SUPPORTING INFORMATION

Fucose, Mannose and β-N-Acetylglucosamine Glycopolymers Initiate the Mouse Sperm Acrosome Reaction Through Convergent Signaling Pathways

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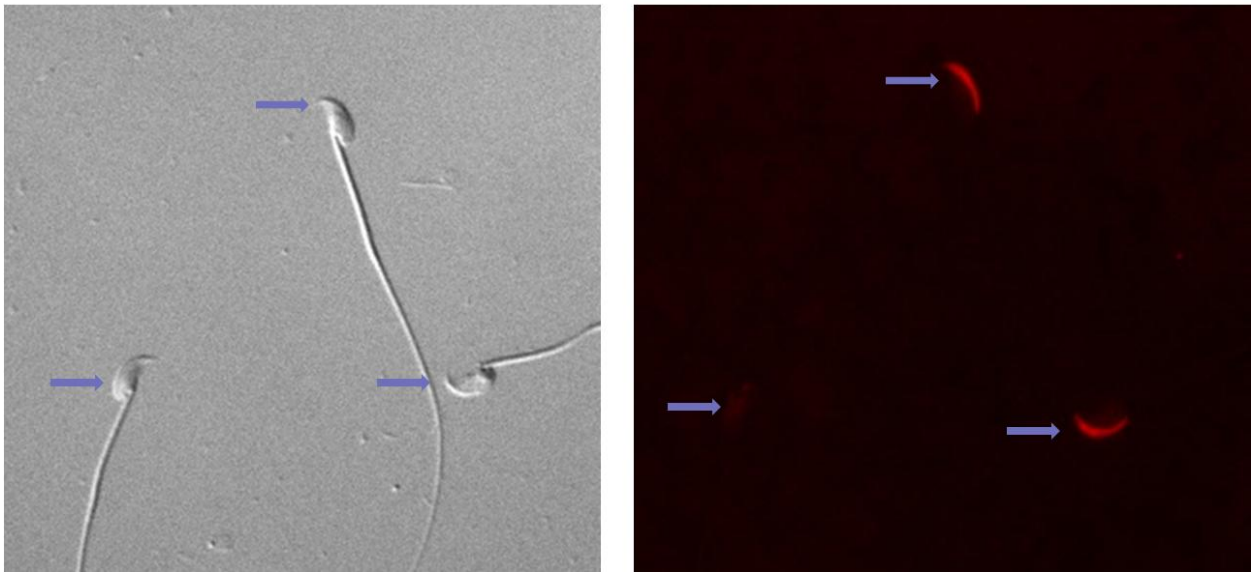


DIC **Cy3.5**

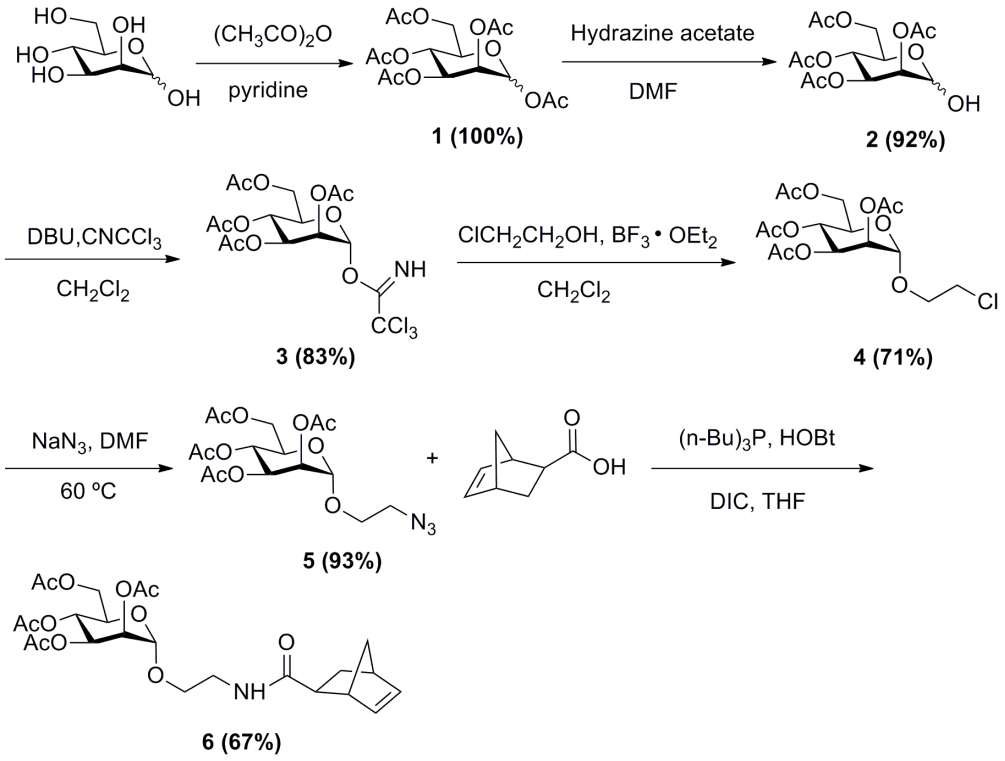
Figure 1 Sperm acrosome reaction assay. Left: Differential interference contrast (DIC) image. Right: Fluorescence image with Cy3.5 (585 nm). Sperm that displayed continuous red fluorescence along their acrosomal arcs were scored as acrosome-intact; those that displayed no red or punctuate fluorescence were scored as acrosome-reacted.

Methods for preparation of glycopolymers

General Methods and Materials. Sugars and other chemicals used were purchased from Sigma-Aldrich (Milwaukee, WI) or Fisher Scientific, Inc. (Springfield, NJ). CH_2Cl_2, CH_3OH, THF and Et_2O were purified with a pushstill solvent dispensing system (Pure Process Technology LLC, Nashua, NH); pyridine, hexane, pentane were used without further purification. $(H_2IMes)(3\text{-}BrPyr)_2Cl_2Ru{=}CHPh$, **32**, was prepared according to the literature.[1] All reactions

were carried out under an N_2 atmosphere in oven-dried glassware unless otherwise specified. Moisture and oxygen-sensitive reagents were handled in an N_2 filled dry box.

Analytical thin layer chromatography (TLC) was performed on precoated silica gel plates (60F254). TLC spots were detected by UV and by staining with 10% phosphomolybdic acid (PMA) in ethanol. The usual workup mentioned in the following syntheses was three washes of the organic layer with 5% aq $NaHCO_3$, followed by three washes with 1 N aq HCl, and drying of the organic layer over Na_2SO_4. All intermediates and monomers were purified by Combiflash personal flash chromatography system (Teledyne Isco, NE), and analyzed on Inova500, Inova600, Bruker400 and Bruker 500 MHz NMR spectrometers. ^{1}H-NMR spectra are reported as chemical shift in parts per million (multiplicity, coupling constant in Hz, integration) and assumed to be first order. The molecular weight of the polymers was assessed by gel permeation chromatography (Phenogel 5 μ Linear(2) GPC column, Phenomenex, CA) and light scattering (Brookhaven Instruments) eluting with THF.



Scheme 1. Synthesis of NB-mannose.

Penta-acetyl-D-mannopyranose 1. To a solution of D-mannopyranose (16.65 mmol, 3 g) in pyridine (64 mL) was added Ac_2O (333.04 mmol, 32 mL).[2] After stirring 24 h at rt the mixture was concentrated. The residue was diluted with CH_2Cl_2, followed by workup and concentrated to yield **1** as a colorless oil (6.49 g, 100%). The product is a mixture of α and β diastereomers (α:β = 8:1). The spectrum for the desired α isomer was the same as reported previously.[3] α isomer ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.11 (d, *J* = 2.0 Hz, 1H), 5.38 – 5.35 (m, 2H), 5.28 (t, *J* = 2.2 Hz, 1H), 4.30 (dd, *J* = 12.4, 5.0 Hz, 1H), 4.12 (dd, *J* = 12.4, 2.5 Hz, 1H), 4.09 – 4.03 (m, 1H), 2.19 (d, *J* = 4.1 Hz, 6H), 2.11 (s, 3H), 2.07 (s, 3H), 2.03 (d, *J* = 0.8 Hz, 3H).

2,3,4,6-tetra-*O*-acetyl-D-mannopyranose 2. To a solution of compound **1** (5.02 mmol, 1.96 g) in dry DMF (60 mL) was added hydrazine acetate (5.53 mmol, 0.51 g).[2] After stirring for 2 h at 40 °C, the mixture was concentrated. The residue was diluted with EtOAc, and washed with cold brine, followed by the usual workup, and concentrated to yield **2** as a colorless oil (1.37 g, 92%). The product is a mixture of α and β diastereomers (α:β = 8:1). The spectrum for the desired α isomer was the same as reported previously.[4] α isomer ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.44 (dd, *J* = 10.0, 3.4 Hz, 1H), 5.36 – 5.25 (m, 3H), 4.31 – 4.22 (m, 2H), 4.19 – 4.11 (m, 1H), 3.32 (d, *J* = 4.0 Hz, 1H), 2.18 (s, 3H), 2.12 (s, 3H), 2.07 (s, 3H), 2.02 (s, 3H).

