

**Supporting Information**  
**for**  
**End-labeled amino terminated monotelechelic**  
**glycopolymers generated by ROMP and Cu(I)-**  
**catalyzed azide–alkyne cycloaddition**

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## 1. Experimental procedures

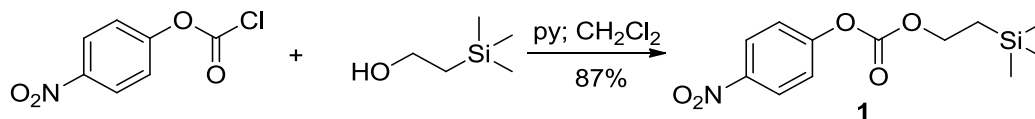
*General procedures and materials.* Dry solvents were obtained from a commercially available solvent purification system based on protocols reported by Grubbs [1]. All reactions were carried out under nitrogen atmosphere unless otherwise stated. Automatic flash chromatography was performed using Teledyne ISCO COMBI Flash Rf instrument using Redi Sep Rf silica columns (24 g and 40 g) and self packed silica cartridges. Water, pyridine and DMF were evaporated using a Centrifan PE from Modular SFC unless otherwise stated. Dialysis was done using 6 Spectra/Por regenerated cellulose dialysis membrane 1000 MWCO from Spectrum. Concentration by centrifugal filtration was done using Amicon Ultra centrifugal filters (regenerated cellulose 3000 MWCO) filter devices in a Sorvall ST 16 centrifuge from Thermo Scientific operated at 4000x g. Centrifugation of the precipitated polymers **6** was done using an Adams physician's compact centrifuge. NMR spectra were recorded in BRUKER 400 MHz or 300 MHz instruments for  $^1\text{H}$  NMR, 100 MHz or 75 MHz for  $^{13}\text{C}$  NMR and referenced at 2.05 ppm for  $d_6$ -acetone, 4.79 ppm for  $\text{D}_2\text{O}$ , 7.26 ppm for  $\text{CDCl}_3$ , and 7.16 ppm for  $\text{C}_6\text{D}_6$  in  $^1\text{H}$  NMR and 128.06 ppm for  $\text{C}_6\text{D}_6$  77.16 ppm for  $\text{CDCl}_3$  in  $^{13}\text{C}$  NMR.  $^1\text{H}$  NMR for all polymer products were obtained with a delay time D[1] of 5 seconds. MALDI-ToF spectra were obtained using a VOYAGER-DE PRO bio-spectrometry workstation instrument using super DHB matrix (2,5-dihydroxybenzoic acid doped with 2-hydroxy-5-methoxybenzoic acid). GPC of polymers **6** were obtained using AM GPC Gel column with linear 10  $\mu\text{m}$  porosity from American Polymer Standards Corporation mounted in a Hewlett Packard 1090 liquid chromatography machine with a UV detector. Agilent 8453 UV-visible spectroscopy

system was used to obtain UV–vis spectra of **15** and pyrene-labeled glycopolymers **16** DMF solutions in a 1 cm quartz cell.

TLC stains were prepared as follows; KMnO<sub>4</sub> (3 g KMnO<sub>4</sub>, 20 g K<sub>2</sub>CO<sub>3</sub>, 5 mL of 5% NaOH, 300 mL H<sub>2</sub>O); anisaldehyde (9.2 mL anisaldehyde, 3.75 mL AcOH, 338 mL 95% EtOH, 12.5 mL conc. H<sub>2</sub>SO<sub>4</sub>) TLC Silica Gel 60 F<sub>254</sub> plates from EMD Chemicals were used.

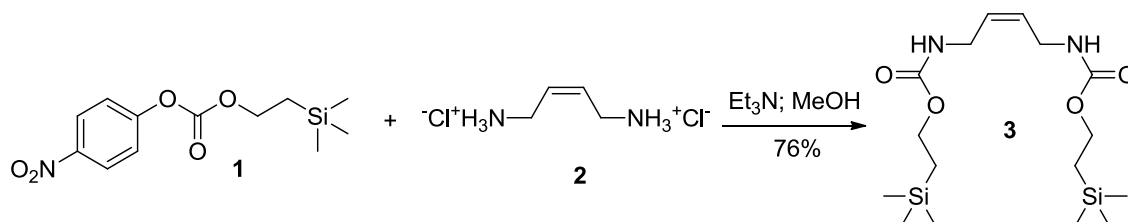
4-Nitrophenyl (2-(trimethylsilyl)ethyl) carbonate (**1**) was prepared by a slight variation of the protocol reported by Rosowsky [2]. *cis*-1,4-Diamino-but-2-ene•2HCl salt (**2**) was prepared as reported by Greenaway [3]. Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid *N*-hydroxysuccinimide ester (**4**) was prepared by a slight variation of the protocol reported by Kiessling [4]. Catalyst **5** was prepared as reported by Grubbs [5]. 1,11-Diazido-3,6,9-trioxaundecane was prepared as reported by Schwabacher [6]. Propargyl galactoside **10a**, propargyl mannoside **10b** and propargyl 3' sulfogalactoside **10c** were prepared as reported by Basu [7]. 2-(2-(2-Aminoethoxy)ethoxy)ethanol tris(3-hydroxy-propyltriazolylmethyl)amine (THPTA) ligand was prepared as reported by Finn [8]. *N*-(1-pyrene)butyryloxysuccinimide **13** was prepared as reported by Wu [9].

4-nitrophenyl (2-(trimethylsilyl)ethyl) carbonate (**1**) [2]



To a solution of 4-nitrophenyl chloroformate (6.00 g, 30 mmol) in 40 mL dry  $\text{CH}_2\text{Cl}_2$  at  $0^\circ\text{C}$  was added a solution of 2-trimethylsilylethanol (3.8 mL, 3.14 g, 26.5 mmol) and pyridine (2.2 mL, 2.13 g, 26.5 mmol) in 20 mL dry  $\text{CH}_2\text{Cl}_2$  via a syringe dropwise over 10 min, and the reaction mixture was allowed to warm to room temperature. After 24 h the reaction mixture was washed four times with 100 mL saturated  $\text{NaHCO}_3$  and twice with brine, and then dried over  $\text{Na}_2\text{SO}_4$ . The  $\text{CH}_2\text{Cl}_2$  solution was concentrated in vacuo, and the pale yellow oily residue was purified by automatic flash chromatography (EtOAc:Hexanes 1:9 to 4:6) to give **1** (6.52 g, 23 mmol) 87% as pale yellow oil which solidified upon refrigeration. TLC (Silica – EtOAc:hexanes 1:3 – UV)  $R_f$  0.69.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.30–8.23 (m, 2H) 7.40–7.32 (m, 2H) 4.44–4.29 (m, 2H) 1.21–1.09 (m, 2H) 0.08 (s 9H)  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.8, 152.6, 145.4, 125.4, 122.0, 68.4, 17.7,  $-1.4$  HRMS (FAB) calculated for  $\text{C}_{12}\text{H}_{17}\text{NO}_5\text{Si}$   $[\text{M} + \text{Na}]^+$  306.0774 found 306.0780.

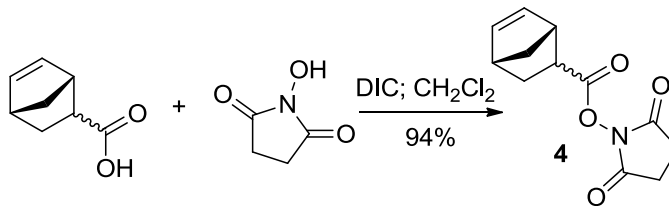
*cis*-Bis(2-(trimethylsilyl)ethyl) but-2-ene-1,4-diyl dicarbamate (**3**)



*cis*-1,4-Diamino-but-2-ene•2HCl salt **2** [3] (1.17 g, 7.35 mmol) was dissolved in 50 mL dry MeOH, 2.1 mL  $\text{Et}_3\text{N}$  (1.50 g, 14.7 mmol) was added to the flask followed by **1** (4.17 g, 14.7 mmol). The reaction was stirred at room temperature overnight. The MeOH

was evaporated, and the yellow oily residue was dissolved in 100 mL CH<sub>2</sub>Cl<sub>2</sub> and washed with saturated NaHCO<sub>3</sub> until the aqueous layer was clear. The CH<sub>2</sub>Cl<sub>2</sub> layer was then washed with 100 mL brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The light brown oily residue was purified by column chromatography (silica, 1:3 EtOAc: Hexanes) to give **3** (2.16 g, 5.77 mmol) 76% as a clear oil. TLC (silica–EtOAc:hexanes 1:3 – KMnO<sub>4</sub> stain) *R*<sub>f</sub> 0.55. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.54 (t, *J* = 4.6 Hz, 2H) 5.03 (bs, 2H) 4.17 (t, *J* = 8.4 Hz, 4H) 3.82 (t, *J* = 5.7 Hz, 4H) 0.97 (t, *J* = 8.4 Hz, 4H) 0.02 (s, 18H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 156.9, 128.9, 63.2, 37.5, 17.9, –1.3 HRMS (FAB) calculated for C<sub>16</sub>H<sub>34</sub>N<sub>2</sub>O<sub>4</sub>Si<sub>2</sub> [M + Na]<sup>+</sup> 397.1955 found 397.1966.

