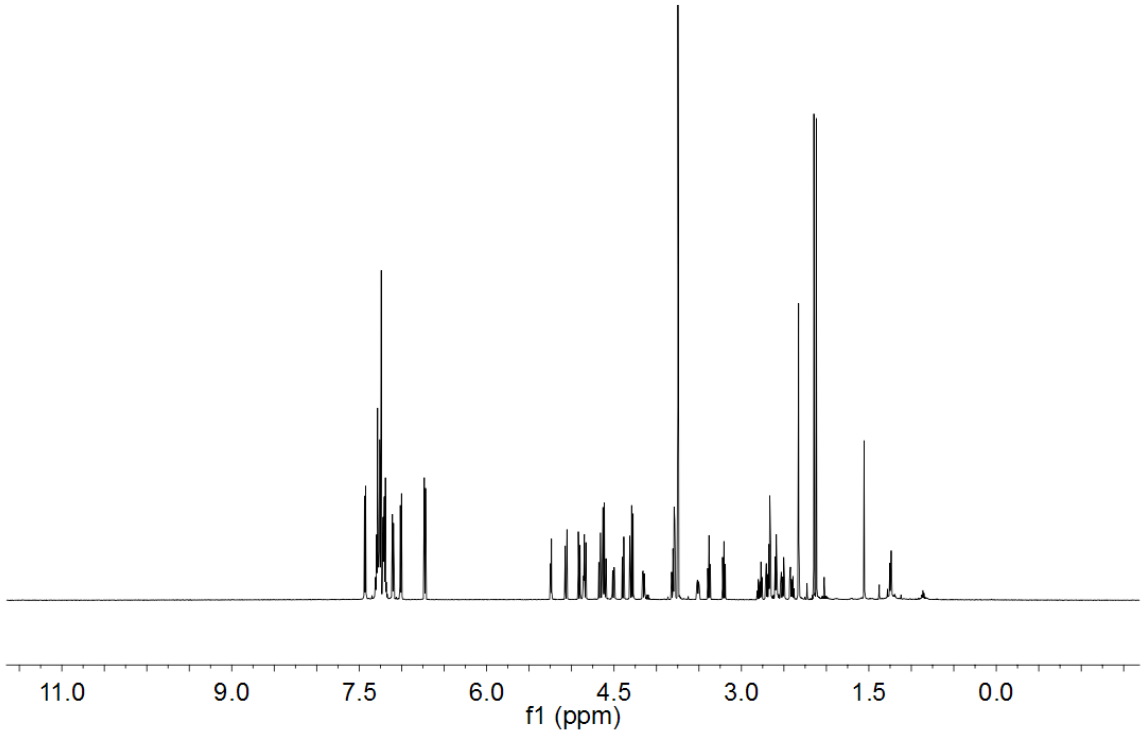
gCOSY ($CDCl_3$, 500 MHz) of **15**



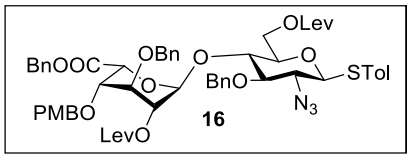


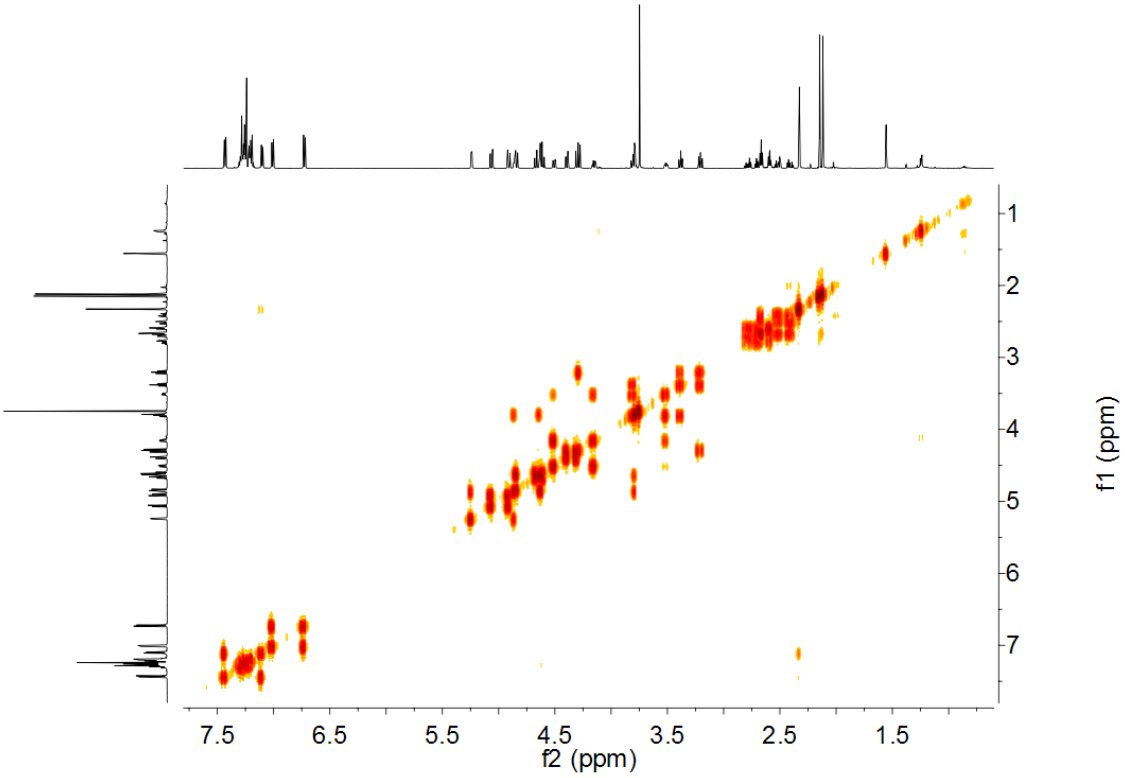
^{1}H-NMR ($CDCl_3$, 500 MHz) of **16**



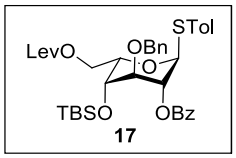


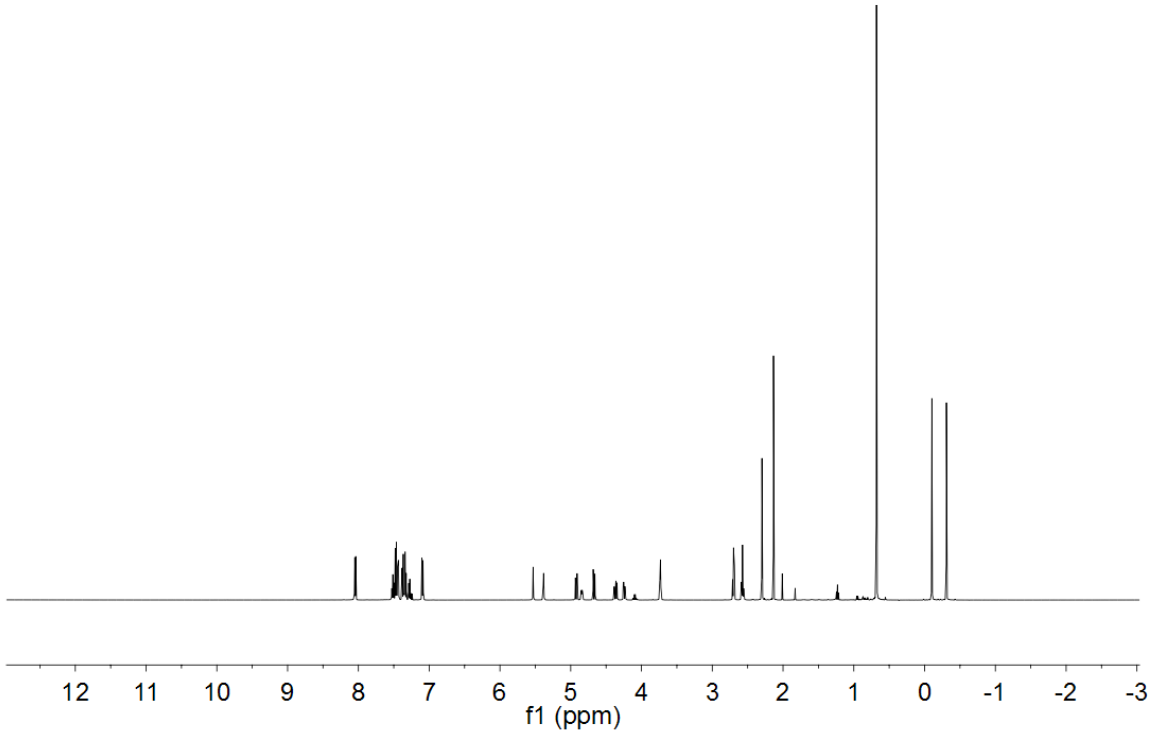
gCOSY ($CDCl_3$, 600 MHz) of **16**



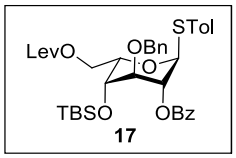


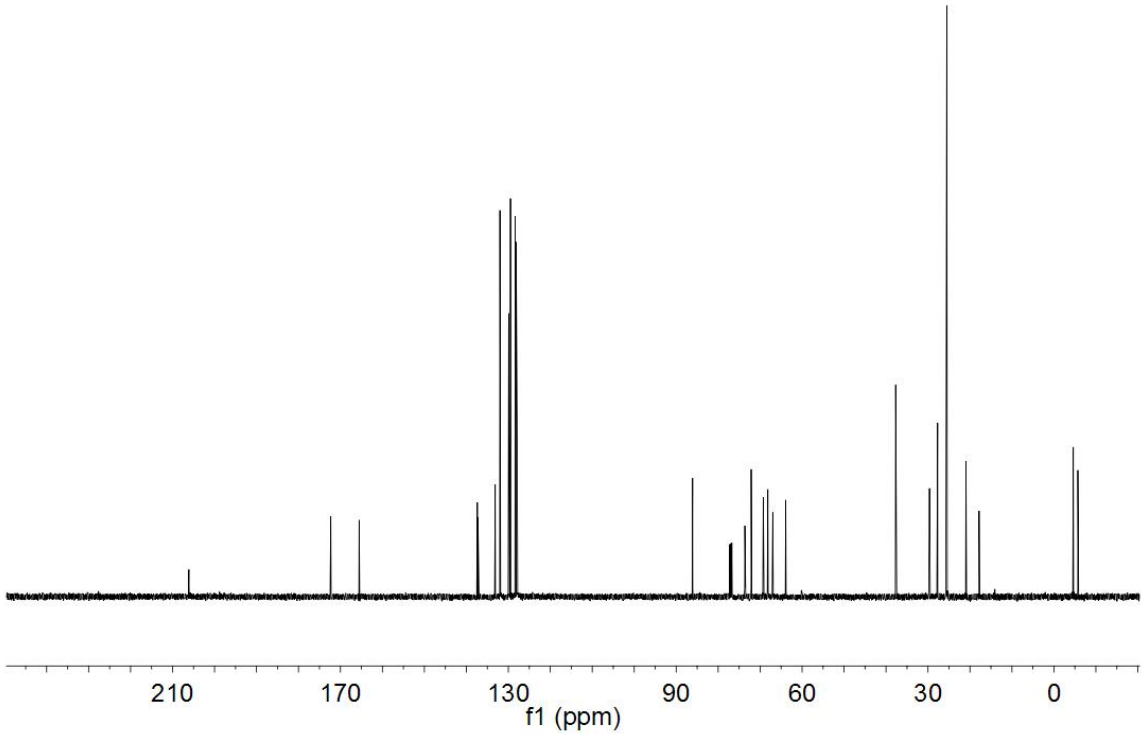
^{1}H-NMR ($CDCl_3$, 500 MHz) of **17**



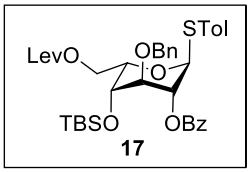


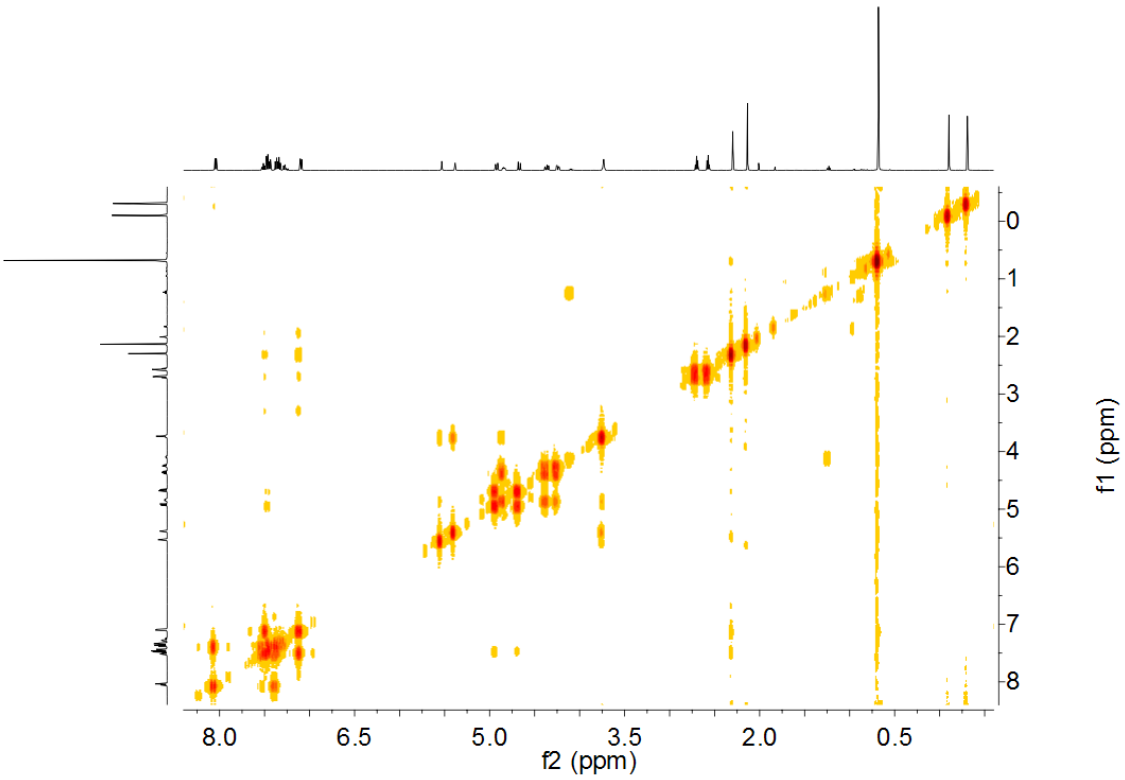
^{13}C-NMR ($CDCl_3$, 125 MHz) of **17**



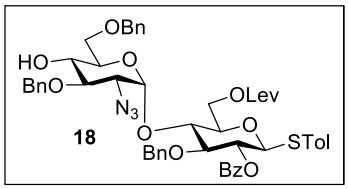


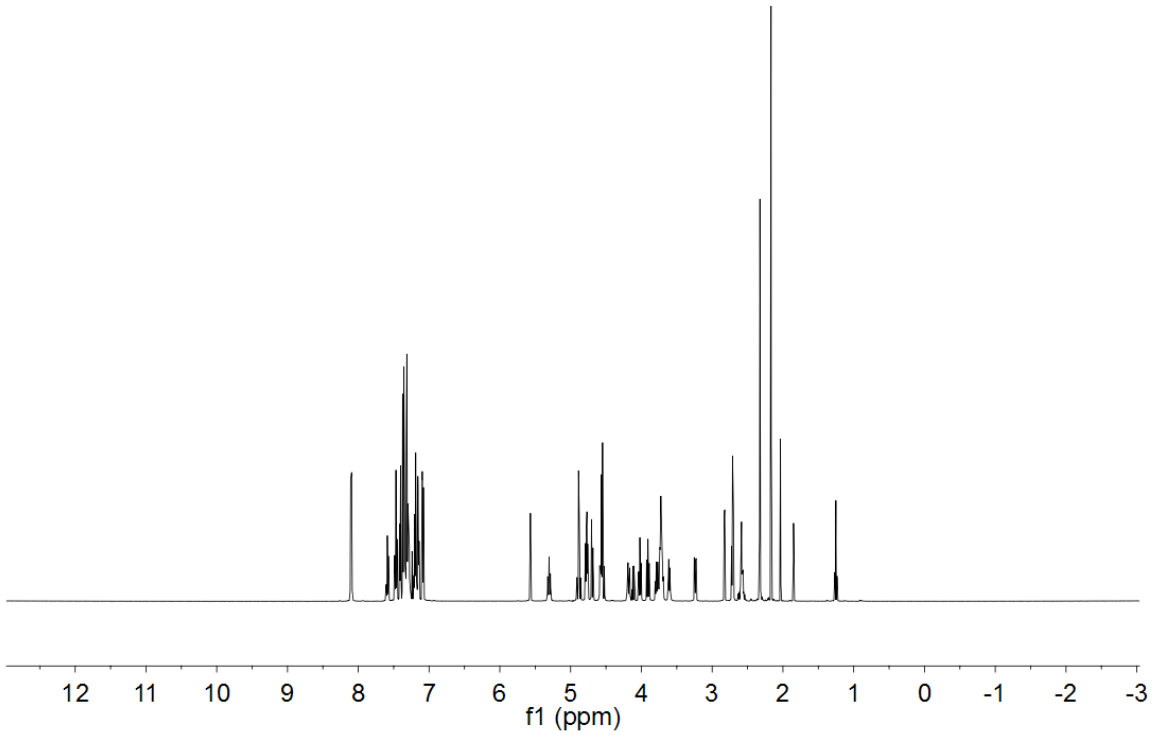
gCOSY ($CDCl_3$, 500 MHz) of **17**



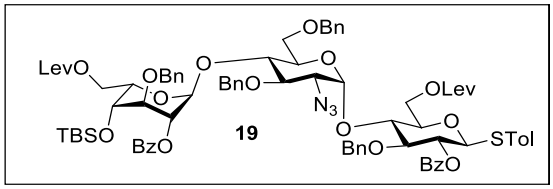


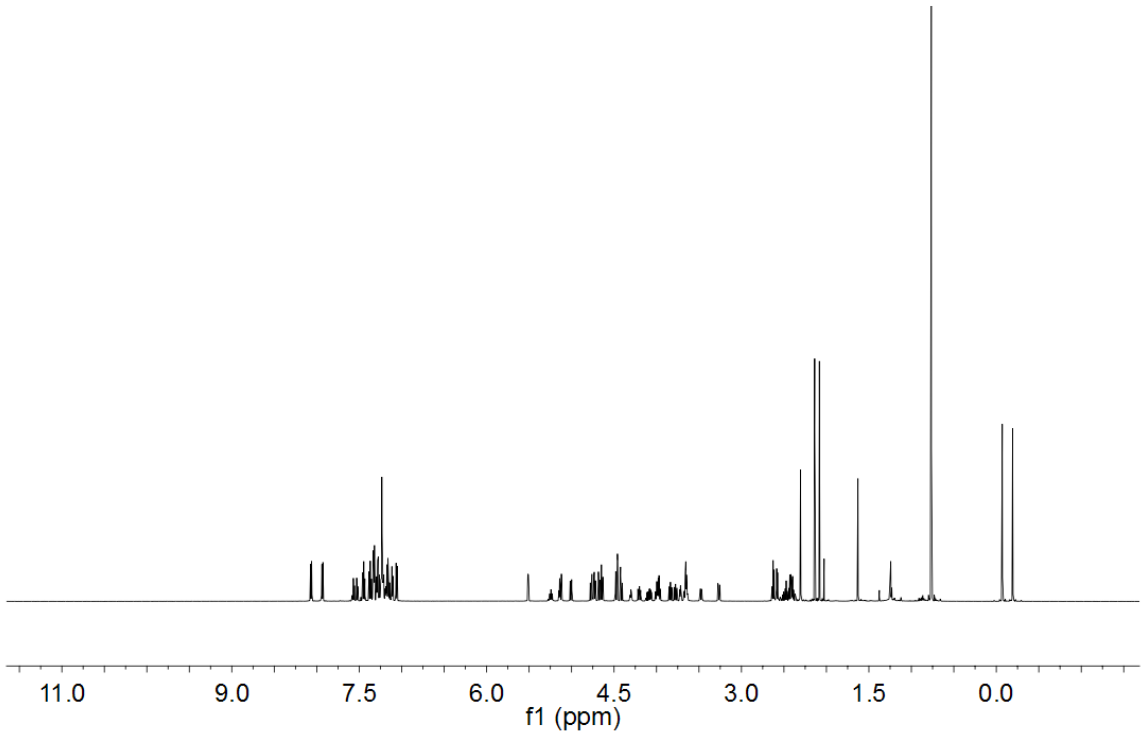
^{1}H-NMR ($CDCl_3$, 500 MHz) of **18**



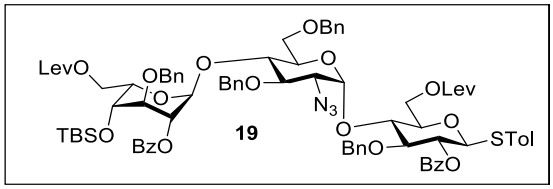


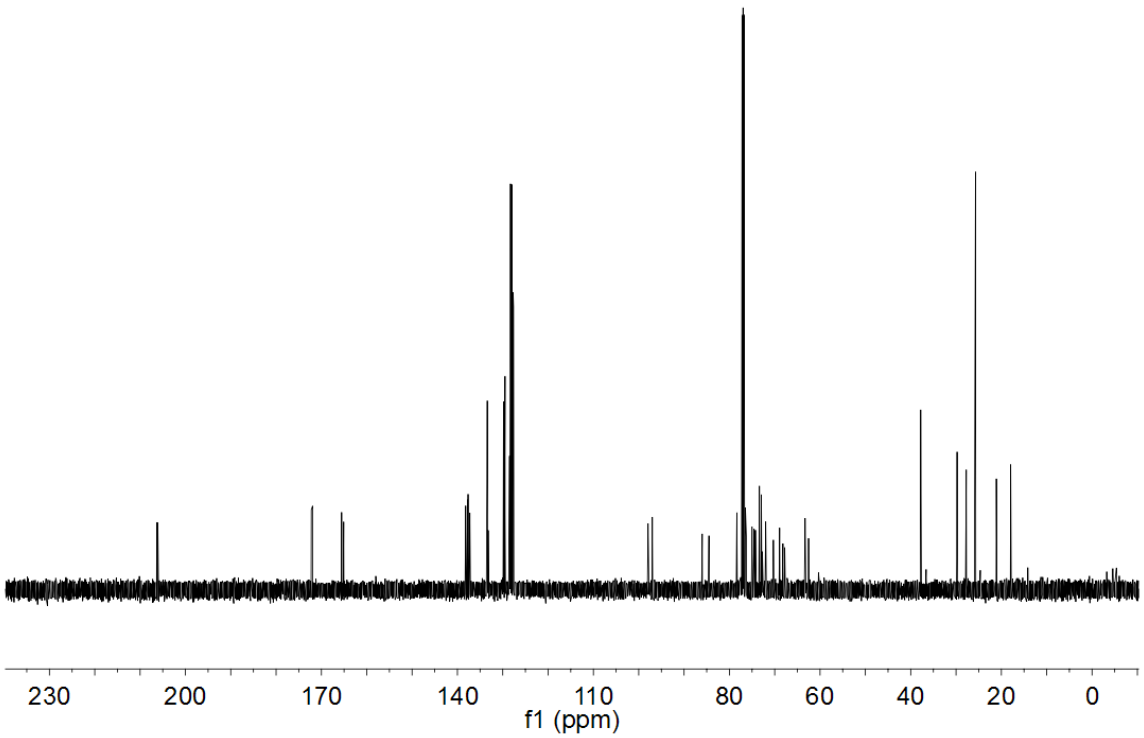
^{1}H-NMR ($CDCl_3$, 600 MHz) of **19**



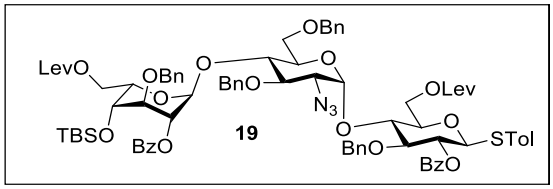


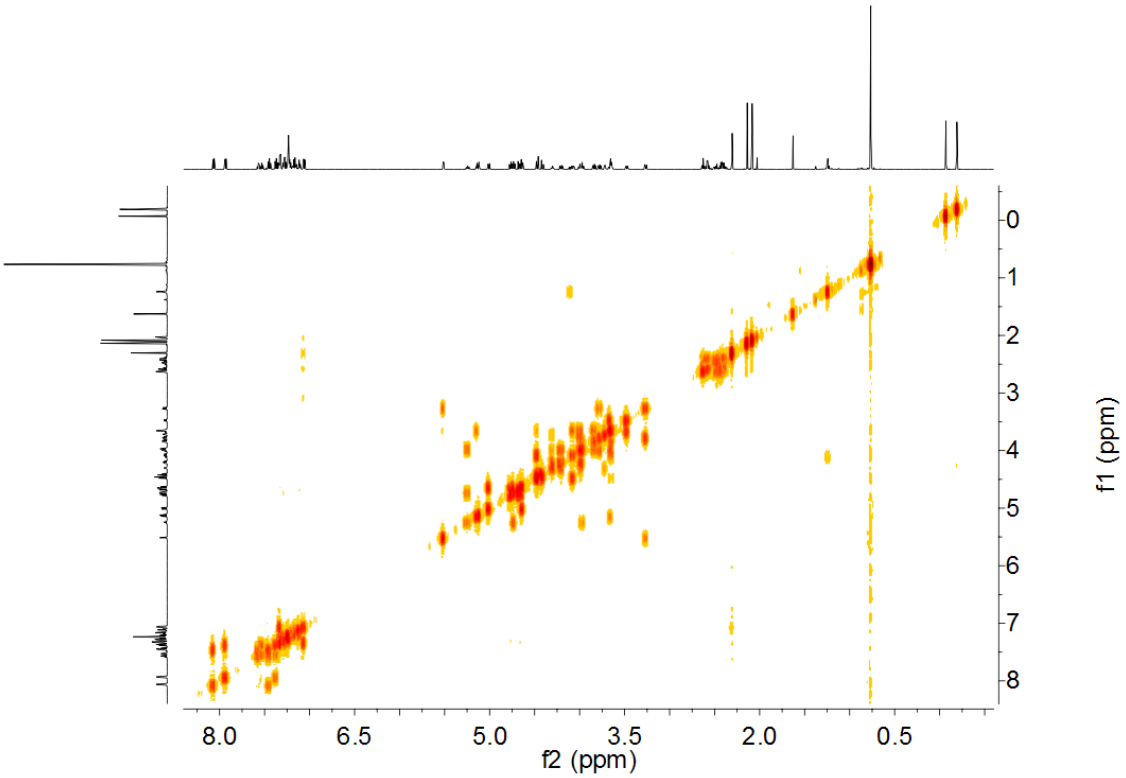
^{13}C-NMR ($CDCl_3$, 150 MHz) of **19**



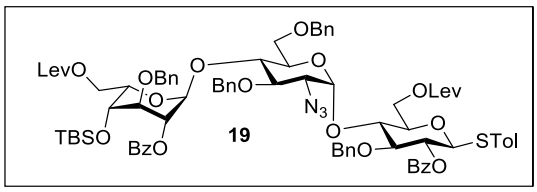


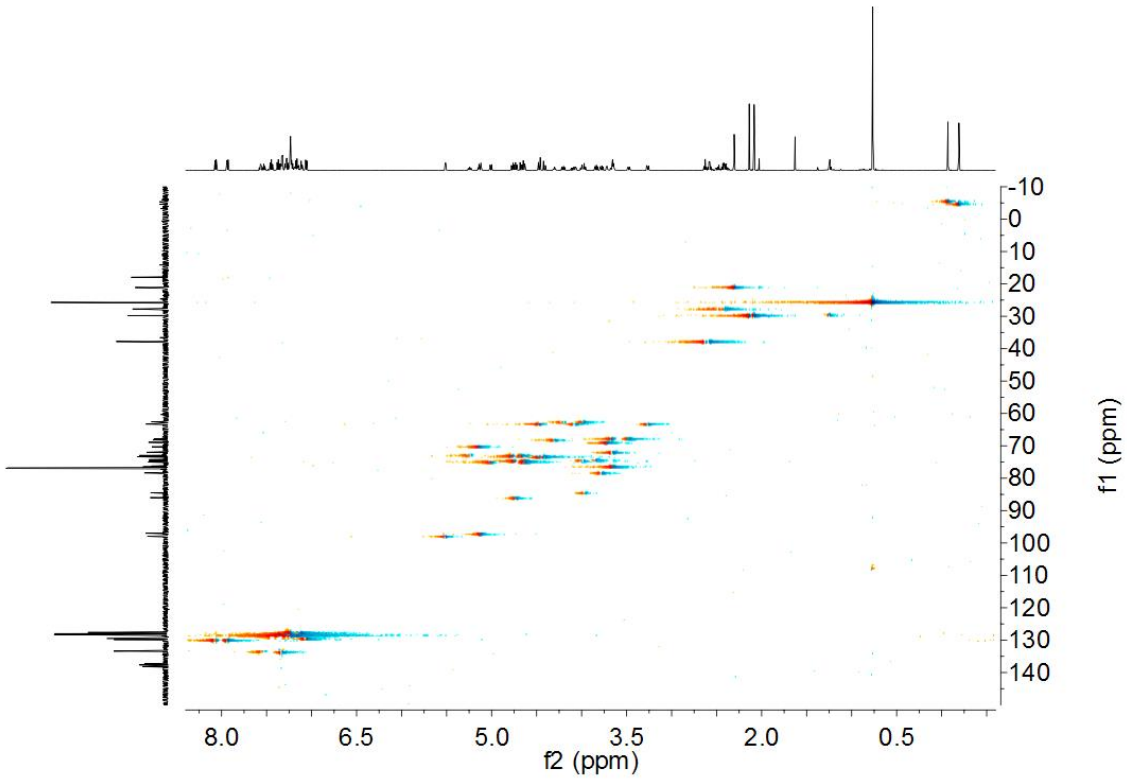
gCOSY ($CDCl_3$, 600 MHz) of **19**



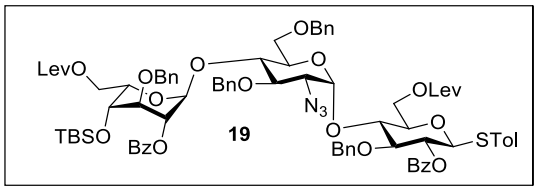


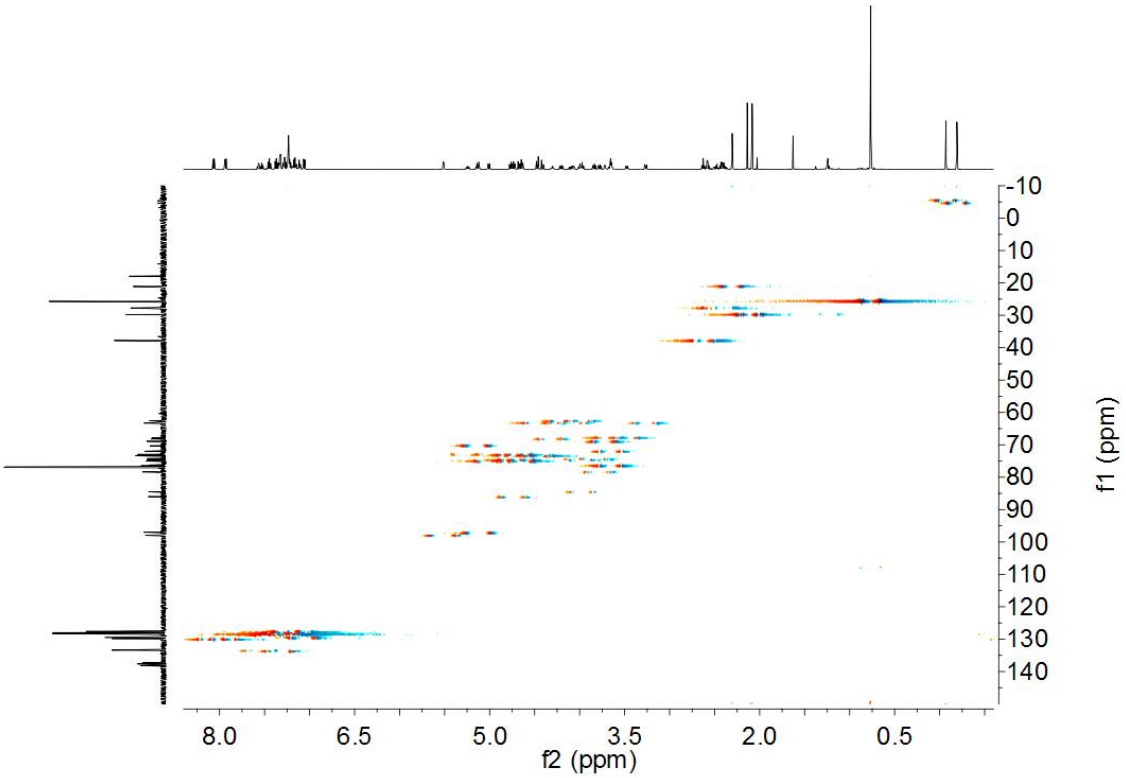
gHMQC ($CDCl_3$, 600 MHz) of **19**



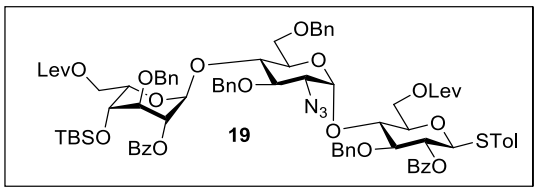


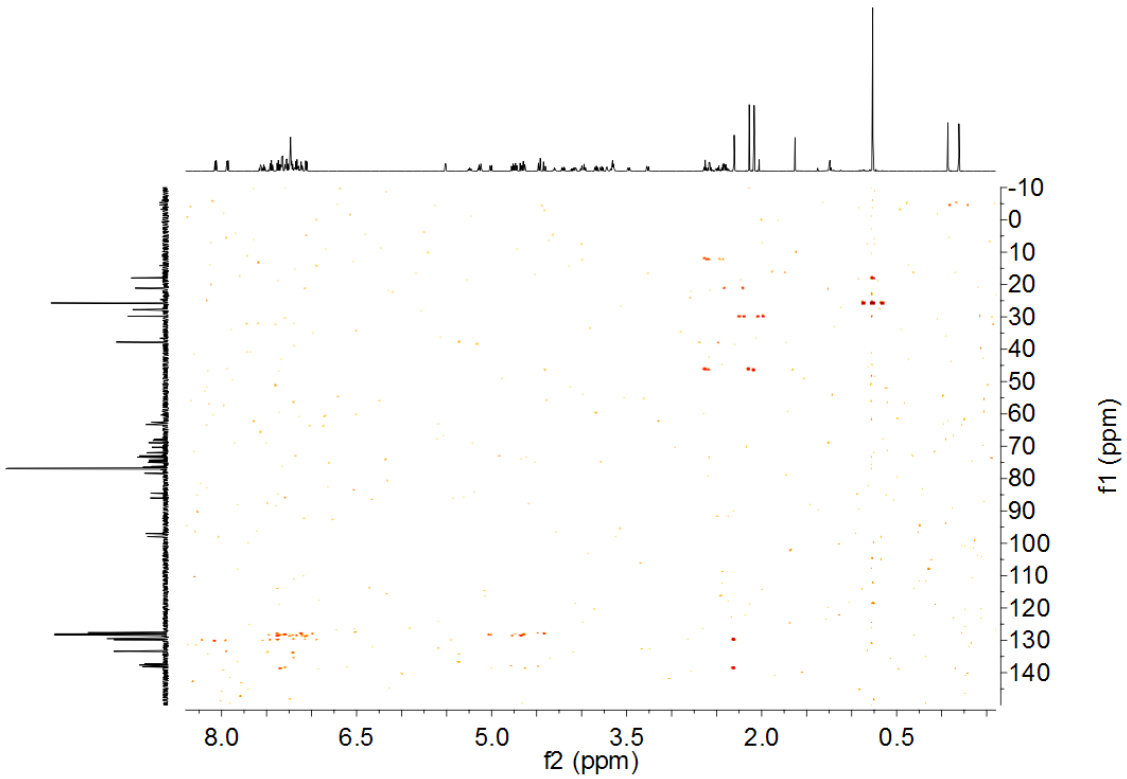
gHMQC (without ^{1}H decoupling) ($CDCl_3$, 600 MHz) of **19**



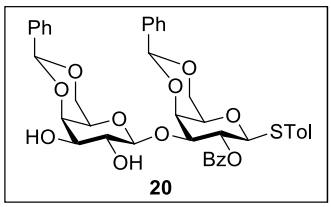


gHMBC ($CDCl_3$, 600 MHz) of **19**





^{1}H-NMR ($(CD_3)_2CO$, 500 MHz) of **20**



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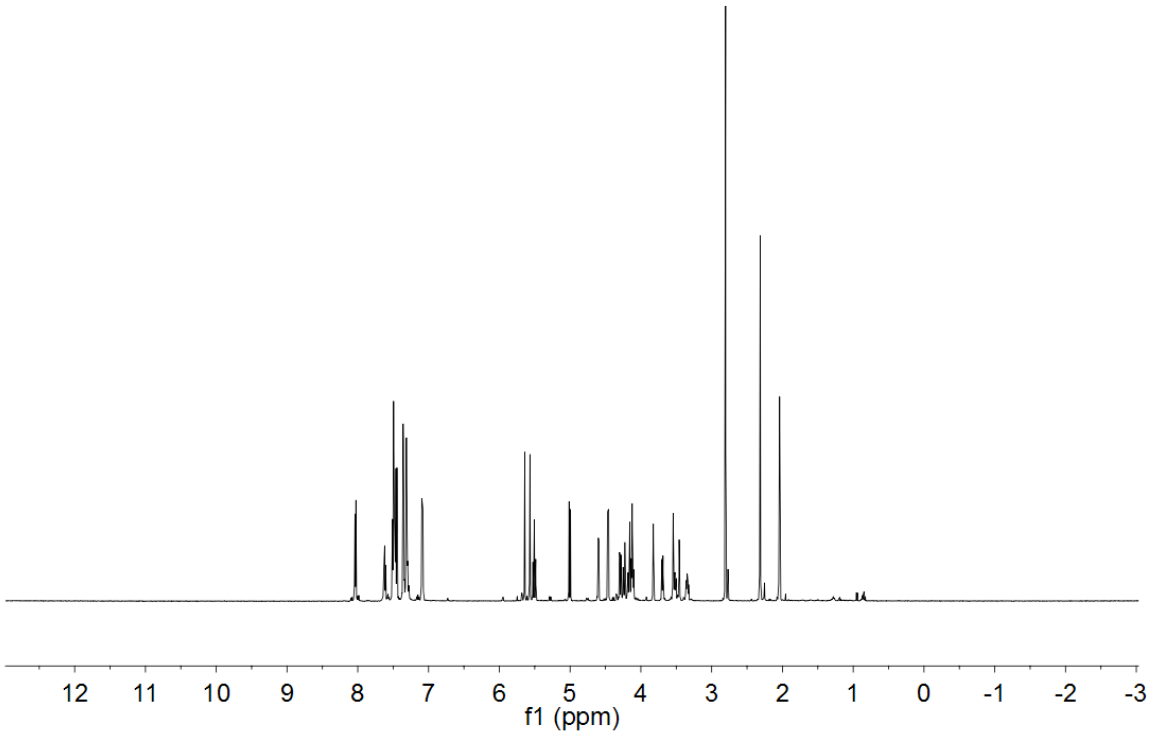
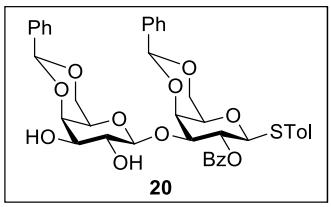


^{13}C-NMR ($(CD_3)_2CO$, 150 MHz) of **20**



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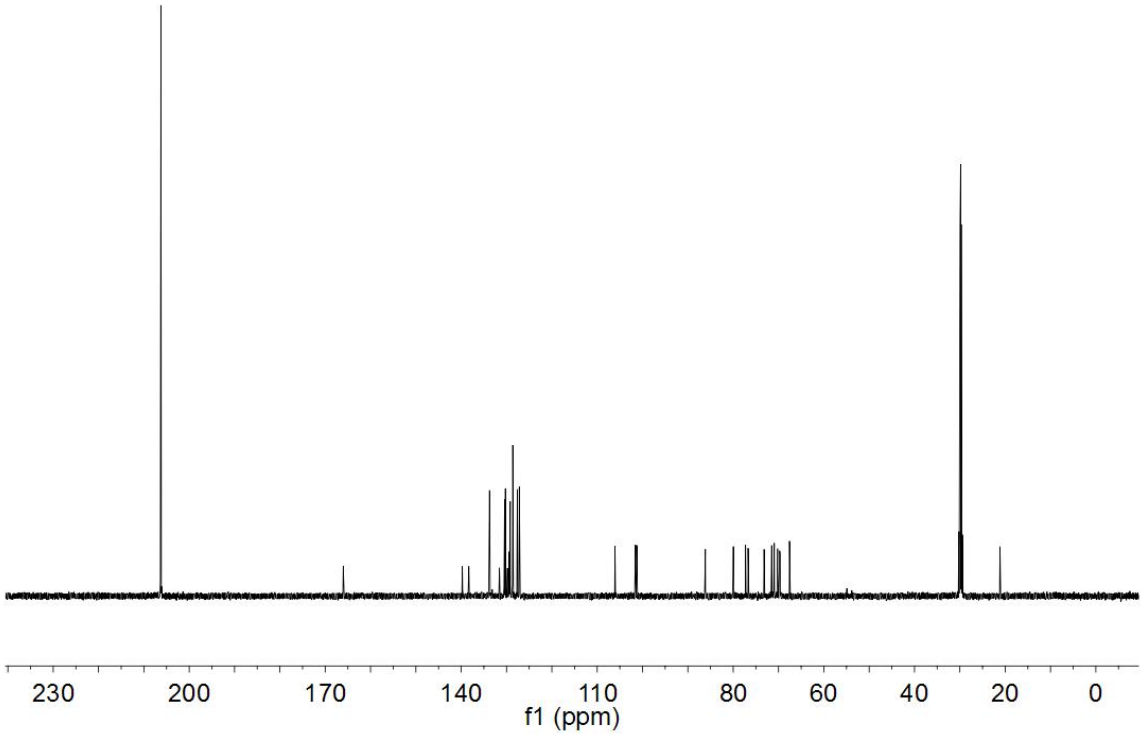
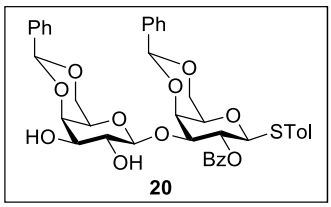


gCOSY ($(CD_3)_2CO$, 600 MHz) of **20**



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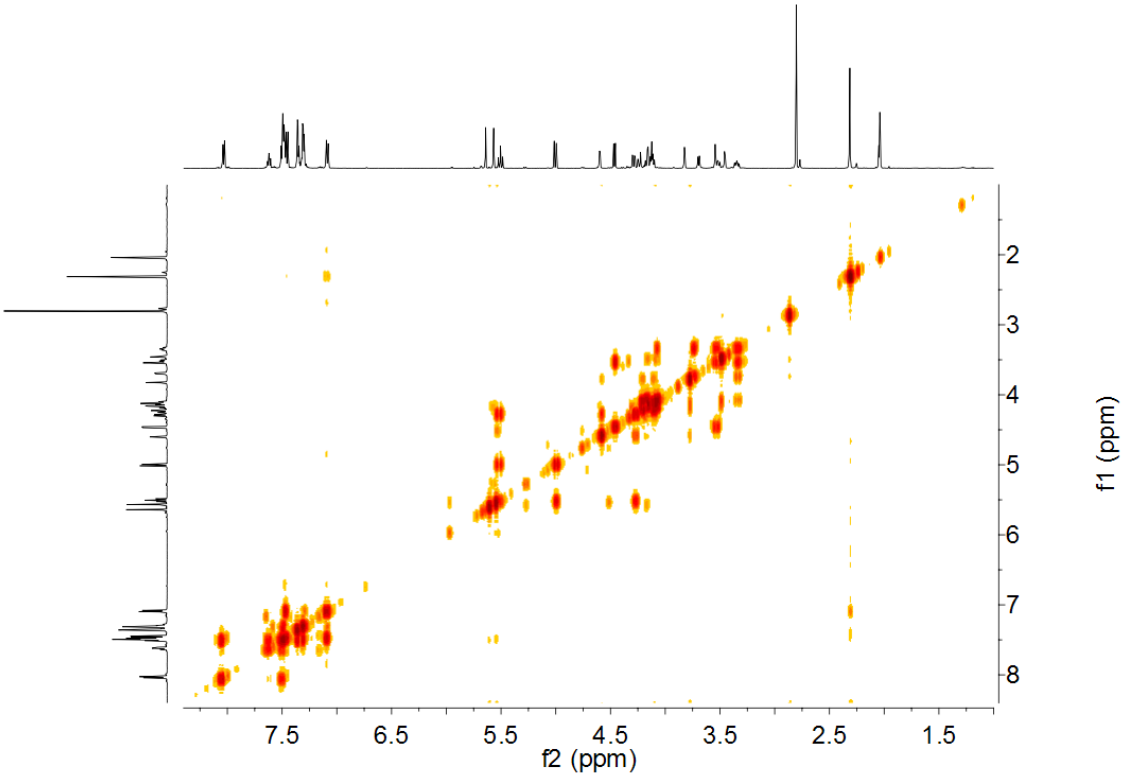
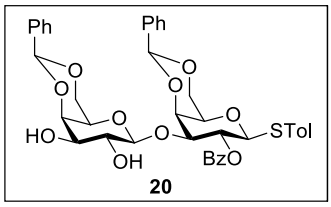


gHMQC ($(CD_3)_2CO$, 600 MHz) of **20**



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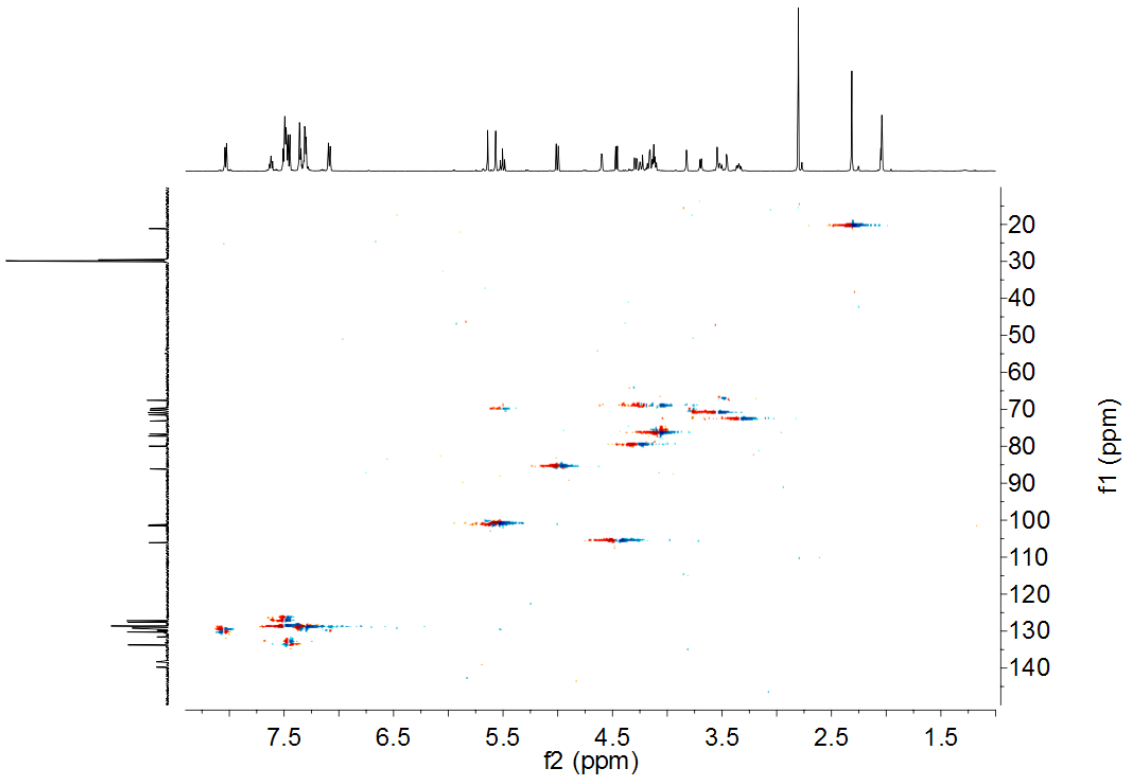
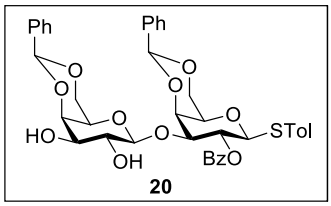


gHMQC (without ^{1}H decoupling) ($(CD_3)_2CO$, 600 MHz) of **20**



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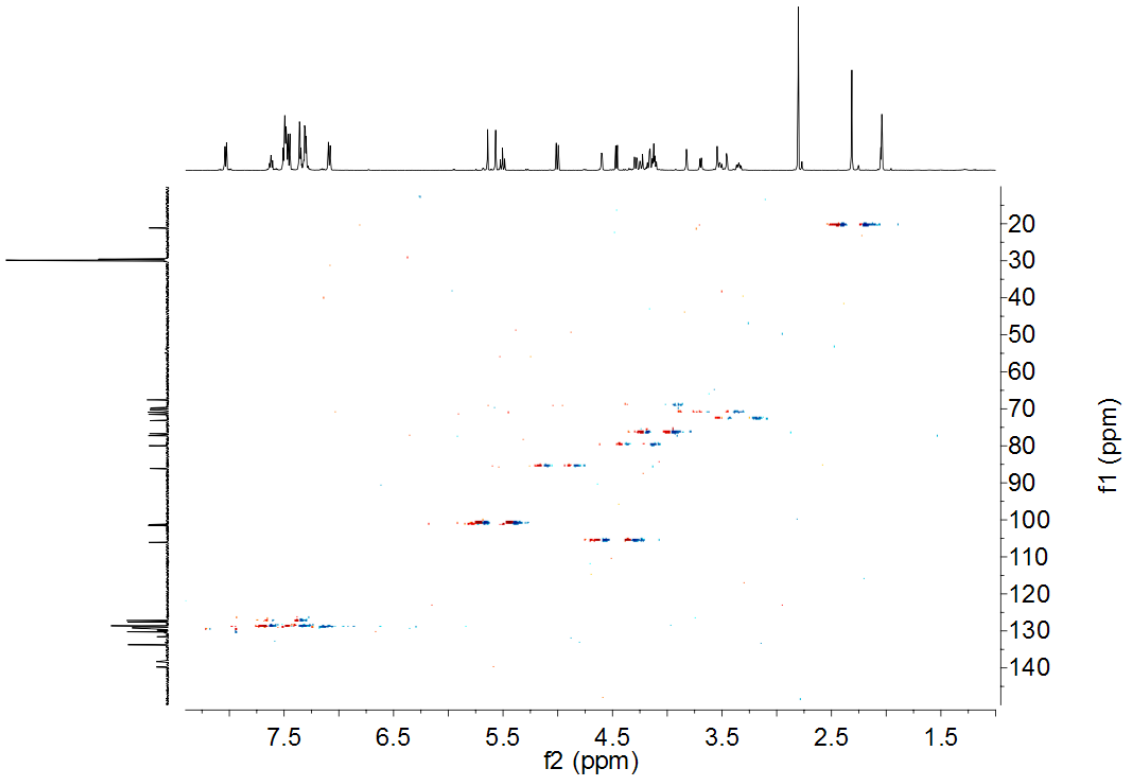
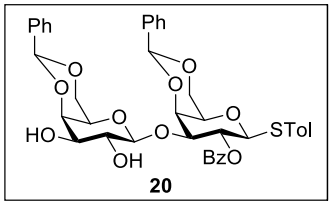
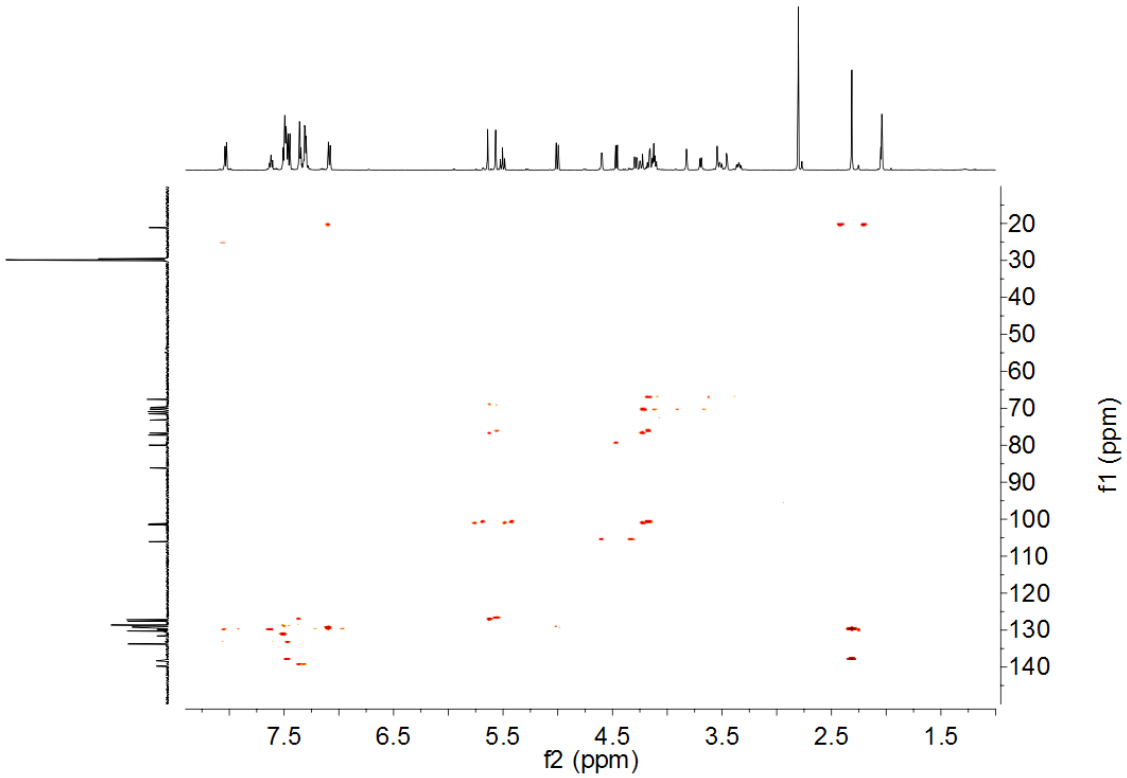
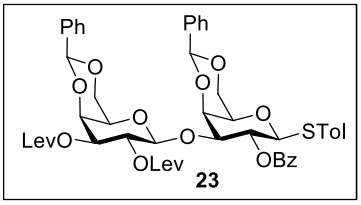


gHMBC ($(CD_3)_2CO$, 600 MHz) of **20**

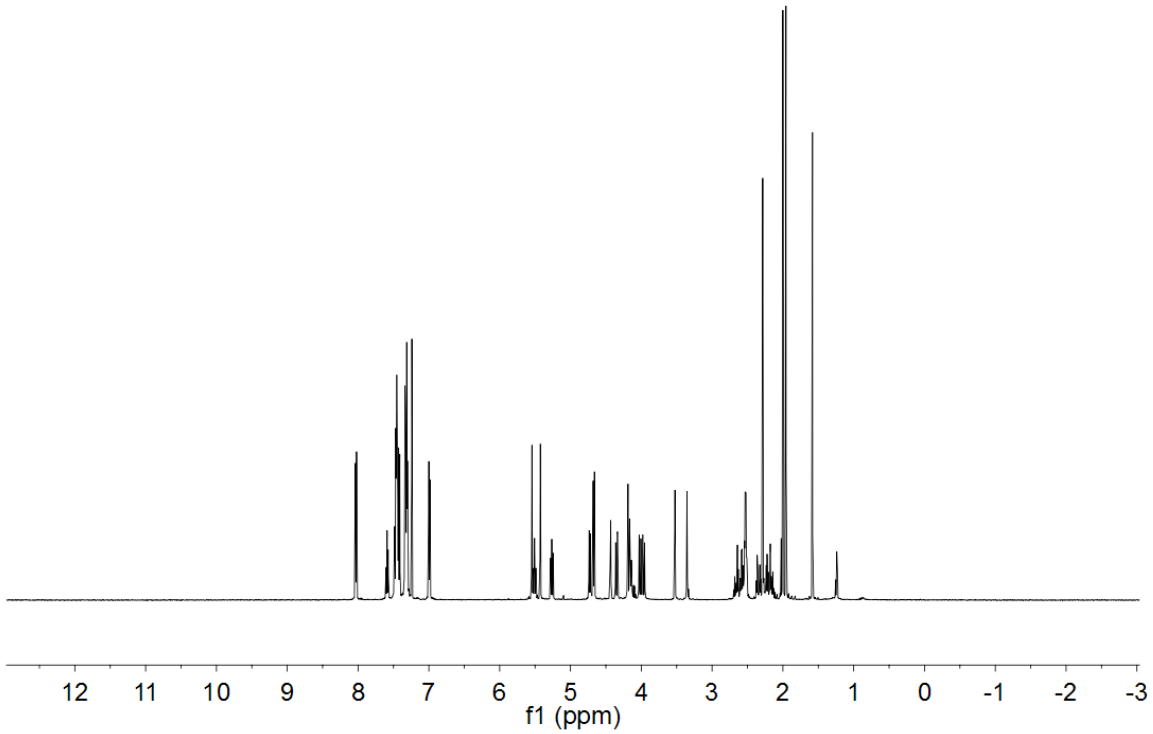




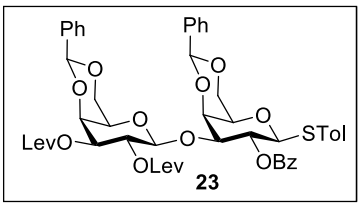
^{1}H-NMR ($CDCl_3$, 500 MHz) of **23**

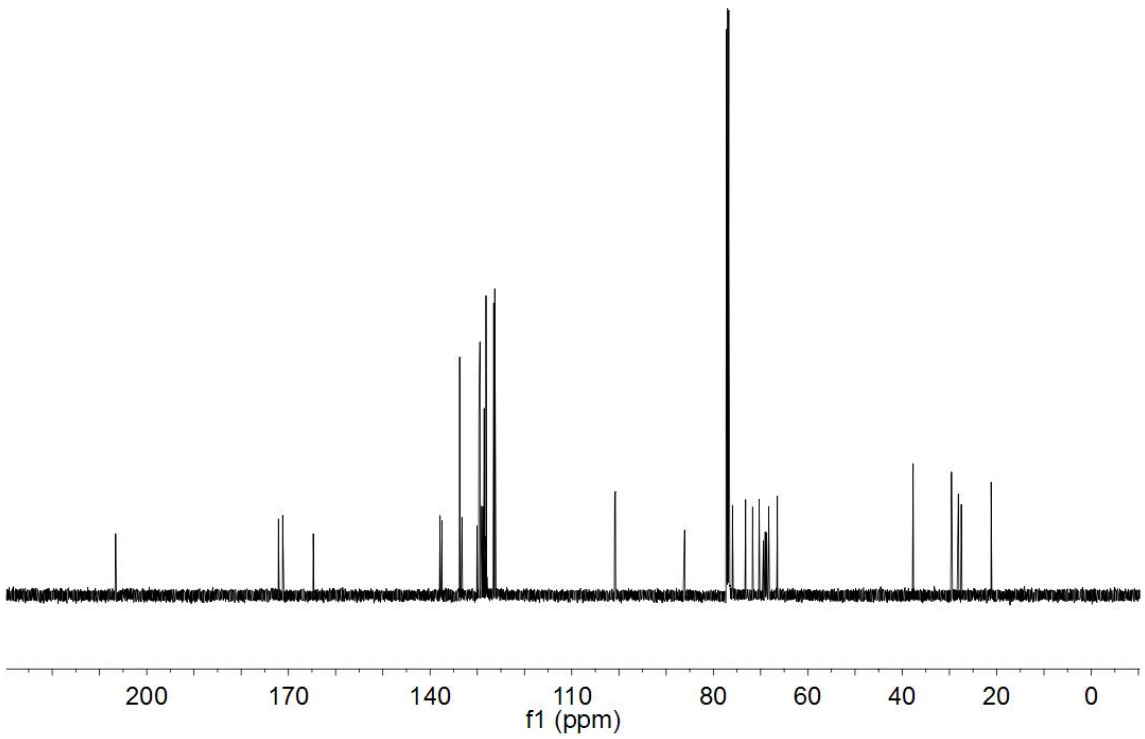


23

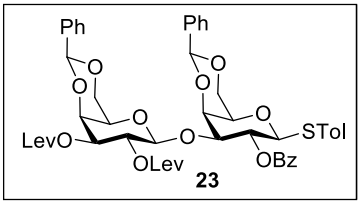


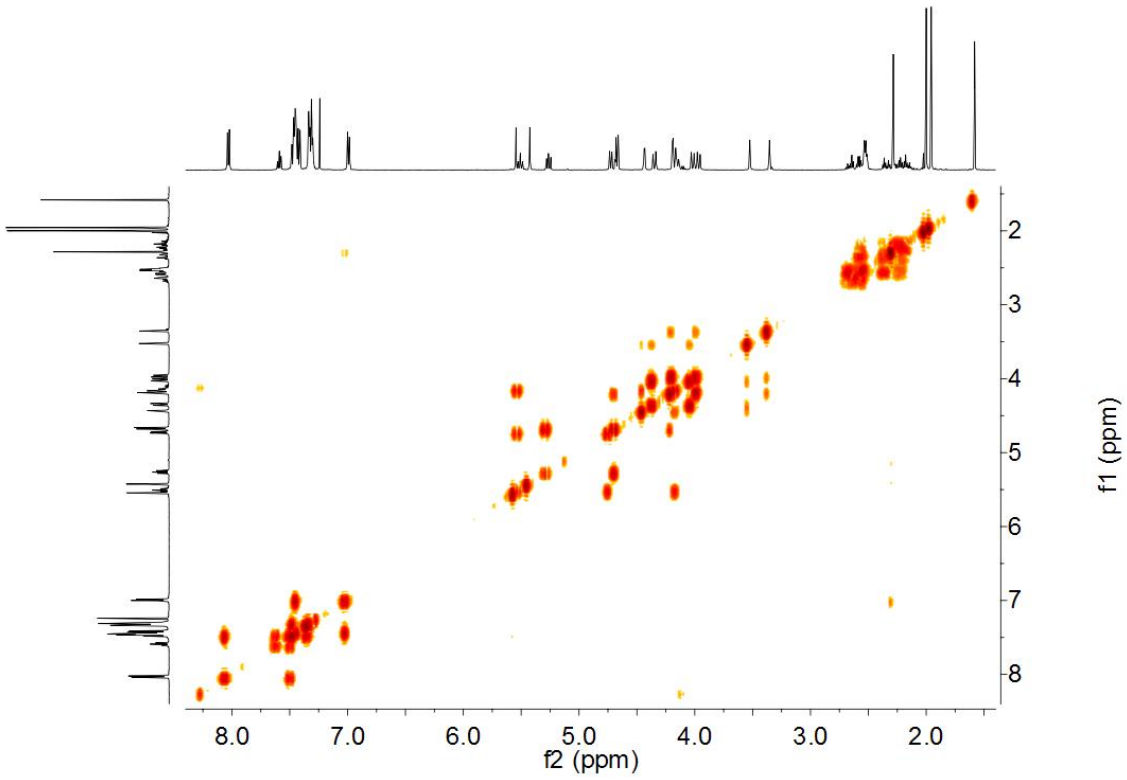
^{13}C-NMR ($CDCl_3$, 125 MHz) of **23**



