Supporting information

Synthesis of Chondroitin Sulfate A Bearing Syndecan-1 Glycopeptide

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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 vacuum. Glycosylation solvents were dried using a solvent purification system and used directly without further drying. The chemicals used were reagent grade as supplied, except where noted. Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F254 glass plates. Compounds spots 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 (500 mL). 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. Optical rotations were recorded on a Perkin Elemer 341 Polarimeter (λ= 589 nm, 1 dm cell).

Characterization of anomeric stereochemistry:

The stereochemistry of the newly formed glycosidic linkages in the oligosaccharide and intermediates are determined by $^3J_{(H1,H2)}$ through ^{1}H-NMR and/or $^1J_{C1,H1}$ through gHMQC 2-D NMR (without ^{1}H decoupling). For glucosyl and galactosamine building blocks, the smaller coupling constants of $^3J_{(H1,H2)}$ (around 3 Hz) indicate *α* linkages and larger coupling constants $^3J_{(H1,H2)}$ (7.2 Hz or larger) indicate *β* linkages. For all glycosyl linkages, the stereochemistry can be further confirmed via $^1J_{(C1,H1)}$ (around 170 Hz) suggests *α* linkages and $^1J_{(C1,H1)}$ (around 160 Hz) for *β* linkages.[1]

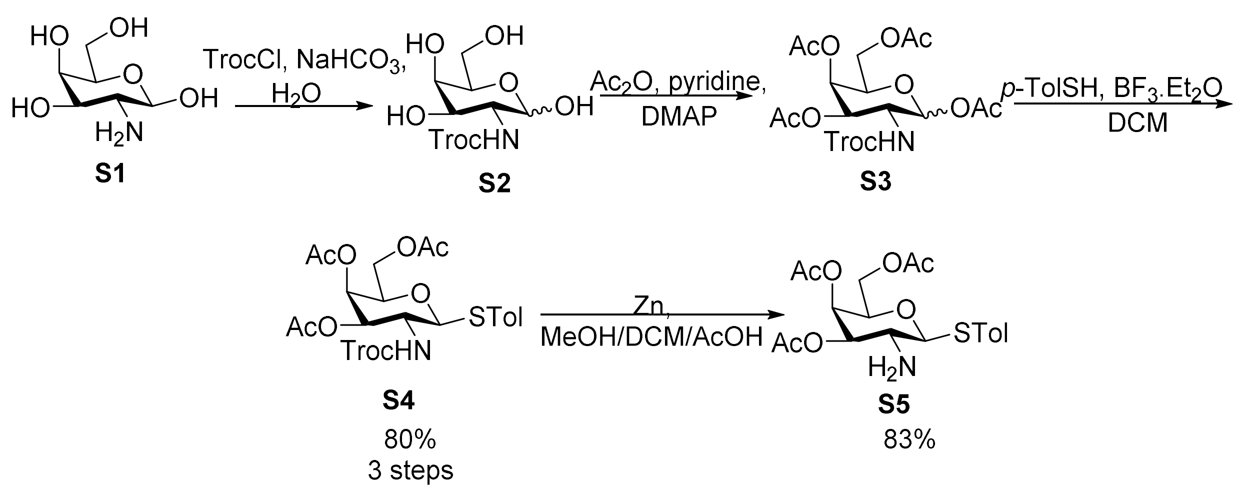
General procedure for pre-activation based single-step glycosylation:

A solution of donor (60 μmol) and freshly activated molecular sieve MS 4Å (200 mg) in CH_2Cl_2 (DCM) (2 mL) was stirred for 30 minutes at room temperature, and then cooled to -78°C. A solution of AgOTf (47 mg, 180 μmol) in anhydrous Et_2O/DCM (0.8 mL/0.2 mL) was added to reaction solution without touching the wall of the flask. After 5 min., orange colored *p*-TolSCl (9.5 μL, 60 μmol) was added to the reaction mixture through a microsyringe. *p*-TolSCl should be added directly to the reaction solution to prevent it from freezing on the flask wall. The characteristic orange color of *p*-TolSCl in the reaction solution dissipated rapidly in a few second indicating depletion of *p*-TolSCl. After the donor was completely activated according to TLC analysis (in 5 minutes), a solution of acceptor (54 μmol) with one equivalent TTBP in DCM (1.2 mL) was slowly added dropwise to the reaction via a syringe. The reaction was stirred for 1 h at -78°C then warmed up to 0 °C under stirring in 2 h (For acceptor contains PMB protective group, the reaction should be quenched at lower temperature to prevent cyclization). Upon reaction completion, the reaction mixture was diluted with DCM (20 mL), quenched by Et_3N and filtered over Celite. The Celite was washed with DCM till no organic compounds were observed in the filtrate by TLC. All DCM solutions were combined and washed twice with saturated aqueous solution $NaHCO_3$ (20mL) and twice with saturated aqueous solution of NaCl (10 mL). The organic layer was collected and dried over Na_2SO_4. After removal of the solvent, the desired oligosaccharide was purified via silica gel flash chromatography.

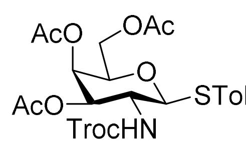
General method for the peptide synthesis:

All peptide syntheses were synthesized according to the Fmoc-chemistry based solid phase peptide synthesis procedure.[2] Resin with pre-loaded amino acid was loaded into a plastic syringe fitted with a filter and swelled in DCM for at least 1h. For the coupling reactions, the Fmoc-amino acids (5 equiv) was activated by *O*-(benzotriazol-1-yl)-*N*, *N*, *N*', *N*'-tetramethyluronium hexafluorophosphate (HBTU, 4.9 equiv), 1-hydroxybenzotriazole (HOBt, 4.9 equiv), DIPEA (10 equiv) and anhydrous DMF (5 mL) for 30 min. Then this mixture containing activated Fmoc amino acid was transferred to the syringe containing the resin preloaded with amino acid and allowed to rotate on a rotator for 30 min. at 70 ^{o}C. After completion of coupling, the resin was washed with DCM (3×5 mL) and DMF (3×5 mL) for 1min, each time followed by cleavage of the Fmoc group by treatment of the resin with a solution of piperidine (20%) in DMF for at least 2 × 20 min at rt. After every coupling step, unreacted amino groups were capped by treatment with a mixture of Ac_2O (0.5 mL), and DIPEA (1 mL) in DMF (3.5 mL) (capping reagent) for 2 times 15 min each. After completion of the peptide chain, the resin was washed and the peptide was cleaved from the resin by treatment with TFA/TIPS/H_2O (95%: 2.5%: 2.5%) solution for 2.5 h. After filtration, the resins were washed with trifluoroacetic acid (2× 10 mL), and the volume of the combined filtrates was concentrated to 1 mL, then absolute Et_2O (20 mL) at 0°C were added dropwise to the residues. The precipitates were separated from the mother liquor by centrifugation and washed with cold Et_2O (10 mL). The crude products were dissolved in H_2O and subjected to semipreparative RP-HPLC for purification.

Synthesis of monosaccharide building blocks:



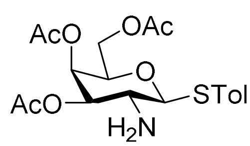
***p*-Tolyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-*N*-trichloroethoxycarbonylamino-1-thio-*β*-D-galactopyranoside S4:**



S4

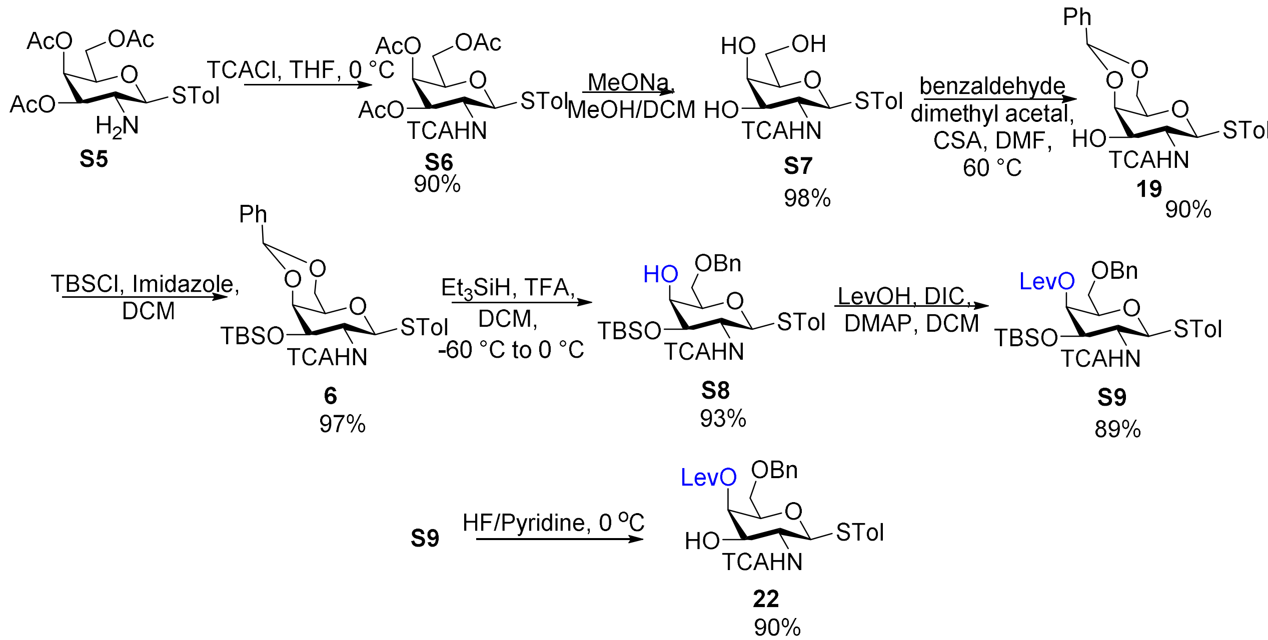
To a solution of D-galactosamine hydrochloride **S1** (20 g, 92 mmol) in water (150 mL), sodium bicarbonate ($NaHCO_3$) (23.4 g, 278 mmol) was added. Then the reaction mixture was cooled down to 0 °C and 2,2,2-trichloroethoxycarbonyl chloride (TrocCl) (15.2 mL, 112 mmol) was added dropwise. The reaction mixture was allowed to stir at room temperature for 3 h, then the precipitate was collected via filtration and dried under reduced pressure to afford crude product **S2** as white solid. Then the obtained crude solid was dissolved in pyridine (90 mL), cooled to 0 °C and acetic anhydride (Ac_2O) (75 mL) was added slowly followed by catalytic amount of 4-(dimethylamino)pyridine (DMAP) (0.01 eq.). The reaction was allowed to stir overnight at room temperature. Upon completion, excess acetic anhydride was quenched by slow addition of methanol (MeOH) at 0 °C. The mixture was concentrated under vacuum, diluted with ethyl acetate (EtOAc) and washed with 1 M HCl, saturated $NaHCO_3$ solution, water and brine. The organic phase was then dried over anhydrous Na_2SO_4, filtered and concentrated. Without purification, the obtained crude as thick syrup **S3** (42 g, 80 mmol) and *p*-toluenethiol (11.98 g, 96.4 mmol) were dissolved in dry DCM (200 mL), followed by slow addition of boron trifluoride etherate (40.7 mL, 321 mmol) at 0 °C. The reaction was stirred at room temperature overnight under nitrogen. Upon completion, the reaction was quenched with a sat. solution of $NaHCO_3$, then diluted with DCM (100 mL) and extracted with DCM (3 × 100 mL), washed with NaCl, dried over Na_2SO_4, concentrated and purified using silica gel column chromatography (Hexane/EtOAc, 8:1 → 3:1) to afford the *p*-tolyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-*N*-trichloroethoxycarbonylamino-1-thio-*β*-D-galactopyranoside **S4** as a white solid in 80% yield (43.5 g, 74.2 mmol) over three steps. Comparison with literature data[3] confirms its identity.

***p*-Tolyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-1-thio-*β*-D-galactopyranoside S5:**

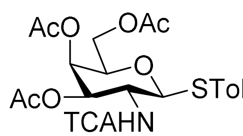


S5

Compound **S4** (37.5 g, 63.9 mmol) was dissolved in MeOH/AcOH/DCM (2:1:1, 160 mL:80 mL:80 mL), followed by careful and slow addition of zinc dust (79 g, 1.2 mol). The reaction was allowed to stir for 1h, then filtered over Celite, concentrated to dryness. The residue was diluted with DCM (30 mL), washed with saturated aqueous solution of $NaHCO_3$, then the organic layer was dried over Na_2SO_4, concentrated and purified with column chromatography (Hexane/EtOAc, 2:1 → 0:1) to afford *p*-tolyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-1-thio-*β*-D-galactopyranoside **S5** as a white solid in 83% yield (22.5, 54.7 mmol). Comparison with literature data[3] confirms its identity.



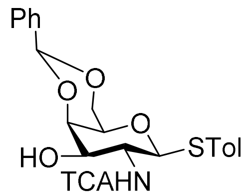
p-Tolyl 3,4,6-tri-O-acetyl- 2-deoxy-2-N-trichloroacetamido-1-thio-β-D-galactopyranoside S6:



S6

Thioglycoside **S5** (30 g, 72.9 mmol) was dissolved in THF (180 mL), the solution was cooled to 0 °C, then trichloroacetyl chloride (40.7 mL, 364 mmol) was added and triethylamine (Et_3N) (61 mL, 437 mmol) was added dropwise at 0 °C. The reaction mixture was stirred at 0 °C until completion (30 min.). The reaction was diluted with DCM (400 mL), washed with 10% HCl, saturated aqueous $NaCO_3$ solution. The organic layer was dried over Na_2SO_4, concentrated and the residue was purified by silica gel column chromatography (Hexane/EtOAc, 6:1 → 2:1) affording *p*-tolyl 3,4,6-tri-*O*-acetyl- 2-deoxy-2-*N*-trichloroacetamido-1-thio-*β*-D-galactopyranoside **S6** as a white solid in 90% yield (36.5 g, 65.6 mmol). [α_D^{20}] = +24 (C = 0.25, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, J = 8.1 Hz, 2H, 2 x aromatic CH), 7.11 (d, J = 8.1 Hz, 2H, 2 x aromatic CH), 6.91 (d, J = 9.0 Hz, 1H, TCANH), 5.38 (d, J = 3.1 Hz, 1H, H-4), 5.32 (dd, J = 10.8, 3.2 Hz, 1H, H-6), 4.91 (d, J = 10.4 Hz, 1H, H-1), 4.20 – 4.09 (m, 3H, H-2, H-5, H-6), 3.94 (t, J = 6.6 Hz, 1H, H-3), 2.33 (s, 3H, $SPhCH_3$), 2.12 (s, 3H, CH_3CO), 2.03 (s, 3H, CH_3CO), 1.95 (s, 3H, CH_3CO). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.48, 170.33, 170.13, 161.75, 138.64, 133.27, 129.72, 128.30, 92.28, 86.77, 74.53, 70.58, 66.90, 61.73, 51.31, 21.18, 20.69, 20.64, 20.53. HRMS: $C_{21}H_{24}Cl_3NO_8S$ $[M+NH_4]^+$ calcd: 573.0632, obsd: 573.0643.

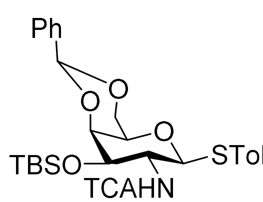
p-Tolyl 4,6-O-benzylidine-2-deoxy-2-N-trichloroacetamido-1-thio-β-D-galactopyranoside 19:



19

The trichloroacetamide **S6** (10 g, 18 mmol) was dissolved in MeOH/DCM (3/2) (150 mL) followed by addition of sodium metal until pH ≈ 14. The reaction was stirred for 2-3 h at room temperature then Amberlite resin was added to adjust pH around 7. After filtration, the filtrate was concentrated and dried under *vacuo* to give product as yellow solid S**7** in 98% yield (7.6 g, 17.6 mmol). HRMS: $C_{15}H_{18}C_{l3}NO_5S$ $[M+Na]^+$ calcd: 451.9869, obsd: 451.9872. The crude triol **S7** (7.58 g, 17.6 mmol) was dissolved in in dry DMF (40 mL), and benzaldehyde dimethylacetal (3.96 mL, 26.4 mmol) was added. The pH was adjusted to 4 with a catalytic amount of camphorsulfonic acid (2.04 g, 8.8 mmol). The reaction mixture was stirred overnight at 60 °C. After the reaction completed, it was neutralized with triethylamine (4-5 drops). Then the solvent was concentrated *in vacuo* and diluted with EtOAc, washed with saturated aqueous $NaHCO_3$ solution, water, dried over Na_2SO_4. Purification of the resulting residue by flash chromatography (Hexane/EtOAc/DCM, 10:1:1 → 5:1:1) gave *p*-tolyl 4,6-*O*-benzylidine-2-deoxy-2-*N*-trichloroacetamido-1-thio-*β*-D-galactopyranoside **19** in 90% yield (8.2 g, 15.8 mmol) as a colorless amorphous solid. $[\alpha_D^{20}]$ = +12.8 (C = 1.25, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, J = 8.0 Hz, 2H, 2 x aromatic CH), 7.44 – 7.32 (m, 5H, 5 x aromatic CH), 7.10 (d, J = 8.0 Hz, 2H, 2 x aromatic CH), 6.96 (d, J = 8.0 Hz, 1H, TCANH), 5.46 (s, 1H, PhCH), 4.95 (d, J = 10.1 Hz, 1H, H-1), 4.33 (d, J = 12.4 Hz, 1H, H-6), 4.13 (d, J = 3.3 Hz, 1H), 4.10 – 4.03 (m, 1H, H-3), 3.96 (d, J = 12.4 Hz, 1H, H-5), 3.75 (td, J = 10.1, 8.4 Hz, 1H, H-2), 3.42 (dd, J = 8.3, 4.5 Hz, 1H, H-4), 2.82 (d, J = 10.2 Hz, 1H), 2.35 (s, 3H, $SPhCH_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.02, 138.63, 137.54, 134.17, 129.97, 129.81, 129.40, 128.54, 128.25, 127.14, 126.82, 126.57, 101.16, 92.53, 84.12, 77.40, 77.15, 76.89, 74.92, 70.82, 70.79, 70.58, 69.87, 62.65, 60.50, 53.91, 45.09, 30.22, 29.55, 27.08, 26.86, 26.43, 26.41, 21.31, 21.10, 14.21. ESI-MS: $C_{22}H_{22}Cl_3NO_5S$ $[M+NH_4]^+$ calcd: 535.0623, obsd: 535.0590.

***p*-Tolyl 4,6-*O*-benzylidine-3-*O*-*t*-butyldimethylsilyl-2-deoxy-2-*N*-trichloroacetamido-1-thio-*β*-D-galactopyranoside 6**:

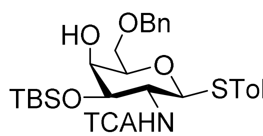


6

97%

Compound **19** (10 g, 19.3 mmol) and *tert*-butyldimethylsilyl chloride (TBSCl) (4.65 g, 30.8 mmol) were dissolved DCM (50 mL), then imidazole (1.3 g, 19.3 mmol) was added and the reaction mixture was stirred at room temperature. After complete conversion of the starting material, the reaction was diluted with DCM (100 mL) and washed with saturated aqueous $NaHCO_3$ solution. The organic layer was dried over Na_2SO_4, concentrated and the residue was purified by silica gel flash column chromatography (Hexane/EtOAc/DCM, 20:1:1 → 5:1:1) to afford *p*-tolyl 4,6-*O*-benzylidine-3-*O*-*t*-butyldimethylsilyl-2-deoxy-2-*N*-trichloroacetamido-1-thio-*β*-D-galactopyranoside **6** as a colorless amorphous solid in 87% yield (10.6 g, 16.8 mmol). [α_D^{20}] = +32 (C = 0.125, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, J = 8.1 Hz, 2H, 2 x aromatic CH), 7.48 (dd, J = 6.8, 2.7 Hz, 2H, 2 x aromatic CH), 7.40 – 7.36 (m, 3H, 3 x aromatic CH), 7.04 (d, J = 8.0 Hz, 2H, 2 x aromatic CH), 6.81 (d, J = 7.1 Hz, 1H, TCANH), 5.52 (s, 1H, PhCH), 5.40 (d, J = 10.1 Hz, 1H, H-1), 4.59 (dd, J = 10.2, 3.2 Hz, 1H, H-3), 4.41 (dd, J = 12.3, 1.3 Hz, 1H, H-5), 4.12 (d, J = 3.1 Hz, 1H, H-4), 4.05 (dd, J = 12.3, 1.5 Hz, 1H, H-6), 3.67 (td, J = 10.0, 7.4 Hz, 1H, H-2), 3.59 (s, 1H, H-6), 2.33 (s, 3H, $SPhCH_3$), 0.85 (s, 9H, $C(CH_3)_3$), 0.08 (s, 3H, $Si(CH_3)_2$), 0.06 (s, 3H, $Si(CH_3)_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.26, 138.32, 137.93, 133.83, 129.82, 128.87, 128.51, 128.24, 128.03, 127.61, 126.26, 100.68, 82.95, 76.14, 70.05, 69.44, 63.02, 54.32, 29.56, 26.51, 25.97, 25.71, 25.59, 21.24, 18.09, -4.37, -4.67, -5.28. HRMS: $C_{28}H_{36}Cl_3NO_5SSi$ $[M+NH_4]^+$ calcd: 649.1487, obsd: 649.1463.

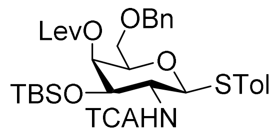
***p*-Tolyl 6-*O*-benzyl-3-*O*-*t*-butyldimethylsilyl-2-deoxy-2-*N*-trichloroacetamido-1-thio-*β*-D-galactopyranoside S8:**



S8

A solution of compound **6** (7.4 g, 11.7 mmol) in anhydrous DCM (100 mL) was cooled to -60 °C, followed by addition of triethylsilane (Et_3SiH)[4] (18.7 mL, 116.9 mmol), then trifluoroacetic acid (TFA) (9 mL, 116.9 mmol) was added dropwise. The reaction mixture was stirred at -60 °C to 0 °C for 2 h. After completion, the reaction was diluted with DCM and neutralized with Et_3N till the pH around 7. The solution was washed with a saturated aqueous $NaHCO_3$ solution, dried over Na_2SO_4 and concentrated. Silica gel column chromatography (Hexane/EtOAc, 8:1 → 3:1) gave *p*-tolyl 6-*O*-benzyl-3-*O*-tert-butyldimethylsilyl-2-deoxy-2-*N*-trichloroacetamido-1-thio-*β*-D-galactopyranoside **S8** in 93% yield as colorless oil (6.9 g, 1.9 mmol). [α_D^{20}] = +17 (C = 0.125, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.1 Hz, 2H, 2 x aromatic CH), 7.39 – 7.28 (m, 5H, 5 x aromatic CH), 7.06 (d, *J* = 8.0 Hz, 2H, 2 x aromatic CH), 6.97 (d, *J* = 8.3 Hz, 1H, TCANH), 5.11 (d, *J* = 10.4 Hz, 1H, H-1), 4.61 – 4.52 (m, 2H, $PhCH_2$), 4.24 (dd, *J* = 9.6, 2.8 Hz, 1H, H-3), 3.92 (d, *J* = 3.2 Hz, 1H, H-4), 3.87 – 3.75 (m, 4H, H-2, H-5, 2 x H-6), 2.56 (s, 1H), 2.31 (s, 3H, $SPhCH_3$), 0.91 (s, 9H, $C(CH_3)_3$), 0.14 (s, 3H, $Si(CH_3)_2$), 0.13 (s, 3H, $Si(CH_3)_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.55, 138.13, 138.05, 132.93, 129.76, 129.09, 128.40, 127.72, 127.68, 92.48, 85.54, 77.23, 73.59, 71.99, 69.54, 69.35, 54.58, 25.74, 21.21, 17.91, 6.69, 5.83, -4.38, -4.59. HRMS: $C_{28}H_{38}Cl_3NO_5SSi$ $[M+NH_4]^+$ calcd: 651.1644, obsd: 651.1628.

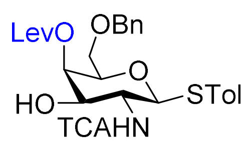
***p*-Tolyl 6-*O*-benzyl-3-*O*-*t*-butyldimethylsilyl-4-*O*-levulinoyl-2-deoxy-2-*N*-trichloroacetamido-1-thio-*β*-D-galactopyranoside S9:**



S9

Compound **S8** (8.43 g, 13.3 mmol) was dissolved in dry DCM (50 mL), followed by addition of *N,N'*-diisopropylcarbodiimide (DIC) (9.15 mL, 59.1 mmol), levulinic acid (LevOH) (6.8 mL, 66.4 mmol) and DMAP (4.9 g, 40.1 mmol). The reaction mixture was stirred overnight at room temperature. After the reaction was completed, it was diluted with DCM, washed with 10% aqueous HCl solution, saturated $NaHCO_3$, brine and dried over Na_2SO_4. The organic phase was concentrated and the residue was purified with silica gel column chromatography (Hexane/EtOAc, 8:1 → 3:1) to afford *p*-tolyl 6-*O*-benzyl-3-*O*-tert-butyldimethylsilyl-4-*O*-levulinoyl-2-deoxy-2-*N*-trichloroacetamido-1-thio-*β*-D-galactopyranoside **S9** as a colorless amorphous solid in 89% yield (8.6 g, 11.8 mmol). [α_D^{20}] = +25 (C = 0.701, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.1 Hz, 2H, 2 x aromatic CH), 7.36 – 7.25 (m, 5H, 5 x aromatic CH), 7.06 (d, *J* = 8.0 Hz, 2H, 2 x aromatic CH), 6.89 (d, *J* = 8.2 Hz, 1H, TCANH), 5.36 (d, *J* = 3.0 Hz, 1H, H-6), 5.11 (m, 1H, H-1), 4.49 (m, 2H, $PhCH_2$), 4.20 (m, 1H, H-6), 3.82 (t, *J* = 6.0 Hz, 2H, H-2, H-5), 3.63 (dd, *J* = 9.9, 6.2 Hz, 1H, H-4), 3.53 (dd, *J* = 10.0, 6.0 Hz, 1H, H-3), 2.80 – 2.74 (m, 1H, $CH_3COCH_2CH_2$), 2.71 – 2.60 (m, 2H, $CH_3COCH_2CH_2$), 2.56 – 2.49 (m, 1H, $CH_3COCH_2CH_2$), 2.31 (s, 3H, $SPhCH_3$), 2.18 (s, 3H, $CH_3COCH_2CH_2$), 0.82 (s, 9H, $C(CH_3)_3$), 0.10 (s, 3H, $Si(CH_3)_2$), 0.06 (s, 3H, $Si(CH_3)_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.31, 171.60, 161.39, 138.14, 137.94, 132.88, 129.70, 129.11, 128.35, 127.97, 127.69, 92.45, 85.90, 76.56, 73.62, 70.48, 70.10, 68.63, 55.07, 37.87, 29.91, 27.94, 25.58, 21.18, 17.70, -4.45, -4.91. HRMS: $C_{33}H_{44}Cl_3NO_7SSi$ $[M+NH_4]^+$ calcd: 749.2012, obsd: 749.2014.

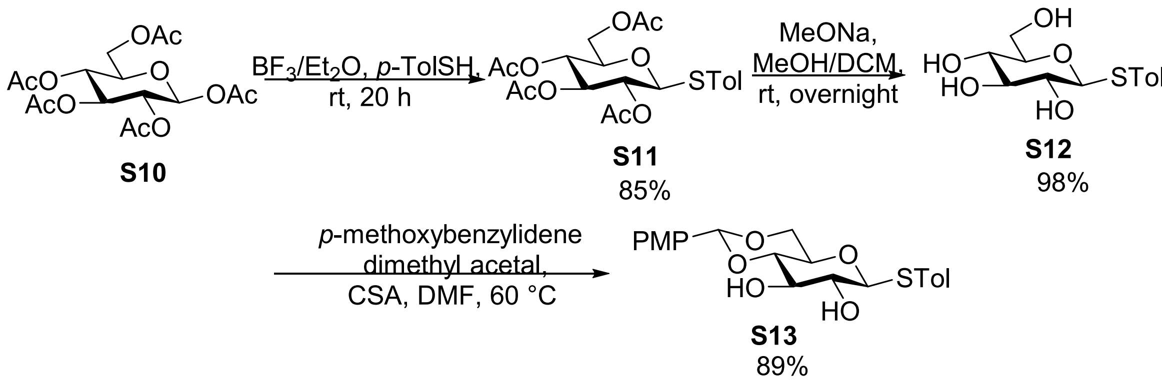
***p*-Tolyl 6-*O*-benzyl-4-*O*-levulinoyl-2-deoxy-2-*N*-trichloroacetamido-1-thio-*β*-D-galactopyranoside 22:**



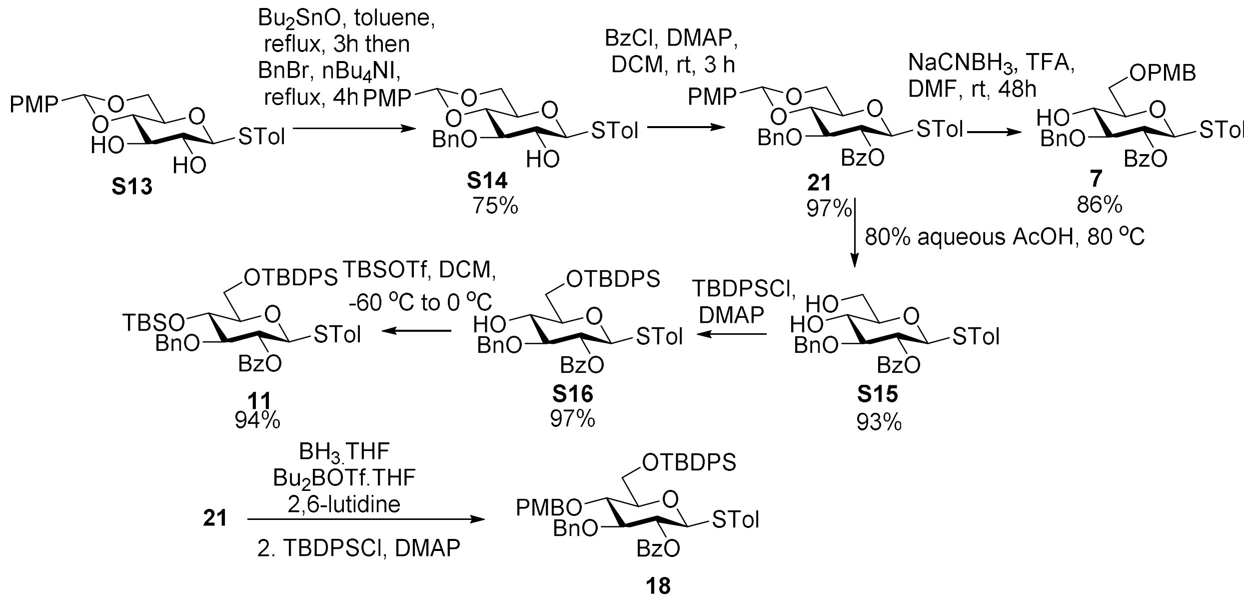
22

Compound **S9** (1.3 g, 1.8 mmol) was dissolved in pyridine (10 mL) in a plastic flask, followed by the addition of HF-pyridine solution (5 mL) at 0 °C. The reaction mixture was stirred until the starting material was consumed as judged by TLC analysis, then it was diluted with EtOAc, washed with saturated $CuSO_4$ solution, saturated $NaHCO_3$ solution, and brine, dried over Na_2SO_4 and concentrated. The crude was purified by silica gel column chromatography (Hexane/EtOAc, 8:1 → 2:1) to afford compound **22** as a white solid in 90% yield (0.99 g, 1.6 mmol). [α_D^{20}] = -119.8 (C = 0.017, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.1 Hz, 2H, 2 x aromatic CH), 7.39 – 7.26 (m, 6H, 6 x aromatic CH), 7.06 (d, *J* = 8.1 Hz, 2H, TCANH), 5.40 (d, *J* = 3.1 Hz, 1H, H-6), 4.93 (d, *J* = 10.3 Hz, 1H, H-1), 4.48 (q, *J* = 11.7 Hz, 2H, $PHCH_2$), 4.12 – 4.06 (m, 1H, H-5), 3.85 – 3.76 (m, 2H, H-2), 3.68 (d, *J* = 7.7 Hz, 1H), 3.59 (dd, *J* = 10.0, 6.4 Hz, 1H, H-4), 3.51 (dd, *J* = 10.0, 5.8 Hz, 1H, H-3), 2.76 – 2.69 (m, 2H, $CH_3COCH_2CH_2$), 2.59 – 2.52 (m, 2H, $CH_3COCH_2CH_2$), 2.31 (s, 3H, $SPhCH_3$), 2.16 (s, 3H, $CH_3COCH_2CH_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.45, 172.57, 162.38, 138.14, 137.90, 132.86, 129.75, 129.72, 129.09, 128.43, 128.38, 127.94, 127.78, 127.74, 92.54, 86.55, 76.36, 73.50, 70.52, 70.41, 68.60, 54.38, 38.21, 29.89, 28.14, 21.19. HRMS: $C_{27}H_{30}Cl_3NO_7S$ $[M+NH_4]^+$ calcd: 635.1147, obsd: 635.1139.

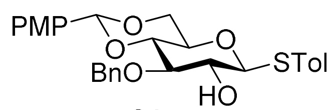
***p*-Tolyl 4,6-*O*-*p*-methoxybenzylidene-1-thio-*β*-D-glucopyranoside S13:**[5,6]



β-D-Glucopyranosyl pentaacetate **S10** (30 g, 68.4 mmol), *p*-toluenethiol (11.05 g, 89 mmol) were dissolved in dry DCM (400 mL) and the solution was cooled to 0 °C. Then boron trifluoride etherate (34.68 mL, 273 mmol) was added dropwise at 0 °C. The mixture was stirred under N_2 at room temperature for 20 h and then diluted with DCM (500 mL). The organic phase was washed with saturated aqueous solution of $NaHCO_3$ until the pH is 7 and then dried over Na_2SO_4, filtered and concentrated. The crude was subjected to silica gel column chromatography (Hexane/EtOAc, 20:1 → 4:1) for purification and afforded thioglycoside **S11** in 85% yield (29.7 g, 65.3 mmol) as a white solid. The thioglycoside **S11** (29 g, 63.8 mmol) was dissolved in MeOH/DCM (3/2) (300 mL), then Na metal was added the mixture was stirred overnight. The mixture was neutralized with Amberlite resin until the pH is around 7 was added to adjust pH around 7. After filtration, the filtrate was concentrated and dried under vacuo to give *p*-tolyl 1-thio-*β*-D-glucopyranoside **S12** in 98% yield (17.9 g, 62.5 mmol) as white solid crude. The mixture of *p*-tolyl 1-thio-*β*-D-glucopyranoside **S12** (29 g, 101.4 mmol), *p*-anisaldehyde dimethylacetal (27.6 mL, 162.2 mmol) and camphorsulfonic acid (11.8 g, 50.7 mmol) in anhydrous DMF (100 mL) was stirred overnight at 60 °C. After the reaction was completed as judged by TLC, the mixture was diluted with EtOAc (200 mL) followed by washing with saturated aqueous solution of $NaHCO_3$, water and then dried over Na_2SO_4, filtered and concentrated. Silica gel column chromatography (Hexane/EtOAc, 10:1 → 3:1) afforded *p*-tolyl 4,6-*O*-*p*-methoxybenzylidene-1-thio-*β*-D-glucopyranoside **S13** in 89% yield (33.8 g, 90.2 mmol) as white solid. Comparison with literature data[4] confirms its identity.



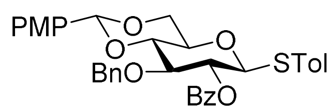
***p*-Tolyl 3-*O*-benzyl-4,6-*O*-*p*-methoxybenzylidene-1-thio-*β*-D-glucopyranoside S14**:



S14

The mixture of dibutyltin oxide (nBu_2SnO) (11.9 g, 47.8 mmol) and diol thioglycoside **S13** (12.9 g, 31.9 mmol) in anhydrous toluene (250 mL) was heated under reflux in a flask equipped with a Dear-Stark apparatus for 3 h. The reaction mixture was cooled down to room temperature and followed by addition of tetrabutylammonium iodide (nBu_4NI) (2.95 g, 7.97 mmol) and BnBr (6.4 mL, 54.2 mmol). The mixture was heated again under reflux for 4h followed by addition of H_2O (3 mL) to quench the reaction after the reaction was completed. Toluene was removed under reduced pressure and the residue was subjected into silica gel column chromatography (Hexane/EtOAc, 12:1 → 5:1) to afford *p*-tolyl 3-*O*-benzyl-4,6-*O*-*p*-methoxybenzylidene-1-thio-*β*-D-glucopyranoside **S14** in 75% yield (12.4 g, 25.8 mmol) as white solid. Comparison with literature data[4] confirms its identity.

***p*-Tolyl 2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-*p*-methoxybenzylidene-1-thio-*β*-D-glucopyranoside 21:**

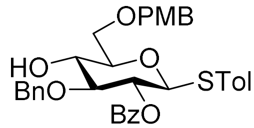


21

p-Tolyl 3-*O*-benzyl-4,6-*O*-*p*-methoxybenzylidene-1-thio-*β*-D-glucopyranoside **S14** (10 g, 20.2 mmol) was dissolved in DCM and treated with benzoyl chloride (5.1 mL, 40.4 mmol), *N*,*N*-dimethylaminopyridine (DMAP) (4.94 g, 40.4 mmol) and stirred for 3h till completion. The reaction was diluted with ethyl acetate and washed with saturated aqueous solution of $NaHCO_3$, water and then dried over Na_2SO_4, filtered and concentrated. *p*-Tolyl 2-*O*-benzoyl-3-

O-benzyl-4,6-*O*-*p*-methoxybenzylidene-1-thio-*β*-D-glucopyranoside **21** was obtained after purification with flash column chromatography (Hexane/EtOAc, 15:1 → 6:1) in 97% yield (12.1 g, 20.3 mmol) as white solid. Comparison with literature data[4] confirms its identity.

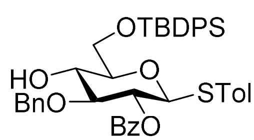
***p*-Tolyl 2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*p*-methoxybenzyl-1-thio-*β*-D-glucopyranoside 7:**



7

Compound **21** (15 g, 25.05 mmol) was dissolved in anhydrous DMF (200 mL) and sodium cyanoborohydride ($NaCNBH_3$)[7] (15.74 g, 250.5 mmol) was added. The mixture was cooled down to 0 °C, then TFA (19.19 mL, 250.5 mmol) was added dropwise over 30 minutes. The resulting suspension solution was stirred for 24 h till the reaction was completed (the solution became clear). The solution was neutralized with Et_3N, diluted with EtOAc, followed by washing with saturated aqueous solution of $NaHCO_3$, water and then dried over Na_2SO_4, filtered and concentrated. The crude was purified with silica gel column chromatography (Hexane/EtOAc, 20:1 → 6:1) to afford *p*-tolyl 2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*p*-methoxybenzyl-1-thio-*β*-D-glucopyranoside **7** in 86% yield (12.9 g, 21.5 mmol) as white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 8.3, 1.2 Hz, 2H, 2 x aromatic CH), 7.60 (t, *J* = 7.4 Hz, 1H, aromatic CH), 7.48 (t, *J* = 7.8 Hz, 2H, 2 x aromatic CH), 7.36 (d, *J* = 8.1 Hz, 2H, 2 x aromatic CH), 7.27 (d, *J* = 8.2 Hz, 2H, 2 x aromatic CH), 7.20 – 7.13 (m, 5H, 2 x aromatic CH), 7.03 (d, *J* = 8.0 Hz, 2H, 2 x aromatic CH), 6.90 (d, *J* = 8.7 Hz, 2H, 2 x aromatic CH), 5.24 (dd, *J* = 9.9, 9.1 Hz, 1H, H-2), 4.71 (m, 10.7 Hz, 3H, H-1, CH_3OPhCH_2), 4.52 (q, *J* = 11.4 Hz, 2H, $PhCH_2$), 3.82 (s, 3H, CH_3OPh), 3.80 – 3.74 (m, 3H, H-4, 2 x H-6), 3.69 (t, *J* = 8.9 Hz, 1H, H-3), 3.56 (dt, *J* = 9.5, 4.8 Hz, 1H, H-5), 2.81 (s, 1H), 2.30 (s, 3H, $SPhCH_3$). ^{13}C NMR (126 MHz, $cdcl_3$) δ 165.19, 159.31, 138.09, 137.84, 133.22, 133.17, 129.88, 129.86, 129.75, 129.72, 129.58, 129.45, 128.90, 128.44, 128.38, 128.25, 128.02, 127.79, 113.84, 86.62, 83.59, 78.21, 74.68, 73.43, 72.10, 72.08, 70.15, 55.30, 21.15. HRMS: $C_{35}H_{36}O_7S$ $[M+NH_4]^+$ calcd: 618.2520, obsd: 618.2529.

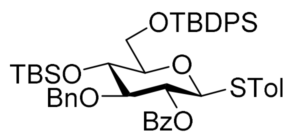
***p*-Tolyl 2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-1-thio-*β*-D-glucopyranoside S16**:



S16

The solution of compound **21** (3.7 g, 6.2 mmol) in 80% aqueous AcOH (50 mL) was stirred at 80 °C for 3 h. Upon completion, the reaction mixture was concentrated and coevaporated with toluene (3x 10 mL), then flash column chromatography afforded the diol **S15** in 93% yield. Diol **S15** (5 g, 10.4 mmol) was dissolved in DCM (40 mL), followed by addition of TBDPSCl (2.98 mL, 11.4 mmol) and DMAP (1.27 g, 10.4 mmol). The reaction mixture was stirred at room temperature. After the reaction was completed as indicated by TLC analysis, the mixture was diluted with DCM and washed with 10% aqueous HCl solution, saturated $NaHCO_3$ and brine. The organic phase was dried over Na_2SO_4, concentered and the residue was purified through silica gel column chromatography (Hexane/EtOAc, 15:1 → 6:1) to afford *p*-tolyl 2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-1-thio-*β*-D-glucopyranoside **S16** as white foaming solid in 97% yield (7.3 g, 10.1 mmol). $[\alpha_D^{20}]$ = +54.6 (C = 0.092, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.3, 1.2 Hz, 2H, 2 x aromatic CH), 7.85 (m, 4H, 4 x aromatic CH), 7.68 – 7.64 (m, 1H, aromatic CH), 7.56 – 7.47 (m, 10H, 10 x aromatic CH), 7.29 – 7.24 (m, 5H, 5 x aromatic CH), 7.09 (d, *J* = 7.9 Hz, 2H, 2 x aromatic CH), 5.37 – 5.33 (m, 1H, H-2), 4.87 (d, *J* = 10.0 Hz, 1H, H-1), 4.79 (q, *J* = 11.4 Hz, 2H, $PhCH_2$), 4.08 (m, 2H, H-4, H-6), 3.94 (t, *J* = 9.2 Hz, 1H, H-6), 3.81 (t, *J* = 9.0 Hz, 1H, H-3), 3.61 (dt, *J* = 9.1, 4.2 Hz, 1H, H-5), 2.80 (br, 1H, OH), 2.37 (s, 3H, $SPhCH_3$), 1.20 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.31, 138.03, 137.93, 135.80, 135.73, 133.34, 133.17, 133.00, 130.05, 129.97, 129.94, 129.69, 129.10, 128.57, 128.52, 128.16, 127.93, 127.92, 86.64, 84.02, 79.60, 74.83, 72.24, 71.23, 64.15, 26.97, 21.27, 19.38. HRMS: $C_{43}H_{46}O_6SSi$ $[M+NH_4]^+$ calcd: 736.3123, obsd: 736.3123.

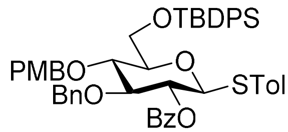
***p*-Tolyl 2-*O*-benzoyl-3-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-6-*O*-*t*-butyldiphenylsilyl-1-thio-*β*-D-glucopyranoside 11:**



11

A solution of compound **S16** (2.073 g, 2.9 mmol) in anhydrous DCM (25 mL) was cooled down to –40 °C followed by sequential addition of 2,6-lutidine (0.672 mL, 5.8 mmol) and TBSOTf (0.993 mL, 4.3 mmol). The resulting solution was warmed up to 0 °C slowly until no starting material was left judged by TLC analysis. The mixture was diluted with DCM (50 mL) and washed with saturated $NaHCO_3$ solution. The organic phase was collected and dried over Na_2SO_4 followed by separation by flash column chromatography (Hexane/EtOAc, 15:1 → 10:1) to afford *p*-tolyl 2-*O*-benzoyl-3-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-6-*O*-*t*-butyldiphenylsilyl-1-thio-*β*-D-glucopyranoside **11** as a white solid in 94% yield (2.2 g, 2.6 mmol). $[\alpha_D^{20}]$ = +53.3 (C = 0.075, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 8.3, 1.2 Hz, 2H, 2 x aromatic CH), 7.78 – 7.75 (m, 4H, 4 x aromatic CH), 7.59 – 7.55 (m, 1H, aromatic CH), 7.45 – 7.35 (m, 11H, 11 x aromatic CH), 7.15 – 7.12 (m, 5H, 5 x aromatic CH), 6.98 (d, *J* = 8.0 Hz, 2H, 2 x aromatic CH), 5.36 – 5.31 (m, 1H, H-2), 4.88 (d, *J* = 10.1 Hz, 1H, H-1), 4.69 – 4.64 (m, 2H, $PhCH_2$), 4.01 (dd, *J* = 11.0, 2.0 Hz, 1H, H-5), 3.79 (dd, *J* = 11.0, 6.8 Hz, 1H, H-6), 3.73 – 3.67 (m, 2H, H-3, H-6), 3.60 – 3.56 (m, 1H, H-4), 2.29 (s, 3H, $SPhCH_3$), 1.13 (s, 9H, $C(CH_3)_3$), 0.79 (s, 9H, $C(CH_3)_3$), -0.05 (s, 3H, $Si(CH_3)_2$), -0.17 (s, 3H, $Si(CH_3)_2$). ^{13}C NMR (126 MHz, $cdcl_3$) δ 165.33, 137.76, 137.29, 135.88, 135.77, 133.53, 133.37, 133.10, 131.71, 130.81, 129.97, 129.81, 129.61, 129.60, 128.35, 128.05, 127.68, 127.65, 127.64, 127.32, 87.37, 84.71, 81.97, 75.21, 73.02, 71.02, 63.87, 31.66, 29.68, 26.97, 25.87, 25.60, 21.12, 19.30, 17.88, -3.81, -4.74. HRMS: $C_{49}H_{60}O_6SSi_2$ $[M+NH_4]^+$ calcd: 850.3987, obsd: 850.3989.

***p*-Tolyl 2-*O*-benzoyl-3-*O*-benzyl-4-*O*-*p*-methoxybenzyl-6-*O*-*t*-butyldiphenylsilyl-1-thio-*β*-D-glucopyranoside 18:**

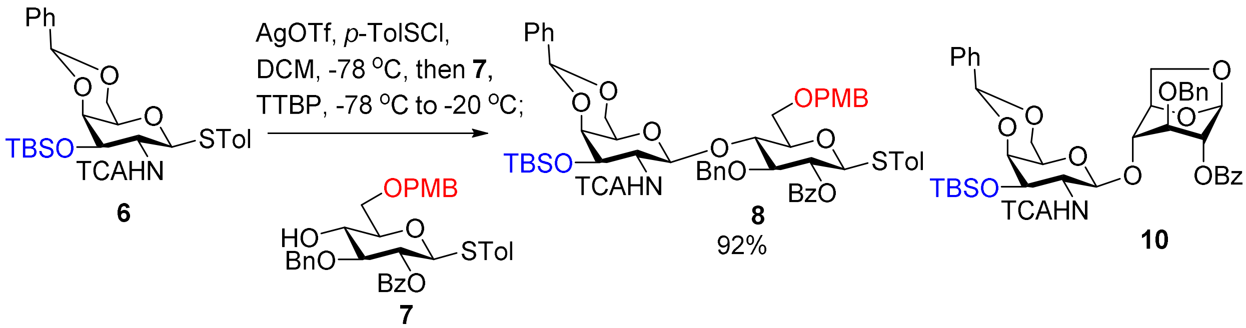


18

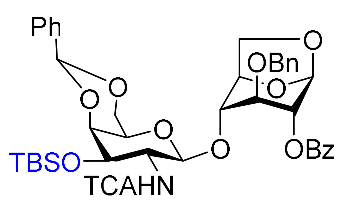
Compound **21** (12 g, 20 mmol) was dissolved in 1M BH_3 solution in THF (226.6 mL, 200 mmol), then treated with 1 M Bu_2BOTf solution in THF (18.9 mL, 24.1 mmol) at 0 °C in the presence of 2,6-lutidine (7 mL, 60 mmol). The reaction mixture was stirred at 0 °C for 10 h, then cooled to -78 °C and quenched with Et_3N, followed by slow addition of cold MeOH. The mixture was slowly warmed to room temperature, the solution was concentrated and subjected to silica gel column chromatography (Hexane/EtOAc, 10:1 → 4:1) to afford *p*-Tolyl 2-*O*-benzoyl-3-*O*-benzyl-4-*O*-*p*-methoxybenzyl-1-thio-*β*-D-glucopyranoside in 69% yield (8.3 g, 13.8 mmol). The resulting product (5.384 g, 9 mmol) was dissolved in DCM (25 mL), followed by addition of TBDPSCl (2.8 mL, 10.8 mmol) and imidazole (1.22 g, 17.9 mmol). The reaction mixture was stirred at room temperature. After the reaction was completed as indicated by TLC analysis, the mixture was diluted with DCM and washed with 10% aqueous HCl solution, saturated $NaHCO_3$ and brine. The organic phase was dried over Na_2SO_4, concentered and the residue was purified through silica gel column chromatography (Hexane/EtOAc, 15:1 → 6:1) to afford **18** as a white solid in 91% yield (6.7 g, 8 mmol)**.** $[\alpha_D^{20}]$ = +90 (C = 0.1, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.2 Hz, 2H, 2 x aromatic CH), 7.84 (m, 4H, 4 x aromatic CH), 7.64 (t, *J* = 7.4 Hz, 1H, aromatic CH), 7.53 – 7.43 (m, 10H, 10 x aromatic CH), 7.23 – 7.17 (m, 5H, 5 x aromatic CH), 7.11 (d, *J* = 8.6 Hz, 2H, 2 x aromatic CH), 7.05 (d, *J* = 8.0 Hz, 2H, 2 x aromatic CH), 6.84 (d, *J* = 8.6 Hz, 2H, 2 x aromatic CH), 5.33 (dd, *J* = 18.7, 9.7 Hz, 1H, H-2), 4.87 – 4.79 (m, 3H, H-1, CH_2PhOCH_3, $PhCH_2$), 4.72 (d, *J* = 11.0 Hz, 1H, $PhCH_2$), 4.66 (d, *J* = 10.3 Hz, 1H, CH_2PhOCH_3), 4.09 (d, *J* = 10.1 Hz, 1H, H-6), 4.01 (dd, *J* = 11.3, 3.9 Hz, 1H, H-5), 3.91 (m, 2H, H-3, H-6), 3.83 (s, 3H, $PhOCH_3$), 3.54 (dd, *J* = 9.3, 2.3 Hz, 1H, H-4), 2.33 (s, 3H, $SPhCH_3$), 1.17 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.25, 159.35, 137.95, 137.79, 136.00, 135.73, 133.54, 133.18, 132.97, 130.15, 130.10, 129.92, 129.76, 129.74, 129.63, 129.20, 128.46, 128.34, 128.15, 127.86, 127.76, 127.75, 113.90, 86.56, 84.54, 80.35, 77.18, 75.51, 74.91, 72.57, 62.66, 55.32, 26.92, 21.21, 19.35. HRMS: $C_{51}H_{54}O_7SSi$ $[M+NH_4]^+$ calcd: 856.3698, obsd: 856.3690.

Synthesis of disaccharides:

***p*-Tolyl 4,6-*O*-benzylidine-3-*O*-*t*-butyldimethylsilyl-2-deoxy-2-*N*-trichloroacetamido-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*p*-methoxybenzyl-1-thio-*β*-D-glucopyranoside 8:**

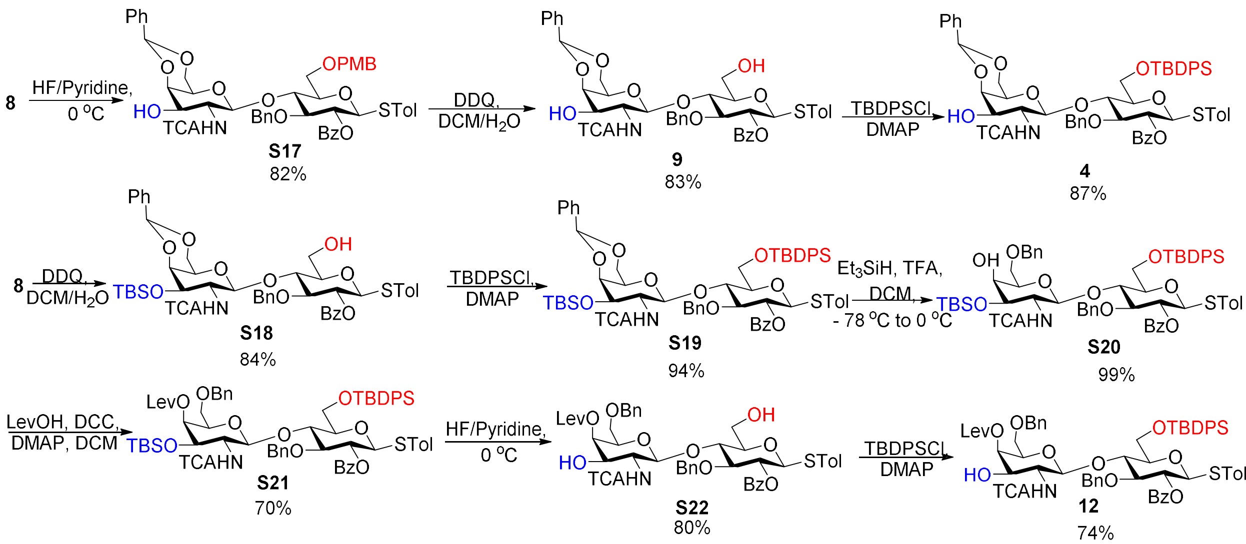


Compound **8** was synthesized from donor **6** and acceptor **7** as a white solid in 92% yield following the general procedure of single step glycosylation. [α_D^{20}] = +33.3 (C = 0.09, DCM). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.99 (d, *J* = 7.1 Hz, 2H, 2 x aromatic CH), 7.58 (t, *J* = 7.4 Hz, 1H, aromatic CH), 7.46 – 7.42 (m, 4H, 4 x aromatic CH), 7.37 (d, *J* = 8.1 Hz, 2H, 2 x aromatic CH), 7.31 (d, *J* = 8.6 Hz, 2H, 2 x aromatic CH), 7.28 – 7.22 (m, 4H, 4 x aromatic CH), 7.06 (d, *J* = 7.2 Hz, 2H, 2 x aromatic CH), 7.01 (d, *J* = 8.0 Hz, 2H, 2 x aromatic CH), 6.97 (t, *J* = 7.4 Hz, 1H, aromatic CH), 6.92 – 6.84 (m, 4H, 4 x aromatic CH), 6.77 (d, *J* = 7.6 Hz, 1H, TCANH), 5.48 (s, 1H, PhCH), 5.21 (t, *J* = 9.5 Hz, 1H,Glc H-2), 5.02 (m, 2H, GalN H-1, GalN H-3), 4.68 (d, *J* = 10.1 Hz, 1H, Glc H-1), 4.61 (dd, *J* = 14.8, 11.6 Hz, 2H, GalN H-4), 4.48 (d, *J* = 11.4 Hz, 1H, GalN H-5), 4.30 (dd, *J* = 10.6, 3.6 Hz, 1H), 4.25 (dd, *J* = 19.6, 10.7 Hz, 2H, Glc H-4, Glc H-6), 4.01 (d, *J* = 3.4 Hz, 1H, GalN H-6), 3.89 (d, *J* = 11.3 Hz, 1H, Glc H-6), 3.83 (d, *J* = 3.0 Hz, 3H, CH_3OPh), 3.78 (dd, *J* = 13.5, 5.7 Hz, 4H, GalN H-2, GalN H-6, Glc H-3, Glc H-5), 3.47 (d, *J* = 9.8 Hz, 1H), 3.10 (s, 1H), 2.28 (s, 3H, $SPhCH_3$), 0.88 (s, 9H, $C(CH_3)_3$), 0.10 (d, *J* = 5.9 Hz, 6H, $Si(CH_3)_2$). ^{13}C NMR (126 MHz, cdcl$_3$) δ 165.09, 161.44, 159.18, 138.45, 138.06, 137.83, 133.53, 132.95, 130.61, 130.10, 129.86, 129.51, 129.48, 128.67, 128.62, 128.28, 128.15, 127.99, 127.81, 126.94, 126.12, 113.64, 100.70, 97.85, 92.52, 86.20, 82.30, 79.16, 75.80, 74.97, 74.77, 72.76, 71.93, 69.30, 68.90, 68.31, 66.37, 57.05, 55.33, 25.69, 25.63, 21.13, 18.07, -4.37, -4.49. HRMS: $C_{56}H_{64}Cl_3NO_{12}SSi$ [M+NH$_4$]$^+$ calcd: 1125.3322, obsd: 1125.3304.

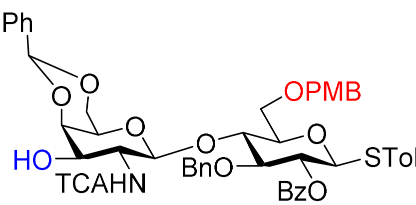


10

[α_D^{20}] = +197.6 (C = 0.658, DCM). ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.05 – 8.00 (m, 2H, 2 x aromatic CH), 7.41 – 7.18 (m, 14H, 14 x aromatic CH), 7.00 (d, *J* = 6.6 Hz, 1H, TCANH), 5.59 (d, *J* = 1.5 Hz, 1H, Glc H-1), 5.40 (s, 1H), 5.21 (d, *J* = 8.3 Hz, 1H, GalN H-1), 4.91 (q, *J* = 1.4 Hz, 1H, Glc H-2), 4.84 (d, *J* = 12.6 Hz, 1H, $PhCH_2$), 4.71 (d, *J* = 12.7 Hz, 1H, $PhCH_2$), 4.64 (dd, *J* = 6.2, 1.5 Hz, 1H, Glc H-4), 4.46 (dd, *J* = 10.5, 3.6 Hz, 1H, GalN H-3), 4.17 (dd, *J* = 7.3, 1.1 Hz, 1H, Glc H-6), 4.07 (t, *J* = 1.6 Hz, 1H, Glc H-3), 3.97 (dd, *J* = 3.7, 1.1 Hz, 1H, GalN H-4), 3.81 – 3.75 (m, 4H, 2 x GalN H-6, Glc H-5, Glc H-6), 3.62 (d, *J* = 8.9 Hz, 1H, GalN H-2), 3.01 (q, *J* = 1.5 Hz, 1H, GalN H-5), 0.88 (s, 9H, $C(CH_3)_3$), 0.08 (d, *J* = 4.5 Hz, 6H, $Si(CH_3)_2$). ^{13}C NMR (126 MHz, CDCl$_3$) δ 166.04, 161.80, 138.15, 137.82, 133.01, 129.88, 129.51, 128.67, 128.65, 128.43, 128.34, 127.97, 127.82, 127.67, 126.02, 100.33, 99.41, 99.03, 92.26, 78.52, 77.27, 77.21, 77.01, 76.76, 75.77, 74.69, 74.49, 71.55, 69.36, 68.91, 68.70, 66.48, 64.91, 57.08, 25.68, 18.06, -4.52, -4.57. HRMS: $C_{41}H_{48}Cl_3NO_{11}Si$ $[M+NH_4]^+$ calcd: 881.2400, obsd: 881.2407.



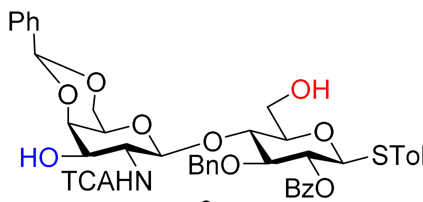
***p*-Tolyl 4,6-*O*-benzylidine-2-deoxy-2-*N*-trichloroacetamido-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*p*-methoxybenzyl-1-thio-*β*-D-glucopyranoside S17:**



S17

Compound **8** (1.163 g, 1.04 mmol) was dissolved in pyridine (8 mL) in a plastic flask followed by addition of 65-70% HF-pyridine (4 mL) under 0 °C. The reaction mixture was stirred overnight until all the starting material was consumed as judged by TLC analysis. The reaction mixture was diluted with EtOAc, washed with 10% HCl, saturated aqueous solution of $NaHCO_3$, water and then dried over Na_2SO_4, filtered and concentrated. Silica gel column purification (Hexane/EtOAc, 8:1 → 3:1) afforded *p*-tolyl 4,6-*O*-benzylidine-2-deoxy-2-*N*-trichloroacetamido-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*p*-methoxybenzyl-1-thio-*β*-D-glucopyranoside **S17** as a white solid in 82% yield (0.86 g, 0.86 mmol). $[\alpha_D^{20}]$ = -93.3 (C = 0.075, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.1 Hz, 2H, 2 x aromatic CH), 7.59 (dd, *J* = 10.6, 4.3 Hz, 1H, aromatic CH), 7.47 – 7.42 (m, 4H, 4 x aromatic CH), 7.37 (d, *J* = 8.1 Hz, 2H, 2 x aromatic CH), 7.32 – 7.25 (m, 6H, 6 x aromatic CH), 7.17 – 7.13 (m, 2H, 2 x aromatic CH), 7.05 (d, *J* = 8.0 Hz, 2H, 2 x aromatic CH), 7.01 (d, *J* = 7.4 Hz, 1H, aromatic CH), 6.96 – 6.91 (m, 4H, 4 x aromatic CH), 6.79 (d, *J* = 8.2 Hz, 1H, TCANH), 5.53 (s, 1H, PhCH), 5.25 – 5.20 (m, 1H, Glc H-2), 5.05 (d, *J* = 11.4 Hz, 1H), 4.69 (d, *J* = 10.1 Hz, 1H, Glc H-1), 4.65 (dd, *J* = 11.5, 6.5 Hz, 2H, $PhCH_2$), 4.59 (d, *J* = 8.3 Hz, 1H, GalN H-1), 4.45 (d, *J* = 11.5 Hz, 1H, CH_2PhOCH_3), 4.22 (d, *J* = 11.9 Hz, 1H, GalN H-6), 4.08 (dd, *J* = 12.2, 6.2 Hz, 2H, GalN H-4, GalN H-5), 3.99 (dt, *J* = 10.7, 8.3 Hz, 1H, GalN H-2), 3.92 (dd, *J* = 12.4, 1.3 Hz, 1H, Glc H-6), 3.84 (s, 3H, CH_3OPh), 3.83 (dd, *J* = 4.3, 2.8 Hz, 1H, Glc H-5), 3.81 – 3.77 (m, 1H, GalN H-5), 3.74 (dd, *J* = 11.2, 2.7 Hz, 1H, Glc H-3), 3.57 – 3.48 (m, 2H, GalN H-3, Glc H-4), 3.18 (s, 1H, GalN H-6), 2.56 (s, 1H), 2.30 (s, 3H, $SPhCH_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.14, 162.61, 159.64, 138.25, 138.24, 137.46, 133.62, 133.08, 130.21, 129.98, 129.88, 129.77, 129.59, 129.20, 128.48, 128.36, 128.21, 127.99, 127.92, 127.17, 126.34, 113.93, 101.23, 99.71, 92.64, 86.40, 81.93, 78.73, 77.40, 75.18, 74.70, 73.39, 71.96, 70.63, 68.71, 68.68, 66.53, 56.17, 55.41, 21.16. HRMS: $C_{50}H_{50}Cl_3NO_{12}S$ $[M+NH_4]^+$ calcd: 1011.2458, obsd: 1011.2452.

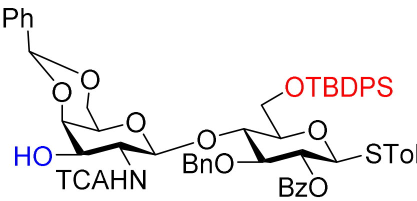
***p*-Tolyl 4,6-*O*-benzylidine-2-deoxy-2-*N*-trichloroacetamido-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-1-thio-*β*-D-glucopyranoside 9:**



9

Compound **S17** (0.9, 0.9 mmol) was dissolved in DCM/H_2O (10:1, 16 mL) followed by addition of DDQ (0.49 g, 2.17 mmol). The reaction mixture was stirred at room temperature and after the reaction was completed (≈5 h), it was quenched with saturated aqueous $NaHCO_3$ solution, diluted with DCM. The organic phase was washed with H_2O until the solution became colorless. The solvent was concentrated *in vacuo* and the residue was purified by silica gel column chromatography (Hexane/EtOAc, 8:1 → 1:2) to afford *p*-tolyl 4,6-*O*-benzylidine-2-deoxy-2-*N*-trichloroacetamido-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-1-thio-*β*-D-glucopyranoside **9** as white solid in 83% yield (0.66 g, 0.75 mmol). $[\alpha_D^{20}]$ = +20 (C = 0.05, DCM). ^1H NMR (500 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.1, 0.9 Hz, 2H, 2 x aromatic CH), 7.63 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H, 2 x aromatic CH), 7.44 (dd, *J* = 7.7, 1.6 Hz, 2H, 2 x aromatic CH), 7.33 – 7.26 (m, 5H, 5 x aromatic CH), 7.10 (dd, *J* = 13.1, 7.6 Hz, 4H, 4 x aromatic CH), 7.03 (t, *J* = 7.4 Hz, 1H, aromatic CH), 6.93 (t, *J* = 7.6 Hz, 2H, 2 x aromatic CH), 5.37 (s, 1H, PhCH), 5.27 – 5.22 (m, 1H, Glc H-2), 5.14 (d, *J* = 11.1 Hz, 1H, $PhCH_2$), 4.83 (d, *J* = 8.3 Hz, 1H, GalN H-1), 4.78 (d, *J* = 10.2 Hz, 1H, Glc H-1), 4.61 (d, *J* = 11.1 Hz, 1H, $PhCH_2$), 4.23 (t, *J* = 9.2 Hz, 1H, Glc H-4), 4.14 (m, 2H, GalN H-2, GalN H-5), 4.00 (d, *J* = 10.9 Hz, 1H, GalN H-3), 3.92 – 3.82 (m, 4H, 2 x GalN H-6, Glc H-3, Glc H-6), 3.60 (dt, *J* = 29.3, 13.3 Hz, 2H, Glc H-6), 3.41 (d, *J* = 9.6 Hz, 1H, Glc H-5), 3.34 (m, 1H, GalN H-4), 2.70 (s, 2H), 2.31 (s, 3H, $SPhCH_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.88, 138.45, 138.32, 137.51, 134.48, 133.50, 132.61, 129.95, 129.84, 129.76, 129.53, 129.15, 129.00, 128.56, 128.19, 128.06, 127.32, 126.32, 101.08, 100.37, 92.86, 87.25, 82.21, 79.37, 75.49, 74.32, 72.30, 69.95, 68.80, 66.36, 61.00, 56.21, 21.13. HRMS: $C_{42}H_{42}Cl_3NO_{11}S$ $[M+NH_4]^+$ calcd: 891.1882, obsd: 891.1860.

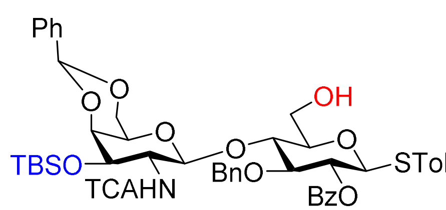
***p*-Tolyl 4,6-*O*-benzylidine-2-deoxy-2-*N*-trichloroacetamido-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-1-thio-*β*-D-glucopyranoside 4:**



4

Compound **9** (2 g, 2.3 mmol) was dissolved in DCM (25 mL) followed by the addition of DMAP (0.42 g, 3.4 mmol) and TBDPSCl (0.654 mL, 2.5 mmol). The resulting mixture was stirred at room temperature until the reaction was completed (≈6 h). The reaction was diluted with DCM, washed with 10% HCl, saturated aqueous $NaHCO_3$ solution and dried over Na_2SO_4. After concentration, column purification (Hexane/EtOAc, 7:1 → 2:1) afforded *p*-tolyl 4,6-*O*-benzylidine-2-deoxy-2-*N*-trichloroacetamido-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-1-thio-*β*-D-glucopyranoside **4** as a white solid in 87% yield (2.2 g, 2 mmol). $[\alpha_D^{20}]$ = -179.96 (C = 0.017, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.3, 1.2 Hz, 2H, 2 x aromatic CH), 7.75 (td, *J* = 8.2, 1.4 Hz, 4H, 4 x aromatic CH), 7.63 – 7.58 (m, 1H, aromatic CH), 7.53 (m, 1H, aromatic CH), 7.51 – 7.45 (m, 5H, 5 x aromatic CH), 7.43 (dd, *J* = 7.7, 6.0 Hz, 6H, 6 x aromatic CH), 7.30 (m, 1H, aromatic CH), 7.26 (m, 3H, 3 x aromatic CH), 7.18 – 7.13 (m, 2H, 2 x aromatic CH), 7.05 – 6.98 (m, 3H, 3 x aromatic CH), 6.95 – 6.89 (m, 2H, 2 x aromatic CH), 6.00 (d, *J* = 8.8 Hz, 1H, TCANH), 5.54 (s, 1H, PhCH), 5.23 – 5.17 (m, 1H, Glc H-2), 5.09 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.69 (dd, *J* = 12.8, 10.8 Hz, 2H, Glc H-1, $PhCH_2$), 4.60 (d, *J* = 8.3 Hz, 1H, GalN H-1), 4.37 (d, *J* = 9.7 Hz, 1H GalN H-3), 4.33 (d, *J* = 4.2 Hz, 1H, Glc H-5), 4.16 – 4.11 (m, 2H, 2 x GalN H-6), 4.02 – 3.94 (m, 2H, GalN H-2, Glc H-6b), 3.86 – 3.80 (m, 2H, Glc H-3), 3.38 – 3.30 (m, 2H, Glc H-4, Glc H-6b), 3.20 (s, 1H), 2.45 (d, *J* = 11.4 Hz, 1H), 2.28 (s, 3H, $SPhCH_3$), 1.12 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.03, 162.16, 138.25, 137.29, 136.02, 135.65, 134.15, 133.78, 132.98, 132.10, 130.36, 130.19, 130.16, 129.89, 129.54, 129.30, 128.65, 128.32, 128.24, 128.13, 127.91, 127.85, 127.16, 126.36, 101.45, 99.69, 92.39, 85.75, 81.86, 79.43, 75.20, 74.97, 74.49, 71.84, 70.25, 68.72, 66.45, 61.81, 55.82, 26.87, 21.16, 19.41. HRMS: $C_{58}H_{60}Cl_3NO_{11}SSi$ $[M+NH_4]^+$ calcd: m/z: 1129.3060, obsd: 1129.3032.

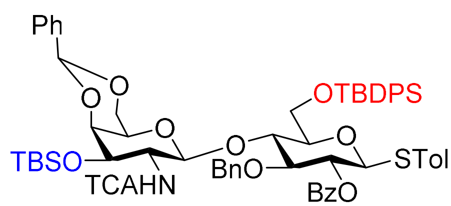
***p*-Tolyl 4,6-*O*-benzylidine-3-*O*-*t*-butyldimethylsilyl-2-deoxy-2-*N*-trichloroacetamido-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-1-thio-*β*-D-glucopyranoside S18:**



S18

Compound **8** (13.27 g, 11.96 mmol) was dissolved in DCM/H_2O (10:1, 55 mL) followed by addition of DDQ (6.52 g, 28.7 mmol). The mixture was stirred at room temperature till all starting material was consumed (4-6 h). The reaction was diluted with DCM (150 mL), quenched with saturated $NaHCO_3$ solution and the organic phase was washed with water till the solution become clear, dried over Na_2SO_4 and concentrated. Silica gel column purification (Hexane/EtOAc, 10:1 → 2:1) afforded compound **S18** as a white solid in 84% yield (9.94 g, 10 mmol). $[\alpha_D^{20}]$ = +236.4 (C = 0.258, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, J = 7.5 Hz, 2H, 2 x aromatic CH), 7.64 (t, J = 7.1 Hz, 1H, aromatic CH), 7.49 (t, J = 7.5 Hz, 4H, 4 x aromatic CH), 7.44 – 7.22 (m, 6H, 6 x aromatic CH), 7.11 (d, J = 7.3 Hz, 3H, 3 x aromatic CH), 7.02 (t, J = 7.1 Hz, 1H, aromatic CH), 6.88 (t, J = 7.2 Hz, 2H, 2 x aromatic CH), 5.39 (s, 1H, PhCH), 5.28 (t, J = 9.6 Hz, 1H, Glc H-2), 5.19 (d, J = 11.4 Hz, 1H, $PhCH_2$), 5.04 (d, J = 8.0 Hz, 1H, GalN H-1), 4.79 (d, J = 10.1 Hz, 1H, $PhCH_2$), 4.67 (d, J = 11.5 Hz, 1H, Glc H-1), 4.33 (dd, J = 22.8, 10.9 Hz, 2H, Glc H-5, Glc H-6), 4.22 (d, J = 9.3 Hz, 1H, GalN H-5), 4.12 – 4.01 (m, 2H, GalN H-2, GalN H-4), 3.93 (dd, J = 26.4, 10.5 Hz, 3H, GalN H-3, GalN H-6, Glc H-3), 3.64 (m, 1H, GalN H-6), 3.45 (m, 2H, Glc H-4, Glc H-6), 2.83 (s, 1H), 2.33 (s, 3H, $SPhCH_3$), 0.89 (s, 9H, $C(CH_3)_3$), 0.05 (s, 3H, $Si(CH_3)_2$), 0.00 (s, 3H, $Si(CH_3)_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.70, 161.88, 138.63, 138.30, 137.93, 133.34, 132.84, 129.97, 129.82, 129.75, 129.15, 128.73, 128.47, 128.00, 127.17, 126.37, 109.99, 100.85, 99.35, 92.82, 87.20, 82.37, 79.62, 75.37, 75.25, 74.22, 72.16, 70.22, 69.07, 66.37, 61.14, 56.50, 25.79, 21.17, 18.21, -4.09, -4.24. ESI-MS: $C_{100}H_{112}Cl_3NO_{17}SSi_3$ $[M+NH_4]^+$ calcd: 1837.6363, obsd: 1837.6073.

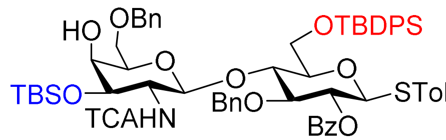
***p*-Tolyl 4,6-*O*-benzylidine-3-*O*-*t*-butyldimethylsilyl-2-deoxy-2-*N*-trichloroacetamido-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-1-thio-*β*-D-glucopyranoside S19:**



S19

Compound **S18** (6.618 g, 6.7 mmol) was dissolved in DCM (25 mL) followed by the addition of TBDPSCl (2.26 mL, 8.7 mmol) and imidazole (0.911 g, 13.4 mmol). The mixture was stirred overnight at room temperature. After reaction completion, it was diluted with DCM, washed with saturated $NaHCO_3$, dried over Na_2SO_4, concentrated and purified with silica gel column (Hexane/EtOAc, 20:1 → 5:1) to afford compound **S19** as a white solid in 94% yield (7.72 g, 6.3 mmol). $[\alpha_D^{20}]$ = +51.6 (C = 1.125, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 7.6 Hz, 2H, 2 x aromatic CH), 7.92 (dd, J = 16.6, 5.8 Hz, 4H, 4 x aromatic CH), 7.65 (t, J = 7.3 Hz, 1H, aromatic CH), 7.62 – 7.46 (m, 12H, 12 x aromatic CH), 7.36 (d, J = 4.6 Hz, 3H, 3 x aromatic CH), 7.20 (d, J = 7.4 Hz, 2H, 2 x aromatic CH), 7.13 – 7.06 (m, 3H, 3 x aromatic CH), 6.99 (t, J = 7.4 Hz, 2H, 2 x aromatic CH), 6.47 (d, J = 7.9 Hz, 1H, TCANH), 5.61 (s, 1H, PhCH), 5.40 (t, J = 9.5 Hz, 1H, Glc H-2), 5.22 (d, J = 11.6 Hz, 1H, $PhCH_2$), 5.13 (d, J = 8.1 Hz, 1H, GalN H-1), 4.86 (d, J = 10.0 Hz, 1H, Glc H-1), 4.79 (d, J = 11.6 Hz, 1H, $PhCH_2$), 4.56 (t, J = 9.1 Hz, 1H, GalN H-3), 4.43 (d, J = 12.2 Hz, 1H, Glc H-4), 4.24 (d, J = 11.5 Hz, 1H, Glc H-6), 4.18 – 3.97 (m, 6H, GalN H-2, GalN H-5, 2 x GalN H-6, Glc H-3, Glc H-6), 3.52 (d, J = 9.4 Hz, 1H, GalN H-4), 3.27 (m, 1H, Glc H-5), 2.37 (s, 3H, $SPhCH_3$), 1.25 (s, 9H, $C(CH_3)_3$), 1.01 (s, 9H, $C(CH_3)_3$), 0.23 (d, J = 2.7 Hz, 6H, $Si(CH_3)_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.24, 161.49, 138.61, 138.13, 137.97, 136.21, 135.85, 134.03, 133.68, 133.13, 132.58, 130.28, 130.13, 129.98, 129.71, 128.86, 128.81, 128.45, 128.35, 128.13, 128.09, 127.98, 127.92, 127.09, 126.31, 100.92, 98.55, 92.51, 86.39, 82.54, 79.92, 75.71, 75.04, 74.24, 72.15, 70.10, 68.99, 66.53, 62.53, 56.56, 26.99, 25.84, 21.30, 19.63, 18.22, -4.05, -4.23. HRMS: $C_{64}H_{74}Cl_3NO_{11}SSi_2$ $[M+NH_4]^+$ calcd: m/z 1243.3925, obsd: 1243.3917.

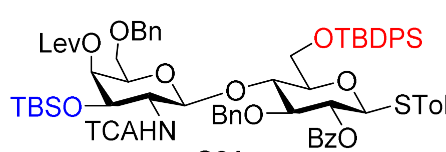
***p*-Tolyl 6-benzyl-3-*O*-*t*-butyldimethylsilyl-2-deoxy-2-*N*-trichloroacetamido-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-1-thio-*β*-D-glucopyranoside S20:**



S20

Compound **S19** (3.3 g, 2.7 mmol) was dissolved in anhydrous DCM (20 mL) and the solution was cooled to -60 °C, followed by addition of Et_3SiH (4.29 mL, 26.9 mmol), then TFA (2.06 mL, 26.9 mmol) was added dropwise. The reaction mixture was stirred at -60 °C to -5 °C for 2 h. After completion, the reaction diluted with DCM and was neutralized with Et_3N till the pH around 7. The solution was washed with saturated aqueous $NaHCO_3$ solution, dried over Na_2SO_4 and concentrated. Silica gel column chromatography (Hexane/EtOAc, 15:1 → 5:1) gave compound **S20** as a white solid in 99% yield (3.3 g, 2.7 mmol). $[\alpha_D^{20}]$ = +74.96 (C = 0.067, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.6 Hz, 2H, 2 x aromatic CH), 7.82 (m, 4H, 4 x aromatic CH), 7.64 (t, *J* = 7.2 Hz, 1H, aromatic CH), 7.48 (m, 10H, 10 x aromatic CH), 7.38 (m, 5H, 5 x aromatic CH), 7.28 – 7.23 (m, 2H, 2 x aromatic CH), 7.10 (m, 5H, 5 x aromatic CH), 6.13 (d, *J* = 9.1 Hz, 1H, TCANH), 5.27 (t, *J* = 9.5 Hz, 1H, Glc H-2), 5.00 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.77 (d, *J* = 10.0 Hz, 1H, Glc H-1), 4.69 (d, *J* = 8.3 Hz, 1H, GalN H-1), 4.63 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.55 – 4.49 (m, 2H, $PhCH_2$), 4.43 (t, *J* = 9.2 Hz, 1H, GalN H-5), 4.16 (d, *J* = 11.4 Hz, 1H, Glc H-4), 3.98 (dd, *J* = 22.0, 12.8 Hz, 2H, GalN H-2, GalN H-4), 3.89 – 3.77 (m, 3H, Glc H-3, Glc H-5), 3.71 – 3.67 (m, 1H, Glc H-6), 3.62 (dd, *J* = 9.3, 5.1 Hz, 1H, GalN H-3), 3.56 – 3.52 (m, 1H, GalN H-6), 3.42 (d, *J* = 9.5 Hz, 1H, GalN H-6), 2.52 (s, 1H), 2.34 (s, 3H, $SPhCH_3$), 1.14 (s, 9H, $C(CH_3)_3$), 0.98 (s, 9H, $C(CH_3)_3$), 0.23 (s, 3H, $Si(CH_3)_2$), 0.19 (s, 3H, $Si(CH_3)_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.09, 161.47, 138.37, 138.21, 138.17, 136.09, 135.85, 133.94, 133.90, 133.08, 132.39, 130.25, 130.13, 130.01, 129.91, 129.63, 128.58, 128.46, 128.43, 128.31, 128.05, 127.98, 127.82, 127.71, 127.30, 98.89, 92.45, 85.98, 82.08, 79.70, 75.18, 73.72, 73.66, 72.80, 72.09, 71.96, 68.21, 68.16, 61.86, 56.07, 26.86, 25.73, 21.25, 19.29, 17.95, -4.12, -4.49. HRMS: $C_{64}H_{76}Cl_3NO_{11}SSi_2$ $[M+NH_4]^+$ calcd: m/z 1245.4081, obsd: 1245.4069.

***p*-Tolyl 6-benzyl-3-*O*-*t*-butyldimethylsilyl-4-*O*-levulinoyl-2-deoxy-2-*N*-trichloroacetamido-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-1-thio-*β*-D-glucopyranoside S21:**

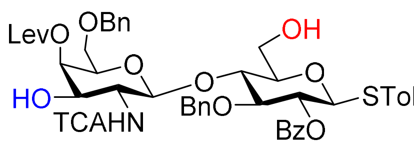


S21

The mixture of compound **S20** (3.384 g, 2.9 mmol), DMAP (1.76 g, 14.4 mmol) and DCC (4.16 g, 20.2 mmol) was dissolved in DCM (40 mL) followed by addition of LevOH (2.66 mL, 26 mmol). The resulting solution was stirred at

50 °C overnight, then the reaction was diluted with DCM, washed with 10% HCl solution, saturated $NaHCO_3$ solution, dried over Na_2SO_4, concentrated and purified with silica gel column (Hexane/EtOAc, 15:1 → 5:1) to afford compound **S21** as a white solid in 70% yield (2.6 g, 1.9 mmol). [α_D^{20}] = +21.02 (C = 0.33, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.3 Hz, 2H, 2 x aromatic CH), 7.78 (m, 4H, 4 x aromatic CH), 7.65 – 7.60 (m, 1H, aromatic CH), 7.54 – 7.41 (m, 10H, 10 x aromatic CH), 7.39 – 7.31 (m, 5H, 5 x aromatic CH), 7.19 (d, *J* = 6.1 Hz, 2H, 2 x aromatic CH), 7.10 (d, *J* = 6.9 Hz, 3H, 3 x aromatic CH), 7.05 (d, *J* = 7.5 Hz, 2H, 2 x aromatic CH), 6.06 (d, *J* = 9.1 Hz, 1H, TCANH), 5.43 (s, 1H, GalN H-4), 5.22 (t, *J* = 9.4 Hz, 1H, Glc H-2), 4.99 (d, *J* = 10.6 Hz, 1H, $PhCH_2$), 4.74 (d, *J* = 9.9 Hz, 1H, Glc H-1), 4.63 (m, 2H, GalN H-1, $PhCH_2$), 4.42 (dd, *J* = 19.5, 10.3 Hz, 3H, GlC H-6a), 4.15 (d, *J* = 11.3 Hz, 1H, Glc H-4), 4.00 – 3.94 (m, 1H, GalN H-2), 3.83 (m, 2H, Glc H-3, Glc H-5), 3.61 (d, *J* = 7.2 Hz, 2H, GalN H-3), 3.54 – 3.37 (m, 3H, GalN H-5, 2 x GalN H-6, Glc H-6b), 2.84 – 2.77 (m, 1H, $CH_3COCH_2CH_2$), 2.67 (m, 1H, $CH_3COCH_2CH_2$), 2.62 – 2.50 (m, 2H, $CH_3COCH_2CH_2$), 2.32 (s, 3H, $SPhCH_3$), 2.12 (s, 3H, $CH_3COCH_2CH_2$), 1.12 (s, 9H, $C(CH_3)_3$), 0.86 (s, 9H, $C(CH_3)_3$), 0.18 (s, 3H, $Si(CH_3)_2$), 0.11 (s, 3H, $Si(CH_3)_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.90, 171.57, 165.02, 161.42, 138.26, 138.21, 137.95, 136.04, 135.78, 135.48, 133.99, 133.81, 133.06, 132.30, 130.22, 130.01, 129.89, 129.61, 128.66, 128.42, 128.37, 128.17, 128.06, 127.82, 127.72, 127.40, 109.99, 99.27, 92.33, 85.87, 81.84, 79.61, 75.06, 73.82, 73.74, 72.14, 71.94, 70.34, 68.97, 67.37, 61.77, 56.42, 53.29, 37.77, 29.78, 27.87, 26.85, 25.92, 25.58, 21.21, 19.27, 17.71, -4.33, -4.62. HRMS: $C_{69}H_{82}Cl_3NO_{13}SSi_2$ $[M+NH_4]^+$ calcd: 1343.4449, obsd: 1343.4418.

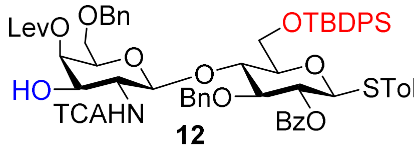
***p*-Tolyl 6-benzyl-4-*O*-levulinoyl-2-deoxy-2-*N*-trichloroacetamido-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-1-thio-*β*-D-glucopyranoside S22:**



S22

Compound **S21** (2.45 g, 1.8 mmol) was dissolved in pyridine (14 mL) in a plastic flask followed by addition of 65-70% HF-pyridine solution (7 mL) at 0 °C and the solution was stirred overnight. Then the reaction mixture was diluted with EtOAc, washed with 10% HCl solution, saturated $NaHCO_3$ solution, dried over Na_2SO_4 and concentrated. Purification with silica gel column (Hexane/EtOAc, 8:1 → 0:1) afforded compound **S22** as white solid in 80% yield (1.4 g, 1.5 mmol). [α_D^{20}] = -60.2 (C = 0.083, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.2 Hz, 2H, 2 x aromatic CH), 7.59 (t, *J* = 7.4 Hz, 1H, aromatic CH), 7.45 (t, *J* = 7.8 Hz, 2H, 2 x aromatic CH), 7.31 (dd, *J* = 14.3, 7.4 Hz, 4H, 4 x aromatic CH), 7.25 (dd, *J* = 12.6, 6.0 Hz, 4H, 3 x aromatic CH, TCANH), 7.14 (d, *J* = 6.8 Hz, 2H, 2 x aromatic CH), 7.09 – 7.02 (m, 5H, 5 x aromatic CH), 5.42 (d, *J* = 2.5 Hz, 1H, GalN H-3), 5.15 (t, *J* = 9.6 Hz, 1H, Glc H-2), 4.91 (d, *J* = 11.0 Hz, 1H, $PhCH_2$), 4.74 (dd, *J* = 11.0, 9.0 Hz, 2H, GalN H-1, Glc H-1), 4.60 (d, *J* = 11.1 Hz, 1H, $PhCH_2$), 4.38 (d, *J* = 11.8 Hz, 1H), 4.26 (d, *J* = 11.8 Hz, 1H), 4.05 – 3.95 (m, 3H, GalN H-4, GalN H-6, Glc H-5), 3.95 – 3.90 (m, 1H, GalN H-2), 3.83 – 3.74 (m, 3H, GalN H-6, Glc H-3, Glc H-6), 3.41 (d, *J* = 9.6 Hz, 1H, GalN H-5), 3.37 (dd, *J* = 9.7, 5.7 Hz, 1H, Glc H-6), 3.31 (dd, *J* = 9.9, 7.4 Hz, 2H, Glc H-4), 2.76 – 2.66 (m, 3H, $CH_3COCH_2CH_2$), 2.56 (dt, *J* = 12.5, 6.1 Hz, 1H, $CH_3COCH_2CH_2$), 2.51 – 2.43 (m, 1H, $CH_3COCH_2CH_2$), 2.29 (s, 3H, $SPhCH_3$), 2.15 (s, 3H, $CH_3COCH_2CH_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.97, 172.47, 165.20, 162.89, 138.35, 138.29, 137.86, 133.19, 133.00, 129.84, 129.77, 129.74, 128.62, 128.40, 128.37, 127.96, 127.89, 127.88, 127.64, 127.31, 100.31, 92.59, 86.58, 81.37, 79.13, 77.27, 77.02, 76.77, 75.93, 74.74, 73.47, 72.33, 71.99, 70.40, 69.93, 67.60, 61.52, 56.46, 38.27, 29.74, 28.01, 21.14. HRMS: $C_{47}H_{50}Cl_3NO_{13}S$ $[M+NH_4]^+$ calcd: 991.2407, obsd: 991.2411.

***p*-Tolyl 6-benzyl-4-*O*-levulinoyl-2-deoxy-2-*N*-trichloroacetamido-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-t-butyldiphenylsilyl-1-thio-*β*-D-glucopyranoside 12:**

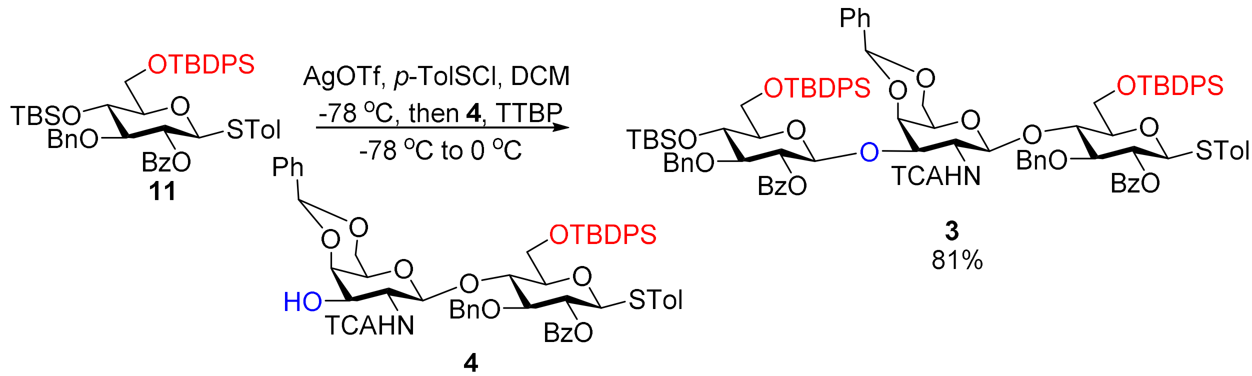


12

Compound **S22** (1.312, 1.35 mmol) was dissolved in DCM (15 mL), followed by addition of DMAP (0.328, 2.7 mmol) and TBDPSCl (0.385 mL, 1.48 mmol). The mixture was stirred at room temperature for 6 h till completion. The reaction was diluted with DCM, washed with10% HCl solution, saturated $NaHCO_3$ solution, dried over Na_2SO_4 and concentrated. Purification with silica gel column (Hexane/EtOAc, 10:1 → 3:1) afforded compound **12** as a white solid in 74% yield (1.2 g, 1 mmol). $[\alpha_D^{20}]$ = -150.2 (C = 0.033, DCM). ^1H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.2 Hz, 2H, 2 x aromatic CH), 7.75 – 7.70 (m, 4H, 4 x aromatic CH), 7.61 (t, *J* = 7.4 Hz, 1H, 2 x aromatic CH), 7.53 – 7.40 (m, 11H, 11 x aromatic CH), 7.37 – 7.33 (m, 2H, 2 x aromatic CH), 7.31 – 7.27 (m, 3H, 3 x aromatic CH), 7.14 (d, *J* = 7.1 Hz, 2H, 2 x aromatic CH), 7.07 (d, *J* = 7.4 Hz, 1H, aromatic CH), 7.05 – 6.99 (m, 4H, 4 x aromatic CH), 5.94 (d, *J* = 8.8 Hz, 1H, TCANH), 5.45 (d, *J* = 3.0 Hz, 1H, Glc H-6), 5.17 (t, *J* = 9.6 Hz, 1H, Glc H-2), 4.90 (d, *J* = 10.7 Hz, 1H, $PhCH_2$), 4.69 (d, *J* = 10.0 Hz, 1H, Glc H-1), 4.56 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.47 (d, *J* = 2.1 Hz, 1H), 4.45 (m, 1H, GalN H-1), 4.35 – 4.29 (m, 2H, GalN H-6, Glc H-4), 4.12 (d, *J* = 10.9 Hz, 1H), 3.85 – 3.81 (m, 1H, Glc H-3), 3.80 – 3.75 (m, 2H, GalN H-2, GalN H-6), 3.57 (dd, *J* = 7.8, 5.6 Hz, 1H, GalN H-4), 3.43 (dd, *J* = 9.3, 5.2 Hz, 1H, Glc H-6), 3.39 – 3.33 (m, 3H, GalN H-3, GalN H-5,Glc H-5), 2.93 (d, *J* = 8.7 Hz, 1H), 2.71 (dd, *J* = 11.6, 5.1 Hz, 2H, $CH_3COCH_2CH_2$), 2.47 (dd, *J* = 11.1, 6.1 Hz, 2H, $CH_3COCH_2CH_2$), 2.30 (s, 3H, $SPhCH_3$), 2.13 (s, 3H), 1.09 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.95, 172.37, 164.95, 162.19, 138.30, 138.26, 137.83, 136.00, 135.72, 134.24, 133.64, 133.03, 132.14, 130.37, 130.14, 130.09, 129.84, 129.56, 128.40, 128.38, 128.28, 128.19, 127.98, 127.91, 127.85, 127.72, 127.68, 127.34, 99.70, 92.43, 85.59, 81.72, 79.45, 74.98, 74.06, 73.56, 72.08, 71.83, 70.52, 69.45, 67.01, 61.47, 56.04, 38.36, 29.68, 28.07, 26.78, 21.19, 19.22. HRMS: $C_{63}H_{68}Cl_3NO_{13}SSi$ $[M+NH_4]^+$ calcd: m/z 1229.3584, obsd: 1229.3540.

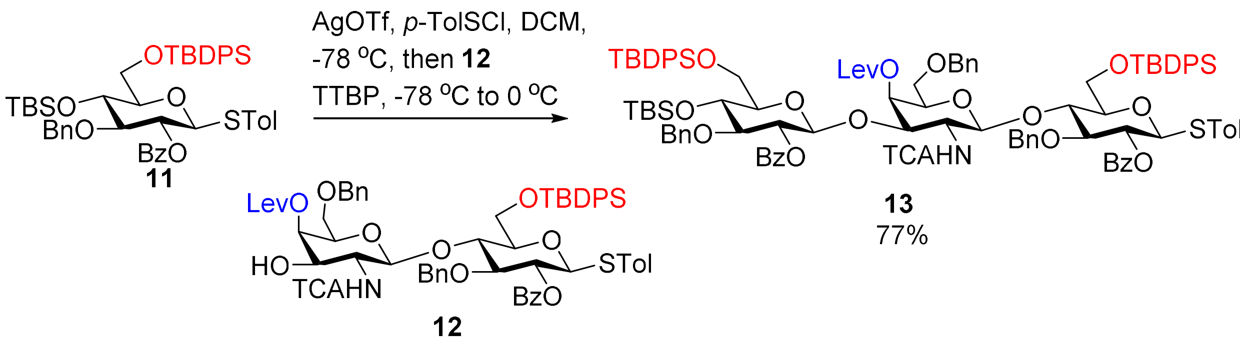
Synthesis of trisaccharides:

***p*-Tolyl 2-*O*-benzoyl-3-*O*-benzyl-4-*O*-t-butyldimethylsilyl-6-*O*-t-butyldiphenylsilyl-*β*-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidine-2-deoxy-2-*N*-trichloroacetamido-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-t-butyldiphenylsilyl-1-thio-*β*-D-glucopyranoside 3:**



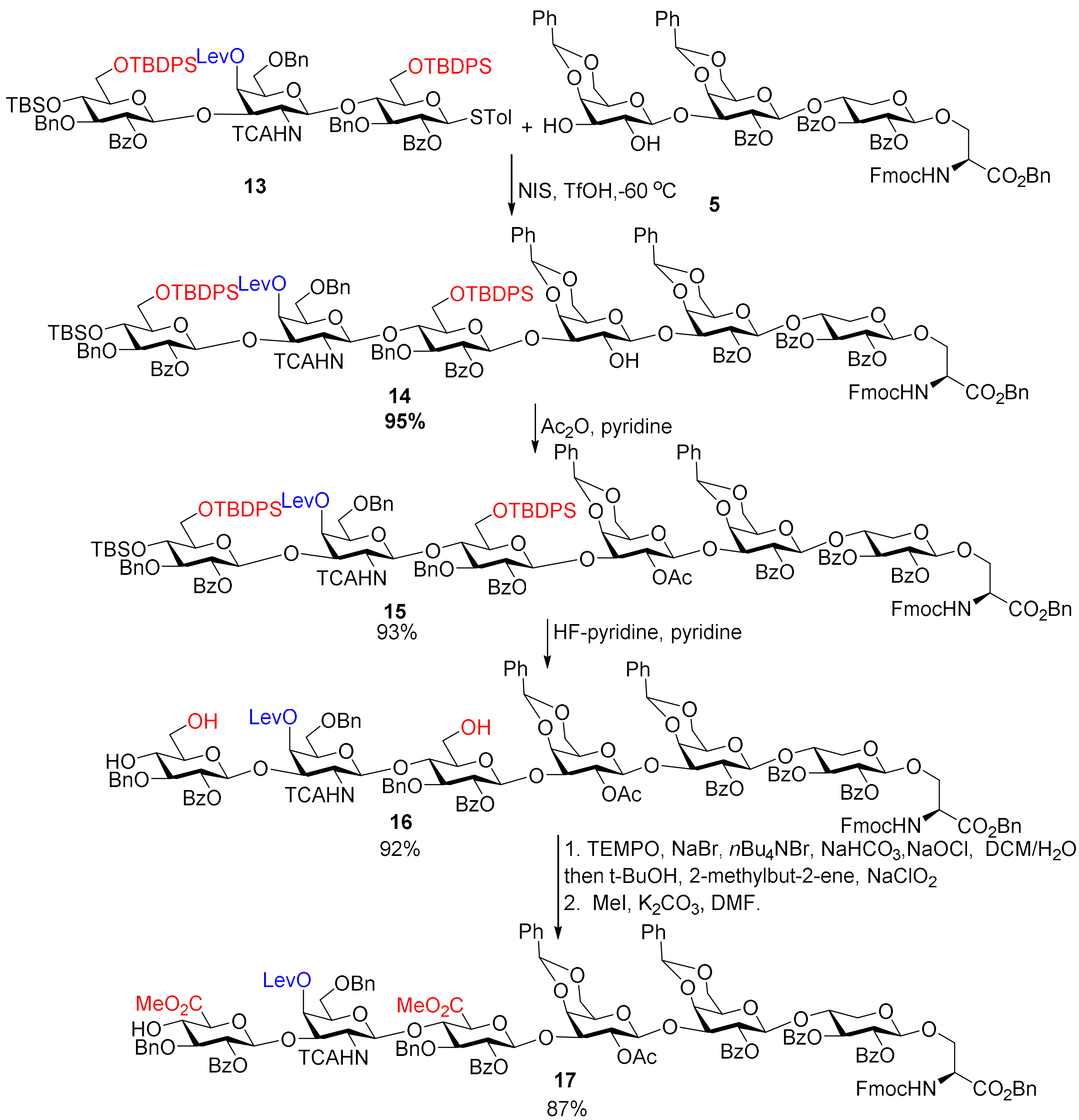
The trisaccharide **3** was synthesized from donor **11** and acceptor **4** in 81% yield following the general procedure of single step glycosylation. $[\alpha_D^{20}]$ = +103.4 (C = 0.058, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 11.8, 4.2 Hz, 4H, 4 x aromatic CH), 7.76 – 7.66 (m, 9H, 9 x aromatic CH), 7.59 – 7.49 (m, 5H, 5 x aromatic CH), 7.45 – 7.41 (m, 5H, 5 x aromatic CH), 7.38 – 7.34 (m, 8H, 8 x aromatic CH), 7.31 (dd, *J* = 7.4, 4.6 Hz, 6H, 6 x aromatic CH), 7.11 – 7.05 (m, 6H, 6 x aromatic CH), 6.97 (t, *J* = 7.7 Hz, 4H, 4 x aromatic CH), 6.82 (t, *J* = 7.5 Hz, 2H, 2 x aromatic CH), 6.38 (d, *J* = 6.9 Hz, 1H, TCANH), 5.42 (s, 1H, PhCH), 5.36 – 5.32 (m, 1H, H-2a), 5.23 (dd, *J* = 13.5, 5.5 Hz, 2H, H-1b, H-2c), 4.94 (m, 2H, H-1a, $PhCH_2$), 4.70 (d, *J* = 10.1 Hz, 1H, H-1c), 4.61 (d, *J* = 5.2 Hz, 2H, $PhCH_2$), 4.53 – 4.51 (m, 1H, $PhCH_2$), 4.44 – 4.39 (m, 2H, H-3b, H-6c), 4.28 – 4.23 (m, 1H, H-6b), 4.09 (d, *J* = 11.7 Hz, 1H, H-4a), 4.02 (dd, *J* = 10.8, 2.2 Hz, 1H, H-4c), 3.96 – 3.88 (m, 3H, H-4b, H-6b, H-6a), 3.72 (dd, *J* = 10.8, 8.1 Hz, 2H, H-5a), 3.58 (dd, *J* = 9.5, 5.7 Hz, 3H, H-3c, H-6c, H-3a), 3.54 – 3.49 (m, 1H, H-2b), 3.35 (dd, *J* = 9.7, 2.2 Hz, 1H, H-5b), 3.06 (m, 1H, H-5c), 2.27 (s, 3H, $SPhCH_3$), 1.07 (s, 9H, $C(CH_3)_3$), 1.03 (s, 9H, $C(CH_3)_3$), 0.70 (s, 9H, $C(CH_3)_3$), -0.15 (s, 3H, $Si(CH_3)_2$), -0.30 (s, 3H, $Si(CH_3)_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.11, 165.07, 161.64, 138.38, 138.12, 137.76, 137.65, 135.98, 135.75, 135.50, 135.49, 133.62, 133.19, 133.13, 133.06, 133.00, 132.96, 132.88, 132.76, 130.08, 129.98, 129.91, 129.83, 129.81, 129.70, 129.67, 129.58, 129.53, 128.53, 128.37, 128.34, 128.28, 127.99, 127.95, 127.90, 127.83, 127.80, 127.71, 127.65, 127.33, 127.23, 126.87, 126.17, 101.39, 100.18, 97.28, 91.90, 86.73, 83.19, 82.82, 79.95, 77.82, 75.63, 74.70, 74.54, 74.16, 74.08, 72.27, 71.38, 69.21, 68.46, 66.52, 64.62, 64.01, 62.96, 55.91, 29.71, 26.95, 26.78, 25.78, 21.11, 19.44, 19.28, 17.75, 14.15, -4.03, -4.69. ESI-MS: $C_{100}H_{112}Cl_3NO_{17}SSi_3$ $[M+NH_4]^+$ calcd: 1837.6363, obsd: 1837.6099.

***p*-Tolyl 2-*O*-benzoyl-3-*O*-benzyl-4-*O*-t-butyldimethylsilyl-6-*O*-*t*-butyldiphenylsilyl-*β*-D-glucopyranosyl-(1→3)-6-*O*-benzyl-4-*O*-levulinoyl-2-deoxy-2-*N*-trichloroacetamido-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-t-butyldiphenylsilyl-1-thio-*β*-D-glucopyranoside 13:**

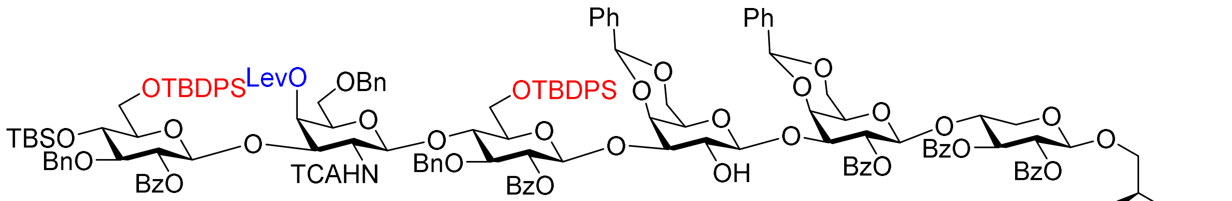


Compounds **13** were synthesized from donor **11** and acceptors **12** in 77% yield, following the general procedure of single step glycosylation. [α_D^{20}] = +83.1 (C = 0.12, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 8.2, 1.1 Hz, 2H, 2 x aromatic CH), 7.96 – 7.91 (m, 2H, 2 x aromatic CH), 7.79 – 7.71 (m, 8H, 8 x aromatic CH), 7.60 (dd, *J* = 11.7, 4.3 Hz, 1H, aromatic CH), 7.53 (t, *J* = 7.4 Hz, 1H, aromatic CH), 7.50 – 7.37 (m, 18H, 18 x aromatic CH), 7.29 – 7.20 (m, 5H, 5 x aromatic CH), 7.16 – 7.10 (m, 5H, 5 x aromatic CH), 7.10 – 7.00 (m, 7H, 7 x aromatic CH), 5.76 – 5.74 (m, 1H, TCANH), 5.22 – 5.17 (m, 2H, H-2a, H-2c), 4.88 (d, *J* = 10.6 Hz, 1H, $PhCH_2$), 4.74 – 4.66 (m, 3H, H-1a, H-1b, H-1c), 4.63 (d, *J* = 11.5 Hz, 2H, $PhCH_2$), 4.50 (d, *J* = 10.6 Hz, 1H, $PhCH_2$), 4.35 (d, *J* = 12.0 Hz, 1H, H-6c), 4.31 – 4.23 (m, 2H, H-6b, H-5c), 4.17 (dd, *J* = 10.8, 3.4 Hz, 1H, H-4c), 4.02 – 3.96 (m, 2H, H-3b, H-4a), 3.83 (dd, *J* = 10.8, 7.8 Hz, 1H, H-4b), 3.66 (m, 8H, H-2b, H-6b, H-3c, H-3a, H-5a, H-6a), 3.41 (m, 2H, H-5b), 3.31 (d, *J* = 9.5 Hz, 1H, H-6c), 3.02 – 2.95 (m, 1H), 2.84 – 2.61 (m, 4H, $CH_3COCH_2CH_2$), 2.31 (s, 3H, $SPhCH_3$), 2.20 (s, 3H, $CH_3COCH_2CH_2$), 1.05 (d, *J* = 7.3 Hz, 18H, 2 x $C(CH_3)_3$), 0.78 (s, 9H, $C(CH_3)_3$), -0.07 (s, 3H, $Si(CH_3)_2$), -0.25 (s, 3H, $Si(CH_3)_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.81, 171.58, 165.07, 165.00, 161.01, 138.21, 138.17, 138.09, 137.66, 136.02, 135.96, 135.71, 135.65, 133.81, 133.71, 133.39, 133.03, 132.85, 132.47, 130.16, 129.93, 129.87, 129.83, 129.75, 129.73, 129.69, 129.54, 128.38, 128.35, 128.23, 128.19, 128.16, 128.04, 127.98, 127.93, 127.88, 127.84, 127.80, 127.47, 127.35, 127.33, 100.63, 98.23, 92.45, 85.90, 82.82, 81.93, 79.54, 78.11, 74.85, 74.75, 74.07, 73.63, 73.41, 72.93, 72.75, 71.95, 71.60, 69.44, 67.76, 64.33, 61.85, 56.00, 38.28, 29.84, 27.99, 26.84, 26.80, 25.89, 21.18, 19.19, 19.17, 17.89, -3.79, -4.70. HRMS: $C_{105}H_{120}Cl_3NO_{19}SSi_3$ $[M+2NH_4]^{2+}$ calcd: 1937.6887, obsd: 1937.6815. HRMS: $C_{105}H_{120}Cl_3NO_{19}SSi_3$ $[M+NH_4]^+$ calcd: m/z 1937.6887, obsd: 1937.6927.

Synthesis of Hexasaccharide 17:



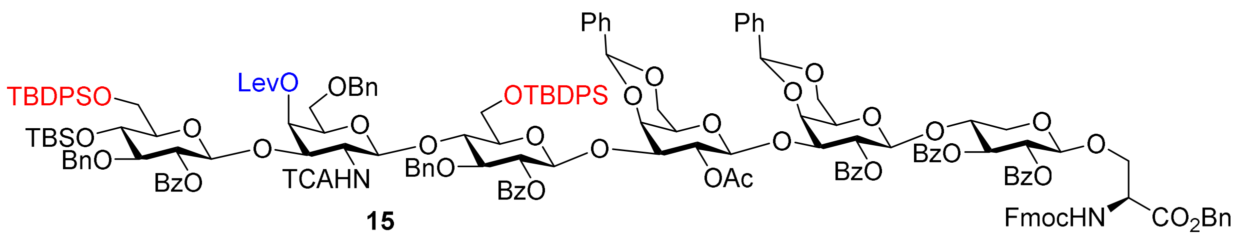
***N*-Fluorenylmethyloxycarbonyl-*O*-[2-*O*-benzoyl-3-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-6-*O*-*t*-butyldiphenylsilyl-*β*-D-glucopyranosyl-(1→3)-6-*O*-benzyl-4-*O*-levulinoyl-2-deoxy-2-*N*-trichloroacetamido-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-*β*-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-*β*-D-galactopyranosyl-(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 14:**



14

Trisaccharide acceptor **5**[8] (0.273g, 0.2 mmol) and trisaccharide donor **13** (0.5 g, 0.26 mmol) were dissolved in anhydrous DCM (10 mL) followed by addition of freshly activated MS. The mixture was stirred at room temperature for 1 h then cooled to -60 °C. NIS (0.076 g, 0.34 mmol) was added followed by the addition of TfOH (8.05 µL, 91 µmol). The reaction was stirred for 2 h from -60 °C to room temperature. After the reaction was completed, the mixture was diluted with DCM, neutralized with DIPEA, filtered through Celite, washed with saturated $NaHCO_3$, brine, dried over Na_2SO_4, concentrated and purified with silica gel column chromatography (toluene/acetone, 30:1 → 3:1) to give hexasaccharide **14** as a colorless oil in 95% yield (0.6 g, 0.19 mmol). [α_D^{20}] = +285.7 (C = 0.005, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.9 Hz, 4H, 4 x aromatic CH), 7.95 – 7.92 (m, 4H, 4 x aromatic CH), 7.92 – 7.90 (m, 2H, 2 x aromatic CH), 7.78 (dd, *J* = 7.5, 3.5 Hz, 2H, 2 x aromatic CH), 7.70 – 7.66 (m, 4H, 4 x aromatic CH), 7.61 (d, *J* = 7.1 Hz, 4H, 4 x aromatic CH), 7.56 – 7.50 (m, 4H, 4 x aromatic CH), 7.49 – 7.45 (m, 3H, 3 x aromatic CH), 7.39 (dd, *J* = 11.2, 4.5 Hz, 7H, 7 x aromatic CH), 7.37 – 7.34 (m, 12H, 12 x aromatic CH), 7.33 (m, 3H, 3 x aromatic CH), 7.28 (m, 8H, 8 x aromatic CH), 7.23 (m, 10H, 10 x aromatic CH), 7.20 (dd, *J* = 5.9, 2.7 Hz, 3H, 3 x aromatic CH), 7.18 – 7.15 (m, 4H, 4 x aromatic CH), 7.10 (dd, *J* = 6.3, 2.7 Hz, 4H, 4 x aromatic CH), 7.05 (dd, *J* = 6.6, 3.0 Hz, 3H, 3 x aromatic CH), 7.02 (dd, *J* = 5.1, 1.7 Hz, 2H, 2 x aromatic CH), 6.03 (d, *J* = 8.0 Hz, 1H, TCANH), 5.67 (d, *J* = 3.4 Hz, 1H), 5.63 – 5.55 (m, 3H), 5.50 (dd, *J* = 10.0, 8.2 Hz, 2H), 5.34 (d, *J* = 5.5 Hz, 2H, 2 x PhCH), 5.18 – 5.11 (m, 4H, GalN H-3), 5.10 – 5.03 (m, 3H, $COOCH_2Ph$), 4.84 (dd, 2H, GalN H-1, H-1), 4.79 (d, *J* = 11.0 Hz, 1H), 4.74 (d, *J* = 7.9 Hz, 1H, H-1), 4.67 (d, *J* = 7.7 Hz, 1H, H-1), 4.60 – 4.57 (m, 3H, H-1, $PhCH_2$), 4.51 (d, *J* = 8.5 Hz, 1H), 4.48 (d, *J* = 11.0 Hz, 1H), 4.34 (d, *J* = 3.1 Hz, 1H), 4.33 – 4.29 (m, 2H), 4.25 (dd, *J* = 9.8, 7.0 Hz, 3H), 4.20 (m, 2H, H-1), 4.15 (dd, *J* = 11.7, 6.4 Hz, 3H), 4.08 (d, *J* = 12.0 Hz, 1H), 3.94 (d, *J* = 3.7 Hz, 4H, GalN H-6), 3.85 (d, *J* = 12.0 Hz, 1H), 3.77 (d, *J* = 5.8 Hz, 3H, GalN H-5, GalN H-6), 3.75 (s, 1H), 3.68 (d, *J* = 13.0 Hz, 3H, GalN H-4), 3.64 (d, *J* = 9.0 Hz, 1H), 3.58 (t, *J* = 6.3 Hz, 1H), 3.54 (t, *J* = 6.3 Hz, 3H), 3.51 – 3.47 (m, 2H, GalN H-2), 3.36 (d, *J* = 6.1 Hz, 2H), 3.18 (s, 1H), 3.10 (s, 1H), 2.94 (dd, *J* = 14.5, 11.4 Hz, 2H), 2.81 – 2.73 (m, 2H), 2.62 (m, 4H, $CH_3COCH_2CH_2$), 2.17 (s, 3H, $CH_3COCH_2CH_2$), 0.97 (s, 9H, $C(CH_3)_3$), 0.96 (s, 9H, $C(CH_3)_3$), 0.74 (s, 9H, $C(CH_3)_3$), -0.11 (s, 3H, $Si(CH_3)_2$), -0.28 (s, 3H, $Si(CH_3)_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.79, 171.60, 169.52, 165.58, 165.33, 165.19, 165.14, 165.04, 161.15, 155.96, 143.87, 143.72, 141.30, 141.27, 138.37, 138.18, 137.89, 137.76, 137.70, 137.60, 135.93, 135.74, 135.68, 135.63, 135.18, 133.79, 133.47, 133.23, 133.17, 133.00, 130.29, 130.01, 129.97, 129.82, 129.76, 129.70, 129.53, 129.15, 129.08, 128.84, 128.54, 128.45, 128.39, 128.32, 128.27, 128.20, 128.07, 128.00, 127.94, 127.90, 127.85, 127.77, 127.70, 127.52, 127.36, 127.25, 127.16, 127.14, 126.70, 125.97, 125.34, 125.23, 120.04, 103.77, 102.09, 101.05, 100.65, 100.55, 100.20, 97.69, 92.44, 82.87, 80.47, 78.12, 76.58, 75.63, 75.49, 74.91, 74.23, 74.03, 73.94, 73.40, 73.23, 72.77, 72.28, 71.62, 71.35, 70.80, 69.90, 69.14, 67.96, 67.36, 67.26, 67.06, 66.93, 62.34, 56.71, 54.31, 47.12, 38.31, 29.87, 28.02, 27.12, 26.87, 26.76, 26.10, 25.89, 21.53, 19.35, 19.17, 17.89, -3.80, -4.67. HRMS: $C_{175}H_{183}Cl_3N_2O_{41}Si_3$ $[M+2NH_4]^{2+}$ calcd: m/z 1597.0690, obsd: 1597.1101.