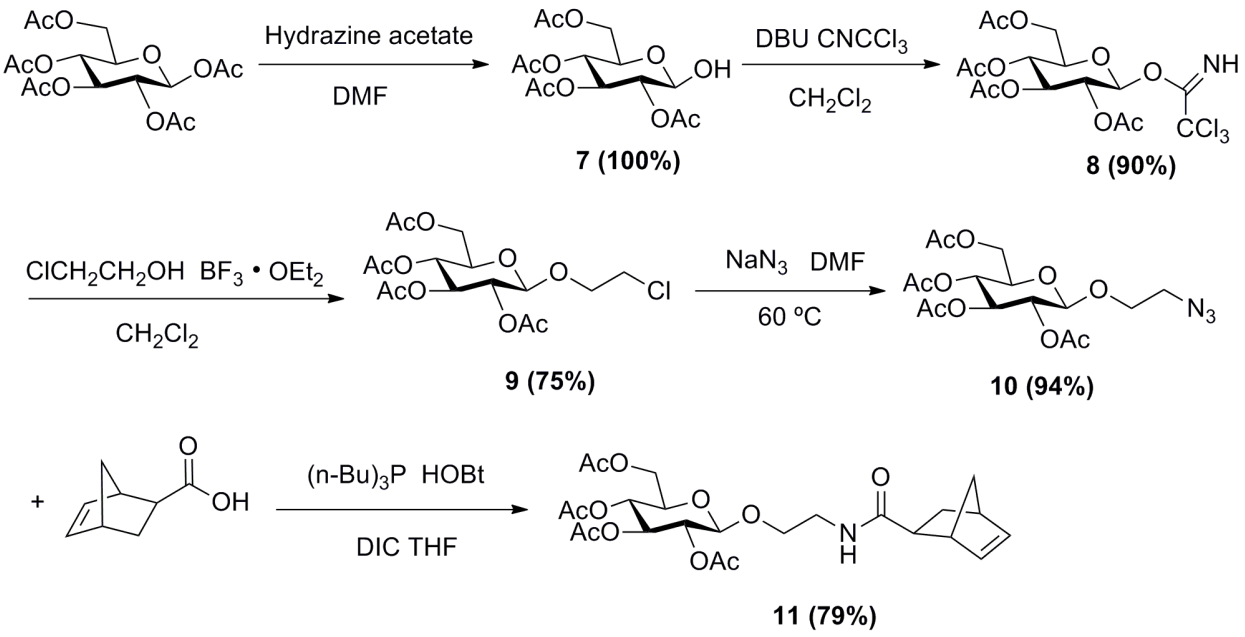
2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl trichloroacetimidate 3. To a solution of compound **2** (1.17 mmol, 0.41 g) in dry CH_2Cl_2 (25 mL) was added trichloroacetonitrile (1.17 mmol, 1.18 mL) and DBU (0.12 mmol, 18 μL).[2] After stirring for 3 h at rt, the mixture was concentrated. The crude product was purified by Combiflash (EtOAc:hexane = 3:7, v/v) to yield **3** as a colorless oil (0.40 g, 83%). The spectrum for compound **3** was the same as reported previously for the α isomer.[5] ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.43 (dd, *J* = 10.1, 3.4 Hz, 1H), 5.36 – 5.24 (m, 3H), 4.32 – 4.19 (m, 2H), 4.18 – 4.11 (m, 1H), 2.92 – 2.82 (m, 1H), 2.16 (s, 3H), 2.11 (s, 3H), 2.05 (s, 3H), 2.00 (s, 3H).

1-Chloroethyl-2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside 4. To a cooled solution of compound **3** (1.97 mmol, 0.97 g) and 2-chloroethanol (19.7 mmol, 1.32 ml) in dry CH_2Cl_2 (15 mL) was added BF_3-etherate (0.39 mmol, 36.5 μL).[6] The solution was stirred for 3 h at -80 °C and followed by the usual workup. The crude product was concentrated and purified by Combiflash (EtOAc:hexane = 4:6, v/v) to yield **4** as a white solid (0.60 g, 71%). The spectrum for compound **4** was the same as reported previously.[6] ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.35 (dd, *J*

= 10.1, 3.4 Hz, 1H), 5.31 – 5.25 (m, 2H), 4.87 (d, *J* = 1.8 Hz, 1H), 4.27 (dd, *J* = 12.2, 5.4 Hz, 1H), 4.17 – 4.09 (m, 2H), 3.92 (dt, *J* = 11.5, 5.8 Hz, 1H), 3.82 (dt, *J* = 11.0, 5.4 Hz, 1H), 3.68 (t, *J* = 5.7 Hz, 2H), 2.16 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 2.00 (s, 3H).

1-Azidoethyl-2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside 5. To a solution of compound **4** (1.02 mmol, 0.42 g) in dry DMSO (10 mL) was added sodium azide (10.2 mmol, 0.67 g). Then the reaction mixture was stirred for 72 h at 60 °C.[6] After the usual workup, the mixture was concentrated and purified by Combiflash (EtOAc:hexane = 4:6, v/v) to yield **5** as a white solid (0.35 g, 93%). The spectrum for compound **5** was the same as reported previously.[6] ^{1}H NMR (600 MHz, $CDCl_3$) : δ 5.40 – 5.33 (m, 1H), 5.32 – 5.25 (m, 2H), 4.87 (d, *J* = 1.8 Hz, 1H), 4.29 (ddd, *J* = 12.3, 5.4, 1.3 Hz, 1H), 4.17 – 4.09 (m, 1H), 4.06 – 4.01 (m, 1H), 3.91 – 3.82 (m, 1H), 3.67 (m, 1H), 3.53 – 3.40 (m, 2H), 2.16 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 1.99 (s, 3H).

1-Aminoethyl-2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl bicyclo[2.2.1]hept-5-ene-exo-2-carboxamide 6. Compound **5** (0.22 mmol, 91 mg) and *exo*-5-norbornenecarboxylic acid (0.39 mmol, 54.2 mg) were combined with HOBt • H_2O (0.39mmol, 60.2 mg) in a round-bottomed flask and dried for more than 1 h in vacuo. This mixture was dissolved in dry THF under N_2 and cooled to 0 °C. Then N,N-diisopropylcarbodiimide (0.39 mmol, 49.6 mg) was added and the solution was stirred for 10 min, followed by the addition of tri-*n*-butylphosphine (0.39 mmol, 79.5 mg) and stirring for 1 h at 0 °C. Then the reaction mixture was stirred for 15 h at rt.[7] After the usual workup, the crude was concentrated and purified by Combiflash (acetone:CH_2Cl_2 = 1:4, v/v) to yield **6** as colorless oil (74 mg, 67%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.16 (ddd, *J* = 8.9, 5.5, 2.9 Hz, 2H), 5.92 (s, 1H), 5.36 (dt, *J* = 10.0, 3.8 Hz, 1H), 5.31 – 5.25 (m, 2H), 4.84 (d, *J* = 1.8 Hz, 1H), 4.28 (ddd, *J* = 12.3, 5.7, 2.8 Hz, 1H), 4.13 (dd, *J* = 12.3, 2.5 Hz, 1H), 4.02 – 3.95 (m, 1H), 3.86 – 3.78 (m, 1H), 3.56 (ddd, *J* = 13.4, 7.4, 4.3 Hz, 2H), 3.48 (d, *J* = 6.4 Hz, 1H), 2.95 (s, 2H), 2.18 (s, 3H), 2.11 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 1.99 – 1.89 (m, 1H), 1.72 (t, *J* = 7.5 Hz, 1H), 1.36 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 178.53, 178.44, 173.25, 172.71, 172.28, 140.86, 138.62, 100.28, 79.97, 72.01, 71.66, 71.34, 70.08, 68.82, 65.12, 49.92, 48.94, 47.28, 44.24, 41.73, 33.24, 33.06, 23.51, 23.35. HRMS (ESI) Calcd for $C_{24}H_{33}NO_{11}$ $[M+H]^+$ 512.2127; found 512.2164.



Scheme 2. Synthesis of NB-glucose.

2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranose 7. Compound **7** was synthesized following the same procedure to prepare **2**, and the spectrum for compound **7** was the same as reported previously.[8] Yield: 100%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.53 (td, *J* = 9.8, 1.5 Hz, 1H), 5.46 (t, *J* = 3.7 Hz, 1H), 5.12 – 5.04 (m, 1H), 4.94 – 4.83 (m, 1H), 4.29 – 4.20 (m, 2H), 4.17 – 4.08 (m, 1H), 2.93 – 2.89 (m, 1H), 2.12 – 2.06 (d, *J* = 10 Hz, 6H), 2.02 (d, *J* = 10.7 Hz, 6H).

