Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

End-functionalised glycopolymers as glycosaminoglycan mimetics inhibit HeLa cell proliferation

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1. Materials and characterization.

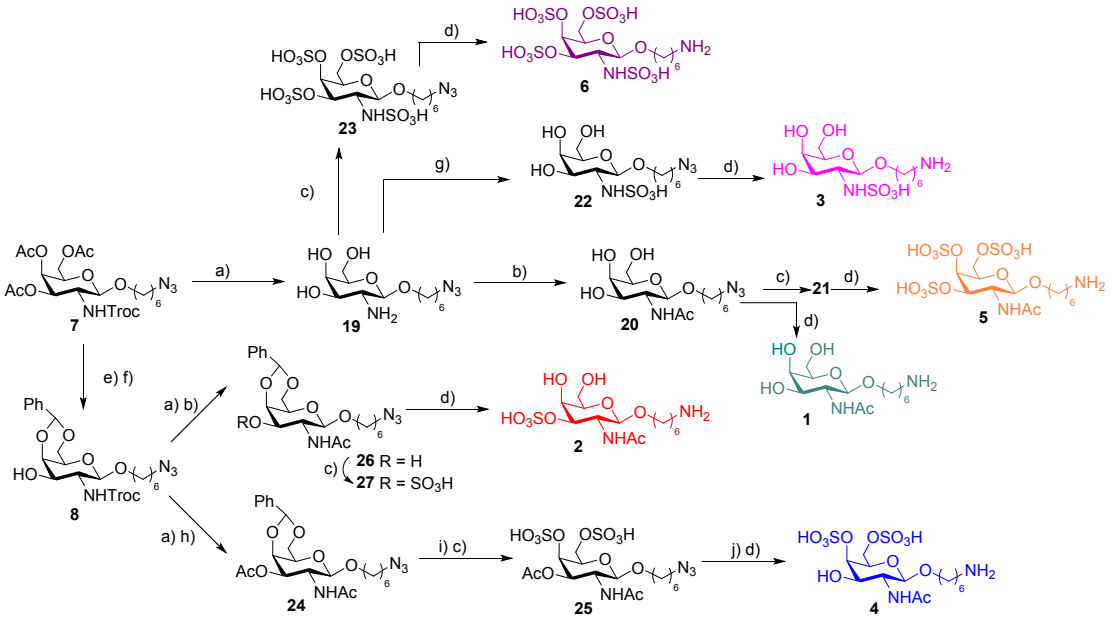
1.1 Materials

Sodium azide (99.5%), cis-5-norbornene-exo-2,3dicarboxylic anhydride (98%, NDA), ethyl vinyl ether (97%, EVE), 3-amiqnopropyne (97%), 6-Chlorohexanol (95%), maleic acid (99%), *N*-(3-Dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (98%, EDC), *N*-hydroxysuccinimide (98%, NHS), *N,N'*-Dicyclohexylcarbodiimide (99%, DCC), 4-Dimethylaminopyridine (99%, DMAP), 2-chloro-4,6-dimethoxy-1,3,5-triazine (CDMT, 97%), *N*-methylmorpholine (NMM, 99.5%), palladium hydroxide on carbon (20% $Pd(OH)_2$), benzaldehyde dimethyl acetal (98%), (+/-)-10-camphorsulfonic acid (99%), sodium methylate (97%), 2,2,2-trichloroethyl chloroformate (99%, Troc-Cl), triethylamine(99.5%), sulfur trioxide pyridine complex (SO_3·Py, 97%), Amberlite® IR-120 cation exchange resin (H^+ form) were purchased from Aladdin (Shanghai, China) and used without further purification. 6-maleimidohexanoic acid (98%), nucleic acid dye DAPI, and 3-(4, 5-dimethyl-2-thiazolyl)-2, 5-diphenyl-2-H-tetrazolium bromide (MTT) and Grubbs-type catalysts (G 3rd) were purchased from Sigma Aldrich (St. Louis, MO, USA). SephadexTM LH-20 was purchased from GE healthcare. Sulfur trioxide triethylamine complex (96%) were purchased from Tokyo Chemical Industry (Tokyo, Japan). Other chemical reagents were purchased from Energy Chemical and used directly. Minimum essential medium (MEM) was obtained from Gibco (Rockville, MD, USA). Fetal bovine serum (FBS) and trypsin were obtained from Gibco-Invitrogen (Grand Island, NY, USA). The primary antibodies p-ERK, ERK, p-AKT, AKT, p-PI_3K, PI_3K, p-mTOR, mTOR, and Actin were obtained from CST (Boston, MA, USA). The secondary antibodies were obtained from HuaBio (Hangzhou, China). Heparanase assay toolbox were purchased from Cisbio Assay (France) and heparinase ((human recombinant heparanase 7570-GH) purchased from R&D systems (Minneapolis, MN, USA).

1.2 Characterization

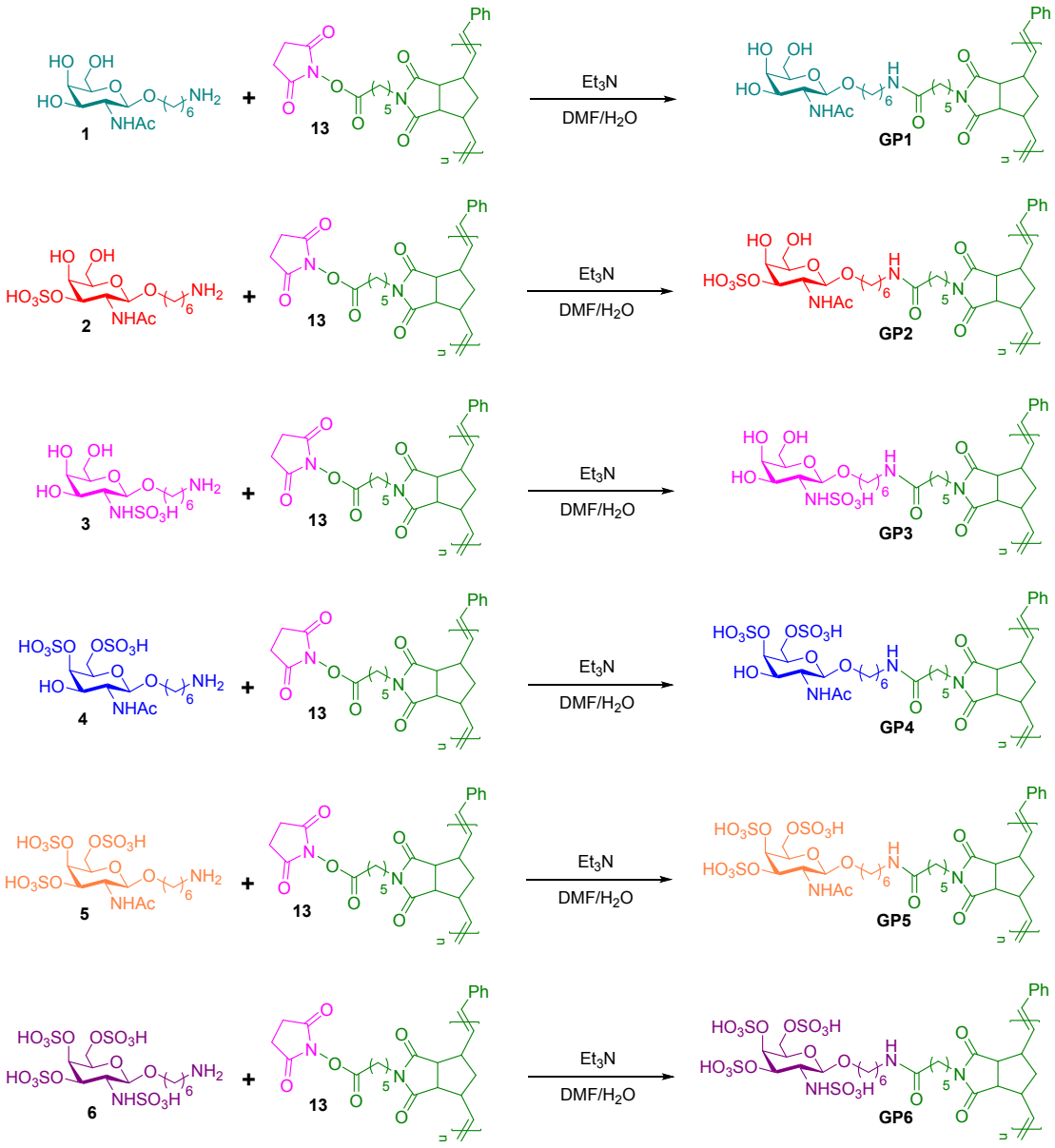
Nuclear magnetic resonance (NMR) spectra were recorded on an Agilent DD2 spectrometer (500 MHz). The chemical shifts of all the NMR spectra were reported in delta (δ) units and expressed as parts per million (ppm). The NMR spectra were referenced using CD_3OD (^1H NMR δ = 3.31 ppm, ^{13}C NMR δ = 49.00 ppm), and D_2O (^1H NMR δ = 4.79 ppm). Zeta potential and spherical nanomicelle diameters analysis of GP1-6 were performed by dynamic light scattering measurement using the zetasizer Nanoparticle Analyser (Nano ZS 90; Malvern Instruments, Ltd., Malvern, United Kingdom). Transmission electron microscope (TEM) images of samples were obtained by a JEOL JSM 5410 transmission electron microscope (Japan) and statistics by Nano Measurer. Absorbance and fluorescence intensity measurements were performed by microplate reader Tecan *SparkControl™ V2.3.5*. Confocal laser scanning microscope (CLSM) images were taken by a LSM 700 confocal scanning microscope (A1+A1R+, Nikon, Japan).

2. Synthetic routes of the galactosamine building blocks with diverse sulfation patterns.



Scheme S1. Synthetic routes of the diverse sulfated monosaccharide (**1**, **2**, **3**, **4**, **5**, **6**). Reagents and conditions: (a) 0.6 M NaOH in water/1,4-dioxane (1:1), 80 °C, 1 h. (b) Et_3N, Ac_2O, CH_3OH, rt, 1 h. (c) $SO_3{\cdot}Et_3N$, DMF, 50 °C, 10 h. (d) Pd/C, H_2, CH_3OH/H_2O(1:1), rt, 2 h. (e) CH_3ONa, CH_3OH, rt, 1 h. (f) α,α-Dimethoxytoluene, CSA, CH_3CN, rt, 3 h. (g) $SO_3{\cdot}Et_3N$, Et_3N, Py, rt, 6 h. (h) Ac_2O, Py, rt, 12 h. (i) 70% CH_3COOH in H_2O, 60 °C, 2 h. (j) CH_3ONa, CH_3OH, -5 °C, 6 h.

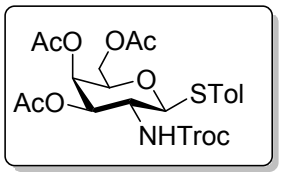
3. Synthetic routes of the distinct glycopolymers with diverse sulfation patterns.



Scheme S2. Synthetic routes of sulfated glycopolymers (**GP1, GP2, GP3, GP4, GP5, GP6**).

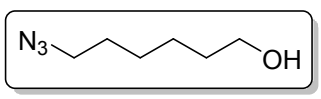
4. Synthetic procedure of compounds.

4-Methylphenyl 3,4,6-tri-*O*-acetyl-2-deoxy-1-thio-2-(2',2',2'-trichloroethoxycarbonylamino)-β-D-galactopyranoside (17)



To a solution of D-glucosamine hydrochloride (2 g, 9.28 mmol) in 40 mL H_2O, sodium bicarbonate (1.95 g, 23.19 mmol, 2.5 eq.) was added. The mixture was cooled to 0 ºC and TrocCl (1.92 mL, 13.92 mmol, 1,5 eq.) was added. The mixture was stirred at room temperature for 5 h after which TLC indicated full conversion. The solution was concentration under reduced pressure. The residue was acetylated by adding pyridine (20 mL) and Ac_2O (10 mL) and stirred at room temperature for 2 h after which TLC indicated full conversion. The mixture was concentrated and the residue was cooled to 0 ºC. The residue was re-dissolved in 25 mL CH_2Cl_2. $BF_3{\cdot}Et_2O$ (0.99 mL, 6.8 mmol, 1.5 eq.) and TolSH (1.13 g, 9.05 mmol, 2 eq.) were added and the solution was warmed up to room temperature. The mixture was stirred at room temperature overnight after which TLC indicated full conversion and quenched by adding sodium bicarbonate aqueous. The mixture was then extracted with CH_2Cl_2. the combined organic layers were dried over Na_2SO_4, concentrated and purified by column chromatography to afford **17** as a white solid (3.02 g, 70%). ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.48 - 7.37 (m, 2H), 7.26 (d, *J* = 3.0 Hz, 1H), 7.09 (t, *J* = 19.9 Hz, 2H), 5.37 (t, *J* = 8.3 Hz, 1H), 5.19 (dd, *J* = 10.7, 2.4 Hz, 1H), 5.10 (d, *J* = 9.0 Hz, 1H), 4.83 (d, *J* = 10.3 Hz, 1H), 4.79 (d, *J* = 12.0 Hz, 1H), 4.72 (d, *J* = 12.0 Hz, 1H), 4.18 (dd, *J* = 11.3, 7.0 Hz, 1H), 4.11 (dd, *J* = 11.4, 6.2 Hz, 1H), 3.94 - 3.84 (m, 2H), 2.34 (s, 3H), 2.12 (s, 3H), 2.04 (d, *J* = 4.9 Hz, 3H), 1.97 (d, *J* = 3.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.40, 170.14, 170.21, 153.93, 138.52, 133.22, 129.70, 128.58, 87.54, 74.50, 74.43, 70.90, 66.91, 61.67, 51.35, 29.69, 21.16, 20.67, 20.64, 20.60.

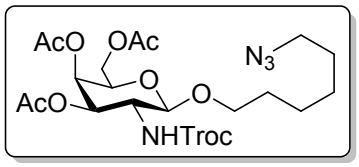
6-Azidohexan-1-ol (18)



6-Chlorohexanol (2.5 mL, 18.74 mmol), sodium azide (3.65 g, 56.2 mmol) and sodium hydroxide (0.038 g, 0.9 mmol) were dissolved in 200 mL H_2O and stirred at room temperature for 3 days after which TLC indicated full conversion. The mixture was then extracted with CH_2Cl_2 till the product was completely

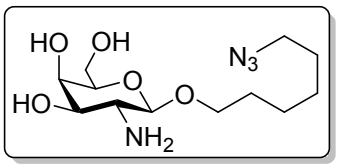
transferred from aqueous layer to organic layer. The organic layer was dried (Na_2SO_4) and evaporated under reduced pressure giving the colourless oil (2.47 g, 92%). ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 3.64 (t, J = 6.5 Hz, 2H), 3.27 (t, J = 6.9 Hz, 2H), 1.73 – 1.51 (m, 4H), 1.50 – 1.32 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): *δ* 62.71, 51.38, 32.53, 28.80, 26.52, 25.33.

6-Azidohexyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2',2',2'-trichloroethoxycarbonylamino)-β-D-galactopyranoside (7)



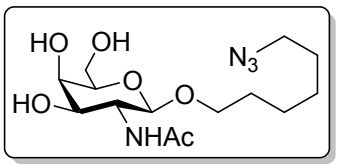
To a solution of compound **17** (500 mg, 1.08 mmol) and **18** (308.82 mg, 2.16 mmol) in 12 mL anhyd DCM with argon protection was added 4 Å molecule sieve. The mixture was stirred at room temperature for 0.5 h and then cooled to -20 ºC, NIS (392.75 mg, 2.16 mmol, 2 eq.) and TMSOTf (47.4 µL, 0.32 mmol, 0.3 eq.) were added. The mixture was stirred for 0.5 h after which TLC indicated full conversion and quenched with Et_3N. The mixture was filtered, evaporated and purified by column chromatography to afford **7** as light yellow syrup (574.9 mg, 88%). ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 5.37 (d, *J* = 2.6 Hz, 1H), 5.23 (d, *J* = 9.9 Hz, 1H), 5.11 (d, *J* = 6.2 Hz, 1H), 4.80 - 4.56 (m, 3H), 4.14 (ddd, *J* = 26.8, 11.2, 6.8 Hz, 2H), 3.93 - 3.85 (m, 2H), 3.77 (d, *J* = 8.9 Hz, 1H), 3.48 (dd, *J* = 16.2, 6.9 Hz, 1H), 3.25 (t, *J* = 6.8 Hz, 2H), 2.13 (d, *J* = 9.9 Hz, 3H), 2.04 (s, 3H), 1.99 (s, 3H), 1.58 (s, 4H), 1.36 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): *δ* 170.40, 170.32, 170.20, 154.02, 101.09, 95.48, 77.21, 74.40, 70.59, 70.11, 69.63, 66.69, 61.33, 53.00, 51.31, 29.27, 28.70, 26.39, 25.41, 20.67, 20.60.

6-Azidohexyl 2-deoxy-2-amino-β-D-galactopyranoside (19)



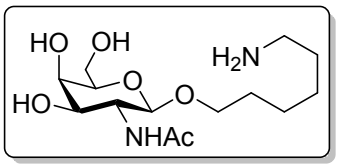
To a solution of compound **7** (200 mg) in MeOH was added MeONa to adjust the pH to 10. The mixture was stirred at room temperature for 30 min then neutralized with Dowex 50-X8 resin (H^+ form), filtered, and concentrated. The residue was re-dissolved in 2 mL 1,4-dioxane and 0.6 M NaOH (2 mL) was added. The solution was refluxed at 80 ºC for 1 h after which TLC indicated full conversion. The mixture was neutralized with 1 M HCl and concentrated to afford compound **19** for further use without purification.

6-Azidohexyl 2-deoxy-2-acetamido-β-D-galactopyranoside (20)



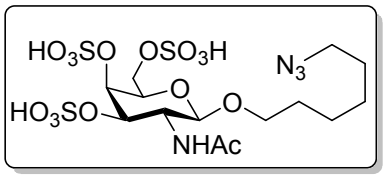
Compound **19** was dissolved in 1.5 mL CH_3OH, Et_3N (20 μL) and Ac_2O (20 μL) were added to the solution and stirred at room temperature for 1 h after which TLC indicated full conversion. The mixture was concentrated to afford compound **20** (32 mg, 95%). ^{1}H NMR (500 MHz, CD_3OD): *δ* 4.37 (d, *J* = 8.4 Hz, 1H), 3.95 - 3.86 (m, 2H), 3.85 (d, *J* = 3.0 Hz, 1H): 3.75 (h, *J* = 4.5 Hz, 2H), 3.60 (dd, *J* = 10.7, 3.1 Hz, 1H), 3.52 - 3.46 (m, 2H), 3.29 (t, *J* = 6.9 Hz, 2H), 1.99 (s, 3H), 1.59 (dd, *J* = 12.6, 5.9 Hz, 4H), 1.39 (dt, *J* = 14.0, 7.0 Hz, 4H). ^{13}C NMR (126 MHz, CD_3OD): *δ* 101.73, 75.20, 71.85, 68.95, 68.25, 68.14, 61.08, 52.87, 51.00, 29.28, 29.14, 28.50, 26.13, 25.27, 21.69.

6-Aminohexyl 2-deoxy-2-acetamido-β-D-galactopyranoside (1)



To a solution of compound **20** (30 mg, 0.086 mmol) in 1:1 CH_3OH/H_2O was added $Pd(OH)_2/C$. The mixture was filled with H_2 and stirred at room temperature for 2 h after which TLC indicated full conversion. $Pd(OH)_2/C$ was separated by filtration through a Celite pad and the filtrate was concentrated to give the desired compound **1** as white solid (20.53 mg, 74%). ^{1}H NMR (500 MHz, D_2O): *δ* 4.32 (d, *J* = 8.5 Hz, 1H), 3.81 (d, *J* = 3.2 Hz, 1H), 3.80 - 3.72 (m, 2H), 3.71 - 3.61 (m, 2H), 3.59 (dd, *J* = 10.7, 3.0 Hz, 1H), 3.56 - 3.52 (m, 1H), 3.50 - 3.43 (m, 1H), 2.93 - 2.84 (m, 2H), 1.91 (s, 3H), 1.79 (s, 1H), 1.54 (d, *J* = 7.4 Hz, 4H), 1.49 - 1.40 (m, 4H). ^{13}C NMR (126 MHz, D_2O): *δ* 101.37, 75.00, 70.93, 70.15, 67.69, 60.87, 52.36, 47.33, 28.26, 25.30, 24.55, 22.14.

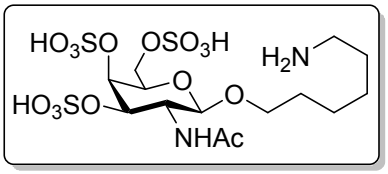
6-Azidohexyl 2-deoxy-2-acetamido-3,4,6-tri-*O*-sulfo-β-D-galactopyranoside (21)



To a solution of compound **20** (40 mg, 0.12 mmol) in DMF (1 mL) was added SO_3•Et_3N (500 mg, 3.6 mmol, 10 eq. per OH). The reaction mixture was stirred at 50 °C for 10 h. Upon confirmation of the completely conversion by TLC, the mixture was purified by Sephadex LH-20 gel filtration (MeOH) to give the desired product **21** as a syrup (57.6 mg, 85%). ^{1}H NMR (500 MHz, CD_3OD): *δ* 4.96 (d, J = 2.8 Hz, 1H), 4.43 (d, J = 8.4 Hz, 2H), 4.35 (dd, J = 11.2, 2.9 Hz, 1H), 4.27 (dd, J = 11.8, 8.3 Hz, 1H), 4.11 (dd, J = 11.1, 8.4 Hz, 1H), 3.94 (dd, J = 8.2, 2.8 Hz, 1H), 3.88 (dt, J = 9.8, 6.2 Hz, 1H), 3.51 (dt, J = 9.8, 6.5 Hz, 1H), 3.29 (d, J = 6.9 Hz, 2H), 1.95 (s, 4H), 1.58 (td, J = 13.0, 11.6, 7.2 Hz, 3H), 1.38 (p,

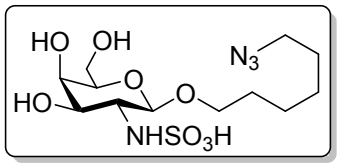
J = 4.5, 4.1 Hz, 4H). ^{13}C NMR (126 MHz, CD_3OD): *δ* 174.39, 100.82, 75.24, 74.05, 72.14, 70.48, 67.80, 67.75, 50.94, 28.42, 27.96, 25.57, 24.62, 22.25.

6-Aminohexyl 2-deoxy-2-acetamido-3,4,6-tri-*O*-sulfo-β-D-galactopyranoside (5)

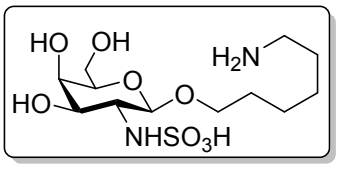


As the same procedure for the compound **1** preparation, the compound **21** (32 mg, 0.054 mmol) was hydrogenated to afford **5** as a white solid (21.4 mg, 70%). ^{1}H NMR (500 MHz, D_2O): *δ* 4.84 (s, 1H), 4.59 (d, *J* = 8.5 Hz, 1H), 4.39 (dd, *J* = 11.0, 2.5 Hz, 1H), 4.21 (dd, *J* = 11.3, 2.7 Hz, 1H), 4.15 - 4.08 (m, 1H), 4.00 (d, *J* = 6.0 Hz, 1H), 3.92 - 3.85 (m, 1H), 3.80 (d, *J* = 5.4 Hz, 1H), 3.61 - 3.54 (m, 1H), 2.90 (dd, J = 15.7, 7.8 Hz, 2H), 1.91 (s, 3H), 1.61 - 1.43 (m, 4H), 1.25 (d, *J* = 30.1 Hz, 4H). ^{13}C NMR (126 MHz, CD_3OH): δ 174.57, 101.76, 75.19, 73.97, 72.09, 70.61, 67.88, 50.94, 39.35, 28.21, 26.48, 24.98, 24.39, 22.18.

6-Azidohexyl 2-deoxy-2-*N*-sulfo-β-D-galactopyranoside (22)



To a solution of compound 19 (45 mg, 0.15 mmol) in 1 mL pyridine was added 0.1 mL Et_3N and $SO_3{\cdot}Et_3N$ (35 mg, 1.5 eq.). The mixture was stirred at room temperature for 6 h. Upon confirmation of the completely conversion by TLC, the mixture was purified by Sephadex LH-20 gel filtration (MeOH) to give the desired product **22** as a syrup (46.6 mg, 82%). ^{1}H NMR (500 MHz, CD_3OD): *δ* 4.38 (d, *J* = 8.2 Hz, 1H), 3.90 (dt, *J* = 9.3, 6.6 Hz, 1H), 3.85 (d, *J* = 3.0 Hz, 1H), 3.78 (d, *J* = 3.1 Hz, 1H), 3.76 (d, *J* = 5.1 Hz, 2H), 3.57 (dt, *J* = 9.4, 6.6 Hz, 1H), 3.50 (t, *J* = 6.1 Hz, 1H), 3.35 (m, 1H), 2.90 (t, *J* = 6.5 Hz, 2H), 1.67 - 1.56 (m, 4H), 1.49 - 1.39 (m, 4H). ^{13}C NMR (126 MHz, CD_3OD): *δ* 101.58, 75.21, 73.69, 68.93, 67.85, 61.14, 56.80, 51.02, 29.20, 28.46, 26.21, 25.26.