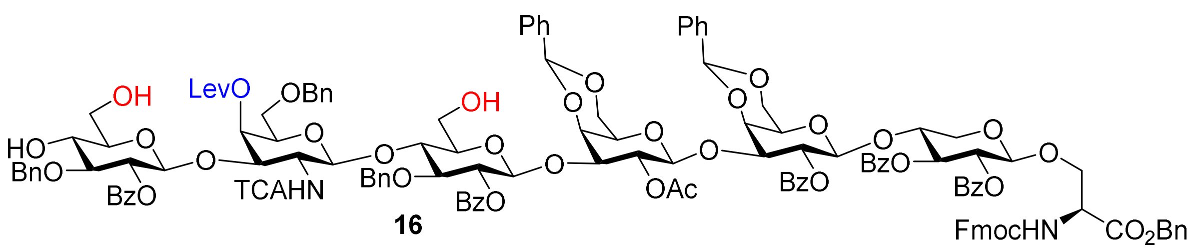
***N*-Fluorenylmethyloxycarbonyl-*O*-[2-*O*-benzoyl-3-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-6-*O*-*t*-butyldiphenylsilyl-*β*-D-glucopyranosyl-(1→3)-6-*O*-benzyl-4-*O*-levulinoyl-2-deoxy-2-*N*-trichloroacetamido-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*t*-butyldiphenylsilyl-*β*-D-glucopyranosyl-(1→3)-2-*O*-acetyl-4,6-*O*-benzylidene-*β*-D-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 15:**



15

Hexasaccharide **14** (0.6 g, 0.19 mmol) was dissolved in pyridine (7 mL) followed by addition of Ac_2O (4 mL). The reaction mixture was stirred overnight, then diluted with EtOAc, washed with 10% HCl solution, saturated $NaHCO_3$ solution, dried over Na_2SO_4 and concentrated. The crude was purified with silica gel column chromatography (Toluene/Acetone, 30:1 → 3:1) to afford compound **15** in 92% yield (0.56 g, 0.17 mmol). $[\alpha_D^{20}]$ = +48.01 (C = 0.042, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.7 Hz, 2H, 2 x aromatic CH), 7.96 (d, *J* = 8.2 Hz, 4H, 4 x aromatic CH), 7.92 – 7.88 (m, 4H, 4 x aromatic CH), 7.78 (dd, *J* = 7.4, 3.6 Hz, 2H, 2 x aromatic CH), 7.71 – 7.67 (m, 4H, 4 x aromatic CH), 7.59 (d, *J* = 6.6 Hz, 4H, 4 x aromatic CH), 7.55 (m, 3H, 3 x aromatic CH), 7.53 – 7.50 (m, 2H, 2 x aromatic CH), 7.49 – 7.45 (m, 2H, 2 x aromatic CH), 7.43 – 7.39 (m, 7H, 7 x aromatic CH), 7.38 (dd, *J* = 4.7, 2.3 Hz, 8H, 8 x aromatic CH), 7.35 (d, *J* = 7.6 Hz, 8H, 8 x aromatic CH), 7.32 – 7.28 (m, 7H, 7 x aromatic CH), 7.26 – 7.24 (m, 2H, 2 x aromatic CH), 7.24 – 7.20 (m, 10H, 10 x aromatic CH), 7.16 (dd, *J* = 9.7, 4.5 Hz, 4H, 4 x aromatic CH), 7.10 (m, 3H, 3 x aromatic CH), 7.06 – 7.03 (m, 4H, 4 x aromatic CH), 7.02 – 6.99 (m, 3H, 3 x aromatic CH), 5.78 (d, *J* = 8.4 Hz, 1H, TCANH), 5.63 – 5.61 (m, 1H), 5.60 – 5.55 (m, 2H), 5.46 – 5.42 (m, 1H, GalN H-4), 5.33 (s, 1H, PHCH), 5.30 (s, 1H, PhCH), 5.17 – 5.13 (m, 3H), 5.11 – 5.07 (m, 2H, $COOCH_2Ph$), 5.03 (d, *J* = 12.2 Hz, 1H), 4.77 (d, *J* = 10.9 Hz, 1H), 4.69 (d, *J* = 7.8 Hz, 1H, H-1), 4.65 (dd, *J* = 11.4, 8.0 Hz, 2H, GalN H-1, H-1), 4.59 (d, *J* = 10.2 Hz, 2H, GalN H-5), 4.57 – 4.54 (m, 2H, 2 x H-1), 4.53 – 4.50 (m, 1H, H-1), 4.46 (d, *J* = 10.9 Hz, 1H), 4.33 (d, *J* = 3.3 Hz, 1H), 4.30 (d, *J* = 14.7 Hz, 1H), 4.24 (m, 3H), 4.20 – 4.17 (m, 2H), 4.15 (d, *J* = 7.2 Hz, 2H, GalN H-3), 4.10 (dd, *J* = 10.9, 3.4 Hz, 1H), 4.03 – 4.00 (m, 1H), 3.98 – 3.94 (m, 2H), 3.92 – 3.89 (m, 1H), 3.87 (d, *J* = 10.3 Hz, 1H), 3.77 – 3.74 (m, 2H), 3.73 – 3.68 (m, 5H), 3.57 – 3.55 (m, 2H, GalN H-2), 3.54 – 3.48 (m, 4H), 3.37 – 3.34 (m, 1H), 3.30 (d, *J* = 6.1 Hz, 2H), 3.26 (d, *J* = 4.2 Hz, 1H), 3.09 (s, 1H), 3.02 – 2.91 (m, 3H), 2.78 (dd, *J* = 6.9, 5.9 Hz, 1H), 2.66 – 2.53 (m, 4H, $CH_3COCH_2CH_2$), 2.18 (s, 3H, $CH_3COCH_2CH_2$), 1.27 (s, 3H, CH_3CO), 1.01 (s, 9H, $C(CH_3)_3$), 1.00 (s, 9H, $C(CH_3)_3$), 0.74 (s, 9H, $C(CH_3)_3$), -0.11 (s, 3H, $Si(CH_3)_2$), -0.28 (s, 3H, $Si(CH_3)_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.79, 176.93, 171.54, 169.47, 168.81, 165.54, 165.07, 164.99, 164.75, 164.57, 161.02, 155.93, 143.84, 143.69, 141.24, 141.22, 138.04, 138.03, 137.80, 137.63, 137.61, 135.69, 135.67, 135.60, 135.57, 135.13, 133.56, 133.32, 133.14, 133.10, 133.01, 132.97, 132.90, 132.83, 130.13, 130.04, 129.96, 129.93, 129.83, 129.79, 129.75, 129.69, 129.67, 129.63, 129.53, 129.13, 129.04, 128.73, 128.49, 128.45, 128.40, 128.37, 128.34, 128.28, 128.23, 128.17, 128.10, 128.06, 128.02, 127.95, 127.87, 127.82, 127.75, 127.70, 127.45, 127.39, 127.33, 127.22, 127.11, 127.09, 126.45, 126.21, 125.30, 125.20, 119.98, 102.32, 101.65, 100.58, 100.53, 100.50, 98.24, 92.36, 82.84, 80.23, 78.13, 76.02, 75.79, 75.06, 74.87, 74.39, 74.11, 73.76, 73.36, 73.18, 72.72, 72.55, 71.82, 71.53, 71.28, 70.85, 69.50, 69.21, 69.10, 68.19, 67.95, 67.31, 67.21, 67.10, 66.78, 64.23, 64.02, 62.76, 62.44, 56.01, 54.25, 47.06, 38.22, 31.64, 29.83, 29.71, 29.56, 27.92, 27.04, 26.81, 26.78, 26.01, 25.83, 22.72, 21.49, 20.08, 19.32, 19.19, 17.84, -3.85, -4.72. HRMS: $C_{177}H_{185}Cl_3N_2O_{42}Si_3$ $[M+2NH_4]^{2+}$ calcd: 1618.0743, obsd: 1618.0773.

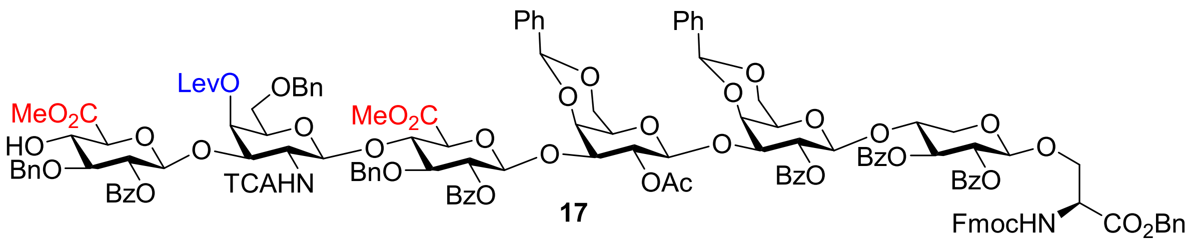
***N*-Fluorenylmethyloxycarbonyl-*O*-[2-*O*-benzoyl-3-*O*-benzyl-*β*-D-glucopyranosyl-(1→3)-6-*O*-benzyl-4-*O*-levulinoyl-2-deoxy-2-*N*-trichloroacetamido-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-*β*-D-glucopyranosyl-(1→3)-2-*O*-acetyl-4,6-*O*-benzylidene-*β*-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-*β*-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzoyl-*β*-D-xylopyranosyl]-L-serine benzyl ester 16:**



16

Compound **15** (0.784 g, 0.24 mmol) was dissolved in pyridine (2 mL) in a plastic flask, followed by addition of HF-pyridine solution (1 mL) at 0 °C. The mixture was stirred over 2 days until the reaction was completed. Then the reaction was diluted with EtOAc, washed with saturated $CuSO_4$ solution, saturated $NaHCO_3$ solution, and brine, dried over Na_2SO_4 and concentrated. The crude was purified with silica gel column chromatography (MeOH/DCM, 40:1 → 10:1) to afford compound **16** as a white solid in 93% yield (0.59 g, 0.23 mmol). $[\alpha_D^{20}]$ = +480.2 (C = 0.0083, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 7.2, 4.1 Hz, 4H, 4 x aromatic CH), 7.97 (d, *J* = 7.6 Hz, 4H, 4 x aromatic CH), 7.89 (d, *J* = 7.2 Hz, 2H, 2 x aromatic CH), 7.78 (dd, *J* = 7.5, 3.9 Hz, 2H, 2 x aromatic CH), 7.61 – 7.52 (m, 5H, 5 x aromatic CH), 7.50 – 7.33 (m, 17H, 17 x aromatic CH), 7.32 – 7.21 (m, 19H, 19 x aromatic CH), 7.18 – 7.15 (m, 3H, 3 x aromatic CH), 7.13 – 7.05 (m, 7H, 7 x aromatic CH), 6.93 (d, *J* = 6.0 Hz, 1H, TCANH), 5.66 (d, *J* = 3.2 Hz, 1H, GalN H-4), 5.59 (m, 2H), 5.49 (dd, *J* = 9.8, 8.2 Hz, 1H), 5.34 (d, *J* = 9.9 Hz, 2H, 2 x PhCH), 5.18 – 5.08 (m, 5H, $COOCH_2Ph$), 5.07 – 4.97 (m, 3H, GalN H-1), 4.79 (t, *J* = 8.5 Hz, 2H, 2 x H-1), 4.74 – 4.69 (m, 2H, 2 x H-1), 4.66 (d, *J* = 8.5 Hz, 1H, H-1), 4.61 (d, *J* = 8.6 Hz, 1H, H-1), 4.54 (d, *J* = 5.8 Hz, 1H), 4.52 – 4.48 (m, 2H), 4.41 (dd, *J* = 10.5, 3.0 Hz, 1H, GalN H-3), 4.36 – 4.29 (m, 3H), 4.27 – 4.22 (m, 3H), 4.16 – 4.11 (m, 3H), 4.10 – 4.06 (m, 1H), 3.90 (m, 6H), 3.79 – 3.69 (m, 6H, GalN H-5), 3.67 – 3.57 (m, 5H, GalN H-2), 3.42 (d, *J* = 4.5 Hz, 1H), 3.38 – 3.31 (m, 3H), 3.26 (dd, *J* = 10.9, 7.3 Hz, 2H), 3.19 (s, 1H), 3.13 (s, 1H), 2.83 – 2.75 (m, 2H, , $CH_3COCH_2CH_2$), 2.68 (dd, *J* = 15.3, 9.2 Hz, 1H), 2.58 (dd, *J* = 8.8, 4.8 Hz, 2H, $CH_3COCH_2CH_2$), 2.35 (s, 2H), 2.15 (s, 3H, $CH_3COCH_2CH_2$), 1.42 (s, 3H, CH_3CO). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.37, 172.65, 171.22, 169.48, 165.57, 165.12, 164.83, 164.56, 161.83, 155.93, 143.84, 143.69, 141.25, 141.23, 138.12, 137.90, 137.80, 137.75, 137.46, 135.12, 133.40, 133.26, 133.17, 130.08, 129.93, 129.76, 129.56, 129.11, 129.05, 129.00, 128.56, 128.52, 128.49, 128.41, 128.39, 128.36, 128.31, 128.29, 128.24, 128.18, 128.02, 127.89, 127.86, 127.78, 127.73, 127.70, 127.63, 127.33, 127.11, 126.40, 126.15, 125.20, 120.00, 102.29, 101.14, 100.76, 100.51, 100.32, 100.23, 98.21, 91.98, 82.27, 80.20, 75.77, 75.71, 75.62, 75.35, 74.83, 74.65, 74.15, 74.06, 73.62, 73.56, 73.03, 72.42, 71.73, 71.30, 70.81, 69.97, 69.72, 69.09, 68.91, 68.74, 68.22, 67.92, 67.32, 67.22, 67.09, 66.62, 62.35, 61.28, 60.92, 60.44, 56.41, 54.25, 47.06, 37.95, 31.95, 29.84, 29.72, 29.39, 28.13, 22.72, 21.10, 20.28, 14.23. HRMS: $C_{139}H_{135}Cl_3N_2O_{42}$ $[M+2NH_4]^{2+}$ calcd: 1323.4101, obsd: 1323.4023.

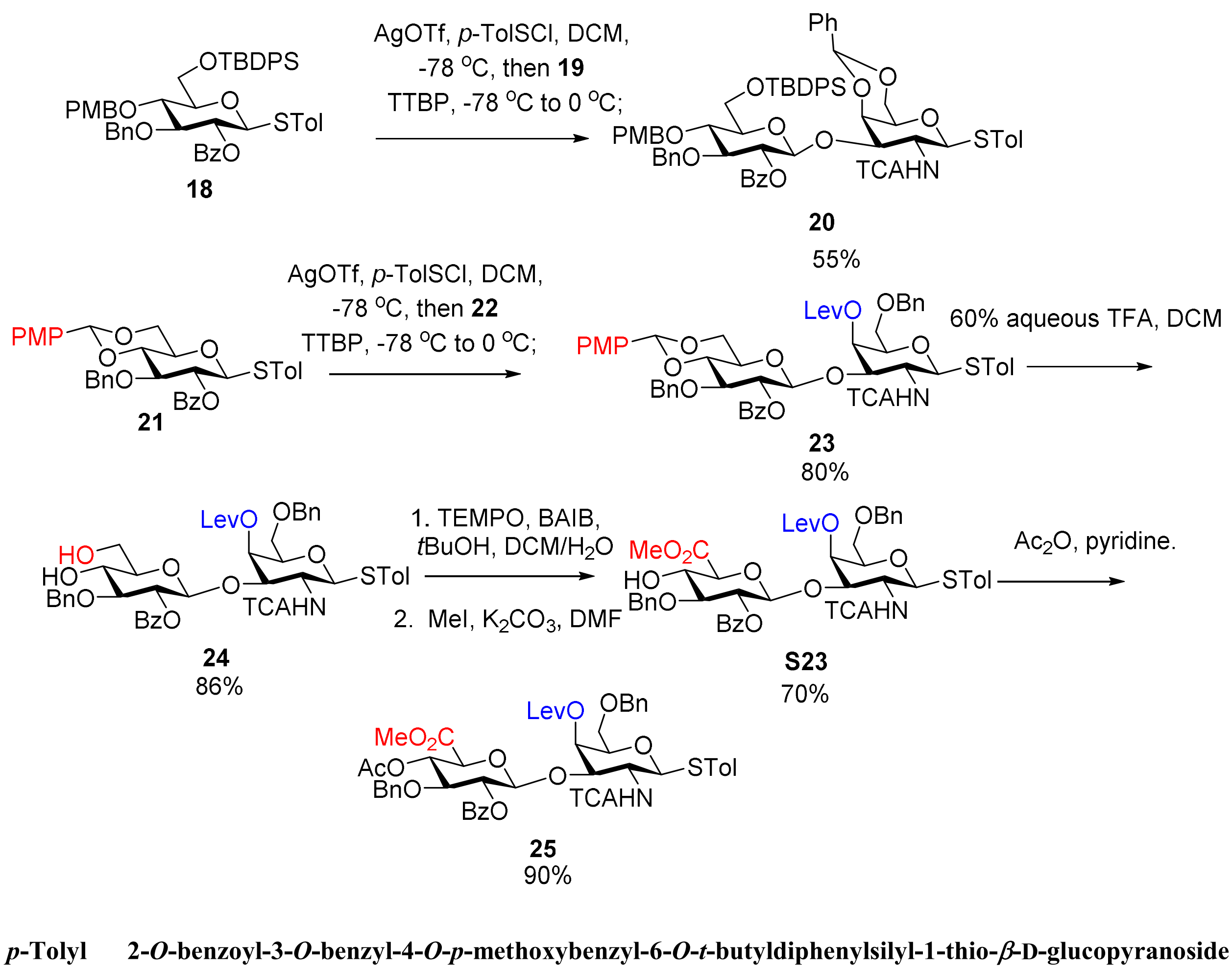
***N*-Fluorenylmethyloxycarbonyl-*O*-[methlyl-2-*O*-benzoyl-3-*O*-benzyl-*β*-D-glucopyranosyluronate-(1→3)-6-*O*-benzyl-4-*O*-levulinoyl-2-deoxy-2-*N*-trichloroacetamido-*β*-D-galactopyranosyl-(1→4)-methyl-2-*O*-benzoyl-3-*O*-benzyl-*β*-D-glucopyranosyluronate-(1→3)-2-*O*-acetyl-4,6-*O*-benzylidene-*β*-D-galactopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-*β*-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzoyl-*β*-D-xylopyranosyl]-L-serine benzyl ester 17:**



17

To a cooled solution of triol **16** (50 mg, 19.1 µmol) in DCM (1.5 mL) and H_2O (250 µL) in an ice –water bath, an aqueous solution of NaBr (1 M, 50 µL), an aqueous solution of tetrabutylammonium bromide (1 M, 100 µL), TEMPO (2 mg, 0.013 mmol, 0.3 equiv per hydroxyl group) and a saturated aqueous solution of $NaHCO_3$ (250 µL) were added. Then NaOCl (300 µL, chlorine content not less than 4%) was added and the mixture was continuously stirred for 1 hour as the temperature increased from 0 °C to room temperature. The reaction was neutralized with HCl (1 N, about 50 µL) to pH 6– 7. Then, *t*BuOH (1.4 mL), 2- methylbut-2-ene in THF (2 M, 2.8 mL) and a solution of $NaClO_2$ (100 mg, 0.44 mm) and NaH_2PO_4 (80 mg, 0.34 mm) in water (400 µL) were added. The reaction mixture was kept at room temperature for 2–3 h, diluted with saturated aqueous NaH_2PO_4 solution (10 mL), and extracted with EtOAc (3x10 mL). The organic layers were combined and dried over Na_2SO_4. After removal of the solvent, the crude was dissolved in DMF (2 mL) followed by addition of K_2CO_3 (63 mg, 0.48 mmol) and MeI (0.03 mL, 0.48 mmol). The reaction mixture was stirred overnight, then diluted with EtOAc, washed with $NaHCO_3$and brine and concentrated. The residue was purified with silica gel column chromatography (Toluene/Acetone, 30:1 → 3:1) to give hexasaccharide acceptor **17** as a white solid in 87% yield (44.4 mg, 16.7 µmol). $[\alpha_D^{20}]$ = +240.1 (C = 0.008, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 13.1, 7.5 Hz, 4H, 4 x aromatic CH), 7.96 (d, *J* = 7.9 Hz, 4H, 4 x aromatic CH), 7.88 (d, *J* = 7.5 Hz, 2H, 2 x aromatic CH), 7.77 (dd, *J* = 7.4, 3.8 Hz, 2H, 2 x aromatic CH), 7.56 (m, 5H, 5 x aromatic CH), 7.49 – 7.34 (m, 17H, 17 x aromatic CH), 7.33 – 7.19 (m, 20H, 20 x aromatic CH), 7.13 (m, 6H, 6 x aromatic CH), 7.09 – 7.07 (m, 2H, 2 x aromatic CH), 6.60 (d, *J* = 8.1 Hz, 1H, TCANH), 5.61 – 5.52 (m, 3H), 5.50 – 5.45 (m, 1H, GalN H-4), 5.36 (d, *J* = 8.9 Hz, 2H, 2 x PhCH), 5.17 – 5.07 (m, 5H), 5.02 (d, *J* = 12.1 Hz, 1H), 4.84 (d, *J* = 8.4 Hz, 1H, GalN H-1), 4.74 (dd, *J* = 13.0, 6.8 Hz, 3H, H-1, $PhCH_2$), 4.71 – 4.68 (m, 2H, 2 x H-1), 4.60 (d, *J* = 7.9 Hz, 1H, H-1), 4.52 (m, 4H, H-

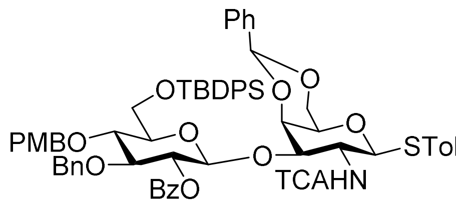
1, $PhCH_2$), 4.35 – 4.20 (m, 8H, GalN H-3), 4.12 (m, 6H, GalN H-6), 3.92 – 3.84 (m, 5H, GalN H-5, GalN H-6), 3.82 – 3.76 (m, 2H), 3.74 (s, 3H, CO_2CH_3), 3.73 – 3.66 (m, 4H, GalN H-2), 3.62 (s, 3H, CO_2CH_3), 3.61 – 3.56 (m, 2H), 3.34 (dd, J = 6.0, 2.4 Hz, 2H), 3.24 (m, 3H), 3.12 (s, 1H), 2.90 – 2.83 (m, 1H, $CH_3COCH_2CH_2$), 2.70 (m, 1H, $CH_3COCH_2CH_2$), 2.55 (m, 3H, $CH_3COCH_2CH_2$), 2.14 (s, 3H, $CH_3COCH_2CH_2$), 1.27 (s, 3H, CH_3CO). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.78, 171.63, 169.63, 169.46, 169.28, 168.97, 166.55, 165.54, 165.08, 164.95, 164.76, 164.56, 161.44, 155.91, 143.83, 143.68, 141.24, 141.22, 137.91, 137.88, 137.73, 137.57, 135.12, 133.21, 133.15, 133.00, 130.01, 129.92, 129.75, 129.66, 129.56, 129.46, 129.11, 128.85, 128.51, 128.48, 128.40, 128.37, 128.34, 128.28, 128.25, 128.11, 128.05, 128.04, 127.95, 127.84, 127.75, 127.71, 127.69, 127.64, 127.44, 127.11, 127.09, 126.40, 126.22, 125.18, 119.98, 102.30, 100.72, 100.61, 100.55, 100.50, 100.27, 100.10, 99.01, 92.52, 80.43, 79.56, 77.78, 75.80, 75.26, 75.05, 74.32, 74.22, 73.94, 73.63, 73.50, 72.91, 72.78, 72.43, 71.73, 71.30, 70.82, 69.20, 69.13, 69.09, 68.79, 68.20, 68.01, 67.30, 67.20, 67.09, 66.69, 64.01, 62.38, 55.41, 54.24, 52.84, 47.06, 38.05, 31.93, 31.64, 29.81, 29.70, 29.67, 29.65, 29.37, 28.95, 27.84, 22.71, 19.97, 14.15. HRMS: $C_{141}H_{135}Cl_3N_2O_{44}$ $[M+2NH_4]^{2+}$ calcd: 1351.9067, obsd: 1351.9071.



***p*-Tolyl 2-*O*-benzoyl-3-*O*-benzyl-4-*O*-*p*-methoxybenzyl-6-*O*-*t*-butyldiphenylsilyl-1-thio-*β*-D-glucopyranoside 18:** see page S14**.**

***p*-Tolyl 4,6-*O*-benzylidine-2-deoxy-2-*N*-trichloroacetamido-1-thio-*β*-D-galactopyranoside 19:** see page S8.

***p*-Tolyl 2-*O*-benzoyl-3-*O*-benzyl-4-*O*-*p*-methoxybenzyl-6-*O*-t-butyldiphenylsilyl-*β*-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidine-2-deoxy-2-*N*-trichloroacetamido-*β*-D-galactopyranoside 20:**



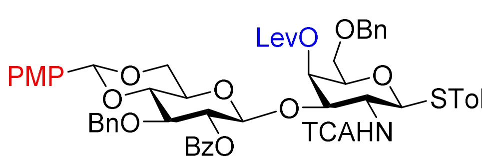
20

Disaccharide **20** was synthesized from donor **18** (1.94 g, 2.3 mmol) and acceptor **19** (1 g, 1.9 mmol) in 55% yield (1.3 g, 1 mmol) as a white solid following the general procedure of single step glycosylation. [α_D^{20}] = +120.01 (C = 0.033, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.6 Hz, 1H, aromatic CH), 7.97 (d, *J* = 7.6 Hz, 2H, 2 x aromatic CH), 7.77 (d, *J* = 6.8 Hz, 1H, aromatic CH), 7.72 (m, 4H, 4 x aromatic CH), 7.57 (t, *J* = 8.0 Hz, 1H, aromatic CH), 7.43 (m, 17H, 17 x aromatic CH), 7.23 (d, *J* = 7.5 Hz, 1H, aromatic CH), 7.20 – 7.06 (m, 7H, 7 x aromatic CH), 6.99 (m, 3H, 3 x aromatic CH), 6.83 (d, *J* = 8.5 Hz, 1H, aromatic CH), 6.75 (m, 3H, TCANH), 6.43 (d, *J* = 5.8 Hz, 1H), 5.51 (s, 1H), 5.40 (s, 1H, PhCH), 5.37 (d, *J* = 10.0 Hz, 1H, GalN H-1), 5.31 (dd, *J* = 15.7, 7.3 Hz, 1H, Glc H-2), 5.15 (d, *J* = 8.1 Hz, 1H), 4.86 – 4.79 (m, 2H, Glc H-1), 4.76 – 4.60 (m, 5H, GalN H-3), 4.48 – 4.34 (m, 3H, Glc H-6, GalN H-4), 4.23 (d, *J* = 12.6 Hz, 1H, Glc H-4), 4.04 (d, *J* = 10.2 Hz, 1H), 4.00 – 3.95 (m, 1H), 3.93 – 3.86 (m, 2H), 3.78 (s, 3H, $PhOCH_3$), 3.76 – 3.63 (m, 4H, Glc H-3, Glc H-6, GalN H-2, GalN H5), 3.60 – 3.56 (m, 1H), 3.28 (m, 1H, Glc H-5), 2.32 (s, 3H, $SPhCH_3$), 1.13 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.53, 165.16, 162.06, 161.80, 159.36, 159.32, 138.38, 138.00, 137.86, 137.58, 137.24, 135.85, 135.64, 135.57, 135.55, 133.67, 133.49, 133.25, 133.17, 132.95, 130.22, 130.09, 129.97, 129.95, 129.92, 129.89, 129.81, 129.78, 129.74, 129.71, 128.78, 128.74, 128.41, 128.36, 128.33, 128.26, 128.16, 128.09, 128.00, 127.97, 127.91, 127.90, 127.80, 127.72, 127.69, 127.62, 127.39, 126.41, 125.77, 113.90, 113.82, 105.65, 101.20, 100.30, 100.11, 99.87, 92.10, 82.93, 82.88, 82.80, 77.57, 77.41, 77.35, 77.10, 76.84, 76.56, 76.37, 76.13, 75.97, 75.25, 75.13, 74.91, 74.55, 74.34, 73.90, 73.62, 73.54, 70.67, 70.15, 69.03, 68.67, 67.49, 63.29, 62.76, 55.30, 55.27, 52.84, 27.02, 26.92, 21.27, 19.54, 19.45. HRMS: $C_{66}H_{68}Cl_3NO_{12}SSi$ $[M+NH_4]^+$ calcd: 1249.3635, obsd: 1249.3653.

***p*-Tolyl 2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-*p*-methoxybenzylidene-1-thio-*β*-D-glucopyranoside 21:** see page S11.

***p*-Tolyl 6-*O*-benzyl-4-*O*-levulinoyl-2-deoxy-2-*N*-trichloroacetamido-1-thio-*β*-D-galactopyranoside 22:** see page S10.

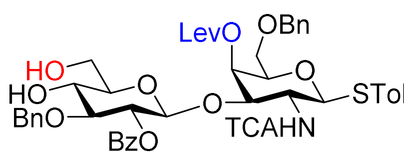
***p*-Tolyl 2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-*p*-methoxybenzylidene-*β*-D-glucopyranosyl-(1→3)-6-*O*-benzyl-4-*O*-levulinoyl-2-deoxy-2-*N*-trichloroacetamido-1-thio-*β*-D-galactopyranoside 23:**



23

23 was synthesized from donor **21** (1.32 g, 2.2 mmol) and acceptor **22** (0.904 g, 1.46 mmol) in 80% yield (1.28 g, 1.17 mmol) as a white solid following the general procedure of single step glycosylation. [α_D^{20}] = +685.7 (C = 0.006, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.2, 1.1 Hz, 2H, 2 x aromatic CH), 7.64 – 7.60 (m, 1H, aromatic CH), 7.48 – 7.43 (m, 4H, 4 x aromatic CH), 7.38 – 7.28 (m, 8H, 8 x aromatic CH), 7.18 – 7.14 (m, 1H, aromatic CH), 7.11 – 7.08 (m, 4H, 4 x aromatic CH), 7.02 (d, *J* = 8.0 Hz, 2H, 2 x aromatic CH), 6.94 – 6.91 (m, 2H, 2 x aromatic CH), 6.67 (d, *J* = 7.1 Hz, 1H, TCANH), 5.58 (s, 1H, PhCH), 5.55 (d, *J* = 3.3 Hz, 1H, GalN H-4), 5.25 (d, *J* = 10.4 Hz, 1H, GalN H-1), 5.17 (dd, *J* = 8.6, 7.6 Hz, 1H, Glc H-2), 4.79 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.72 (d, *J* = 7.4 Hz, 1H, Glc H-1), 4.66 (d, *J* = 12.0 Hz, 1H, GalN H-3), 4.61 (dd, *J* = 10.3, 3.4 Hz, 1H, GalN H-6), 4.50 (m, 2H, $PhCH_2$), 4.35 (dd, *J* = 10.6, 5.0 Hz, 1H, Glc H-5), 3.88 – 3.80 (m, 7H, $PhOCH_3$, Glc H-4, GalN H-5, GalN H-6), 3.74 (t, *J* = 8.9 Hz, 1H, Glc H-3), 3.63 (dd, *J* = 10.0, 6.2 Hz, 1H, Glc H-6), 3.55 (dd, *J* = 10.0, 5.9 Hz, 1H), 3.45 (m, 2H, Glc H-6, GalN H-2), 2.93 – 2.86 (m, 1H, $CH_3COCH_2CH_2$), 2.75 – 2.63 (m, 2H, $CH_3COCH_2CH_2$), 2.57 – 2.51 (m, 1H, $CH_3COCH_2CH_2$), 2.31 (s, 3H, $SPhCH_3$), 2.23 (s, 3H, $CH_3COCH_2CH_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.66, 171.69, 164.88, 161.62, 160.06, 138.48, 137.93, 137.69, 133.37, 133.18, 129.90, 129.79, 129.66, 129.53, 128.49, 128.38, 128.17, 128.16, 128.11, 127.98, 127.74, 127.61, 127.35, 113.62, 101.17, 101.04, 92.04, 84.30, 81.16, 77.65, 76.68, 73.88, 73.62, 73.42, 73.35, 69.82, 68.61, 68.50, 66.28, 55.32, 54.62, 38.16, 29.91, 28.00, 21.18. HRMS: $C_{55}H_{56}C_{l3}NO_{14}S$ [M+NH$_4$]$^+$ calcd: 1109.2831, obsd: 1109.2773.

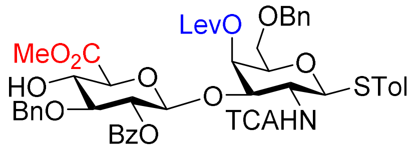
***p*-Tolyl 2-*O*-benzoyl-3-*O*-benzyl-*β*-D-glucopyranosyl-(1→3)-6-*O*-benzyl-4-*O*-levulinoyl-2-deoxy-2-*N*-trichloroacetamido-1-thio-*β*-D-galactopyranoside 24:**



24

Compound **23** (1.28 g, 1.17 mmol) was dissolved in DCM, then treated with 60% aqueous TFA. The reaction was stirred for 2 h. After the reaction was completed, it was diluted with DCM and washed with saturated $NaHCO_3$ solution. The aqueous layer was extracted with DCM three times. The organic layers were combined, washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography (Hexane/EtOAc, 8:1 → 1:1) on silica gel to provide compound **24** as a white solid in 86% yield (0.98 g, 1 mmol). [α_D^{20}] = +120.0 (C = 0.108, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 8.2, 1.1 Hz, 2H, 2 x aromatic CH), 7.61 – 7.57 (m, 1H, aromatic CH), 7.45 (t, *J* = 7.8 Hz, 2H, 2 x aromatic CH), 7.39 – 7.28 (m, 7H, 7 x aromatic CH), 7.18 – 7.09 (m, 5H, 5 x aromatic CH), 7.05 (d, *J* = 8.0 Hz, 2H, 2 x aromatic CH), 6.83 (d, *J* = 7.0 Hz, 1H, TCANH), 5.74 (d, *J* = 3.4 Hz, 1H, GalN H-4), 5.31 (d, *J* = 10.4 Hz, 1H, GalN H-1), 5.16 (dd, *J* = 9.6, 7.8 Hz, 1H, Glc H-2), 4.74 (d, *J* = 7.7 Hz, 1H, Glc H-1), 4.65 (q, *J* = 11.5 Hz, 2H, $PhCH_2$), 4.59 (dd, *J* = 10.3, 3.5 Hz, 1H, GalN H-3), 4.46 (m, 2H, $PhCH_2$), 3.89 – 3.81 (m, 3H, GalN H-6, Glc H-4), 3.77 (dd, *J* = 12.4, 2.9 Hz, 1H, GalN H-5), 3.64 – 3.58 (m, 2H, Glc H-3, Glc H-5), 3.54 – 3.45 (m, 2H, GalN H-2, Glc H-6), 3.35 (d, *J* = 9.6 Hz, 1H, GalN H-6), 2.82 – 2.77 (m, 1H, $CH_3COCH_2CH_2$), 2.74 – 2.68 (m, 1H, $CH_3COCH_2CH_2$), 2.67 – 2.58 (m, 2H, $CH_3COCH_2CH_2$), 2.32 (s, 3H, $SPhCH_3$), 2.20 (s, 3H, $CH_3COCH_2CH_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.53, 172.82, 165.16, 161.68, 138.49, 137.86, 137.75, 133.44, 133.13, 130.00, 129.83, 129.49, 128.57, 128.41, 128.37, 128.26, 127.96, 127.92, 127.85, 127.74, 101.40, 91.79, 84.29, 82.27, 76.38, 75.67, 75.17, 74.70, 73.60, 73.57, 70.51, 68.83, 68.54, 60.83, 54.25, 38.00, 29.87, 28.20, 21.19. HRMS: $C_{47}H_{50}Cl_3NO_{13}S$ $[M+NH_4]^+$ calcd: 991.2412, obsd: 991.2359.

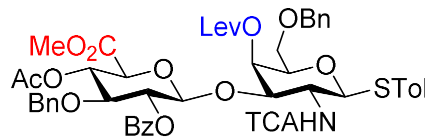
***p*-Tolyl methyl-2-*O*-benzoyl-3-*O*-benzyl-*β*-D-glucopyranosyluronate-(1→3)-6-*O*-benzyl-4-*O*-levulinoyl-2-deoxy-2-*N*-trichloroacetamido-1-thio-*β*-D-galactopyranoside S23:**



S23

Compound **24** (108 mg, 0.11 mmol) was dissolved in DCM/*t*BuOH/H_2O (4:4:1, 4.5 mL), followed by addition of TEMPO (3.5 mg) and BAIB (107 mg). The resulting mixture was stirred at room temperature until all starting material was consumed as indicated by TLC analysis (≈5 h). Then it was neutralized by 1 M HCl solution to adjust pH around 6, diluted with EtOAc, washed with H_2O, dried over Na_2SO_4. After concentration, the crude was dissolved in dry DMF (5 mL), followed by addition of MeI (63 µL, 1 mmol) and K_2CO_3 (209 mg, 1.5 mmol). The resulting mixture was stirred under room temperature overnight, then diluted with EtOAc, washed with $NaHCO_3$, brine, dried over Na_2SO_4 and concentrated. The residue underwent silica gel column chromatography (Hexane/EtOAc, 10:1 → 2:1) to give compound **S23** as a white solid in 70% yield (77.8 mg, 77.5 µmol). $[\alpha_D^{20}]$ = +600 (C = 0.01, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.3, 1.2 Hz, 2H, 2 x aromatic CH), 7.63 – 7.59 (m, 1H, aromatic CH), 7.45 (dd, *J* = 10.8, 4.8 Hz, 2H, 2 x aromatic CH), 7.38 – 7.28 (m, 7H, 7 x aromatic CH), 7.18 – 7.12 (m, 5H, 5 x aromatic CH), 7.02 (d, *J* = 8.0 Hz, 2H, 2 x aromatic CH), 6.73 (d, *J* = 7.2 Hz, 1H, TCANH), 5.60 (d, *J* = 3.2 Hz, 1H, GalN H-4), 5.25 (d, *J* = 10.4 Hz, 1H, GalN H-1), 5.12 (dd, *J* = 9.1, 7.4 Hz, 1H, Glc H-2), 4.77 (d, *J* = 11.6 Hz, 1H, Glc H-1), 4.70 (dd, *J* = 9.5, 5.8 Hz, 2H, $PhCH_2$), 4.64 (dd, *J* = 10.4, 3.3 Hz, 1H, GalN H-3), 4.51 – 4.46 (m, 2H, $PhCH_2$), 4.08 – 4.02 (m, 1H, Glc H-4), 3.85 (dd, *J* = 7.7, 4.4 Hz, 2H, GalN H-5), 3.74 (s, 3H, CO_2CH_3), 3.64 – 3.46 (m, 5H, GalN H-3, 2 x GalN H-6, Glc H-3), 3.26 (d, *J* = 2.7 Hz, 1H, Glc H5), 2.86 (m, 1H, $CH_3COCH_2CH_2$), 2.72 – 2.60 (m, 2H, $CH_3COCH_2CH_2$), 2.51 (m, 1H, $CH_3COCH_2CH_2$), 2.31 (s, 3H, $SPhCH_3$), 2.20 (s, 3H, $CH_3COCH_2CH_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.78, 171.58, 169.64, 164.91, 161.61, 138.45, 137.97, 137.71, 133.39, 133.12, 129.86, 129.78, 129.46, 128.49, 128.33, 128.25, 128.07, 127.96, 127.70, 127.67, 100.63, 92.08, 84.42, 80.31, 76.84, 74.35, 73.81, 73.67, 73.61, 72.76, 71.89, 69.81, 68.73, 60.43, 54.47, 52.81, 38.13, 29.87, 27.94, 21.17, 14.21. HRMS: $C_{48}H_{50}Cl_{3}NO_{14}S$ $[M+NH_4]^+$ calcd: 1019.2361, obsd: 1019.2306.

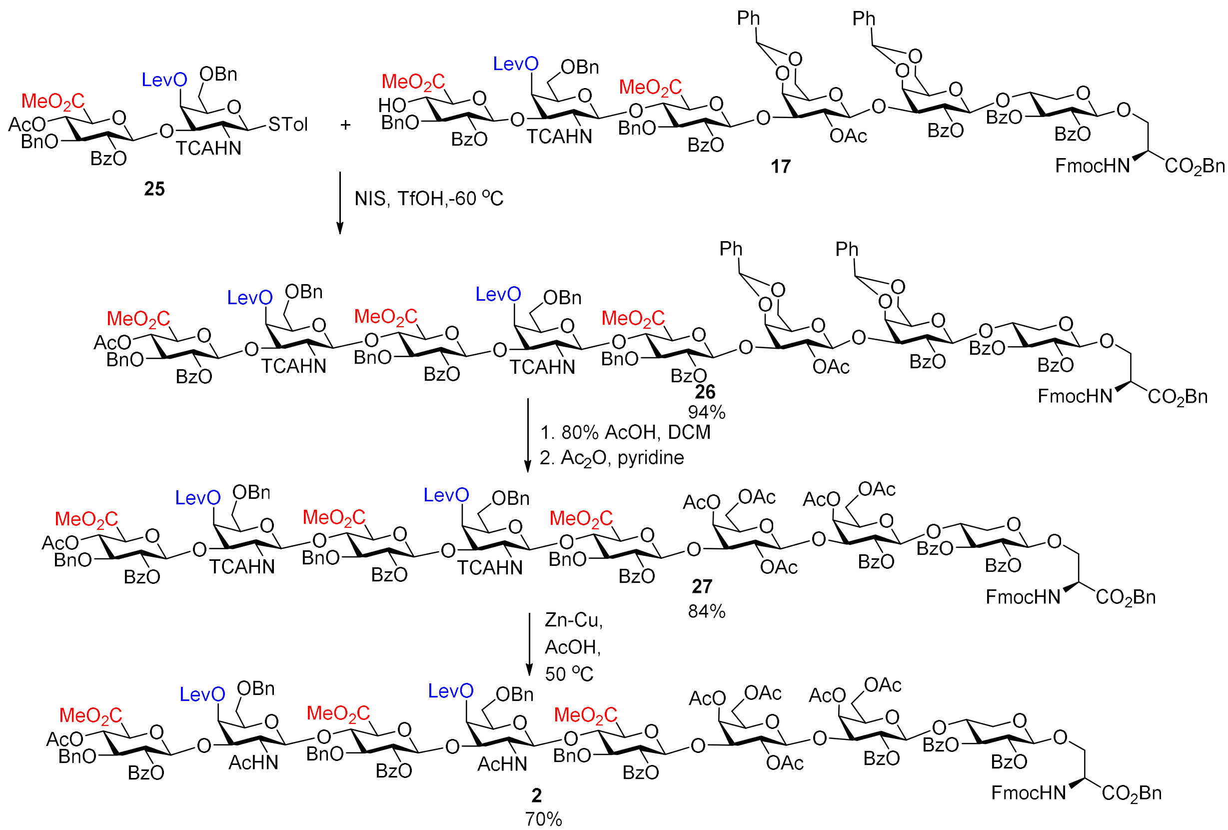
***p*-Tolyl methyl-4-*O*-acetyl-2-*O*-benzoyl-3-*O*-benzyl-*β*-D-glucopyranosyluronate-(1→3)-6-*O*-benzyl-4-*O*-levulinoyl-2-deoxy-2-*N*-trichloroacetamido-1-thio-*β*-D-galactopyranoside 25:**



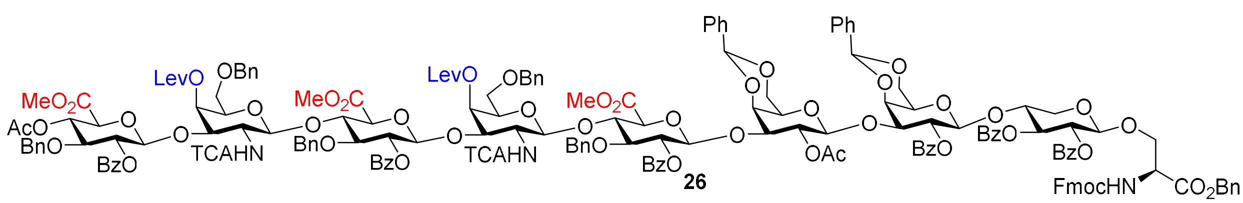
25

Compound **S23** (0.5 g, 0.5 mmol) was dissolved in pyridine (8 mL) allowed by addition of Ac_2O (4 mL). The mixture was stirred overnight, diluted with EtOAc, washed with 10% HCl solution, saturated $NaHCO_3$ solution, dried over Na_2SO_4 and concentrated. The crude was purified with silica gel column chromatography (Hexane/EtOAc, 10:1 → 2:1) to afford compound **25** as a white solid in 90% yield (0.47 g, 0.45 mmol). [α_D^{20}] = +120 (C = 0.025, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.3, 1.2 Hz, 2H, 2 x aromatic CH), 7.63 – 7.59 (m, 1H, aromatic CH), 7.46 (t, *J* = 7.8 Hz, 2H, 2 x aromatic CH), 7.37 (d, *J* = 8.1 Hz, 2H, 2 x aromatic CH), 7.35 – 7.28 (m, 5H, 5 x aromatic CH), 7.18 – 7.13 (m, 3H, 3 x aromatic CH), 7.07 (dd, *J* = 7.5, 1.8 Hz, 2H, 2 x aromatic CH), 7.02 (d, *J* = 8.0 Hz, 2H, 2 x aromatic CH), 6.71 (d, *J* = 7.2 Hz, 1H, TCANH), 5.57 (d, *J* = 3.2 Hz, 1H, GalN H-4), 5.30 – 5.20 (m, 3H, GalN H-1, Glc H-2, GalN H-6), 4.75 (d, *J* = 7.5 Hz, 1H, Glc H-1), 4.63 (dd, *J* = 10.4, 3.3 Hz, 1H, GalN H-3), 4.56 (s, 2H, $PhCH_2$), 4.48 (s, 2H, $PhCH_2$), 3.94 (d, *J* = 9.8 Hz, 1H, Glc H-5), 3.83 (t, *J* = 6.0 Hz, 1H, GalN H-5), 3.77 (t, *J* = 9.0 Hz, 1H, Glc H-3), 3.71 (s, 3H, CO_2CH_3), 3.61 (dd, *J* = 10.1, 6.4 Hz, 1H, Glc H-4), 3.57 – 3.50 (m, 2H, GalN H-2, GalN H-6), 2.91 – 2.84 (m, 1H, $CH_3COCH_2CH_2$), 2.72 – 2.60 (m, 2H, $CH_3COCH_2CH_2$), 2.55 – 2.48 (m, 1H, $CH_3COCH_2CH_2$), 2.31 (s, 3H, $SPHCH_3$), 2.21 (s, 3H, $CH_3COCH_2CH_2$), 1.98 (s, 3H, CH_3CO). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.79, 171.49, 169.23, 167.25, 164.68, 161.58, 138.46, 138.00, 137.18, 133.47, 133.13, 133.00, 129.86, 129.78, 129.66, 129.32, 128.53, 128.33, 128.29, 128.20, 127.95, 127.92, 127.82, 127.64, 99.98, 92.10, 84.38, 78.88, 76.94, 73.90, 73.84, 73.59, 72.73, 72.65, 70.59, 69.43, 69.20, 68.83, 64.01, 54.34, 52.77, 38.10, 31.93, 29.88, 29.71, 29.38, 27.89, 22.71, 21.17, 20.68, 14.15. HRMS: $C_{50}H_{52}Cl_3NO_{15}S$ $[M+NH_4]^+$ calcd: m/z: 1061.2461, obsd: 1061.2513.

Synthesis of Octasaccharide:

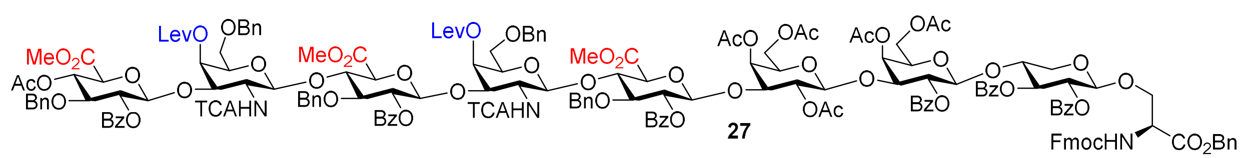


***N*-Fluorenylmethyloxycarbonyl-*O*-[methyl-4-*O*-acetyl-2-*O*-benzoyl-3-*O*-benzyl-*β*-D-glucopyranosyluronate-(1→3)-6-*O*-benzyl-4-*O*-levulinoyl-2-deoxy-2-*N*-trichloroacetamido-*β*-D-galactopyranosyl-(1→4)-methyl-2-*O*-benzoyl-3-*O*-benzyl-*β*-D-glucopyranosyluronate-(1→3)-6-*O*-benzyl-4-*O*-levulinoyl-2-deoxy-2-*N*-trichloroacetamido-*β*-D-galactopyranosyl-(1→4)-methyl-2-*O*-benzoyl-3-*O*-benzyl-*β*-D-glucopyranosyluronate-(1→3)-2-*O*-acetyl-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 26:**



A mixture of hexasaccharide acceptor **17** (166 mg, 62.2 μmol) and disaccharide donor **25** (195 mg, 0.19 mmol) was dissolved in anhydrous DCM (10 mL) followed by addition of freshly activated MS. The mixture was stirred at room temperature for 1 h then cooled to -60 °C. NIS (40.4 mg, 0.18 mmol) was added followed by addition of TfOH (0.82 μL, 9.2 μmol). The reaction was stirred for 3 h from -60 °C to room temperature. The mixture was diluted with DCM, neutralized with DIPEA, filtered through Celite, washed with saturated $NaHCO_3$, brine, dried over Na_2SO_4, concentrated and purified with silica gel column chromatography (Toluene/Acetone, 30:1 → 3:1) to give octasaccharide **26** as a white solid in 94% yield (209 mg,58.5 μmol). [α_D^{20}] = +240.0 (C = 0.083, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 8.00 (m, 4H, 4 x aromatic CH), 7.99 – 7.93 (m, 6H, 6 x aromatic CH), 7.89 (dd, J = 8.3, 1.2 Hz, 2H, 2 x aromatic CH), 7.78 (dd, J = 7.5, 3.9 Hz, 2H, 2 x aromatic CH), 7.61 – 7.53 (m, 6H, 6 x aromatic CH), 7.50 – 7.35 (m, 19H, 19 x aromatic CH), 7.33 – 7.23 (m, 22H, 22 x aromatic CH), 7.23 – 7.16 (m, 12H, 12 x aromatic CH), 7.11 (m, 12H, 12 x aromatic CH), 6.88 (d, J = 8.3 Hz, 1H, TCANH), 6.57 (d, J = 8.1 Hz, 1H, TCANH), 5.60 (t, J = 7.5 Hz, 1H), 5.57 – 5.54 (m, 2H), 5.51 – 5.47 (m, 2H), 5.37 (d, J = 9.8 Hz, 2H, 2 x PhCH), 5.34 – 5.24 (m, 3H), 5.18 – 5.12 (m, 3H), 5.11 (s, 1H), 5.09 (d, J = 4.4 Hz, 1H), 5.05 – 5.02 (m, 1H), 4.91 (d, J = 8.4 Hz, 1H, GalN H-1'), 4.84 (dd, J = 7.9, 2.3 Hz, 2H, GalN H-1"), 4.74 (m, 6H, 3 x H-1), 4.62 – 4.60 (m, 1H, H-1), 4.59 – 4.54 (m, 5H, H-1), 4.52 – 4.48 (m, 1H), 4.36 – 4.31 (m, 2H), 4.29 – 4.27 (m, 3H), 4.24 (d, J = 10.8 Hz, 5H), 4.21 – 4.08 (m, 7H), 3.96 (d, J = 9.8 Hz, 2H, GalN H-2'), 3.93 – 3.89 (m, 4H), 3.81 (m, 3H), 3.77 – 3.73 (m, 3H, GalN H-2"), 3.72 (s, 3H, CO_2CH_3), 3.69 (dd, J = 6.5, 5.0 Hz, 3H), 3.66 (s, 3H, CO_2CH_3), 3.62 (s, 3H, CO_2CH_3), 3.61 – 3.56 (m, 2H), 3.38 – 3.31 (m, 4H), 3.26 (t, J = 5.9 Hz, 2H), 3.13 (s, 1H), 2.93 – 2.85 (m, 2H), 2.78 – 2.70 (m, 2H, $CH_3COCH_2CH_2$), 2.66 – 2.46 (m, 7H, $CH_3COCH_2CH_2$), 2.15 (s, 3H, $CH_3COCH_2CH_2$), 2.10 (s, 3H, $CH_3COCH_2CH_2$), 1.99 (s, 3H, CH_3CO), 1.35 (s, 3H, CH_3CO). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.85, 206.83, 171.55, 171.52, 169.46, 169.30, 169.22, 169.18, 168.97, 167.45, 165.55, 165.08, 164.87, 164.80, 164.75, 164.55, 161.57, 155.92, 143.84, 143.69, 141.25, 141.23, 137.96, 137.93, 137.91, 137.88, 137.75, 137.59, 137.27, 135.13, 133.26, 133.17, 133.15, 133.01, 130.07, 130.03, 129.93, 129.76, 129.56, 129.54, 129.51, 129.49, 129.12, 129.04, 128.85, 128.52, 128.49, 128.41, 128.38, 128.35, 128.32, 128.29, 128.23, 128.11, 128.06, 128.00, 127.98, 127.96, 127.93, 127.84, 127.80, 127.76, 127.72, 127.65, 127.58, 127.47, 127.43, 127.12, 127.10, 126.41, 126.23, 125.30, 125.19, 119.99, 102.31, 100.72, 100.59, 100.56, 100.50, 100.12, 100.02, 99.69, 99.60, 99.08, 92.68, 92.43, 79.87, 79.58, 78.90, 75.81, 75.27, 75.03, 74.41, 74.36, 74.13, 73.96, 73.87, 73.79, 73.64, 73.60, 73.05, 72.97, 72.86, 72.69, 72.56, 72.40, 71.76, 71.30, 70.82, 70.69, 69.10, 68.84, 68.17, 67.31, 67.21, 67.10, 66.71, 62.39, 55.23, 55.12, 54.25, 52.90, 52.82, 47.07, 38.13, 38.03, 31.94, 31.65, 29.85, 29.71, 29.68, 27.89, 27.82, 22.72, 21.49, 20.69, 19.98, 14.16. ESI-MS: $C_{184}H_{179}Cl_6N_3O_{59}$ $[M+2NH_4]^{2+}$ calcd: 1811.4955, obsd: 1811.4644.

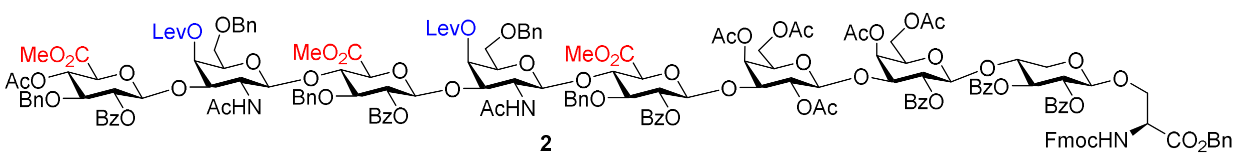
***N*-Fluorenylmethyloxycarbonyl-*O*-[2-*O*-benzoyl-3-*O*-benzyl-*β*-D-glucopyranosyl-(1→3)-6-*O*-benzyl-4-*O*-levulinoyl-2-deoxy-2-*N*-trichloroacetamido-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-*β*-D-glucopyranosyl-(1→3)-6-*O*-benzyl-4-*O*-levulinoyl-2-deoxy-2-*N*-trichloroacetamido-*β*-D-galactopyranosyl-(1→4)2-*O*-benzoyl-3-*O*-benzyl-*β*-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-*β*-D-galactopyranosyl-(1→3)-4,6-di-*O*-acetyl-2-*O*-benzoyl-*β*-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzoyl-*β*-D-xylopyranosyl]-L-serine benzyl ester 27:**



27

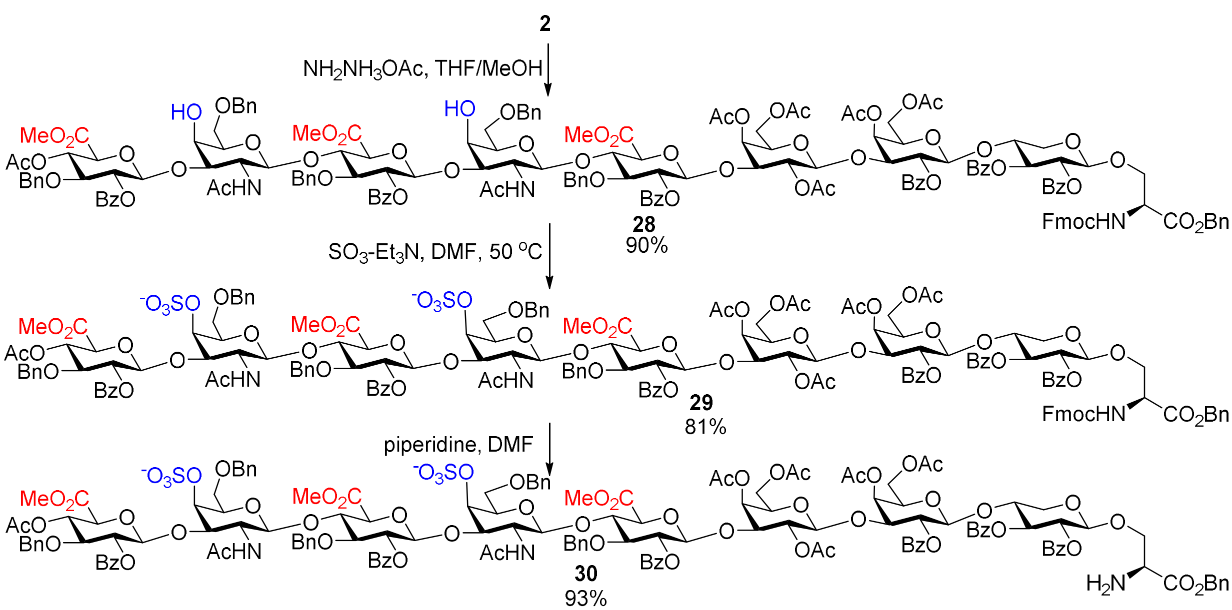
Octasaccharide **26** (150 mg, 41.8 μmol) was treated with 80% aqueous acetic acid (10 mL), and the mixture was heated at 60 °C until the reaction was completed. The solvent was removed *in vacuo* and the residue was co-evaporated with toluene to afford the tetraol. ESI-MS: $C_{170}H_{171}Cl_6N_3O_{59}$ $[M+2NH_4]^{2+}$ calcd: 1724.9644, obsd: 1724.9280. The crude was dissolve in pyridine (5 mL), then treated with Ac_2O (3 mL). The reaction mixture was stirred overnight till completion. The mixture was diluted with EtOAc, washed with 10% HCl solution, saturated $NaHCO_3$ solution, dried over Na_2SO_4 and concentrated. The residue was purified with silica gel column chromatography (Toluene/Acetone, 30:1 → 3:1) to provide compound **27** as a white solid in 84% yield (125.7 mg, 35.1 μmol) over two steps. $[\alpha_D^{20}]$ = -30.03 (C = 0.033, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 – 7.93 (m, 10H, 10 x aromatic CH), 7.89 – 7.85 (m, 2H, 2 x aromatic CH), 7.78 (dd, *J* = 7.5, 2.5 Hz, 2H, 2 x aromatic CH), 7.56 (m, 7H, 7 x aromatic CH), 7.48 – 7.38 (m, 13H, 13 x aromatic CH), 7.37 – 7.22 (m, 16H, 16 x aromatic CH), 7.20 – 7.08 (m, 18H, 18 x aromatic CH), 6.88 (d, *J* = 8.3 Hz, 1H, TCANH), 6.78 (d, *J* = 8.2 Hz, 1H, TCANH), 5.57 – 5.50 (m, 4H), 5.34 – 5.22 (m, 6H), 5.14 (m, 3H), 4.99 (dd, *J* = 9.2, 7.0 Hz, 2H), 4.94 – 4.89 (m, 2H, GalN H-1'), 4.88 (d, *J* = 8.4 Hz, 1H), 4.81 (dd, *J* = 15.2, 6.9 Hz, 2H), 4.76 (dd, *J* = 10.9, 6.7 Hz, 2H), 4.63 (d, *J* = 8.0 Hz, 1H), 4.60 – 4.55 (m, 4H), 4.52 (m, 4H, GalN H-2"), 4.39 – 4.34 (m, 2H), 4.32 (d, *J* = 7.2 Hz, 1H), 4.27 (dd, *J* = 9.8, 4.5 Hz, 3H), 4.25 – 4.19 (m, 3H), 4.17 (d, *J* = 8.3 Hz, 1H), 4.13 (dd, *J* = 10.9, 3.4 Hz, 1H), 4.09 (dd, *J* = 11.6, 5.3 Hz, 1H), 3.97 – 3.87 (m, 7H, GalN H-1', GalN H-2"), 3.85 – 3.80 (m, 2H), 3.77 (s, 3H, CO_2CH_3), 3.76 – 3.73 (m, 2H), 3.71 (s, 3H, CO_2CH_3), 3.68 (d, *J* = 7.3 Hz, 2H), 3.65 (s, 3H, CO_2CH_3), 3.62 (dd, *J* = 12.2, 6.8 Hz, 3H), 3.55 (dd, *J* = 10.1, 3.5 Hz, 1H), 3.38 – 3.35 (m, 2H), 3.32 (d, *J* = 6.7 Hz, 2H), 3.12 (dd, *J* = 12.2, 6.1 Hz, 1H), 2.89 (m, 2H), 2.74 – 2.67 (m, 2H, $CH_3COCH_2CH_2$), 2.64 – 2.43 (m, 7H, $CH_3COCH_2CH_2$), 2.15 (s, 3H, $CH_3COCH_2CH_2$), 2.08 (s, 3H, $CH_3COCH_2CH_2$), 2.08 (s, 3H, CH_3CO), 2.02 (s, 3H, CH_3CO), 1.99 (s, 3H, CH_3CO), 1.98 (s, 3H, CH_3CO), 1.92 (s, 3H, CH_3CO), 1.31 (s, 3H, CH_3CO). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.86, 171.55, 170.59, 170.57, 170.22, 169.68, 169.22, 169.21, 169.08, 168.53, 167.44, 165.27, 164.85, 164.80, 164.51, 164.29, 161.62, 161.54, 143.80, 143.65, 141.28, 141.24, 137.95, 137.93, 137.90, 137.26, 133.41, 133.23, 133.18, 133.00, 130.10, 130.06, 129.93, 129.87, 129.73, 129.66, 129.61, 129.49, 129.26, 129.03, 128.66, 128.46, 128.44, 128.34, 128.33, 128.31, 128.27, 128.11, 128.05, 128.00, 127.97, 127.93, 127.89, 127.79, 127.73, 127.64, 127.58, 127.46, 127.43, 127.10, 127.07, 125.14, 125.11, 120.01, 99.96, 99.76, 99.74, 99.68, 99.67, 99.58, 99.24, 73.92, 73.77, 73.61, 73.03, 72.85, 72.68, 72.48, 70.69, 69.20, 68.92, 68.19, 67.30, 67.18, 64.01, 62.28, 52.90, 52.81, 52.80, 47.10, 38.15, 38.03, 31.93, 31.63, 29.84, 29.70, 29.69, 29.67, 29.65, 29.64, 29.52, 29.37, 29.17, 27.82, 22.71, 20.87, 20.72, 20.70, 20.68, 20.51, 19.66. HRMS: $C_{178}H_{179}Cl_6N_3O_{63}$ $[M+2NH_4]^{2+}$ calcd: 1807.4853, obsd: 1807.4600.

***N*-Fluorenylmethyloxycarbonyl-*O*-[2-*O*-benzoyl-3-*O*-benzyl-*β*-D-glucopyranosyl-(1→3)-2-*N*-acetyl-6-*O*-benzyl-4-*O*-levulinoyl-2-deoxy-*β*-D-galactopyranosyl-(1→4)-2-*O*-benzoyl-3-*O*-benzyl-*β*-D-glucopyranosyl-(1→3)-2-*N*-acetyl-6-*O*-benzyl-4-*O*-levulinoyl-2-deoxy-*β*-D-galactopyranosyl-(1→4)2-*O*-benzoyl-3-*O*-benzyl-*β*-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-*β*-D-galactopyranosyl-(1→3)-4,6-di-*O*-acetyl-2-*O*-benzoyl-*β*-D-galactopyranosyl-(1→4)-2,3-di-*O*-benzoyl-*β*-D-xylopyranosyl]-L-serine benzyl ester 2:**

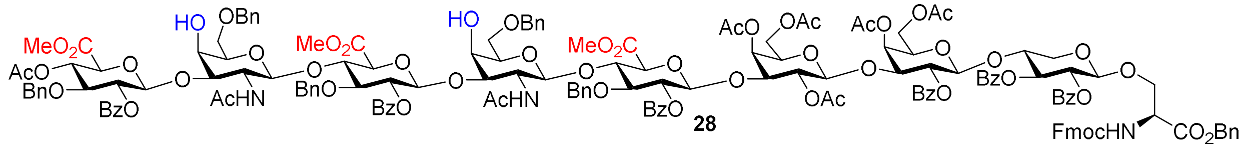


2

To a solution of octasaccharide **27** (90 mg, 25.1 μmol) in anhydrous AcOH (2 mL), Zn-Cu couple (97.3 mg, 0.75 mmol, 5 equiv/Cl) was added in five portions at 2 h. The mixture was stirred at 50 °C for 24 h. After the reaction was consumed as indicated from mass spectrometry, the mixture was cooled to room temperature and filtered through Celite, washed with DCM, EtOAc, and toluene. The filtrate was concentrated and subjected to silica gel column chromatography (Toluene/Acetone, 30:1 → 1:1) to afford compound **2** as a white solid in 70% yield (59.4 mg, 17.6 μmol). [α_D^{20}] = +95.9 (C = 0.0417, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 7.94 (m, 10H, 10 x aromatic CH), 7.91 (d, *J* = 7.4 Hz, 2H, 2 x aromatic CH), 7.77 (dd, *J* = 7.4, 2.5 Hz, 2H, 2 x aromatic CH), 7.55 (m, 7H, 7 x aromatic CH), 7.51 – 7.40 (m, 12H, 12 x aromatic CH), 7.39 – 7.33 (m, 4H, 4 x aromatic CH), 7.30 – 7.19 (m, 16H, 16 x aromatic CH), 7.16 (m, 13H, 13 x aromatic CH), 7.11 – 7.07 (m, 3H, 3 x aromatic CH), 5.99 (d, *J* = 8.3 Hz, 1H, AcNH), 5.75 (d, *J* = 7.9 Hz, 1H, AcNH), 5.63 (s, 1H), 5.56 (t, *J* = 6.8 Hz, 2H), 5.51 (d, *J* = 2.5 Hz, 1H), 5.43 (d, *J* = 3.0 Hz, 1H), 5.37 – 5.33 (m, 1H), 5.30 – 5.23 (m, 3H), 5.17 – 5.11 (m, 3H), 5.04 (dd, *J* = 9.8, 8.2 Hz, 1H), 4.99 (dd, *J* = 7.7, 4.1 Hz, 2H), 4.92 (d, *J* = 4.7 Hz, 1H), 4.79 (dd, *J* = 8.1, 4.3 Hz, 2H, GalN H-1”), 4.69 – 4.62 (m, 3H, GalN H-1’), 4.60 – 4.47 (m, 8H), 4.41 – 4.27 (m, 10H), 4.23 (d, *J* = 8.2 Hz, 1H), 4.16 (t, *J* = 7.0 Hz, 1H), 4.09 (d, *J* = 10.6 Hz, 1H), 4.05 (dd, *J* = 10.8, 5.0 Hz, 2H), 3.98 – 3.91 (m, 4H, GalN H-2’), 3.87 – 3.78 (m, 5H), 3.75 (s, 3H), 3.72 (s, 3H), 3.69 (s, 6H, GalN H-2”), 3.64 (dd, *J* = 15.5, 9.2 Hz, 3H), 3.48 (dd, *J* = 13.0, 8.1 Hz, 2H), 3.43 – 3.34 (m, 4H), 3.13 (dd, *J* = 12.1, 6.0 Hz, 1H), 2.86 – 2.77 (m, 2H), 2.67 – 2.57 (m, 3H, $CH_3COCH_2CH_2$), 2.53 – 2.28 (m, 6H, $CH_3COCH_2CH_2$), 2.14 (s, 3H, $CH_3COCH_2CH_2$), 2.05 (s, 3H, $CH_3COCH_2CH_2$), 2.03 (s, 3H, CH_3CO), 2.02 (s, 3H, CH_3CO), 1.96 (s, 6H, 2 x CH_3CO), 1.77 (s, 2H, CH_3CO), 1.75 (s, 2H, CH_3CO), 1.59 (s, 3H, CH_3CO), 1.53 (s, 3H, CH_3CO). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.75, 206.74, 171.66, 170.91, 170.61, 170.53, 169.75, 169.46, 169.23, 168.90, 167.55, 165.26, 155.91, 143.80, 143.64, 141.27, 141.24, 138.04, 137.93, 137.75, 137.37, 135.66, 135.06, 133.53, 133.47, 133.39, 133.35, 133.29, 133.17, 130.11, 129.88, 129.80, 129.72, 129.60, 129.49, 129.28, 129.07, 128.70, 128.44, 128.34, 128.30, 128.25, 128.08, 128.06, 127.92, 127.89, 127.86, 127.77, 127.73, 127.65, 127.56, 127.10, 127.06, 125.13, 120.65, 120.00, 109.99, 101.91, 101.90, 101.36, 101.32, 101.26, 100.73, 100.17, 100.16, 99.76, 79.11, 75.24, 73.63, 73.61, 73.58, 73.05, 72.81, 72.62, 71.67, 71.56, 70.63, 69.49, 69.44, 69.03, 68.92, 67.30, 67.17, 62.01, 54.16, 52.67, 47.09, 38.12, 29.81, 29.44, 28.02, 23.28, 23.07, 20.84, 20.81, 20.74, 20.67, 20.56, 19.96. HRMS: $C_{178}H_{185}N_3O_{63}$ $[M+2H]^{2+}$ calcd: m/z: 1688.0776, obsd: 1688.0627.



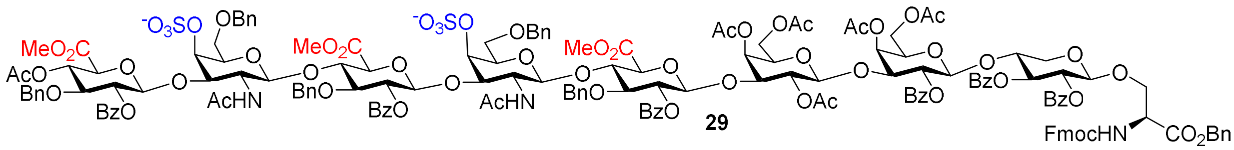
N-Fluorenylmethyloxycarbonyl-O-[2-O-benzoyl-3-O-benzyl-β-D-glucopyranosyl-(1→3)-2-N-acetyl-6-O-benzyl-2-deoxy-β-D-galactopyranosyl-(1→4)-2-O-benzoyl-3-O-benzyl-β-D-glucopyranosyl-(1→3)-2-N-acetyl-6-O-benzyl-2-deoxy-β-D-galactopyranosyl-(1→4)2-O-benzoyl-3-O-benzyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-O-acetyl-β-D-galactopyranosyl-(1→3)-4,6-di-O-acetyl-2-O-benzoyl-β-D-galactopyranosyl-(1→4)-2,3-di-O-benzoyl-β-D-xylopyranosyl]-L-serine benzyl ester 28:



28

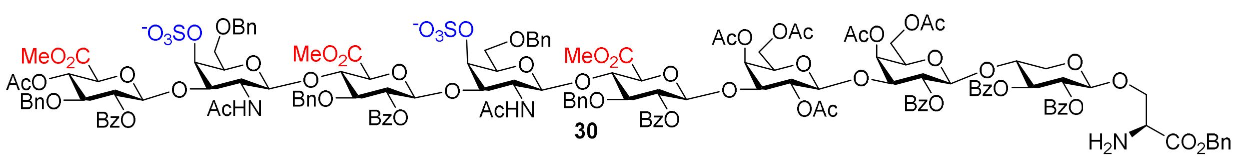
Compound **2** (90 mg, 26.7 μmol) was dissolved in THF/MeOH (10:1, 3.3 mL). The mixture was cooled to 0 °C then hydrazine acetate (NH_2NH_3OAc) (25 mg, 0.27 mmol) was added. The mixture was stirred at 0 °C for 2 h. After the reaction was completed, it was quenched with acetone (0.2 mL), stirred for another 0.5-1 h from 0 °C to room temperature and then, acetone was evaporated under vacuum. The residue was diluted with EtOAc, washed with saturated $NaHCO_3$ solution, 10% HCl and water and the organic layer was dried over Na_2SO_4 and concentrated *in vacuo* and the residue was purified with silica gel chromatography (DCM/MeOH, 40:1 → 15:1) to give compound **28** as a white solid in 90% yield (76.3 mg, 24 μmol). [α_D^{20}] = +400 (C = 0.0075, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (m, 10H), 7.87 (d, *J* = 7.2 Hz, 2H, 2 x aromatic CH), 7.77 (dd, *J* = 7.4, 2.5 Hz, 2H, 2 x aromatic CH), 7.62 – 7.57 (m, 2H, 2 x aromatic CH), 7.56 – 7.52 (m, 4H, 4 x aromatic CH), 7.48 – 7.39 (m, 12H, 12 x aromatic CH), 7.39 – 7.32 (m, 4H, 4 x aromatic CH), 7.30 – 7.23 (m, 10H, 10 x aromatic CH), 7.21 (m, 4H, 4 x aromatic CH), 7.17 – 7.07 (m, 19H, 19 x aromatic CH), 5.60 (d, *J* = 6.5 Hz, 2H, 2 x AcNH), 5.57 – 5.53 (m, 2H), 5.42 (d, *J* = 3.2 Hz, 1H), 5.36 – 5.30 (m, 2H), 5.27 (dd, *J* = 11.3, 7.3 Hz, 3H), 5.15 (m, 5H), 5.00 – 4.94 (m, 4H, GalN H-1'), 4.79 (dd, *J* = 11.2, 7.2 Hz, 2H, GalN H-1", H-1), 4.74 – 4.68 (m, 3H, H-1), 4.64 (dd, *J* = 13.8, 8.1 Hz, 3H, 2 x H-1), 4.60 – 4.56 (m, 4H, H-1), 4.50 (m, 4H), 4.42 (m, 2H), 4.35 (m, 4H, H-1), 4.32 – 4.27 (m, 2H), 4.25 (d, *J* = 7.5 Hz, 1H), 4.21 (d, *J* = 7.7 Hz, 1H), 4.16 (dd, *J* = 13.4, 7.3 Hz, 2H), 4.09 (s, 1H), 4.04 – 3.96 (m, 6H), 3.92 – 3.87 (m, 3H), 3.86 – 3.81 (m, 2H), 3.78 – 3.71 (m, 4H), 3.70 (s, 3H, CO_2CH_3), 3.68 (s, 3H, , CO_2CH_3), 3.66 – 3.63 (m, 3H), 3.62 (s, 3H, , CO_2CH_3), 3.60 (d, *J* = 2.5 Hz, 1H), 3.51 (m, 4H, GalN H-2"), 3.32 (dd, *J* = 15.5, 7.6 Hz, 2H, GalN H-1'), 3.12 (dd, *J* = 12.3, 6.0 Hz, 1H), 2.73 (s, 2H), 2.04 (s, 3H, CH_3CO), 2.02 (s, 3H, CH_3CO), 2.00 (s, 3H, CH_3CO), 1.93 (s, 3H, CH_3CO), 1.88 (s, 3H, CH_3CO), 1.43 (s, 3H, CH_3CO), 1.25 (s, 6H, 2 x CH_3CO). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.08, 170.89, 170.60, 170.58, 170.53, 169.72, 169.46, 169.41, 168.93, 168.77, 168.69, 167.43, 165.25, 165.18, 164.82, 164.63, 164.46, 164.32, 155.91, 143.80, 143.64, 141.27, 141.23, 138.14, 138.09, 137.97, 137.81, 137.17, 135.06, 133.63, 133.43, 133.39, 133.28, 133.17, 130.10, 129.87, 129.84, 129.83, 129.75, 129.57, 129.48, 129.36, 129.30, 129.26, 129.23, 128.67, 128.64, 128.46, 128.43, 128.34, 128.33, 128.29, 128.05, 128.04, 127.93, 127.88, 127.86, 127.76, 127.72, 127.65, 127.56, 127.53, 127.52, 127.35, 127.33, 127.09, 127.06, 125.11, 119.99, 109.99, 101.92, 101.28, 101.15, 100.97, 99.75, 99.54, 98.57, 80.33, 79.74, 79.48, 78.74, 78.67, 76.55, 76.06, 75.24, 74.74, 74.11, 73.67, 73.44, 73.42, 73.05, 73.01, 72.89, 72.69, 72.25, 72.12, 71.64, 71.58, 71.30, 70.68, 70.06, 69.48, 69.12, 68.97, 68.80, 67.29, 67.17, 62.08, 61.91, 60.91, 55.99, 54.38, 54.16, 53.06, 52.89, 52.83, 52.73, 47.09, 31.93, 29.70, 29.66, 29.37, 23.06, 22.85, 22.70, 20.81, 20.73, 20.70, 20.68, 20.53, 19.78, 14.14. HSMS: $C_{168}H_{173}N_3O_{59}$ $[M+2Na]^{2+}$ calcd: m/z: 1612.0240, obsd: 1612.0148.

CS-A octasaccharide 29:



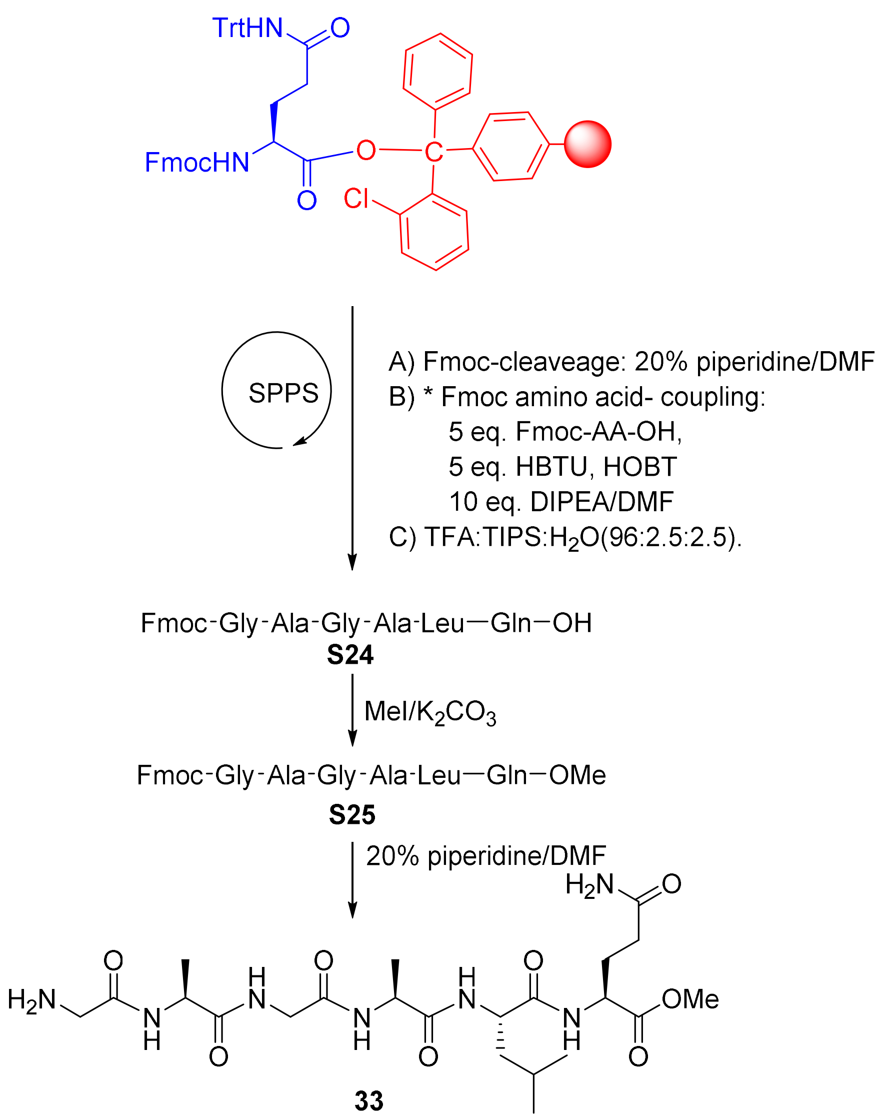
Compound **28** (40 mg, 12.6 μmol) was dissolved in anhydrous DMF (1 mL), followed by addition of SO_3-NEt_3 (91.2 mg, 0.05 mmol). The resulting mixture was stirred at 50 °C overnight. After cooling down to room temperature, it was diluted with MeOH-DCM (0.5 mL) and subjected into LH-20 column chromatography (DCM/MeOH, 1:1) for purification to provide compound **29** as a white solid in 81% yield (34 mg, 10.2 μmol). $[\alpha_D^{20}]$ = -117.6 (C = 0.017, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 – 7.88 (m, 12H, 12 x aromatic CH), 7.77 (dd, *J* = 7.4, 2.5 Hz, 2H, 2 x aromatic CH), 7.55 (m, 6H, 6 x aromatic CH), 7.50 – 7.41 (m, 9H, 9 x aromatic CH), 7.41 – 7.32 (m, 9H, 9 x aromatic CH), 7.28 (m, 3H, 3 x aromatic CH), 7.25 – 7.08 (m, 23H, 23 x aromatic CH), 7.05 – 6.96 (m, 5H, 5 x aromatic CH), 5.62 – 5.49 (m, 5H, 2 x AcNH), 5.39 – 5.23 (m, 7H), 5.14 (d, *J* = 8.8 Hz, 2H), 4.97 (dd, *J* = 19.3, 8.3 Hz, 5H), 4.90 – 4.73 (m, 7H), 4.65 (d, *J* = 8.4 Hz, 3H), 4.59 – 4.50 (m, 5H), 4.39 – 4.28 (m, 7H), 4.23 (d, *J* = 9.1 Hz, 3H), 4.15 (dd, *J* = 14.1, 6.7 Hz, 3H), 4.04 (dd, *J* = 22.4, 9.8 Hz, 5H), 3.93 (m, 6H), 3.82 – 3.76 (m, 4H), 3.72 – 3.58 (m, 13H), 3.49 (s, 2H), 3.13 (d, *J* = 12.8 Hz, 3H), 2.04 (dd, *J* = 13.4, 7.4 Hz, 9H, 3 x CH_3CO), 1.98 – 1.89 (m, 9H, 3 x CH_3CO), 1.61 (d, *J* = 7.6 Hz, 6H, 2 x CH_3CO). ^{13}C NMR (126 MHz, cdcl$_3$) δ 171.70, 170.62, 170.54, 169.81, 169.63, 169.46, 168.97, 168.18, 165.26, 165.19, 164.45, 164.39, 155.91, 143.79, 143.64, 141.26, 141.23, 138.44, 137.78, 135.05, 133.48, 133.39, 133.17, 130.11, 129.87, 129.80, 129.72, 129.49, 129.37, 129.27, 128.99, 128.70, 128.58, 128.52, 128.45, 128.43, 128.36, 128.33, 128.30, 128.28, 128.26, 128.23, 128.19, 128.12, 128.05, 128.03, 127.91, 127.80, 127.76, 127.72, 127.56, 127.39, 127.09, 127.06, 125.13, 125.10, 119.99, 101.89, 101.86, 101.30, 99.75, 97.74, 97.71, 80.89, 79.76, 77.26, 76.32, 75.23, 74.46, 73.51, 73.15, 72.35, 71.68, 71.54, 71.22, 70.65, 70.43, 69.63, 69.47, 69.08, 68.80, 67.29, 67.16, 62.01, 60.88, 54.16, 52.67, 52.46, 51.82, 47.09, 45.68, 29.69, 23.11, 20.80, 20.77, 20.73, 20.65, 20.56, 20.00. HRMS: $C_{168}H_{171}N_3O_{65}S_2^{2-}$ $[M-2H]^{2-}$ calcd: 1667.9844, obsd: 1667.9734.

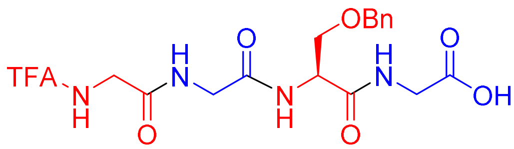
CS-A octasaccharide 30:



Compound **29** (10 mg, 3 μmol) was dissolved in dry DMF (0.4 mL), followed by addition of piperidine (20 μL). The mixture was stirred under room temperature for 20 minutes and the product **30** (8.6 mg, 2.7 μmol) (93% yield) was purified with LH-20 (DCM/MeOH, 1:1) and prep. TLC as a white solid. $[\alpha_D^{20}]$ = -58.6 (C = 0.0583, DCM). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 – 7.89 (m, 12H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.60 – 7.49 (m, 7H), 7.48 – 7.37 (m, 11H), 7.30 (d, *J* = 5.3 Hz, 3H), 7.26 – 7.11 (m, 19H), 7.09 – 6.96 (m, 6H), 6.83 (d, *J* = 2.7 Hz, 1H), 5.56 (dd, *J* = 18.9, 16.6 Hz, 3H), 5.39 – 5.23 (m, 6H), 5.15 (dd, J = 17.1, 5.5 Hz, 3H), 5.09 – 4.94 (m, 7H), 4.81 (dd, J = 30.3, 19.5 Hz, 5H), 4.67 (d, J = 4.8 Hz, 4H), 4.60 – 4.44 (m, 6H), 4.40 – 4.29 (m, 5H), 4.26 – 4.14 (m, 4H), 4.12 – 4.00 (m, 7H), 3.99 – 3.88 (m, 7H), 3.79 (dd, J = 11.3, 6.5 Hz, 4H), 3.67 (dd, J = 28.7, 11.3 Hz, 12H), 3.49 (s, 2H), 3.19 (dd, J = 15.0, 9.2 Hz, 2H), 2.09 – 2.00 (m, 9H), 1.99 – 1.89 (m, 9H), 1.58 (d, J = 38.3 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.05, 171.89, 170.62, 169.73, 168.96, 165.29, 165.12, 164.38, 164.33, 137.72, 135.40, 133.50, 133.34, 133.12, 130.93, 130.55, 130.10, 129.85, 129.49, 129.48, 129.40, 128.68, 128.47, 128.37, 128.29, 128.24, 128.20, 128.15, 128.11, 127.96, 127.85, 127.80, 127.51, 127.44, 127.24, 102.07, 101.98, 101.97, 101.96, 99.67, 99.62, 99.62, 99.59, 77.23, 75.39, 73.21, 73.20, 71.66, 71.62, 70.70, 69.52, 69.03, 66.84, 54.60, 31.94, 29.71, 29.38, 22.71, 20.82, 20.81, 20.73, 20.56, 14.15, 1.03. HRMS: $C_{153}H1_{61}N_3O_{63}S_2^{2-}$ $[M-2H]^{2-}$ calcd: 1556.9503, obsd: 1556.9376.

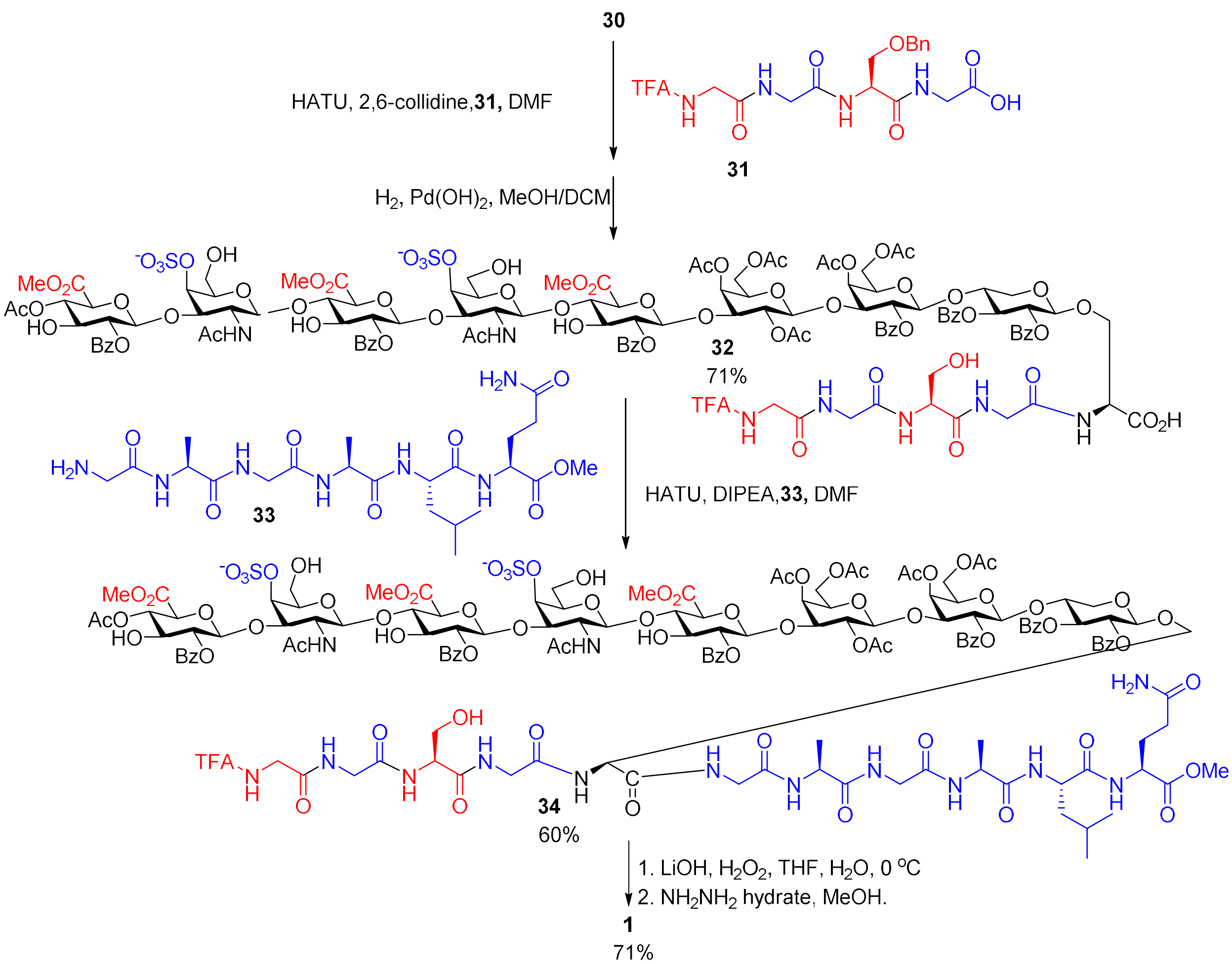
Synthesis of Glycopeptide:



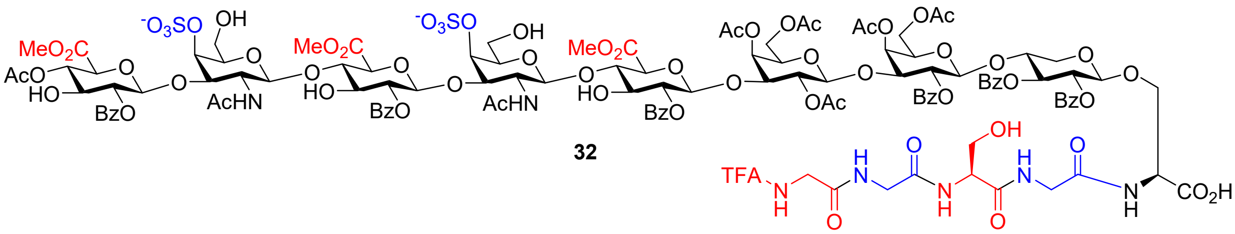


31

Peptide 31 was synthesized following the general procedure for solid phase peptide synthesis. The crude peptide was purified using HPLC (solvent A: H_2O (0.01% TFA; solvent B: acetonitrile, 5 to 40% in 40 min) to afford pure peptide **31** as a white solid in 55% yield. ^1H NMR (500 MHz, CD_3OD) δ 7.40 – 7.21 (m, 5H, 5 x aromatic CH), 4.66 (dd, J = 5.8, 4.7 Hz, 1H, Ser-CH), 4.59 – 4.50 (m, 2H, $PhCH_2$), 4.04 – 3.86 (m, 6H, 3 x Gly-CH_2), 3.80 (dd, J = 9.9, 5.8 Hz, 1H, Ser-CH_2), 3.74 (dd, J = 9.9, 4.7 Hz, 1H, Ser-CH_2). ^{13}C NMR (126 MHz, CD_3OD) δ 171.17, 170.93, 170.12, 169.23, 158.23, 157.93, 137.80, 127.94, 127.50, 127.31, 117.13, 114.85, 72.80, 69.14, 53.31, 48.09, 48.04, 47.92, 47.87, 47.84, 47.82, 47.81, 47.78, 47.75, 47.71, 47.71, 47.61, 47.60, 47.58, 47.54, 47.46, 47.44, 47.43, 47.41, 47.24, 47.23, 47.07, 42.16, 41.84, 40.46. HRMS: $C_{18}H_{21}F_3N_4O_7$ $[M+H]^+$ calcd: 463.1435, obsd: 463.1427.



Glycopeptide **32**:



32

Compound **30** (5 mg, 1.6 μmol) and tetrapeptide **31** (5.2 mg, 11.2 μmol) were dissolved in anhydrous DMF (0.4 mL), followed by addition of HATU (4.3 mg, 11.2 μmol) and 2,6-collidine (2.7 μL, 16.1 μmol). The mixture was stirred for 3 h at room temperature, then loaded onto a LH-20 column (DCM/MeOH, 1:1) followed by prep. TLC for purification to provide the glycopeptide as a white solid in 90% yield (5 mg, 1.4 μmol). Then the resulting glycopeptide (3 mg, 1.15 μmol) was dissolved in MeOH/DCM (4:1, 1 mL) followed by adding $Pd(OH)_2C$ (10 mg). The resulting mixture was stirred under H_2 atmosphere. The reaction was monitored by mass spectrometry till completion, then diluted with MeOH and filtered. After concentration, the residue was purified by LH-20 (pure MeOH) to afford compound **32** as a white solid in 75% yield (2.6 mg, 0.86 μmol). $[\alpha_D^{20}]$ = -117.6 (C = 0.017, DCM). ^{1}H NMR (500 MHz, CD_3OD) δ 8.09 – 7.89 (m, 12H), 7.66 – 7.38 (m, 18H), 5.57 – 5.49 (m, 2H), 5.37 – 5.26 (m, 4H), 5.21 – 5.06 (m, 7H), 5.00 – 4.96 (m, 2H), 4.86 – 4.74 (m, 5H), 4.64 (dd, J = 11.3, 5.2 Hz, 3H), 4.51 – 4.42 (m, 4H), 4.36 – 4.29 (m, 3H), 4.22 (dd, J = 5.7, 3.2 Hz, 1H), 4.16 (d, J = 9.9 Hz, 1H), 4.09 (dd, J = 11.0, 4.4 Hz, 3H), 4.05 – 4.00 (m, 4H), 3.99 – 3.92 (m, 7H), 3.86 – 3.79 (m, 8H), 3.79 – 3.72 (m, 11H), 3.72 – 3.64 (m, 6H), 3.56 – 3.44 (m, 5H), 3.35 (d, J = 2.2 Hz, 2H), 3.23 – 3.13 (m, 3H), 2.37 – 2.26 (m, 4H), 2.09 – 2.02 (m, 9H), 1.98 (s, 3H), 1.87 (s, 3H), 1.63 (s, 6H), 1.53 (s, 3H). ^{13}C NMR (126 MHz, CD_3OD) δ 129.52, 129.38, 128.17, 128.13, 109.98, 48.10, 47.93, 47.88, 47.76, 47.59, 47.42, 47.25, 47.08, 31.67, 29.37, 29.35, 29.33, 29.31, 29.07, 22.34, 19.33, 13.04. HRMS: $C_{122}H_{138}F_3N_7O_{69}S_2^{2-}$ $[M-2H]^{2-}$ calcd: 1463.3471, obsd: 1463.3422; $[M-3H]^{3-}$ calcd: 975.2290, obsd: 975.2247.

Peptide 33:

Peptide **S24** was synthesized following the general procedure for solid phase peptide synthesis. Then the crude peptide **S24** (258.6 mg, 0.35 mmol) was dissolved in DMF (1 mL), followed by addition of MeI (0.125 mL, 1 mmol) and DIPEA (0.183 mL, 1 mmol). The mixture was stirred under room temperature overnight. The product was precipitated from diethyl ether and the crude was dissolved in DMF (1 mL), followed by addition of piperidine (26 μL). The resulting mixture was stirred for 1 h, then diluted with diethyl ether and the precipitate was collected and purified with HPLC (solvent A: H_2O (0.01% TFA; solvent B: acetonitrile, 5 to 40% in 40 min) to afford peptide **33** as a white solid in 30% yield over three steps. ^{1}H NMR (500 MHz, CD_3OD) δ 4.38 – 4.32 (m, 2H), 3.98 – 3.92 (m, 3H), 3.71 (s, 3H, CO_2CH_3), 3.61 – 3.55 (m, 1H), 3.40 (q, J = 7.4 Hz, 3H), 1.71 (dt, J = 9.2, 3.3 Hz, 2H), 1.45 – 1.43 (m, 6H, 2 x Ala-CH_3), 1.39 – 1.38 (m, 2H), 1.37 – 1.37 (m, 2H), 0.96 (d, J = 6.2 Hz, 3H, Leu-CH_3), 0.91 (d, J = 6.0 Hz, 3H, Leu-CH_3). ^{13}C NMR (126 MHz, CD_3OD) δ 174.09, 173.78, 172.02, 170.50, 63.00, 62.98, 62.97, 52.09, 52.07, 52.05, 51.78, 51.72, 51.40, 49.67, 49.60, 48.99, 48.12, 47.95, 47.78, 47.60, 47.43, 47.26, 47.09, 46.49, 42.59, 42.23, 42.20, 42.17, 40.15, 39.64, 29.58, 26.73, 25.43, 24.65, 24.53, 24.42, 22.88, 22.03, 20.48, 20.45, 17.33, 16.27, 16.25, 16.14, 15.98, 15.25, 8.88. HRMS: $C_{22}H_{39}N_7O_8$ $[M+H]^+$ calcd: 530.2933, obsd: 530.2956.

Glycopeptide **32** (3 mg, 1μmol) and hexapeptide **33** (5.3 mg, 10 μmol) were dissolved in anhydrous DMF. To that solution, HATU (0.57 mg, 1.5 μmol) and DIPEA (0.26 μL, 1.5 μmol) were added. The reaction was stirred for 4 h, then loaded to LH-20 (pure MeOH), and HPLC was used for purification to give glycopeptide **34** as a white solid in 60% yield (2.1 mg, 0.6 μmol). [α_D^{20}] = +20 (C = 0.05, DCM). ^{1}H NMR (500 MHz, CD_3OD) δ 8.09 – 7.88 (m, 12H), 7.67 – 7.37 (m, 18H), 5.52 (dd, *J* = 8.7, 2.9 Hz, 2H), 5.35 (t, *J* = 4.8 Hz, 2H), 5.28 (t, *J* = 2.8 Hz, 2H), 5.21 – 5.07 (m, 7H), 5.00 – 4.96 (m, 2H), 4.82 – 4.75 (m, 4H), 4.49 – 4.27 (m, 12H), 4.16 (d, *J* = 9.8 Hz, 6H), 4.10 – 3.90 (m, 14H), 3.90 – 3.68 (m, 20H), 3.50 – 3.43 (m, 4H), 3.21 – 3.11 (m, 6H), 2.31 (q, *J* = 6.8 Hz, 6H), 2.19 (q, *J* = 7.4 Hz, 7H), 2.10 – 1.85 (m, 18H), 1.67 (m, 22H), 1.41 – 1.31 (m, 12H), 1.01 – 0.94 (m, 5H), 0.91 (m, 5H). ^{13}C NMR (based on bsgHSQCAD) (126 MHz, CD_3OD) δ 133.39, 133.48, 132.14, 132.05, 55.84, 51.89, 51.84, 51.94, 23.41, 29.80, 26.53, 33.31, 22.57, 17.10, 13.94, 22.63, 4.12. HRMS: $C_{144}H_{175}F_3N_{14}O_{76}S_2^{2-}$ [M-2H]$^{2-}$ calcd: 1718.9849, obsd: 1718.9774; [M-3H]$^{3-}$ calcd: 1145.6542, obsd: 1145.6510.

Glycopeptide 1:

Compound **34** (2 mg), was dissolved in THF/H_2O (1:1, 0.4 mL) to which 0.25 M LiOH and H_2O_2 solution were added to maintain pH around 9.0 under 0 °C. When MS analysis showed the complete disappearance of the resulting material (2 h at 0 °C), the mixture was neutralized by 1 M AcOH solution. Then the solution was loaded onto a LH-20 column (pure MeOH) to remove Li salt. The resulting glycopeptide was dissolved in MeOH (0.4 mL), followed by addition of hydrazine hydrate (0.1 mL). The mixture was stirred overnight at room temperature and then neutralized by acetone under 0 °C for 30 minutes. The solution was concentrated and loaded onto a Sephadex G-15 column (H_2O) to afford compound **1** (1 mg, 71% yield). [α_D^{20}] = -240.04 (C = 0.0042, DCM). ^{1}H NMR (500 MHz, D_2O) δ 4.64 – 4.48 (m, 5H), 4.44 – 4.35 (m, 3H), 4.34 – 4.25 (m, 3H), 4.18 (m, 3H), 4.02 (dd, *J* = 12.6, 6.7 Hz, 2H), 3.92 (m, 7H), 3.80 (m, 5H), 3.70 – 3.62 (m, 8H), 3.57 (m, 7H), 3.53 – 3.49 (m, 3H), 3.46 – 3.41 (m, 2H), 3.34 (m, 4H), 3.25 – 3.14 (m, 4H), 2.06 – 1.93 (m, 4H), 1.92 – 1.83 (m, 6H), 1.64 (m, 3H), 1.52 – 1.42 (m, 4H), 1.24 (m, 5H), 1.17 (d, *J* = 6.9 Hz, 3H), 1.13 (m, 3H), 0.93 (m, 2H), 0.79 (d, *J* = 5.6 Hz, 3H), 0.73 (d, *J* = 5.5 Hz, 3H). ^{13}C NMR (126 MHz, D_2O) based on HSQC data δ 152.42, 152.00, 104.56, 103.87, 103.72, 103.34, 102.98, 101.29, 101.06, 101.03, 82.63, 80.20, 76.65, 76.43, 75.32, 74.47, 73.79, 72.25, 72.04, 71.56, 69.81, 69.18, 68.70, 68.06, 60.96, 60.33, 51.48, 49.73, 49.52, 42.21, 38.44, 37.81, 28.96, 25.68, 23.03, 22.55, 21.91, 21.01, 20.17, 16.62, 15.93, 0.82. HRMS: $C_{84}H_{132}N_{14}O_{63}S_2^{2-}$ [M-2H]$^{2-}$ calcd: 1204.3504, obsd 1204.3486; [M-3H]$^{3-}$ calcd: 802.5645, obsd: 802.5599.

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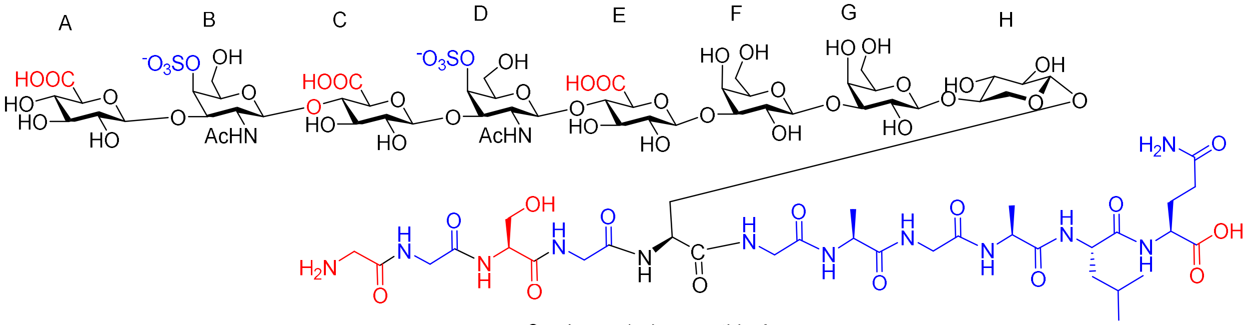
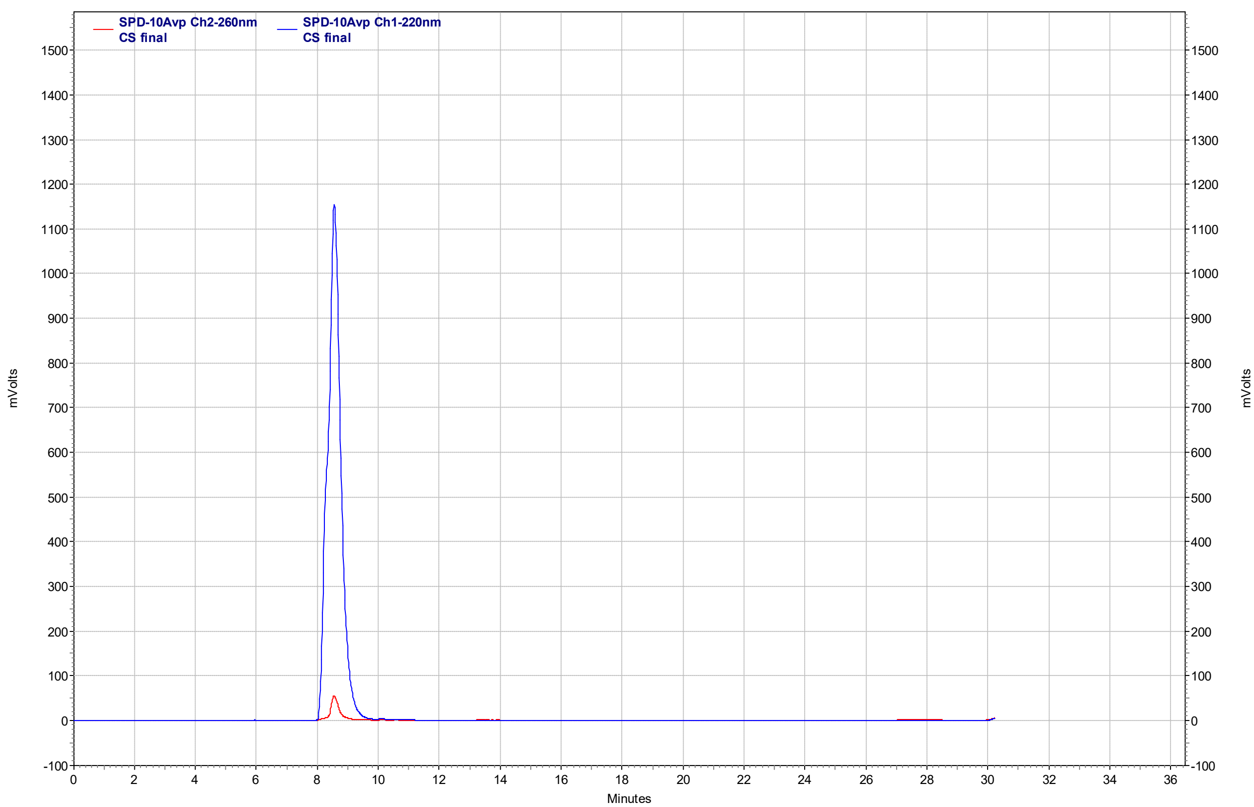


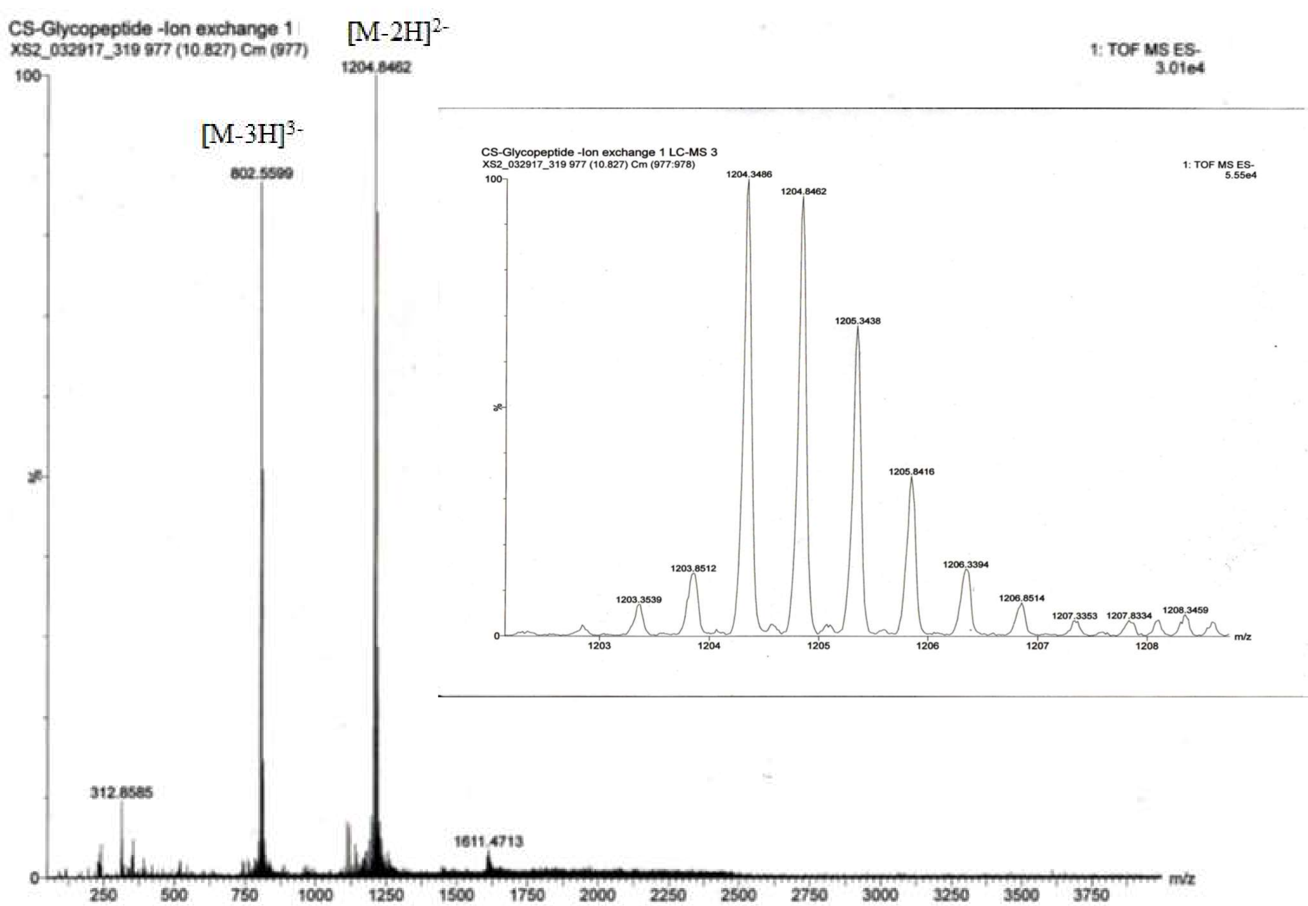
Syndecan-1 glycopeptide **1**

HPLC:

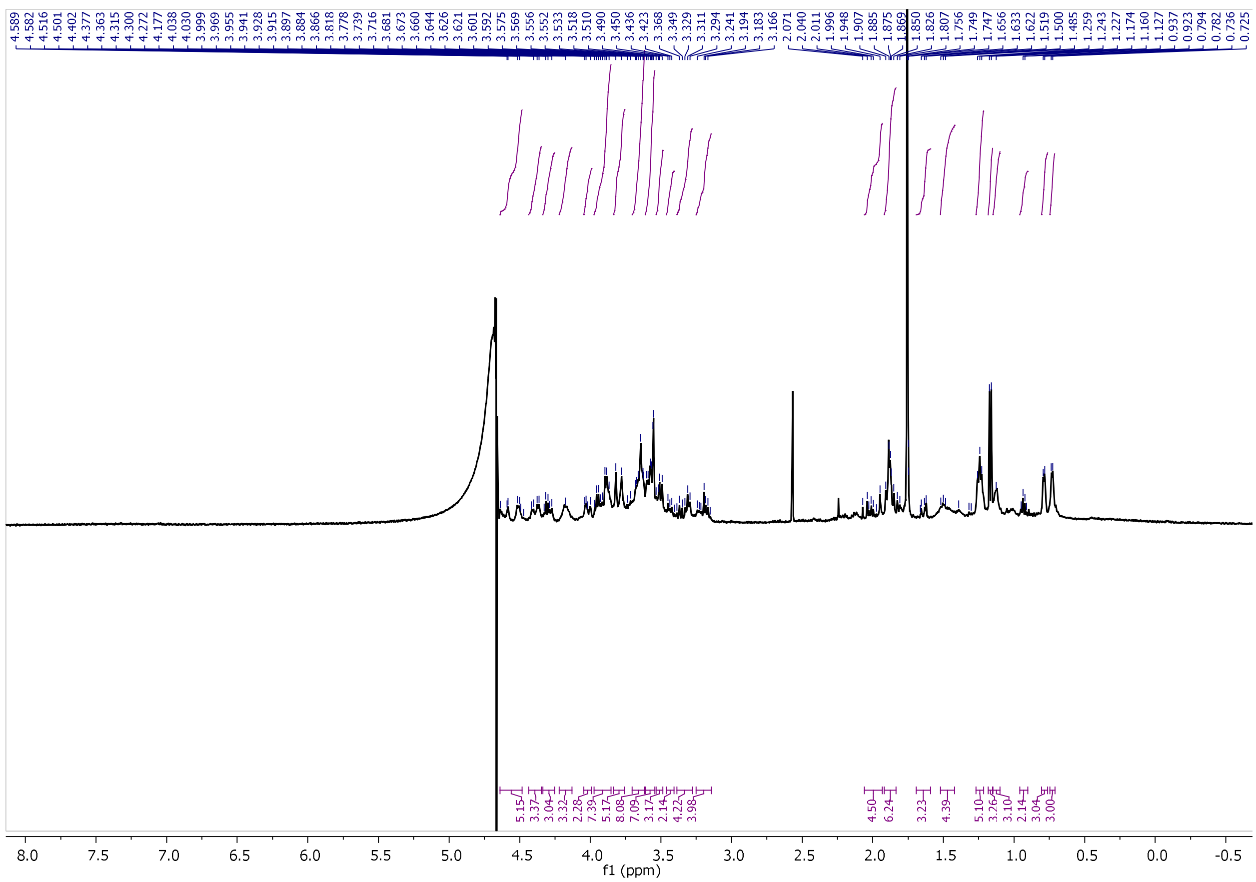
HPLC mobile phase: 40% to 95% B in A over 30 min (solvent A: H_2O; solvent B: CH_3CN). Flow rate: 0.4 mL/min. Detection wavelength: 220 nm. HPLC column: Agilent, ZPRBAX 300SB-C18, 3.5 µm, 4.6x150 mm.



