Supplementary Information

for

Non-enzymatic Stereoselective *S*-glycosylation of Polypeptides and Proteins

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1. General Information

Flash column chromatography was performed using silica gel (300-400 mesh) purchased from Qindao Haiyang. Reverse-phase flash column chromatography was performed on Biotage Isolera One equipped with a Spherigel C18 column (25-40 μm, 100Å, 114 mm ×12.4 mm). The preparative reverse-phase-HPLC separation was performed on a Prep-HPLC system (NS4600 series, Hanbon Sci. & Tech.) using a Dubhe C18 column (10 μm, 100Å, 250 ×10 mm) at 25 °C and a flow rate of 3 mL/min with MeCN/0.1% TFA and water/0.1% TFA as eluents. Reaction solvents (e.g., CH_3CN, H_2O, THF, and CH_2Cl_2) and deuterated solvents were purchased from Energy Chemicals and used as received. Eosin Y was purchased from Sigma-Aldrich and used as received. Ir-based photosensitizers were prepared according to literature procedures.[1] Peptides used in this study were purchased from Dechi Bio (Shanghai, China) or GL Biochem (Shanghai) Ltd., where they were synthesized following conventional solid phase peptide synthesis technologies. The light source was provided by WATTECS WP-TEC-1020 parallel reactor (Figure S1). The distance between the bottom of reaction vial to light bulb is ca. 0.5 cm.

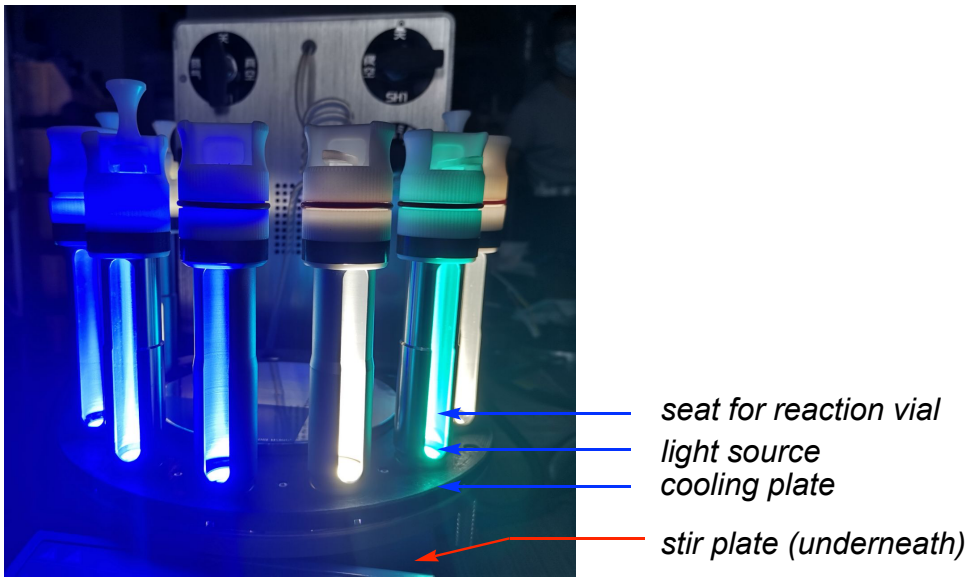


Figure S1 | Photoreactor used in this study.

All new small molecules were characterized by ^{1}H and ^{13}C NMR spectroscopy and high-resolution mass spectroscopy (HR-MS). NMR spectra were recorded on a Bruker AMX 400, 600 or 800 spectrometer and were calibrated using TMS (0.00 ppm) or residual non-deuterated solvent as an internal reference ($CDCl_3$: 7.26 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR; DMSO-d_6: 2.50 ppm for ^{1}H NMR and 49.50 ppm for ^{13}C NMR), and the tabulated data were reported in ppm. HR-MS spectra were recorded on a Waters Q-TOF Premier.

LC-MS/MS analysis of polypeptide products

The peptides were first desalted using C18 ZipTip (Millipore) according to the manufacturer's instructions. After vacuum freeze drying, the peptides were lyophilized and suspended in buffer A (2% CH_3CN, 0.1% TFA). LC-MS/MS analysis was performed using an EASY-nLC 1000 nanoflow LC instrument coupled to a Q Exactive™ Quadrupole-Orbitrap mass spectrometer (Thermo Fisher Scientific). An in-house packed reverse-phase C18 trap column (2 cm length × 360 μm OD × 75 μm ID, 5 μm particle, DIKMA) and in-house packed reversed-phase C18 analytical column (30 cm length × 360 μm OD × 75 μm ID, 3 μm particle, DIKMA) were used in peptide separation. Mobile phase A was 100/0.1% water/formic acid (v/v) and mobile phase B was 95/5/0.1% acetonitrile/water/formic acid (v/v/v). LC gradient elution condition was initially 10% B for 2 min, then raised from 10% to 33% B in 28 min, from 33% to 47% B in 8 min, from 47% to 90% B in 5 min, and held at 90% B for the final 2 min, with a flow rate of 330 nL/min. Data dependent acquisition (DDA) was performed in positive ion mode. MS spectra were acquired from 350 m/z to 1800 m/z with a resolution of 70,000 at m/z = 200. The automatic gain control value was set at 3e6, with maximum fill time of 20 ms. For MS/MS scans, the top 20 most intense parent ions were selected with a 1.6 m/z isolation window and fragmented with a normalized collision energy of 27%. The AGC value for MS/MS was set to a target value of 1e6, with a maximum fill time of 64 ms. Parent ions with a charge state of z = 1 or with unassigned charge states were excluded from fragmentation and the intensity threshold for selection was set to 3.1e5. Fragmentation was performed with an HCD collision cell (mass resolution 17, 000 at m/z = 200). A dynamic exclusion period of 60 s was used after one repeat count.

All raw files were analyzed and searched using Sequest-HT algorithm (version 1.17) by Proteome Discoverer (PD2.3, Thermo Fisher Scientific). The searches were against the peptide sequences using a reverse decoy database with a false discovery rate (FDR) < 1%. Searches were carried out with a precursor peptide mass tolerance of 10 ppm and a fragment ion mass tolerance of 0.02 Da. Oxidation of methionine were set as variable modifications.

Determination of the configuration of the newly formed glycosidic bonds

The stereochemistry of the newly formed glycosidic bonds could be readily determined by coupling constant analysis. For 1,2-*cis* products, *J*(H1-H2) falls within 5–6 Hz, whereas for 1,2-*trans* products, *J*(H1-H2) falls within 9–10 Hz. For all products except the glycosylated protein, the *J*(H1-H2) determined indicate formation of 1,2-*cis* (axially configured) products.

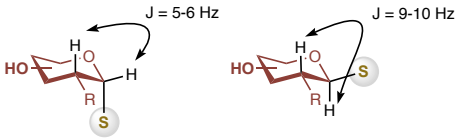
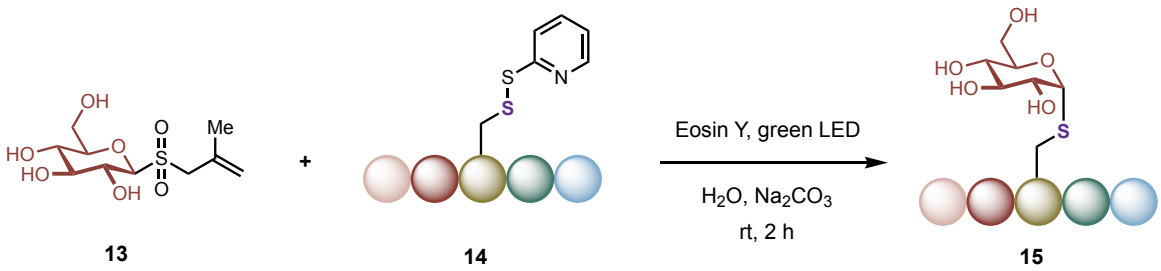


Figure S2 | Determination of the stereochemistry of *S*-glycosidic bonds.

2. General Procedures for *S*-Glycosylation of Peptides

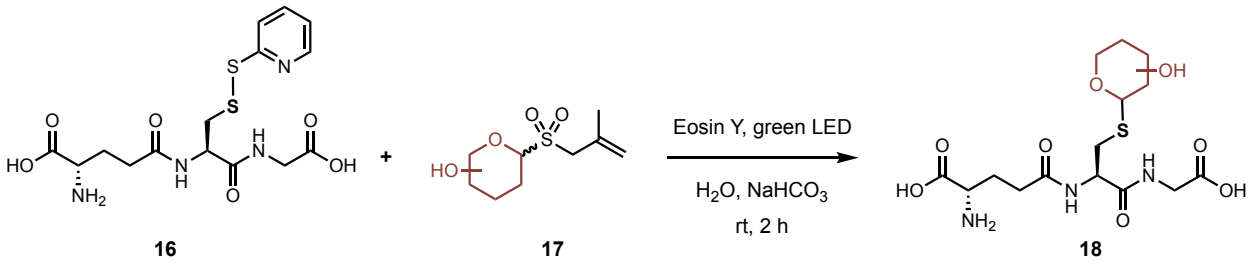
2.1 General Procedure I (for products in Fig. 3, top)



13 14 15

Under N_2 atmosphere, the glycosyl donor **13**, disulfide **14**, Eosin Y, and solvent (0.05 M aqueous solution of Na_2CO_3) were sequentially added to an 8 mL screw-capped glass vial containing a magnetic stirring bar. The reaction vial was then capped and placed onto the WATTECS WP-TEC-1020 parallel reactor and irradiated with green LED for 2 h. The resulting solution was subjected to reverse phase HPLC for purification.

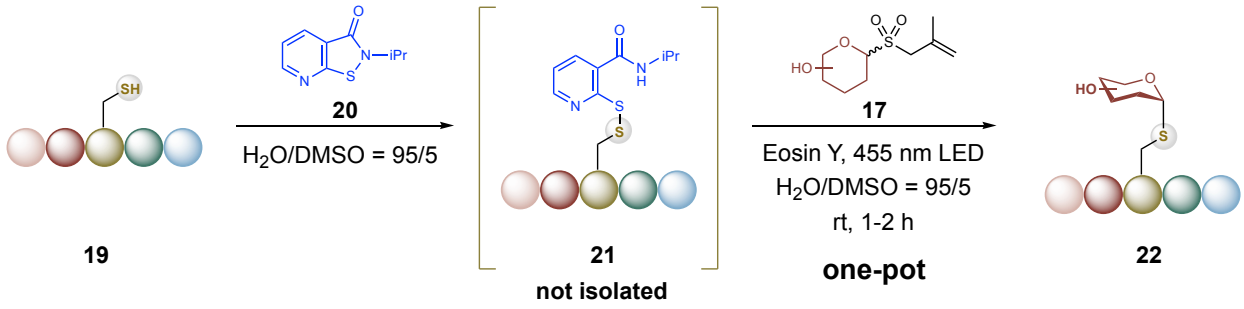
2.2 General Procedure II (for products in Fig. 3, bottom)



16 17 18

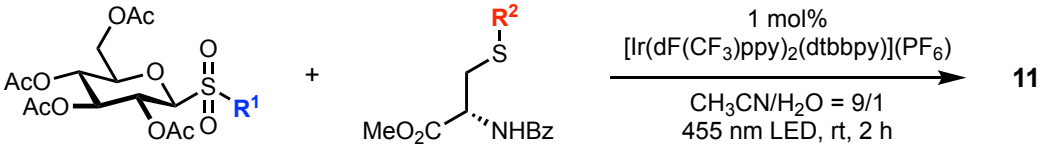
Under N_2 atmosphere, the glycosyl donor **17**, disulfide **16,** Eosin Y, and and solvent (0.1 M aqueous solution of $NaHCO_3$) were sequentially added to a 8 mL screw-capped glass vial containing a magnetic stirring bar. The reaction vial was then capped and placed onto the WATTECS WP-TEC-1020 parallel reactor and irradiated with green LED for 2h. The resulting solution was subjected to reverse phase HPLC for purification.

2.3 General Procedure III (for products in Fig. 4)



Under N_2 atmosphere, the Cys-containing peptide **27** was added to a "glycosylation kit" made from 2-isopropylisothiazolo[5,4-b]pyridin-3(2*H*)-one **28**, glycosyl donor **25**, Eosin Y, and 95/5 H_2O/DMSO. The tube was capped and held at room temperature for 5 min before placed onto the WATTECS WP-TEC-1020 parallel reactor and irradiated with blue LED for 2 h. The resulting solution was subjected to reverse phase HPLC for purification.

3. Optimization Tables



SI-1 **SI-2**

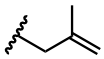
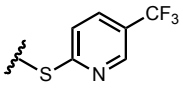
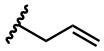
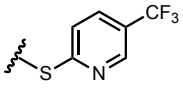
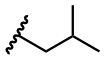
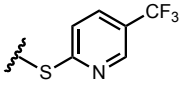
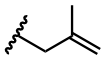
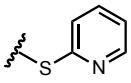
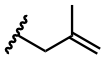
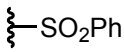
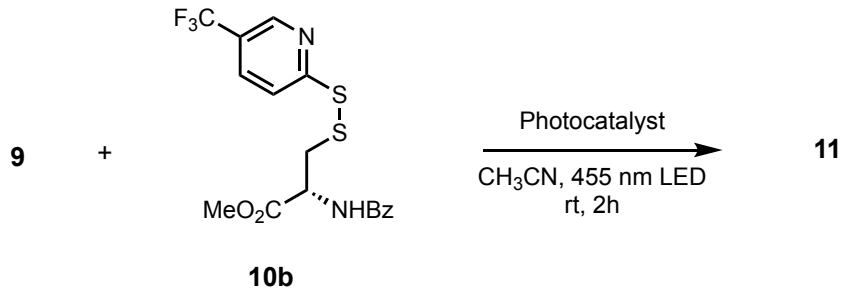
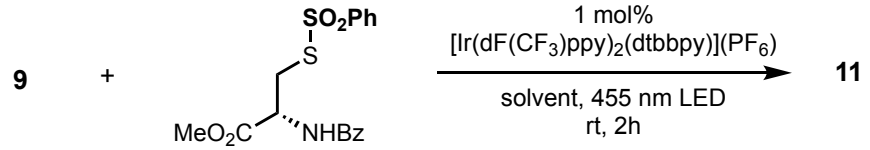
Entry	R^1	R^2	Conv. (%)	Yield (%)
1			100	98
2			82	72
3			0	0
4			100	86
5			100	95

Figure S3. Condition Optimization: Impact of Leaving Groups on Each Substrate.



Entry	Photocatalyst	Conv. (%)	Yield (%)
1	2 mol% $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF_6)$	100	98
2	10 mol% 9-Fluorenone	95	70
3	2 mol% *fac*-$Ir(ppy)_3$	71	57
4	2 mol% $Ru(bpy)_3$	0	0
5	2 mol% Eosin Y	100	75

Figure S4. Condition Optimization: Impact of Photocatalysts.

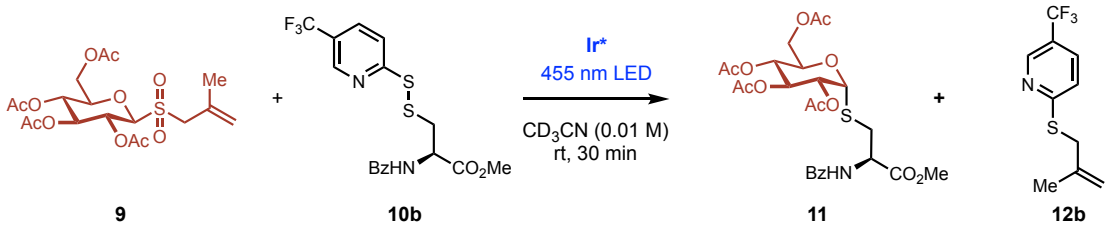


SI-3

Entry	Solvent	Conv. (%)	Yield (%)
1	MeCN	100	95
2	1,2-DCE	89	81
3	EtOAc	75	62
4	glyme	92	70
5	THF	73	61
6	MeOH	90	64
7	DMF	95	74
8	DMSO	95	75

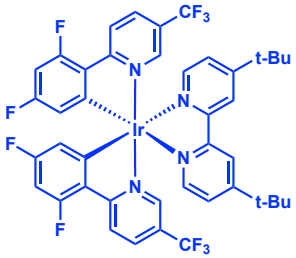
Figure S5. Condition Optimization: Impact of Solvent Properties.

4. Experimental Details of Kinetic Studies



9 **10b** **11** **12b**

Ir* =



4.1 Procedures for "same excess" and "different excess" experiments (Fig. 2C, left):

Step I: Prepare stock solutions.

Solution A: Catalyst Ir* (2.8 mg, 0.0025 mmol) was dissolved in CD_3CN (400 μL).

Solution B: Compound **9** (5.5 mg, 0.012 mmol) was dissolved in CD_3CN (1000 μL).

Solution C: Compound **10b** (5.0 mg, 0.012 mmol) was dissolved in CD_3CN (1000 μL).

Solution D: Compound **9** (9.2 mg, 0.020 mmol), **10b** (10.0 mg, 0.024 mmol), $PhCF_3$ (2.9 mg, 0.020 mmol), and 16 μL solution **A** were dissolved in CD_3CN (984 μL).

Step II: Prepare reaction solutions.

Tube **I** ([**9**] = 0.010 M, [**10b**] = 0.012 M): 250 μL of **Solution D** and 250 μL CD_3CN were added to a NMR tube.

Tube **II** ([**9**] = 0.010 M, [**10b**] = 0.015 M): 250 μL of **Solution D**, 125 μL **Solution C** and 125 μL CD_3CN were added to a NMR tube.

Tube **III** ([**9**] = 0.013 M, [**10b**] = 0.015 M): 250 μL of **Solution D**, 125 μL **Solution B** and 125 μL **Solution C** were added to a NMR tube.

Step **III**: Monitor reaction progress.

1) At time 0, tube **I**, tube **II**, and tube **III** were recorded by ^{19}F NMR respectively.
2) Tube **I**, tube **II**, and tube **III** were bundled together with a rubber rope, and exposed to the same 10 W blue LED bulb for 30 seconds. Each tube was then recorded by ^{19}F NMR.

3) The above operation was repeated for 10 times at 30 seconds intervals, and then 5 times at 1 minute intervals.

Discussion:

The only difference between reactions in Tube II and Tube III is the initial concentration of compound **9**. However, these two reactions have almost identical progress curve, suggesting the concentration of **9** is not impacting the reaction rate. To put it differently, the reaction has a zeroth order of dependence on [**9**].

In all of the three reactions, ln[**10b**] decreases linearly with time. This is consistent with the following scenario:

$$d[\mathbf{10b}]/dt = C \bullet [\mathbf{10b}], \text{ where } C \text{ is a constant.}$$

$$\text{thus, } d[\mathbf{10b}]/[\mathbf{10b}] = C \bullet dt,$$

$$\text{therefore, } \ln[\mathbf{10b}] = C \bullet t, \text{ which is in agreement with our experimental observation.}$$

$$\text{Since } d[\mathbf{11}]/dt = -d[\mathbf{10b}]/dt,$$

$$d[\mathbf{11}]/dt = -C \bullet [\mathbf{10b}].$$

Consequently, the product formation has a first order of dependence on [**10b**].

4.2 Procedures for determining the relationship between rate and [Ir*] (Fig. 2C, right):

Step I: Prepare stock solutions.

Solution E: Catalyst Ir* (2.8 mg, 0.0025 mmol) was dissolved in CD_3CN (2000 μL).

Solution F: Compound **9** (18.4 mg, 0.040 mmol), **10** (20.0 mg, 0.048 mmol) and $PhCF_3$ (as an internal standard, 5.8 mg, 0.040 mmol) were dissolved in CD_3CN (2000 μL).

Step II: Prepare reaction solutions.

Tube **IV** (0 mol % Ir*): 250 μL of solvent **F** and 250 μL CD_3CN were added to a NMR tube.

Tube **V** (0.25 mol % Ir*): 250 μL of solvent **F**, 10 μL solvent **E** and 240 μL CD_3CN were added to a NMR tube.

Tube **VI** (0.5 mol % Ir*): 250 μL of solvent **F**, 20 μL solvent **E** and 230 μL CD_3CN were added to a NMR tube.

Tube **VII** (1 mol % Ir*): 250 μL of solvent **F**, 40 μL solvent **E** and 210 μL CD_3CN were added to a NMR tube.

Step **III**: Monitor reaction progress.

1) At time 0, tube **IV**, tube **V**, tube **VI** and tube **VII** were recorded by ^{19}F NMR respectively.
2) Tube **IV**, tube **V**, tube **VI** and tube **VII** were bundled together with a rubber rope, and exposed to the same 10 W blue LED bulb for 30 seconds. Each tube was then recorded by ^{19}F NMR.
3) The above step was repeated for 10 times at 30 seconds intervals.

The rate constant (-*C*) of each reaction could be determined by plotting ln[**10**] against **t**. Plotting -*C* against catalyst loading gave the data shown in Fig. S2. Therefore, the reaction rate constant is increasing, but less than linearly with the catalyst loading.

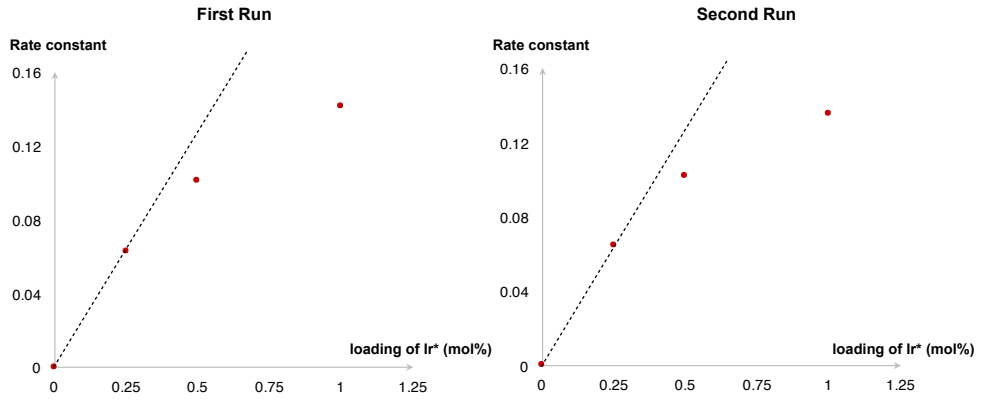
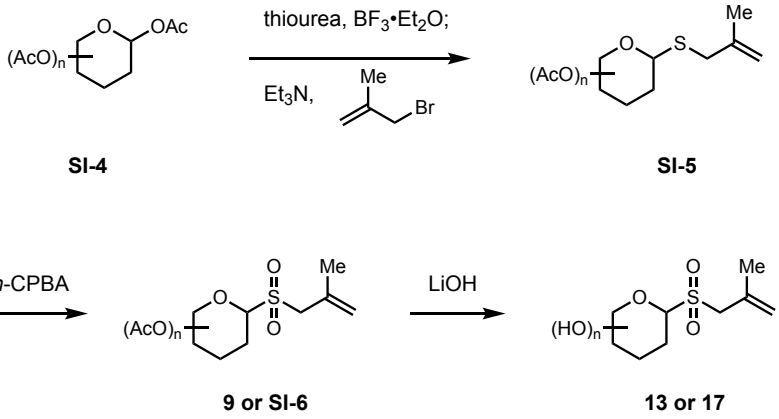


Fig. S6. Relationship between rate constant and photocatalyst loading. For reference, the straight dashed line indicates a (hypothetical) linear relationship.

5. Synthesis and Characterization Data of Glycosyl Donors

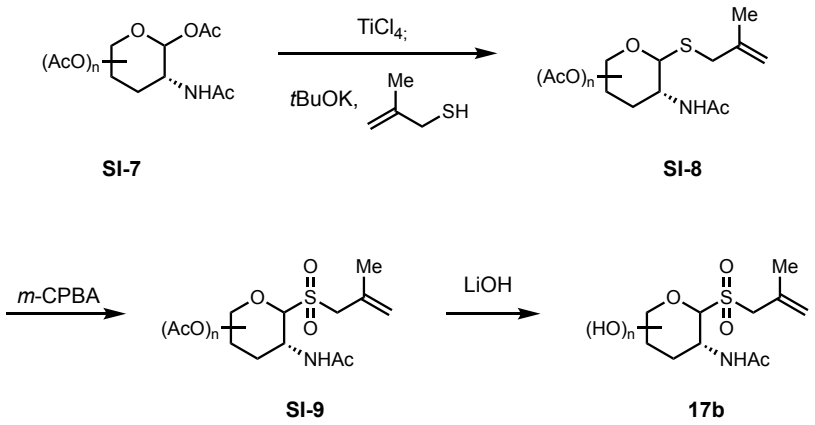


General Procedures IV:

Step 1: To a 100 mL round bottom flask containing **SI-4** (10 mmol) and 25 mL CH_3CN thiourea (15 mmol, 1.1g) and BF_3•Et_2O (30 mmol, 3.75 mL) were added sequentially. The reaction solution was refluxed for 8 h, until **SI-4** was fully consumed as indicated by TLC. To the resulting solution was added Et_3N (30 mmol, 5.2 mL), 3-bromo-2-methyl propene (15 mmol, 1.5 mL). The resulting solution was stirred at 80 °C and monitored by TLC analysis. The resulting solution was concentrated and dissolved in CH_2Cl_2, washed with H_2O. The organic layer was separated and washed with brine, dried, and concentrated to give **SI-5** as a crude mixture, which is used for the next step without further purification.

Step 2: SI-5 was dissolved in 20 mL CH_2Cl_2 and cooled at 0 °C. *m*-CPBA (25 mmol, 4.3g) was slowly added to the reaction solution with stirring. The mixture was allowed to stir for an additional 1 h at room temperature. The resulting mixture was filtered, and the filtrate was washed with H_2O. The organic layer was separated and washed with saturated Na_2SO_3 solution, saturated $NaHCO_3$ solution, brine respectively, then dried and concentrated. The residue was subjected to flash chromatography to give the sulfone **SI-6**.

Step 3: SI-6 was dissolved in 20 mL MeOH at 0 °C, to which LiOH (5 mmol, 120 mg) was added. The reaction was allowed to stir at 0 °C for 4 h. Silica gel was added to the mixture, which is then concentrated in vacuo. The resulting mixture was dry-loaded onto silica gel column, and eluted to give the corresponding polyols.

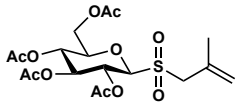


General Procedures V:

Step 1: To a 25 mL round bottom flask containing **SI-7** (1.3 mmol) and 15 mL $CHCl_3$ was added $TiCl_4$ (5 mmol, 0.6 mL). The reaction solution was refluxed for 8 h, until **SI-7** was fully consumed as indicated by TLC. The resulting solution was concentrated. To the resulting residue was added *t*BuOK (0.89 mmol, 100 mg), 2-methylprop-2-ene-1-thiol (0.89 mmol, 93 μL) and 10 mL DMF. The resulting solution was stirred at room temperature and monitored by TLC analysis. The resulting solution was concentrated and dissolved in EtOAc, washed with H_2O. The organic layer was separated and washed with brine, dried, and concentrated. The residue was purified by flash chromatography to give **SI-8**.

Step 2: SI-8 was dissolved in 5 mL CH_2Cl_2 and cooled at 0 °C. *m*-CPBA (0.5 mmol, 86 mg) was slowly added to the reaction solution with stirring. The mixture was allowed to stir for an additional 1 h at room temperature. The resulting mixture was filtered, and the filtrate was washed with H_2O. The organic layer was separated and washed with saturated Na_2SO_3 solution, saturated $NaHCO_3$ solution, brine respectively, then dried and concentrated. The residue was purified by flash chromatography to give **SI-9**.

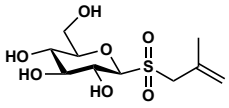
Step 3: SI-9 was dissolved in 5 mL MeOH, to which LiOH (0.25 mmol, 6 mg) was added. The reaction was allowed to stir at room temperature for 4h. Silica gel was added to the mixture, which is then concentrated in vacuo. The resulting mixture was dry-loaded onto a silica gel column, and purified to afford to corresponding polyols.



9

1-((2-Methylallyl)sulfonyl)-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (9)

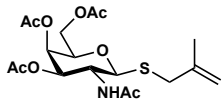
9 was prepared following **General Procedure IV** from peracetylated glucose (10 mmol, 3.9 g), thiourea (15 mmol, 1.1 g), BF_3•Et_2O (30 mmol, 3.75 mL), Et_3N (30 mmol, 4.3 mL), 3-bromo-2-methyl propene (15 mmol, 2 g) and *m*-CPBA (25 mmol, 4.3 g). **9** was isolated by flash chromatography (DCM:EtOAc = 10:1) as a white solid (2.82 g, 63%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.53 (dd, *J* = 9.6, 9.6 Hz, 1H), 5.31 (dd, *J* = 9.4, 9.4 Hz, 1H), 5.27 (br s, 1H), 5.20 (br s, 1H), 5.10 (dd, *J* = 9.8, 9.8 Hz, 1H), 4.58 (d, *J* = 9.9 Hz, 1H), 4.26 (dd, *J* = 12.6, 2.6 Hz, 1H), 4.21 (dd, *J* = 12.6, 5.1 Hz, 1H), 3.98 (d, *J* = 13.6 Hz, 1H), 3.80 (ddd, *J* = 10.1, 5.1, 2.7 Hz, 1H), 3.65 (d, *J* = 13.6 Hz, 1H), 2.09 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.48, 170.19, 169.32, 169.26, 133.00, 121.20, 85.82, 76.73, 73.30, 67.69, 66.29, 61.80, 57.65, 23.01, 20.79, 20.72, 20.66, 20.63. **M.P.**:166-168 °C. **HRMS (DART-TOF)** calculated for $C_{18}H_{26}NaO_{11}S^+$ $[M+Na]^+$ m/z 473.1088, found 473.1091.



13

1-((2-Methylallyl)sulfonyl)-β-D-glucopyranoside (13)

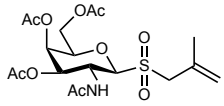
13 was prepared following **General Procedure IV** from **9** (2 mmol, 900 mg) and LiOH (1 mmol, 24 mg). **13** was isolated by flash chromatography (DCM:MeOH = 10:1) as a white solid (472 mg, 84%). **^{1}H NMR (400 MHz, CD_3OD)** δ 5.20 (overlapping m, 2H), 4.43 (d, *J* = 9.6 Hz, 1H), 4.11 (d, *J* = 13.6 Hz, 1H), 3.87 (dd, *J* = 12.5, 2.1 Hz, 1H), 3.80 (d, *J* = 13.5 Hz, 1H), 3.77 (dd, *J* = 9.2, 9.2 Hz, 1H), 3.64 (dd, *J* = 12.5, 6.2 Hz, 1H), 3.42 (dd, *J* = 8.9, 8.9 Hz, 1H), 3.36 (ddd, *J* = 9.2, 6.2, 2.0 Hz, 1H), 3.27 (dd, *J* = 9.4, 9.4 Hz, 1H), 1.93 (s, 3H). **^{13}C NMR (101 MHz, CD_3OD)** δ 135.09, 121.86, 90.11, 83.33, 79.52, 71.15, 70.96, 63.12, 59.73, 23.83. **HRMS (DART-TOF)** calculated $C_{10}H_{18}NaO_7S^+$ $[M+Na]^+$ m/z 305.0665, found 305.0674.



SI-8

1-((2-Methylallyl)thio)-2-deoxy-2-*N*-acetyl-3,4,6-tri-*O*-acetyl-β-D-galactopyranoside (SI-8)

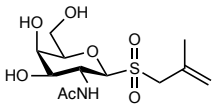
SI-8 was prepared following **General Procedure V** from peracetylated galactocose (3.33 mmol, 1.3 g), $TiCl_4$ (5 mmol, 0.6 mL), BF_3•Et_2O (30 mmol, 3.8 mL), *t*BuOK (0.89 mmol, 100 mg), and 2-methylprop-2-ene-1-thiol (0.89 mmol, 93 μL). **SI-8** was isolated by flash chromatography (PE:EtOAc = 1:1) as a white solid (203 mg, 71%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.71 (d, *J* = 9.4 Hz, 1H), 5.38 (dd, *J* = 3.4, 1.1 Hz, 1H), 5.14 (dd, *J* = 10.8, 3.4 Hz, 1H), 4.88 (br s, 1H), 4.85 (br s, 1H), 4.55 (d, *J* = 10.4 Hz, 1H), 4.29 (td, *J* = 10.6, 9.3 Hz, 1H), 4.12 (dd, *J* = 11.3, 6.9 Hz, 1H), 4.08 (dd, *J* = 11.3, 6.1 Hz, 1H), 3.86 (td, *J* = 6.5, 0.7 Hz, 1H), 3.47 (d, *J* = 13.2 Hz, 1H), 3.12 (d, *J* = 13.2 Hz, 1H), 2.16 (s, 3H), 2.05 (s, 3H), 2.00 (s, 3H), 1.96 (s, 3H), 1.81 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.77, 170.51, 170.43, 170.34, 140.80, 114.22, 83.34, 74.54, 71.48, 67.19, 62.05, 49.51, 37.44, 23.39, 20.81, 20.78, 20.76, 20.71. **HRMS (DART-TOF)** calculated for $C_{15}H_{27}NaO_8S^+$ $[M+Na]^+$ m/z 440.1350, found 440.1350.



SI-9

1-((2-Methylallyl)sulfonyl)-2-deoxy-2-*N*-acetyl-3,4,6-tri-*O*-acetyl-β-D-galactopyranoside (SI-9)

SI-9 was prepared following **General Procedure V** from **SI-8** (0.44 mmol, 180 mg) and *m*-CPBA (1.1 mmol, 220 mg). **SI-9** was isolated by flash chromatography (PE:EtOAc = 1:1) as a white solid (121 mg, 61%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 6.28 (d, *J* = 8.0 Hz, 1H), 5.72 (dd, *J* = 10.8, 3.3 Hz, 1H), 5.46 (d, *J* = 3.3 Hz, 1H), 5.25 (s, 1H), 5.21 (s, 1H), 5.17 (d, *J* = 10.1 Hz, 1H), 4.25 (td, *J* = 10.2, 8.3 Hz, 1H), 4.21 – 4.13 (m, 3H), 4.02 (d, *J* = 13.5 Hz, 1H), 3.73 (d, *J* = 13.5 Hz, 1H), 2.18 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.96 (s, 3H), 1.94 (s, 3H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.82, 170.37, 170.23, 170.14, 132.53, 121.28, 85.81, 75.53, 69.18, 67.11, 61.97, 57.32, 46.64, 23.43, 23.20, 20.78, 20.74. **M.P.**:170-171℃. **HRMS (DART-TOF)** calculated for $C_{15}H_{27}NNaO_{10}S^+$ $[M+Na]^+$ m/z 472.1248, found 472.1242.

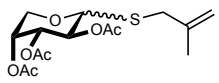


17b

1-((2-Methylallyl)sulfonyl)-2-acetamido-2-deoxy-β-D-galactopyranoside (17b)

17b was prepared following **General Procedure V** from **SI-9** (0.5 mmol, 225 mg) and LiOH (0.25 mmol, 6 mg). **17b** was isolated by flash chromatography (DCM:MeOH = 10:1) as a white solid (159 mg, 97%).

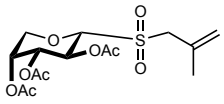
^{1}H NMR (400 MHz, D_2O) δ 5.34 (t, *J* = 1.4 Hz, 1H), 5.22 (br s, 1H), 4.75 (d, *J* = 10.3 Hz, 1H), 4.46 (dd, *J* = 10.3, 10.3 Hz, 1H), 4.20 (d, *J* = 13.7 Hz, 1H), 4.05 (d, *J* = 3.2 Hz, 1H), 4.00 (d, *J* = 13.7 Hz, 1H), 3.86 – 3.76 (m, 4H), 2.01 (s, 3H), 1.93 (s, 3H). **^{13}C NMR (101 MHz, D_2O)** δ 174.54, 131.87, 121.67, 86.73, 80.12, 71.31, 67.71, 61.03, 56.81, 46.07, 22.20. **HRMS (DART-TOF)** calculated $C_{12}H_{21}NNaO_7S^+$ $[M+Na]^+$ m/z 346.0931, found 346.0941.



SI-10

1-((2-Methylallyl)thio)-2,3,4-tri-*O*-acetyl-*D*-arabinopyran-oside (SI-10)

SI-10 was prepared following **General Procedure IV** from peracetylated arabinose (10 mmol, 3.2 g), thiourea (15 mmol, 1.14 g), BF_3•Et_2O (30 mmol, 3.8 mL), Et_3N (30 mmol, 4.3 mL), and 3-bromo-2-methyl propene (15 mmol, 2 g). **SI-10** was isolated by flash chromatography (PE:EtOAc = 10:1) as a colorless oil (1.6 g, 45%, a 9:1 mixture of both isomers). Characterization data of the major isomer is provided. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.28 (td, *J* = 3.7, 2.0 Hz, 1H), 5.23 (dd, *J* = 8.4, 8.4 Hz, 1H), 5.08 (dd, *J* = 8.6, 3.5 Hz, 1H), 4.90 (t, *J* = 1.6 Hz, 1H), 4.88 (s, 1H), 4.50 (d, *J* = 8.2 Hz, 1H), 4.10 (dd, *J* = 12.8, 3.8 Hz, 1H), 3.61 (dd, *J* = 12.8, 2.0 Hz, 1H), 3.42 (d, *J* = 12.9 Hz, 1H), 3.13 (d, *J* = 12.2 Hz, 1H), 2.13 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 1.81 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.38, 170.08, 169.62, 140.51, 114.67, 82.48, 70.75, 68.42, 67.93, 65.82, 37.85, 21.03, 20.90, 20.81, 20.69. **HRMS (DART-TOF)** calculated for $C_{15}H_{22}NaO_7S^+$ $[M+Na]^+$ m/z 369.0978, found 369.0978.

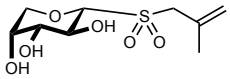


SI-11

1-(2-Methylallyl)sulfonyl)-2,3,4-tri-*O*-acetyl-α-*D*-arabinopyranoside (SI-11)

SI-11 was prepared following **General Procedure IV** from **SI-10** (2 mmol, 620 mg) and *m*-CPBA (5 mmol, 860 mg). **SI-11** was isolated by flash chromatography (PE:EtOAc = 10:1) as a white solid (467 mg, 62%). Only one isomer was isolated.

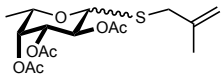
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73 (dd, *J* = 9.4, 9.4 Hz, 1H), 5.34 (ddd, *J* = 3.8, 2.8, 1.5 Hz, 1H), 5.27 (br s, 1H), 5.17 – 5.12 (m, 2H), 4.47 (d, *J* = 9.3 Hz, 1H), 4.24 (dd, *J* = 13.0, 2.7 Hz, 1H), 3.92 (dd, *J* = 13.4, 0.8 Hz, 1H), 3.79 (dd, *J* = 13.0, 1.6 Hz, 1H), 3.75 (d, *J* = 13.4 Hz, 1H), 2.17 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 1.98 (t, *J* = 1.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.28, 170.10, 169.49, 132.48, 121.48, 87.68, 70.66, 68.22, 67.57, 63.89, 57.34, 23.16, 21.03, 20.87, 20.72. **M.P.**:107-109 °C. **HRMS (DART-TOF)** calculated for $C_{15}H_{22}NaO_9S^+$ $[M+Na]^+$ m/z 401.0877, found 401.0887.



17c

1-((2-Methylallyl)sulfonyl)-α-*D*-arabinopyranoside (17c)

17c was prepared following **General Procedure IV** from **SI-11** (0.5 mmol, 168 mg) and LiOH (0.25 mmol, 6 mg). **17c** was isolated by flash chromatography (DCM:MeOH = 10:1) as a white solid (77 mg, 65%). **^{1}H NMR (400 MHz, D_2O)** δ 5.35 (t, *J* = 1.6 Hz, 1H), 5.21 (s, 1H), 4.57 (d, *J* = 9.6 Hz, 1H), 4.18 – 4.04 (m, 4H), 4.00 (d, *J* = 13.8 Hz, 1H), 3.83 (d, *J* = 12.8 Hz, 1H), 3.78 (dd, *J* = 9.4, 3.4 Hz, 1H), 1.95 (s, 3H). **^{13}C NMR (101 MHz, D_2O)** δ 131.91, 121.65, 89.33, 72.91, 70.87, 68.12, 65.62, 57.95, 22.24. **HRMS (DART-TOF)** calculated $C_9H_{16}NaO_6S^+$ $[M+Na]^+$ m/z 275.0560, found 275.0562.

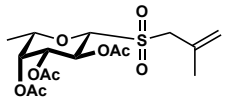


SI-12

1-((2-Methylallyl)thio)-2,3,4-tri-*O*-acetyl-*L*-fucopyranoside (SI-12)

SI-12 was prepared following **General Procedure IV** from peracetylated *L*-fucose (10 mmol, 3.3 g), thiourea (15 mmol, 1.14 g), BF_3•Et_2O (30 mmol, 3.8 mL), Et_3N (30 mmol, 4.3 mL) and 3-bromo-2-methyl propene (15 mmol, 2 g). **SI-12** was isolated by flash chromatography (PE:EtOAc = 10:1) as a colorless oil (2.7 g, 81%, an 8:1 mixture of two isomers). Characterization data of the major isomer is

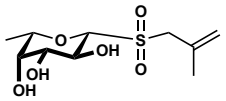
provided. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.25 (dd, *J* = 3.2, 1.2 Hz, 1H), 5.22 (dd, *J* = 9.9, 9.9 Hz, 1H), 5.05 (dd, *J* = 9.9, 3.5 Hz, 1H), 4.89 (m, 1H), 4.86 (br s, 1H), 4.42 (d, *J* = 10.0 Hz, 1H), 3.76 (qd, *J* = 6.4, 1.2 Hz, 1H), 3.44 (dd, *J* = 12.4, 0.9 Hz, 1H), 3.15 (dd, *J* = 12.1. 1.2 Hz, 1H), 2.17 (s, 3H), 2.05 (s, 3H), 1.99 (s, 3H), 1.81 (s, 3H), 1.21 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.71, 170.16, 169.67, 140.67, 114.35, 82.17, 73.13, 72.44, 70.56, 67.38, 37.49, 20.84, 20.75, 20.68, 20.63, 16.38. **HRMS (DART-TOF)** calculated for $C_{16}H_{24}NaO_7S^+$ $[M+Na]^+$ m/z 383.1135, found 383.1137.



SI-13

1-((2-Methylallyl)sulfonyl)-2,3,4-tri-*O*-acetyl-β-L-fucopyranoside (SI-13)

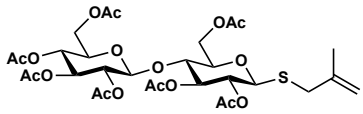
SI-13 was prepared following **General Procedure IV** from **SI-12** (3.2 mmol, 1.06 g) and *m*-CPBA (8.1 mmol, 1.4 g). **SI-13** was isolated by flash chromatography (PE:EtOAc = 5:1) as a white solid (840 mg, 67%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.68 (dd, *J* = 9.9, 9.9 Hz, 1H), 5.31 (m, 1H), 5.27 (br s, *J* = 1.4 Hz, 1H), 5.17 – 5.11 (m, 2H), 4.49 (d, *J* = 9.9 Hz, 1H), 3.96 (qd, *J* = 6.5, 1.0 Hz, 1H), 3.91 (dd, *J* = 13.3, 1.0 Hz, 1H), 3.73 (d, *J* = 13.3 Hz, 1H), 2.20 (s, 3H), 2.06 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H), 1.28 (dd, *J* = 6.6, 1.8 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.45, 170.02, 169.46, 132.51, 121.21, 87.56, 74.35, 71.77, 69.82, 63.53, 57.00, 23.05, 20.80, 20.69, 20.59, 16.33. **M.P.**:144-146 °C. **HRMS (DART-TOF)** calculated for $C_{16}H_{24}NaO_9S^+$ $[M+Na]^+$ m/z 415.1033, found 415.1039.



17d

1-((2-Methylallyl)sulfonyl)-β-*L*-focupyranoside (17d)

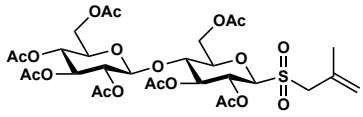
17d was prepared following **General Procedure IV** from **SI-13** (0.2 mmol, 70 mg) and LiOH (0.1 mmol, 2.4 mg). **17d** was isolated by flash chromatography (DCM:MeOH = 10:1) as a white solid (42 mg, 90%). **^{1}H NMR (400 MHz, D_2O)** δ 5.35 (br s, 1H), 5.20 (s, 1H), 4.60 (d, *J* = 9.6 Hz, 1H), 4.15 (d, *J* = 13.8 Hz, 1H), 4.09 (dd, *J* = 9.5, 9.5 Hz, 1H), 3.97 (d, *J* = 13.8 Hz, 1H), 3.94 (q, *J* = 6.5 Hz, 1H), 3.85 (d, *J* = 3.3 Hz, 1H), 3.76 (dd, *J* = 9.6, 3.4 Hz, 1H), 1.95 (s, 3H), 1.32 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (101 MHz, D_2O)** δ 132.06, 121.59, 88.87, 76.07, 73.71, 70.95, 65.39, 57.92, 22.26, 15.62. **HRMS (DART-TOF)** calculated for $C_{10}H_{18}NaO_6S^+$ $[M+Na]^+$ m/z 289.0716, found 289.0732.



SI-14

1-((2-Methylallyl)thio)-2,3,6-tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-β-D-glucopyranoside (SI-14)

SI-14 was prepared following **General Procedure IV** from peracetylated cellobiose (4.2 mmol, 2.8 g), thiourea (6.3 mmol, 482 mg), BF_3•Et_2O (12.7 mmol, 1.8 mL), Et_3N (12.7 mmol, 1.76 g) and 3-bromo-2-methyl propene (6.3 mmol, 851 mg). **SI-14** was isolated by flash chromatoraphy (PE:EtOAc = 2:1) as a yellow solid (1.8 g, 64%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.19 (dd, *J* = 9.2, 9.2 Hz, 1H), 5.13 (dd, *J* = 9.3, 9.3 Hz, 1H), 5.06 (dd, *J* = 9.6, 9.6 Hz, 1H), 4.95 (dd, *J* = 10.0, 10.0 Hz, 1H), 4.90 (dd, *J* = 9.3, 8.2 Hz, 1H), 4.98 (br s, 1H), 4.84 (s, 1H), 4.51 (d, *J* = 7.8 Hz, 1H), 4.51 (dd, *J* = 11.8, 1.5 Hz, 1H), 4.43 (d, *J* = 10.2 Hz, 1H), 4.36 (dd, *J* = 12.5, 4.4 Hz, 1H), 4.08 (dd, *J* = 12.0, 5.7 Hz, 1H), 4.02 (dd, *J* = 12.1, 1.0 Hz, 1H), 3.74 (dd, *J* = 9.5, 9.5 Hz, 1H), 3.66 (ddd, *J* = 9.8, 4.5, 2.3Hz, 1H), 3.53 (ddd, *J* = 9.9, 5.7, 2.0 Hz, 1H), 3.41 (d, *J* = 13.3 Hz, 1H), 3.09 (d, *J* = 13.2 Hz, 1H), 2.12 (s, 3H), 2.08 (s, 3H), 2.03 (d, *J* = 1.6 Hz, 6H), 2.02 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.80 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.57, 170.36, 170.29, 169.88, 169.71, 169.40, 169.17, 140.45, 114.66, 100.95, 81.78, 76.75, 76.73, 73.77, 73.07, 72.09, 71.75, 70.27, 67.91, 62.36, 61.69, 37.75, 20.92, 20.78, 20.75, 20.64, 20.49. **HRMS (DART-TOF)** calculated for $C_{30}H_{42}NaO_{17}S^+$ $[M+Na]^+$ m/z 729.2035, found 729.2038.

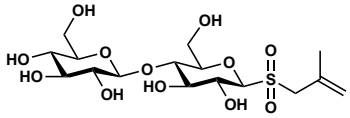


SI-15

1-((2-Methylallyl)sulfonyl)-2,3,6-tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-β-D-glucopyranoside (SI-15)

SI-15 was prepared following **General Procedure IV** from **SI-14** (2.7 mmol, 1.8 g) and *m*-CPBA (6.6 mmol, 1.15 g). **SI-15** was isolated by flash chromatography (PE:EtOAc = 2:1) as a white solid (1.3 g, 65%). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 5.49 (dd, *J* = 9.4, 9.4 Hz, 1H), 5.28 (dd, *J* = 9.0, 9.0 Hz, 1H), 5.25 (br s, 1H), 5.18 (s, 1H), 5.15 (dd, *J* = 9.4, 9.4 Hz, 1H), 5.06 (dd, *J* = 9.7, 9.7 Hz, 1H), 4.92 (dd, *J* = 9.4, 7.9 Hz, 1H), 4.62 (dd, *J* = 12.3, 1.9 Hz, 1H), 4.59 (d, *J* = 9.8 Hz, 1H), 4.56 (d, *J* = 7.9 Hz, 1H), 4.37 (dd, *J* = 12.5, 4.4 Hz, 1H), 4.08 (ddd, *J* = 14.7, 12.4, 3.9 Hz, 2H), 3.98 (d, *J* = 13.7 Hz, 1H), 3.81 (dd, *J* = 9.4, 9.4 Hz, 1H), 3.75 – 3.67 (m, 2H), 3.58 (d, *J* = 13.7 Hz, 1H), 2.12 (s, 3H), 2.09 (s, 3H), 2.04 (s, 3H), 2.03 (s, 6H), 2.01 (s, 3H), 1.98 (s, 3H), 1.97 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ

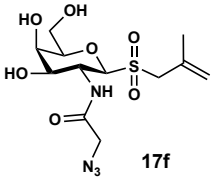
170.54, 170.25, 170.19, 169.79, 169.37, 169.25, 169.10, 133.19, 120.98, 100.84, 84.87, 77.31, 75.71, 72.95, 72.87, 72.16, 71.70, 67.79, 66.01, 61.59, 61.54, 57.77, 29.37, 22.91, 20.81, 20.73, 20.64, 20.59, 20.53. **M.P.**:87-89℃. **HRMS (DART-TOF)** calculated for $C_{30}H_{42}NaO_{19}S^+$ $[M+Na]^+$ m/z 761.1933, found 761.1934.



