Supporting Information

Cationic Charged Helical Glycopolypeptide using Ring Opening Polymerization Of 6-deoxy-6-azido-Glyco-N-Carboxyanhydride

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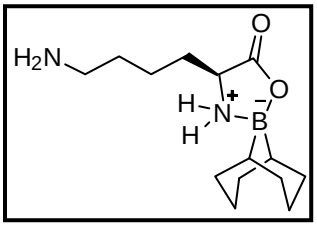
General Experimental Techniques and Apparatus

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Unless otherwise reported all reactions were performed under argon atmosphere. Removal of solvent *in vacuo* refers to distillation using a rotary evaporator attached to an efficient vacuum pump. Products obtained as solids or syrups were dried under high vacuum. 9-BBN dimer was purchased from Sigma Aldrich. Analytical thin-layer chromatography was performed on pre-coated silica plates (F_{254}, 0.25 mm thickness); compounds were visualized by UV light or by staining with anisaldehyde spray. ^{1}H NMR spectra were recorded on Bruker Spectrometers (200 MHz, 400 or 500 MHz). ^{13}C NMR and DEPT spectra were recorded on Bruker Spectrometer (50, 100, or 125 MHz) and reported relative signals according to deuterated solvent used. HRMS data was recorded on Synapat G-2 waters LC-MS system.Chemical shifts (δ_H) are quoted in ppm and are referenced to tetramethylsilane (internal).

Preparation of 9-BBN complex of Lysine (1)

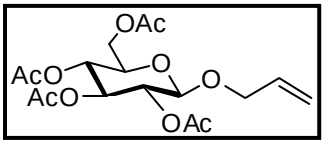


L-lysine mono hydrochloride salt was treated with Aq. NH_3 solution to neutralize acid salt in round bottom flask for 30 min kept at 0˚C and then concentrated under vacuum to remove excess of ammonia. This was directly used for 9-BBN complex formation reactions.

To 150mL methanol in a 250mL round bottom flask at room temperature under argon was added 1.1 eq. 9-BBN dimer (Aldrich). The mixture was heated at reflux until the 9-BBN was completely dissolved (30min) and to this solution 25 mmol of amino acid was added. The resultant reaction mixture was heated for additional 3 h until gas evolution ceased and the

suspension became a clear homogenous solution. The methanol was removed on rotary evaporator and the residue dissolved in hot THF (100mL), filtered and the filtrate was concentrated to get a white gummy residue of 9-BBN-L-lysine complex. Excess of 9-BBN was removed by treatment with hot hexane or diethyl ether and then subjected to high vacuum for 1 h during which time it became an amorphous solid. This material was used without any further purification for coupling reaction.

Preparation of (allyl)-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (2)

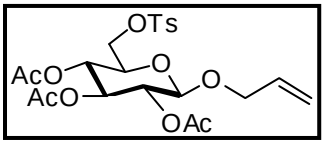


To a solution of D-glucose (5g, 27.75 mmol) in dry pyridine (20 mL) was added acetic anhydride (18.4 mL, 194.25 mmol) and the reaction mixture was stirred at room temperature until the completion of reaction followed by TLC. After completion of reaction, most of the pyridine was removed on the rotary evaporator. The crude reaction mixture was dissolved in dichloromethane and washed with dil. HCl solution to remove traces of pyridine. The crude reaction mixture was purified by column chromatography to get penta-*O*-acetyl-β-D-glucopyranoside.

To a solution of penta-*O*-acetyl-β-D-glucopyranoside (10g, 25.6 mmol) and allyl alcohol (2.1 mL, 30.7 mmol) in dry dichloromethane was placed in 100 mL round bottom covered by aluminium foil and fitted with a dropping funnel. At 0˚C $BF_3.Et_2O$ (2.5 equivalent) was added drop wise over period of 25 minutes. The reaction mixture was then stirred at 0˚C for 1h, further at room temperature for 12 h. Completion of reaction was monitored by TLC. The reaction mixture was diluted by dichloromethane and poured onto ice water while stirring. The organic layer was separated and washed successively with water, saturated sodium bicarbonate and brine. The organic layer was dried on Na_2SO_4, concentrated on rotary evaporator and the resulting residue was purified by column chromatography on silica gel using ethyl acetate-petroleum ether as eluent to get allyl-penta-*O*-acetyl-β-D-glucopyranoside (7.0 g, 60%) as a crystalline solid.

HRMS (ESI):calcd for $C_{17}H_{24}NaO_{10}$ $[M + Na]^+$ 411.1267, found 411.1265

Preparation of (allyl)-6-*O*-tosyl-2,3,4,-tri-*O*-acetyl-β-D-glucopyranoside (2a)



To a solution of allyl-2,4,5,6-tetra-*O*-acetyl-β-D-glucopyranoside (5g, 12.9 mmol) in anhydrous methanol (10 mL) was added freshly

prepared solution NaOMe in MeOH (1 M, 1 mL) at 0˚C. The reaction mixture was stirred for 1h and progress of reaction was monitored by TLC. After complete conversion, reaction mixture was neutralized with amberlite IR 120 H^+ resin and filtered. The crude reaction product was obtained by removal of solvent on rotary evaporator and purified by coloumn chromatography to get desired tetraol of allylglucoside (2.7g, 96% yield).

The above tetraol (2.7g, 12.3 mmol) was dissolved in pyridine (15mL) and to this crystallized tosyl chloride (2.8g, 14.7 mmol) was added at 0˚C under argon. The reaction mixture was then allowed to attain room temperature and was further stirred for 12 h. Excess tosyl chloride was quenched by addition of methanol at 0˚C and then solvents were evaporated. The crude product obtained was purified by column chromatography to get 6-*O*-tosyl-allyl glucoside (3.2g, 70%). Starting material was isolated (30%) and used again in tosyl protection reaction.

The unprotected 6-*O*-tosyl derivative of ally glucoside (3.2g, 8.6 mmol) was dissolved in dry pyridine and the solution was cooled to -10˚C. To this ice-cold solution acetic anhydride (4.06 mL, 43.0 mmol) was added slowly while stirring. The reaction mixture was kept at 4˚C for 12 h and was then concentrated. The crude product was purified by column chromatography to afford allyl-6-*O*-tosyl-2,3,4,-tri-*O*-acetyl-β-D-glucopyranoside (4.2g, 98%).

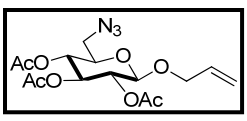
$[\alpha]^{RT}_D$ (c = 1.0 M, $CHCl_3$) = −1.76

^{1}H NMR (200.13 MHz, $CDCl_3$):δ (ppm) 1.99 (s, 3H), 2.00 (s, 3H), 2.03 (s, 3H), 2.46 (s, 3H), 3.69-3.79 (m, 1H), 3.77-4.11 (m, 3H), 4.21-4.29 (m, 1H), 4.50 (d, J = 7.83 Hz, 1H), 4.86-4.98 (m, 2H), 5.31-5.32 (m, 3H), 5.72-5.91 (m, 1H), 7.35 (d, J = 8.08, 2H), 7.78 (d, J = 8.08, 2H)

^{13}C NMR (50.32 MHz, $CDCl_3$):δ (ppm) 20.4(2C), 20.5, 21.6, 67.7, 68.6, 69.8, 70.1, 71.4, 72.4, 99.2, 117.6, 128.0(2C), 129.9(2C), 132.3, 133.0, 145.1, 169.2, 169.4, 170.1

HRMS (ESI):calcd for $C_{22}H_{28}NaO_{11}S$ $[M + Na]^+$ 523.1250, found 523.1253

Preparation of (allyl)-6-*deoxy*-6-azido-2,3,4,-tri-*O*-acetyl-β-D-glucopyranoside (2b)



To a solution of allyl-6-*O*-tosyl-2,3,4-tri-*O*-acetyl-β-D-glucopyranoside (4g, 8 mmol) in dry DMF (20 mL) was added NaN_3 (1.6g, 24 mmol) and

the reaction mixture was stirred at 80˚C for 24 h. After completion of the reaction, the reaction was diluted by diethyl ether. The organic layer was washed with saturated brine to remove excess of DMF for 5-6 times and then by water wash. The organic layer was dried on Na_2SO_4 and concentrated to get crude product. The crude product was purified by column chromatography to get allyl-6-*deoxy*-6-azido-2,3,4-tri-*O*-acetyl-β-D-glucopyranoside (2.9g, 97%).

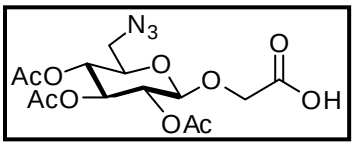
$[\alpha]^{RT}_D$ (c = 1.0 M, $CHCl_3$) = −45.1

^{1}H NMR (200.13 MHz, $CDCl_3$):δ (ppm) 2.01 (s, 3H), 2.04 (s, 3H), 2.06 (s, 3H), 3.15 (dd, *J* = 2.4, 13.3 Hz, 1H), 3.4 (dd, *J* = 7.58, 13.26 Hz, 1H), 3.69-3.79 (m, 1H), 4.12(qt, *J* = 1.39, 6.19, 13.26 Hz, 1H), 4.35 (qt, *J* = 1.52, 4.9, 13.26 Hz, 1H), 4.60(d, *J* = 7.96 Hz, 1H), 4.90-5.08 (m, 2H), 5.77-5.96 (m, 1H)

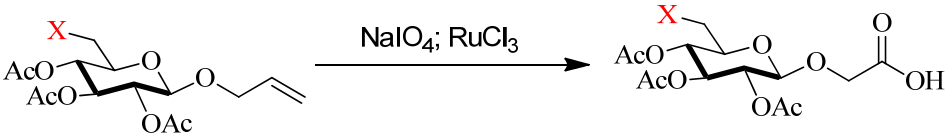
^{13}C NMR (50.32 MHz, $CDCl_3$):δ (ppm) 20.5(2C), 20.6, 51.1, 69.8, 71.2, 72.5, 73.6, 99.2, 117.7, 133.1, 169.2, 169.5, 170.2

HRMS (ESI):calcd for $C_{15}H_{21}N_3NaO_8$ $[M + Na]^+$ 394.1226, found 394.1233

Preparation of 6-*deoxy*-6-azido-2,3,4-tri-*O*-acetyl-β-D-glucopyranoside ethyl carboxylic acid (2c)



To a stirring solution of 6-*deoxy*-6-azido-2,3,4-allyl glucoside (2.8g, 7.5 mmol) in CCl_4 (23mL), CH_3CN (23mL) and H_2O (30mL) at 0˚C in a round bottom flask was added NaIO4 (6.5g, 30.2 mmol) and $RuCl_3.H_2O$ (23mg, 0.150 mmol). After 4 hr of vigorous stirring of the suspension at room temperature, the reaction mixture was concentrated on a rotary evaporator and diluted with 1M HCl (70mL) and brine (70mL). The aqueous layer was extracted with CH_2Cl_2 (4X100ml) and dried extensively over Na_2SO_4. The crude product was used in next step without any further purification.



2c, X=N_3 2d, X=OAc

SI Figure 1. Oxidation of allyl moiety of 6-*deoxy*-6-azido allyl glycoside.

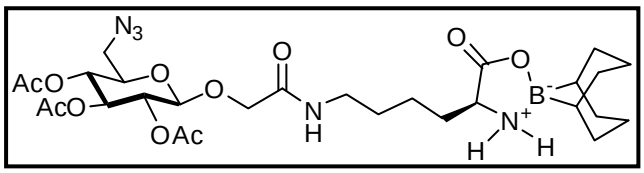
^{1}H NMR (200.13 MHz, $CDCl_3$):δ (ppm) 2.02 (s, 3H), 2.05 (s, 3H), 2.08 (s, 3H), 3.21-3.48 (m, 2H), 3.66-3.77 (m, 1H), 4.29-4.30 (d, J = 6.76 Hz, 1H), 4.37 (s, 1H), 4.68(dd, J = 7.8, 11.7 Hz, 1H), 4.95-5.14 (m, 2H), 5.25 (td, J = 2.65, 9.35 Hz, 1H), 9.69 (bs, 1H)

^{13}C NMR (50.32 MHz, $CDCl_3$): δ (ppm) 20.5(2C), 20.6, 50.9, 64.8, 69.4, 71.0, 72.2, 73.8, 100.1, 169.2, 169.7, 170.2, 172.7

Preparation of 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside ethyl carboxylic acid (2d)

Same procedure followed which is described below for compound**2c**.

Coupling of 6-*deoxy*-6-azido-2,3,4-tri-*O*-acetyl-β-D-glucopyranoside ethyl carboxylic acid with 9-BBN-L-lysine complex (3a)



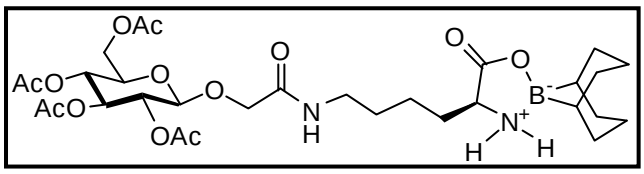
To a solution of 6-*deoxy*-6-azido-2,3,4-tri-*O*-acetyl-β-D-glucopyranoside ethyl carboxylic acid (1g, 2.6 mmol) and 9-BBN-L-lysine complex (0.684g, 2.57 mmol) in dry THF (10mL) was added EDCI (0.548g, 3.1 mmol) and HOBt (0.475g, 3.1 mmol)). The reaction mixture was stirred for 6 h and progress of reaction was monitored by TLC. After completion of the reaction, the solvent in reaction mixture was removed by rotary evaporator and directly loaded onto the column for further purification. The desired coupling product was obtained by using ethyl acetate/methanol as eluent (1.2g, 75%).

^{1}H NMR (200.13 MHz, $CDCl_3$):δ (ppm) 0.55 (s, 2H), 1.25-1.90 (m, 18H), 2.03 (s, 3H), 2.04 (s, 3H), 2.09 (s, 3H), 3.25-3.40 (m, 2H), 3.71-3.80 (m, 2H), 4.03 (d, J = 14.91 Hz, 1H), 4.12 (q, J = 7.20 Hz, 1H), 4.31 (d, , J = 14.91 Hz, 1H), 4.55 (d, J = 7.96 Hz, 1H), 4.80-5.10 (m, 3H), 5.26 (t, J = 9.40 Hz, 1H), 6.78 (t, J = 6.30 Hz, 1H)

^{13}C NMR (50.32 MHz, $CDCl_3$):δ (ppm) 20.5(2C), 20.6, 20.8, 22.2, 22.9, 23.9, 24.1, 24.3, 28.9, 29.8, 31.1, 31.2, 31.3, 31.5, 37.7, 55.2, 61.5, 68.0, 68.4, 71.4, 71.9, 72.0, 100.4, 169.2, 169.5, 169.9, 170.1, 170.2.

Coupling of 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside ethyl carboxylic acid with 9-BBN-L-lysine complex (3b)

Same procedure followed which is described above for **3a**.



^{1}H NMR (200.13 MHz, $CDCl_3$):δ (ppm) 0.55 (s, 2H), 1.25-1.90 (m, 18H), 2.03 (s, 3H), 2.04 (s, 3H), 2.09 (s, 6H), 2.58 (bs, 1H), 3.20-3.40 (m, 2H), 3.70-3.80 (m, 2H), 4.03 (d, J = 14.8 Hz, 1H), 4.12 (dd, J = 2.0, 12.5 Hz, 1H), 4.22-4.35 (m, 2H), 4.55 (d, J = 7.83 Hz, 1H), 4.90-5.14 (m, 3H), 5.26 (t, J = 9.40 Hz, 1H), 5.50 (m, 1H), 6.78 (t, J = 5.94 Hz, 1H)

^{13}C NMR (50.32 MHz, $CDCl_3$):δ (ppm) 20.4(2C), 20.6, 20.8, 22.2, 22.9, 23.9, 24.1, 24.3, 28.9, 29.8, 31.1, 31.2, 31.3, 31.5, 37.7, 55.2, 61.5, 68.0, 68.4, 71.4, 71.9, 72.0, 100.4, 168.9, 169.4, 169.4, 170.1, 170.3, 170.6

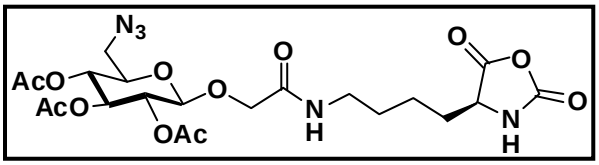
Cleavage of 9-BBN complex

6-*deoxy*-6-azido-2,3,4-tri-*O*-acetyl-β-D-glucopyranoside-L-lysine **3a** derivative was dissolved in MeOH:$CHCl_3$ (1:5) mixture and stirred it for 24 h at room temperature. After complete cleavage of 9-BBN complex, the reaction mixture was concentrated and treated with hot petroleum ether to remove excess 9-BBN. If sometime complete cleavage was not occurred then 1-2 drops of conc. HCl was added for complete cleavage. The crude product was directly subjected for next reaction without any further purification.

Same procedure followed for normal glycol-aminoacid derivative which is described above for **3b**.

Reference: Syed, B. M.; Gustafsson. T.; Kihlberg. J. *Tetrahedron,* 2004, *60*, 5571-5575.

Preparation of *N*-Carboxyanhydride of 6-*deoxy*-6-azido-2,3,4-tri-*O*-acetyl-β-D-glucopyranoside-L-lysine derivative (4a)



To a solution of 6-*deoxy*-6-azido-2,3,4-tri-*O*-acetyl-β-D-glucopyranoside-L-lysine derivative (0.1 mmol) in freshly distilled anhydrous tetrahydrofuran (30 mL) was added a solution of triphosgene (0.05 mmol) in anhydrous tetrahydrofuran (5 mL) under argon atmosphere. α-Pinene (0.3 mmol) was added and the reaction mixture was heated to 55˚C for 1 h and cooled to room temperature, poured into dry hexane. The white precipitate of the *N*-carboxyanhydride (**4a**) was vacuum filtered

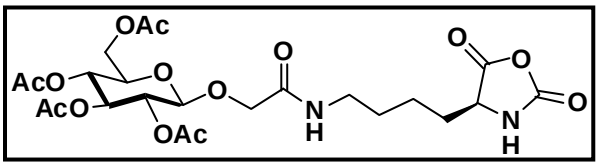
quickly and reprecipitated (2 times) by dissolving in ethyl acetate followed by addition of light petroleum. The resulting precipitate was filtered and dried under vacuum (Yield 80%).