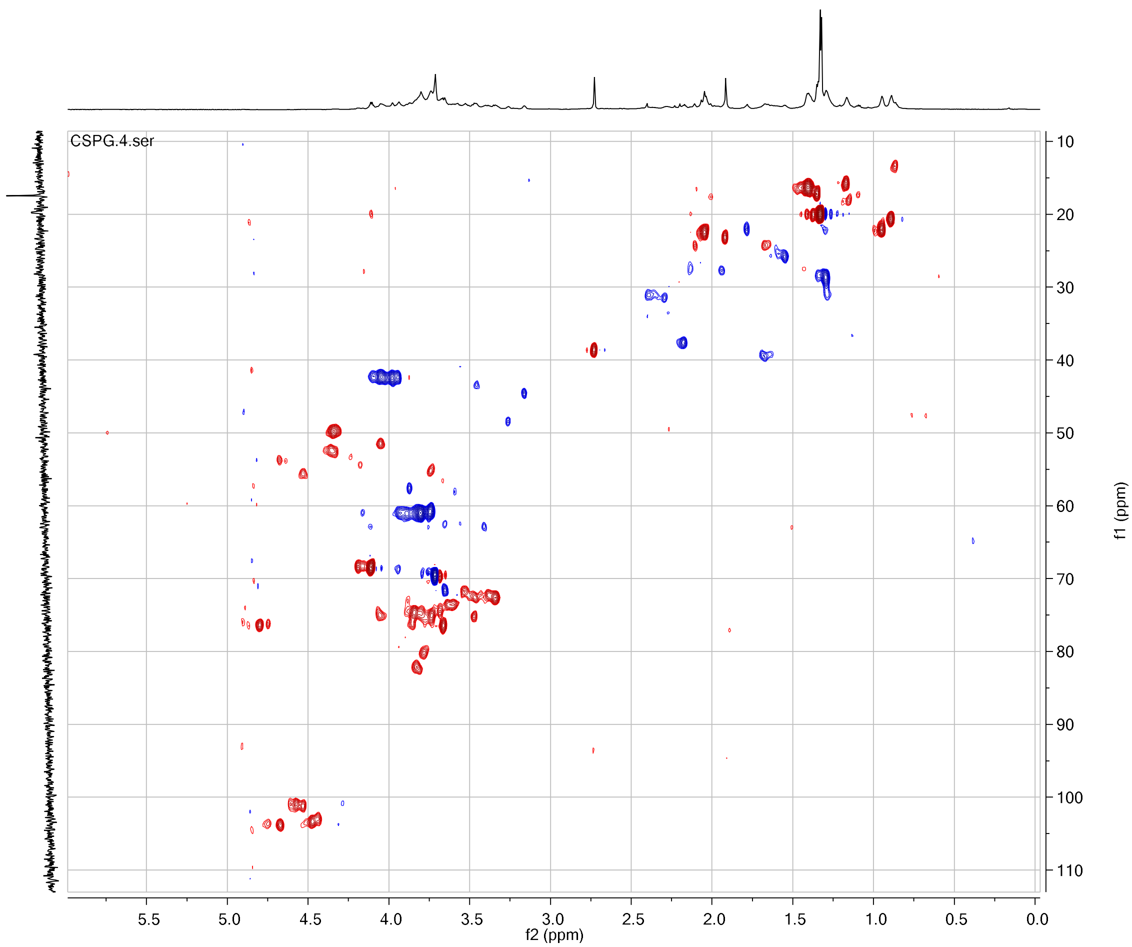
HRMS of CSPG **1**



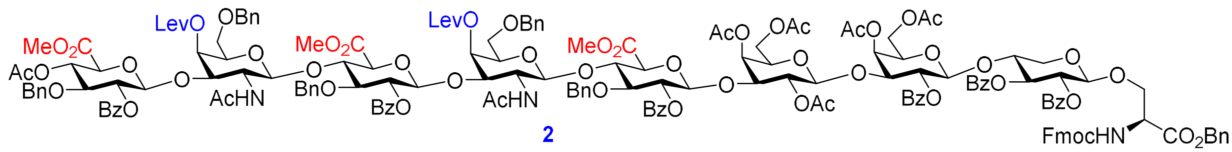
^{1}H-NMR (CD_3OD, 900 MHz) of **1**



bsgHSQC (CD_3OD, 500 MHz) of **1**



^{1}H-NMR ($CDCl_3$, 500 MHz) of **2**



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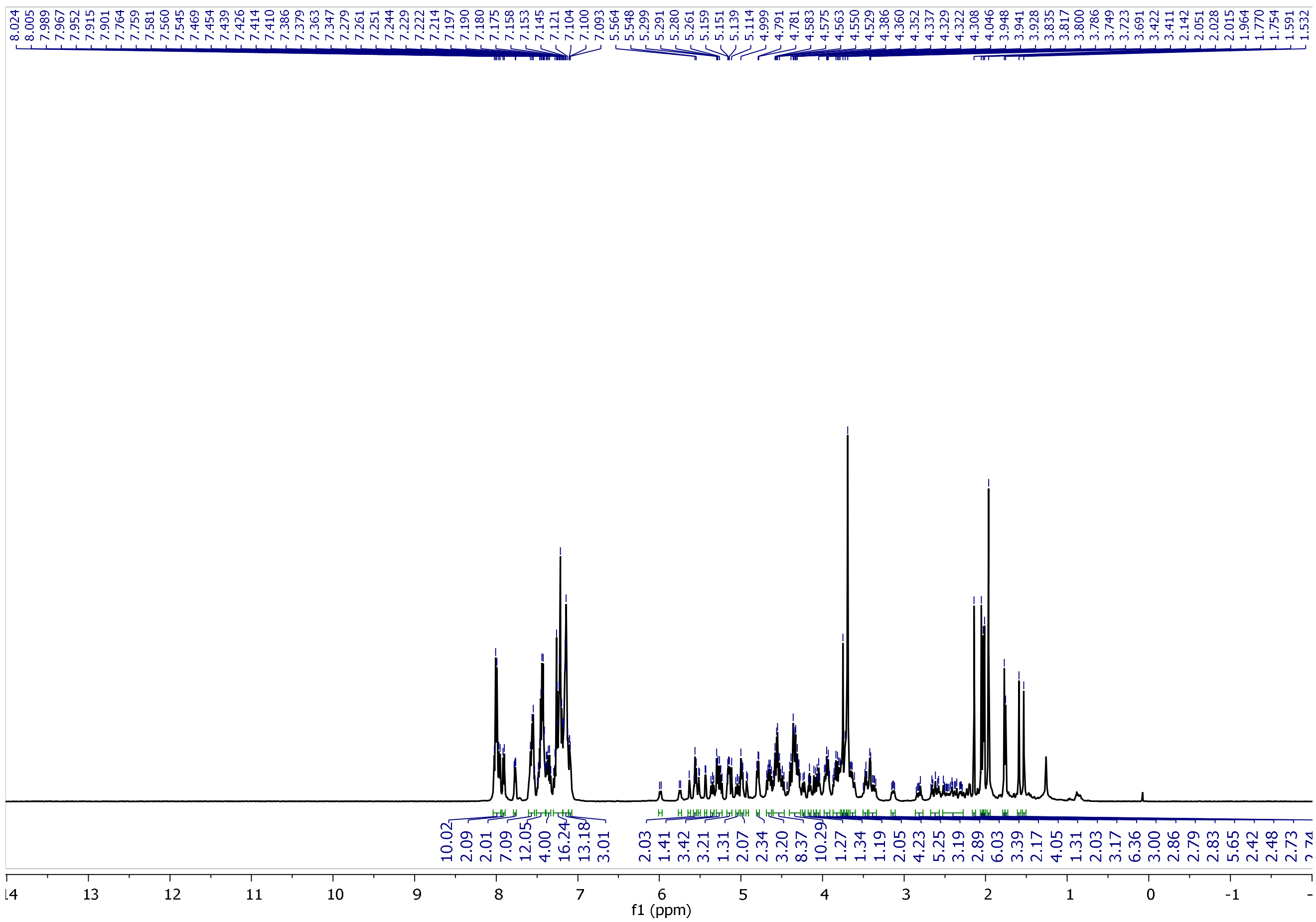
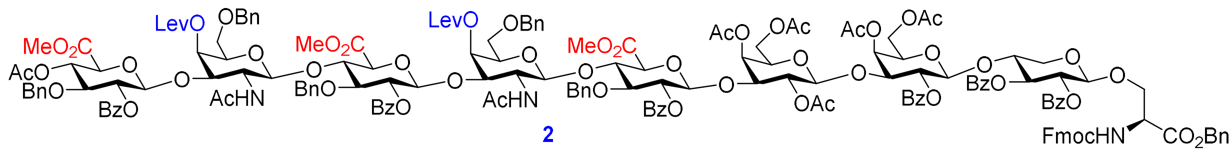


^{13}C-NMR ($CDCl_3$, 126 MHz) of **2**



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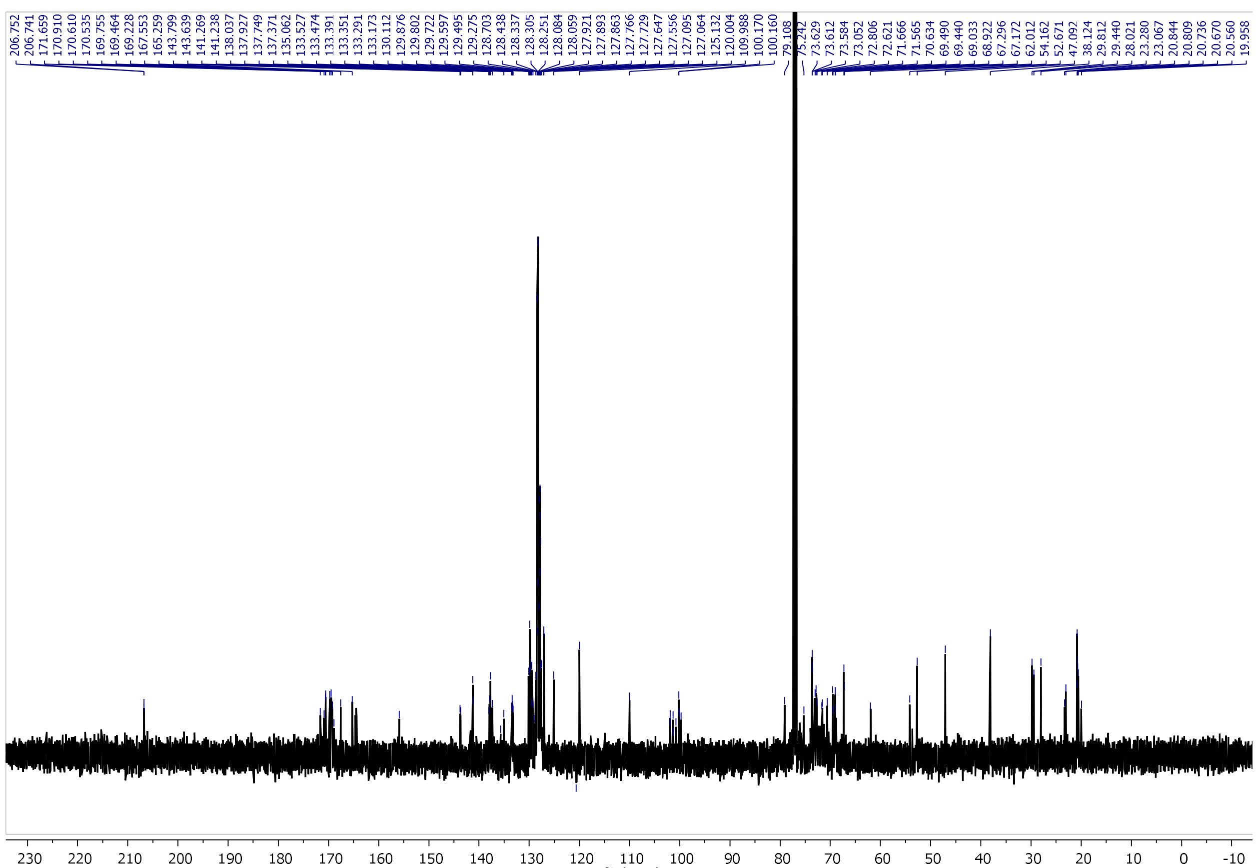
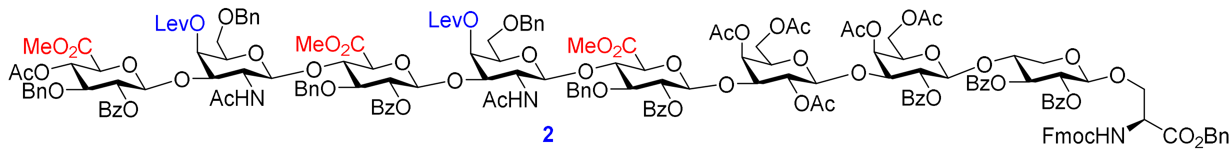


gCOSY ($CDCl_3$, 500 MHz) of **2**



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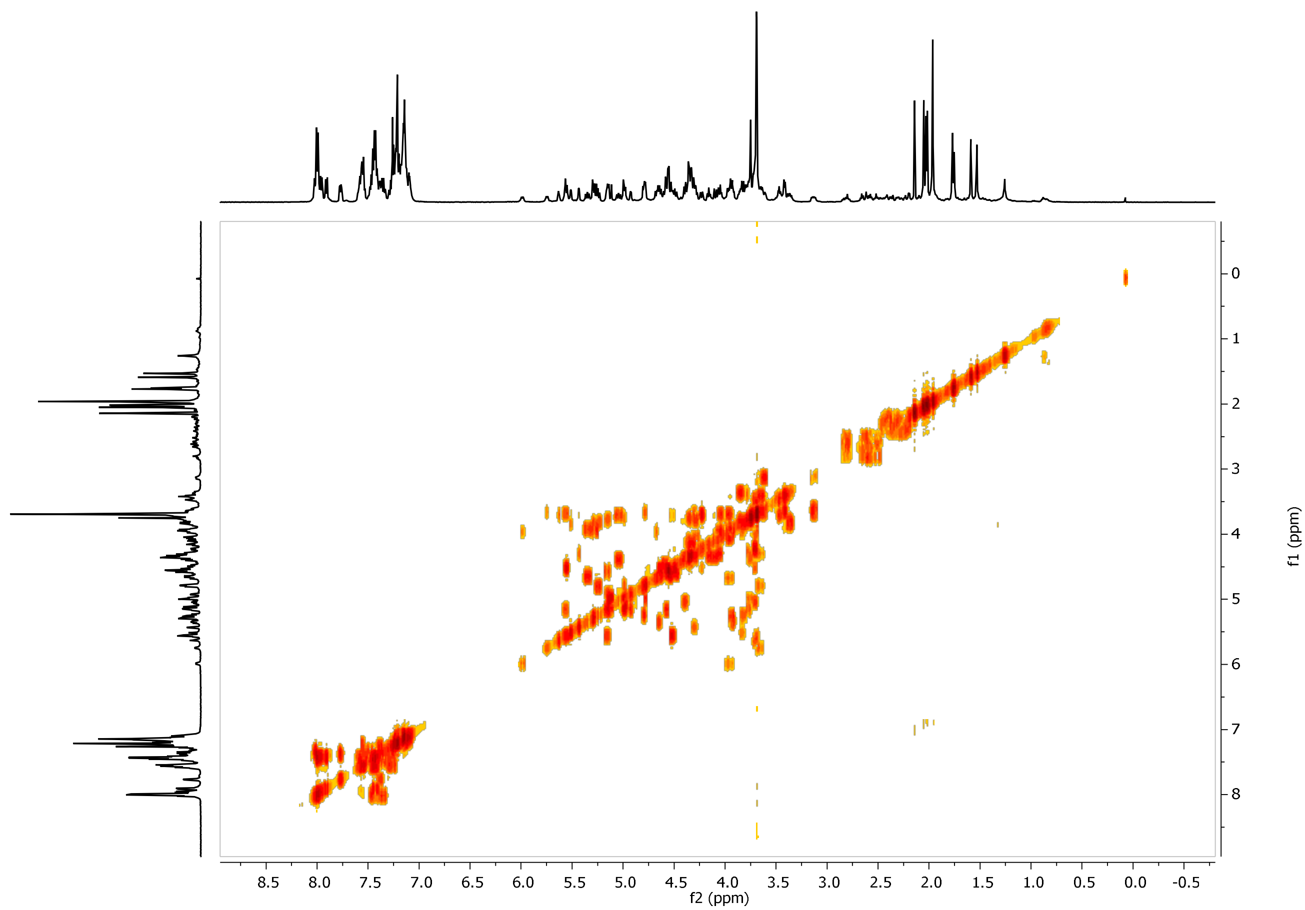
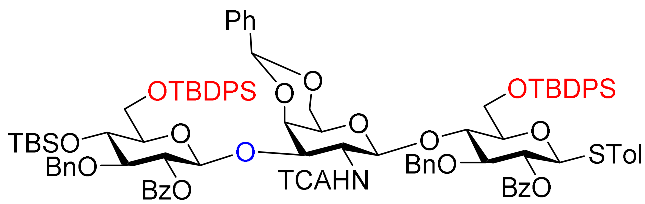


^{1}H-NMR ($CDCl_3$, 500 MHz) of **3**



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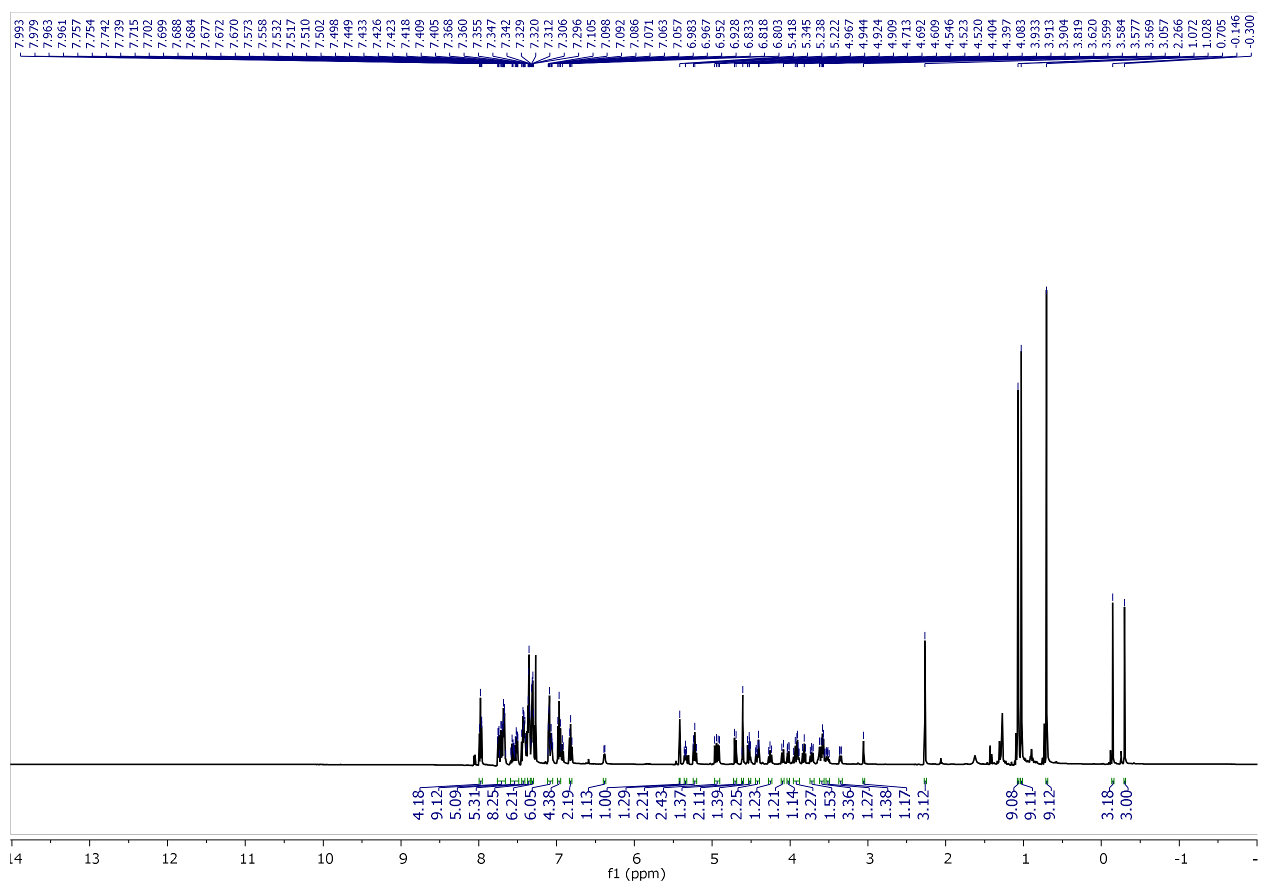
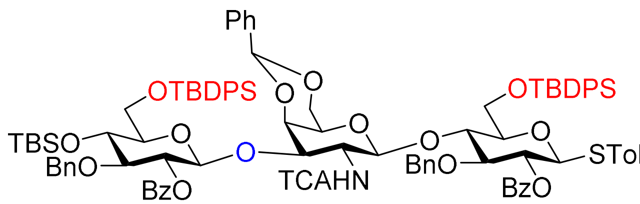


^{13}C-NMR (CDCl$_3$, 126 MHz) of **3**



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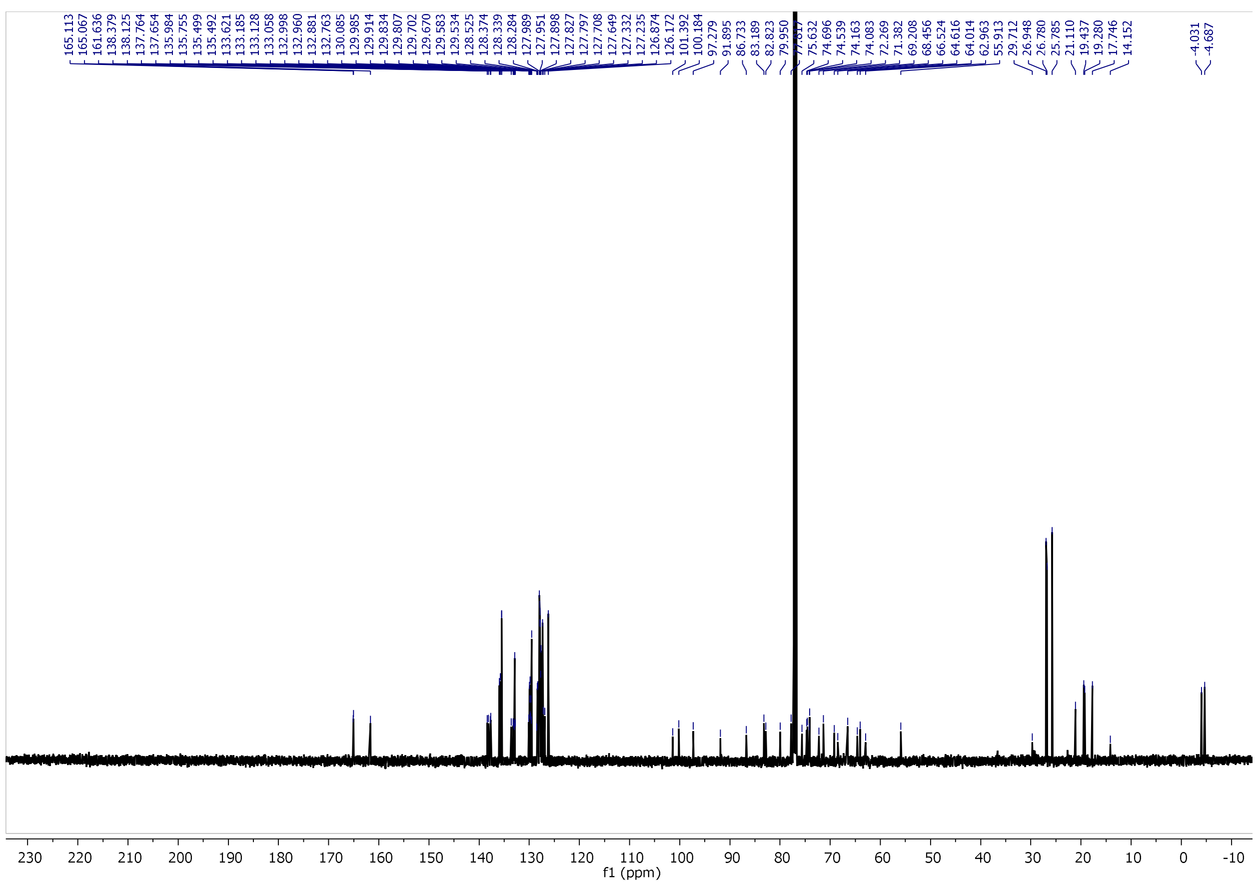
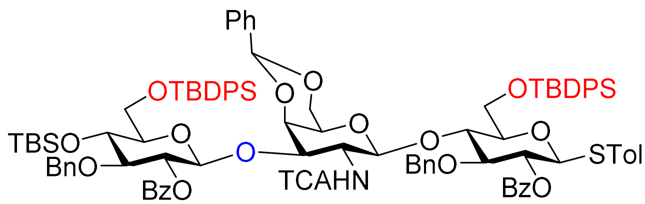


gCOSY ($CDCl_3$, 500 MHz) of **3**



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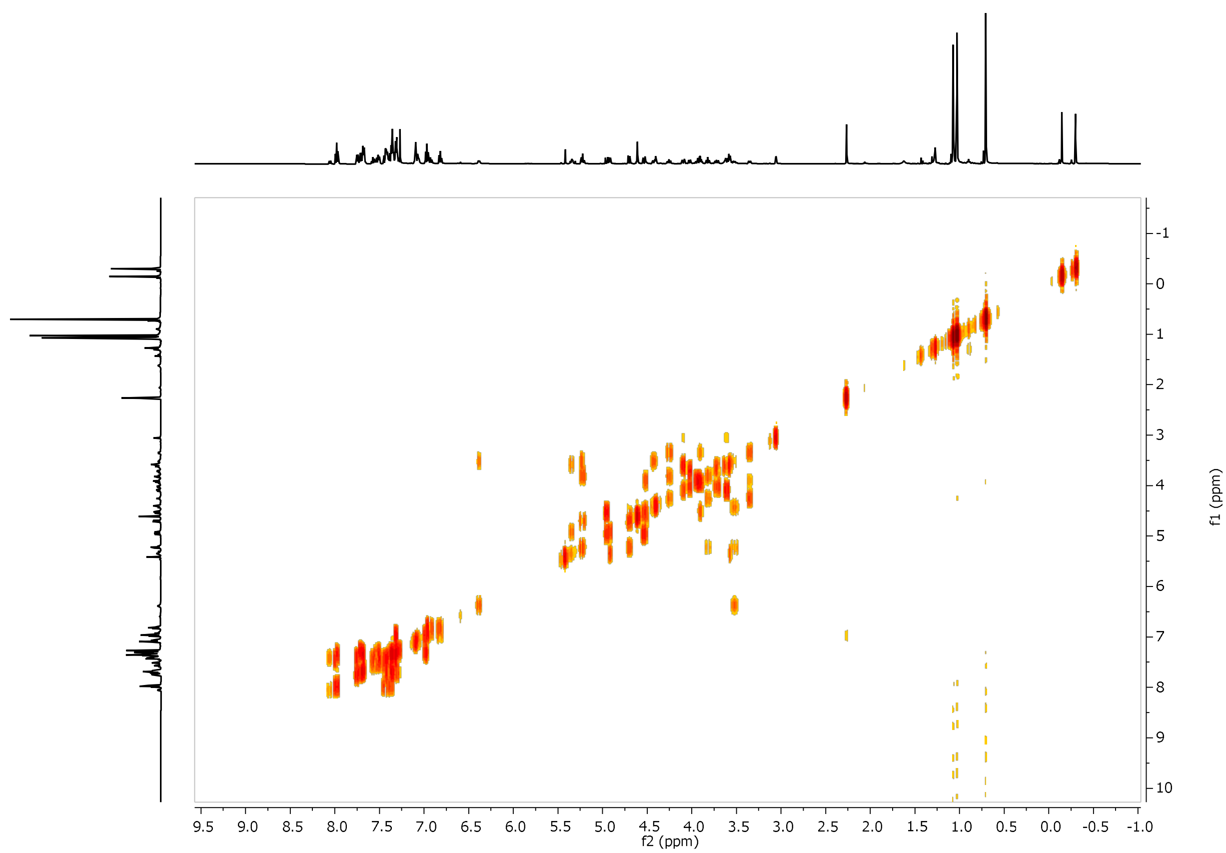
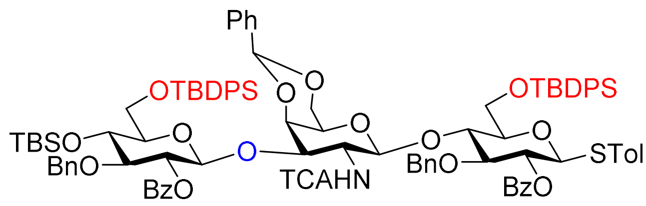


bsgHSQC ($CDCl_3$, 500 MHz) of **3**



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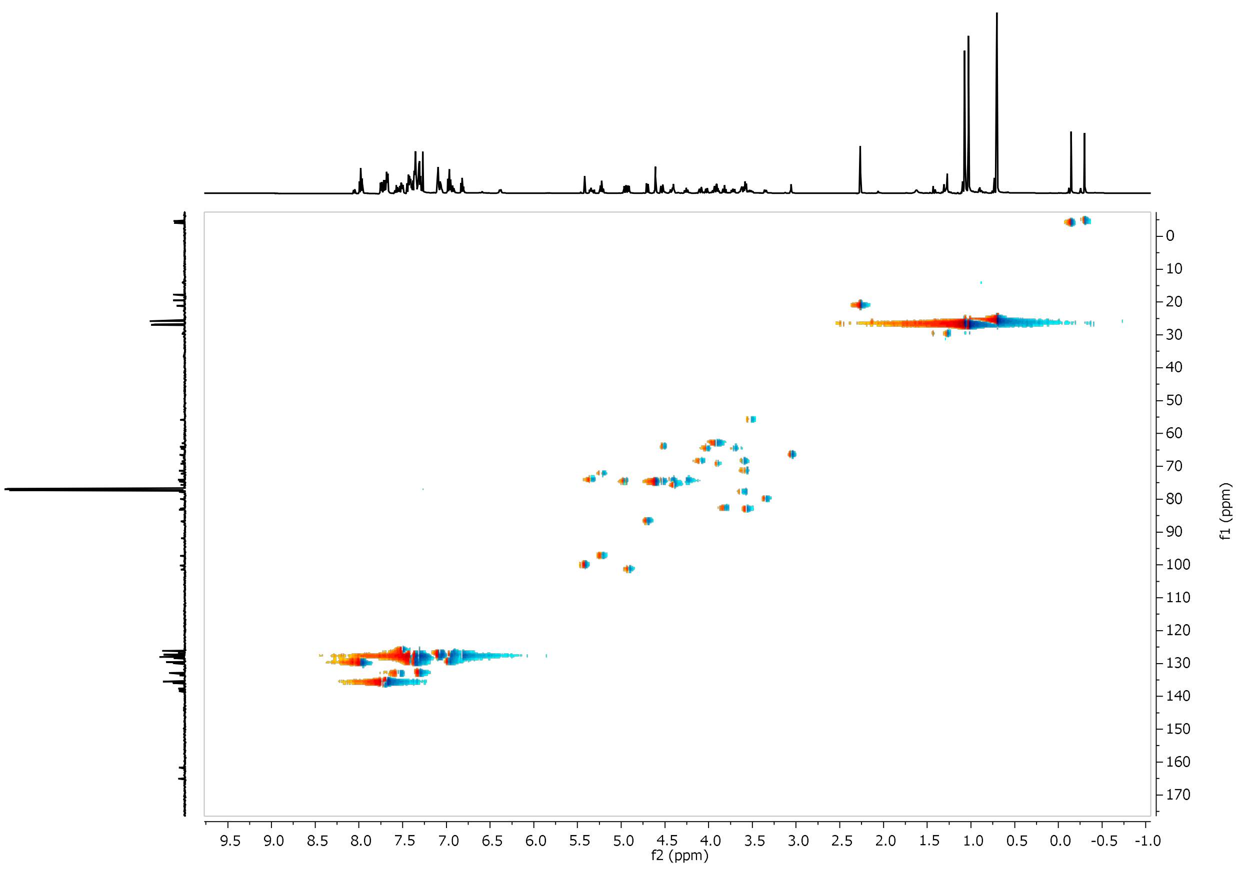
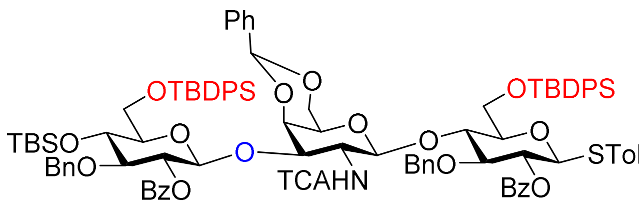


gHSQC ($CDCl_3$, 500 MHz) of **3**



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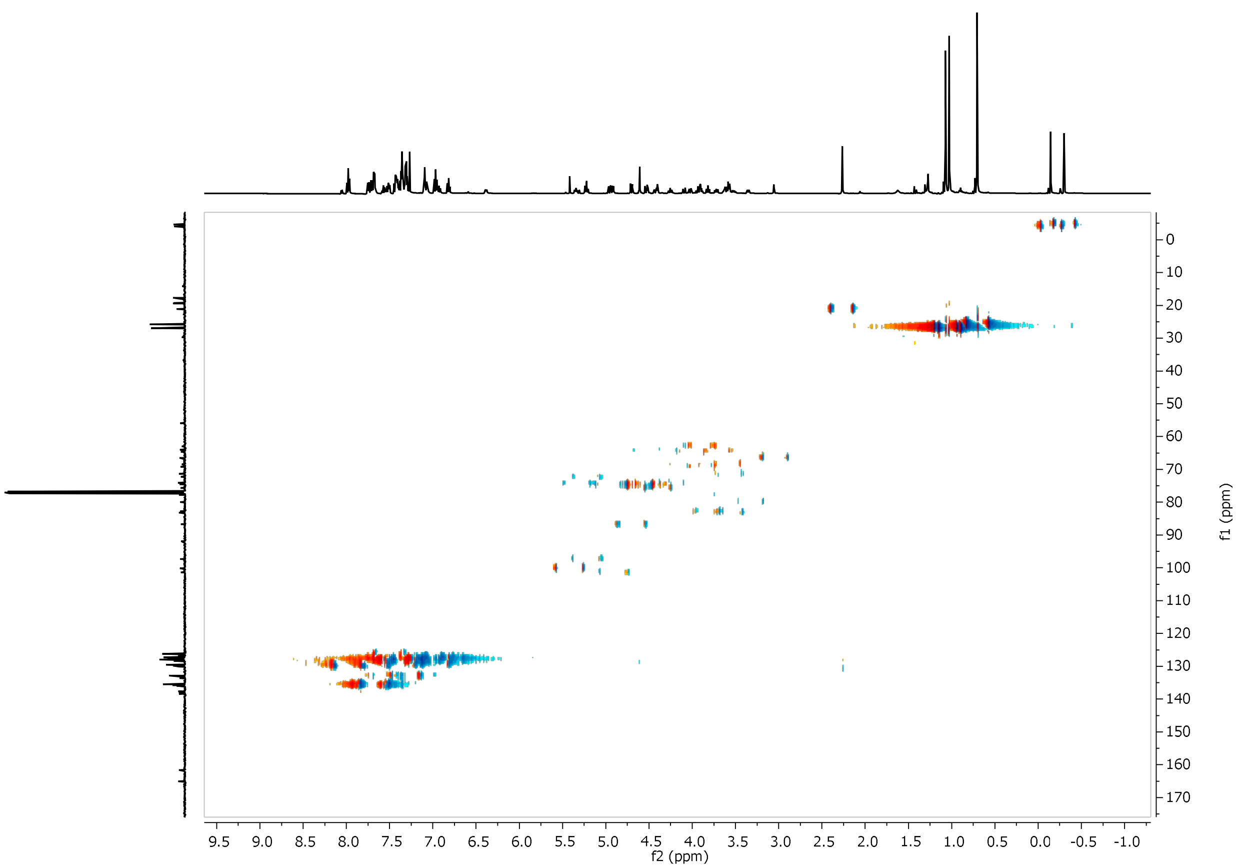

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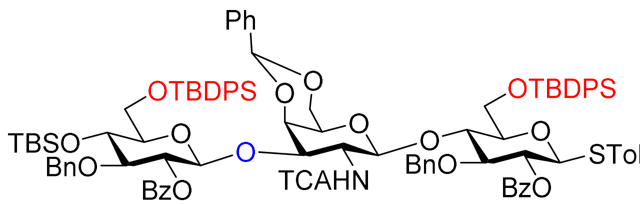

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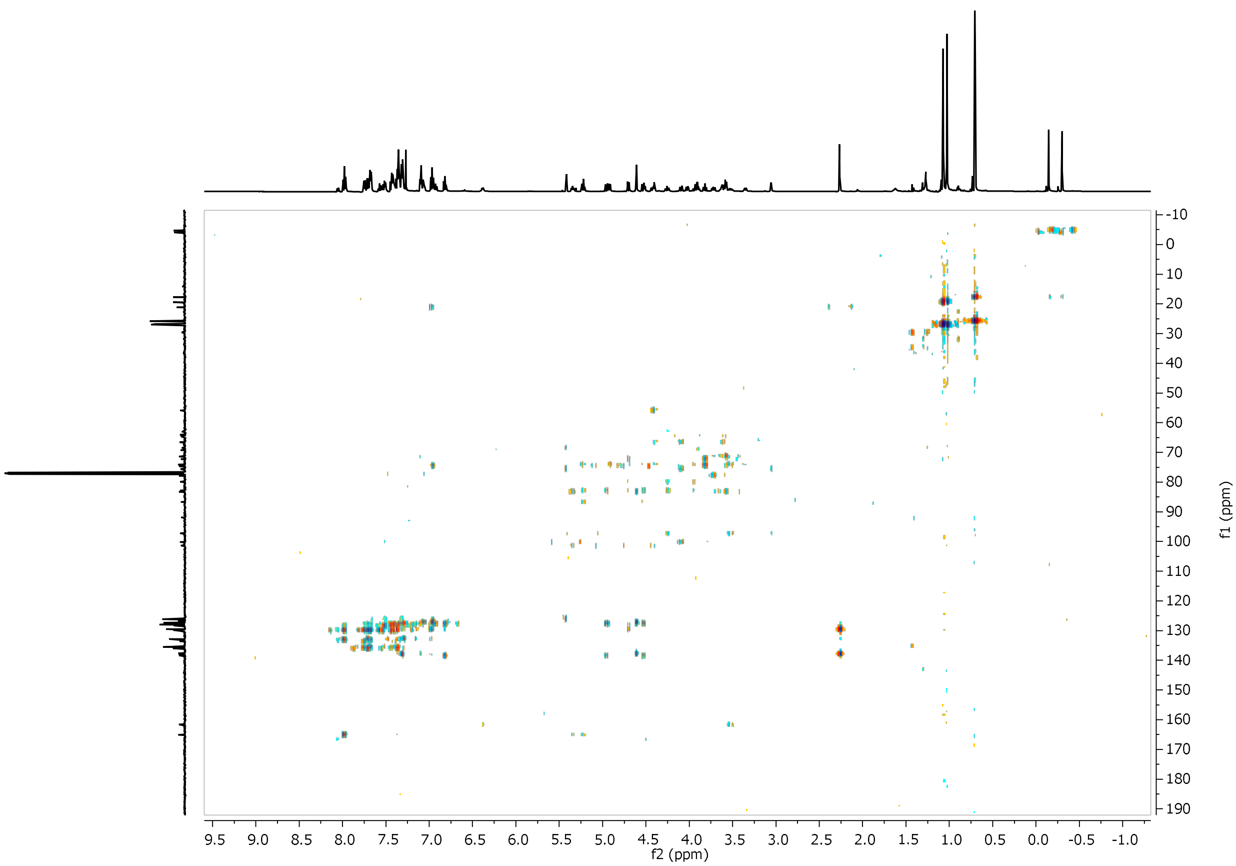
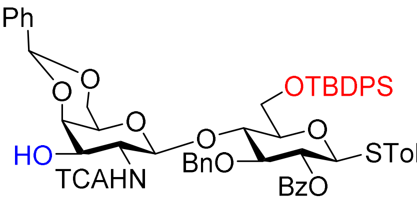


^{1}H-NMR ($CDCl_3$, 500 MHz) of **4**



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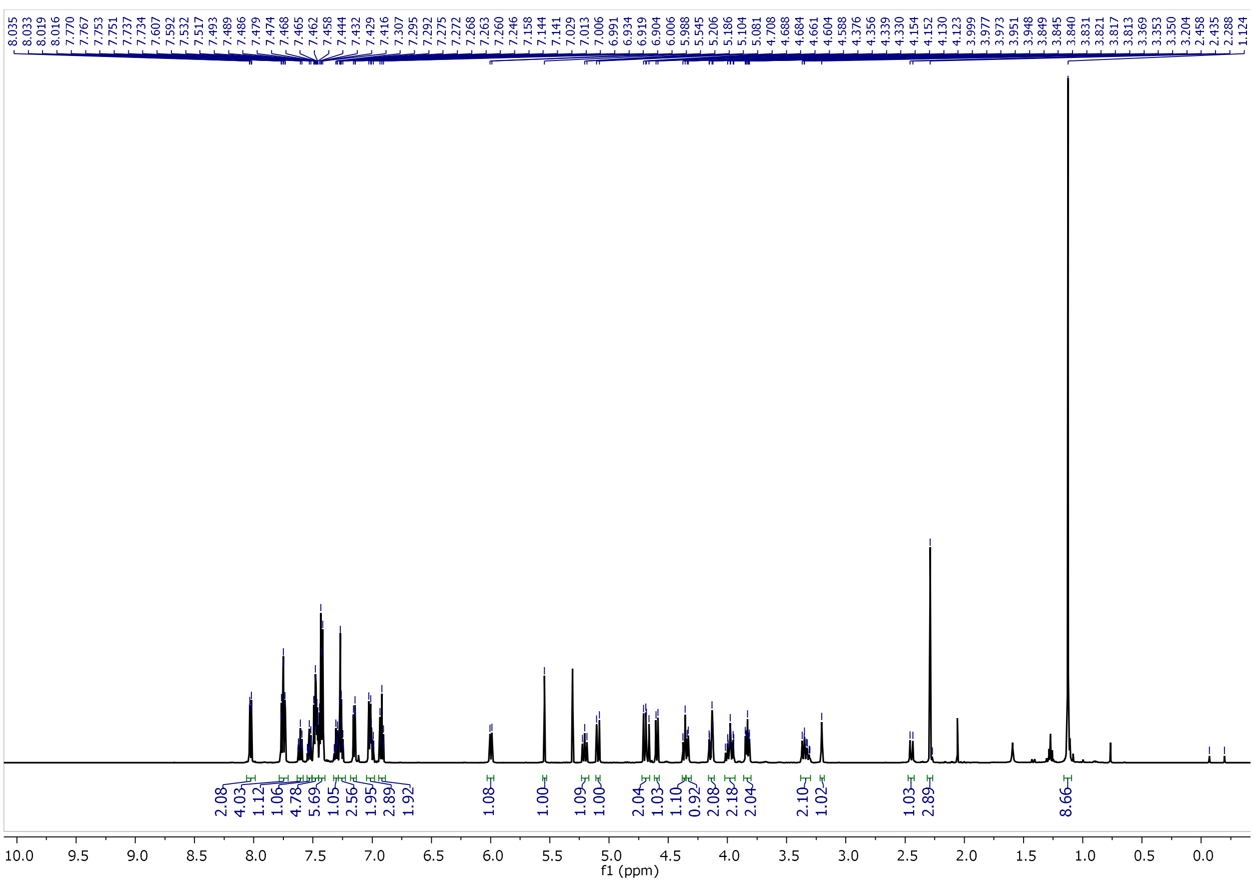
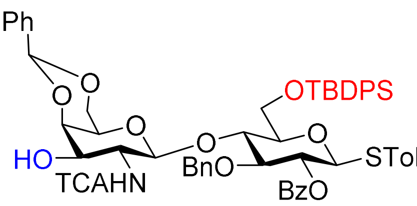


^{13}C-NMR (CDCl$_3$, 126 MHz) of **4**



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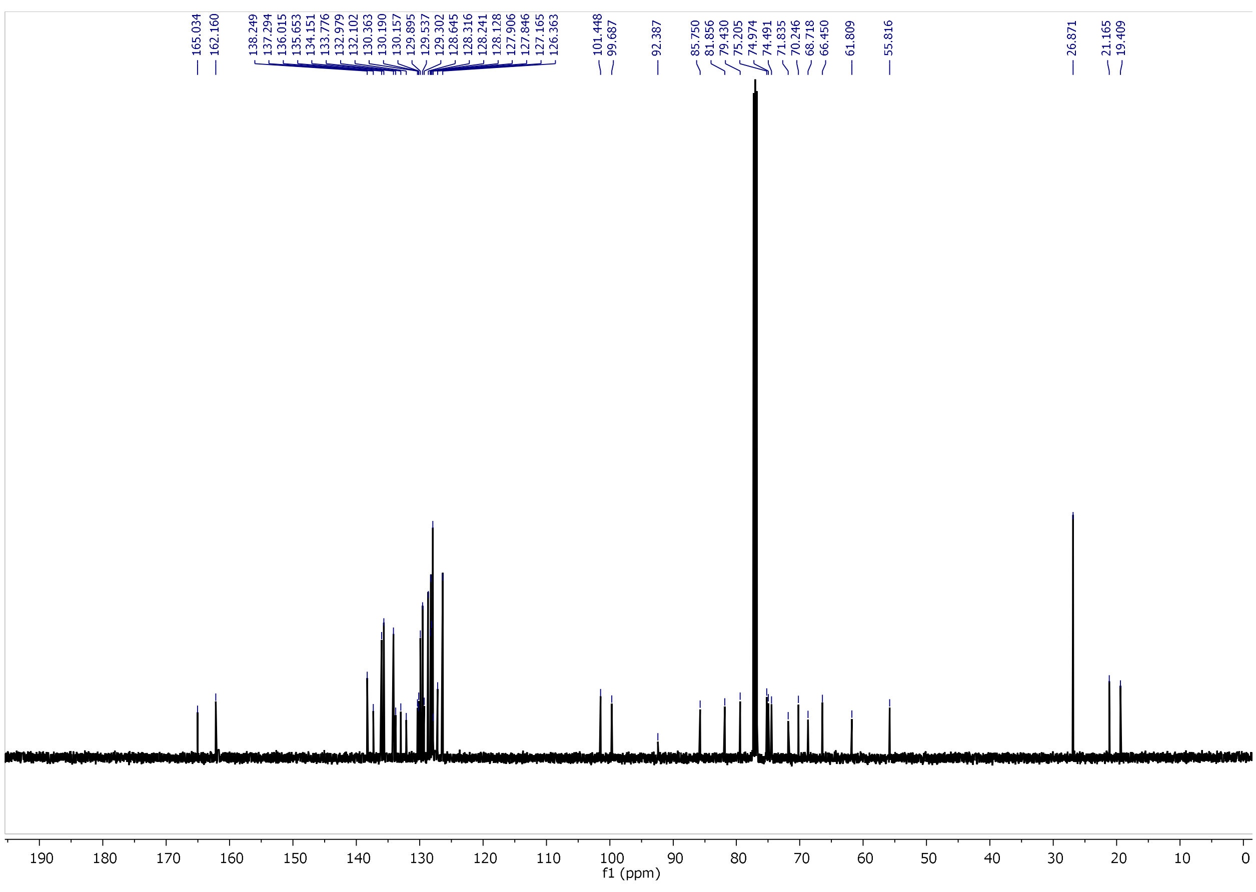
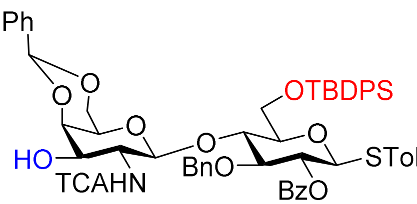


gCOSY ($CDCl_3$, 500 MHz) of **4**



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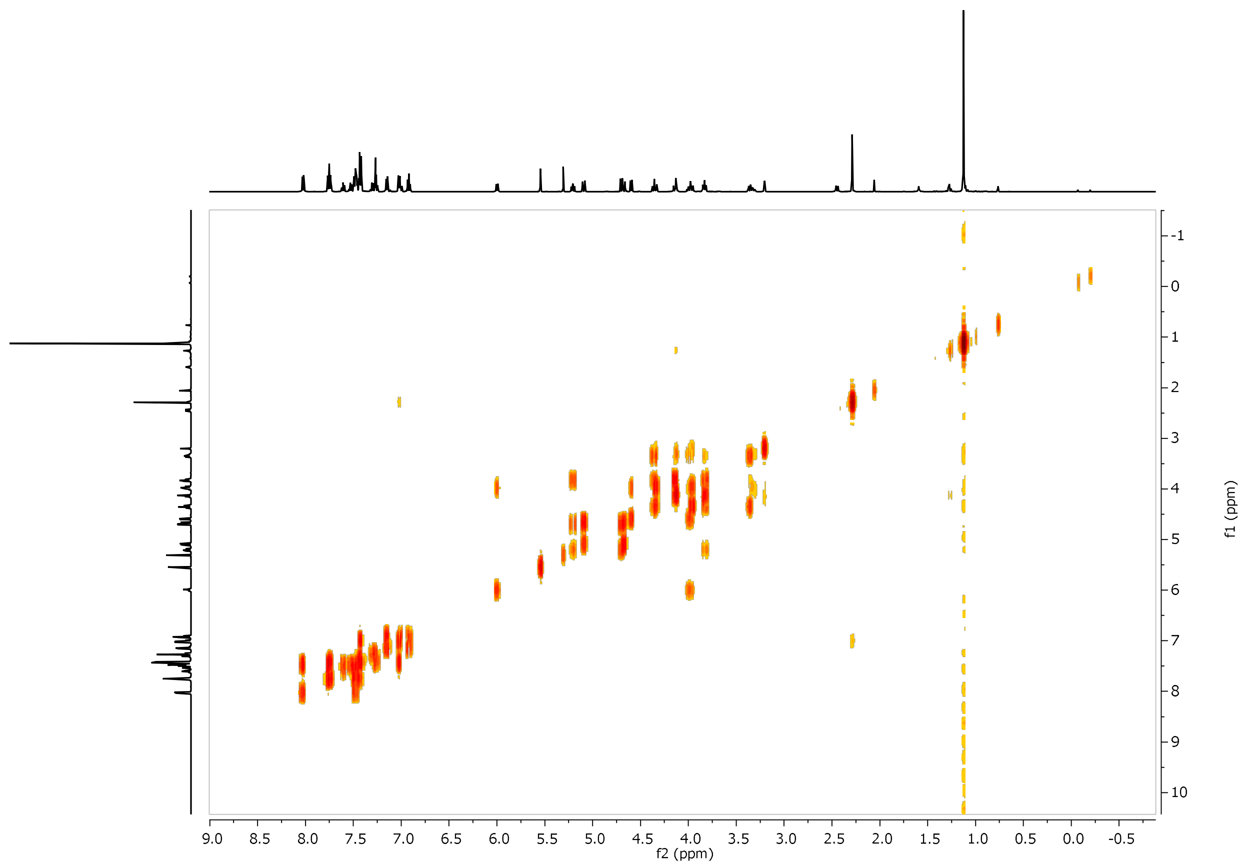

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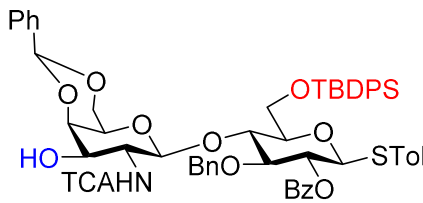

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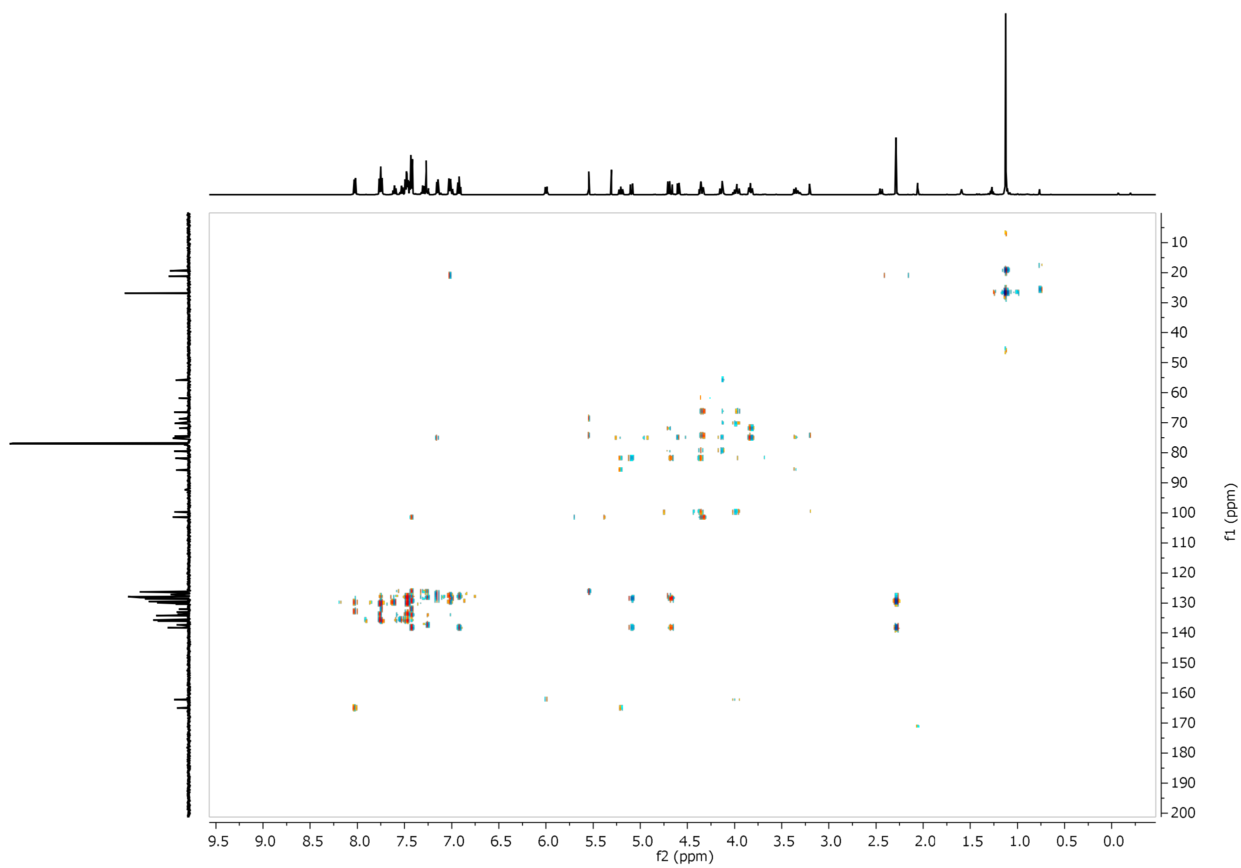
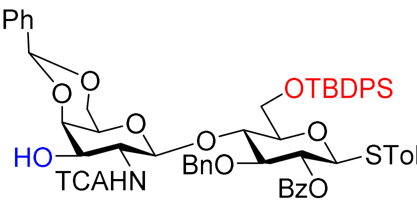


gHSQC (CDCl$_3$, 500 MHz) of **4**



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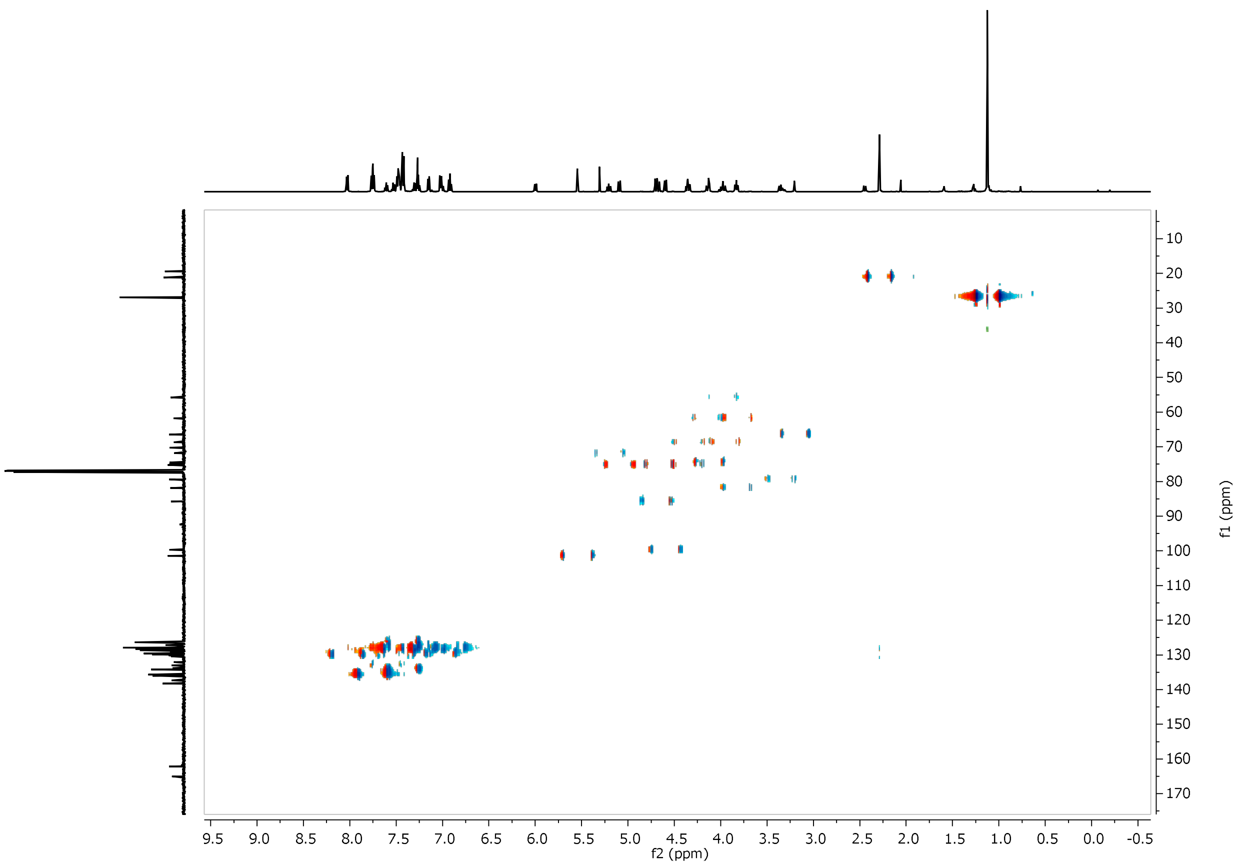
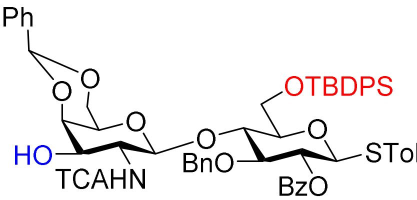


bsgHSQC ($CDCl_3$, 500 MHz) of **4**



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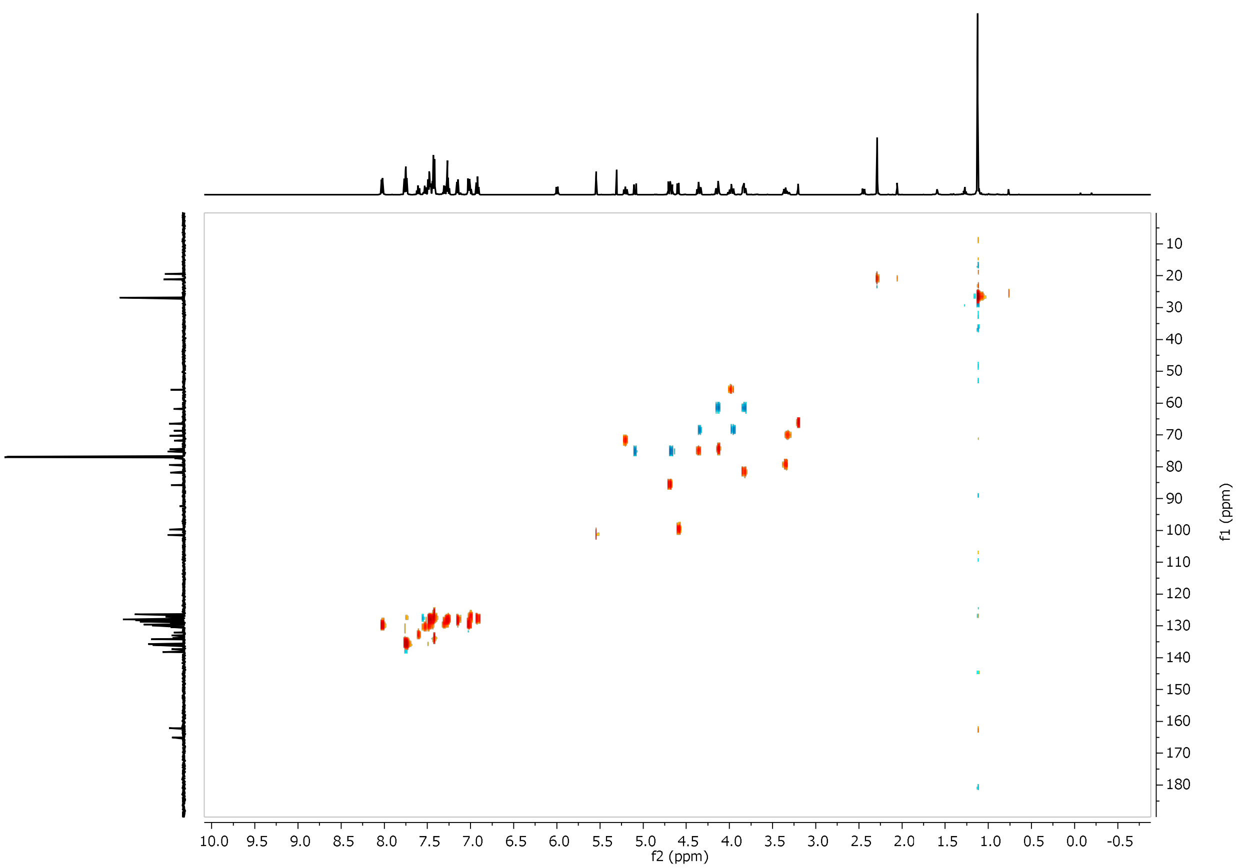
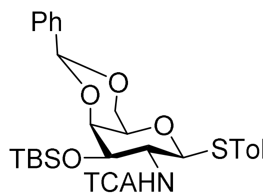


^{1}H-NMR ($CDCl_3$, 500 MHz) of **6**



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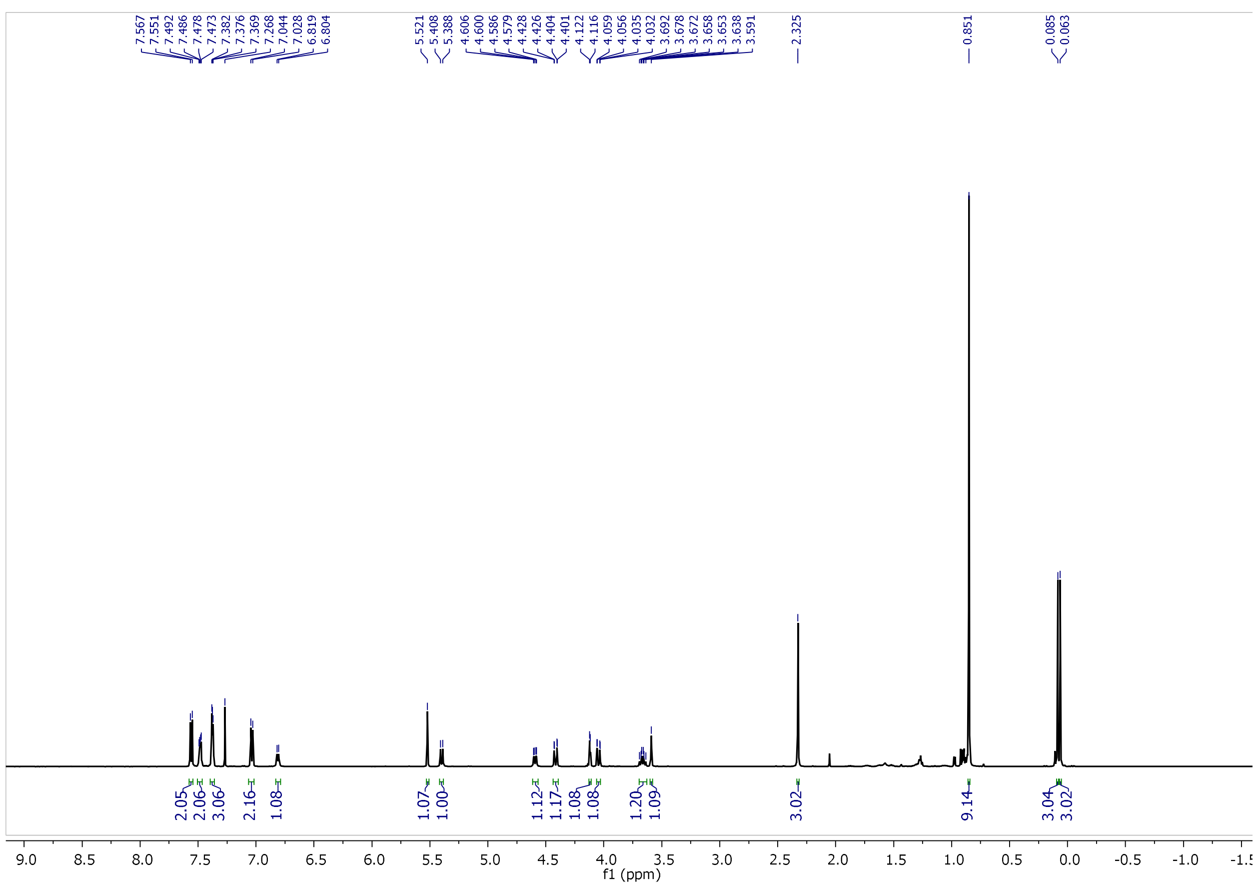
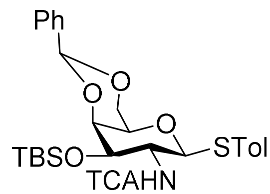


^{13}C-NMR ($CDCl_3$, 126 MHz) of **6**



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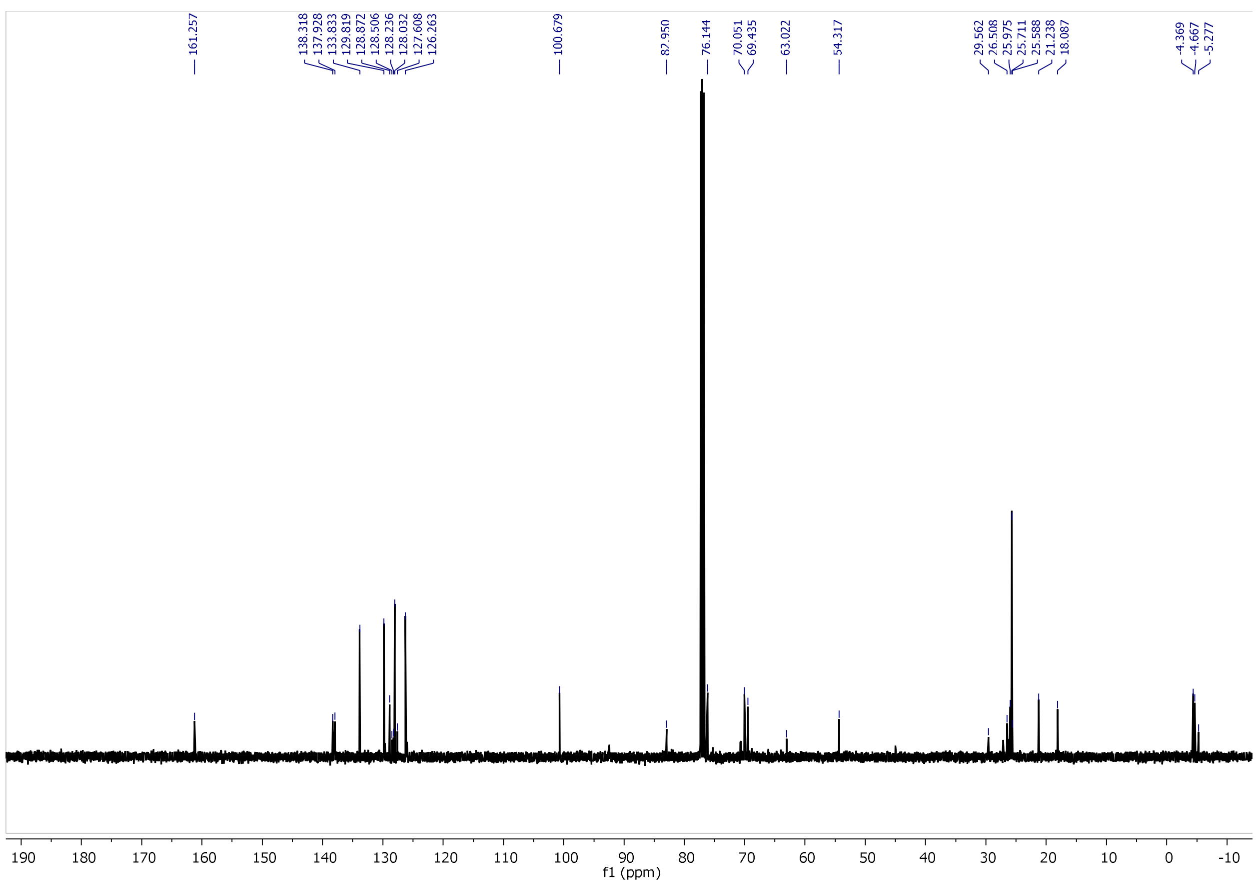
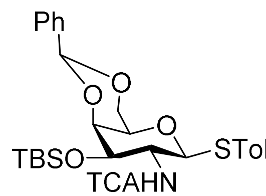


gCOSY ($CDCl_3$, 500 MHz) of **6**



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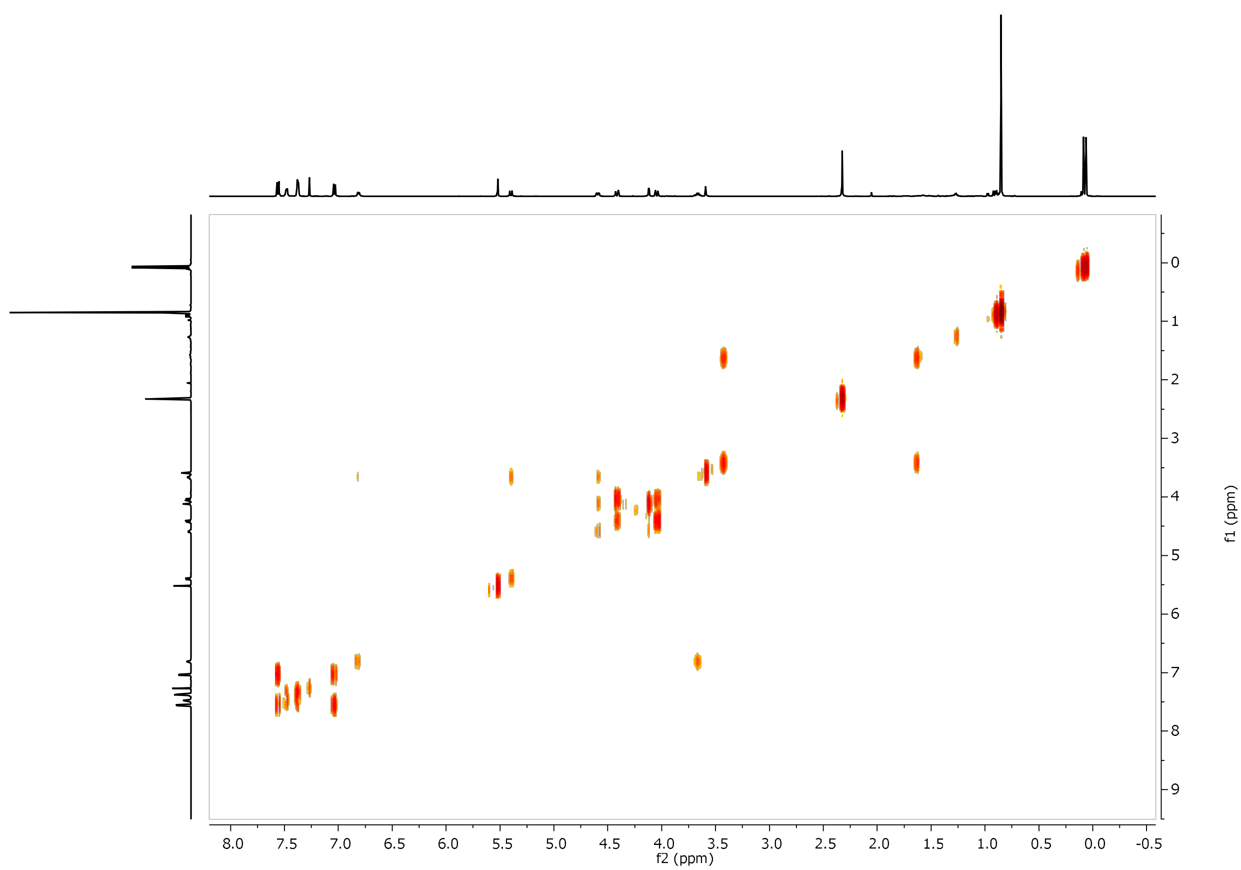
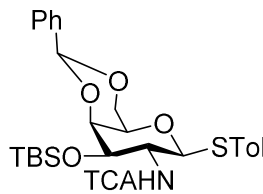


gHSQC ($CDCl_3$, 500 MHz) of **6**



6

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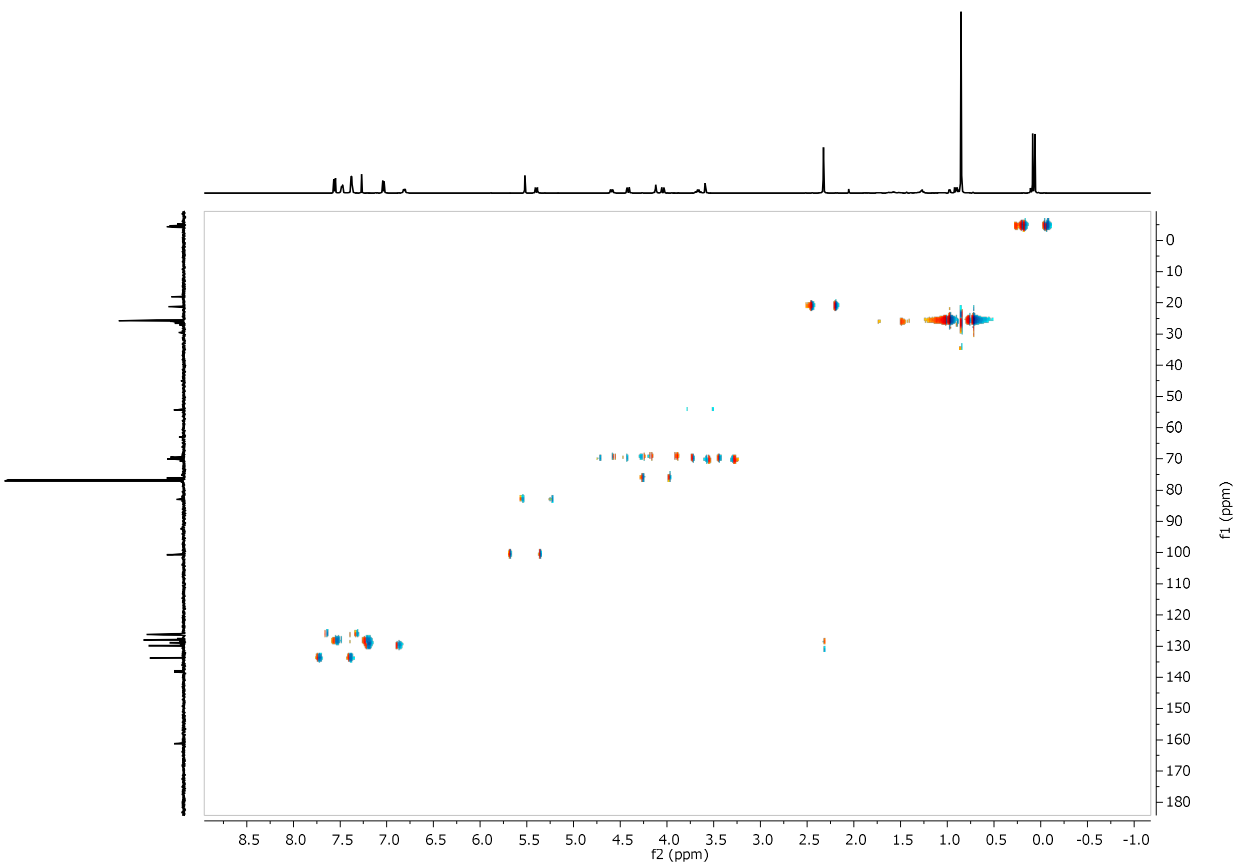
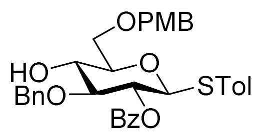


^{1}H-NMR ($CDCl_3$, 500 MHz) of **7**



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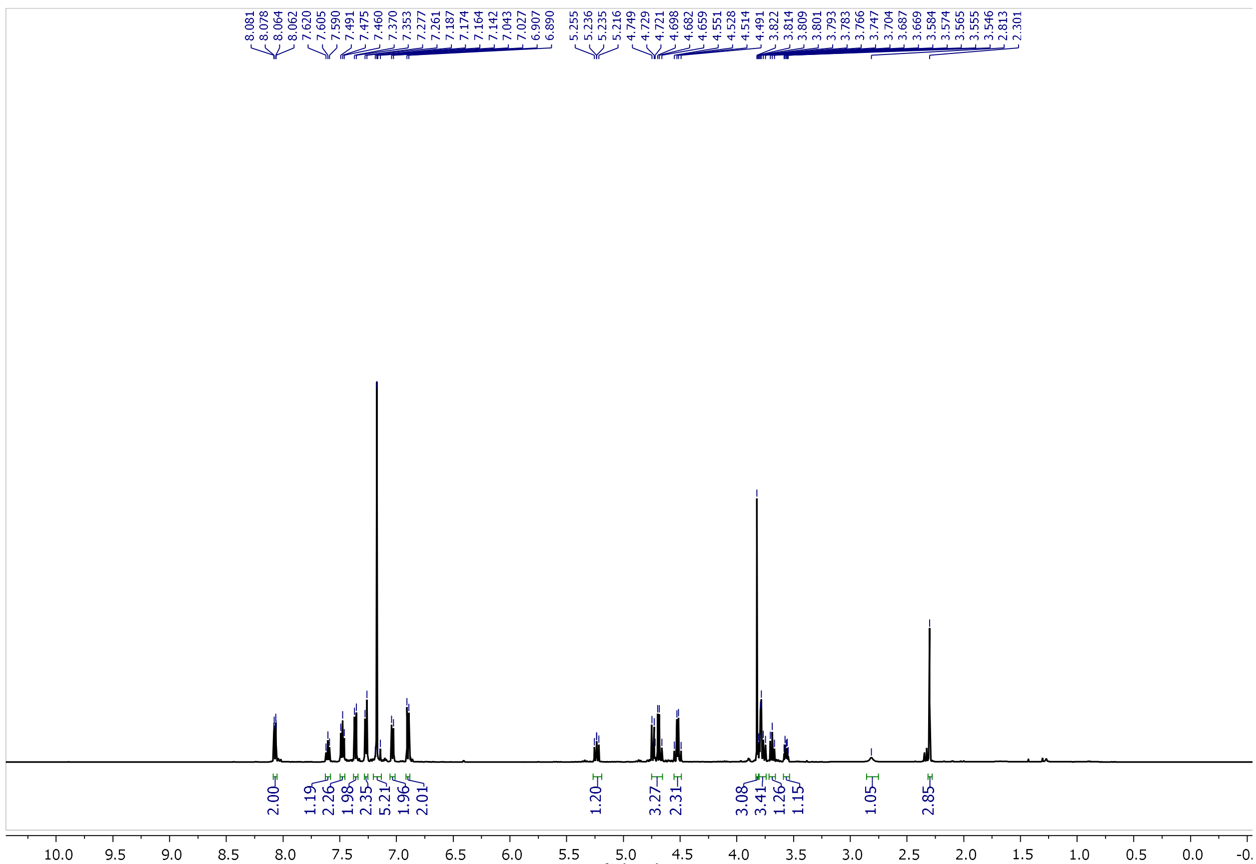
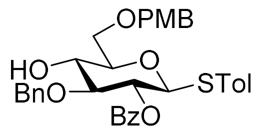


^{13}C-NMR ($CDCl_3$, 126 MHz) of **7**



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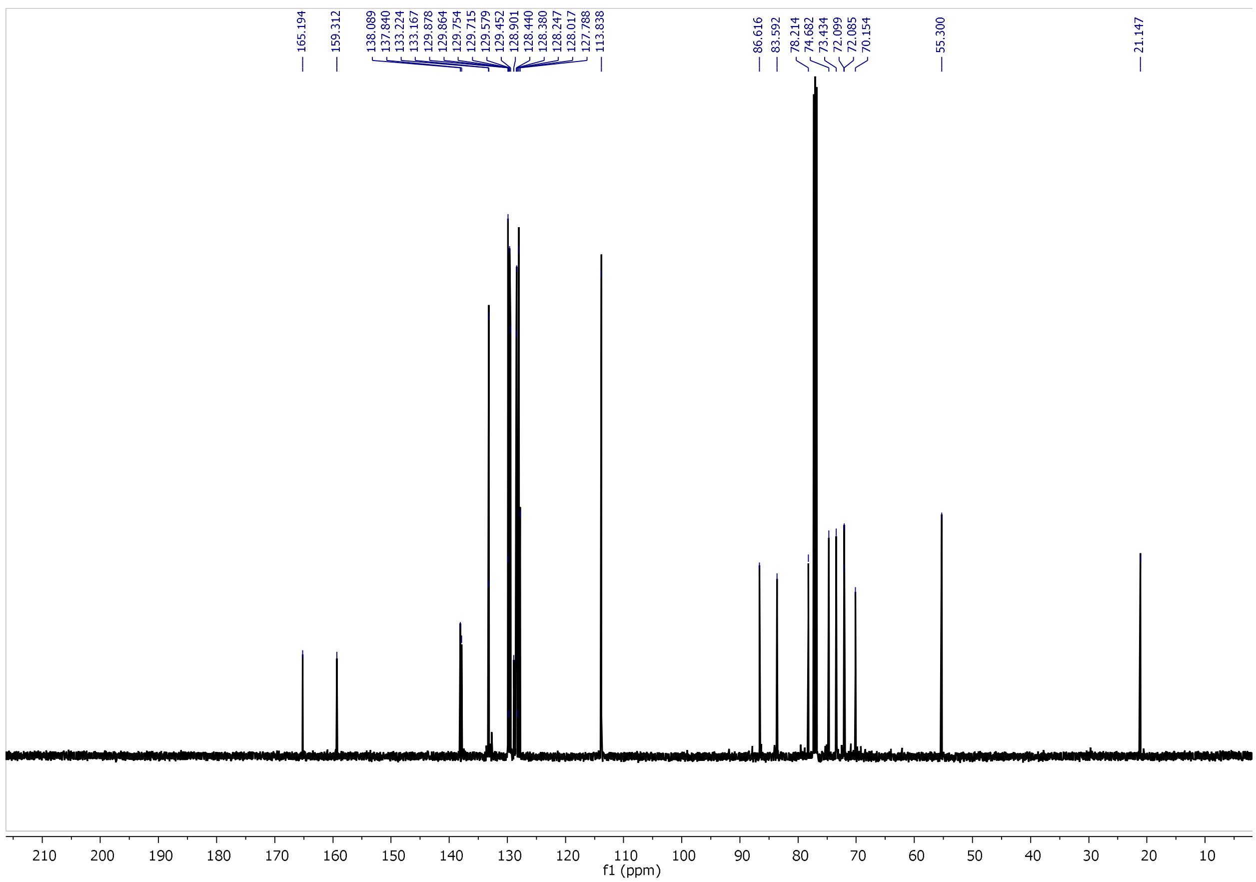
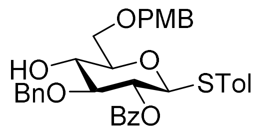


gCOSY ($CDCl_3$, 500 MHz) of **7**



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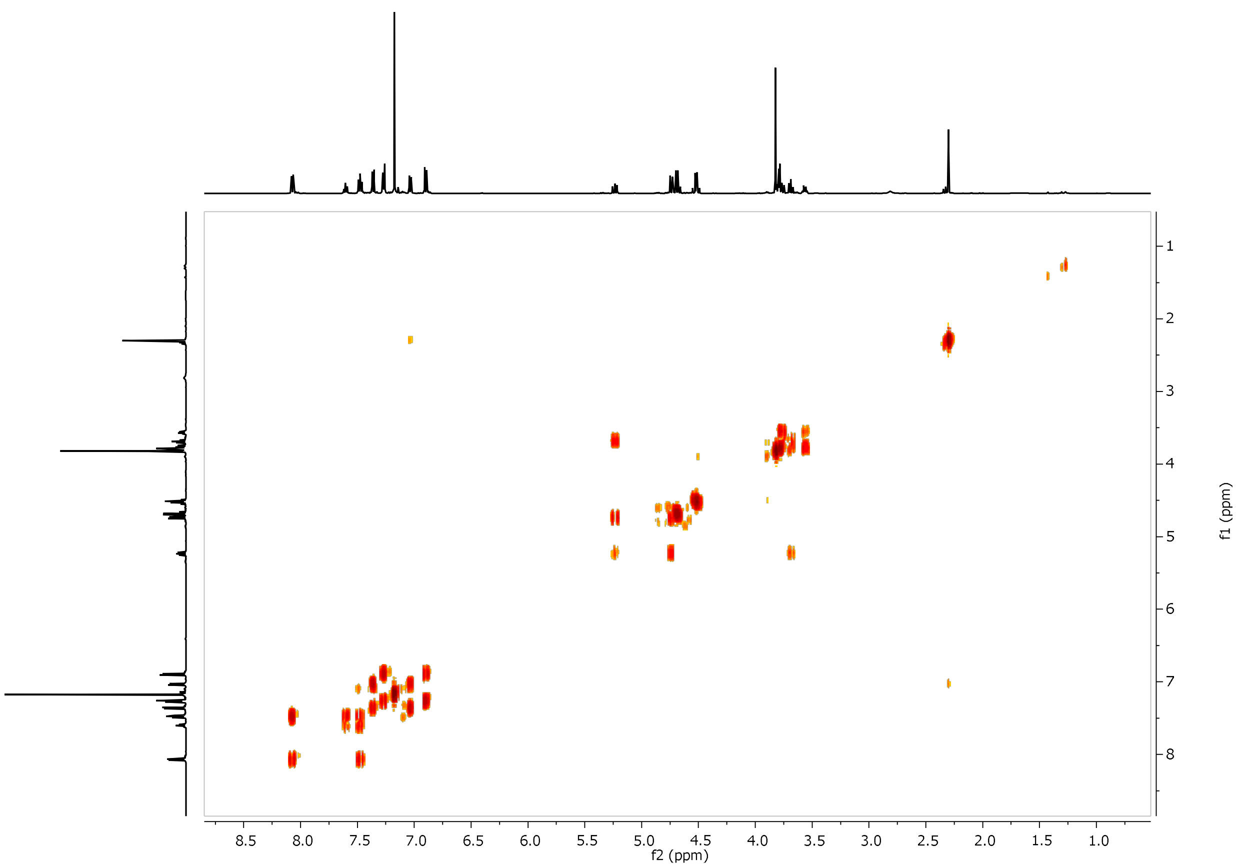
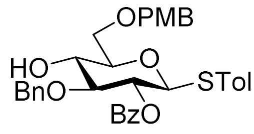


bsgHSQC ($CDCl_3$, 500 MHz) of **7**



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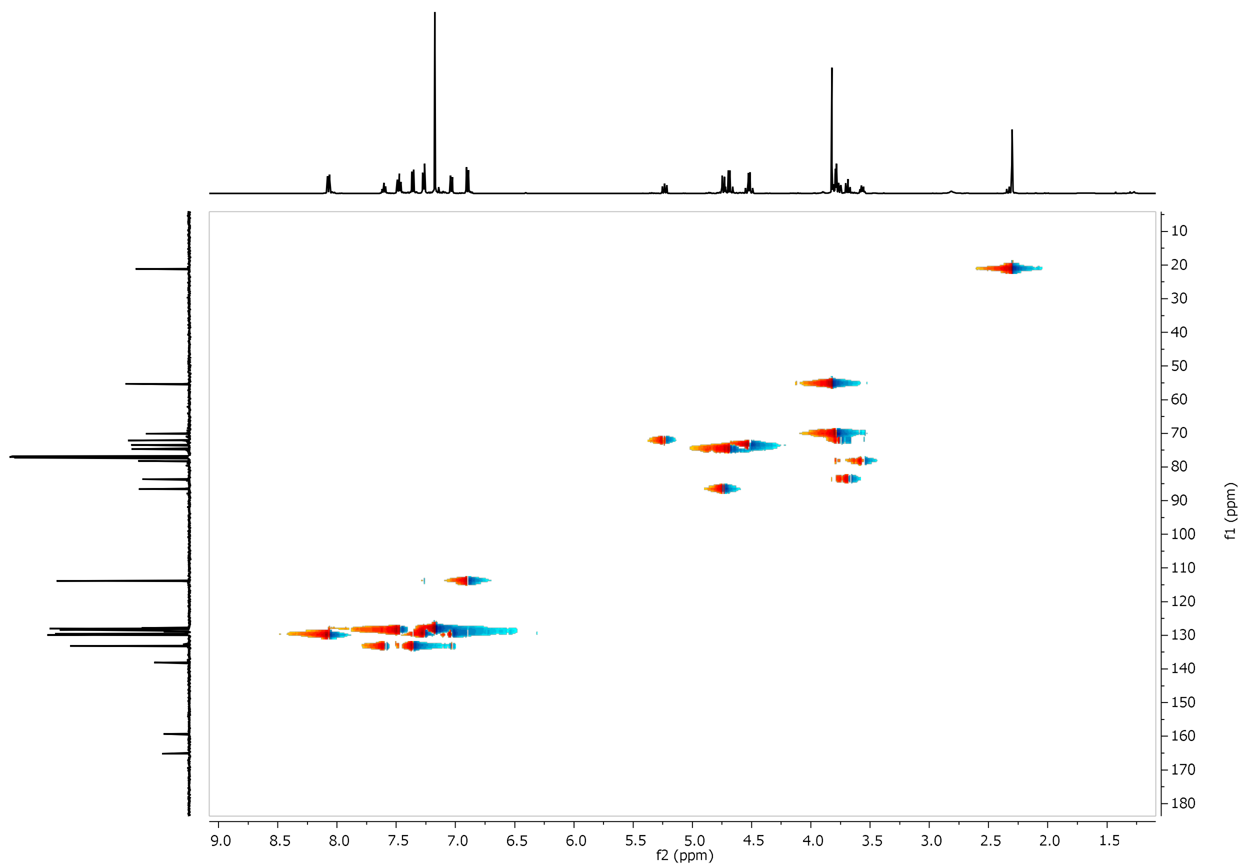
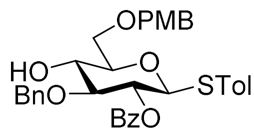


gHMBC ($CDCl_3$, 500 MHz) of **7**



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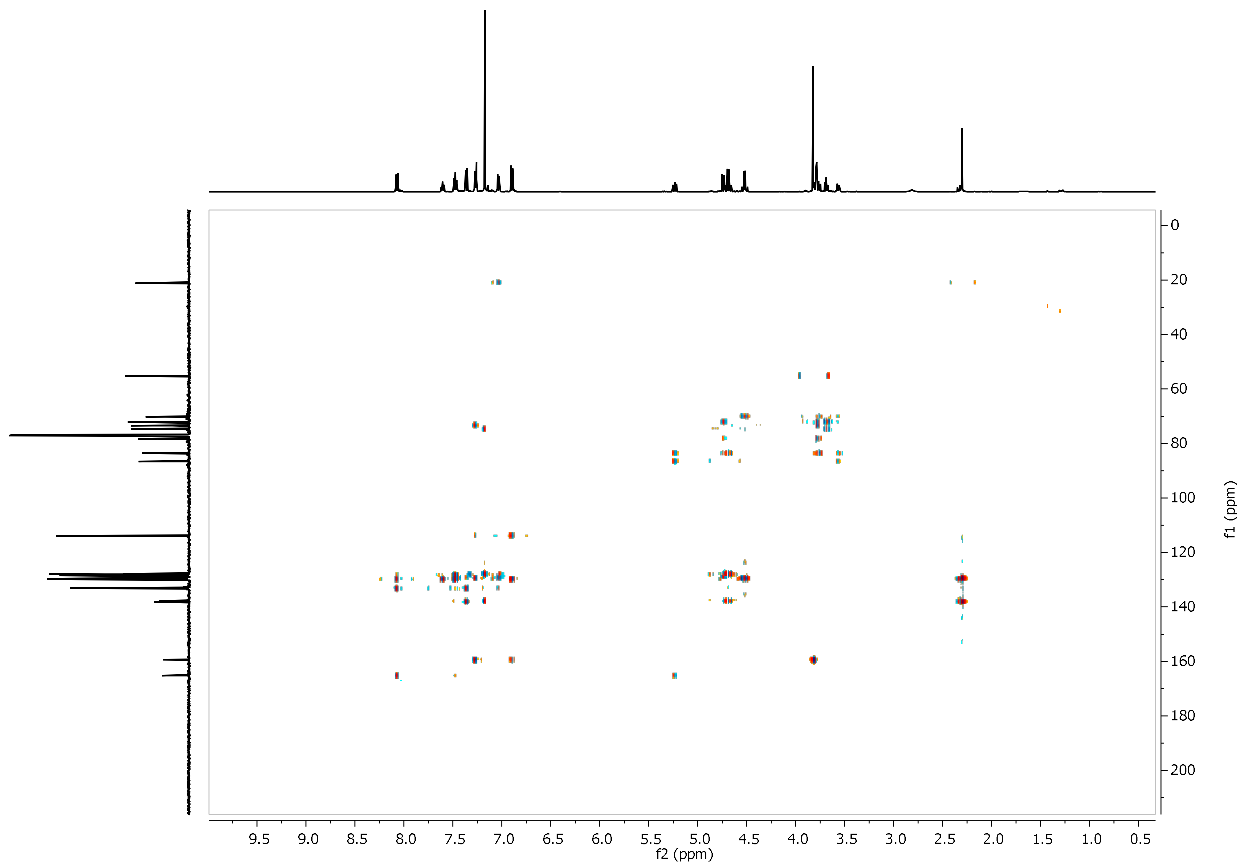
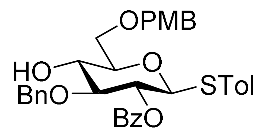


gHSQC ($CDCl_3$, 500 MHz) of **7**



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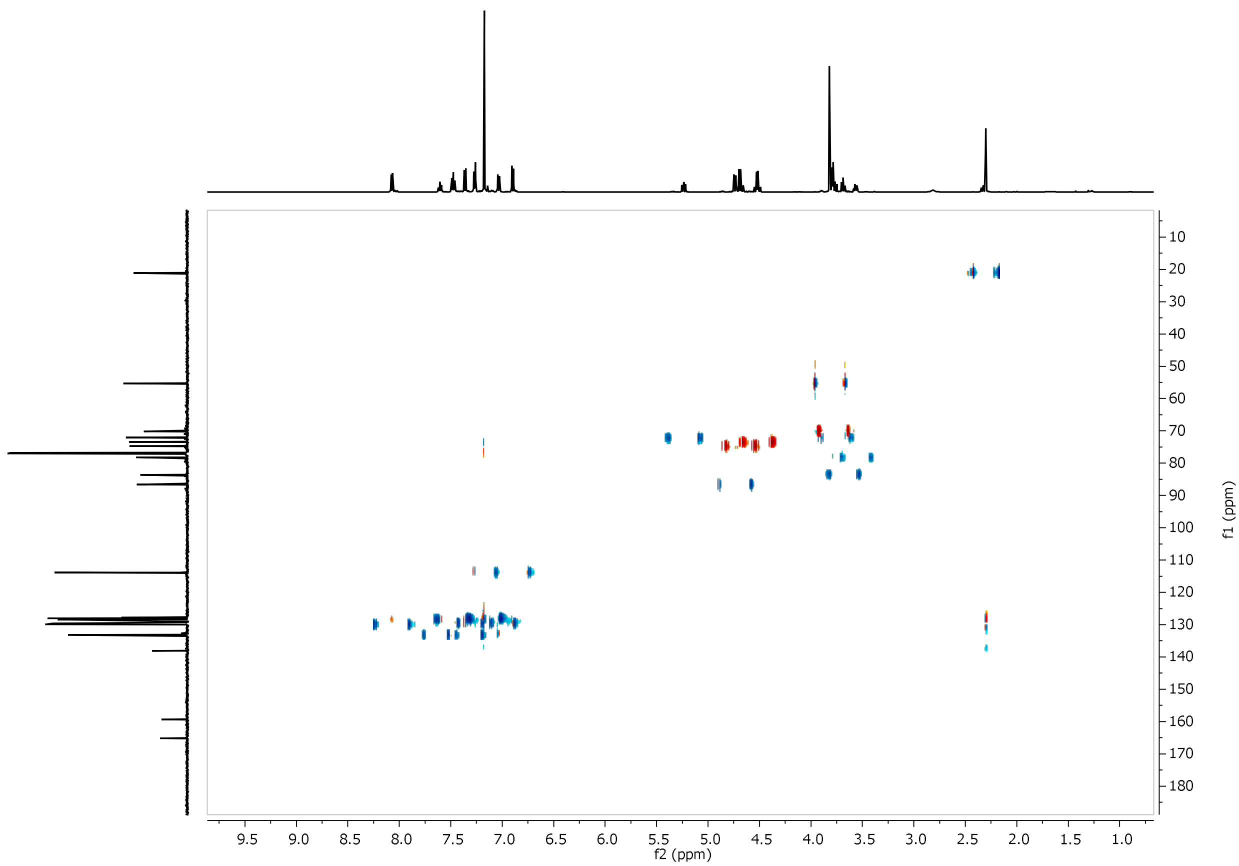
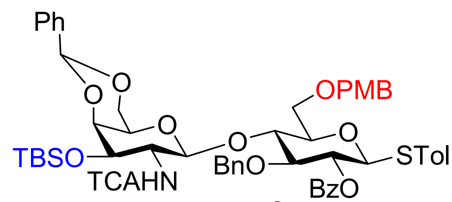


^{1}H-NMR ($CDCl_3$, 500 MHz) of **8**



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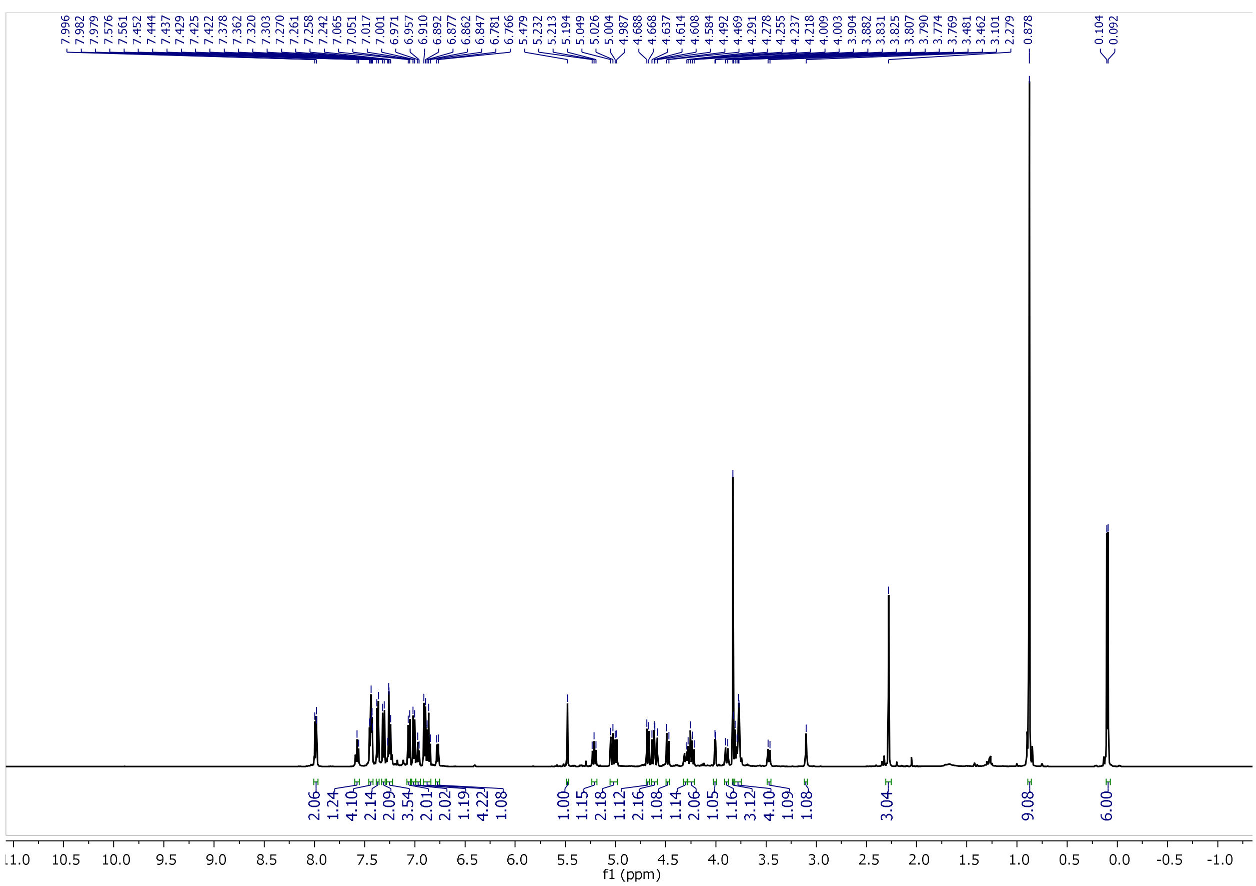
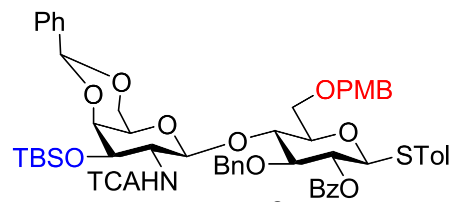


^{13}C-NMR ($CDCl_3$, 126 MHz) of **8**



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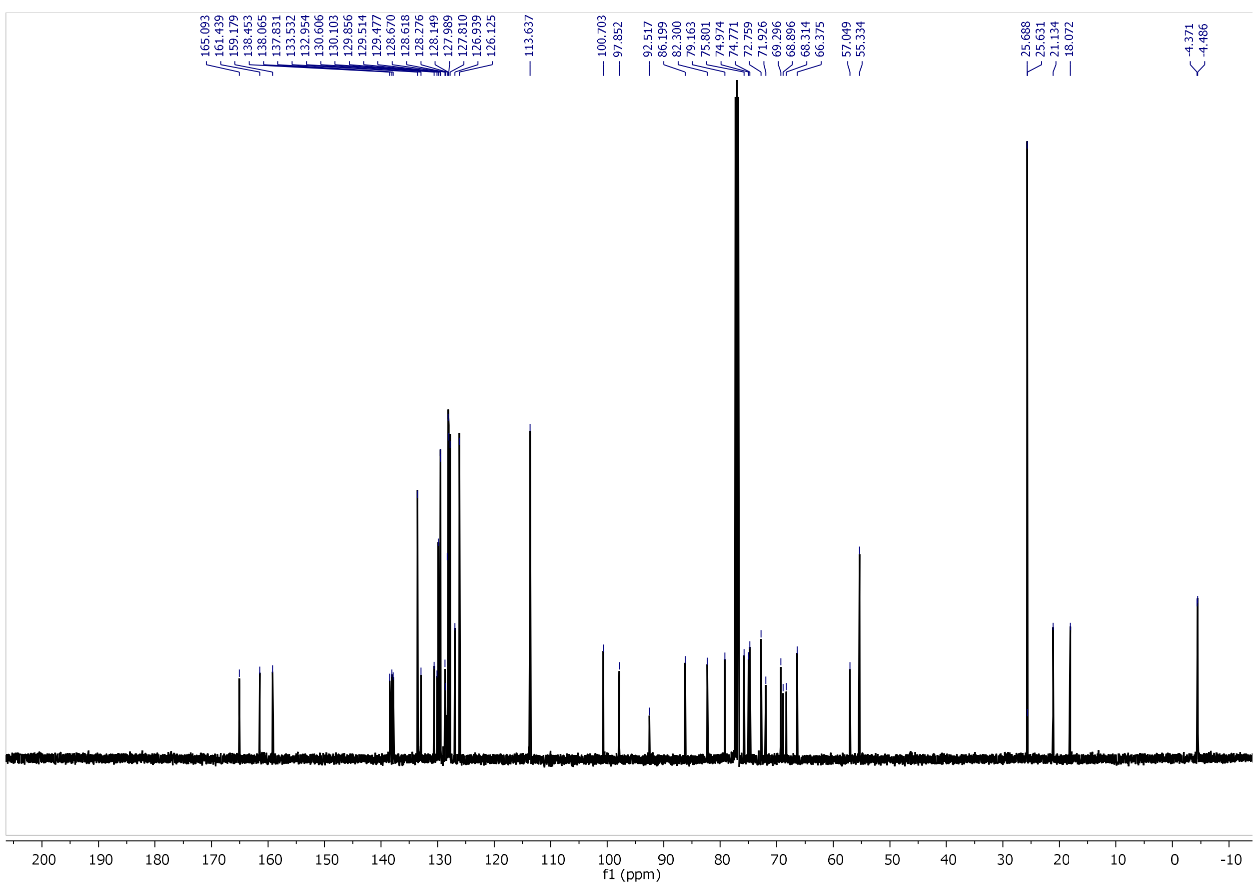
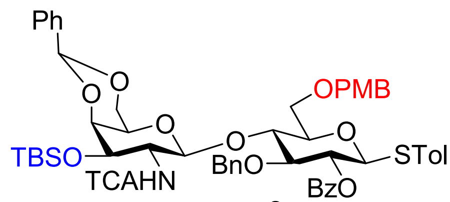


gCOSY ($CDCl_3$, 500 MHz) of **8**



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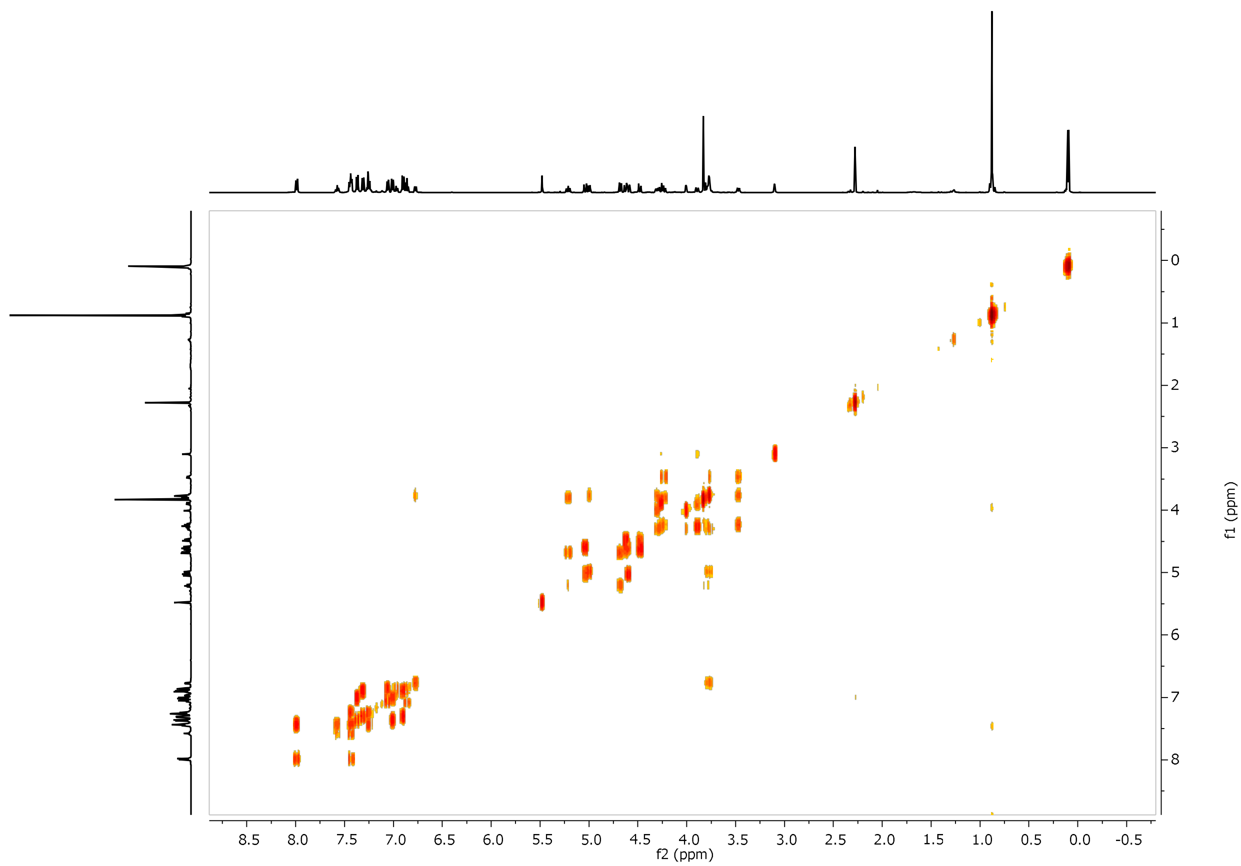
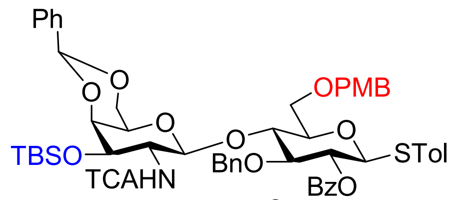


gHSQC ($CDCl_3$, 500 MHz) of **8**



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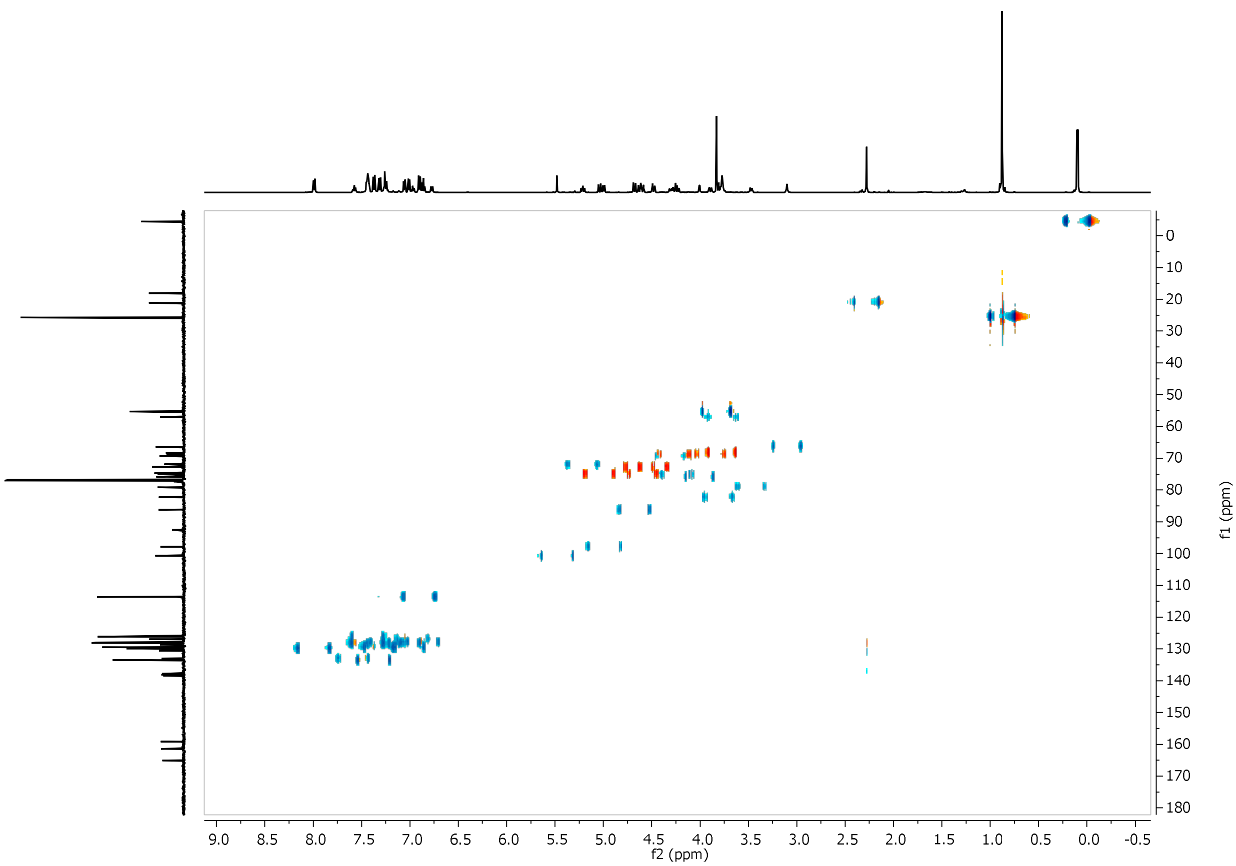
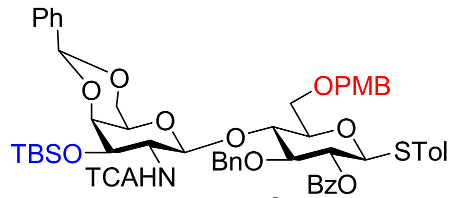


gHMBC ($CDCl_3$, 500 MHz) of **8**



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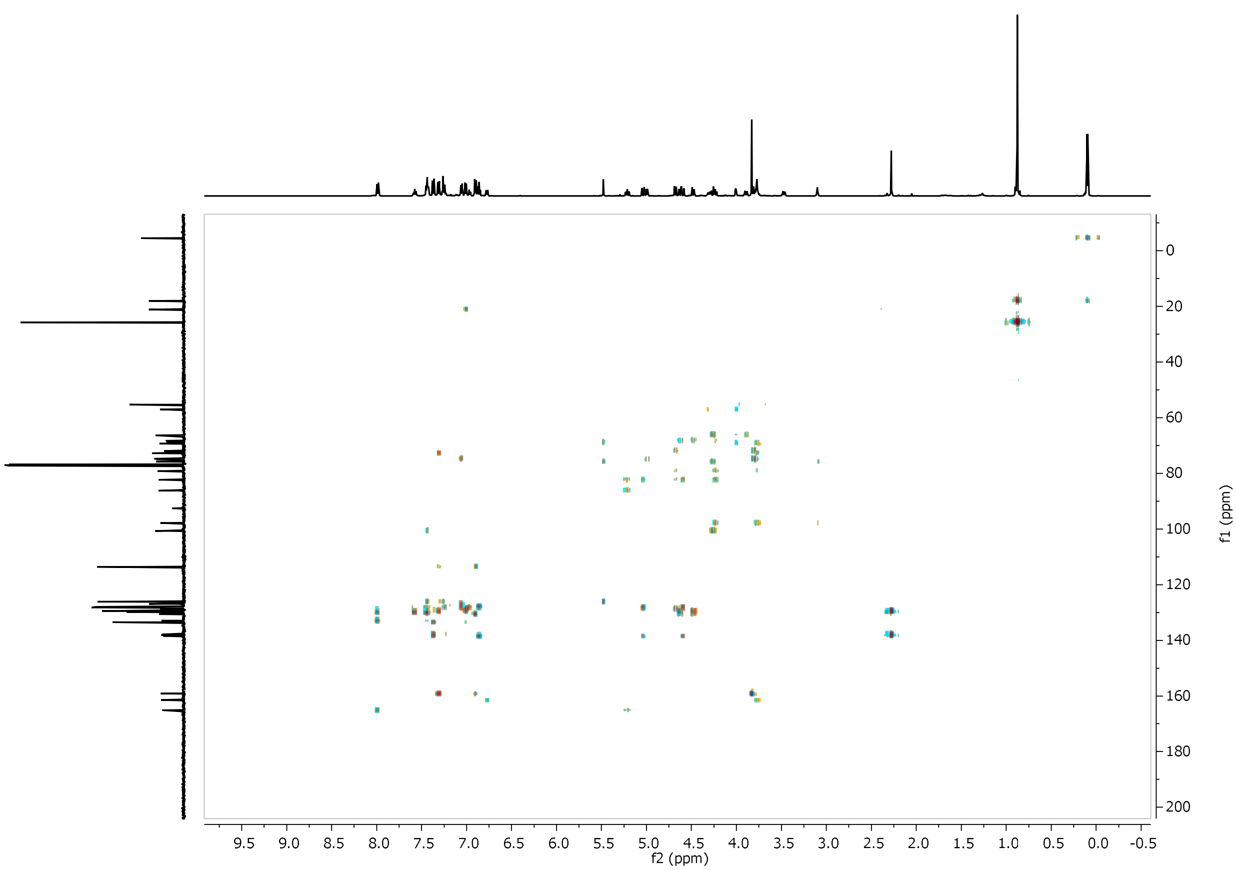
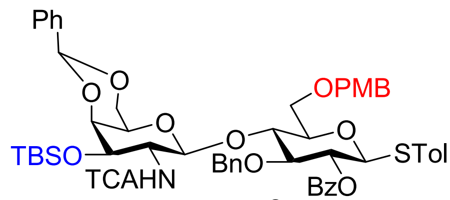


bsgHSQC ($CDCl_3$, 500 MHz) of **8**



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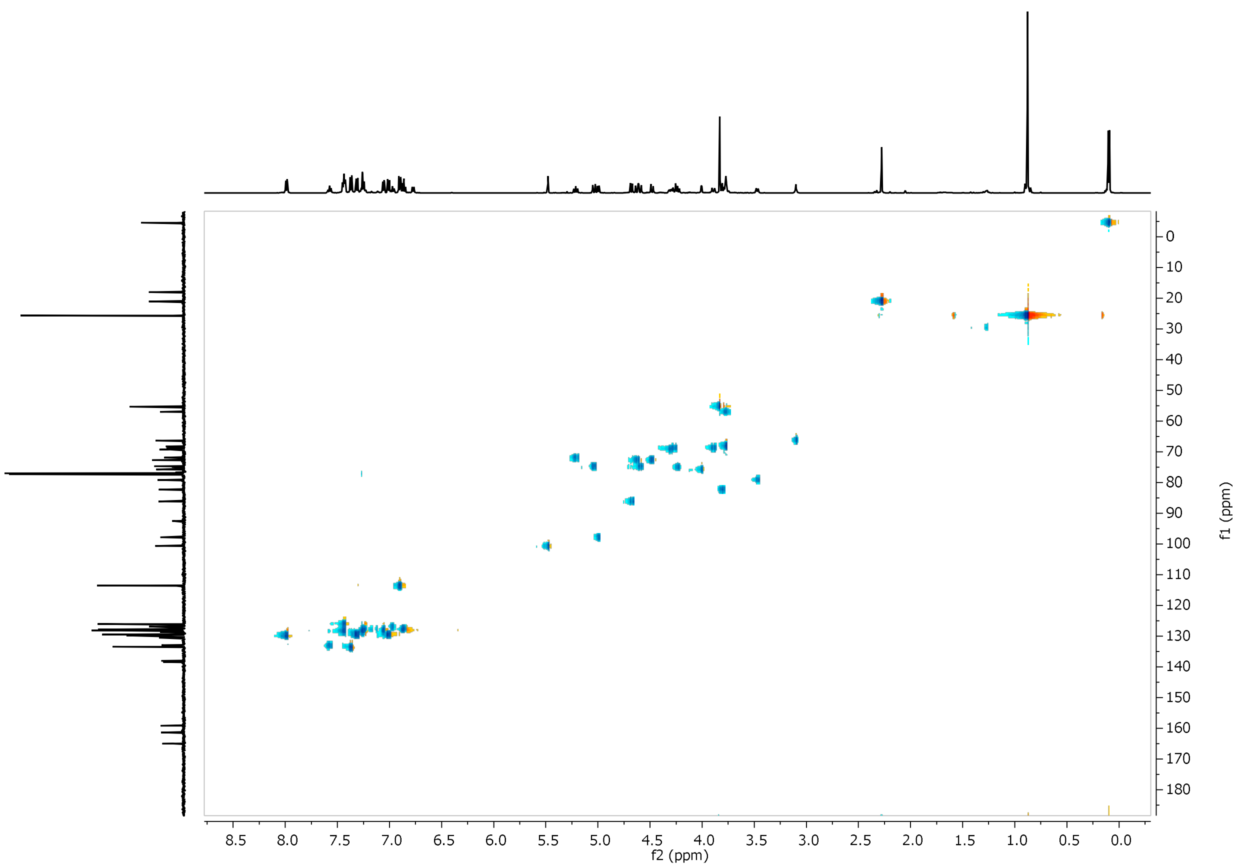
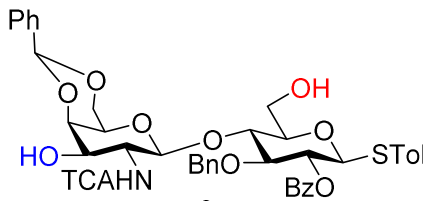


^{1}H-NMR ($CDCl_3$, 500 MHz) of **9**



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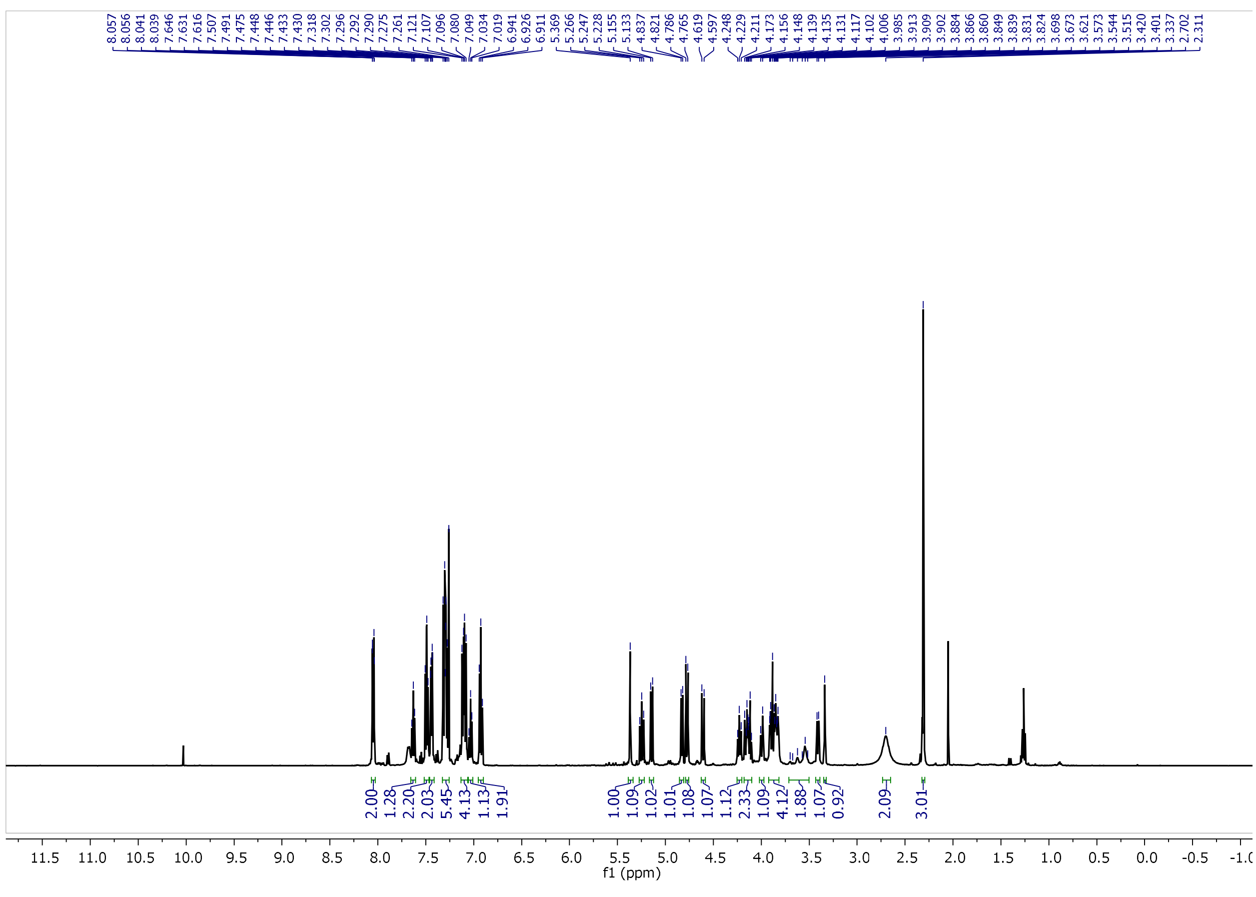
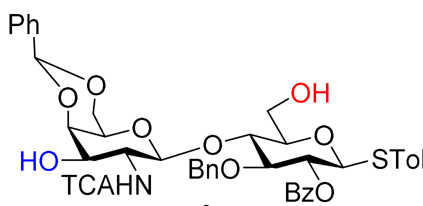