17e

1-((2-Methylallyl)sulfonyl)-β-D-cellobioside (17e)

17e was prepared following **General Procedure IV** from **SI-15** (0.5 mmol, 369 mg) and LiOH (0.25 mmol, 6 mg). **17e** was isolated by flash chromatography (DCM:MeOH = 10:1) as a yellow solid (200 mg, 90%). **^{1}H NMR (400 MHz, D_2O)** δ 5.36 (br s, 1H), 5.23 (br s, 1H), 4.54 (d, *J* = 8.0 Hz, 1H), 4.20 (d, *J* = 14.0 Hz, 1H), 4.06 – 3.94 (m, 5H), 3.81 – 3.70 (m, 4H), 3.56 – 3.30 (m, 5H), 1.95 (s, 3H). **^{13}C NMR (101 MHz, D_2O)** δ 131.93, 121.74, 102.42, 87.63, 79.25, 77.02, 76.00, 75.45, 75.14, 73.10, 69.43, 68.32, 60.57, 59.67, 57.99, 22.17. **HRMS (DART-TOF)** calculated $C_{16}H_{28}NaO_{12}S^+$ $[M+Na]^+$ m/z 467.1194, found 467.1191.

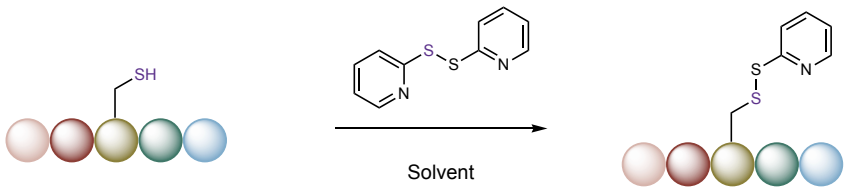


17f

2-azido-N-((2S,3R,4R,5R,6R)-4,5-dihydroxy-6-(hydroxymethyl)-2-((2-methylallyl)sulfonyl) tetrahydro-2H-pyran-3-yl) acetamide (17f)

17f was prepared following **General Procedure V** and isolated by flash chromatography (DCM:MeOH = 10:1) as a white solid. **^{1}H NMR (400 MHz, MeOD)** δ 5.22 (br s, 2H), 4.67 (d, *J* = 10.3 Hz, 1H), 4.44 (dd, *J* = 10.2, 10.2 Hz, 1H), 4.15 (d, *J* = 13.5 Hz, 1H), 3.95 (d, *J* = 2.8 Hz, 1H) 3.92 – 3.78 (m, 5H), 3.72 (dd, *J* = 11.9, 4.2 Hz, 1H), 3.67 (dd, *J* = 7.5, 4.3 Hz, 1H), 1.95 (s, 3H). **^{13}C NMR (101 MHz, MeOD)** δ 171.42, 134.93, 121.87, 88.69, 82.59, 73.31, 70.16, 63.26, 58.05, 53.68, 24.60. **HRMS (DART-TOF)** calculated $C_{12}H_{20}N_4NaO_7S^+$ $[M+Na]^+$ m/z 387.0945, found 387.0954.

6. Synthesis and Characterization Data of Disulfides in Fig. 2



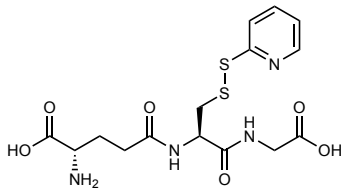
General Procedure VI:

A cysteine containing peptide (0.17 mmol) was added to a 8.5 mL CH_3OH solution of dipyridine disulfide (0.34 mmol, 75 mg). The reaction was incubated for 8 h until full consumption of the thiol. Addition of CH_2Cl_2 to the reaction mixture caused precipitation of the peptide product, which is then filtered and air dried.

General Procedure VII:

A cysteine containing peptide (0.17 mmol) was added to a 8.5 mL DMSO solution of dipyridine disulfide (0.34 mmol, 75 mg). The reaction was incubated for 8 h until full consumption of the thiol. Water (10 mL) was added to the reaction mixture. The resulting solution was subjected to reverse phase column for purification.

Characterization Data for Disulfides in Fig. 3:

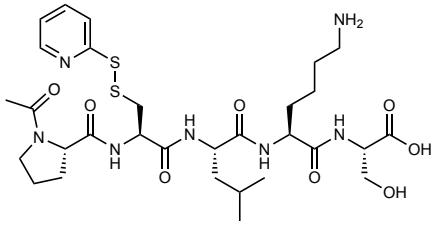


16

Method 1: 16 was prepared using the following procedure. Reduced glutathione (0.02 mmol, 6.1 mg) was added to a 1 mL stock solution (H_2O:MeOH:TFA = 9:1:0.01) of dipyridine disulfide (0.04 mmol, 8.8 mg). The reaction was incubated for 0.5 h until full consumption of the thiol. The resulting solution was neutralized by adding 12 mg $NaHCO_3$ and was subjected to reverse phase flash column chromatography for purification to afford a white solid (8.3 mg, 98%).

Method 2: Reduced glutathione (2 mmol, 614 mg) was added to a 20 mL solution (MeOH:H_2O = 1:1) of dipyridine disulfide (6 mmol, 1.32 g). The reaction was incubated for 8 h until full consumption of the thiol. **16** was subjected to reverse phase flash column chromatography for purification to afford a white solid (480 mg, 58%).

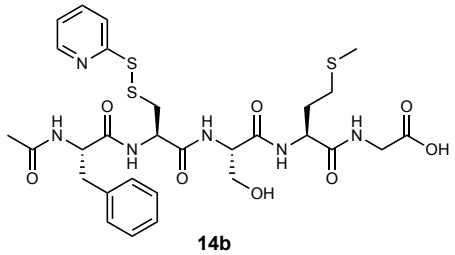
^{1}H NMR (400 MHz, D_2O) δ 8.46 (d, *J* = 5.1 Hz, 1H), 7.97 – 7.86 (m, 2H), 7.41 (t, *J* = 5.9 Hz, 1H), 4.64 (dd, *J* = 9.6, 4.3 Hz, 1H), 3.92 (s, 2H), 3.80 (t, *J* = 6.4 Hz, 1H), 3.40 (dd, *J* = 14.5, 4.3 Hz, 1H), 3.15 (dd, *J* = 14.5, 9.6 Hz, 1H), 2.46 – 2.32 (m, 2H), 2.19 – 2.05 (m, 2H). **^{13}C NMR (101 MHz, D_2O)** δ 174.59, 173.99, 173.65, 172.13, 157.78, 148.50, 139.48, 122.50, 122.34, 53.90, 52.71, 41.95, 39.38, 31.25, 26.04.



14a

14a was prepared following **General Procedure VII** from cysteine containing peptide (0.17 mmol, 100 mg) and dipyridine disulfide (0.34 mmol, 75 mg) in 8.5 mL DMSO. 10 mL water was added to the reaction mixture. The resulting solution was subjected to reverse phase flash column chromatography for purification to afford a white solid (66 mg, 55%).

^{1}H NMR (400 MHz, D_2O) δ 8.57 (d, *J* = 5.9 Hz, 1H), 8.18 (td, *J* = 8.0, 1.7 Hz, 1H), 8.08 (d, *J* = 8.3 Hz, 1H), 7.62 (dd, *J* = 7.6, 6.0 Hz, 1H), 4.67 (dd, *J* = 8.9, 5.4 Hz, 1H), 4.50 (t, *J* = 4.4 Hz, 1H), 4.43 – 4.35 (m, 3H), 3.97 (dd, *J* = 11.7, 4.8 Hz, 1H), 3.86 (dd, *J* = 11.7, 4.0 Hz, 1H), 3.72 – 3.61 (m, 2H), 3.37 (dd, *J* = 14.2, 5.5 Hz, 1H), 3.18 (dd, *J* = 14.3, 9.0 Hz, 1H), 2.99 (t, *J* = 7.6 Hz, 2H), 2.34 – 2.25 (m, 1H), 2.14 (s, 3H), 2.04 – 1.98 (m, 2H), 1.96 – 1.74 (m, 4H), 1.73 – 1.55 (m, 6H), 1.51 – 1.38 (m, 2H), 0.93 (d, *J* = 5.4 Hz, 3H), 0.87 (d, *J* = 5.3 Hz, 3H). **^{13}C NMR (101 MHz, D_2O)** δ 174.63, 174.19, 173.41, 173.29, 173.21, 171.31, 156.29, 145.40, 142.89, 124.07, 123.39, 117.76, 61.02, 60.19, 54.83, 53.26, 52.45, 52.29, 48.67, 39.63, 39.14, 39.04, 30.39, 29.89, 26.20, 24.30, 24.21, 22.09, 21.89, 21.42, 20.55. **HRMS (DART-TOF)** calculated for $C_{30}H_{48}N_7O_8S_2^+$ $[M+H]^+$ m/z 698.3000, found 601.2993.



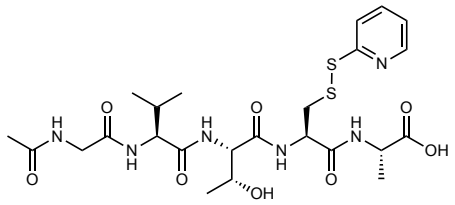
14b

14b was prepared following **General Procedure VI** from cysteine containing peptide (0.17 mmol, 100 mg) and dipyridine disulfide (0.34 mmol, 75 mg) in 8.5 mL CH_3OH. **14b** was filtered and air dried as a white solid (112 mg, 95%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.48 (dd, *J* = 13.6, 6.3 Hz, 2H), 8.24 – 8.15 (m, 2H), 8.09 (dd, *J* = 17.1, 7.7 Hz, 2H), 7.84 – 7.74 (m, 2H), 7.29 – 7.22 (m, 5H), 7.21 – 7.16 (m, 1H), 4.60 – 4.50 (m, 2H), 4.42 – 4.28 (m, 2H), 3.74 (ddd, *J* = 23.5, 17.8, 5.8 Hz, 2H), 3.60 (ddd, *J* = 29.4, 10.8, 5.8 Hz, 2H), 3.27 (dd, *J* = 13.5, 5.1 Hz, 1H), 3.09 – 3.00 (m, 2H), 2.75 (dd, *J* = 13.9, 10.2 Hz, 1H), 2.49 – 2.38 (m, 2H), 2.00 (s, 4H), 1.78 (s, 4H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 171.74, 171.25, 170.98, 169.68, 169.47, 159.05, 149.56, 137.97, 137.89, 129.13, 128.05, 126.25, 121.15, 119.22, 61.55, 55.13, 54.06, 52.13, 51.79, 40.80, 40.69, 37.33, 31.82, 29.37, 22.48, 14.60.

HRMS (DART-TOF) calculated for $C_{29}H_{39}N_6O_8S_3^+$ $[M+H]^+$ m/z 695.1986, found 695.1994.



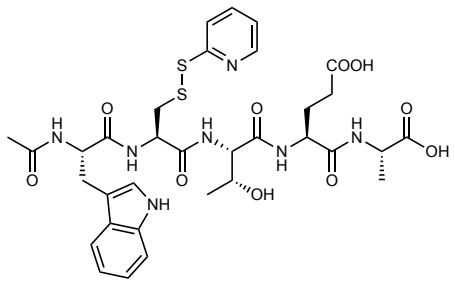
14c

14c was prepared following **General Procedure VI** from cysteine containing peptide (0.2 mmol, 100 mg) and dipyridine disulfide (0.4 mmol, 88 mg) in 8.5 mL CH_3OH. **14c** was filtered and air dried as a white solid (102 mg, 84%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.45 (d, *J* = 4.8 Hz, 1H), 8.26 (d, *J* = 7.2 Hz, 1H), 8.19 (d, *J* = 7.9 Hz, 1H), 8.14 – 8.07 (m, 1H), 7.87 (t, *J* = 8.1 Hz, 2H), 7.84 – 7.74 (m, 2H), 7.24 (t, *J* = 5.9 Hz, 1H), 5.07 (s, 1H), 4.58 – 4.50 (m, 1H), 4.30 – 4.24 (m, 2H), 4.15 (p, *J* = 6.8 Hz, 1H), 4.01– 3.93 (m, 1H), 3.74 (d, *J* = 5.8 Hz, 2H), 3.22 (dd, *J* = 13.5, 4.8 Hz, 1H), 3.05 (dd, *J* = 13.4, 9.1 Hz, 1H), 2.05 – 1.95 (m, 1H), 1.85 (s, 3H), 1.25 (d, *J* = 7.0 Hz, 3H), 1.05 (d, *J* = 6.1 Hz, 3H), 0.83 (dd, *J* = 9.8, 4.9 Hz, 6H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 173.63, 171.08, 169.82, 169.73, 169.20, 169.11, 159.05, 149.58, 137.94, 121.17, 119.16, 66.59, 58.21, 57.67, 51.87, 47.81, 42.05, 40.80, 30.55, 22.45, 19.44, 19.28, 18.02, 16.97.

HRMS (DART-TOF) calculated for $C_{24}H_{37}N_6O_8S_2^+$ $[M+H]^+$ m/z 601.2109, found 601.2104.



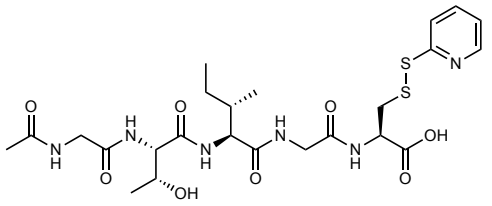
14d

14d was prepared following **General Procedure VI** from cysteine containing peptide (0.15 mmol, 100 mg) and dipyridine disulfide (0.3 mmol, 66 mg) in 8.5 mL CH_3OH. **14d** was filtered and air dried as a white solid (100 mg, 86%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.22 (s, 2H), 10.78 (s, 1H), 8.59 (d, *J* = 7.7 Hz, 1H), 8.47 (d, *J* = 4.9 Hz, 1H), 8.18 (d, *J* = 7.1 Hz, 1H), 8.13 (d, *J* = 7.9 Hz, 1H), 7.88 (dd, *J* = 8.2, 3.2 Hz, 2H), 7.81 – 7.75 (s, 2H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.24 (td, *J* = 5.7, 4.8, 2.1 Hz, 1H), 7.15 (d, *J* = 2.4 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 4.99 (s, 1H), 4.63 – 4.54 (m, 2H), 4.36 – 4.28 (m, 1H), 4.24 (dd, *J* = 8.3, 4.0 Hz, 1H), 4.15 (t, *J* = 7.2 Hz, 1H), 4.01 (t, *J* =4.6 Hz, 1H), 3.18 – 3.05 (m, 3H), 2.92 (dd, *J* = 14.8, 9.9 Hz, 1H), 2.27 (t, *J* = 8.2 Hz, 2H), 2.04 – 1.89 (m, 2H), 1.79 (s, 3H), 1.24 (d, *J* = 6.9 Hz, 3H), 1.04 (d, *J* = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 174.09, 173.89, 172.27, 170.73, 169.73, 169.55, 169.41, 159.11, 149.58, 137.91, 136.09, 127.30, 123.63, 121.17, 120.89, 119.30, 118.49, 118.24, 111.32, 110.17, 66.56, 58.29, 53.52, 52.33, 51.51, 47.58, 40.55, 29.96, 27.70, 27.54, 22.56, 19.56, 16.91.

HRMS (DART-TOF) calculated for $C_{33}H_{42}N_7O_{10}S_2^+$ $[M+H]^+$ m/z 760.2429, found 760.2426.



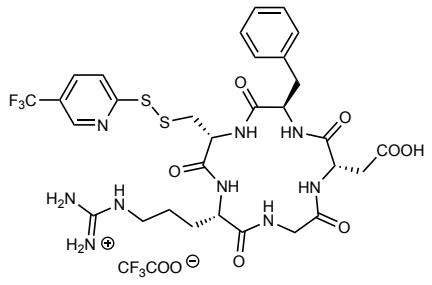
14e

14e was prepared following **General Procedure VII** from cysteine containing peptide (0.2 mmol, 100 mg) and dipyridine disulfide (0.4 mmol, 88 mg) in 10 mL DMSO. 10 mL water was added to the reaction mixture. The resulting solution was subjected to reverse phase flash column chromatography for purification to afford a white solid (80 mg, 65%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.45 (d, *J* = 4.2 Hz, 1H), 8.30 (d, *J* = 7.8 Hz, 1H), 8.19 (dt, *J* = 9.5, 5.8 Hz, 2H), 7.82 (td, *J* = 7.7, 1.9 Hz, 1H), 7.78 – 7.70 (m, 3H), 7.24 (dd, *J* = 7.2, 4.8 Hz, 1H), 4.94 (s, 1H), 4.50 – 4.43 (m, 1H), 4.29 (dd, *J* = 8.4, 4.1 Hz, 1H), 4.18 (t, *J* = 7.6 Hz, 1H), 4.03 – 3.96 (m, 1H), 3,82 – 3.70 (m, 4H), 3.23 (dd, *J* = 13.7, 4.7 Hz, 1H), 3.09 (dd, *J* = 13.7, 8.8 Hz, 1H), 1.85 (s, 3H), 1.79 – 1.71 (m, 1H), 1.52– 1.43 (m, 1H), 1.15 – 1.05 (m, 1H), 1.01 (d, *J* = 6.3 Hz, 3H), 0.88 – 0.78 (m, 6H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 171.62, 171.19, 170.04, 169.89, 169.32, 168.85, 158.80, 149.67, 137.97, 121.30, 119.33, 66.63, 57.91, 57.35, 51.50, 42.27, 41.67, 40.43, 36.59, 24.38, 22.47, 19.71, 15.36, 11.28.

HRMS (DART-TOF) calculated for $C_{24}H_{37}N_6O_8S_2^+$ $[M+H]^+$ m/z 601.2109, found 601.2189.

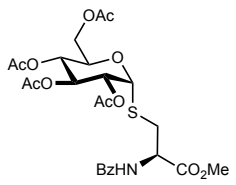


14f

The cysteine containing peptide (0.086 mmol, 57.9 mg) was added to a 8 mL CH_3OH solution of 2,2'-bis(5-trifluoromethylpyridyl)disulfide (0.3 mmol, 106.8 mg). The reaction was incubated for 8h until full consumption of the thiol. CH_3OH was evaporated under the reduced pressure. Addition of CH_2Cl_2 to the reaction mixture caused precipitation of the peptide product, which is then filtered and air dried as a white solid (60.2 mg, 80%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.86 (s, 1H), 8.40 – 8.30 (m, 2H), 8.21 (d, J = 7.3 Hz, 1H), 8.14 (dd, J = 8.6, 2.1 Hz, 1H), 8.09 – 7.86 (m, 3H),7.59 – 7.50 (m, 1H), 7.28 – 7.11 (m, 6H), 4.67 – 4.59 (m, 1H), 4.49 – 4.36 (m, 2H), 4.17 – 4.01 (m, 2H), 3.25 (dd, J = 15.5, 3.6 Hz, 1H), 3.12 – 2.96 (m, 4H), 2.80 (dd, J = 13.6, 6.4 Hz, 1H), 2.68 (dd, J = 16.4, 8.2 Hz, 1H), 2.36 (dd, J = 16.2, 5.7 Hz, 1H), 1.82 – 1.68 (m, 1H), 1.56 – 1.32 (m, 3H). **^{13}C NMR (101 MHz, DMSO-d_6)** δ 172.08, 171.25, 171.05, 170.51, 170.17, 169.86, 164.72, 157.09, 146.95, 146.91, 137.73, 135.34, 129.50, 128.63, 126.76, 123.23, 122.91, 122.79, 120.00, 54.74, 54.07, 52.72, 49.40, 43.69, 40.81, 37.25, 35.78, 28.49, 25.64. **^{19}F NMR (376 MHz, DMSO-d_6)** δ -60.61, -73.95. **HRMS (DART-TOF)** calculated for $C_{30}H_{45}N_8O_{12}S^+$ $[M\text{-}CF_3COO^-]^+$ m/z 756.2204, found 756.2206.

7. Synthesis and Characterization Data for Compounds in Fig. 2

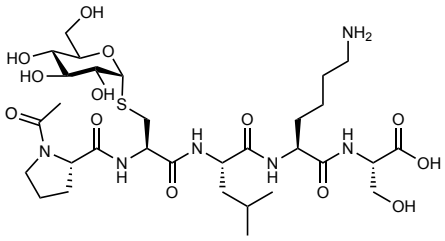


11

Methyl N-(benzoyl)-S-(2,3,4,6-tetra-O-acetyl-α-*D*-glucopyranoside)-L-cysteinate

Product **11** was prepared following **General Procedure VIII** from **9** (0.2 mmol, 90 mg), **10b** (0.22 mmol, 70 mg) and $Ir[dF(CF_3)(ppy)_2(dtbbpy)]PF_6$ (0.001 mmol, 1.1 mg). **11** was isolated by flash chromatography (SiO_2, PE:EtOAc = 3:1) as a white solid (108 mg, 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (br d, *J* = 8.5 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 5.66 (d, *J* = 5.8 Hz, 1H), 5.24 (dd, *J* = 10.3, 9.5 Hz, 1H), 5.19 (ddd, *J* = 8.5, 5.0, 3.5 Hz, 1H), 4.99 (dd, *J* = 10.3, 9.2 Hz, 1H), 4.97 (dd, *J* = 10.4, 5.7 Hz, 1H), 4.37 (ddd, *J* = 10.3, 5.0, 2.1 Hz, 1H), 4.25 (dd, *J* = 12.6, 5.0 Hz, 1H), 4.15 (dd, *J* = 12.6, 2.2 Hz, 1H), 3.79 (s, 3H), 3.32 (dd, *J* = 14.5, 5.1 Hz, 1H), 3.13 (dd, *J* = 14.6, 3.5 Hz, 1H), 2.06 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.65, 170.42, 169.80, 169.78, 169.47, 167.01, 133.47, 131.95, 128.52, 127.27, 84.19, 70.49, 69.97, 68.65, 68.18, 61.77, 52.73, 52.70, 35.07, 20.66, 20.57, 20.52, 20.48. **HRMS (DART-TOF)** calculated $C_{25}H_{31}NNaO_{12}S^+$ $[M+Na]^+$ m/z 592.1459, found 592.1469.



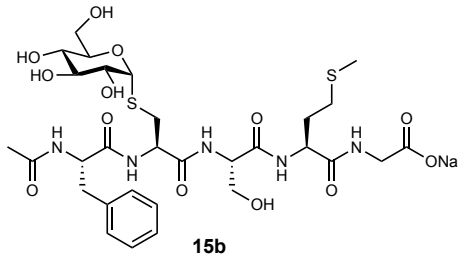
15a

15a was prepared following **General Procedure I** from the glycosyl donor **13** (0.022 mmol, 6.2 mg), disulfide **14a** (0.02 mmol, 13.9 mg), Eosin Y (65 μL, 4 mg/mL in 0.05 mol/L aqueous solution of Na_2CO_3), and 1 mL aqueous solution of Na_2CO_3 (0.05 mmol/L). **15a** was obtained following reverse phase preparative HPLC for purification as a white solid (8.4 mg, 58%). **Reverse phase HPLC details**: Column type: Dubhe C18, 250 x10 mm, 10 μm. Temperature = 25°C. Flow rate = 3 mL/min. Solvents used for the eluents are MeCN and water, both with 0.1% TFA. The eluent was kept constant at 5% MeCN for 15 min, then raised from 5% MeCN to 10% MeCN for 10 min, and from 10% MeCN to 90% MeCN for 80 min. The product was generally eluted from 36.2 min to 38.6 min.

^{1}H NMR (600 MHz, D_2O) δ 5.48 (d, *J* = 5.5 Hz, 1H), 4.55 (dd, *J* = 8.7, 5.5 Hz, 1H), 4.48 (t, *J* = 4.2 Hz, 1H), 4.38– 4.32 (m, 3H), 3.95 (dd, *J* = 11.8, 4.8 Hz, 1H), 3.94–3.91 (m, 1H), 3.83 (dd, *J* = 11.7, 3.9 Hz, 1H), 3.81 – 3.77 (m, 2H), 3.73 (dd, *J* = 12.5, 5.0 Hz, 1H), 3.67 – 3.56 (m, 2H), 3.50 (t, *J* = 9.6 Hz, 1H), 3.39 (t, *J* = 9.5 Hz, 1H), 3.06 –2.94 (m, 4H), 2.30 – 2.20 (m, 1H), 2.08 (s, 3H), 1.98 – 1.95 (m, 3H), 1.92 –1.80 (m, 2H), 1.78 – 1.70 (m, 1H), 1.69 – 1.51 (m, 6H), 1.48 – 1.37 (m, 2H), 0.89 (d, *J* = 5.8 Hz, 3H), 0.83 (d, *J* = 5.9 Hz, 3H).

^{13}C NMR (151 MHz, D_2O) δ 174.62, 174.28, 173.50, 173.35, 173.30, 172.05, 86.98, 73.66, 72.58, 71.05, 69.56, 61.15, 60.47, 60.24, 54.91, 53.86, 53.32, 52.47, 48.76, 39.74, 39.29, 31.87, 30.45, 29.97, 26.26, 24.39, 24.30, 22.18, 21.97, 21.50, 20.72.

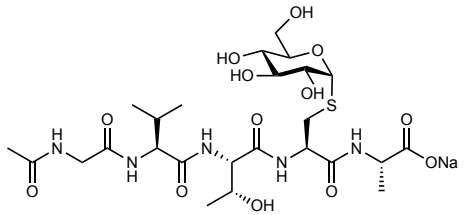
HRMS (DART-TOF) calculated for $C_{31}H_{55}N_6O_{13}S^+$ $[M+H]^+$ m/z 751.3542, found 751.3538.



15b

15b was prepared following **General Procedure I** from the glycosyl donor **13** (0.022 mmol, 6.2 mg), disulfide **14b** (0.02 mmol, 11.7 mg), Eosin Y (65 μL, 4 mg/mL in 0.05 mol/L Na_2CO_3 aqueous solution), and 1 mL aqueous solution of Na_2CO_3 (0.05 mmol/L). **15b** was obtained following reverse phase preparative HPLC for purification as a white solid (8.0 mg, 52%). **Reverse phase HPLC details**: Column type: Dubhe C18, 250 x10 mm, 10 μm. Temperature = 25°C. Flow rate = 3 mL/min. Solvents used for the eluents are MeCN and water, both with 0.1% TFA. The eluent was kept constant at 5% MeCN for 15 min, then raised from 5% MeCN to 10% MeCN for 10 min, and from 10% MeCN to 90% MeCN for 80 min. The product was generally eluted from 44.2 min to 45.2 min.

^{1}H NMR (600 MHz, D_2O) δ 7.35 (dd, *J* = 7.0, 7.0 Hz, 2H), 7.30 (dd, *J* = 7.3, 7.3 Hz, 1H), 7.26 (d, *J* = 7.0 Hz, 2H), 5.45 (d, *J* = 5.5 Hz, 1H), 4.58 (dd, *J* = 8.2, 6.3 Hz, 2H), 4.54 (dd, *J* = 9.2, 5.0 Hz, 1H), 4.37 (t, *J* = 5.5 Hz, 1H), 3.99 (d, *J* = 18 Hz, 1H), 3.96 (d, *J* = 18 Hz, 1H), 3.90 (ddd, *J* = 10.0, 4.8, 2.4 Hz, 1H), 3.86 (dd, *J* = 14.6, 5.8 Hz, 1H), 3.83 (dd, *J* = 11.6, 5.6 Hz, 1H), 3.81 – 3.77 (m ,2H), 3.74 (dd, *J* = 12.5, 4.9 Hz, 1H), 3.51 (t, *J* = 9.5 Hz, 1H), 3.40 (t, *J* = 9.6 Hz, 1H), 3.09 (dd, *J* = 13.9, 6.8 Hz, 1H), 3.04 – 2.94 (m, 3H), 2.62 (ddd, *J* = 13.4, 8.1, 5.2 Hz, 1H), 2.53 (dt, *J* = 13.4, 7.8 Hz, 1H), 2.17 – 2.10 (m, 1H), 2.08 (s, 3H), 2.05 – 1.98 (m, 1H), 1.93 (s, 3H). **^{13}C NMR (151 MHz, D_2O)** δ 174.10, 173.64, 173.29, 173.19, 171.76, 171.63, 136.38, 129.20, 128.81, 127.22, 86.82, 73.63, 72.68, 71.02, 69.48, 60.93, 60.45, 55.76, 55.17, 53.68, 52.71, 41.34, 36.99, 32.11, 30.25, 29.34, 21.69, 14.19. **HRMS (DART-TOF)** calculated for $C_{30}H_{44}N_5Na_2O_{13}S_2^+$ $[M+Na]^+$ m/z 792.2167, found 792.2167.

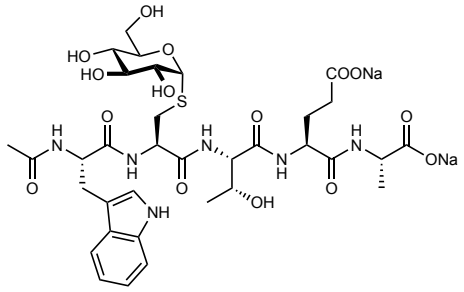


15c

15c was prepared following **General Procedure I** from the glycosyl donor **13** (0.022 mmol, 6.1 mg), disulfide **14c** (0.02 mmol, 12 mg), Eosin Y (65 μL, 4 mg/mL in 0.05 mol/L Na_2CO_3 aqueous solution), and 1 mL aqueous solution of Na_2CO_3 (0.05 mmol/L). **14c** was obtained following reverse

phase preparative HPLC for purification as a white solid (7.3 mg, 54%). **Reverse phase HPLC details**: Column type: Dubhe C18, 250 x10 mm, 10 μm. Temperature = 25°C. Flow rate = 3 mL/min. Solvents used for the eluents are MeCN and water, both with 0.1% TFA. The eluent was kept constant at 5% MeCN for 15 min, then raised from 5% MeCN to 10% MeCN for 10 min, and from 10% MeCN to 90% MeCN for 80 min. The product was generally eluted from 32.2 min to 35.0 min.

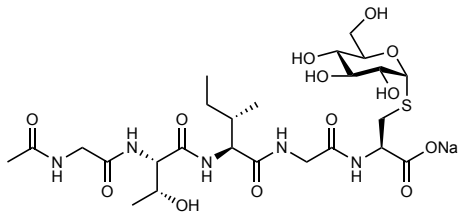
^{1}H NMR (600 MHz, D_2O) δ 5.50 (d, *J* = 5.5 Hz, 1H), 4.61 (dd, *J* = 8.7, 5.0 Hz, 1H), 4.41 – 4.35 (m, 2H), 4.24 (d, *J* = 7.3 Hz, 1H), 4.22 – 4.16 (m, 1H), 4.00 – 3.91 (m, 3H), 3.85 – 3.80 (m, 2H), 3.77 (dd, *J* = 12.5, 4.9 Hz, 1H), 3.54 (t, *J* = 9.5 Hz, 1H), 3.43 (t, *J* = 9.5 Hz, 1H), 3.10 (dd, *J* = 14.2, 5.0 Hz, 1H), 3.04 (dd, *J* = 14.3, 8.7 Hz, 1H), 2.15– 2.08 (m, 1H), 2.05 (s, 3H), 1.43 (d, *J* = 7.4 Hz, 3H), 1.21 (d, *J* = 6.4 Hz, 3H), 0.95 (dd, *J* = 8.6, 6.8 Hz, 6H). **^{13}C NMR (151 MHz, D_2O)** δ 176.04, 174.88, 173.83, 171.80, 171.46, 171.45, 87.15, 73.62, 72.59, 71.10, 69.53, 67.17, 60.48, 59.52, 59.04, 53.91, 48.81, 42.59, 32.36, 30.22, 21.76, 18.80, 18.57, 17.60, 16.22.



15d was prepared following **General Procedure I** from the glycosyl donor **13** (0.022 mmol, 6.2 mg), disulfide **14d** (0.02 mmol, 15.2 mg), Eosin Y (65 μL, 4 mg/mL in 0.05 mol/L Na_2CO_3 aqueous solution), and 1 mL aqueous solution of Na_2CO_3 (0.05 mmol/L). **15d** was obtained following reverse phase preparative HPLC for purification as a white solid (8.5 mg, 51%). **Reverse phase HPLC details**: Column type: Dubhe C18, 250 x10 mm, 10 μm. Temperature = 25°C. Flow rate = 3 mL/min. Solvents used for the eluents are MeCN and water, both with 0.1% TFA. The eluent was kept constant at 5% MeCN for 15 min, then raised from 5% MeCN to 10% MeCN for 10 min, and from 10% MeCN to 90% MeCN for 80 min. The product was generally eluted from 42.5 min to 44.4 min.

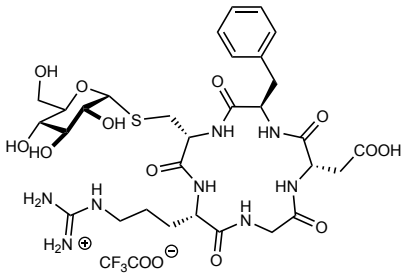
^{1}H NMR (600 MHz, D_2O) δ 7.59 (d, *J* = 7.9 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.22 – 7.18 (m, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 5.34 (d, *J* = 5.5 Hz, 1H), 4.61 (t, *J* = 7.3 Hz, 1H), 4.51 (dd, *J* = 7.7, 5.8 Hz, 1H), 4.34 (dd, *J* = 8.7, 5.8 Hz, 1H), 4.28 (q, *J* = 7.3 Hz, 1H), 4.20 (d, *J* = 4.8 Hz, 1H), 4.14 – 4.09 (m, 1H), 3.80 (ddd, *J* = 9.9, 4.7, 2.4 Hz, 1H), 3.75 – 3.67 (m, 3H), 3.44 (t, *J* = 9.5 Hz, 1H), 3.36 (t, *J* = 9.5 Hz, 1H), 3.23 (dd, *J* = 14.6, 7.0 Hz, 1H), 3.16 (dd, *J* = 14.7, 7.4 Hz, 2H), 2.93 – 2.85 (m, 2H), 2.44 (t, *J* = 7.4 Hz, 2H), 2.12 – 2.05 (m, 1H), 1.98– 1.92 (m, 4H), 1.36 (d, *J* = 7.3 Hz, 3H), 1.14 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR (151 MHz, D_2O)** δ 176.99, 174.01, 173.50, 172.51, 171.65, 171.34, 136.07, 126.77,

124.28, 121.87, 119.23, 118.19, 111.80, 108.71, 86.74, 73.43, 72.48, 70.85, 69.28, 66.81, 60.23, 59.13, 54.62, 53.56, 52.68, 48.78, 32.08, 29.69, 26.84, 26.03, 21.59, 18.64, 16.02. **HRMS (DART-TOF)** calculated for $C_{34}H_{47}N_6Na_2O_{15}S^+$ $[M+H]^+$ m/z 857.2610, found 857.2632.



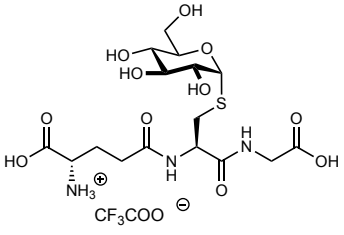
15e

15e was prepared following **General Procedure I** from the glycosyl donor **13** (0.022 mmol, 6.2 mg), disulfide **14e** (0.02 mmol, 12 mg), Eosin Y (65 μL, 4 mg/mL in 0.05 mol/L Na_2CO_3 aqueous solution), and 1 mL aqueous solution of Na_2CO_3 (0.05 mmol/L). **15e** was obtained following reverse phase preparative HPLC for purification as a white solid (7.6 mg, 56%). **Reverse phase preparative HPLC details**: Column type: Dubhe C18, 250 x10 mm, 10 μm. Temperature = 25°C. Flow rate = 3 mL/min. Solvents used for the eluents are MeCN and water, both with 0.1% TFA. The eluent was kept constant at 5% MeCN for 15 min, then raised from 5% MeCN to 10% MeCN for 10 min, and from 10% MeCN to 90% MeCN for 80 min. The product was generally eluted from 25.3 min to 28.7 min. **^{1}H NMR (600 MHz, D_2O)** δ 5.45 (d, *J* = 5.5 Hz, 1H), 4.59 (dd, *J* = 7.9, 4.6 Hz, 1H), 4.40 (d, *J* = 5.0 Hz, 1H), 4.23 – 4.19 (m, 2H), 3.99 – 3.94 (m, 5H), 3.84 – 3.77 (m, 3H), 3.53 (t, *J* = 9.5 Hz, 1H), 3.43 (t, *J* = 9.5 Hz, 1H), 3.16 – 3.07 (m, 2H), 2.06 (s, 3H), 1.92 – 1.86 (m, 1H), 1.54 – 1.47 (m, 1H), 1.24 – 1.18 (m, 4H), 0.94 (d, *J* = 6.9 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (151 MHz, D_2O)** δ 174.97, 173.83, 172.00, 171.96, 170.87, 87.20, 73.64, 72.53, 71.11, 69.57, 67.13, 60.45, 58.99, 58.64, 54.15, 42.65, 42.43, 36.10, 32.80, 24.67, 21.79, 18.90, 14.79, 10.18. **HRMS (DART-TOF)** calculated for $C_{25}H_{43}N_5NaO_{13}S^+$ $[M+H]^+$ m/z 676.2470, found 676.2473.



15f

The glycosyl donor **13** (0.0165 mmol, 4.7 mg), disulfide **14f** (0.013 mmol, 11.3 mg), $Ir[dF(CF_3)(ppy)_2(dtbbpy)]PF_6$ (1.5 mol %, 0.2 mg), and 0.65 mL DMSO were added to a reaction vial under N_2. The vial was irradiated with blue light for 2 h. The reaction mixture was directly subjected to the preparative RP-HPLC for purification to afford a white solid (4.0 mg, 36%). **Reverse phase HPLC details**: Column type: Dubhe C18, 250 x10 mm, 10 μm. Temperature = 25°C. Flow rate = 3 mL/min. Solvents used for the eluents are MeCN and water, both with 0.1% TFA. The eluent was kept constant at 5% MeCN for 15 min, then raised from 5% MeCN to 10% MeCN for 10 min, and from 10% MeCN to 90% MeCN for 80 min. The product was generally eluted from 36.3 min to 37.7 min. **^{1}H NMR (800 MHz, D_2O)** δ 7.40 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 2H), 4.94 (d, *J* = 5.7 Hz, 1H), 4.72 (t, *J* = 7.3 Hz, 1H), 4.63 (t, *J* = 7.8 Hz, 1H), 4.46 (t, *J* = 6.2 Hz, 1H), 4.35 (dd, *J* = 16.8, 5.5 Hz, 1H), 4.22 (d, *J* = 15.1 Hz, 1H), 3.85 (d, *J* = 11.8 Hz, 1H), 3.82 – 3.75 (m, 3H), 3.50 (d, *J* = 15.1 Hz, 1H), 3.45 – 3.40 (m, 2H), 3.23 (dt, *J* = 14.0, 6.9 Hz, 1H), 3.17 (dt, *J* = 13.9, 7.1 Hz, 1H), 3.06 (dt, *J* = 13.4, 6.9 Hz, 2H), 3.00 (dd, *J* = 13.6, 9.3 Hz, 1H), 2.92 (dd, *J* = 16.9, 8.0 Hz, 1H), 2.73 (dd, *J* = 16.8, 6.6 Hz, 1H), 2.68 (dd, *J* = 14.8, 4.8 Hz, 1H), 1.93 – 1.87 (m, 1H), 1.71 – 1.65 (m, 1H), 1.65 – 1.60 (m, 1H), 1.59 – 1.53 (m, 1H). **^{13}C NMR (201 MHz, D_2O)** δ 174.21, 172.73, 172.57, 172.16, 171.39, 171.22, 163.20, 163.02, 162.85, 162.67, 156.62, 136.14, 129.20, 128.79, 127.18, 118.45, 117.00, 115.55, 114.10, 87.55, 73.53, 72.98, 70.65, 69.24, 60.38, 55.42, 54.92, 52.81, 49.71, 43.23, 40.51, 36.74, 34.11, 32.95, 27.11, 24.62. **^{19}F NMR (376 MHz, D_2O)** δ -75.62. **HRMS (DART-TOF)** calculated for $C_{30}H_{45}N_8O_{12}S^+$ $[M\text{-}CF_3COO^-]^+$ m/z 741.2872, found 741.2876.

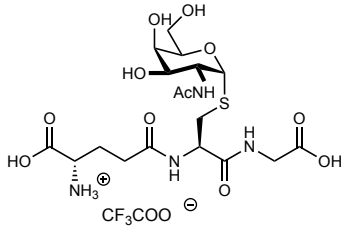


18a

18a was prepared following **General Procedure II** from the glycosyl donor **13** (0.05 mmol, 14.1 mg), disulfide **16** (0.05 mmol, 20.8 mg), Eosin Y (5 mol%, 1.6 mg), and 1 mL aqueous $NaHCO_3$ solution

(0.1 M). **18a** was obtained following reverse phase preparative HPLC for purification as a white solid (16.6 mg, 57%). **Reverse phase HPLC details**: Column type: Dubhe C18, 250 x10 mm, 10 µm. Temperature = 25°C. Flow rate = 3 mL/min. Solvents used for the eluents are MeCN and water, both with 0.1% TFA. The eluent was kept constant at 1% MeCN for 20 min. The product generally eluted from 6.9 min to 8.4 min.

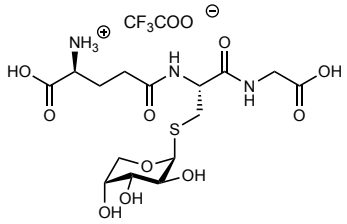
^{1}H NMR (400 MHz, D_2O) δ 5.50 (d, *J* = 5.5 Hz, 1H), 4.64 (dd, *J* = 8.3, 5.1 Hz, 1H), 4.04 – 3.94 (m, 4H), 3.87 – 3.77 (m, 3H), 3.55 (t, *J* = 9.4 Hz, 1H), 3.44 (t, *J* = 9.3 Hz, 1H), 3.16 – 3.04 (m, 2H), 2.64 – 2.54 (m, 2H), 2.27 – 2.19 (m, 2H). **^{13}C NMR (101 MHz, D_2O)** δ 174.42, 172.94, 172.69, 172.21, 87.10, 73.47, 72.53, 70.91, 69.36, 60.28, 53.92, 52.72, 41.12, 32.44, 30.99, 25.63. **^{19}F NMR (376 MHz, D_2O)** δ -75.61. **HRMS (DART-TOF)** calculated for $C_{16}H_{27}N_3NaO_{11}S^+$ $[M\text{-}CF_3COOH+Na]^+$ m/z 492.1259, found 492.1259.



18b

18b was prepared following **General Procedure II** from the glycosyl donor **17b** (0.022 mmol, 7.1 mg), disulfide **16** (0.02 mmol, 8.3 mg), Eosin Y (2 mol%, 0.3 mg), and 1 mL aqueous $NaHCO_3$ solution (0.1 M). **18b** was obtained following reverse phase preparative HPLC for purification as a white solid (7.1 mg, 57%). **Reverse phase HPLC details**: Column type: Dubhe C18, 250 x10 mm, 10 µm. Temperature = 25°C. Flow rate = 3 mL/min. Solvents used for the eluents are MeCN and water, both with 0.1% TFA. The eluent was kept constant at 1% MeCN for 20 min. The product generally eluted from 3.8 min to 4.9 min.

^{1}H NMR (400 MHz, D_2O) δ 5.58 (d, *J* = 5.5 Hz, 1H), 4.66 (d, *J* = 7.1 Hz, 5.7Hz, 1H), 4.36 (dd, *J* = 11.4, 5.5 Hz, 1H), 4.27 (t, *J* = 6.1 Hz, 1H), 4.06 – 3.98 (m, 4H), 3.83 (dd, *J* = 11.4, 3.2 Hz, 1H), 3.79 (d, *J* = 6.2 Hz, 2H), 3.14 – 3.01 (m, 2H), 2.58 (td, *J* = 7.4, 3.5 Hz, 2H), 2.26 – 2.19 (m, 2H), 2.03 (s, 3H). **^{13}C NMR (101 MHz, D_2O)** δ 174.55, 174.31, 172.88, 172.49, 172.11, 114.85, 111.95, 84.97, 71.78, 68.36, 67.40, 61.10, 53.83, 52.63, 50.04, 41.07, 32.07, 30.95, 25.51, 21.87. **^{19}F NMR (376 MHz, D_2O)** δ -75.61. **HRMS (DART-TOF)** calculated for $C_{18}H_{30}N_4NaO_{11}S^+$ $[M\text{-}CF_3COOH+Na]^+$ m/z 533.1524, found 533.1553.



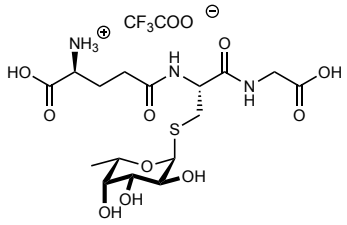
18c

18c was prepared following **General Procedure II** from the glycosyl donor **17c** (0.011 mmol, 2.7 mg), disulfide **16** (0.01 mmol, 4.2 mg), Eosin Y (3 mol%, 0.2 mg), and 0.5 mL aqueous $NaHCO_3$ solution (0.1 M). **18c** was obtained following reverse phase preparative HPLC for purification as a white solid (3.6 mg, 65%). **Reverse phase HPLC details**: Column type: Dubhe C18, 250 x10 mm, 10 µm. Temperature = 25°C. Flow rate = 3 mL/min. Solvents used for the eluents are MeCN and water, both with 0.1% TFA. The eluent was kept constant at 1% MeCN for 20 min. The product generally eluted from 5.1 min to 9.2 min.

^{1}H NMR (400 MHz, D_2O) δ 5.38 (d, *J* = 4.8 Hz, 1H), 4.64 (dd, *J* = 8.7, 5.2 Hz, 1H), 4.13 (dd, *J* = 12.6, 2.1 Hz, 1H), 4.09 (dd, *J* = 9.2, 4.7 Hz, 1H), 4.04 – 3,98 (m, 4H), 3.77 (dd, *J* = 9.1, 3.4 Hz, 1H), 3.69 (dd, *J* = 12.6, 3.7 Hz, 1H), 3.16 (dd, *J* = 14.1, 5.3 Hz, 1H), 2.91 (dd, *J* = 14.1, 8.8 Hz, 1H), 2.63 – 2.54 (m, 2H), 2.27 – 2.18 (m, 2H).

^{13}C NMR (101 MHz, D_2O) δ 174.45, 172.94, 172.60, 172.29, 163.15, 162.79, 117.76, 114.86, 85.53, 69.45, 68.52, 67.76, 63.80, 52.98, 52.76, 41.14, 31.31, 30.99, 25.62.

^{19}F NMR (376 MHz, D_2O) δ -75.61.



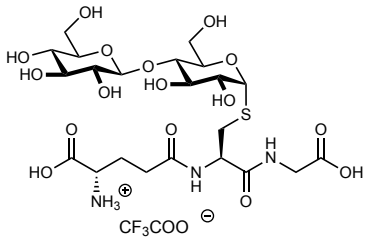
18d

18d was prepared following **General Procedure II** from the glycosyl donor **17d** (0.022 mmol, 5.8 mg), disulfide **16** (0.02 mmol, 8.3 mg), Eosin Y (2.5 mol%, 0.3 mg), and 1 mL aqueous $NaHCO_3$ solution (0.1 M). **18d** was obtained following reverse phase preparative HPLC for purification as a white solid (6.9 mg, 61%). **Reverse phase HPLC details**: Column type: Dubhe C18, 250 x10 mm, 10 µm. Temperature = 25°C. Flow rate = 3 mL/min. Solvents used for the eluents are MeCN and water, both with 0.1% TFA. The eluent was kept constant at 1% MeCN for 20 min. The product generally eluted from 5.2min to 6.6 min.

^{1}H NMR (400 MHz, D_2O) δ 5.44 (d, *J* = 5.7 Hz, 1H), 4.65 (dd, *J* = 8.6, 5.1 Hz, 1H), 4.32 (q, *J* = 6.6 Hz, 1H), 4.11–4.05 (m, 2H), 4.02 (s, 2H), 3.81 (d, *J* = 3.4 Hz, 1H), 3.74 (dd, *J* = 10.3, 3.4 Hz, 1H), 3.10 (dd, *J* = 14.0, 5.1 Hz, 1H), 2.89 (dd, *J* = 14.0, 8.6 Hz, 1H), 2.68 – 2.53 (m, *J* = 8.1 Hz, 2H), 2.32 – 2.18 (m, 2H), 1.24 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, D_2O) δ 174.77, 173.30, 172.64, 85.33, 71.66, 70.27, 67.64, 67.59, 53.64, 52.86, 41.44, 31.25, 30.95, 25.98, 15.42.