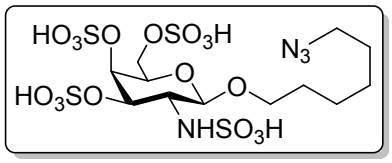


6-Aminohexyl 2-deoxy-2-*N*-sulfo-β-D-galactopyranoside (3)

As the same procedure for the compound **1** preparation, the compound **22** (20 mg, 0.052 mmol) was hydrogenated to afford **3** as a white solid (14.36 mg, 77%). ^{1}H NMR (500 MHz, D_2O): δ 4.40 – 4.36 (m, 1H), 3.83 (d, J = 3.3 Hz, 2H), 3.68-3.57 (m, 3H), 3.54 – 3.42 (m, 2H), 3.06 (d, 1H), 2.90 (J = 7.21, 2H), 1.61 – 1.48 (m, 4H), 1.38 – 1.24 (m,

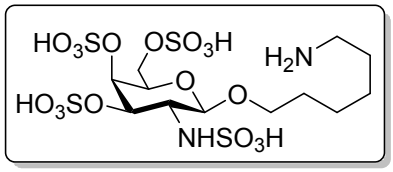
4H). ^{13}C NMR (126 MHz, D_2O): δ 101.65, 74.81, 72.15, 70.13, 67.76, 60.96, 56.60, 39.30, 28.32, 26.50, 25.10, 24.49.

6-Azidohexyl 2-deoxy-2-*N*-sulfo-3,4,6-tri-*O*-sulfo-β-D-galactopyranoside (23)



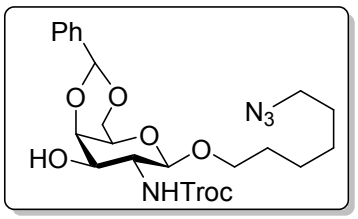
As the same procedure for the compound **21** preparation, the compound **19** (28 mg, 0.092 mmol) was sulfated to afford **23** as syrup (41.4 mg, 72%). ^{1}H NMR (500 MHz, CD_3OD): δ, 4.94 (d, J = 2.2 Hz, 1H), 4.62 (d, J = 8.2 Hz, 1H), 4.51 - 4.45 (m, 1H), 4.41 (dd, J = 15.2, 6.2 Hz, 2H), 4.27 (dd, J = 11.7, 8.1 Hz, 1H), 4.05 - 4.00 (m, 1H), 3.95 (dd, J = 15.4, 6.4 Hz, 1H), 3.28 (m, 2H) , 3.59 (m, 1H), 1.61 (d, J = 5.5 Hz, 4H), 1.41 (s, 4H). ^{13}C NMR (126 MHz, D_2O): δ 99.87, 74.59, 73.73, 73.09, 69.38, 67.71, 59.48, 50.97, 29.13, 28.46, 26.11, 25.27.

6-Aminohexyl 2-deoxy-2-*N*-sulfo-3,4,6-tri-*O*-sulfo-β-D-galactopyranoside (6)



As the same procedure for the compound **1** preparation, the compound **23** (22 mg, 0.035 mmol) was hydrogenated to afford **6** as a white solid (16.9 mg, 80%). ^{1}H NMR (500 MHz, D_2O): δ ^{1}H NMR (500 MHz, Deuterium Oxide) δ 4.86 (t, J = 6.0 Hz, 1H), 4.56 (d, J = 12.1 Hz, 1H), 4.51 – 4.41 (m, 1H), 4.22 (d, J = 12.0 Hz, 1H), 4.10 (dt, J = 24.2, 8.2 Hz, 2H), 3.92 – 3.77 (m, 1H), 3.74 – 3.57 (m, 1H), 3.57 – 3.48 (m, 1H), 2.89 (t, J = 7.5 Hz, 2H), 1.54 (d, J = 20.9 Hz, 4H), 1.37 – 1.24 (m, 4H).

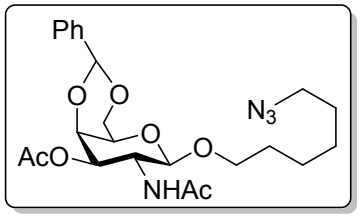
6-Azidohexyl 4,6-*O*-benzylidene-2-deoxy-2-(2',2',2'-trichloroethoxycarbonylamino)-β-D-galactopyranoside (8)



To a solution of compound **7** (200 mg, 0.33 mmol) in MeOH was added MeONa to adjust the pH to 10. The mixture was stirred at room temperature for 30 min then neutralized with Dowex 50-X8 resin (H^+ form), filtered, and concentrated. The residue was re-dissolved in 7 mL CH_3CN, a catalytic amount of (+/-)-10-camphorsulfonic acid (8 mg, 0.035 mmol) and benzaldehyde dimethyl acetal (102.7 µL, 0.68 mmol) were added. The mixture was stirred at room temperature for 4 h until the TLC showed full conversion, and 500 µL Et_3N was added to quench the reaction. CH_3CN was evaporated and the residue was purified to afford **8** as a white solid (167 mg, 89%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 - 7.46 (m, 2H), 7.39 - 7.32 (m, 3H), 5.56 (s, 1H), 5.27 (s, 1H), 4.72 (t, J = 11.4 Hz, 2H), 4.57 (d, J =

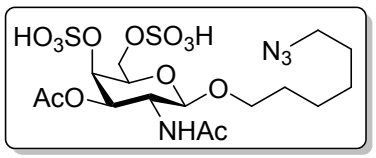
6.1 Hz, 1H), 4.32 (d, *J* = 12.4 Hz, 1H), 4.19 (d, *J* = 2.8 Hz, 1H), 4.07 (d, *J* = 12.4 Hz, 1H), 4.02 - 3.88 (m, 2H), 3.64 (s, 1H), 3.51 - 3.40 (m, 2H), 3.25 (t, *J* = 6.8 Hz, 2H), 2.84 (s, 1H), 1.58 (s, 4H), 1.35 (d, *J* = 22.9 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): *δ* 154.63, 137.38, 129.27, 128.38, 126.40, 101.35, 100.38, 77.22, 75.03, 74.55, 70.18, 69.32, 69.14, 66.56, 55.83, 51.34, 30.93, 29.28, 28.72, 26.42, 25.48.

6-Azidohexyl 3-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-2-acetamido-β-D-galactopyranoside (24)



To a solution of compound **8** (130 mg, 0.23 mmol) in 4 mL 1,4-dioxanewas added 0.6 M NaOH (4 mL). The solution was refluxed at 80 ºC for 1 h after which TLC indicated full conversion. The mixture was neutralized with 1 M HCl and concentrated. The residue was dissolved in pyridine (4 mL) and Ac_2O (2 mL) and stirred at room temperature overnight. The solution was concentrated and purified to afford compound **24** (100 mg, 92%). ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.57 – 7.45 (m, 2H), 7.36 (p, J = 5.5, 4.4 Hz, 3H), 5.54 (d, J = 12.9 Hz, 2H), 5.42 (dd, J = 11.3, 3.6 Hz, 1H), 4.92 (d, J = 8.3 Hz, 1H), 4.36 (d, J = 3.6 Hz, 1H), 4.32 (d, J = 12.0 Hz, 1H), 4.09 – 4.03 (m, 1H), 3.92 (ddd, J = 11.5, 6.3, 2.9 Hz, 2H), 3.54 (s, 1H), 3.50 (dd, J = 9.4, 6.6 Hz, 1H), 3.25 (t, J = 6.9 Hz, 2H), 2.08 (s, 3H), 1.95 (s, 3H), 1.59 (t, J = 6.7 Hz, 4H), 1.38 (d, J = 7.5 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): *δ* 170.87, 170.28, 137.65, 128.97, 128.13, 126.31, 100.85, 100.00, 73.21, 70.46, 69.20, 69.03, 66.32, 52.06, 51.37, 45.76, 28.77, 26.43, 25.50, 23.56, 20.96.

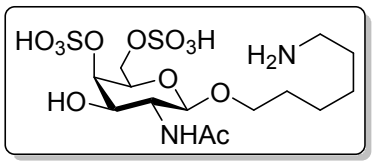
6-Azidohexyl 3-*O*-acetyl-4,6-di-*O*-sulfo-2-deoxy-2-acetamido-β-D-galactopyranoside (25)



Compound **24** (60 mg, 0.13 mmol) was heated to 60 ºC and 70% (v/v) CH_3COOH (3 mL) was added. The mixture was stirred for 2 h after which TLC indicated full conversion. The mixture was concentrated and the residue was dissolved in DMF (1 mL). SO_3•Et_3N (500 mg, 3.6 mmol, 10 eq. per OH) was added and the reaction mixture was stirred at 50 °C for 10 h. Upon confirmation of the completely conversion by TLC, the mixture was purified by Sephadex LH-20 gel filtration (MeOH) to give the desired product **25** as a syrup (57.7 mg, 85%). ^{1}H NMR (500 MHz, CD_3OD): *δ* 4.90 (d, *J* = 3.2 Hz, 1H), 4.77 (d, *J* = 2.7 Hz, 1H), 4.47 (d, *J* = 8.4 Hz,

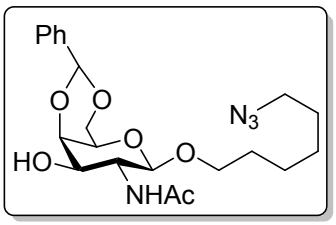
1H), 4.42 (d, *J* = 9.5 Hz, 1H), 4.21 (dd, *J* = 11.8, 8.3 Hz, 1H), 4.12 (dd, *J* = 11.0, 8.7 Hz, 1H), 4.01 (d, *J* = 6.0 Hz, 1H), 3.89 (dd, *J* = 9.8, 5.9 Hz, 1H), 3.51 (d, *J* = 9.5 Hz, 1H), 3.27 (t, 2H), 1.80 - 2.18 (m, 6H), 1.58 (d, *J* = 6.2 Hz, 4H), 1.39 (s, 4H). ^{13}C NMR (126 MHz, CD_3OD): *δ* 171.87, 171.30, 101.31, 72.56, 71.60, 71.38, 69.05, 67.85, 50.98, 50.06, 56.53, 29.08, 28.49, 26.10, 25.22, 21.45, 19.62.

6-Aminohexyl 4,6-di-*O*-sulfo-2-deoxy-2-acetamido-β-D-galactopyranoside(4)



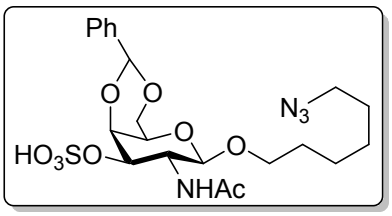
To a solution of **25** (28 mg, 0.051 mmol) in CH_3OH (2 mL), MeONa was added to adjust the pH to 9. The mixture was stirred at -5 ºC for 30 min then neutralized with Dowex 50-X8 resin (H^+ form), filtered, and concentrated. The residue was dissolved in 1:1 CH_3OH/H_2O and $Pd(OH)_2/C$ was added. The mixture was filled with H_2 and stirred at room temperature for 2 h after which TLC indicated full conversion. $Pd(OH)_2/C$ was separated by filtration through a Celitepad and the filtrate was concentrated to give the desired compound **4** as white solid (29 mg, 58%). ^{1}H NMR (500 MHz, D_2O): *δ* 4.61 (s, 1H), 4.41 (t, *J* = 4.2 Hz, 1H), 4.21 (dd, *J* = 11.5, 3.3 Hz, 1H), 4.13 – 4.07 (m, 1H), 3.95 (dd, *J* = 8.8, 3.2 Hz, 1H), 3.79 (dd, *J* = 10.4, 5.6 Hz, 3H), 3.55(m, 1H), 2.94 – 2.84 (m, 2H), 2.00 – 1.87 (m, 3H), 1.61 – 1.43 (m, 4H), 1.27 (dd, *J* = 9.3, 4.7 Hz, 4H). ^{13}C NMR (126 MHz, CD_3OD): *δ* 172.20, 101.58, 75.55, 72.67, 70.95, 69.05, 67.71, 53.47, 51.01, 29.11, 28.50, 26.12, 25.24, 21.62.

6-Azidohexyl 4,6-*O*-benzylidene-2-deoxy-2-acetamido-β-D-galactopyranoside(26)



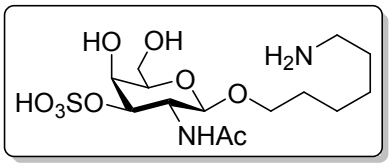
To a solution of compound **8** (130 mg, 0.23 mmol) in 4 mL 1,4-dioxane was added 0.6 M NaOH (4 mL). The solution was refluxed at 80 ºC for 1 h after which TLC indicated full conversion. The mixture was neutralized with 1 M HCl and concentrated. The residue was dissolved in CH_3OH (2 mL), Et_3N (20 µL) and Ac_2O (20 µL) were added and stirred at room temperaturefor 1 h. The solution was concentrated and purified to afford **26** as a syrup (85 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.50 (dd, *J* = 7.2, 2.1 Hz, 2H), 7.39 - 7.31 (m, 3H), 5.43 (s, 1H), 4.57 (d, *J* = 8.3 Hz, 1H), 4.19 (d, *J* = 12.4 Hz, 1H), 4.00 (d, *J* = 3.0 Hz, 1H), 3.97 - 3.85 (m, 3H), 3.83 - 3.75 (m, 1H), 3.50 - 3.43 (m, 1H), 3.34 (s, 1H), 3.25 (t, *J* = 6.9 Hz, 2H), 2.00(s, 3H), 1.64 -1.52 (m, 4H), 1.42 - 1.30 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): *δ* 171.82, 137.85, 129.10, 128.21, 126.51, 101.13, 100.55, 75.21, 70.40, 69.14,

69.01, 66.51, 54.26, 51.33, 29.30, 28.77, 26.43, 25.50, 23.58.



6-Azidohexyl 4,6-*O*-benzylidene-2-deoxy-2-acetamido -3-*O*-sulfo-β-D-galactopyranoside (27)

As the same procedure for the preparation of compound **21**, the compound **26** (28 mg, 0.092 mmol) was sulfated to give the desired product **27** as a syrup (24 mg, 61%). ^{1}H NMR (500 MHz, CD_3OD): δ 7.54 (d, J = 7.8 Hz, 2H), 7.34 (d, J = 6.0 Hz, 3H), 5.63 (s, 1H), 4.60 (d, J = 8.3 Hz, 2H), 4.48 (dd, J = 11.1, 3.3 Hz, 1H), 4.24 – 4.09 (m, 3H), 3.95 – 3.85 (m, 1H), 3.58 (s, 1H), 3.52 (d, J = 9.6 Hz, 1H), 3.28 (t, J = 6.9 Hz, 2H), 3.14 (q, J = 7.0 Hz, 1H), 1.96 (s, 3H), 1.59 (s, 4H), 1.40 (s, 4H). ^{13}C NMR (126 MHz, CD_3OD): δ 172.30, 138.27, 128.36, 127.47, 126.23, 101.52, 100.82, 75.30, 73.84, 69.02, 68.84, 66.44, 50.97, 50.48, 46.42, 29.06, 28.49, 26.08, 25.21, 21.74.

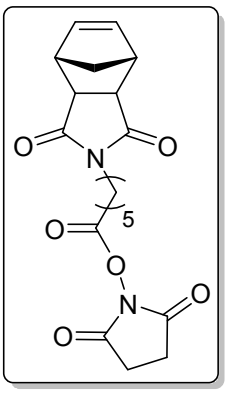


6-Aminohexyl 2-deoxy-2-acetamido-3-*O*-sulfo-β-D-gala ctopyranoside (2)

As the same procedure for the compound **1** preparation, the compound **27** (24 mg, 0.047 mmol) was hydrogenated to afford **2** as a syrup (13.45 mg, 72%). ^{1}H NMR (500 MHz, CD_3OD): δ 4.44 (d, J = 8.4 Hz, 1H), 4.23 (s, 1H), 4.09 (s, 1H), 3.85 (s, 1H), 3.76 (s, 1H), 3.60 (d, J = 33.4 Hz, 3H), 3.48 (s, 1H), 2.83 (s, 2H), 1.87 (s, 3H), 1.46 (d, J = 41.4 Hz, 4H), 1.22 (s, 4H). ^{13}C NMR (126 MHz, CD_3OD): δ 172.25, 101.86, 77.82, 74.83, 69.09, 66.35, 60.94, 50.57, 39.38, 28.81, 26.97, 25.63, 25.21, 21.89.

6-(*exo*-*N*-norbornene-2,3-dicarboximide)hexanoic acid (11)

Cis-5-norbornene-exo-2,3-dicarboxylic anhydride (2.0 g, 12.20 mmol) was dissolved in 60 mL of anhydrous toluene purged with argon gas. Then 6-Aminocaproic acid (1.9 g, 14.64 mmol) and Et_3N (1.5 g, 14.64 mmol) were added and the flask was fitted with a Dean-Stark trap and a condenser. The reaction mixture was refluxed in oil bath at 120 °C for 15 h after which TLC indicated full conversion. The solvent was evaporated under reduced pressure. The product was purified by column chromatography to give a white solid (3.2 g, 95%). The spectrum for the desired product was the same as reported previously.[1]



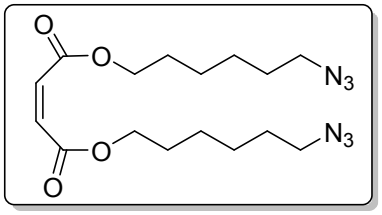
6-(*exo*-*N*-norbornene-2,3-dicarboximide)hexanoic acid *N*-succinim ide ester (12)

To a solution of compound **11** (2.00 g, 9.04 mmol) in 30 mL CH_2Cl_2, EDC

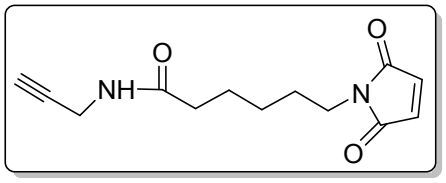
(1.935 g, 12.66 mmol, 1.4 eq.) and NHS (1.162 g, 12.7 mmol, 1.4 eq.) were added and stirred at room temperature for 4 h. The mixture was concentrated and purified to afford **12** as white solid (2.76 g, 96%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.24 (s, 2H), 3.49 – 3.35 (m, 2H), 3.21 (s, 2H), 2.78 (s, 4H), 2.63 (s, 2H), 2.55 (t, J = 7.4 Hz, 2H), 1.79 – 1.64 (m, 2H), 1.55 (dt, J = 15.1, 7.6 Hz, 2H), 1.45 (t, J = 11.6 Hz, 1H), 1.37 (dt, J = 15.3, 7.8 Hz, 2H), 1.16 (d, J = 9.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 178.00, 169.17, 168.33, 137.76, 47.74, 45.09, 42.72, 38.20, 30.66, 27.20, 25.96, 25.55, 24.02.

***Cis*-butenedioic-bis(6-azidohexyl) ester (15)**

To a solution of maleic acid (300 mg, 2.58 mmol) in 10 mL CH_2Cl_2 was added compound **18** (740 mg, 5.17 mmol, 2 eq.). The mixture was cooled to 0 ºC and DCC (640 mg, 3.11 mmol, 1.2 eq.) and DMAP (95 mg, 0.78 mmol, 0.3 eq.) were added. The mixture was stirred at room temperature and white precipitation was occurred. After TLC indicated full conversion, the mixture was concentrated under reduced pressure. The residue was re-dissolved in minimal amount of CH_2Cl_2, filtrated to remove white precipitation, and CH_2Cl_2 was evaporated. The residue was purified by silica gel column to afford compound **15** as white solid (540 mg, 57%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.24 (s, 2H), 4.19 (t, *J* = 6.6 Hz, 4H), 3.27 (t, *J* = 6.9 Hz, 4H), 1.71 - 1.66 (m, 4H), 1.63 - 1.59 (m, 4H), 1.43 - 1.38 (m, 8H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.27, 129.77, 65.13, 51.30, 28.71, 28.30, 26.33, 25.45.



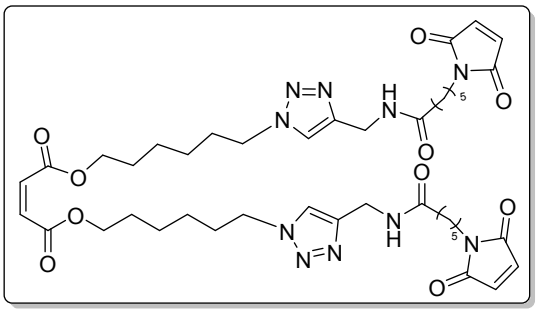
6-(*N*-Maleimido)-*N*-(2-propynyl)hexanamide (14)



To a solute of 6-maleimidohexanoic acid (300 mg, 1.42 mmol) in 8 mL CH_3OH was added propargylamine (182 µL, 3.30 mmol, 2.3 eq.) and DMTMM (786 mg, 2.84 mmol, 2 eq.). The mixture was stirred at 40 ºC for 3 h after which TLC indicated full conversion. The mixture was concentrated under reduced pressure and purified to give compound 14 as white solid (257.4 mg, 73%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.68 (s, 2H), 5.71 (s, 1H), 4.03 (dd, *J* = 5.0, 2.3 Hz, 2H), 3.50 (t, *J* = 7.2 Hz, 2H), 2.22 (t, *J* = 2.0 Hz, 1H), 2.18 (t, *J* = 7.5 Hz, 2H), 1.72 - 1.64 (m, 2H), 1.59 (dd, *J* = 14.9, 7.5 Hz, 2H), 1.36 - 1.27 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.26, 170.83, 134.05, 79.58, 71.53, 37.54, 36.08,

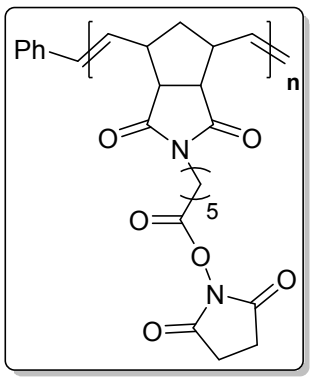
29.13, 28.17, 26.20, 24.83.

***Cis*-butenedioic-bis[6-(4-(6-(*N*-maleimido)-hexanamide)methyl-1*H*-1,2,3-triazol-4-yl)hexyl] ester (16)**



Compound **15** (36 mg, 0.1 mmol) and compound **14** (48.78 mg, 0.2 mmol, 2 eq.) were dissolved in 2 mL THF and 1.5 mL H_2O was added. To this was added freshly prepared stock solutions of $CuSO_4 \cdot 5H_2O$ (200 µL, 25 mg/mL, 0.2 eq.) and Na-ascorbate (212 µL, 99.055 mg/mL, 1.2 eq.). The mixture was stirred at 40 ^{o}C for 1 h after which TLC indicated full conversion. The mixture was concentrated and washed with CH_2Cl_2. The organic layer was dried (Na_2SO_4) and evaporated under reduced pressure. The residue was purified by silica gel column to give compound **16** as white solid (35 mg, 47 %). ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.57 (s, 1H), 6.68 (s, 4H), 6.23 (s, 2H), 5.30 (s, 1H), 4.50 (d, *J* = 5.6 Hz, 4H), 4.33 (t, *J* = 7.2 Hz, 4H), 4.15 (t, *J* = 6.5 Hz, 4H), 3.49 (t, *J* = 7.2 Hz, 6H), 2.18 (t, *J* = 7.5 Hz, 4H), 1.94 - 1.86 (m, 4H), 1.65 (dd, *J* = 13.3, 7.1 Hz, 11H), 1.45 - 1.30 (m, 11H). ^{13}C NMR (126 MHz, $CDCl_3$): *δ* 172.88, 170.85, 165.29, 134.04, 129.79, 122.27, 64.98, 54.27, 50.18, 37.60, 36.16, 34.87, 30.06, 28.17, 26.29, 26.02, 25.24, 24.95.

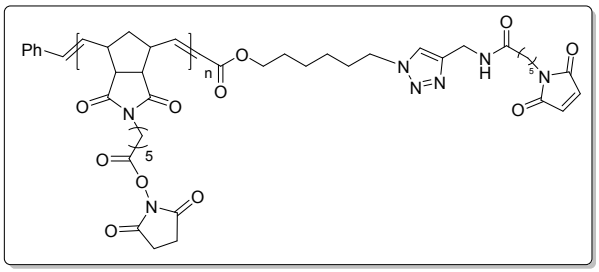
General procedure for the preparation of polymer containing NHS ester (13)



A solution of **12** (30 mg, 1 eq.) in 1 mL CH_2Cl_2 was stirred at -78 ºC for 30 min with argon protection. A stock solution of the Grubbs 3rd catalyst was freshly prepared at 14.2 mg•mL^{-1} in CH_2Cl_2. Following the addition of desirable amounts of the catalyst solution, the mixture was stirred vigorously at -78 ºC for 20 min and then stirred at room temperature protected from light. The reaction time for the complete consumption of the monomer was monitored by thin layer chromatography (TLC). Following the end of the reaction, excess ethyl vinyl ether was added to quench the reaction, after which the mixture was stirred for 30 min. Following stirring, the excess Et_2O (×5 Volume) was added and light brown precipitate was formed. The suspension was centrifuged and then the ether was decanted. Repeat the process

of centrifuging and decanting to afford the final polynorbornyl NHS ester as a grey solid. The polymer was stored at -20 ºC and characterized by ^{1}H-NMR.