^{13}C-NMR (CDCl$_3$, 126 MHz) of **9**



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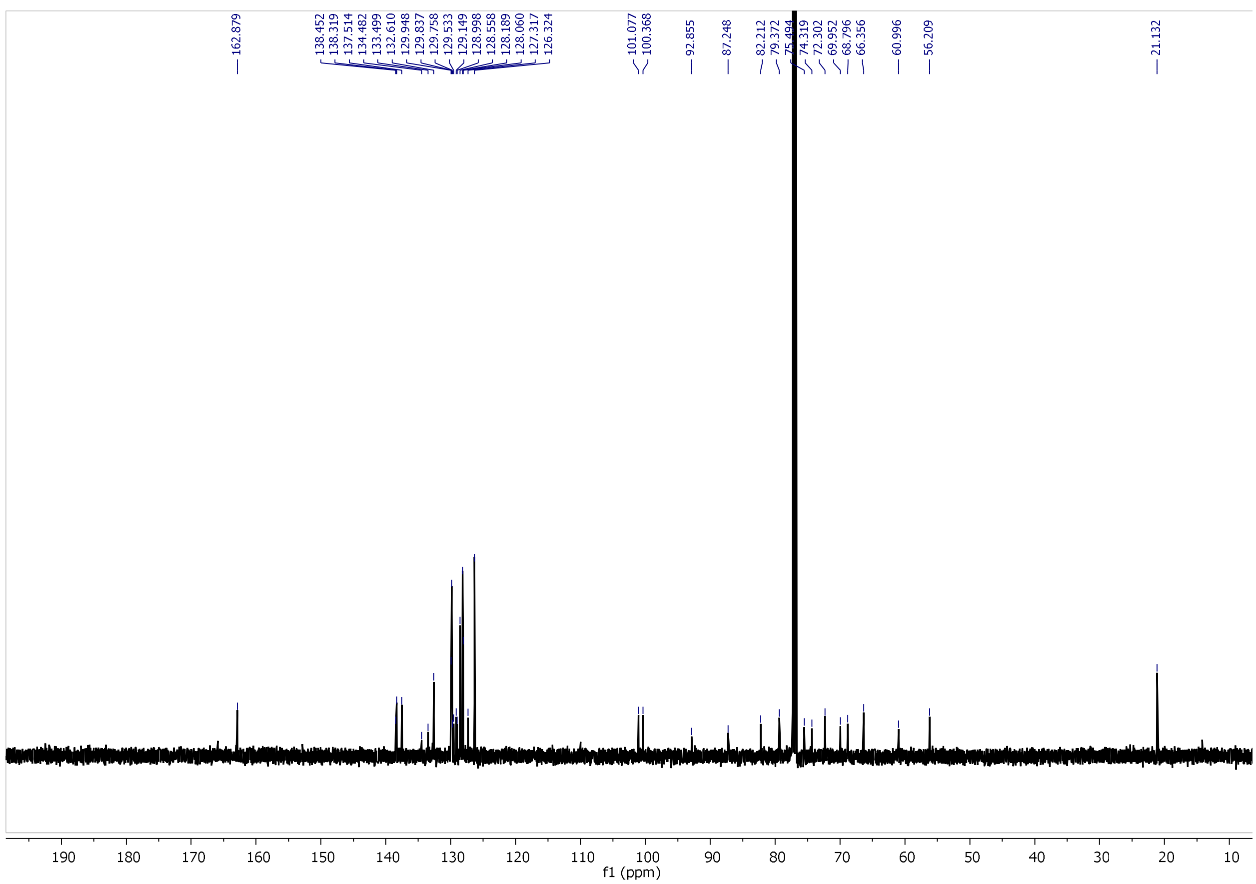
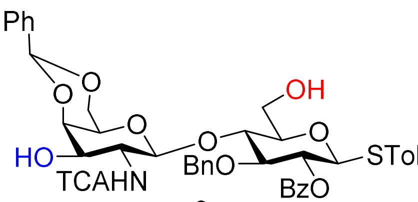


gCOSY ($CDCl_3$, 500 MHz) of **9**



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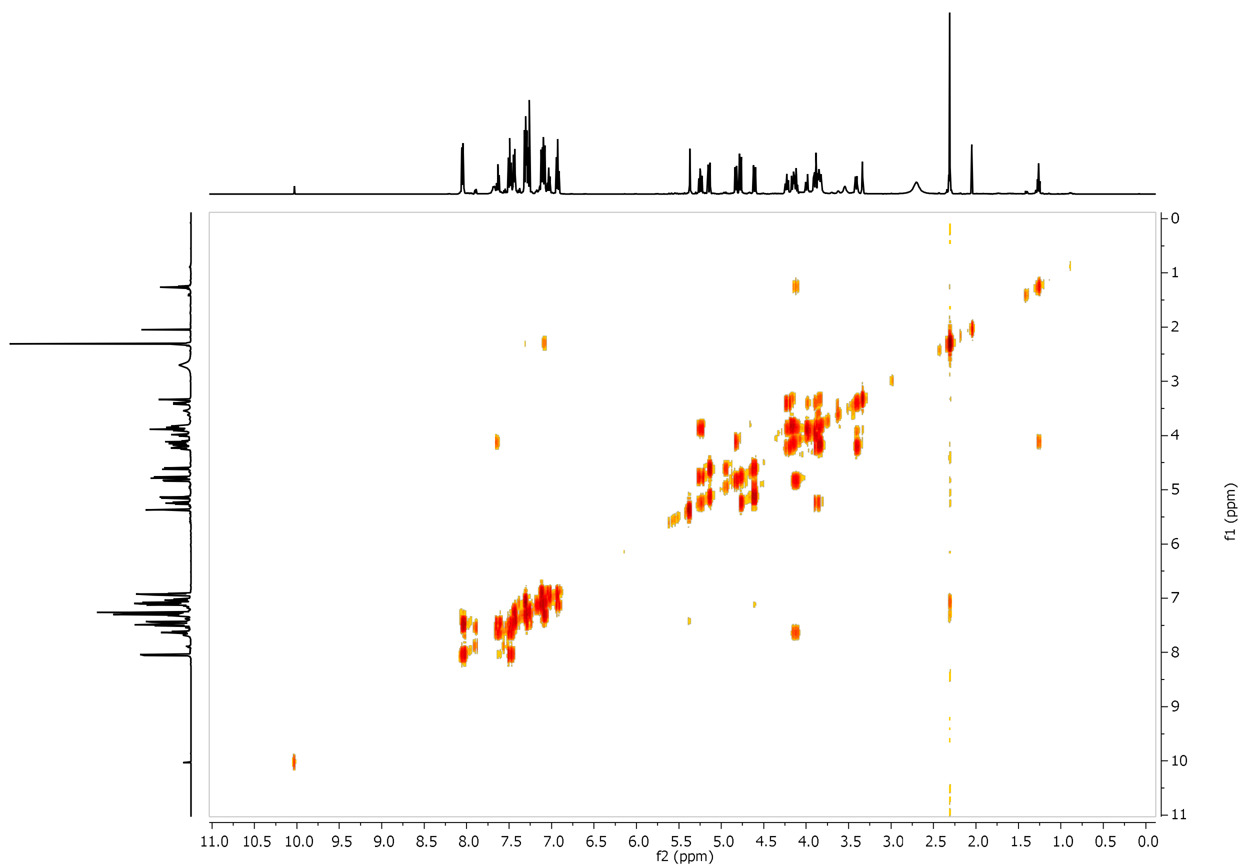
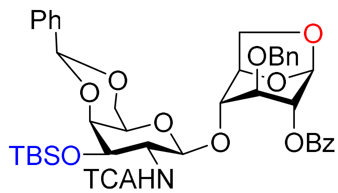


[1]H-NMR ($CDCl_3$, 500 MHz) of **10**



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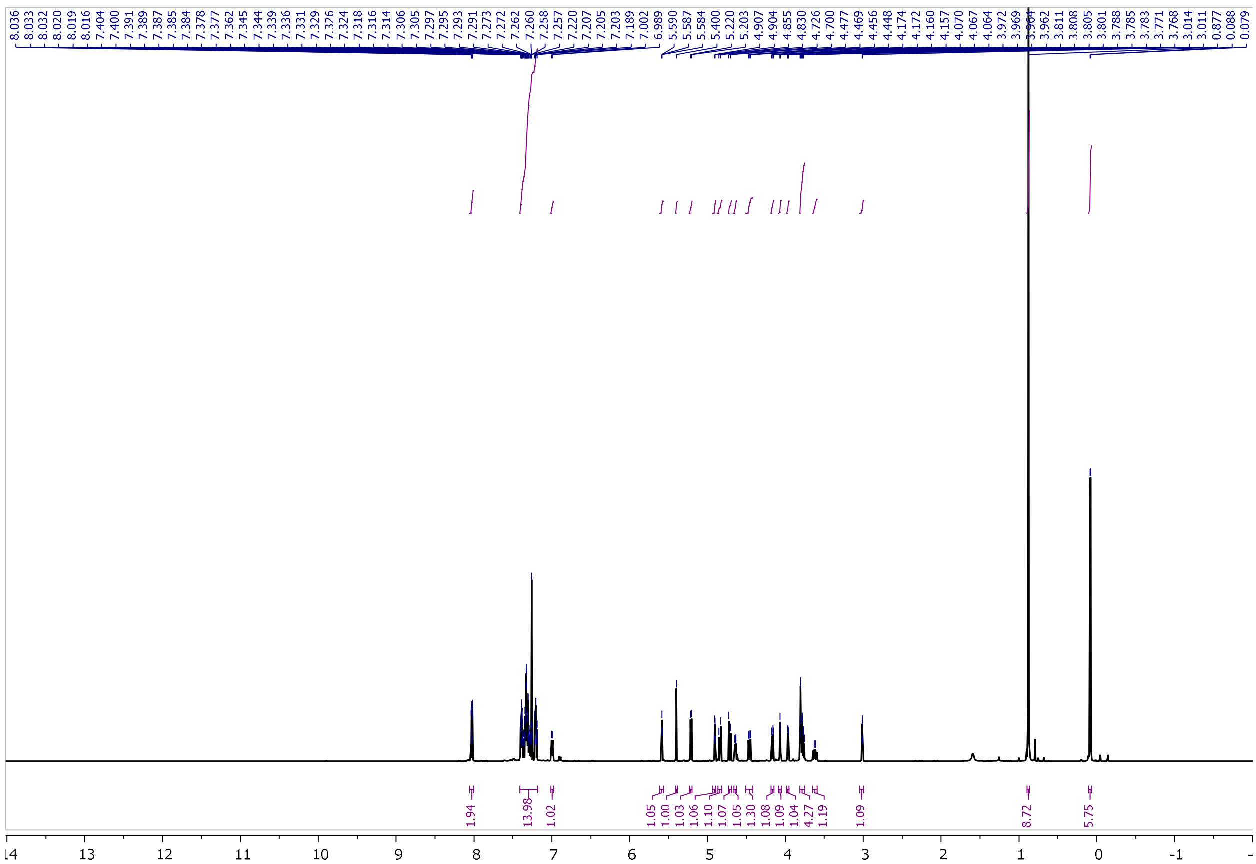
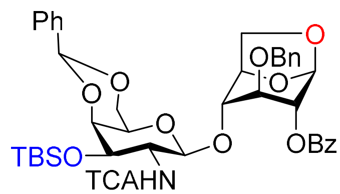


^{13}C-NMR ($CDCl_3$, 126 MHz) of **10**



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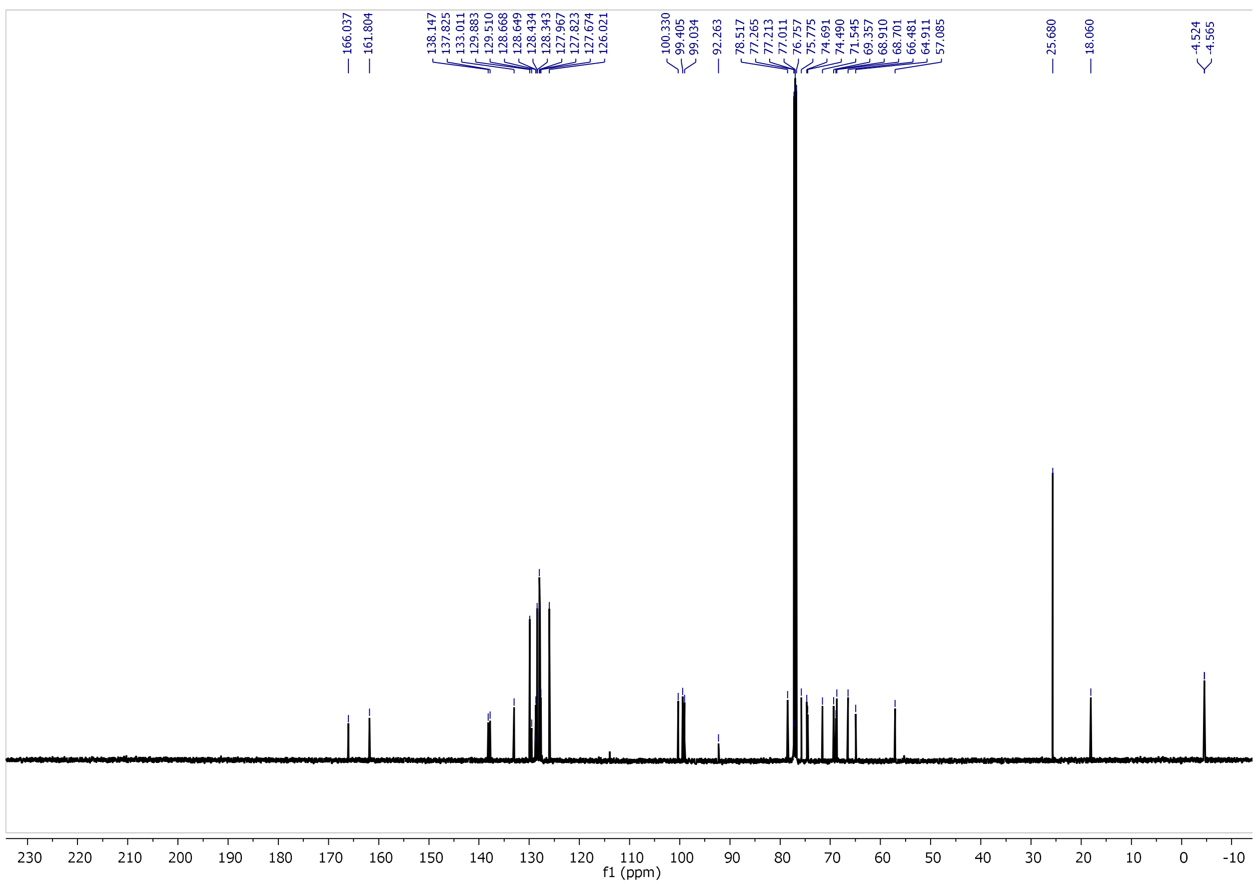
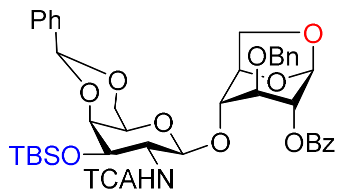


gCOSY ($CDCl_3$, 500 MHz) of **10**



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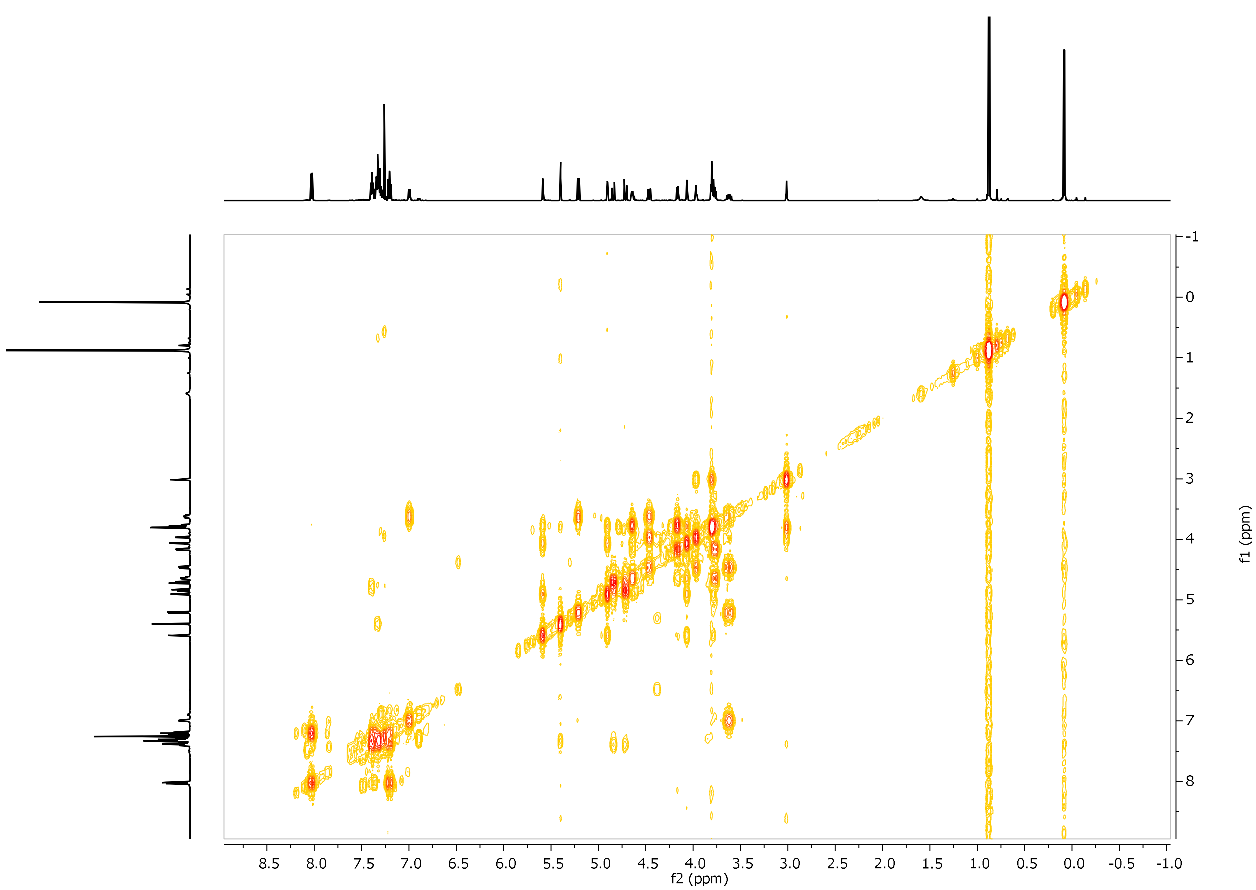
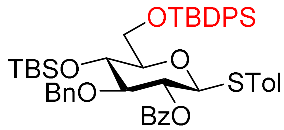


^{1}H-NMR ($CDCl_3$, 500 MHz) of **11**



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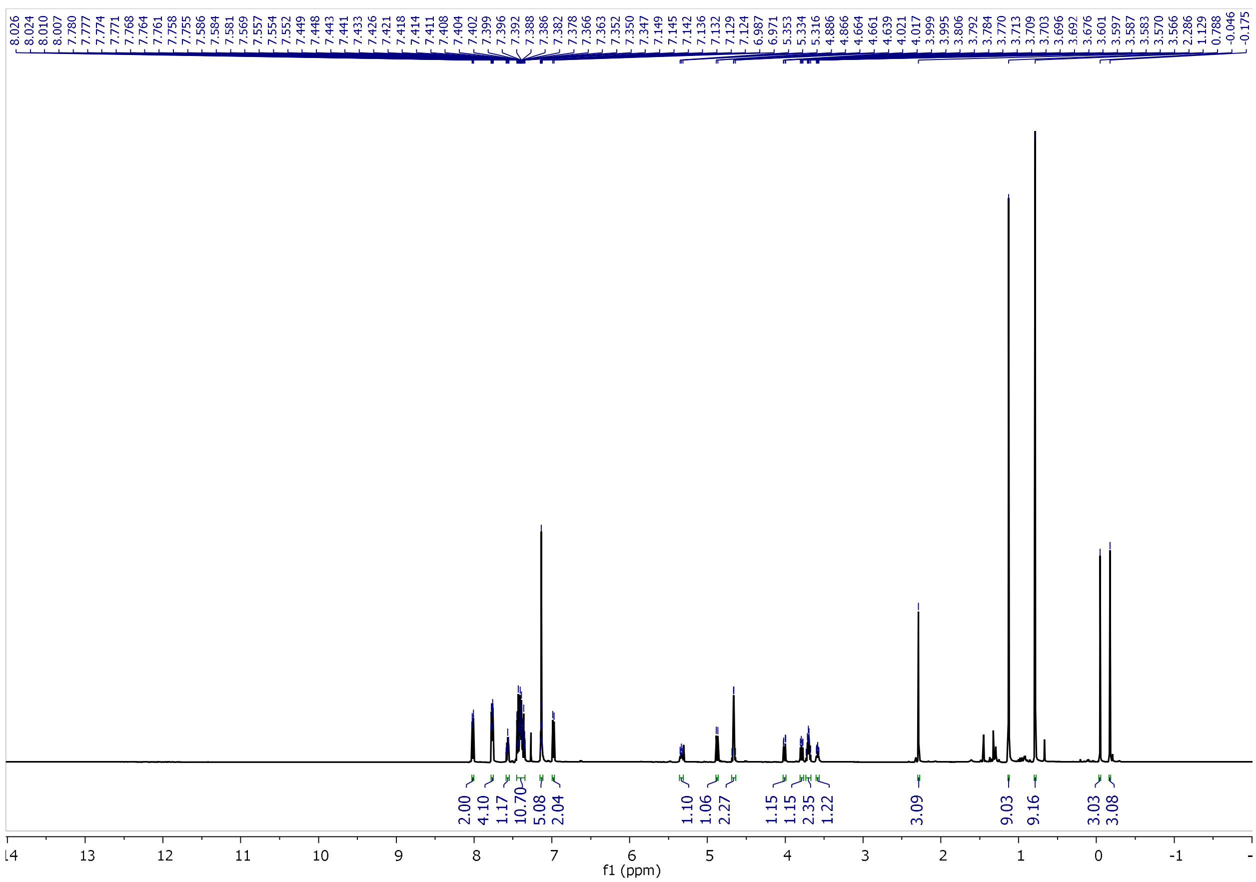
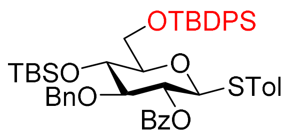


^{13}C-NMR ($CDCl_3$, 126 MHz) of **11**



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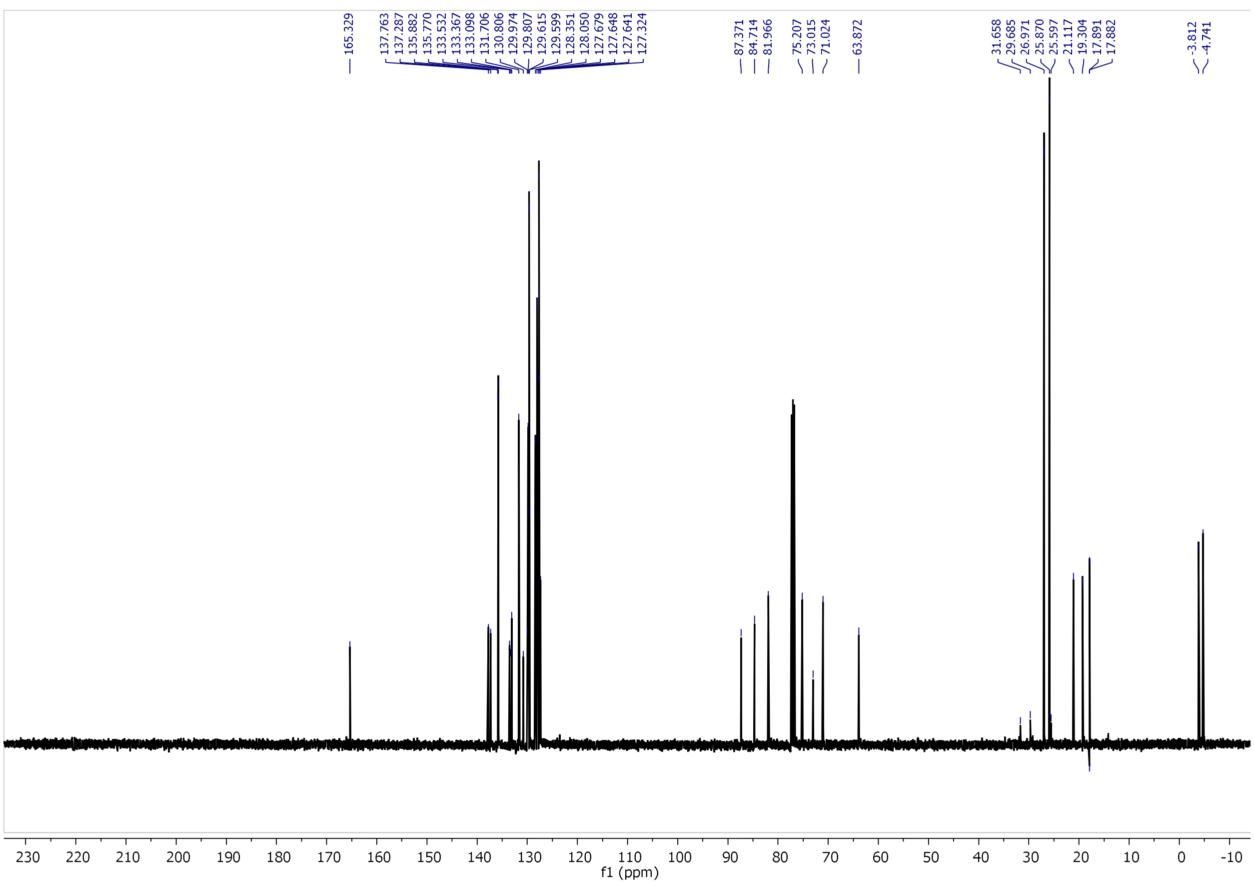
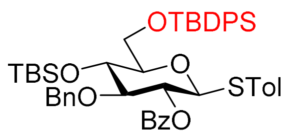


gCOSY ($CDCl_3$, 500 MHz) of **11**



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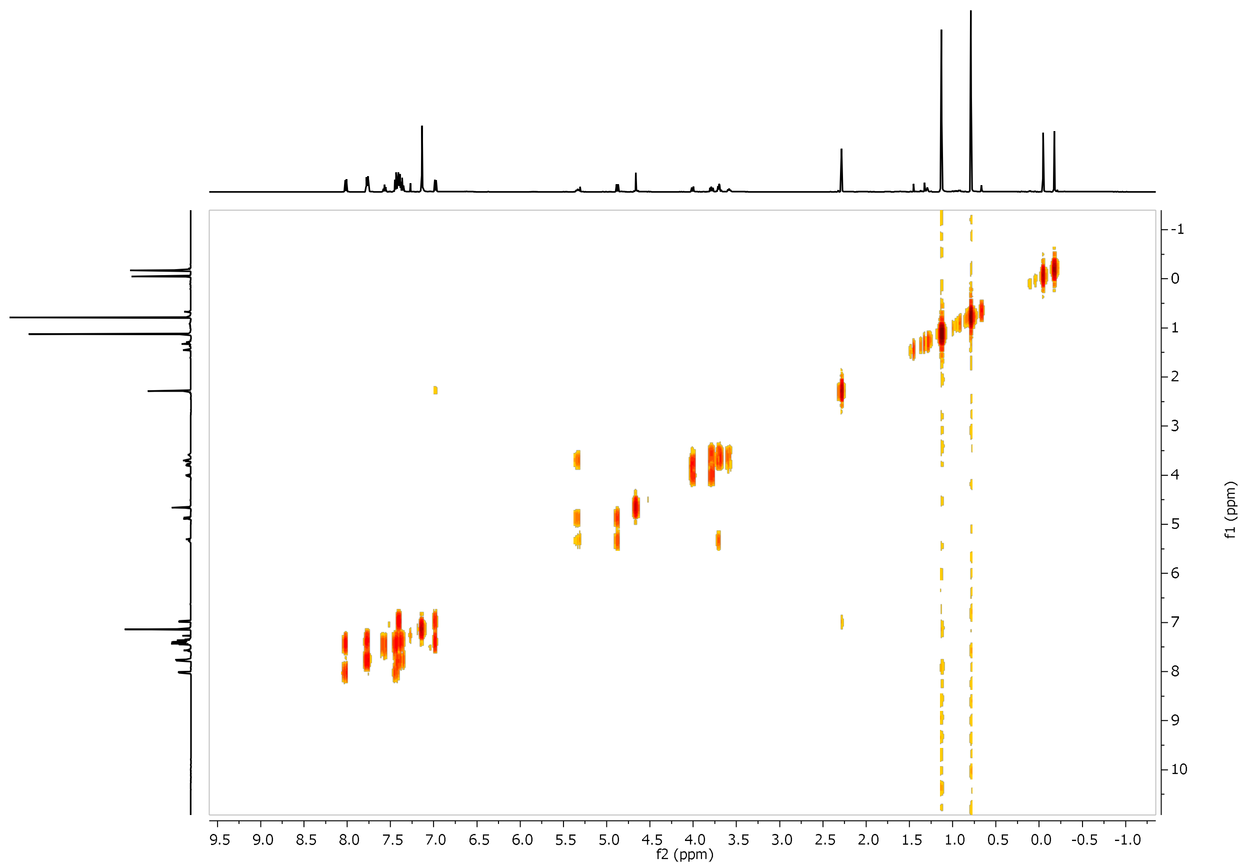
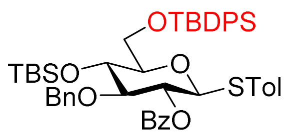


gHMBC ($CDCl_3$, 500 MHz) of **11**



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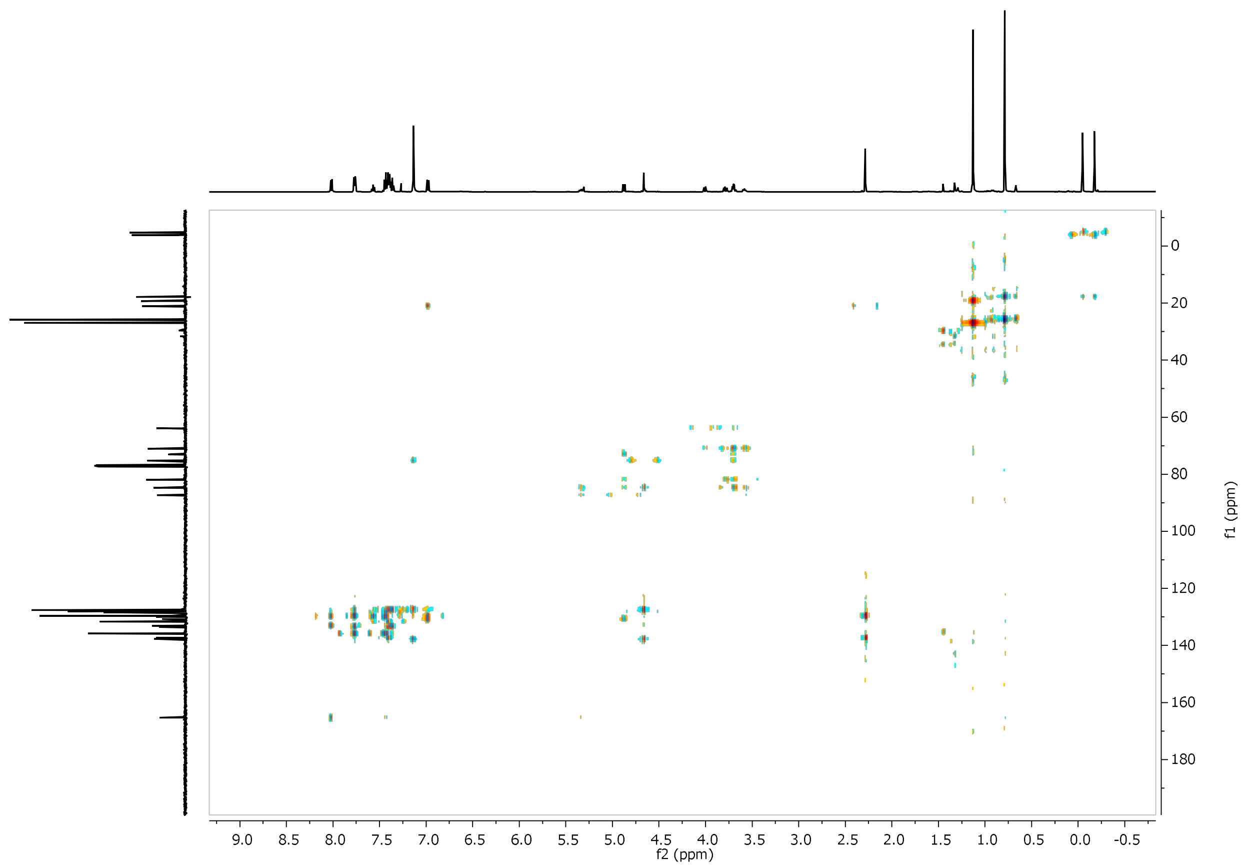
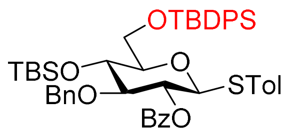


gHSQC ($CDCl_3$, 500 MHz) of **11**



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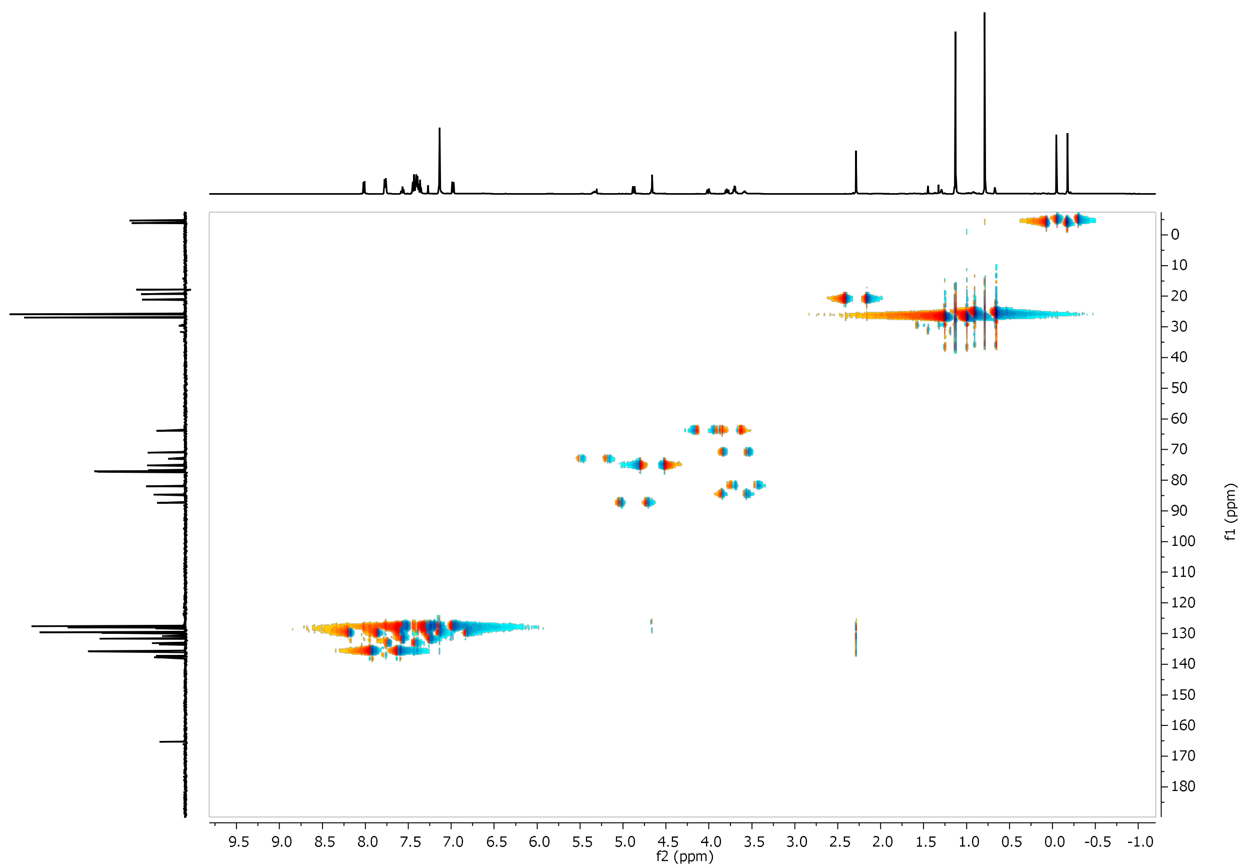
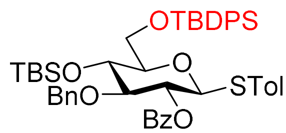


bsgHSQC ($CDCl_3$, 500 MHz) of **11**



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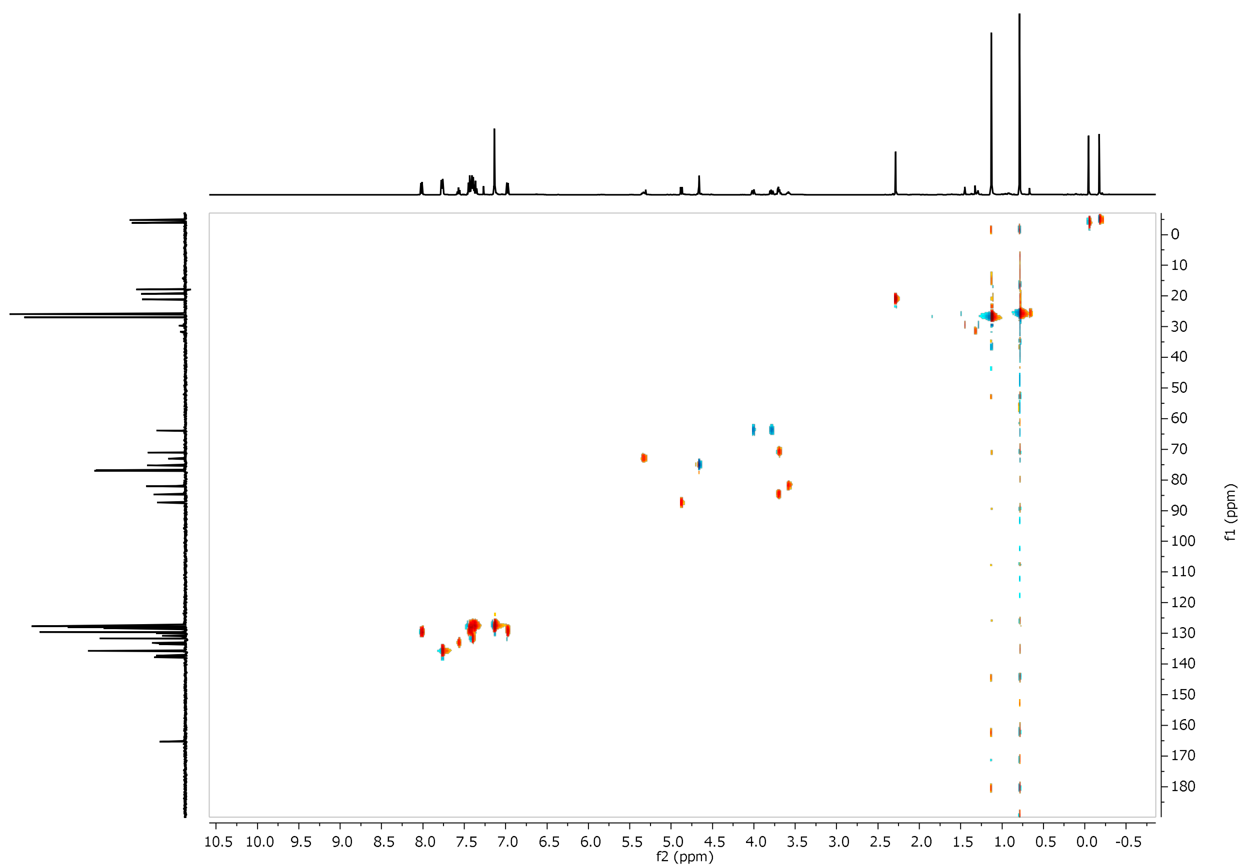
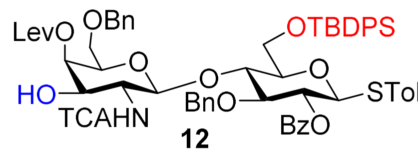


[1]H-NMR (CDCl$_3$, 500 MHz) of **12**



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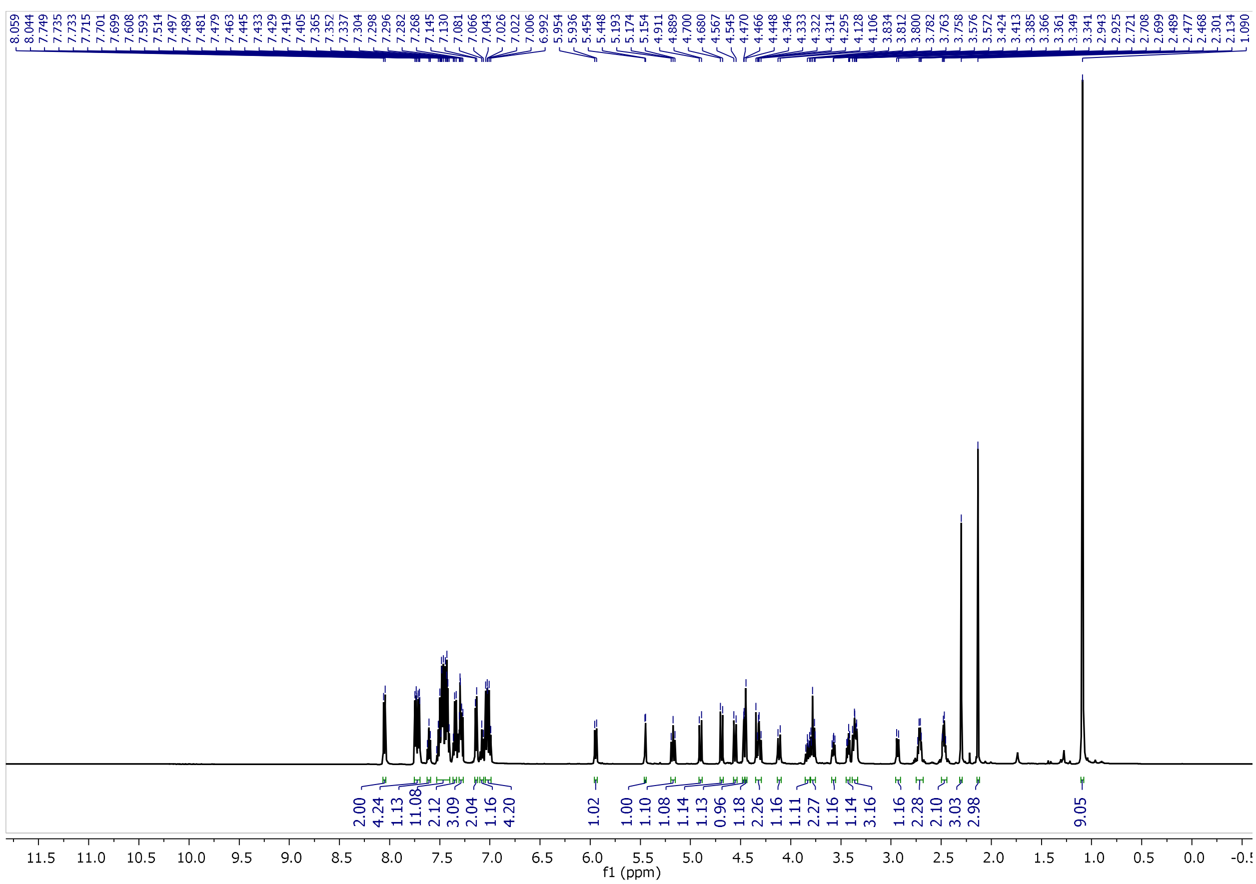
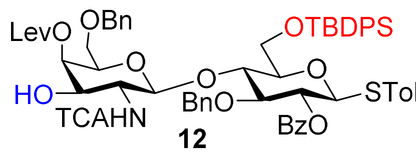
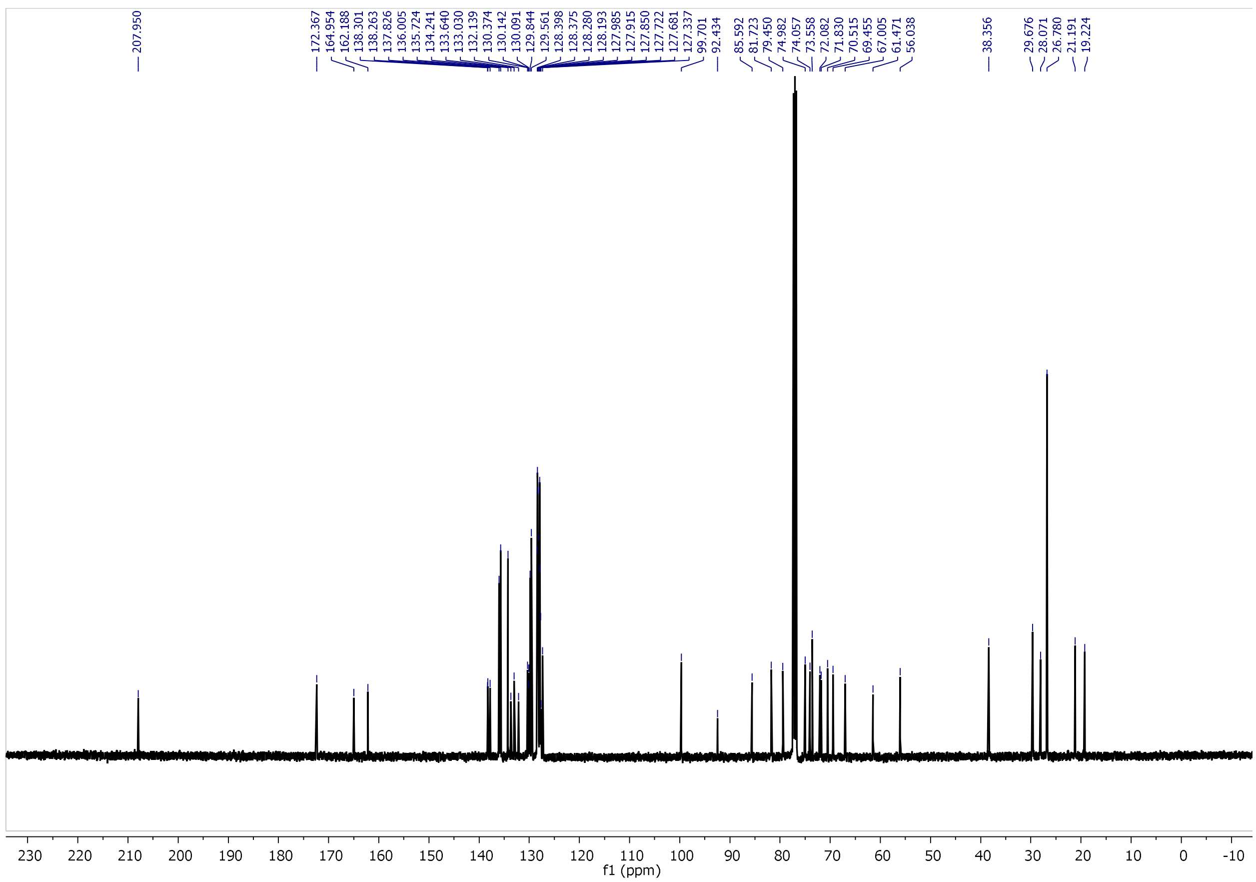
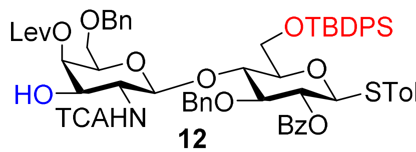


^{13}C-NMR ($CDCl_3$, 126 MHz) of **12**





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



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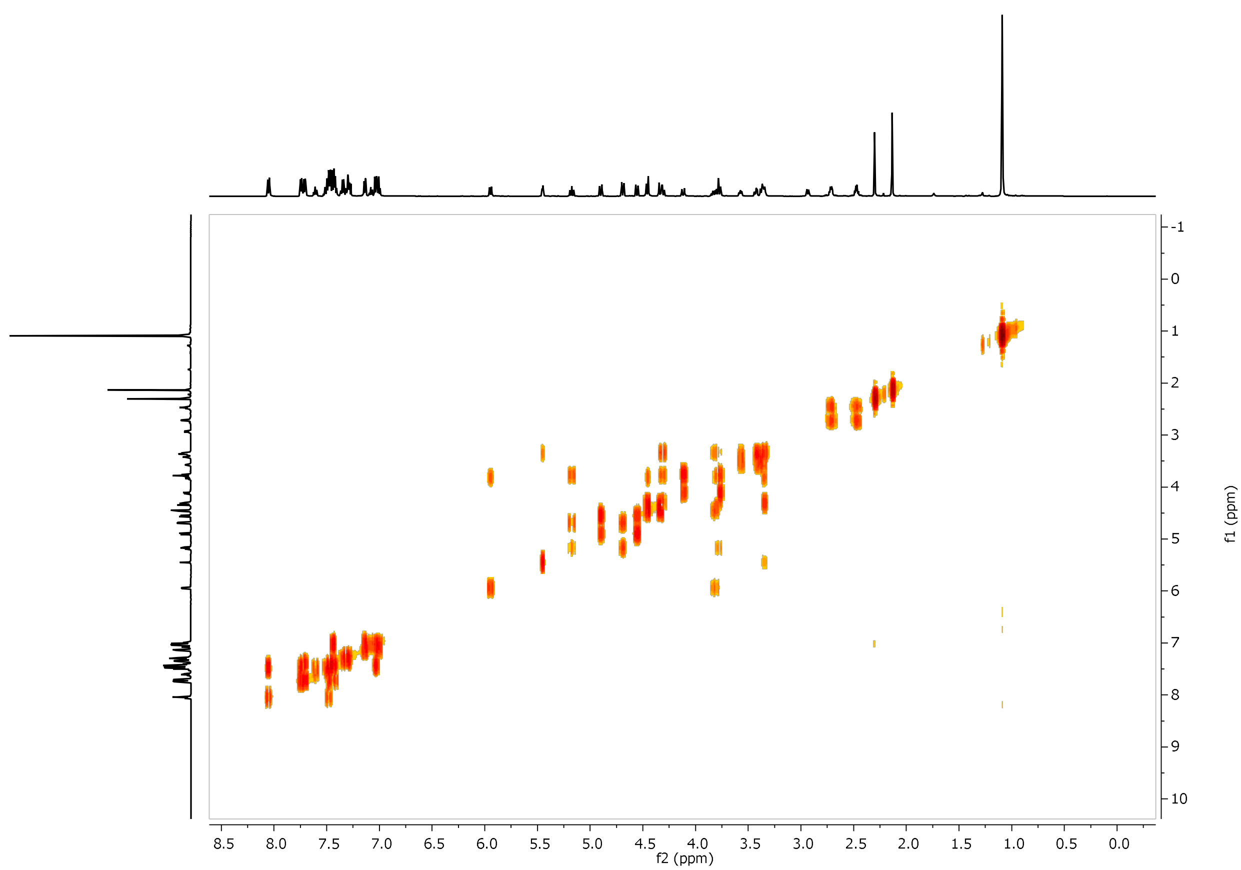
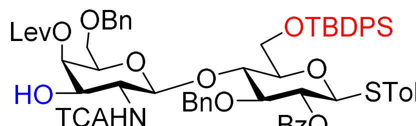


bsgHSQC ($CDCl_3$, 500 MHz) of **12**



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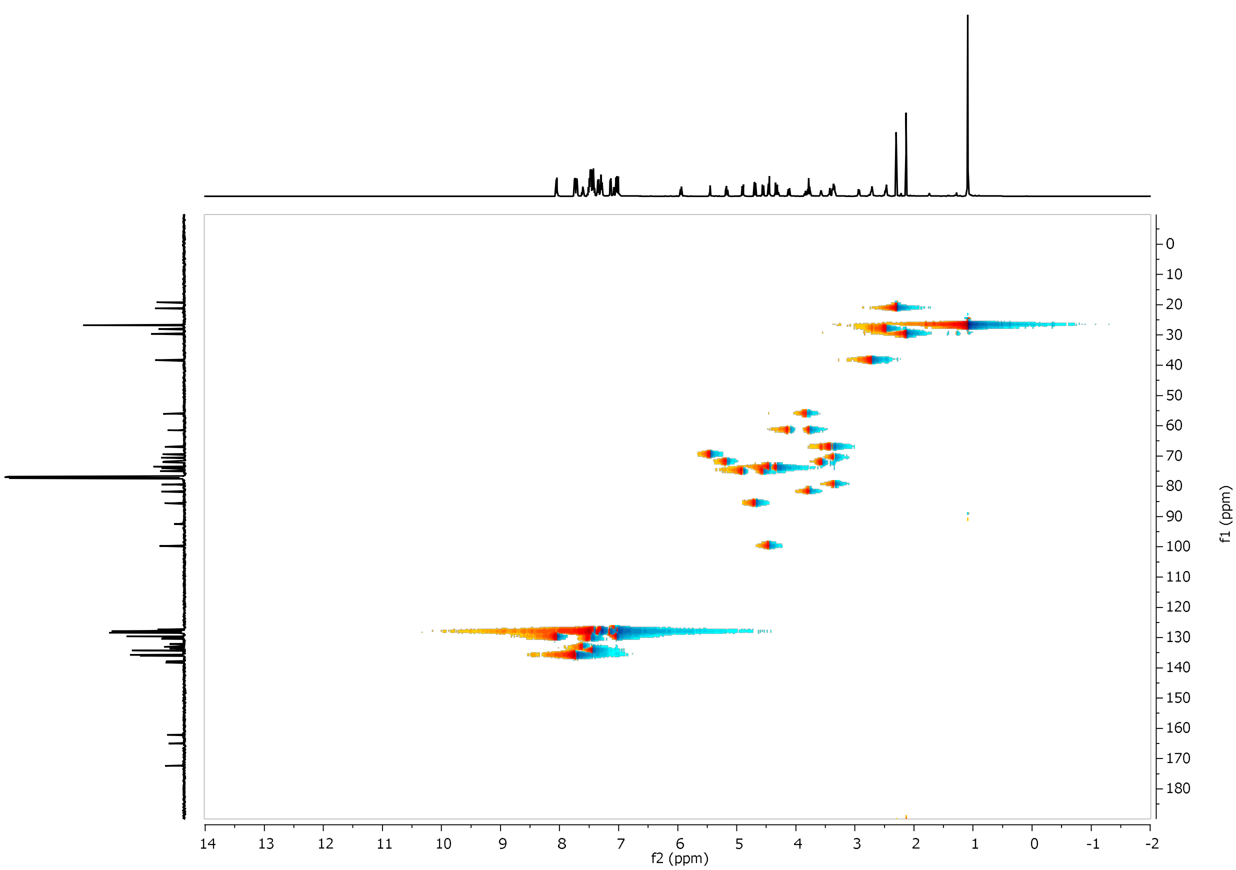
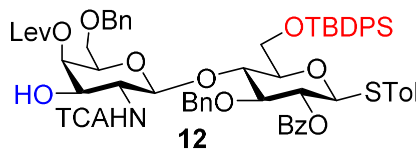
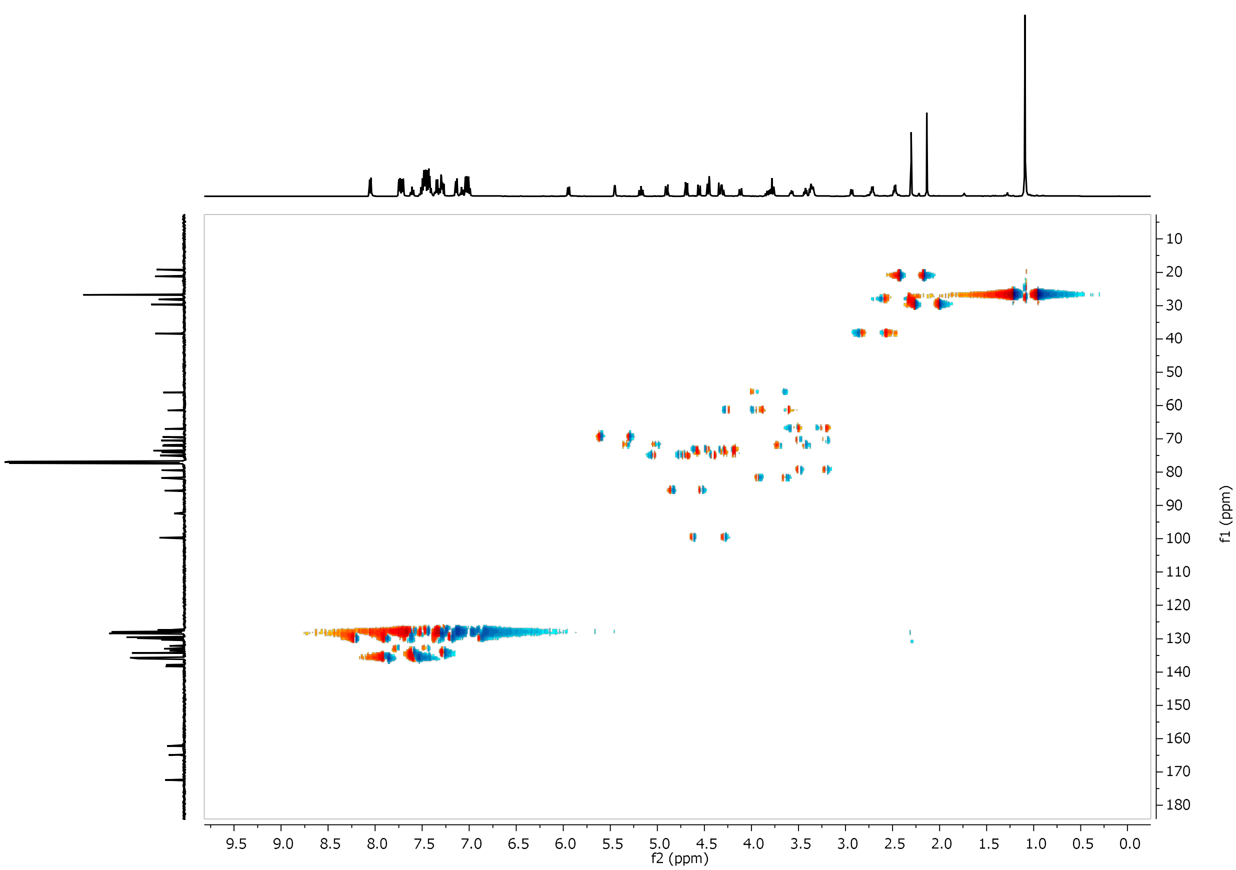
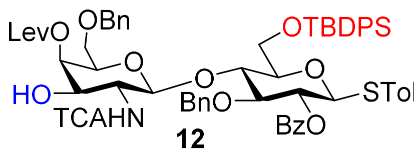


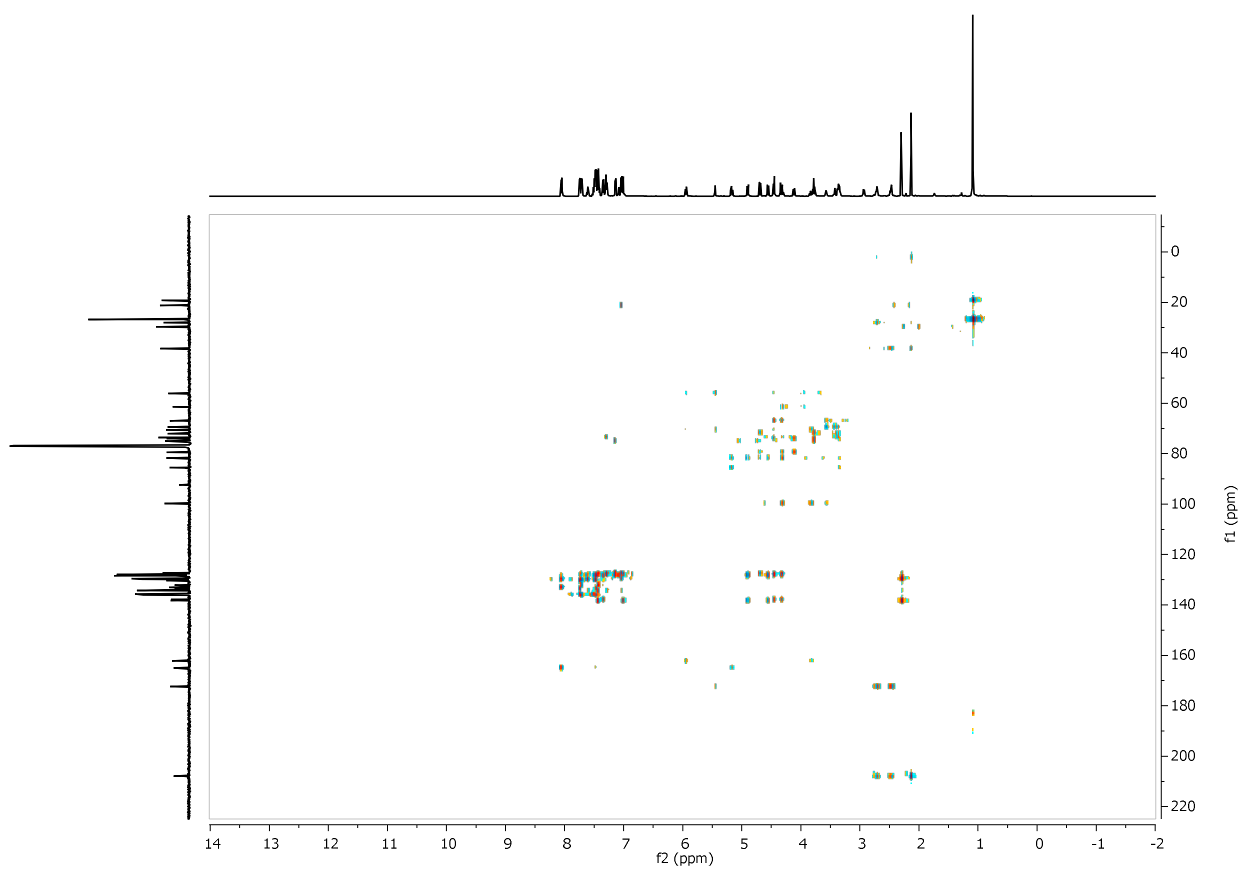
gHSQC ($CDCl_3$, 500 MHz) of **12**



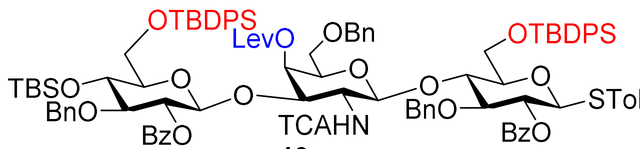


gHMBC ($CDCl_3$, 500 MHz) of **12**





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



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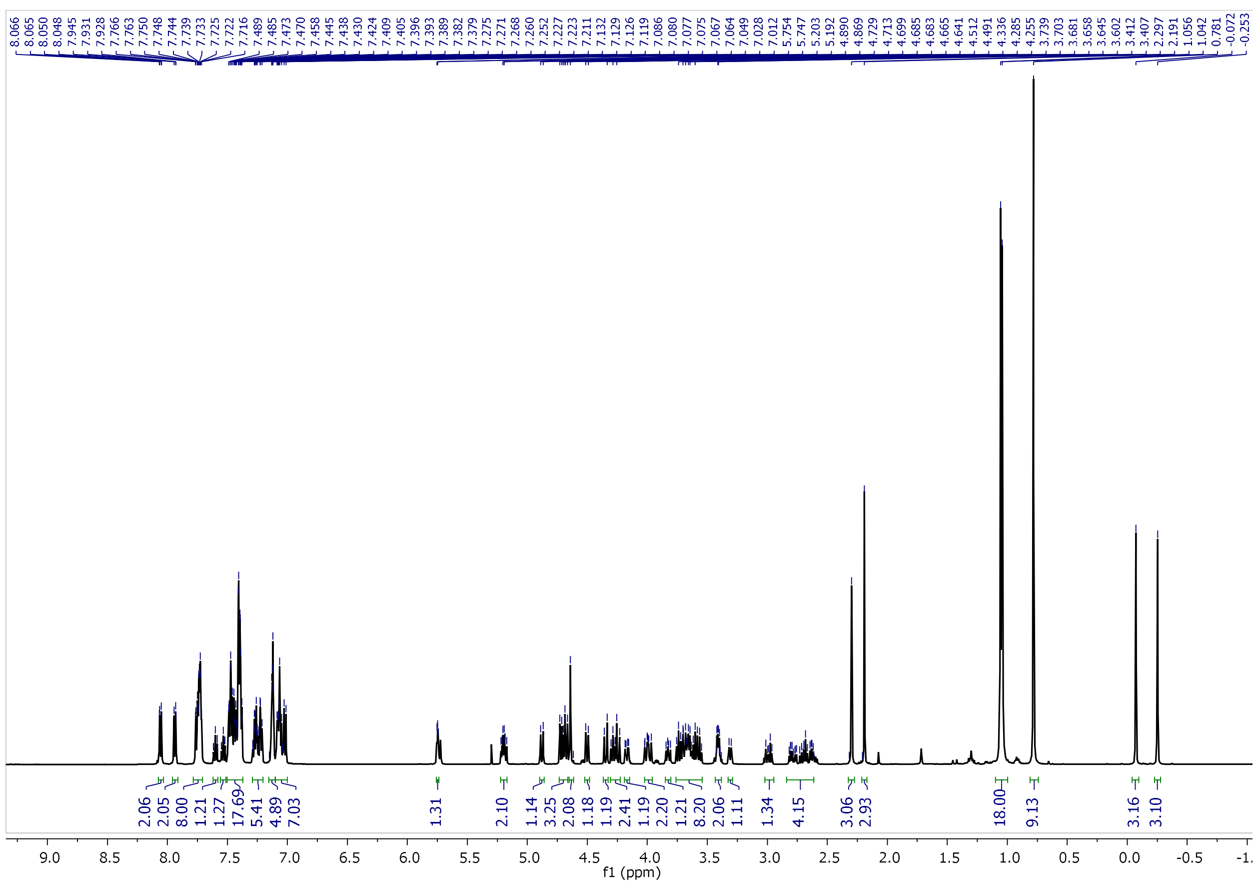
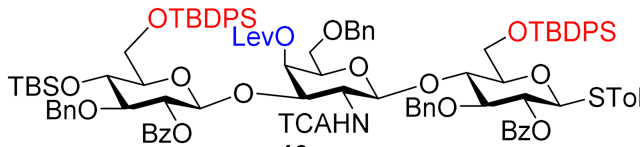
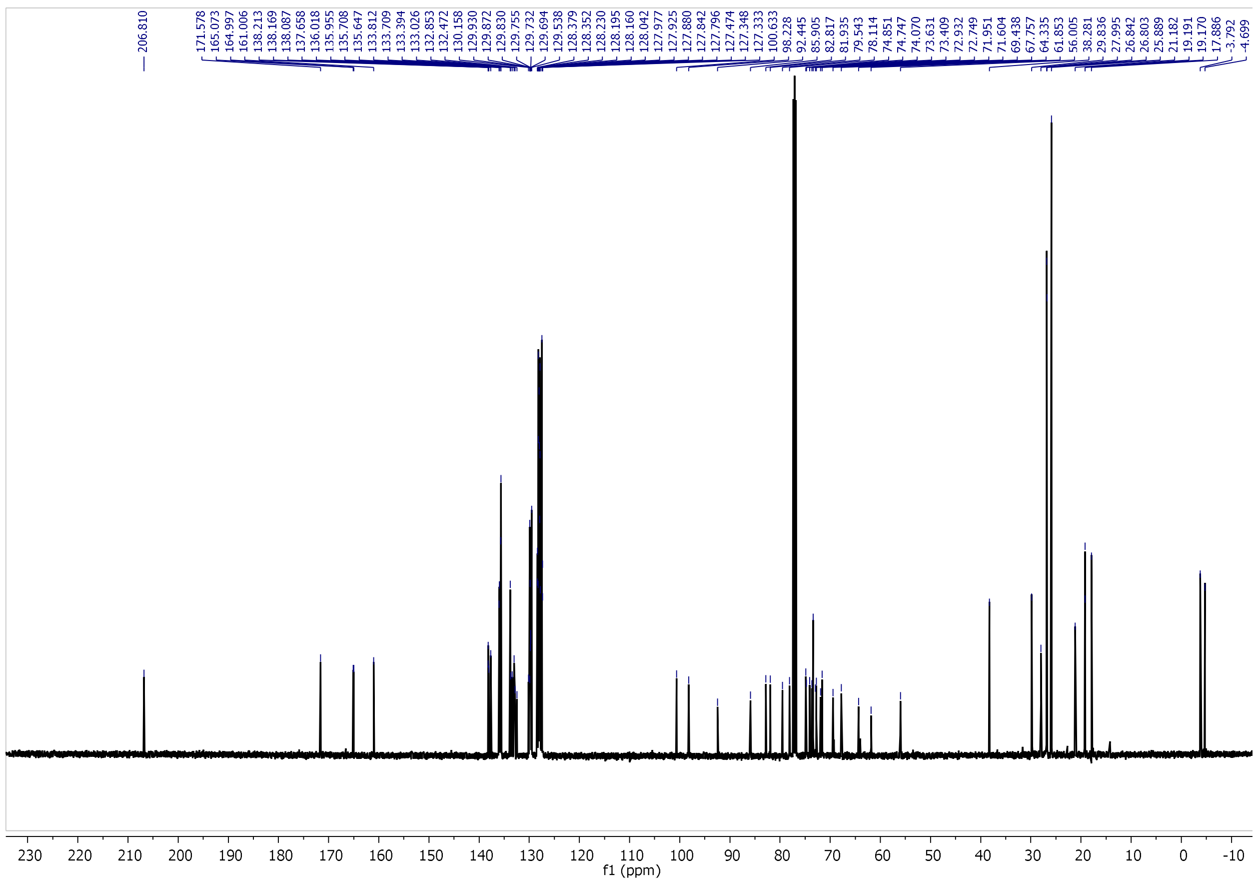
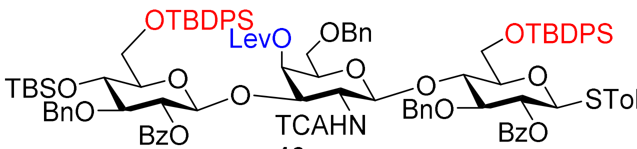


^{13}C-NMR (CDCl$_3$, 126 MHz) of **13**





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



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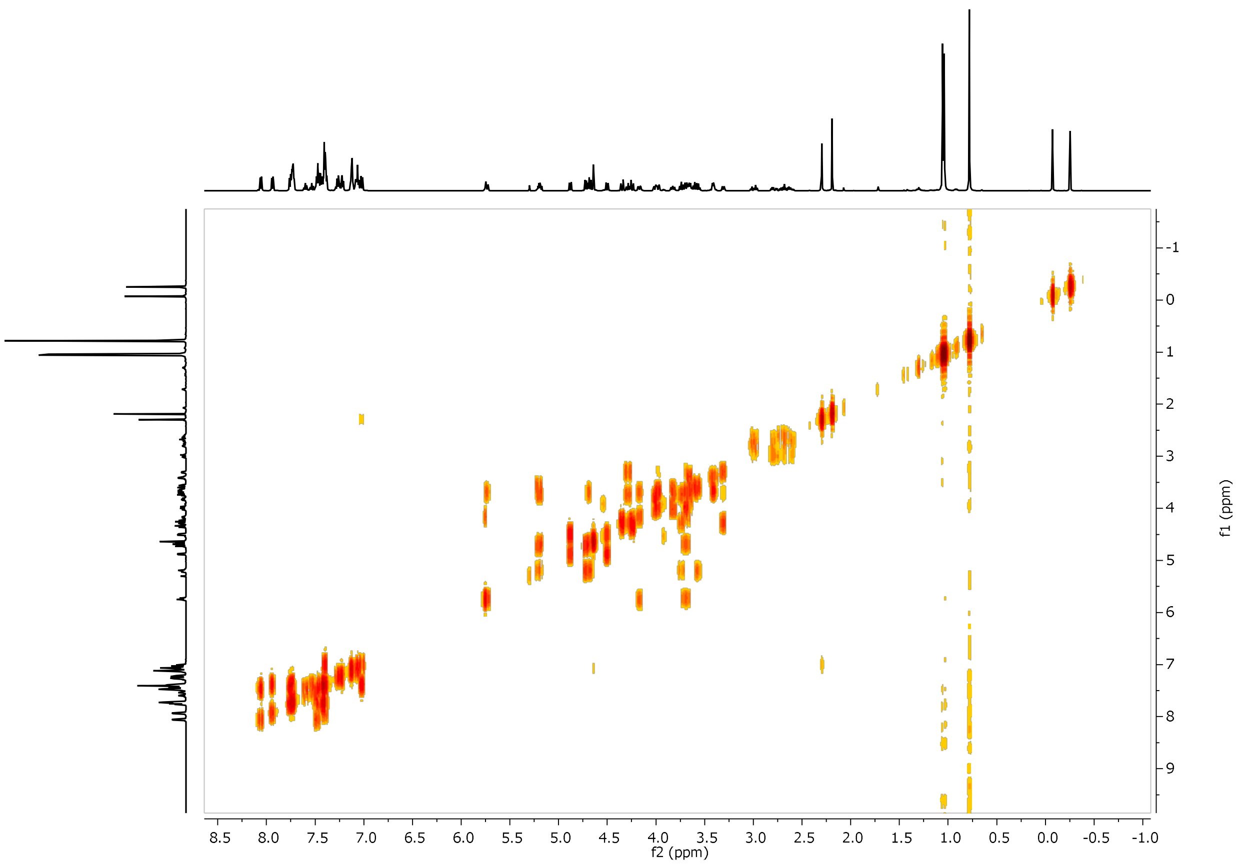
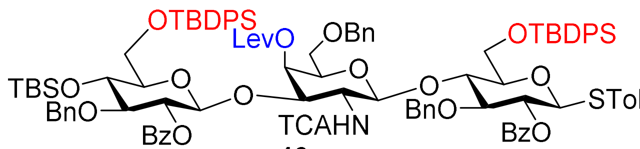


bsgHSQC ($CDCl_3$, 500 MHz) of **13**



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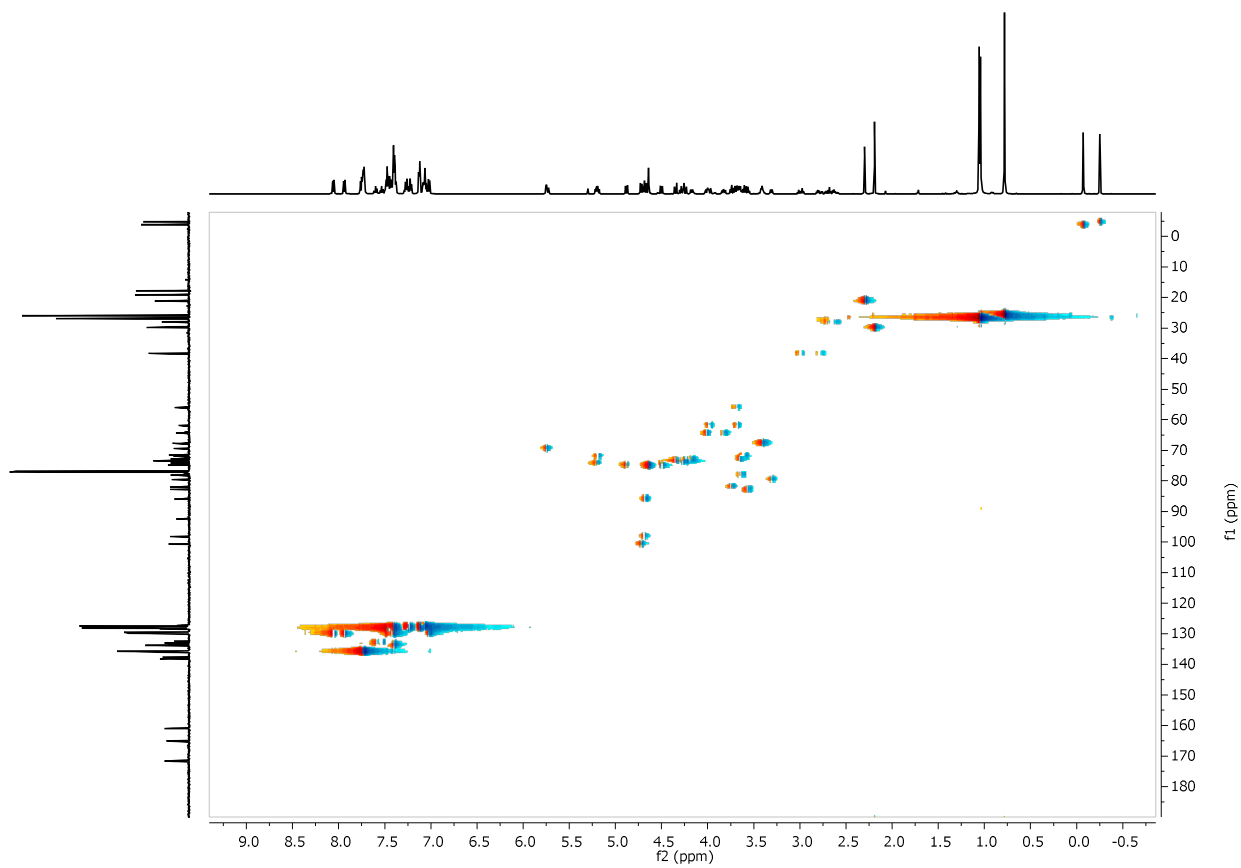
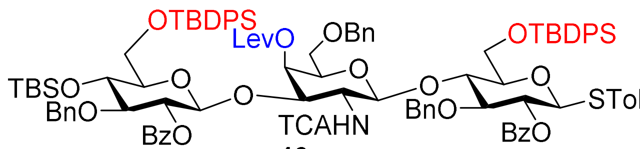


gHSQC ($CDCl_3$, 500 MHz) of **13**



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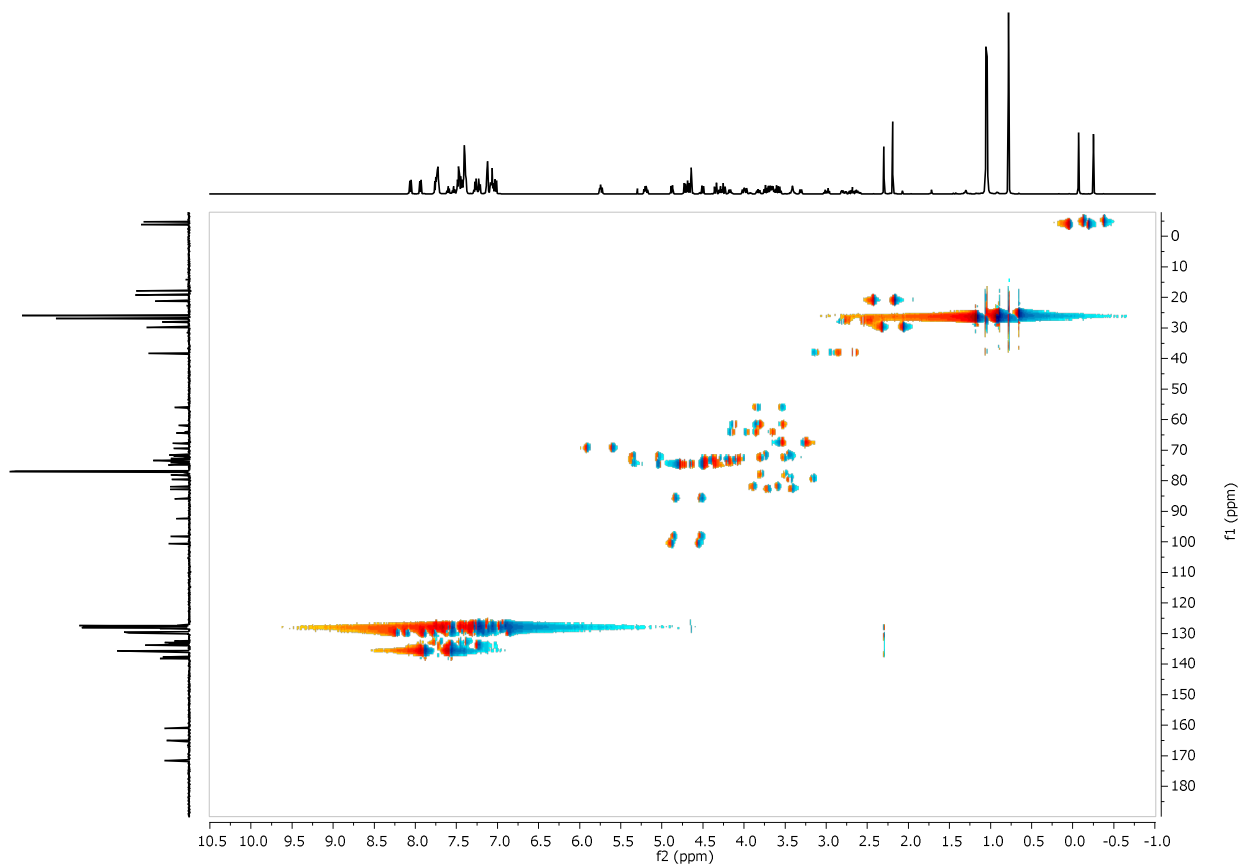
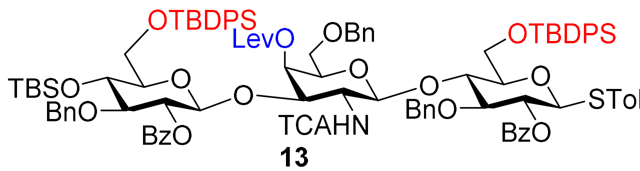
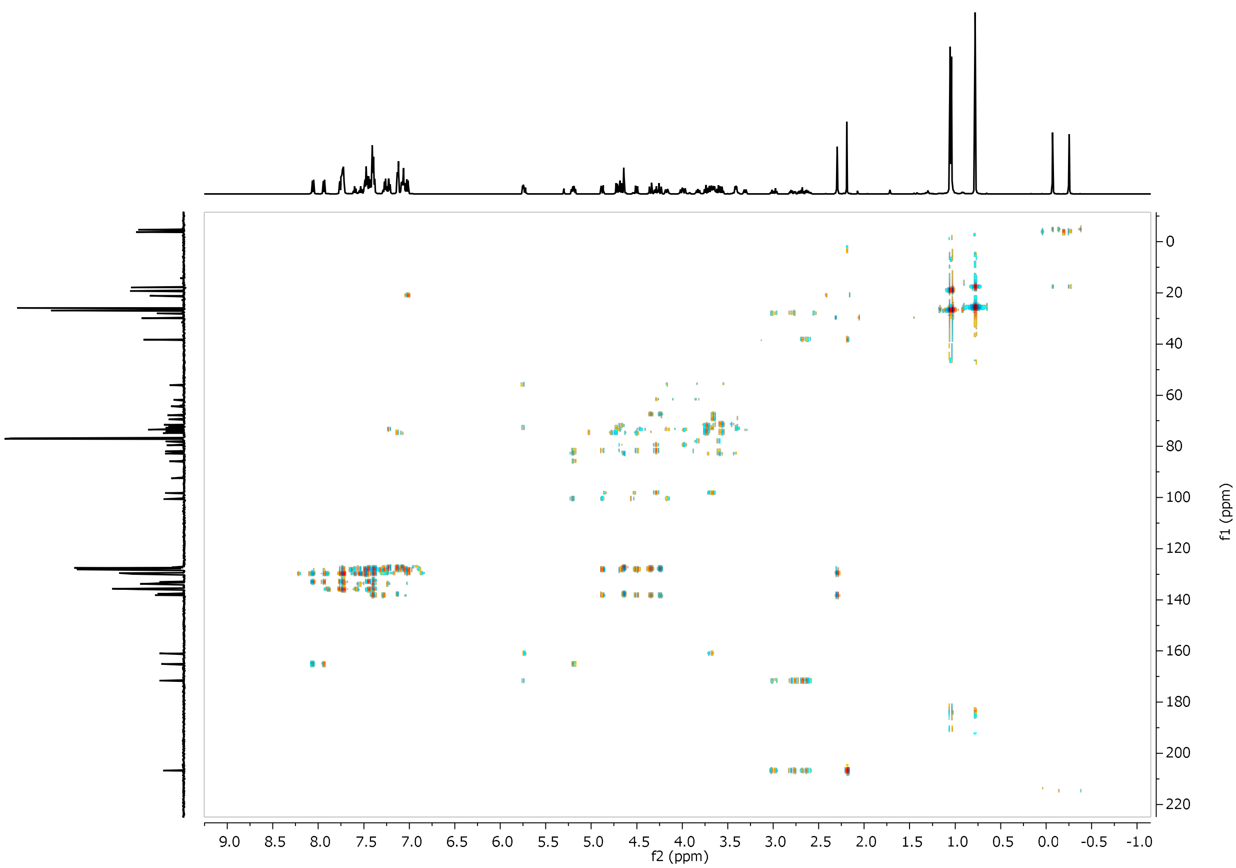
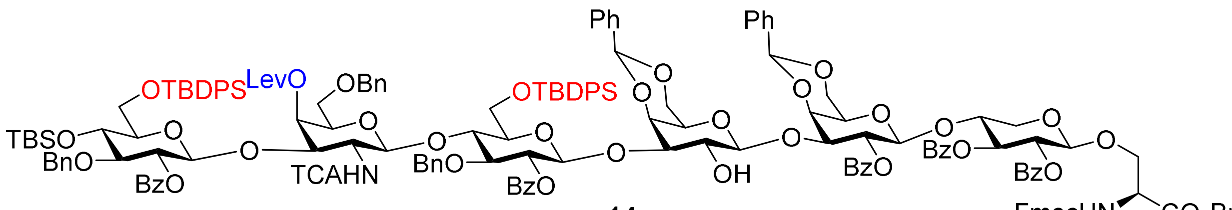


gHMBC (CDCl$_3$, 500 MHz) of **13**





[1]H-NMR ($CDCl_3$, 500 MHz) of **14**



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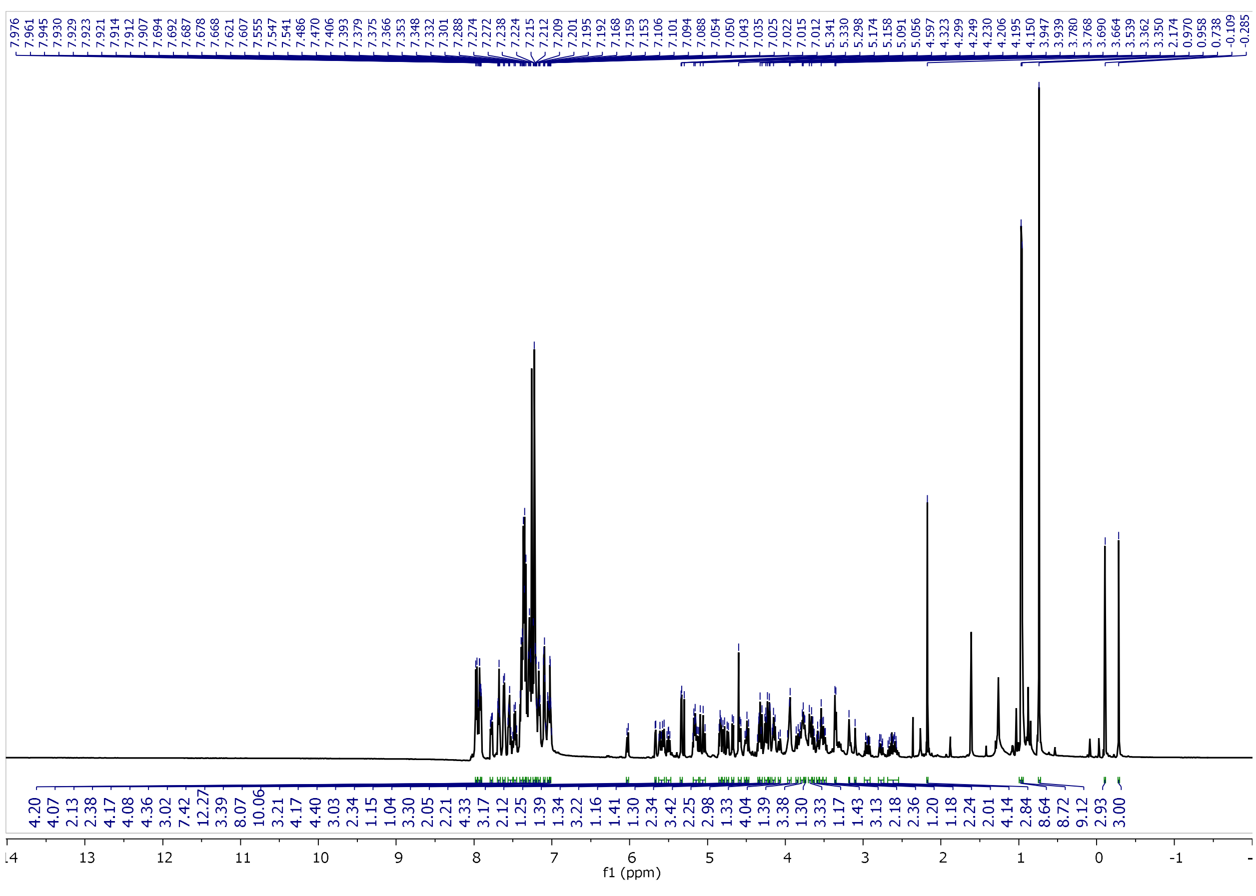
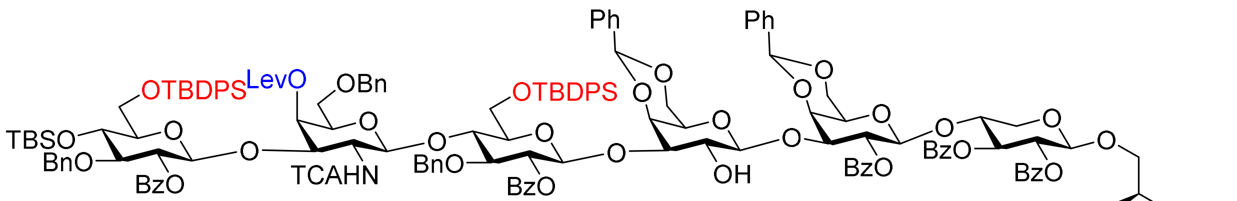


^{13}C-NMR ($CDCl_3$, 126 MHz) of **14**



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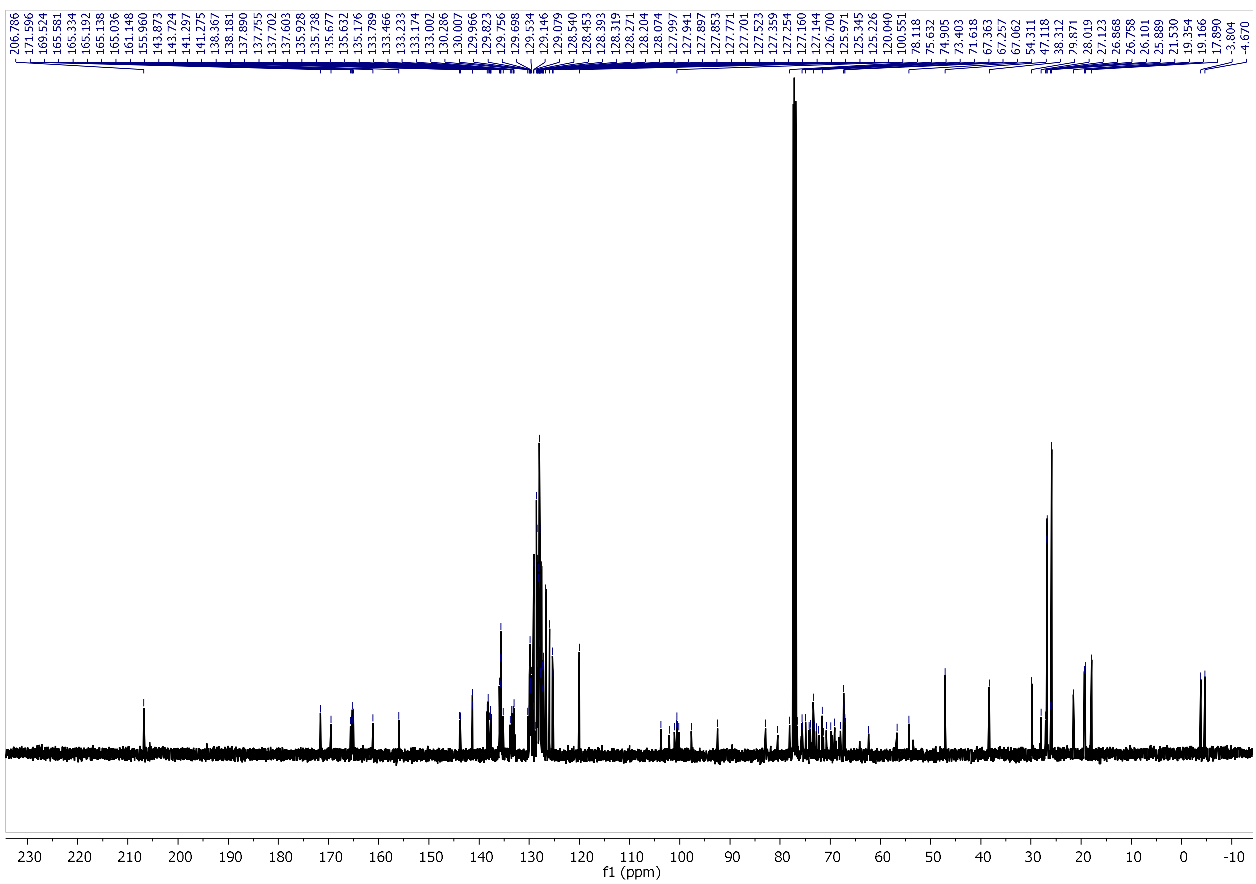
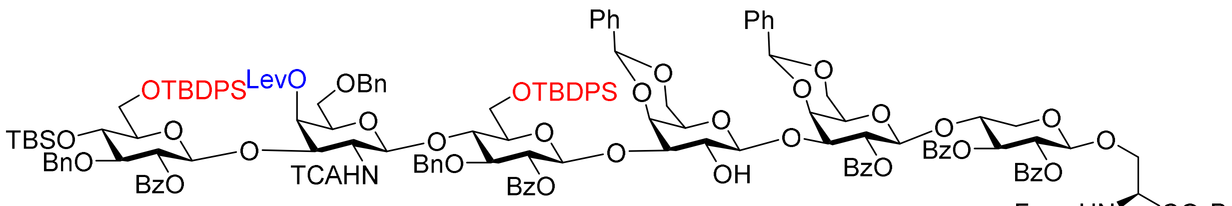


gCOSY ($CDCl_3$, 500 MHz) of **14**



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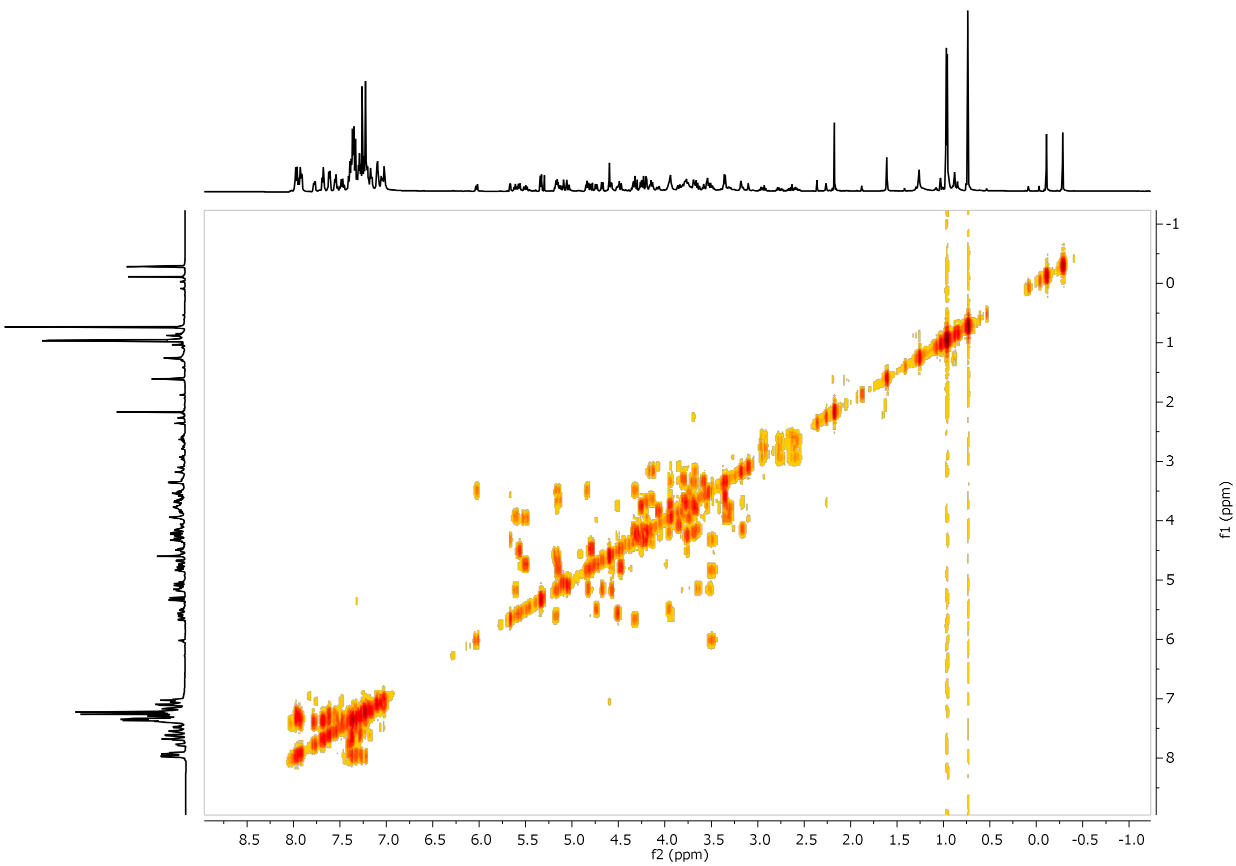
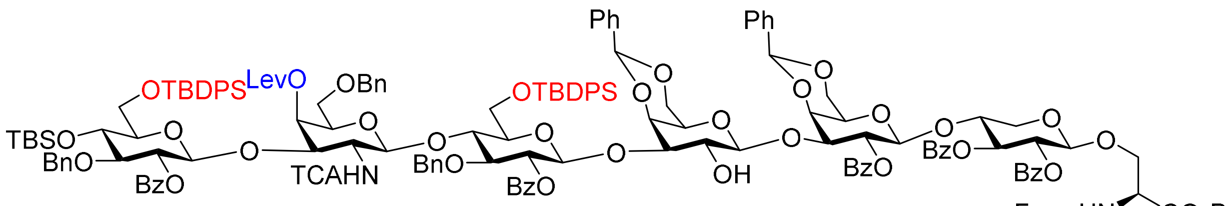


bsgHSQC ($CDCl_3$, 500 MHz) of **14**



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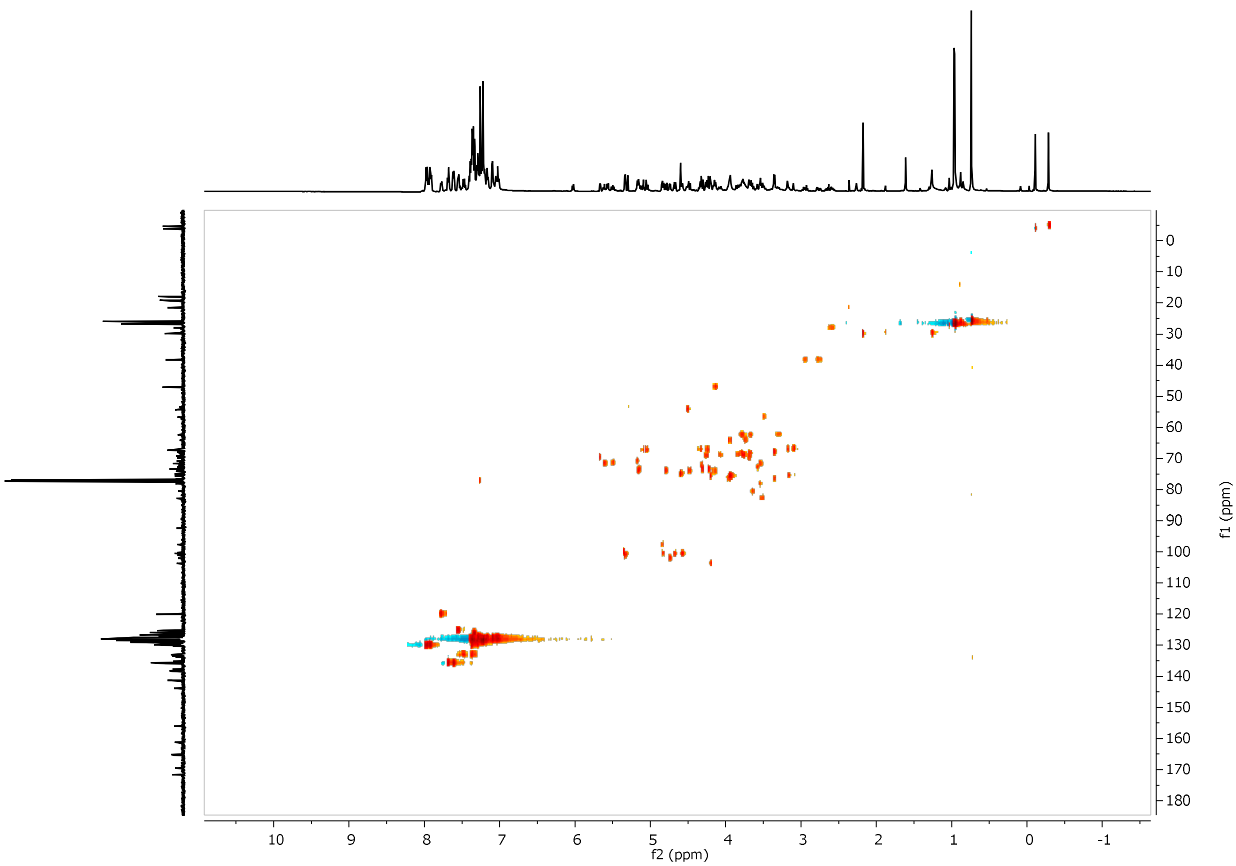
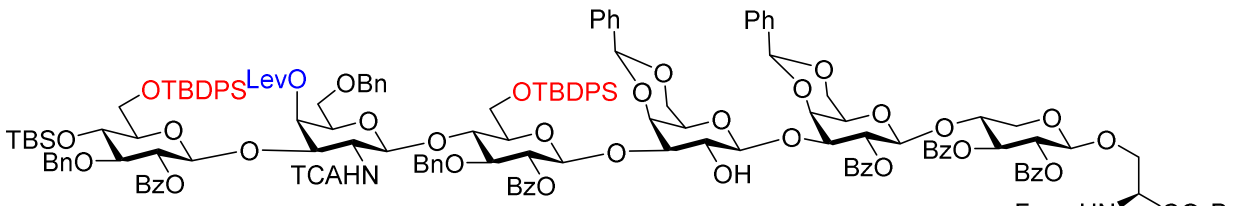


gHSQC ($CDCl_3$, 500 MHz) of **14**



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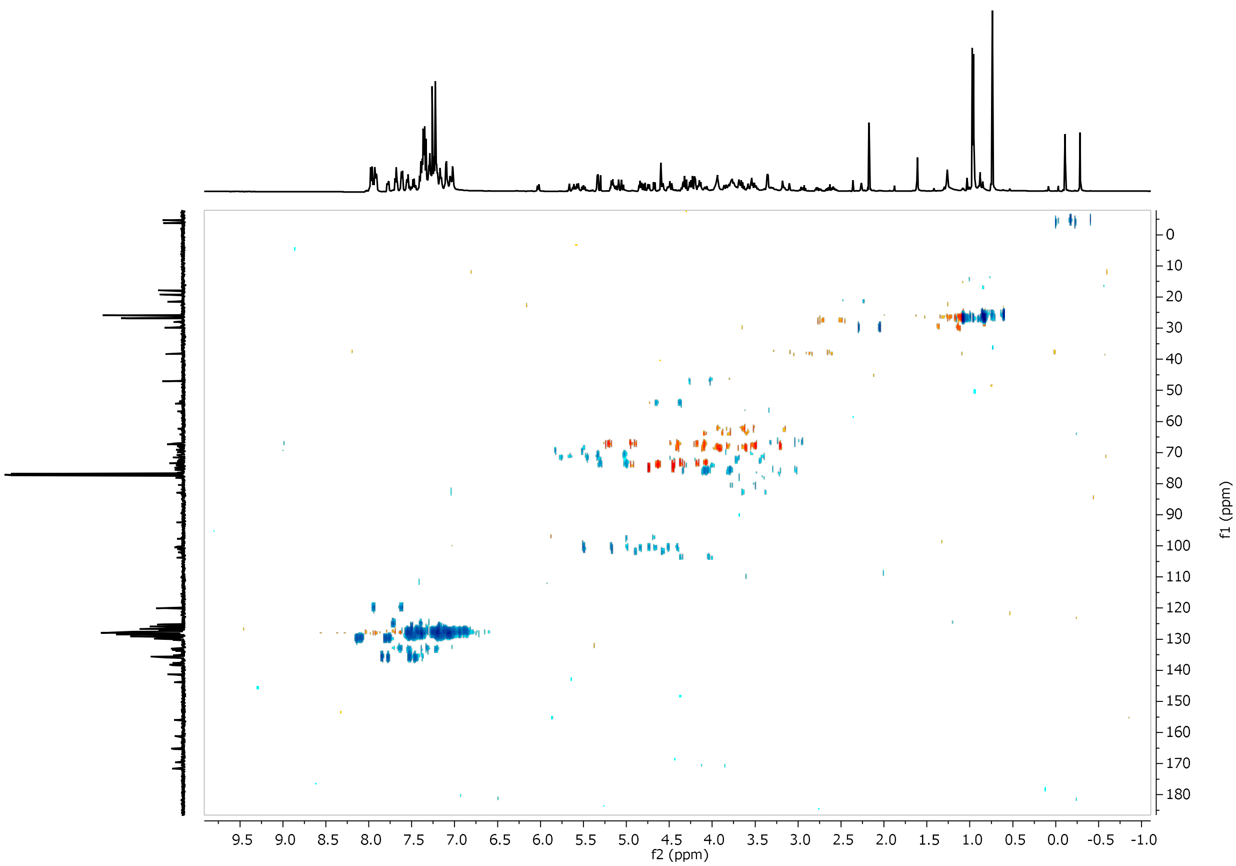
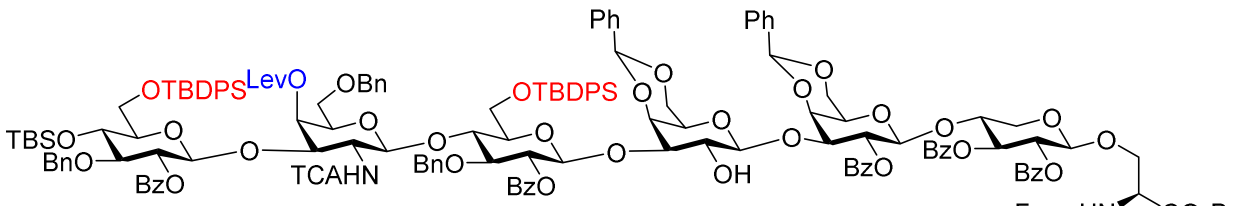


gHMBC ($CDCl_3$, 500 MHz) of **14**



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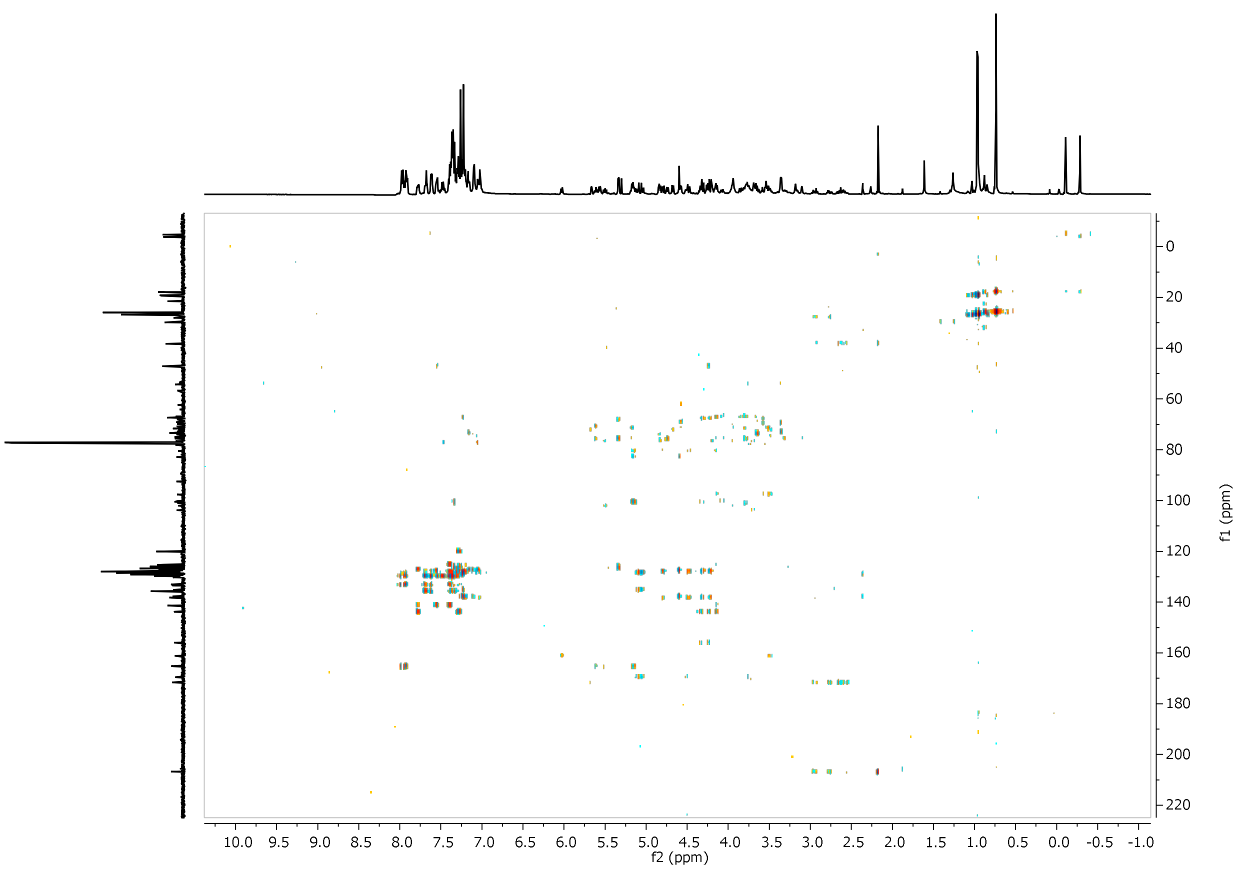
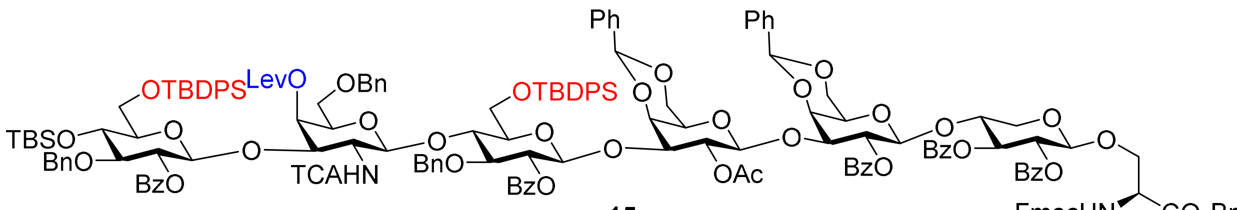
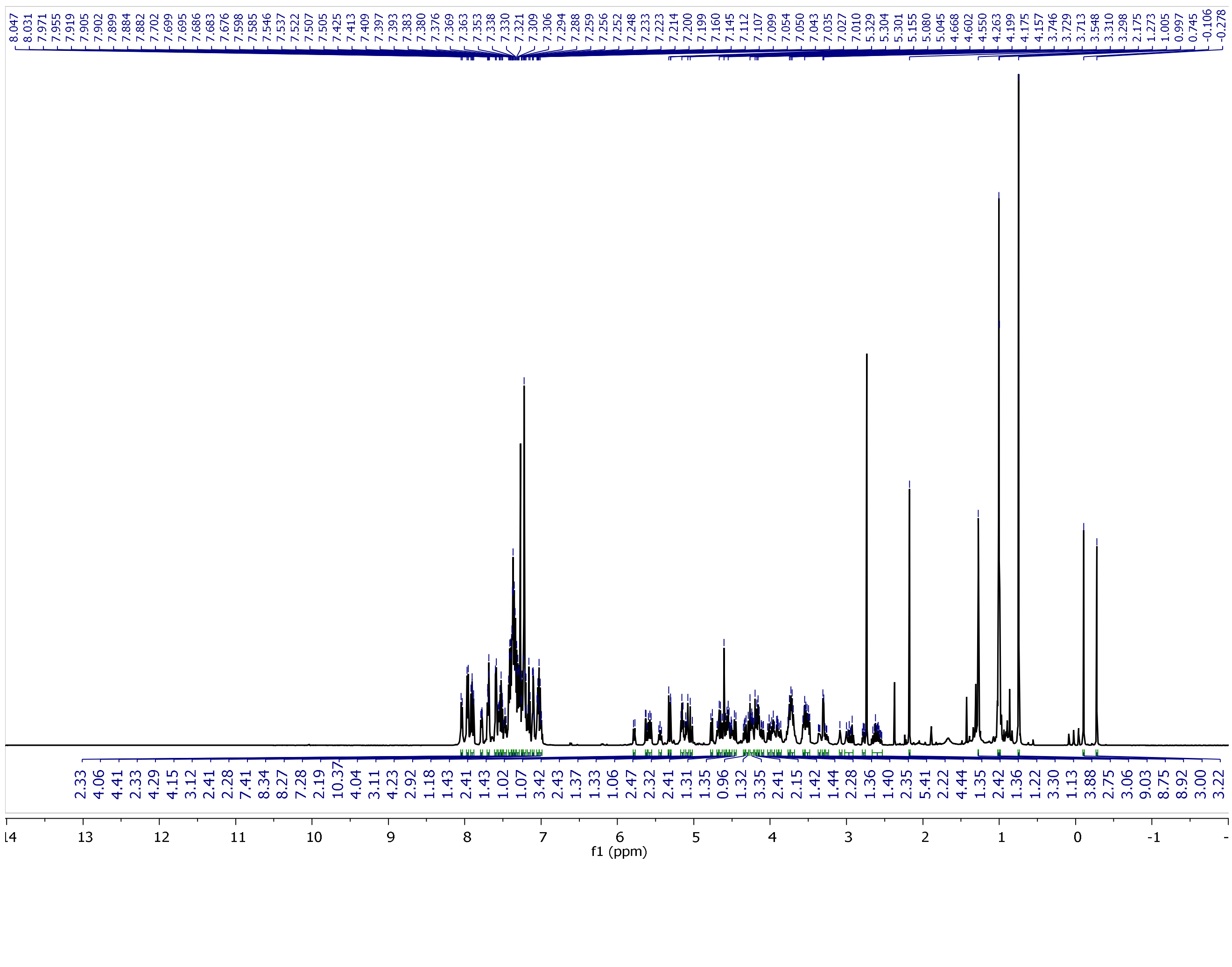
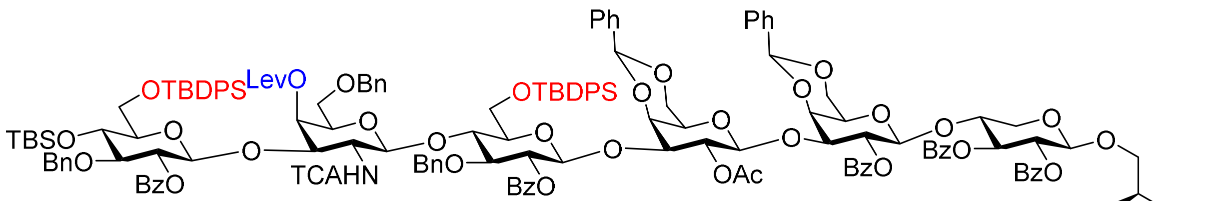