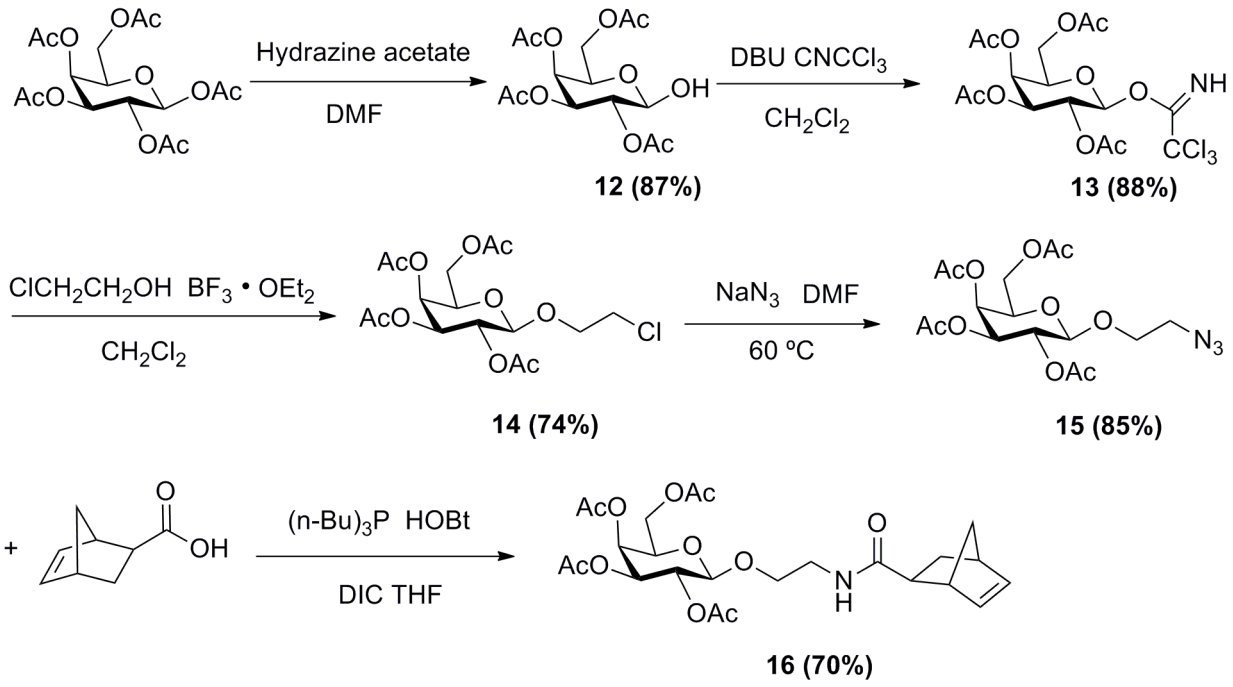
2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl trichloroacetimidate 8. Compound **8** was synthesized following the same procedure to prepare **3**, and the spectrum for compound **8** was the same as reported previously.[8] Yield: 90%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.69 (s, 1H), 6.56 (d, *J* = 3.7 Hz, 1H), 5.57 (t, *J* = 9.9 Hz, 1H), 5.18 (t, *J* = 9.9 Hz, 1H), 5.14 (dd, *J* = 10.2, 3.7 Hz, 1H), 4.27 (dd, *J* = 12.4, 4.2 Hz, 1H), 4.22 (ddd, *J* = 10.3, 4.2, 2.1 Hz, 1H), 4.13 (dd, *J* = 12.5, 2.2 Hz, 1H), 2.08 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H).

1-Chloroethyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside 9. Compound **9** was synthesized following the same procedure to prepare **4**, and the spectrum for compound **9** was the same as reported previously.[9] Yield: 75%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.21 (dd, *J* = 10.1, 9.0 Hz, 1H), 5.08 (t, *J* = 9.7 Hz, 1H), 5.04 – 4.98 (m, 1H), 4.57 (dd, *J* = 8.1, 1.1 Hz, 1H), 4.26 (dd, *J* = 12.4, 4.8 Hz, 1H), 4.15 (dd, *J* = 12.3, 2.4 Hz, 1H), 4.09 (dt, *J* = 10.8, 5.2 Hz, 1H), 3.80 – 3.73 (m, 1H),

3.71 (ddd, *J* = 9.9, 4.8, 2.4 Hz, 1H), 3.65 – 3.59 (m, 2H), 2.09 (d, *J* = 1.2 Hz, 3H), 2.06 (d, *J* = 1.1 Hz, 3H), 2.02 (s, 3H), 2.00 (d, *J* = 1.0 Hz, 3H).

1-Azidoethyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside 10. Compound **10** was synthesized following the same procedure to prepare **5**, and the spectrum for compound **10** was the same as reported previously.[10] Yield: 94%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.20 (td, *J* = 9.5, 0.9 Hz, 1H), 5.12 – 5.05 (m, 1H), 5.00 (ddd, *J* = 9.4, 8.0, 1.0 Hz, 1H), 4.59 (dd, *J* = 7.9, 0.9 Hz, 1H), 4.28 – 4.21 (m, 1H), 4.18 – 4.11 (m, 1H), 4.06 – 3.98 (m, 1H), 3.75 – 3.64 (m, 2H), 3.53 – 3.43 (m, 1H), 3.28 (dt, *J* = 13.4, 4.1 Hz, 1H), 2.07 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.99 (s, 3H).

1-Aminoethyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl bicyclo[2.2.1]hept-5-ene-exo-2-carboxamide 11. Compound **11** was synthesized following the same procedure to prepare **6**. Yield: 79%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.14 (dt, *J* = 5.2, 2.4 Hz, 1H), 6.09 (dt, *J* = 5.8, 3.0 Hz, 1H), 5.91 (s, 1H), 5.21 (t, *J* = 9.5 Hz, 1H), 5.07 (td, *J* = 9.7, 2.4 Hz, 1H), 4.99 (dd, *J* = 9.6, 8.0 Hz, 1H), 4.51 (dd, *J* = 8.0, 1.6 Hz, 1H), 4.26 (ddd, *J* = 12.3, 7.4, 4.9 Hz, 1H), 4.14 (dt, *J* = 12.4, 2.4 Hz, 1H), 3.89 – 3.80 (m, 1H), 3.71 (dtd, *J* = 10.2, 5.1, 1.7 Hz, 2H), 3.46 (t, *J* = 5.6 Hz, 2H), 2.91 (dt, *J* = 3.7, 1.8 Hz, 2H), 2.08 (d, *J* = 1.9 Hz, 3H), 2.05 (d, *J* = 9.6 Hz, 3H), 2.03 (s, 3H), 2.01 (d, *J* = 1.0 Hz, 3H), 1.93 – 1.87 (m, 1H), 1.70 (dt, *J* = 8.6, 2.9 Hz, 1H), 1.32 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 178.38, 173.19, 172.78, 172.05, 159.74, 140.92, 138.60, 103.55, 75.32, 74.60, 74.01, 71.91, 70.92, 64.48, 49.83, 48.99, 48.92, 47.25, 44.60, 44.21, 41.91, 33.09, 26.16, 23.30. HRMS (ESI) Calcd for $C_{24}H_{33}NO_{11}$ $[M+H]^+$ 512.2127; found 512.2180.



Scheme 3. Synthesis of NB-galactose.