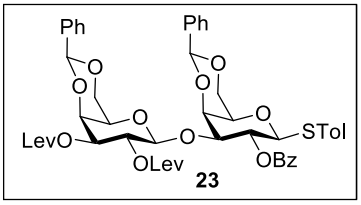


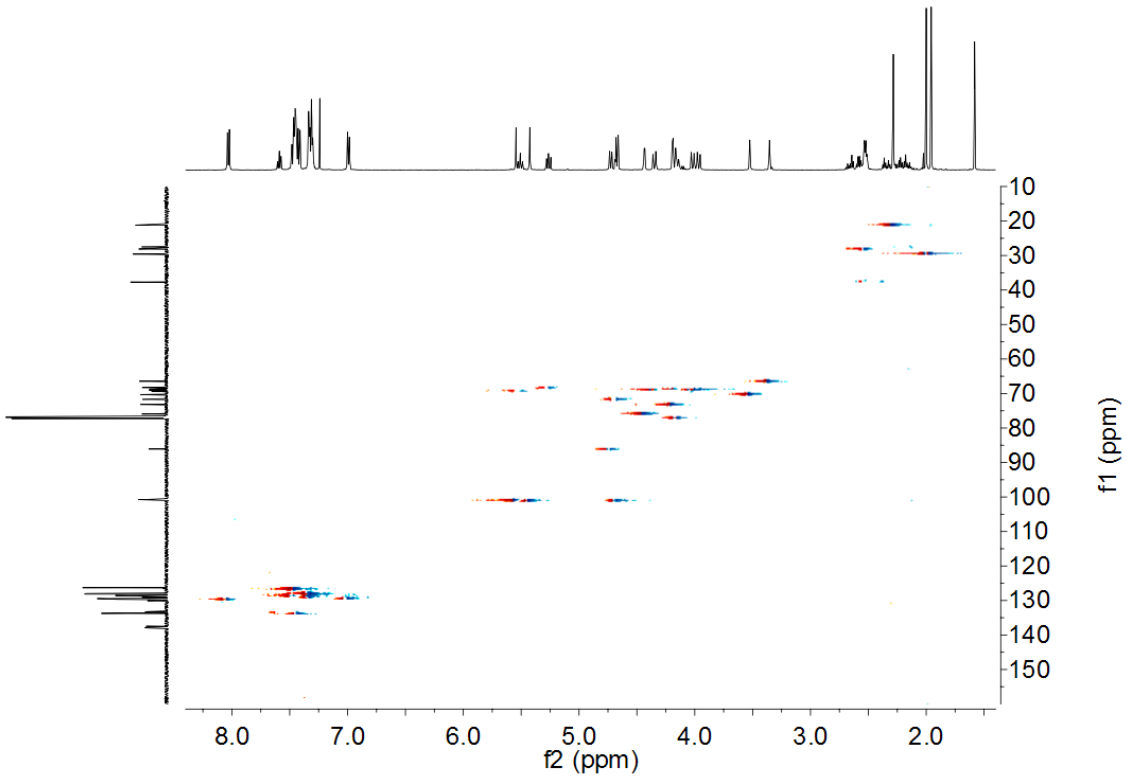
gCOSY ($CDCl_3$, 500 MHz) of **23**



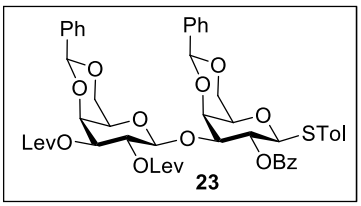


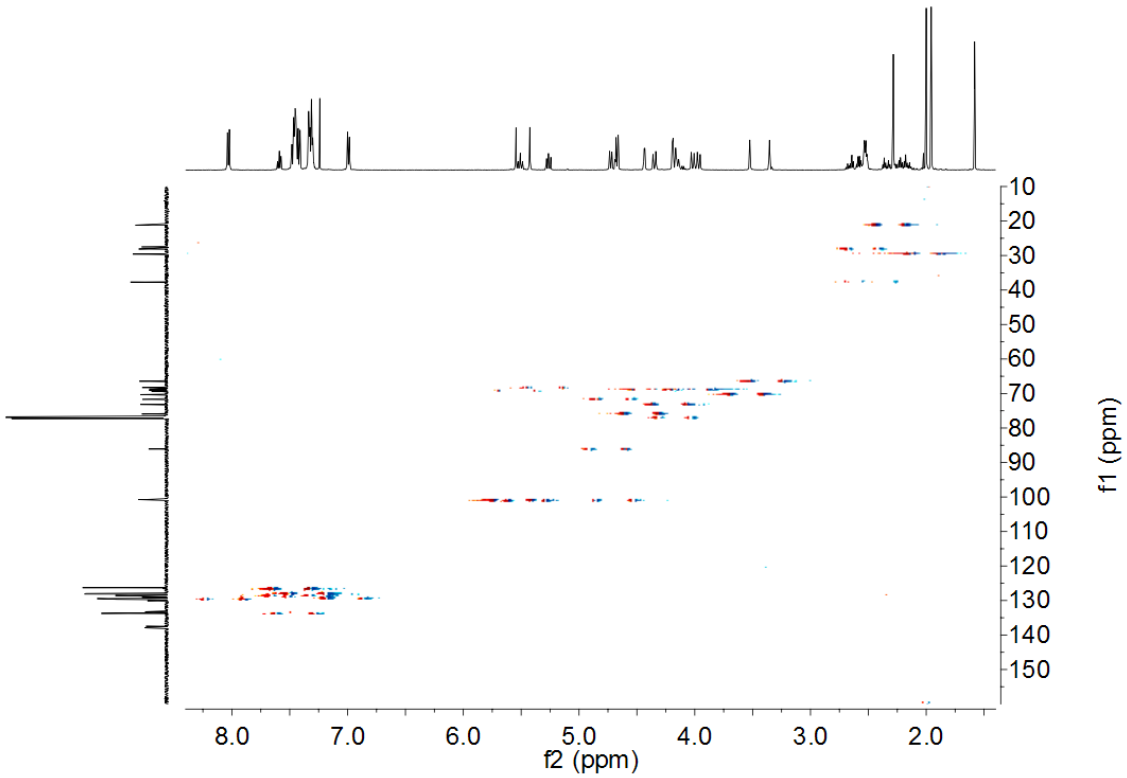
gHMQC ($CDCl_3$, 500 MHz) of **23**



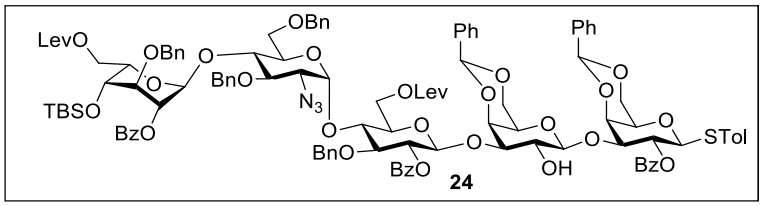


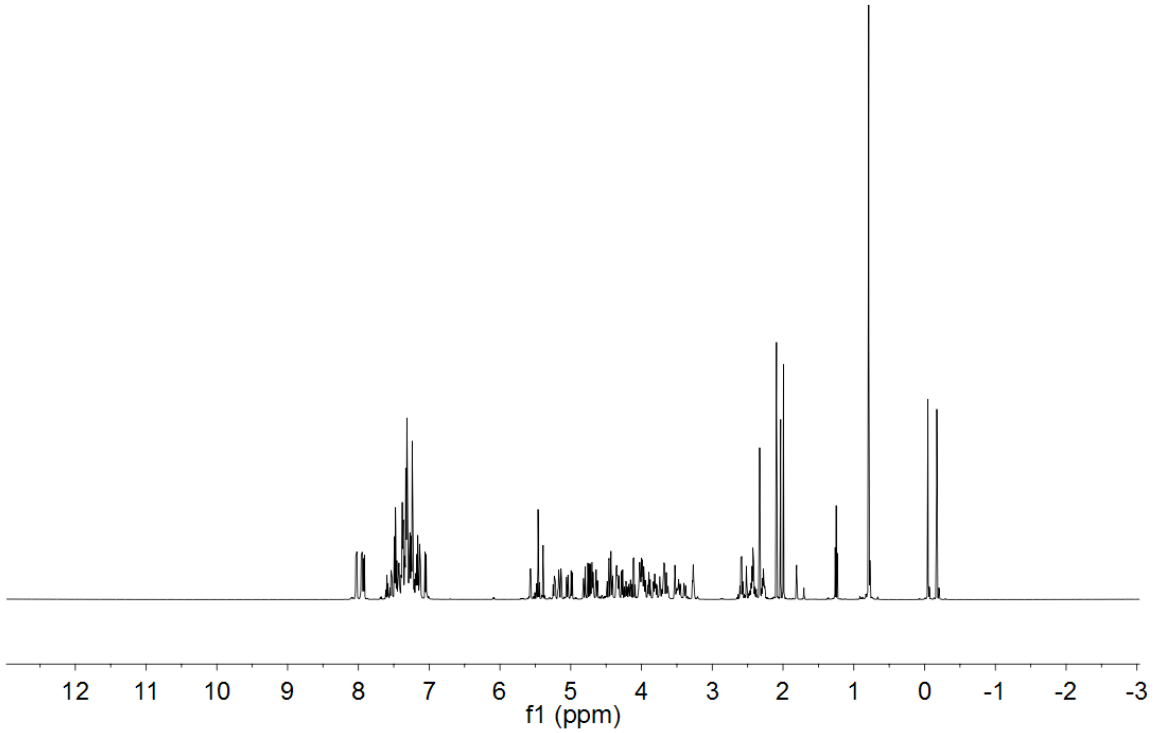
gHMQC (without ^{1}H decoupling) ($CDCl_3$, 500 MHz) of **23**



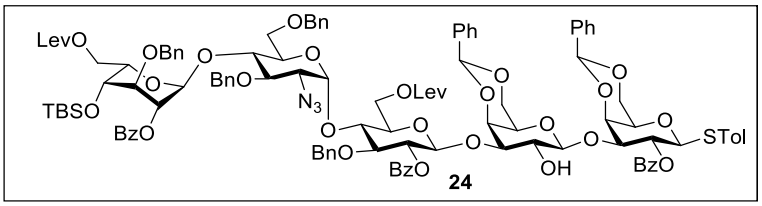


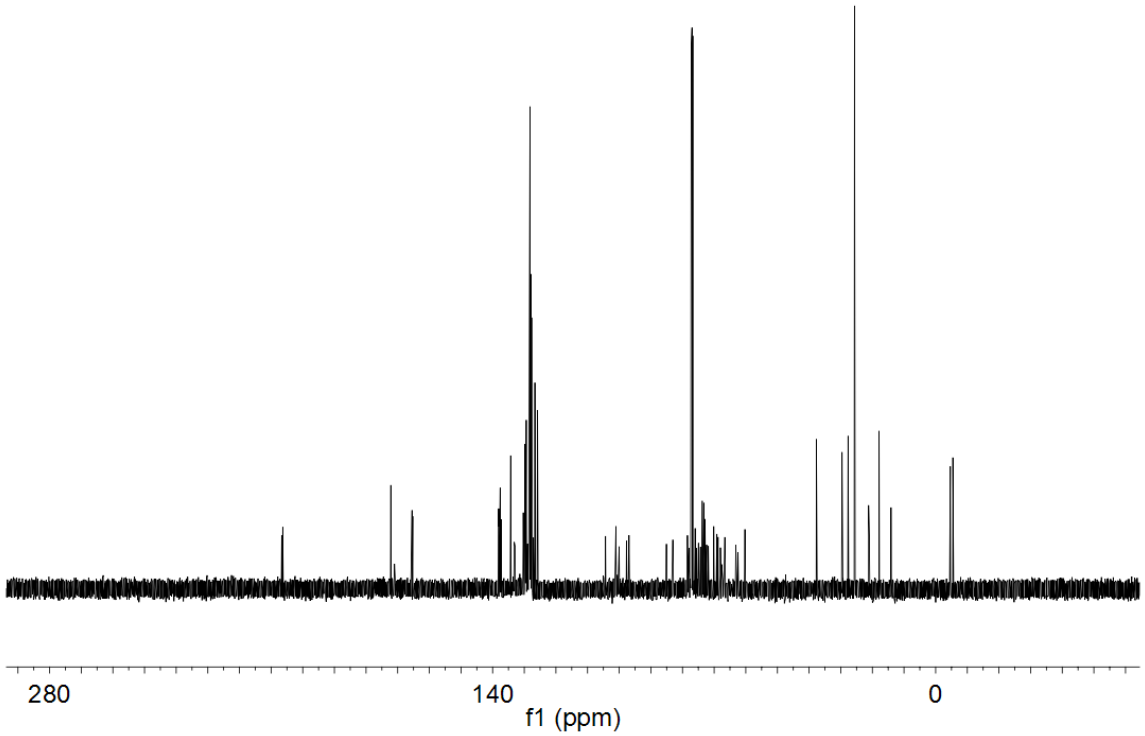
^{1}H-NMR ($CDCl_3$, 500 MHz) of **24**



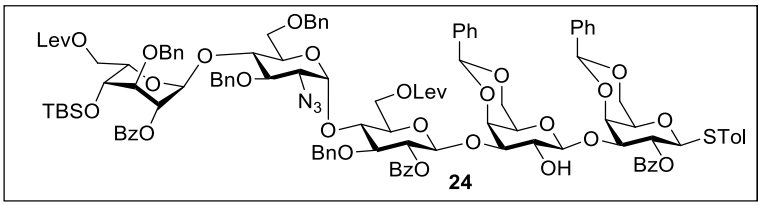


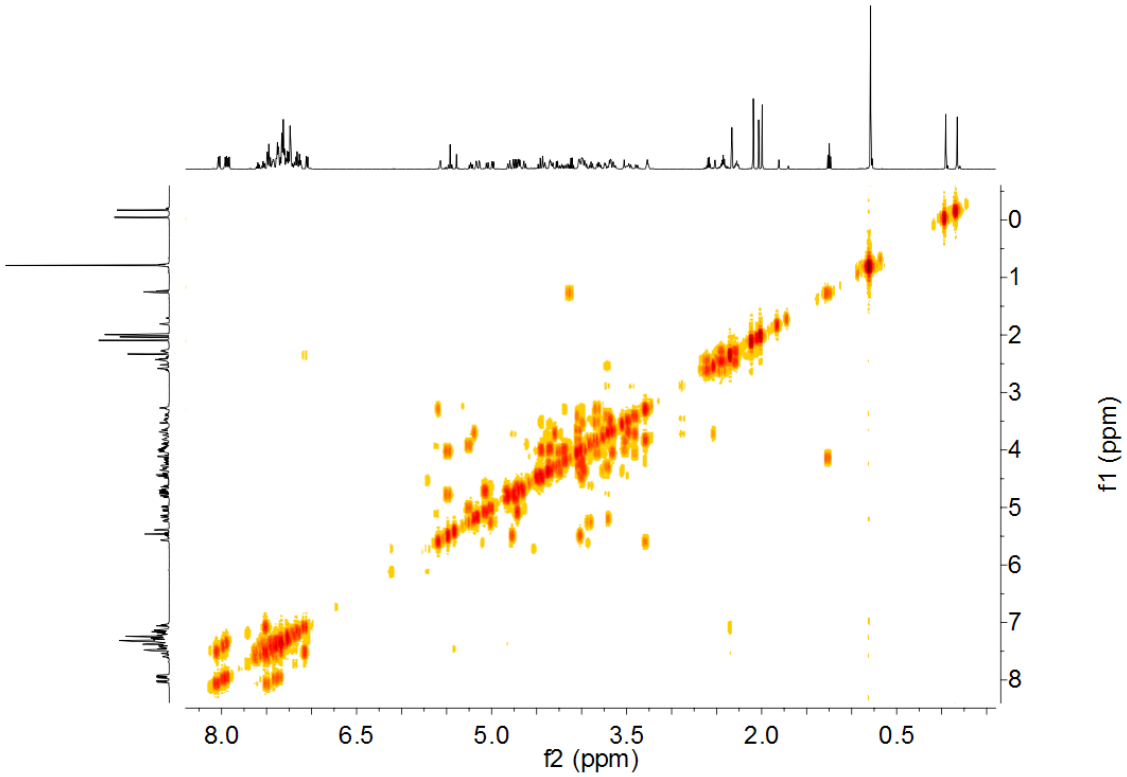
^{13}C-NMR ($CDCl_3$, 125 MHz) of **24**



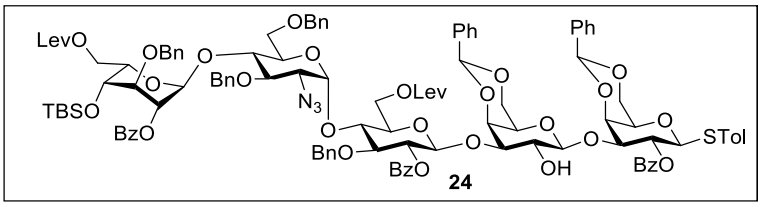


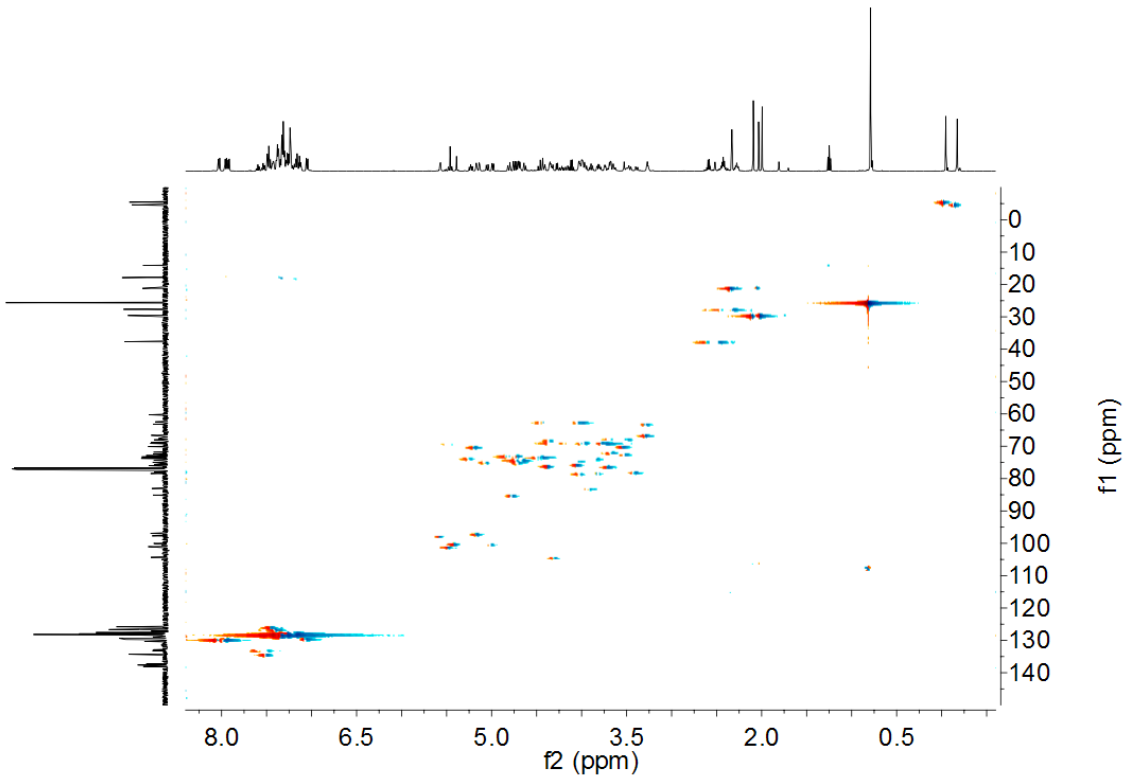
gCOSY ($CDCl_3$, 500 MHz) of **24**



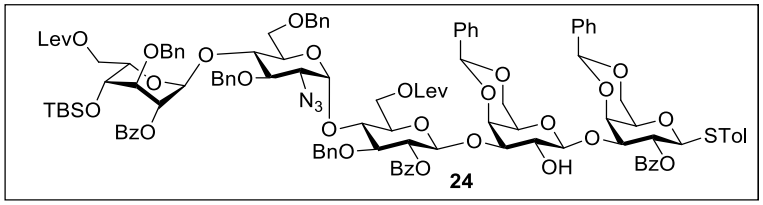


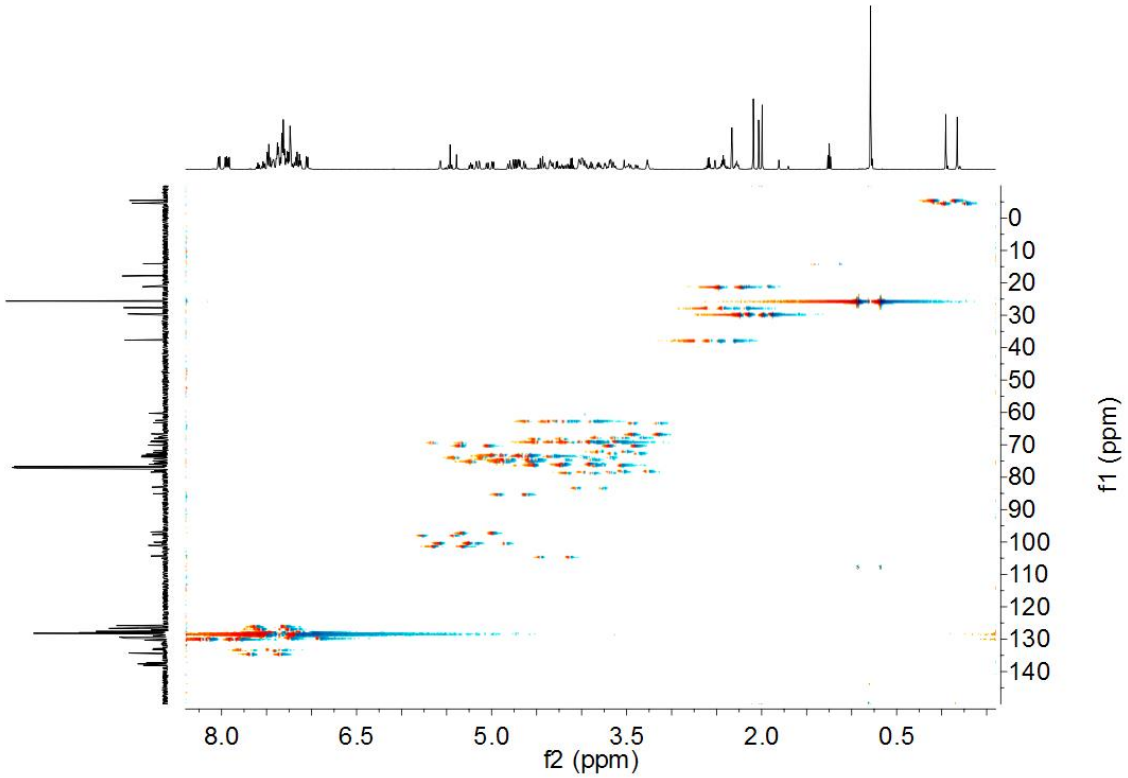
gHMQC ($CDCl_3$, 500 MHz) of **24**



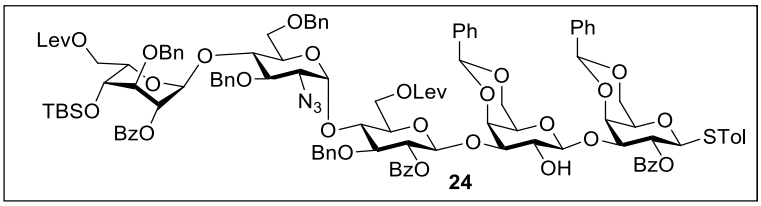


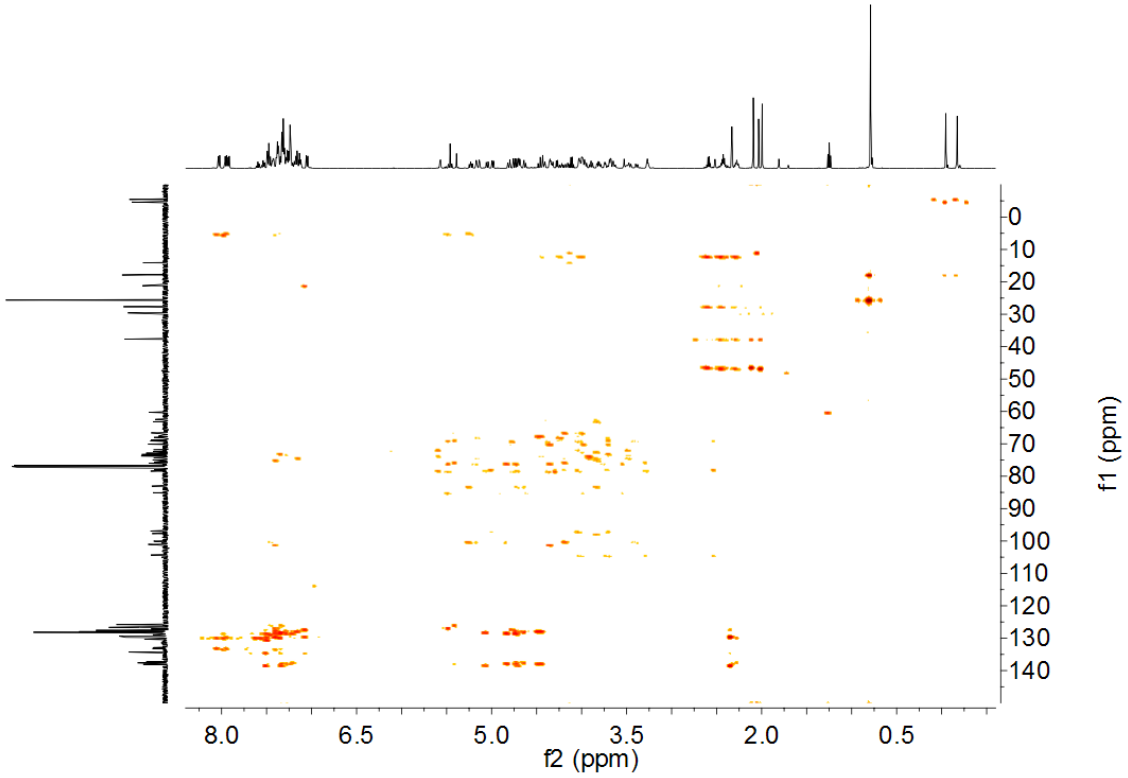
gHMQC (without ^{1}H decoupling) ($CDCl_3$, 500 MHz) of **24**



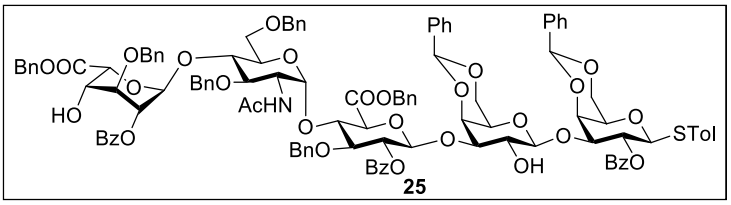


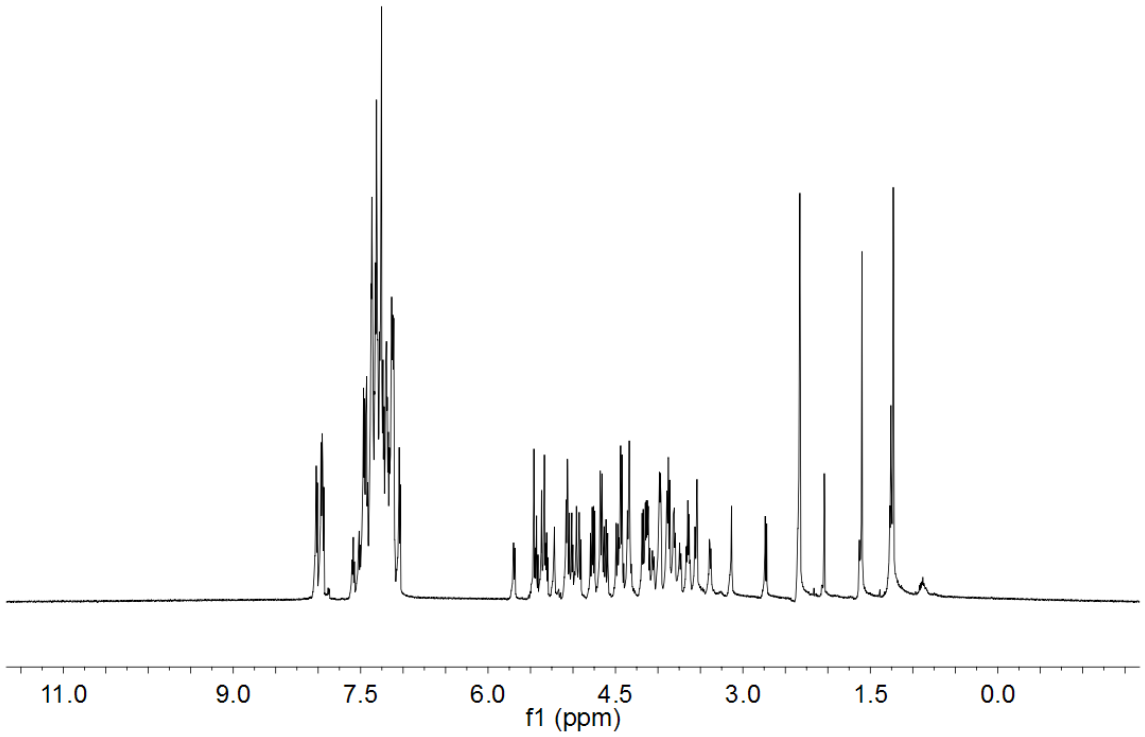
gHMBC ($CDCl_3$, 500 MHz) of **24**



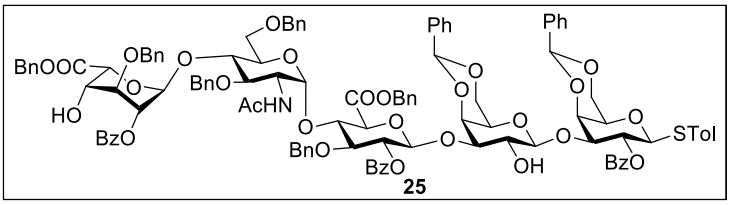


^{1}H-NMR ($CDCl_3$, 500 MHz) of **25**





^{13}C-NMR ($CDCl_3$, 150 MHz) of **25**



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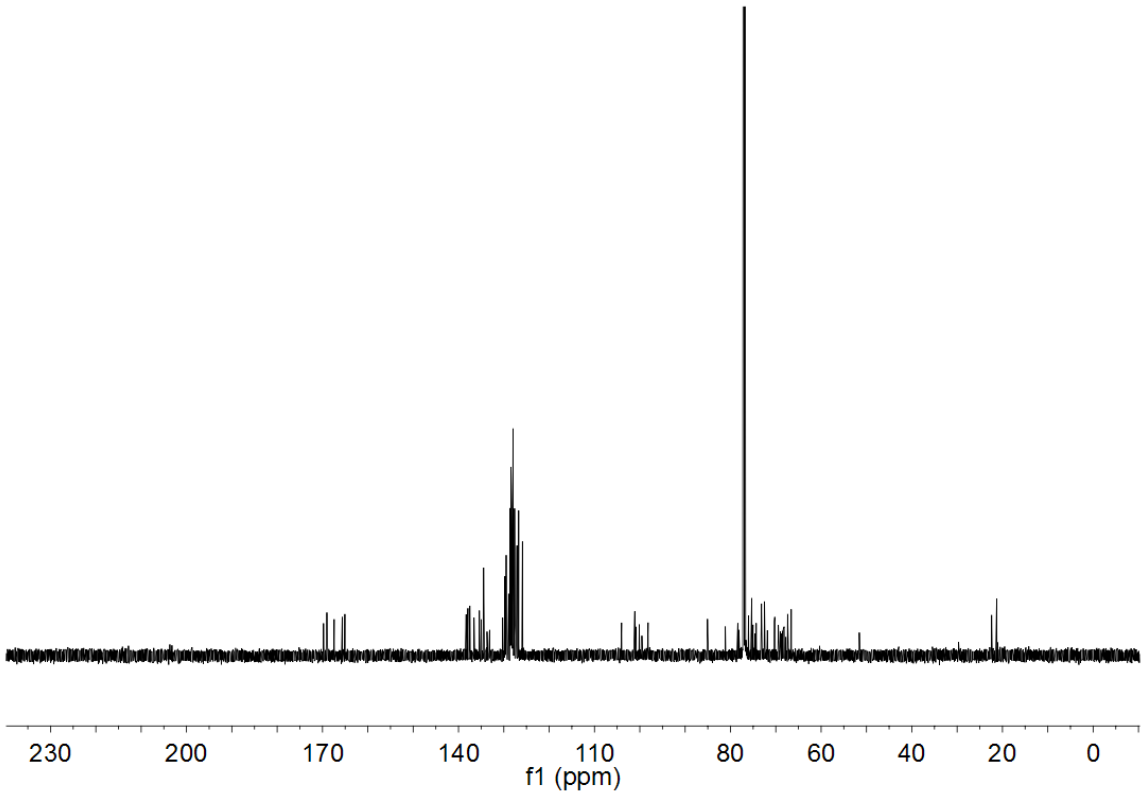
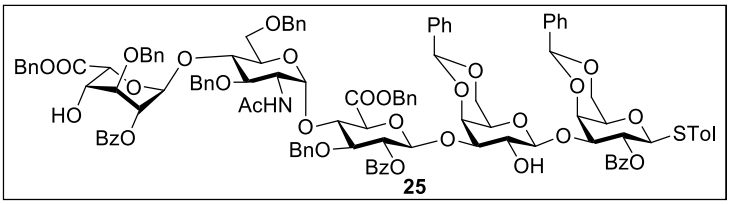
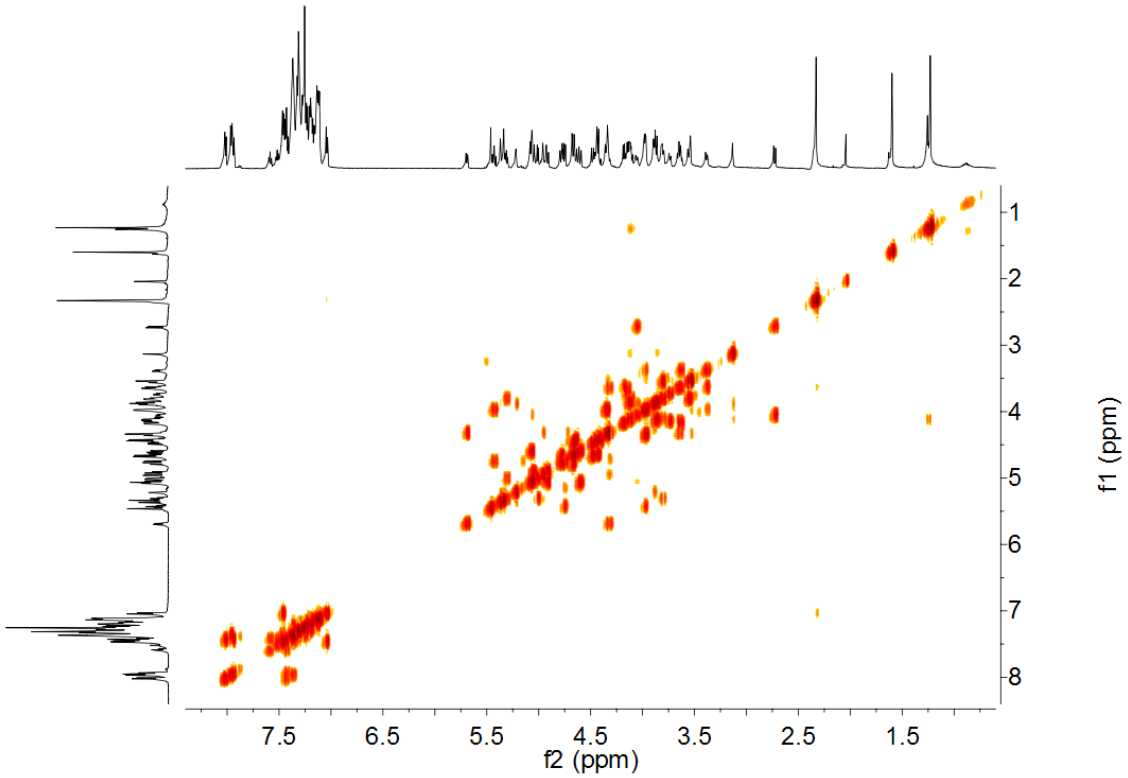
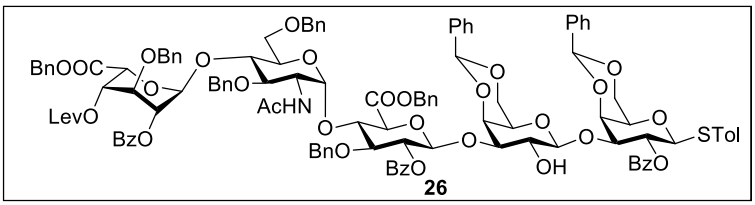


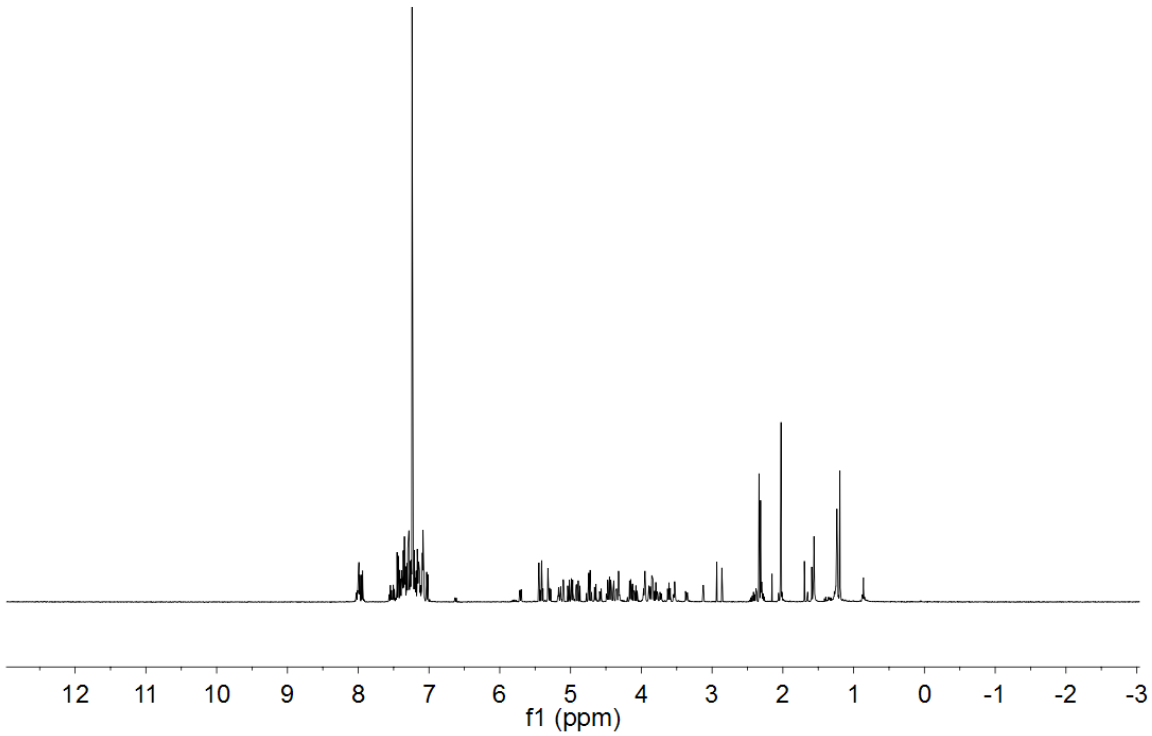
gCOSY ($CDCl_3$, 600 MHz) of **25**



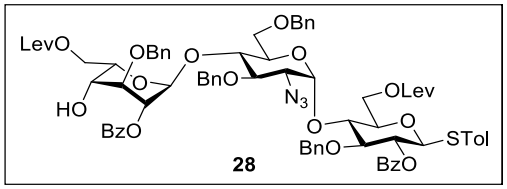


^{1}H-NMR ($CDCl_3$, 500 MHz) of **26**





^{1}H-NMR ($CDCl_3$, 500 MHz) of **28**



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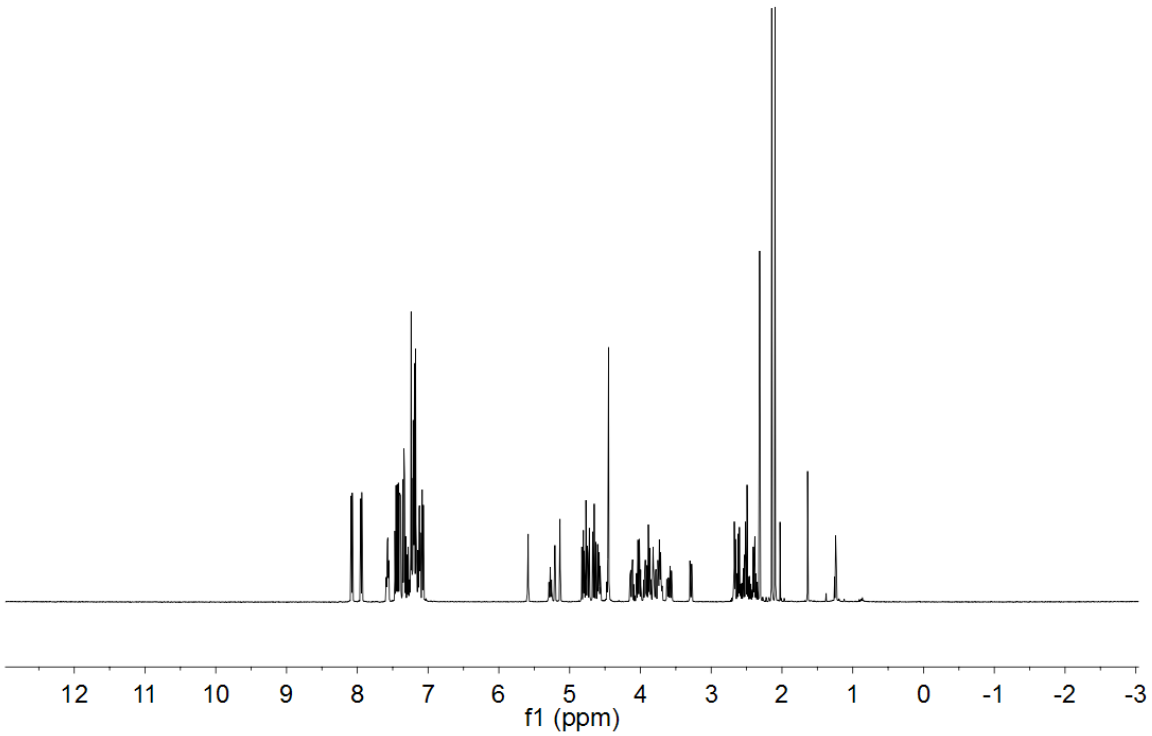
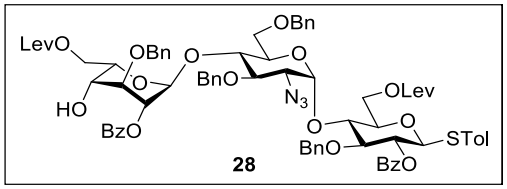


^{13}C-NMR ($CDCl_3$, 125 MHz) of **28**



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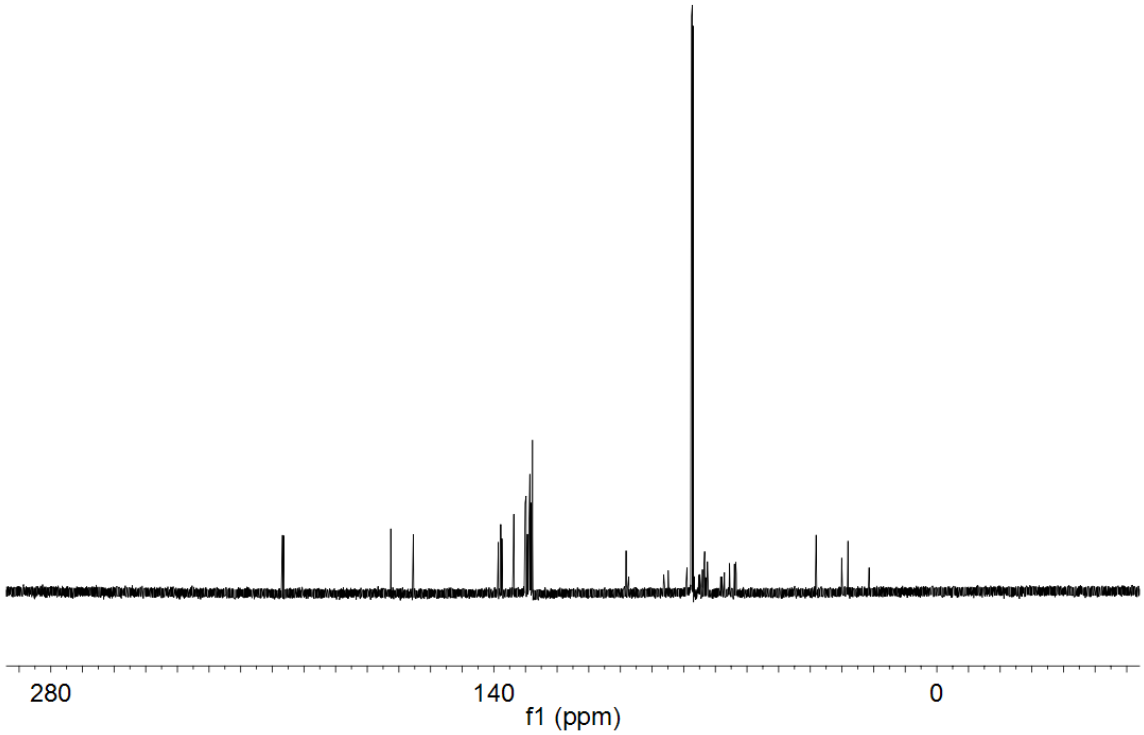
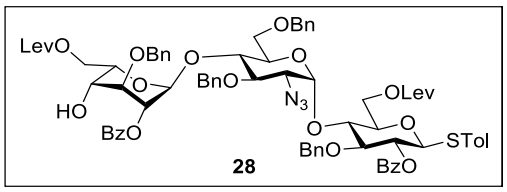


gCOSY ($CDCl_3$, 500 MHz) of **28**



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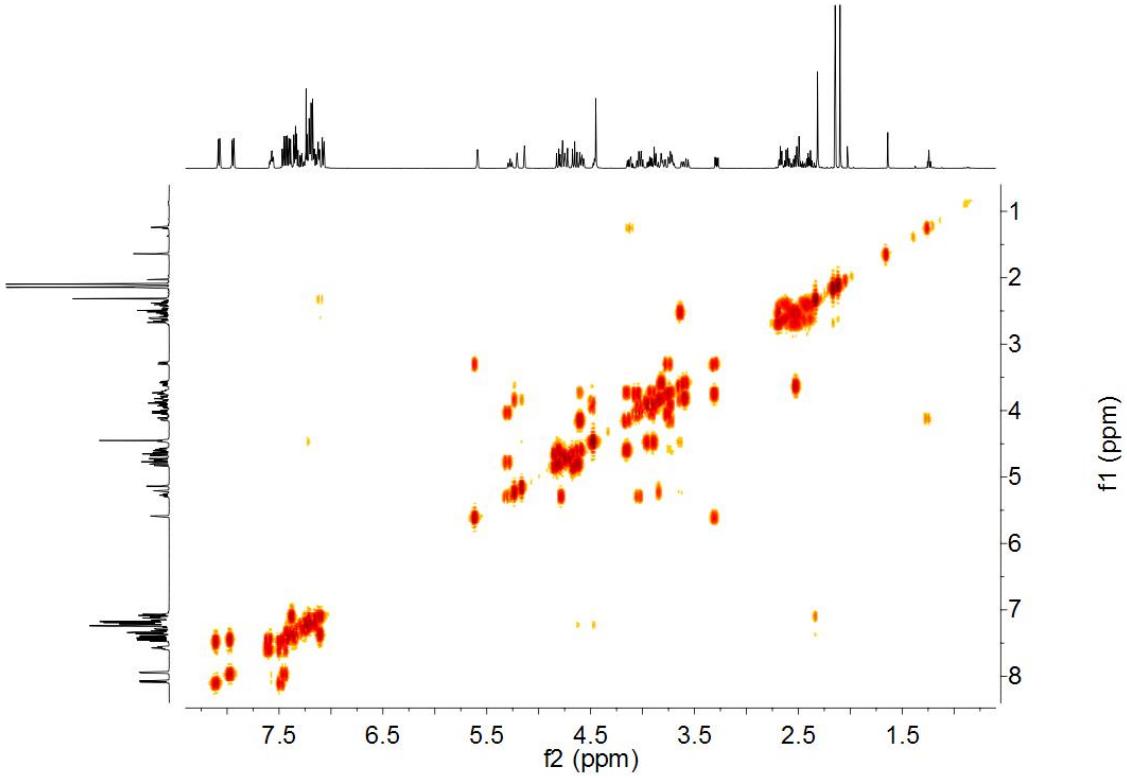
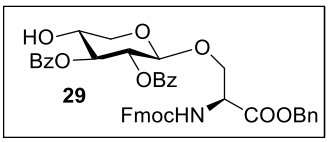
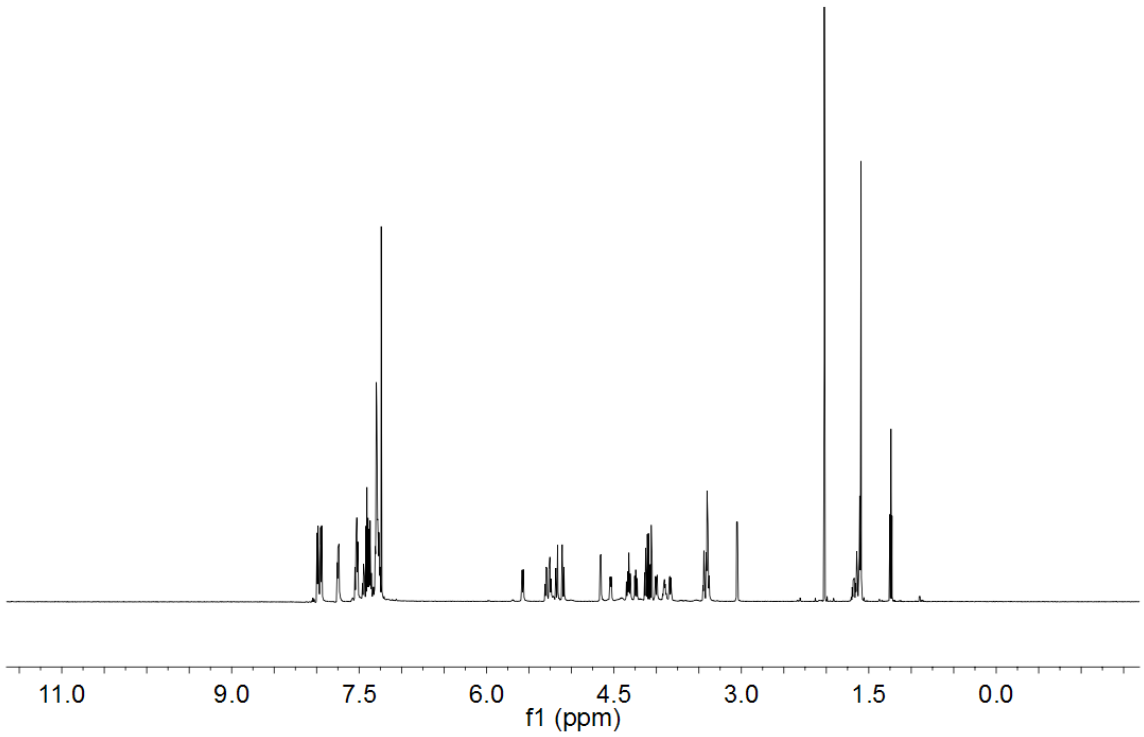
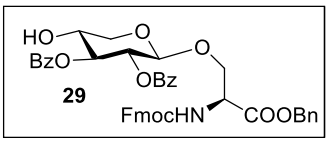


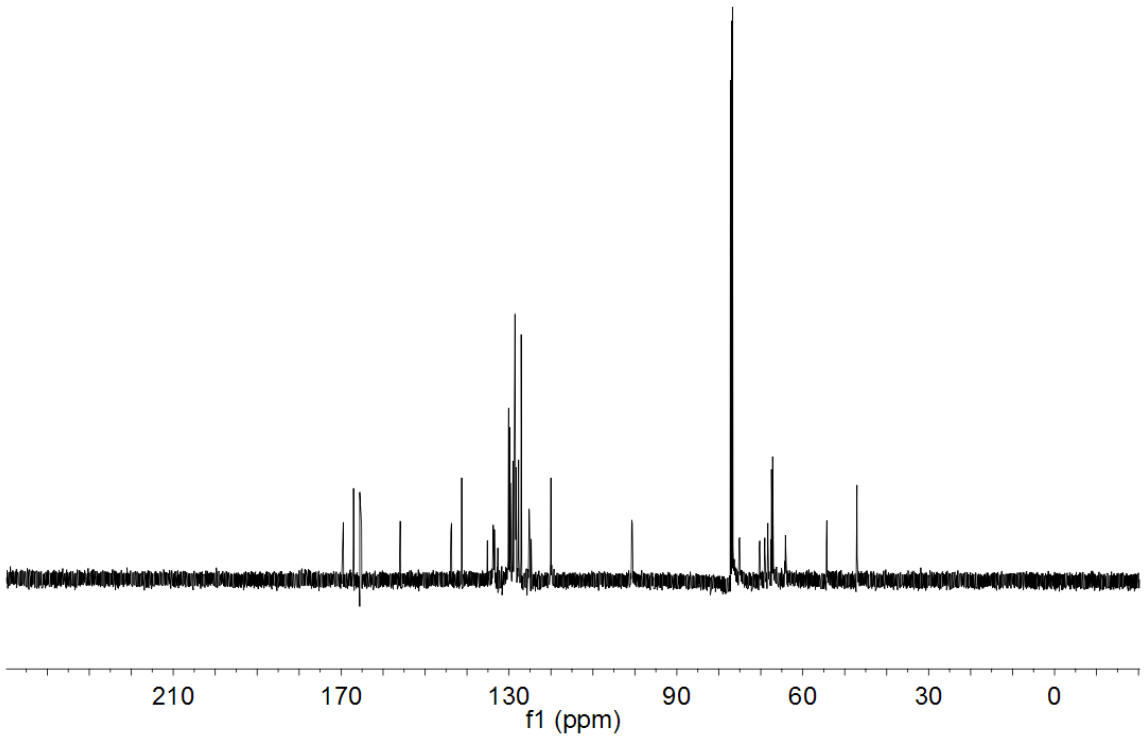
^{1}H-NMR ($CDCl_3$, 500 MHz) of **29**



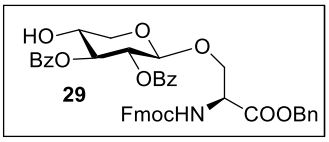


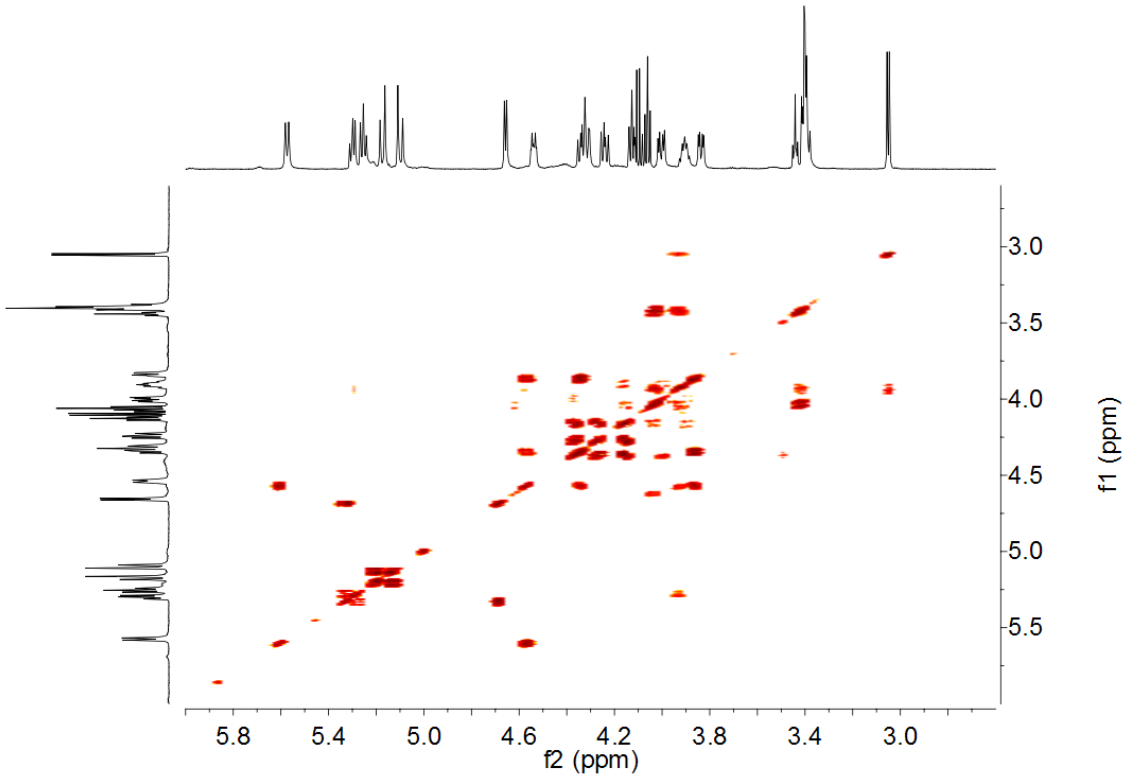
^{13}C-NMR ($CDCl_3$, 125 MHz) of **29**



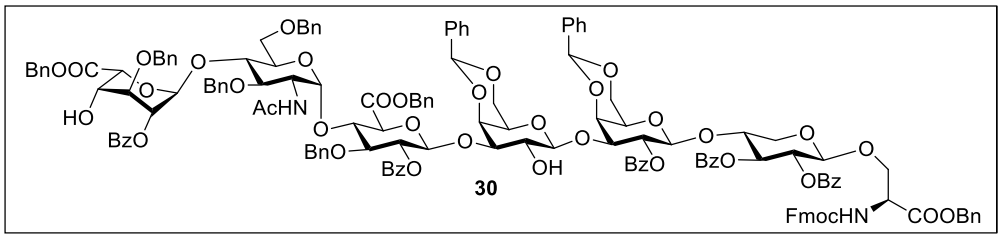


gCOSY ($CDCl_3$, 500 MHz) of **29**





^{1}H-NMR ($CDCl_3$, 500 MHz) of **30**



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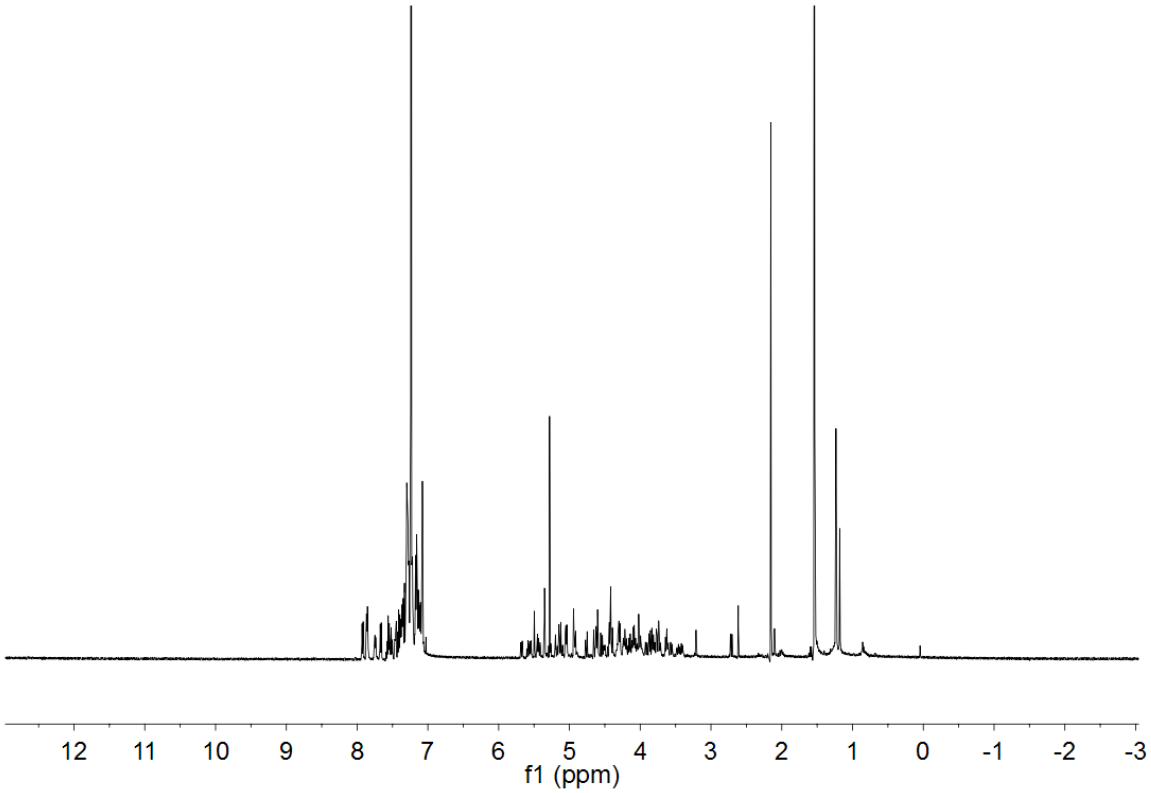
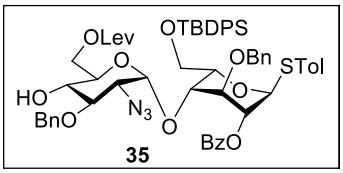
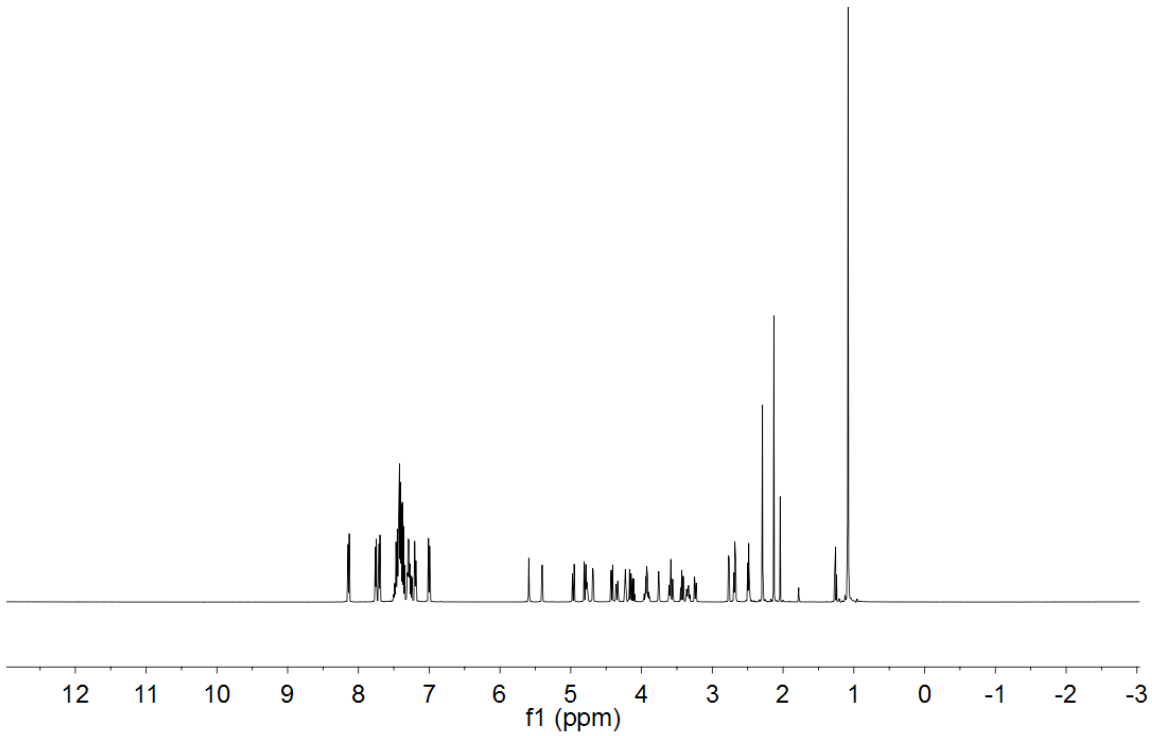
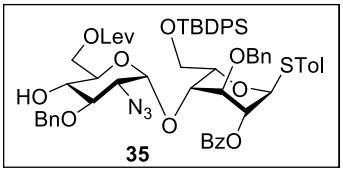


^{1}H-NMR ($CDCl_3$, 500 MHz) of **35**





^{13}C-NMR ($CDCl_3$, 125 MHz) of **35**



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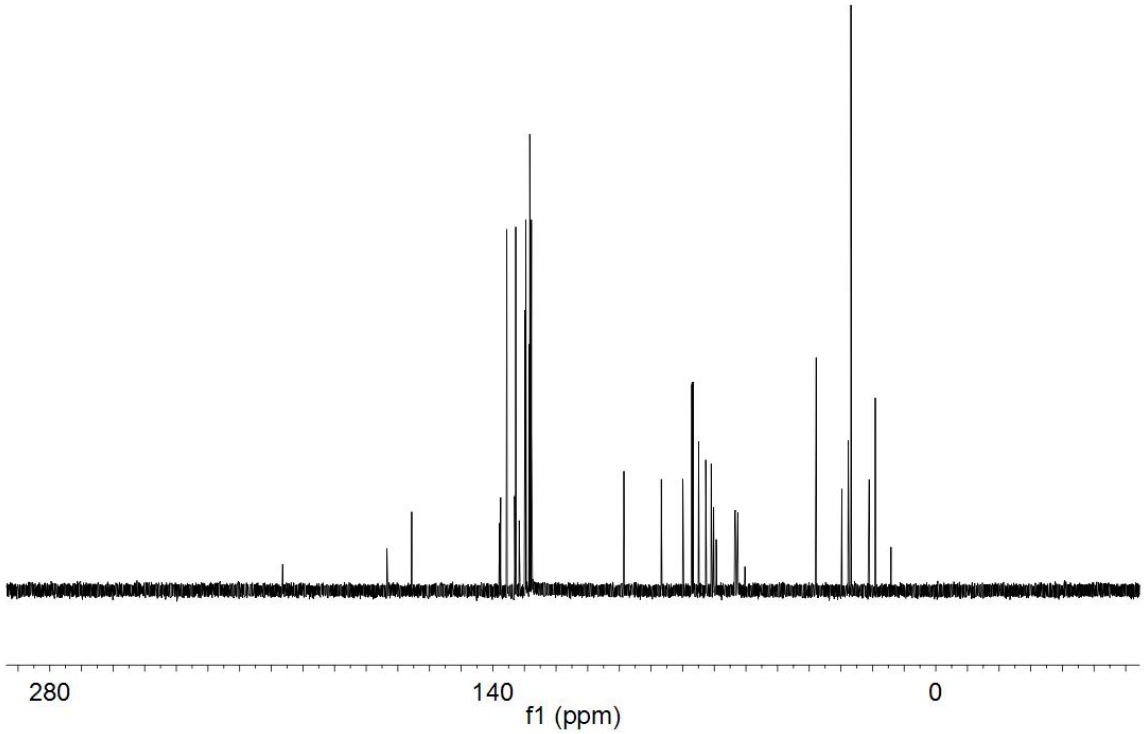
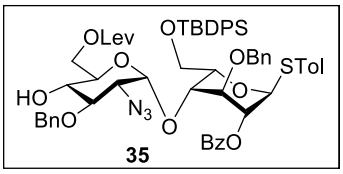
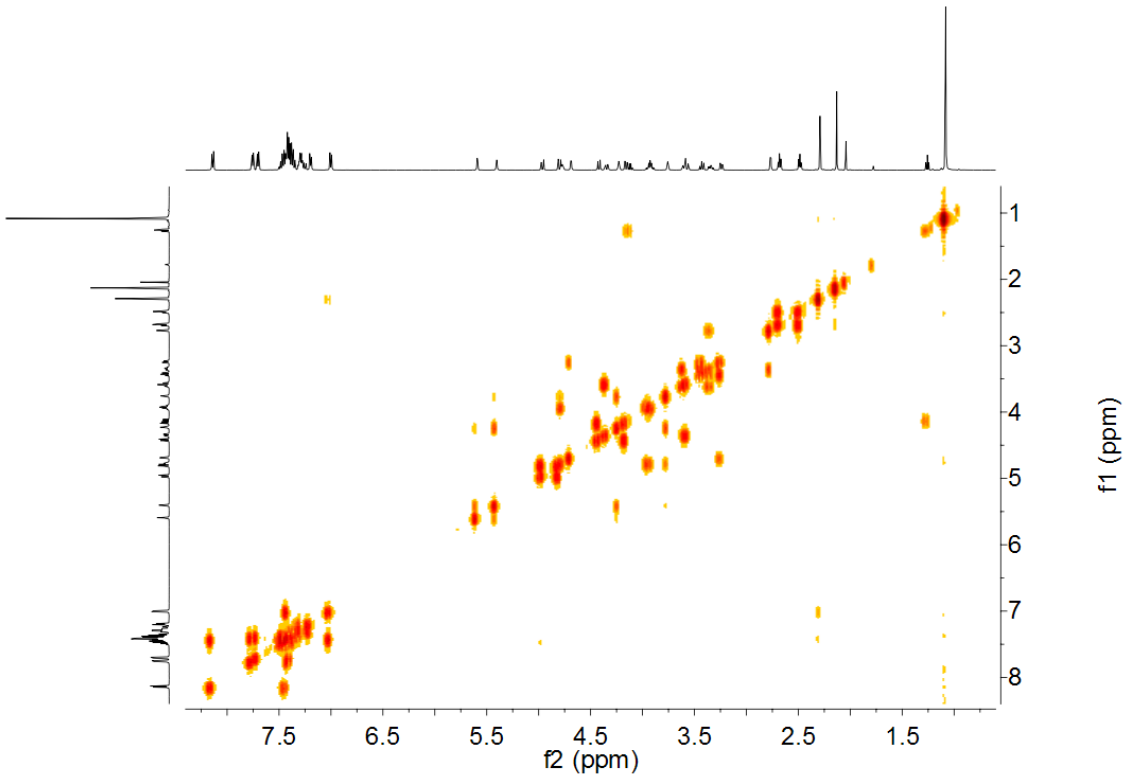
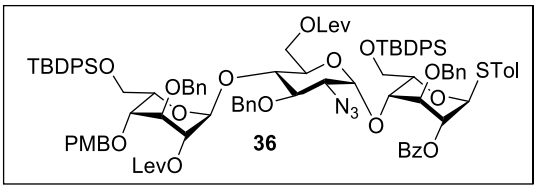