^{1}H NMR (400.13 MHz, CD_2Cl_2):δ (ppm) 1.42-1.50 (m, 2H), 1.55-1.61 (m, 2H), 1.78-1.85 (m, 2H), 2.00 (s, 3H), 2.02 (s, 3H), 2.06 (s, 3H), 3.24-3.37 (m, 4H), 3.75-3.80 (m, 1H), 4.09-4.12 (d, J = 15.1 Hz, 1H), 4.29-4.33 (m, 2H), 4.61-4.63 (d, J = 7.8 Hz, 1H), 5.00-5.05 (m, 2H), 5.22-5.27 (t, J = 1.8, 9.5 Hz, 1H), 6.62 (bs, 1H), 7.34 (bs, 1H).

^{13}C NMR (100.61 MHz, CD_2Cl_2): δ (ppm) 20.9 (2C), 21.2, 22.2, 28.8, 31.4, 38.4, 51.4, 58.1, 69.1, 69.7, 72.0, 72.4, 74.1, 100.9, 152.5, 169.4, 170.0, 170.4, 170.7, 170.9.

Preparation of *N*-Carboxyanhydride of 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside-L-lysine derivative (4b)

Same procedure followed for normal glycoaminoacid derivative **4b** which is described above for **4a**.



^{1}H NMR (399.78 MHz, $CDCl_3$):δ (ppm) 1.40-1.42 (m, 2H), 1.51-1.54 (m, 2H), 1.77-1.79 (m, 2H), 1.96 (s, 3H), 1.97 (s, 3H), 2.03 (s, 3H), 2.04 (s, 3H), 3.21-3.30 (m, 2H), 3.68-3.70 (m, 1H), 4.01-4.08 (t, J = 15.0 Hz, 1H), 4.20-4.27 (m, 3H), 4.47-4.49 (d, J = 7.8 Hz, 1H), 4.97-5.02 (m, 2H), 5.16-5.21 (t, J = 9.6 Hz, 1H), 6.56 (t, J = 5.5 Hz, 1H), 7.26 (bs, 1H).

^{13}C NMR (100.53 MHz, $CDCl_3$): *δ* (ppm) 20.5, 20.6, 20.7, 20.9, 21.3, 28.2, 30.6, 37.7, 57.4, 61.6, 68.1, 68.6, 71.6, 72.0, 72.1, 100.5, 152.1, 169.0, 169.4, 170.1(2C), 170.3, 170.7

SI Table 1: Different glycopolypeptides synthesized

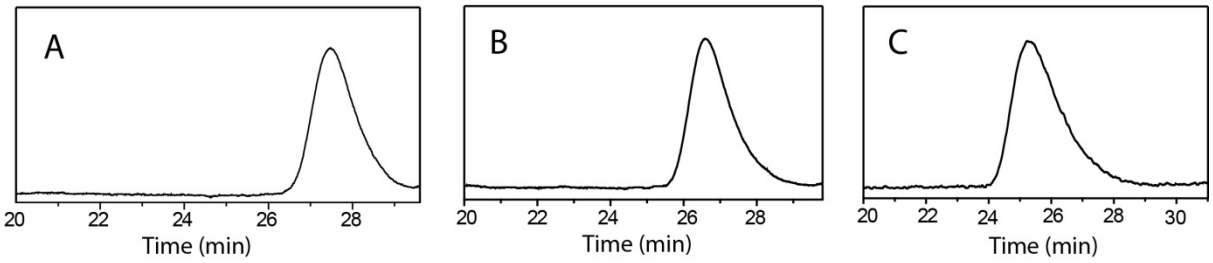
Run No.	Monomer	Protected Polymer					
		M/I[a]	**Polymer**	**M_n**[b] ($\times 10^3$ g/mol)	**M_w/M_n**[c]	**DP**[d]	**% Yield**[e]
1	6-*deoxy*-6-azido-glyco-NCA (**4a**)	30	Ac30GP-N_3 (**5a**)	17.7	1.03	34	98
2	6-*deoxy*-6-azido-glyco-NCA (**4a**)	40	Ac40GP-N_3 (**6a**)	22.4	1.08	42	95
3	6-*deoxy*-6-azido-glyco-NCA (**4a**)	50	Ac50GP-N_3 (**7a**)	29.8	1.16	56	98
4	6-*deoxy*-6-azido-glyco-NCA (**4a**) / 6-OAc-glyco-NCA (**4b**) (1:9)	30	30GP[OAc-*co*-(10%)-N_3] (**8a**)	16.2	1.08	31	94
5	6-*deoxy*-6-azido--glyco-NCA (**4a**) / 6-OAc-glyco-NCA (**4b**) (1:4)	30	30GP[OAc-*co*-(20%)-N_3] (**9a**)	16.6	1.08	31	92

[a]M/I=monomer to initiator ratio [Initiator (I) is hexylamine]; [b,c]Calculated from gel permeation chromatography in DMF containing 0.025 M LiBr as eluent at 60 °C. GPC samples were prepared at concentrations of 5 mg/mL. [d]Degree of polymerization (DP) were calculated from ^{1}H-NMR. [e]Total isolated yield of the glycopolypeptides.

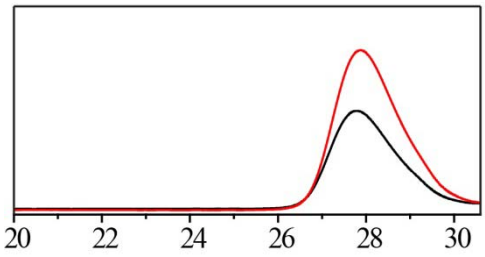
SI Table 2: Secondary conformation analysis of different glycopolypeptide synthesized.

Entry	Protected polymer	Deprotected polymer		After reduction[a]	
		Polymer	**% helicity**[b]	**Polymer**	**% helicity**[b]
1	Ac30GP-N_3 (**5a**)	(OH)30GP-N_3 (**5b**)	52	(OH)30GP-NH_2 (**5c**)	36
2	Ac40GP-N_3 (**6a**)	(OH)40GP-N_3 (**6b**)	64	(OH)40GP-NH_2 (**6c**)	53
3	Ac50GP-N_3 (**7a**)	(OH)50GP-N_3 (**7b**)	85	(OH)50GP-NH_2 (**7c**)	83
4	30GP[OAc-*co*-(10%)-N_3] (**8a**)	30GP[(OH)-*co*-(10%)-N_3] (**8b**)	49	30GP[(OH)-*co*-(10%)-NH_2] (**8c**)	47
5	30GP[OAc-*co*-(20%)-N_3] (**9a**)	30GP[(OH)-*co*-(20%)-N_3](**9b**)	49	30GP[(OH)-*co*-(20%)-NH_2] (**9c**)	40

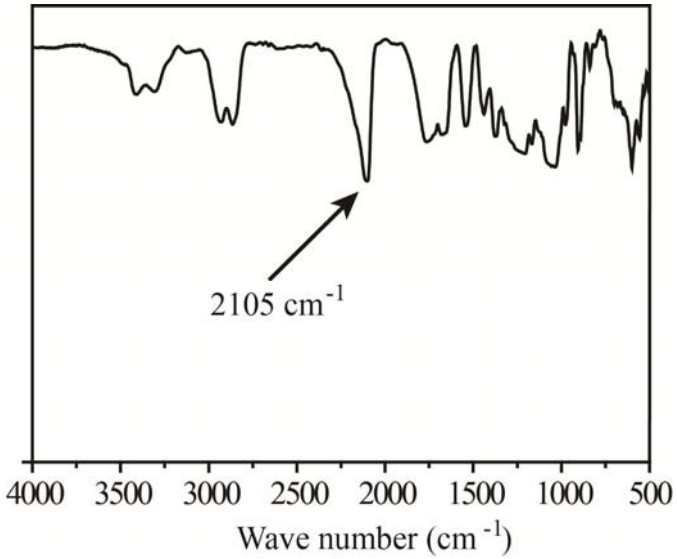
[a]The reduction of 6-*deoxy*-6-azido moiety was done by using trimethylphosphine in THF-water. [b]The molar ellipticity was calculated using the standard formula, $[\theta] = (\theta \times 100 \times M_w)/(C \times l)$, where θ = experimental ellipticity in millidegrees, M_w = average molecular weight, C = concentration in mg/mL, and l = path length in cm. The % α helicity was calculated by using the formula: % α helicity = $[(-[\theta]_{222}\ \text{nm} + 3000)/ 39000]\times 100$.



SI Figure 2: Size exclusion chromatogram of 6-*deoxy*-6-azido- functionalized glycopolypeptides (**A**) Ac30GP-N_3, **5a**, (**B**) Ac40GP-N_3, **6a** and (**C**) Ac50GP-N_3, **7a**.



SI Figure 3: Size exclusion chromatogram of glycopolypeptides. Black line indicates Ac30GP[OAc-co-(10%)-N_3] (8a) and red line indicates Ac30GP[OAc-co-(20%)-N_3] (9a).

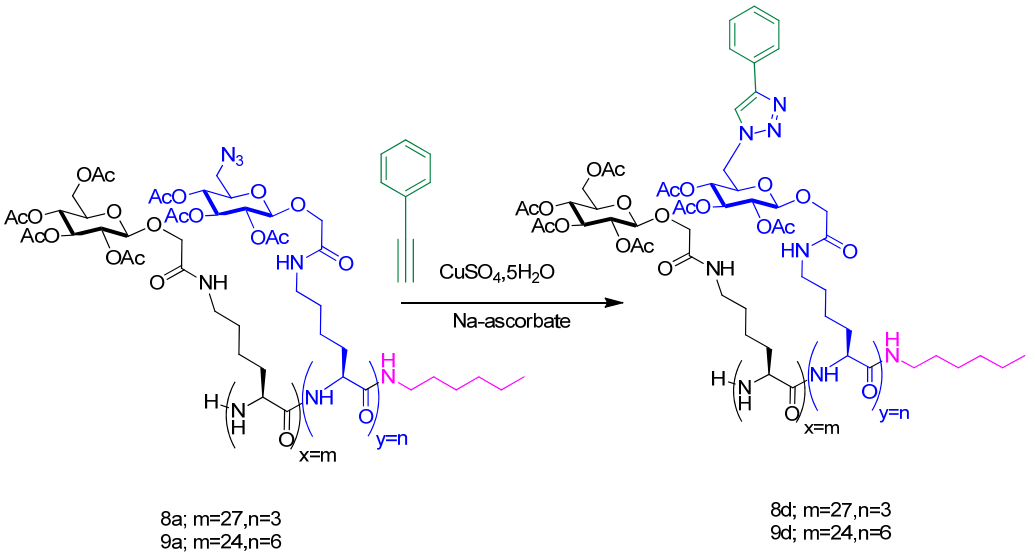


SI Figure 4: FT-IR spectra of 6-*deoxy*-6-azido functionalized glycopolypeptides **5a.**

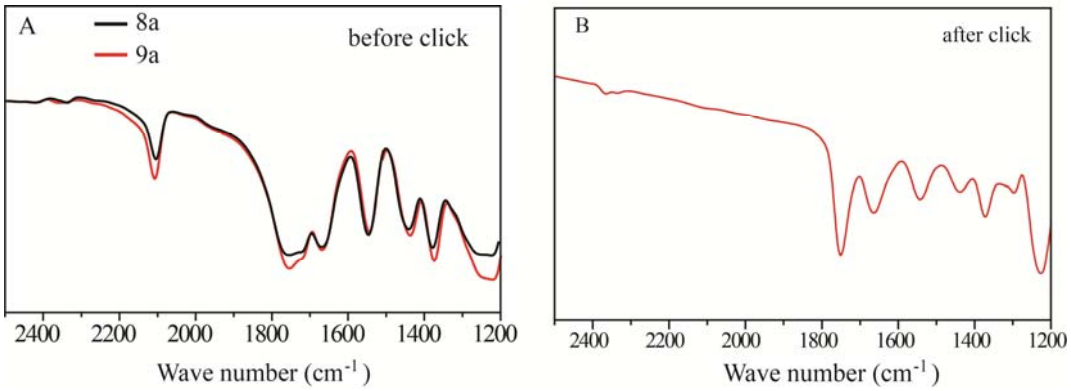
Estimation of azide incorporation by ^{1}H NMR analysis

The azide functionalized glycopolypeptide **8a** and **9a** was reacted with excess amount of phenyl acetylene (10 equivalent) in presence of $CuSO_4$, $5H_2O$ (5 equivalent) and sodium ascorbate (5 equivalent) in a solvent mixture THF: MeOH: H_2O (2: 2: 0.1). The reaction was

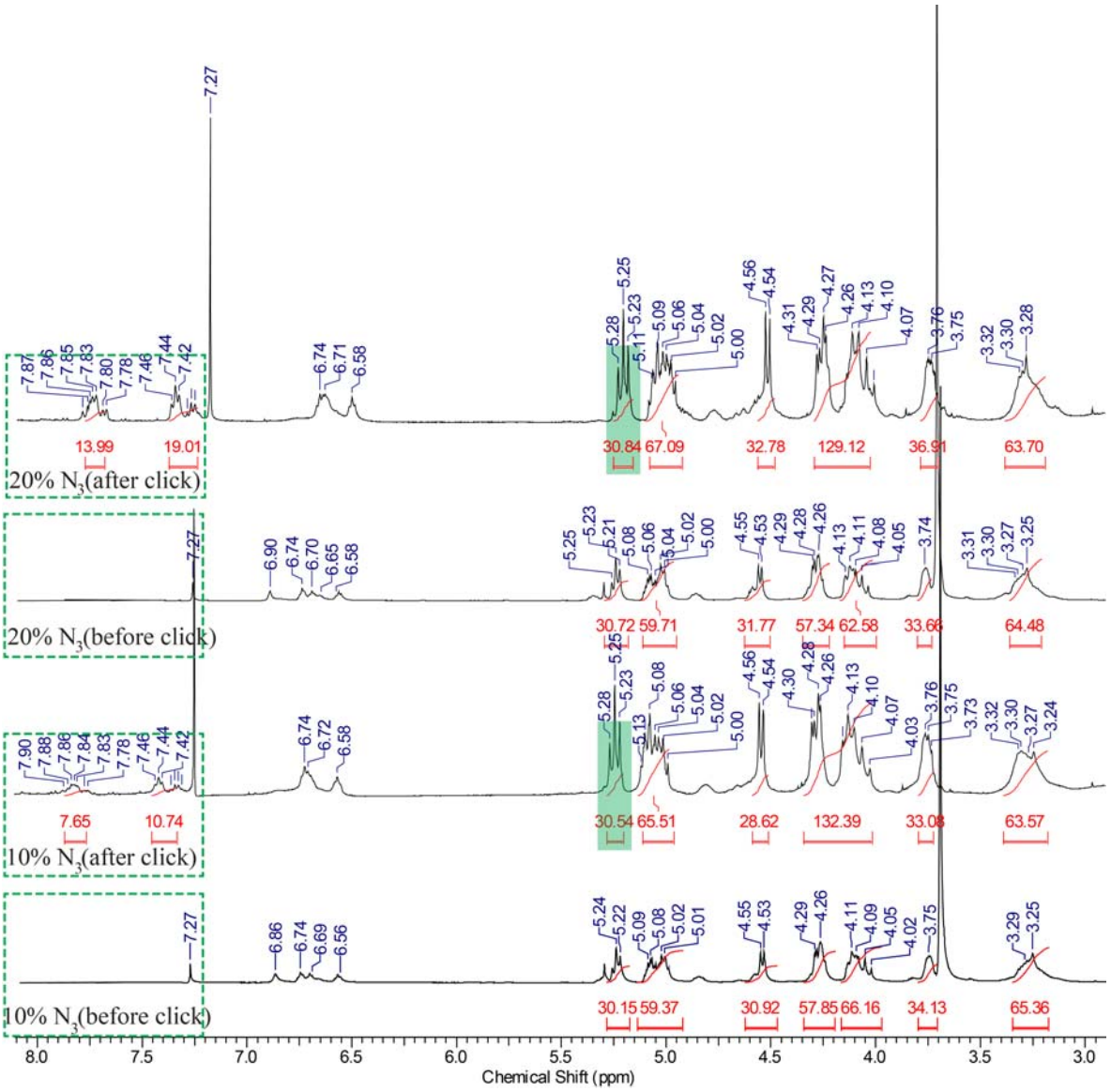
left for 24 hr under argon atmosphere. Then solvent was removed under reduced pressure and residue was re-dissolved in dichloromethane. It was then washed multiple times using dilute aqueous ammonia solution to remove copper salt. The dichloromethane was removed and the residue was re-dissolved in acetonitrile and washed with hexane. Then the polymer was dried thoroughly and analysed by ^{1}H NMR (SI figure 7). The % incorporation of azide monomer was estimated from ^{1}H NMR by comparing the relative intensity of the peak at 5.2 ppm due to characteristic proton present in the glucose moiety (methine; -CH) with the proton peaks of the aromatic group (C_6H_5-) present in the phenyl acetylene moiety (7.42-7.90) ppm.



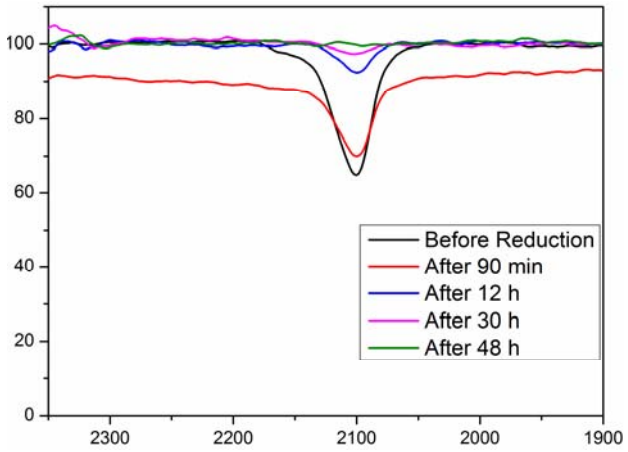
SI Figure 5: click reaction between the 6-N_3 and phenyl acetylene for the polymer **8a** and **9a**.