^{19}F NMR (376 MHz, D_2O) δ -75.61.



18e

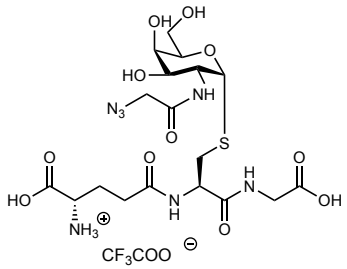
18e was prepared following **General Procedure II** from the glycosyl donor **17e** (0.05 mmol, 22.2 mg), disulfide **16** (0.05 mmol, 20.8 mg), Eosin Y (5 mol%, 1.7 mg), and 1 mL aqueous $NaHCO_3$ solution (0.1 M). **18e** was obtained following reverse phase preparative HPLC for purification as a white solid (18.2 mg, 49%). **Reverse phase HPLC details**: Column type: Dubhe C18, 250 x10 mm, 10 µm. Temperature = 25°C. Flow rate = 3 mL/min. Solvents used for the eluents are MeCN and water, both with 0.1% TFA. The eluent was kept constant at 1% MeCN for 20 min. The product generally eluted from 4.3 min to 6.3 min.

^{1}H NMR (600 MHz, D_2O) δ 5.46 (d, *J* = 5.5 Hz, 1H), 4.58 (dd, *J* = 9.2, 4.5 Hz, 1H), 4.46 (d, *J* = 7.9 Hz, 1H), 4.05 – 4.03 (m, 1H), 3.90 – 3.80 (m, 5H), 3.75 – 3.72 (m, 2H), 3.69 (dd, *J* = 12.4, 5.8 Hz, 1H), 3.65 – 3.60 (m, 3H), 3.48 – 3.43 (m, 2H), 3.38 (t, *J* = 9.5 Hz, 1H), 3.28 (t, *J* = 8.6 Hz, 1H), 3.11 (dd, *J* = 14.5, 4.5 Hz, 1H), 3.03 (dd, *J* = 14.4, 9.2 Hz, 1H), 2.52 – 2.42 (m, 2H), 2.10 – 2.04 (m, 2H).

^{13}C NMR (151 MHz, D_2O) δ 176.30, 175.76, 175.30, 171.88, 163.35, 163.12, 162.88, 162.65, 119.37, 117.44, 115.51, 113.57, 102.69, 87.14, 78.78, 76.09, 75.65, 73.25, 72.18, 71.41, 70.87, 69.60, 60.74, 59.86, 54.55, 54.18, 43.52, 32.89, 31.81, 27.33.

^{19}F NMR (376 MHz, D_2O) δ -75.60.

HRMS (DART-TOF) calculated for $C_{22}H_{37}N_3NaO_{16}S^+$ $[M\text{-}CF_3COOH+Na]^+$ m/z 654.1787, found 654.1791.



18f

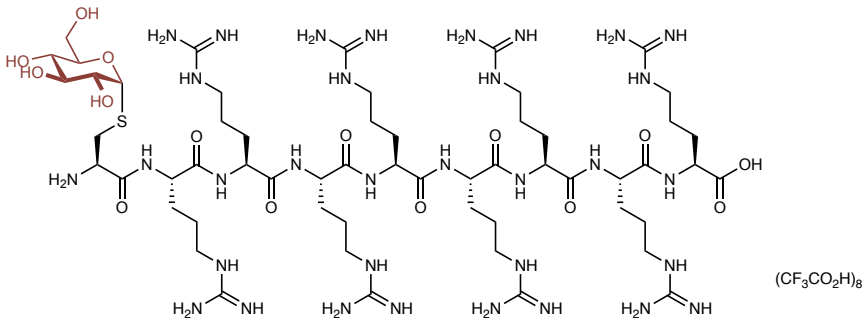
18f was prepared following **General Procedure III** from the Cys-containing peptide (0.02 mmol, 6.1 mg), the glycosyl donor **17f** (0.02 mmol, 7.6 mg), 2-methylisothiazolo[5,4-b]pyridin-3(*2H*)-one (0.02 mmol, 3.3 mg), Eosin Y (0.3 mg, 2 mol%), and 1 mL $NaHCO_3$ solution (0.1 M in water). **18f** was obtained following reverse phase preparative HPLC for purification as a white solid (4.5 mg, 34%). **Reverse phase HPLC details**: Column type: Dubhe C18, 250 x10 mm, 10 μm. Temperature = 25°C. Flow rate = 3 mL/min. Solvents used for the eluents are MeCN and water, both with 0.1% TFA. The eluent was kept constant at 1% MeCN for 20 min. The product generally eluted from 6.1 min to 6.5 min.

^{1}H NMR (800 MHz, Deuterium Oxide) δ 5.60 (d, *J* = 5.7 Hz, 1H), 4.66 (t, *J* = 6.4 Hz, 1H), 4.41 (dd, *J* = 11.5, 5.5 Hz, 1H), 4.28 (t, *J* = 6.3 Hz, 1H), 4.09 – 4.00 (m, 6H), 3.87 (dd, *J* = 11.7, 3.0 Hz, 1H), 3.81 – 3.75 (m, 2H), 3.11 – 3.04 (m, 2H), 2.62 – 2.53 (m, 2H), 2.26 – 2.18 (m, *J* = 7.2 Hz, 2H).

^{13}C NMR (201 MHz, D_2O) δ 174.29, 172.86, 172.43, 172.08, 170.83, 163.05, 162.88, 117.01, 115.56, 84.76, 71.83, 68.36, 67.28, 61.08, 53.77, 52.61, 51.69, 50.16, 48.82, 41.06, 32.03, 30.94, 25.49.

^{19}F NMR (376 MHz, D_2O) δ -75.61.

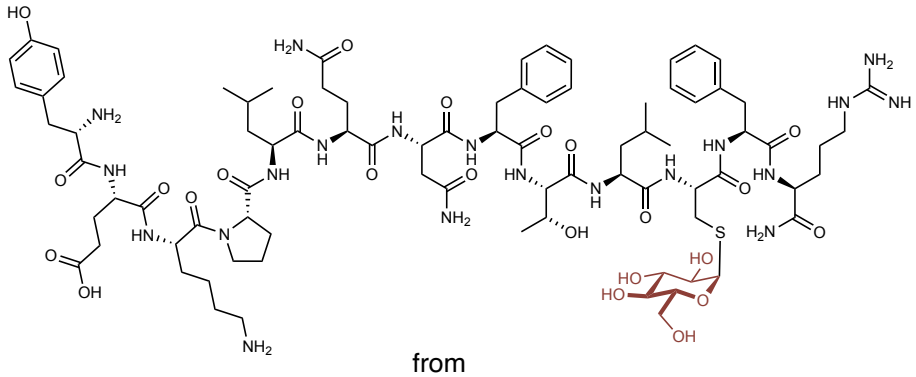
8. Synthesis and Characterization Data for Products in Fig. 3



23

23 was prepared following **General Procedure III** from the Cys-containing peptide (0.005 mmol, 11.4 mg), the glycosyl donor **13** (0.015 mmol, 4.2 mg), **20** (0.015 mmol, 2.9 mg), Eosin Y (25 μL, 4 mg/mL in DMSO), and 1 mL H_2O. **23** was obtained following reverse phase preparative HPLC for purification as a white solid (7.2 mg, 59%). **Reverse phase HPLC details**: Column type: Dubhe C18, 250 x10 mm, 10 μm. Temperature = 25 °C. Flow rate = 3 mL/min. Solvents used for the eluents are MeCN and water, both with 0.1% TFA. The eluent was kept constant at 5% MeCN for 15 min, then raised from 5% MeCN to 10% MeCN for 10 min, and from 10% MeCN to 90% MeCN for 80 min. The product was generally eluted from 27.9 min to 31.9 min.

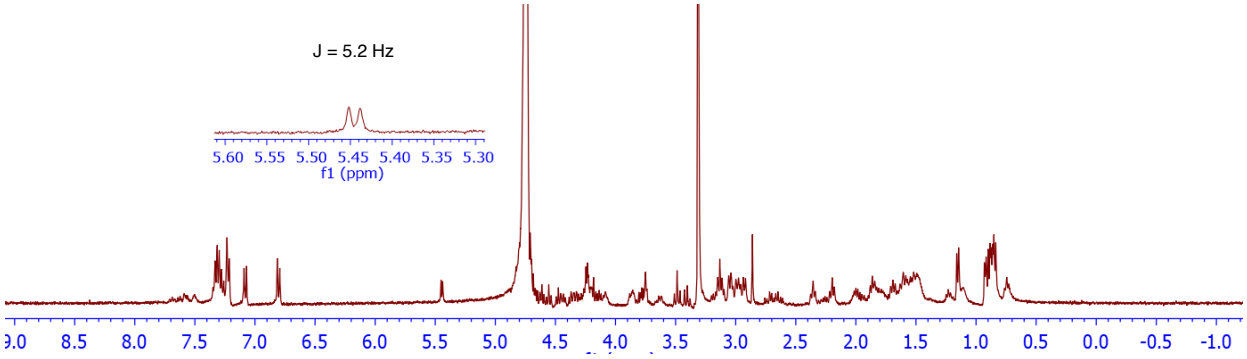
^{1}H NMR (800 MHz, D_2O) δ 5.47 (d, *J* = 5.5 Hz, 1H), 4.40 (t, *J* = 7.2 Hz, 1H), 4.34 – 4.32 (m, 7H), 4.22 (t, *J* = 6.5 Hz, 1H), 3.97 (t, *J* = 8.3 Hz, 1H), 3.93 – 3.90 (m, 1H), 3.87 (dd, *J* = 10.1, 5.5 Hz, 1H), 3.77 (dd, *J* = 12.5, 6.4 Hz, 1H), 3.53 (t, *J* = 9.6 Hz, 1H), 3.41 (t, *J* = 9.6 Hz, 1H), 3.25 (dd, *J* = 14.9, 6.1 Hz, 1H), 3.22 – 3.18 (m, 16H), 3.16 (dd, *J* = 15.0, 5.7 Hz, 1H), 1.87 – 1.74 (m, 16H), 1.68 – 1.61 (m, 16H). **^{13}C NMR (201 MHz, D_2O)** δ 177.01, 173.23, 173.22, 173.20, 173.18, 172.80, 172.78, 167.98, 163.19, 163.02, 162.84, 162.66, 156.69, 156.68, 118.49, 117.04, 115.59, 114.14, 86.16, 73.46, 72.98, 70.78, 69.52, 60.56, 54.04, 53.45, 53.40, 53.30, 53.19, 53.16, 53.11, 52.40, 40.55, 40.50, 31.26, 28.34, 28.27, 28.25, 28.22, 28.12, 24.49, 24.42, 24.40, 24.37, 24.31, 24.27. **^{19}F NMR (376 MHz, D_2O)** δ -75.57.



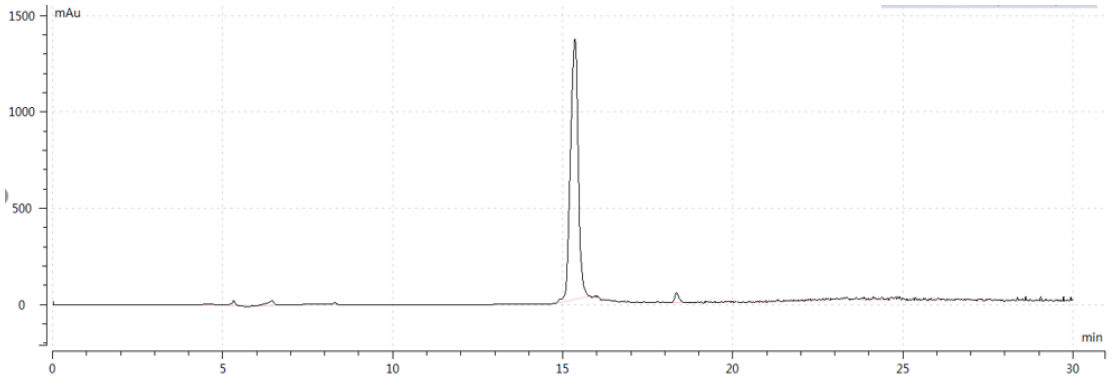
from
Tyr-amyloid P component (27-38)
24

24 was prepared following **General Procedure III** from the from the Cys-containing peptide (0.0025 mmol, 4.1 mg), the glycosyl donor **13** (0.01 mmol, 2.8 mg), **20** (0.01mmol, 1.9 mg), Eosin Y (25 µL, 4 mg/mL DMSO), and 0.5 mL H_2O. **24** was obtained following reverse phase preparative HPLC for purification as a white solid (2.5 mg, 55%). **Reverse phase HPLC details**: Column type: Dubhe C18, 250 x10 mm, 10 µm. Temperature = 25 °C. Flow rate = 3 mL/min. Solvents used for the eluents are MeCN and water, both with 0.1% TFA. The eluent was kept constant at 5% MeCN for 3 min, then raised from 5% MeCN to 10% MeCN for 2 min, and from 10% MeCN to 90% MeCN for 55 min. The product was generally eluted from 31.4 min to 32.1 min.

^{1}H NMR: 400 MHz, D_2O



HPLC Trace:

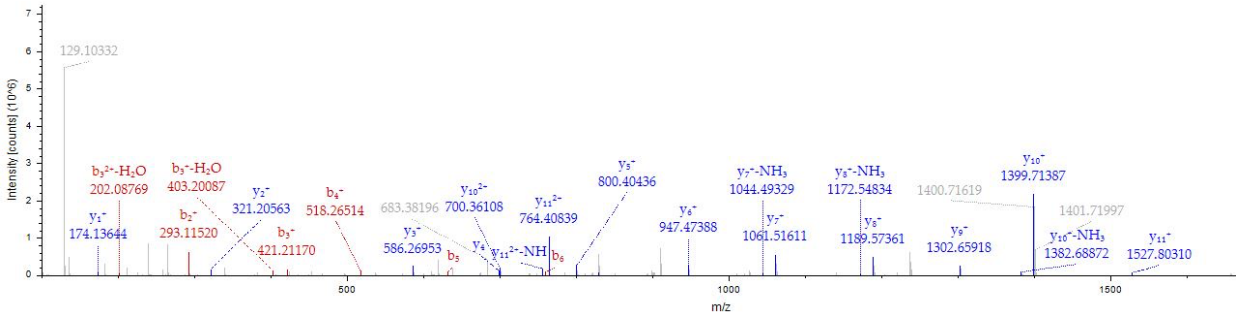


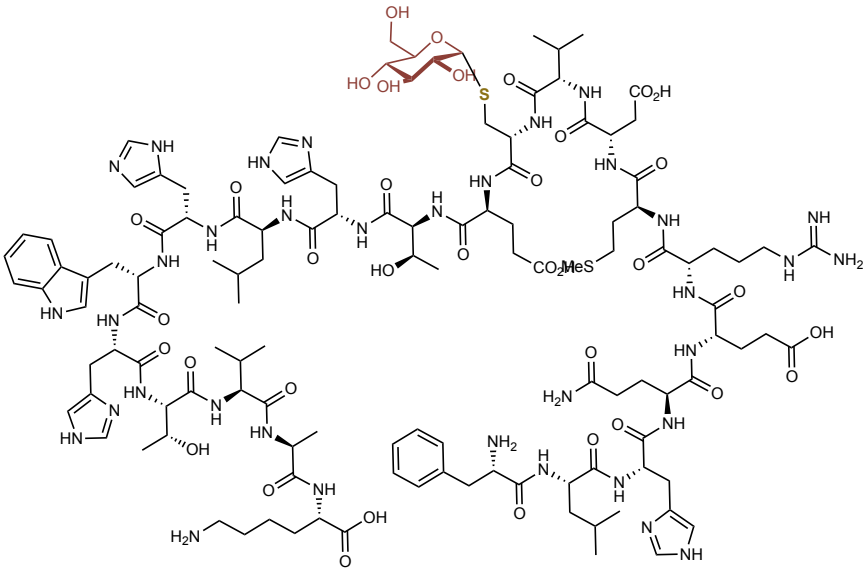
Theoretical Mass: YEKPLQNFTLC(Glu)FR-NH_2

Ion Series | Neutral Losses | Precursor Ions | Internal Fragments

#1	b^+	b^{2+}	Seq.	y^+	y^{2+}	#2
1	164.07061	82.53894	Y			13
2	293.11320	147.06024	E	1656.84140	828.92434	12
3	421.20816	211.10772	K	1527.79880	764.40304	11
4	518.26092	259.63410	P	1399.70384	700.35556	10
5	631.34499	316.17613	L	1302.65108	651.82918	9
6	759.40357	380.20542	Q	1189.56701	595.28714	8
7	873.44649	437.22689	N	1061.50843	531.25786	7
8	1020.51491	510.76109	F	947.46551	474.23639	6
9	1121.56259	561.28493	T	800.39709	400.70218	5
10	1234.64665	617.82696	L	699.34941	350.17835	4
11	1499.70863	750.35796	C-21-B	586.26535	293.63631	3
12	1646.77705	823.89216	F	321.20337	161.10532	2
13			R-R-13	174.13495	87.57111	1

Observed Mass:

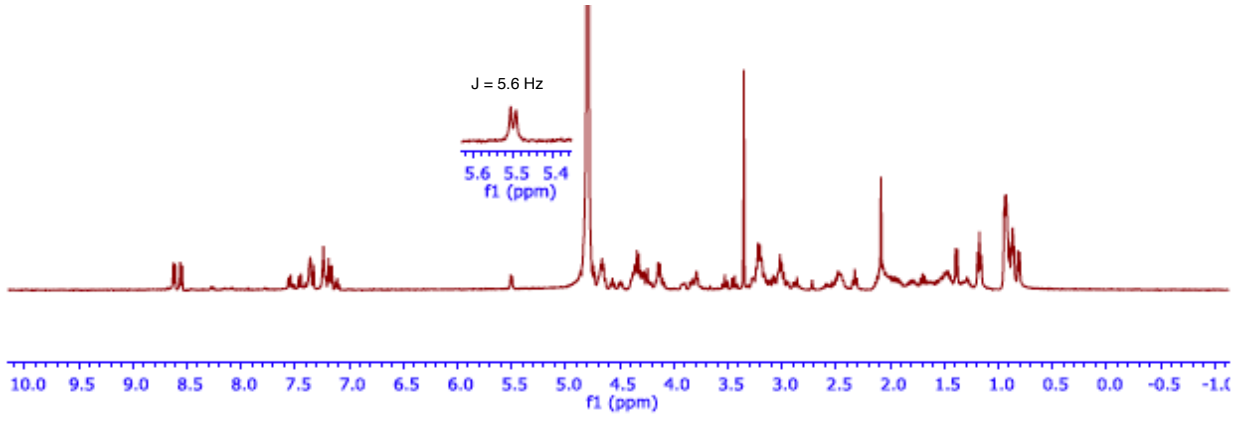




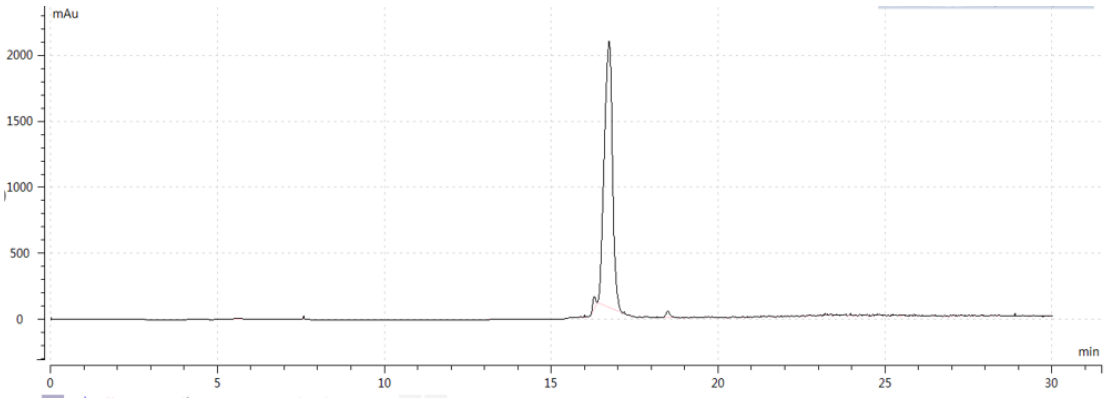
25

25 was prepared following **General Procedure III** from the Cys-containing peptide (0.0038 mmol, 10.0 mg), glycosyl donor **13** (0.015 mmol, 4.3 mg), **20** (0.015 mmol, 3.0 mg), Eosin Y (38 µL, 4 mg/mL DMSO), and 760 µL H_2O. **25** was obtained following reverse phase preparative HPLC for purification as a white solid (6.6 mg, 62%). **Reverse phase HPLC details**: Column type: Dubhe C18, 250 x10 mm, 10 µm. Temperature = 25 °C. Flow rate = 3 mL/min. Solvents used for the eluents are MeCN and water, both with 0.1% TFA. The eluent was kept constant at 5% MeCN for 15 min, then raised from 5% MeCN to 10% MeCN for 10 min, and from 10% MeCN to 90% MeCN for 80 min. The product was generally eluted from 43.1 min to 45.2 min.

^{1}H NMR: 400 MHz, D_2O



HPLC Trace:

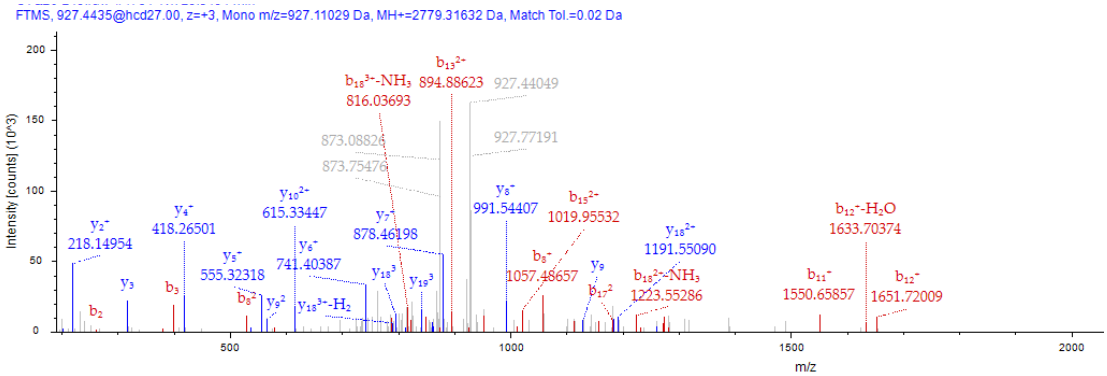


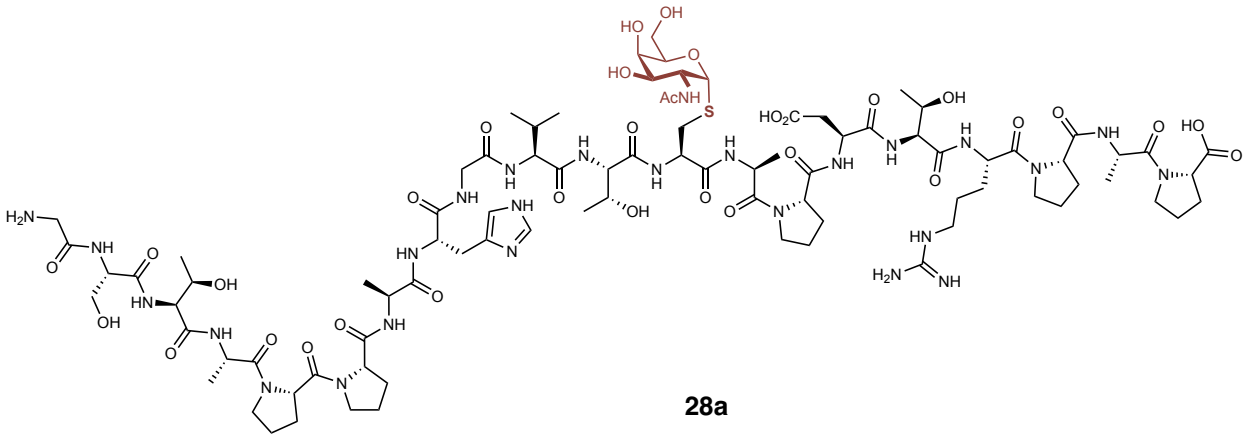
Theoretical Mass: FLHQERMDVC(Glu)ETHLHWHTVAK

Ion Series | Neutral Losses | Precursor Ions | Internal Fragments

#1	b^{+}	b^{2+}	b^{3+}	Seq.	y^{+}	y^{2+}	y^{3+}	#2
1	148.07569	74.54148	50.03008	F				21
2	261.15975	131.08352	87.72477	L	2632.23948	1316.62338	878.08468	20
3	398.21867	199.61297	133.41107	H	2519.15541	1260.08134	840.38999	19
4	526.27724	263.64226	176.09727	Q	2382.09650	1191.55189	794.70368	18
5	655.31984	328.16356	219.11146	E	2254.03792	1127.52260	752.01749	17
6	811.42095	406.21411	271.14517	R	2124.99533	1063.00130	709.00329	16
7	942.46143	471.73435	314.82533	M	1968.89422	984.95075	656.96959	15
8	1057.48838	529.24783	353.16764	D	1837.85374	919.43051	613.28943	14
9	1156.55679	578.78203	386.19045	V	1722.82679	861.91703	574.94712	13
10	1421.61877	711.31303	474.54444	C-21-B	1623.75838	812.38283	541.92431	12
11	1550.66137	775.83432	517.55864	E	1358.69639	679.85184	453.57032	11
12	1651.70904	826.35816	551.24120	T	1229.65380	615.33054	410.55612	10
13	1788.76796	894.88762	596.92750	H	1128.60612	564.80670	376.87356	9
14	1901.85202	951.42965	634.62219	L	991.54721	496.27724	331.18725	8
15	2038.91093	1019.95910	680.30850	H	878.46315	439.73521	293.49257	7
16	2224.99025	1112.99876	742.33493	W	741.40423	371.20576	247.80626	6
17	2362.04916	1181.52822	788.02124	H	555.32492	278.16610	185.77983	5
18	2463.09684	1232.05206	821.70380	T	418.26601	209.63664	140.09352	4
19	2562.16525	1281.58626	854.72660	V	317.21833	159.11280	106.41096	3
20	2633.20236	1317.10482	878.40564	A	218.14992	109.57860	73.38816	2
21				K	147.11280	74.06004	49.70912	1

Observed Mass

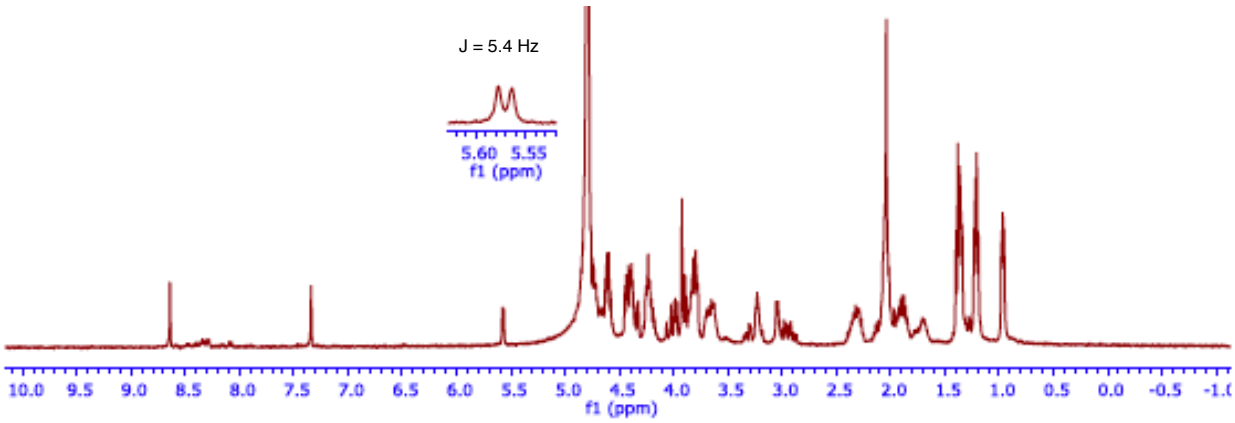




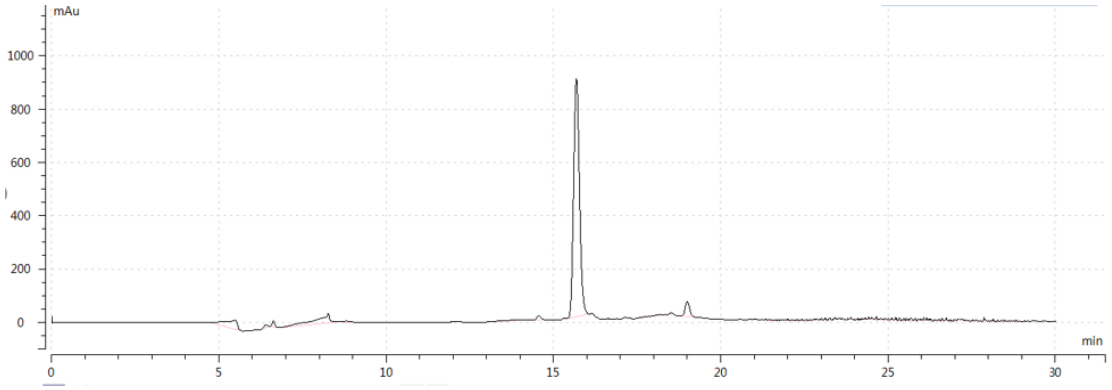
28a

28a was prepared following **General Procedure III** from the Cys-containing peptide (0.005 mmol, 9.5 mg), glycosyl donor **17b** (0.02 mmol, 6.5 mg), **20** (0.02 mmol, 3.9 mg), Eosin Y (48 µL, 4 mg/mL in DMSO), and 1 mL H_2O. **28a** was obtained following reverse phase preparative HPLC for purification as a white solid (5.6 mg, 53%). **Reverse phase HPLC details**: Column type: Dubhe C18, 250 x10 mm, 10 µm. Temperature = 25°C. Flow rate = 3 mL/min. Solvents used for the eluents are MeCN and water, both with 0.1% TFA. The eluent was kept constant at 5% MeCN for 15 min, then raised from 5% MeCN to 10% MeCN for 10 min, and from 10% MeCN to 90% MeCN for 80 min. The product was generally eluted from 37.0 min to 38.2 min.

^{1}H NMR: 400 MHz, D_2O



HPLC Trace:

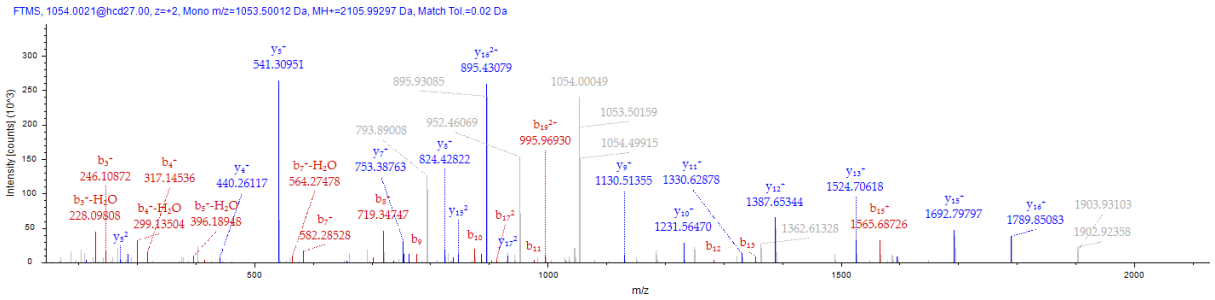


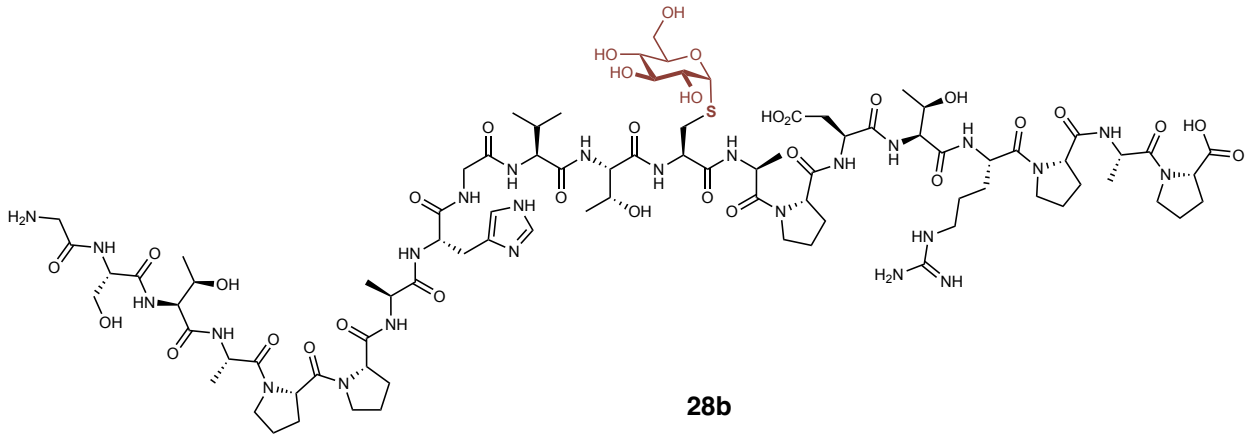
Theoretical Mass: GSTAPPAHGVTC(GalNac)APDTRPAP

Ion Series | Neutral Losses | Precursor Ions | Internal Fragments

#1	b⁺	b²⁺	Seq.	y⁺	y²⁺	#2
1	58.02874	29.51801	G			20
2	145.06077	73.03402	S	2048.97061	1024.98894	19
3	246.10845	123.55786	T	1961.93858	981.47293	18
4	317.14556	159.07642	A	1860.89090	930.94909	17
5	414.19832	207.60280	P	1789.85379	895.43053	16
6	511.25109	256.12918	P	1692.80102	846.90415	15
7	582.28820	291.64774	A	1595.74826	798.37777	14
8	719.34711	360.17720	H	1524.71114	762.85921	13
9	776.36858	388.68793	G	1387.65223	694.32975	12
10	875.43699	438.22213	V	1330.63077	665.81902	11
11	976.48467	488.74597	T	1231.56236	616.28482	10
12	1282.57325	641.79027	C-20-3	1130.51468	565.76098	9
13	1353.61037	677.30882	A	824.42609	412.71668	8
14	1450.66313	725.83520	P	753.38898	377.19813	7
15	1565.69007	783.34868	D	656.33621	328.67175	6
16	1666.73775	833.87251	T	541.30927	271.15827	5
17	1822.83886	911.92307	R	440.26159	220.63444	4
18	1919.89163	960.44945	P	284.16048	142.58388	3
19	1990.92874	995.96801	A	187.10772	94.05750	2
20			P	116.07061	58.53894	1

Observed Mass

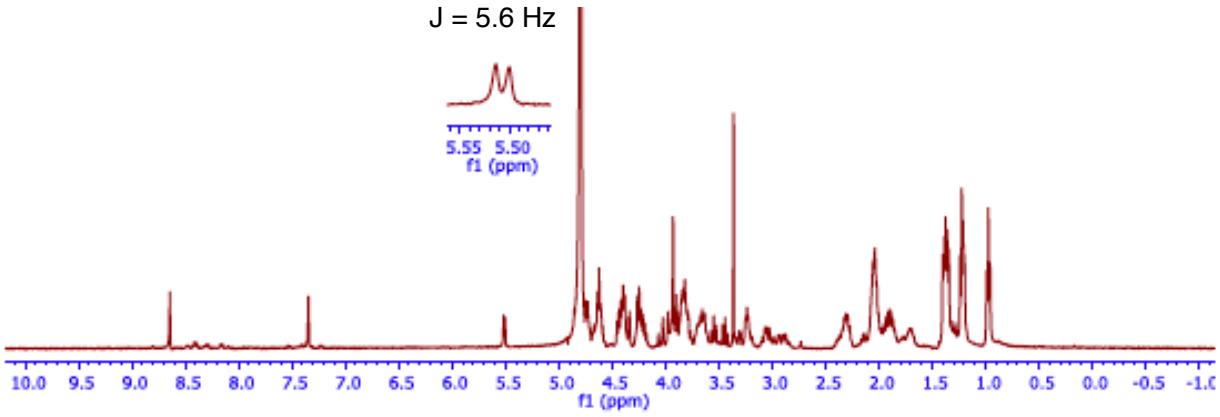




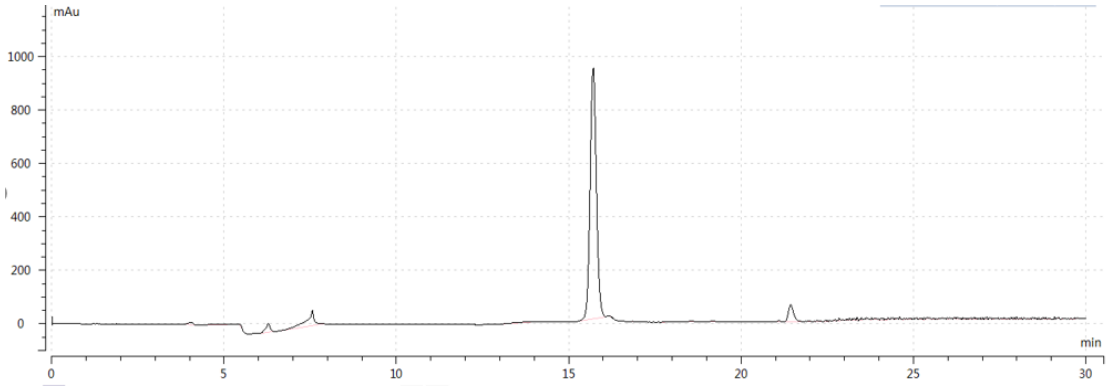
28b

28b was prepared following **General Procedure III** from the Cys-containing peptide (0.005 mmol, 9.5 mg), glycosyl donor **13** (0.02 mmol, 5.6 mg), **20** (0.02 mmol, 3.9 mg), Eosin Y (48 µL, 4 mg/mL in DMSO), and 1 mL H_2O. **28b** was obtained following reverse phase preparative HPLC for purification as a white solid (6.8 mg, 66%). **Reverse phase HPLC details**: Column type: Dubhe C18, 250 x10 mm, 10 µm. Temperature = 25 °C. Flow rate = 3 mL/min. Solvents used for the eluents are MeCN and water, both with 0.1% TFA. The eluent was kept constant at 5% MeCN for 15 min, then raised from 5% MeCN to 10% MeCN for 10 min, and from 10% MeCN to 90% MeCN for 80 min. The product was generally eluted from 36.0 min to 37.2 min.

^{1}H NMR: 400 MHz, D_2O



HPLC Trace:

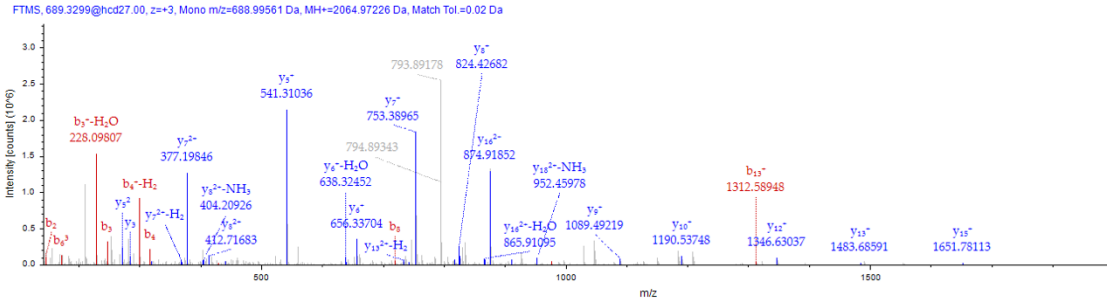


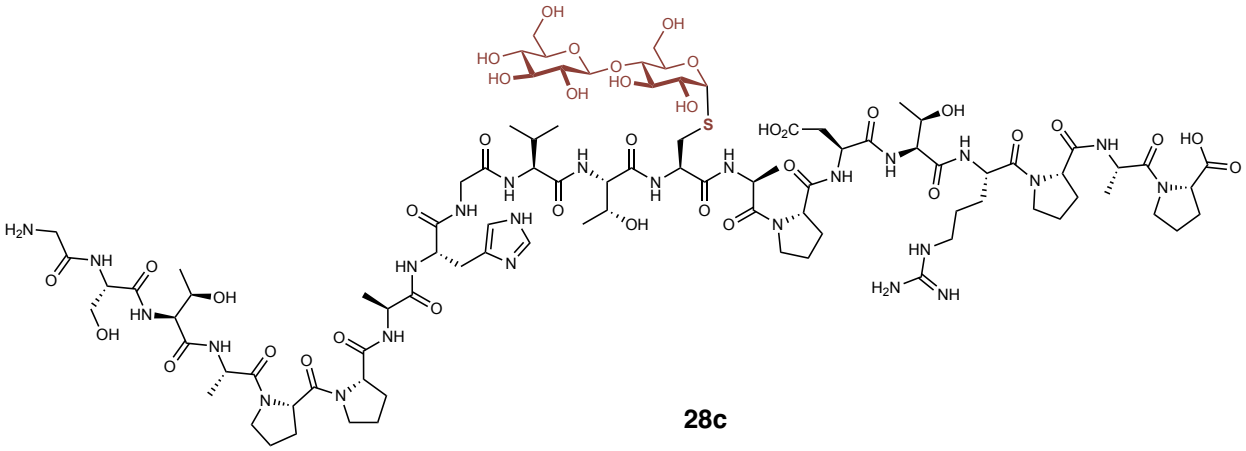
Theoretical Mass: GSTAPPAHGVTC(Glu)APDTRPAP

Ion Series | Neutral Losses | Precursor Ions | Internal Fragments

#1	b^+	b^{2+}	b^{3+}	Seq.	y^+	y^{2+}	y^{3+}	#2
1	58.02874	29.51801	20.01443	G				20
2	145.06077	73.03402	49.02511	S	2007.95181	1004.47954	669.98879	19
3	246.10845	123.55786	82.70767	T	1920.91978	960.96353	640.97811	18
4	317.14556	159.07642	106.38670	A	1819.87210	910.43969	607.29555	17
5	414.19832	207.60280	138.73763	P	1748.83499	874.92113	583.61651	16
6	511.25109	256.12918	171.08855	P	1651.78222	826.39475	551.26559	15
7	582.28820	291.64774	194.76759	A	1554.72946	777.86837	518.91467	14
8	719.34711	360.17720	240.45389	H	1483.69234	742.34981	495.23563	13
9	776.36858	388.68793	259.46104	G	1346.63343	673.82035	449.54933	12
10	875.43699	438.22213	292.48385	V	1289.61197	645.30962	430.54217	11
11	976.48467	488.74597	326.16641	T	1190.54356	595.77542	397.51937	10
12	1241.55445	621.28087	414.52300	C-20-2	1089.49588	545.25158	363.83681	9
13	1312.59157	656.79942	438.20204	A	824.42609	412.71668	275.48022	8
14	1409.64433	705.32580	470.55296	P	753.38898	377.19813	251.80118	7
15	1524.67127	762.83928	508.89528	D	656.33621	328.67175	219.45026	6
16	1625.71895	813.36311	542.57784	T	541.30927	271.15827	181.10794	5
17	1781.82006	891.41367	594.61154	R	440.26159	220.63444	147.42538	4
18	1878.87283	939.94005	626.96246	P	284.16048	142.58388	95.39168	3
19	1949.90994	975.45861	650.64150	A	187.10772	94.05750	63.04076	2
20				P	116.07061	58.53894	39.36172	1

Observed Mass

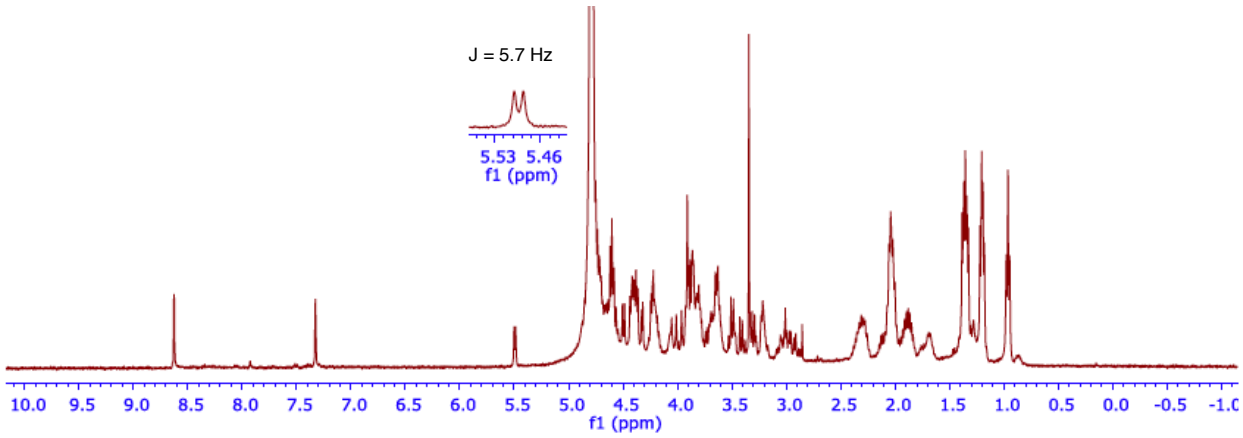




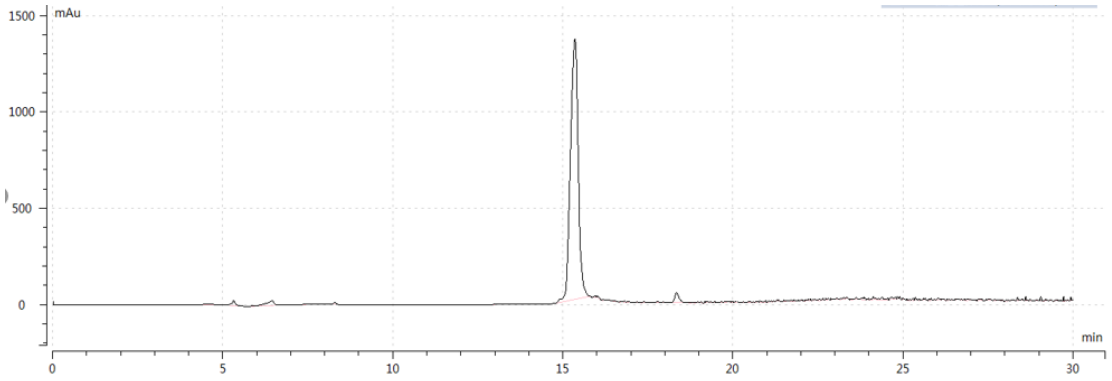
28c

28c was prepared following **General Procedure III** from the Cys-containing peptide (0.005 mmol, 9.5 mg), glycosyl donor **17e** (0.02 mmol, 8.9 mg), **20** (0.02 mmol, 3.9 mg), Eosin Y (48 µL, 4 mg/mL in DMSO), and 1 mL H_2O. **28c** was obtained following reverse phase preparative HPLC for purification as a white solid (6.1 mg, 55%). **Reverse phase HPLC details**: Column type: Dubhe C18, 250 x10 mm, 10 µm. Temperature = 25 °C. Flow rate = 3 mL/min. Solvents used for the eluents are MeCN and water, both with 0.1% TFA. The eluent was kept constant at 5% MeCN for 15 min, then raised from 5% MeCN to 10% MeCN for 10 min, and from 10% MeCN to 90% MeCN for 80 min. The product was generally eluted **from** 38.2 min to 40.0 min.