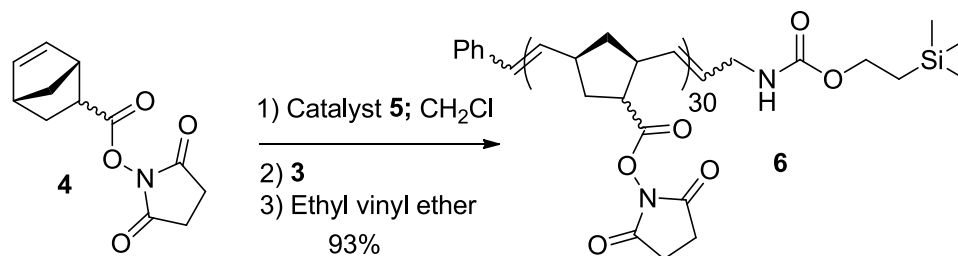
Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid *N*-succinimide ester (**4**) [4]



To a solution of 5-norbornene-2-carboxylic acid (3.49 g, 25.2 mmol) and *N*-hydroxysuccinimide (3.48 g, 30.3 mmol) in 50 mL dry CH<sub>2</sub>Cl<sub>2</sub> at 0 °C was added 4.7 mL *N,N'*-diisopropylcarbodiimide (DIC) (3.83 g, 30.3 mmol) dropwise via a syringe, and the reaction was stirred overnight. The white precipitate was filtered and washed with 10 mL CH<sub>2</sub>Cl<sub>2</sub> twice, and the filtrate was concentrated and purified by automatic flash chromatography (EtOAc:DCM 1:9 to 6:4) to give **4** (5.55 g, 23.6 mmol) in 94% yield as a white solid. TLC (Silica–DCM - KMnO<sub>4</sub> stain) *R*<sub>f</sub> = 0.34. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 6.27–6.09 (m, 2H) 3.40 (s, 1H) 3.24 (dt, *J* = 9.1, 3.8 Hz, 1H) 2.99 (s, 1H) 2.81 (bs, 4H) 2.51 (ddd, *J* = 9.0, 4.6, 1.4 Hz, 1H) 2.09–1.93 (m, 1H) 1.56–1.23 (m, 3H); <sup>13</sup>C NMR

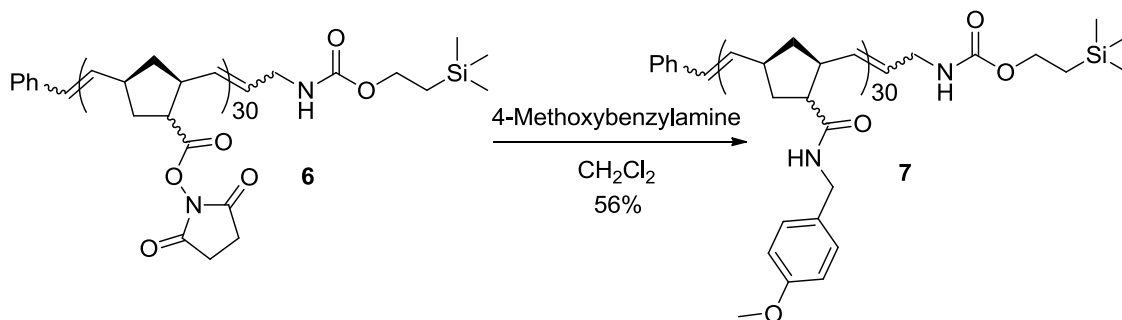
(100 MHz, CDCl<sub>3</sub>)  $\delta$  170.1, 169.4, 138.7, 138.3, 135.4, 132.3, 49.8, 47.3, 46.60, 46.56, 41.9, 40.8, 40.4, 31.1, 29.7, 25.8, 25.7; HRMS (FAB) calculated for C<sub>12</sub>H<sub>13</sub>NO<sub>4</sub> [M + Na]<sup>+</sup> 258.0742 found 258.0750.

Polymerization of **4** to give **6**



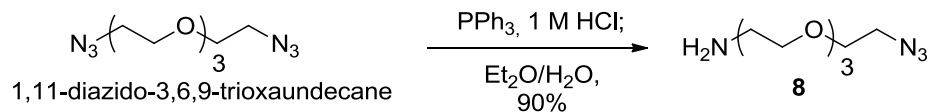
To a solution of **4** (0.48 g, 2.05 mmol) in 10 mL dry CH<sub>2</sub>Cl<sub>2</sub> in a capped vial at -78 °C was added a solution of catalyst **5** [**5**] (0.06 g, 0.07 mmol) in 5 mL dry CH<sub>2</sub>Cl<sub>2</sub> quickly via a syringe. The reaction was allowed to warm to room temperature upon which the solution turned from bright green to brown after about 2 minutes. After 40 minutes a solution of **3** (0.13 g, 0.34 mmol) in 5 mL dry CH<sub>2</sub>Cl<sub>2</sub> was added to the reaction via a syringe. After 20 min 0.5 mL of ethyl vinyl ether (0.38 g, 5.22 mmol) was added via a syringe, and the reaction solution was transferred using a Pasteur pipette to 4 different test tubes each containing about 10 mL of ether, forming a light brown precipitate. The test tubes were centrifuged and the ether decanted, and the precipitate was washed by adding 10 mL of ether into the test tubes and agitating the mixture with a Pasture pipette then centrifuging and decanting the ether. Washing was repeated until the ether was clear. The grey precipitate was collected and dried under vacuum to give **6** (0.44 g, 0.06 mmol) as a grey solid 93%. Partial <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-acetone)  $\delta$  7.24–7.21 (m, 5H, **H-Ph**) 5.8–5.4 (m, 84H, **H-olefinic**) 0.0 (s, 9H, **H-TMS**).

## Preparation of **7**



To a solution of **6** (0.09 g, 0.013 mmol) in 5 mL dry  $\text{CH}_2\text{Cl}_2$  was added 250  $\mu\text{L}$  of 4-methoxybenzyl amine (0.26 g, 0.93 mmol), and the mixture was stirred for 24 h. The solvent was evaporated, the residue was dissolved in 20 mL THF and filtered through a plug of cotton, and then the cotton was washed with 10 mL THF. The filtrate was then transferred to a dialysis tube and dialyzed in 200 mL THF reservoir (12 h  $\times$  3). The solution in the tube was collected, and the excess solvent was evaporated and dried to give **7** (0.06 g) 56% as a white film partial  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.13 (bs, 77H, **H-aromatic**) 6.80 (bs, 77H, **H-aromatic**) 5.28–5.17 (m, 77H, **H-olefinic**) 3.74–3.72 (m, 120H, **H-OMe**) 0.02 (s, 9H, **H-TMS**) MW 6372, PDI 1.38 (MALDI-ToF).