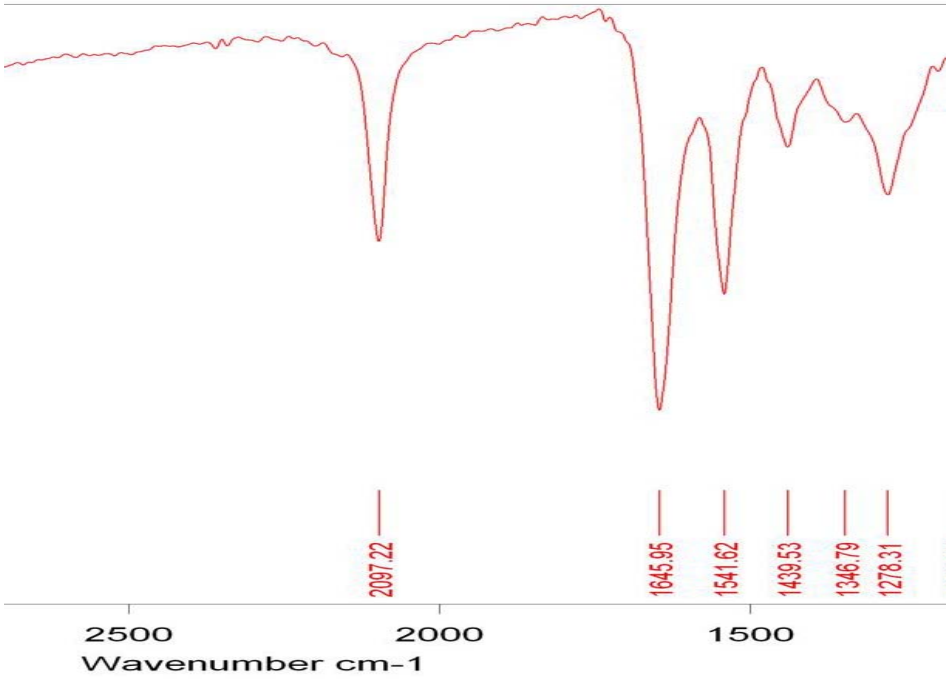
SI Figure 6: FT-IR spectrum of polymer **8a** and **9a** before click (A) and after click **9d** (B).



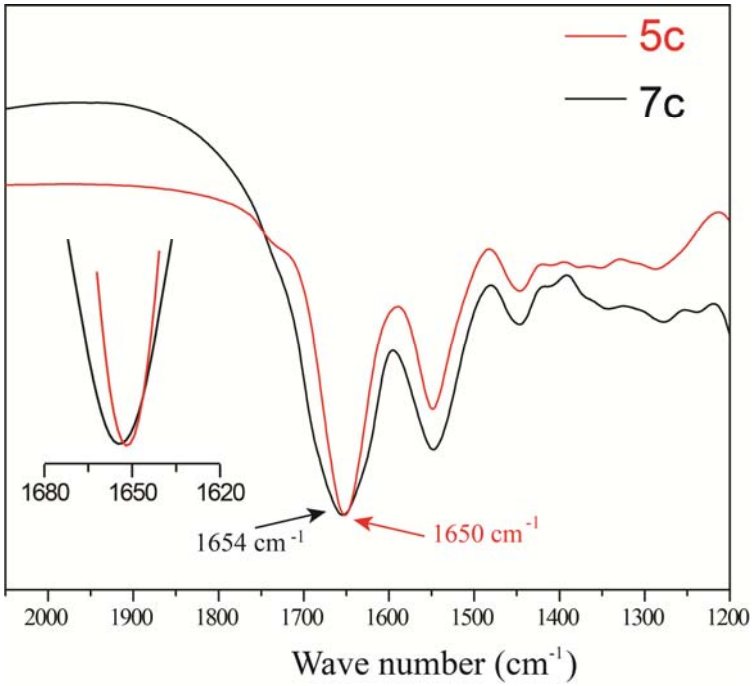
SI Figure 7: Comparison of ^{1}H NMR of the polymer **8a** and **9a** before click and after click.



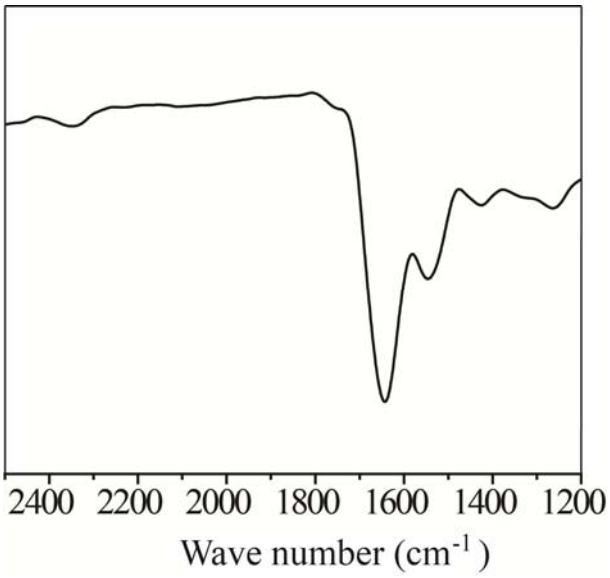
SI Figure 8: FT-IR spectra of Azide to Amine reduction using PMe_3 on Zn-Se plate.



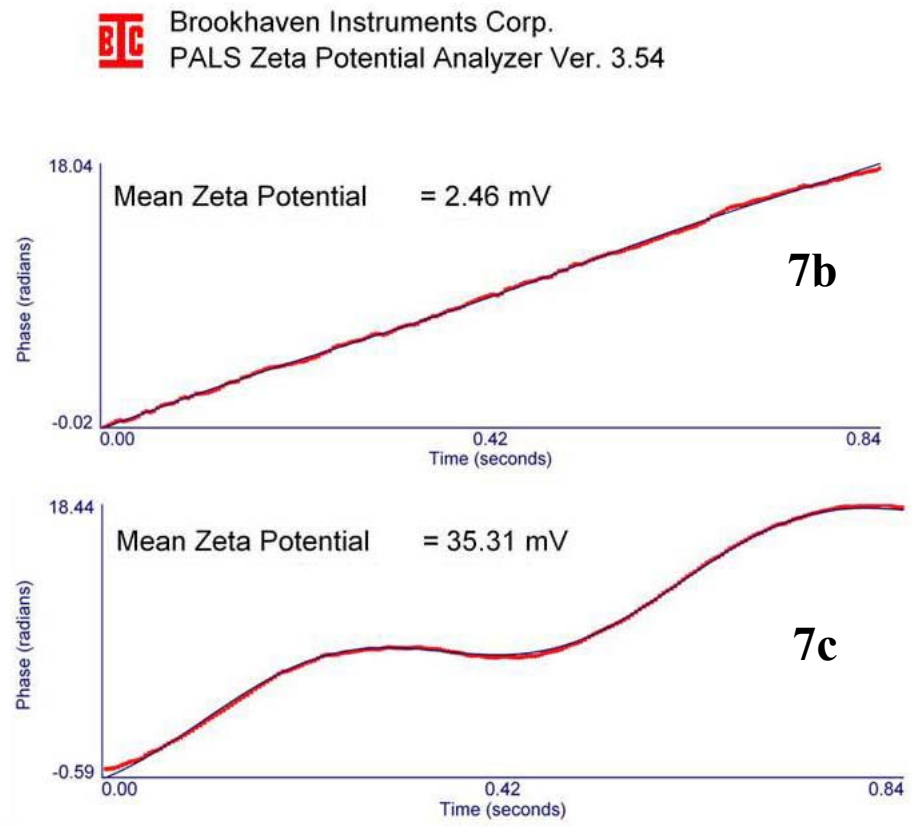
SI Figure 9: FT-IR spectra of **7b** (before click).



SI Figure 10: FT-IR spectra of cationic glycopolypeptide (OH)30GP-NH_2(**5c**) and (OH)50GP-NH_2(**7c**).



SI Figure 11: FT-IR spectra of **7d** (after click).

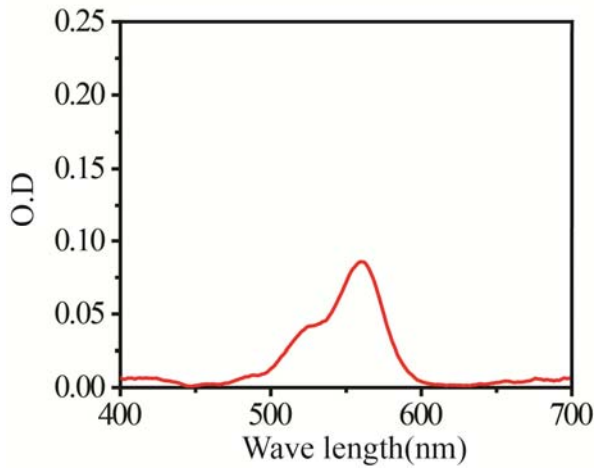


SI Figure 12: Zeta potentials measurement of the polymer **7b** and **7c**

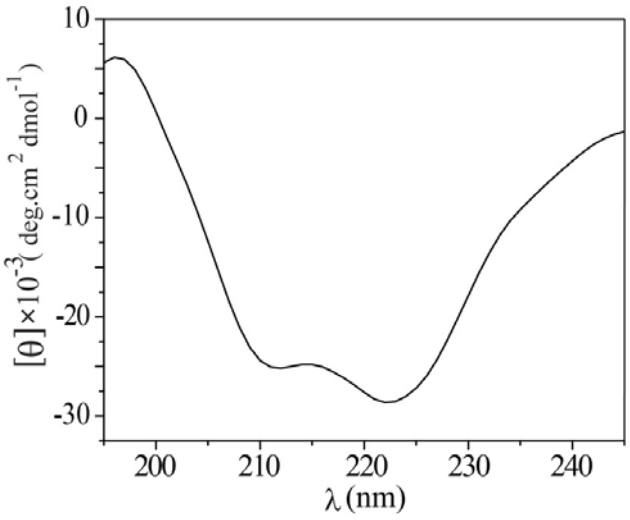
Labelling of the Ac50GP-NH_2 by Rhodamine-B isothiocyanate

To a solution of Ac50GP-NH_2 (20 mg/mL solution in THF) was added Rhodamine-B isothiocyanate (0.05 equivalents with respect to the polymer) and the reaction mixture was

incubated overnight under inert atmosphere. Solvent was removed from the crude reaction mixture followed by addition of hydrazine hydrate for removal of the acetate groups from carbohydrate moiety. The reaction mixture was dialysed against deionised water for long time for complete removal of the unreacted rhodamine dye. The resultant glycopolypeptide was lypholized to get solid product. This rhodamine labelled glycopolypeptide was used further for cellular uptake studies.



SI Figure 13: UV-vis spectra of Rhodamine-B labelled polymer.

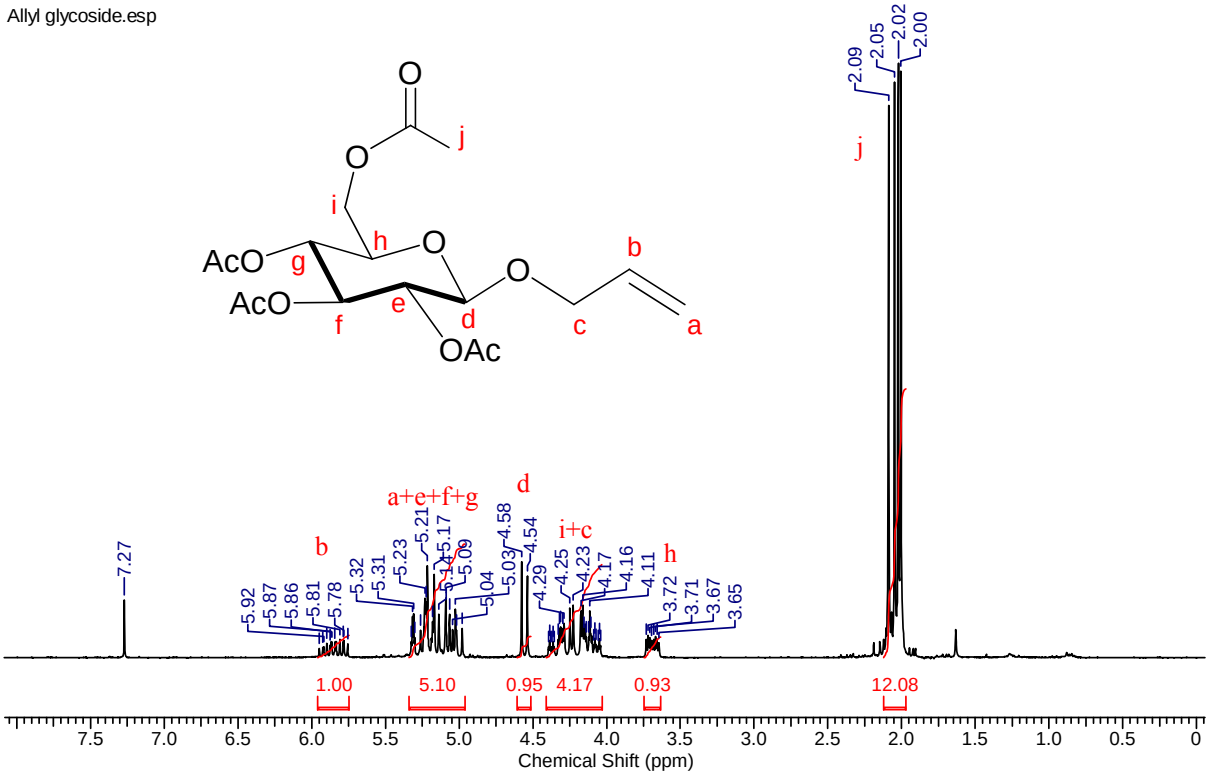


SI Figure 14: Circular dichroism spectra of the polymer **7d**.

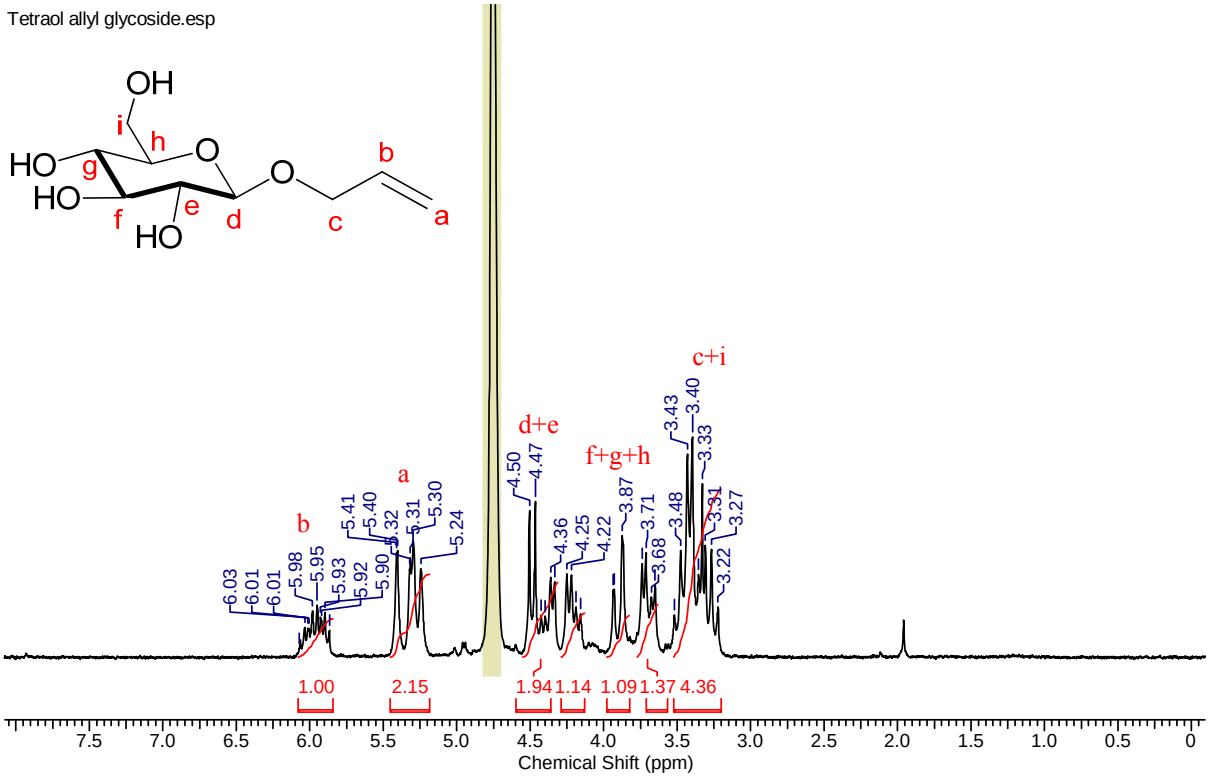
^{1}H NMR, ^{13}C and DEPT Spectra of the compounds

(* peak in NMR indicates residual solvents peak)

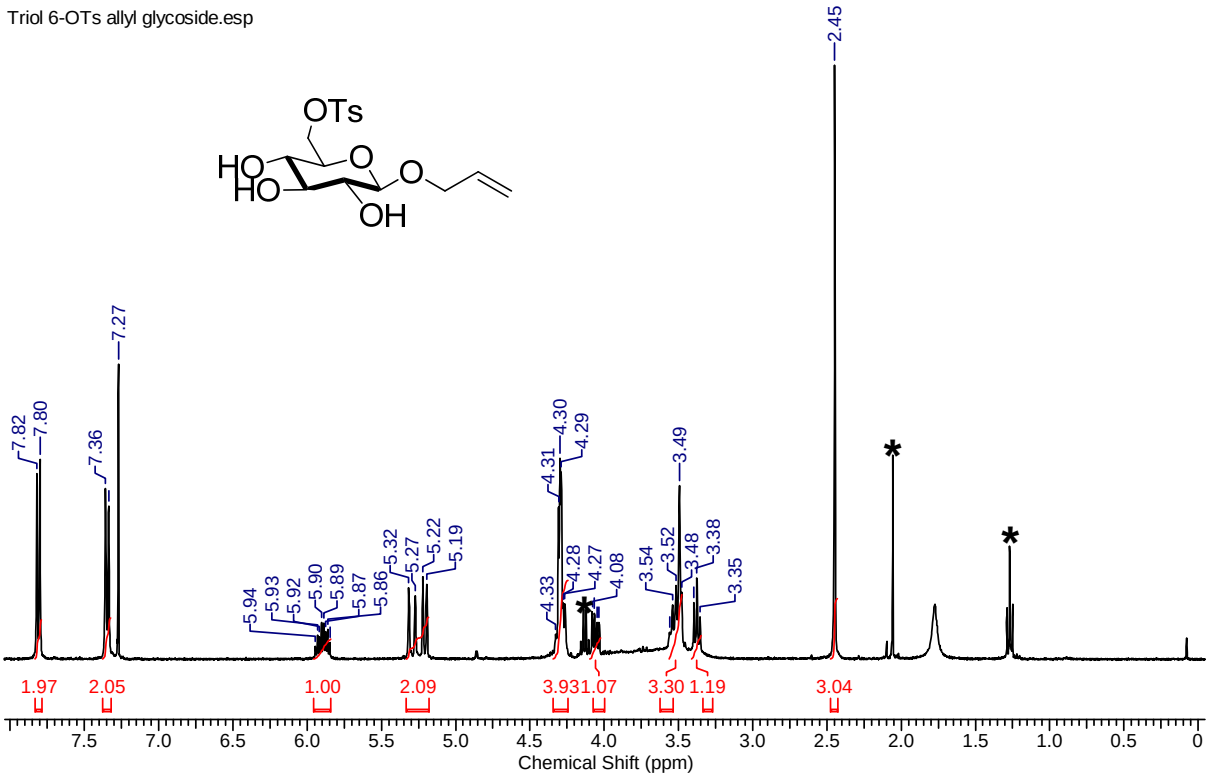
^{1}H NMR ($CDCl_3$, 200.13 MHz) Spectrum