^{1}H NMR: 400 MHz, D_2O



HPLC Trace:

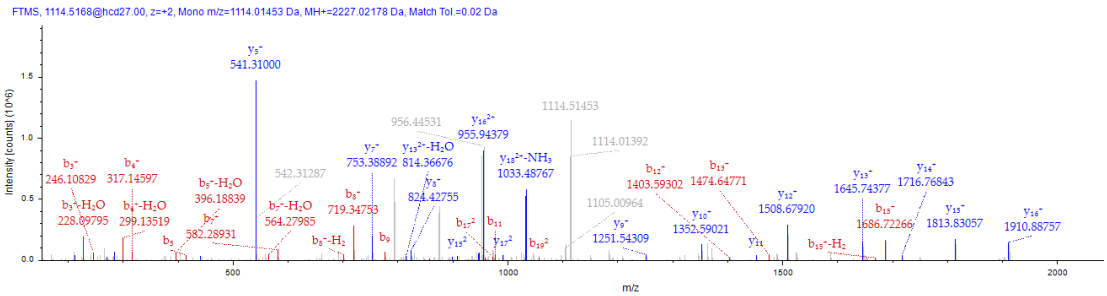


Theoretical Mass: GSTAPPAHGVTC(maltosyl)APDTRPAP

Ion Series | Neutral Losses | Precursor Ions | Internal Fragments

#1	b⁺	b²⁺	Seq.	y⁺	y²⁺	#2
1	58.02874	29.51801	G			20
2	145.06077	73.03402	S	2170.00471	1085.50599	19
3	246.10845	123.55786	T	2082.97268	1041.98998	18
4	317.14556	159.07642	A	1981.92500	991.46614	17
5	414.19832	207.60280	P	1910.88789	955.94758	16
6	511.25109	256.12918	P	1813.83512	907.42120	15
7	582.28820	291.64774	A	1716.78236	858.89482	14
8	719.34711	360.17720	H	1645.74524	823.37626	13
9	776.36858	388.68793	G	1508.68633	754.84680	12
10	875.43699	438.22213	V	1451.66487	726.33607	11
11	976.48467	488.74597	T	1352.59646	676.80187	10
12	1403.60735	702.30732	C-20-4	1251.54878	626.27803	9
13	1474.64447	737.82587	A	824.42609	412.71668	8
14	1571.69723	786.35225	P	753.38898	377.19813	7
15	1686.72417	843.86573	D	656.33621	328.67175	6
16	1787.77185	894.38956	T	541.30927	271.15827	5
17	1943.87296	972.44012	R	440.26159	220.63444	4
18	2040.92573	1020.96650	P	284.16048	142.58388	3
19	2111.96284	1056.48506	A	187.10772	94.05750	2
20			P	116.07061	58.53894	1

Observed Mass



9. Glycosylation of Affibody

9.1 Protein Expression and Purification

Cysteine mutations were introduced into affibody by site-directed mutagenesis using QuickChange Lightning Single Site-directed Mutagenesis Kit (Agilent) following manufacturer's instructions. *E. coli* BL21 (DE3) cells transformed with pBAD-affibody (D36C)-His_6 plasmid were grown in 1 L of LB medium containing ampicillin (50 μg/mL) at 37 °C until OD600 equaled to 0.6. Expression was induced by addition of 0.2% arabinose at 37 °C for 6 h. Harvested cell pellet was lysed by sonicating in 25 mL of 20 mM Tris and 300 mM NaCl (pH 7.4) buffer containing 0.25 mL of protease inhibitor cocktail (MedChemExpress, USA). The resulting suspension was centrifuged at 16,000 g for 50 min at 4 °C to remove cell debris. The supernatant was loaded onto columns containing 1 mL of HisPur Ni-NTA resin (Cube Biotech, Germany), washed with 40 mL of 20 mM Tris and 300 mM NaCl (pH 7.4), and then washed with 100 mL of 25 mM imidazole in 20 mM Tris and 300 mM NaCl (pH 7.4). The protein was eluted from the column with buffer containing 250 mM imidazole in 20 mM Tris and 300 mM NaCl (pH 7.4). Imidazole was removed from protein using an ultrafiltration centrifugation tube (Millipore, MWCO = 3 kDa, USA). The protein was analyzed by SDS-PAGE and LC/MS to confirm its purity. Protein aliquots were flash frozen and stored in a -80 °C freezer. The weight concentration of the protein was determined by NanoDrop to be ca. 1.67 mM.

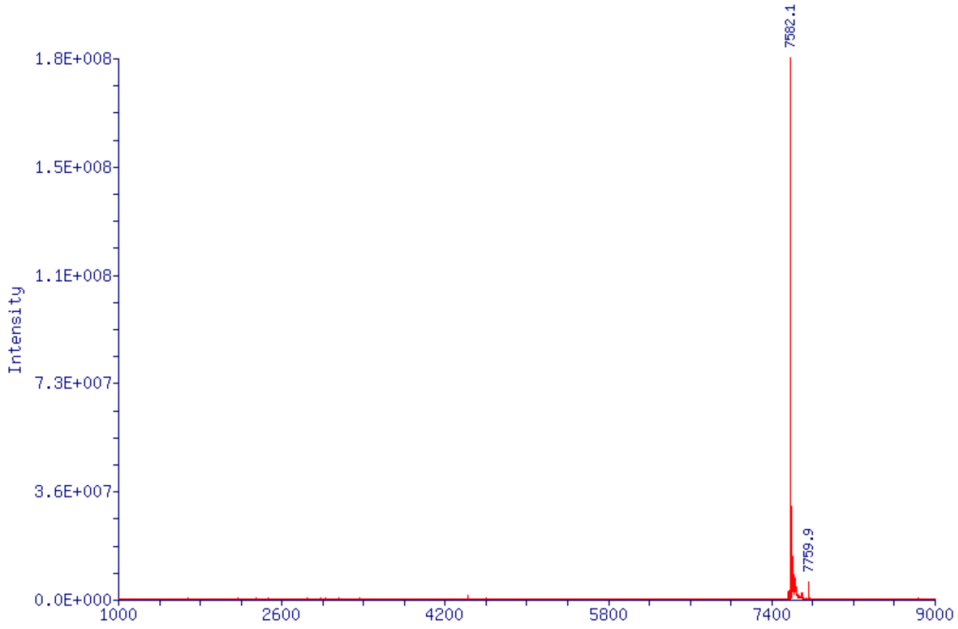
Sequence:

MTSVDNKFNKELSVAGREIVTLPNLNDPQKKAFIFSLWCDPSQSANLLAEAKKLNDAQA
PKGSHHHHHH

Calculated Mass: 7582.5 (-M).

Observed Mass Spectra:

Deconvoluted Mass:



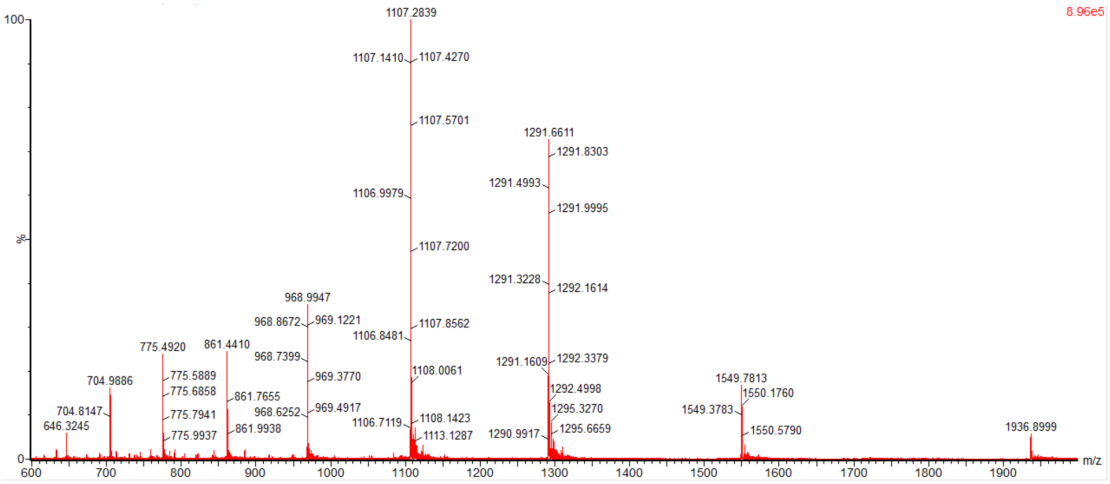
9.2 Protein Modification

A "glycosylation kit" was prepared by dissolving **21** (4.2 mg, 0.015 mmol), **28** (3.7 mg, 0.0225 mmol), and Eosin Y (25 μL, 4 mg/mL in DMSO) in 500 μL H_2O.

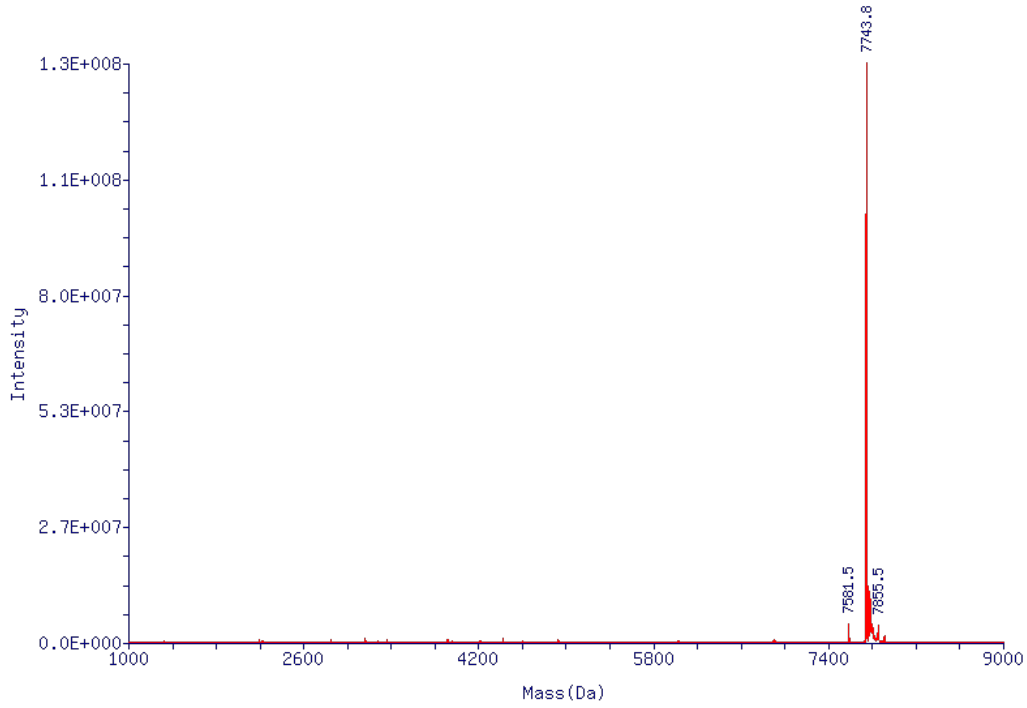
An aliquot of the affibody solution in pH 7.4 Tris buffer (2 μL, 1.67 mM) was added to 20 μL of the above stock solution in a 100 μL Eppendorf tube. The tube was then placed in a screw-capped 8 mL vial, and sealed. The vial was then placed in the photoreactor (Fig. S1), and irradiated with blue LED for 1 h. Without any further purification, the resulting solution was directly analyzed by LC/MS, which indicated full consumption of the protein starting material. LC-MS analysis was performed using Waters I-class equipped with a reverse-phase column (Aeris 3.6 μm WIDEPORE XB-C18 50×2.1 mm, phenomenex) for separation, and coupled to a XEVO G2-XS QTOF. The mobile phase A was 100/0.1% water/formic acid (v/v) and the mobile phase B was 100/0.1% methanol/formic acid (v/v). The LC gradient elution condition was initially 15% B for 0.5 min, from 15% to 60% B in 6.5 min, from 60% to 95% B in 3 min, then maintained at 95% B for 2.0 min, and followed by re-equilibration to starting conditions in 3.0 min, with a flow rate of 0.4 mL/min.

Fig. S7. Reaction setup for protein modification.

Observed Mass Spectra:



Deconvoluted Mass:



9.3 Protein Digestion and MS/MS Analysis

The reaction solution containing glycosylated protein was vacuum dried, and then dissolved in 50 mM ammonium bicarbonate. In-solution digestion was carried out overnight with trypsin in a 1:50 (w/w, trypsin/protein) ratio at 37 °C. Digestion was stopped by heating at 95 °C for 5 min. The resulting solution was subjected to MS/MS analysis following the protocol described in General Information. Glycosylation at cysteine was confirmed.

Peptide Fragments Identified: The green segment refers to the sequence of glycosylated affibody that is identified by mass spectrometry.

Sequence | Modification List

		1	11	21	31	41	51	61
Modifications	1		R		B			
P02769		TSVDNKFNKE	LSVAGREIVT	LPNLNDPQKK	AFIFSLWCDP	SQSANLLAEA	KKLNDAQAPK	GSHHHHHH

Peptide chain with glycosylated cysteine residue:

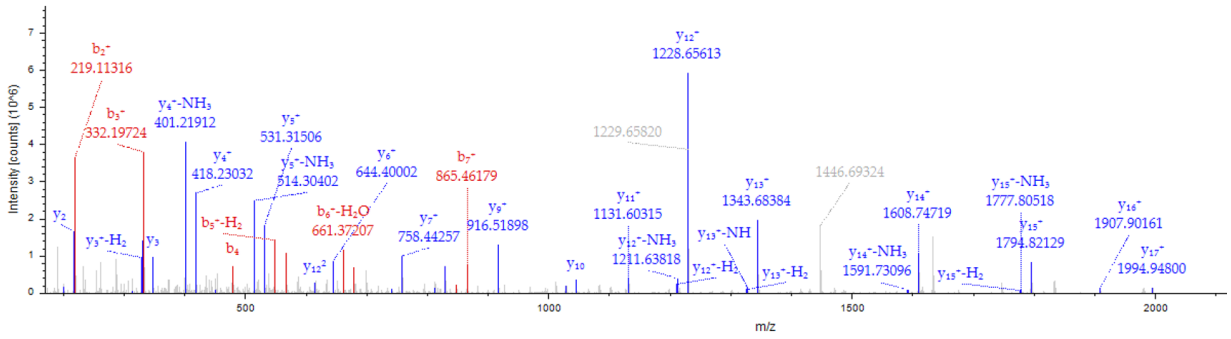
AFIFSLWC(Glu)DPSQSANLLAEAK

Calculated Mass:

Ion Series | Neutral Losses | Precursor Ions | Internal Fragments

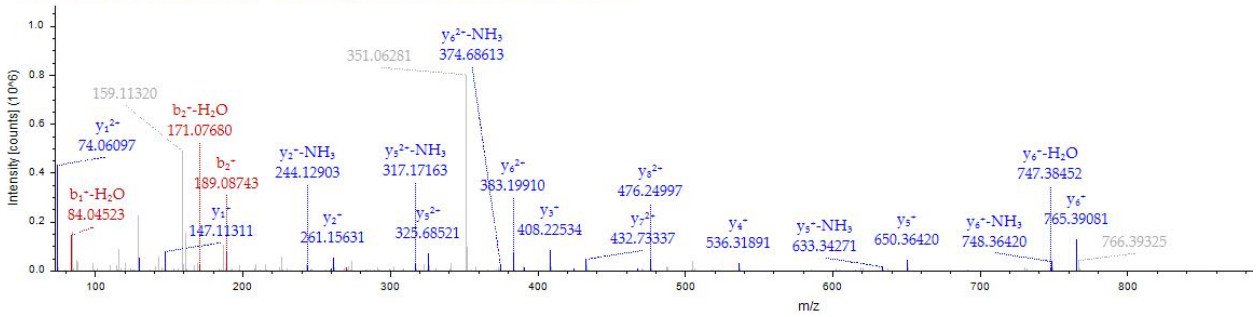
#1	b⁺	b²⁺	Seq.	y⁺	y²⁺	#2
1	72.04439	36.52583	A			21
2	219.11280	110.06004	F	2402.15842	1201.58285	20
3	332.19687	166.60207	I	2255.09000	1128.04864	19
4	479.26528	240.13628	F	2142.00594	1071.50661	18
5	566.29731	283.65229	S	1994.93752	997.97240	17
6	679.38137	340.19433	L	1907.90550	954.45639	16
7	865.46069	433.23398	W	1794.82143	897.91435	15
8	1130.52267	565.76497	C-21-B	1608.74212	804.87470	14
9	1245.54961	623.27845	D	1343.68013	672.34371	13
10	1342.60238	671.80483	P	1228.65319	614.83023	12
11	1429.63441	715.32084	S	1131.60043	566.30385	11
12	1557.69298	779.35013	Q	1044.56840	522.78784	10
13	1644.72501	822.86614	S	916.50982	458.75855	9
14	1715.76213	858.38470	A	829.47779	415.24254	8
15	1829.80505	915.40617	N	758.44068	379.72398	7
16	1942.88912	971.94820	L	644.39775	322.70251	6
17	2055.97318	1028.49023	L	531.31369	266.16048	5
18	2127.01030	1064.00879	A	418.22962	209.61845	4
19	2256.05289	1128.53008	E	347.19251	174.09989	3
20	2327.09000	1164.04864	A	218.14992	109.57860	2
21			K	147.11280	74.06004	1

Observed Mass:

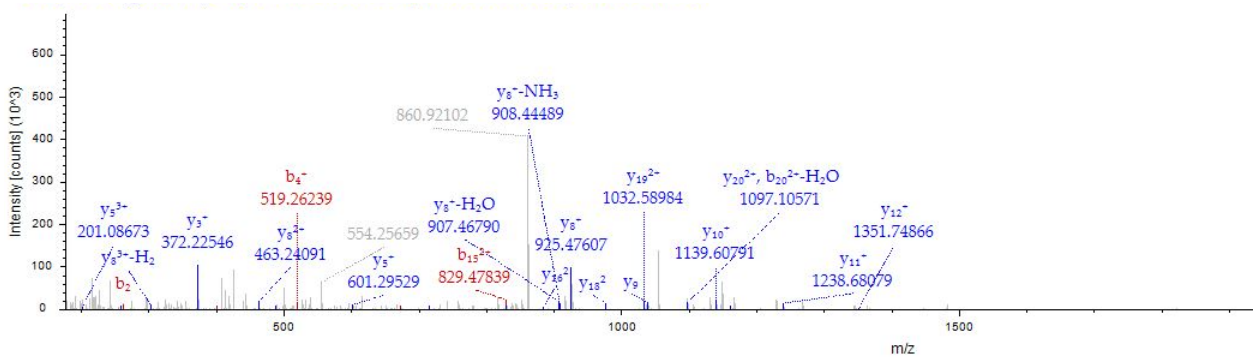


Other peptide fragments identified:

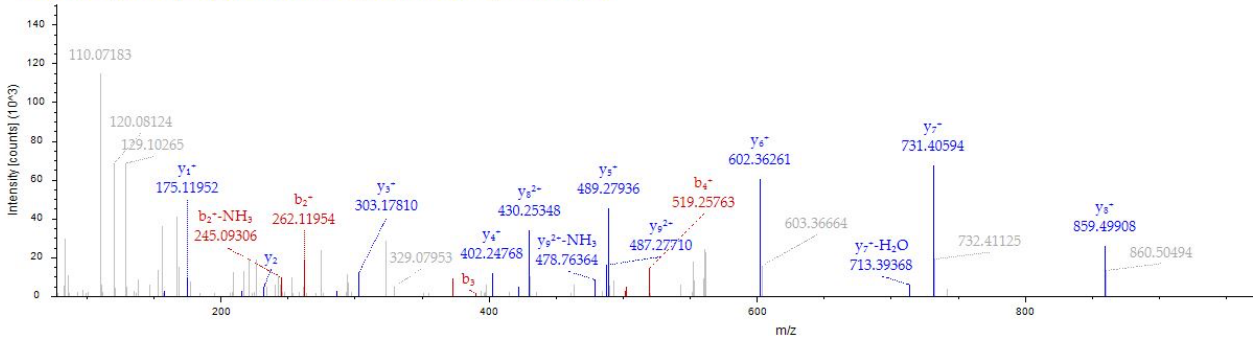
TSVDNKFNK



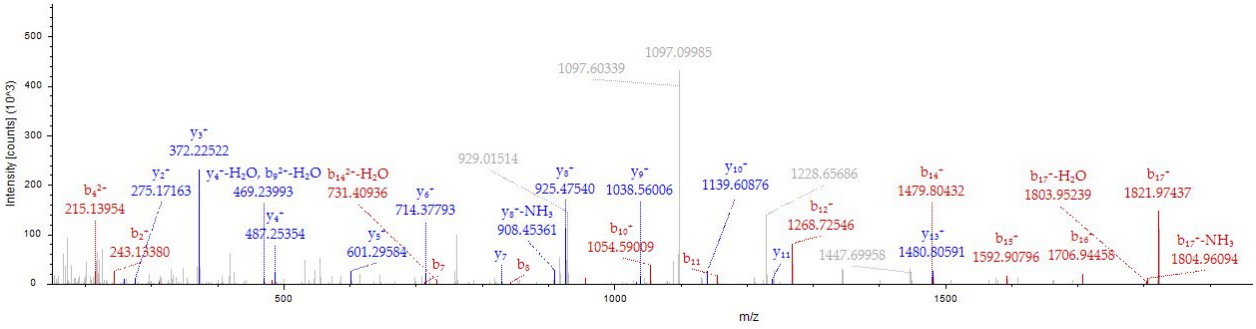
FNKELSVAGREIVTLPNLNDPQK



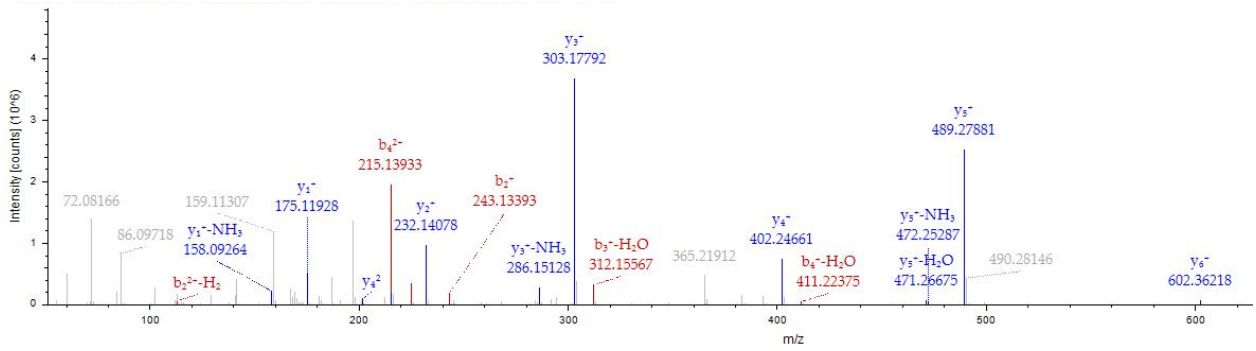
FNKELSVAGR



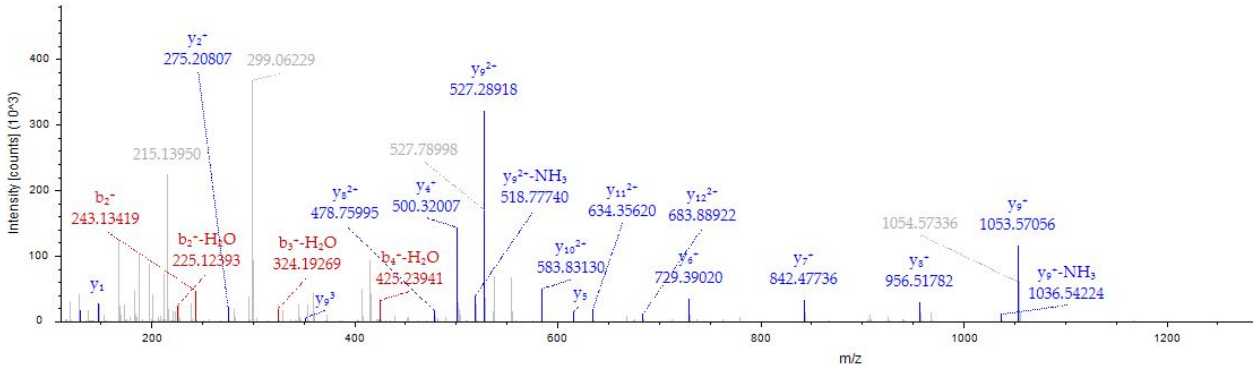
ELSVAGREIVTLPNLNDPQK



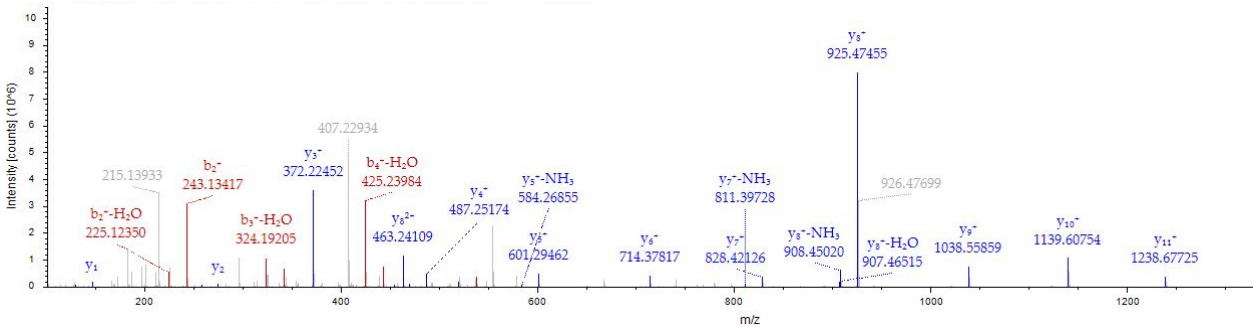
ELSVAGR



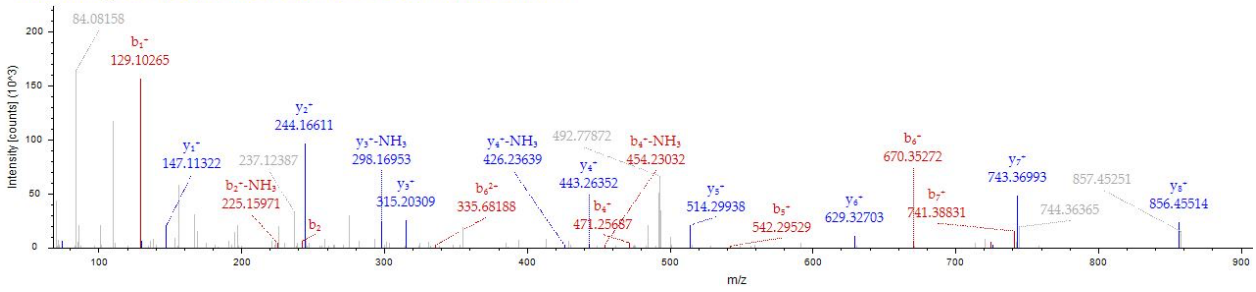
EIVTLPNLNDPQKK



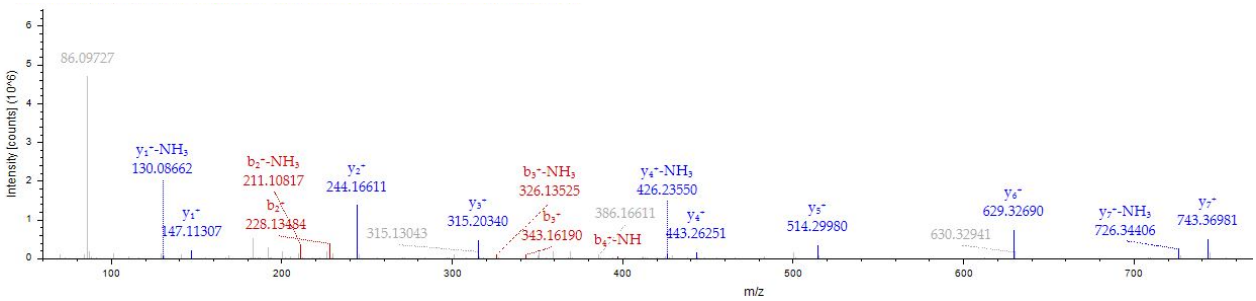
EIVTLPNLNDPQK



KLNDAQAPK



LNDAQAPK


Intensity (counts) (10^6)
m/z
86.09727
y1*-NH3
130.08662
y1*
147.11307
b2*-NH3
211.10817
b2*
228.13484
y2*
244.16611
315.13043
y3*
315.20340
b3*-NH3
326.13525
b3*
343.16190
386.16611
b4*-NH
y4*-NH3
426.23550
y4*
443.26251
y5*
514.29980
630.32941
y6*
629.32690
y7*-NH3
726.34406
y7*
743.36981

10. Glycosylation of NSP7

10.1 Protein Expression and Purification

The DNA of SARS-CoV-2 nsp7 was amplified by PCR and inserted into pHis-parallel2 plasmid using BamHI and XhoI sites. *E. coli* BL21 (DE3) cells transformed with pHis-parallel2 -His_6-TEV-nsp7 plasmid were grown in 1 L of LB medium containing ampicillin (50 μg/mL) and chloromycetin (17 μg/mL) at 37 °C until OD_{600} equaled to 0.8.

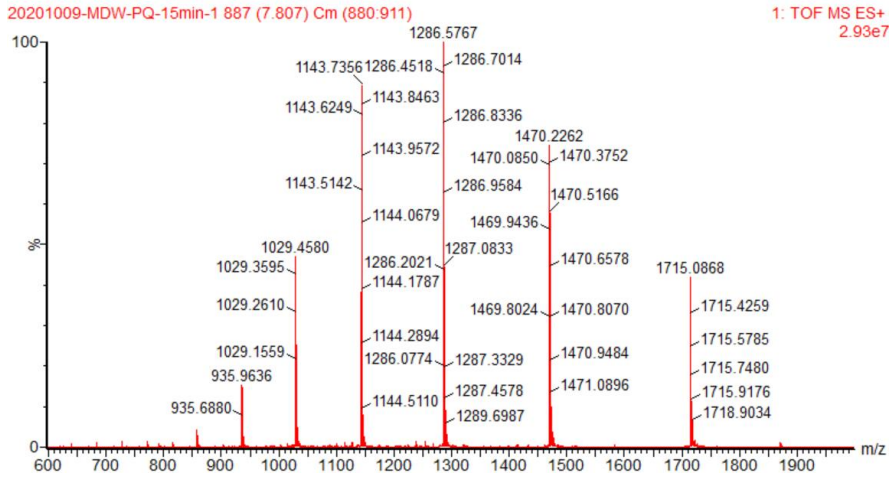
Expression was induced by addition of 0.2 mM IPTG at 16 °C overnight. Pellet was resuspended in lysis buffer (25 mM Tris pH 8.0, 150 mM NaCl) containing 1mM PMSF. The lysate was cleared by centrifugation and loaded onto a Ni-NTA (Qiagen) column. The His_6-tagged protein was eluted in lysis buffer containing 250 mM imidazole pH 8.0. The eluate was diluted 5-fold with 25 mM Tris pH 8.0, then loaded onto a Hi-Trap Q HP column. His_6-TEV-nsp7 was eluted and treated with TEV protease overnight to remove the His_6-tag. The protein was load onto a Hi-Trap Q HP column to remove the His_6-tag and protease. Fractions were concentrated and further purified by Superdex 75(10/300 GL) column equilibrated with 25 mM Tris pH 8.0, 150 mM NaCl. The protein was analyzed by SDS-PAGE to confirm its purity. Protein was aliquoted and stored in -80 °C. The concentration was 11.1 mg/mL, which was measured based on the UV_{280} absorption.

Sequence:

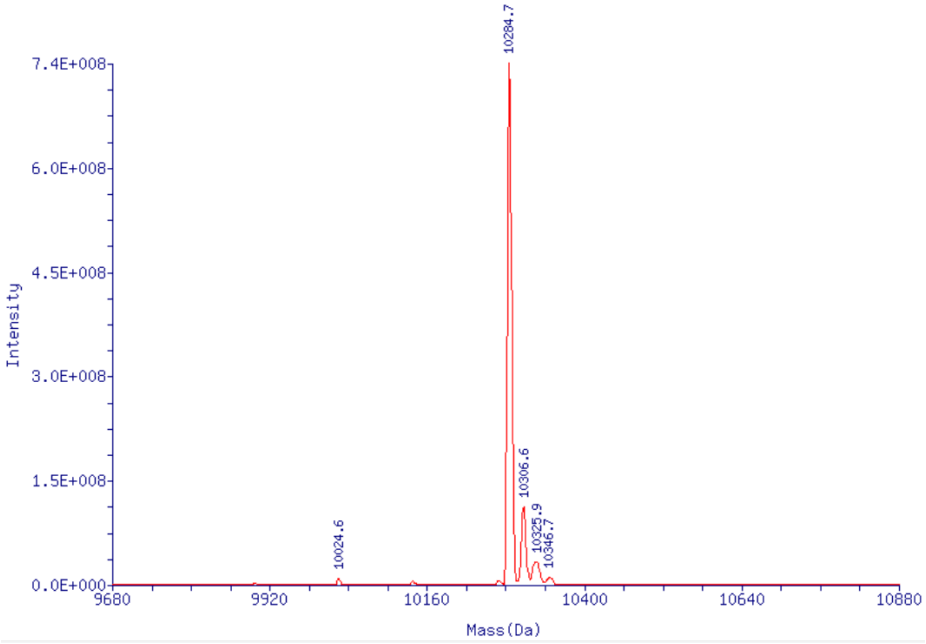
GAMGSMHMSKMSDVKCTSVVLLSVLQQLRVESSSKLWAQCVQLHNDILLAKDTTEAF
EKMVSLLSVLLSMQGAVDINKLCEEMLDNRATLQLE

Calculated Mass: 10284.7.

Observed Mass Spectra:



Deconvoluted Mass:

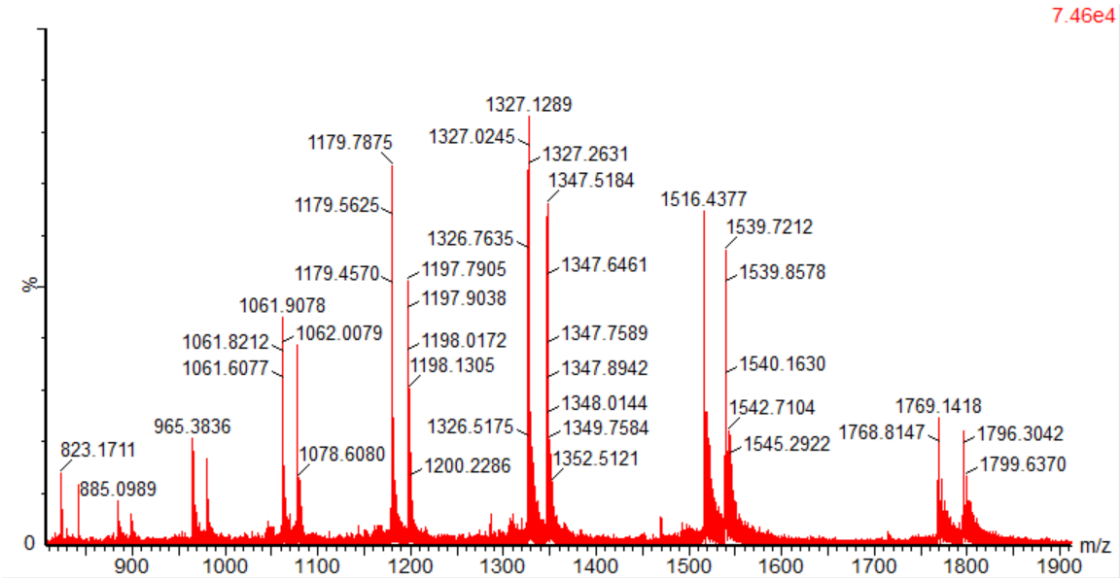


10.2 Protein Modification

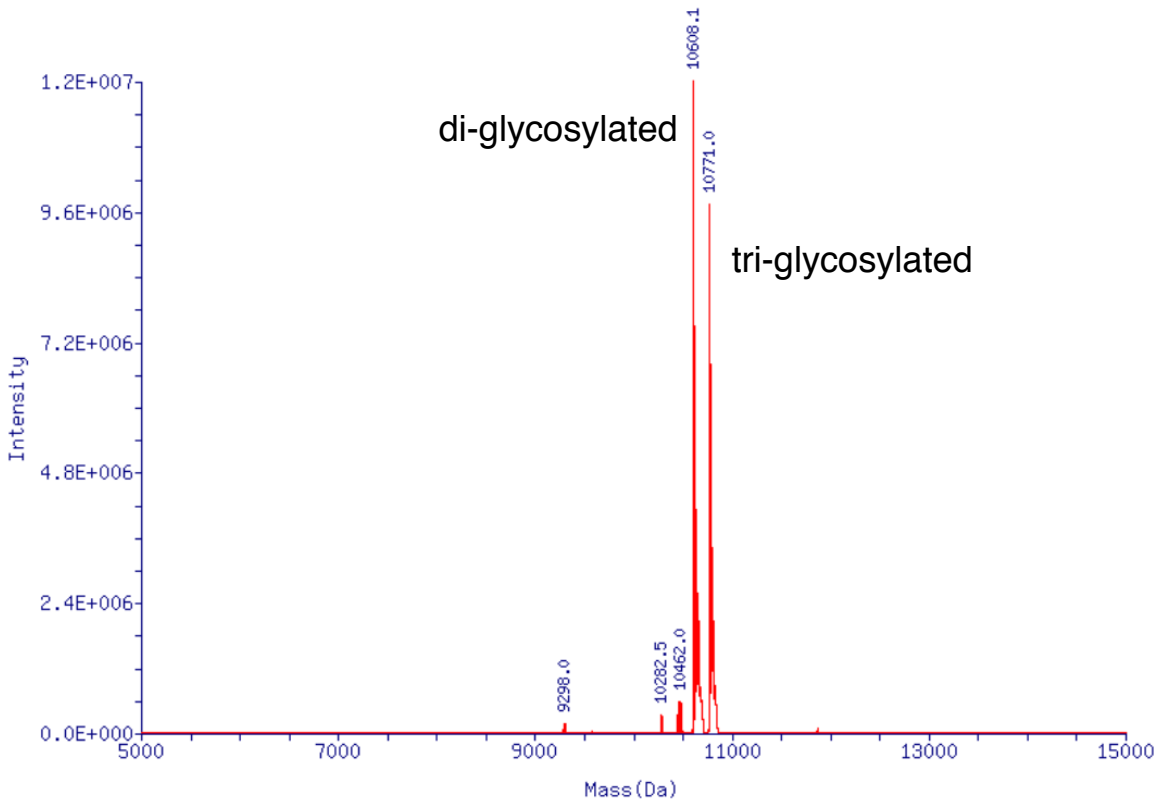
A "glycosylation kit" was prepared by dissolving **21** (4.2 mg, 0.015 mmol), **28** (3.7 mg, 0.0225 mmol), and Eosin Y (25 μL, 4 mg/mL in DMSO) in 500 μL H_2O.

An aliquot of the nsp7 solution in pH 7.4 Tris buffer (2 μL, 1.06 mM) was added to 20 μL of the above stock solution in a 100 μL Eppendorf tube. The tube was then placed in a screw-capped 8 mL vial, and sealed. The vial was then placed in the photoreactor, and irradiated with blue LED for 30 min. The resulting solution was treated with DTT, and then directly analyzed by LC/MS. LC-MS analysis was performed using Waters I-class equipped with a reverse-phase column (Aeris 3.6 μm WIDEPORE XB-C18 50×2.1 mm, phenomenex) for separation, and coupled to a XEVO G2-XS QTOF. The mobile phase A was 100/0.1% water/formic acid (v/v) and the mobile phase B was 100/0.1% methanol/formic acid (v/v). The LC gradient elution condition was initially 15% B for 0.5 min, from 15% to 60% B in 6.5 min, from 60% to 95% B in 3 min, then maintained at 95% B for 2.0 min, and followed by re-equilibration to starting conditions in 3.0 min, with a flow rate of 0.4 mL/min.

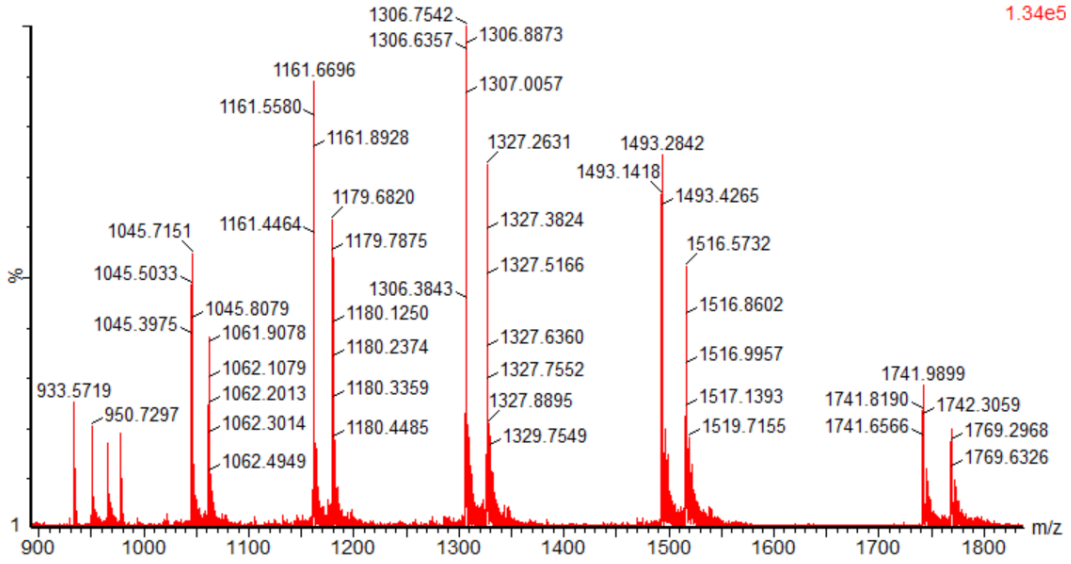
Observed Spectra of di- and triglycosylated proteins.



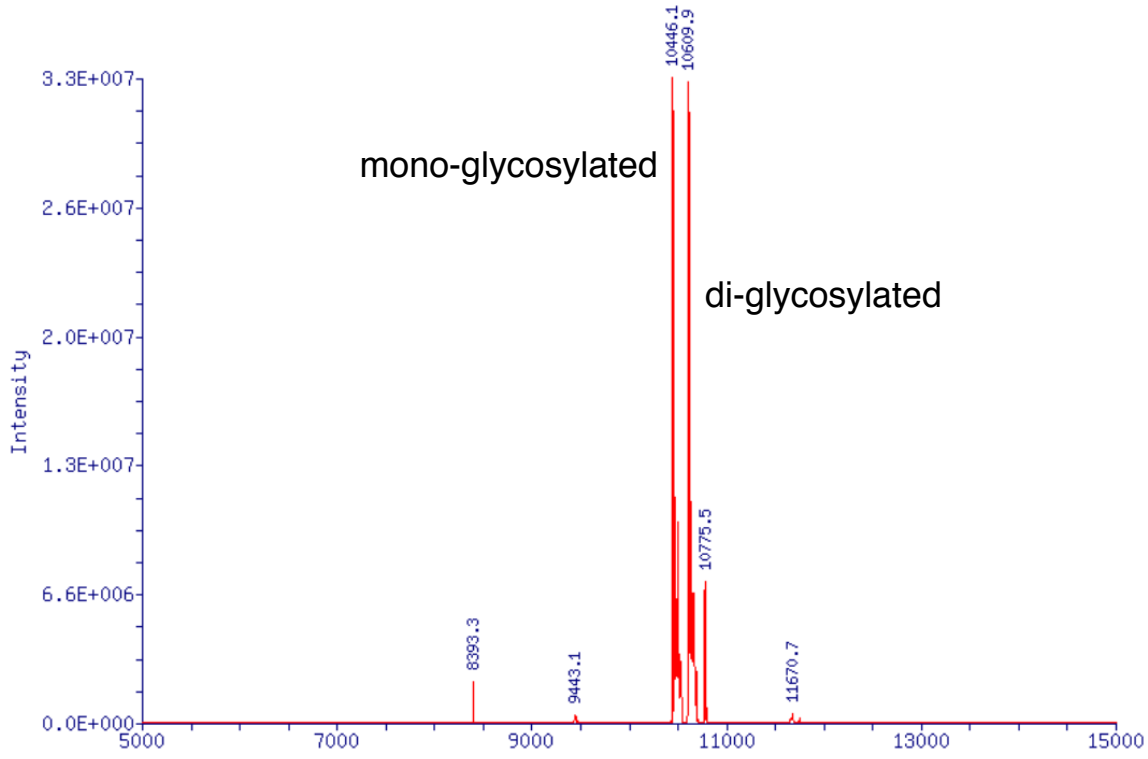
Deconvoluted Mass:



Observed Spectra of mono- and diglycosylated proteins.



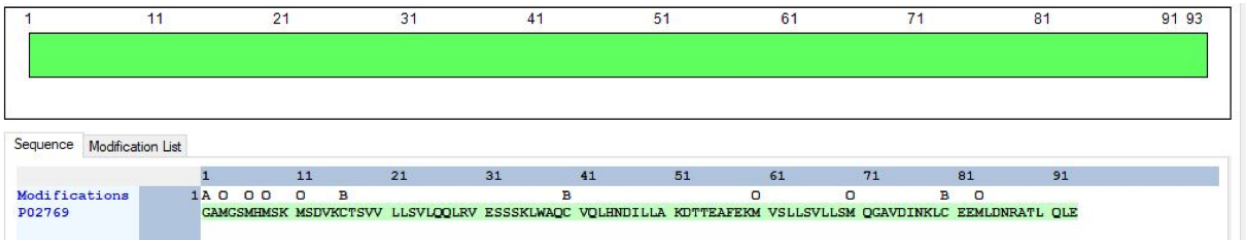
Deconvoluted Mass:



10.4 Protein Digestion and MS/MS Analysis

The reaction solution containing glycosylated protein was vacuum dried, and then dissolved in 50 mM ammonium bicarbonate. In-solution digestion was carried out overnight with trypsin in a 1:50 (w/w, trypsin/protein) ratio at 37 °C. Digestion was stopped by heating at 95 °C for 5 min. The resulting solution was subjected to MS/MS analysis following the protocol described in General Information. Glycosylation at cysteine was confirmed.

Peptide Fragments Identified: The green segment refers to the sequence of glycosylated nsp7 that is identified by mass spectrometry.