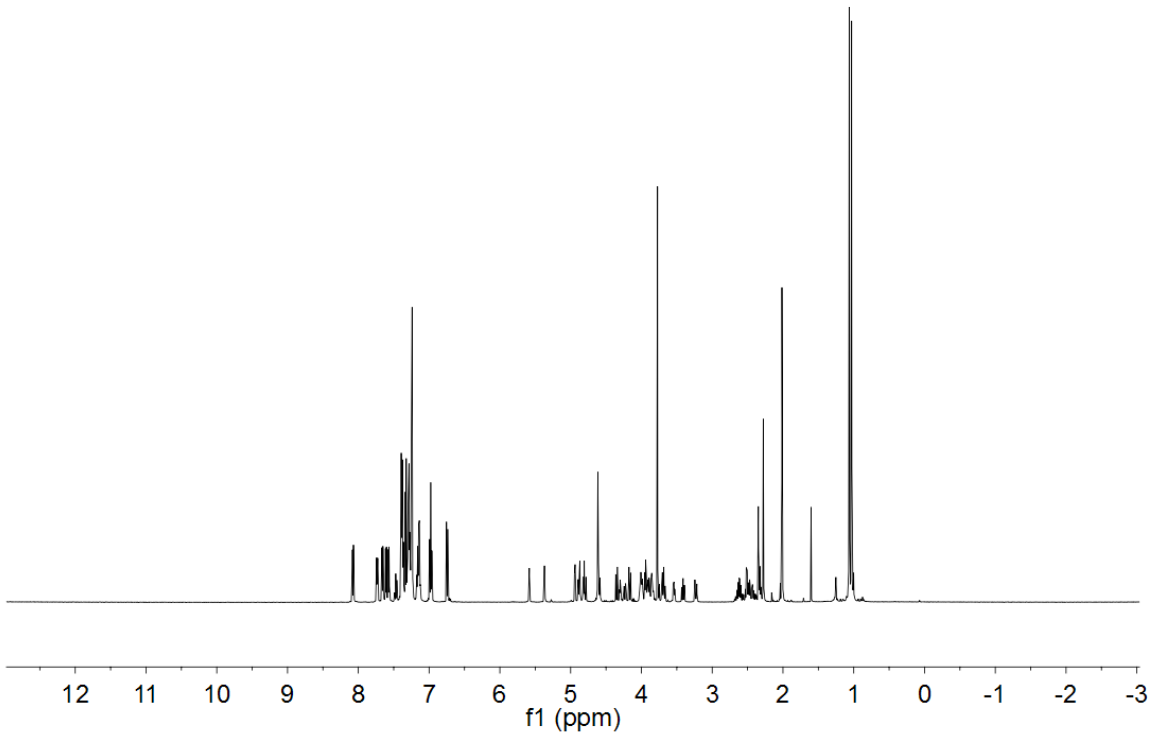
gCOSY ($CDCl_3$, 500 MHz) of **35**



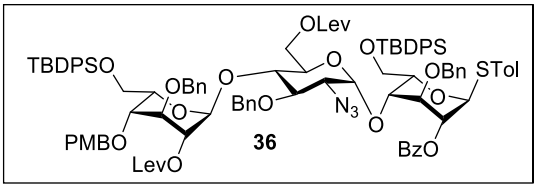


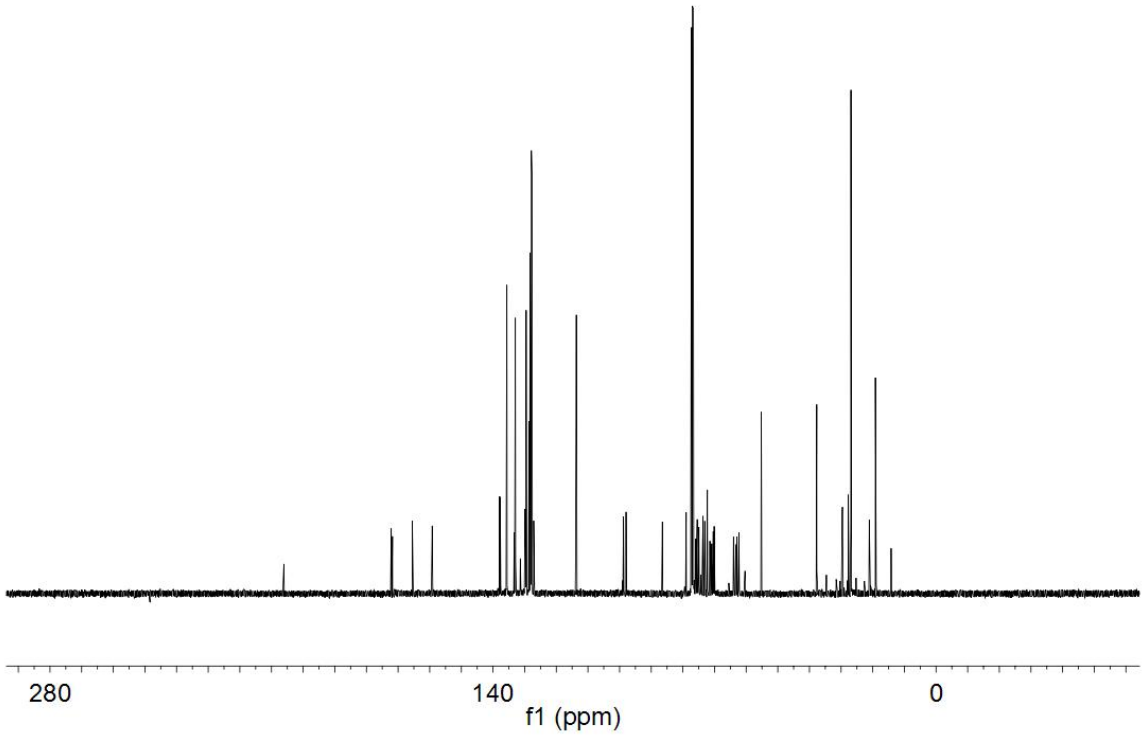
^{1}H-NMR ($CDCl_3$, 500 MHz) of **36**



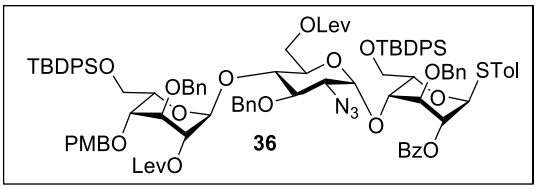


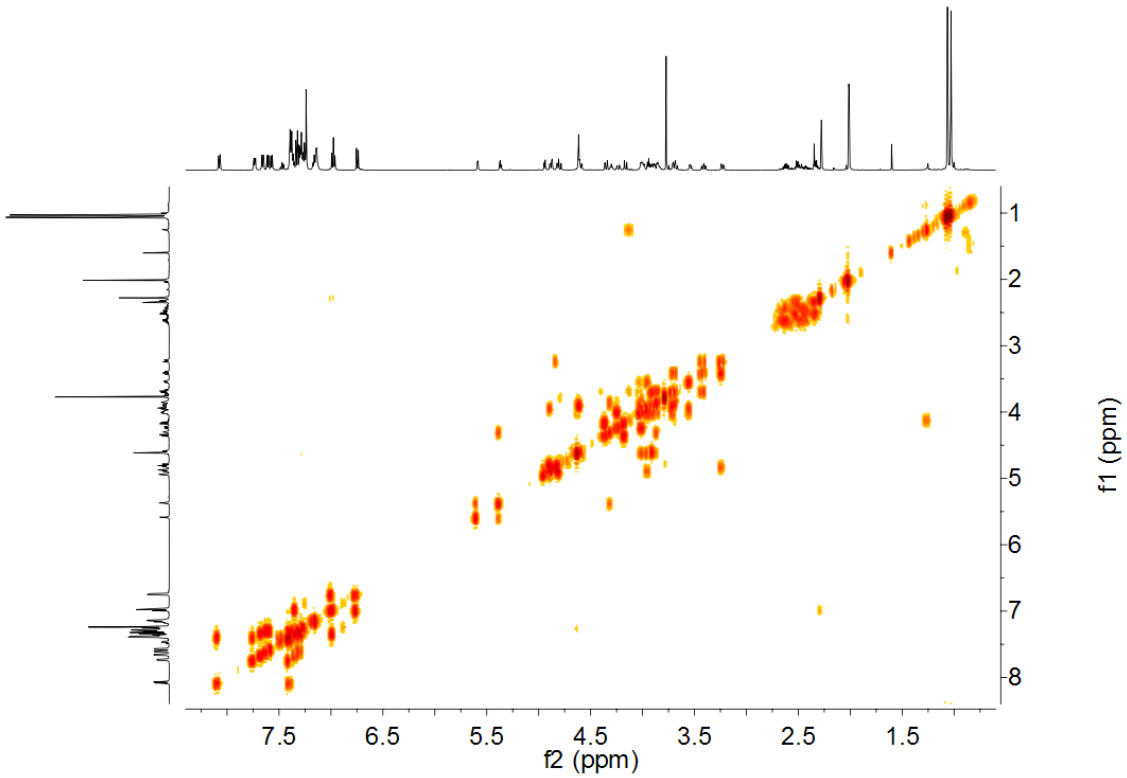
^{13}C-NMR ($CDCl_3$, 125 MHz) of **36**



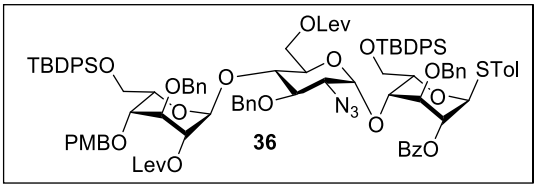


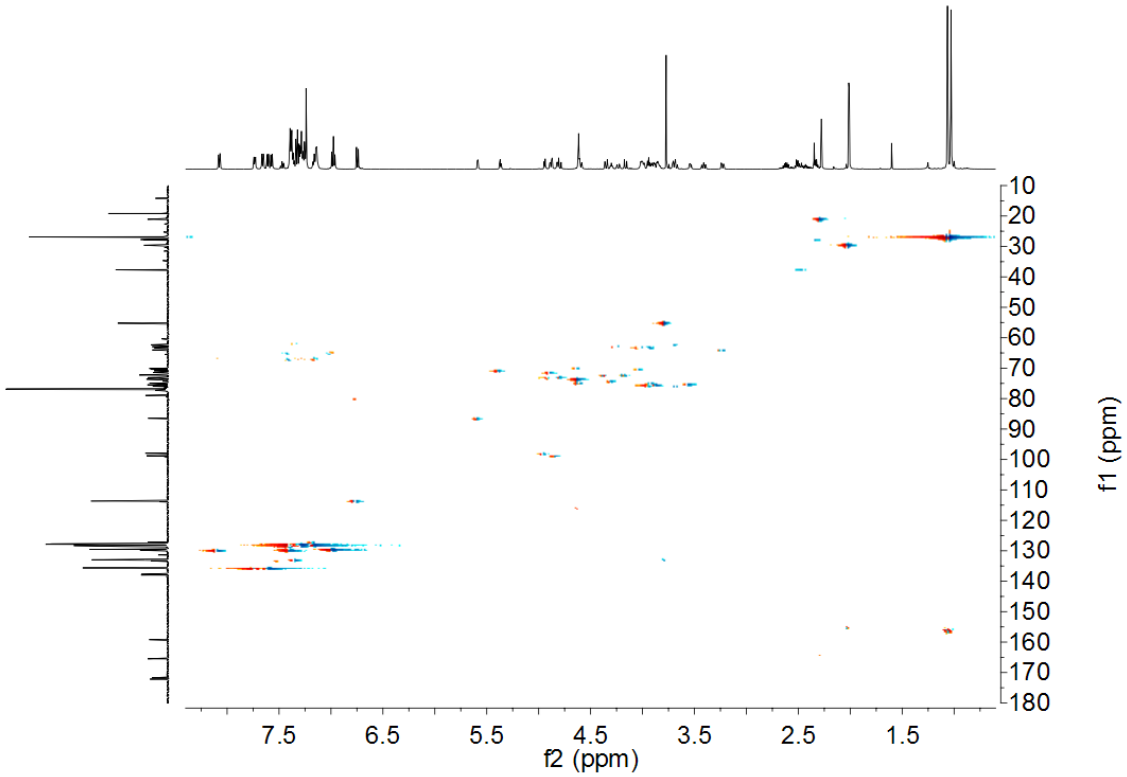
gCOSY ($CDCl_3$, 500 MHz) of **36**



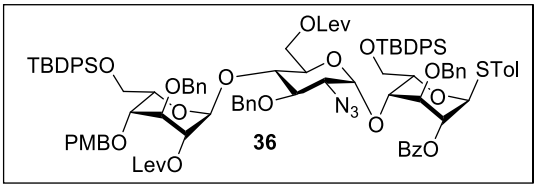


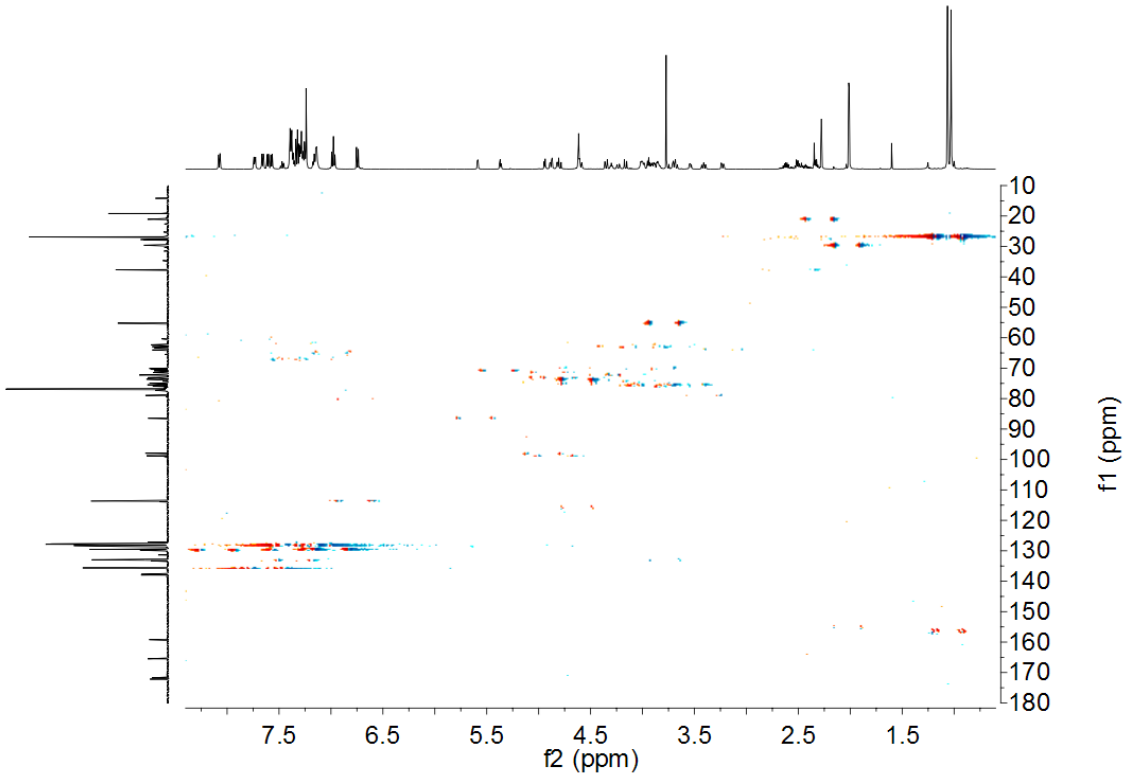
gHMQC ($CDCl_3$, 500 MHz) of **36**



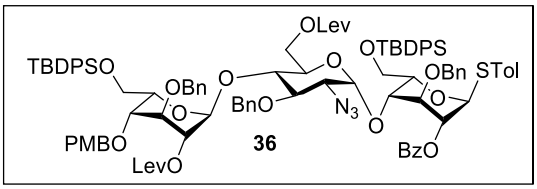


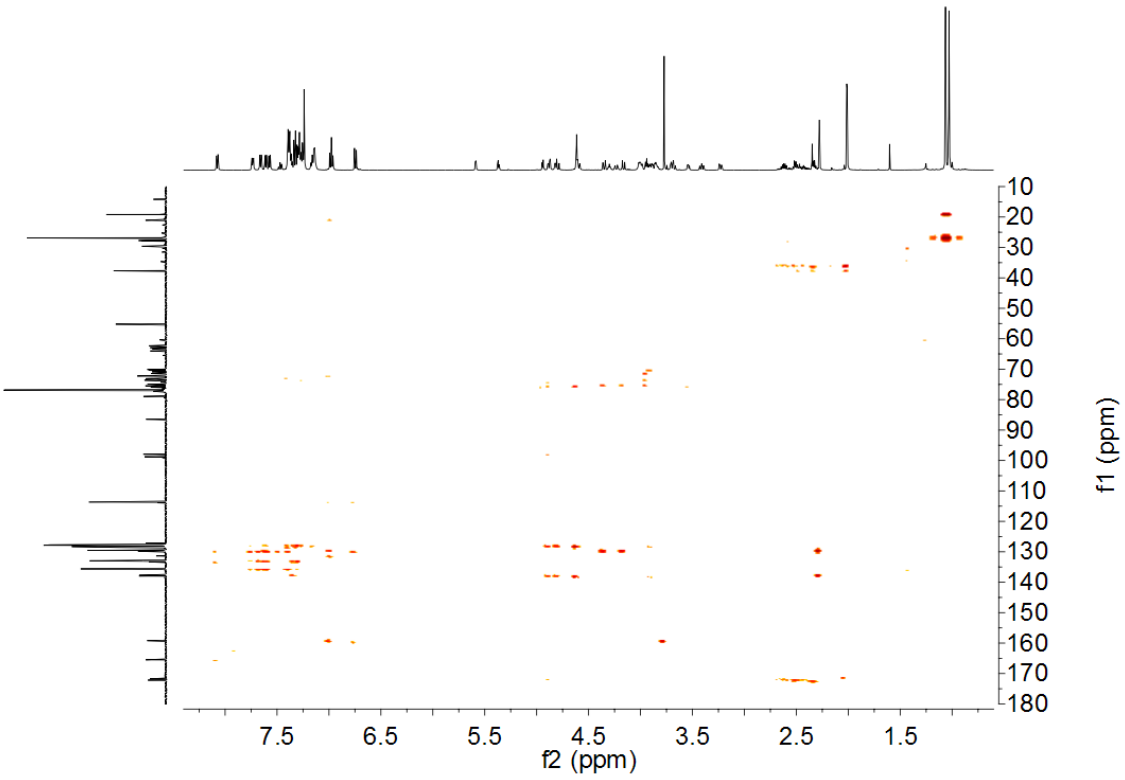
gHMQC (without ^{1}H decoupling) ($CDCl_3$, 500 MHz) of **36**



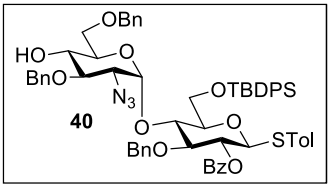


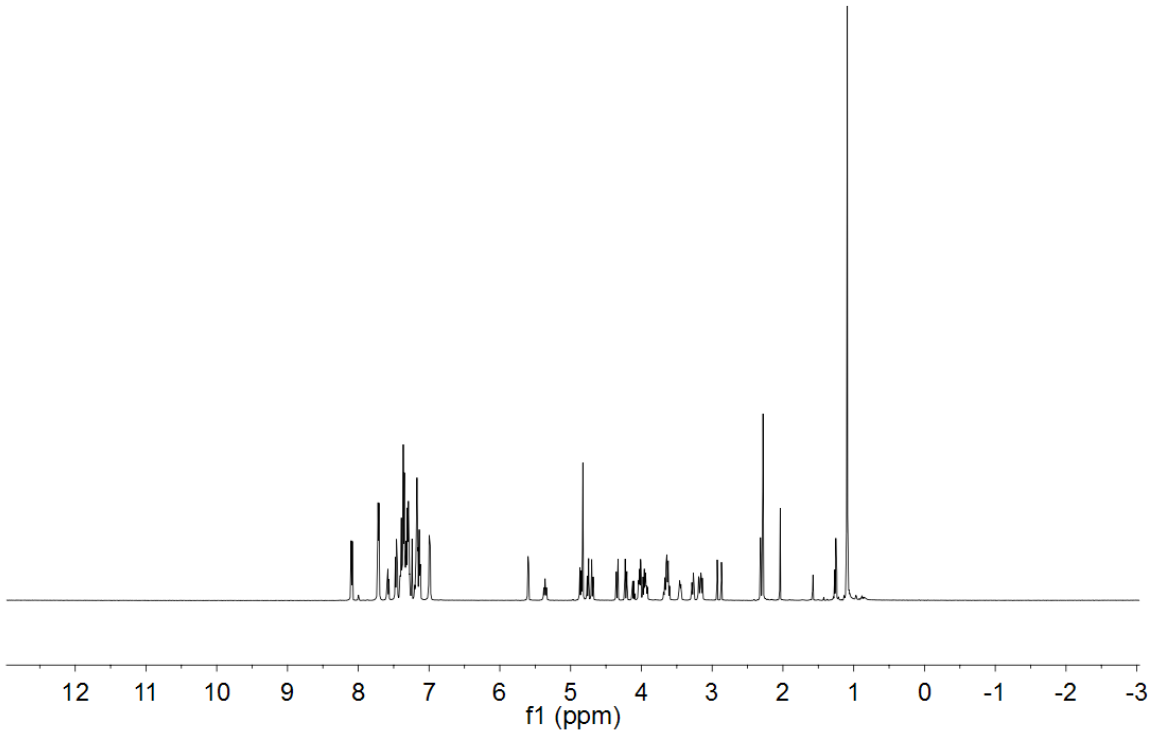
gHMBC ($CDCl_3$, 500 MHz) of **36**



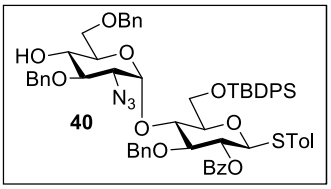


^{1}H-NMR ($CDCl_3$, 500 MHz) of **40**





^{13}C-NMR ($CDCl_3$, 125 MHz) of **40**



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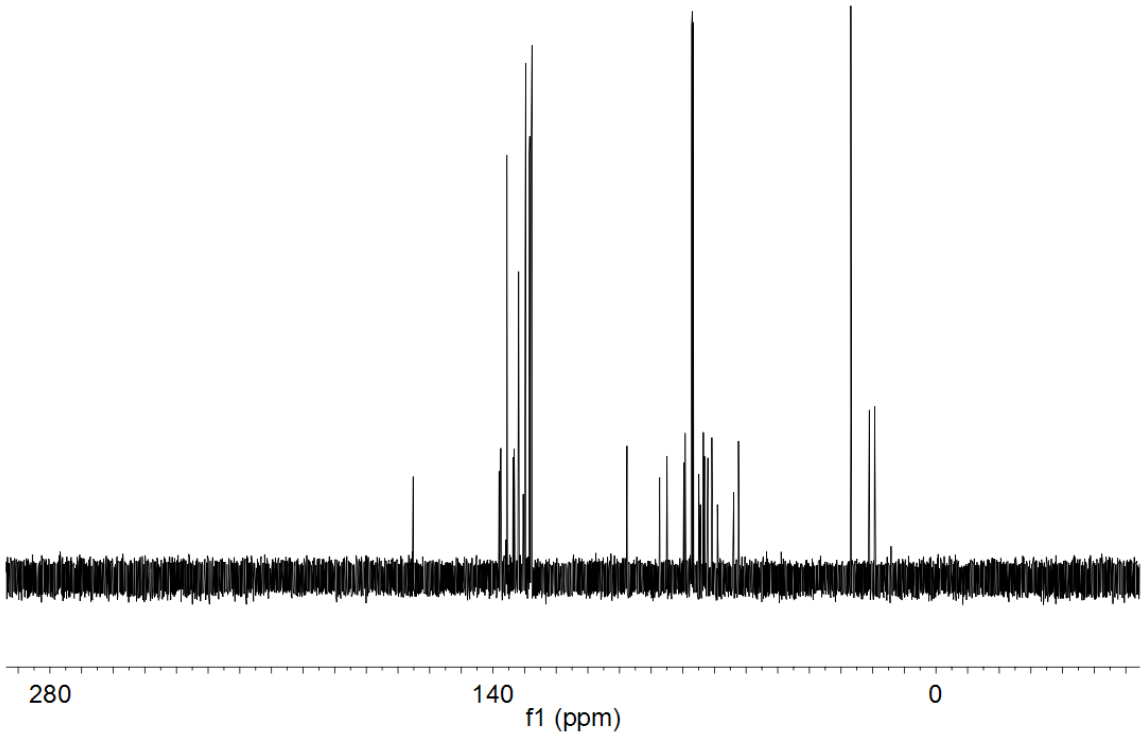
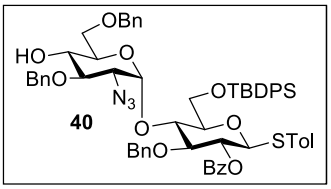
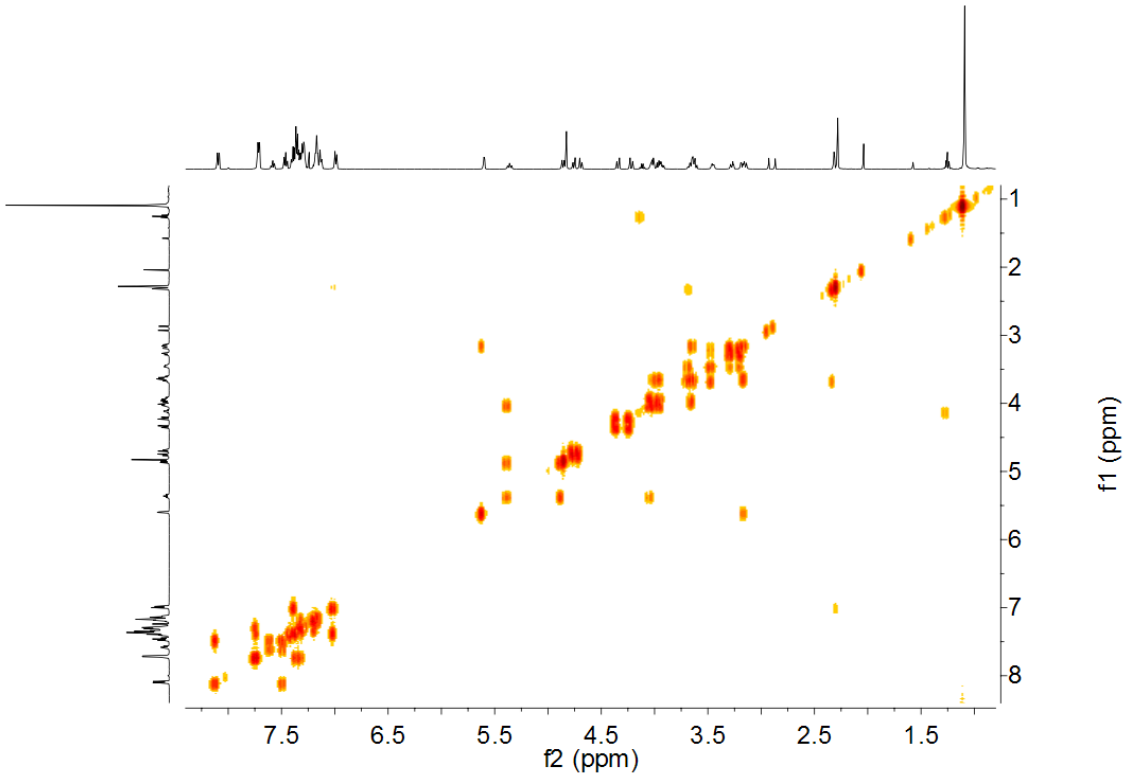
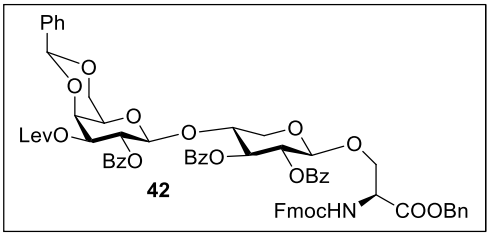


gCOSY ($CDCl_3$, 500 MHz) of **40**

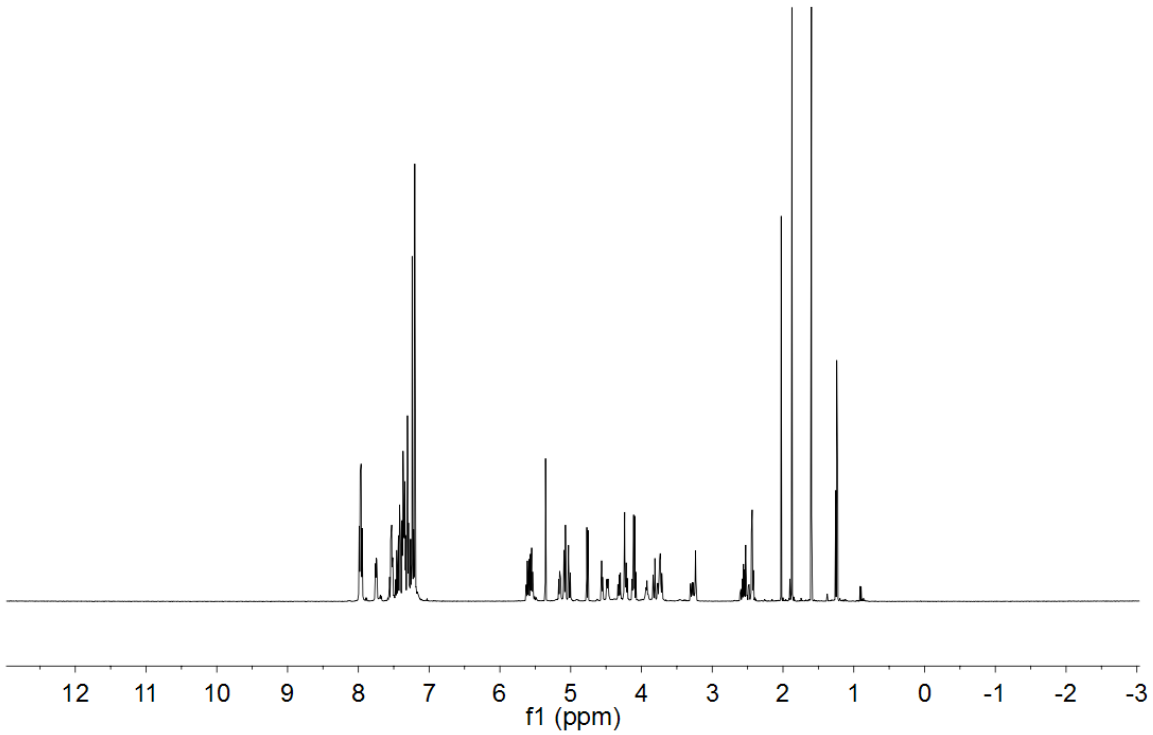




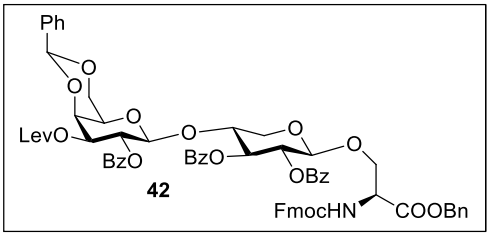
^{1}H-NMR ($CDCl_3$, 500 MHz) of **42**



42



^{13}C-NMR ($CDCl_3$, 150 MHz) of **42**



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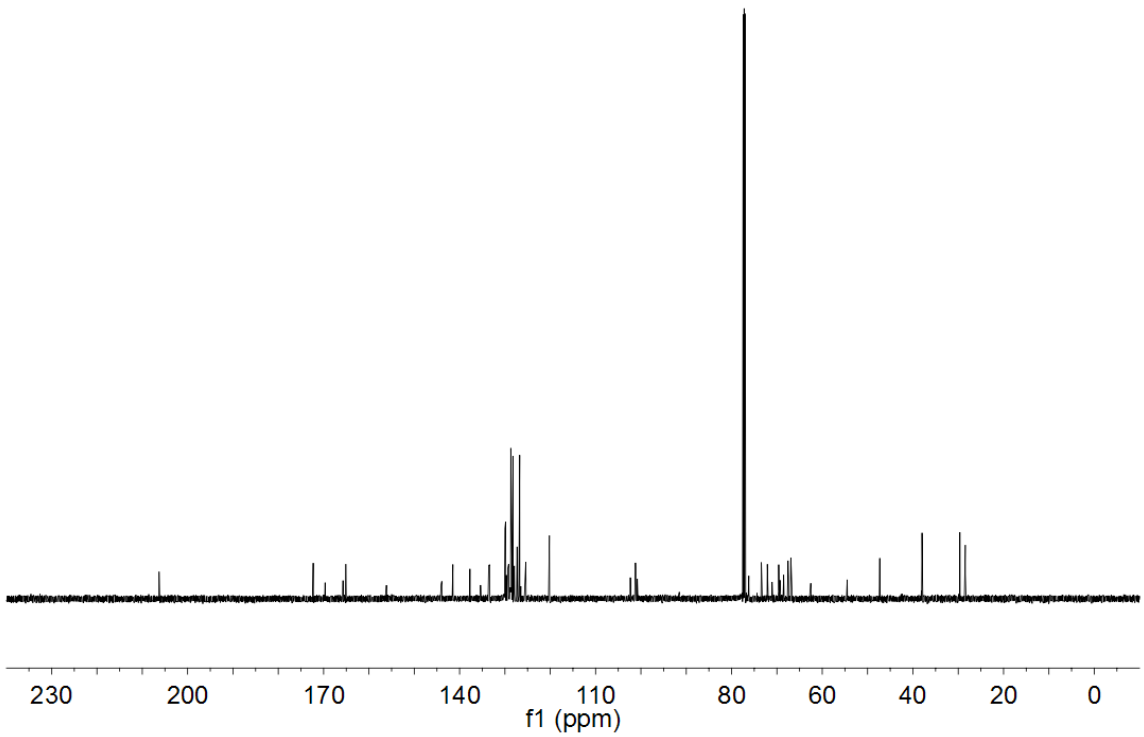
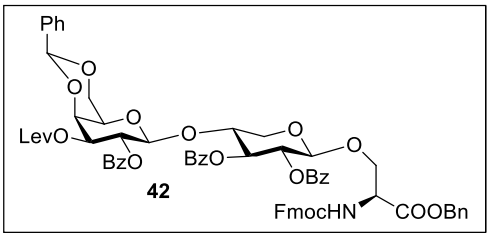
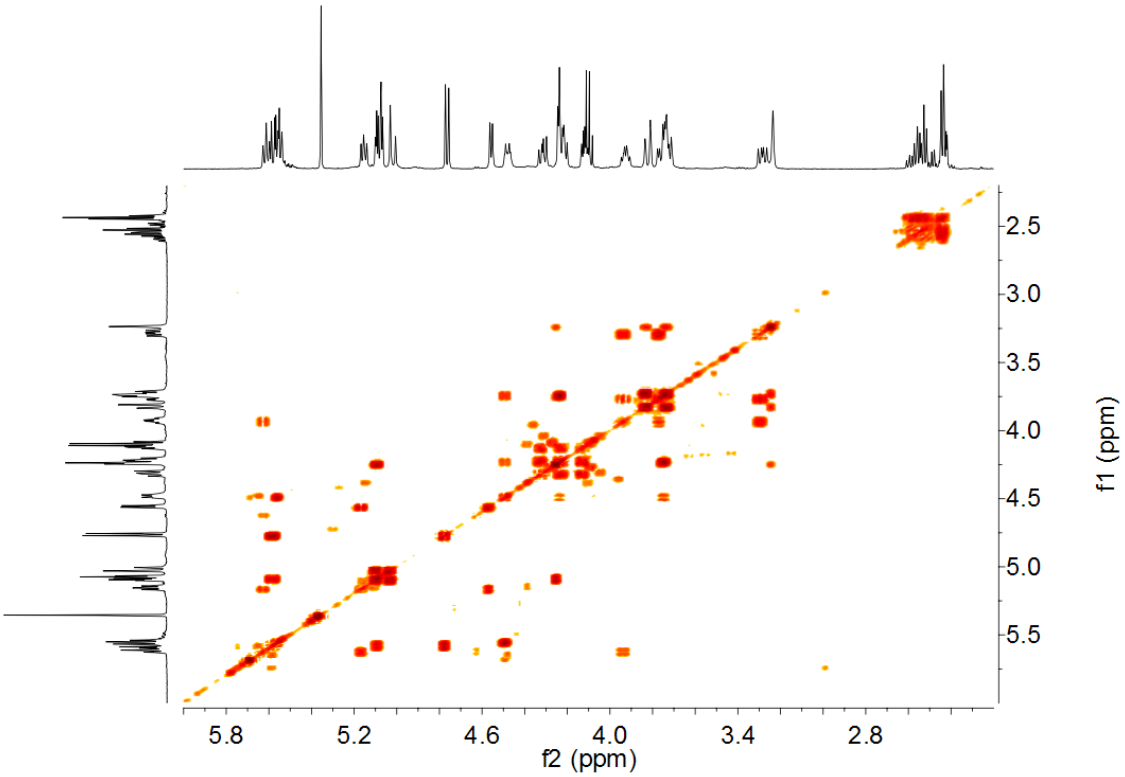
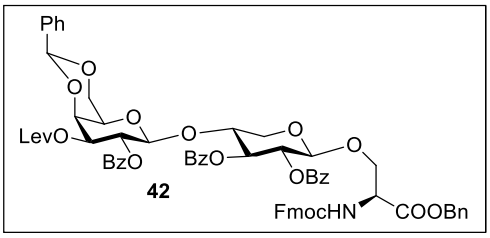


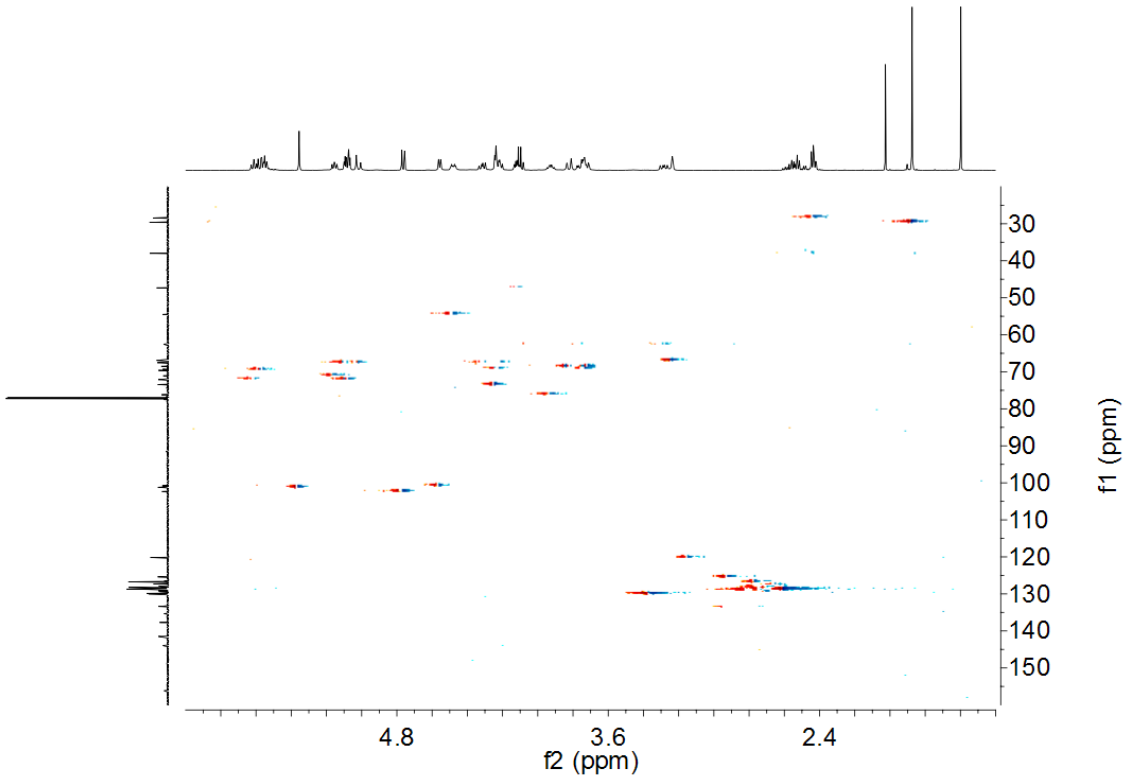
gCOSY ($CDCl_3$, 600 MHz) of **42**



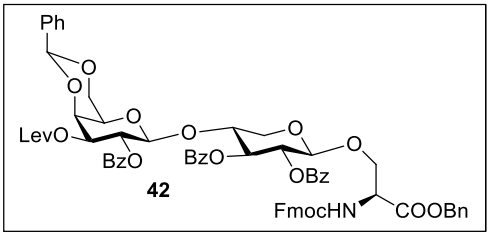


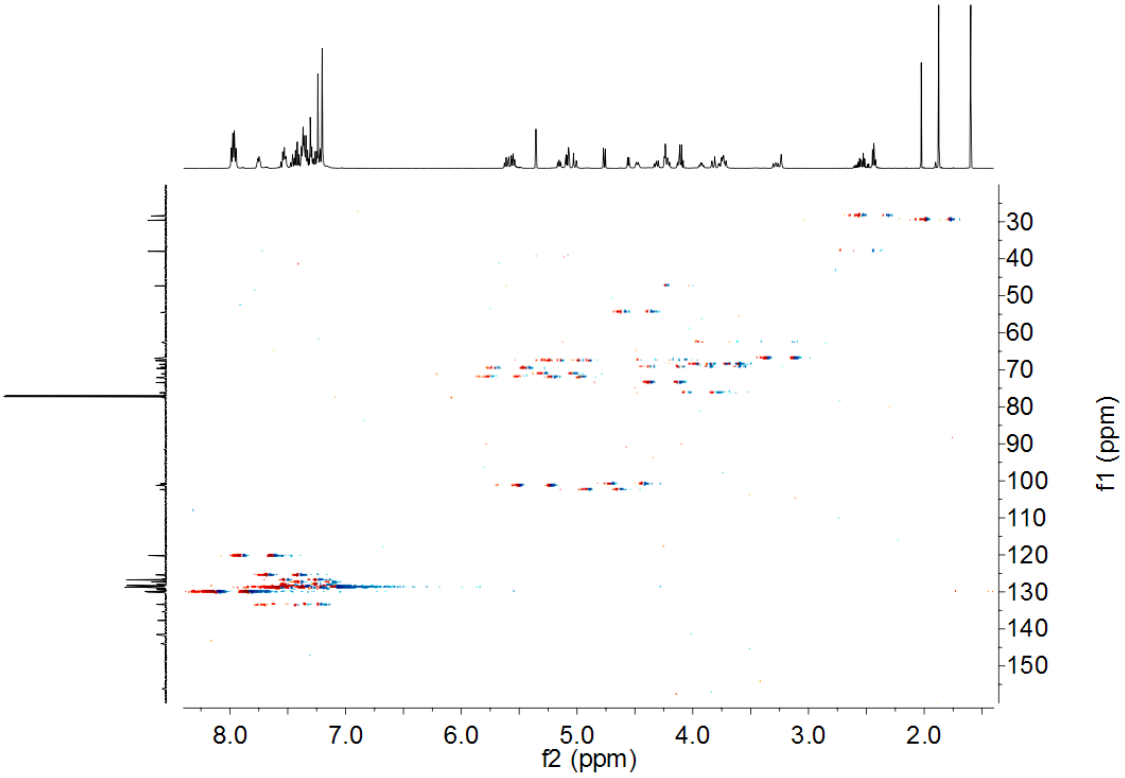
gHMQC ($CDCl_3$, 600 MHz) of **42**



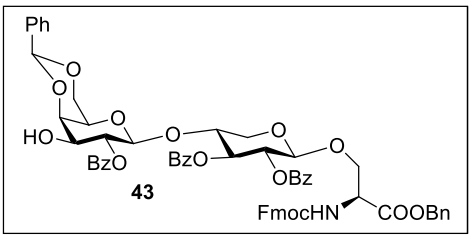


gHMQC (without ^{1}H decoupling) ($CDCl_3$, 600 MHz) of **42**

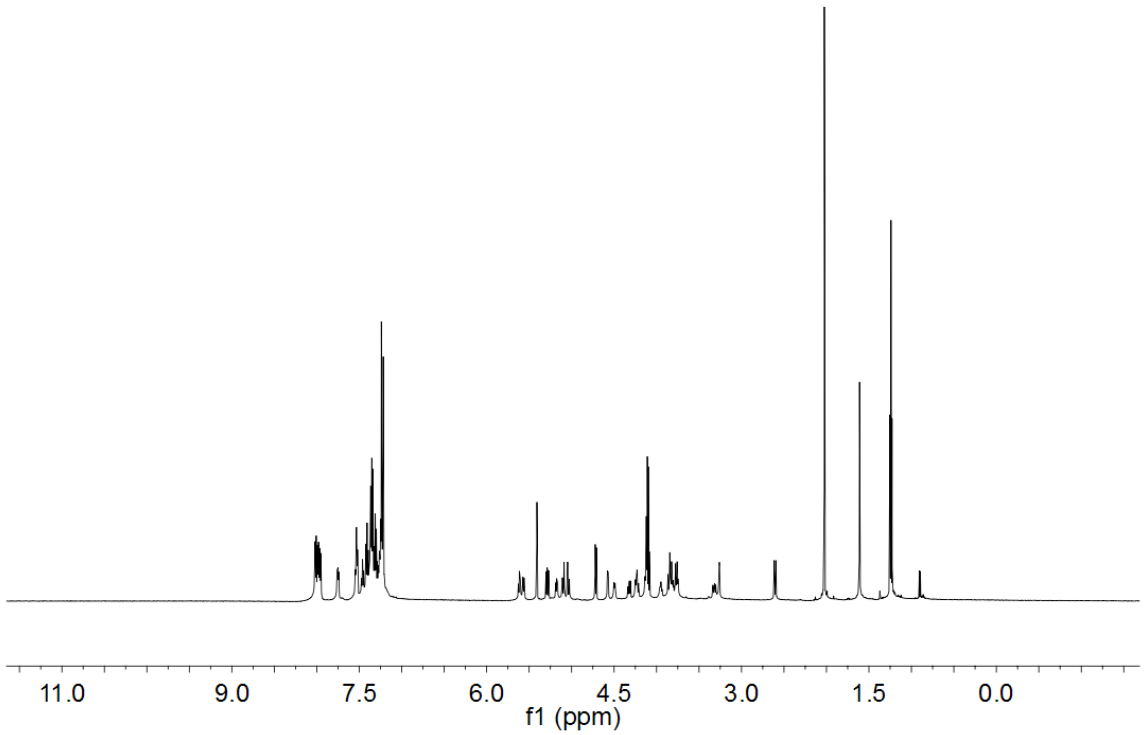




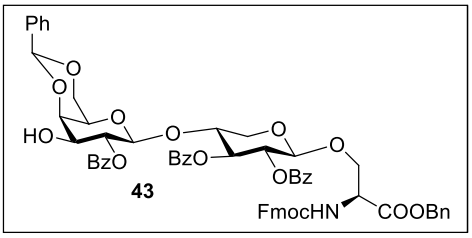
^{1}H-NMR ($CDCl_3$, 600 MHz) of **43**



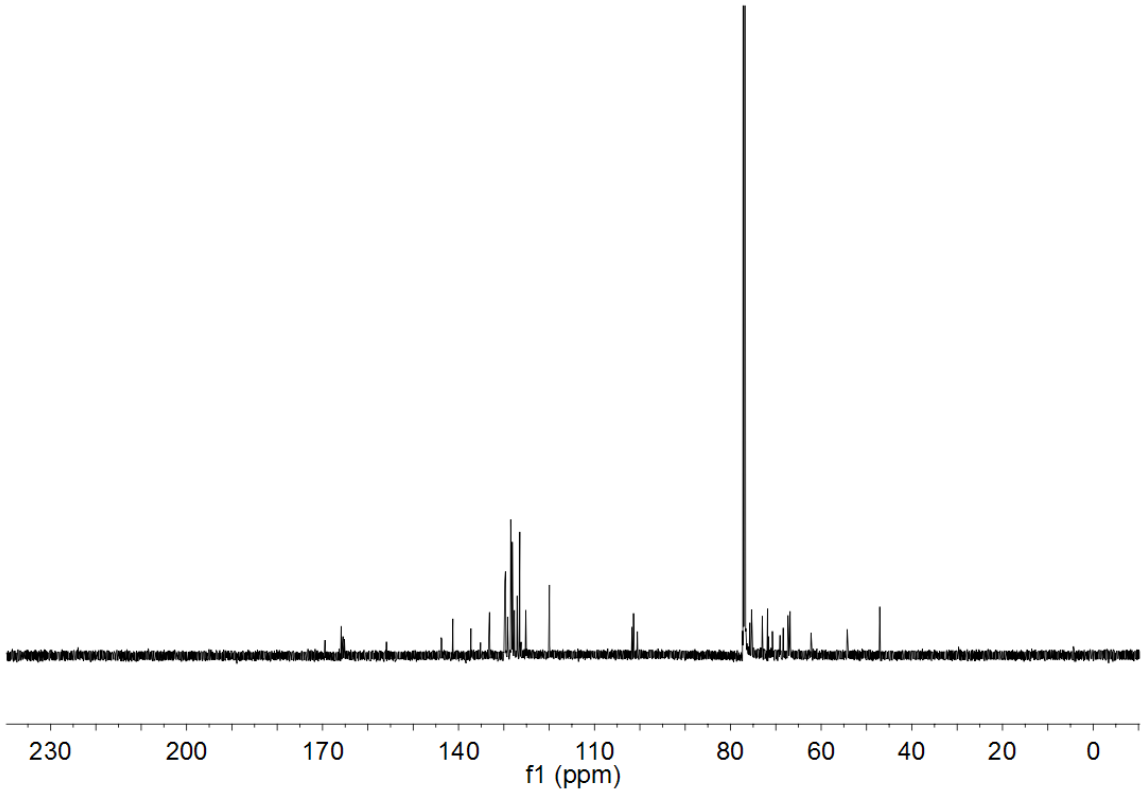
43



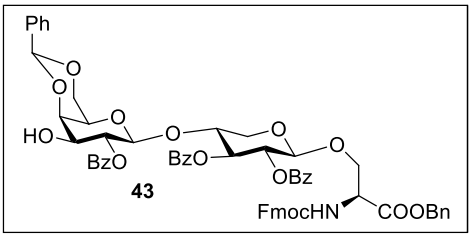
^{13}C-NMR ($CDCl_3$, 150 MHz) of **43**



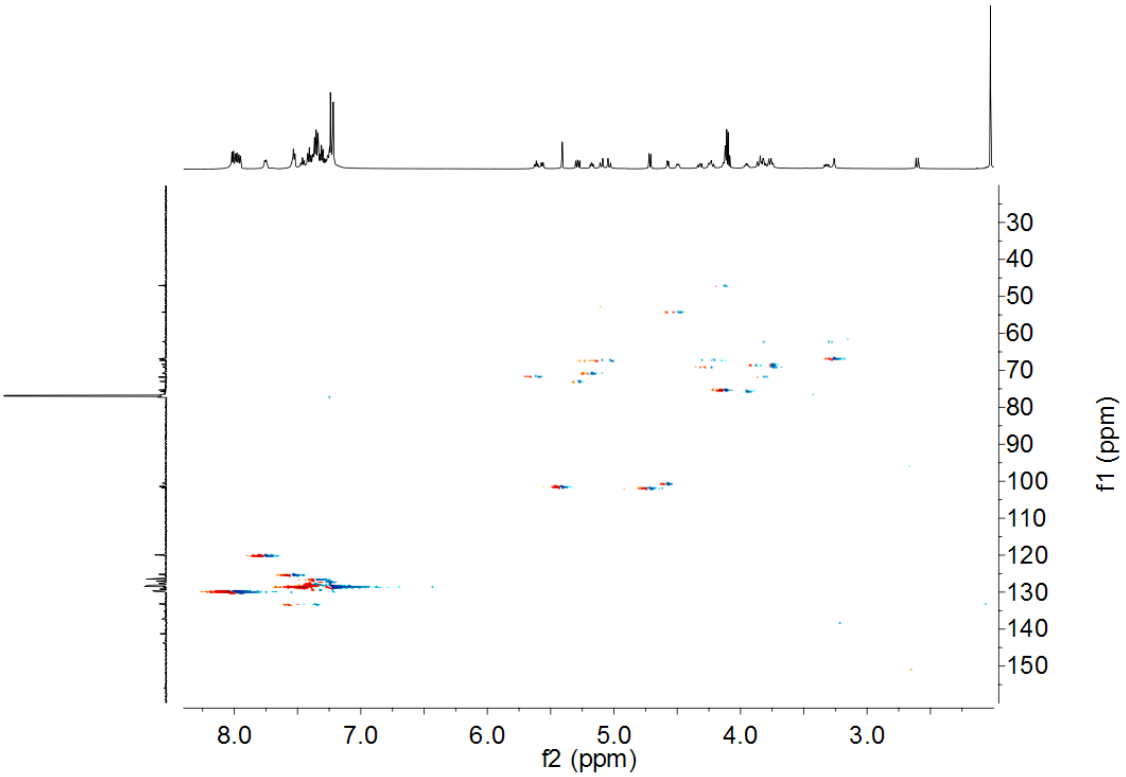
43



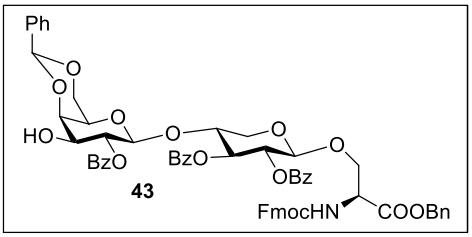
gHMQC ($CDCl_3$, 600 MHz) of **43**



43



gHMQC (without ^{1}H decoupling) ($CDCl_3$, 500 MHz) of **43**



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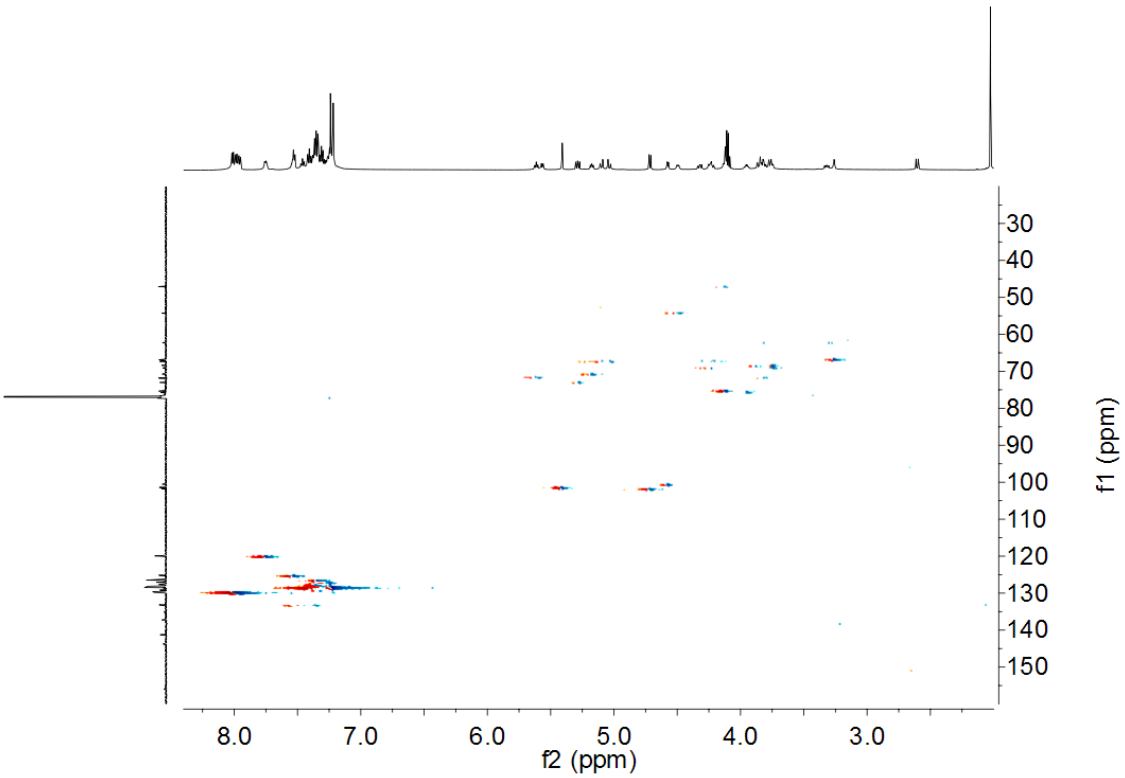
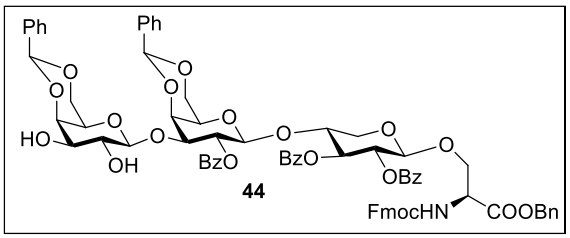


^{1}H-NMR ($CDCl_3$, 500 MHz) of **44**



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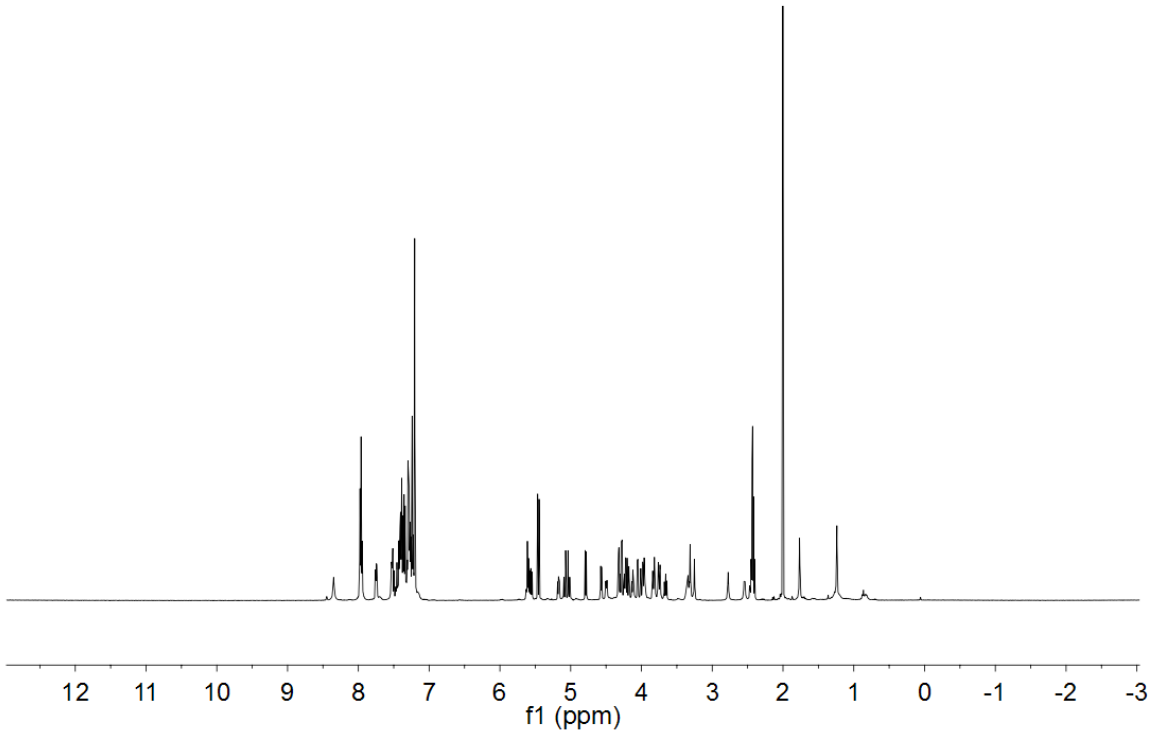
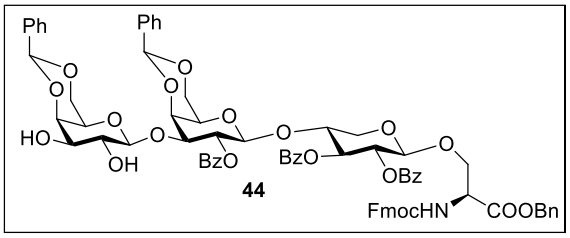


^{13}C-NMR ($CDCl_3$, 150 MHz) of **44**



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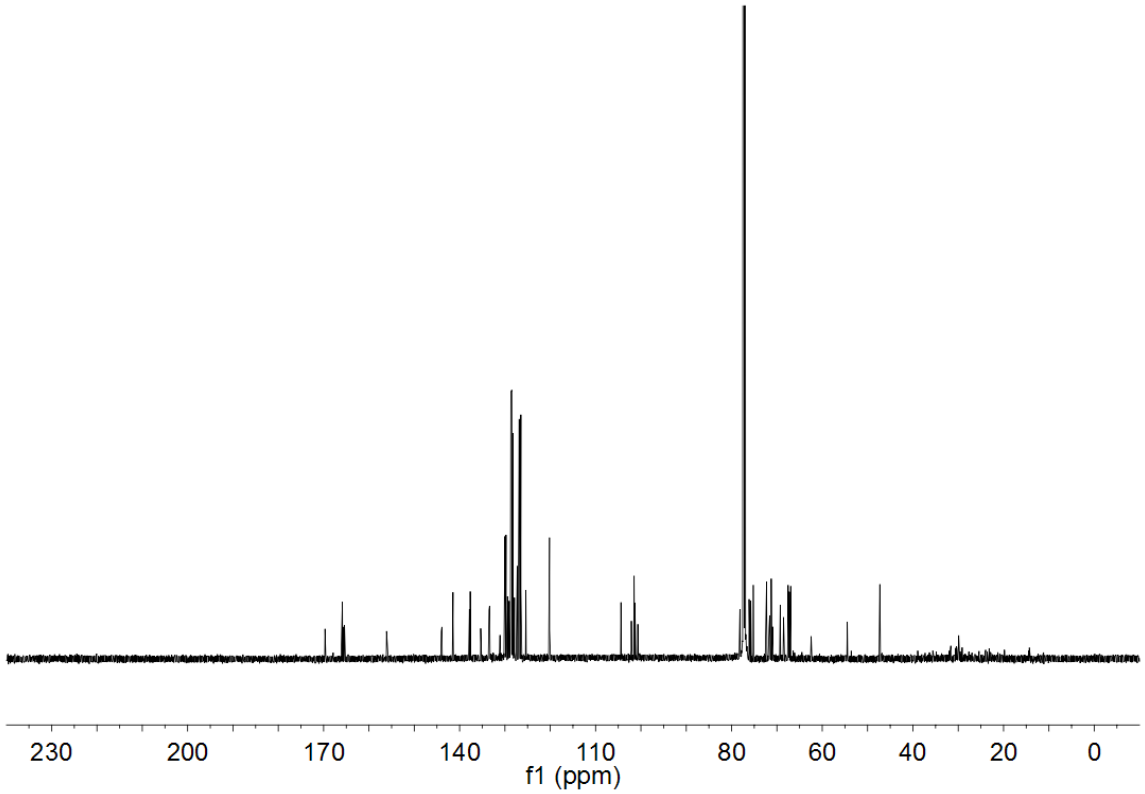
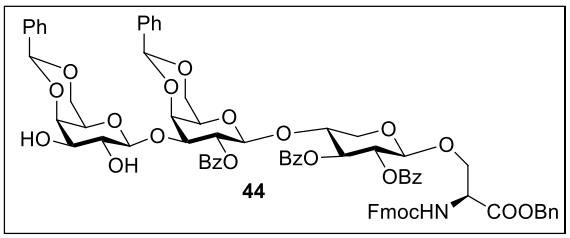
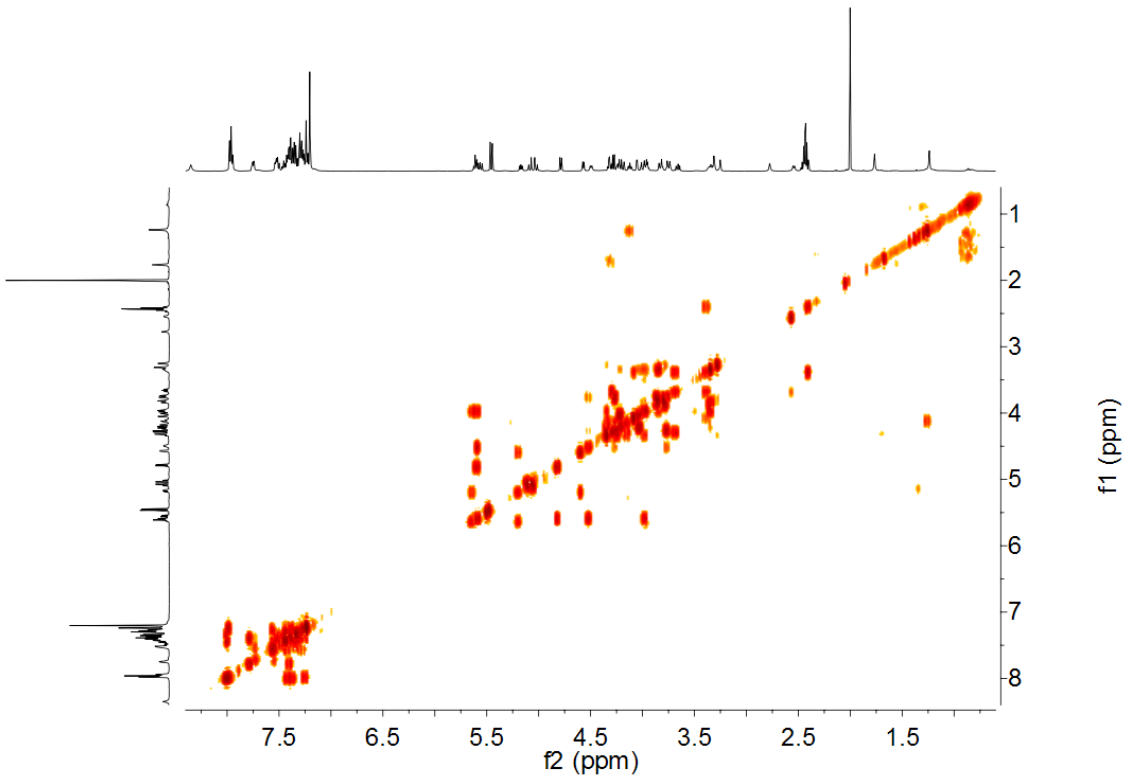
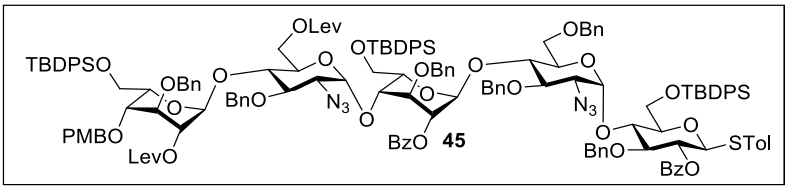