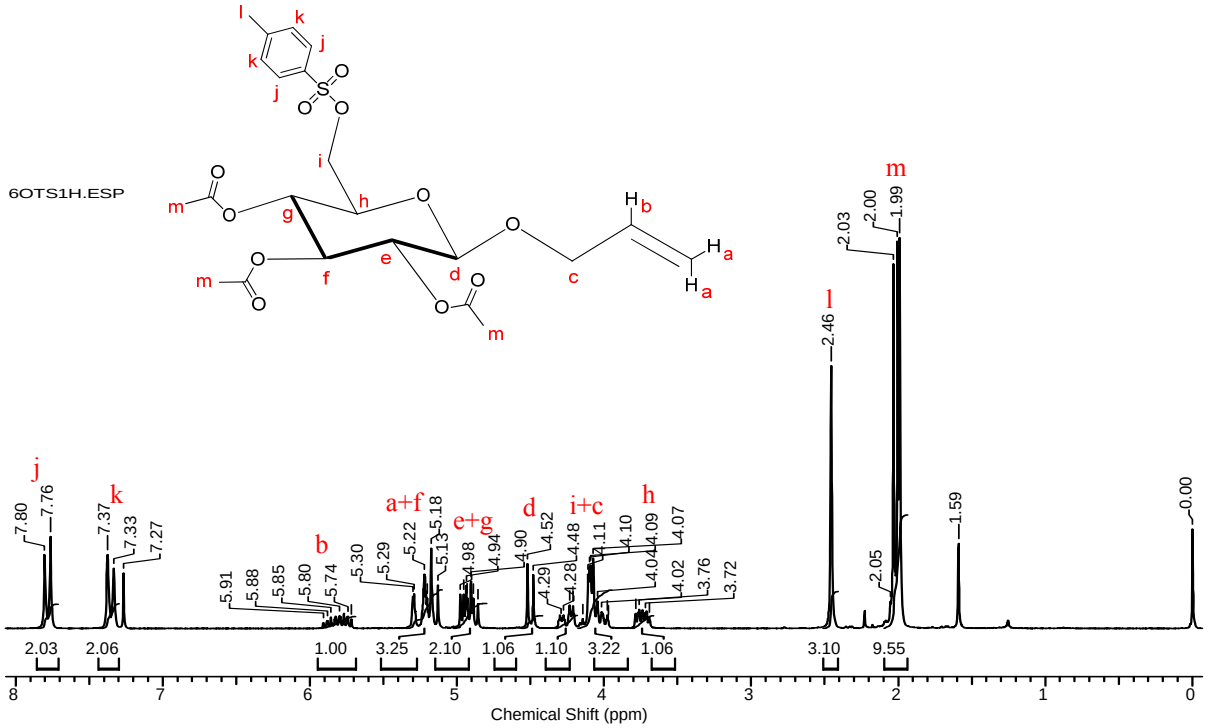
^{1}H NMR (D_2O, 200.13 MHz) Spectrum



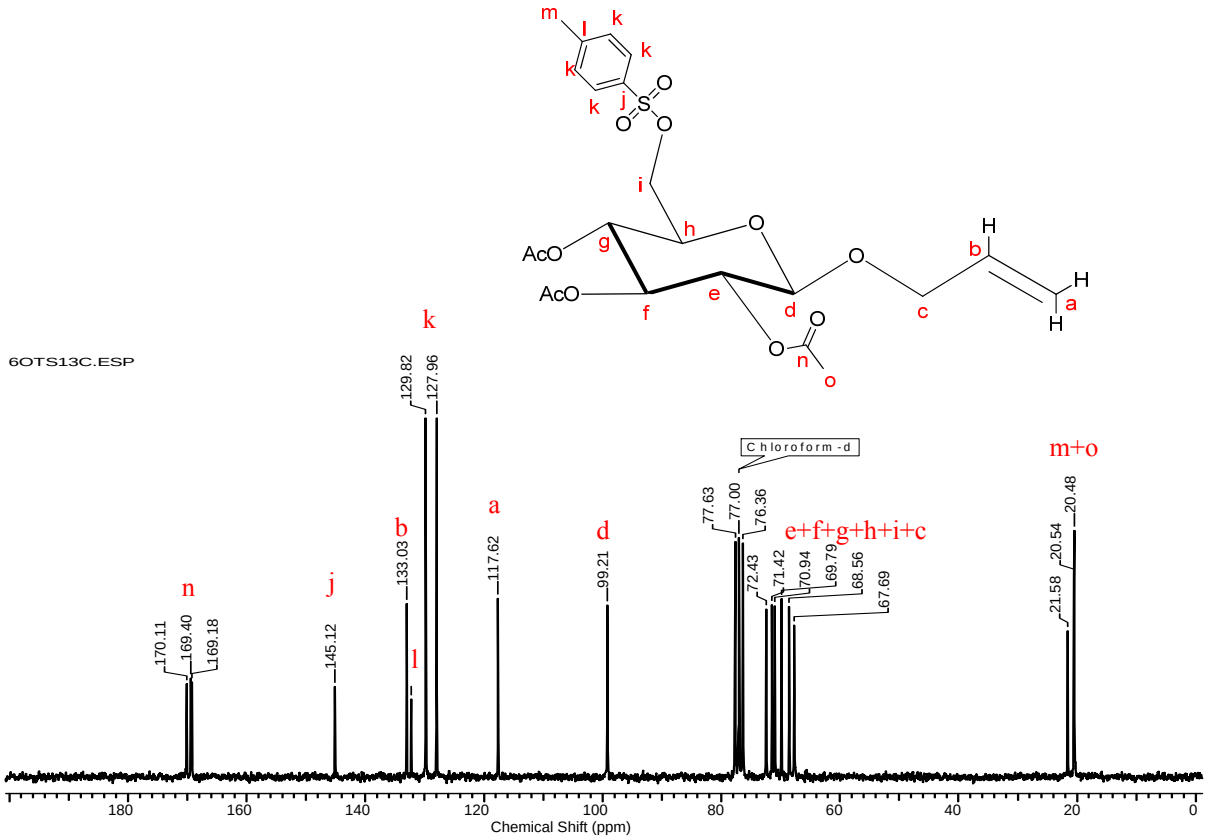
^{1}H NMR ($CDCl_3$, 200.13 MHz) Spectrum



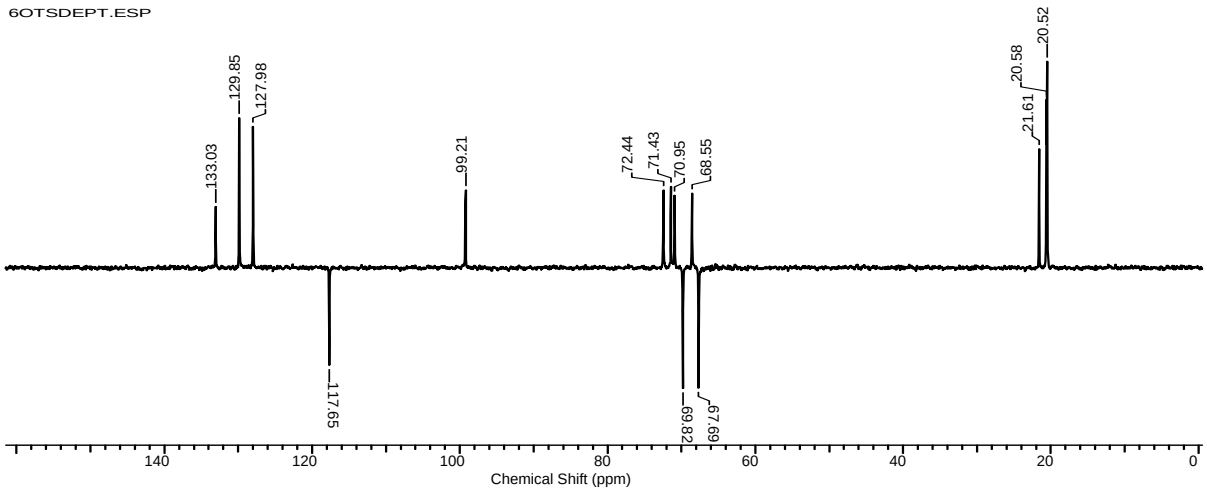
^{1}H NMR ($CDCl_3$, 200.13 MHz) Spectrum of Compound **2a**



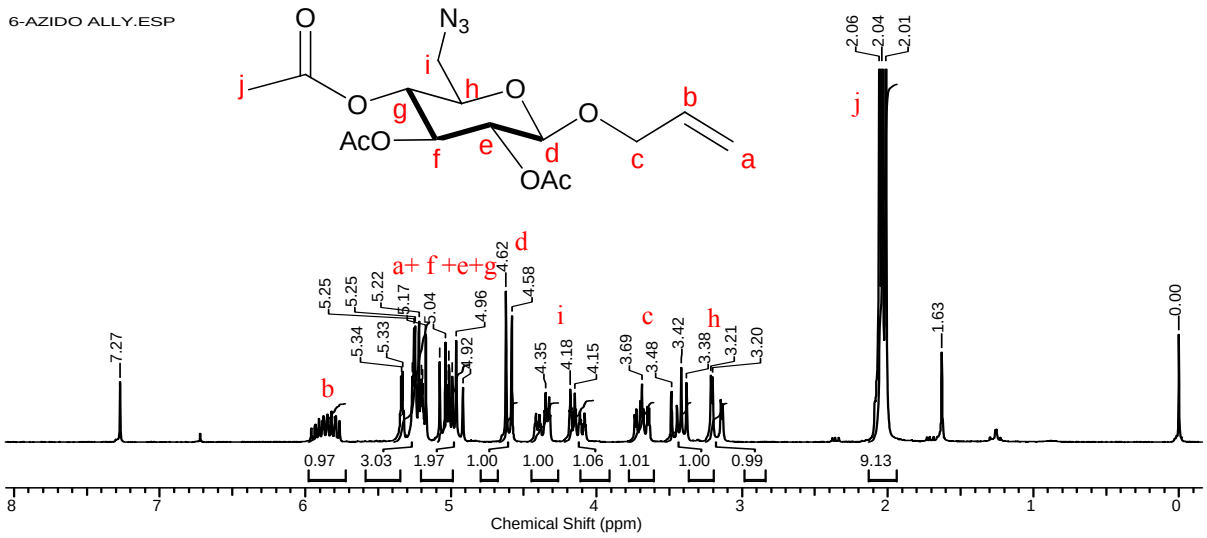
^{13}C NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **2a**



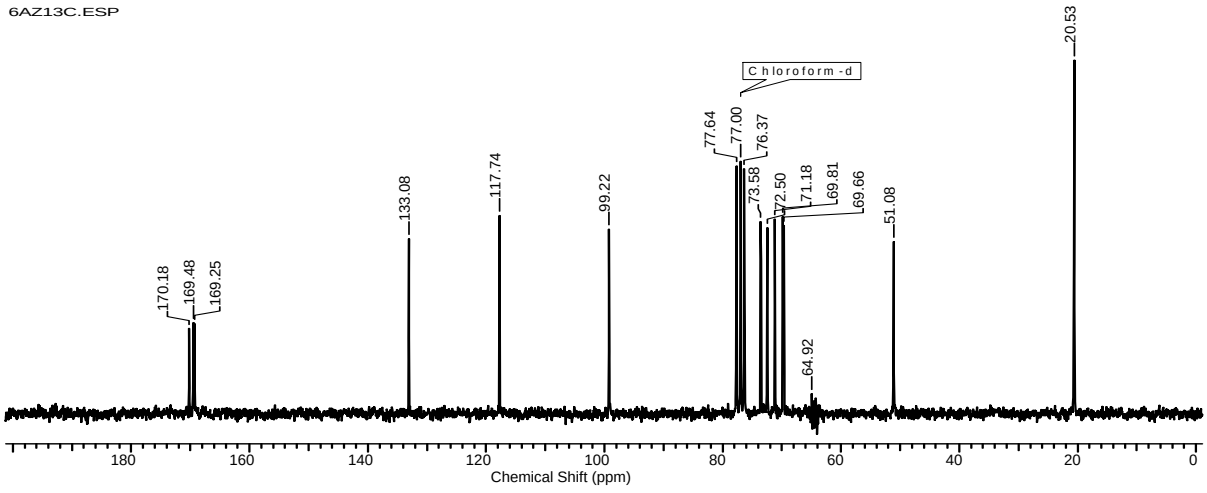
DEPT NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **2a**



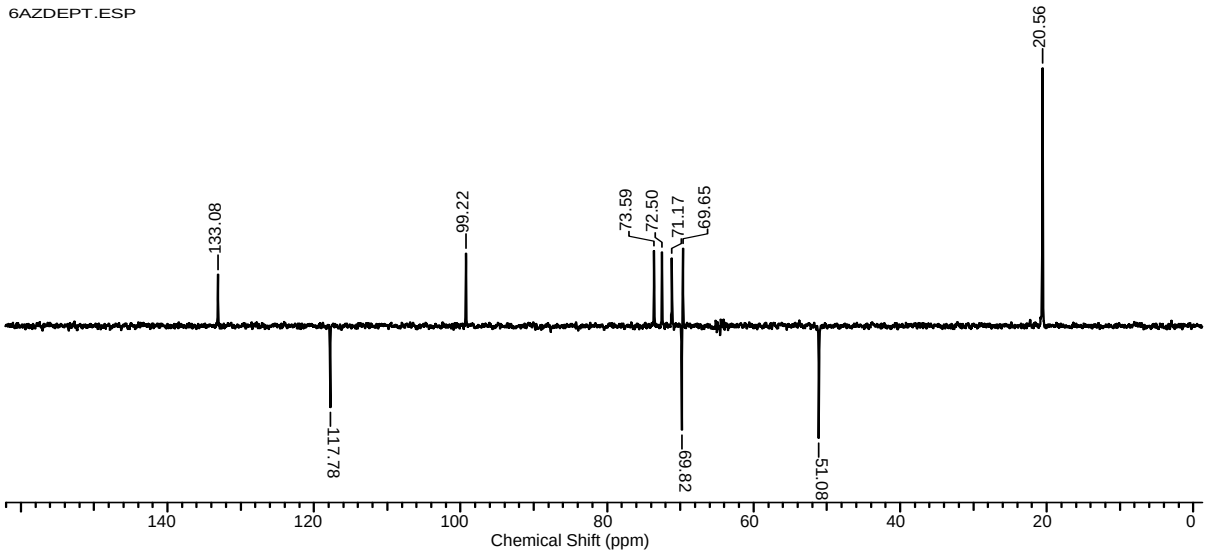
^{1}H NMR ($CDCl_3$, 200.13 MHz) Spectrum of Compound **2b**



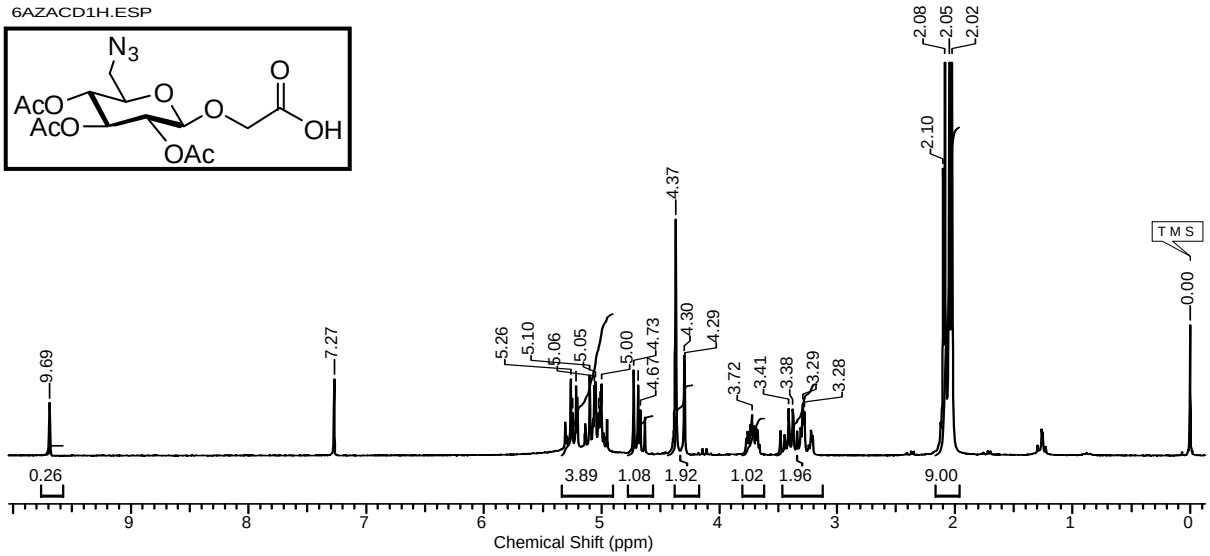
^{13}C NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **2b**



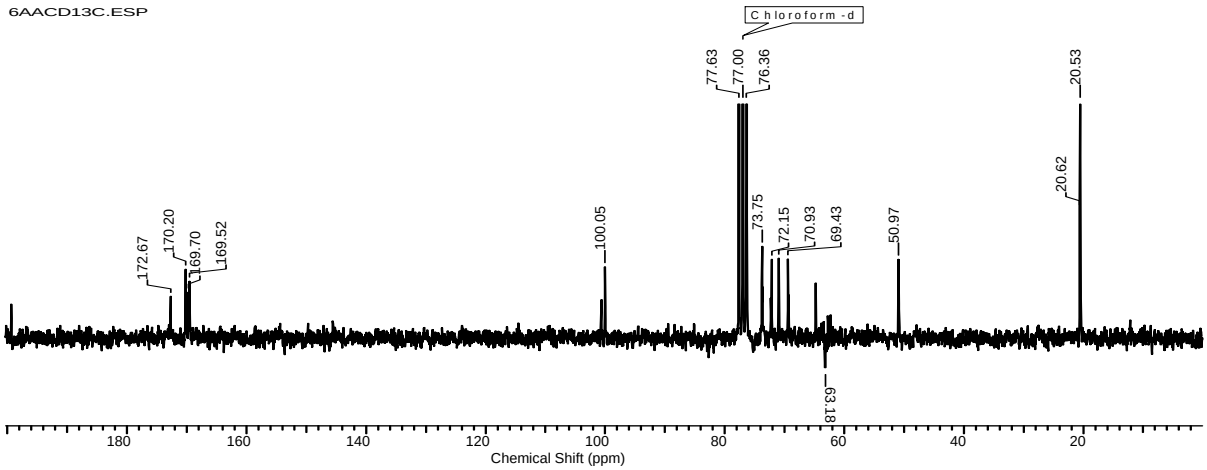
DEPT NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **2b**



