Supporting information for

Inherent Antibacterial Properties of Mannose-containing Polynorbornene Glycomaterials

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Table of Contents

Instrumentation

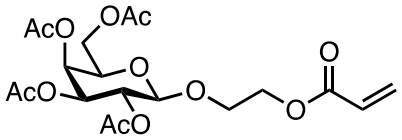
Size exclusion chromatography (SEC) was performed using instrumentation consisting of Wyatt Technologies TRIOS II light scattering, Optilab T-REX refractive index detectors, and a Shimadzu LC-20aD with pump operating at 1.0 mL min^{-1}. Two Agilent Technologies PLgel 10 μm mixed-bed columns heated to 50 °C were used with a mobile phase consisting of *N*,*N*-dimethylacetamide with 50 mM lithium chloride as the eluent. All nuclear magnetic resonance (NMR) spectra were acquired using an Agilent U4-DD2 400 MHz instrument; samples were dissolved in deuterated chloroform at a concentration of ~40 mg mL^{-1}. Flash chromatography was carried out using a Biotage® Isolera One with Sfär Silica HC D High Capacity Duo 20 μm 25 g columns as the stationary phase. 96-Well plates were read on the Cytation3 BioTek instrument to give absorbance values for the minimum inhibitory concentration (MIC) and hemolysis concentration (HC_{xx}) data.

Materials

1,2,3,4,6-Penta-*O*-acetyl-β-D-galactopyranose (Gal-**1**), 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (Glc-**1**), 2-acetamido-1,3,4,6-tetra-*O*-acetyl-β-D-glucopyranose (GlcNAc-**1**), and 1,2,3,4,6-penta-*O*-acetyl-β-D-mannopyranose (Man-**1**) were acquired from Biosynth. 2-Hydroxyethylacrylate (**2**) was received from Ambeed Chemicals. Acetone, CH_2Cl_2, dichloroethane (DCE) hexanes, and CH_3OH were acquired from Spectrum Chemicals. Grubbs 3rd generation catalyst (G3) was prepared according to literature procedure.[1] Dicyclopentadiene, ethyl vinyl ether, linear polyethyleneimine (PEI, 2.5 KDa), and LB broth were obtained from Millipore Sigma. Cyclopentadiene was distilled from dicyclopentadiene and used within 24 hours of preparation. Liquid cultures of *E. coli* and *Staphylococcus aureus* were prepared in 3 mL of LB broth. All other chemicals were obtained from Oakwood Chemicals.

Glycomonomer Synthesis

1-*O*-Acryloyloxyethyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (Gal-**3**)



Boron trifluoride diethyl etherate (BF_3•OEt_2, 3.51 mL, 28.5 mmol) was added at a rate of 0.1 mL min^{-1} to a solution of Gal-**1** (1.95 g, 5 mmol) and **2** (0.79 mL, 7.5 mmol) in 10 mL DCM under a nitrogen atmosphere and cooled to 0 °C and allowed to react for 1 hour. The solution was then warmed to 25 °C and allowed to react for an additional 4 hours, after which point it was diluted with ~50 mL of DCM and neutralized by the addition of ~50 mL of saturated $NaHCO_3$ solution. The organic layer was then separated and washed with 1x 50 mL saturated $NaHCO_3$ solution, 2x 50 mL cold DI H_2O, and 1x 50 mL brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure to afford 1-*O*-acryloyloxyethyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (Gal-**3**, 2.01 g, 4.5 mmol, 91%). The acrylate was obtained as a clear oil and was used without further purification. ^{1}H NMR ($CDCl_3$, δ): 1.91 (s, 3H), 1.96 (s, 3H), 1.98 (s, 3H), 2.08 (s, 3H), 3.73-3.80 (m, 1H), 3.83-3.88 (m, 1H), 3.95-4.02 (m, 1H), 4.00-4.11 (m, 2H), 4.23-4.26 (m, 2H), 4.47 (d, 1H), 4.95 (dd, 1H), 5.11-5.17 (m, 1H), 5.31-5.33 (m, 1H), 5.77-5.82 (m, 1H), 6.02-6.11 (m, 1H), 6.33-6.39 (m, 1H). ^{13}C NMR ($CDCl_3$, δ): 20.47, 20.55, 20.56, 20.59, 61.22, 63.21, 66.95, 67.33, 68.57, 70.70, 70.77, 101.2, 128.0, 131.2, 165.8, 169.3, 170.0, 170.1, 170.3.

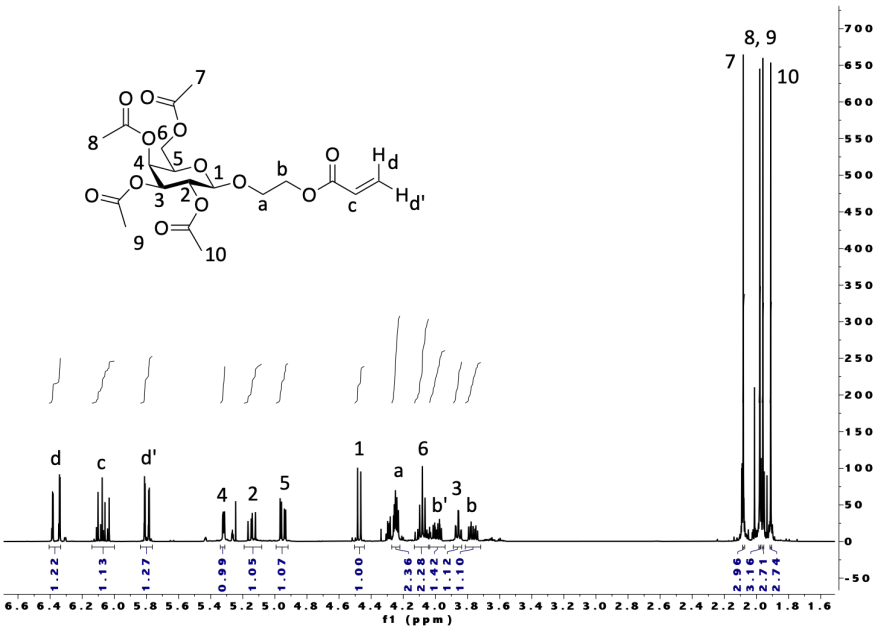


Figure S1. ^{1}H NMR spectrum of Gal-**3**

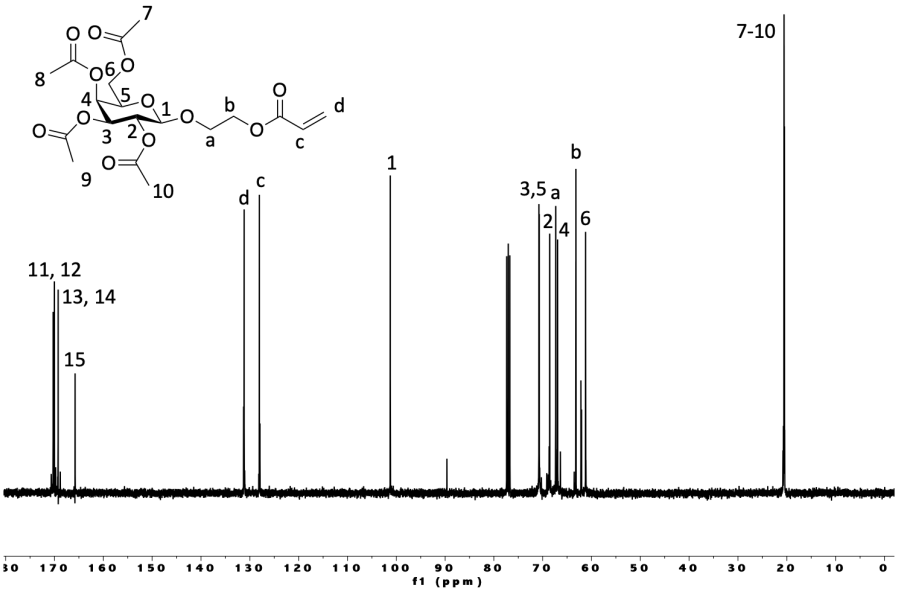


Figure S2. ^{13}C NMR spectrum of Gal-**3**

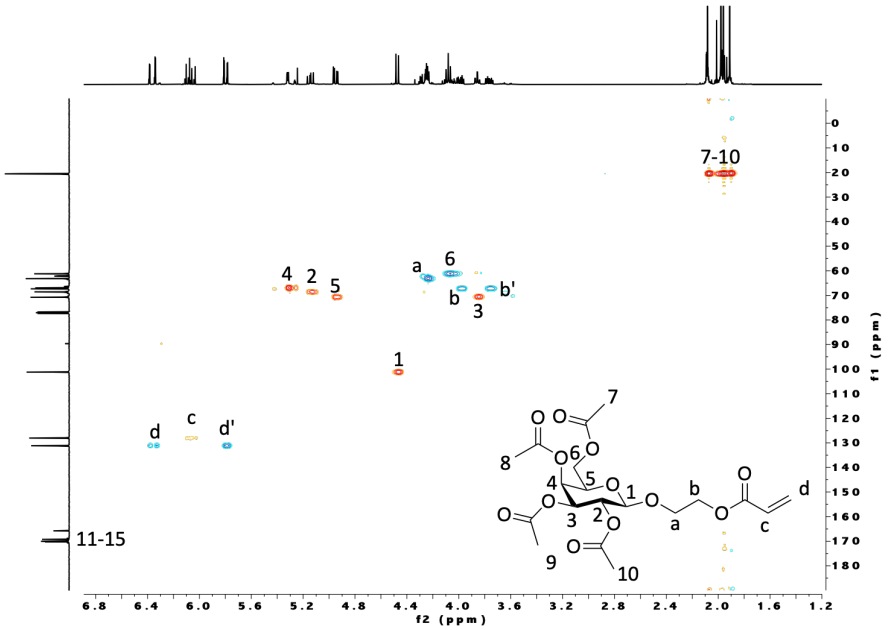
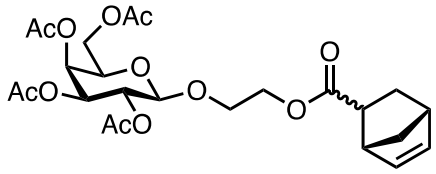


Figure S3. HSQC NMR spectrum of Gal-**3**

2-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)hydroxyethyl 5-norbornene-2-carboxylate (Gal-**5**)



Cyclopentadiene (0.79 mL, 9.40 mmol) was added to a solution of Gal-**3** (2.00 g, 4.48 mmol) in 50 mL toluene under a nitrogen atmosphere. The mixture was heated to reflux and allowed to react overnight, after which point it was concentrated under reduced pressure, diluted in 15 mL of hexanes/DCM (2:1), and purified via flash chromatography (3 column volumes of 100% Hexanes, 3 column volumes of 100% DCM, DCM→acetone 100→97%). The solvent was removed under reduced pressure to afford 2-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)hydroxyethyl 5-norbornene-2-carboxylate as a viscous oil (Gal-**5**, 1.94 g, 3.79 mmol, 85%). The product was a mixture of endo/exo norbornene (71/29) that was used in polymerizations without separation. ^{1}H NMR ($CDCl_3$, δ): 1.18-1.23 (m, 1H), 1.85-1.94 (m, 2H), 1.97 (s, 3H), 2.04 (s, 6H), 2.14 (s, 3H), 2.90-2.97 (m, 3H), 3.17-3.22 (m, 1H), 3.91 (t, 2H), 4.08-4.18 (m, 5H) 4.52 (d, 1H), 5.00 (dd, 1H), 5.21 (dd, 1H), 5.38 (dd, 1H), 5.89-5.94 (m, 1H), 6.16-6.20 (m, 1H). ^{13}C NMR ($CDCl_3$, δ): 20.71, 20.78, 20.79, 29.35, 42.66, 43.35, 45.82, 49.72, 61.39, 61.40, 63.12, 66.99, 68.60, 70.88, 71.04, 101.1, 132.1, 137.8, 169.5, 170.3, 170.4, 170.5, 174.7.

