Supporting information

Chemical synthesis and anti-inflammatory activity of bikunin associated chondroitin sulfate 24-mer

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List of abbreviation:

Name	Abbreviation
Acetic acid	AcOH
Acetic anhydride	Ac_2O
Acetyl chloride	AcCl
***tert*-Butyldimethylsilyl chloride**	TBSCl
tert-Butyldimethylsilyl trifluoromethanesulfonate	TBSOTf
Camphorsulfonic acid	CSA
1,8-Diazabicyclo[5.4.0]undec-7-ene	DBU
Dichloromethane	DCM
2,5-Dihydroxy-benzoic acid	DHB
***N,N′*-Diisopropylcarbodiimide**	DIC
Dynamic light scattering	DLS
4-Dimethylaminopyridine	DMAP
Dimethylsulfoxide	DMSO
Equivalent	Equiv.
Ethyl acetate	EtOAc
Fluorescence activated cell sorting	FACS
Fluorescein isothiocyanate	FITC
***N*-Iodosuccinimide**	NIS
Levulinic acid	LevOH
***p*-Methoxyphenyl**	PMP
Molecular sieve	MS
2-Picolinic acid	PicoOH
Pyridine	Py.
Enzyme-linked immunosorbent assay	ELISA
Thin layer chromatography	TLC
Trichloroacetyl	TCA

Triethylamine	Et_3N
Trifluroacetyl	TFA
Trifluoromethanesulfonic acid	TfOH
2,4,6-Tri-ter-butylpyrimidine	TTBP
Silver trifluoromethanesulfonate	AgOTf

1. Experimental Section:

1.1.General experimental procedures and safety statement:

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. Chemicals used were reagent grade as supplied except where noted. Analytical thin-layer chromatography was performed using silica gel 60 F254 glass plates. Compounds were visualized by UV light (254 nm) and by staining with a yellow solution containing $Ce(NH_4)_2(NO_3)_6$ (0.5 g) and $(NH_4)_6Mo_7O_{24}$ $4H_2O$ (24.0 g) in 6% H_2SO_4 (500 mL). Flash column chromatography was performed on silica gel 60 (230-400 Mesh). Optical rotations were recorded on a Perkin Elmer 341 polarimeter (λ= 589 nm, 1 dm cell).

No unexpected or unusually high safety hazards were encountered during this work.

1.2.Mass spectrometry (MS) analysis:

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

1.3.Nuclear magnetic resonance analysis:

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

1.4.Characterization of anomeric stereochemistry:

The stereochemistry of the newly formed glycosidic linkages in the oligosaccharide and intermediates are determined by$^3JH_{1,H2}$ through ^{1}H-NMR and/or $^1J_{C1,H1}$ through gHMQC 2-D

NMR (without ^{1}H decoupling).The smaller coupling constants of $^{3}J_{H1,H2}$ (around 3 Hz) indicate α linkages and larger coupling constants $^{3}J_{H1,H2}$ (7.2 Hz or larger) indicate β linkages in glucose and galactosamine linkages. $^{1}J_{C1,H1}$ around 170 Hz suggests α linkages and 160 Hz suggests β linkages.[2]

1.5. General procedure for pre-activation based single-step glycosylation with *p*-TolSCl/AgOTf promoter:

A solution of donor and freshly activated molecular sieve (MS) Å (700 mg) in DCM (0.01M donor concentration) was stirred for 30 min. under room temperature (rt) and cooled to -78 °C. A solution of silver trifluoromethanesulfonate (AgOTf) (3 equiv. to donor) in anhydrous Et_2O/DCM (2 :1 v/v) was added to reaction solution without touching the wall of the flask. After 5 min., orange colored *p*-TolSCl (1 equiv. to donor) 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 disappeared in a few second indicating consumption of *p*-TolSCl promoter. TLC analysis could confirm the complete activation of donor in 5 minutes. A solution of acceptor with one equivalent 2,4,6-tri-*ter*-butylpyrimidine (TTBP) in DCM (2 mL) was added to the reaction via a syringe. The reaction was stirred for 1 h at -78 °C then it could be warmed up to 0 °C under stirring in 2 hours depending on the reactivity of donor and acceptor. Upon reaction completion, the reaction mixture was diluted with DCM, quenched by triethylamine (Et_3N) and filtered over Celite with DCM. The DCM solution was washed with $NaHCO_3$ and NaCl solution. The organic layer was collected, dried over Na_2SO_4, concentrated and purified by silica gel chromatography.

1.6. General procedure for glycosylation promoted by NIS/TfOH promoter:

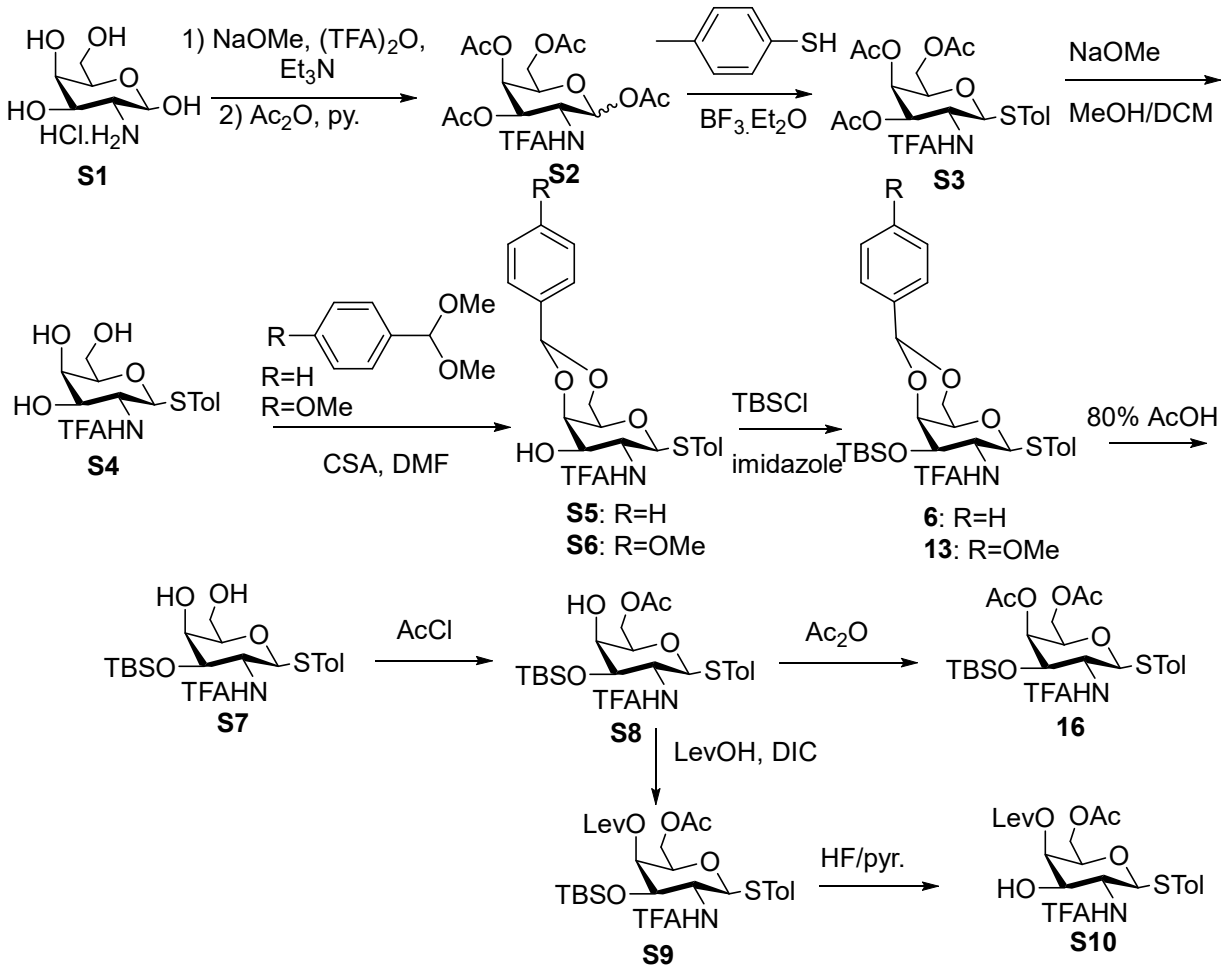
A mixture of acceptor (1 equiv.) and thioglycoside donor (1.5 to 2 equiv.) was dissolved and co-evaporated with anhydrous toluene (2× 20 mL) and dried in high vacuum. Then the mixture was dissolved in anhydrous DCM (typical final donor concentration 0.010 M), 4 Å molecular sieves was added and stirred at rt for 30 min. Then it was cooled to −30 °C followed by the addition of *N*-iodosuccinimide (NIS) (1.2 equiv. to donor) and trifluoromethanesulfonic acid (TfOH) (0.3 equiv. to donor). The reaction was stirred at −30 °C for 2 hours, if the reaction did not complete, the temperature was raised to 0 °C or rt till completion, after which it was quenched by

triethylamine (Et_3N) and filtered by Celite, and the filtrate was concentrated under reduced pressure. Then the residue was purified by flash column chromatography.

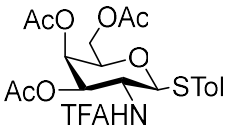
1.7.General procedure for removal of TBS:

The TBS-protected compound was dissolved in pyridine (Py.) (0.2 M) in a plastic flask and cooled down to 0 °C, then followed by the addition of 65–70% HF.pyridine solution (v/v 1:2 with respect to pyridine). The solution was stirred until complete disappearance of the starting material as judged from TLC analysis. The reaction mixture was diluted with ethylacetate (EtOAc) (30 mL) and washed with saturated aqueous $CuSO_4$ solution (20 mL). The aqueous phase was extracted with EtOAc (30 mL) twice and the combined organic layers were washed with 1 M HCl solution, then with saturated aqueous $NaHCO_3$ solution (3×50 mL). After drying over Na_2SO_4 and concentrated, the obtained residue was purified by flash column chromatography (Toluene/Acetone) to give the desired product.

1.8.Synthesis of monosaccharide building blocks:



***p*-Tolyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-*N*-trifluoroacetamido-1-thio-*β*-D-galactopyranoside S3:**

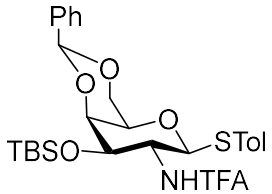


S3

To a solution of galactosamine hydrochloride **S1** (21 g, 93.4 mmol) in dry MeOH (250 mL), NaOMe (105 mL, 1.3 M solution in MeOH) was added at rt. After stirring for 40 min, the mixture was cooled down to 0 °C, then TFA anhydride (14.2 mL, 98.1 mmol) was added followed by adding Et_3N (13.6 mL, 94.0 mmol). The reaction mixture was stirred overnight at rt, then it was concentrated in vacuo. The residue was dissolved in pyridine (Py.) (300 mL) and acetic anhydride (Ac_2O) (150 mL) and 4-dimethylaminopyridine (DMAP) (6.4 g, 46.7 mmol) was added at 0 °C. The reaction was stirred for 24 hours at rt, then it was diluted with EtOAc, washed with 1 M HCl, $NaHCO_3$, and NaCl solutions, dried over Na_2SO_4, filtered, and concentrated. Flash chromatography (Hex:EtOAc, 3 : 1) gave a mixture of α,β anomers of 1,3,4,6-tetra-*O*-acetyl-2-

deoxy-2-trifluoroacetamido-D-galactopyranose **S2** (32.5 g, 75.5%). Comparison with literature data[3] confirms its identity. Compound **S2** (38.29 g, 86.4 mmol) and 4-methylbenzenethiol (11.8 g, 95 mmol) were dissolved in dry DCM (300 mL), followed by slow addition of boron trifluoride etherate (32.85 mL, 295 mmol) at 0 ^{O}C. The reaction was stirred at rt overnight under nitrogen. Upon completion, the reaction was quenched with a sat. $NaHCO_3$ solution, then diluted with DCM (100 mL) and extracted with DCM (3×100mL), washed with NaCl, dried over Na_2SO_4, concentrated and purified using column chromatography (Hex:EtOAc, 3:1) to afford the product **S3** (35.9 g, in 82%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 8.1 Hz, 2H), 7.14 – 7.10 (m, 2H), 7.07 (d, *J* = 9.4 Hz, 1H), 5.37 (dd, *J* = 3.3, 1.0 Hz, 1H), 5.22 (dd, *J* = 10.8, 3.3 Hz, 1H), 4.82 (d, *J* = 10.3 Hz, 1H), 4.27 – 4.07 (m, 3H), 3.97 – 3.91 (m, 1H), 2.33 (s, 3H), 2.11 (s, 3H), 2.02 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.75, 170.65, 170.27, 157.48, 157.18, 138.72, 133.35, 129.71, 127.98, 116.74, 114.45, 86.60, 74.49, 70.91, 66.71, 61.86, 49.91, 21.14, 20.65, 20.58, 20.40. ESI-MS: $C_{21}H_{24}F_3NO_8S$ $[M+NH_4]^+$ calcd: 525.1513, obsd: 525.1565.

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

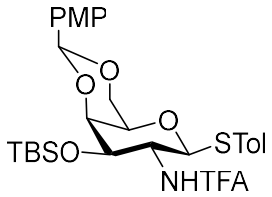


6

Compound **S3** (1 g, 2 mmol) was dissolved in DCM/MeOH (2:3, 50 mL), followed by addition of sodium metal at 0 ^{o}C until pH≈14 and the reaction was stirred for 2-3 h at 0 ^{o}C then Amberlite resin was added to adjust pH around 7. After filtration, the filtrate was concentrated and dried under vacuo to give product **S4** (0.68 g**,** 90%), which was used in the next step without further purification. Compound **S4** (0.3 g, 0.79 mmol) was dissolved in dry DMF (10 mL), and benzaldehyde dimethylacetal (0.21 mL, 1.4 mmol) was added. The pH was adjusted to 4 with a catalytic amount of camphorsulfonic acid (CSA) (91.4 mg, 0.39 mmol). The reaction mixture was stirred overnight at 60 ^{o}C. After the reaction was completed, it was neutralized with Et_3N (4-5 drops). Then it was diluted with EtOAc, washed with water, dried over Na_2SO_4, and purification of the resulting residue by flash chromatography (Hex:EtOAc:DCM, 5:1:1) gave compound **S5** (0.26 g, 70%) as a colorless amorphous solid. Compound **S5** (0.26 g, 0.55 mmol) was dissolved in

DMF (50 mL), then *tert*-butyldimethylsilyl chloride (TBSCl) (0.1 g, 0.66 mmol) and imidazole (75.4 mg, 1.1 mmol) were added. The reaction was stirred at rt for 2 h and upon completion, it was diluted with EtOAc, washed with H_2O, dried over Na_2SO_4, concentrated and purified by silica gel chromatography (Hex:EtOAc:DCM, 8:1:1) to afford **6** (0.29 g, 90%) as a white solid. $[\alpha_D{}^{20}]$ = -1.9 (C = 0.7, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.54 – 7.51 (m, 2H), 7.48 – 7.45 (m, 2H), 7.40 – 7.36 (m, 3H), 7.03 (d, *J* = 7.8 Hz, 2H), 6.34 (d, *J* = 7.4 Hz, 1H), 5.52 (s, 1H), 5.31 (d, *J* = 10.1 Hz, 1H), 4.51 (dd, *J* = 10.2, 3.3 Hz, 1H), 4.41 (dd, *J* = 12.3, 1.7 Hz, 1H), 4.10 (dd, *J* = 3.5, 1.0 Hz, 1H), 4.04 (dd, *J* = 12.4, 1.7 Hz, 1H), 3.72 – 3.65 (m, 1H), 3.59 – 3.58 (m, 1H), 2.32 (s, 3H), 0.84 (s, 9H), 0.06 (s, 3H), 0.02 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 138.39, 137.86, 133.75, 129.85, 128.90, 128.05, 127.40, 126.23, 100.65, 83.09, 75.99, 70.11, 70.02, 69.39, 53.82, 29.71, 25.51, 21.22, 18.00, -4.72, -4.82. ESI-MS: $C_{28}H_{36}F_3NO_5SSi$ $[M+NH_4]^+$ calcd: 601.2374, obsd: 601.2329.

***p*-Tolyl 4,6-*O*-(4-methoxy)benzylidene-3-*O*-*t*-butyldimethylsilyl-2-deoxy-2-*N*-trifluoroacetamido-1-thio-*β*-D-galactopyranoside 13:**

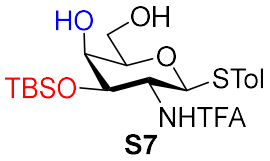


13

Compound **S4** (0.18 g, 0.47 mmol) was dissolved in in dry DMF (10 mL), and 4-methoxybenzaldyhyde dimethylacetal (0.14 mL, 0.85 mmol) was added. The pH was adjusted to 4 with a catalytic amount of CSA (54.8 mg, 0.24 mmol). The reaction mixture was stirred overnight at 60 ^{o}C. After the reaction completed, it was neutralized with Et_3N (4-5 drops), diluted with EtOAc, washed with water, and dried over Na_2SO_4. Purification of the resulting residue by flash chromatography (Hex:EtOAc:DCM, 7:1:1) gave compound **S6** (0.15 g, 65%) as a colorless amorphous solid. Compound **S6** (0.15 g, 0.30 mmol) was dissolved in DMF (50 mL), then TBSCl (54 mg, 0.36 mmol) and imidazole (41 mg, 0.60 mmol) were added. The reaction was stirred at rt for 2 h. Upon completion, it was diluted with EtOAc, washed with H_2O, dried over Na_2SO_4, concentrated and purified by silica gel chromatography (Hex:EtOAc:DCM, 8:1:1) to afford **13** (0.17 g, 92%) as a white solid. $[\alpha_D{}^{20}]$ = +2.1 (C = 1.35, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.54 – 7.50 (m, 2H), 7.40 – 7.37 (m, 2H), 7.06 (d, *J* = 7.9 Hz, 2H), 6.91 – 6.88 (m, 2H), 6.34

(d, J = 7.5 Hz, 1H), 5.47 (s, 1H), 5.29 (d, J = 10.1 Hz, 1H), 4.49 (dd, J = 10.4, 3.4 Hz, 1H), 4.38 (dd, J = 12.4, 1.6 Hz, 1H), 4.08 (d, J = 3.4 Hz, 1H), 4.02 (dd, J = 12.4, 1.7 Hz, 1H), 3.84 (s, 3H), 3.72 – 3.65 (m, 1H), 3.57 (q, J = 1.5 Hz, 1H), 2.34 (s, 3H), 0.83 (s, 9H), 0.06 (s, 3H), 0.02 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.98, 157.18, 138.37, 133.78, 130.45, 129.85, 127.55, 127.45, 113.38, 100.62, 83.18, 75.94, 70.19, 70.02, 69.36, 55.31, 53.82, 25.52, 21.25, 18.00, -4.70, -4.81. ESI-MS: $C_{29}H_{38}F_3NO_6SSi$ $[M+NH_4]^+$ calcd: 631.2479, obsd: 631.2491.

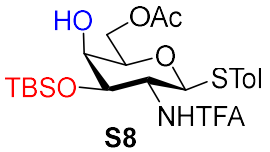
***p*-Tolyl 3-*O*-*t*-butyldimethylsilyl-2-deoxy-2-*N*-trifluoroacetamido-1-thio-*β*-D-galactopyranoside S7:**



S7

Compound **9** (1.5 g, 2.3 mmol) was dissolved in aqueous acetic acid (AcOH) 80% (50 mL). The mixture was stirred at 80 °C for 3 h. Upon completion, the mixture was concentrated *in vacuo*, and the residue was purified with flash chromatography (DCM:MeOH, 20:1) to give **S7** (1 g, 89.3%) as white solid. $[\alpha_D{}^{20}]$ = -2.2 (C = 0.09, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.36 (d, J = 7.9 Hz, 2H), 7.10 (d, J = 7.9 Hz, 2H), 6.67 (d, J = 7.4 Hz, 1H), 4.69 (d, J = 9.5 Hz, 1H), 3.91 – 3.72 (m, 4H), 3.60 – 3.54 (m, 2H), 2.49 – 2.39 (m, 1H), 2.32 (s, 3H), 0.84 (s, 9H), 0.06 (s, 3H), 0.04 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 158.29, 157.99, 139.01, 134.05, 129.94, 125.70, 116.85, 114.55, 83.92, 80.22, 73.90, 69.89, 62.77, 52.19, 25.75, 21.18, 18.19, -4.10, -4.76. ESI-MS: $C_{21}H_{32}F_3NO_5SSi$ $[M+NH_4]^+$ calcd: 513.2061, obsd: 513.2081.

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

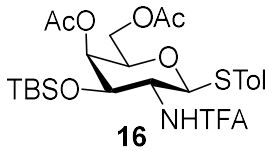


S8

To a solution of **S7** (3 g, 6.1 mmol) in DCM (30 mL), acetyl chloride (AcCl) (0.475 mL, 6.7 mmol) and lutidine (1.6 mL, 13.7 mmol) were added at 0 °C. The reaction was stirred at 0 °C for 2 h, then the temperature was raised to rt. Upon completion, the mixture was washed with 1M HCl, $NaHCO_3$, and NaCl, dried over Na_2SO_4, concentrated and the residue was purified with silica gel chromatography (Hex:EtOAc:DCM, 4:1:1) to give **S8** (3 g, 92%) as white solid. ^{1}H NMR (500

MHz, Chloroform-*d*) δ 7.47 (d, *J* = 9.0 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 4.88 (d, *J* = 10.4 Hz, 1H), 4.39 (dd, *J* = 11.6, 7.9 Hz, 1H), 4.21 (dd, *J* = 11.6, 4.3 Hz, 1H), 4.08 (dd, *J* = 9.8, 3.2 Hz, 1H), 3.98 (t, *J* = 9.7 Hz, 1H), 3.81 – 3.76 (m, 2H), 2.48 (s, 1H), 2.28 (s, 3H), 1.97 (s, 3H), 0.85 (s, 9H), 0.09 (s, 3H), 0.04 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.18, 157.89, 157.60, 137.95, 132.61, 129.55, 128.98, 116.85, 114.56, 85.83, 75.48, 72.15, 68.80, 63.66, 52.79, 25.46, 21.09, 20.76, 17.73, -4.55, -5.12. ESI-MS: $C_{23}H_{34}F_3NO_6SSi$ $[M+NH_4]^+$ calcd: 555.2166, obsd: 555.2208.

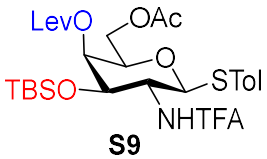
***p*-Tolyl 4,6-di-*O*-acetyl-3-*O*-*t*-butyldimethylsilyl-2-deoxy-2-*N*-trifluoroacetamido-1-thio-*β*-D-galactopyranoside 16:**



16

Compound **S7** (1 g, 2 mmol) was dissolved in pyridine (8 mL), then Ac_2O (4 mL) was added and the reaction was stirred for 4 h. After completion, the reaction was diluted with EtOAc, washed with 1 M HCl, $NaHCO_3$, and NaCl, dried over Na_2SO_4, concentrated and purified by flash chromatography (Hex:EtOAc:DCM, 4:1:1) to give **16** (1.1 g, 94%) as white solid. $[\alpha_D{}^{20}]$ = +15.1 (C = 0.57, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 7.7 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 1H), 5.24 (d, *J* = 3.3 Hz, 1H), 4.98 (d, *J* = 10.4 Hz, 1H), 4.15 – 4.04 (m, 3H), 3.94 – 3.83 (m, 2H), 2.31 (s, 3H), 2.07 (s, 3H), 2.00 (s, 3H), 0.79 (s, 9H), 0.06 (s, 3H), -0.00 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.74, 170.12, 157.51, 157.21, 138.31, 132.85, 129.64, 128.73, 116.77, 114.48, 74.85, 69.30, 62.62, 25.30, 21.12, 20.67, 20.65, 17.56, -4.67, -5.38. ESI-MS: $C_{25}H_{36}F_3NO_7SSi$ $[M+H]^+$ calcd: 580.2007, obsd: 580.2026.

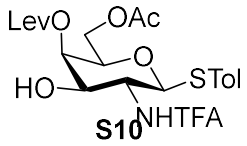
***p*-Tolyl 6-*O*-acetyl-3-*O*-*t*-butyldimethylsilyl-2-deoxy-4-*O*-levulinoyl-2-*N*-trifluoroacetamido-1-thio-*β*-D-galactopyranoside S9:**



S9

Compound **S8** (3 g, 5.6 mmol) was dissolved in DCM (30 mL), then levulinic acid (LevOH) (0.86 mL, 8.4 mmol), *N,N'*-diisopropylcarbodiimide (DIC) (1.1 mL, 7.4 mmol) and DMAP (0.886 g, 7.3 mmol) were added. The reaction mixture was stirred at 40 °C. Upon completion, the mixture was washed with 1 M HCl, $NaHCO_3$, and NaCl solutions, dried over Na_2SO_4, concentrated and the crude was purified with silica gel chromatography (Hex:EtOAc:DCM, 5:1:1) to afford **S9** (3 g, 84.7%) as white solid. $[\alpha_D^{20}] = +17.0$ (C = 0.54, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.41 – 7.37 (m, 2H), 7.12 – 7.08 (m, 2H), 6.80 (d, *J* = 8.6 Hz, 1H), 5.25 (dd, *J* = 3.3, 0.9 Hz, 1H), 5.01 (d, *J* = 10.4 Hz, 1H), 4.16 – 4.11 (m, 3H), 3.91 – 3.83 (m, 2H), 2.79 – 2.73 (m, 1H), 2.71 – 2.63 (m, 2H), 2.58 – 2.51 (m, 1H), 2.33 (s, 3H), 2.18 (s, 3H), 2.03 (s, 3H), 0.79 (s, 9H), 0.06 (s, 3H), 0.00 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.37, 171.67, 170.79, 157.35, 157.06, 138.41, 133.11, 129.66, 128.48, 116.77, 114.47, 77.26, 74.91, 69.51, 62.49, 37.88, 29.80, 27.88, 25.71, 25.36, 21.19, 21.16, 20.74, 17.60, 17.59, -4.64, -5.41. ESI-MS: $C_{28}H_{40}F_3NO_8SSi$ $[M+NH_4]^+$ calcd: 653.2534, obsd: 653.2578.

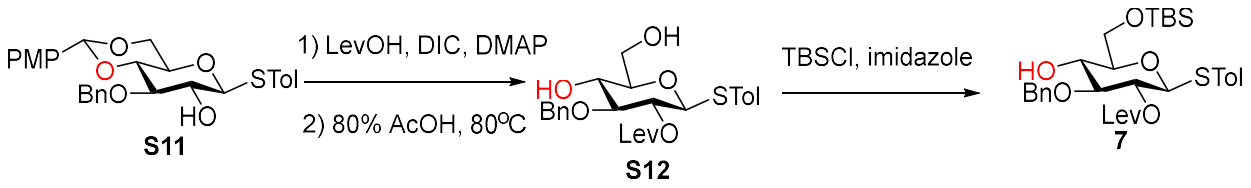
***p*-Tolyl 6-*O*-acetyl-2-deoxy-4-*O*-levulinoyl-2-*N*-trifluoroacetamido-1-thio-*β*-D-galactopyranoside S10:**



S10

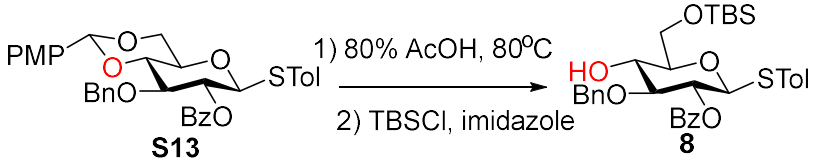
Following the general procedure for TBS removal, monosaccharide acceptor **S10** was obtained (1.11 g, 90%) from **S9** (1.5 g, 2.36 mmol). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 8.9 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 5.28 (d, *J* = 3.2 Hz, 1H), 4.81 (d, *J* = 10.3 Hz, 1H), 4.07 (d, *J* = 6.3 Hz, 2H), 3.99 (ddd, *J* = 11.1, 8.4, 3.3 Hz, 1H), 3.89 – 3.78 (m, 3H), 2.76 – 2.68 (m, 2H), 2.61 – 2.48 (m, 2H), 2.30 (s, 3H), 2.10 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 209.50, 172.47, 170.81, 158.08, 157.78, 138.30, 133.13, 129.57, 128.47, 116.90, 114.62, 86.08, 74.68, 70.40, 69.74, 62.30, 52.71, 38.16, 29.63, 28.11, 21.10, 20.65, 14.12. ESI-MS: $C_{22}H_{26}F_3NO_8S$ $[M+NH_4]^+$ calcd: 539.1669, obsd: 539.1698.

***p*-Tolyl 3-*O*-benzyl-6-*O*-*t*-butyldimethylsilyl-2-*O*-levulinoyl-1-thio-*β*-D-glucopyranoside 7**:



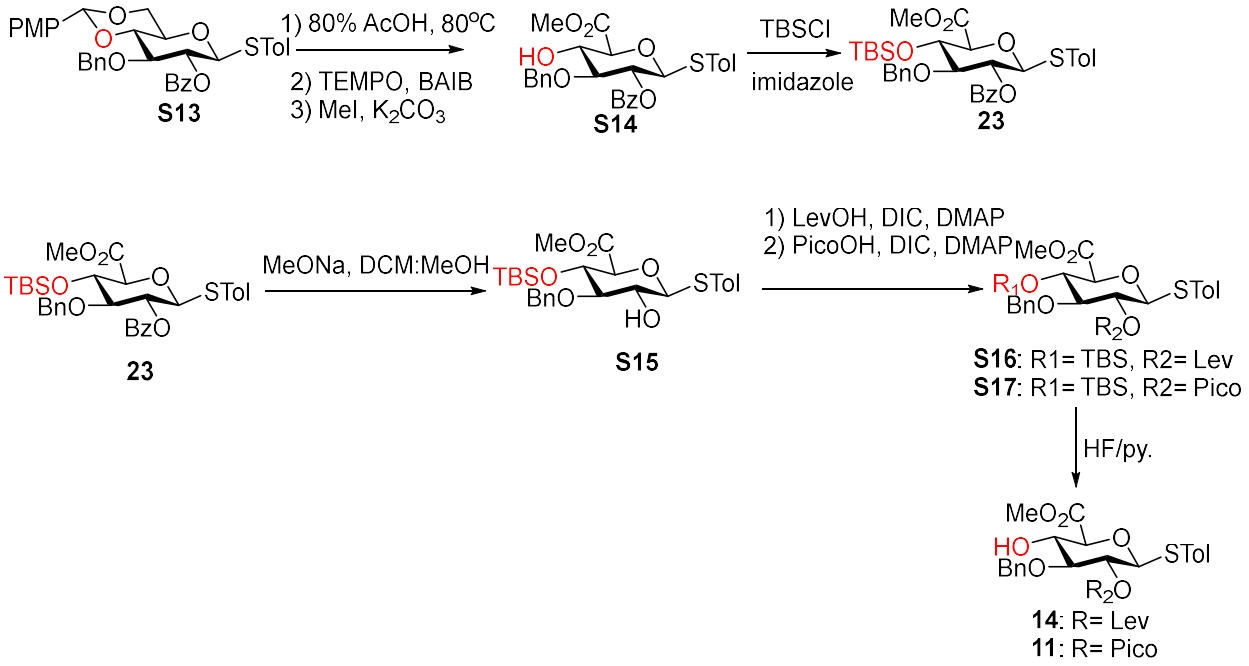
Compound **S11**[4] (0.11 g, 0.23 mmol) was dissolved in DCM (15 mL), then LevOH (0.05 mL, 0.49 mmol), DIC (0.07 mL, 0.48 mmol) and DMAP (0.056 g, 0.46 mmol) were added and the reaction was stirred at 40 °C for 2h. The mixture was washed with 1 M HCl, $NaHCO_3$, and NaCl solutions, dried over Na_2SO_4, concentrated. The crude mixture was then dissolved in DCM (4 mL) and 80% AcOH (25 mL) was added. The reaction mixture was stirred at 80 °C for 2 h. Upon completion, the mixture was concentrated and the crude was purified with silica gel chromatography (Hex:EtOAc, 2:1) to afford **S12** (0.102 g, 93.6% in 2 steps) as white solid. Next, compound **S12** (0.102 g, 0.21 mmol) was dissolved in DCM (10 mL) and TBSCl (0.036 g, 0.24 mmol) and imidazole (0.016 g, 0.24 mmol) were added. The reaction was stirred and after completion, it was concentrated and purified through silica gel chromatography (Hex:EtOAc, 5:1) to afford **7** (0.115 g, 90.5%) as colorless glassy solid. $[\alpha_D{}^{20}]$ = -6.5 (C = 8.9, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.40 – 7.36 (m, 2H), 7.35 – 7.24 (m, 5H), 7.12 – 7.07 (m, 2H), 4.93 (dd, *J* = 10.1, 9.1 Hz, 1H), 4.57 (d, *J* = 10.0 Hz, 1H), 3.92 – 3.84 (m, 2H), 3.70 (t, *J* = 9.2 Hz, 1H), 3.54 (d, *J* = 8.9 Hz, 1H), 3.37 (dt, *J* = 9.8, 5.0 Hz, 1H), 3.02 (s, 1H), 2.79 – 2.68 (m, 2H), 2.64 – 2.51 (m, 2H), 2.33 (s, 3H), 2.18 (s, 3H), 0.91 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.29, 171.42, 138.32, 138.00, 132.86, 129.60, 129.08, 128.46, 127.92, 127.77, 86.53, 83.68, 78.61, 74.64, 72.37, 71.66, 64.21, 37.85, 29.90, 28.14, 25.87, 21.16, 18.26, -5.44. ESI-MS: $C_{31}H_{44}O_7SSi$ $[M+NH_4]^+$ calcd: 606.2915, obsd: 606.2990.

***p*-Tolyl 2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*t*-butyldimethylsilyl-1-thio-*β*-D-glucopyranoside 8**:

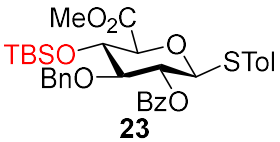


Compound **S13**[4] (0.12 g, 0.2 mmol) was dissolved in DCM (4 mL) and 80% AcOH (25 mL) was added. The reaction mixture was stirred at 80 °C for 2 h. Upon completion, the mixture was concentrated and the crude was purified with silica gel chromatography (Hex:EtOAc, 2:1) to afford the diol (0.091 g, 95.7%) as white solid. Next, the diol (0.091 g, 0.19 mmol) was dissolved in DCM (10 mL), and TBSCl (0.031 g, 0.21 mmol) and imidazole (0.019 g, 0.28 mmol) were added.

The reaction was stirred and after completion, it was concentrated and purified through silica gel chromatography (Hex:EtOAc, 5:1) to afford **8** (0.1 g, 91%) as colorless glassy solid. [α_D ^{20}] = +13.3 (C = 6.2, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.09 – 8.04 (m, 2H), 7.62 – 7.58 (m, 1H), 7.50 – 7.44 (m, 2H), 7.37 – 7.33 (m, 2H), 7.23 – 7.12 (m, 5H), 7.09 – 7.05 (m, 2H), 5.21 (dd, *J* = 10.0, 9.0 Hz, 1H), 4.75 (d, *J* = 10.1 Hz, 1H), 4.72 – 4.71 (d, *J* = 1.1 Hz, 2H), 3.98 – 3.88 (m, 2H), 3.80 (td, *J* = 9.2, 1.9 Hz, 1H), 3.71 (t, *J* = 8.9 Hz, 1H), 3.47 (dt, *J* = 9.8, 5.0 Hz, 1H), 3.07 (d, *J* = 2.0 Hz, 1H), 2.32 (s, 3H), 0.94 (s, 9H), 0.14 (s, 3H), 0.12 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.18, 138.03, 137.91, 133.18, 133.06, 129.94, 129.87, 129.57, 129.02, 128.42, 128.34, 128.03, 127.72, 86.64, 83.57, 78.63, 74.69, 72.65, 72.00, 64.35, 25.90, 21.16, 18.29, -5.41. ESI-MS: $C_{33}H_{42}O_6SSi$ $[M+NH_4]^+$ calcd: 612.2810, obsd: 612.2868.



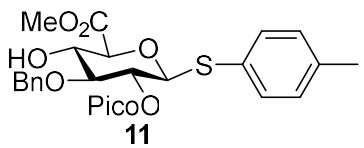
Methyl (*p*-tolyl 3-*O*-benzyl-2-*O*-benzoyl-4-*O*-*t*-butyldimethylsilyl-1-thio-*β*-D-glucopyranosyluronate) 23:



Compound **S13**[4] (1.5 g, 2.5 mmol) was dissolved in DCM (10 mL) and then 80% AcOH solution (30 mL) was added. The reaction mixture was stirred at 80 °C for 2 h. Upon completion, the mixture was concentrated and the crude was purified with silica gel chromatography (Hex:EtOAc,

2:1) to afford the diol (1.1 g, 91.7%) as white solid. To a solution of the resulting diol (1.1 g, 2.6 mmol) in DCM/*t*BuOH/H_2O (4:1:1, 18 mL), TEMPO (0.107 g, 0.69 mmol) and BAIB (1.47 g, 4.6 mmol) were added. The reaction was stirred for 5 h till oxidation of **17** was completed (monitored by TLC). Then the reaction was quenched with brine (5 mL) and extracted with DCM (3*15 mL). The organic layers were combined and dried over Na_2SO_4 and concentrated under vacuo. The residue was then dissolved in dry DMF (6 mL) and methyl iodide (1.4 mL, 22.9 mmol) and K_2CO_3 (1.6 g, 11.4 mmol) were added. The mixture was stirred overnight, then diluted with EtOAc (50 mL), washed with saturated $NaHCO_3$, brine, dried over Na_2SO_4, concentrated and the residue was purified using column chromatography (Hex:EtOAc, 4:1) to give **S14** (1 g, 86%% in 2 steps). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.83 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.58 – 7.54 (m, 3H), 7.39 – 7.36 (m, 2H), 7.16 – 7.06 (m, 7H), 5.41 – 5.36 (m, 1H), 4.76 (d, *J* = 11.6 Hz, 1H), 4.68 (d, *J* = 11.6 Hz, 1H), 4.65 (d, *J* = 9.5 Hz, 1H), 4.03 (d, *J* = 9.4 Hz, 1H), 3.78 (s, 3H), 3.63 (d, *J* = 3.7 Hz, 1H), 2.25 (s, 3H).^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.90, 164.74, 142.07, 137.51, 134.80, 133.39, 129.91, 129.83, 129.47, 129.07, 128.36, 128.30, 128.25, 128.10, 127.71, 125.99, 93.09, 81.51, 77.81, 74.61, 71.39, 67.89, 52.81, 21.39. Compound **S14** (1 g, 1.97 mmol) was dissolved in py. (15 mL), then TBSCl (0.89 g, 5.9 mmol) was added. The reaction was heated at 50 °C overnight till the reaction was completed. The mixture was diluted with EtOAc (50 mL), washed with 1M HCl, $NaHCO_3$, NaCl, concentrated and purified with silica gel chromatography (Hex:EtOAc, 6:1) to afford **23** (1 g, 81.9% yield) as white solid.^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.04 – 8.00 (m, 2H), 7.44 – 7.32 (m, 5H), 7.15 – 7.06 (m, 7H), 5.34 (dd, *J* = 9.9, 8.7 Hz, 1H), 4.86 (d, *J* = 9.9 Hz, 1H), 4.67 (s, 2H), 4.08 – 4.01 (m, 2H), 3.79 (s, 3H), 3.75 (t, *J* = 8.3 Hz, 1H), 2.30 (s, 3H), 0.87 (s, 9H), -0.00 (d, *J* = 3.7 Hz, 6H).^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.45, 165.10, 162.37, 138.30, 137.56, 133.30, 133.21, 129.80, 129.74, 129.70, 128.77, 128.60, 128.45, 128.10, 127.60, 127.45, 87.17, 83.87, 80.25, 77.44, 75.15, 72.30, 72.14, 52.43, 25.76, 21.18, 17.90, -3.94, -5.17. ESI-MS: $C_{33}H_{42}O_5SSi$ $[M+H]^+$ calcd: 579.2595, obsd: 579.2589.

Methyl (*p*-tolyl 3-*O*-benzyl-2-*O*-picolinoyl-1-thio-*β*-D-glucopyranosyluronate) 11:

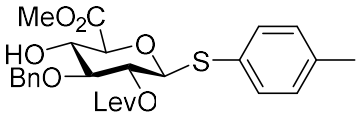


11

Compound **23** (1.5 g, 2.4 mmol) was dissolved in dry DCM/MeOH (2:3, 50 mL), followed by the addition of sodium metal until pH≈14 and the reaction was stirred for 2-3 h at rt. Amberlite resin

was then added to adjust pH to around 7. After filtration, the filtrate was concentrated and the residue was purified with silica gel chromatography (Hex:EtOAc, 8:1) to give **S15** (1 g**,** 80%) as a white solid. To a solution of **S15** (0.3 g, 0.58 mmol) in DCM (5 mL), 2-picolinic acid (PicoOH) (0.14 g, 1.2 mmol), DIC (0.179 mL, 1.2 mmol) and DMAP (0.14 g, 1.2 mmol) were added and the reaction mixture was stirred at 40 °C for 2 h. Upon completion, the mixture was washed with 1 M HCl, $NaHCO_3$, and NaCl solutions, dried over Na_2SO_4, concentrated and the crude was purified with silica gel chromatography (Hex:EtOAc, 4:1) to afford the product **S17** (0.32 g, 89%) as a white solid. Following the general procedure for TBS removal, monosaccharide acceptor **11** was obtained (0.24 g, 92%) as a white solid. $[\alpha_D{}^{20}]$ = +10 (C = 0.2, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.75 (d, *J* = 5.0 Hz, 1H), 8.11 (d, *J* = 7.8 Hz, 1H), 7.82 (t, *J* = 7.8 Hz, 1H), 7.49 – 7.43 (m, 1H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.13 – 7.03 (m, 7H), 5.29 (t, *J* = 9.5 Hz, 1H), 4.89 (d, *J* = 10.1 Hz, 1H), 4.78 (d, *J* = 11.5 Hz, 1H), 4.70 (d, *J* = 11.6 Hz, 1H), 4.03 – 3.94 (m, 2H), 3.88 (t, *J* = 8.8 Hz, 1H), 3.79 (s, 3H), 3.67 (s, 1H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.28, 163.74, 149.88, 147.37, 138.41, 137.86, 137.11, 133.44, 129.63, 128.18, 128.15, 127.88, 127.56, 127.20, 125.76, 86.77, 82.59, 77.90, 74.91, 72.30, 71.93, 52.83, 21.17. ESI-MS: $C_{27}H_{27}NO_7S$ $[M+NH_4]^+$ calcd: 527.1846, obsd: 527.1876.

Methyl (*p*-tolyl 3-*O*-benzyl-2-*O*-levulinoyl-1-thio-*β*-D-glucopyranosyluronate) 14:

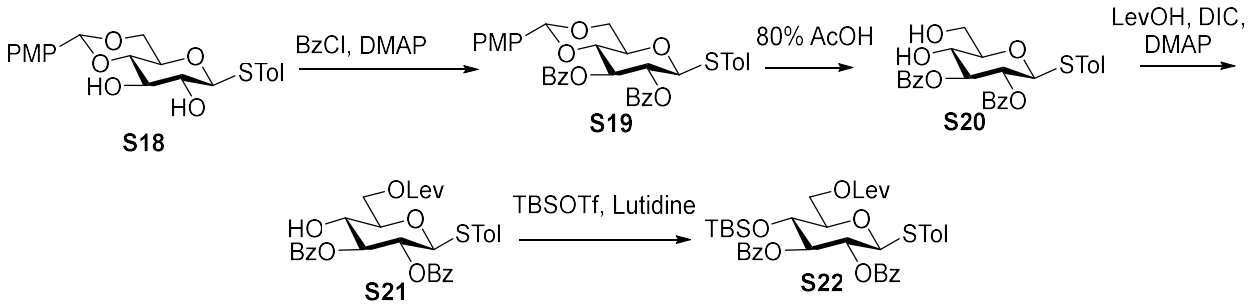


14

Compound **23** (1.5 g, 2.4 mmol) was dissolved in dry DCM/MeOH (2:3, 50 mL), followed by addition of sodium metal until pH≈14 and the reaction was stirred for 2-3 h at rt. Amberlite resin was added to adjust pH around 7. After filtration, the filtrate was concentrated and the residue was purified with silica gel chromatography (Hex:EtOAc, 8:1) to give product **S15** (1 g**,** 80%) as a white solid. To a solution of **S15** (0.5 g, 0.96 mmol) in DCM (5 mL), LevOH (0.197 mL, 1.9 mmol), DIC (0.299 mL, 1.9 mmol), and DMAP (0.236 g, 1.9 mmol) were added and the reaction mixture was stirred at 40 °C for 2 h. Upon completion, the mixture was washed with 1 M HCl, $NaHCO_3$, and NaCl, dried over Na_2SO_4, concentrated and the crude was purified with silica gel chromatography (Hex:EtOAc, 8:1) to afford the product **S16** (0.52, 87.5%) as white solid. Following the general procedure for TBS removal, monosaccharide acceptor **14** was obtained (0.39 g, 92%) as a white solid. $[\alpha_D{}^{20}]$ = -14 (C = 0.05, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*)

δ 7.42 – 7.38 (m, 2H), 7.35 – 7.23 (m, 5H), 7.13 – 7.09 (m, 2H), 4.95 (dd, *J* = 10.1, 9.1 Hz, 1H), 4.82 – 4.73 (m, 2H), 4.59 (d, *J* = 10.1 Hz, 1H), 3.92 (ddd, *J* = 9.7, 8.7, 3.0 Hz, 1H), 3.85 (d, *J* = 9.8 Hz, 1H), 3.81 (s, 3H), 3.57 (t, *J* = 8.9 Hz, 1H), 3.27 (d, *J* = 3.0 Hz, 1H), 2.73 (td, *J* = 6.7, 4.8 Hz, 2H), 2.62 – 2.48 (m, 2H), 2.33 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.34, 171.33, 169.25, 138.44, 138.14, 133.20, 129.71, 128.51, 128.43, 127.97, 127.80, 87.25, 82.52, 77.72, 74.73, 71.74, 71.08, 52.86, 37.80, 29.90, 28.05, 21.19. ESI-MS: $C_{26}H_{30}O_8S$ $[M+NH_4]^+$ calcd: 520.2000, obsd: 520.1986.

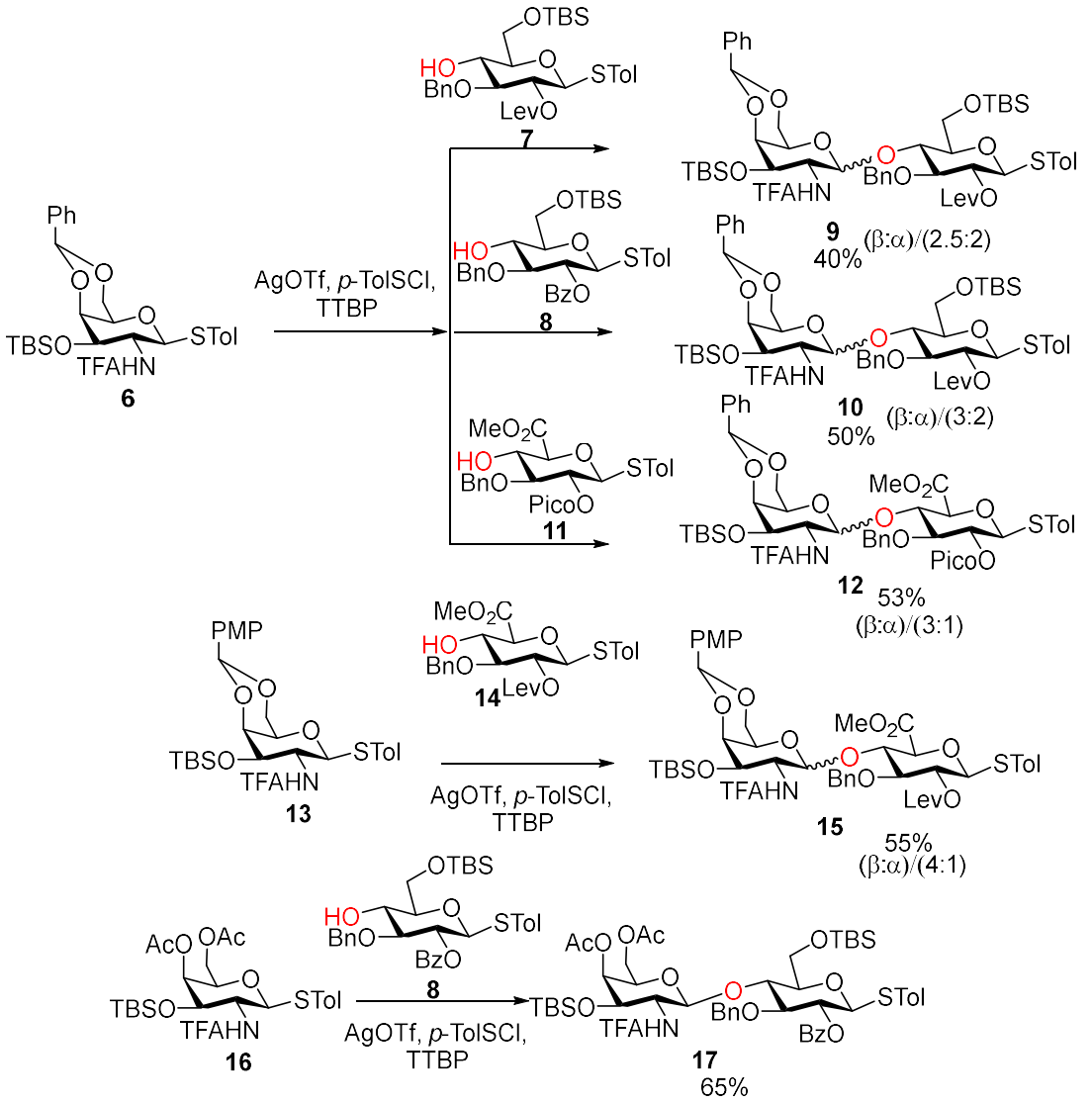
***p*-Tolyl 2,3-di-*O*-benzoyl-4-*O*-*t*-butyldimethylsilyl-6-levulinoyl-1-thio-*β*-D-glucopyranoside S22**:



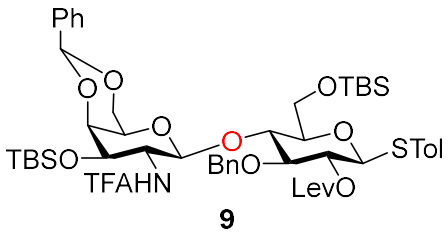
Compound **S18**[4] (8.6 g, 21.3 mmol) was dissolved in Py. (30 mL), then benzoyl chloride (14.8 mL, 127.6 mmol) and DMAP (10.39 g, 85 mmol) were added. The reaction was stirred at rt till completion. The reaction mixture was diluted with EtOAc, washed with 1 M HCl, $NaHCO_3$, and NaCl solutions, dried over Na_2SO_4, concentrated and the crude was purified through crystallization (Hex:EtOAc) to afford **S19** (10 g, 77%). Then **S19** (1 g, 1.6 mmol) was dissolved in aqueous AcOH 80%. The reaction was stirred at 80 ºC for 2 h till completion. The mixture was concentrated in vacuo and the residue was purified with flash chromatography (DCM:MeOH, 20:1) to afford the diol **S20** as white solid. The diol **S20** (8.45 g, 17.1 mmol) was dissolved in DCM (80 mL) and LevOH (2.1 mL, 20.5 mmol), DIC (3.05 mL, 20.5 mmol), and DMAP (2.5 g, 20.5 mmol) were added. The reaction mixture was stirred at rt for 6 h. The mixture was washed with 1 M HCl, $NaHCO_3$, and NaCl, dried over Na_2SO_4, concentrated and the crude was purified with silica gel chromatography (Hex:EtOAc, 8:1) to afford the product **S21** (6.53, 61%) as white solid. Then **S21** (6.53g, 11 mmol) was dissolved in DCM (40 mL). The reaction was cooled to -60 ºC, followed by adding tert-butyldimethylsilyl trifluoromethanesulfonate (TBSOTf) (2.53 mL, 11 mmol) and lutidine (1.27 mL, 11 mmol). The reaction was stirred at -60 ºC for 1 h, then warmed up to 0 ºC.

Upon completion, the reaction was washed with 1 M HCl, $NaHCO_3$, and NaCl, dried over Na_2SO_4, concentrated and the crude was purified through silica gel chromatography (Hex:EtOAc, 8:1) to afford **S22** (7.2 g, 92%) as white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92 – 7.86 (m, 4H), 7.51 – 7.45 (m, 2H), 7.40 – 7.31 (m, 6H), 7.12 – 7.08 (m, 2H), 5.61 (t, *J* = 9.2 Hz, 1H), 5.29 (t, *J* = 9.8 Hz, 1H), 4.88 (d, *J* = 10.0 Hz, 1H), 4.58 (dd, *J* = 11.8, 2.2 Hz, 1H), 4.18 (dd, *J* = 11.8, 5.4 Hz, 1H), 3.97 (t, *J* = 9.2 Hz, 1H), 3.72 (ddd, *J* = 9.5, 5.4, 2.2 Hz, 1H), 2.84 – 2.78 (m, 2H), 2.71 – 2.64 (m, 2H), 2.34 (s, 3H), 2.23 (s, 3H), 0.76 (s, 9H), 0.04 (s, 3H), -0.19 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.34, 172.38, 165.77, 165.26, 138.33, 133.35, 133.15, 133.08, 129.79, 129.70, 129.60, 129.25, 128.41, 128.29, 86.14, 78.52, 76.94, 70.90, 69.31, 63.13, 37.88, 29.94, 27.87, 25.54, 21.20, 17.81, -4.17, -4.78. ESI-MS: $C_{38}H_{46}O_9SSi$ $[M+NH_4]^+$ calcd: 724.2970, obsd: 724.2995.

1.9.Synthesis of disaccharides containing *N*-TFA groups:



_p_-Tolyl 4,6-*O*-benzylidine-3-*O*-*t*-butyldimethylsilyl-2-deoxy-2-*N*-trifluoroacetamido-*β*-D-galactopyranoside-(1→4)-3-*O*-benzyl-6-*O*-*t*-butyldimethylsilyl-2-*O*-levulinoyl-1-thio-*β*-D-glucopyranoside 9:

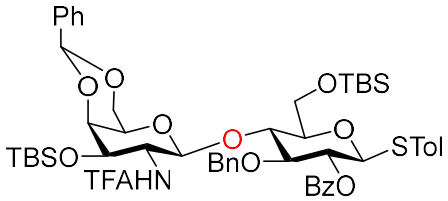


9

Following the general procedure for pre-activation based single-step glycosylation, disaccharide **9** was obtained (0.96 g, 40%) in (2.5:2) (β:α) ratio, by coupling between donor **6** (2.0 g, 3.4 mmol)

and acceptor **7** (1.35 g, 2.3 mmol). For β-anomer, ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.43 – 7.40 (m, 2H), 7.38 – 7.36 (m, 2H), 7.29 – 7.25 (m, 5H), 7.23 – 7.19 (m, 3H), 7.09 – 7.06 (m, 2H), 6.37 (d, *J* = 7.8 Hz, 1H), 5.49 (s, 1H), 5.12 – 5.07 (m, 2H), 4.88 (dd, *J* = 10.0, 8.9 Hz, 1H), 4.58 (d, *J* = 11.9 Hz, 1H), 4.50 (d, *J* = 10.0 Hz, 1H), 4.34 (dd, *J* = 10.6, 3.6 Hz, 1H), 4.29 (dd, *J* = 12.4, 1.5 Hz, 1H), 4.08 – 4.05 (m, 2H), 3.96 (dd, *J* = 12.4, 1.8 Hz, 1H), 3.87 – 3.78 (m, 3H), 3.70 (dd, *J* = 12.0, 3.4 Hz, 1H), 3.64 (t, *J* = 8.8 Hz, 1H), 3.33 (q, *J* = 1.5 Hz, 1H), 3.24 (ddd, *J* = 9.6, 3.4, 1.6 Hz, 1H), 2.69 – 2.60 (m, 2H), 2.57 – 2.50 (m, 2H), 2.32 (s, 3H), 2.15 (s, 3H), 0.92 (s, 9H), 0.87 (s, 9H), 0.12 (d, *J* = 4.1 Hz, 6H), 0.09 (s, 3H), 0.04 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.39, 171.27, 138.97, 138.08, 137.76, 133.44, 129.55, 129.36, 128.72, 128.66, 128.51, 128.06, 128.05, 128.01, 127.59, 127.17, 126.11, 116.73, 100.73, 98.52, 86.20, 82.41, 79.78, 75.70, 75.48, 74.87, 71.67, 69.54, 68.91, 66.46, 61.64, 56.08, 37.93, 29.90, 29.71, 28.13, 25.99, 25.88, 25.80, 25.72, 25.49, 25.23, 21.16, 18.25, 18.00, -4.55, -4.93, -5.03, -5.36. ESI-MS: $C_{52}H_{72}F_3NO_{12}SSi_2$ $[M+Na]^+$ calcd: 1070.4158, obsd: 1070.4101.

***p*-Tolyl 4,6-*O*-benzylidine-3-*O*-*t*-butyldimethylsilyl-2-deoxy-2-*N*-trifluoroacetamido-*β*-D-galactopyranoside-(1→4)-3-*O*-benzyl-2-*O*-benzoyl-6-*O*-*t*-butyldimethylsilyl-1-thio-*β*-D-glucopyranoside 10:**

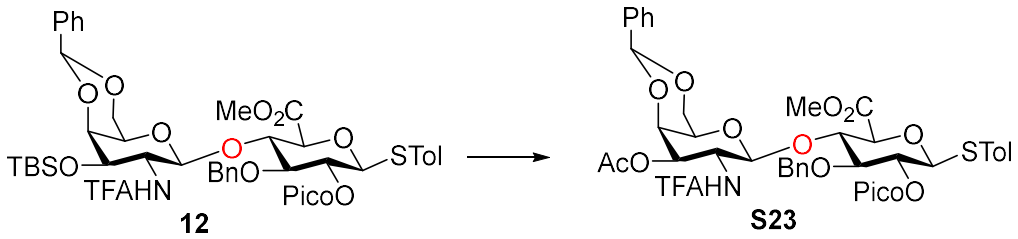


10

Following the general procedure for pre-activation based single-step glycosylation, disaccharide **10** was obtained (1.2 g, 50%) in (3:2) (β:α) ratio, by coupling between donor **6** (2.0 g, 3.4 mmol) and acceptor **8** (1.36 g, 2.3 mmol). For β-anomer, ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.01 – 7.97 (m, 2H), 7.60 – 7.56 (m, 1H), 7.47 – 7.42 (m, 4H), 7.39 – 7.34 (m, 3H), 7.29 – 7.26 (m, 3H), 7.12 – 7.04 (m, 4H), 6.98 (dd, *J* = 8.2, 6.9 Hz, 1H), 6.92 – 6.89 (m, 1H), 6.35 (d, *J* = 7.9 Hz, 1H), 5.51 (s, 1H), 5.15 (dd, *J* = 10.1, 9.0 Hz, 1H), 5.10 (d, *J* = 8.4 Hz, 1H), 5.05 (d, *J* = 11.6 Hz, 1H), 4.69 – 4.63 (m, 2H), 4.59 (d, *J* = 11.7 Hz, 1H), 4.36 – 4.29 (m, 2H), 4.17 – 4.13 (m, 1H), 4.10 – 4.06 (m, 1H), 4.01 – 3.95 (m, 1H), 3.90 (dd, *J* = 12.0, 1.5 Hz, 1H), 3.88 – 3.85 (m, 1H), 3.79 (d, *J* = 8.9 Hz, 1H), 3.74 (dd, *J* = 12.0, 3.4 Hz, 1H), 3.35 – 3.29 (m, 2H), 2.31 (s, 3H), 0.94 (s, 9H), 0.88 (s, 9H), 0.15 (d, *J* = 6.3 Hz, 6H), 0.10 (s, 3H), 0.05 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ

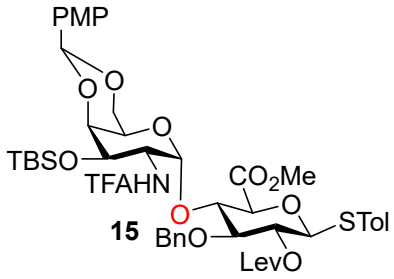
165.09, 138.43, 138.08, 137.81, 133.59, 132.95, 130.13, 129.85, 129.79, 129.72, 129.52, 128.71, 128.65, 128.51, 128.36, 128.27, 128.22, 128.14, 128.04, 128.02, 127.84, 127.56, 127.01, 126.15, 126.12, 100.74, 98.72, 86.39, 82.33, 79.88, 75.71, 74.94, 72.16, 69.74, 68.92, 66.54, 61.68, 56.00, 25.92, 25.90, 25.82, 25.54, 25.50, 25.47, 25.42, 21.15, 18.27, 18.01, -4.92, -4.97, -5.34. ESI-MS: $C_{54}H_{70}F_3NO_{11}SSi_2$ $[M+NH_4]^+$ calcd: 1071.4498, obsd: 1071.4471.

Methyl (*p*-tolyl [3-*O*-Acetyl-4,6-*O*-benzylidine-2-deoxy-2-*N*-trifluoroacetamido-*β*-D-galactopyranoside]-(1→4)-3-*O*-benzyl-2-*O*-picolinoyl-1-thio-*β*-D-glucopyranosyluronate) S23:



Following the general procedure for pre-activation based single-step glycosylation, disaccharide **12** was obtained (0.39 g, 53%) in (3:1) (β:α) ratio, by coupling between donor **6** (0.33 g, 0.56 mmol) and acceptor **11** (0.21 g, 0.4 mmol). Then, compound **12** (0.2 g, 0.21 mmol) was subjected to the general procedure for TBS deprotection, and the resulting crude was dissolved in a mixture of pyridine/Ac_2O (4:2, 6 mL). The mixture was stirred at rt till the reaction was completed. The mixture was diluted with EtOAc (30 mL), washed with 1M HCl, saturated $NaHCO_3$, and brine solutions. The organic layer was dried over Na_2SO_4, concentrated and purified using silica gel chromatography to afford disaccharide **S23** (0.16 g, 89% over 2 steps). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.71 (dt, *J* = 4.6, 1.3 Hz, 1H), 8.15 – 8.11 (m, 1H), 7.86 (td, *J* = 7.7, 1.6 Hz, 1H), 7.52 – 7.49 (m, 3H), 7.40 – 7.34 (m, 5H), 7.16 – 7.07 (m, 7H), 6.97 (d, *J* = 9.7 Hz, 1H), 5.53 (s, 1H), 5.42 (dd, *J* = 9.2, 8.2 Hz, 1H), 5.39 (d, *J* = 3.5 Hz, 1H), 5.14 (dd, *J* = 11.3, 3.2 Hz, 1H), 4.93 (d, *J* = 9.3 Hz, 1H), 4.79 (ddd, *J* = 11.3, 9.7, 3.5 Hz, 1H), 4.72 (d, *J* = 11.4 Hz, 1H), 4.64 (d, *J* = 11.3 Hz, 1H), 4.37 (dd, *J* = 3.2, 1.2 Hz, 1H), 4.27 – 4.22 (m, 2H), 4.05 – 4.00 (m, 3H), 3.82 (s, 3H), 3.70 (d, *J* = 1.7 Hz, 1H), 2.33 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.31, 167.96, 163.72, 157.31, 157.01, 149.63, 147.11, 138.56, 137.18, 136.44, 133.37, 129.70, 129.13, 128.36, 128.24, 127.88, 127.60, 127.35, 126.20, 126.00, 100.79, 98.61, 87.04, 81.89, 78.16, 75.70, 74.50, 73.02, 72.78, 69.00, 68.66, 63.51, 52.91, 48.21, 29.71, 21.18, 20.82. ESI-MS: $C_{44}H_{43}F_3N_2O_{13}S$ $[M+NH_4]^+$ calcd: 914.2776, obsd: 914.2706.

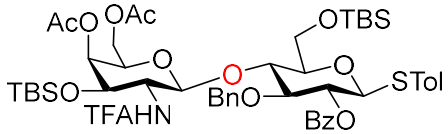
Methyl (*p*-tolyl [4,6-*O*-(4-methoxy)benzylidene-3-*O*-*t*-butyldimethylsilyl-2-deoxy-2-*N*-trifluoroacetamido-*α*-D-galactopyranoside]-(1→4)-3-*O*-benzyl-2-*O*-levulinoyl-1-thio-*β*-D-glucopyranosyluronate) 15:



15

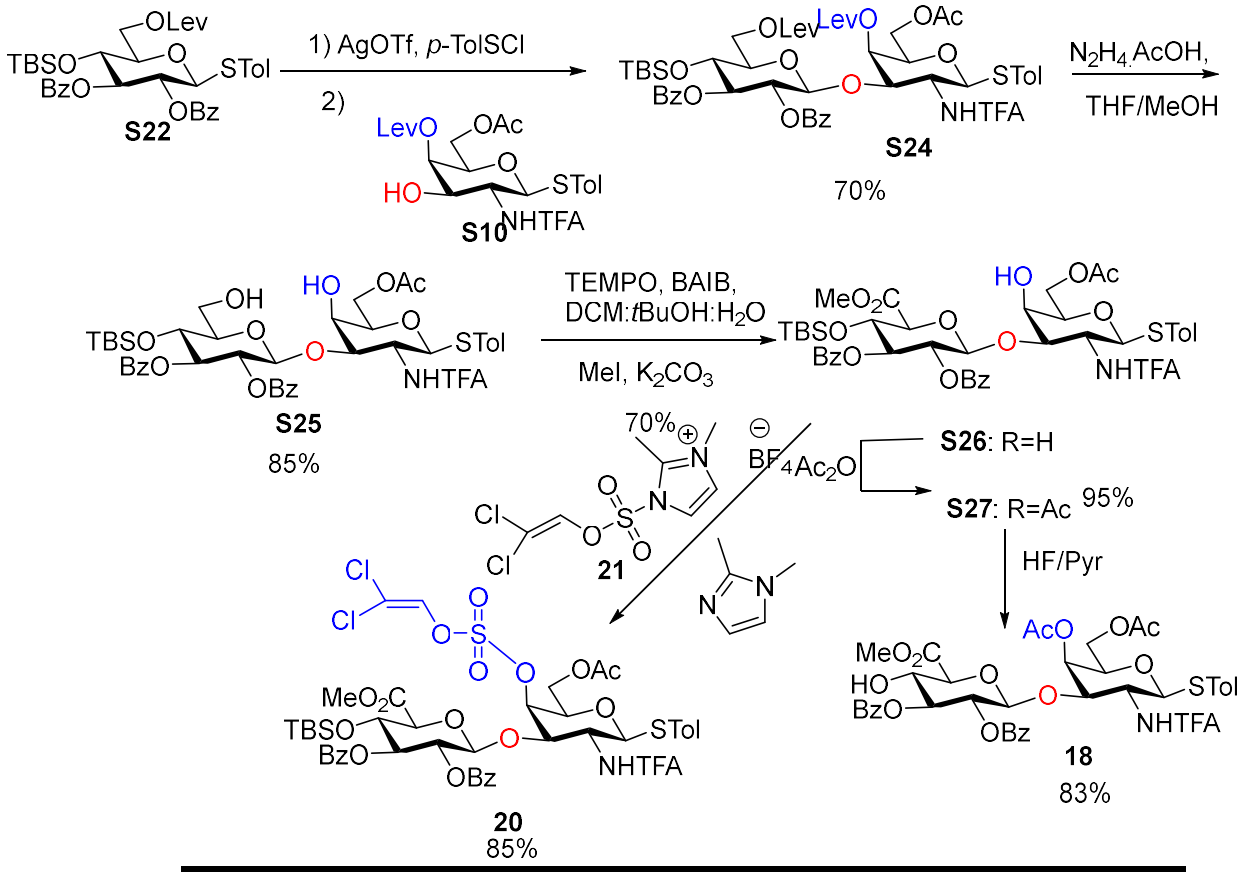
Following the general procedure for pre-activation based single-step glycosylation, disaccharide **15** was obtained (1.33 g, 55 %) in (4:1) (β:α) ratio, by coupling between donor **13** (2.9 g, 4.8 mmol) and acceptor **14** (1.2 g, 2.4 mmol). For α-anomer, ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.43 – 7.41 (m, 2H), 7.38 – 7.35 (m, 2H), 7.33 – 7.29 (m, 2H), 7.21 – 7.18 (m, 2H), 7.13 – 7.11 (m, 2H), 6.89 – 6.86 (m, 2H), 6.59 (d, *J* = 9.5 Hz, 1H), 5.44 (s, 1H), 5.39 (d, *J* = 3.6 Hz, 1H), 5.06 (dd, *J* = 9.6, 8.1 Hz, 1H), 4.67 – 4.61 (m, 3H), 4.58 (td, *J* = 10.0, 3.7 Hz, 1H), 4.20 – 4.16 (m, 2H), 4.05 – 4.02 (m, 2H), 3.98 – 3.93 (m, 2H), 3.79 (s, 3H), 3.78 (s, 3H), 3.75 (d, *J* = 8.2 Hz, 1H), 3.54 (d, *J* = 1.5 Hz, 1H), 2.69 – 2.66 (m, 2H), 2.53 (dt, *J* = 17.2, 6.4 Hz, 1H), 2.39 – 2.35 (m, 1H), 2.34 (s, 3H), 2.15 (s, 3H), 0.82 (s, 9H), 0.03 (d, *J* = 8.2 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.28, 171.31, 168.05, 159.97, 157.05, 156.75, 138.53, 136.90, 133.01, 129.93, 129.76, 128.56, 128.49, 127.85, 127.43, 127.28, 116.89, 113.49, 100.73, 98.60, 87.08, 82.28, 78.25, 77.26, 75.75, 75.27, 73.78, 71.58, 69.05, 68.45, 63.77, 55.27, 52.82, 50.31, 37.81, 29.74, 27.97, 25.51, 25.41, 21.18, 17.92, -4.18, -4.79. ESI-MS: $C_{48}H_{60}F_3NO_{14}SSi$ $[M+NH_4]^+$ calcd: 1009.3794, obsd: 1009.3801.

***p*-Tolyl 4,6-di-*O*-acetyl-3-*O*-*t*-butyldimethylsilyl-2-deoxy-2-*N*-trifluoroacetamido-*β*-D-galactopyranoside-(1→4)-3-*O*-benzyl-2-*O*-benzoyl-6-*O*-*t*-butyldimethylsilyl-1-thio-*β*-D-glucopyranoside 17:**

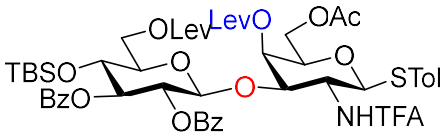


17

Following the general procedure for pre-activation based single-step glycosylation, disaccharide **17** was obtained (0.22 g, 50 %), by coupling between donor **16** (0.37 g, 0.64 mmol) and acceptor **8** (0.25 g, 0.43 mmol). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.01 – 7.96 (m, 2H), 7.60 – 7.55 (m, 1H), 7.46 – 7.42 (m, 2H), 7.36 – 7.32 (m, 2H), 7.17 – 7.13 (m, 2H), 7.12 – 7.03 (m, 5H), 6.29 (d, *J* = 8.6 Hz, 1H), 5.22 (dd, *J* = 3.5, 1.0 Hz, 1H), 5.12 (dd, *J* = 10.0, 8.9 Hz, 1H), 4.99 (d, *J* = 8.4 Hz, 1H), 4.86 (d, *J* = 11.2 Hz, 1H), 4.67 (d, *J* = 10.0 Hz, 1H), 4.56 (d, *J* = 11.2 Hz, 1H), 4.12 – 4.03 (m, 3H), 3.90 (dd, *J* = 12.1, 1.5 Hz, 1H), 3.85 – 3.69 (m, 5H), 3.30 (ddd, *J* = 9.6, 3.2, 1.5 Hz, 1H), 2.31 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 0.95 (s, 9H), 0.81 (s, 9H), 0.15 (d, *J* = 8.3 Hz, 6H), 0.09 (s, 3H), 0.01 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.42, 169.83, 165.05, 157.25, 156.96, 138.29, 138.15, 133.53, 133.04, 129.98, 129.81, 129.71, 129.54, 128.70, 128.32, 127.99, 127.80, 127.33, 116.76, 114.46, 98.65, 86.56, 81.61, 79.81, 75.18, 74.40, 72.09, 70.93, 69.33, 68.72, 61.67, 61.65, 56.05, 25.92, 25.34, 21.14, 20.72, 20.67, 18.24, 17.59, -4.65, -4.89, -5.37, -5.41. ESI-MS: $C_{51}H_{70}F_3NO_{13}SSi_2$ $[M+Na]^+$ calcd: 1072.4, obsd: 1072.4.



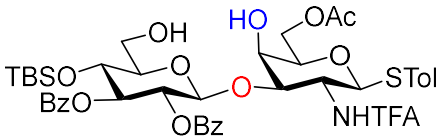
***p*-Tolyl 2,3-di-*O*-benzoyl-4-*O*-*t*-butyldimethylsilyl-6-*O*-levulinoyl-*β*-D-glucopyranosyl-(1→3)-6-*O*-acetyl-2-deoxy-4-*O*-levulinoyl-2-*N*-trifluoroacetamido-1-thio-*β*-D-galactopyranoside S24:**



S24

Following the general procedure for pre-activation based single-step glycosylation, disaccharide **S24** was obtained (3.05 g, 70 %), by coupling between donor **S22** (3.34 g, 4.7 mmol) and acceptor **S10** (2.06 g, 3.9 mmol). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.84 – 7.80 (m, 2H), 7.76 – 7.71 (m, 2H), 7.61 (d, *J* = 9.3 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.36 – 7.33 (m, 2H), 7.33 – 7.27 (m, 4H), 7.06 – 7.02 (m, 2H), 5.47 – 5.41 (m, 2H), 5.16 (dd, *J* = 9.9, 7.9 Hz, 1H), 4.79 (d, *J* = 7.9 Hz, 1H), 4.67 – 4.62 (m, 2H), 4.48 (dd, *J* = 10.5, 3.2 Hz, 1H), 4.15 – 4.05 (m, 4H), 3.91 – 3.85 (m, 2H), 3.64 (ddd, *J* = 9.2, 6.7, 2.2 Hz, 1H), 2.94 (ddd, *J* = 18.6, 9.6, 4.2 Hz, 1H), 2.71 – 2.57 (m, 4H), 2.56 – 2.43 (m, 4H), 2.27 (s, 3H), 2.12 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 0.74 (s, 9H), 0.02 (s, 3H), -0.24 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 209.66, 206.54, 172.08, 171.55, 170.61, 165.54, 165.19, 157.16, 156.87, 138.30, 133.24, 133.06, 133.02, 129.63, 129.52, 129.47, 129.01, 128.82, 128.30, 128.24, 128.11, 116.91, 114.62, 99.79, 86.59, 77.32, 75.50, 74.96, 74.70, 73.02, 72.10, 69.68, 69.39, 62.73, 62.58, 51.27, 38.13, 38.02, 29.72, 29.66, 29.61, 27.99, 25.52, 25.49, 21.09, 20.76, 17.78, 17.76, -4.21, -4.74. ESI-MS: $C_{53}H_{64}F_3NO_{17}SSi$ $[M+NH_4]^+$ calcd: 1121.3955, obsd: 1121.3999.

***p*-Tolyl 2,3-di-*O*-benzoyl-4-*O*-*t*-butyldimethylsilyl-*β*-D-glucopyranosyl-(1→3)-6-*O*-acetyl-2-deoxy-2-*N*-trifluoroacetamido-1-thio-*β*-D-galactopyranoside S25:**

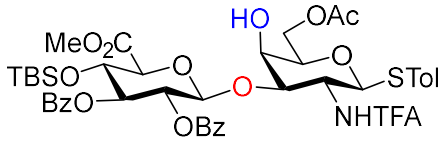


S25

Compound **S24** (3.27 g, 2.96 mmol) was dissolved in THF/MeOH (10:1, 15 mL), then hydrazine acetate (1.64 g, 17.8 mmol) was added at 0 °C. The reaction was stirred for 5 h at rt. Upon completion, the mixture was cooled down to 0 °C, and quenched with acetone, concentrated under vacuo, diluted with ethyl acetate (50 mL), washed with saturated $NaHCO_3$, and brine. The organic

layer was concentrated and the residue was purified with silica gel chromatography (Hex:EtOAc, 3:1) to afford **S25** (2.28 g, 85%) as a white powder. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.85 – 7.81 (m, 2H), 7.71 – 7.67 (m, 2H), 7.45 – 7.36 (m, 5H), 7.26 – 7.20 (m, 4H), 7.08 – 7.03 (m, 2H), 5.61 (dd, *J* = 10.1, 9.0 Hz, 1H), 5.42 – 5.36 (m, 2H), 5.00 (d, *J* = 7.9 Hz, 1H), 4.56 (dd, *J* = 10.4, 3.1 Hz, 1H), 4.40 – 4.34 (m, 2H), 4.29 – 4.23 (m, 2H), 3.98 – 3.82 (m, 6H), 3.65 – 3.61 (m, 1H), 3.39 (dd, *J* = 8.2, 4.2 Hz, 1H), 2.29 (s, 3H), 1.98 (s, 3H), 0.75 (s, 9H), 0.11 (s, 3H), -0.20 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.24, 165.81, 165.75, 157.78, 157.48, 138.14, 133.29, 132.99, 132.95, 129.81, 129.70, 129.62, 129.35, 129.20, 128.19, 128.13, 128.10, 116.33, 114.03, 101.44, 85.10, 78.91, 75.83, 75.59, 72.30, 68.53, 68.11, 63.81, 60.74, 52.99, 25.65, 25.59, 21.11, 20.73, 17.79, -4.16, -4.85. ESI-MS: $C_{43}H_{52}F_3NO_{13}SSi$ $[M+NH_4]^+$ calcd: 925.3219, obsd: 925.3202.

***p*-Tolyl methyl-2,3-di-*O*-benzoyl-4-*O*-*t*-butyldimethylsilyl-*O*-*β*-D-glucopyranosyluronate-(1→3)-6-*O*-acetyl-2-deoxy-2-*N*-trifluoroacetamido-1-thio-*β*-D-galactopyranoside S26:**

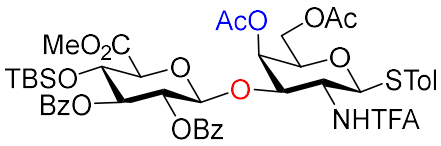


S26

To a solution of **S25** (2.4 g, 2.6 mmol) in DCM/*t*BuOH/H_2O (4:1:1, 18 mL), TEMPO (0.123 g, 0.8 mmol) and BAIB (1.87 g, 5.8 mmol) were added. The reaction was stirred for 5 h till oxidation of **17** was completed (monitored by TLC). Then the reaction was quenched with brine (5 mL) and extracted with DCM (3*15 mL). The organic layers were combined and dried over Na_2SO_4 and concentrated under vacuo. The residue was then dissolved in dry DMF (6 mL) and methyl iodide (0.7 mL, 13.8 mmol) and K_2CO_3 (1.4 g, 10.1 mmol) were added. The mixture was stirred overnight, then diluted with EtOAc (50 mL), washed with saturated $NaHCO_3$, brine, dried over Na_2SO_4, and concentrated. The residue was purified using column chromatography (Hex:EtOAc, 5:1) to give **S26** (1.73 g, 70% in 2 steps). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.88 – 7.83 (m, 2H), 7.83 – 7.78 (m, 2H), 7.50 – 7.45 (m, 2H), 7.37 – 7.29 (m, 6H), 7.10 – 7.05 (m, 2H), 6.47 (d, *J* = 7.3 Hz, 1H), 5.52 (t, *J* = 8.7 Hz, 1H), 5.32 (dd, *J* = 8.9, 7.2 Hz, 1H), 5.14 (d, *J* = 10.3 Hz, 1H), 4.93 (d, *J* = 7.2 Hz, 1H), 4.42 – 4.29 (m, 4H), 4.15 – 4.10 (m, 2H), 3.80 (s, 3H), 3.79 – 3.75 (m, 1H), 3.68 – 3.62 (m, 1H), 2.87 (dd, *J* = 3.0, 1.4 Hz, 1H), 2.32 (s, 3H), 2.06 (s, 3H), 0.73 (s, 9H), -0.04 (s, 3H), -0.19 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.88, 168.54, 165.45, 165.20,

157.48, 157.18, 138.44, 133.45, 133.27, 133.14, 129.78, 129.70, 129.68, 129.14, 128.37, 128.34, 128.32, 128.23, 116.21, 113.92, 101.02, 84.41, 78.46, 76.25, 75.70, 74.72, 71.96, 70.32, 67.89, 63.53, 52.80, 52.43, 25.37, 21.15, 20.84, 17.72, -4.44, -5.17. ESI-MS: $C_{44}H_{52}F_3NO_{14}SSi$ $[M+NH_4]^+$ calcd: 953.3168, obsd: 953.3177.

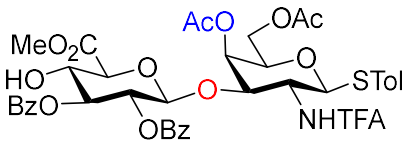
_p_-Tolyl methyl-2,3-di-_O_-benzoyl-4-_O_-_t_-butyldimethylsilyl-_β_-D-glucopyranosyluronate-(1→3)-4,6-di-_O_-acetyl-2-deoxy-2-_N_-trifluoroacetamido-1-thio-_β_-D-galactopyranoside S27:



S27

Compound **S26** (1 g, 1 mmol) was dissolved in py./ Ac_2O (2:1, 6 mL) and the reaction was stirred for 3 h at rt. The mixture was diluted with EtOAc (30 mL), washed with 1M HCl, saturated $NaHCO_3$, and brine solutions. The organic layer was dried over Na_2SO_4, concentrated and purified using silica gel chromatography (Hex:EtOAc, 5:1) to afford disaccharide **S27** (0.99g, 95%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.85 – 7.78 (m, 4H), 7.48 – 7.43 (m, 2H), 7.36 – 7.29 (m, 6H), 7.09 – 7.06 (m, 2H), 6.57 (d, *J* = 7.6 Hz, 1H), 5.50 (dd, *J* = 9.5, 8.8 Hz, 1H), 5.42 (d, *J* = 3.2 Hz, 1H), 5.27 (dd, *J* = 9.5, 7.8 Hz, 1H), 5.12 (d, *J* = 10.4 Hz, 1H), 4.85 (d, *J* = 7.7 Hz, 1H), 4.49 (dd, *J* = 10.4, 3.3 Hz, 1H), 4.26 (t, *J* = 9.0 Hz, 1H), 4.14 (dd, *J* = 11.7, 4.8 Hz, 1H), 4.06 – 3.99 (m, 2H), 3.88 (ddd, *J* = 7.7, 4.8, 1.0 Hz, 1H), 3.81 (s, 3H), 3.71 – 3.64 (m, 1H), 2.32 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 0.71 (s, 9H), -0.05 (s, 3H), -0.21 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.61, 169.73, 167.92, 165.47, 165.14, 157.44, 157.14, 138.63, 133.30, 133.25, 133.18, 129.74, 129.66, 129.63, 129.26, 128.61, 128.29, 128.23, 128.07, 116.25, 113.96, 100.44, 84.81, 77.27, 76.40, 75.30, 75.24, 74.96, 71.74, 70.48, 68.54, 62.68, 52.77, 52.62, 25.36, 21.15, 20.72, 20.64, 20.60, 17.70, -4.48, -5.17. ESI-MS: $C_{46}H_{54}F_3NO_{15}SSi$ $[M+NH_4]^+$ calcd: 995.3274, obsd: 995.3245.

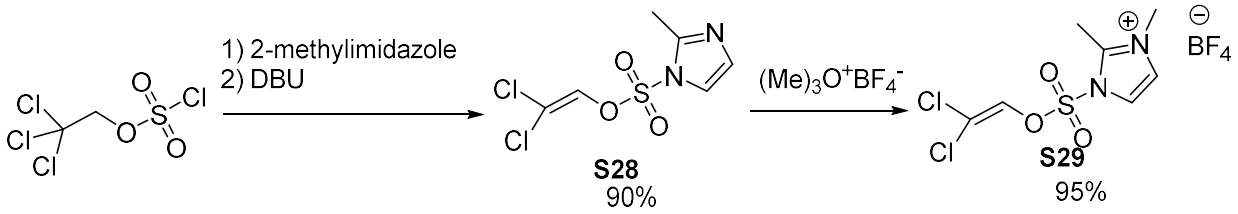
_p_-Tolyl methyl-2,3-di-_O_-benzoyl-_O_-_β_-D-glucopyranosyluronate-(1→3)-4,6-di-_O_-acetyl-2-deoxy-2-_N_-trifluoroacetamido-1-thio-_β_-D-galactopyranoside 18:



18

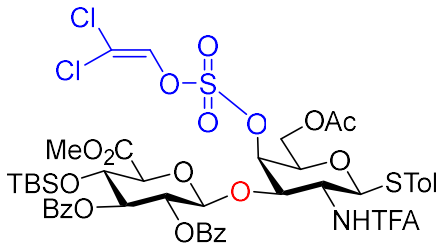
Following the general procedure for TBS removal, disaccharide acceptor **18** was obtained (1.3 g, 83%) from **S27** (1.77 g, 1.7 mmol). [α_D^{20}] = +36.5 (C = 0.2, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93 – 7.85 (m, 4H), 7.54 – 7.47 (m, 2H), 7.39 – 7.31 (m, 6H), 7.11 – 7.06 (m, 2H), 6.49 (d, *J* = 7.5 Hz, 1H), 5.55 – 5.47 (m, 2H), 5.33 (dd, *J* = 9.6, 7.6 Hz, 1H), 5.16 (d, *J* = 10.4 Hz, 1H), 4.88 (d, *J* = 7.6 Hz, 1H), 4.59 (dd, *J* = 10.5, 3.3 Hz, 1H), 4.18 – 4.13 (m, 2H), 4.08 – 4.03 (m, 2H), 3.91 (ddd, *J* = 7.6, 4.8, 1.0 Hz, 1H), 3.86 (s, 3H), 3.66 (td, *J* = 10.4, 7.3 Hz, 1H), 3.41 (d, *J* = 3.7 Hz, 1H), 2.34 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.60, 169.79, 168.75, 166.42, 165.15, 157.51, 157.21, 138.69, 133.51, 133.47, 133.24, 129.85, 129.78, 129.67, 128.78, 128.62, 128.41, 128.39, 128.00, 116.28, 113.99, 100.65, 84.67, 75.27, 75.07, 74.73, 74.41, 71.28, 70.16, 68.90, 62.73, 53.04, 53.01, 21.17, 20.74, 20.64. ESI-MS: $C_{40}H_{40}F_3NO_{15}S$ $[M+NH_4]^+$ calcd: 881.2409, obsd: 881.2379.

1-(2,2-Dichlorovinyloxysulfuryl) 2,3-dimethylimidazolium tetrafluoroborate S29[5]:



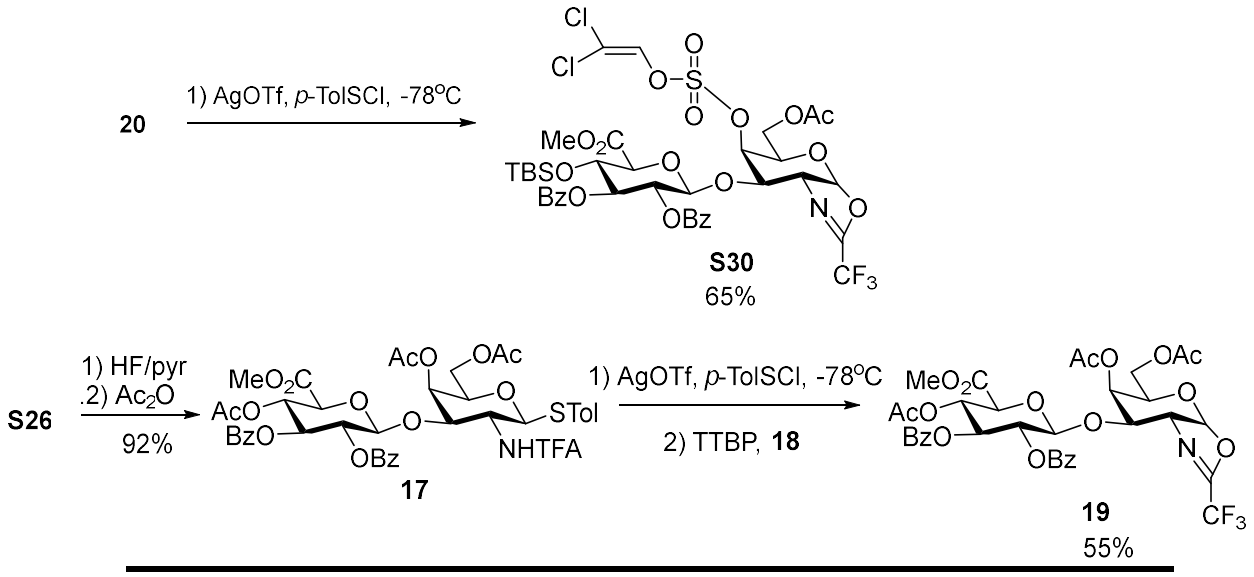
2-Methyl imidazole (6.0 g, 97.4 mmol) was dissolved in dry THF (56 mL). To this solution 2,2,2-trichloroethoxy sulfurylchloride (6.8 g, 27.4 mmol) in dry THF (72 mL) was added at 0 °C. The reaction mixture was stirred for 1 h at 0 °C, and another 1 h at rt, then filtered. To the filtrate, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (6.2 mL, 41.2 mmol, 1.5 equiv.) was added dropwise at 0 °C, and the reaction was stirred at the same temperature for 1 h followed by 2 h at rt. The reaction was filtered, washed with brine, dried over Na_2SO_4, concentrated in *vacuo*. The residue was purified with flash chromatography to afford **S28** in 90% yield. Compound **S28** (7.07 g, 27.5 mmol) was dissolved in DCM (70 mL) and then added to a solution of trimethyloxonium tetrafluoroborate (4.07 g, 27.5 mmol) in DCM (35 mL) at 0 °C. The reaction was stirred overnight at rt, then the solvent was concentrated and triturated with hot THF (10 mL), filtered and concentrated to afford pure compound **29** (9.37 g, 95%). Comparison with literature data[5] confirms its identity. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.25 (d, *J* = 2.4 Hz, 1H), 7.95 (d, *J* = 2.4 Hz, 2H), 3.85 (s, 3H), 2.81 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 149.60, 134.53, 124.49, 122.18, 121.39, 36.46, 12.22.^{19}F NMR (470 MHz, DMSO-d_6) δ -148.34.

***p*-Tolyl methyl-2,3-di-*O*-benzoyl-4-*O*-*t*-butyldimethylsilyl-*O*-*β*-D-glucopyranosyluronate-(1→3)-6-*O*-acetyl-4-*O*-dichlorovinyl sulfate-2-deoxy-2-*N*-trifluoroacetamido-1-thio-*β*-D-galactopyranoside 20:**

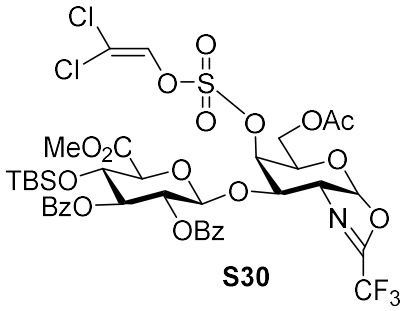


20

To a solution of disaccharide **S26** (0.6 g, 0.64 mmol) in DCM (10 mL), 1,2-dimethylimidazole (0.57 mL, 6.4 mmol) followed by dropwise addition of the DCV reagent **S29** (2.3 g, 6.4 mmol). The reaction mixture was stirred at rt for 4 h, then at 50 ºC for 8 h. The reaction mixture was diluted with another 20 mL of DCM, washed with brine and H_2O, then dried over Na_2SO_4 and concentrated. The residue was purified using flash chromatography (EtOAc:Hex., 3:1) to give pure compound **20** (0.6 g, 85%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.87 – 7.79 (m, 4H), 7.49 – 7.44 (m, 2H), 7.35 – 7.29 (m, 6H), 7.26 (s, 1H), 7.12 – 7.09 (m, 2H), 6.68 (d, *J* = 7.3 Hz, 1H), 5.57 (t, *J* = 9.1 Hz, 1H), 5.35 – 5.30 (m, 2H), 5.16 (d, *J* = 10.3 Hz, 1H), 4.93 (d, *J* = 7.7 Hz, 1H), 4.71 (dd, *J* = 10.7, 2.9 Hz, 1H), 4.31 – 4.21 (m, 3H), 4.12 (d, *J* = 9.1 Hz, 1H), 3.95 (t, *J* = 6.5 Hz, 1H), 3.80 (s, 3H), 3.59 – 3.52 (m, 1H), 2.33 (s, 3H), 2.06 (s, 3H), 0.73 (s, 9H), -0.04 (s, 3H), -0.19 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.49, 167.78, 165.42, 165.08, 157.72, 157.42, 139.10, 134.23, 133.56, 133.40, 133.27, 129.97, 129.72, 129.65, 129.15, 128.47, 128.35, 128.27, 127.14, 117.40, 116.14, 113.84, 101.70, 84.62, 82.91, 77.29, 76.45, 74.69, 74.60, 74.37, 71.64, 70.33, 61.76, 52.64, 52.50, 25.36, 21.18, 20.58, 17.71, -4.44, -5.11. ESI-MS: $C_{46}H_{52}Cl_2F_3NO_{17}S_2Si$ $[M+Na]^+$ calcd: 1127.2, obsd: 1127.2.