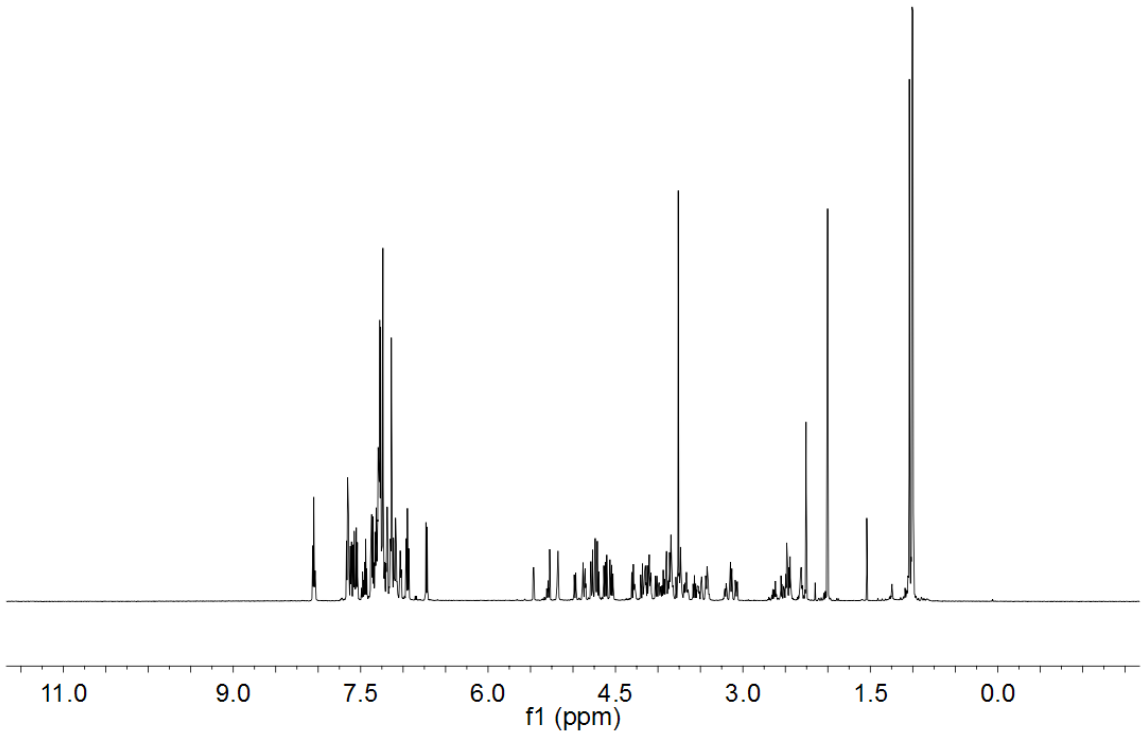
gCOSY ($CDCl_3$, 500 MHz) of **44**



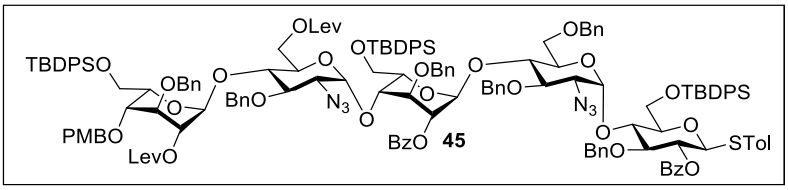


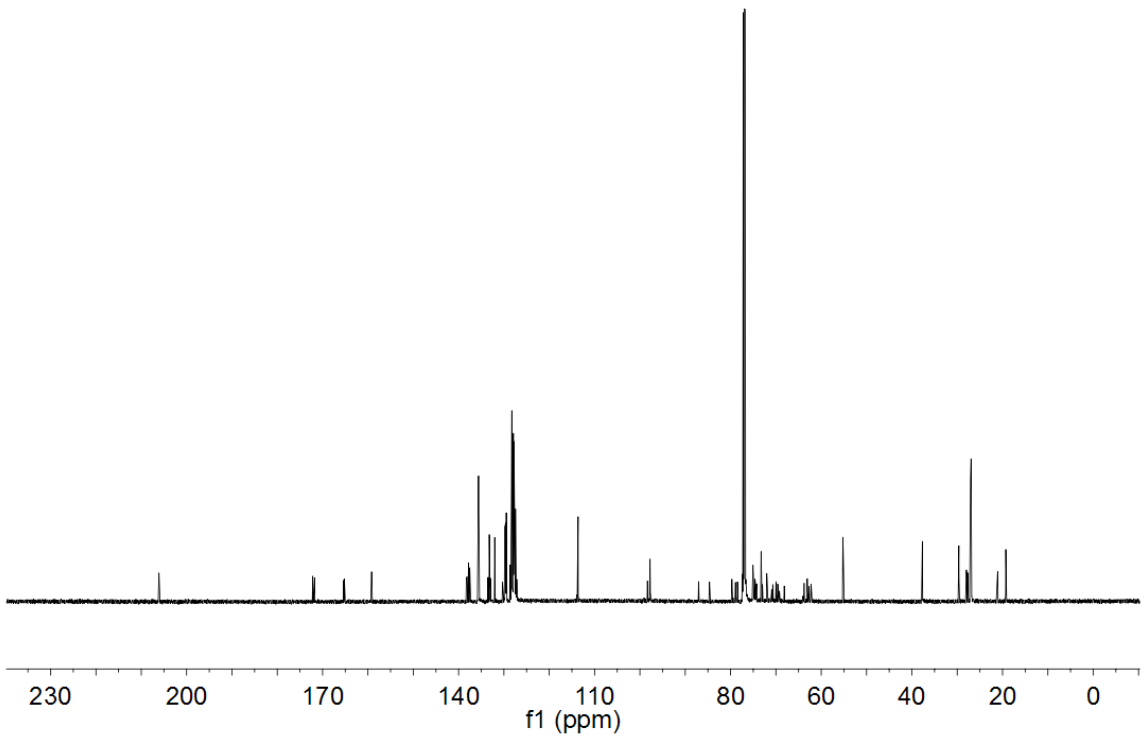
^{1}H-NMR ($CDCl_3$, 600 MHz) of **45**



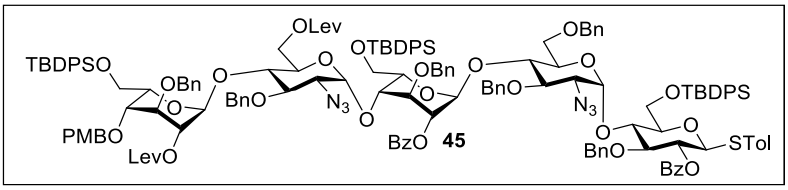


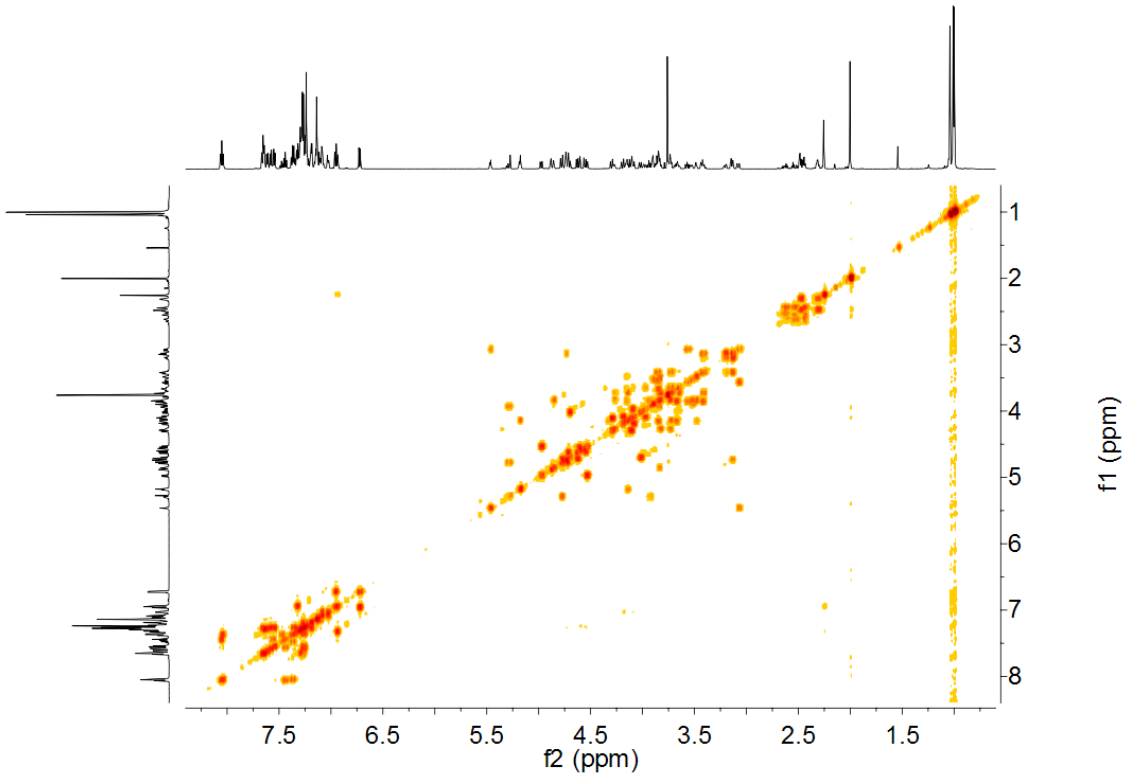
^{13}C-NMR ($CDCl_3$, 150 MHz) of **45**



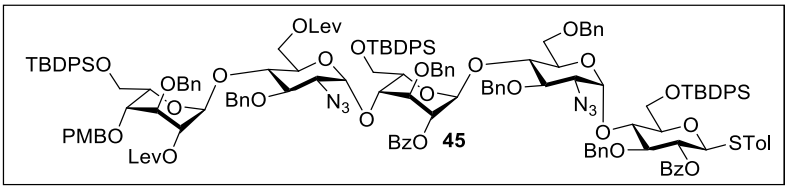


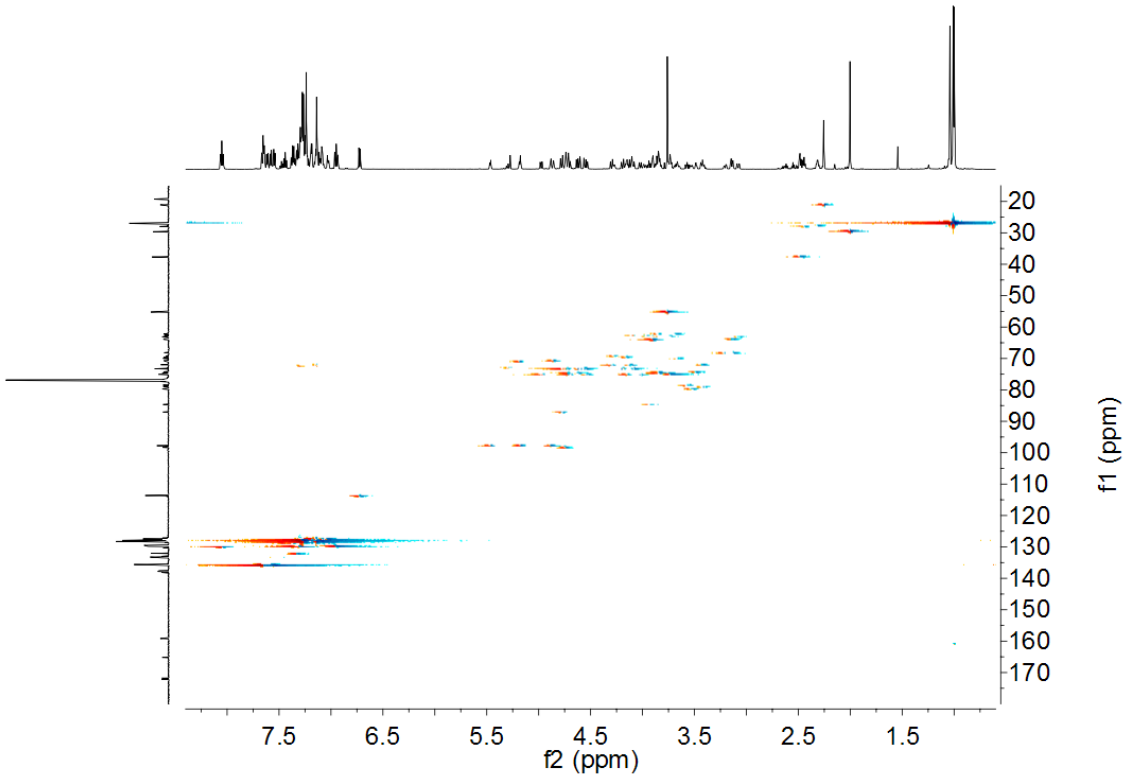
gCOSY ($CDCl_3$, 600 MHz) of **45**



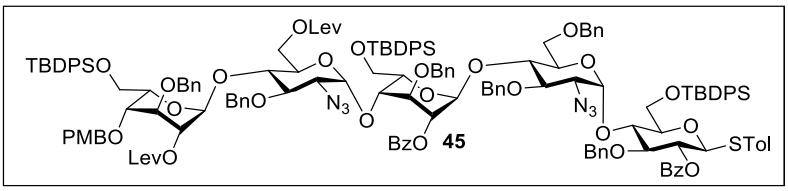


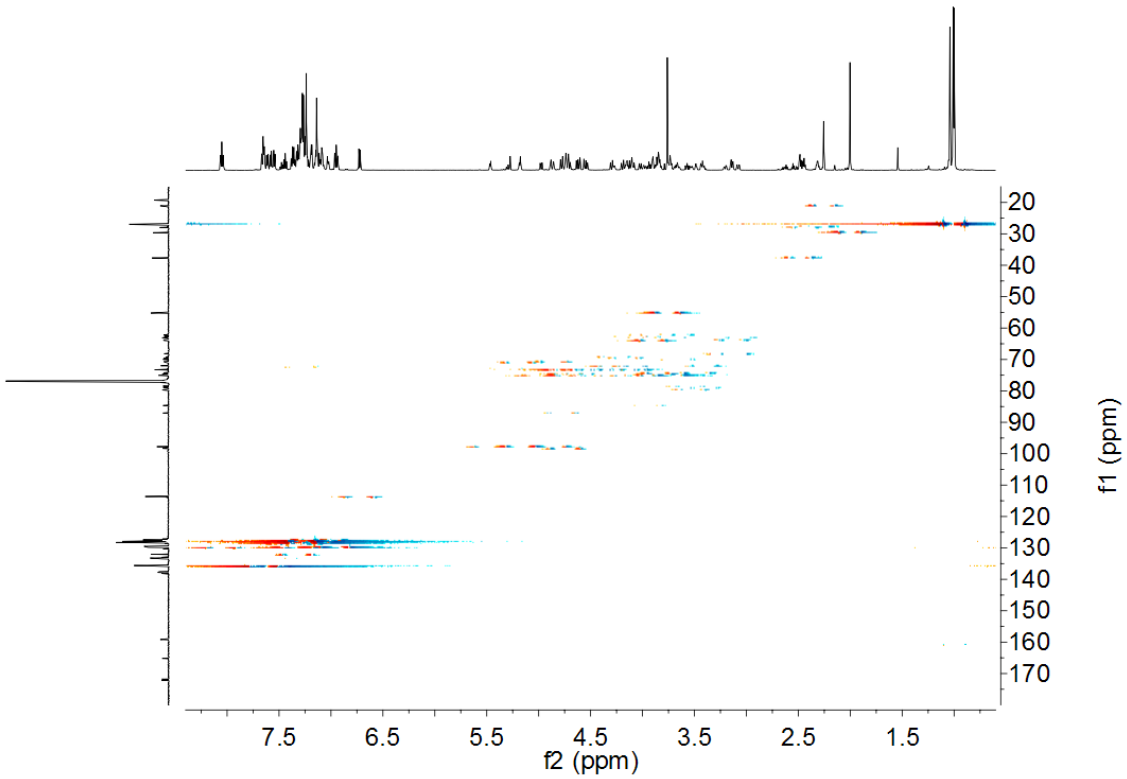
gHMQC ($CDCl_3$, 600 MHz) of **45**



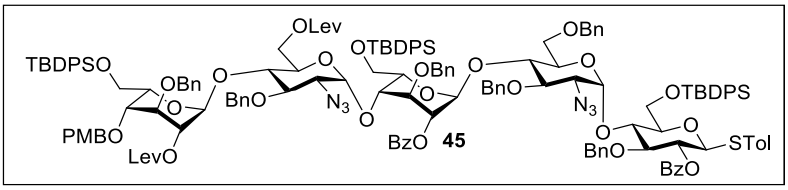


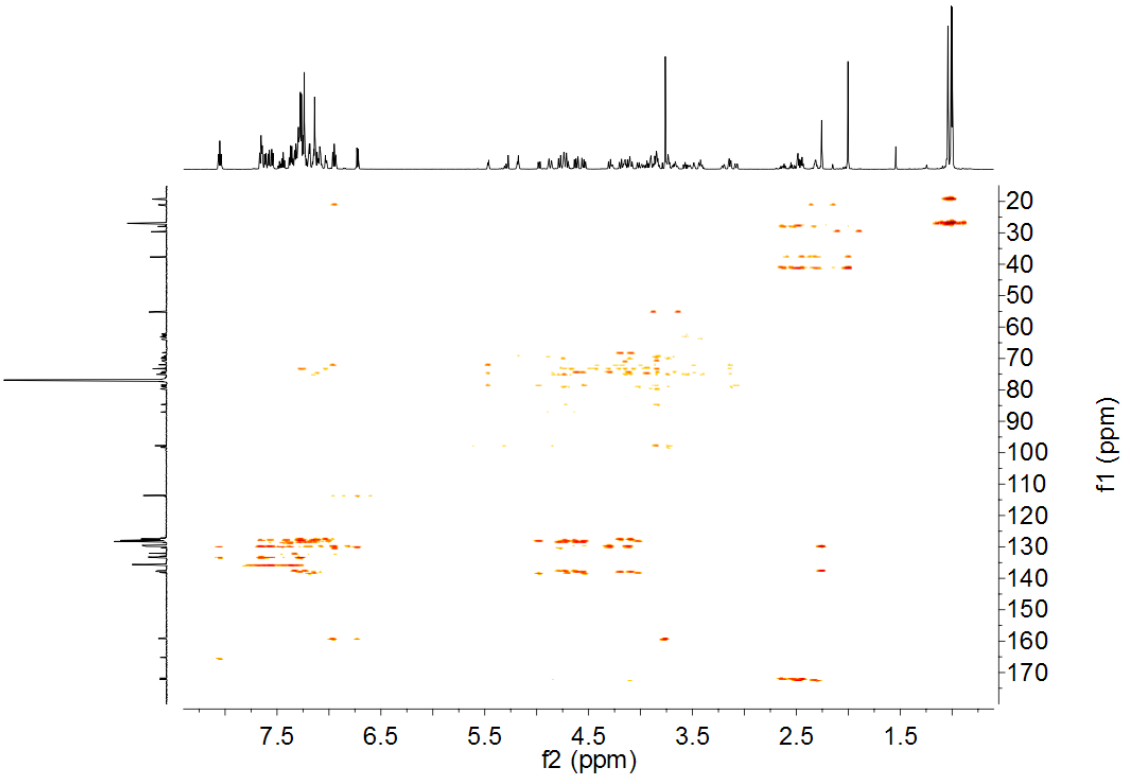
gHMQC (without ^{1}H decoupling) ($CDCl_3$, 600 MHz) of **45**



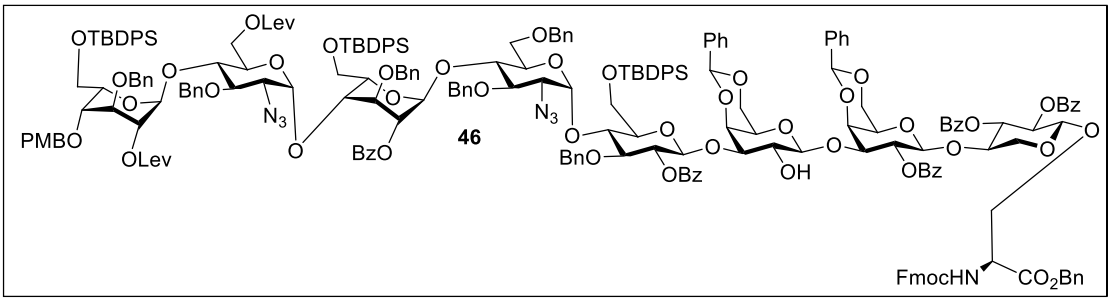


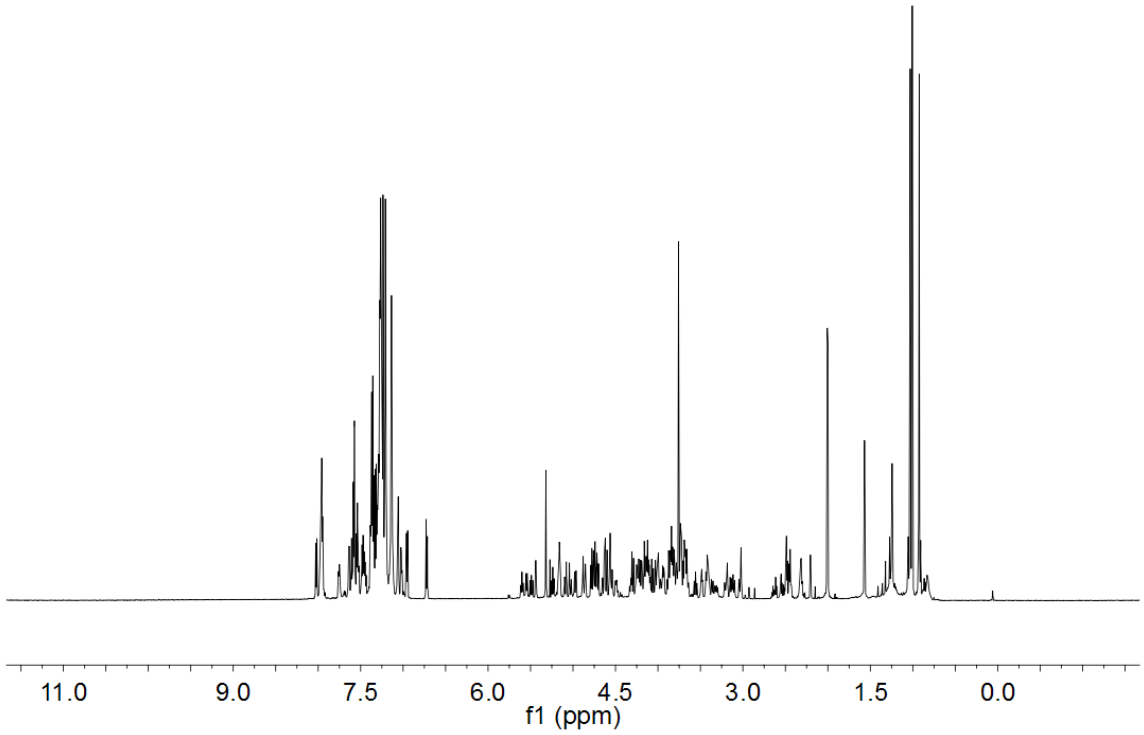
gHMBC ($CDCl_3$, 600 MHz) of **45**



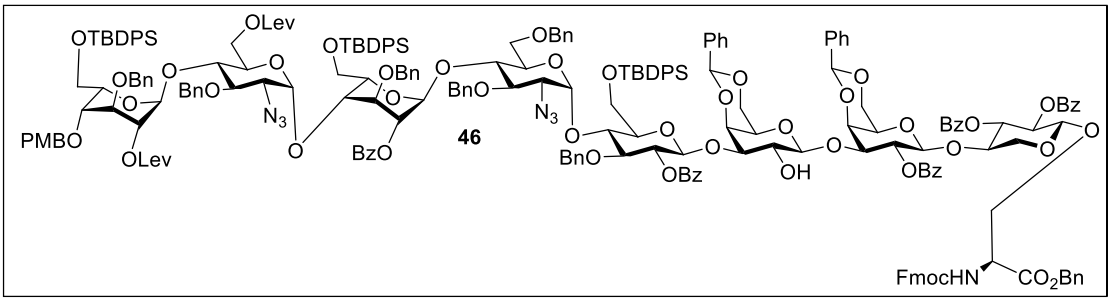


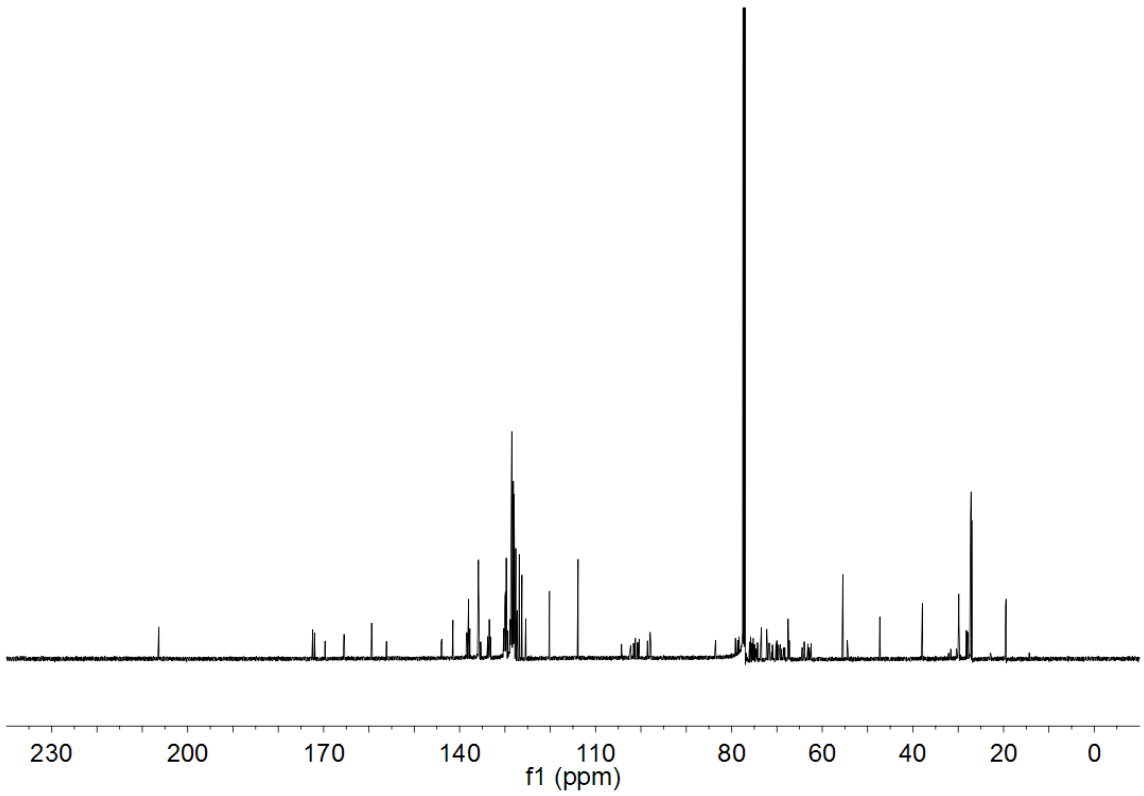
^{1}H-NMR ($CDCl_3$, 600 MHz) of **46**



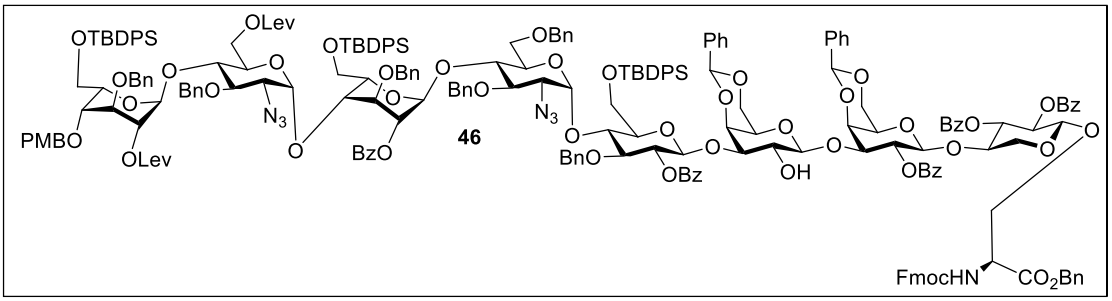


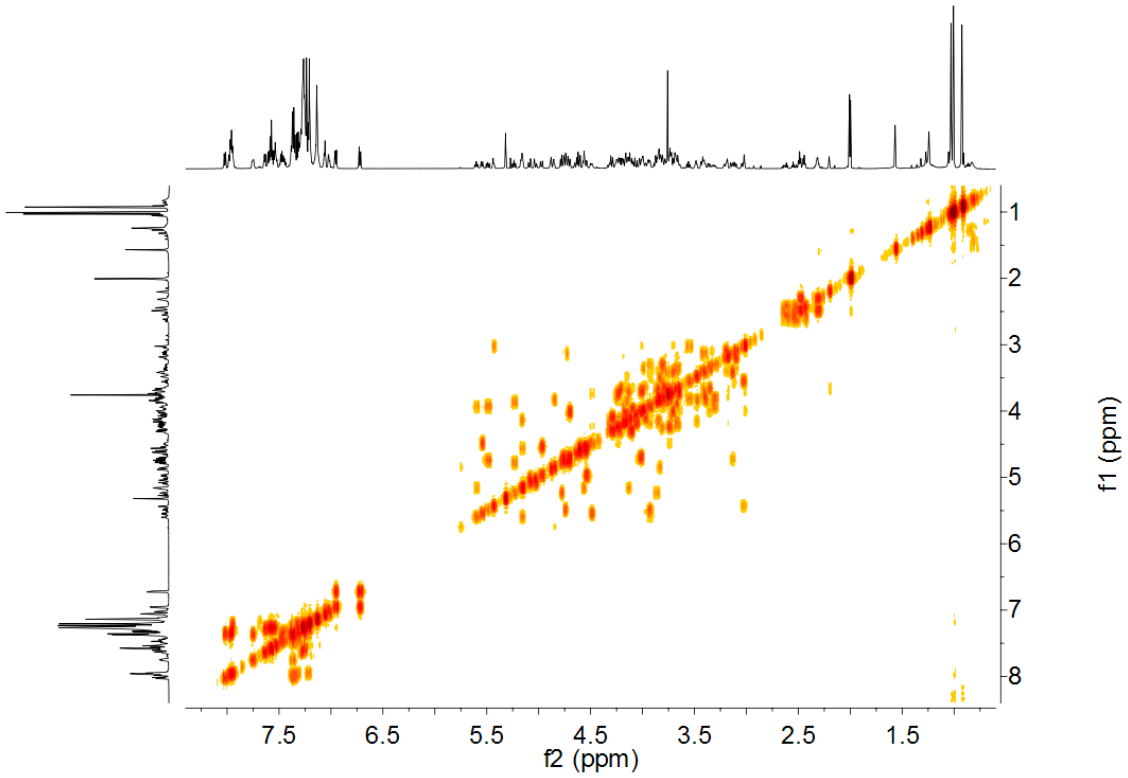
^{13}C-NMR ($CDCl_3$, 150 MHz) of **46**



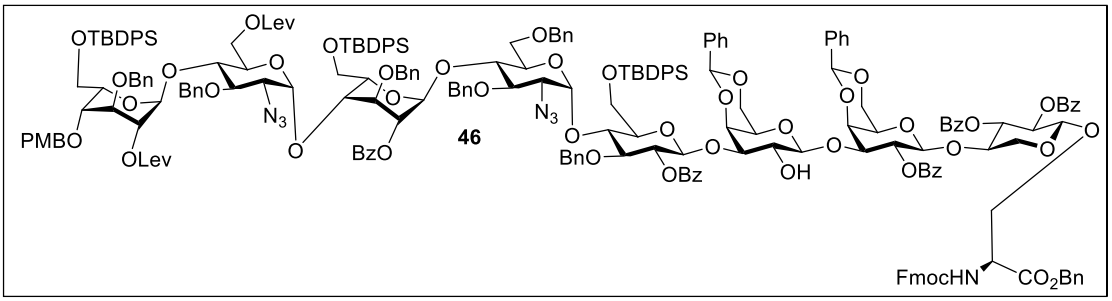


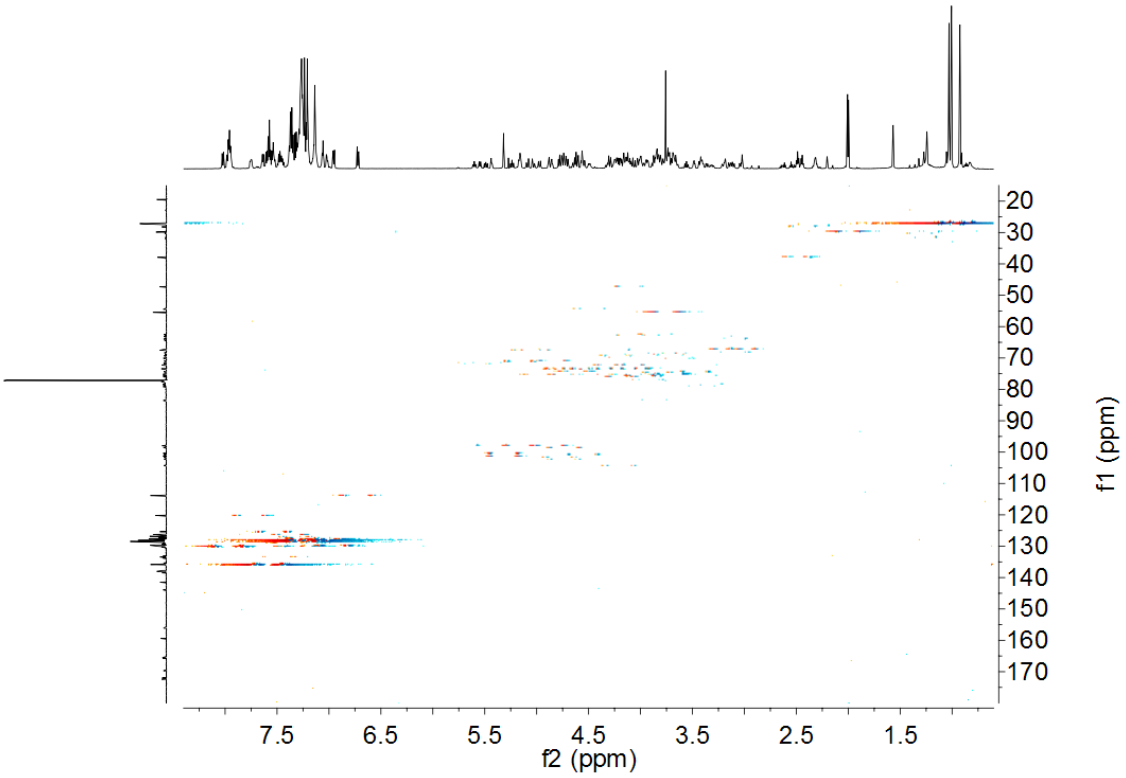
gCOSY ($CDCl_3$, 600 MHz) of **46**



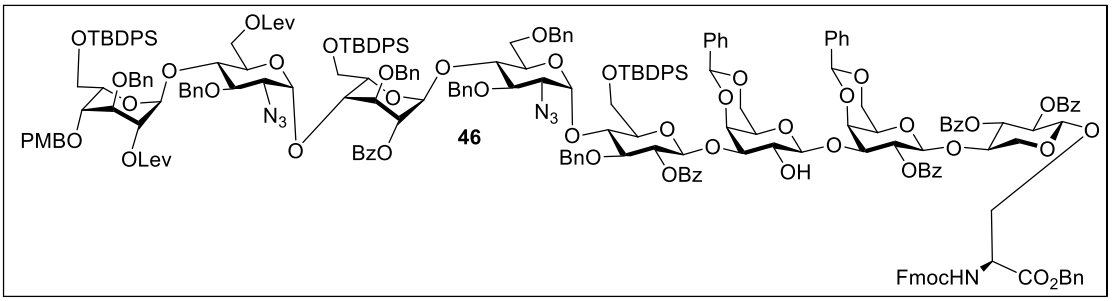


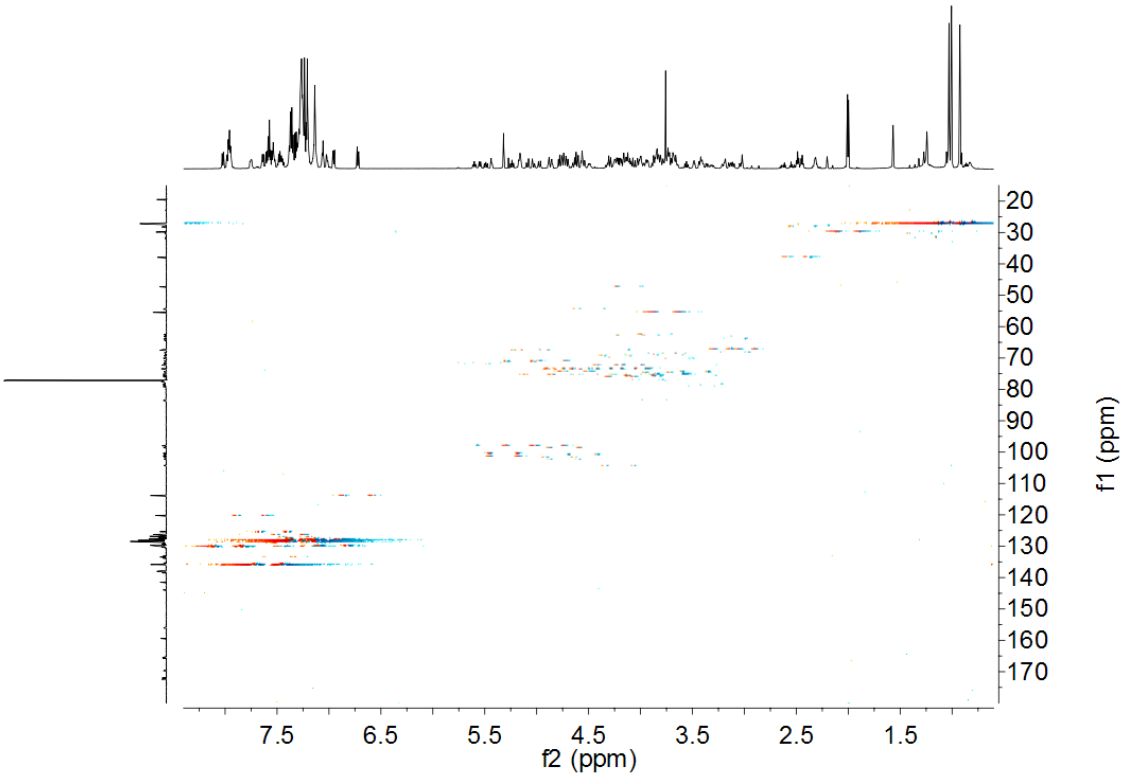
gHMQC ($CDCl_3$, 500 MHz) of **46**



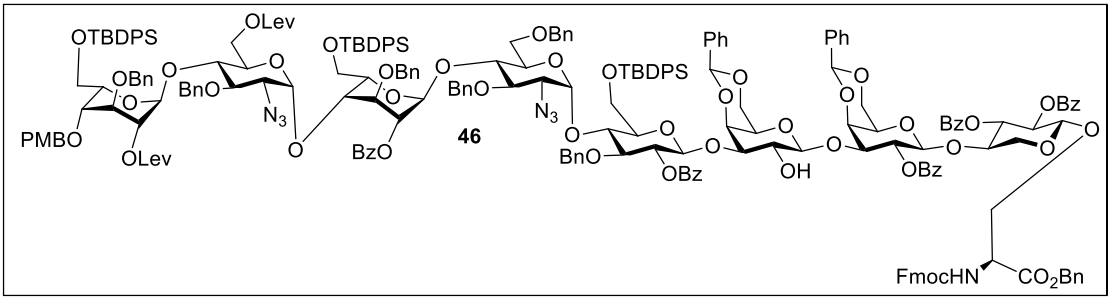


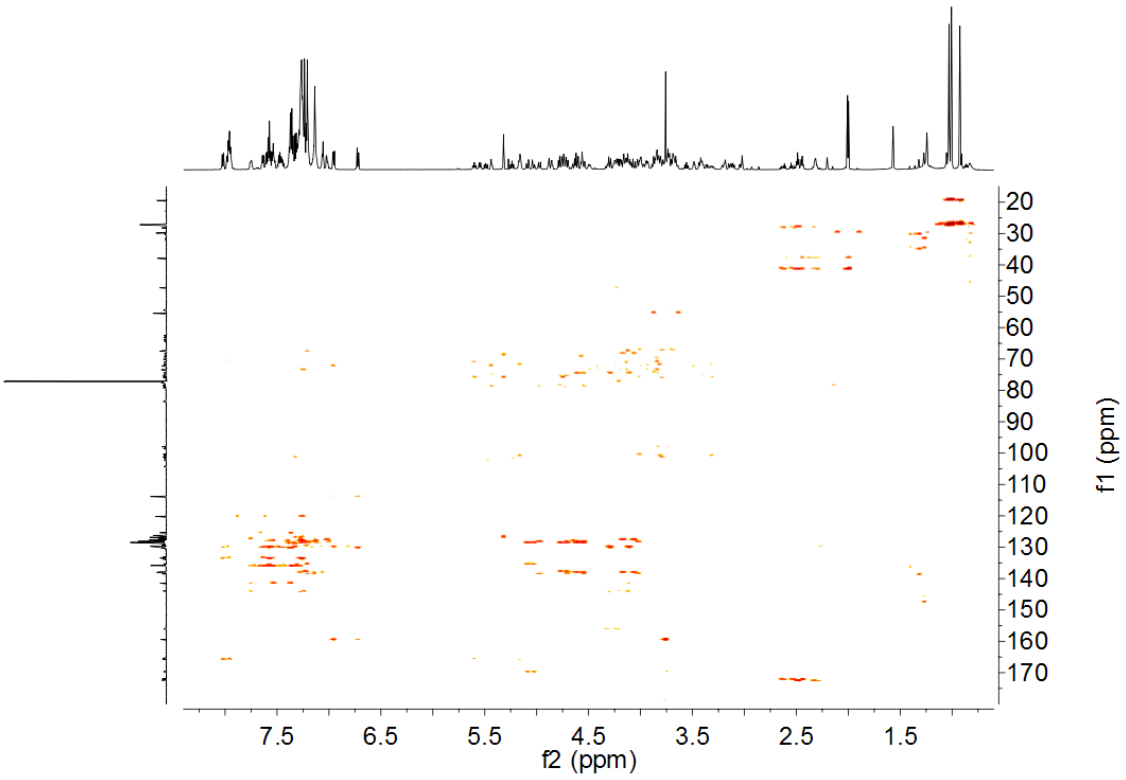
gHMQC (without ^{1}H decoupling) ($CDCl_3$, 500 MHz) of **46**