Terminal maleimidation of NHS-containing polymer chain (13-TA)



In a typical polymerization experiment, a solution of **12** (70 mg, 0.19 mmol) in 2 mL CH_2Cl_2 was stirred at -78 ºC for 30 min with argon protection. A stock solution of the Grubbs 3rdcatalyst was freshly prepared at 14.2 mg•mL^{-1} in DCE. Following the addition of 100 μL catalyst solution, the mixture was stirred vigorously at -78 ºC for 20 min and then stirred at room temperature protected from light. Upon TLC indicated full conversion, excess compound **16** was added to quench the reaction, after which the mixture was stirred for 30 min. Following stirring, the excess Et_2O (×5 Volume) was added and light brown precipitate was formed. The suspension was centrifuged and then the ether was decanted. Repeat the process of centrifuging and decanting to afford the final polynorbornyl NHS ester as a grey solid. The polymer was stored at -20 ºC and characterized by ^{1}H-NMR.

General procedure for post-modification of NHS-containing polymer with sugar units

Before the condensation of NHS-containing polymer with sugar units, NHS-containing polymer (1 eq., based on monomer) was dissolved in 1.2 mL DMF to prepared solution A, and terminal amine functionalized galactosamine (1.2 eq.) was dissolved in 200 μL deionized water to prepare solution B. Afterward, solution A and Et_3N (5 eq.) were added to solution B quickly. The mixture was stirred vigorously under room temperature for 5 h after which TLC indicated full conversion. The mixture was dialyzed against deionized water for 3 days using cellulose membranes with a molecular weight cut off of 3.5 kDa and lyophilized to obtain the purified glycopolymer and maleimide containing glycopolymer as a white powder. The glycopolymers were stored at -20 ºC and characterized by ^{1}H-NMR.

General procedure for coupling glycopolymer with Cy3-NH_2

Glycopolymer with NHS activated esters and Cy3-NH_2 (2 eq., based on glycopolymer) was dissolved in 1.2 mL PBS buffer (0.1 M, pH = 8.5). The mixture was stirred vigorously under room temperature for 5 h after which TLC indicated successful coupling. The mixture was

dialyzed against deionized water for 3 days using cellulose membranes with a molecular weight cut off of 3.5 kDa and lyophilized to obtain the purified glycopolymer with Cy3 a pink powder. The glycopolymers were stored at -20 ºC.

General procedure for the end-capping of glycopolymers with iRGD cyclic peptide (GP-iRGD)

The maleimide containing glycopolymer (1 eq., based on maleimide) was dissolved in HEPES buffer and iRGD cyclic peptide (1.5 eq.) was added. The mixture was stirred gently at room temperature for 24 h. The mixture was dialyzed against deionized water for 3 days using cellulose membranes with a molecular weight cutoff of 3.5 kDa to remove inorganic salt and excess iRGD cyclic peptide. The dialysate was lyophilized to obtain iRGD cyclic peptide capped glycopolymer as a white powder. The glycopolymers were stored at -20 ºC.

5. NMR spectra of compounds.

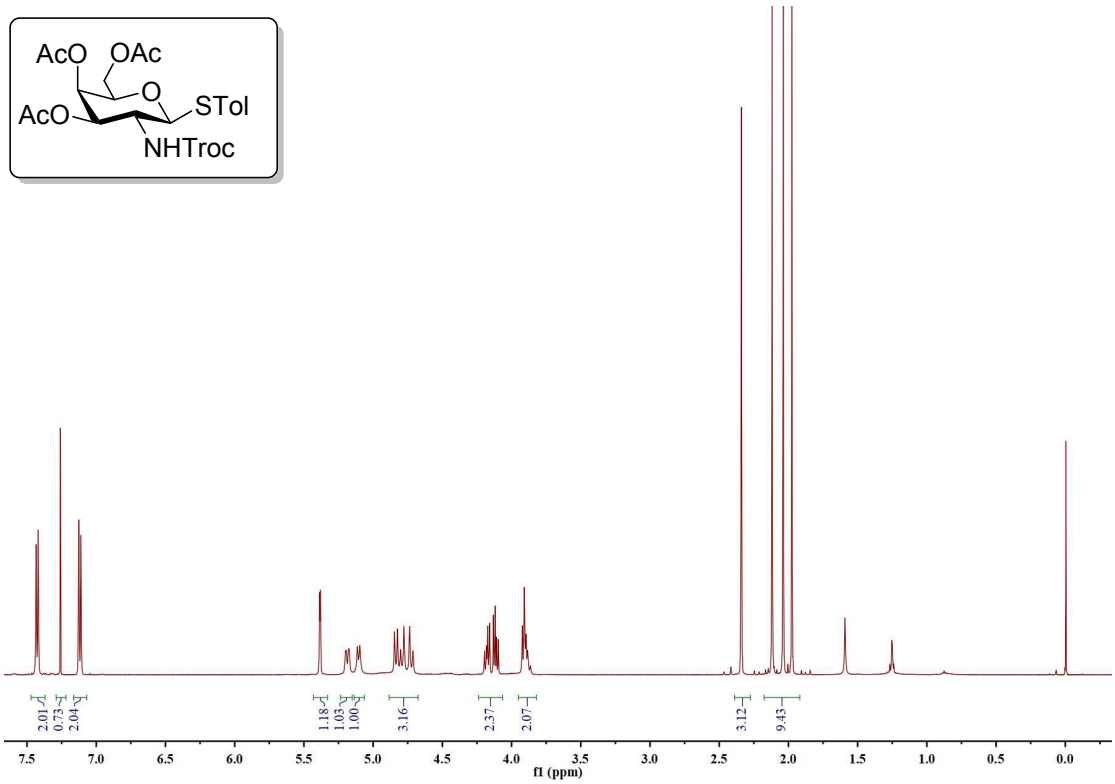


Figure S1-1. ^{1}H NMR spectrum of compound **17**

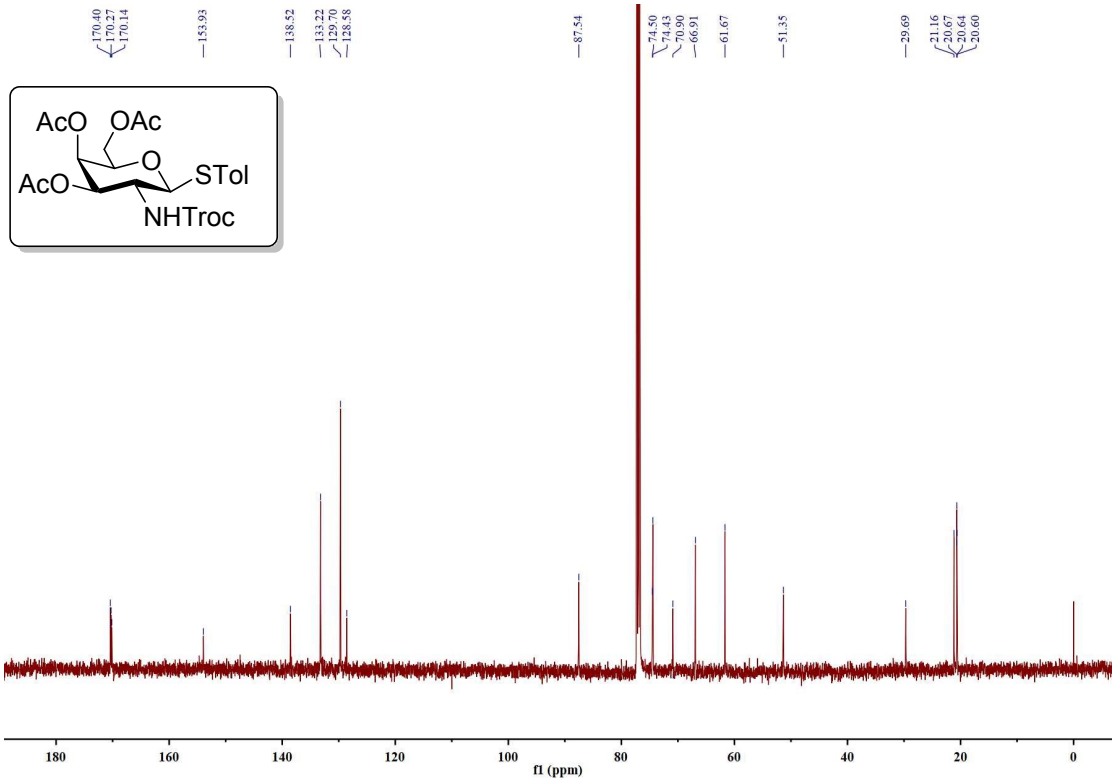
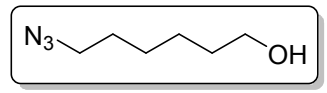


Figure S1-2. ^{13}C NMR spectrum of compound **17**



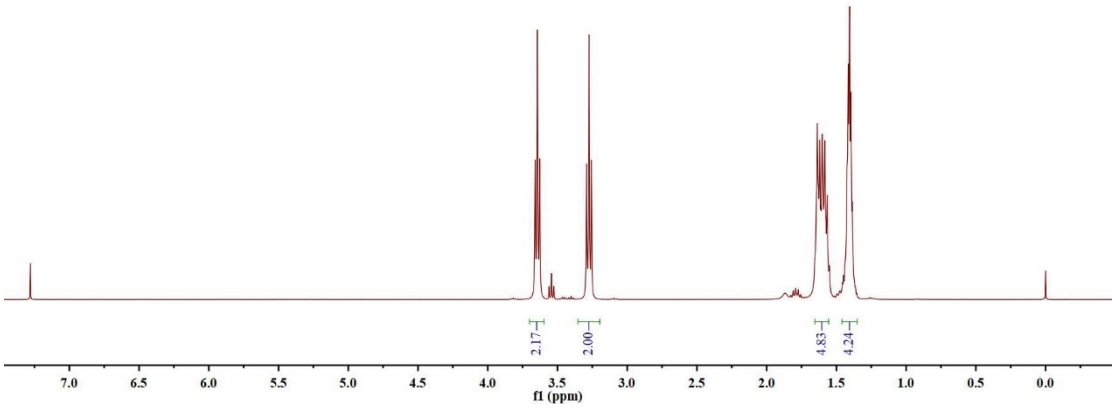


Figure S2-1. ^{1}H NMR spectrum of compound **18**

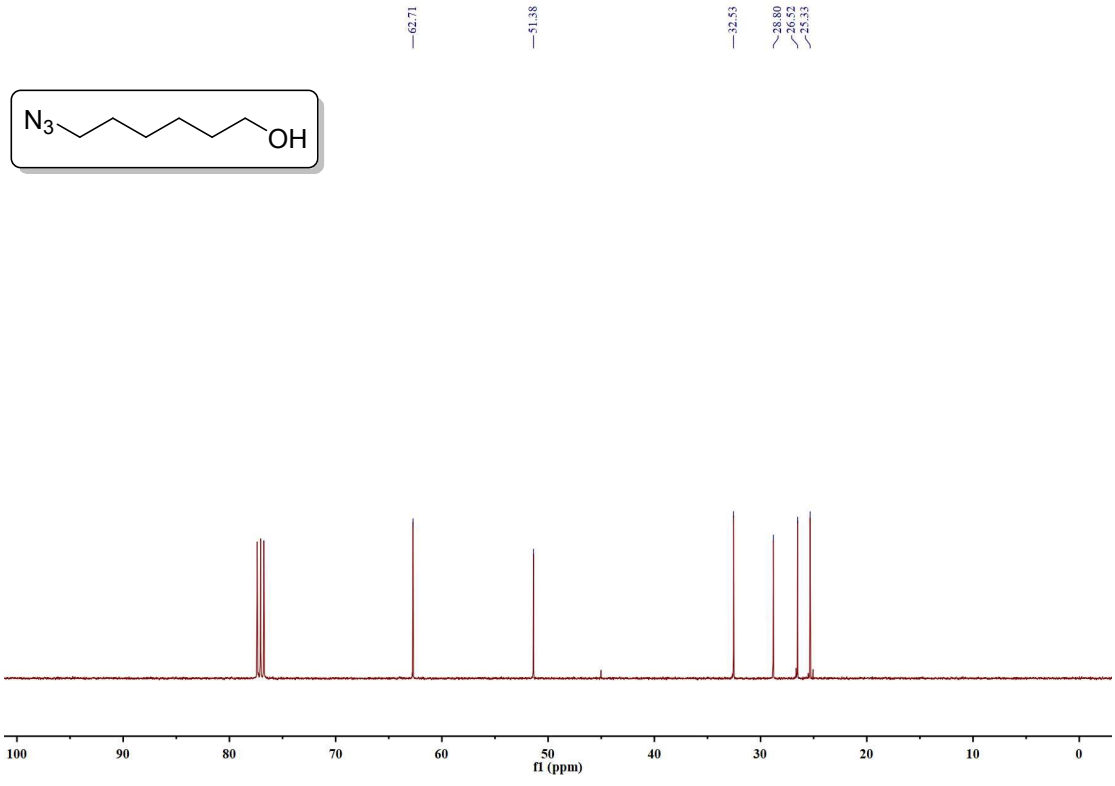


Figure S2-2. ^{13}C NMR spectrum of compound **18**

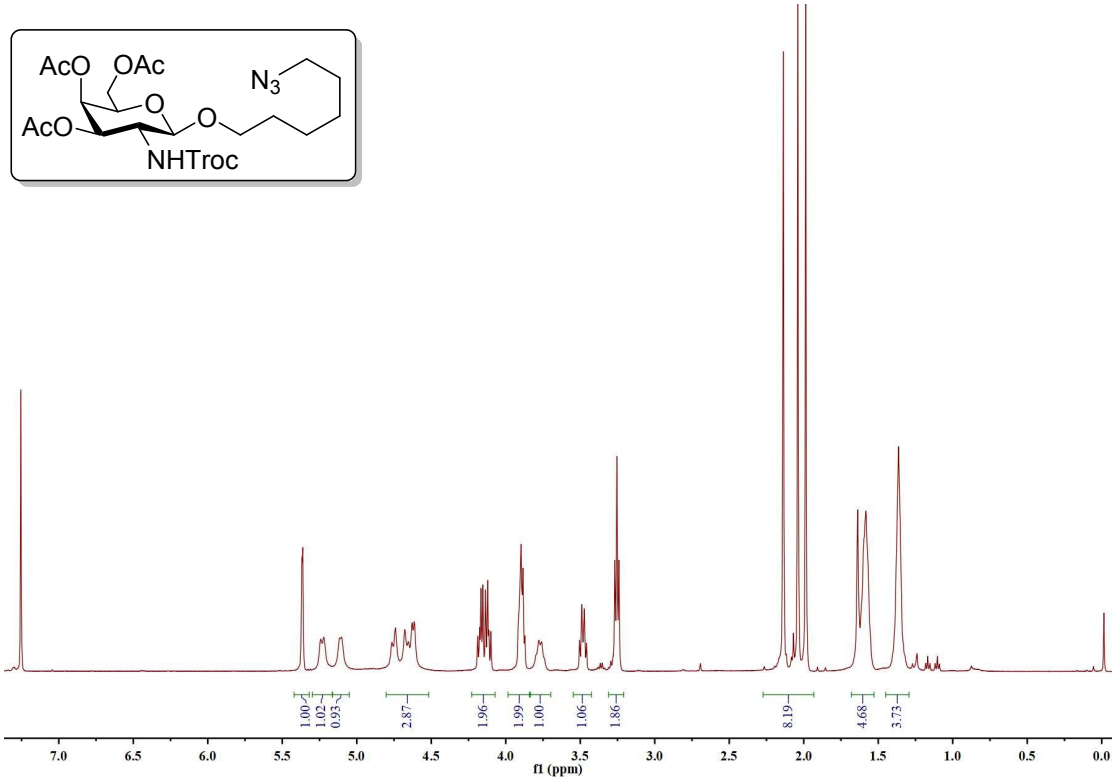


Figure S3-1. ^{1}H NMR spectrum of compound **7**

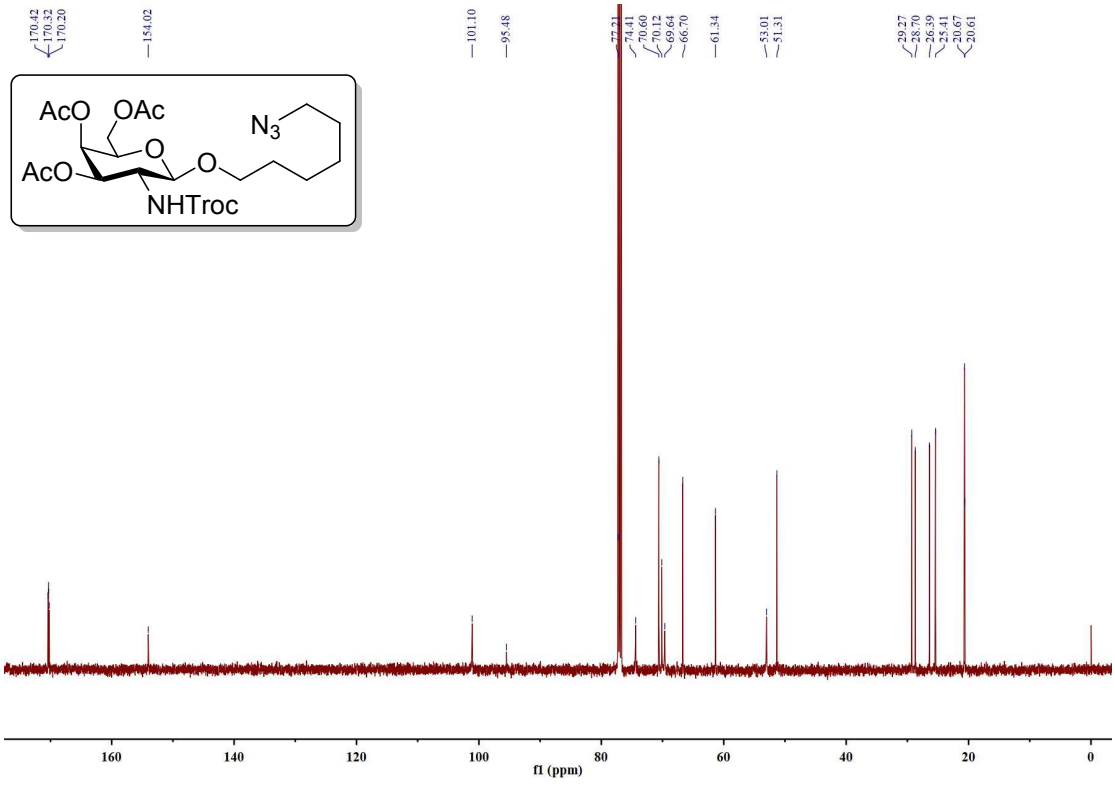


Figure S3-2. ^{13}C NMR spectrum of compound **7**.

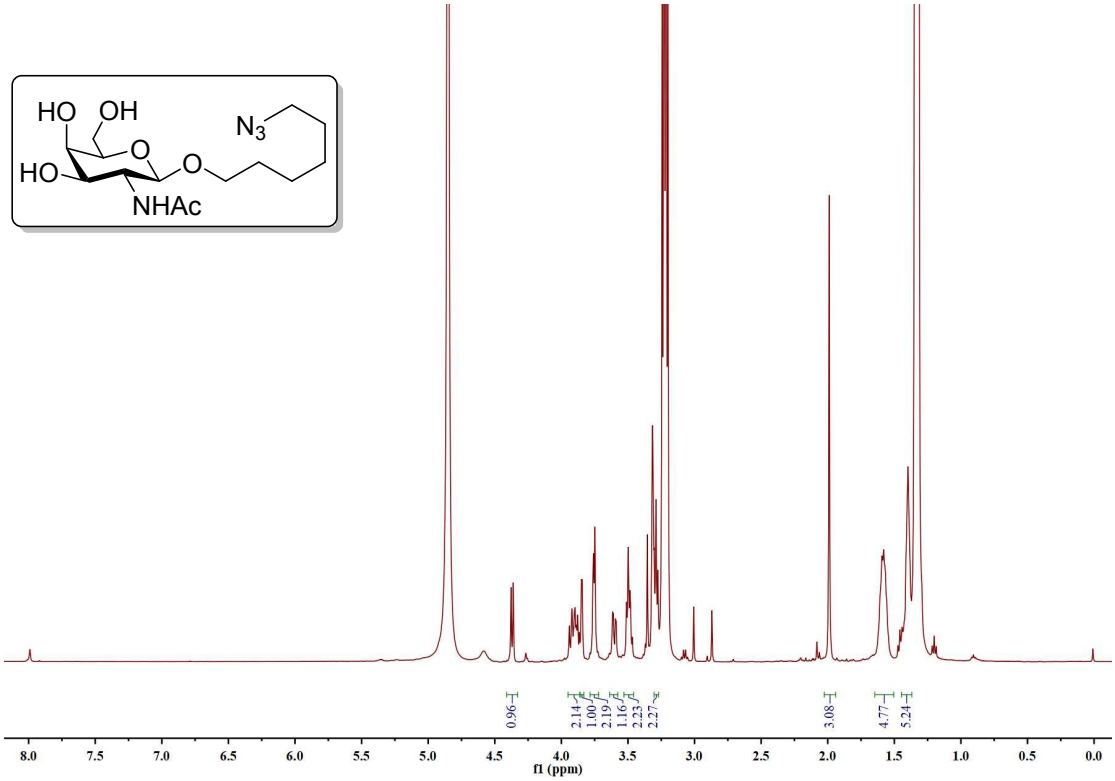


Figure S4-1. ^{1}H NMR spectrum of compound **20**

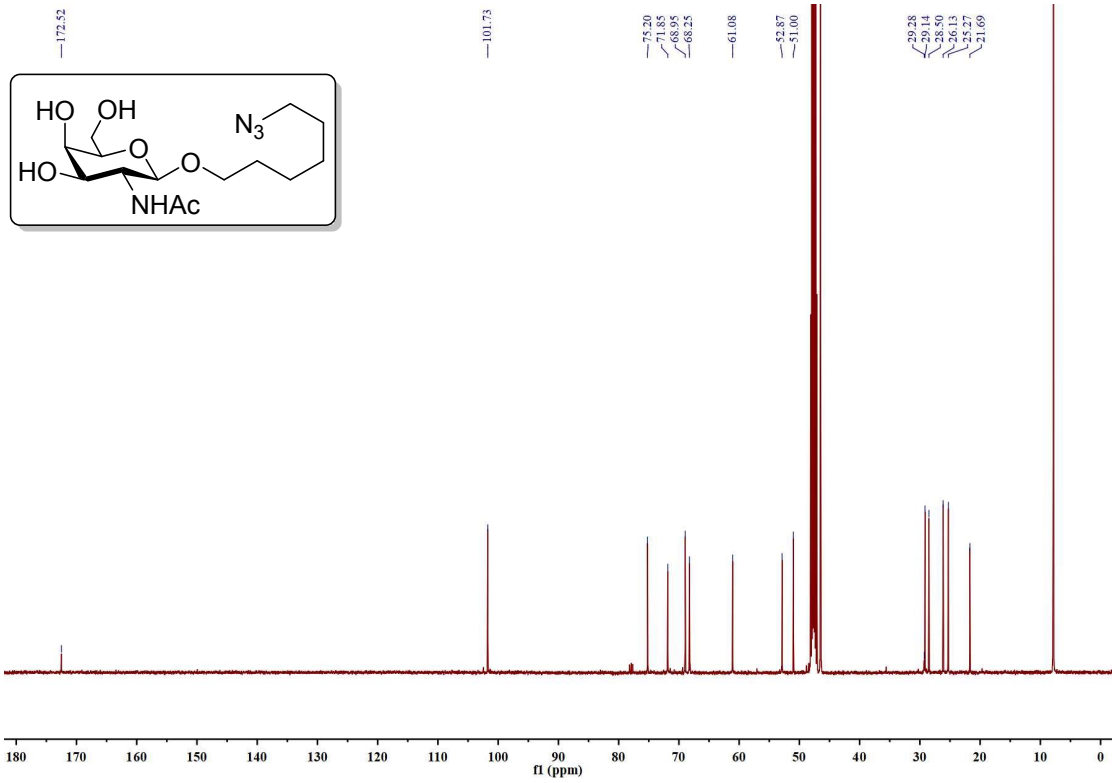


Figure S4-2. ^{13}C NMR spectrum of compound **20**.