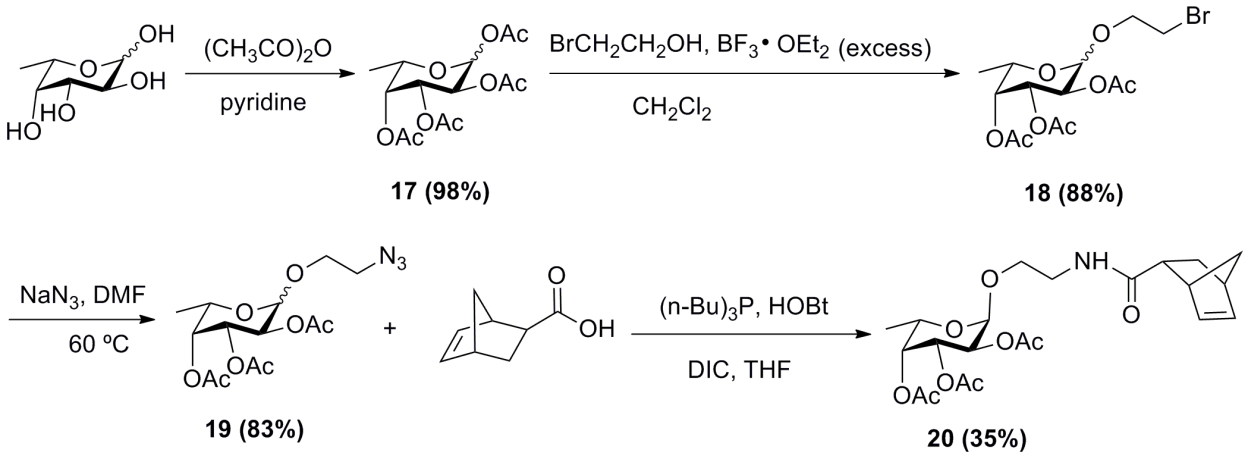
2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranose 12. Compound **12** was synthesized following the same procedure to prepare **2**, and the spectrum for compound **12** was the same as reported previously.[8] Yield: 87%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.52 (t, *J* = 3.5 Hz, 1H), 5.44 – 5.39 (m, 1H), 5.17 (dd, *J* = 10.9, 3.6 Hz, 1H), 5.07 (dd, *J* = 3.4, 2.2 Hz, 1H), 4.47 (t, *J* = 6.6 Hz, 1H), 4.18 – 4.05 (m, 3H), 2.89 (s, 1H), 2.15 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 1.99 (s, 3H).

2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl trichloroacetimidate 13. Compound **13** was synthesized following the same procedure to prepare **3**, and the spectrum for compound **13** was the same as reported previously.[8] Yield: 88%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.66 (s, 1H), 6.60 (d, *J* = 3.6 Hz, 1H), 5.56 (dd, *J* = 3.2, 1.3 Hz, 1H), 5.45 – 5.34 (m, 2H), 4.48 – 4.40 (m, 1H), 4.17 (dd, *J* = 11.3, 6.6 Hz, 1H), 4.08 (dd, *J* = 11.4, 6.6 Hz, 1H), 2.16 (s, 3H), 2.03 – 2.01 (m, 9H).

1-Chloroethyl-2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside 14. Compound **14** was synthesized following the same procedure to prepare **4**, and the spectrum for compound **14** was the same as reported previously.[6] Yield: 74%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.43 – 5.37 (m, 1H), 5.23 (ddd, J = 10.2, 7.9, 1.5 Hz, 1H), 5.03 (ddd, J = 10.5, 3.5, 1.3 Hz, 1H), 4.54 (dd, J = 7.8, 1.3 Hz, 1H), 4.22 – 4.07 (m, 3H), 3.92 (ddd, J = 7.9, 6.0, 1.5 Hz, 1H), 3.77 (dtd, J = 11.1, 6.5, 1.4 Hz, 1H), 3.63 (ddd, J = 6.5, 5.0, 1.4 Hz, 2H), 2.15 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 1.99 (s, 3H).

1-Azidoethyl-2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside 15. Compound **15** was synthesized following the same procedure to prepare **5**, and the spectrum for compound **15** was the same as reported previously.[6] Yield: 85%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.39 (dd, *J* = 3.4, 1.3 Hz, 1H), 5.24 (dd, *J* = 10.5, 7.9 Hz, 1H), 5.02 (dd, *J* = 10.4, 3.4 Hz, 1H), 4.56 (d, *J* = 7.9 Hz, 1H), 4.23 – 4.09 (m, 2H), 4.04 (m, 1H), 3.92 (td, *J* = 6.6, 1.3 Hz, 1H), 3.69 (ddd, *J* = 10.7, 8.4, 3.4 Hz, 1H), 3.50 (ddd, *J* = 13.5, 8.5, 3.6 Hz, 1H), 3.30 (ddd, *J* = 13.4, 4.8, 3.4 Hz, 1H), 2.15 (s, 3H), 2.05 (d, *J* = 8.9 Hz, 6H), 1.98 (s, 3H).

1-Aminoethyl-2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl bicyclo[2.2.1]hept-5-ene-exo-2-carboxamide 16. Compound **16** was synthesized following the same procedure to prepare **6**. Yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.22 – 6.08 (m, 2H), 5.93 (s, 1H), 5.42 (dd, *J* = 3.5, 1.2 Hz, 1H), 5.22 (ddd, *J* = 10.5, 7.9, 1.2 Hz, 1H), 5.04 (ddd, *J* = 10.5, 3.4, 0.9 Hz, 1H), 4.50 (dd, *J* = 7.9, 1.7 Hz, 1H), 4.17 (ddd, *J* = 6.4, 2.1, 1.0 Hz, 2H), 3.98 – 3.86 (m, 2H), 3.72 (ddt, *J* = 10.6, 7.6, 3.9 Hz, 1H), 3.50 (m, 2H), 2.94 (dd, *J* = 3.6, 1.9 Hz, 2H), 2.18 (s, 3H), 2.12 – 2.06 (m, 6H), 2.01 (s, 3H), 1.94 (m, 1H), 1.73 (d, *J* = 8.4 Hz, 1H), 1.41 – 1.25 (m, 2H). ^{13}C NMR(125 MHz, $CDCl_3$): δ 175.83, 170.44, 170.25, 170.21, 169.68, 138.16, 135.98, 101.58, 70.97, 69.10, 68.99, 67.0, 61.30, 47.35, 47.22, 46.32, 44.62, 41.57, 39.33, 30.49, 29.73, 20.84, 20.66, 20.51. HRMS (ESI) Calcd for $C_{24}H_{33}NO_{11}$ $[M+H]^+$ 512.2127; found 512.2136.



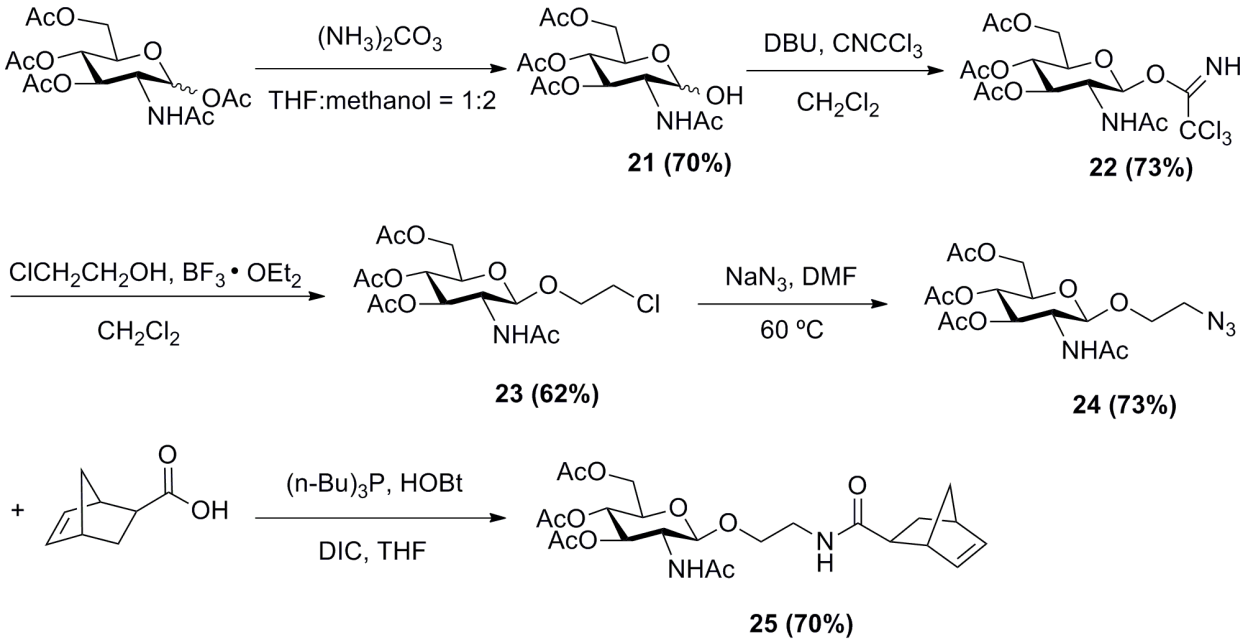
Scheme 4. Synthesis of NB-fucose.

Tetra-acetyl-L-fucopyranose 17. Compound **17** was synthesized following the same procedure to prepare **1**, and the spectrum for the α isomer was the same as reported previously.[3] Yield: 98%. (α:β = 1:1). α isomer ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.34 (d, *J* = 2.8 Hz, 1H), 5.34 (m, 2H), 4.27 (q, *J* = 6.5 Hz, 1H), 2.18 (s, 3H), 2.15 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.16 (d, *J* = 6.5 Hz, 3H).

1-Bromoethyl-2,3,4-tri-*O*-acetyl-L-fucopyranoside 18. Compound **18** was synthesized according to the literature,[11] and the product is a mixture of α and β diastereomers (α:β = 1:1). Yield: 88%. The mixture was used for the next step without further separation.