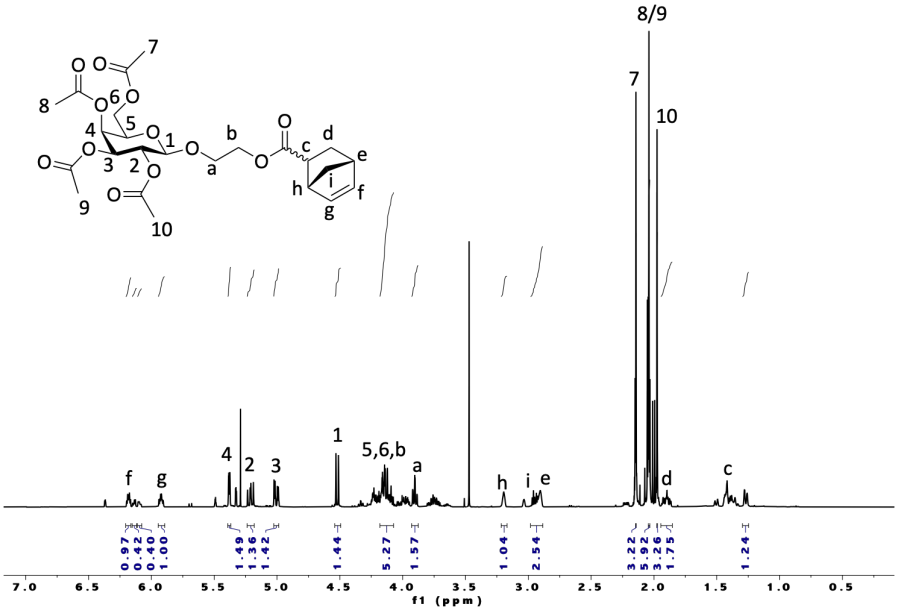


Figure S4. ^{1}H NMR spectrum of Gal-**5**

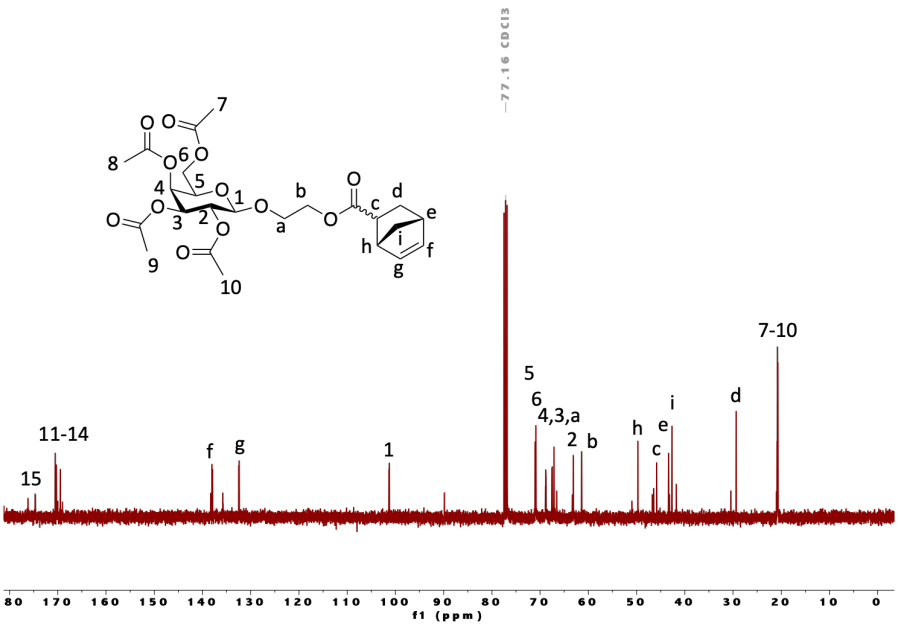


Figure S5. ^{13}C NMR spectrum of Gal-**5**

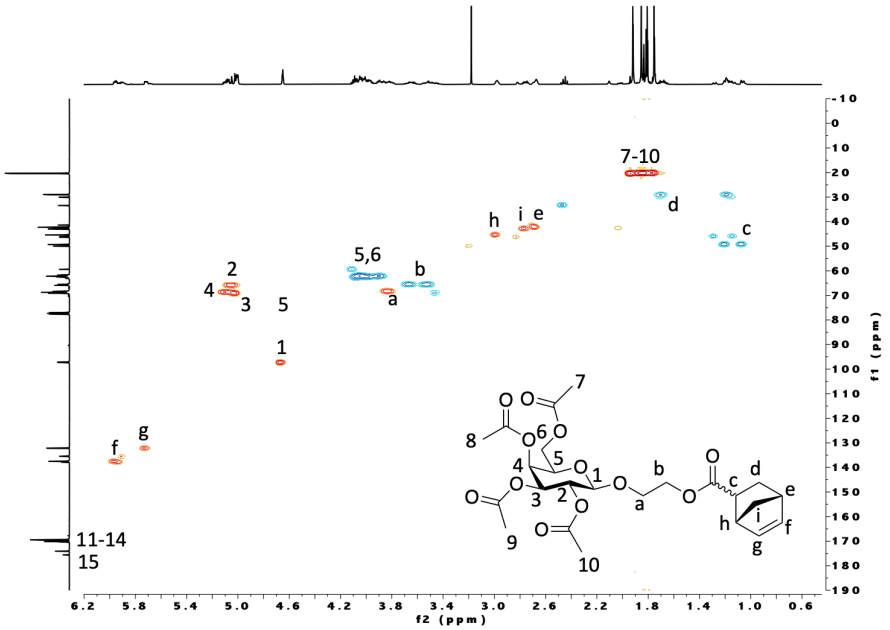
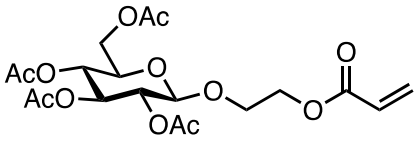


Figure S6. HSQC NMR spectrum of Gal-**5**

1-*O*-Acryloyloxyethyl 2,3,4,6-tetra-*O*-acetyl β-D-glucopyranoside (Glc-**3**)



Boron trifluoride diethyl etherate (BF_3•OEt_2, 3.51 mL, 28.5 mmol) was added at a rate of 0.1 mL min^{-1} to a solution of Glc-**1** (1.95 g, 5 mmol) and **2** (0.79 mL, 7.5 mmol) in 10 mL DCM under a nitrogen atmosphere and cooled to 0 °C and allowed to react for 1 hour. The solution was then warmed to 25 °C and allowed to react for an additional 4 hours, after which point it was diluted with ~50 mL of DCM and neutralized by the addition of ~50 mL of saturated $NaHCO_3$ solution. The organic layer was then separated and washed with 1x 50 mL saturated $NaHCO_3$ solution, 2x 50 mL cold DI H_2O, and 1x 50 mL brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure to afford 1-*O*-acryloyloxyethyl 2,3,4,6-tetra-*O*-acetyl-β-

D-glucopyranoside (Glc-**3**, 1.98 g, 4.43 mmol, 89%). The acrylate was obtained as a clear oil and was used without further purification.

^{1}H NMR ($CDCl_3$, δ): 1.99 (s, 3H), 2.01 (s, 6H), 2.07 (s, 3H), 3.66-3.72 (m, 2H), 3.77-3.84 (m, 1H), 4.08-4.15 (m, 2H), 4.27-4.31 (m, 2H), 5.56 (d, 1H), 4.93-5.03 (m, 1H), 5.03-5.11 (m, 2H), 5.15-5.23 (m, 1H), 5.80-5.90 (m, 1H), 6.01-6.20 (m, 1H), 6.36-6.45 (m, 1H). ^{13}C NMR ($CDCl_3$, δ): 20.56, 20.57 (2C), 20.69, 61.47, 63.14, 67.46, 68.31, 71.08, 71.88, 72.70, 100.8, 128.1, 131.3, 165.9, 169.2, 169.4, 170.3, 170.7.

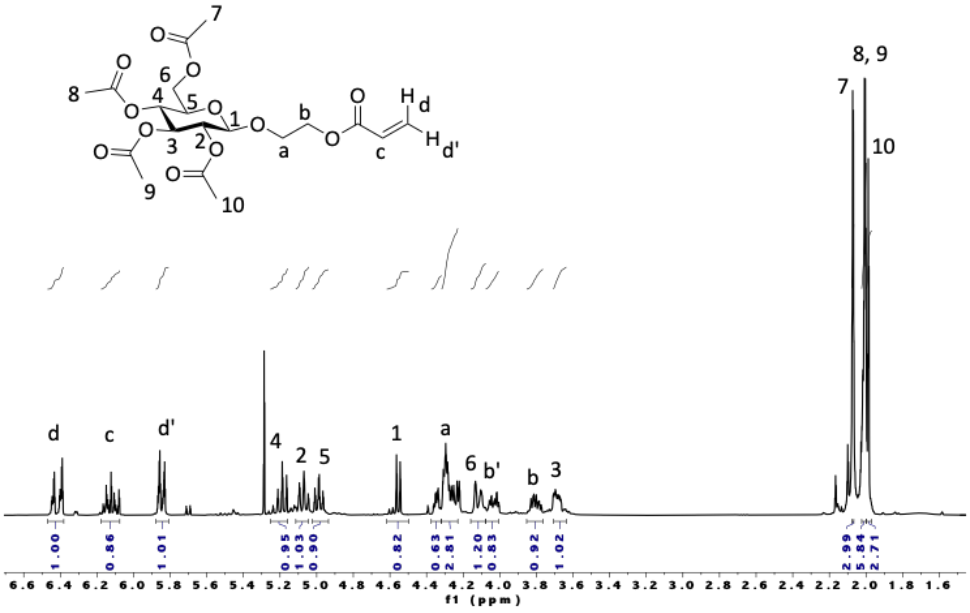


Figure S7. ^{1}H NMR spectrum of Glc-**3**

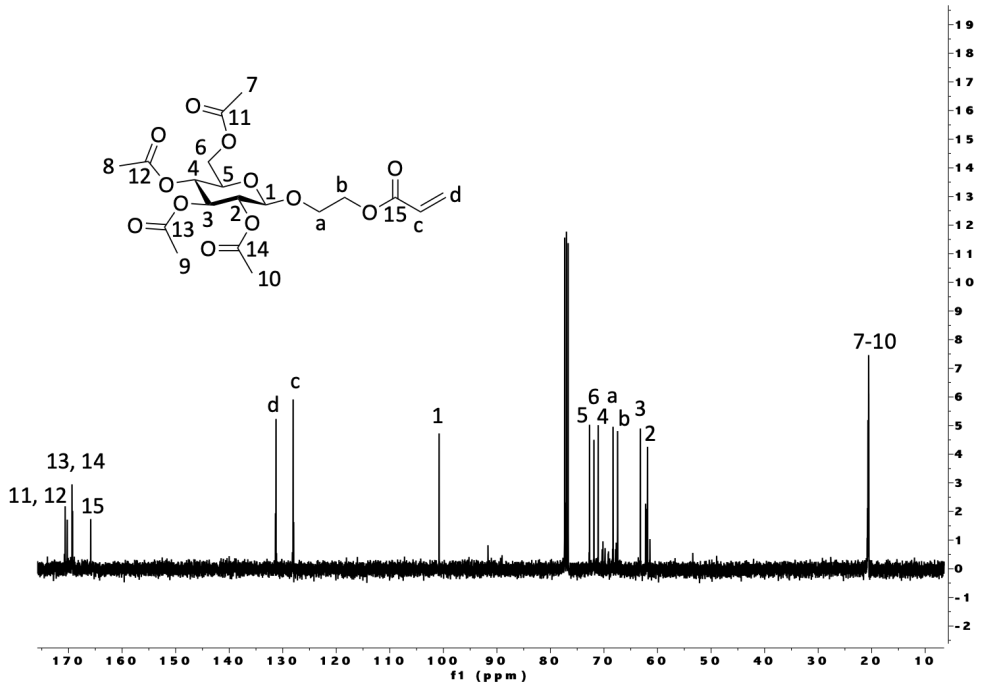


Figure S8. ^{13}C NMR spectrum of Glc-**3**

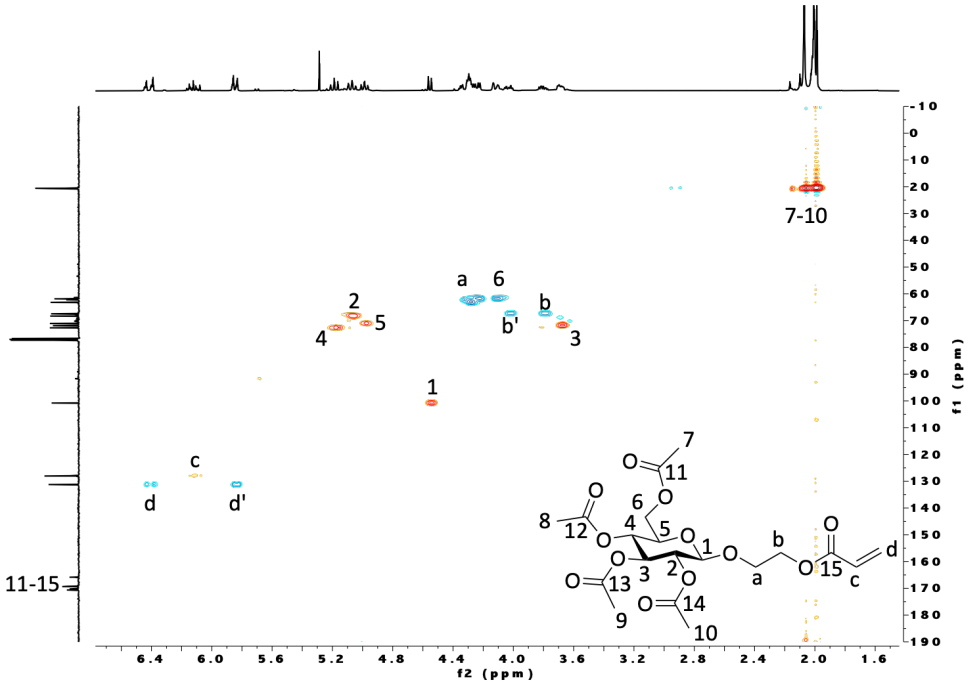
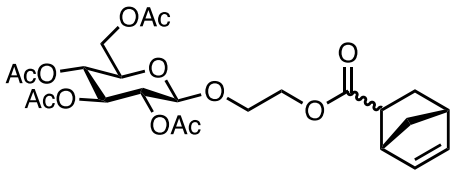