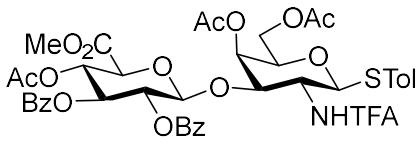


2-Trifluoromethyl-[methyl-2,3-di-*O*-benzoyl-4-*O*-*t*-butyldimethylsilyl-*O*-*β*-D-glucopyranosyluronate-(1→3)-6-*O*-acetyl-4-*O*-dichlorovinyl sulfate-2-deoxy-*α*-D-galactopyranose]-[2,1-d]-oxazoline S30:



Glycosylation reaction between donor **20** (0.086 g, 0.77 μmol) and acceptor **18** (0.056 g, 0.64 μmol) was performed following the general procedure for pre-activation based single-step glycosylation. No glycosylation product was obtained and oxazoline **S30** was isolated using flash column chromatography (toluene:acetone, 6:1) (29 mg, 65%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.01 – 7.86 (m, 4H), 7.56 – 7.46 (m, 2H), 7.38 (m, 4H), 7.20 (m, 1H), 6.14 (m, 1H), 5.61 (m, 1H), 5.40 – 5.34 (m, 1H), 5.28 – 5.23 (m, 2H), 4.39 (m, 2H), 4.29 – 4.15 (m, 3H), 4.10 – 4.04 (m, 1H), 3.94 (m, 1H), 3.82 (s, 3H), 2.13 (s, 3H), 0.75 (s, 9H), -0.01 (s, 3H), -0.16 (s, 3H). ESI-MS: $C_{39}H_{44}Cl_2F_3NO_{17}SSi$ $[M+H]^+$ calcd: 986.1501, obsd: 986.1378, $[M+Na]^+$ calcd: 1008.1, obsd: 1008.1.

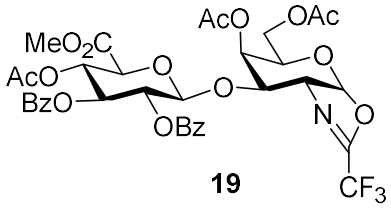
***p*-Tolyl methyl-4-*O*-acetyl-2,3-di-*O*-benzoyl-*O*-*β*-D-glucopyranosyluronate-(1→3)-4,6-di-*O*-acetyl-2-deoxy-2-*N*-trifluoroacetamido-1-thio-*β*-D-galactopyranoside 17:**



18

Compound **18** (0.12 g, 0.14 mmol) was dissolved in pyridine/Ac_2O (2:1, 3 mL). The reaction was stirred for 5 h. The mixture was diluted with ethyl acetate (30 mL), washed with 1M HCl, saturated $NaHCO_3$, and brine. The organic layer was dried over Na_2SO_4, concentrated and purified using silica gel chromatography (Hex:EtOAc, 3:1) to afford disaccharide **17** (0.12 g, 92%). $[\alpha_D^{20}] = +50$ (C = 0.05, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 – 7.79 (m, 4H), 7.53 – 7.45 (m, 2H), 7.40 – 7.29 (m, 6H), 7.11 – 7.03 (m, 2H), 6.52 (d, *J* = 7.4 Hz, 1H), 5.62 (t, *J* = 9.5 Hz, 1H), 5.50 (d, *J* = 3.2 Hz, 1H), 5.45 – 5.33 (m, 2H), 5.14 (d, *J* = 10.4 Hz, 1H), 4.88 (d, *J* = 7.7 Hz, 1H), 4.58 (dd, *J* = 10.5, 3.3 Hz, 1H), 4.18 – 4.11 (m, 2H), 4.06 (dd, *J* = 11.6, 7.5 Hz, 1H), 3.91 – 3.86 (m, 1H), 3.78 (s, 3H), 3.66 (td, *J* = 10.4, 7.4 Hz, 1H), 2.33 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.55, 169.66, 169.27, 166.77, 165.44, 164.94, 157.52, 157.22, 138.72, 133.50, 133.31, 129.78, 129.76, 129.70, 128.52, 128.50, 128.43, 128.37, 127.90, 116.27, 113.97, 100.17, 84.65, 75.24, 75.06, 72.58, 72.17, 71.33, 69.04, 68.56, 62.57, 52.97, 52.95, 21.16, 20.73, 20.60, 20.42. ESI-MS: $C_{42}H_{42}F_3NO_{16}S$ $[M+NH_4]^+$ calcd: 923.2515, obsd: 923.2543.

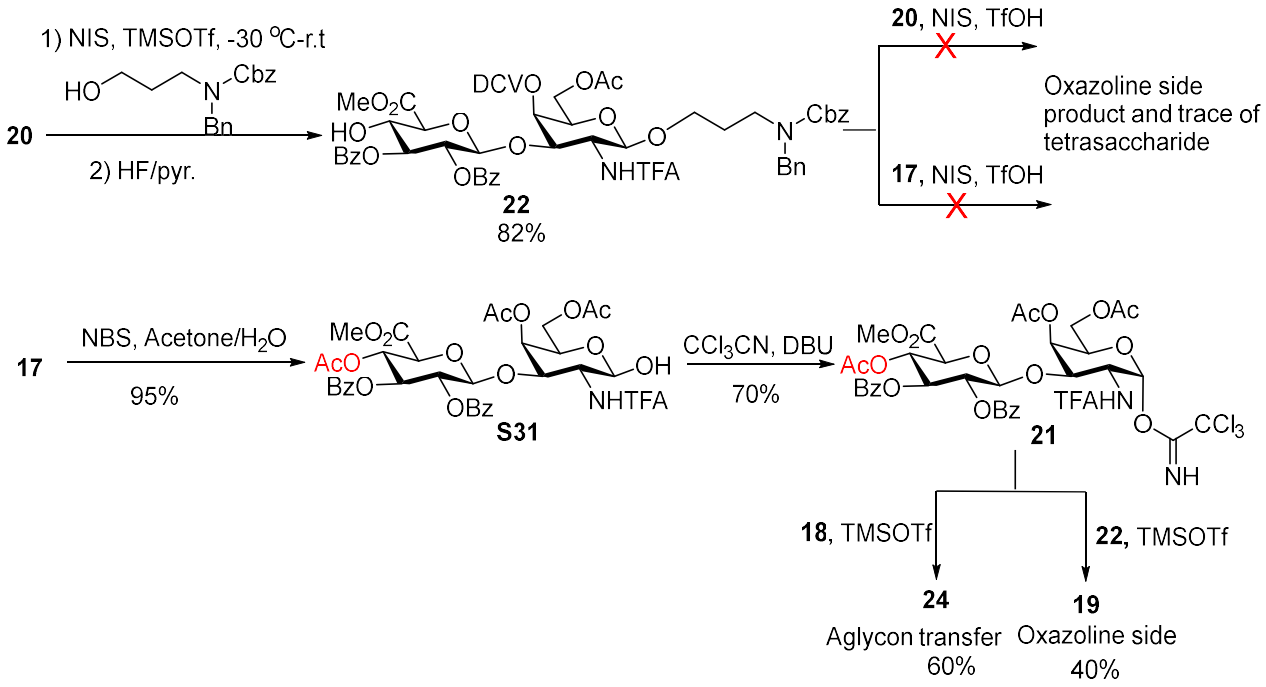
2-Trifluoromethyl-[methyl-4-*O*-acetyl-2,3-di-*O*-benzoyl-*O*-*β*-D-glucopyranosyluronate-(1→3)-4,6-di-*O*-acetyl-2-deoxy-*α*-D-galactopyranose]-[2,1-d]-oxazoline 19:



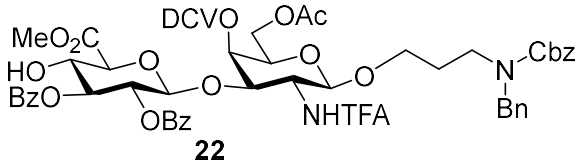
19

Glycosylation between donor **17** (0.191 g, 0.21 μmol) and acceptor **18** (0.140 g, 0.162 μmol) was performed following general procedure for pre-activation based single-step glycosylation. No glycosylation product was separated and oxazoline **19** was obtained using flash column chromatography (toluene:acetone, 6:1) (0.06 g, 55%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.01 – 7.89 (m, 4H), 7.58 – 7.50 (m, 2H), 7.44 – 7.35 (m, 4H), 6.14 (d, *J* = 6.2 Hz, 1H), 5.75 (t, *J* = 9.4 Hz, 1H), 5.50 – 5.41 (m, 3H), 5.29 (d, *J* = 7.5 Hz, 1H), 4.25 – 4.16 (m, 2H), 4.14 – 4.08 (m, 2H),

4.02 – 3.95 (m, 2H), 3.79 (s, 3H), 2.08 (s, 3H), 1.96 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.45, 169.37, 169.34, 167.12, 165.52, 164.66, 133.51, 133.47, 129.86, 129.75, 128.97, 128.67, 128.52, 128.47, 105.51, 98.67, 74.91, 72.63, 72.00, 71.51, 70.90, 69.35, 65.34, 64.81, 61.76, 52.94, 20.70, 20.47, 20.19. ESI-MS: $C_{35}H_{34}F_3NO_{16}$ $[M+NH_4]^+$ calcd: 782.1902, obsd: 782.1886.



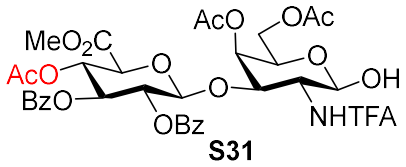
_N_-(Benzyl)-benzyloxycarbonyl-3-aminopropyl methyl-2,3-di-_O_-benzoyl-_O_-_β_-D-glucopyranosyluronate-(1→3)-6-_O_-acetyl-4-_O_-dichlorovinyl sulfate-2-deoxy-2-_N_-trifluoroacetamido-_β_-D-galactopyranoside 22:



Following the general procedure for glycosylation catalyzed by NIS/TfOH, coupling between donor **20** (0.051 g, 0.46 μmol) and *N*-(benzyl)-benzyloxycarbonyl-3-aminopropanol (0.021 g, 0.70 μmol) was performed, which was followed by TBS cleavage using the general procedure for TBS removal to afford disaccharide **22** (0.044 g, 82% yield for the 2 steps). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 – 7.92 (m, 2H), 7.90 (t, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.52 – 7.44

(m, 2H), 7.38 – 7.27 (m, 13H), 7.13 (d, *J* = 7.2 Hz, 1H), 5.56 (t, *J* = 9.3 Hz, 1H), 5.44 – 5.40 (m, 2H), 5.13 – 5.07 (m, 2H), 4.96 (d, *J* = 7.7 Hz, 1H), 4.90 – 4.77 (m, 1H), 4.60 – 4.50 (m, 3H), 4.37 (t, *J* = 14.6 Hz, 1H), 4.29 – 4.24 (m, 2H), 4.23 – 4.10 (m, 3H), 3.89 (s, 3H), 3.85 – 3.79 (m, 2H), 3.70 (dt, *J* = 10.9, 7.7 Hz, 1H), 3.53 – 3.45 (m, 2H), 3.33 (ddd, *J* = 9.9, 7.7, 4.4 Hz, 1H), 3.21 – 3.06 (m, 2H), 2.13 (s, 3H), 1.72 – 1.65 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 134.63, 133.36, 133.26, 130.02, 129.82, 126.68, 101.88, 98.96, 82.69, 74.70, 73.94, 70.73, 70.23, 69.73, 67.21, 66.20, 61.74, 52.80, 50.03, 43.05, 27.38, 20.39. ESI-MS: $C_{51}H_{51}Cl_2F_3N_2O_{20}S$ $[M+H]^+$ calcd: 1171.2, obsd: 1171.2, $[M+NH_4]^+$ calcd: 1188.2, obsd: 1188.2.

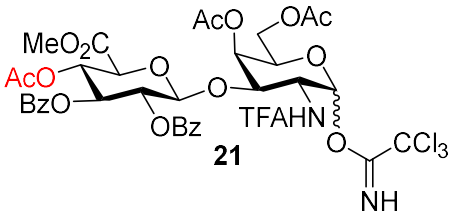
Methyl-4-*O*-acetyl-2,3-di-*O*-benzoyl-*β*-D-glucopyranosyluronate-(1→3)-4,6-di-*O*-acetyl-2-deoxy-2-*N*-trifluoroacetamido-*β*-D-galactopyranoside S31:



S31

To a solution of thioglycoside **17** (0.034 g, 0.38 µmol) in acetone/H_2O (15:1, 3 mL) at 0 ºC, *N*-bromosuccinimide (0.01g, 0.85 µmol) was added. After stirring in ice bath for 1 h, the solvents were evaporated under reduced pressure. The residue was dissolved in ethyl acetate and washed successively with 10% $Na_2S_2O_3$(aq) and brine. The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (Hex:EtOAc., 2:1) to give the hemiacetal **S31** (0.028 g, 95%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.87 – 7.83 (m, 4H), 7.51 – 7.46 (m, 2H), 7.36 – 7.32 (m, 4H), 7.20 (d, *J* = 8.1 Hz, 1H), 5.67 (t, *J* = 9.6 Hz, 1H), 5.49 – 5.41 (m, 3H), 5.36 (t, *J* = 3.4 Hz, 1H), 5.05 (d, *J* = 7.9 Hz, 1H), 4.49 – 4.35 (m, 4H), 4.23 (d, *J* = 10.0 Hz, 1H), 4.17 (dd, *J* = 11.5, 5.3 Hz, 1H), 3.97 (dd, *J* = 11.6, 7.2 Hz, 1H), 3.78 (s, 3H), 2.08 (s, 3H), 2.05 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 178.07, 170.06, 169.41, 167.19, 133.53, 133.25, 129.79, 129.76, 128.84, 128.44, 128.20, 99.38, 91.27, 72.69, 72.24, 70.96, 70.84, 69.30, 68.65, 67.33, 62.67, 53.09, 50.04, 29.58, 20.77, 20.63, 20.44. ESI-MS: $C_{35}H_{36}F_3NO_{17}$ $[M+NH_4]^+$ calcd: 817.2274, obsd: 817.2266.

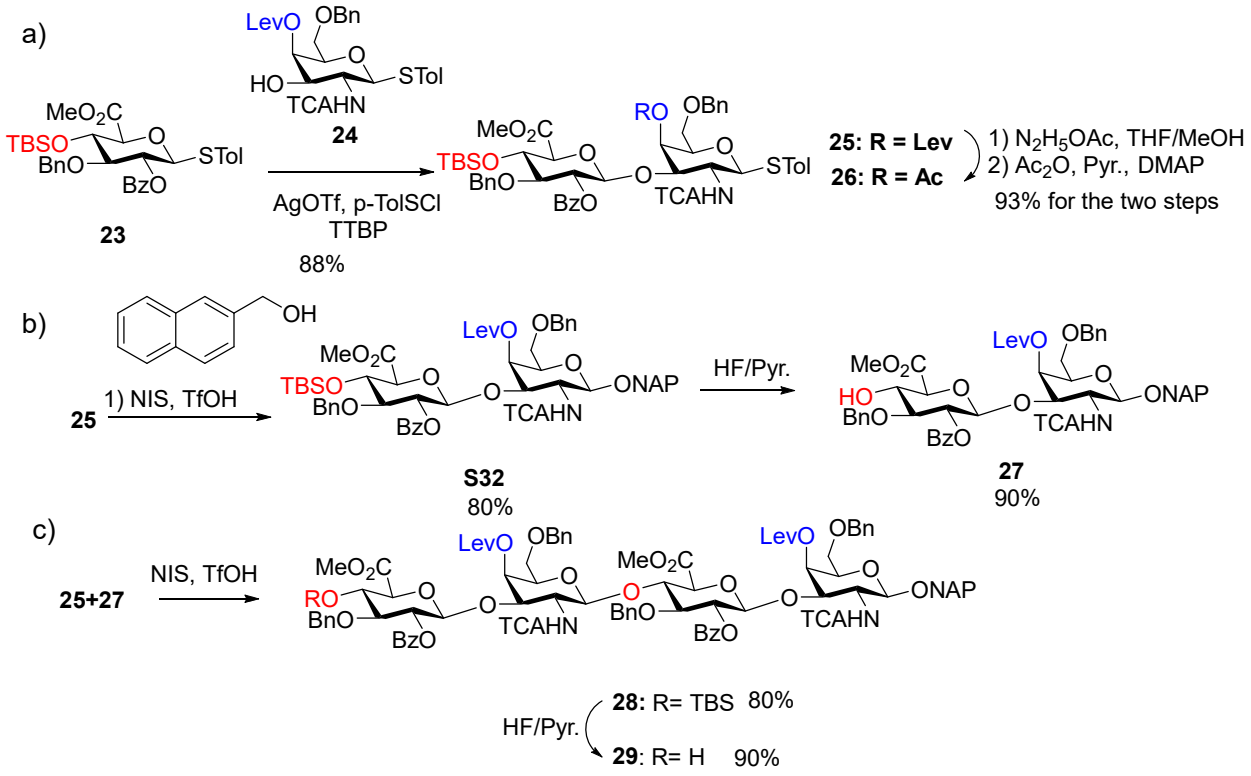
***O*-(Methyl-4-*O*-acetyl-2,3-di-*O*-benzoyl-*O*-*β*-D-glucopyranosyluronate-(1→3)-4,6-di-*O*-acetyl-2-deoxy-2-*N*-trifluoroacetamido-*α*-D-galactopyranosyl)trichloroacetimidate 21:**



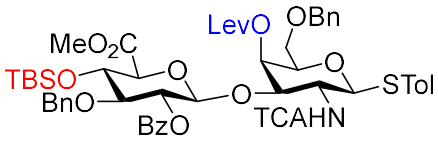
21

DBU (2.4 µL, 0.16 µmol) was added to a solution of the hemiacetal **S31** (0.032 g, 0.4 µmol) and CCl_3CN (0.06 mL, 0.6 µmol) in DCM (2 mL) at 0 °C under a nitrogen atmosphere. The reaction was stirred at rt for 10 h, then concentrated under reduced pressure. The crude was purified using flash chromatography (Hex:EtOAc., 2:1) to afford trichloroacetamidate **21** (0.026 g, 70%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.74 (s, 1H), 8.06 – 8.02 (m, 1H), 7.88 (tt, *J* = 8.4, 1.4 Hz, 4H), 7.57 – 7.50 (m, 3H), 7.43 – 7.34 (m, 6H), 6.87 (d, *J* = 7.1 Hz, 1H), 6.58 (d, *J* = 3.4 Hz, 1H), 5.72 (t, *J* = 9.5 Hz, 1H), 5.62 – 5.60 (m, 1H), 5.48 (dd, *J* = 9.5, 8.0 Hz, 1H), 5.06 (d, *J* = 8.0 Hz, 1H), 4.77 – 4.72 (m, 1H), 4.67 – 4.62 (m, 1H), 4.53 – 4.49 (m, 1H), 4.37 – 4.32 (m, 2H), 4.24 (d, *J* = 9.8 Hz, 1H), 4.19 (dd, *J* = 11.5, 6.1 Hz, 1H), 4.12 – 4.08 (m, 1H), 3.98 (dd, *J* = 11.5, 6.9 Hz, 1H), 3.91 – 3.89 (m, 1H), 3.81 (d, *J* = 7.8 Hz, 1H), 3.77 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 1.99 (s, 1H), 1.97 (s, 3H), 1.95 (s, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) from coupled HSQC δ 133.31, 129.43, 128.02, 98.02, 94.13, 72.87, 71.81, 69.34, 66.52, 63.78, 61.31, 52.93, 49.40, 20.37. ESI-MS: $C_{37}H_{36}Cl_3F_3N_2O_{17}$ $[M+H]^+$ calcd: 943.1, obsd: 943.1.

1.10. Chemical synthesis of 24-mer 1:



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

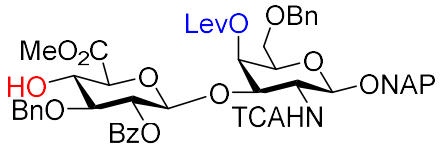


25

Following the general procedure for pre-activation based single-step glycosylation, coupling between donor **23** (1.32 g, 2.1 mmol) and acceptor **24** (1.01 g, 1.6 mmol) afford the desired disaccharide **25** (1.52 g, 88%). $[\alpha_D^{20}]$ = +7.5 (C = 0.12, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 – 7.87 (m, 2H), 7.58 – 7.54 (m, 1H), 7.45 – 7.30 (m, 9H), 7.17 – 7.10 (m, 5H), 7.06 – 7.00 (m, 2H), 6.79 (d, *J* = 7.6 Hz, 1H), 5.55 (d, *J* = 3.6 Hz, 1H), 5.23 (t, *J* = 7.2 Hz, 1H), 5.18 – 5.15 (m, 1H), 4.85 (d, *J* = 6.9 Hz, 1H), 4.68 – 4.60 (m, 2H), 4.56 (dd, *J* = 10.4, 3.3 Hz, 1H), 4.49 (s, 2H), 4.14 – 4.09 (m, 2H), 3.96 (d, *J* = 8.9 Hz, 1H), 3.74 (s, 3H), 3.67 – 3.60 (m, 2H), 3.59 – 3.54 (m, 2H), 2.86 – 2.78 (m, 1H), 2.66 – 2.56 (m, 2H), 2.51 – 2.43 (m, 1H), 2.31 (s, 3H), 2.17 (s,

3H), 0.86 (s, 9H), 0.00 (d, J = 1.6 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.78, 206.61, 171.44, 171.32, 168.53, 164.88, 161.53, 138.34, 138.07, 137.67, 137.57, 133.38, 133.34, 133.09, 129.79, 129.75, 129.65, 129.62, 129.41, 128.53, 128.48, 128.45, 128.39, 128.33, 128.10, 128.00, 127.96, 127.77, 127.63, 127.62, 127.57, 127.47, 127.43, 107.35, 99.77, 98.69, 92.22, 84.85, 82.43, 82.35, 77.35, 76.95, 76.48, 76.46, 74.87, 74.57, 74.24, 73.68, 73.67, 73.63, 73.58, 73.29, 72.09, 71.87, 71.63, 69.42, 68.89, 68.13, 65.81, 65.19, 60.46, 54.09, 52.36, 38.09, 37.89, 29.85, 29.78, 27.91, 27.49, 25.75, 25.73, 21.18, 17.89, 14.22, -4.03, -4.08, -5.19, -5.23. ESI-MS: $C_{54}H_{64}Cl_3NO_{14}SSi$ $[M+NH_4]^+$ calcd: 1133.3221, obsd: 1133.3201.

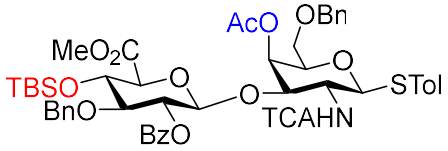
2-Naphthylmethyl (methyl 3-*O*-benzyl-2-*O*-benzoyl-*O*-*β*-D-glucopyranosyluronate)-(1→3)-6-*O*-benzyl-4-*O*-levulinoyl-2-deoxy-2-*N*-trichloroacetamido-*β*-D-galactopyranoside 27:



27

Following the general procedure for glycosylation catalyzed by NIS/TfOH, disaccharide **S32** was synthesized in (0.12 g, 80%) by coupling between donor **25** (0.15 g, 0.13 mmol) and acceptor **24** (0.028 g, 0.18 mmol). Then compound **S32** (122 mg, 0.105 mmol) was subjected to the general procedure for TBS removal to give disaccharide acceptor **27** (0.1 g, 90%). $[\alpha_D^{20}]$ = +4.6 (C = 0.13, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.96 – 7.92 (m, 2H), 7.83 – 7.68 (m, 5H), 7.60 – 7.56 (m, 1H), 7.48 – 7.41 (m, 4H), 7.40 – 7.35 (m, 5H), 7.33 – 7.29 (m, 1H), 7.18 – 7.11 (m, 5H), 6.77 (d, J = 7.0 Hz, 1H), 5.59 (dd, J = 3.5, 0.9 Hz, 1H), 5.14 (dd, J = 9.3, 7.5 Hz, 1H), 5.04 (d, J = 8.3 Hz, 1H), 5.01 (d, J = 11.7 Hz, 1H), 4.78 – 4.66 (m, 5H), 4.59 – 4.52 (m, 2H), 4.06 (ddd, J = 9.8, 8.7, 2.5 Hz, 1H), 3.88 – 3.83 (m, 2H), 3.75 (s, 3H), 3.68 – 3.58 (m, 3H), 3.53 (ddd, J = 10.9, 8.3, 7.0 Hz, 1H), 3.31 (d, J = 2.8 Hz, 1H), 2.90 (dt, J = 17.9, 7.2 Hz, 1H), 2.78 – 2.66 (m, 2H), 2.60 (ddd, J = 16.8, 6.9, 5.6 Hz, 1H), 2.21 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.92, 171.70, 169.65, 164.90, 161.93, 138.00, 137.74, 133.90, 133.38, 133.14, 133.10, 129.86, 129.45, 128.50, 128.42, 128.34, 128.26, 128.10, 127.97, 127.91, 127.76, 127.70, 127.67, 127.33, 126.19, 126.13, 126.01, 100.65, 97.26, 92.11, 80.19, 77.28, 74.37, 73.87, 73.71, 72.95, 72.71, 72.43, 72.00, 71.34, 69.67, 68.70, 56.64, 52.82, 38.18, 29.88, 28.00. ESI-MS: $C_{48}H_{50}Cl_3NO_{14}S$ $[M+H]^+$ calcd: 1002.2090, obsd: 1002.2065, $[M+NH_4]^+$ calcd: 1019.2356, obsd: 1019.2306.

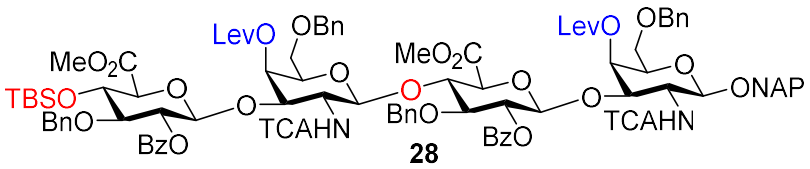
***p*-Tolyl methyl-3-*O*-benzyl-2-*O*-benzoyl-4-*O*-*t*-butyldimethylsilyl-*β*-D-glucopyranosyluronate-(1→3)-4-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-*N*-trichloroacetamido-1-thio-*β*-D-galactopyranoside 26:**



26

To a solution of **25** (1 g, 0.89 mmol) in THF/MeOH (10:1, 20 mL), hydrazine acetate (0.247 g, 2.7 mmol) was added at 0 °C. The reaction was stirred for 5 h at rt. Upon completion, the mixture was cooled down to 0 °C, and quenched with acetone, concentrated under vacuo, diluted with ethyl acetate (50 mL), washed with saturated $NaHCO_3$, and brine. The organic layer was concentrated and the residue was dissolved in Py:Ac_2O (2:1, 20 mL) and the mixture was stirred at rt till the reaction was completed. Then the mixture was diluted with EtOAc, washed with 1M HCl, $NaHCO_3$ and NaCl solutions, concentrated and purified with silica gel chromatography to afford **26** (0.88 g, 93% in 2 steps) as a white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 – 7.91 (m, 2H), 7.57 – 7.54 (m, 1H), 7.43 – 7.38 (m, 4H), 7.37 – 7.30 (m, 5H), 7.16 – 7.12 (m, 5H), 7.04 – 7.01 (m, 2H), 6.70 (d, *J* = 7.4 Hz, 1H), 5.52 (d, *J* = 3.2 Hz, 1H), 5.26 – 5.20 (m, 2H), 4.85 (d, *J* = 6.9 Hz, 1H), 4.68 – 4.63 (m, 2H), 4.58 (dd, *J* = 10.4, 3.3 Hz, 1H), 4.53 – 4.46 (m, 2H), 4.12 (dd, *J* = 8.8, 7.8 Hz, 1H), 3.97 (d, *J* = 8.7 Hz, 1H), 3.87 – 3.84 (m, 1H), 3.76 (s, 3H), 3.67 – 3.61 (m, 1H), 3.59 – 3.54 (m, 3H), 2.31 (s, 3H), 2.03 (s, 3H), 0.85 (s, 9H), -0.01 (d, *J* = 4.1 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 169.90, 168.53, 164.87, 161.55, 138.31, 137.96, 137.63, 133.36, 132.95, 129.84, 129.80, 129.75, 129.42, 128.60, 128.46, 128.35, 128.06, 128.00, 127.83, 127.66, 127.45, 127.40, 99.75, 92.08, 84.85, 82.37, 77.27, 76.52, 74.14, 73.90, 73.53, 73.28, 71.61, 69.34, 69.17, 54.17, 52.36, 25.71, 21.17, 20.66, 17.87, -4.15, -5.22. ESI-MS: $C_{51}H_{60}Cl_3NO_{13}SSi$ $[M+H]^+$ calcd: 1002.2090, obsd: 1002.2065, $[M+NH_4]^+$ calcd: 1077.3, obsd: 1077.3.

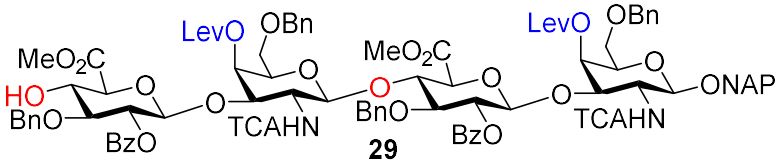
2-Naphthylmethyl (methyl 3-*O*-benzyl-2-*O*-benzoyl-4-*O*-*t*-butyldimethylsilyl-*β*-D-glucopyranosyluronate-(1→3)-6-*O*-benzyl-4-*O*-levulinoyl-2-deoxy-2-*N*-trichloroacetamido-*β*-D-galactopyranosyl-(1→4)-(methyl 3-*O*-benzyl-2-*O*-benzoyl-*O*-*β*-D-glucopyranosyluronate)-(1→3)-6-*O*-benzyl-4-*O*-levulinoyl-2-deoxy-2-*N*-trichloroacetamido-*β*-D-galactopyranoside 28:



28

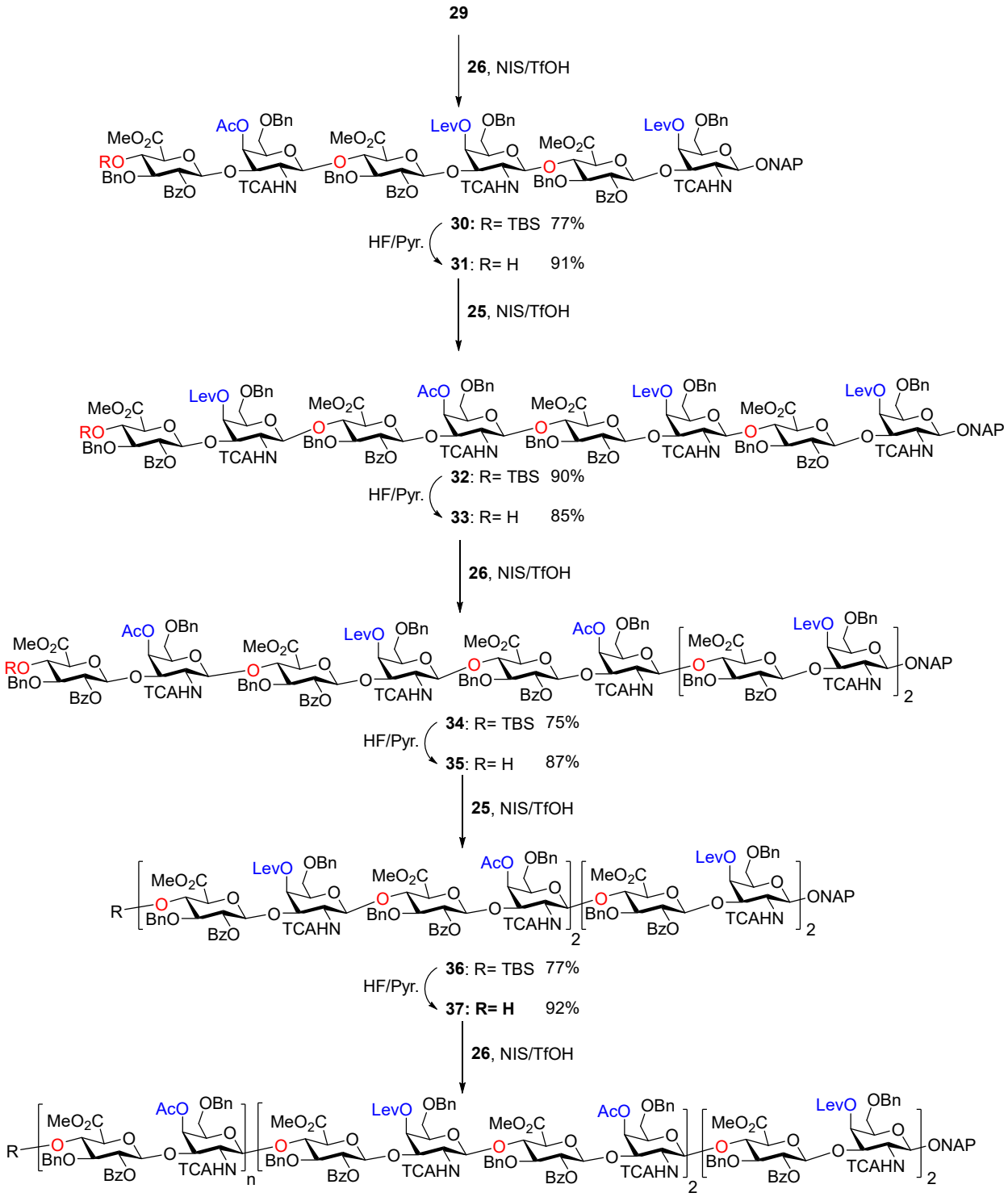
Following the general procedure for glycosylation catalyzed by NIS/TfOH, tetrasaccharide **28** was obtained (0.78 g, 80%) by coupling between donor **25** (0.7 g, 0.6 mmol) and acceptor **27** (0.5 g, 0.48 mmol). $[\alpha_D^{20}]$ = +20 (C = 0.01, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.98 – 7.94 (m, 2H), 7.92 – 7.89 (m, 2H), 7.81 – 7.70 (m, 4H), 7.56 – 7.51 (m, 2H), 7.48 – 7.44 (m, 2H), 7.42 – 7.33 (m, 9H), 7.32 – 7.23 (m, 7H), 7.16 (t, *J* = 2.4 Hz, 5H), 7.12 – 7.07 (m, 5H), 6.97 (d, *J* = 8.5 Hz, 1H), 6.83 (d, *J* = 7.0 Hz, 1H), 5.55 – 5.51 (m, 2H), 5.24 (t, *J* = 6.9 Hz, 1H), 5.11 (dd, *J* = 8.4, 7.1 Hz, 1H), 5.02 (d, *J* = 1.3 Hz, 1H), 5.00 (d, *J* = 4.7 Hz, 1H), 4.92 – 4.87 (m, 2H), 4.81 (d, *J* = 11.0 Hz, 1H), 4.73 – 4.68 (m, 3H), 4.61 – 4.56 (m, 2H), 4.55 – 4.50 (m, 3H), 4.30 – 4.24 (m, 2H), 4.19 – 4.13 (m, 3H), 4.07 – 4.01 (m, 1H), 3.97 (d, *J* = 9.1 Hz, 1H), 3.90 – 3.87 (m, 1H), 3.83 – 3.80 (m, 1H), 3.74 (s, 3H), 3.73 – 3.70 (m, 1H), 3.66 (s, 3H), 3.65 – 3.61 (m, 2H), 3.60 – 3.52 (m, 3H), 3.38 – 3.32 (m, 2H), 2.84 – 2.75 (m, 2H), 2.70 – 2.63 (m, 3H), 2.60 – 2.52 (m, 3H), 2.16 (s, 3H), 2.09 (s, 3H), 0.85 (s, 9H), 0.00 (d, *J* = 1.8 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.91, 206.76, 177.57, 171.61, 171.46, 169.33, 168.71, 164.91, 164.90, 161.99, 161.63, 138.02, 137.99, 137.93, 137.57, 133.92, 133.31, 133.17, 133.12, 133.07, 133.01, 129.94, 129.82, 129.66, 129.53, 129.40, 128.46, 128.40, 128.34, 128.30, 128.28, 128.09, 128.05, 128.03, 127.99, 127.89, 127.78, 127.75, 127.66, 127.54, 127.45, 127.28, 126.17, 126.10, 125.99, 100.37, 99.86, 99.45, 97.38, 92.70, 92.05, 82.42, 79.75, 77.27, 76.50, 74.74, 74.10, 73.70, 73.65, 73.57, 73.15, 73.11, 72.98, 72.95, 72.70, 71.52, 71.27, 69.58, 69.18, 68.91, 68.69, 68.17, 64.02, 56.35, 54.97, 52.91, 52.39, 38.19, 37.93, 29.83, 29.78, 29.70, 29.69, 29.65, 29.55, 28.01, 27.75, 25.72, 17.88, -4.07, -5.24. ESI-MS: $C_{99}H_{108}C_{l6}N_2O_{29}Si$ $[M+2NH_4]^{2+}$ calcd: 1032.2778, obsd: 1032.2792, $[M+NH_4]^+$ calcd: 2046.5, obsd: 2046.4.

2-Naphthylmethyl (methyl 3-*O*-benzyl-2-*O*-benzoyl-*O*-*β*-D-glucopyranosyluronate)-(1→3)-6-*O*-benzyl-4-*O*-levulinoyl-2-deoxy-2-*N*-trichloroacetamido-*β*-D-galactopyranosyl-(1→4)-(methyl 3-*O*-benzyl-2-*O*-benzoyl-*O*-*β*-D-glucopyranosyluronate)-(1→3)-6-*O*-benzyl-4-*O*-levulinoyl-2-deoxy-2-*N*-trichloroacetamido-*β*-D-galactopyranoside 29:



29

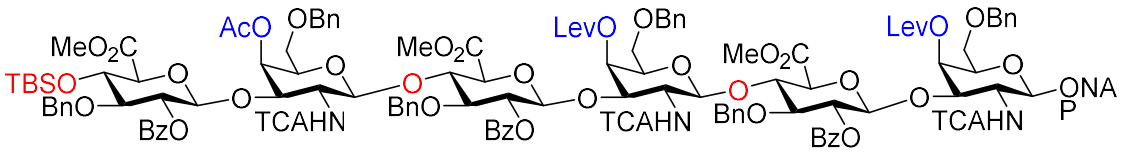
Following the general procedure for TBS removal, tetrasaccharide acceptor **29** (0.334 g, 90%) was obtained from **28** (0.39 g, 0.19 mmol). $[\alpha_D^{20}]$ = +3.6 (C = 0.11, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.01 – 7.97 (m, 2H), 7.93 – 7.90 (m, 2H), 7.82 – 7.71 (m, 4H), 7.59 – 7.53 (m, 2H), 7.48 – 7.45 (m, 2H), 7.44 – 7.40 (m, 3H), 7.40 – 7.35 (m, 5H), 7.34 – 7.29 (m, 3H), 7.28 – 7.23 (m, 4H), 7.18 – 7.13 (m, 5H), 7.11 – 7.07 (m, 5H), 6.87 (d, *J* = 8.3 Hz, 1H), 6.80 (d, *J* = 7.0 Hz, 1H), 5.58 – 5.53 (m, 2H), 5.17 – 5.10 (m, 2H), 5.04 – 4.99 (m, 2H), 4.97 (d, *J* = 8.4 Hz, 1H), 4.82 – 4.77 (m, 2H), 4.75 – 4.69 (m, 4H), 4.61 (dd, *J* = 10.9, 3.4 Hz, 1H), 4.56 – 4.49 (m, 3H), 4.32 – 4.24 (m, 3H), 4.19 (dd, *J* = 9.1, 8.1 Hz, 1H), 4.09 (dd, *J* = 9.9, 8.8 Hz, 1H), 3.93 – 3.86 (m, 3H), 3.84 – 3.80 (m, 1H), 3.76 (s, 3H), 3.67 (s, 3H), 3.66 – 3.53 (m, 6H), 3.37 – 3.33 (m, 2H), 2.92 – 2.86 (m, 1H), 2.85 – 2.79 (m, 1H), 2.73 – 2.65 (m, 3H), 2.63 – 2.53 (m, 3H), 2.17 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.91, 206.86, 171.71, 171.58, 169.64, 169.12, 165.01, 164.89, 162.00, 161.58, 137.99, 137.88, 137.75, 133.91, 133.35, 133.19, 133.13, 133.09, 130.06, 129.81, 129.67, 129.59, 129.39, 128.49, 128.41, 128.32, 128.26, 128.07, 128.05, 128.00, 127.98, 127.90, 127.77, 127.70, 127.67, 127.60, 127.48, 127.28, 126.18, 126.12, 125.98, 100.45, 100.29, 99.34, 97.35, 92.61, 92.03, 80.51, 79.77, 77.07, 74.75, 74.33, 74.06, 73.74, 73.71, 73.60, 72.98, 72.95, 72.76, 72.70, 71.72, 71.34, 69.58, 69.17, 68.69, 68.05, 56.44, 55.29, 52.92, 52.85, 38.20, 38.07, 29.83, 28.03, 27.89. ESI-MS: $C_{93}H_{94}Cl_6N_2O_{29}$ $[M+2NH_4]^{+2}$ calcd: 975.7377, obsd: 975.7313, $[M+NH_4]^+$ calcd: 1933.4, obsd: 1933.4.



R= TBS, **38** (n=1) (89%); **40** (n=2) (82%); **42** (n=3) (91%); **44** (n=4) (86%); **46** (n=5) (95%); **48** (n=6) (90%)

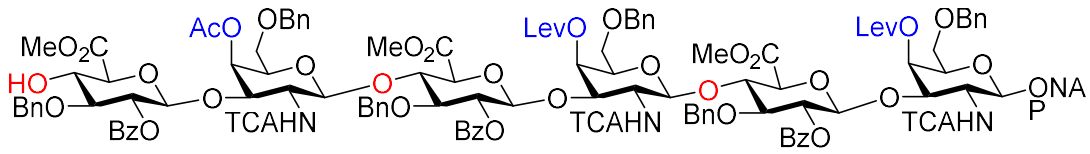
R= H, **39**(n=1) (70%); **41** (n=2) (88%); **43** (n=3) (95%); **45** (n=4 (94%); **47** (n=5) (90%); **49** (n=6 (94%)

6-mer 30:



30

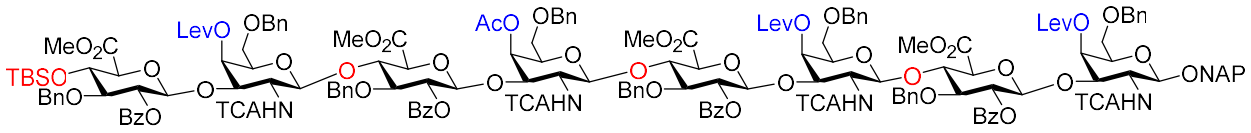
Following the general procedure for glycosylation catalyzed by NIS/TfOH, hexasaccharide **30** was obtained (0.383 g, 77%) through coupling between donor **29** (0.296 g, 0.28 mmol) and acceptor **26** (0.334 g, 0.17 mmol). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.06 – 8.04 (m, 1H), 7.96 (m, 4H), 7.91 – 7.89 (m, 2H), 7.81 – 7.70 (m, 5H), 7.54 (m, 4H), 7.47 – 7.44 (m, 2H), 7.40 (m, 7H), 7.37 – 7.35 (m, 4H), 7.31 (m, 5H), 7.26 – 7.23 (m, 4H), 7.17 (d, *J* = 4.3 Hz, 5H), 7.13 – 7.11 (m, 2H), 7.10 – 7.06 (m, 8H), 6.92 – 6.87 (m, 2H), 6.76 (d, *J* = 6.9 Hz, 1H), 5.52 (t, *J* = 3.7 Hz, 2H), 5.50 (d, *J* = 3.1 Hz, 1H), 5.28 – 5.25 (m, 1H), 5.14 – 5.09 (m, 2H), 5.02 (s, 1H), 5.00 (d, *J* = 3.8 Hz, 1H), 4.96 – 4.93 (m, 2H), 4.91 (d, *J* = 8.4 Hz, 1H), 4.83 – 4.80 (m, 1H), 4.79 – 4.77 (m, 1H), 4.73 – 4.69 (m, 3H), 4.60 – 4.59 (m, 1H), 4.57 – 4.56 (m, 1H), 4.54 – 4.50 (m, 4H), 4.33 – 4.30 (m, 1H), 4.29 – 4.27 (m, 1H), 4.26 – 4.25 (m, 1H), 4.24 – 4.22 (m, 1H), 4.17 (m, 4H), 4.06 – 4.02 (m, 1H), 3.99 (d, *J* = 9.0 Hz, 1H), 3.96 – 3.93 (m, 1H), 3.91 – 3.85 (m, 3H), 3.81 (t, *J* = 6.1 Hz, 1H), 3.76 (s, 3H), 3.74 – 3.68 (m, 3H), 3.67 (s, 3H), 3.66 (s, 3H), 3.64 – 3.61 (m, 2H), 3.59 – 3.53 (m, 3H), 3.34 – 3.27 (m, 4H), 2.84 – 2.68 (m, 4H), 2.66 – 2.60 (m, 2H), 2.57 – 2.47 (m, 4H), 2.16 (s, 3H), 2.10 (s, 3H), 1.97 (s, 3H), 0.84 (s, 9H), -0.01 (s, 3H), -0.02 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.86, 171.61, 171.57, 169.82, 169.18, 169.09, 168.79, 164.89, 164.86, 161.97, 161.72, 161.66, 138.11, 137.98, 137.90, 137.87, 137.61, 133.89, 133.33, 133.16, 133.12, 133.07, 133.00, 129.94, 129.81, 129.66, 129.55, 129.39, 128.47, 128.40, 128.34, 128.30, 128.05, 128.03, 127.98, 127.95, 127.92, 127.89, 127.87, 127.75, 127.67, 127.66, 127.59, 127.45, 127.38, 127.36, 127.27, 126.16, 126.10, 125.97, 100.40, 100.00, 99.76, 99.41, 99.38, 97.36, 92.63, 92.51, 82.38, 79.95, 79.75, 76.47, 74.67, 74.35, 74.18, 73.91, 73.78, 73.70, 73.62, 73.59, 73.54, 73.18, 73.10, 73.03, 72.95, 72.67, 72.50, 71.49, 71.33, 69.57, 69.24, 69.20, 68.80, 68.69, 68.38, 68.15, 64.01, 56.42, 55.08, 54.99, 52.89, 52.36, 38.19, 38.12, 33.84, 31.63, 29.82, 29.71, 29.67, 29.37, 29.17, 28.01, 27.90, 25.70, 22.71, 20.56, 17.87, 14.15, -4.17, -5.28. ESI-MS: $C_{137}H_{146}Cl_9N_3O_{42}Si$ $[M+2NH_4]^{+2}$ calcd: 1444.3499, obsd: 1444.3450, $[M+NH_4]^{+}$ calcd: 2870.7, obsd: 2870.6.



31

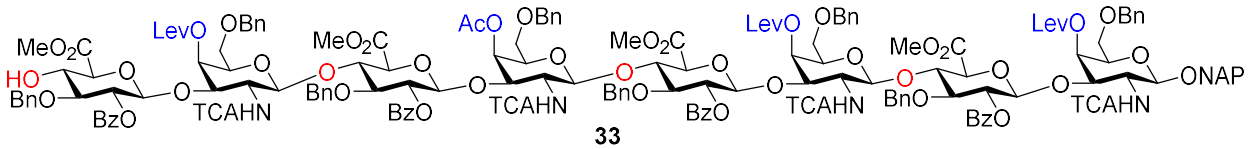
Following the general procedure for TBS removal, hexasaccharide acceptor **31** was obtained (0.454 g, 91%) from **30** (0.519 g, 0.18 mmol). $[\alpha_D^{20}]$ = +12.5 (C = 0.04, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.02 – 7.99 (m, 2H), 7.97 – 7.94 (m, 2H), 7.92 – 7.88 (m, 2H), 7.81 – 7.70 (m, 4H), 7.60 – 7.53 (m, 3H), 7.48 – 7.36 (m, 13H), 7.32 m, 5H), 7.28 – 7.25 (m, 6H), 7.18 – 7.14 (m, 5H), 7.12 – 7.04 (m, 10H), 6.88 – 6.83 (m, 2H), 6.78 (d, *J* = 7.0 Hz, 1H), 5.55 – 5.51 (m, 3H), 5.17 (dd, *J* = 8.8, 7.1 Hz, 1H), 5.14 – 5.09 (m, 2H), 5.02 (s, 1H), 5.00 (d, *J* = 4.6 Hz, 1H), 4.98 – 4.94 (m, 2H), 4.82 – 4.79 (m, 3H), 4.76 (d, *J* = 3.9 Hz, 1H), 4.74 – 4.68 (m, 4H), 4.61 – 4.58 (m, 1H), 4.57 – 4.51 (m, 4H), 4.36 – 4.30 (m, 2H), 4.29 – 4.26 (m, 2H), 4.25 – 4.22 (m, 2H), 4.21 – 4.17 (m, 2H), 4.09 (dd, *J* = 9.8, 8.7 Hz, 1H), 3.90 (m, 5H), 3.81 (t, *J* = 6.2 Hz, 1H), 3.78 (s, 3H), 3.74 (d, *J* = 6.3 Hz, 1H), 3.71 (t, *J* = 6.3 Hz, 1H), 3.67 (s, 3H), 3.66 (s, 3H), 3.65 (d, *J* = 3.1 Hz, 1H), 3.63 (d, *J* = 3.9 Hz, 1H), 3.62 – 3.61 (m, 1H), 3.60 – 3.52 (m, 3H), 3.33 (d, *J* = 6.3 Hz, 2H), 3.30 (d, *J* = 6.2 Hz, 2H), 2.85 – 2.73 (m, 3H), 2.72 – 2.61 (m, 3H), 2.59 – 2.48 (m, 4H), 2.17 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.89, 206.87, 171.57, 169.91, 169.63, 169.10, 169.02, 164.94, 164.90, 164.87, 161.99, 161.69, 161.58, 138.06, 137.98, 137.90, 137.82, 137.75, 133.89, 133.34, 133.17, 133.13, 133.08, 130.07, 129.95, 129.81, 129.63, 129.56, 129.39, 128.48, 128.41, 128.37, 128.34, 128.32, 128.26, 128.04, 128.02, 127.99, 127.92, 127.90, 127.76, 127.67, 127.60, 127.46, 127.38, 127.28, 126.18, 126.11, 125.98, 100.42, 100.24, 100.13, 99.37, 99.25, 97.36, 92.57, 92.51, 92.02, 80.53, 79.92, 79.75, 74.69, 74.36, 74.31, 74.22, 74.09, 73.80, 73.73, 73.71, 73.69, 73.59, 73.57, 72.99, 72.96, 72.94, 72.91, 72.68, 72.53, 71.59, 71.34, 69.58, 69.19, 68.90, 68.69, 68.12, 56.43, 55.33, 55.10, 52.93, 52.90, 52.82, 38.20, 38.13, 29.82, 29.71, 28.02, 27.92, 20.66. ESI-MS: $C_{131}H_{132}Cl_9N_3O_{42}$ $[M+2NH_4]^{+2}$ calcd: 1387.3067, obsd: 1387.3064, $[M+NH_4]^+$ calcd: 2756.6, obsd: 2756.6.

8-mer 32:



32

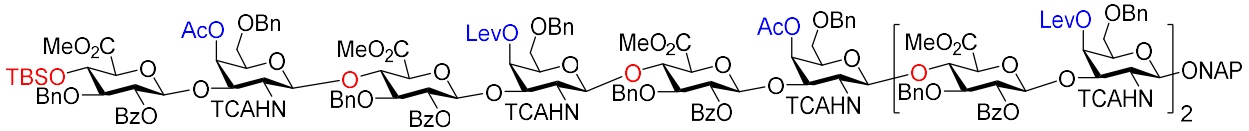
Following the general procedure for glycosylation catalyzed by NIS/TfOH, octasaccharide **32** was obtained (0.557 g, 90%) through coupling between donor **25** (0.333 g, 0.29 mmol) and acceptor **31** (0.454 g, 0.166 mmol). $[\alpha_D^{20}]$ = +22 (C = 0.05, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.98 – 7.93 (m, 6H), 7.92 – 7.89 (m, 2H), 7.82 – 7.69 (m, 5H), 7.55 (m, 4H), 7.47 – 7.45 (m, 2H), 7.44 – 7.38 (m, 8H), 7.38 – 7.35 (m, 4H), 7.33 – 7.29 (m, 7H), 7.28 – 7.23 (m, 10H), 7.17 (m, 4H), 7.15 – 7.11 (m, 6H), 7.09 (m, 6H), 7.07 – 7.03 (m, 3H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.88 – 6.85 (m, 2H), 6.76 (d, *J* = 7.0 Hz, 1H), 5.54 – 5.50 (m, 4H), 5.24 (t, *J* = 6.7 Hz, 1H), 5.15 – 5.13 (m, 1H), 5.13 – 5.09 (m, 2H), 5.02 (s, 1H), 5.00 (d, *J* = 3.9 Hz, 1H), 4.97 – 4.92 (m, 3H), 4.87 – 4.84 (m, 2H), 4.81 – 4.76 (m, 4H), 4.73 – 4.68 (m, 3H), 4.61 – 4.50 (m, 8H), 4.36 – 4.30 (m, 2H), 4.28 – 4.22 (m, 7H), 4.20 – 4.16 (m, 2H), 4.16 – 4.11 (m, 2H), 4.08 – 4.01 (m, 2H), 4.00 – 3.97 (m 2H), 3.93 – 3.90 (m, 2H), 3.89 – 3.85 (m, 2H), 3.81 (t, *J* = 6.1 Hz, 1H), 3.74 (s, 3H), 3.73 – 3.70 (m, 3H), 3.69 (s, 3H), 3.67 (s, 3H), 3.66 (s, 3H), 3.64 – 3.61 (m, 2H), 3.59 – 3.57 (m, 1H), 3.56 – 3.52 (m, 2H), 3.35 – 3.32 (m, 3H), 3.28 (d, *J* = 6.1 Hz, 1H), 2.85 – 2.73 (m, 4H), 2.70 (t, *J* = 6.1 Hz, 1H), 2.67 – 2.60 (m, 3H), 2.58 – 2.50 (m, 5H), 2.47 – 2.40 (m, 2H), 2.17 (s, 3H), 2.09 (s, 3H), 2.09 (s, 3H), 1.96 (s, 3H), 0.85 (s, 9H), 0.02 – -0.02 (m, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.85, 206.73, 171.57, 171.42, 169.93, 169.49, 169.10, 168.96, 168.74, 164.91, 164.90, 164.86, 161.98, 161.73, 161.69, 138.07, 137.99, 137.98, 137.90, 137.81, 137.58, 133.89, 133.33, 133.17, 133.13, 133.08, 129.96, 129.95, 129.81, 129.67, 129.55, 129.39, 128.47, 128.40, 128.37, 128.34, 128.31, 128.29, 128.10, 128.04, 128.01, 127.98, 127.92, 127.90, 127.82, 127.76, 127.66, 127.59, 127.56, 127.47, 127.40, 127.37, 127.28, 126.17, 126.11, 125.97, 100.40, 100.11, 99.98, 99.92, 99.41, 99.33, 99.25, 97.35, 92.51, 92.47, 82.41, 79.92, 79.82, 79.76, 76.48, 74.68, 74.39, 74.31, 74.25, 74.03, 73.74, 73.71, 73.68, 73.58, 73.56, 73.10, 73.05, 73.01, 72.96, 72.85, 72.67, 72.53, 71.46, 71.33, 69.58, 69.20, 68.89, 68.85, 68.68, 68.16, 68.13, 68.09, 56.43, 55.21, 55.07, 54.93, 52.92, 52.89, 52.39, 38.19, 38.12, 37.92, 29.82, 29.78, 29.71, 29.66, 28.01, 27.91, 27.74, 25.71, 20.66, 17.87, -4.09, -5.25. ESI-MS: $C_{178}H_{188}Cl_{12}N_4O_{56}Si$ $[M+3NH_4]^{+3}$ calcd: 1261.9659, obsd: 1261.9602, $[M+2NH_4]^{+2}$ calcd: 1884.4, obsd: 1884.4.



33

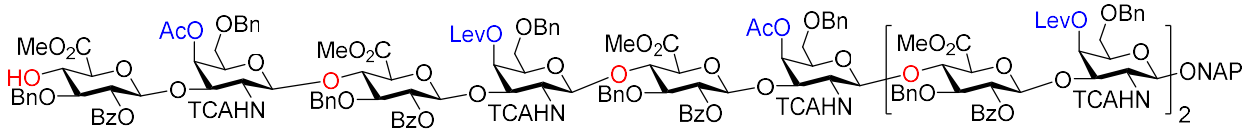
Following the general procedure for TBS removal, octasaccharide acceptor **33** was obtained (0.46 g, 85%) from **32** (0.56 g, 0.15 mmol). $[\alpha_D^{20}]$ = +2 (C = 0.05, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.01 – 7.93 (m, 6H), 7.91 – 7.88 (m, 2H), 7.81 – 7.73 (m, 3H), 7.70 (s, 1H), 7.61 – 7.52 (m, 5H), 7.47 – 7.44 (m, 3H), 7.41 (m, 6H), 7.38 – 7.35 (m, 4H), 7.33 – 7.28 (m, 7H), 7.26 (m, 10H), 7.16 (m, 5H), 7.14 – 7.02 (m, 15H), 6.87 – 6.82 (m, 3H), 6.76 (d, *J* = 7.1 Hz, 1H), 5.56 – 5.49 (m, 4H), 5.16 – 5.09 (m, 4H), 5.02 (s, 1H), 5.00 (d, *J* = 4.7 Hz, 1H), 4.98 – 4.91 (m, 3H), 4.84 – 4.76 (m, 6H), 4.74 – 4.68 (m, 4H), 4.62 – 4.49 (m, 7H), 4.36 – 4.30 (m, 2H), 4.29 – 4.15 (m, 11H), 4.11 – 4.06 (m, 1H), 3.96 – 3.84 (m, 8H), 3.81 (t, *J* = 6.2 Hz, 1H), 3.76 (s, 3H), 3.74 – 3.71 (m, 2H), 3.69 (s, 3H), 3.67 (s, 3H), 3.66 (s, 3H), 3.63 (d, *J* = 3.0 Hz, 1H), 3.62 – 3.57 (m, 3H), 3.56 – 3.53 (m, 1H), 3.34 – 3.31 (m, 3H), 3.29 – 3.26 (m, 2H), 3.21 (d, *J* = 2.7 Hz, 1H), 2.91 – 2.76 (m, 4H), 2.75 – 2.66 (m, 3H), 2.57 (m, 7H), 2.17 (s, 3H), 2.15 (s, 3H), 2.10 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.86, 206.84, 171.67, 171.56, 169.87, 169.69, 169.29, 169.10, 168.95, 164.99, 164.92, 164.89, 164.86, 161.98, 161.70, 161.68, 161.58, 138.06, 137.97, 137.94, 137.90, 137.81, 137.75, 133.89, 133.34, 133.18, 133.12, 133.08, 130.06, 129.96, 129.81, 129.59, 129.56, 129.54, 129.39, 128.47, 128.40, 128.37, 128.35, 128.32, 128.26, 128.07, 128.03, 127.99, 127.92, 127.90, 127.89, 127.76, 127.69, 127.66, 127.61, 127.59, 127.46, 127.41, 127.37, 127.28, 126.17, 126.11, 125.97, 100.42, 100.24, 100.13, 100.05, 99.41, 99.38, 99.18, 97.34, 92.62, 92.45, 80.49, 79.93, 79.78, 79.76, 76.94, 74.69, 74.38, 74.36, 74.30, 73.97, 73.83, 73.78, 73.71, 73.67, 73.59, 73.56, 73.00, 72.94, 72.85, 72.76, 72.66, 72.53, 71.70, 71.34, 69.58, 69.19, 69.08, 68.85, 68.68, 68.12, 67.93, 56.44, 55.28, 55.24, 55.09, 52.92, 52.90, 52.85, 38.19, 38.12, 38.07, 29.82, 29.71, 29.66, 28.01, 27.91, 27.88, 20.65. ESI-MS: $C_{172}H_{174}Cl_{12}N_4O_{56}$ $[M+3NH_4]^{+3}$ calcd: 1223.93, obsd: 1223.93, $[M+2NH_4]^{+2}$ calcd: 1826.9, obsd: 1826.9.

10-mer 34:



34

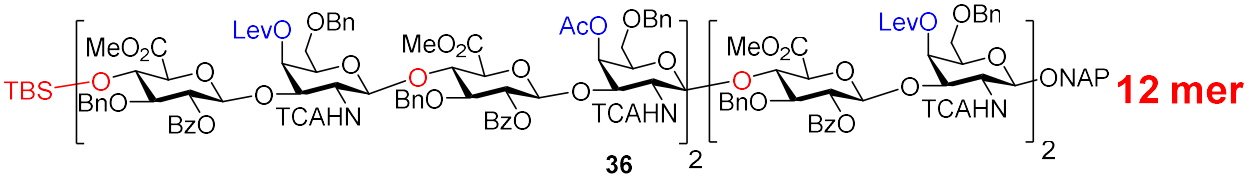
Following the general procedure for glycosylation catalyzed by NIS/TfOH, decasaccharide **34** was obtained (0.5 g, 75%) through coupling between donor **26** (0.28 g, 0.26 mmol) and acceptor **33** (0.53 g, 0.15 mmol). $[\alpha_D^{20}]$ = -20 (C = 0.01, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.00 – 7.95 (m, 8H), 7.93 – 7.90 (m, 2H), 7.81 – 7.79 (m, 1H), 7.77 (m, 1H), 7.76 – 7.73 (m, 1H), 7.71 (m, 1H), 7.58 – 7.53 (m, 5H), 7.46 (m, 2H), 7.42 (m, 9H), 7.37 (m, 5H), 7.34 – 7.30 (m, 9H), 7.29 (d, *J* = 1.6 Hz, 1H), 7.28 – 7.24 (m, 11H), 7.19 (m, 5H), 7.17 – 7.09 (m, 18H), 7.07 (m, 3H), 6.99 – 6.94 (m, 2H), 6.92 – 6.88 (m, 2H), 6.80 (d, *J* = 7.0 Hz, 1H), 5.53 (m, 5H), 5.30 – 5.27 (m, 2H), 5.18 – 5.11 (m, 5H), 5.02 (d, *J* = 2.2 Hz, 1H), 5.00 (s, 1H), 4.98 – 4.96 (m, 2H), 4.95 – 4.90 (m, 3H), 4.89 – 4.87 (m, 2H), 4.85 – 4.82 (m, 2H), 4.81 – 3.97 (m, 2H), 4.78 (d, *J* = 2.7 Hz, 1H), 4.75 – 4.71 (m, 3H), 4.63 – 4.58 (m, 5H), 4.55 – 4.51 (m, 3H), 4.36 – 4.32 (m, 3H), 4.30 – 4.25 (m, 8H), 4.24 – 4.15 (m, 7H), 4.09 – 4.05 (m, 1H), 4.03 – 3.97 (m, 4H), 3.97 – 3.88 (m, 5H), 3.81 (d, *J* = 6.2 Hz, 1H), 3.77 (s, 3H), 3.74 – 3.71 (m, 4H), 3.70 (s, 3H), 3.68 (s, 6H), 3.67 (s, 3H), 3.58 (m, 4H), 3.32 (m, 9H), 2.85 – 2.68 (m, 6H), 2.67 – 2.60 (m, 3H), 2.58 – 2.46 (m, 7H), 2.16 (s, 3H), 2.09 (s, 6H), 1.98 (s, 3H), 1.97 (s, 3H), 0.86 (s, 9H), -0.01 (s, 3H), -0.00 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.91, 206.89, 206.87, 171.63, 171.61, 171.59, 169.95, 169.85, 169.36, 169.24, 169.14, 169.02, 168.83, 164.93, 164.91, 164.89, 161.99, 161.79, 161.75, 161.73, 161.71, 138.12, 138.08, 137.98, 137.94, 137.92, 137.87, 137.81, 137.62, 133.91, 133.36, 133.20, 133.14, 133.09, 129.96, 129.82, 129.56, 129.40, 128.49, 128.42, 128.39, 128.36, 128.33, 128.08, 128.05, 128.01, 127.99, 127.96, 127.94, 127.92, 127.90, 127.77, 127.70, 127.68, 127.63, 127.62, 127.48, 127.41, 127.28, 126.20, 126.13, 125.98, 100.37, 100.06, 99.87, 99.62, 99.46, 99.36, 97.40, 92.58, 92.54, 92.49, 82.39, 79.95, 79.79, 77.04, 76.79, 76.47, 74.64, 74.46, 74.14, 74.01, 73.91, 73.79, 73.71, 73.69, 73.60, 73.57, 73.20, 72.99, 72.84, 72.69, 72.53, 71.51, 71.31, 69.59, 69.22, 68.86, 68.68, 68.44, 68.17, 56.39, 55.17, 55.07, 54.97, 52.91, 52.38, 38.20, 38.14, 29.82, 29.71, 29.69, 28.04, 27.93, 25.73, 20.67, 20.58, 17.89, -4.14, -5.25. ESI-MS: $C_{216}H_{226}Cl_{15}N_5O_{69}Si$ $[M+3NH_4]^{+3}$ calcd: 1536.0140, obsd: 1536.010.



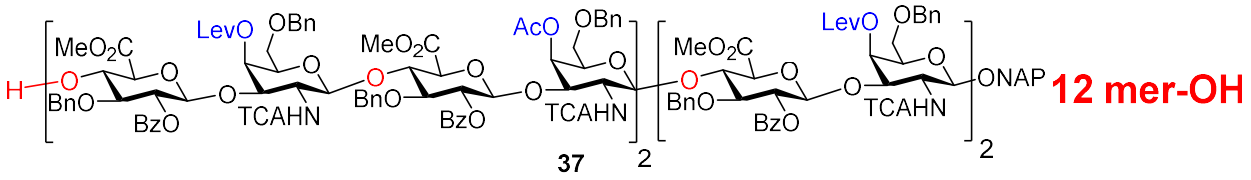
35

Following the general procedure for TBS removal, decasaccharide acceptor **35** was obtained (0.56 g, 87%) from **34** (0.66 g, 0.145 mmol). $[\alpha_D^{20}]$ = -2.5 (C = 0.12, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.03 – 7.97 (m, 8H), 7.94 – 7.91 (m, 2H), 7.82 – 7.72 (m, 5H), 7.60 – 7.54 (m, 5H), 7.48 – 7.41 (m, 11H), 7.41 – 7.39 (m, 1H), 7.39 – 7.37 (m, 3H), 7.35 – 7.31 (m, 9H), 7.29 – 7.25 (m, 12H), 7.12 (m, 26H), 6.98 – 6.94 (m, 2H), 6.93 – 6.90 (m, 2H), 6.84 (d, *J* = 7.1 Hz, 1H), 5.56 – 5.52 (m, 5H), 5.21 – 5.12 (m, 6H), 5.03 (d, *J* = 4.2 Hz, 1H), 5.01 (s, 1H), 4.99 – 4.97 (m, 3H), 4.93 (d, *J* = 8.4 Hz, 1H), 4.89 (d, *J* = 6.3 Hz, 1H), 4.87 – 4.82 (m, 4H), 4.81 – 4.76 (m, 4H), 4.75 (s, 1H), 4.74 – 4.70 (m, 2H), 4.63 – 4.58 (m, 4H), 4.57 – 4.53 (m, 3H), 4.38 – 3.33 (m, 3H), 4.31 – 4.24 (m, 10H), 4.22 – 4.16 (m, 3H), 4.12 – 4.08 (m, 1H), 4.01 – 3.90 (m, 10H), 3.83 (t, *J* = 6.2 Hz, 1H), 3.78 (s, 3H), 3.74 – 3.72 (m, 3H), 3.71 (s, 3H), 3.70 – 3.68 (m, 6H), 3.68 (s, 3H), 3.66 – 3.63 (m, 2H), 3.62 – 3.59 (m, 2H), 3.33 (m, 9H), 2.84 – 2.67 (m, 6H), 2.64 – 2.48 (m, 9H), 2.17 (s, 3H), 2.10 (d, *J* = 1.6 Hz, 6H), 2.05 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.97, 206.94, 206.91, 171.60, 169.97, 169.57, 169.36, 169.16, 169.10, 169.04, 165.00, 164.93, 164.91, 162.01, 161.77, 161.75, 161.62, 138.08, 138.00, 137.99, 137.95, 137.93, 137.82, 137.76, 133.94, 133.38, 133.22, 133.15, 133.10, 130.10, 129.98, 129.84, 129.64, 129.57, 129.40, 128.51, 128.43, 128.40, 128.35, 128.34, 128.27, 128.06, 128.02, 128.00, 127.96, 127.93, 127.92, 127.79, 127.70, 127.68, 127.66, 127.63, 127.50, 127.43, 127.28, 126.21, 126.14, 125.99, 100.37, 100.23, 100.06, 99.99, 99.59, 99.48, 97.44, 92.61, 80.55, 79.92, 79.79, 77.10, 76.80, 74.63, 74.30, 74.21, 73.82, 73.72, 73.61, 73.58, 73.04, 72.96, 72.87, 72.70, 72.55, 71.63, 71.30, 69.61, 69.24, 68.92, 68.71, 68.19, 68.09, 56.36, 55.27, 55.18, 55.07, 52.94, 52.92, 52.83, 38.22, 38.16, 38.15, 29.83, 29.72, 29.70, 28.06, 27.96, 20.68. ESI-MS: $C_{210}H_{212}Cl_{15}N_5O_{69}$ $[M+2NH_4]^{+2}$ calcd: 2238.4, obsd: 2238.4.

12-mer 36:

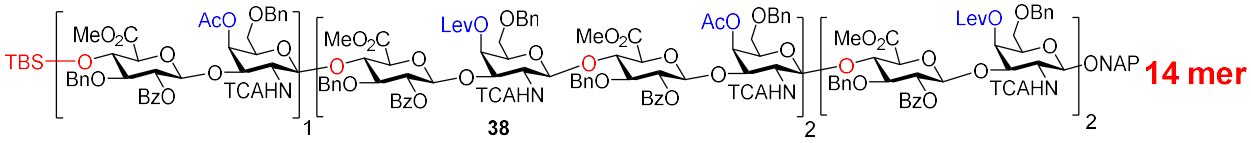


Following the general procedure for glycosylation catalyzed by NIS/TfOH, dodecasaccharide **36** was obtained (0.53 g, 77%) through coupling between donor **25** (0.255 g, 0.23 mmol) and acceptor **35** (0.562 g, 0.13 mmol). $[\alpha_D^{20}]$ = +0.2 (C = 1.03, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.00 – 7.95 (m, 10H), 7.93 – 7.90 (m, 2H), 7.82 – 7.71 (m, 5H), 7.59 – 7.54 (m, 6H), 7.48 – 7.45 (m, 2H), 7.45 – 7.39 (m, 12H), 7.38 (m, 4H), 7.35 – 7.30 (m, 11H), 7.29 – 7.25 (m, 15H), 7.20 – 7.18 (m, 5H), 7.11 (m, 25H), 7.00 (d, *J* = 8.5 Hz, 1H), 6.95 – 6.88 (m, 4H), 6.80 (d, *J* = 7.0 Hz, 1H), 5.56 – 5.50 (m, 6H), 5.29 – 5.24 (m, 2H), 5.17 – 5.12 (m, 5H), 5.03 (s, 1H), 5.01 (d, *J* = 2.7 Hz, 1H), 4.99 – 4.94 (m, 4H), 4.92 – 4.89 (mz, 2H), 4.88 – 4.82 (m, 5H), 4.80 – 4.71 (m, 8H), 4.61 – 4.57 (m, 5H), 4.56 – 4.54 (m, 2H), 4.53 – 4.51 (m, 1H), 4.37 (d, *J* = 5.6 Hz, 1H), 4.34 (d, *J* = 5.6 Hz, 1H), 4.32 (d, *J* = 3.1 Hz, 1H), 4.30 – 4.27 (m, 6H), 4.27 – 4.23 (m, 6H), 4.21 – 4.14 (m, 5H), 4.08 (t, *J* = 8.4 Hz, 1H), 4.02 – 3.99 (m, 2H), 3.97 (d, *J* = 2.6 Hz, 1H), 3.96 – 3.93 (m, 3H), 3.92 (d, *J* = 2.4 Hz, 1H), 3.91 – 3.88 (m, 2H), 3.82 (t, *J* = 6.2 Hz, 1H), 3.75 (s, 3H), 3.74 – 3.72 (m, 4H), 3.71 – 3.69 (m, 6H), 3.69 – 3.67 (m, 6H), 3.67 (s, 3H), 3.66 – 3.63 (m, 2H), 3.61 – 3.54 (m, 4H), 3.37 – 3.28 (m, 10H), 2.85 – 2.69 (m, 7H), 2.64 – 2.44 (m, 13H), 2.17 (s, 3H), 2.11 – 2.07 (m, 9H), 1.97 (s, 6H), 0.87 (s, 9H), 0.04 – 0.01 (m, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.87, 206.72, 171.58, 171.42, 169.96, 169.92, 169.51, 169.34, 169.12, 169.01, 168.77, 164.92, 164.90, 164.88, 161.98, 161.71, 138.07, 137.98, 137.92, 137.91, 137.80, 137.58, 133.90, 133.19, 133.13, 133.08, 129.96, 129.81, 129.67, 129.56, 129.39, 128.48, 128.41, 128.38, 128.36, 128.32, 128.29, 128.24, 128.11, 128.05, 128.01, 127.99, 127.94, 127.91, 127.82, 127.76, 127.68, 127.63, 127.60, 127.57, 127.48, 127.41, 127.28, 126.18, 126.12, 125.98, 100.38, 99.99, 99.32, 97.37, 92.72, 92.48, 82.41, 79.92, 79.80, 76.49, 74.66, 74.48, 74.32, 74.19, 74.03, 73.71, 73.59, 73.57, 72.96, 72.85, 72.53, 71.46, 71.32, 69.58, 69.19, 68.86, 68.68, 64.02, 56.41, 55.18, 55.08, 54.93, 52.90, 52.40, 38.20, 38.13, 37.92, 29.82, 29.78, 29.70, 29.67, 28.03, 27.93, 27.75, 25.73, 20.66, 17.88, -4.08, -5.23. ESI-MS: $C_{257}H_{268}Cl_{18}N_6O_{83}Si$ $[M+2NH_4]^{+2}$ calcd: 2734.59, obsd: 2734.59. $[M+3NH_4]^{+3}$ calcd: 1829.1, obsd: 1829.0.



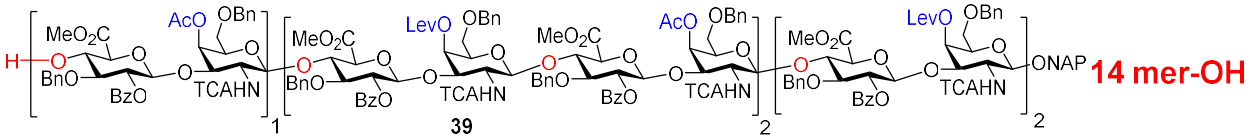
Following the general procedure for TBS removal, dodecasaccharide acceptor **37** was obtained (0.568 g, 92%) from **36** (0.63 g, 0.12 mmol). $[\alpha_D^{20}]$ = +20 (C = 0.01, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.03 – 7.95 (m, 10H), 7.94 – 7.91 (m, 2H), 7.82 – 7.71 (m, 5H), 7.62 – 7.52 (m, 7H), 7.49 – 7.37 (m, 18H), 7.33 (m, 11H), 7.29 – 7.25 (m, 14H), 7.12 (m, 30H), 6.93 (m, 5H), 6.82 (d, *J* = 7.0 Hz, 1H), 5.58 – 5.51 (m, 6H), 5.19 – 5.12 (m, 6H), 5.03 (d, *J* = 3.4 Hz, 1H), 5.01 (s, 1H), 4.99 – 4.95 (m, 3H), 4.94 – 4.91 (m, 2H), 4.89 – 4.87 (m, 2H), 4.86 – 4.83 (m, 2H), 4.82 – 4.77 (m, 5H), 4.76 – 4.71 (m, 4H), 4.63 – 4.57 (m, 5H), 4.57 – 4.50 (m, 4H), 4.39 – 4.32 (m, 4H), 4.31 – 4.24 (m, 13H), 4.23 – 4.14 (m, 4H), 4.13 – 4.10 (m, 2H), 4.00 – 3.89 (m, 11H), 3.84 – 3.82 (m, 1H), 3.76 (s, 3H), 3.75 – 3.72 (m, 4H), 3.72 – 3.70 (m, 6H), 3.69 (s, 6H), 3.67 (s, 3H), 3.66 – 3.63 (m, 2H), 3.62 – 3.59 (m, 2H), 3.39 – 3.29 (m, 10H), 2.92 – 2.70 (m, 8H), 2.67 – 2.45 (m, 13H), 2.17 (s, 3H), 2.15 (s, 3H), 2.10 (d, *J* = 2.0 Hz, 6H), 1.98 (s, 3H), . ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.92, 206.90, 206.87, 171.69, 171.60, 169.95, 169.93, 169.63, 169.37, 169.34, 169.15, 169.03, 165.04, 164.96, 164.92, 164.90, 162.00, 161.76, 161.62, 138.09, 137.99, 137.96, 137.94, 137.81, 137.77, 133.93, 133.38, 133.22, 133.15, 133.10, 130.08, 129.98, 129.83, 129.62, 129.56, 129.40, 128.50, 128.43, 128.40, 128.38, 128.35, 128.27, 128.10, 128.06, 128.02, 128.01, 127.96, 127.93, 127.78, 127.70, 127.65, 127.62, 127.49, 127.43, 127.29, 126.21, 126.14, 125.99, 100.38, 100.24, 99.33, 97.42, 92.58, 92.50, 80.53, 79.95, 79.79, 76.79, 74.64, 74.31, 74.17, 73.85, 73.72, 73.71, 73.61, 73.58, 73.03, 72.96, 72.87, 72.76, 72.54, 71.72, 71.31, 69.61, 68.88, 68.70, 68.19, 67.99, 56.38, 55.20, 55.08, 52.94, 52.91, 52.86, 38.22, 38.15, 38.08, 29.83, 29.72, 29.70, 28.05, 27.95, 27.92, 20.68. ESI-MS: $C_{251}H_{254}C_{118}N_6O_{83}$ $[M+3NH_4]^{+3}$ calcd: 1791.4, obsd: 1791.4, $[M+2NH_4]^{+2}$ calcd: 2677.5, obsd: 2677.6.

14-mer 38:



Following the general procedure for glycosylation catalyzed by NIS/TfOH, tetradecasaccharide **38** was obtained (0.59 g, 89%) through coupling between donor **26** (0.204 g, 0.19 mmol) and

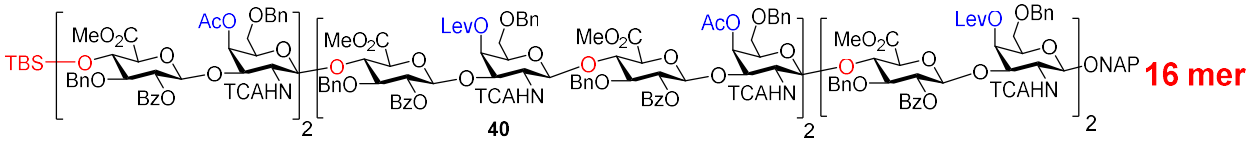
acceptor **37** (0.568 g, 0.045 mmol). [α_D^{20}] = +10 (C = 0.01, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.08 – 8.04 (m, 1H), 8.01 – 7.95 (m, 11H), 7.93 – 7.90 (m, 2H), 7.82 – 7.71 (m, 5H), 7.59 – 7.53 (m, 7H), 7.49 – 7.35 (m, 21H), 7.35 – 7.22 (m, 31H), 7.20 – 7.17 (m, 5H), 7.11 (m, 29H), 6.98 – 6.93 (m, 3H), 6.92 – 6.88 (m, 3H), 6.80 (d, *J* = 7.0 Hz, 1H), 5.56 – 5.46 (m, 7H), 5.30 – 5.27 (m, 1H), 5.18 – 5.10 (m, 6H), 5.03 (s, 1H), 5.01 (d, *J* = 2.5 Hz, 1H), 4.99 – 4.82 (m, 14H), 4.81 – 4.76 (m, 5H), 4.75 – 4.71 (m, 3H), 4.64 – 4.50 (m, 12H), 4.37 – 4.32 (m, 4H), 4.30 – 4.23 (m, 14H), 4.21 – 4.13 (m, 6H), 4.09 – 4.05 (m, 1H), 4.03 – 3.88 (m, 14H), 3.82 (d, *J* = 6.3 Hz, 1H), 3.77 (s, 3H), 3.72 (s, 5H), 3.71 – 3.68 (m, 15H), 3.67 (s, 3H), 3.61 – 3.55 (m, 4H), 3.38 – 3.27 (m, 12H), 2.83 – 2.67 (m, 7H), 2.64 – 2.46 (m, 12H), 2.17 (s, 3H), 2.12 – 2.07 (m, 9H), 2.01 – 1.94 (m, 9H), 0.86 (s, 9H), 0.01 (s, 3H), 0.00 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.91, 206.89, 206.87, 171.63, 171.59, 169.94, 169.85, 169.36, 169.24, 169.14, 169.01, 164.93, 164.91, 164.89, 161.99, 161.79, 161.75, 161.71, 138.13, 138.08, 137.99, 137.93, 137.88, 137.80, 137.62, 133.91, 133.20, 133.14, 133.09, 129.96, 129.83, 129.68, 129.57, 129.40, 128.49, 128.42, 128.39, 128.36, 128.34, 128.08, 128.05, 128.01, 128.00, 127.96, 127.93, 127.90, 127.78, 127.70, 127.68, 127.65, 127.62, 127.48, 127.41, 127.29, 126.20, 126.13, 125.99, 100.39, 99.87, 99.60, 99.37, 97.39, 92.57, 92.49, 82.39, 79.95, 79.80, 76.79, 76.47, 74.67, 74.15, 74.03, 73.92, 73.79, 73.72, 73.69, 73.60, 73.57, 73.20, 73.09, 72.97, 72.83, 72.68, 72.52, 71.52, 71.33, 69.60, 69.21, 68.69, 68.43, 68.16, 56.41, 52.93, 52.90, 52.38, 38.21, 38.15, 29.83, 29.72, 29.70, 29.68, 28.04, 27.94, 25.73, 20.67, 20.58, -4.14, -5.25. ESI-MS: $C_{295}H_{306}Cl_{21}N_7O_{96}Si$ $[M+3NH_4]^{3+}$ calcd: 2104.4, obsd: 2104.4.



Following the general procedure for TBS removal, tetradecasaccharide acceptor **39** was obtained (0.42 g, 70%) from **38** (0.61 g, 0.097 mmol). [α_D^{20}] = -5 (C = 0.04, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.07 – 7.87 (m, 16H), 7.82 – 7.02 (m, 96H), 6.94 – 6.85 (m, 6H), 6.79 (d, *J* = 7.0 Hz, 1H), 5.55 – 5.47 (m, 7H), 5.19 – 5.07 (m, 8H), 5.02 (d, *J* = 3.7 Hz, 1H), 5.01 – 4.88 (m, 9H), 4.87 – 4.67 (m, 16H), 4.62 – 4.50 (m, 11H), 4.37 – 4.05 (m, 26H), 3.97 – 3.85 (m, 14H), 3.81 (t, *J* = 6.2 Hz, 1H), 3.78 (s, 3H), 3.76 – 3.70 (m, 5H), 3.69 – 3.65 (m, 18H), 3.64 – 3.51 (m, 7H), 3.35 – 3.25 (m, 11H), 3.17 (d, *J* = 2.8 Hz, 1H), 2.85 – 2.65 (m, 8H), 2.65 – 2.42 (m, 13H), 2.17 (s, 3H), 2.10 – 2.03 (m, 12H), 1.96 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.90,

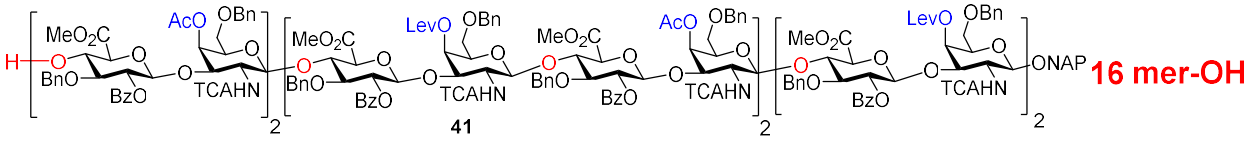
171.57, 169.93, 169.64, 169.32, 164.90, 161.99, 161.73, 161.59, 138.06, 137.96, 137.91, 137.79, 133.18, 133.01, 130.07, 129.96, 129.81, 129.67, 129.55, 128.47, 128.41, 128.37, 128.35, 128.32, 128.26, 128.03, 128.01, 127.99, 127.93, 127.90, 127.76, 127.67, 127.63, 127.39, 127.28, 126.17, 126.11, 125.97, 114.08, 100.02, 99.96, 99.29, 80.54, 79.90, 79.78, 74.21, 73.71, 73.58, 72.52, 71.58, 69.20, 68.13, 64.02, 52.89, 52.81, 38.19, 38.13, 33.84, 31.94, 31.64, 29.82, 29.71, 29.68, 29.66, 29.63, 29.52, 29.38, 29.17, 28.96, 28.01, 27.92, 22.71, 20.65, 14.16. ESI-MS: $C_{289}H_{292}Cl_{21}N_7O_{96}$ $[M+3NH_4]^{+3}$ calcd: 2065.8, obsd: 2065.7.

16-mer 40:



Following the general procedure for glycosylation catalyzed by NIS/TfOH, hexadecasaccharide **40** was obtained (0.39 g, 82%) through coupling between donor **26** (0.143 g, 0.13 mmol) and acceptor **39** (0.42 g, 0.07 mmol). $[\alpha_D^{20}] = +25$ (C = 0.02, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.04 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.99 – 7.93 (m, 12H), 7.91 – 7.88 (m, 2H), 7.80 – 7.69 (m, 5H), 7.59 – 7.00 (m, 106H), 6.95 – 6.87 (m, 7H), 6.78 (d, *J* = 7.0 Hz, 1H), 5.53 – 5.47 (m, 7H), 5.29 – 5.24 (m, 2H), 5.16 – 5.08 (m, 7H), 5.01 (s, 1H), 4.99 (d, *J* = 3.6 Hz, 1H), 4.96 – 4.92 (m, 5H), 4.90 – 4.87 (m, 3H), 4.86 – 4.74 (m, 12H), 4.72 – 4.68 (m, 3H), 4.61 – 4.49 (m, 12H), 4.35 (d, *J* = 3.6 Hz, 1H), 4.33 – 4.28 (m, 4H), 4.28 – 4.21 (m, 16H), 4.19 – 4.11 (m, 6H), 4.05 (d, *J* = 8.4 Hz, 1H), 4.00 – 3.97 (m, 2H), 3.96 – 3.84 (m, 13H), 3.80 (d, *J* = 6.2 Hz, 1H), 3.75 (s, 3H), 3.72 – 3.69 (m, 6H), 3.69 – 3.65 (m, 21H), 3.644 – 3.59 (m, 3H), 3.59 – 3.50 (m, 5H), 3.35 – 3.23 (m, 14H), 2.82 – 2.65 (m, 8H), 2.63 – 2.43 (m, 13H), 2.16 (s, 3H), 2.11 – 2.05 (m, 9H), 1.95 (s, 12H), 0.84 (s, 9H), -0.01 (s, 3H), -0.02 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.88, 171.58, 169.92, 169.80, 169.32, 169.00, 168.81, 164.90, 161.73, 138.06, 137.96, 137.90, 137.85, 137.78, 133.17, 129.95, 129.80, 129.66, 129.55, 128.47, 128.40, 128.36, 128.34, 128.31, 128.22, 128.06, 128.02, 127.99, 127.92, 127.90, 127.87, 127.83, 127.75, 127.67, 127.62, 127.60, 127.45, 127.38, 127.32, 127.27, 126.17, 126.10, 125.97, 99.95, 99.85, 99.41, 99.33, 79.89, 76.48, 73.70, 73.58, 73.55, 73.53, 72.93, 72.81, 69.19, 64.01, 52.90, 52.89, 38.19, 38.12, 31.93, 31.64, 29.81, 29.70, 29.68, 29.66, 29.52, 29.16, 28.01, 27.91, 25.70, 22.70, 20.65, 20.54, 17.86, 14.15, -4.17, -5.28. ESI-MS:

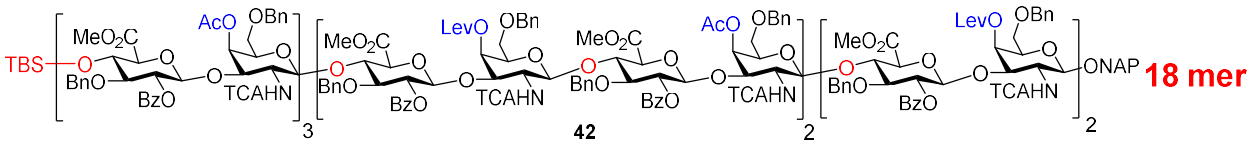
$C_{333}H_{344}Cl_{24}N_8O_{109}Si$ $[M+3NH_4]^{3+}$ calcd: 2377.8, obsd: 2378.0, $[M+4NH_4]^{4+}$ calcd: 1787.4, obsd: 1787.4.



41

Following the general procedure for TBS removal, hexadecasaccharide acceptor **41** was obtained (0.372 g, 88%) from **40** (0.428 g, 0.061 mmol). $[\alpha_D^{20}]$ = -12.5 (C = 0.04, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.09 – 7.89 (m, 17H), 7.82 – 7.01 (m, 110H), 6.93 – 6.83 (m, 7H), 6.78 (d, *J* = 7.0 Hz, 1H), 5.55 – 5.49 (m, 7H), 5.19 – 5.10 (m, 8H), 5.02 (s, 1H), 5.01 – 4.69 (m, 28H), 4.62 – 4.50 (m, 11H), 4.37 – 4.04 (m, 31H), 3.97 – 3.86 (m, 14H), 3.82 (t, *J* = 6.2 Hz, 1H), 3.78 (s, 3H), 3.75 – 3.71 m, 5H), 3.70 – 3.66 (m, 21H), 3.65 – 3.51 (m, 8H), 3.34 – 3.26 (m, 12H), 3.20 (d, *J* = 2.8 Hz, 1H), 2.85 – 2.68 (m, 7H), 2.67 – 2.46 (m, 13H), 2.17 (s, 3H), 2.10 – 2.08 (m, 6H), 2.01 – 1.94 (m, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.88, 206.86, 171.58, 169.89, 169.33, 169.12, 169.01, 164.91, 161.73, 138.07, 137.97, 137.92, 137.80, 133.90, 133.18, 133.09, 130.06, 129.96, 129.81, 129.67, 129.56, 128.48, 128.41, 128.38, 128.35, 128.33, 128.26, 128.23, 128.03, 128.00, 127.94, 127.91, 127.89, 127.78, 127.76, 127.67, 127.63, 127.60, 127.47, 127.39, 127.33, 127.28, 126.18, 126.12, 125.98, 100.20, 100.01, 99.54, 99.31, 92.55, 92.47, 80.52, 79.92, 79.79, 76.95, 74.21, 74.15, 74.08, 73.71, 73.59, 73.57, 72.94, 72.83, 72.52, 71.59, 71.33, 69.20, 68.86, 68.69, 68.15, 68.05, 64.03, 55.06, 52.92, 52.89, 52.83, 38.20, 38.13, 31.66, 29.82, 29.71, 29.69, 29.67, 29.52, 28.02, 27.93, 20.65, 14.17. ESI-MS: $C_{327}H_{330}Cl_{24}N_8O_{109}$ $[M+3NH_4]^{3+}$ calcd: 2339.8, obsd: 2339.8.

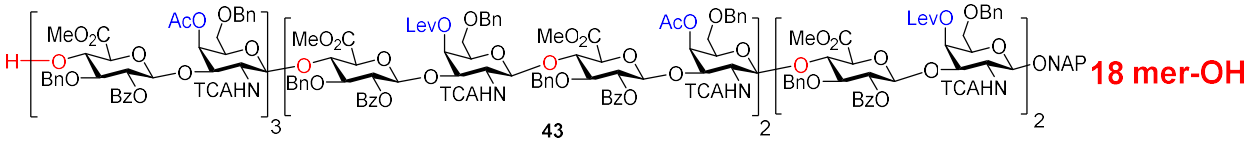
18-mer 42:



42

Following the general procedure for glycosylation catalyzed by NIS/TfOH, octadecasaccharide **42** was obtained (0.382 g, 91%) through coupling between donor **26** (0.17 g, 0.16 mmol) and acceptor

41 (0.372 g, 0.053 mmol). $[\alpha_D^{20}]$ = +30 (C = 0.01, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.01 – 7.95 (m, 15H), 7.93 – 7.91 (m, 2H), 7.82 – 7.72 (m, 5H), 7.59 – 7.53 (m, 9H), 7.49 – 7.23 (m, 66H), 7.21 – 7.04 (m, 45H), 6.97 – 6.88 (m, 8H), 6.80 (d, *J* = 7.1 Hz, 1H), 5.56 – 5.49 (m, 9H), 5.18 – 5.11 (m, 8H), 5.03 (d, *J* = 2.1 Hz, 1H), 5.01 (s, 1H), 4.99 – 4.94 (m, 5H), 4.92 – 4.83 (m, 11H), 4.81 – 4.76 (m, 7H), 4.75 – 4.72 (m, 3H), 4.63 – 4.52 (m, 13H), 4.37 – 4.23 (m, 26H), 4.21 – 4.15 (m, 6H), 4.09 – 3.89 (m, 20H), 3.82 (d, *J* = 6.1 Hz, 1H), 3.77 (s, 3H), 3.75 – 3.72 (m, 5H), 3.71 – 3.67 (m, 24H), 3.66 – 3.55 (m, 8H), 3.37 – 3.26 (m, 16H), 2.85 – 2.46 (m, 23H), 2.17 (s, 3H), 2.12 – 2.08 (m, 9H), 2.02 – 1.92 (m, 15H), 0.87 (s, 9H), 0.02 (s, 3H), 0.01 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.89, 206.86, 171.59, 169.94, 169.36, 169.32, 169.14, 169.05, 168.82, 164.93, 164.91, 164.88, 161.75, 138.09, 137.99, 137.93, 137.89, 137.81, 133.21, 129.97, 129.83, 129.57, 128.50, 128.42, 128.39, 128.37, 128.34, 128.09, 128.05, 128.01, 128.00, 127.96, 127.93, 127.88, 127.86, 127.81, 127.78, 127.70, 127.65, 127.62, 127.48, 127.42, 127.35, 127.29, 126.20, 126.14, 125.99, 99.94, 99.60, 99.45, 99.34, 97.41, 82.38, 79.94, 79.81, 76.49, 74.65, 73.94, 73.83, 73.72, 73.61, 73.58, 73.56, 72.97, 72.85, 72.69, 72.54, 71.49, 71.32, 68.88, 68.69, 68.34, 68.17, 56.40, 52.93, 52.90, 52.88, 52.40, 38.21, 38.15, 29.83, 29.71, 29.69, 28.04, 27.94, 25.73, 20.67, -4.14, -5.24. ESI-MS: $C_{371}H_{382}Cl_{27}N_9O_{122}Si$ $[M+4NH_4]^{4+}$ calcd: 1993.7, obsd: 1993.6.