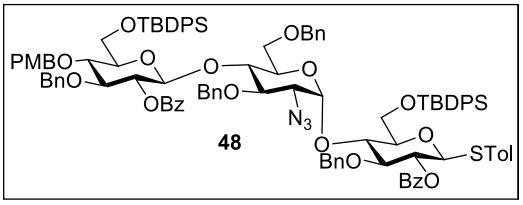


gHMBC ($CDCl_3$, 500 MHz) of **46**

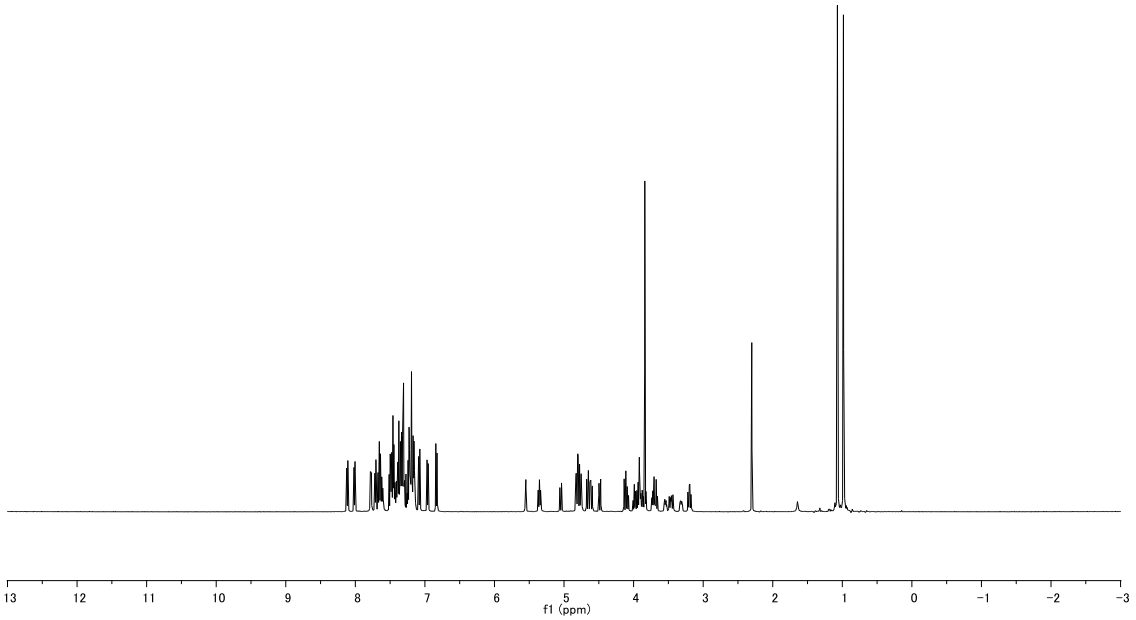




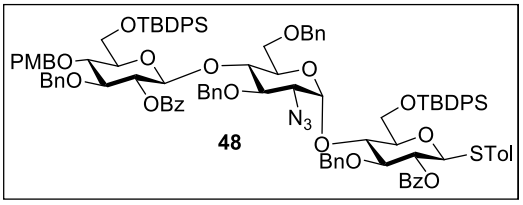
^{1}H-NMR (500 MHz) of **48**



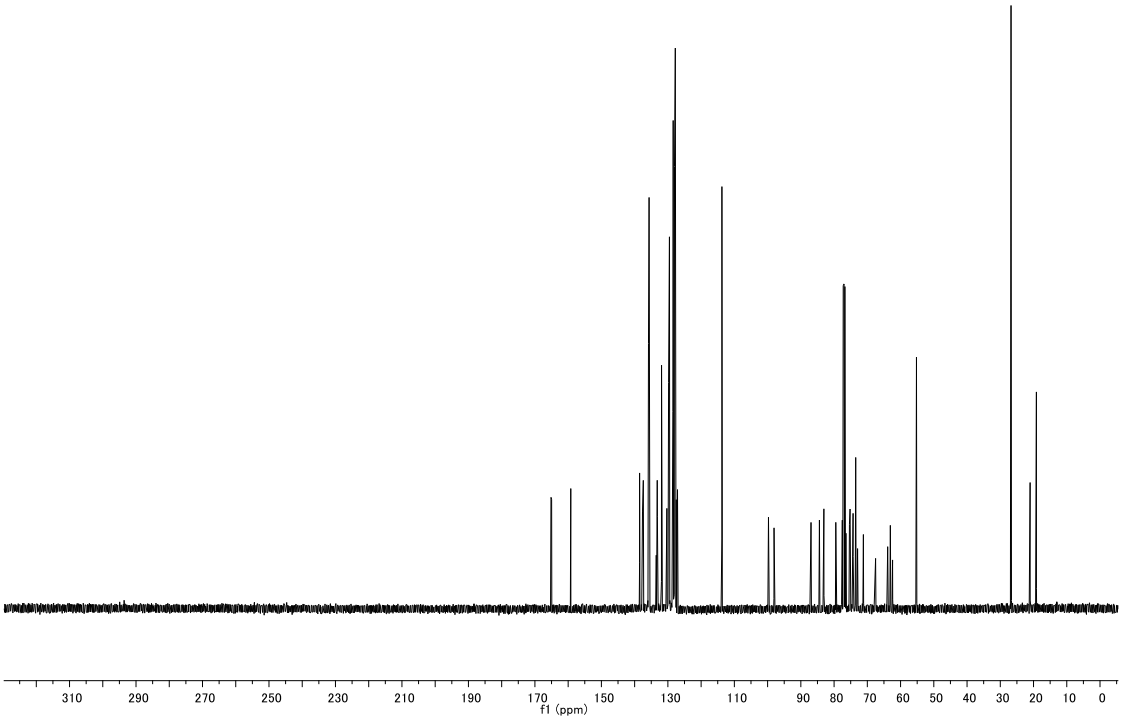
48



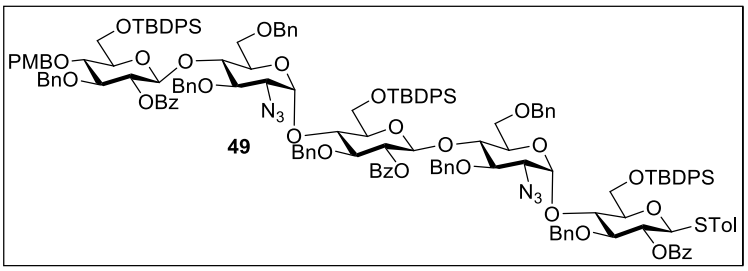
^{13}C-NMR (125 MHz) of **48**

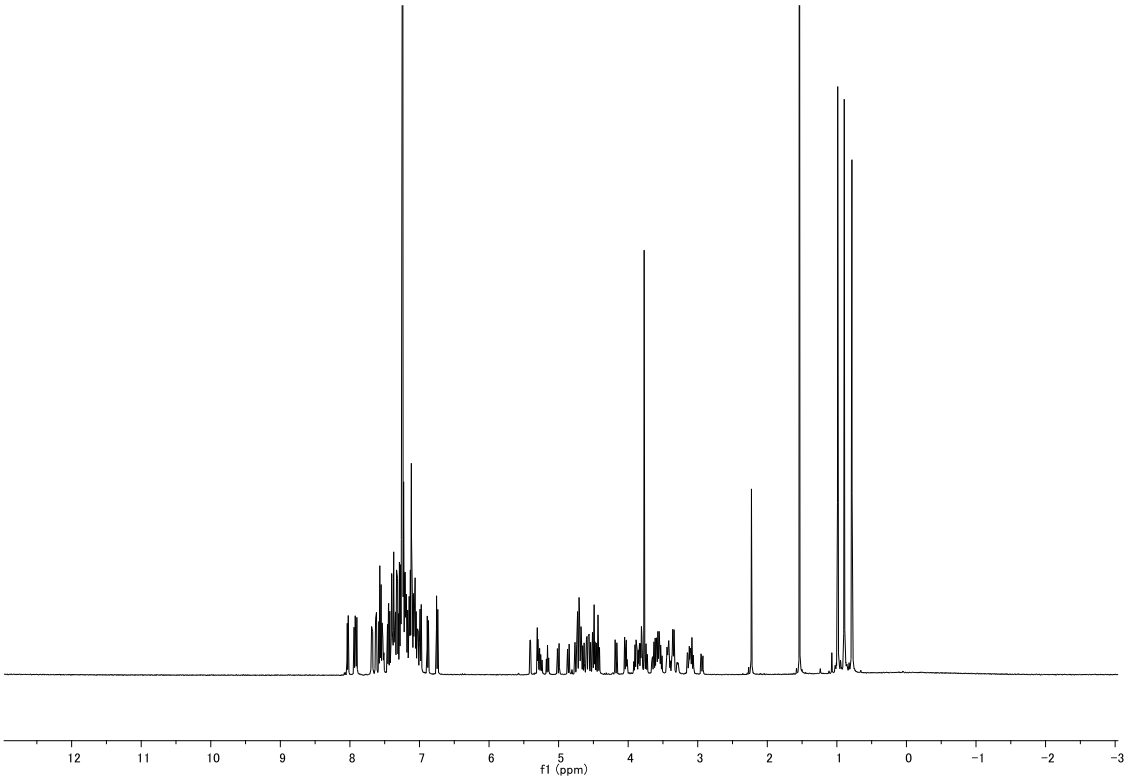


48

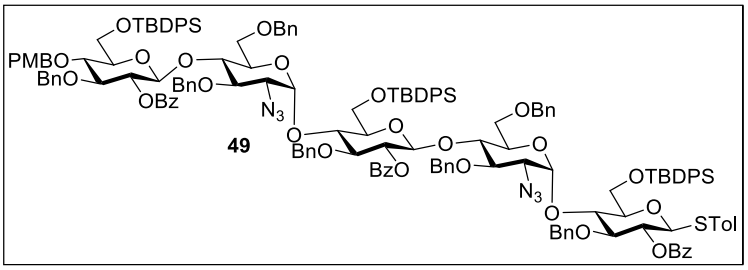


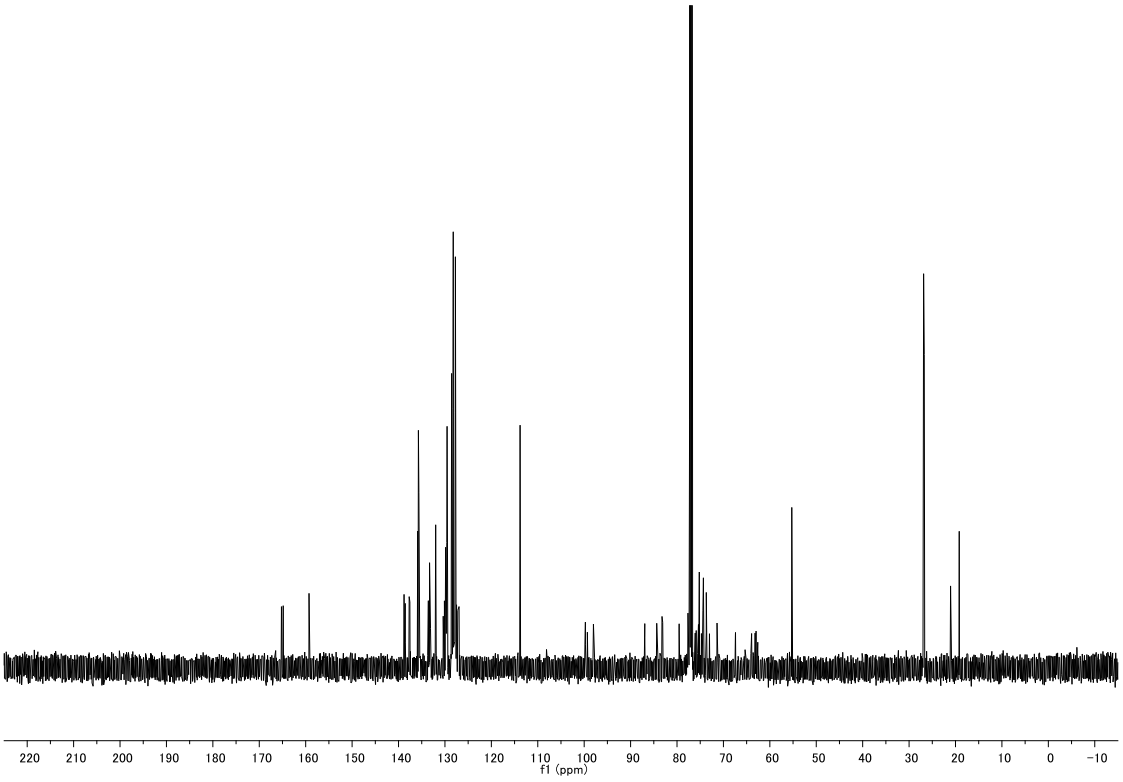
^{1}H-NMR (500 MHz) of **49**



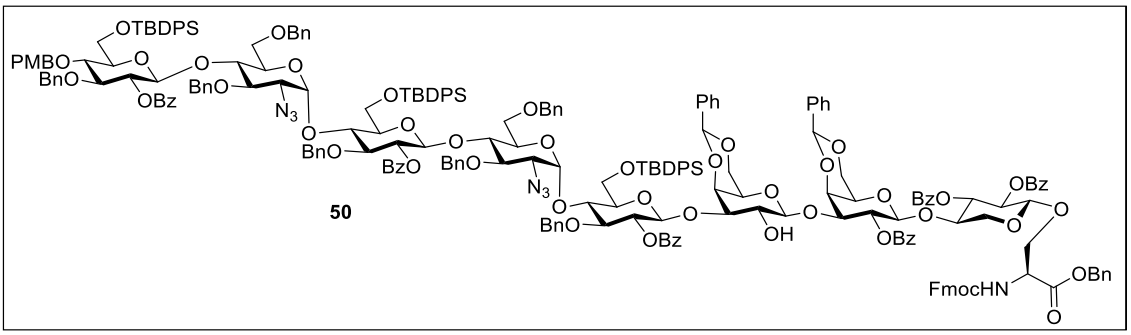


^{13}C-NMR (125 MHz) of **49**

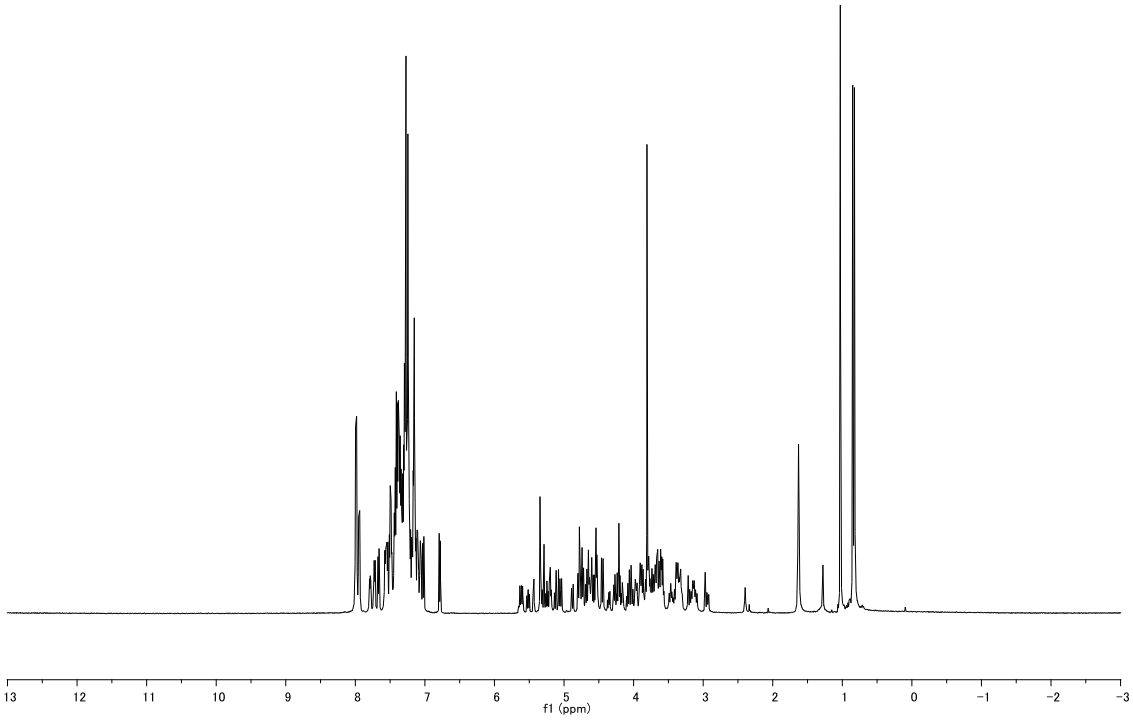




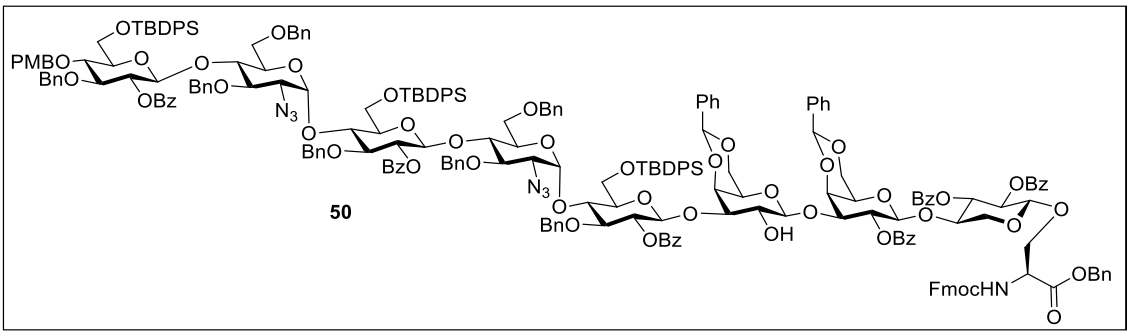
^{1}H-NMR (500 MHz) of **50**



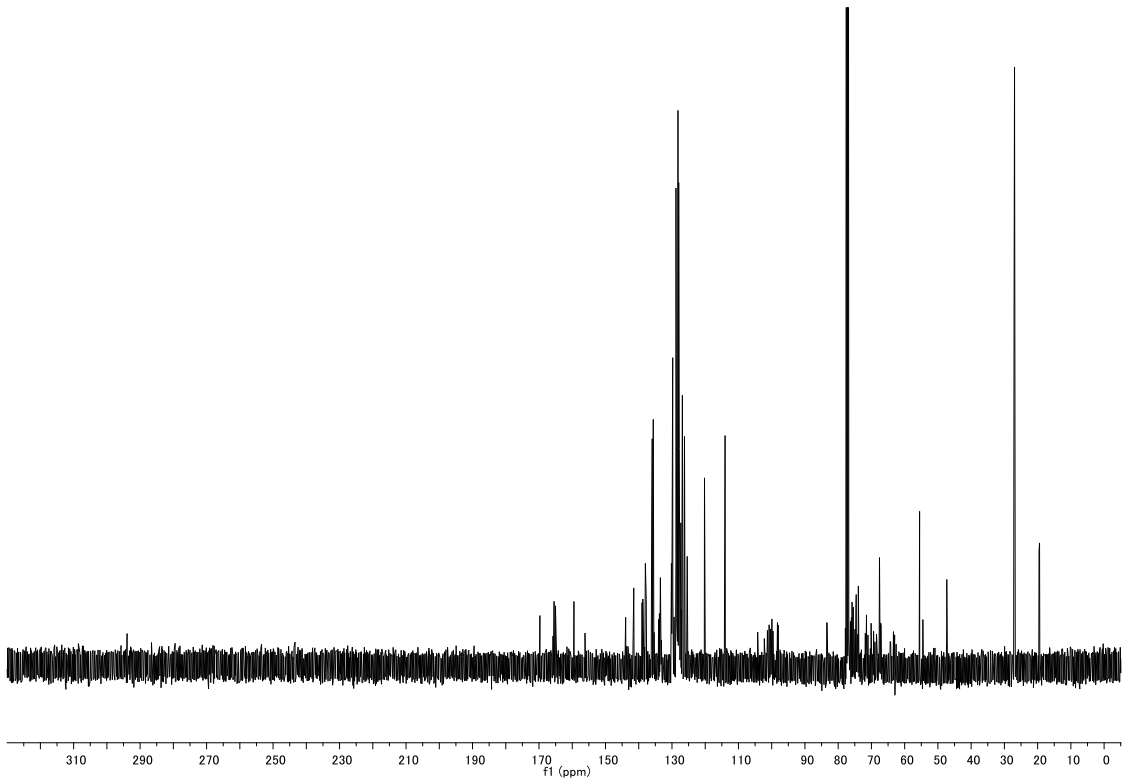
50



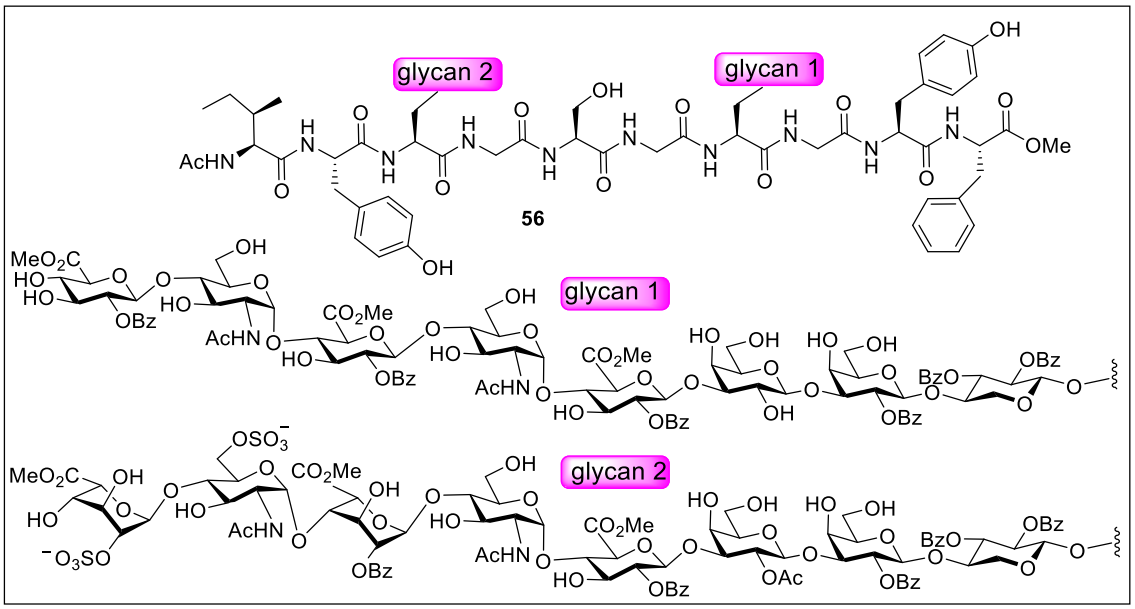
^{13}C-NMR (125 MHz) of **50**

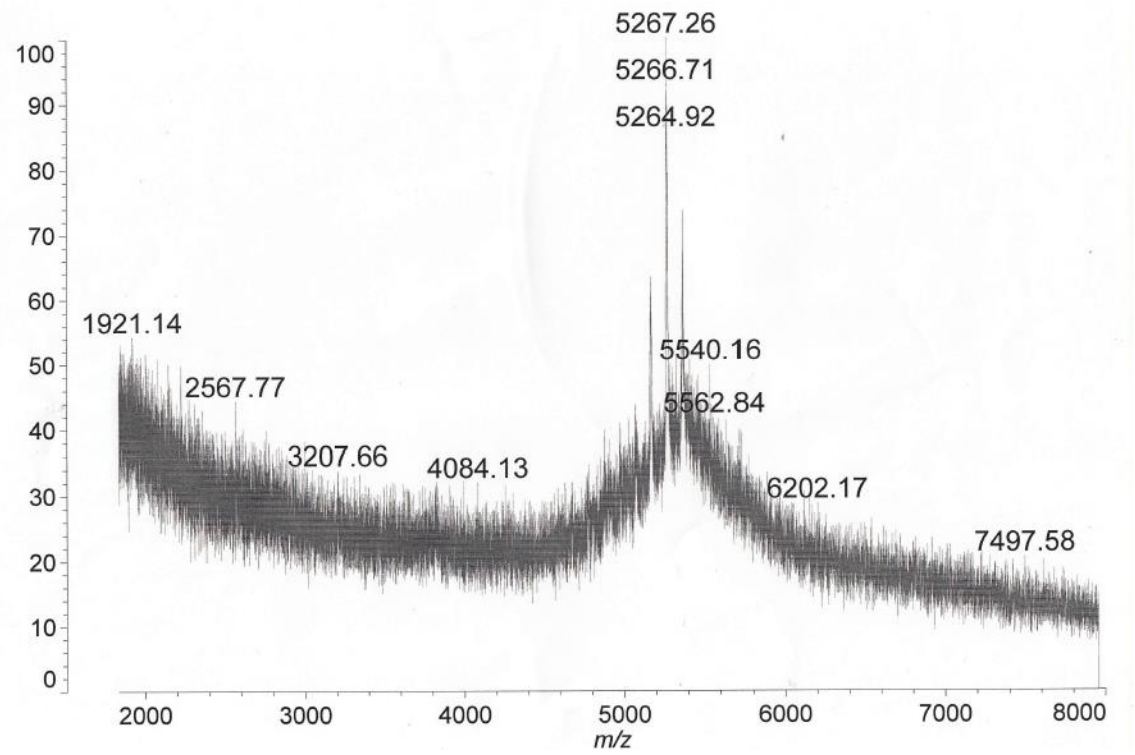


50

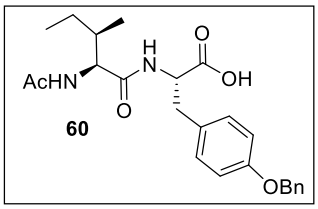


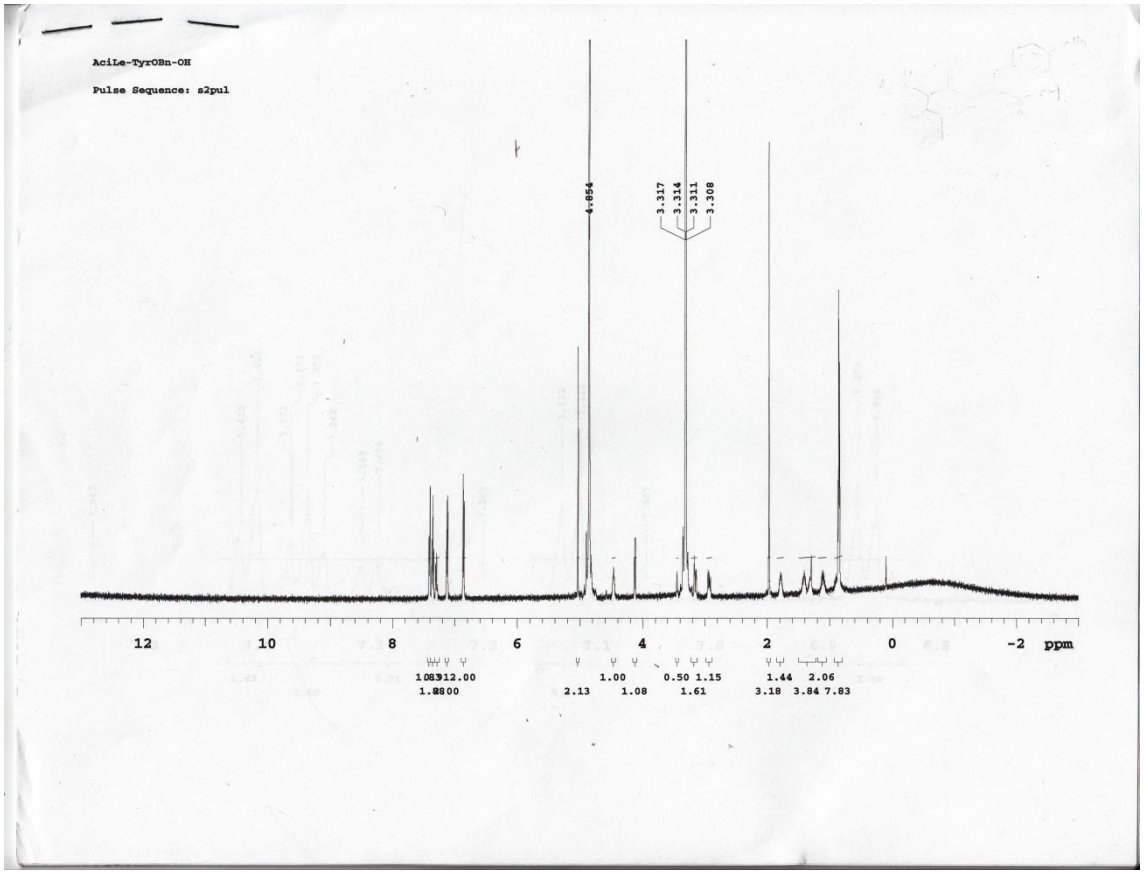
MALDI-MS of **56**



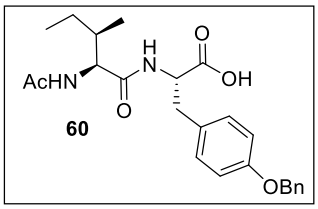


^{1}H-NMR (500 MHz) of **60**





^{13}C-NMR (125 MHz) of **60**



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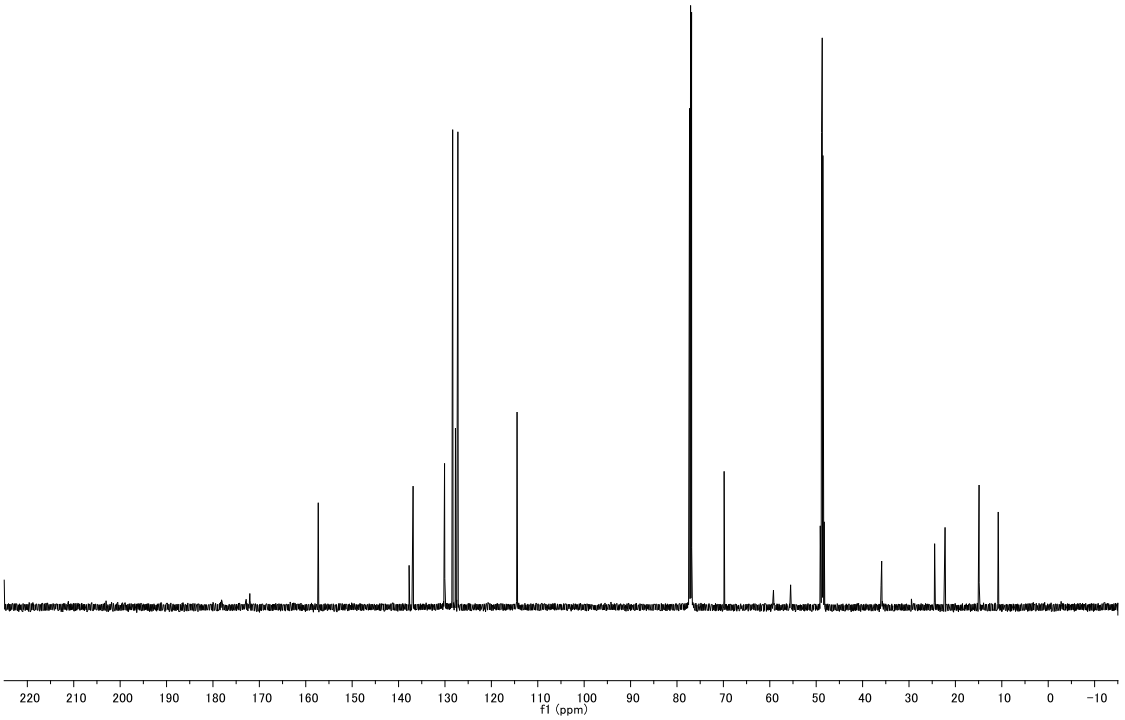
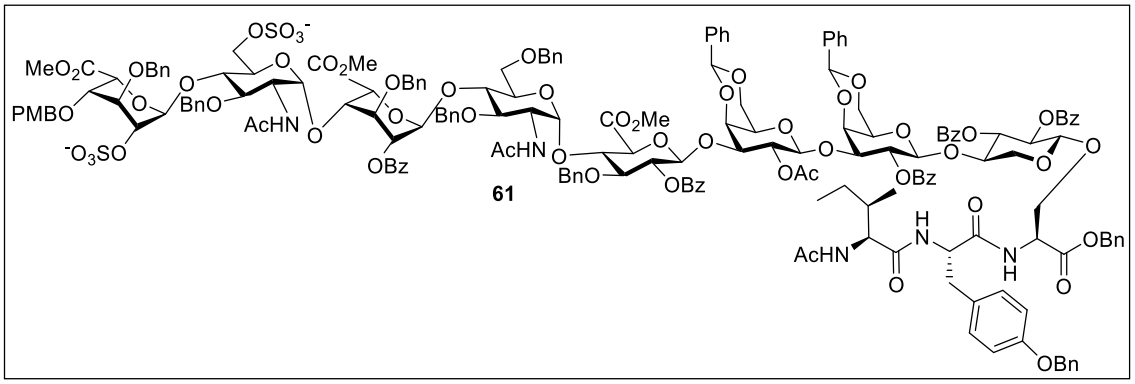
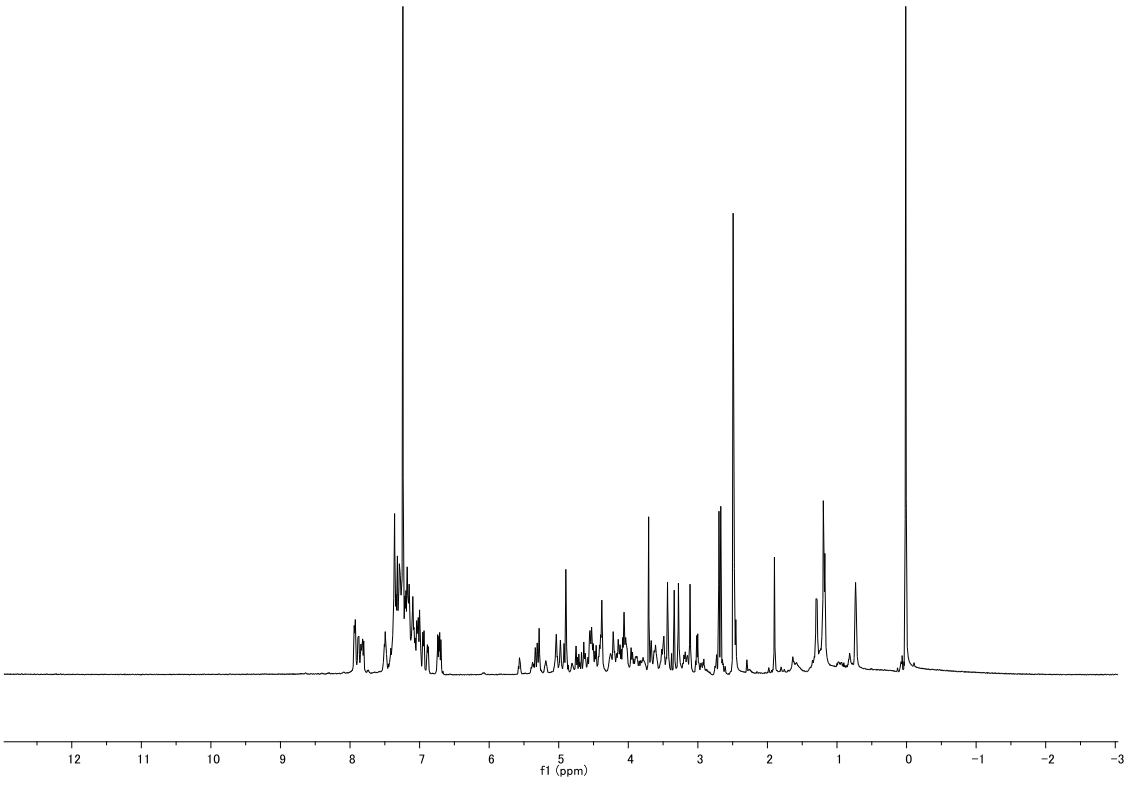
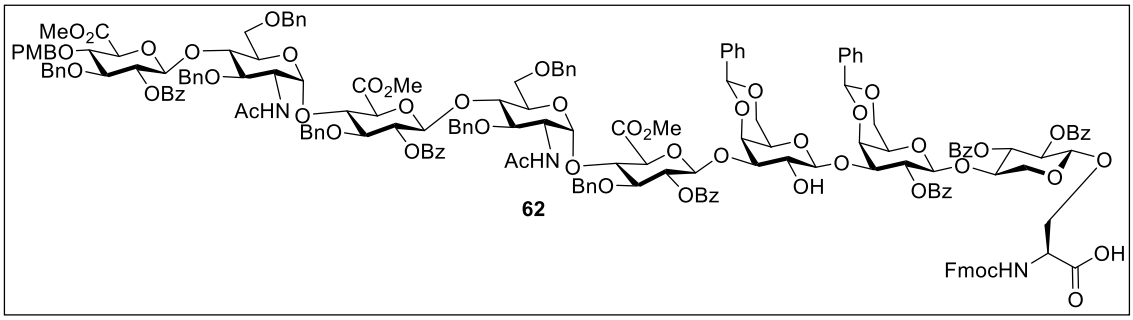


^{1}H-NMR (500 MHz) of **61**

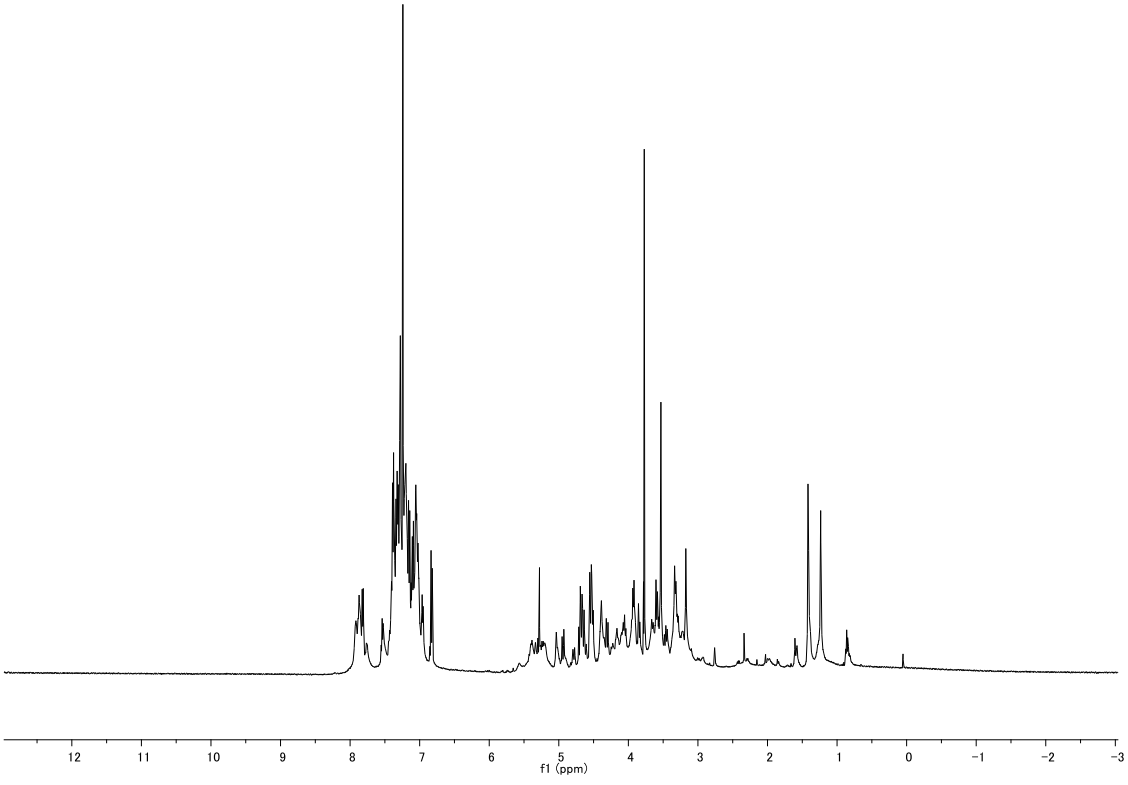




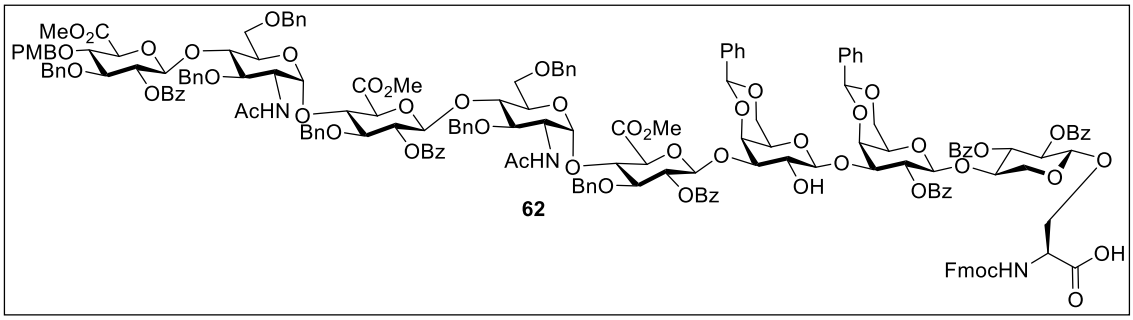
^{1}H-NMR (500 MHz) of **62**



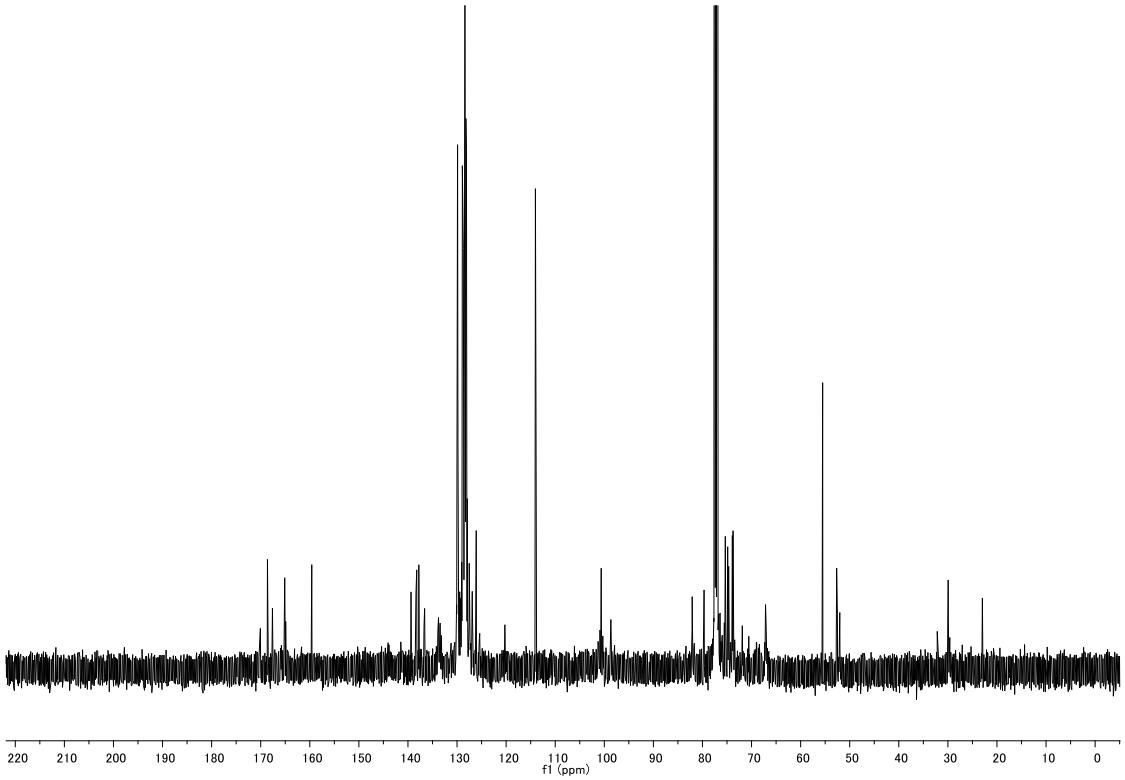
62



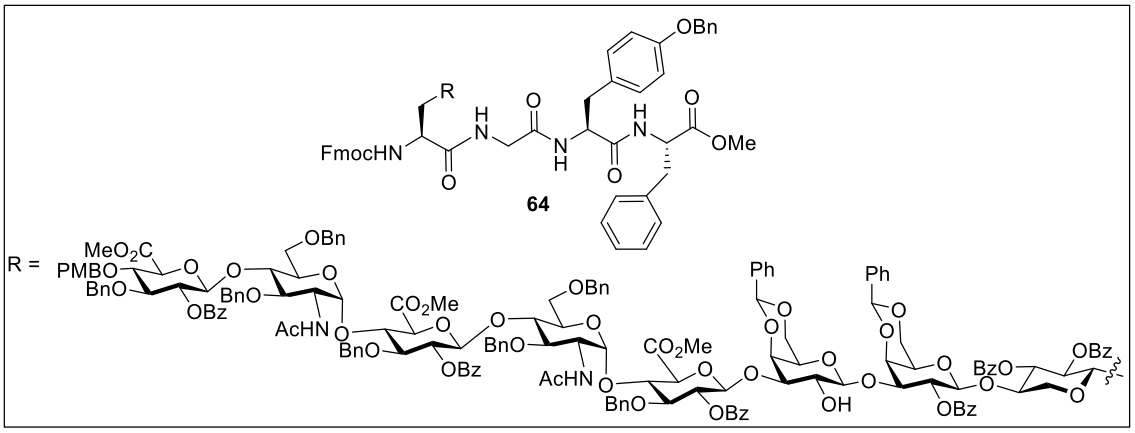
^{13}C-NMR (125 MHz) of **62**

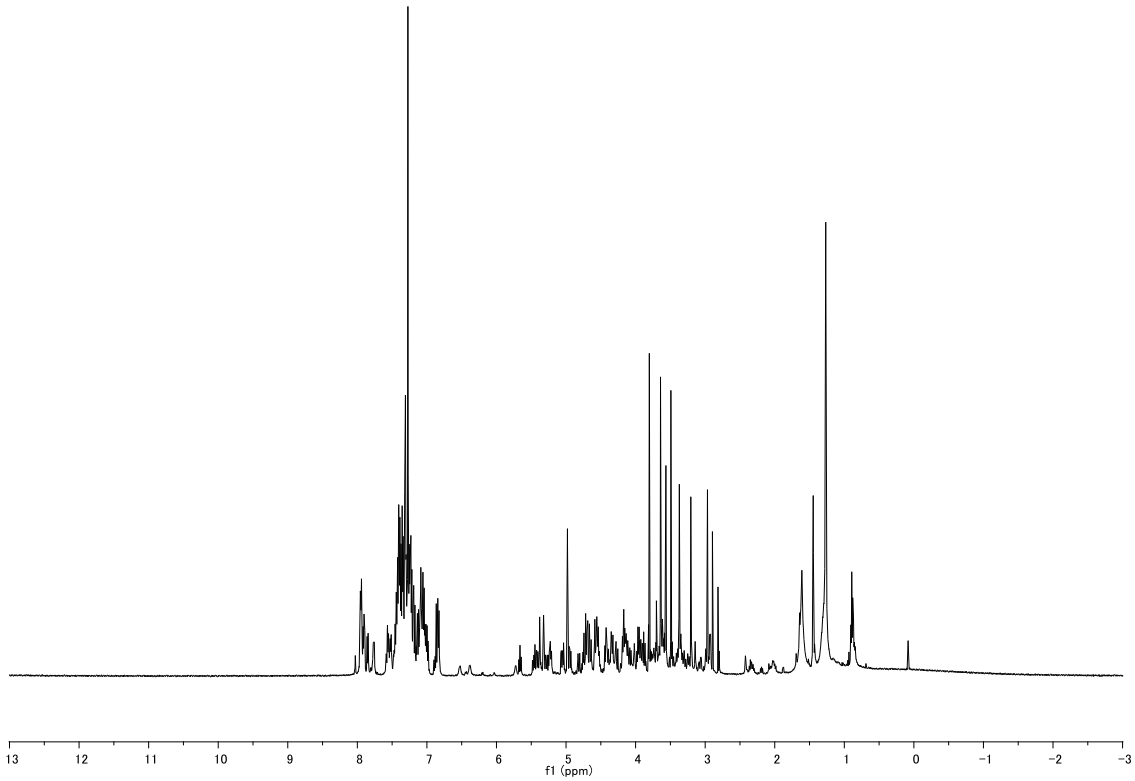


62

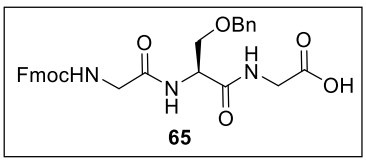


^{1}H-NMR (500 MHz) of **64**

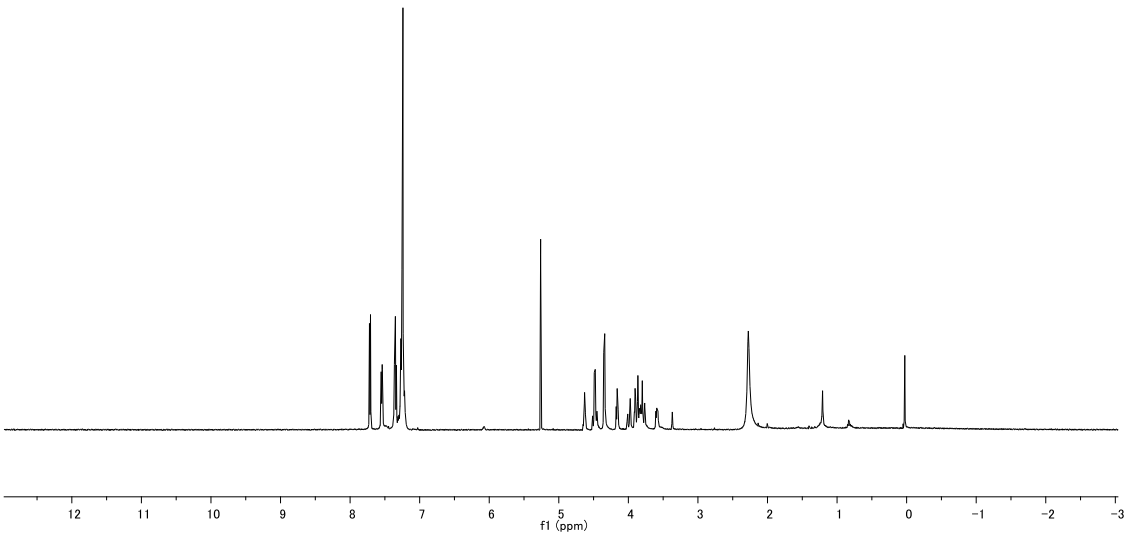




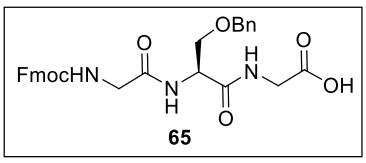
^{1}H-NMR (500 MHz) of **65**



65



^{13}C-NMR (125 MHz) of **65**



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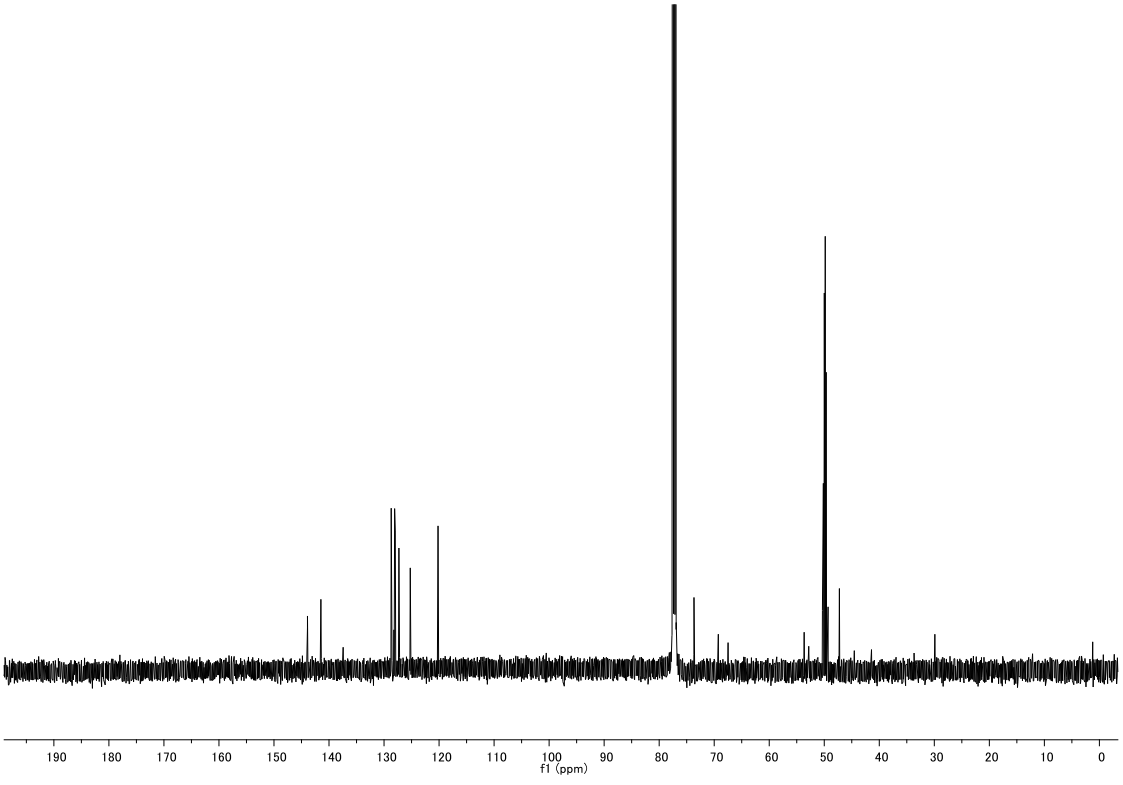
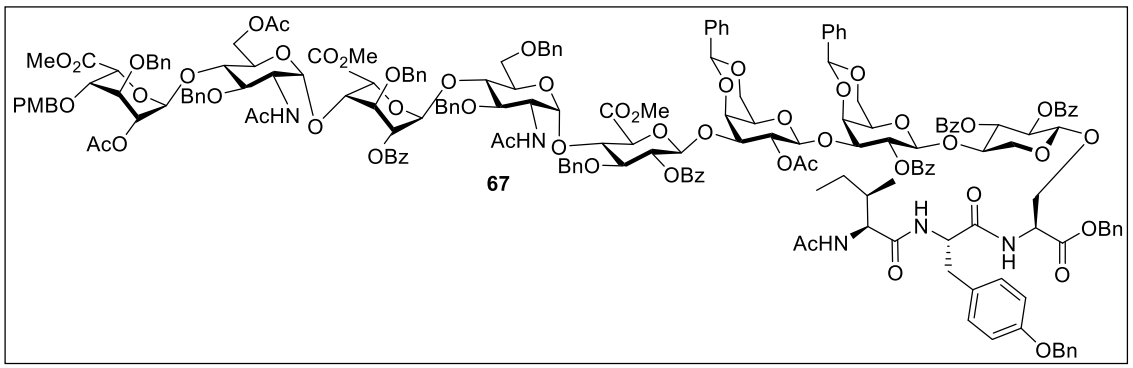
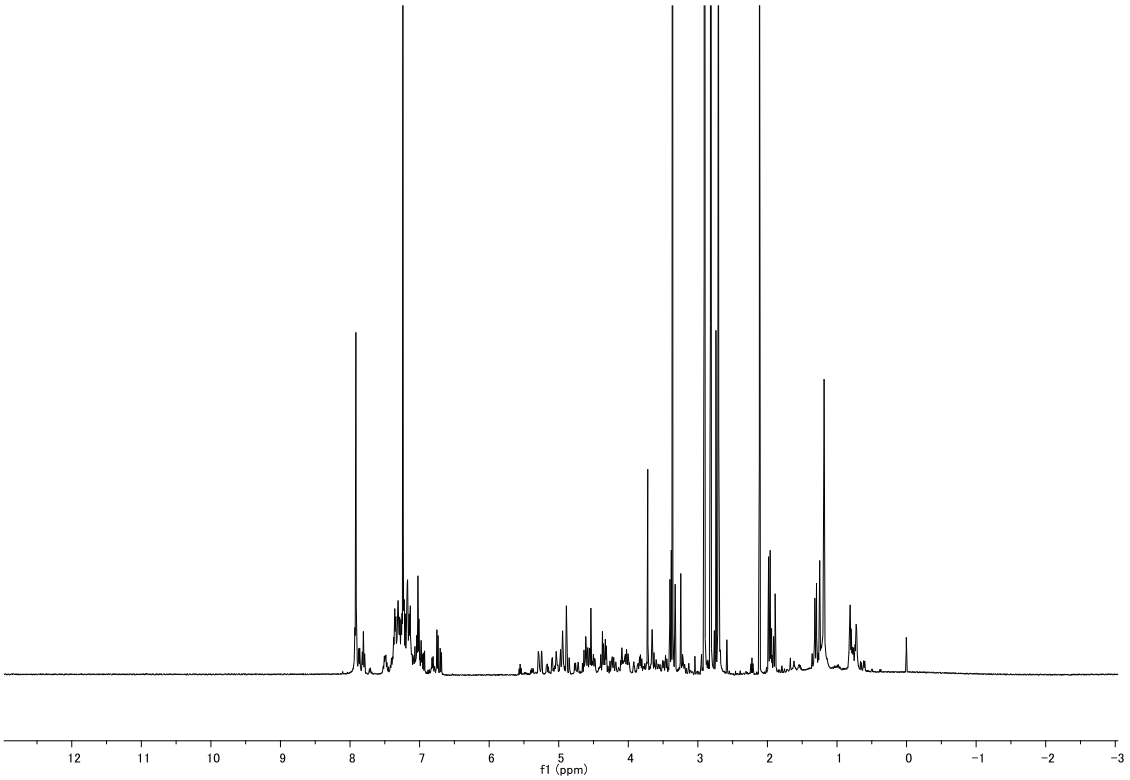


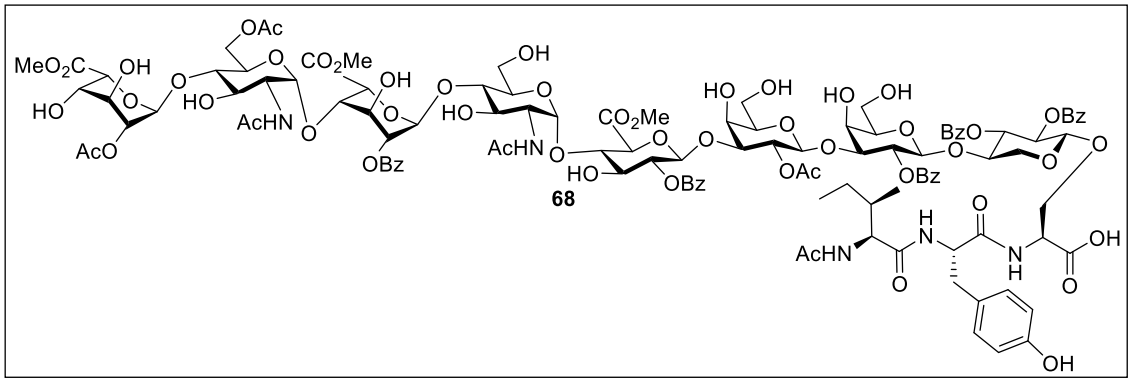
^{1}H-NMR (500 MHz) of **67**



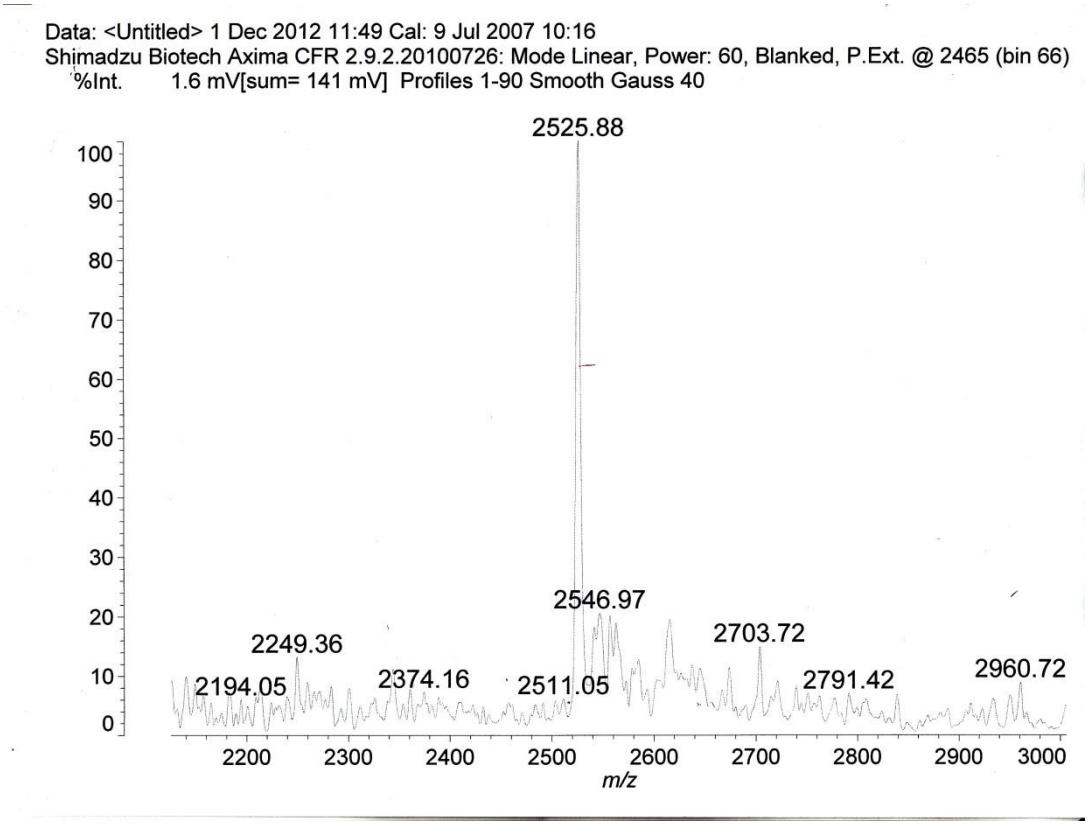
67



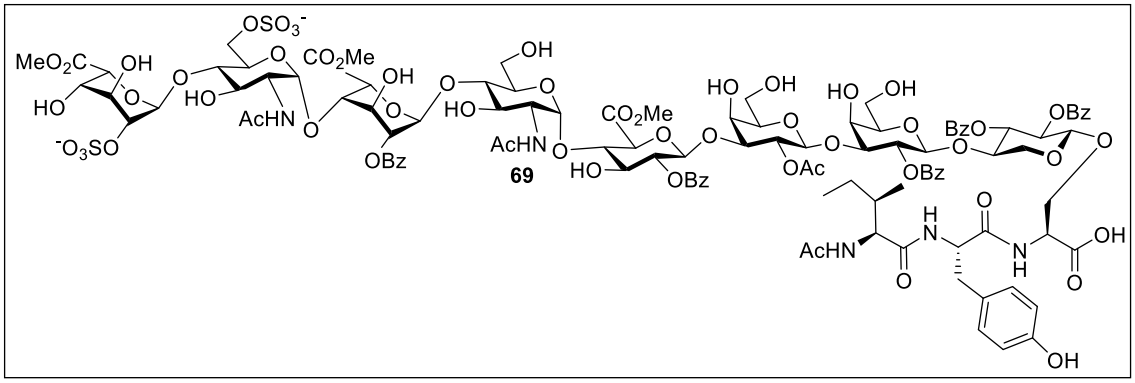
MALDI-MS of **68**

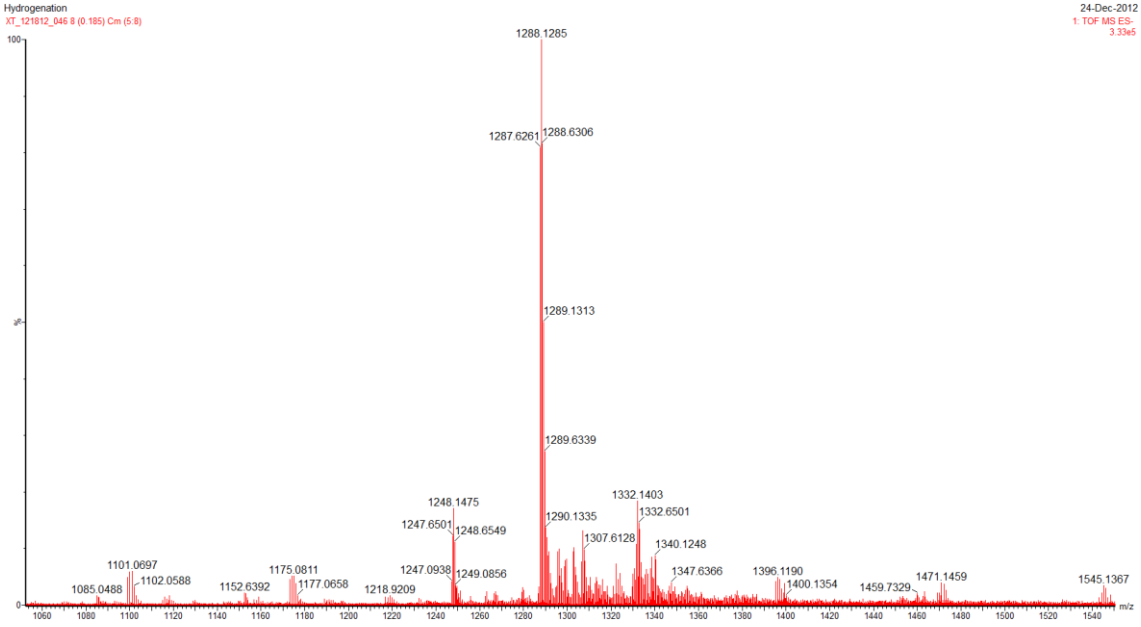


68



ESI-MS of **69**


69


Hydrogenation
XT_121812_046 8 (0.185) Cm (5:8)
24-Dec-2012
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1288.1285
1287.6261
1288.6306
1289.1313
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1248.1475
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1290.1335
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1340.1248
1101.0697
1102.0588
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1175.0811
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1152.6392
1247.0938
1249.0856
1218.9209
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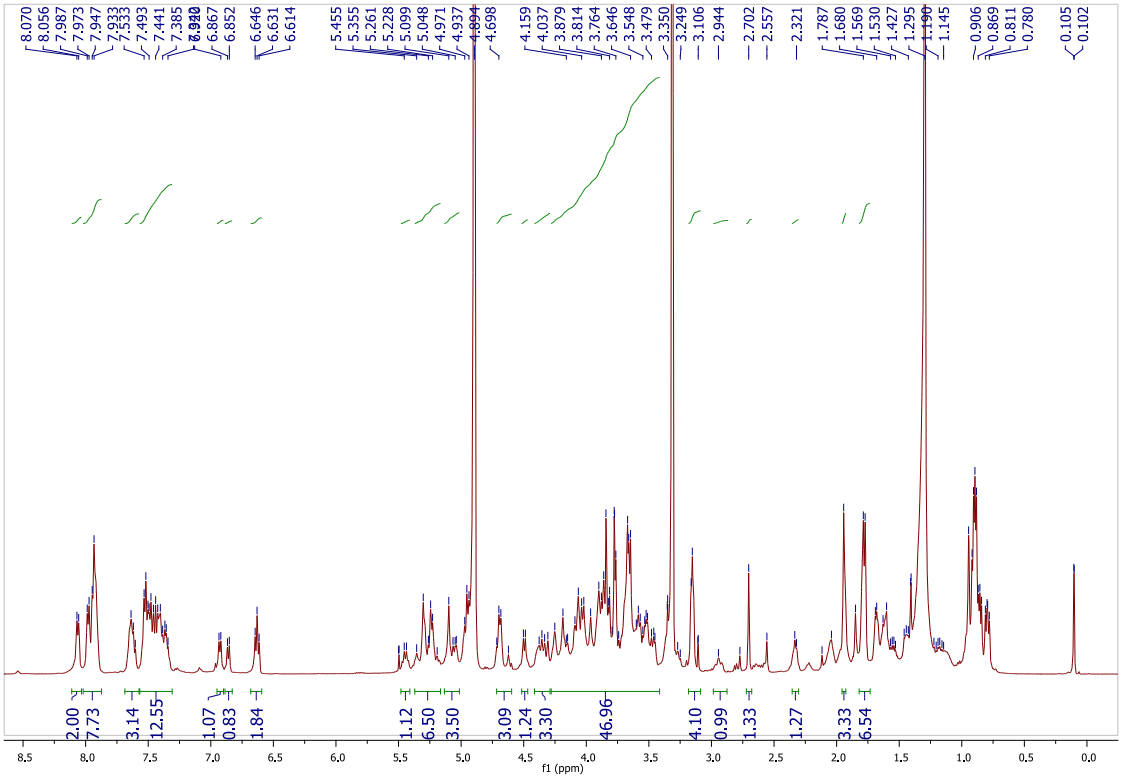
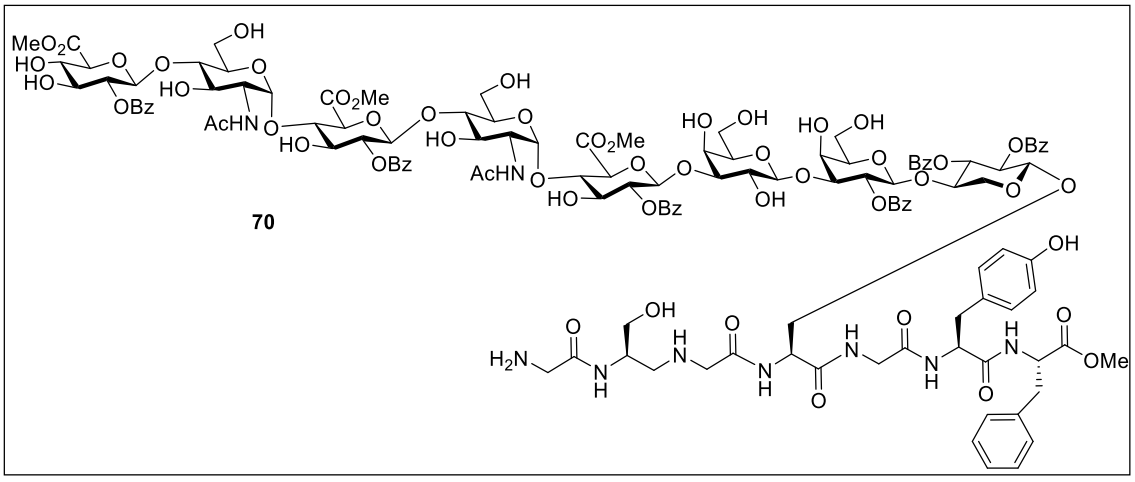
m/z

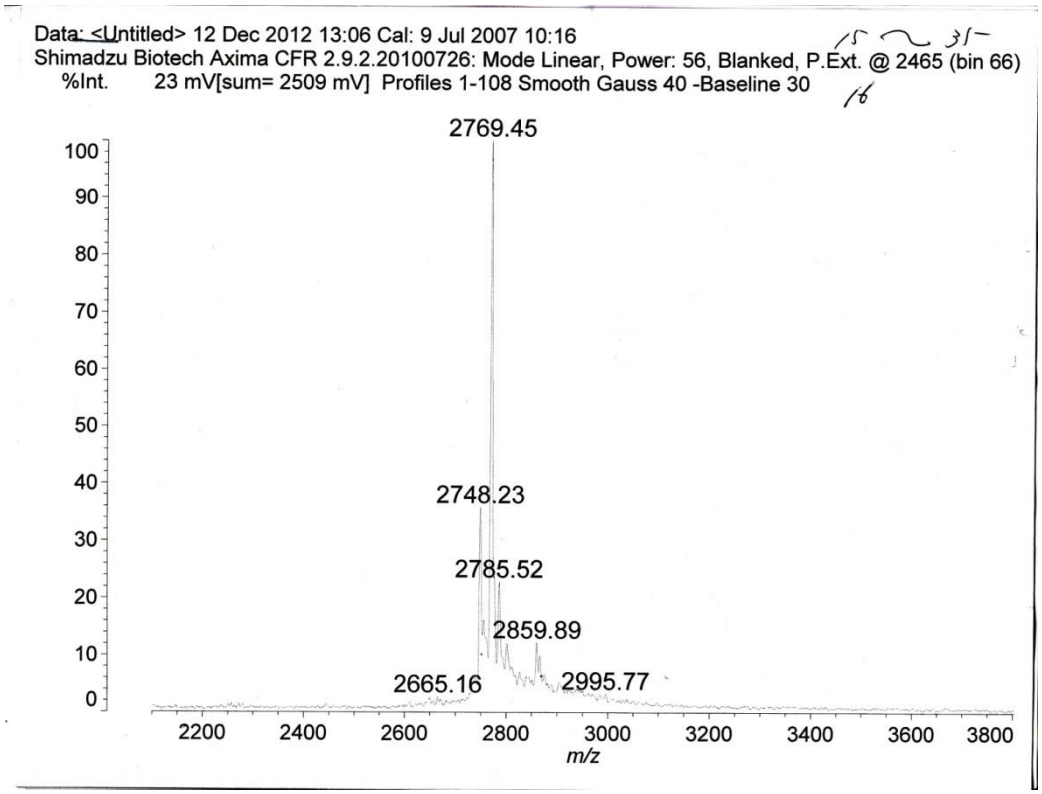
^{1}H-NMR (500 MHz) of **69**



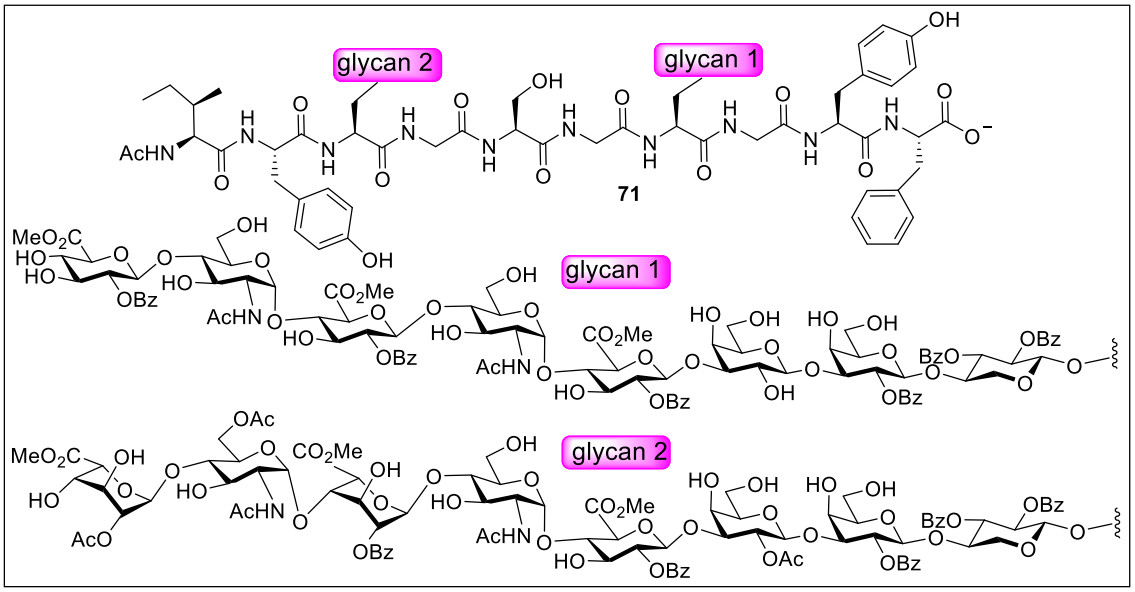
MALDI-MS of **70**

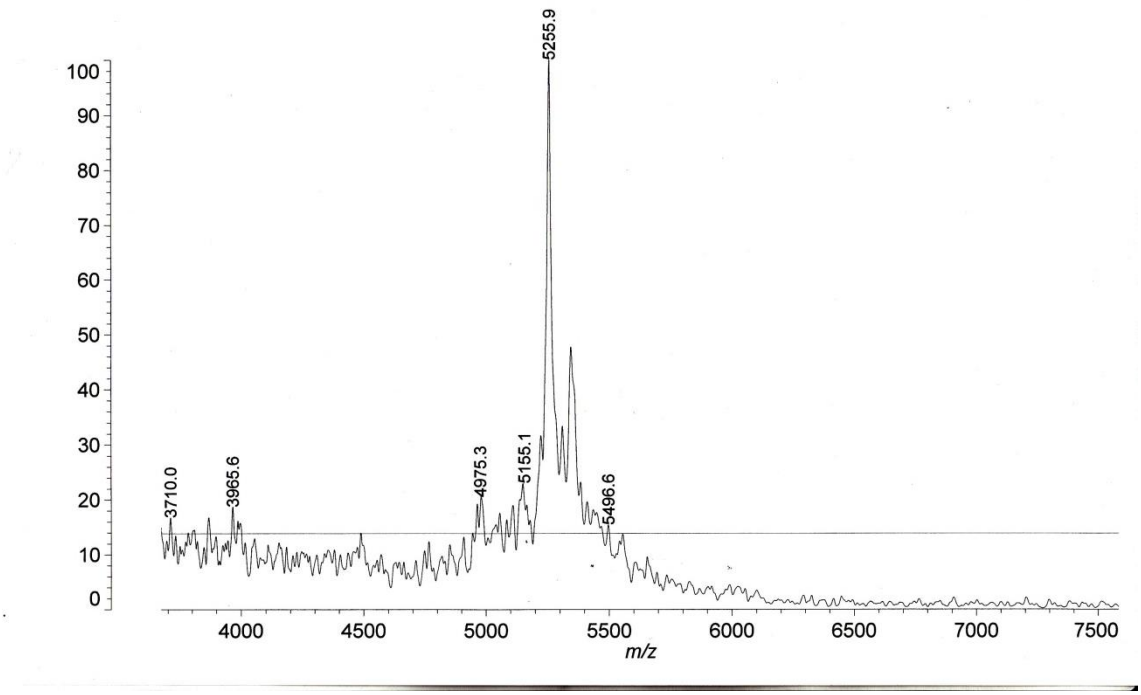


70

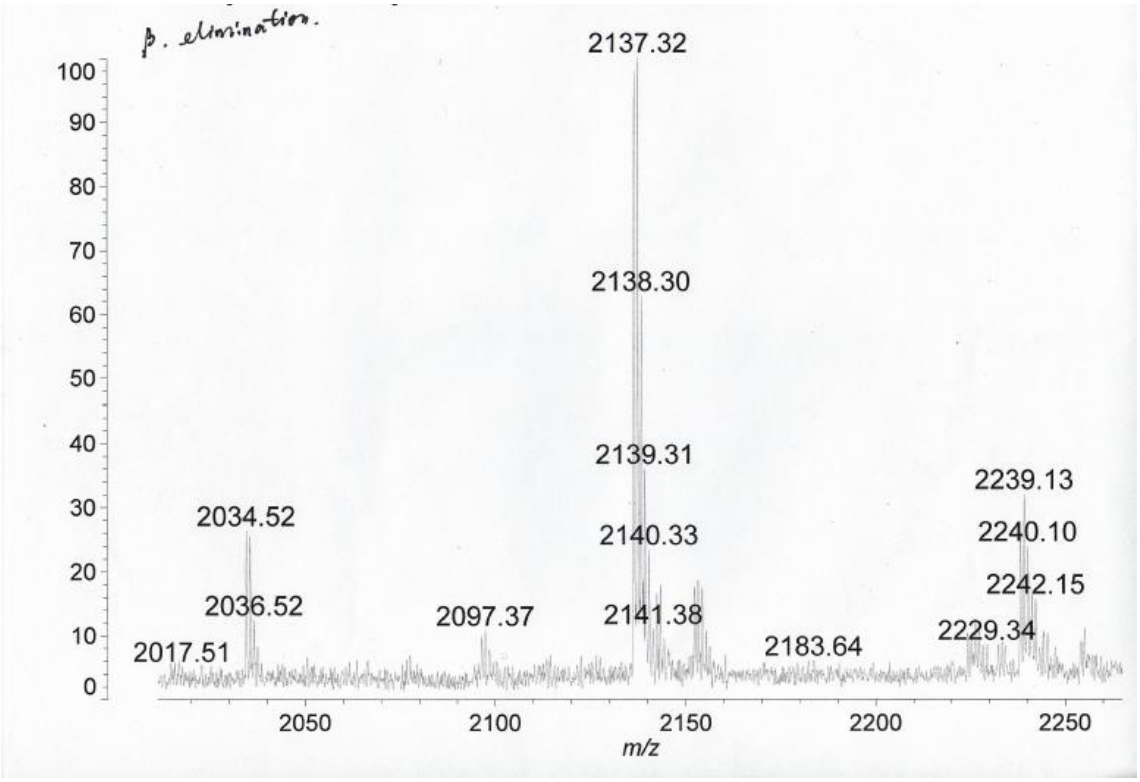


MALDI-MS of **71**

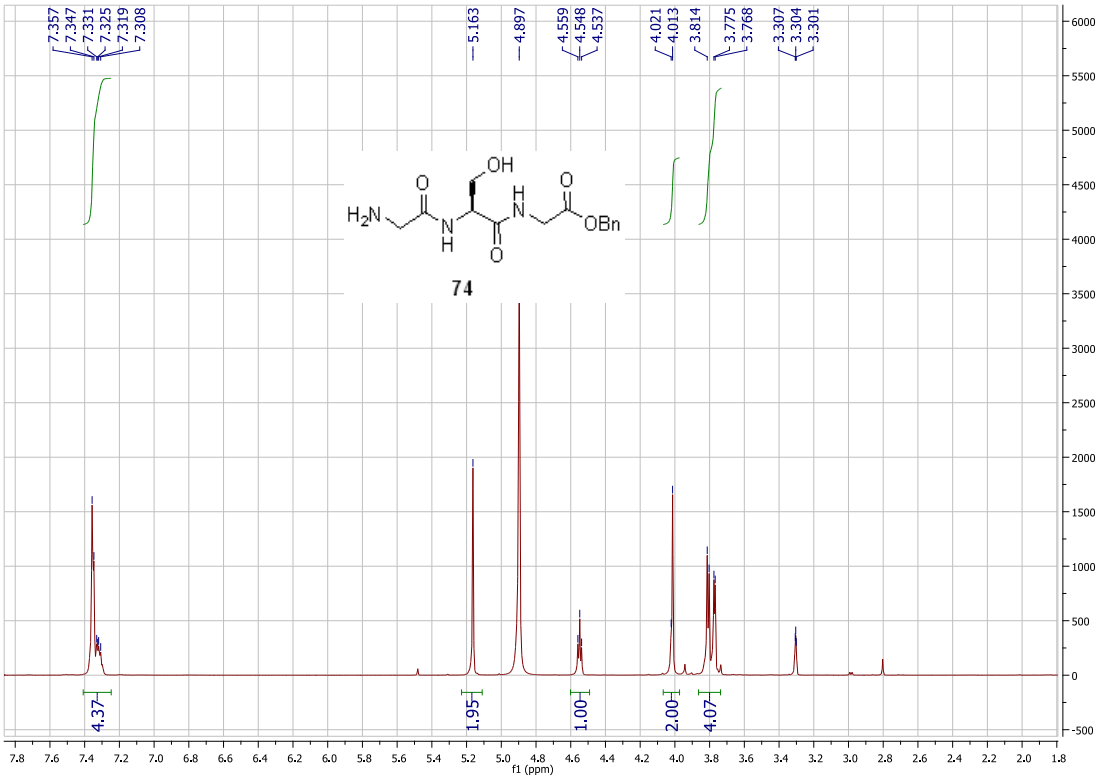




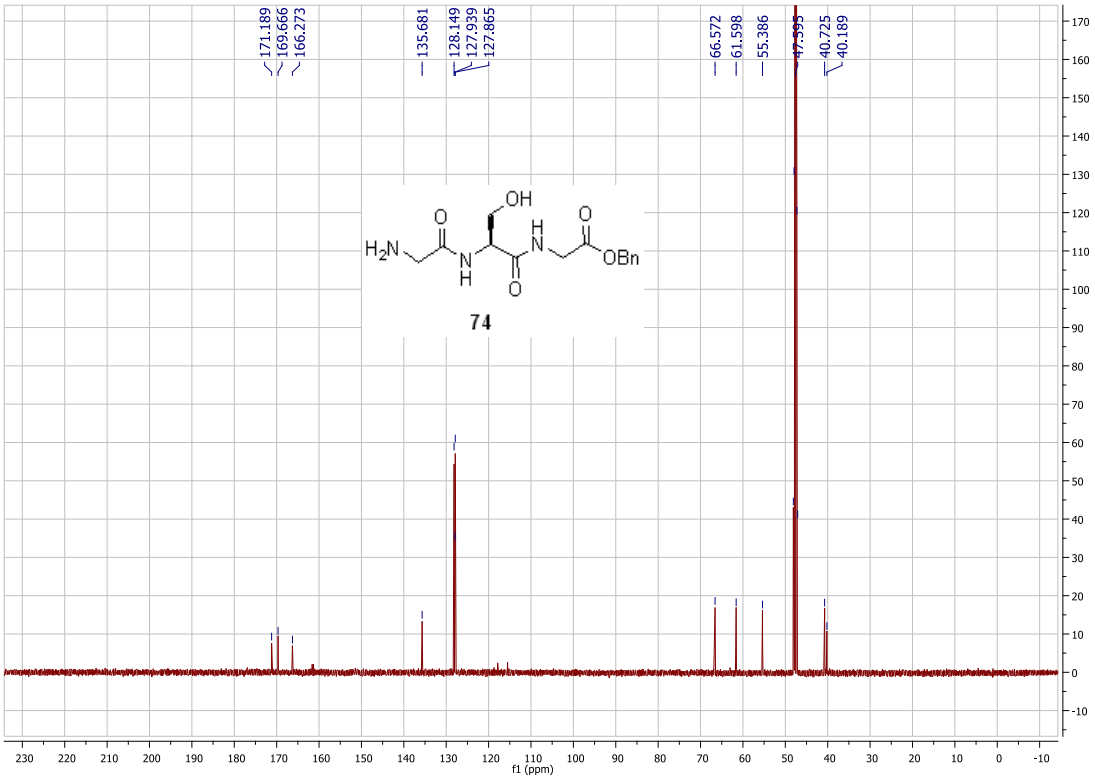
MALDI-MS of **72**



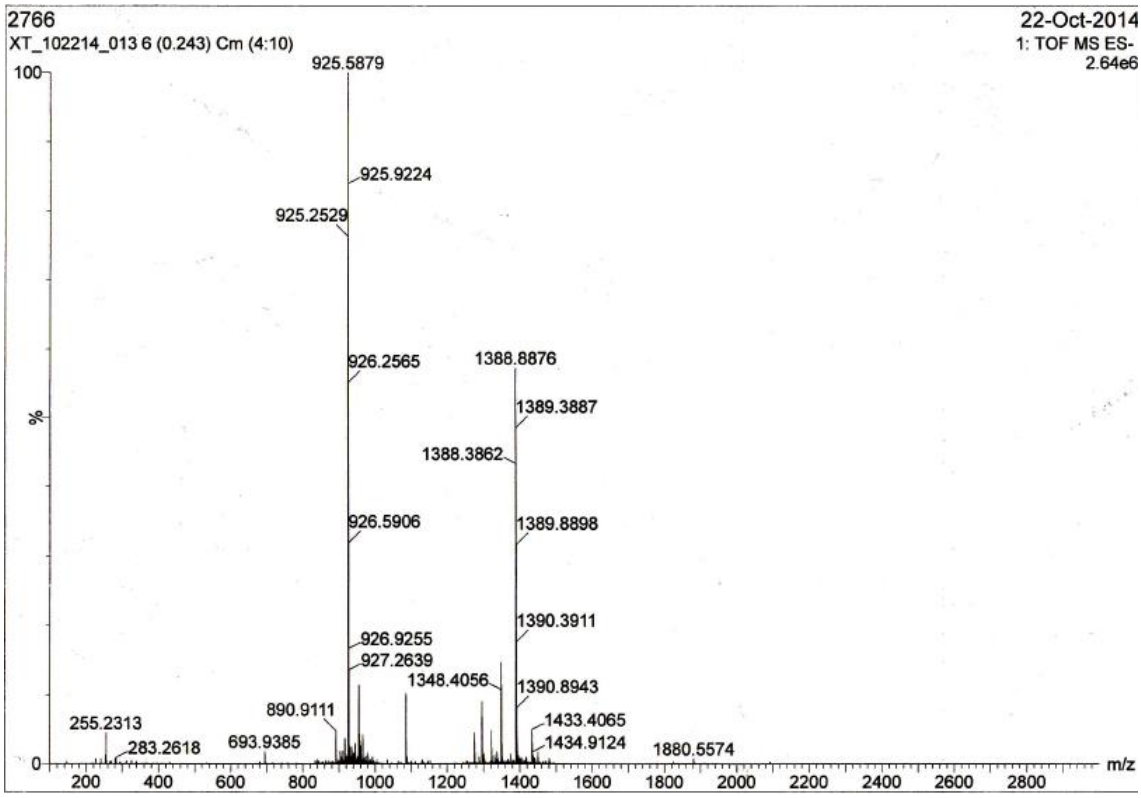
^{1}H-NMR ($CDCl_3$, 500 MHz) and ^{13}C-NMR ($CDCl_3$, 125 MHz) of **73**