Figure S9. HSQC NMR spectrum of Glc-**3**

2-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)hydroxyethyl 5-norbornene-2-carboxylate (Glc-**5**)



Cyclopentadiene (0.79 mL, 9.40 mmol) was added to a solution of Glc-**3** (2.00 g, 4.48 mmol) in 50 mL toluene under a nitrogen atmosphere. The mixture was heated to reflux and allowed to react overnight, after which point it was concentrated under reduced pressure, diluted in 15 mL of hexanes/DCM (2:1), and purified via flash chromatography (3 column volumes of 100% Hexanes, 3 column volumes of 100% DCM, DCM→acetone 100→97%). The solvent was removed under reduced pressure to afford 2-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl) hydroxyethyl 5-norbornene-2-carboxylate (Glc-**5**) as a viscous oil (2.04 g, 3.99 mmol, 89%). The product was a mixture of endo/exo norbornene (67/33) that was used in polymerizations without separation. ^{1}H NMR ($CDCl_3$, δ): 1.23-1.29 (m, 1H), 1.85-1.93 (m, 2H), 1.99 (s, 3H), 2.00 (s, 6H), 2.07 (s, 3H), 2.87-2.97 (m, 3H), 3.16-3.21 (m, 1H), 3.65-3.75 (m, 3H), 4.11-4.17 (m, 3H), 4.25-4.28 (m, 1H), 4.55 (d, 1H), 5.07 (t, 2H), 5.19 (t, 1H), 5.88-5.93 (m, 1H), 6.15-6.19 (m, 1H). ^{13}C NMR ($CDCl_3$, δ): 20.70, 20.72, 20.77, 20.84, 29.33, 42.65, 43.34, 45.83, 49.68, 62.02, 63.03, 67.57, 67.63, 68.43, 72.03, 72.91, 100.7, 132.6, 137.9, 169.4, 169.5, 170.4, 170.8, 174.7.

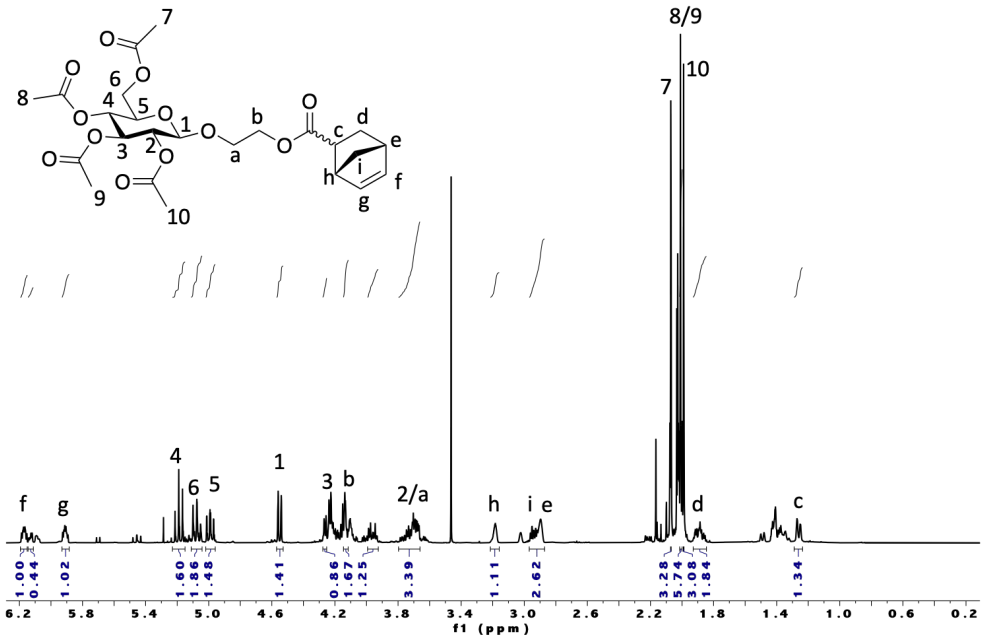


Figure S10. ^{1}H NMR spectrum of Glc-**5**

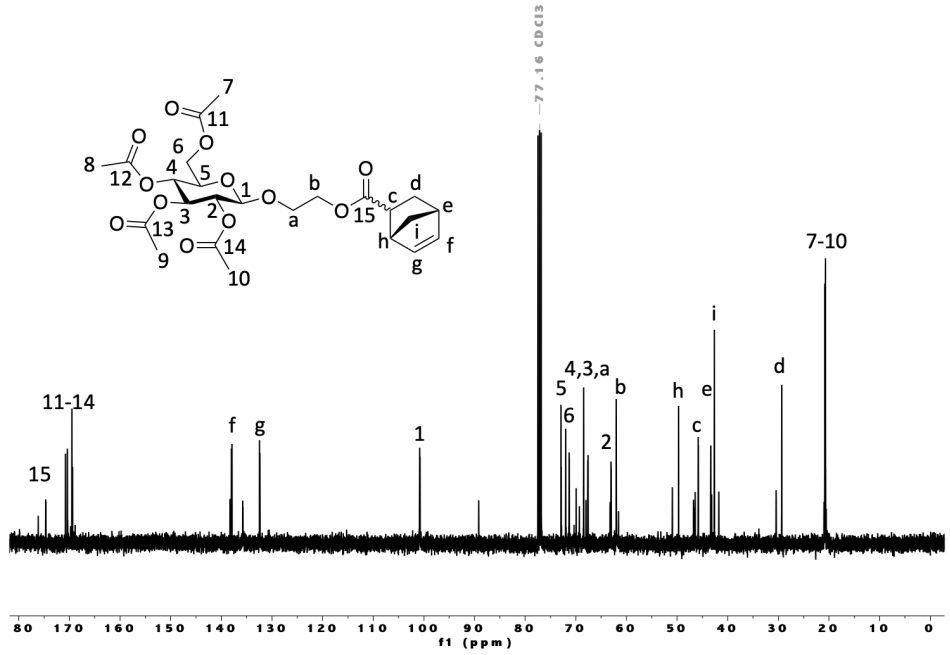


Figure S11. ^{13}C NMR spectrum of Glc-**5**

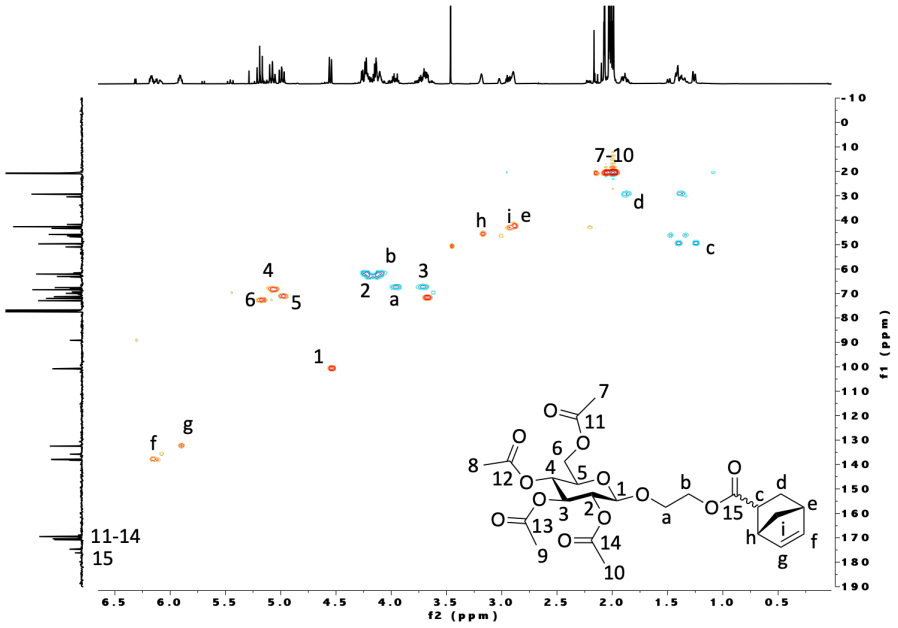
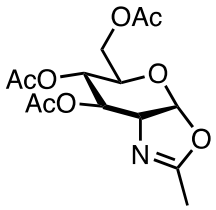


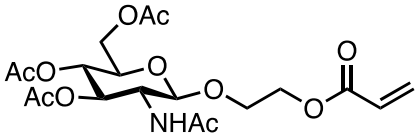
Figure S12. HSQC NMR spectrum of Glc-**5**

2-methyl (3,4,6-tri-*O*-acetyl-α-D-glucopyranosyl)-[2,1-d]-2-oxazoline (Glc-oxazoline)



GlcNAc-**1** (1.00 g, 2.58 mmol) was dissolved in 25 mL DCE heated to 60 °C. After sparging the solution with N_2 for 10 minutes, TMSOTf (1.61 mL, 5.2 mmol) was added and the mixture allowed to stir. After 3 hours, the solution was cooled to room temperature, neutralized using triethylamine and diluted with 50 mL of toluene/acetone (50/50). The solution was filtered through silica gel and concentrated to afford 2-methyl (3,4,6-tri-*O*-acetyl-α-D-glucopyranosyl)-[2,1-d]-2-oxazoline (Glc-oxazoline) as a dark yellow oil and was used without further purification.

1-*O*-Acryloyloxyethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-acetamido-β-D-glucopyranoside (GlcNAc-**3**)



A mixture of Glc-oxazoline (0.75 g, 2.3 mmol) and **2** (0.69 mL, 6.8 mmol) and 25 mL DCE was sparged with nitrogen for 25 minutes. The solution was allowed to stir at 25 °C for 1 hour, after which point it was placed in an oil bath heated to 70 °C, and camphor sulfonic acid (CSA, 0.053 g, 0.23 mmol) was added after 5 minutes. The mixture was vigorously stirred for 2 hours, after which point additional CSA (0.042 g, 0.18 mmol) was added. After 2 hours, the solution was cooled to room temperature, neutralized with triethylamine and diluted with 75 mL of DCM. The organic layer was then washed with 2x 100 mL saturated $NaHCO_3$, 2x 100 mL of cold DI H_2O, dried over $MgSO_4$, and concentrated under reduced pressure to afford 1-*O*-acryloyloxyethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-acetamido β-D-glucopyranoside (GlcNAc-**3**). The acrylate was obtained as a yellow oil and used without further purification. ^{1}H NMR ($CDCl_3$, δ): 1.94 (s, 3H), 2.99 (s, 3H), 2.01 (s, 3H), 2.11 (s, 3H), 3.75-3.84 (m, 1H), 3.85-3.91 (t, 1H), 3.95-4.06 (m, 1H), 4.06-4.18 (m, 2H), 4.24-4.30 (m, 2H), 4.50 (d, 1H), 4.97 (dd, 1H), 5.17 (dd, 1H), 5.34 (dd, 1H), 5.82 (dd, 1H), 6.09 (dd, 1H) 6.49 (dd, 1H). ^{13}C NMR ($CDCl_3$, δ): 20.51, 20.60 (2C), 20.64, 61.23, 63.24, 66.95, 67.38, 68.58, 70.72, 70.80, 101.3, 128.0, 131.3, 165.9, 169.3, 170.1, 170.2, 170.4.