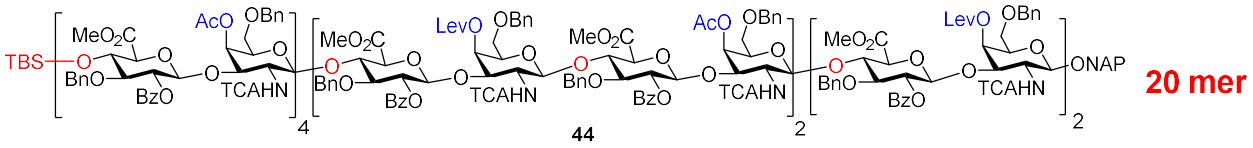


43

Following the general procedure for TBS removal, octadecasaccharide acceptor **43** was obtained (0.374 g, 95%) from **42** (0.39 g, 0.051 mmol). $[\alpha_D^{20}]$ = +5 (C = 0.06, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.03 – 7.94 (m, 15H), 7.92 – 7.89 (m, 2H), 7.81 – 7.70 (m, 5H), 7.61 – 7.00 (m, 120H), 6.95 – 6.85 (m, 8H), 6.80 (d, *J* = 7.0 Hz, 1H), 5.55 – 5.47 (m, 9H), 5.19 – 5.10 (m, 9H), 5.02 (s, 1H), 5.00 (s, 1H), 4.98 – 4.69 (m, 29H), 4.61 – 4.50 (m, 11H), 4.37 – 4.21 (m, 26H), 4.20 – 4.13 (m, 5H), 4.11 – 4.06 (m, 2H), 3.99 – 3.87 (m, 16H), 3.83 – 3.79 (m, 2H), 3.77 (s, 3H), 3.75 – 3.70 (m, 8H), 3.70 – 3.66 (m, 24H), 3.64 – 3.52 (m, 7H), 3.35 – 3.25 (m, 15H), 2.86 – 2.45 (m, 22H), 2.16 (s, 6H), 2.11 – 2.06 (m, 9H), 2.03 (s, 3H), 1.98 – 1.94 (m, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.90, 171.59, 169.93, 169.13, 169.04, 164.92, 161.74, 138.07, 137.97, 137.80, 130.05, 129.88, 129.56, 128.65, 128.23, 128.07, 127.65, 127.35, 127.08, 100.26, 99.71, 99.69,

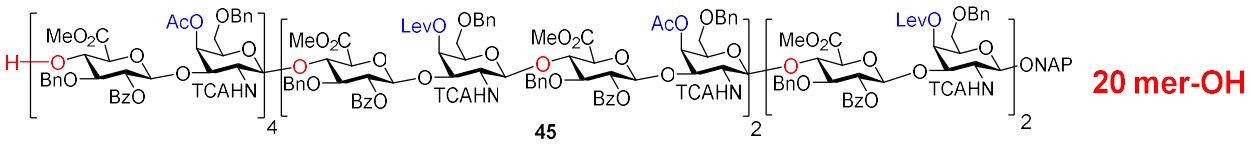
92.56, 92.48, 79.89, 74.22, 73.88, 73.71, 73.59, 73.27, 69.01, 68.67, 52.81, 20.60. ESI-MS: $C_{365}H_{368}Cl_{27}N_9O_{122}$ $[M+3NH_4]^{3+}$ calcd: 2614.2, obsd: 2614.1.

20-mer 44:



44

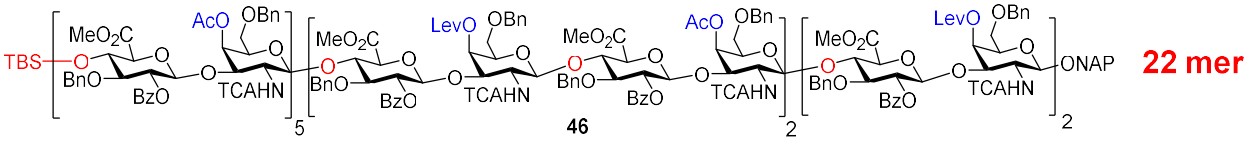
Following the general procedure for glycosylation catalyzed by NIS/TfOH, icosasaccharide **44** was obtained (0.36 g, 86%) through coupling between donor **26** (0.153 g, 0.14 mmol) and acceptor **43** (0.374 g, 0.048 mmol). $[\alpha_D^{20}]$ = +2.5 (C = 0.08, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.06 – 7.94 (m, 18H), 7.91 (d, *J* = 7.7 Hz, 2H), 7.81 – 7.70 (m, 6H), 7.59 – 7.00 (m, 131H), 6.94 (m, 9H), 6.82 (d, *J* = 7.1 Hz, 1H), 5.50 (m, 11H), 5.29 – 5.25 (m, 2H), 5.17 – 5.09 (m, 9H), 5.01 (d, *J* = 5.3 Hz, 1H), 4.99 (d, *J* = 1.9 Hz, 1H), 4.97 – 4.81 (m, 19H), 4.79 – 4.70 (m, 11H), 4.60 – 4.53 (m, 11H), 4.52 – 4.50 (m, 1H), 4.36 – 4.31 (m, 6H), 4.30 – 4.21 (m, 21H), 4.20 – 4.13 (m, 7H), 4.08 – 4.03 (m, 2H), 4.02 – 3.87 (m, 19H), 3.83 – 3.79 (m, 2H), 3.76 (s, 3H), 3.73 – 3.70 (m, 8H), 3.69 – 3.65 (m, 27H), 3.65 – 3.61 (m, 3H), 3.60 – 3.54 (m, 4H), 3.36 – 3.23 (m, 18H), 2.82 – 2.44 (m, 23H), 2.16 (s, 3H), 2.11 – 2.05 (m, 9H), 2.00 – 1.88 (m, 18H), 0.85 (s, 9H), 0.00 (s, 3H), -0.01(s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.89, 206.86, 171.58, 169.93, 169.34, 169.30, 169.12, 169.00, 168.81, 164.91, 161.98, 161.74, 138.08, 137.97, 137.92, 137.87, 137.80, 133.19, 133.13, 129.96, 129.82, 129.67, 129.56, 129.39, 128.47, 128.41, 128.37, 128.35, 128.32, 128.07, 128.04, 128.00, 127.94, 127.91, 127.89, 127.87, 127.84, 127.79, 127.76, 127.68, 127.63, 127.60, 127.47, 127.40, 127.33, 127.27, 126.18, 126.12, 125.98, 99.97, 99.94, 99.92, 99.46, 99.44, 99.33, 92.57, 92.50, 79.79, 74.43, 73.71, 73.59, 73.57, 72.96, 72.84, 72.53, 71.48, 69.18, 68.86, 68.16, 55.06, 52.88, 38.20, 38.13, 29.82, 29.71, 29.69, 28.03, 27.93, 25.71, 20.65, 20.55, 17.88, -4.15, -5.26. MALDI-MS: $C_{409}H_{420}Cl_{30}N_{10}O_{135}Si$ $[M+H]^+$ calcd: 8719.7, obsd: 8719.1.



45

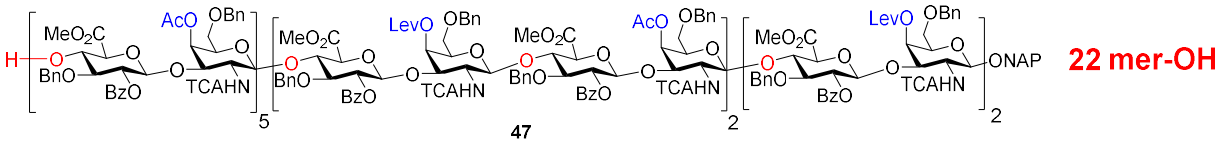
Following the general procedure for TBS removal, icosasaccharide acceptor **45** was obtained (0.33 g, 94%) from **44** (0.356 g, 0.041 mmol). $[\alpha_D^{20}]$ = +20 (C = 0.01, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.07 – 7.03 (m, 158H), 6.94 – 6.84 (m, 9H), 6.81 (d, *J* = 7.0 Hz, 1H), 5.56 – 5.47 (m, 10H), 5.21 – 5.09 (m, 11H), 5.03 (s, 1H), 5.01 (d, *J* = 2.1 Hz, 1H), 4.99 – 4.70 (m, 32H), 4.62 – 4.51 (m, 12H), 4.36 – 4.17 (m, 33H), 4.16 – 4.06 (m, 5H), 3.99 – 3.88 (m, 18H), 3.84 – 3.80 (m, 2H), 3.78 (s, 3H), 3.74 – 3.71 (m, 6H), 3.71 – 3.67 (m, 27H), 3.65 – 3.55 (m, 7H), 3.37 – 3.25 (m, 18H), 2.85 – 2.44 (m, 23H), 2.18 – 1.96 (m, 30H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.89, 171.58, 169.92, 169.35, 169.13, 169.03, 164.92, 161.75, 138.09, 137.99, 137.93, 137.81, 133.20, 130.07, 129.97, 129.83, 129.58, 128.42, 128.38, 128.33, 128.26, 128.05, 128.03, 128.01, 127.99, 127.95, 127.92, 127.90, 127.89, 127.80, 127.77, 127.68, 127.64, 127.61, 127.48, 127.40, 127.34, 127.29, 126.19, 126.13, 125.99, 100.21, 99.99, 99.57, 99.39, 99.37, 80.53, 79.94, 79.79, 74.66, 74.44, 74.22, 74.16, 73.89, 73.72, 73.69, 73.60, 73.57, 72.94, 72.53, 71.33, 68.86, 68.70, 55.08, 52.90, 38.21, 38.14, 29.71, 29.69, 28.04, 27.94, 20.66. MALDI-MS: $C_{403}H_{406}Cl_{30}N_{10}O_{135}$ $[M+H]^+$ calcd: 8594.6, obsd: 8594.5.

22-mer 46:



Following the general procedure for glycosylation catalyzed by NIS/TfOH, docosasaccharide **46** was obtained (0.347 g, 95%) through coupling between donor **26** (0.123 g, 0.12 mmol) and acceptor **45** (0.33 g, 0.038 mmol). $[\alpha_D^{20}]$ = -20 (C = 0.04, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.07 – 7.94 (m, 21H), 7.91 (d, *J* = 7.7 Hz, 2H), 7.81 – 7.71 (m, 6H), 7.56 (m, 11H), 7.47 – 7.36 (m, 29H), 7.34 – 7.24 (m, 49H), 7.12 (m, 55H), 6.91 (m, 10H), 6.79 (d, *J* = 7.0 Hz, 1H), 5.55 – 5.48 (m, 11H), 5.30 – 5.26 (m, 2H), 5.17 – 5.09 (m, 11H), 5.02 (s, 1H), 5.00 (s, 1H), 4.97 – 4.94 (m, 4H), 4.93 – 4.86 (m, 11H), 4.85 – 4.81 (m, 4H), 4.80 – 4.71 (m, 13H), 4.61 – 4.50 (m, 15H), 4.36 – 4.31 (m, 8H), 4.30 – 4.22 (m, 24H), 4.20 – 4.15 (m, 7H), 4.0 – 4.03 (m, 2H), 4.02 – 3.89 (m, 21H), 3.82 (t, *J* = 6.1 Hz, 2H), 3.76 (s, 3H), 3.74 – 3.71 (m, 7H), 3.70 – 3.66 (m, 30H), 3.63 – 3.54 (m, 7H), 3.35 – 3.24 (m, 20H), 2.84 – 2.66 (m, 10H), 2.64 – 2.47 (m, 14H), 2.16 (s, 3H), 2.10 – 2.07 (m, 9H), 2.01 – 1.90 (m, 21H), 0.86 (s, 9H), 0.01 (s, 3H), -0.00 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.89, 171.59, 169.93, 169.88, 169.35, 169.13, 169.04, 164.93, 164.90,

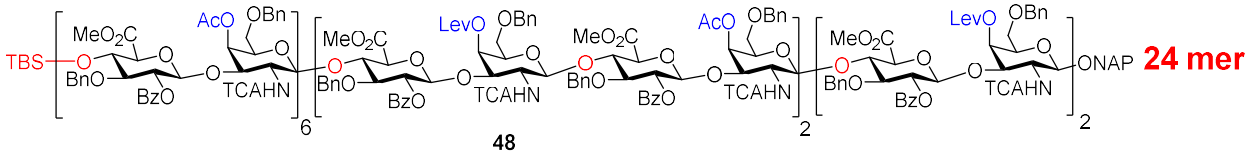
161.99, 161.75, 138.08, 137.98, 137.92, 137.88, 137.80, 133.20, 129.96, 129.82, 129.56, 128.48, 128.41, 128.38, 128.35, 128.33, 128.08, 128.04, 128.00, 127.99, 127.95, 127.93, 127.90, 127.88, 127.85, 127.80, 127.77, 127.69, 127.63, 127.47, 127.41, 127.34, 127.28, 126.19, 126.13, 125.98, 99.94, 99.94, 99.45, 99.32, 97.38, 92.49, 79.80, 76.69, 74.43, 73.71, 73.60, 73.56, 72.95, 72.84, 72.52, 71.48, 71.32, 69.18, 68.86, 68.68, 68.15, 55.09, 52.89, 38.20, 38.13, 29.82, 29.71, 29.69, 28.03, 27.93, 25.72, 20.66, -4.15, -5.26. MALDI-MS: $C_{447}H_{458}Cl_{33}N_{11}O_{148}Si$ $[M+H]^+$ calcd: 9529.8, obsd: 9529.8.



47

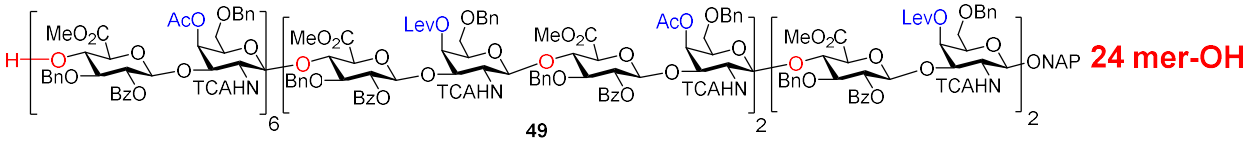
Following the general procedure for TBS removal, docosasaccharide acceptor **47** was obtained (0.29 g, 90%) from **46** (0.326 g, 0.034 mmol). $[\alpha_D^{20}] = -3.3$ (C = 0.06, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.04 – 7.02 (m, 172H), 6.98 – 6.89 (m, 10H), 6.81 (d, *J* = 7.0 Hz, 1H), 5.55 – 5.46 (m, 11H), 5.19 – 5.08 (m, 12H), 5.02 (s, 1H), 5.00 (d, *J* = 2.2 Hz, 1H), 4.97 – 4.69 (m, 35H), 4.61 – 4.51 (m, 13H), 4.36 – 4.06 (m, 42H), 3.99 – 3.87 (m, 19H), 3.83 – 3.79 (m, 2H), 3.78 (s, 3H), 3.74 – 3.70 (m, 7H), 3.70 – 3.66 (m, 30H), 3.64 – 3.53 (m, 7H), 3.38 – 3.23 (m, 21H), 2.85 – 2.44 (m, 24H), 2.17 (s, 3H), 2.11 – 2.07 (m, 15H), 2.03 (s, 3H), 1.98 – 1.95 (m, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.90, 171.59, 169.95, 169.90, 169.34, 169.13, 169.03, 164.95, 161.76, 138.07, 137.96, 137.91, 137.79, 133.20, 130.06, 129.96, 129.82, 129.57, 128.48, 128.41, 128.38, 128.33, 128.26, 128.03, 128.00, 127.94, 127.92, 127.90, 127.79, 127.77, 127.68, 127.64, 127.61, 127.40, 127.34, 127.28, 126.18, 126.12, 125.98, 99.95, 99.57, 99.42, 99.37, 92.48, 80.54, 79.90, 79.76, 76.94, 76.69, 74.66, 74.22, 74.13, 73.91, 73.71, 73.59, 73.56, 72.54, 71.56, 71.33, 68.84, 68.68, 68.12, 56.39, 55.07, 52.89, 52.84, 38.20, 38.12, 29.82, 29.71, 29.69, 28.03, 27.93, 20.65. MALDI-MS: $C_{441}H_{444}Cl_{33}N_{11}O_{148}$ $[M+H]^+$ calcd: 9437.7, obsd: 9437.6.

24-mer 48:



48

Following the general procedure for glycosylation catalyzed by NIS/TfOH, tetracosasaccharide **48** was obtained (0.287 g, 90%) through coupling between donor **26** (0.098 g, 0.092 mmol)and acceptor **47** (0.29 g, 0.031 mmol). [α_D^{20}] = -40 (C = 0.01, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.06 – 7.04 (m, 188H), 6.95 – 6.86 (m, 11H), 6.78 (d, *J* = 7.0 Hz, 1H), 5.55 – 5.46 (m, 12H), 5.29 – 5.25 (m, 2H), 5.17 – 5.9 (m, 11H), 5.02 (s, 1H), 5.00 (d, *J* = 2.6 Hz, 1H), 4.98 – 4.69 (m, 38H), 4.61 – 4.51 (m, 15H), 4.36 – 4.14 (m, 43H), 4.08 – 3.86 (m, 26H), 3.83 –3.79 (m, 2H), 3.76 (s, 3H), 3.73 – 3.70 (m, 7H), 3.70 – 3.66 (m, 33H), 3.63 – 3.54 (m, 8H), 3.35 – 3.24 (m, 20H), 2.83 – 2.46 (m, 24H), 2.17 – 2.13 (m, 6H), 2.11 – 2.06 (m, 9H), 1.99 – 1.92 (m, 21H), 0.85 (s, 9H), 0.00 (m, 3H), -0.01 (m, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.88, 171.58, 169.92, 169.87, 169.11, 169.02, 164.92, 161.74, 138.08, 137.97, 137.92, 137.80, 133.19, 129.96, 129.56, 128.41, 128.37, 128.35, 128.32, 128.07, 128.04, 128.00, 127.98, 127.94, 127.92, 127.89, 127.87, 127.84, 127.79, 127.76, 127.68, 127.62, 127.40, 127.33, 127.28, 126.19, 125.98, 99.94, 99.94, 99.54, 99.42, 92.48, 79.92, 79.81, 79.80, 76.68, 74.42, 73.71, 73.59, 73.55, 72.95, 72.83, 68.85, 68.14, 55.10, 52.89, 38.20, 38.13, 29.71, 29.68, 27.93, 25.71, 20.65, -5.26. MALDI-MS: $C_{485}H_{496}Cl_{36}N_{12}O_{161}Si$ $[M+H]^+$ calcd: 10349.9, obsd: 10348.3.

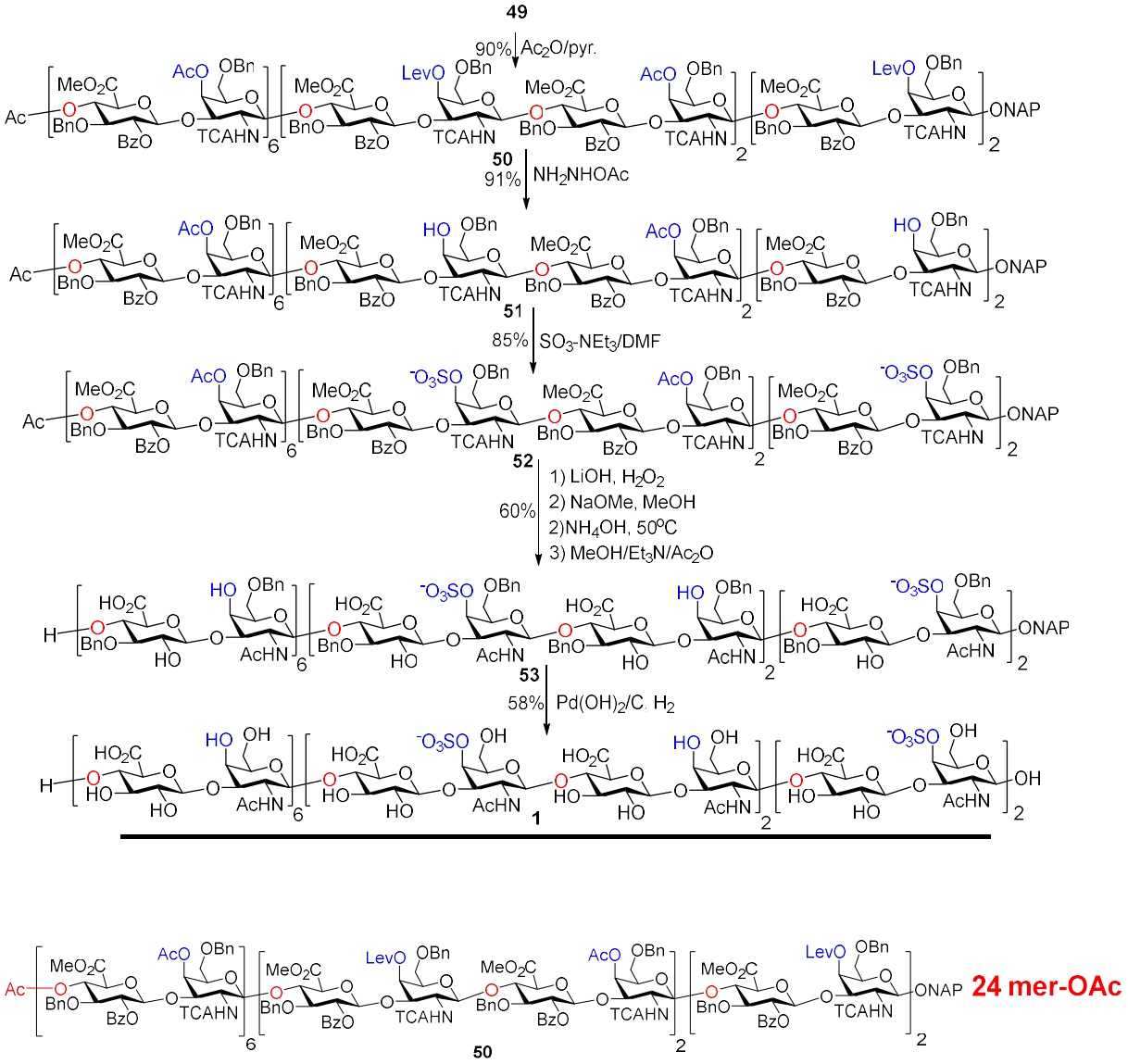


49

Following the general procedure for TBS removal, tetracosasaccharide acceptor **49** was obtained (0.293 g, 94%) from **48** (0.287 g, 0.028 mmol). [α_D^{20}] = -10 (C = 0.01, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.04 – 7.05 (m, 188H), 6.99 – 6.90 (m, 11H), 6.86 (d, *J* = 7.1 Hz, 1H), 5.54 – 5.46 (m, 11H), 5.15 (m, 12H), 5.02 (s, 1H), 5.00 (d, *J* = 3.0 Hz, 1H), 4.97 – 4.69 (m, 39H), 4.59 – 4.50 (m, 14H), 4.36 – 4.12 (m, 44H), 4.09 – 4.06 (m, 2H), 3.99 – 3.87 (m, 22H), 3.82 – 3.79 (m, 2H), 3.77 (s, 3H), 3.73 – 3.70 (m, 8H), 3.69 – 3.65 (m, 33H), 3.64 – 3.55 (m, 9H), 3.35 – 3.21 (m, 22H), 2.82 – 2.45 (m, 24H), 2.17 – 1.94 (m, 36H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.90, 171.58, 169.87, 169.10, 169.02, 164.92, 162.66, 161.75, 138.08, 137.97, 137.92, 137.80, 133.18, 129.96, 129.82, 129.58, 128.41, 128.37, 128.32, 128.25, 128.04, 128.02, 128.00, 127.98, 127.93, 127.91, 127.89, 127.78, 127.67, 127.63, 127.38, 127.33, 127.25, 126.18, 126.11, 125.98, 99.99, 99.97, 99.96, 99.93, 99.45, 99.44, 99.39, 92.50, 79.78, 76.67, 74.44, 74.18, 73.92, 73.71, 73.59, 73.56, 71.61, 68.84, 68.14, 55.06, 52.88, 38.20, 38.13, 36.55, 31.50, 29.81, 29.71, 29.69, 27.92,

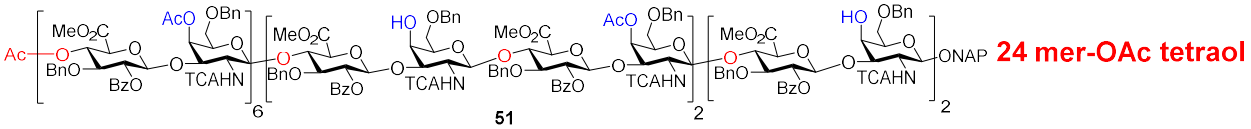
20.65. ESI-MS: $C_{479}H_{482}Cl_{36}N_{12}O_{161}$ $[M+5NH_4]^{5+}$ calcd: 2068.8, obsd: 2068.8, $[M+4NH_4]^{4+}$ calcd: 2582.7, obsd: 2582.7, $[M+3NH_4]^{3+}$ calcd: 3437.7, obsd: 3437.5.

1.11. Sulfation and deprotection of the 24-mer 49:



Compound **49** (121 mg, 11.7 µm) was dissolved in Py. (4 mL), followed by addition of Ac_2O (2 mL). The reaction mixture was stirred at rt till completion. Then the mixture was diluted with EtOAc (40 mL), washed with 10% HCl (3*10 mL), saturated $NaHCO_3$ solution (2*10 mL), saturated brine solution (10 mL). The organic layer was dried over Na_2SO_4, concentrated and the residue was introduced to silica gel column chromatography (Toluene/Acetone, 15:1 → 6:1) to afford the desired tetracosasaccharide **50** (0.109 g, 90%) as a white solid. $[\alpha_D^{20}]$ = -15 (C = 0.02,

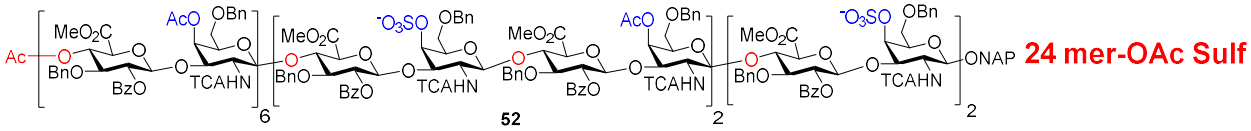
DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.18 – 6.99 (m, 187H), 6.92 (dd, *J* = 17.0, 7.9 Hz, 11H), 6.80 (d, *J* = 7.1 Hz, 1H), 5.50 (d, *J* = 10.6 Hz, 12H), 5.35 – 5.26 (m, 5H), 5.13 (q, *J* = 9.1, 8.0 Hz, 11H), 5.03 (s, 1H), 5.00 (s, 1H), 4.98 – 4.70 (m, 35H), 4.62 – 4.51 (m, 15H), 4.38 – 4.11 (m, 43H), 4.01 – 3.86 (m, 22H), 3.83 – 3.79 (m, 2H), 3.76 – 3.62 (m, 47H), 3.62 – 3.52 (m, 7H), 3.37 – 3.22 (m, 21H), 2.82 – 2.44 (m, 24H), 2.18 – 2.03 (m, 21H), 2.01 – 1.94 (m, 18H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 206.88, 171.58, 169.87, 169.10, 164.92, 161.74, 138.08, 137.98, 137.93, 137.81, 133.19, 130.06, 129.96, 129.58, 128.41, 128.38, 128.33, 128.27, 128.04, 128.00, 127.94, 127.91, 127.89, 127.79, 127.77, 127.67, 127.64, 127.61, 127.40, 127.33, 127.28, 126.19, 126.12, 125.98, 99.96, 99.57, 99.55, 99.42, 99.40, 92.49, 79.79, 74.42, 74.07, 73.89, 73.71, 73.60, 73.56, 72.93, 72.67, 72.53, 71.32, 69.20, 68.85, 68.69, 68.14, 55.10, 52.88, 38.20, 38.14, 29.71, 29.68, 27.93, 20.65, 14.17. MALDI-MS: $C_{481}H_{484}Cl_{36}N_{12}O_{162}$ $[M+NH_4]^+$ calcd: 10315.9, obsd: 10315.9.



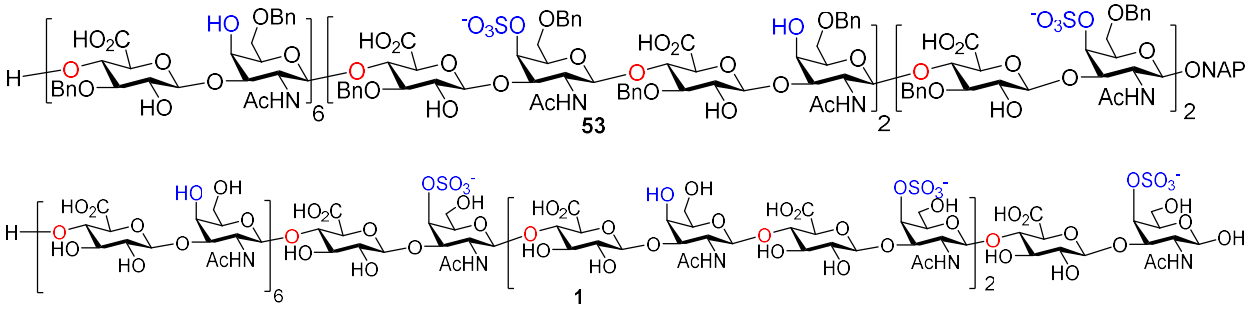
51

Tetracosasaccharide **50** (238 mg, 23.1 μmol) was dissolved in THF/MeOH (10:1, 4.4 mL). The mixture was cooled to 0 °C then hydrazine acetate (NH_2NHOAc) (26 mg, 0.28 mmol) was added. The mixture was stirred at 0 °C for 2 h. Upon completion, the reaction was quenched with acetone (0.2 mL), stirred for another 0.5-1 h from 0 °C to r.t. and then, the solvent was evaporated under vaccum. The residue was diluted with EtOAc, washed with saturated $NaHCO_3$ solution, 10% HCl, water. The organic layer was dried over Na_2SO_4, concentrated in vacuo and the residue was purified with silica gel chromatography (DCM/MeOH, 40:1 → 15:1) to give tetraol **51** as a white solid (0.208 g, 91%). $[\alpha_D^{20}]$ = +5.7 (C = 0.07, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.09 – 7.00 (m, 188H), 6.92 – 6.78 (m, 12H), 5.55 – 5.38 (m, 11H), 5.33 – 5.24 (m, 4H), 5.22 – 5.10 (m, 12H), 5.02 (s, 1H), 4.99 (d, *J* = 7.8 Hz, 2H), 4.95 – 4.81 (m, 20H), 4.78 – 4.69 (m, 12H), 4.64 – 4.50 (m, 16H), 4.39 – 4.35 (m, 5H), 4.33 – 4.15 (m, 36H), 4.13 – 4.01 (m, 12H), 3.99 – 3.85 (m, 16H), 3.85 – 3.76 (m, 11H), 3.75 – 3.57 (m, 52H), 3.47 – 3.41 (m, 4H), 3.35 (d, *J* = 3.6 Hz, 1H), 3.31 – 3.19 (m, 16H), 3.09 – 3.02 (m, 3H), 2.04 – 1.89 (m, 27H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.07, 164.91, 138.06, 137.79, 133.17, 133.13, 130.01, 129.95, 129.58, 128.43, 128.36, 128.25, 128.05, 127.99, 127.97, 127.90, 127.87, 127.85, 127.81, 127.77, 127.69, 127.66, 127.64, 127.59, 127.47, 127.32, 126.00, 79.77, 78.85, 73.86, 73.59, 73.54, 73.49, 72.91, 55.11, 52.88,

52.86, 29.71, 20.62. ESI-MS: $C_{461}H_{460}Cl_{36}N_{12}O_{154}$ $[M+4NH_4]^{4+}$ calcd: 2495.7, obsd: 2495.7, $[M+3NH_4]^{3+}$ calcd: 3320.9, obsd: 3320.8.



Compound **51** (73.6 mg, 7.4 μmol) was dissolved in anhydrous DMF (1.5 mL), followed by addition of SO_3-NEt_3 (215.4 mg, 1.19 mmol). The resulting mixture was stirred at 50 °C for 1d. 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 **52** as a white solid (60 mg, 85%). $[\alpha_D^{20}]$ = -10 (C = 0.01, DCM). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.14 – 6.88 (m, 188H), 5.40 – 5.28 (m, 8H), 5.26 – 5.17 (m, 6H), 5.10 – 5.00 (m, 10H), 4.97 (m, 3H), 4.94 – 4.79 (m, 16H), 4.74 – 4.46 (m, 35H), 4.29 – 3.88 (m, 68H), 3.78 – 3.52 (m, 53H), 3.39 – 3.34 (m, 4H), 3.28 – 3.08 (m, 17H), 2.77 (m, 11H), 2.01 (s, 6H), 1.95 – 1.82 (m, 21H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.39, 169.28, 165.19, 165.17, 165.17, 137.99, 137.99, 137.64, 137.58, 137.58, 129.94, 129.56, 128.33, 128.31, 128.22, 128.17, 128.03, 127.94, 127.88, 127.86, 127.82, 127.76, 127.69, 127.65, 127.56, 127.39, 127.39, 127.29, 126.04, 126.04, 125.95, 125.92, 99.67, 99.64, 99.55, 99.53, 79.39, 74.63, 73.50, 73.36, 69.11, 68.71, 62.32, 62.29, 61.97, 52.86, 52.79, 52.66, 49.86, 49.69, 49.52, 49.35, 49.17, 49.01, 48.83, 45.40, 34.15, 34.04, 33.99, 31.69, 29.65, 29.48, 29.46, 29.38, 29.18, 29.15, 29.03, 28.98, 25.27, 25.22, 24.79, 22.53, 21.24, 20.83, 20.63, 20.52, 14.00. ESI-MS: $C_{461}H_{456}Cl_{36}N_{12}O_{166}S_4^{4-}$ $[M-4H]^{4-}$ calcd: 2556.1, obsd: 2556.2, $[M+NH_4-3H]^{3-}$ calcd: 3413.5, obsd: 3413.6.

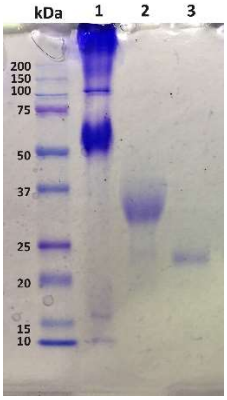


Compound **52** (24.65 mg, 2.4 μmol) was dissolved in [THF:H_2O, 4:1 (1 mL)], then a mixture of LiOH (1 M) (15 equiv. per CO_2Me) and H_2O_2 (2:1) was added at 0 ºC and the reaction mixture was stirred at r.t over night. The reaction was monitored by mass spectrometer to ensure the

hydrolysis of all methyl esters. The crude was neutralized with 0.1 M HCl till PH=7, concentrated and passed through LH-20. Then the product was dissolved in MeOH, NaOMe was added till pH=9 and the mixture was heated at 50 ºC till cleavage of all ester protected groups (MS shows incompletion of TCA cleavage). After passing through LH-20, it was dissolved in concentrated aqueous NH_4OH and heated at 50 ºC for 2d, till cleavage of all TCA protected groups. The mixture was concentrated, then dissolved in MeOH:Et_3N:Ac_2O (0.5 mL:200 µL:100 µL) and the mixture was stirred at rt for 2 h, evaporated to dryness and the residue was passed through LH-20 to obtain **53** (10.4 mg, 60% yield over 4 steps). ESI-MS: $C_{347}H_{402}N_{12}O_{145}S_4^{4-}$ $[M-4H]^{4-}$ calcd: 1797.3, obsd: 1797.3, $[M+5Li-5H-4H]^{4-}$ calcd: 1804.6, obsd: 1804.6, $[M-3H]^{3-}$ calcd: 1437.5, obsd: 1437.5, $[M+5Li-5H-3H]^{3-}$ calcd: 1443.3, obsd: 1443.3. The 24-mer **53** (10.4 mg, 1.4 µmol) was dissolved in a mixture of EtOH/H_2O (1 mL / 1 mL). Then $Pd(OH)_2/C$ (32 mg,10-20%) was added and the flask was flushed with nitrogen. A hydrogen balloon was placed on the flaks and the flask was subjected to vacuum and hydrogen gas 5 times to put the reactant under a hydrogen atmosphere. The reaction was vigorously stirred. After reaction completion as indicated by mass spectrometer, the product mixture was filtered through Celite and washed with EtOH/water 1:2 (3x2 mL). The combined filtrate was then evaporated and purified by a short Sephadex G-15 column to give the final 24-mer **1 (**4.1 mg, 58%) as a glassy solid. $[\alpha_D^{20}] = +10$ (C = 0.05, DCM). ^{1}H NMR (500 MHz, Deuterium Oxide) δ 5.07 – 5.04 (m, 3H), 4.59 – 4.56 (m, 5H), 4.53 – 4.48 (m, 5H), 4.40 – 4.30 (m, 22H), 3.99 – 3.97 (m, 3H), 3.95 – 3.91 (m, 8H), 3.87 – 3.79 (m, 18H), 3.69 – 3.57 (m, 56H), 3.55 – 3.52 (m, 10H), 3.47 – 3.41 (m, 14H), 3.34 – 3.29 (m, 6H), 3.25 – 3.13 (m, 18H), 1.905 – 1.79 (m, 36H). ^{13}C NMR (126 MHz, Deuterium Oxide), based on HSQC: δ 103.96, 100.98, 80.136, 79.22, 75.15, 74.92, 74.47, 73.78, 72.18, 71.49, 69.48, 67.88, 67.42, 62.67, 60.83, 50.87. ESI-MS: $C_{168}H_{250}N_{12}O_{145}S_4^{4-}$ $[M-3SO_3+2Na-4H]^{3-}$ calcd: 1563.8, obsd: 1563.7, $[M-4H]^{4-}$ calcd: 1221.3, obsd: 1221., $[M-SO_3^-\text{-}4H]^{4-}$ calcd: 1200.8, obsd: 1200.8, $[M-2SO_3^-\text{-}7H+NH_4+2Na]^{4-}$ calcd: 1196. 3, obsd: 1196.3, $[M-2SO_3^-\text{-}6H+3Na]^{5-}$ calcd: 957.8, obsd: 957.9, $[M-3SO_3^-\text{-}6H+NH_4+Na]^{5-}$ calcd: 939.9, obsd: 939.9.

Enzyme digestion and deglycosylation of bikunin PG: Bikunin (41.6 mg) was dissolved with 1 U of chondroitinase ABC (Sigma C2905) in reaction buffer (0.1 M Tris-HCl, 30 mM sodium acetate, pH 8.0, 20 mL). The mixture was incubated at 37 ^{o}C and the reaction progress was monitored by SDS-PAGE. After 48 h, the crude mixture was purified and concentrated using 10 KDa MWCO centrifugal filters against PBS buffer and centrifuged at 4000 rpm for 30 min. The process was repeated at least three times. The resulting core protein was quantified using Bradford assay (BSA as standard) to give the bikunin core protein (9.7 mg).

Figure S1. SDS-PAGE of proteolytic cleavage of CS from bikunin. Lanes: 1, commercial chondroitinase ABC (Sigma C2905); 2, intact bikunin; 3, product after cleavage of CS. The gel was run under non-reducing conditions and stained by Coomassie blue for visualization.



Preparation of bikunin CS chain:

The bikunin proteoglycan (7 mg) was digested with 5% (w/w) actinase E at pH 7.5 in 50 mM tris-HCl in sodium acetate buffer. The mixture was incubated at 45 ^{o}C for 18 h. The CS chain was isolated from the digestion mixture through strong-anion exchange spin column chromatography. First, the spin column was equilibrated with 50 mM NaCl, then the reaction mixture was diluted with 50 mM NaCl and loaded into the column using centrifugation at 500g. The column was then washed three times with 50 mM NaCl, then eluted with 1.5 M NaCl. The fractions collected were concentrated and desalted using 10 KDa MWCO centrifugal filter with deionized water. The resulting concentrate was collected and lyophilized to afford the bikunin CS (2.7 mg). The CS chain was characterized using ^{1}H-NMR and ESI-MS.

Anti-inflammatory activity measurement:

Mouse macrophage cells (RAW264.7) were used for the determination of anti-inflammatory effects of 24-mer **1,** CS-A polysaccharide, bikunin CS, bikunin core protein and bikunin proteoglycan. As the bikunin core protein was generated by chondroitinase ABC mediated digestion of bikunin proteoglycan, chondroitinase ABC was incubated with RAW264.7 cells, which did not lead to significant amounts of TNF-α over the background, suggesting the chondroitinase ABC itself is not inflammatory.

Preparation of macrophage and cell culture treatment:

Raw 264.7 murine macrophage cells were plated in 100mm cell culture dish in 10 mL of growth medium (Dulbecco's Modified Eagle Medium (Gibco) with 10% fetal bovine serum and 1% Pen/Strep (Gibco)). The cells were incubated at 37 °C in a humidified atmosphere with 5% CO_2, harvested for use by Versene solution (Gibco), and seeded at 0.4×10^6 cells/well in 96-well plates.

After incubation overnight, the nonadherent cells and the medium was removed. FBS free medium containing 24-mer **1,** CS-A polysaccharide, bikunin CS, core protein and Bikunin were added and incubated for 1 h, which were followed by stimulation of LPS (E. *coli*, Sigma) at 100 ng/mL for 24 h. The growth medium from each well was harvested for the measurement of the amount of TNF-α generated.

Quantitative enzyme-linked immunosorbent assay (ELISA) for TNF-α quantification:

Mouse TNF-α uncoated ELISA kit was purchased from Thermo-Fisher scientific.

a- Reagent preparation:

- **Wash Buffer:** 1X PBS, 0.05% Tween-20 wash buffer.
- **Stop Solution:** 1M H_3PO_4.
- **Coating buffer:** make a 1:10 dilution of PBS in deionized water.
- **Capture Antibody:** dilute capture antibody (250X) in coating buffer (1X).
- **5X ELISA/ELISASPOT Diluent:** dilute diluent concentrate 1:5 in deionized water.
- **Detection Antibody:** dilute detection antibody 1:250 in ELISA/ELISASPOT Diluent (1X).
- **Enzyme:** dilute HRP concentrate (250X) 1:250 in ELISA/ELISASPOT Diluent (1X).

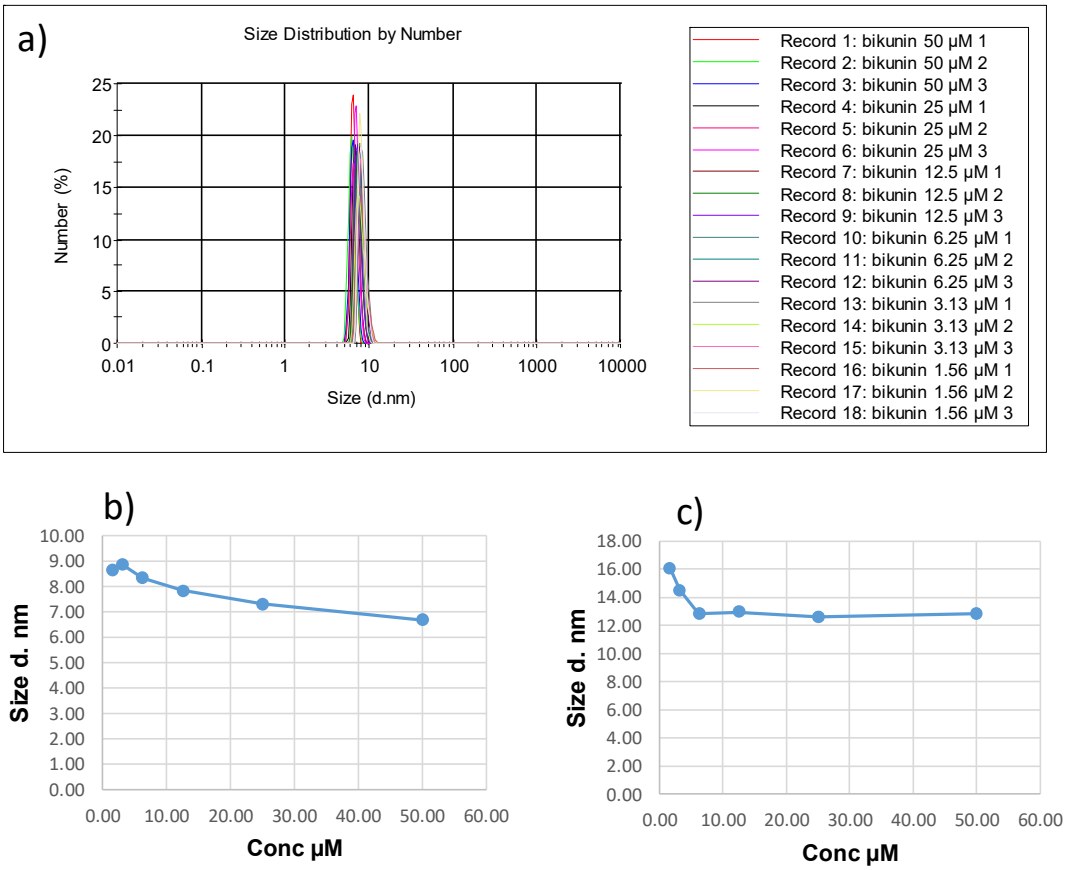
b- Experimental steps:

1- Coat an ELISA plate with the capture antibody in coating buffer (50 µL) to each individual well, seal the plate with parafilm and incubate at 4 ºC overnight.
2- Wash the plate 5 times with ELISA washing buffer and discard remaining solution in the plate. In every washing step, keep the plate for 1 min., and the last step for 2 min. (to remove any residual buffer, blot the plate on adsorption paper)
3- Add 100 µL of ELISA diluent to each individual well and incubate at rt for 1h.
4- Wash the plate following the same procedure as step 2.
5- Add all samples in desired concentration (100 µL/well) and the last columns were kept for standard. Seal the plates and incubate at 4 ºC overnight.
6- Follow step 2 for washing.
7- Add 50 µL/well diluted detection antibody to all wells, then cover the plate and incubate at rt for 1h.
8- Follow step 2 for washing.
9- Add 50 µL/well of diluted Advin-HRP, then seal the plate and incubate for 15 min. at rt.
10- Wash the plate for 7 times for 2 min. each.
11- Add 50 µL/well of substrate solution (offered as mixture of 3,3',5,5'-tetramethylbenzidine (TMB), hydrogen peroxide (H_2O_2), and proprietary catalyzing and stabilizing agents) and incubate at rt for 15 min.
12- Add 50 µL of stop solution.
13- Read the plate at 450 nm by TECAN reader.

Aggregation state test of bikunin and CS-A polysaccharide:

The hydrodynamic diameters of bikunin and CS-A polysaccharide (1.56 – 50.0 µM) in PBS were measured by dynamic light scattering (DLS) analyzer Zetasizer (Malvern).

Figure S2. a) Hydrodynamic diameters of bikunin were measured at different concentrations (1.56 – 50.0 µM) in PBS. For each concentration, three independent batches of samples were measured. Changes of hydrodynamic diameters of b) bikunin based on data in a). c) Changes of hydrodynamic diameters of CS-A polysaccharide. CS and bikunin showed similar small size decreases at higher concentrations supporting that CS and bikunin are soluble and not aggregated at concentrations studied.



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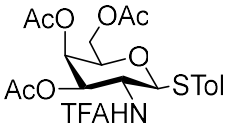
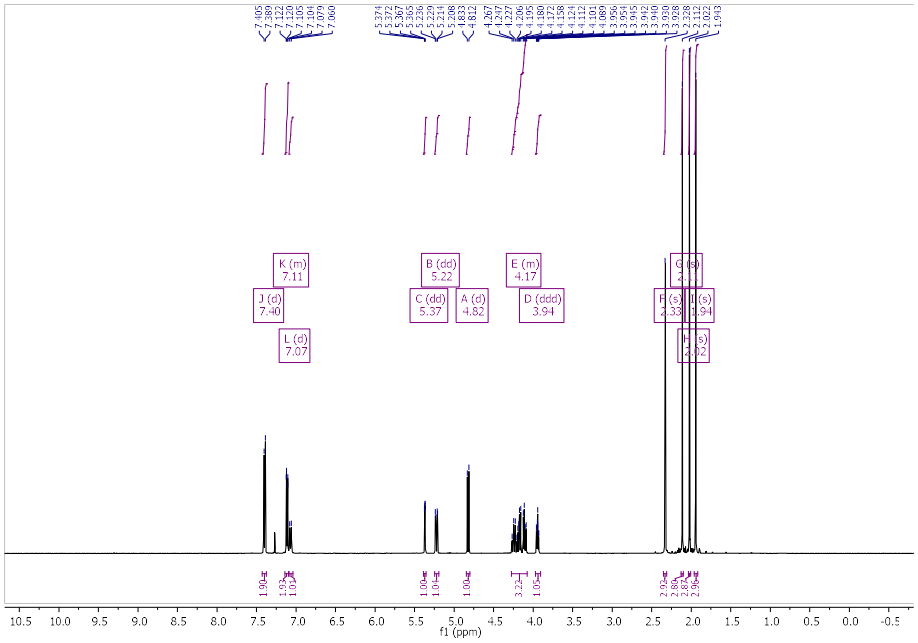
NMR Spectra

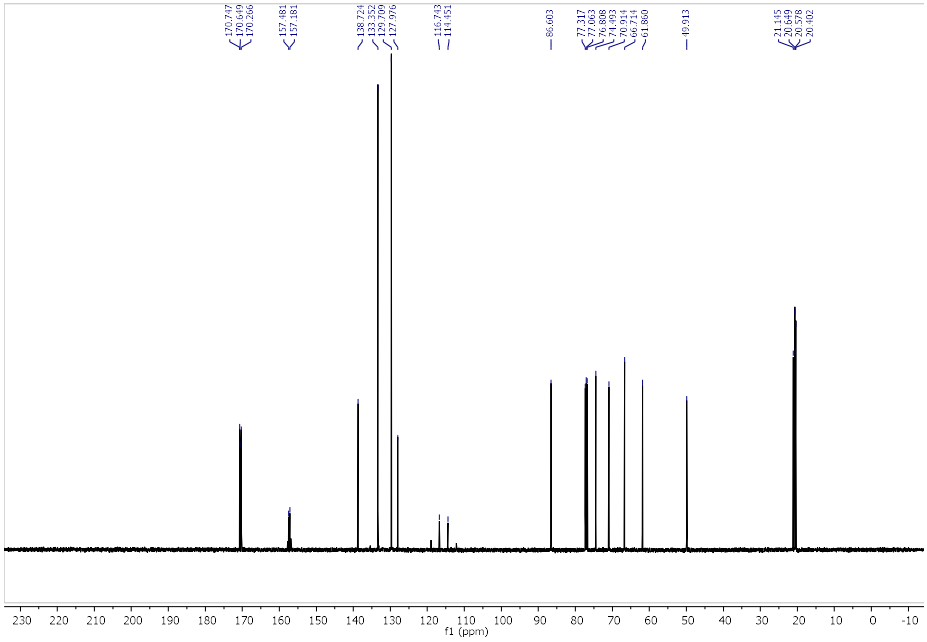


S3

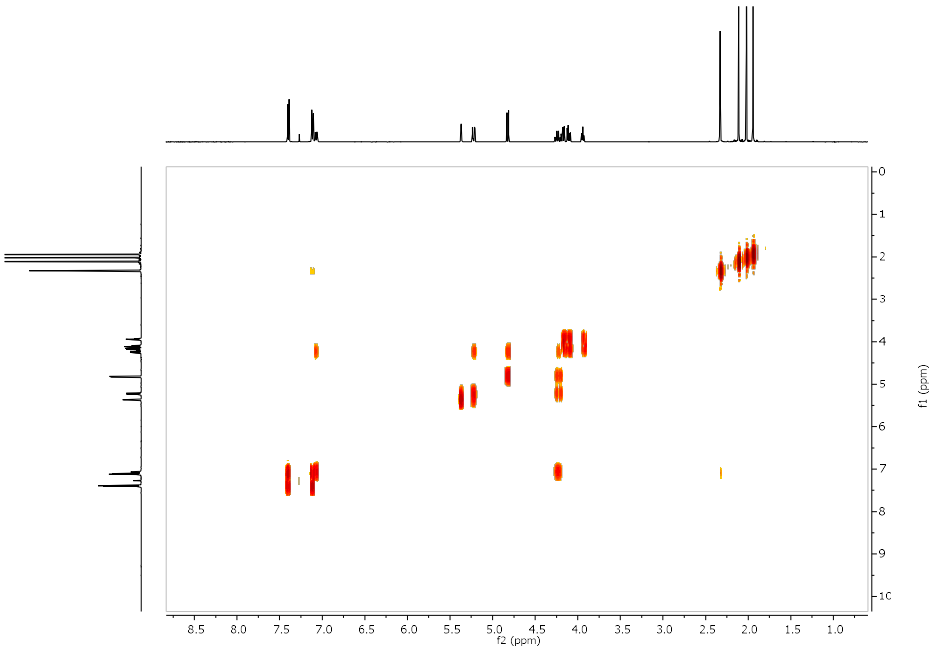
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S3**



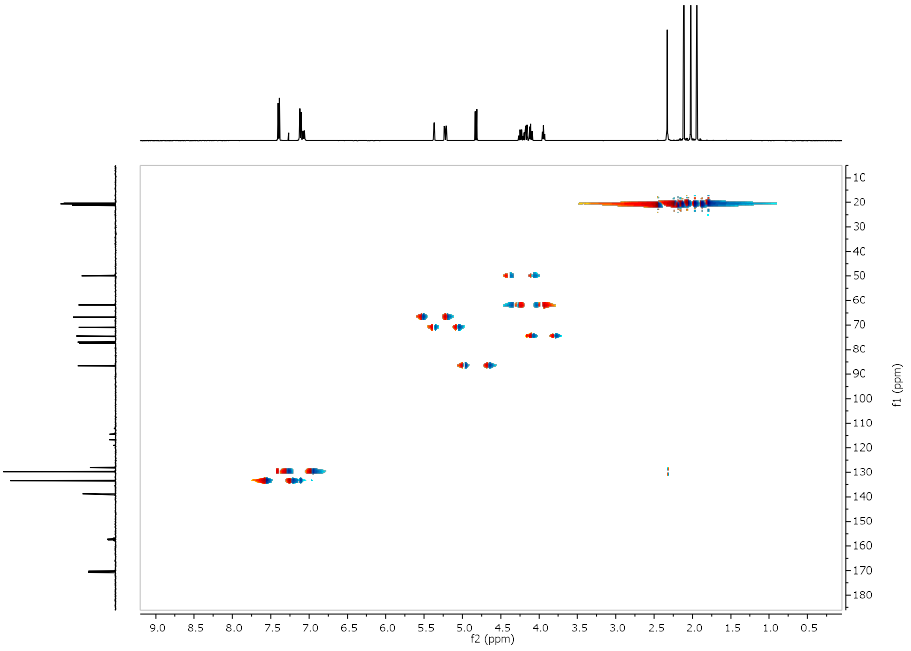
^{13}C-NMR ($CDCl_3$, 126 MHz) of **S3**

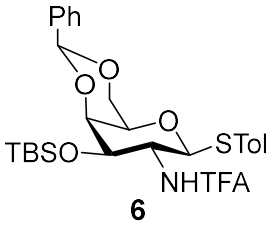


gCOSY ($CDCl_3$, 500 MHz) of **S3**



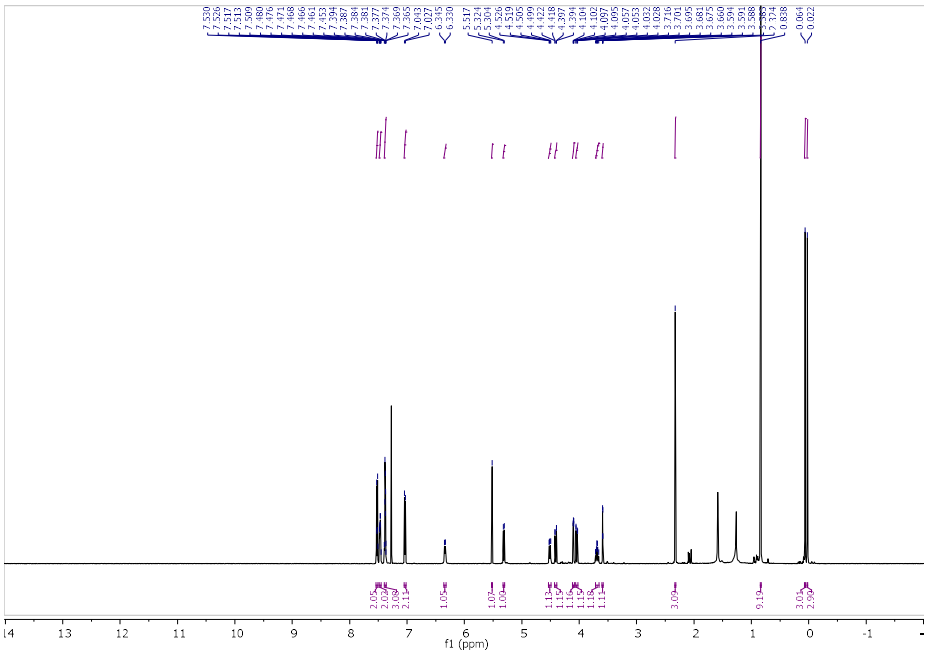
gHSQC ($CDCl_3$, 500 MHz) of **S3**



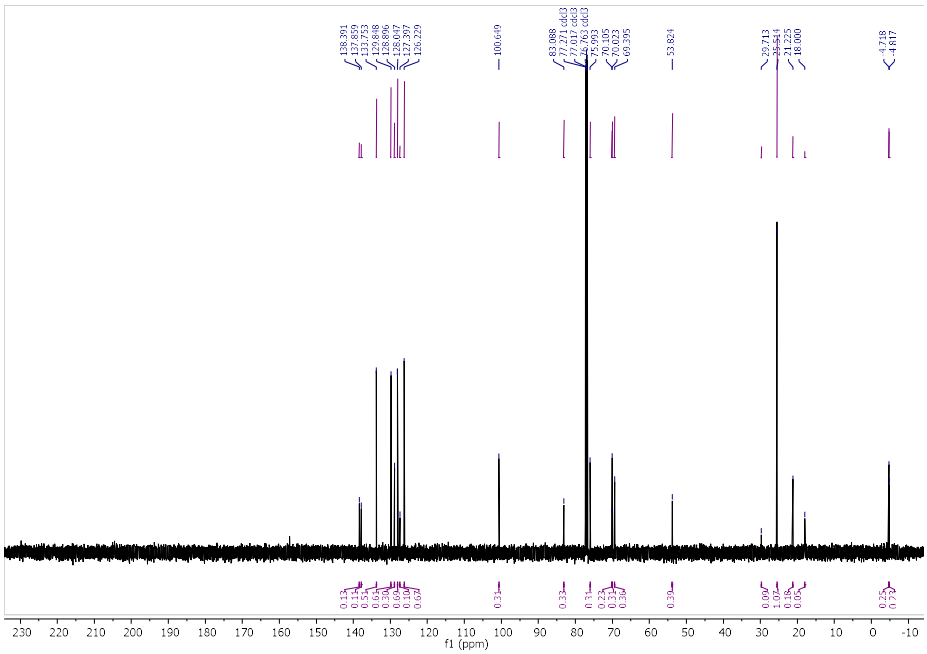


6

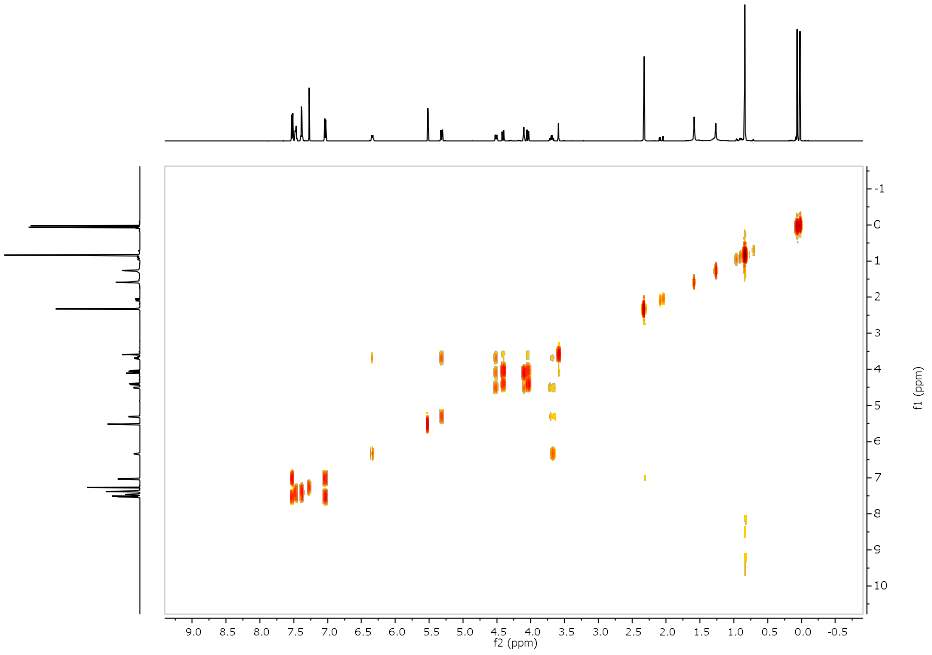
^{1}H-NMR ($CDCl_3$, 500 MHz) of **6**



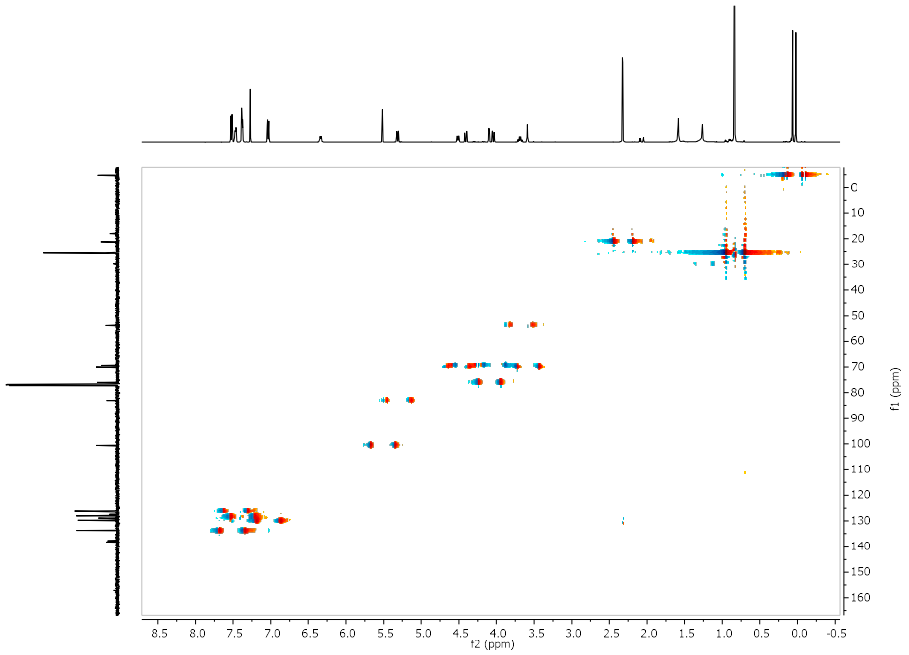
^{13}C-NMR ($CDCl_3$, 126 MHz) of **6**

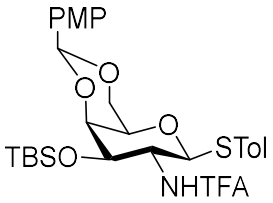


gCOSY ($CDCl_3$, 500 MHz) of **6**



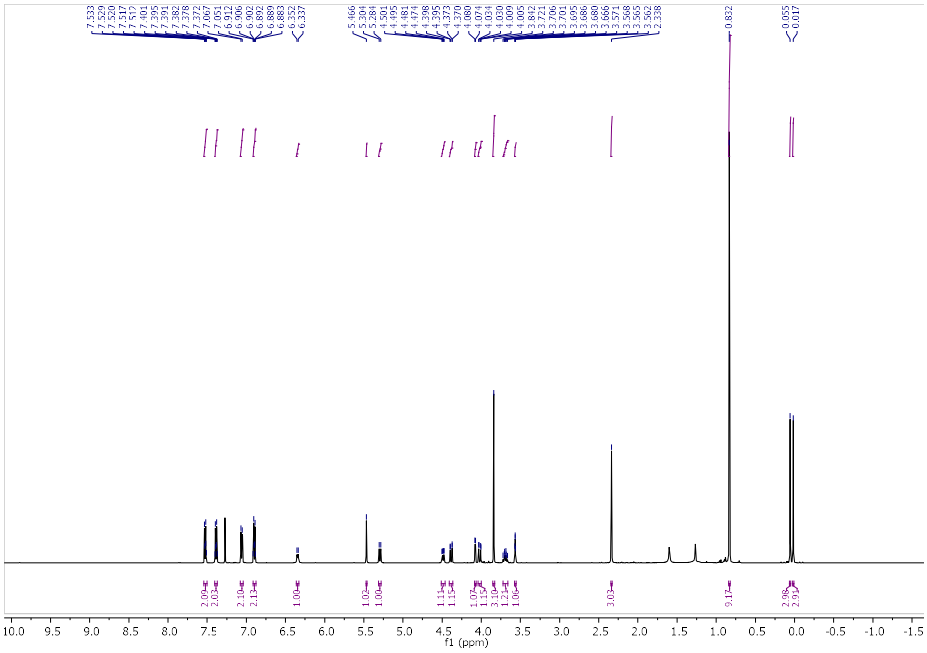
gHSQC ($CDCl_3$, 500 MHz) of **6**



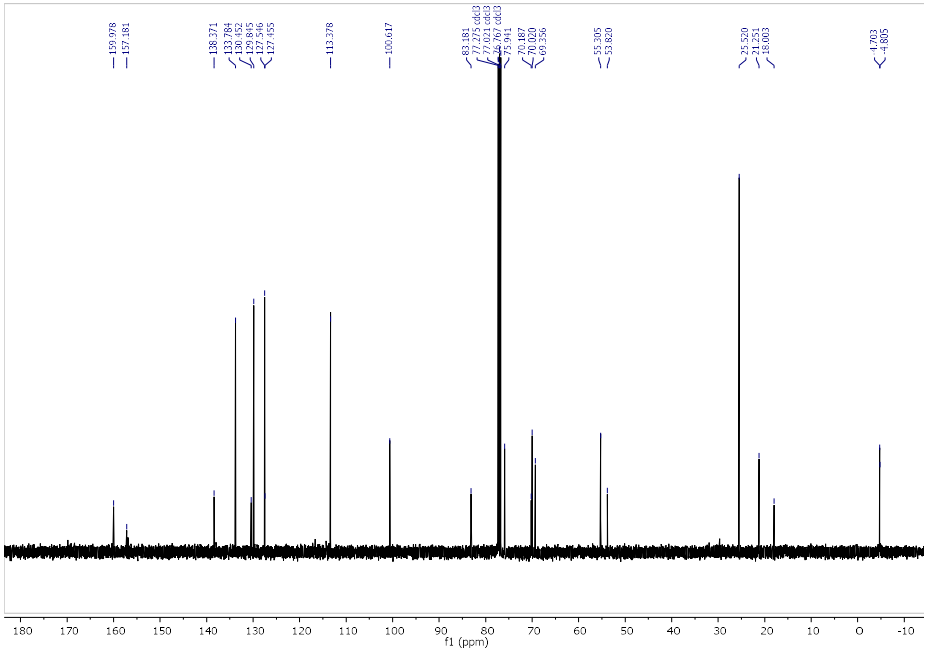


13

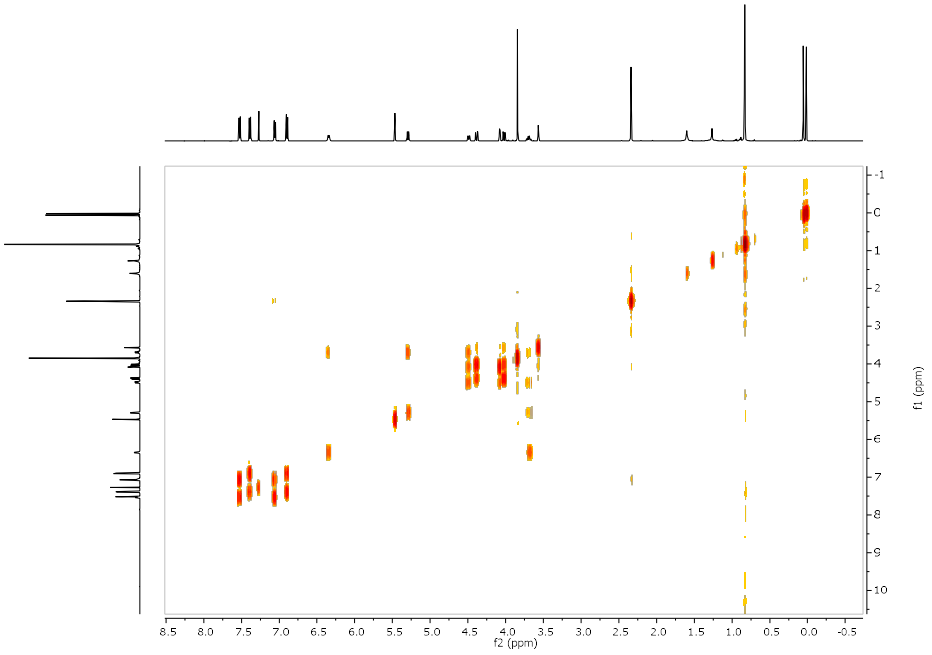
^{1}H-NMR ($CDCl_3$, 500 MHz) of **13**



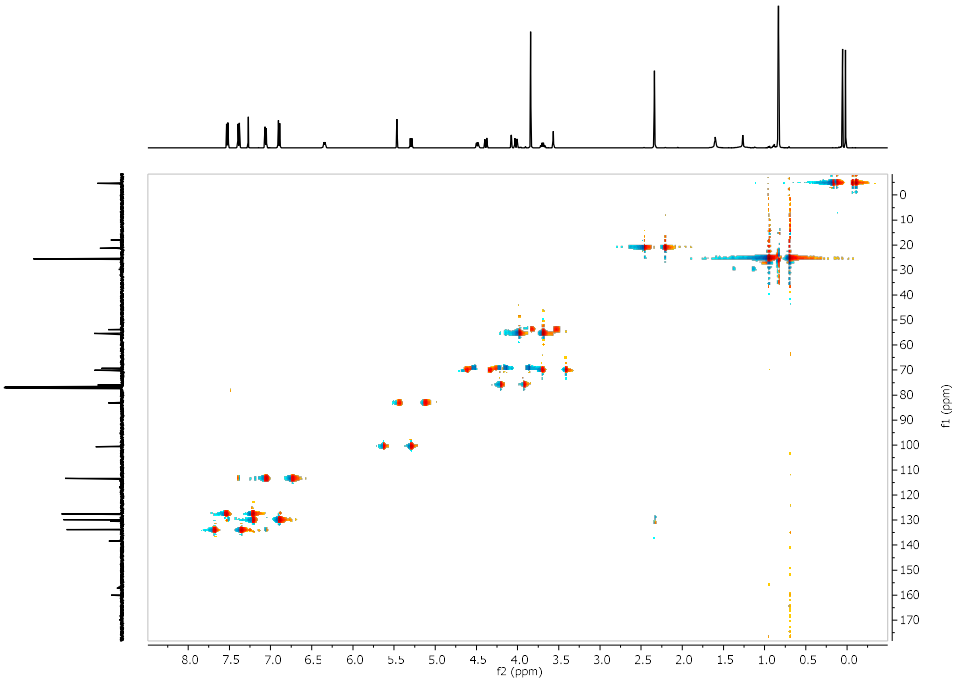
^{13}C-NMR ($CDCl_3$, 126 MHz) of **13**

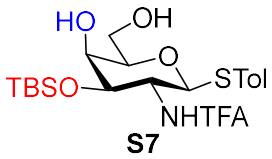


gCOSY ($CDCl_3$, 500 MHz) of **13**



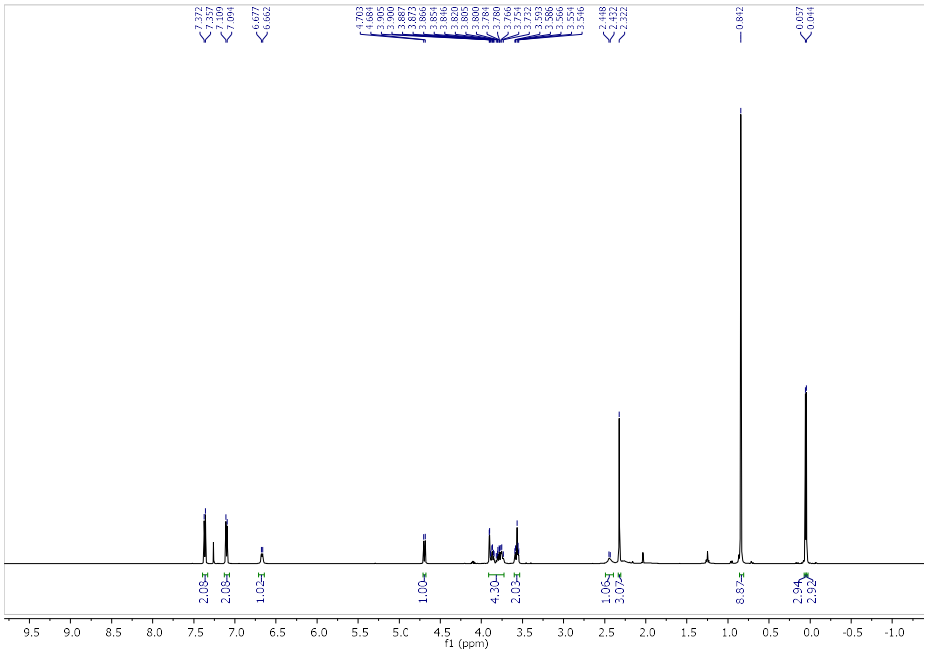
gHSQC ($CDCl_3$, 500 MHz) of **13**



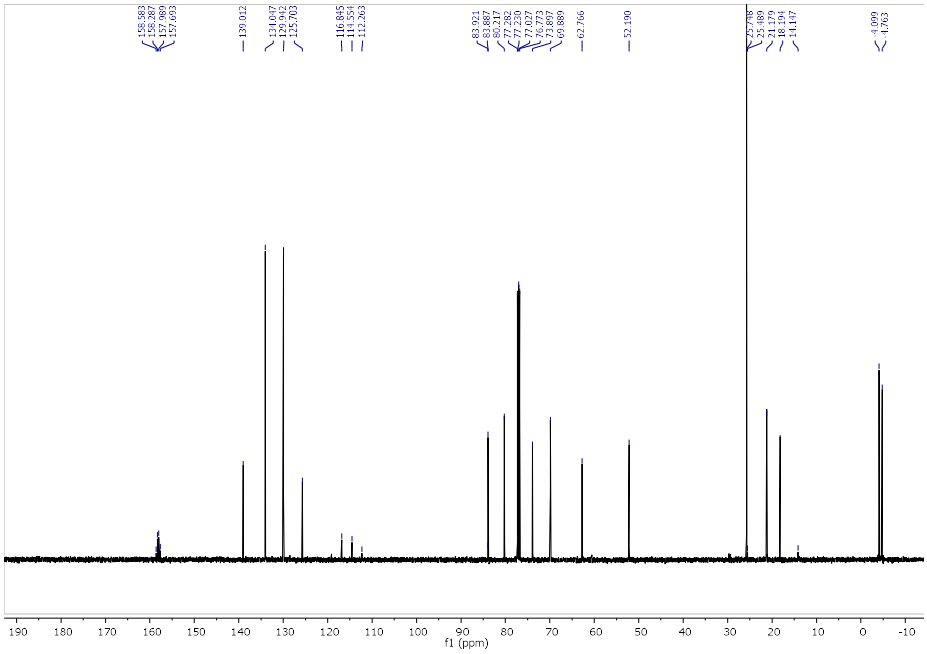


S7

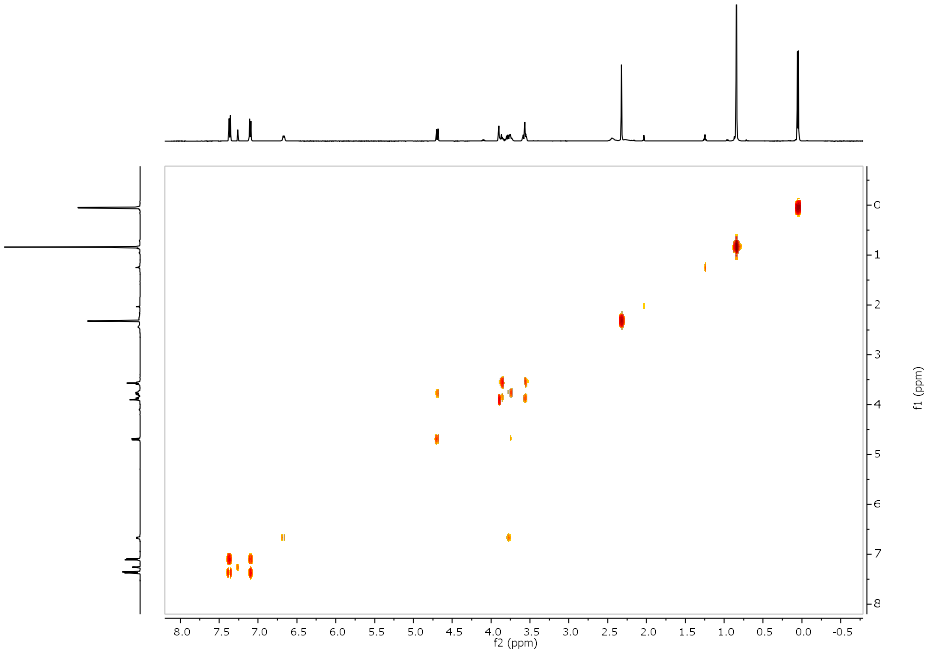
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S7**



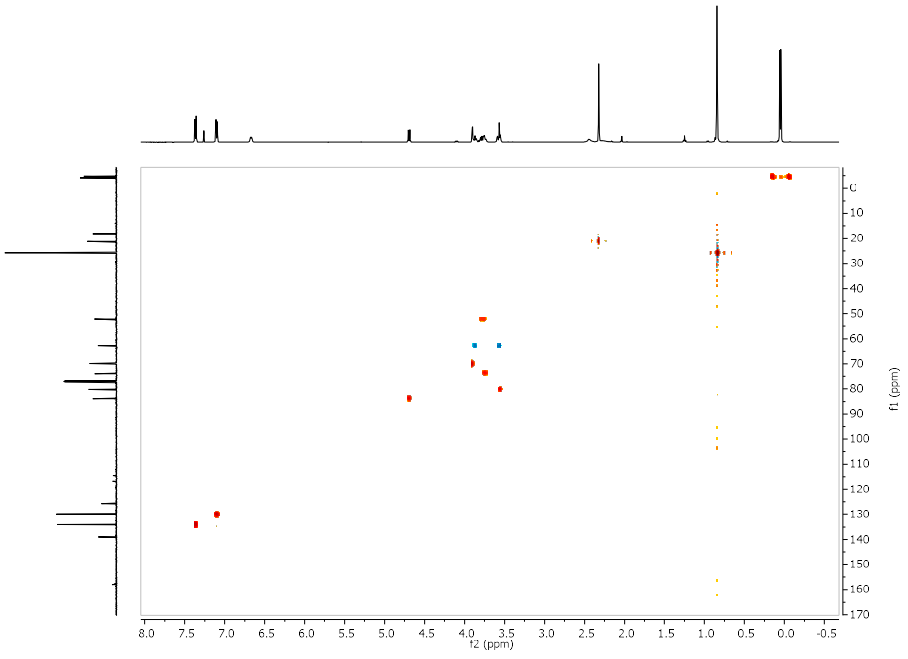
^{13}C-NMR ($CDCl_3$, 126 MHz) of **S7**

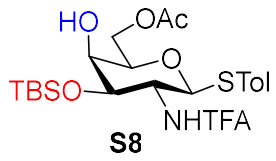


gCOSY ($CDCl_3$, 500 MHz) of **S7**



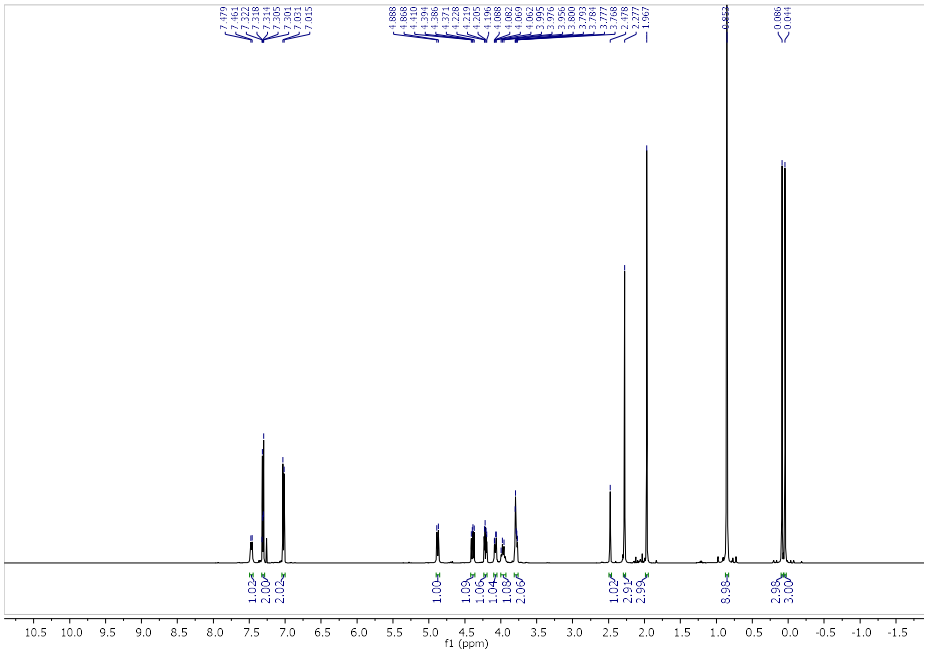
gHSQC ($CDCl_3$, 500 MHz) of **S7**



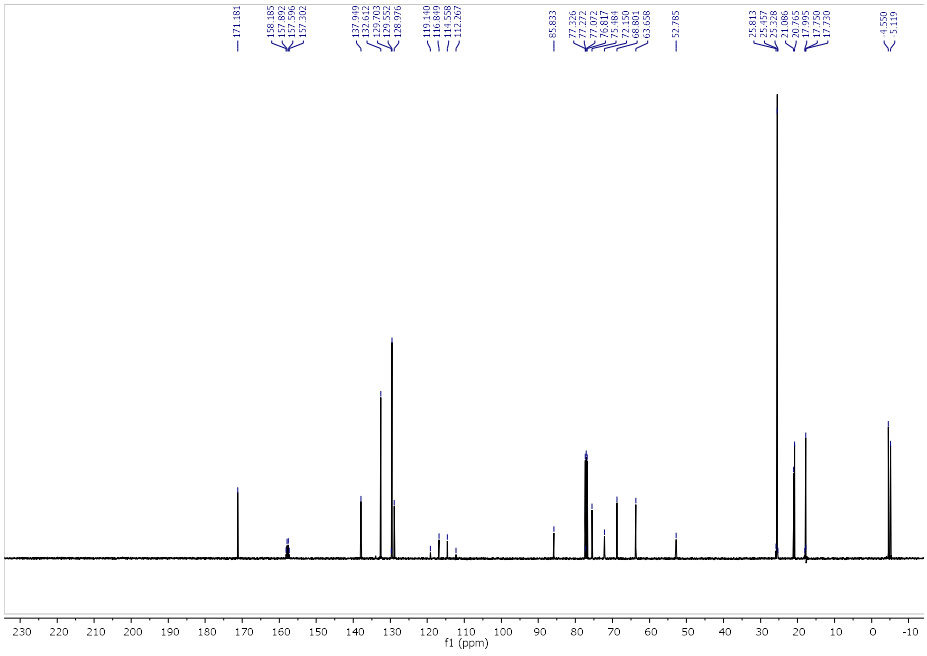


S8

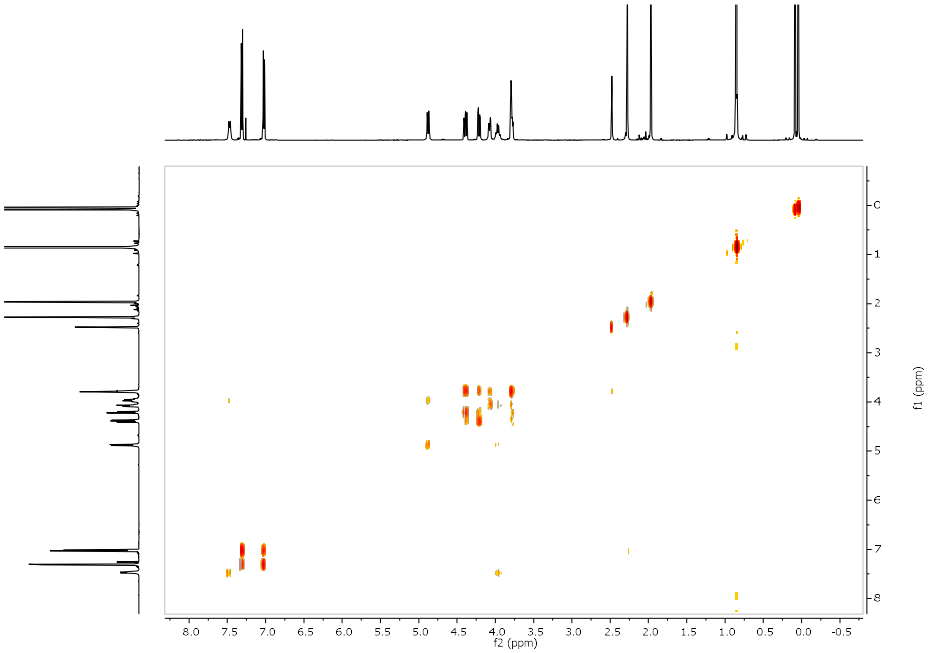
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S8**



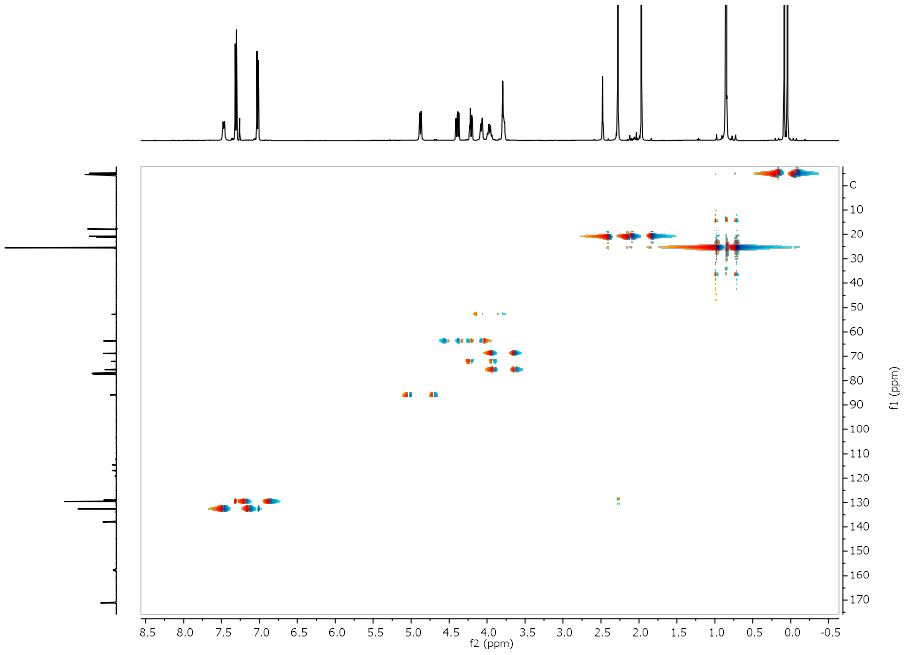
^{13}C-NMR ($CDCl_3$, 126 MHz) of **S8**

