Supporting Information

A double-click approach to the protecting group free synthesis of glycoconjugates

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Synthesis of VTSAPDCRPAPGSTAPPAHG peptide 9

Materials: 9-Fluorenylmethoxycarbonyl (Fmoc) protected L-a-amino acids, 2-(6-chloro-1H-benzotriazole-1-yl)-1,1,3,3-tetramethylaminium hexafluorophosphate (HCTU) and benzotriazol-1-yl-oxytripyrrolidinophosphonium hexafluorophosphate (PyBOP) were purchased from Bachem (Switzerland). Dimethylformamide (DMF) and acetonitrile were purchased from Global Science (Auckland, NZ). Acetic anhydride, triisopropylsilane (TIPS), 4-methylmorpholine (NMM), 2,4,6-trimethylpyridine and piperidine were purchased from Sigma Aldrich. Trifluoroacetic acid (TFA) was obtained from Oakwood Products, Inc (West Colombia, SC). Preloaded (Wang-type linker) polystyrene resin was obtained from Rapp Polymere GmbH (Tübingen).

General Methods: Analytical HPLC employed a Dionex Ultimate 3000 HPLC system fitted with a Phenomenex Gemini C18 3mm 110Å 4.6x150mm column, with water/0.1% TFA as eluent A and MeCN/0.1% TFA as eluent B. Mass spectra were recorded using an Agilent 1100MSD spectrometer.

Solid-Phase Peptide Synthesis: Fmoc synthesis was carried out at room temperature on Tentagel resin using a Tribute peptide synthesiser (Protein Technologies International, Tucson, Az) and conducted on a 0.1 mmol scale. Generally, individual peptide couplings employed a 5-fold molar excess (relative to resin) of the protected amino acid in DMF activated by a 4.8-fold molar excess of HCTU in the presence of a 10-fold molar excess of 4-methylmorpholine in DMF, with a coupling time of 60 minutes. After the coupling step 20% acetic anhydride in DMF (20-fold excess) was added prior to draining and washing the resin. The Fmoc protecting group was removed using two separate treatments of 20% piperidine in DMF (three minutes then seven minutes) in in preparation for coupling of the next Fmoc-amino-acid residue. For the coupling of Fmoc-histidine residues, PyBOP was used as the coupling agent and 2,4,6 trimethylpyridine (5-fold excess) was used in place of 4-methylmorpholine.

The side-chains of the amino acids were protected where necessary with TFA-labile groups. Cleavage from resin with concomitant deprotection of the peptide was achieved by incubating the resin in 6 mL/mmol (resin) of cleavage medium comprised of 94% TFA, 5% water and 1% TIPS for 2.5 h at room temperature. The crude peptide was recovered by draining the TFA solution into chilled diethyl ether (5 vol) to induce precipitation. After centrifugation the peptide pellet was washed twice with ether, allowed to air-dry, dissolved in

1:1 water/MeCN (approx. 10 mL) and heated at 65 °C for 20 minutes to degrade residual carboxylated Trp. The solution was then freeze-dried.

Purification: Semi-preparative HPLC purification employed a Dionex Ultimate 3000 HPLC system fitted with a Phenomenex Gemini C18 5mm 110Å 10x250mm column, with water/0.1% TFA as eluent A and MeCN/0.1% TFA as eluent B operating at room termperature. Approximately 60 mg of crude peptide was dissolved to a concentration of 20 mg/mL in in water/0.1%TFA and a series of 0.2 mL aliquots of this solution were purified on the column using the following gradient: 0-1min, 5%B; 1-2min, 10%B; 2-15min 20%B, eluting at 4 mL/min. The main peak from each run, eluting at approximately 11 minutes, was collected and, after pooling this purified product from all runs, it was analysed by HPLC and freeze-dried to afford 25 mg of pure material.

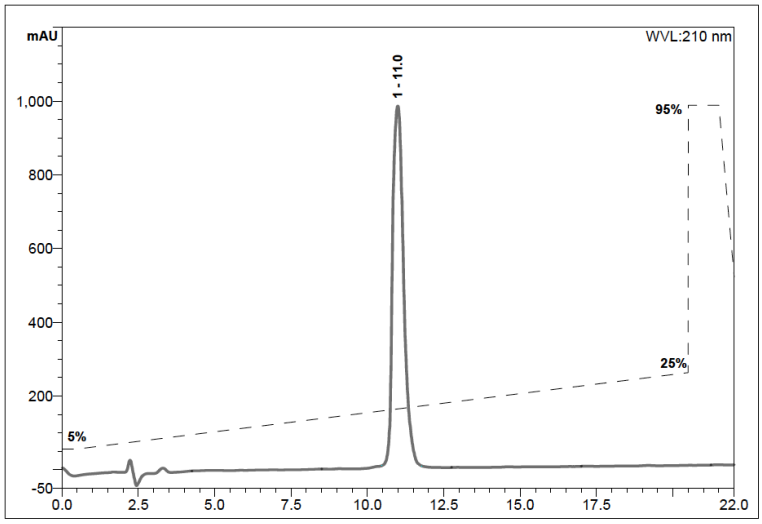


Fig S1. HPLC analysis of purified VTSAPDCRPAPGSTAPPAHG: Column: Phenomenex Gemini C18 3mm 110Å 4.6x150mm column, with water/0.1% TFA as eluent A and MeCN/0.1% TFA as eluent B; Gradient: 0-0.5min, 5%B; 0.5-20.5min, 25%B; 20.5min, 95%B; flow 1 mL/min.

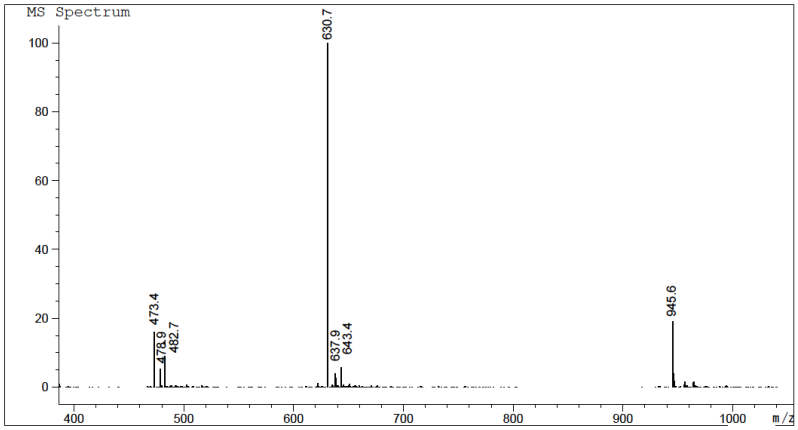
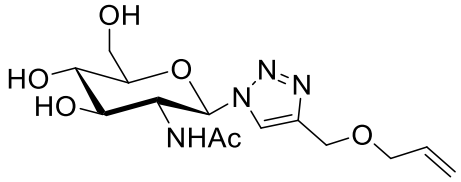


Fig. S2 Low-resolution MS analysis of purified VTSAPDCRPAPGSTAPPAHG: Observed *m/z* [M+2H$^+$], 945.6; [M+2H$^+$] requires 944.9. The sodium and potassium adducts in the [M+3] and [M+4] charge states are clearly visible.

General Experimental

Melting points were recorded on an Electrothermal melting point apparatus and are uncorrected. Optical rotations were measured on a Perkin-Elmer Polarimeter 341 with a path length of 1 dm. Concentrations are given in g / 100 mL. Infrared spectra were recorded on a Perkin-Elmer Spectrum One. Proton and carbon nuclear magnetic resonance (δ_H, δ_C) spectra were recorded on Agilent Technologies 400 MR (400 MHz) or Varian VNMR500 (500 MHz) spectrometers. All chemical shifts are quoted on the δ-scale in ppm using residual solvent as an internal standard. High-resolution mass spectra were recorded with a Bruker maXis 3G UHR-TOF mass spectrometer. Thin Layer Chromatography (t.l.c.) was carried out on Merck silica gel $60F_{254}$ aluminium-backed plates. Visualization of the plates was achieved using a u.v. lamp (λ_{max} = 254 or 365 nm), and/or 5% w/v ammonium molybdate in 2 M sulfuric acid. Flash column chromatography was carried out using Sorbsil C60 40/60 silica. Unless preparative details are provided, all reagents were commercially available or made following literature procedures. "Petrol" refers to the fraction of light petroleum ether boiling in the range of 40-60 °C. Reverse phase high performance liquid chromatography (RP-HPLC) was performed on a Dionex P680 HPLC instrument.

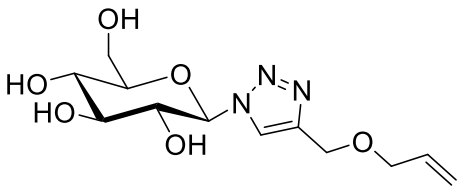
3-((1'-(2"-Acetamido-2"-deoxy-β-D-glucopyranosyl)-[1',2',3']-triazo-4'-yl)methyloxy)-1-propene 4[1]



N-Acetyl-D-glucosamine **2** (500 mg, 2.26 mmol) and triethylamine (1.55 mL, 11.3 mmol) were dissolved in D_2O/MeCN (4:1, 10 mL) and the reaction mixture was cooled to 0 °C. 2-Azido-1,3-dimethylimidazolinium hexafluorophosphate **3** (1.925 g, 6.75 mmol) was added and the reaction mixture was stirred for 1 h. The reaction mixture was then acidified to pH 2 by addition of HCl (1 M, 10 mL), stirred for 10 min, and then neutralised by the addition of NaHCO3 (sat. aqueous soln., 20 mL). The mixture was concentrated *in vacuo*. The residue was dissolved in *tert*-butanol/water (2:1, 25 mL) and 3-allyloxy-1-propyne **1** (0.45 mL,

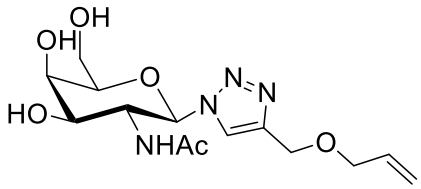
4.0 mmol), $CuSO_4.5H_2O$ (112 mg, 0.45 mmol), and sodium ascorbate (178 mg, 0.9 mmol) were added. The reaction mixture was then heated to 50 °C and stirred for 16 h. The reaction mixture was then concentrated *in vacuo* and the residue was dissolved in EtOH (50 mL), filtered through Celite®, and concentrated *in vacuo*. The residue was dissolved in water (50 mL), and the aqueous layer was washed with CH_2Cl_2 (2 x 100 mL), filtered through a column of Amberlite® IR-120 (Na^+ form, produced by treating the H^+ form with 1 M aqueous NaOH solution and then washing with water until pH 7), and concentrated *in vacuo*. The residue was pre-absorbed onto silica and purified by flash column chromatography (CH_2Cl_2:MeOH 8:1) to afford 3-((1'-(2"-acetamido-2"-deoxy-β-D-glucopyranosyl)-[1',2',3']-triazo-4'-yl)methyloxy)-1-propene **4** (615 mg, 79%) as a white solid; m.p. 95-100 °C (CH_2Cl_2); $[\alpha]_D^{20}$ -5.9 (*c*, 1.0 in MeOH); υ_{max} (neat) 3410 cm^{-1} (OH), 1651 cm^{-1} (NHC=O); δ_H (400 MHz, D_2O) 1.80 (3H, s, NHC(O)C$\underline{H}_3$), 3.66 - 3.85 (4 H, m, H-3, H-4, H-5 & H-6), 3.92 (1H, dd, $J_{5,6'}$ 1.6 Hz, $J_{6,6'}$ 12.5 Hz, H-6'), 4.04 (2H, d, *J* 6.3 Hz, CH_2=CHC$\underline{H}_2$), 4.25 (1H, t, *J* 10.0 Hz, H-2), 4.66 (2H, s, NCH=CC$\underline{H}_2$), 5.26 (1H, d, J_Z 10.6 Hz, $CH_E\underline{H}_Z$=$CHCH_2$), 5.32 (1H, d, J_E 17.2 Hz, C$\underline{H}_E H_Z$=$CHCH_2$), 5.84 (1H, d, $J_{1,2}$ 9.8 Hz, H-1), 5.92 (1H, ddt, J_E 17.2 Hz, J_Z 10.6, 2 x *J* 5.9 Hz, CH_2=C$\underline{H}CH_2$), 8.22 (1H, s, NC$\underline{H}$=C); δ_C (100.5 MHz, D_2O) 21.5 (q, NHC(O)C$\underline{H}_3$), 55.3 (d, C-2), 60.3 (t, C-6), 61.8 (t, NCH=C$\underline{C}H_2$), 69.2 (d, C-4), 70.8 (t, CH_2=CH$\underline{C}H_2$), 73.4 (d, C-3), 78.8 (d, C-5), 86.3 (d, C-1), 118.7 (t, $\underline{C}H_2$=$CHCH_2$), 123.7 (d, N$\underline{C}$H=C), 133.2 (d, CH_2=$\underline{C}CH_2$), 144.0 (s, NCH=$\underline{C}CH_2$), 174.0 (s, NH$\underline{C}$(O)CH_3); HRMS (ESI-TOF): calcd. for $C_{14}H_{23}N_4O_6^+$: 343.1612. Found: 343.1611 (MH^+).

3-((1'-β-D-Glucopyranosyl-[1',2',3']-triazo-4'-yl)methyloxy)-1-propene 6a[1]



Glucose **5a** (90.1 mg, 0.5 mmol) and triethylamine (0.35 mL, 2.5 mmol) were dissolved in D_2O/MeCN (4:1, 2 mL) and the reaction mixture was cooled to 0 °C. 2-Azido-1,3-dimethylimidazolinium hexafluorophosphate **3** (428 g, 1.5 mmol) was added and the reaction mixture was stirred for 1 h. The reaction mixture was then concentrated *in vacuo* and the residue was dissolved in *tert*-butanol/water (2:1, 6 mL). 3-Allyloxy-1-propyne **1** (0.11 mL, 1.0 mmol), $CuSO_4.5H_2O$ (25.0 mg, 0.1 mmol), and sodium ascorbate (39.6 mg, 0.2 mmol) were added. The reaction mixture was then heated to 50 °C and stirred for 16 h. The reaction mixture was then concentrated *in vacuo* and the residue was dissolved in EtOH (25 mL), filtered through Celite®, and concentrated *in vacuo*. The residue was dissolved in water (20 mL), and the aqueous layer was washed with CH_2Cl_2 (3 x 20 mL), filtered through a column of Amberlite® IR-120 (Na^+ form, produced by treating the H^+ form with 1 M aqueous NaOH solution and then washing with water until pH 7), and concentrated *in vacuo*. The residue was pre-absorbed onto silica and purified by flash column chromatography (CH_2Cl_2:MeOH 8:1) to afford 3-((1'-β-D-glucopyranosyl-[1',2',3']-triazo-4'-yl)methyloxy)-1-propene **6a** (100 mg, 66%) as a colourless oil; $[\alpha]_D^{20}$ -3 (*c*, 1.0 in MeOH); υ_{max} 3334 cm^{-1} (OH); δ_H (400 MHz, D_2O) 3.58 - 3.64 (1H, m, H-4), 3.67 - 3.80 (3H, m, H-3, H-5 & H-6'), 3.90 (1H, d, $J_{6,6'}$ 10.6 Hz, H-6'), 3.99 (1H, t, *J* 9.2 Hz, H-2), 4.10 (2H, d, *J* 5.9 Hz, CHC$\underline{H}_2$), 4.70 (2H, s, CC$\underline{H}_2$O), 5.27 (1H, d, J_Z 10.6 Hz, C$\underline{H}_Z$H$_E$=CH), 5.33 (1H, d, J_E 17.2 Hz, CH$_Z\underline{H}_E$=CH), 5.75 (1H, d, $J_{1,2}$ 9.4 Hz, H-1), 5.94 (1H, ddt, J_E 17.0 Hz, J_Z 10.6 Hz, 2 x *J* 6.2 Hz, CH_2=C$\underline{H}CH_2$), 8.25 (1H, s, NC$\underline{H}$=C); δ_C (100.5 MHz, D_2O) 60.3 (t, C-6), 62.0 (t, C$\underline{C}H_2$O), 68.9 (d, C-4), 71.1 (t, CH_2=CH$\underline{C}H_2$), 72.2 (d, C-2), 75.8 (d, C-3), 78.8 (d, C-5), 87.4 (d, C-1), 118.8 (t, $\underline{C}H_2$=CH), 124.3 (d, N$\underline{C}$H=C), 133.3 (d, CH_2=$\underline{C}$H), 144.2 (s, NCH=$\underline{C}CH_2$); HRMS (ESI-TOF): calcd. for $C_{12}H_{20}N_3O_6^+$: 302.1347. Found: 302.1348 (MH^+).

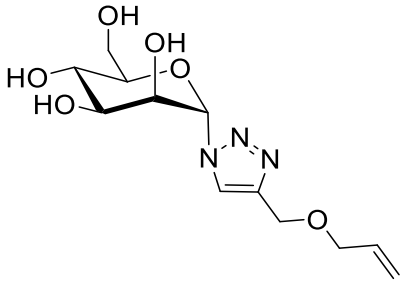
3-((1'-(2"-Acetamido-2"-deoxy-β-D-galactopyranosyl)-[1',2',3']-triazo-4'-yl)methyloxy)-1-propene 6b[1]



N-Acetyl-D-galactosamine **5b** (111 mg, 0.5 mmol) and triethylamine (0.35 mL, 2.5 mmol) were dissolved in D_2O/MeCN (4:1, 2 mL) and the reaction mixture was cooled to 0 °C. 2-Azido-1,3-dimethylimidazolinium hexafluorophosphate **3** (428 mg, 1.5 mmol) was added and the reaction mixture was stirred for 1 h. The reaction mixture was then acidified to pH 2 by addition of aqueous HCl (1 M, 2.5 mL), stirred for 10 min, and then neutralised by the addition of NaHCO3 (sat. aqueous soln., 5 mL). The mixture was concentrated *in vacuo*. The residue was dissolved in *tert*-butanol/water (2:1, 6 mL) and 3-allyloxy-1-propyne **1** (0.11 mL, 2.0 mmol), $CuSO_4.5H_2O$ (25 mg, 0.5 mmol), and sodium ascorbate (40 mg, 0.2 mmol) were added. The reaction mixture was then heated to 50 °C and stirred for 16 h. The reaction mixture was then concentrated *in vacuo* and the residue was dissolved in EtOH (20 mL), filtered through Celite®, and concentrated *in vacuo*. The residue was dissolved in water (10 mL), and the aqueous layer was washed with CH_2Cl_2 (3 x 20 mL), filtered through a column of Amberlite® IR-120 (Na^+ form, produced by treating the H^+ form with 1 M aqueous NaOH solution and then washing with water until pH 7), and concentrated *in vacuo*. The residue was pre-absorbed onto silica and purified by flash column chromatography (CH_2Cl_2:MeOH 8:1) to afford 3-((1'-(2"-acetamido-2"-deoxy-β-D-galactopyranosyl)-[1',2',3']-triazo-4'-yl)methyloxy)-1-propene **6b** (75.3 mg, 44%) as a white solid; $[\alpha]_D^{20}$ +6 (*c*, 1.0 in MeOH); υ_{max} (neat) 3290 cm^{-1} (OH), 1652 cm^{-1} (NHC=O); δ_H (400 MHz, D_2O) 1.80 (3H, s, NHC(O)C$\underline{H}_3$), 3.79 - 3.84 (2H, m, H-6 & H-6'), 3.95 - 4.02 (2H, m, H-3 & H-5), 4.05 (2H, d, *J* 5.9 Hz, CH_2=CHC$\underline{H}_2$), 4.10 (1H, d, $J_{3,4}$ 3.1 Hz, H-4), 4.42 (1H, t, *J* 10.2 Hz, H-2), 4.67

(2H, s, CC$\underline{H}_2$O), 5.27 (1H, dd, J_Z 10.6 Hz, J_{gem} 0.8 Hz, C$\underline{H}_Z$H$_E$=CH), 5.32 (1H, dd, J_E 17.4 Hz, J_{gem} 1.4 Hz, CH$_Z\underline{H}_E$=CH), 5.78 (1H, d, $J_{1,2}$ 9.8 Hz, H-1), 5.92 (1H, ddt, J_E 17.1 Hz, J_Z 10.7 Hz, 2 x J 5.9 Hz, CH$_2$=C$\underline{H}$), 8.27 (1H, s, NC$\underline{H}$=C); δ_C (100.5 MHz, D$_2$O) 21.6 (q, $\underline{C}$H$_3$), 52.0 (d, C-2), 60.8 (t, C-6), 61.8 (t, C$\underline{C}$H$_2$O), 67.6 (d, C-4), 70.6 (d, C-3), 70.8 (t, CH$_2$=CH$\underline{C}$H$_2$), 78.3 (d, C-5), 86.9 (d, C-1), 118.8 (t, $\underline{C}$H$_2$=CH), 123.6 (d, N$\underline{C}$H=C), 133.3 (d, CH$_2$=$\underline{C}$H), 144.1 (s, NCH=$\underline{C}$CH$_2$), 174.2 (s, NH$\underline{C}$(O)CH$_3$); HRMS (ESI-TOF): calcd. for $C_{14}H_{23}N_4O_6^+$: 343.1612. Found: 343.1613 (MH^+).

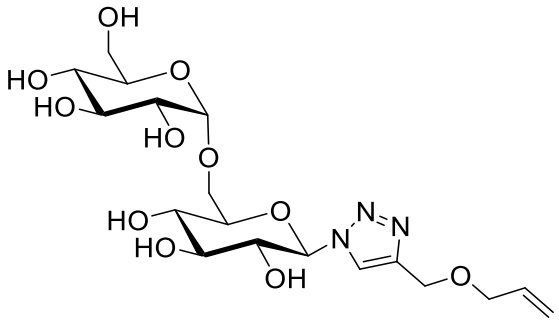
3-((1'-α-D-Mannopyranosyl-[1',2',3']-triazo-4'-yl)methyloxy)-1-propene 6c[1]



Mannose **5c** (90.1 mg, 0.5 mmol) and triethylamine (0.35 mL, 2.5 mmol) were dissolved in D$_2$O/MeCN (4:1, 2 mL) and the reaction mixture was cooled to 0 °C. 2-Azido-1,3-dimethylimidazolinium hexafluorophosphate **3** (428 g, 1.5 mmol) was added and the reaction mixture was stirred for 1 h. The reaction mixture was then concentrated *in vacuo* and the residue was dissolved in *tert*-butanol/water (2:1, 6 mL). 3-Allyloxy-1-propyne **1** (0.11 mL, 1.0 mmol), $CuSO_4.5H_2O$ (25.0 mg, 0.1 mmol), and sodium ascorbate (39.6 mg, 0.2 mmol) were added. The reaction mixture was then heated to 50 °C and stirred for 40 h. The reaction mixture was then concentrated *in vacuo* and the residue was dissolved in EtOH (25 mL), filtered through Celite®, and concentrated *in vacuo*. The residue was dissolved in water (20 mL), and the aqueous layer was washed with CH_2Cl_2 (3 x 20 mL), filtered through a column of Amberlite® IR-120 (Na^+ form, produced by treating the H^+ form with 1 M aqueous NaOH solution and then washing with water until pH 7), and concentrated *in vacuo*. The

residue was pre-absorbed onto silica and purified by flash column chromatography (CH_2Cl_2:MeOH 8:1) to afford 3-((1'-α-D-mannopyranosyl-[1',2',3']-triazo-4'-yl)methyloxy)-1-propene **6c** (120 mg, 80%) as a colourless oil; $[\alpha]_D^{20}$ +42 (*c*, 1.0 in MeOH); υ_{max} 3353 cm^{-1} (OH); δ_H (400 MHz, D_2O) 3.27 - 3.32 (1H, m, H-5), 3.75 - 3.85 (3H, m, H-4, H-6 & H-6'), 4.07 - 4.16 (3H, m, H-3 & CHC$\underline{H}_2$O), 4.69 (2H, s, CC$\underline{H}_2$O), 4.79 (1H, t, *J* 3.1 Hz, H-2), 5.26 (1H, dd, J_Z 10.6 Hz, J_{gem} 0.8 Hz, C$\underline{H}_Z$$H_E$=CH), 5.32 (1H, dd, J_E 17.2 Hz, J_{gem} 1.6 Hz, $CH_Z\underline{H}_E$=CH), 5.93 (1H, ddt, J_E 17.0 Hz, J_Z 10.6 Hz, 2 x *J* 6.2 Hz, CH_2=C$\underline{H}$), 6.12 (1H, d, $J_{1,2}$ 2.3 Hz, H-1), 8.19 (1H, s, NC$\underline{H}$=C); δ_C (100.5 MHz, D_2O) 60.4 (t, C-6), 62.0 (t, C$\underline{C}H_2$O), 66.5 (d, C-4), 68.2 (d, C-2), 70.5 (d, C-3), 71.1 (t, CH$\underline{C}H_2$O), 76.1 (d, C-5), 86.7 (d, C-1), 118.7 (t, $\underline{C}H_2$=CH), 124.7 (d, N$\underline{C}$H=C), 133.4 (d, CH_2=$\underline{C}$H), 144.3 (s, NCH=$\underline{C}CH_2$); HRMS (ESI-TOF): calcd. for $C_{12}H_{20}N_3O_6^+$: 302.1347. Found: 302.1339 (MH^+).