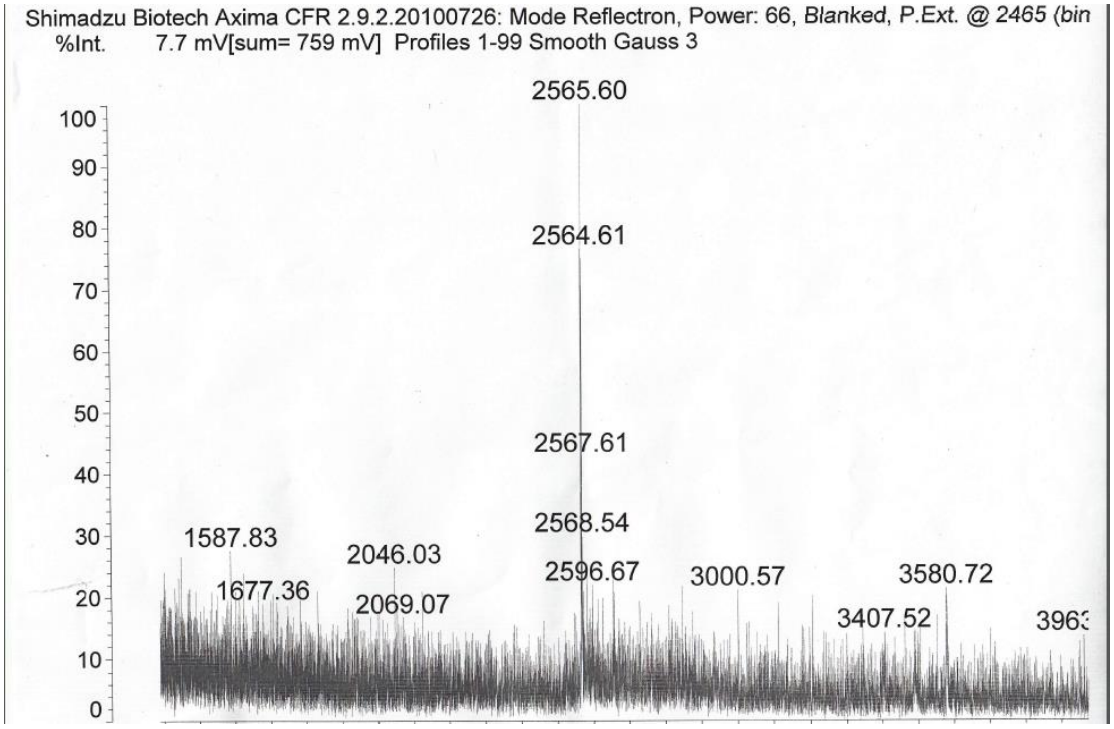
^{13}C-NMR ($CDCl_3$, 125 MHz) of **73**



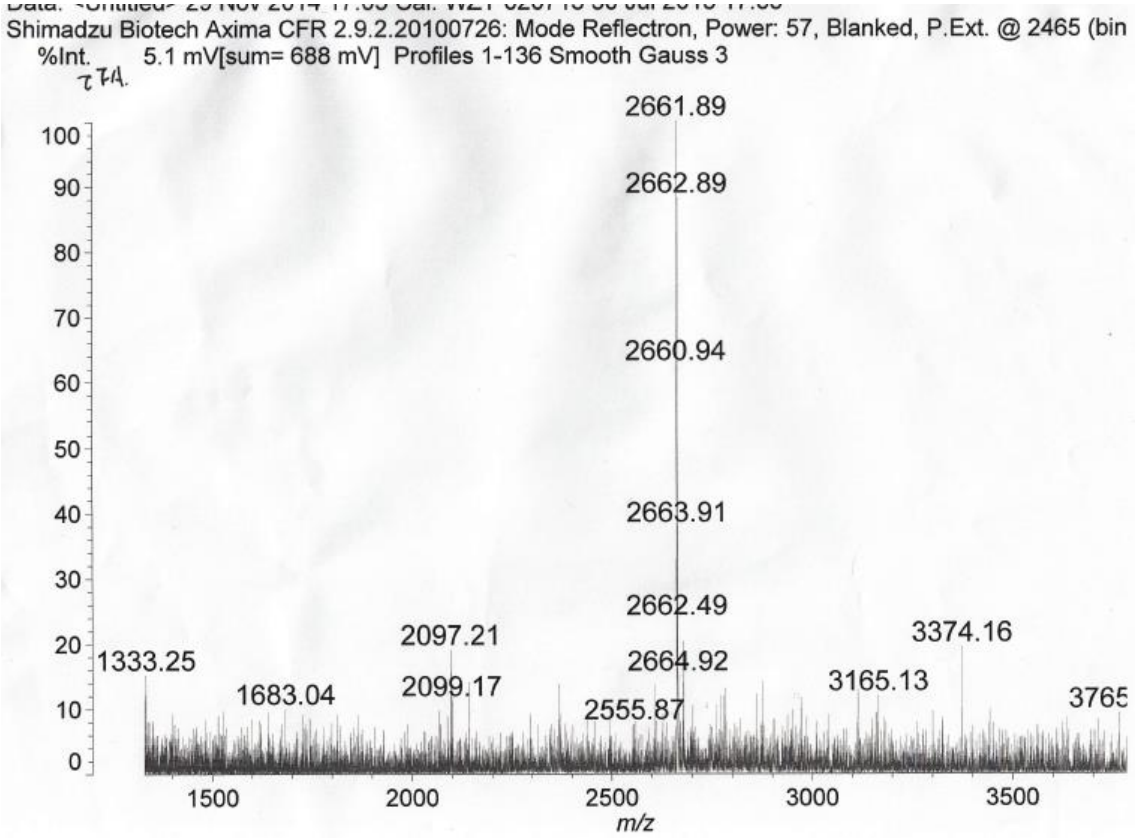
HRMS of **75**


2766
XT_102214_013 6 (0.243) Cm (4:10)
22-Oct-2014
1: TOF MS ES-
2.64e6
100
%
0
925.5879
925.9224
925.2529
926.2565
1388.8876
1389.3887
1388.3862
926.5906
1389.8898
1390.3911
926.9255
927.2639
1348.4056
1390.8943
890.9111
255.2313
283.2618
693.9385
1433.4065
1434.9124
1880.5574
m/z
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
2600
2800

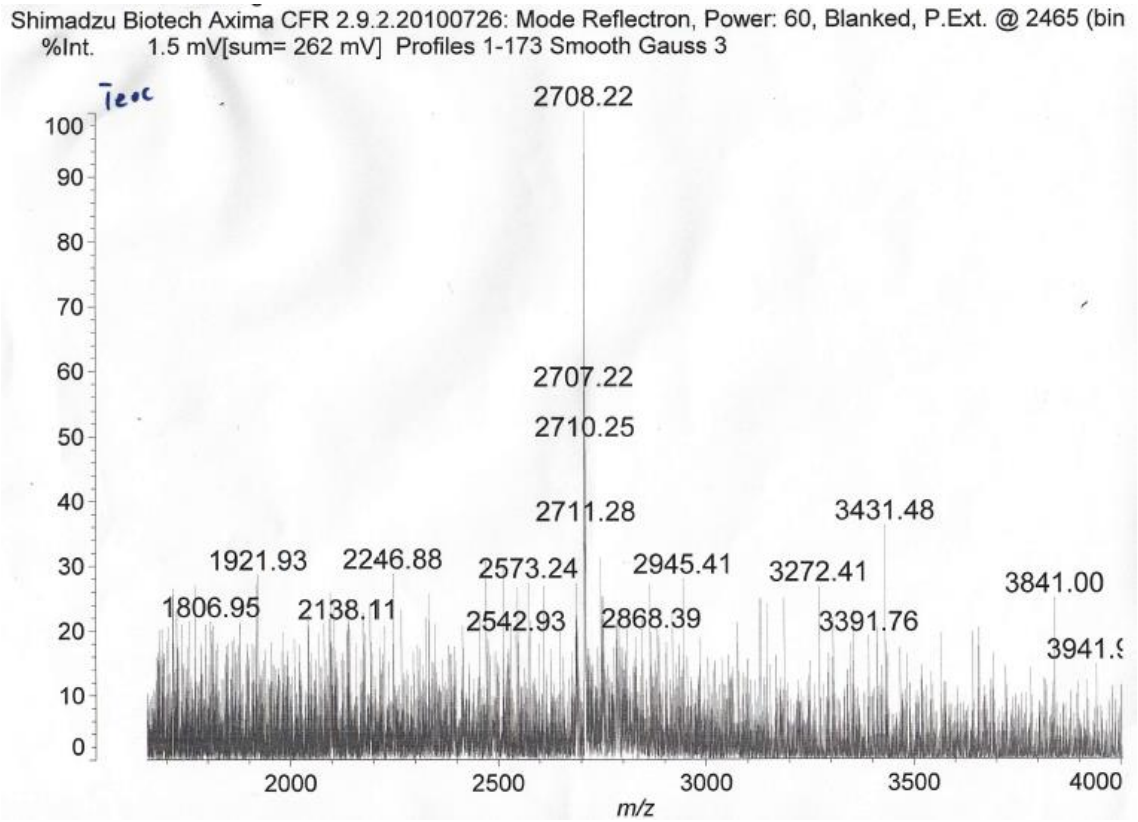
MALDI-MS of **77**



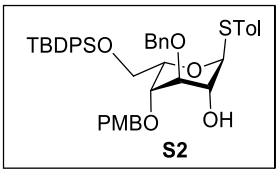
MALDI-MS of **78**

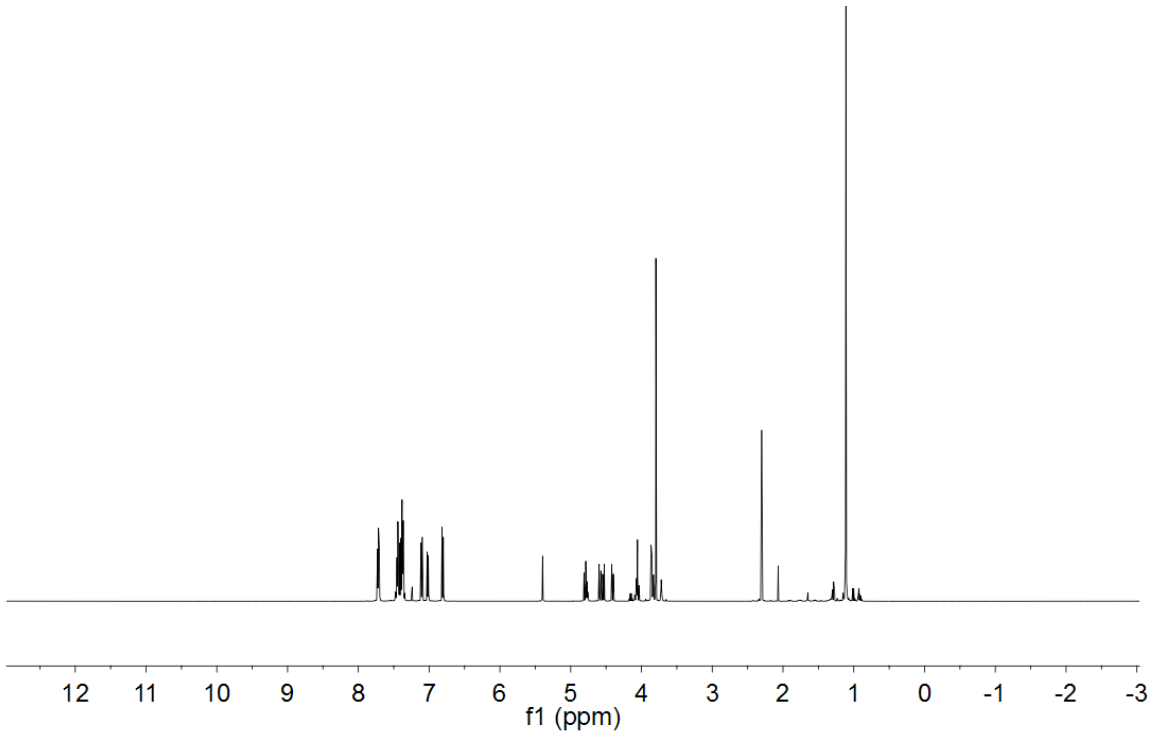


MALDI-MS of **79**

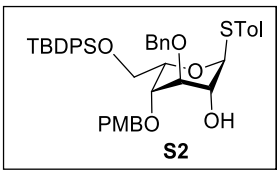


^{1}H-NMR ($CDCl_3$, 500 MHz) of **S2**

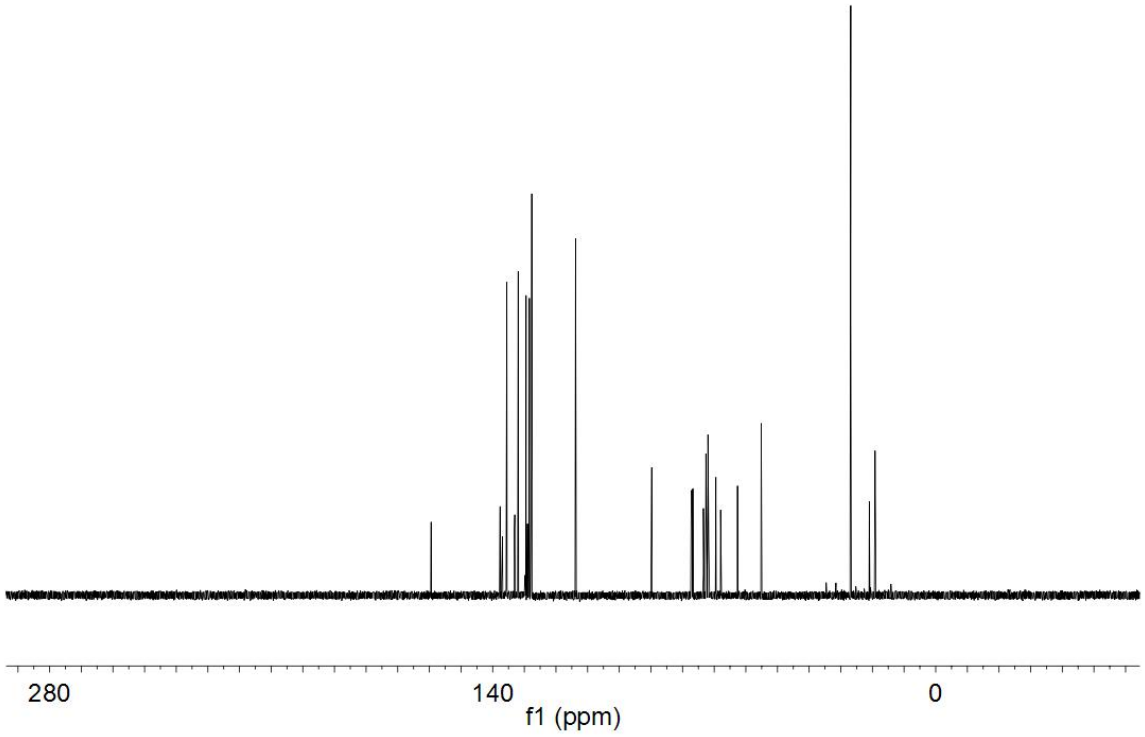




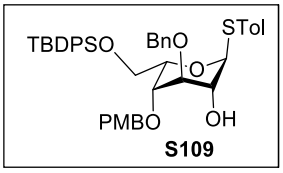
^{13}C-NMR ($CDCl_3$, 125 MHz) of **S2**



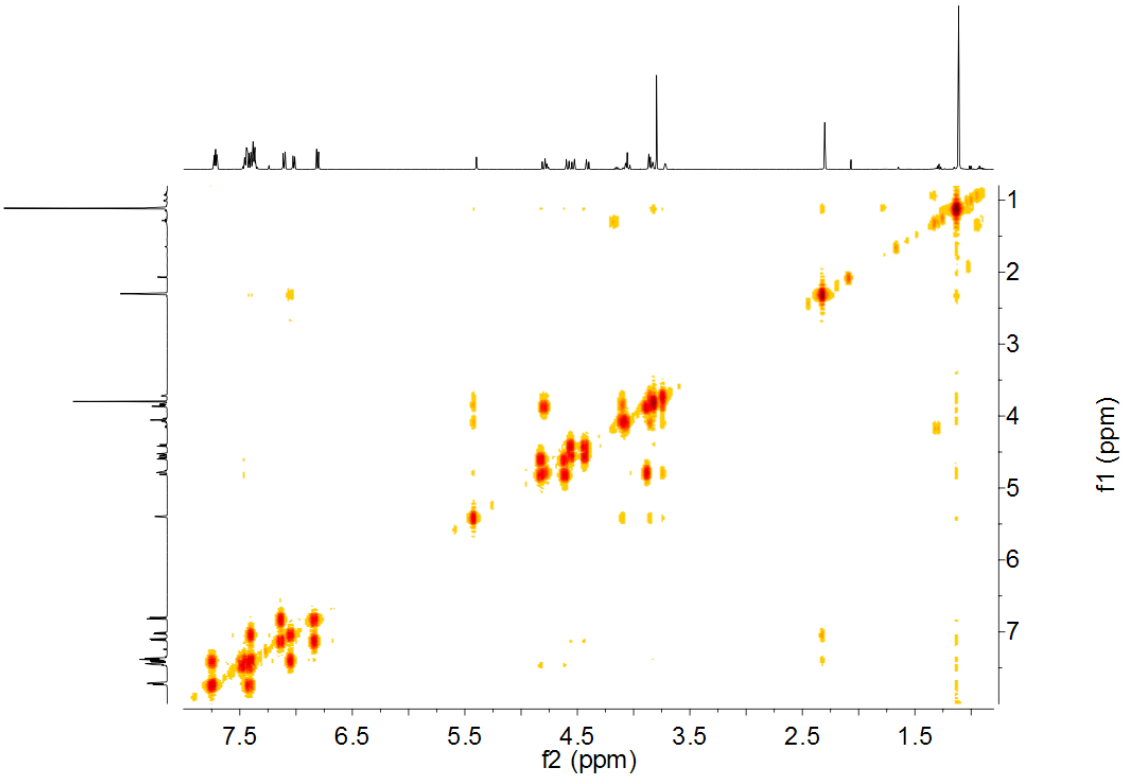
S2



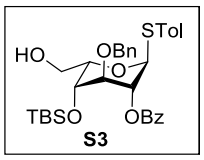
gCOSY ($CDCl_3$, 500 MHz) of **S2**

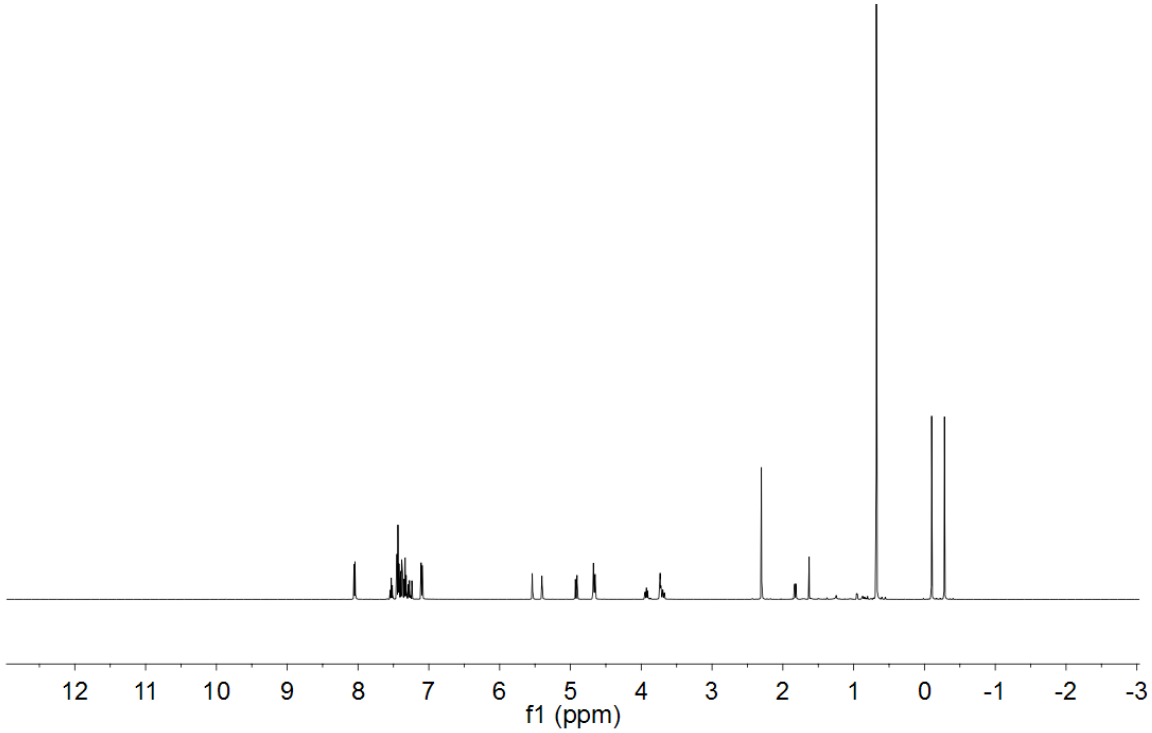


S109

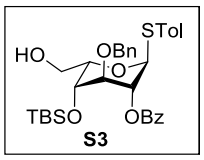


^{1}H-NMR (500 MHz) of **S3**

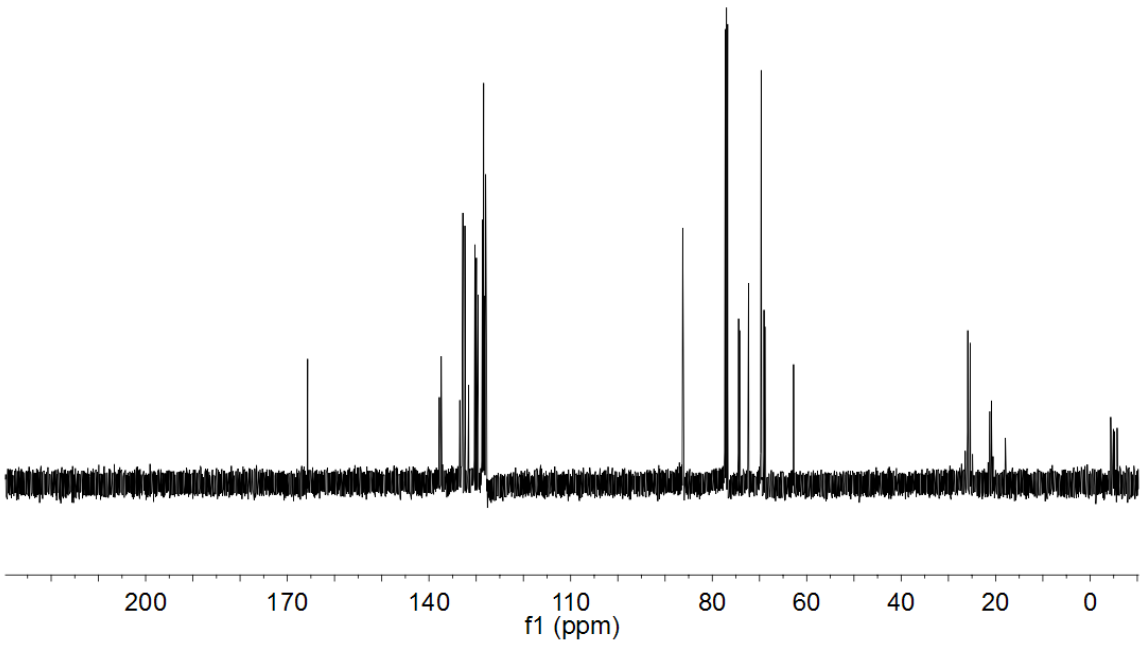




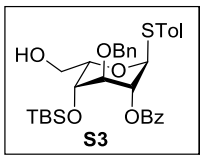
^{13}C-NMR (125 MHz) of **S3**



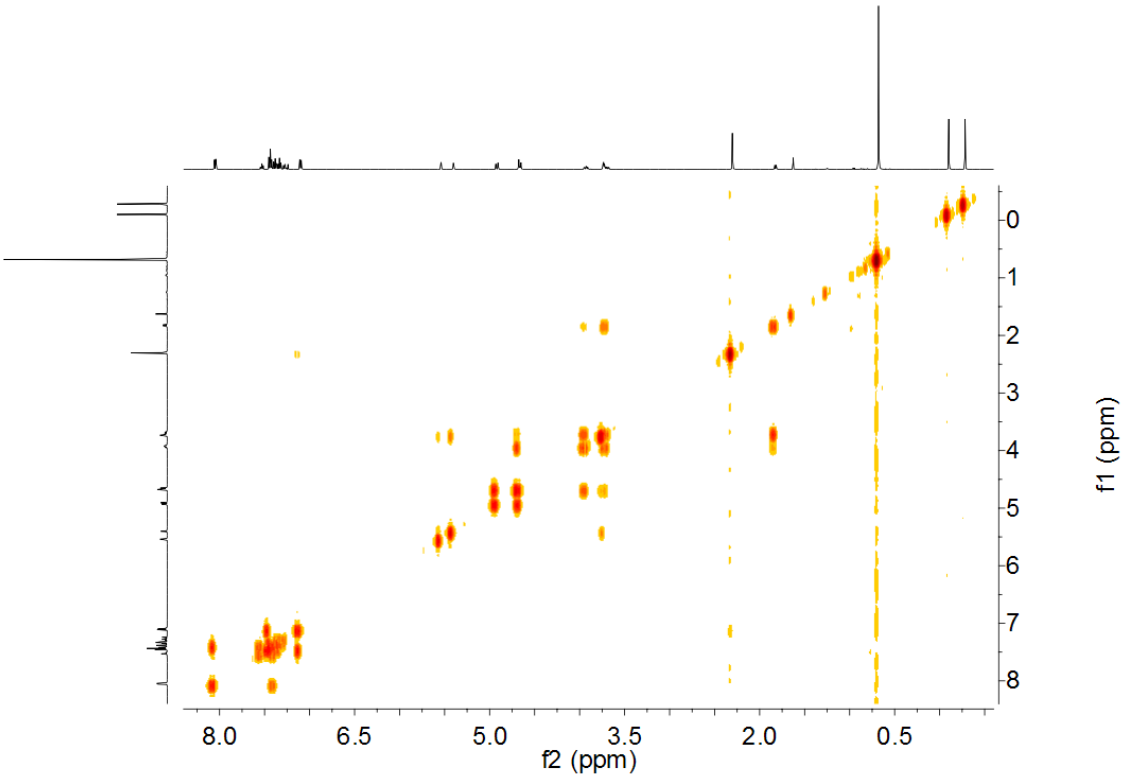
S3



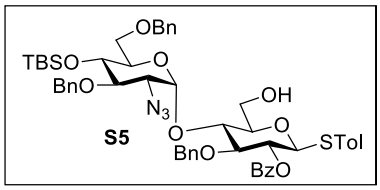
gCOSY (500 MHz) of **S3**



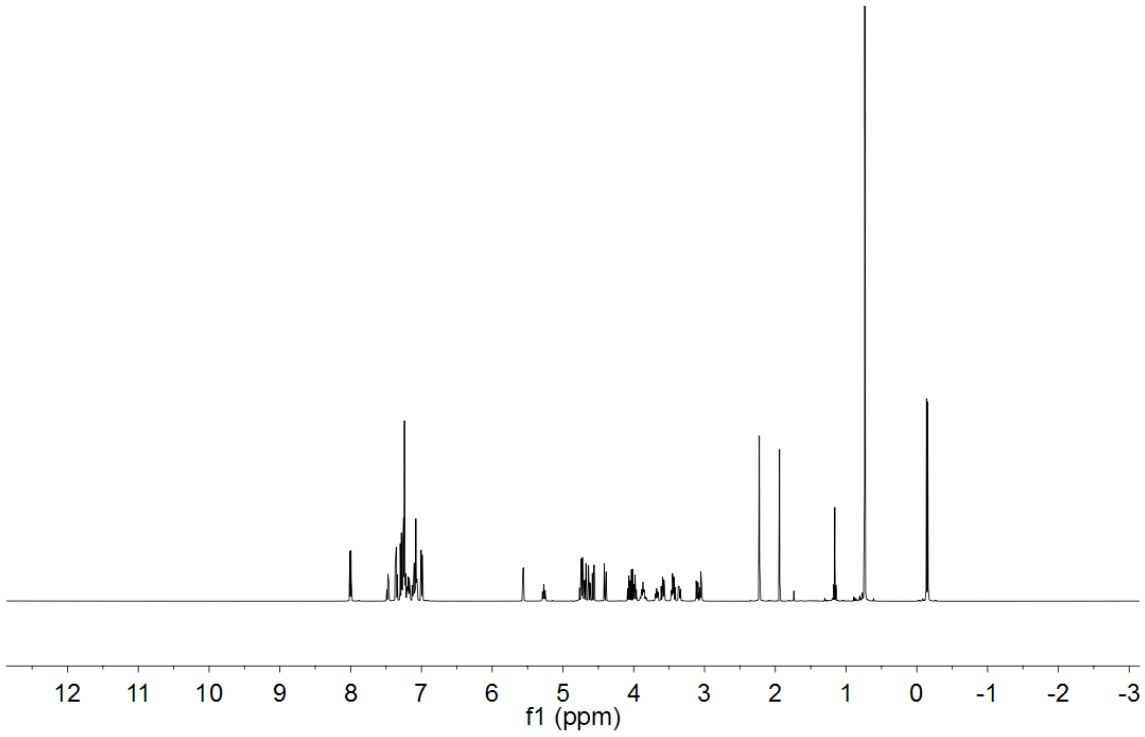
S3



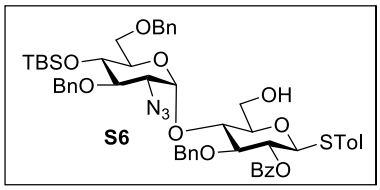
^{1}H-NMR (500 MHz) of **S5**

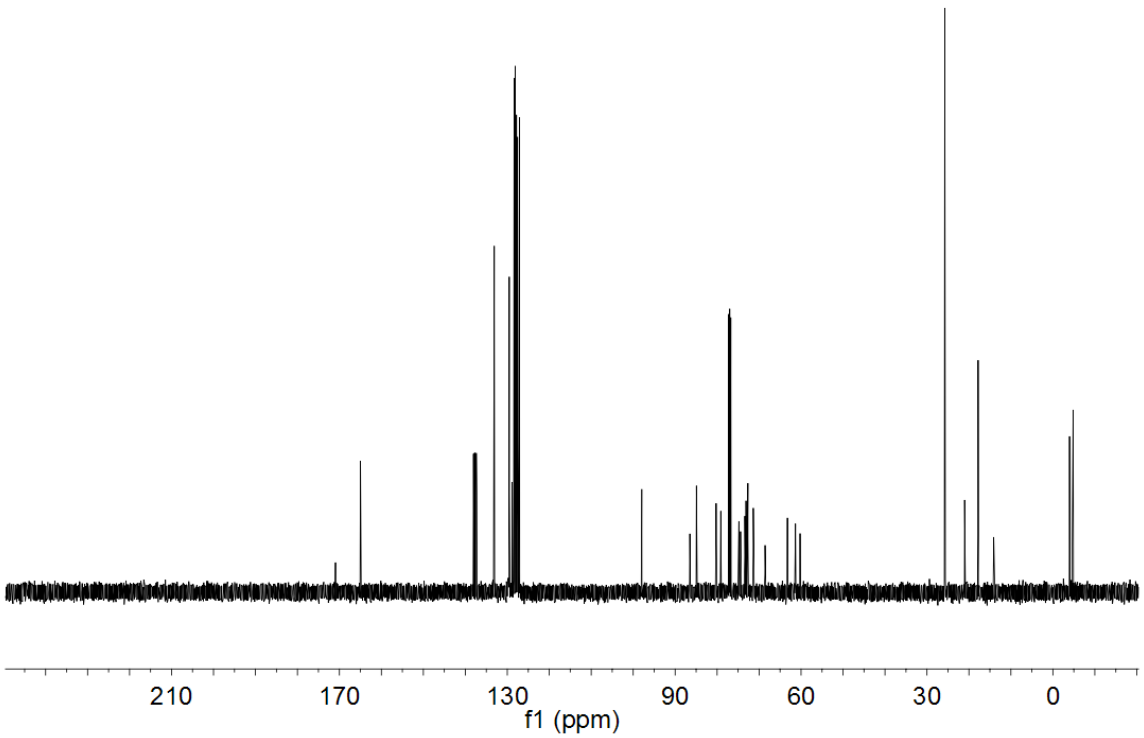


S5

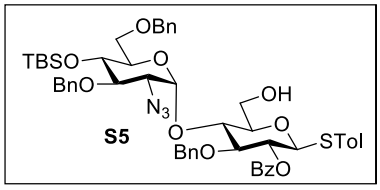


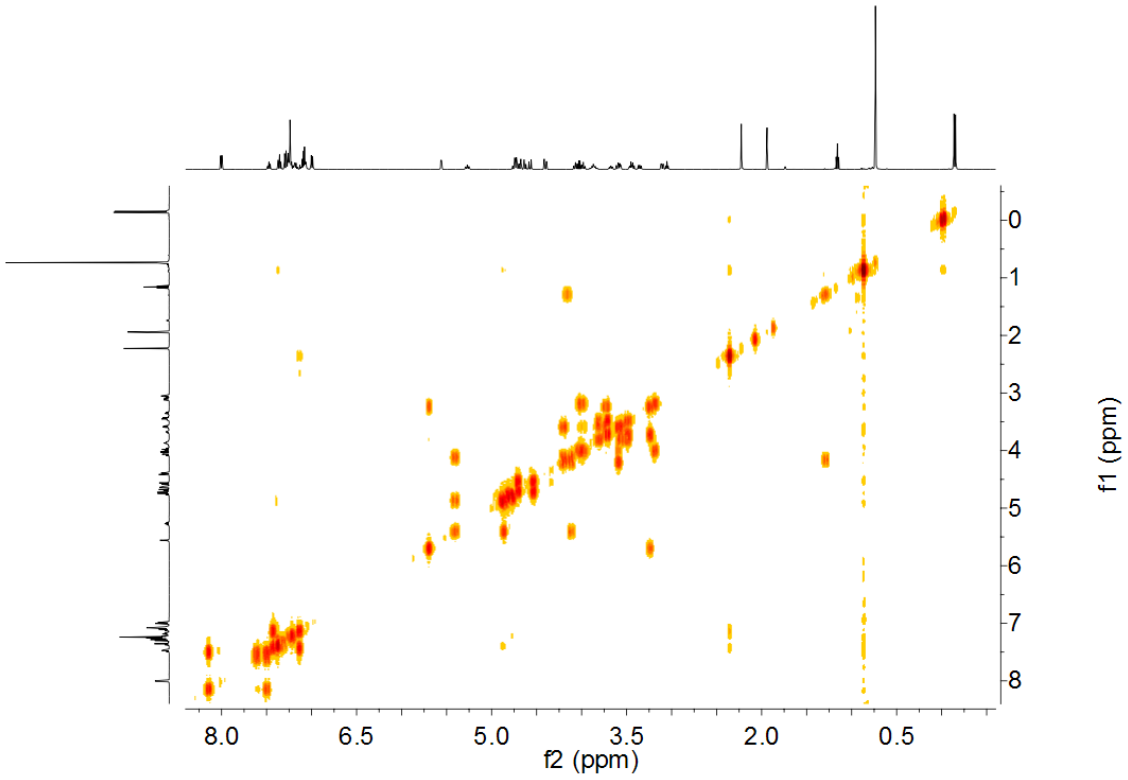
^{13}C-NMR (125 MHz) of **S5**



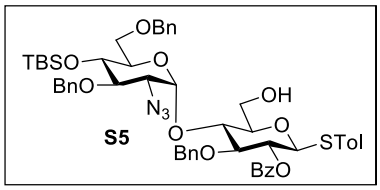


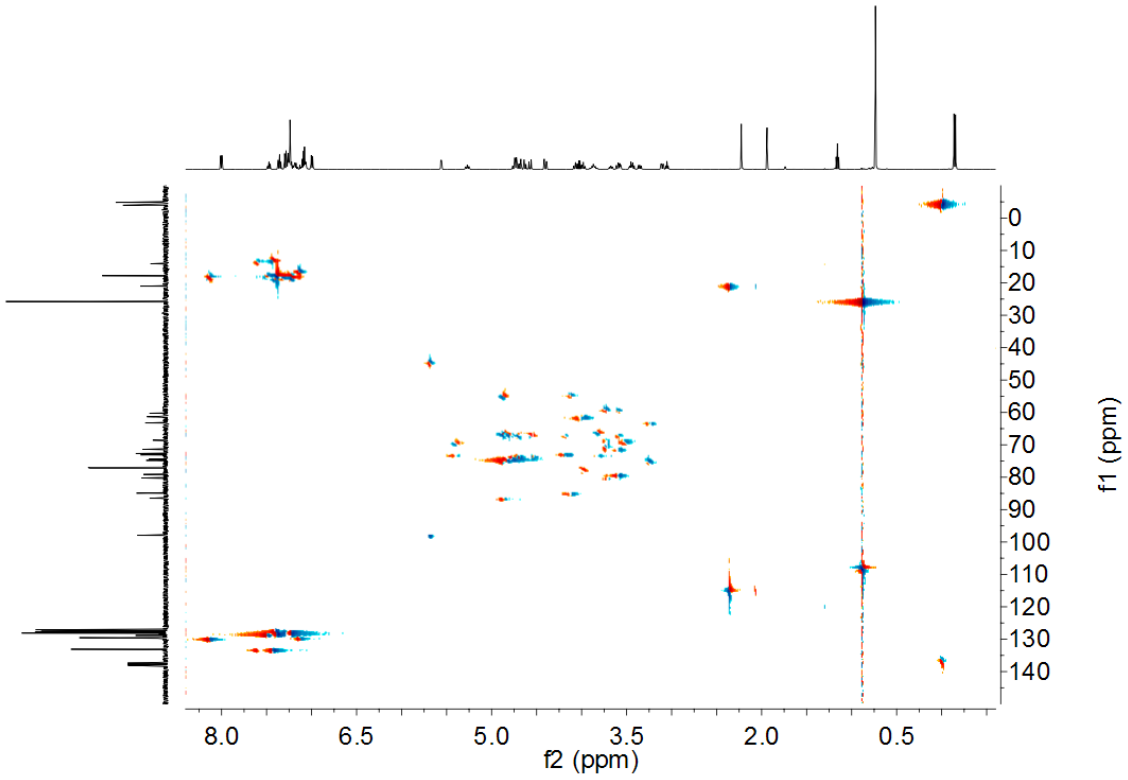
gCOSY (500 MHz) of **S5**



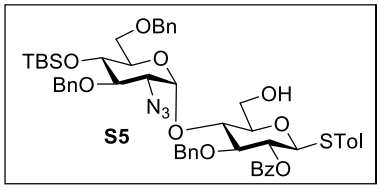


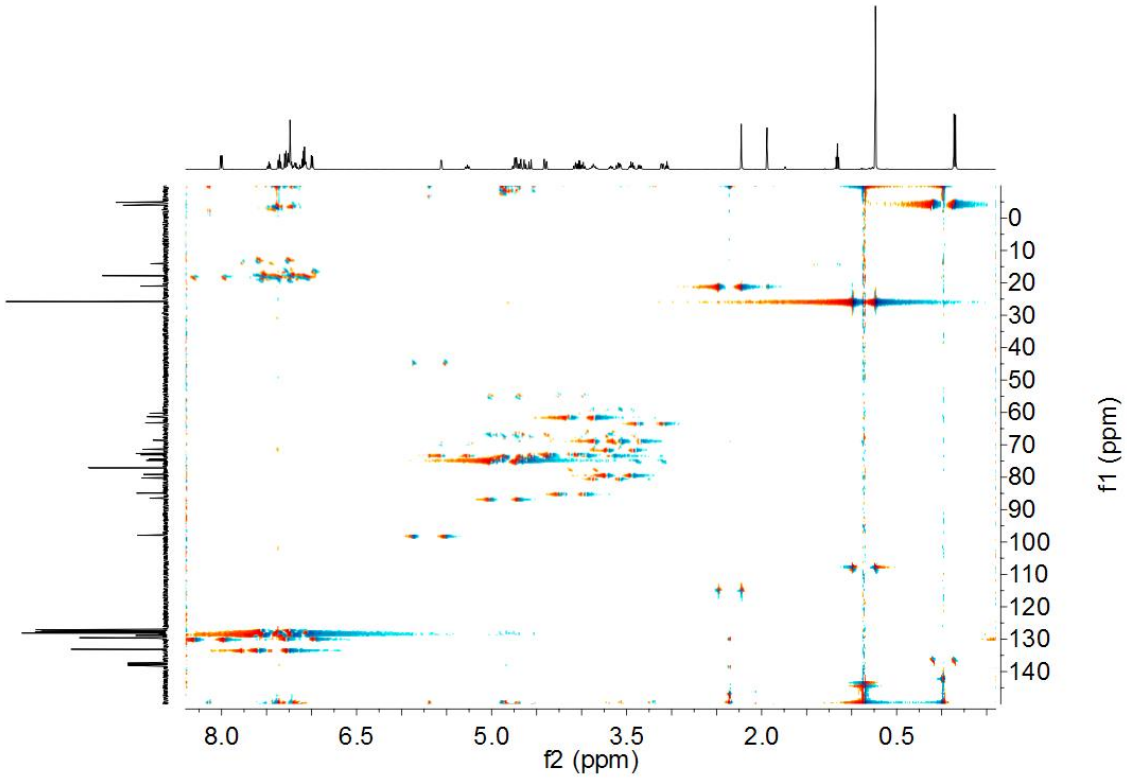
gHMQC (500 MHz) of **S5**



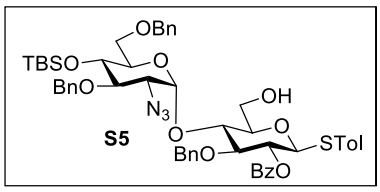


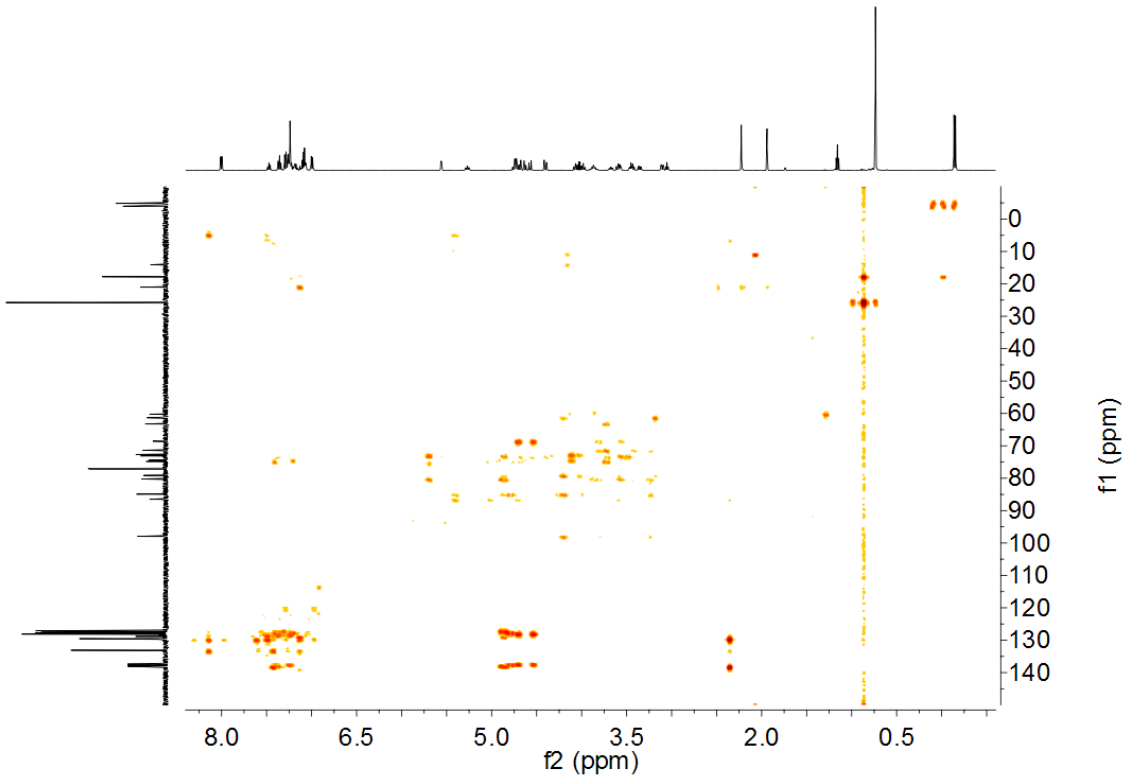
gHMQC (without ^{1}H decoupling) (500 MHz) of **S5**



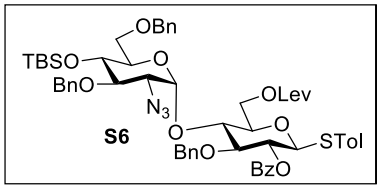


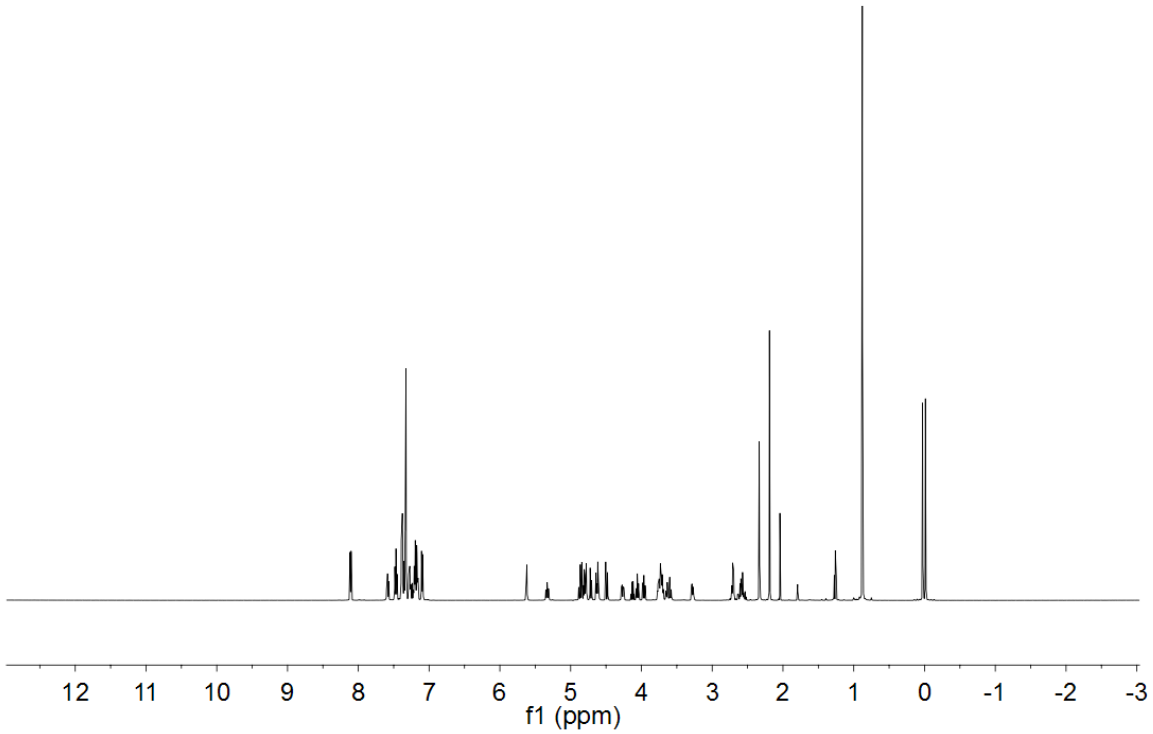
gHMBC (500 MHz) of **S5**



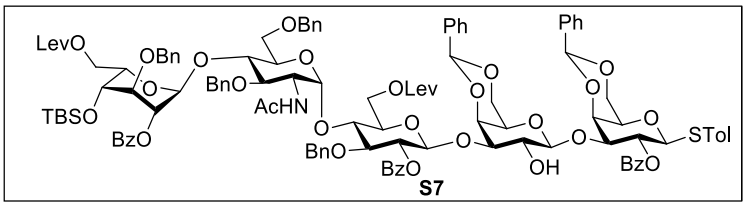


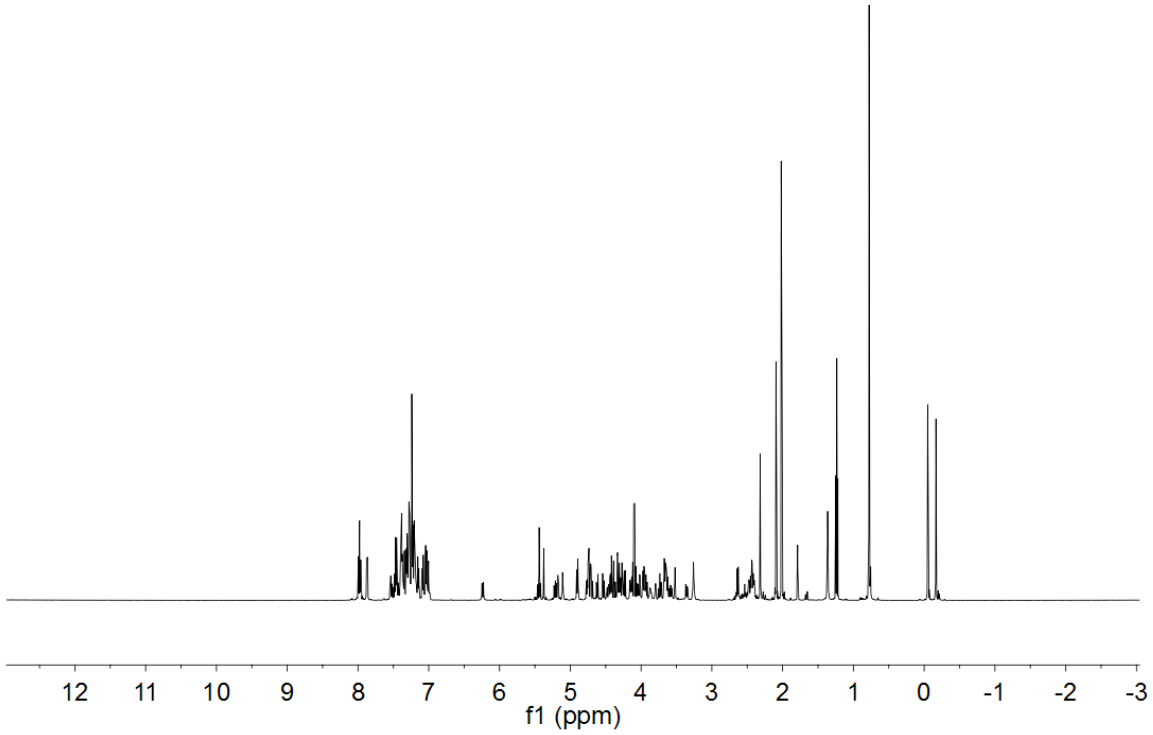
^{1}H-NMR (500 MHz) of **S6**



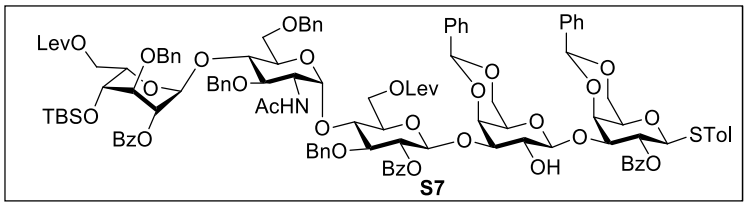


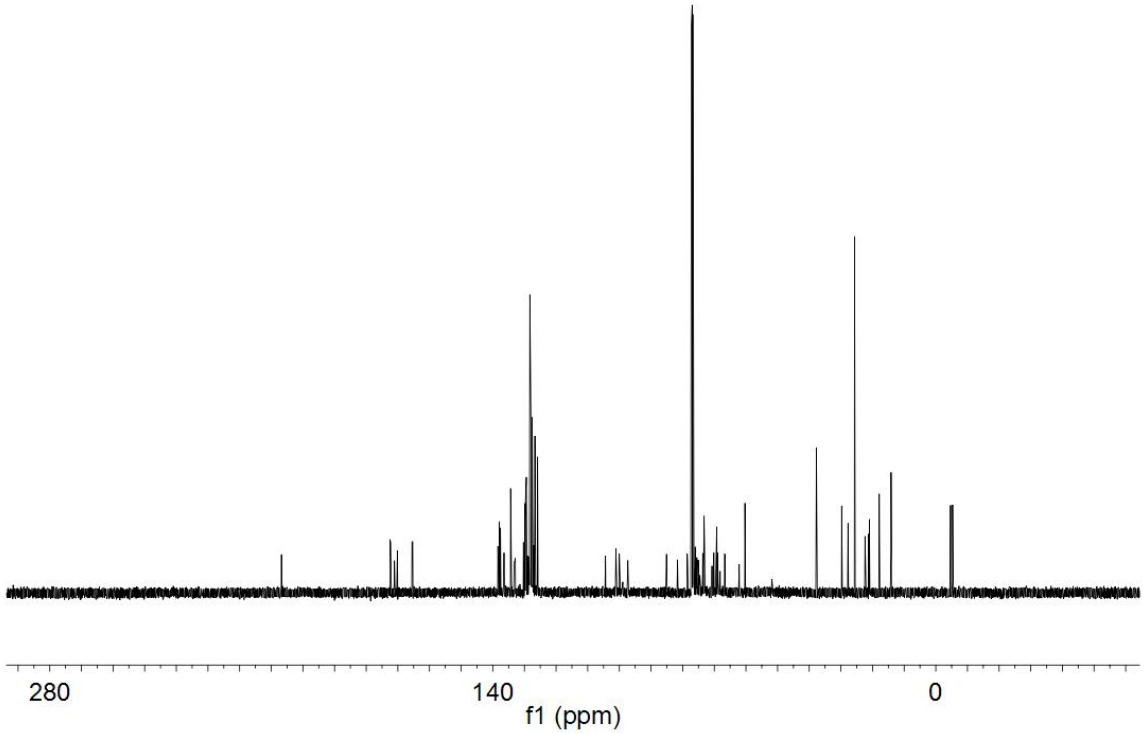
^{1}H-NMR (500 MHz) of **S7**



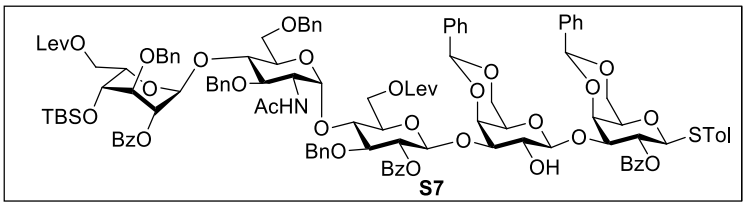


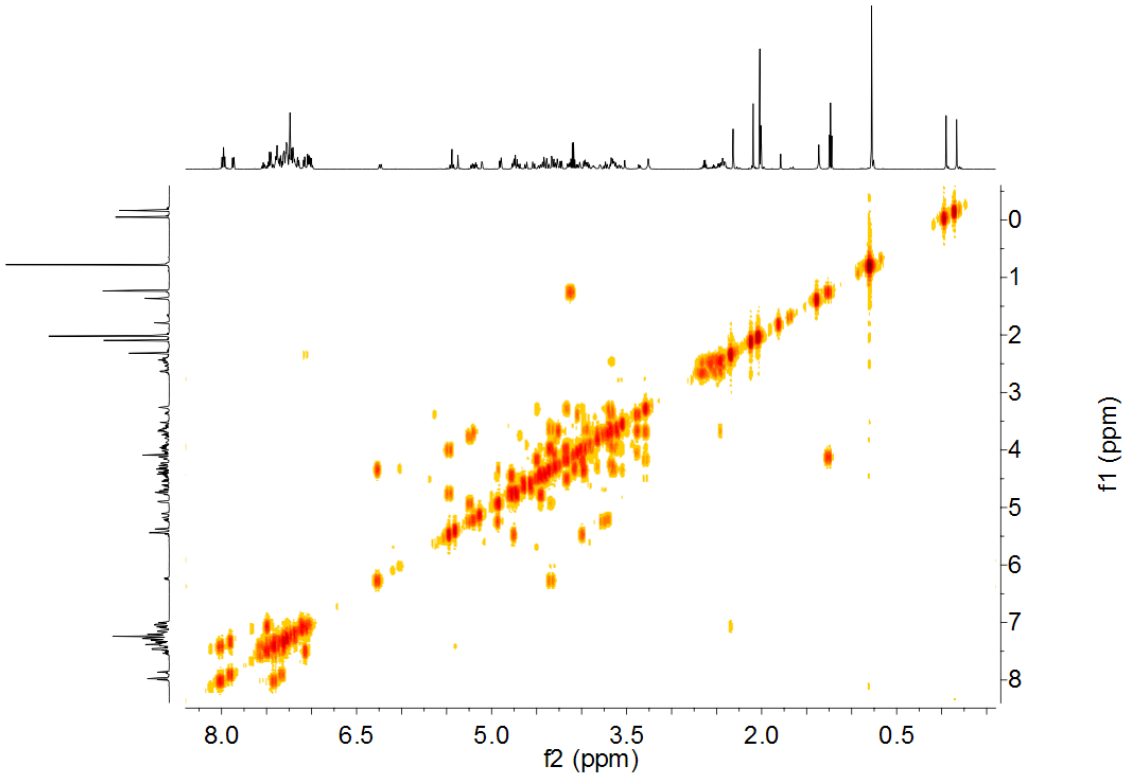
^{13}C-NMR (125 MHz) of **S7**



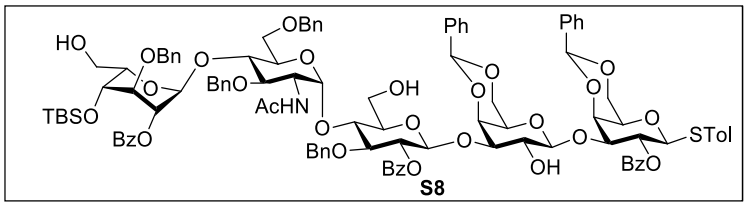


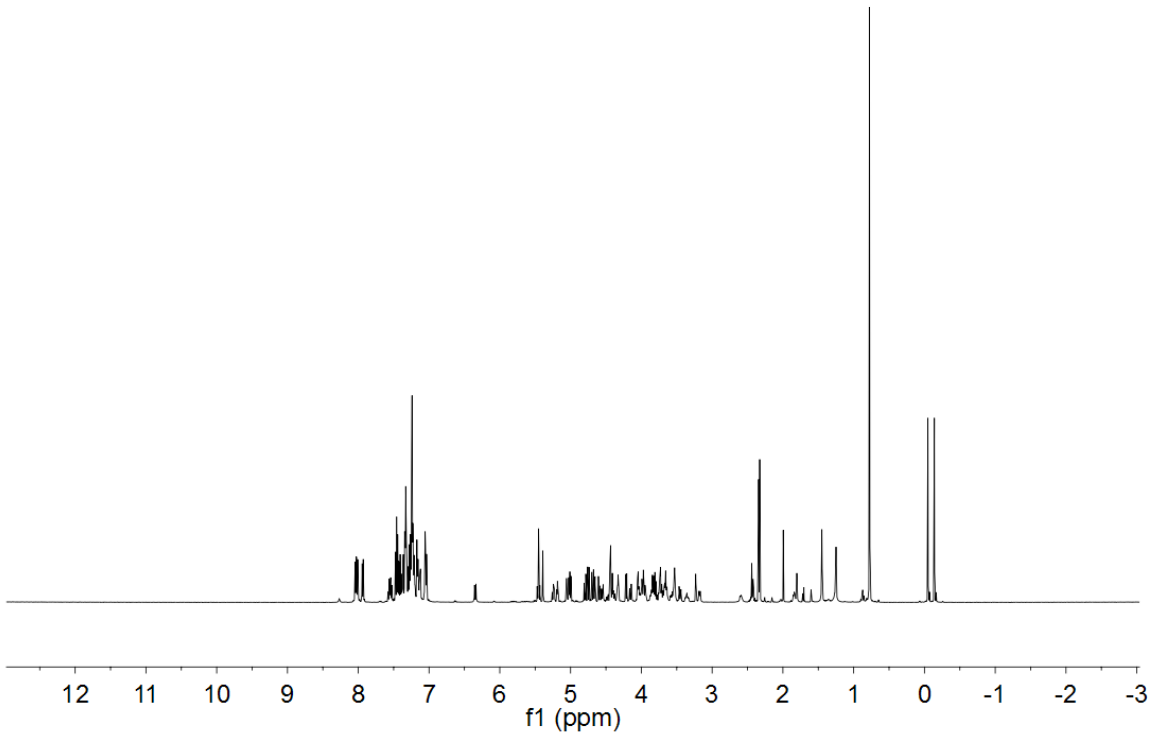
gCOSY (500 MHz) of **S7**



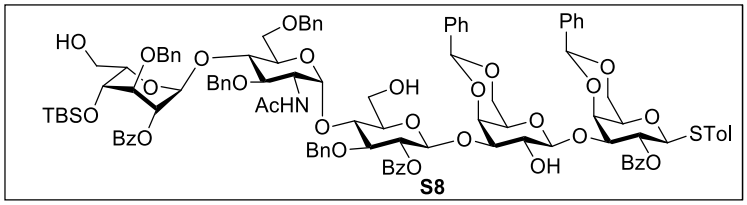


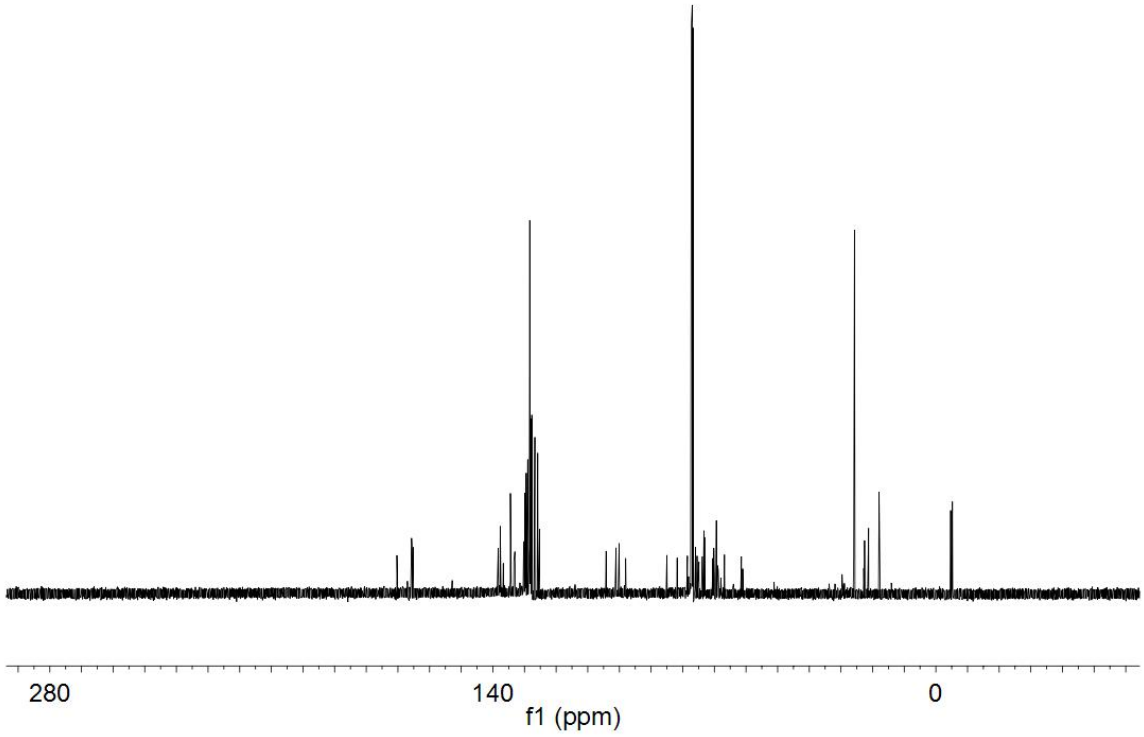
^{1}H-NMR (500 MHz) of **S8**



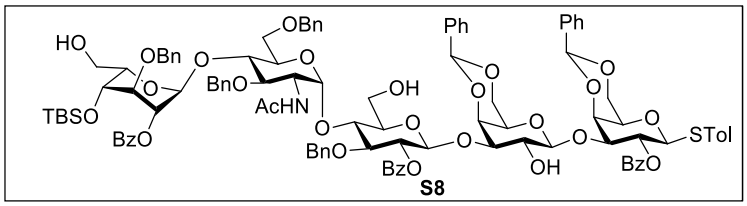


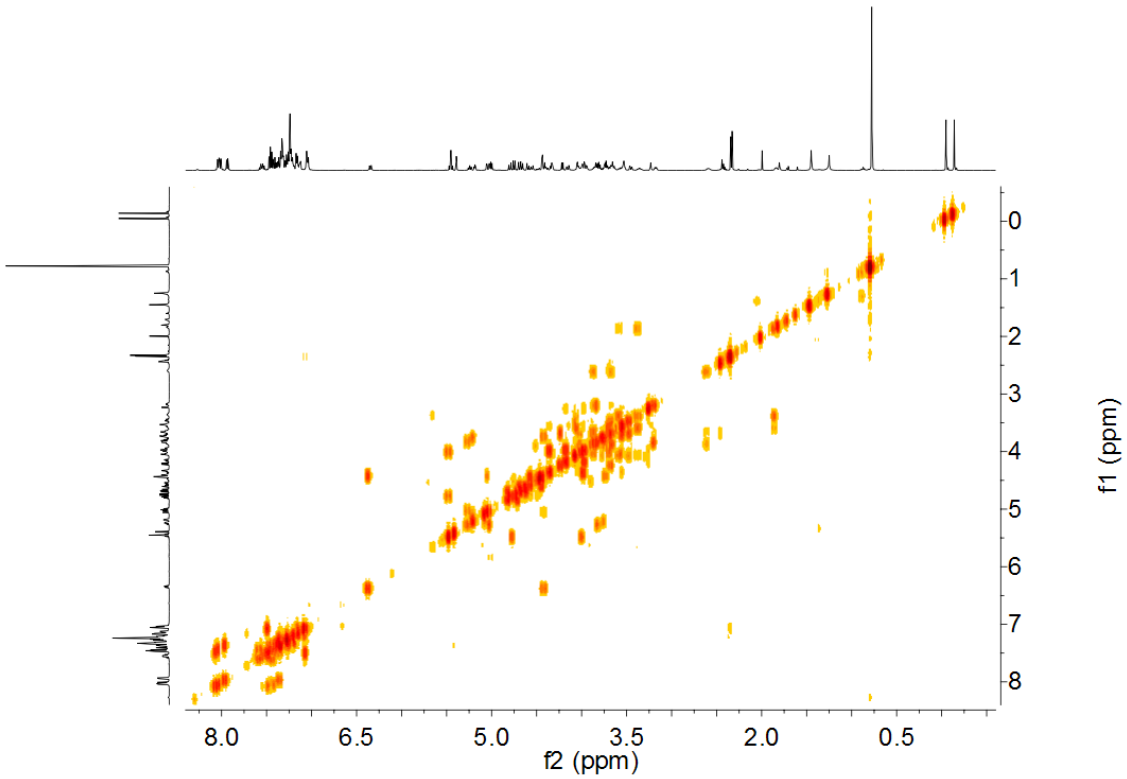
^{13}C-NMR (125 MHz) of **S8**



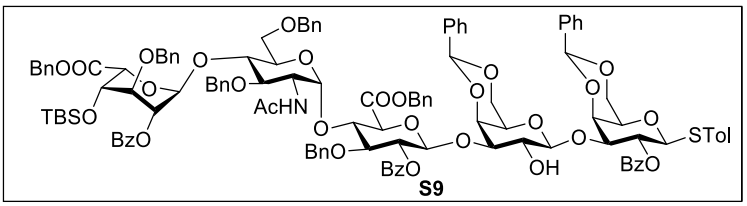


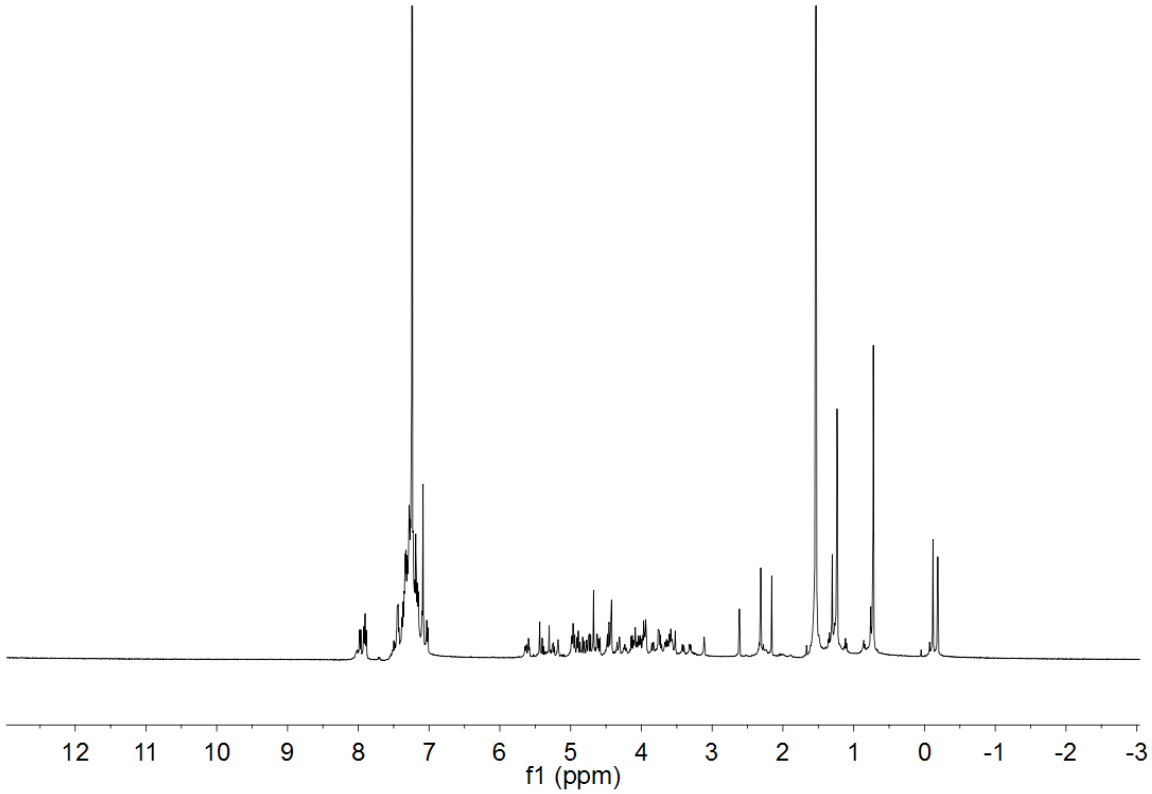
gCOSY (500 MHz) of **S8**



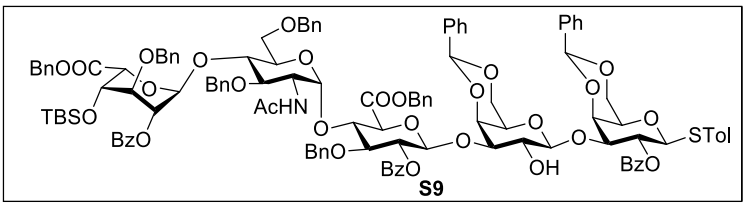


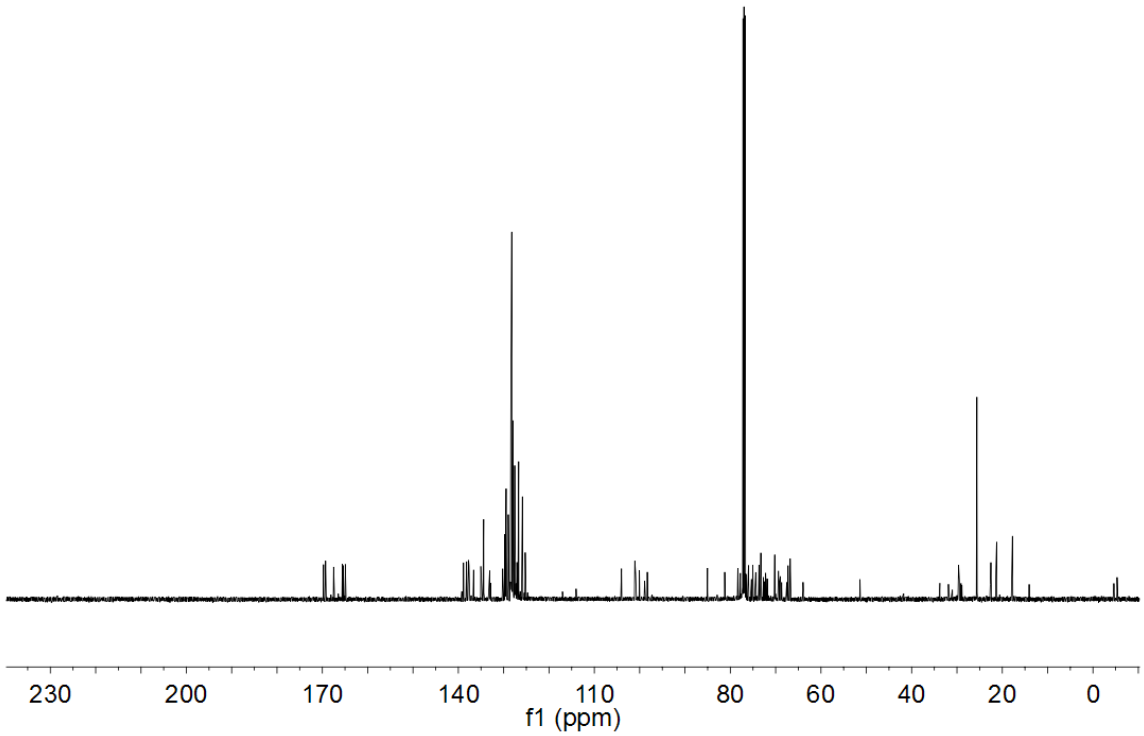
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S9**