[1]H-NMR ($CDCl_3$, 500 MHz) of **15**





^{13}C-NMR ($CDCl_3$, 126 MHz) of **15**



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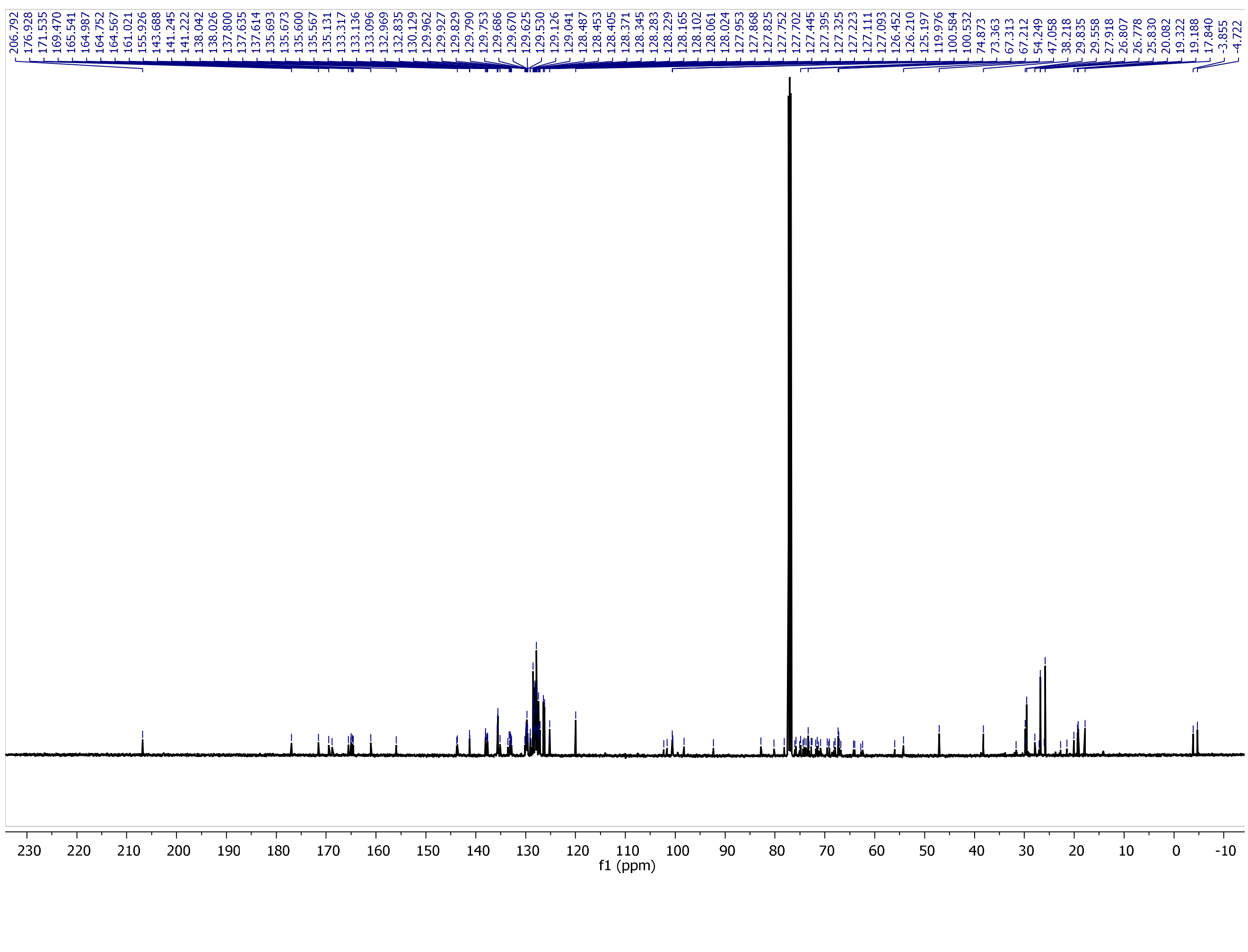
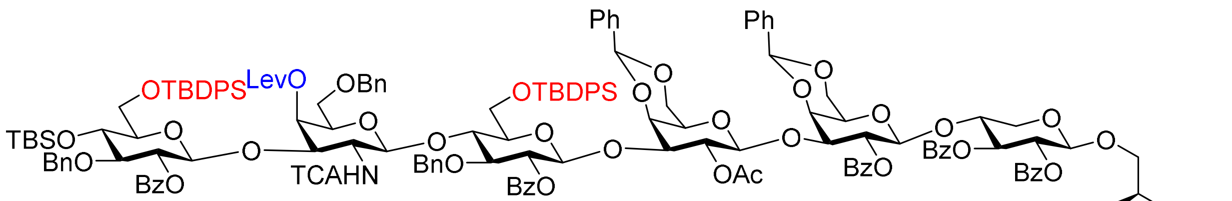


gCOSY ($CDCl_3$, 500 MHz) of **15**



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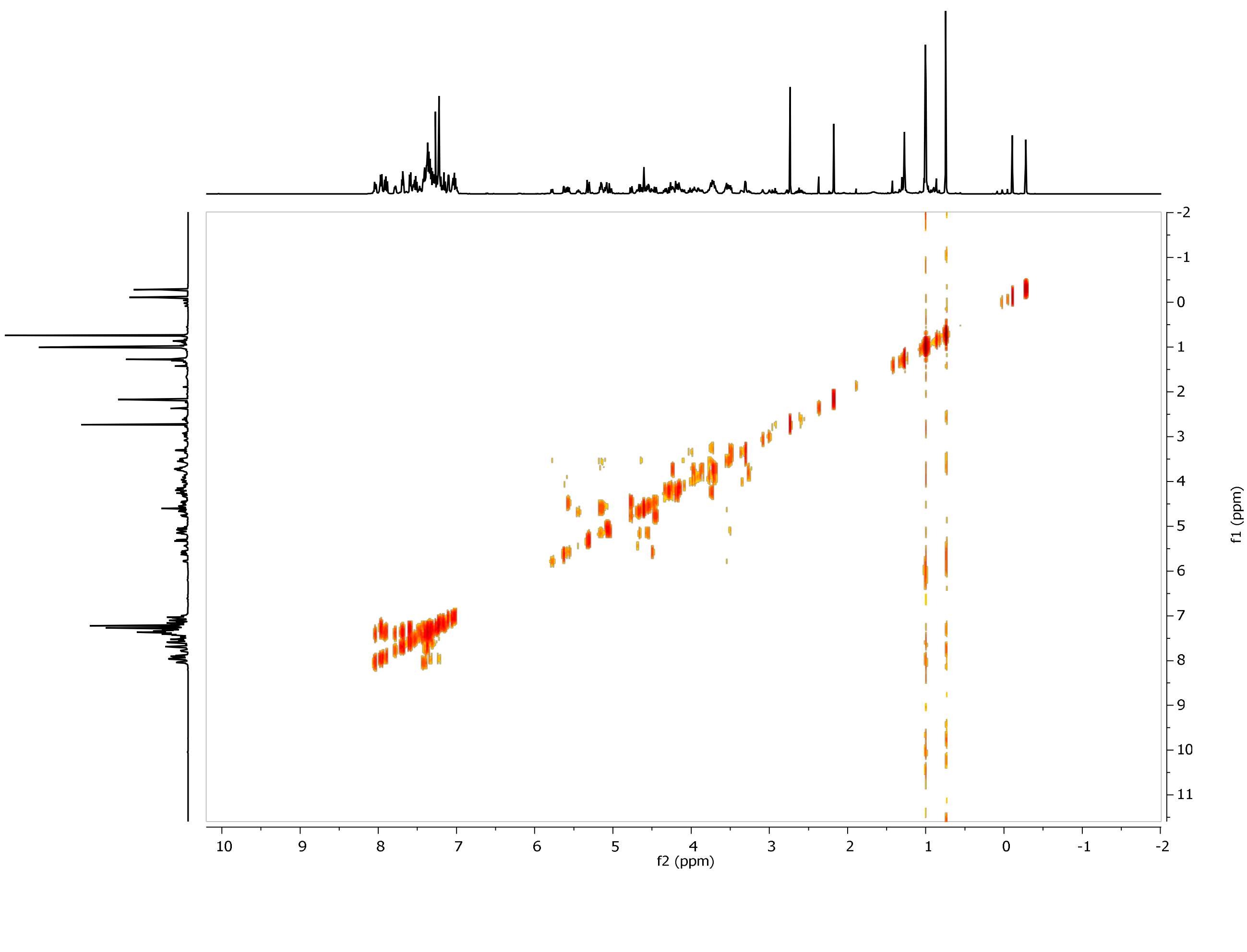
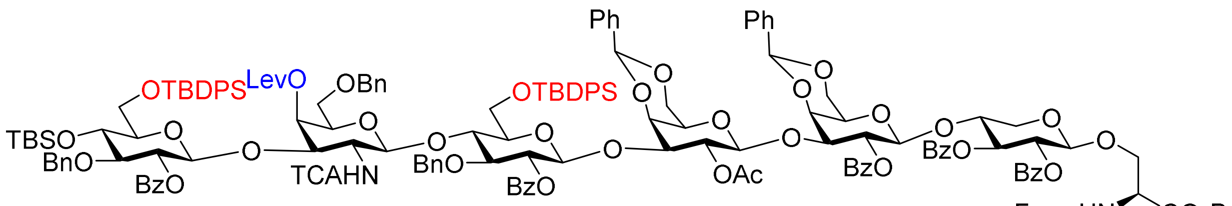


bsgHSQC ($CDCl_3$, 500 MHz) of **15**



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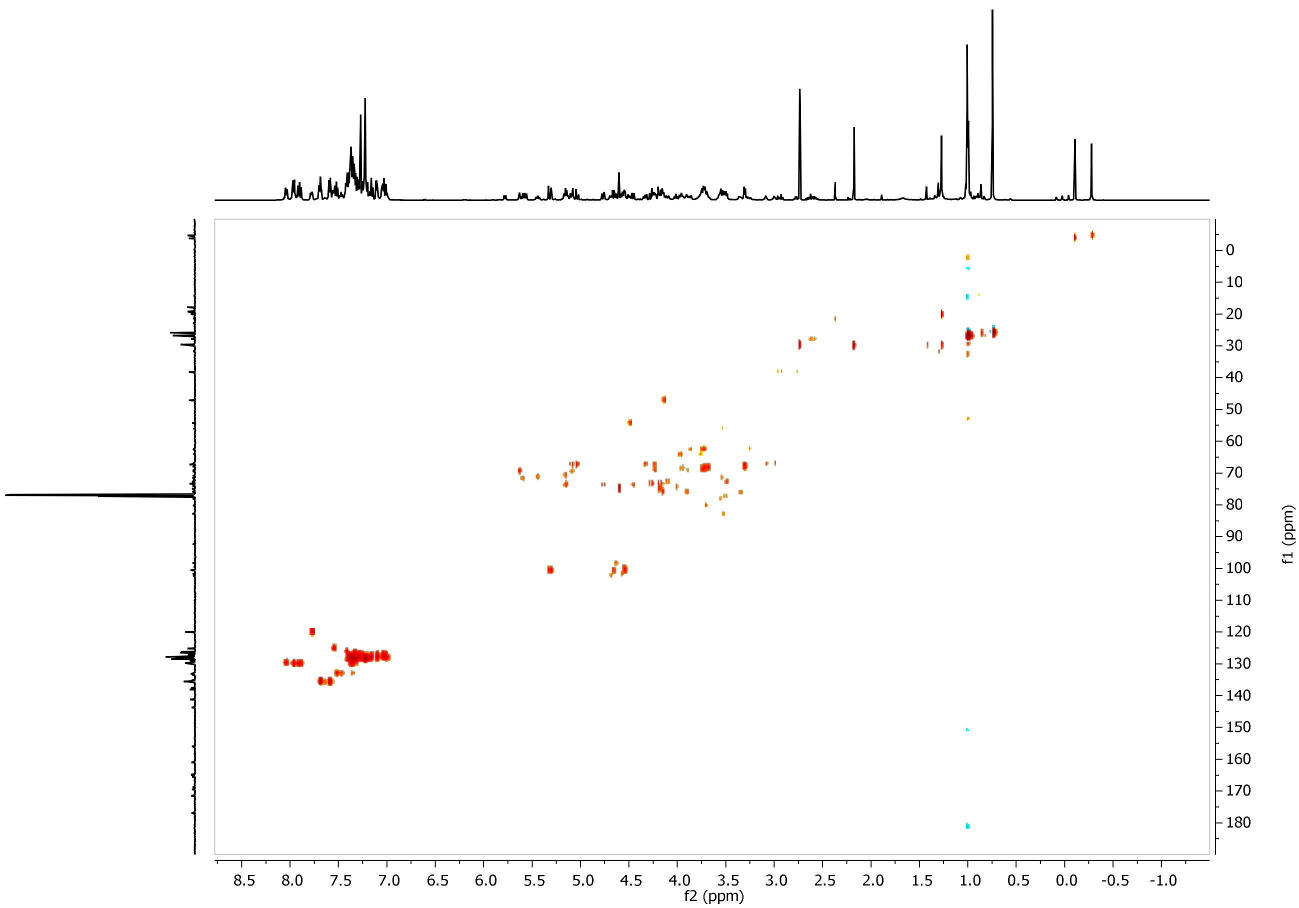
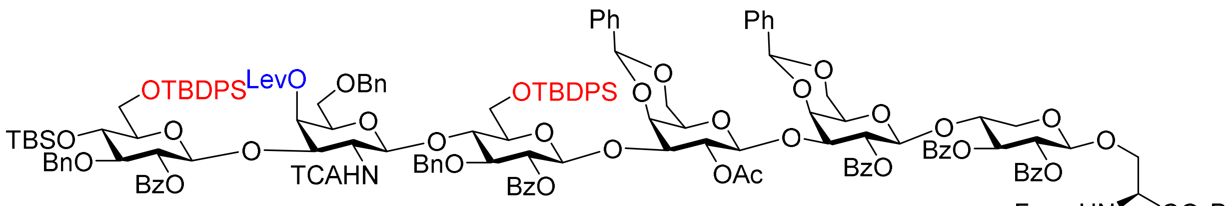


bHSQC ($CDCl_3$, 500 MHz) of **15**



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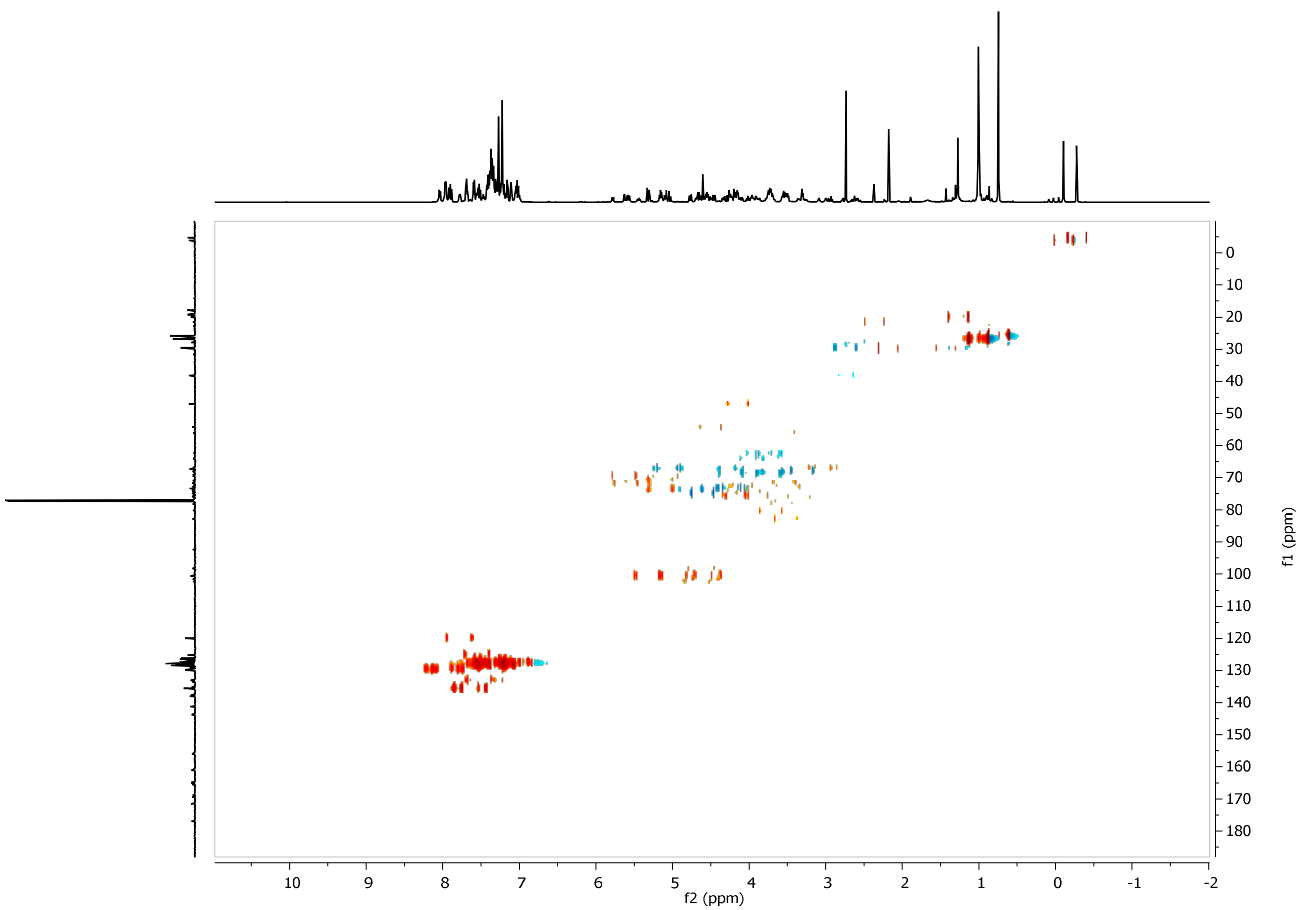
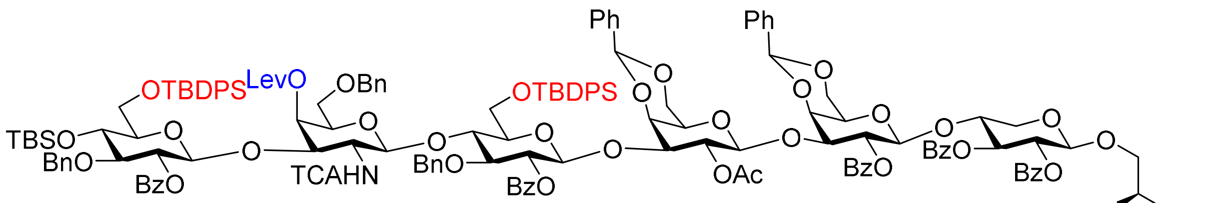


gHMBC ($CDCl_3$, 500 MHz) of **15**



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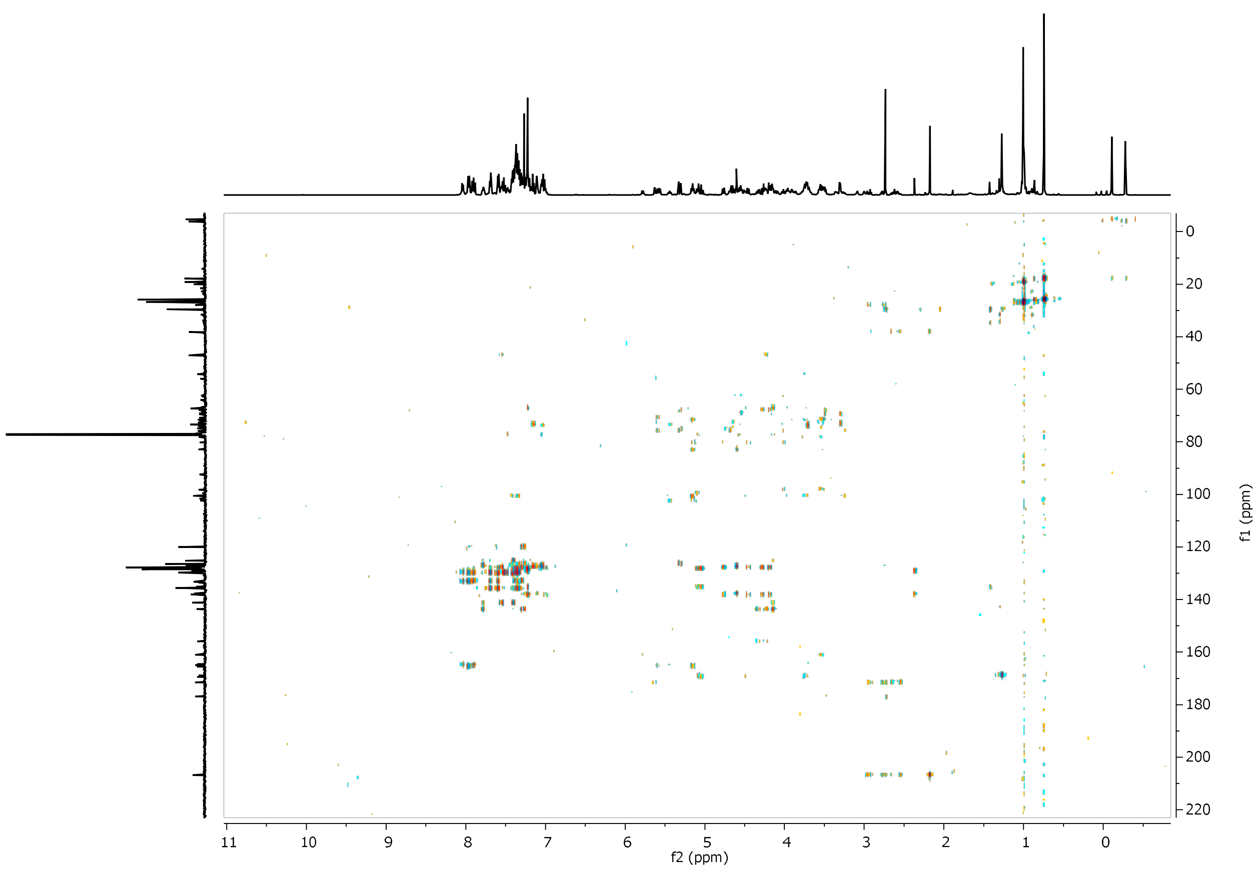
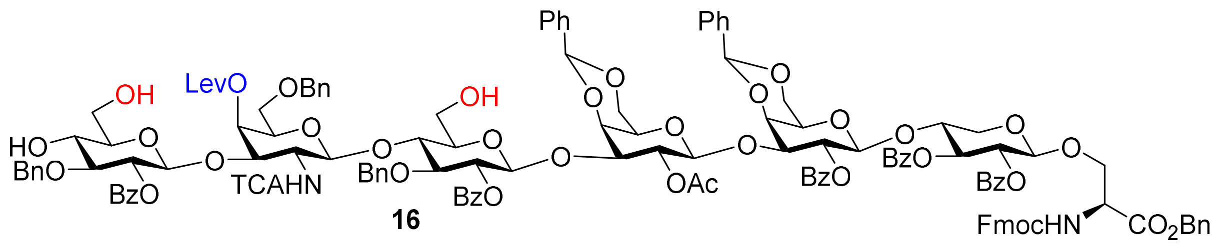


[1]H-NMR ($CDCl_3$, 500 MHz) of **16**



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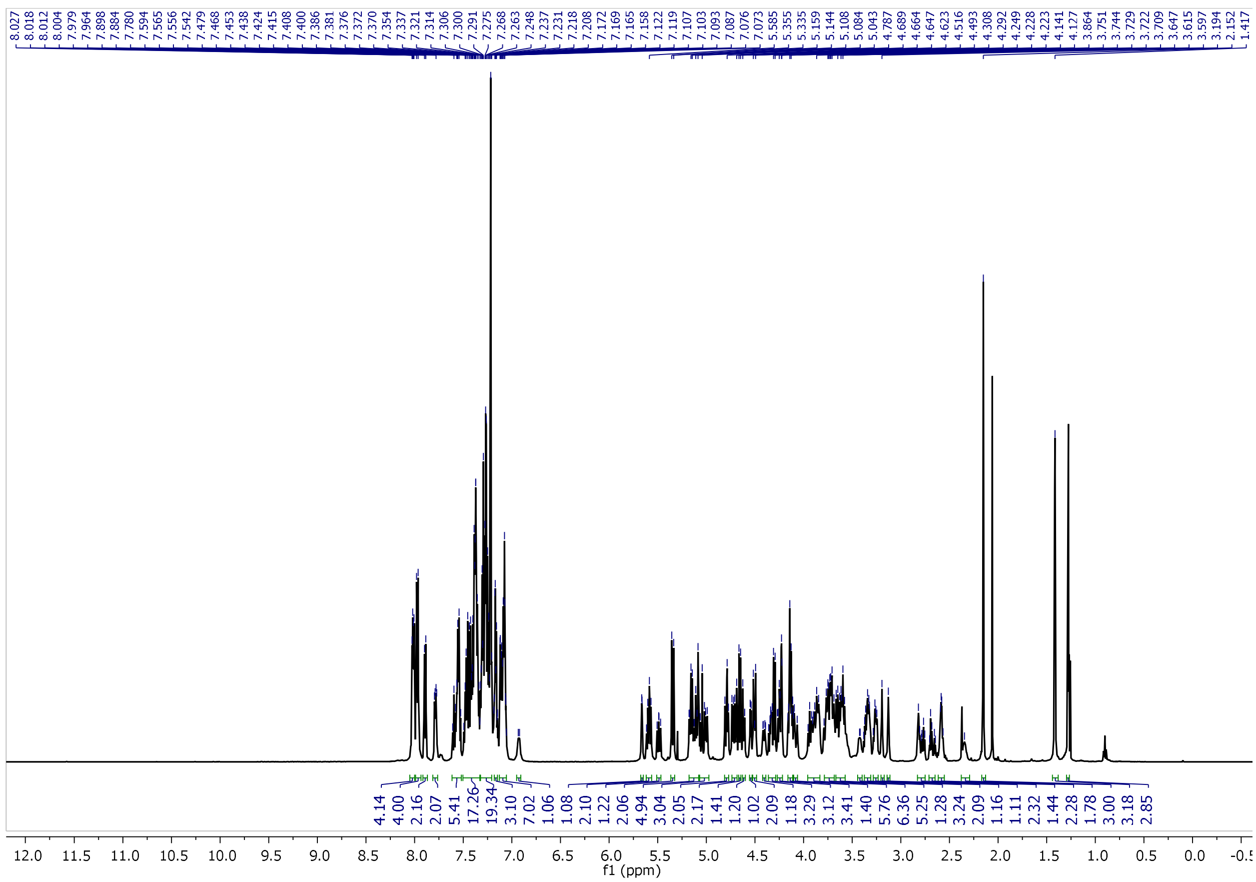
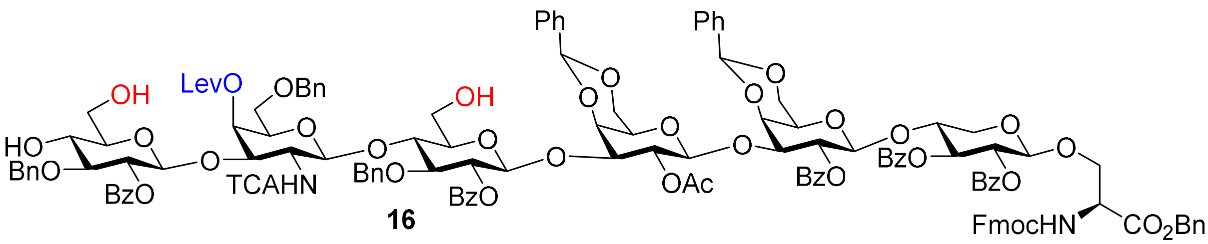


^{13}C-NMR ($CDCl_3$, 126 MHz) of **16**



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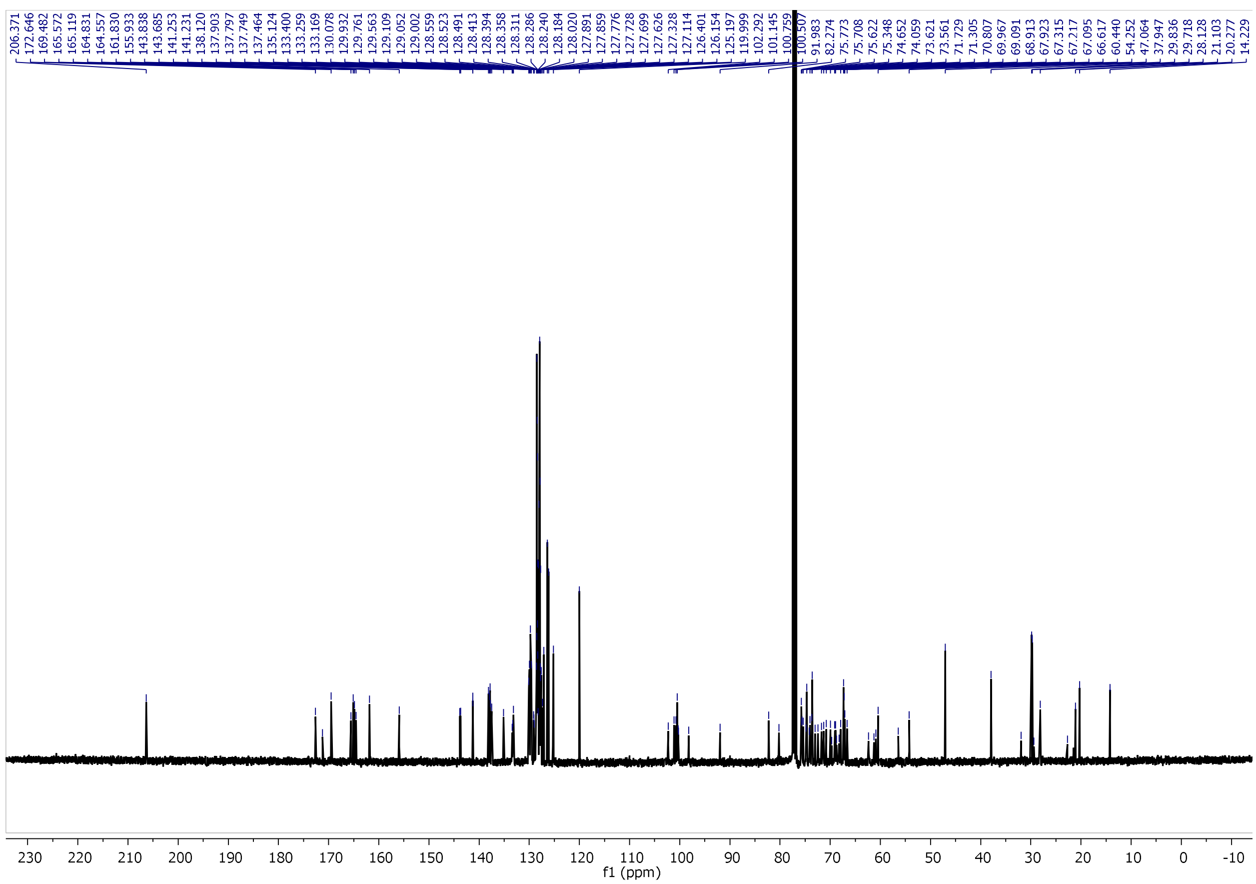
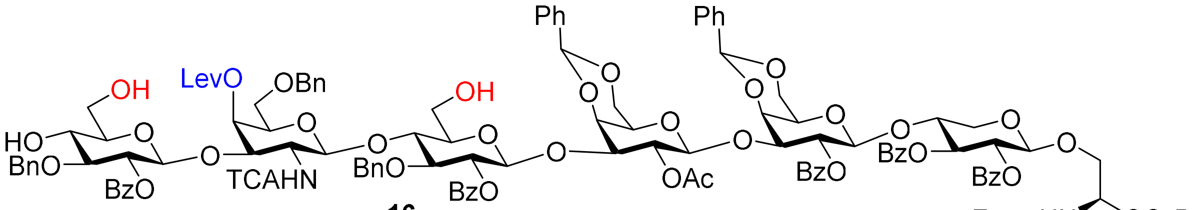
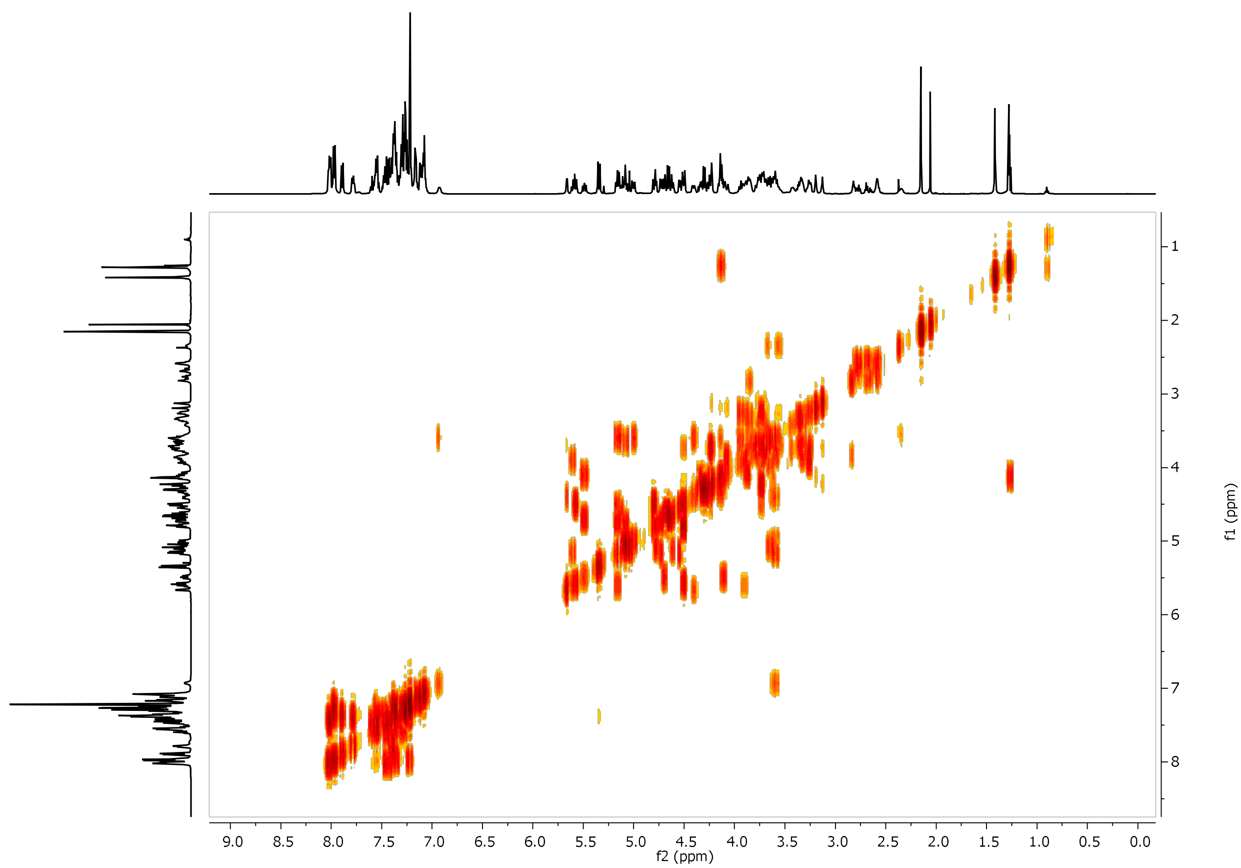
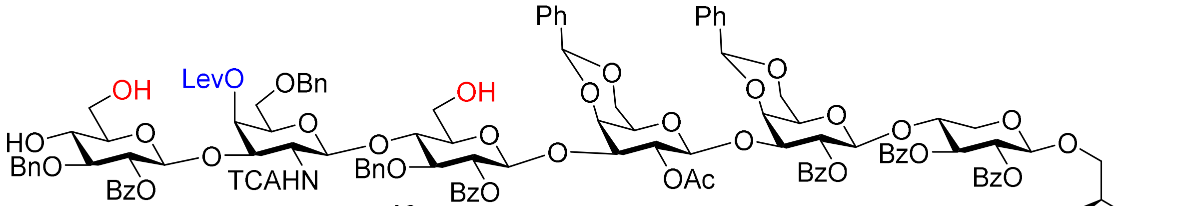


gCOSY ($CDCl_3$, 500 MHz) of **16**





gHMBC ($CDCl_3$, 500 MHz) of **16**



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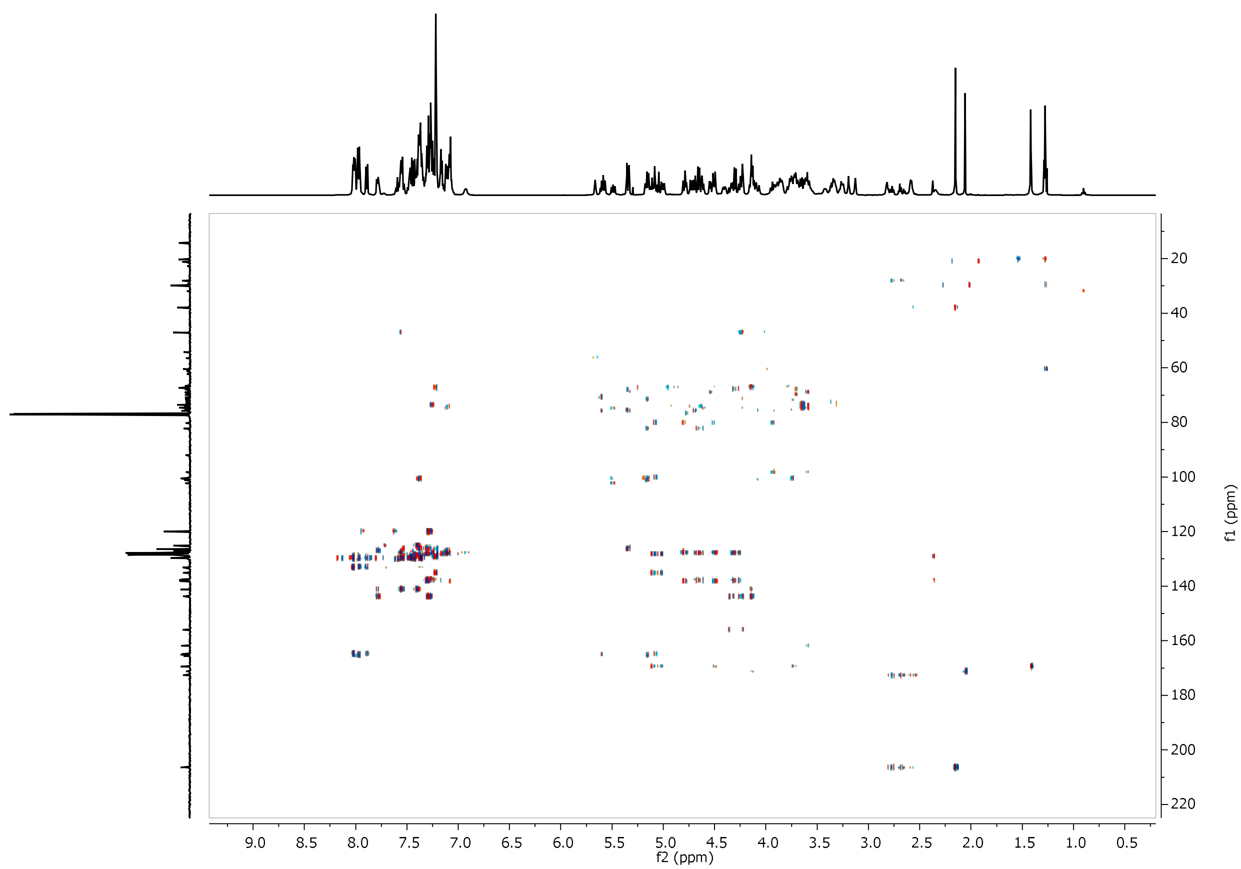
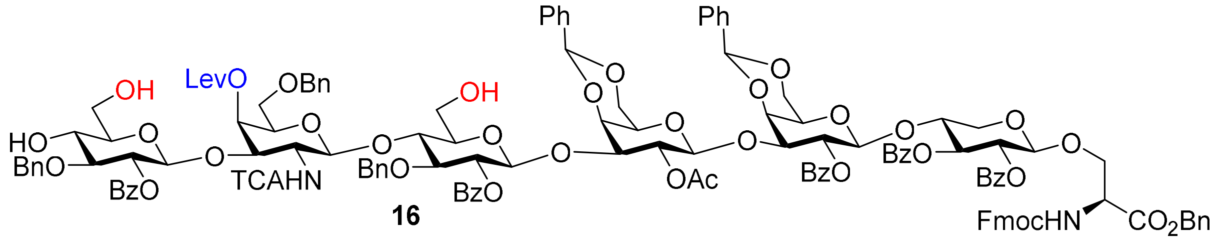


bsgHSQC ($CDCl_3$, 500 MHz) of **16**



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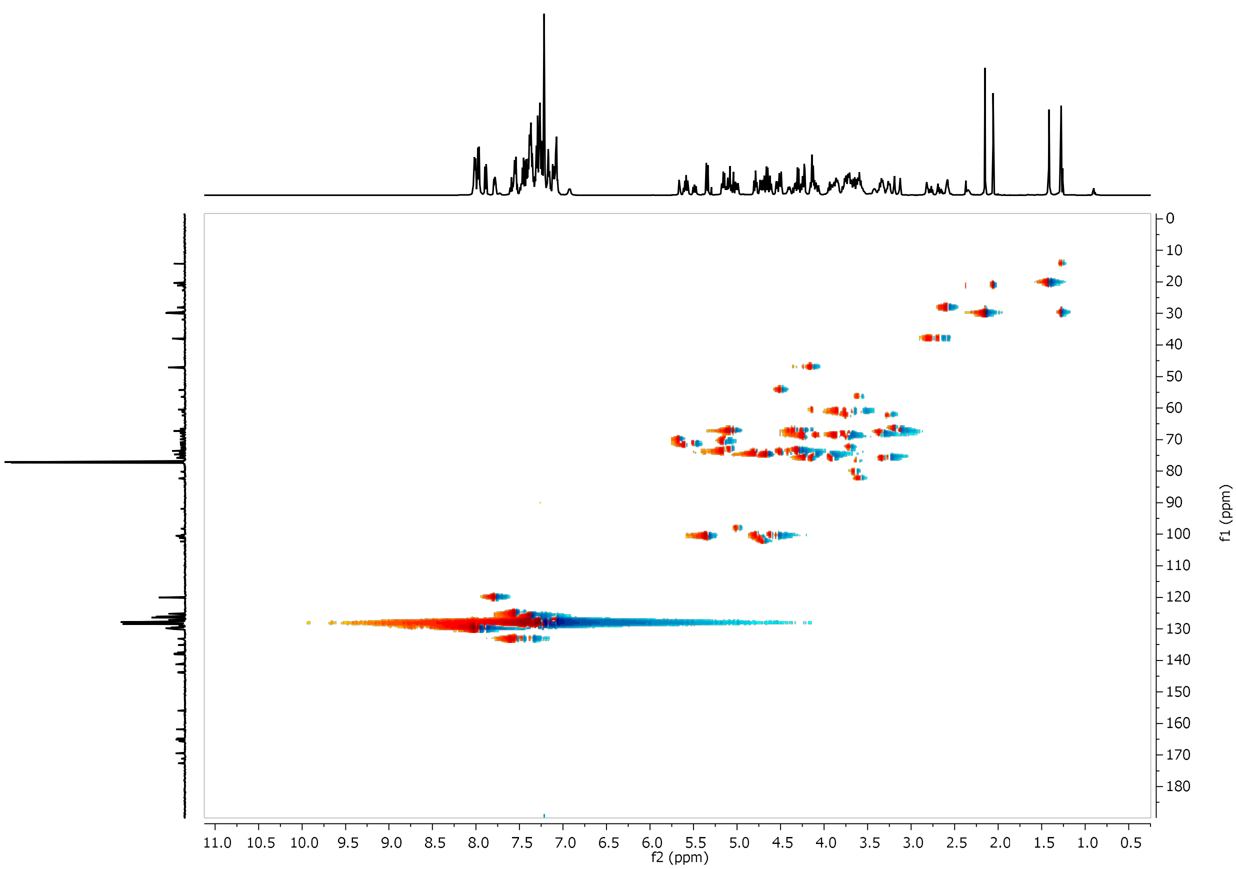
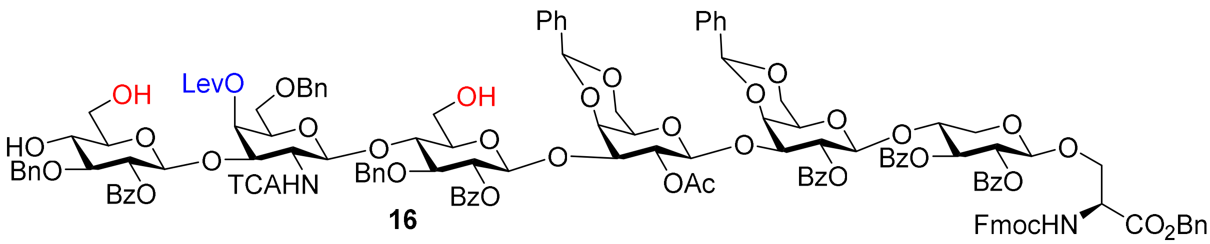
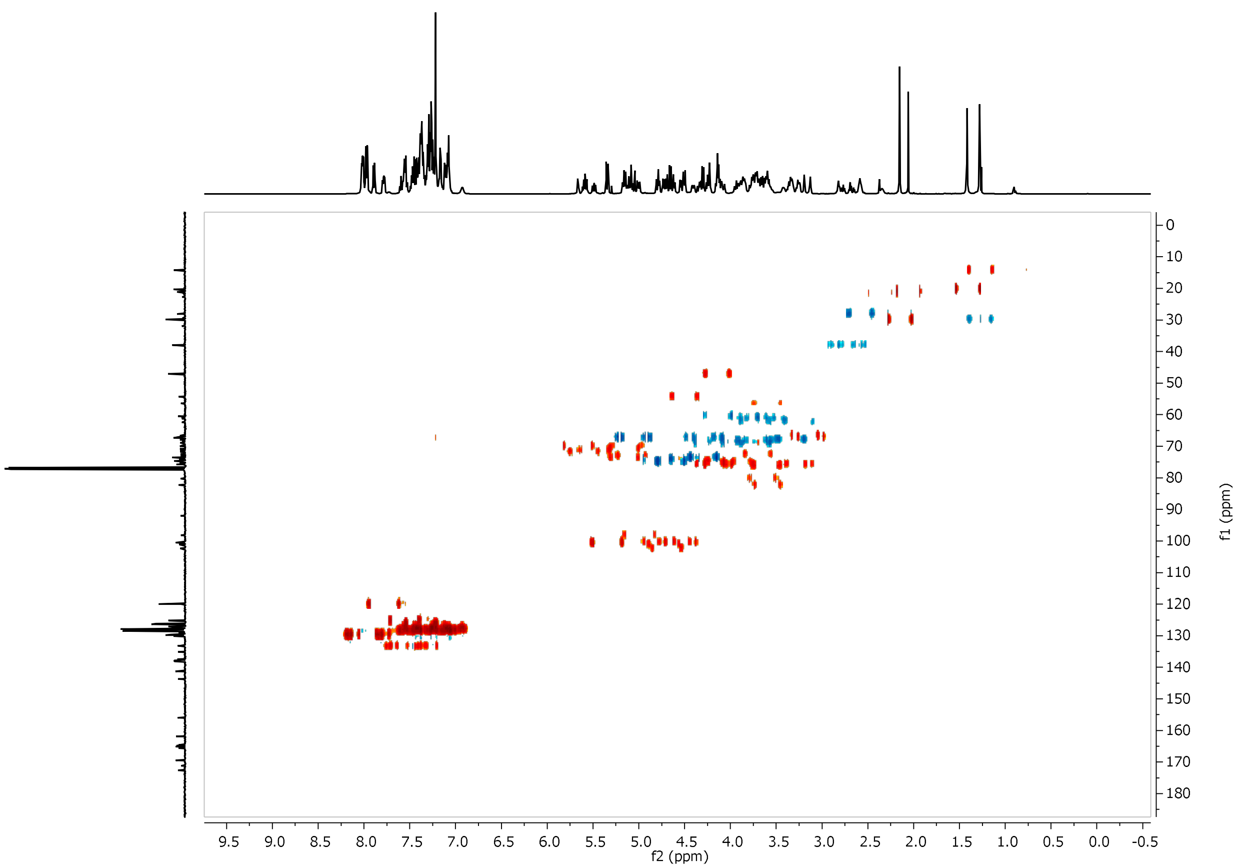
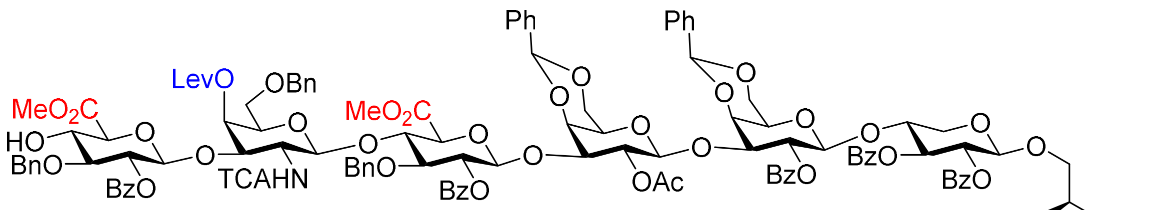


gHSQC ($CDCl_3$, 500 MHz) of **16**





[1]H-NMR ($CDCl_3$, 500 MHz) of **17**



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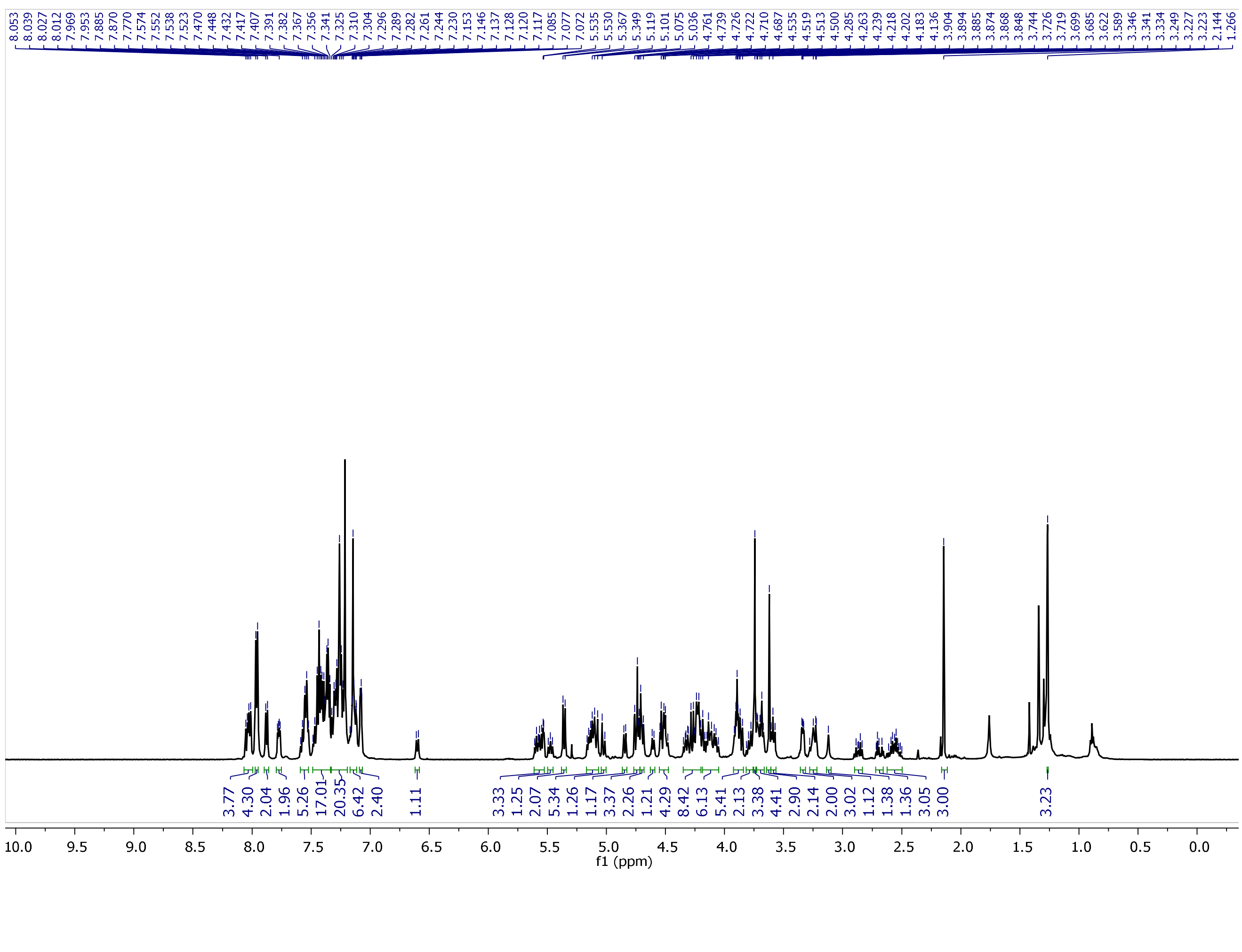
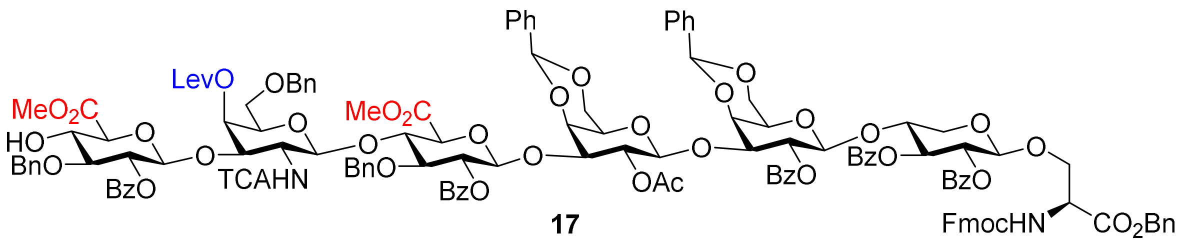


[13]C-NMR (CDCl$_3$, 126 MHz) of **17**



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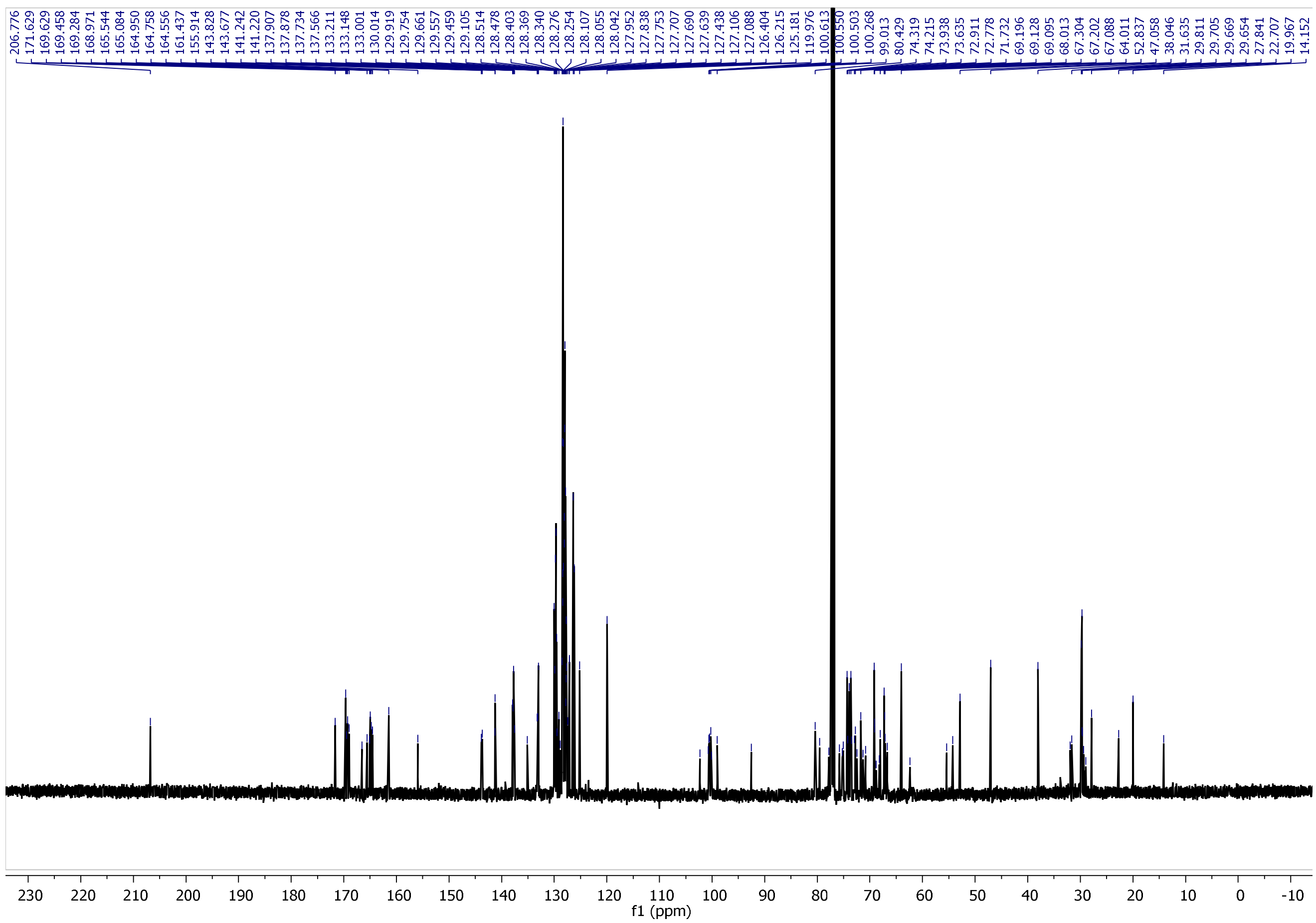
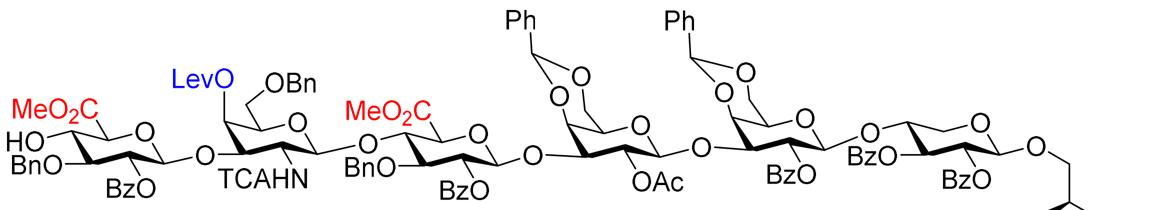


gCOSY ($CDCl_3$, 500 MHz) of **17**



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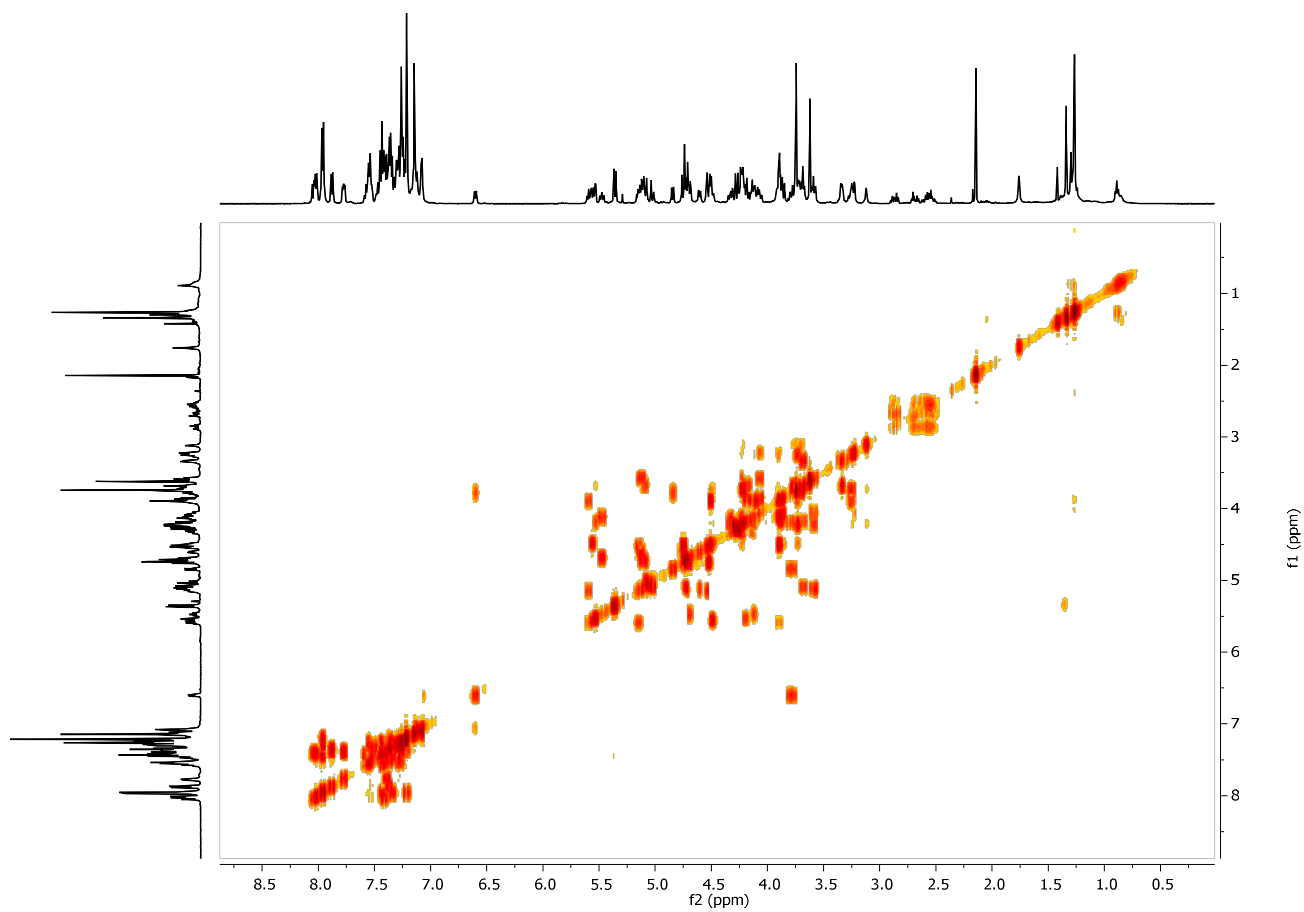
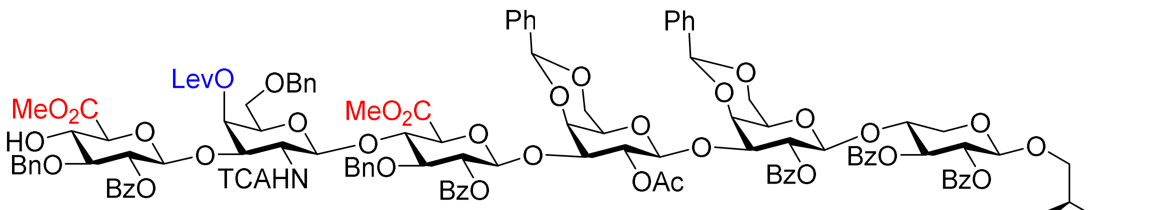


gHMBC ($CDCl_3$, 500 MHz) of **17**



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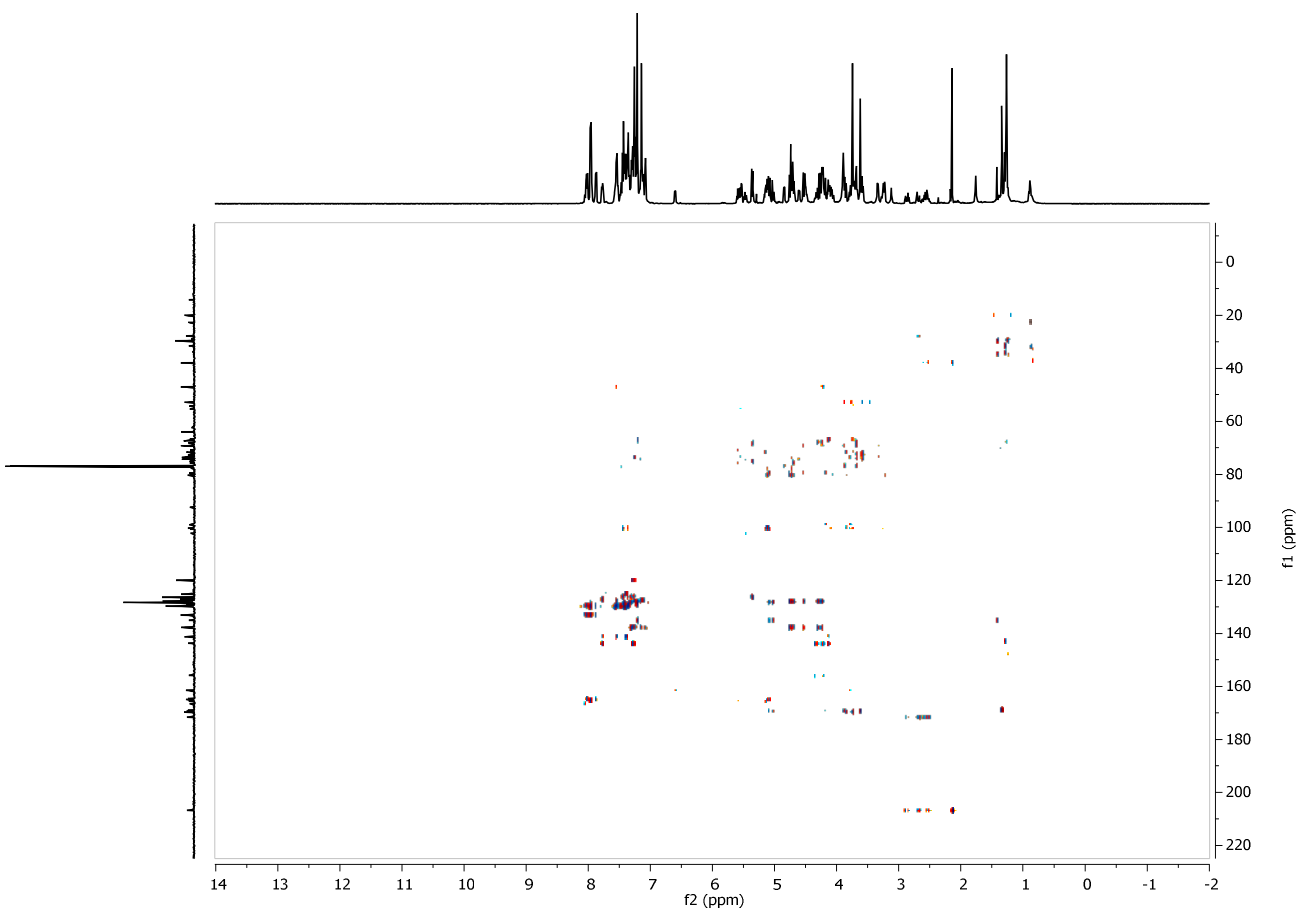
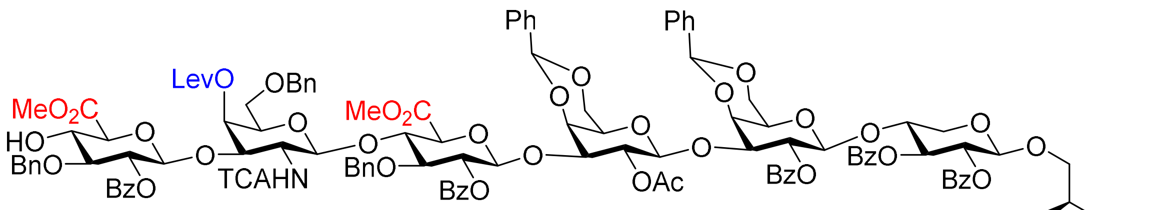


bsgHSQC ($CDCl_3$, 500 MHz) of **17**



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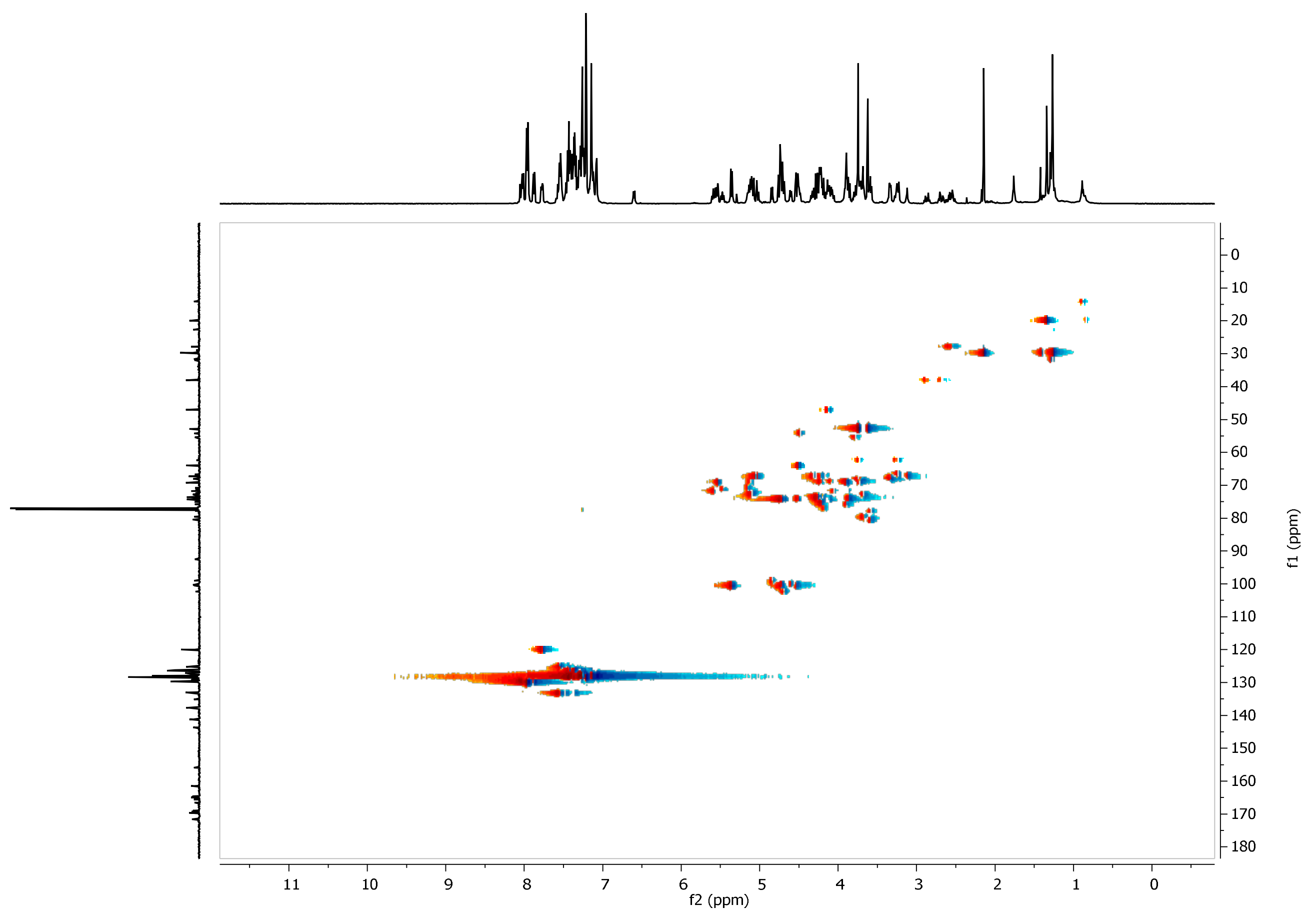
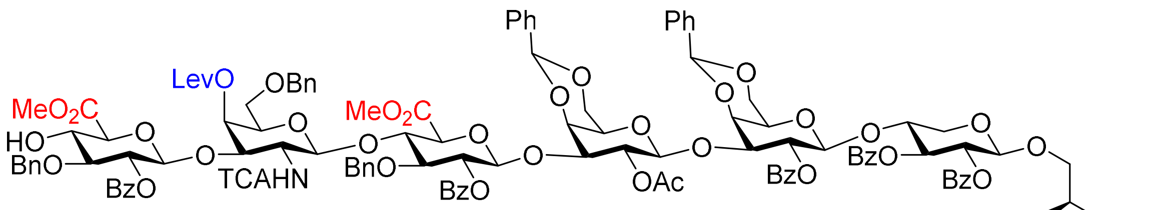


gHSQC ($CDCl_3$, 500 MHz) of **17**



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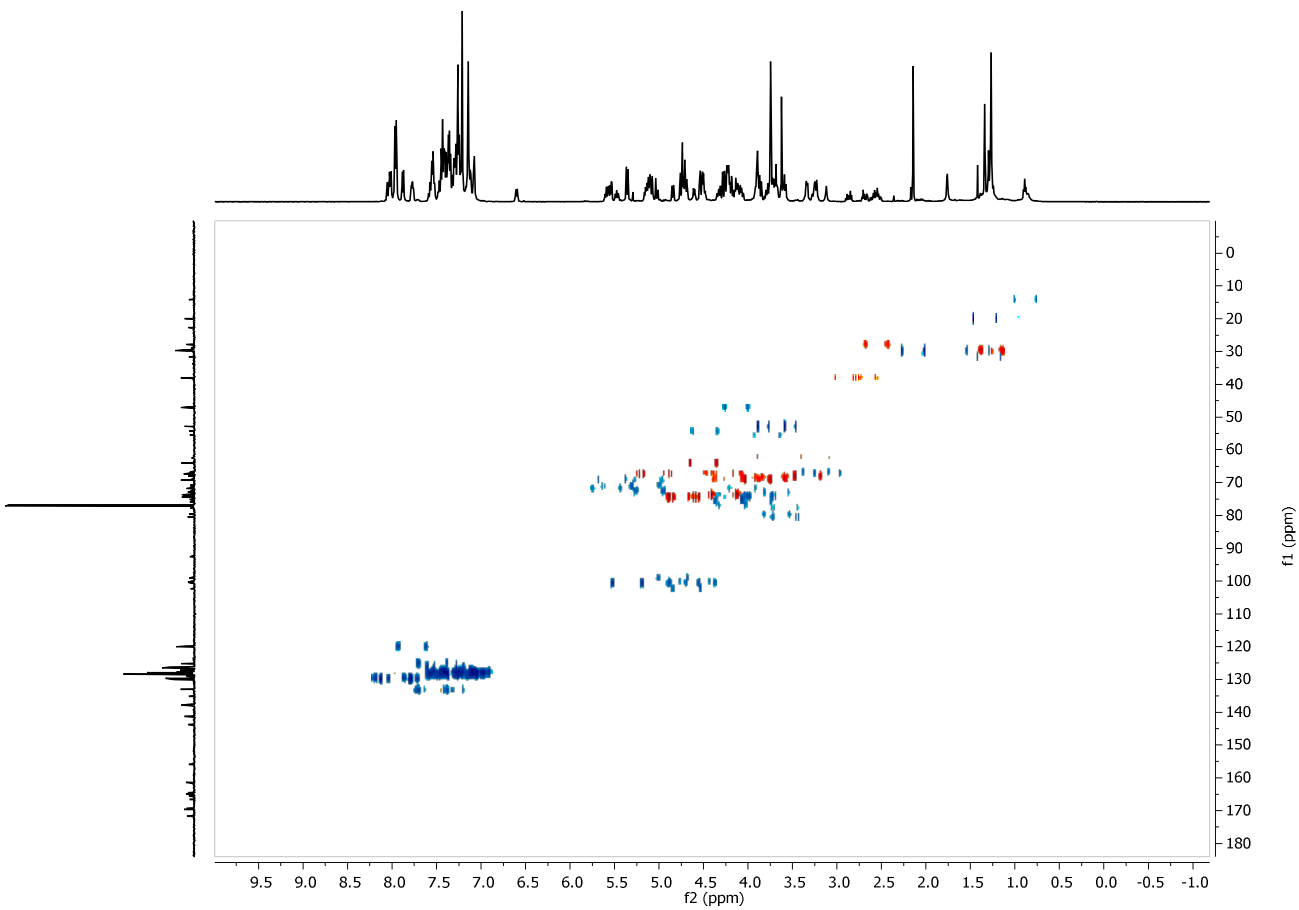
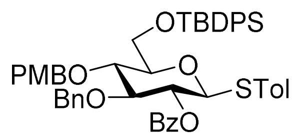


[1]H-NMR ($CDCl_3$, 500 MHz) of **18**



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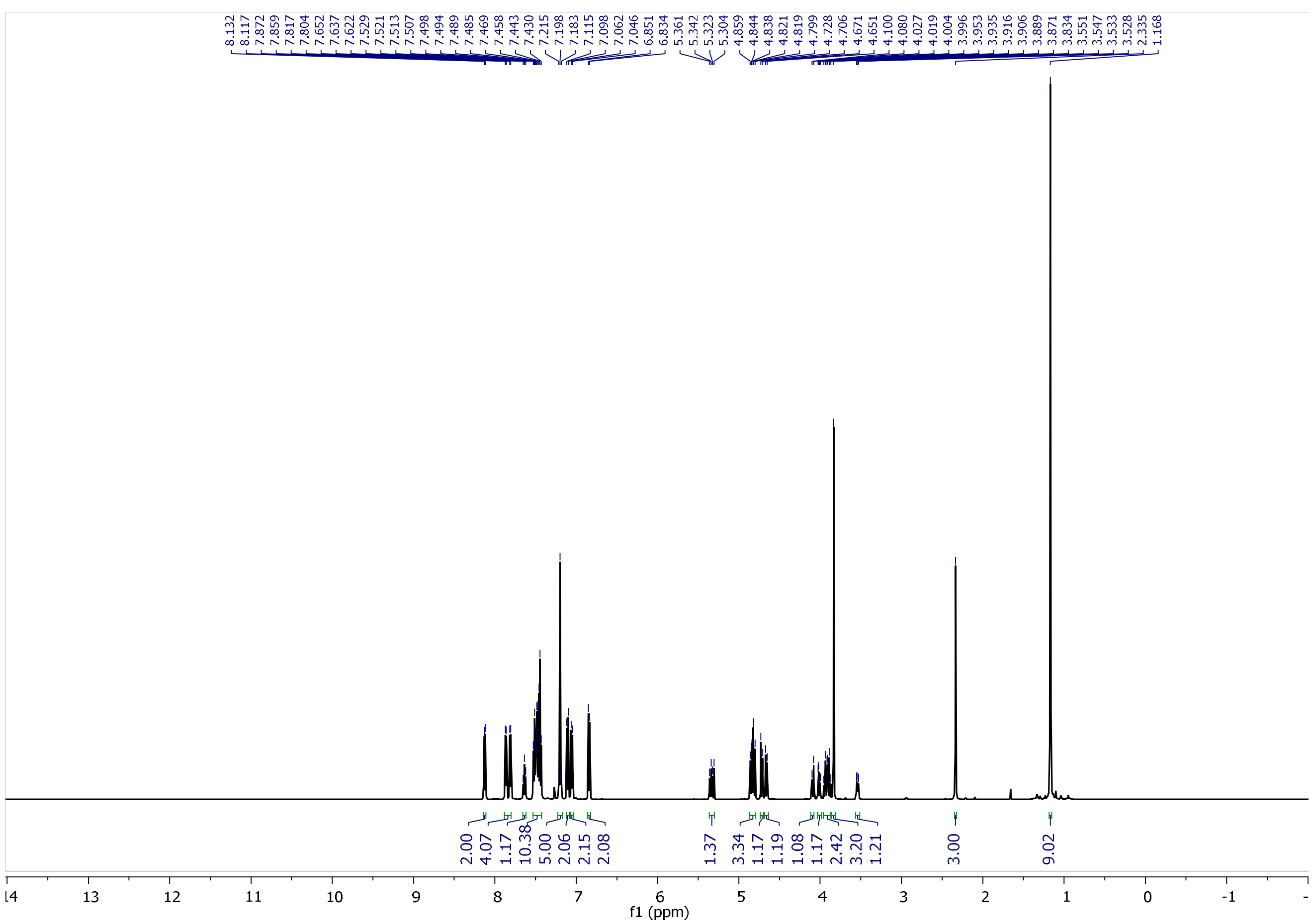
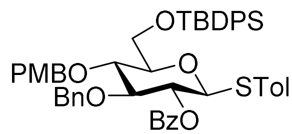


^{13}C-NMR ($CDCl_3$, 126 MHz) of **18**



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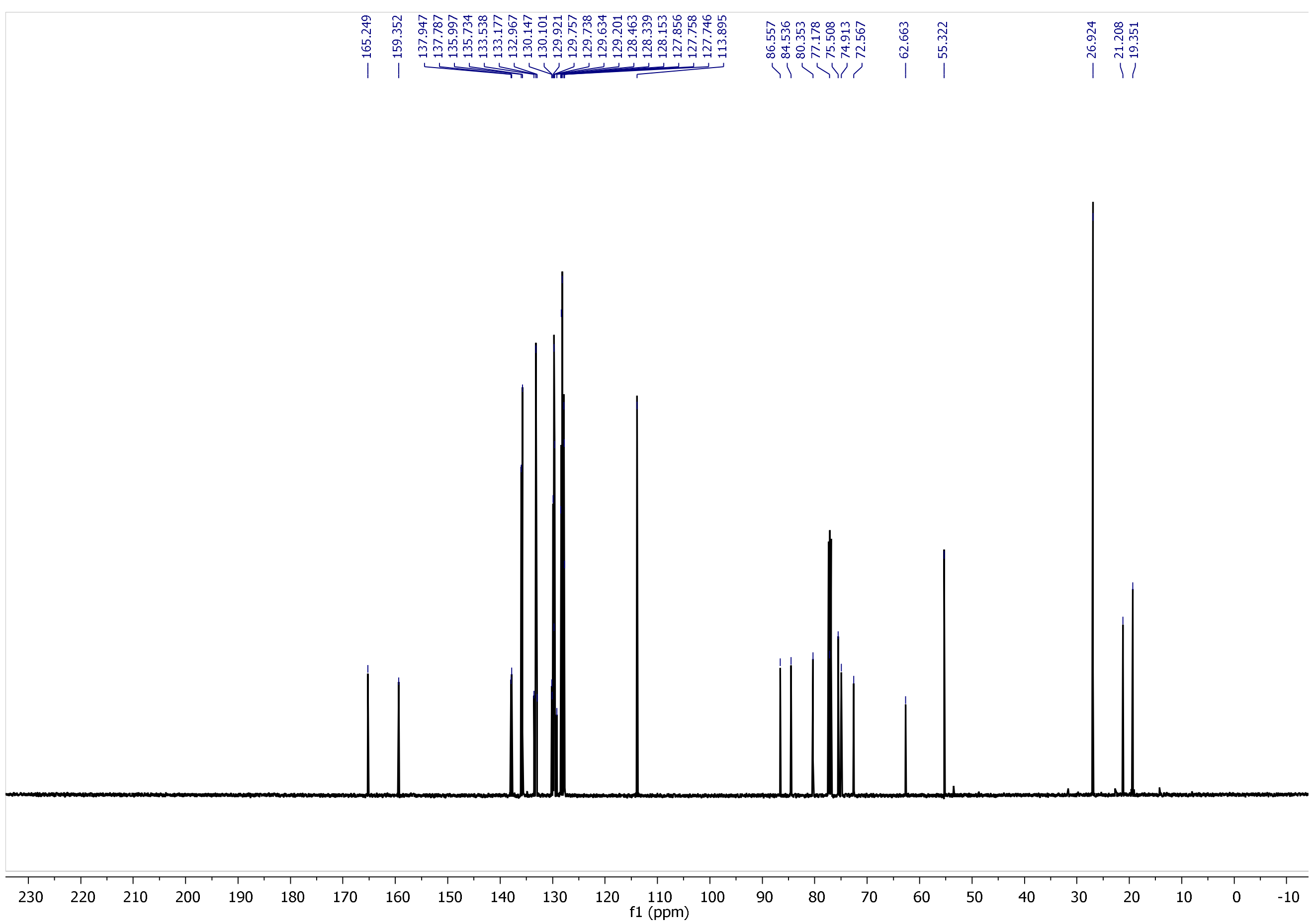
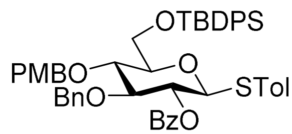


gCOSY ($CDCl_3$, 500 MHz) of **18**



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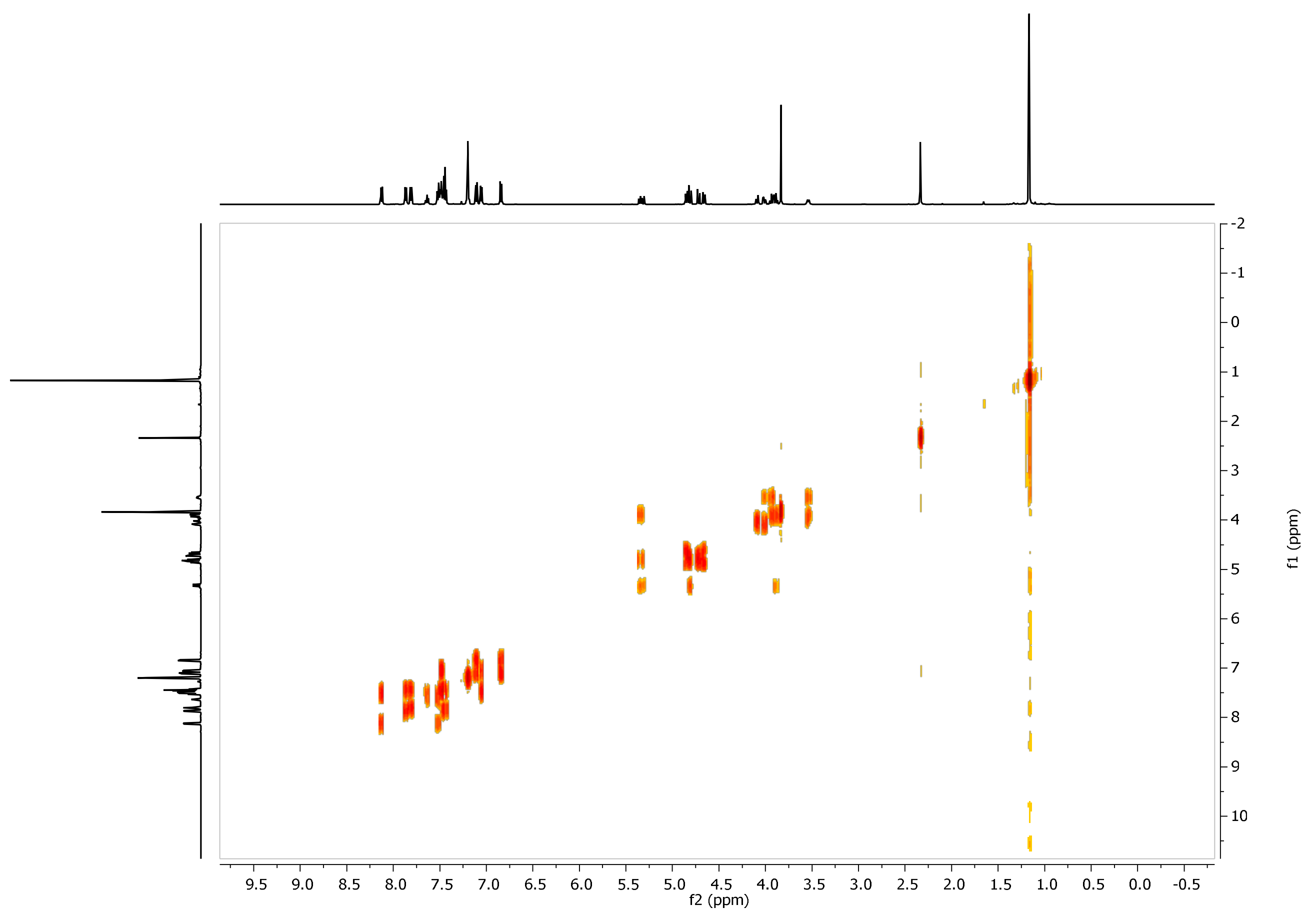
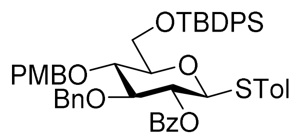


gHMBC ($CDCl_3$, 500 MHz) of **18**



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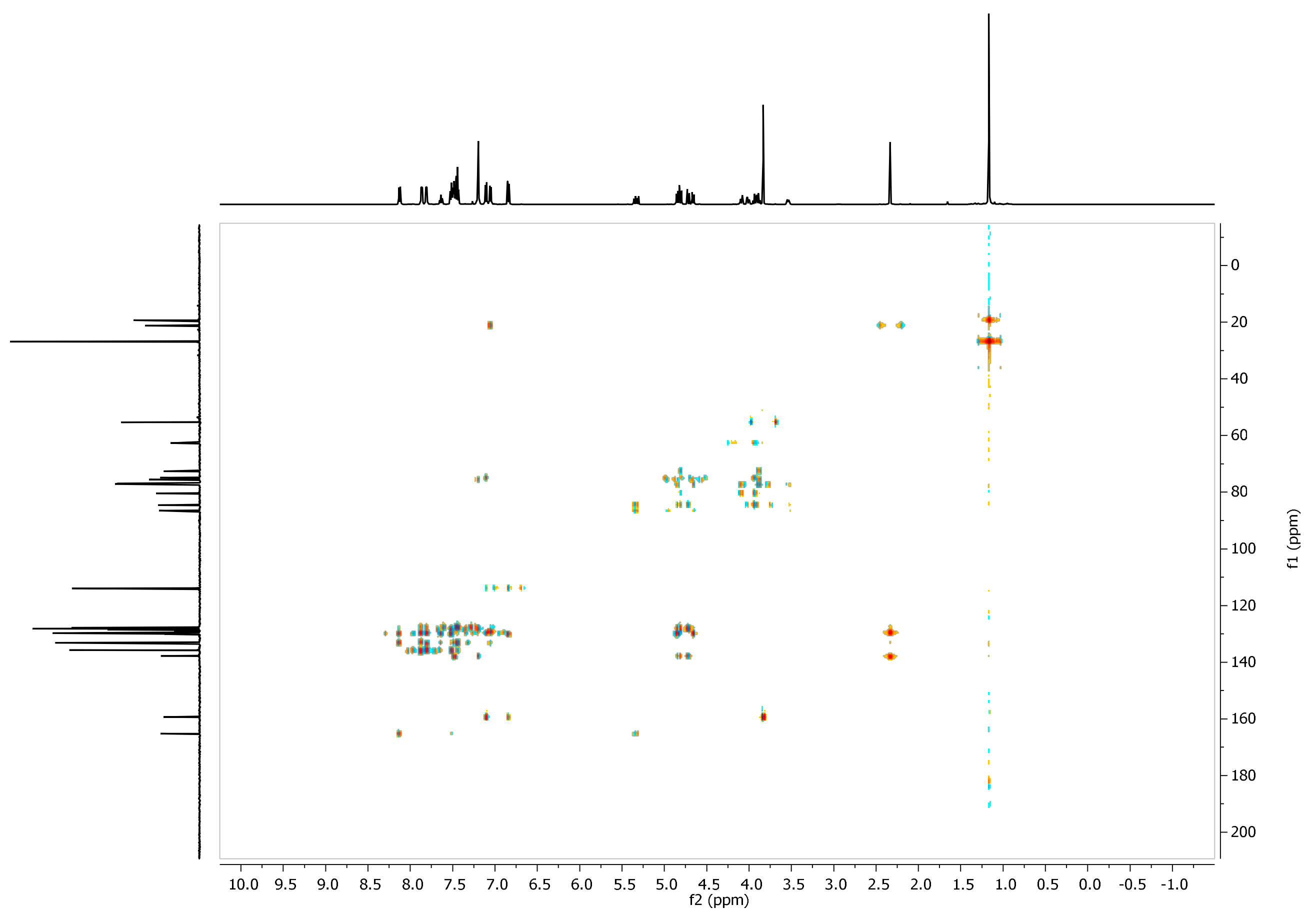
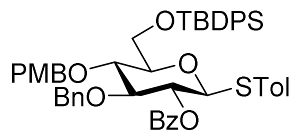


bsgHSQC ($CDCl_3$, 500 MHz) of **18**



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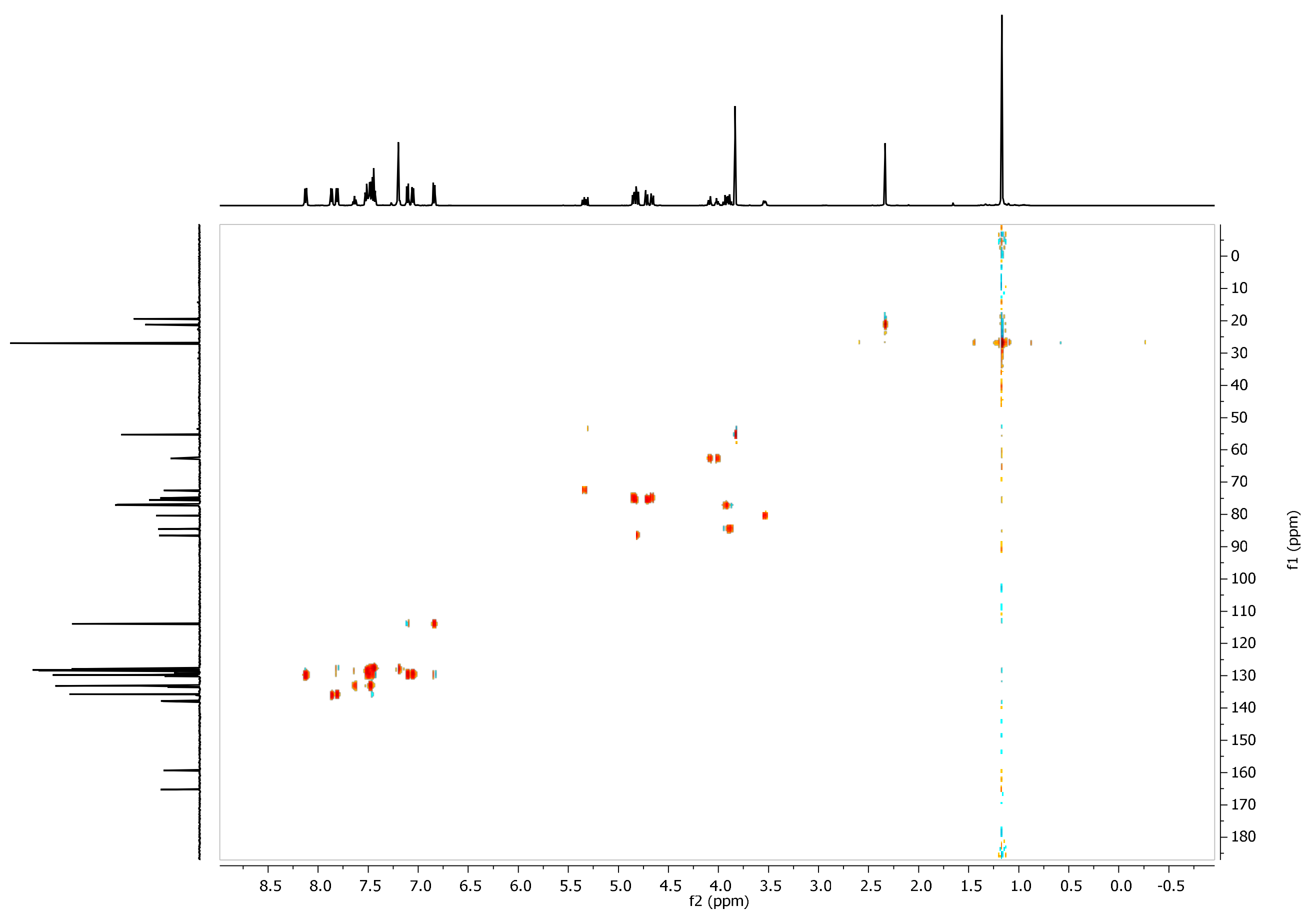
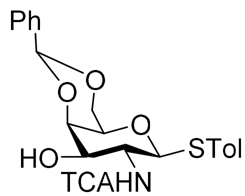


^{1}H-NMR ($CDCl_3$, 500 MHz) of **19**



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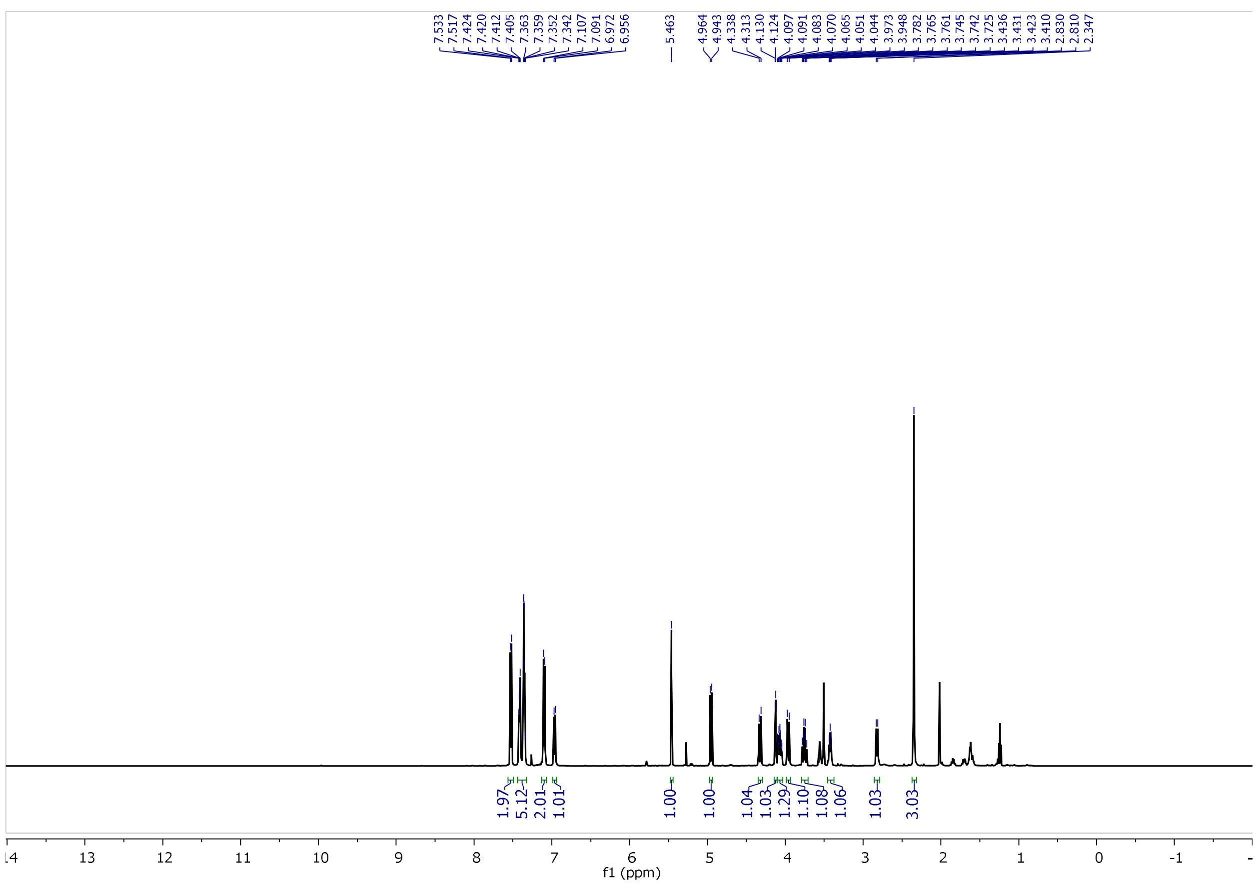
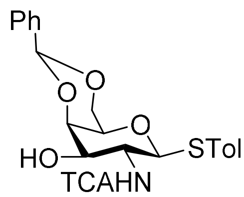


^{13}C-NMR ($CDCl_3$, 126 MHz) of **19**



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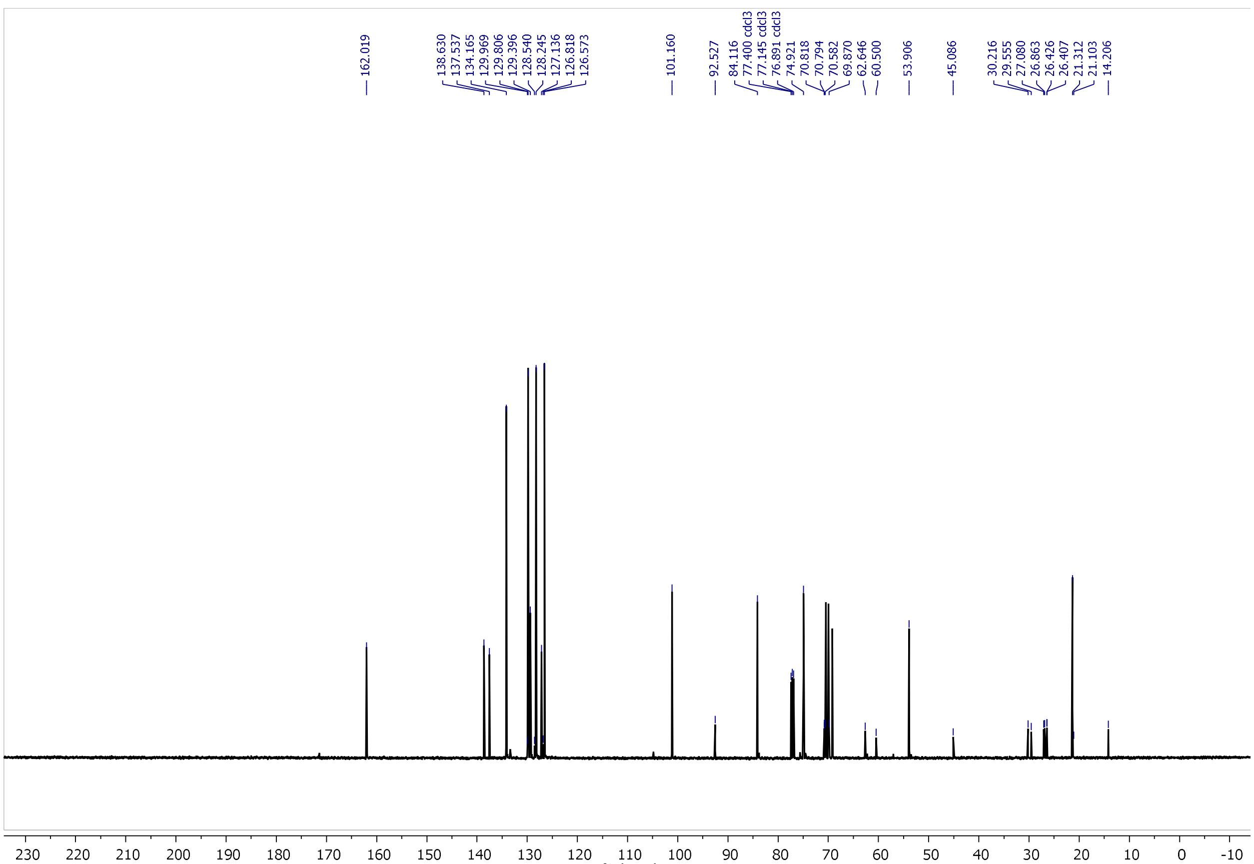
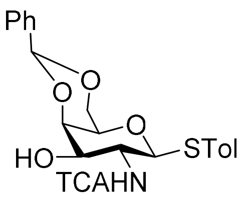


gCOSY ($CDCl_3$, 500 MHz) of **19**



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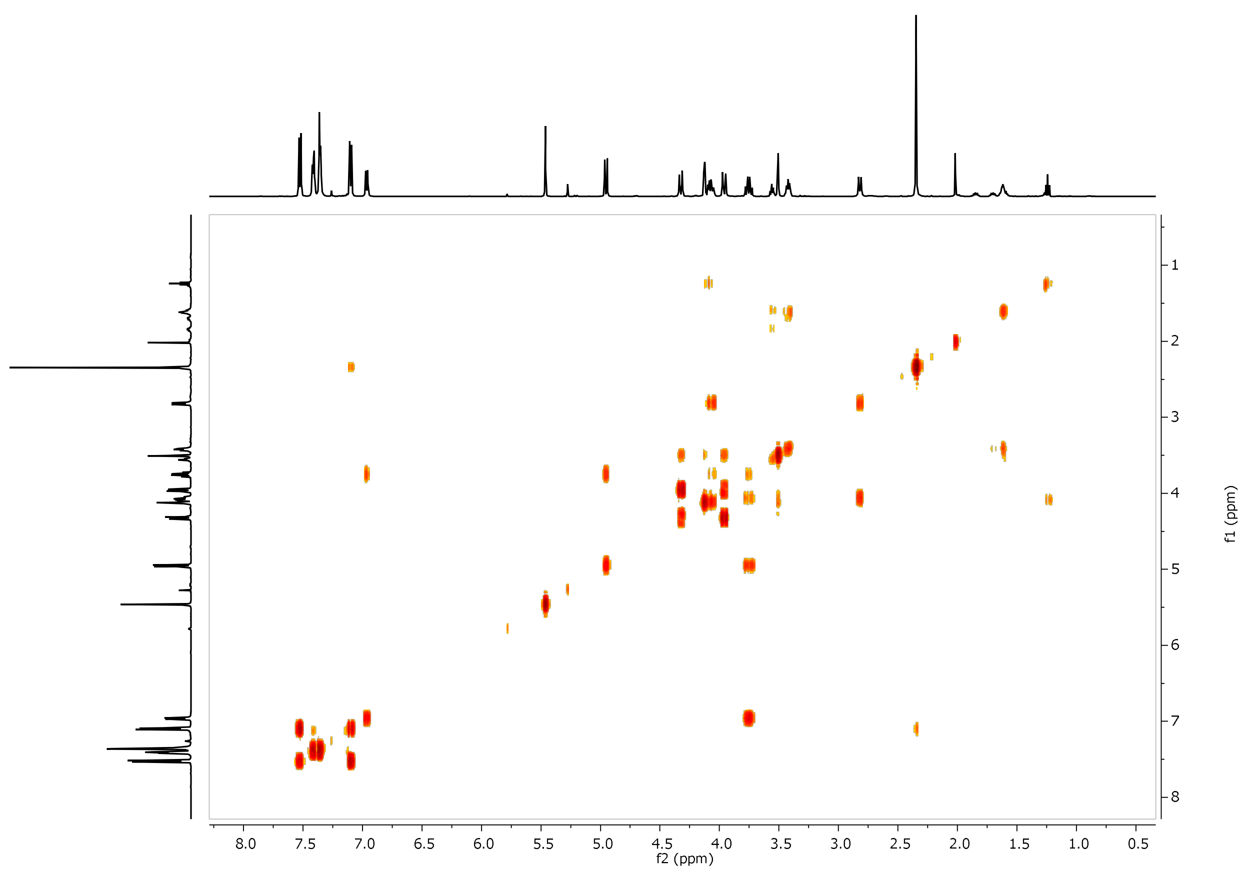
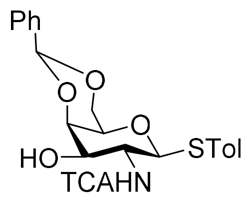


gHSQC ($CDCl_3$, 500 MHz) of **19**



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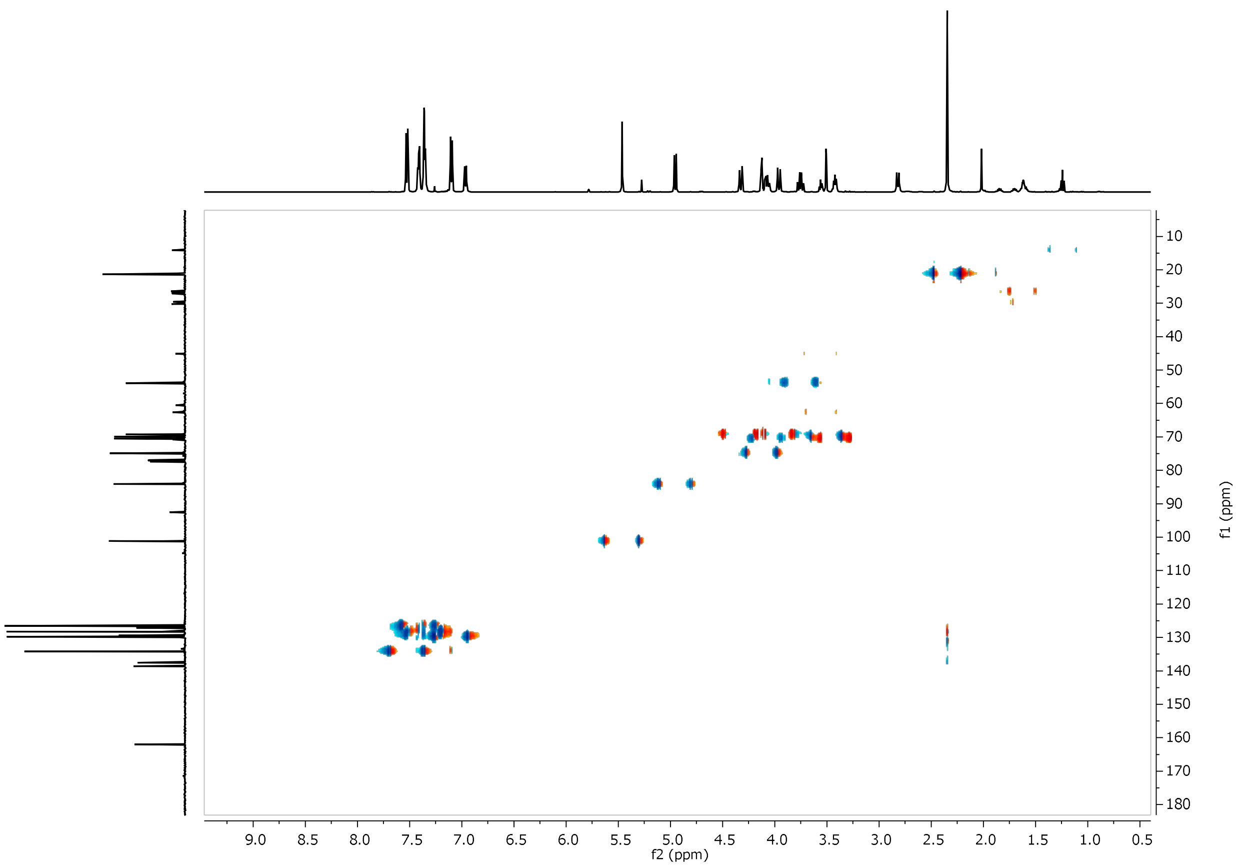
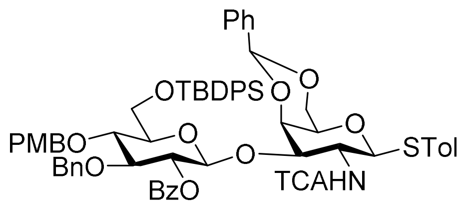


[1]H-NMR (CDCl$_3$, 500 MHz) of **20**



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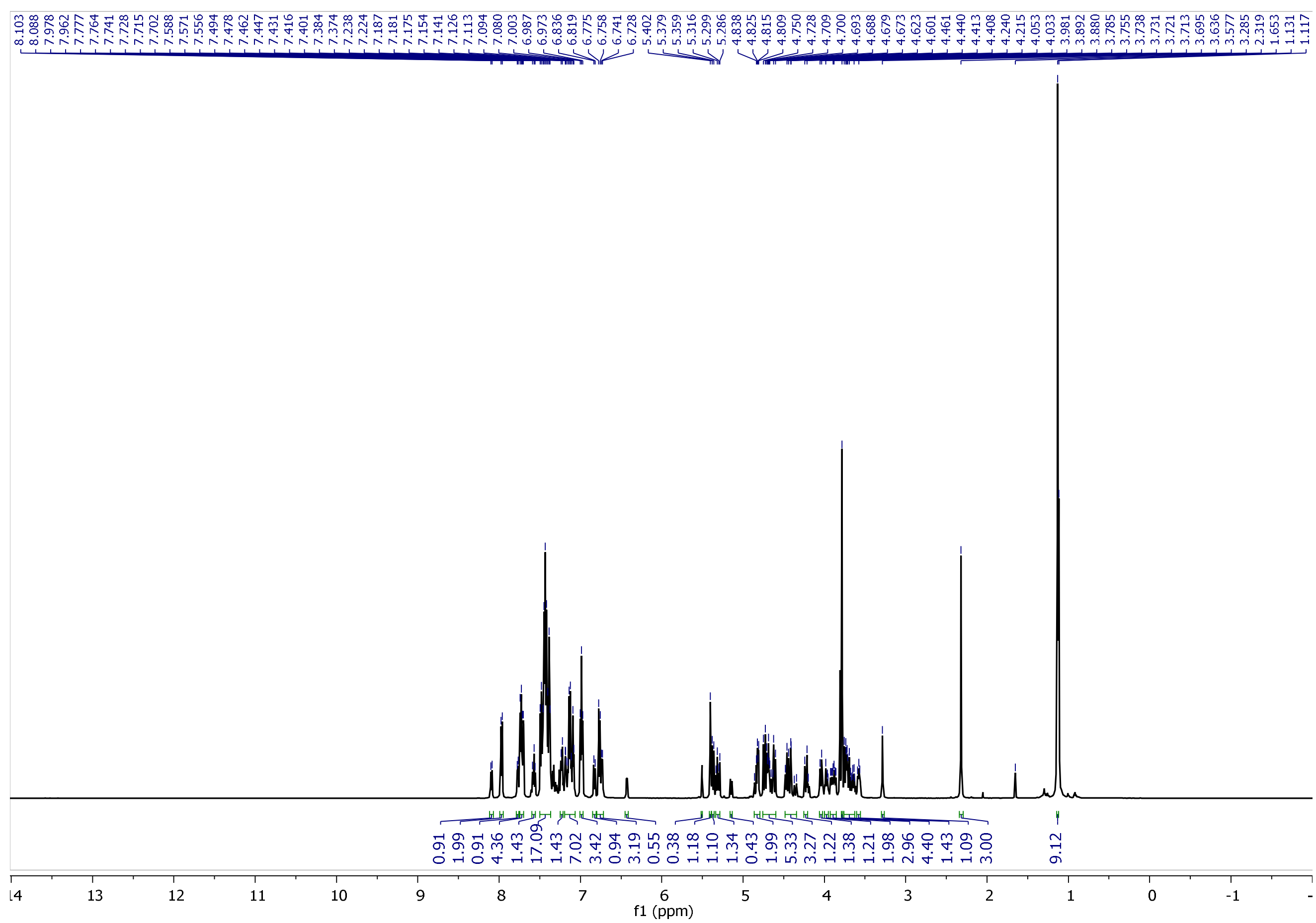
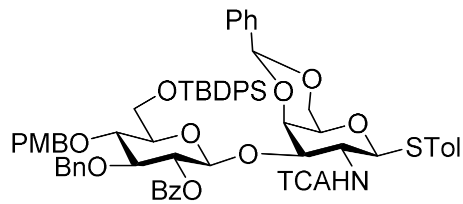