Peptide chain with glycosylated cysteine residue:

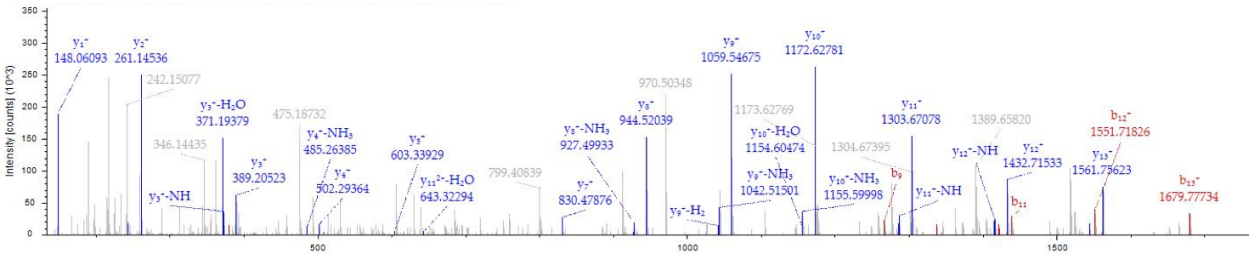
LC(glu)EEMLDNRATLQLE

Calculated Mass:

Ion Series | Neutral Losses | Precursor Ions | Internal Fragments

#1	b^+	b^{2+}	Seq.	y^+	y^{2+}	#2
1	114.09134	57.54931	L			15
2	379.15333	190.08030	C-21-B	1826.81463	913.91095	14
3	508.19592	254.60160	E	1561.75265	781.37996	13
4	637.23851	319.12289	E	1432.71005	716.85867	12
5	768.27900	384.64314	M	1303.66746	652.33737	11
6	881.36306	441.18517	L	1172.62698	586.81713	10
7	996.39000	498.69864	D	1059.54291	530.27509	9
8	1110.43293	555.72010	N	944.51597	472.76162	8
9	1266.53404	633.77066	R	830.47304	415.74016	7
10	1337.57115	669.28922	A	674.37193	337.68960	6
11	1438.61883	719.81305	T	603.33482	302.17105	5
12	1551.70290	776.35509	L	502.28714	251.64721	4
13	1679.76147	840.38438	Q	389.20308	195.10518	3
14	1792.84554	896.92641	L	261.14450	131.07589	2
15			E	148.06043	74.53386	1

Observed Mass:



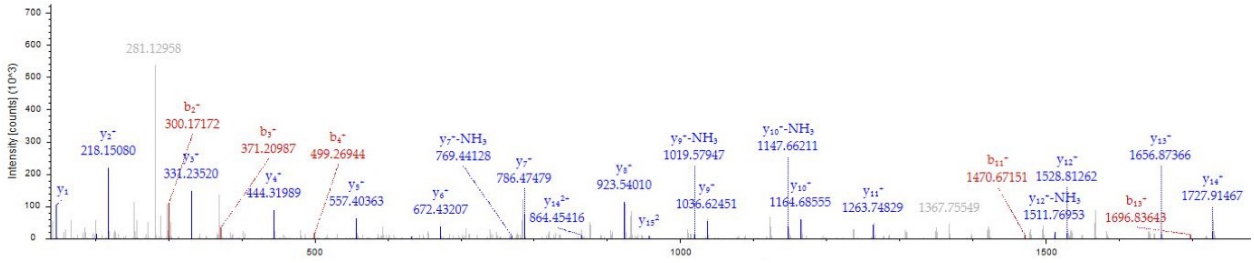
LWAQC(glu)VQLHNDILLAKDTTEAF

Calculated Mass:

Ion Series | Neutral Losses | Precursor Ions | Internal Fragments

#1	b+	b2+	Seq.	y+	y2+	#2
1	114.09134	57.54931	L			16
2	300.17065	150.58897	W	1913.97894	957.49311	15
3	371.20777	186.10752	A	1727.89962	864.45345	14
4	499.26634	250.13681	Q	1656.86251	828.93489	13
5	764.32833	382.66780	C-21-B	1528.80393	764.90560	12
6	863.39674	432.20201	V	1263.74195	632.37461	11
7	991.45532	496.23130	Q	1164.67353	582.84040	10
8	1104.53938	552.77333	L	1036.61496	518.81112	9
9	1241.59830	621.30279	H	923.53089	462.26908	8
10	1355.64122	678.32425	N	786.47198	393.73963	7
11	1470.66817	735.83772	D	672.42905	336.71816	6
12	1583.75223	792.37975	I	557.40211	279.20469	5
13	1696.83629	848.92179	L	444.31805	222.66266	4
14	1809.92036	905.46382	L	331.23398	166.12063	3
15	1880.95747	940.98237	A	218.14992	109.57860	2
16			K	147.11280	74.06004	1

Observed Mass:



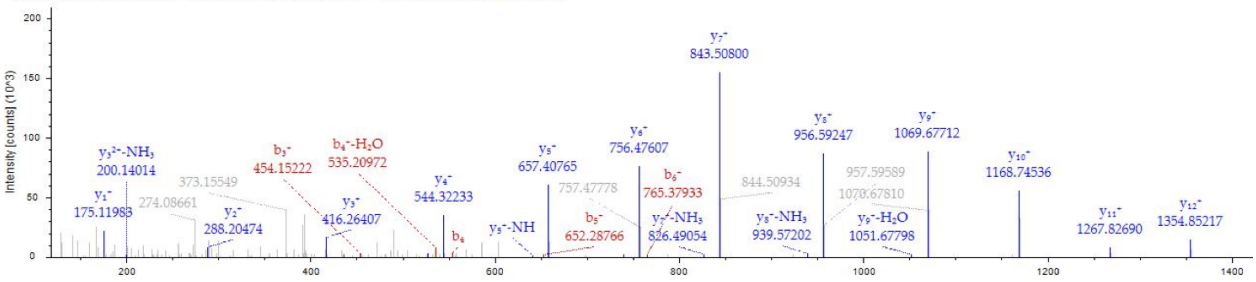
C(glu)TSVVLLSVLQQLR

Calculated Mass:

Ion Series | Neutral Losses | Precursor Ions | Internal Fragments

#1	b^+	b^{2+}	Seq.	y^+	y^{2+}	#2
1	266.06926	133.53827	C-21-B			14
2	367.11694	184.06211	T	1455.88934	728.44831	13
3	454.14897	227.57812	S	1354.84166	677.92447	12
4	553.21738	277.11233	V	1267.80963	634.40845	11
5	652.28580	326.64654	V	1168.74122	584.87425	10
6	765.36986	383.18857	L	1069.67281	535.34004	9
7	878.45392	439.73060	L	956.58874	478.79801	8
8	965.48595	483.24661	S	843.50468	422.25598	7
9	1064.55437	532.78082	V	756.47265	378.73996	6
10	1177.63843	589.32285	L	657.40423	329.20576	5
11	1305.69701	653.35214	Q	544.32017	272.66372	4
12	1433.75558	717.38143	Q	416.26159	208.63444	3
13	1546.83965	773.92346	L	288.20302	144.60515	2
14			R	175.11895	88.06311	1

Observed Mass:

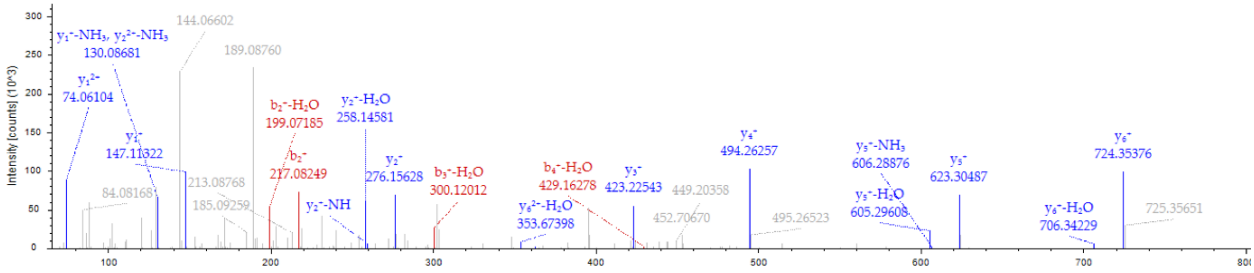


Other peptide fragments identified:

DTTEAFEK

Ion Series | Neutral Losses | Precursor Ions | Internal Fragments

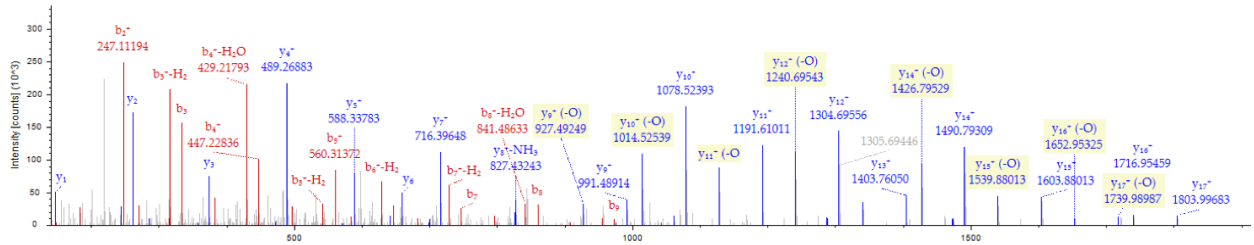
#1	b⁺	b²⁺	Seq.	y⁺	y²⁺	#2
1	116.03422	58.52075	D			8
2	217.08190	109.04459	T	825.39887	413.20308	7
3	318.12958	159.56843	T	724.35120	362.67924	6
4	447.17217	224.08972	E	623.30352	312.15540	5
5	518.20928	259.60828	A	494.26092	247.63410	4
6	665.27770	333.14249	F	423.22381	212.11554	3
7	794.32029	397.66378	E	276.15540	138.58134	2
8			K	147.11280	74.06004	1



MVSLLSVLLSMQGAVDINK

Ion Series | Modification Losses | Neutral Losses | Multiple Neutral Losses | Precursor Ions | Internal Fragments

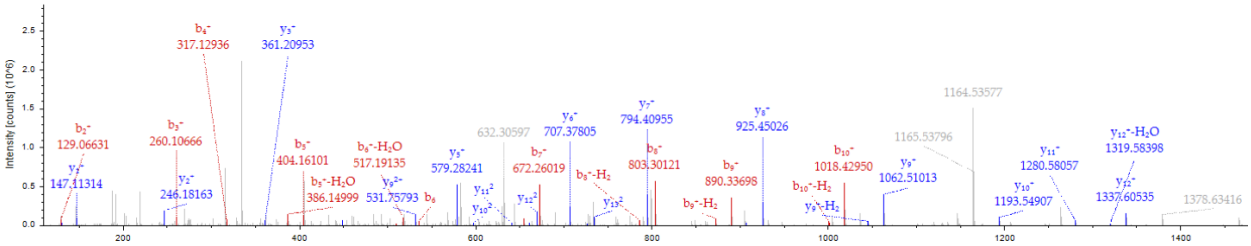
#1	b⁺	b²⁺	Seq.	y⁺	y²⁺	#2
1	148.04268	74.52498	M-Oxidation			19
2	247.11109	124.05918	V	1903.05688	952.03208	18
3	334.14312	167.57520	S	1803.98846	902.49787	17
4	447.22718	224.11723	L	1716.95643	858.98185	16
5	560.31125	280.65926	L	1603.87237	802.43982	15
6	647.34327	324.17528	S	1490.78831	745.89779	14
7	746.41169	373.70948	V	1403.75628	702.38178	13
8	859.49575	430.25151	L	1304.68786	652.84757	12
9	972.57982	486.79355	L	1191.60380	596.30554	11
10	1059.61184	530.30956	S	1078.51974	539.76351	10
11	1206.64724	603.82726	M-Oxidation	991.48771	496.24749	9
12	1334.70582	667.85655	Q	844.45231	422.72979	8
13	1391.72729	696.36728	G	716.39373	358.70050	7
14	1462.76440	731.88584	A	659.37227	330.18977	6
15	1561.83281	781.42004	V	588.33515	294.67121	5
16	1676.85976	838.93352	D	489.26674	245.13701	4
17	1789.94382	895.47555	I	374.23980	187.62354	3
18	1903.98675	952.49701	N	261.15573	131.08150	2
19			K	147.11280	74.06004	1



GAMGSMHMSKMSDVK

Ion Series | Neutral Losses | Precursor Ions | Internal Fragments

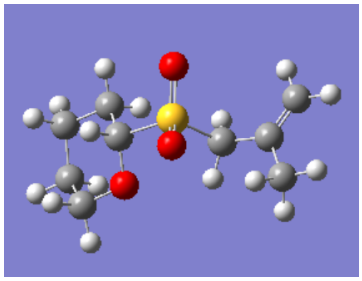
#1	b⁺	b²⁺	Seq.	y⁺	y²⁺	#2
1	58.02874	29.51801	G			15
2	129.06585	65.03657	A	1539.67864	770.34296	14
3	260.10634	130.55681	M	1468.64152	734.82440	13
4	317.12780	159.06754	G	1337.60104	669.30416	12
5	404.15983	202.58355	S	1280.57957	640.79343	11
6	535.20032	268.10380	M	1193.54755	597.27741	10
7	672.25923	336.63325	H	1062.50706	531.75717	9
8	803.29971	402.15349	M	925.44815	463.22771	8
9	890.33174	445.66951	S	794.40767	397.70747	7
10	1018.42670	509.71699	K	707.37564	354.19146	6
11	1149.46719	575.23723	M	579.28067	290.14398	5
12	1236.49922	618.75325	S	448.24019	224.62373	4
13	1351.52616	676.26672	D	361.20816	181.10772	3
14	1450.59457	725.80092	V	246.18122	123.59425	2
15			K	147.11280	74.06004	1



11. Details of Computational Studies

All geometries were optimized via density functional theory (DFT) using the B3-LYP[2,3] functional and a standard 6-31G(d) basis set for all atoms using Gaussian09.[4] Analytical frequencies of all optimized structures were computed to verify the nature of stationary points. Transition-state vibrations were verified as connecting reactants and products by viewing normal mode vibrations with imaginary frequencies.

32
G (A.U.) = -976.162077



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C	-2.75767200	-1.49171900	0.16477800
C	-3.54825700	-0.65197200	-0.83863000
H	-1.38770100	1.06655800	-1.45083300
H	-1.69137200	2.22048900	-0.14530200
H	-3.83958100	1.10486400	0.39653800
H	-3.83011900	1.45440200	-1.32959700
H	-2.77090400	-2.55495700	-0.08859200
H	-3.17093200	-1.37414100	1.17966900
H	-3.19675200	-0.88721700	-1.85158800
H	-4.60975300	-0.92488100	-0.78968500
H	-1.54894600	0.42400200	1.55252900
O	-1.37243300	-1.11963200	0.17574900
S	0.63803800	0.48258100	0.70269100
C	1.33347900	-0.25483700	-0.83686000
H	0.98369700	0.38807500	-1.64841700
H	0.86340300	-1.23854200	-0.91967400
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H	4.52660800	-1.48991200	-0.09765700
H	3.08569500	-1.59644100	0.94195800
H	3.12419100	-2.45858300	-0.59762000
C	2.83975500	-0.32534100	-0.77698700

O	1.08015200	-0.32179300	1.85403800
O	0.86133400	1.93918100	0.68280900
C	3.57834600	0.65813200	-1.30214700
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H	3.12819400	1.52629200	-1.77552800

33
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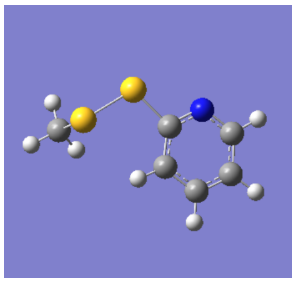

XYZ coordinates
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S	-2.38702600	0.23793000	-0.55042800
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C	0.83127500	0.99520300	-0.35732300
C	2.13108400	1.48586800	-0.25774600
H	0.00350600	1.63133200	-0.65020100
C	2.84781400	-0.71236500	0.35350700
C	3.16582200	0.62203400	0.10552900
H	2.33284200	2.53338100	-0.46635700
H	3.61927300	-1.42635500	0.63594500
H	4.19020800	0.96992700	0.19289400
C	-2.79990800	0.86917600	1.12480400
H	-1.93653100	1.35657600	1.58341400
H	-3.59915700	1.60384000	0.98340300
H	-3.15889200	0.05971600	1.76336400
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34
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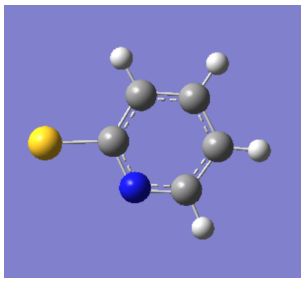

XYZ coordinates
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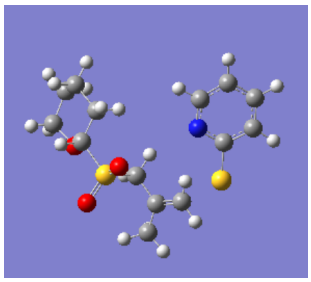
C	1.59645000	1.15372300	0.00019100
C	2.20772200	-0.10350800	0.00032700
C	1.38942700	-1.23101300	0.00029100
N	0.05089900	-1.17002200	-0.00000100
H	2.19617000	2.06008800	0.00026400
H	-0.30202300	2.19686000	-0.00004800
H	3.28801500	-0.20715400	0.00047800
H	1.81734400	-2.23159100	0.00032200
S	-2.29259500	-0.01201400	-0.00030800

TS-I
G (A.U.) = -1621.93834



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C	-4.05658600	1.11275900	-1.46532600
C	-3.50354300	2.53069100	-1.32454600
H	-1.20610300	1.73938900	0.12657000
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H	-4.00003600	2.84504100	0.76180100
H	-2.60721900	3.77830700	0.22305200
H	-4.23323500	0.84209100	-2.50944300
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C	1.53100900	-2.26037600	0.63004600
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S	3.25032700	-1.33834900	-0.99187600
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C	4.62026900	0.92506900	-0.25735100
C	2.33281500	2.18068000	0.52063300
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C	3.53109900	2.88481900	0.60634400
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35
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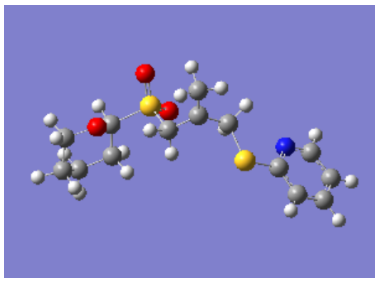

XYZ coordinates
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H	-2.15688300	1.89752300	0.45575700
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S	-2.52665200	0.31147500	-1.35056400
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C	-6.12874900	-1.26621500	0.88330500
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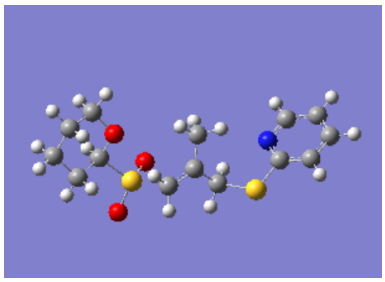
G (A.U.) = -1621.944500



XYZ coordinates
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H	4.18271100	-0.74751400	-1.34610100
H	5.04084700	-1.44965500	0.02903700
H	6.25989200	0.67412500	0.41521100
H	6.45450700	0.24004000	-1.28065500
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H	4.35993100	2.46437200	1.04231100
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H	5.84402500	2.70460000	-0.93040500
H	3.92256300	0.11660800	1.59655500
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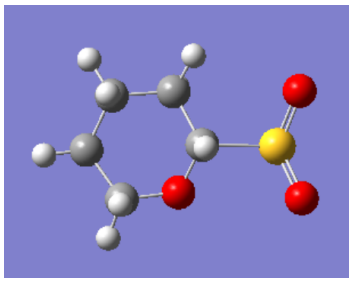
H	-0.56719100	1.45713700	0.61303500
H	0.26781200	1.75369900	-0.92287700
C	-0.40234200	-0.27505400	-0.62975700
O	1.34149300	-0.71963600	1.94117200
O	2.69524600	-2.53593000	0.72915700
C	-1.50848900	-1.15700600	-0.14364500
H	-1.88687700	-0.83174800	0.83120000
H	-1.20045600	-2.20324700	-0.08251100
S	-2.98950000	-1.12976900	-1.26859200
C	-4.16730800	-0.14266700	-0.34835600
C	-5.43307400	0.05655500	-0.92932200
C	-4.73828500	1.08802700	1.49970400
C	-6.36420500	0.81144900	-0.22942100
H	-5.66918300	-0.37415300	-1.89768200

C	-6.01709000	1.34387700	1.01714900
H	-4.41698300	1.47960100	2.46307200
H	-7.35179900	0.98340800	-0.64922100
H	-6.71668000	1.93939300	1.59476400
N	-3.82629300	0.36224600	0.83546300

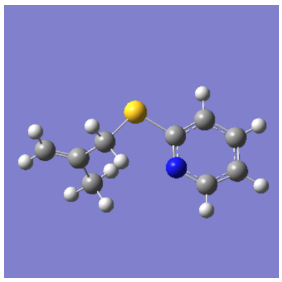
36
G (A.U.) = -819.608214



XYZ coordinates
0 2

C	-2.18334700	1.19544500	0.25892600
C	-0.69434400	1.29356000	-0.13115800
C	-0.00431100	0.00814700	0.30047700
C	-1.94179300	-1.30645700	0.16126200
C	-2.79504200	-0.11260000	-0.26674500
H	-0.60142800	1.40229800	-1.21903600
H	-0.21064900	2.15571300	0.33619200
H	-2.27425900	1.22953900	1.35382800
H	-2.72625400	2.06420400	-0.12987900
H	-2.26964400	-2.23830500	-0.30546800
H	-1.97448000	-1.43654500	1.25522100
H	-2.84352300	-0.08755400	-1.36278600
H	-3.81945500	-0.24214400	0.10364700
H	0.08416400	-0.06744400	1.39760000
O	-0.57624200	-1.13689300	-0.25327100
S	1.81078200	-0.02518600	-0.27653800
O	2.39962000	-1.27776900	0.26651900
O	2.34862800	1.30899400	0.11909100

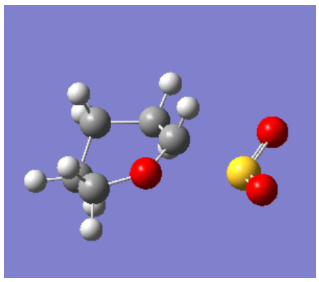
SI-II-p
G (A.U.) = -802.361759



XYZ coordinates
0 1

C	-4.03963200	-0.08542300	0.06138800
H	-4.40405200	0.62446400	0.80016700
H	-4.78705300	-0.54290700	-0.58177500
C	-2.21477300	-1.36432700	-1.06657200
H	-1.49657000	-0.88080500	-1.74034800
H	-1.67948700	-2.18820400	-0.57737400
H	-3.02358300	-1.78419100	-1.67193300
C	-2.74062700	-0.38470000	-0.04904600
C	-1.73128400	0.23871700	0.88146400
H	-1.09645100	-0.51806500	1.35394500
H	-2.22186200	0.83245900	1.65646400
S	-0.54990700	1.38523800	0.03298800
C	0.98608500	0.46627600	0.05024800
C	2.11352000	1.09009500	-0.51576700
C	2.20055700	-1.40445500	0.58313300
C	3.31811200	0.40122900	-0.51105900
H	2.03483700	2.08600500	-0.94122800
C	3.37263900	-0.87934700	0.05078500
H	2.18889100	-2.39645600	1.03139700
H	4.20730500	0.85614900	-0.93954100
H	4.29486600	-1.45094300	0.07340200
N	1.02772600	-0.75281300	0.58594000

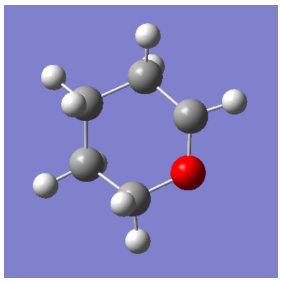
TS-III
G (A.U.) = -819.602781



XYZ coordinates
0 2

C	-2.24506600	1.15174700	0.19042600
C	-0.72029400	1.31759700	0.16254100
C	-0.01699100	0.03823000	0.61287600
C	-1.97868600	-1.32188300	-0.03233900
C	-2.59845700	-0.07596600	-0.65265100
H	-0.42548900	1.56943100	-0.86376800
H	-0.37458100	2.14021400	0.79390700
H	-2.60626500	1.02251500	1.21989300
H	-2.72142800	2.05430800	-0.20686800
H	-1.97079700	-2.16635300	-0.72717100
H	-2.55353300	-1.61871900	0.85524500
H	-2.23187100	0.06680300	-1.67759200
H	-3.68223000	-0.22958500	-0.71585800
H	0.39340500	0.08511900	1.62778800
O	-0.61256700	-1.17408100	0.41264000
S	1.76142200	-0.02324100	-0.36701700
O	2.41998100	-1.27519500	0.09022000
O	2.36096000	1.29799700	-0.01766200

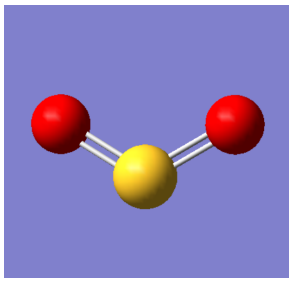
37
G (A.U.) = -271.006025



XYZ coordinates
0 2

C	1.00715300	1.01863800	0.25870900
C	1.40617600	-0.41090500	-0.14540000
C	-1.38479500	0.26951400	0.19913300
C	-0.39464300	1.32703500	-0.28514800
H	1.63416100	-0.41575600	-1.22939100
H	2.32734100	-0.72407500	0.36147000
H	0.99686400	1.10123300	1.35413800
H	1.73999200	1.74364900	-0.11428400
H	-2.37304600	0.40082300	-0.25039000
H	-1.49108800	0.32698800	1.29309000
H	-0.37728300	1.33029200	-1.38349400
H	-0.73996600	2.31737200	0.03809700
O	-0.98377200	-1.06245200	-0.15125800
C	0.31180300	-1.39145300	0.15831300
H	0.47903300	-2.45789000	0.02719000

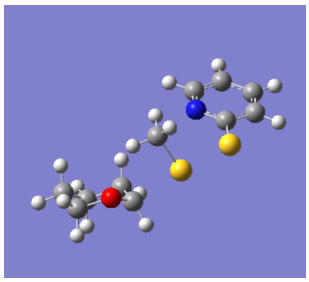
SI-III-p
G (A.U.) = -548.604899



XYZ coordinates
0 1

S	0.00000000	0.00000000	0.37079200
O	0.00000000	1.26188700	-0.37079200
O	0.00000000	-1.26188700	-0.37079200

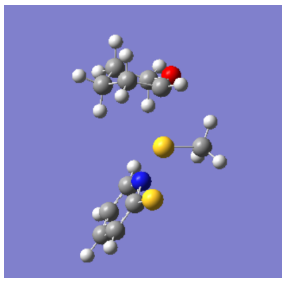
TS-IV
G (A.U.) = -1354.876251



XYZ coordinates
0 2

S	0.29697600	1.44255400	-0.24213000
S	-1.88998500	1.88890900	-0.26895400
C	-2.66405400	0.28787800	-0.06633000
C	-3.96212800	0.12563100	-0.58435000
C	-4.60851300	-1.08863100	-0.38670200
H	-4.43639100	0.93400000	-1.13169400
C	-2.65231100	-1.85313500	0.75241100
C	-3.94270400	-2.10997900	0.29589900
H	-5.61297600	-1.24189300	-0.77287500
H	-2.09207000	-2.62143900	1.28355600
H	-4.40636800	-3.07669200	0.46568500
N	-2.02054400	-0.68259700	0.59106300
C	0.53223800	1.31482700	1.57361400
H	-0.02838300	0.45881800	1.95109100
H	1.60393600	1.19203800	1.74480200
H	0.18696500	2.23584600	2.04638500
C	3.40798500	-1.92739800	-0.69515500
H	3.20555800	-2.99448800	-0.54440200
H	3.90914600	-1.83038600	-1.66863300
C	4.52327300	0.12033800	0.22934500
H	5.09551100	0.32103300	-0.68957700
H	5.05586400	0.57051400	1.07101900
C	4.32208700	-1.38117900	0.40984700
H	5.30109600	-1.87733200	0.39791600
H	3.87198100	-1.57098300	1.39323700
C	2.08464800	-1.12954200	-0.70520600
H	1.52531800	-1.35779700	0.21160300
H	1.44631400	-1.41441900	-1.54755600
C	2.36312800	0.34837200	-0.76369500
H	2.43758300	0.82219800	-1.74636500
O	3.26837100	0.83533300	0.15220700

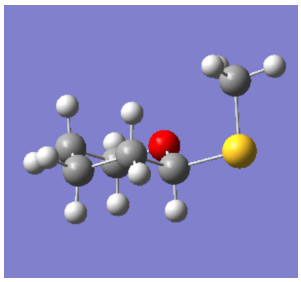
TS-V
G (A.U.) = -1354.886441



XYZ coordinates
0 2

S	0.66117800	1.52002200	-0.07101300
S	-1.48357800	1.91800300	-0.52286000
C	-2.29562500	0.35889100	-0.18383400
C	-3.54000700	0.13301800	-0.80238500
C	-4.22190600	-1.04237900	-0.51499400
H	-3.94651900	0.86509400	-1.49302400
C	-2.40475900	-1.65482400	0.90890500
C	-3.64582800	-1.96651400	0.36155300
H	-5.18531000	-1.24178400	-0.97727700
H	-1.91512900	-2.34572500	1.59387600
H	-4.14086000	-2.89995600	0.61032300
N	-1.73773400	-0.51925900	0.65659500
C	2.46581900	-1.27937200	-1.54154600
H	1.38441100	-1.11139200	-1.60532200
H	2.78154200	-1.75268300	-2.47816900
C	2.76945000	-2.18551900	-0.34079600
H	2.21062900	-3.12744900	-0.40391300
H	3.83747500	-2.44149300	-0.31760100
C	2.39051100	-1.47369000	0.95388300
H	2.69035900	-2.03845000	1.84001900
H	1.30900800	-1.28950600	0.99147100
C	3.17936900	0.06895100	-1.36245100
H	2.84275100	0.80304900	-2.10282700
H	4.26292900	-0.06968700	-1.52678300
C	2.98242700	0.63534400	0.01850000
H	3.45423800	1.58754200	0.25421700
O	3.06006900	-0.19923300	1.08899700
C	0.57796500	1.73564800	1.75271100
H	-0.14982000	1.03085500	2.15690500
H	1.56754100	1.51335700	2.15834400
H	0.29424300	2.76120300	1.99631400

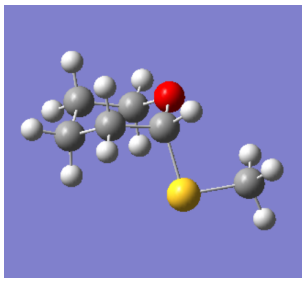
38
G (A.U.) = -709.128690



XYZ coordinates
0 1

S	-2.04493500	0.05921700	-0.59548300
C	-2.36597700	-0.11640600	1.19783900
H	-1.76481400	-0.93343500	1.60147100
H	-2.16790500	0.80754600	1.74777800
H	-3.42526400	-0.36597600	1.29860700
C	1.67187200	-1.29545200	-0.17448500
C	2.43152200	-0.16915500	0.52657100
C	1.96369000	1.19003900	-0.01190200
C	0.42910500	1.29164000	0.05226900
C	-0.21279600	0.07357600	-0.62343200
H	2.42323300	2.01267200	0.54905100
H	2.23831900	-0.22991900	1.60566700
H	3.51101100	-0.30205100	0.37934100
H	1.94479000	-1.32863200	-1.24368100
H	1.89879500	-2.27252500	0.26230400
H	0.10766800	1.32794000	1.10036500
H	0.07356800	2.20666700	-0.43379200
H	0.02449000	0.08929300	-1.70120400
H	2.29121100	1.29971400	-1.05623400
O	0.25742000	-1.13802700	-0.04788800

39
G (A.U.) = -709.131033

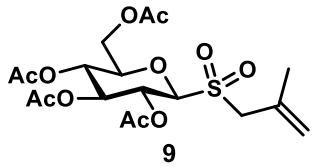


XYZ coordinates
0 1

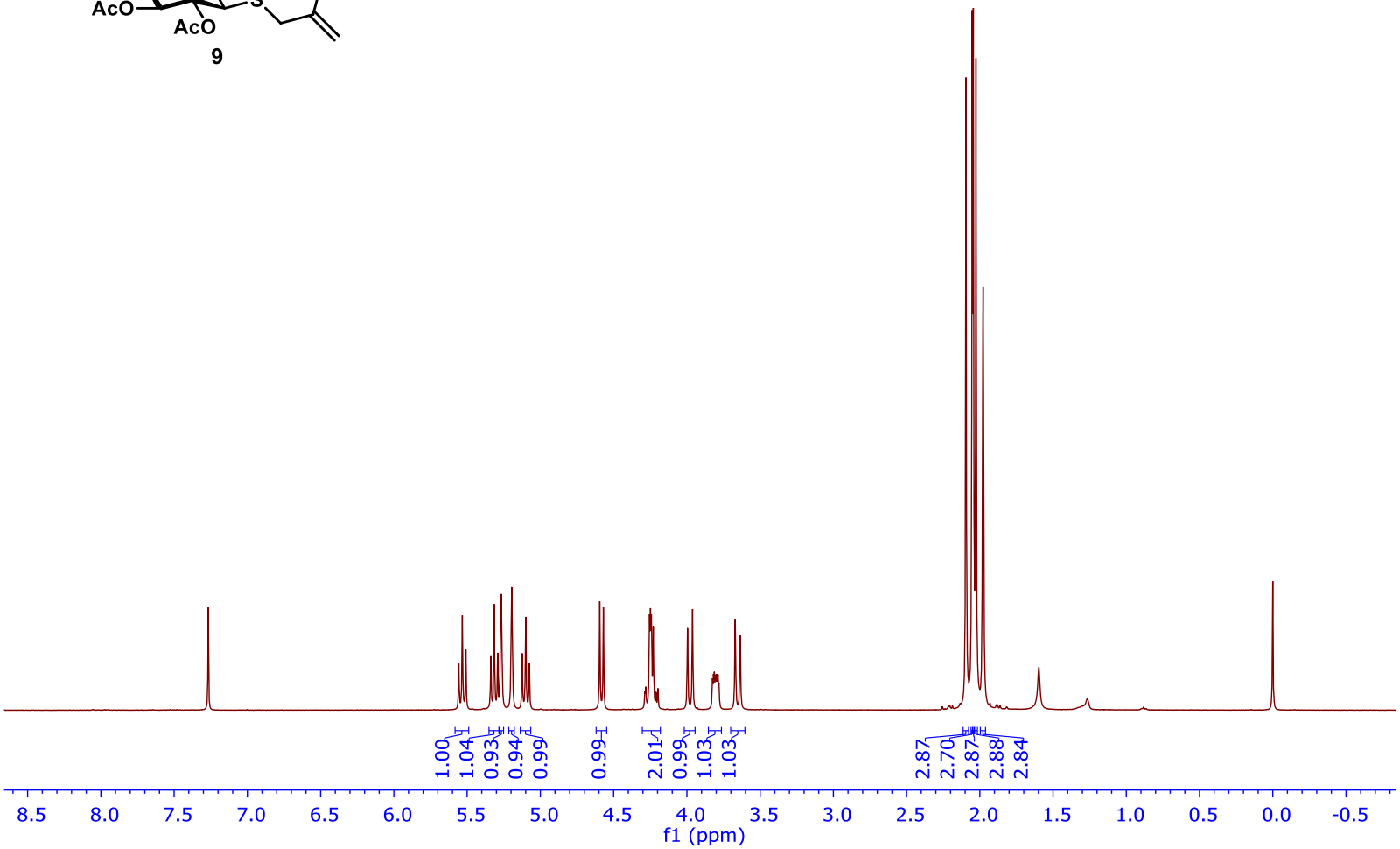
S	1.49803500	-0.63384500	-0.54131400
C	-1.87505500	-0.92275800	-0.47163300
H	-1.37701700	-1.10968900	-1.43174100
H	-2.75973100	-1.56998000	-0.44136600
C	-2.27895000	0.55639800	-0.38101100
H	-2.87501500	0.85646600	-1.25227000
H	-2.89908200	0.71915600	0.51080900
C	-1.03225200	1.43528000	-0.28791900
H	-1.28802200	2.48216000	-0.10078900
H	-0.45625600	1.37962500	-1.22245800
C	-0.92818900	-1.27576200	0.68555900
H	-0.54466500	-2.29782400	0.59360500
H	-1.48191200	-1.21948100	1.63244400
C	0.24121600	-0.28643300	0.79464200
H	0.76429000	-0.41735600	1.74633400
O	-0.19542000	1.05667800	0.81253300
C	2.77406800	0.56720700	-0.02020200
H	3.52802200	0.60778200	-0.81013900
H	2.32636700	1.55559100	0.10545800
H	3.25278800	0.25805700	0.91424900