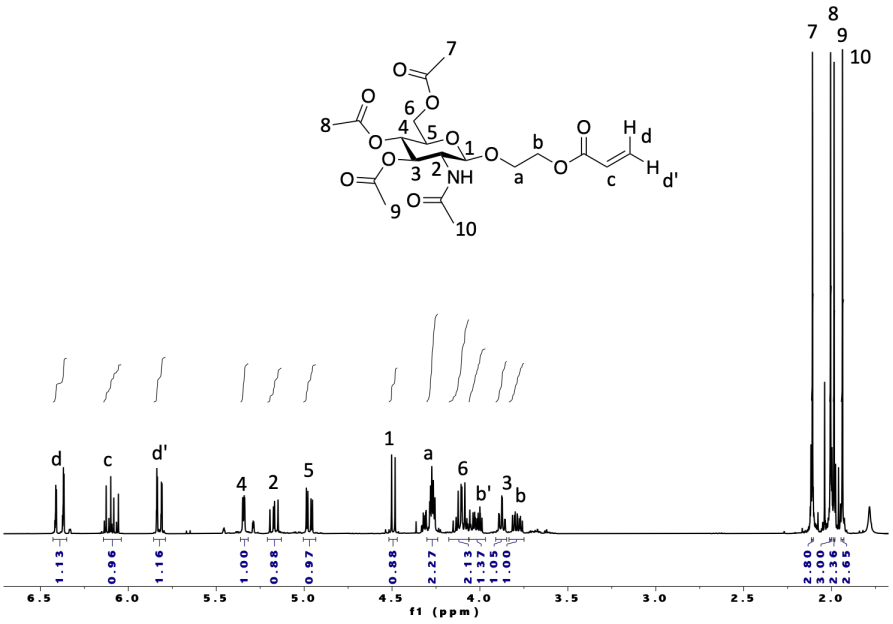


Figure S13. ^{1}H NMR spectrum of GlcNAc-**3**

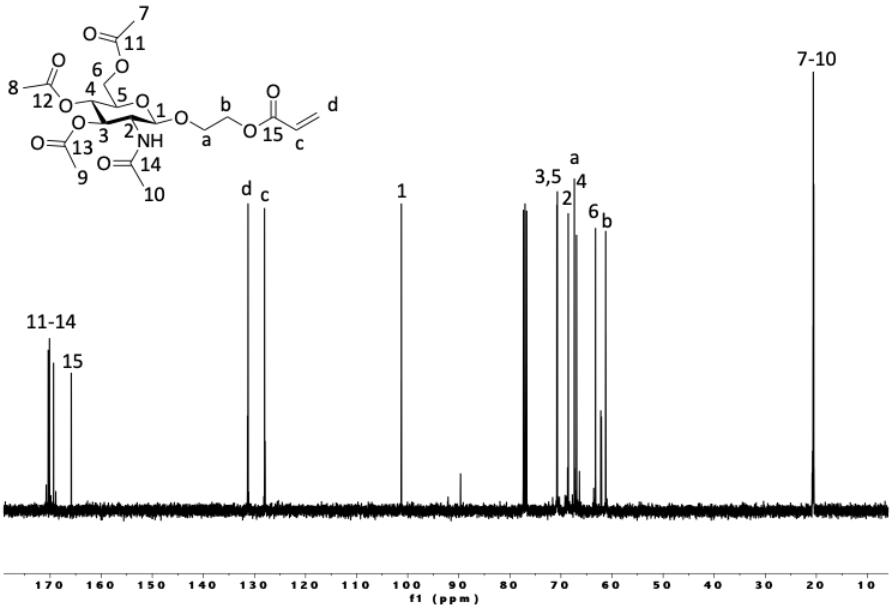


Figure S14. ^{13}C NMR spectrum of GlcNAc-**3**

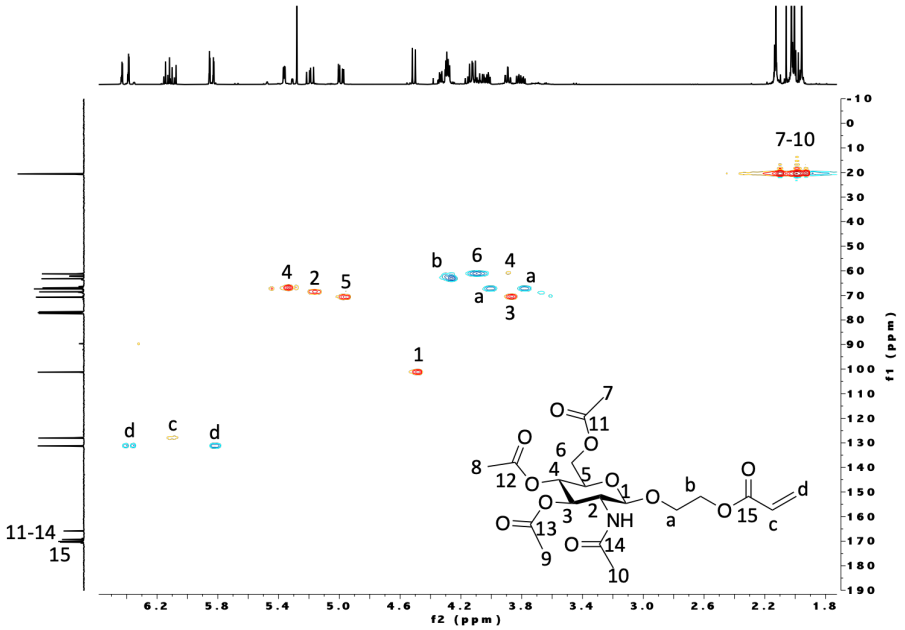
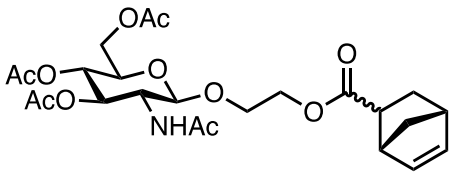


Figure S15. COSY NMR Spectrum of GlcNAc-**3**

2-*O*-(3,4,6-tetra-*O*-acetyl-2-deoxy-2-acetamido-β-D-galactopyranosyl) hydroxyethyl 5-norbornene-2-carboxylate (GlcNAc-**5**)



Cyclopentadiene (0.79 mL, 9.40 mmol) was added to a solution of GlcNAc-**3** (1.00 g, 2.25 mmol) in 50 mL toluene under a nitrogen atmosphere. The mixture was heated to reflux and allowed to react overnight, after which point it was concentrated under reduced pressure, diluted in 15 mL of hexanes/DCM (2:1), and purified via flash chromatography (3 column volumes of 100% Hexanes, 3 column volumes of 100% DCM, DCM→acetone 100→97%). The solvent was removed under reduced pressure to afford 2-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-acetamido-β-D-glucopyranosyl)hydroxyethyl 5-norbornene-2-carboxylate (Glc-**5**) as a viscous oil (0.942 g, 1.84 mmol, 82%). The product was a mixture of endo/exo norbornene (69/31) that was used in polymerizations without separation. ^{1}H NMR ($CDCl_3$, δ): 1.05-1.09 (m, 1H), 1.65-1.73 (m, 2H), 1.74 (s, 3H), 1.74 (s, 6H), 1.93 (s, 3H), 2.67-2.77 (m, 3H), 2.96-3.00 (m, 1H), 2.99-3.61 (m, 2H), 3.49-3.61 (m, 2H), 3.70-3.74 (m, 1H), 3.77-3.83 (m, 1H), 3.92-3.95 (m, 3H), 3.96-4.05 (m, 2H), 4.24 (d, 1H), 4.81 (dd, 1H), 4.98 (dd, 1H), 5.17 (dd, 1H), 5.68-5.74 (m, 1H), 5.93-5.98 (m, 1H). ^{13}C NMR ($CDCl_3$): 20.48, 20.56, 20.66, 29.13, 42.43, 43.15, 45.61, 49.50, 61.20, 62.92, 66.95, 67.26, 67.38, 68.62, 70.64, 101.06, 132.4, 137.7, 169.2, 170.0, 170.2, 170.3, 174.5.

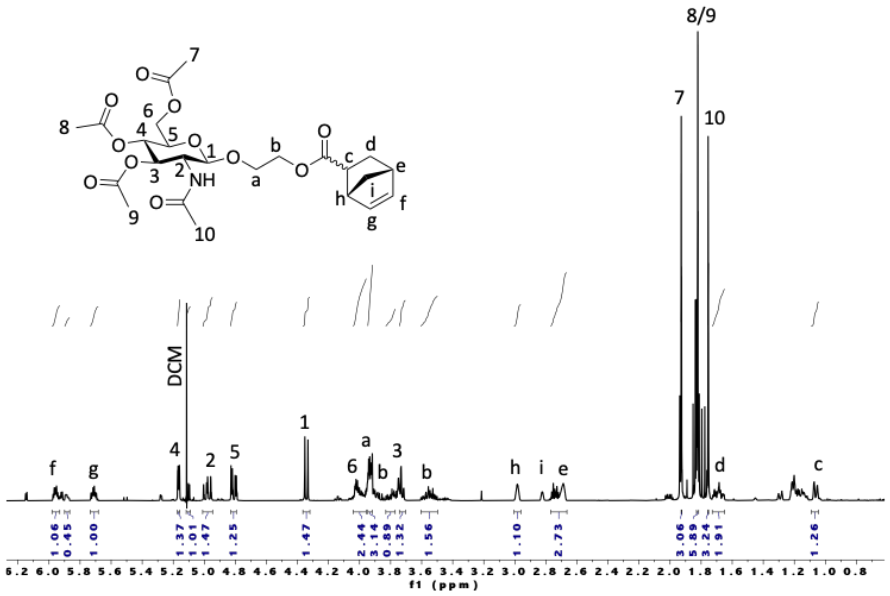


Figure S16. ^{1}H NMR spectrum of GlcNAc-**5**

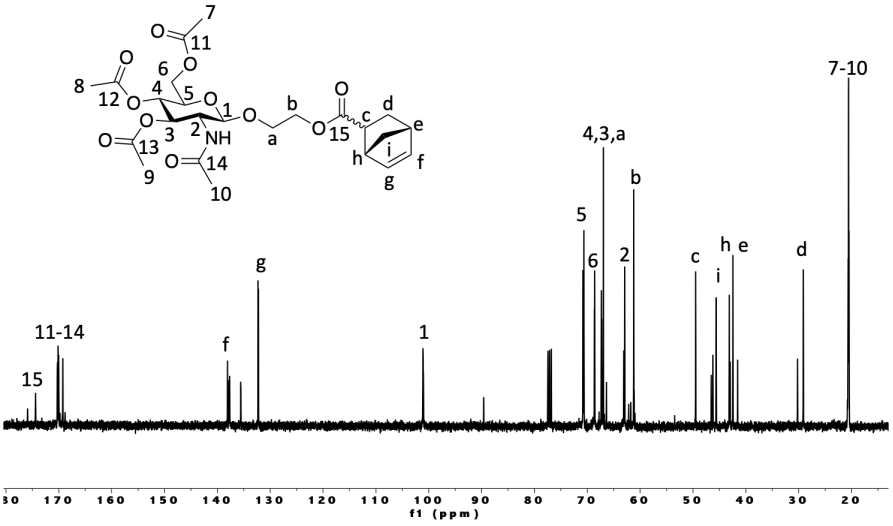


Figure S17. ^{13}C NMR spectrum of GlcNAc-**5**

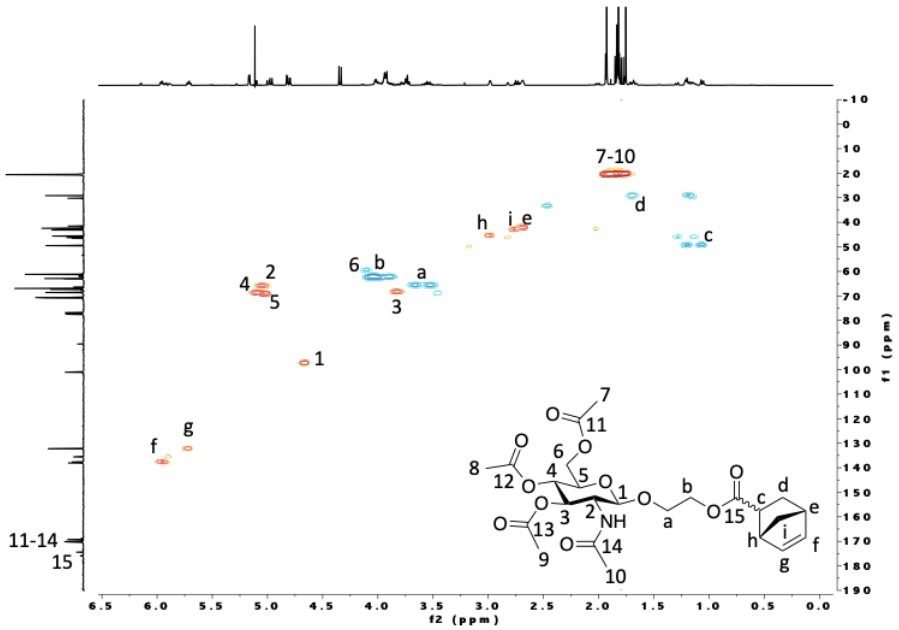
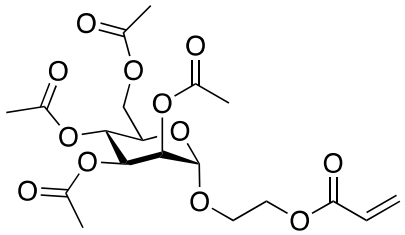


Figure S18. HSQC NMR spectrum of GlcNAc-**5**

1-*O*-Acryloyloxyethyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside (Man-**3**)



Boron trifluoride diethyl etherate (BF_3•OEt_2, 3.51 mL, 28.5 mmol) was added at a rate of 0.1 mL min^{-1} to a solution of Man-**1** (1.95 g, 5 mmol) and **2** (0.79 mL, 7.5 mmol) in 10 mL DCM under a nitrogen atmosphere and cooled to 0 °C and allowed to react for 1 hour. The solution was then warmed to 25 °C and allowed to react for 48 hours, after which point it was diluted with ~50 mL of DCM and neutralized by the addition of ~50 mL of saturated $NaHCO_3$ solution. The organic layer was then separated and washed with 1x 50 mL saturated $NaHCO_3$ solution, 2x 50 mL cold DI H_2O, and 1x 50 mL brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure to afford 1-*O*-acryloyloxyethyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside (Man-**3**). The acrylate was obtained as a clear oil and was used without further purification. ^{1}H NMR ($CDCl_3$, δ): 1.96 (s, 3H), 2.00 (s, 3H), 2.06 (s, 3H), 2.12 (s, 3H), 3.61-3.78 (m, 2H), 3.84-3.91 (m, 1H), 4.03-4.08 (m, 1H), 4.20-4.25 (m, 1H), 4.29-4.33 (m, 2H), 4.82-4.85 (m, 1H), 5.20-5.25 (m, 2H), 5.28-5.34 (m, 1H), 5.84 (dd, 1H), 6.11 (dd, 1H), 6.40 (dd, 1H). ^{13}C NMR ($CDCl_3$, δ): 20.55, 20.58, 20.60, 20.76, 62.33, 62.91, 65.93, 66.00, 68.56, 68.84, 69.33, 97.53, 127.7, 131.3, 165.8, 169.6, 169.7, 169.9, 170.5.