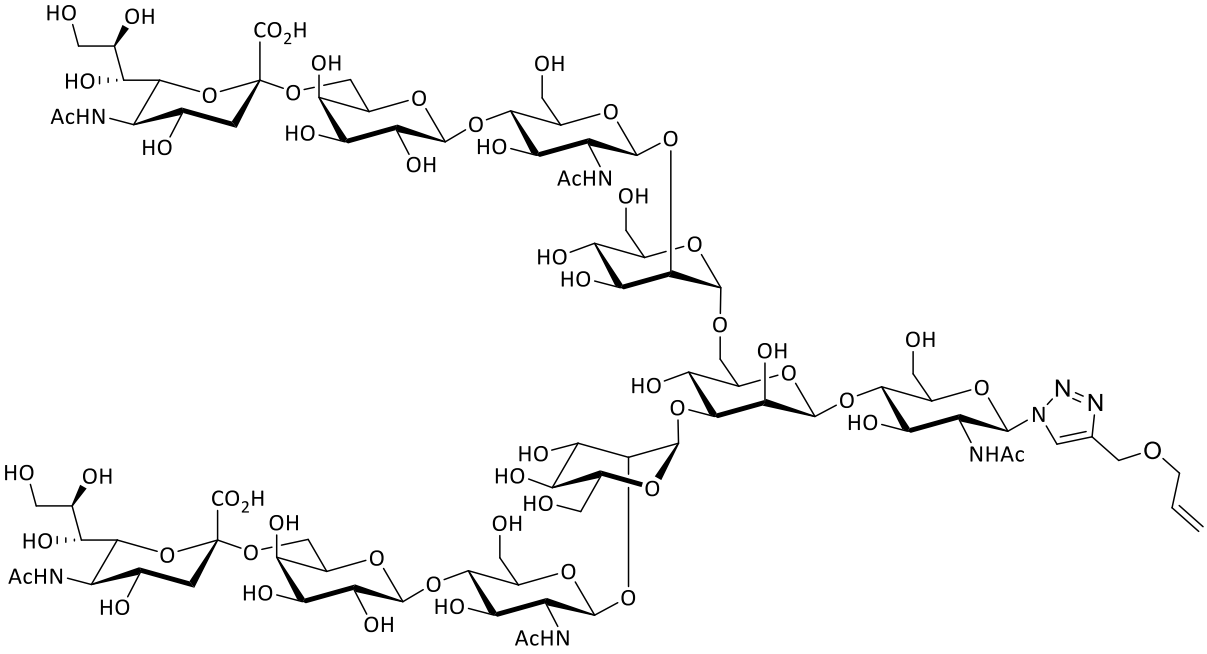
3-((1'-(α-D-Glucopyranosyl-(1→4)-β-D-glucopyranosyl)-[1',2',3']-triazo-4'-yl)methyloxy)-1-propene 6d[1]



Isomaltose **5d** (34.2 mg, 0.1 mmol) and triethylamine (0.07 mL, 0.5 mmol) were dissolved in D_2O/MeCN (4:1, 0.4 mL) and the reaction mixture was cooled to 0 °C. 2-Azido-1,3-dimethylimidazolinium hexafluorophosphate **3** (85.5 g, 0.3 mmol) was added and the reaction mixture was stirred for 1 h. *tert*-Butanol (0.8 mL) was added to the reaction mixture, followed by 3-allyloxy-1-propyne **1** (0.02 mL, 0.2 mmol), $CuSO_4.5H_2O$ (5.0 mg, 0.02 mmol), and sodium ascorbate (7.9 mg, 0.04 mmol). The reaction was heated to 50 °C and stirred for 16 h, then concentrated *in vacuo*. The residue was dissolved in EtOH (5 mL), filtered through Celite®, and concentrated *in vacuo*. The residue was dissolved in water (5 mL), and the aqueous layer was washed with CH_2Cl_2 (3 x 10 mL), filtered through a column of Amberlite® IR-120 (Na^+ form, produced by treating the H^+ form with 1 M aqueous NaOH solution and then washing with water until pH 7), and concentrated *in vacuo*. The residue was pre-absorbed onto silica and purified by flash column chromatography (CH_2Cl_2:MeOH 4:1) to afford 3-((1'-(α-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl)-[1',2',3']-triazo-4'-yl)methyloxy)-1-propene **6d** (34.7 mg, 75%) as a white solid; $[\alpha]_D^{20}$ +47 (*c*, 1.0 in MeOH); υ_{max} 3258 cm^{-1} (OH); δ_H (400 MHz, D_2O) 3.37 (1H, t, *J* 9.8 Hz, H-5_b), 3.51 (1H, dd, $J_{1,2}$ 3.9 Hz, $J_{2,3}$ 10.2 Hz, H-2_b), 3.59 - 3.76 (6H, m, H-3_a, H-5_a, H-3_b, H-4_b, H-6_b & H-$6'_b$), 3.76 - 4.00 (3H, m, H-4_a, H-6_a & H-$6'_a$), 4.06 (1H, t, *J* 9.2 Hz, H-2_a), 4.11 (2H, d, *J* 5.9 Hz, CH_2=CHC$\underline{H}_2$), 4.71 (2H, s, CC$\underline{H}_2$O), 4.91 (1H, d, $J_{1,2}$ 3.9 Hz, H-1_b), 5.28 (1H, d, J_Z 10.6 Hz,

C$\underline{H}_Z$H$_E$=CH), 5.34 (1H, dd, J_E 17.2 Hz, J_{gem} 1.6 Hz, CH$_Z\underline{H}_E$=CH), 5.77 (1H, d, $J_{1,2}$ 9.4 Hz, H-1$_a$), 5.95 (1H, ddt, J_E 17.0 Hz, J_Z 10.6 Hz, 2 x J 6.2 Hz, CH$_2$=C$\underline{H}$), 8.28 (1H, s, NC$\underline{H}$=C); δ_C (100.5 MHz, D$_2$O) 60.0 (t, C-6$_b$), 61.9 (t, C$\underline{C}$H$_2$O), 65.9 (t, C-6$_a$), 69.0 (d, C-5$_a$), 69.2 (d, C-5$_b$), 71.1 (t, CH$_2$=CH$\underline{C}$H$_2$), 71.3 (d, C-2$_b$), 71.6 (d, C-4$_b$), 72.0 (d, C-2$_a$), 72.9 (d, C-3$_b$), 76.0 (d, C-3$_a$), 77.5 (d, C-4$_a$), 87.3 (s, C-1$_a$), 98.0 (s, C-1$_b$), 118.8 (t, $\underline{C}$H$_2$=C), 124.5 (d, N$\underline{C}$H=C), 133.3 (s, CH=$\underline{C}$CH$_2$); HRMS (ESI-TOF): calcd. for $C_{18}H_{30}N_3O_{11}^+$: 464.1875. Found: 464.1878 (MH^+).

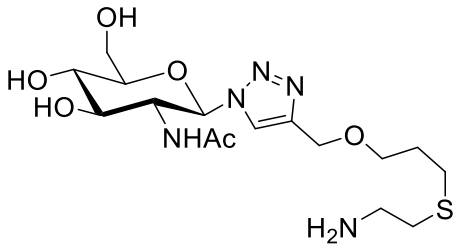
Sialoglycan-linker conjugate 6e



Sialoglycan **5e** (5.0 mg, 2.5 μmol) and triethylamine (24.4 μL, 175 μmol) were dissolved in D$_2$O/MeCN (4:1, 90 μL) and the solution cooled to 0 °C. 2-Azido-1,3-dimethylimidazolinium hexafluorophosphate **3** (21.4 mg, 75 μmol) was added and the mixture was stirred for 6 h. The reaction mixture was then acidified to pH 2 by addition of aqueous HCl over 10 min (1 M, 150 μL). After 20 min the reaction mixture was neutralised

by the addition of $NaHCO_3$ (sat. aqueous soln., 150 µL). The mixture was lyophilised and the residue was dissolved in *tert*-butanol/water (2:1, 150 µL) and 3-allyloxy-1-propyne **1** (5.6 µL, 50 µmol), $CuSO_4.5H_2O$ (1.2 mg, 5 µmol), and sodium ascorbate (2.0 mg, 10 µmol) were added. The reaction mixture was then heated to 50 °C and stirred for 40 h. The reaction was then filtered and the mixture purified by HPLC (t_R = 14.5 min; column: XBridge® Glycan BEH Amide 3.5µm (130 Å) column; gradient: 10% water in MeCN for 7 min, followed by an increase to 40% water over 5 min, followed by 40% water in MeCN for 5 min; column oven: 40 °C; flow rate: 1 mL/min; detection: UV 210 nm) to afford sialoglycan-linker conjugate **6e** (5.0 mg, 94%) as a white solid; $[\alpha]_D^{20}$ -10 (*c*, 0.25 in water); δ_H (400 MHz, D_2O) 4.05 (2H, d, *J* 5.9 Hz, CH_2=CHC<u>H</u>$_2$), 4.67 (2H, s, NCH=CC<u>H</u>$_2$), 5.26 (1H, d, J_Z 10.2 Hz, CH_E<u>H</u>$_Z$=CH), 5.32 (1H, d, J_E 17.2 Hz, C<u>H</u>$_E$H$_Z$=CH), 5.82 - 6.01 (2H, m, CH_2=C<u>H</u> & H-1), 8.24 (1H, m, NC<u>H</u>=C); HRMS (ESI-TOF): calcd. for $C_{82}H_{133}N_8O_{57}^+$: 2141.7749. Found: 2141.7770 (MH^+).

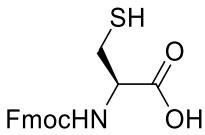
_S_-(3'-((1''-(2'''-Acetamido-2'''-deoxy-β-D-glucopyranosyl)-[1'',2'',3'']-triazo-4''-yl)methyloxy)-1'-propyl)-1-thio-2-aminoethane 8a



3-((1'-(2''-Acetamido-2''-deoxy-β-D-glucopyranosyl)-[1',2',3']-triazo-4'-yl)methyloxy)-1-propene **4** (41 mg, 0.12 mmol) and cysteamine hydrochloride **7a** (42 mg, 0.36 mmol) were dissolved in sodium acetate buffer (2 mL, pH 4.0, 0.2 M). 2,2-Dimethoxy-2-phenylacetophenone (3.1 mg, 0.012 mmol) was added, and the reaction mixture was stirred and irradiated in a Rayonet photoreactor (wavelength: 254 nm) for 6 h. The reaction mixture

was then concentrated *in vacuo* and the residue purified by flash column chromatography (CH_2Cl_2:MeOH:NH_3 75:25:1) to afford *S*-(3'-((1''-(2'''-acetamido-2'''-deoxy-β-D-glucopyranosyl)-[1'',2'',3'']-triazo-4''-yl)methyloxy)-1'-propyl)-1-thio-2-aminoethane **8a** (31.1 mg, 61%) as a colourless oil; υ_{max} (neat) 3246 cm^{-1} (broad, NH & OH), 1649 cm^{-1} (C=O); $[\alpha]_D^{20}$ -8 (*c*, 1.6 in MeOH); δ_H (400 MHz, D_2O) 1.80 (3H, s, C(O)C$\underline{H}_3$), 1.85 (2H, quin, *J* 6.7 Hz, OCH$_2$C$\underline{H}_2$CH$_2$S), 2.61 (2H, t, *J* 7.2 Hz, OCH$_2$CH$_2$C$\underline{H}_2$S), 2.82 (2H, t, *J* 6.7 Hz, SC$\underline{H}_2$CH$_2$NH$_2$), 3.19 (2H, t, *J* 6.7 Hz, SCH$_2$C$\underline{H}_2$NH$_2$), 3.61 (2H, t, *J* 6.1 Hz, OC$\underline{H}_2$CH$_2$CH$_2$S), 3.65 - 3.85 (4H, m, H-3, H-4, H-5 & H-6), 3.93 (1H, dd, $J_{5,6'}$ 1.6 Hz, $J_{6,6'}$ 12.1, H-6'), 4.25 (1H, t, *J* 9.8 Hz, H-2), 4.65 (2H, s, CC$\underline{H}_2$O), 5.84 (1H, d, $J_{1,2}$ 9.8 Hz, H-1), 8.23 (1H, s, NC$\underline{H}$=C); δ_C (100.5 MHz, D_2O) 21.6 (q, C(O)$\underline{C}$H$_3$), 27.2 (t, OCH$_2$CH$_2$$\underline{C}H_2$S), 28.1 (t, S$\underline{C}H_2CH_2NH_2$), 28.3 (t, OCH$_2$$\underline{C}H_2CH_2$S), 38.2 (t, SCH$_2$$\underline{C}H_2NH_2$), 55.3 (d, C-2), 60.3 (t, C-6), 62.4 (t, C$\underline{C}$H$_2$O), 68.3 (t, O$\underline{C}$H$_2$CH$_2$CH$_2$S), 69.2 (d, C-4), 73.4 (d, C-3), 78.9 (d, C-5), 86.3 (d, C-1), 123.7 (d, N$\underline{C}$H=C), 174.0 (s, $\underline{C}$(O)CH$_3$); HRMS (ESI-TOF): calcd. for $C_{16}H_{30}N_5O_6S^+$: 420.1911. Found: 420.1922 (MH^+).

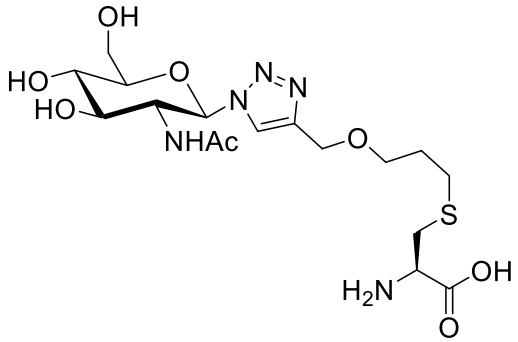
_N_-[(9-Fluorenylmethoxy)carbonyl]-L-cysteine 7b[2]



Trifluoroacetic acid (0.19 mL, 2.5 mmol) and triisopropylsilane (0.37 mL, 2.5 mmol) were added to a solution of *N*-[(9-fluorenylmethoxy)carbonyl]-*S*-trityl-L-cysteine (293 mg, 0.5 mmol) in CH_2Cl_2 (5 mL) under an atmosphere of nitrogen. After 1 h, the reaction was concentrated *in vacuo*. The residue was redissolved in CH_2Cl_2 (20 mL) and concentrated *in vacuo*, and this process was repeated until a white solid was obtained in order to remove all trifluoroacetic acid. The solid was precipitated (CH_2Cl_2/petrol) to afford *N*-[(9-fluorenylmethoxy)carbonyl]-L-cysteine **7b** (142 mg, 83%) was a white solid; $[\alpha]_D^{20}$ -25

(*c*, 2.0 in DMF) [lit. $[\alpha]_D^{20}$ -24.8 (*c*, 2.3 in DMF)][2]; υ_{max} (neat) 3310 cm^{-1} (NH) 1701 cm^{-1}, 1688 cm^{-1} (NC=O & HOC=O); δ_H (400 MHz, DMSO-d_6)[2] 2.65 - 2.76 (1H, m, C<u>H</u>H'SH), 2.82 - 2.91 (1H, m, CH<u>H</u>'SH), 4.09 (1H, td, *J* 8.4 Hz, *J* 4.3 Hz, C<u>H</u>CH_2SH), 4.21 (1H, t, *J* 7.0 Hz, C<u>H</u>CH_2O), 4.26 - 4.31 (2H, m, CHC<u>H</u>$_2$O), 7.25 - 7.35 (2H, m, 2 x Ar-H), 7.35 - 7.45 (2H, m, 2 x Ar-H), 7.66 (1H, d, *J* 8.6 Hz, NH), 7.71 (2H, d, *J* 7.4 Hz, 2 x Ar-H), 7.87 (2H, d, *J* 7.4 Hz, 2 x Ar-H); δ_C (100.5 MHz, DMSO-d_6)[2] 25.9 (t, <u>C</u>H_2SH), 47.1 (d, <u>C</u>HCH_2O), 57.0 (d, <u>C</u>HCH_2SH), 66.2 (t, CH<u>C</u>H_2O), 120.6 (d, Ar-C), 125.7 (d, Ar-C), 127.5 (D, Ar-C), 128.1 (d, Ar-C), 141.2 (s, Ar-C), 144.2 (s, Ar-C), 144.2 (s, Ar-C), 156.5 (s, OC(O)NH), 172.3 (s, COOH); HRMS (ESI-TOF): calcd. for $C_{18}H_{17}NO_4SNa^+$: 366.0770. Found: 366.0756 (MNa^+).

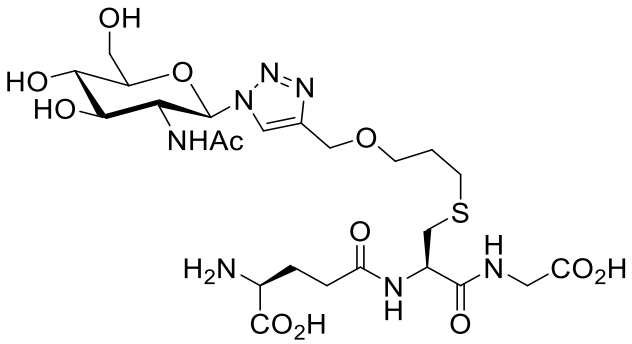
_S_-(3'-((1''-(2'''-Acetamido-2'''-deoxy-β-D-glucopyranosyl)-[1'',2'',3'']-triazo-4''-yl)methyloxy)-1'-propyl)-L-cysteine 8b



3-((1'-(2''-Acetamido-2''-deoxy-β-D-glucopyranosyl)-[1',2',3']-triazo-4'-yl)methyloxy)-1-propene **4** (50 mg, 0.15 mmol) and *N*-[(9-fluorenylmethoxy)carbonyl]-L-cysteine **7b** (60 mg, 0.17 mmol) were dissolved in a mixture of sodium acetate buffer (0.7 mL, pH 4.0, 0.6 M) and *tert*-butanol (1.3 mL). 2,2-Dimethoxy-2-phenylacetophenone (4.0 mg, 0.016 mmol) was added, and the reaction mixture was stirred and irradiated in a Rayonet photoreactor (wavelength: 254 nm) for 2 h. A further portion of *N*-[(9-fluorenylmethoxy)carbonyl]-L-cysteine **7b** (60 mg, 0.17 mmol) was added, and the reaction mixture was stirred and irradiated for a further 2 h. The reaction mixture was then concentrated *in vacuo* and

dissolved in anhydrous DMF (4.5 mL). Piperidine (0.5 mL, 6.8 mmol) was added, and the mixture stirred for 2 h. The mixture was concentrated *in vacuo* and the residue was purified by reverse phase flash column chromatography to afford *S*-(3'-((1''-(2'''-Acetamido-2'''-deoxy-β-D-glucopyranosyl)-[1'',2'',3'']-triazo-4''-yl)methyloxy)-1'-propyl)- L-cysteine **8b** (58 mg, 74%) as a colourless oil; $[\alpha]_D^{20}$ -15 (*c*, 0.9 in water); υ_{max} 3245 cm^{-1} (OH), 1628 cm^{-1} (NC=O); δ_H (400 MHz, D_2O) 1.80 (3H, s, NHC(O)C$\underline{H}_3$), 1.86 (2H, quin, *J* 6.7 Hz, $CH_2C\underline{H}_2CH_2$), 2.63 (2H, t, *J* 6.8 Hz, $CH_2C\underline{H}_2S$), 2.98 (1H, dd, *J* 14.9 Hz, *J* 7.8 Hz, CHC$\underline{H}$H'S), 3.09 (2H, dd, *J* 14.9 Hz, *J* 4.3 Hz, CHCH$\underline{H}$'S), 3.61 (2H, t, *J* 6.1 Hz, $OC\underline{H}_2CH_2$), 3.65 - 3.85 (4H, m, H-3, H-4, H-5 & H-6), 3.86 - 3.97 (2H, m, C$\underline{H}CH_2$ & H-6'), 4.25 (1H, t, *J* 9.8 Hz, H-2), 4.64 (2H, s, $CC\underline{H}_2O$), 5.84 (1H, d, $J_{1,2}$ 9.8 Hz, H-1), 8.23 (1H, s, NC$\underline{H}$=C); δ_C (100.5 MHz, D_2O) 21.6 (q, NHC(O)$\underline{C}H_3$), 27.9 (t, $CH_2\underline{C}H_2S$), 28.3 (t, $CH_2C\underline{H}_2CH_2$), 32.0 (t, $CH\underline{C}H_2S$), 53.5 (d, $\underline{C}HCH_2$), 55.3 (d, C-2), 60.3 (t, C-6), 62.4 (t, $C\underline{C}H_2O$), 68.3 (t, $O\underline{C}H_2CH_2$), 69.2 (d, C-4), 73.4 (d, C-3), 78.8 (d, C-5), 86.3 (d, C-1), 123.7 (d, N$\underline{C}$H=C), 144.1 (s, CH=$\underline{C}CH_2$), 172.7, 174.0 (2 x s, 2 x C=O); HRMS (ESI-TOF): calcd. for $C_{17}H_{30}N_5O_8S^+$: 464.1810. Found: 464.1816 (MH^+).

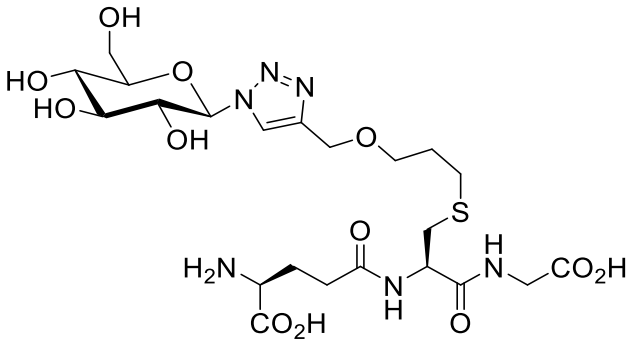
_S_-(3'-((1''-(2'''-Acetamido-2'''-deoxy-β-D-glucopyranosyl)-[1'',2'',3'']-triazo-4''-yl)methyloxy)-1'-propyl)-γ-L-glutamyl-L-cysteinylglycine 8c



3-((1'-(2"-Acetamido-2"-deoxy-β-D-glucopyranosyl)-[1',2',3']-triazo-4'-yl)methyloxy)-1-propene **4** (20.5 mg, 0.06 mmol) and γ-L-glutamyl-L-cysteinylglycine **7c** (18.4 mg,

0.06 mmol) were dissolved in sodium acetate buffer (1 mL, pH 4.0, 0.2 M). 2,2-Dimethoxy-2-phenylacetophenone (1.5 mg, 0.006 mmol) was added, and the reaction mixture was stirred and irradiated in a Rayonet photoreactor (wavelength: 254 nm) for 4 h. The reaction mixture was then concentrated *in vacuo* and the residue purified by reverse phase flash column chromatography (water) to afford *S*-(3'-((1''-(2'''-acetamido-2'''-deoxy-β-D-glucopyranosyl)-[1'',2'',3'']-triazo-4''-yl)methyloxy)-1'-propyl)-γ-L-glutamyl-L-cysteinylglycine **8c** (38.8 mg, quant.) as a colourless oil; $[\alpha]_D^{20}$ -10 (*c*, 0.7 in water); υ_{max} 3246 cm^{-1} (OH), 1728 cm^{-1} (OC=O), 1641 (NHC=O); δ_H (400 MHz, D_2O) 1.79 (3H, s, C(O)C$\underline{H}_3$) 1.84 (2H, quin, *J* 5.9 Hz, $CH_2C\underline{H}_2CH_2$), 2.19 (2H, q, *J* 6.4 Hz, Q-CHC$\underline{H}_2$), 2.50 - 2.58 (2H, m, $CH_2C\underline{H}_2S$), 2.58 - 2.65 (2H, m, Q-CC$\underline{H}_2$), 2.84 (1H, dd, *J* 13.9 Hz, *J* 8.8 Hz, C-C$\underline{H}$H'), 3.01 (1H, dd, *J* 14.3 Hz, *J* 4.9 Hz, C-CH$\underline{H}$'), 3.60 (1H, t, *J* 6.1 Hz, OC$\underline{H}_2CH_2$), 3.65 - 3.85 (4H, m, H-3, H-4, H-5 & H-6), 3.89 - 4.01 (4H, m, G-C$\underline{H}_2$, Q-C$\underline{H}$ & H-6'), 4.25 (1H, t, *J* 10.0 Hz, H-2), 4.54 (2H, dd, *J* 8.6 Hz, *J* 5.1 Hz, C-C$\underline{H}$), 4.64 (1H, s, CC$\underline{H}_2$O), 5.84 (1H, d, $J_{1,2}$ 9.8 Hz, H-1), 8.23 (1H, s, NC$\underline{H}$=C); δ_C (100.5 MHz, D_2O) 25.7 (t, Q-CH$\underline{C}H_2$), 28.1 (t, $CH_2\underline{C}H_2S$), 28.4 (t, $CH_2\underline{C}H_2CH_2$), 31.0 (t, Q-C$\underline{C}H_2$), 32.7 (t, C-$\underline{C}H_2$), 41.2 (t, G-$\underline{C}H_2$), 53.0 (d, Q-$\underline{C}$H), 53.0 (d, C-$\underline{C}$H), 55.3 (d, C-2), 60.4 (t, C-6), 62.4 (t, C$\underline{C}H_2$O), 68.3 (t, O$\underline{C}H_2CH_2$), 69.2 (d, C-4), 73.4 (d, C-3), 78.8 (d, C-5), 86.3 (d, C-1), 123.7 (d, N$\underline{C}$H=C), 172.5, 172.8, 172.9, 174.0, 174.4 (5 x s, 5 x $\underline{C}$=O); HRMS (ESI-TOF): calcd. for $C_{24}H_{40}N_7O_{12}S^+$: 650.2450. Found: 650.2450 (MH^+).