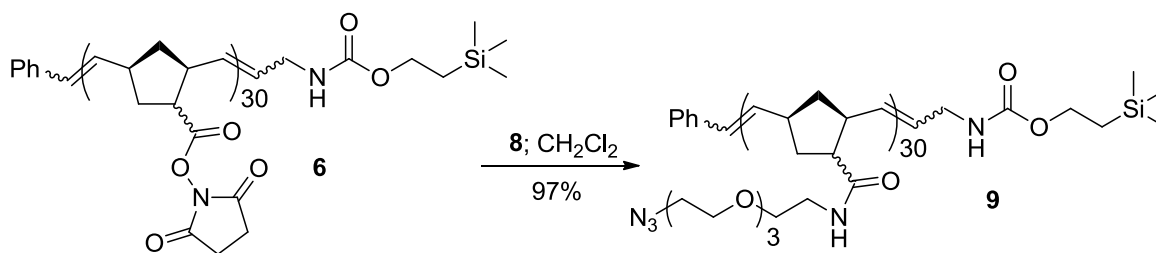
## 1-Amino -11- azido-3,6,9-trioxaundecane (**8**)



60 mL of 1M HCl was added to a flask containing 1,11-diazido-3,6,9-trioxaundecane [6] (4 g, 16.4 mmol) at 0  $^\circ\text{C}$ . While vigorously stirring the mixture a solution of  $\text{PPh}_3$  (5 g, 19.1 mmol) in 60 mL  $\text{Et}_2\text{O}$  was added dropwise to the flask using an addition funnel then 10 mL of  $\text{Et}_2\text{O}$  as used to rinse the funnel. The mixture was allowed to warm to room

temperature. After 24 h the white precipitate was filtered and the aqueous layer washed with 50 mL Et<sub>2</sub>O three times. The aqueous layer was cooled at 0 °C and 30 g of KOH was added. After the effervescence stopped the mixture was extracted in DCM (20 mL × 5). The CH<sub>2</sub>Cl<sub>2</sub> layers were combined and dried over Na<sub>2</sub>SO<sub>4</sub>. Excess solvent was evaporated, and the product was dried under vacuum to give **8** as pale yellow oil 90% (3.23 g, 14.7 mmol). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 3.70–3.51 (m, 10H) 3.48 (t, *J* = 5.2 Hz, 2H) 3.33 (t, *J* = 5.0 Hz, 2H) 2.83 (t, *J* = 5.1 Hz, 2H) 2.78 (s, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 72.7, 70.7, 70.2, 70.0, 50.7, 41.5. HRMS (FAB) calculated for C<sub>8</sub>H<sub>18</sub>N<sub>4</sub>O<sub>3</sub> [M + Na]<sup>+</sup> 241.1277 found 214.1272.

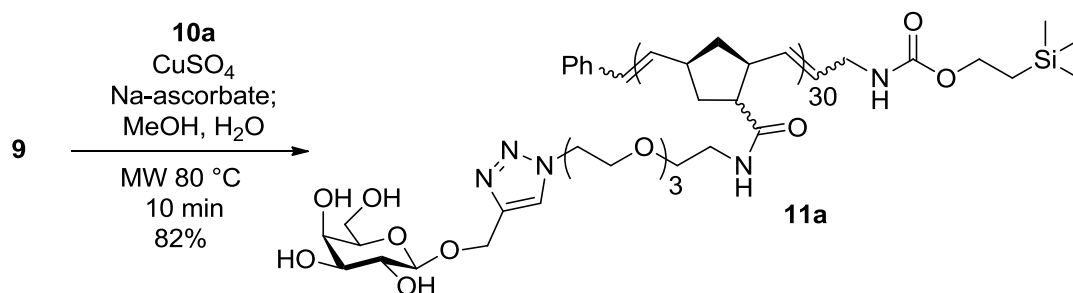
#### Azido-polymer **9**



To a solution of **6** (0.4 g, 0.06 mmol) in 5 mL dry CH<sub>2</sub>Cl<sub>2</sub> was added a solution of **8** (0.7 g, 3.4 mmol) in 5 mL dry CH<sub>2</sub>Cl<sub>2</sub>, and the mixture was stirred for 24 h. The solvent was evaporated, and the brown residue was dissolved in 10 mL MeOH, transferred into a dialysis tube and dialyzed in 200 mL MeOH reservoir (12 h × 3). The solution in the dialysis tube was collected, evaporated and dried under vacuum to give **9** as a light brown sticky gel 97% (0.6 g, 0.06 mmol). Partial <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 5.55–5.02 (m, 75H, **H-olefinic**) 0.00 (s, 9H, **H-TMS**).

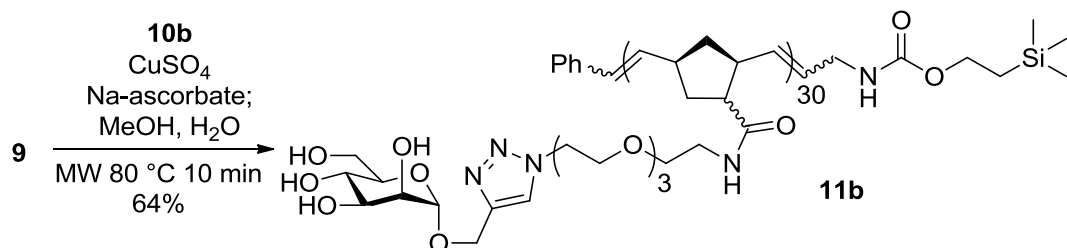


## Galactosyl glycopolymer **11a**



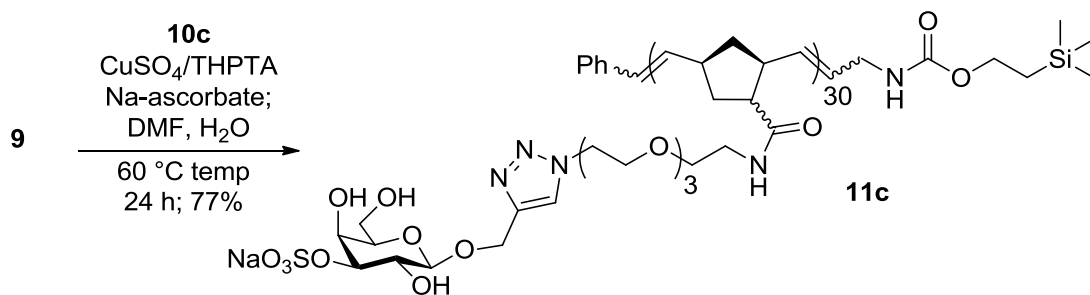
Solutions of poly-azide **9** (0.14 g, 0.013 mmol) in 2 mL MeOH, propargyl galactoside **10a** [7] (0.2 g, 0.92 mmol) in 0.5 mL  $\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (8 mg, 0.03 mmol) in 0.5 mL  $\text{H}_2\text{O}$ , Na-ascorbate (12 mg, 0.06 mmol) in 0.5 mL were added to a 2–5 mL microwave vial charged with a stir bar in that order. The reaction was run in a microwave at 80 °C for 10 min. The resulting solution was transferred into a vial containing 1 g CupriSorb<sup>®</sup> and 5 mL  $\text{H}_2\text{O}$ , stirred overnight to remove copper ions, and filtered through a plug of cotton. The CupriSorb<sup>®</sup> [8] was washed with 10 mL  $\text{H}_2\text{O}$  and the collected filtrate dialyzed against 200 mL  $\text{H}_2\text{O}$  (12 h x 4). The solution was then concentrated to about 2 mL by centrifuge filtration. The  $\text{H}_2\text{O}$  was then azeotroped with 1 mL toluene and evaporated on a rotovap at 40 °C (x 3). The product was dried under vacuum to give glycopolymer **11a** (0.2 g, 0.012 mmol) as a brown film 82%. Partial  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$  8.15 (s, 40H, **H-triazole**) 5.38 (bs, 80H, **H-olefinic**) 5.03 (d,  $J = 12.4$  Hz, 40H, **H-Gal**) 4.88 (d,  $J = 11.7$ , 40H, **H-Gal**) 4.65 (bs, 80H, **H-Gal**) 4.51 (d,  $J = 7.7$  Hz, 40H, **H-Gal**) 0.04 (s, 9H, **H-TMS**).

### Mannosyl glycopolymer **11b**



Mannosyl glycopolymer **11b** was obtained using the same procedure reported for galactose glycopolymer **11a**. 64% of **11b** was recovered. Partial  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ )  $\delta$  8.14 (s, 37H, **H-triazole**) 5.37 (bs, 74H, **H-olefinic**) 4.98 (s, 40H, **H-Man**) 0.02 (s, 9H, **H-TMS**).