^{13}C-NMR (CDCl$_3$, 126 MHz) of **20**



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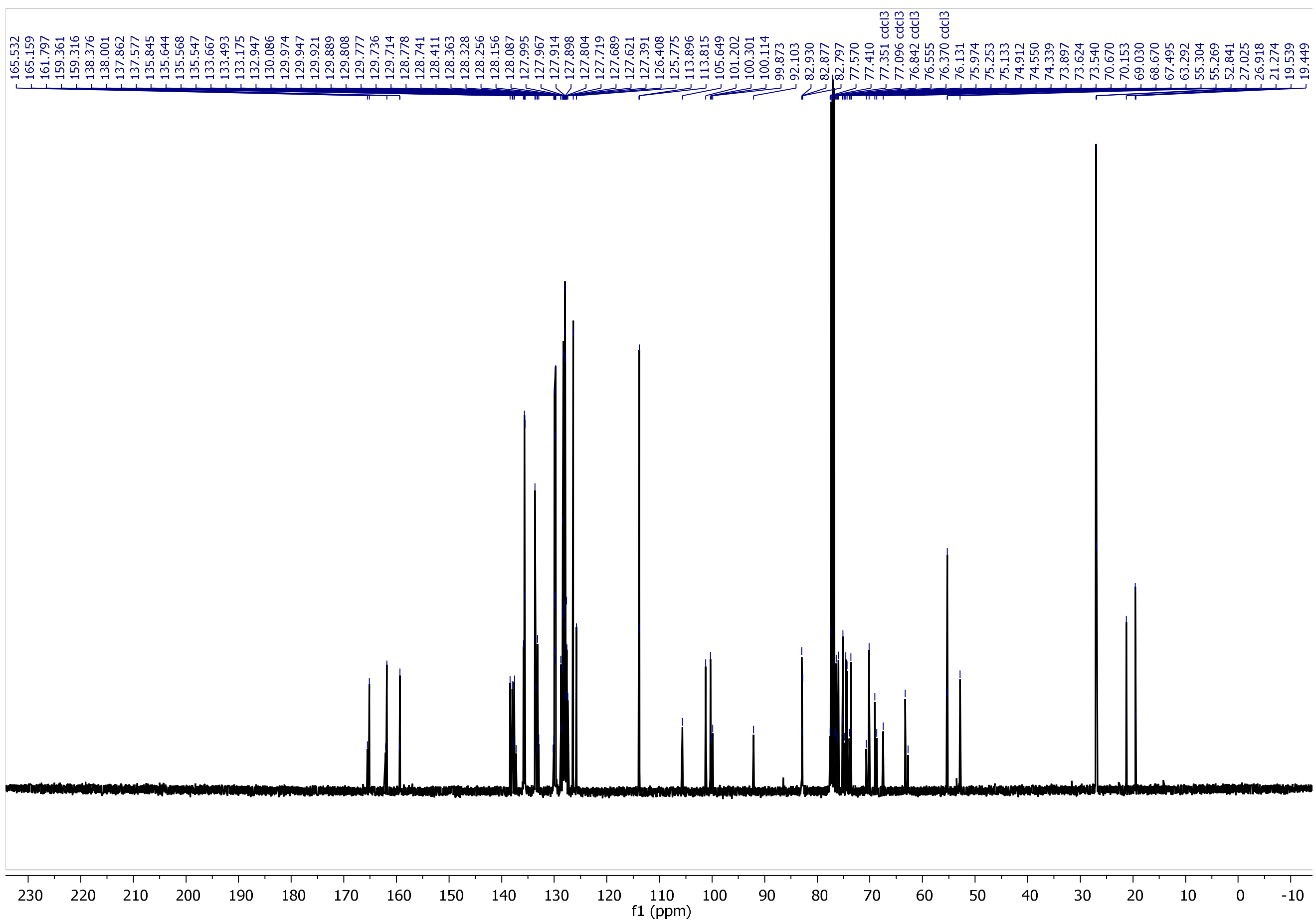
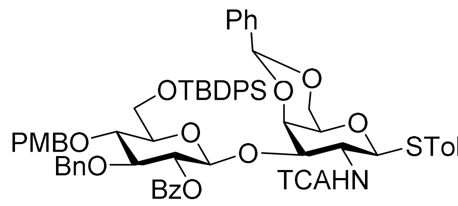


gCOSY ($CDCl_3$, 500 MHz) of **20**



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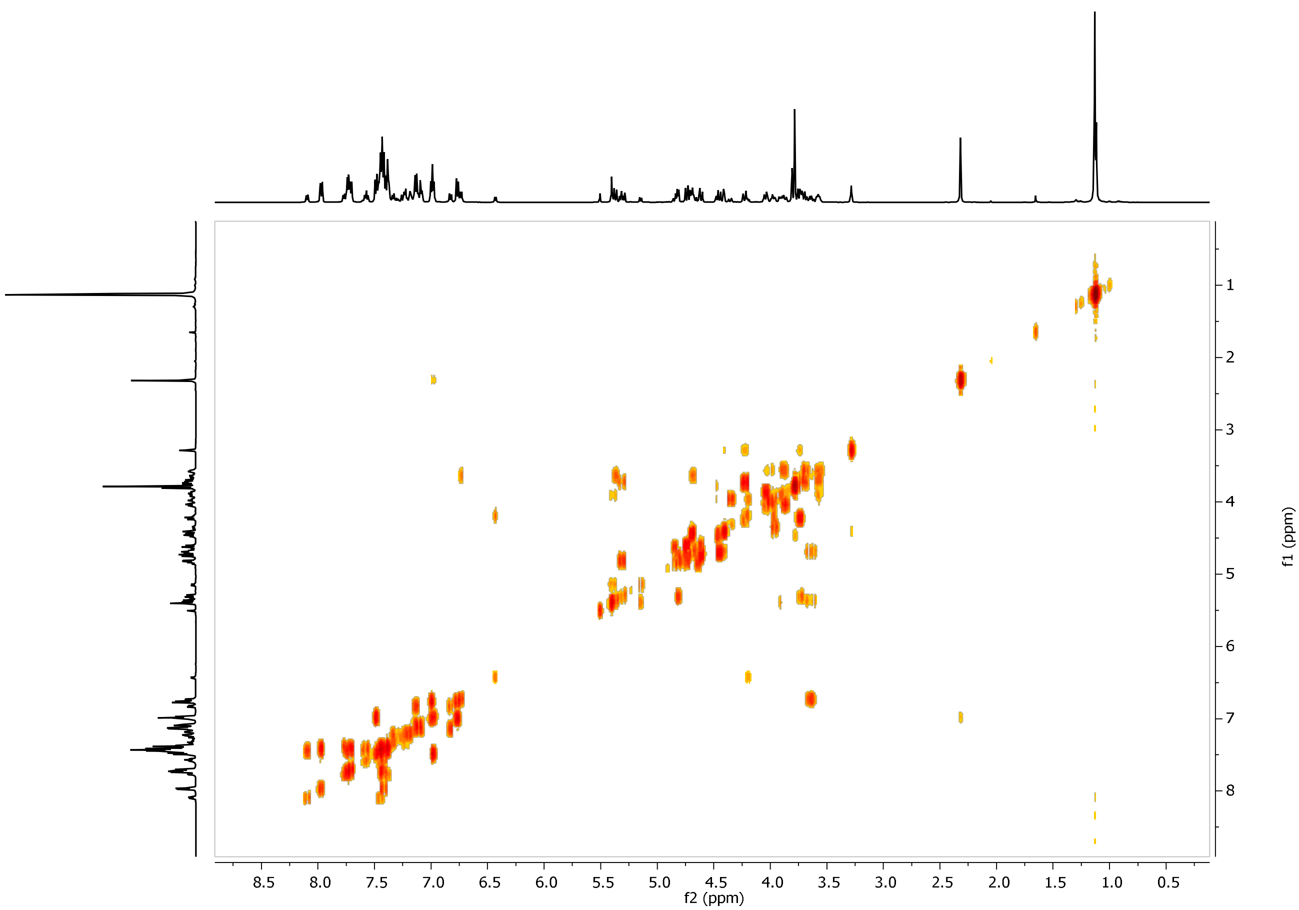
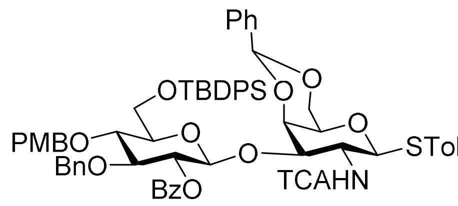


gHMBC ($CDCl_3$, 500 MHz) of **20**



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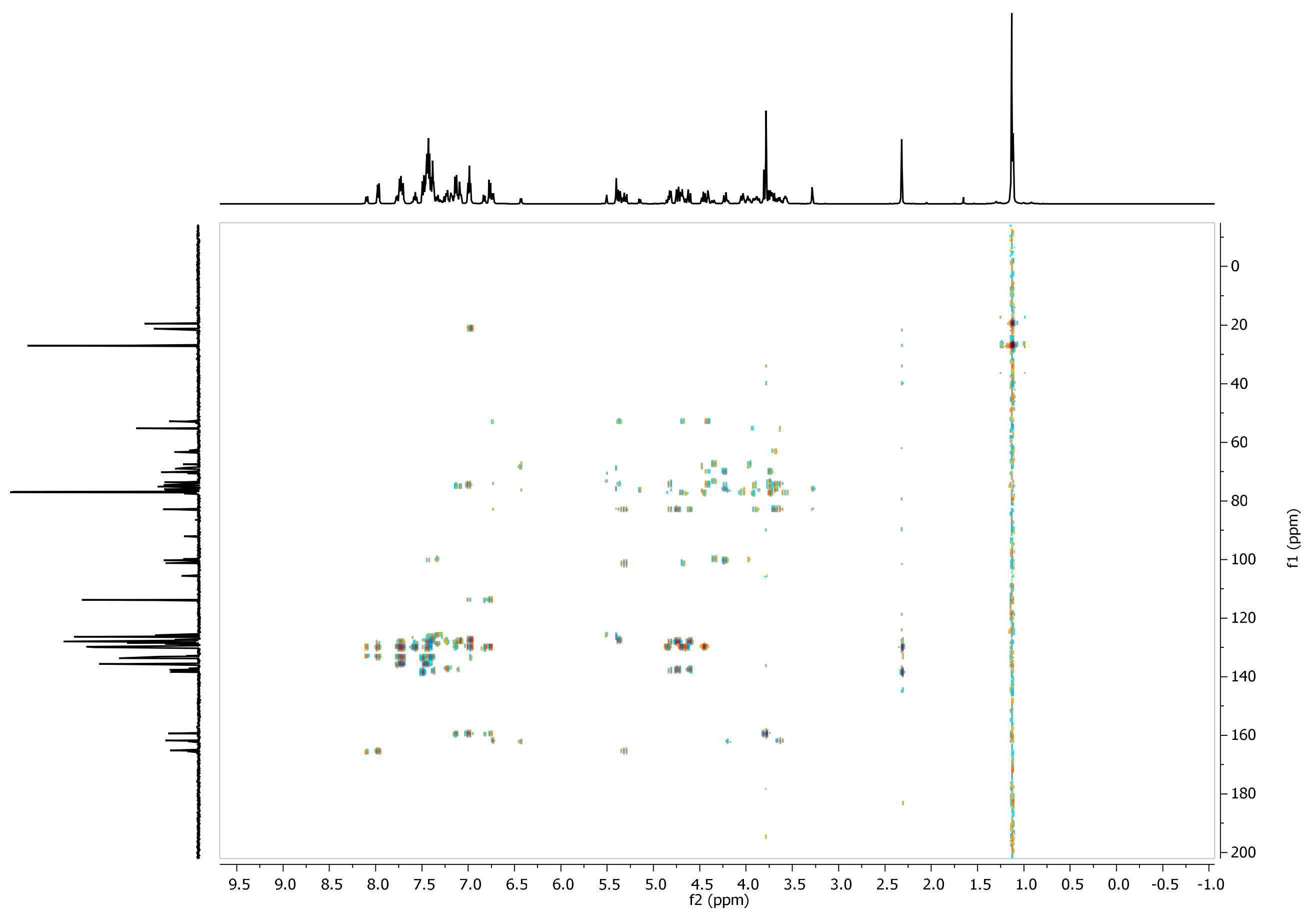
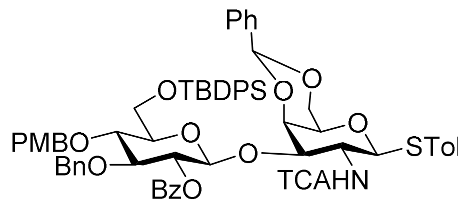


bsgHSQC ($CDCl_3$, 500 MHz) of **20**



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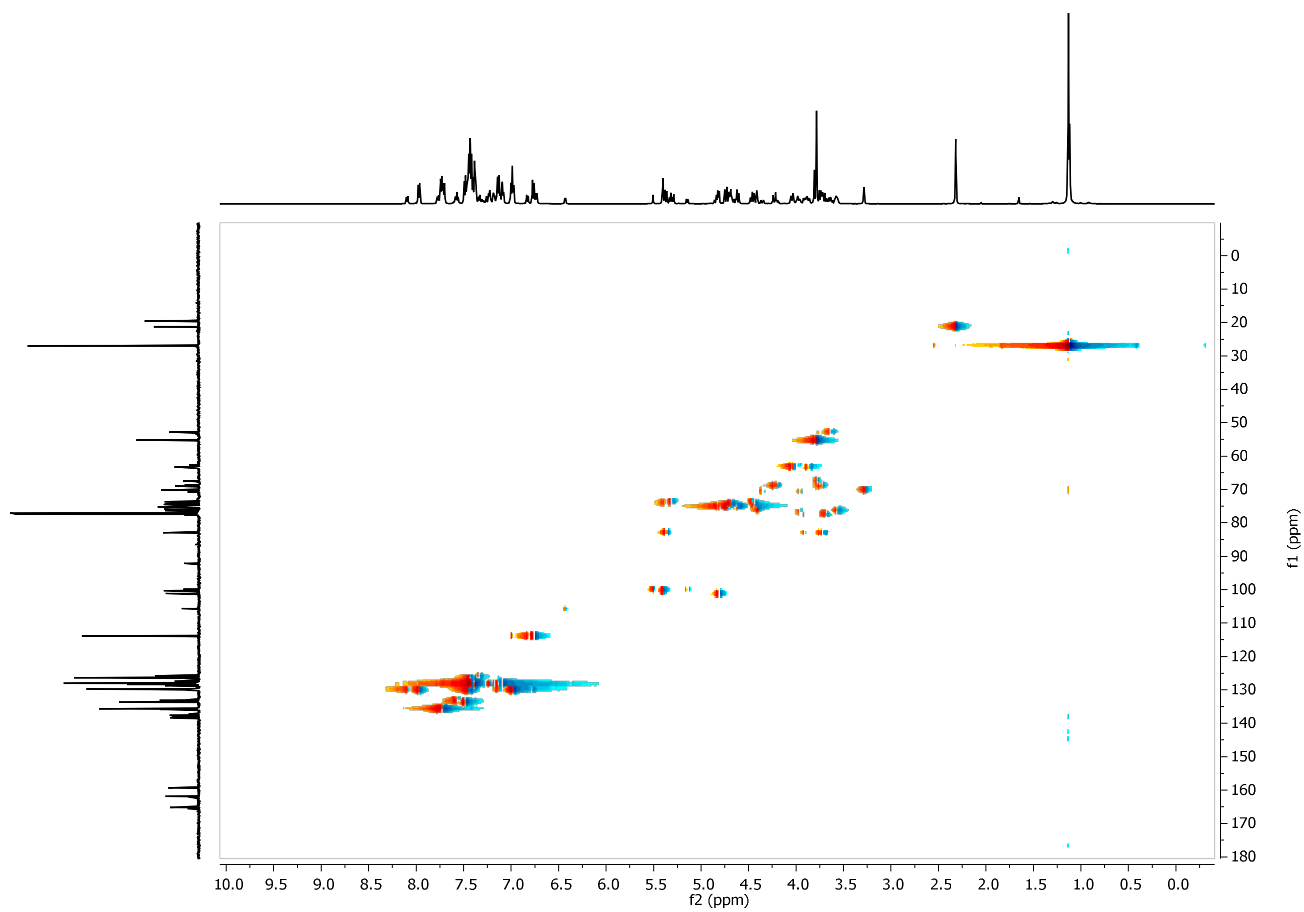
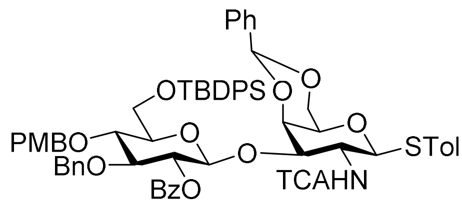


gHSQC ($CDCl_3$, 500 MHz) of **20**



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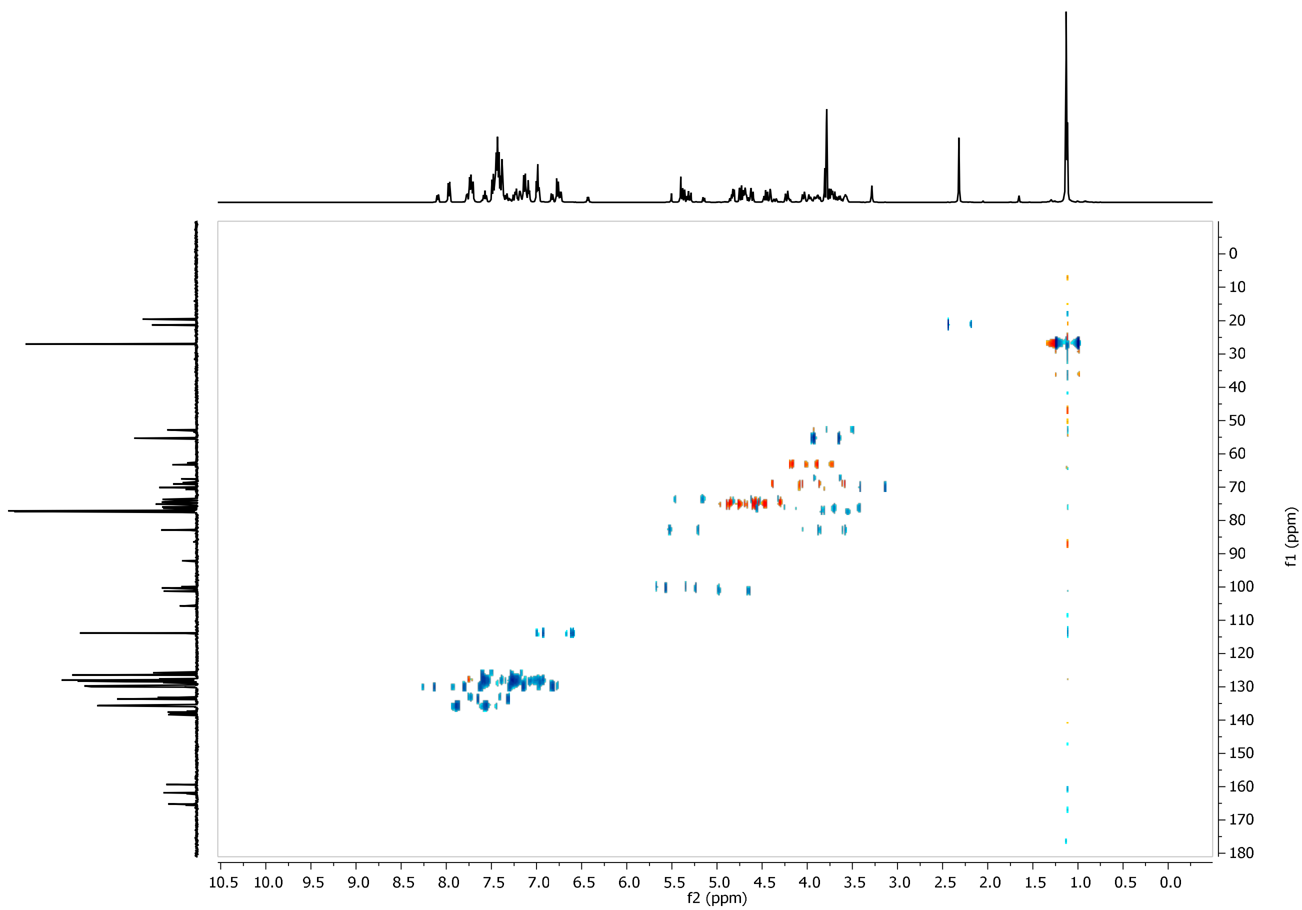
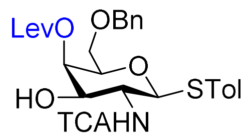


[1]H-NMR (CDCl$_3$, 500 MHz) of **22**



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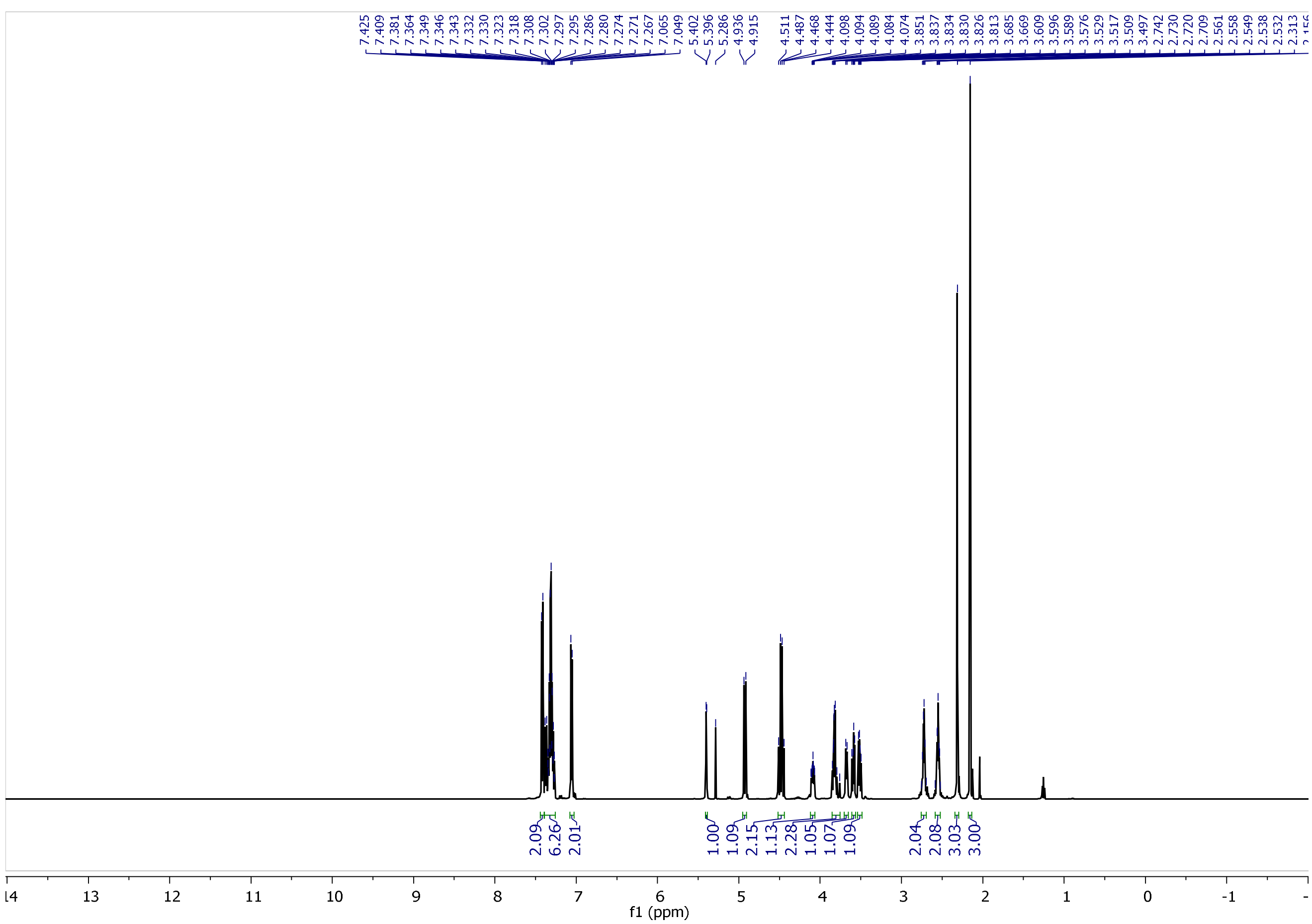
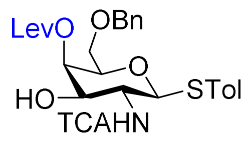
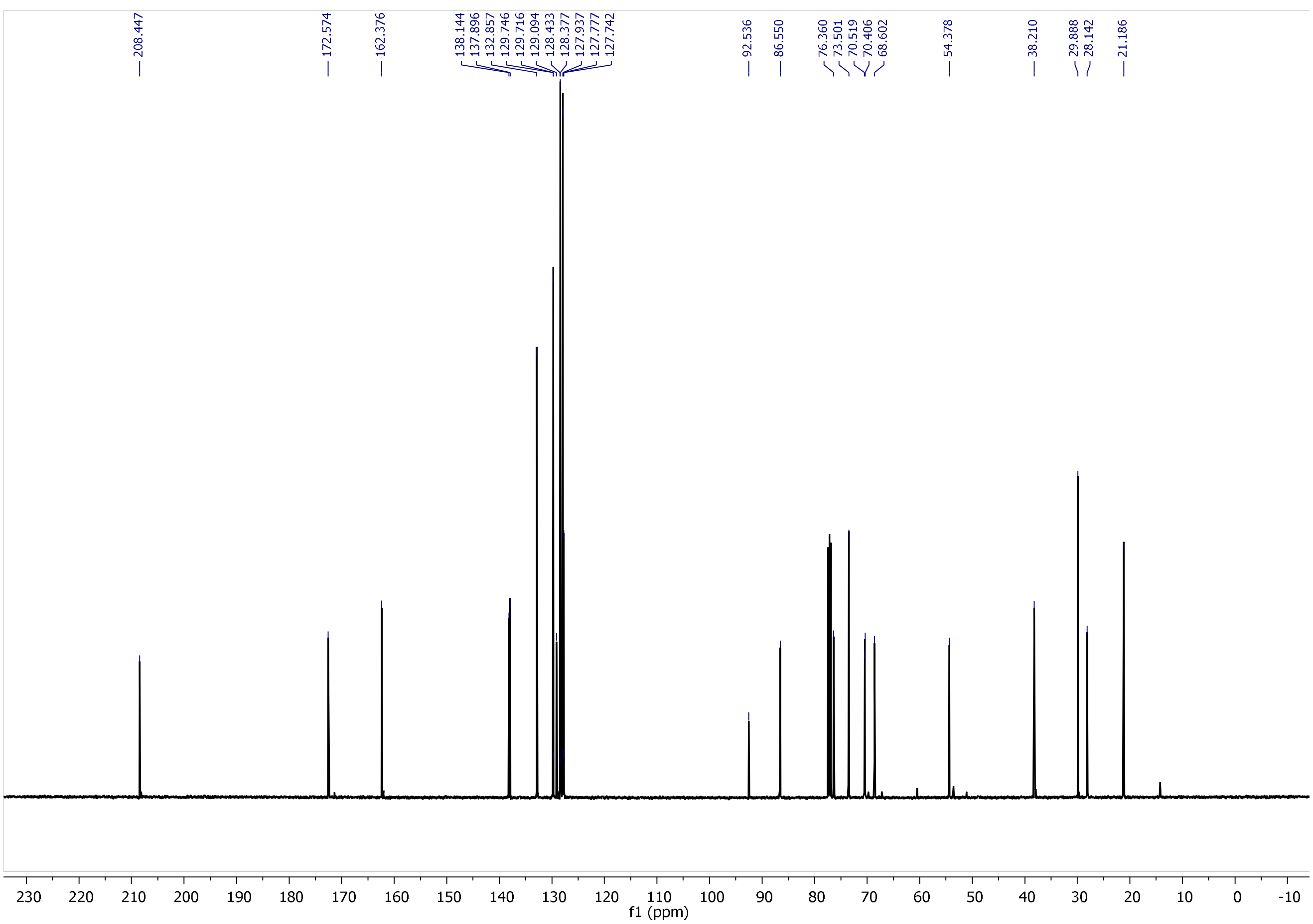
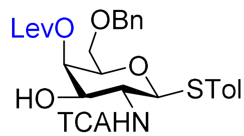


[13]C-NMR (CDCl$_3$, 126 MHz) of **22**





gCOSY ($CDCl_3$, 500 MHz) of **22**



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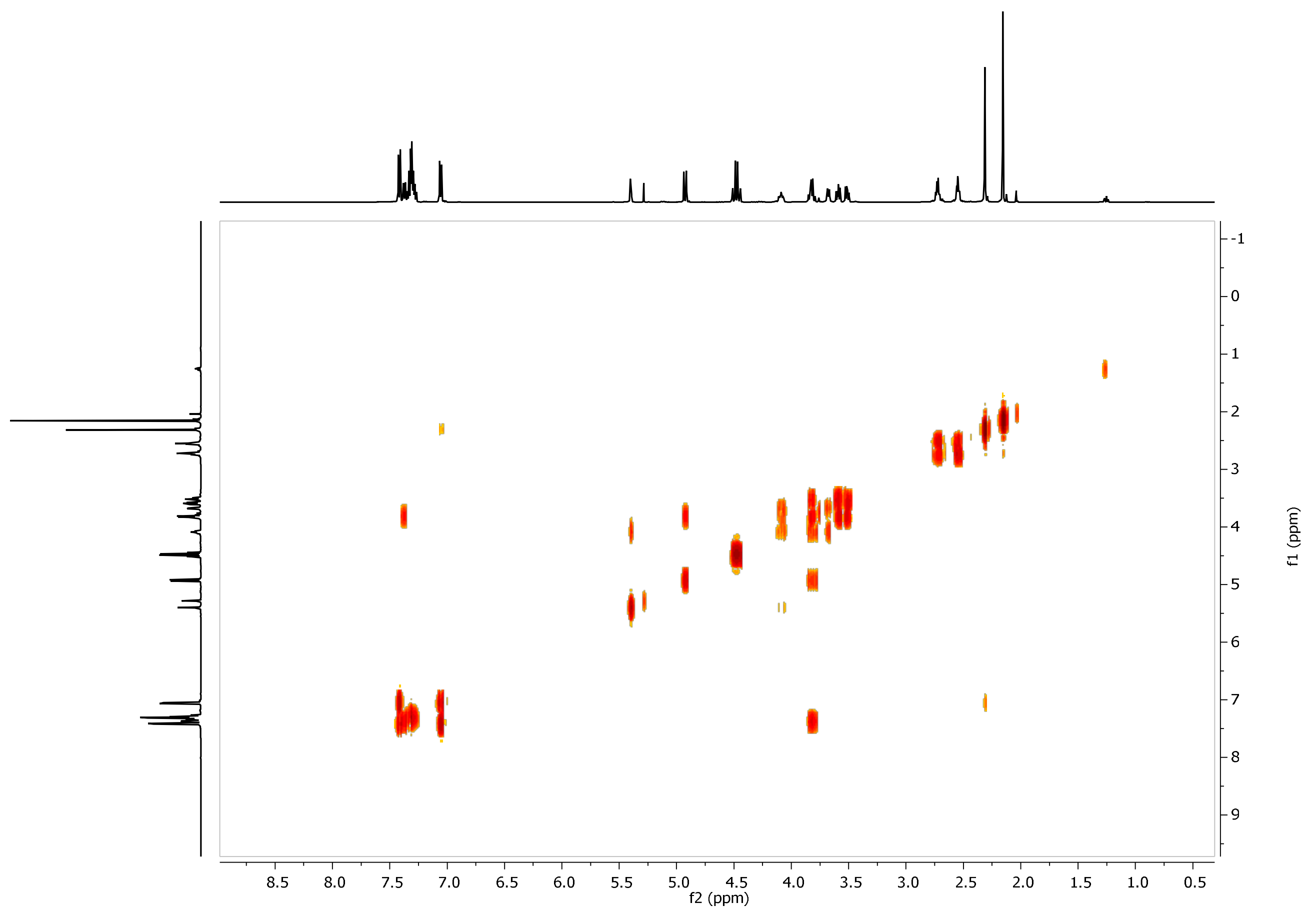
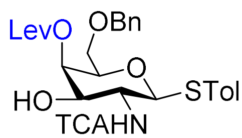


bsgHSQC ($CDCl_3$, 500 MHz) of **22**



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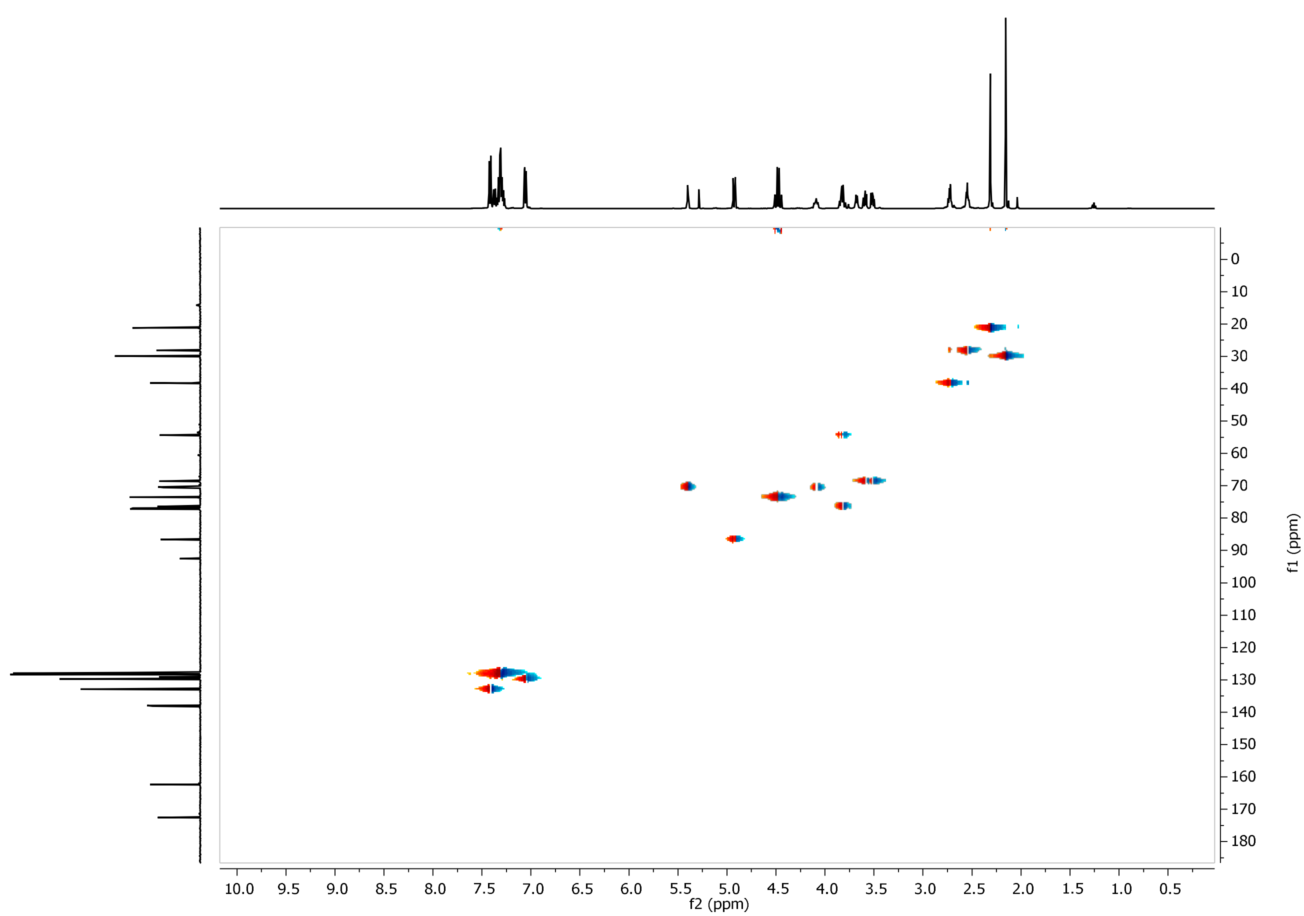
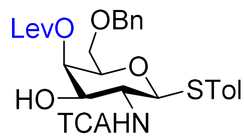


gHSQC ($CDCl_3$, 500 MHz) of **22**



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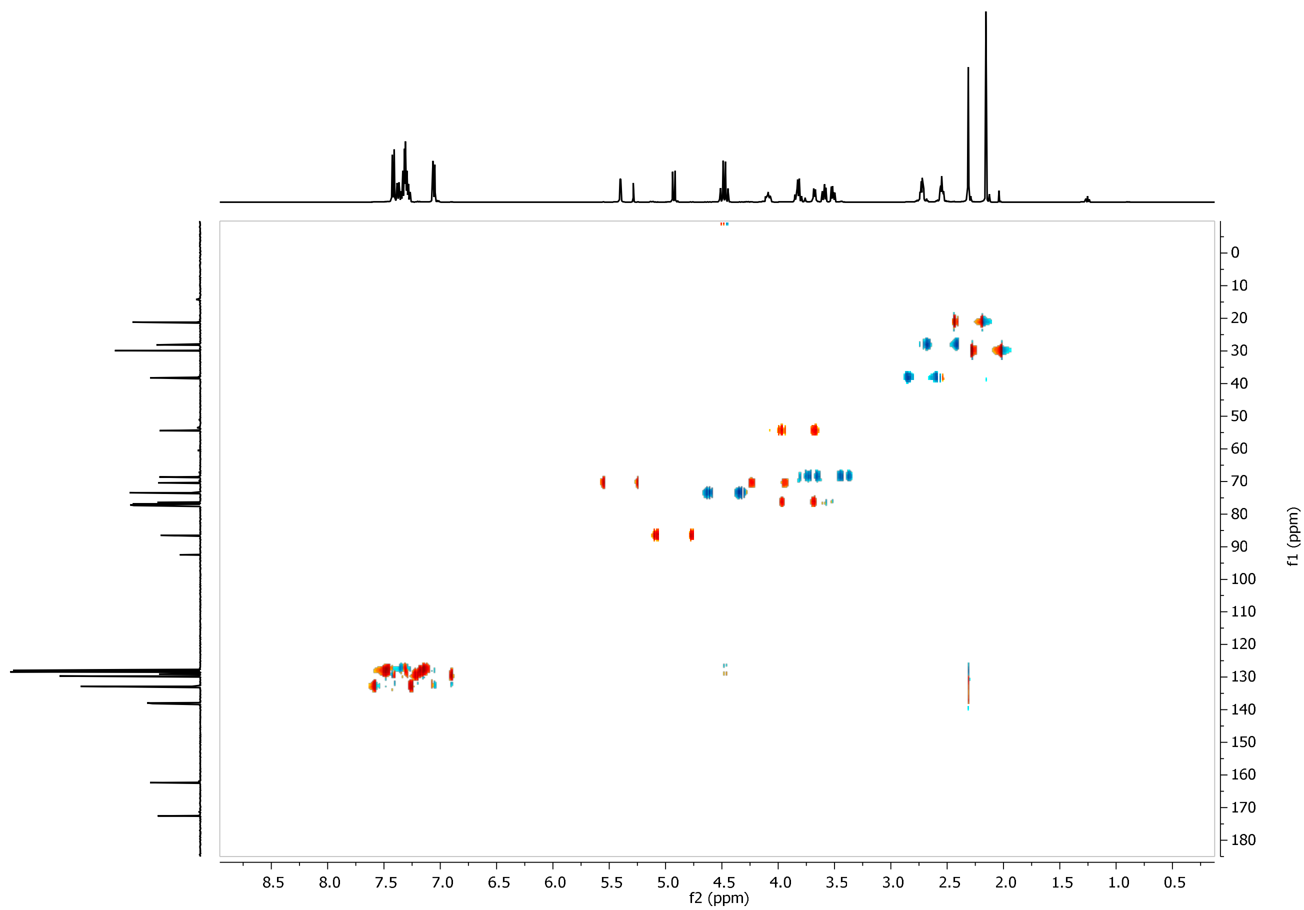
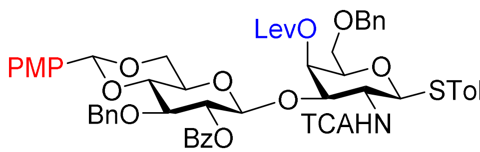


^{1}H-NMR ($CDCl_3$, 500 MHz) of **23**



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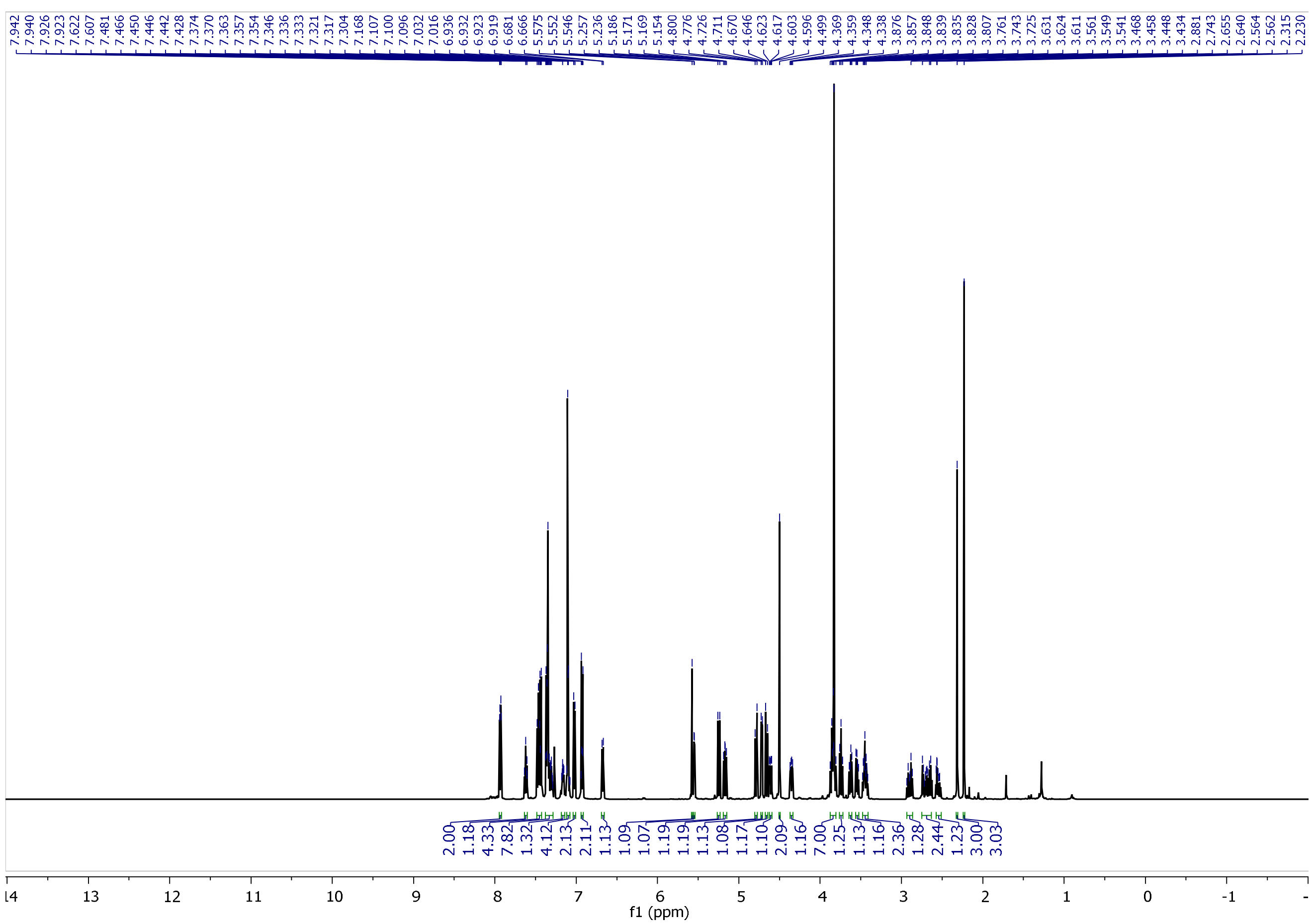
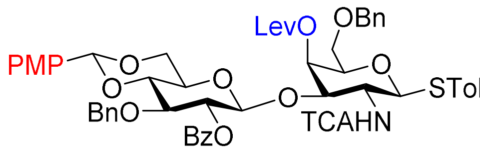


^{13}C-NMR ($CDCl_3$, 126 MHz) of **23**



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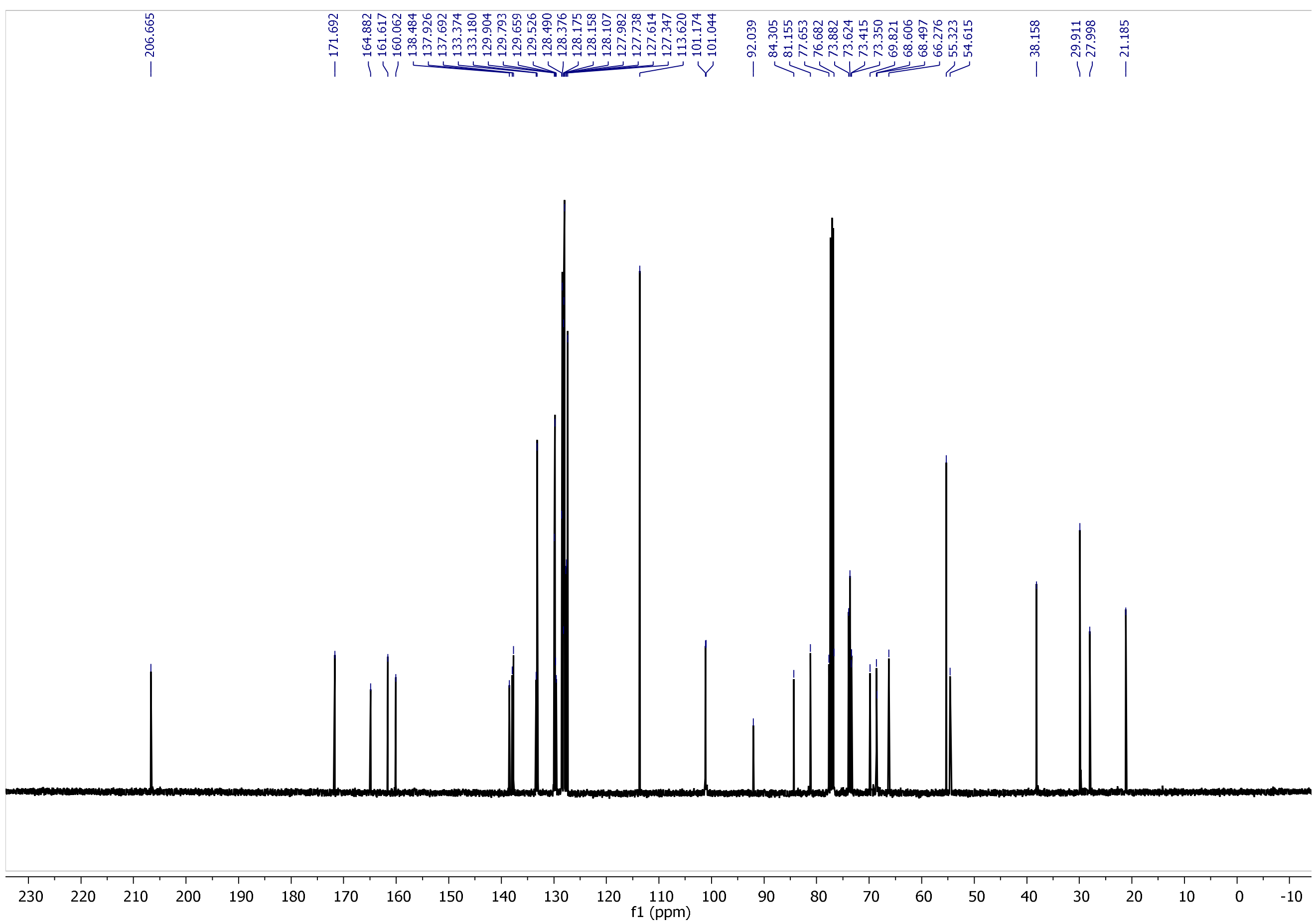
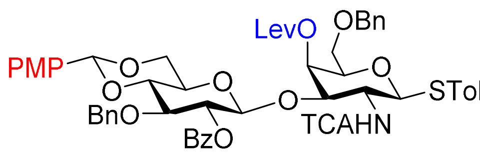


gCOSY ($CDCl_3$, 500 MHz) of **23**



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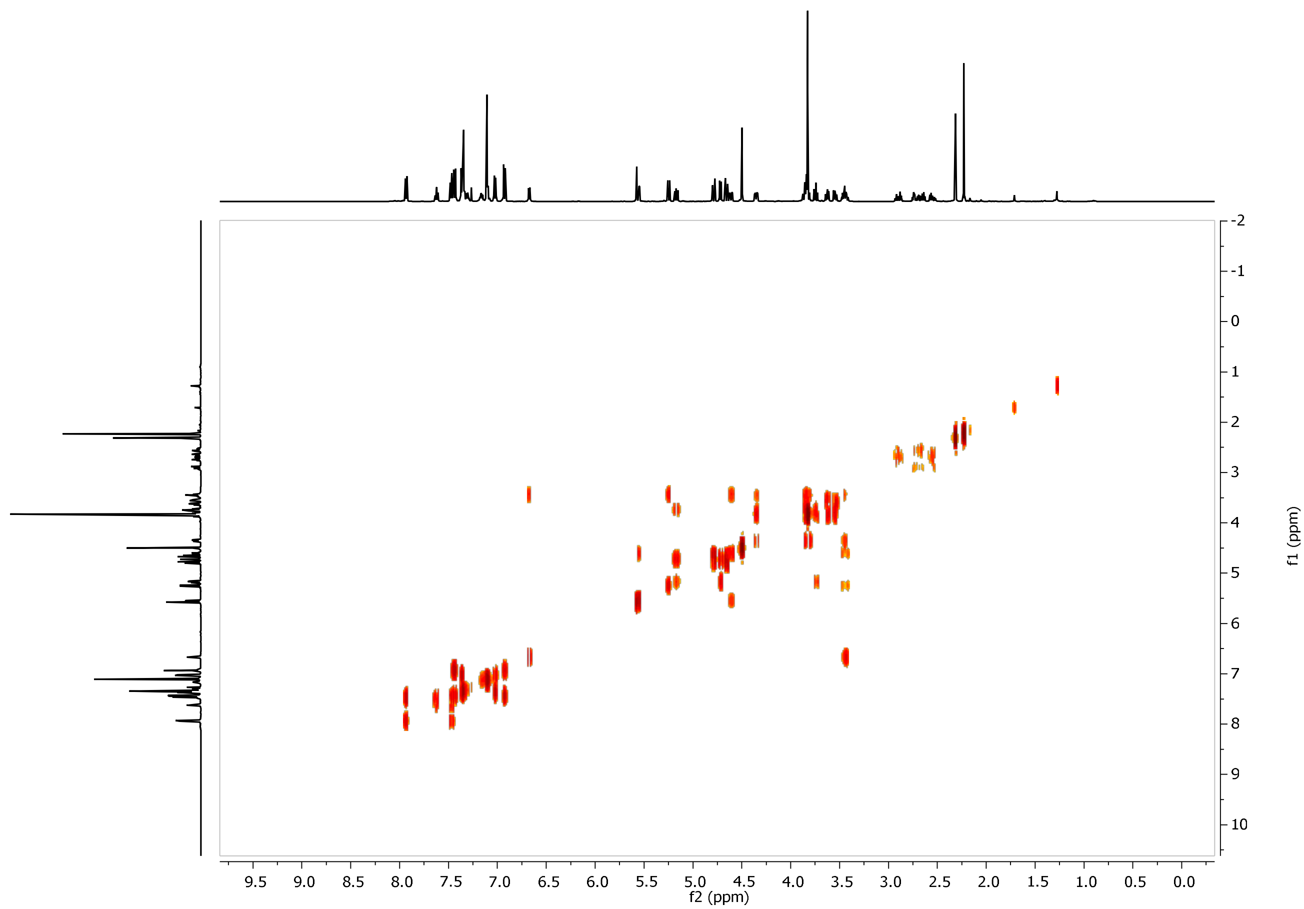
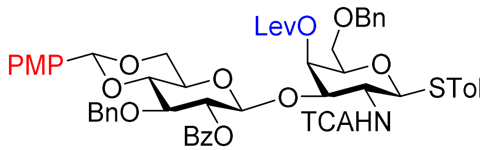


bsgHSQC ($CDCl_3$, 500 MHz) of **23**



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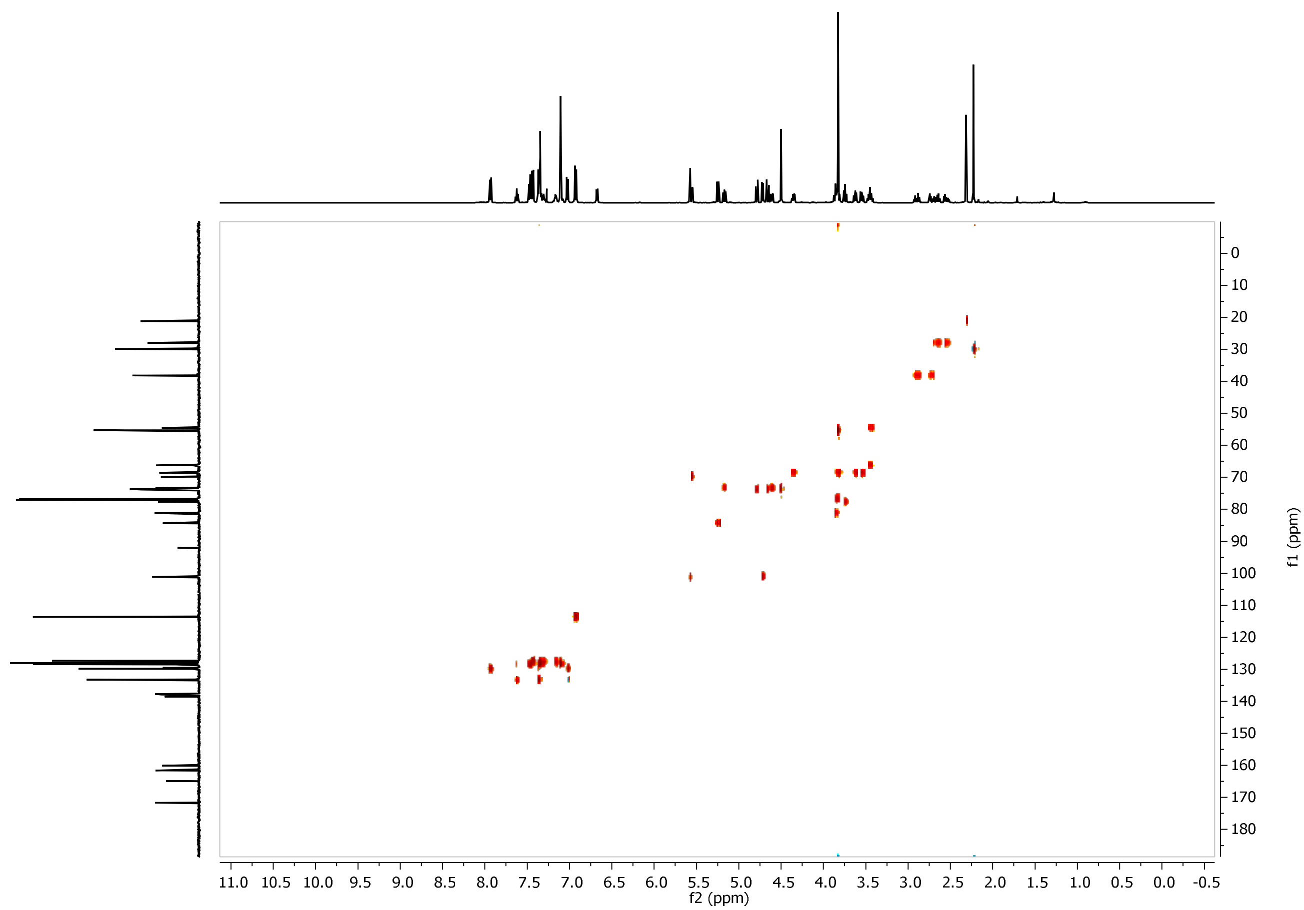
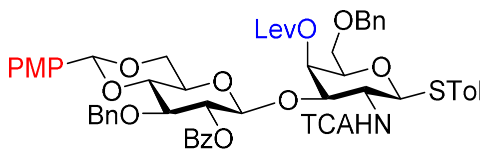


gHSQC ($CDCl_3$, 500 MHz) of **23**



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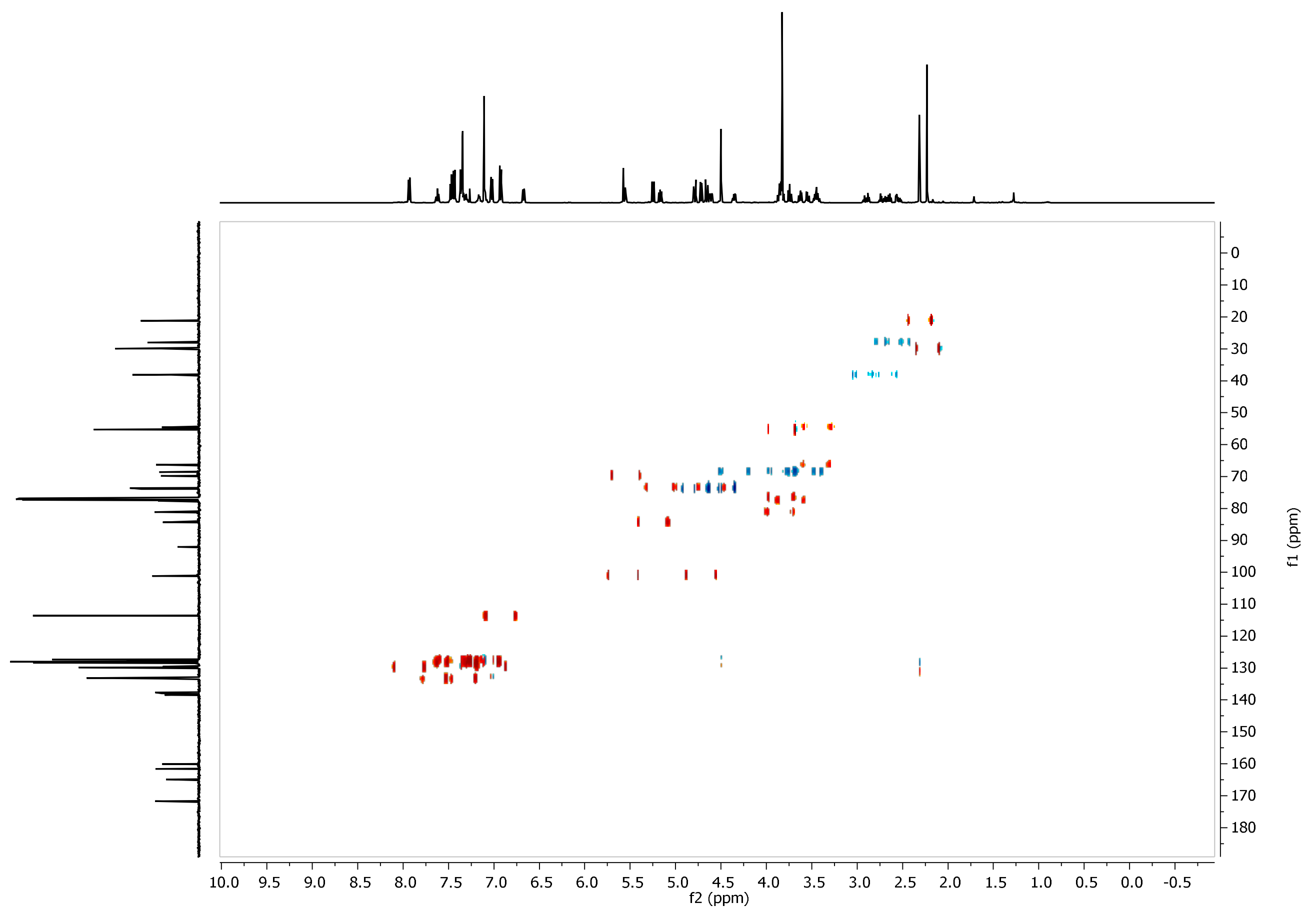
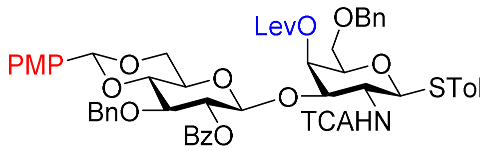


gHMBC ($CDCl_3$, 500 MHz) of **23**



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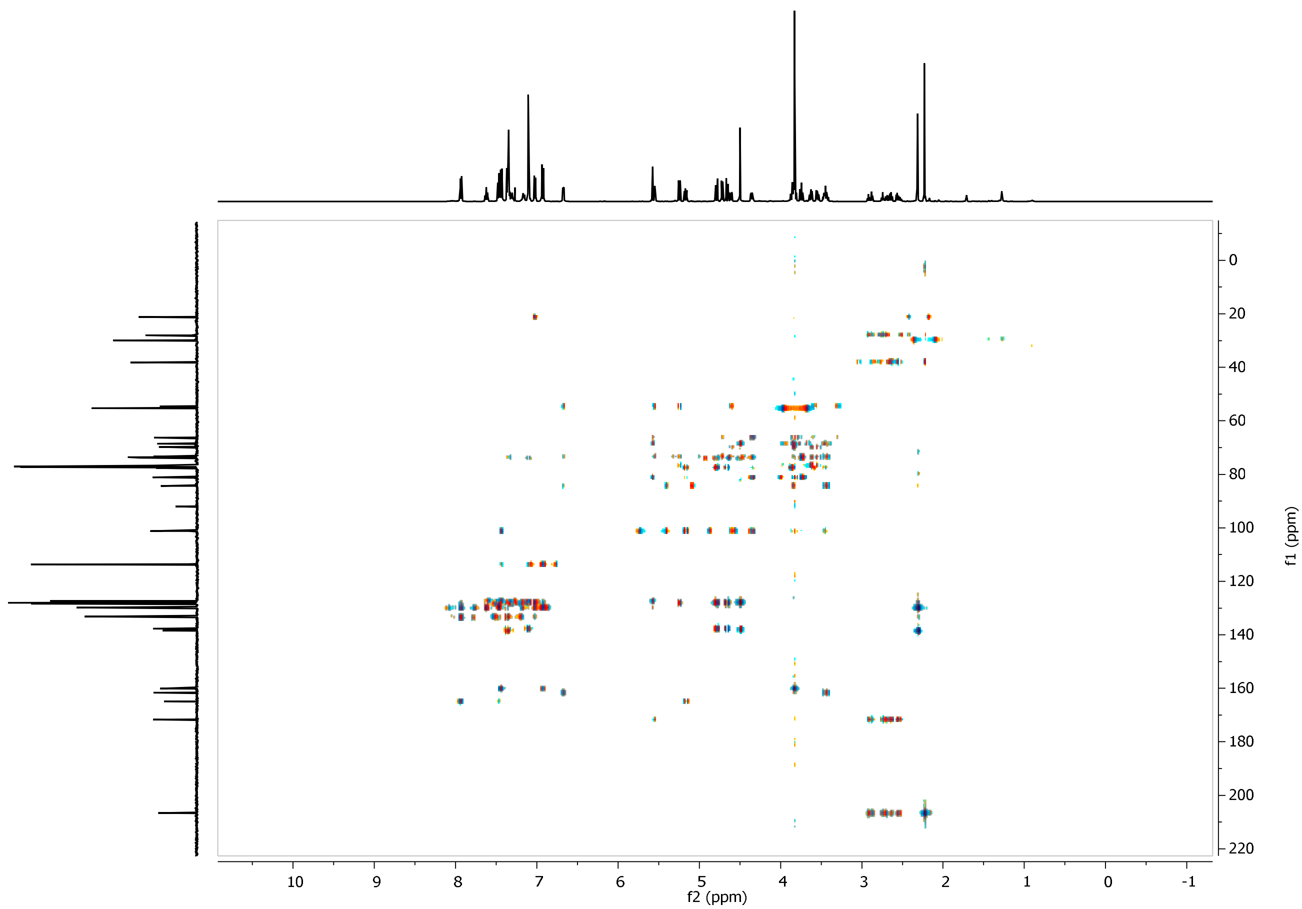
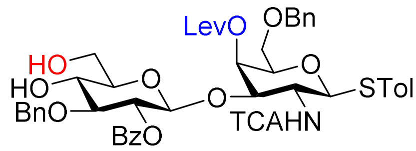


[1]H-NMR (CDCl$_3$, 500 MHz) of **24**



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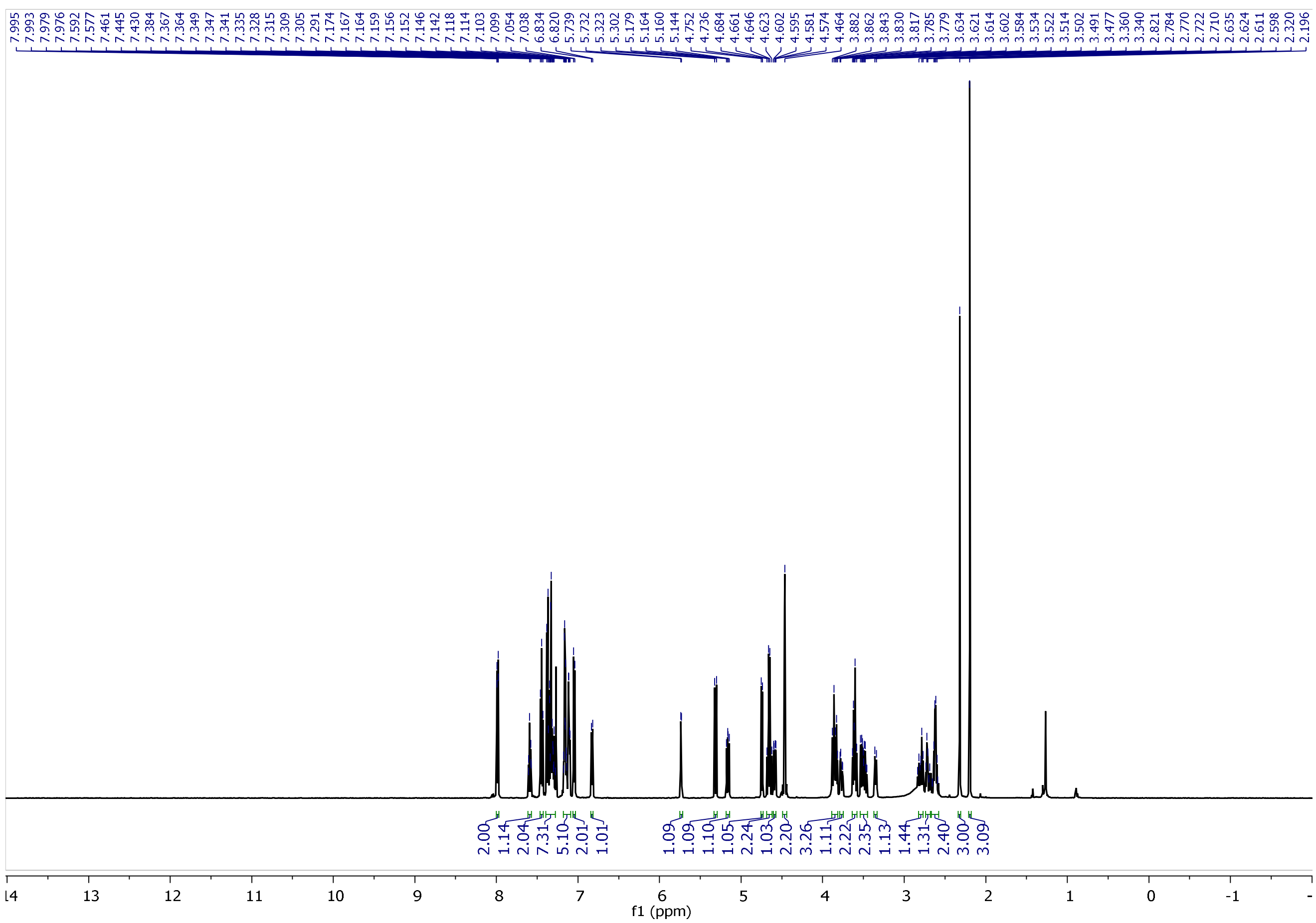
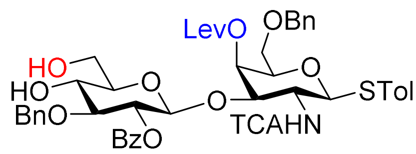


^{13}C-NMR ($CDCl_3$, 126 MHz) of **24**



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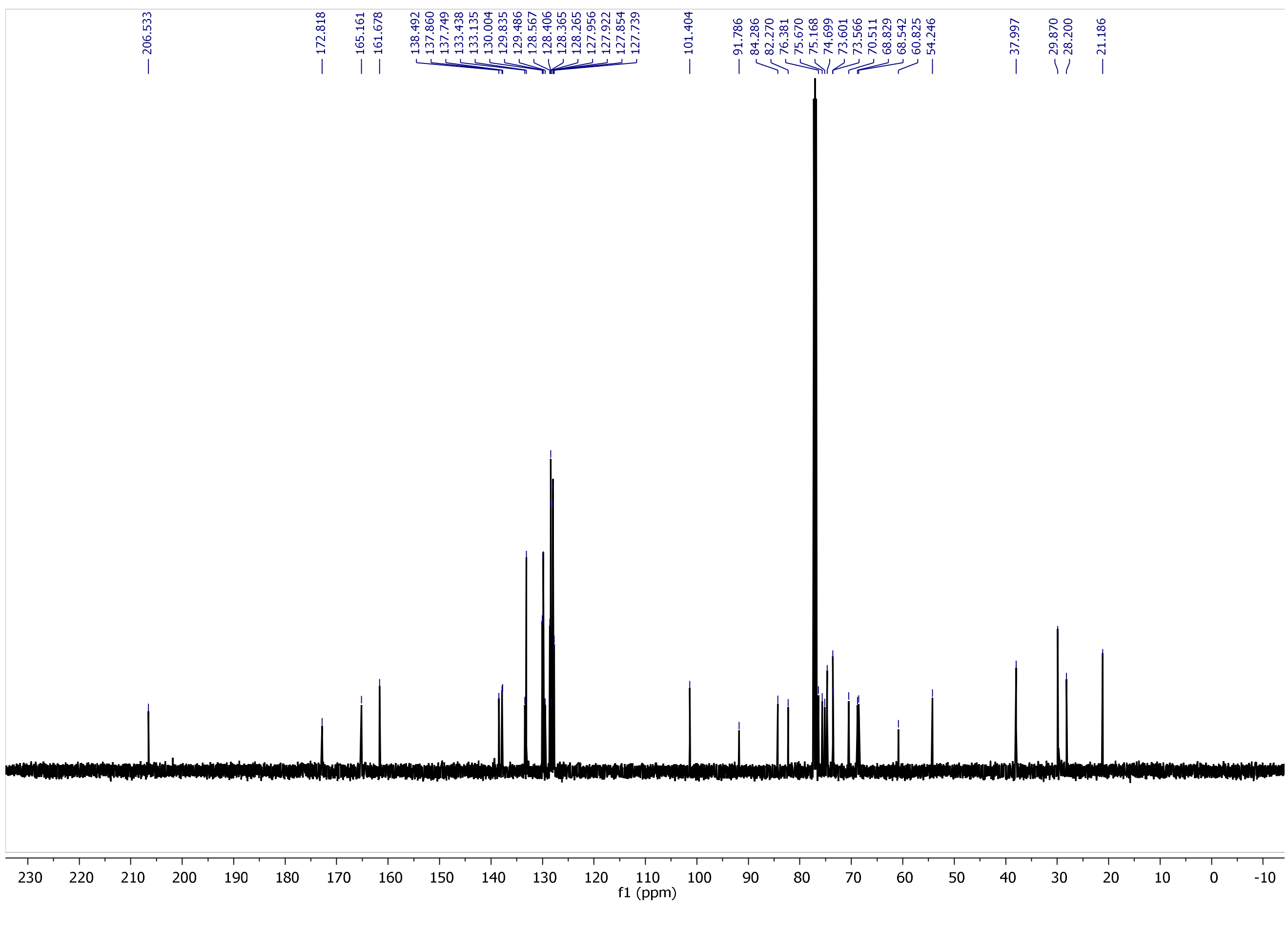
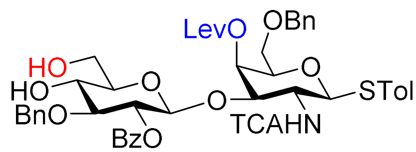


gCOSY ($CDCl_3$, 500 MHz) of **24**



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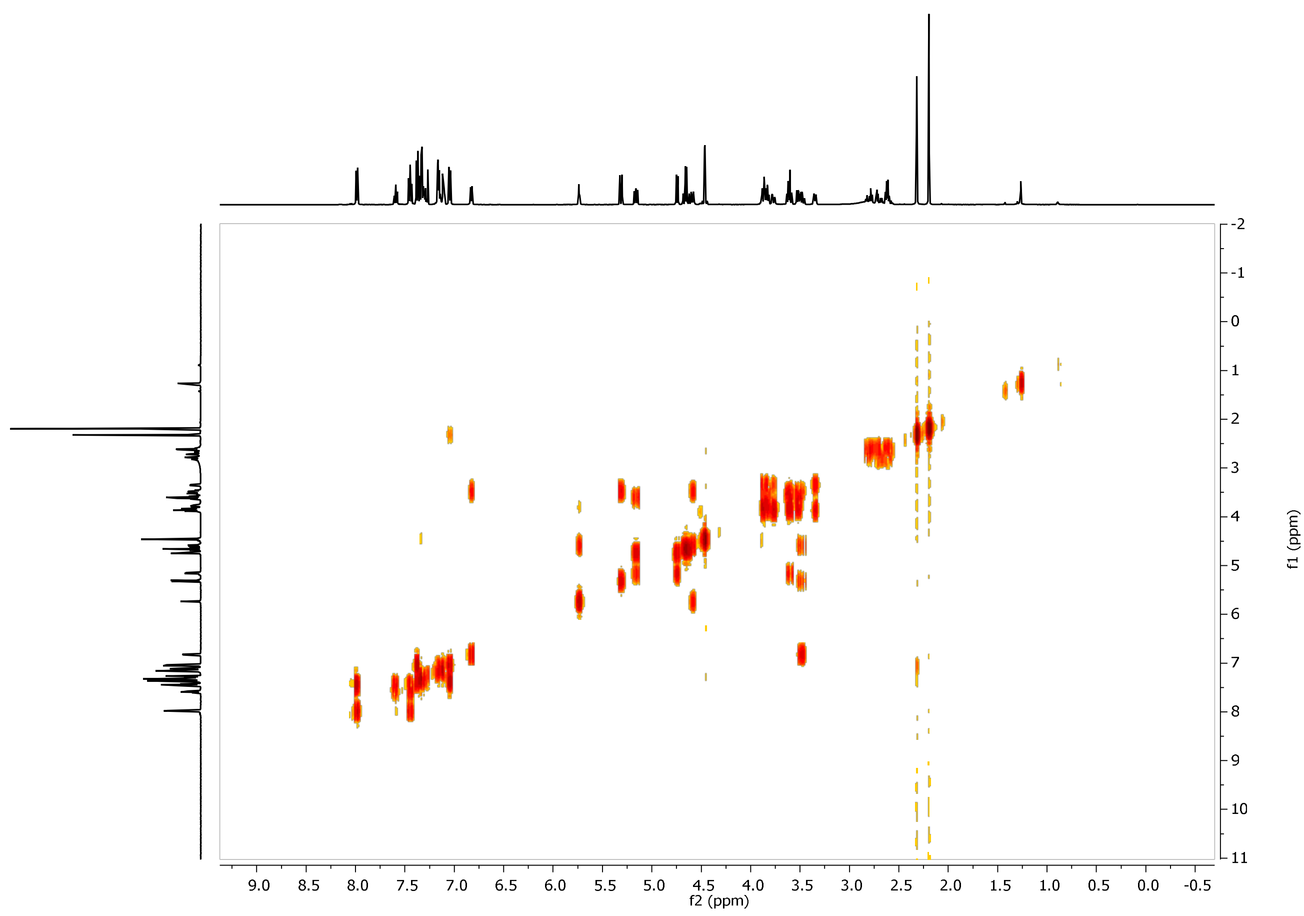
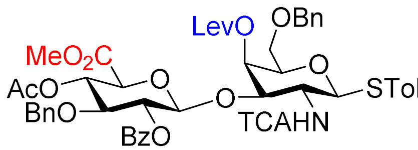


[1]H-NMR ($CDCl_3$, 500 MHz) of **25**



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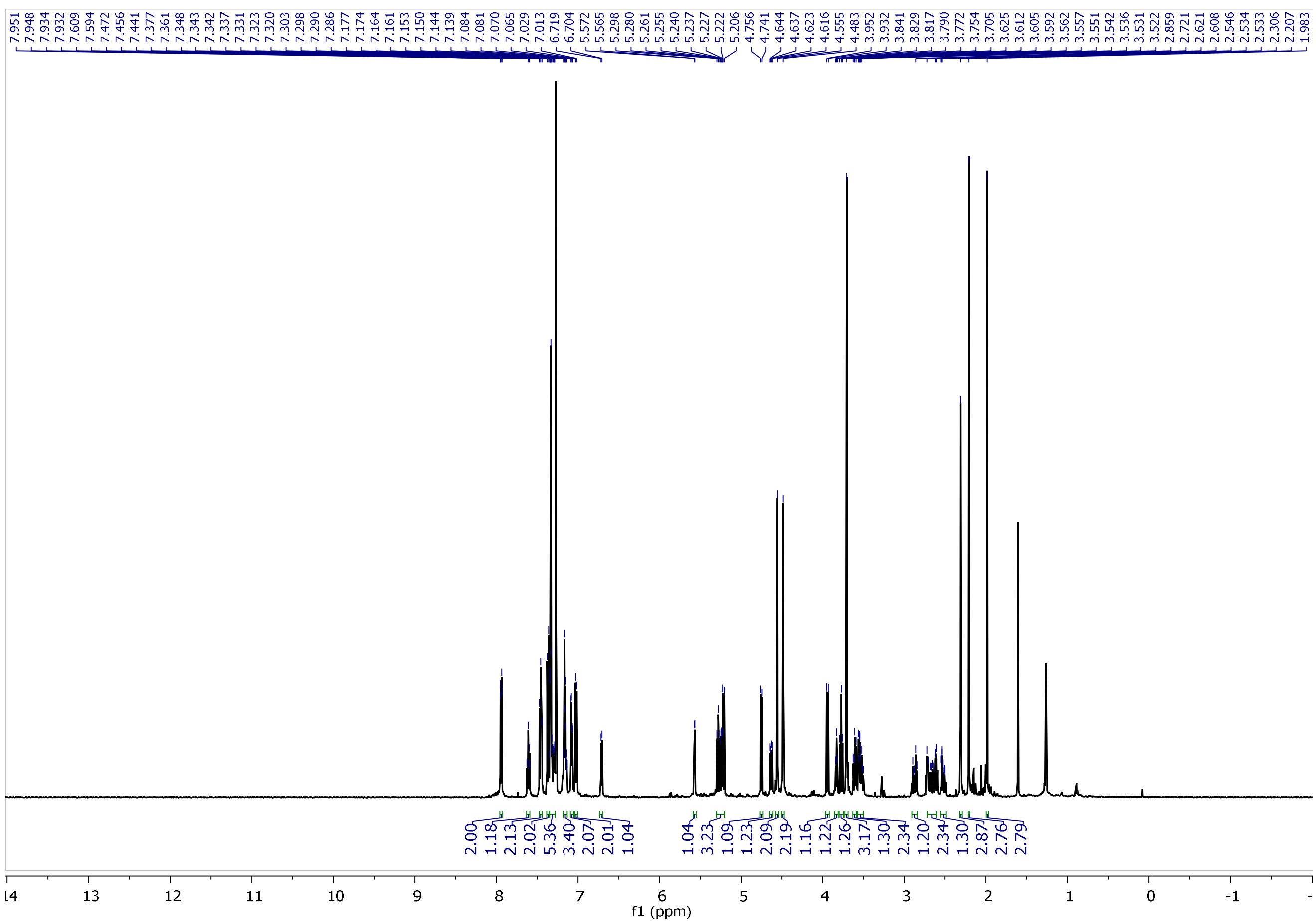
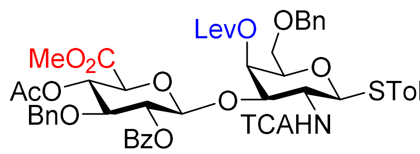


^{13}C-NMR ($CDCl_3$, 126 MHz) of **25**



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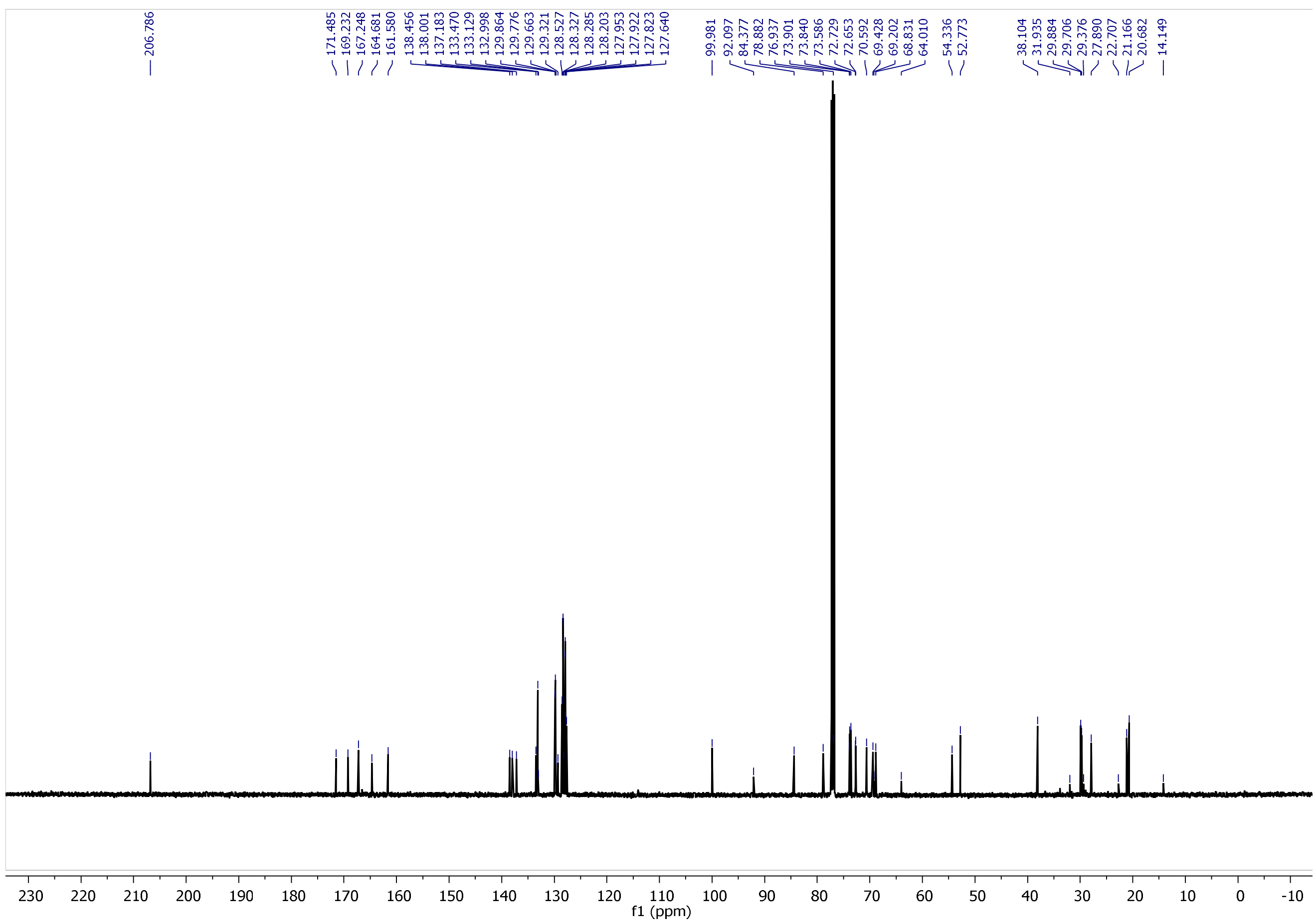
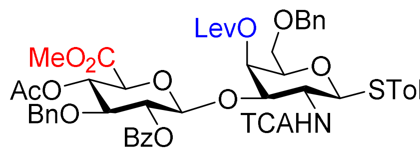


gCOSY ($CDCl_3$, 500 MHz) of **25**



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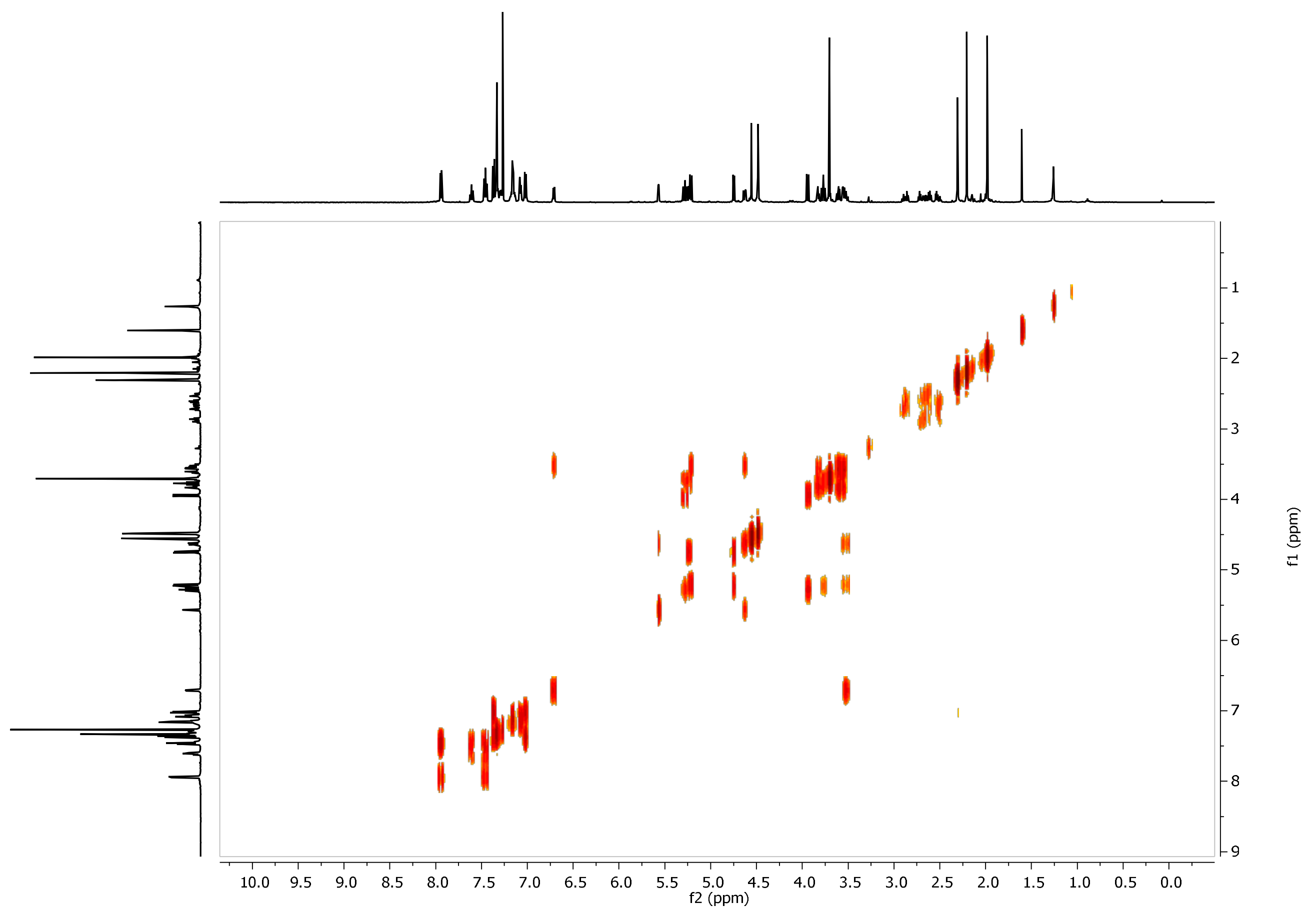
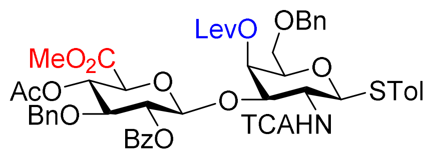


bsgHSQC ($CDCl_3$, 500 MHz) of **25**



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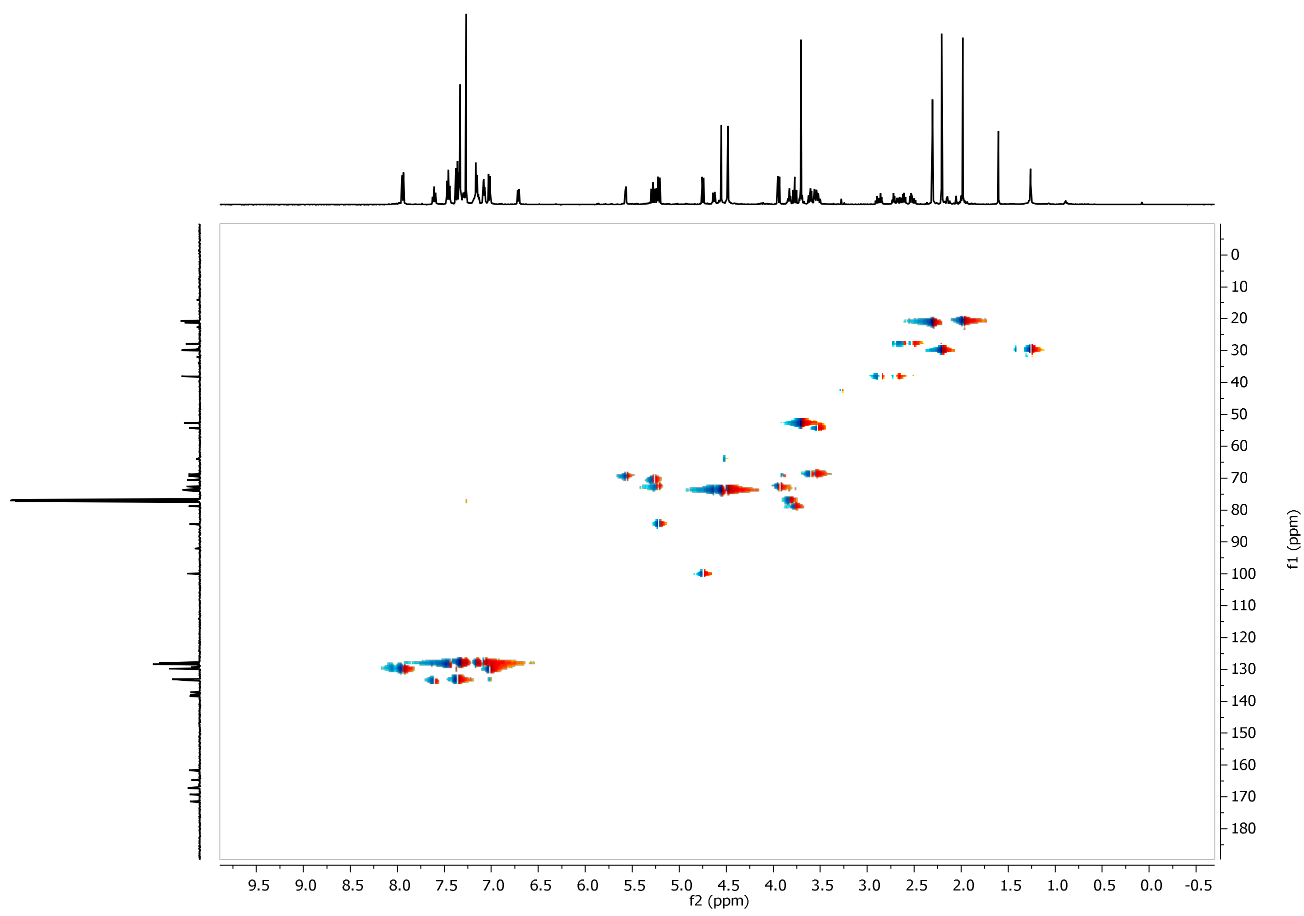
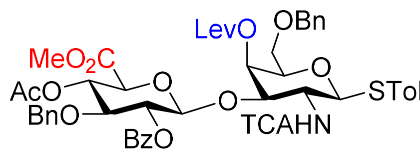


gHSQC ($CDCl_3$, 500 MHz) of **25**



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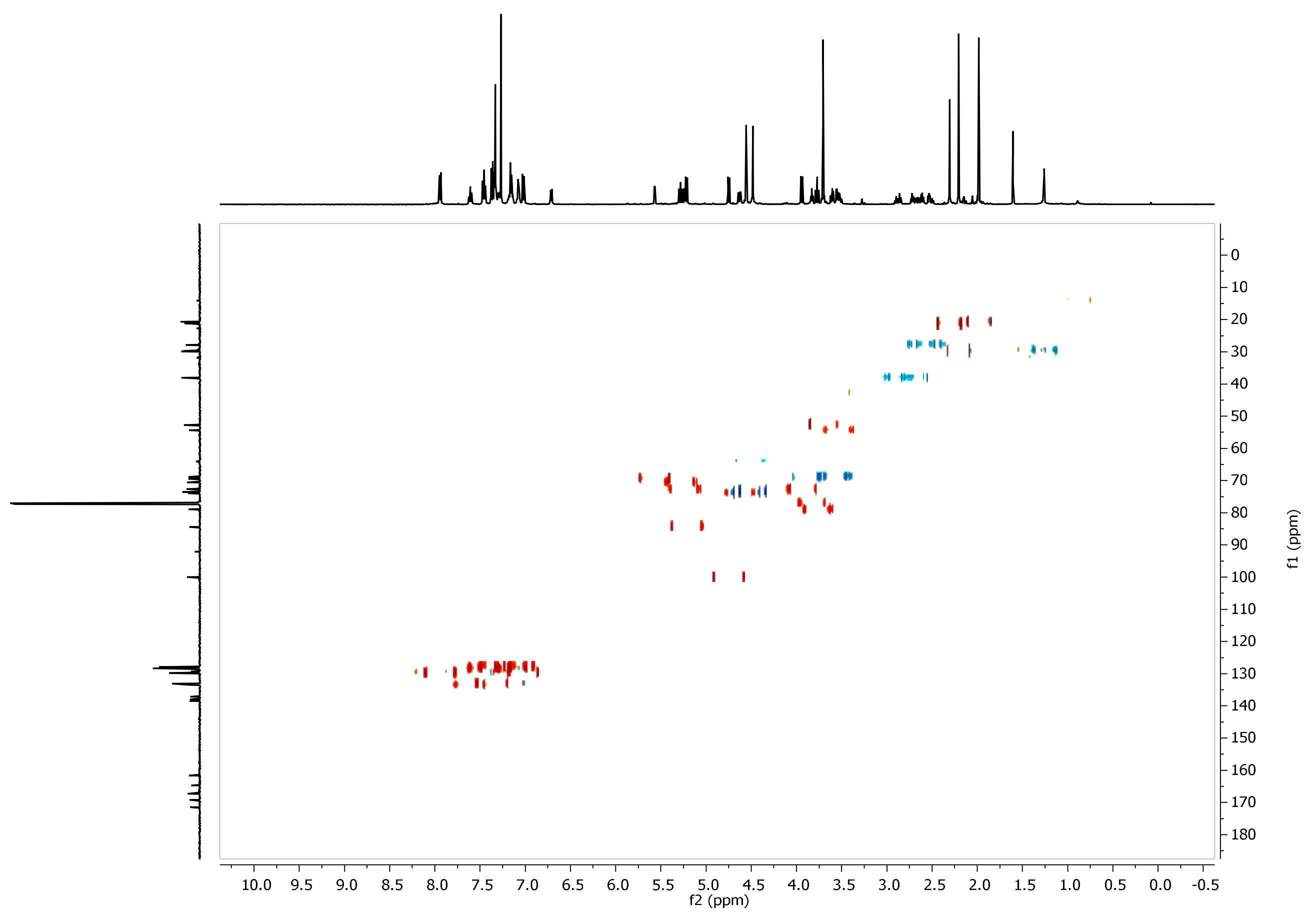
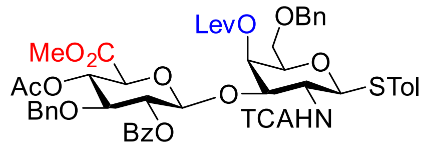


gHMBC ($CDCl_3$, 500 MHz) of **25**



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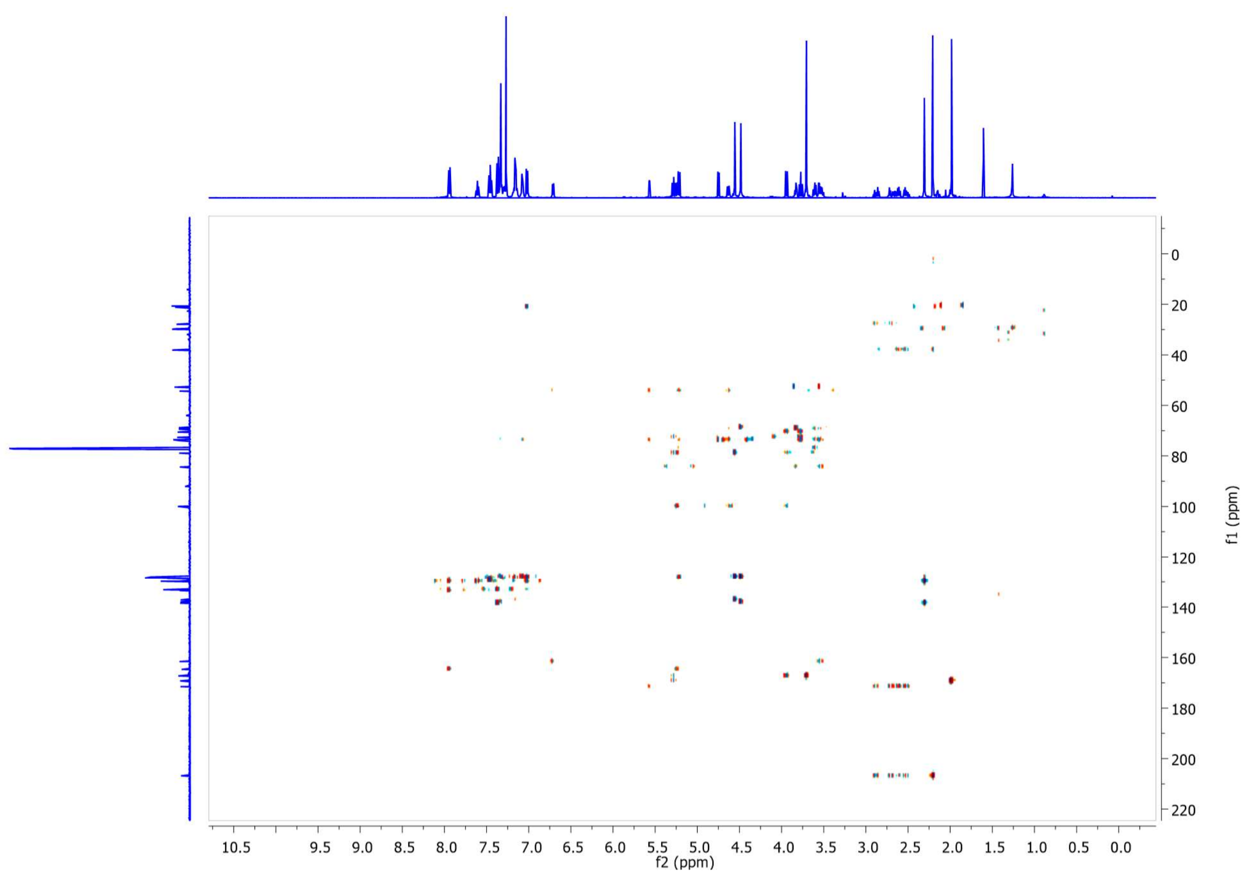
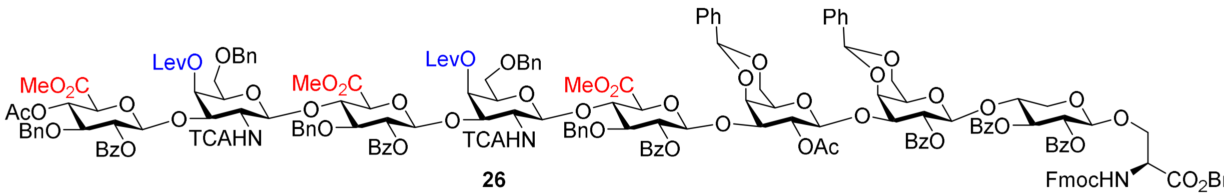


^{1}H-NMR ($CDCl_3$, 500 MHz) of **26**



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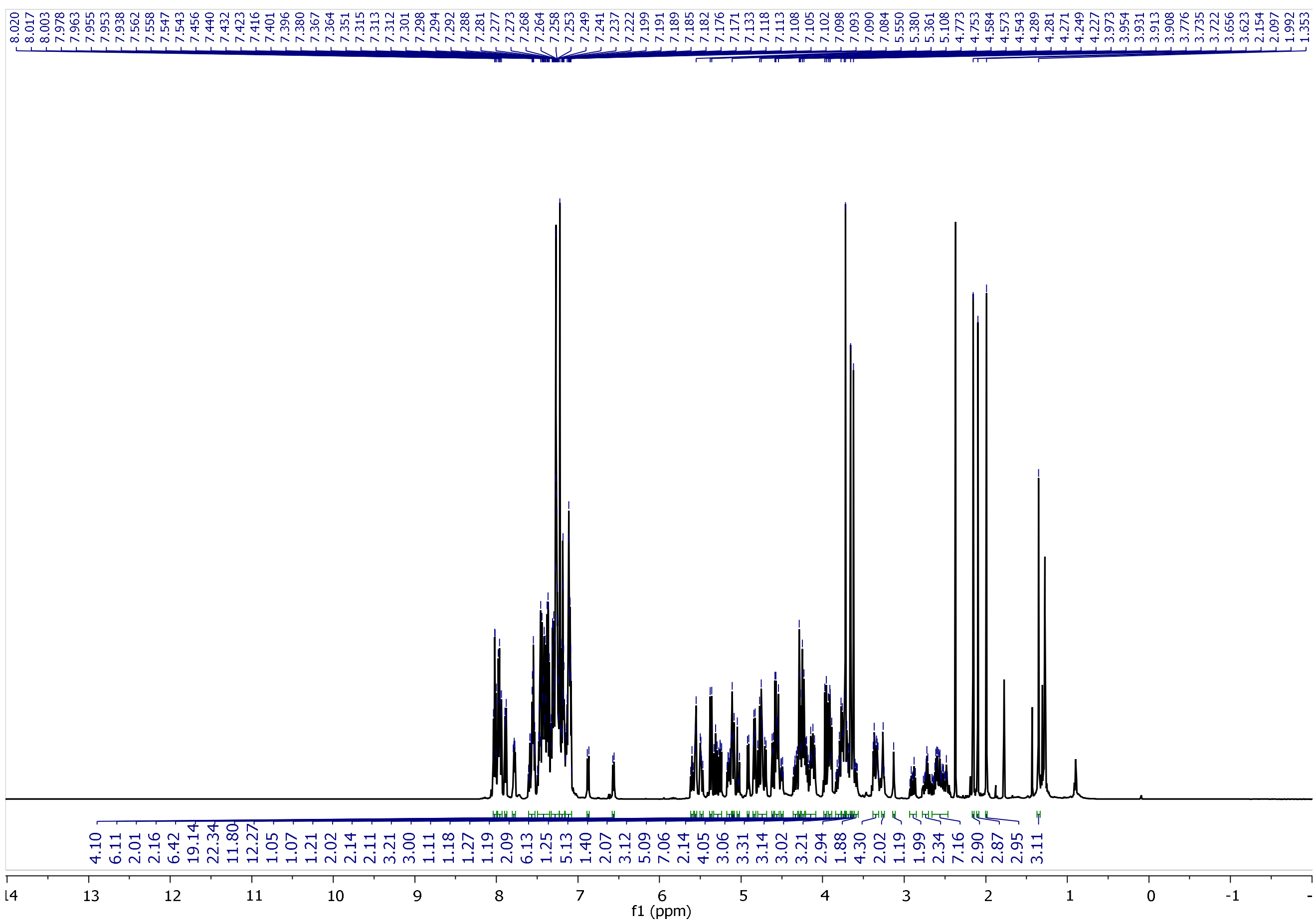
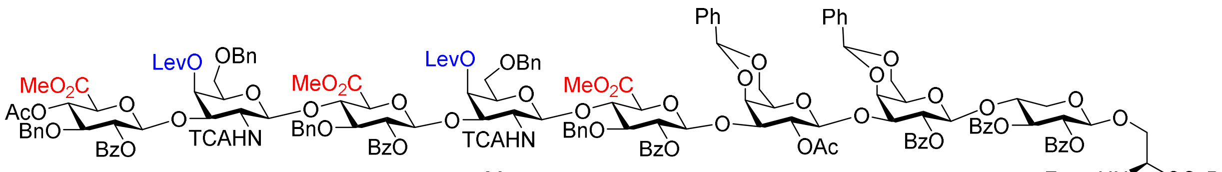


^{13}C-NMR ($CDCl_3$, 126 MHz) of **26**



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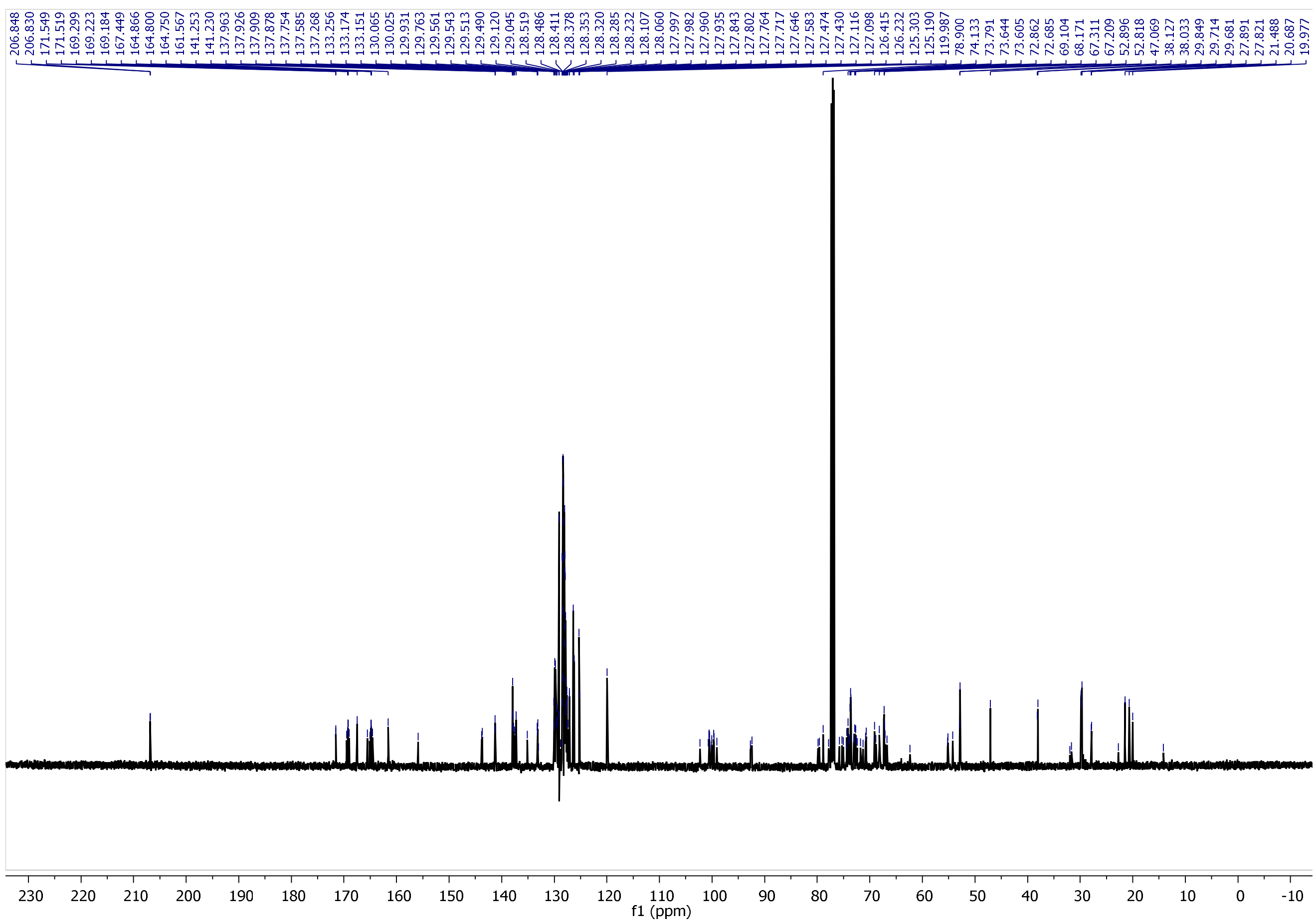
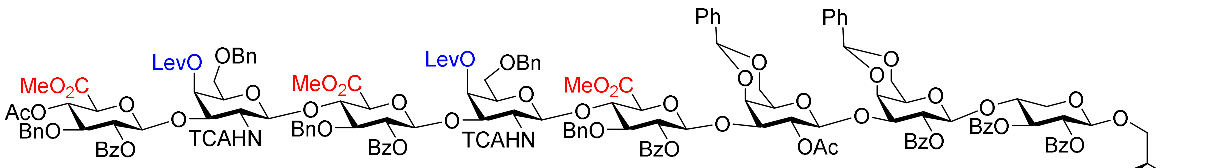


gCOSY ($CDCl_3$, 500 MHz) of **26**



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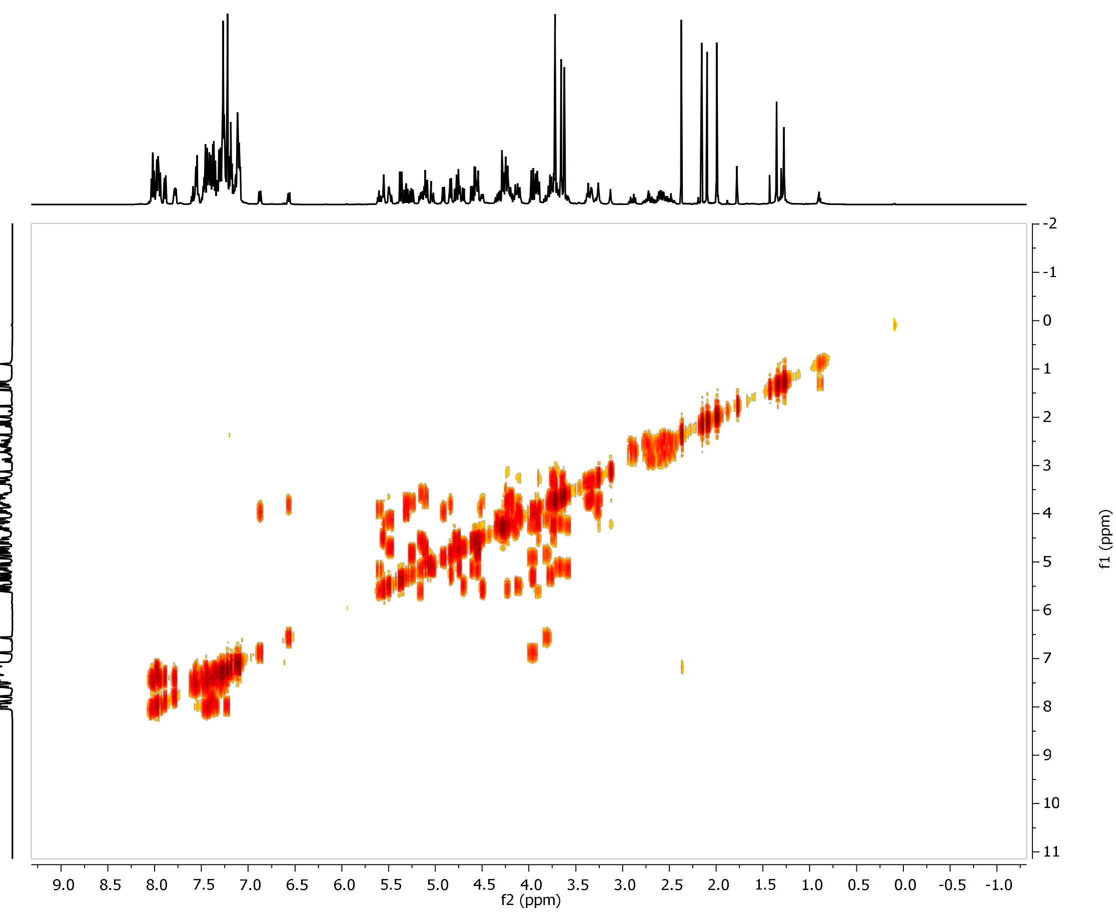
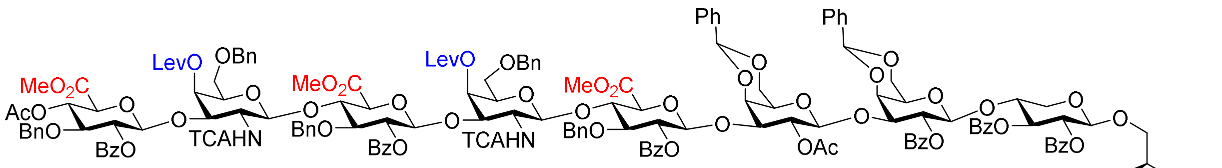


gHMBC (CDCl$_3$, 500 MHz) of **26**



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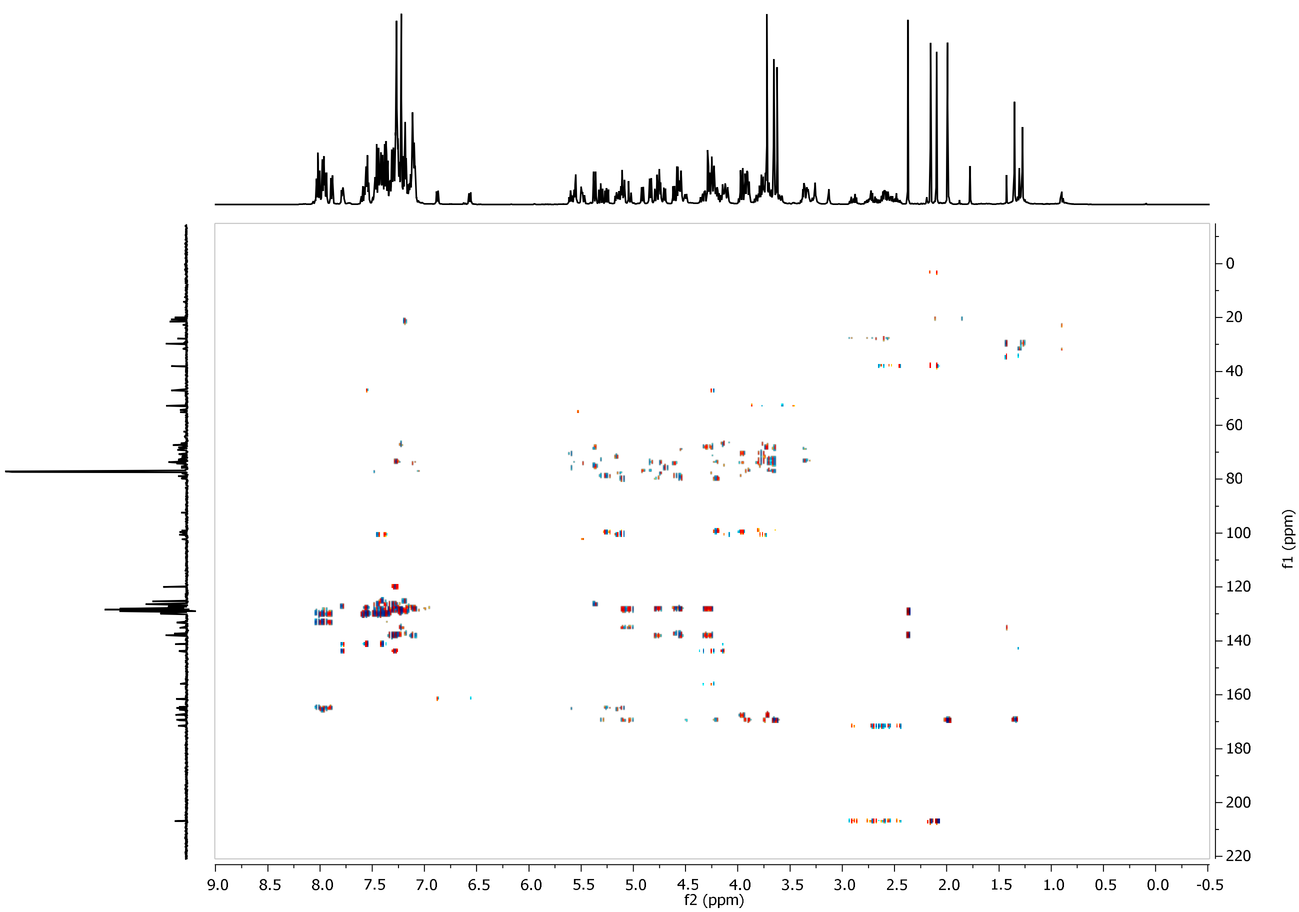
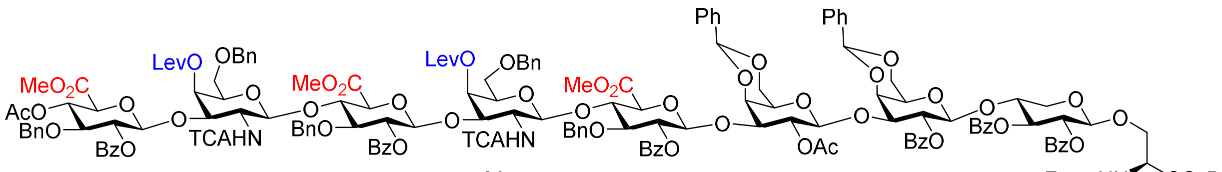


bsgHSQC ($CDCl_3$, 500 MHz) of **26**



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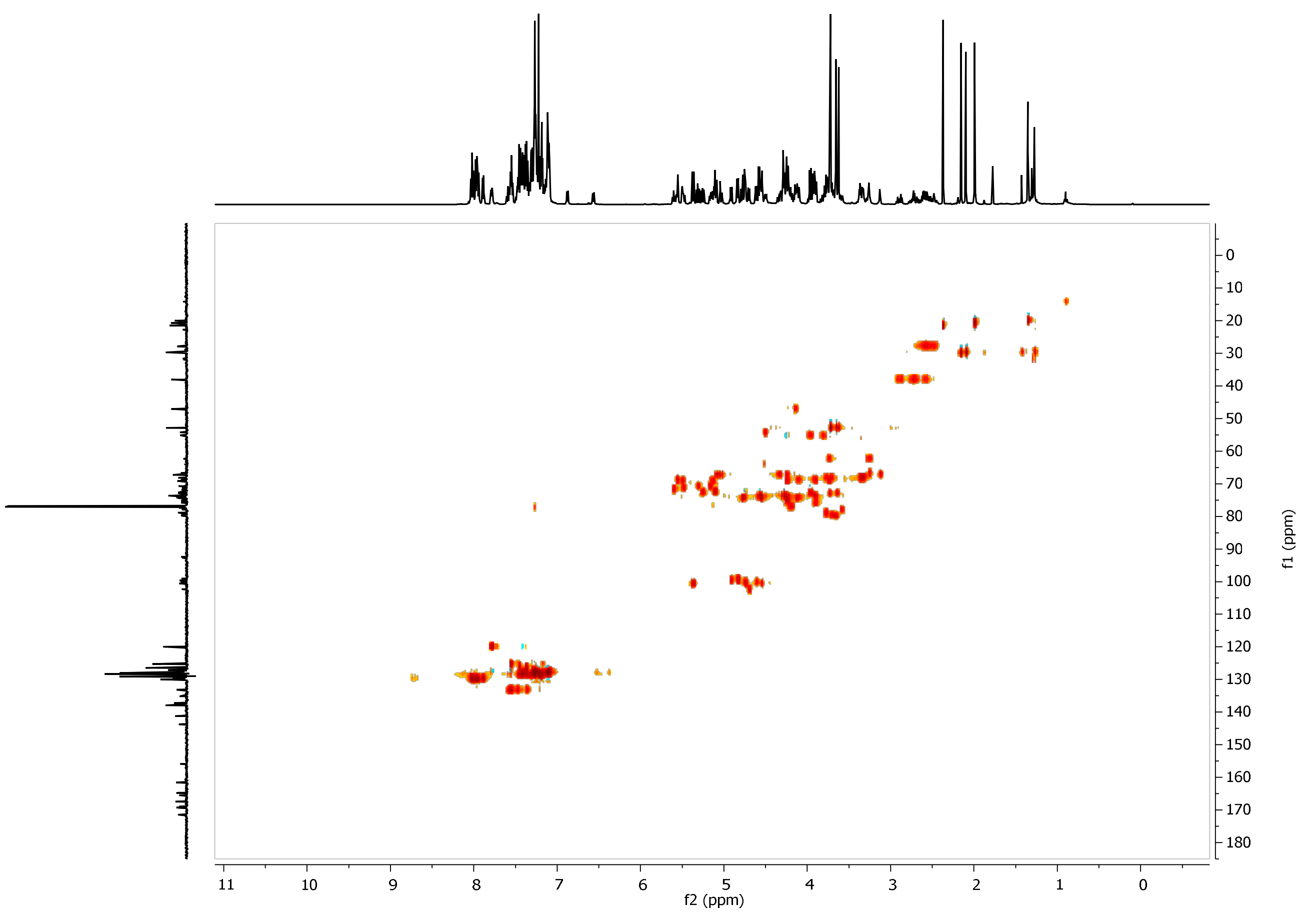
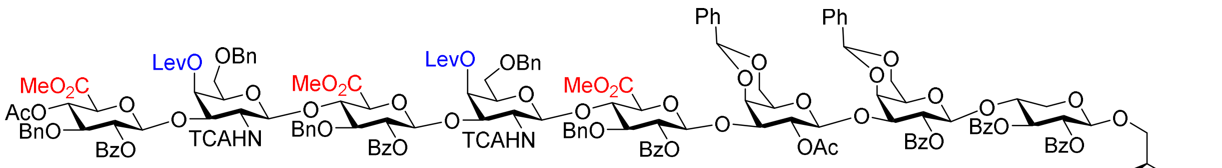


gHSQC ($CDCl_3$, 500 MHz) of **26**



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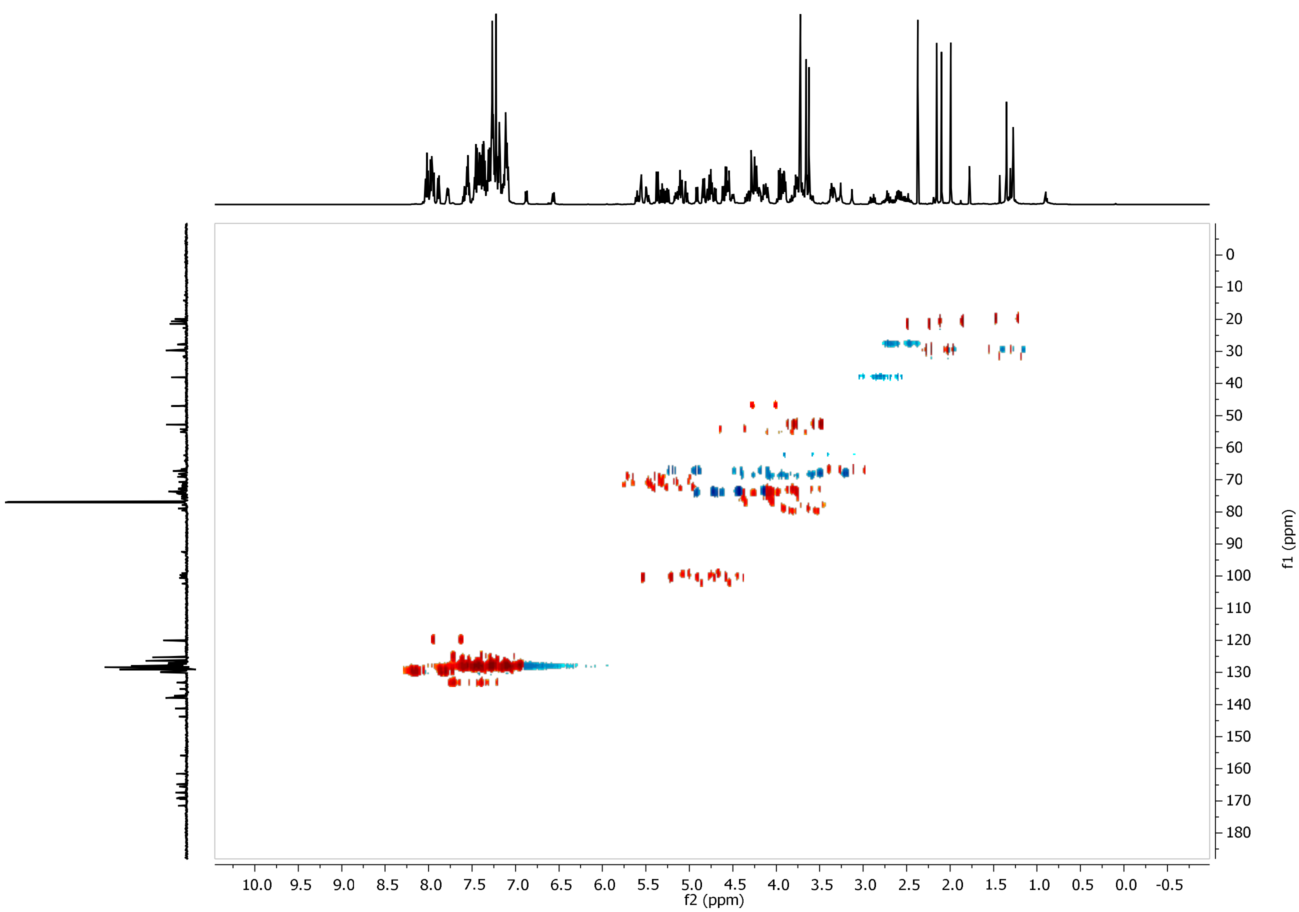
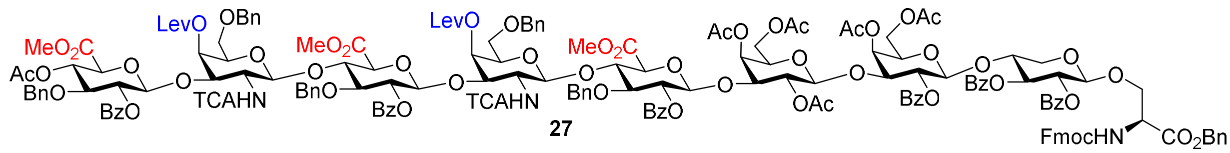


^{1}H-NMR ($CDCl_3$, 500 MHz) of **27**



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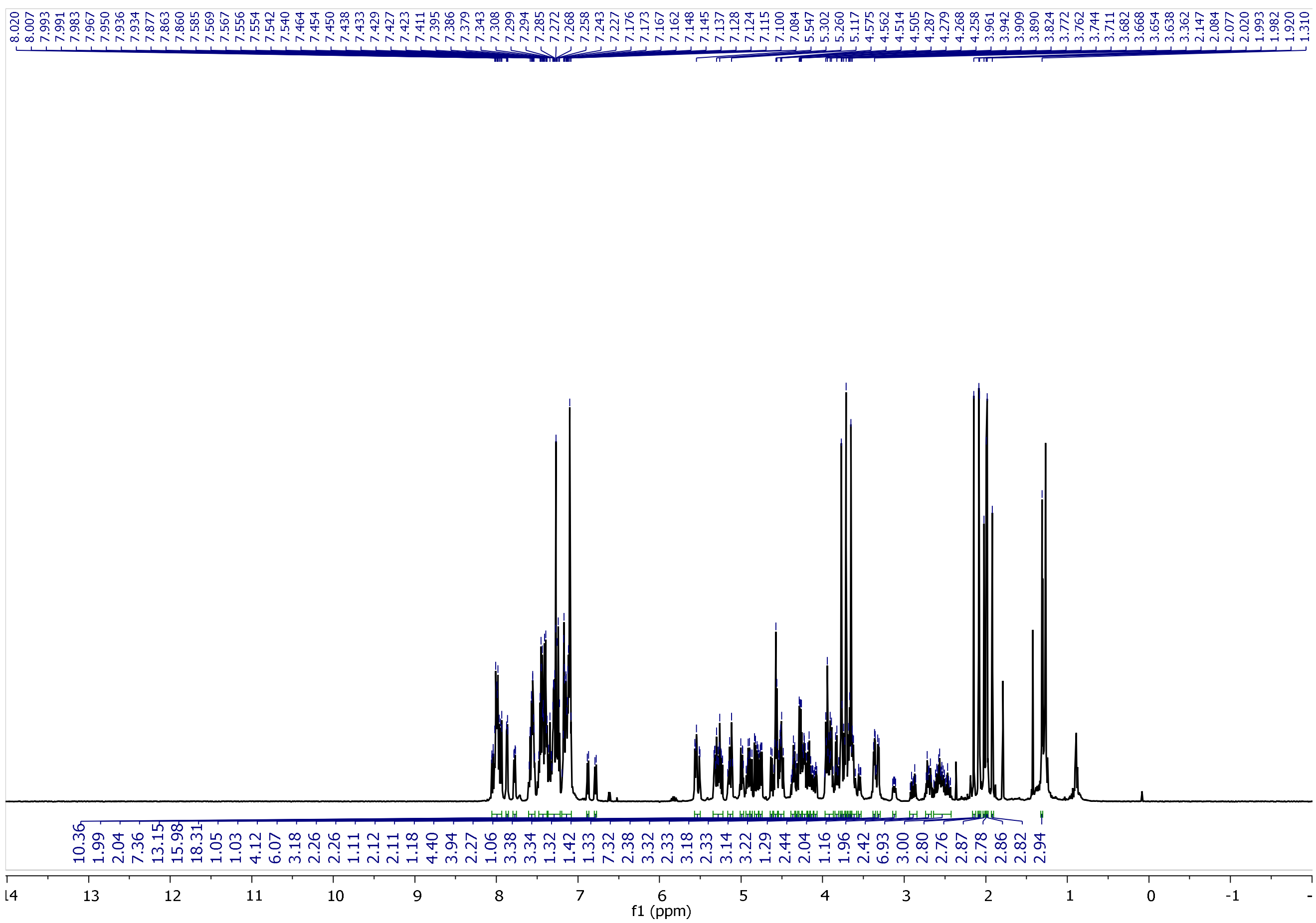
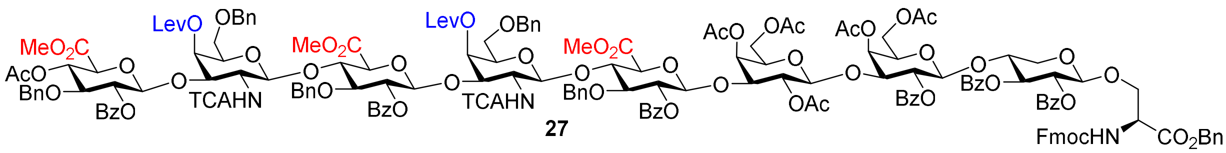