12. NMR Spectra

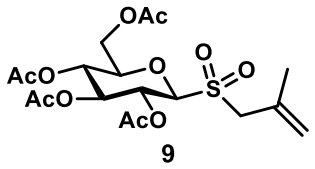
CDCl3, 400 MHz



9

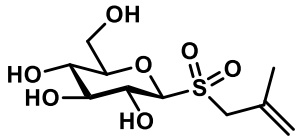


CDCl3, 101 MHz



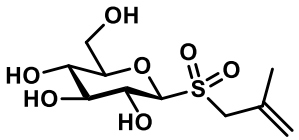
9

CD3OD, 400 MHz



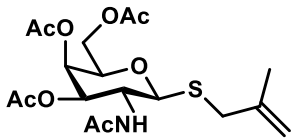
13

CD3OD, 101 MHz

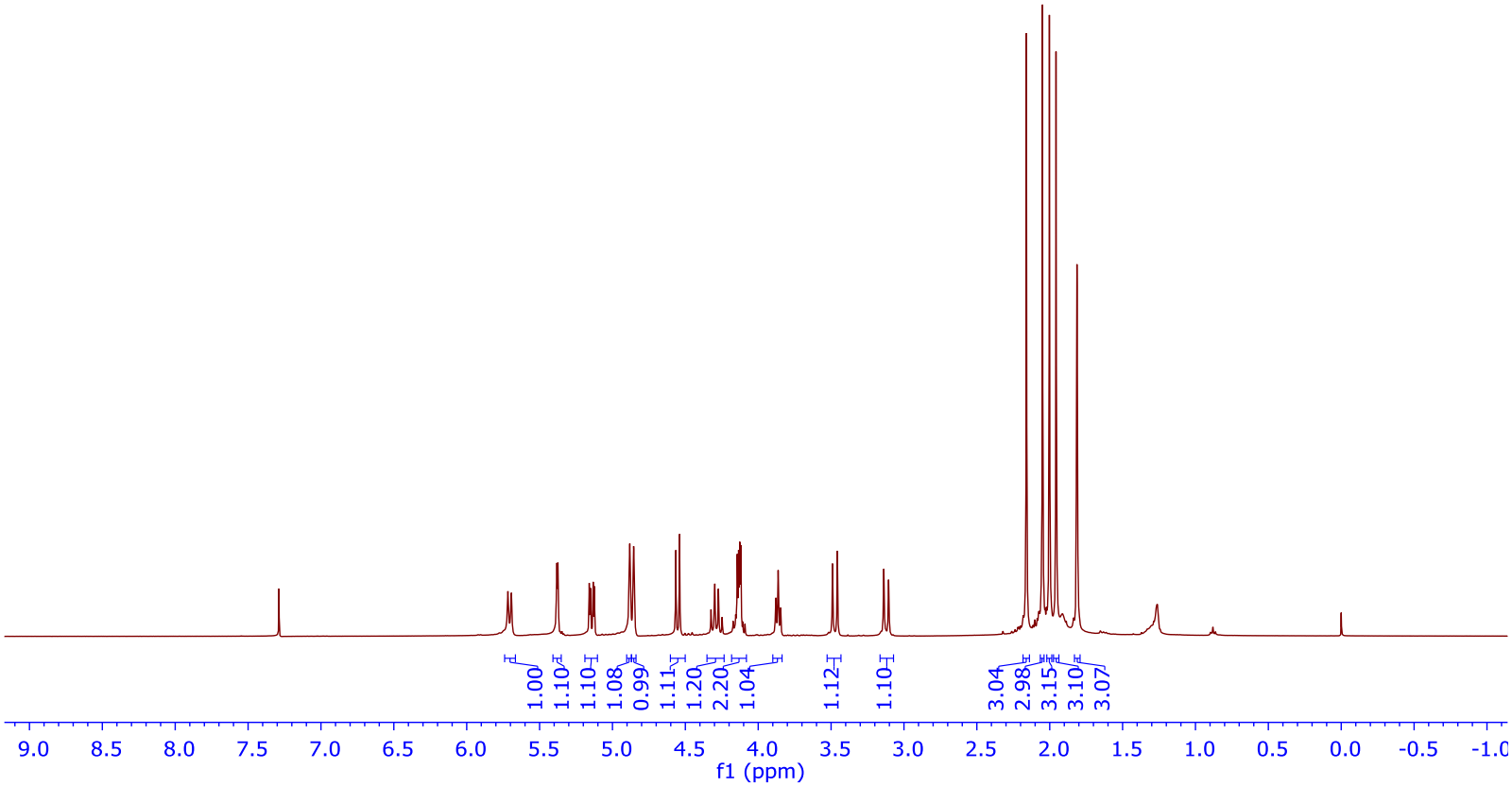


13

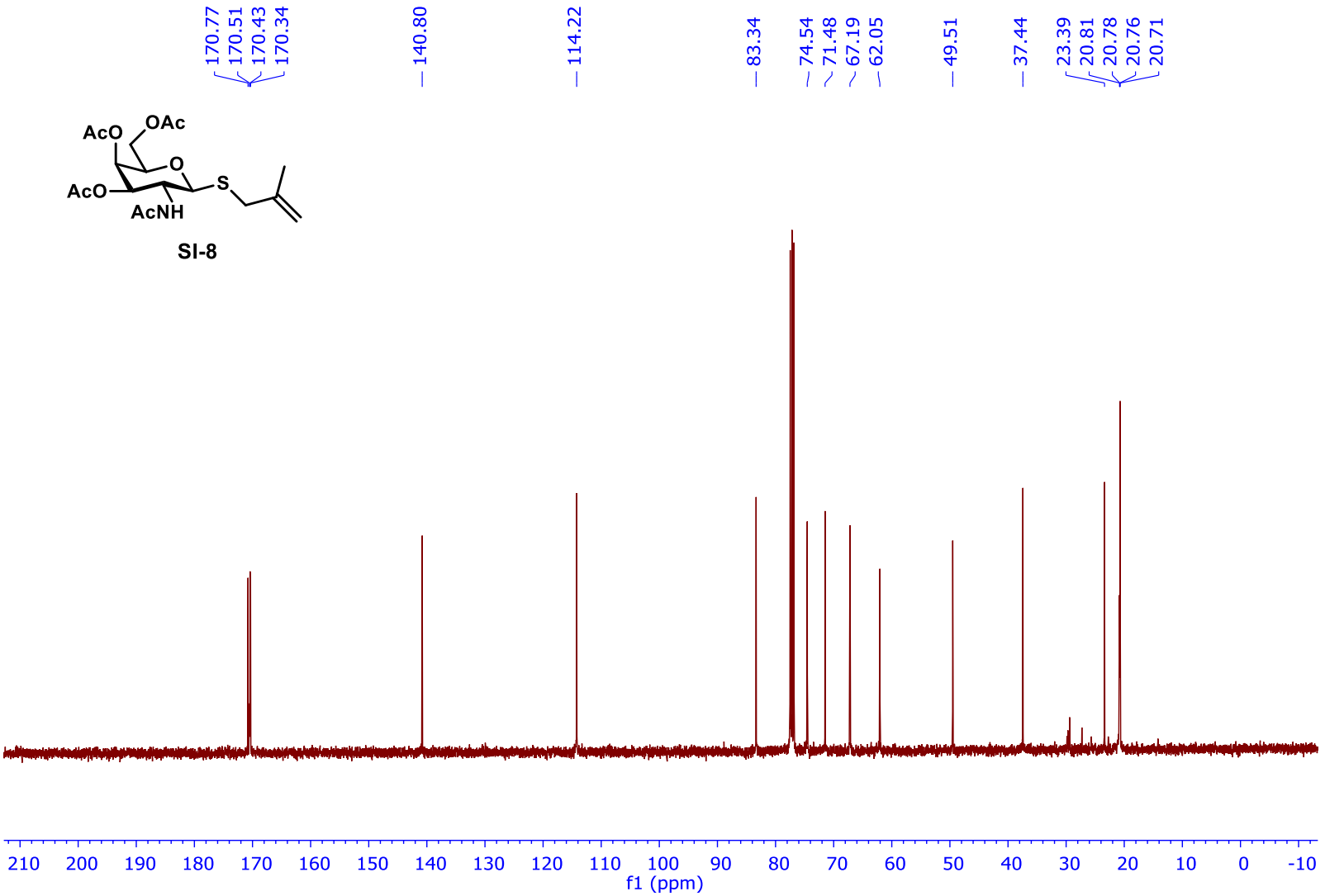
CDCl3, 400 MHz



SI-8

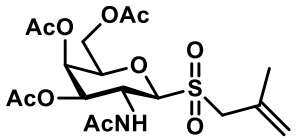


CDCl3, 101 MHz

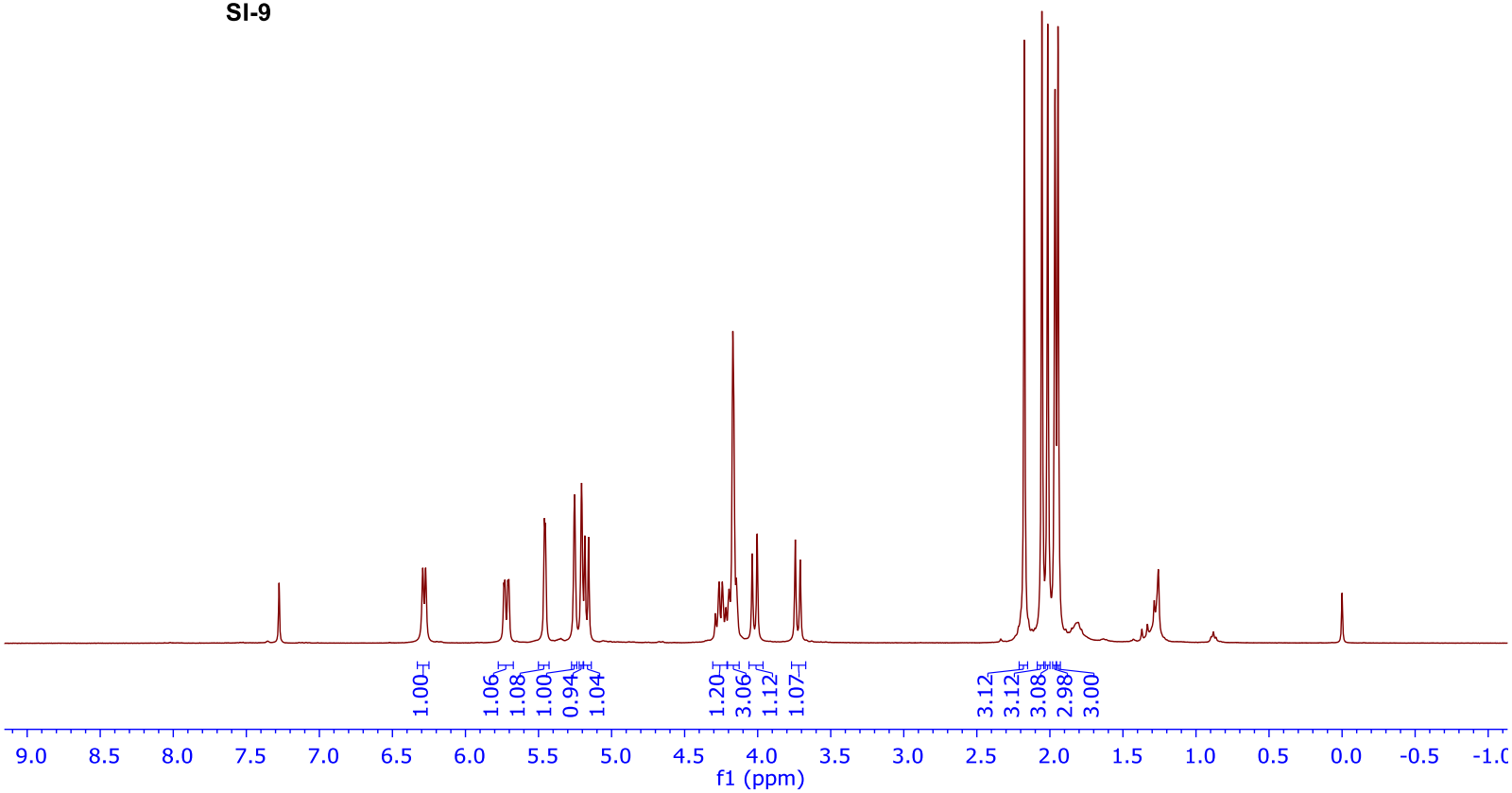


SI-8

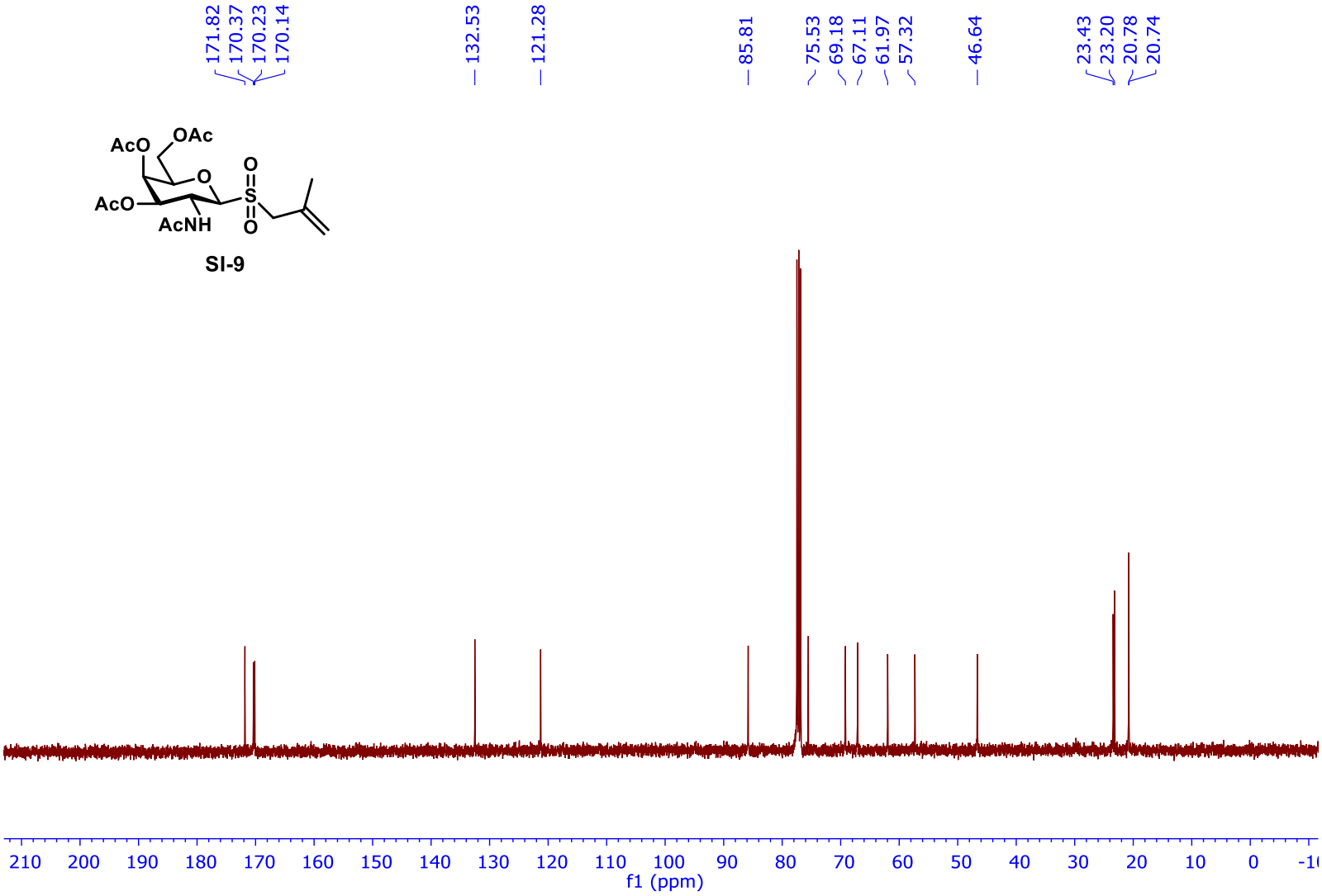
CDCl3, 400 MHz



SI-9

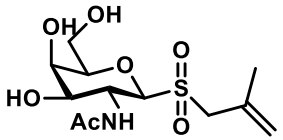


CDCl3, 101 MHz



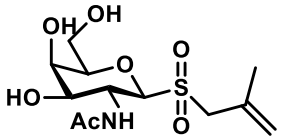
SI-9

D2O, 400 MHz



17b

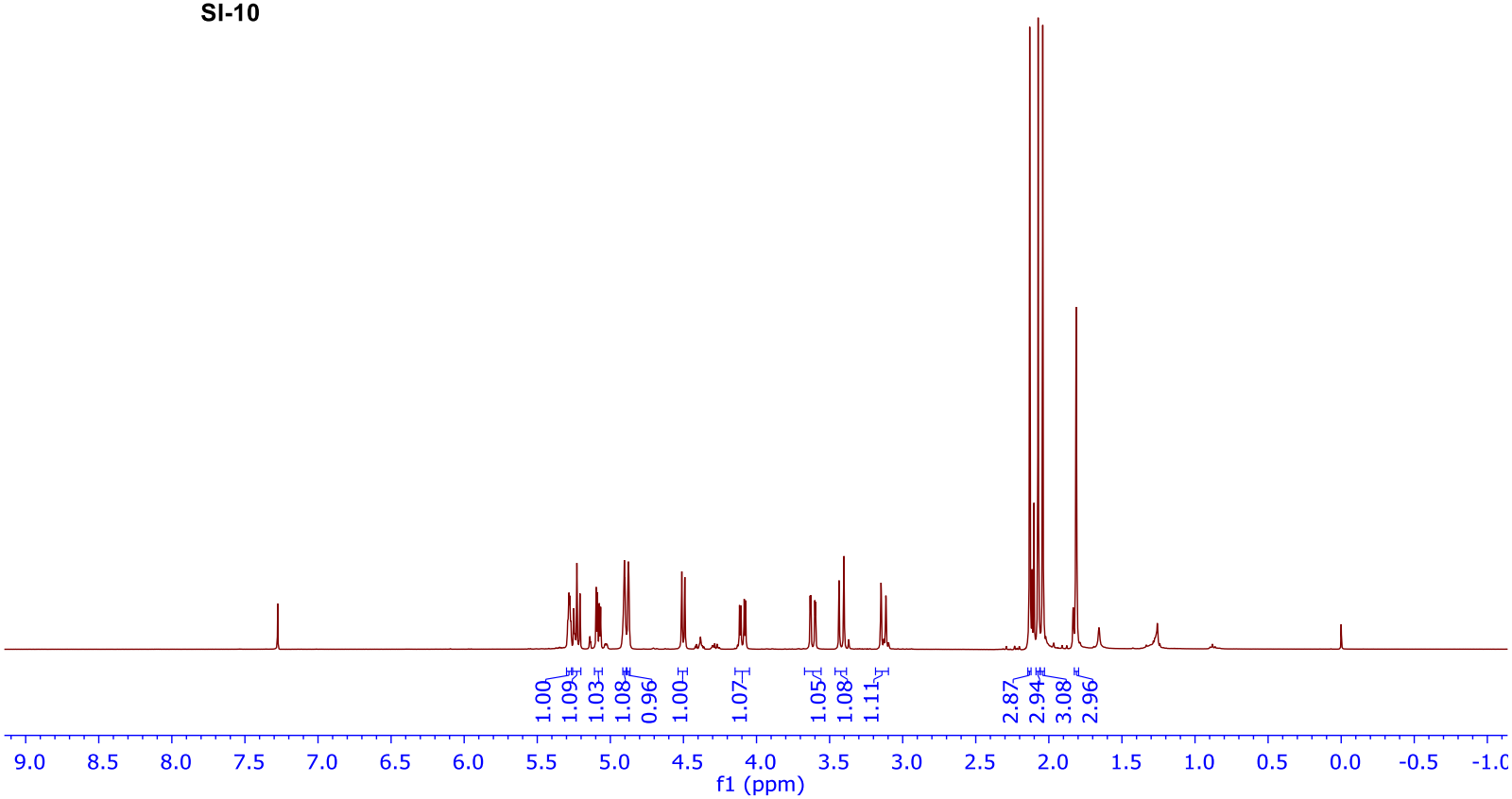
D2O, 101 MHz



17b

CDCl3, 400 MHz

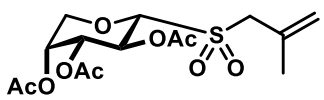
SI-10



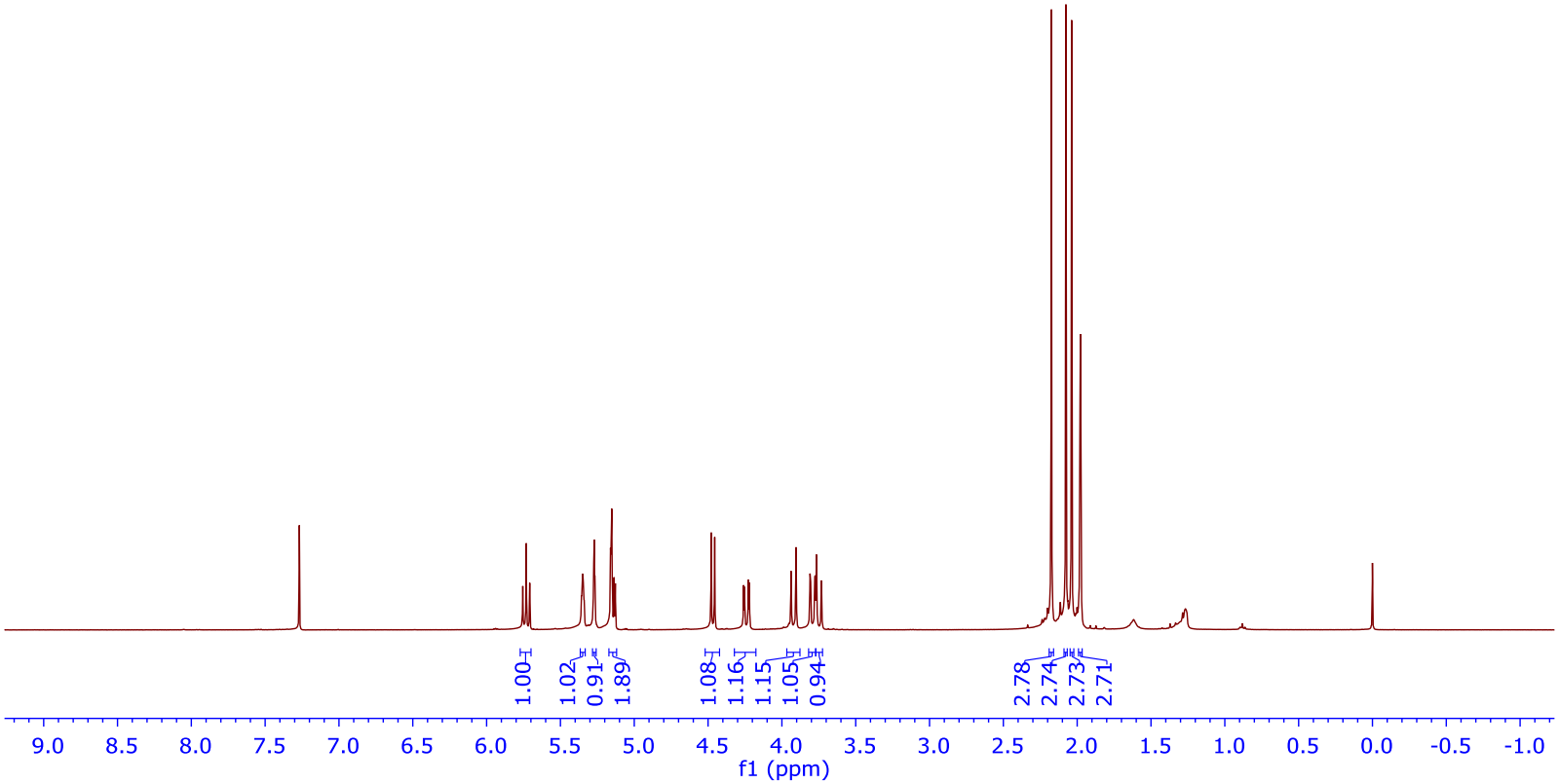
CDCl3, 101 MHz

SI-10

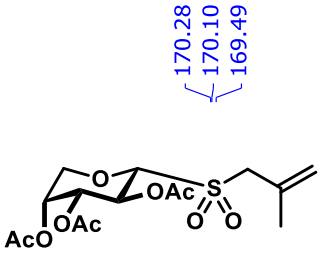
CDCl3, 400 MHz



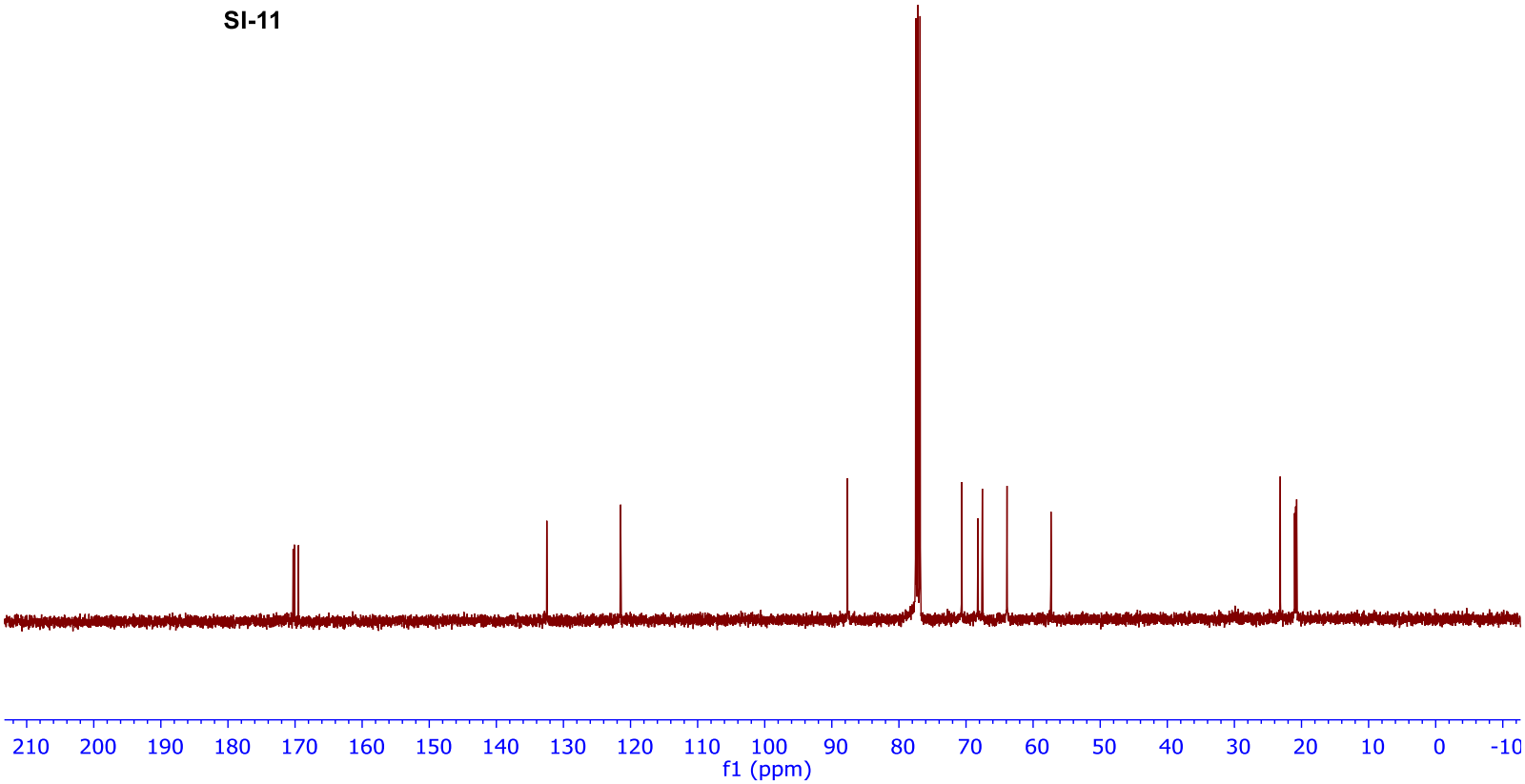
SI-11



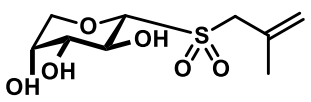
CDCl3, 101 MHz



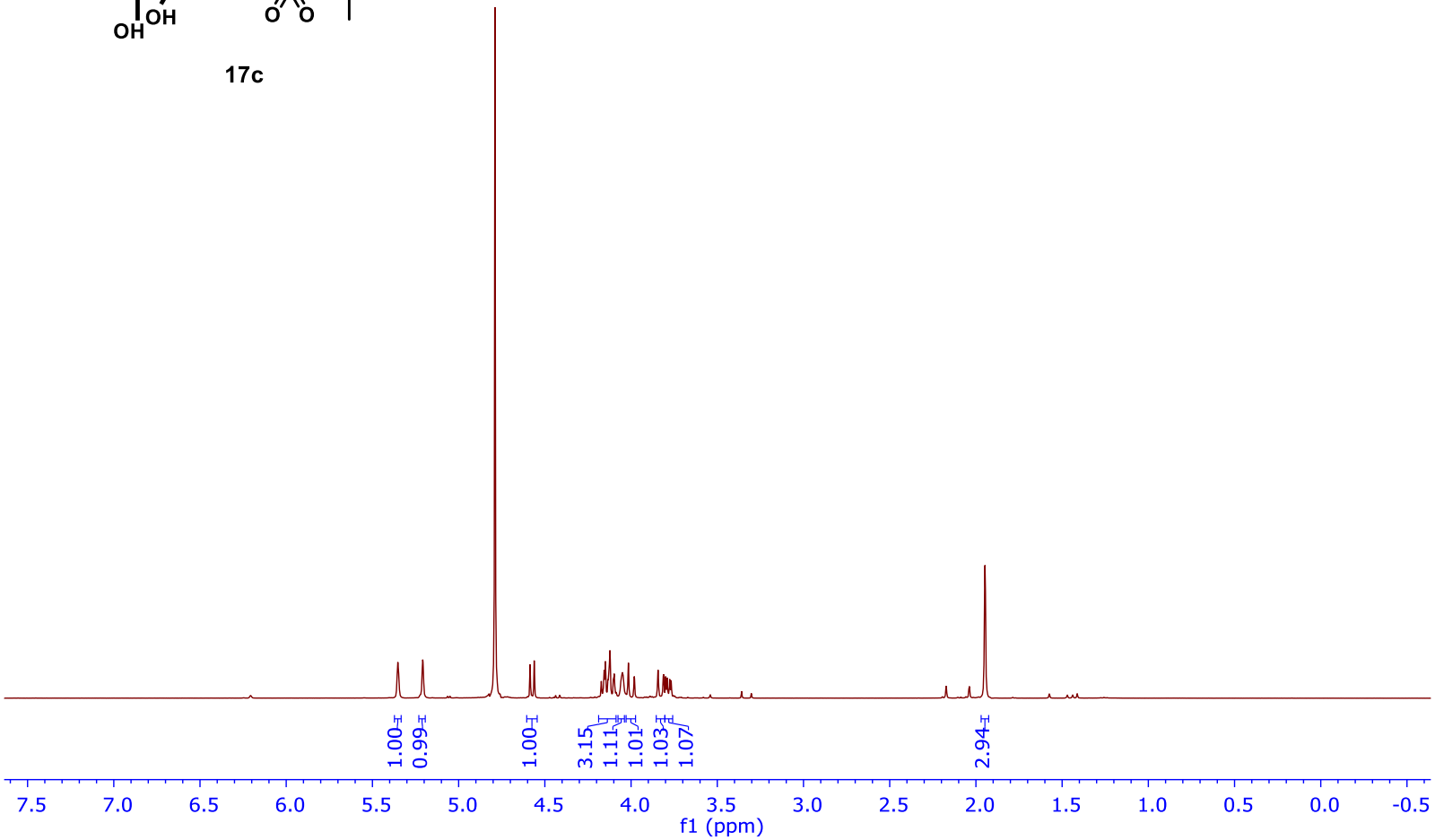
SI-11



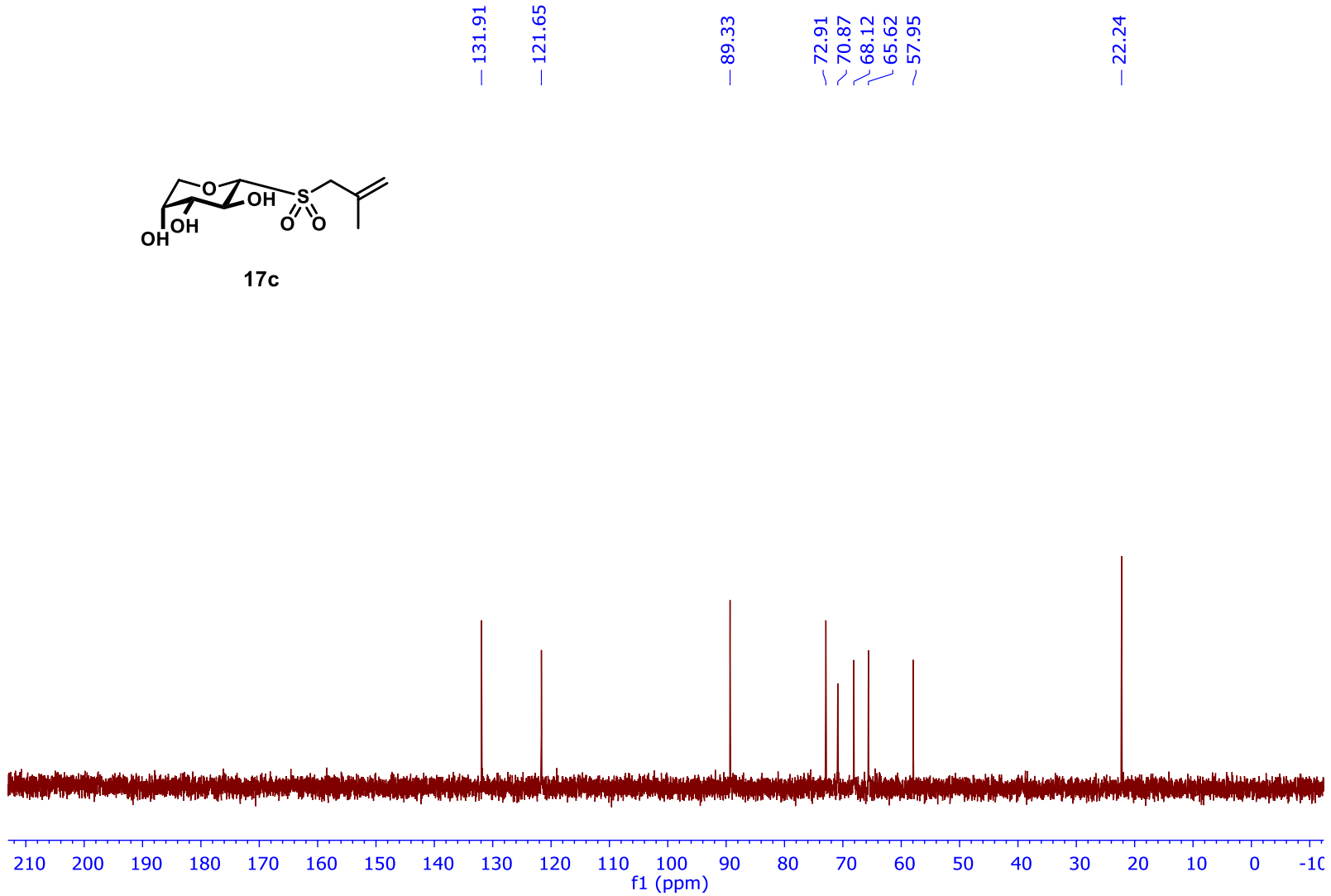
D2O, 400 MHz



17c



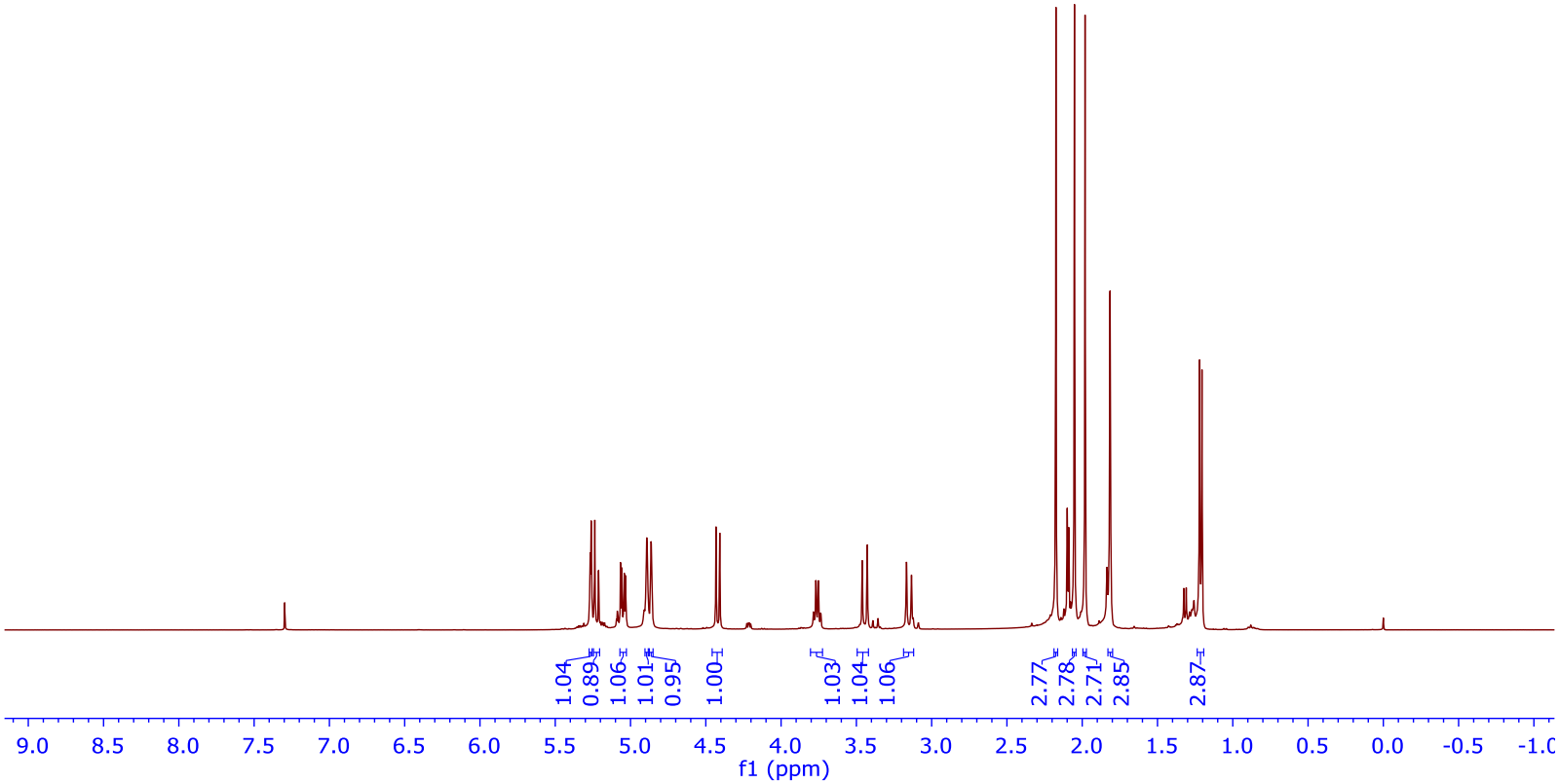
D2O, 101 MHz



17c

CDCl3, 400 MHz

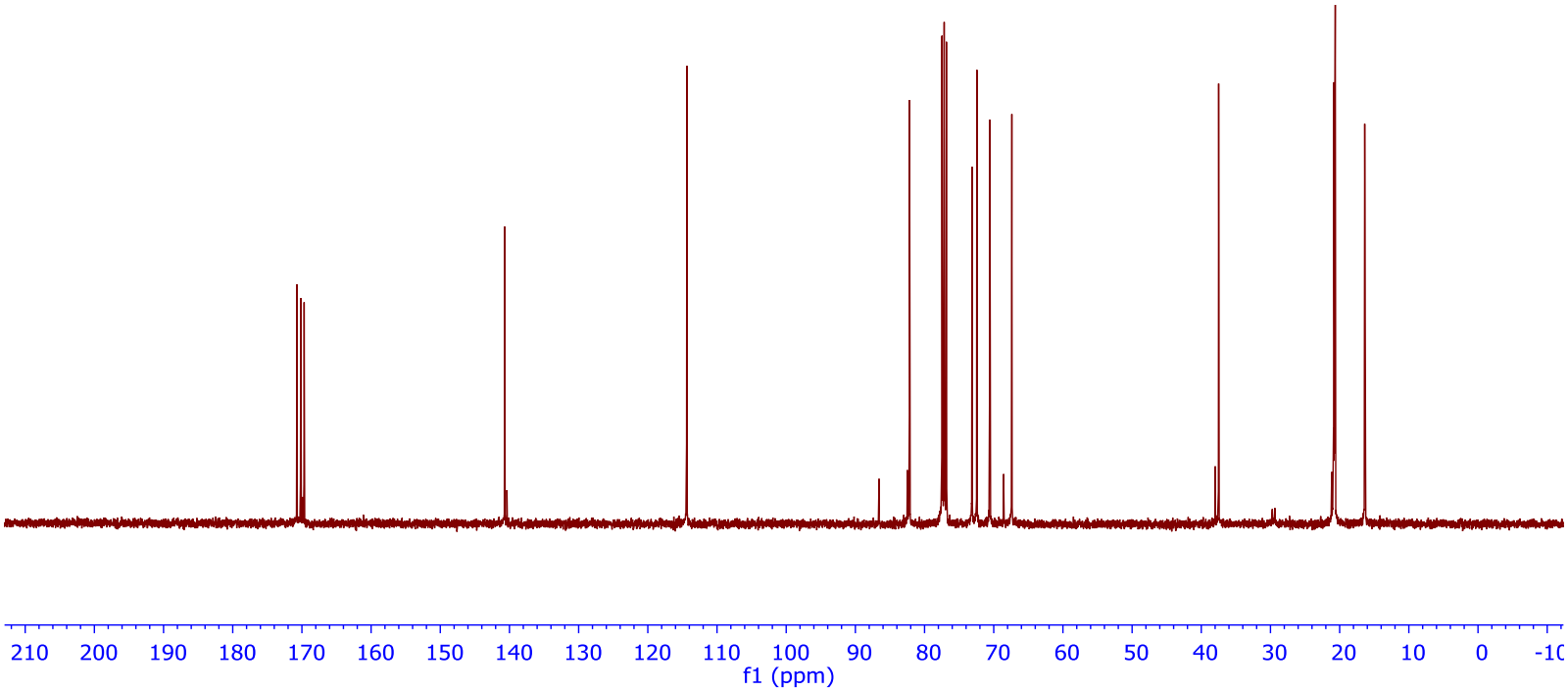
SI-12



CDCl3, 101 MHz

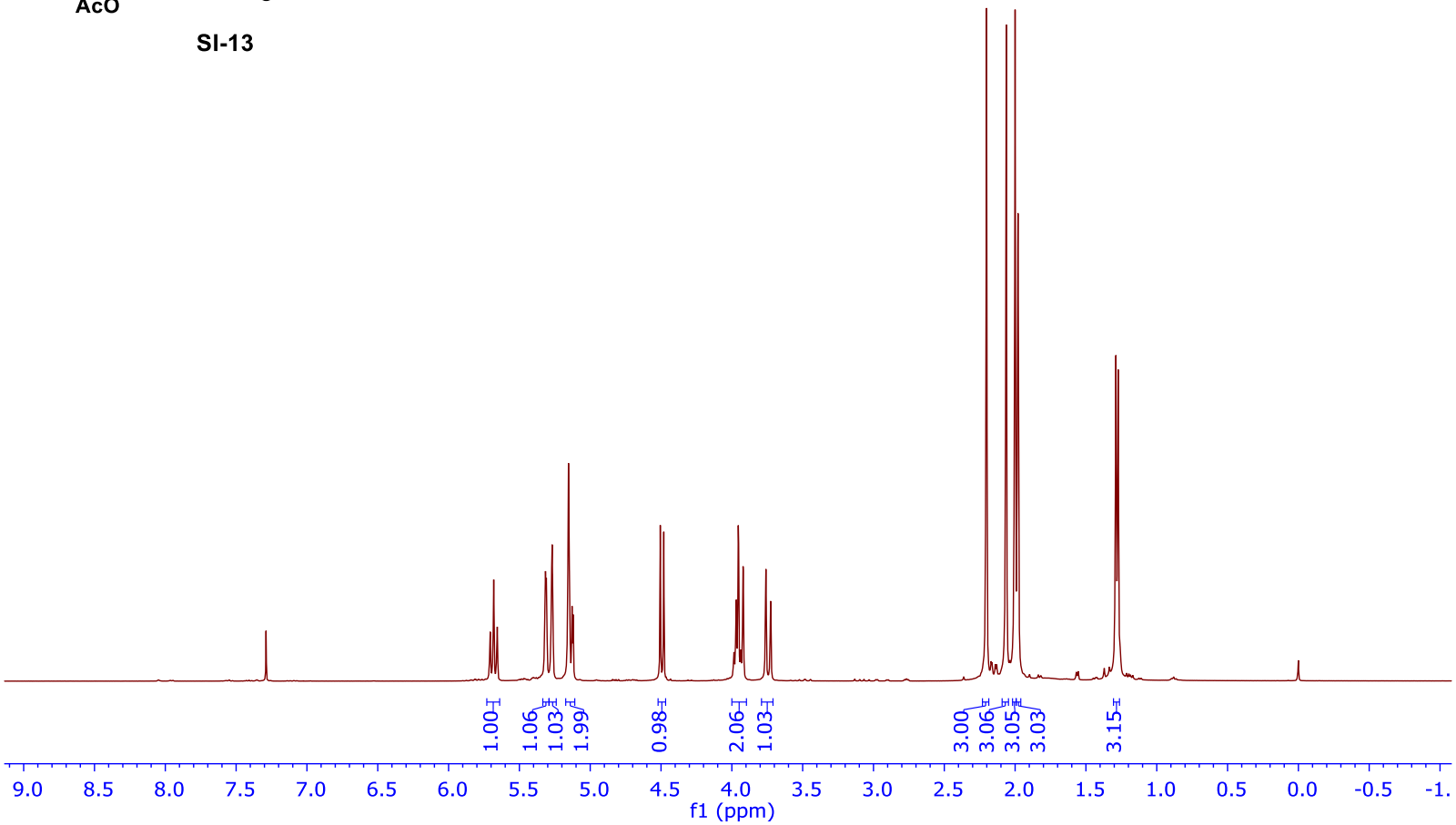
170.71
170.16
169.67
140.67
114.35
82.17
73.13
72.44
70.56
67.38
37.49
20.84
20.75
20.68
20.63
16.38

SI-12

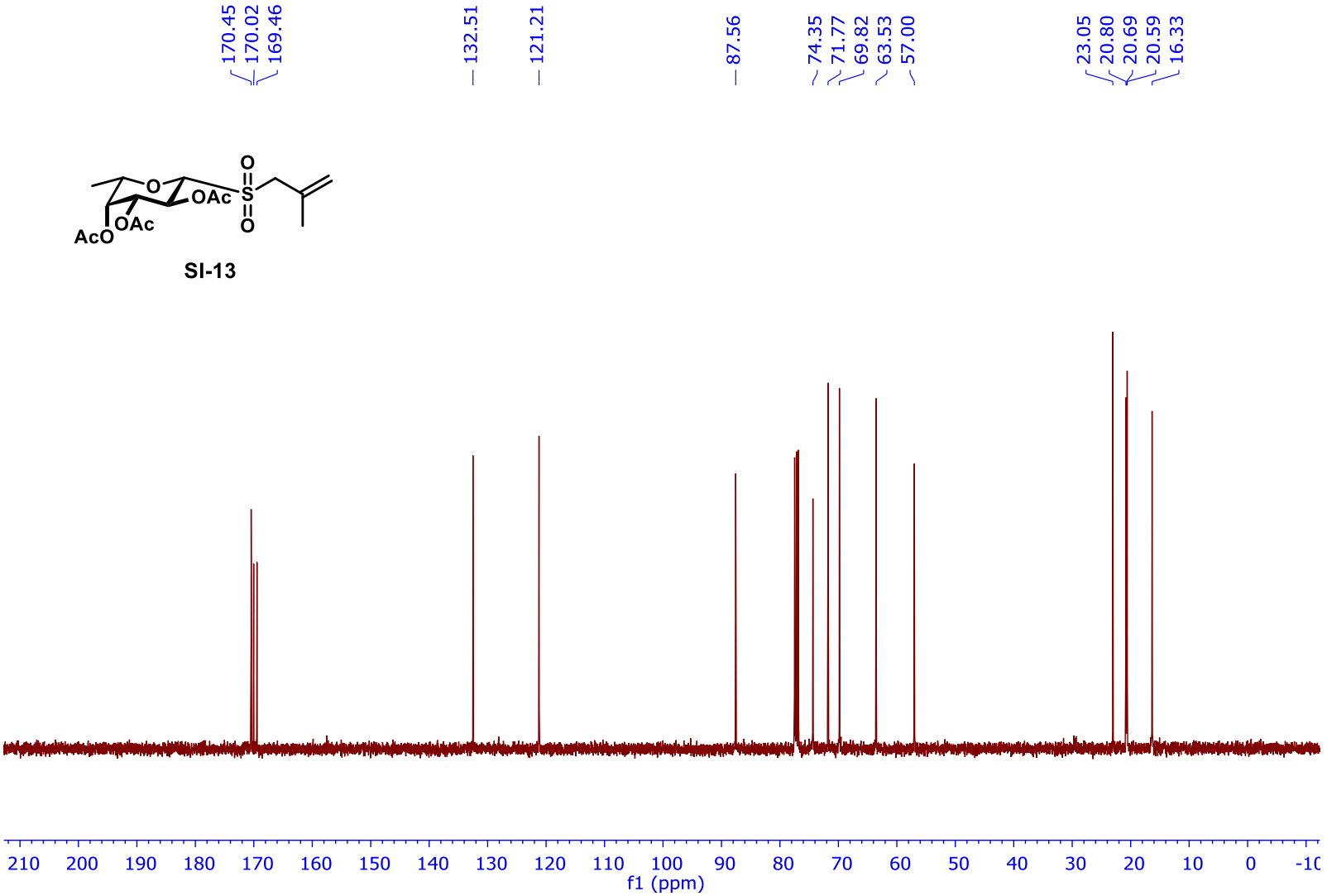


CDCl3, 400 MHz

SI-13

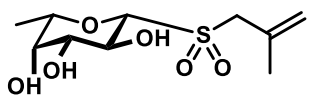


CDCl3, 101 MHz



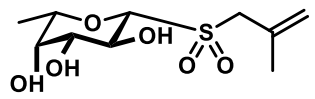
SI-13

D2O, 400 MHz

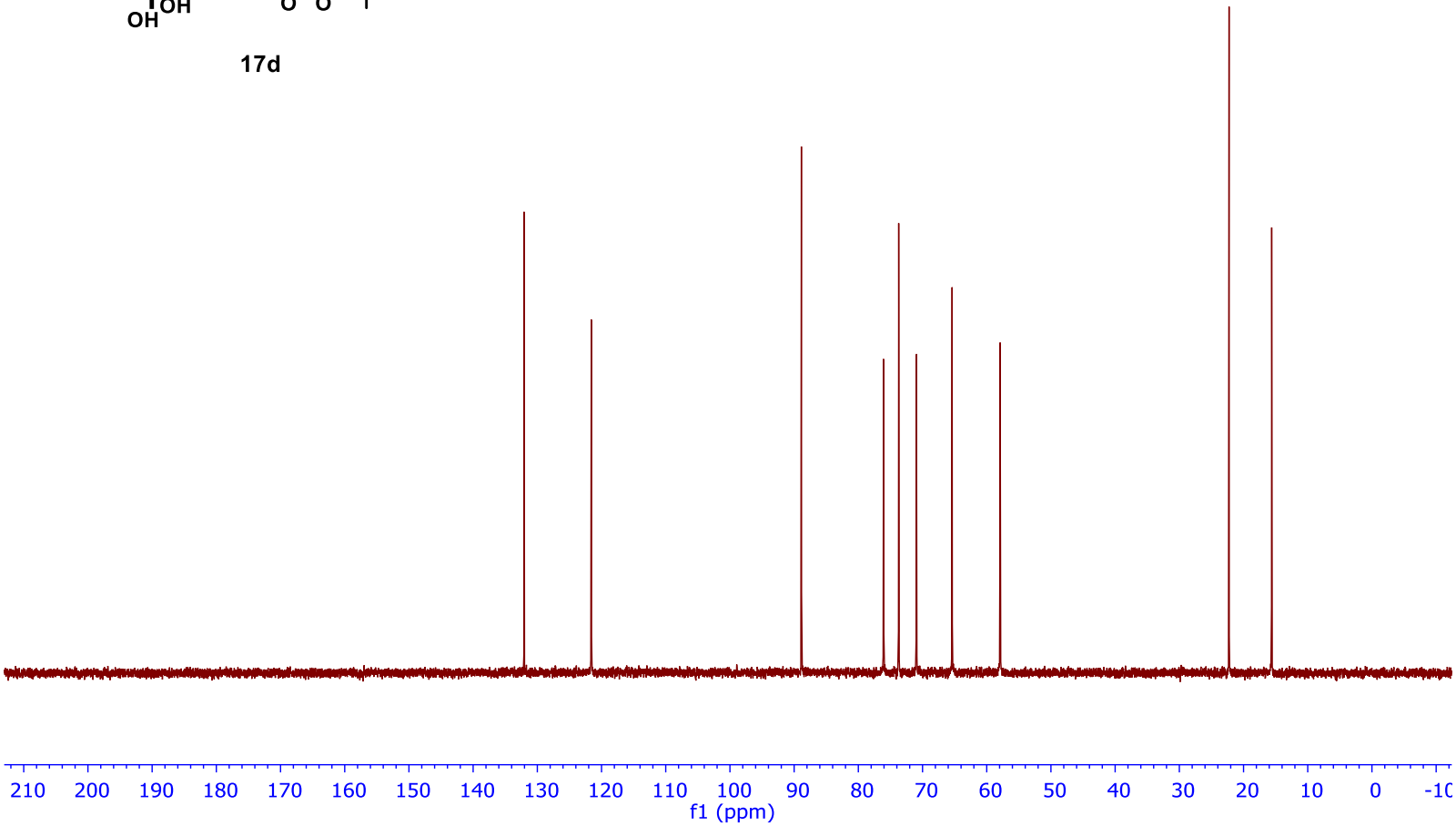


17d

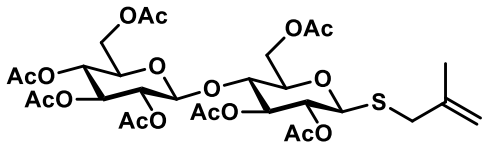
D2O, 101 MHz



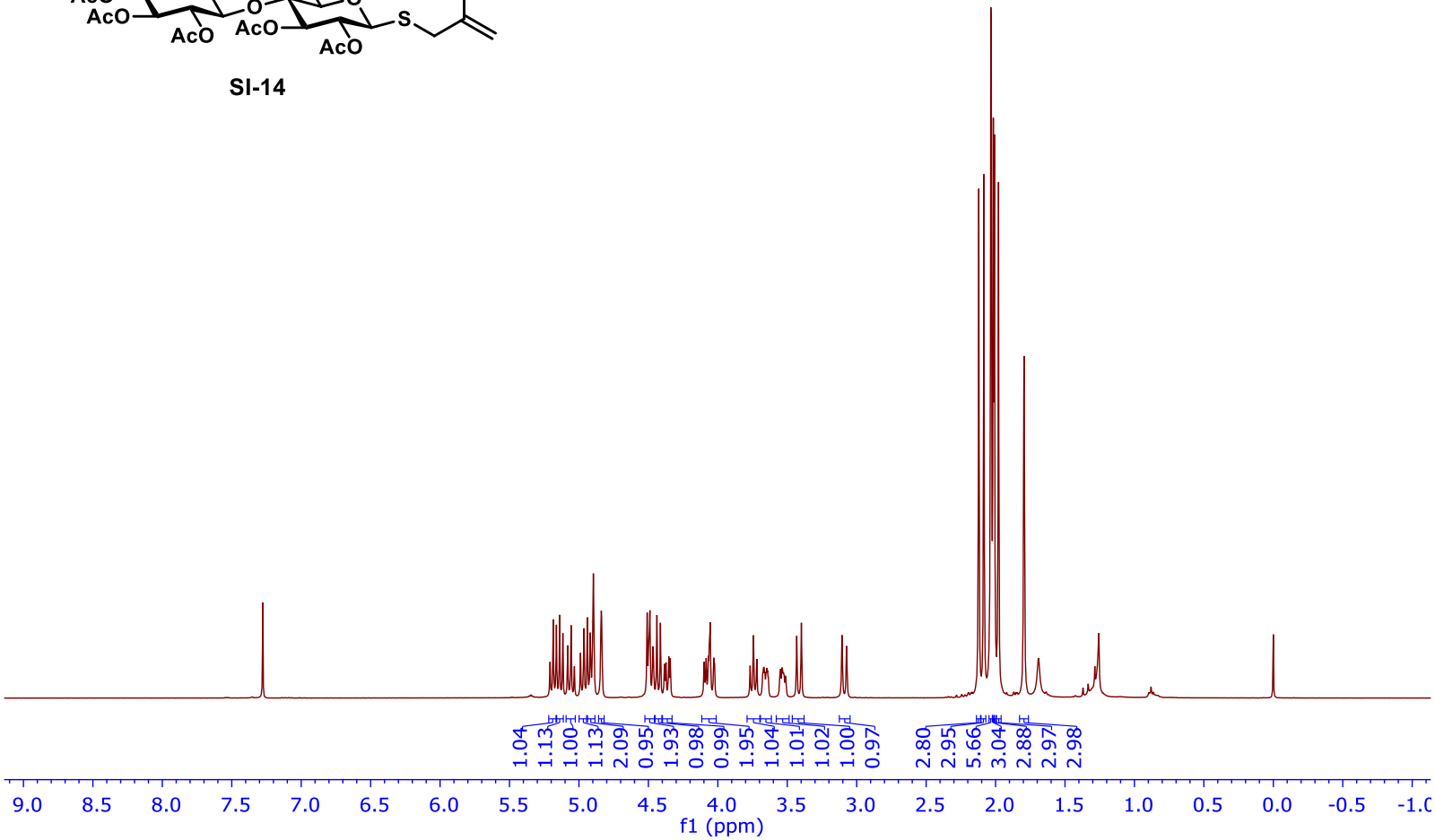
17d



CDCl3, 400 MHz

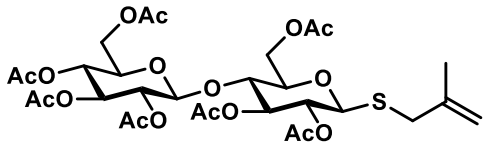


SI-14

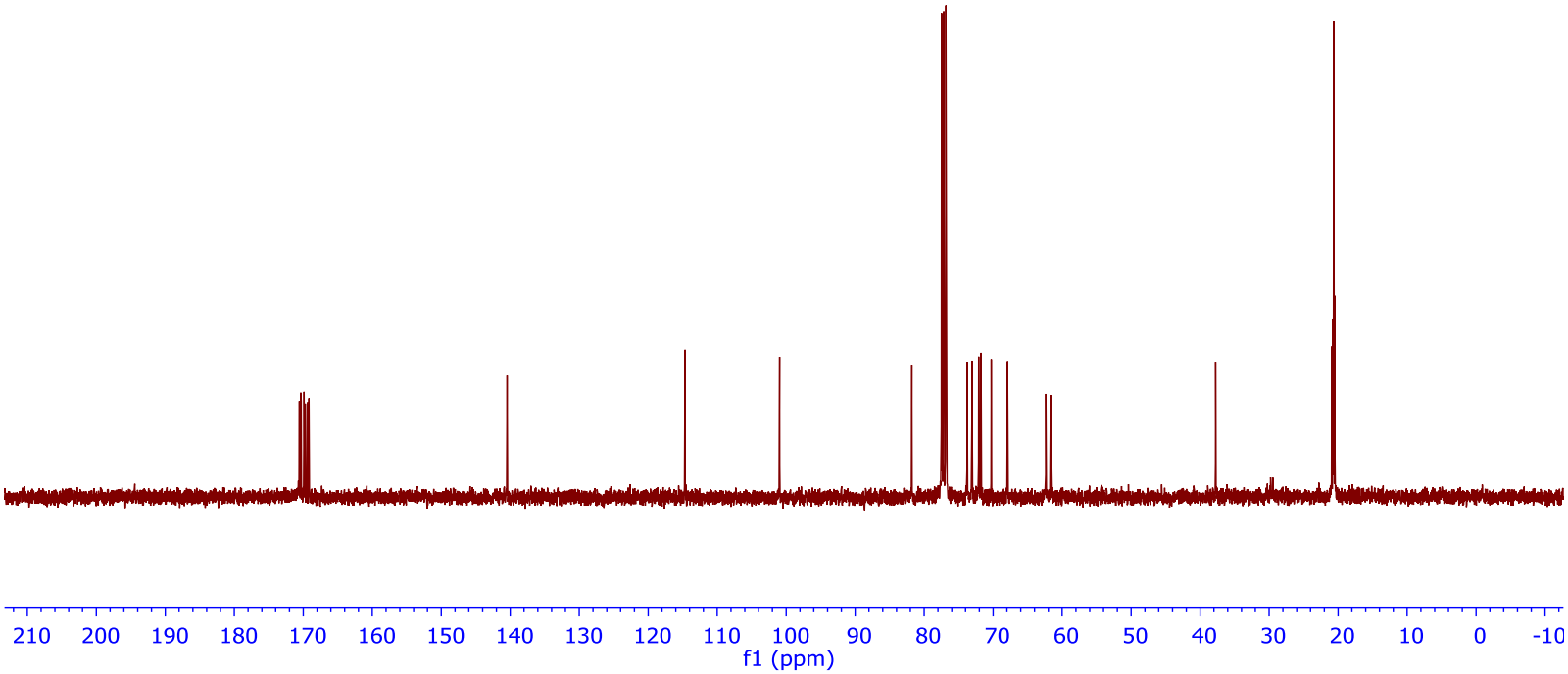


CDCl3, 101 MHz

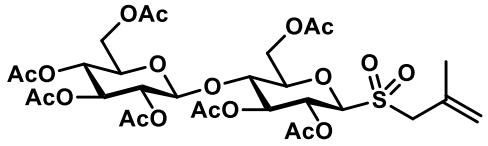
170.57
170.36
170.29
169.88
169.71
169.40
169.17
140.45
114.66
100.95
81.78
76.75
76.73
73.77
73.07
72.09
71.75
70.27
67.91
62.36
61.69
37.75
20.92
20.78
20.75
20.64
20.49