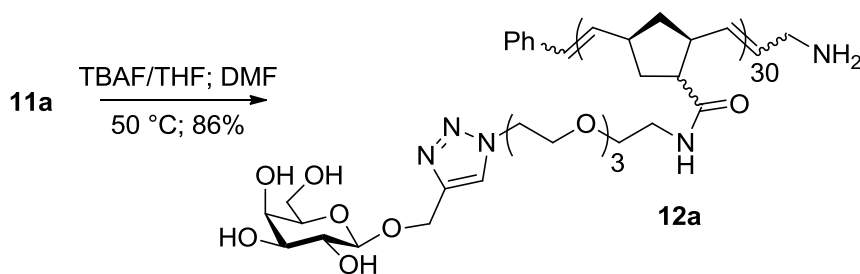
### 3-sulfogalactose glycopolymer **11c**



Solutions of poly-azide **9** (0.15 g, 0.014 mmol) in 2 mL DMF, propargyl 3'-sulfogalactoside **10c** [7] (0.20 g, 0.625 mmol) in 0.5 mL  $\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (8 mg, 0.03 mmol) and THPTA [8] (65 mg, 0.15 mmol) mixture in 0.5 mL  $\text{H}_2\text{O}$ , Na-ascorbate (12 mg, 0.06 mmol) in 0.5 mL  $\text{H}_2\text{O}$  were added to a vial charged with a stir bar in that order. The reaction was run at  $60\text{ }^\circ\text{C}$  for 24 h. 10 mL  $\text{H}_2\text{O}$  was added and the solution transferred into a vial containing 1 g CupriSorb<sup>®</sup> [8], stirred overnight to remove copper ions and filtered through a plug of cotton. The CupriSorb<sup>®</sup> [8] was washed with 10 mL  $\text{H}_2\text{O}$  and the collected filtrate dialyzed against 200 mL  $\text{H}_2\text{O}$  (12 h x 4). The solution was

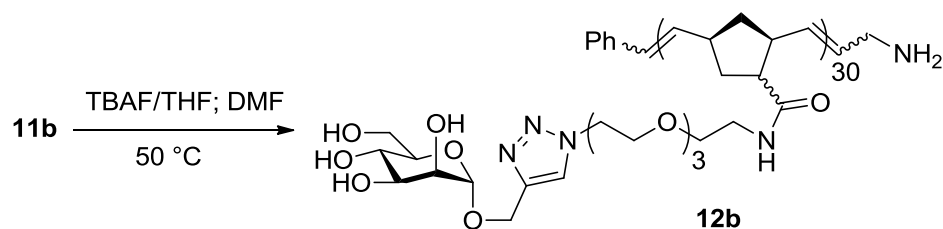
then concentrated to about 2 mL by centrifuge filtration and the H<sub>2</sub>O was then azeotroped with 1 mL toluene and evaporated on a rotovap at 40 °C (x 3) followed by 1 mL heptane. The product was dried under vacuum to give glycopolymer **11c** (0.23 g, 0.011 mmol) as a light brown film 77%. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O) δ 8.17 (s, 40H, **H-triazole**) 5.40 (bs, 80H, **H-olefinic**) 5.05 (d, *J* = 12.6 Hz, 40H, **H-SGal**) 4.91 (d, *J* = 11.9, 40H, **H-SGal**) 4.65 (bs, 80H, **H-SGal**) 4.35 (d, *J* = 7.6 Hz, 40H, **H-SGal**) 0.06 (s, 9H, **H-TMS**).

#### Amino-terminated galactosylated glycopolymer **12a**



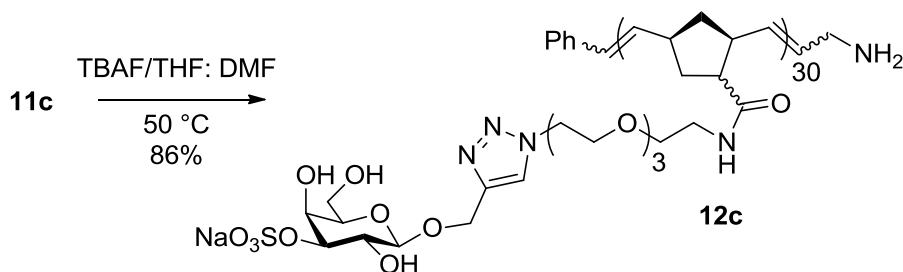
To a solution of glycopolymer **11a** (0.12 g, 7 μmol) in 2 mL dry DMF was added 1 mL of 1 M TBAF solution in THF and the mixture stirred for 24 h at 50 °C. 1 mL of 1% NaCl solution and 10 mL H<sub>2</sub>O was added and the mixture dialyzed against 200 mL H<sub>2</sub>O (12 h x 4). The solution was then concentrated to about 2 mL by centrifuge filtration and the H<sub>2</sub>O was then azeotroped with 1 mL toluene then evaporated on a rotovap at 40 °C (x 3) followed by 1 mL heptane. The product was dried under vacuum to give glycopolymer **12a** (0.10 g, 6 μmol) as a light brown film 86%. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O) δ 8.15 (s, 40H, **H-triazole**) 5.37 (bs, 80H, **H-olefinic**) 5.03 (d, *J* = 12.6 Hz, 40H, **H-Gal**) 4.93-4.83 (m, 40H, **H-Gal**) 4.65 (bs, 80H, **H-Gal**) 4.51 (d, *J* = 7.7 Hz, 40H, **H-Gal**).

### Amino-terminated mannosylated glycopolymer **12b**



Amino-terminated mannosylated glycopolymer **12b** was obtained using the same procedure reported for amino-terminated galactose glycopolymer **12a**. 55% of polymer **12b** was recovered. Partial  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ )  $\delta$  8.13 (s, 37H, **H-triazole**) 5.37 (bs, 77H, **H-olefinic**) 4.98 (s, 39H, **H-Man**).

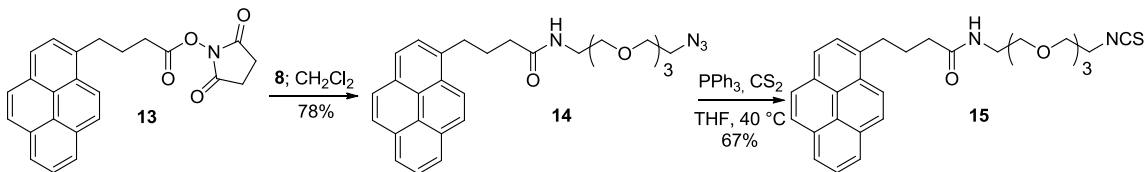
### Amino-terminated 3'-sulfogalactosylated glycopolymer **12c**



To a solution of glycopolymer **11c** (0.15 g, 8  $\mu\text{mol}$ ) in 2 mL dry DMF was added 1 mL of 1 M TBAF solution in THF, and the mixture was stirred for 24 h at 50  $^{\circ}\text{C}$ . 10 mL  $\text{H}_2\text{O}$  was added, and the mixture was dialyzed against 200 mL  $\text{H}_2\text{O}$  (12h x 4). The solution was then subjected to  $\text{Na}^+$  exchange chromatography ( $\text{Na}^+$  form generated from Amberlite IR-I20 resin  $\text{H}^+$  form using brine) to remove TBA cation and concentrated to about 2 mL by centrifuge filtration, and the  $\text{H}_2\text{O}$  was then azeotroped with 1 mL toluene then evaporated on a rotovap at 40  $^{\circ}\text{C}$  (x 3) followed by 1 mL heptane. The product was then dried under vacuum to give glycopolymer **12c** (0.13 g, 7  $\mu\text{mol}$ ) as a light brown film.

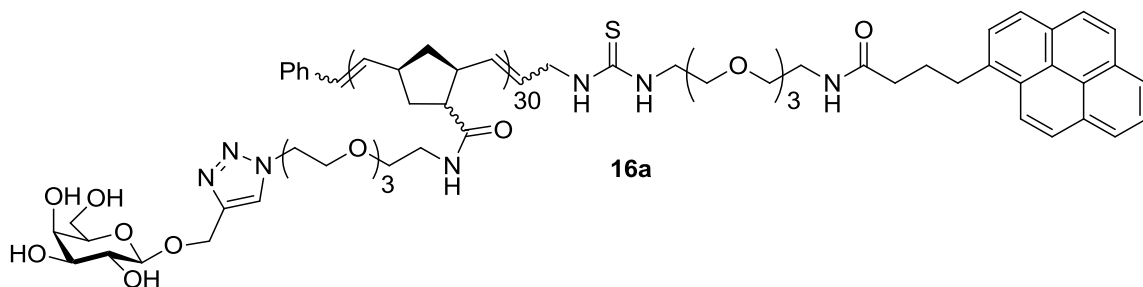
86%.  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$  8.16 (s, 40H, **H-triazole**) 5.46 (bs, 80H, **H-olefinic**) 5.05 (d,  $J = 12.6$  Hz, 40H, **H-SGal**) 4.71–4.58 (m, 40H, **H-SGal**) 4.51 (d,  $J = 7.6$  Hz, 40H, **H-SGal**).