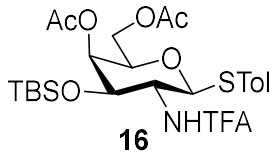


gCOSY ($CDCl_3$, 500 MHz) of **S8**



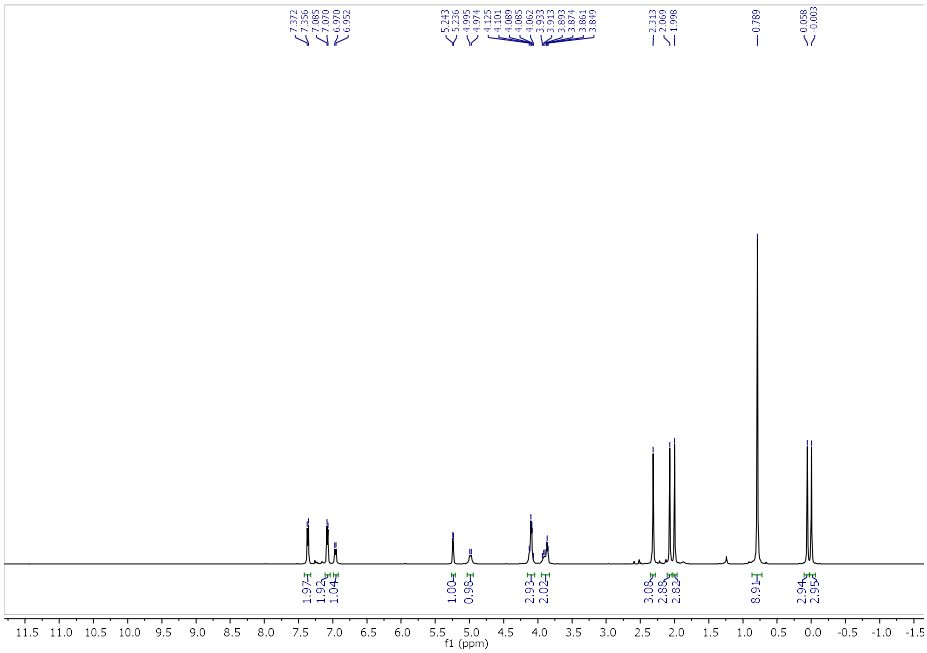
gHSQC ($CDCl_3$, 500 MHz) of **S8**



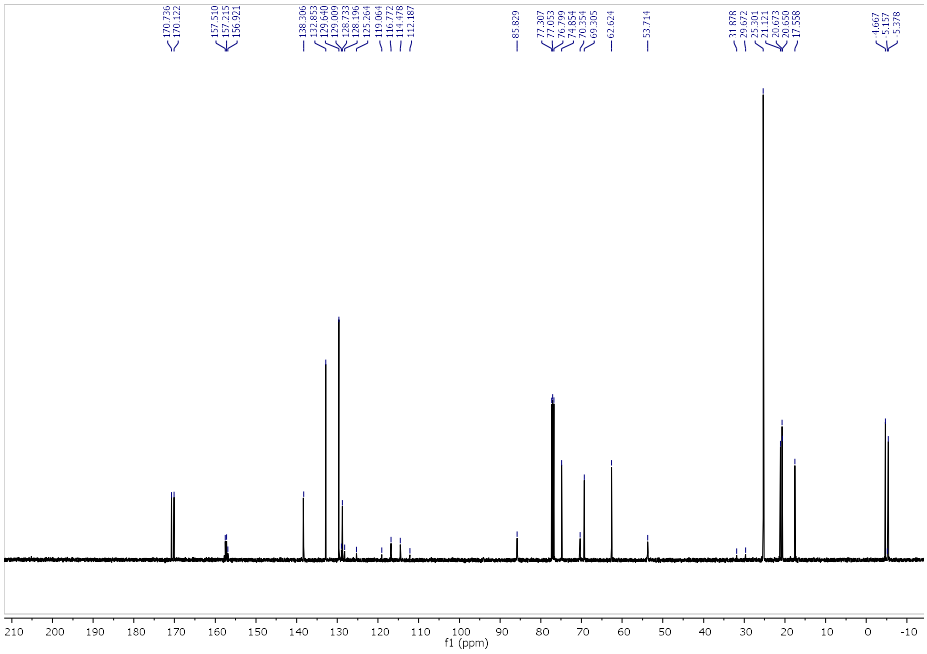


16

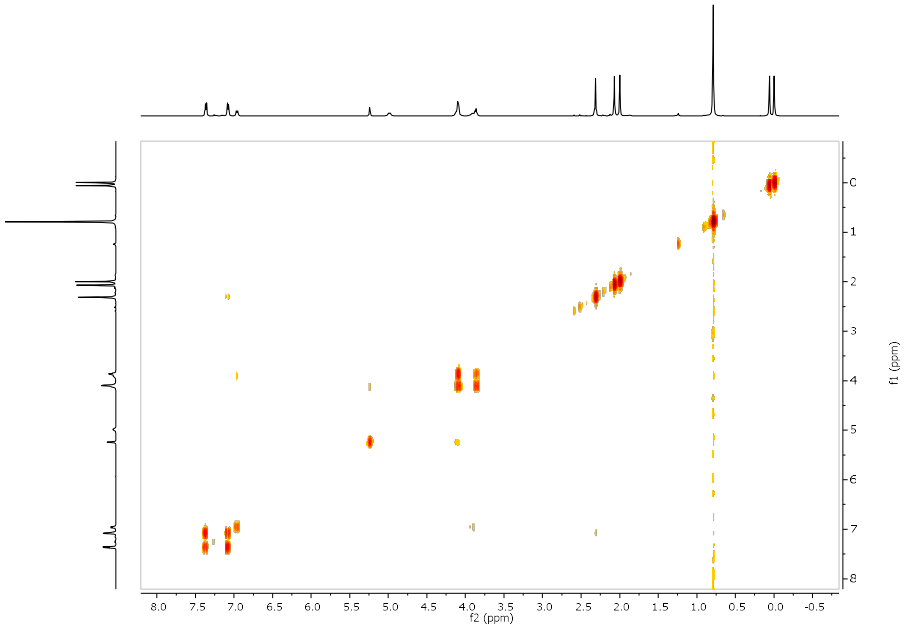
^{1}H-NMR ($CDCl_3$, 500 MHz) of **16**

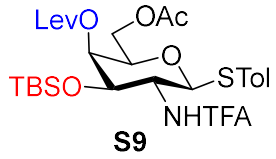


^{13}C-NMR ($CDCl_3$, 126 MHz) of **16**



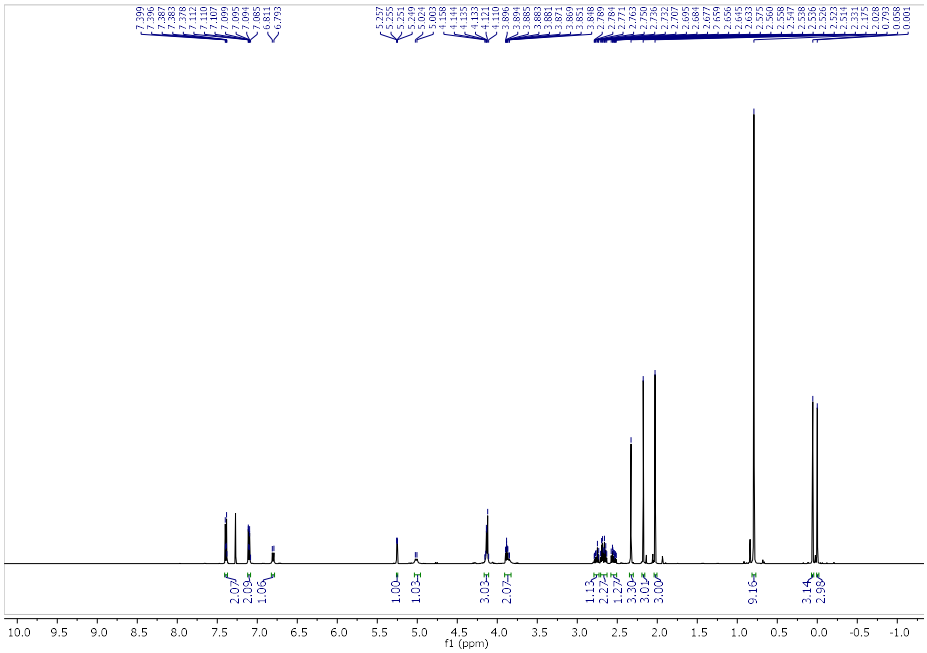
gCOSY ($CDCl_3$, 500 MHz) of **16**



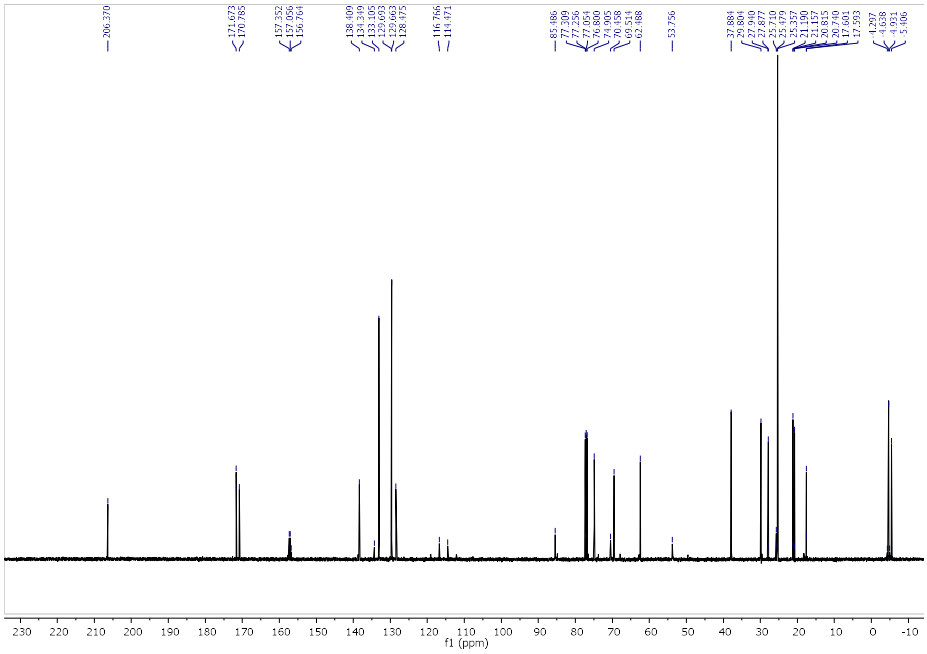


S9

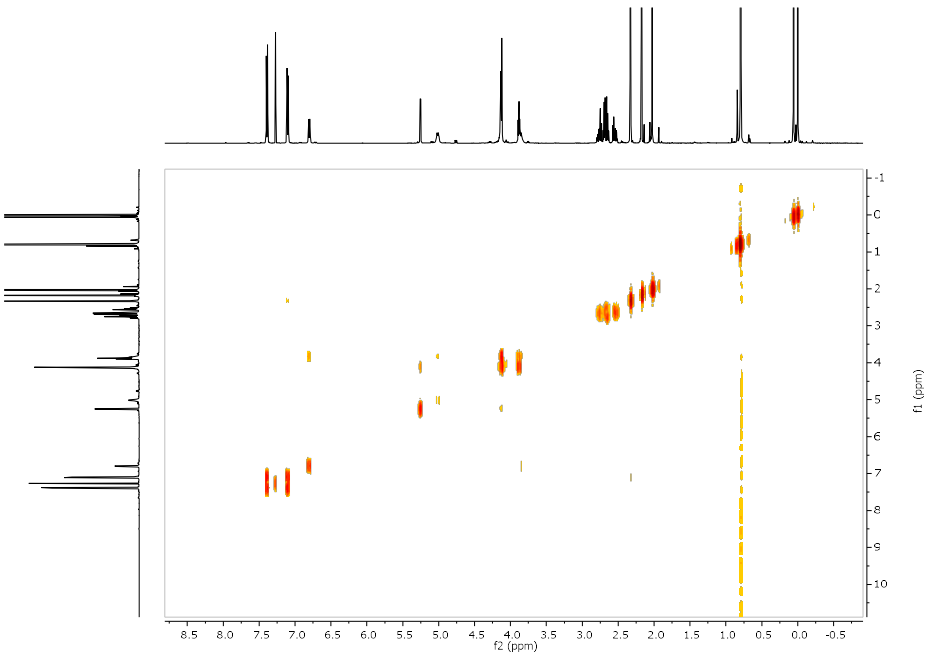
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S9**



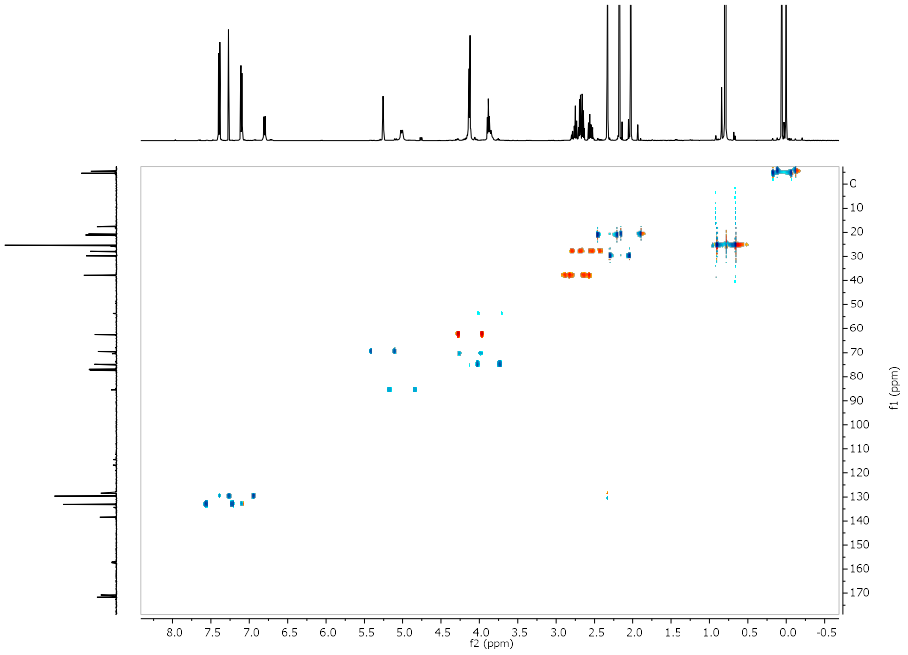
^{13}C-NMR ($CDCl_3$, 126 MHz) of **S9**

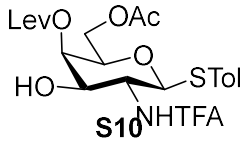


gCOSY ($CDCl_3$, 500 MHz) of **S9**



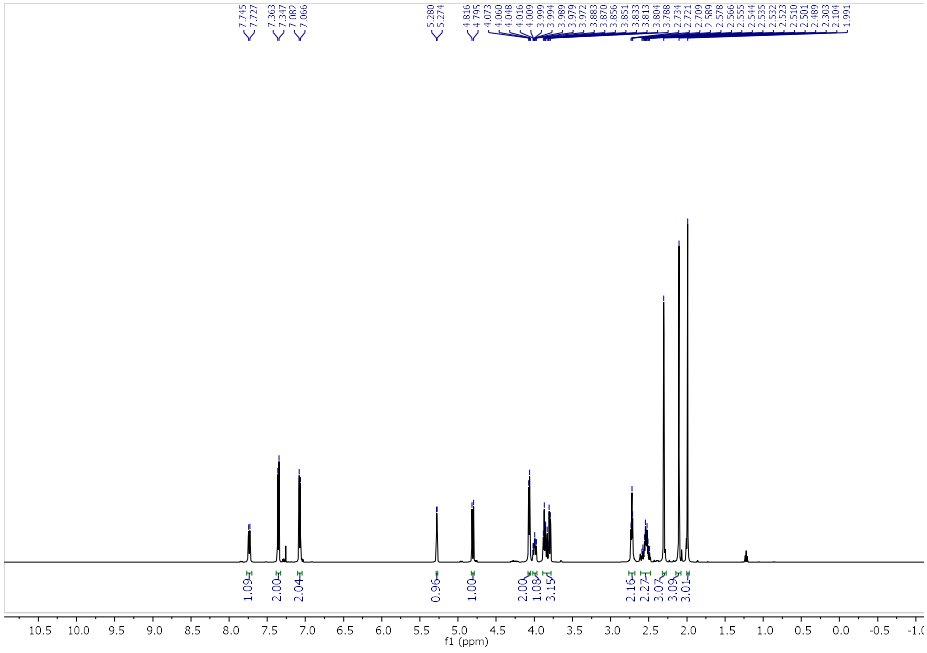
gHSQC ($CDCl_3$, 500 MHz) of **S9**



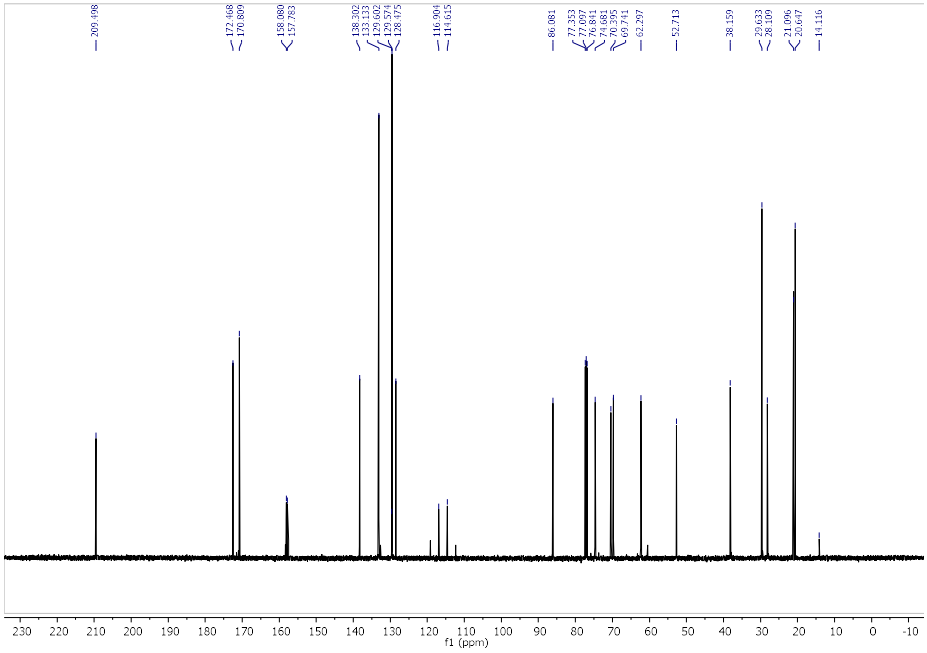


S10

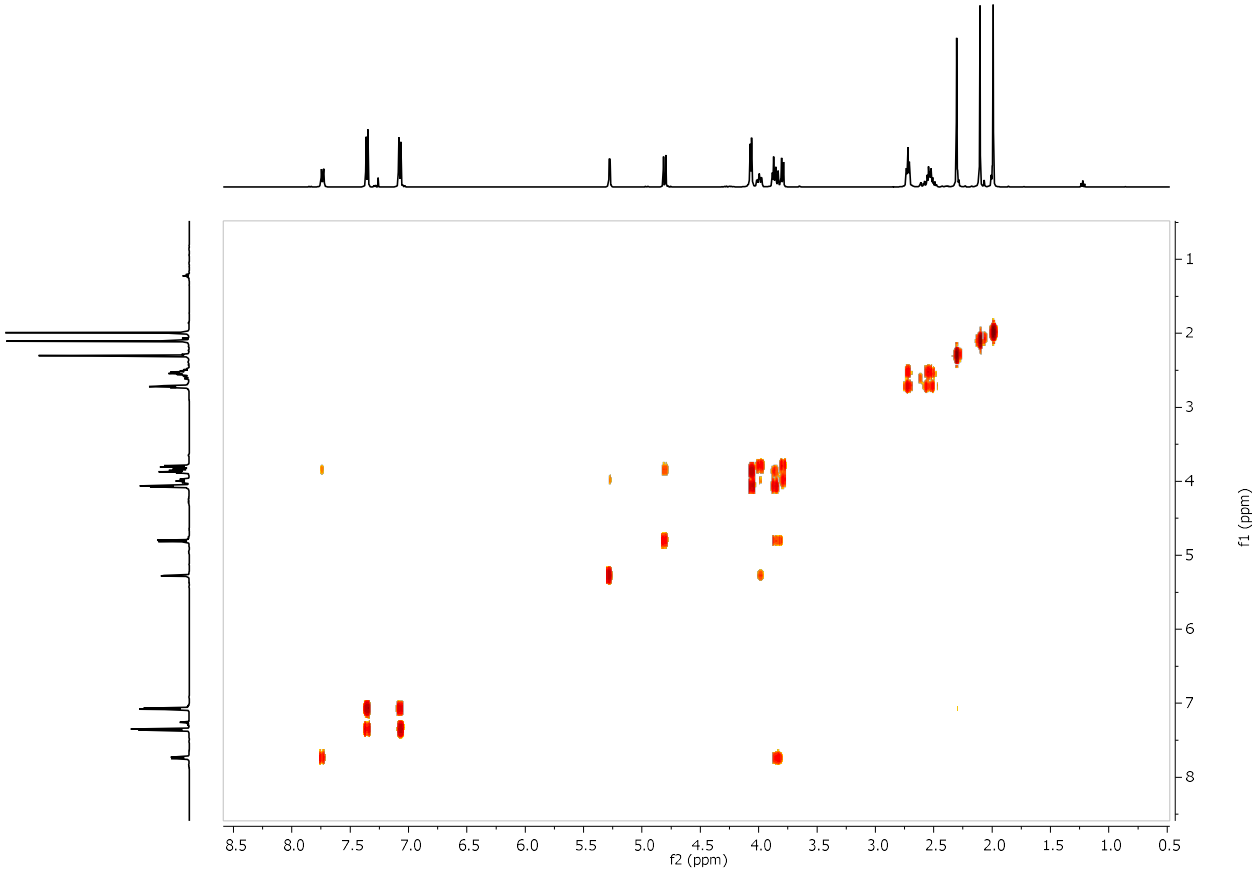
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S10**

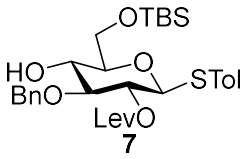


^{13}C-NMR ($CDCl_3$, 126 MHz) of **10**



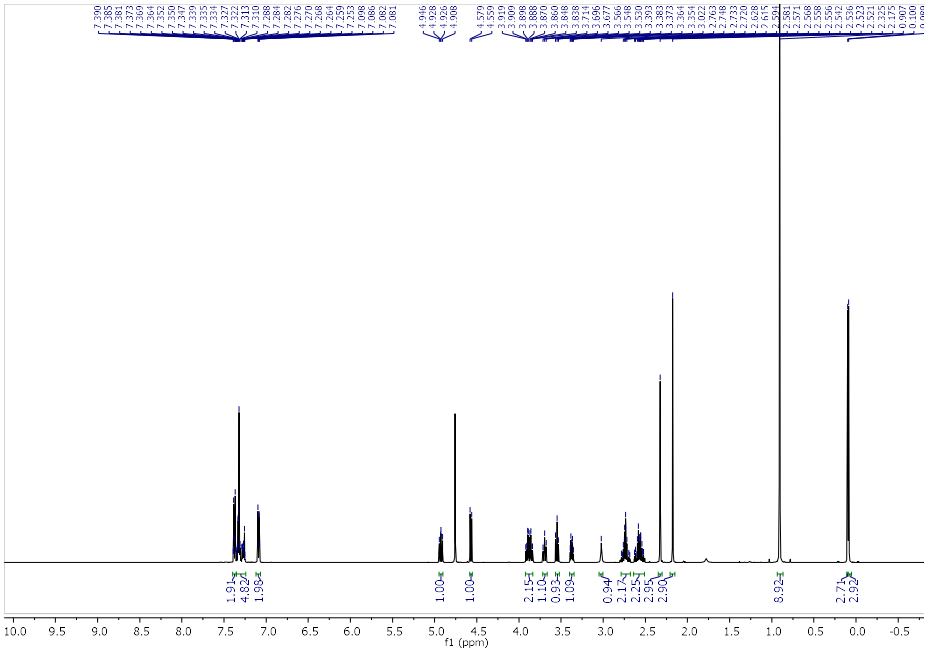
gCOSY ($CDCl_3$, 500 MHz) of **10**



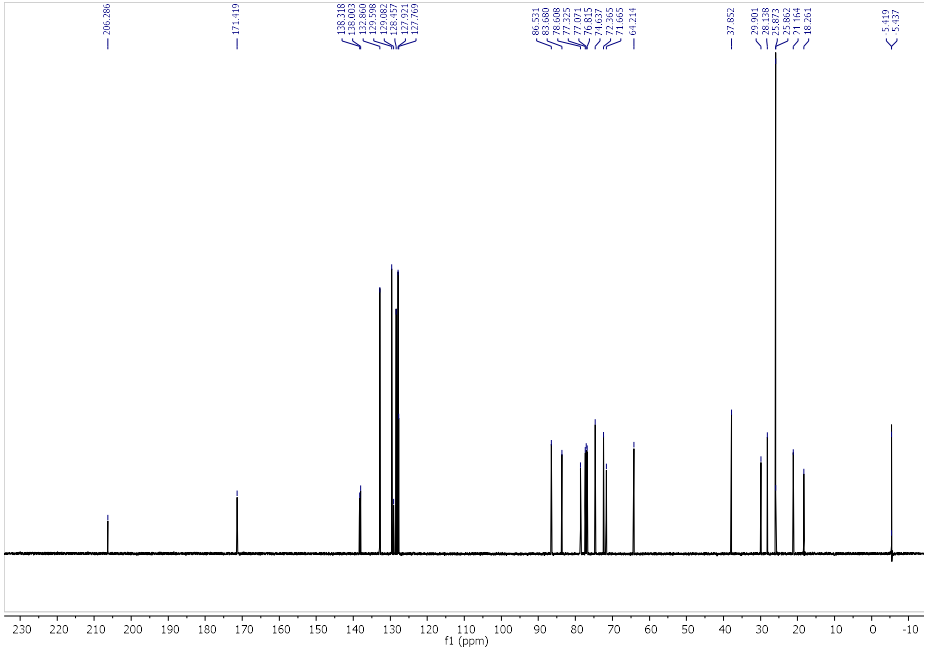


7

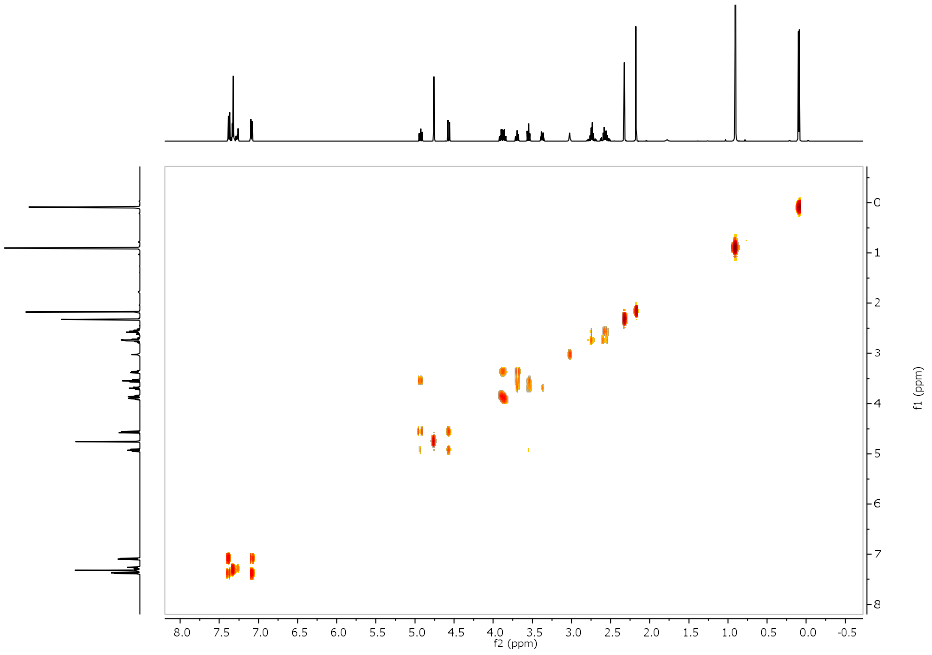
^{1}H-NMR ($CDCl_3$, 500 MHz) of **7**



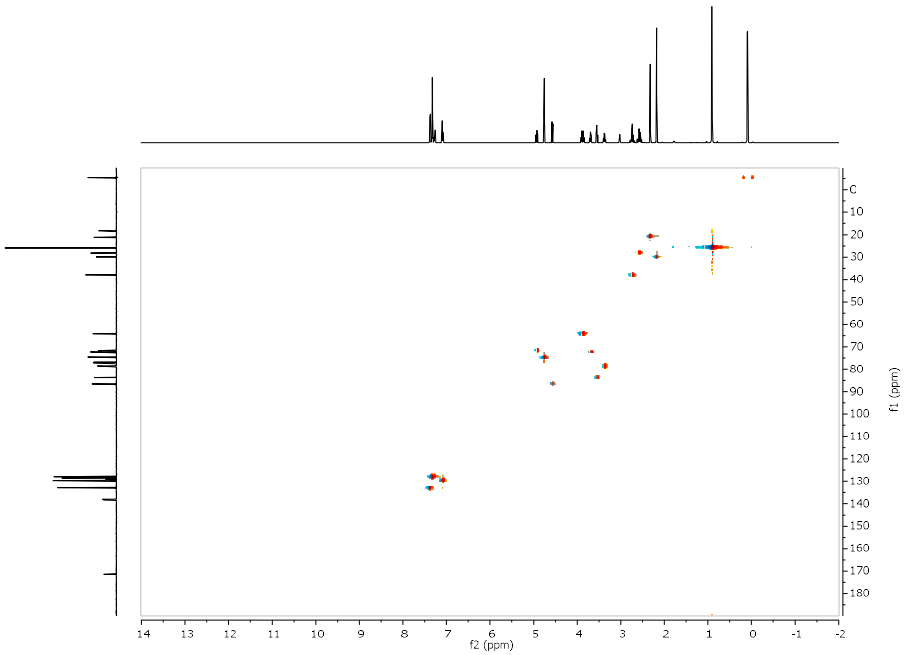
^{13}C-NMR ($CDCl_3$, 126 MHz) of **7**

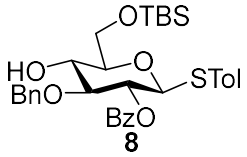


gCOSY ($CDCl_3$, 500 MHz) of **7**



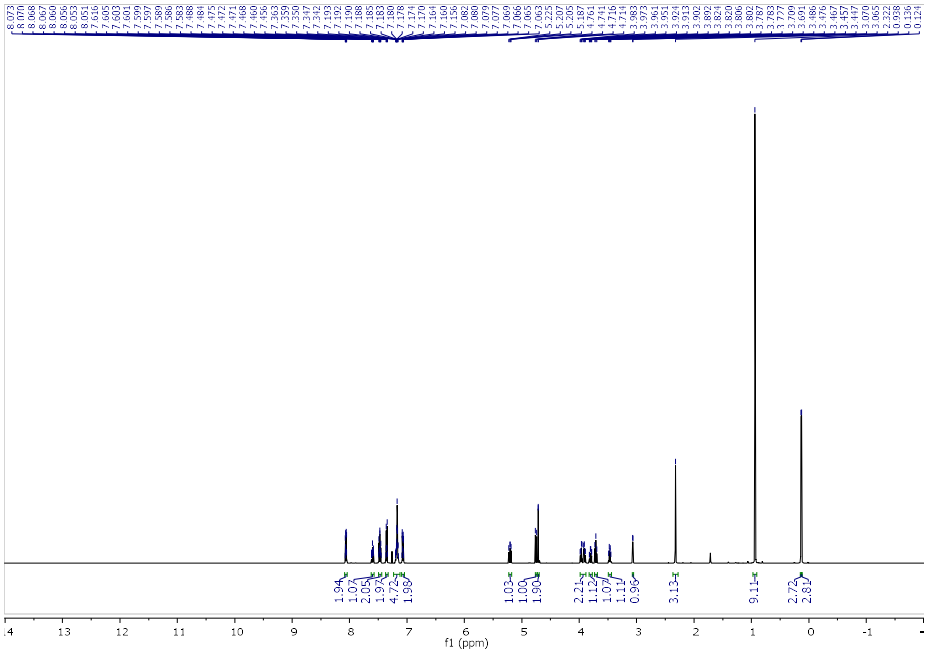
gHSQC ($CDCl_3$, 500 MHz) of **7**



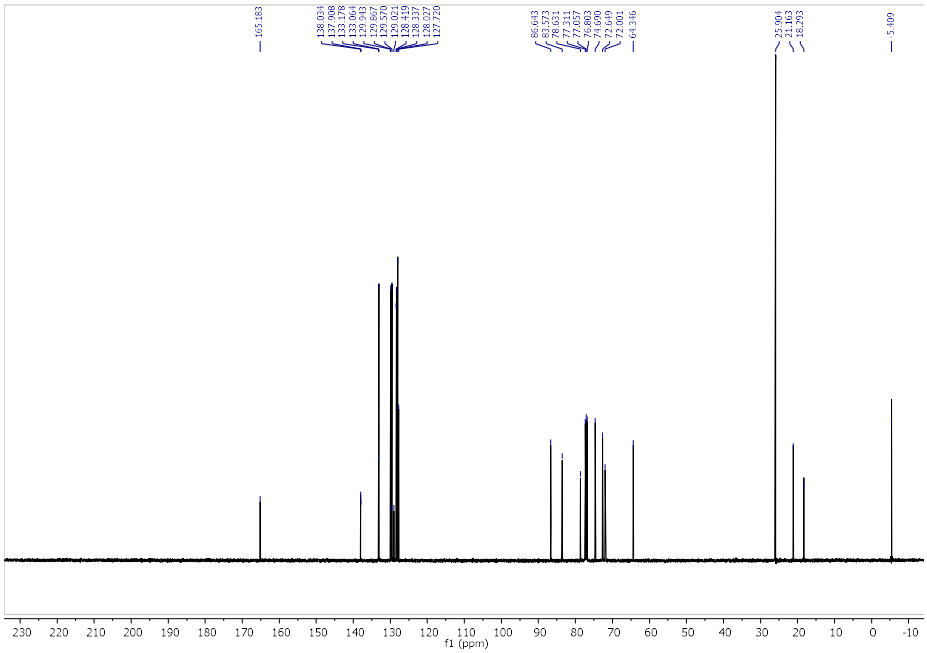


8

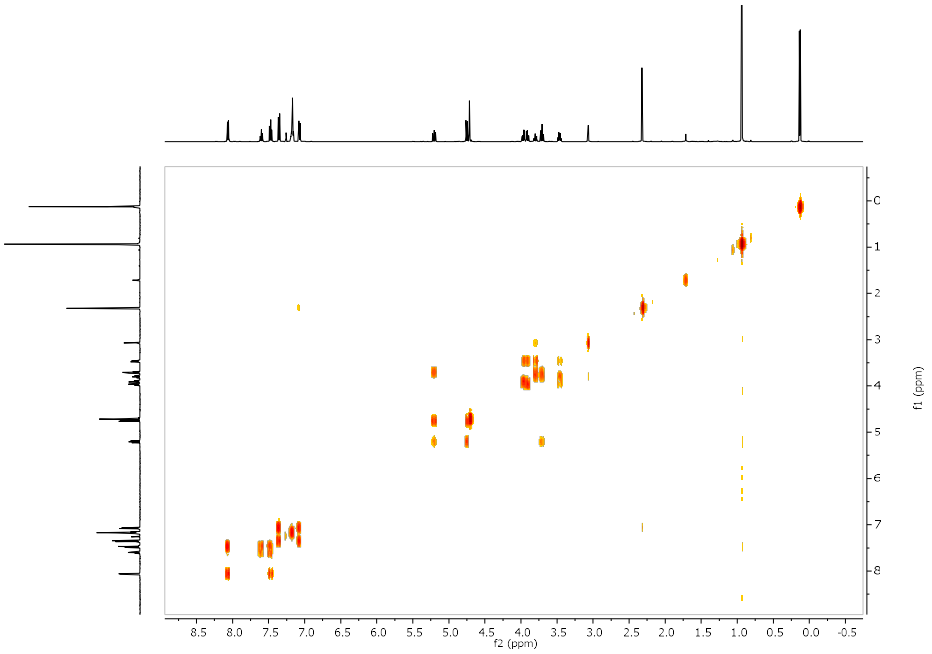
^{1}H-NMR ($CDCl_3$, 500 MHz) of **8**



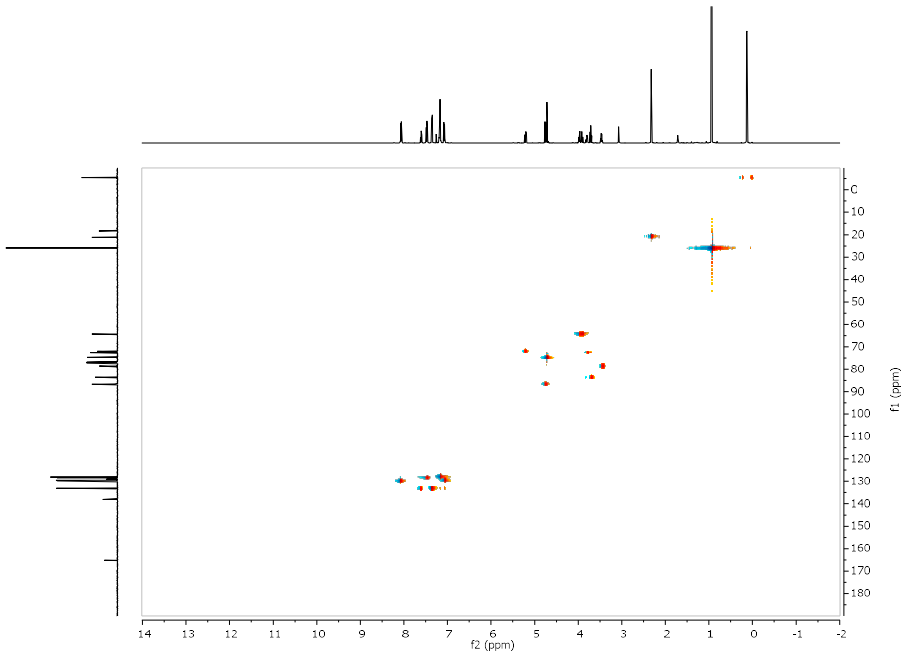
^{13}C-NMR ($CDCl_3$, 126 MHz) of **4**

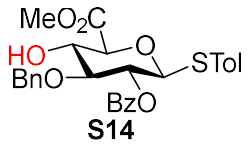


gCOSY ($CDCl_3$, 500 MHz) of **8**

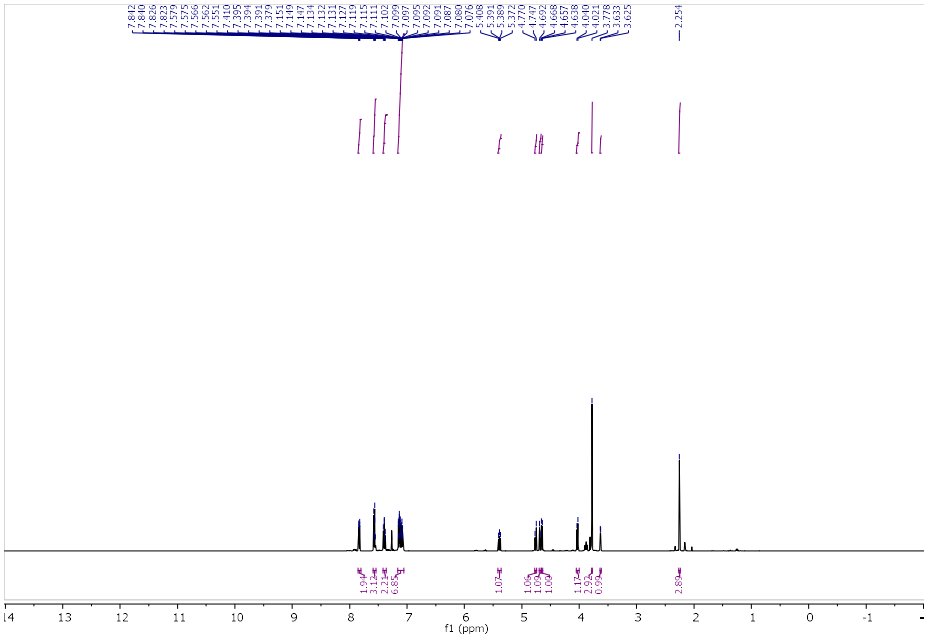


gHSQC ($CDCl_3$, 500 MHz) of **8**

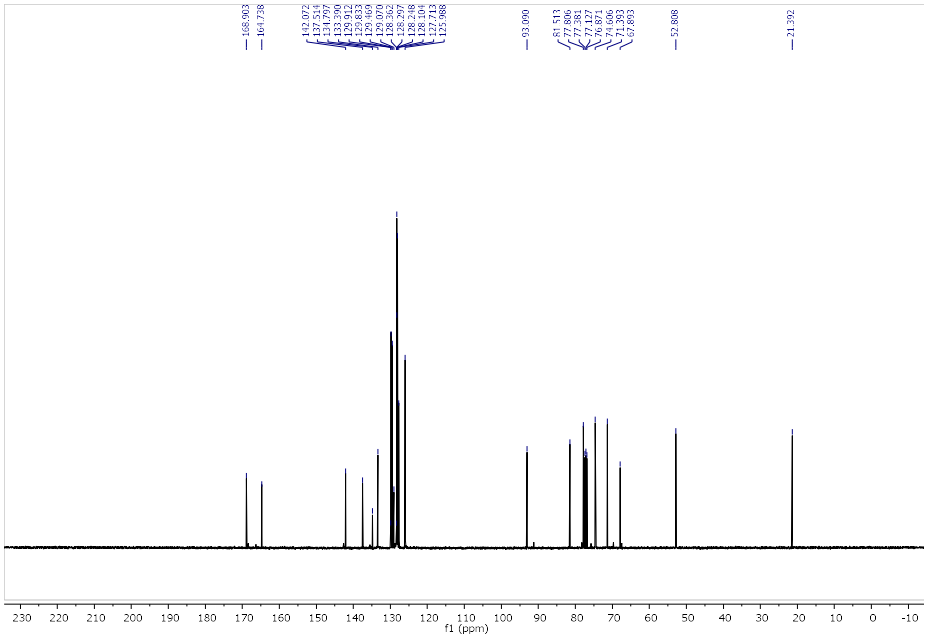




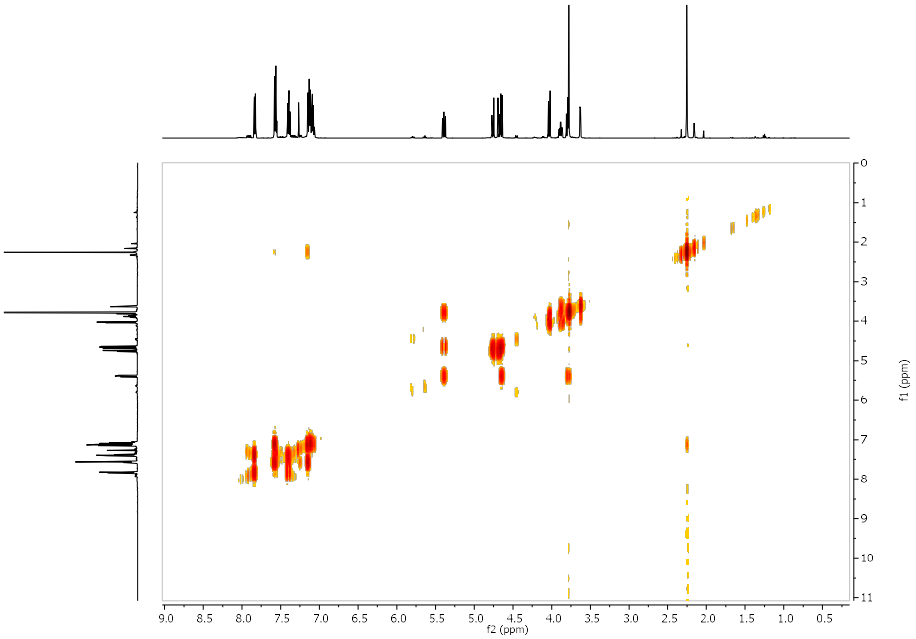
S14



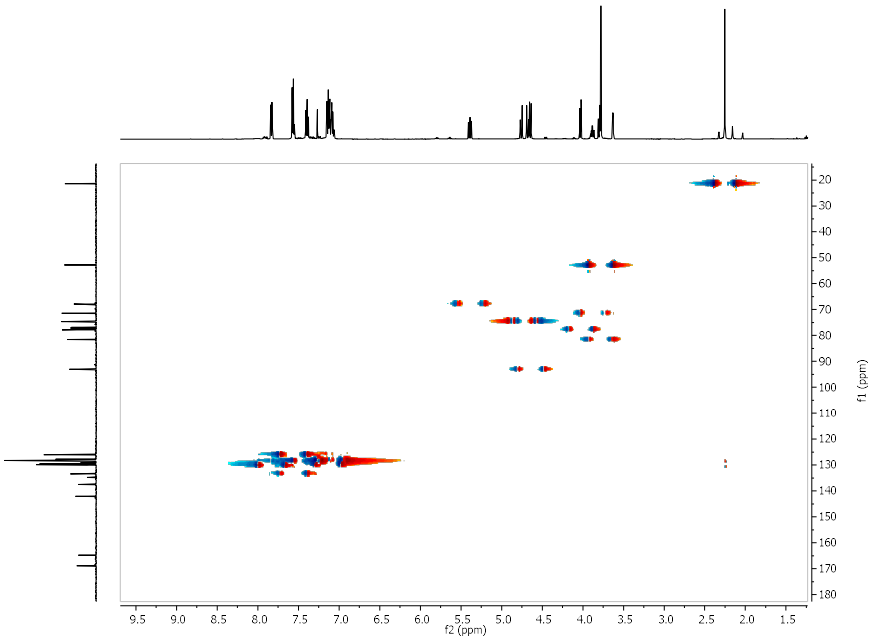
^{13}C-NMR ($CDCl_3$, 126 MHz) of **S14**

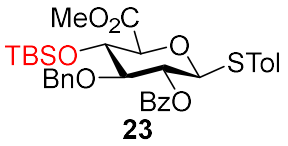


gCOSY ($CDCl_3$, 500 MHz) of **S14**



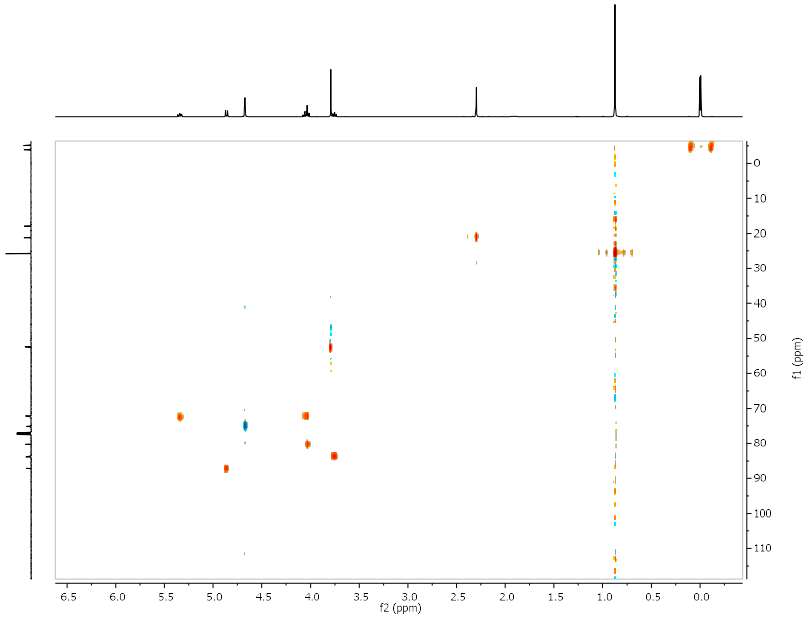
gHSQC ($CDCl_3$, 500 MHz) of **S14**

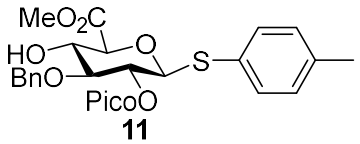




23

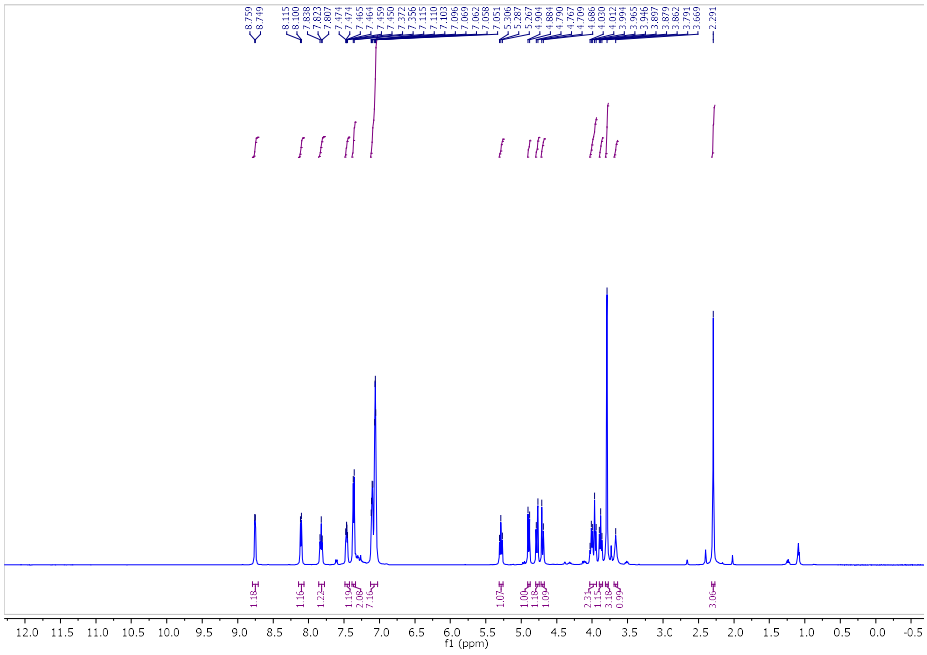
gHSQC ($CDCl_3$, 500 MHz) of **23**



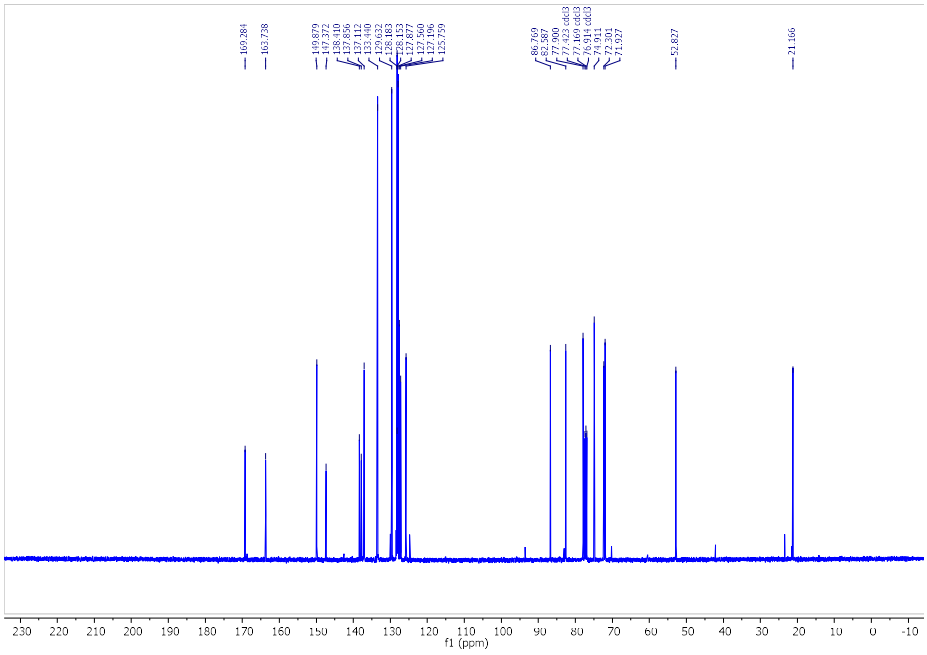


11

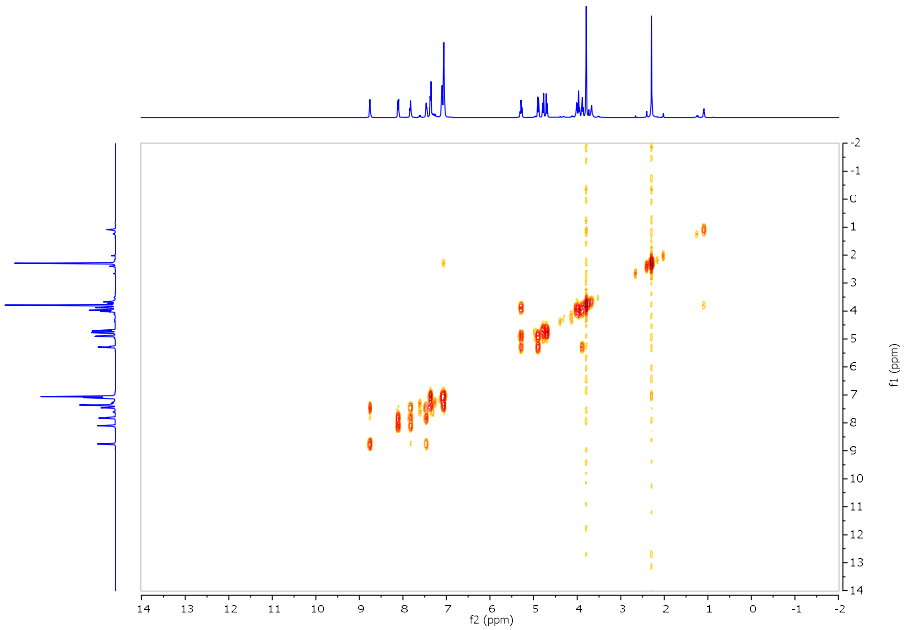
^{1}H-NMR ($CDCl_3$, 500 MHz) of **11**



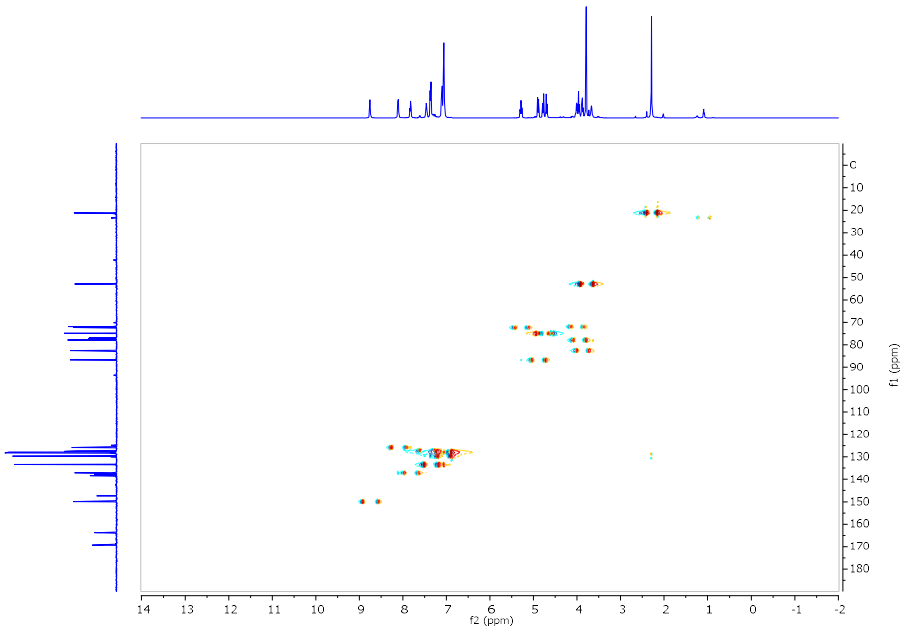
^{13}C-NMR ($CDCl_3$, 126 MHz) of **11**

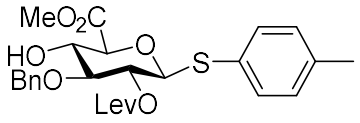


gCOSY ($CDCl_3$, 500 MHz) of **11**



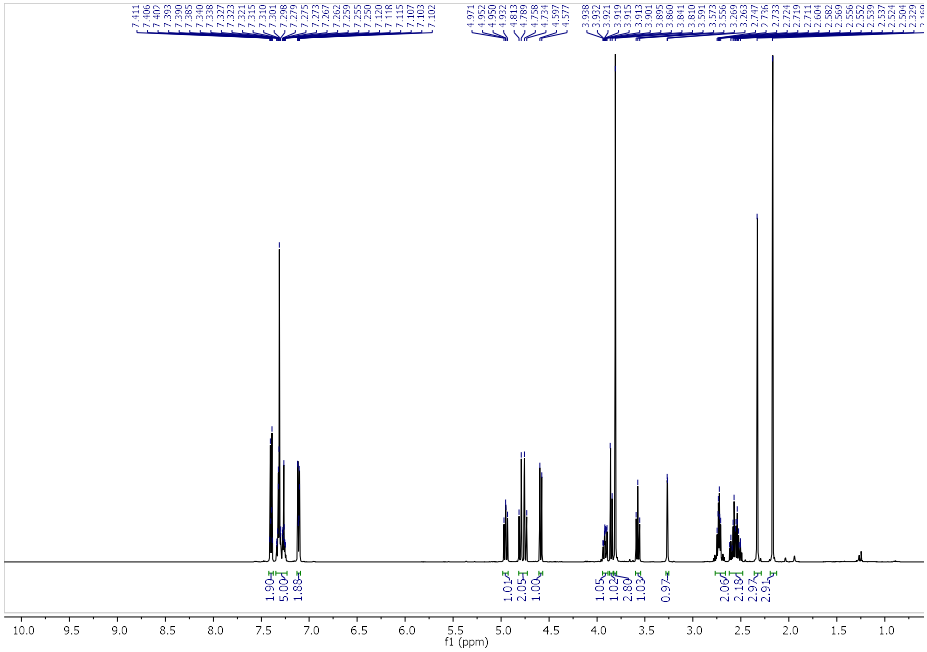
gHSQC ($CDCl_3$, 500 MHz) of **11**



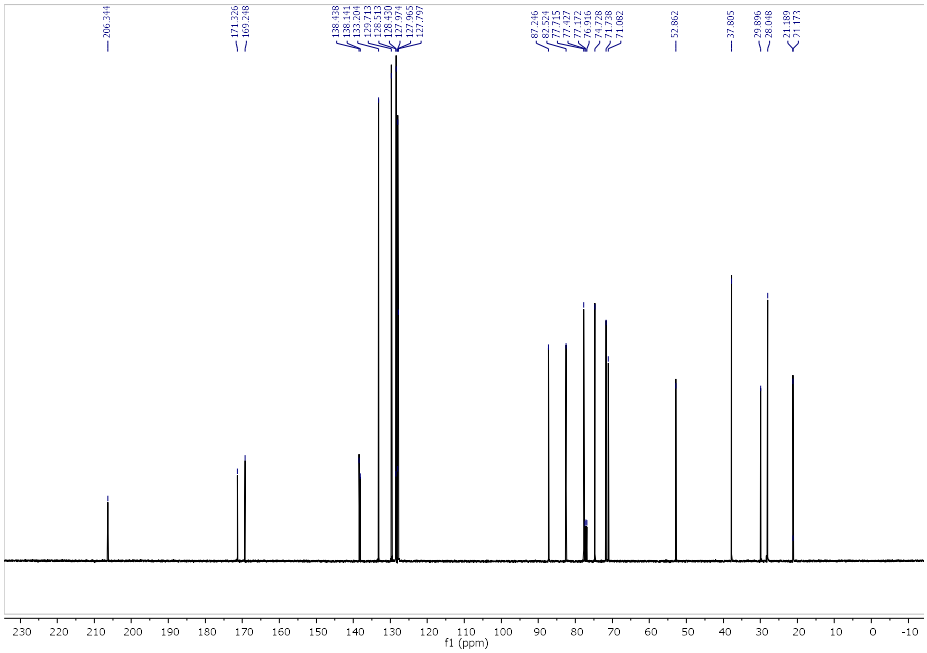


14

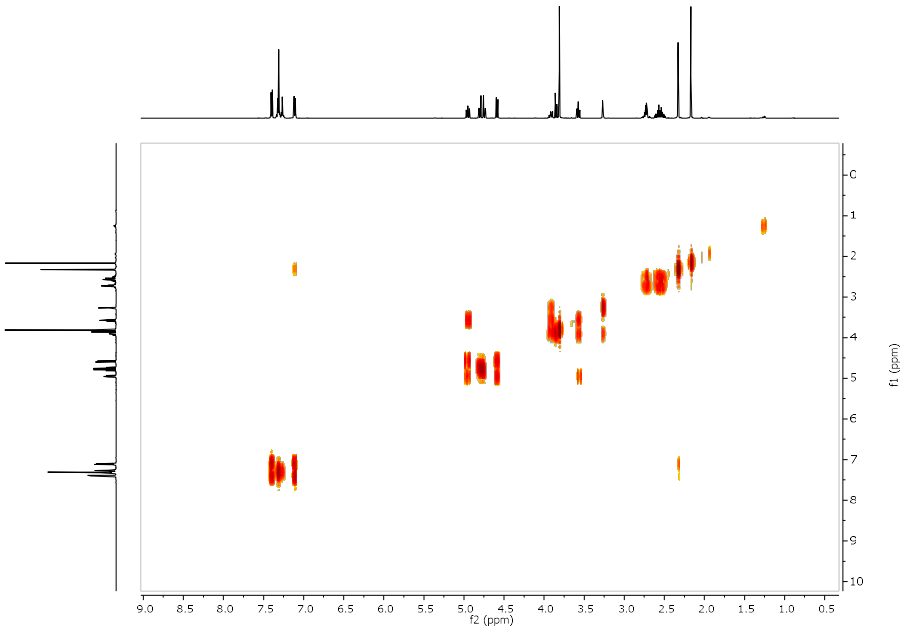
^{1}H-NMR ($CDCl_3$, 500 MHz) of **14**

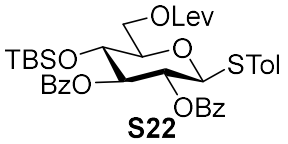


^{13}C-NMR ($CDCl_3$, 126 MHz) of **14**



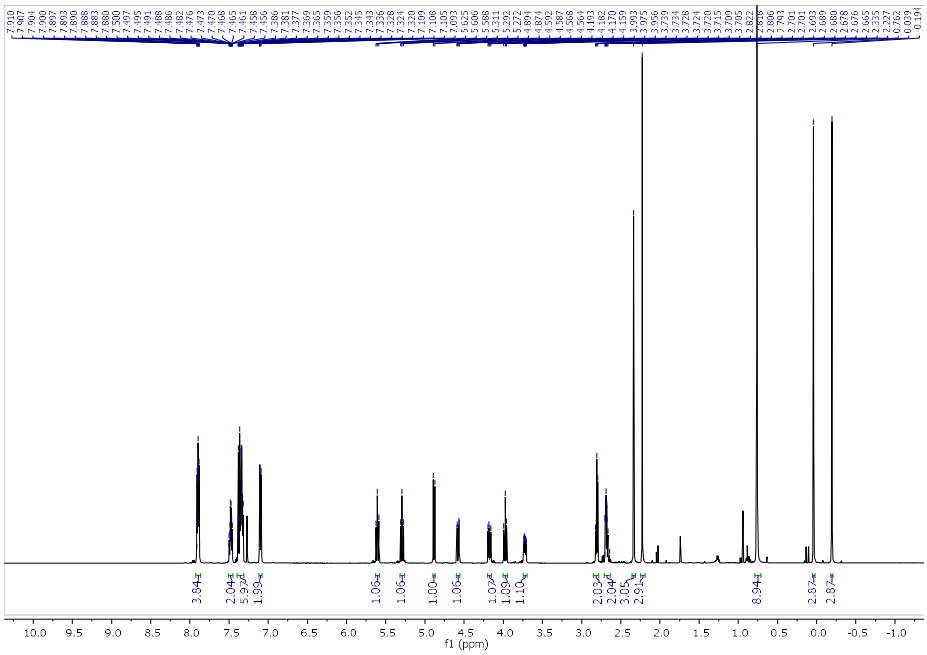
gCOSY ($CDCl_3$, 500 MHz) of **14**



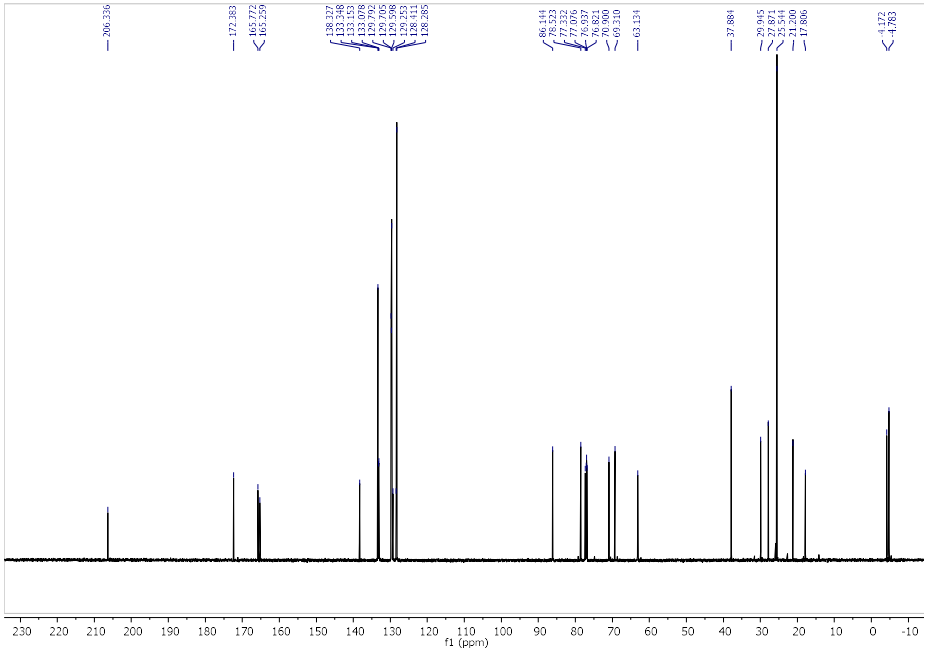


S22

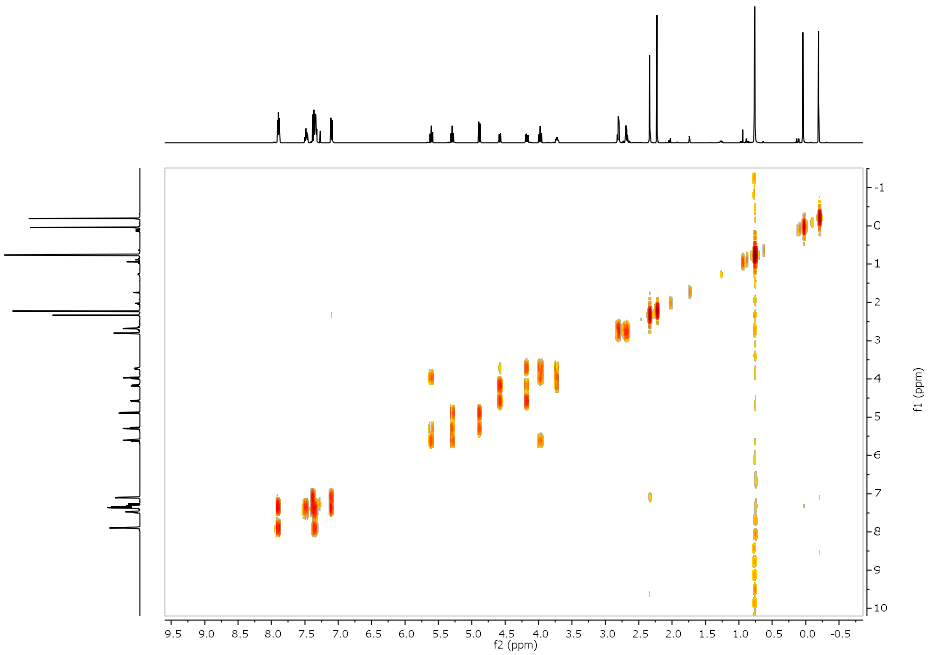
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S22**



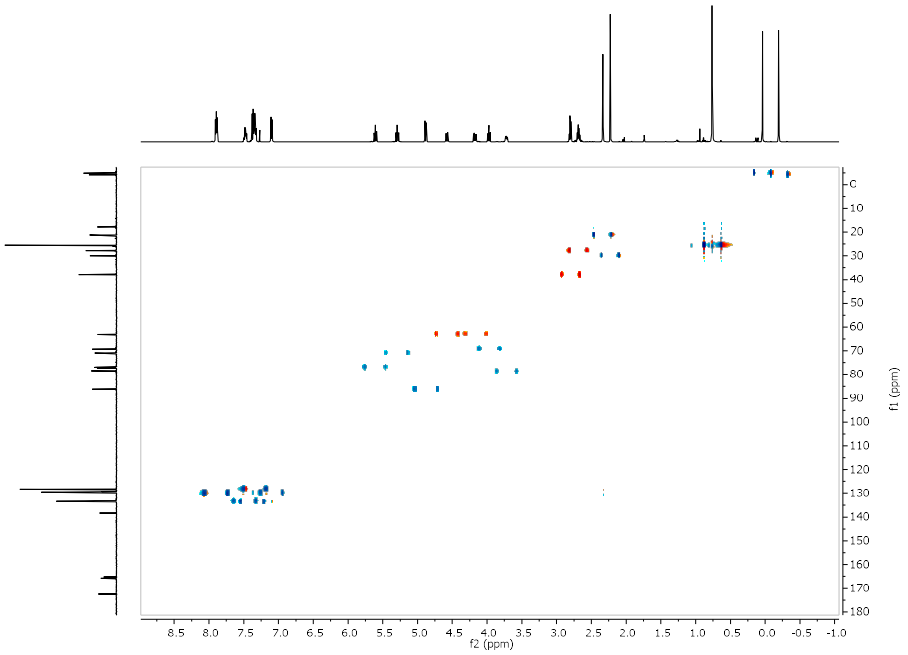
^{13}C-NMR ($CDCl_3$, 126 MHz) of **S22**

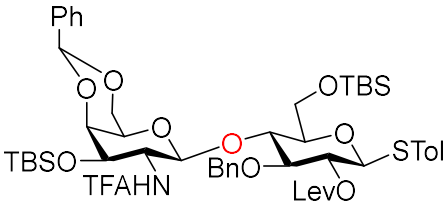


gCOSY ($CDCl_3$, 500 MHz) of **S22**



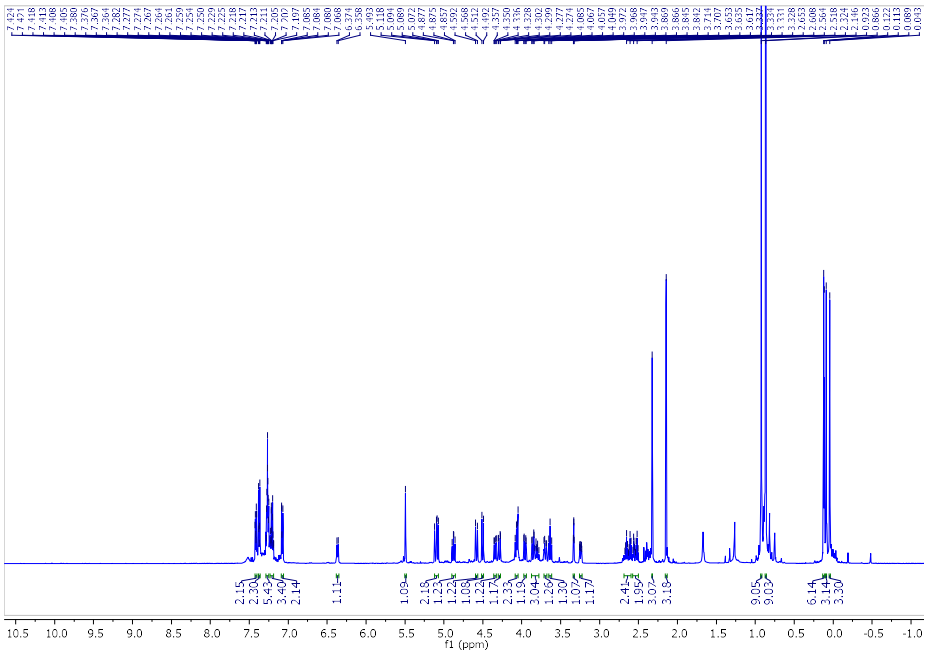
gHSQC ($CDCl_3$, 500 MHz) of **S22**



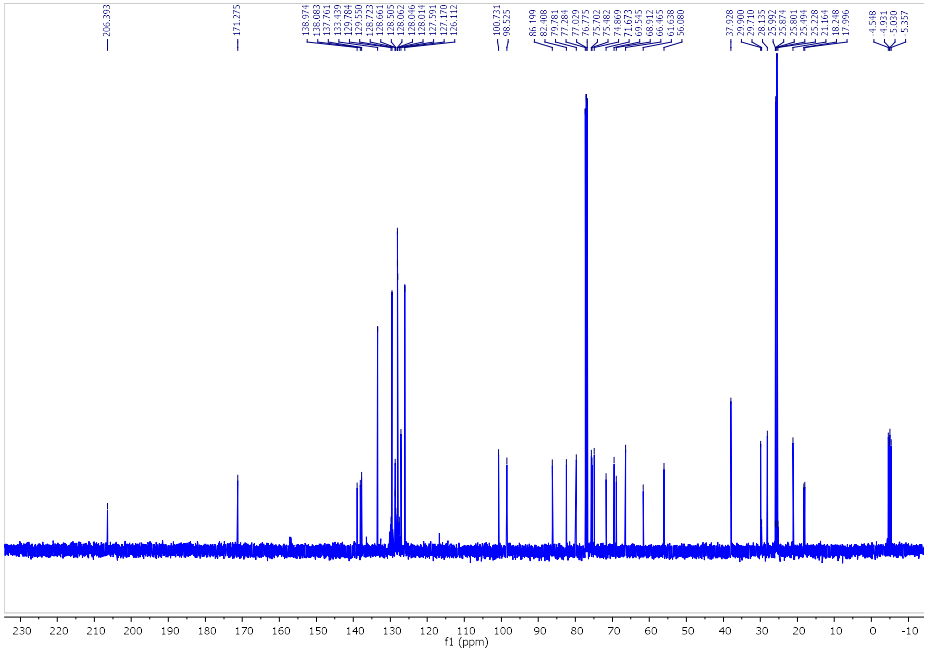


9

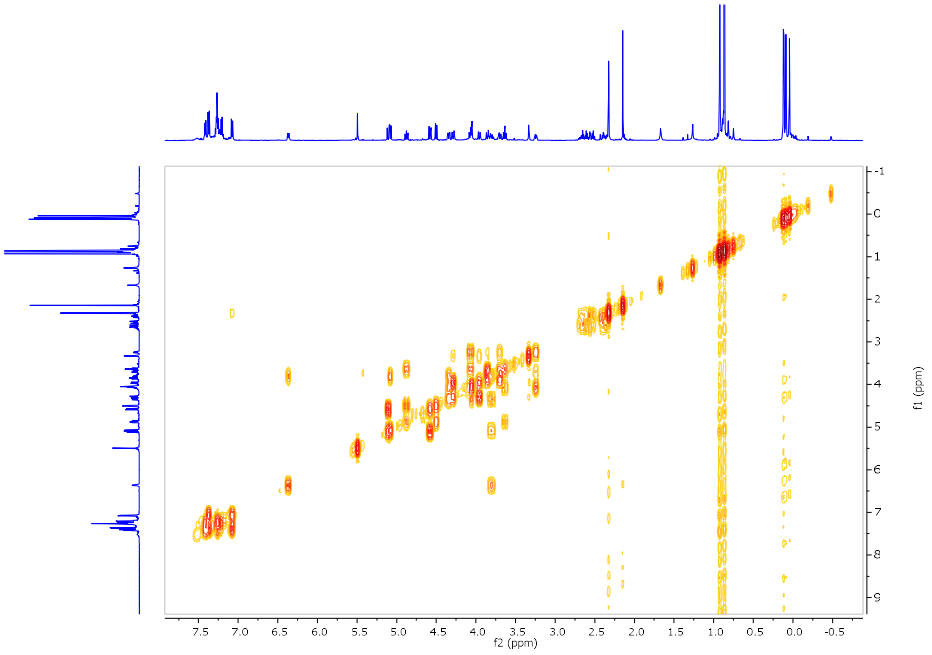
^{1}H-NMR ($CDCl_3$, 500 MHz) of **9**



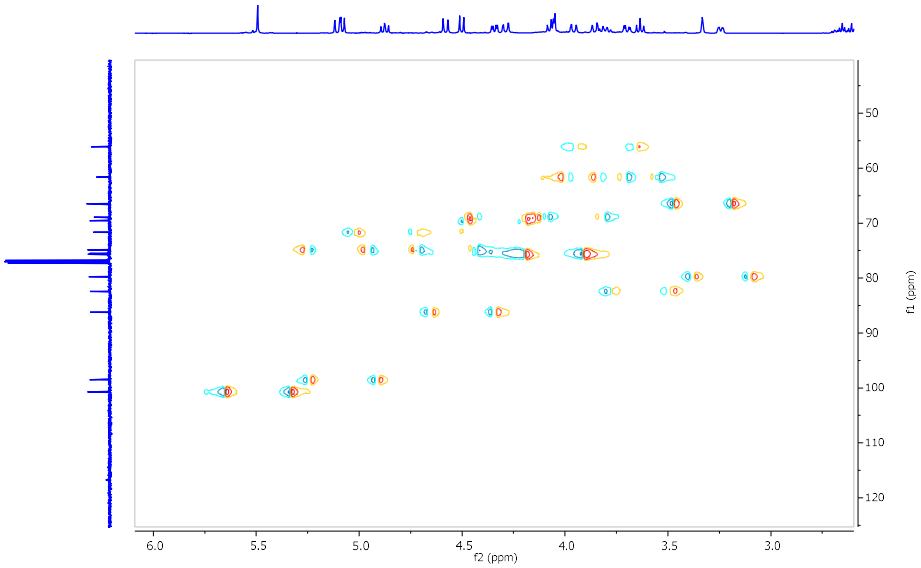
^{13}C-NMR ($CDCl_3$, 126 MHz) of **9**

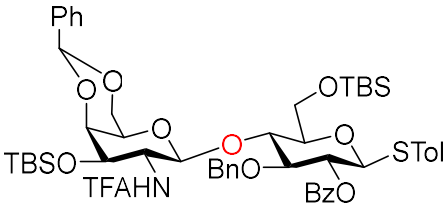


gCOSY ($CDCl_3$, 500 MHz) of **9**



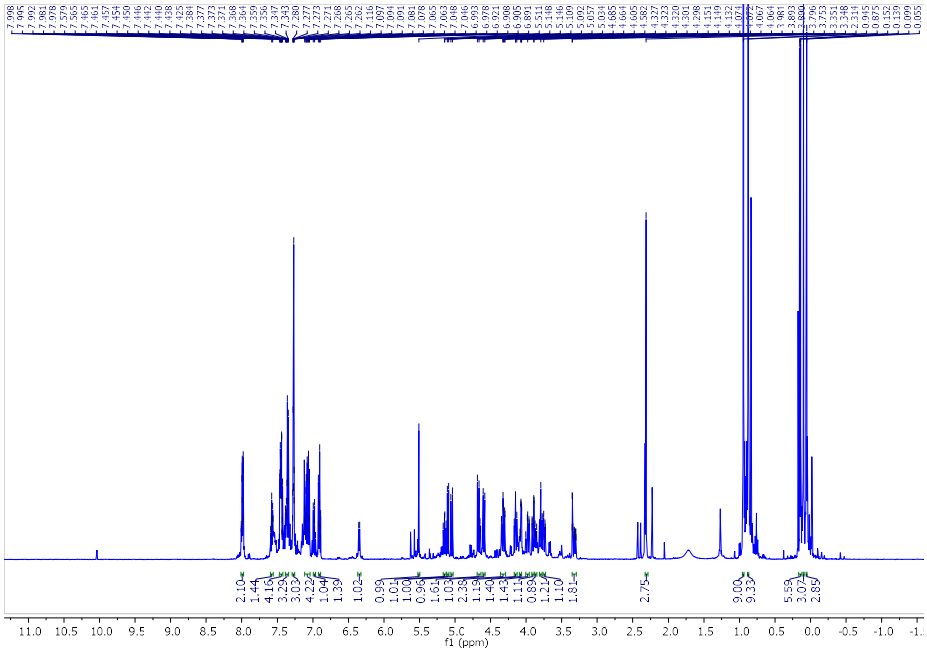
gHSQC ($CDCl_3$, 500 MHz) of **9**



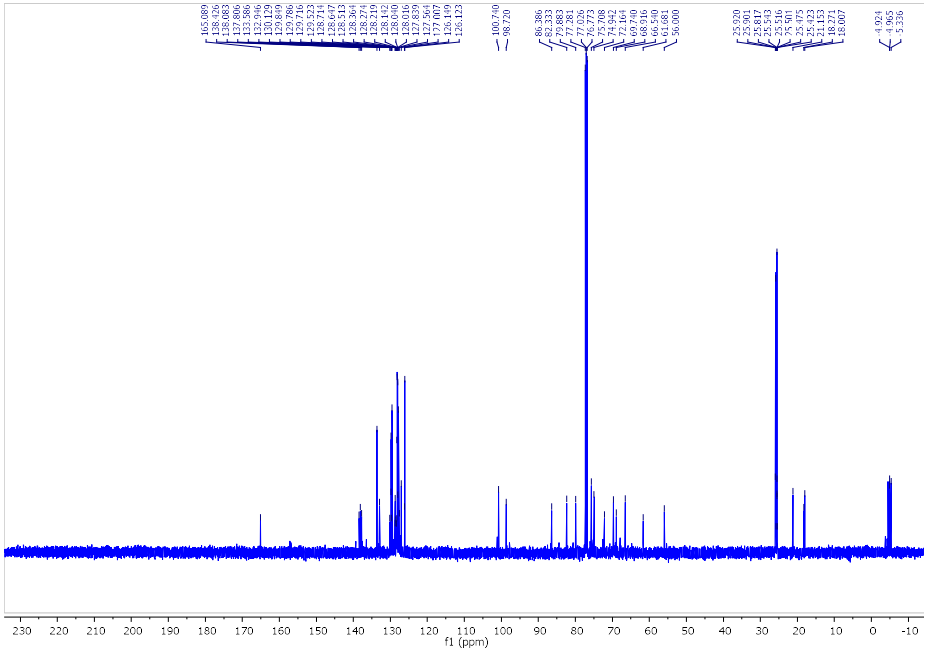


10

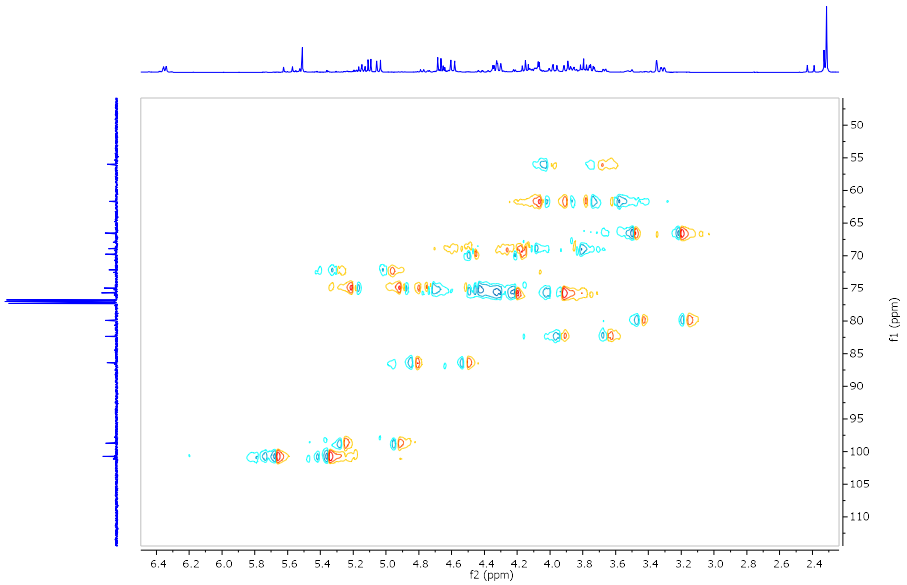
^{1}H-NMR ($CDCl_3$, 500 MHz) of **10**

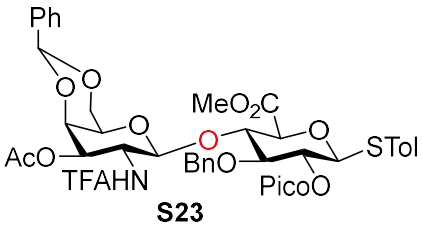


^{13}C-NMR ($CDCl_3$, 126 MHz) of **10**



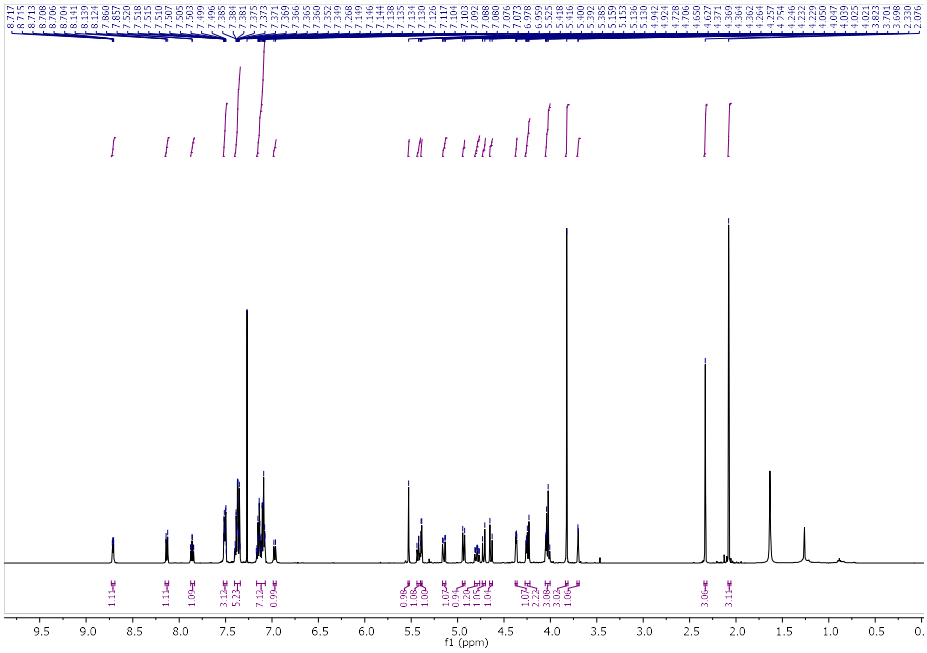
gHSQC ($CDCl_3$, 500 MHz) of **10**



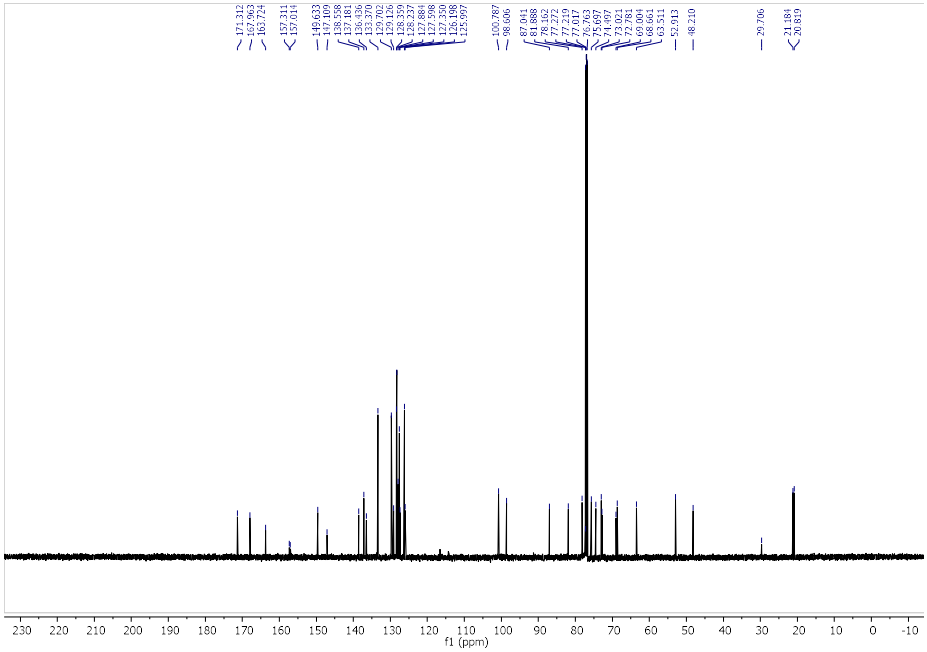


S23

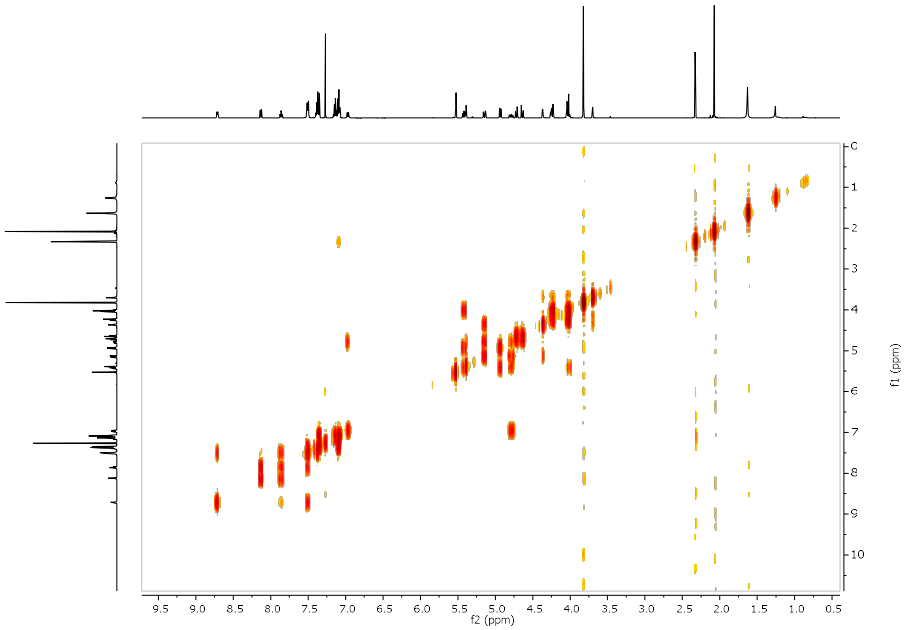
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S23**



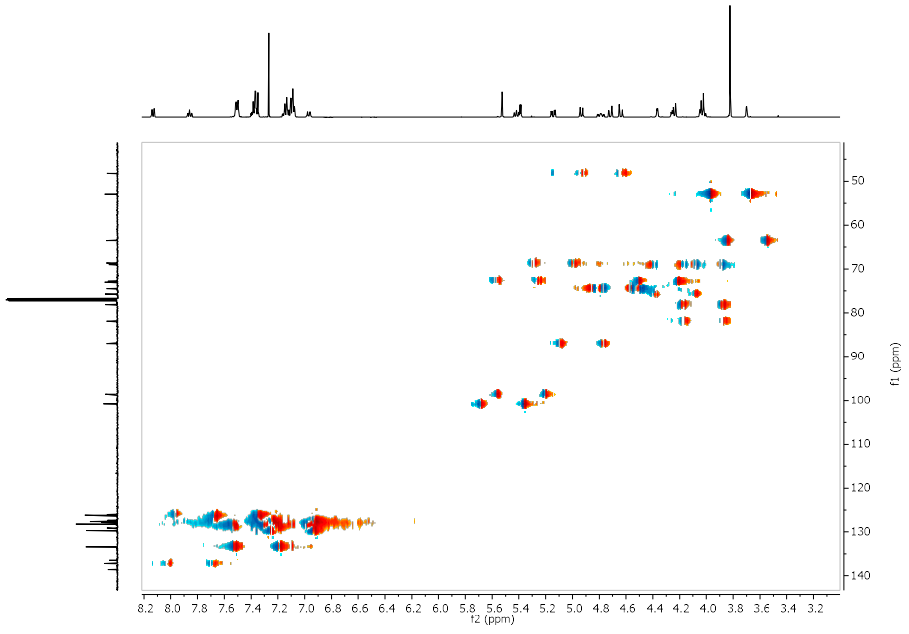
^{13}C-NMR ($CDCl_3$, 126 MHz) of **S23**

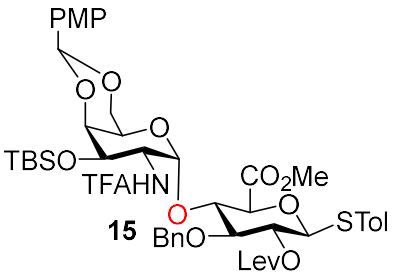


gCOSY ($CDCl_3$, 500 MHz) of **S23**

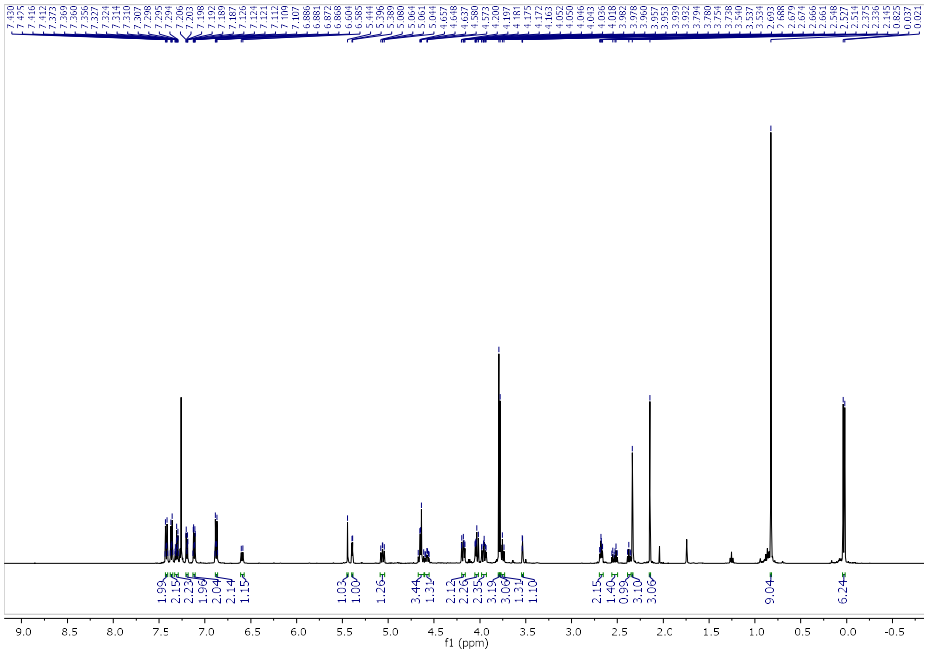


gHSQC ($CDCl_3$, 500 MHz) of **S23**

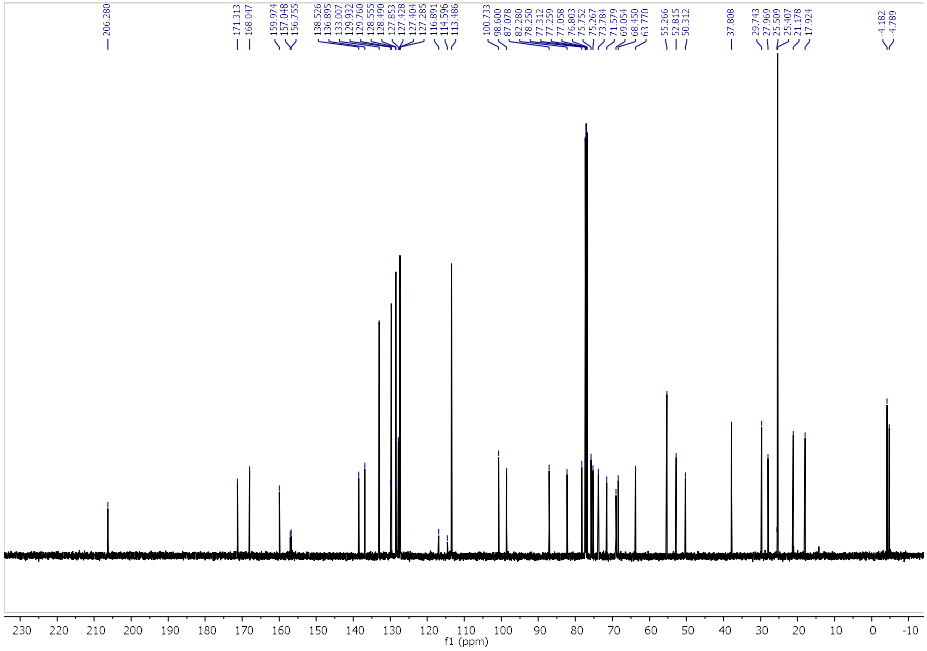




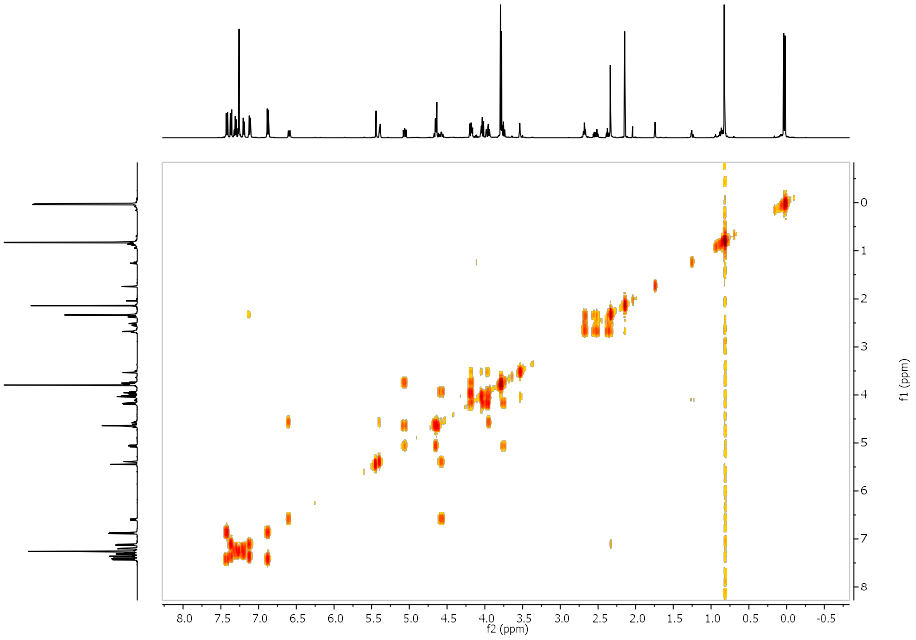
^{1}H-NMR ($CDCl_3$, 500 MHz) of **15**



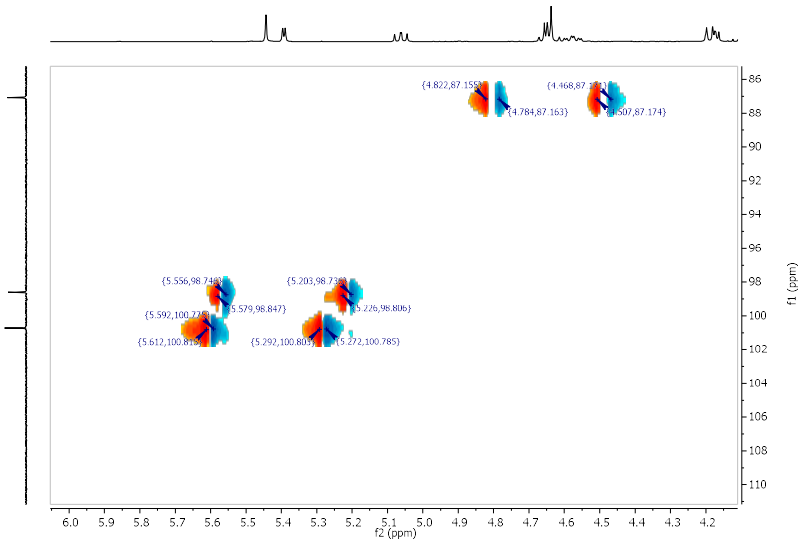
^{13}C-NMR ($CDCl_3$, 126 MHz) of **15**