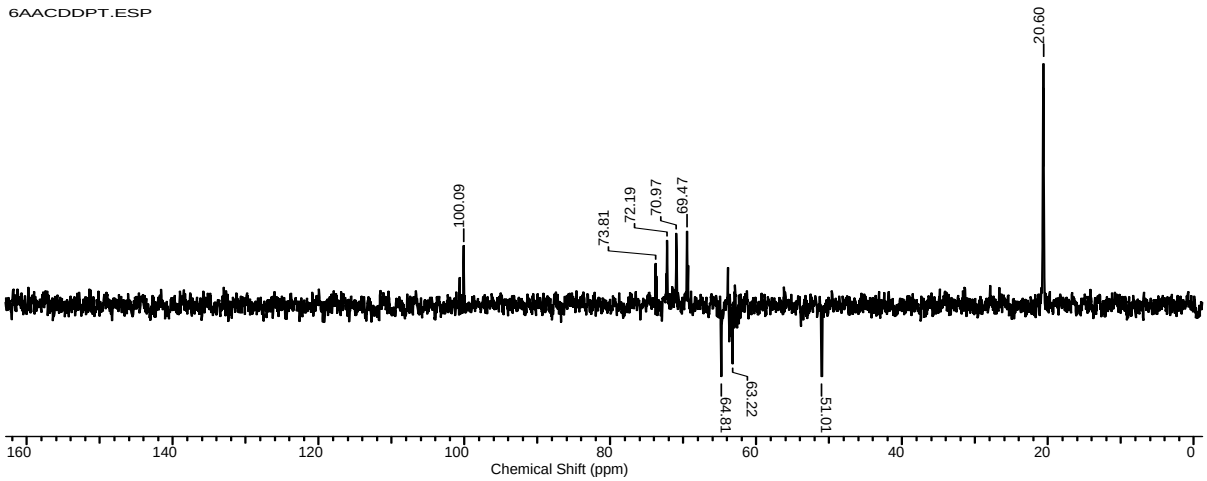
^1H NMR ($CDCl_3$, 200.13 MHz) Spectrum of Compound **2c**



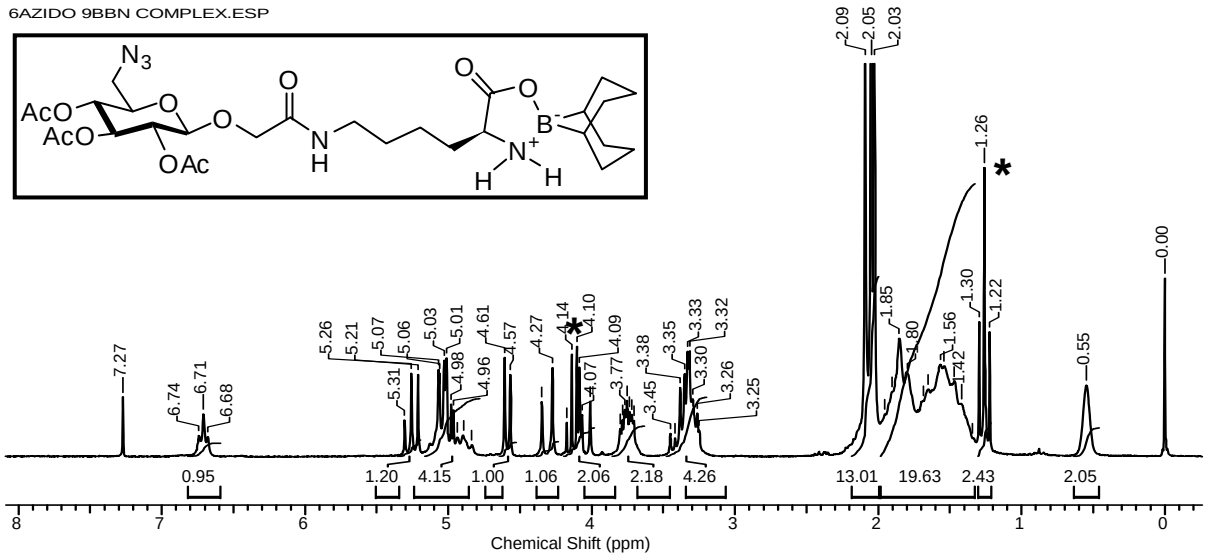
^{13}C NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **2c**



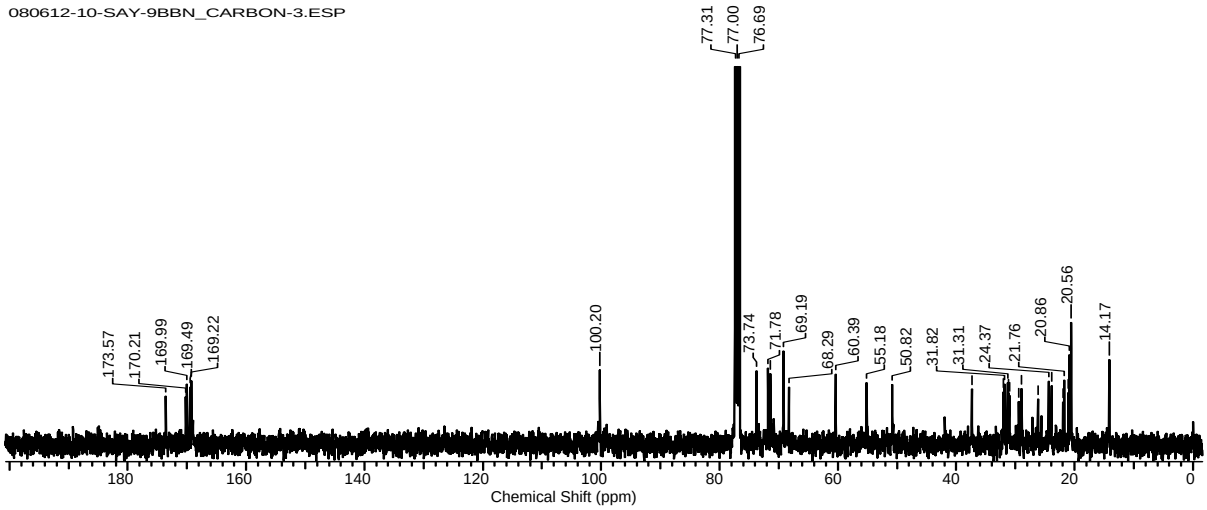
DEPT NMR ($CDCl_3$, 50.32 MHz) Spectrum of Compound **2c**



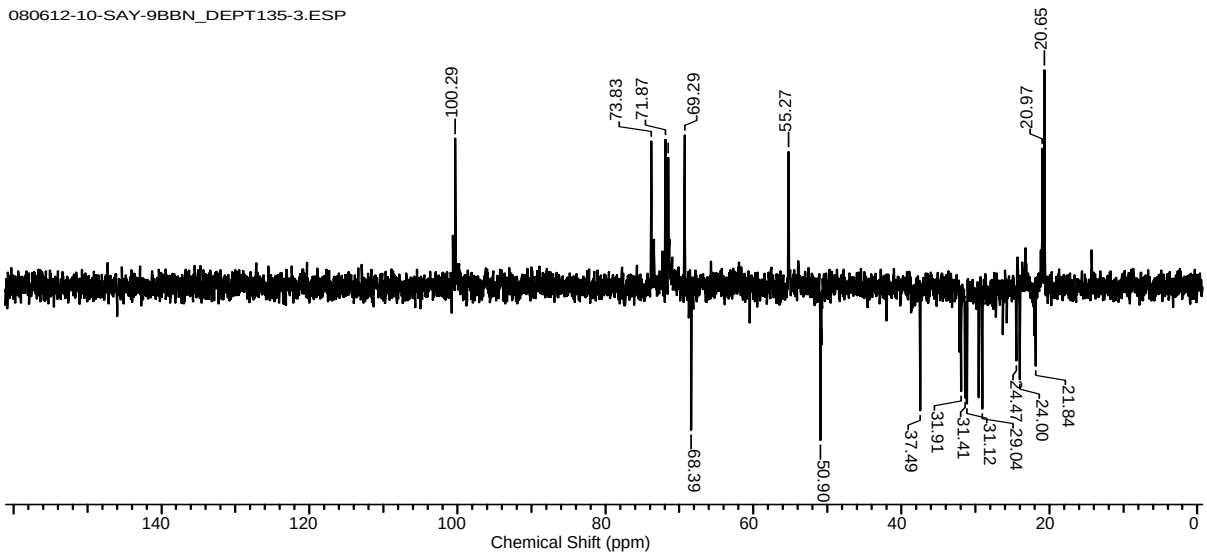
^{1}H NMR ($CDCl_3$, 399.78 MHz) Spectrum of Compound **3a**



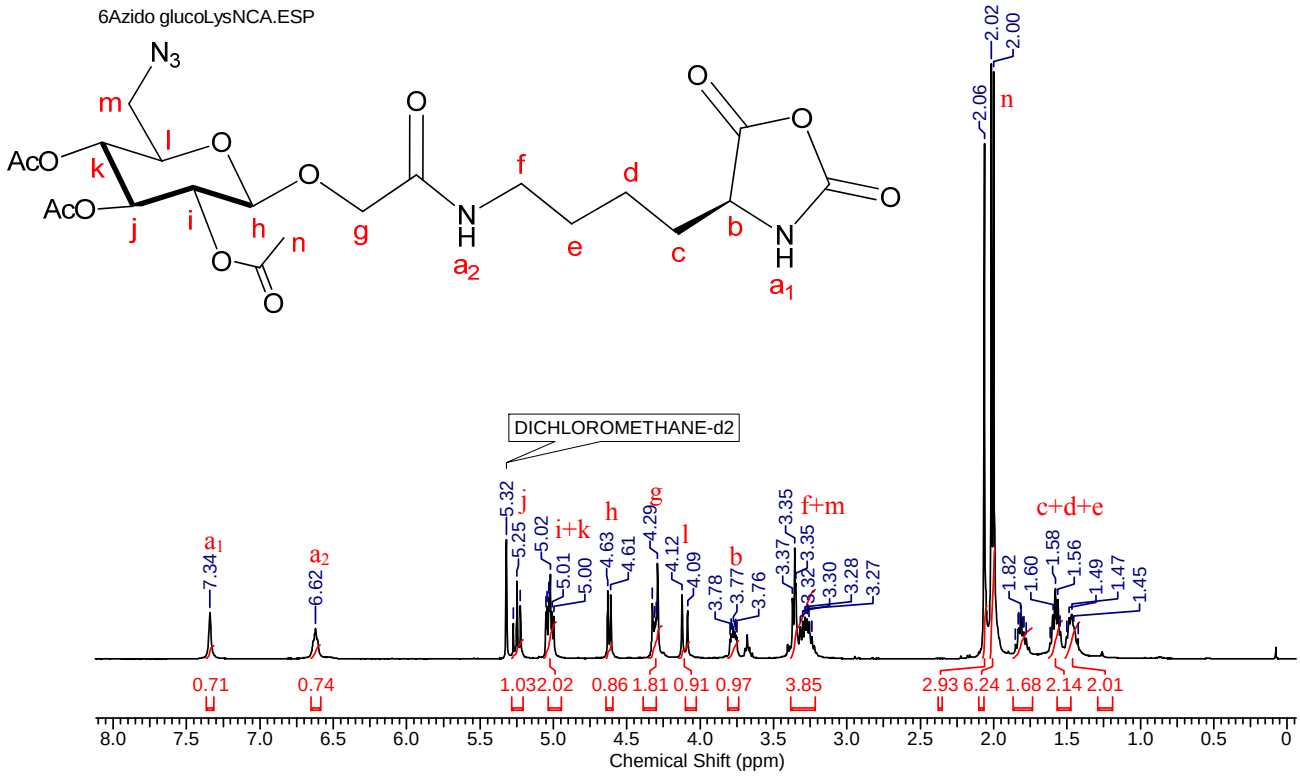
^{13}C NMR ($CDCl_3$, 100.53 MHz) Spectrum of Compound **3a**



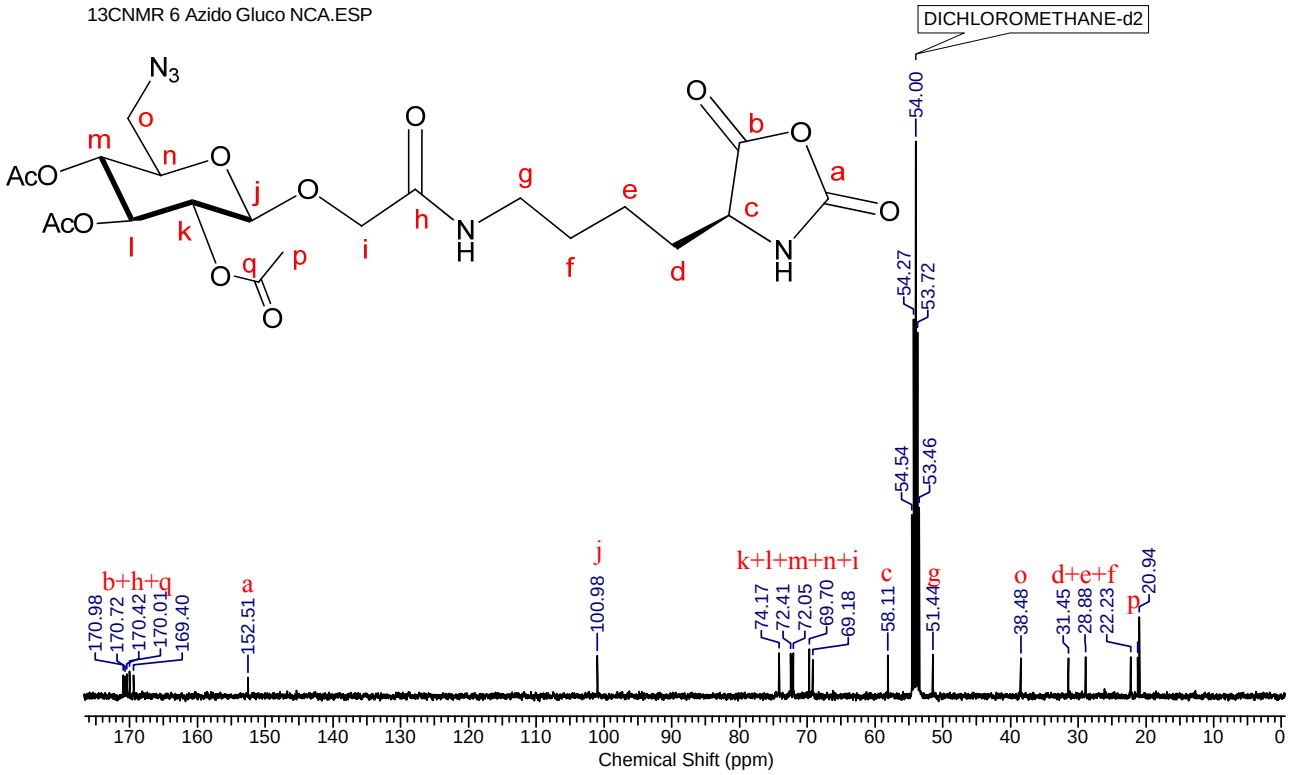
DEPT NMR ($CDCl_3$, 100.53 MHz) Spectrum of Compound **3a**



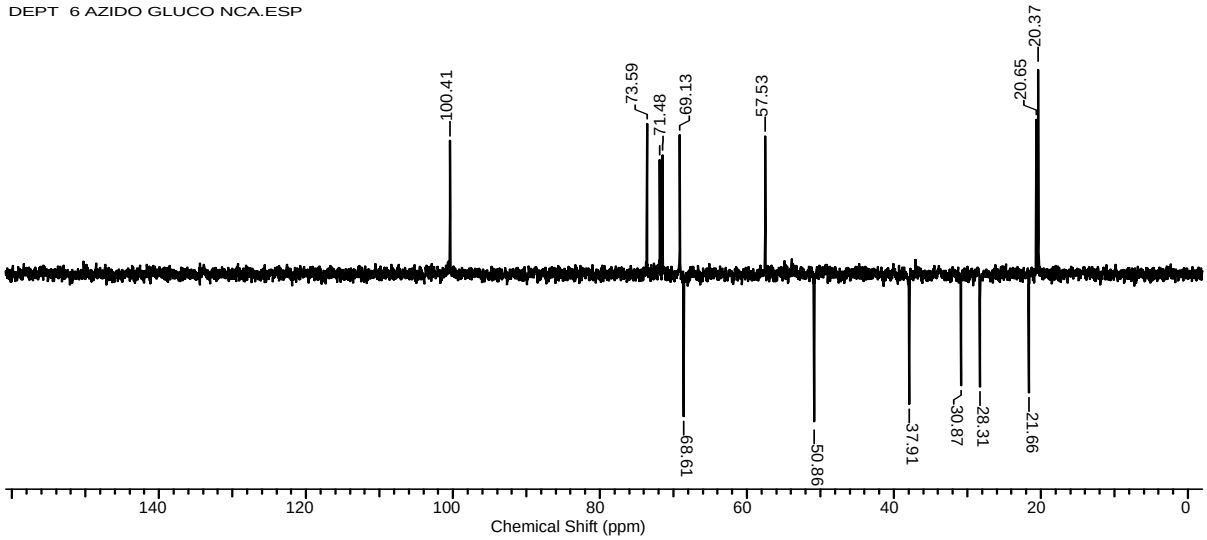
^{1}H NMR (CD_2Cl_2, 400.13 MHz) Spectrum of Compound **4a**