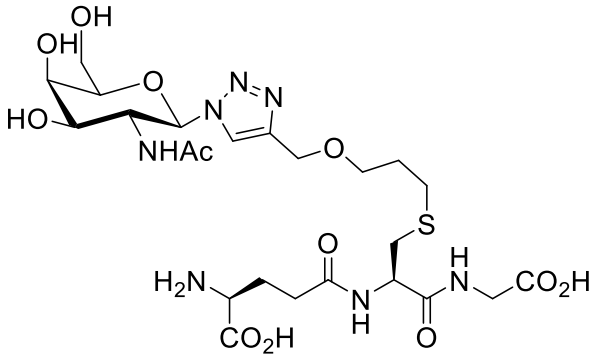
***S*-(3'-((1''-β-D-Glucopyranosyl-[1'',2'',3'']-triazo-4''-yl)methyloxy)-1'-propyl)-γ-L-glutamyl-L-cysteinylglycine 8d**



3-((1'-β-D-Glucopyranosyl-[1',2',3']-triazo-4'-yl)methyloxy)-1-propene **6a** (17.0 mg, 0.06 mmol) and γ-L-glutamyl-L-cysteinylglycine **7c** (17.0 mg, 0.06 mmol) were dissolved in sodium acetate buffer (1 mL, pH 4.0, 0.2 M). 2,2-Dimethoxy-2-phenylacetophenone (1.5 mg, 0.006 mmol) was added, and the reaction mixture was stirred and irradiated in a Rayonet photoreactor (wavelength: 254 nm) for 4 h. The reaction mixture was then concentrated *in vacuo* and the residue purified by reverse phase flash column chromatography (water) to afford *S*-(3'-((1''-β-D-glucopyranosyl-[1'',2'',3'']-triazo-4''-yl)methyloxy)-1'-propyl)-γ-L-glutamyl-L-cysteinylglycine **8d** (30 mg, 93%) as a colourless oil; $[\alpha]_D^{20}$ -23 (*c*, 1.0 in water); υ_{max} 3272 (OH), 1643, 1556 (C(O)N); δ_H (400 MHz, D_2O) 1.85 (2H, quin, *J* 7.0 Hz, $CH_2C\underline{H}_2CH_2$), 2.13 (2H, q, *J* 7.0 Hz, Q-$CHC\underline{H}_2CH_2$), 2.50 (2H, t, *J* 7.0 Hz, Q-$CHCH_2C\underline{H}_2$), 2.60 (2H, t, *J* 6.8 Hz, $CH_2C\underline{H}_2S$), 2.82 (1H, dd, *J* 14.1 Hz, *J* 9.0 Hz, C-C$\underline{H}$H'), 3.03 (1H, dd, *J* 13.9 Hz, *J* 4.9 Hz, CH$\underline{H}$'), 3.57 - 3.81 (9H, m, H-3, H-4, H-5, H-6, G-$C\underline{H}_2$, Q-C$\underline{H}$ & $OC\underline{H}_2CH_2$), 3.89 (1H, d, $J_{6,6'}$ 11.0 Hz, H-6'), 3.99 (1H, t, *J* 9.2 Hz, H-2), 4.54 (1H, dd, *J* 8.8 Hz, *J* 4.9 Hz, C-C$\underline{H}$), 4.67 (2H, s, $CC\underline{H}_2O$), 5.75 (1H, d, $J_{1,2}$ 9.4 Hz, H-1), 8.26 (1H, s, NC$\underline{H}$=C); δ_C (100.5 MHz, D_2O) 26.2 (t, Q-$CHC\underline{H}_2CH_2$), 28.0 (t, $CH_2C\underline{H}_2S$), 28.4 (t, $CH_2C\underline{H}_2CH_2$), 31.4 (t, Q-$CHCH_2C\underline{H}_2$), 32.9 (t, C-$C\underline{H}_2$), 43.4 (t, G-$C\underline{H}_2$), 53.1 (d, C-C$\underline{H}$), 54.1 (d, Q-C$\underline{H}$), 60.4 (t, C-6), 62.6 (t, $CC\underline{H}_2O$), 68.5 (t, $OC\underline{H}_2CH_2$), 68.9 (d, C-4), 72.2 (d, C-2), 75.9 (d, C-3), 78.8 (d, C-5), 87.4 (d, C-1), 124.3 (d, NC$\underline{H}$=C), 144.3 (s, NCH=C$\underline{}$), 171.9,

174.9, 181.4 (3 x s, 3 x C(O)); HRMS (ESI-TOF): calcd. for $C_{22}H_{37}N_6O_{12}S^+$: 609.2185. Found: 609.2204 (MH^+).

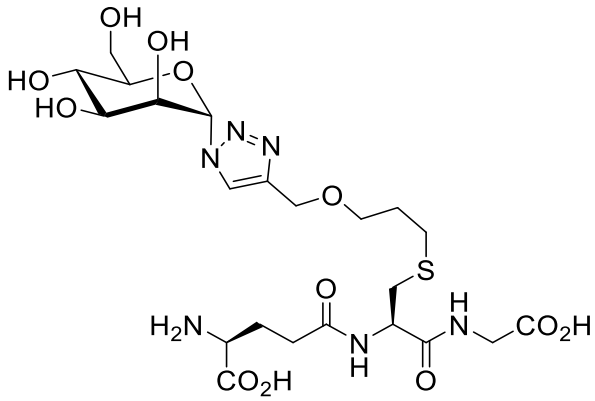
_S_-(3'-((1''-(2'''-Acetamido-2'''-deoxy-β-D-galactopyranosyl)-[1'',2'',3'']-triazo-4''-yl)methyloxy)-1'-propyl)-γ-L-glutamyl-L-cysteinylglycine 8e



3-((1'-(2''-Acetamido-2''-deoxy-β-D-glucopyranosyl)-[1',2',3']-triazo-4'-yl)methyloxy)-1-propene **6b** (20.5 mg, 0.06 mmol) and γ-L-glutamyl-L-cysteinylglycine **7c** (18.4 mg, 0.06 mmol) were dissolved in sodium acetate buffer (1 mL, pH 4.0, 0.2 M). 2,2-Dimethoxy-2-phenylacetophenone (1.5 mg, 0.006 mmol) was added, and the reaction mixture was stirred and irradiated in a Rayonet photoreactor (wavelength: 254 nm) for 4 h. The reaction mixture was then concentrated *in vacuo* and the residue purified by reverse phase flash column chromatography (water) to afford *S*-(3'-((1''-(2'''-acetamido-2'''-deoxy-β-D-galactopyranosyl)-[1'',2'',3'']-triazo-4''-yl)methyloxy)-1'-propyl)-γ-L-glutamyl-L-cysteinylglycine **8e** (27.2 mg, 70%) as a white solid; $[\alpha]_D^{20}$ -9 (*c*, 0.5 in water); υ_{max} 3362 cm^{-1} (OH), 1637 cm^{-1} (C=O); δ_H (400 MHz, D_2O) 1.77 - 1.88 (5H, m, $CH_2C\underline{H}_2CH_2$ & C(O)$C\underline{H}_3$), 2.13 (2H, q, *J* 7.3 Hz, Q-CHC$\underline{H}_2CH_2$), 2.51 (2H, t, *J* 7.6 Hz, Q-$CHCH_2C\underline{H}_2$), 2.60 (2H, t, *J* 7.2 Hz, $CH_2C\underline{H}_2S$), 2.83 (1H, dd, *J* 14.1 Hz, *J* 9.0 Hz, C-C$\underline{H}$H'), 3.03 (1H, dd, *J* 13.9 Hz, *J* 4.9 Hz, C-CH$\underline{H}$'), 3.60 (2H, t, *J* 6.3 Hz, O$C\underline{H}_2CH_2$), 3.72 - 3.77 (3H, m, Q-C$\underline{H}$ & G-$C\underline{H}_2$), 3.79 - 3.84 (2H, m, H-6 & H-6'), 3.94 - 4.02 (2H, m, H-3 & H-5), 4.09 (1H, d, $J_{3,4}$ 2.7

Hz, H-4), 4.43 (1H, t, *J* 10.2 Hz, H-2), 4.54 (1H, dd, *J* 9.0 Hz, *J* 4.7 Hz, C-C<u>H</u>), 4.65 (2H, s, CC<u>H</u>$_2$O), 5.78 (1H, d, $J_{1,2}$ 9.8 Hz, H-1), 8.27 (1H, s, NC<u>H</u>=C); δ_C (100.5 MHz, D_2O) 21.7 (q, C(O)<u>C</u>H$_3$), 26.2 (t, Q-CH<u>C</u>H$_2$CH$_2$), 28.1 (t, CH$_2$<u>C</u>H$_2$S), 28.4 (t, CH$_2$<u>C</u>H$_2$CH$_2$), 31.4 (t, Q-CHCH$_2$<u>C</u>H$_2$), 32.9 (t, C-<u>C</u>H$_2$), 43.3 (t, G-<u>C</u>H$_2$), 51.9 (d, C-2), 53.1 (d, C-<u>C</u>H), 54.1 (d, Q-<u>C</u>H), 60.9 (t, C-6), 62.5 (t, C<u>C</u>H$_2$O), 67.7 (d, C-4), 68.3 (t, O<u>C</u>H$_2$CH$_2$), 70.7 (d, C-3), 78.3 (d, C-5), 86.8 (d, C-1), 123.6 (d, N<u>C</u>H=C), 144.2 (s, CH=<u>C</u>CH$_2$), 171.9, 173.9, 174.2, 174.8, 176.1 (5 x s, 5 x <u>C</u>(O)); HRMS (ESI-TOF): calcd. for $C_{24}H_{40}N_7O_{12}S^+$: 650.2450. Found: 650.2475 (MH^+).

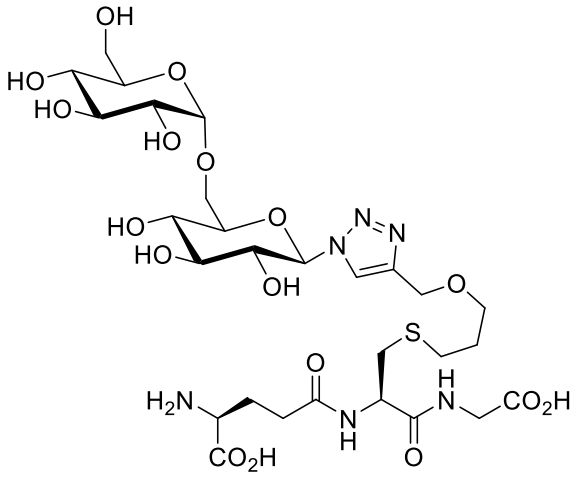
_S_-(3'-((1''-α-D-Mannopyranosyl-[1'',2'',3'']-triazo-4''-yl)methyloxy)-1'-propyl)-γ-L-glutamyl-L-cysteinylglycine 8f



3-((1'-β-D-Mannopyranosyl-[1',2',3']-triazo-4'-yl)methyloxy)-1-propene **6c** (18.1 mg, 0.06 mmol) and γ-L-glutamyl-L-cysteinylglycine **7c** (18.1 mg, 0.06 mmol) were dissolved in sodium acetate buffer (1 mL, pH 4.0, 0.2 M). 2,2-Dimethoxy-2-phenylacetophenone (1.5 mg, 0.006 mmol) was added, and the reaction mixture was stirred and irradiated in a Rayonet photoreactor (wavelength: 254 nm) for 4 h. The reaction mixture was then concentrated *in vacuo* and the residue purified by reverse phase flash column chromatography (water) to afford *S*-(3'-((1''-α-D-mannopyranosyl-[1'',2'',3'']-triazo-4''-yl)methyloxy)-1'-propyl)-γ-L-glutamyl-L-cysteinylglycine **8f** (25.2 mg, 74%) as a colourless oil; $[\alpha]_D^{20}$ -3 (*c*, 1.0 in water);

υ_{max} 3217 cm^{-1} (OH), 1634 (C=O); δ_H (400 MHz, D_2O) 1.84 (2H, quin, *J* 6.7 Hz, $CH_2C\underline{H}_2CH_2$), 2.13 (3H, q, *J* 7.3 Hz, Q-$CHC\underline{H}_2CH_2$), 2.51 (3H, t, *J* 7.8 Hz, Q-$CHCH_2C\underline{H}_2$), 2.60 (2H, t, *J* 7.2 Hz, $CH_2C\underline{H}_2S$), 2.82 (1H, dd, *J* 13.9 Hz, *J* 9.2 Hz, C-C<u>H</u>H'), 3.03 (1H, dd, *J* 14.3 Hz, *J* 4.9 Hz, C-CH<u>H</u>'), 3.25 - 3.34 (1H, m, H-5), 3.65 (2H, t, *J* 5.9 Hz, $OC\underline{H}_2CH_2$), 3.72 - 3.85 (6H, m., H-4, H-6, H-6', Q-C<u>H</u> & G-$C\underline{H}_2$), 4.13 (1H, dd, $J_{2,3}$ 3.5 Hz, $J_{3,4}$ 9.0 Hz, H-3), 4.53 (1H, dd, *J* 8.8 Hz, *J* 4.9 Hz, C-C<u>H</u>), 4.66 (2H, s, $CC\underline{H}_2O$), 4.78 - 4.82 (1H, m, H-2), 6.12 (1H, s, H-1), 8.20 (1H, s, NC<u>H</u>=C); δ_C (100.5 MHz, D_2O) 26.1 (t, Q-$CH\underline{C}H_2CH_2$), 28.0 (t, $CH_2\underline{C}H_2S$), 28.3 (t, $CH_2\underline{C}H_2CH_2$), 31.4 (t, Q-$CHCH_2\underline{C}H_2$), 32.8 (t, C-$\underline{C}H_2$), 43.4 (t, G-$\underline{C}H_2$), 53.1 (d, C-2), 54.1 (d, Q-<u>C</u>H), 60.4 (t, C-6), 62.5 (t, $C\underline{C}H_2O$), 66.5 (d, C-4), 68.2 (d, C-2), 68.4 (t, $O\underline{C}H_2CH_2$), 70.4 (d, C-3), 76.1 (d, C-5), 86.7 (d, C-1), 124.7 (d, N<u>C</u>H=C), 144.4 (s, NCH=<u>C</u>), 171.9, 173.9, 174.8 (3 x s, 3 x <u>C</u>(O)); HRMS (ESI-TOF): calcd. for $C_{22}H_{37}N_6O_{12}S^+$: 609.2185. Found: 609.2211 (MH^+).

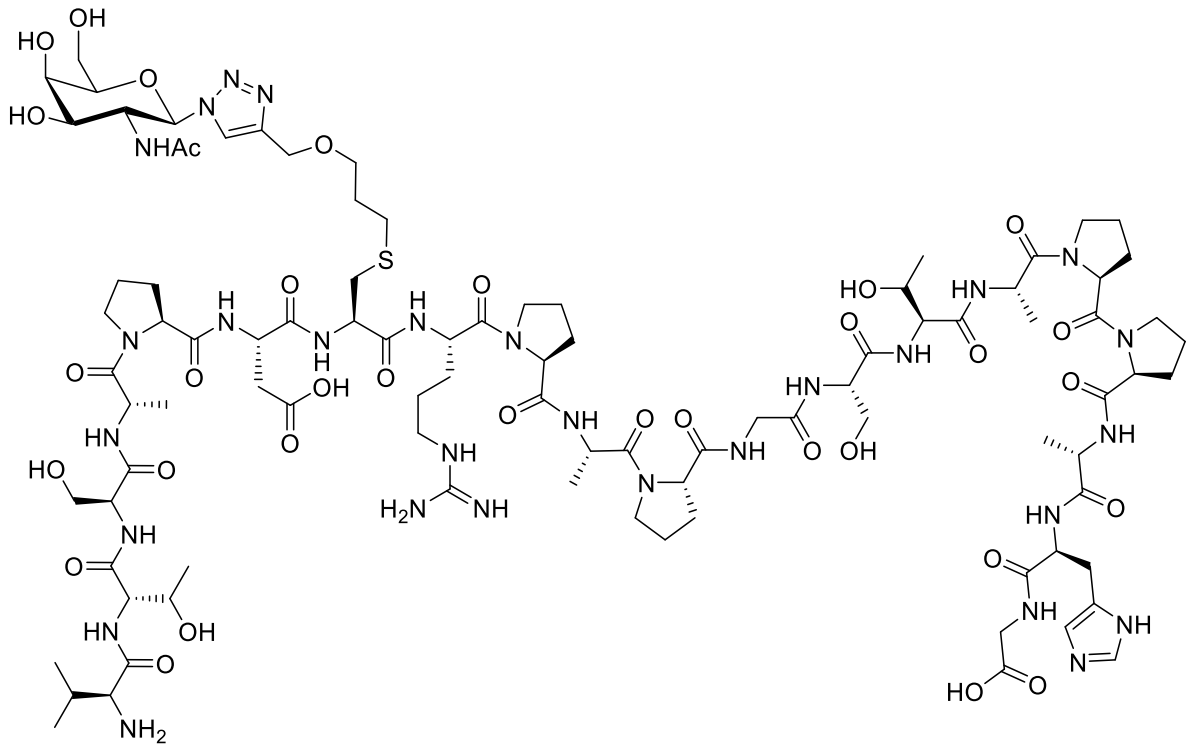
_S_-(5'-((1''-(α-D-Glucopyranosyl-(1→4)-β-D-glucopyranosyl)-[1'',2'',3'']-triazo-4''-yl)methyloxy)-1'-pentyl)-γ-L-glutamyl-L-cysteinylglycine 8g



3-((1'-(α-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl)-[1',2',3']-triazo-4'-yl)methyloxy)-1-propene **6d** (16.0 mg, 0.035 mmol) and γ-L-glutamyl-L-cysteinylglycine **7c** (10.6 mg, 0.035 mmol) were dissolved in sodium acetate buffer (0.5 mL, pH 4.0, 0.2 M). 2,2-

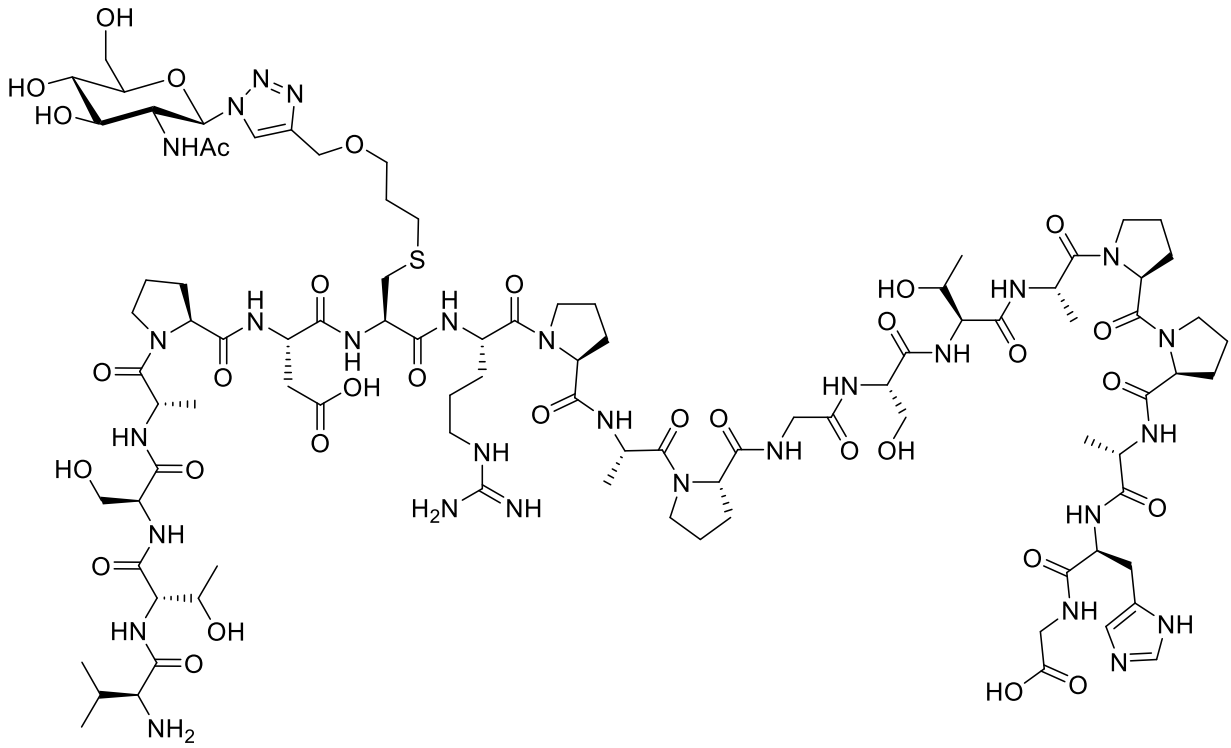
Dimethoxy-2-phenylacetophenone (0.9 mg, 0.0035 mmol) was added, and the reaction mixture was stirred and irradiated in a Rayonet photoreactor (wavelength: 254 nm) for 4 h. The reaction mixture was then concentrated *in vacuo* and the residue purified by HPLC (t_R = 20.5 min, column: Luna 5u C18 (100 Å) column (Phenomenex); gradient: 100% water for 10 min, followed by an increase to 40% MeOH over 5 min, then 40% MeOH for 10 min; column oven: 40 °C; flow rate: 2 mL/min; detection: UV 210 nm) to afford *S*-(5'-((1''-(α-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl)-[1'',2'',3'']-triazo-4''-yl)methyloxy)-1'-pentyl)-γ-L-glutamyl-L-cysteinylglycine **8g** (20.1 mg, 76%) as a white solid; $[\alpha]_D$ +18 (*c*, 0.7 in water); υ_{max} 3306 cm^{-1} (OH), 1727 cm^{-1} (HOC=O), 1658 cm^{-1} (NHC=O); δ_H (400 MHz, D_2O) 1.82 (2H, quin, *J* 6.7 Hz, $OCH_2C\underline{H}_2CH_2S$), 2.12 - 2.28 (2H, m, *J* 7.0 Hz, Q-$CHC\underline{H}_2CH_2$), 2.51 - 2.63 (4H, m, $CH_2C\underline{H}_2S$ & $QCHCH_2C\underline{H}_2$), 2.81 (1H, dd, *J* 14.1 Hz, *J* 8.6 Hz, C-C$\underline{H}$H'), 2.98 (1H, dd, *J* 14.1, 5.5 Hz, C-CH$\underline{H}$'), 3.31 - 3.39 (1H, m, H-5_b), 3.47 (1H, dd, $J_{1,2}$ 3.5 Hz, $J_{2,3}$ 9.8 Hz, H-2_b), 3.56 - 3.71 (8H, m, H-3_a, H-5_a, H-3_b, H-4_b, H-6_b, H-$6'_b$ & $OC\underline{H}_2CH_2$), 3.81 (1H, d, $J_{6,6'}$ 10.2 Hz, H-6_a), 3.85 - 3.94 (2H, m, H-4_a & H-$6'_a$), 3.96 (2H, s, G-CH_2), 4.02 (1H, t, *J* 9.2 Hz, H-2_a), 4.06 (1H, t, *J* 6.7 Hz, Q-CH), 4.51 (1H, dd, *J* 8.4 Hz, *J* 5.3 Hz, C-CH), 4.64 (2H, s, $CC\underline{H}_2O$), 4.86 (1H, d, $J_{1,2}$ 3.5 Hz, H-1_b), 5.73 (1H, d, $J_{1,2}$ 9.4 Hz, H-1_a), 8.23 (1H, s, NC$\underline{H}$=C); δ_C (100.5 MHz, D_2O) 25.4 (t, Q-$CH\underline{C}H_2CH_2$), 28.1 (t, $CH_2\underline{C}H_2S$), 28.4 (t, Q-$CH\underline{C}H_2CH_2$), 30.8 (t, Q-$CHCH_2\underline{C}H_2$), 32.7 (t, C-$\underline{C}H_2$), 41.0 (d, G-$\underline{C}H_2$), 52.1 (t, Q-$\underline{C}$H), 53.0 (d, C-$\underline{C}$H), 60.0 (t, C-6_b), 62.5 (t, $C\underline{C}H_2O$), 65.9 (t, C-6_a), 68.5 (t, $O\underline{C}H_2CH_2$), 69.0 (d, C-5_a), 69.2 (d, C-5_b), 71.3 (d, C-2_b), 71.6 (d, C-4_b), 72.0 (d, C-2_a), 72.9 (d, C-3_b), 76.1 (d, C-3a), 77.5 (d, C-4_a), 87.3 (d, C-1_a), 98.0 (d, C-1_b), 124.5 (d, N$\underline{C}$H=C), 144.2 (s, NCH=$\underline{C}CH_2$), 171.4, 172.7, 172.8, 174.2 (4 x s, 4 x C(O)); HRMS (ESI-TOF): calcd. for $C_{28}H_{47}N_6O_{17}S^+$: 771.2713. Found: 771.2729 (MH^+).