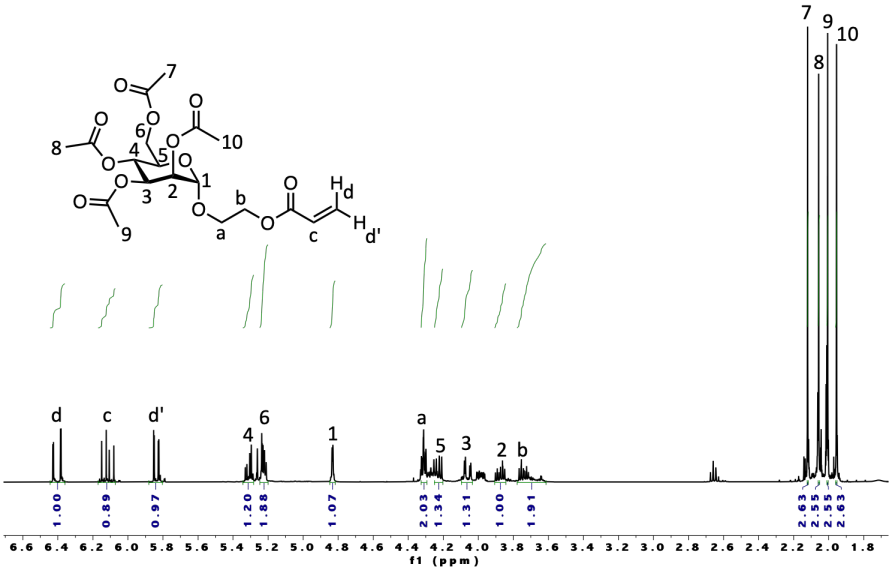


Figure S19. ^{1}H NMR spectrum of Man-**3**

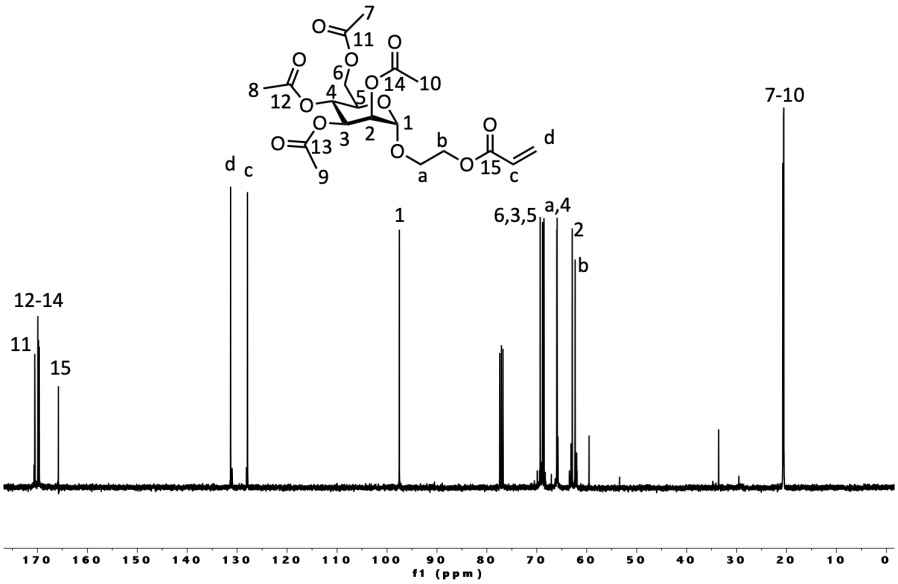


Figure S20. ^{13}C NMR spectrum of Man-**3**

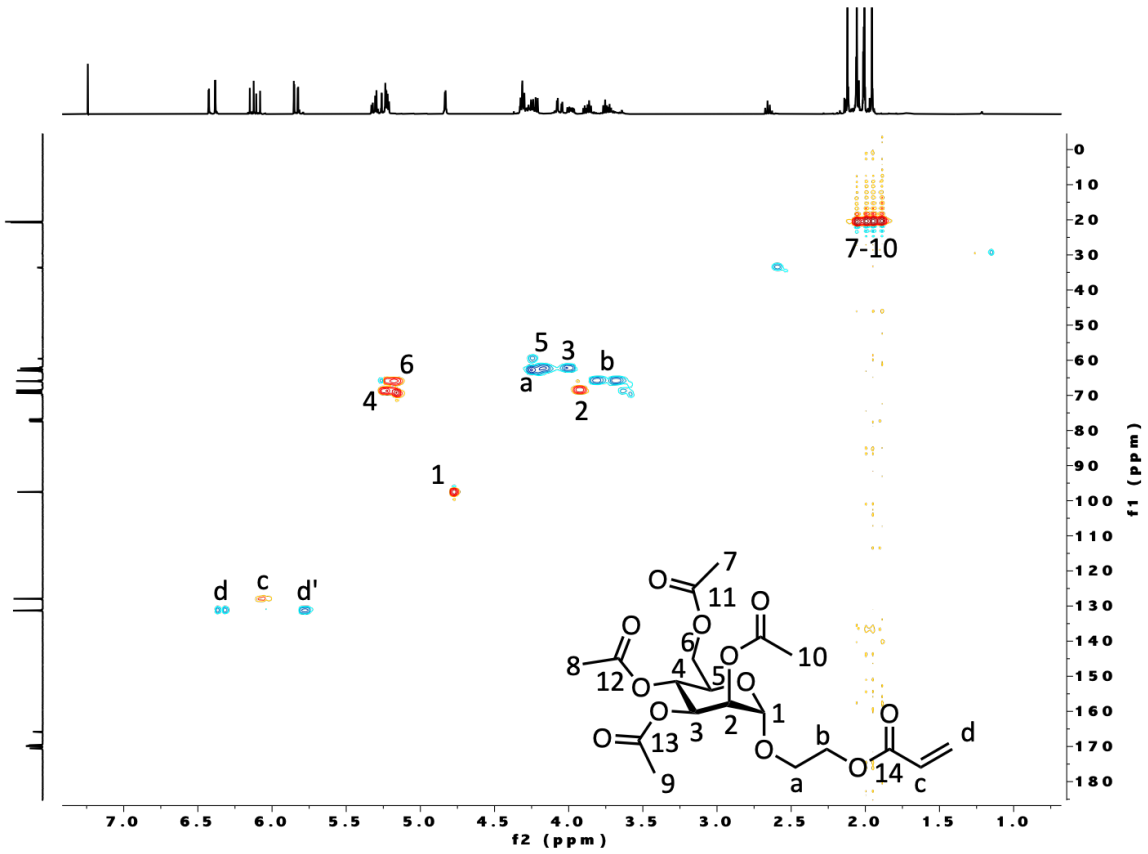
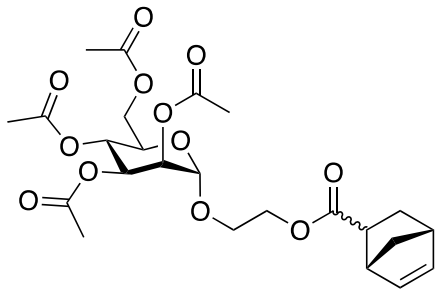


Figure S21. HSQC NMR spectrum of Man-**3**

2-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)hydroxyethyl 5-norbornene-2-carboxylate (Man-**5**)



Cyclopentadiene (0.79 mL, 9.40 mmol) was added to a solution of Man-**3** (2.00 g, 4.48 mmol) in 50 mL toluene under a nitrogen atmosphere. The mixture was heated to reflux and allowed to react overnight, after which point it was concentrated under reduced pressure, diluted in 15 mL of hexanes/DCM (2:1), and purified via flash chromatography (3 column volumes of 100% Hexanes, 3 column volumes of 100% DCM, DCM→acetone 100→97%). The solvent was removed under reduced pressure to afford 2-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)hydroxyethyl 5-norbornene-2-carboxylate (Man-**5**) as a viscous oil (1.923g, 3.76 mmol, 84%). The product was a mixture of endo/exo norbornene (67/33) that was used in polymerizations without separation. ^{1}H NMR ($CDCl_3$): 1.06-1.12 (m, 1H), 1.65-1.75 (m, 2H), 1.77 (s, 3H), 1.83 (s, 3H), 1.87 (s, 3H), 1.94 (s, 3H), 2.68-2.71 (m, 1H), 2.72-2.84 (m, 2H), 2.97-3.03 (m, 1H), 3.63-3.73 (m, 2H), 3.78-3.86 (m, 2H) 3.87-3.92 (m, 1H) 4.04-4.06 (m, 1H), 4.08-4.13 (m, 1H) 4.66-4.68 (m, 1H), 5.02-5.03 (m, 1H), 5.08-5.14 (m, 2H), 5.72-5.75 (m, 1H), 5.96-6.00 (m, 1H). ^{13}C NMR ($CDCl_3$, δ): 20.29 (s, 1C), 20.35 (s, 2C), 20.46 (s, 1C), 29.51 (d, 1C), 42.24 (s, 1C), 43.04 (d, 1C), 45.28 (d, 1C), 49.26 (d, 1C), 59.36 (s, 1C), 62.25 (s, 2C), 65.52 (s, 1C), 68.36 (s, 1C), 68.74 (s, 1C), 69.15 (s, 1C), 97.44 (d, 1C), 132.0 (d, 1C), 137.7 (s, 2C), 169.4 (s, 1C), 169.5 (s, 1C), 170.2 (s, 1C), 174.1 (d, 1C).