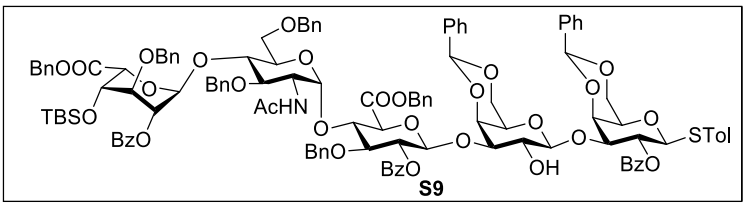


^{13}C-NMR ($CDCl_3$, 150 MHz) of **S9**

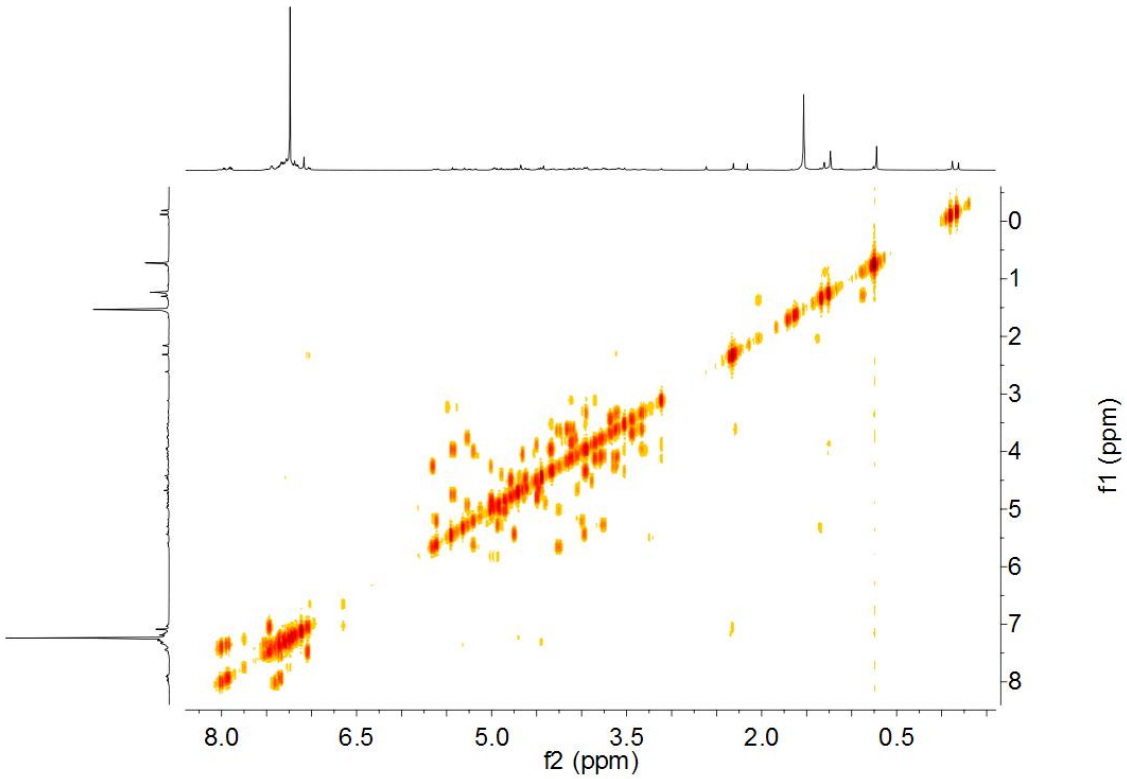




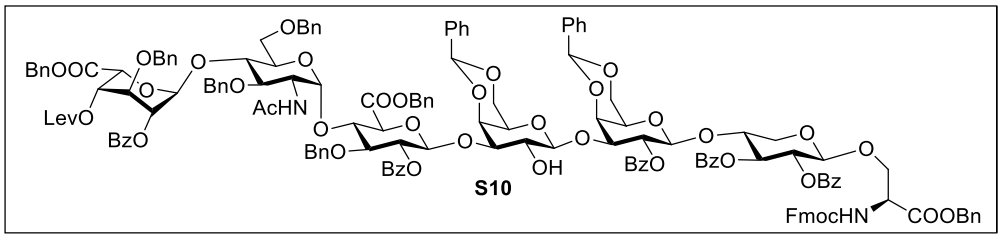
gCOSY ($CDCl_3$, 600 MHz) of **S9**



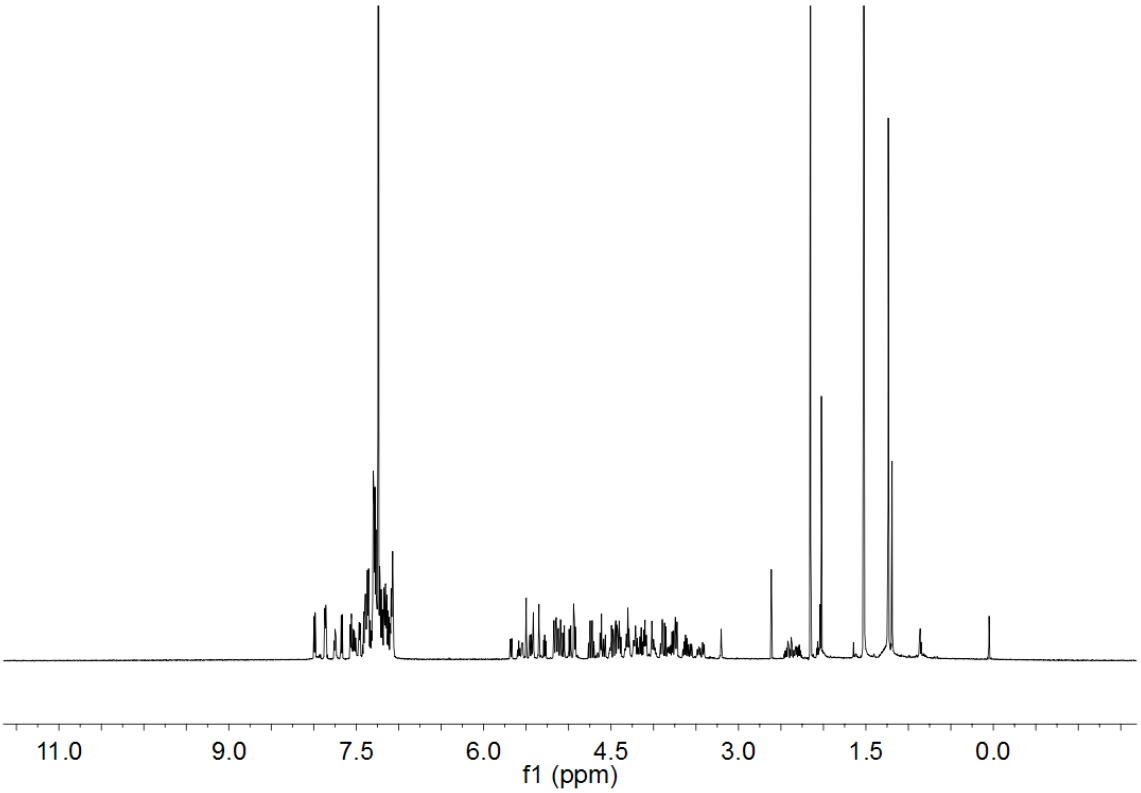
S9



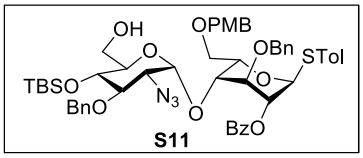
^{1}H-NMR (600 MHz) of **S10**

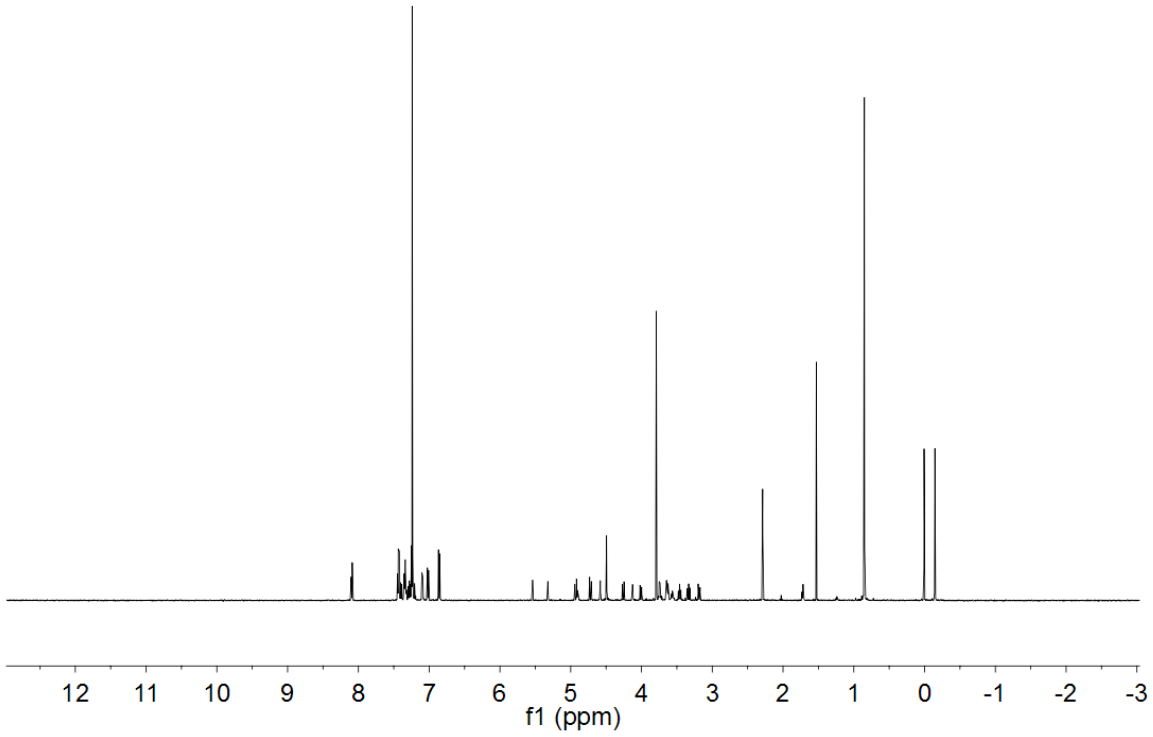


S10

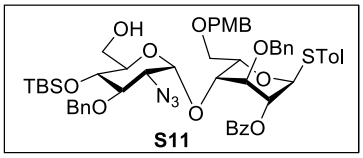


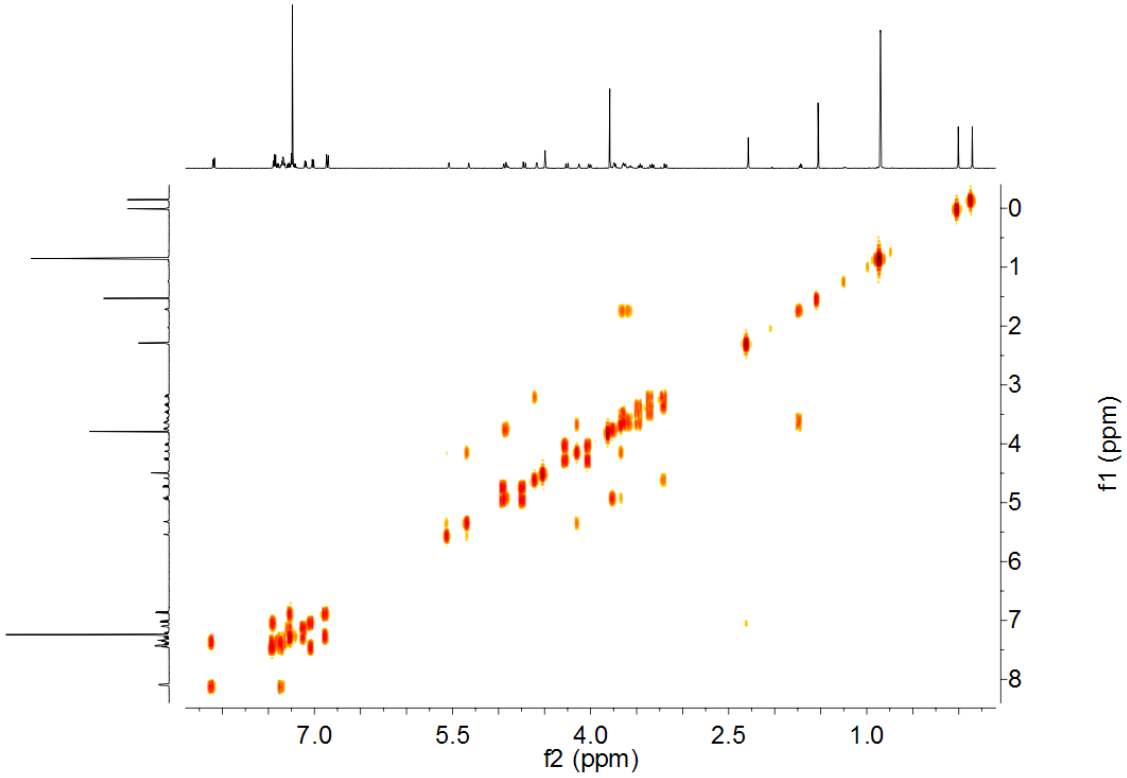
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S11**



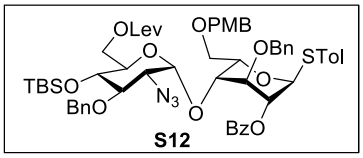


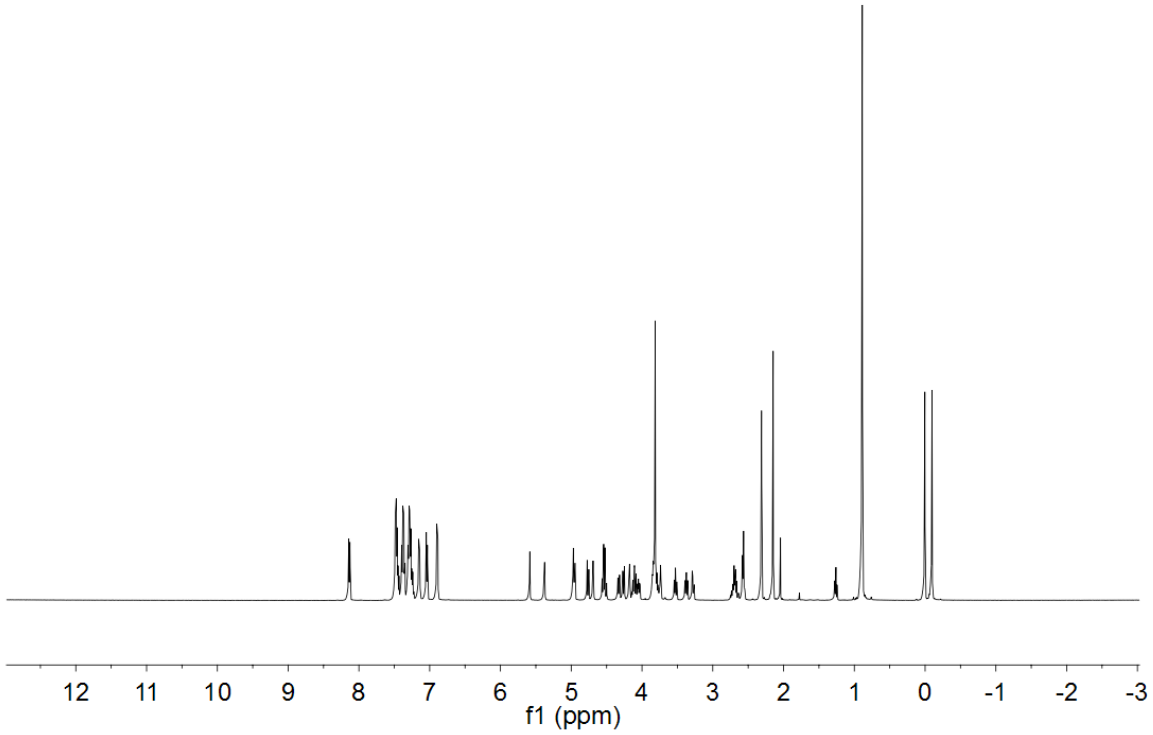
gCOSY ($CDCl_3$, 500 MHz) of **S11**



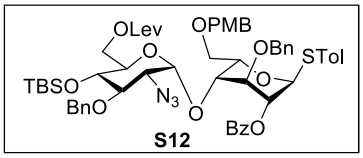


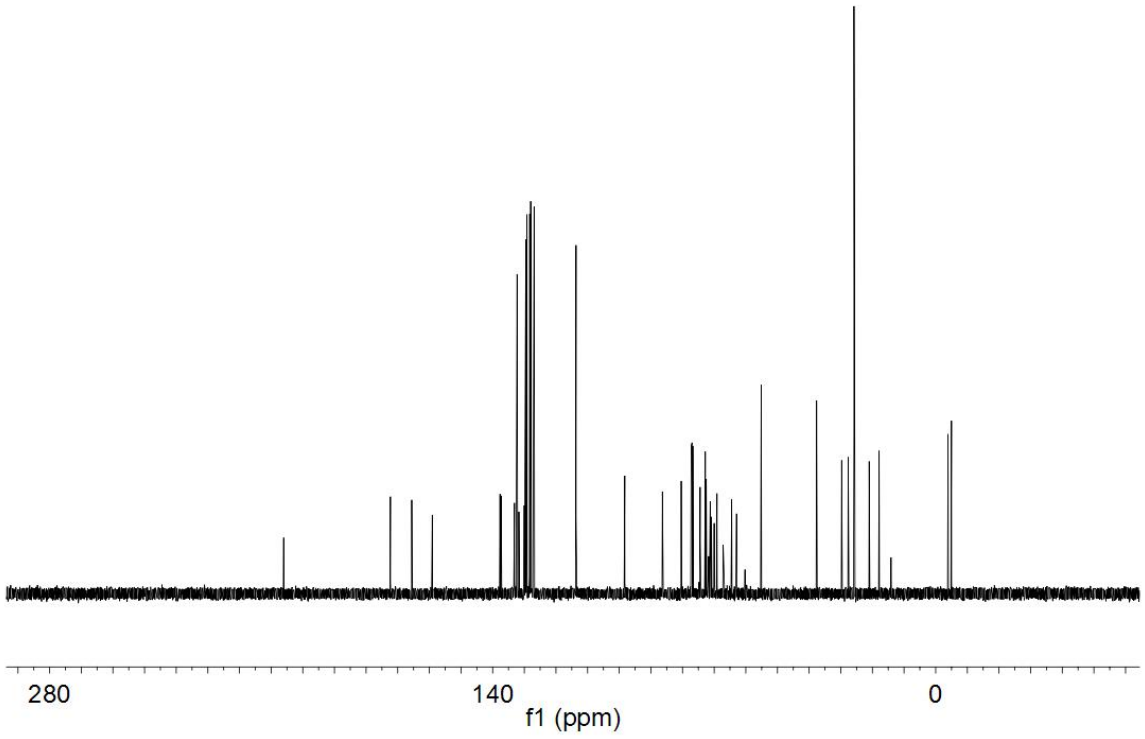
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S12**



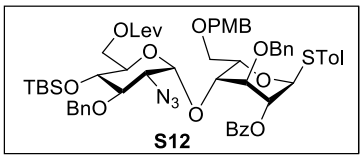


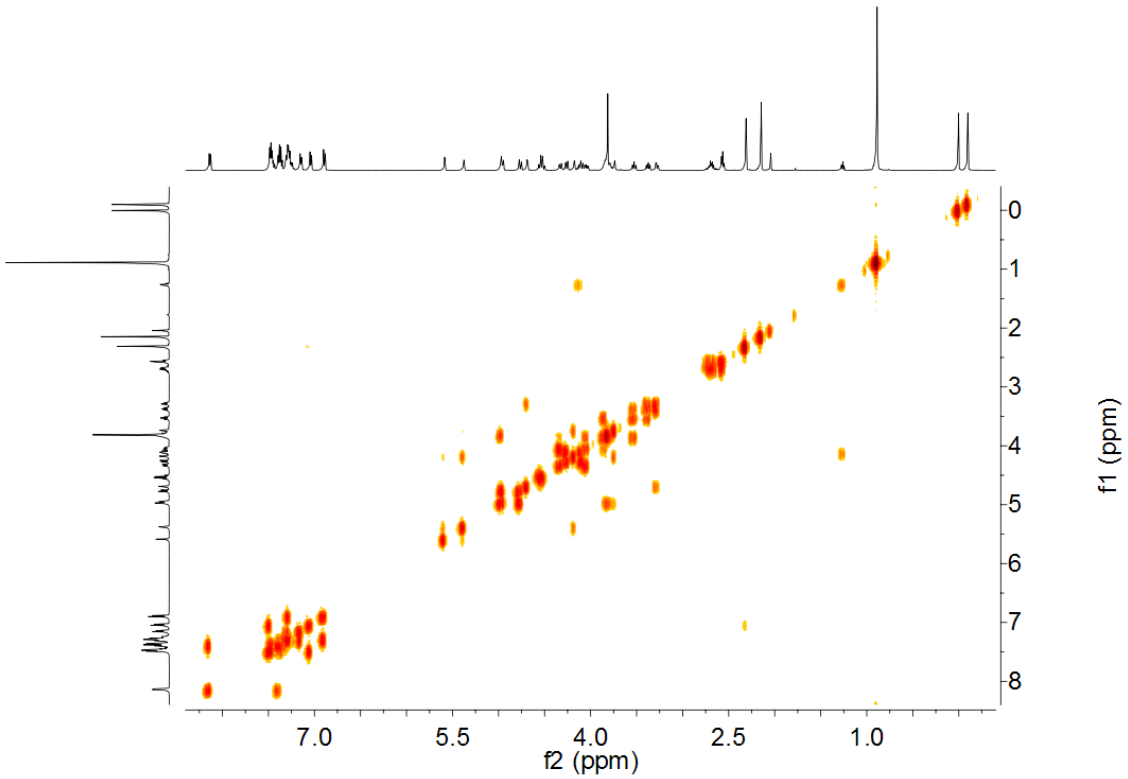
^{13}C-NMR ($CDCl_3$, 125 MHz) of **S12**



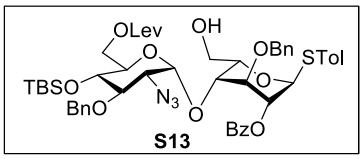


gCOSY ($CDCl_3$, 500 MHz) of **S12**

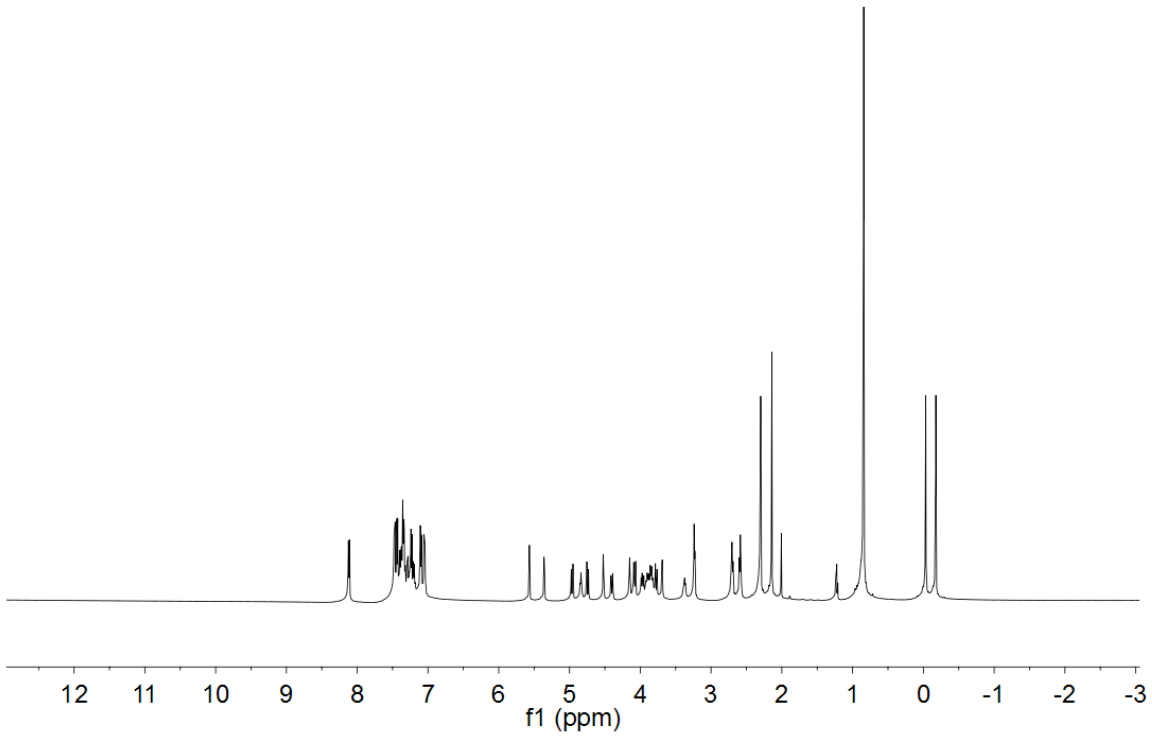




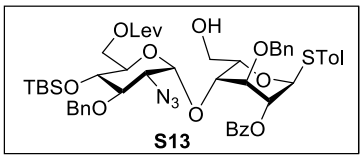
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S13**



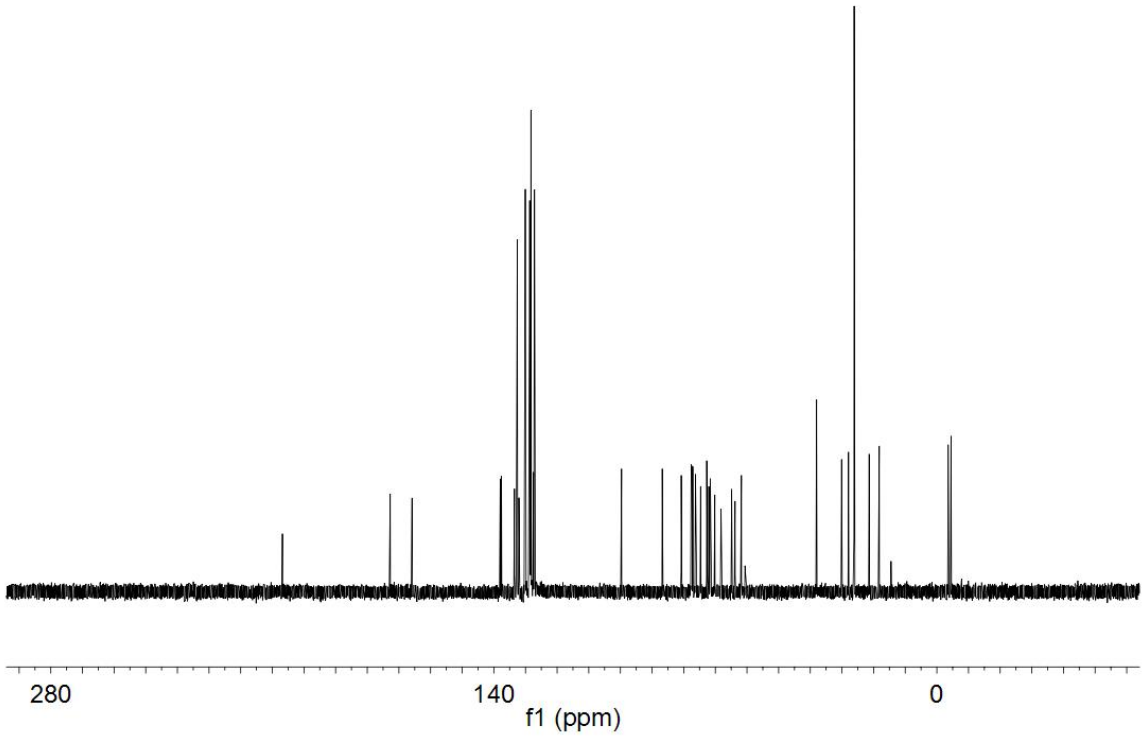
S13



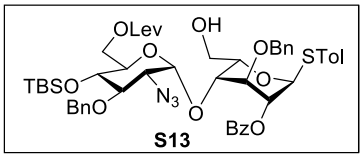
^{13}C-NMR ($CDCl_3$, 125 MHz) of **S13**



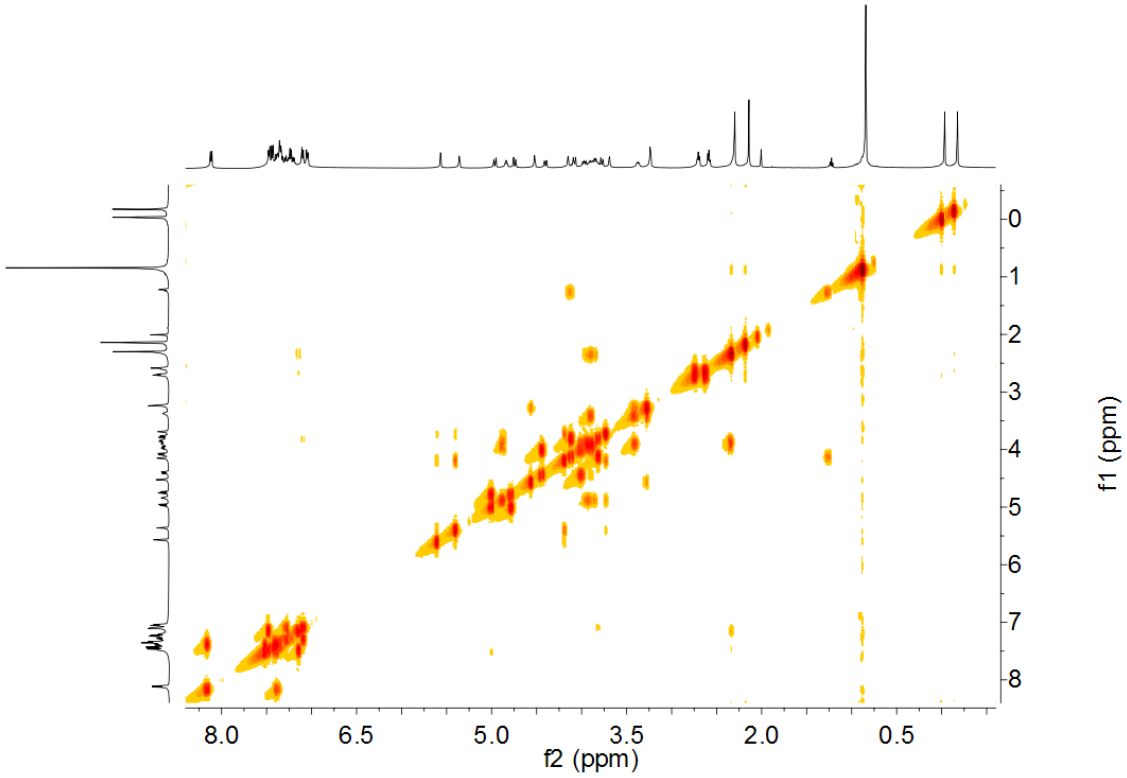
S13



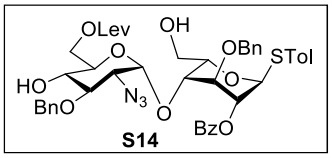
gCOSY ($CDCl_3$, 500 MHz) of **S13**

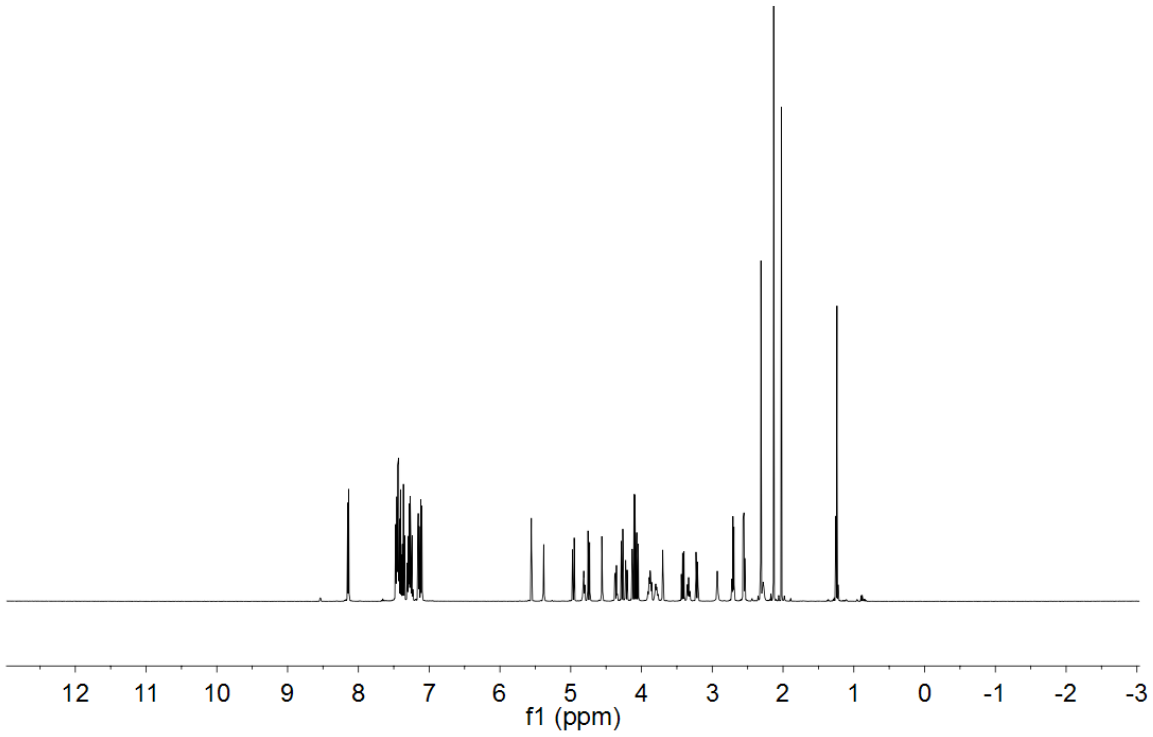


S13

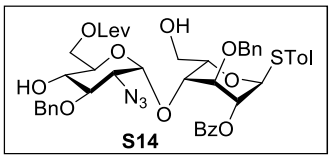


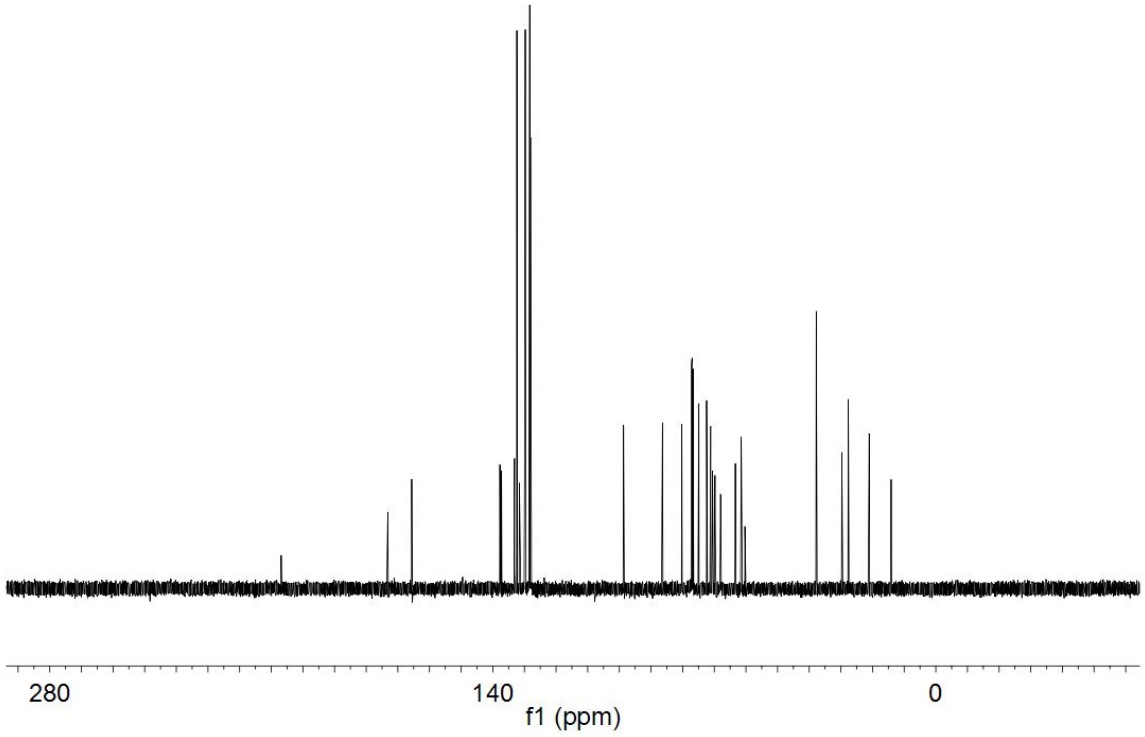
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S14**



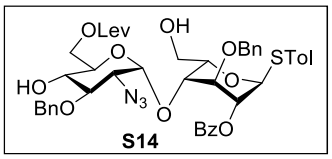


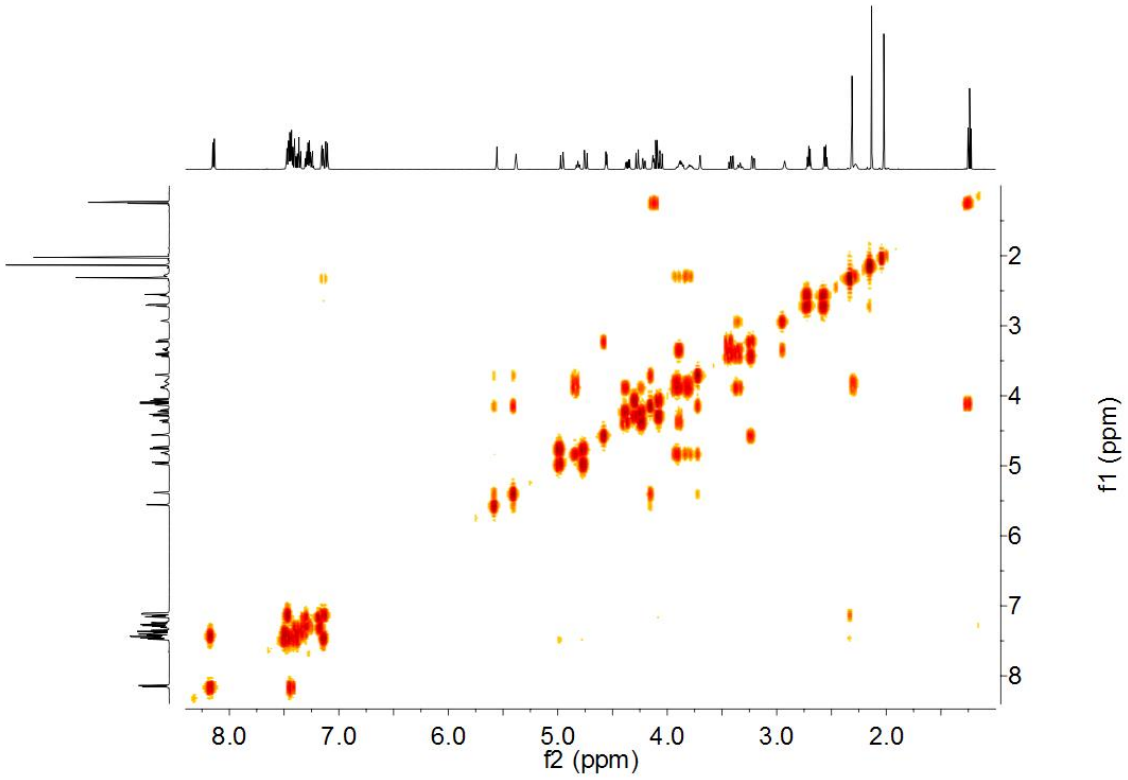
^{13}C-NMR ($CDCl_3$, 125 MHz) of **S14**



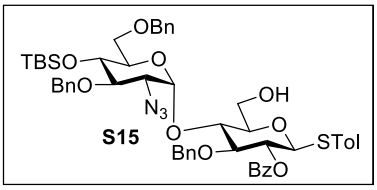


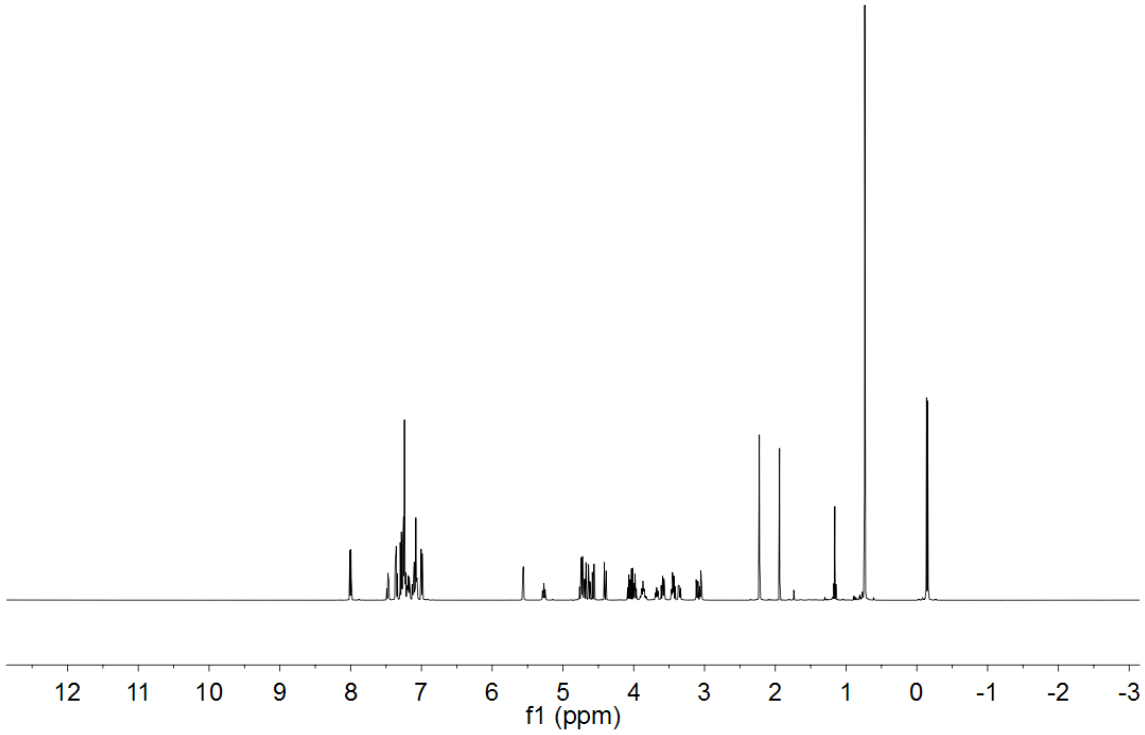
gCOSY ($CDCl_3$, 500 MHz) of **S14**



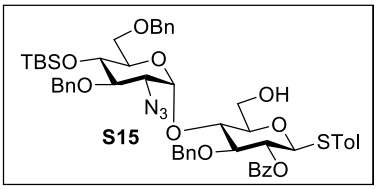


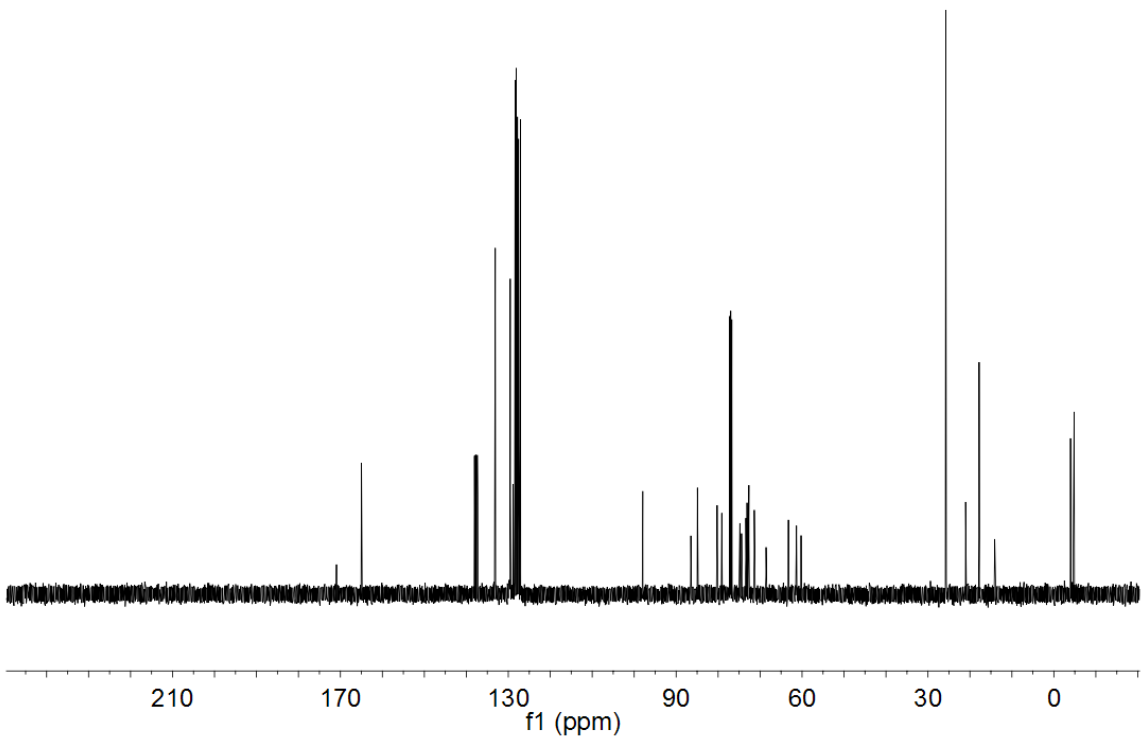
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S15**



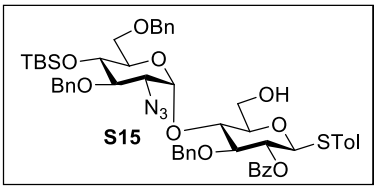


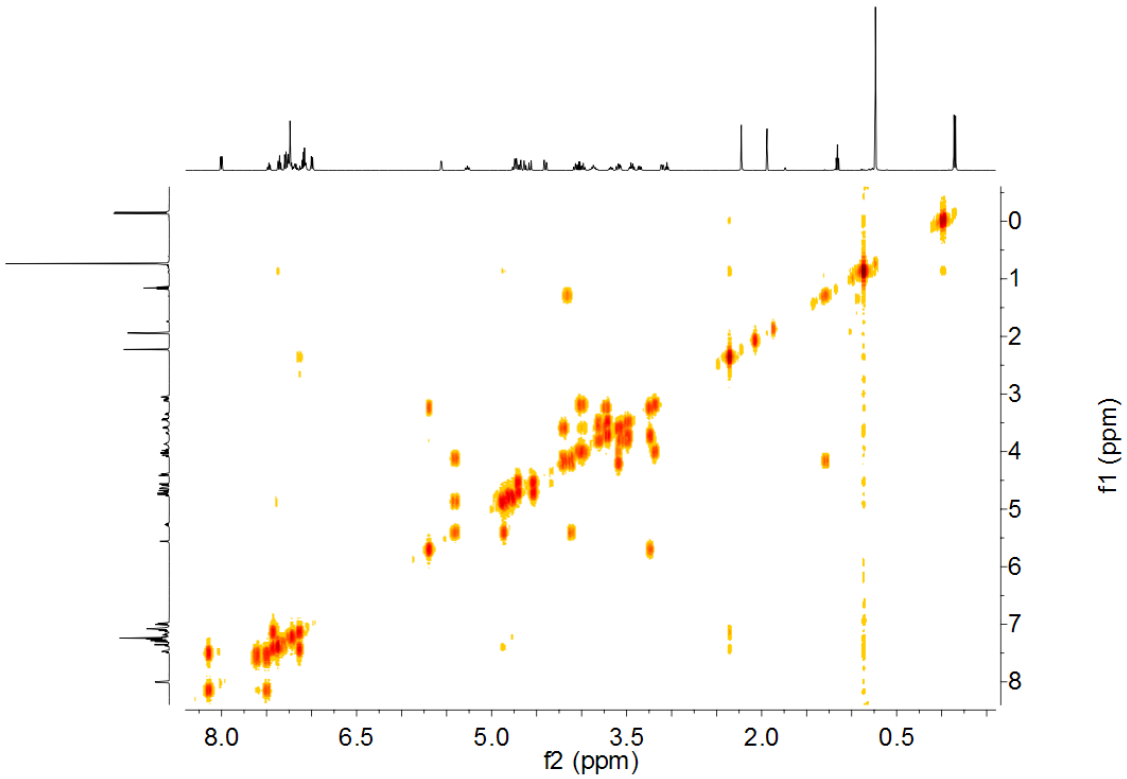
^{13}C-NMR ($CDCl_3$, 125 MHz) of **S15**



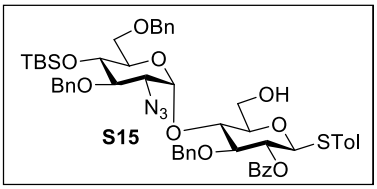


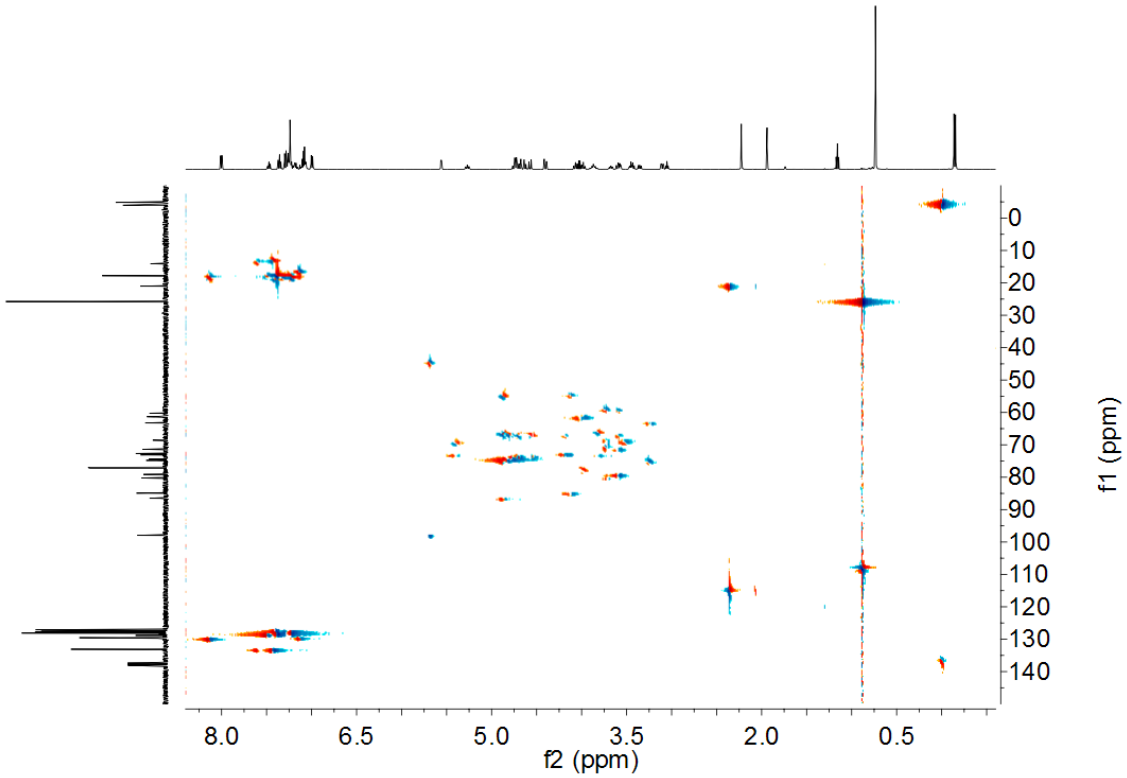
gCOSY ($CDCl_3$, 500 MHz) of **S15**



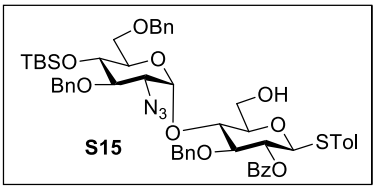


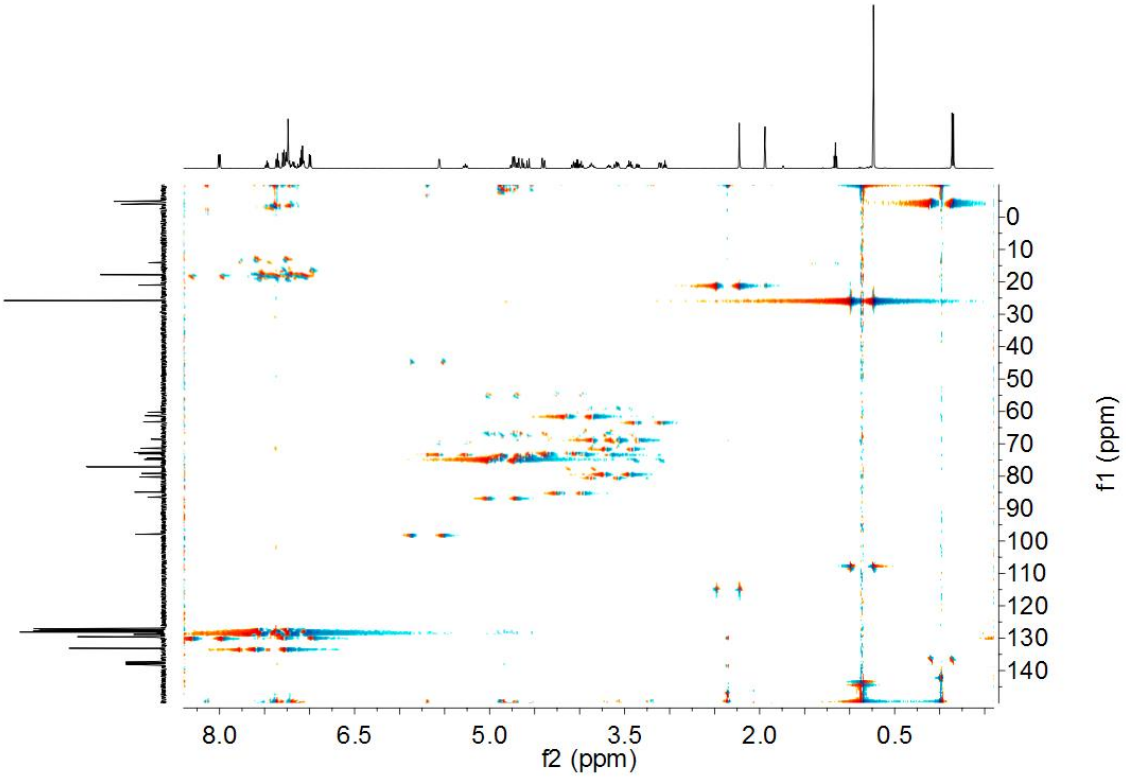
gHMQC ($CDCl_3$, 500 MHz) of **S15**



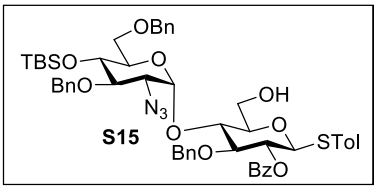


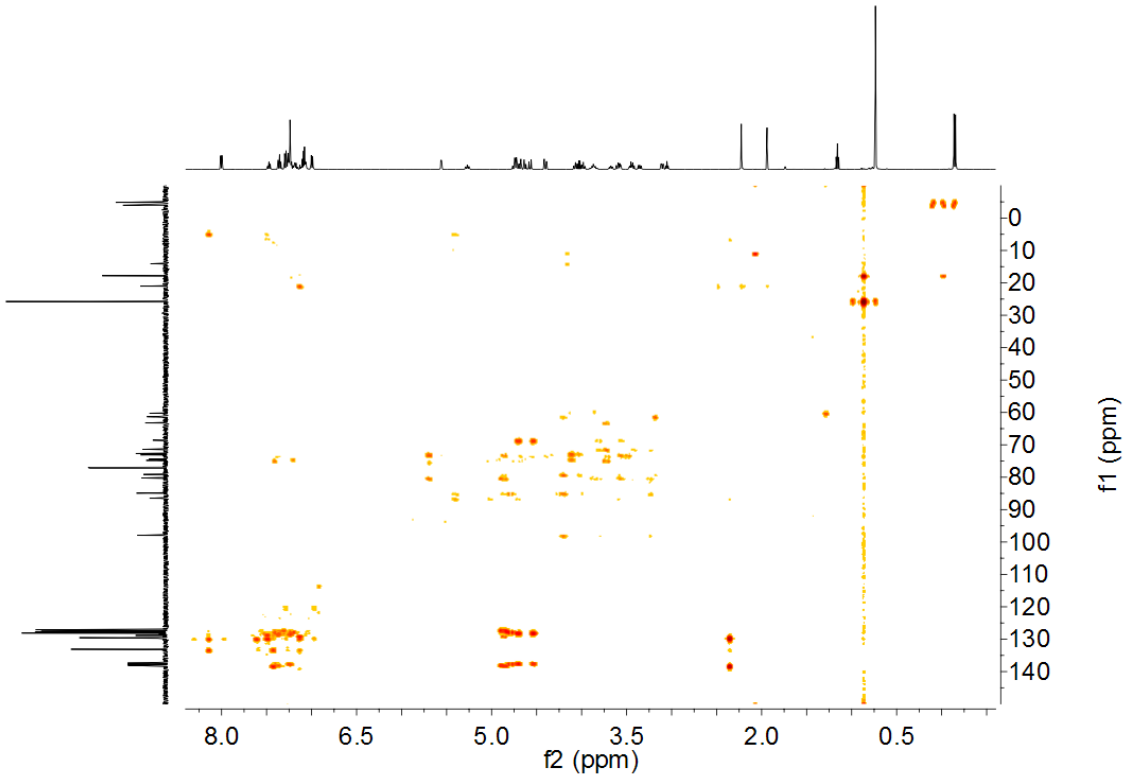
gHMQC (without ^{1}H decoupling) ($CDCl_3$, 500 MHz) of **S15**