MUC1-GalNAc Neoglycopeptide 10



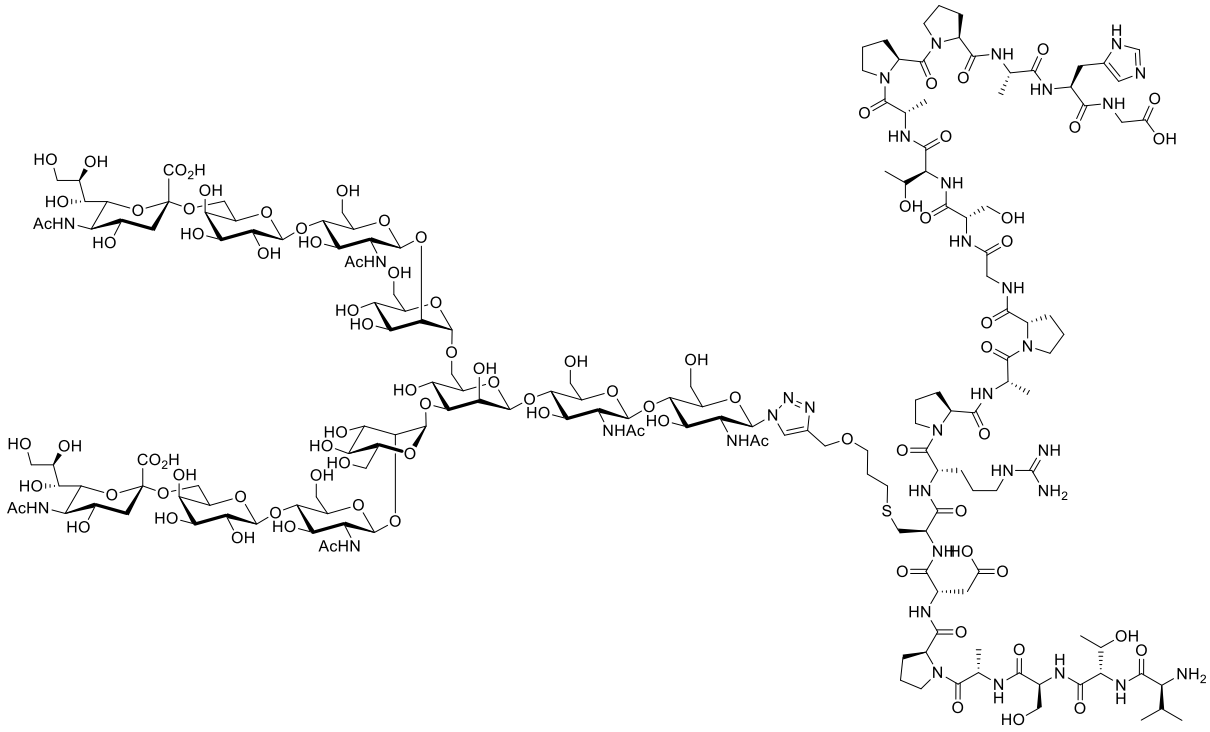
3-((1'-(2"-Acetamido-2"-deoxy-β-D-galactopyranosyl)-[1',2',3']-triazo-4'-yl)methyloxy)-1-propene **6b** (1.7 mg, 5.0 μmol) and modified MUC1 peptide **9** (0.9 mg, 0.5 μmol) were dissolved in sodium acetate buffer (50 μL, pH 4.0, 0.2 M). 2,2-Dimethoxy-2-phenylacetophenone (0.1 mg, 0.4 μmol) was added, and the reaction mixture was stirred and irradiated in a Rayonet photoreactor (wavelength: 254 nm) for 4 h, and then analysed by HPLC (column: Prodigy 5u ODS3 (100 Å) column (Phenomenex); gradient: 5% MeCN in water for 5 min, followed by an increase to 25% MeCN over 20 min; column oven: 40 °C; flow rate: 0.5 mL/min; detection: UV 210 nm) to reveal the presence of MUC1-GalNAc neoglycopeptide **10** (80%); t_R = 19.1 min; HRMS (ESI-TOF): calcd. for $C_{93}H_{148}N_{29}O_{33}S^+$: 2231.0510. Found: 2231.0557 (MH^+).

MUC1-GlcNAc Neoglycopeptide 11



3-((1'-(2"-Acetamido-2"-deoxy-β-D-glucopyranosyl)-[1',2',3']-triazo-4'-yl)methyloxy)-1-propene **4** (0.45 mg, 0.13 μmol) and modified MUC1 peptide **9** (0.25 mg, 0.0.13 μmol) were dissolved in sodium acetate buffer (15 μL, pH 4.0, 0.2 M). 2,2-Dimethoxy-2-phenylacetophenone (33 μg, 0.13 μmol, added as a solution in 1 μL DMF) was added, and the reaction mixture was stirred and irradiated in a Rayonet photoreactor (wavelength: 254 nm) for 4 h, and then analysed by HPLC (column: Jupiter 5u C4 (300 Å) column (Phenomenex); gradient: 5% MeCN in water for 5 min, followed by an increase to 25% MeCN over 20 min; column oven: 40 °C; flow rate: 0.5 mL/min; detection: UV 210 nm) to reveal the presence of MUC1-GlcNAc neoglycopeptide **11** (77%); t_R = 16.0 min; HRMS (ESI-TOF): calcd. for $C_{93}H_{148}N_{29}O_{33}S^+$: 2231.0510. Found: 2231.0532 (MH^+).

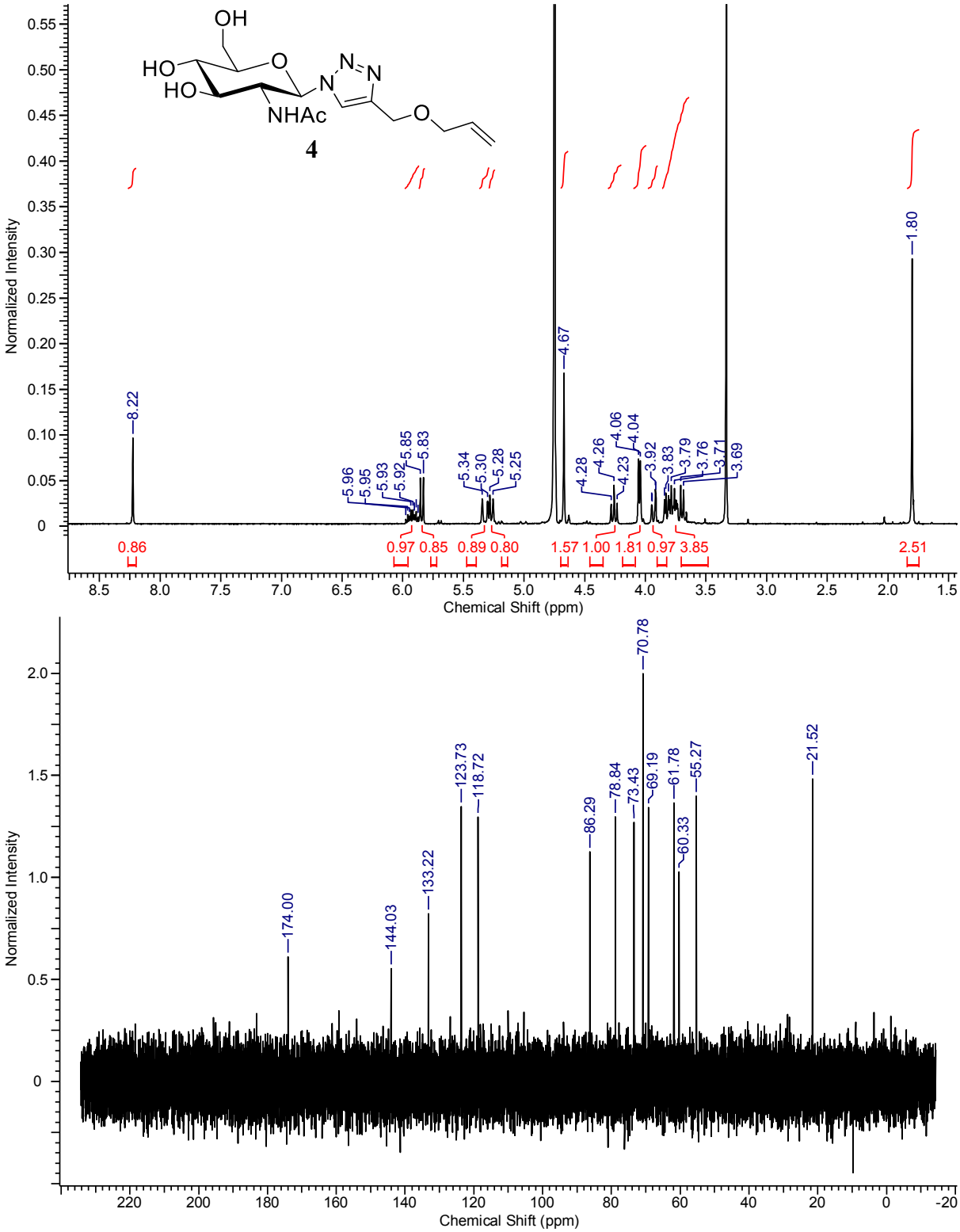
MUC1-Sialoglycan Neoglycopeptide 12[3]



MUC1-GlcNAc Neoglycopeptide **11** (0.2 mg, 0.1 μmol) and complex bi-antennary N-glycan oxazoline (0.8 mg, 0.4 μmol) were dissolved in DMSO (4 μL). The mixture was heated to 37 °C and Endo M N175Q (10 mU, solution in sodium phosphate buffer (10 μL, pH 6.5, 0.1 M)) was added and the reaction was heated at 37 °C. Analysis by HPLC (column: Jupiter 5u C4 (300 Å) column (Phenomenex); gradient: 5% MeCN in water for 5 min, followed by an increase to 25% MeCN over 20 min; column oven: 40 °C; flow rate: 0.5 mL/min; detection: UV 210 nm) indicated complete reaction after 1 h, and the presence of MUC1-sialoglycan neoglycopeptide **12** (40%); t_R = 15.1 min; HRMS (ESI-TOF): calcd. for $C_{169}H_{271}N_{34}O_{89}S^+$: 4232.7740. Found: 4232.7307 (MH^+).