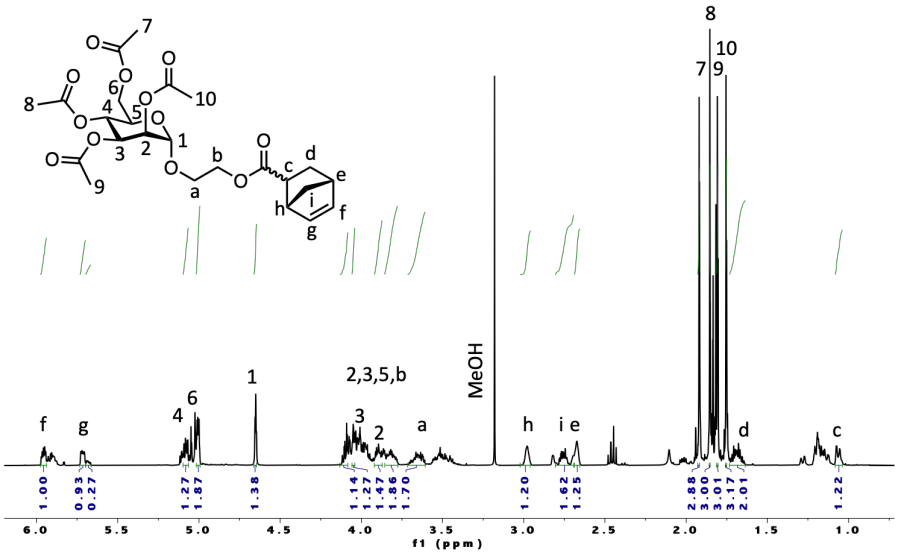


Figure S22. ^{1}H NMR spectrum of Man-**5**

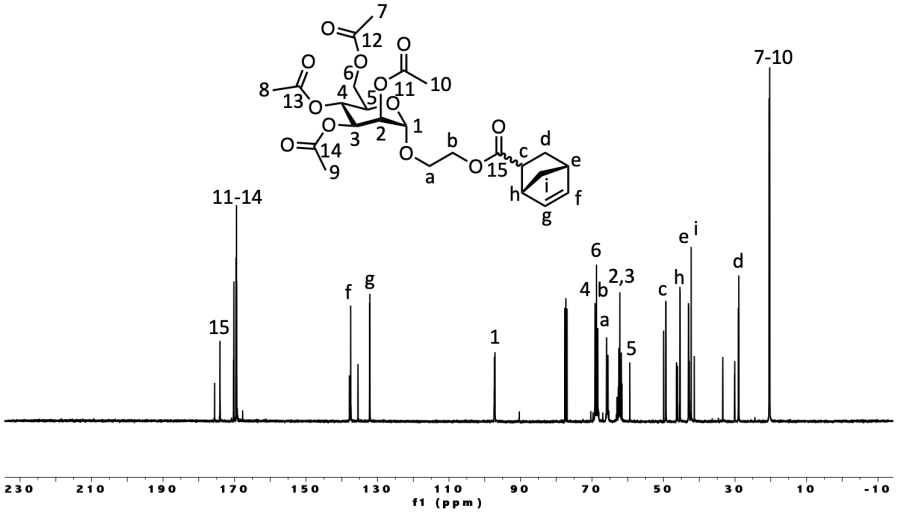


Figure S23. ^{13}C NMR spectrum of Man-**5**

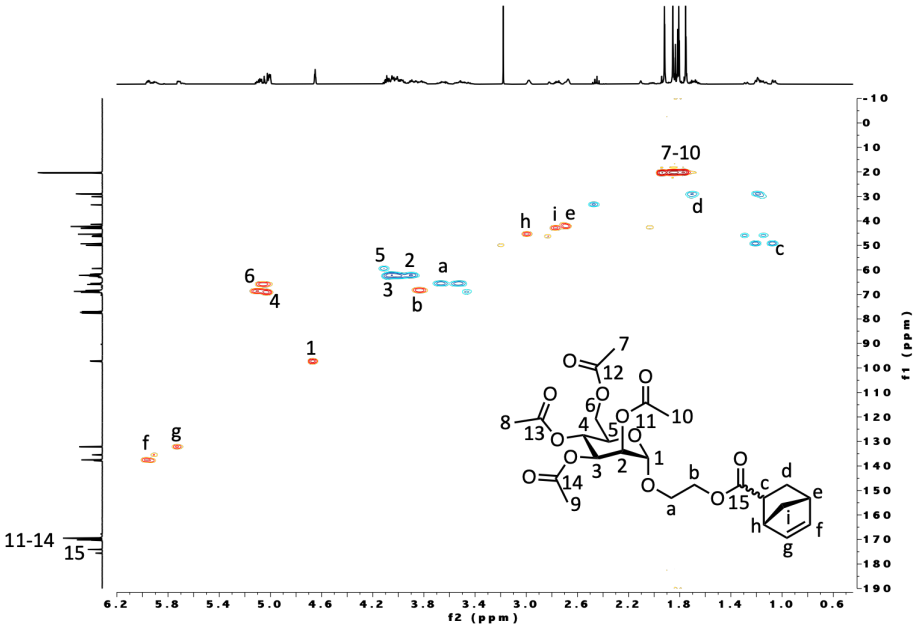
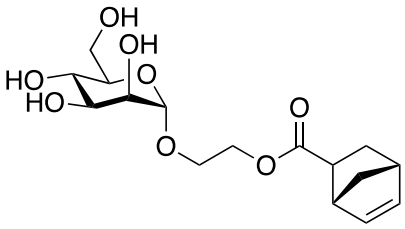


Figure S24. HSQCD NMR spectrum of Man-**5**

2-*O*-(α-D-mannopyranosyl)hydroxyethyl 5-norbornene-2-carboxylate (deacetylated Man-**5**)



1,8-Diazabicyclo(5.4.0)undec-7-ene (DBU, 0.3 mL, 2 mmol) was added to a solution of Man-**5** (0.27 g, 0.53 mmol) in 4 mL methanol. The mixture was heated to 55 °C for 2 min in a Biotage Initiator 4.1.3. Microwave Synthesizer, then neutralized to pH 7 and concentrated to afford deacetylated Man-**5** (quant.). ^{1}H NMR (DMSO-d_6): 1.27 (d, 2H), 1.88-1.34 (m, 2H), 2.49 (s, 1H), 2.84 (s, 1H), 3.58 (m, 3C), 4.00-4.20 (m, 2C), 4.37-4.78 (m, 11H), 5.88 (s, 1H), 6.15 (s, 1H). ^{13}CNMR ($CDCl_3$, δ): 29.08 (s, 1C), 42.19 (s, 1C), 42.84 (s, 1C) , 45.35 (s, 1C), 49.30 (s, 1C), 61.52 (s, 1C), 63.04 (s, 1C), 63.24 (s, 1C), 67.12 (d, 1C), 68.59 (s, 1C), 70.49 (s, 1C), 71.13 (s, 1C), 100.07 (s, 1C), 132.80 (s, 1C), 137.77 (s, 1C), 173.98 (s, 1C).

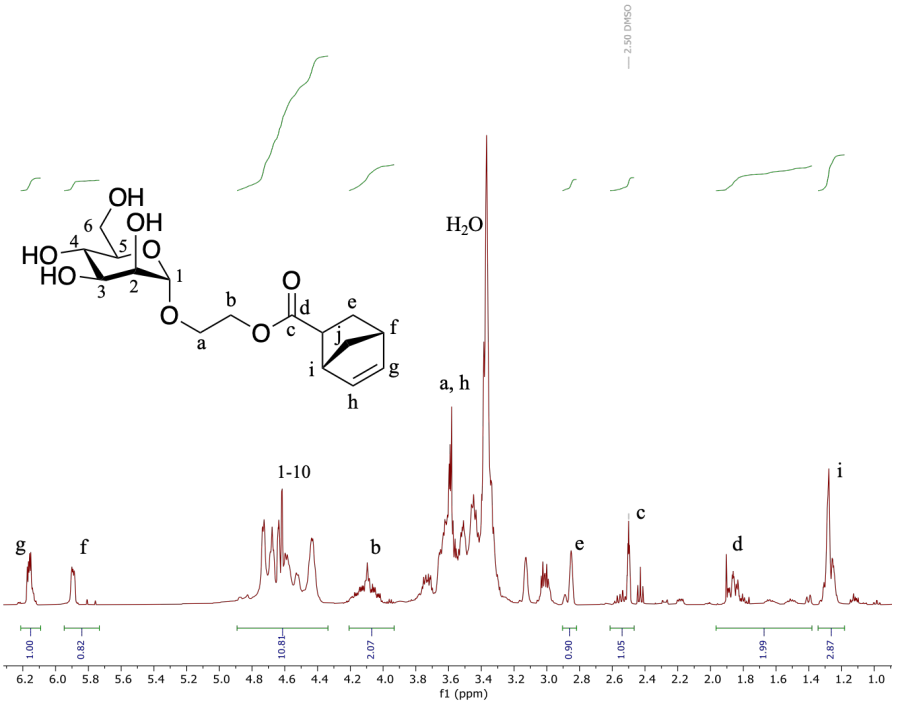


Figure S25. ^{1}H NMR spectrum of deacetylated Man-**5**

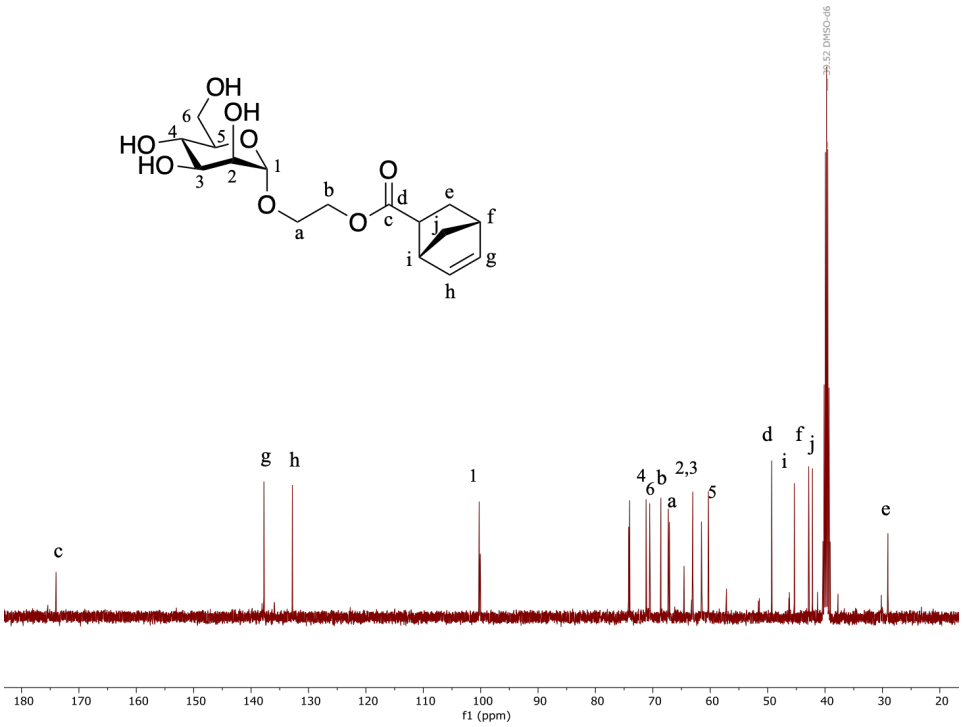


Figure S26. ^{13}CNMR spectrum of deacetylated Man-**5**

Synthesis of Glycopolymers

The general polymerization procedure is illustrated using Gal-**5**, with a targeted degree of polymerization (DP) of 100. A solution of G3 (3.55 mg, 4.88 x10^{-3} mmol, 0.001 g mL^{-1} in DCM) was added in one portion to a vigorously stirred solution of Gal-**5** (0.250 g, 0.488 mmol) in 10 mL DCM under a nitrogen atmosphere. The mixture was allowed to react for 1 h at 25 °C, after which the polymerization was terminated by the addition of ethyl vinyl ether (0.1 mL, 1.05 mmol) to afford Gal-**6**. The solution was diluted with 20 mL of DCM and passed through a silica plug. Sodium methoxide (0.25 mL, 1.09 mmol, 25 wt% in MeOH) was added to the solution. After 30 min, the pH was brought to 7 by the addition of 1 M HCl, and the solution concentrated under reduced pressure. Gal-**7** weas separated from residual sodium chloride by extraction with DMSO, which was removed prior to characterization. All polymers were prepared in an analogous fashion.

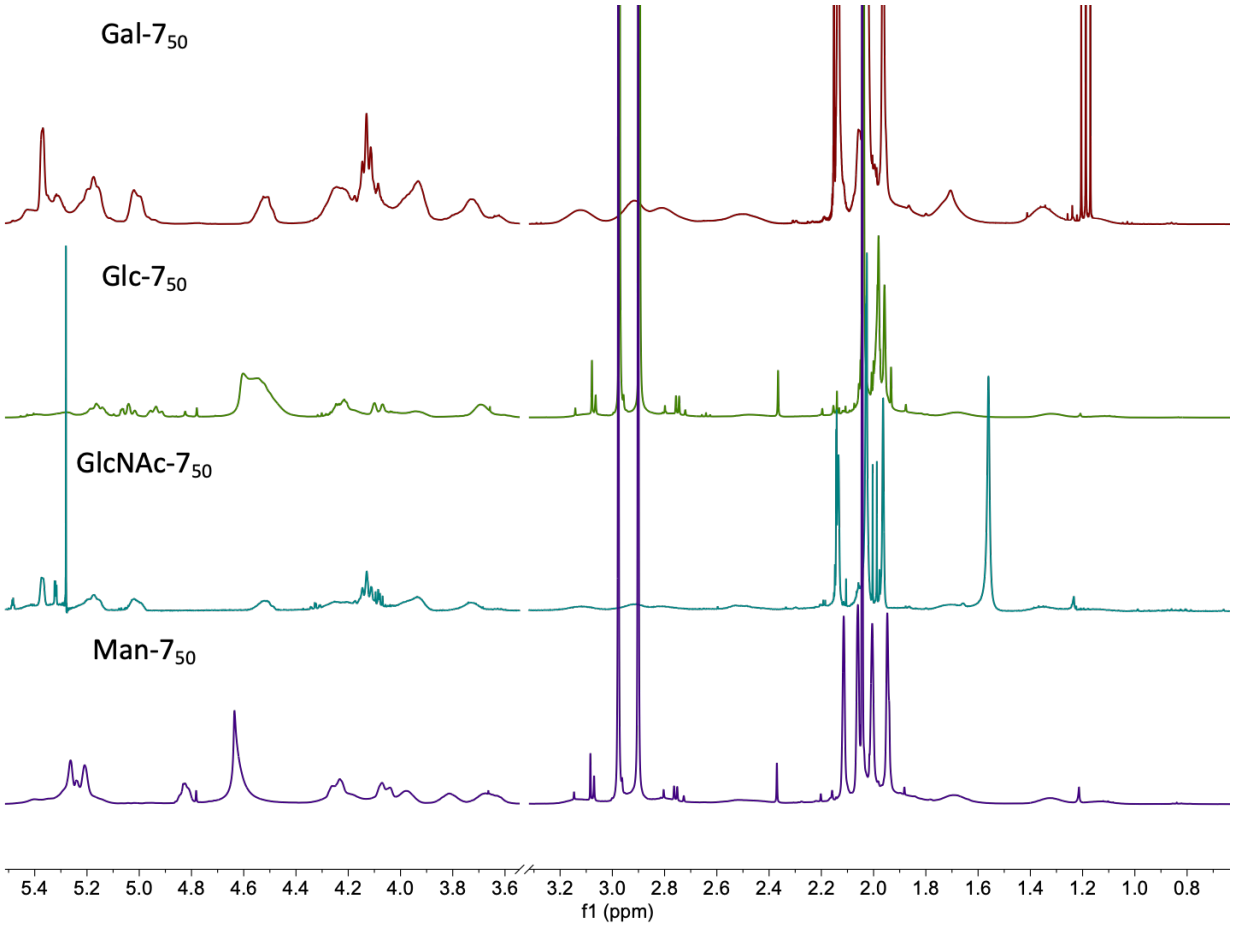


Figure S27. Representative polymer spectra for the protected glycomaterials (Gal-7_{50}, Glc-7_{50}, GlcNAc-7_{50}, and Man-7_{50})