^{13}C NMR (CD_2Cl_2, 100.61 MHz) Spectrum of Compound **4a**

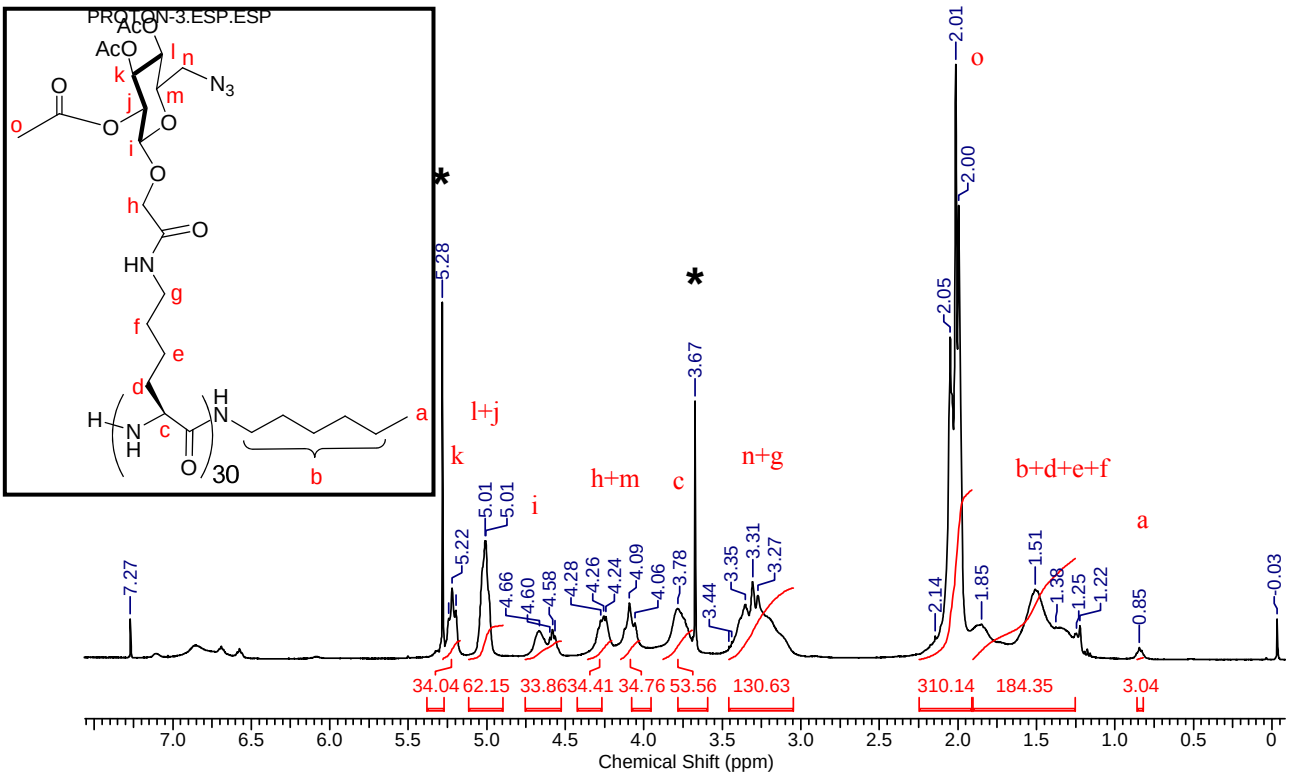


DEPT NMR (CD_2Cl_2, 100.61 MHz) Spectrum of Compound **4a**

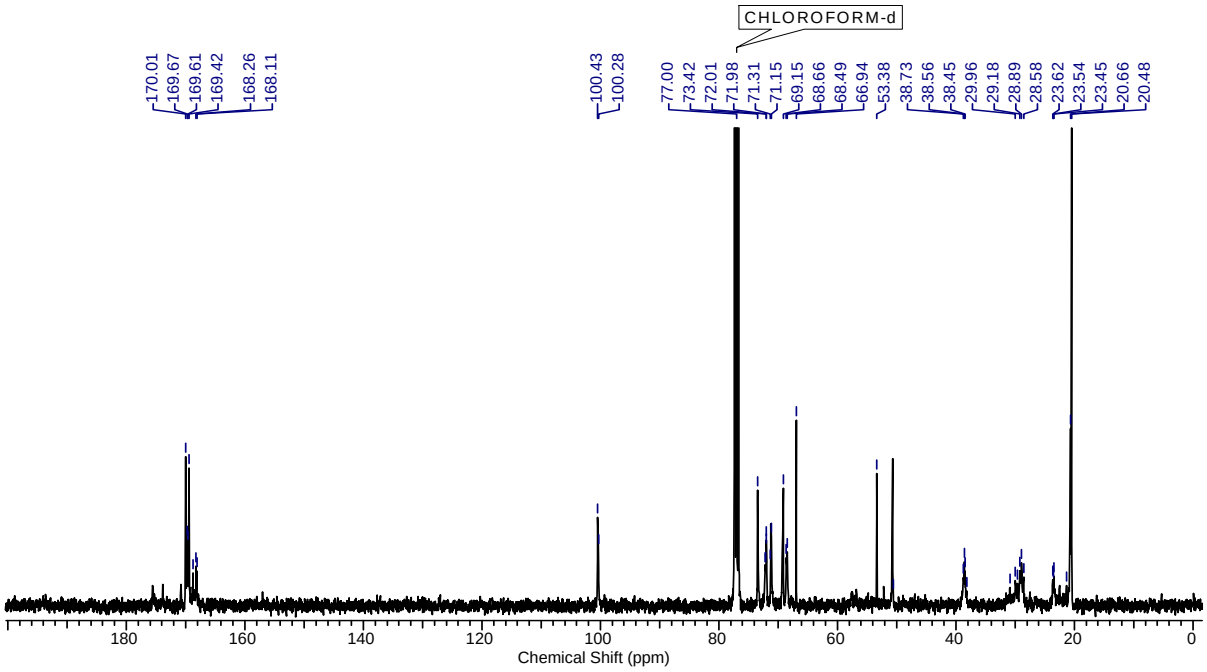


^{1}H NMR ($CDCl_3$, 399.78 MHz) Spectrum of Compound

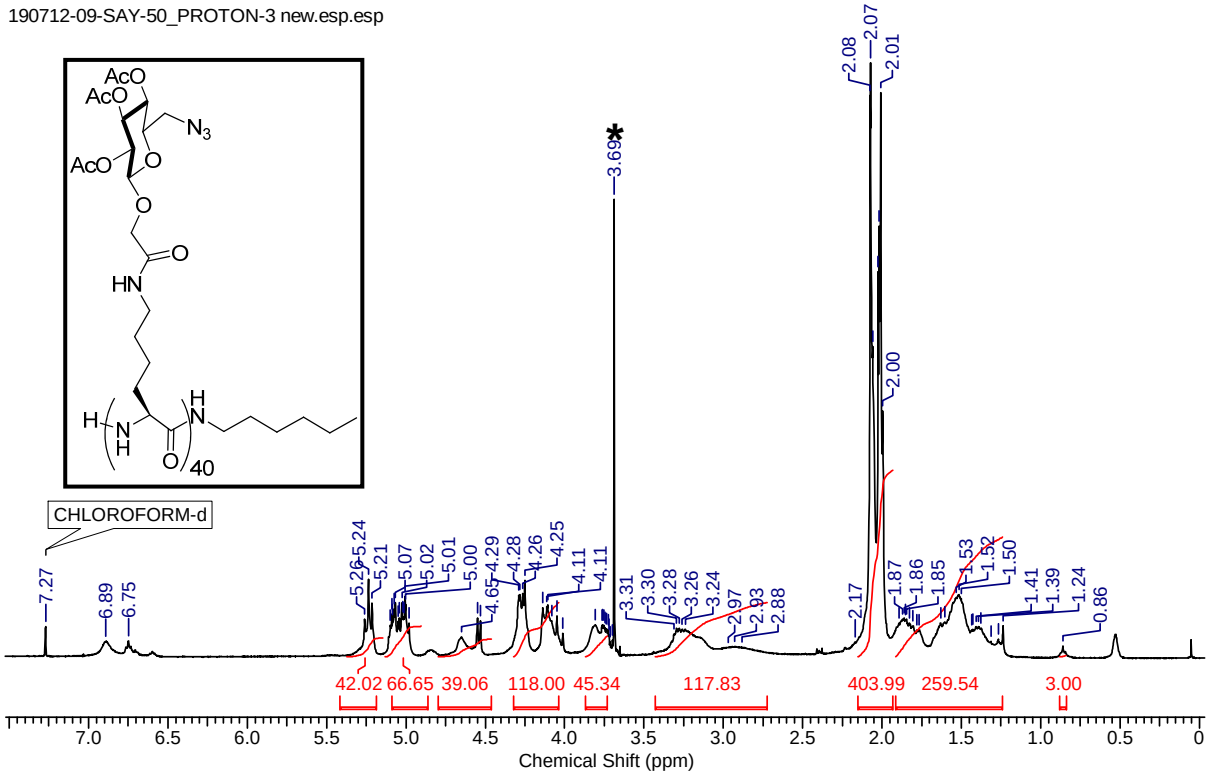
5a



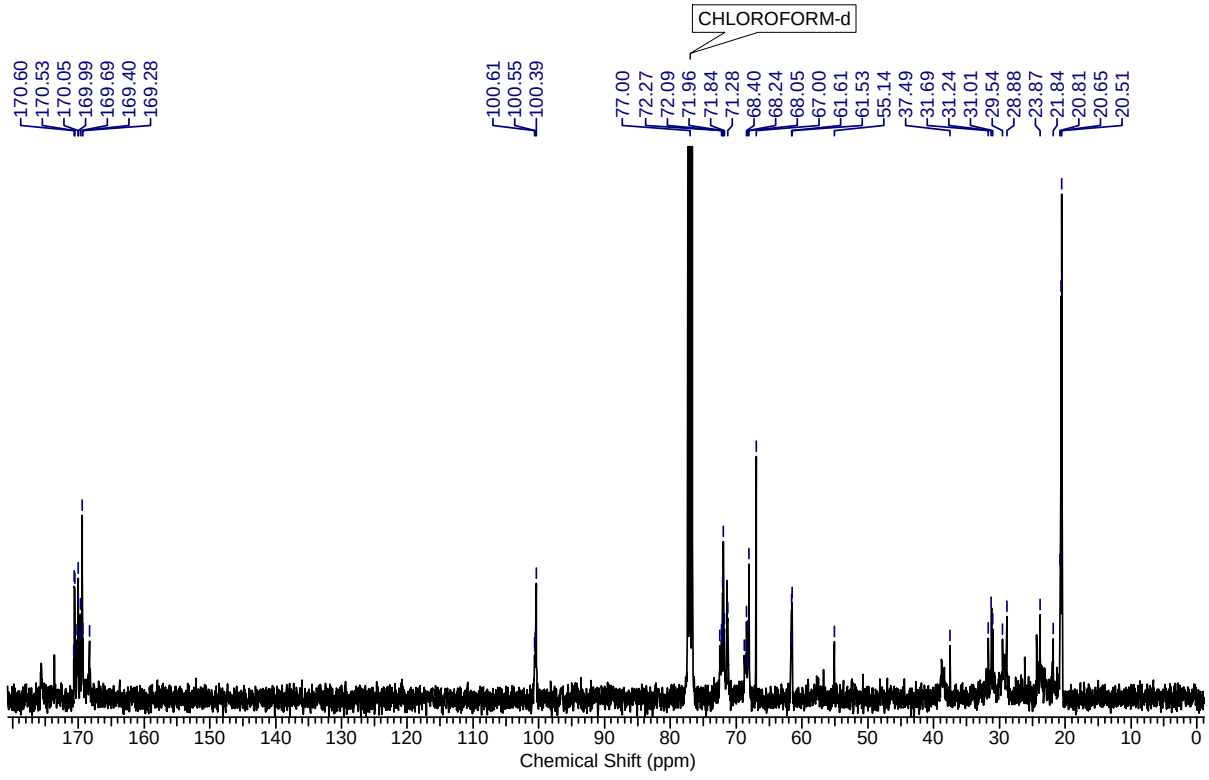
^{13}C NMR ($CDCl_3$, 100.53 MHz) Spectrum of Compound **5a**



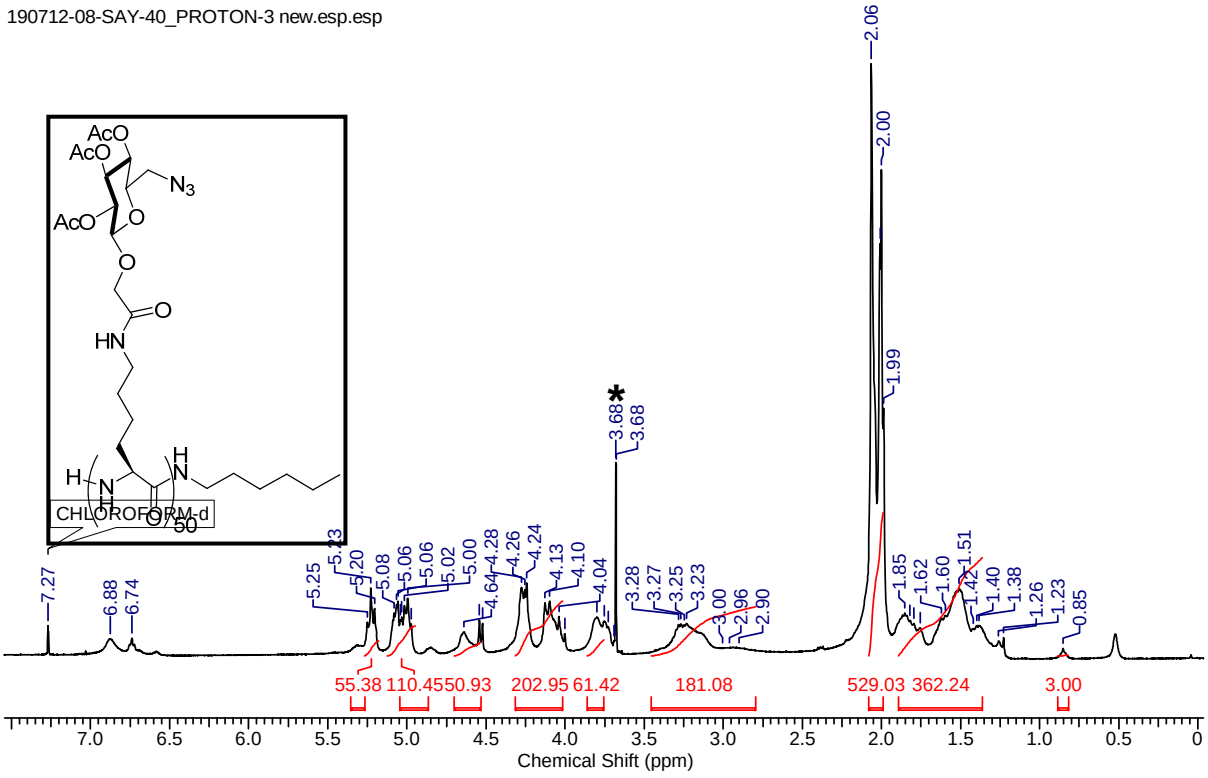
^{1}H NMR ($CDCl_3$, 399.78 MHz) Spectrum of Compound **6a**



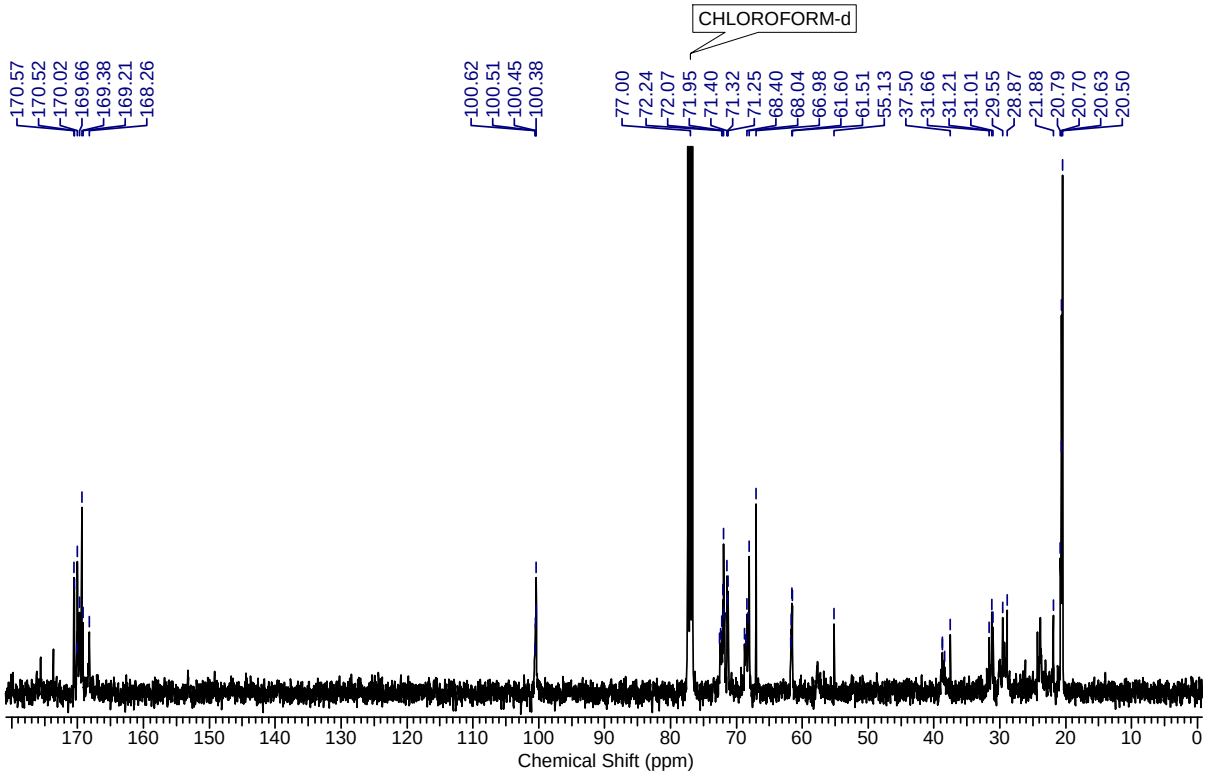
^{13}C NMR ($CDCl_3$, 100.53 MHz) Spectrum of Compound **6a**