SI-14

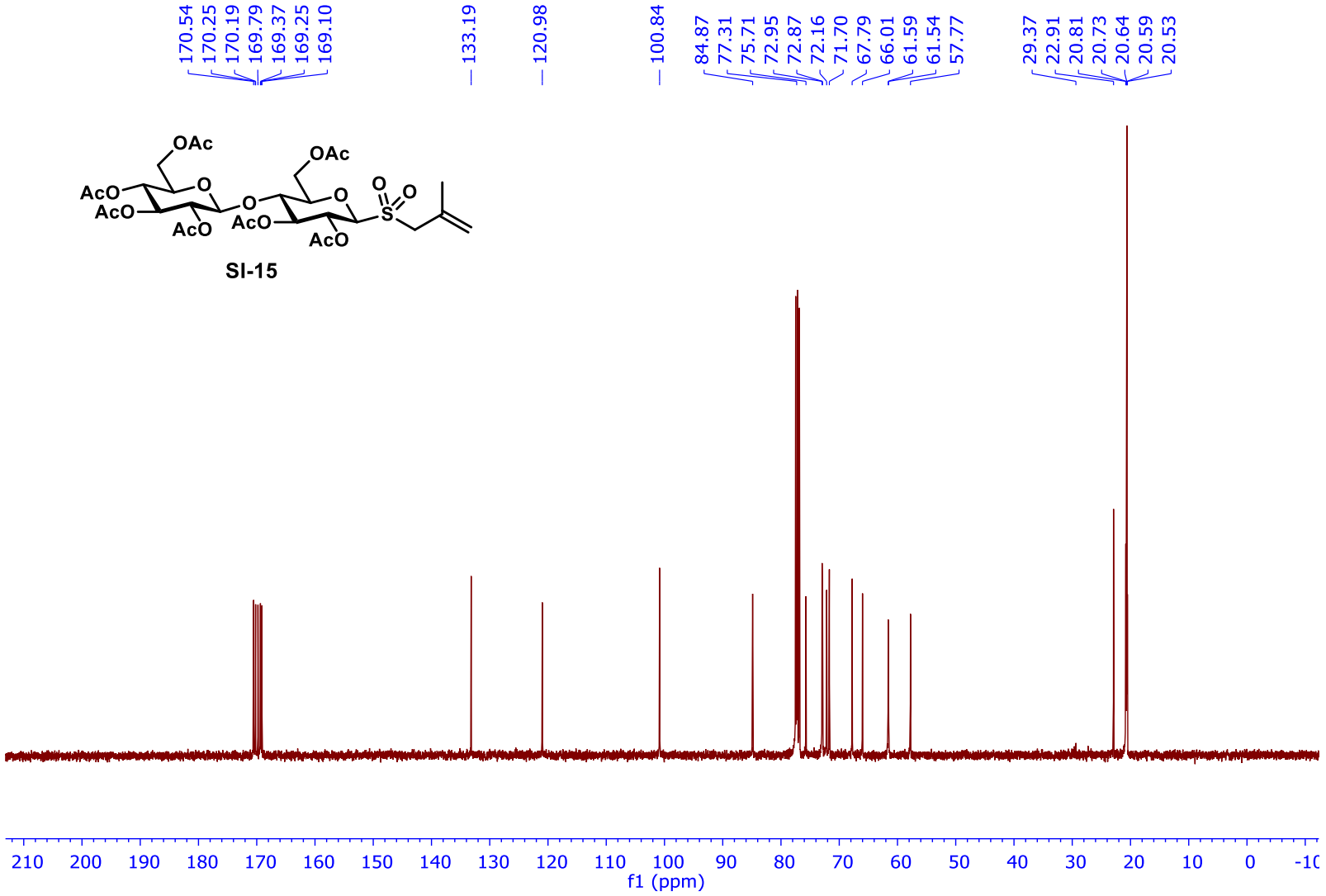


CDCl3, 400 MHz



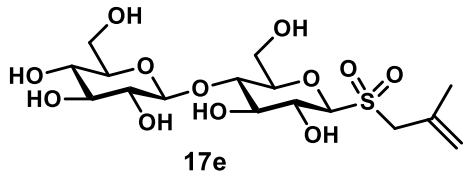
SI-15

CDCl3, 101 MHz



SI-15

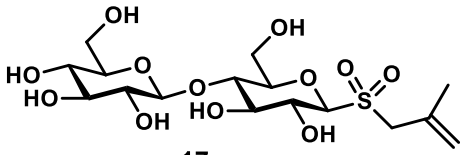
D2O, 400 MHz



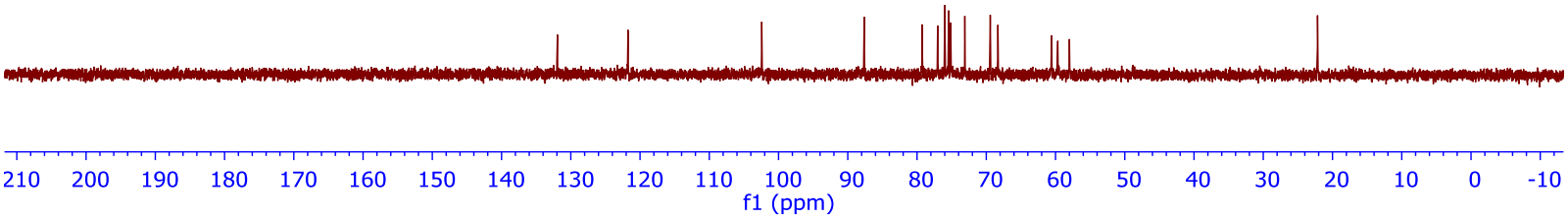
17e

D2O, 101 MHz

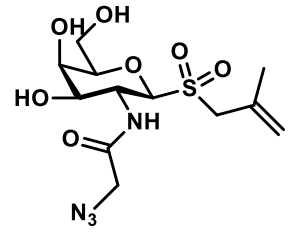
131.93
121.74
102.42
87.63
79.25
77.02
76.00
75.45
75.14
73.10
69.43
68.32
60.57
59.67
57.99
22.17



17e

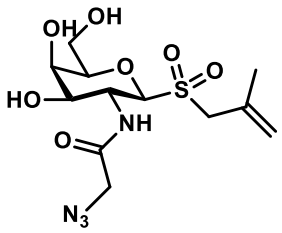


CD3OD, 400 MHz



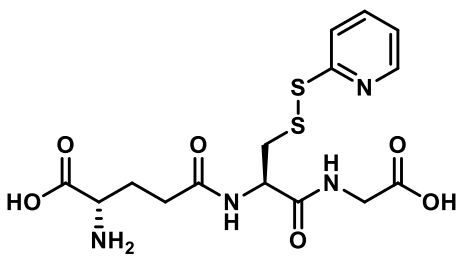
17f

CD3OD, 400 MHz



17f

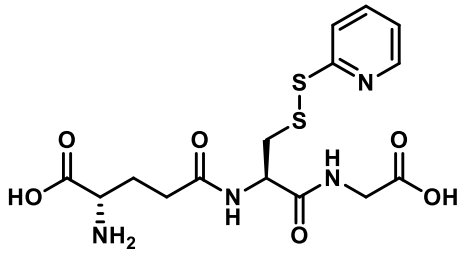
D2O, 400 MHz



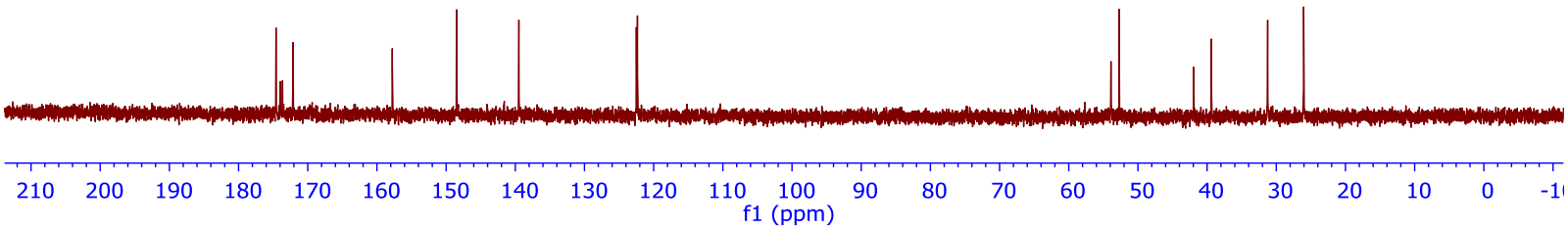
16

D2O, 101 MHz

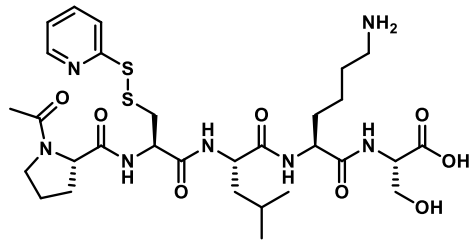
174.59
173.99
173.65
172.13
157.78
148.50
139.48
122.50
122.34
53.90
52.71
41.95
39.38
31.25
26.04



16



D2O, 400 MHz

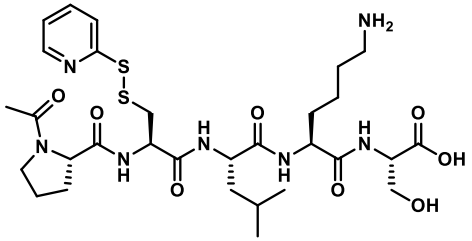


14a

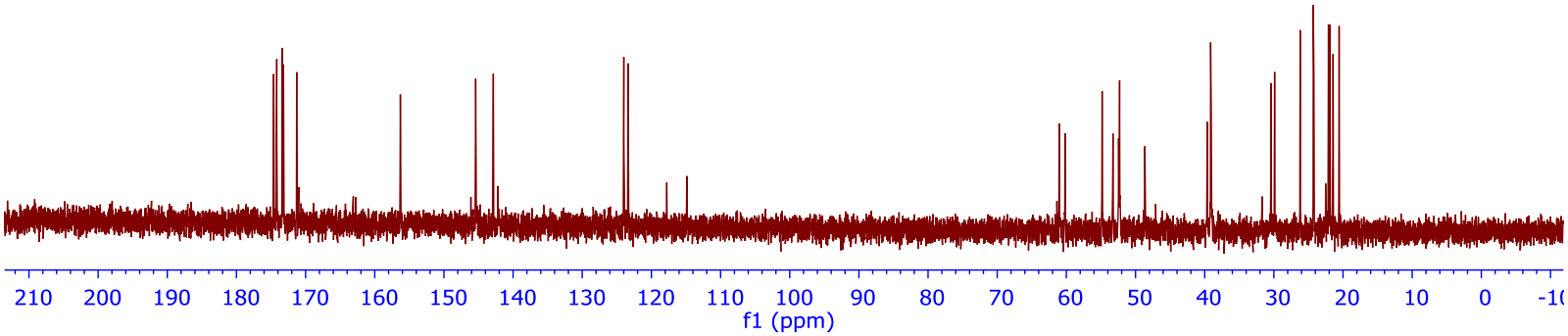
D2O, 101 MHz

174.62
174.17
173.39
173.28
173.20
171.29
156.30
145.41
142.86
123.99
123.37

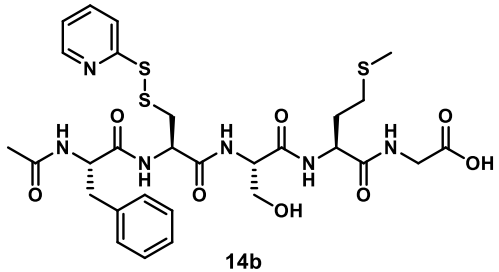
61.03
60.20
54.83
53.27
52.45
52.30
48.65
39.65
39.14
39.06
30.40
29.89
26.19
24.30
24.21
22.10
21.89
21.43
20.56



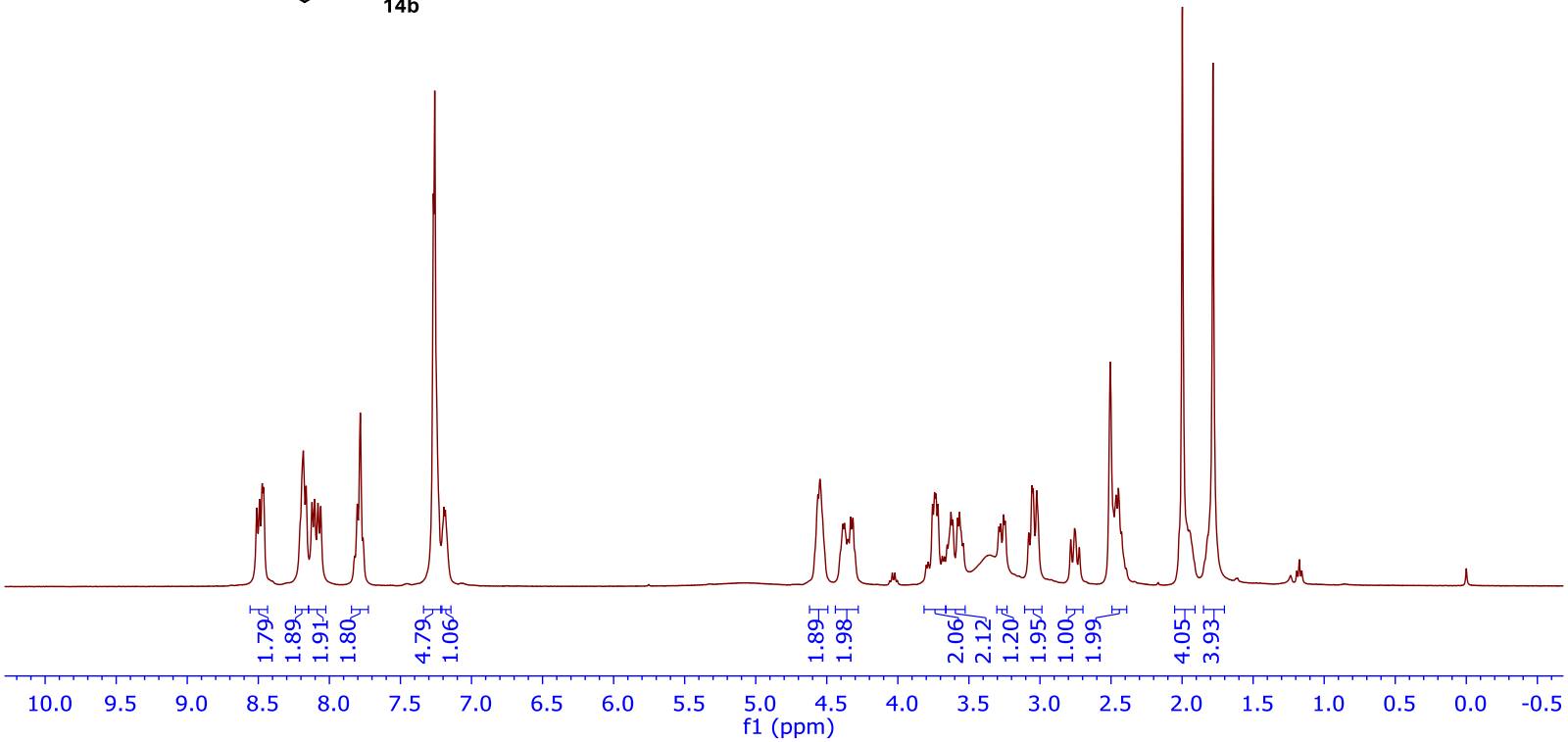
14a



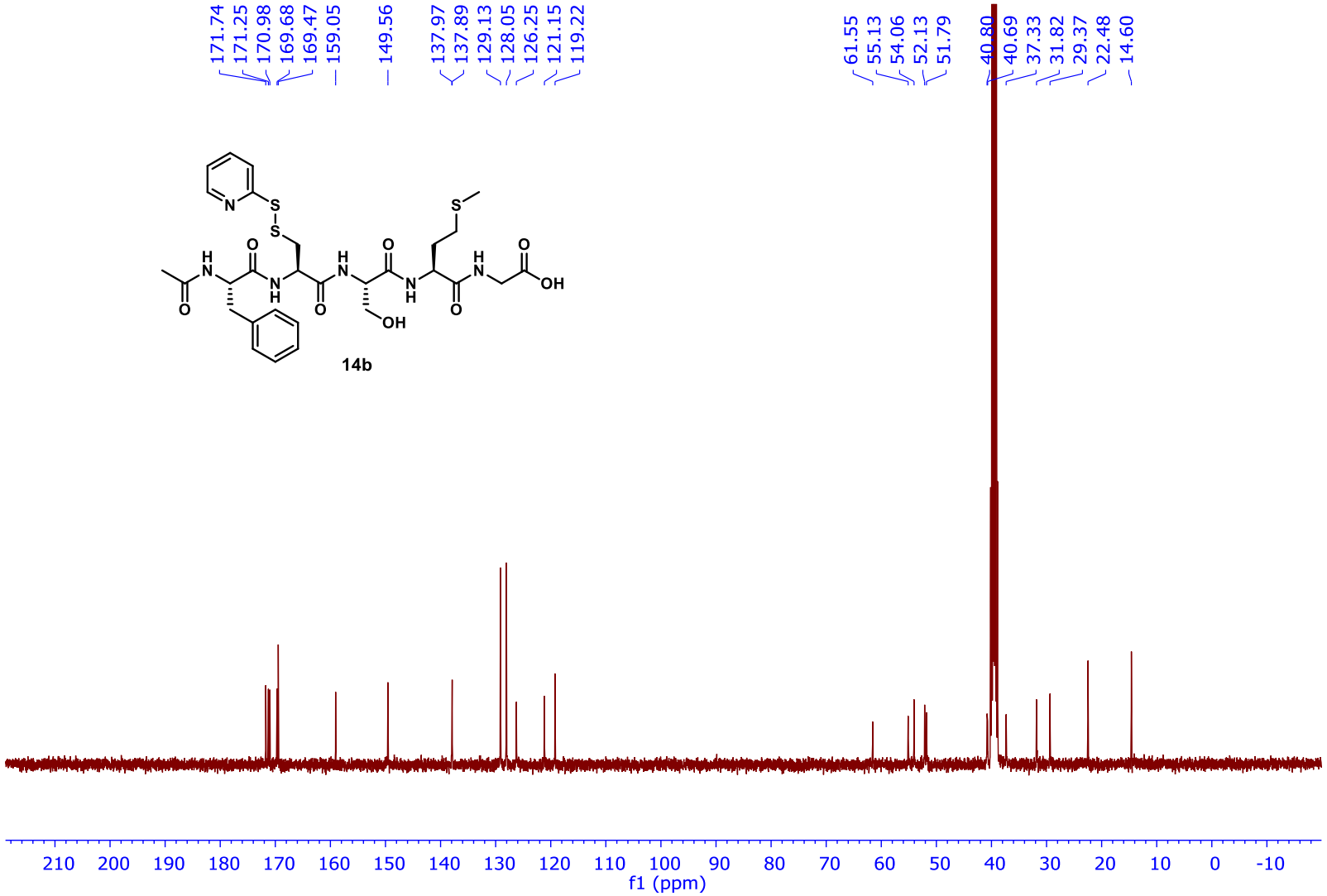
DMSO, 400 MHz



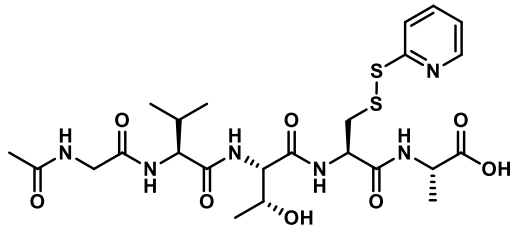
14b



DMSO, 101 MHz

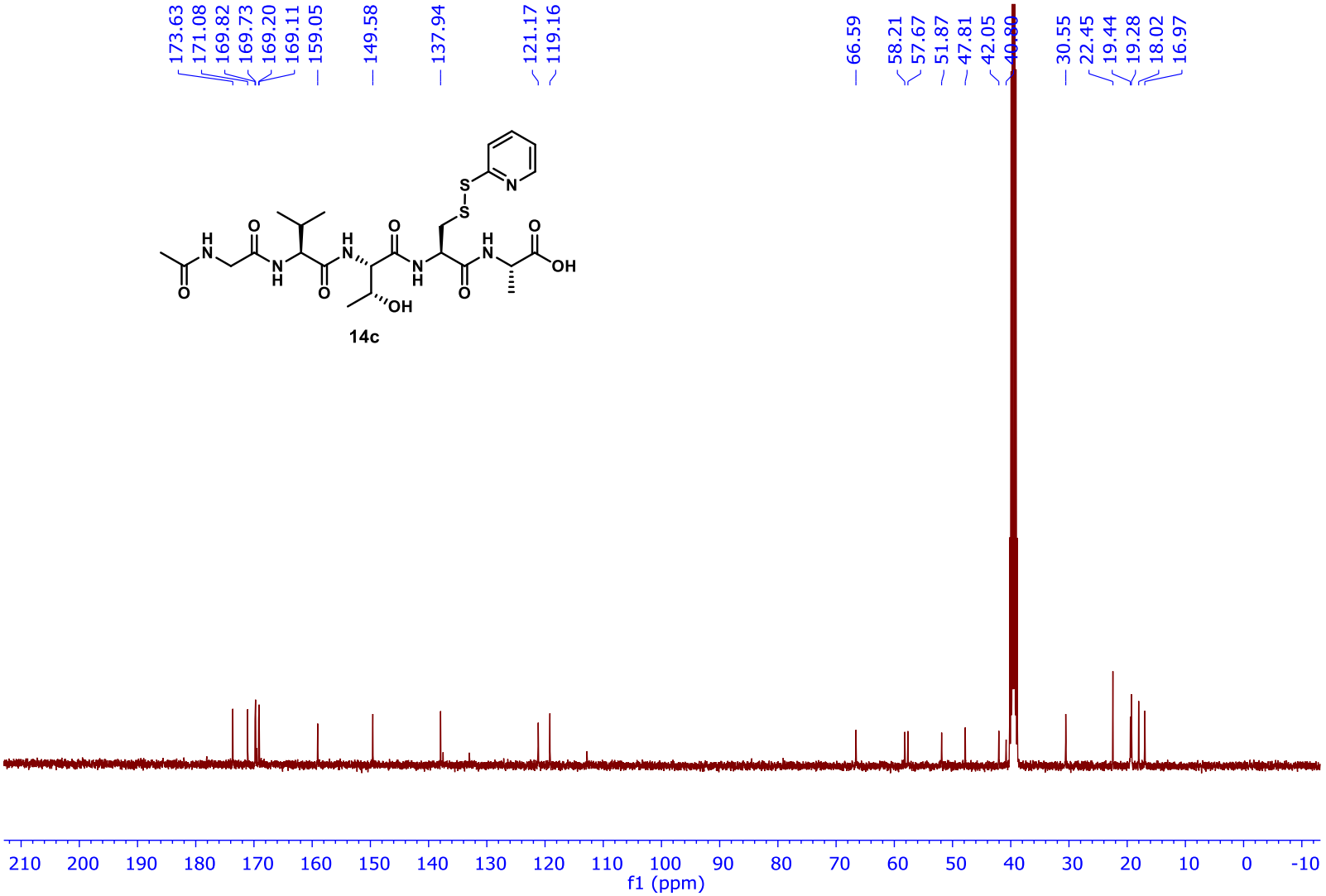

171.74
171.25
170.98
169.68
169.47
159.05
149.56
137.97
137.89
129.13
128.05
126.25
121.15
119.22
61.55
55.13
54.06
52.13
51.79
40.80
40.69
37.33
31.82
29.37
22.48
14.60
14b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

DMSO, 400 MHz

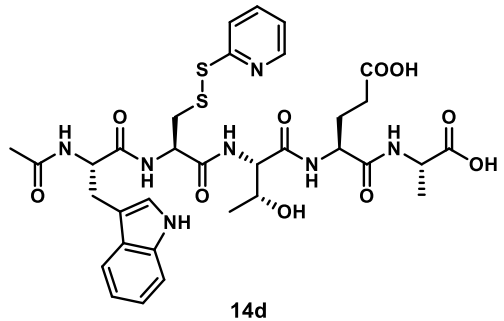


14c

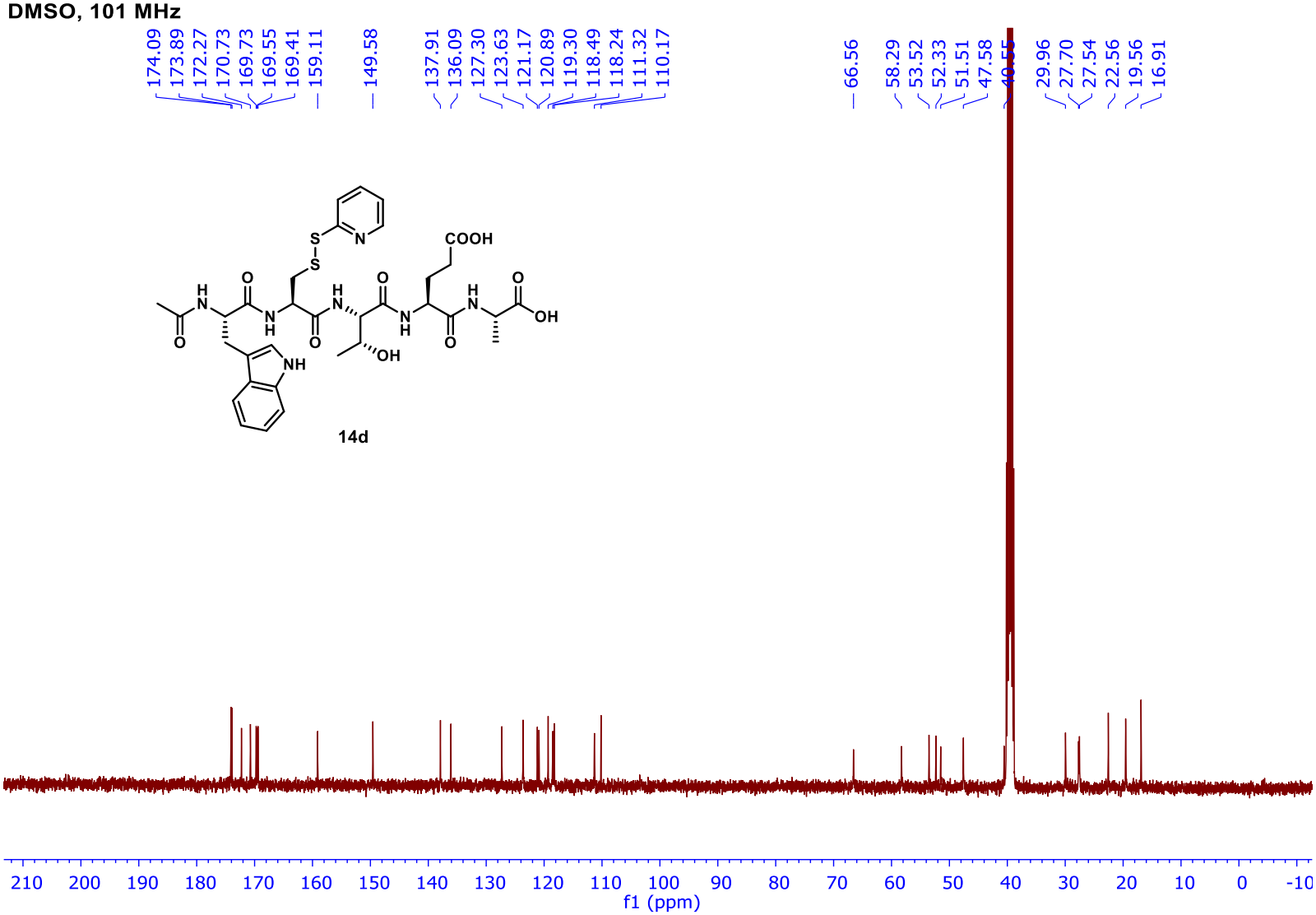
DMSO, 101 MHz


173.63
171.08
169.82
169.73
169.20
169.11
159.05
149.58
137.94
121.17
119.16
66.59
58.21
57.67
51.87
47.81
42.05
40.80
30.55
22.45
19.44
19.28
18.02
16.97
14c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

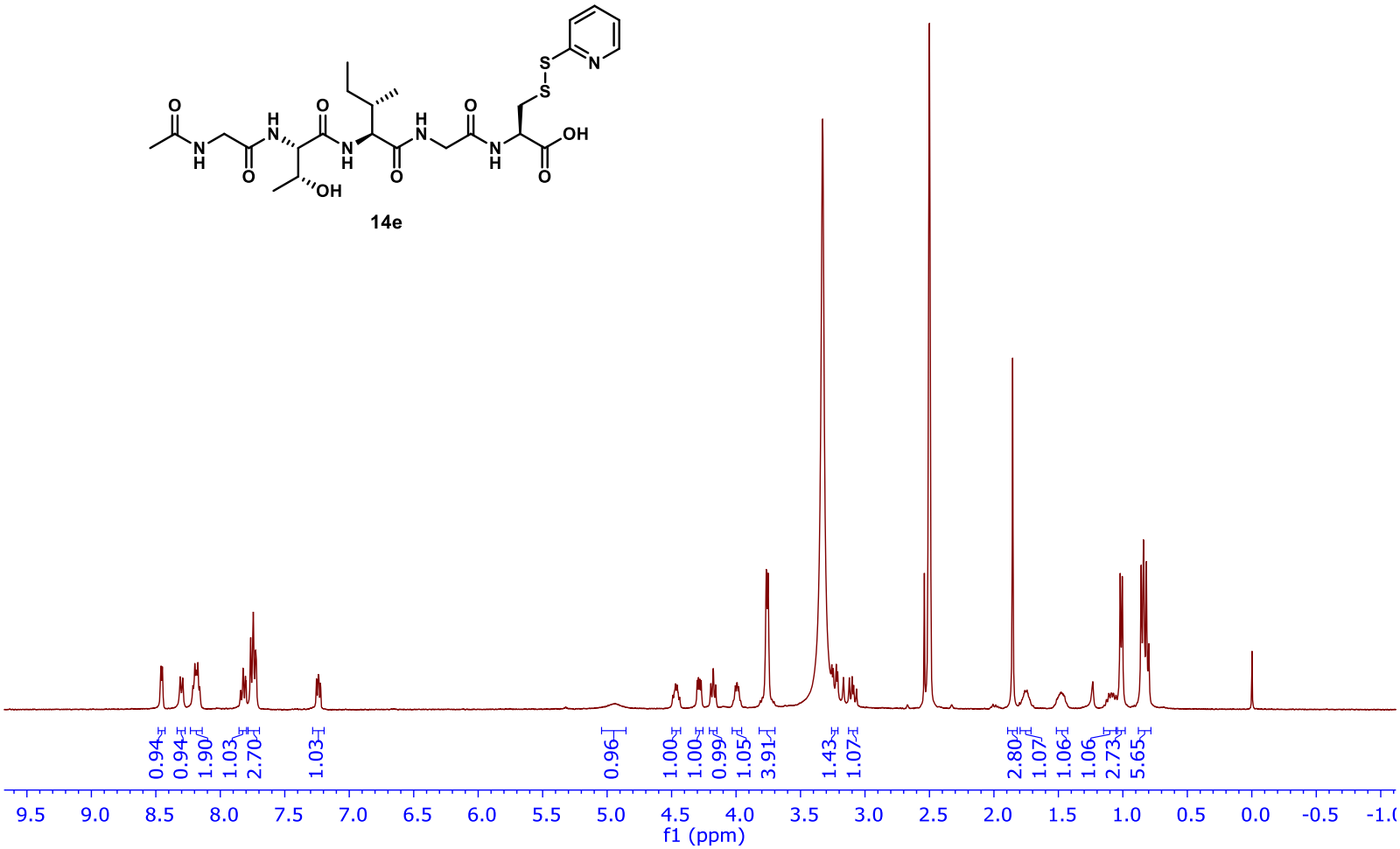
DMSO, 400 MHz

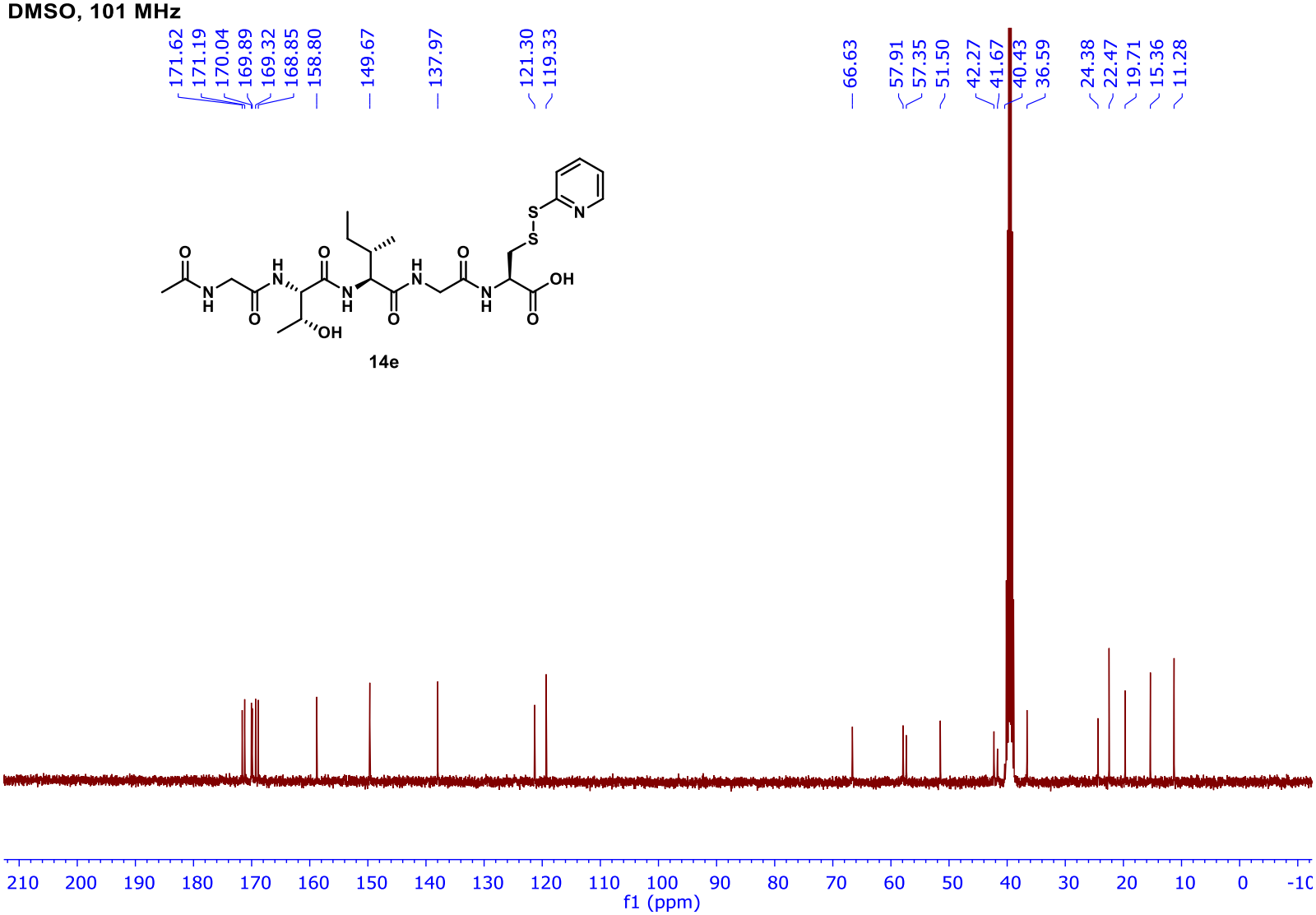


14d

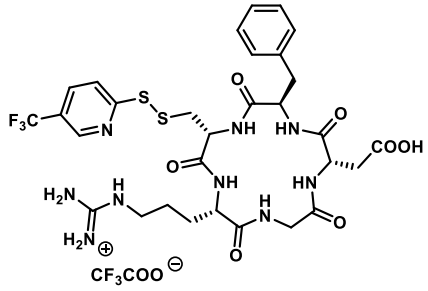

DMSO, 101 MHz
174.09
173.89
172.27
170.73
169.73
169.55
169.41
159.11
149.58
137.91
136.09
127.30
123.63
121.17
120.89
119.30
118.49
118.24
111.32
110.17
66.56
58.29
53.52
52.33
51.51
47.58
40.55
29.96
27.70
27.54
22.56
19.56
16.91
COOH
OH
OH
NH
14d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

DMSO, 400 MHz


14e
0.94
0.94
1.90
1.03
2.70
1.03
0.96
1.00
1.00
0.99
1.05
3.91
1.43
1.07
2.80
1.07
1.06
1.06
2.73
5.65
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

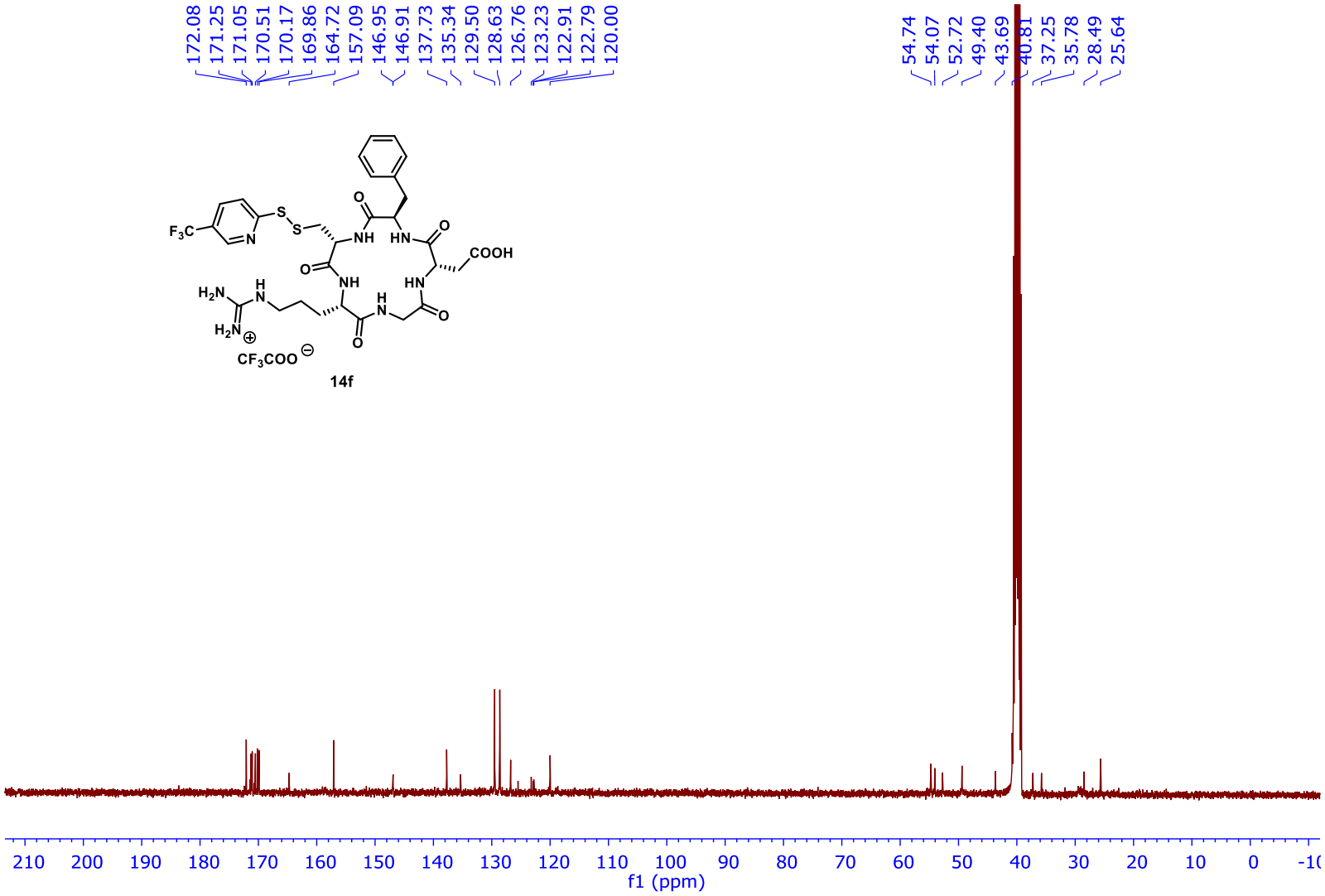

DMSO, 101 MHz
171.62
171.19
170.04
169.89
169.32
168.85
158.80
149.67
137.97
121.30
119.33
66.63
57.91
57.35
51.50
42.27
41.67
40.43
36.59
24.38
22.47
19.71
15.36
11.28
14e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

DMSO 400 MHz

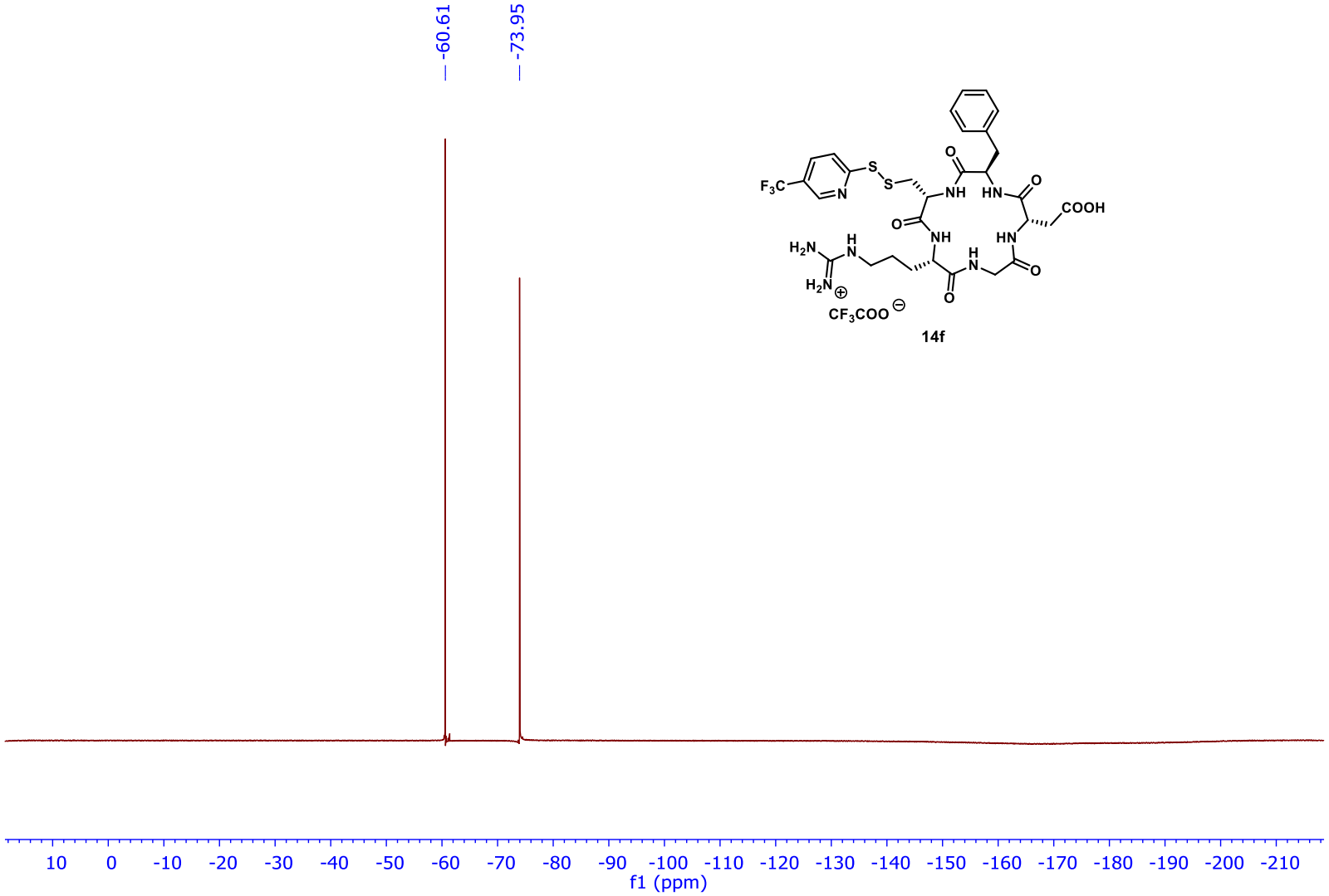


14f

DMSO 101 MHz

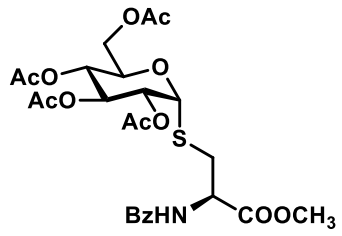

172.08
171.25
171.05
170.51
170.17
169.86
164.72
157.09
146.95
146.91
137.73
135.34
129.50
128.63
126.76
123.23
122.91
122.79
120.00
54.74
54.07
52.72
49.40
43.69
40.81
37.25
35.78
28.49
25.64
14f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

DMSO 376 MHz

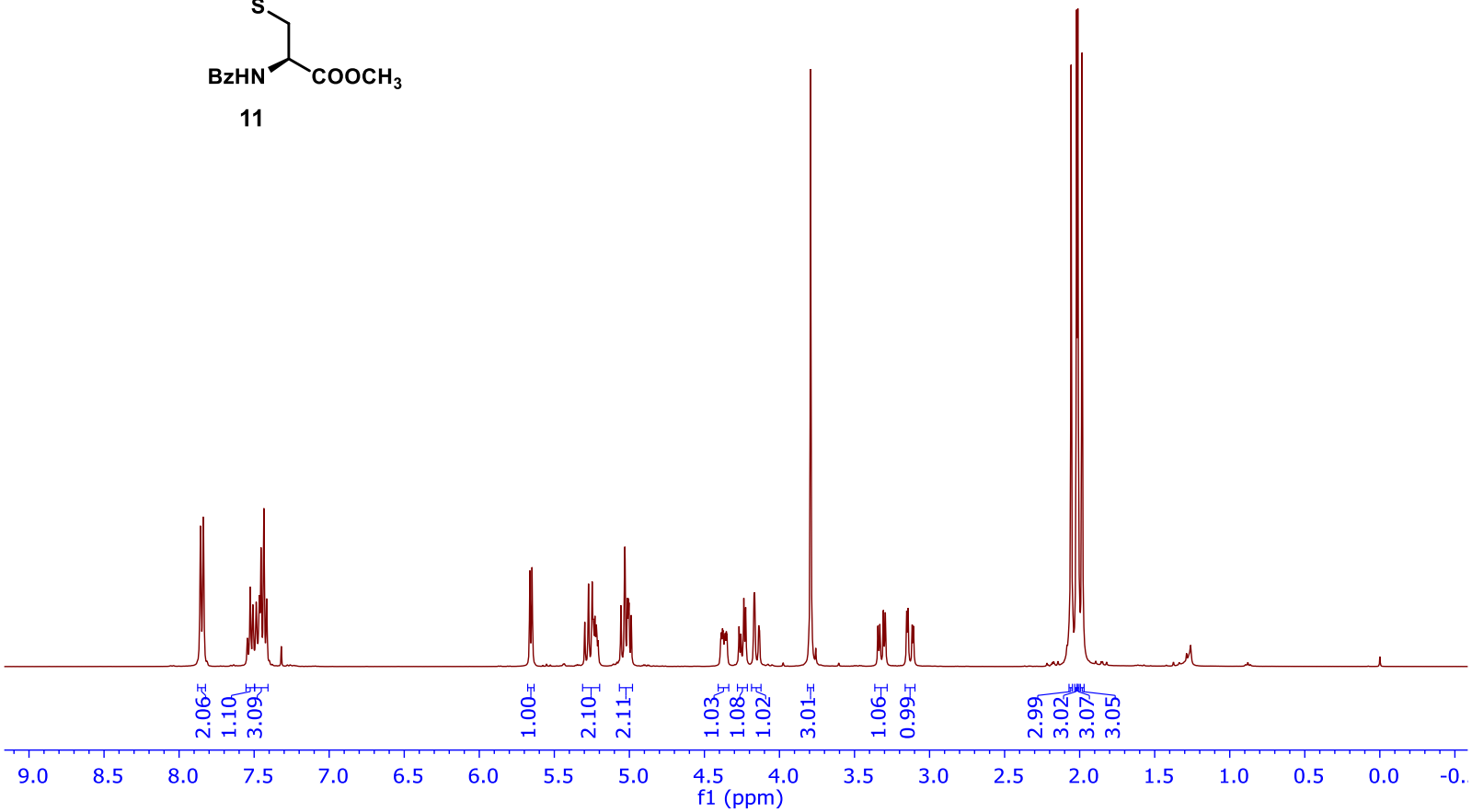


14f

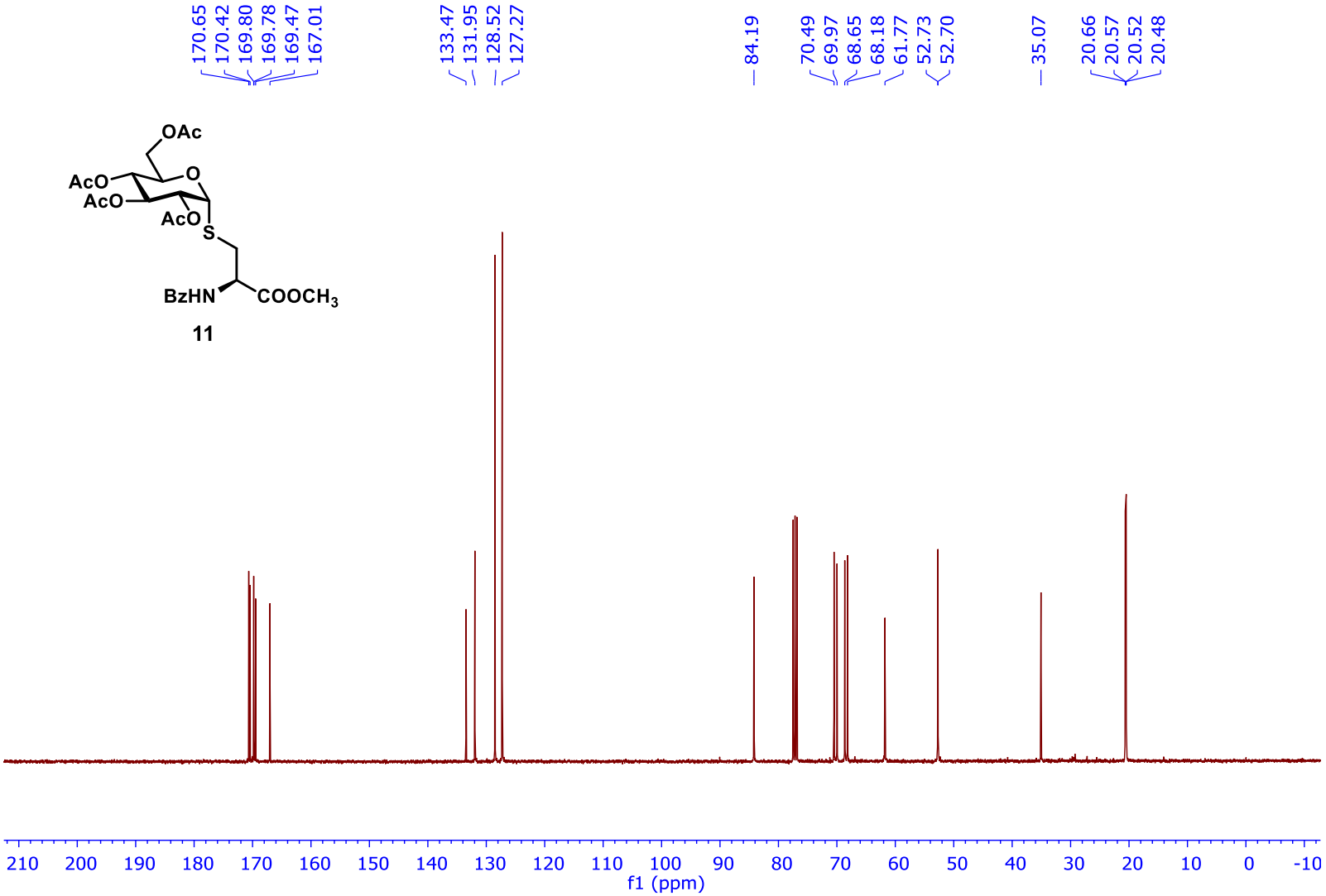
CDCl3, 400 MHz



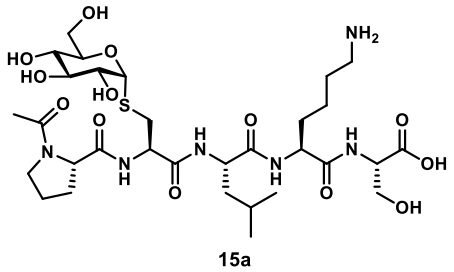
11



CDCl3, 101 MHz



D2O, 600 MHz

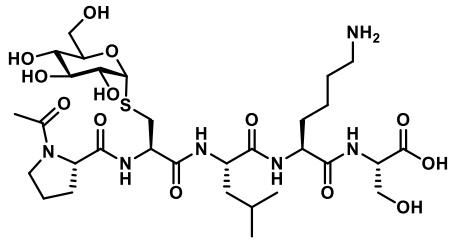


15a

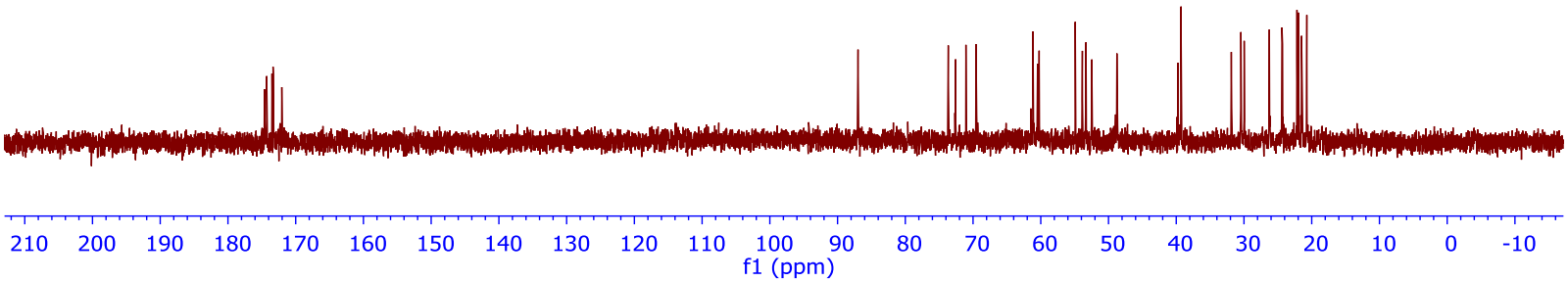
D2O 151 MHz

174.62
174.28
173.50
173.35
173.30
172.05

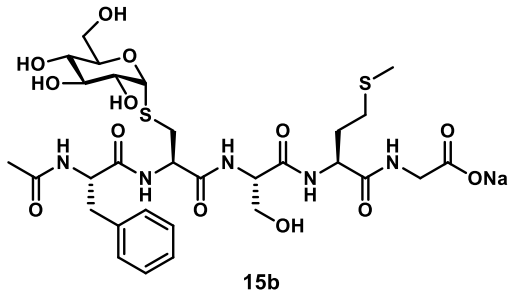
86.98
73.66
72.58
71.05
69.56
61.15
60.47
60.24
54.91
53.86
53.32
52.47
48.76
39.74
39.29
31.87
30.45
29.97
26.26
24.39
24.30
22.18
21.97
21.50
20.72