*N*-(2-(2-(2-(2-isothiocyanatoethoxy)ethoxy)ethoxy)ethyl)-4-(pyren-2-yl)butanamide **15**



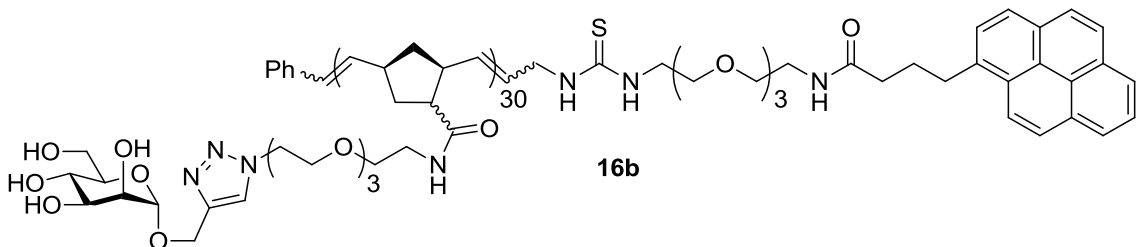
To a solution of **13** [8] (0.15 g, 0.4 mmol) in dry  $\text{CH}_2\text{Cl}_2$  was added a solution of **8** (0.13 g, 0.6 mmol) in dry  $\text{CH}_2\text{Cl}_2$ , and the mixture was stirred until TLC ( $\text{CH}_2\text{Cl}_2$ ) showed that **13** had been completely consumed (ca. 3 h). The solvent was then evaporated and the brown residue purified by automatic flash chromatography (100:0 to 95:5  $\text{CH}_2\text{Cl}_2$ :MeOH). The solvent was evaporated and product dried under vacuum to give **14** (0.15 g, 0.31 mmol) 78% as a yellow oil. To a solution of **14** (0.1 g, 0.2 mmol) in 10 mL  $\text{THF}:\text{CS}_2$  1:1 mixture was added 0.08 g of polymer bound  $\text{PPh}_3$  (3 mmol/g of polymer = 0.065 g, 0.25 mmol of  $\text{PPh}_3$ ), and the reaction mixture was heated at  $40^\circ\text{C}$  for 24 h. The mixture was then filtered, the solvent evaporated, and the product dried under vacuum to give **15** (0.07 g, 0.14 mmol) 67% as a yellow oil.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.32–7.85 (m, 9H) 6.00 (bs, 1H) 3.67–3.46 (m, 16H) 3.39 (t,  $J = 7.43$  Hz, 2H) 2.33–2.17 (m, 4H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  172.8, 136.1, 131.5, 131.0, 130.0, 128.9, 127.6, 127.50, 127.47, 126.8, 126.0, 125.2, 124.90, 124.87, 123.6, 70.8, 70.7, 70.5, 70.3, 69.9, 69.2, 45.2, 39.3, 36.1, 32.9, 27.5 HRMS (FAB) calculated for  $\text{C}_{29}\text{H}_{32}\text{N}_2\text{O}_4\text{S}$  [ $\text{M} + \text{Na}$ ] $^+$  527.1981 found 527.1966.

### Pyrene-end-labeled galactosyl glycopolymer **16a**



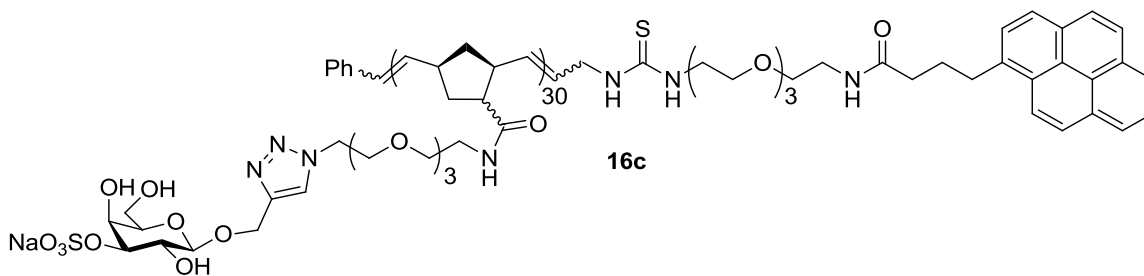
To a solution of galactosyl glycopolymer **12a** (80 mg, 5  $\mu$ M) in 2 mL DMF was added 527  $\mu$ L of 9.5 M **15** (9.6 mg, 19  $\mu$ M) in DMF, and the mixture was stirred at 50  $^{\circ}$ C overnight. The resulting solution was dialyzed from 200 mL DMF for 4 h to remove excess **15** then dialyzed from 200 mL MeOH:H<sub>2</sub>O 1:1 mixture (12 h x 3) and concentrated to about 2 mL by centrifuge filtration, and the H<sub>2</sub>O was then azeotroped with 1 mL toluene and evaporated on a rotovap at 40  $^{\circ}$ C (x 3) followed by 1 mL heptane. The product was then dried under vacuum to give glycopolymer **16a** (0.07 g, 4  $\mu$ mol) as a light brown film, 81% recovered.

### Pyrene-end-labeled mannosyl glycopolymer **16b**



Pyrene-end-labeled mannose glycopolymer **16b** was obtained using the same procedure reported for pyrene-end-labeled galactose glycopolymer **16a**. 96% of **16b** was recovered.

## Pyrene-end-labeled 3'-sulfogalactosyl glycopolymer **16c**



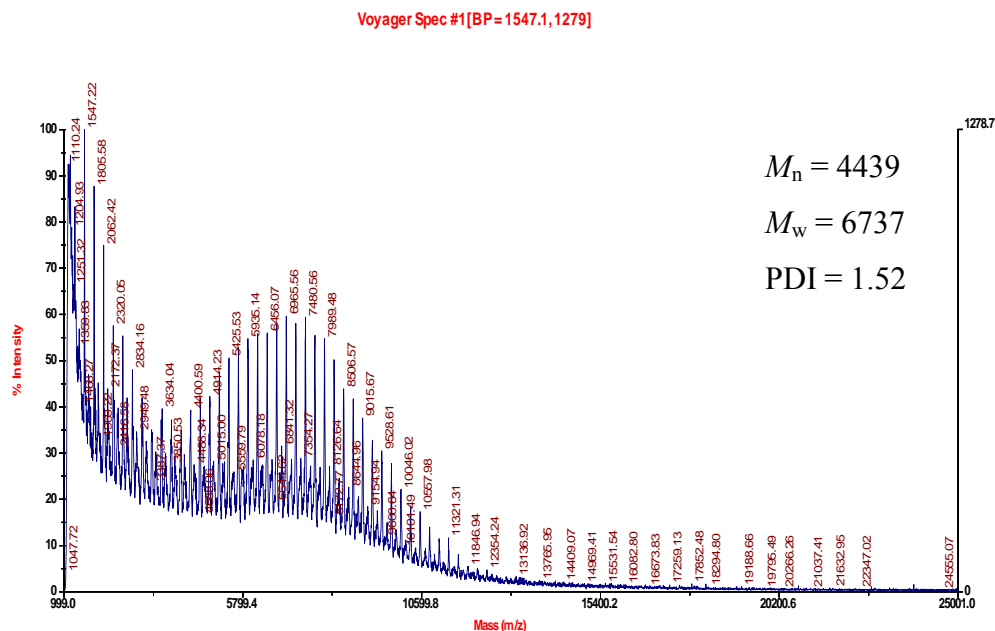
Pyrene-end-labeled 3'-sulfogalactosyl glycopolymer **16c** was obtained using the same procedure reported for pyrene-end-labeled galactose glycopolymer **16a**. 65% of **16c** was recovered.

## 2. References

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### 3. MALDI-ToF analysis

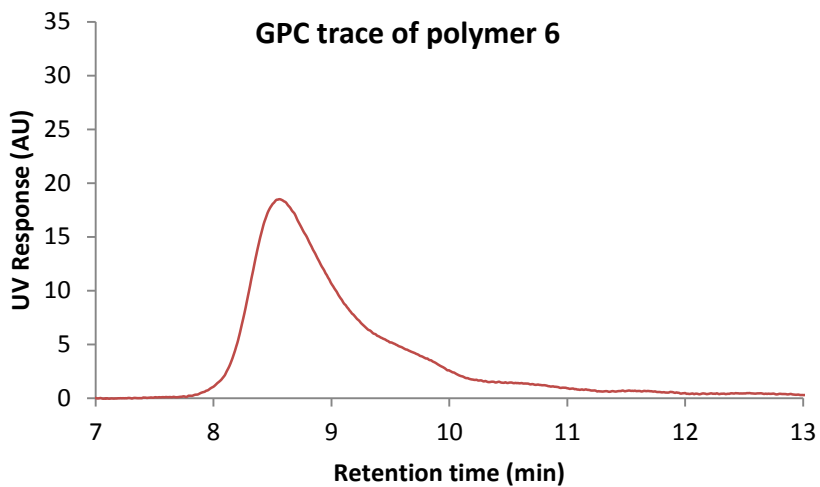
MALDI-ToF samples were prepared as follows; Polymer **7** (ca. 30 mg) was dissolved in 400  $\mu\text{L}$  of THF. 70  $\mu\text{L}$  water containing 0.1% TFA and 30  $\mu\text{L}$  acetonitrile were added to about 6 mg of super DHB, and the mixture was vortexed to provide a clear solution. 10  $\mu\text{L}$  of the polymer solution and 10  $\mu\text{L}$  of the matrix solution were mixed, and then 1  $\mu\text{L}$  of the mixture was applied directly to the MALDI target plate and allowed to dry completely before acquisition.