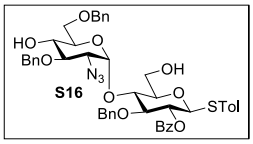


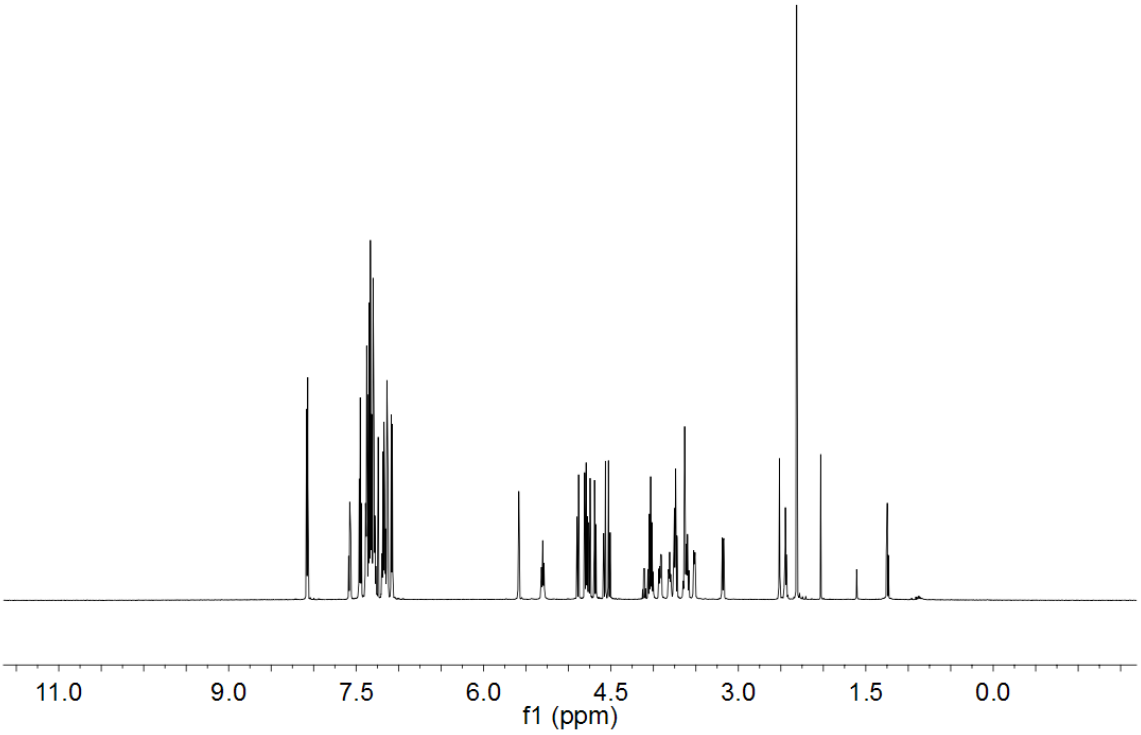
gHMBC ($CDCl_3$, 500 MHz) of **S15**



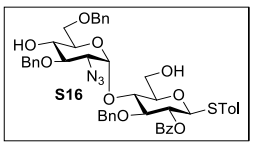


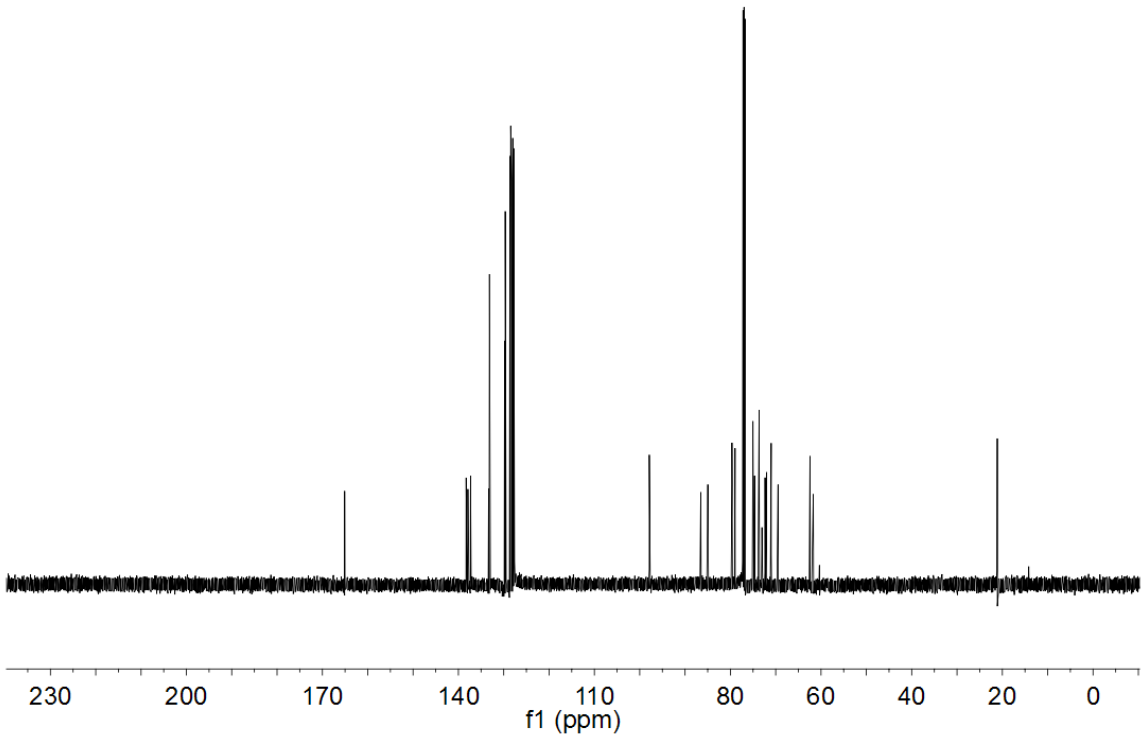
^{1}H-NMR ($CDCl_3$, 600 MHz) of **S16**



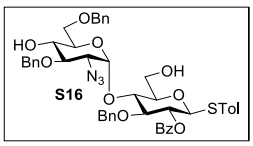


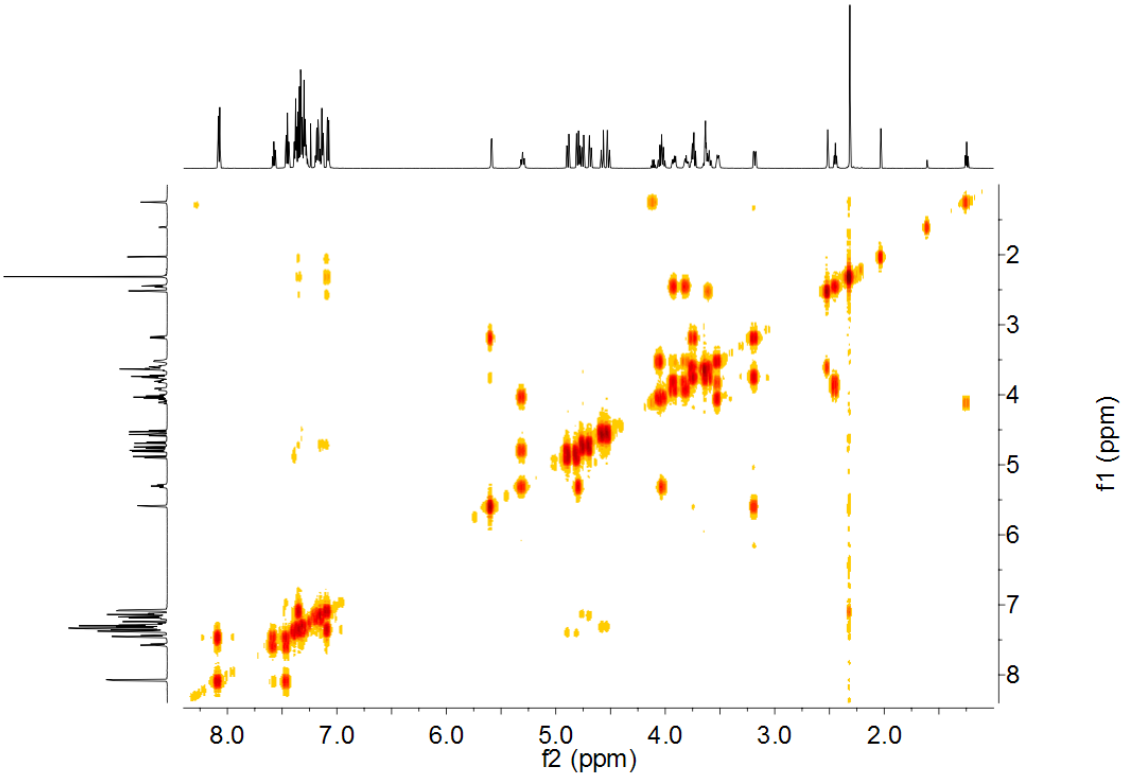
^{13}C-NMR ($CDCl_3$, 150 MHz) of **S16**



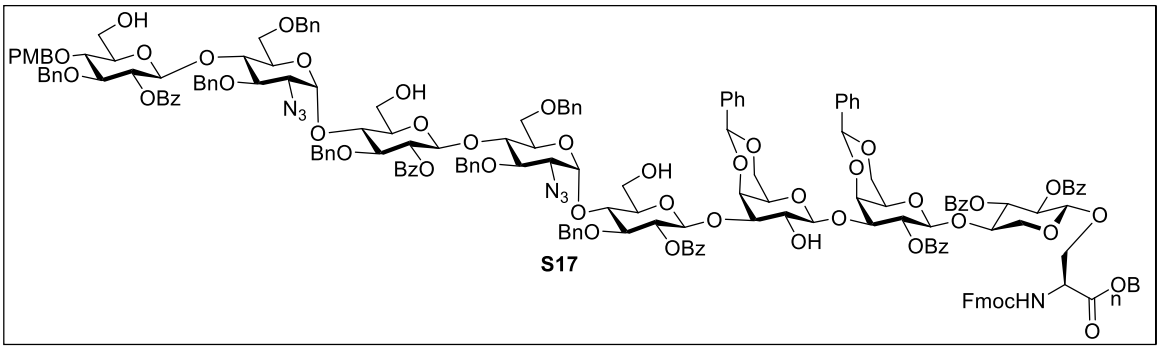


gCOSY ($CDCl_3$, 600 MHz) of **S16**

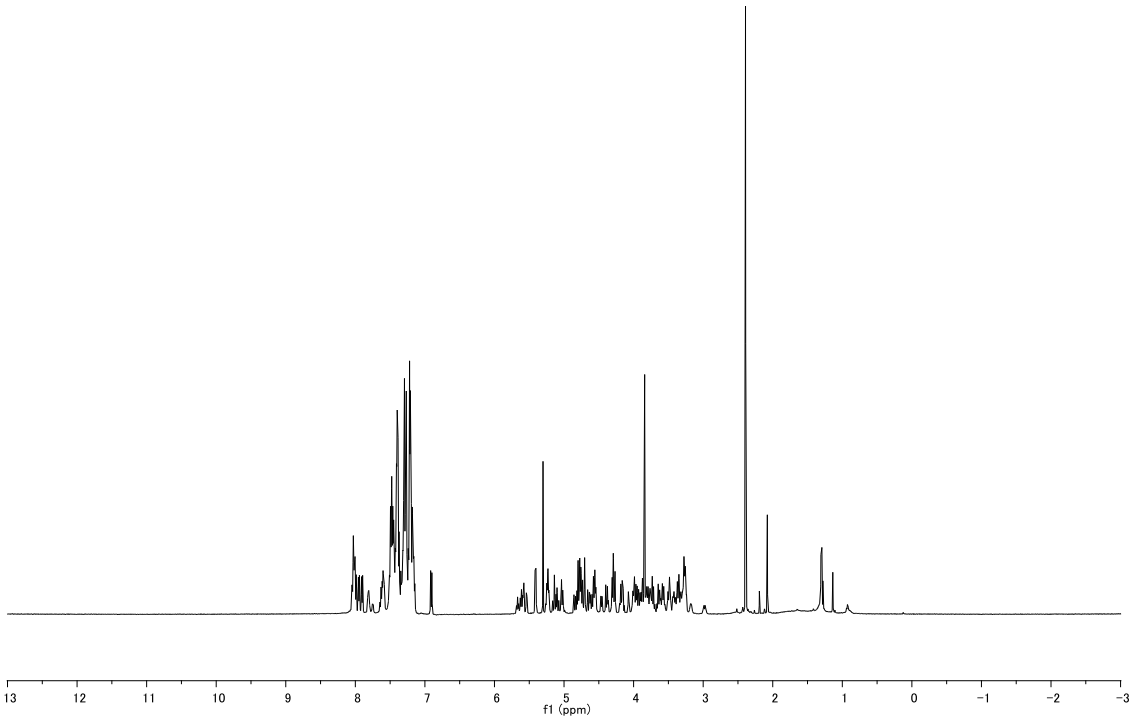




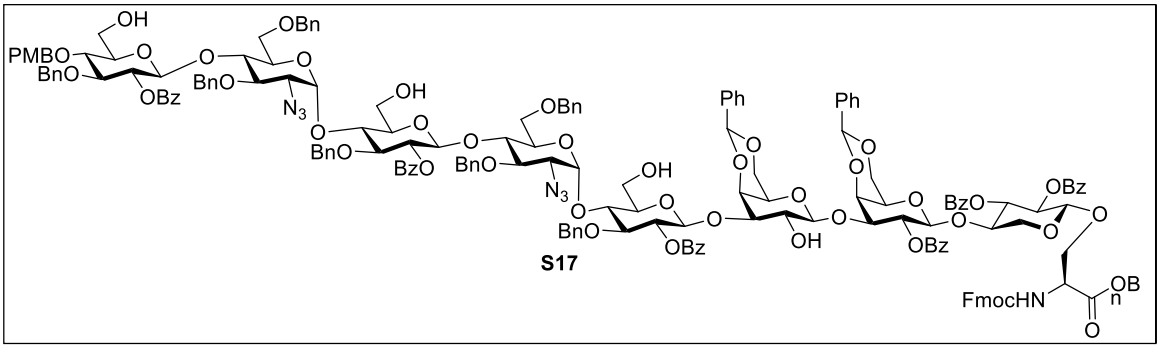
^{1}H-NMR ($CDCl_3$, 500 MHZ) of **S17**

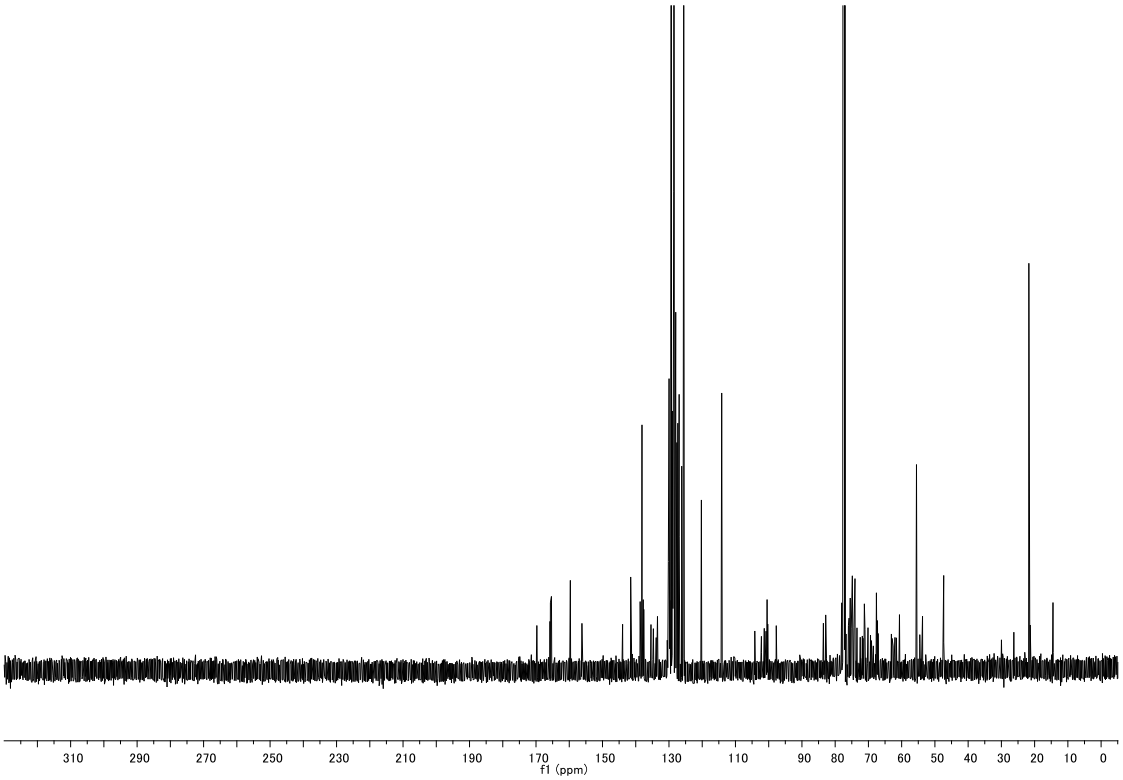


S17

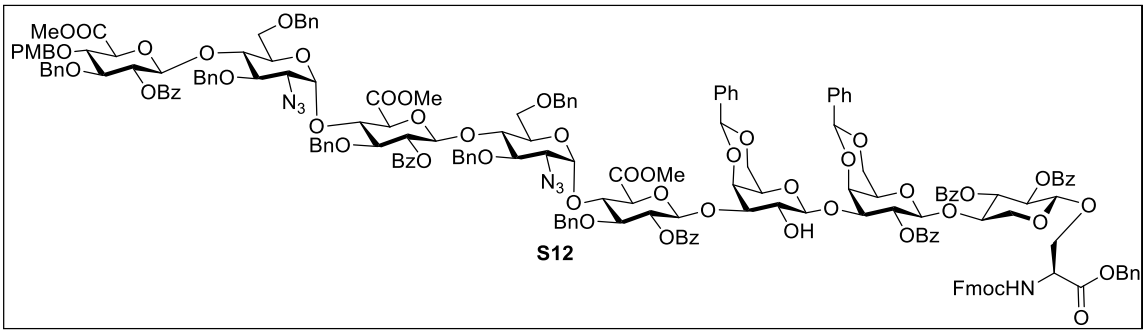


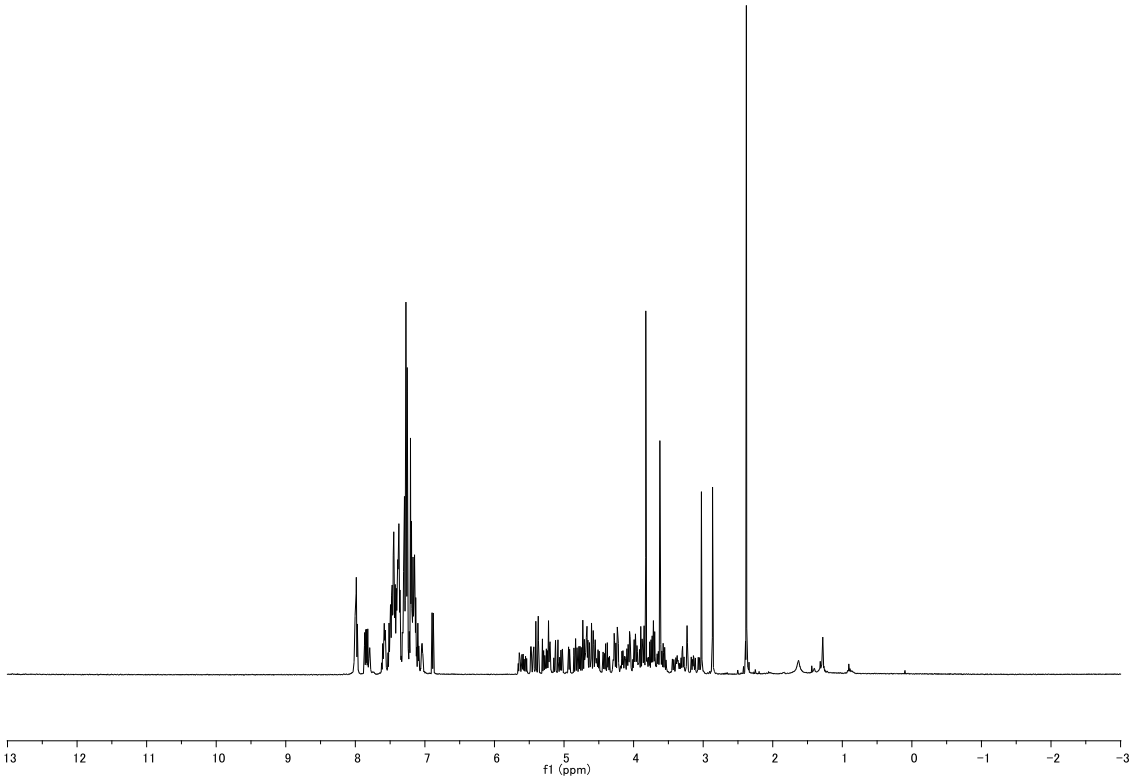
^{13}C-NMR ($CDCl_3$, 125 MHz) of **S17**



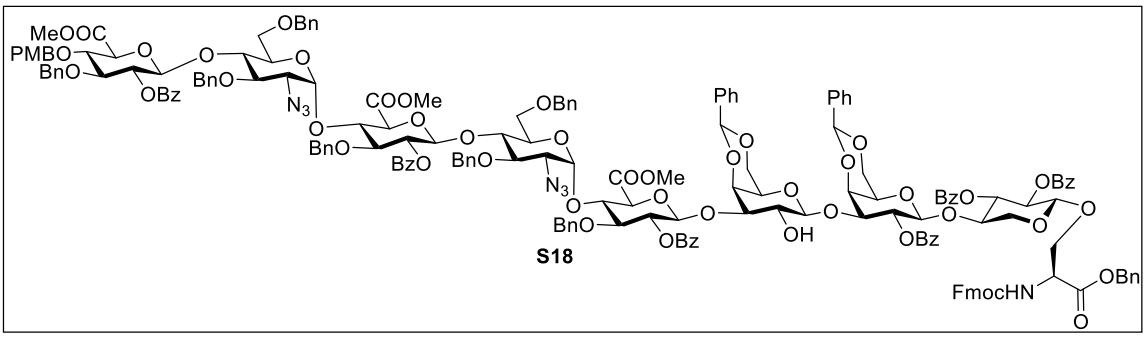


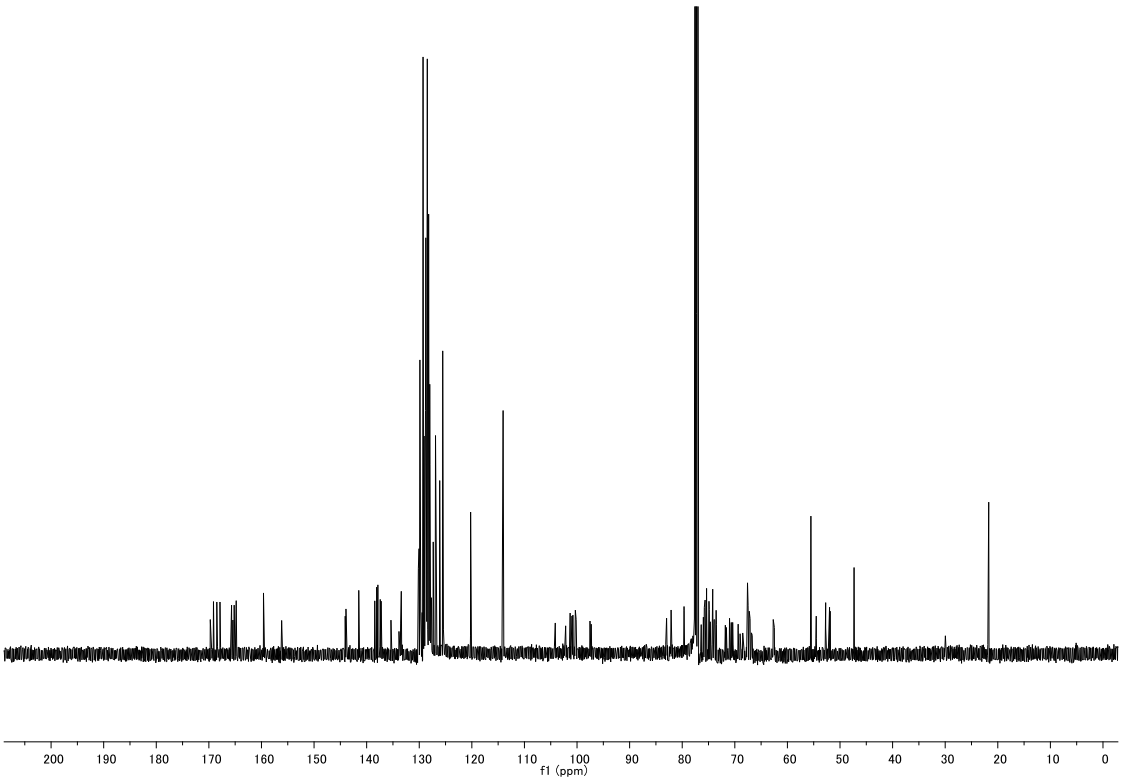
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S18**



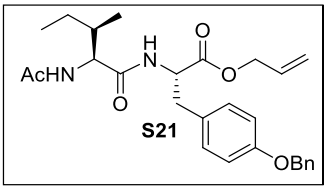


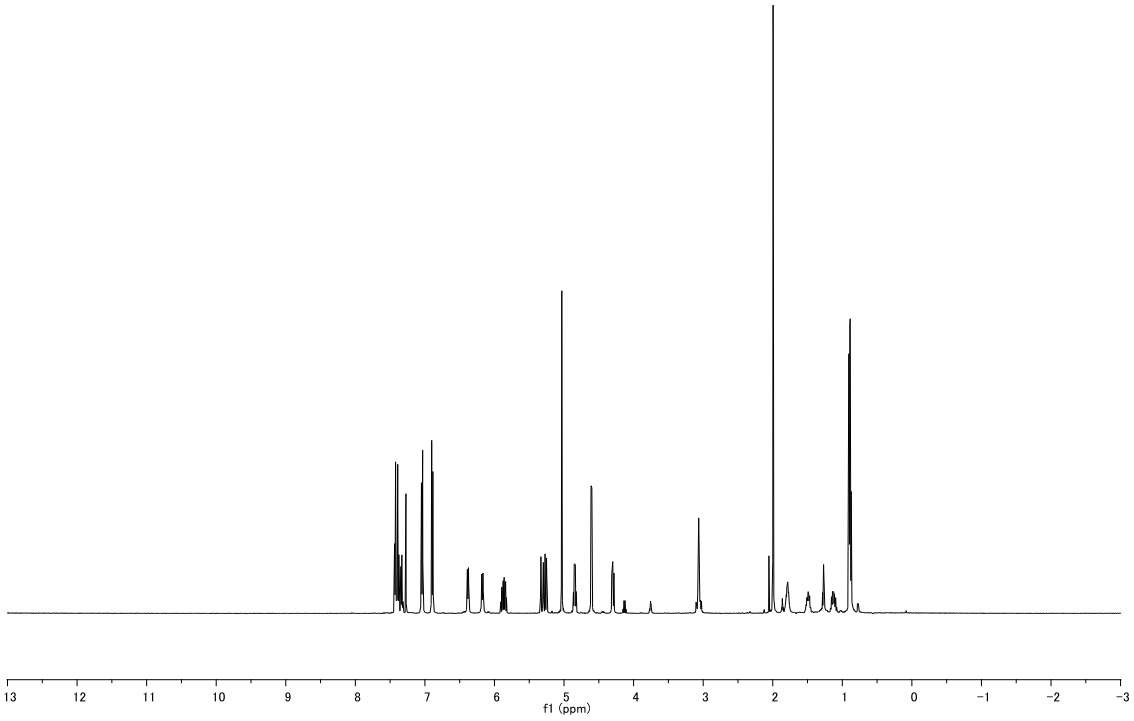
^{13}C-NMR ($CDCl_3$, 125 MHz) of **S18**



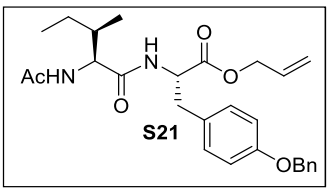


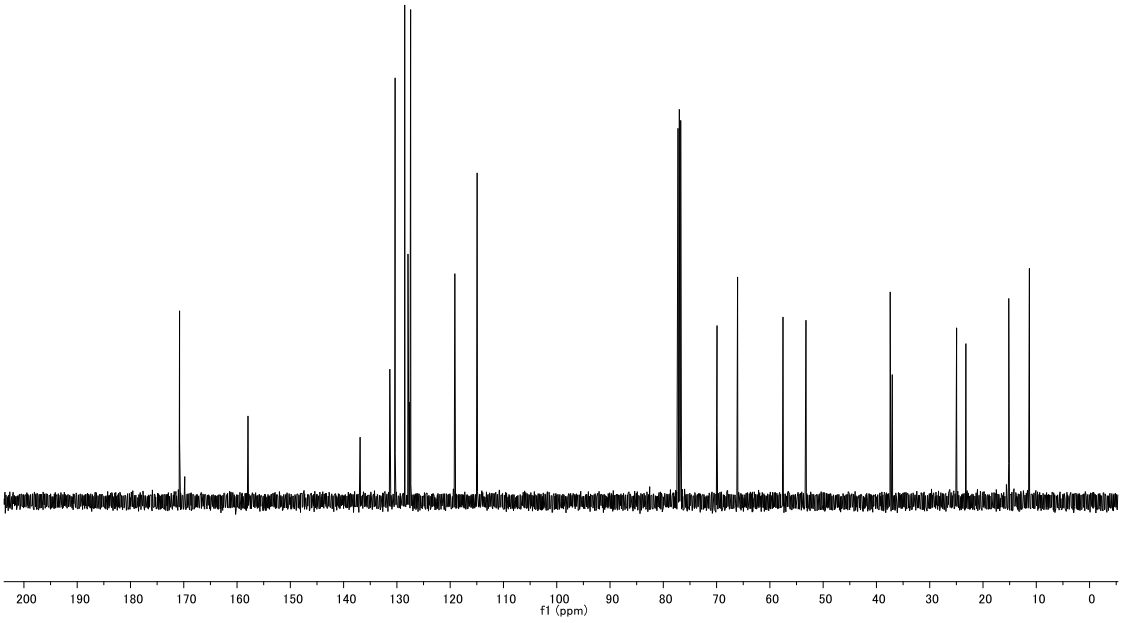
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S21**



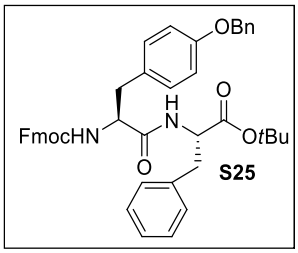


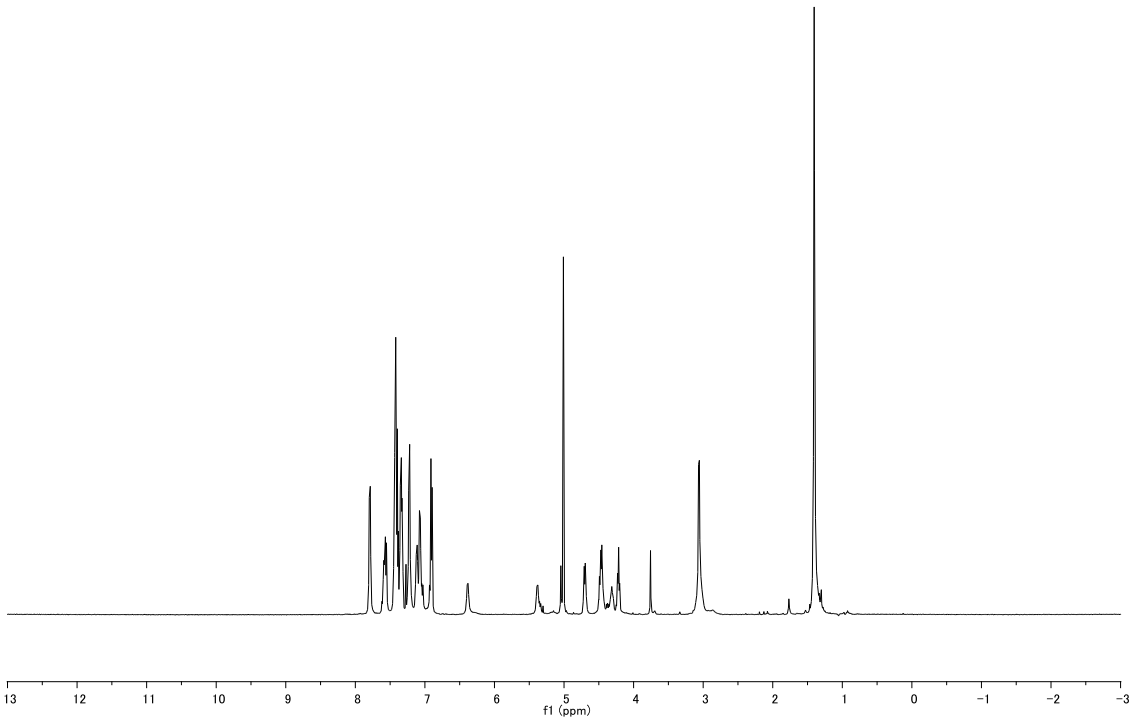
^{13}C-NMR ($CDCl_3$, 125 MHz) of **S21**



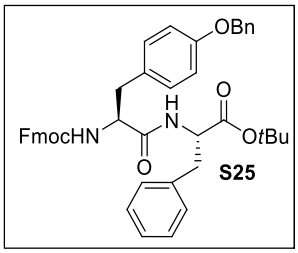


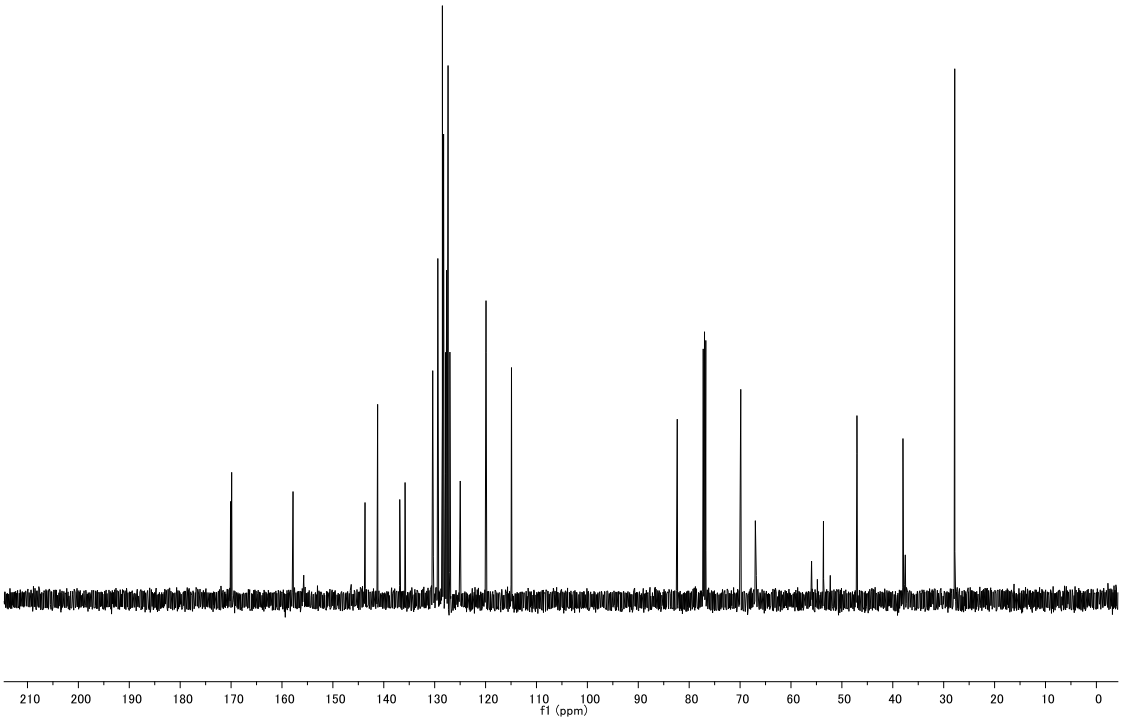
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S25**



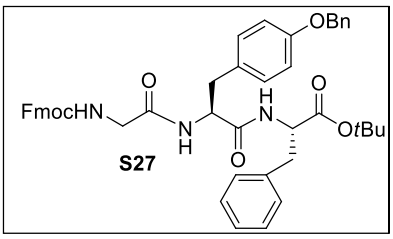


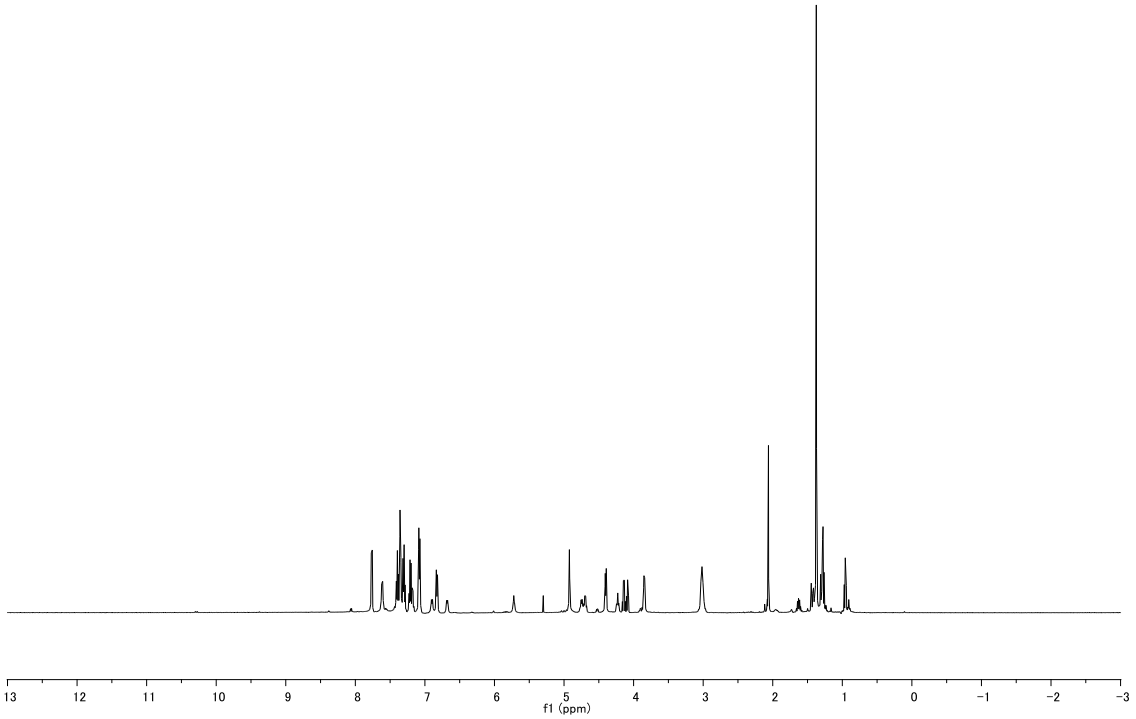
^{13}C-NMR ($CDCl_3$, 125 MHz) of **S25**



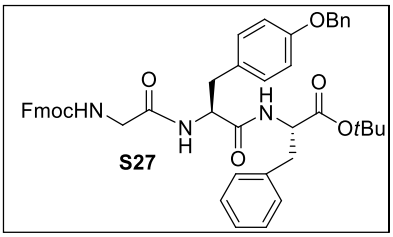


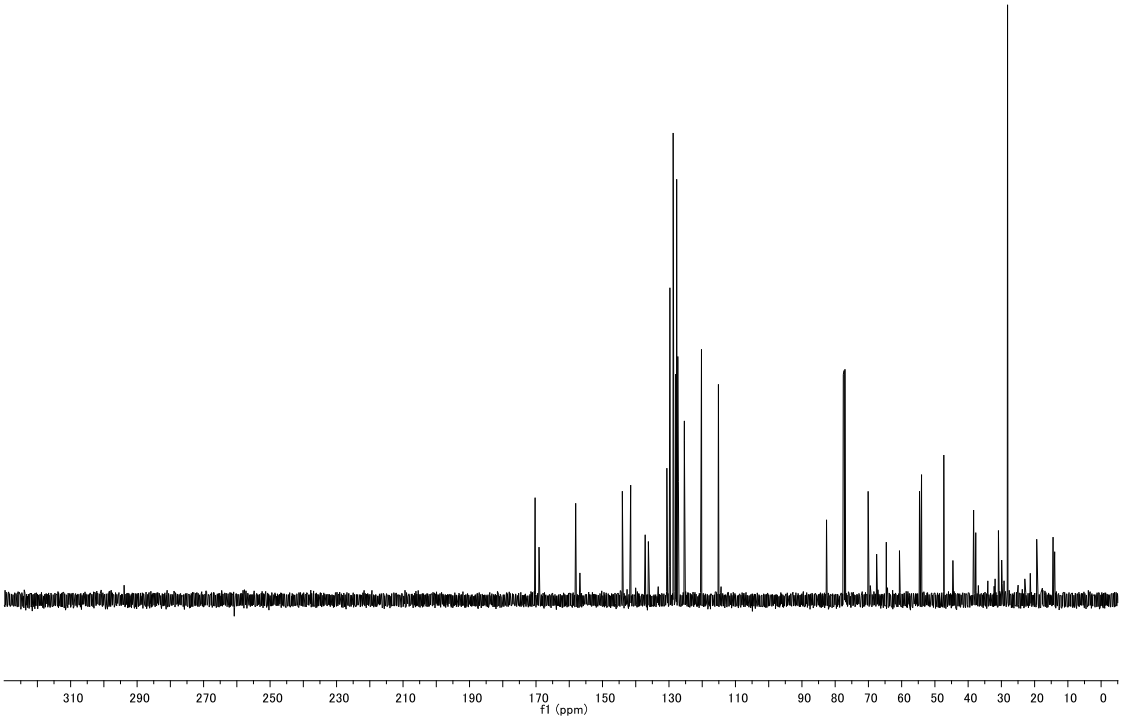
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S27**



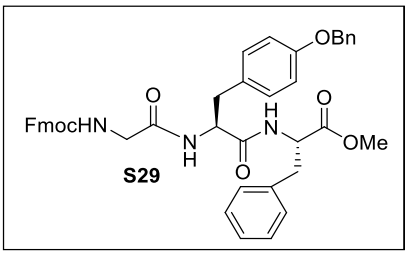


^{13}C-NMR ($CDCl_3$, 125 MHz) of **S27**

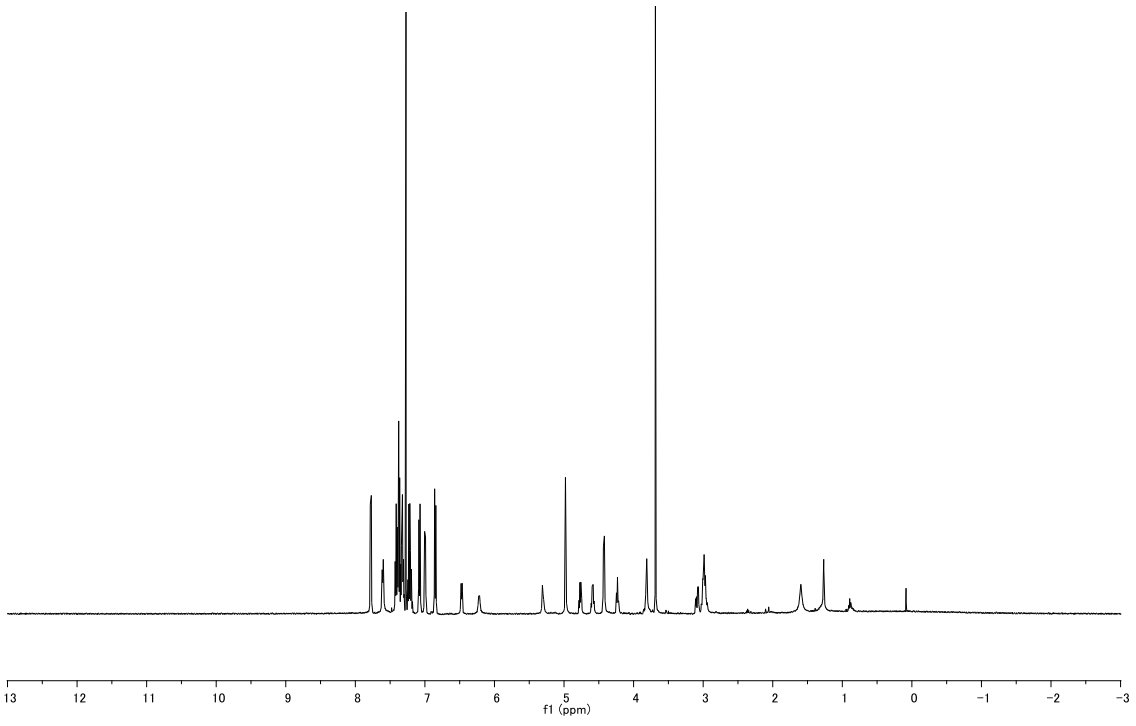




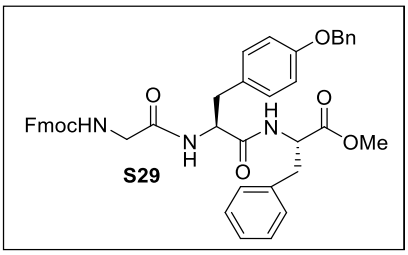
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S29**



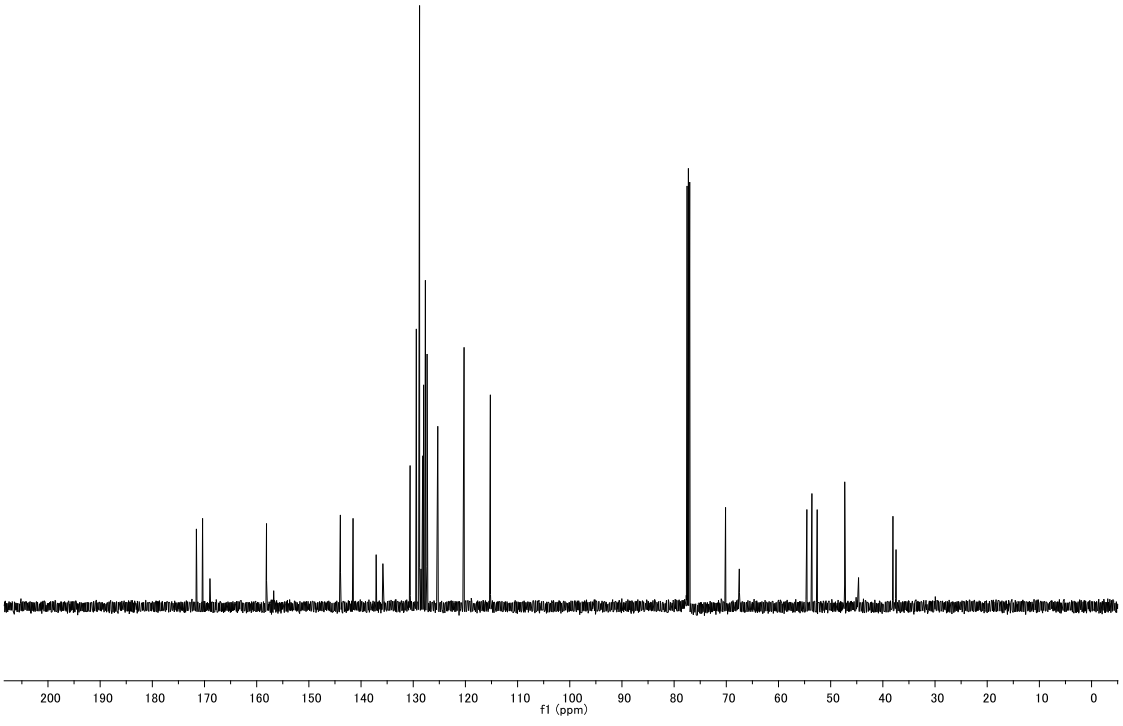
S29



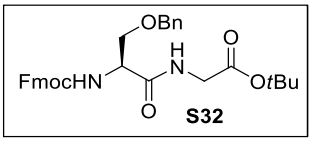
^{13}C-NMR ($CDCl_3$, 125 MHz) of **S29**



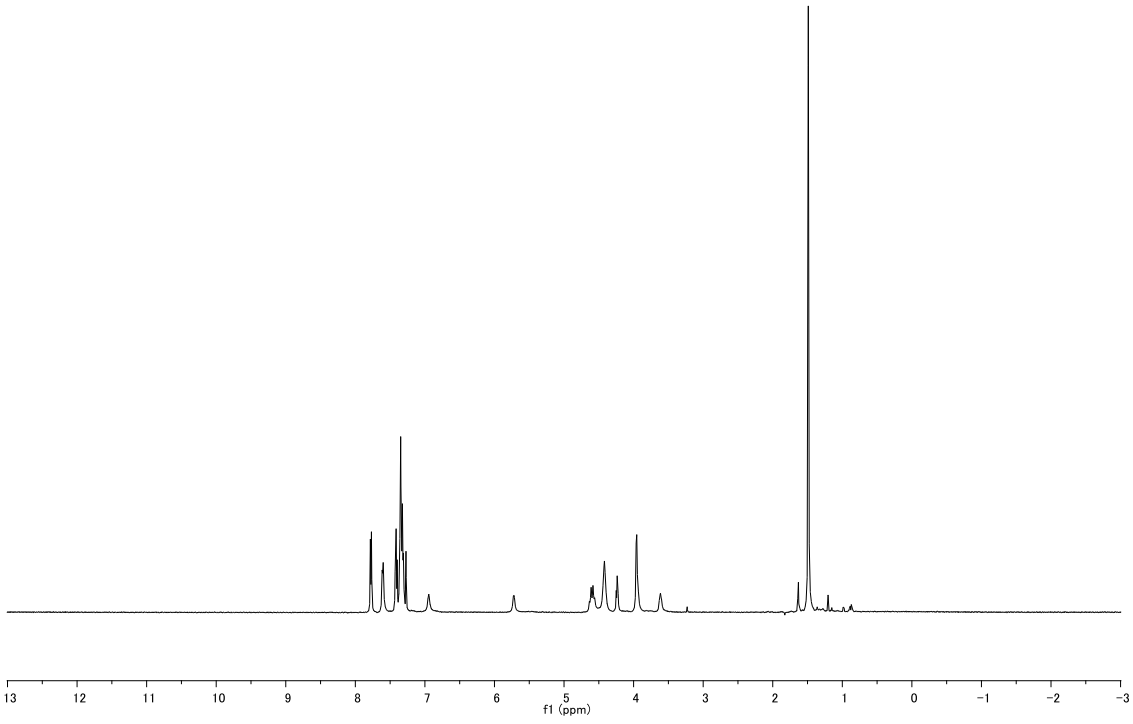
S29



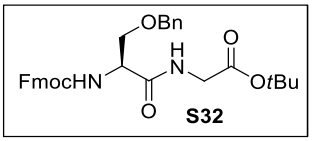
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S32**



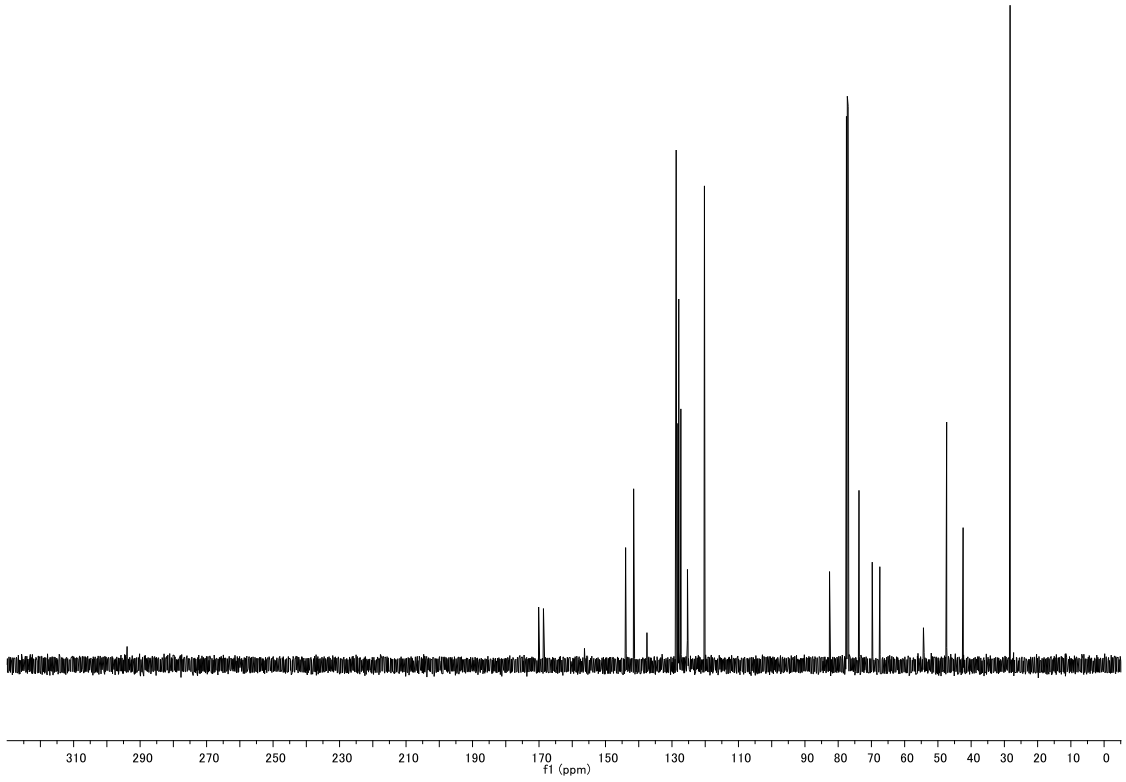
S32



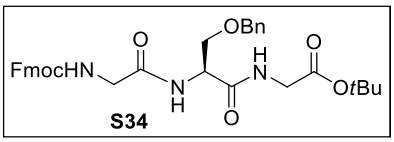
^{13}C-NMR ($CDCl_3$, 125 MHz) of **S32**



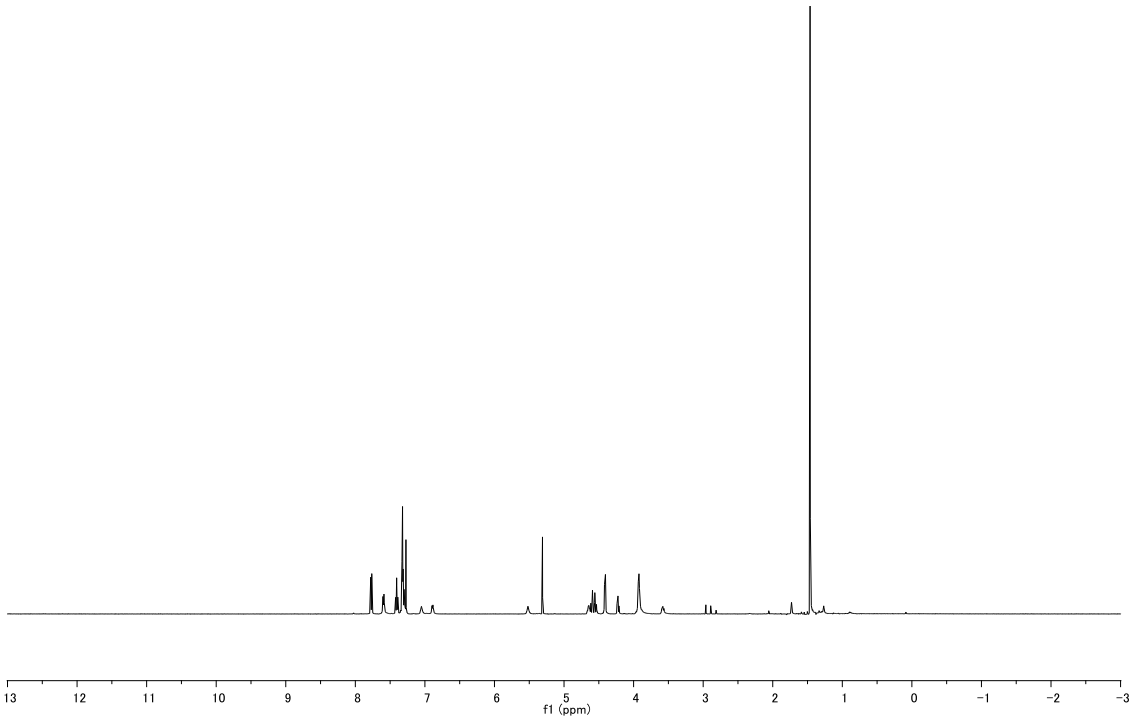
S32



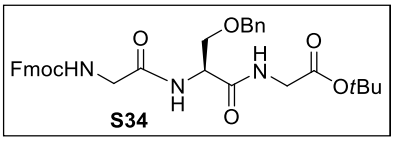
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S34**



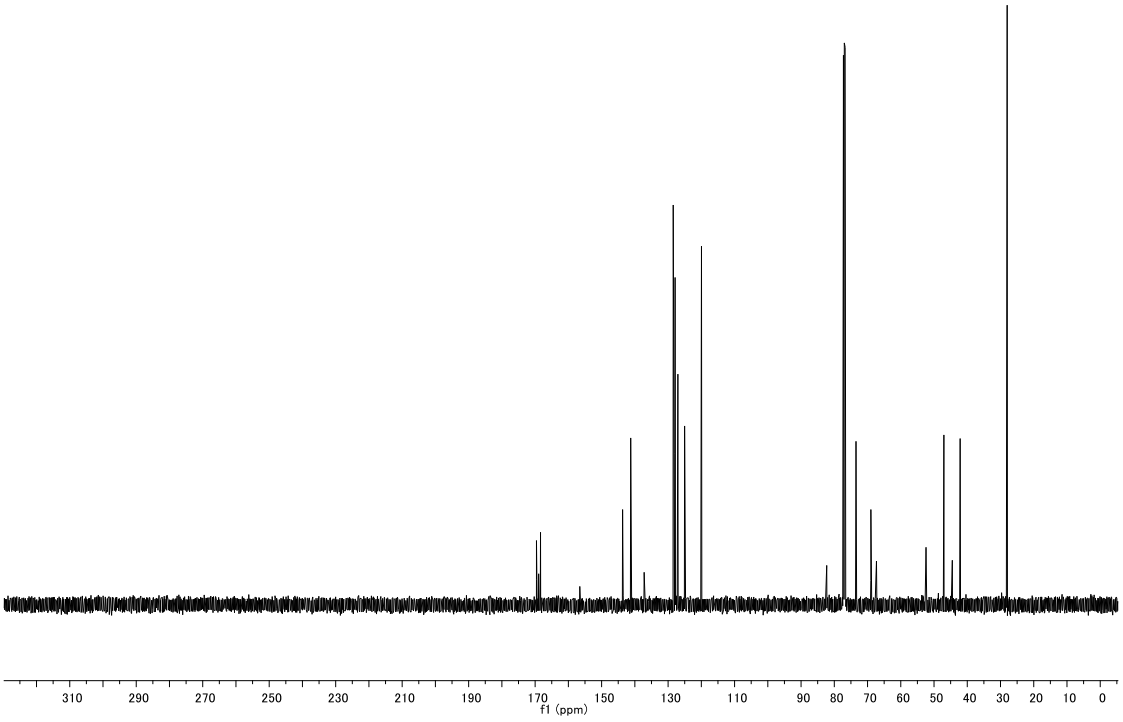
S34



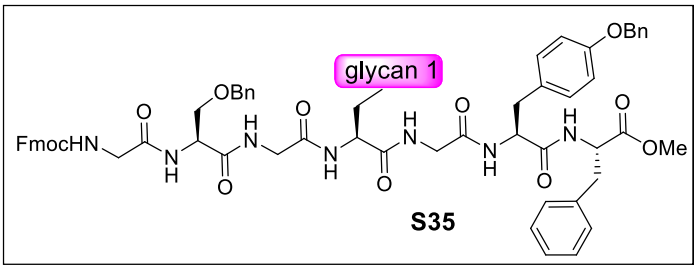
^{13}C-NMR ($CDCl_3$, 125 MHz) of **S34**

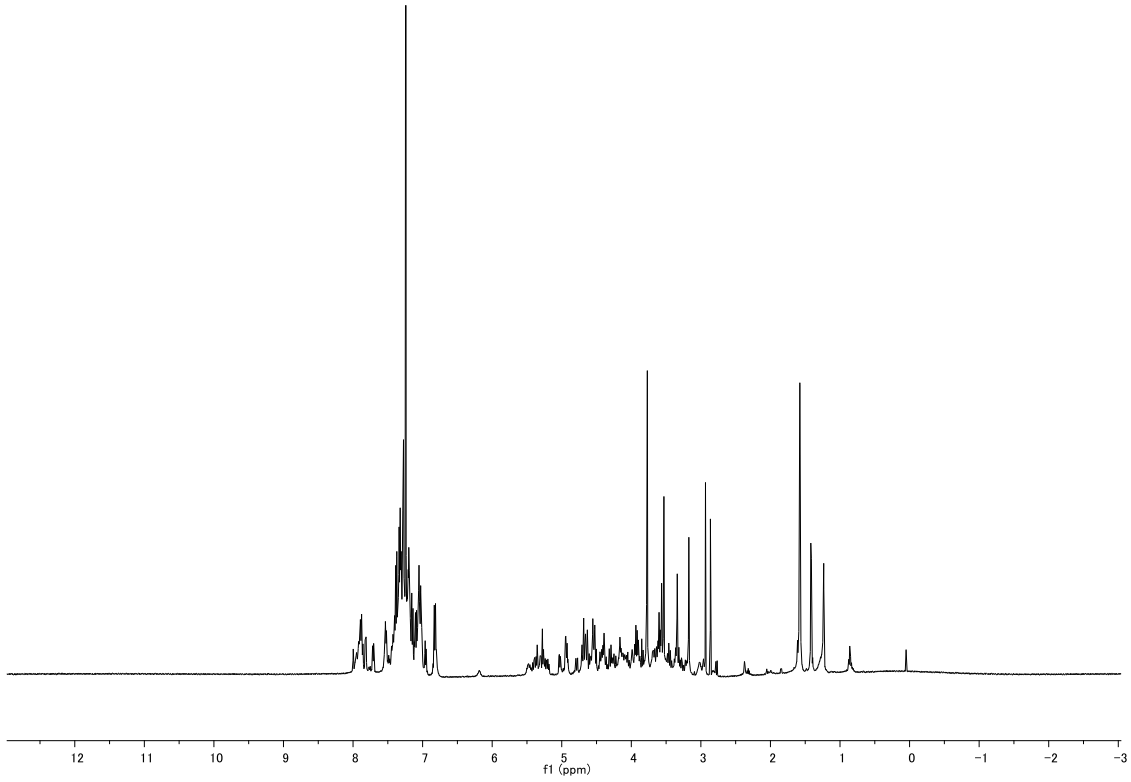


S34

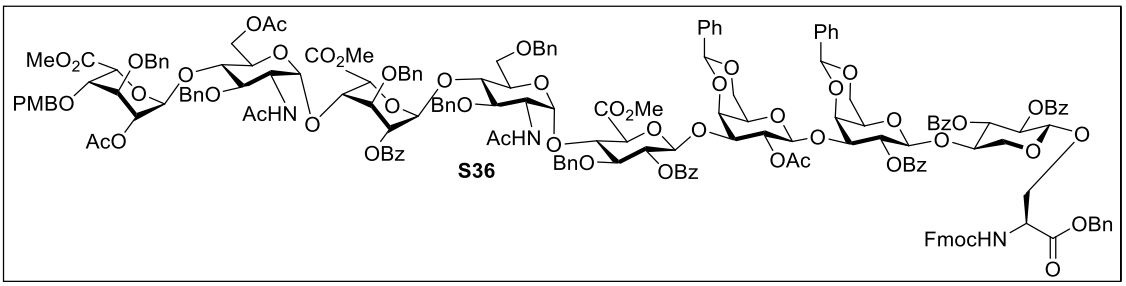


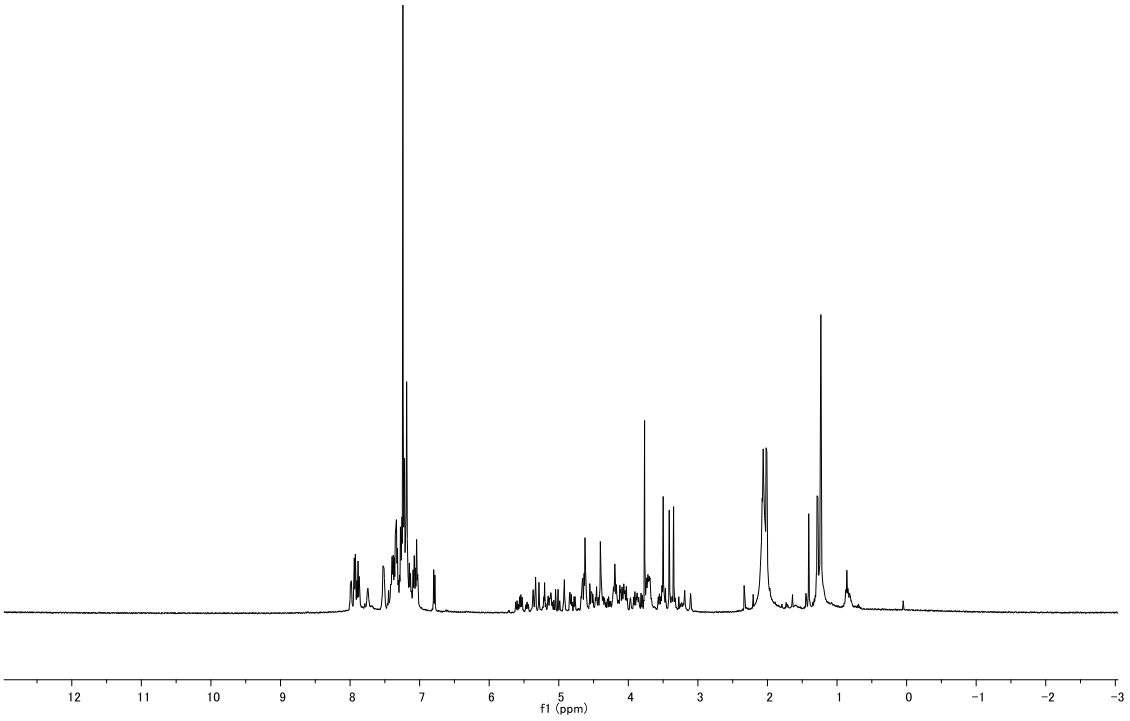
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S35**





^{1}H-NMR ($CDCl_3$, 500 MHz) of **S36**





^{13}C-NMR ($CDCl_3$, 125 MHz) of **S36**