1-Azidoethyl-2,3,4-tri-*O*-acetyl-L-fucopyranoside 19. Compound **19** was synthesized following the same procedure to prepare **5** Yield: 83% (α:β = 1:1). The isomers were separated by Combiflash (EtOAc:hexane = 1:4, v/v) and the spectrum for the α isomer of compound **19** was the same as reported previously.[12]. α isomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.39 (dd, *J* = 10.5, 3.4 Hz, 1H), 5.34 (dd, *J* = 3.4, 1.3 Hz, 1H), 5.21 – 5.09 (m, 2H), 4.20 (dd, *J* = 10.5, 3.4 Hz, 1H), 3.88 (ddd, *J* = 10.8, 6.1, 3.2 Hz, 1H), 3.63 (ddd, *J* = 10.6, 7.1, 3.3 Hz, 1H), 3.44 (dddd, *J* = 41.9, 13.4, 6.6, 3.3 Hz, 2H), 2.19 (s, 3H), 2.10 (s, 3H), 2.01 (s, 3H), 1.17 (d, *J* = 6.5 Hz, 3H).

1-Aminoethyl-2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl bicyclo[2.2.1]hept-5-ene-exo-2-carbox-amide 20. Compound **20** was synthesized following the same procedure to prepare **6** using the α:β mixture of **19**. The isomers of **20** were separated by Combiflash (acetone:CH_2Cl_2 = 1:4, v/v). Yield (α isomer): 35%. α isomer ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.17 (dd, *J* = 5.9, 2.8 Hz, 1H), 6.13 (ddd, *J* = 11.1, 5.7, 3.0 Hz, 1H), 5.94 (s, 1H), 5.38 (dt, *J* = 10.9, 3.4 Hz, 1H), 5.31 (s, 1H), 5.17 (ddd, *J* = 10.8, 3.7, 1.0 Hz, 1H), 5.08 (t, *J* = 3.1 Hz, 1H), 4.16 (dq, *J* = 8.5, 7.1, 6.1 Hz, 1H), 3.79 (m, 1H), 3.53 (m, 3H), 2.94 (dt, *J* = 5.2, 2.6 Hz, 2H), 2.19 (s, 3H), 2.09 (d, *J* = 7.0 Hz, 3H), 2.02 (s, 3H), 1.94 (dt, *J* = 10.9, 3.6 Hz, 1H), 1.73 (d, *J* = 8.3 Hz, 1H), 1.44 – 1.31 (m, 2H), 1.17 (dd, *J* = 6.6, 2.6 Hz, 3H). ^{13}C NMR(125 MHz, $CDCl_3$): δ 175.61, 170.62, 170.21, 170.20, 138.36, 135.91, 96.49, 71.02, 68.15, 67.92, 67.66, 64.68, 47.24, 46.35, 44.78, 41.58, 39.21, 30.53, 20.84, 20.75, 20.68, 20.51, 15.91. HRMS (ESI) Calcd for $C_{22}H_{31}NO_9$ $[M+H]^+$ 454.2078; found 454.2078.



Scheme 5. Synthesis of NB-GlcNAc.

2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranose 21. To a solution of 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-D-glucopyranose (0.77 mmol, 0.3 g) in a dry THF and methanol mixture (1:2, v/v) (6 mL) was added ammonium carbonate (1.54 mmol, 0.15 g).[13] After stirring overnight at rt the mixture was concentrated and purified by Combiflash (EtOAc: CH_2Cl_2 = 3:2, v/v) to yield **21** as a colorless oil (0.19 g, 70%) (α:β = 1:15). The spectrum for the β isomer was the same as reported previously.[14] β isomer ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.76 (d, *J* = 9.3 Hz, 1H), 5.34 – 5.26 (m, 2H), 5.14 (t, *J* = 9.8 Hz, 1H), 4.35 – 4.27 (m, 1H), 4.25 – 4.17 (m, 2H), 4.17 – 4.08 (m, 2H), 3.03 (s, 1H), 2.10 (s, 3H), 2.04 (s, 6H), 1.96 (s, 3H).

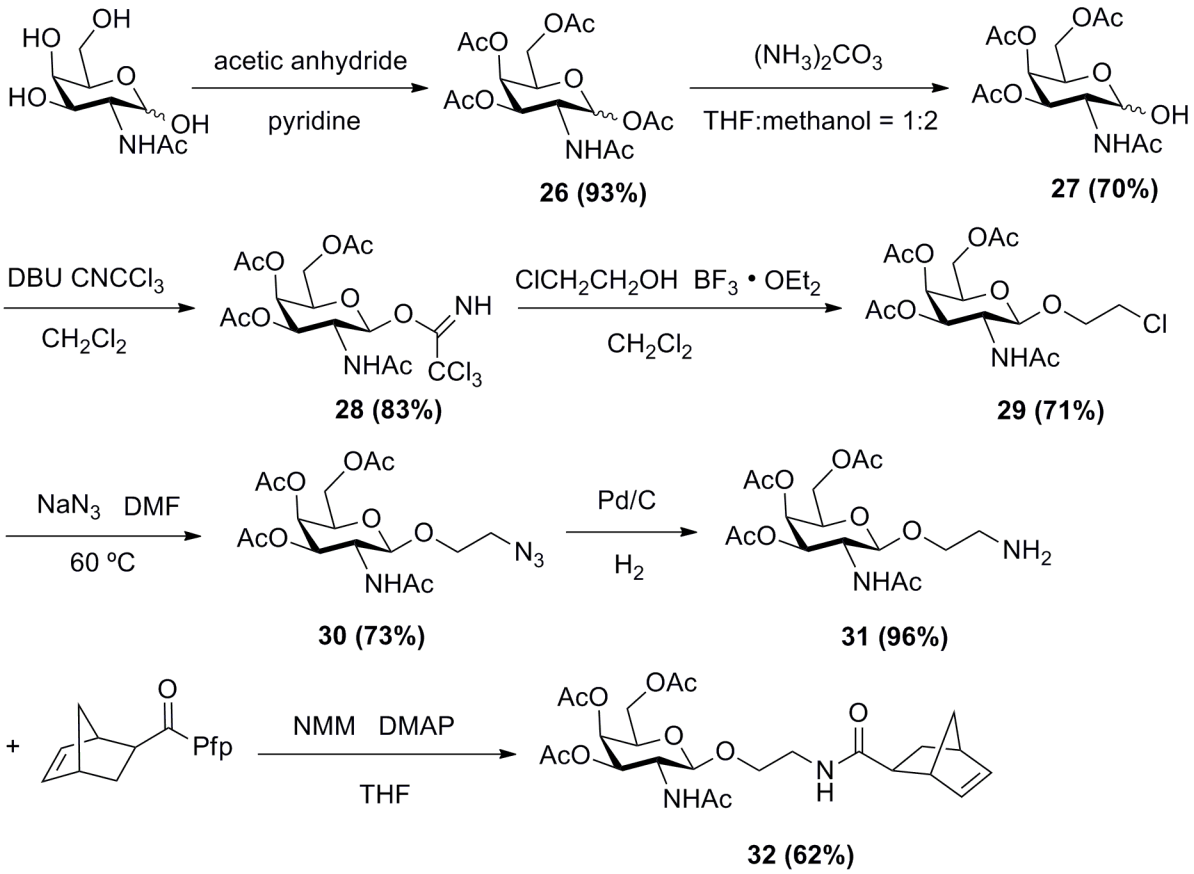
2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl trichloroacetimidate 22. Compound **22** was synthesized following the same procedure to prepare **3**, and the spectrum for compound **22** was the same as reported previously.[15] Yield: 73%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.79 (s, 1H), 5.62 (d, *J* = 8.9 Hz, 1H), 5.35 – 5.22 (m, 2H), 4.55 (ddd, *J* = 10.7, 8.9, 3.7 Hz, 1H), 4.28 – 4.22 (m, 1H), 4.15 – 4.09 (m, 2H), 2.07 (s, 3H), 2.06 (d, *J* = 5.3 Hz, 6H), 1.93 (s, 3H).

1-Chloroethyl-2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside 23. Compound **23** was synthesized following the same procedure to prepare **4**, and the spectrum for compound **23** was the same as reported previously.[16] Yield: 62%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.50 (d, *J*

= 8.9 Hz, 1H), 5.34 – 5.27 (m, 1H), 5.08 (t, *J* = 9.7 Hz, 1H), 4.77 (dd, *J* = 8.4, 0.9 Hz, 1H), 4.26 (dd, *J* = 12.3, 4.7 Hz, 1H), 4.16 – 4.08 (m, 2H), 3.87 (dt, *J* = 10.5, 8.7 Hz, 1H), 3.77 (ddd, *J* = 11.0, 6.8, 5.8 Hz, 1H), 3.71 (ddd, *J* = 10.1, 4.8, 2.4 Hz, 1H), 3.64 (ddd, *J* = 6.1, 4.9, 1.0 Hz, 2H), 2.09 (s, 3H), 2.03 (d, *J* = 5.7, 6H), 1.97 (s, 3H).