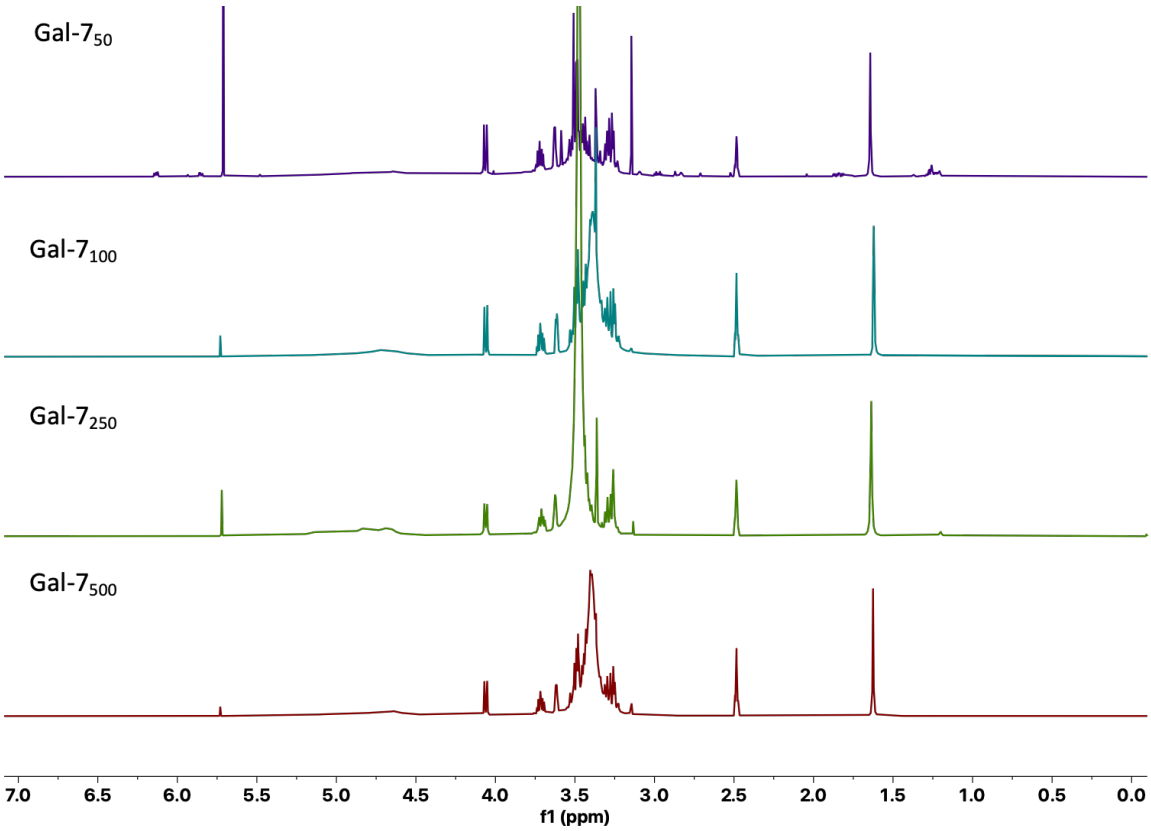


Figure S28. ^{1}H NMR spectra of deprotected galactose polymers (Gal-7)

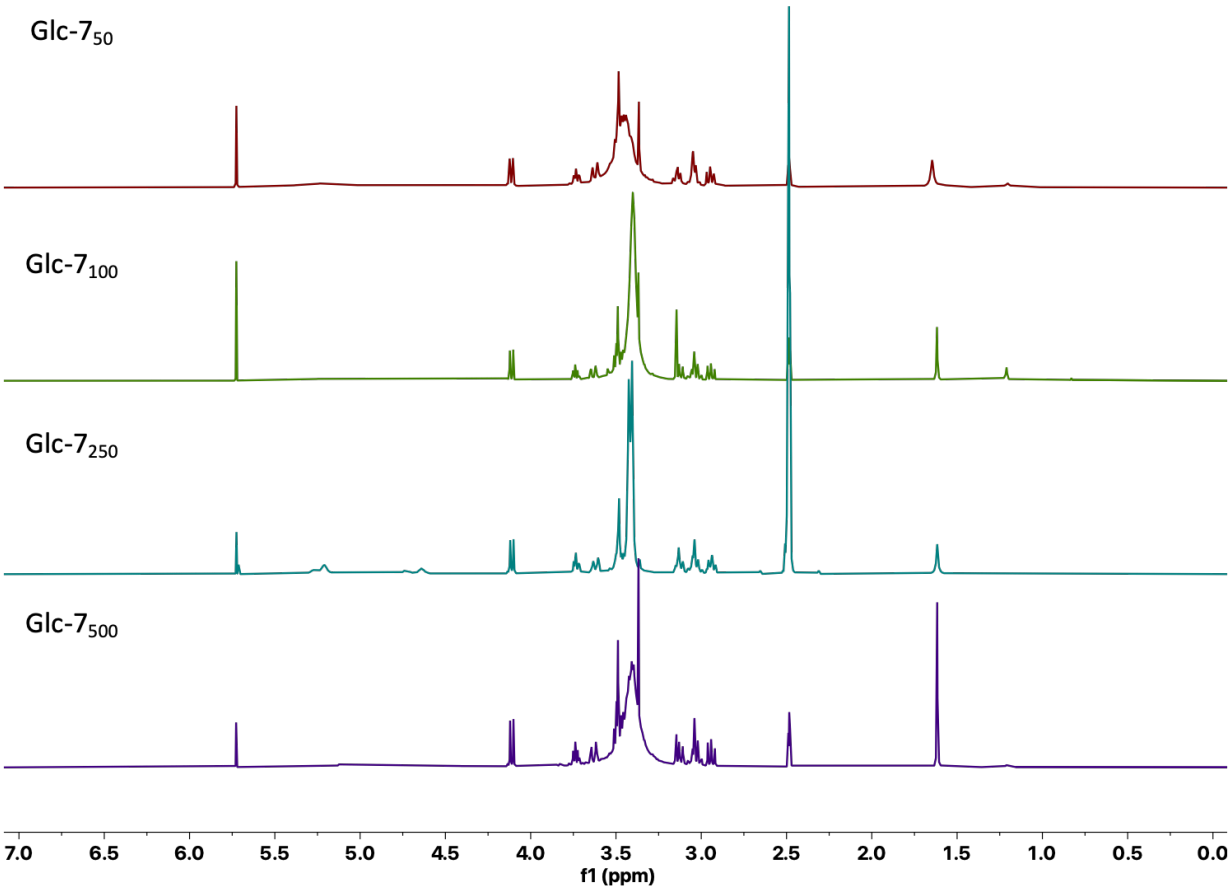


Figure S29. ^{1}H NMR spectra of deprotected glucose polymers (Glc-7)

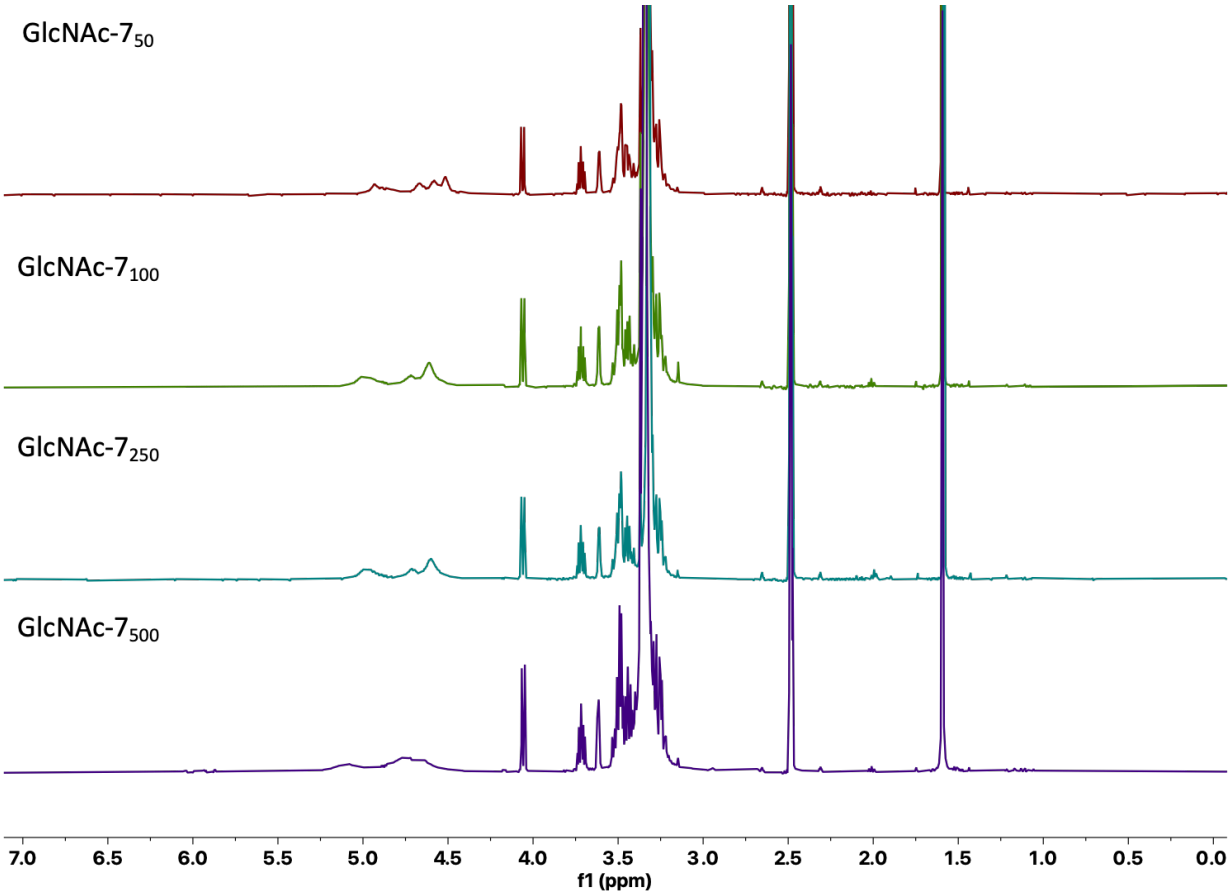


Figure S30. ^{1}H NMR spectra of deprotected *N*-acetyl glucose polymers (GlcNAc-7)

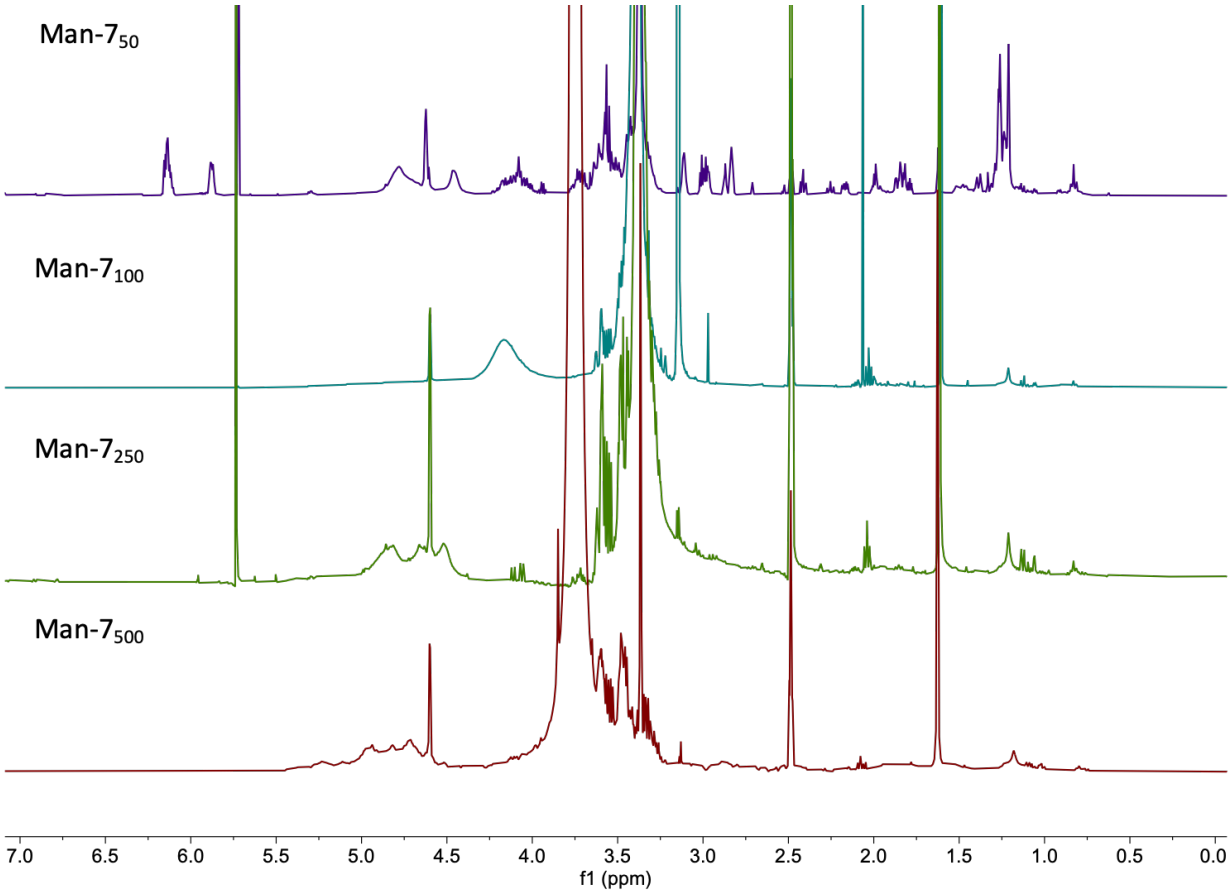


Figure S31. ^{1}H NMR spectra of deprotected mannose polymers (Man-7)

Dynamic Light Scattering

Dynamic light scattering and zeta potential measurements were conducted using a Malvern Instruments (Worchestershire, UK) Zetasizer Nano-ZS. Samples were filtered using .22 µm filters before analysis. Following a 2- minute equilibration, samples were recorded for 120 seconds and three accumulated runs were averaged to obtain the particle size distribution. The particle size distributions are reported as the intensity distribution.