## 4. GPC analysis

GPC samples were prepared as follows; 10  $\mu\text{L}$  of 0.2% **6** (0.004 g in 2 mL THF) was injected and eluted using HPLC-grade THF flowing at 1 mL/min at room temperature; Absorbance was monitored at 254 nm. GPC molecular weight (MW) was obtained from a polystyrene standards calibration curve.  $M_w = 7469$ ;  $M_n = 4791$ ; DPI = 1.56.



**Figure S2:** GPC chromatogram of polymer **6**.

## 5. Capping efficiency table

Table S1

	Time <sup>a</sup>	5 min	20 min	1 h	15 h
<i>n</i> <sup>b</sup>		Ph:TMS <sup>c</sup>	Ph:TMS <sup>c</sup>	Ph:TMS <sup>c</sup>	Ph:TMS <sup>c</sup>
15		5:7 (1)	5:8.3 ± 1.2 (3)	5:8.7 ± 0.6 (3)	5:9 (1)
30		5:6 (1)	5:9.4 ± 0.8 (11)	5:9.7 ± 0.6 (3)	5:9 (1)
50 <sup>d</sup>		5:4	5:11.7 ± 0.6 (3)	5:11 ± 1 (3)	5:11 (1)

<sup>a</sup> Reaction time after addition of a solution of terminating agent **3** to the reaction mixture before quenching with ethyl vinyl ether.

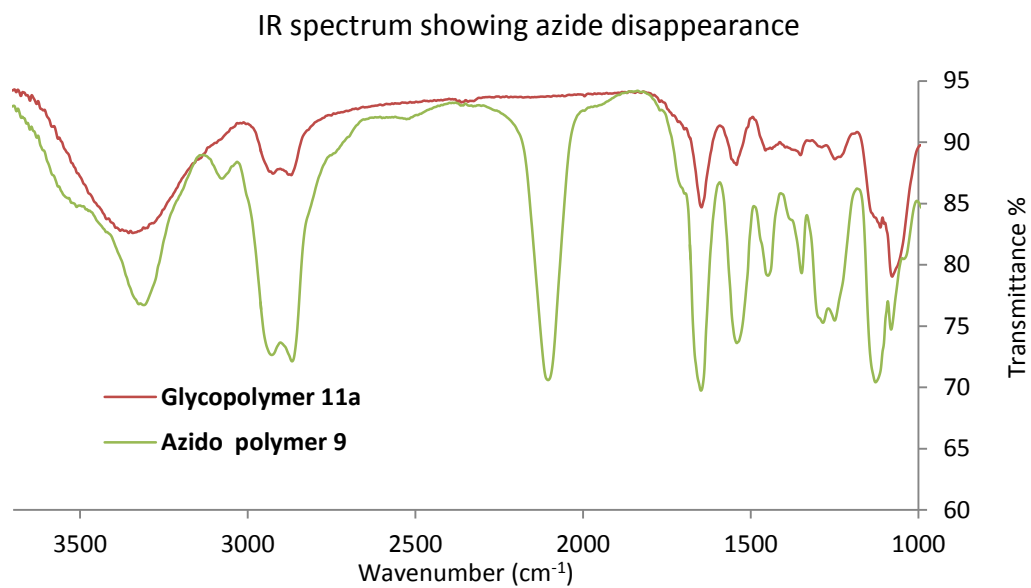
<sup>b</sup> Theoretical degree of polymerization determined by the molar ratios of monomer **4** to catalyst **5** used.

<sup>c</sup> The integral for the aromatic protons (derived from the Ph in catalyst **5**) was set to 5. The values are the ratios of the integral for aromatic protons to the TMS protons in the <sup>1</sup>H NMR spectra of polymers **6**. The number in parentheses refers to the number of times the polymerization and capping reactions were carried out.

<sup>d</sup> Although the TMS integrations for the 50mer are greater than 9 at 20 minutes and beyond, the degree of polymerization corresponding to this integration is also high, at approximately 80. However, if these spectra are reintegrated by setting the integral for the TMS peak to 9, the degree of polymerization is found to be 64. This is in accordance with the *M<sub>w</sub>* determined by GPC - 6693, which corresponds to a degree of polymerization of 63. Thus, we believe that the higher TMS integrations are a result of the error associated with integration of the small and broad aromatic peaks in the spectra of the 50mers. Moreover, the lack of a significant change in the integration values from 20 min to 15 hours indicates that secondary metathesis is unlikely to be the cause of the higher TMS integrations.

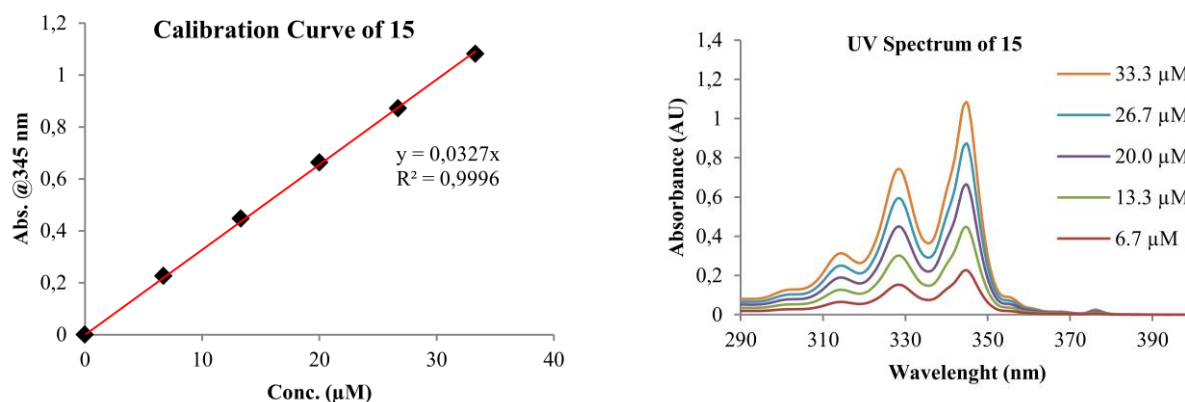
## 6. IR Spectra of Polymers

IR spectra were obtained from a dried film formed from a methanolic solution of polymer on NaCl discs.



**Figure S3:** Overlay IR spectra of azido polymer **9** and glycopolymer **11a**.

## 7. Determination of extent of pyrene end-labeling

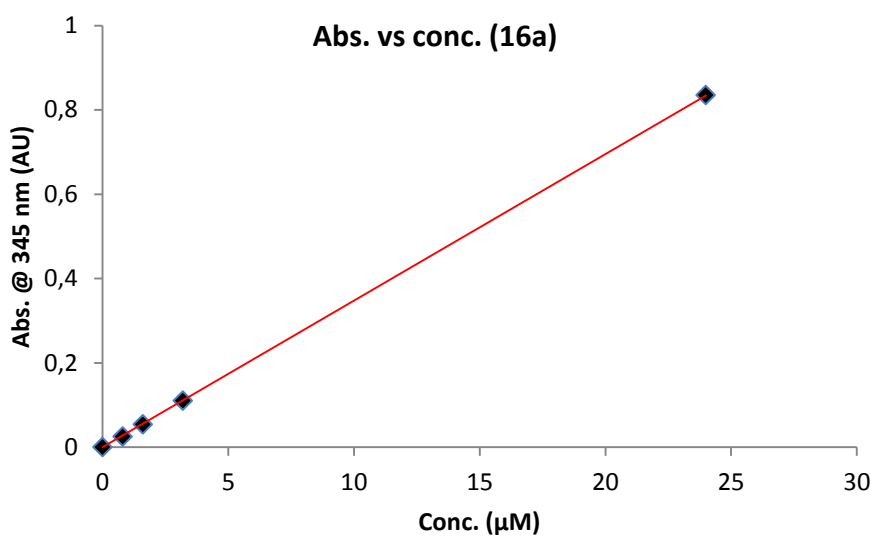
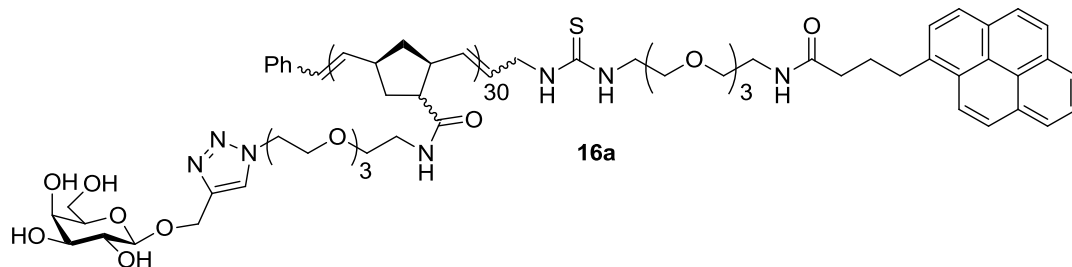


**Figure S4:** UV spectrum and calibration curve of **15**.

Molar extinction coefficient  $\epsilon$  of **15** =  $32,700 \text{ L mol}^{-1} \text{ cm}^{-1}$ .