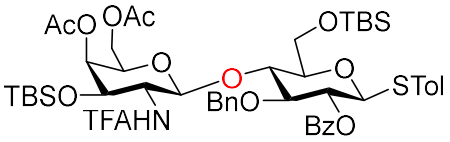


gCOSY ($CDCl_3$, 500 MHz) of **15**



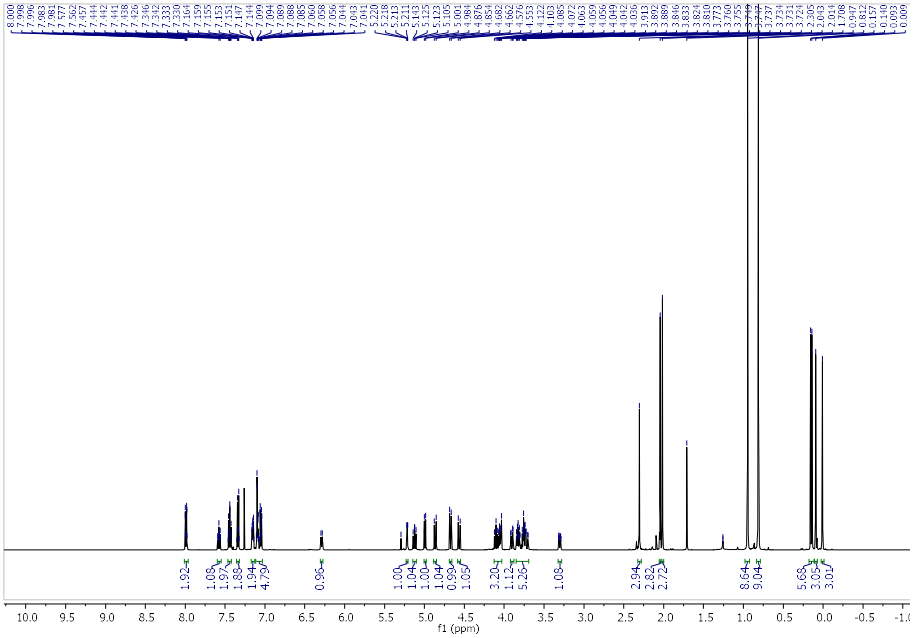
gHSQC ($CDCl_3$, 500 MHz) of **15**



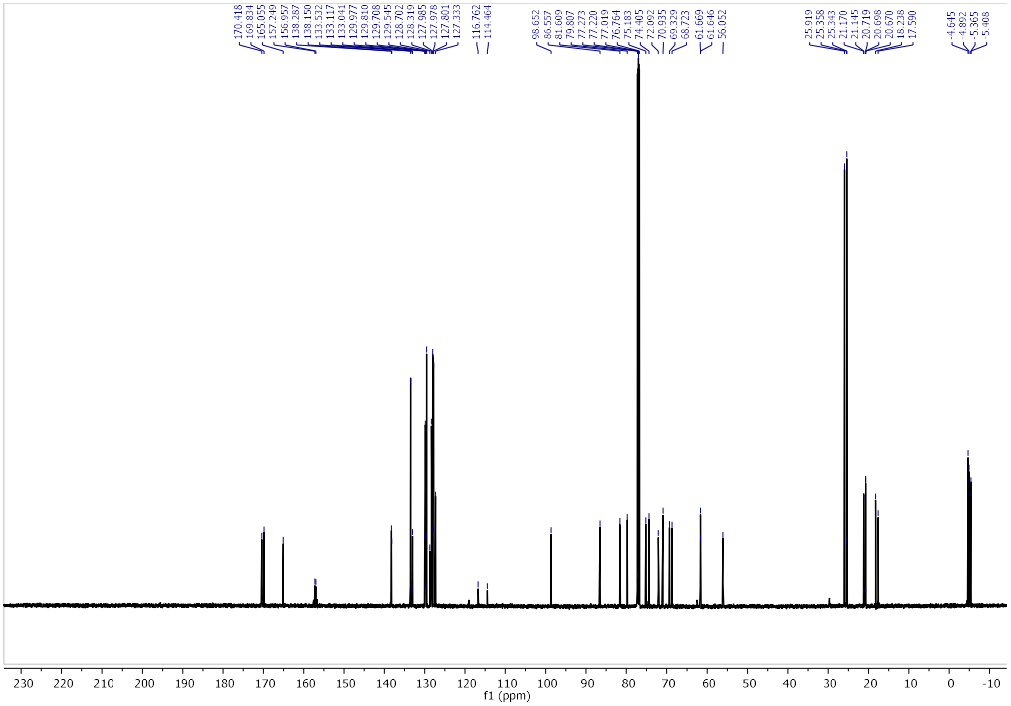


17

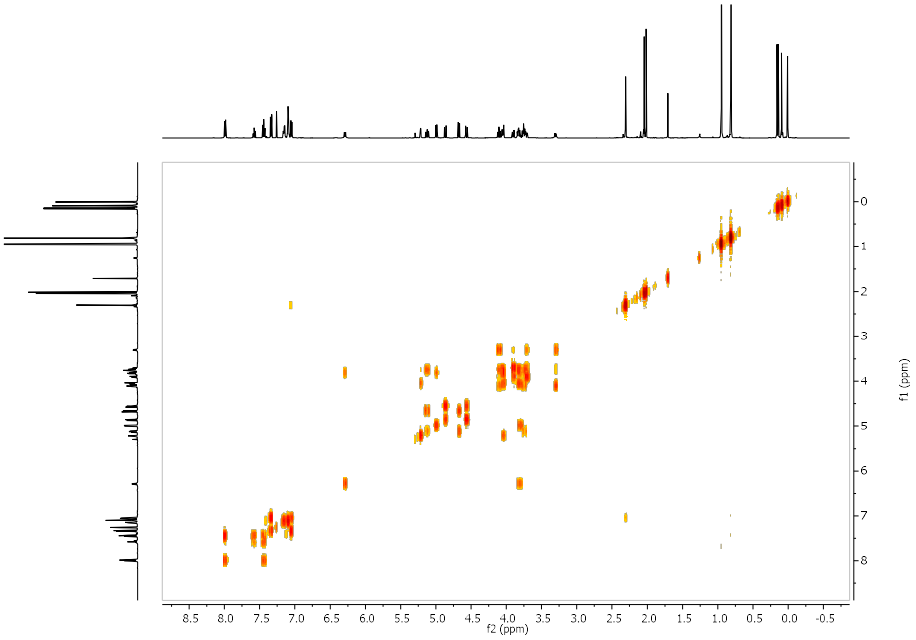
^{1}H-NMR ($CDCl_3$, 500 MHz) of **17**



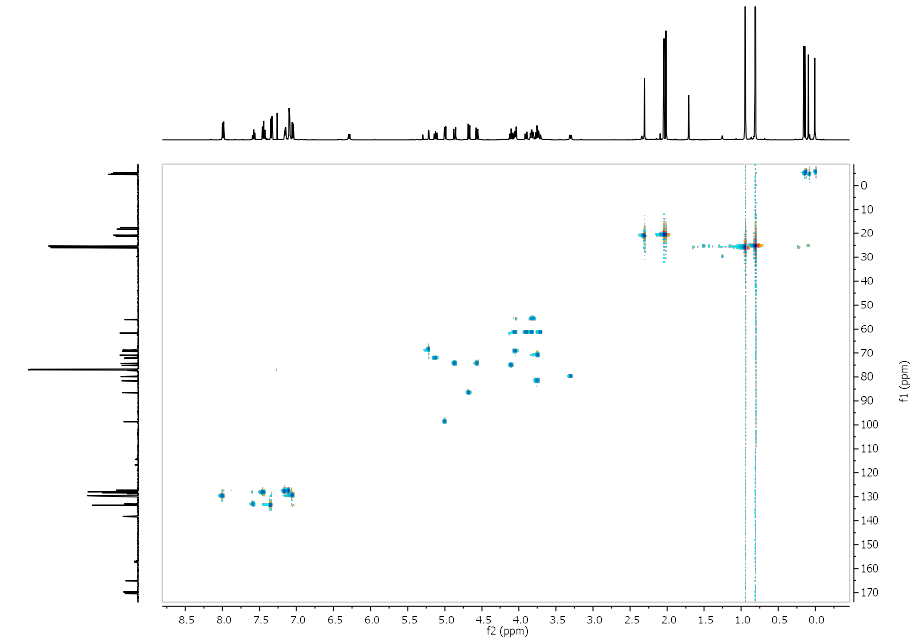
^{13}C-NMR ($CDCl_3$, 126 MHz) of **17**

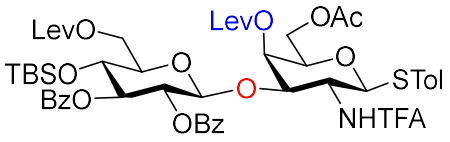


gCOSY ($CDCl_3$, 500 MHz) of **17**



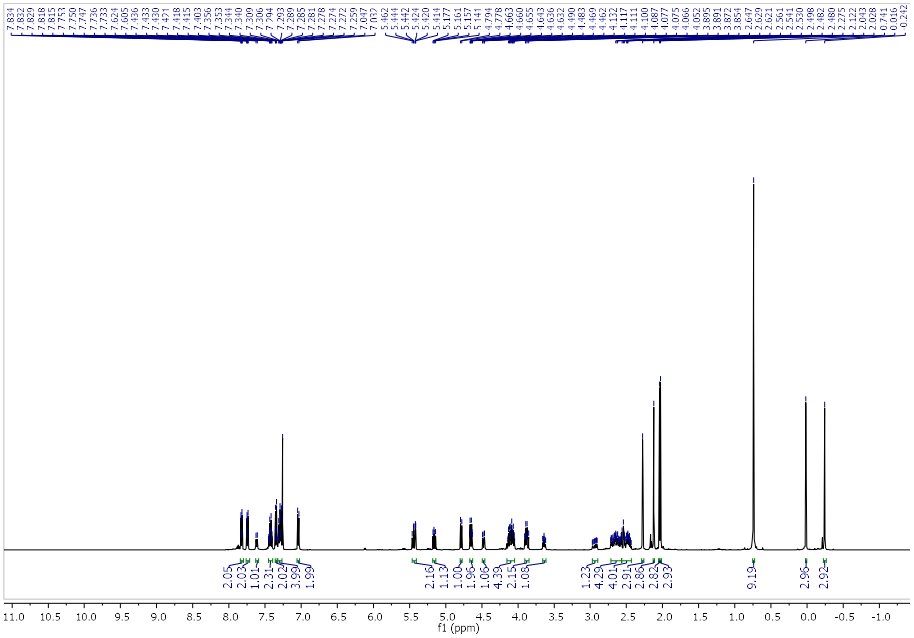
gHSQC ($CDCl_3$, 500 MHz) of **17**



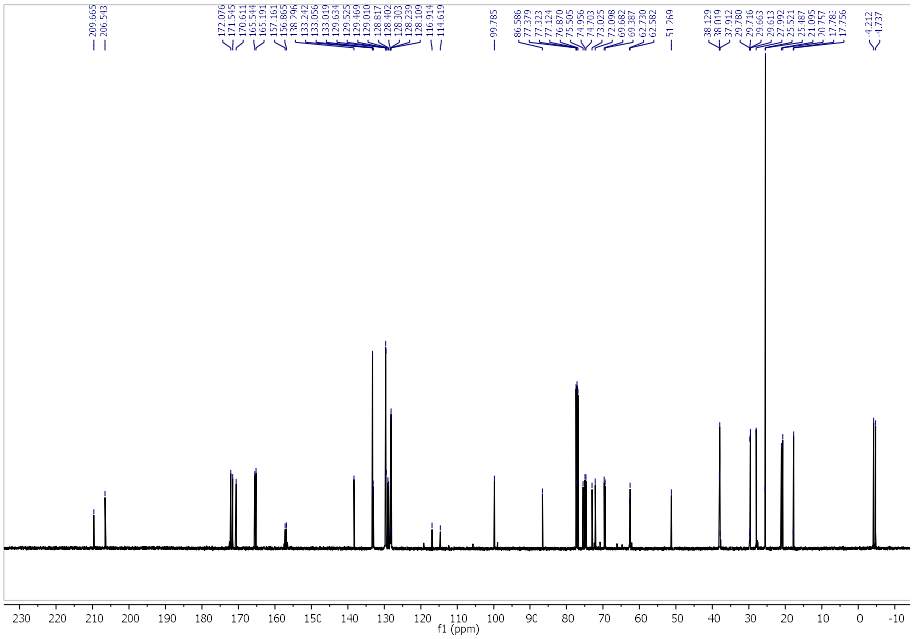


S24

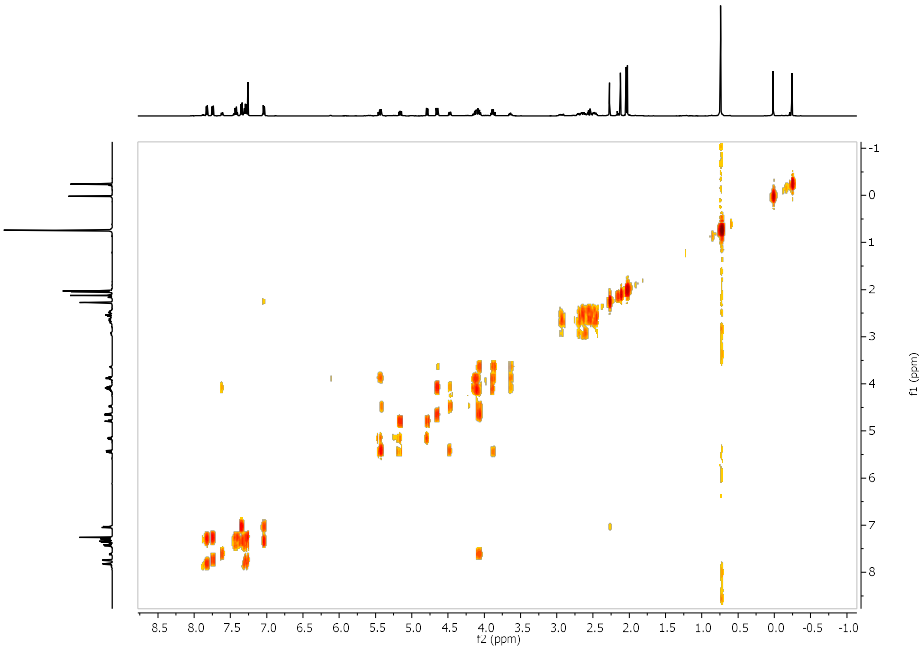
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S24**



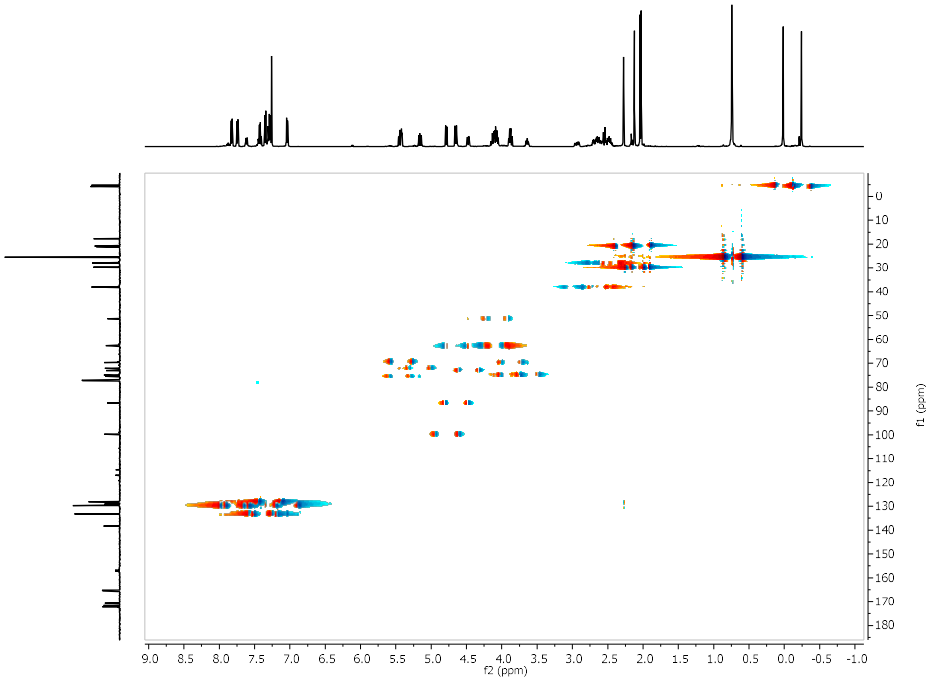
^{13}C-NMR ($CDCl_3$, 126 MHz) of **S24**

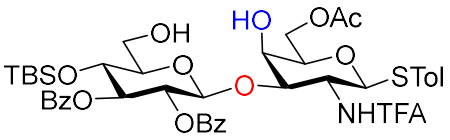


gCOSY ($CDCl_3$, 500 MHz) of **S24**



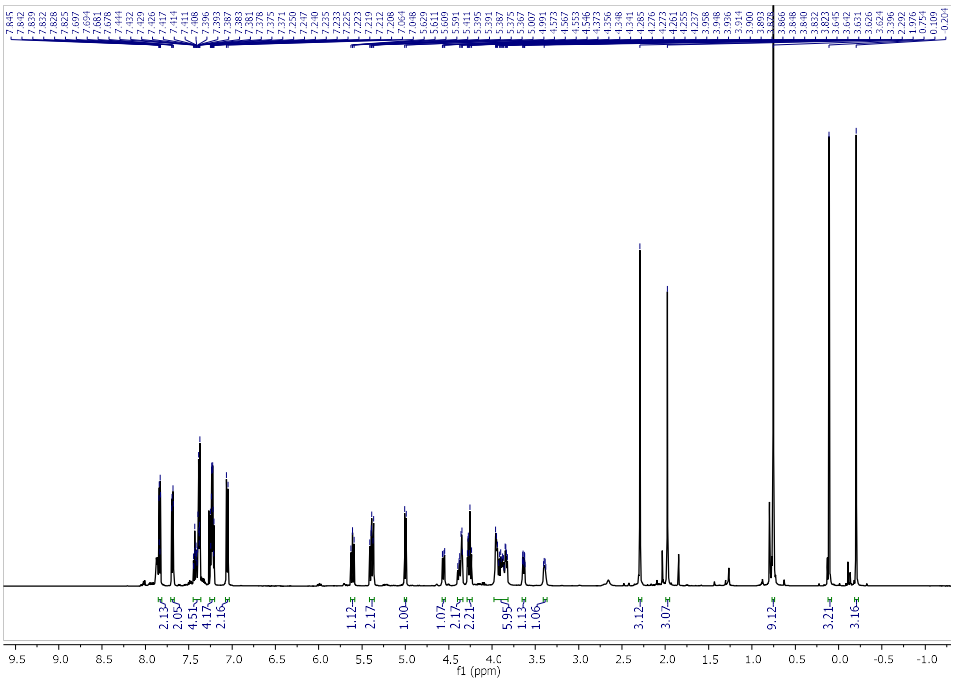
gHSQC ($CDCl_3$, 500 MHz) of **S24**



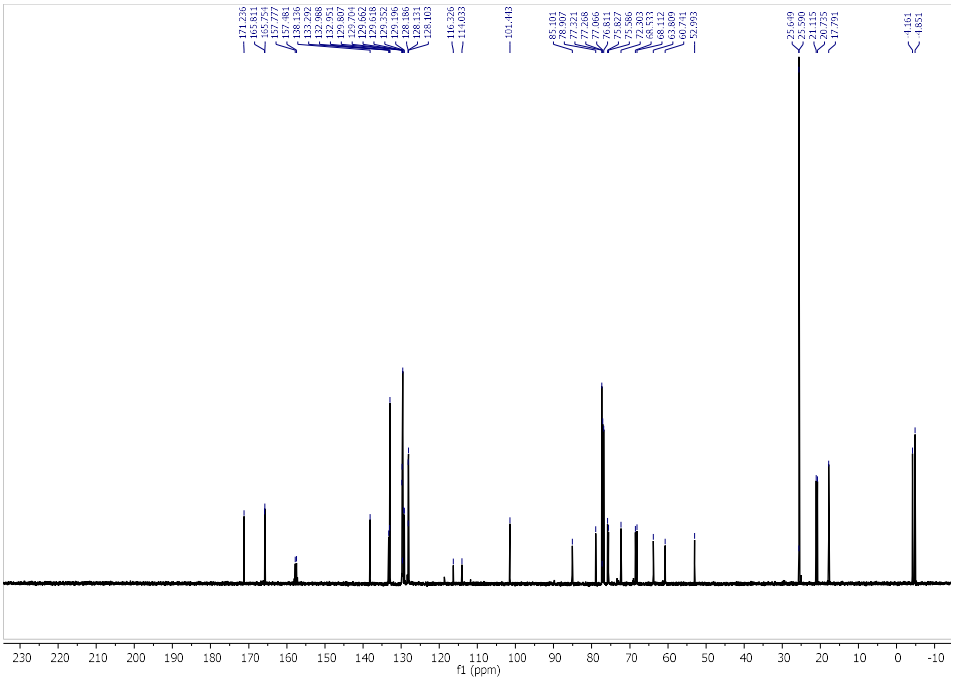


S25

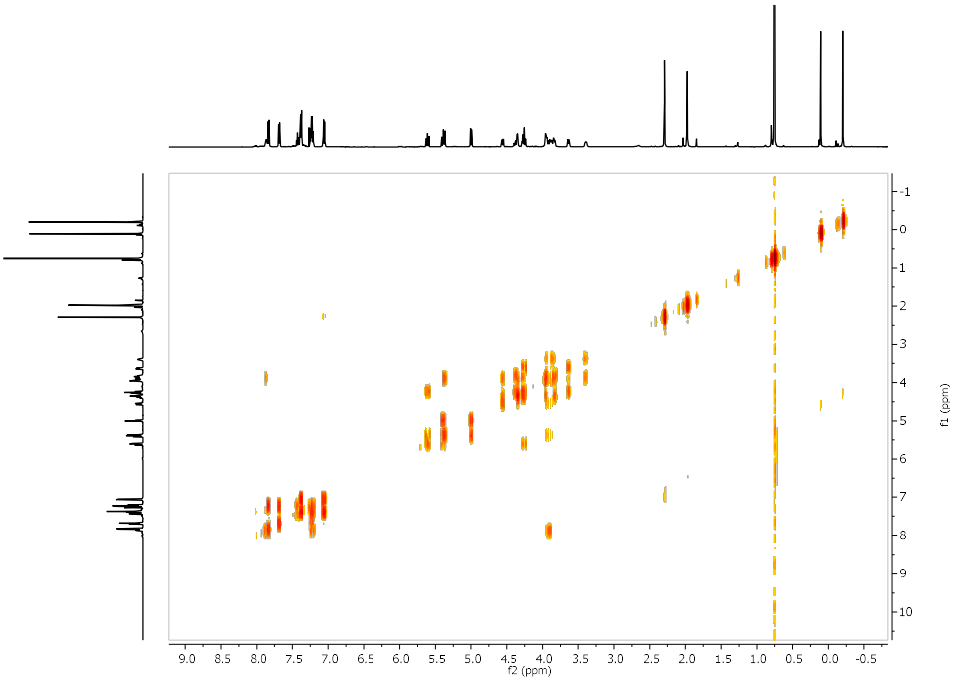
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S25**



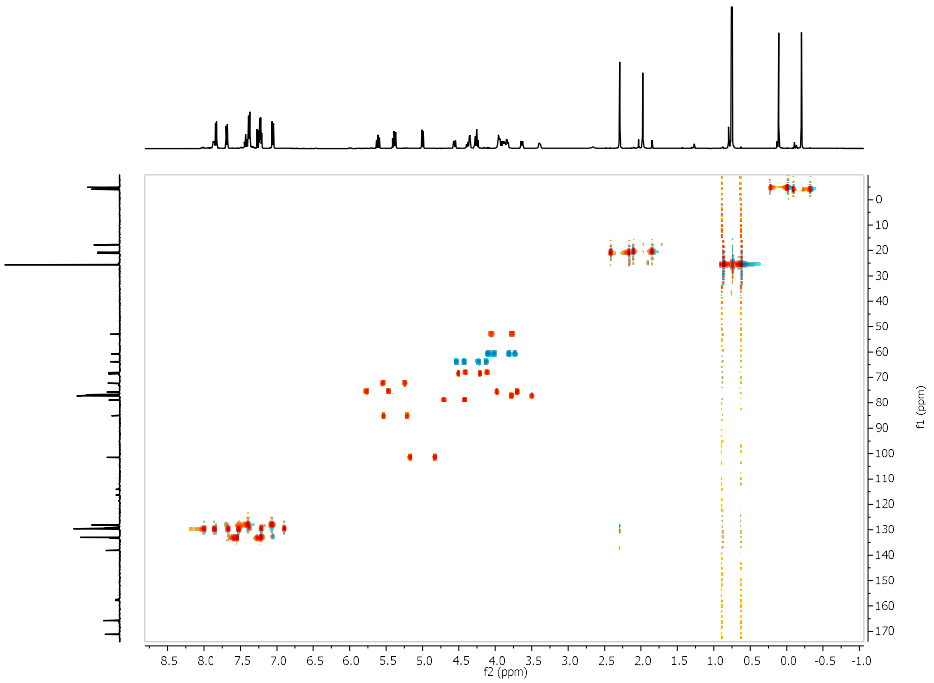
^{13}C-NMR ($CDCl_3$, 126 MHz) of **S25**

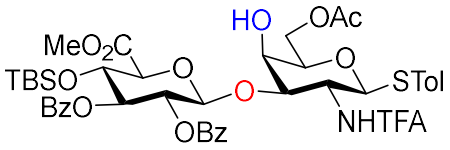


gCOSY ($CDCl_3$, 500 MHz) of **S25**



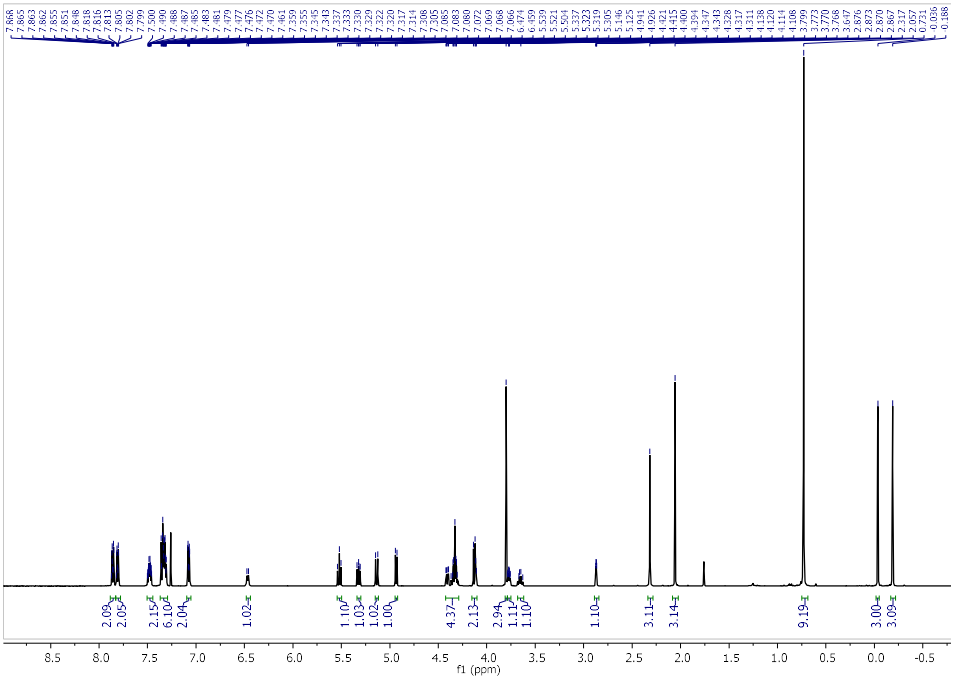
gHSQC ($CDCl_3$, 500 MHz) of **S25**



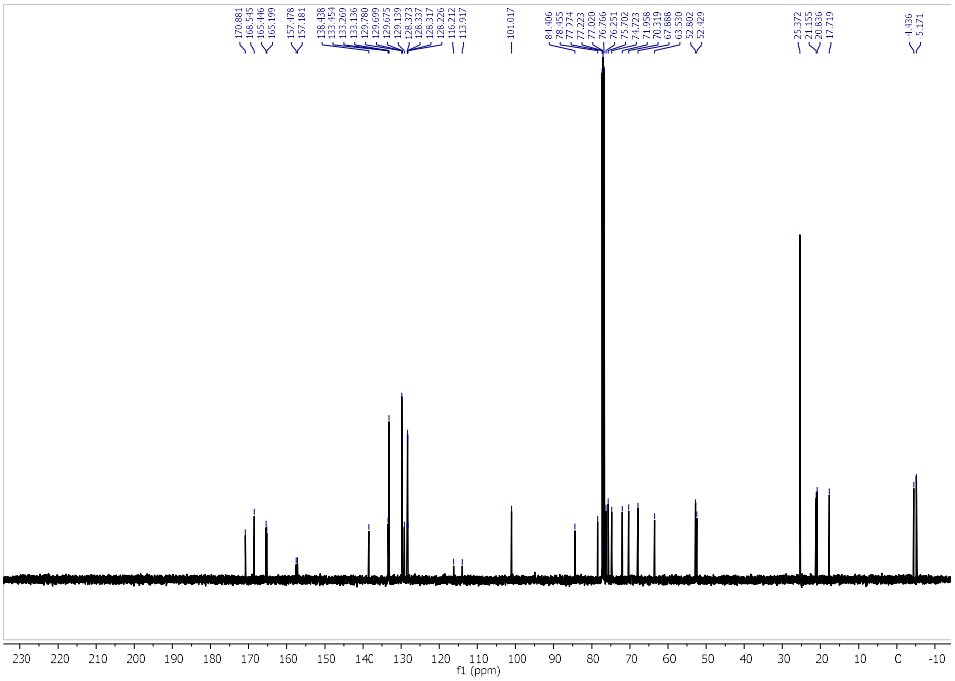


S26

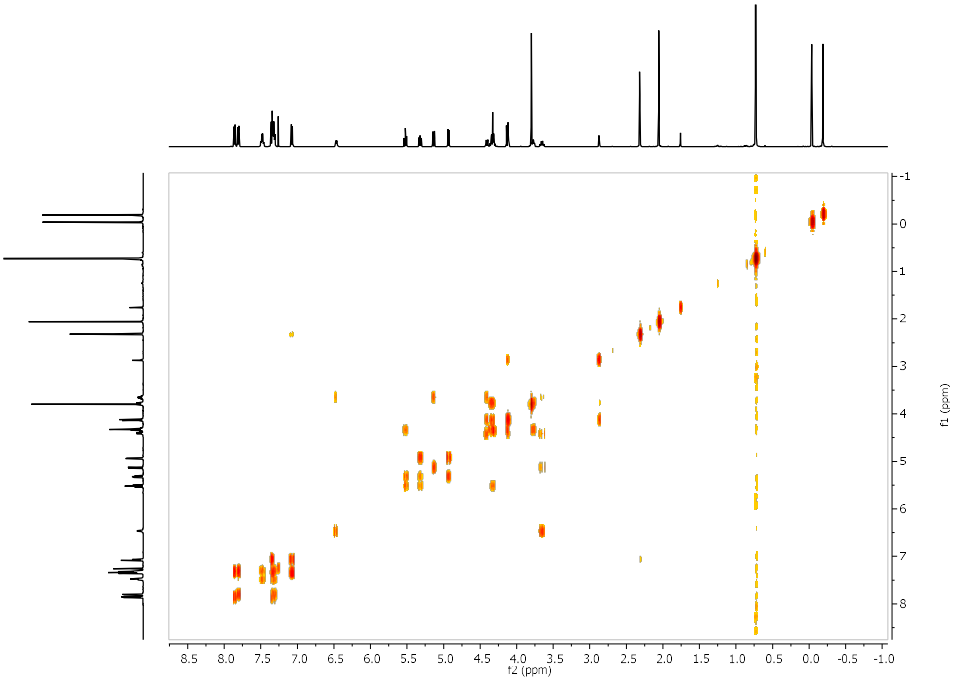
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S26**



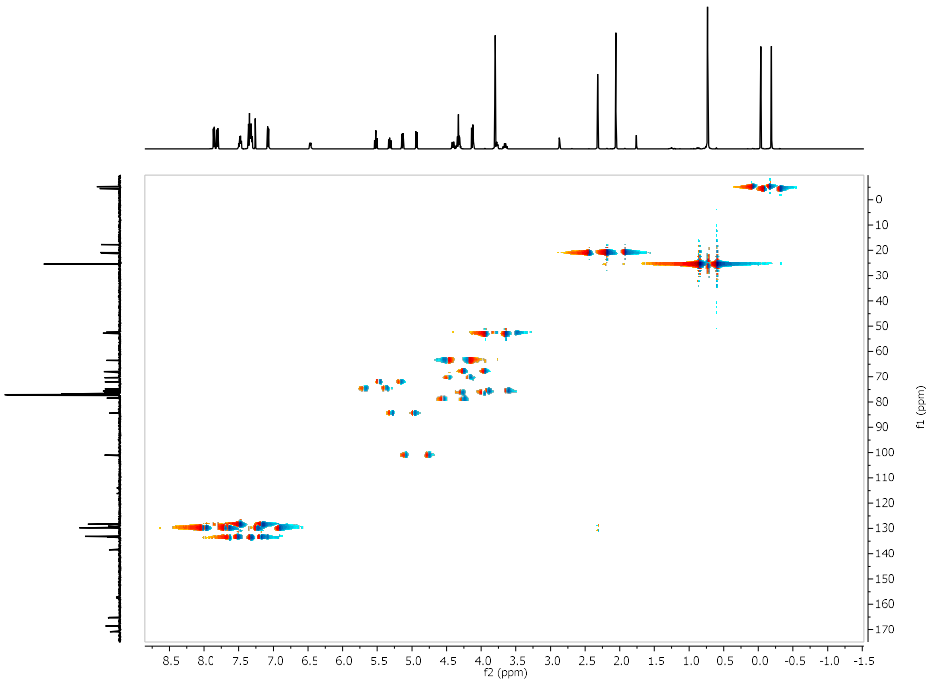
^{13}C-NMR ($CDCl_3$, 126 MHz) of **S26**

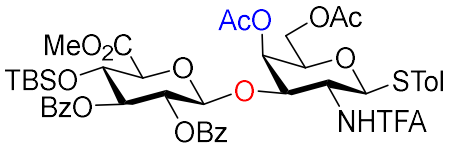


gCOSY ($CDCl_3$, 500 MHz) of **S26**



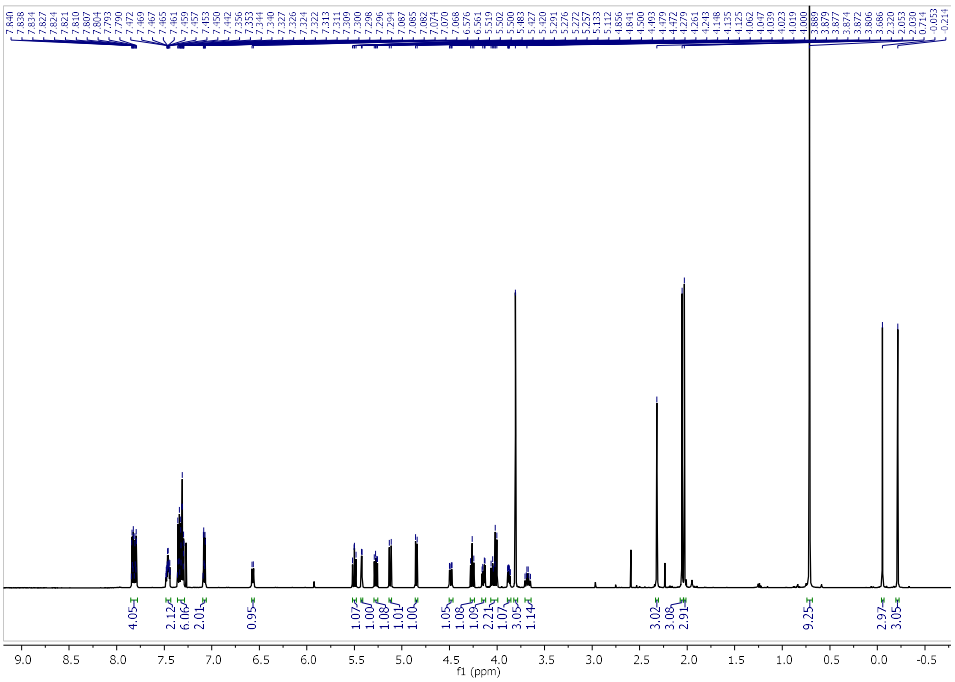
gHSQC ($CDCl_3$, 500 MHz) of **S26**



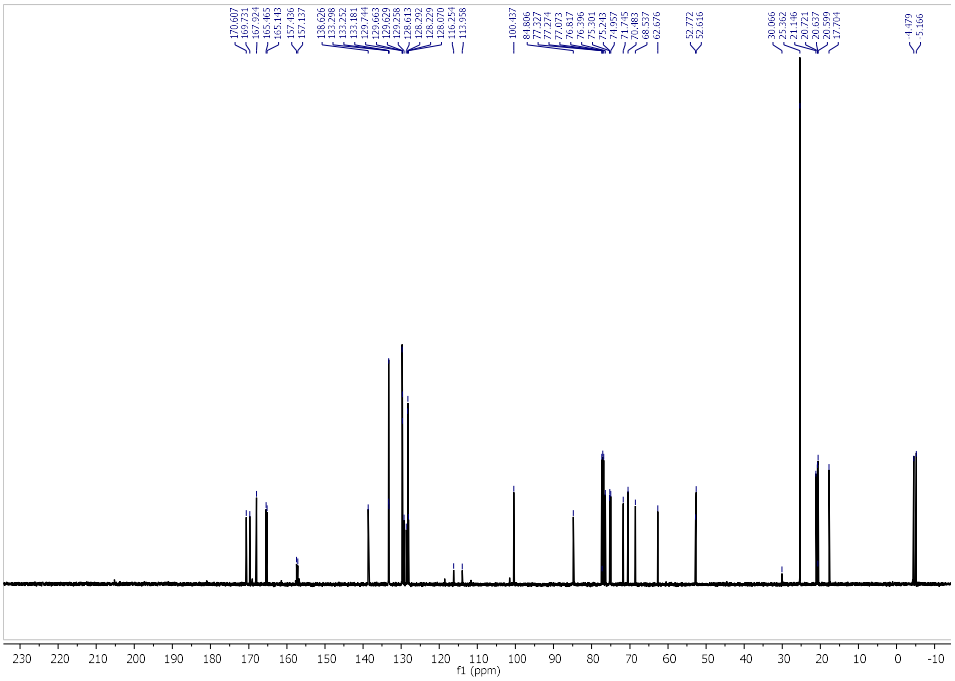


S27

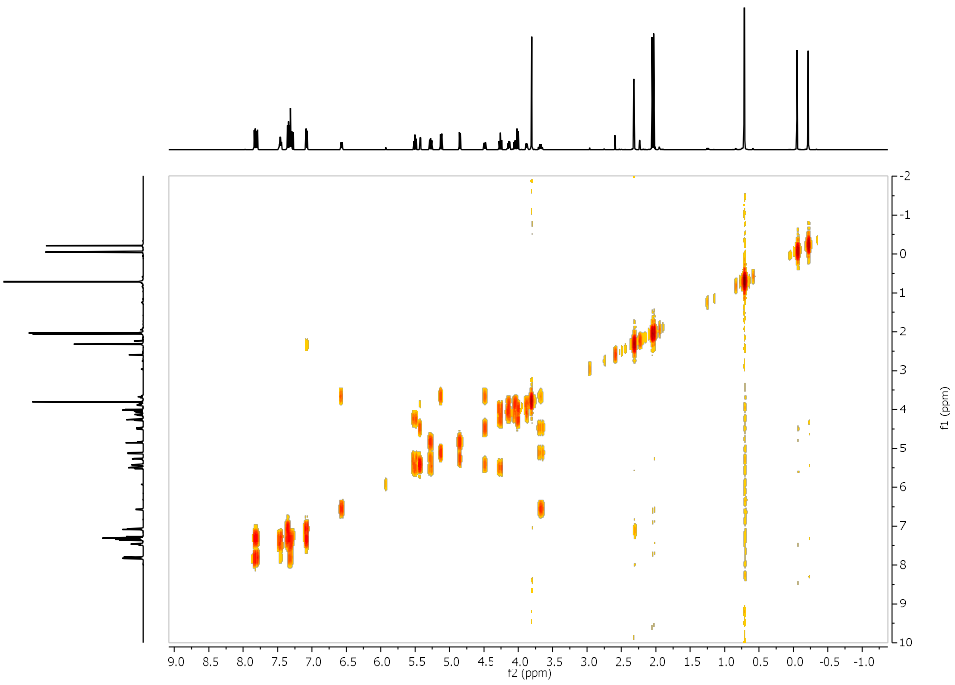
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S27**



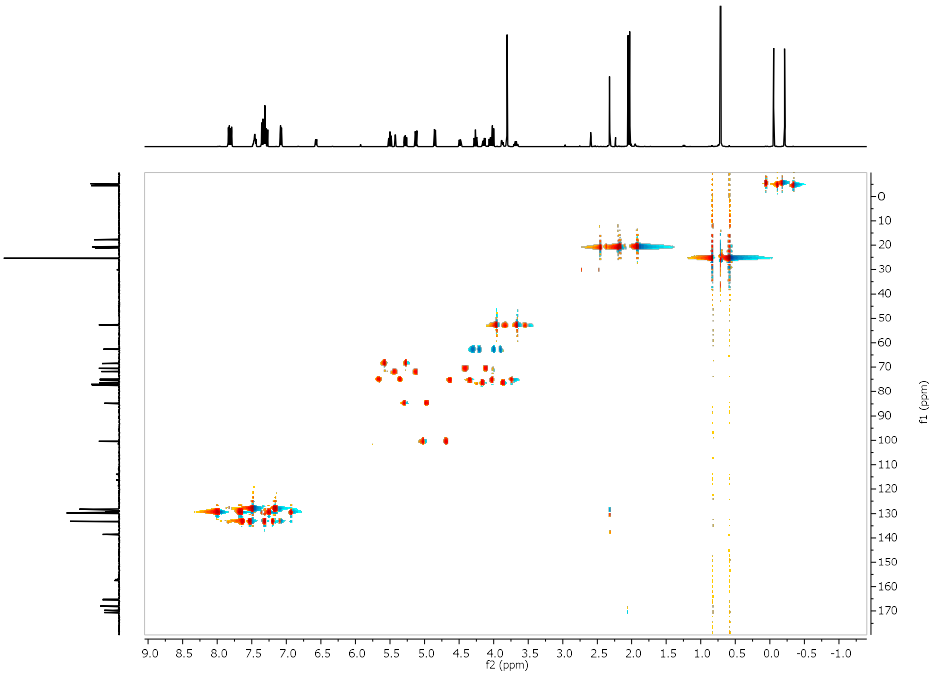
^{13}C-NMR ($CDCl_3$, 126 MHz) of **S27**

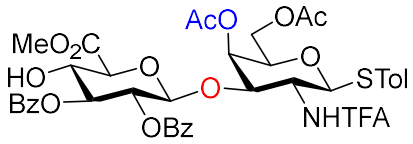


gCOSY ($CDCl_3$, 500 MHz) of **S27**



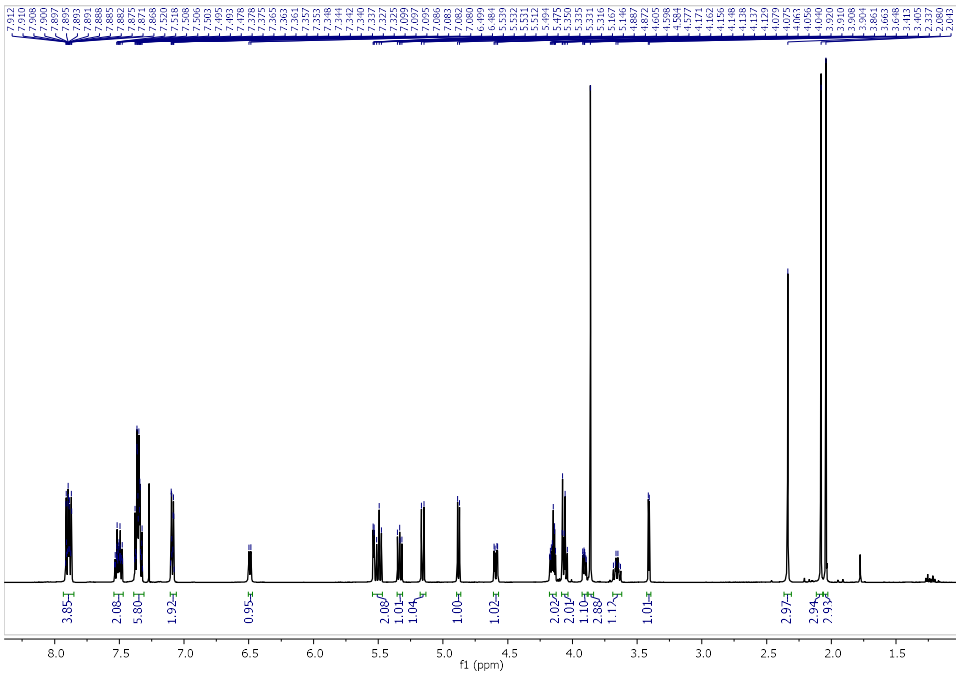
gHSQC ($CDCl_3$, 500 MHz) of **S27**



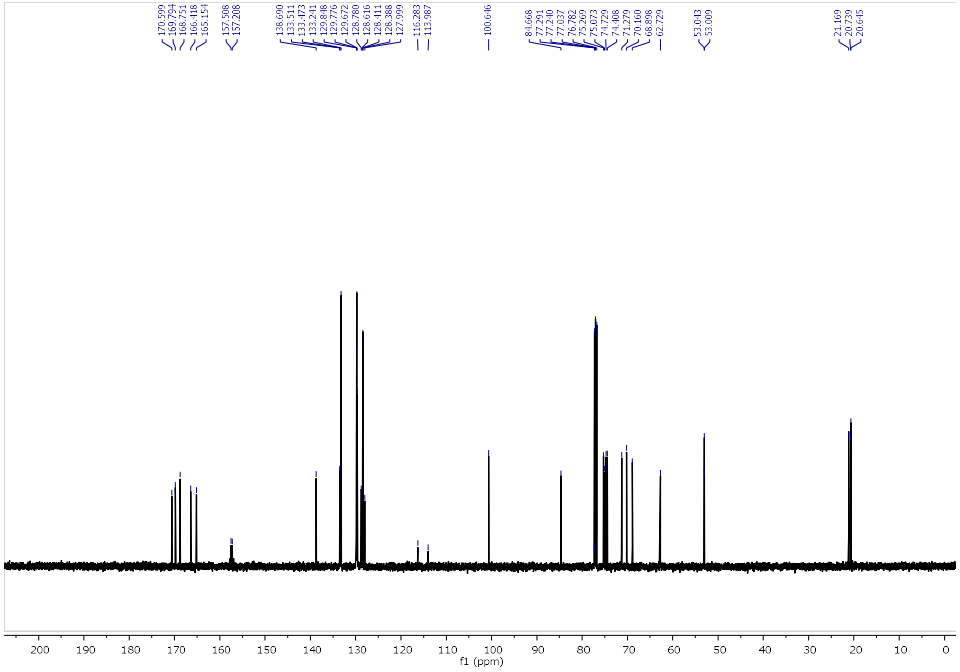


18

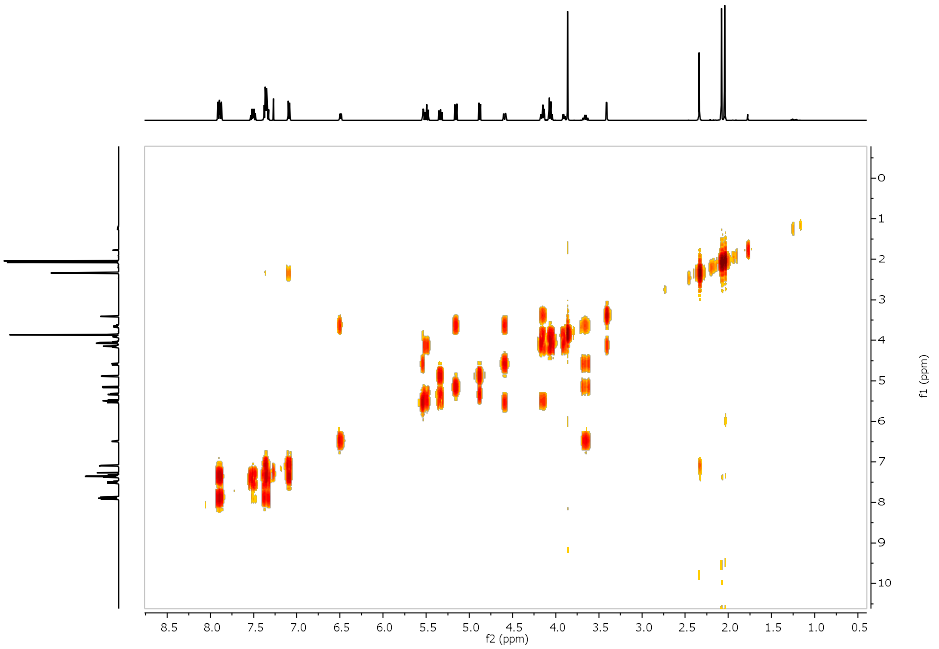
^{1}H-NMR ($CDCl_3$, 500 MHz) of **18**



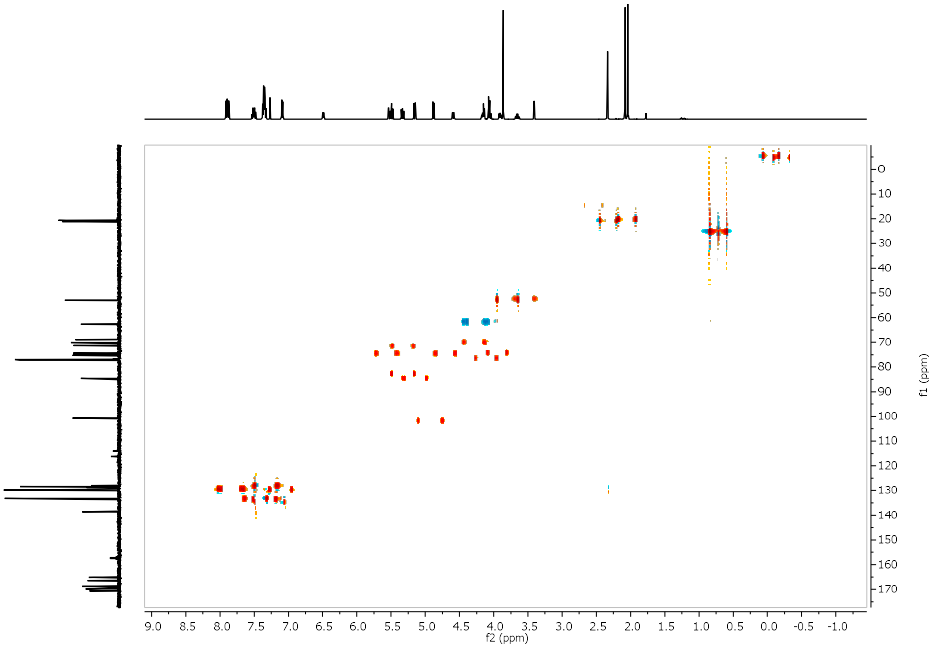
^{13}C-NMR ($CDCl_3$, 126 MHz) of **18**

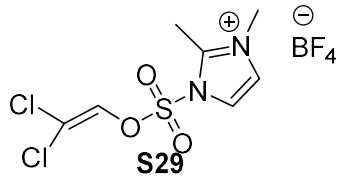


gCOSY ($CDCl_3$, 500 MHz) of **18**



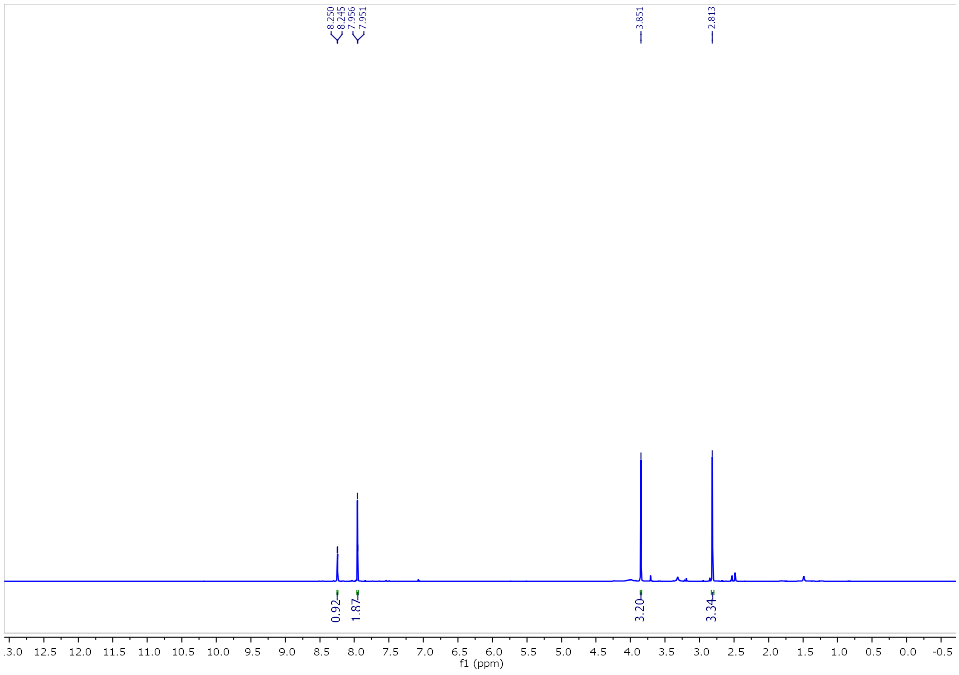
gHSQC ($CDCl_3$, 500 MHz) of **18**



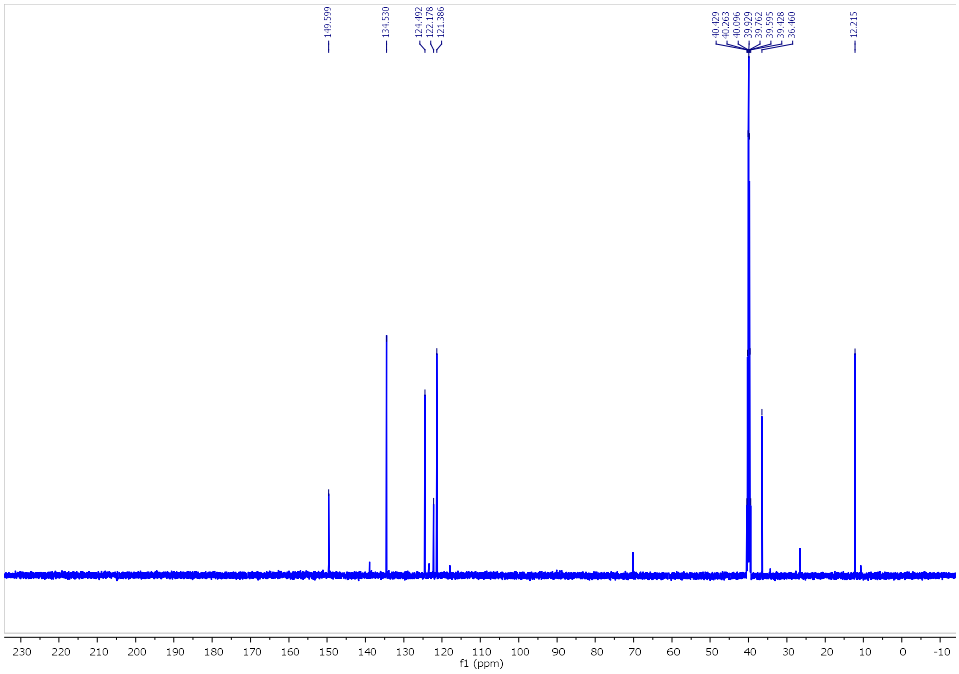


S29

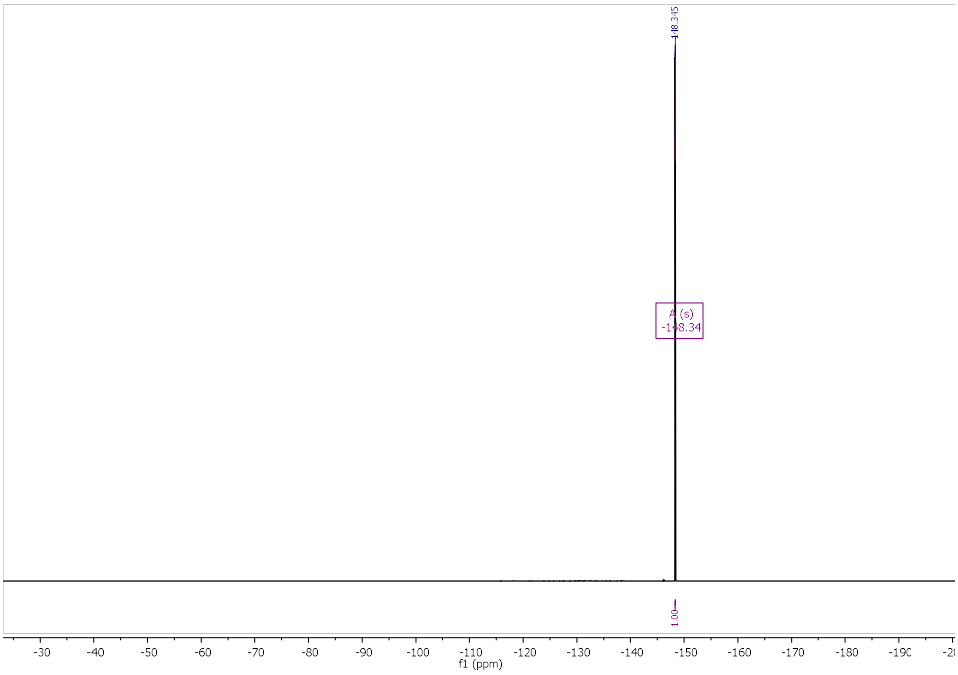
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S29**

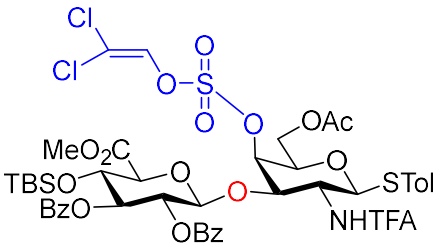


^{13}C-NMR ($CDCl_3$, 126 MHz) of **S29**



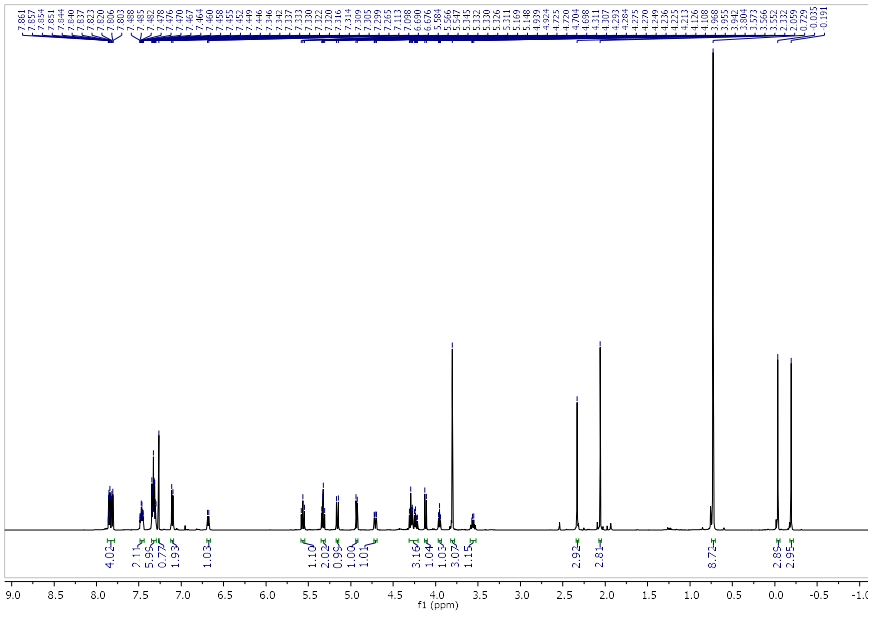
^{19}F-NMR ($CDCl_3$, 500 MHz) of **S29**



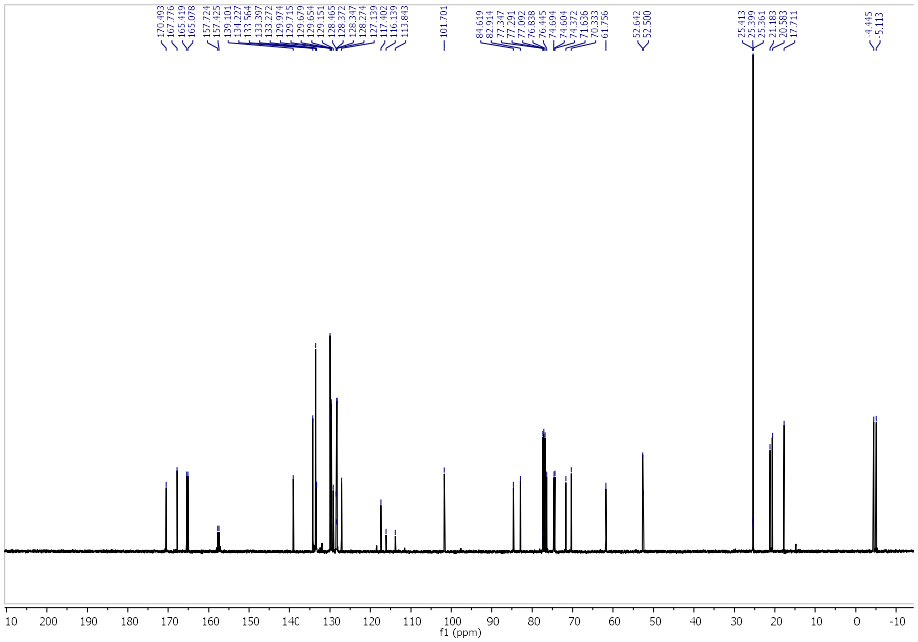


20

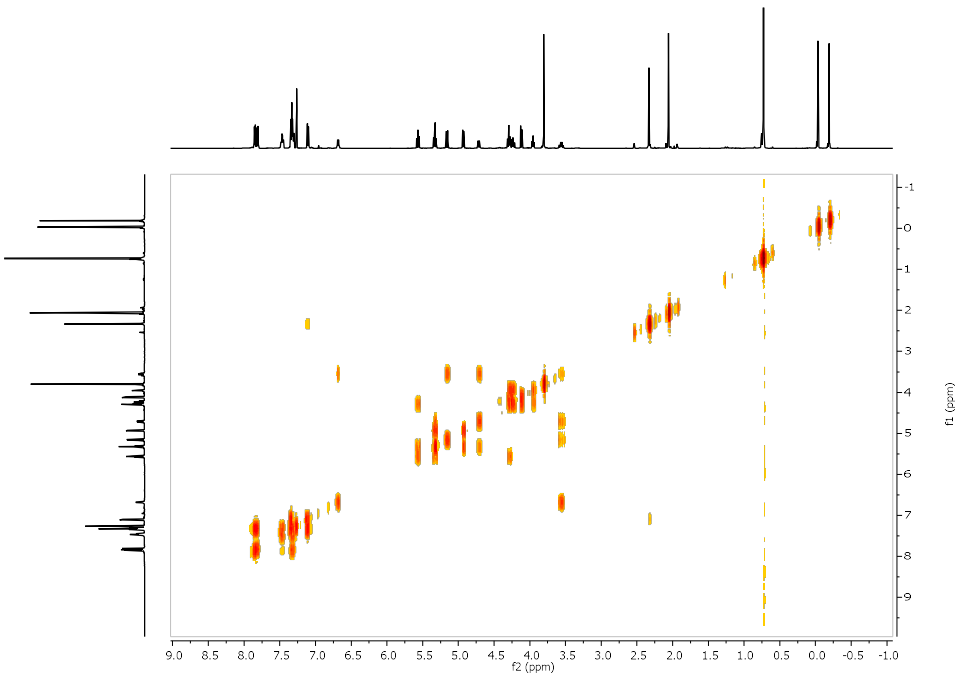
^{1}H-NMR ($CDCl_3$, 500 MHz) of **20**



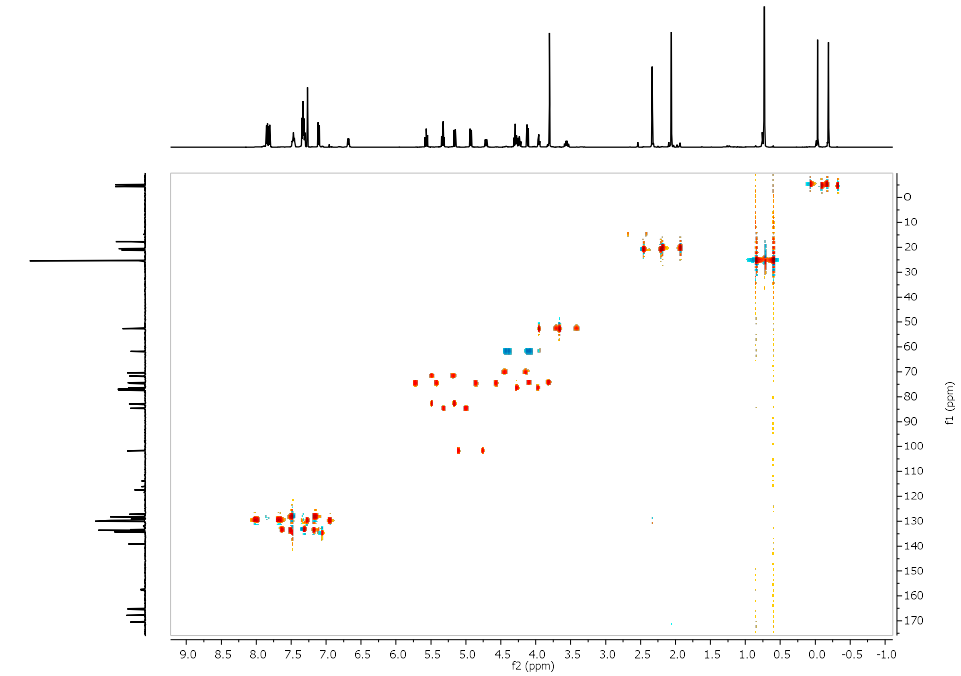
^{13}C-NMR ($CDCl_3$, 126 MHz) of **20**

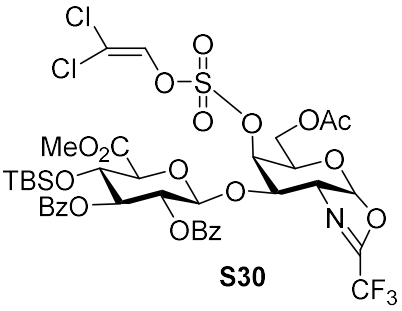


gCOSY ($CDCl_3$, 500 MHz) of **20**



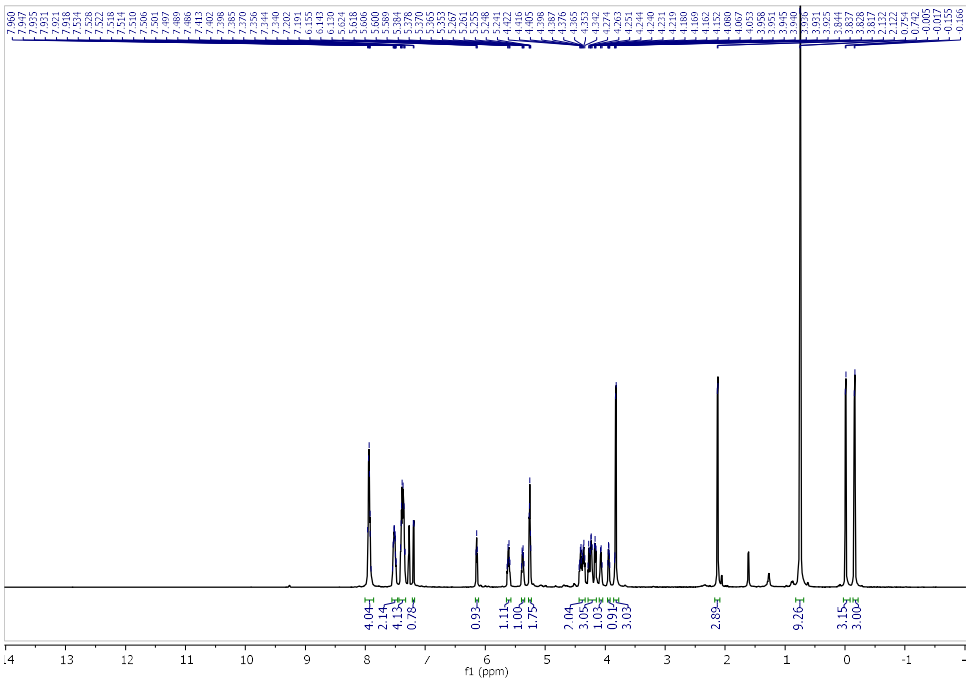
gHSQC ($CDCl_3$, 500 MHz) of **20**

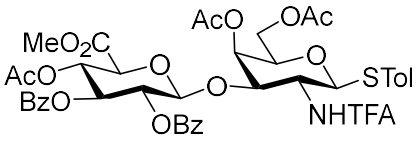




S30

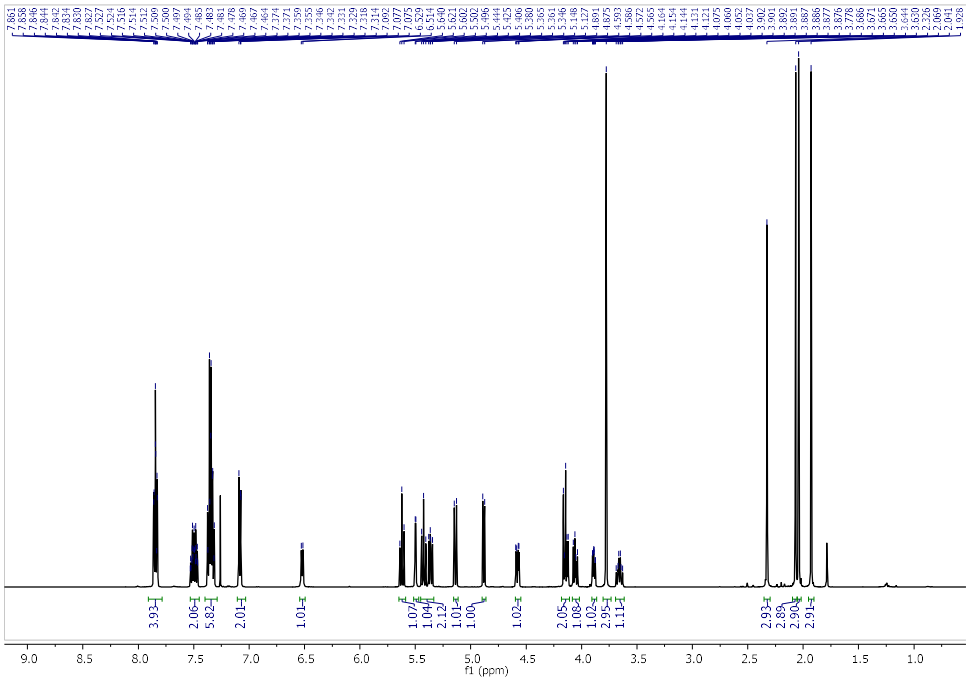
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S30**



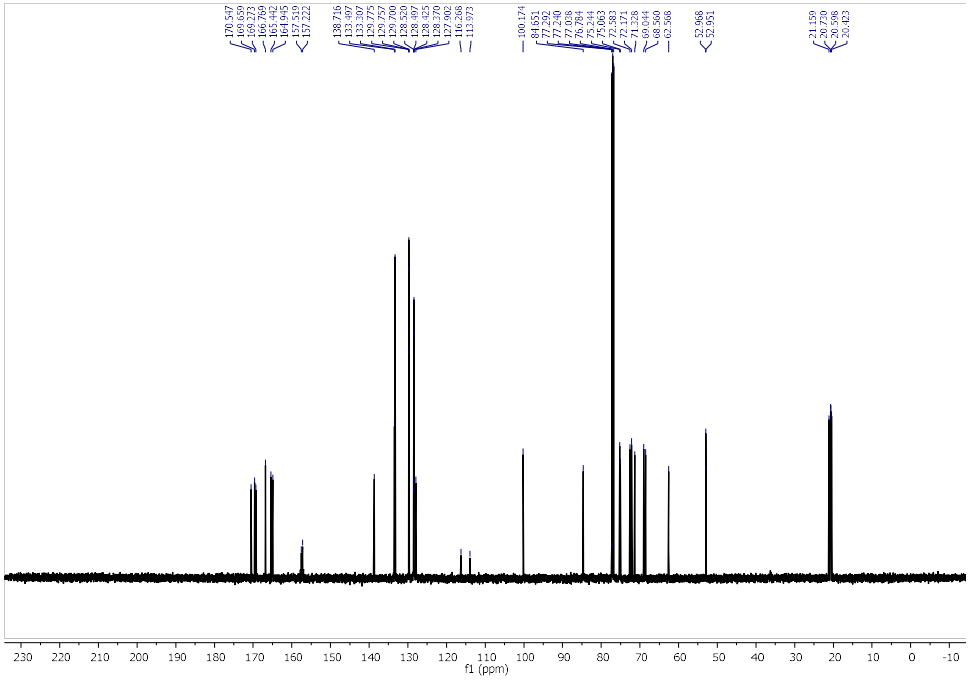


18

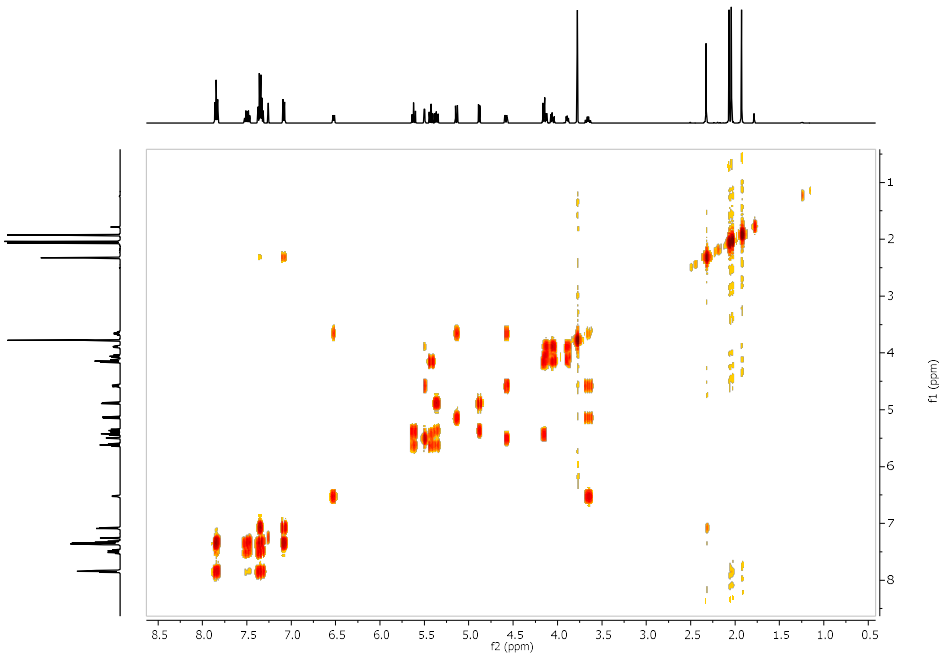
^{1}H-NMR ($CDCl_3$, 500 MHz) of **18**

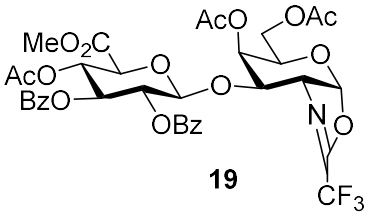


^{13}C-NMR ($CDCl_3$, 126 MHz) of **18**



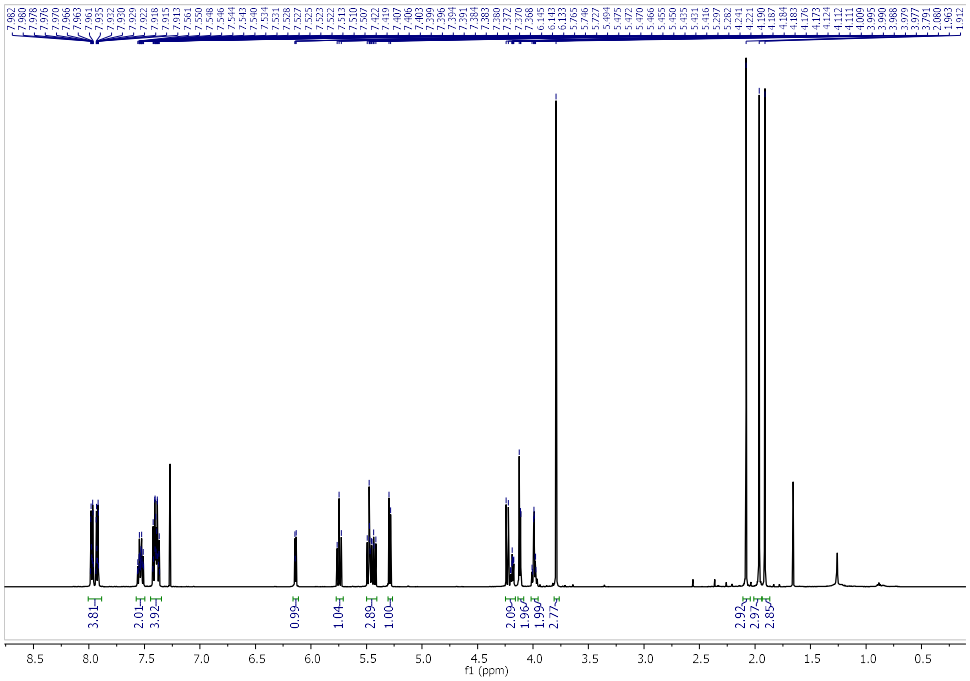
gCOSY ($CDCl_3$, 500 MHz) of **18**



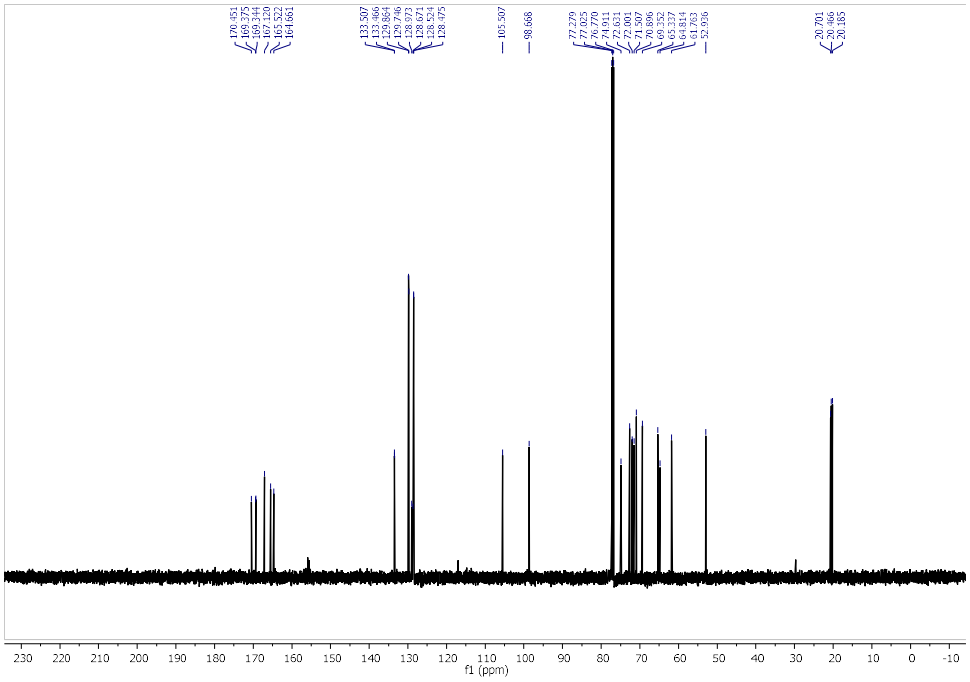


19

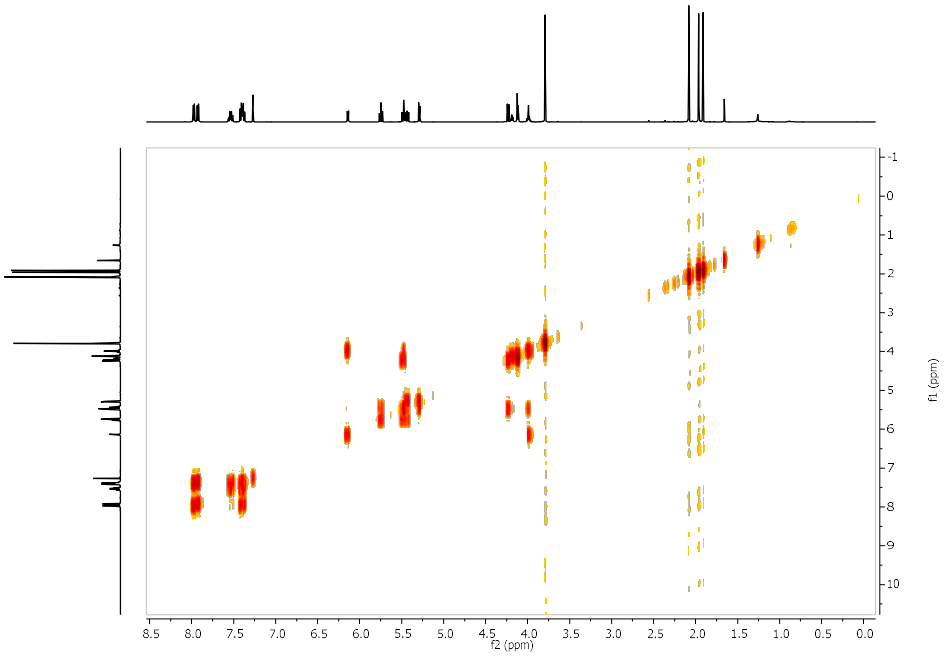
^{1}H-NMR ($CDCl_3$, 500 MHz) of **19**



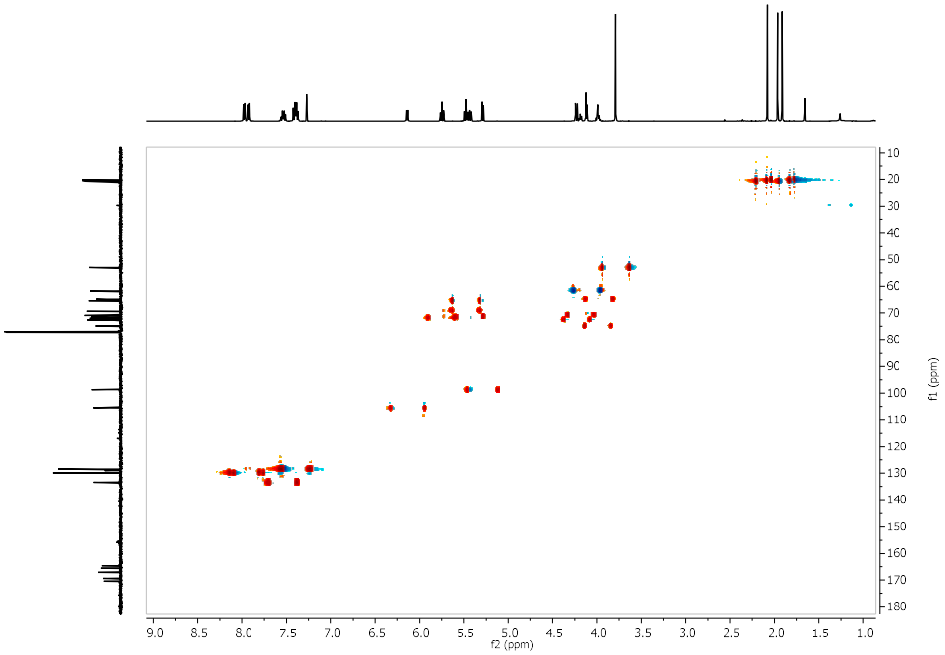
^{13}C-NMR ($CDCl_3$, 126 MHz) of **19**

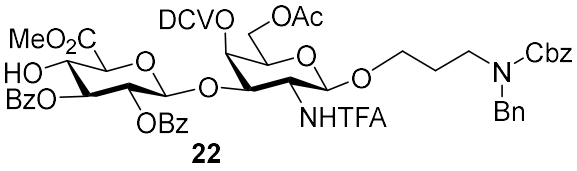


gCOSY ($CDCl_3$, 500 MHz) of **19**



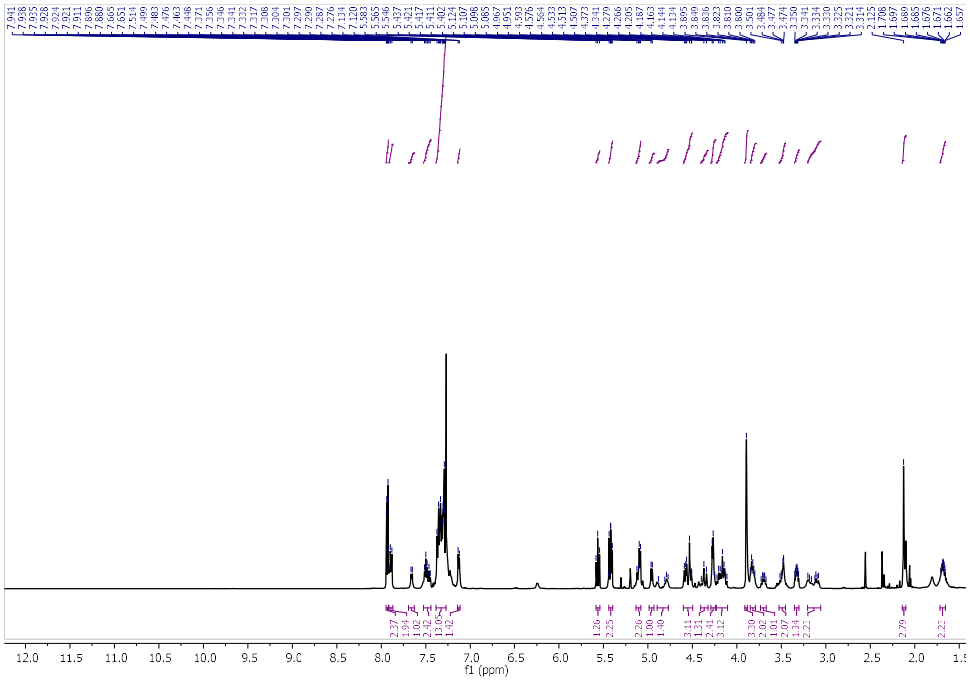
gHSQC ($CDCl_3$, 500 MHz) of **19**



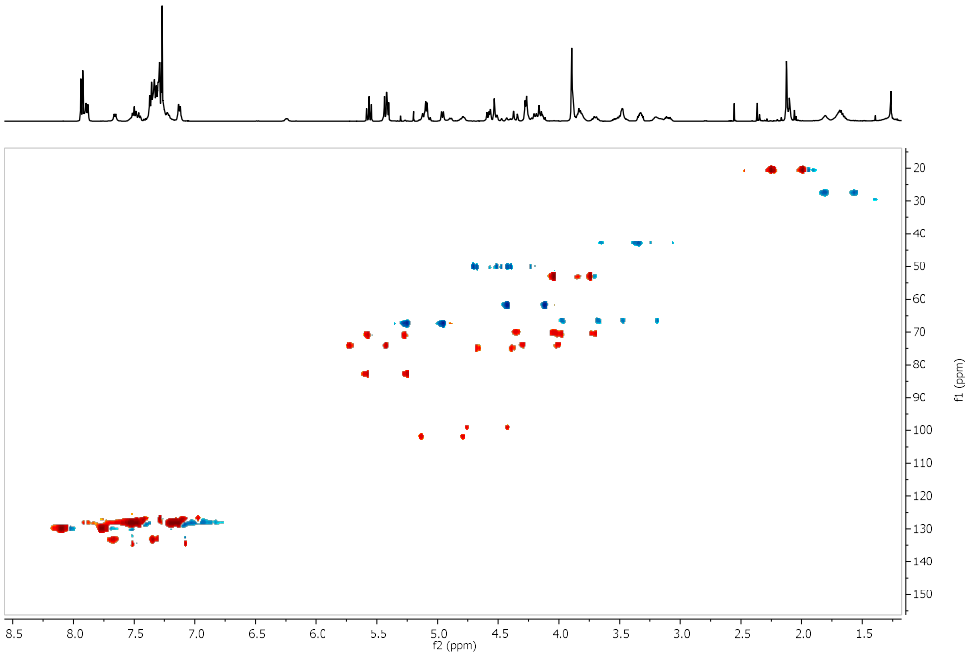


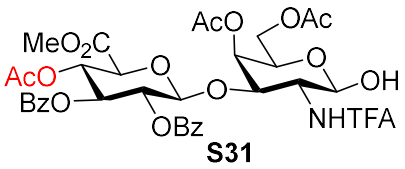
22

^{1}H-NMR ($CDCl_3$, 500 MHz) of **22**



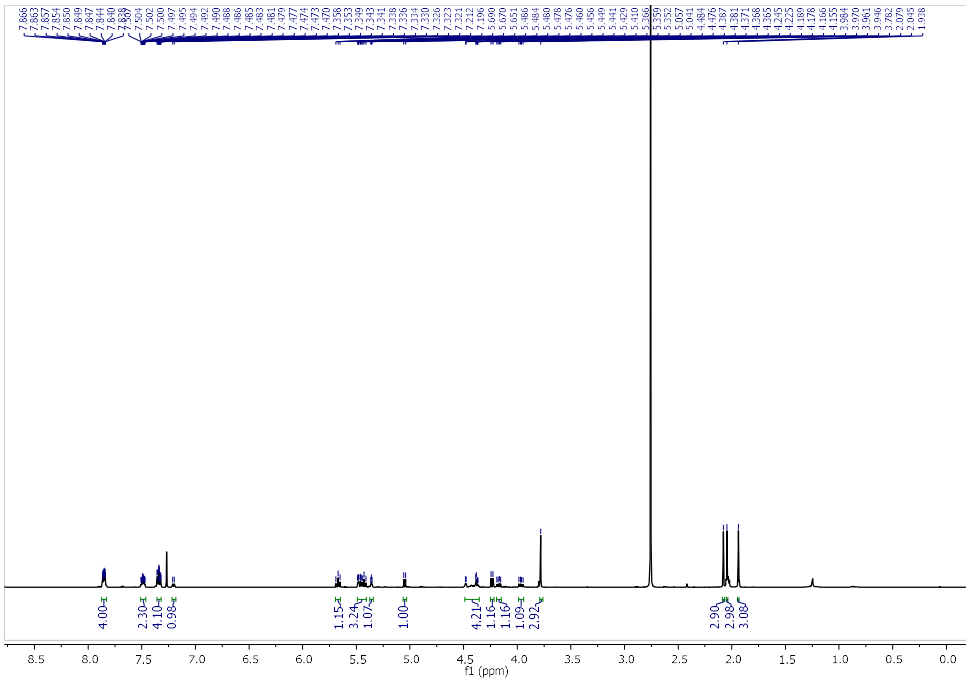
gHSQC ($CDCl_3$, 500 MHz) of **22**



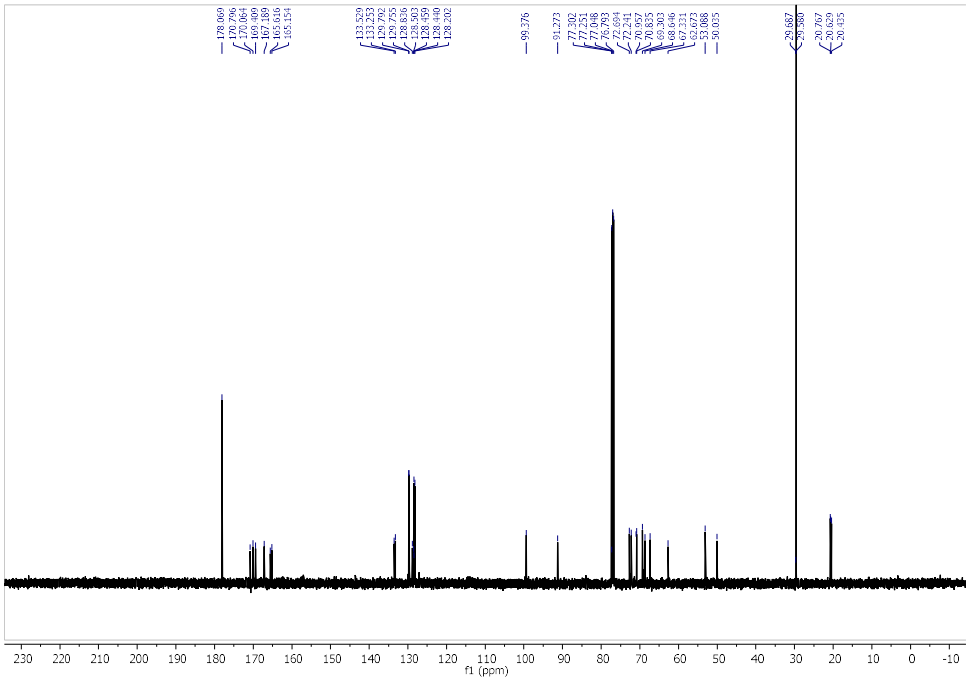


S31

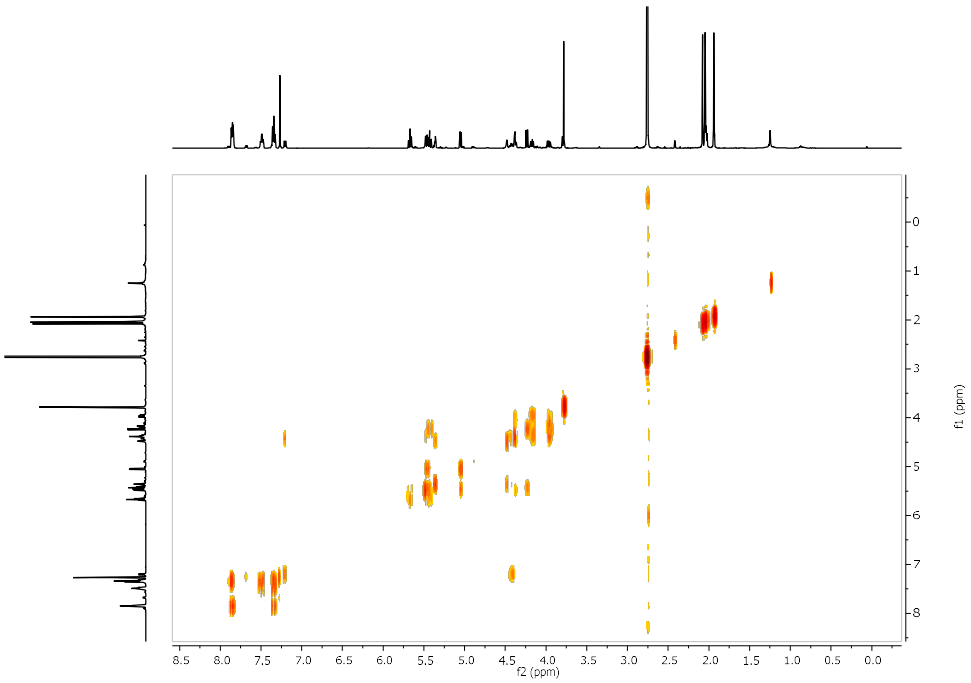
^{1}H-NMR ($CDCl_3$, 500 MHz) of **S31**