^{13}C-NMR ($CDCl_3$, 126 MHz) of **27**



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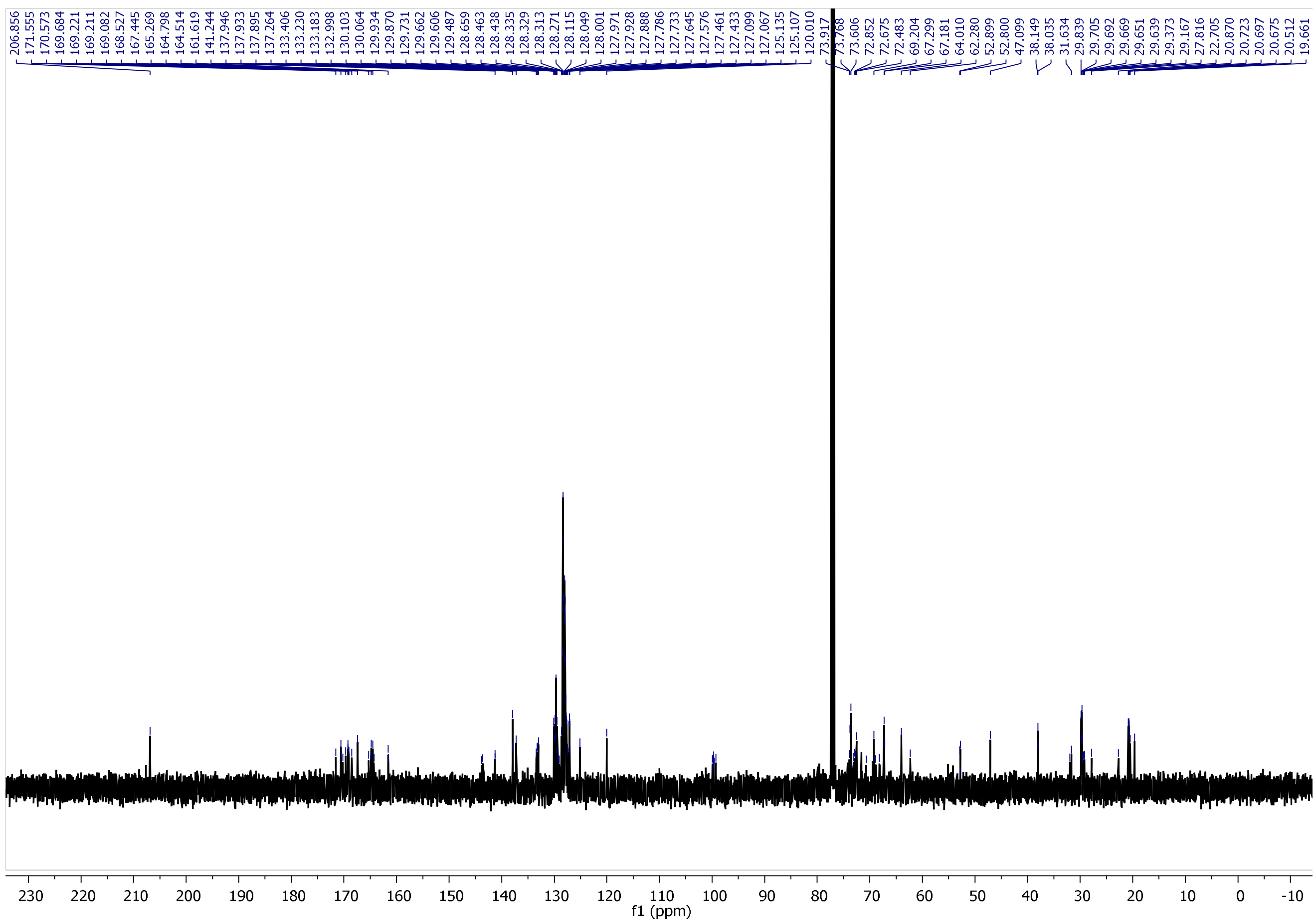
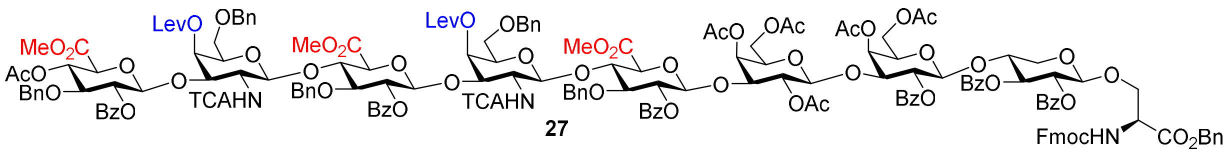
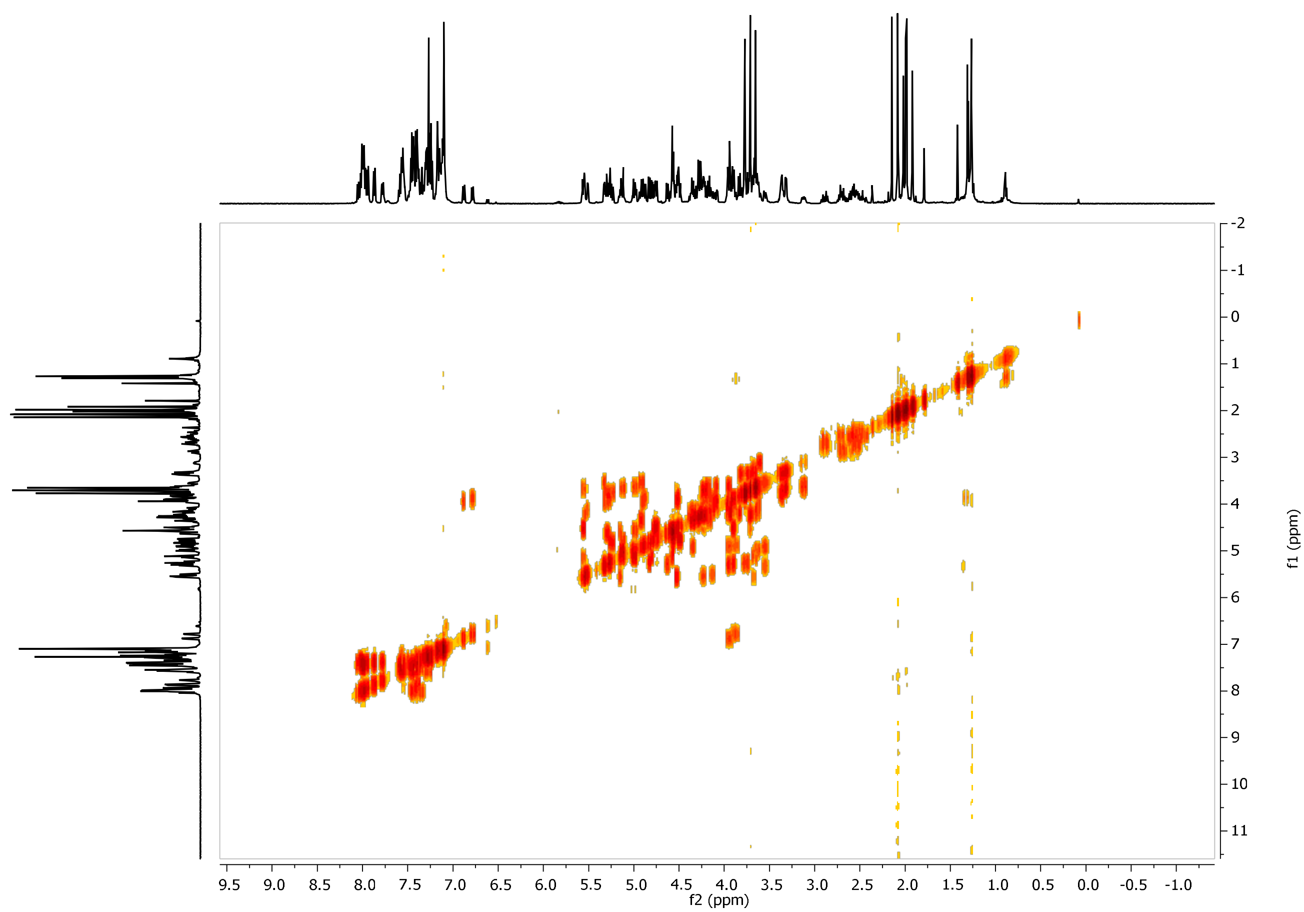
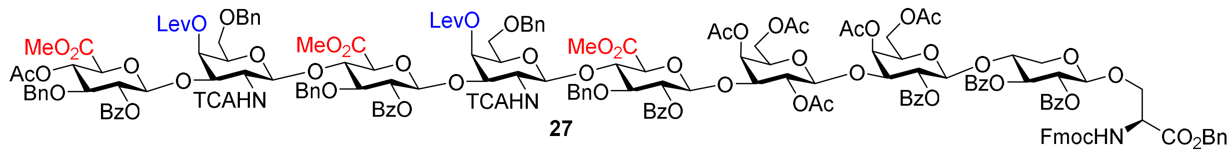


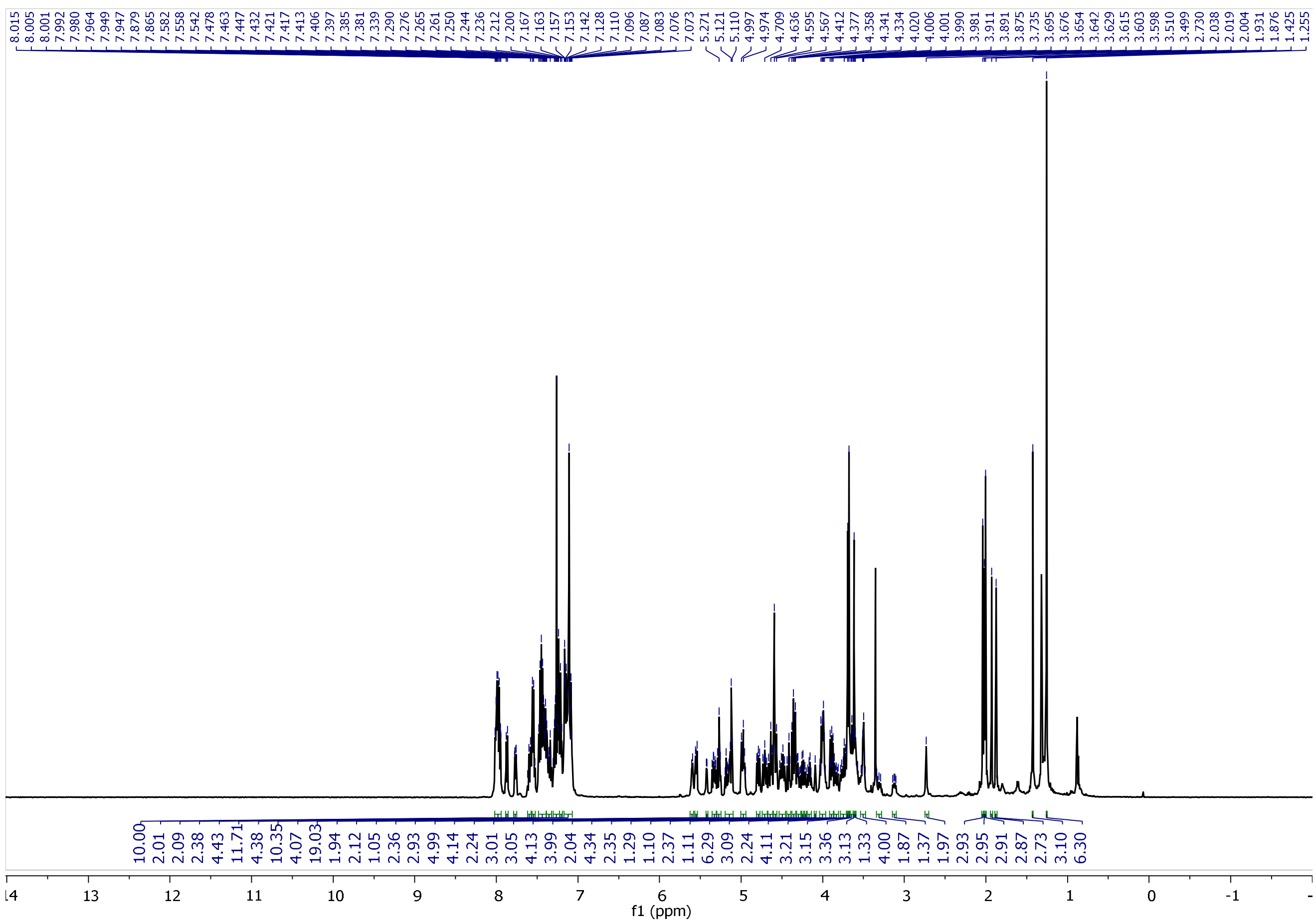
gCOSY ($CDCl_3$, 500 MHz) of **27**



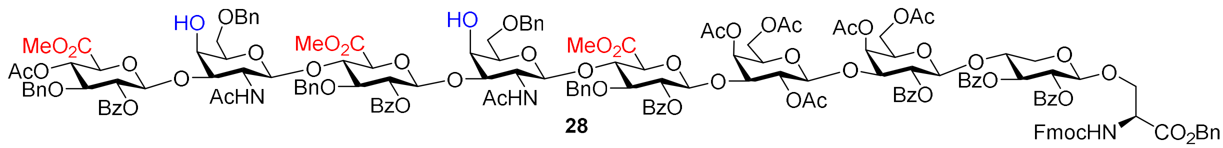


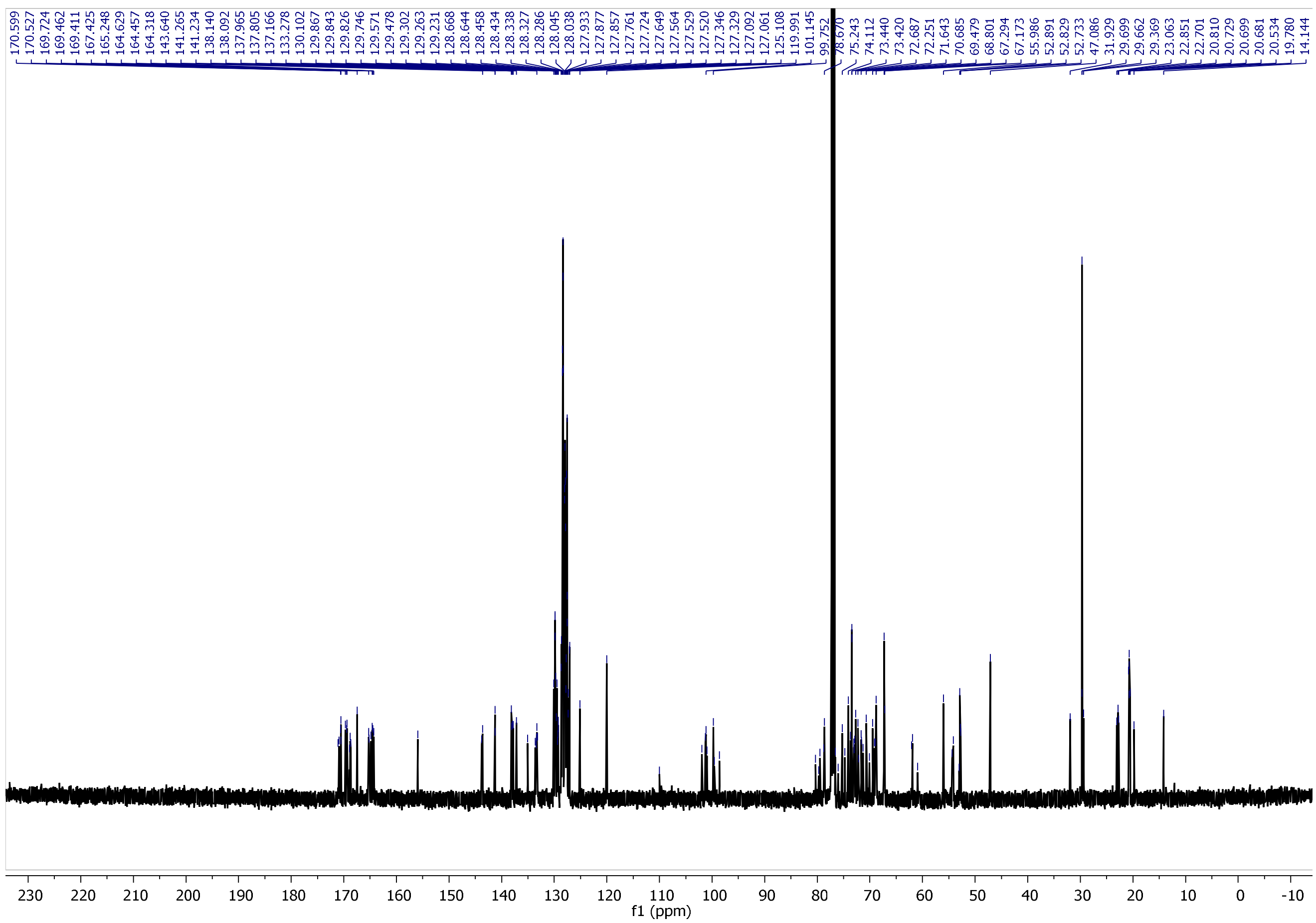
^{1}H-NMR ($CDCl_3$, 500 MHz) of **28**



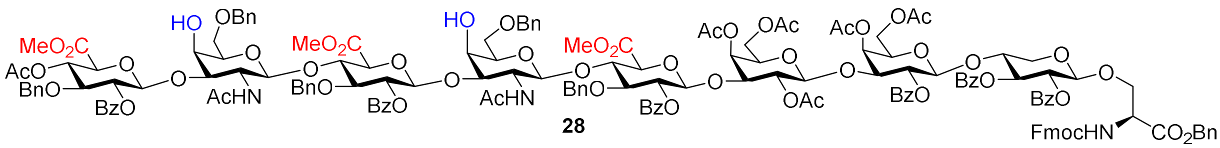


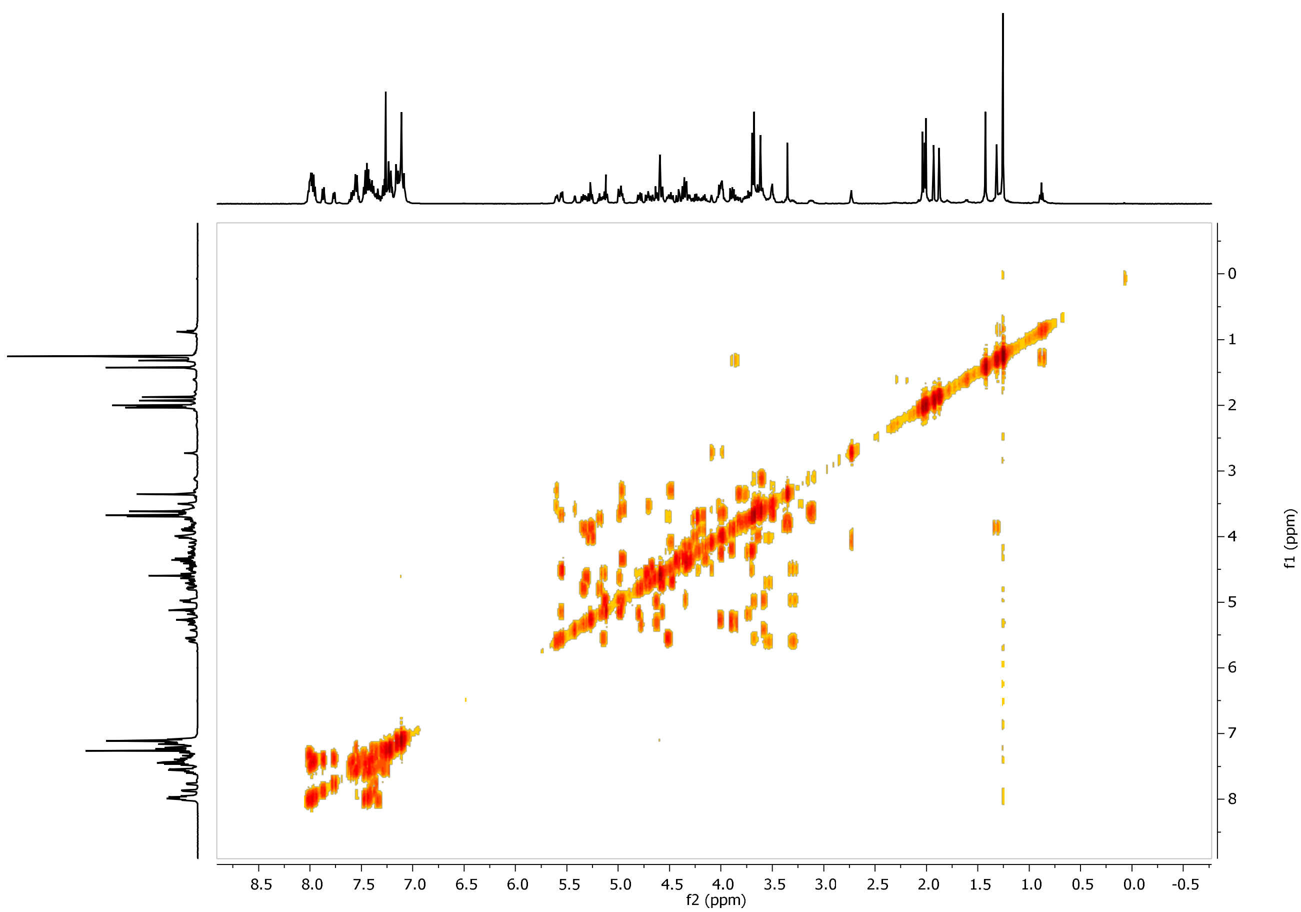
^{13}C-NMR ($CDCl_3$, 126 MHz) of **28**



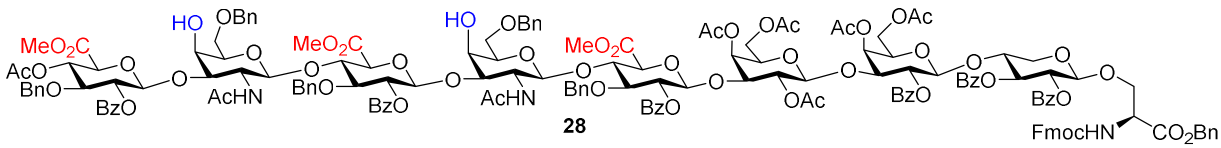


gCOSY ($CDCl_3$, 500 MHz) of **28**





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



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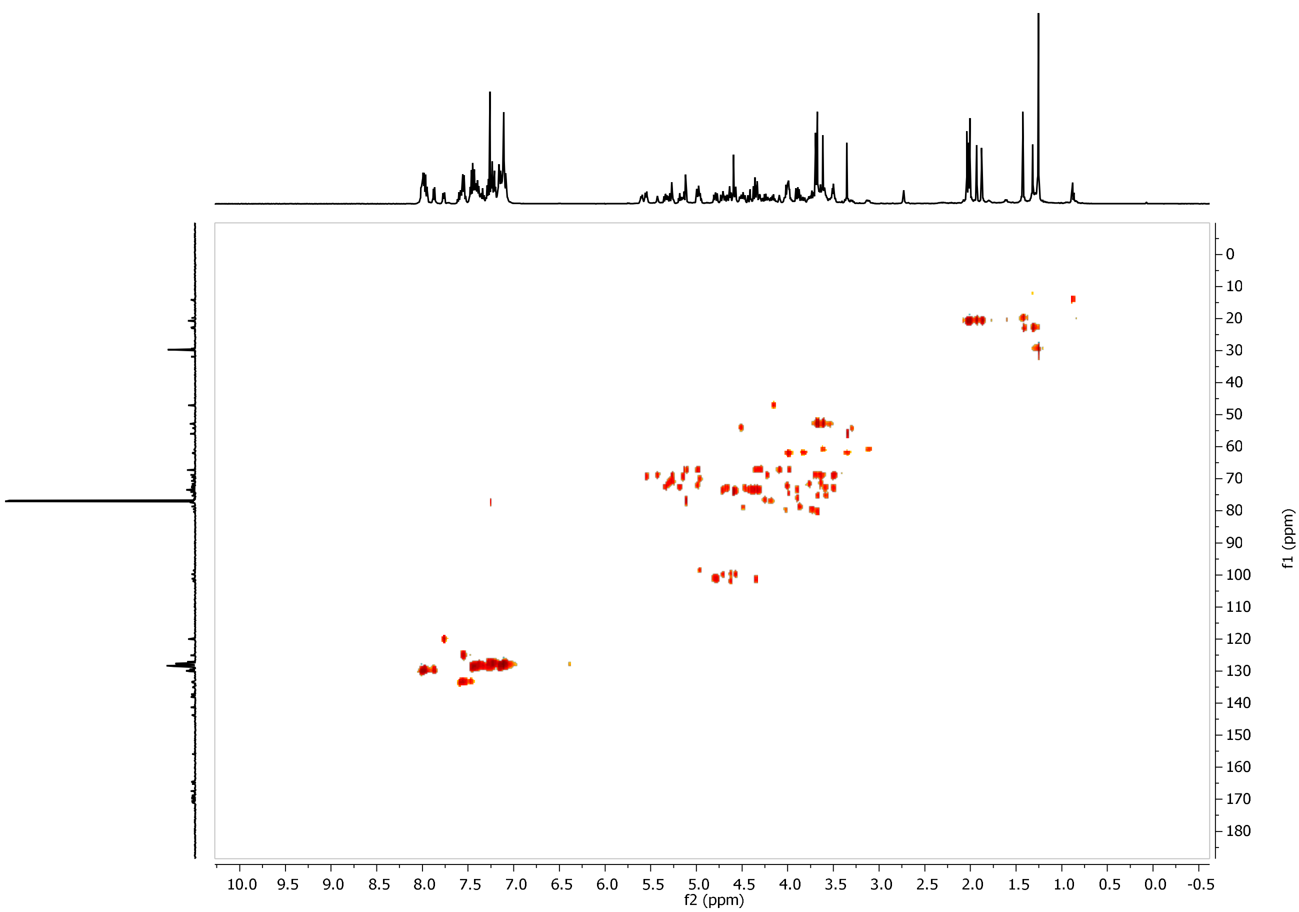
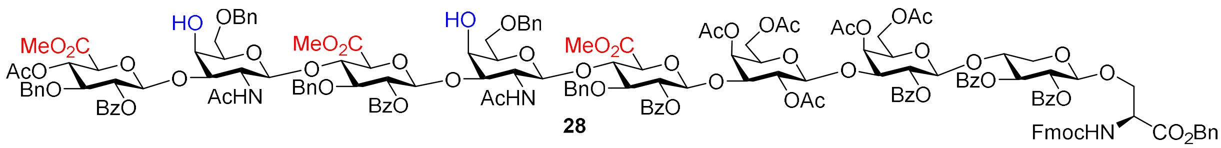


gHSQC ($CDCl_3$, 500 MHz) of **28**



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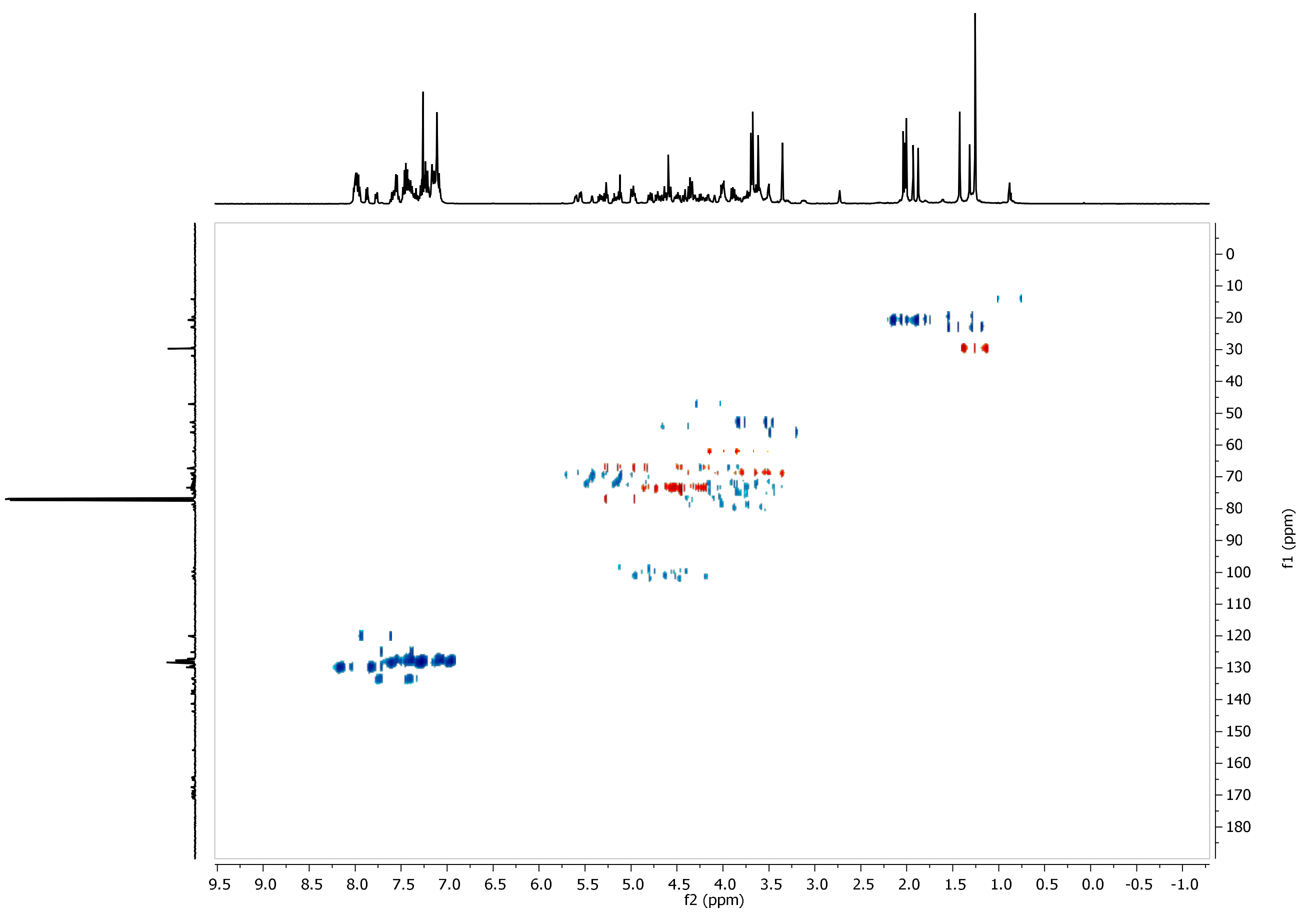
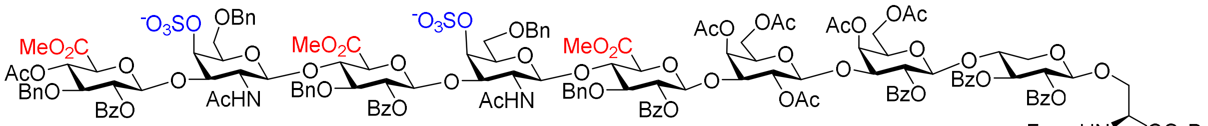


^{1}H-NMR ($CDCl_3$, 500 MHz) of **29**



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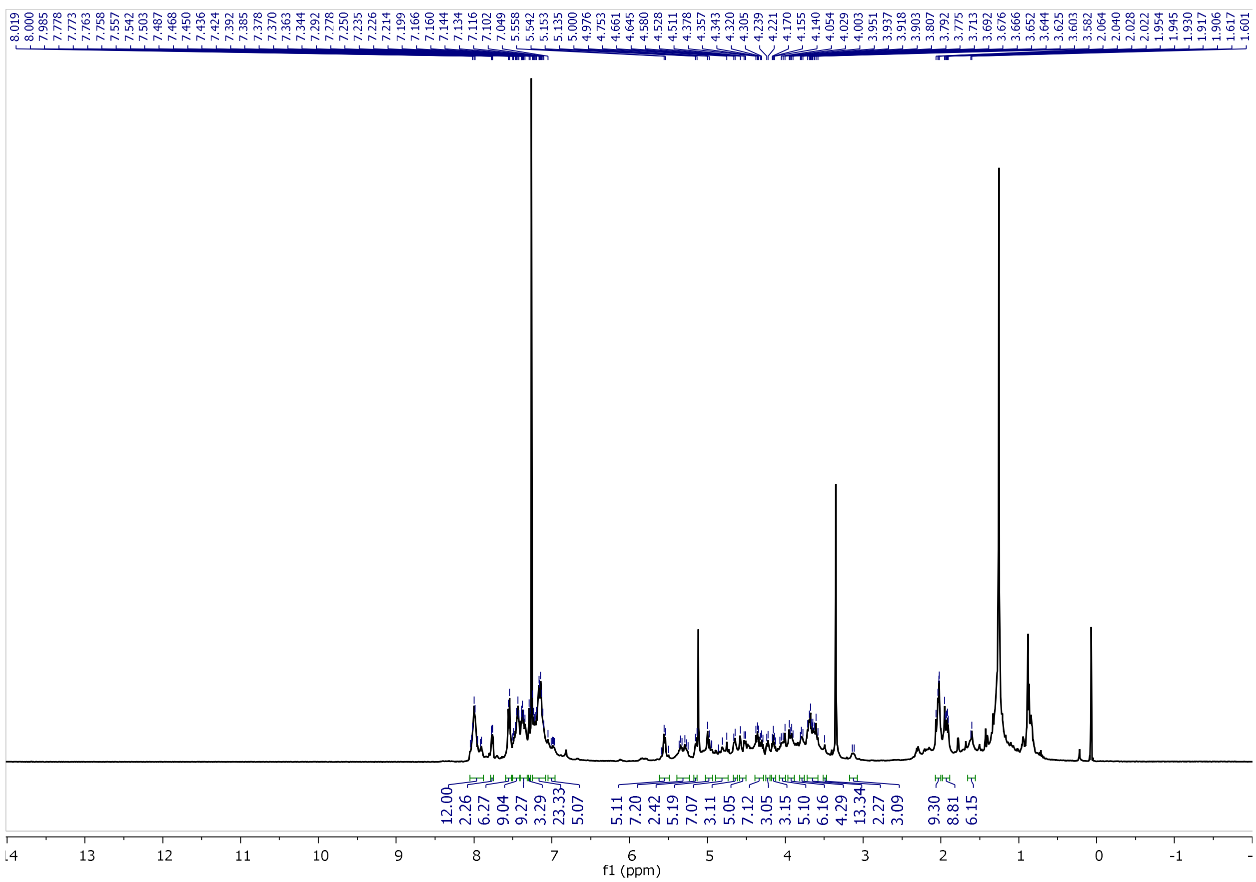
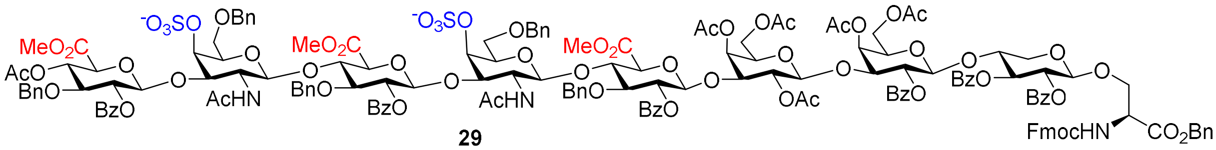


^{13}C-NMR ($CDCl_3$, 126 MHz) of **29**



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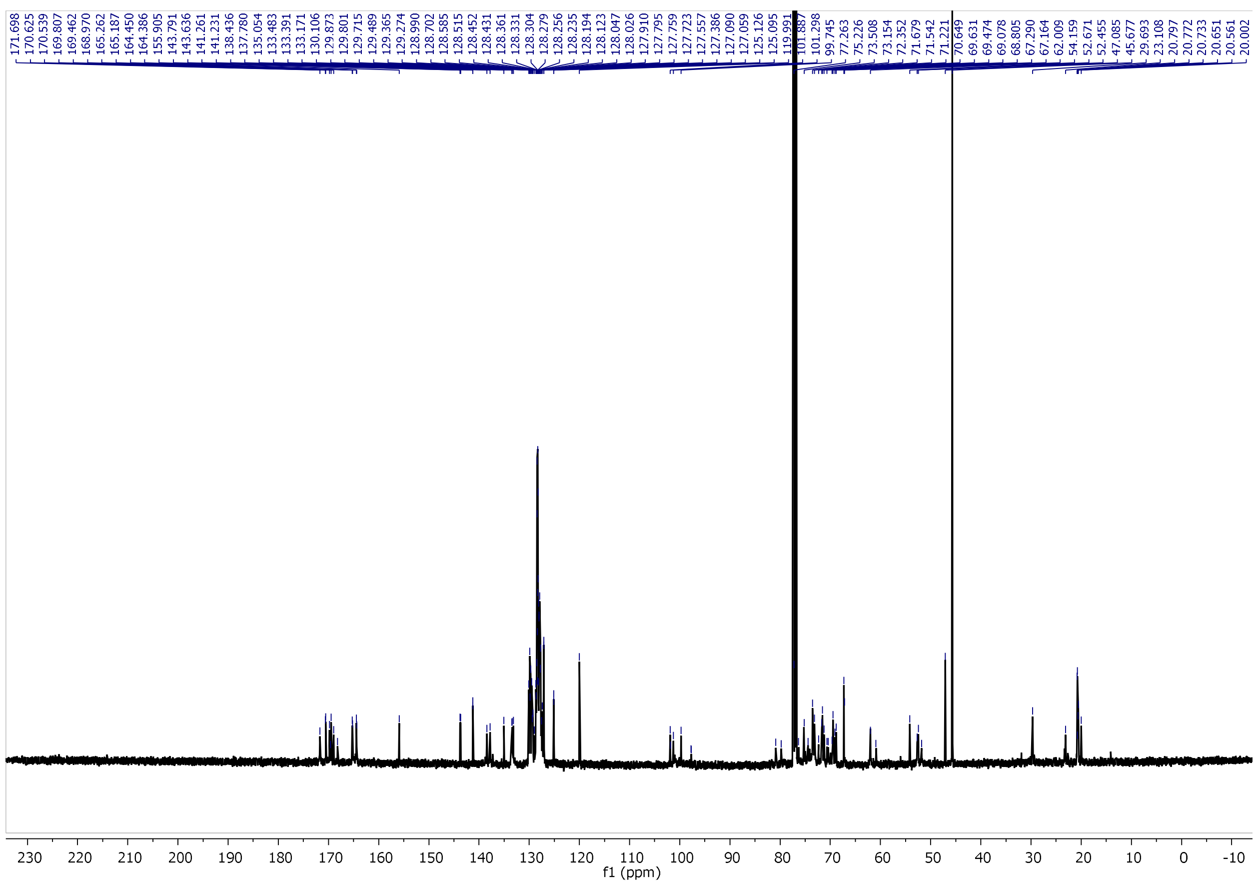
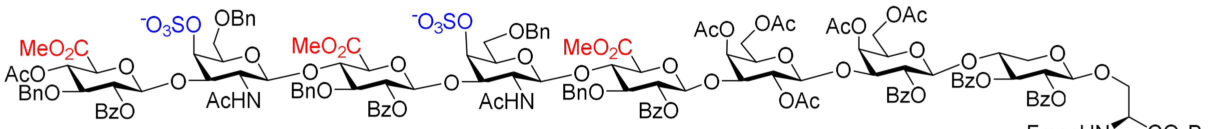


gCOSY ($CDCl_3$, 500 MHz) of **29**



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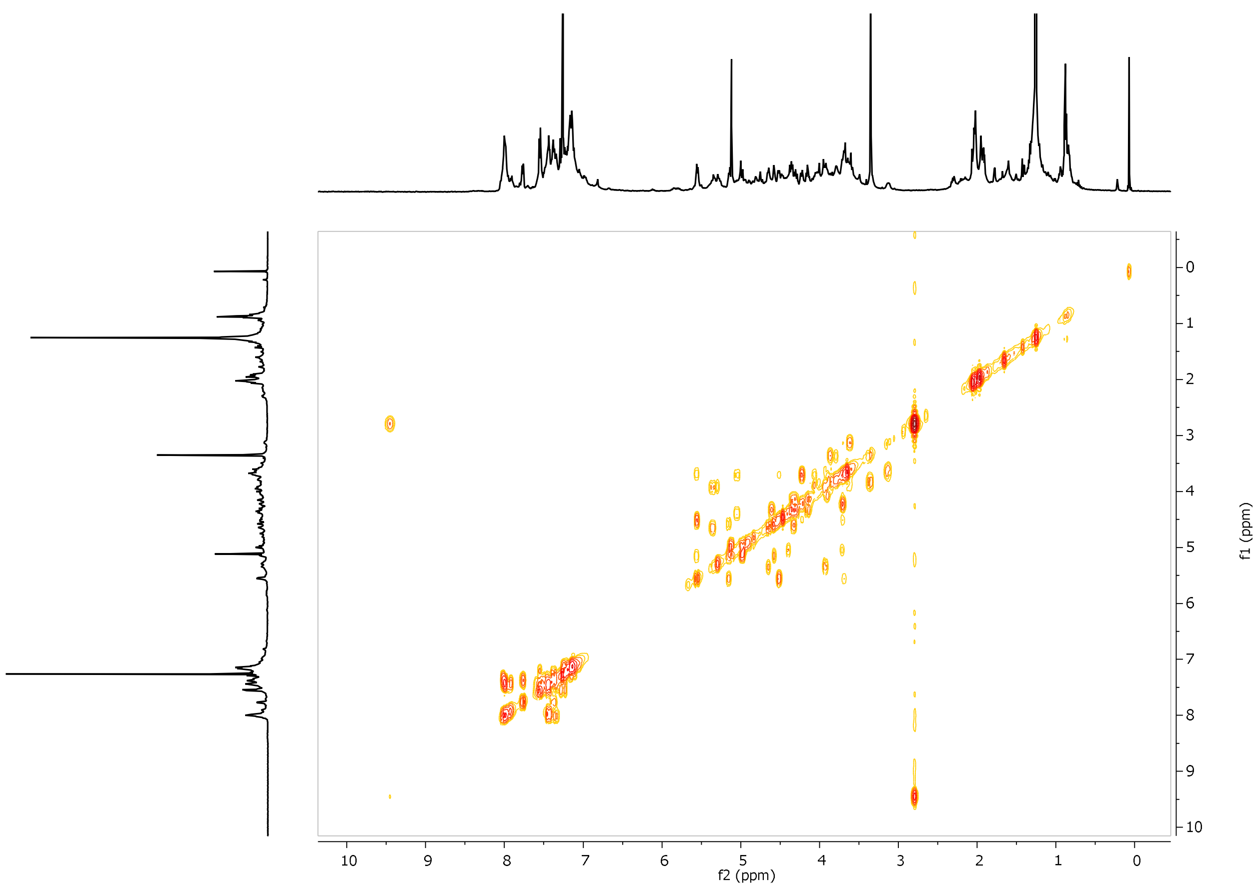
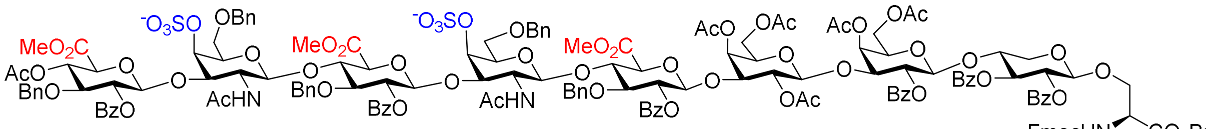


bsgHSQC ($CDCl_3$, 500 MHz) of **29**



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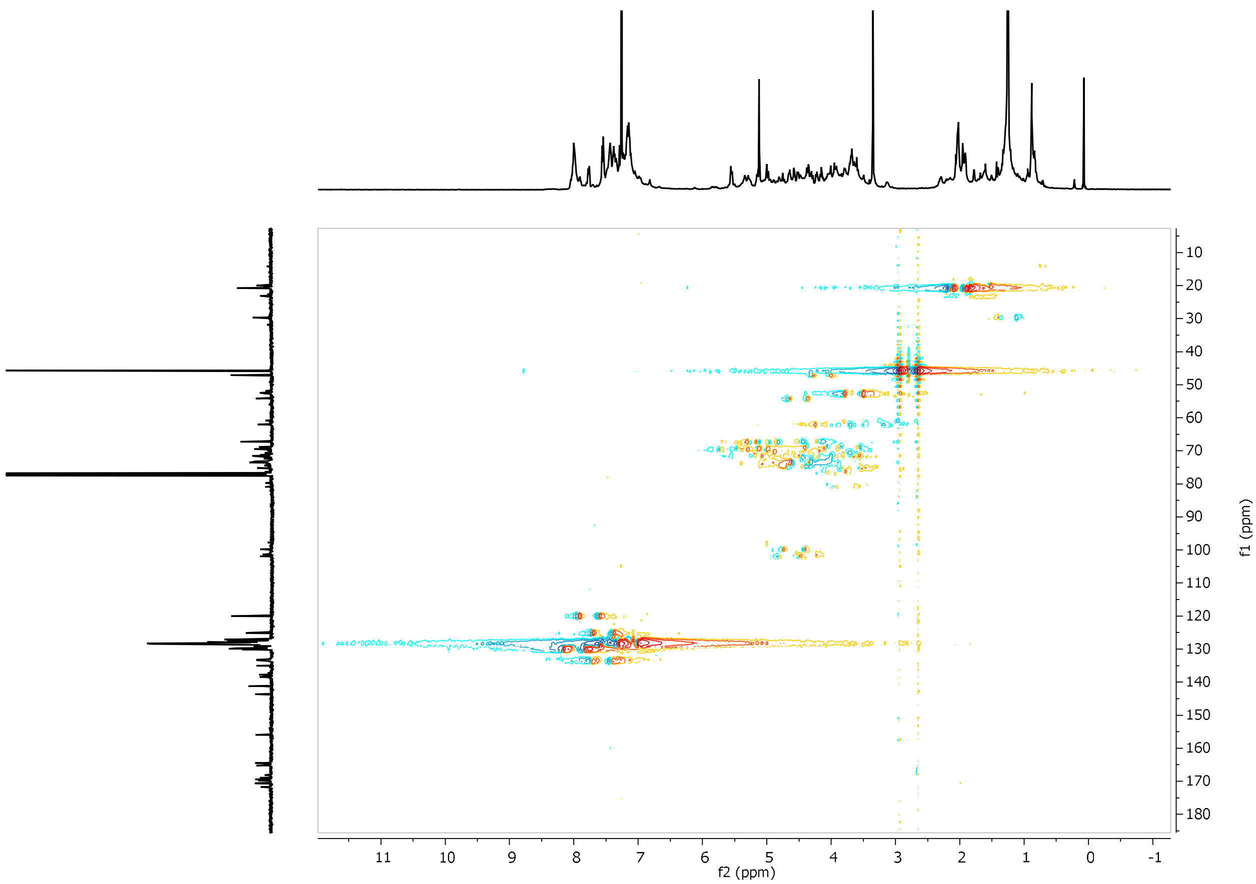
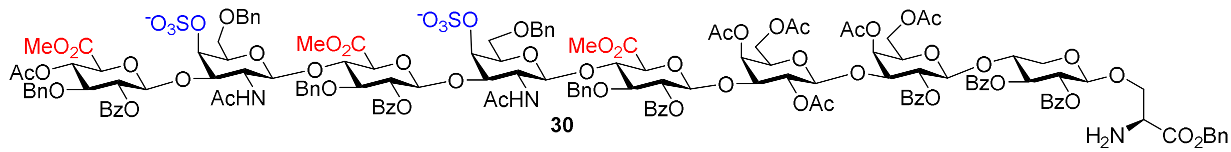


[1]H-NMR (CDCl3, 500 MHz) of **30**



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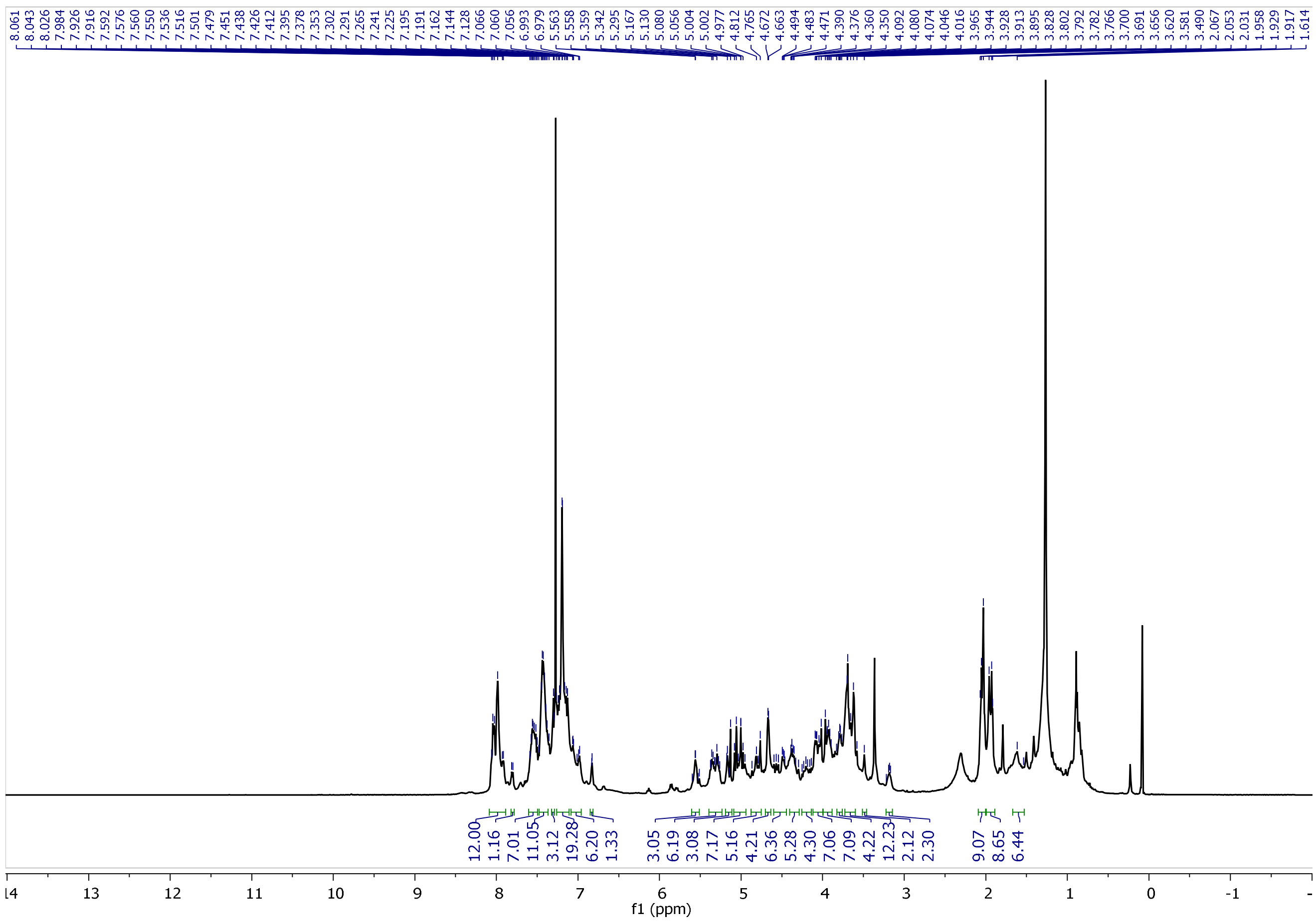
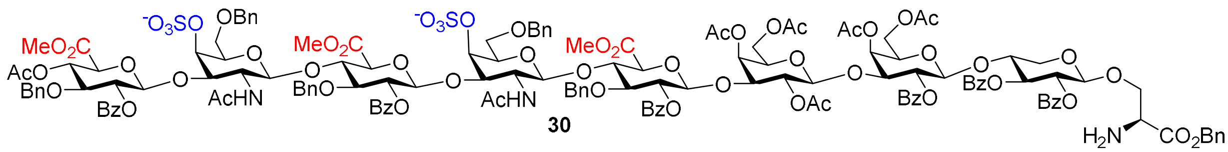
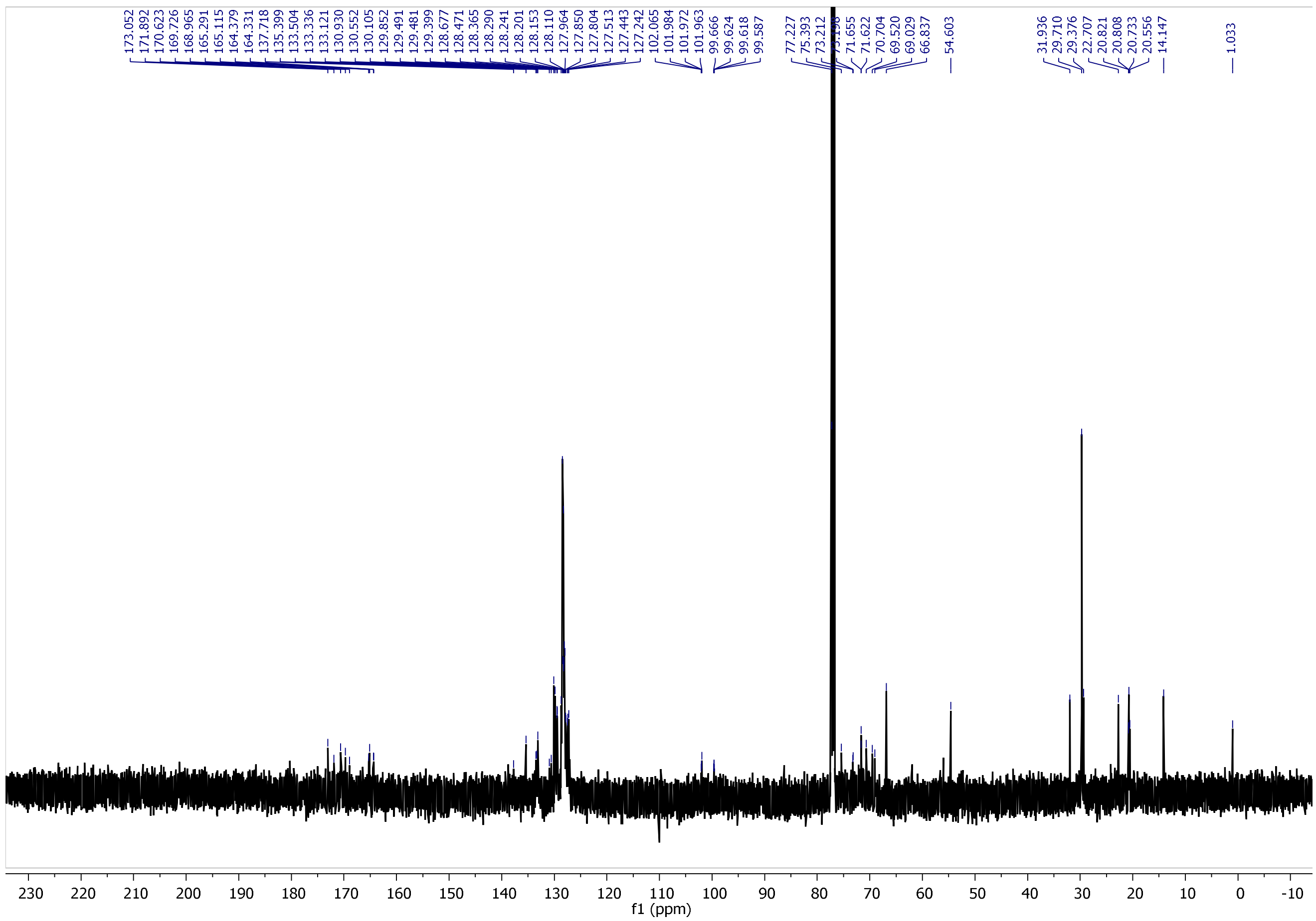
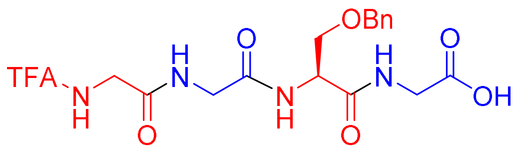


^{13}C-NMR ($CDCl_3$, 126 MHz) of **30**





HPLC Chromatogram of peptide **31**



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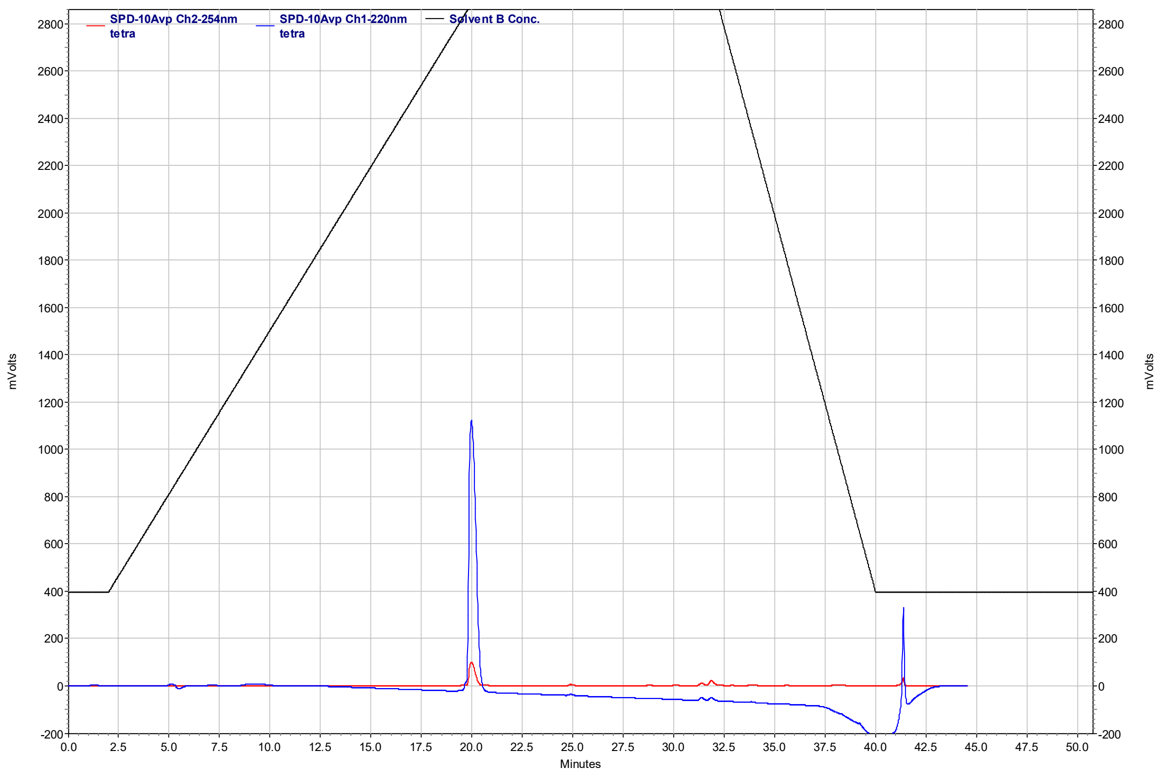
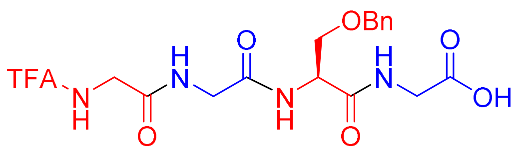


[1]H-NMR (CD_3OD, 500 MHz) of **31**



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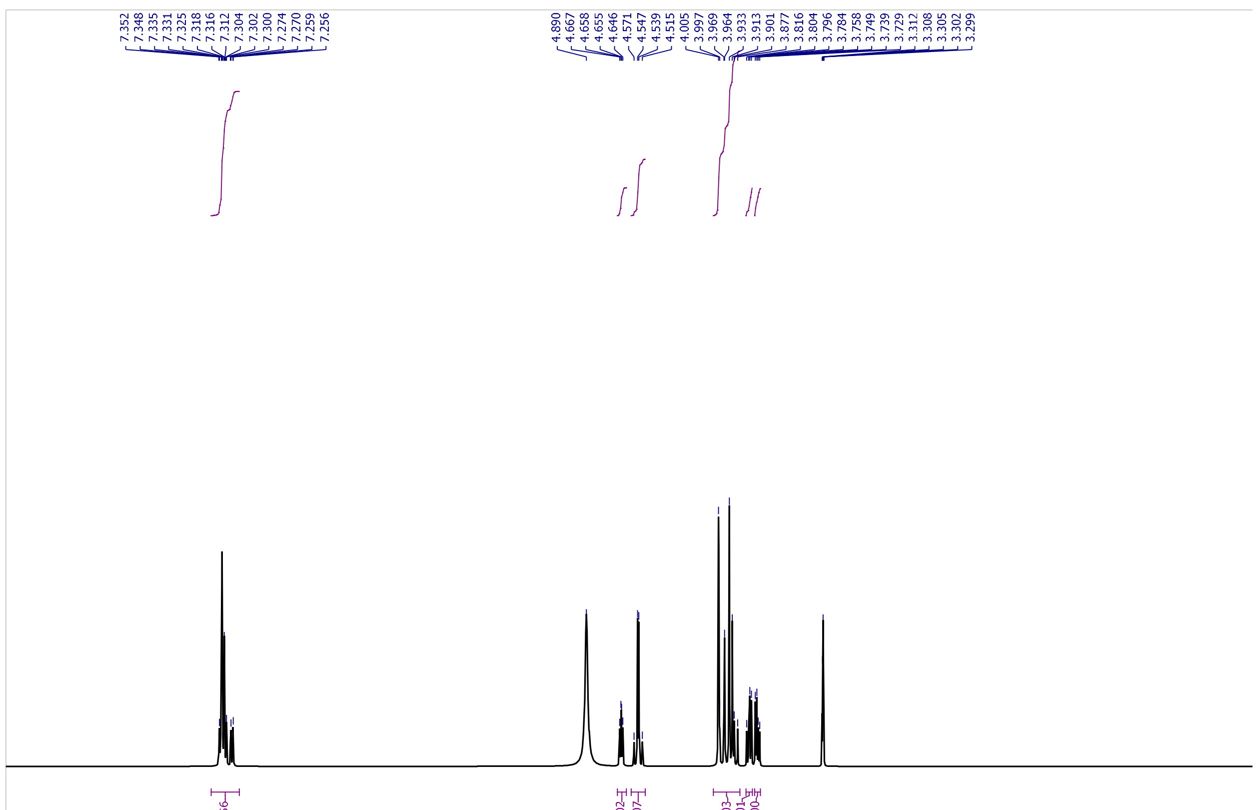
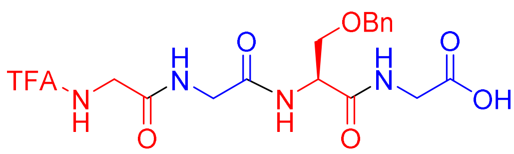


^{13}C-NMR (CD_3OD, 126 MHz) of **31**



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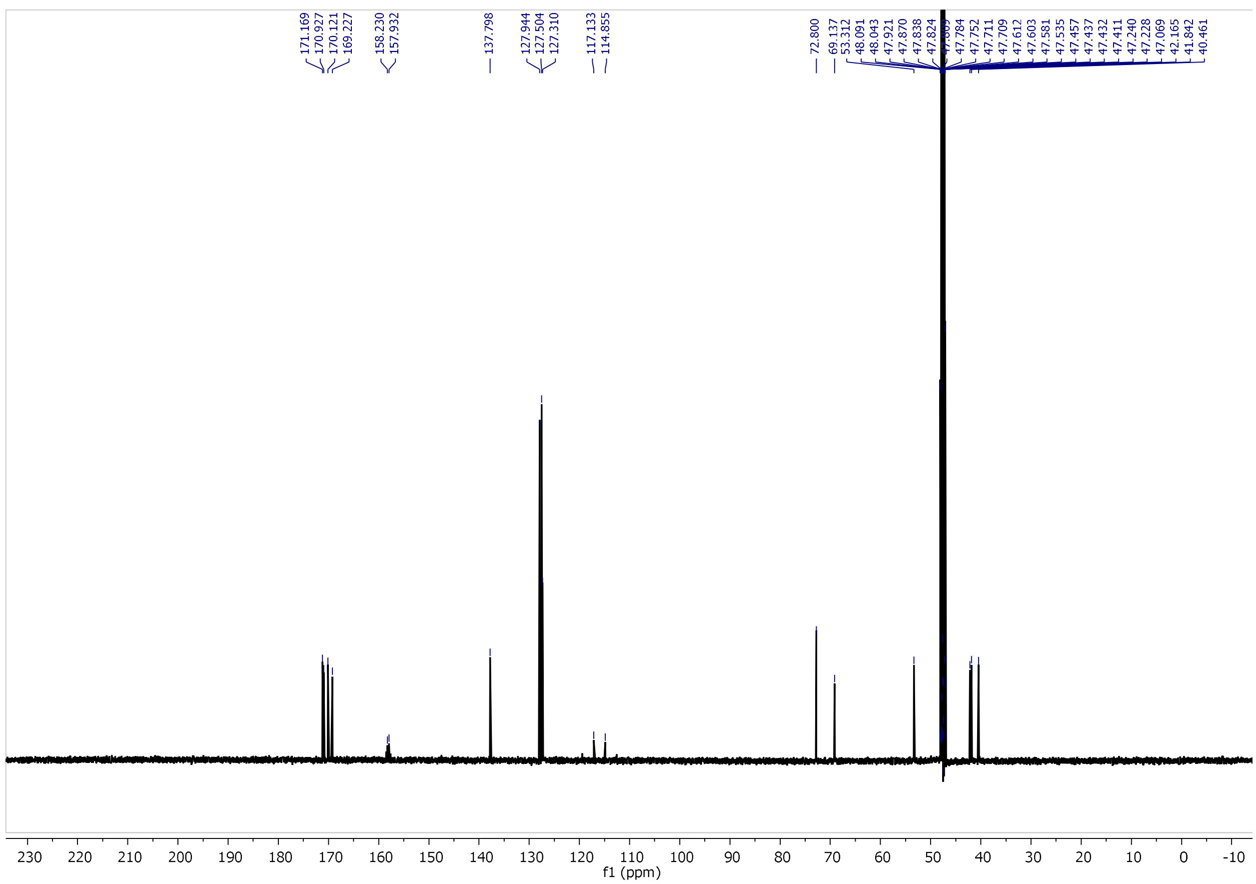
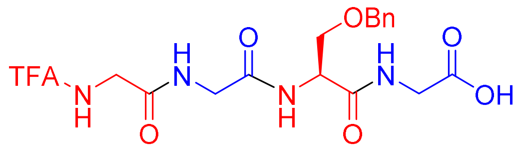


gCOSY (CD_3OD, 500 MHz) of **31**



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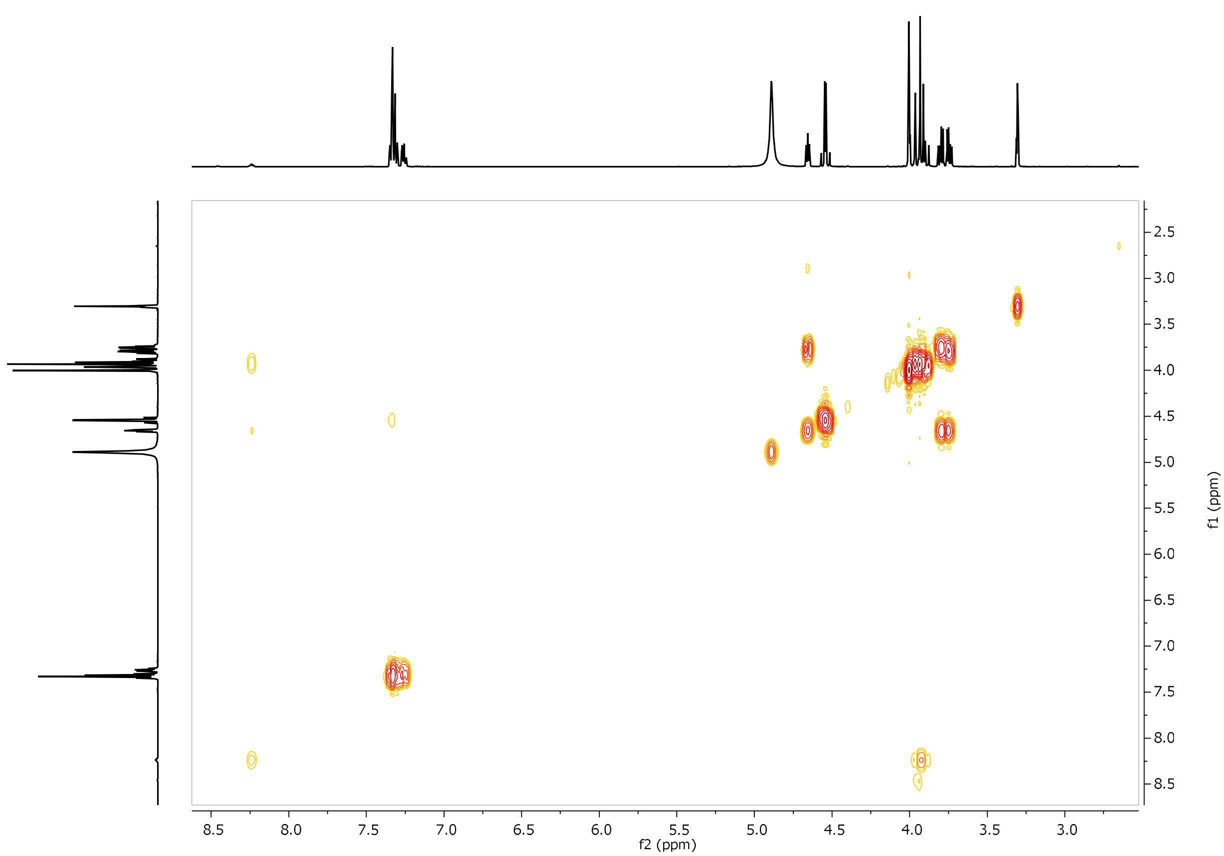
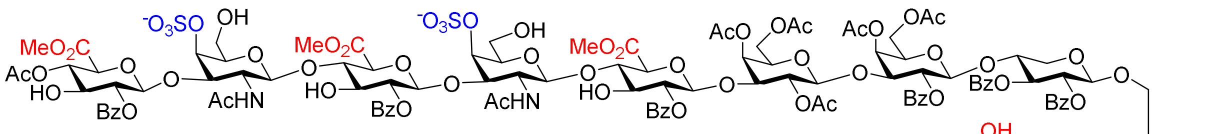


[1]H-NMR (CD_3OD, 500 MHz) of **32**



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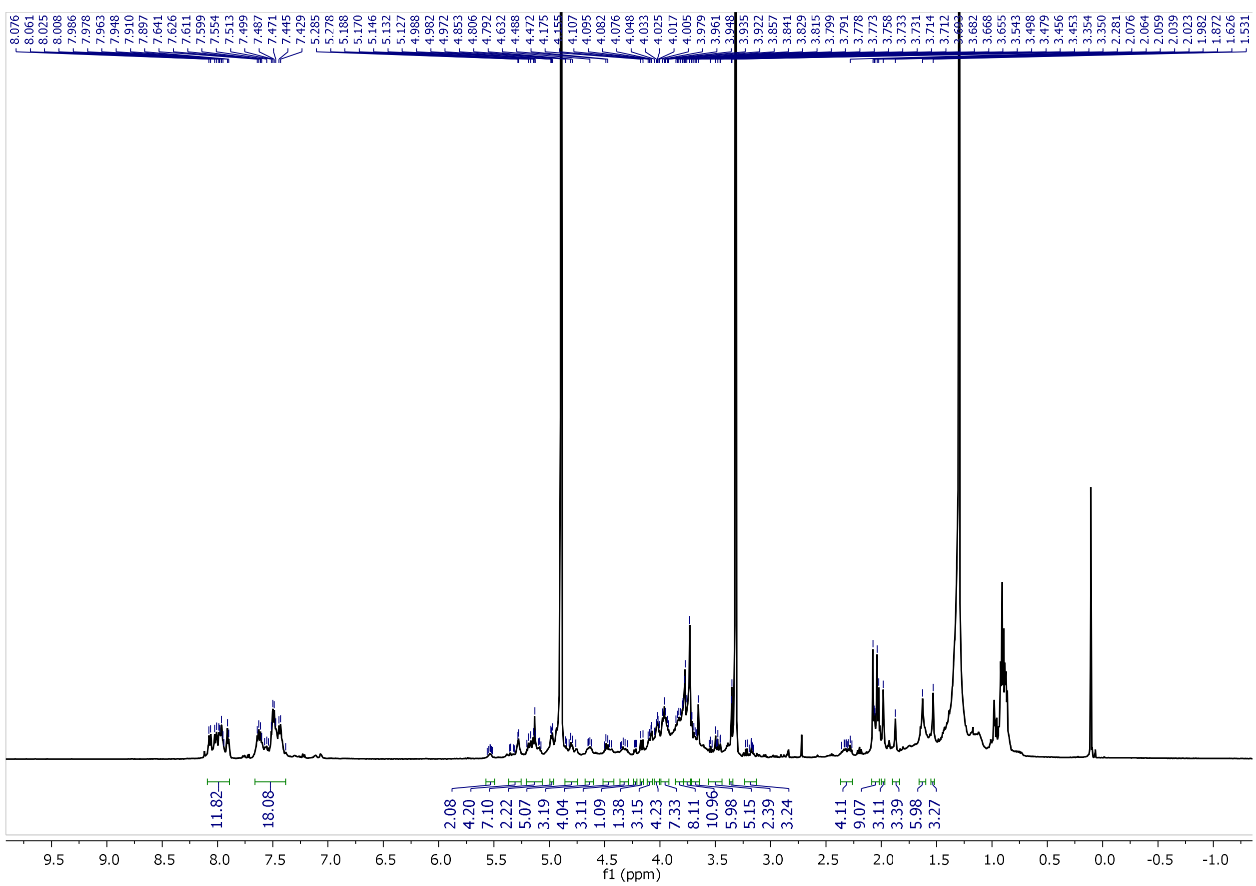
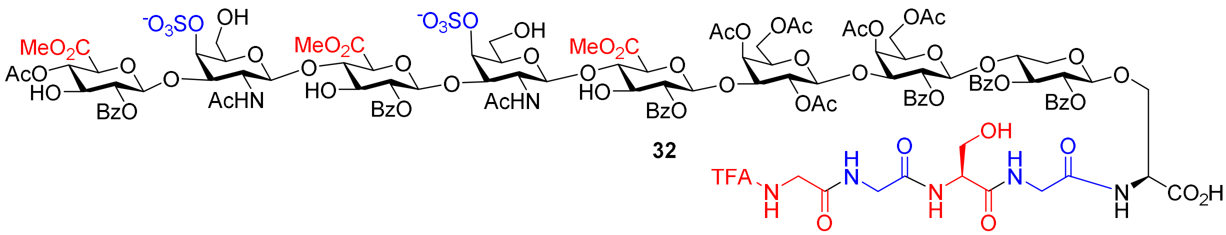


^{13}C-NMR (CD_3OD, 126 MHz) of **32**



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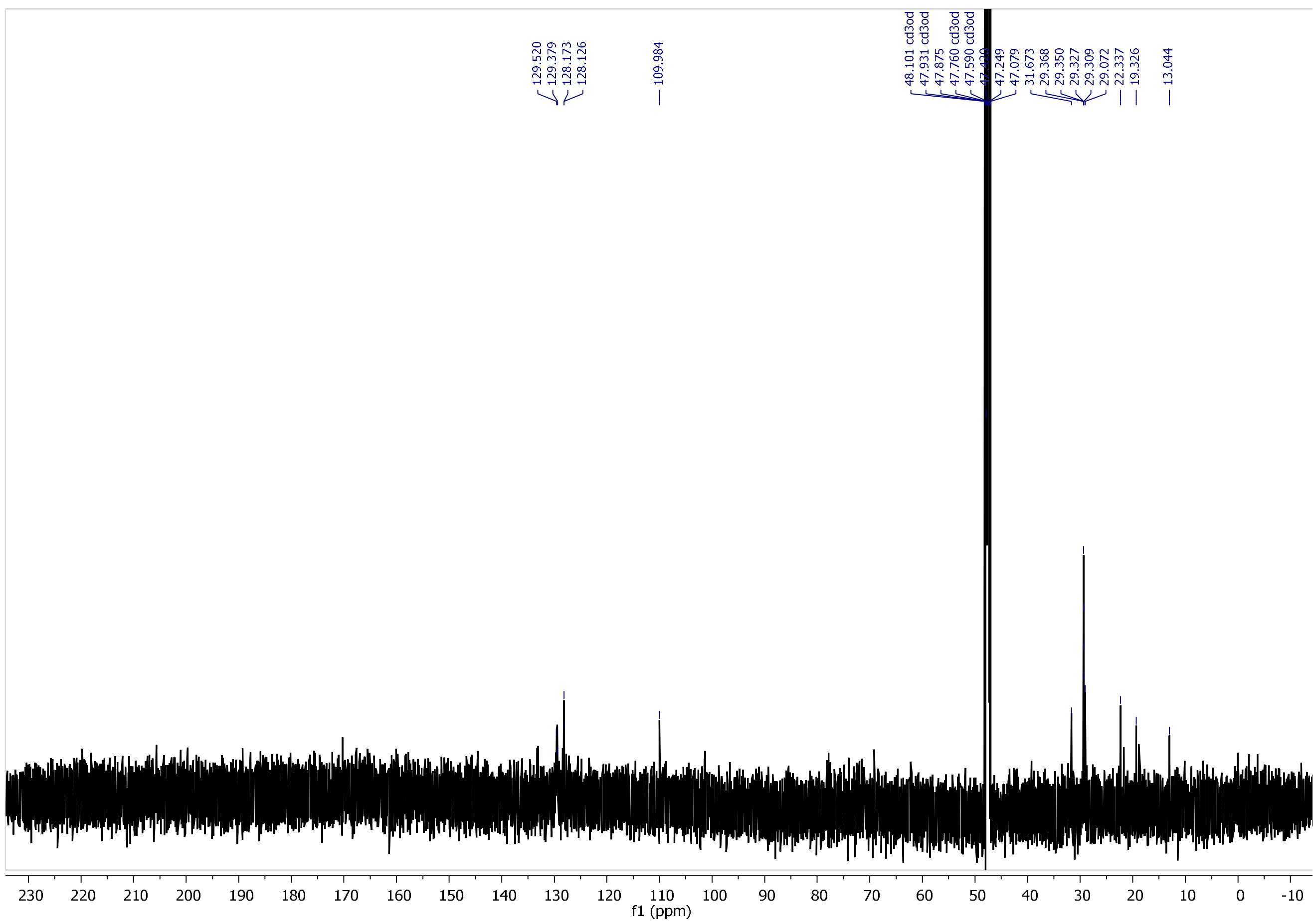
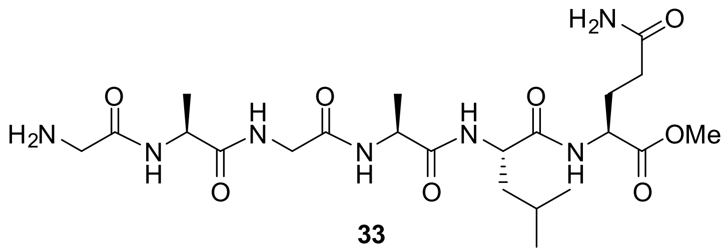


HPLC Chromatogram of glycopeptide **33**



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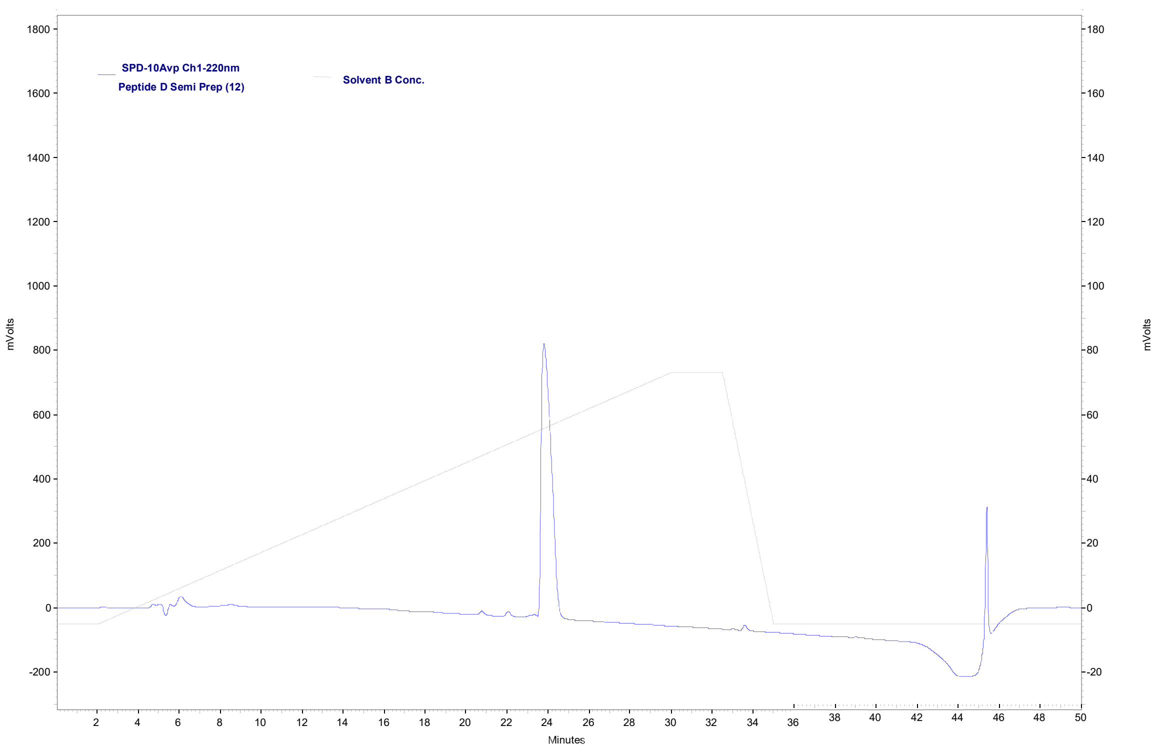
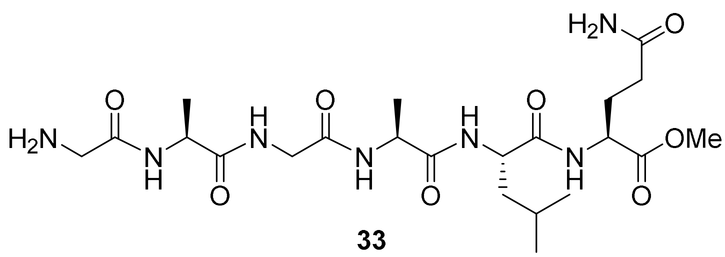


^{1}H-NMR (CD_3OD, 500 MHz) of **33**



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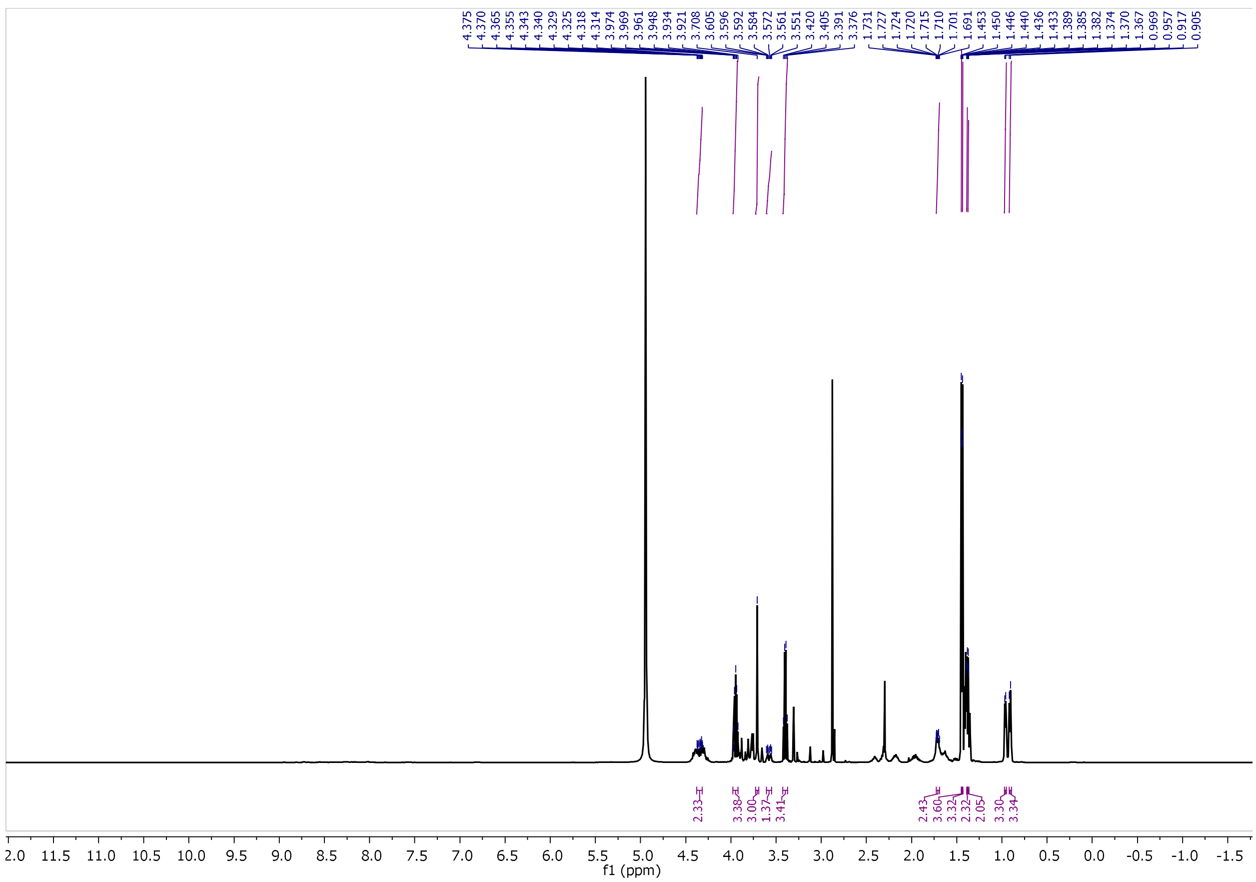
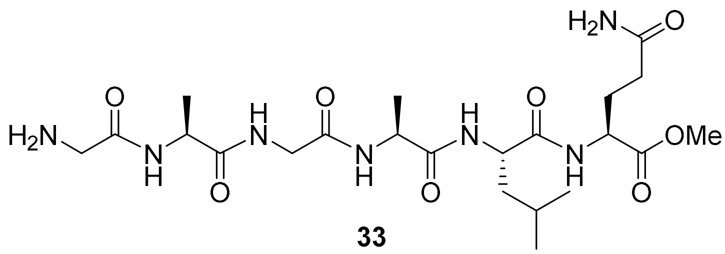


^{13}C-NMR (CD_3OD, 126 MHz) of **33**



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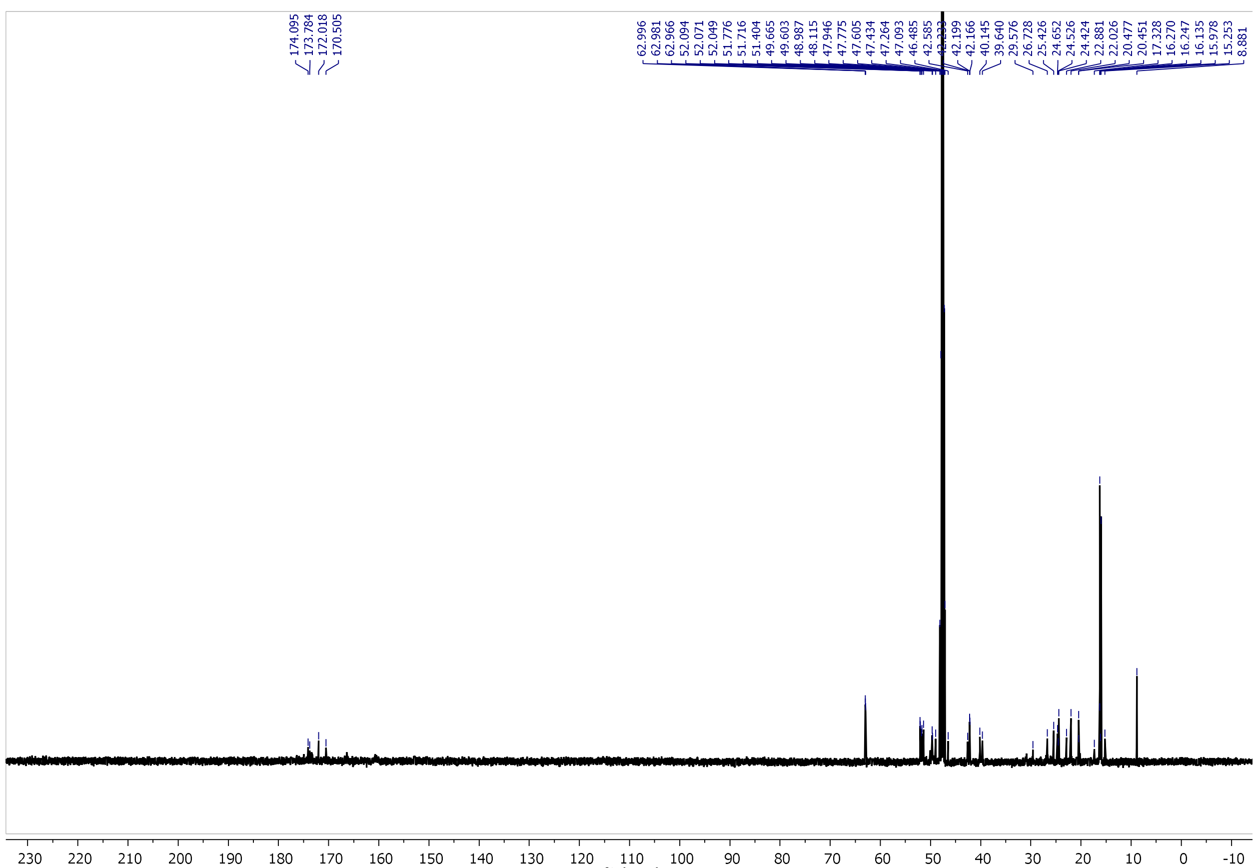
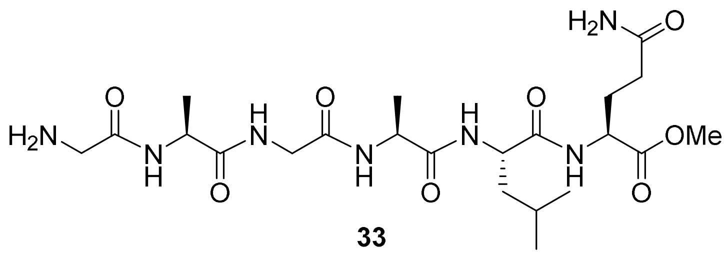


gCOSY (CD_3OD, 500 MHz) of **33**



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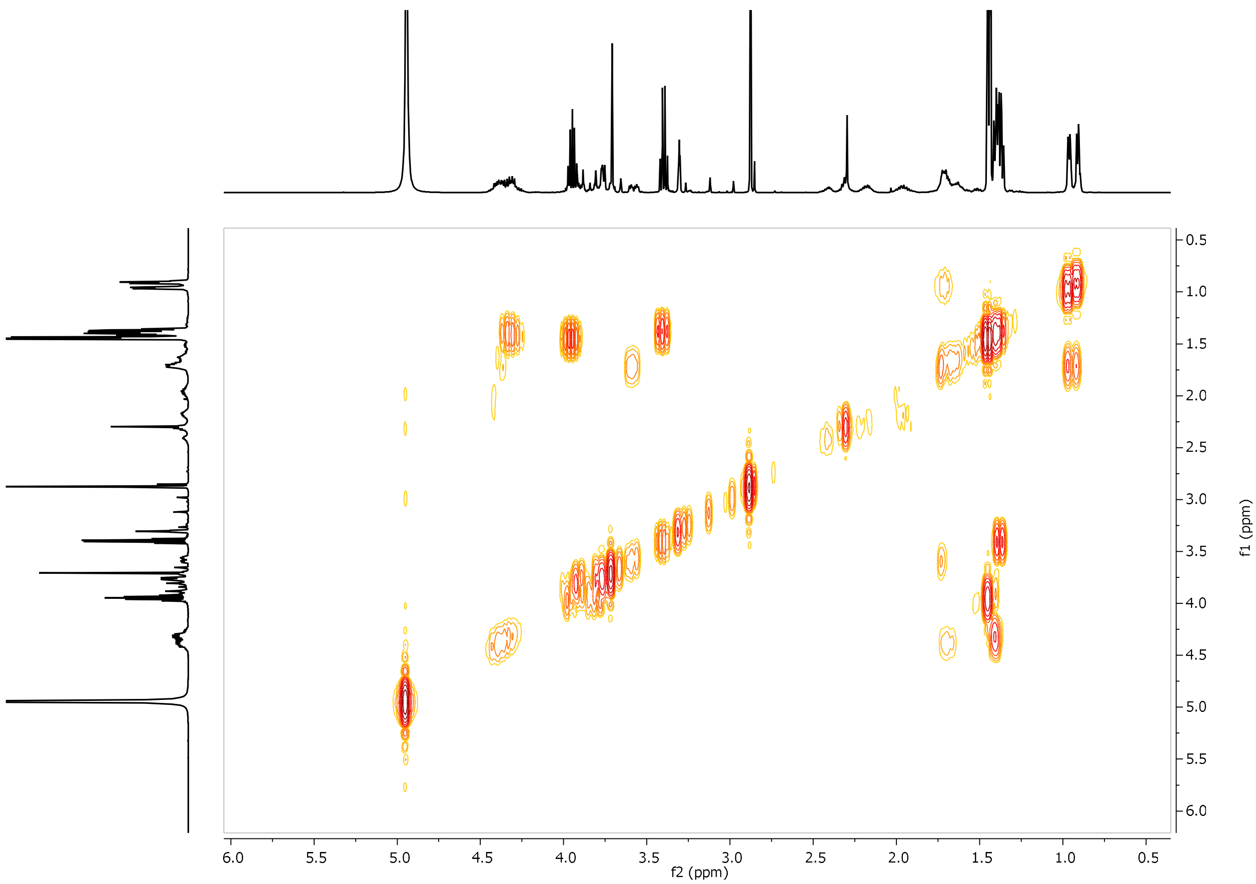
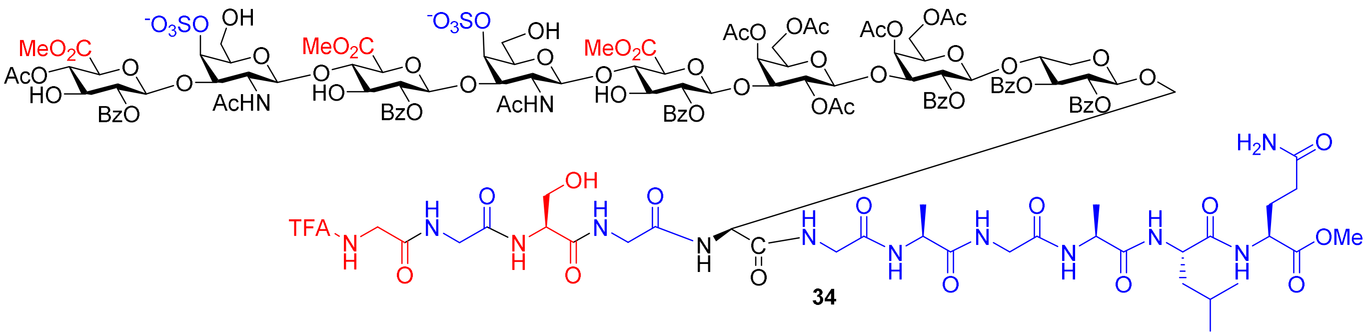


^{1}H-NMR (CD_3OD, 500 MHz) of **34**



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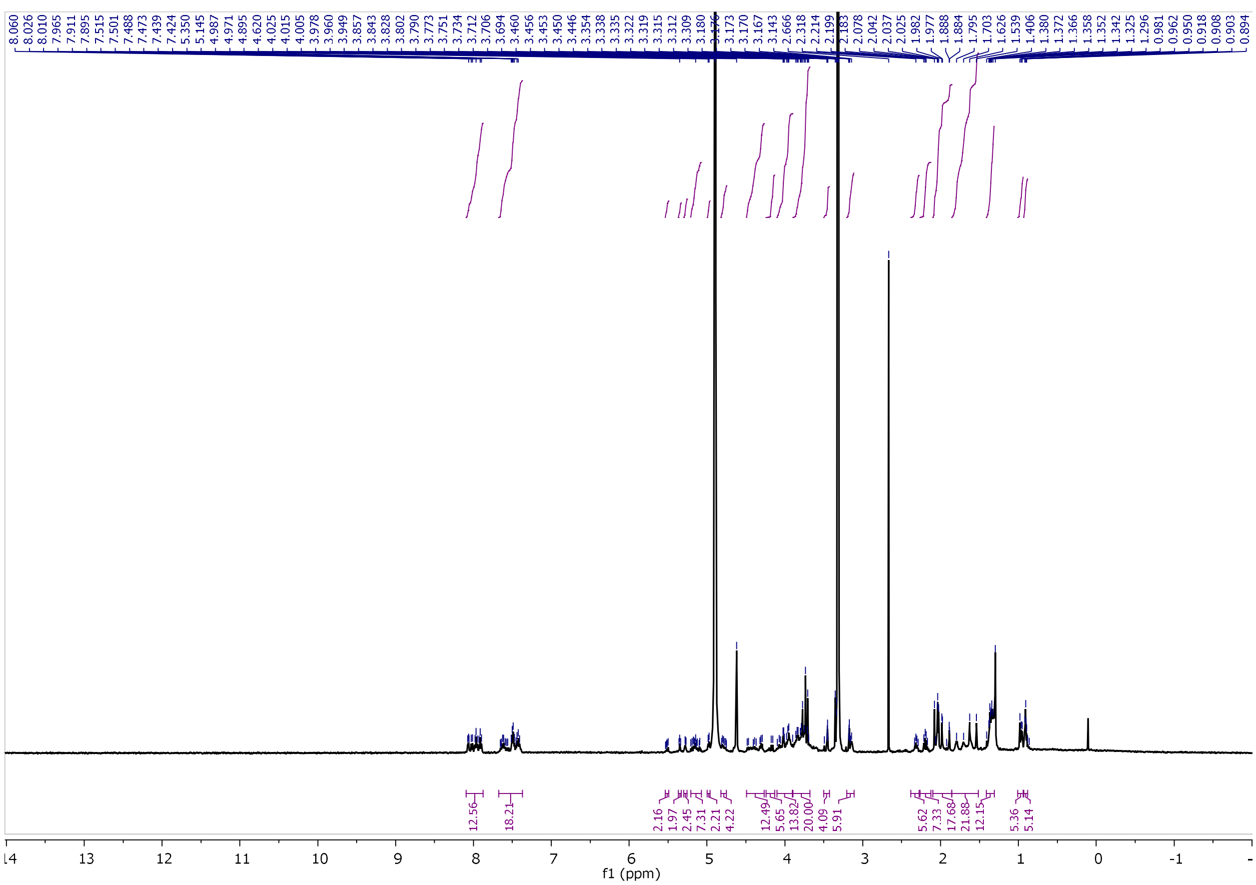
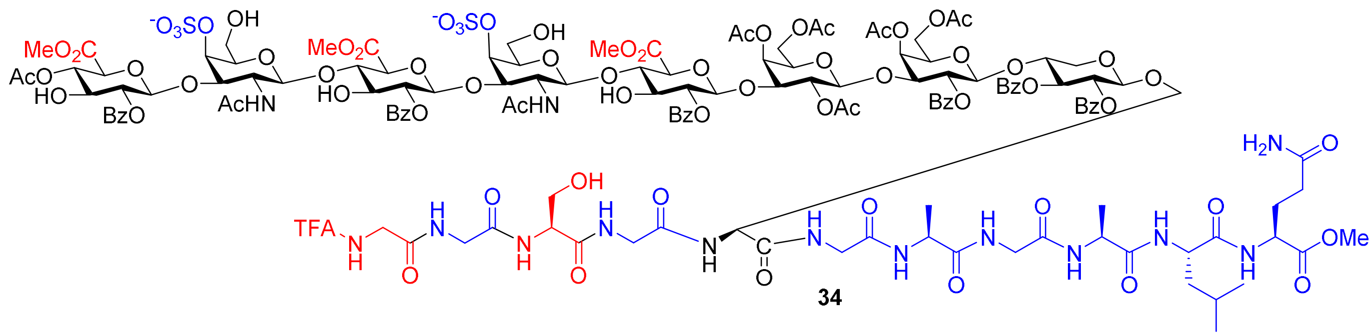
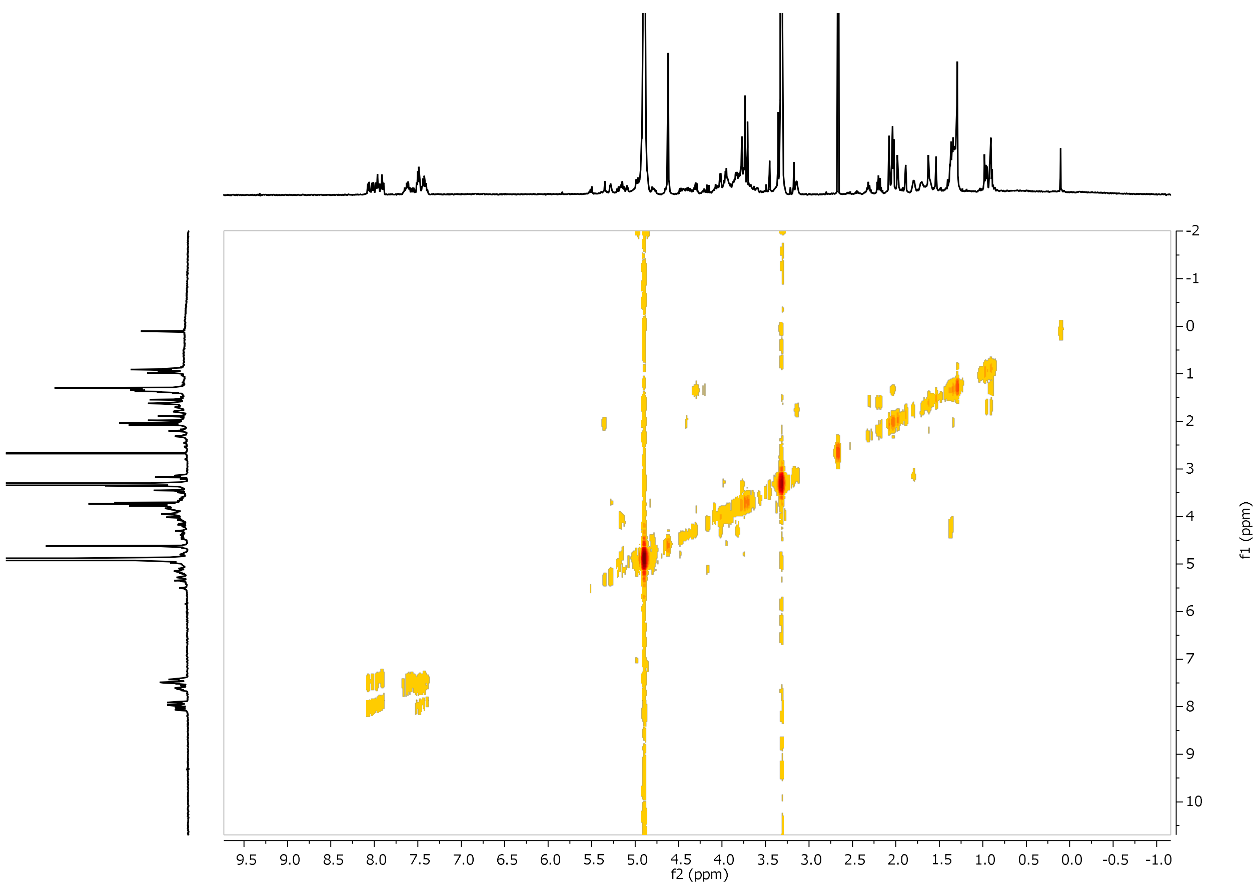
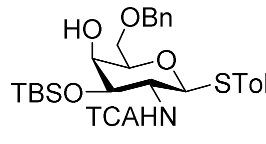


gCOSY (CD₃OD, 500 MHz) of **34**

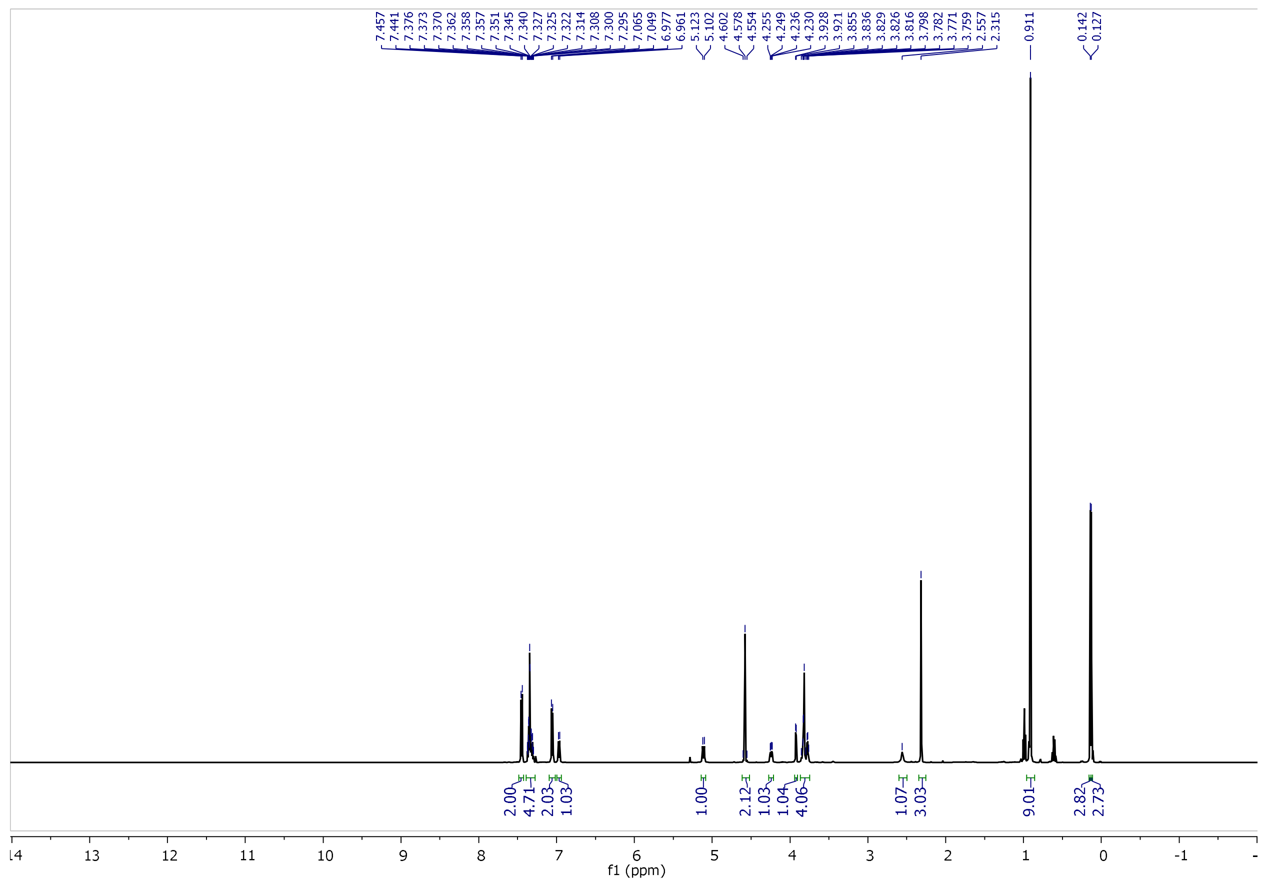




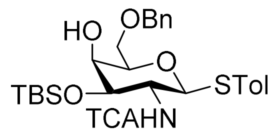
H-NMR ($CDCl_3$, 500 MHz) of **S8**



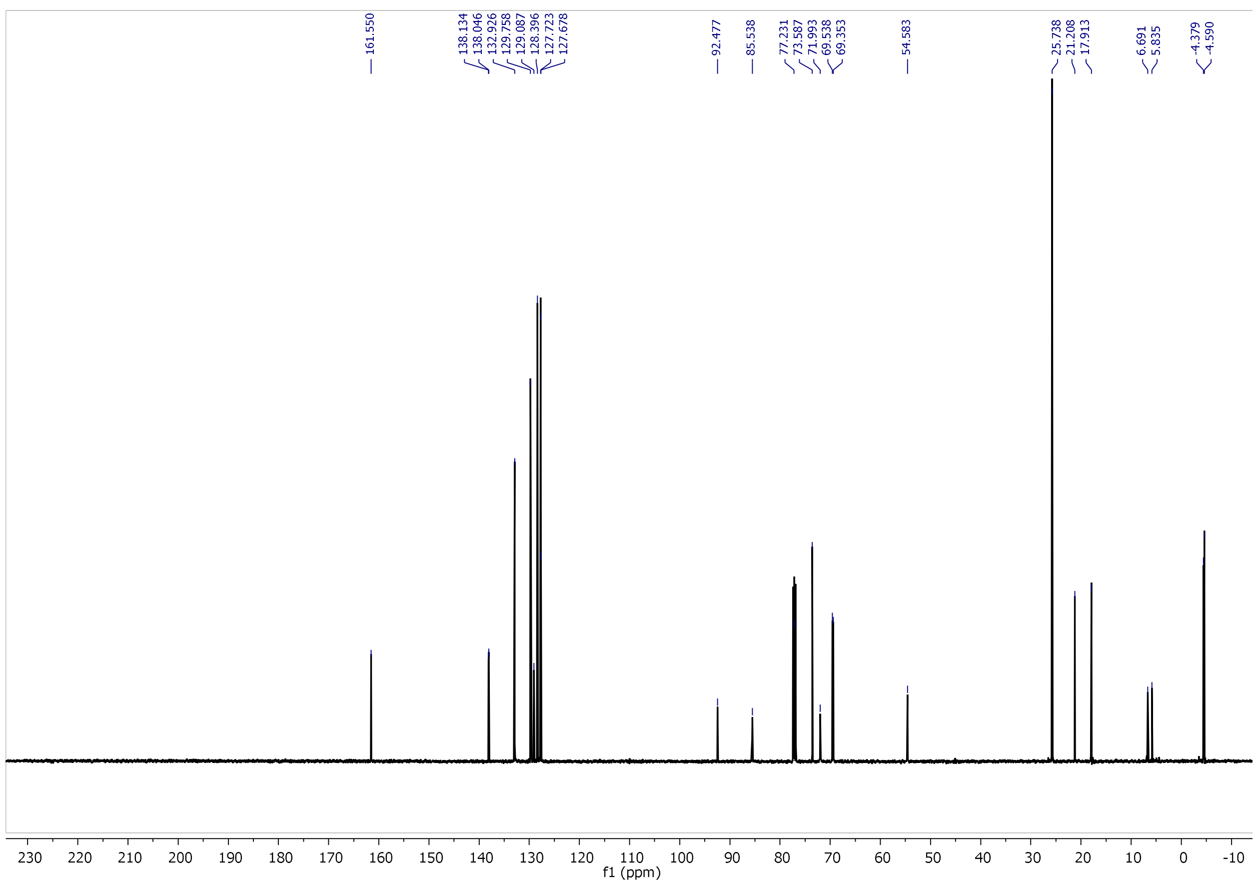
S8



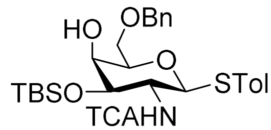
^{13}C-NMR ($CDCl_3$, 126 MHz) of **S8**