## Polymer 16a

25 mg of pyrene labeled galactose glycopolymer **16a** was dissolved in 1 mL DMF to make 1.44 mM stock solution.



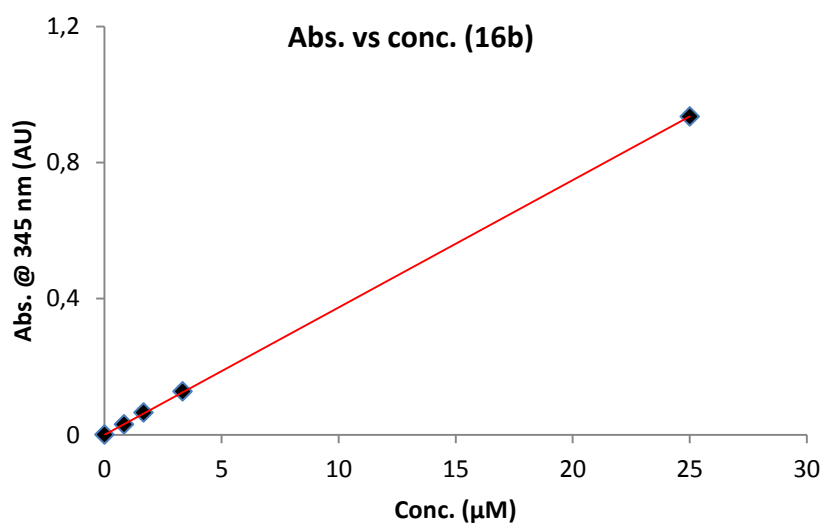
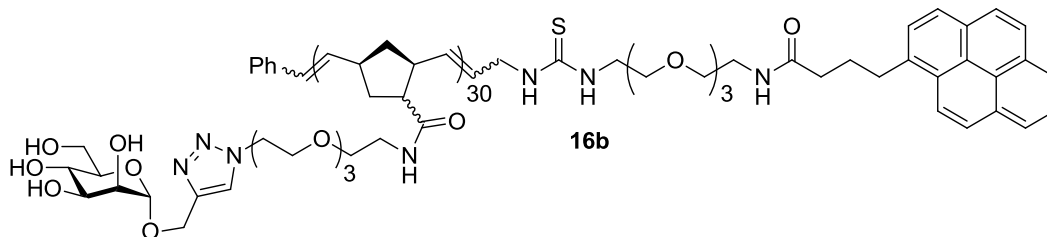
**Figure S5:** Graph of absorbance @ 345 nm against concentration for polymer **16a**.

**Table S2:** Percent pyrene labeling of polymer **16a**.

<b>16a</b> Conc. (μM)	Abs. @ 345 nm	<b>PY</b> μmol/g	<b>%</b> label
0.8	0.0251	<b>55</b>	<b>96</b>
1.6	0.0537	<b>59</b>	<b>103</b>
3.2	0.1099	<b>61</b>	<b>105</b>
24	0.8343	<b>61</b>	<b>106</b>
Average		<b>59</b>	<b>103</b>

## Polymer 16b

26 mg of pyrene labeled mannose glycopolymer **16b** dissolved in 1 mL DMF to make 1.5 mM stock solution.



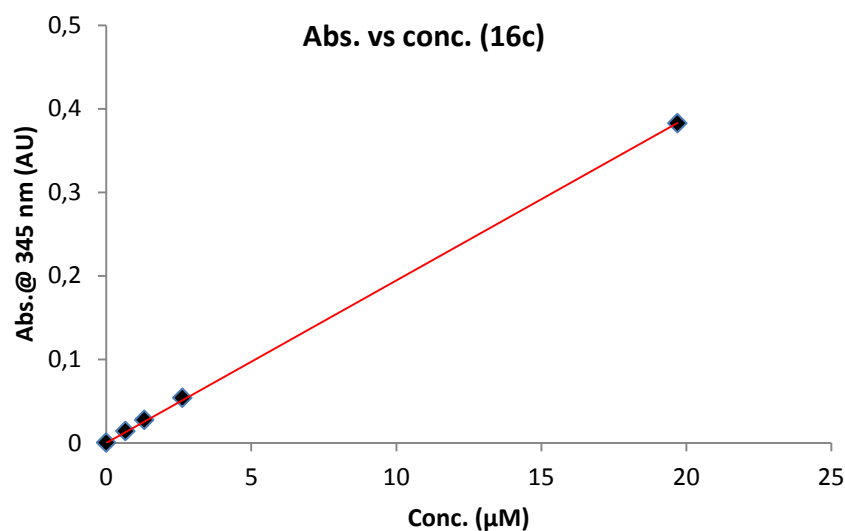
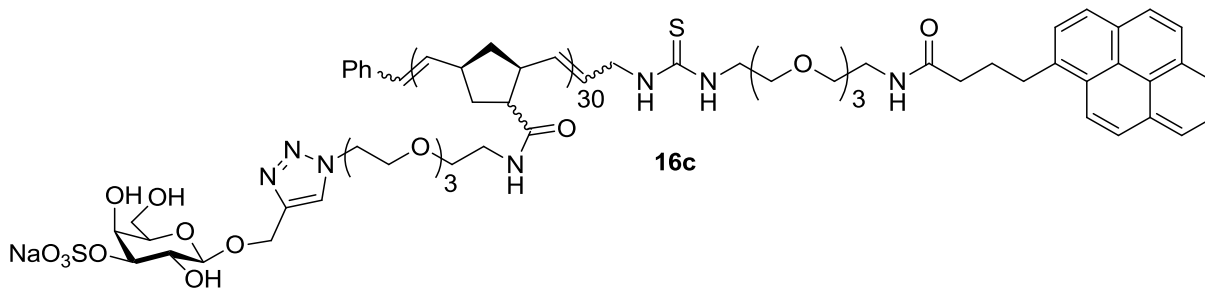
**Figure S6:** Graph of absorbance @ 345 nm against concentration for polymer **16b**.

**Table S3:** Percent pyrene labeling of polymer **16b**.

<b>16b</b> Conc. (μM)	Abs. @ 345 nm	PY μmol/g	% Label
0.83	0.0307	<b>65</b>	<b>113</b>
1.67	0.0648	<b>68</b>	<b>118</b>
3.33	0.1272	<b>67</b>	<b>116</b>
25	0.9350	<b>66</b>	<b>114</b>
Average		<b>68</b>	<b>116</b>

## Polymer 16c

24 mg of pyrene labeled 3'-sulfogalactose glycopolymer **16c** dissolved in 1mL DMF to make 1.18 mM stock solution.