1-Azidoethyl-2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside 24. Compound **24** was synthesized following the same procedure to prepare **5**, and the spectrum for compound **24** was the same as reported previously.[12] Yield: 73%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.60 (d, *J* = 8.6 Hz, 1H), 5.38 (dd, *J* = 10.6, 9.3 Hz, 1H), 5.09 (t, *J* = 9.7 Hz, 1H), 4.85 (d, *J* = 8.3 Hz, 1H), 4.27 (dd, *J* = 12.3, 4.8 Hz, 1H), 4.17 (dd, *J* = 12.3, 2.4 Hz, 1H), 4.06 (ddd, *J* = 10.9, 4.8, 3.3 Hz, 1H), 3.83 (dt, *J* = 10.8, 8.5 Hz, 1H), 3.78 – 3.68 (m, 2H), 3.52 (ddd, *J* = 13.4, 8.6, 3.2 Hz, 1H), 3.28 (ddd, *J* = 13.5, 4.7, 3.2 Hz, 1H), 2.10 (s, 3H), 2.05 (d, *J* = 3.4 Hz, 6H), 1.97 (s, 3H).

1-Aminoethyl-2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl bicyclo[2.2.1] hept-5-ene-exo-2-carboxamide 25. Compound **25** was synthesized following the same procedure to prepare **6**. Yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.25 (d, *J* = 4 Hz, 1H), 6.22 – 6.01 (m, 3H), 5.19 (td, *J* = 9.9, 4.7 Hz, 1H), 5.08 (td, *J* = 9.6, 2.7 Hz, 1H), 4.58 (d, *J* = 8.4 Hz, 1H), 4.26 (dt, *J* = 12.7, 5.0 Hz, 1H), 4.14 (dd, *J* = 12.2, 2.2 Hz, 1H), 3.96 (tq, *J* = 8.7, 3.9 Hz, 1H), 3.86 (ddt, *J* = 9.9, 6.5, 3.3 Hz, 1H), 3.70 (ddd, *J* = 10.0, 5.2, 2.4 Hz, 2H), 3.58 – 3.49 (m, 1H), 3.39 (m, 1H), 2.91 (s, 2H), 2.08 (d, *J* = 1.7 Hz, 3H), 2.04 (d, *J* = 4.6 Hz, 6H), 1.95 (d, *J* = 10.7 Hz, 3H), 1.90 (m, 1H), 1.70 (t, *J* = 8.0 Hz, 1H), 1.38 – 1.22 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 178.55, 173.71, 173.28, 173.10, 171.98, 140.90, 138.65, 109.99, 103.75, 75.15, 74.65, 71.41, 71.02, 64.68, 57.15, 50.02, 49.77, 49.0, 47.19, 44.23, 41.77, 33.12, 26.06, 23.33. HRMS (ESI) Calcd for $C_{24}H_{34}N_2O_{10}$ $[M+H]^+$ 511.2300; found 511.2295.



Scheme 6. Synthesis of NB-GalNAc.

2-Acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-D-galactopyranose 26. Compound **26** was synthesized following the same procedure to prepare **1**, and the spectrum for the β isomer was the same as reported previously.[17] Yield: 93% (α:β = 1:10). β isomer ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.21 (d, *J* = 3.7 Hz, 1H), 5.45 – 5.39 (m, 2H), 5.25 – 5.19 (m, 1H), 4.72 (ddd, *J* = 11.8, 8.7, 3.4 Hz, 1H), 4.23 (t, *J* = 6.8 Hz, 1H), 4.14 – 4.03 (m, 2H), 2.17 (s, 6H), 2.03 (s, 6H), 1.95 (s, 3H).

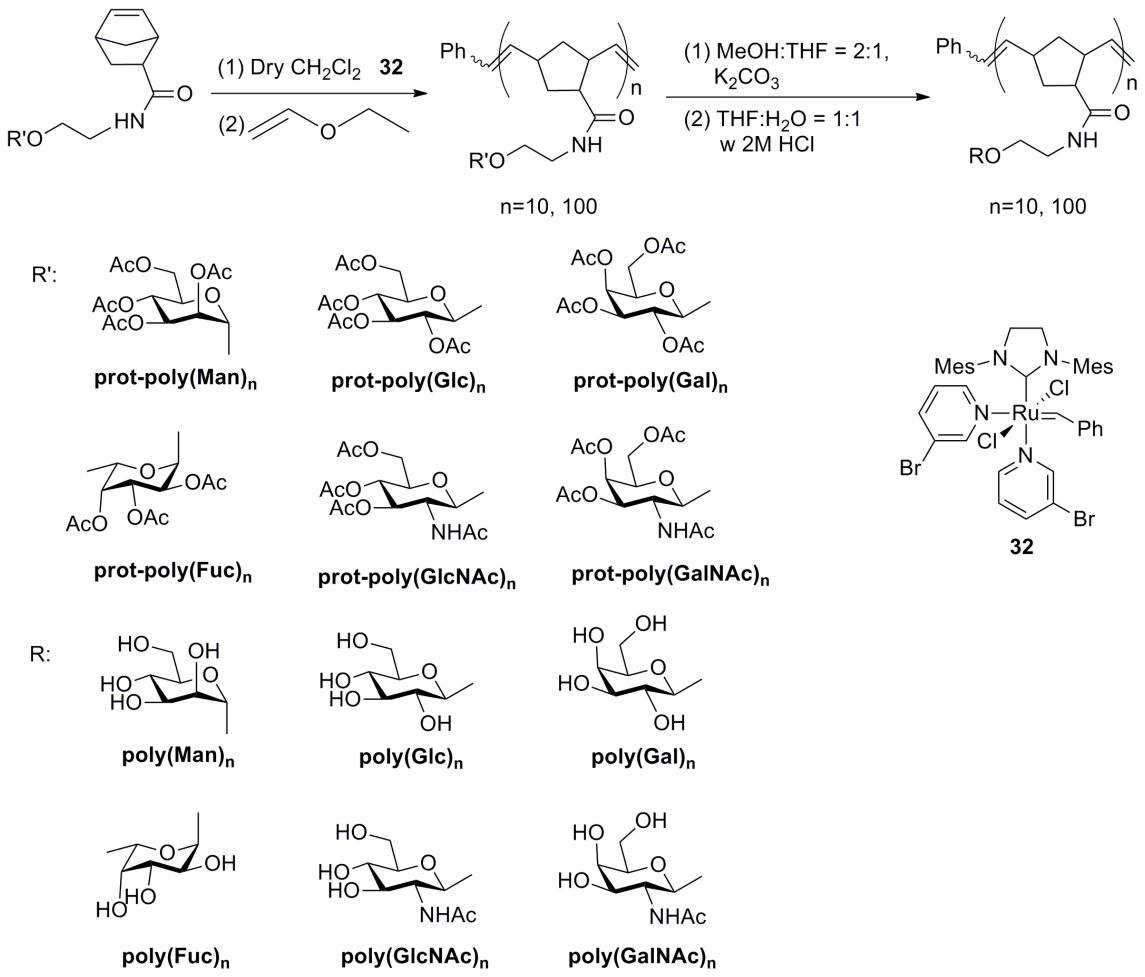
2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-galactopyranose 27. Compound **27** was synthesized following the same procedure to prepare **21**, and the spectrum for the β isomer was the same as reported previously.[18] Yield: 70% (α:β = 1:10). β isomer ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.72 (d, *J* = 9.5 Hz, 1H), 5.39 (dd, *J* = 3.3, 1.4 Hz, 1H), 5.33 (t, *J* = 3.0 Hz, 1H), 5.25 (dd, *J* = 11.4, 3.2 Hz, 1H), 4.56 (td, *J* = 11.2, 10.5, 3.5 Hz, 1H), 4.42 (t, *J* = 6.5 Hz, 1H), 4.16 – 4.02 (m, 2H), 3.25 (s, 1H), 2.16 (s, 3H), 2.05 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H).

2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranosyl trichloroacetimidate 28. Compound **28** was synthesized following the same procedure to prepare **3**, and the spectrum for compound **28** was the same as reported previously.[18] Yield: 83%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.78 (s, 1H), 6.40 (d, *J* = 3.6 Hz, 1H), 5.52 – 5.46 (m, 2H), 5.31 – 5.25 (m, 1H), 4.80 (ddd, *J* = 11.4, 9.2, 3.7 Hz, 1H), 4.38 – 4.32 (m, 1H), 4.17 (dd, *J* = 11.4, 6.7 Hz, 1H), 4.07 (dd, *J* = 11.4, 6.6 Hz, 1H), 2.18 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.94 (s, 3H).