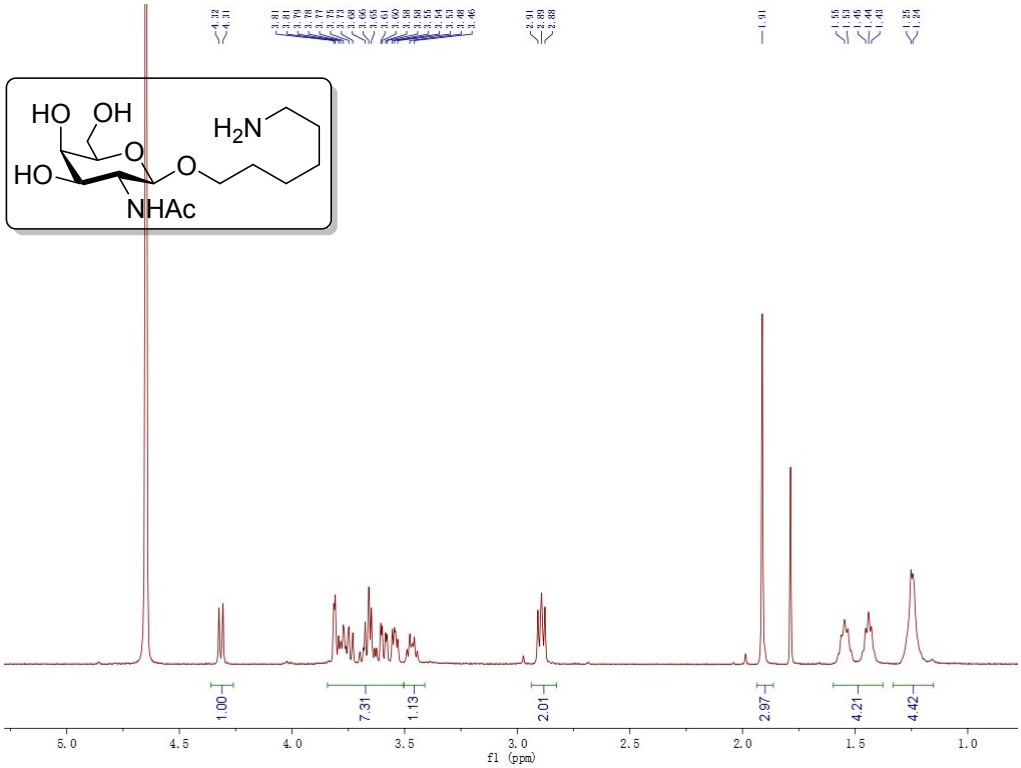


Figure S5-1. ^{1}H NMR spectrum of compound **1**

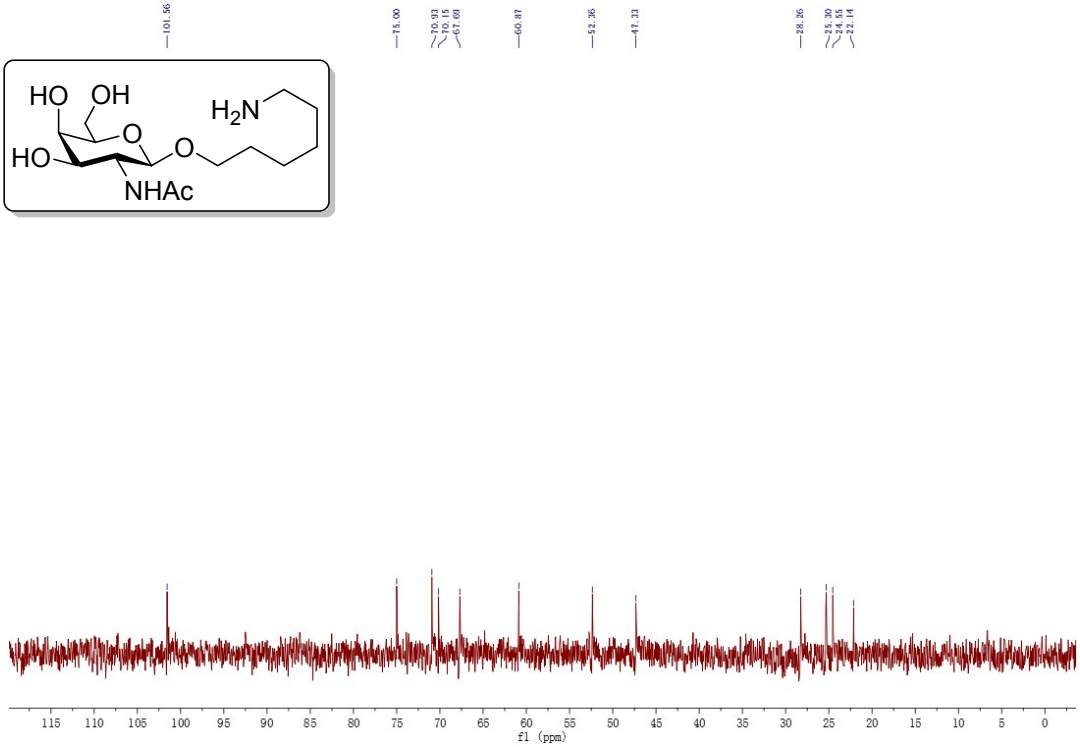


Figure S5-2. ^{13}C NMR spectrum of compound **1**.

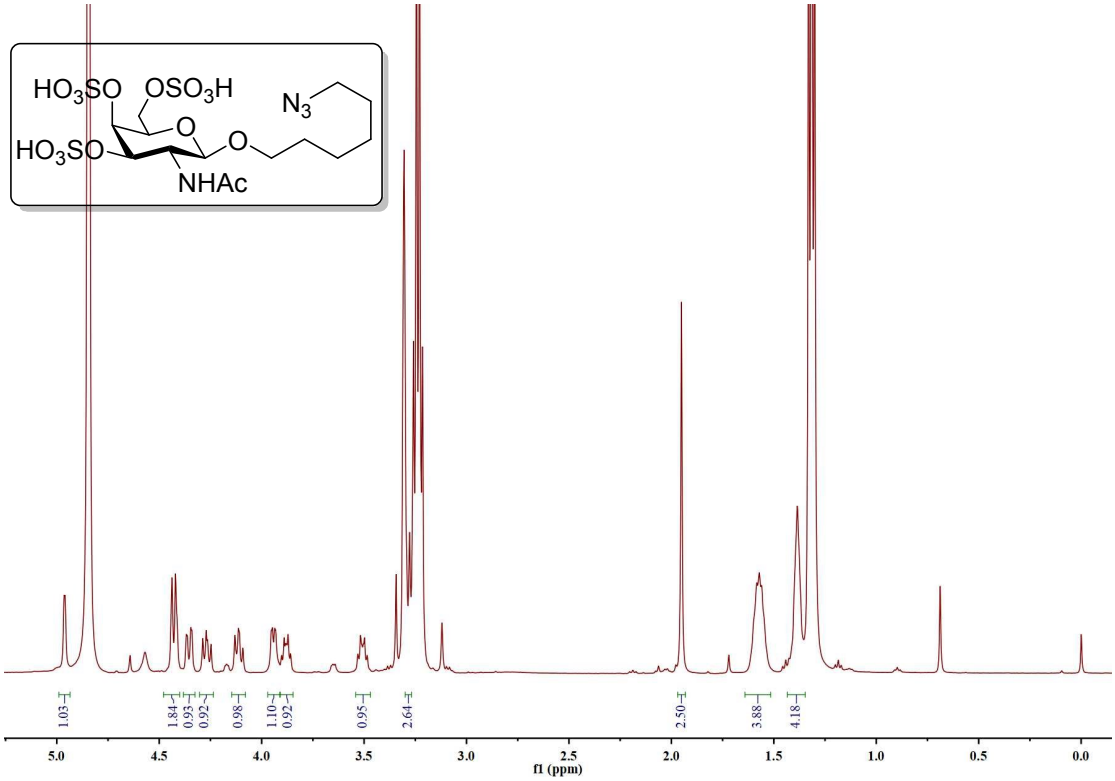


Figure S6-1. ^{1}H NMR spectrum of compound **21**.

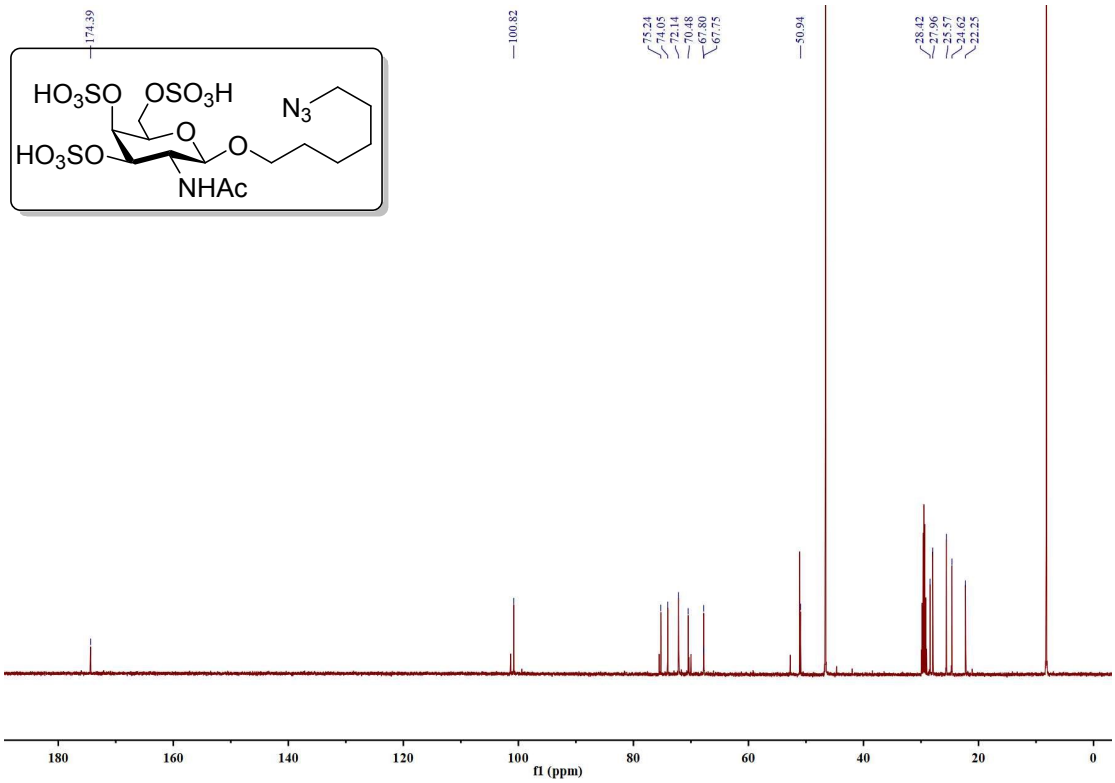


Figure S6-2. ^{13}C NMR spectrum of compound **21**.

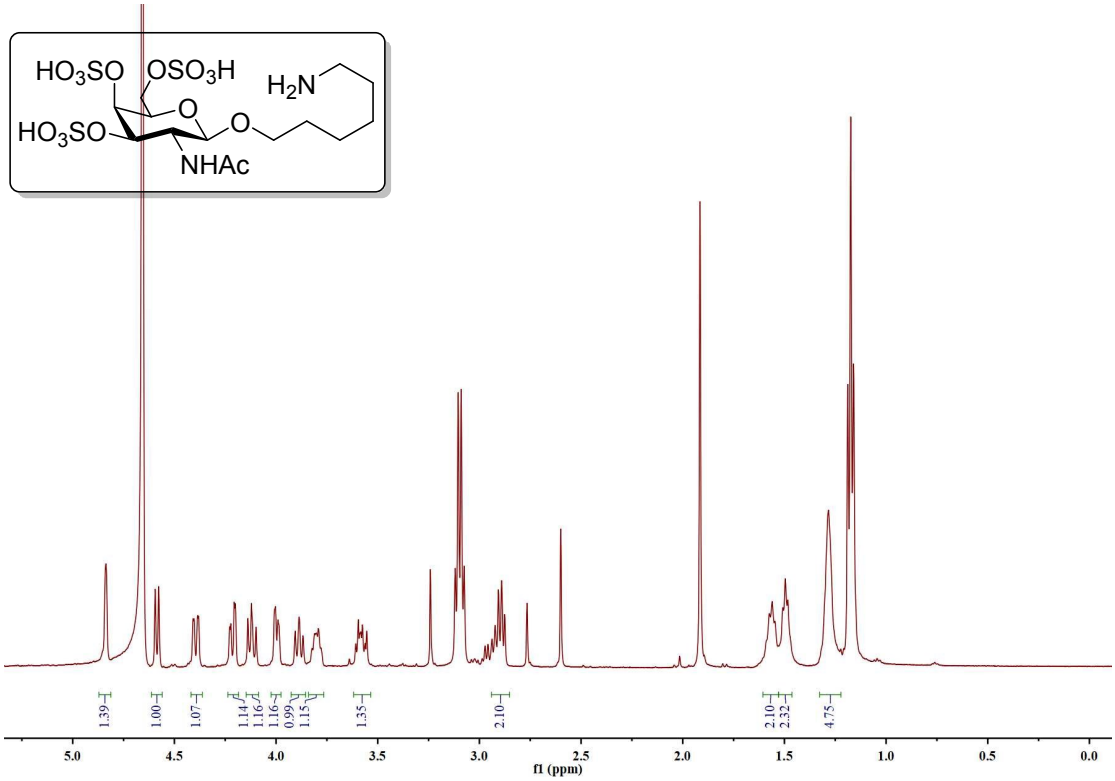


Figure S7-1. ^{1}H NMR spectrum of compound **5**.

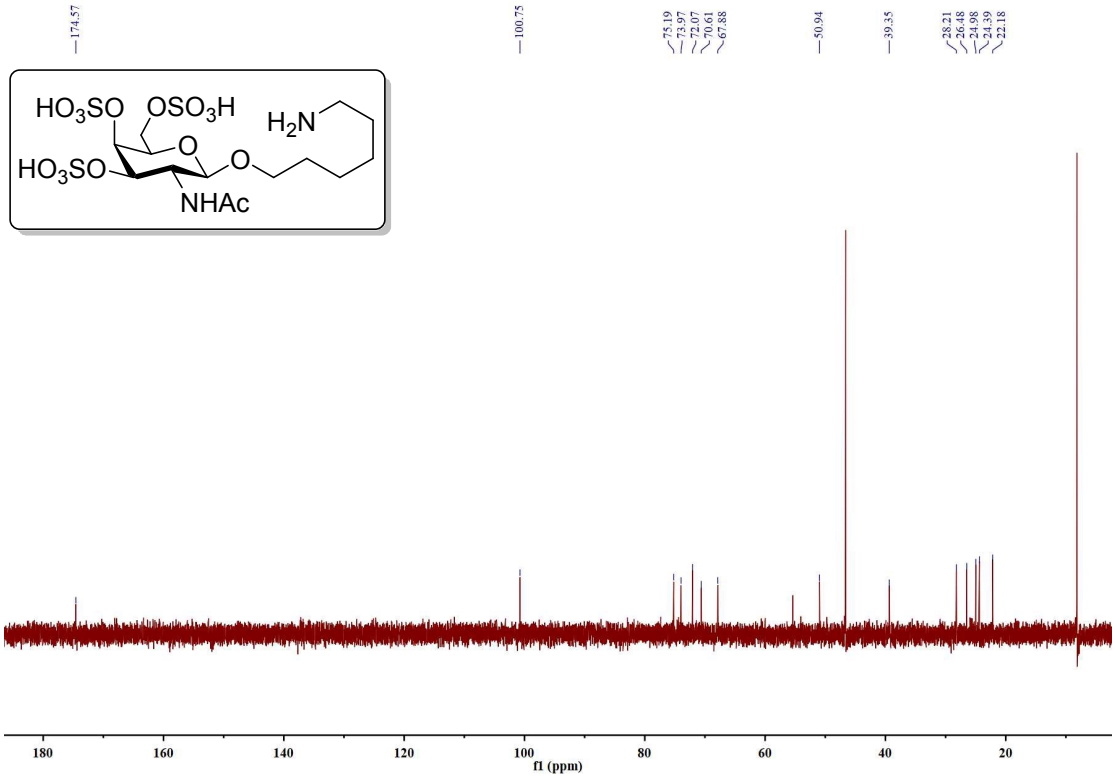


Figure S7-2. ^{13}C NMR spectrum of compound **5**.

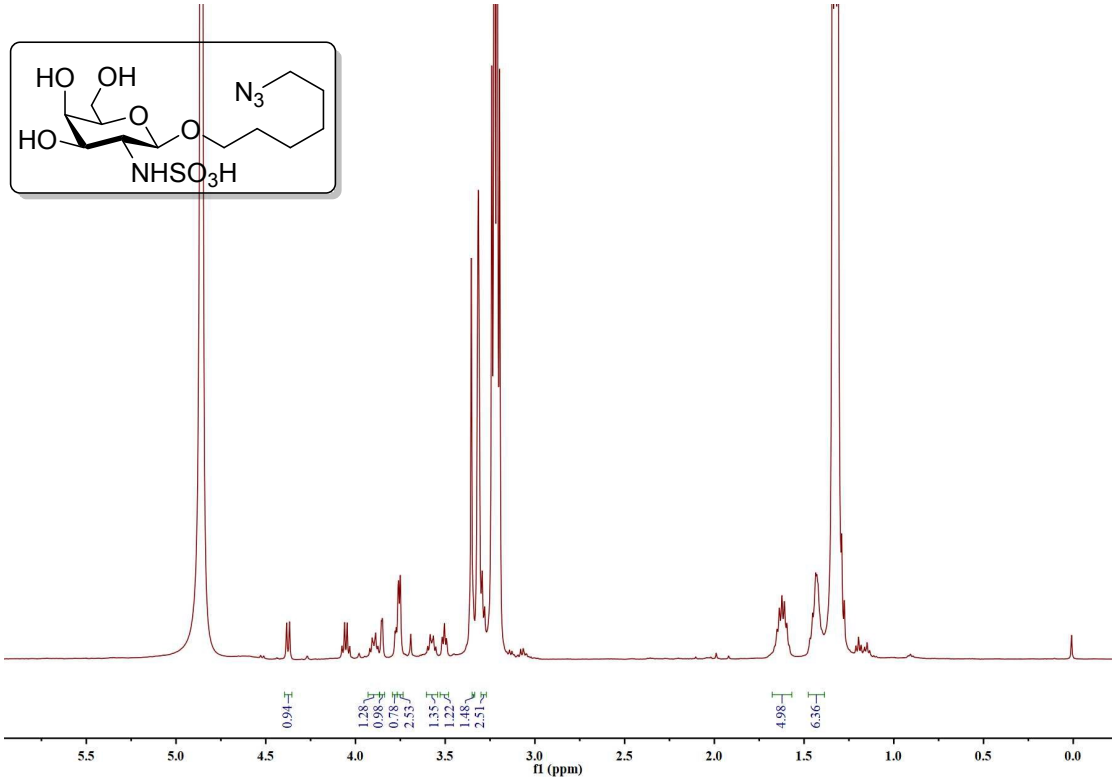


Figure S8-1. ^{1}H NMR spectrum of compound **22**.

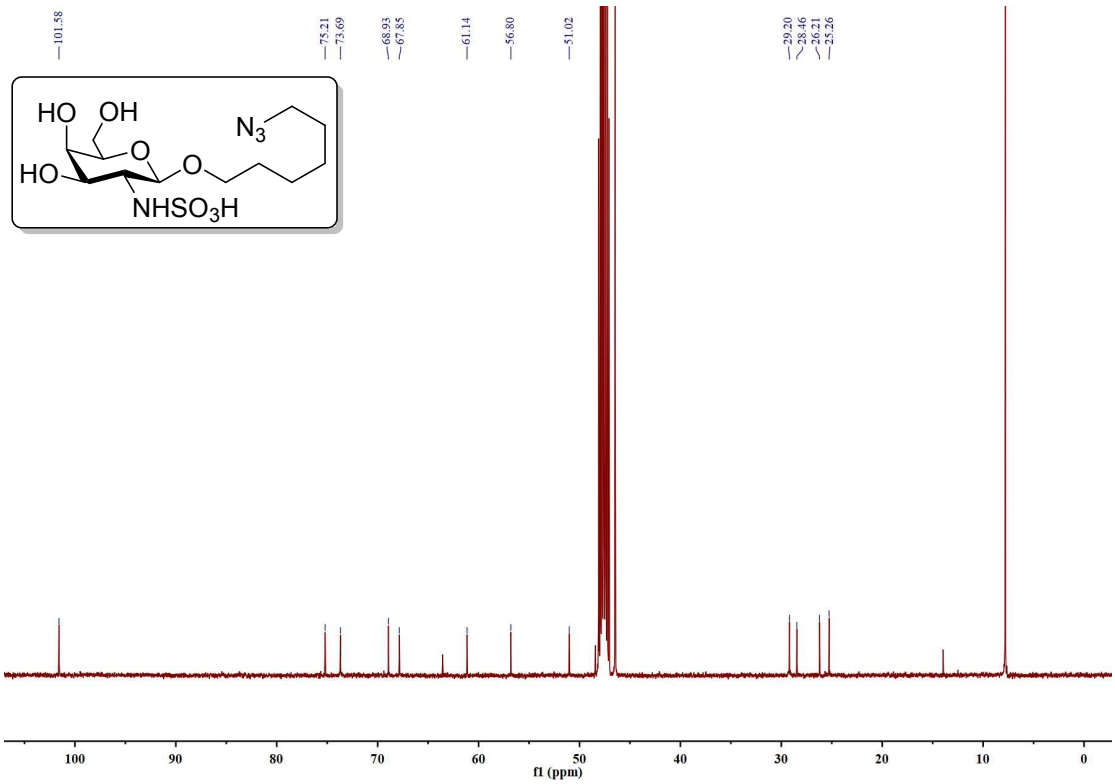


Figure S8-2. ^{13}C NMR spectrum of compound **22**.

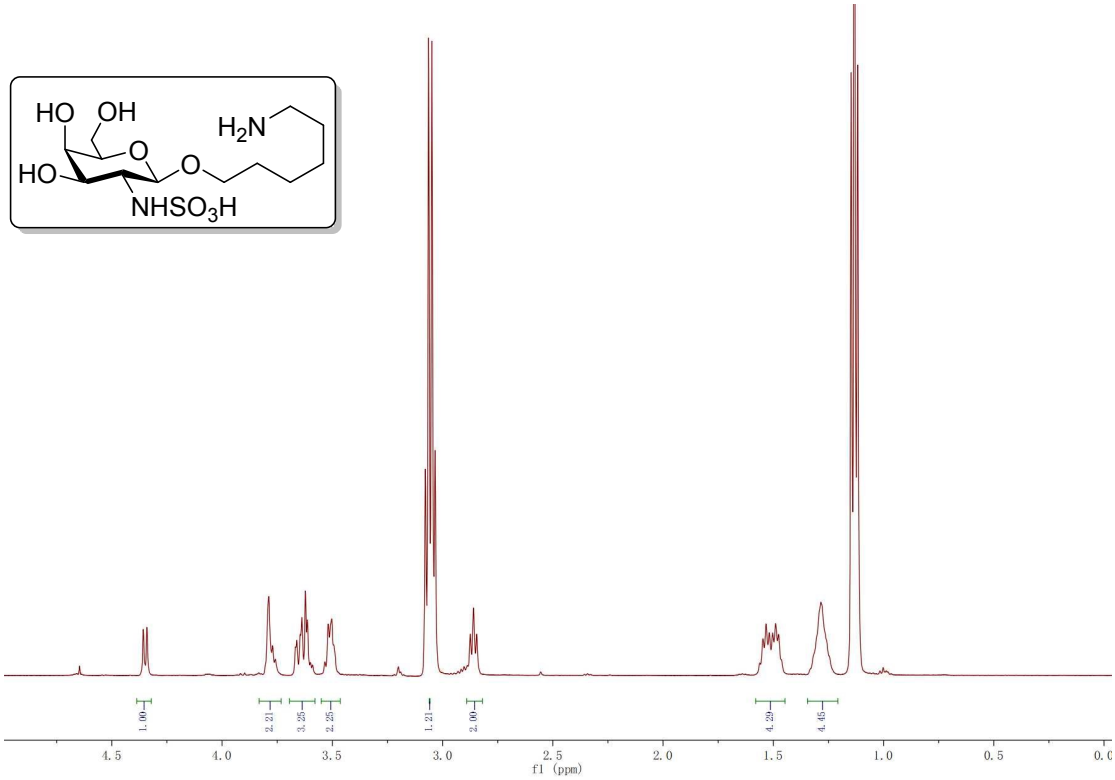


Figure S9-1. ^{1}H NMR spectrum of compound **3**.

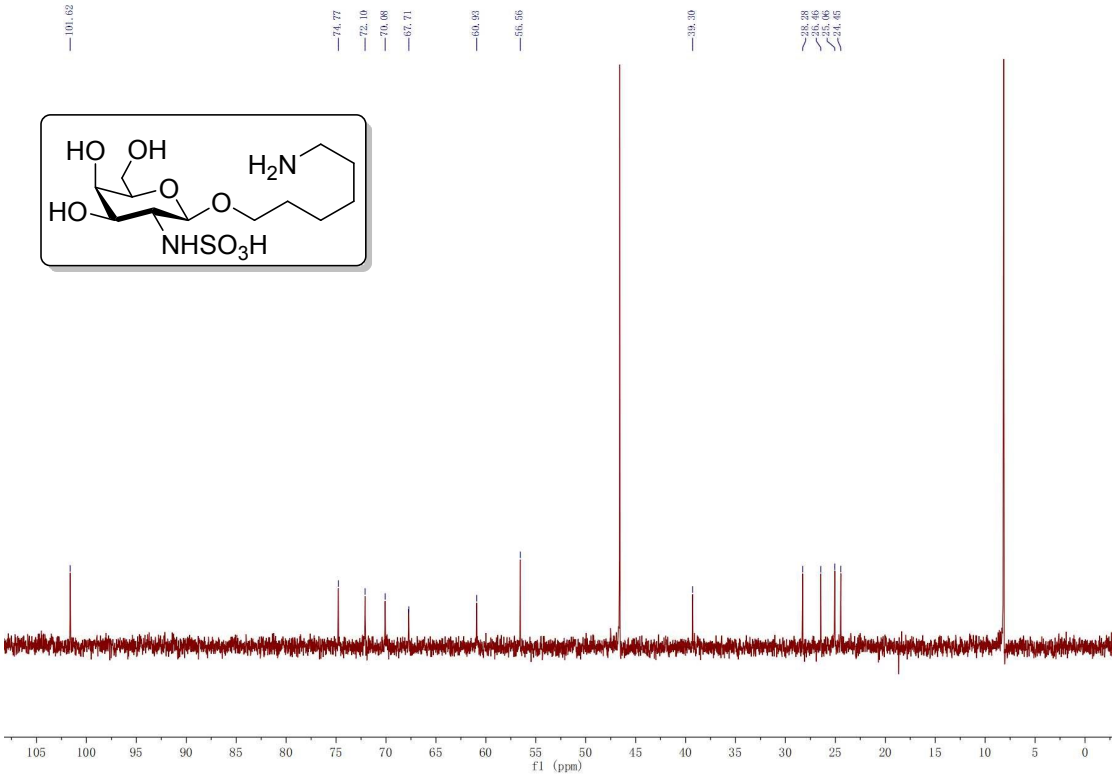


Figure S 9-2. ^{13}C NMR spectrum of compound **3**.