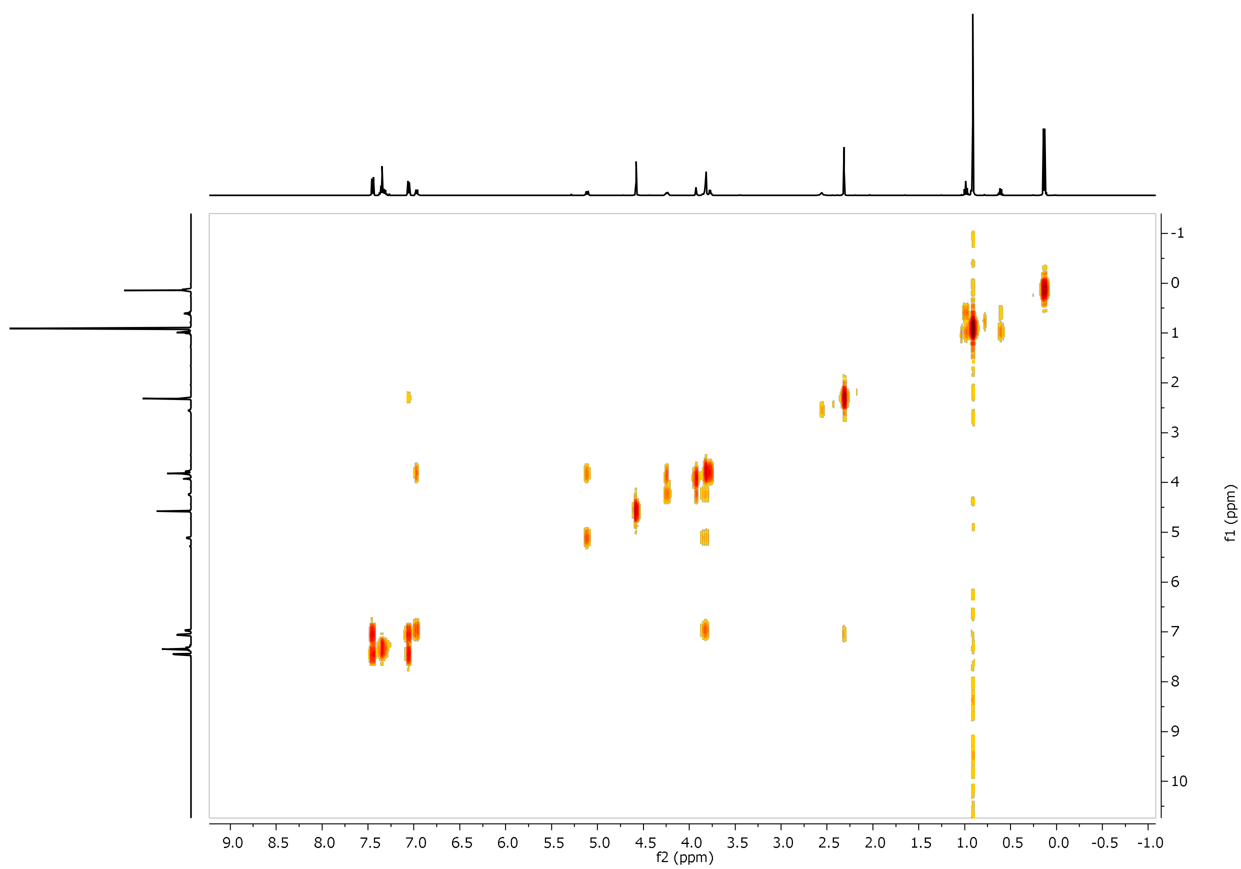
S8



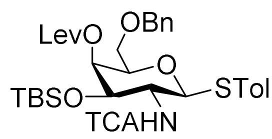
gCOSY ($CDCl_3$, 500 MHz) of **S8**



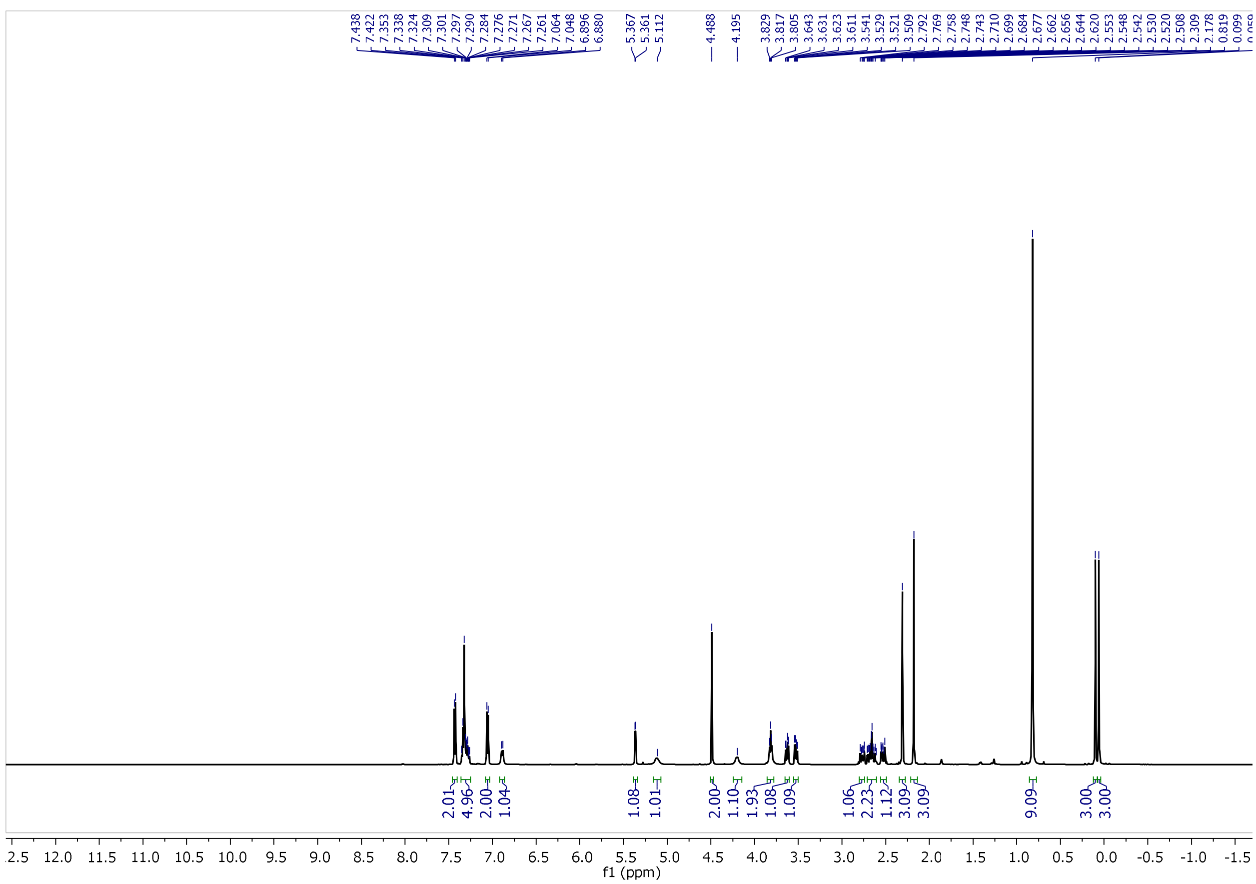
S8



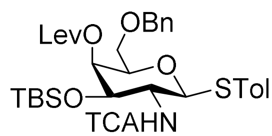
[1]H-NMR ($CDCl_3$, 500 MHz) of **S9**



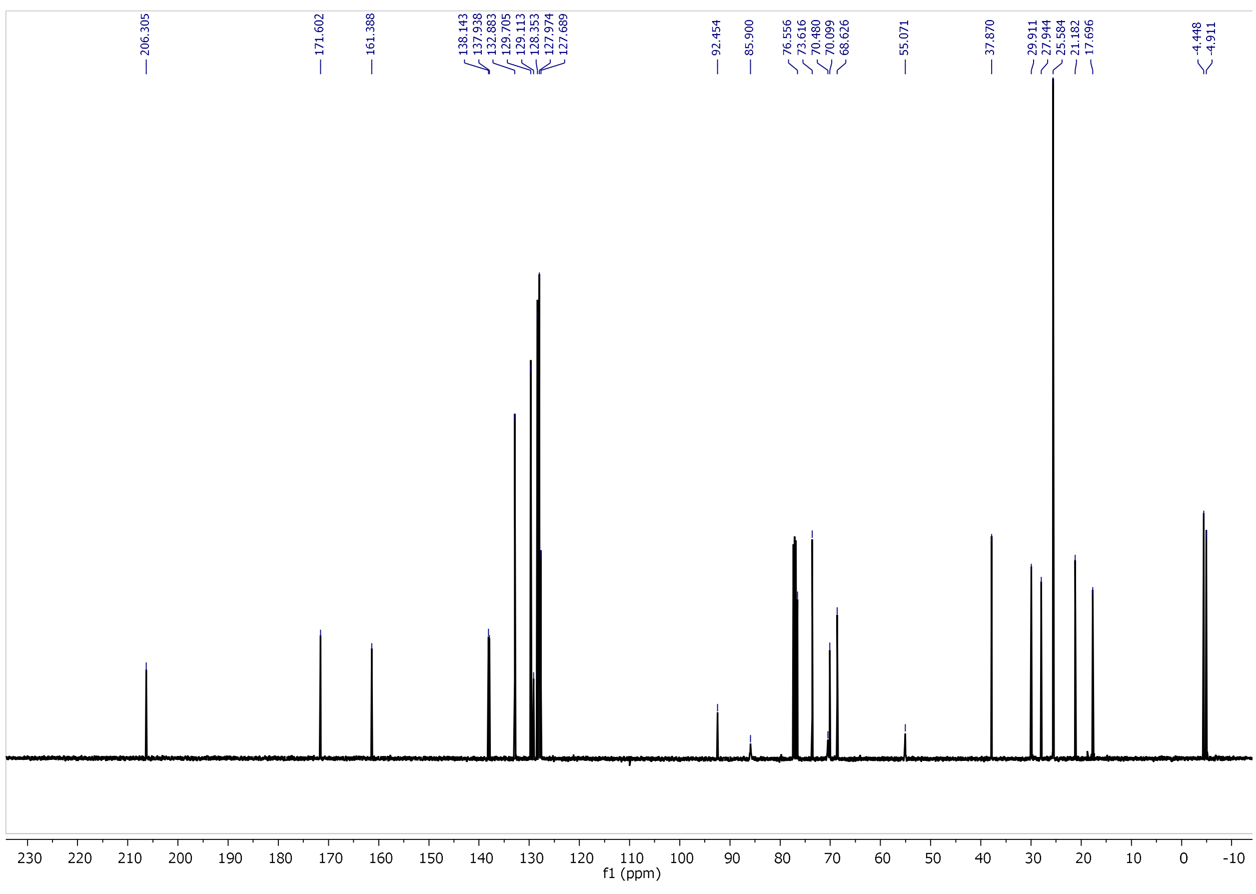
S9



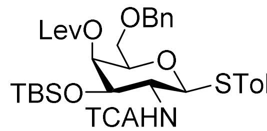
[13]C-NMR ($CDCl_3$, 126 MHz) of **S9**



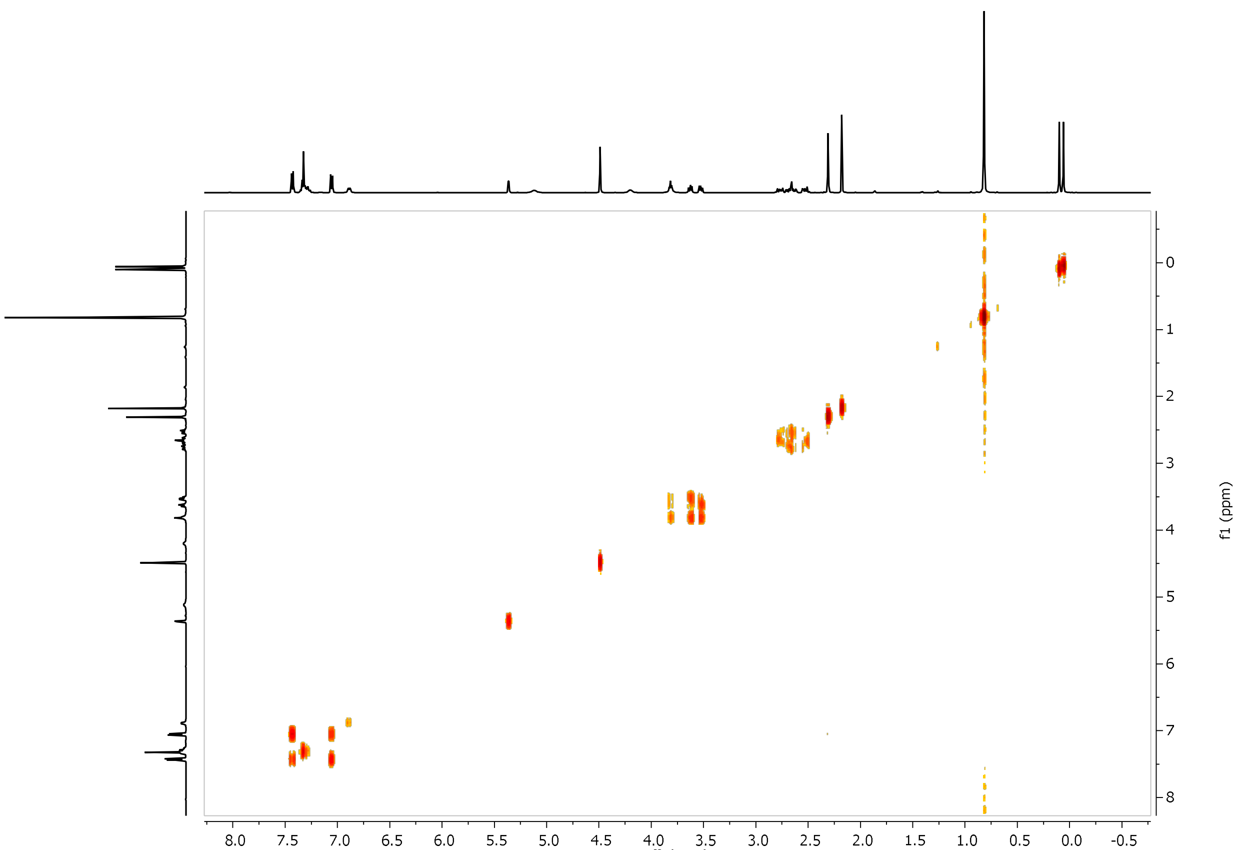
S9



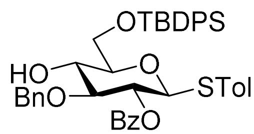
gCOSY ($CDCl_3$, 500 MHz) of **S9**



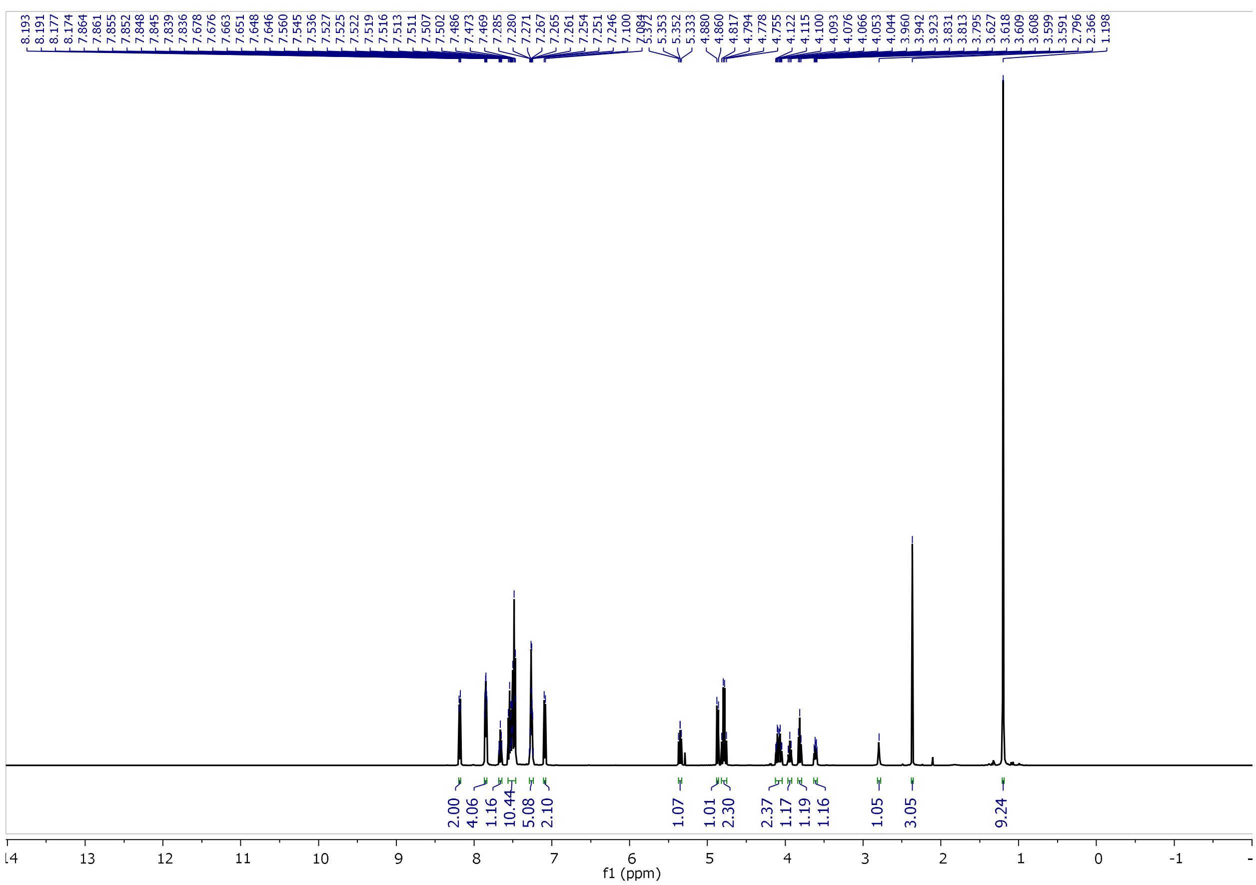
S9



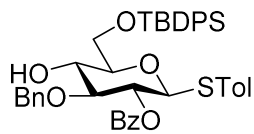
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S16**



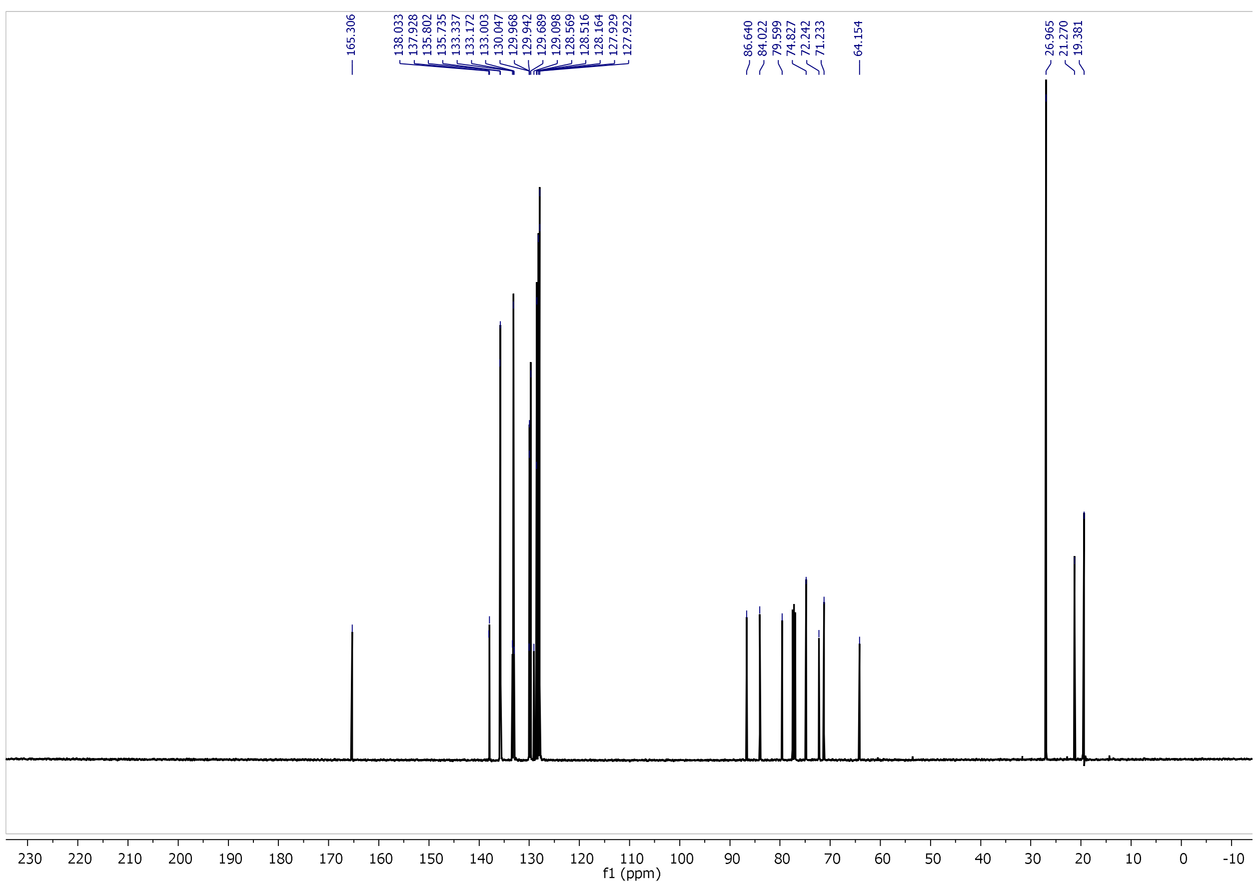
S16



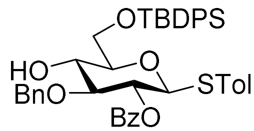
^{13}C-NMR ($CDCl_3$, 126 MHz) of **S16**



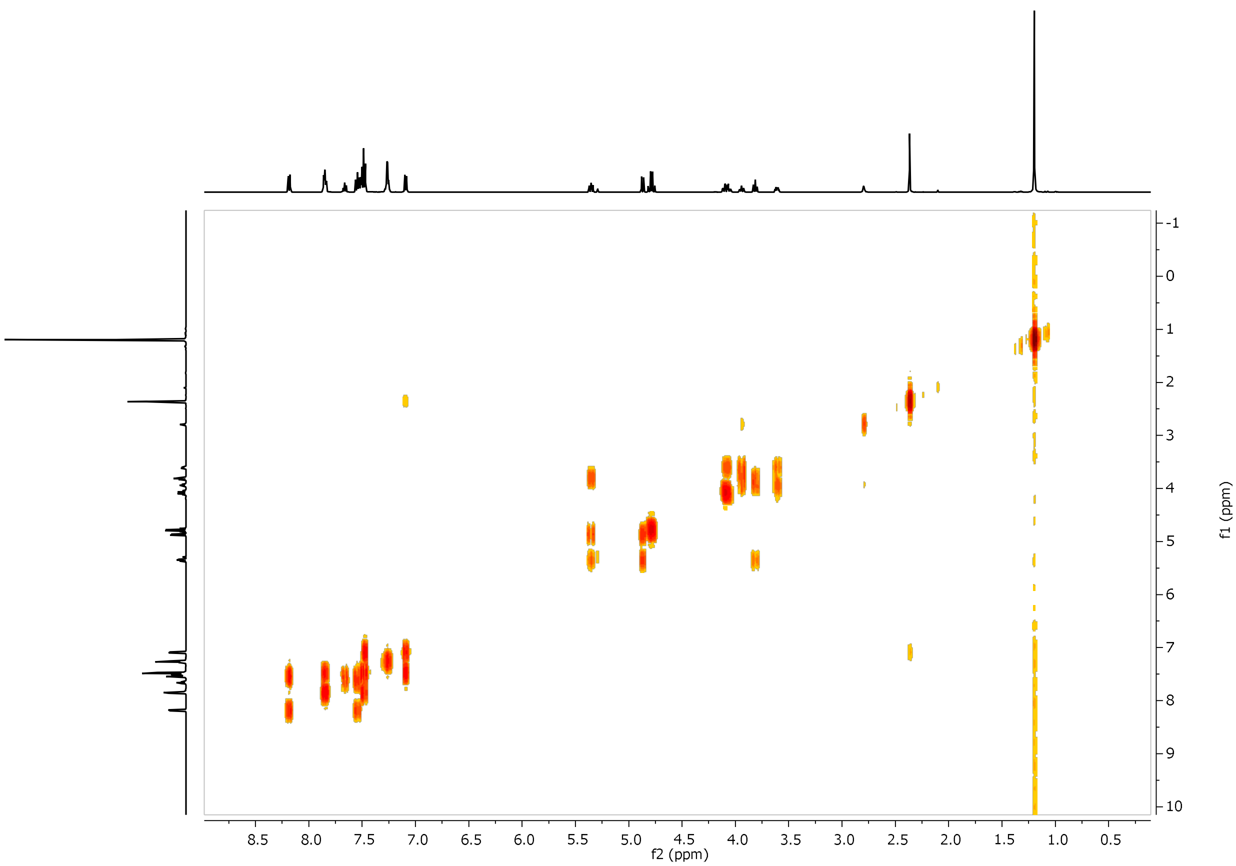
S16



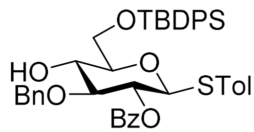
gCOSY ($CDCl_3$, 500 MHz) of **S16**



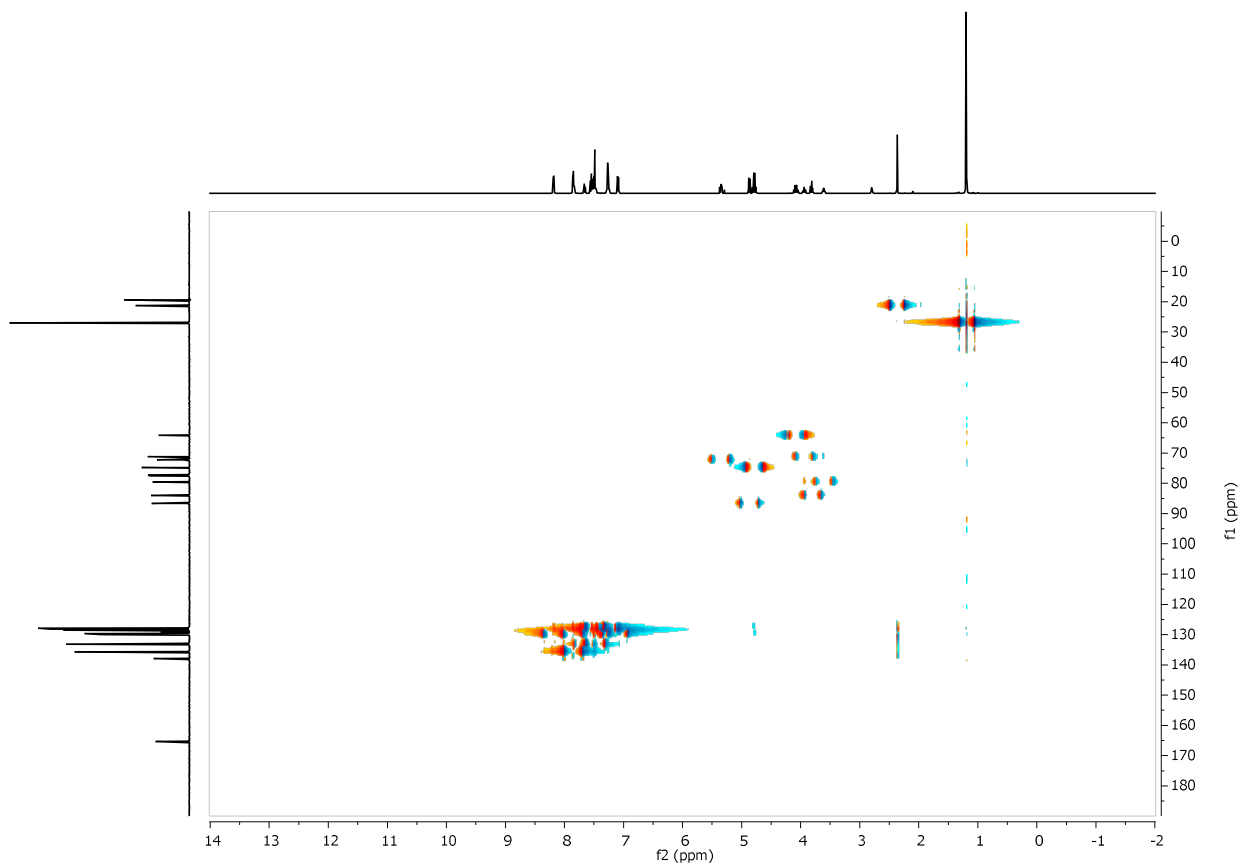
S16



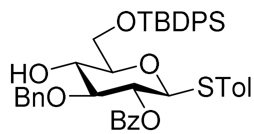
gHSQC ($CDCl_3$, 500 MHz) of **S16**



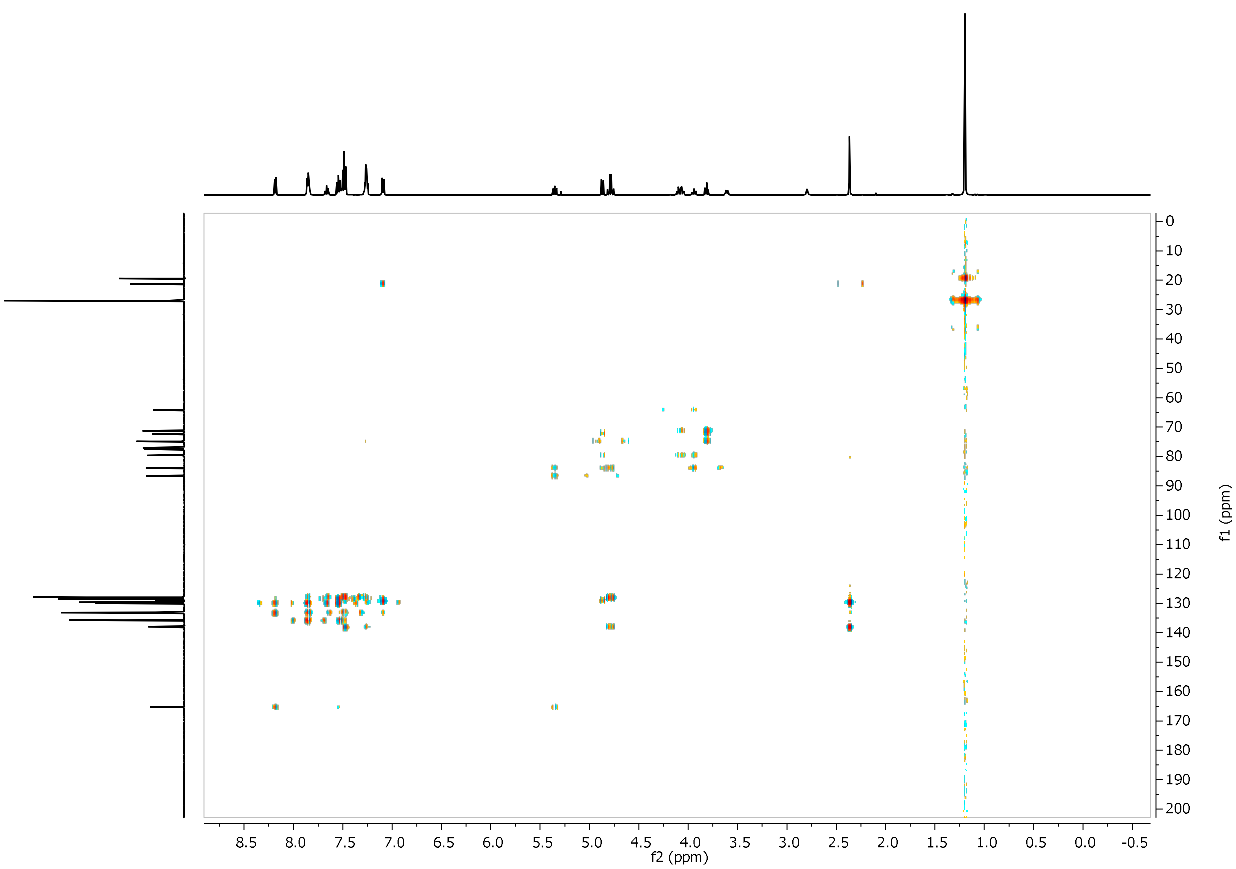
S16



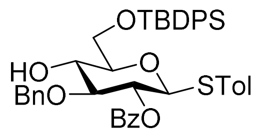
gHMBC ($CDCl_3$, 500 MHz) of **S16**



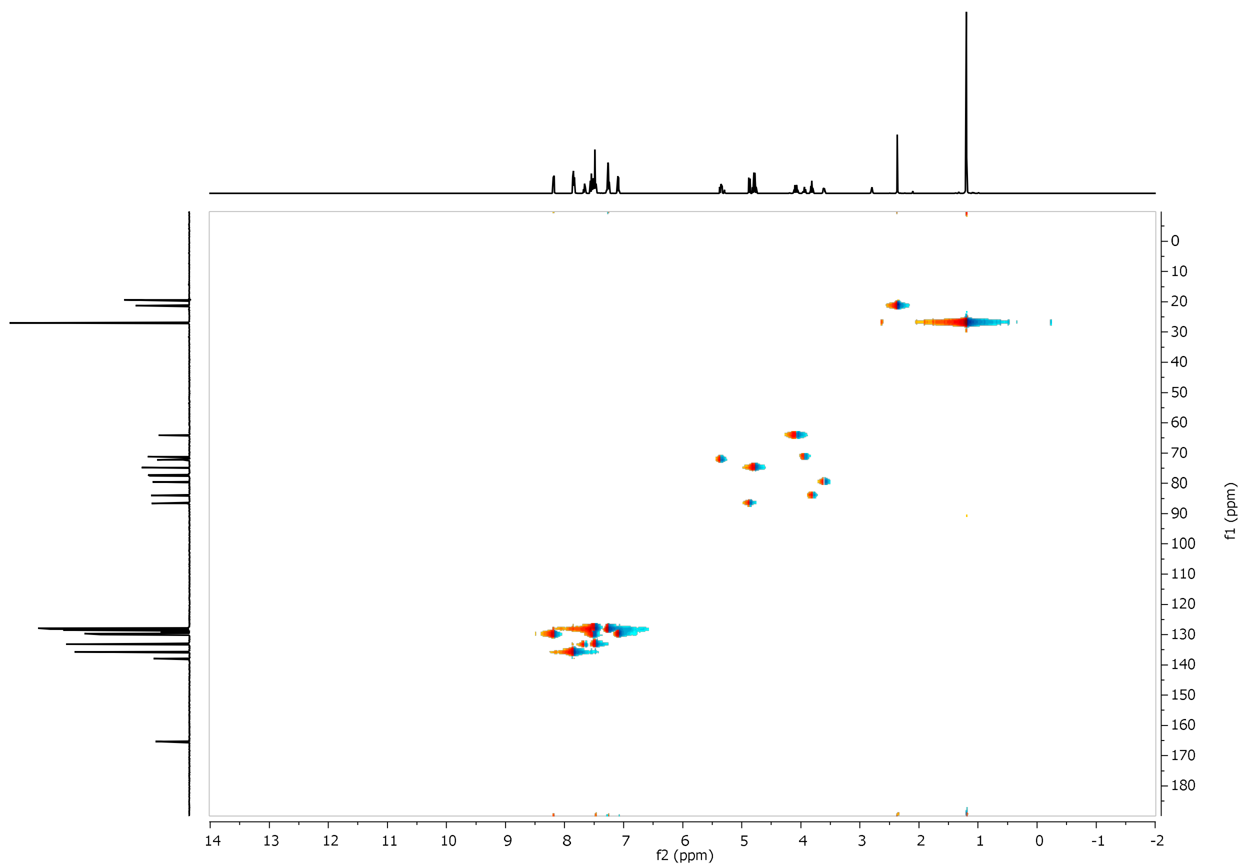
S16



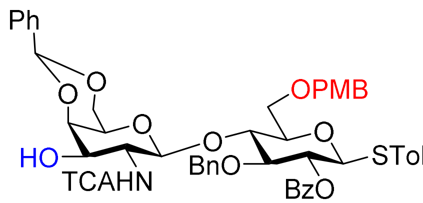
bsgHSQC ($CDCl_3$, 500 MHz) of **S16**



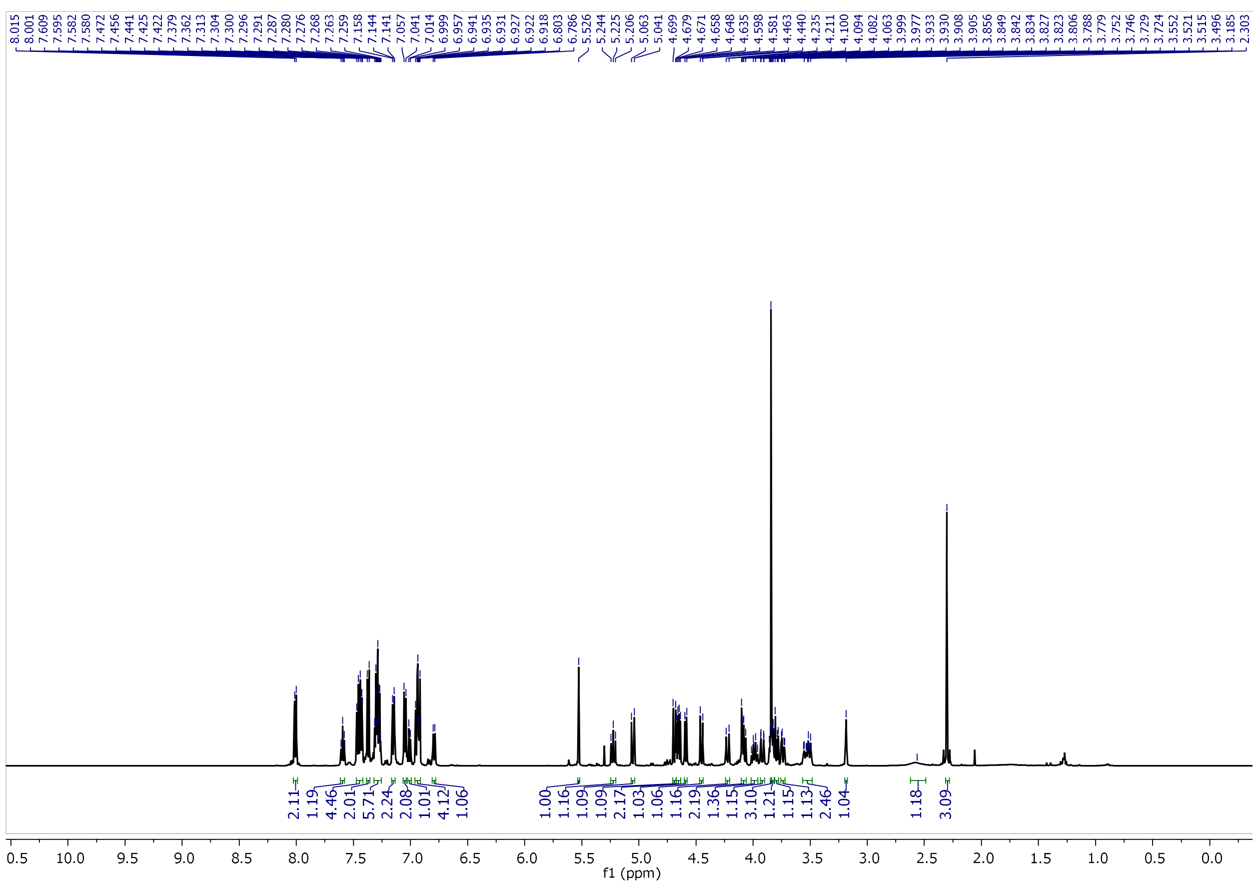
S16



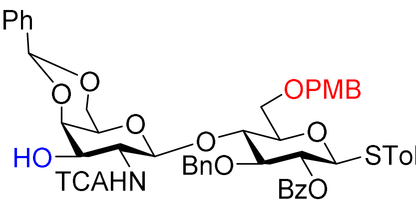
[1]H-NMR ($CDCl_3$, 500 MHz) of **S17**



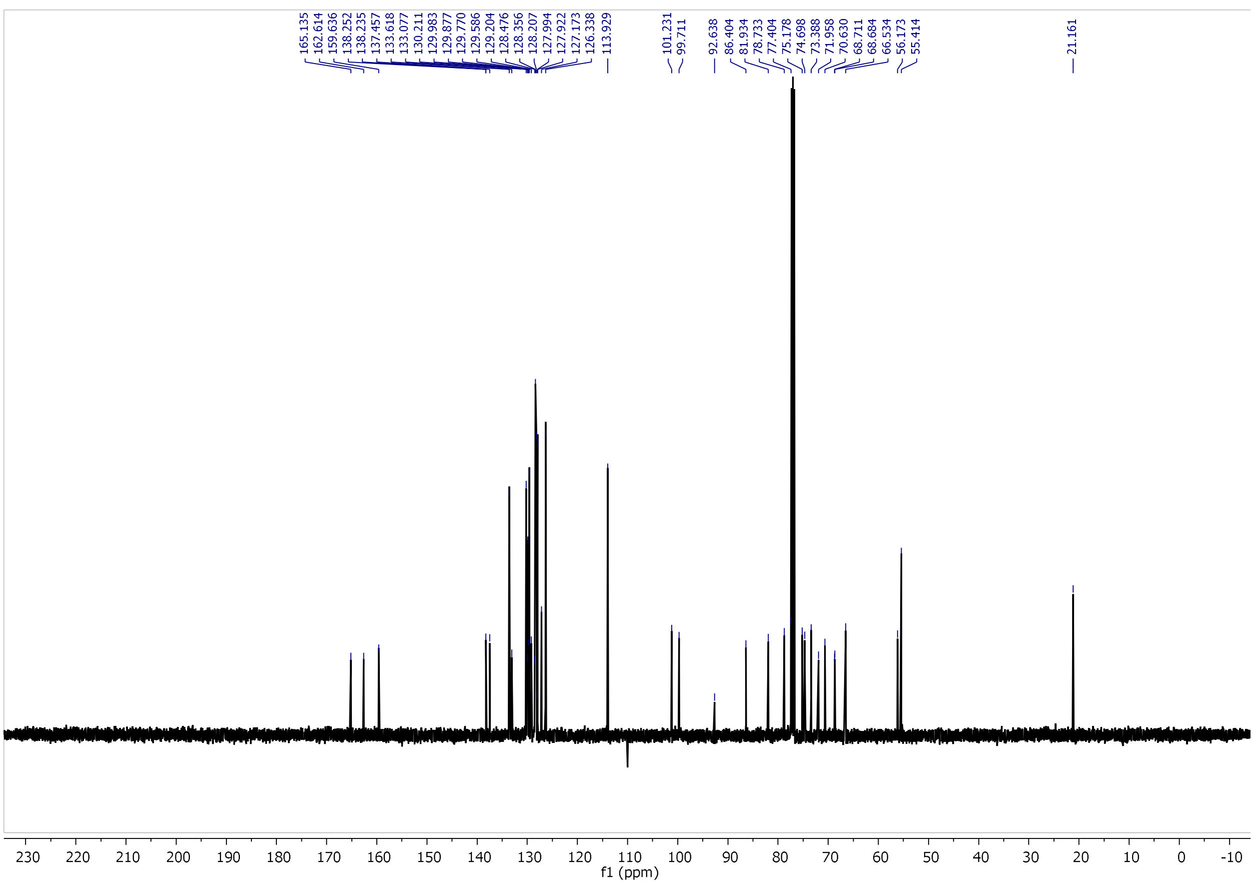
S17



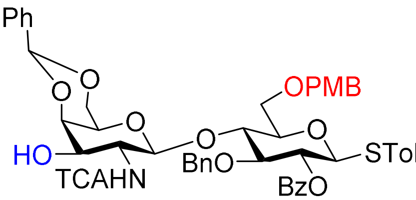
^{13}C-NMR ($CDCl_3$, 126 MHz) of **S17**



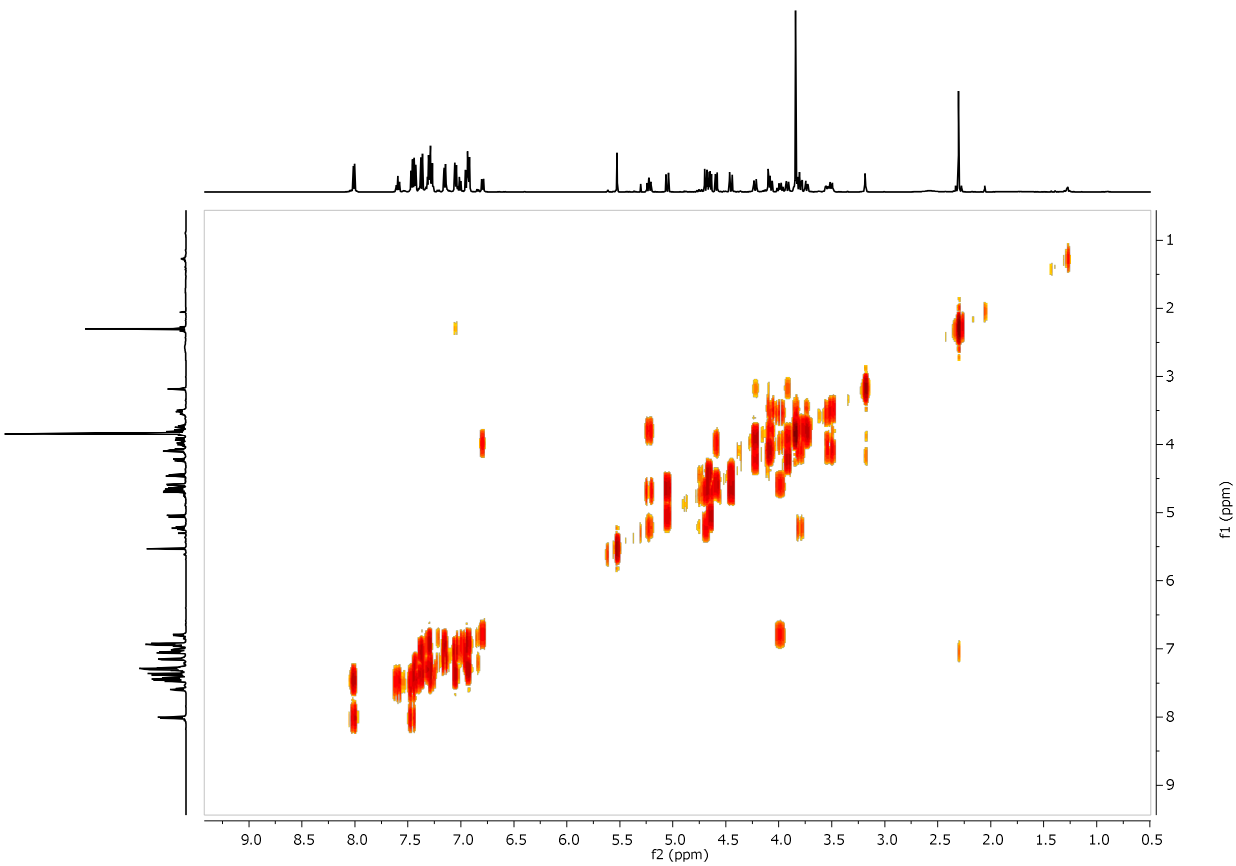
S17



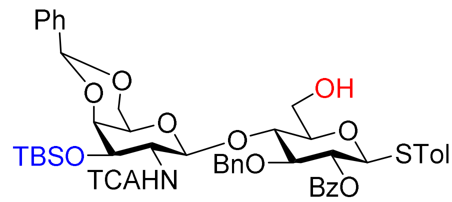
gCOSY ($CDCl_3$, 500 MHz) of **S17**



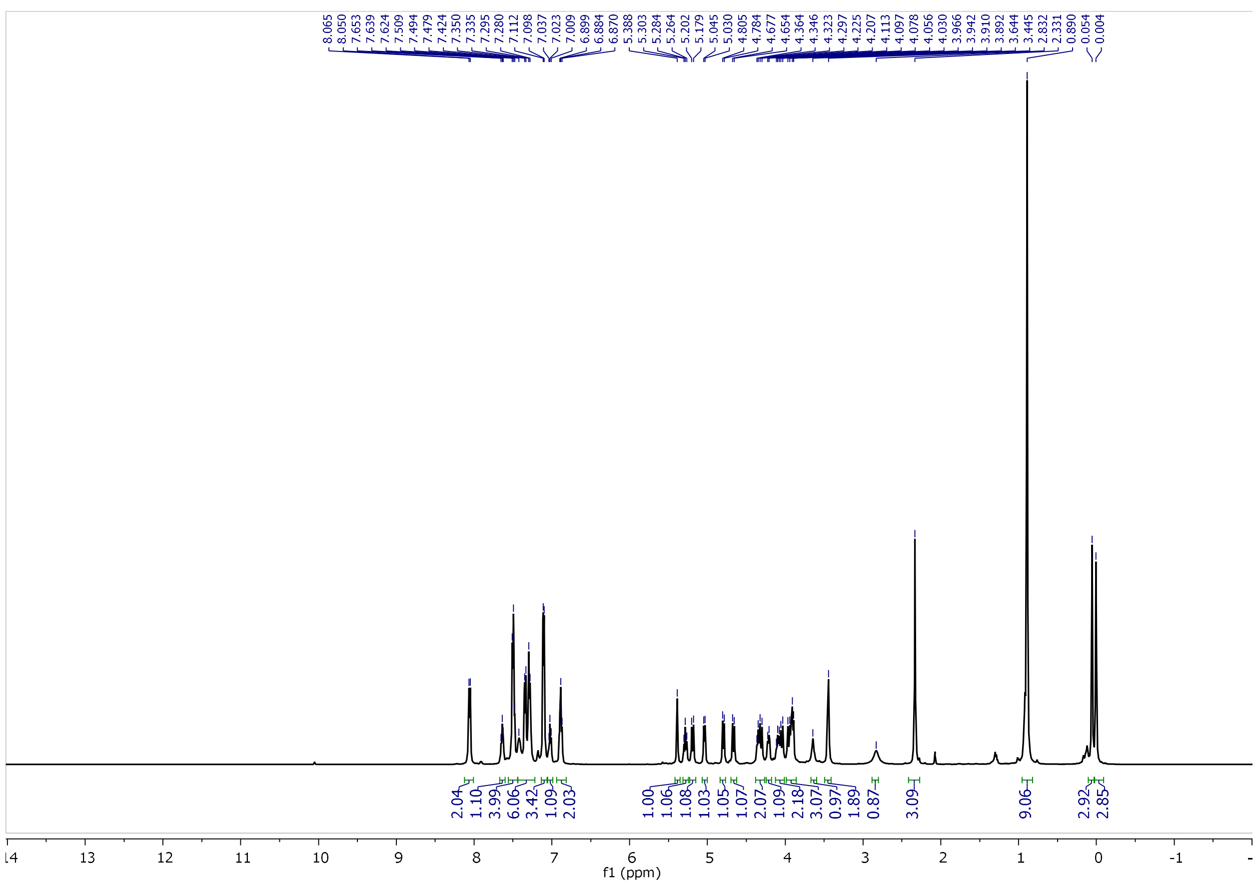
S17



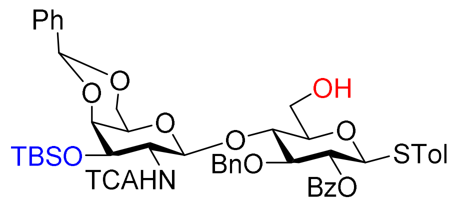
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S18**



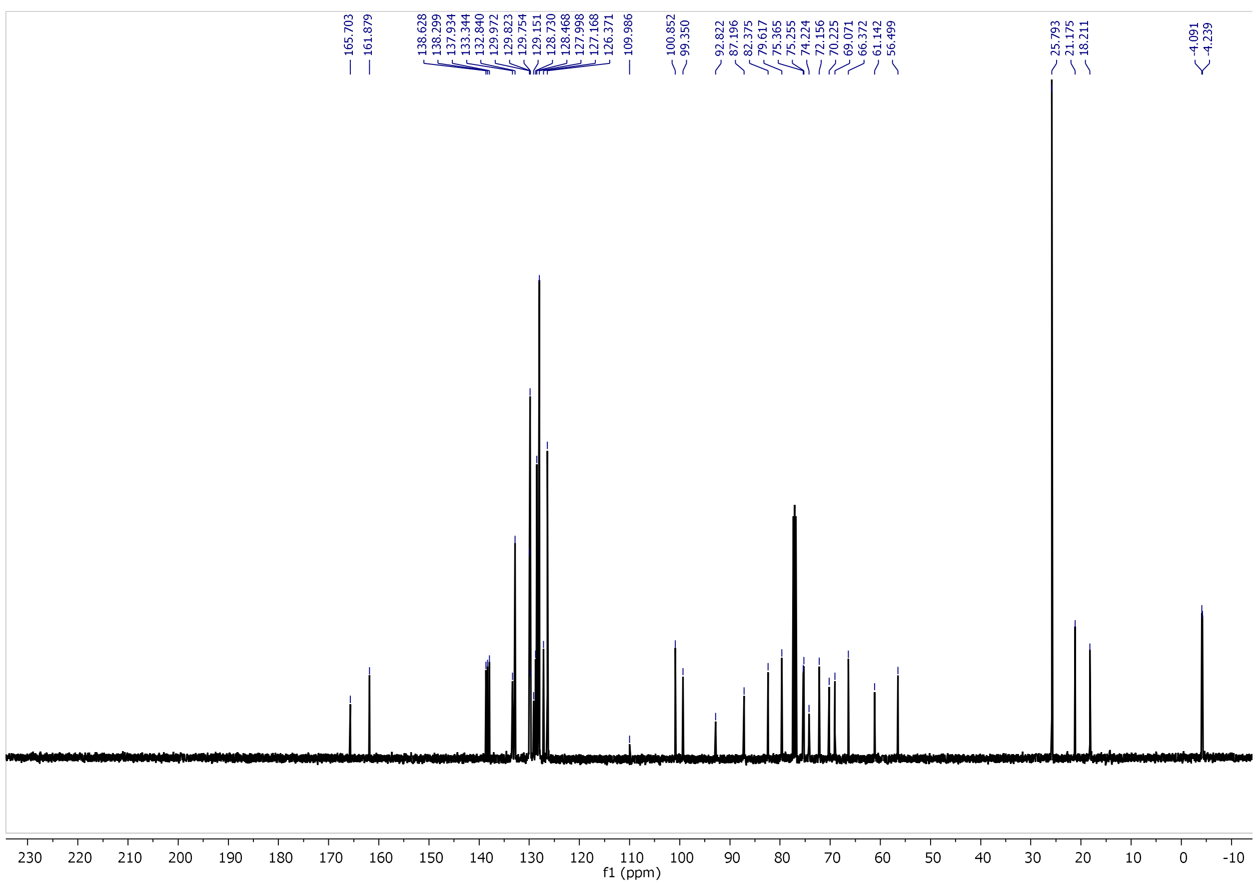
S18



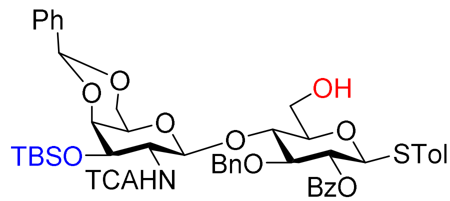
^{13}C-NMR ($CDCl_3$, 126 MHz) of **S18**



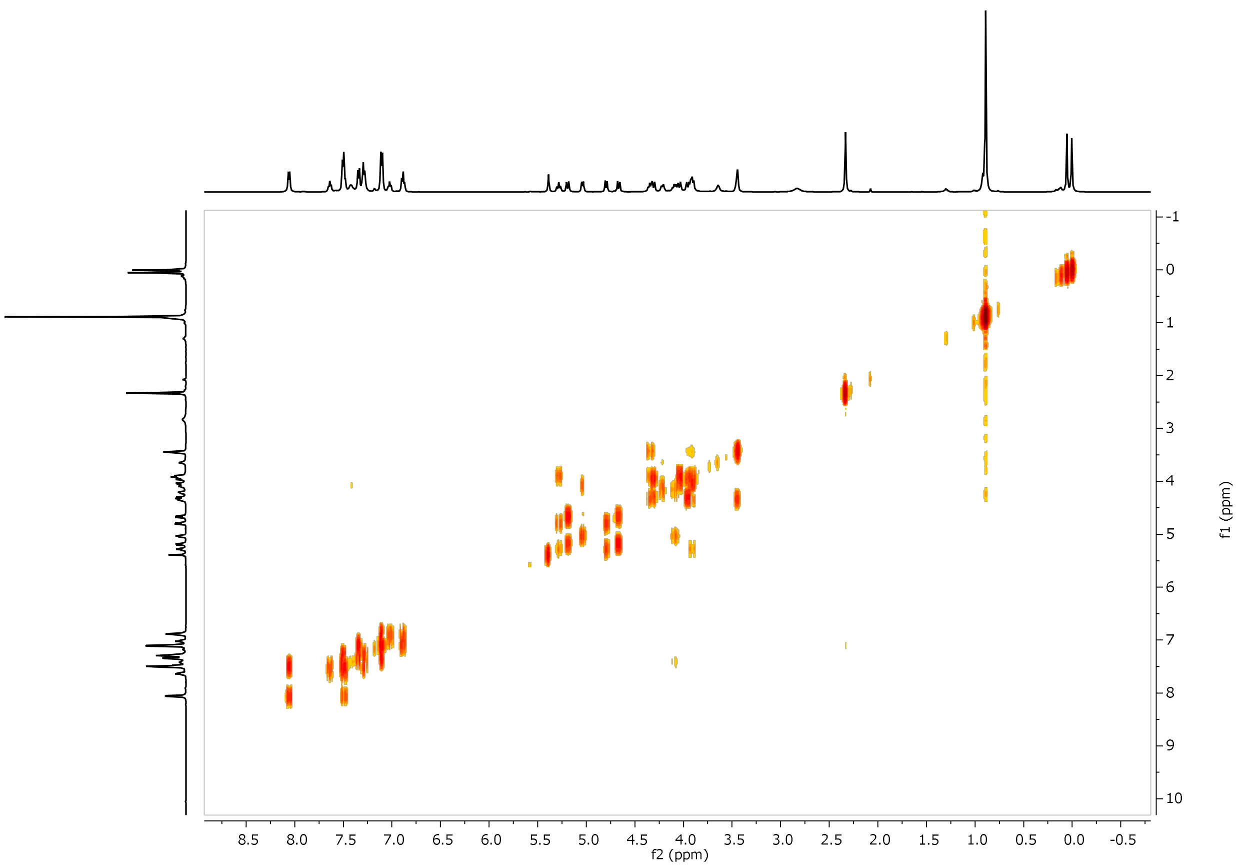
S18



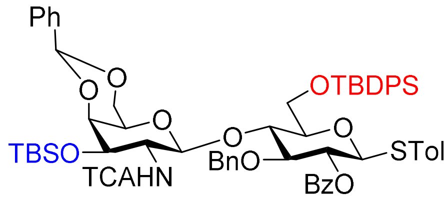
gCOSY (CDCl$_3$, 500 MHz) of **S18**



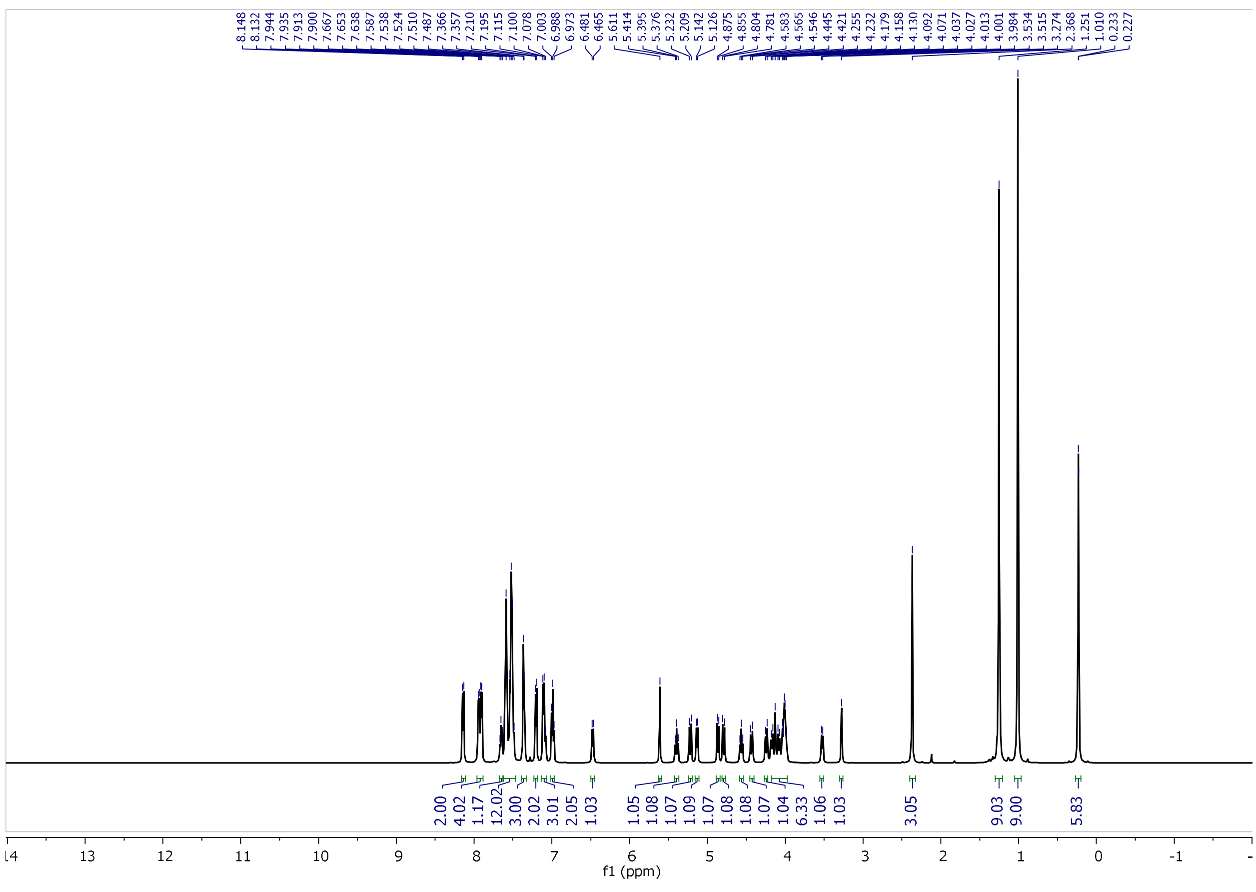
S18



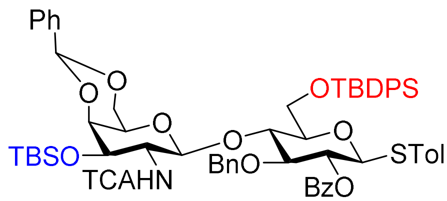
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S19**



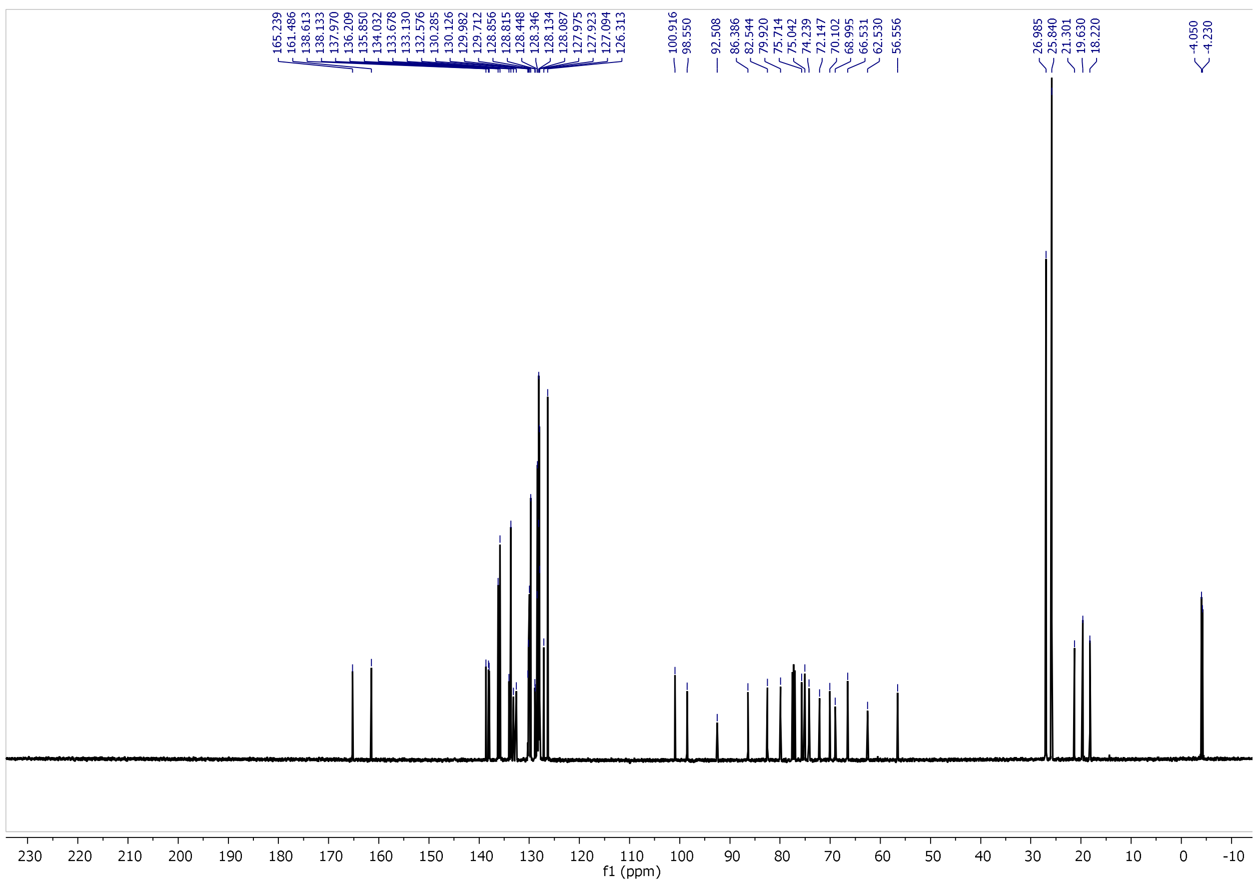
S19



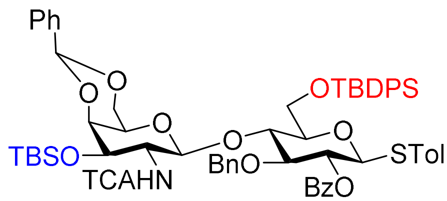
^{13}C-NMR (CDCl$_3$, 126 MHz) of **S19**



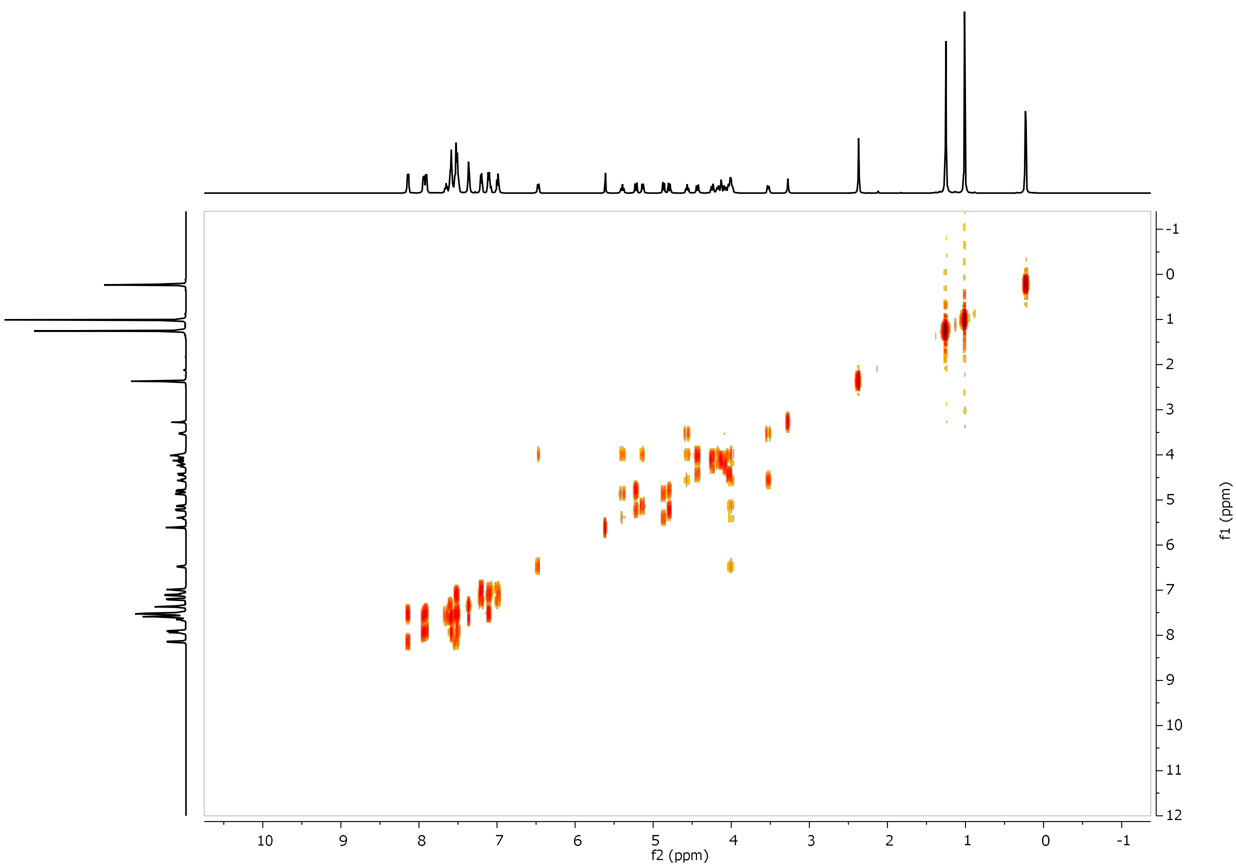
S19



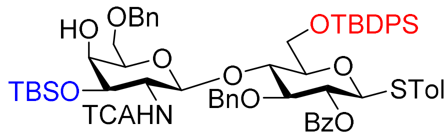
gCOSY ($CDCl_3$, 500 MHz) of **S19**



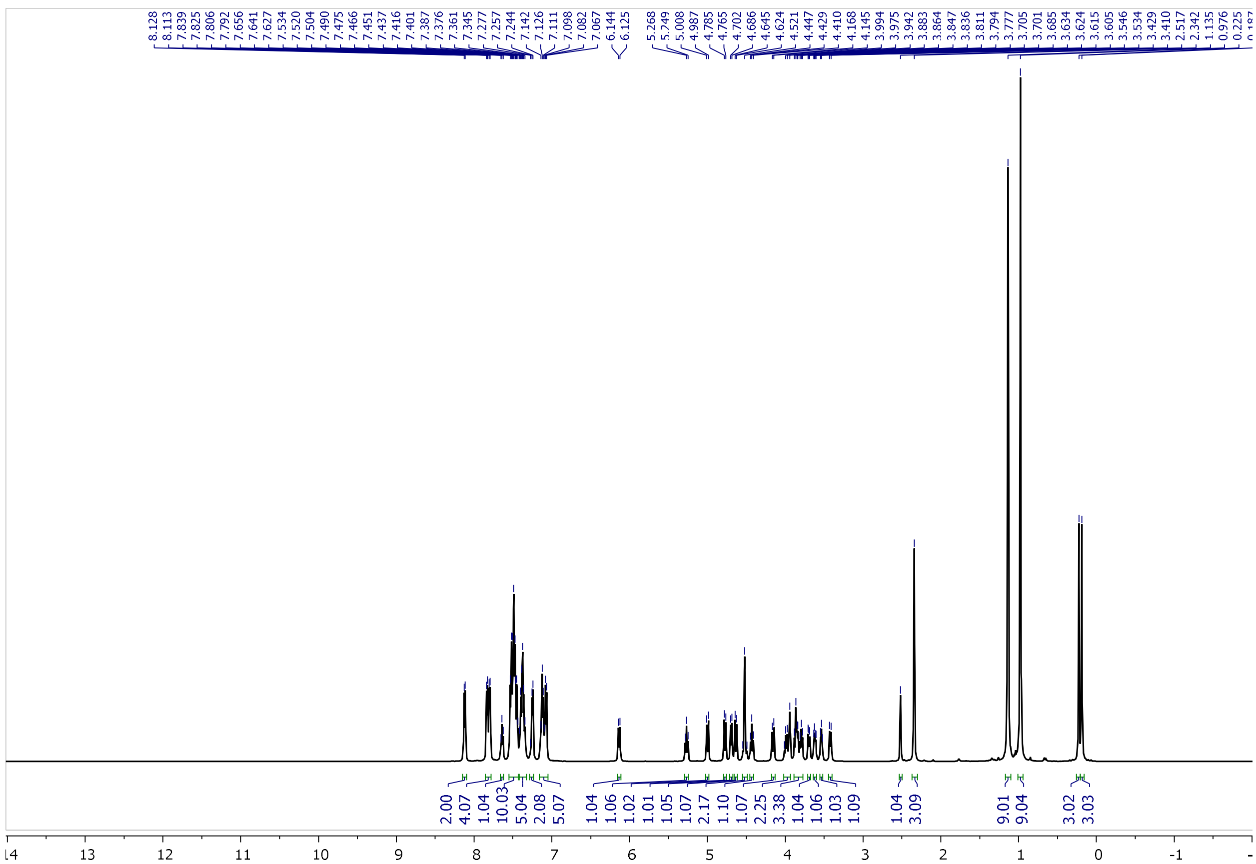
S19



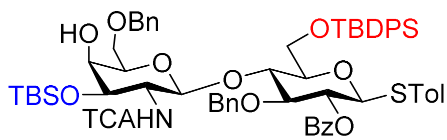
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S20**



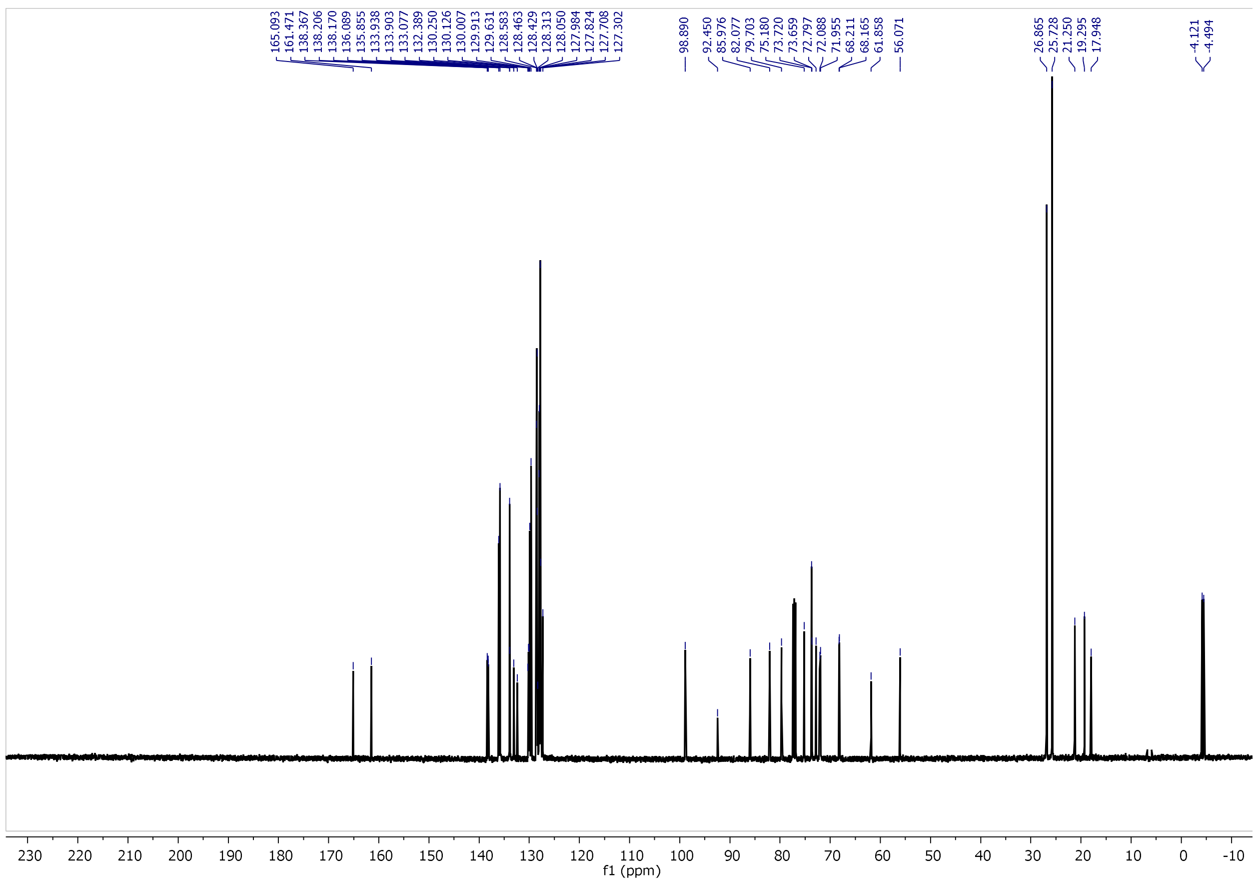
S20



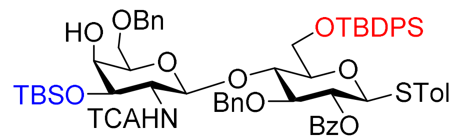
^{13}C-NMR (CDCl$_3$, 126 MHz) of **S20**



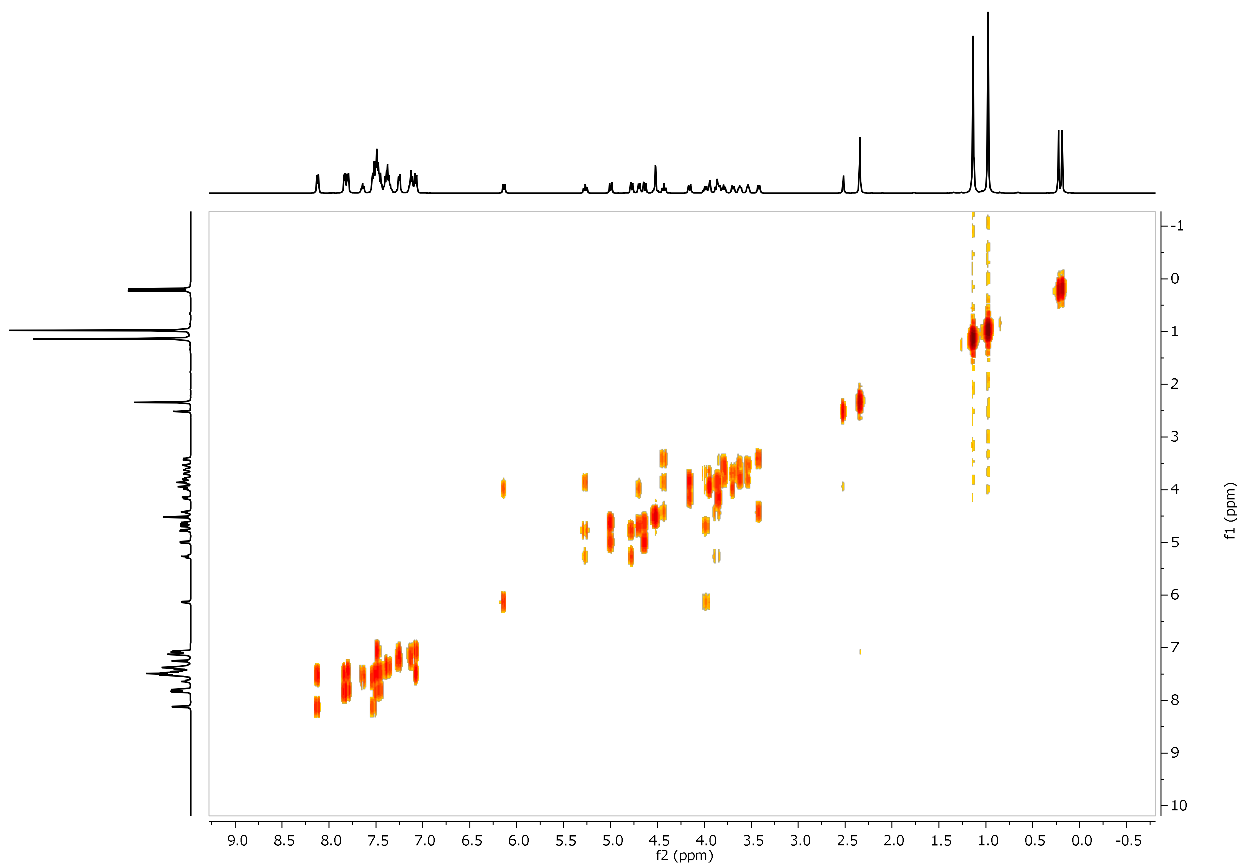
S20



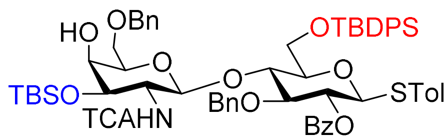
gCOSY ($CDCl_3$, 500 MHz) of **S20**



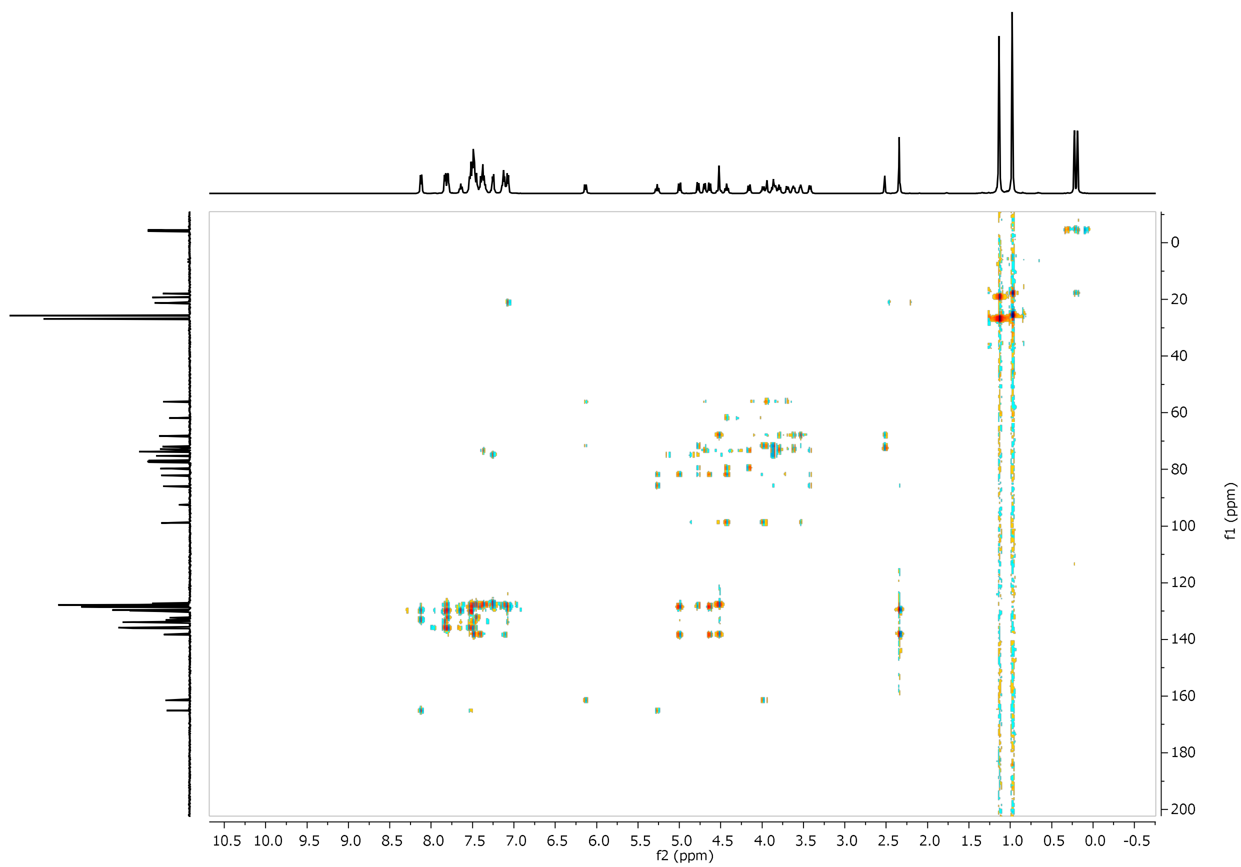
S20



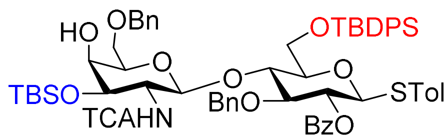
gHMBC ($CDCl_3$, 500 MHz) of **S20**



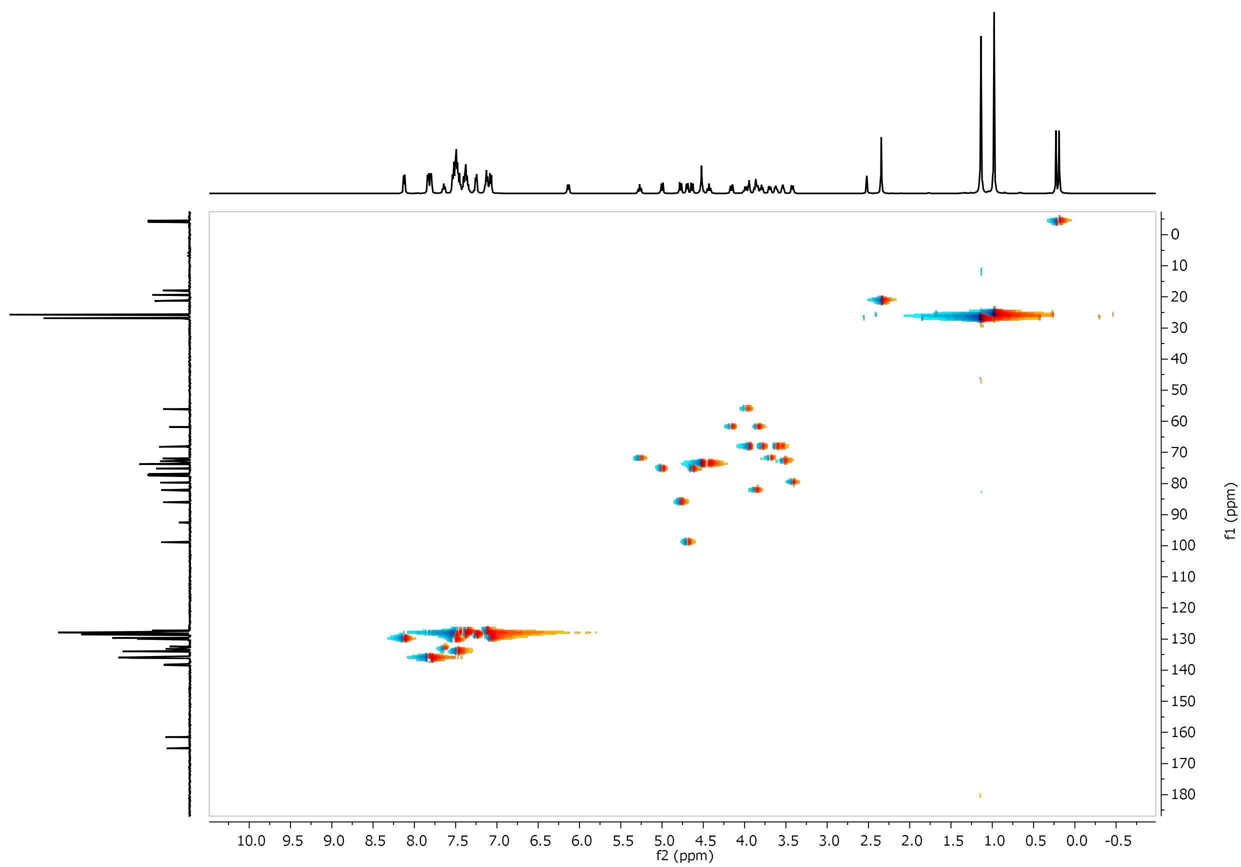
S20



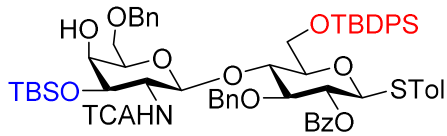
bsgHSQC ($CDCl_3$, 500 MHz) of **S20**



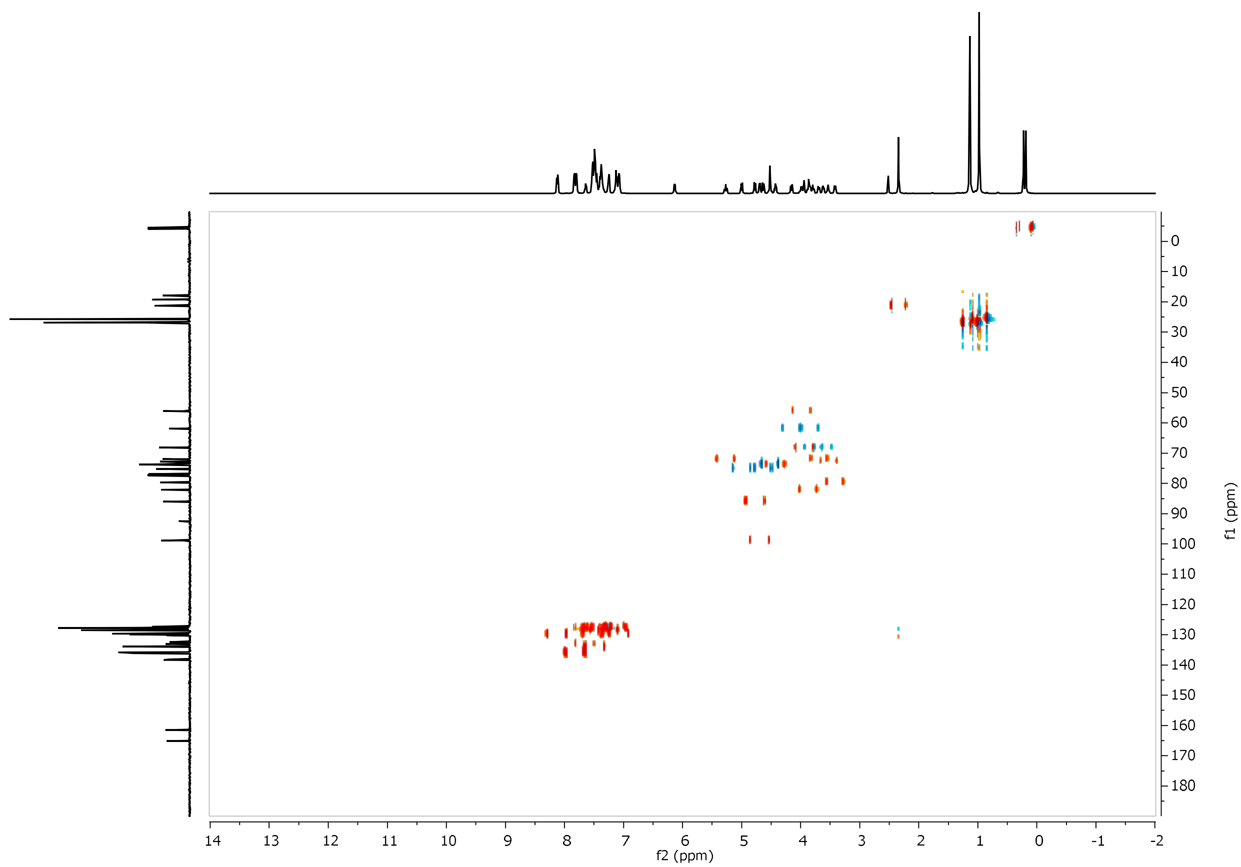
S20



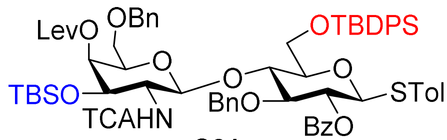
gHSQC ($CDCl_3$, 500 MHz) of **S20**



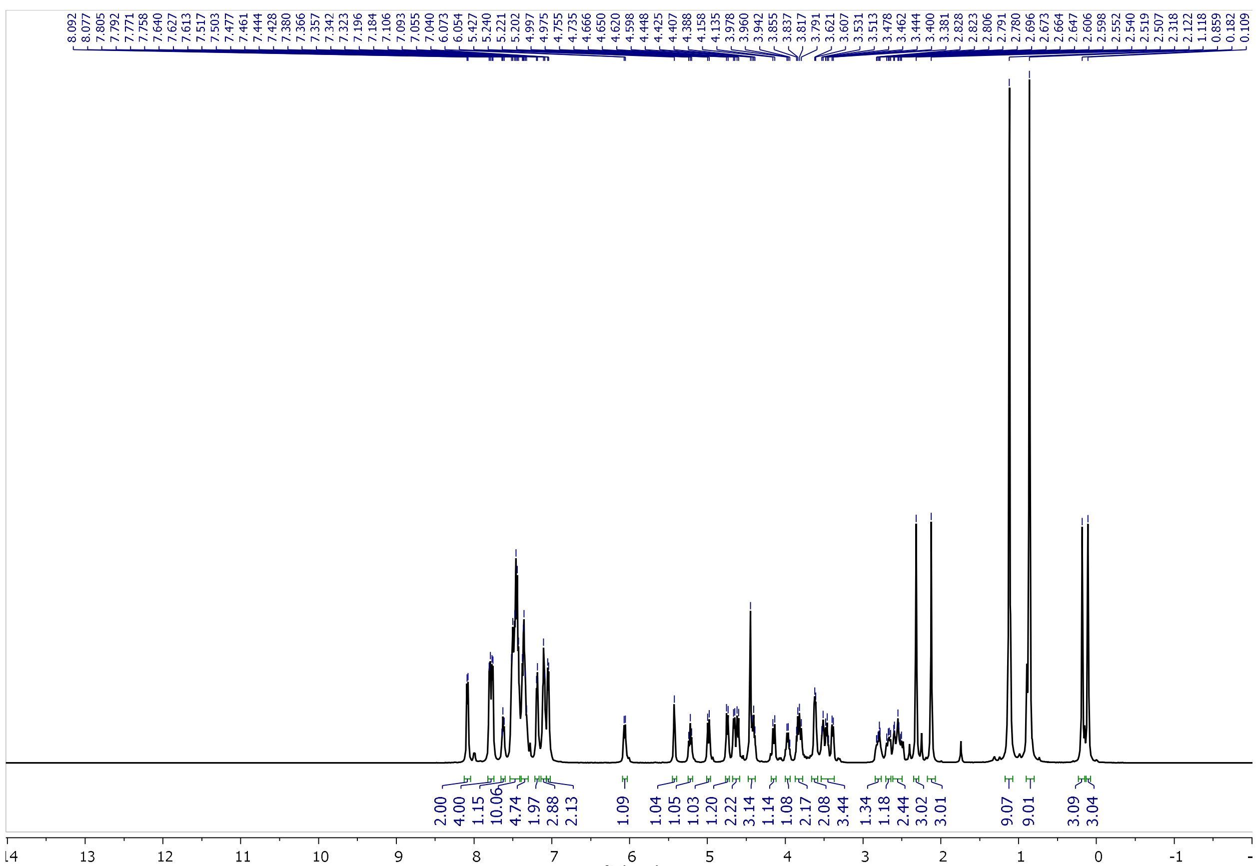
S20



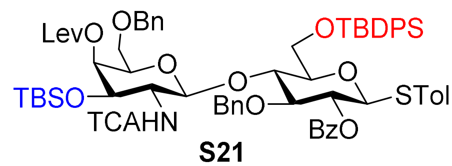
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S21**

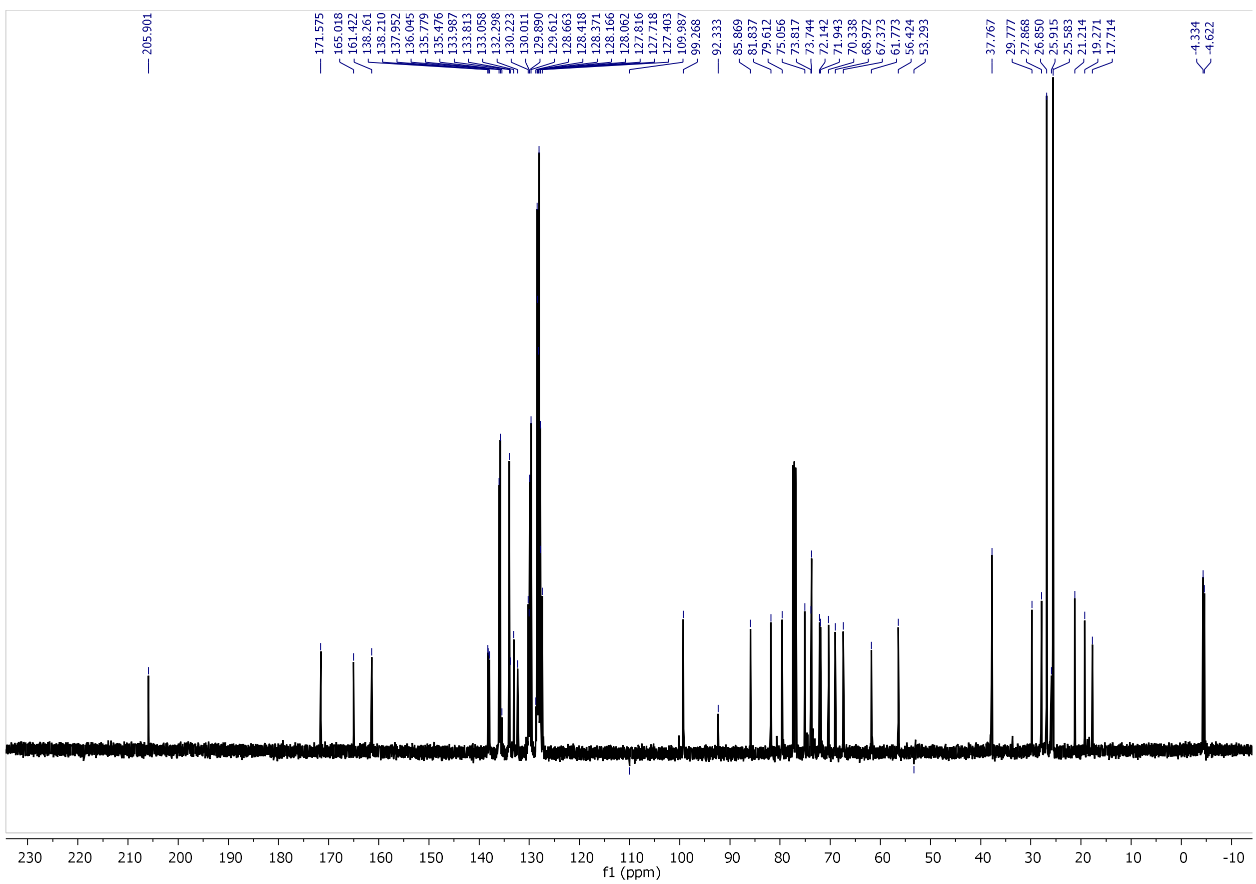


S21

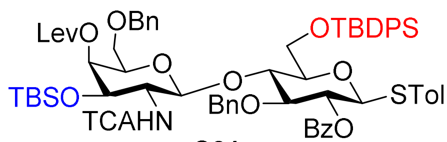


^{13}C-NMR ($CDCl_3$, 126 MHz) of **S21**

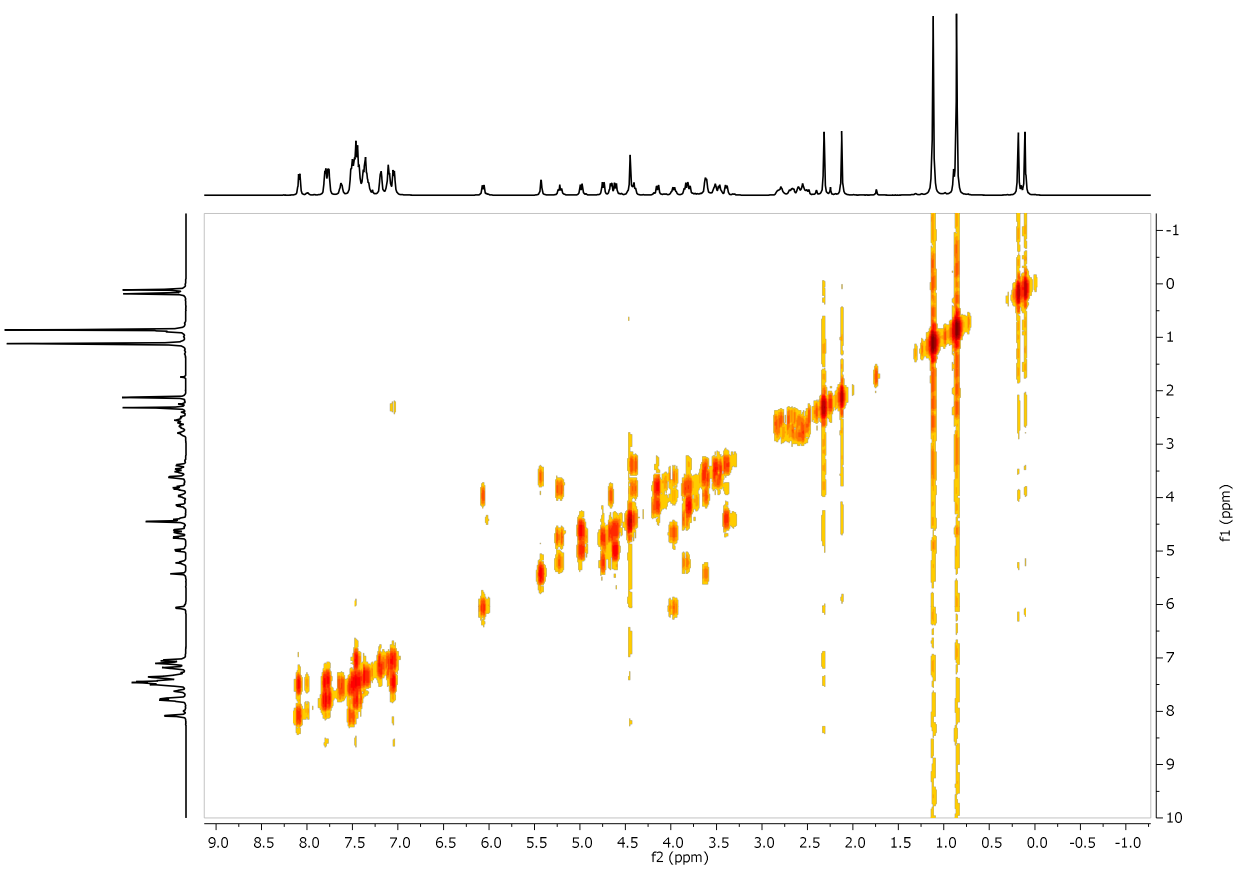




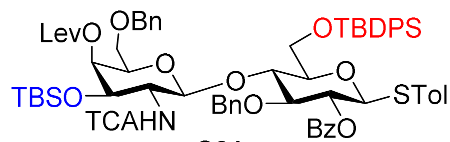
gCOSY ($CDCl_3$, 500 MHz) of **S21**



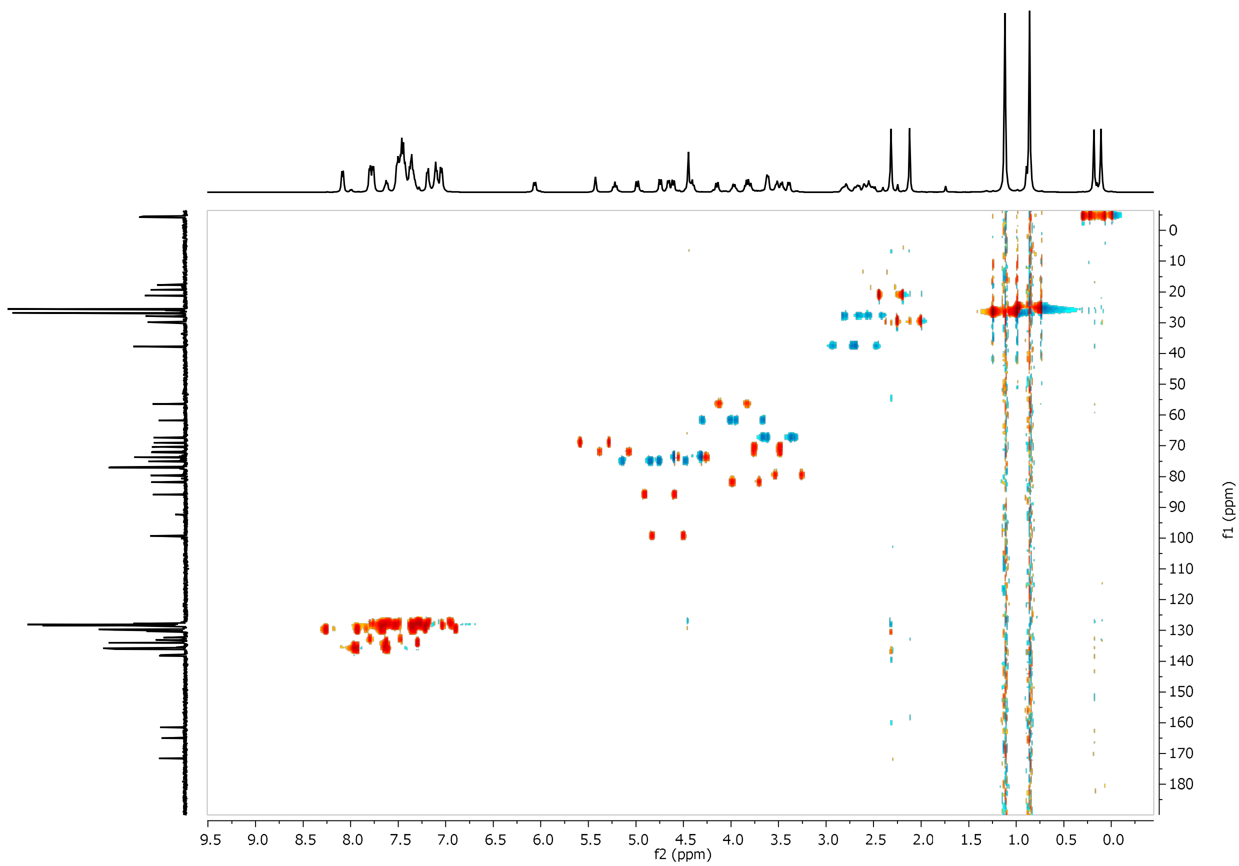
S21



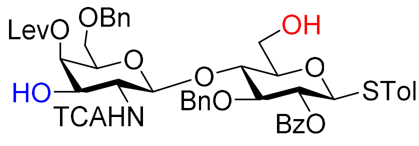
gHSQC ($CDCl_3$, 500 MHz) of **S21**



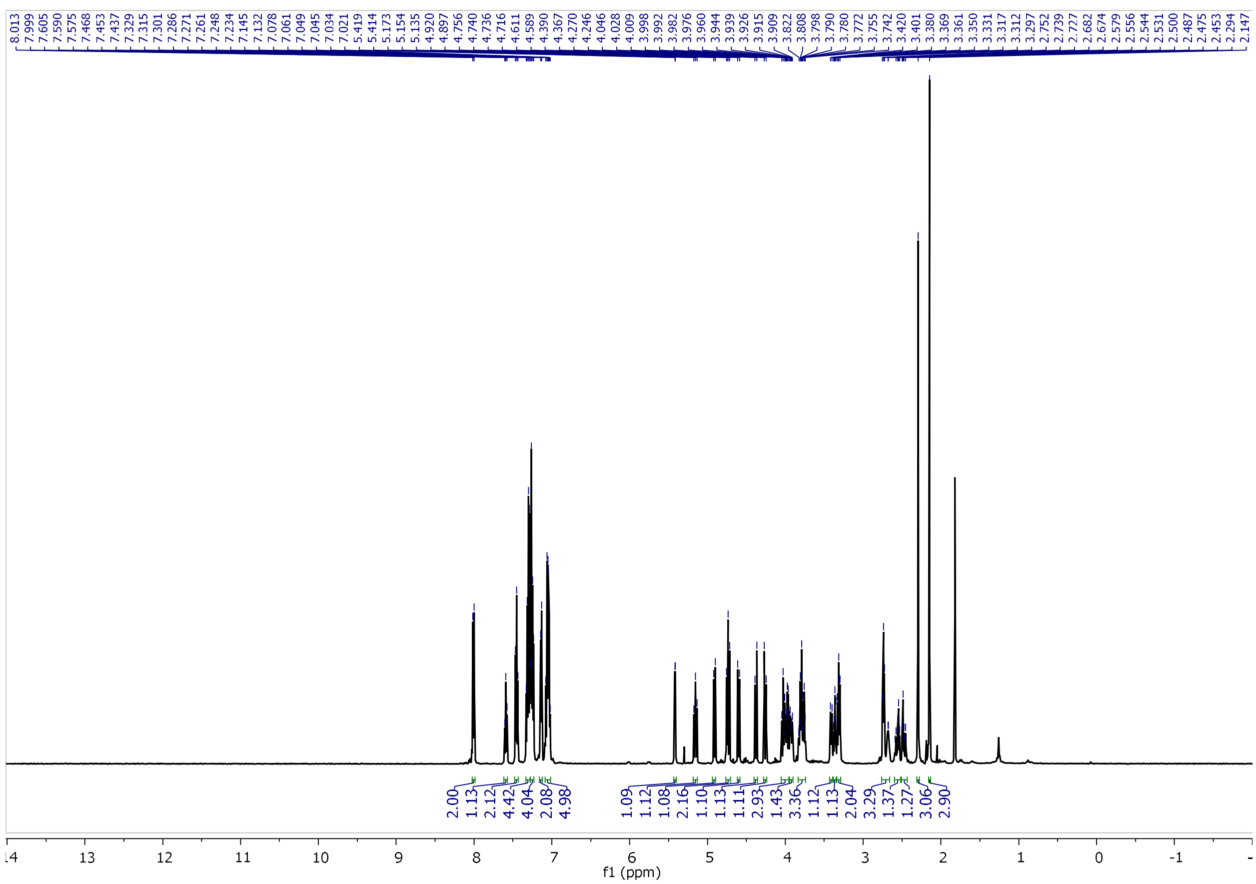
S21



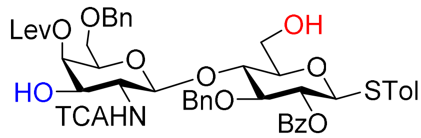
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S22**



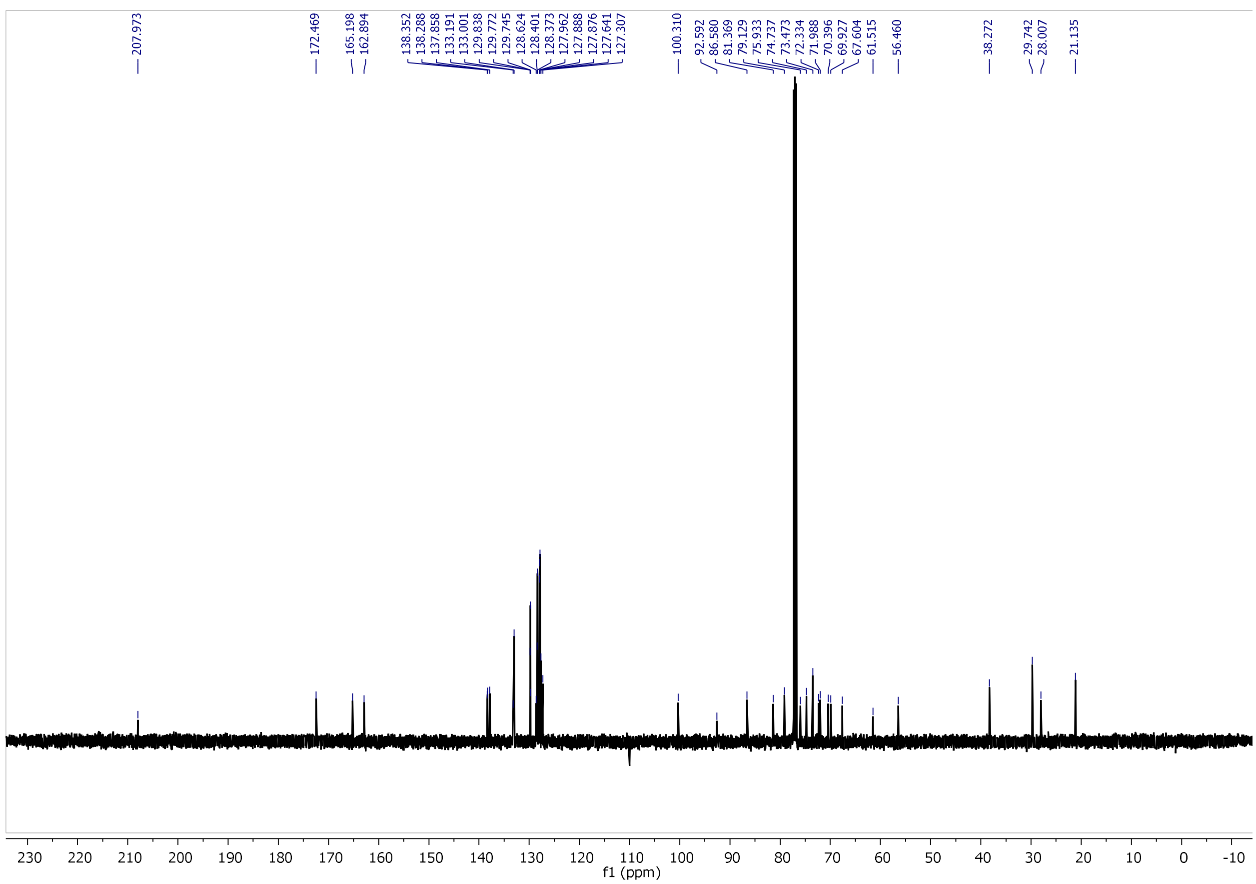
S22



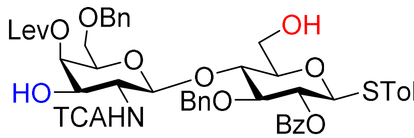
^{13}C-NMR ($CDCl_3$, 126 MHz) of **S22**



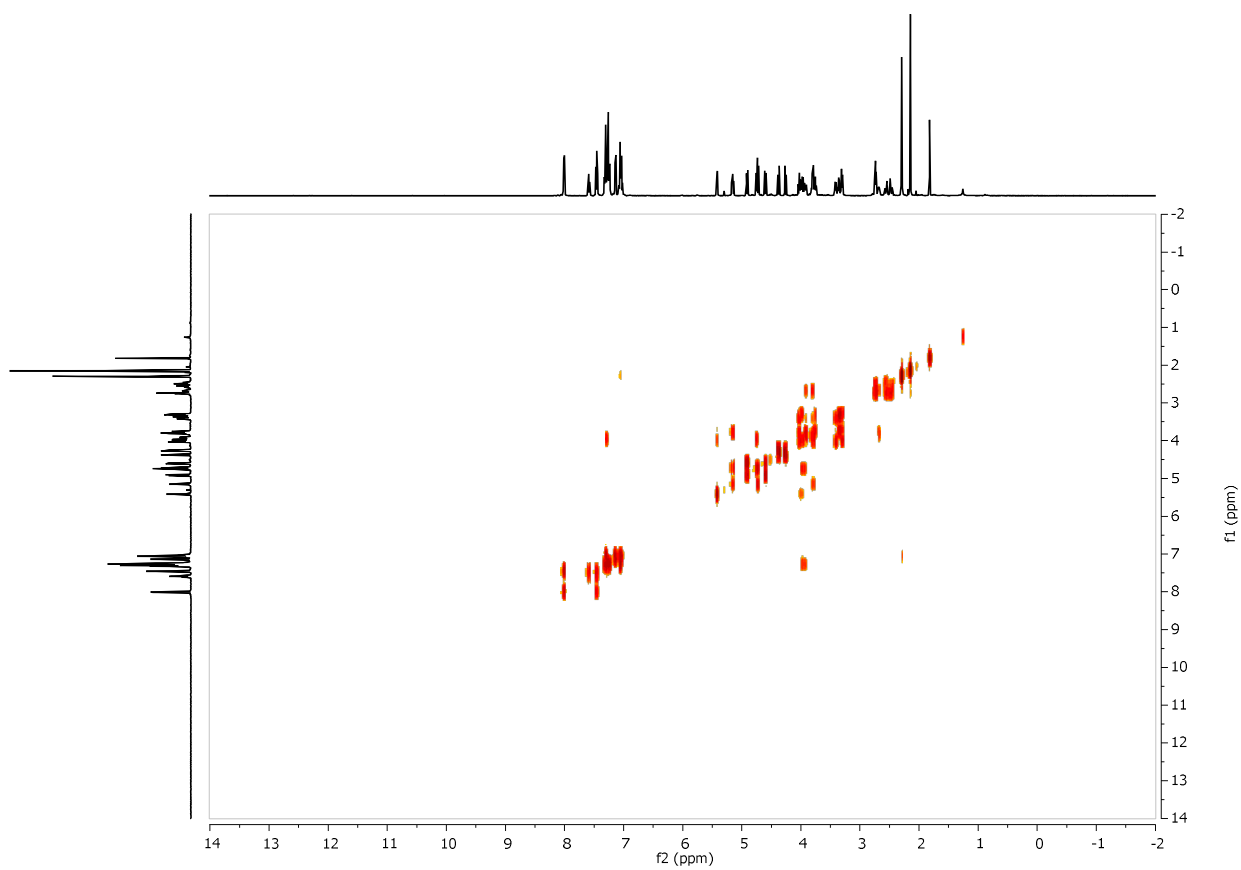
S22



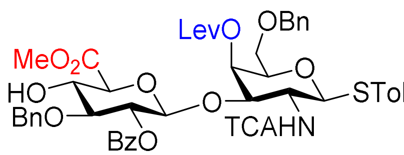
gCOSY ($CDCl_3$, 500 MHz) of **S22**



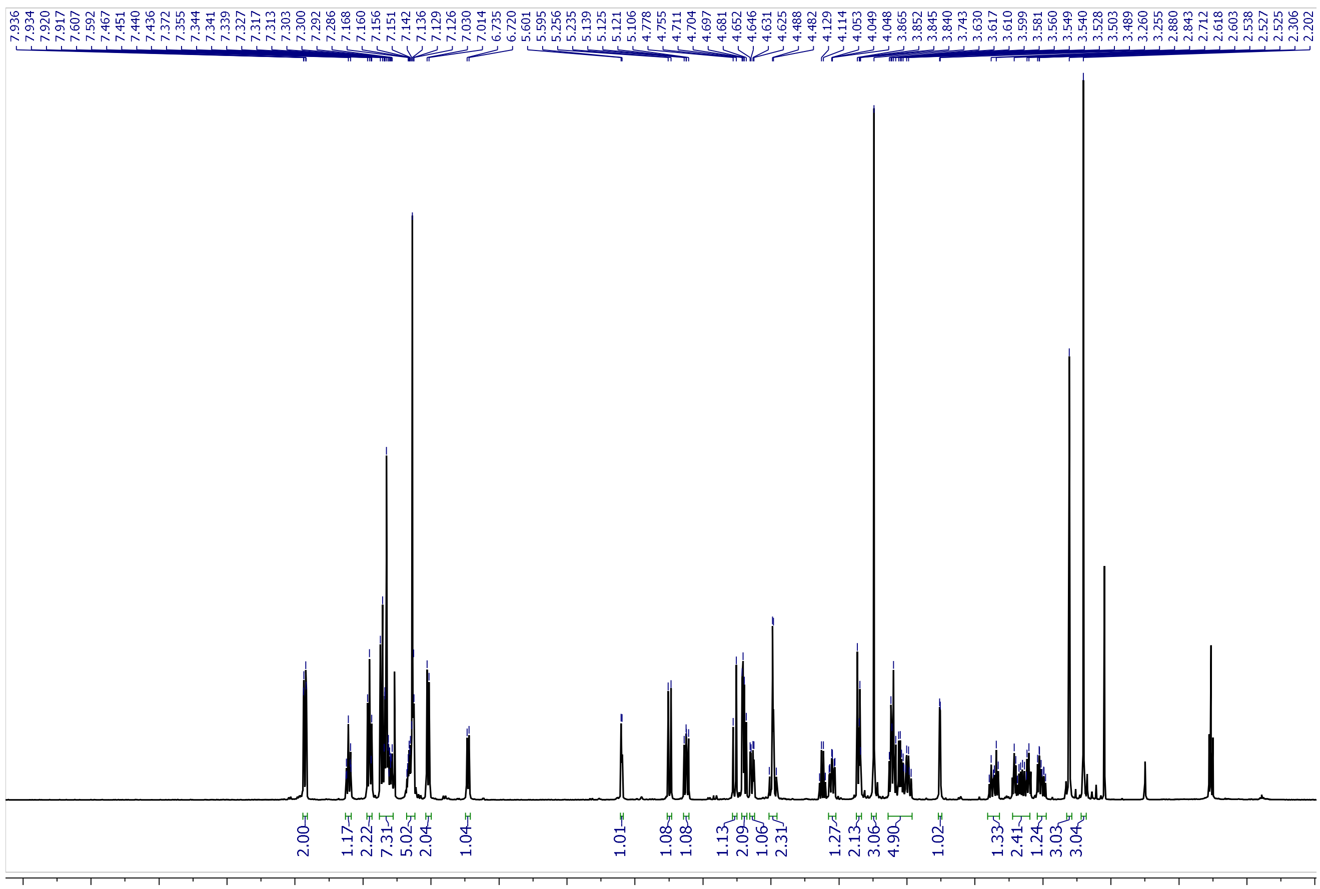
S22



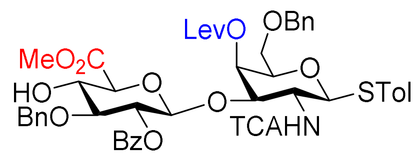
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S23**



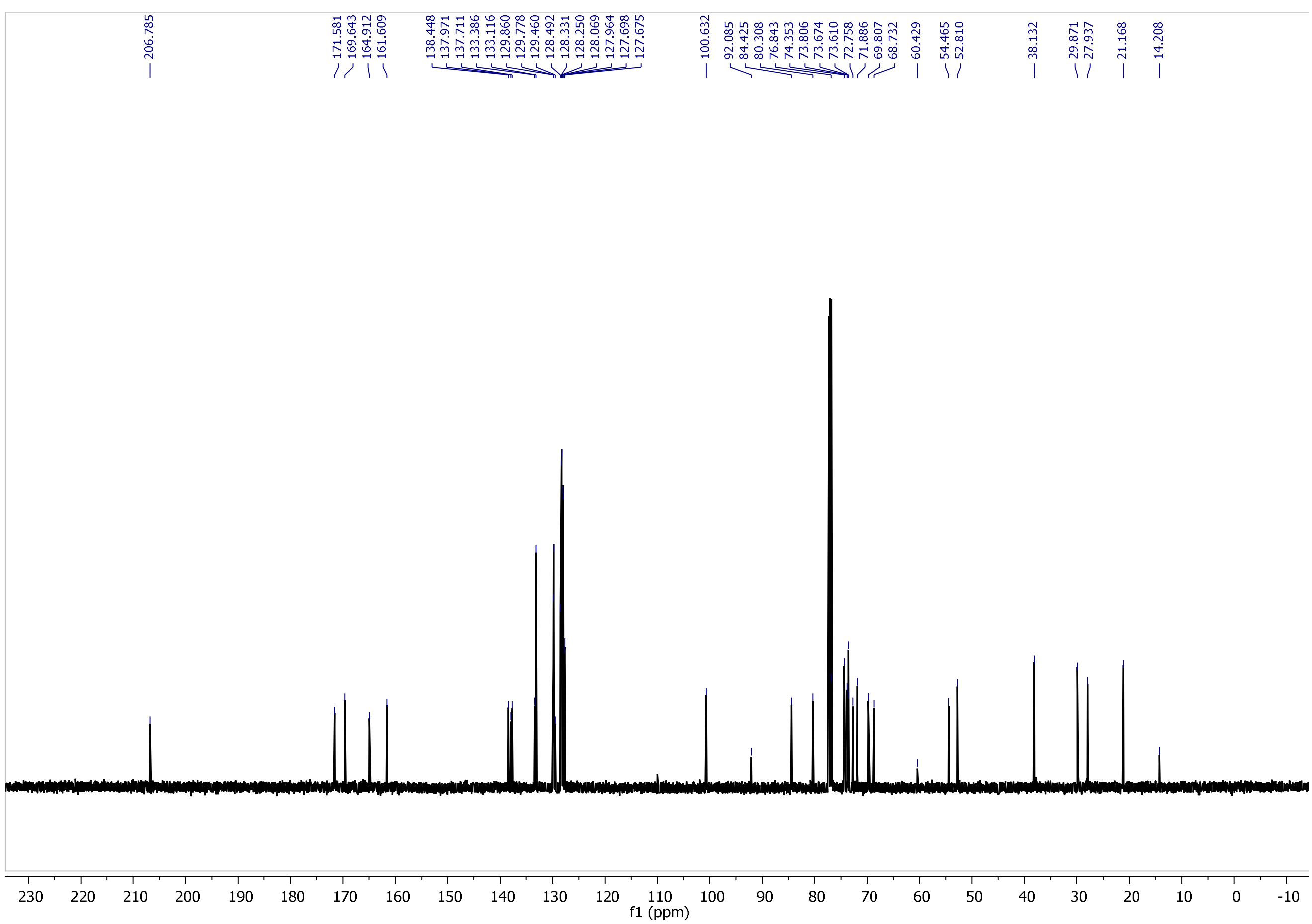
S23



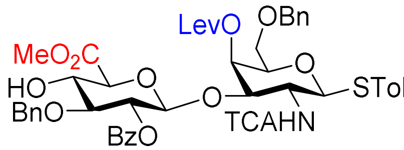
^{13}C-NMR ($CDCl_3$, 126 MHz) of **S23**



S23



gCOSY ($CDCl_3$, 500 MHz) of **S23**



S23