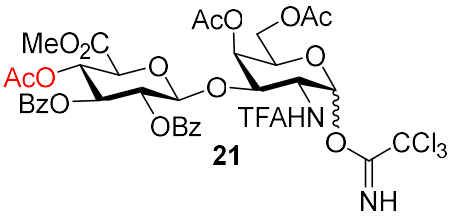


^{13}C-NMR ($CDCl_3$, 126 MHz) of **S31**



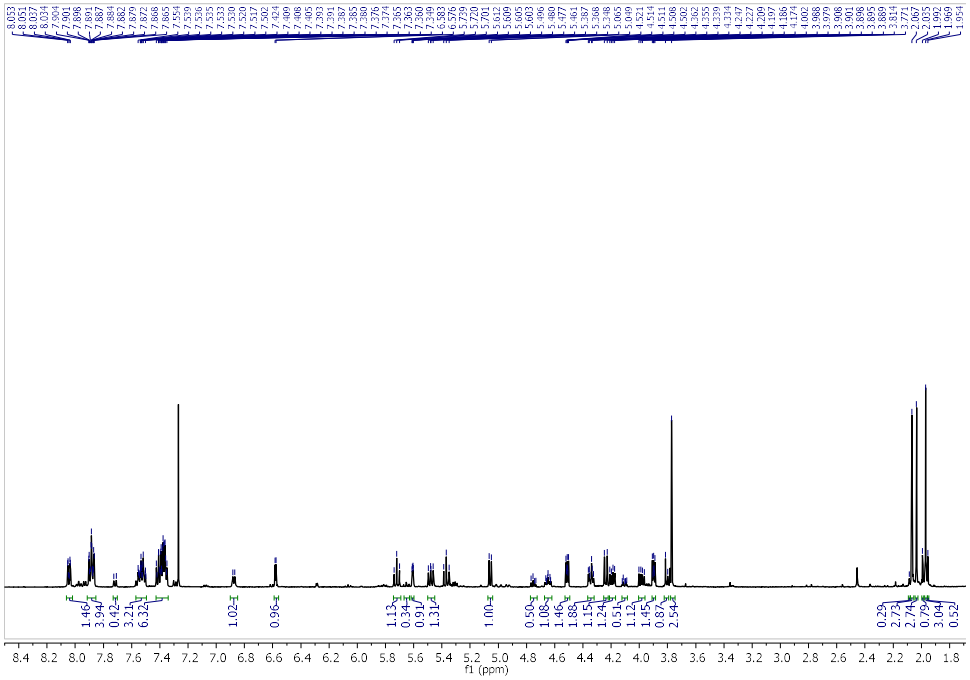
gCOSY ($CDCl_3$, 500 MHz) of **S31**



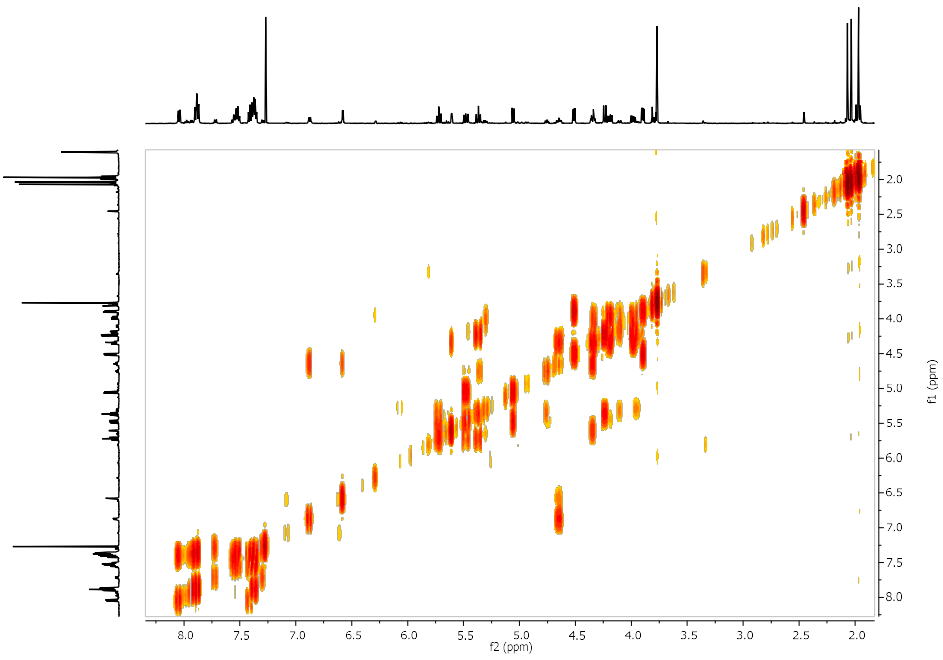


21

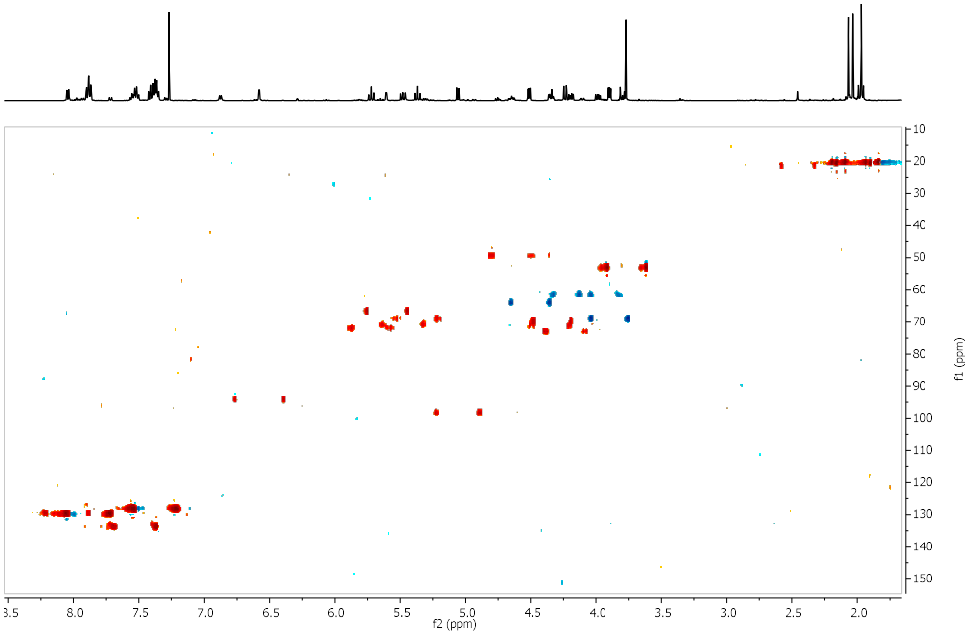
^{1}H-NMR ($CDCl_3$, 500 MHz) of **21**

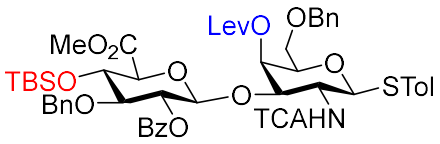


^{13}C-NMR ($CDCl_3$, 126 MHz) of **21**



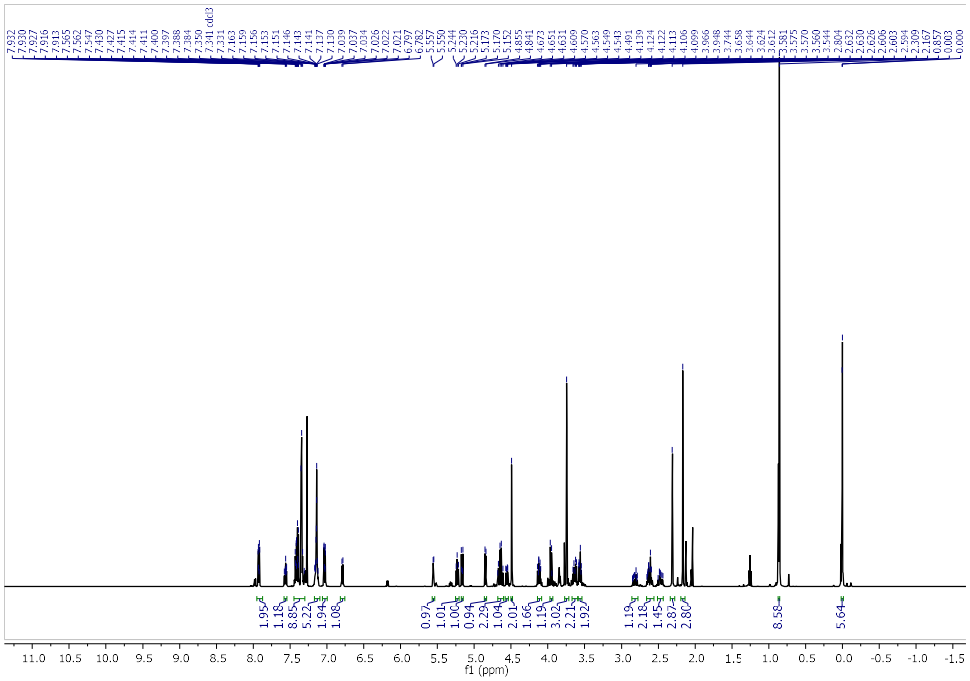
gHSQC ($CDCl_3$, 500 MHz) of **21**



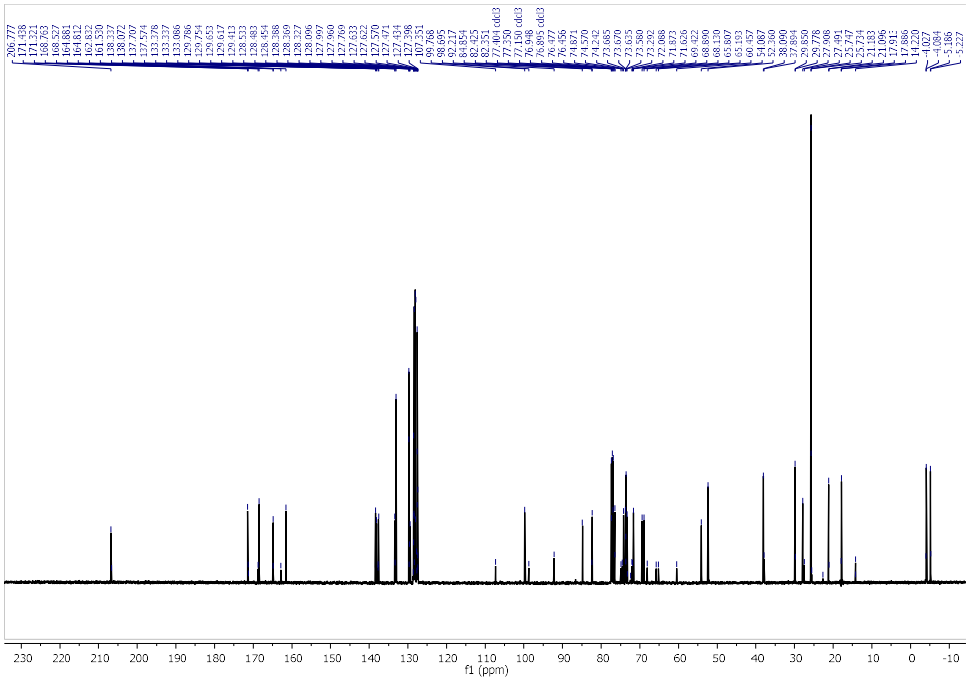


25

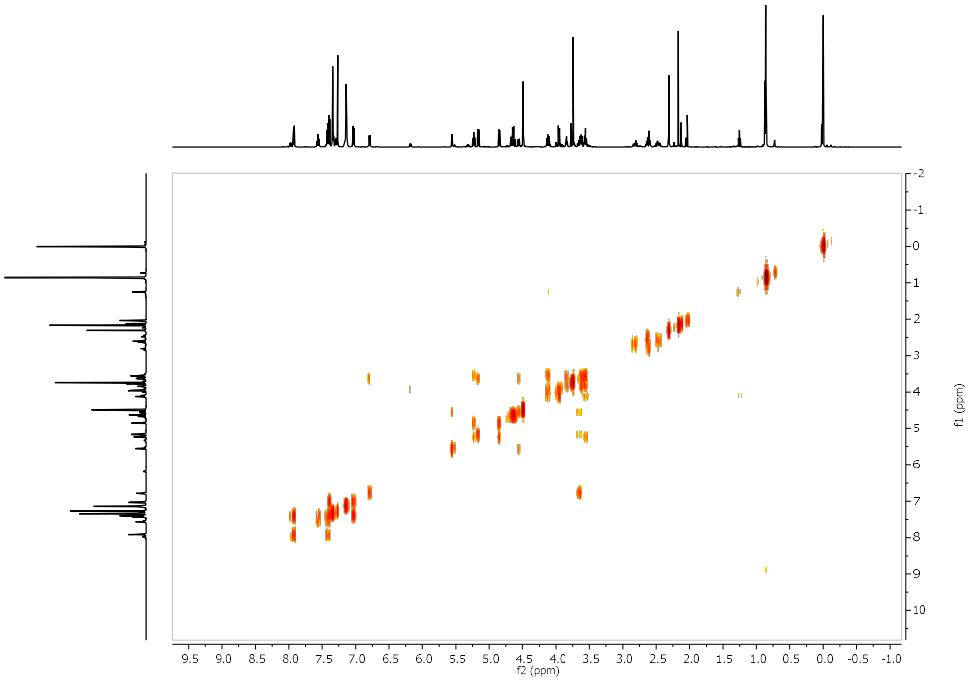
^{1}H-NMR ($CDCl_3$, 500 MHz) of **25**



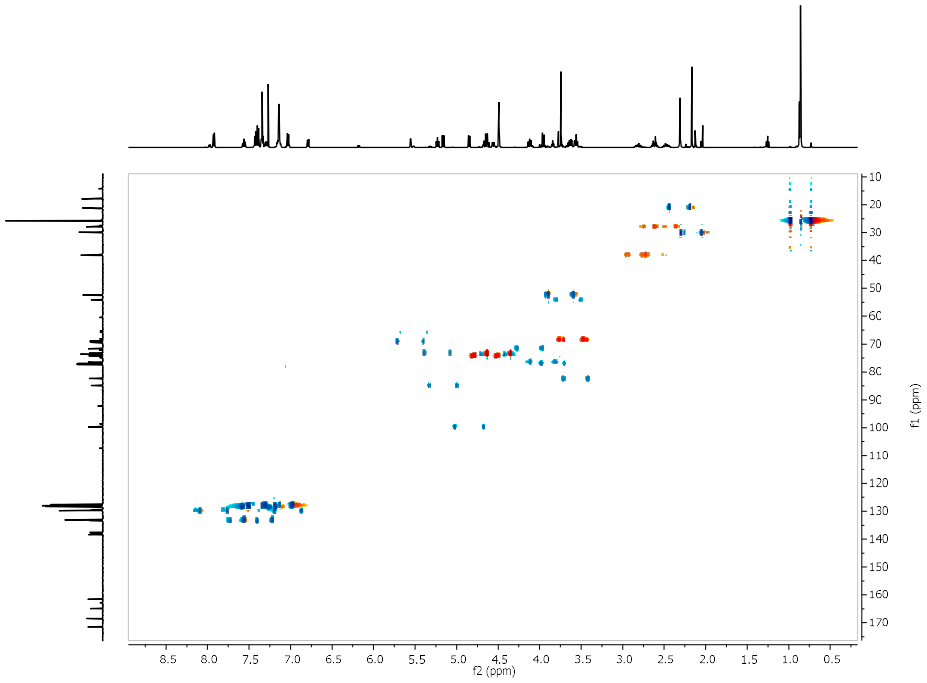
^{13}C-NMR ($CDCl_3$, 126 MHz) of **25**

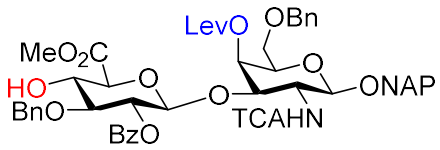


gCOSY ($CDCl_3$, 500 MHz) of **25**



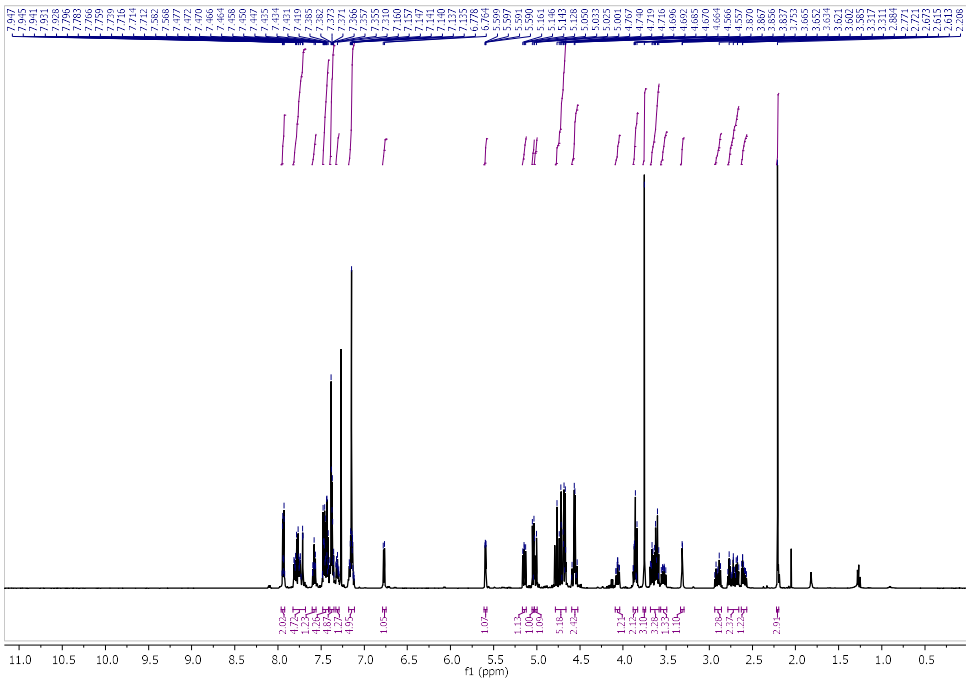
gHSQC ($CDCl_3$, 500 MHz) of **25**



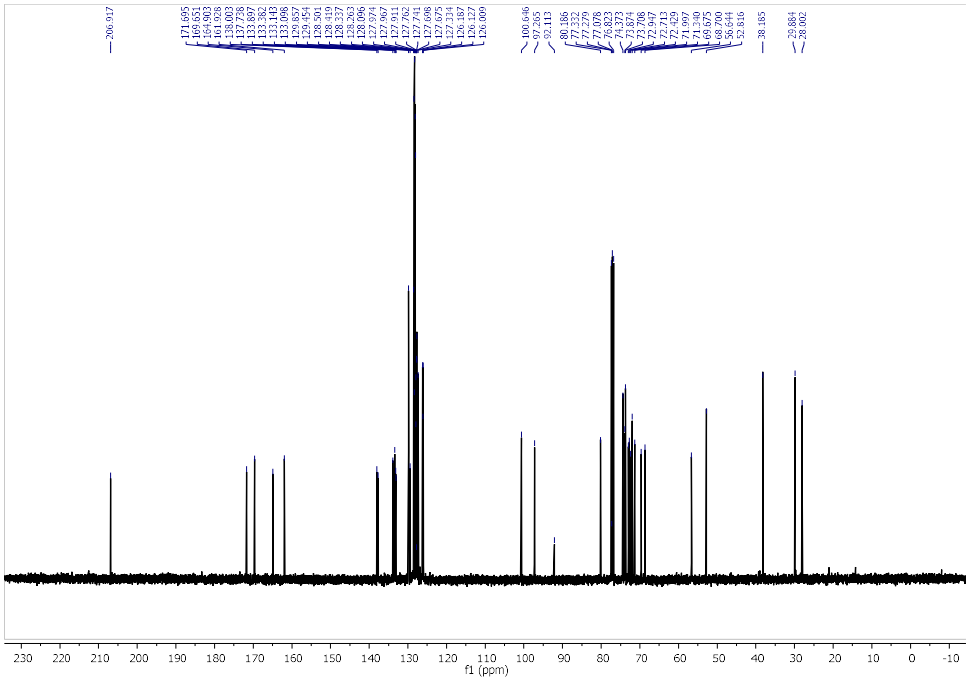


27

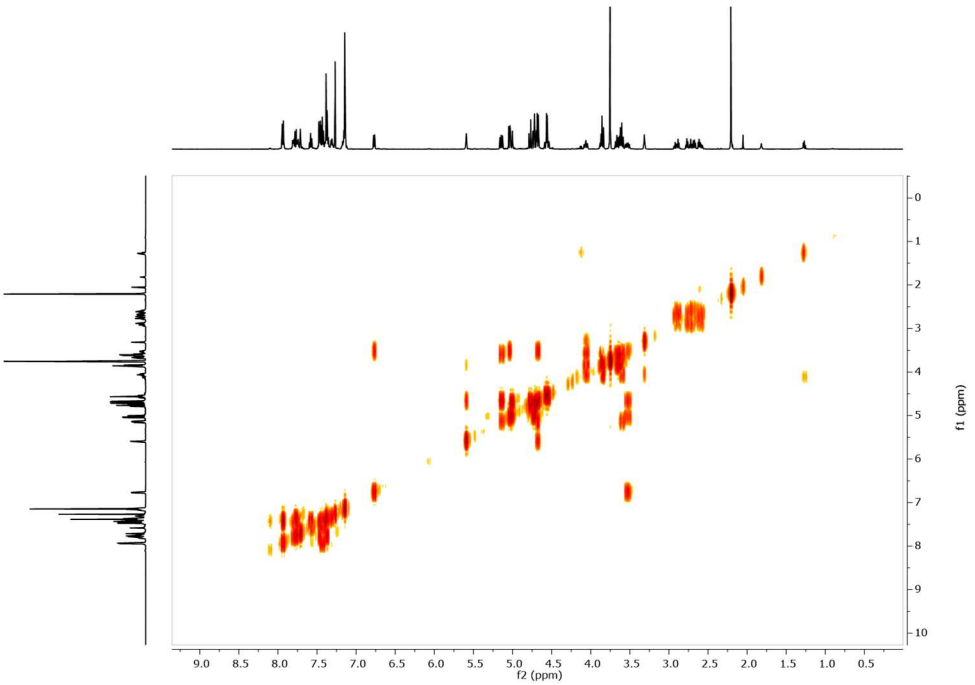
^{1}H-NMR ($CDCl_3$, 500 MHz) of **27**



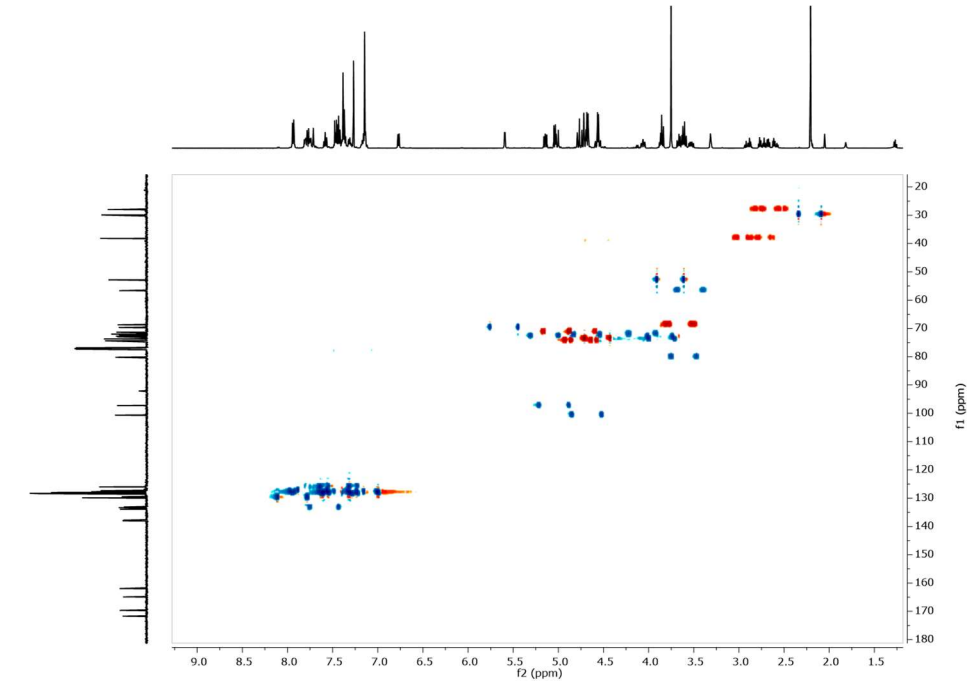
^{13}C-NMR ($CDCl_3$, 126 MHz) of **27**

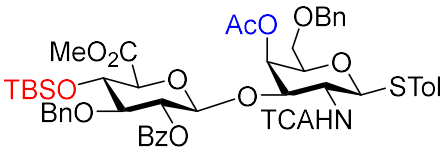


gCOSY ($CDCl_3$, 500 MHz) of **27**



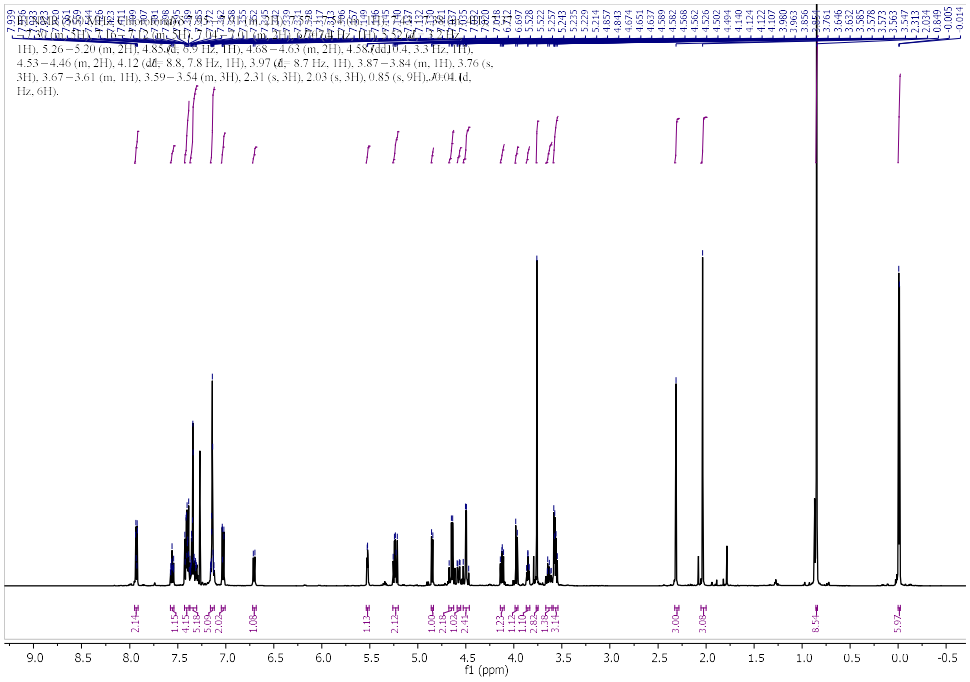
gHSQC ($CDCl_3$, 500 MHz) of **27**



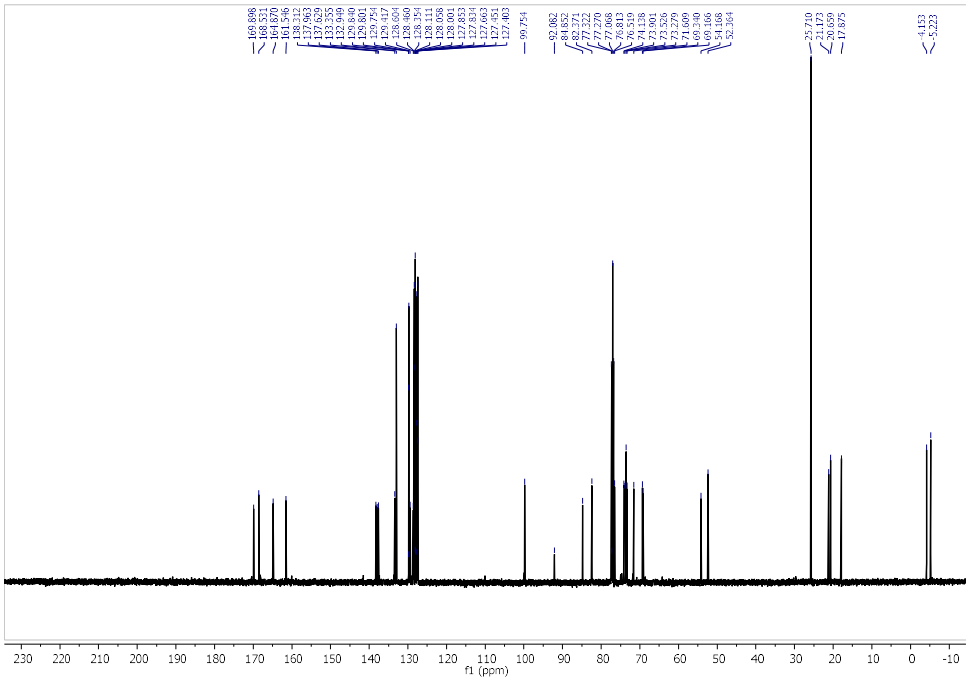


26

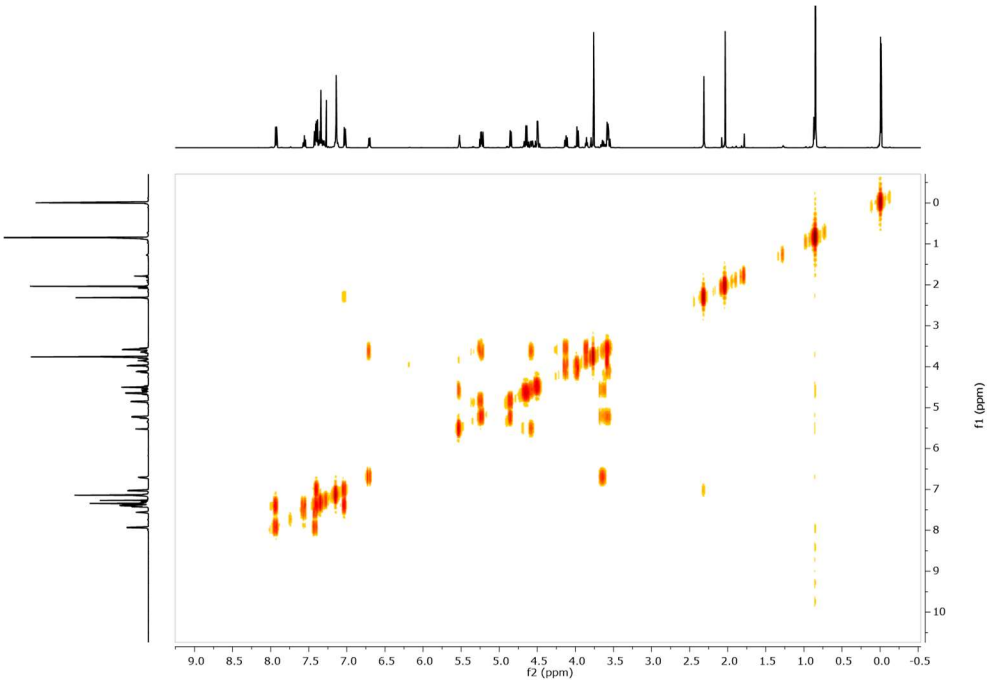
^{1}H-NMR ($CDCl_3$, 500 MHz) of **26**



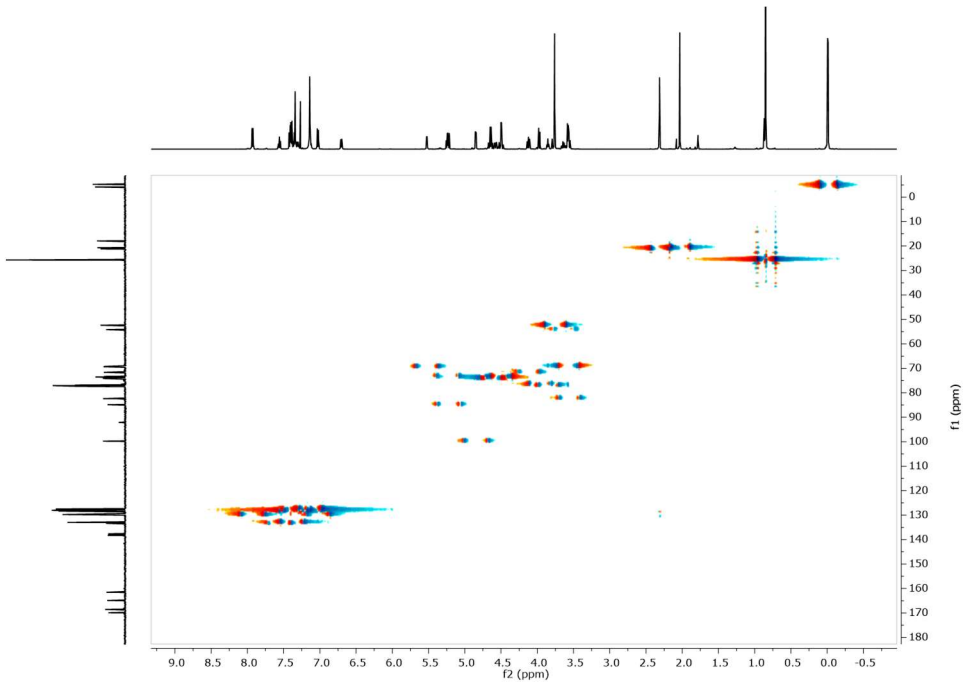
^{13}C-NMR ($CDCl_3$, 126 MHz) of **26**

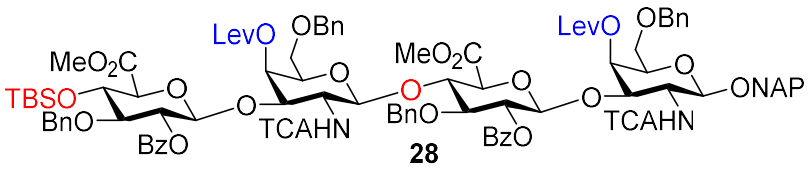


gCOSY ($CDCl_3$, 500 MHz) of **26**



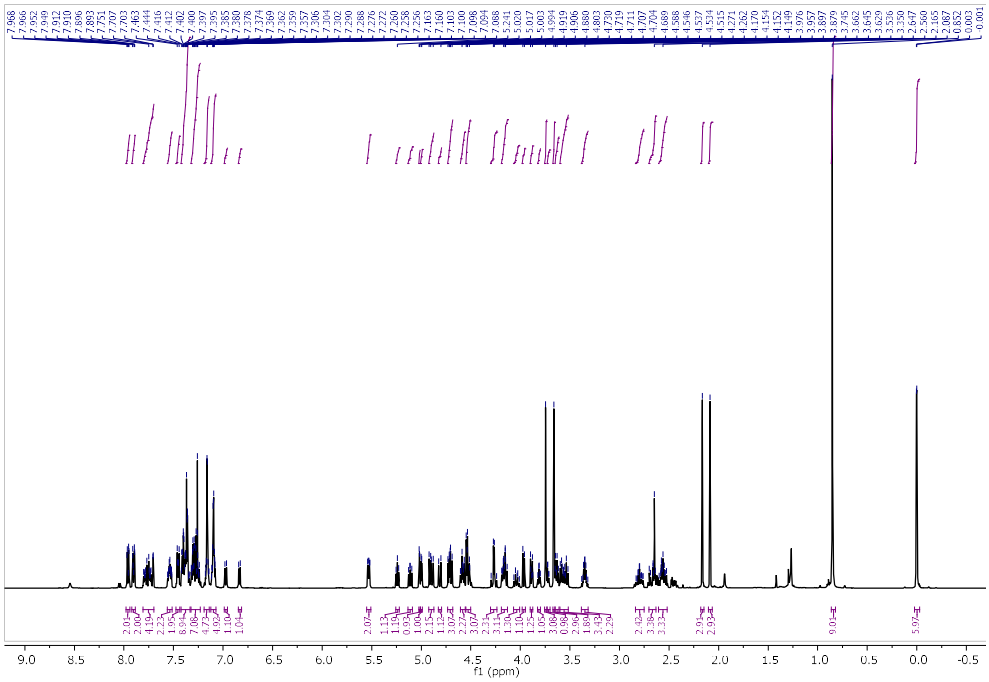
gHSQC ($CDCl_3$, 500 MHz) of **26**



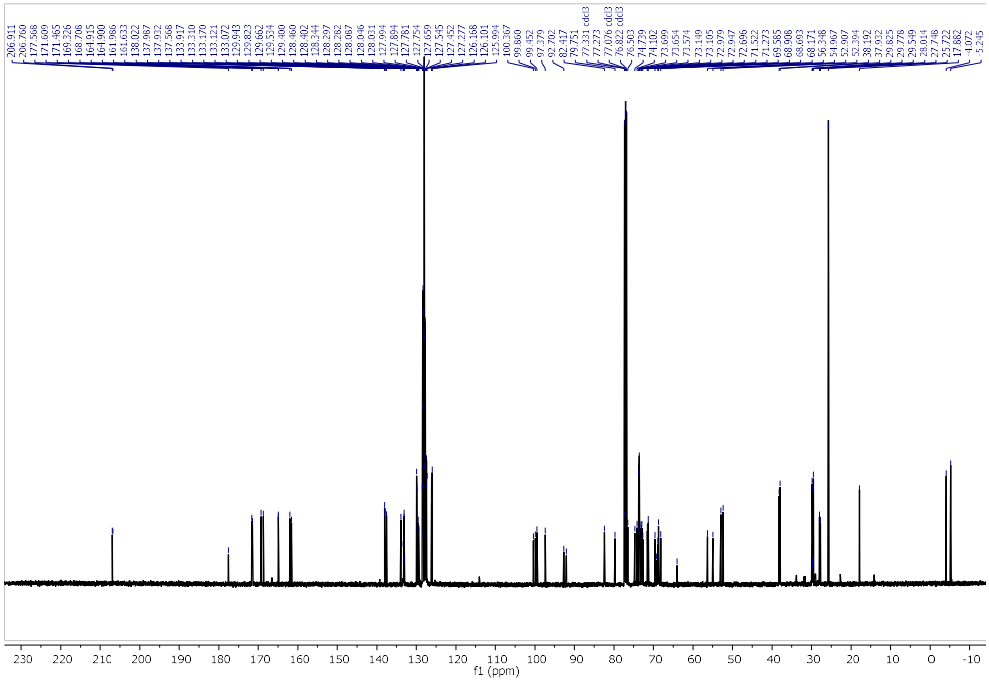


28

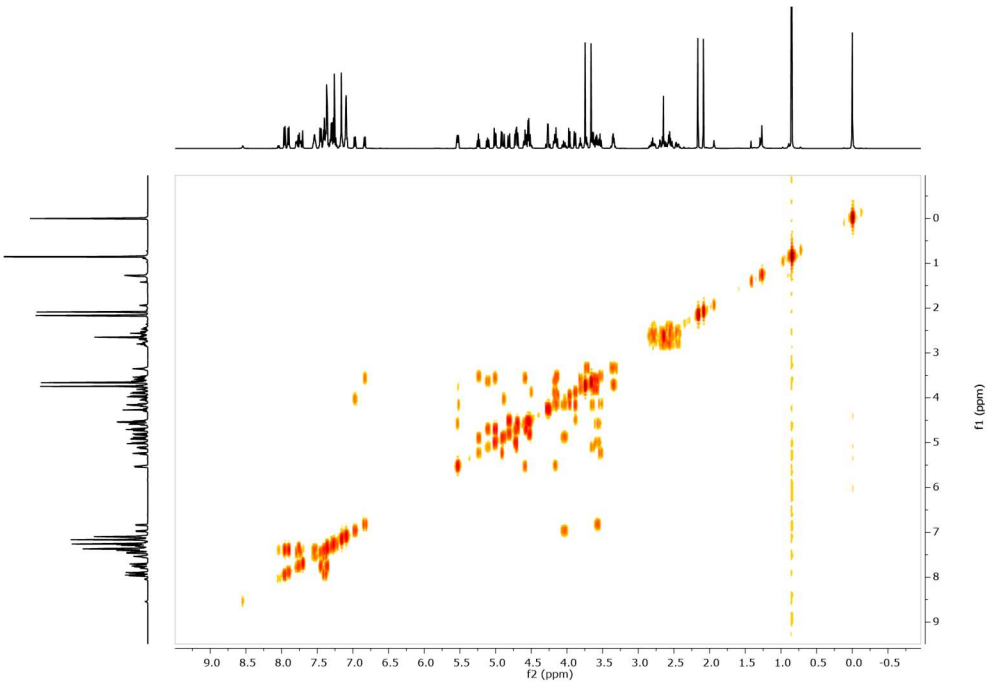
^{1}H-NMR ($CDCl_3$, 500 MHz) of **28**



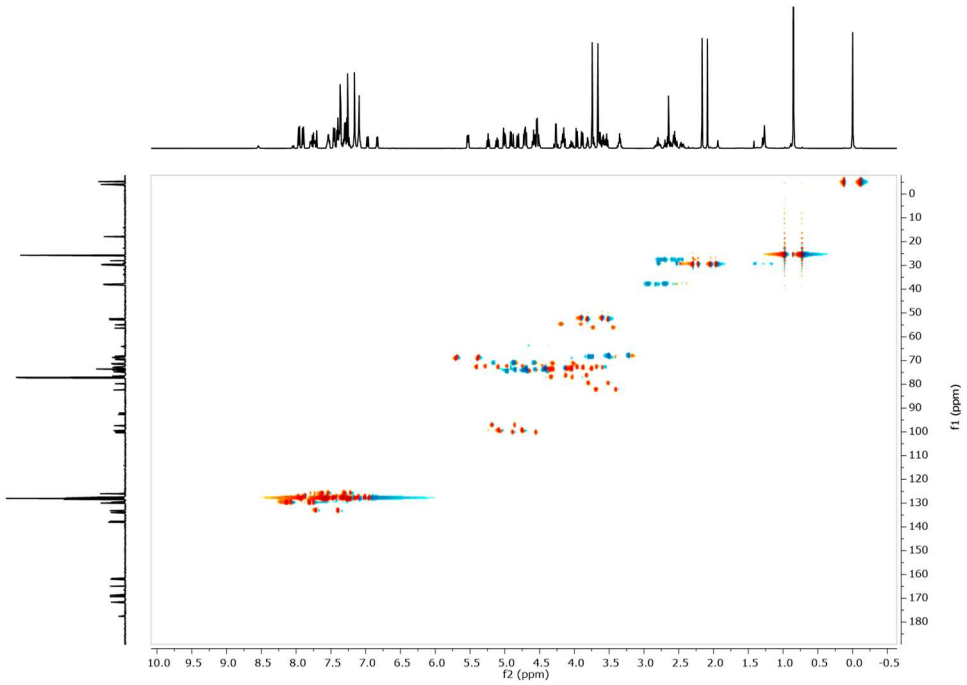
^{13}C-NMR ($CDCl_3$, 126 MHz) of **28**

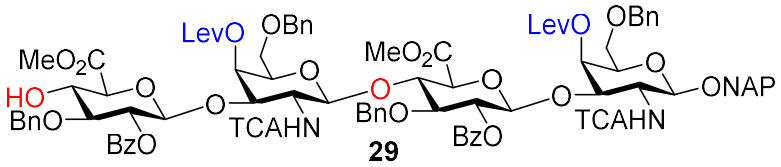


gCOSY ($CDCl_3$, 500 MHz) of **28**



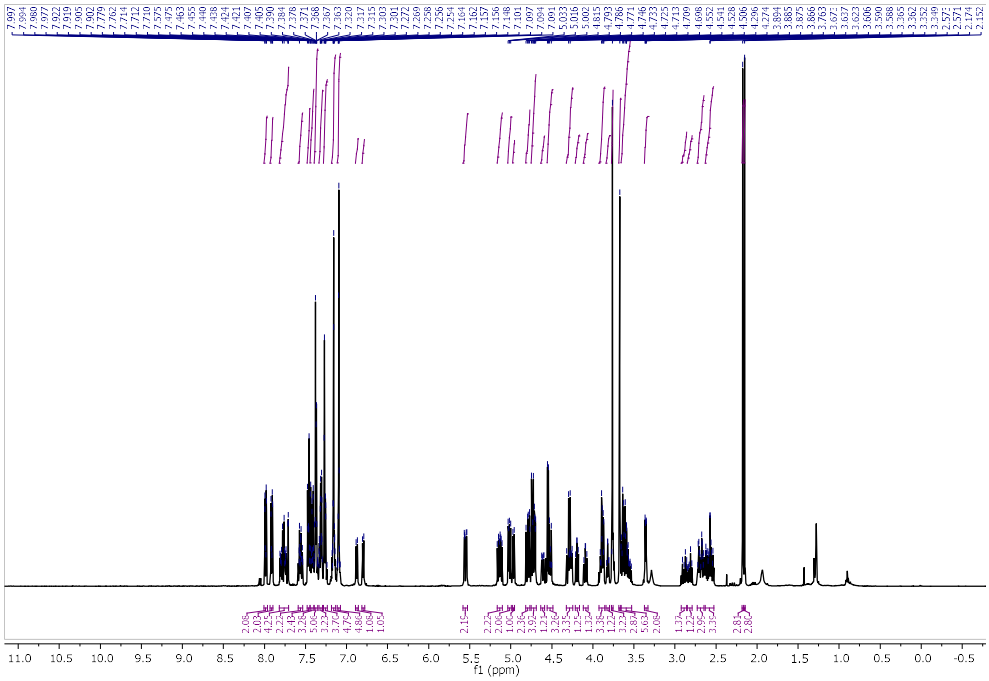
gHSQC ($CDCl_3$, 500 MHz) of **28**



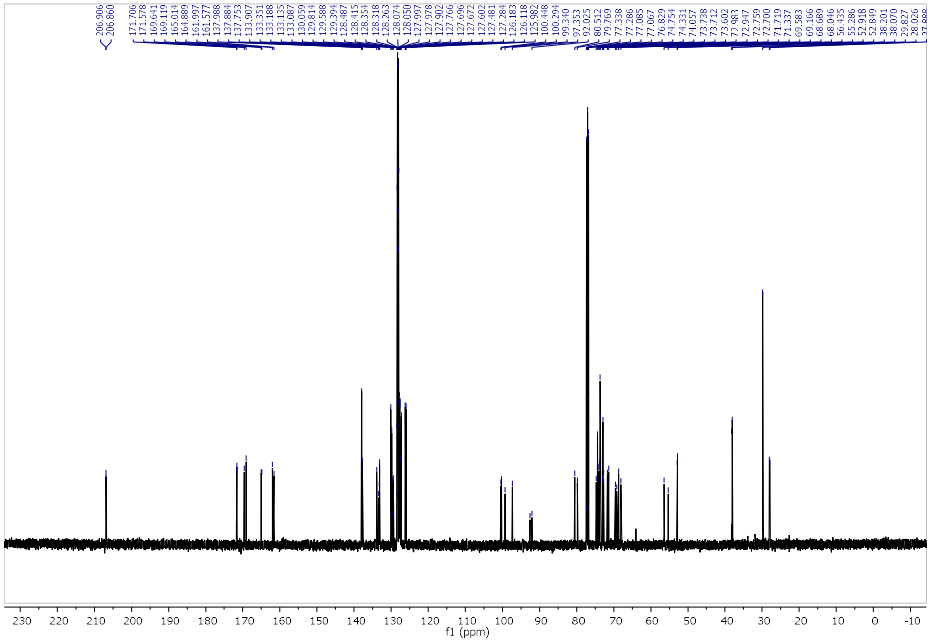


29

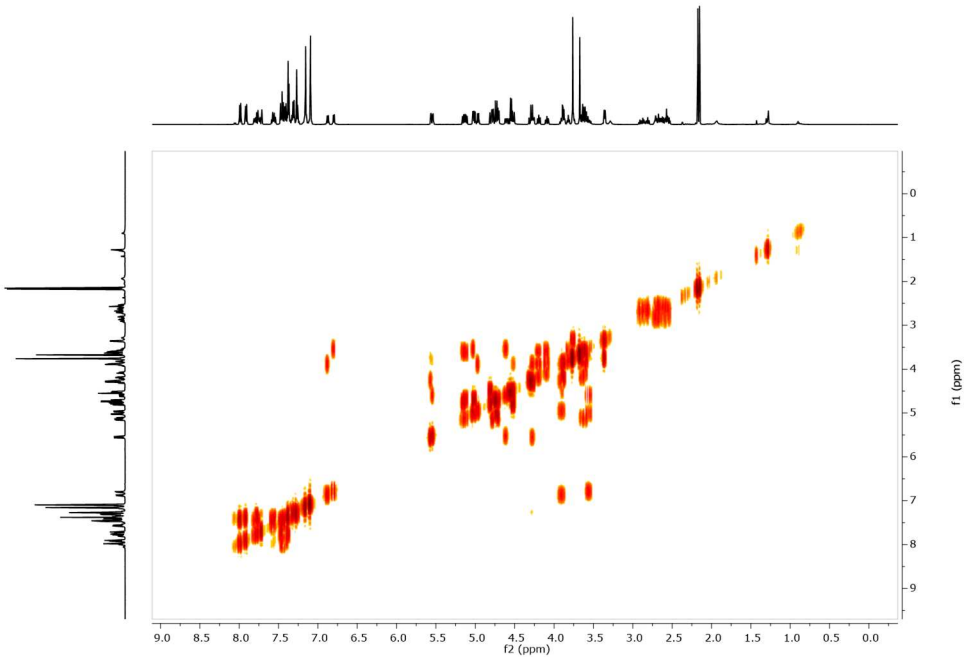
^{1}H-NMR ($CDCl_3$, 500 MHz) of **29**

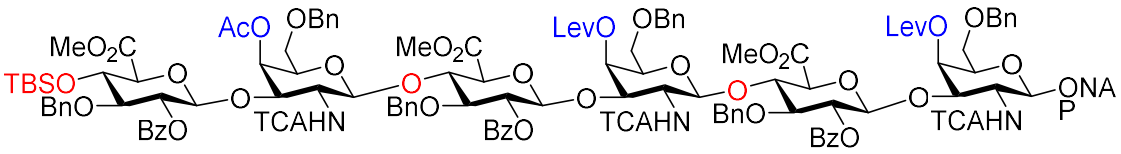


^{13}C-NMR ($CDCl_3$, 126 MHz) of **29**



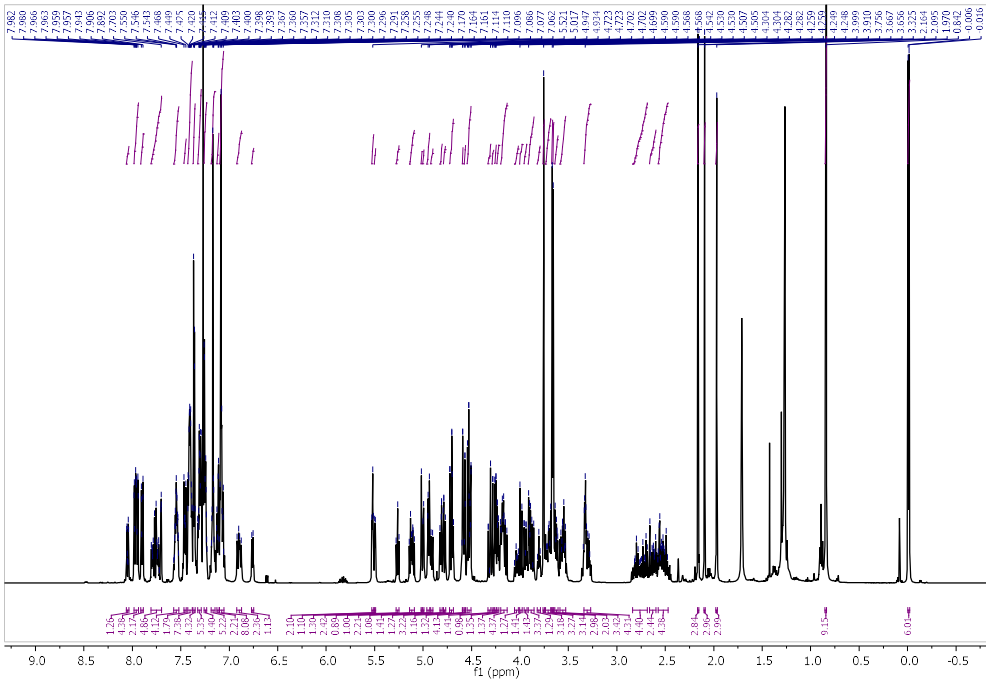
gCOSY ($CDCl_3$, 500 MHz) of **29**



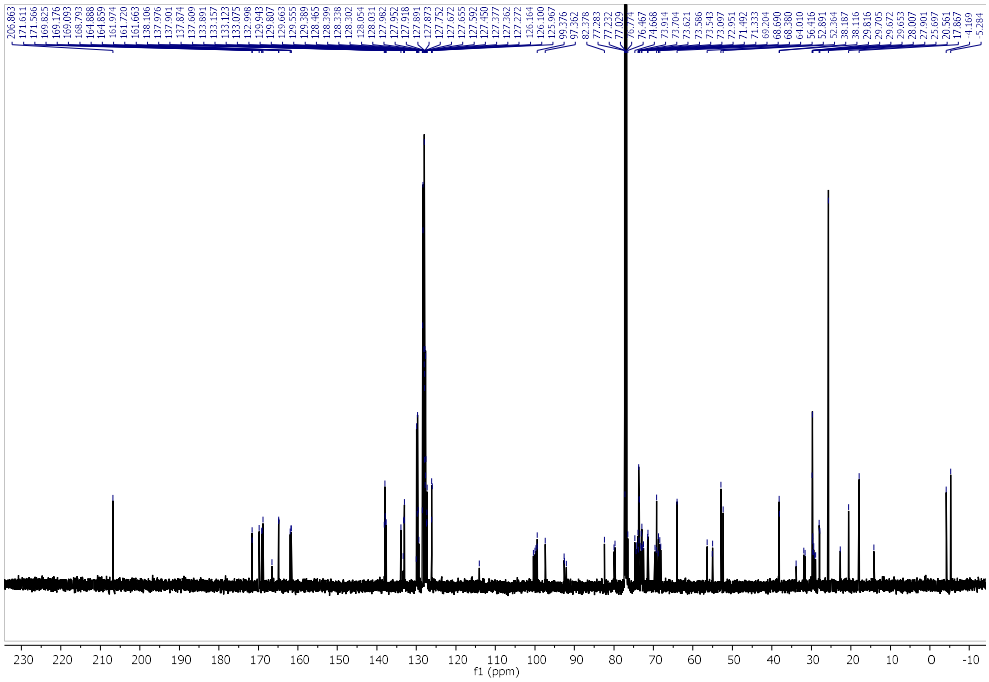


30

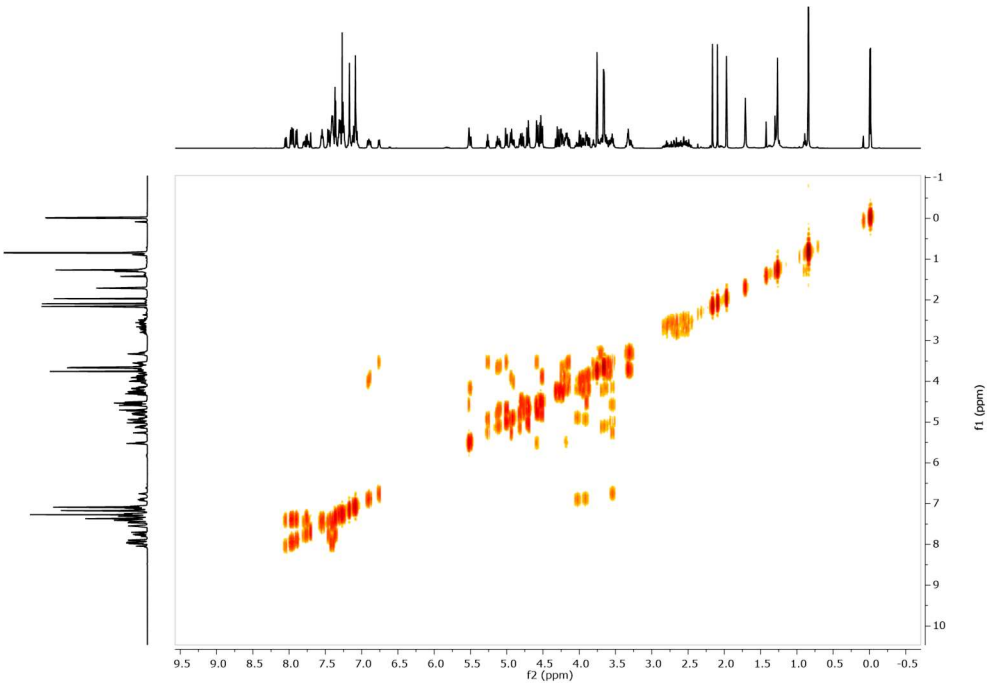
^{1}H-NMR ($CDCl_3$, 500 MHz) of **30**



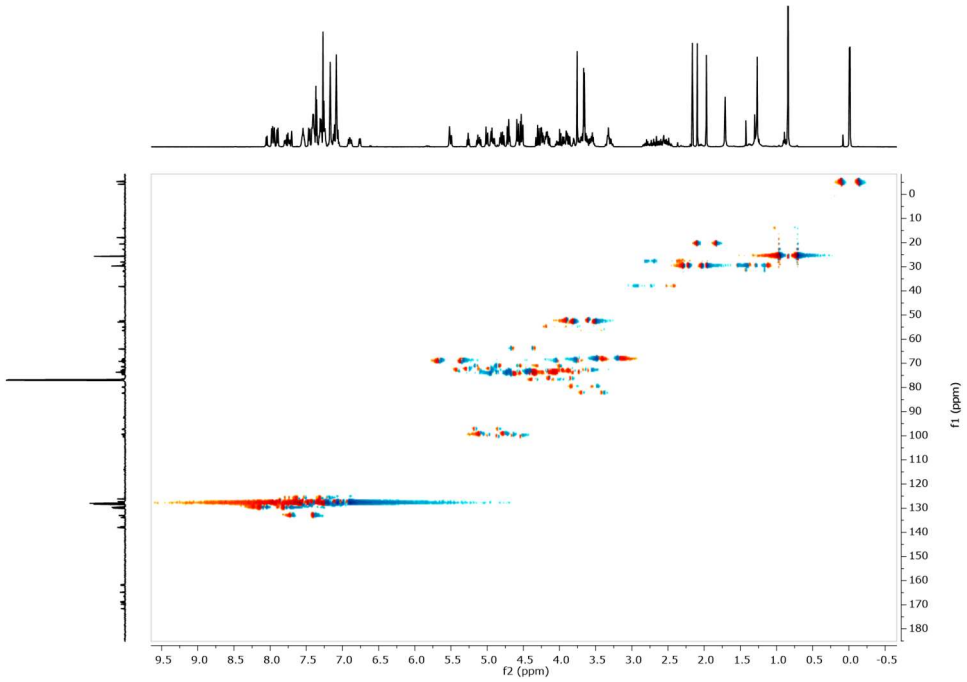
^{13}C-NMR ($CDCl_3$, 126 MHz) of **30**

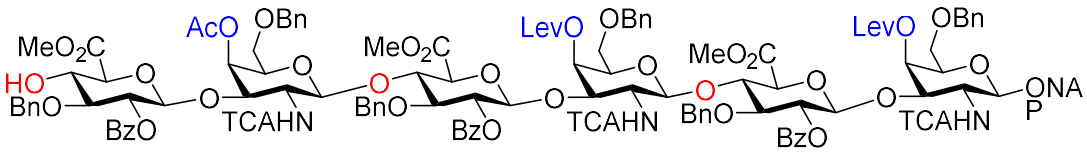


gCOSY ($CDCl_3$, 500 MHz) of **30**



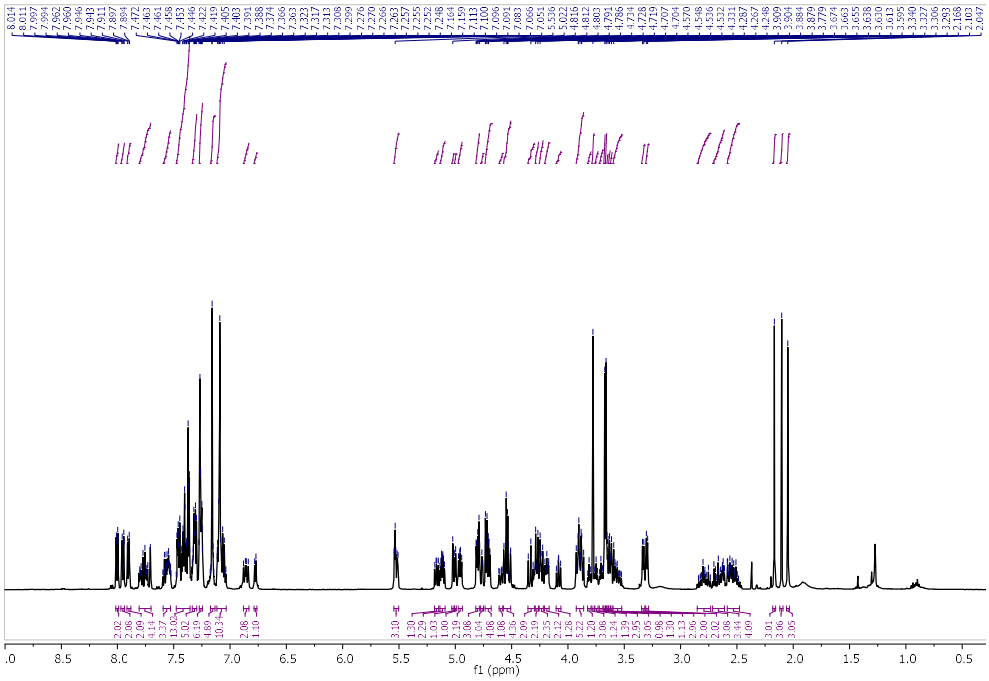
gHSQC ($CDCl_3$, 500 MHz) of **30**



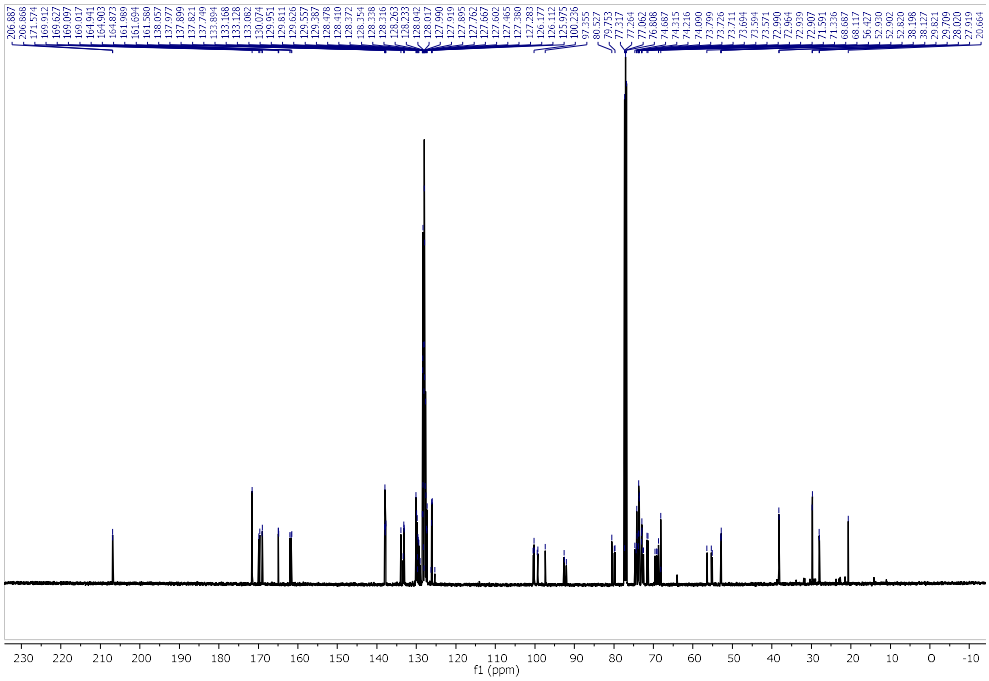


31

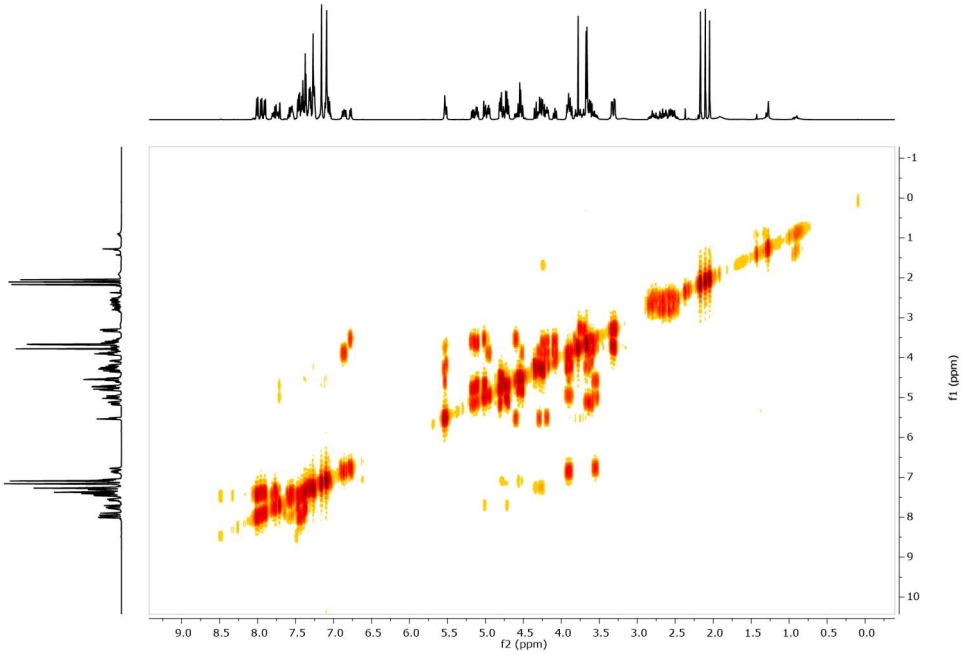
^{1}H-NMR ($CDCl_3$, 500 MHz) of **31**



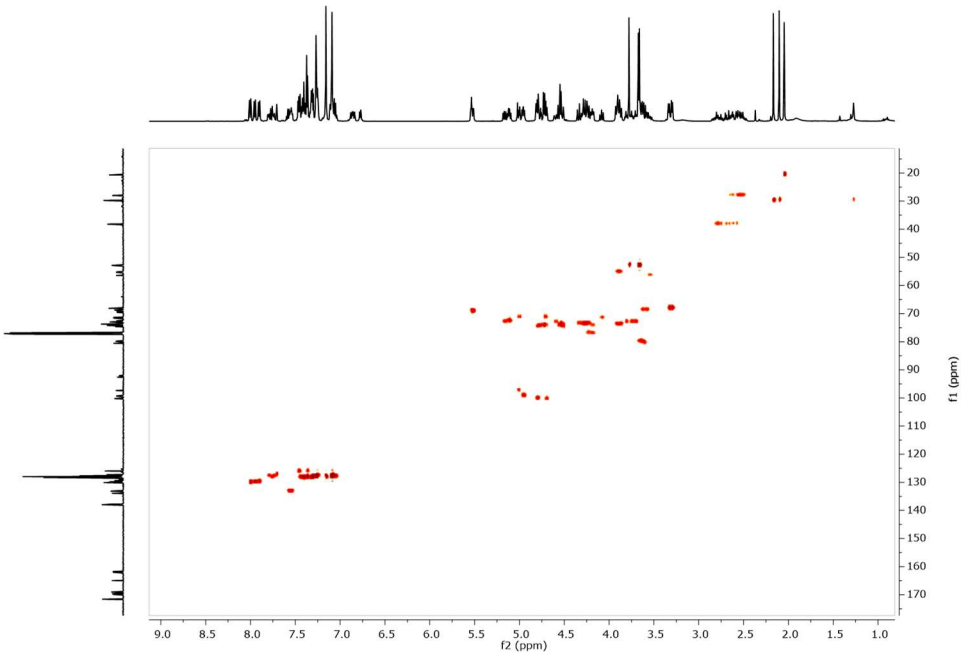
^{13}C-NMR ($CDCl_3$, 126 MHz) of **31**

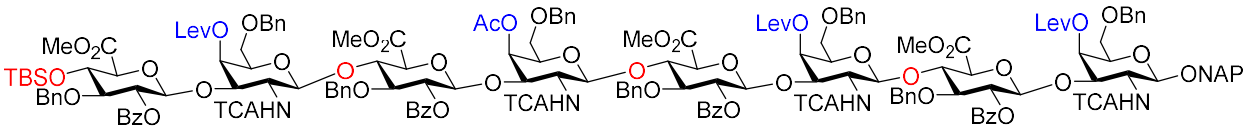


gCOSY ($CDCl_3$, 500 MHz) of **31**



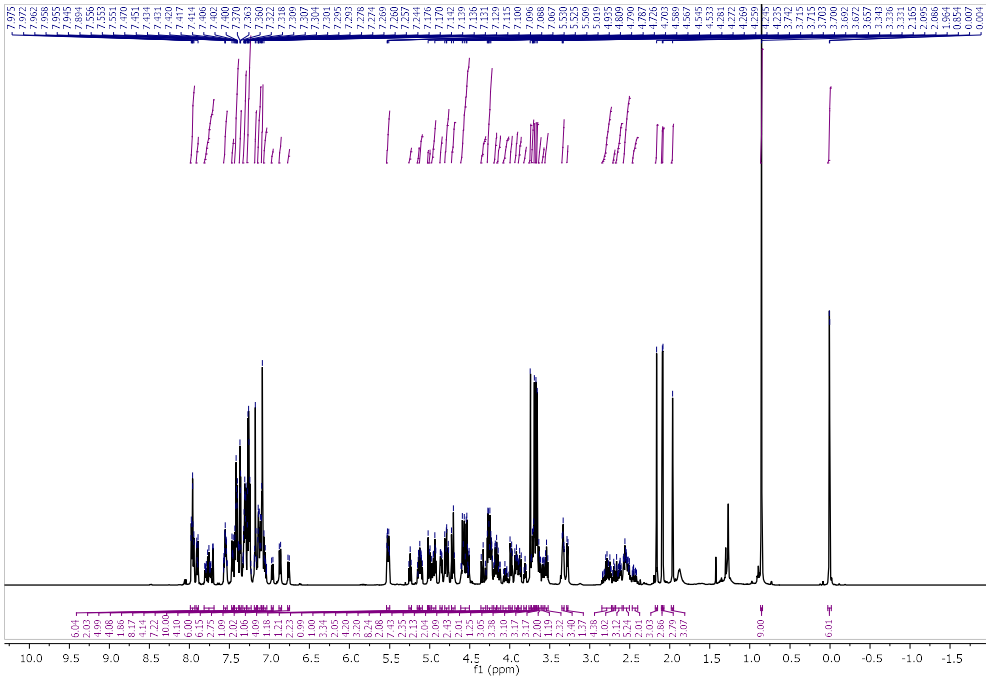
gHSQC ($CDCl_3$, 500 MHz) of **31**



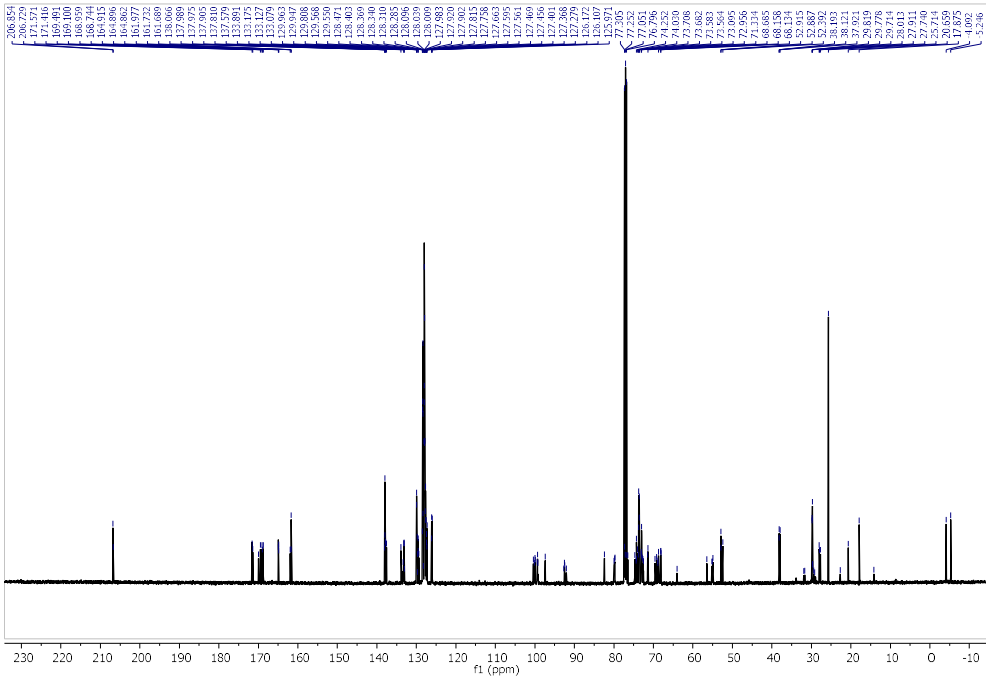


32

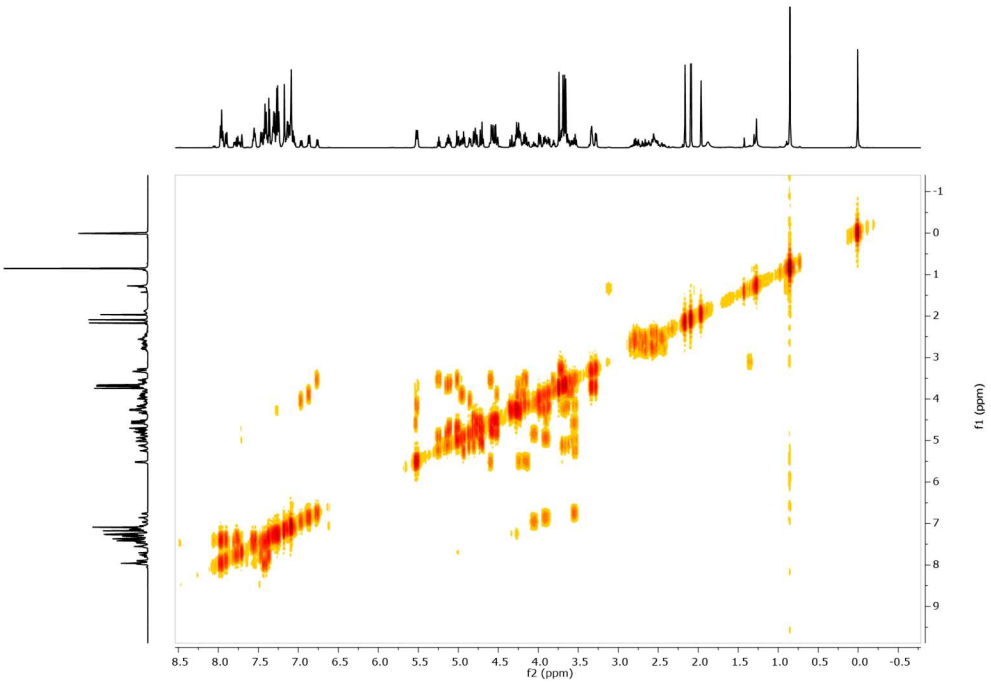
^{1}H-NMR ($CDCl_3$, 500 MHz) of **32**



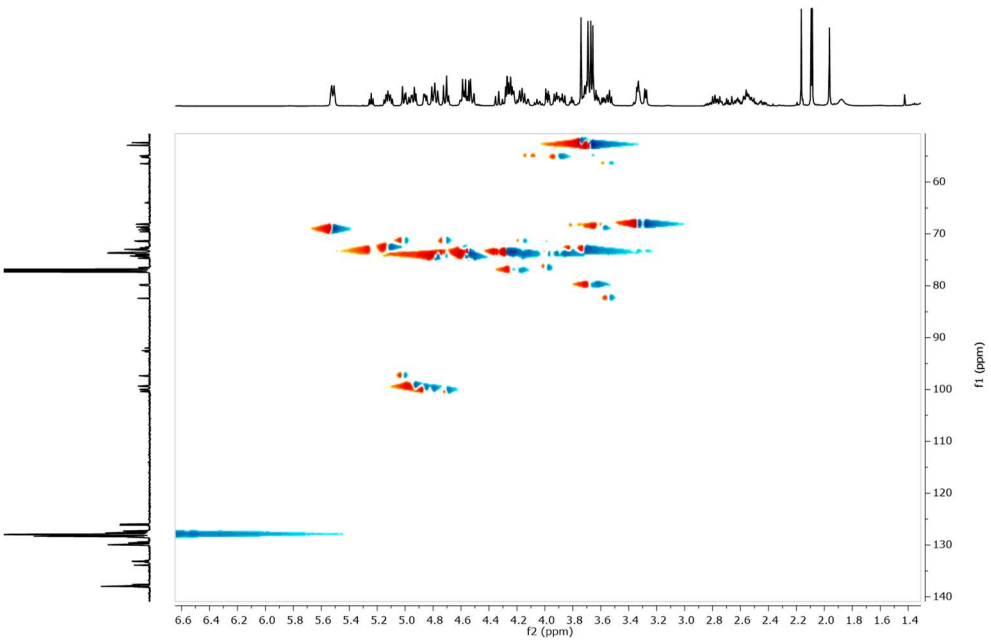
^{13}C-NMR ($CDCl_3$, 126 MHz) of **32**

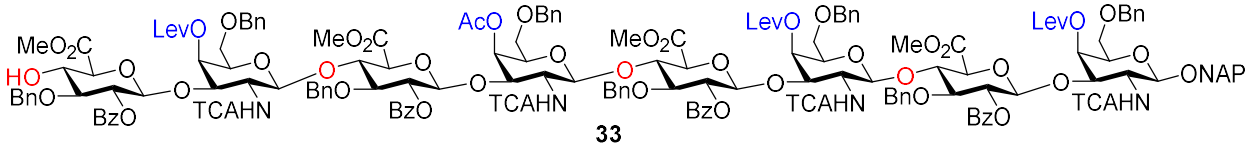


gCOSY ($CDCl_3$, 500 MHz) of **32**



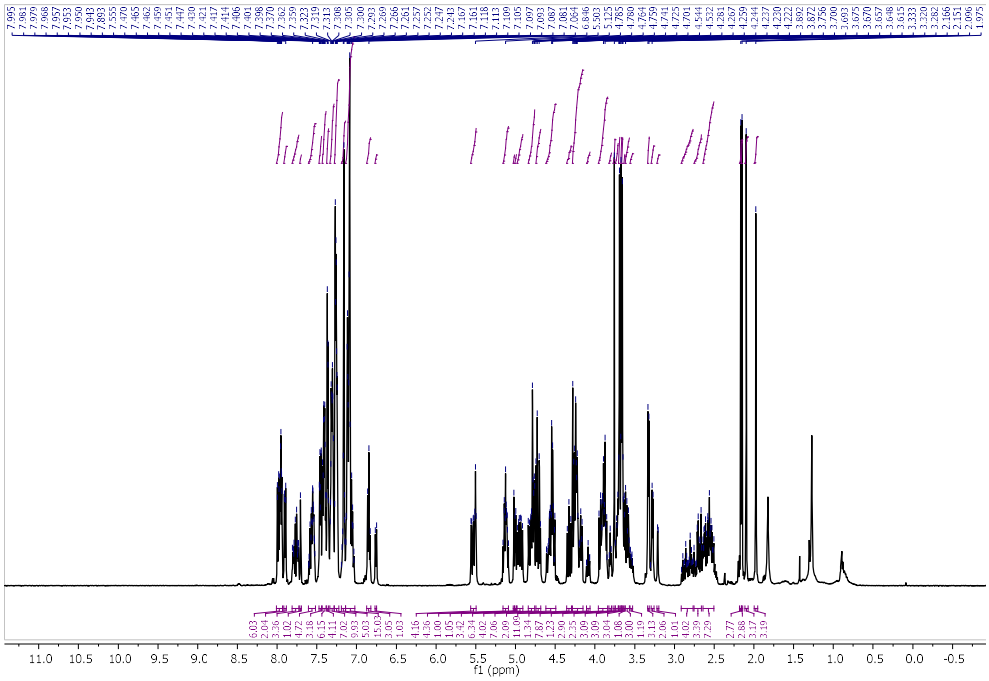
gHSQC ($CDCl_3$, 500 MHz) of **32**



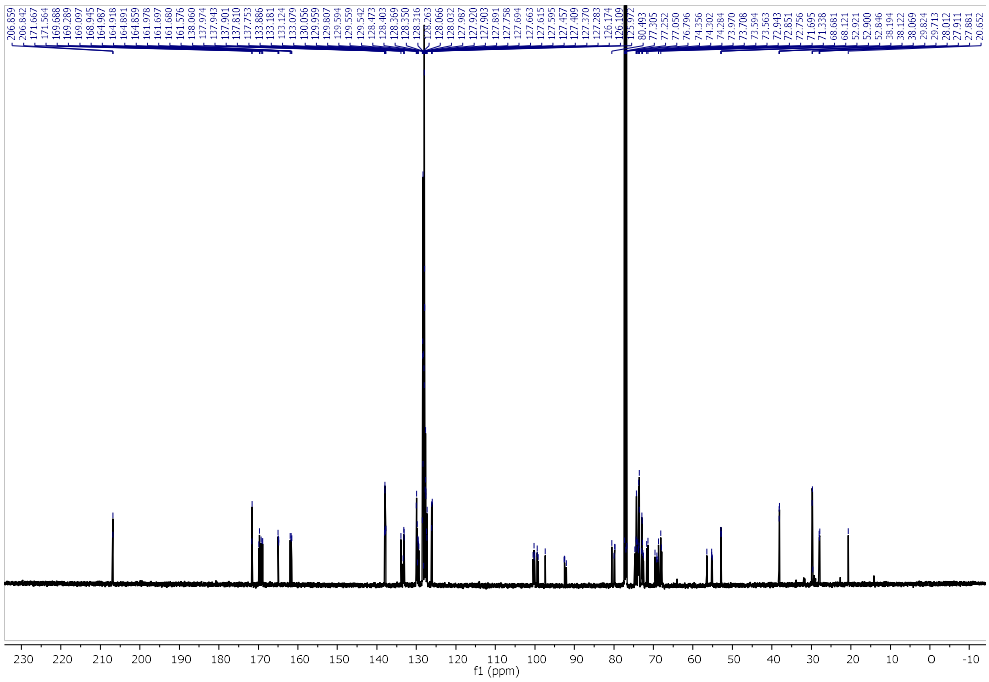


33

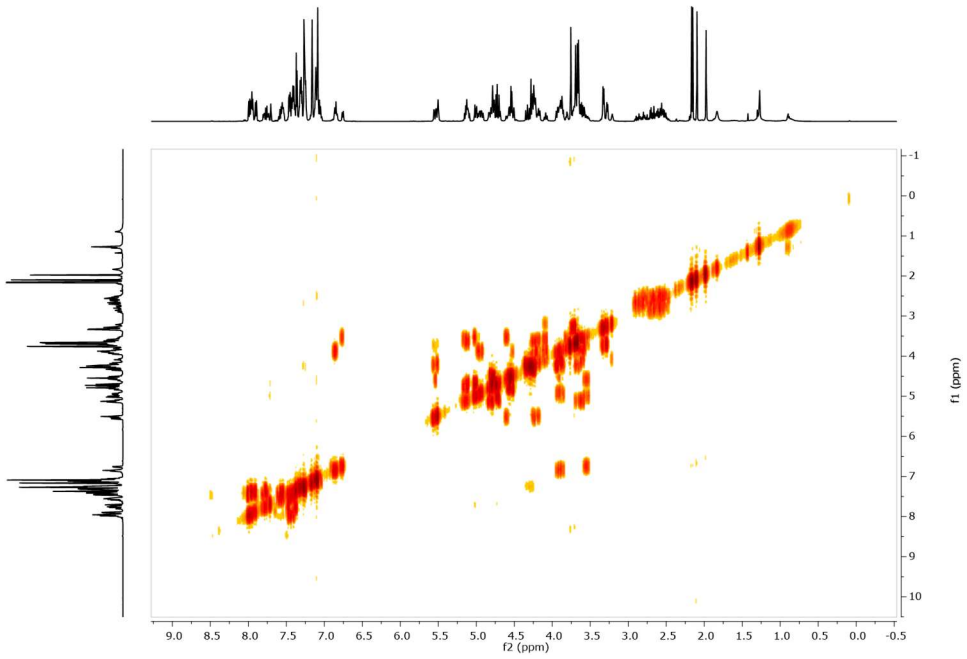
^{1}H-NMR ($CDCl_3$, 500 MHz) of **33**

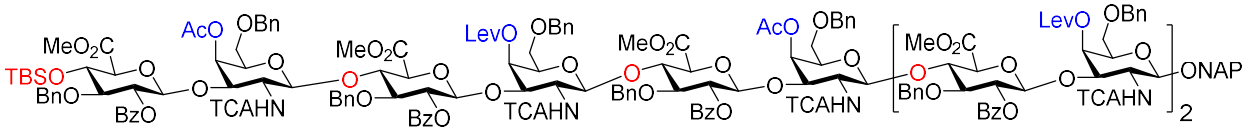


^{13}C-NMR ($CDCl_3$, 126 MHz) of **33**



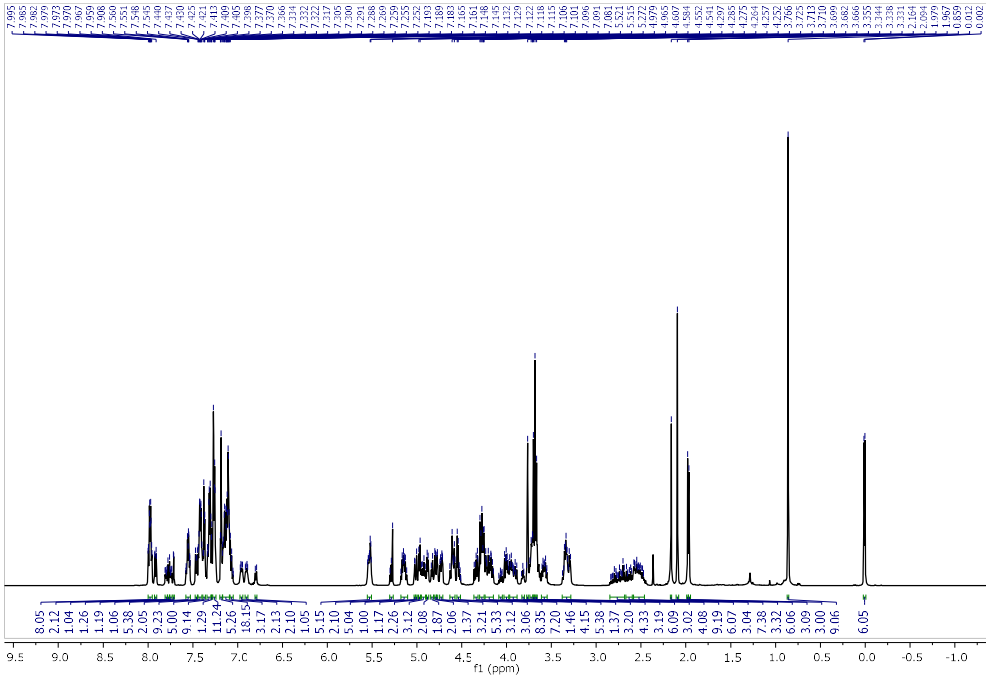
gCOSY ($CDCl_3$, 500 MHz) of **33**



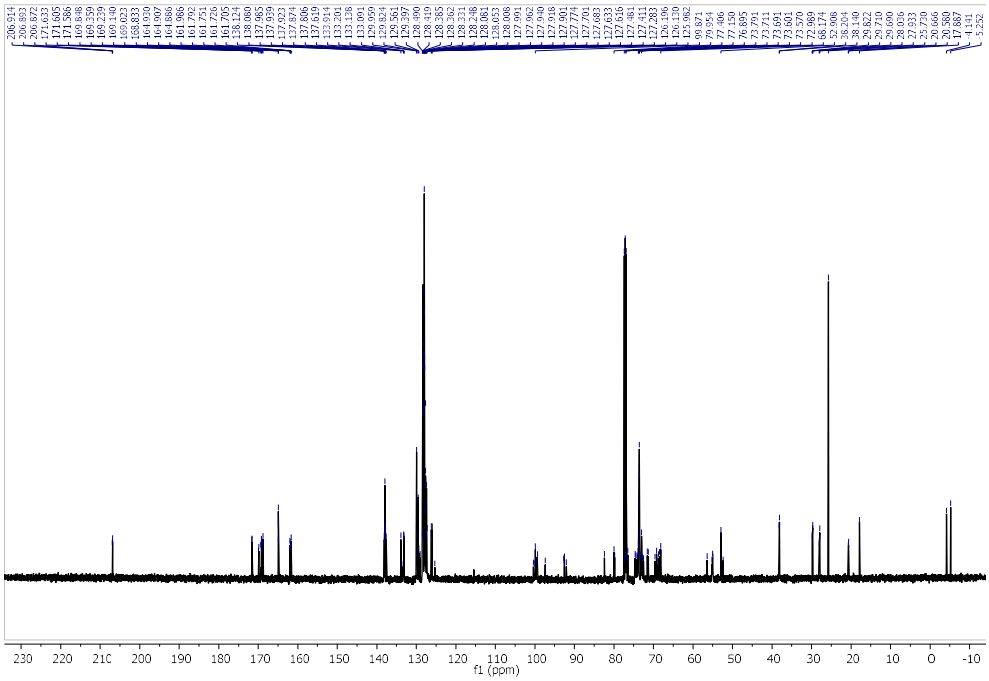


34

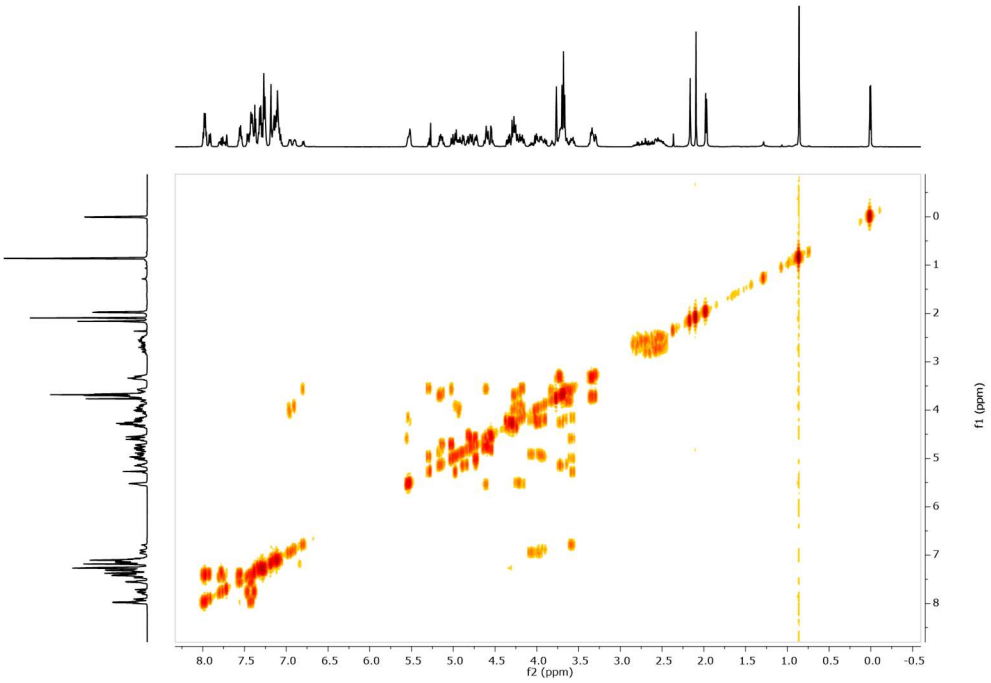
^{1}H-NMR ($CDCl_3$, 500 MHz) of **34**



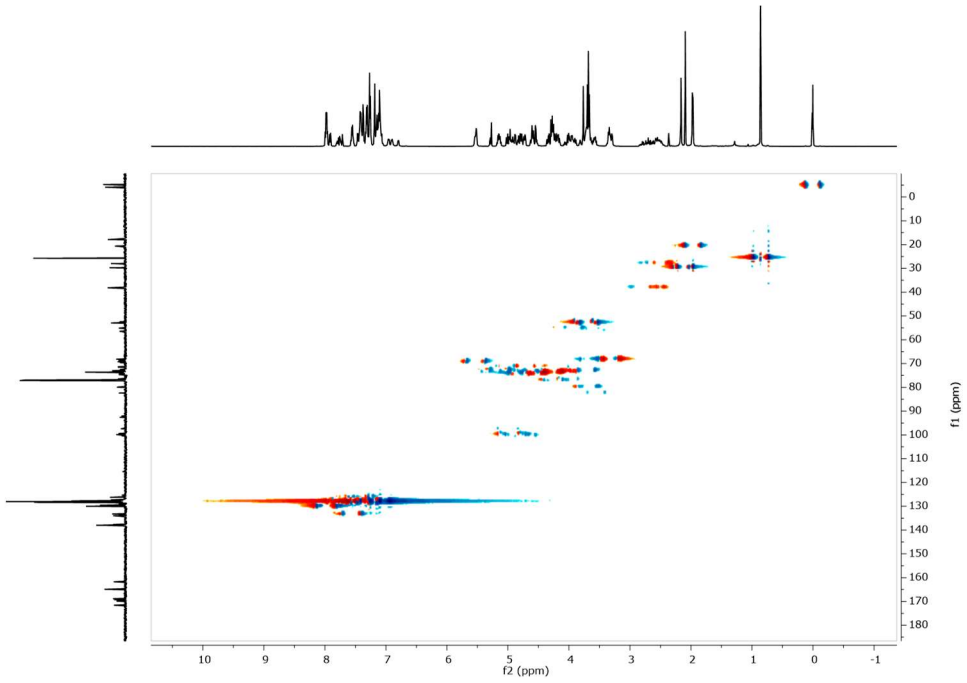
^{13}C-NMR ($CDCl_3$, 126 MHz) of **34**