1-Bromoethyl-2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranoside 29. Compound **29** was synthesized following the same procedure to prepare **4**, and the spectrum for compound **29** was the same as reported previously.[18] Yield: 71%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.58 (d, *J* = 8.4 Hz, 1H), 5.34 – 5.28 (m, 2H), 4.81 (d, *J* = 8.4 Hz, 1H), 4.20 – 4.08 (m, 3H), 4.01 – 3.90 (m, 2H), 3.79 (dt, *J* = 11.5, 6.4 Hz, 1H), 3.65 (dd, *J* = 6.4, 4.9 Hz, 2H), 2.15 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H).

1-Azidoethyl-2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranoside 30. Compound **30** was synthesized following the same procedure to prepare **5**, and the spectrum for compound **30** was the same as reported previously.[12] Yield: 73%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.52 (d, *J* = 8.4 Hz, 1H), 5.44 – 5.28 (m, 2H), 4.87 (d, *J* = 8.3 Hz, 1H), 4.19 – 4.03 (m, 3H), 3.97 – 3.86 (m, 2H), 3.71 (ddd, *J* = 11.2, 8.5, 3.2 Hz, 1H), 3.52 (ddd, *J* = 13.8, 8.5, 3.4 Hz, 1H), 3.27 (ddd, *J* = 13.4, 4.7, 3.1 Hz, 1H), 2.14 (s, 3H), 2.04 (s, 3H), 2.00 (s, 3H), 1.96 (s, 3H).

1-Aminoethyl-2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranosyl bicyclo[2.2.1] hept-5-ene-exo-2-carboxamide 31. Compound **31** was synthesized following the same procedure to prepare **6**. Yield: 62%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.21– 6.07 (m, 3H), 5.89 – 5.80 (m, 1H), 5.36 (dd, *J* = 3.4, 1.1 Hz, 1H), 5.14 (ddd, *J* = 11.3, 6.3, 3.4 Hz, 1H), 4.62 (dd, *J* = 8.4, 4.6 Hz, 1H), 4.22 – 4.05 (m, 3H), 3.98 – 3.85 (m, 2H), 3.71 (m, 1H), 3.63 – 3.50 (m, 1H), 3.46 – 3.33 (m, 1H), 2.93 (s, 1H), 2.17 (d, *J* = 6.2 Hz, 3H), 2.06 (d, *J* = 1.6 Hz, 3H), 2.02 (d, *J* = 0.9 Hz, 3H), 1.97 (d, *J* = 9.6 Hz, 3H), 1.95 – 1.84 (m, 2H), 1.71 (ddd, *J* = 6.0, 4.6, 3.0 Hz, 1H), 1.39 – 1.24 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 176.13, 176.03, 170.84, 170.43, 170.25, 138.26, 136.0, 101.68, 70.77, 70.02, 68.50, 66.34, 61.30, 51.02, 47.35, 47.12, 46.22, 44.56, 41.57, 39.03, 30.39, 30.29, 23.64, 20.61. HRMS (ESI) Calcd for $C_{24}H_{34}N_2O_{10}$ $[M+H]^+$ 511.2300; found 511.2304.



Scheme 7. ROMP and deacetylation of glycopolymers.

The general method of ROMP was as follows:[19] Monomer **6** (0.06 mmol, 30.7 mg) was dissolved in 0.3 mL CH_2Cl_2. To the reaction was added **32** (6 μmol, 5.3 mg for the 10-mers and 0.6 μmol, 0.53 mg for the 100-mers) in CH_2Cl_2 (0.3 mL for the 10-mers and 0.7 mL for the 100-mers). The reaction was monitored by TLC. Ethylvinyl ether (0.1 mL) was added to quench the reaction when it was complete, and the mixture was stirred for an additional 30 min. The polymer was isolated by precipitation with cold Et_2O to yield 10-mers as brown sticky oils and 100-mers as light yellow sticky oils.

prot-poly(Man)$_{10}$ Yield after purification: 58%. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.32 (m), 5.85—6.2 (m), 5.20—5.5 (with max at 5.3, 5.25), 4.82 (br s), 4.27 (br s), 4.12 (br s), 3.97 (br s), 3.12—3.80 (with max at 3.52, 3.74), 3.02 (br s), 2.70 (br s), 2.33 (br s), 1.90—2.24 (with max at 2.0, 2.05, 2.10, 2.15), 1.55 (br s), 1.04—1.40 (m).

prot-poly(Man)$_{100}$ Yield after purification: 90%. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 5.85—6.3 (m), 5.10—5.50 (with max at 5.23, 5.27, 5.34), 4.80 (br s), 4.26 (br s), 4.09 (br s), 3.96 (br s), 3.12—3.80 (with max at 3.52, 3.75), 3.02 (br s), 2.68 (br s), 2.33 (br s), 1.73—2.24 (with max at 2.0, 2.05, 2.10, 2.15), 1.60 (br s), 1.05—1.27 (m).

prot-poly(Glc)$_{10}$ Yield after purification: 68%. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.32 (m), 5.68—6.07 (m), 4.78—5.51 (with max at 4.95, 5.06, 5.18, 5.23, 5.40), 4.51 (br s), 4.25 (br s), 4.12 (br s), 3.18—3.97 (with max at 3.30, 3.48, 3.66, 3.72, 3.81), 3.01 (br s), 2.67 (br s), 2.19—2.49 (with max at 2.24, 2.41), 1.95—2.20 (with max at 1.99, 2.01, 2.03, 2.07), 1.79 (br s), 1.57 (br s), 1.01—1.38 (m).

prot-poly(Glc)$_{100}$ Yield after purification: 75%. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 5.78—6.0 (m), 5.23—5.48 (with max at 5.28, 5.40), 5.20 (br s), 5.07 (br s), 4.96 (br s), 4.54 (br s), 4.26 (br s), 4.13 (br s), 3.82 (br s), 3.63—3.77 (with max at 3.67, 3.71), 3.18—3.62 (with max at 3.29, 3.47), 3.02 (br s), 2.67 (br s), 2.09—2.37 (with max at 2.13, 2.25), 1.94—2.10 (with max at 2.0, 2.02, 2.04, 2.05, 2.08), 1.85—1.94 (m), 1.56 (br s), 0.97—1.39 (m).

prot-poly(Gal)$_{10}$ Yield after purification: 72%. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.32 (m), 5.75—6.10 (m), 4.90—5.50 (with max at 5.07, 5.18, 5.32, 5.42), 4.52 (br s), 4.15 (br s), 3.75—4.00 (with max at 3.80, 3.92), 3.20—3.74 (with max at 3.30, 3.50, 3.67), 3.05 (br s), 2.71 (br s), 2.26 (br, s), 1.80—2.24 (with max at 2.03, 2.11, 2.20), 1.60 (br s), 1.0—1.30 (m).

prot-poly(Gal)$_{100}$ Yield after purification: 93%. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.75—6.20 (m), 4.98—5.51(with max at 5.03, 5.16, 5.29, 5.39), 4.52 (br s), 4.16 (br s), 3.95 (br s), 3.84 (br s), 3.19—3.75 (with max at 3.29, 3.51, 3.65), 3.01 (br s), 2.68 (br s), 2.27 (br s), 1.82—2.20 (with max at 1.98, 2.04, 2.16), 1.59 (br s), 1.0—1.27 (m).

prot-poly(Fuc)$_{10}$ Yield after purification: 59%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.32 (m), 5.66—6.58 (m), 4.85—5.54 (with max at 5.02, 5.12, 5.27, 5.31), 4.12 (br s), 3.20—3.81 (with max at 3.34, 3.51, 3.71), 3.03 (br s), 2.67 (br s), 2.21—2.42 (m), 1.80—2.20 (with max at 1.98, 2.06, 2.15), 1.60 (br s), 0.9—1.33 (with max at 1.13, 1.23).

prot-poly(Fuc)$_{100}$ Yield after purification: 77%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.75—6.47 (m), 4.89—5.56 (with max at 5.06, 5.15, 5.30, 5.34), 4.15 (br s), 3.25—3.94 (with max at 3.38, 3.54,

3.76), 3.07 (br s), 2.70 (br s), 2.26—2.47 (m), 1.78—2.24 (with max at 2.02, 2.09, 2.19), 1.63 (br s), 1.28 (br s), 1.16 (br s), 0.72—0.99 (with max at 0.90).

prot-poly(GlcNAc)$_{10}$ Yield after purification: 67%. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.31 (m), 6.02—6.56 (m), 4.51—5.50 (with max at 4.75, 5.02, 5.18, 5.28), 3.12—4.48 (with max at 3.31, 3.50, 3.67, 3.83, 4.12, 4.26), 2.95 (br s), 2.63 (br s), 2.19—2.47 (with max at 2.33, 2.41), 1.71—2.19 (with max at 1.94, 2.0, 2.06), 1.59 (br s), 0.98—1.34 (with max at 1.14, 1.22).