A: Target DP = 50 B: Target DP = 100 C: Target DP = 250 D: Target DP = 500

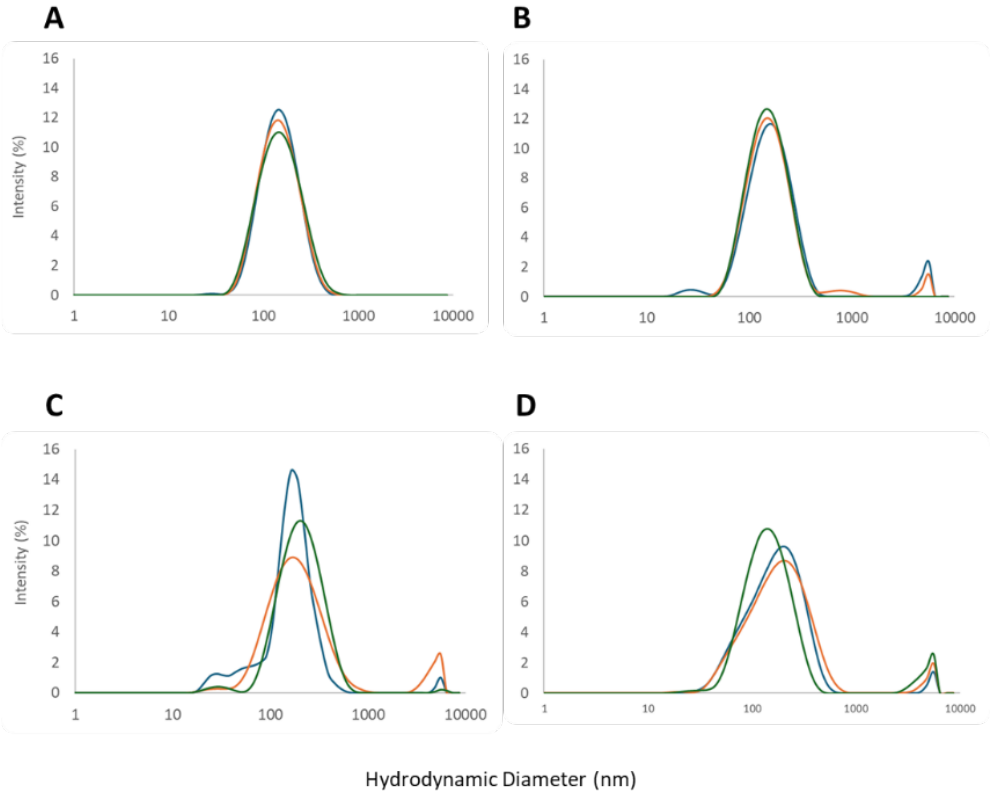


Figure S32. Histogram of hydrodynamic diameters (D_h) of (A) Man_{50}, (B) Man_{100}, (C) Man_{250} and (D) Man_{500} at 0.1 mg/mL (blue), 0.2 mg/mL (orange) and 0.4 mg/mL (green). Sizes are an average of 3 measurements.

Disk-diffusion and MIC Assays

The glycopolymers (20 μL of 100 mg mL^{-1} in DMSO) were applied to sterile discs and allowed to thoroughly dry. Linear polyethyleneimine (4 kDa) and biological grade DMSO were used as positive and negative controls, respectively. A 1 mL aliquot of an overnight culture of *E. coli* TolC and *S. aureus* NorA were used to inoculate 35 mL batches of LB broth which were incubated at 37 °C at a rate of 200 rpm for 3 h (OD = 0.4). A solution of 60 mL of 0.8% LB agar was liquefied for each organism, and 6 mL of the fresh cultures were added once the agar had cooled to 40 °C. The solutions were mixed by autopipette, and plated (~10 mL) onto previous poured petri dishes containing 1% LB agar (~20 mL). After cooling to 20 °C, the discs containing the glycopolymers and controls were applied to the plates using sterile forceps and the plates incubated at 37 °C for 18 h.

Overnight cultures of *E. coli* TolC were used to inoculate (100 μL) 5 mL of LB broth. After incubation (37 °C, 200 rpm, 4 h, OD = 0.4), the culture was back-diluted to OD = 0.004 using fresh LB broth. Polyethyleneimine was used as the positive control at the same stock concentration. Water and DMSO (vehicles) were used as negative controls in all plates. Using a stock concentration of 100 mg mL^{-1} polymers in DMSO, eleven 2-fold dilutions in DMSO were prepared. An aliquot (10 μL) of these working polymer solutions were transferred to polystyrene clear-bottomed 96-well plates in triplicate. The fresh culture of *E. coli* TolC in LB broth (190 μL) was added to each well using a multidrop dispenser, and the plates wrapped in parafilm, damp paper towels, and plastic wrap then incubated at 37 °C for 16 h.

Disk Diffusion Assays

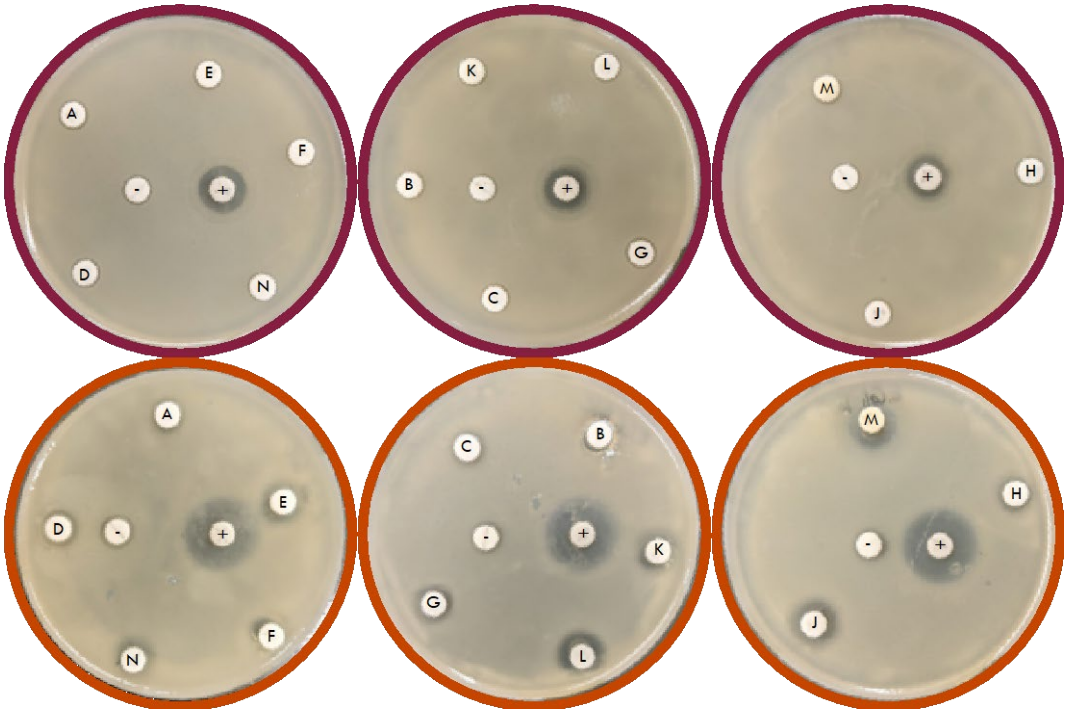


Figure S33. Disk diffusion assays of glycopolymers in S. aureus (top) and E. coli (bottom). Glycopolymers (**7**) used are shown in Table S4. DMSO was used as the negative control and polyethyleneimine as the positive control.

Table S1. Labels for disk diffusion assays

	Label			
Polymer	Gal	Glc	Man	Gal-*co*-Glc
7_{50}	A	E	J	-
7_{100}	B	F	K	N
7_{250}	C	G	L	-
7_{500}	D	H	M	-

Hemolysis Assays

The hemolysis assay was adapted from a literature protocol,[2] and was modified in the following ways: the final suspension of erythrocytes in phosphate-buffered saline (PBS) was made in double the concentration. The stock solutions of the polymers to be tested were made at 10 mg/mL, by dissolution of the polymers into PBS at 85 °C for 72 hours. To polypropylene, V-bottom 96 well plates, 100 µL of PBS was applied to all but the first row. To the first two rows, 100 µL of the polymer stock solutions were applied. The second row was then serial diluted down the remaining ten rows. The negative control contained 100 µL of PBS, and the positive control (Triton) contained 90 µL PBS and 10 µL 20% Triton solution in DI H_2O. The erythrocyte suspension was then applied to each well (100 µL). Another plate was made in the same fashion, but instead of erythrocyte suspension 100 µL of PBS was applied to each well (as a compound control for absorbance subtraction). The highest working concentration was 5 mg/mL for each polymer tested. The plates were then incubated in a 37 °C incubator for one hour. After centrifuging the plates, 100 µL of each well was carefully pipetted into polypropylene, flat-bottomed 96-well plates. These plates were then read at 450 nm in a Cytation3 BioTek Imaging Reader. After subtracting the average compound controls and averaging negative control absorbances, the absorbance values were normalized to the average positive control absorbance values, multiplied by 100, and averaged, giving the average percent lysis for each concentration of polymer.

Table S2. Polymer HC_{10}s

	HC_{10} (mg mL^{-1})
	Man
Monomer	>5.0
7$_{50}$	>5.0
7$_{100}$	>5.0
7$_{250}$	2.5-5.0
7$_{500}$	2.5-5.0
PEI	>5.0

MBC:MIC assay

The MBC:MIC assay was performed according to literature protocol.[4] Stock solutions of the mannose containing polymers (100 mg/mL), serial dilutions, and bacteria application and growth were prepared as per the MIC assay section From the MIC wells and the next two highest concentrations, 100 µL was taken and plated on Luria-Bertani broth agar petri dishes. The MBC was determined as the highest concentration that showed no colony formation after incubation of the petri dishes at 37 °C for 48 h.

Table S3. MBC:MIC comparison of mannose containing polymers

	Man-**7** MBC	Man-**7** MIC
Monomer	>5	5
DP = 50	>5	2.5
DP = 100	>5	2.5
DP = 250	5	1.25
DP = 500	5	1.25

Mannose addition assay

To further elucidate the function of mannose in the antibacterial effects of the polymers, bacteria was incubated in the presence of the polymers and excess mannose. Serial dilutions were performed as in the MIC assay above, and then stock solutions containing either sterile water (control), 50 mg/mL mannose or 500 mg/mL mannose (20 μL) were applied to each well followed by application of bacterial suspension in LB broth medium (0.004 optical density, 170 μL). The plates were then incubated at 37 °C for 20 h, and the MIC was visually determined.

Table S4. MIC of mannose containing polymer in the presence of mannose at 5 mg/mL and 50 mg/mL. MICs reported in mg/mL.

	Man-**7** , 5 mg/mL	Man-**7** , 50 mg/mL
Monomer	>5	>5
DP = 50	>5	>5
DP = 100	5	>5
DP = 250	5	>5
DP = 500	2.5	>5

References:

1. Liu, J.; Gao, A. X.; Johnson, J. A., Particles Without a Box: Brush-first Synthesis of Photodegradable PEG Star Polymers Under Ambient Conditions. *J. Vis. Exp.* **2013**, (80).
2. Evans, B. C.; Nelson, C. E.; Yu, S. S.; Beavers, K. R.; Kim, A. J.; Li, H.; Nelson, H. M.; Giorgio, T. D.; Duvall, C. L., *Ex Vivo* Red Blood Cell Hemolysis Assay for the Evaluation of pH-responsive Endosomolytic Agents for Cytosolic Delivery of Biomacromolecular Drugs. *J. Vis. Exp.* **2013**, *73*.
3. Li, C.; Zhong, D.; Zhang, Y.; Tuo, W.; Li, N.; Wang, Q.; Liu, Z.; Xue, W., The Effect of the Gene Carrier Material Polyethyleneimine on the Structure and Function of Human Red Blood Cells *in vitro*. *J. Mater. Chem. B* **2013**, *1*, 1885-1893.
4. CLSI: Performance Standards for Antimicrobial Susceptibility Testing. 29th Ed. CLSI supplement M100. Wayne, PA: Clinical and Laboratory Standards Institute; 2019.