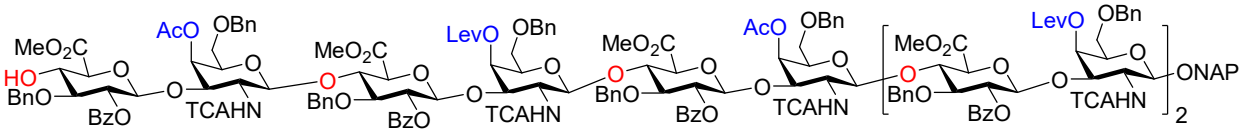


gCOSY ($CDCl_3$, 500 MHz) of **34**



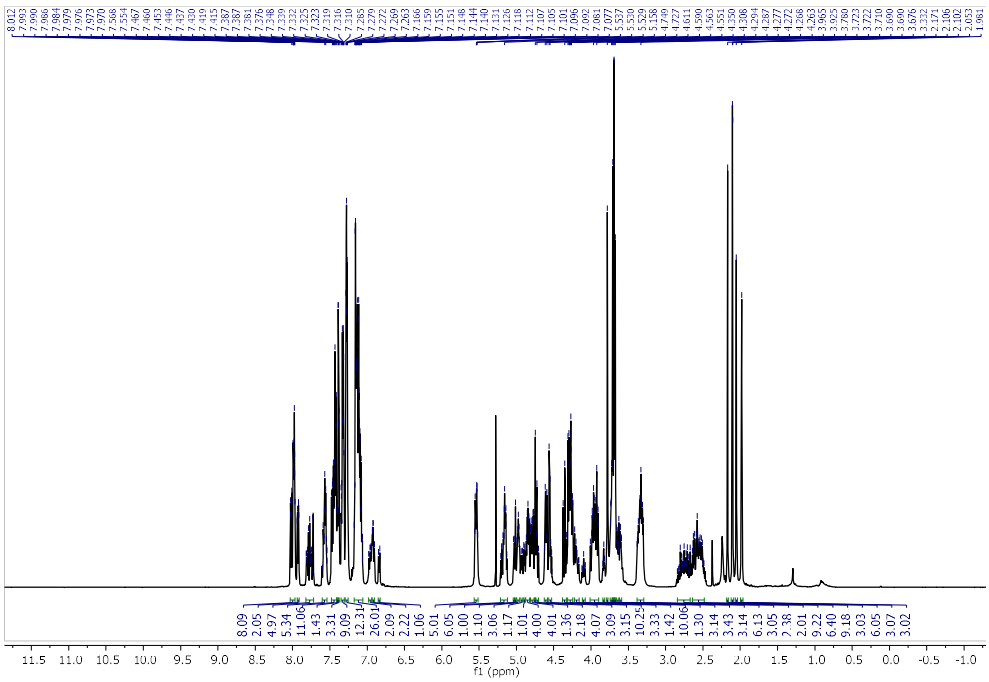
gHSQC ($CDCl_3$, 500 MHz) of **34**



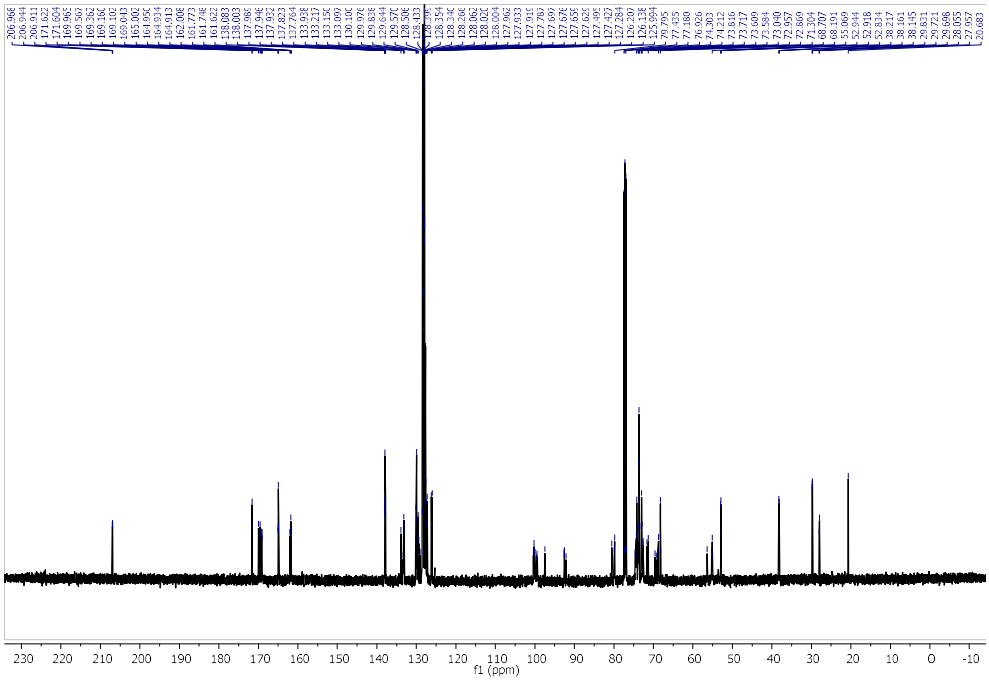


35

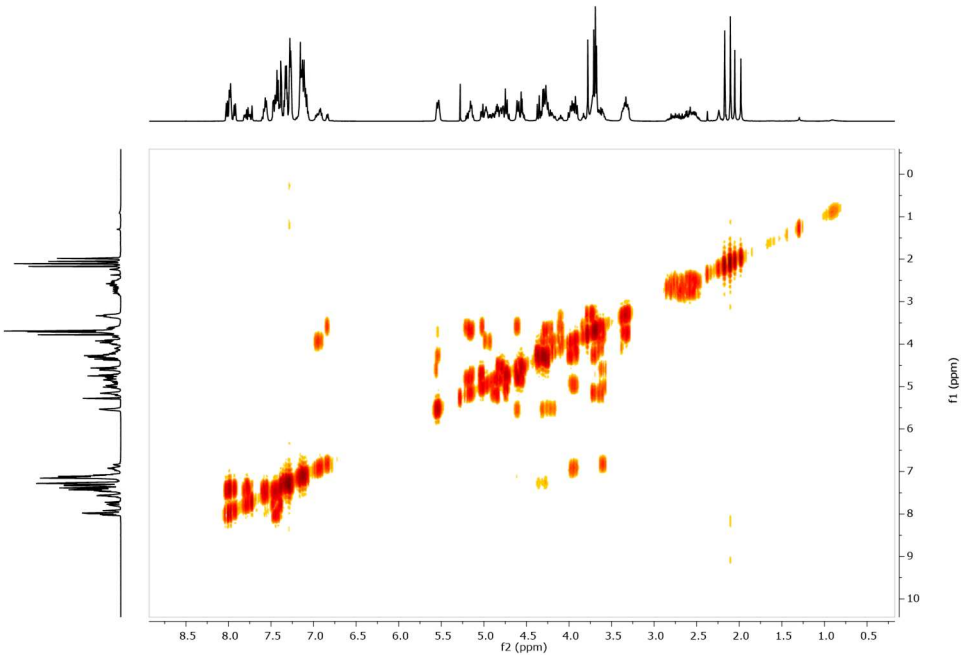
^{1}H-NMR ($CDCl_3$, 500 MHz) of **35**



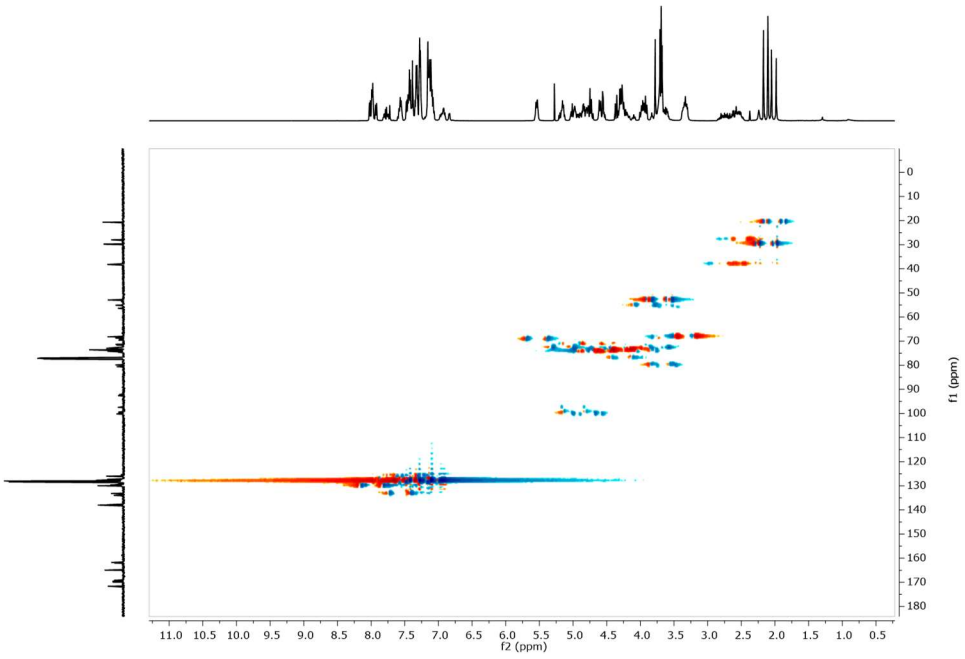
^{13}C-NMR ($CDCl_3$, 126 MHz) of **35**

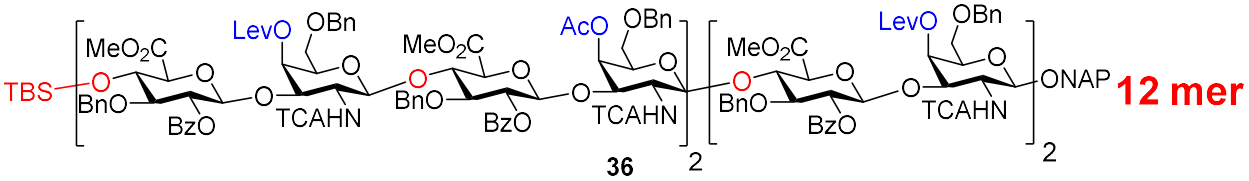


gCOSY ($CDCl_3$, 500 MHz) of **35**



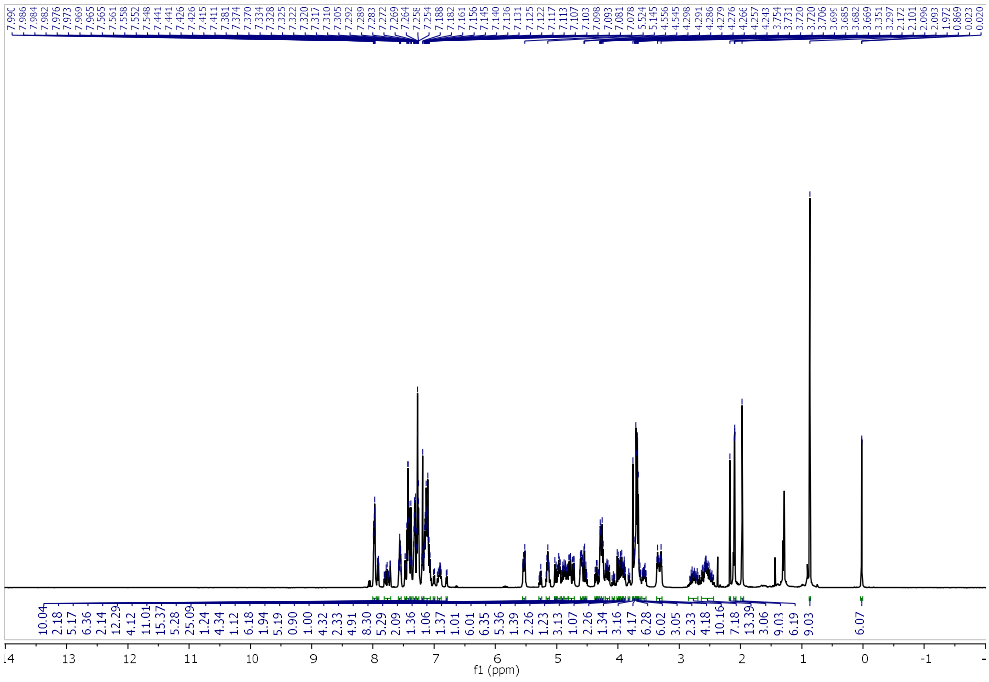
gHSQC ($CDCl_3$, 500 MHz) of **35**



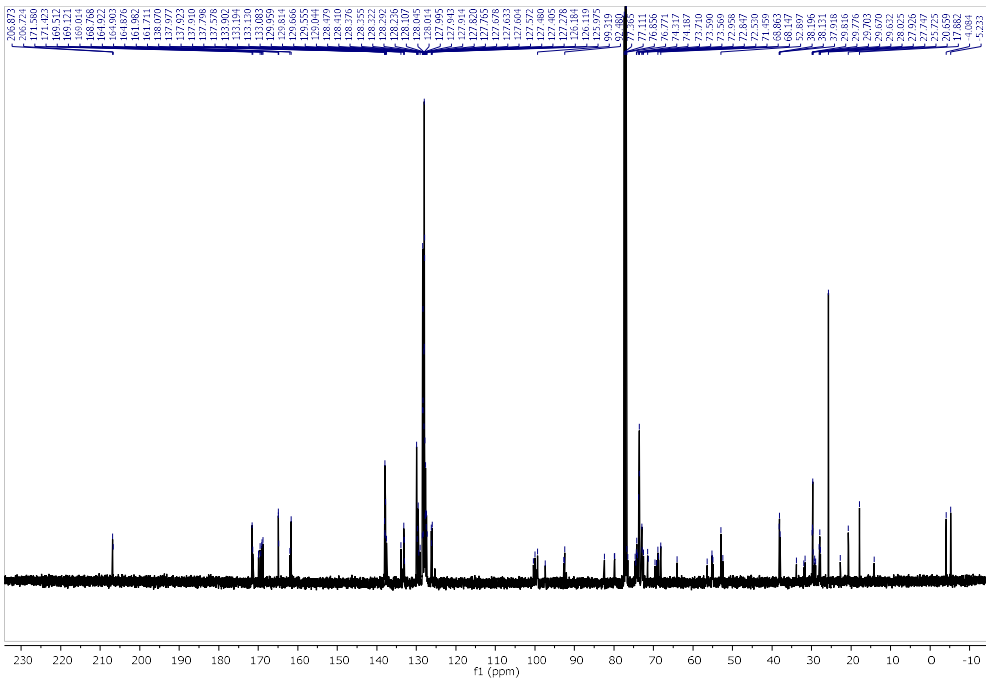


36

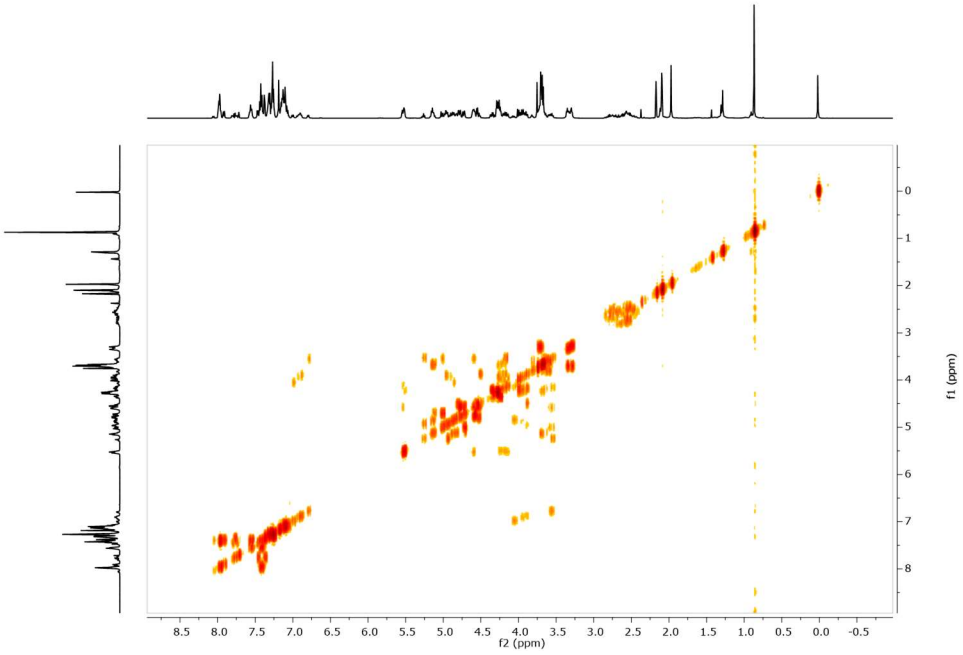
^{1}H-NMR ($CDCl_3$, 500 MHz) of **36**



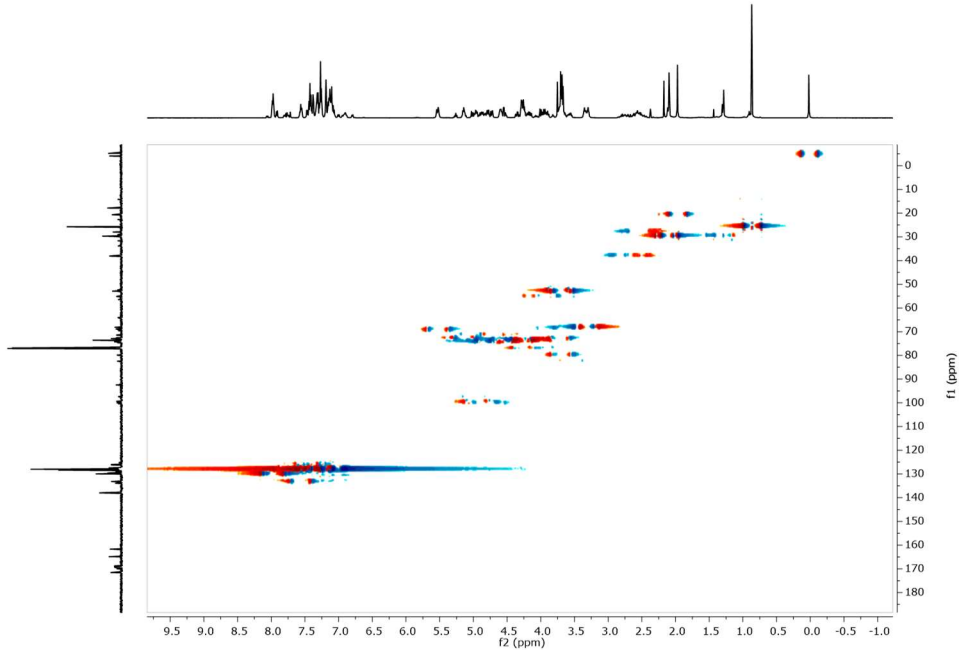
^{13}C-NMR ($CDCl_3$, 126 MHz) of **36**

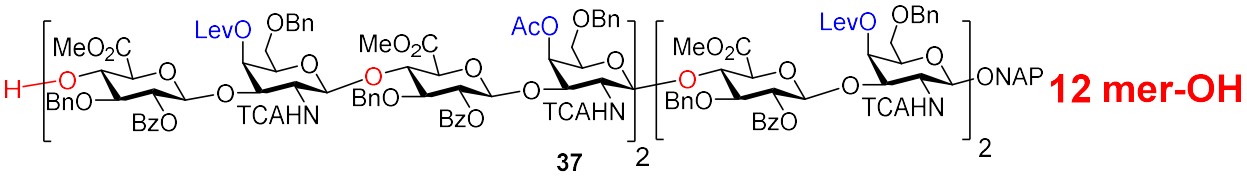


gCOSY ($CDCl_3$, 500 MHz) of **36**

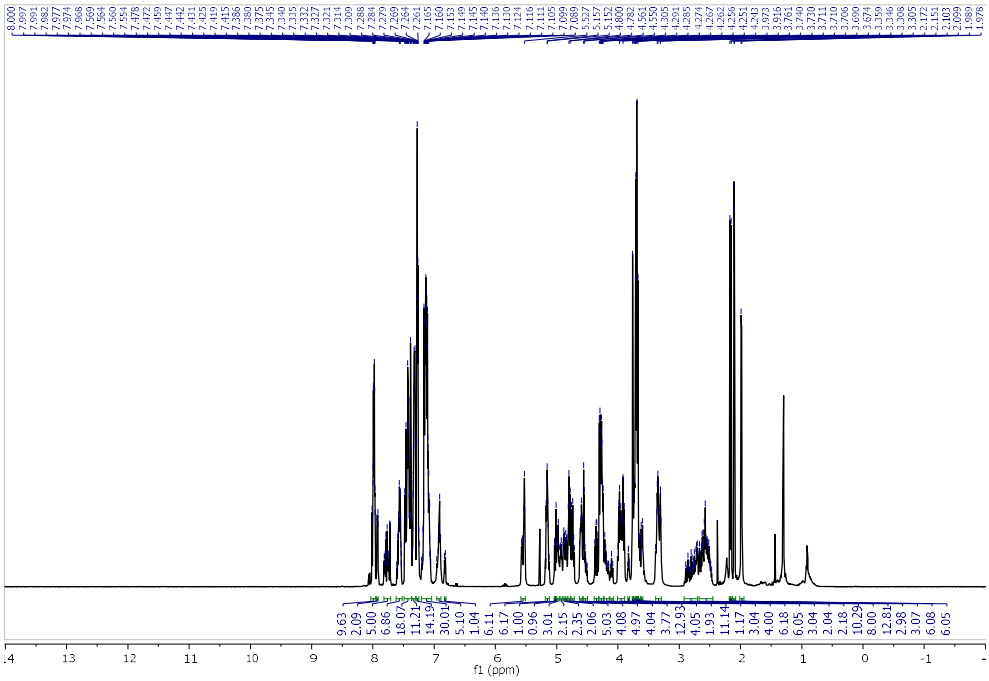


gHSQC ($CDCl_3$, 500 MHz) of **36**

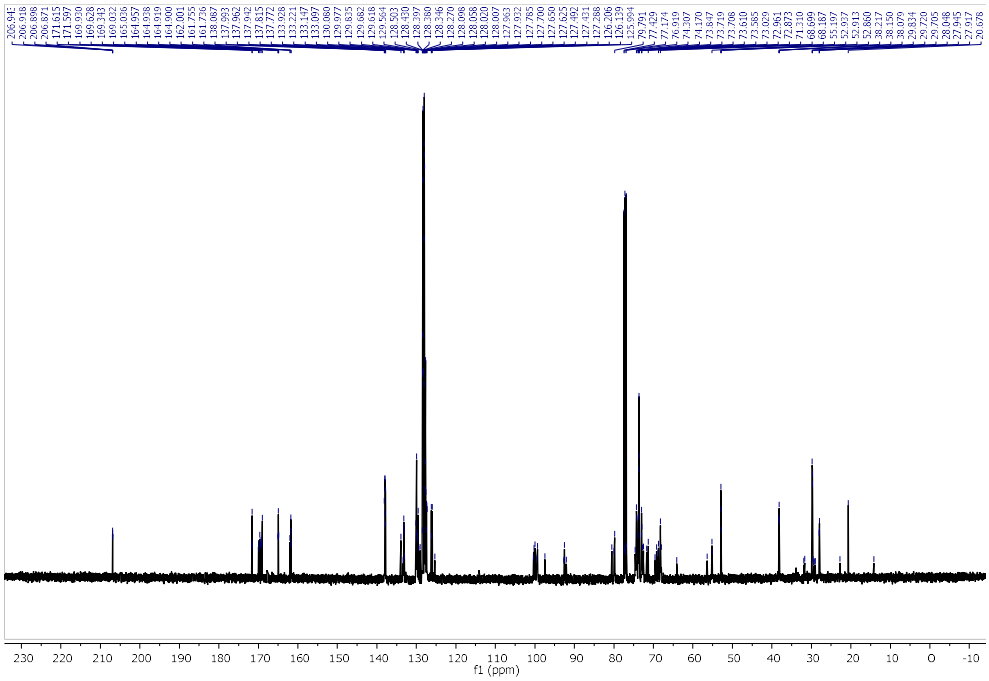




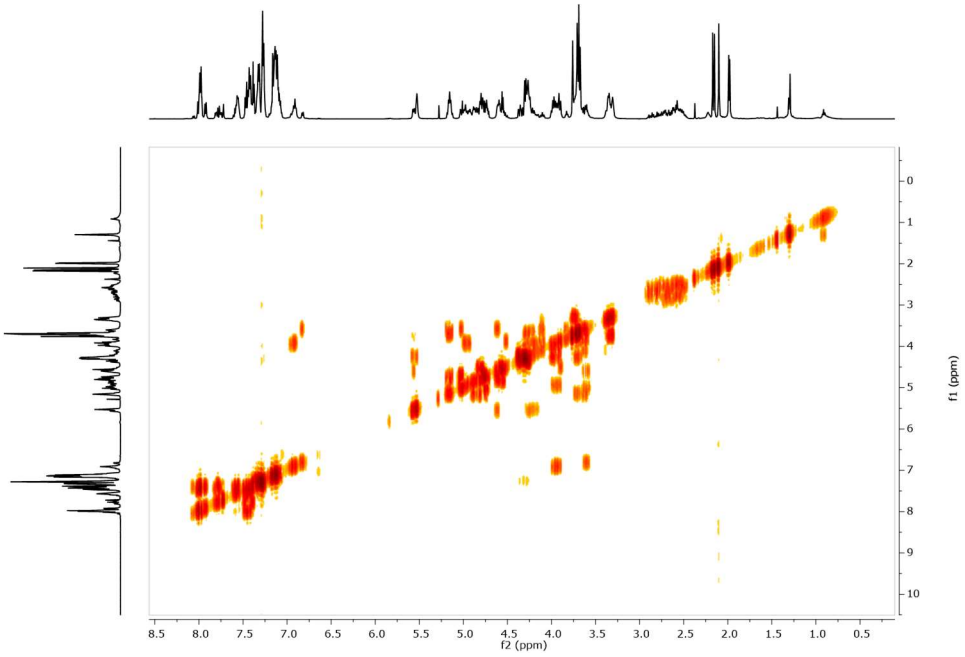
^{1}H-NMR ($CDCl_3$, 500 MHz) of **37**



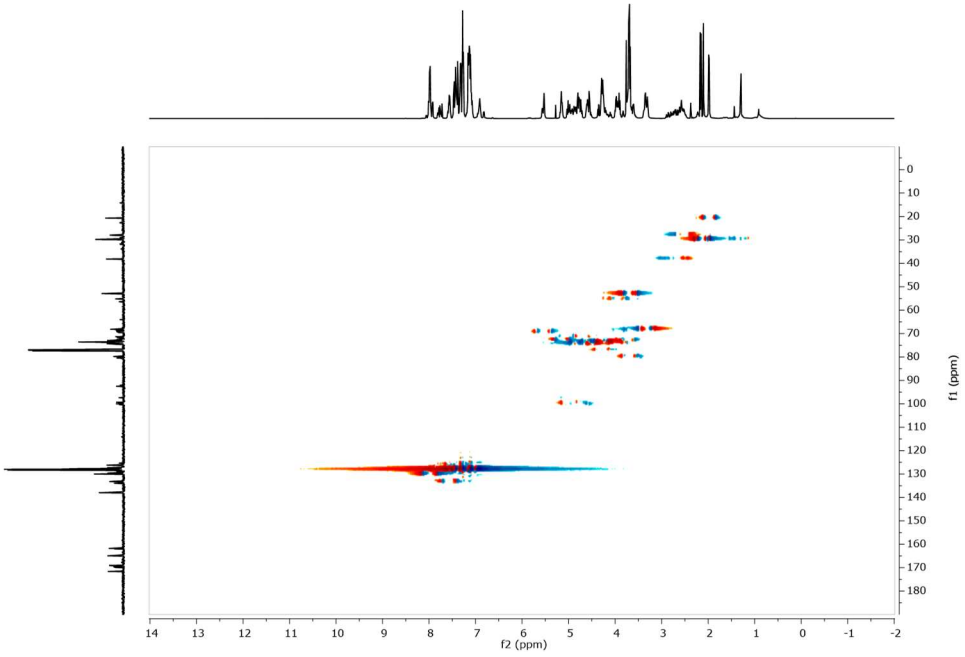
^{13}C-NMR ($CDCl_3$, 126 MHz) of **37**

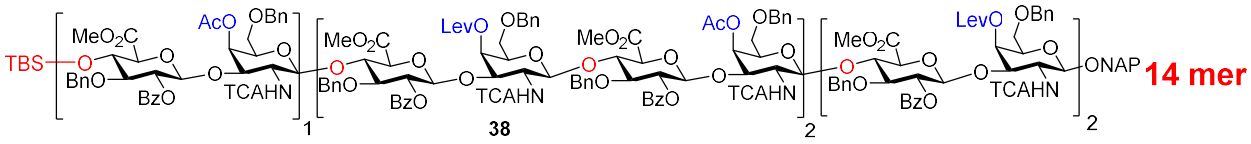


gCOSY ($CDCl_3$, 500 MHz) of **37**

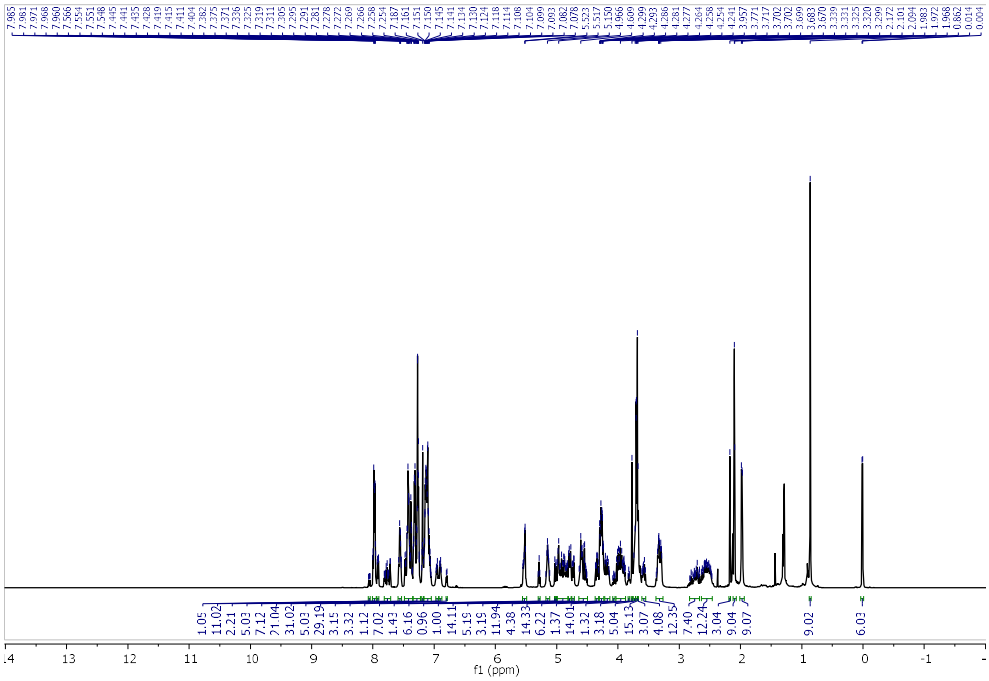


gHSQC ($CDCl_3$, 500 MHz) of **37**

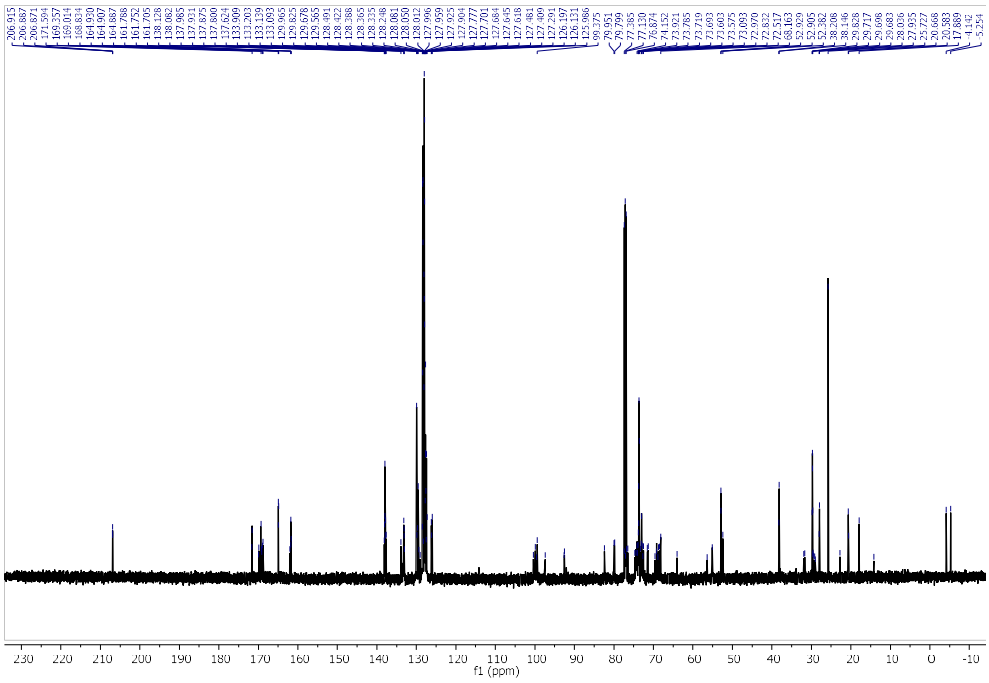




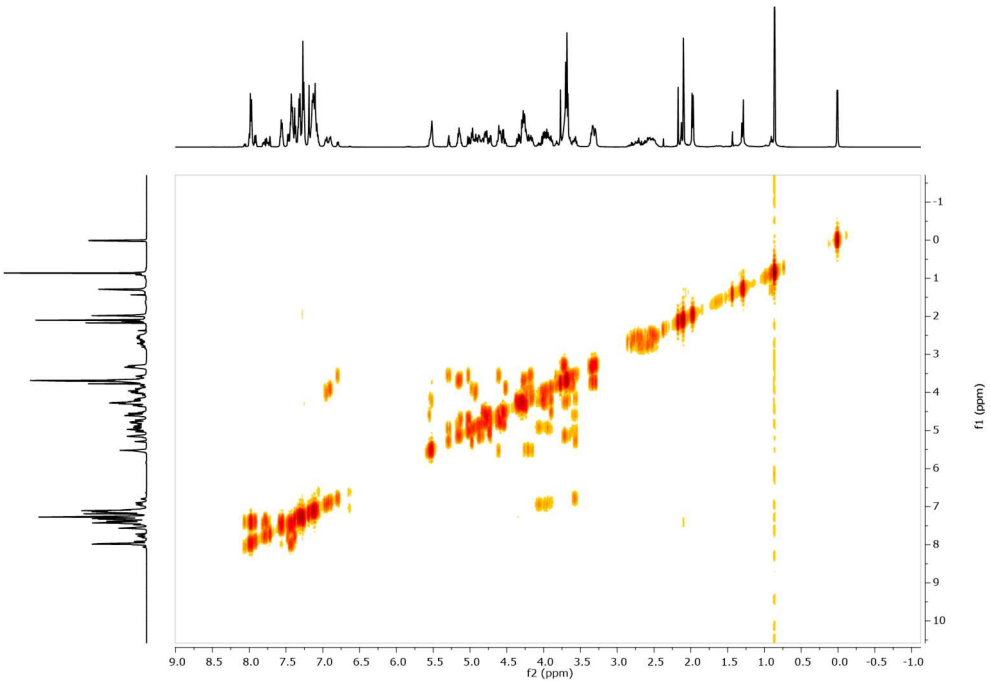
^{1}H-NMR ($CDCl_3$, 500 MHz) of **38**



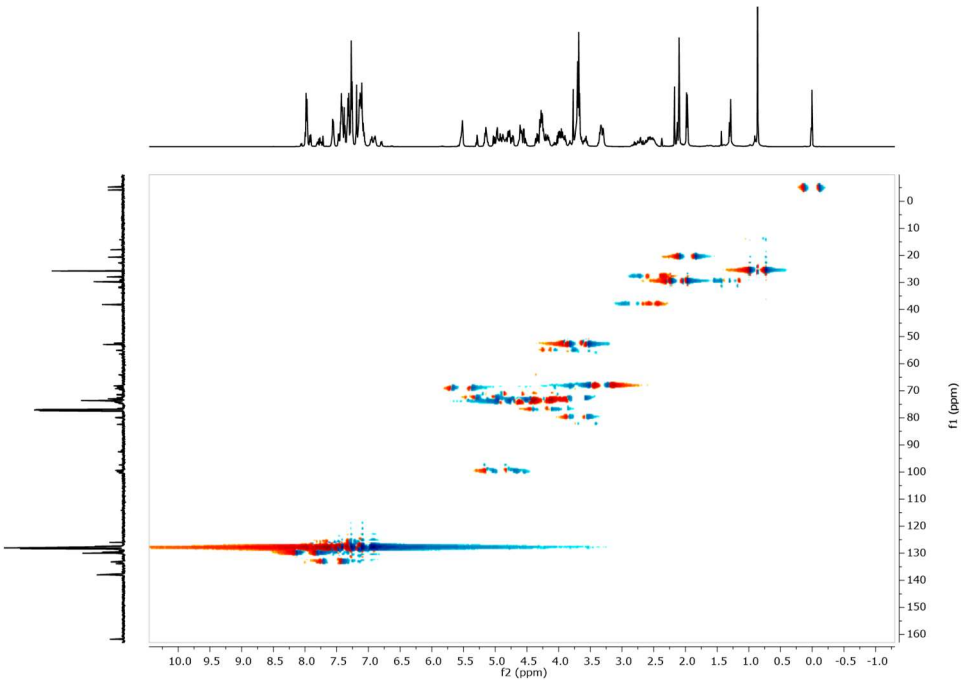
^{13}C-NMR ($CDCl_3$, 126 MHz) of **38**

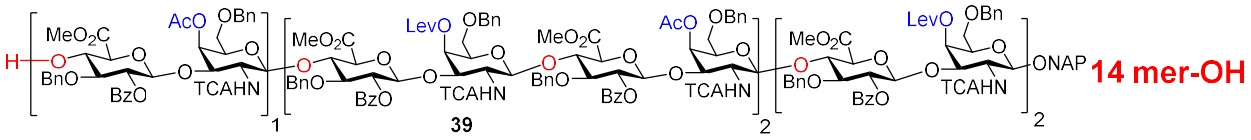


gCOSY ($CDCl_3$, 500 MHz) of **38**

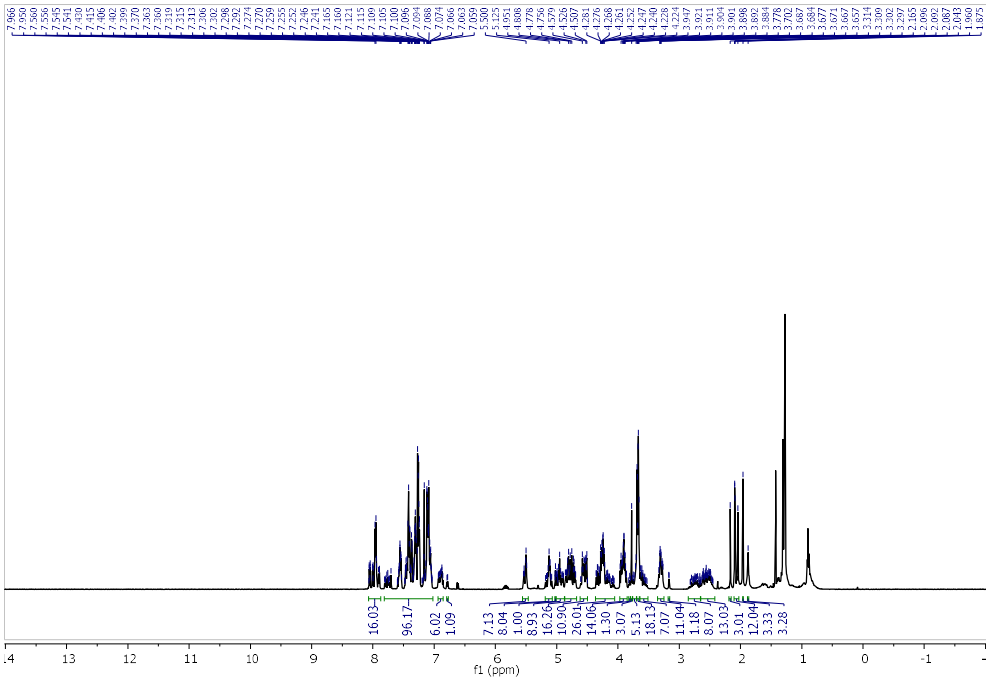


gHSQC ($CDCl_3$, 500 MHz) of **38**

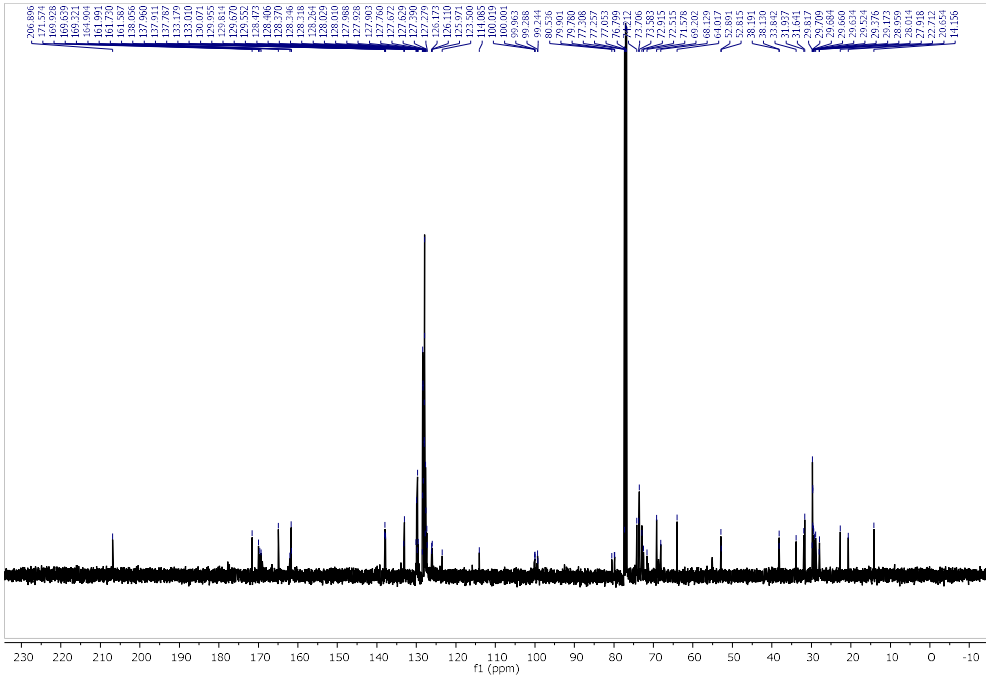




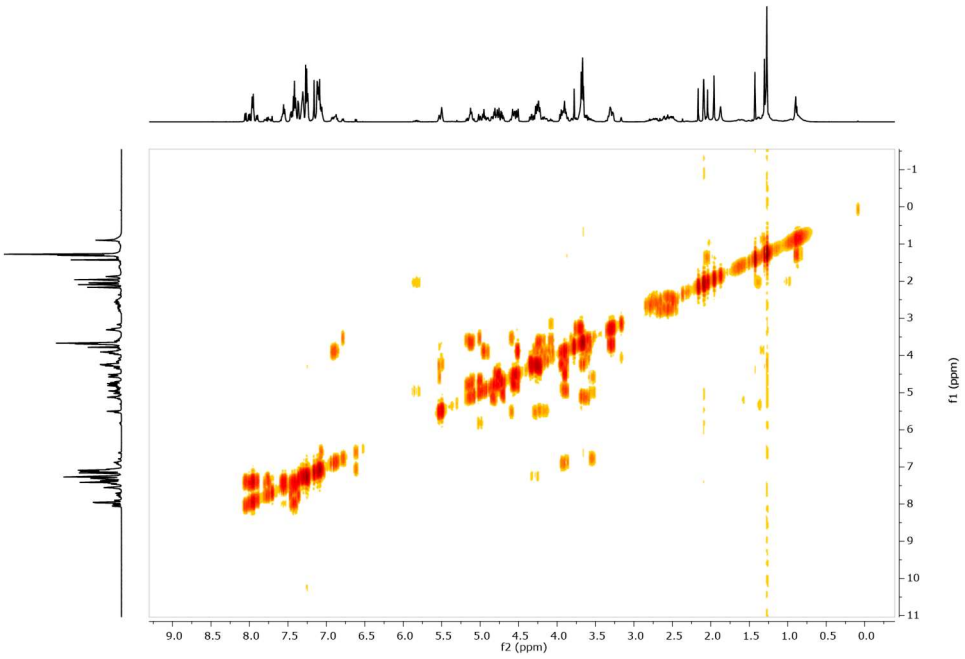
^{1}H-NMR ($CDCl_3$, 500 MHz) of **39**



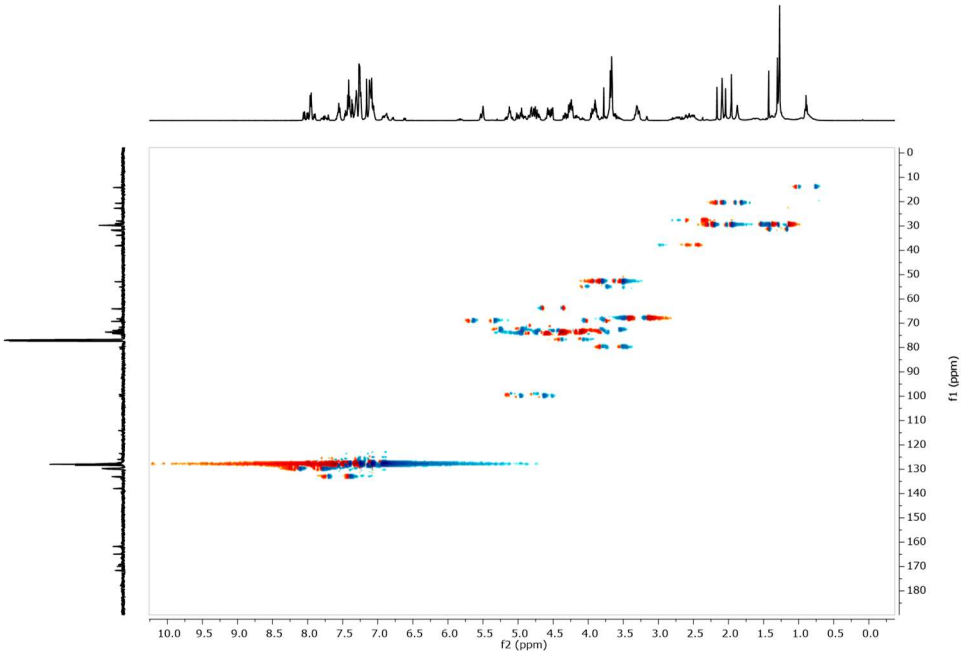
^{13}C-NMR ($CDCl_3$, 126 MHz) of **39**

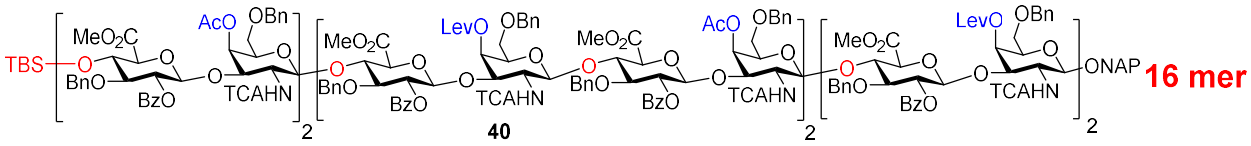


gCOSY ($CDCl_3$, 500 MHz) of **39**

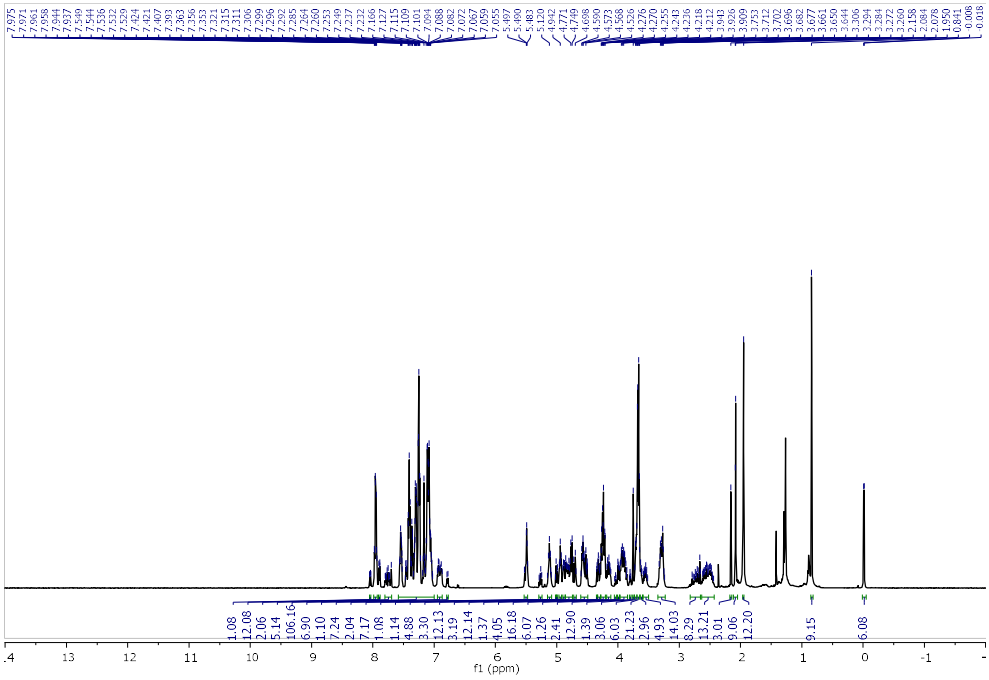


gHSQC ($CDCl_3$, 500 MHz) of **39**

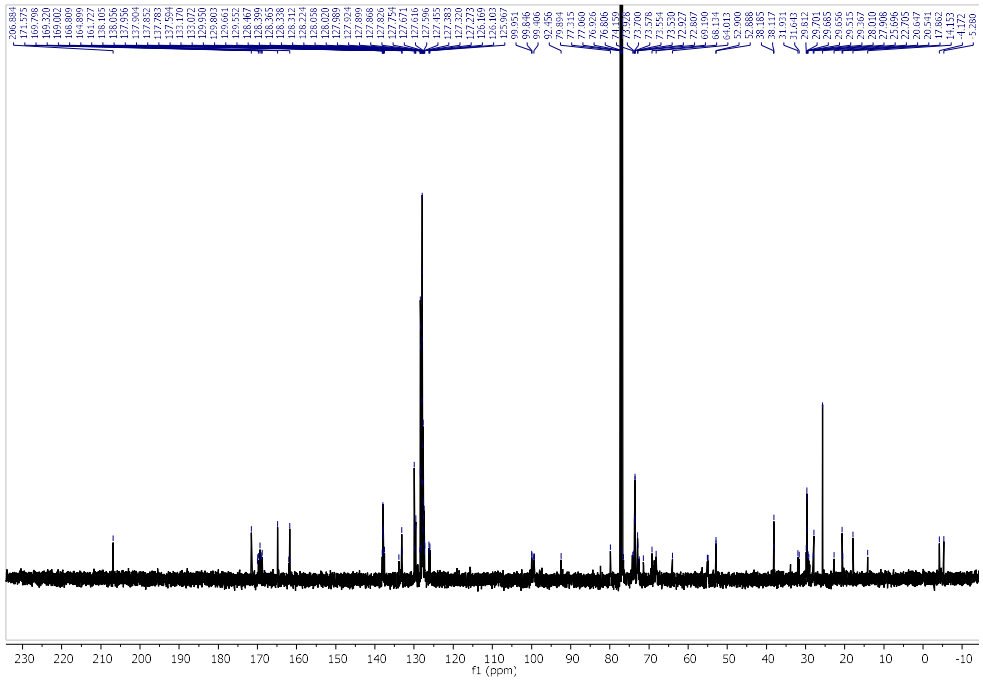




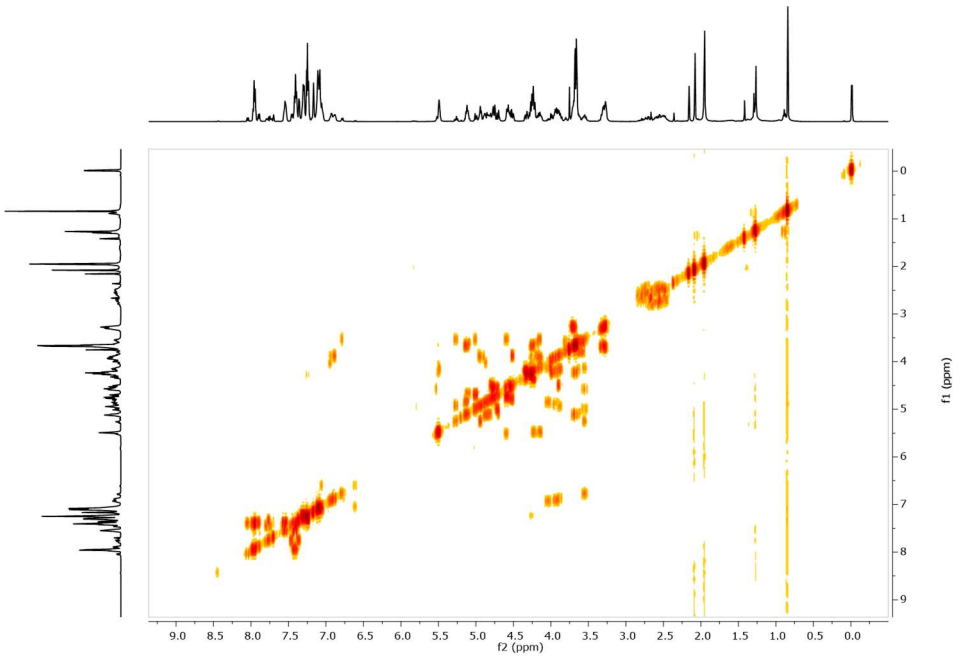
^{1}H-NMR ($CDCl_3$, 500 MHz) of **40**



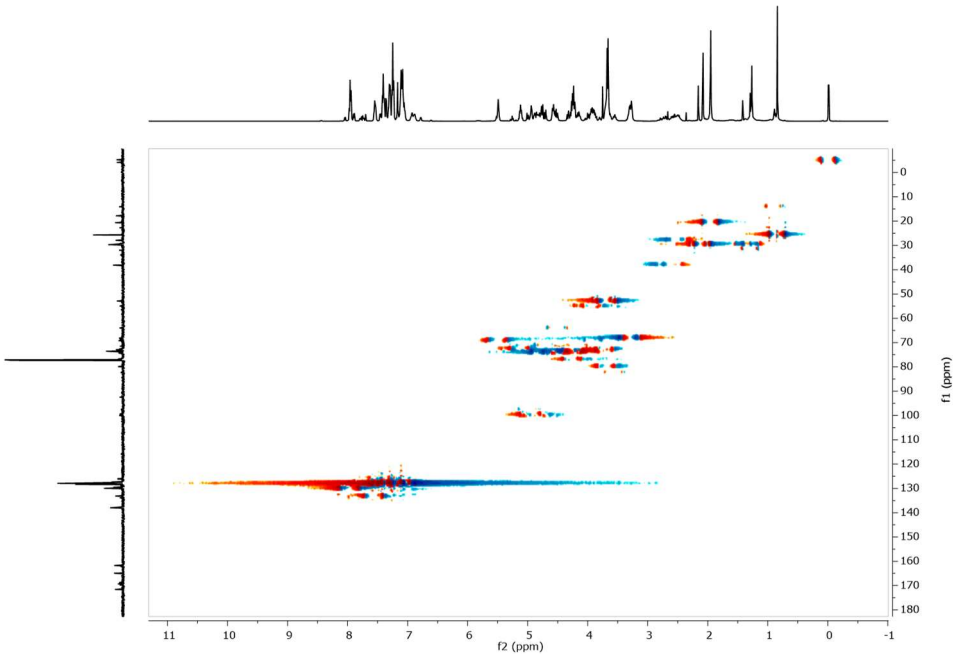
^{13}C-NMR ($CDCl_3$, 126 MHz) of **40**

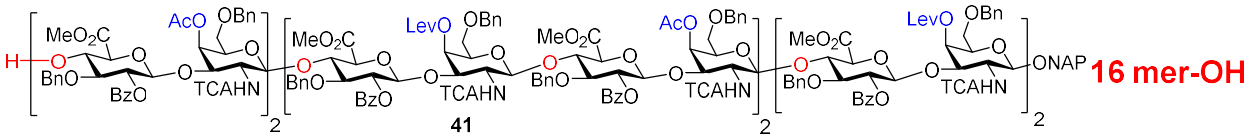


gCOSY ($CDCl_3$, 500 MHz) of **40**



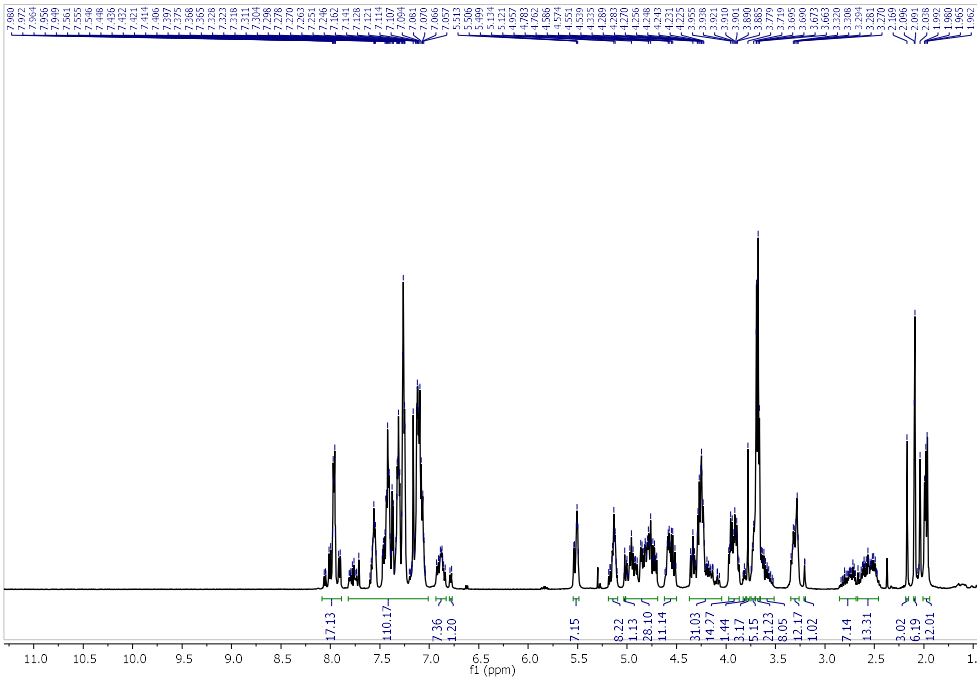
gHSQC ($CDCl_3$, 500 MHz) of **40**



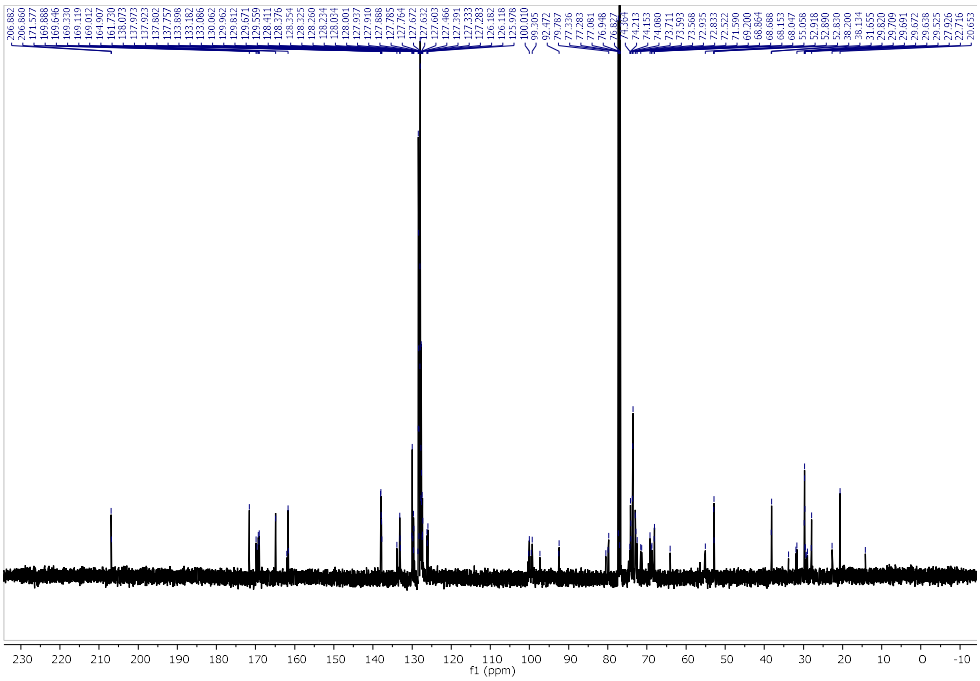


41

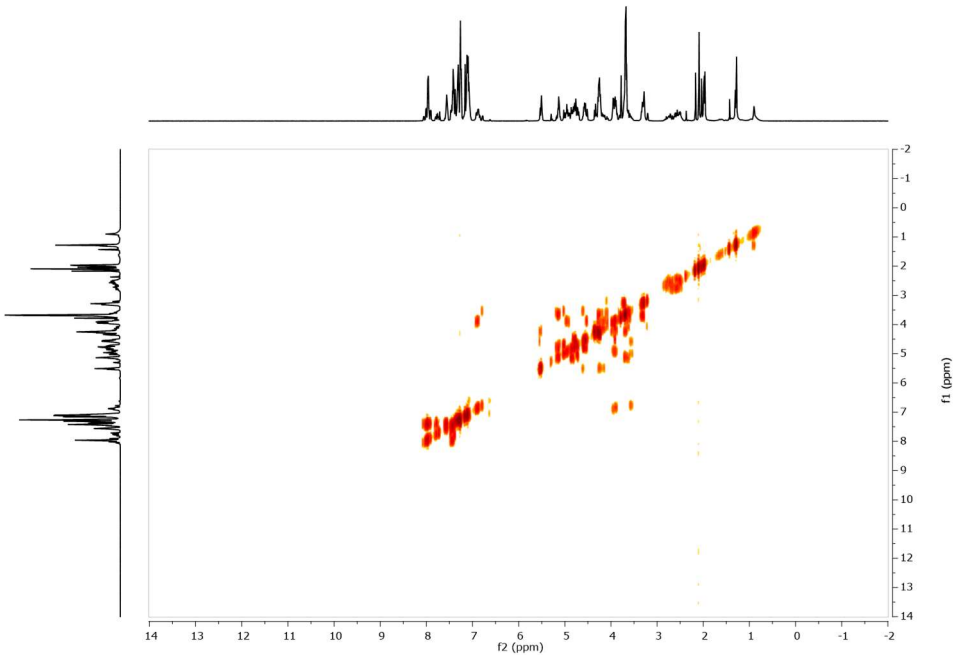
^{1}H-NMR ($CDCl_3$, 500 MHz) of **41**



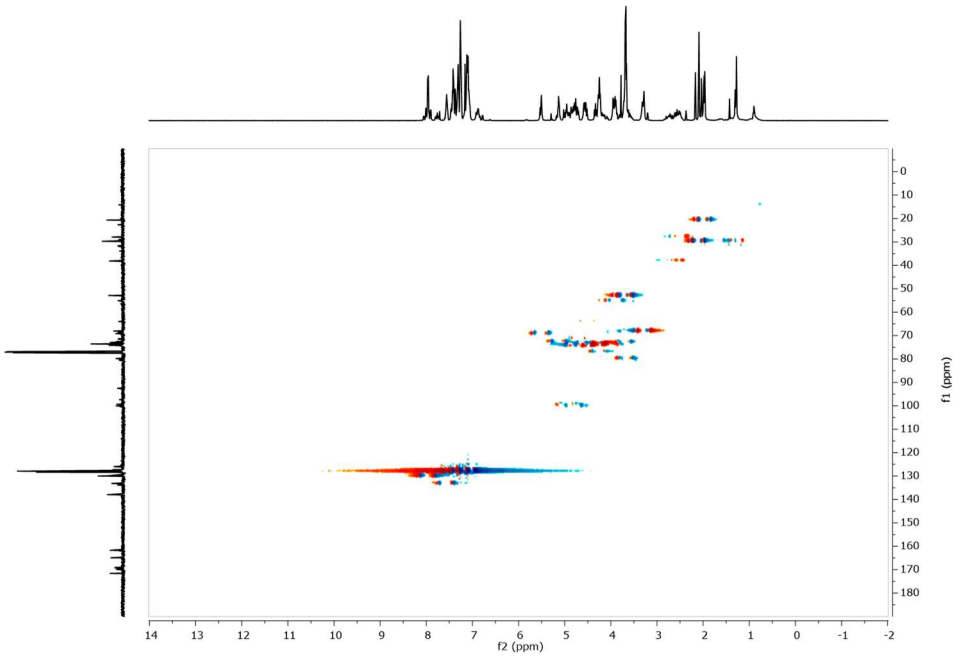
^{13}C-NMR ($CDCl_3$, 126 MHz) of **41**

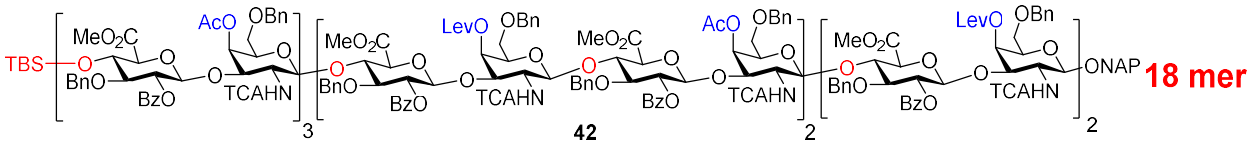


gCOSY ($CDCl_3$, 500 MHz) of **41**

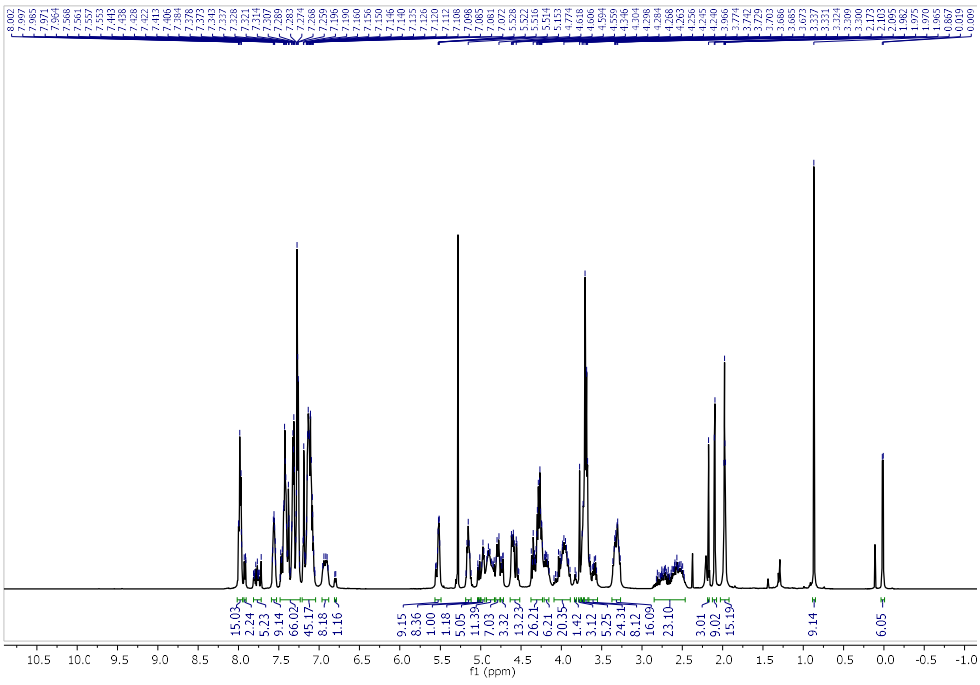


gHSQC ($CDCl_3$, 500 MHz) of **41**

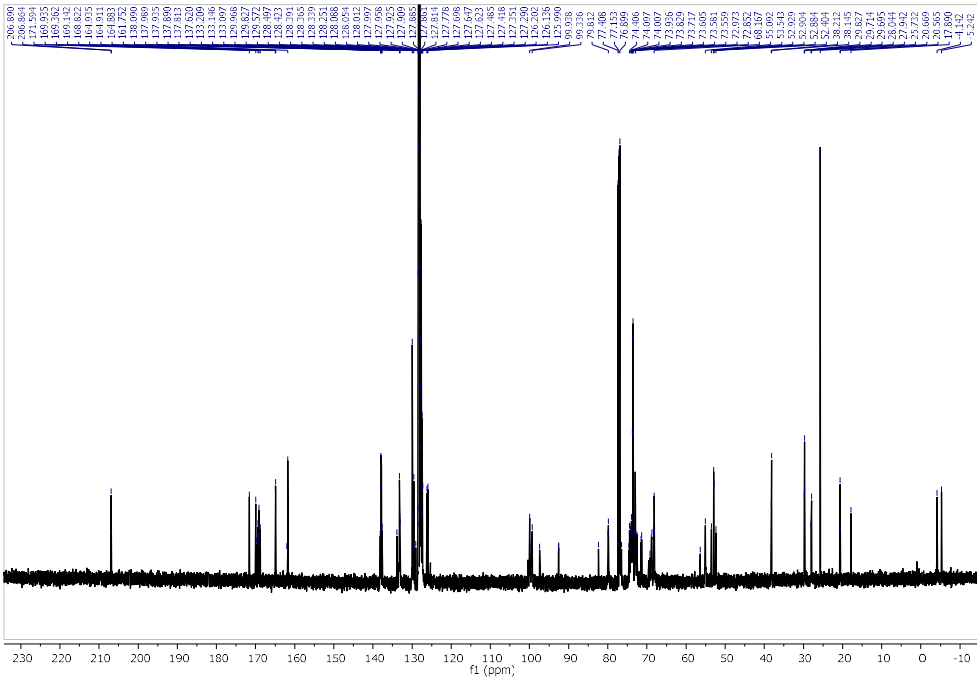




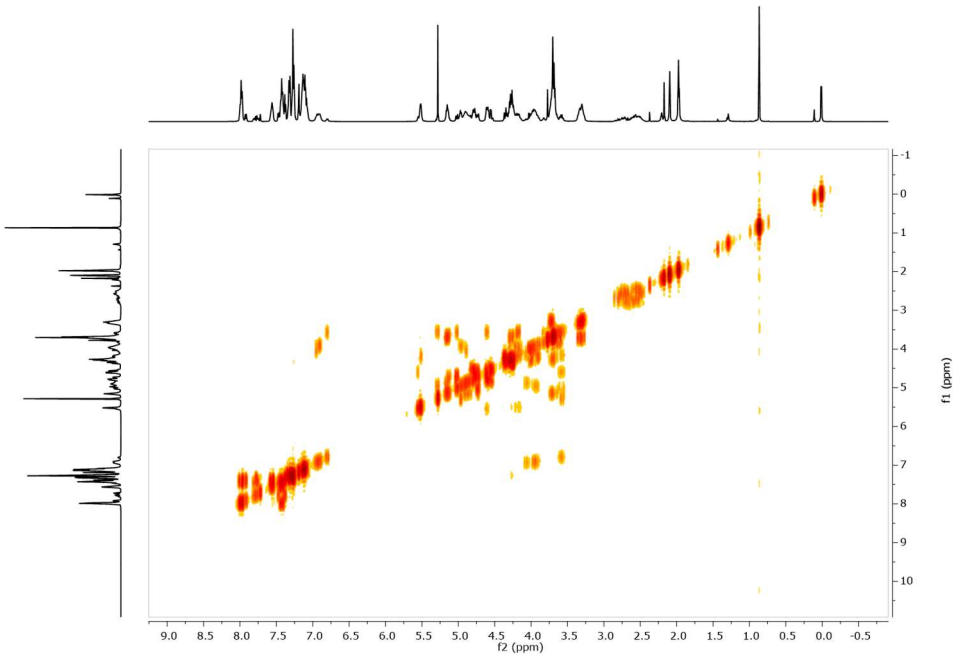
^{1}H-NMR ($CDCl_3$, 500 MHz) of **42**



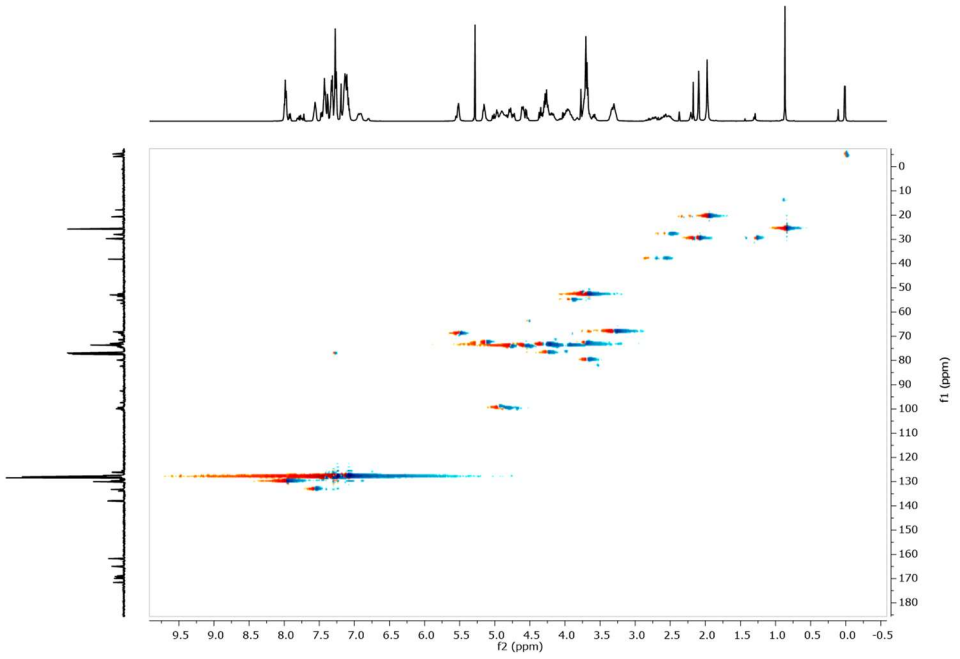
^{13}C-NMR ($CDCl_3$, 126 MHz) of **42**

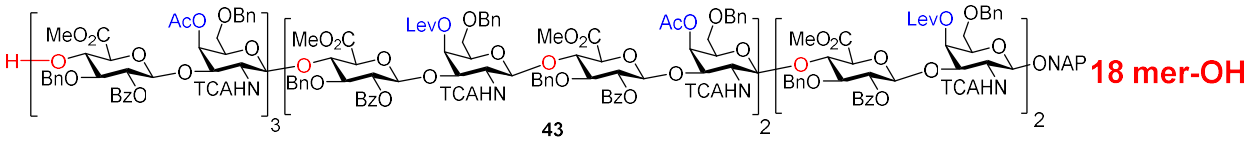


gCOSY ($CDCl_3$, 500 MHz) of **42**



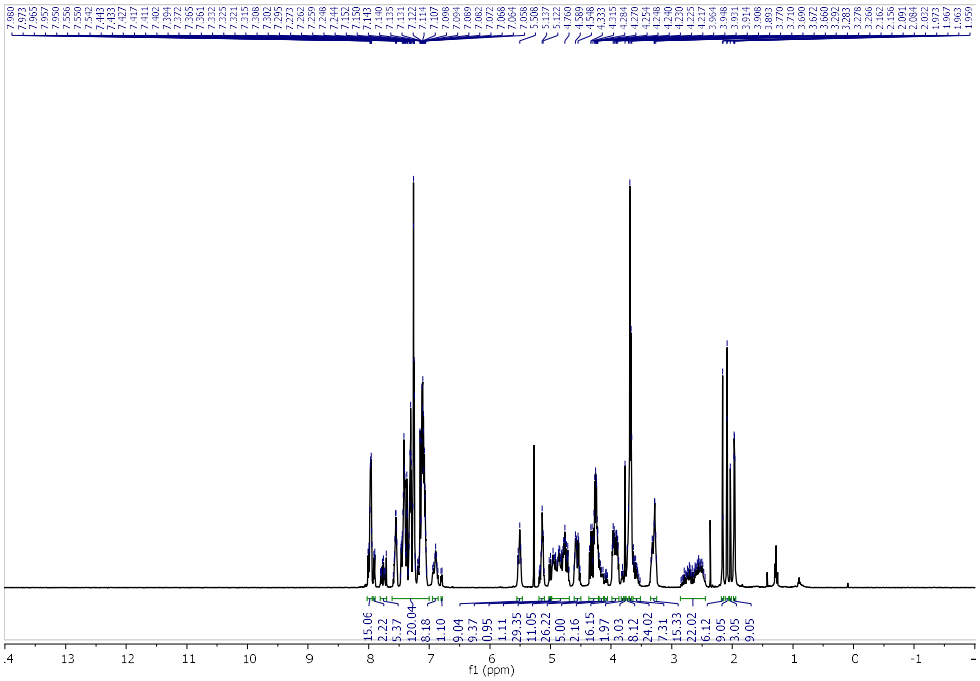
gHSQC ($CDCl_3$, 500 MHz) of **42**



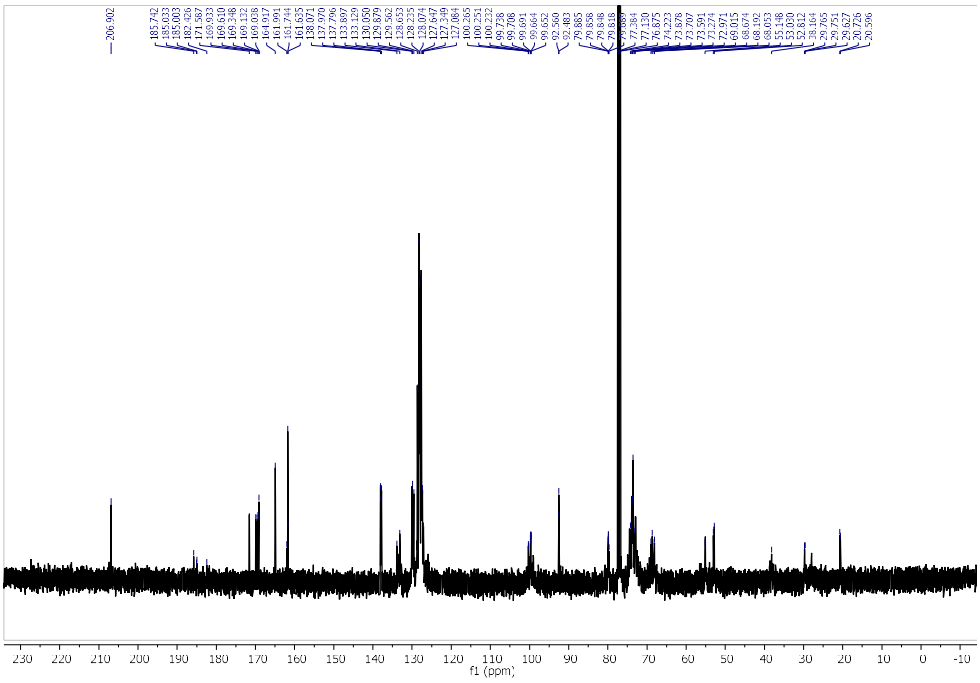


43

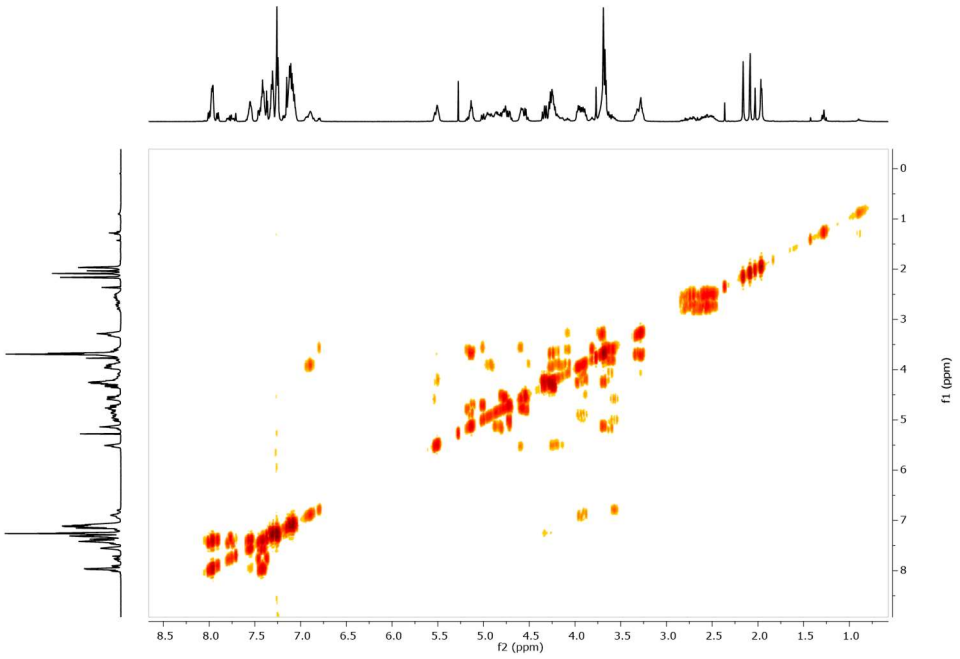
^{1}H-NMR ($CDCl_3$, 500 MHz) of **43**



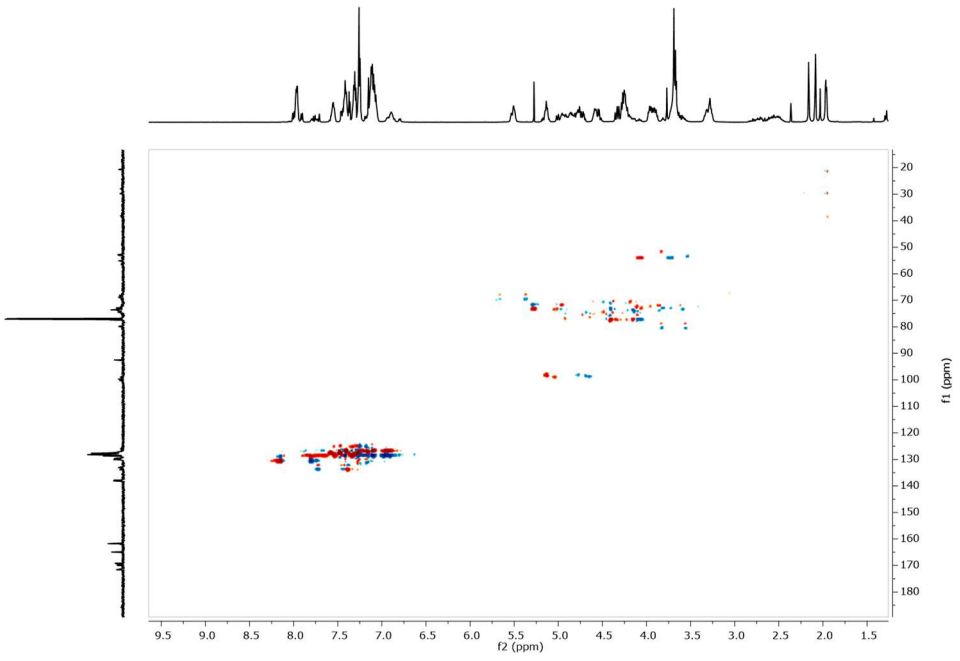
^{13}C-NMR ($CDCl_3$, 126 MHz) of **43**

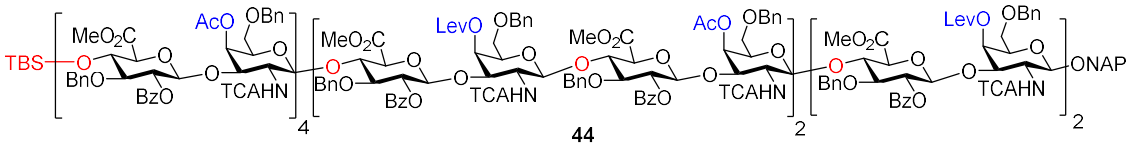


gCOSY ($CDCl_3$, 500 MHz) of **43**



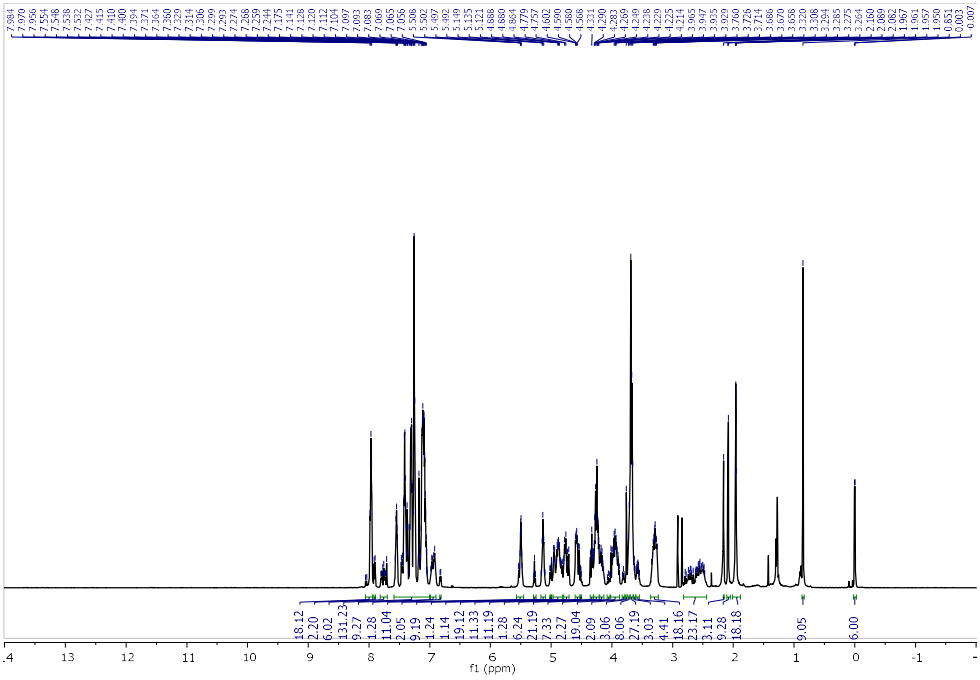
gHSQC ($CDCl_3$, 500 MHz) of **43**



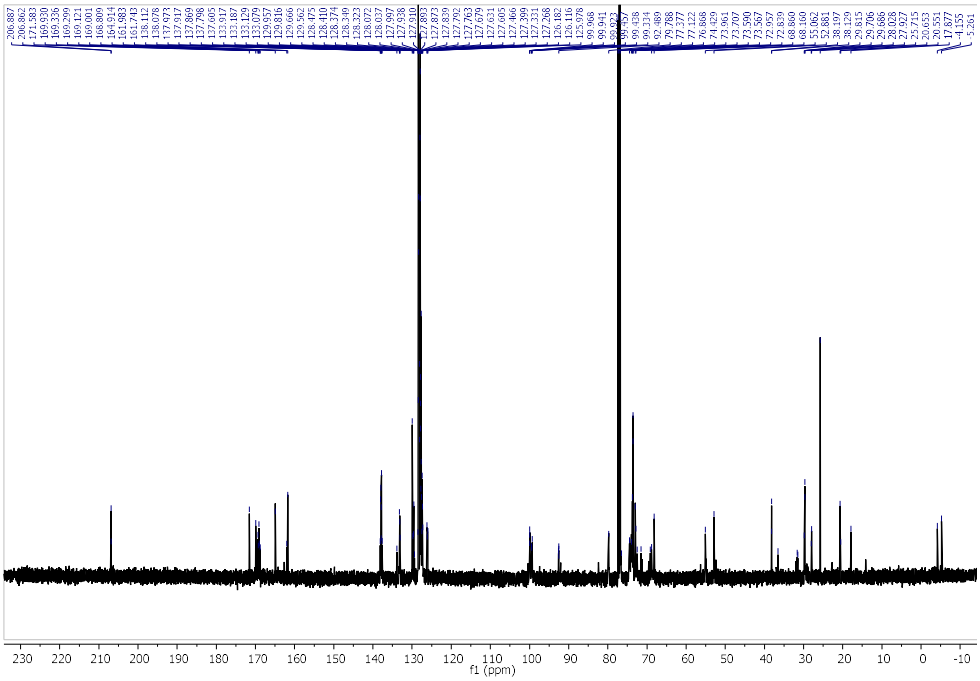


44

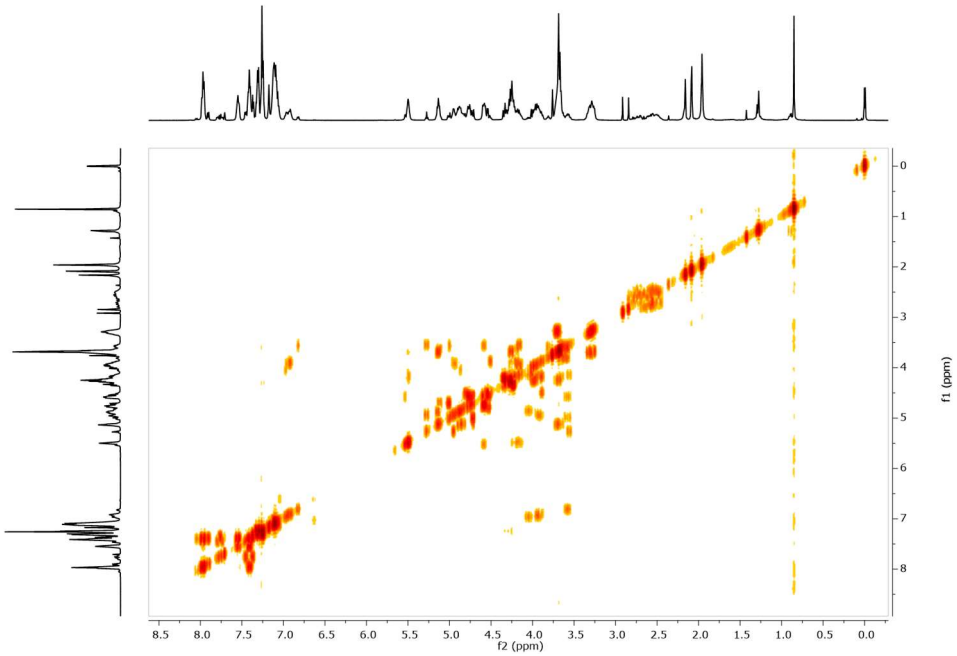
^{1}H-NMR ($CDCl_3$, 500 MHz) of **44**



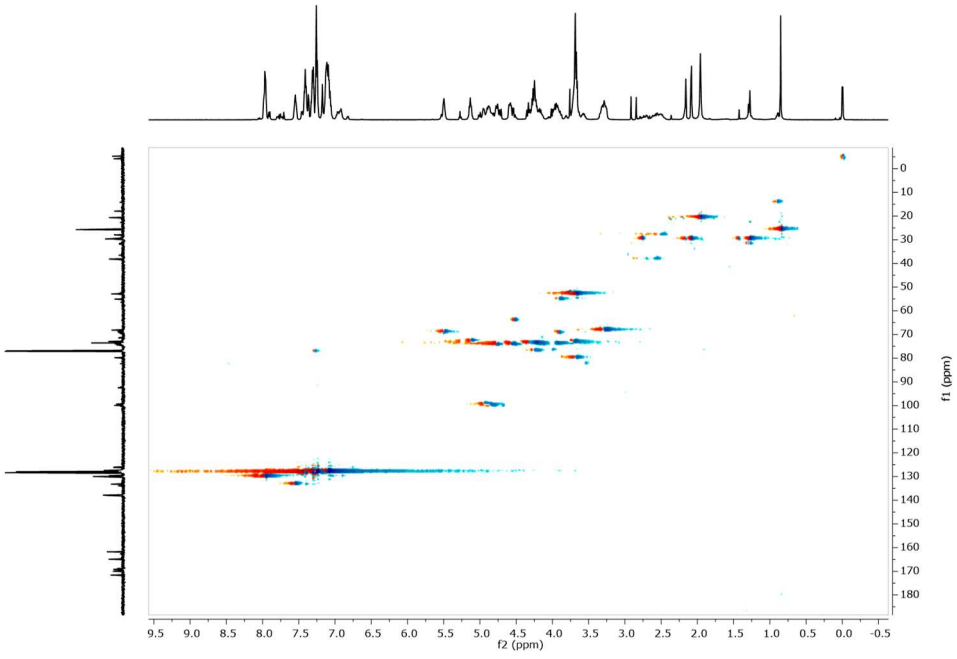
^{13}C-NMR ($CDCl_3$, 126 MHz) of **44**