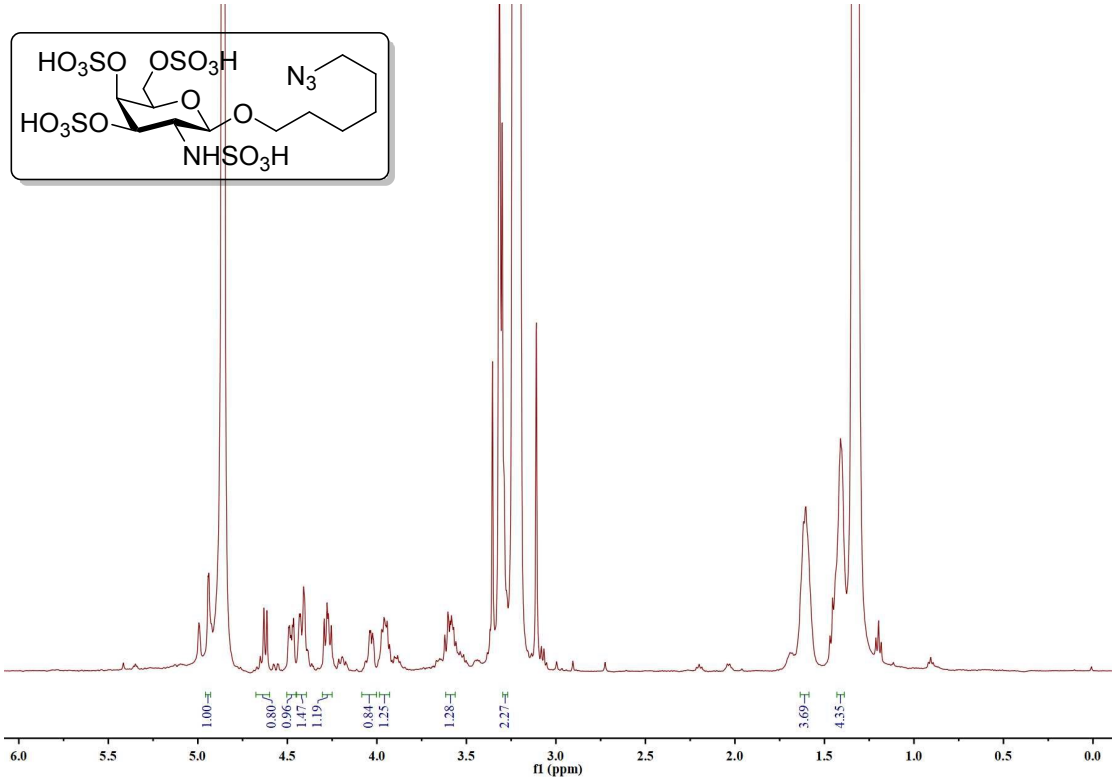


Figure S 10-1.[1]H NMR spectrum of compound **23**.

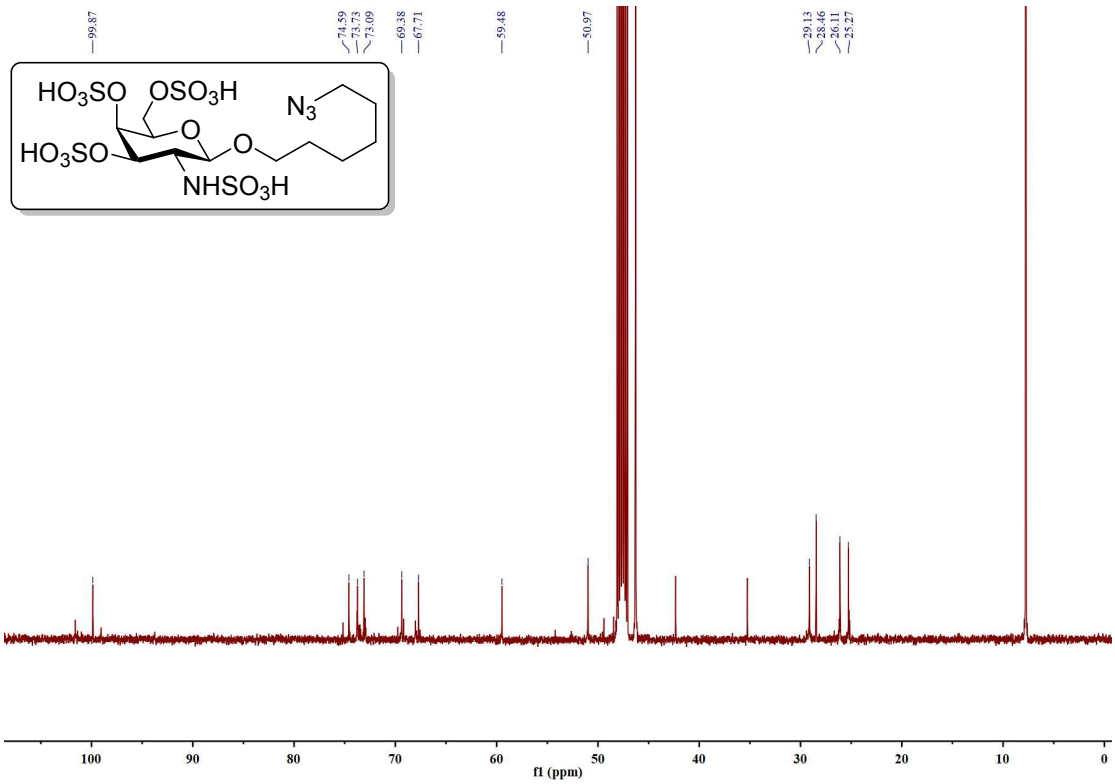


Figure S10-2. [13]C NMR spectrum of compound **23**.

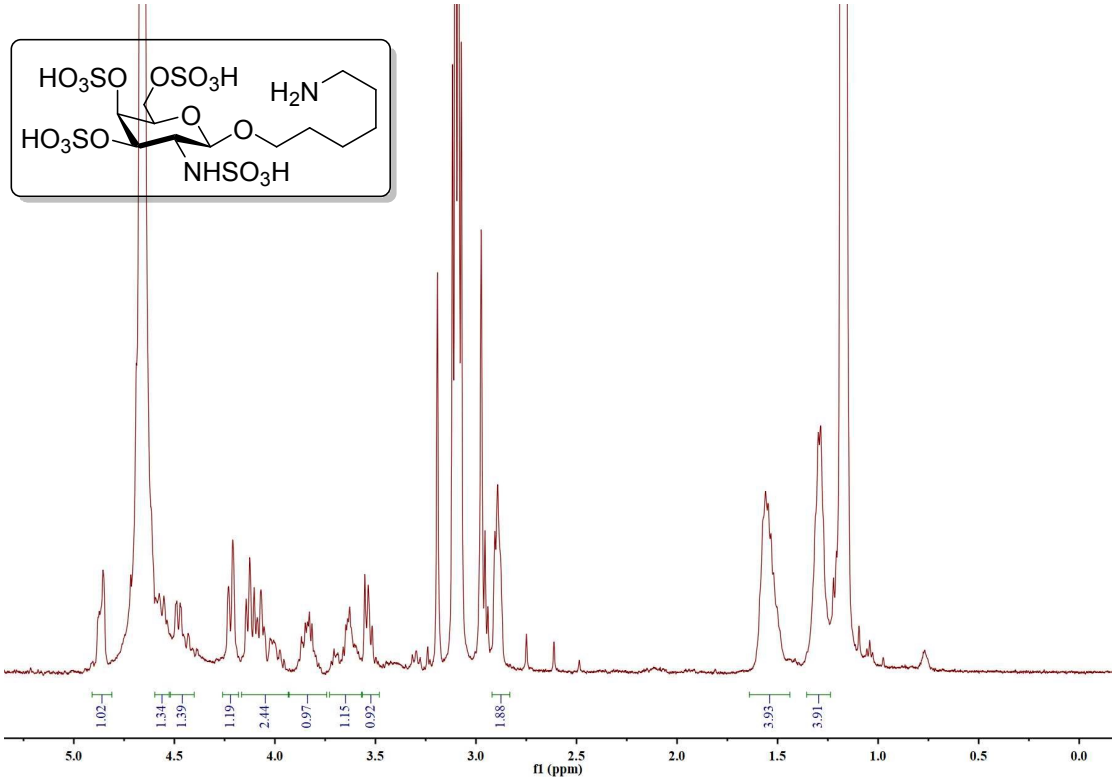


Figure S11-1. ^{1}H NMR spectrum of compound **6**.

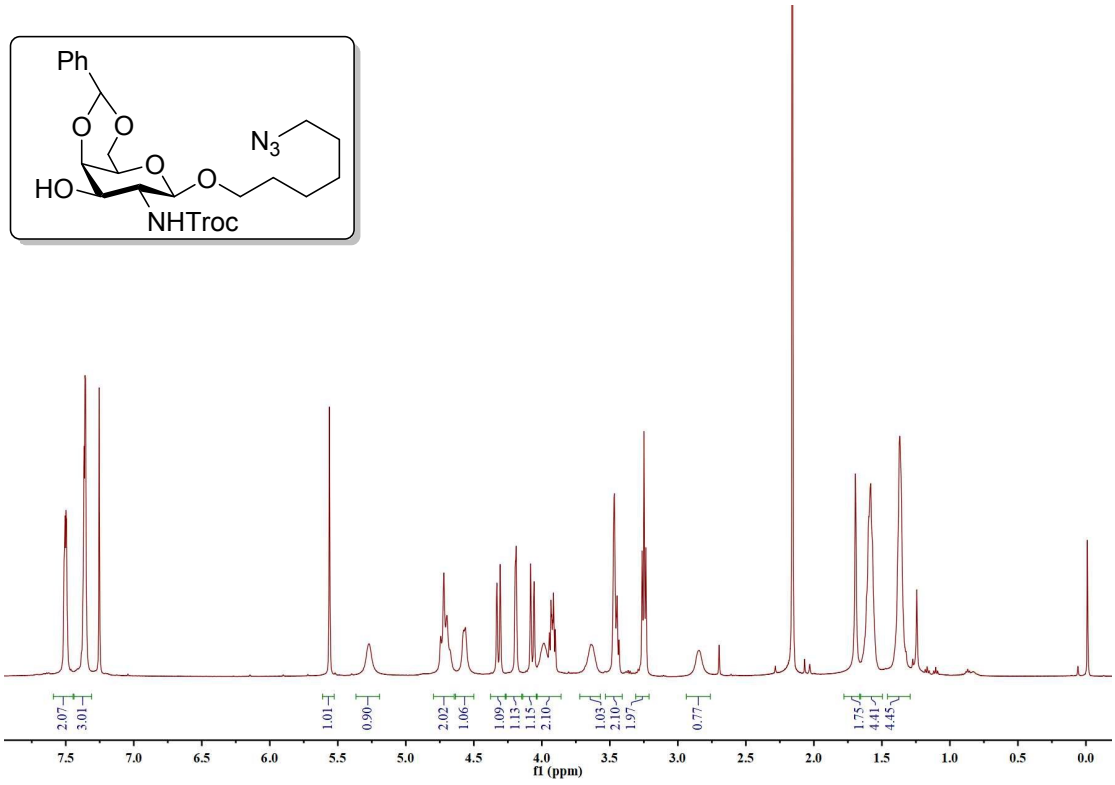


Figure S12-1.^{1}H NMR spectrum of compound **8**.

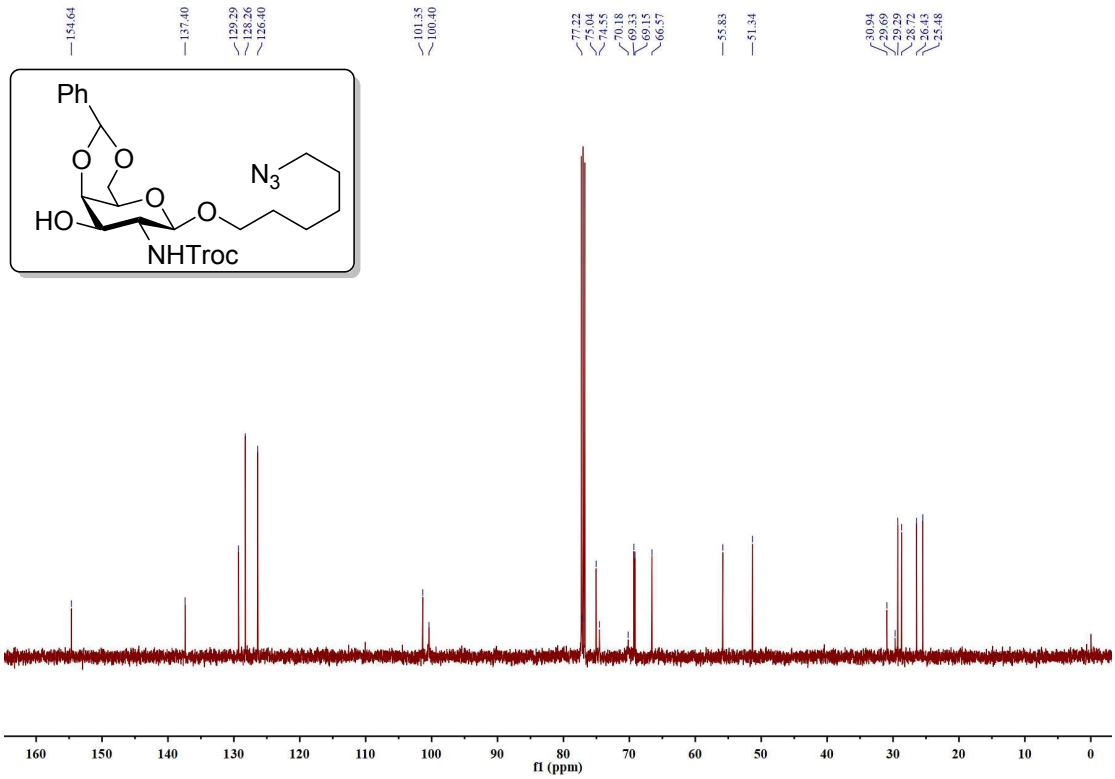


Figure S12-2. ^{13}C NMR spectrum of compound **8**.

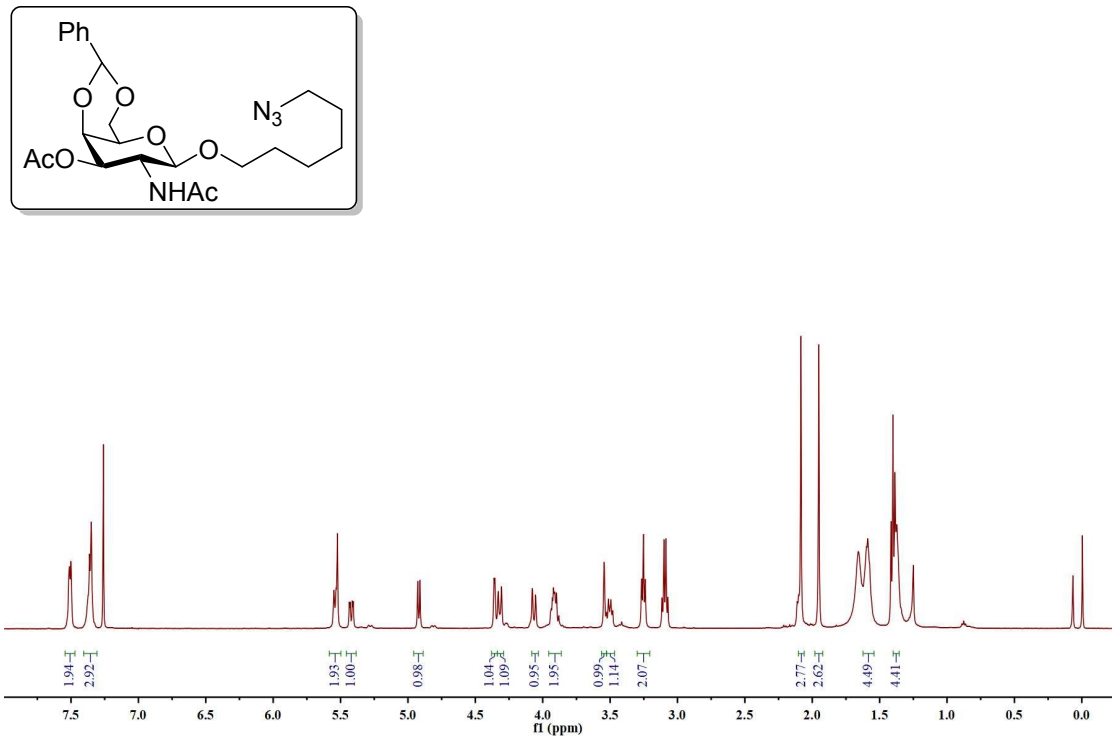


Figure S13-1. ^{1}H NMR spectrum of compound **24**.

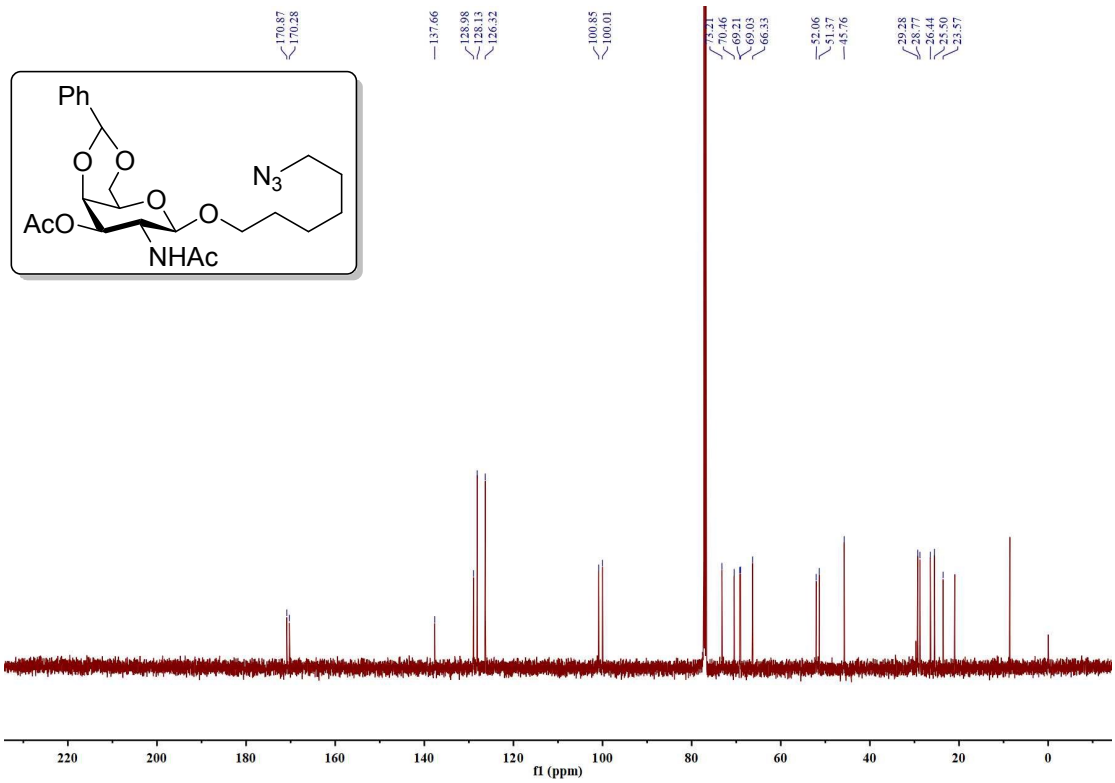


Figure S13-2. ^{13}C NMR spectrum of compound **24**.

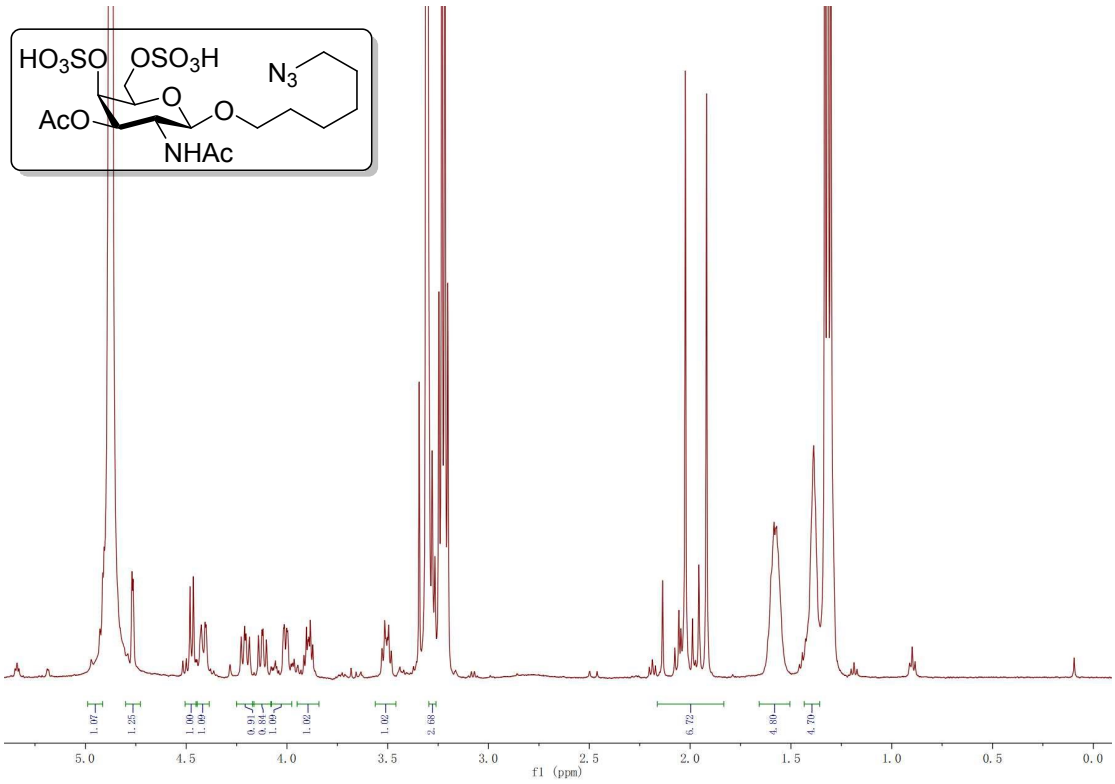


Figure S14-1. ^{1}H NMR spectrum of compound **25**.

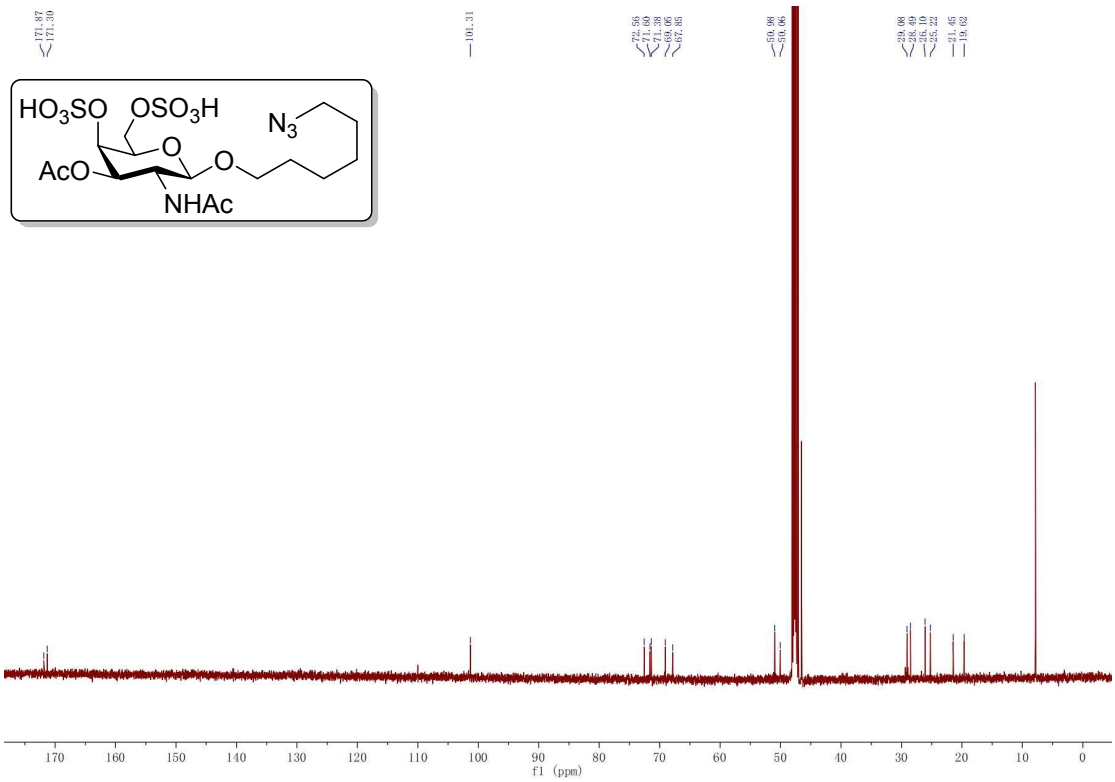


Figure S14-2. ^{13}C NMR spectrum of compound **25**.