References

1. Lim, D.; Brimble, M. A.; Kowalczyk, R.; Watson, A. J. A.; Fairbanks, A. J., *Angew. Chem., Int. Ed.* **2014,** *53* (44), 1907-11911.
2. Schwarz, M. K.; Tumelty, D.; Gallop, M. A., *J. Org. Chem.* **1999,** *64* (7), 2219-2231.
3. Tomabechi, Y.; Squire, M. A.; Fairbanks, A. J., *Org. Biomol. Chem.* **2014,** *12* (6), 942-955.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NHAc
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4.06
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3.83
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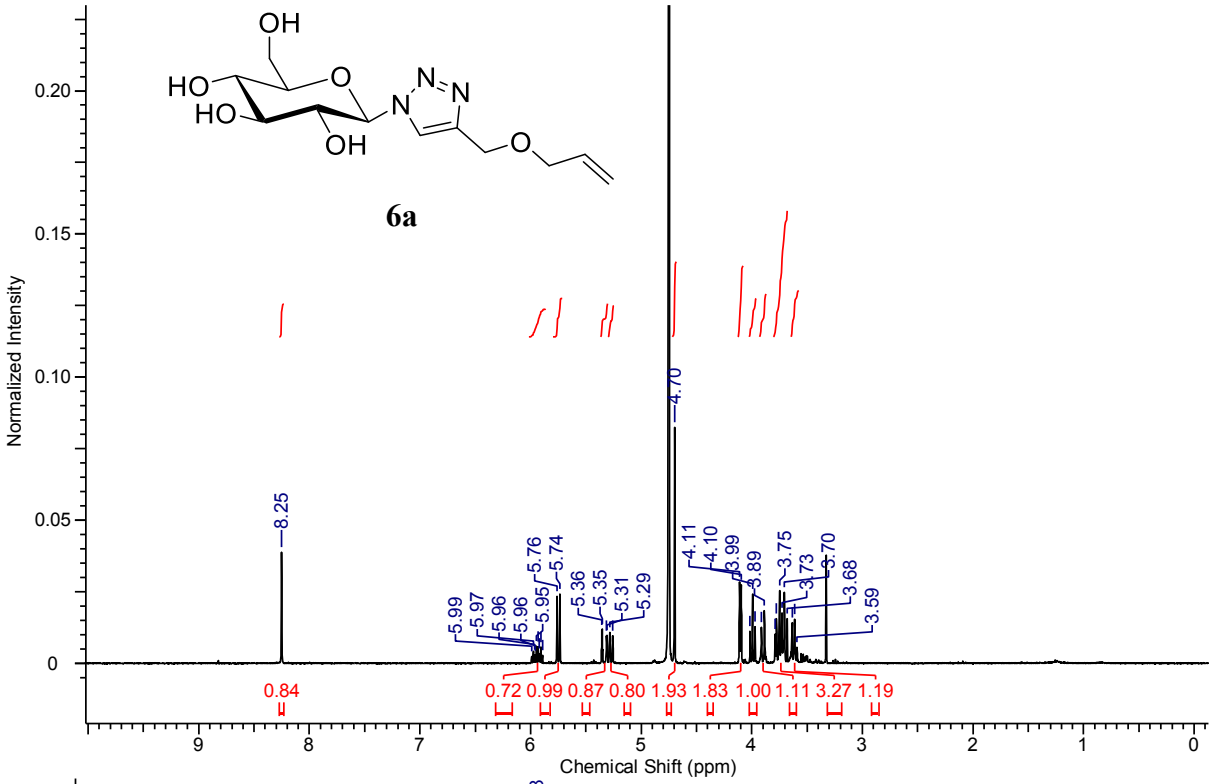
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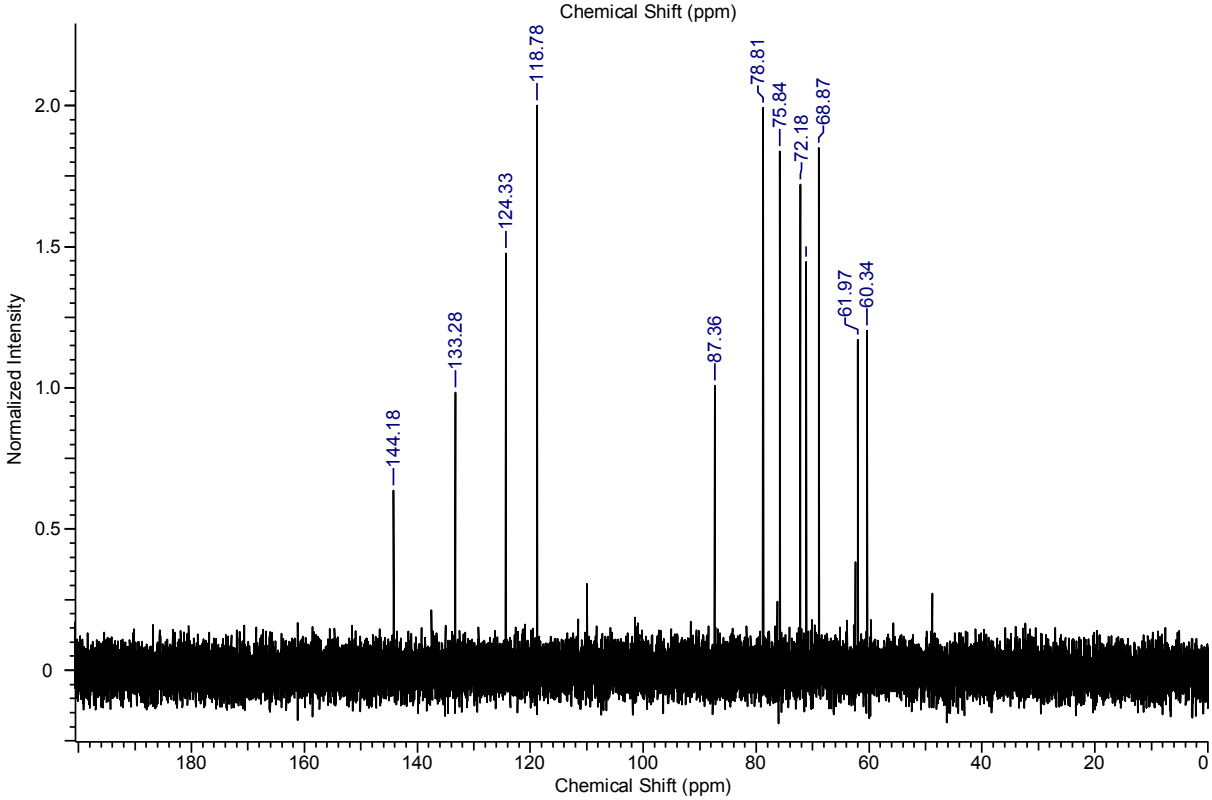
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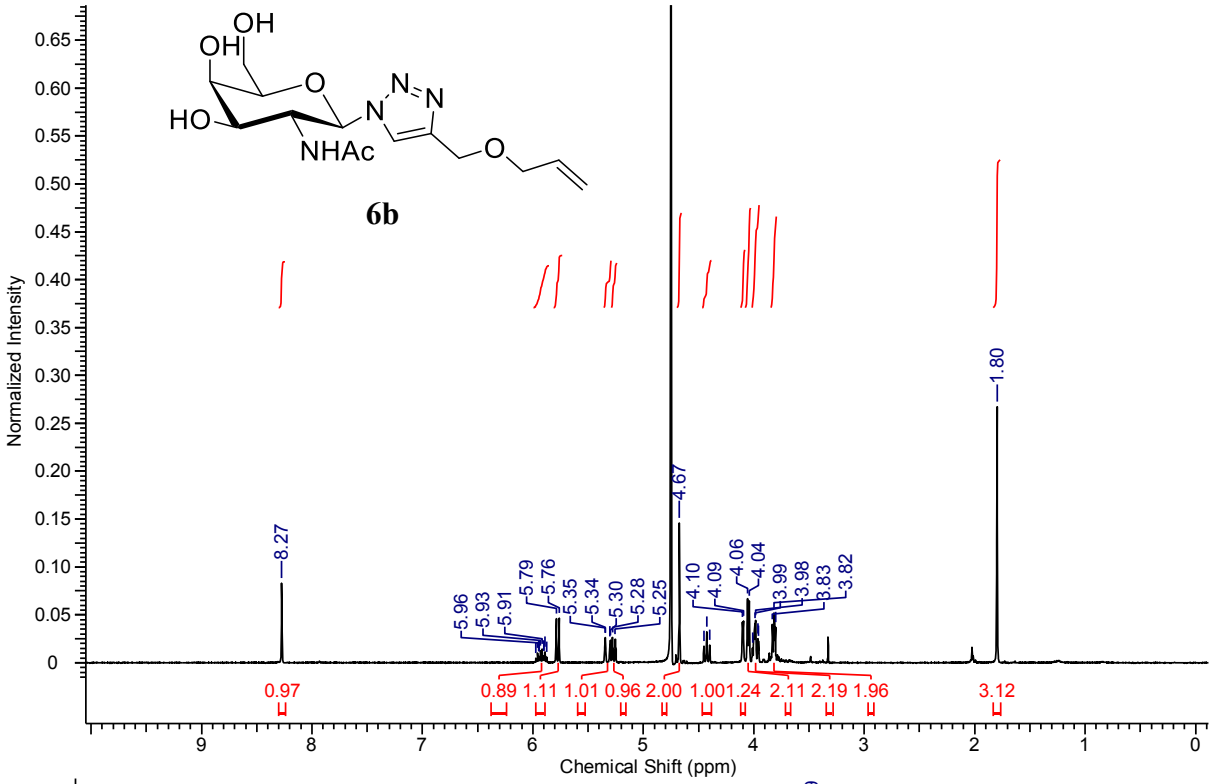
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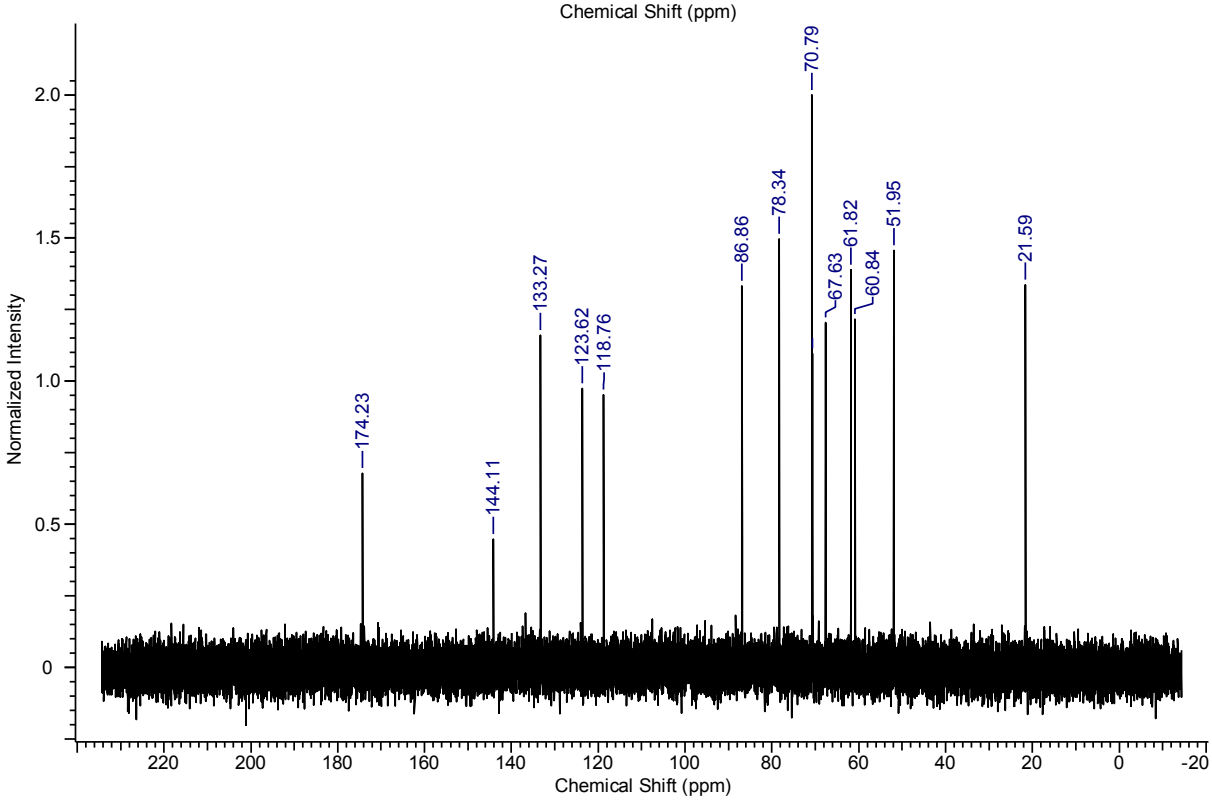
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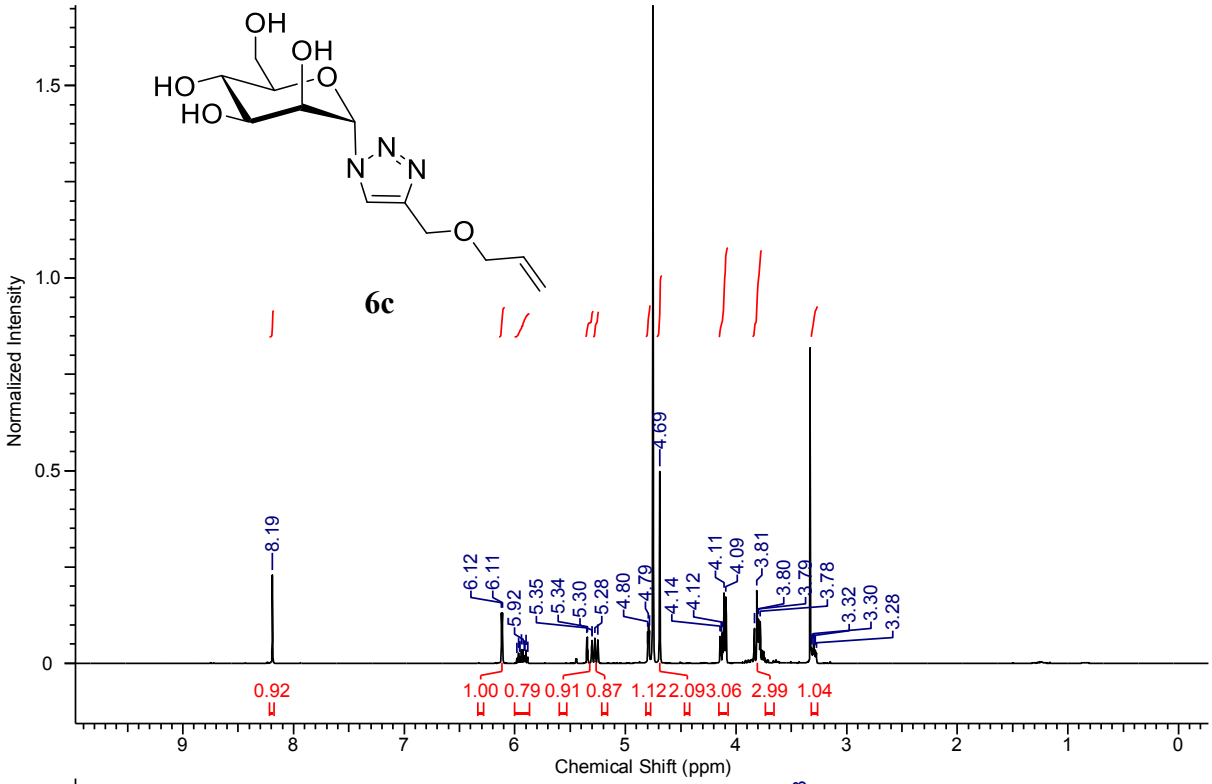
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4.11
4.09
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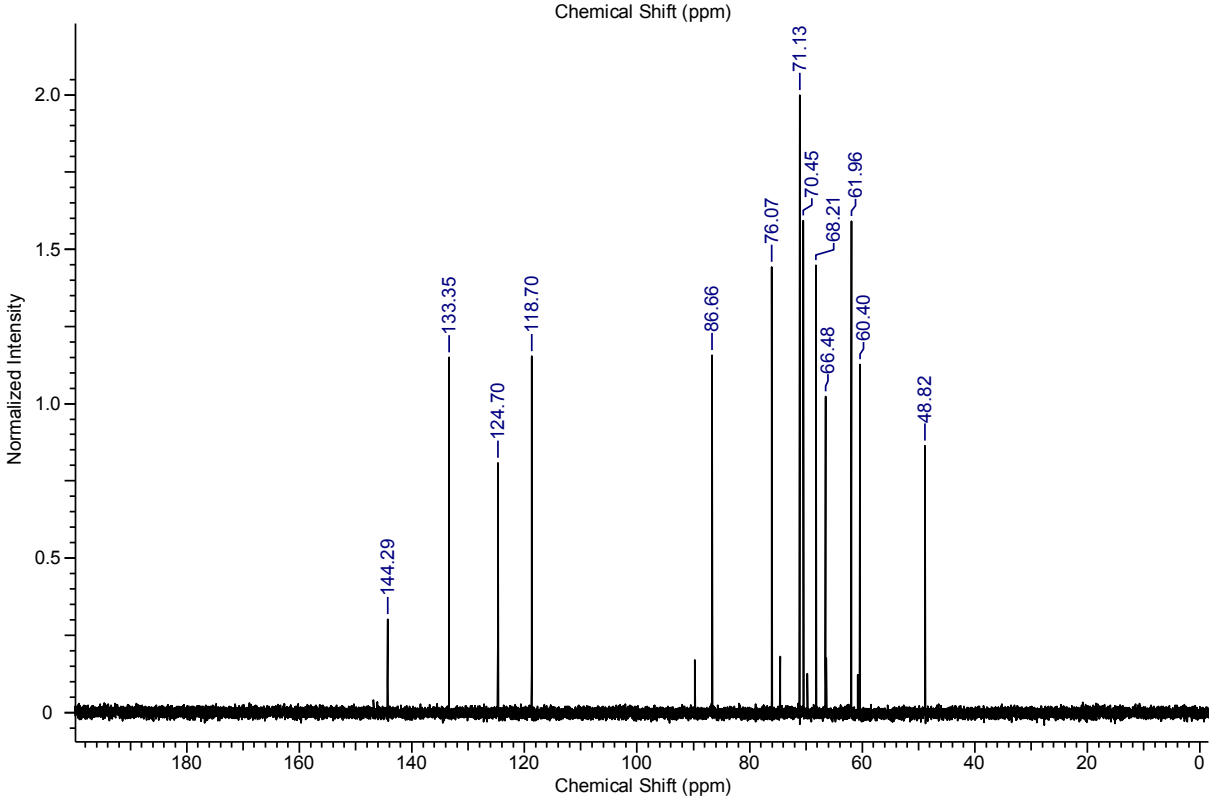
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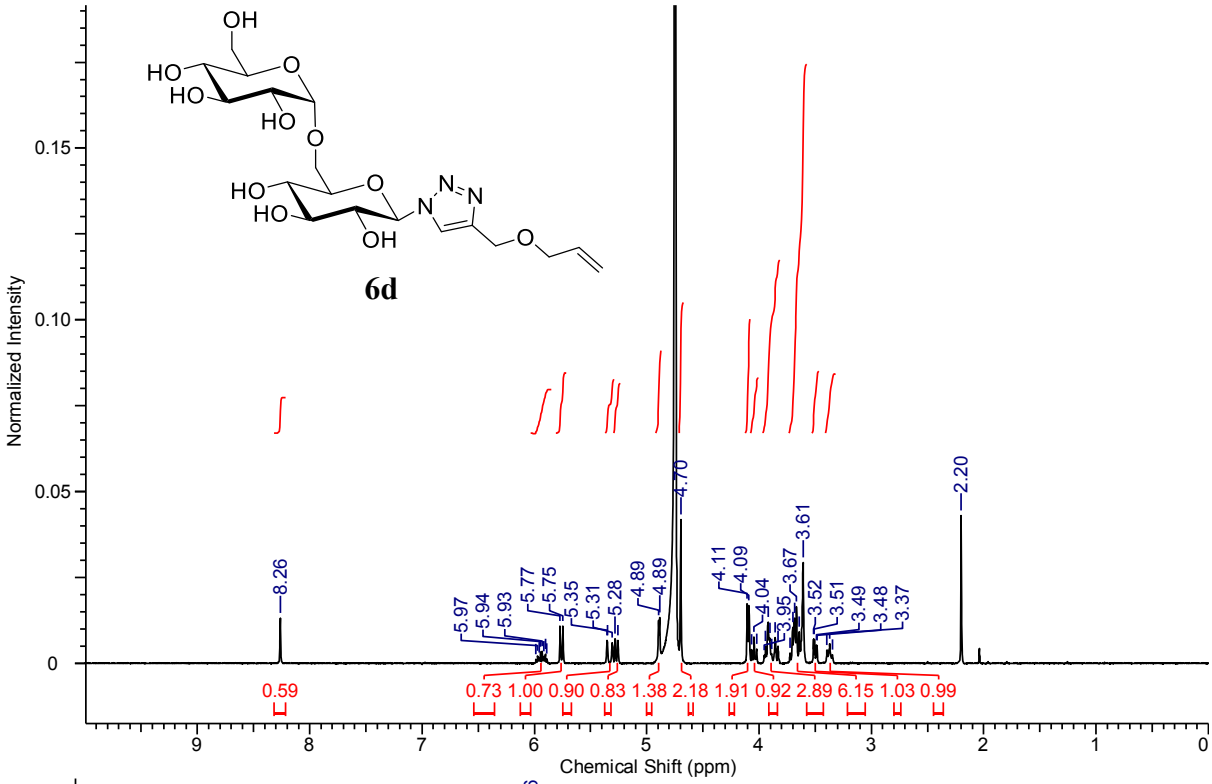
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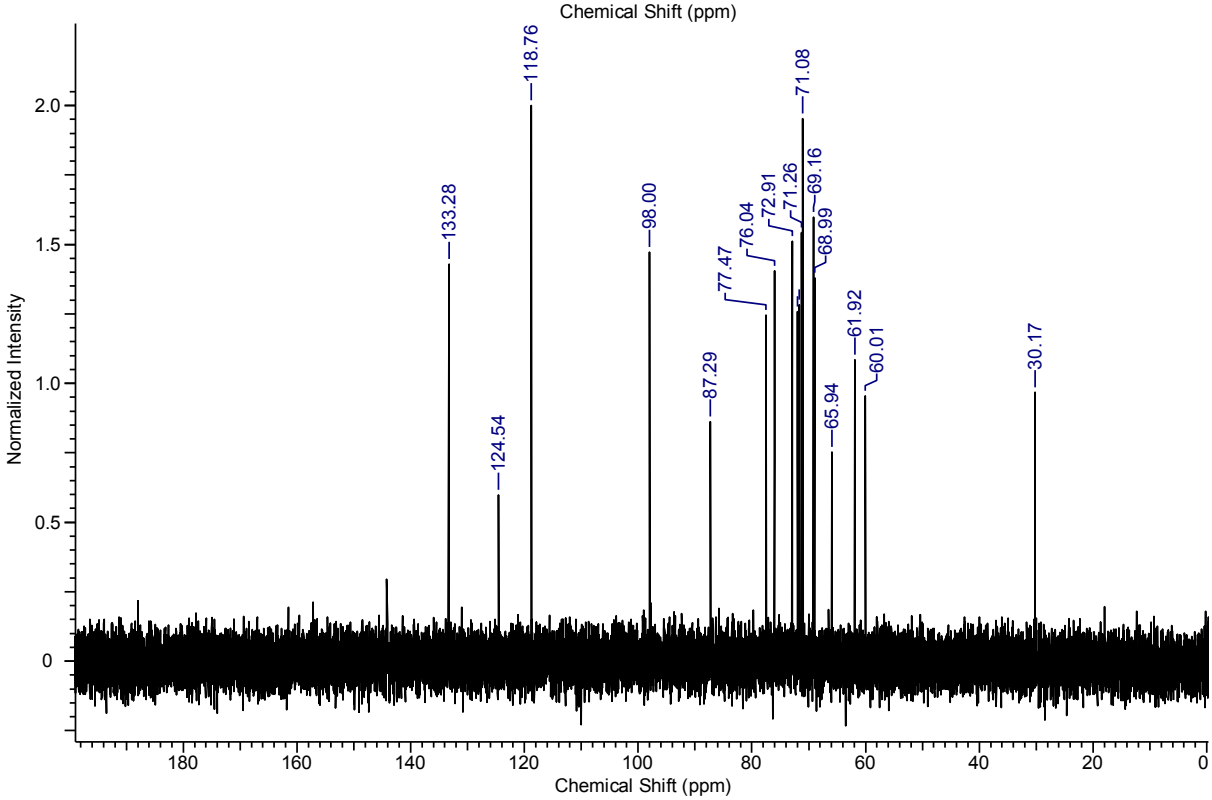
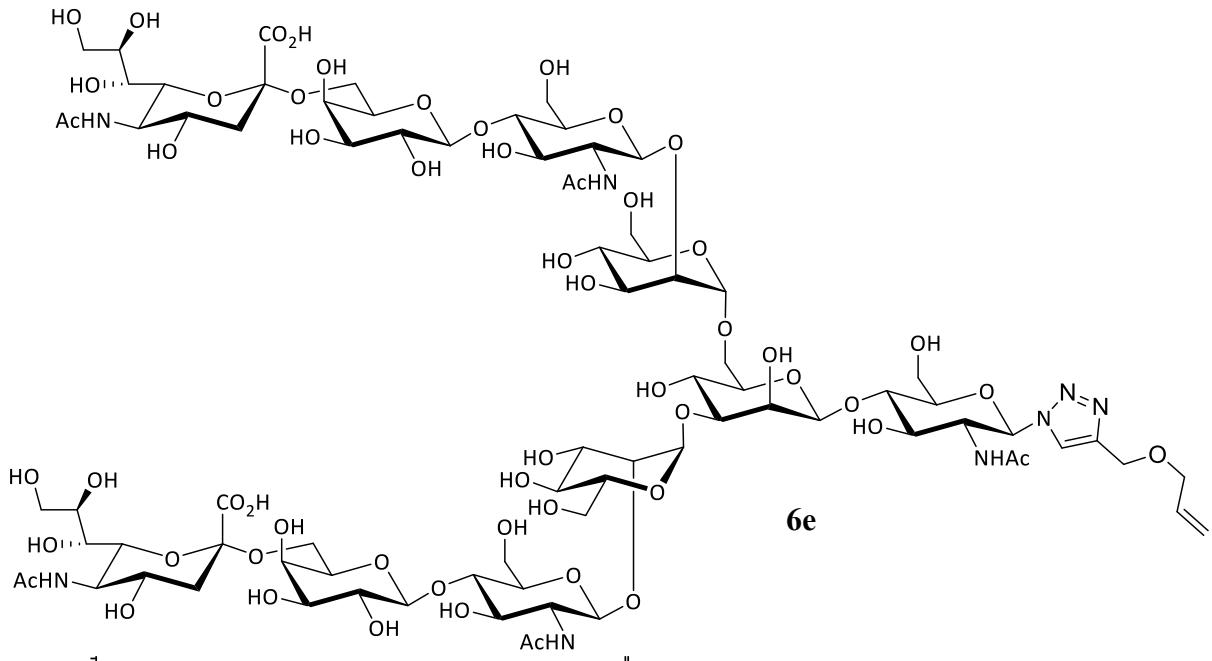
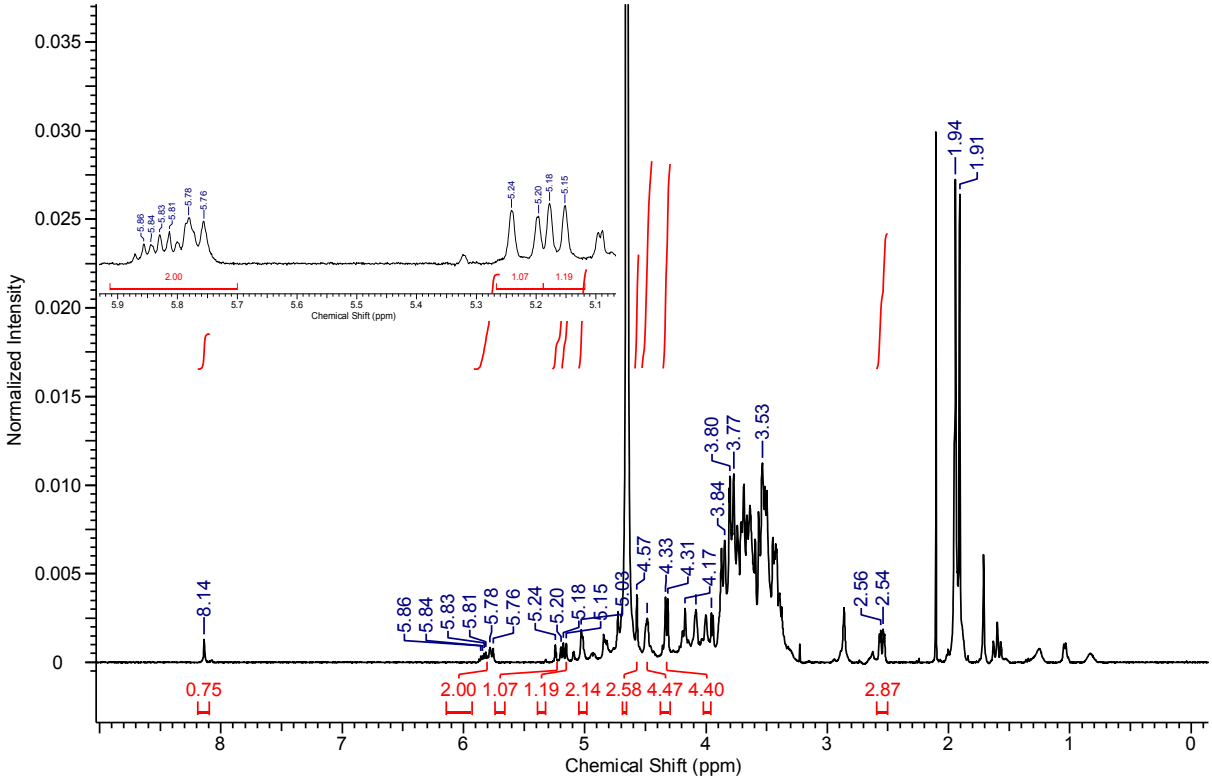
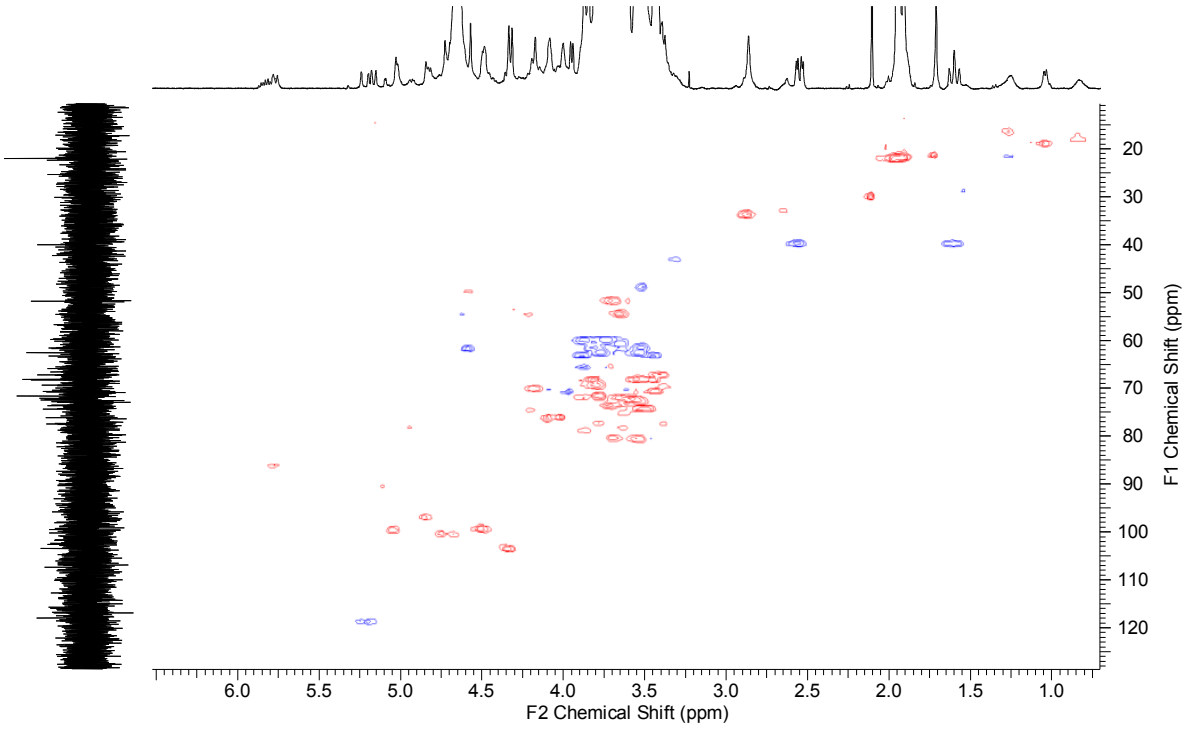
0.05
0
8.26
5.97
5.94
5.93
5.77
5.75
5.35
5.31
5.28
4.89
4.89
4.70
4.11
4.09
4.04
3.95
3.67
3.61
3.52
3.51
3.49
3.48
3.37
2.20
0.59
0.73 1.00 0.90 0.83 1.38 2.18 1.91 0.92 2.89 6.15 1.03 0.99
9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)

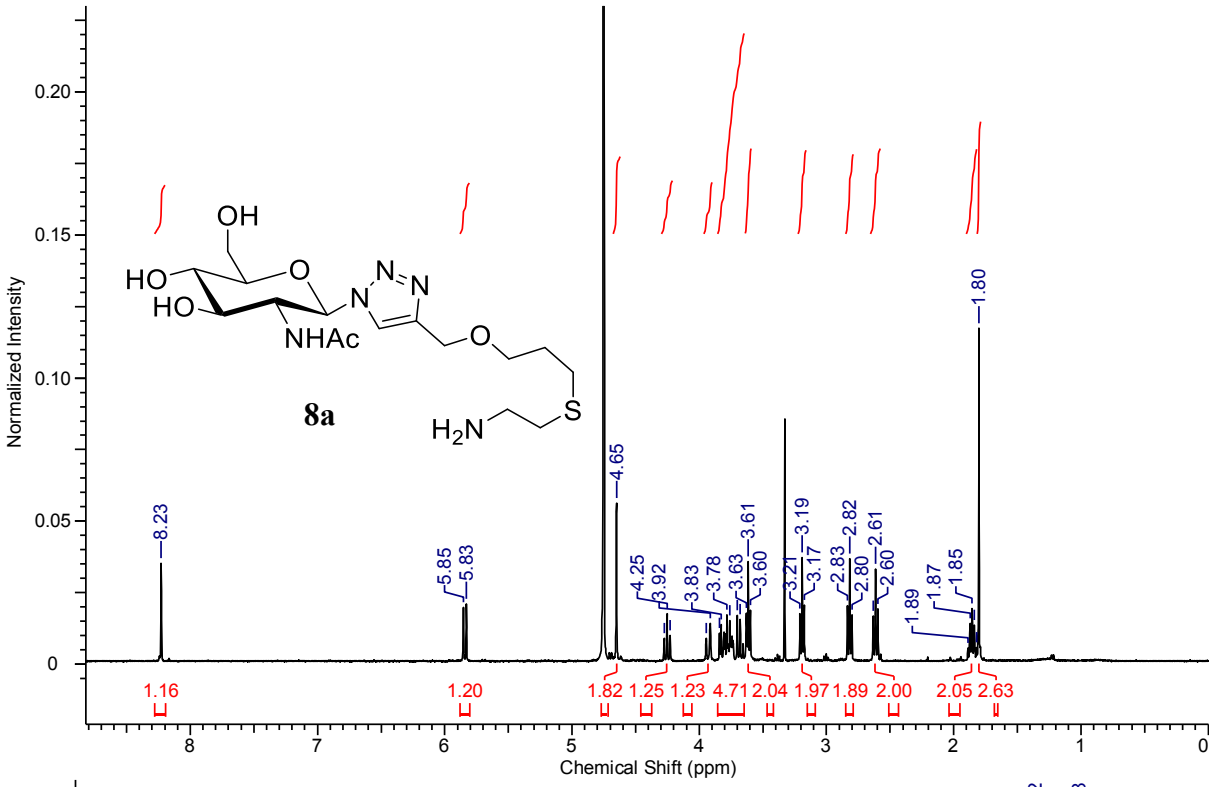

Normalized Intensity
2.0
1.5
1.0
0.5
0
118.76
71.08
133.28
98.00
69.16
72.91
71.26
76.04
77.47
68.99
61.92
60.01
87.29
65.94
124.54
30.17
180 160 140 120 100 80 60 40 20 0
Chemical Shift (ppm)