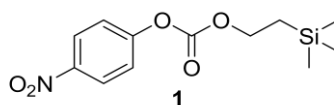


**Figure S7:** Graph of absorbance @ 345 nm against concentration for polymer **16c**.

**Table S4:** Percent pyrene labeling of polymer **16c**.

<b>16c</b> Conc. (μM)	Abs. @ 345 nm	<b>PY</b> μmol/g	<b>%</b> Label
0.66	0.0140	<b>32</b>	<b>65</b>
1.31	0.0275	<b>32</b>	<b>65</b>
2.63	0.0538	<b>31</b>	<b>63</b>
19.7	0.3826	<b>29</b>	<b>59</b>
Average		<b>31</b>	<b>63</b>

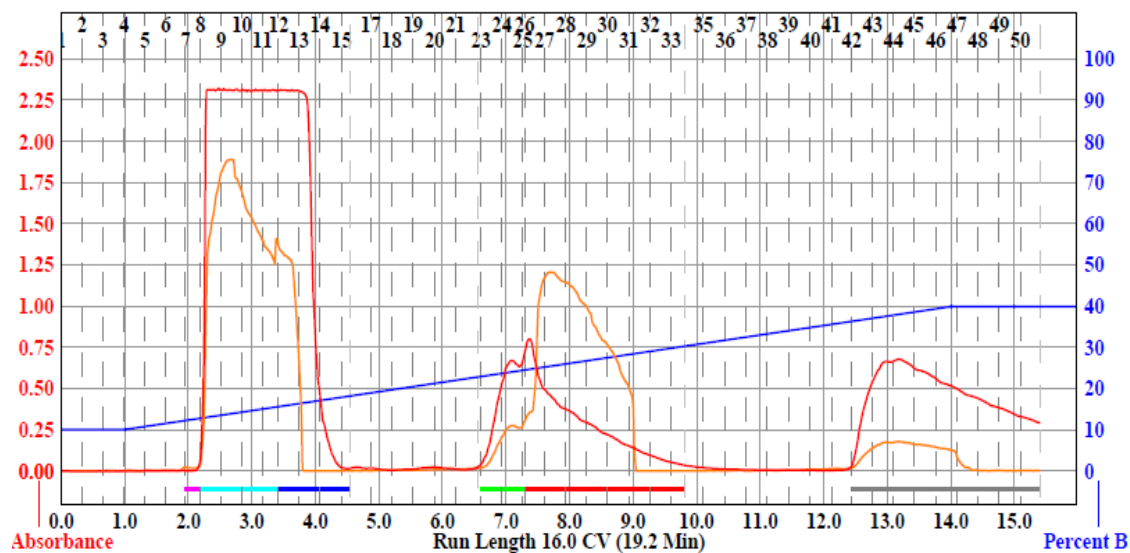
## 8. Teledyne ISCO COMBI flash $R_f$ chromatograms



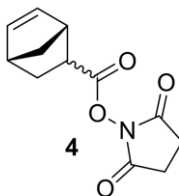
RediSep Column: Silica 40g Gold  
 Flow Rate: 40 ml/min  
 Equilibration Volume: 5.0 CV  
 Initial Waste: 0.0 CV  
 Air Purge: 1.0 min  
 Solvent A: A1 hexane  
 Solvent B: B1 ethyl acetate

Peak Tube Volume: Max.  
 Non-Peak Tube Volume: Max.  
 Loading Type: Solid  
 Wavelength 1 (red): 254nm  
 Peak Width: 2 min  
 Threshold: 0.20 AU  
 All Wavelength (orange): 200nm - 360nm  
 Peak Width: 2 min  
 Threshold: 0.20 AU

Run Notes:



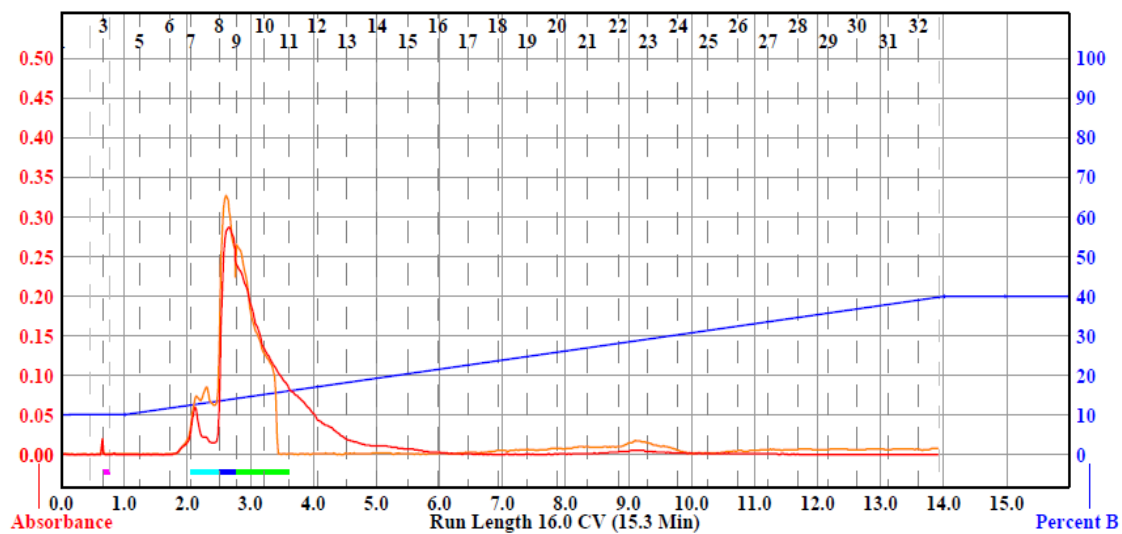


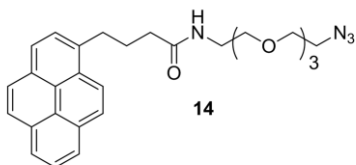


RediSep Column: Silica 24g Gold  
 Flow Rate: 35 ml/min  
 Equilibration Volume: 5.0 CV  
 Initial Waste: 0.0 CV  
 Air Purge: 1.0 min  
 Solvent A: A2 dichloromethane  
 Solvent B: B1 ethyl acetate

Peak Tube Volume: Max.  
 Non-Peak Tube Volume: Max.  
 Loading Type: Solid  
 Wavelength 1 (red): 254nm  
 Peak Width: 1 min  
 Threshold: 0.20 AU  
 All Wavelength (orange): 200nm - 360nm  
 Peak Width: 1 min  
 Threshold: 0.20 AU

Run Notes:

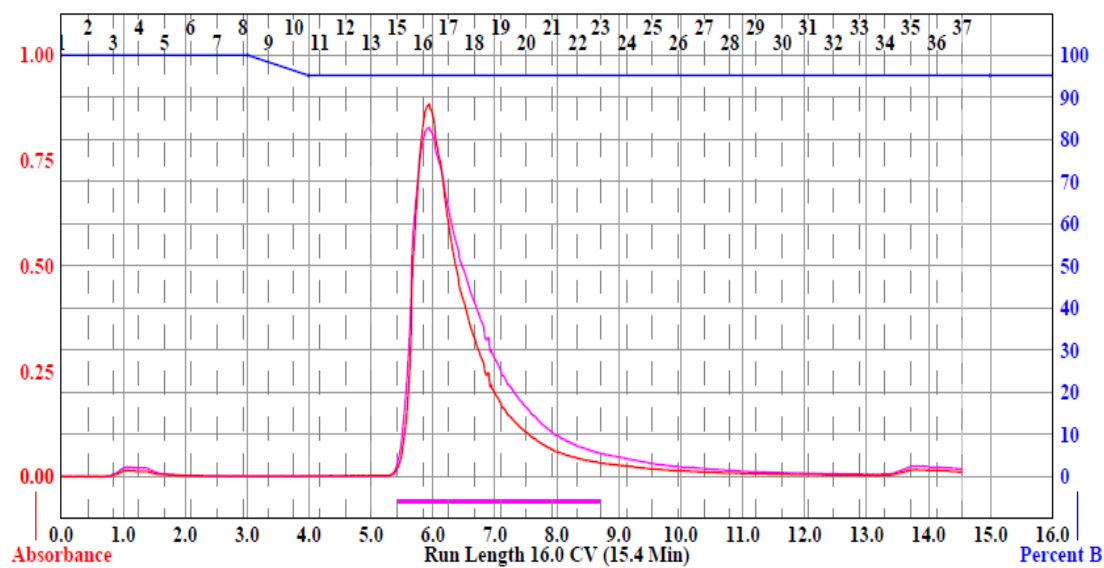




RediSep Column: Silica 24g Gold  
 SN: E0410597DC182 Lot: 2115201090W  
 Flow Rate: 35 ml/min  
 Equilibration Volume: 5.0 CV  
 Initial Waste: 0.0 CV  
 Air Purge: 1.0 min  
 Solvent: A2 methanol  
 Solvent: B2 dichloromethane

Peak Tube Volume: Max.  
 Non-Peak Tube Volume: Max.  
 Loading Type: Solid  
 Wavelength 1 (red): 254nm  
 Peak Width: 1 min  
 Threshold: 0.20 AU  
 Wavelength 2 (purple): 280nm

**Run Notes:**



## 9. NMR Spectra