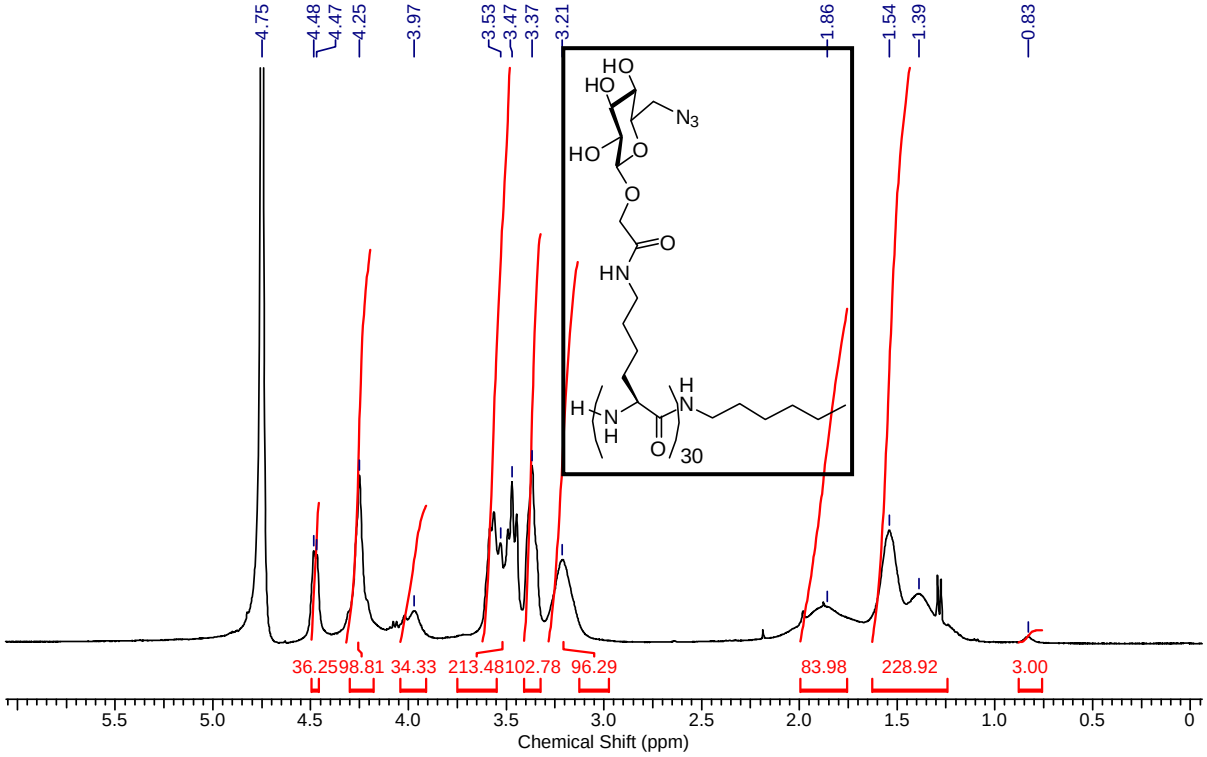
^{1}H NMR ($CDCl_3$, 399.78 MHz) Spectrum of Compound **7a**



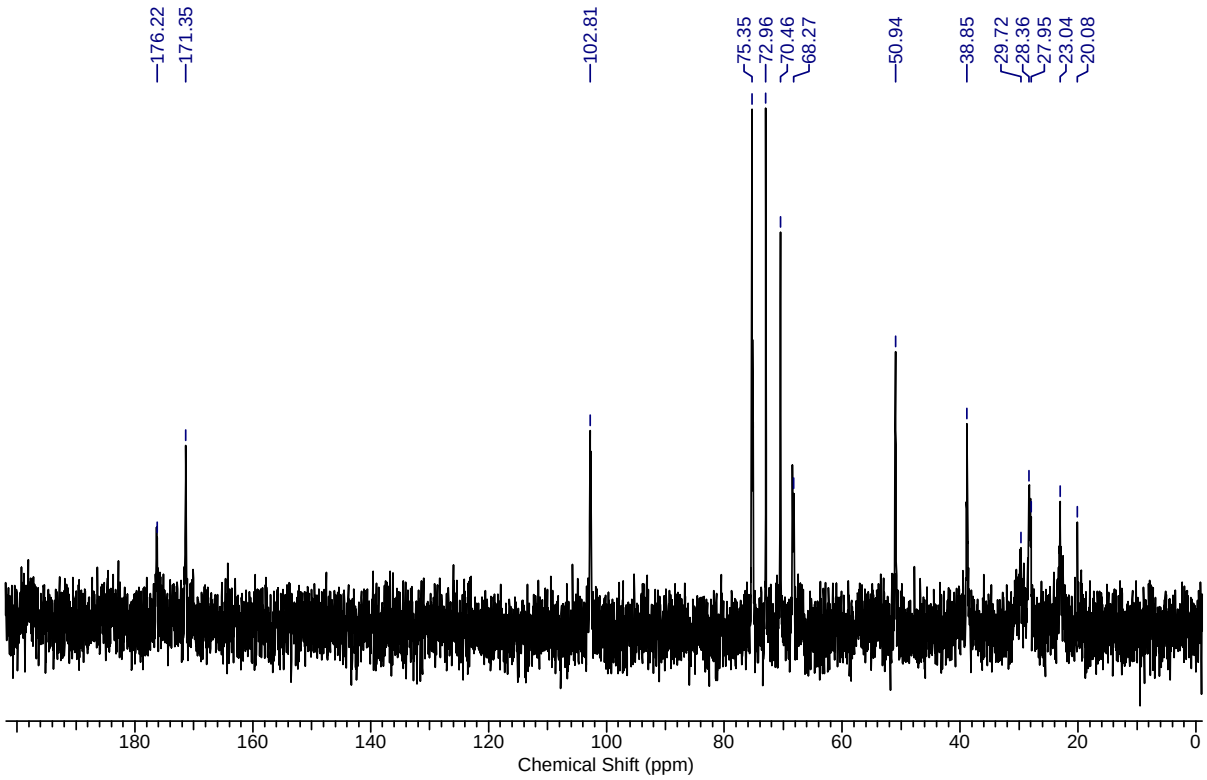
^{13}C NMR ($CDCl_3$, 100.53 MHz) Spectrum of Compound **7a**



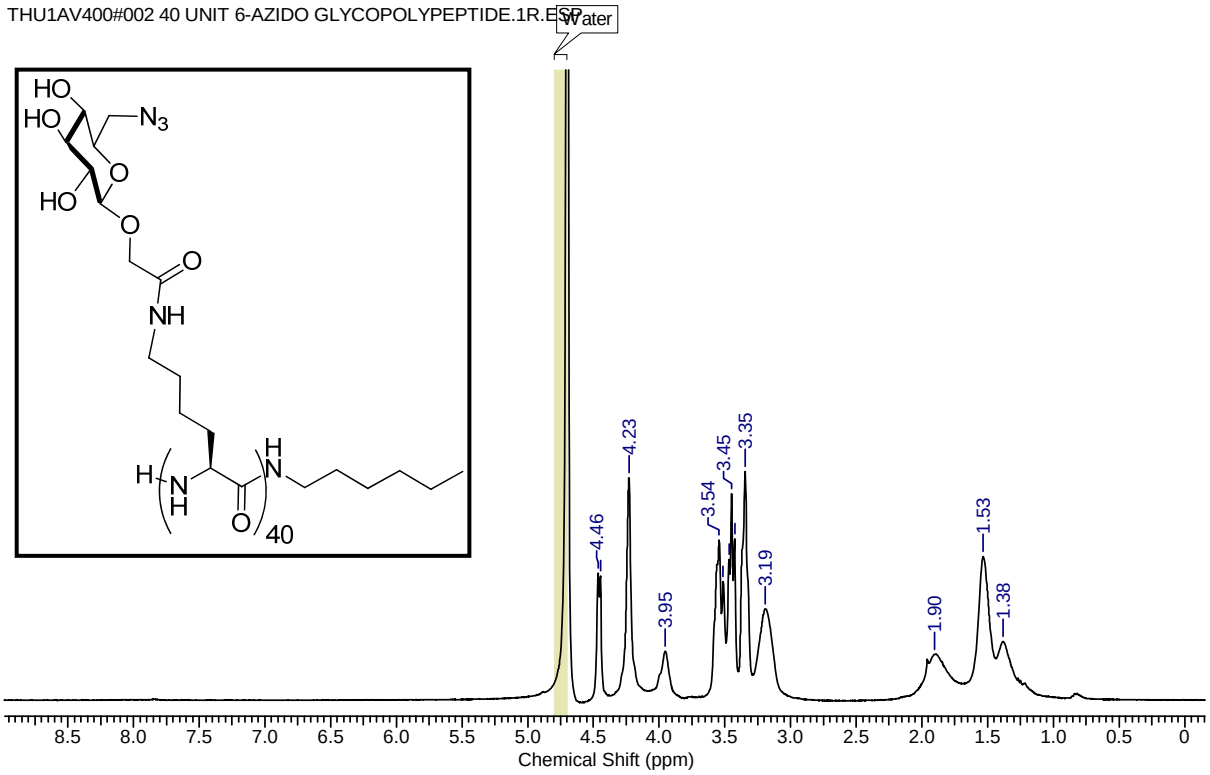
^{1}H NMR (D_2O, 399.78 MHz) Spectrum of Compound **5b**



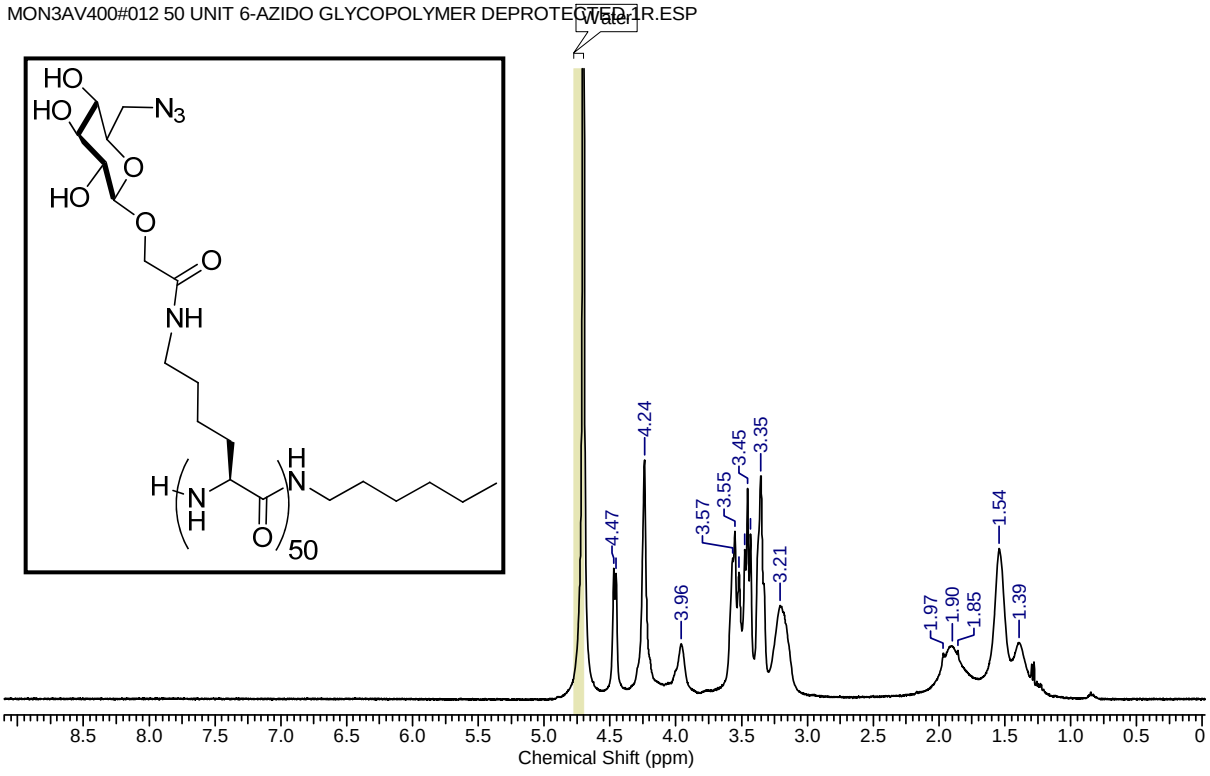
^{13}C NMR (D_2O, 100.53 MHz) Spectrum of Compound **5b**



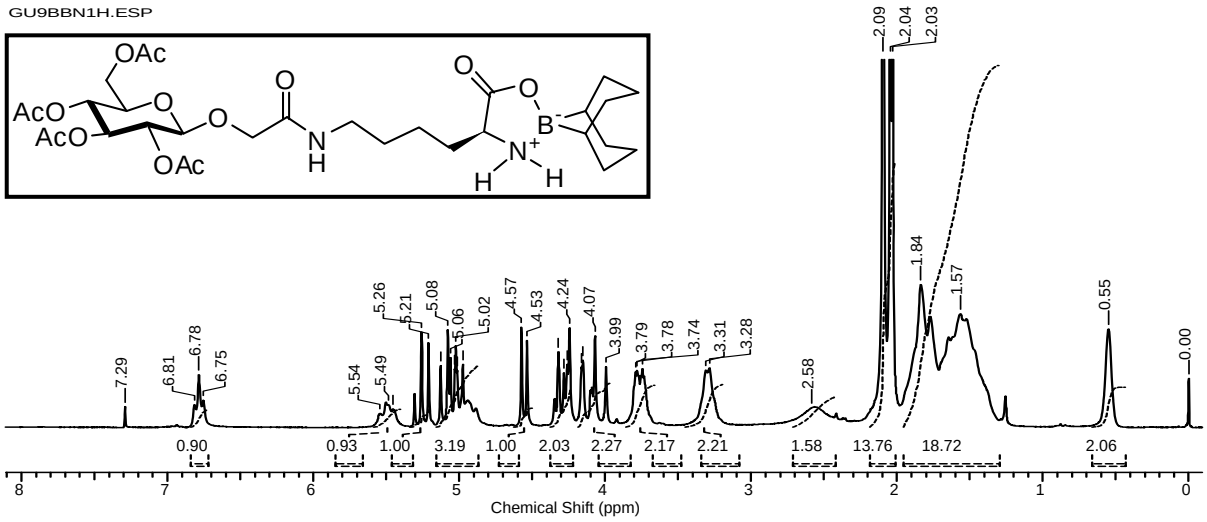
^{1}H NMR (D_2O, 399.78 MHz) Spectrum of Compound **6b**



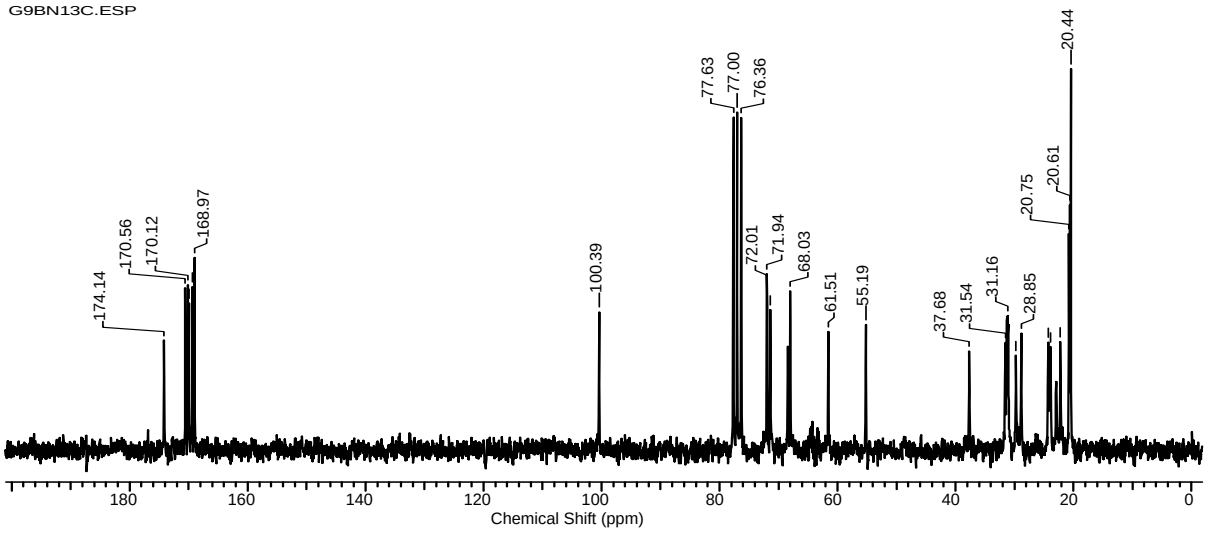
^{1}H NMR (D_2O, 399.78 MHz) Spectrum of Compound **7b**



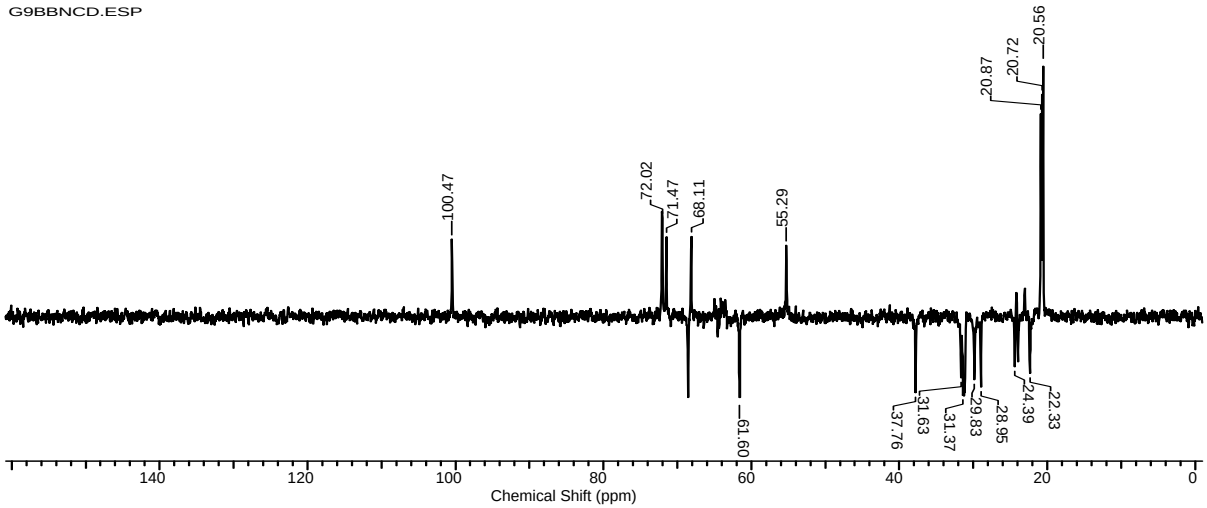
^{1}H NMR ($CDCl_3$, 399.78 MHz) Spectrum of Compound **3b**