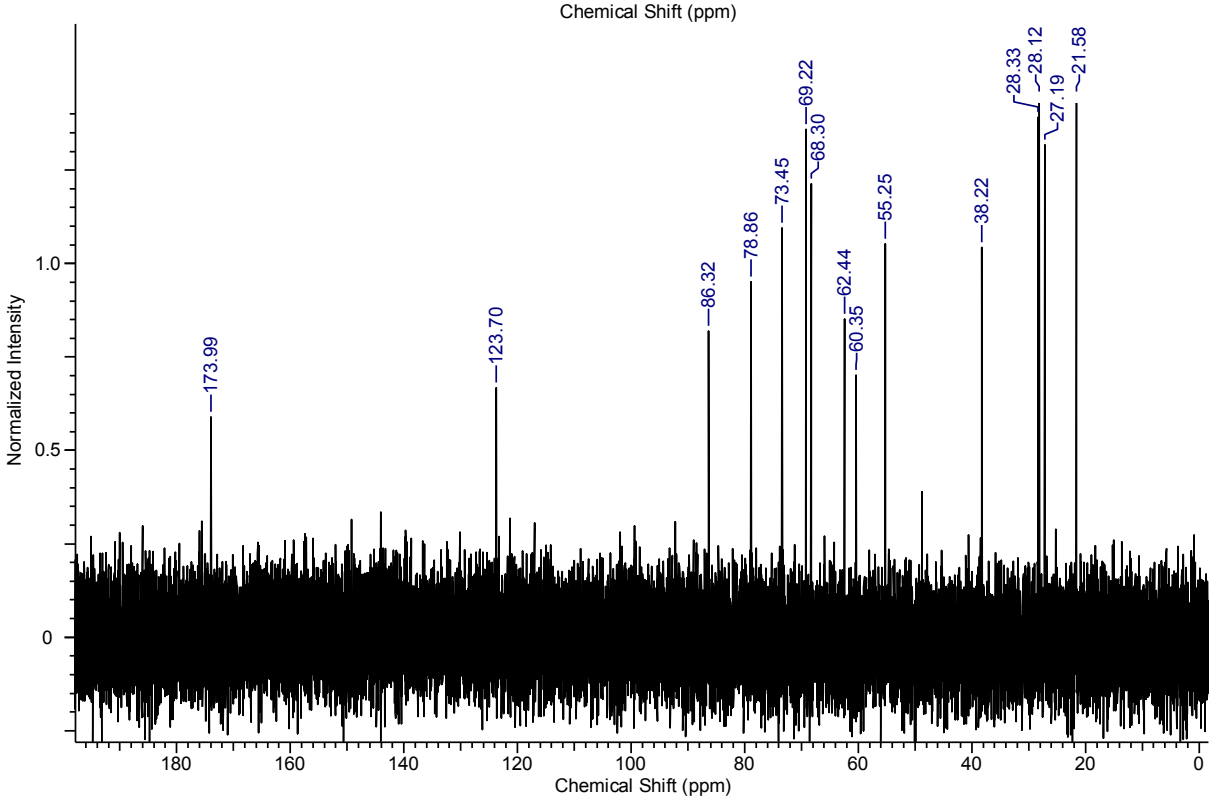


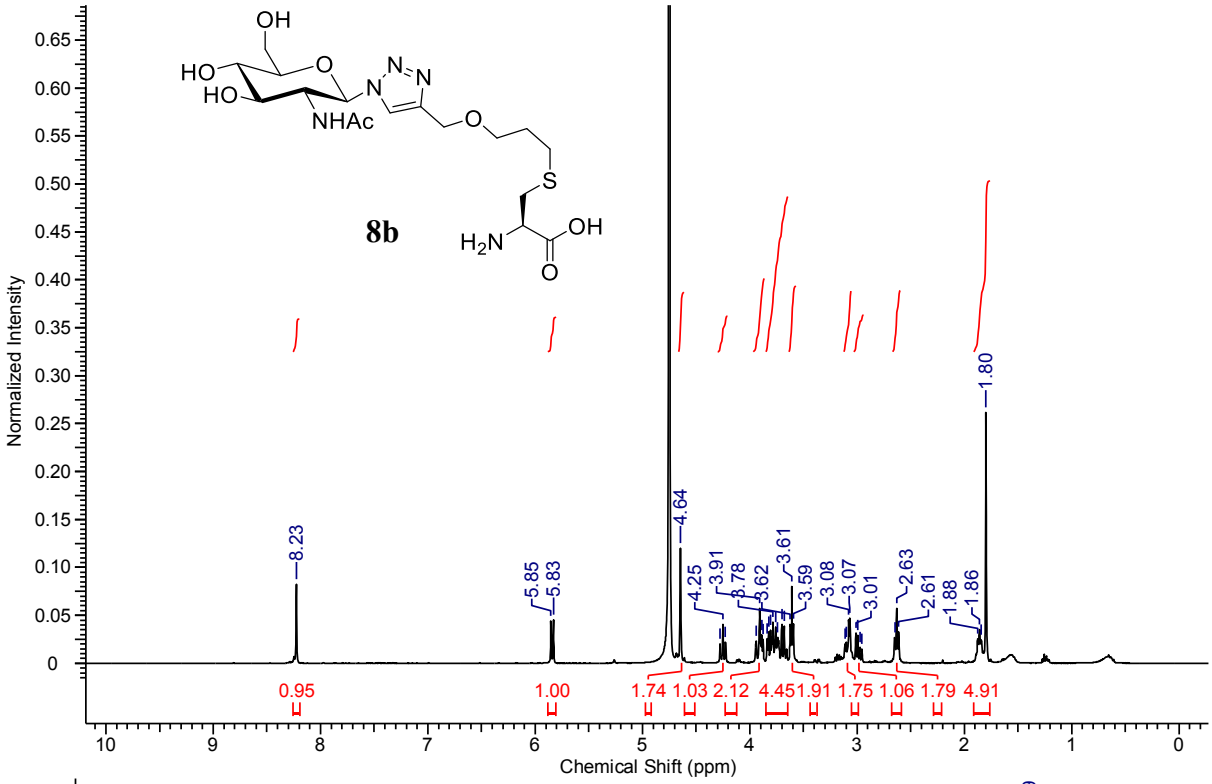
6e

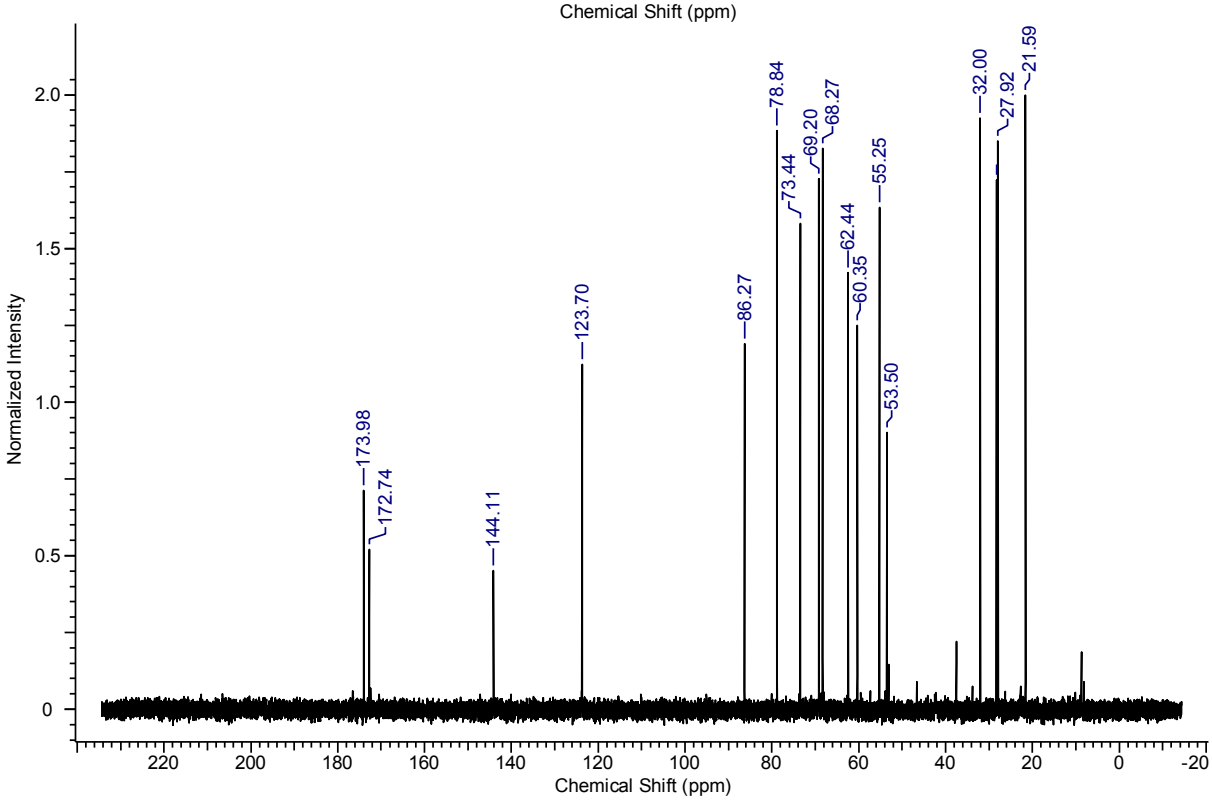

Normalized Intensity
Chemical Shift (ppm)
8.14
5.86
5.84
5.83
5.81
5.78
5.76
5.24
5.20
5.18
5.15
5.03
4.57
4.33
4.31
4.17
3.84
3.80
3.77
3.53
2.56
2.54
1.94
1.91
0.75
2.00
1.07
1.19
2.14
2.58
4.47
4.40
2.87

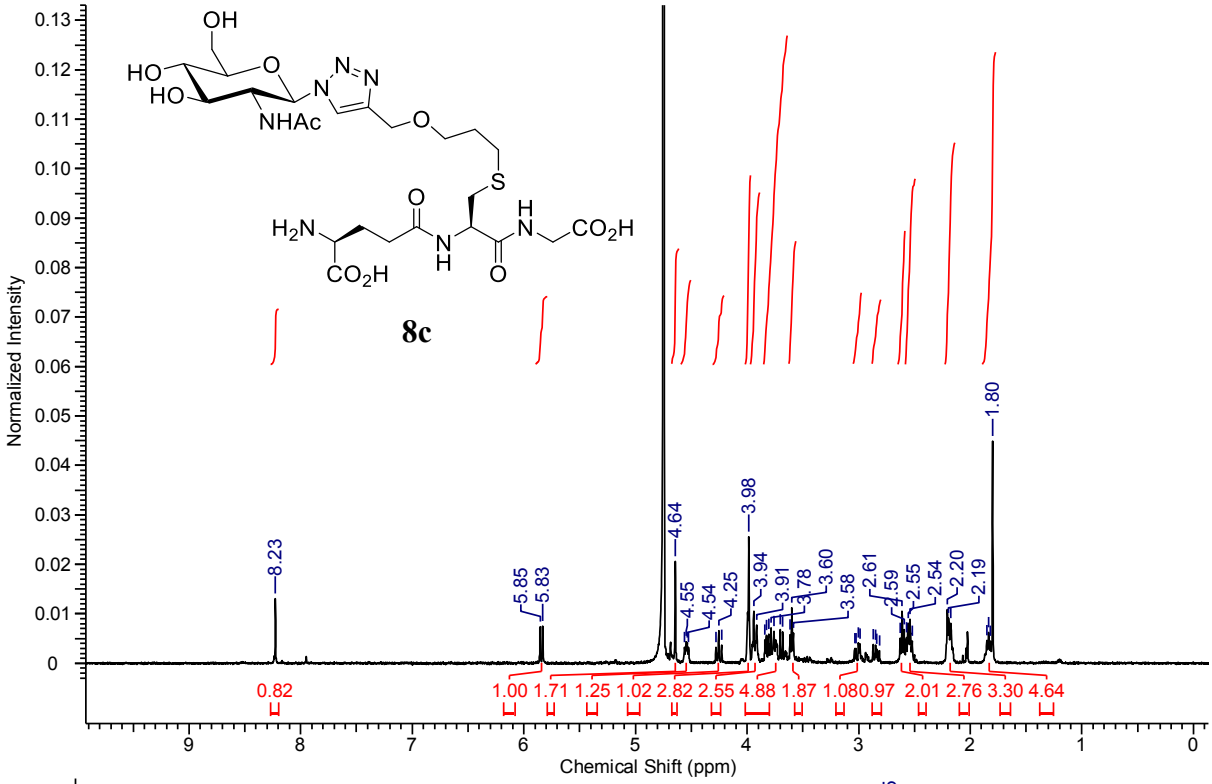

6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
F2 Chemical Shift (ppm)
20
30
40
50
60
70
80
90
100
110
120
F1 Chemical Shift (ppm)

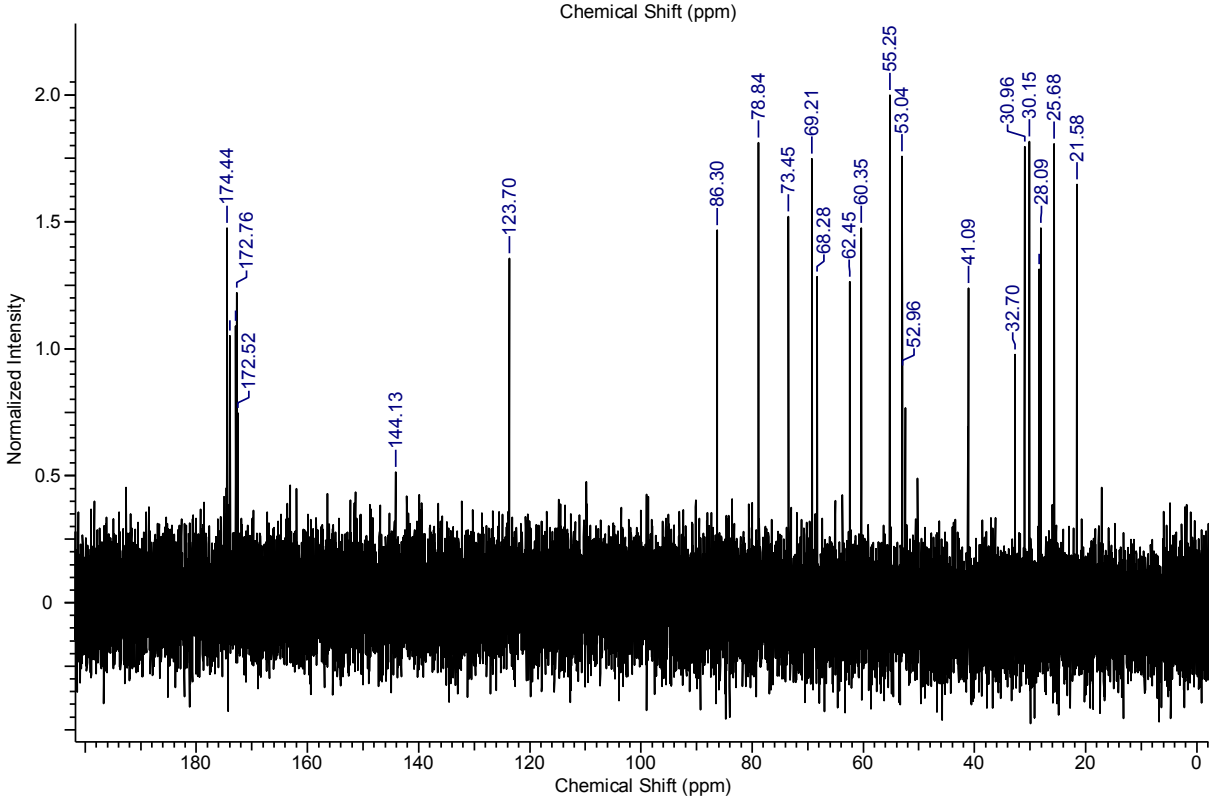

OH
HO
HO
O
N
N
N
NHAc
O
S
H2N
8a
Normalized Intensity
Chemical Shift (ppm)
8.23
5.85
5.83
4.65
4.25
3.92
3.83
3.78
3.63
3.61
3.60
3.21
3.19
3.17
2.83
2.82
2.80
2.61
2.60
1.89
1.87
1.85
1.80
1.16
1.20
1.82
1.25
1.23
4.71
2.04
1.97
1.89
2.00
2.05
2.63

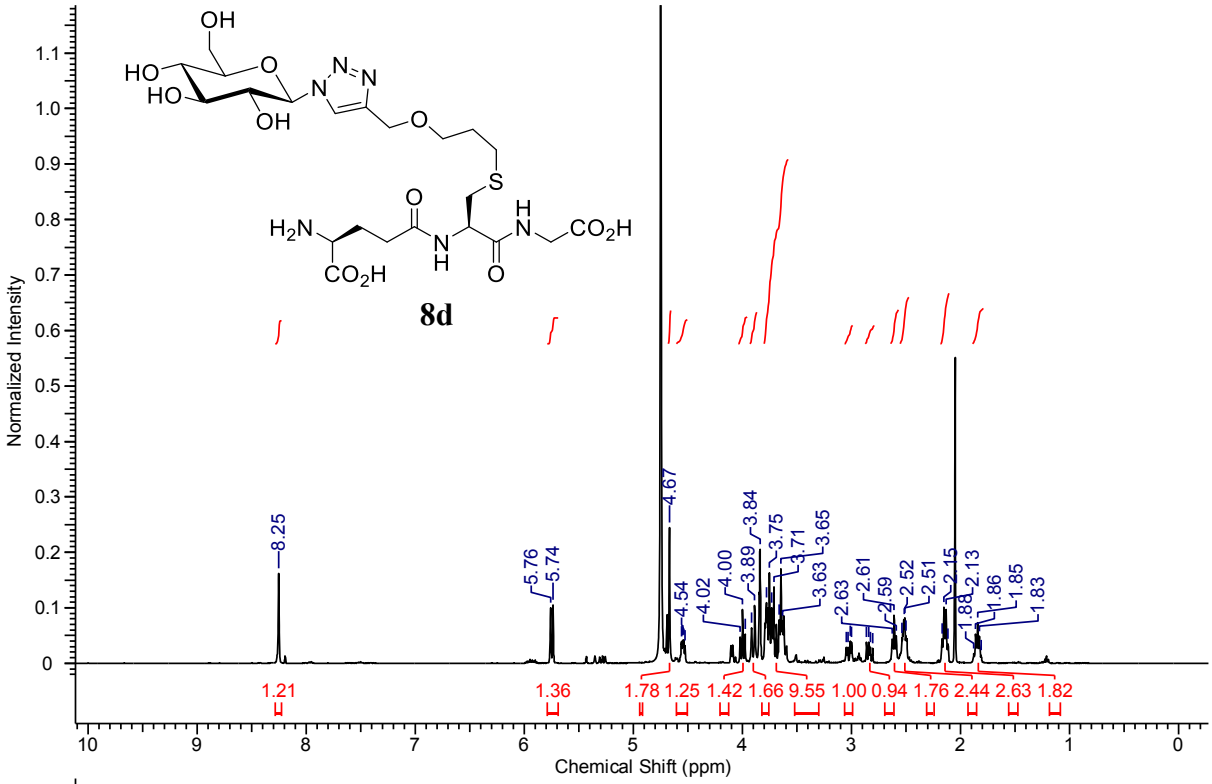

Normalized Intensity
Chemical Shift (ppm)
173.99
123.70
86.32
78.86
73.45
69.22
68.30
62.44
60.35
55.25
38.22
28.33
28.12
27.19
21.58

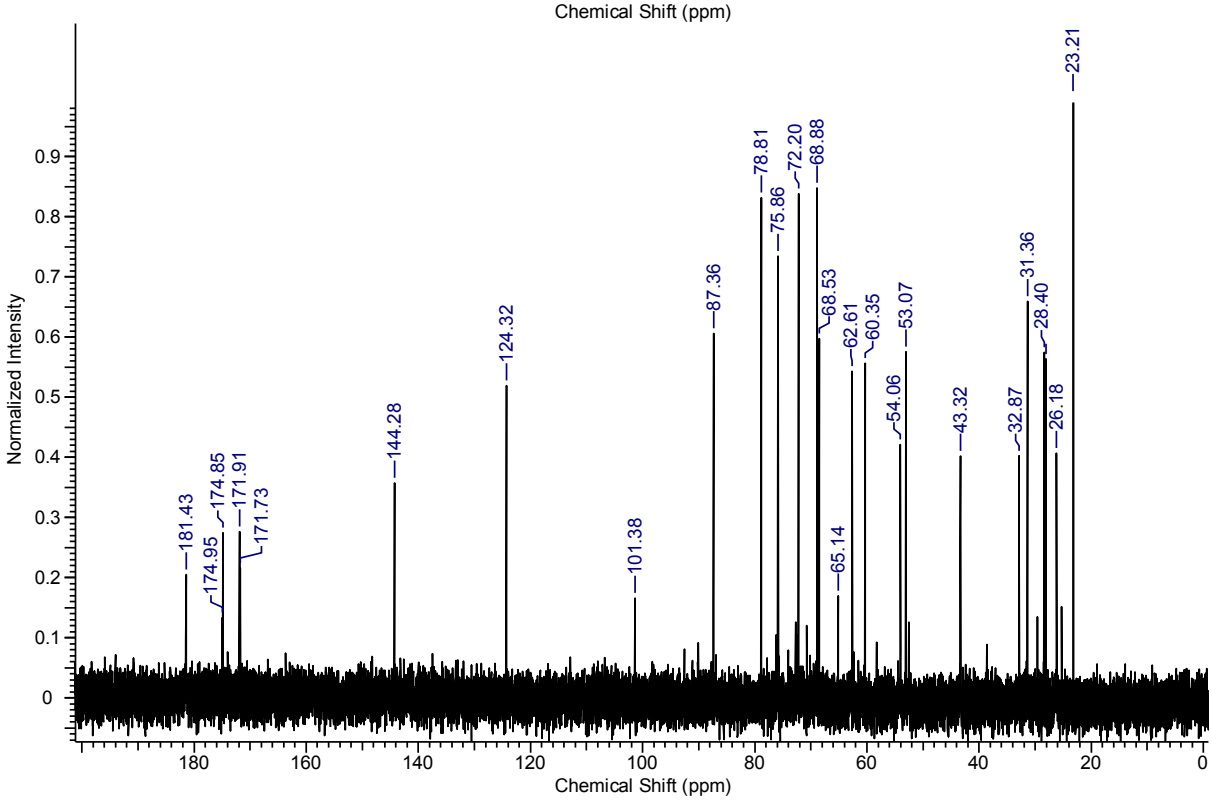

OH
HO
HO
O
N
N
N
NHAc
O
S
OH
H_2N
O
8b
Normalized Intensity
Chemical Shift (ppm)
8.23
5.85
5.83
4.64
4.25
3.91
3.78
3.62
3.61
3.59
3.08
3.07
3.01
2.63
2.61
1.88
1.86
1.80
0.95
1.00
1.74
1.03
2.12
4.45
1.91
1.75
1.06
1.79
4.91

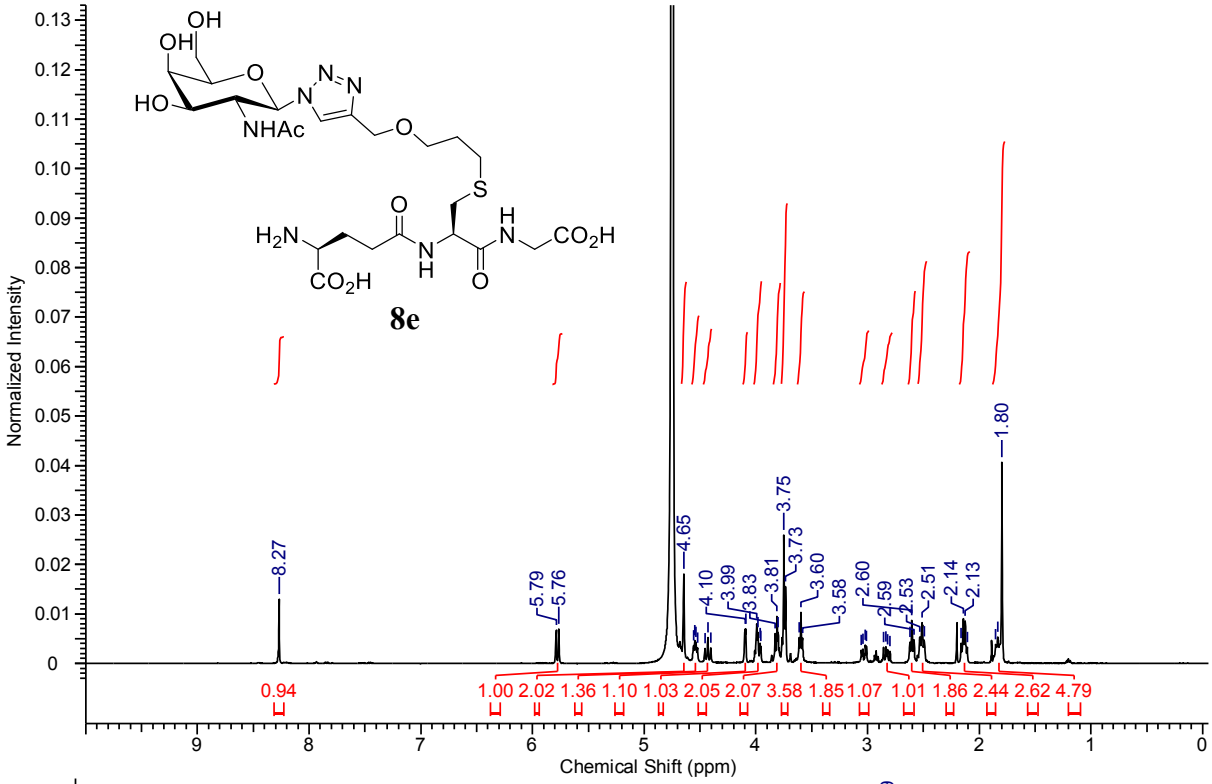

Normalized Intensity
Chemical Shift (ppm)
173.98
172.74
144.11
123.70
86.27
78.84
73.44
69.20
68.27
62.44
60.35
55.25
53.50
32.00
27.92
21.59


OH
HO
HO
O
NHAc
N
N
N
O
S
H
N
CO2H
O
H2N
CO2H
O
N
H
O
8c
Normalized Intensity
Chemical Shift (ppm)
8.23
5.85
5.83
4.64
4.55
4.54
4.25
3.98
3.94
3.91
3.78
3.60
3.58
2.61
2.59
2.55
2.54
2.20
2.19
1.80
0.82
1.00 1.71 1.25 1.02 2.82 2.55 4.88 1.87 1.08 0.97 2.01 2.76 3.30 4.64

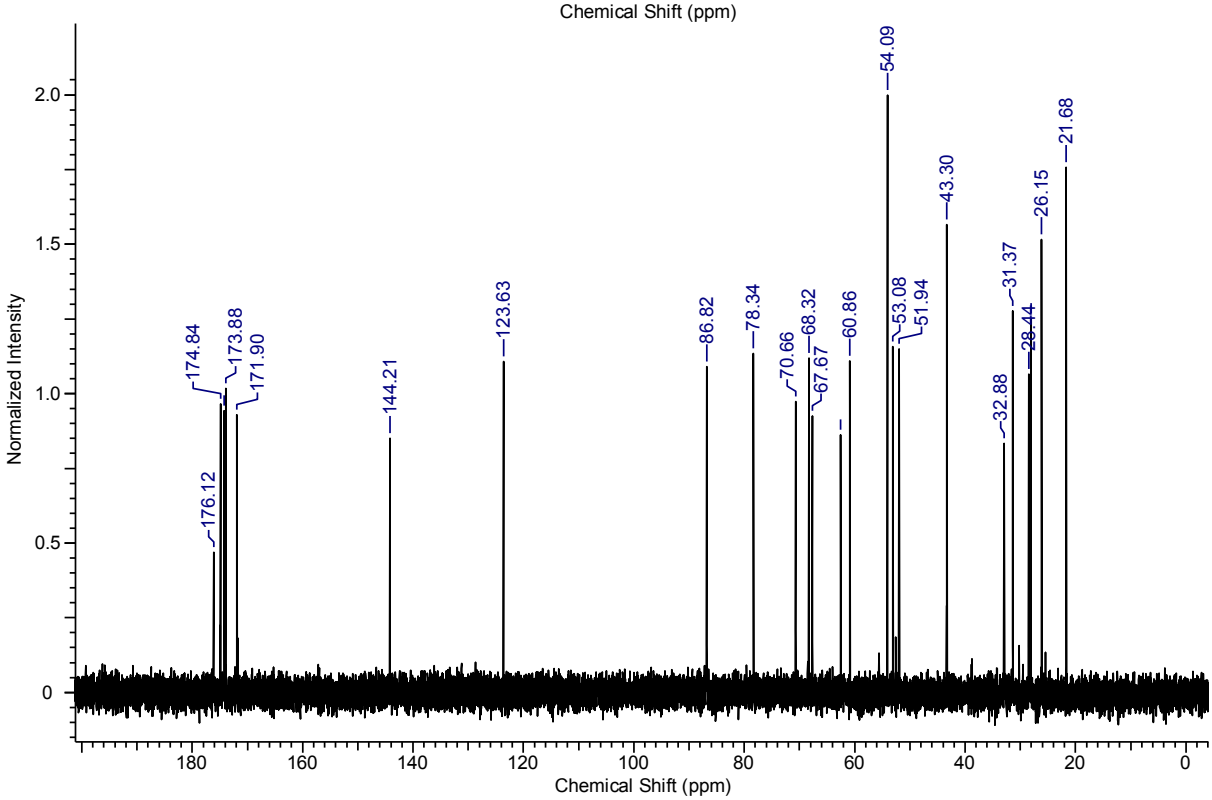

Normalized Intensity
Chemical Shift (ppm)
174.44
172.76
172.52
144.13
123.70
86.30
78.84
73.45
69.21
68.28
62.45
60.35
55.25
53.04
52.96
41.09
32.70
30.96
30.15
28.09
25.68
21.58