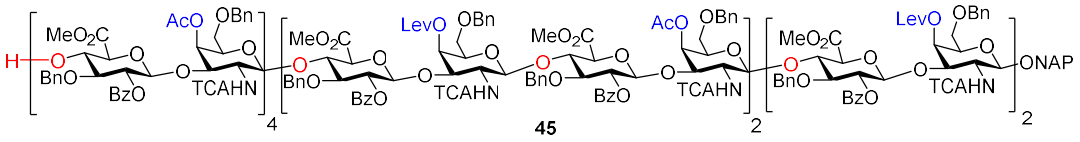


gCOSY ($CDCl_3$, 500 MHz) of **44**



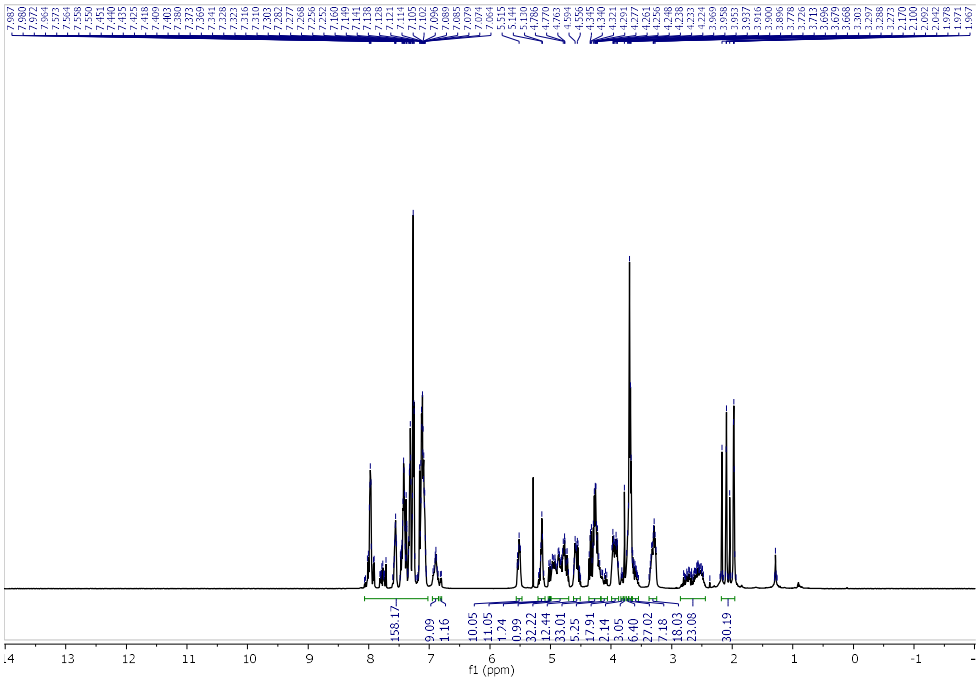
gHSQC ($CDCl_3$, 500 MHz) of **44**



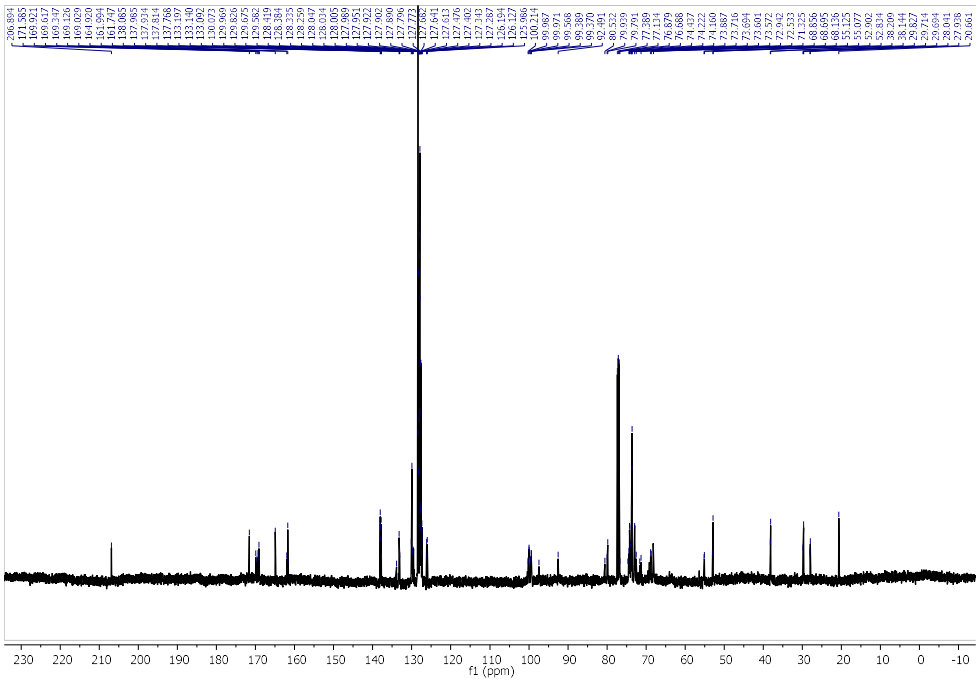


45

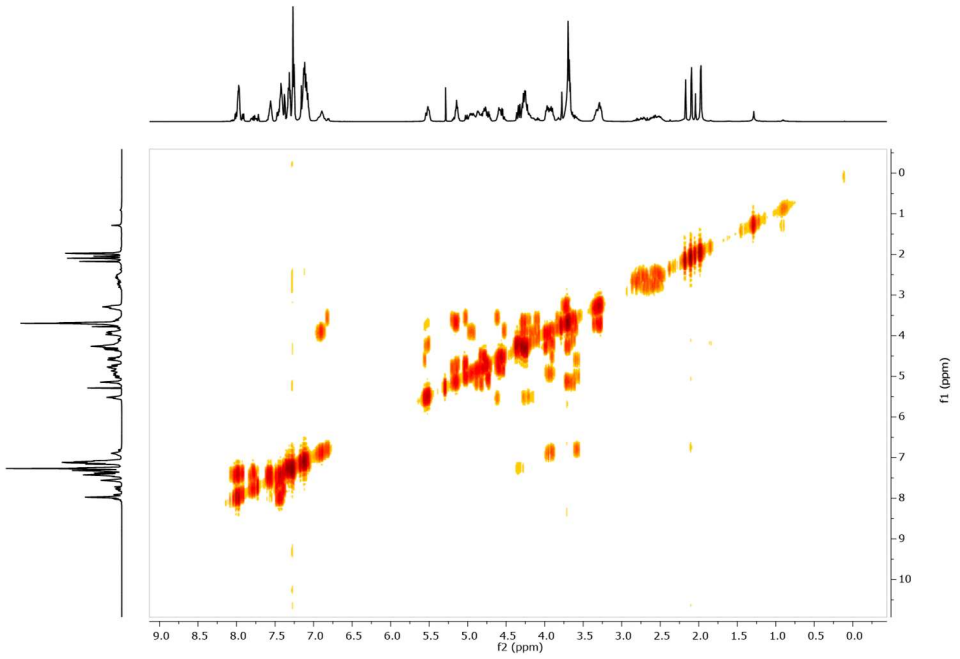
^{1}H-NMR ($CDCl_3$, 500 MHz) of **45**



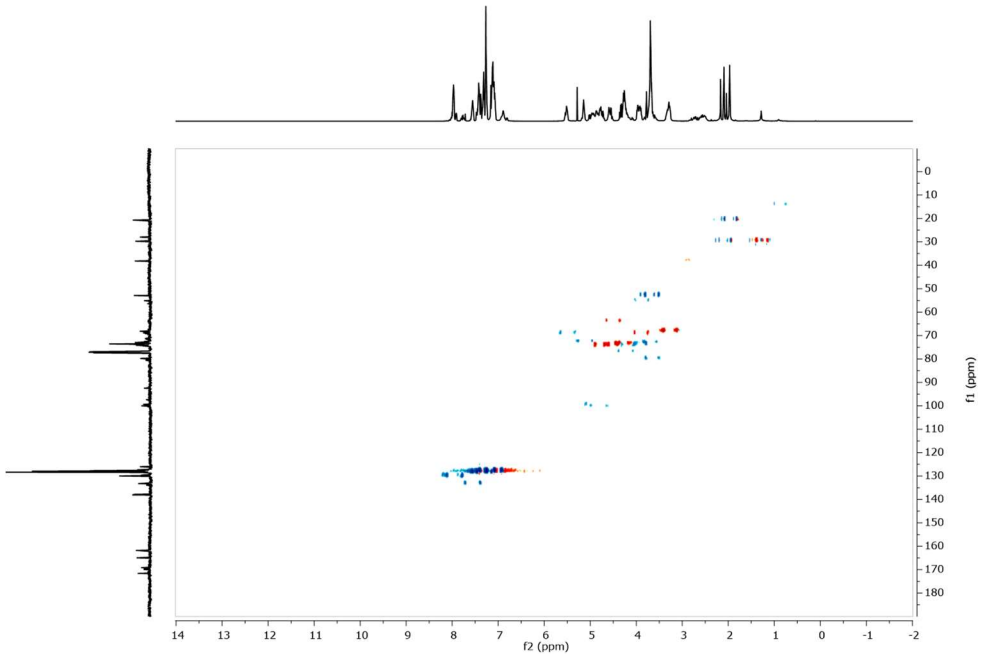
^{13}C-NMR ($CDCl_3$, 126 MHz) of **45**

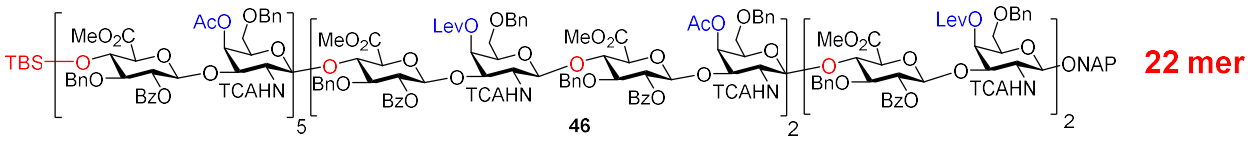


gCOSY ($CDCl_3$, 500 MHz) of **45**



gHSQC ($CDCl_3$, 500 MHz) of **45**





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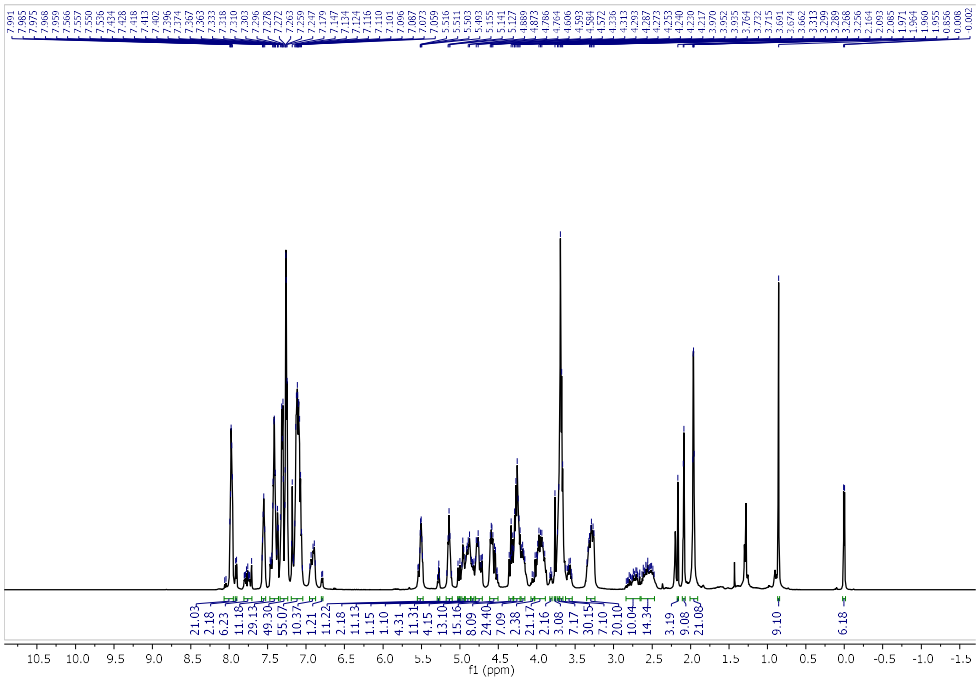
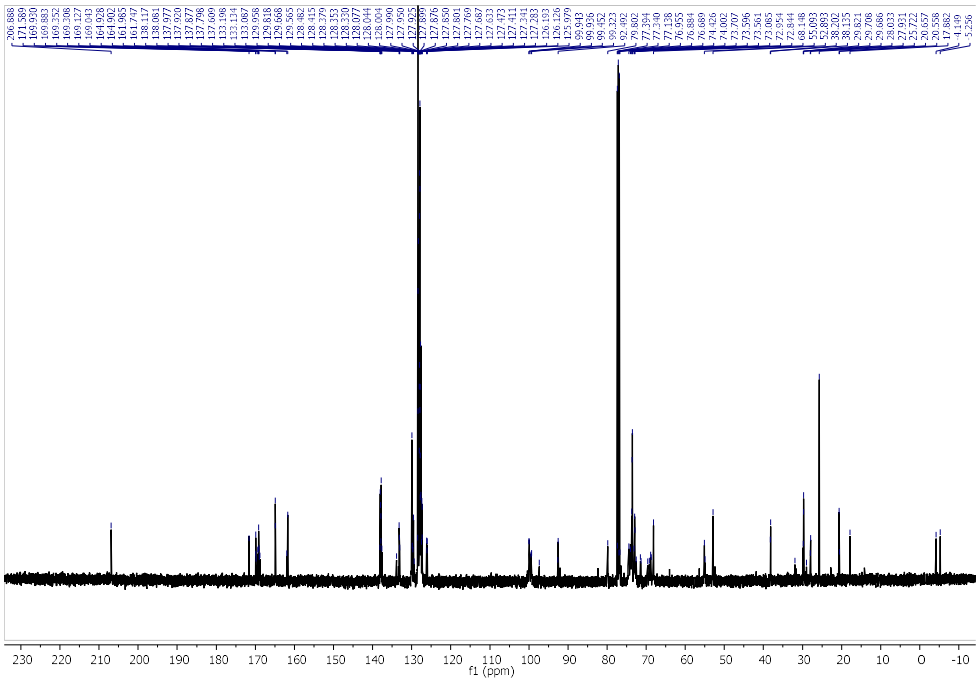
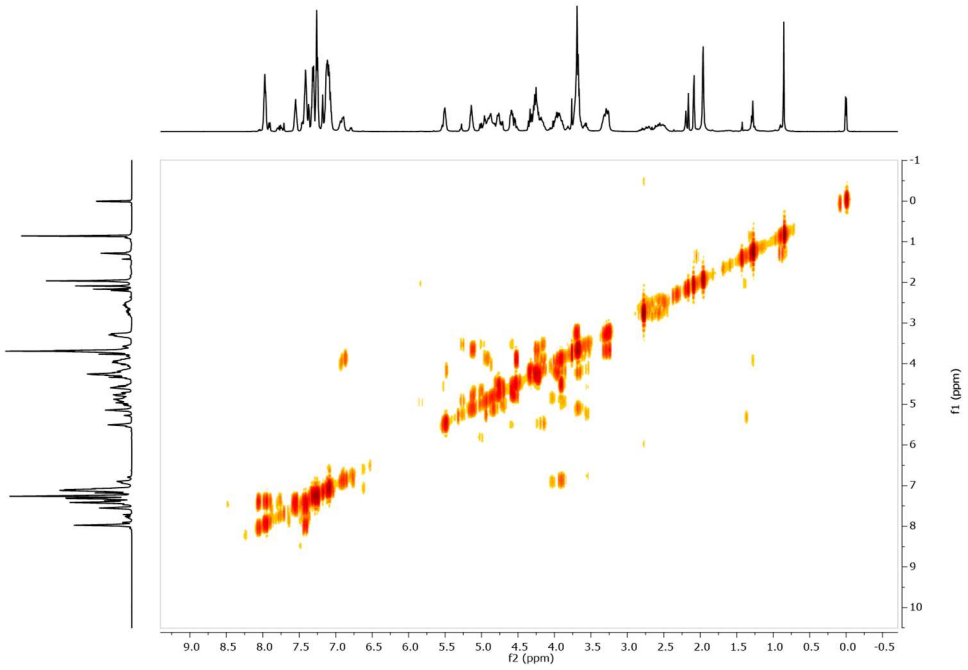
^{1}H-NMR ($CDCl_3$, 500 MHz) of **46**

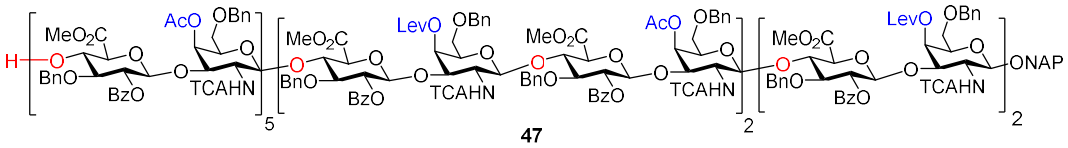


^{13}C-NMR ($CDCl_3$, 126 MHz) of **46**



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





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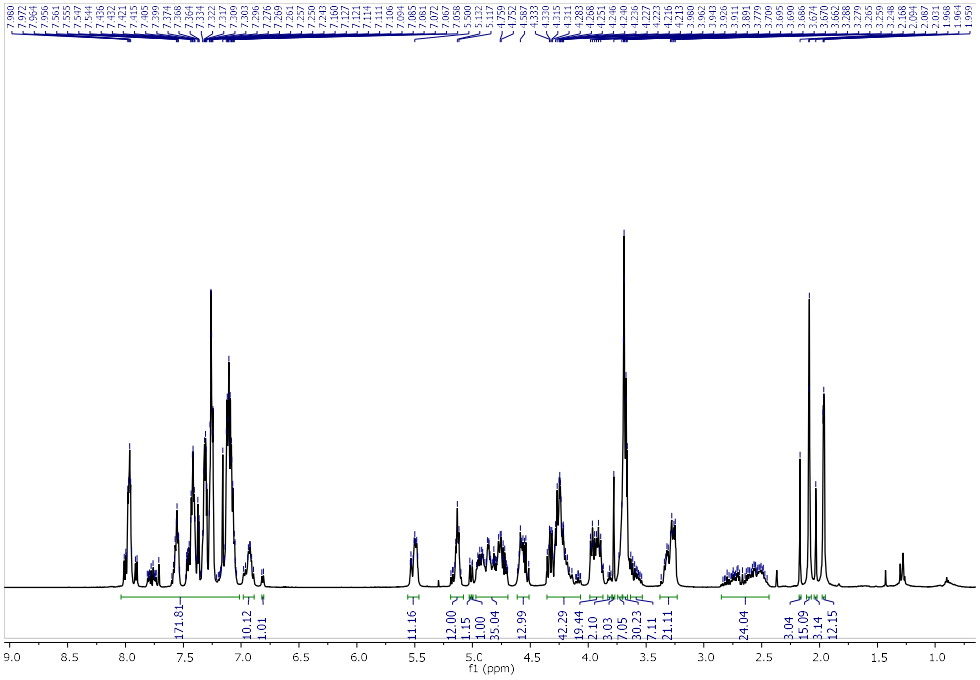
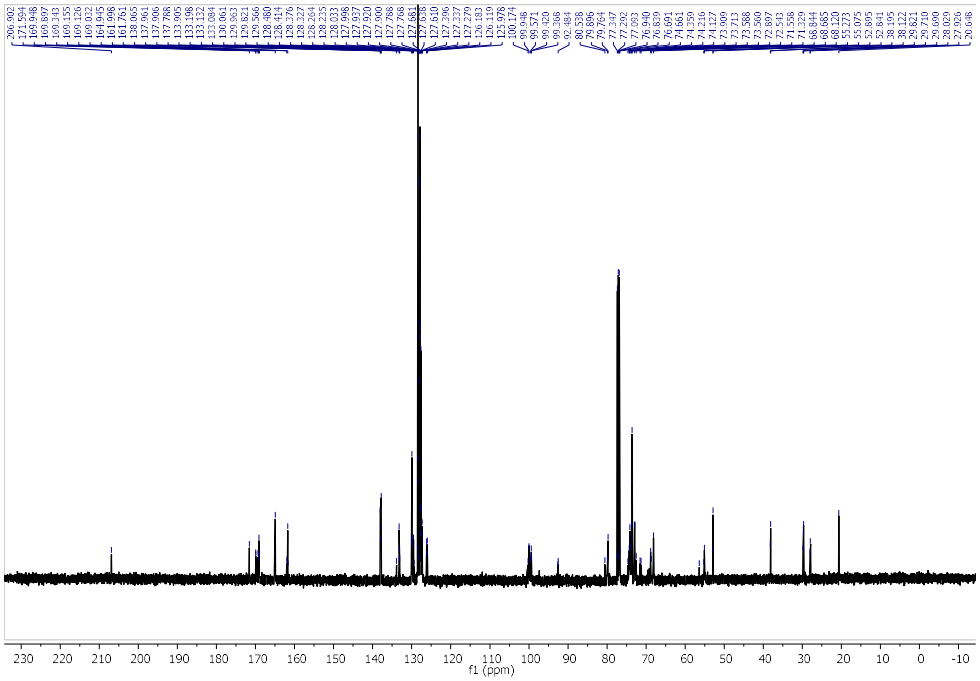
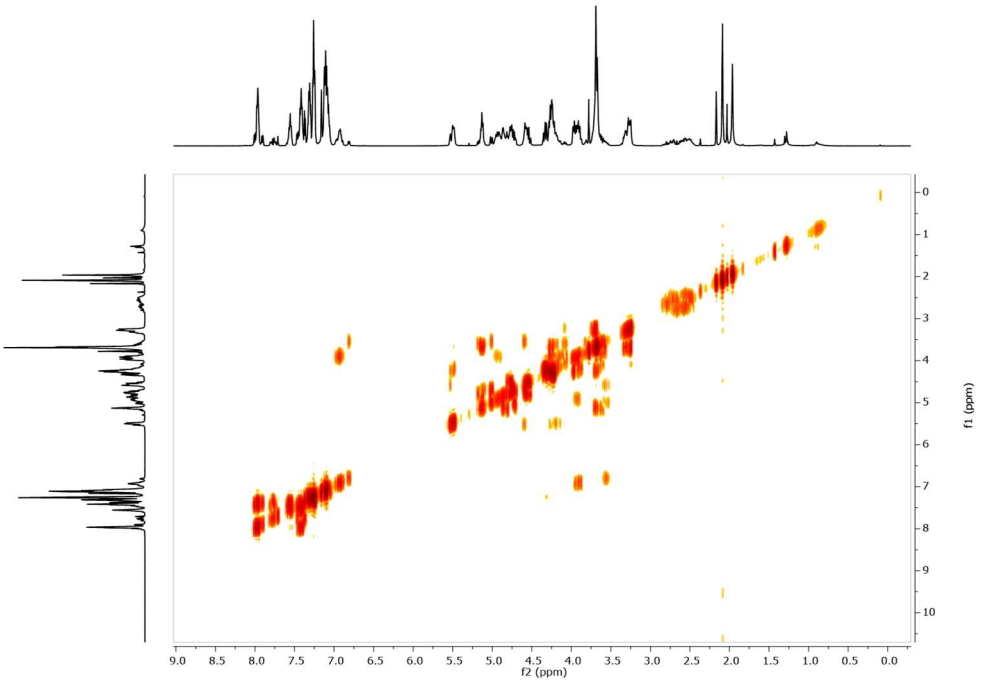
^{1}H-NMR ($CDCl_3$, 500 MHz) of **47**



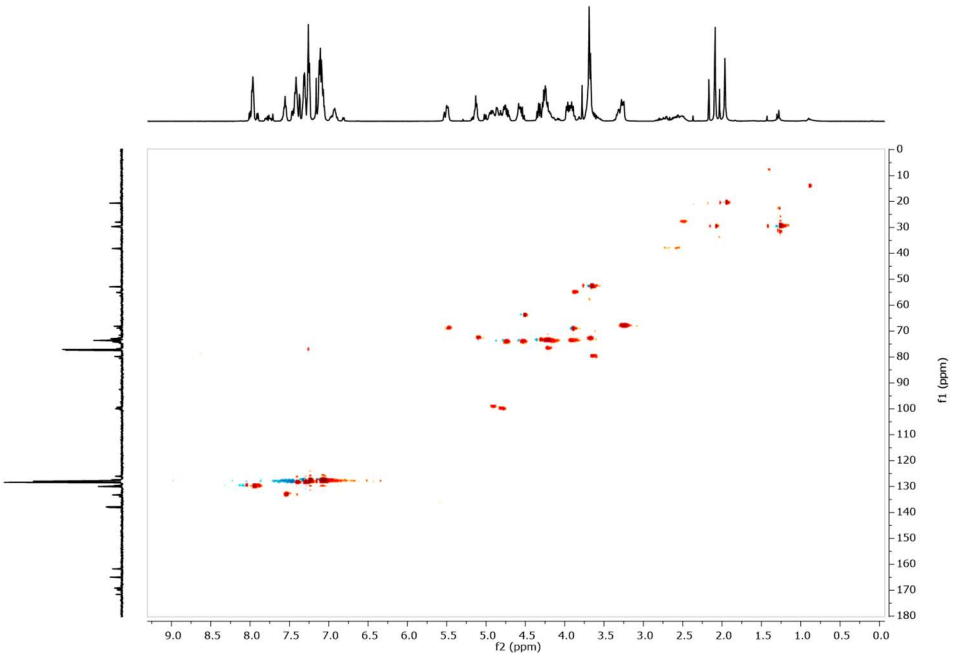
^{13}C-NMR ($CDCl_3$, 126 MHz) of **47**

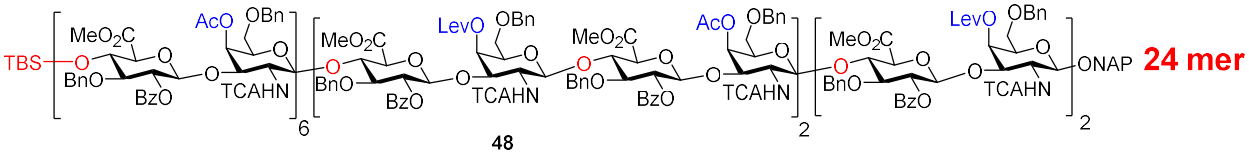


gCOSY ($CDCl_3$, 500 MHz) of **47**



gHSQC ($CDCl_3$, 500 MHz) of **47**





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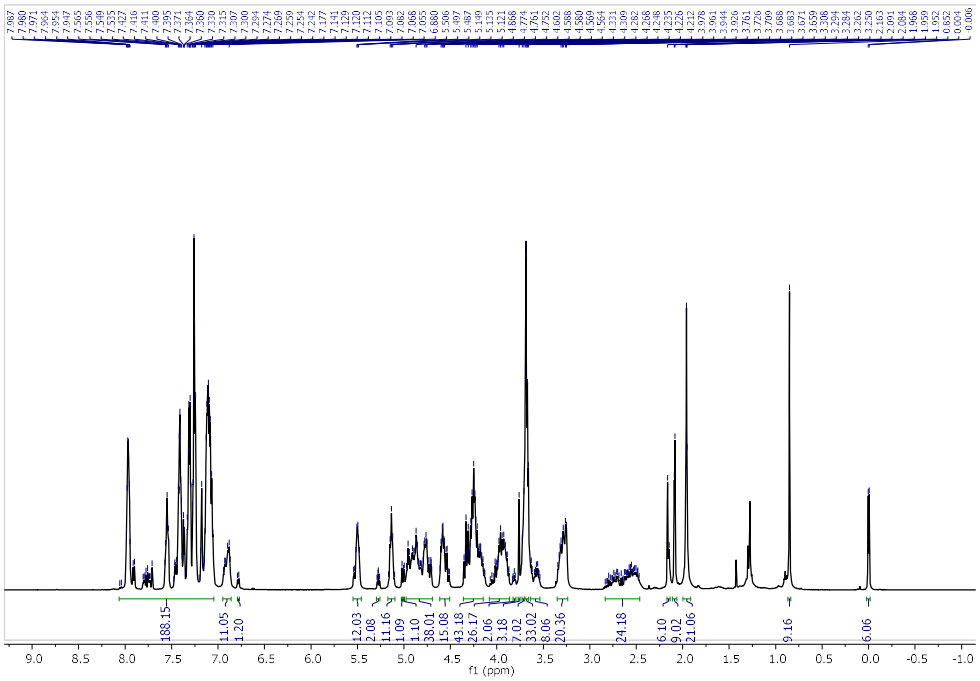
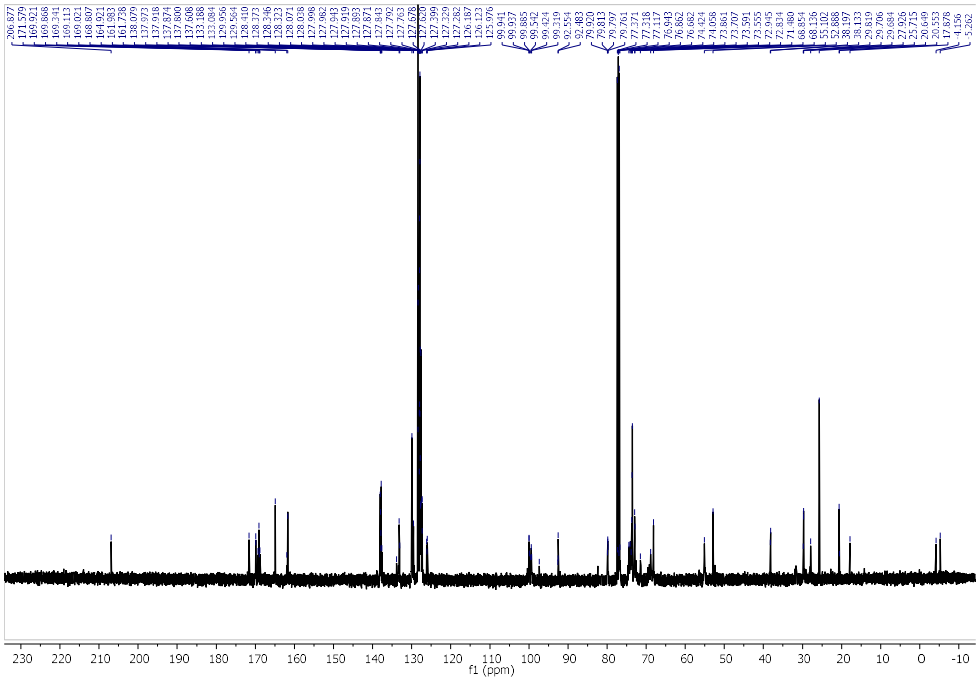
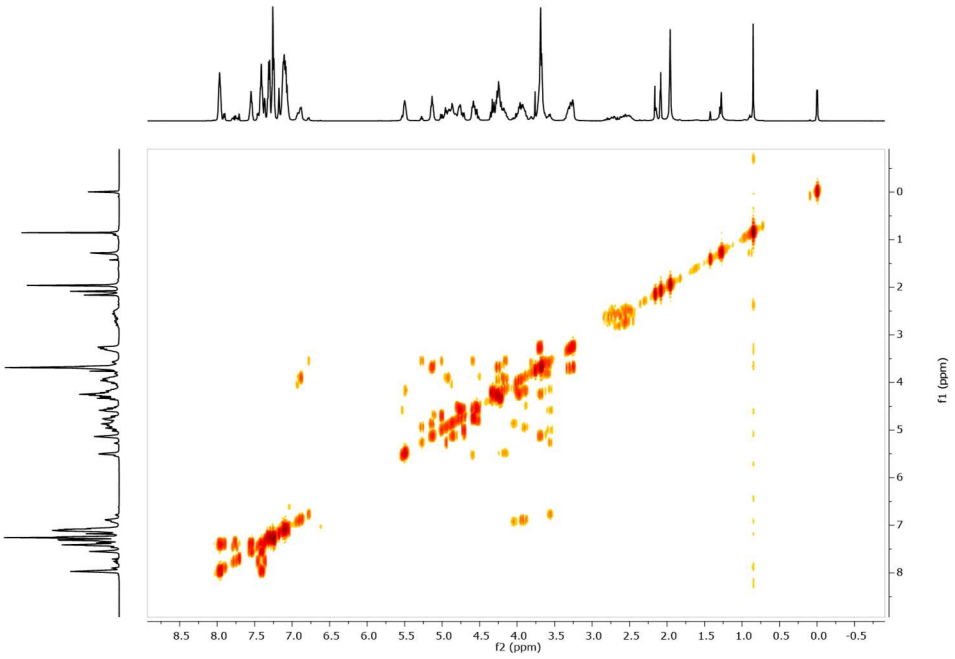
^{1}H-NMR ($CDCl_3$, 500 MHz) of **48**



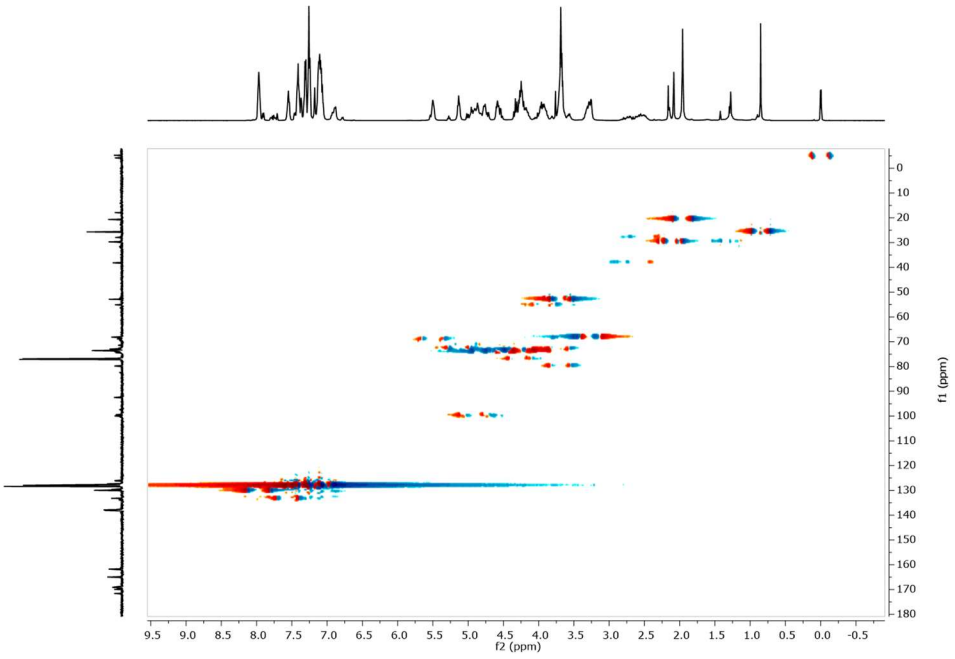
^{13}C-NMR ($CDCl_3$, 126 MHz) of **48**

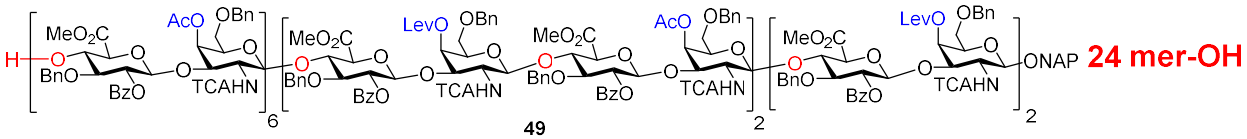


gCOSY ($CDCl_3$, 500 MHz) of **48**



gHSQC ($CDCl_3$, 500 MHz) of **48**





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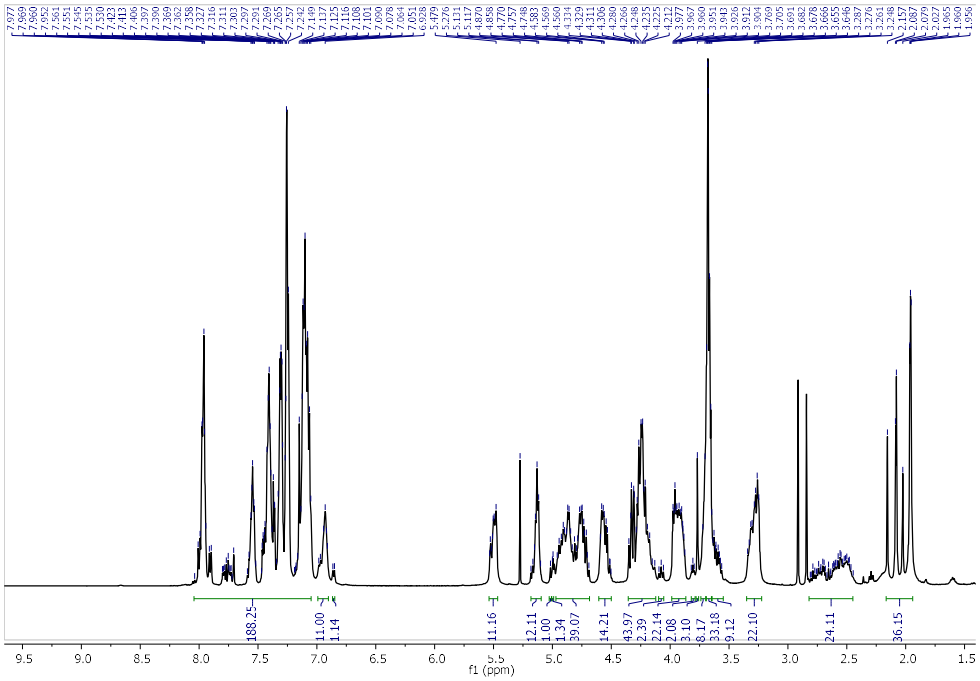
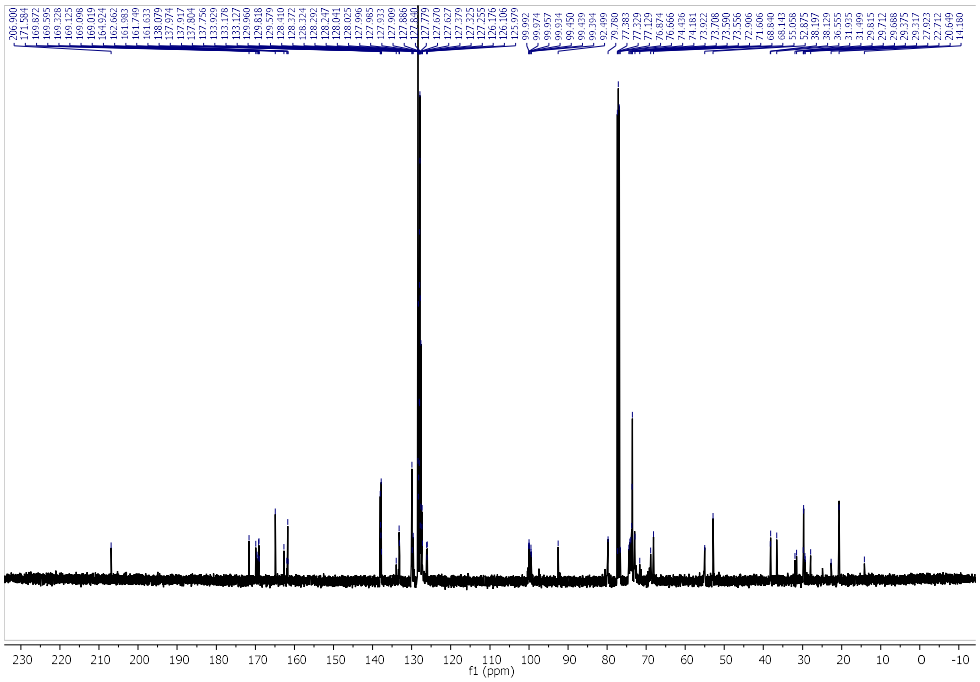
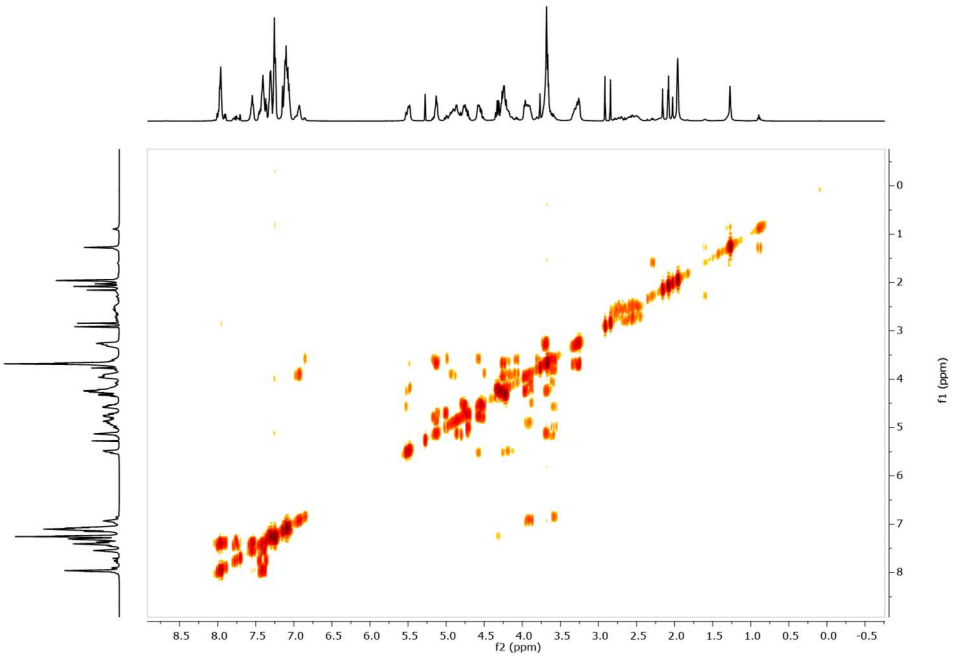
^{1}H-NMR ($CDCl_3$, 500 MHz) of **49**



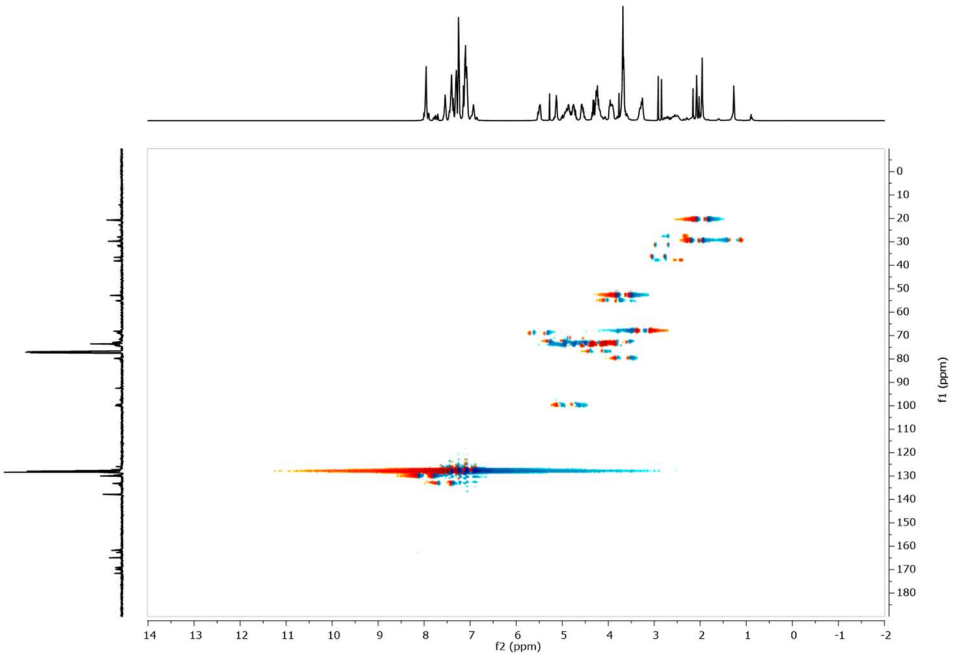
^{13}C-NMR ($CDCl_3$, 126 MHz) of **49**

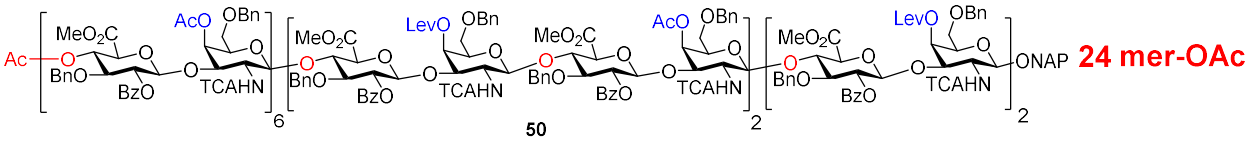


gCOSY ($CDCl_3$, 500 MHz) of **49**



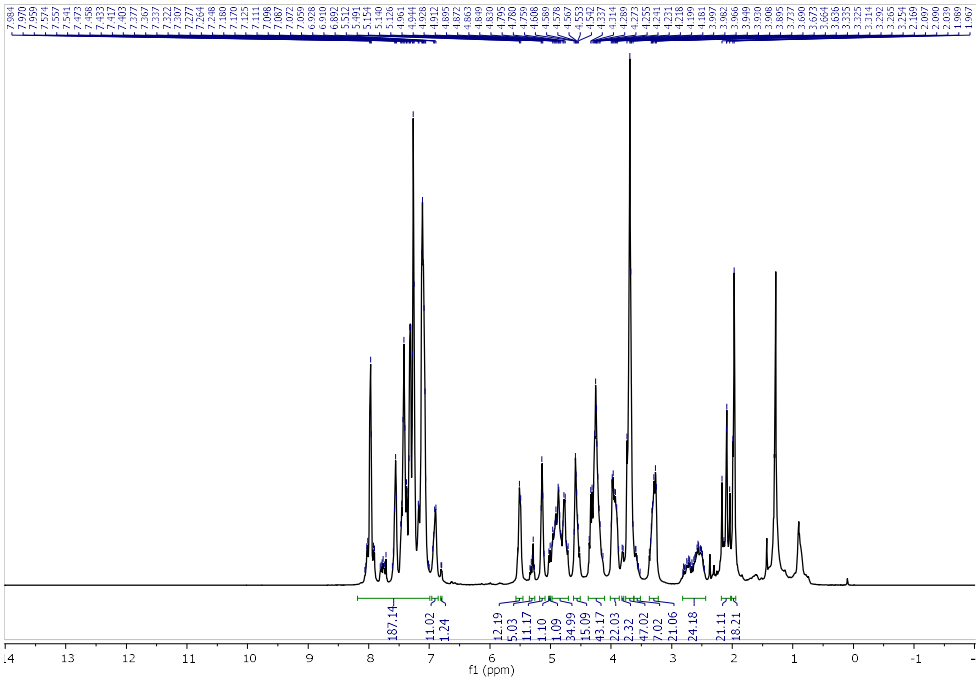
gHSQC ($CDCl_3$, 500 MHz) of **49**



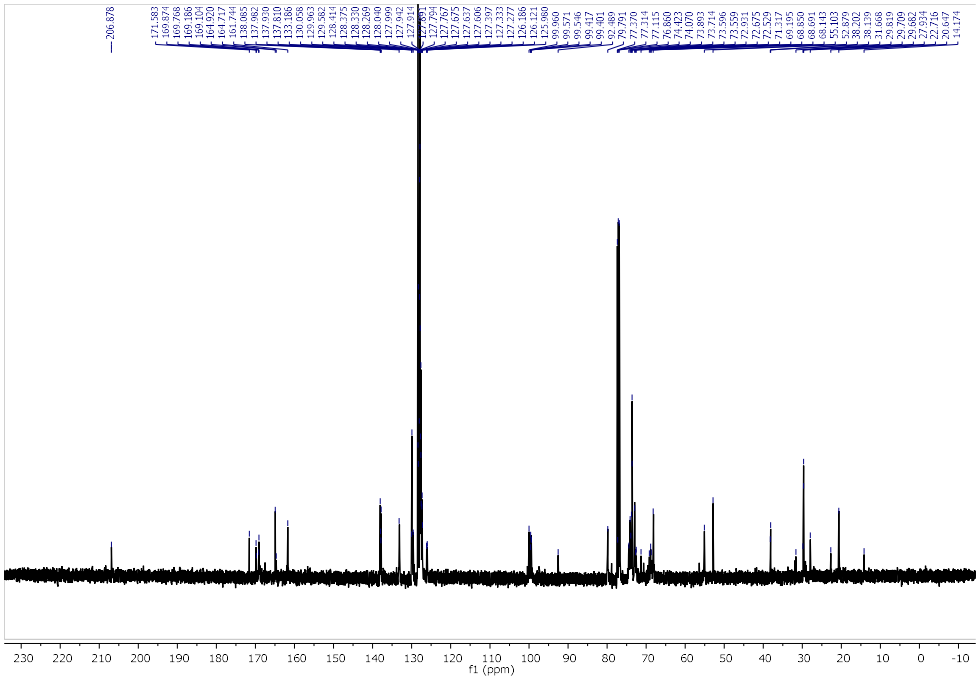


50

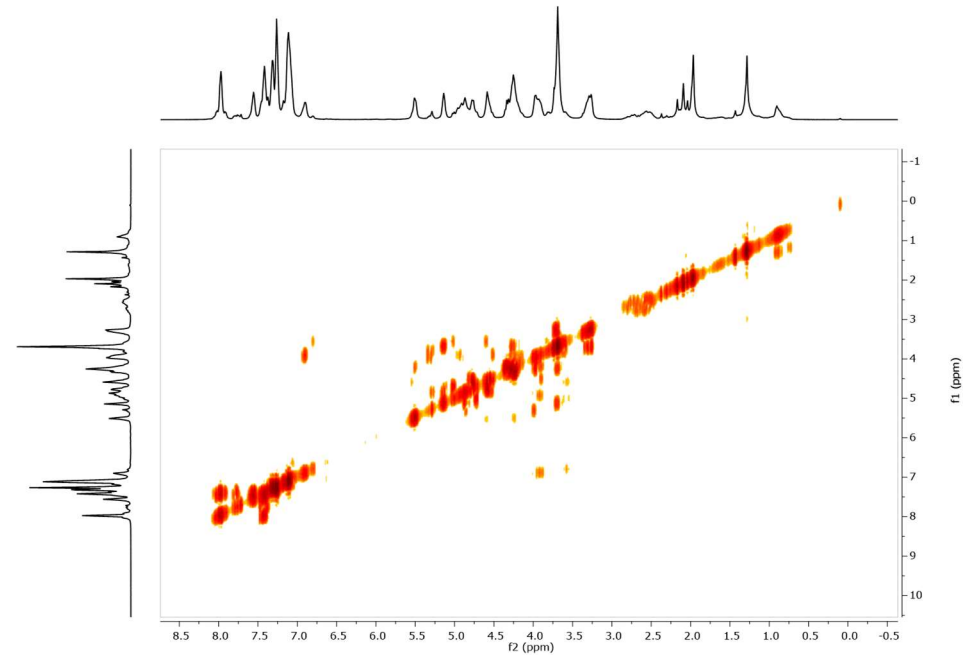
^{1}H-NMR ($CDCl_3$, 500 MHz) of **50**



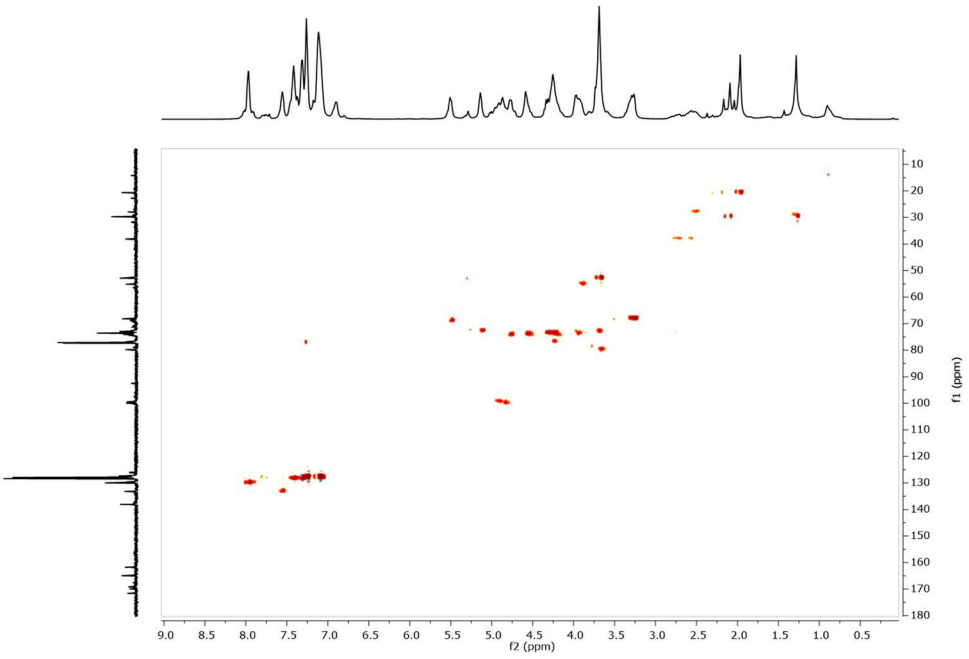
^{13}C-NMR ($CDCl_3$, 126 MHz) of **50**



gCOSY ($CDCl_3$, 500 MHz) of **50**

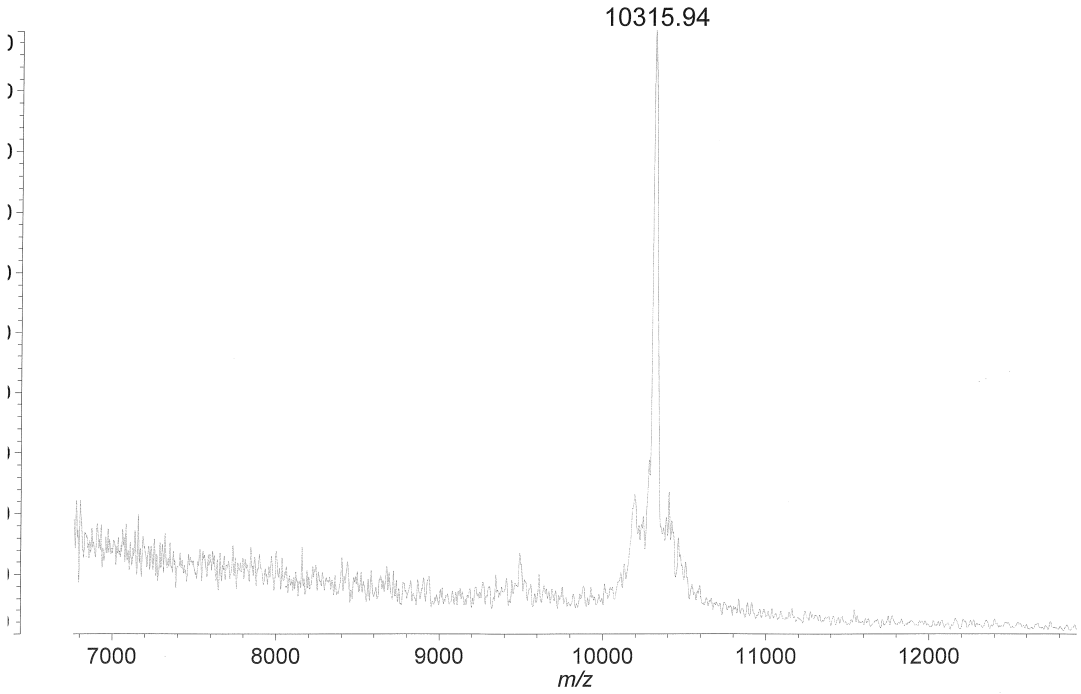


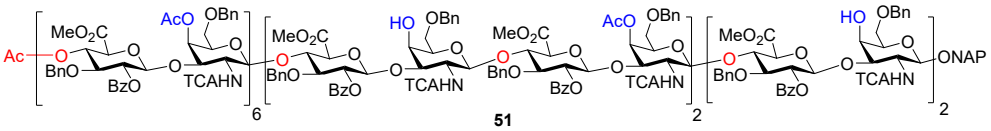
gHSQC ($CDCl_3$, 500 MHz) of **50**



MALDI-TOF. of **50**

<Untitled> 13 Aug 2018 17:24 Cal: 9 Jul 2007 10:16
dzu Biotech Axima CFR 2.9.3.20110624: Mode Linear, Power: 69, Blanked, P.Ext. @ 4244 (bin 79)
ıt. 13 mV[sum= 526 mV] Profiles 1-41 Smooth Av 50 -Baseline 150

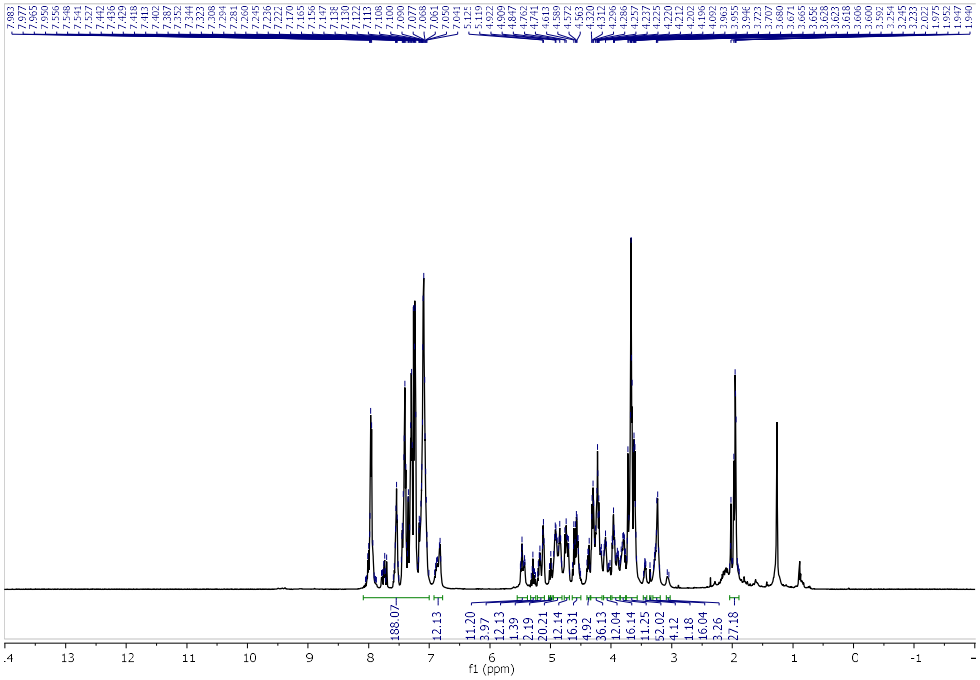




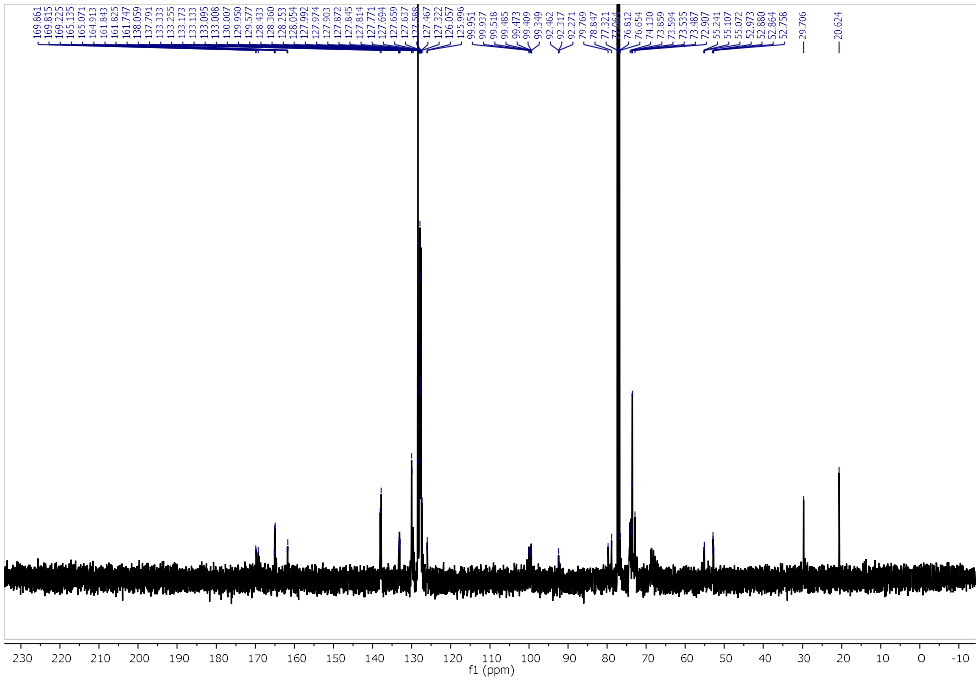
24 mer-OAc tetraol

51

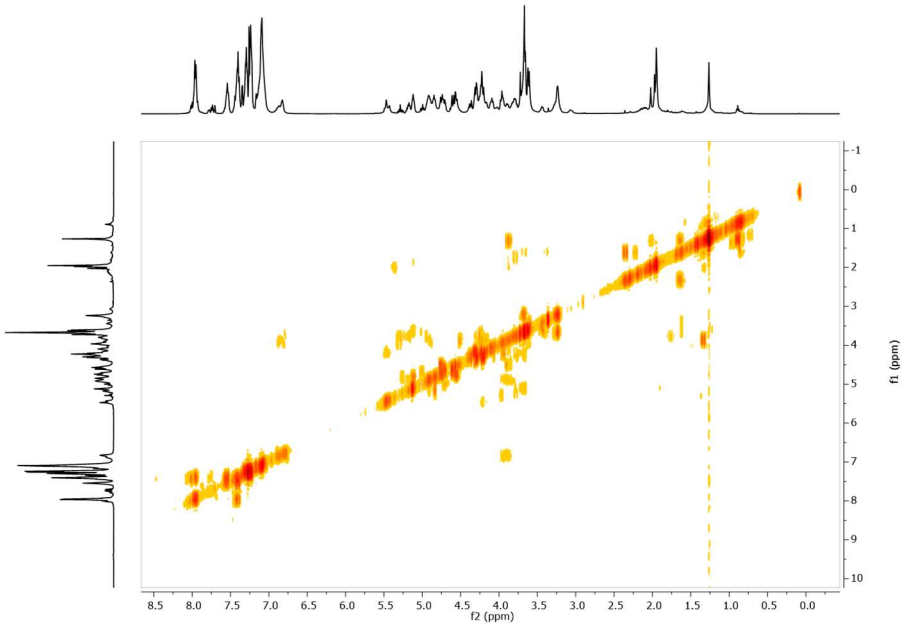
^{1}H-NMR ($CDCl_3$, 500 MHz) of **51**



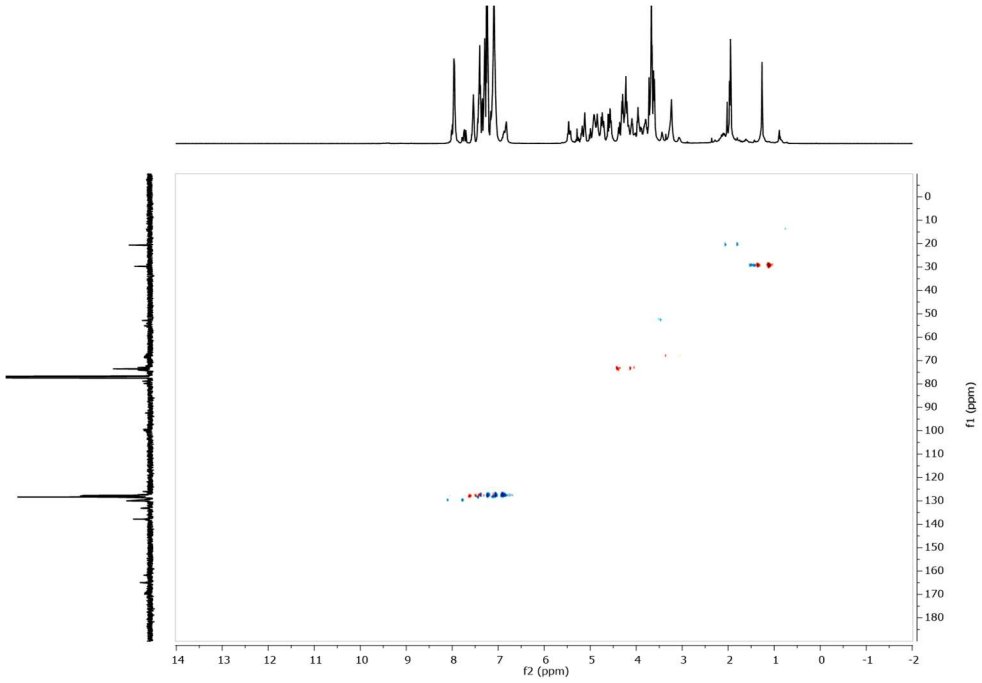
^{13}C-NMR ($CDCl_3$, 126 MHz) of **51**

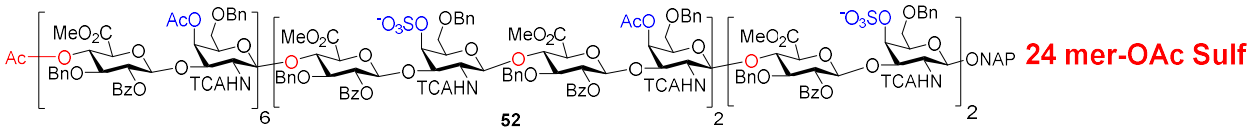


gCOSY ($CDCl_3$, 500 MHz) of **51**



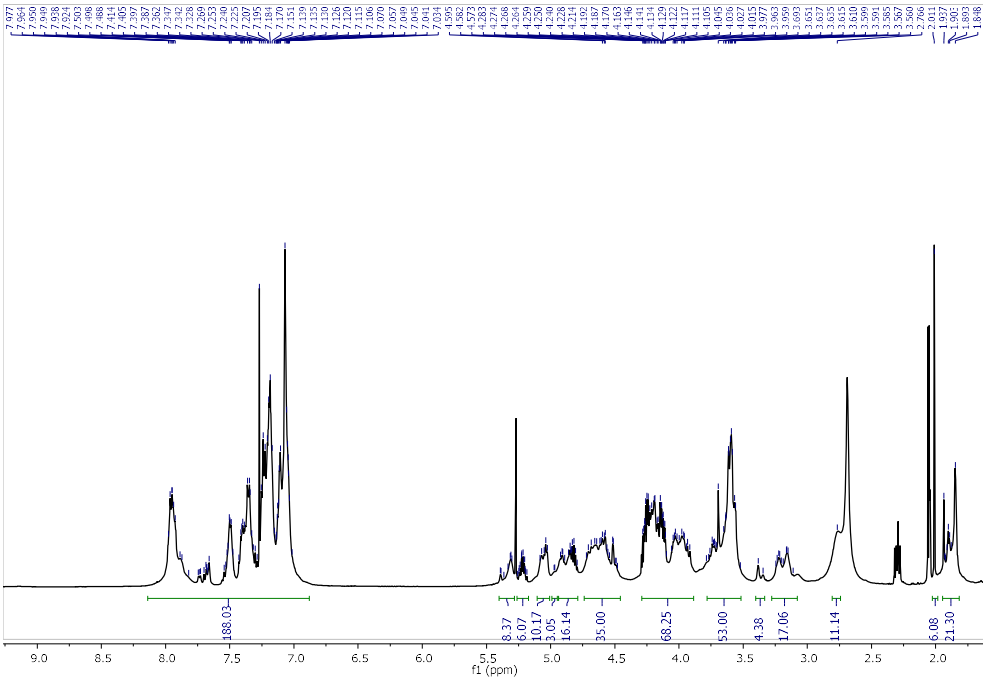
gHSQC ($CDCl_3$, 500 MHz) of **51**



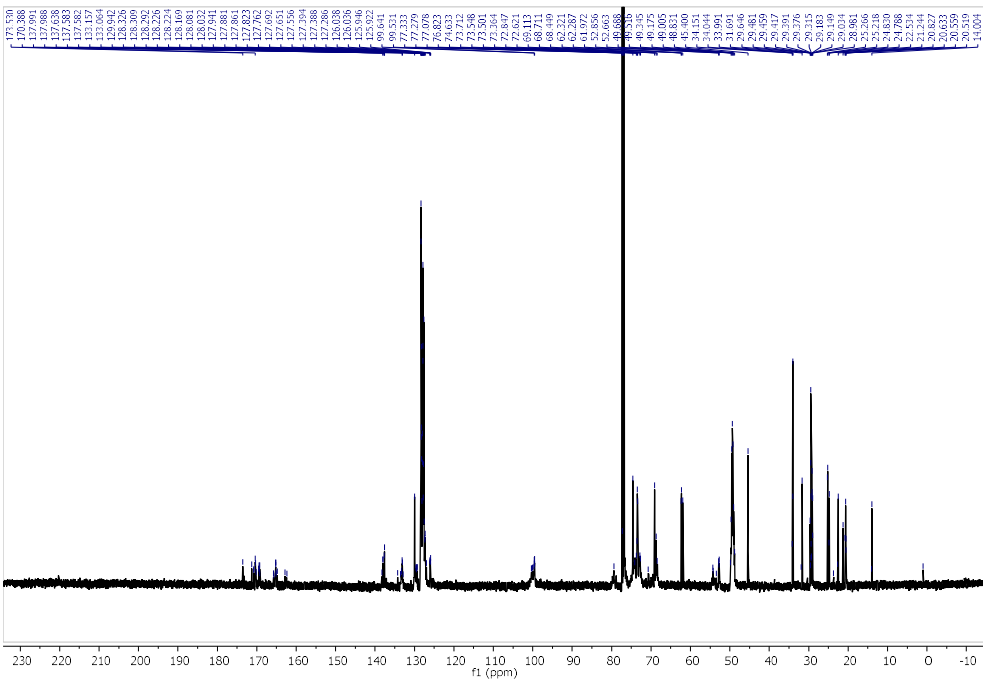


52 **24 mer-OAc Sulf**

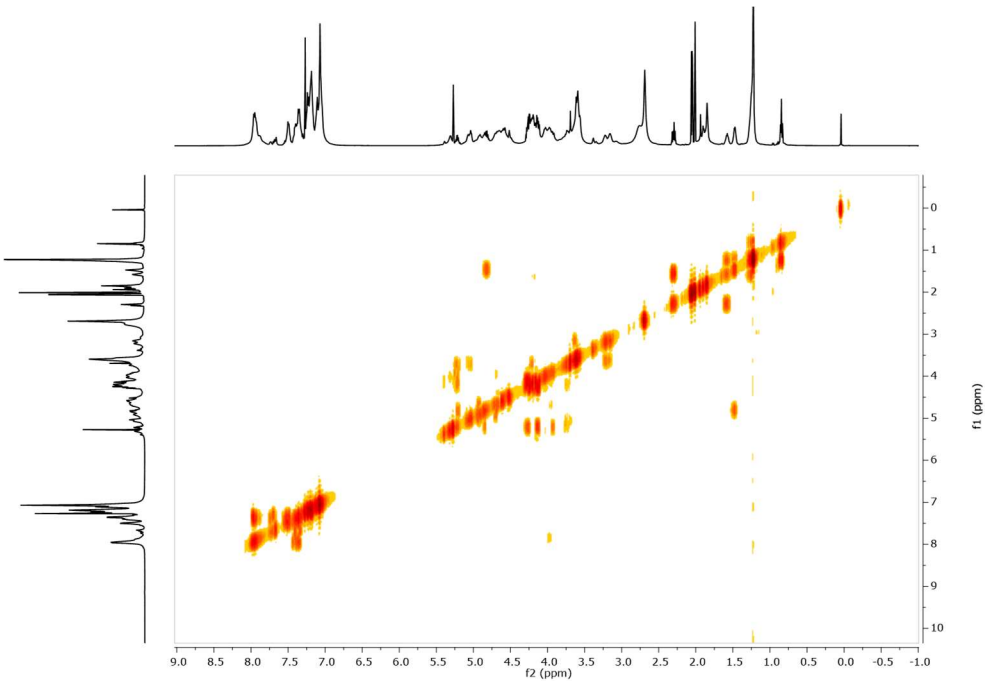
^{1}H-NMR ($CDCl_3$, 500 MHz) of **52**



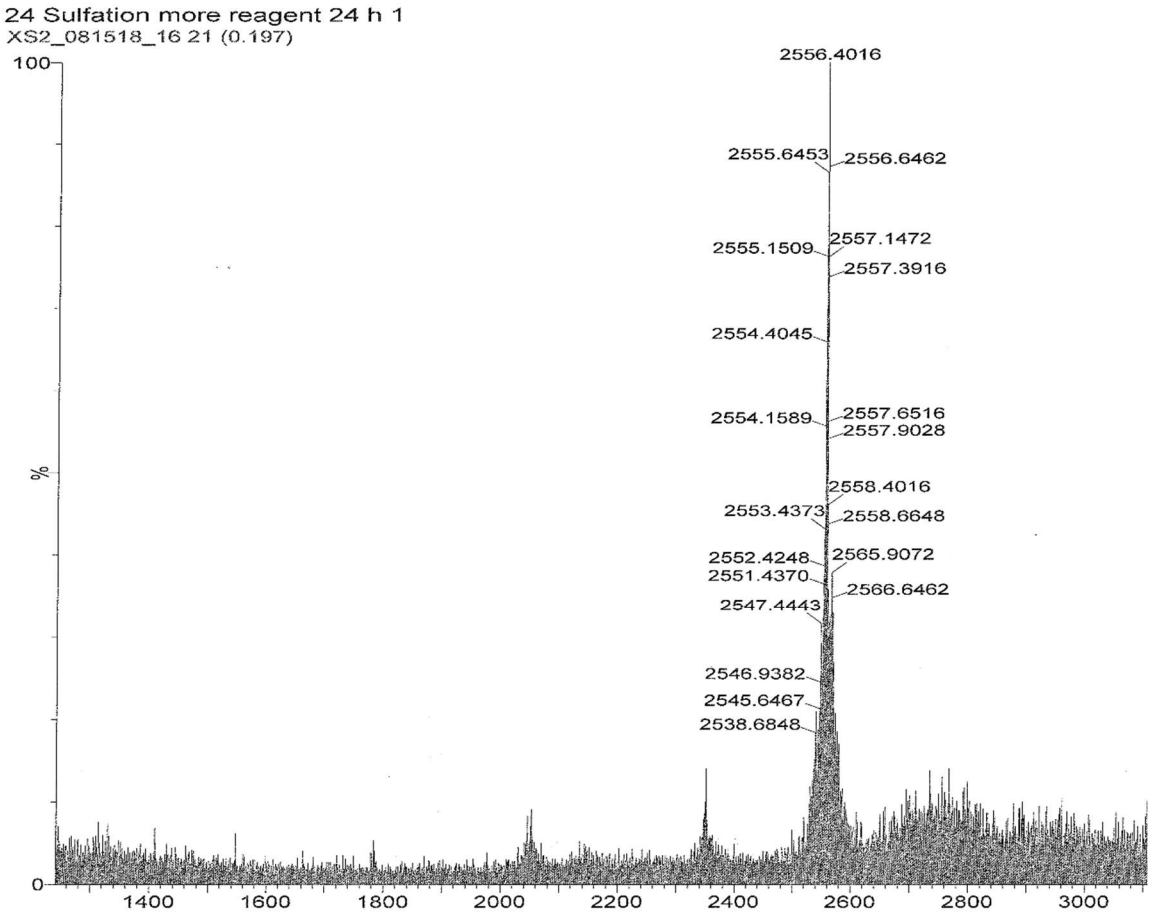
^{13}C-NMR ($CDCl_3$, 126 MHz) of **52**



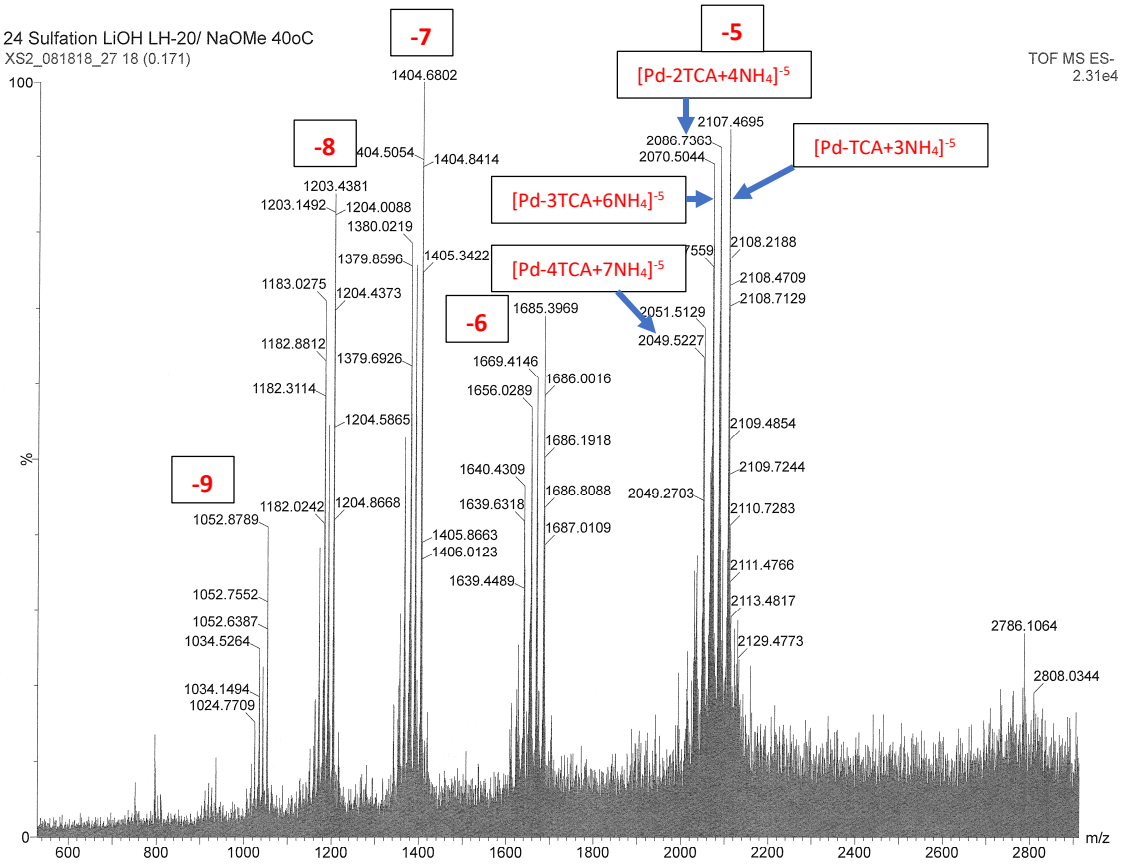
gCOSY ($CDCl_3$, 500 MHz) of **52**

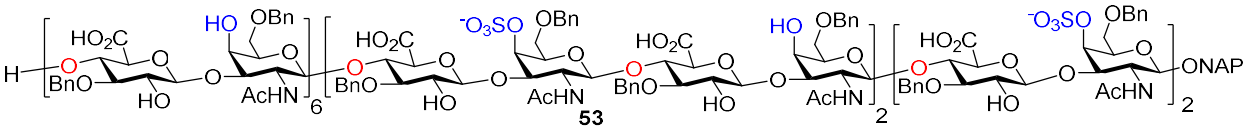


ESI-MS of **52**


24 Sulfation more reagent 24 h 1
XS2_081518_16 21 (0.197)
100
%
0
2556.4016
2555.6453
2556.6462
2555.1509
2557.1472
2557.3916
2554.4045
2554.1589
2557.6516
2557.9028
2558.4016
2553.4373
2558.6648
2552.4248
2565.9072
2551.4370
2566.6462
2547.4443
2546.9382
2545.6467
2538.6848
1400
1600
1800
2000
2200
2400
2600
2800
3000

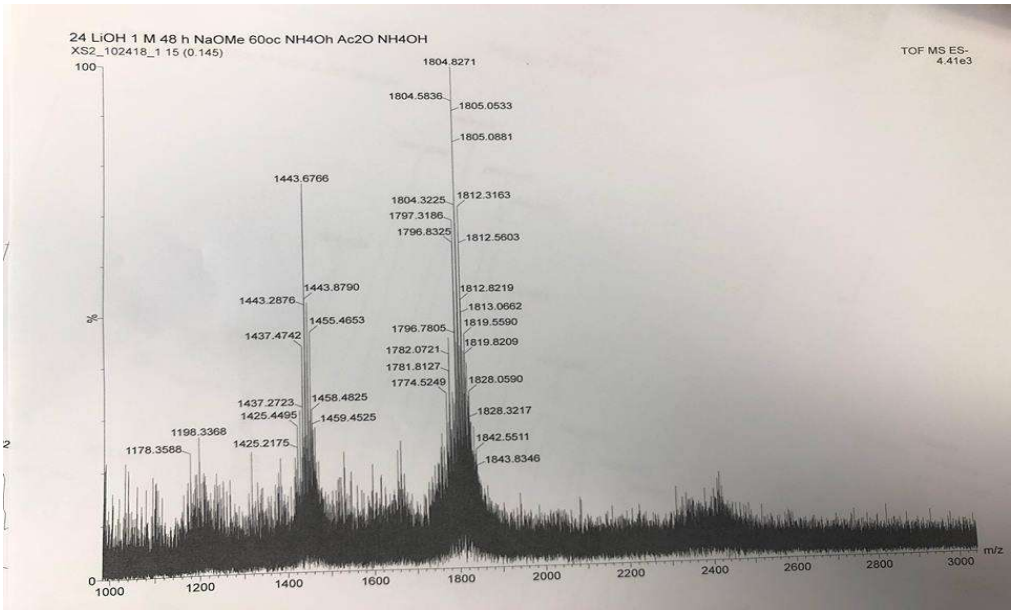
ESI-MS of hydrolysis and TCA removal of **52**

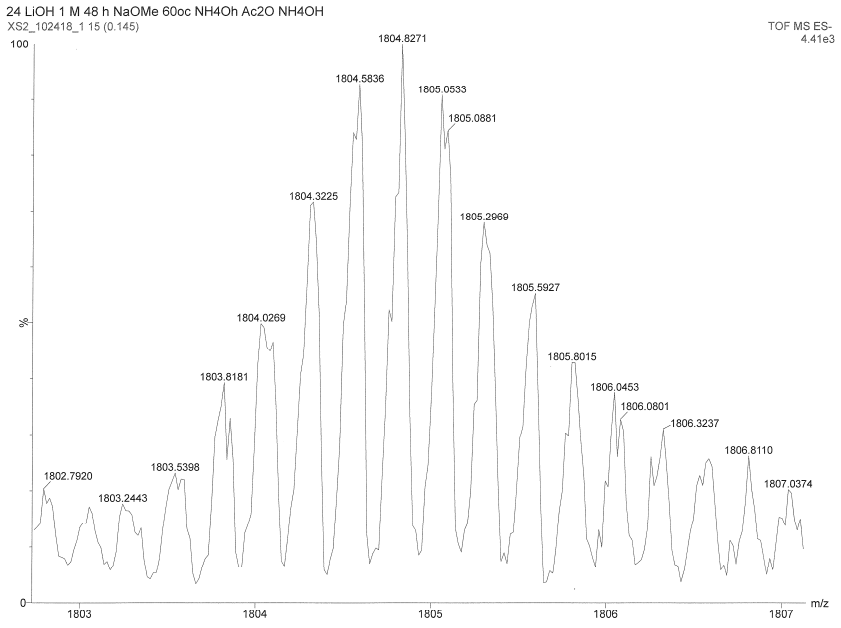


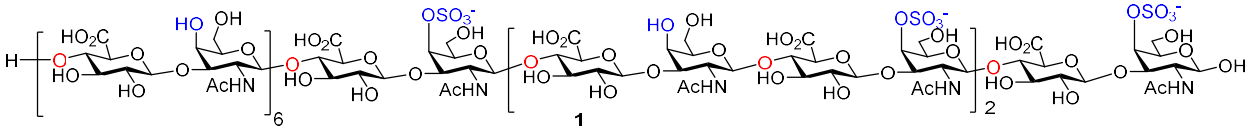


53

ESI-MS. of **53**

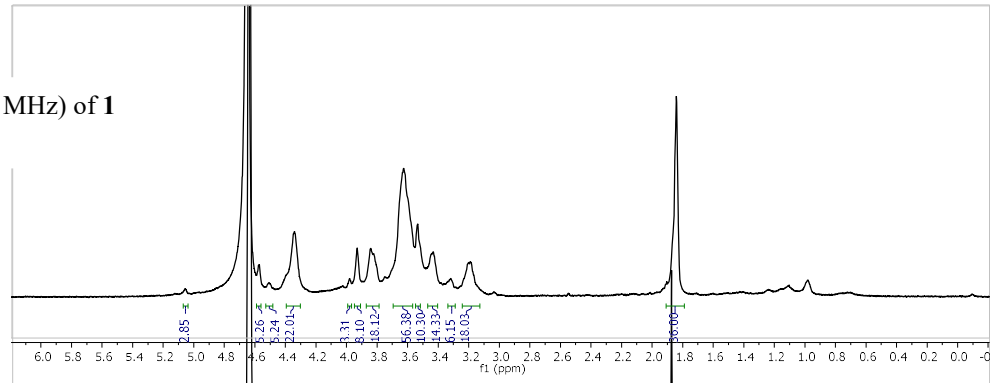




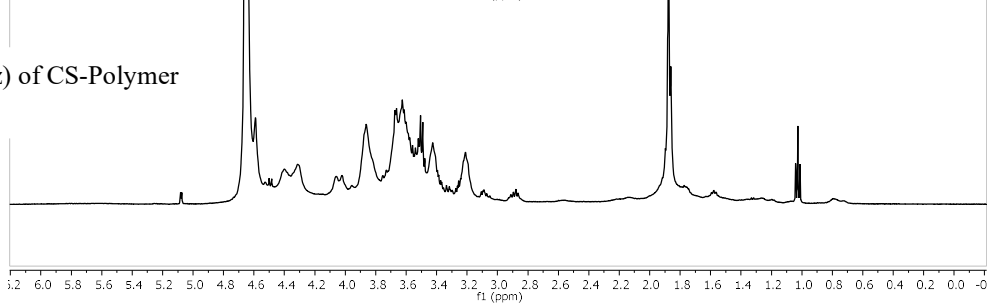


1

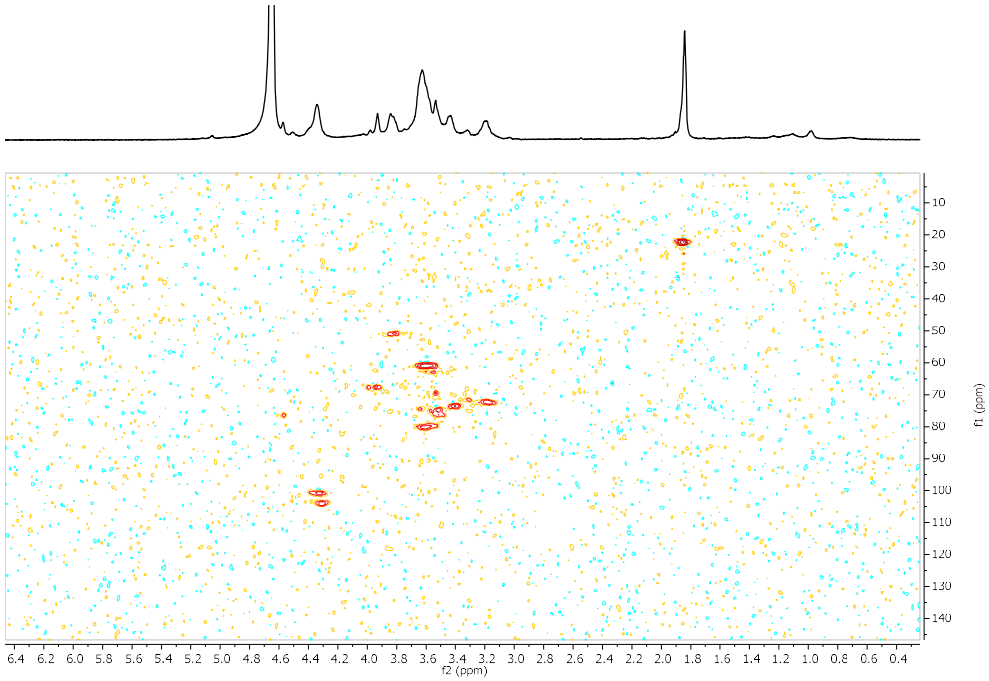
^{1}H-NMR (D_2O, 500 MHz) of **1**



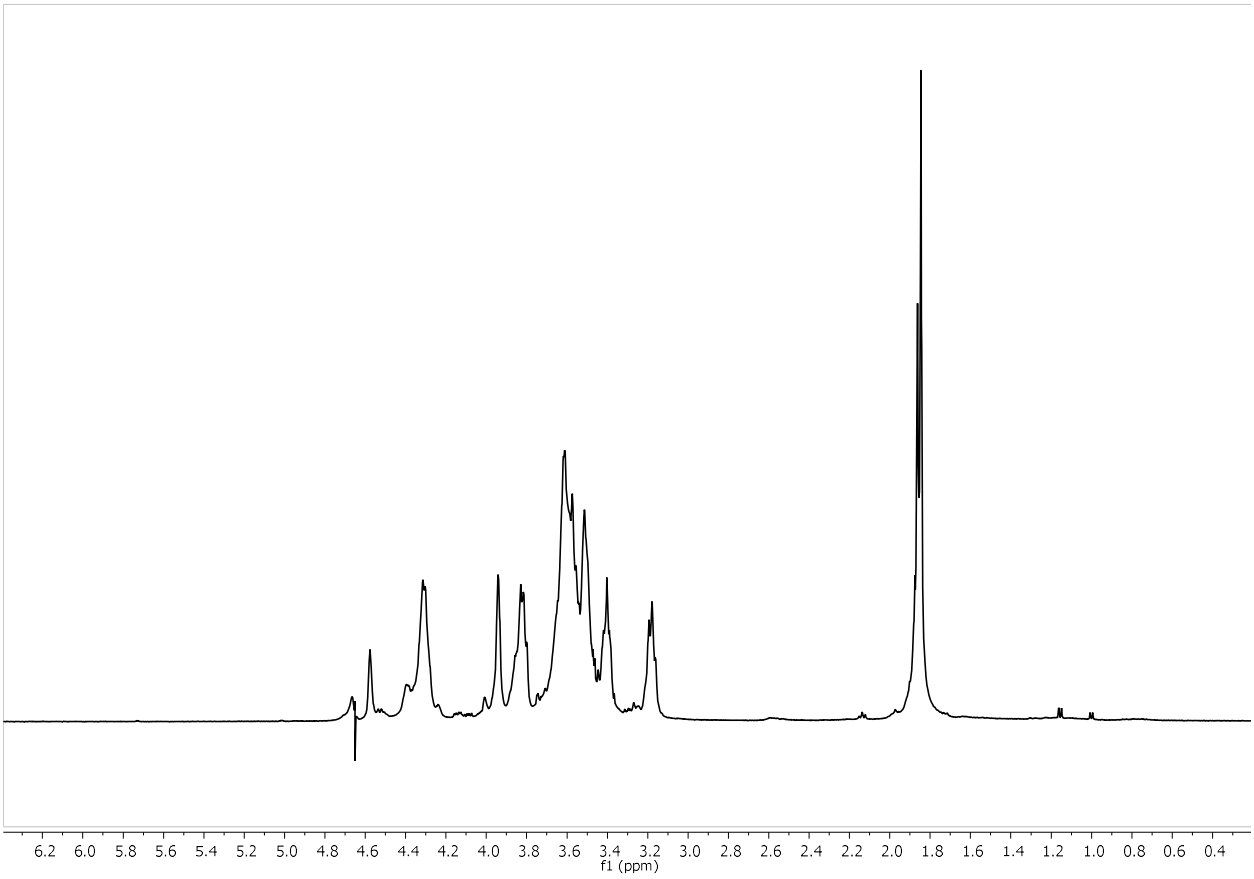
^{1}H-NMR (D_2O, 500 MHz) of CS-Polymer



gHSQC ($CDCl_3$, 500 MHz) of **1**



^{1}H-NMR (D_2O, 500 MHz) of bikunin **CS**



ESI-MS of bikunin **CS**