15a



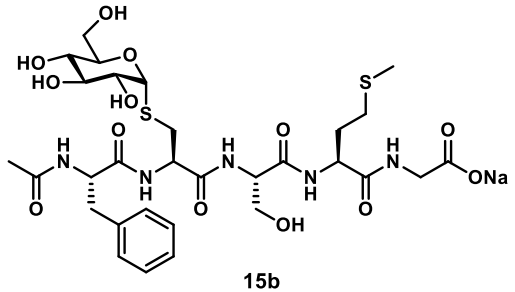
D2O, 600 MHz



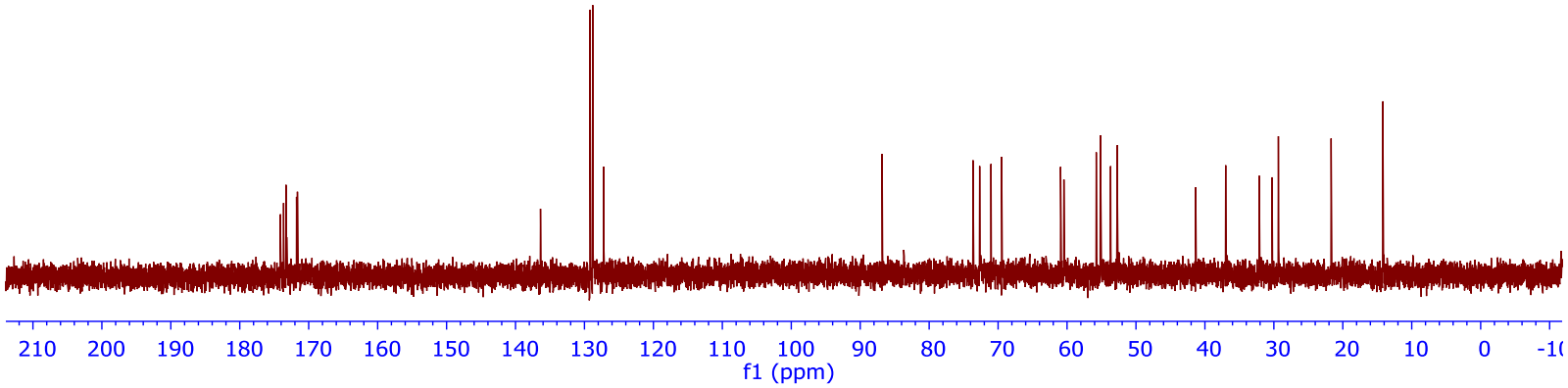
15b

D2O, 151 MHz

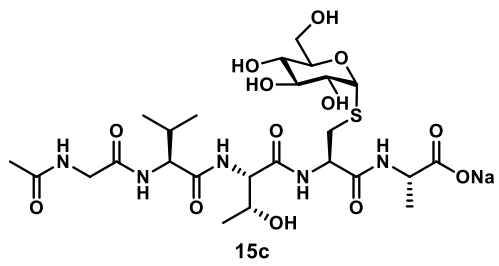
174.10 173.64 173.29 173.20 173.19 171.76 171.63 136.38 129.20 128.81 127.22 86.82 73.63 72.68 71.02 69.48 60.93 60.45 55.76 55.17 53.68 52.71 41.34 36.99 32.11 30.25 29.34 21.69 14.19



15b



D2O, 600 MHz

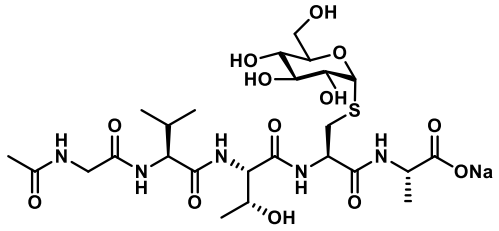


15c

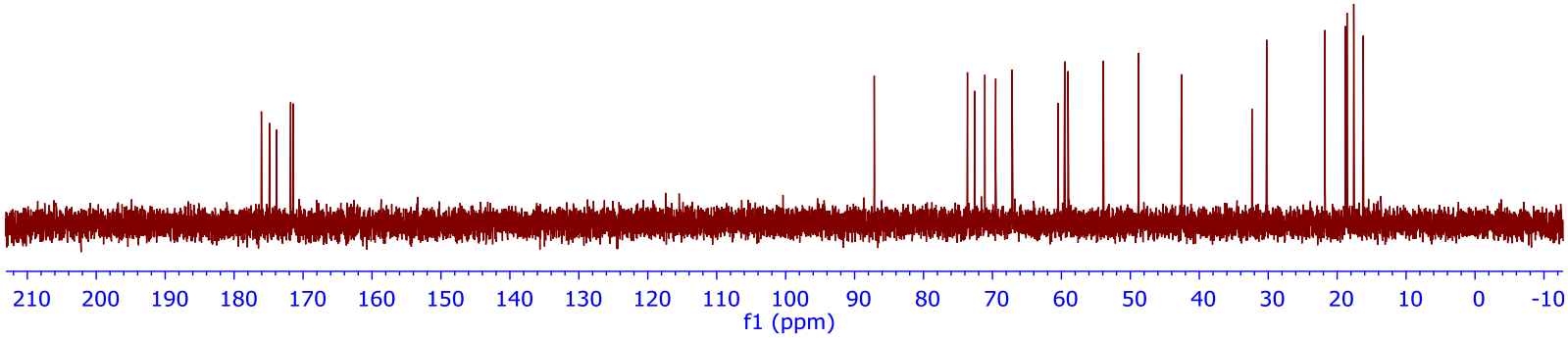
D2O, 151 MHz

176.04
174.88
173.83
171.80
171.46
171.45

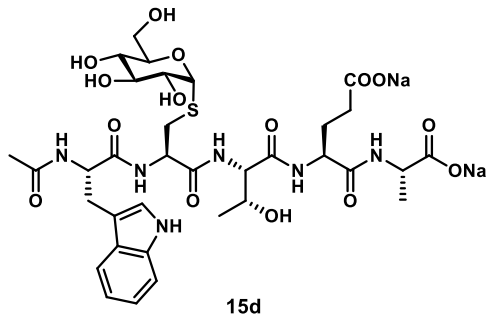
87.15
73.62
72.59
71.10
69.53
67.17
60.48
59.52
59.04
53.91
48.81
42.59
32.36
30.22
21.76
18.80
18.57
17.60
16.22



15c



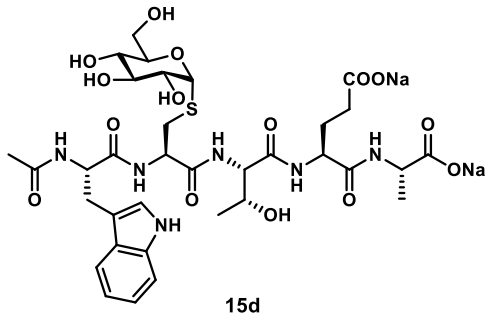
D2O, 600 MHz



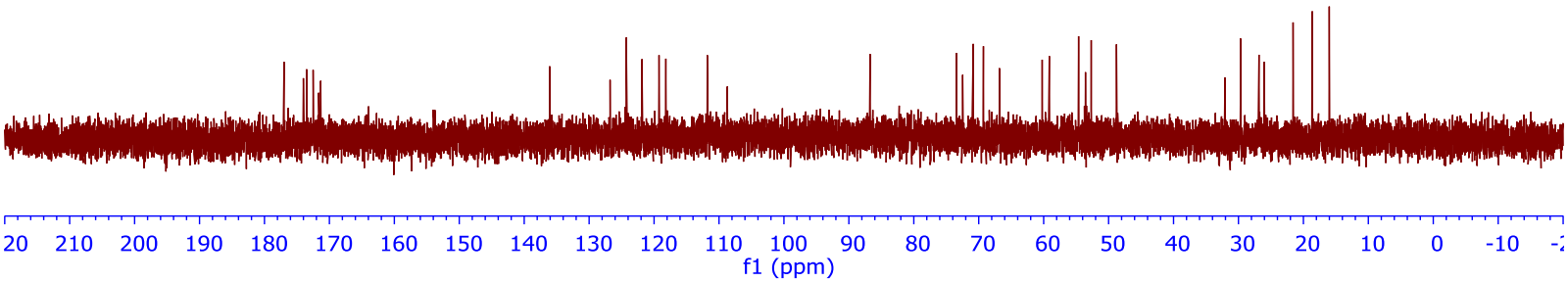
15d

D2O 151 MHz

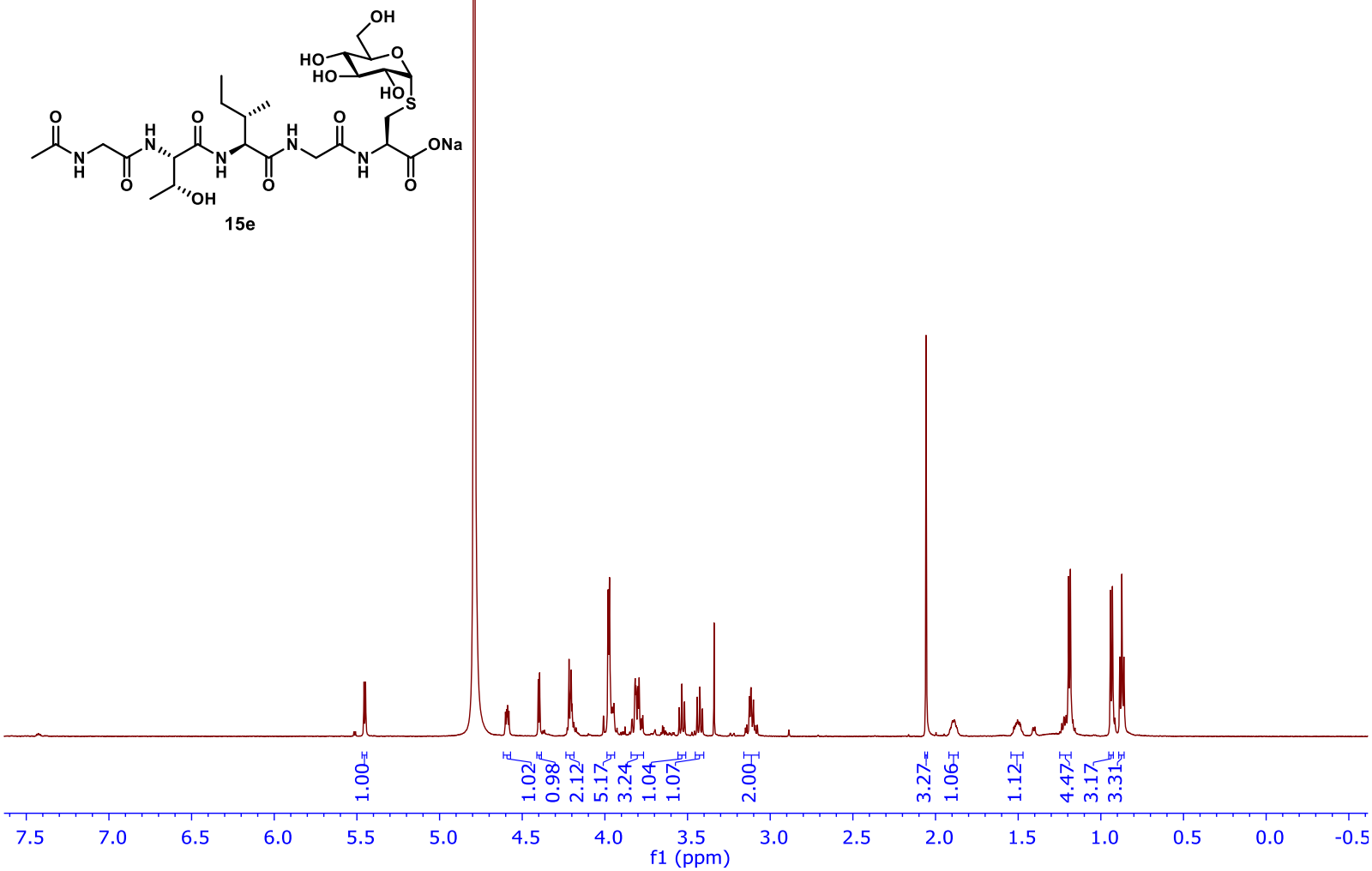
176.99
174.01
173.50
172.51
171.65
171.34
136.07
126.77
124.28
121.87
119.23
118.19
111.80
108.71
86.74
73.43
72.48
70.85
69.28
66.81
60.23
59.13
54.62
53.56
52.68
48.78
32.08
29.69
26.84
26.03
21.59
18.64
16.02



15d



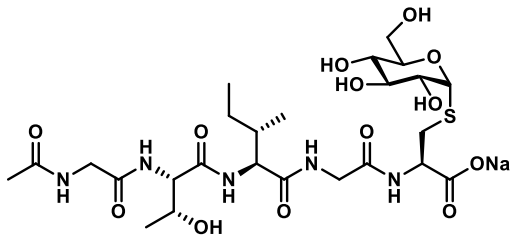
D2O, 600 MHz


15e
1.00
1.02
0.98
2.12
5.17
3.24
1.04
1.07
2.00
3.27
1.06
1.12
4.47
3.17
3.31
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

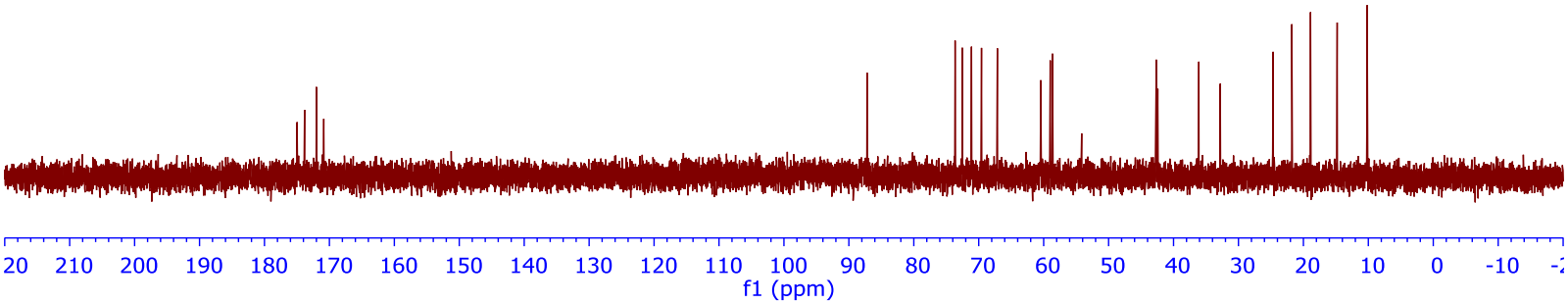
D2O, 151 MHz

174.97
173.83
172.00
171.96
170.87

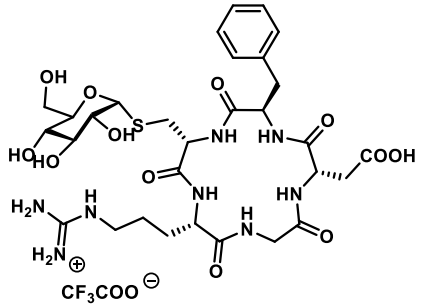
87.20
73.64
72.53
71.11
69.57
67.13
60.45
58.99
58.64
54.15
42.65
42.43
36.10
32.80
24.67
21.79
18.90
14.79
10.18



15e



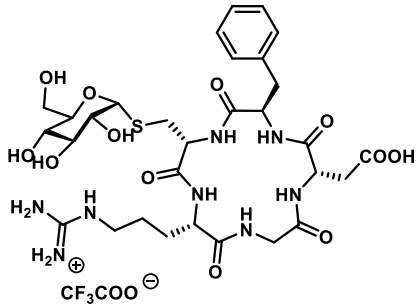
D2O, 800 MHz



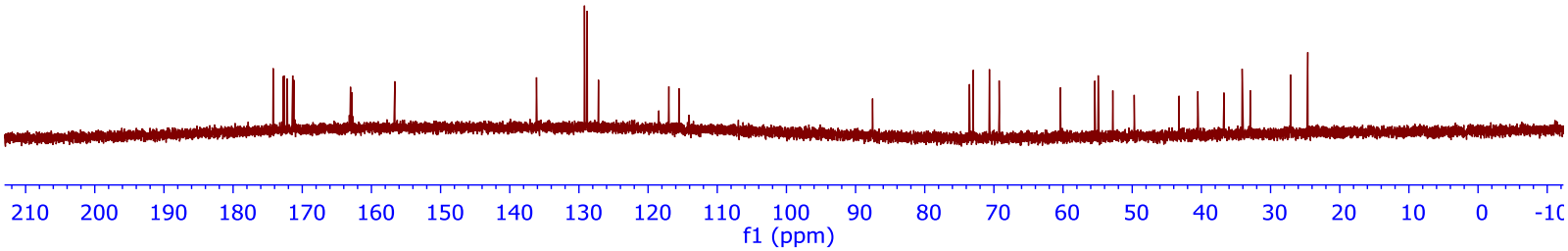
15f

D2O, 201 MHz

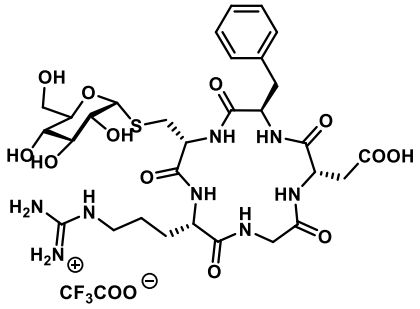
174.21
172.73
172.57
172.16
171.39
171.22
163.20
163.02
162.85
162.67
156.62
136.14
129.20
128.79
127.18
118.45
117.00
115.55
114.10
87.55
73.53
72.98
70.65
69.24
60.38
55.42
54.92
52.81
49.71
43.23
40.51
36.74
34.11
32.95
27.11
24.62



15f

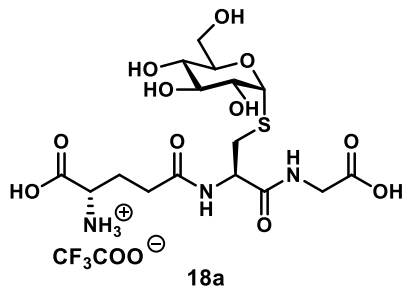


D2O, 376 MHz



15f

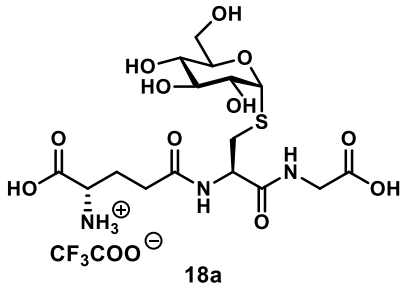
D2O, 400 MHz



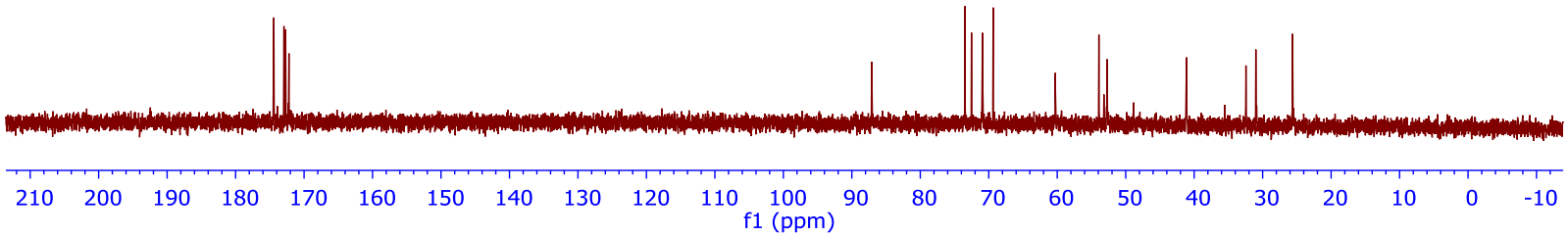
18a

D2O 101 MHz

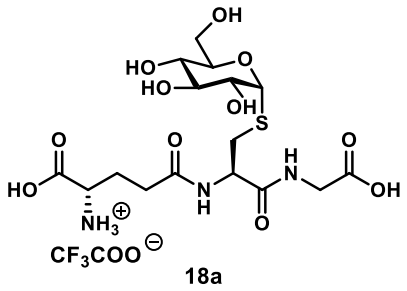
174.42
172.94
172.69
172.21
87.10
73.47
72.53
70.91
69.36
60.28
53.92
52.72
41.12
32.44
30.99
25.63



18a

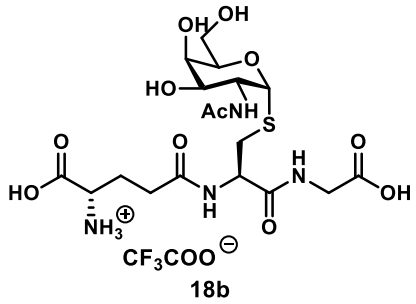


D2O, 376 MHz



18a

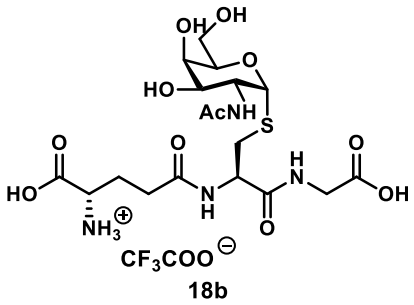
D2O, 400 MHz



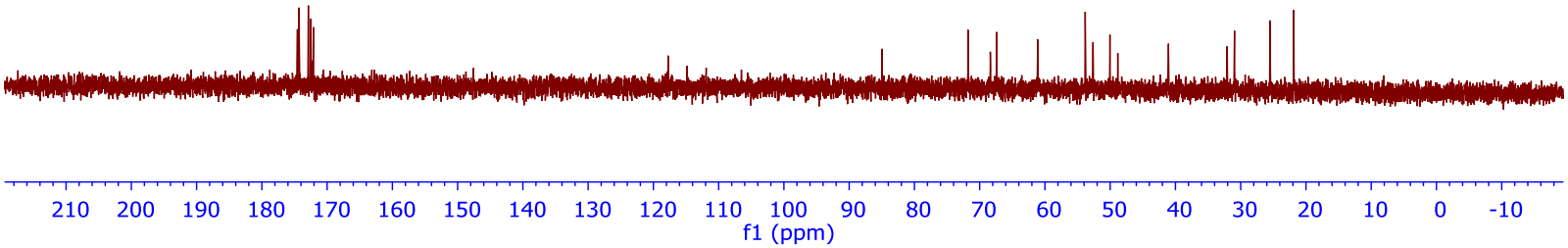
18b

DMSO 400 MHz

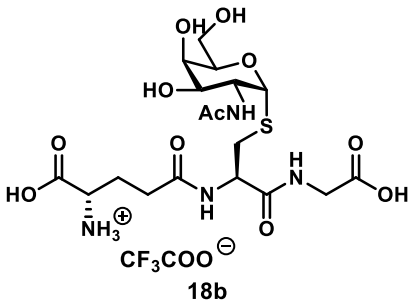
174.55
174.31
172.88
172.49
172.11
114.85
111.91
84.97
71.78
68.36
67.40
61.10
53.83
52.63
50.04
41.07
32.07
30.95
25.51
21.87



18b

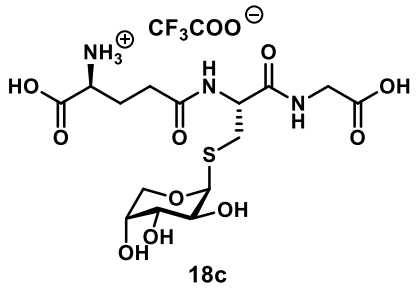


D2O, 376 MHz


OH
OH
O
HO
AcNH
S
O
O
H
N
O
HO
N
H
OH
NH3
CF3COO
18b

-75.61
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

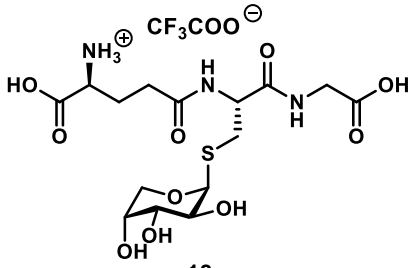
D2O, 400 MHz



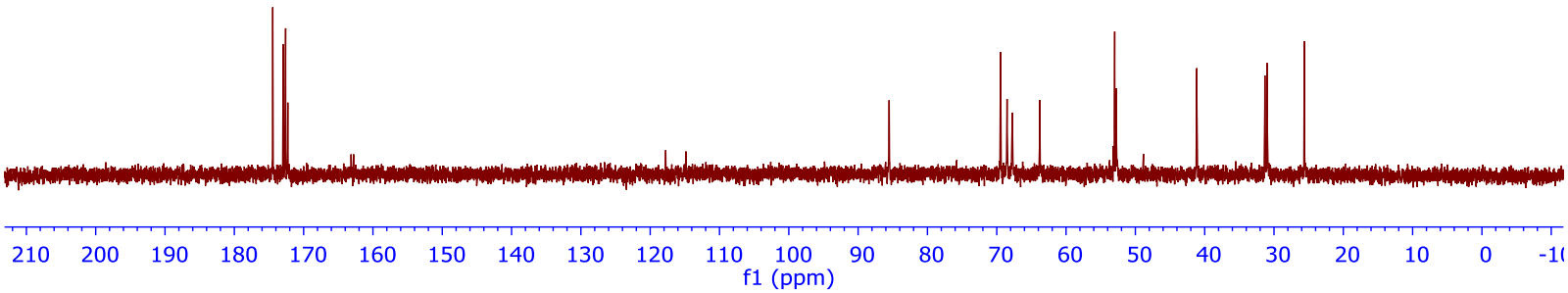
18c

D2O, 101 MHz

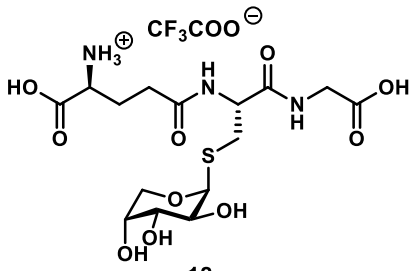
174.45
172.94
172.60
172.29
163.15
162.79
117.76
114.86
85.53
69.45
68.52
67.76
63.80
52.98
52.76
41.14
31.31
30.99
25.62



18c

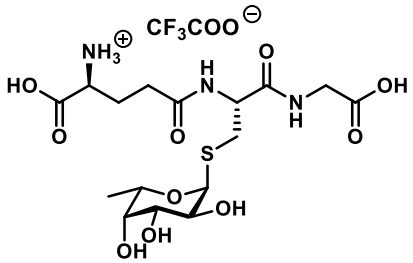


D2O, 376 MHz



18c

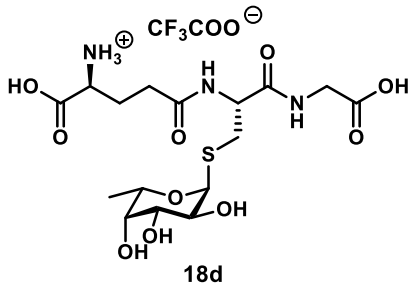
D2O, 400 MHz



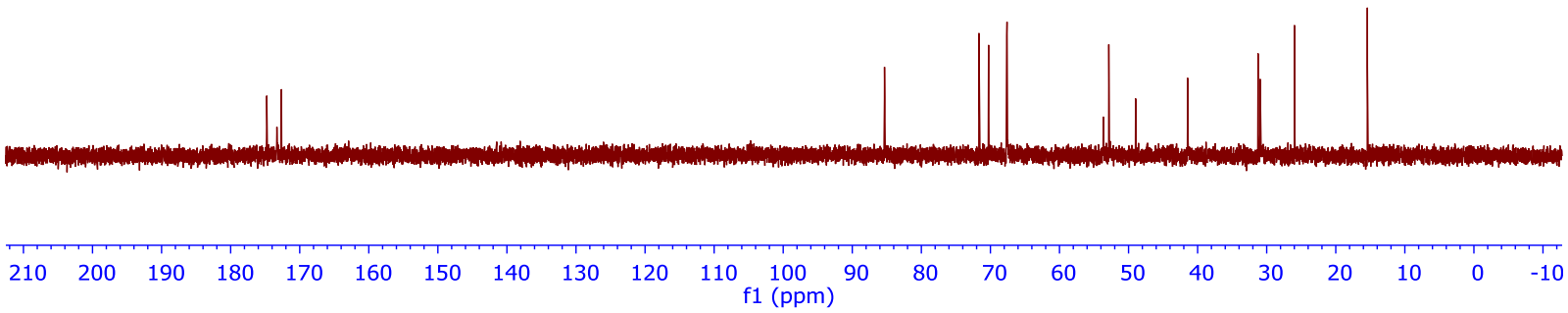
18d

D2O 151 MHz

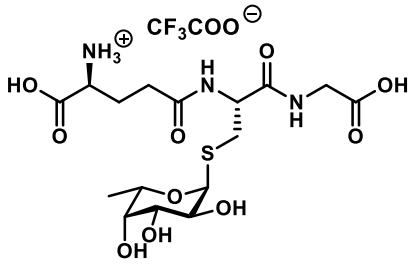
174.77
173.30
172.64
85.33
71.66
70.27
67.64
67.59
53.64
52.86
41.44
31.25
30.95
25.98
15.42



18d

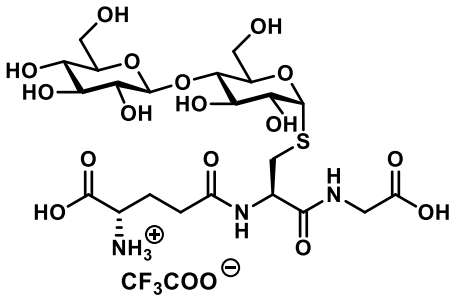


D2O, 376 MHz



18d

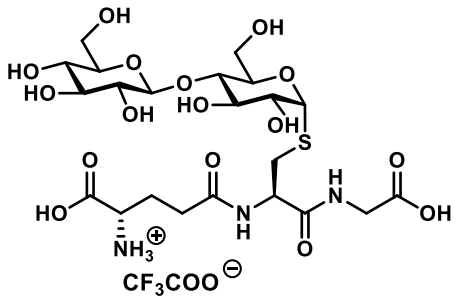
D2O, 600 MHz



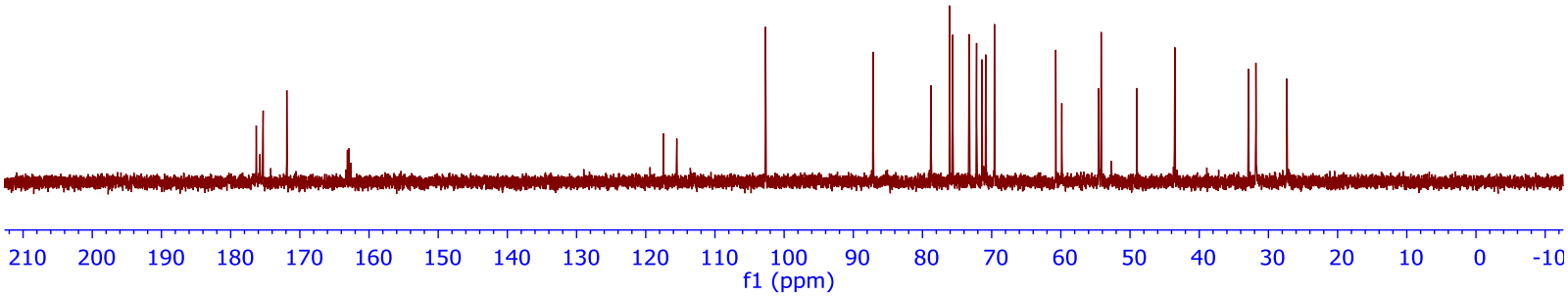
18e

D2O, 151 MHz

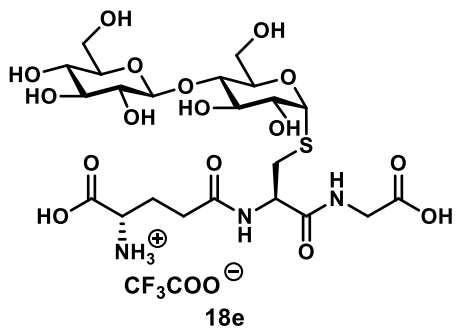
176.30
175.76
175.30
171.88
163.35
163.12
162.88
162.65
119.37
117.44
115.51
113.57
102.69
87.14
78.78
76.09
75.65
73.25
72.18
71.41
70.87
69.60
60.74
59.86
54.55
54.18
43.52
32.89
31.81
27.33



18e

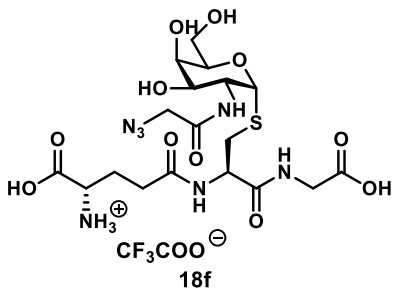


D2O, 376 MHz



18e

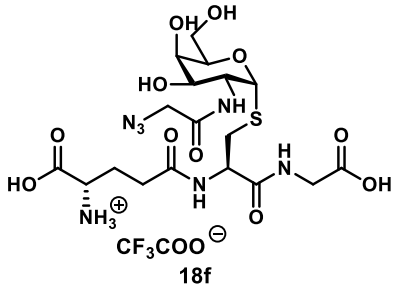
D2O, 800 MHz



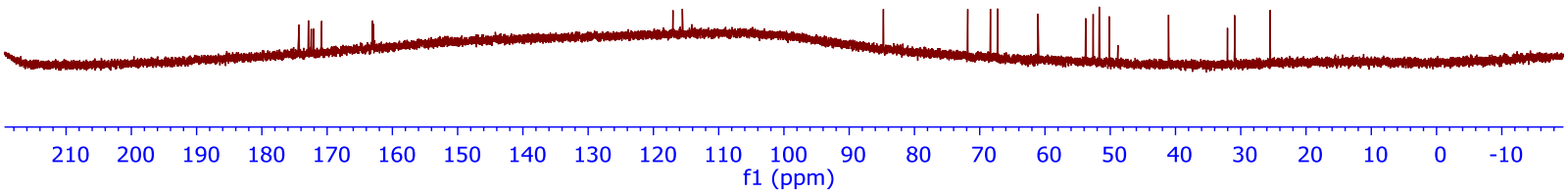
18f

D2O, 201 MHz

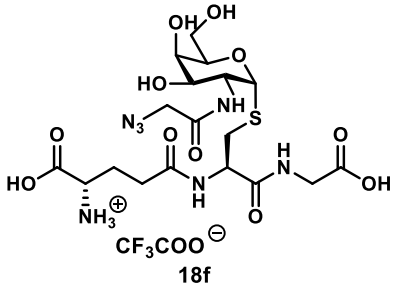
174.29
172.86
172.43
172.08
170.83
163.05
162.88
117.01
115.56
84.76
71.83
68.36
67.28
61.08
53.77
52.61
51.69
50.16
48.82
41.06
32.03
30.94
25.49



18f

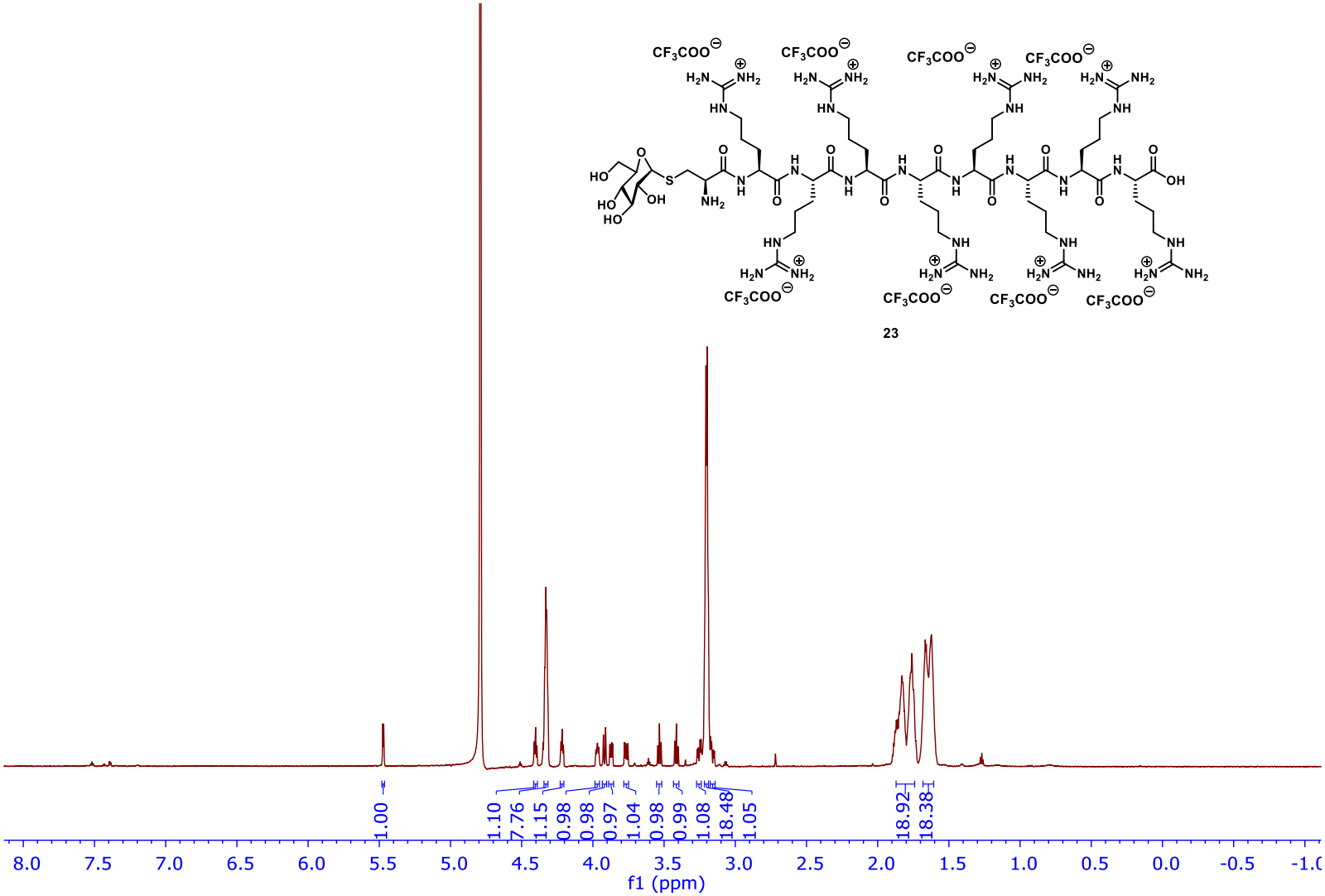


D2O 376 MHz



18f

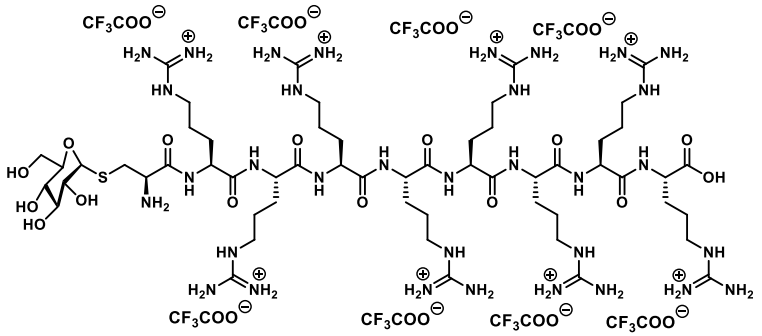
D22O, 800 MHz



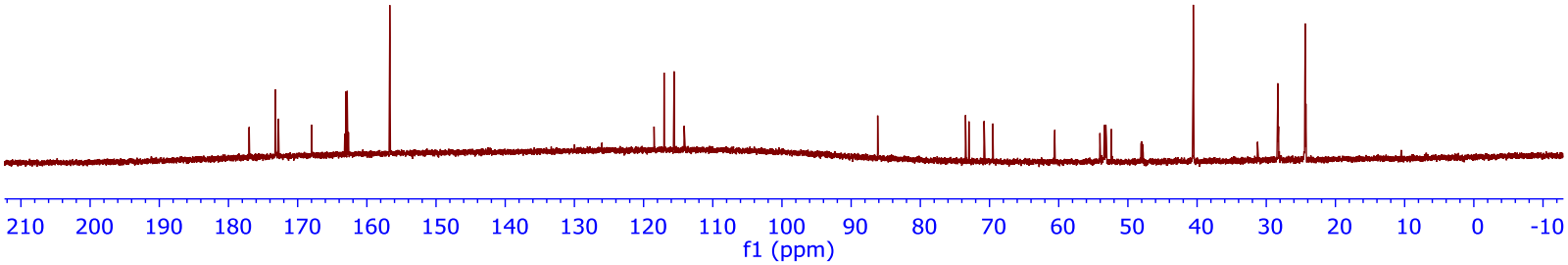
23

D2O, 201 MHz

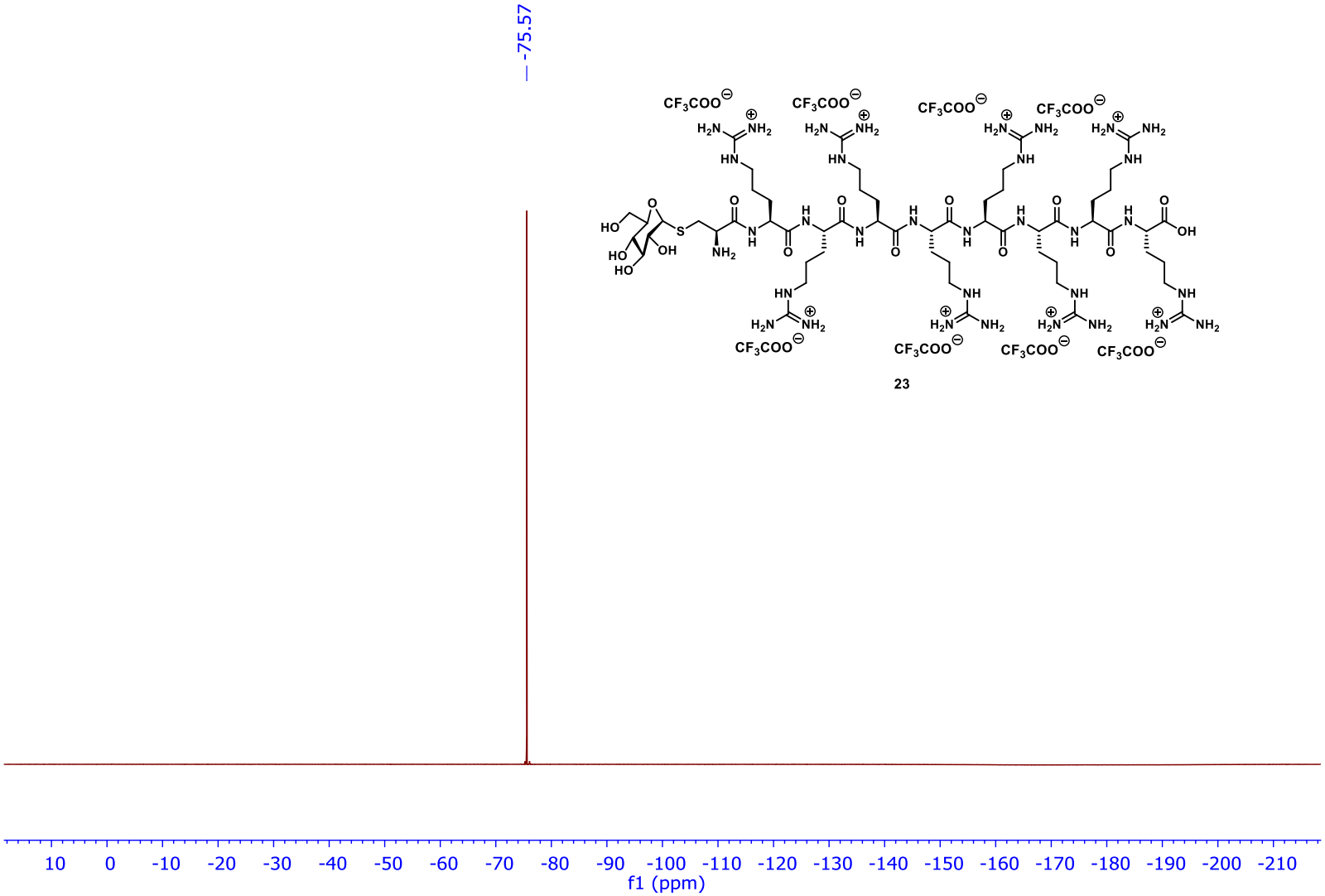
177.01
173.23
173.22
173.20
173.18
172.80
172.78
167.98
163.19
163.02
162.84
162.66
156.69
156.68
118.49
117.04
115.59
114.14
86.16
73.46
72.98
70.78
69.52
60.56
53.45
53.40
53.19
53.16
52.40
40.55
40.50
28.34
28.27
28.25
28.22
28.12
24.49
24.42
24.40
24.37
24.31



23



D2O, 376 MHz



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