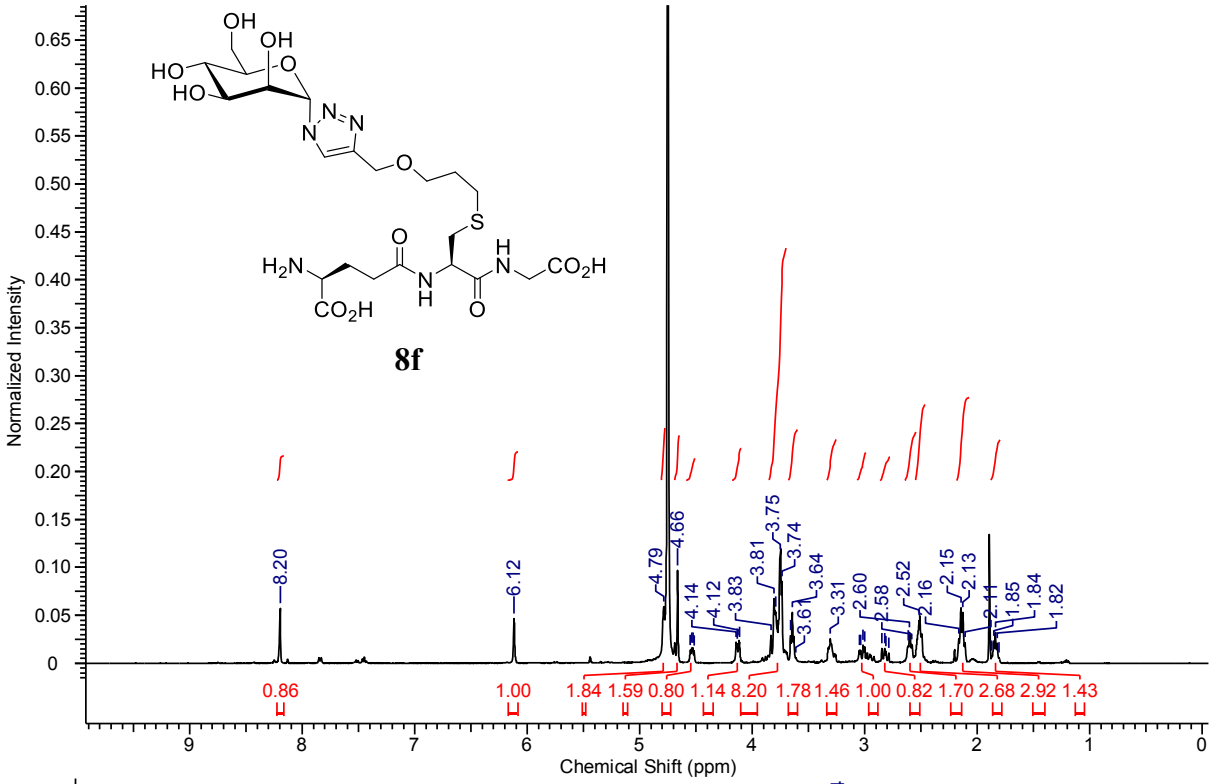

OH
HO
HO
OH
O
N
N
N
O
S
H
N
O
H2N
CO2H
N
H
CO2H
O
8d
Normalized Intensity
8.25
5.76
5.74
4.67
4.54
4.02
4.00
3.89
3.84
3.75
3.71
3.65
3.63
2.63
2.61
2.59
2.52
2.51
2.15
2.13
1.88
1.86
1.85
1.83
1.21
1.36
1.78 1.25 1.42 1.66 9.55 1.00 0.94 1.76 2.44 2.63 1.82
Chemical Shift (ppm)


Normalized Intensity
181.43
174.95
174.85
171.91
171.73
144.28
124.32
101.38
87.36
78.81
75.86
72.20
68.88
68.53
65.14
62.61
60.35
54.06
53.07
43.32
32.87
31.36
28.40
26.18
23.21
Chemical Shift (ppm)

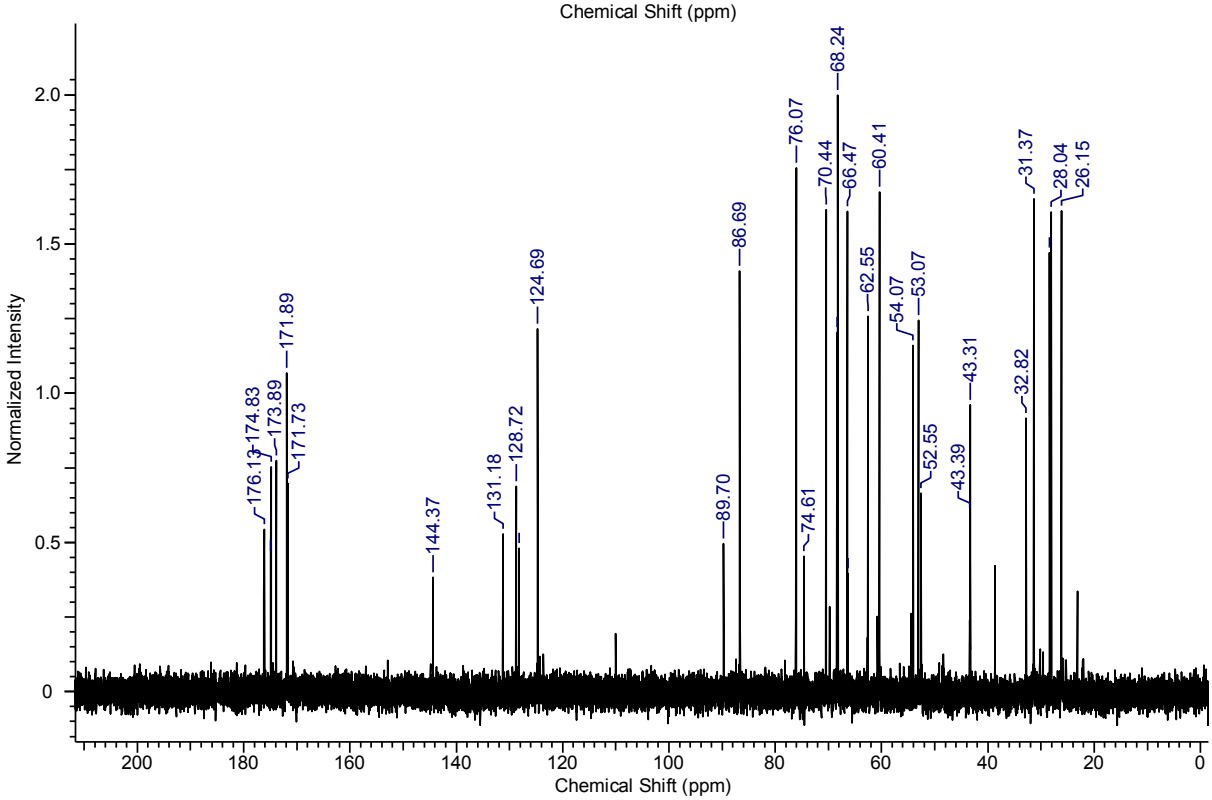

Normalized Intensity
Chemical Shift (ppm)
8.27
5.79
5.76
4.65
4.10
3.99
3.83
3.81
3.75
3.73
3.60
3.58
2.60
2.59
2.53
2.51
2.14
2.13
1.80
0.94
1.00 2.02 1.36 1.10 1.03 2.05 2.07 3.58 1.85 1.07 1.01 1.86 2.44 2.62 4.79

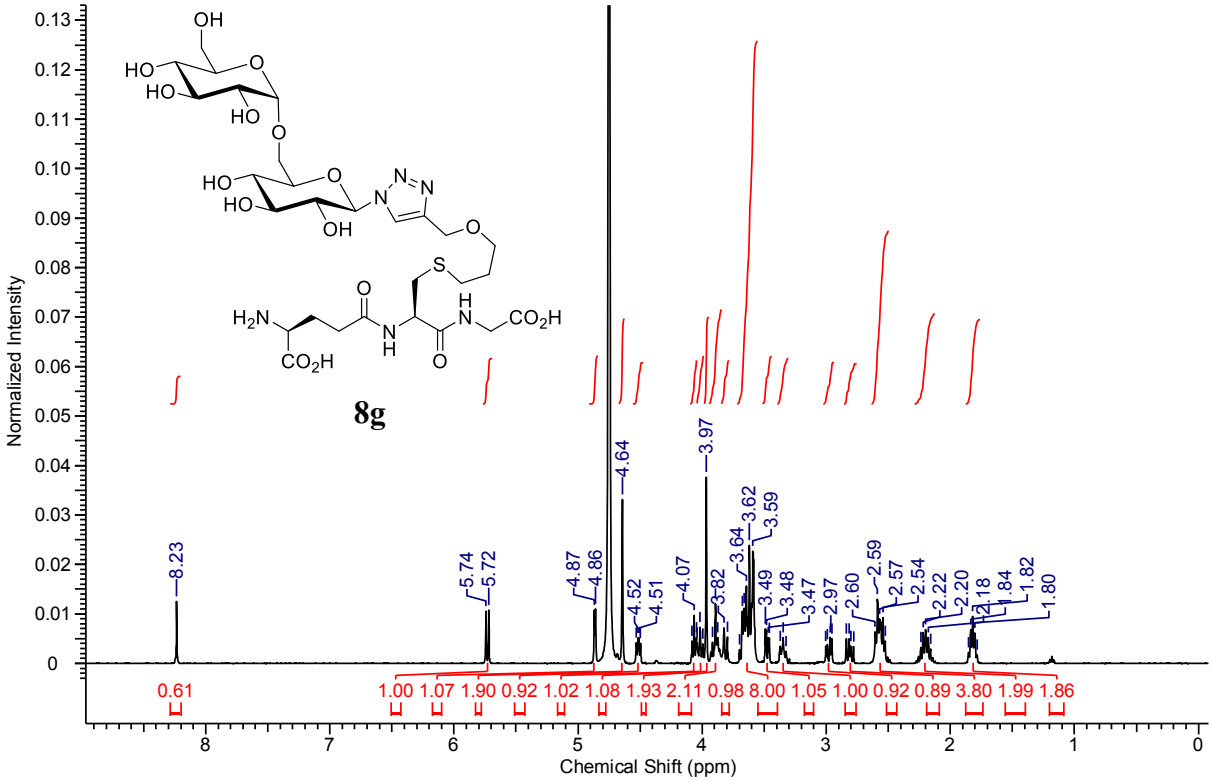
8e

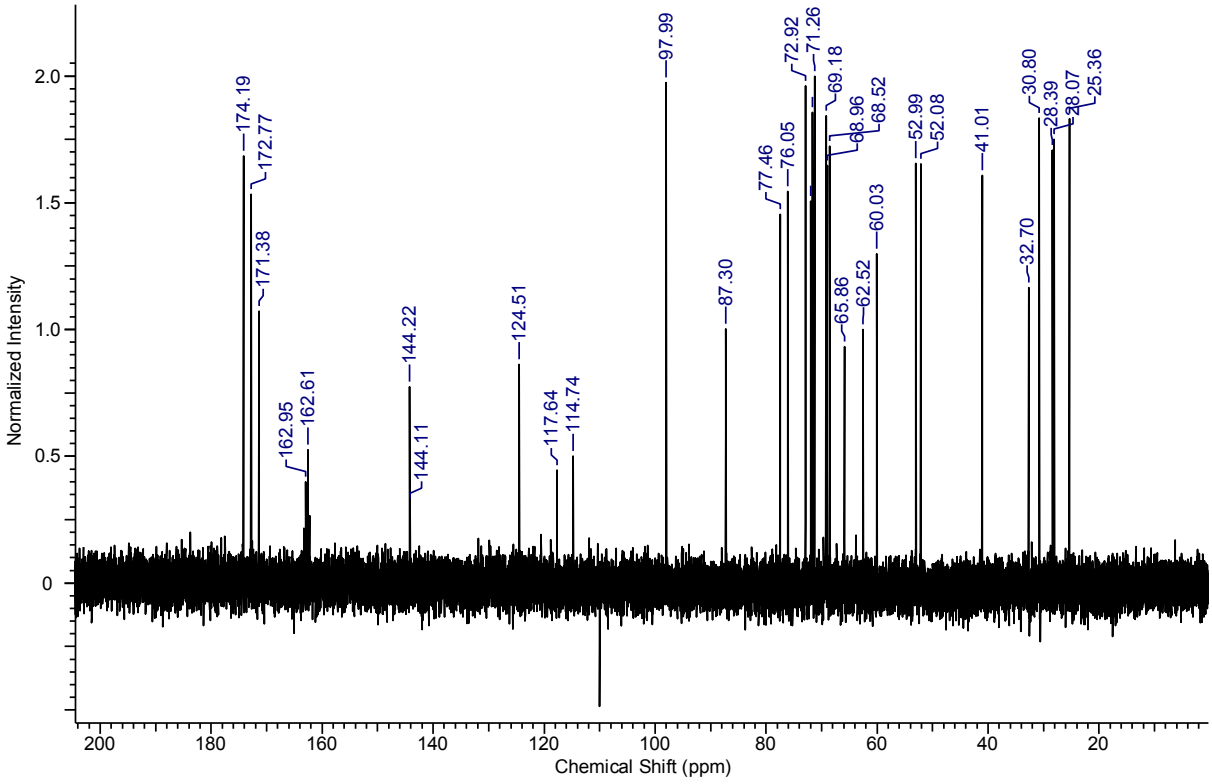

Normalized Intensity
Chemical Shift (ppm)
176.12
174.84
173.88
171.90
144.21
123.63
86.82
78.34
70.66
68.32
67.67
60.86
54.09
53.08
51.94
43.30
32.88
31.37
28.44
26.15
21.68


Normalized Intensity
Chemical Shift (ppm)
8.20
6.12
4.79
4.66
4.14
4.12
3.83
3.81
3.75
3.74
3.64
3.61
3.31
2.60
2.58
2.52
2.16
2.15
2.13
1.85
1.84
1.82
0.86
1.00
1.84 1.59 0.80 1.14 8.20 1.78 1.46 1.00 0.82 1.70 2.68 2.92 1.43

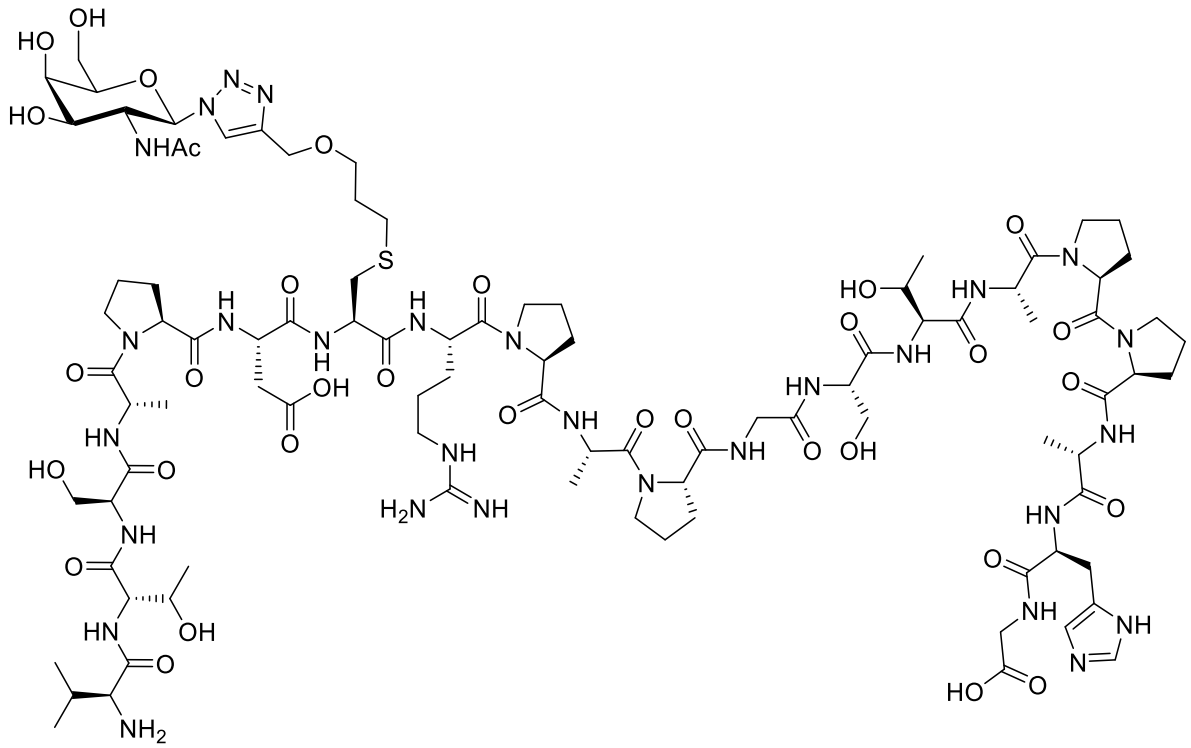
8f

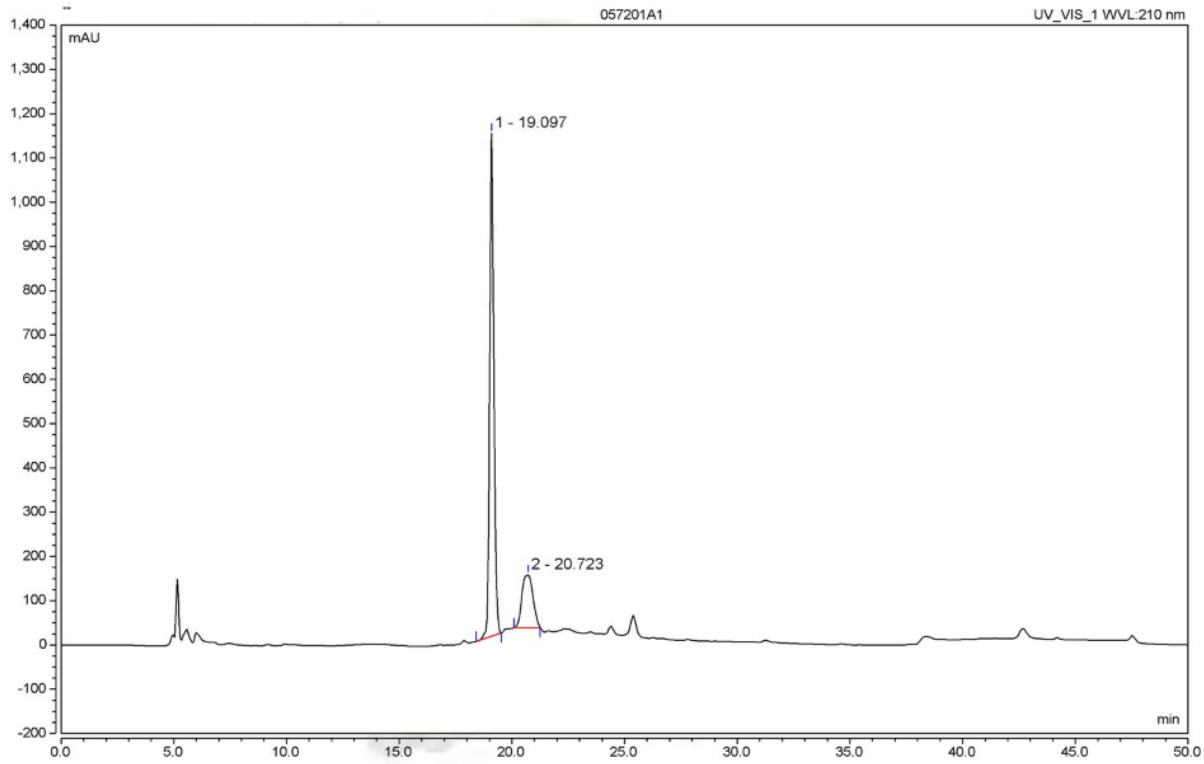

Normalized Intensity
Chemical Shift (ppm)
176.13
174.83
173.89
171.73
171.89
144.37
131.18
128.72
124.69
89.70
86.69
76.07
74.61
70.44
68.24
66.47
62.55
60.41
54.07
53.07
52.55
43.39
43.31
32.82
31.37
28.04
26.15

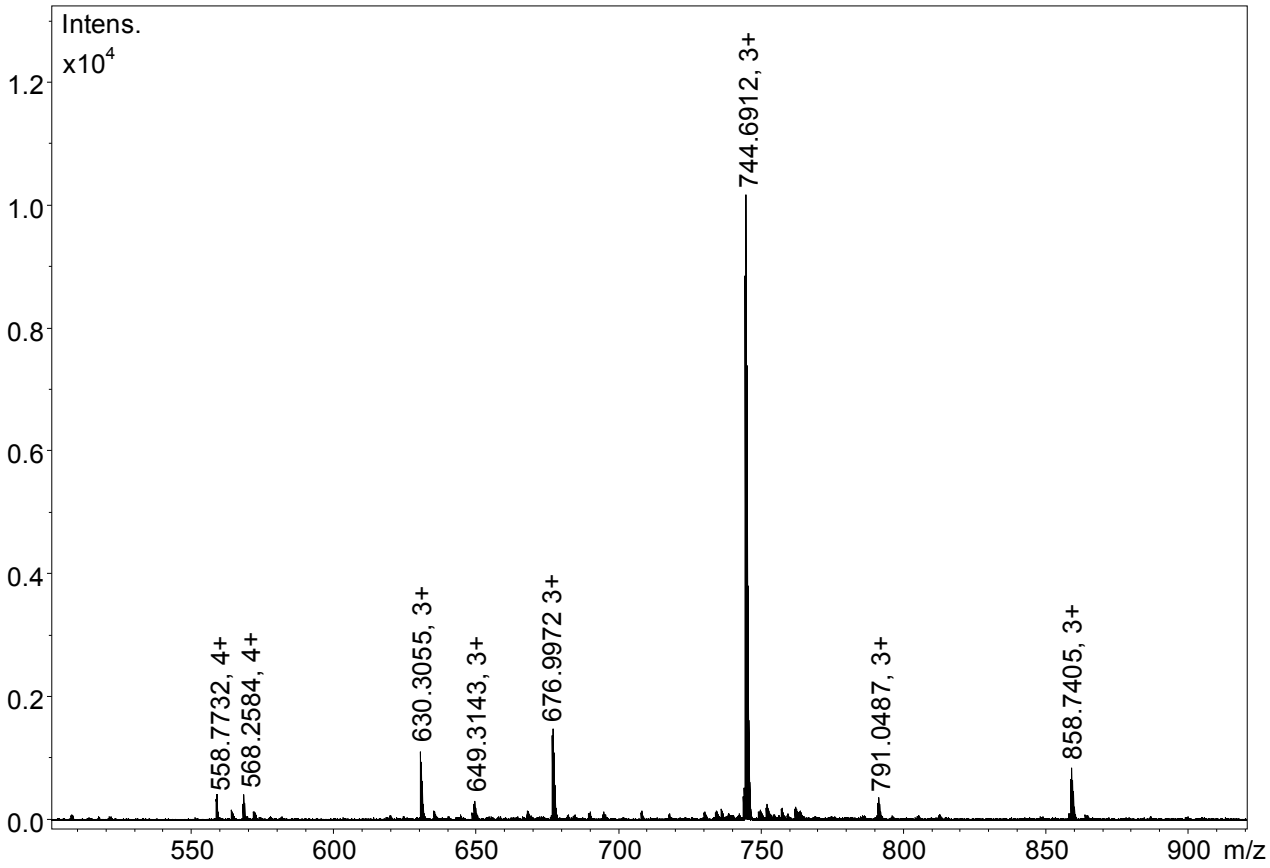

8g
Normalized Intensity
Chemical Shift (ppm)
8.23
5.74
5.72
4.87
4.86
4.64
4.52
4.51
4.07
3.97
3.82
3.64
3.62
3.59
3.49
3.48
3.47
2.97
2.60
2.59
2.57
2.54
2.22
2.20
2.18
1.84
1.82
1.80
0.61
1.00 1.07 1.90 0.92 1.02 1.08 1.93 2.11 0.98 8.00 1.05 1.00 0.92 0.89 3.80 1.99 1.86