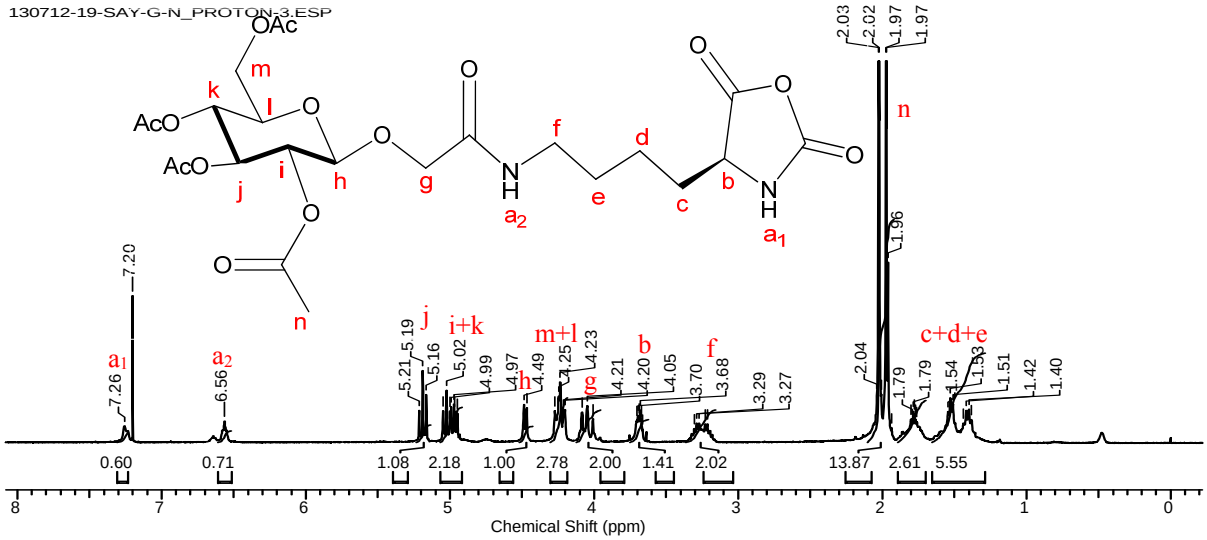
^{13}C NMR ($CDCl_3$, 100.53 MHz) Spectrum of Compound **3b**



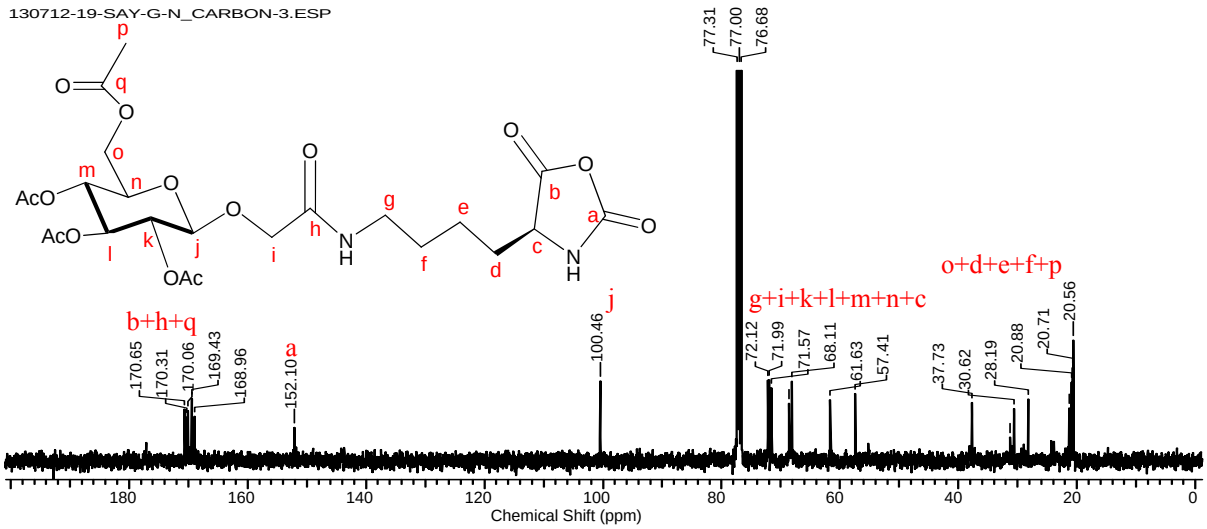
DEPT NMR ($CDCl_3$, 100.53 MHz) Spectrum of Compound **3b**



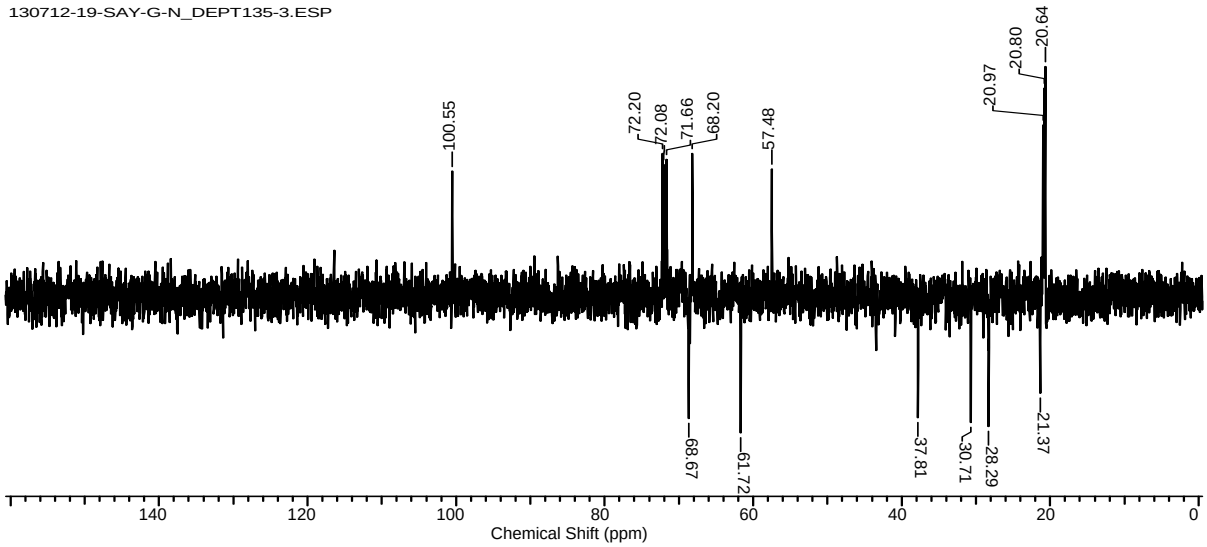
^1H NMR ($CDCl_3$, 399.78 MHz) Spectrum of Compound **4b**



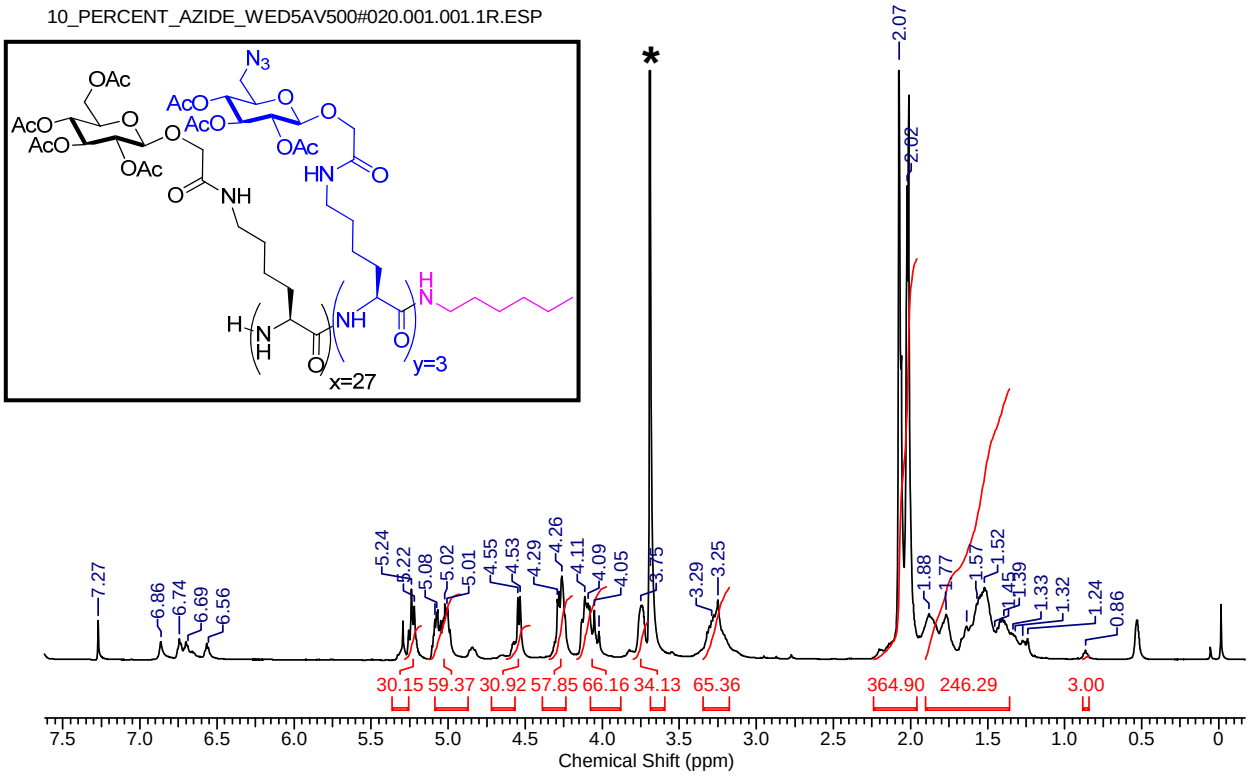
^{13}C NMR ($CDCl_3$, 100.53 MHz) Spectrum of Compound **4b**



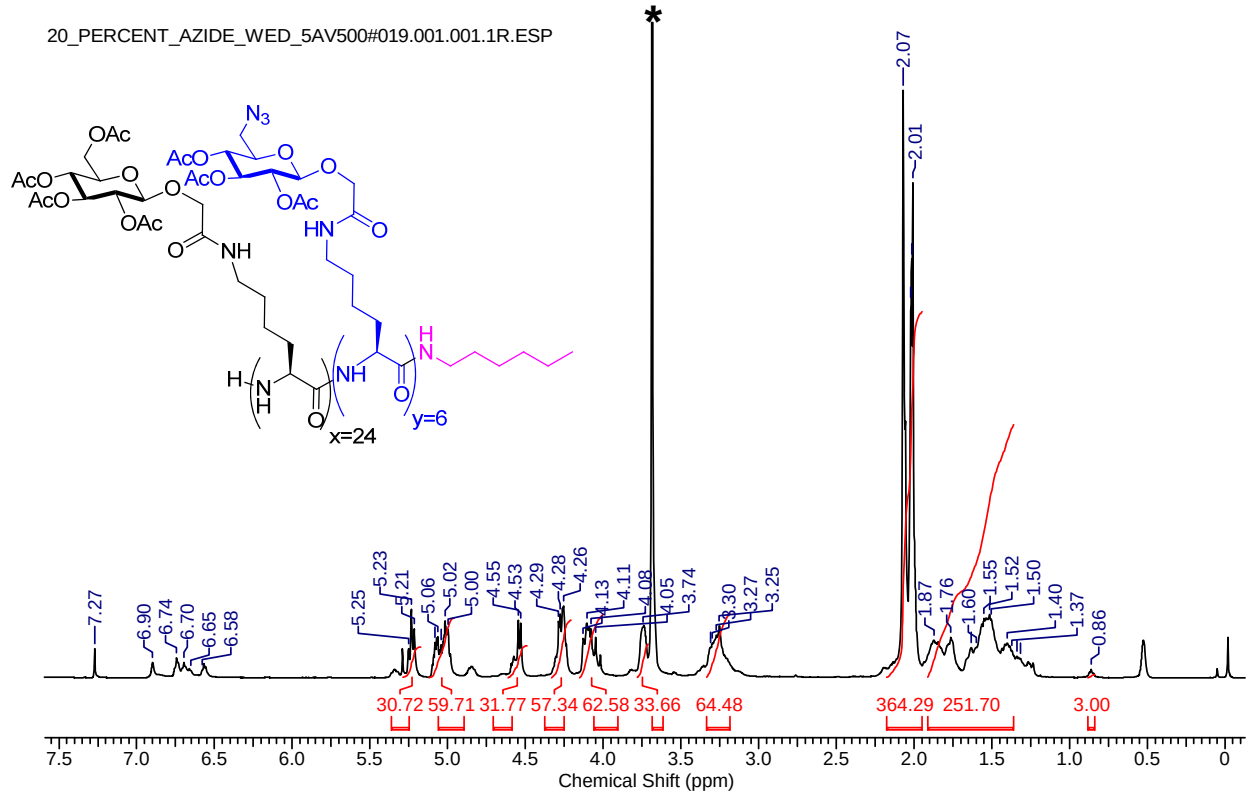
DEPT NMR ($CDCl_3$, 100.53 MHz) Spectrum of Compound **4b**



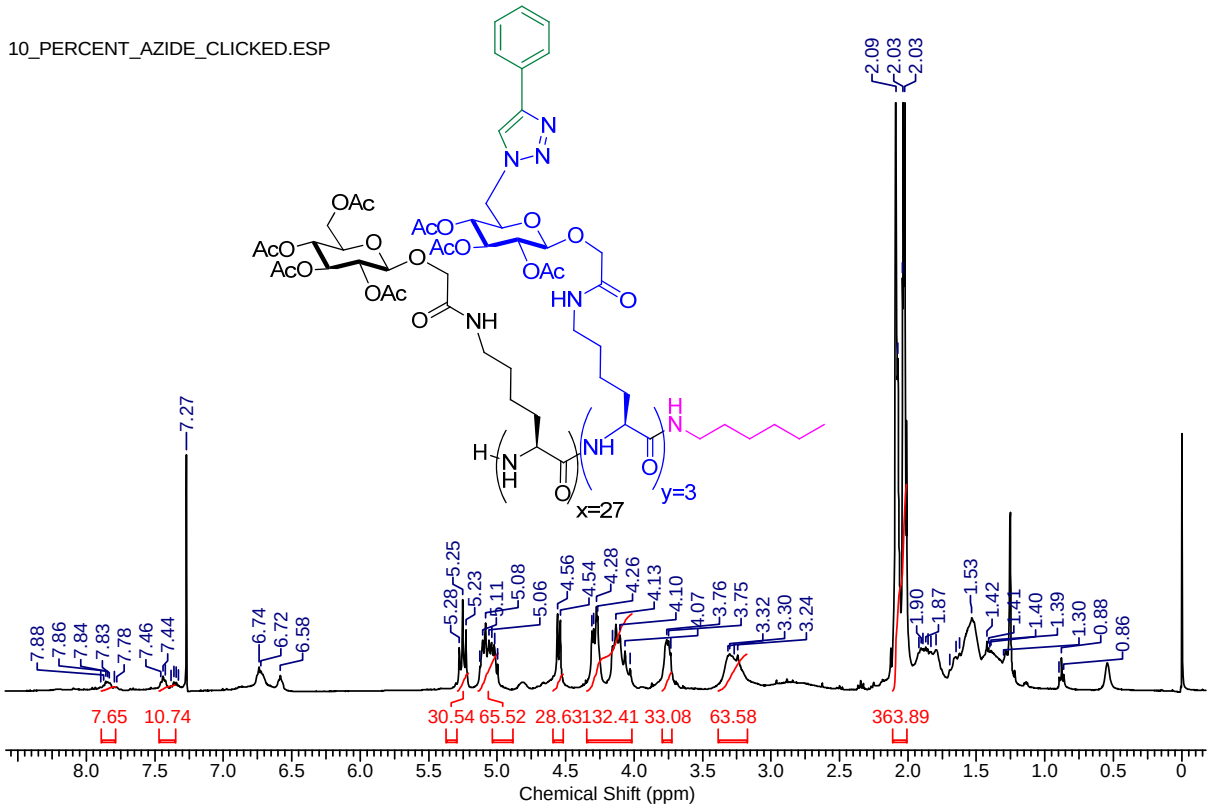
^{1}H NMR ($CDCl_3$, 399.78 MHz) Spectrum of Compound **8a**



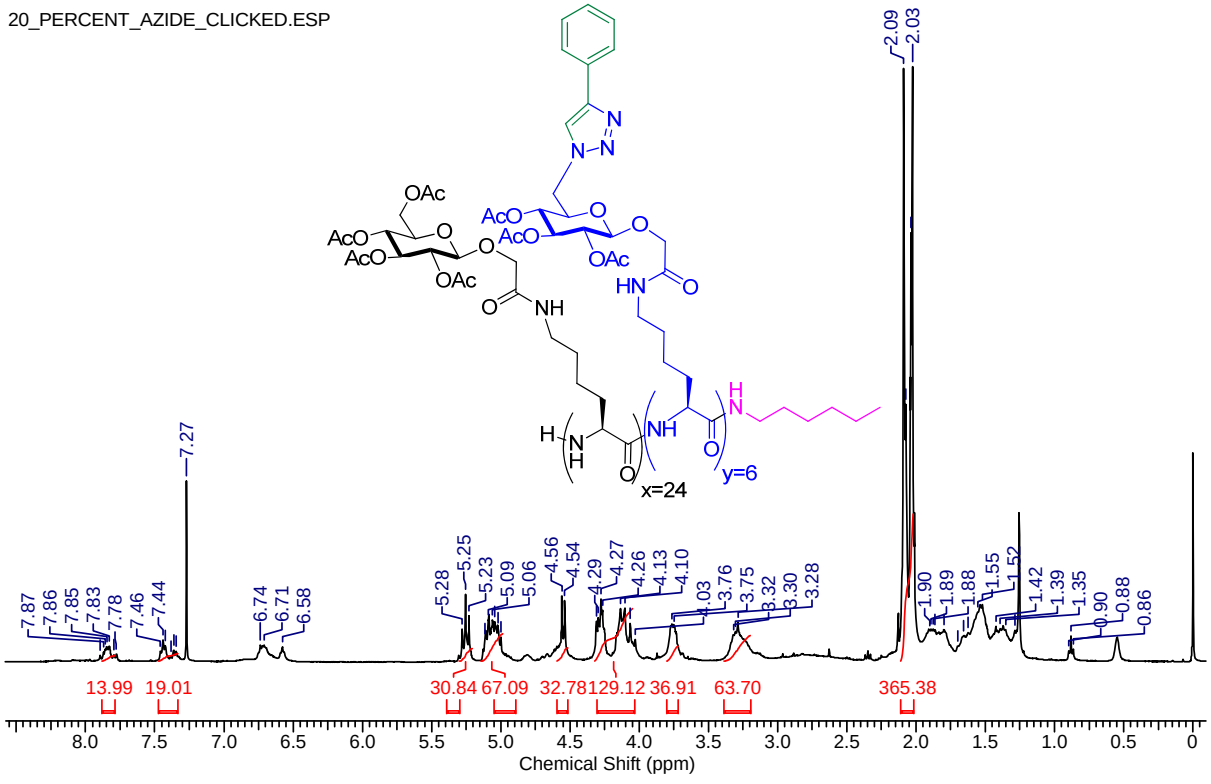
^{1}H NMR ($CDCl_3$, 399.78 MHz) Spectrum of Compound **9a**



^{1}H NMR ($CDCl_3$, 399.78 MHz) Spectrum of Compound **8d**



^{1}H NMR ($CDCl_3$, 399.78 MHz) Spectrum of Compound **9d**



^{1}H NMR (D_2O**,** 399.78 MHz) Spectrum of Compound **7d**