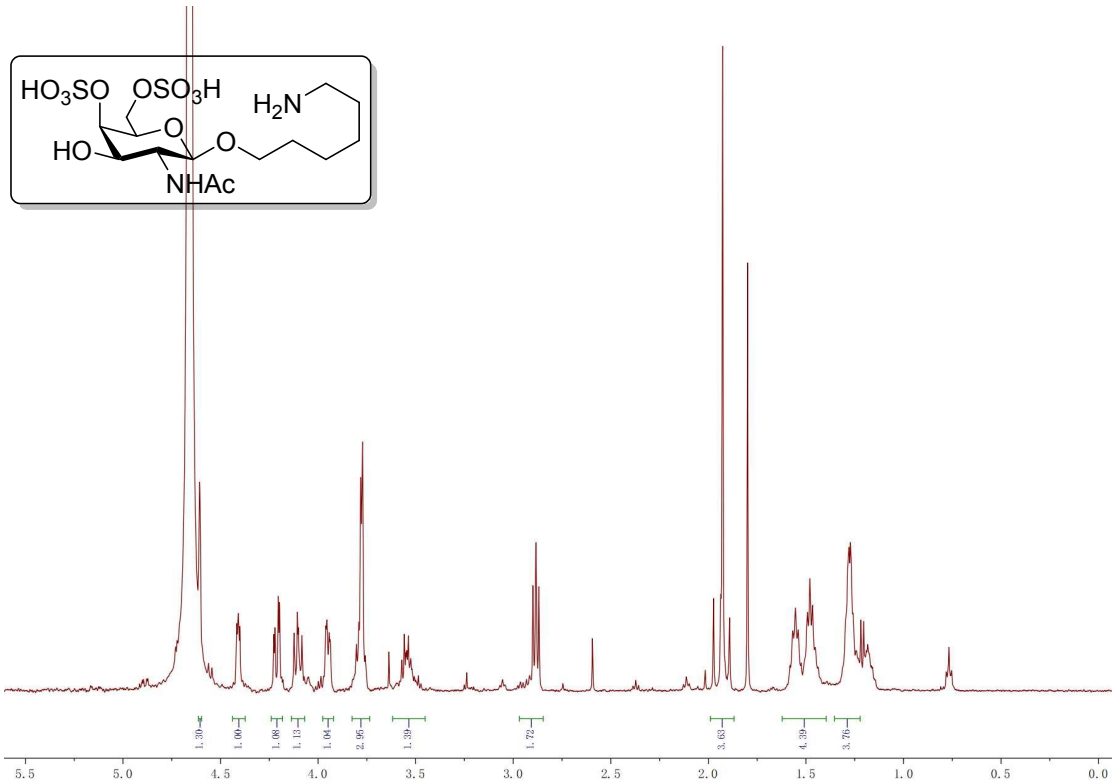


Figure S15-1. ^{1}H NMR spectrum of compound **4**.

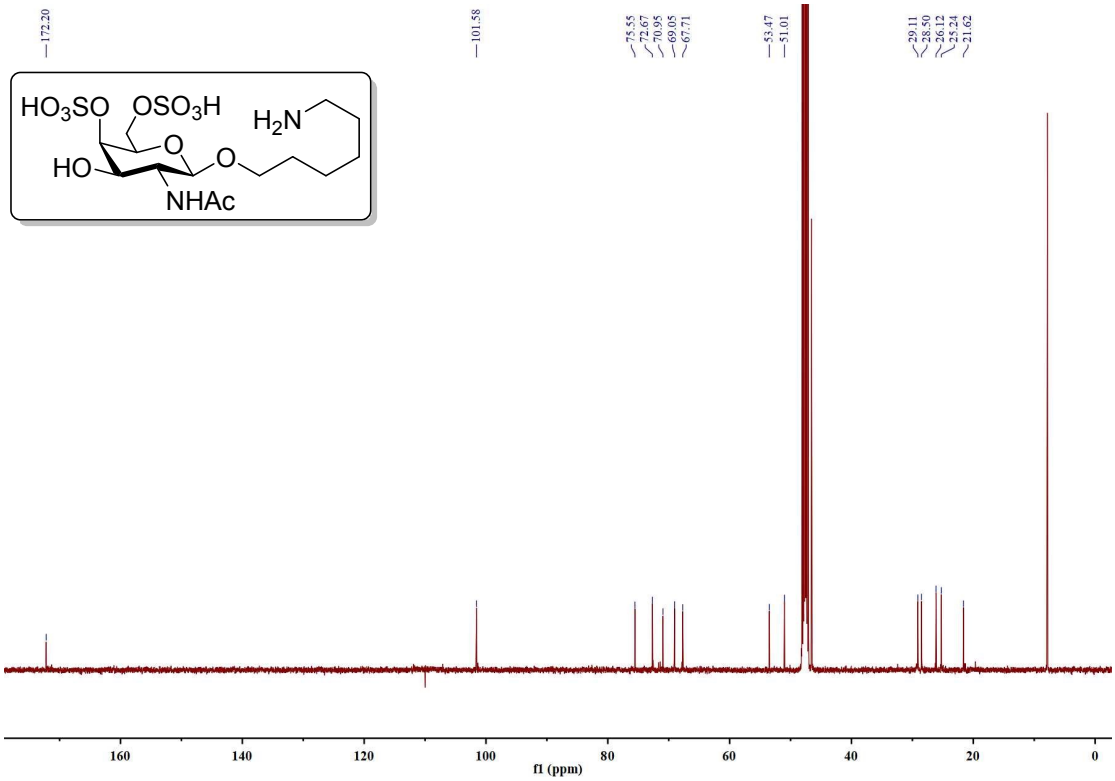


Figure S15-2. ^{13}C NMR spectrum of compound **4**.

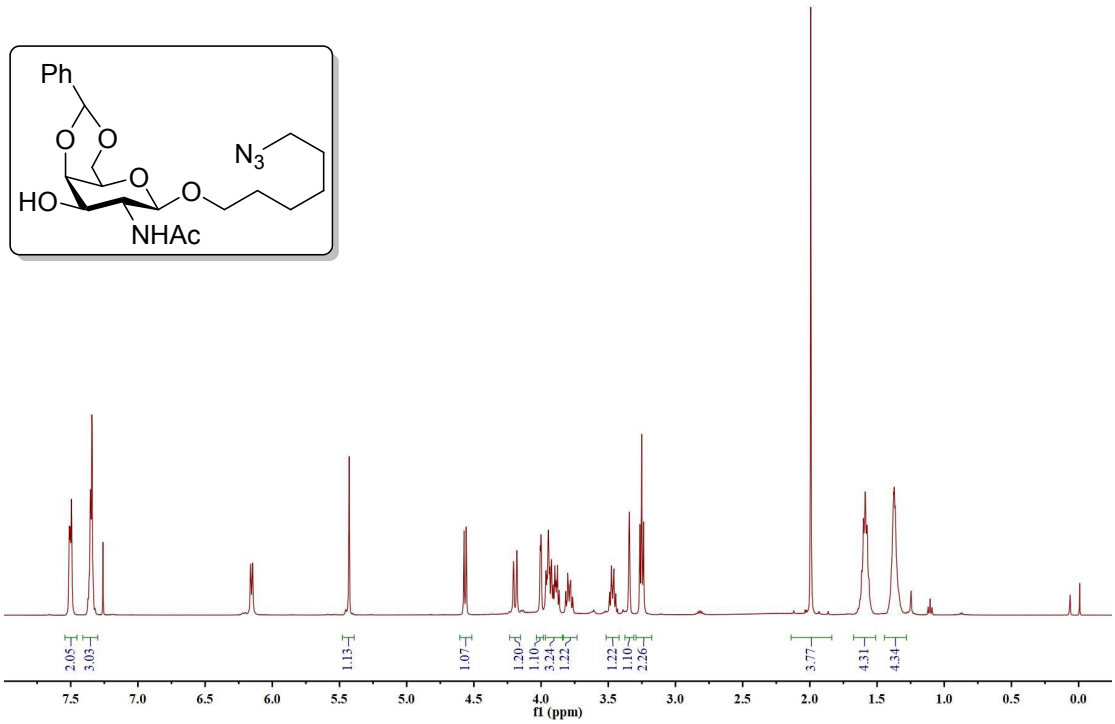


Figure S16-1. ^{1}H NMR spectrum of compound **26**.

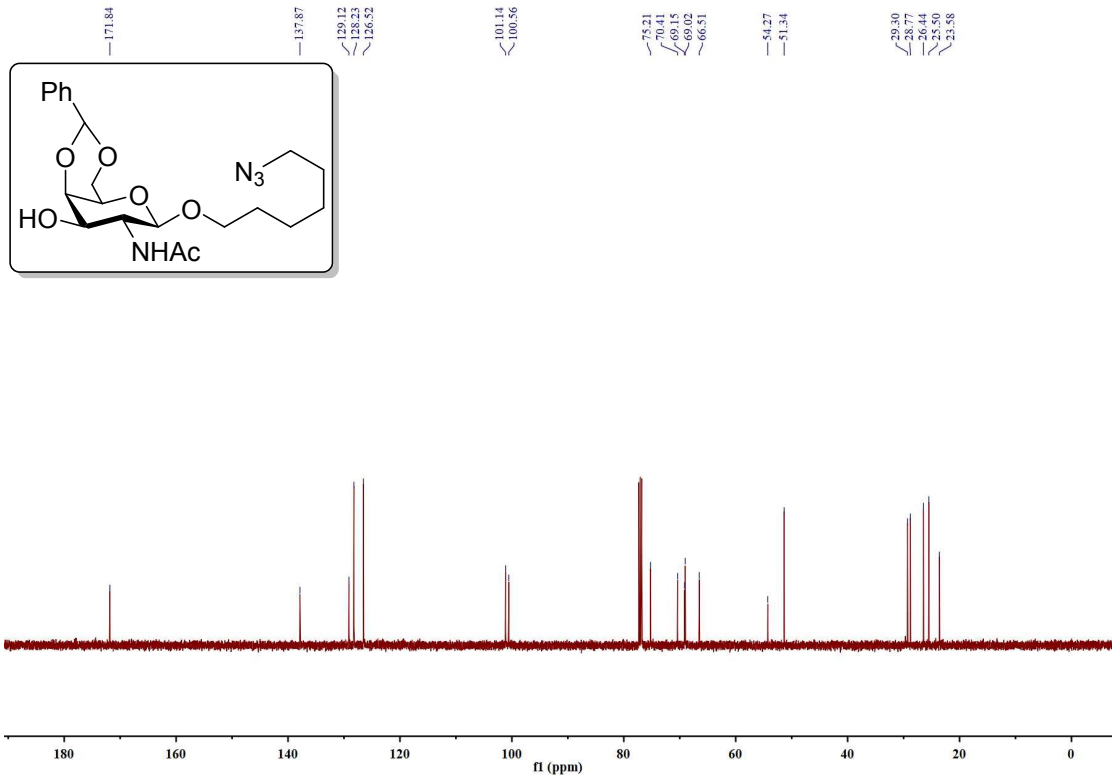


Figure S16-2. ^{13}C NMR spectrum of compound **26**.

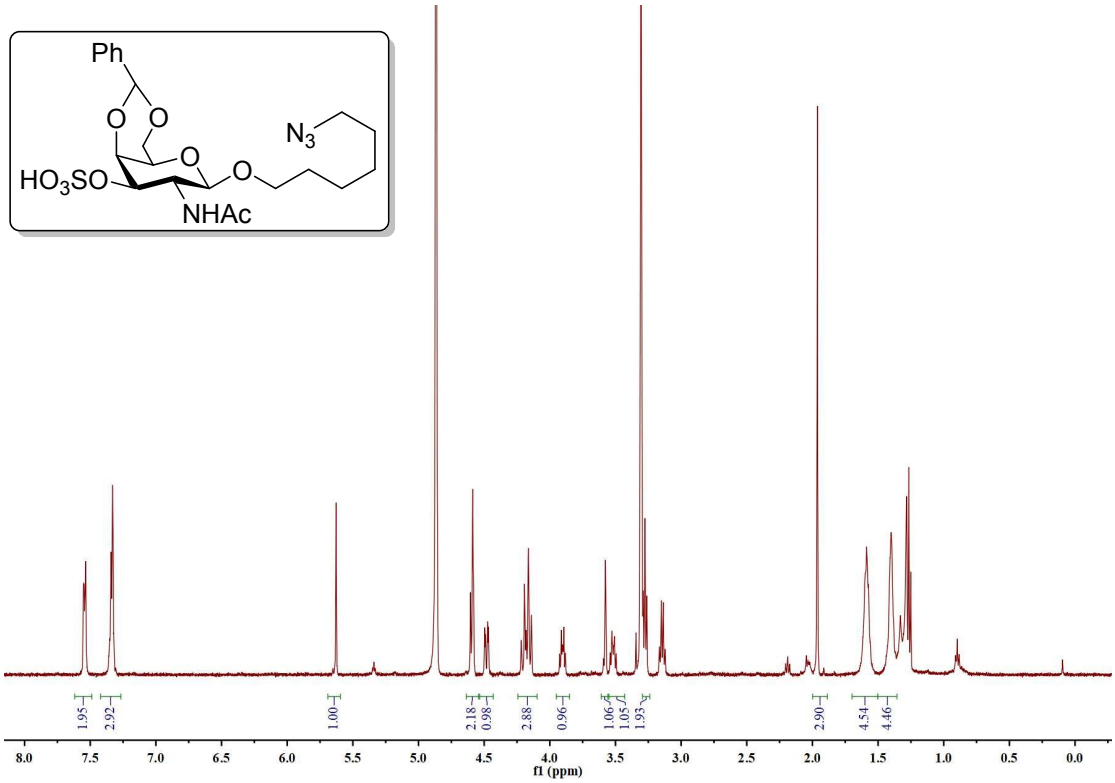


Figure S17-1. ^{1}H NMR spectrum of compound **27**.

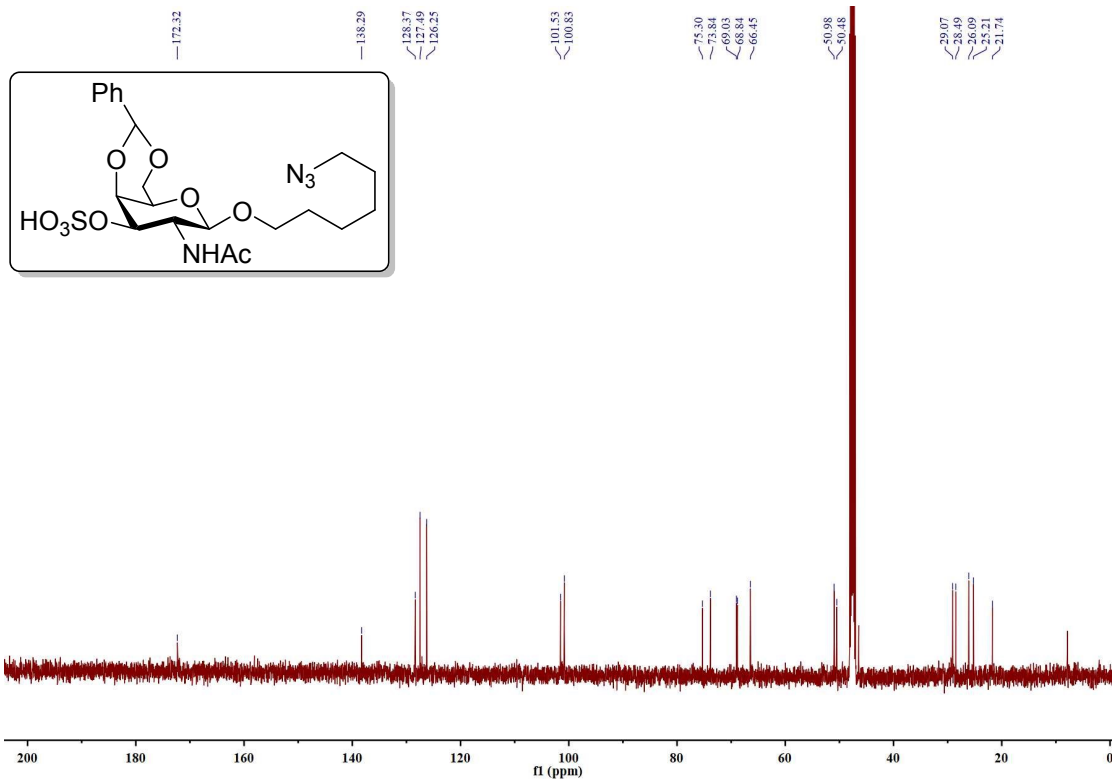


Figure S17-2. ^{13}C NMR spectrum of compound **27**.

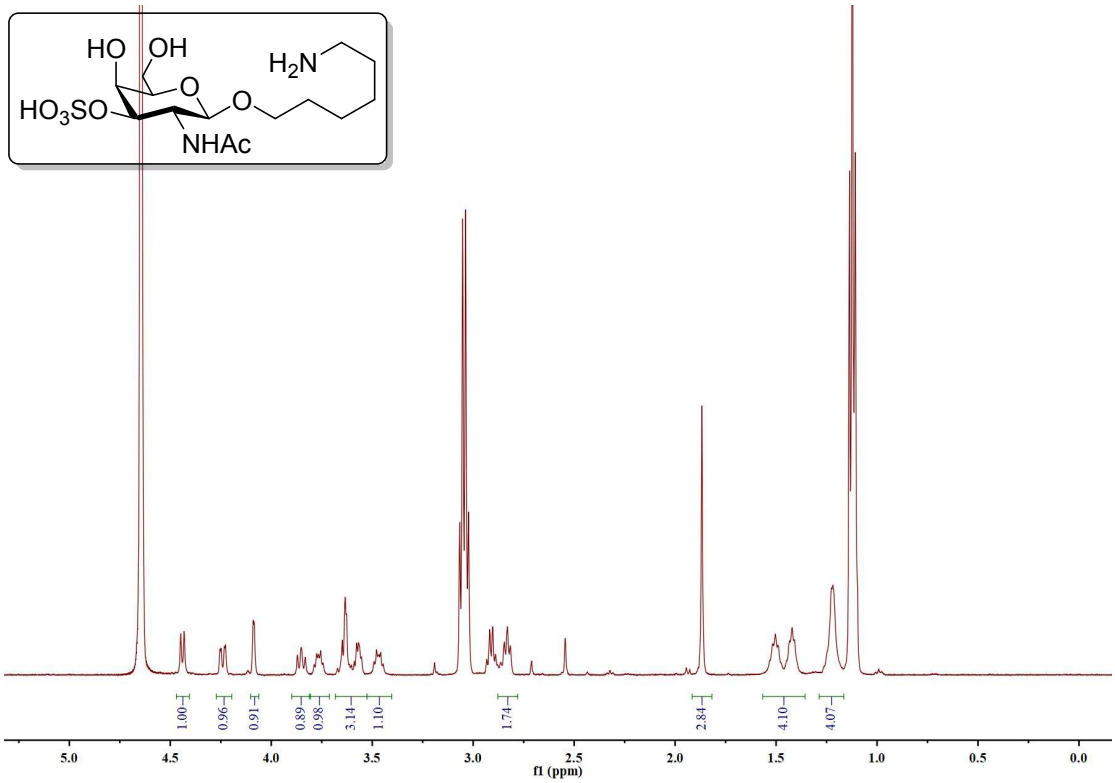


Figure S18-1. ^{1}H NMR spectrum of compound **2**.

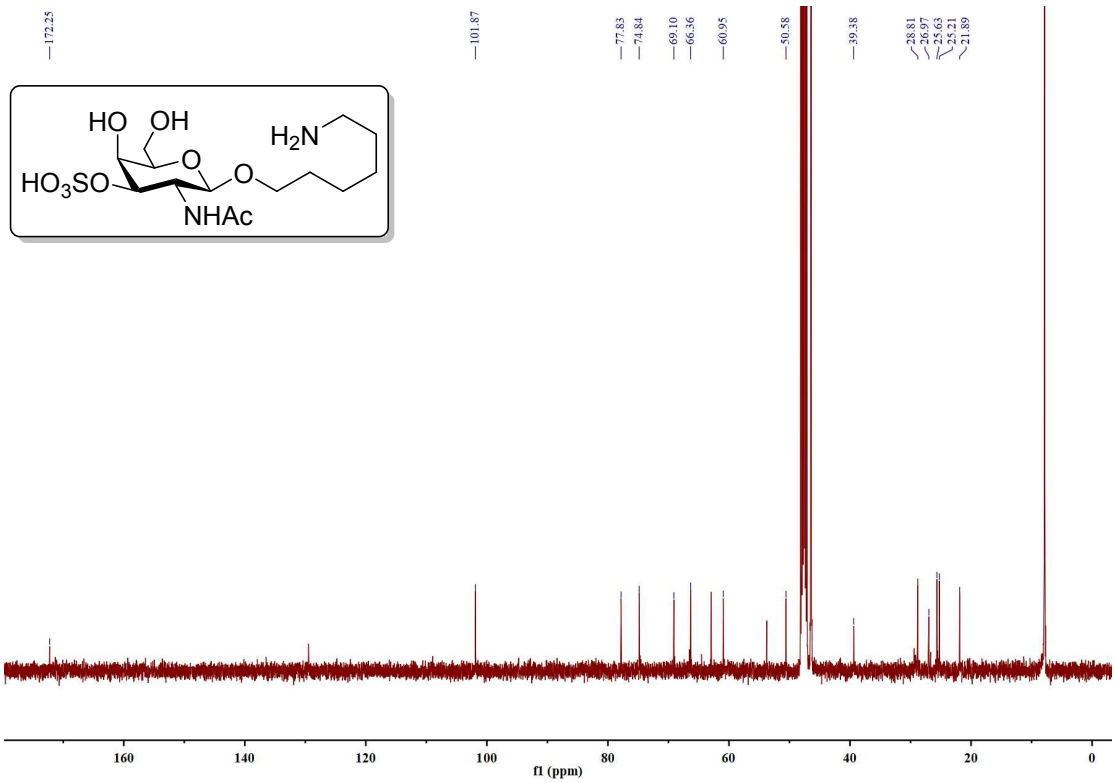


Figure S18-2. ^{13}C NMR spectrum of compound **2**.

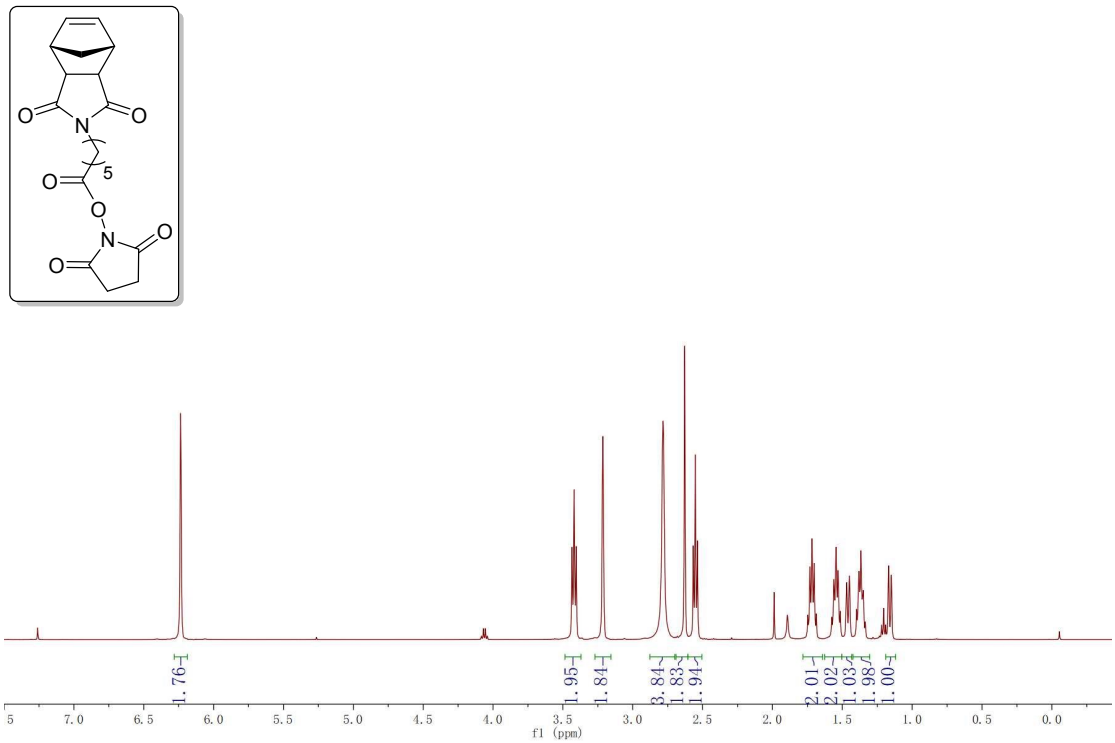


Figure S19-1. ^{1}H NMR spectrum of compound **12**.