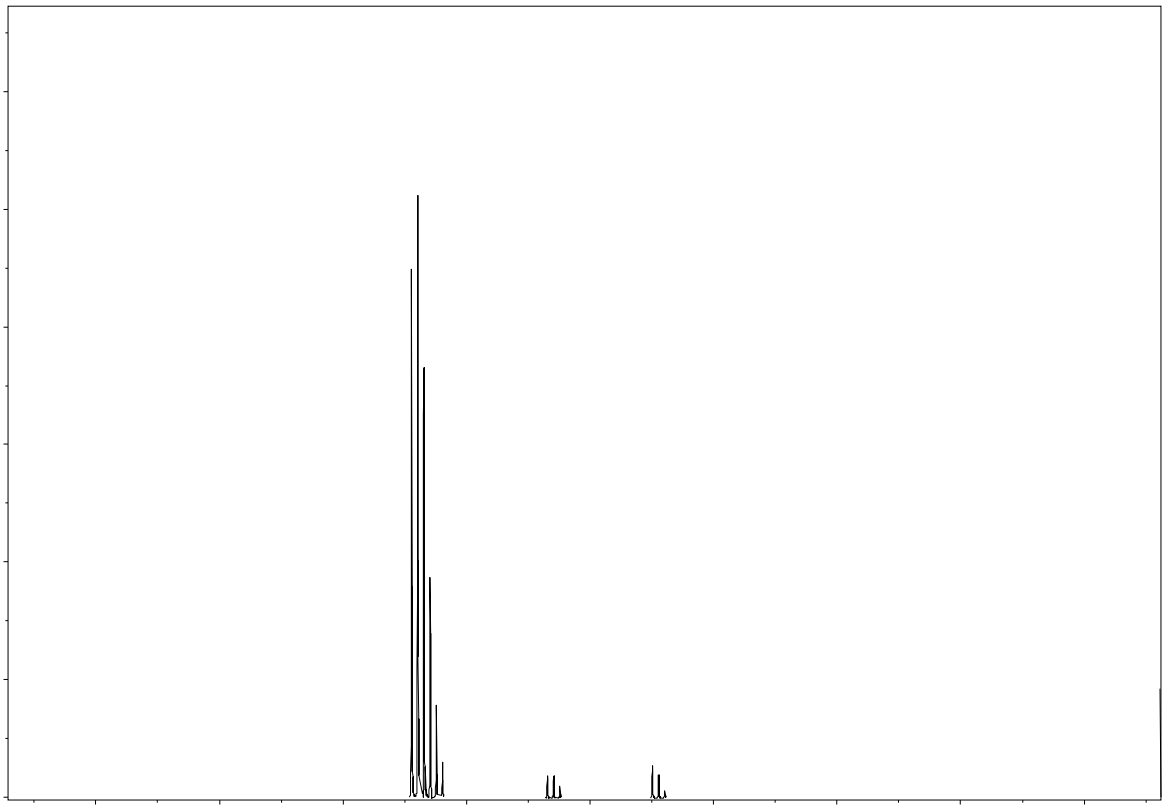

Normalized Intensity
Chemical Shift (ppm)
174.19
172.77
171.38
162.95
162.61
144.22
144.11
124.51
117.64
114.74
97.99
87.30
77.46
76.05
72.92
71.26
69.18
68.96
68.52
65.86
62.52
60.03
52.99
52.08
41.01
32.70
30.80
28.39
28.07
25.36

MUC1-GalNAc Neoglycopeptide 10

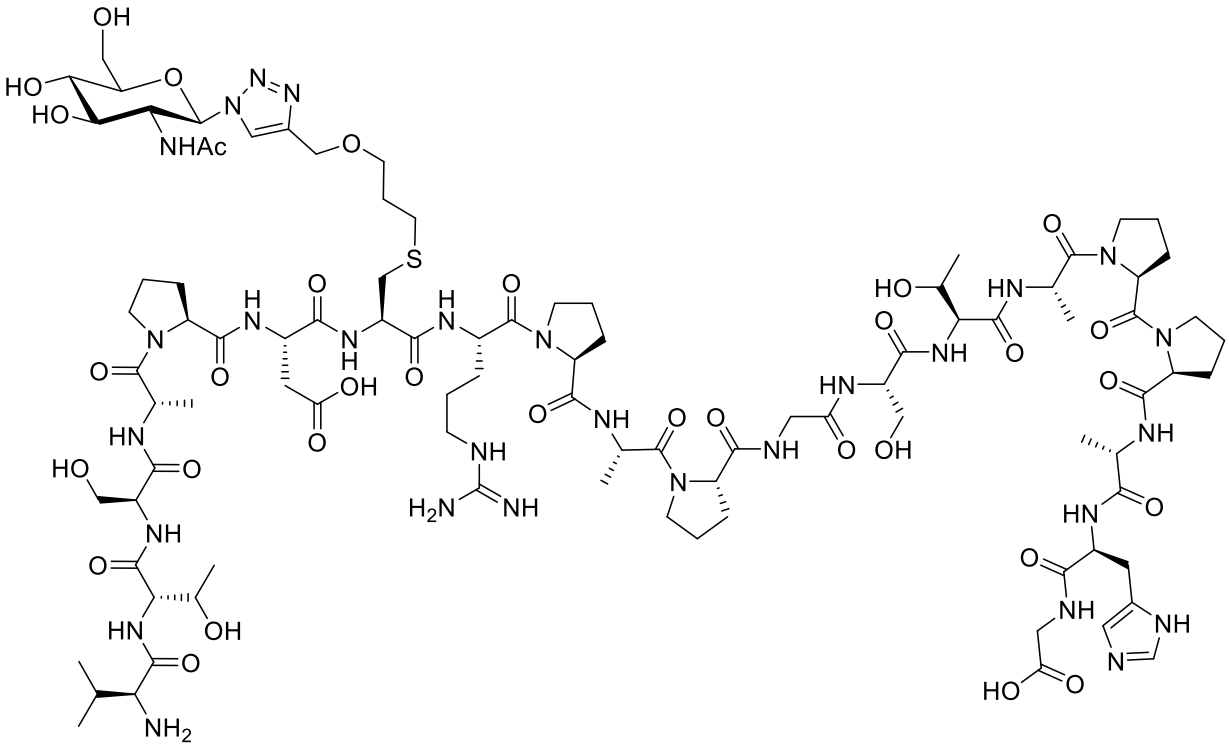


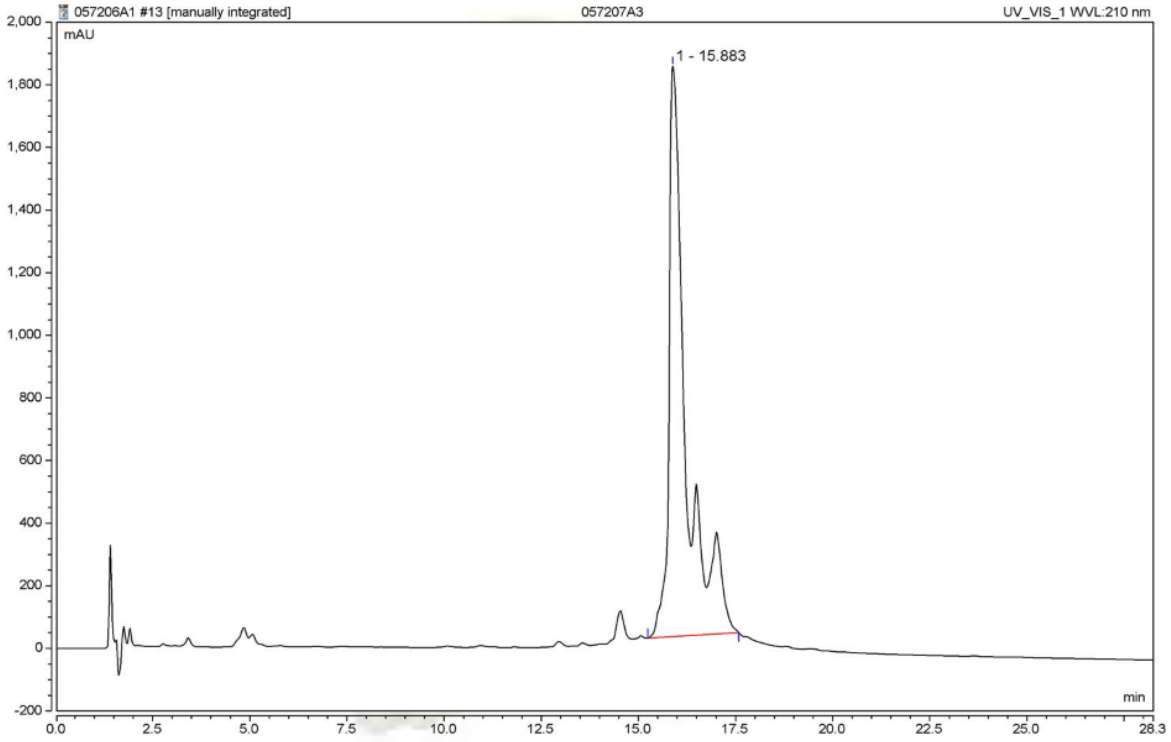


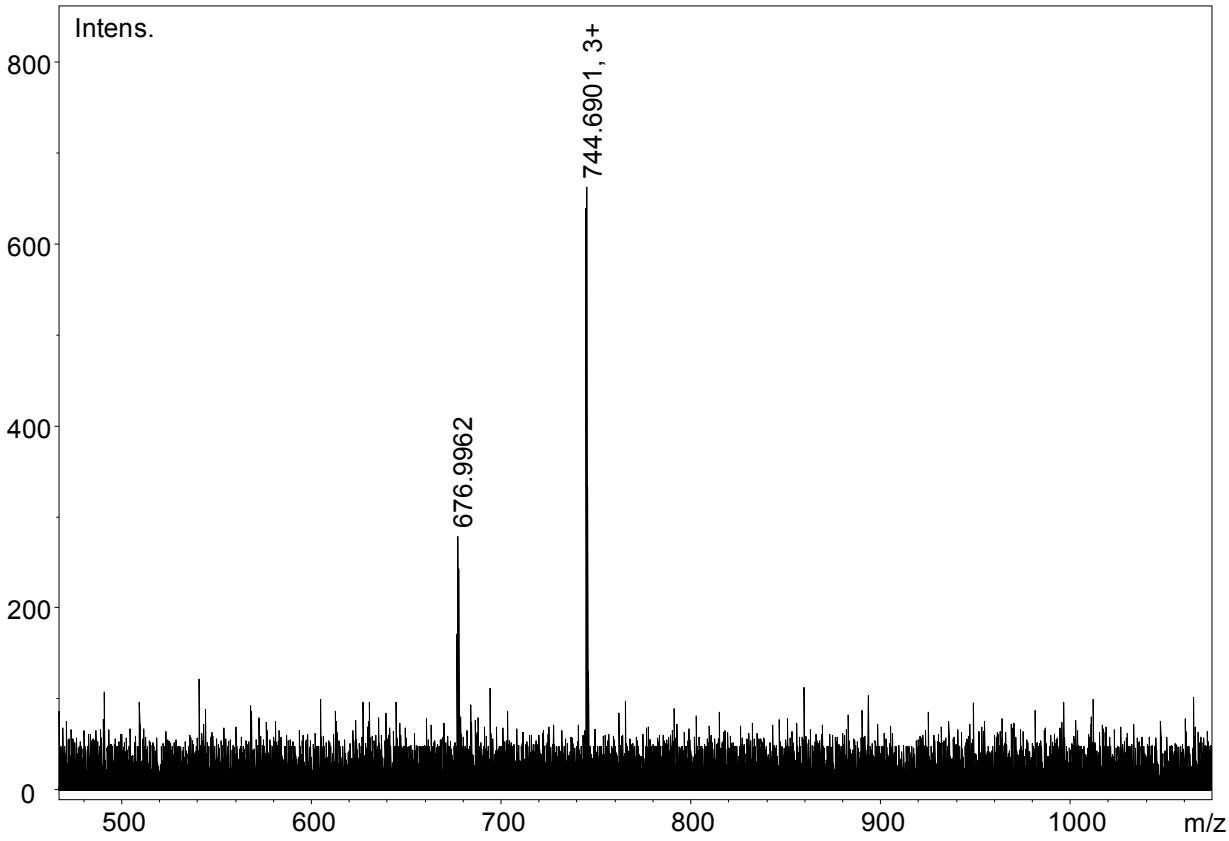


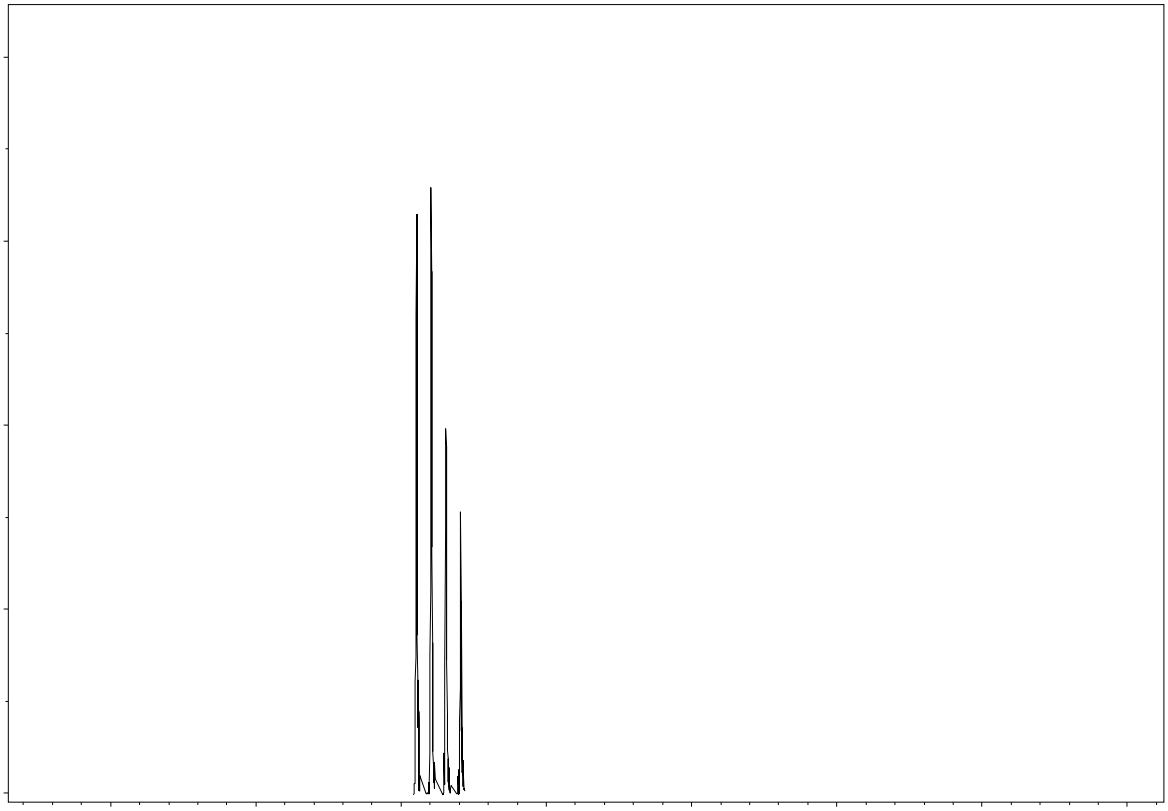


MUC1-GlcNAc Neoglycopeptide 11

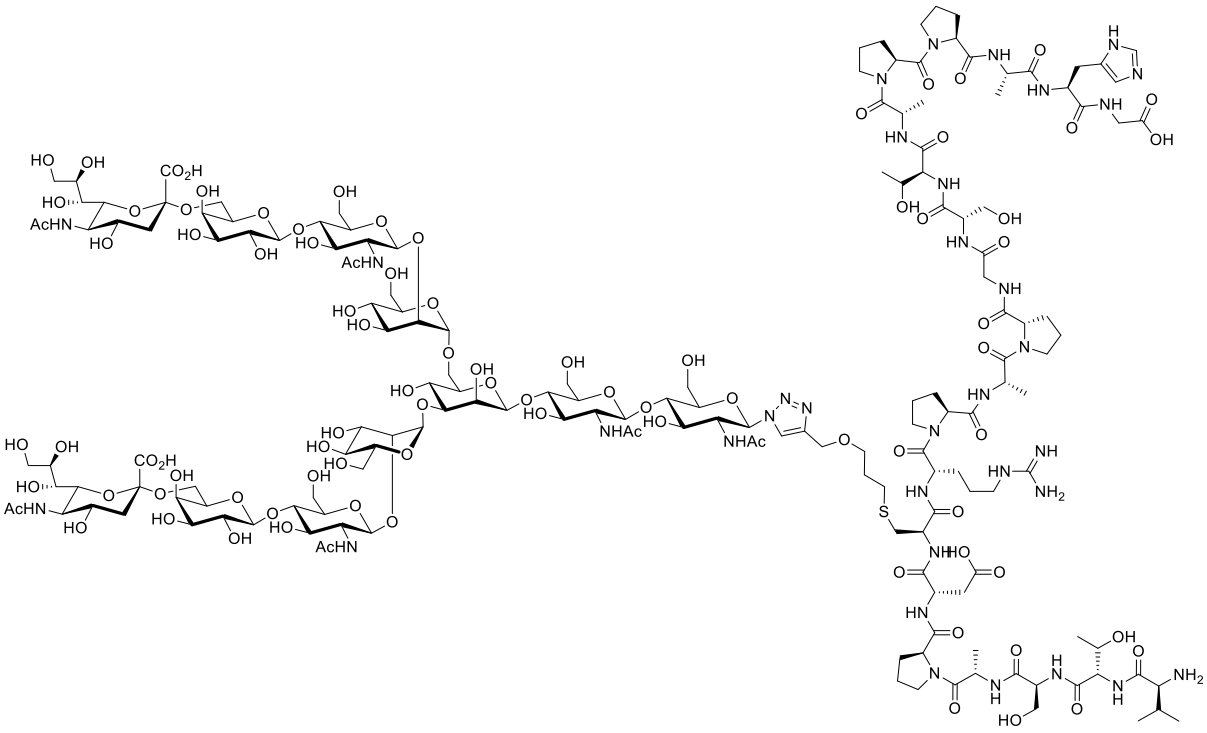


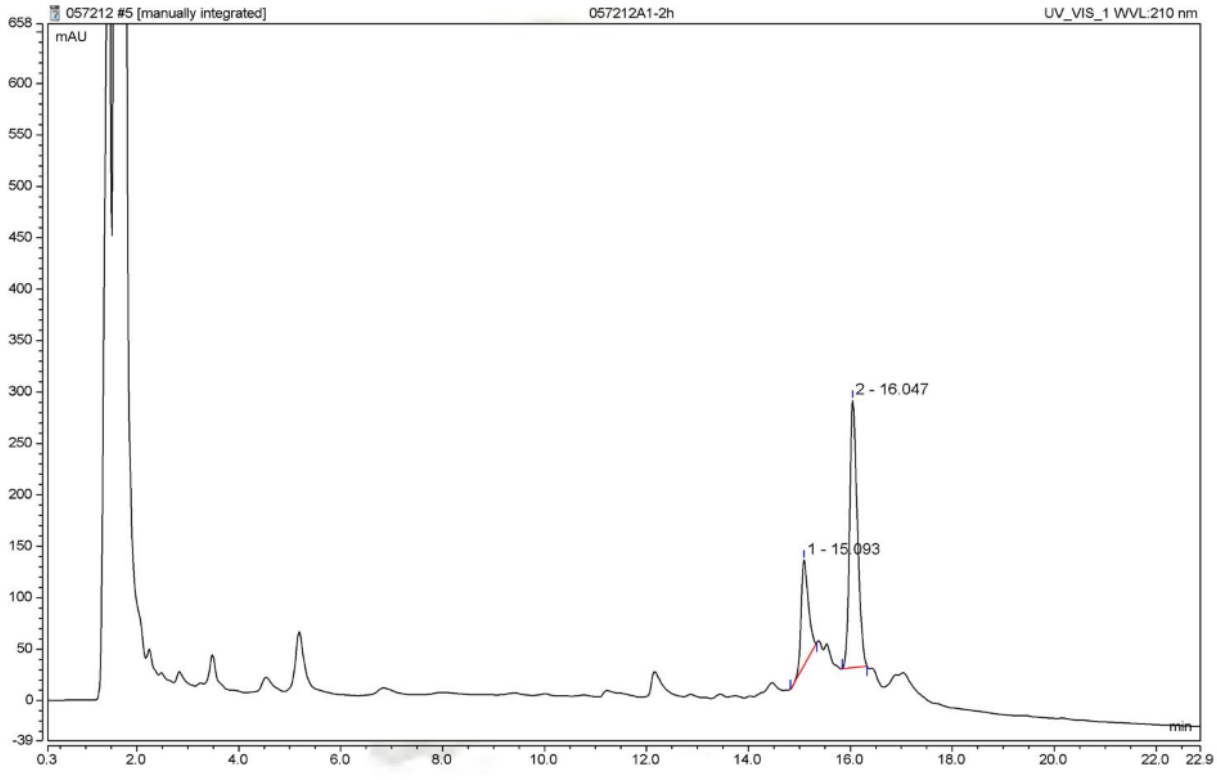

057206A1 #13 [manually integrated]
057207A3
UV_VIS_1 WVL:210 nm
mAU
1 - 15.883
min

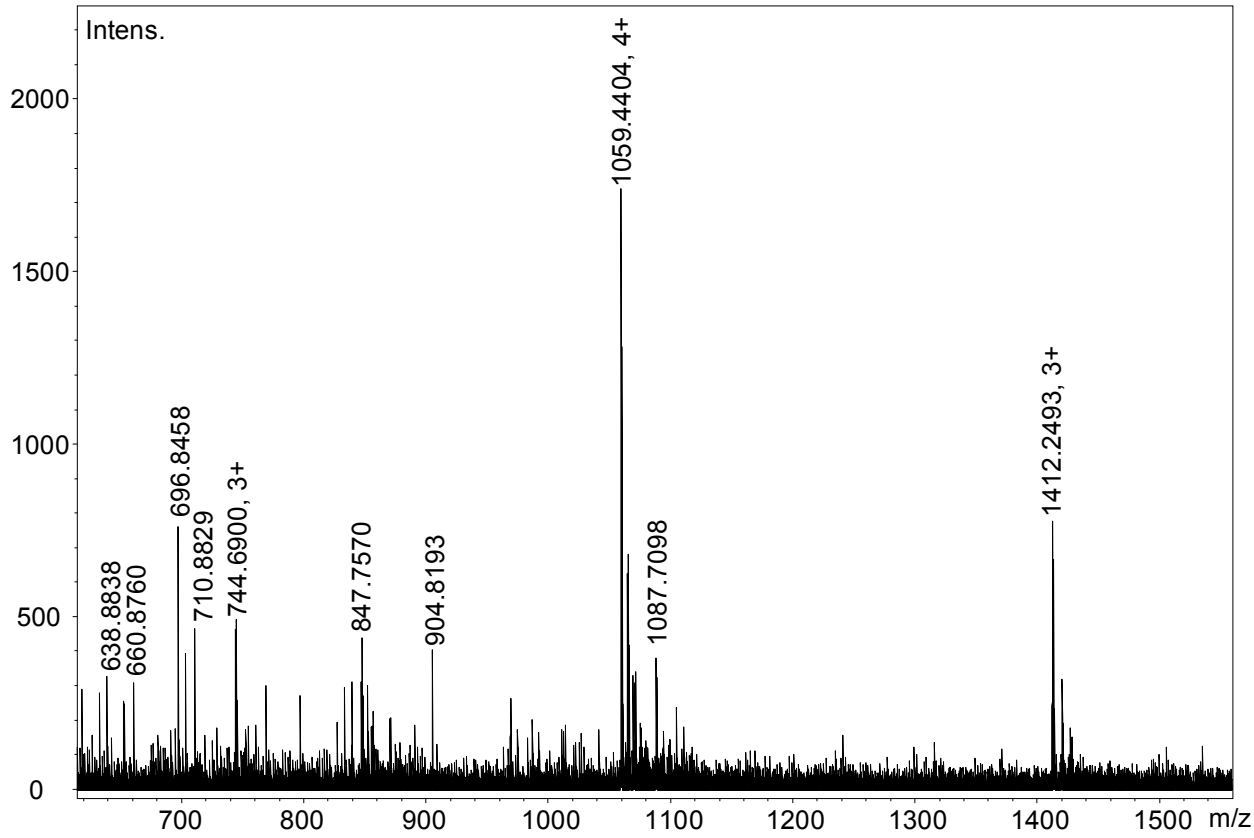

Intens.
800
600
400
200
0
744.6901, 3+
676.9962
500
600
700
800
900
1000
m/z



MUC1-Sialoglycan Neoglycopeptide 12






Intens.
2000
1500
1000
500
0
638.8838
660.8760
696.8458
710.8829
744.6900, 3+
847.7570
904.8193
1059.4404, 4+
1087.7098
1412.2493, 3+
700
800
900
1000
1100
1200
1300
1400
1500
m/z