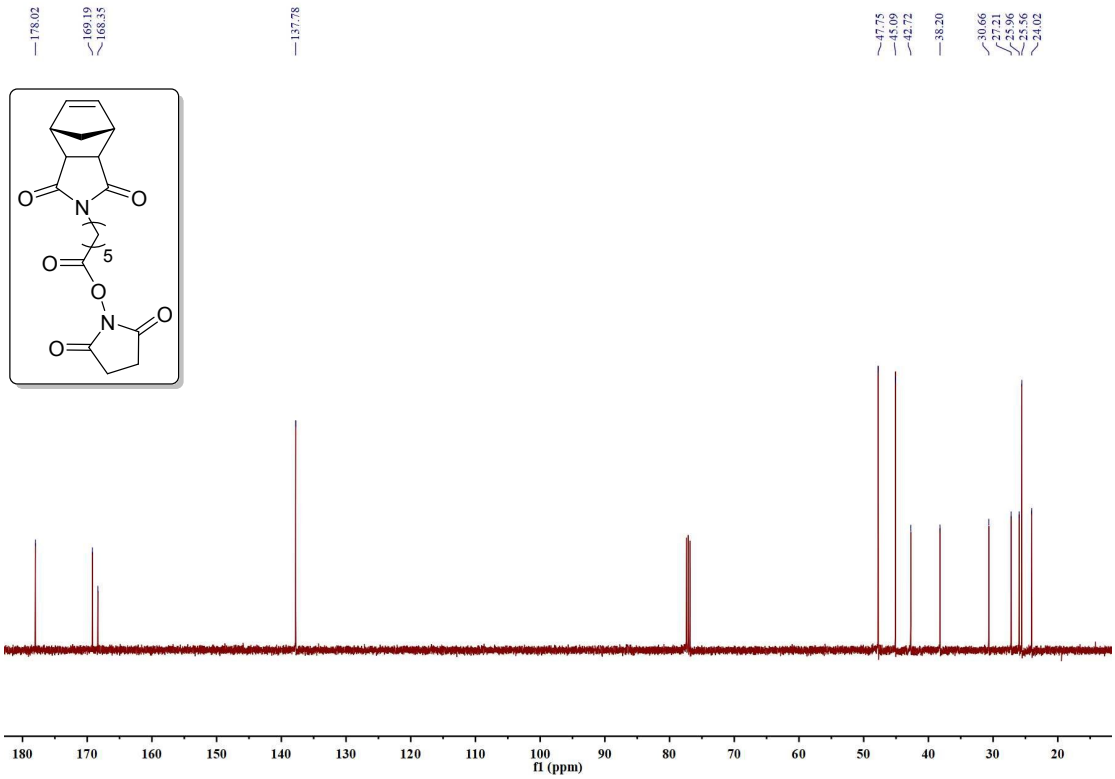


Figure S19-2. ^{13}C NMR spectrum of compound **12**.

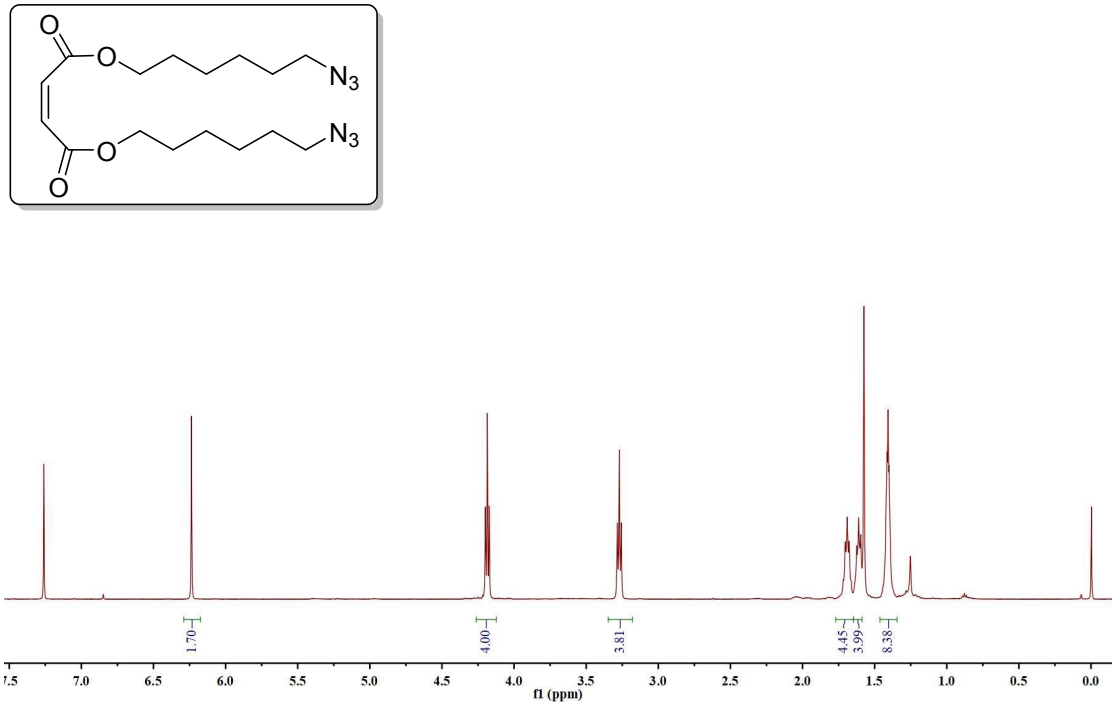


Figure S20-1. ^{1}H NMR spectrum of compound **15**.

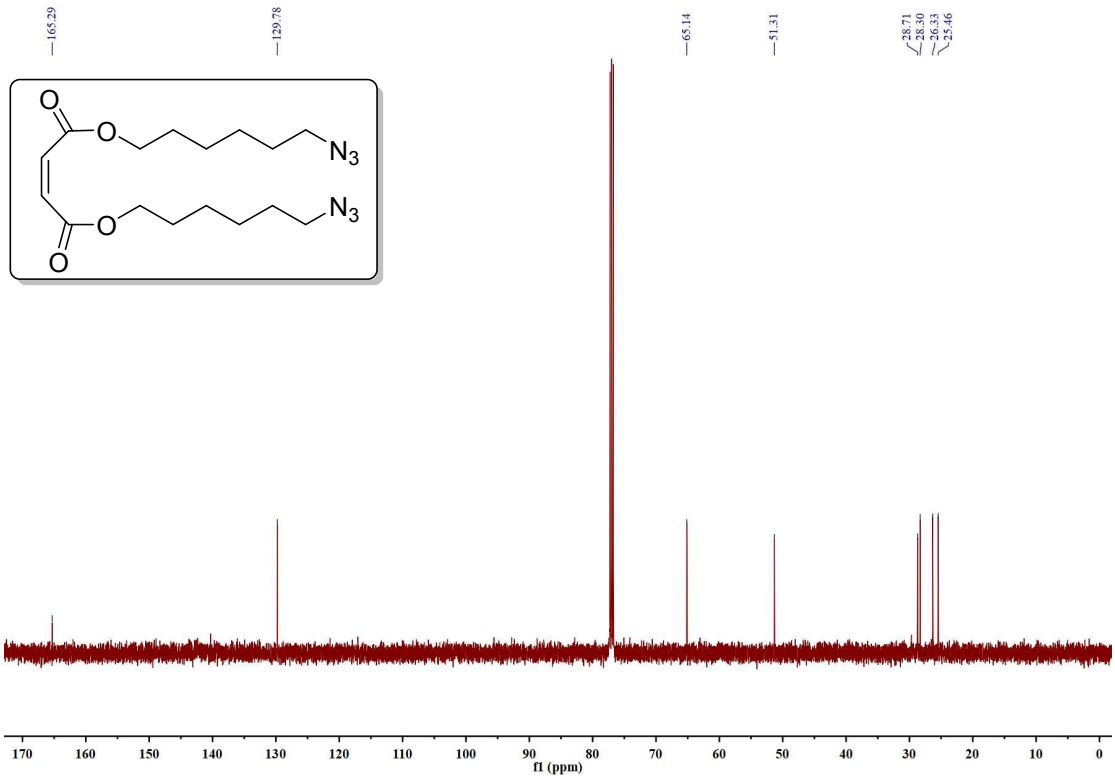


Figure S20-2. ^{13}C NMR spectrum of compound **15**.

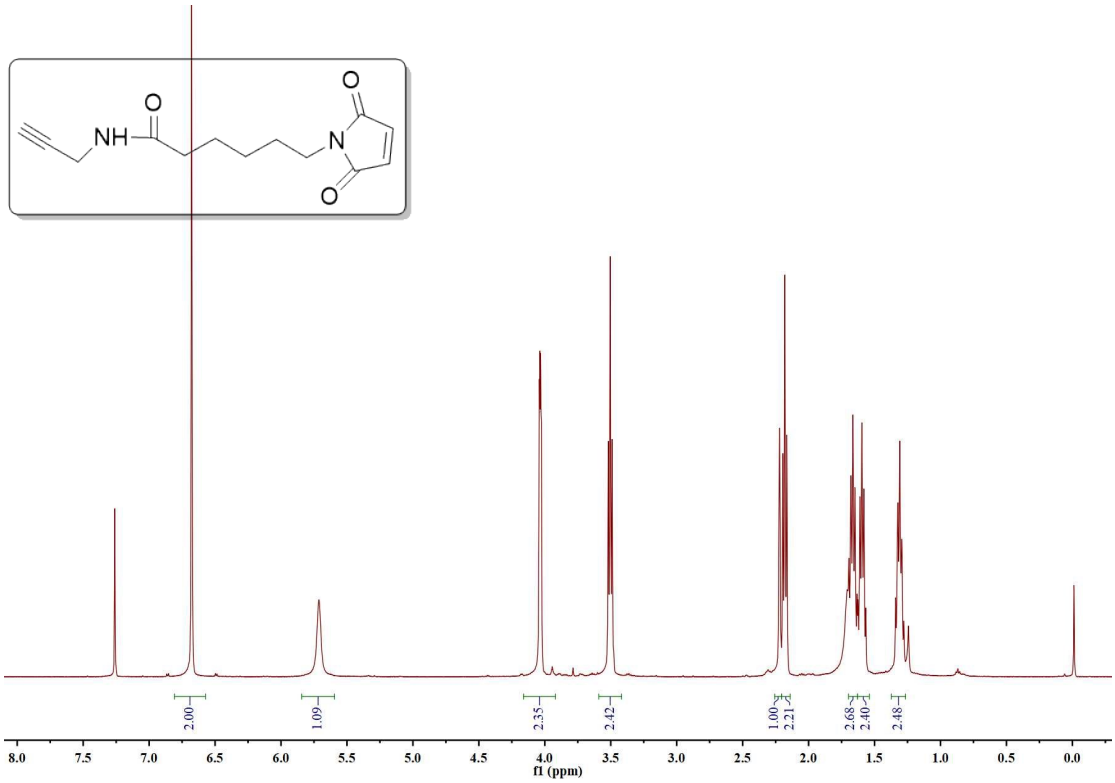


Figure S21-1. ^{1}H NMR spectrum of compound **14**.

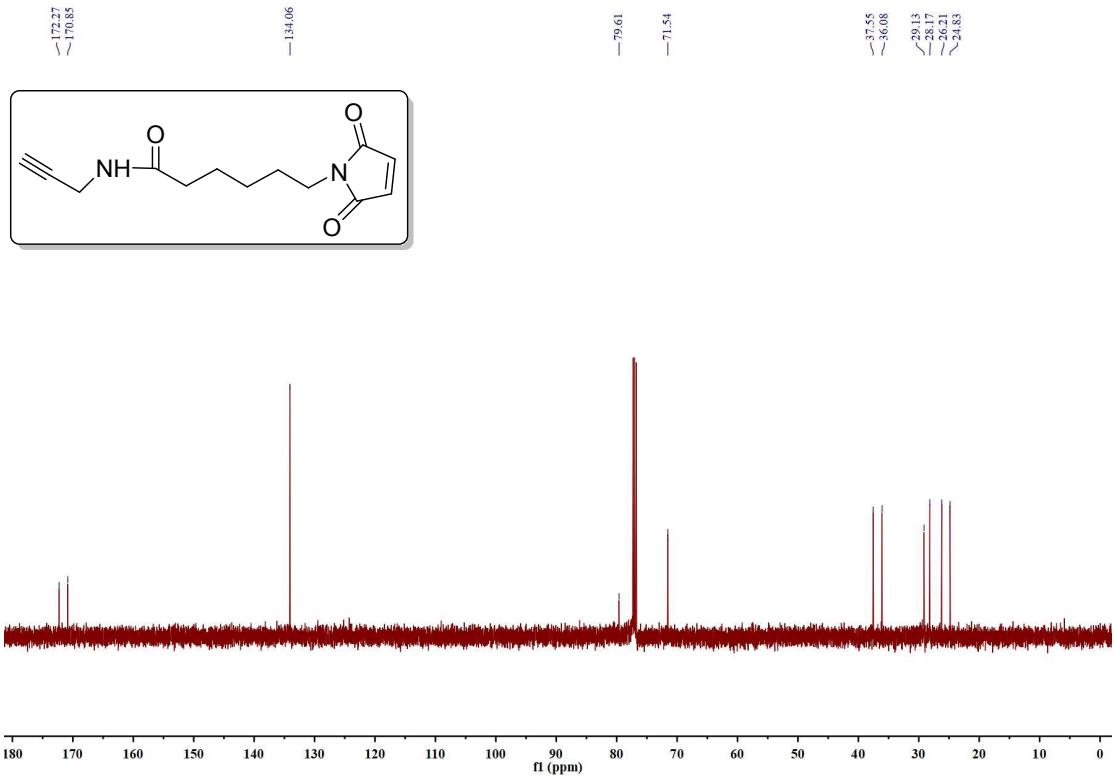


Figure S21-2. ^{13}C NMR spectra of compound **14**.

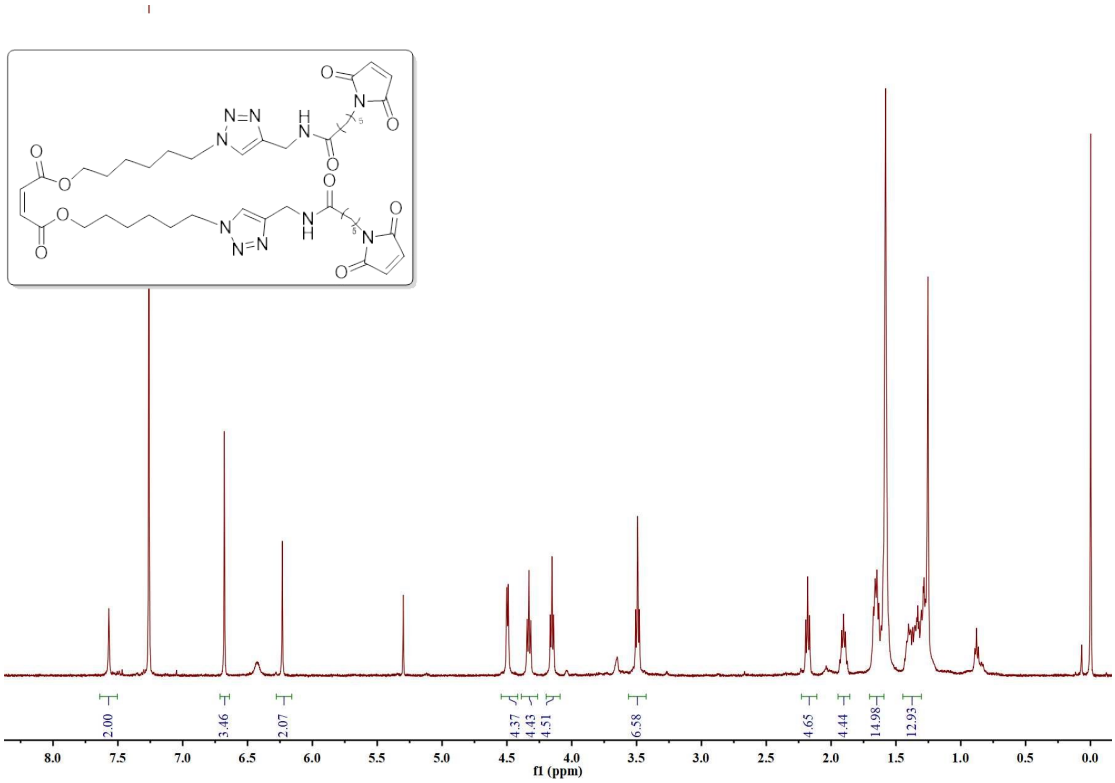


Figure S22-1. ^{1}H NMR spectra of compound **16**.

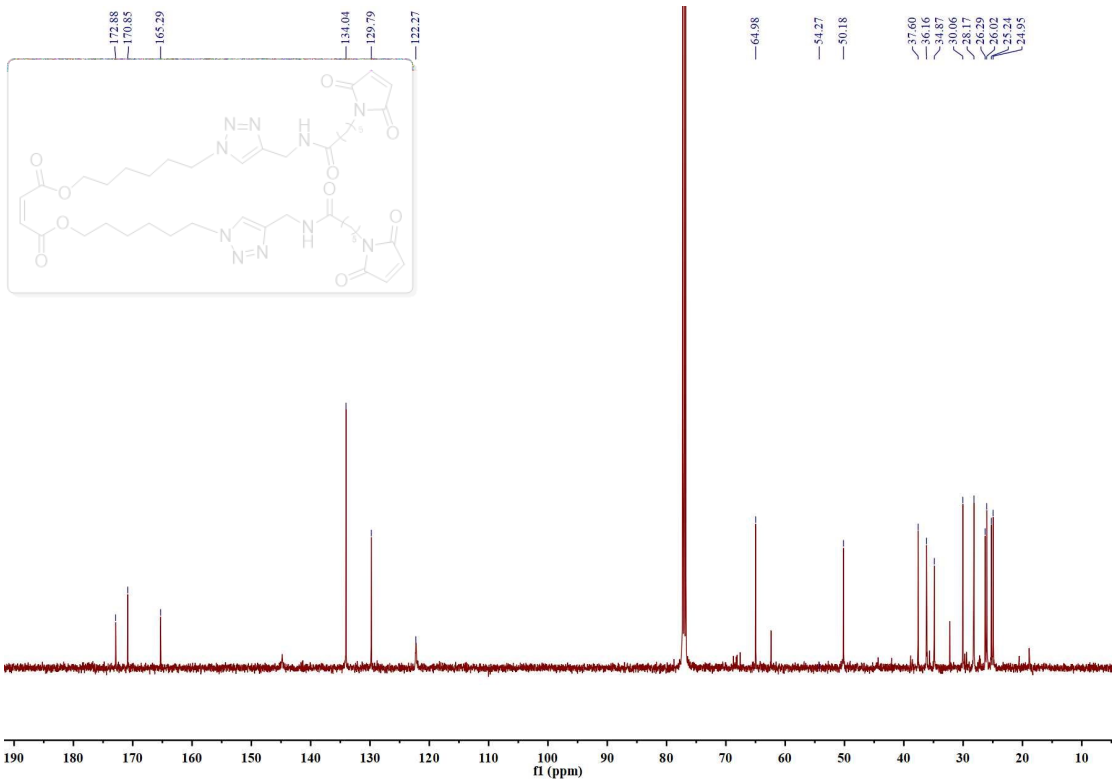


Figure S22-2. ^{13}C NMR spectra of compound **16**.

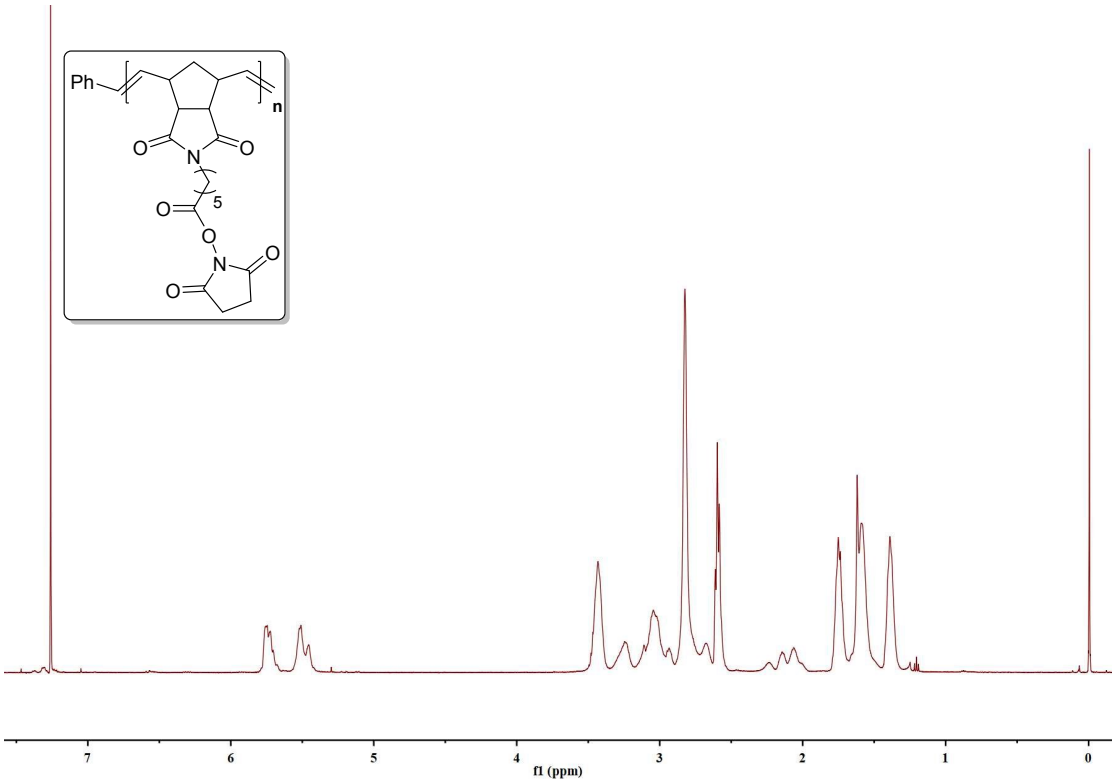


Figure S23. ^{1}H NMR spectra of compound **13**.

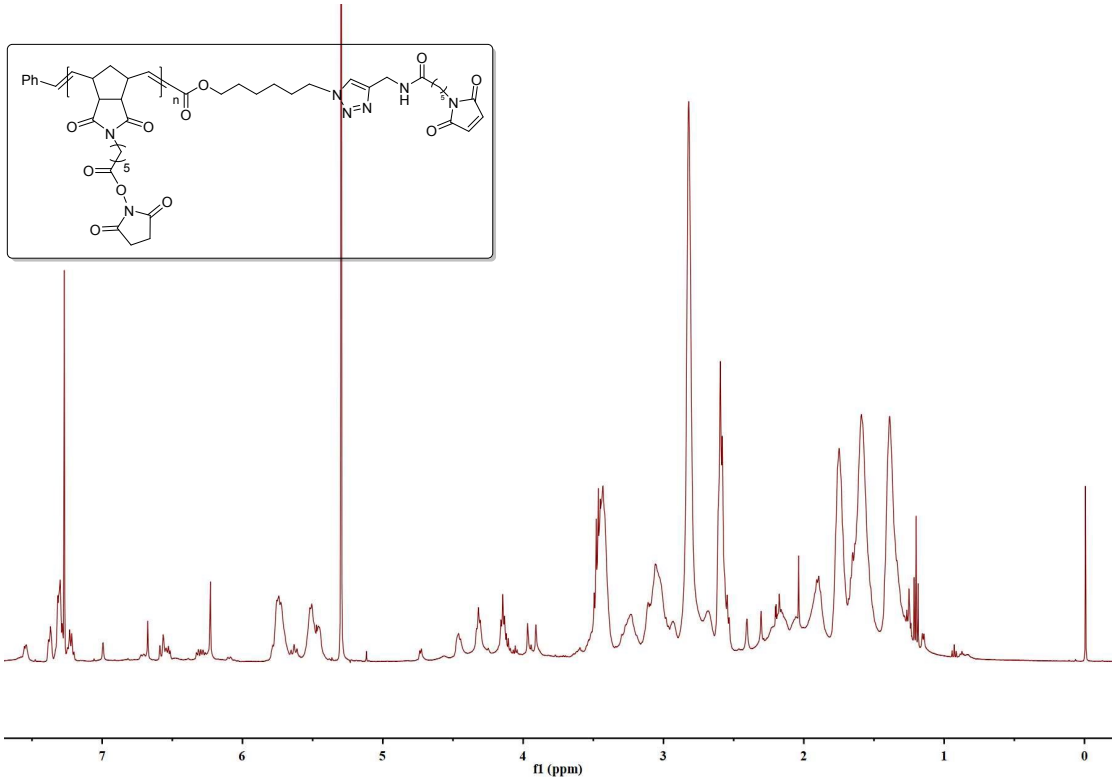


Figure S24. ^{1}H NMR spectra of compound **13-TA**.

6. NMR spectra for glycopolymers with specific sulfation pattern.

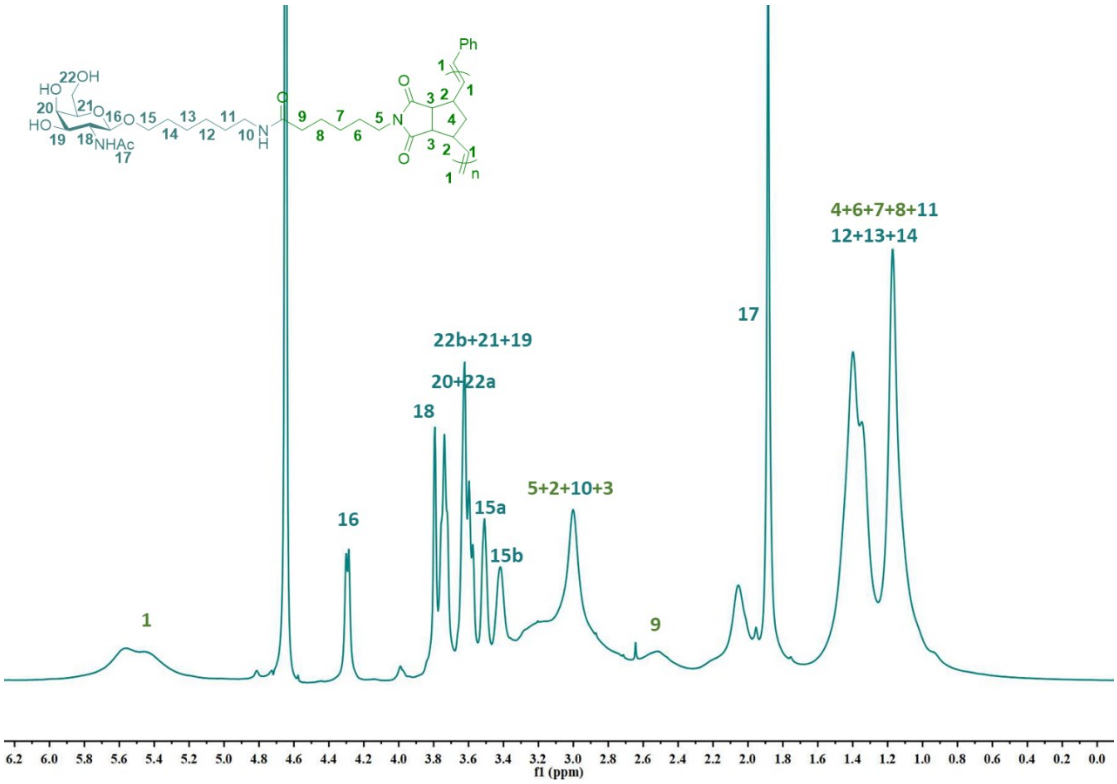


Figure S25. ^{1}H NMR spectra of compound **GP1**.

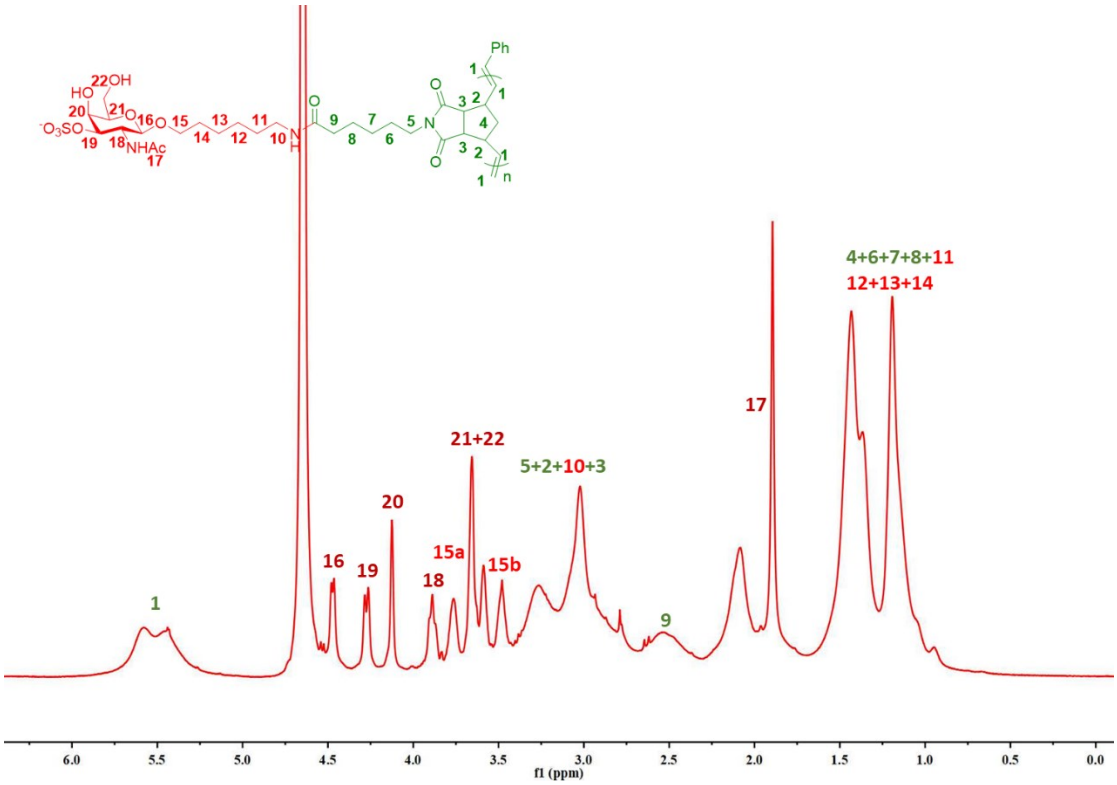


Figure S26. ^{1}H NMR spectra of compound **GP2**.

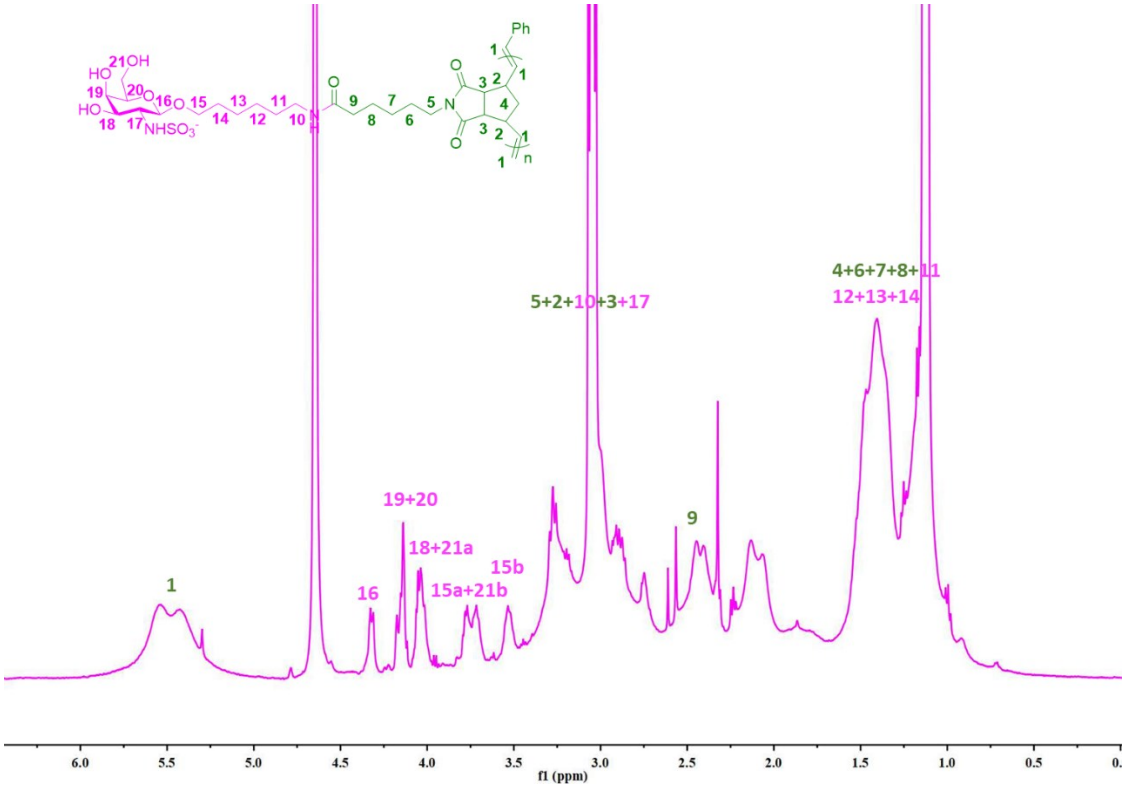


Figure S27.[1]H NMR spectra of compound **GP3**.

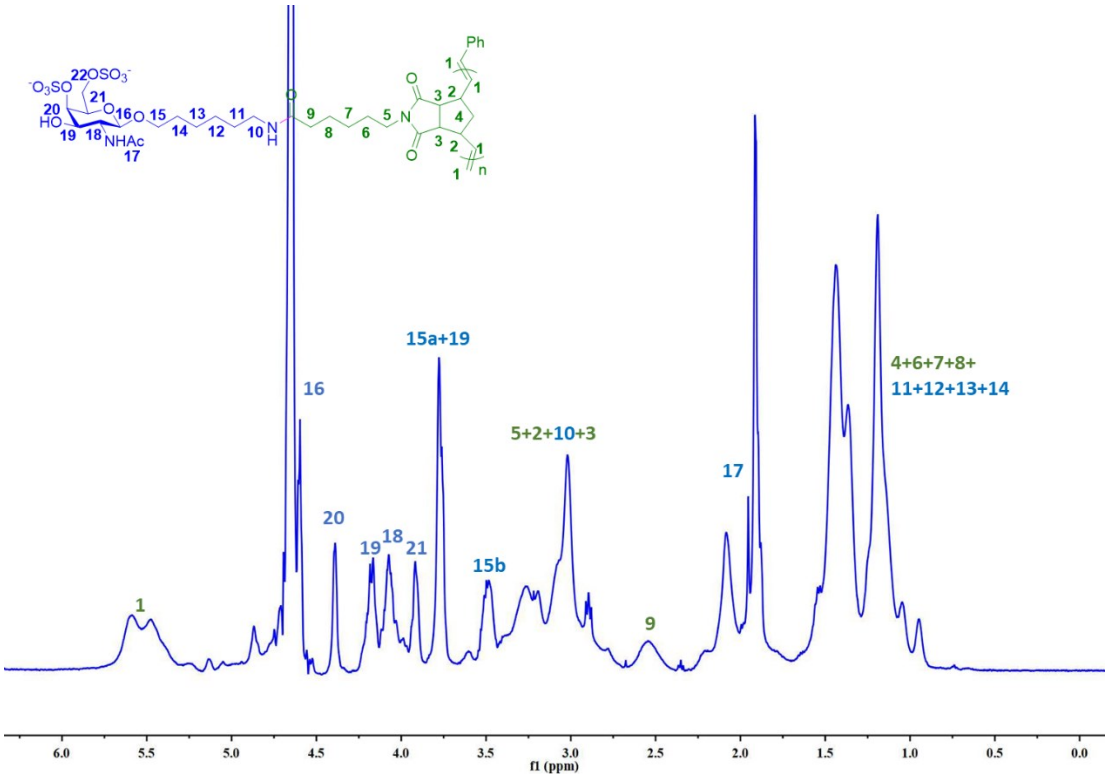


Figure S28. [1]H NMR spectra of compound **GP4**.

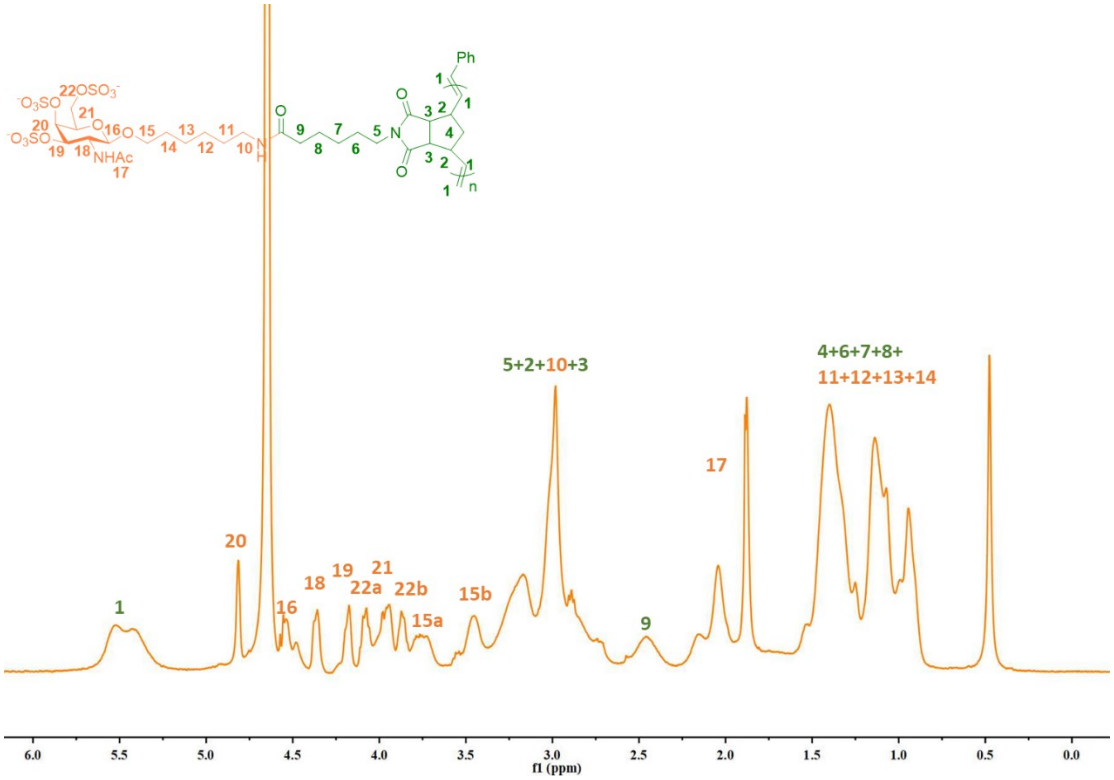


Figure S29. ^{1}H NMR spectra of compound GP**5**.

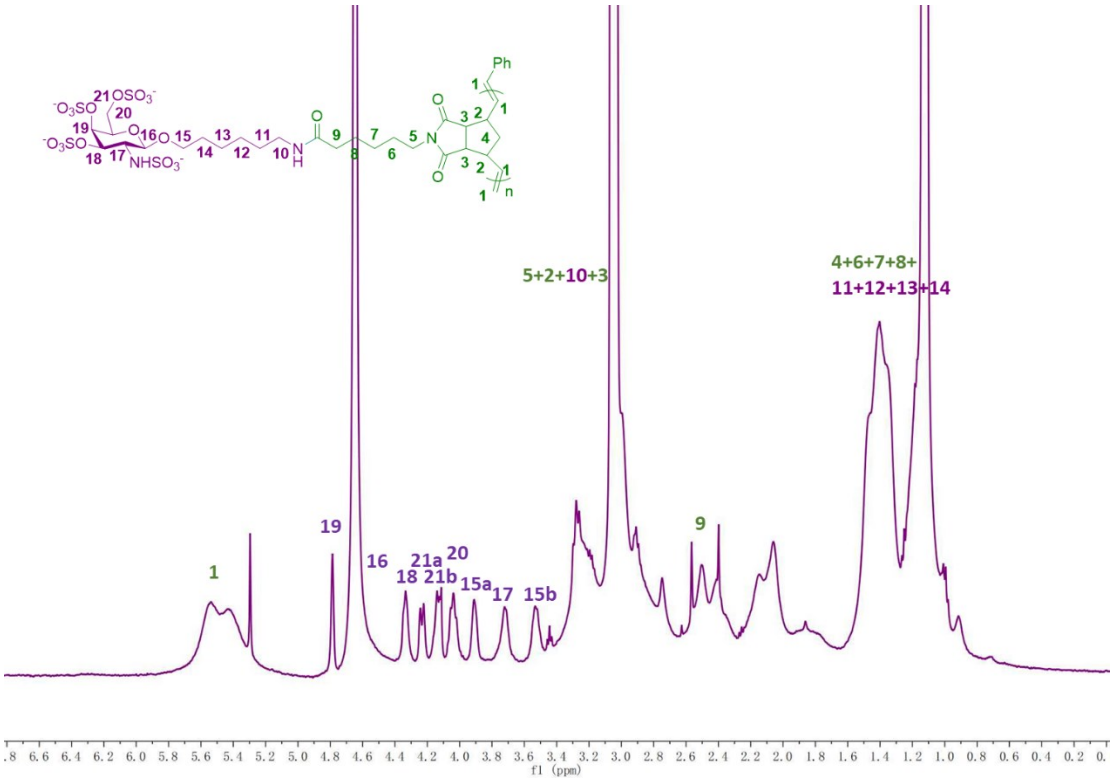


Figure S30. ^{1}H NMR spectra of compound **GP6**.

7. Design of polymer backbone with different lenghth.

Table S1. Properties of the synthesized polymer backbone.

Entry	Moiety	DP	Catalyst	[C]/[M]	M_n(NMR)	yield
1	22	25	Grubbs 3rd	4 %	9.36 kDa	97%
2	22	50	Grubbs 3rd	2 %	18.72 kDa	94%
3	22	100	Grubbs 3rd	1 %	37.44 kDa	95%

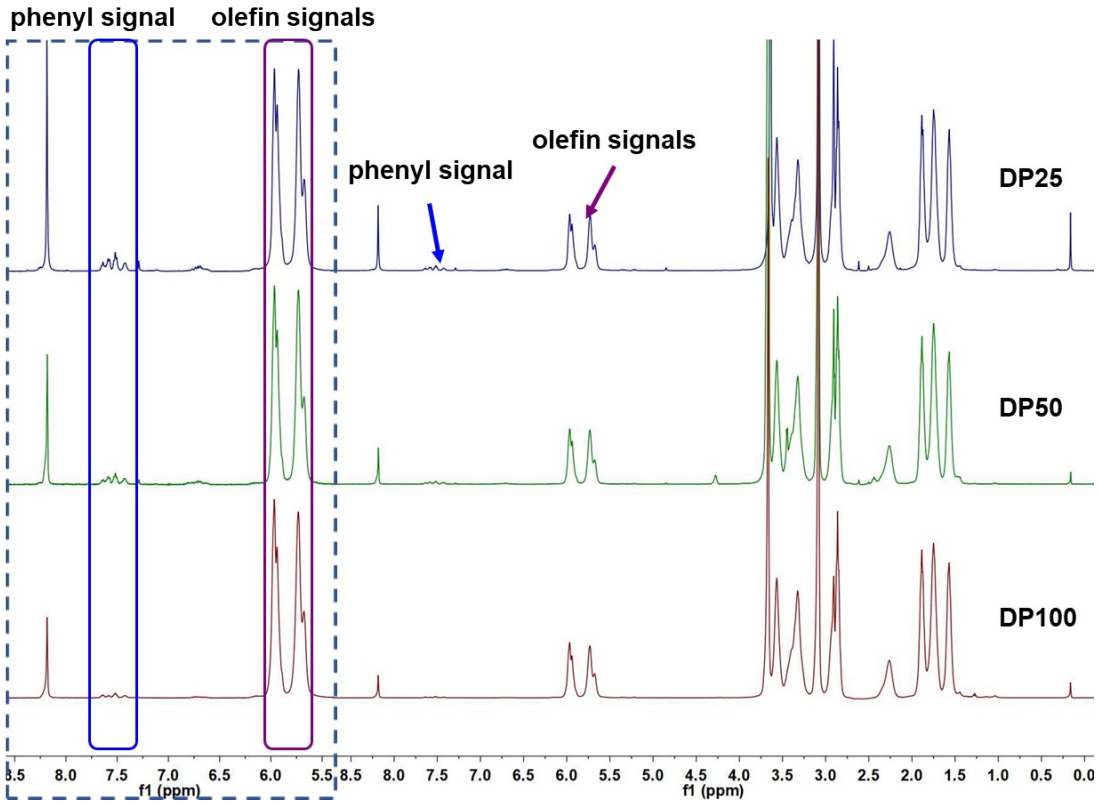


Figure S31. ^{1}H NMR spectra of polymer backbone. Degree of polymerization (DP) were determined by ^{1}H NMR integrations of polymer olefin signals (5.3-5.9 ppm) to phenyl signal (7.5 ppm).

8. Flow cytometric analysis and confocal images of glycopeptide mimetic with different time.

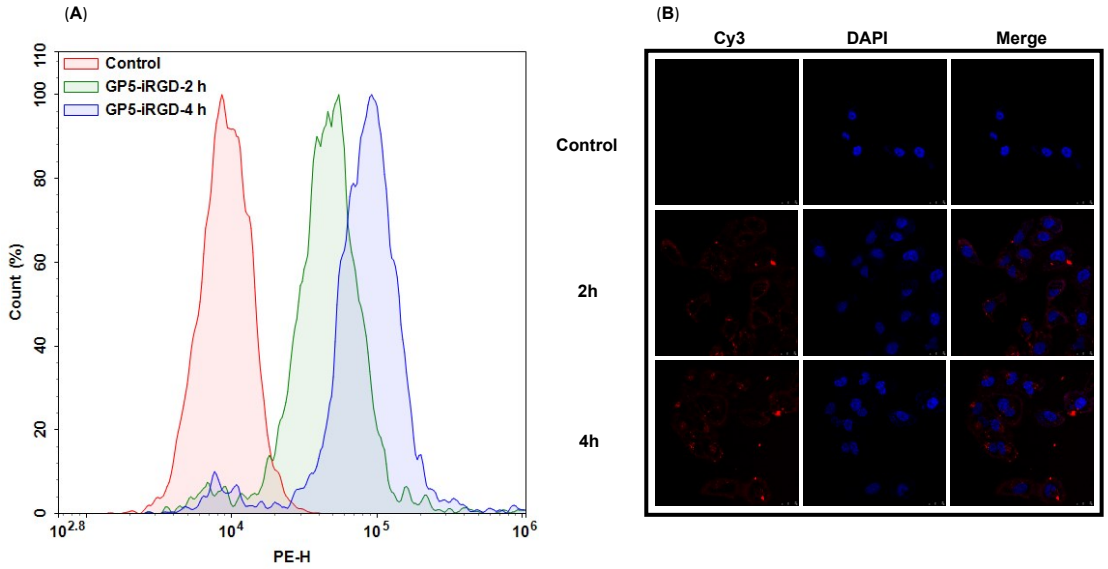


Figure S32. GP5-iRGD localizes to the cytoplasm of HeLa. (**A**) Changes in fluorescence intensity of **GP5-iRGD** with different time. (**B**) Confocal images of HeLa cells incubated with **GP5-iRGD** (20 μg•mL^{-1}) for 2 h and 4 h.

9. NMR spectra for terminating agent

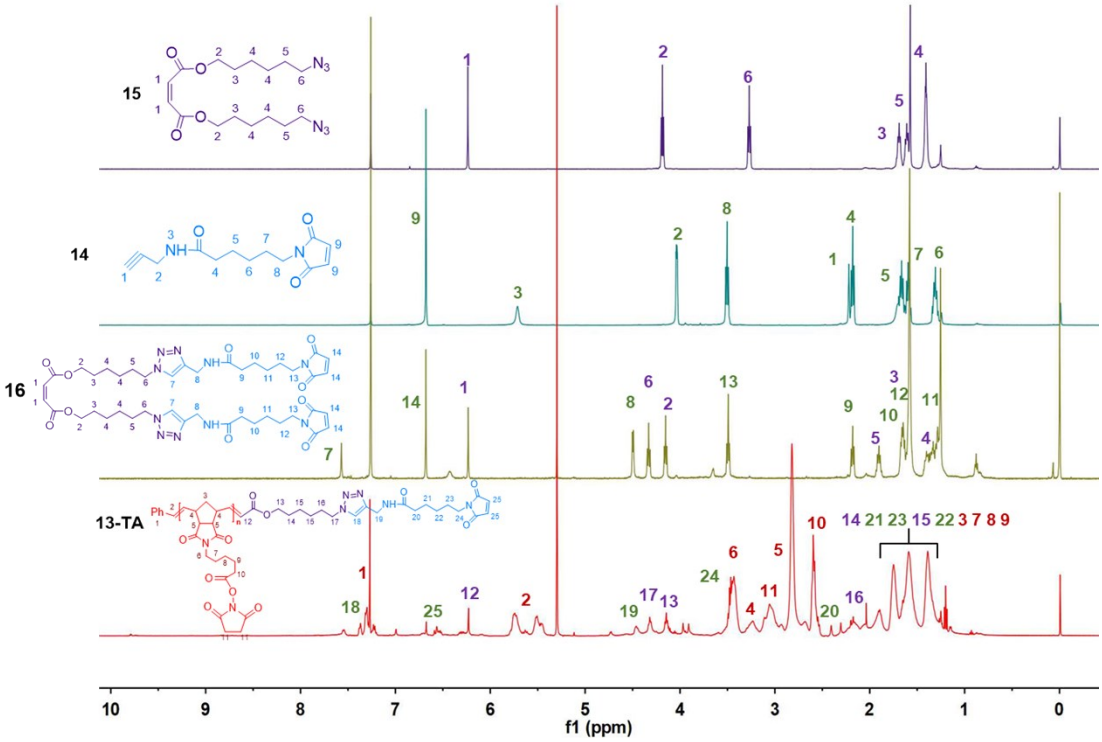


Figure S33. ^{1}H NMR spectra of compound **14**, **15**, **16**, **13-TA**.

10. Reference

1 M. T. Proetto, J. Sanning, M. Peterlechner, M. Thunemann, L. Stegemann, S. Sadegh, A. Devor, N. C. Gianneschi and C. A. Strassert, *Chem. Comm.*, **2019**, *55*, 501-504.