prot-poly(GlcNAc)$_{100}$ Yield after purification: 81%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.01—6.62 (m), 5.14—5.54 (with max at 5.22, 5.31), 5.08 (br s), 4.48—4.96 (m), 4.27 (br s), 4.15 (br s), 2.84—4.06 (with max at 2.92, 2.99, 3.37, 3.54, 3.69, 3.80, 3.87, 3.98), 2.66 (br s), 2.38 (br s), 1.76—2.20 (with max at 1.91, 1.96, 2.04, 2.09), 1.62 (br s), 0.97—1.48 (with max at 1.16, 1.27, 1.35).

prot-poly(GalNAc)$_{10}$ Yield after purification: 90%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.34 (m), 6.01—6.82 (m), 5.01—5.68 (with max at 5.23, 5.28, 5.38), 2.90—4.39 (with max at 3.01, 3.34, 3.51, 3.58, 3.65, 3.89, 3.97, 4.16), 2.67 (br s), 2.39 (br s), 1.78—2.27 (with max at 1.93, 1.98, 2.01, 2.06, 2.16), 1.62 (br s), 1.06—1.41 (m).

prot-poly(GalNAc)$_{100}$ Yield after purification: 92%. ^{1}H-NMR (500 MHz, $CDCl_3$): 6.06—6.77 (m), 5.05—5.58 (with max at 5.23, 5.28, 5.38), 4.67 (br s), 3.77—4.30 (with max at 3.80, 3.93, 4.16), 2.80—3.78 (with max at 3.02, 3.34, 3.86), 2.67 (br s), 2.39 (br s), 1.78—2.27 (with max at 1.93, 1.98, 2.01, 2.06, 2.16), 1.62 (br s), 1.06—1.41 (m).

The general method of deacetylation was as follows:[20] the protected polymer (28 mg) was dissolved in 2 mL MeOH/THF (2:1, v/v) and to this solution was added K_2CO_3 (75 mg) and the reaction stirred for 20–30 min. The solvents were evaporated and the solid was then poured into a solution of 10 mL THF/H_2O (1:1, v/v) containing 1N HCl. This solution was then allowed to stir for 30–60 min and the solvents removed in vacuo, followed by ion exchange chromatography for 10-mers or dialysis for 100-mers to afford the deprotected polymer as a white powder.

poly(Man)$_{10}$ Yield after purification: 78%. ^{1}H-NMR (600 MHz, D_2O): δ 7.24 (m), 5.09—5.43 (m), 4.70—4.82 (with max at 4.75), 3.10—3.90 (with max at 3.25, 3.48, 3.55, 3.60, 3.75, 3.82), 2.23—3.0 (with max at 2.40, 2.85), 1.53—2.10 (with max at 1.57, 1.91), 1.10 (br s).

poly(Man)$_{100}$ Yield after purification: 85%. ^{1}H-NMR (600 MHz, D_2O): δ 5.12—5.43 (m), 4.77 (m), 3.17—3.92 (with max at 3.26, 3.51, 3.68, 3.77, 3.84), 2.29—3.17 (with max at 2.42, 2.94), 1.48—2.13 (with max at 1.59, 1.91), 1.13 (br s).

poly(Glc)$_{10}$ Yield after purification: 83%. ^{1}H-NMR (600 MHz, D_2O): δ 7.25 (m), 4.80—5.50 (with max at 5.03, 5.26), 4.43 (br s), 3.10—4.02 (with max at 3.31, 3.48, 3.55, 3.68, 3.73, 3.81), 2.25—3.04 (with max at 2.39, 2.90), 1.30—2.10 (with max at 1.56, 1.92), 1.09 (br s).

poly(Glc)$_{100}$ Yield after purification: 85%. ^{1}H-NMR (500 MHz, D_2O): δ 5.08—5.50 (m), 4.34 (br s), 3.85 (br s), 3.66 (br s), 3.18—3.50 (with max at 3.73, 3.78, 3.80), 2.20—3.10 (with max at 2.40, 2.68, 2.98), 1.30—2.10 (with max at 1.59, 1.98), 1.09 (br s).

poly(Gal)$_{10}$ Yield after purification: 75%. ^{1}H-NMR (600 MHz, D_2O): δ 7.24 (m), 5.0—5.50 (m), 4.23 (br s), 3.10—4.0 (with max at 3.25, 3.40, 3.51, 3.55, 3.76), 2.25—3.10 (with max at 2.40, 2.90), 1.42—2.05 (with max at 1.54, 1.68, 1.90), 1.10 (br s).

poly(Gal)$_{100}$ Yield after purification: 78%. ^{1}H-NMR (600 MHz, D_2O): δ 5.04—5.45 (m), 4.26 (br s), 3.84 (br s), 3.11—3.78 (with max at 3.28, 3.44, 3.55, 3.63, 3.66), 2.70—3.12 (m), 2.29—2.69 (with max at 2.40), 1.48—2.08 (with max at 1.59, 1.94), 1.10 (br s).

poly(Fuc)$_{10}$ Yield after purification: 77%. ^{1}H-NMR (400 MHz, D_2O): δ 7.34 (m), 5.00—5.58 (m), 4.51—4.68 (m), 4.35 (br s), 4.22 (br s), 3.18—4.12 (with max at 3.37, 3.52, 3.65, 3.76, 3.83, 3.98), 3.00 (br s), 2.36—2.80 (with max at 2.49), 1.48—2.21 (with max at 1.66, 1.87, 2.01), 1.01—1.43 (with max at 1.23, 1.24, 1.27, 1.28).

poly(Fuc)$_{100}$ Yield after purification: 85%. ^{1}H-NMR (400 MHz, D_2O): δ 5.03—5.40 (m), 4.15—4.36 (m), 3.10—3.90 (with max at 3.40, 3.54, 3.61, 3.64), 2.12—3.08 (with max at 2.39, 2.60, 2.98), 1.45—2.21 (with max at 1.56, 2.01), 1.0—1.40 (with max at 1.11, 1.16).

poly(GlcNAc)$_{10}$ Yield after purification: 78%. ^{1}H-NMR (600 MHz, D_2O): δ 7.24 (m), 4.94—5.50 (with max at 5.03, 5.26), 4.43 (br s), 3.04—4.02 (with max at 3.31, 3.48, 3.55, 3.68, 3.73, 3.81), 2.25—3.04 (with max at 2.39, 2.90), 1.30—2.10 (with max at 1.56, 1.92), 1.17 (br s).

poly(GlcNAc)$_{100}$ Yield after purification: 77%. ^{1}H-NMR (600 MHz, D_2O): δ 5.02—5.40 (m), 4.38 (br s), 3.66—3.83 (with max at 3.73, 3.78, 3.80), 3.47—3.66 (with max at 3.51, 3.57, 3.62), 3.32 (br s), 3.15 (br s), 2.86 (m), 2.42—2.66 (with max at 2.33, 2.57), 1.91 (br s), 1.52 (br s).

poly(GalNAc)$_{10}$ Yield after purification: 90%. ^{1}H-NMR (500 MHz, D_2O): δ 7.24 (br s), 5.02—5.40 (m), 4.35 (br s), 3.48—4.10 (with max at 3.59, 3.68, 3.70, 3.88), 2.30—3.44 (with max at 2.40, 2.60, 2.91, 3.22), 1.98 (br s), 0.98—1.70 (with max at 1.10, 1.60).

poly(GalNAc)$_{100}$ Yield after purification: 92%. ^{1}H-NMR (500 MHz, D_2O): δ 5.09—5.45 (m), 4.36 (br s), 3.50—3.91 (with max at 3.59, 3.69, 3.70, 3.81, 3.90), 2.30—3.41 (with max at 2.38, 2.62, 2.90, 3.20, 3.35), 1.98 (br s), 1.59 (br s), 1.01—1.23 (m).

Table 1. Analytical data for homoglycopolymers.

polymers	[Monomer]/ [Catalyst]	Rxn time (h)	Theo Mn[a]	Calcd Mn[b]	Calcd Mw[b]	PDI[b]
poly(Man)$_{10}$	10/1	1	5189	3509	4316	1.23
poly(Man)$_{100}$	100/1	1.5	51197	34397	38180	1.11
poly(Glc)$_{10}$	10/1	1	5189	3509	4280	1.22
poly(Glc)$_{100}$	100/1	1.5	51197	34397	44372	1.29
poly(Gal)$_{10}$	10/1	1	5189	3509	4245	1.21
poly(Gal)$_{100}$	100/1	1.5	51197	34397	41276	1.20
poly(Fuc)$_{10}$	10/1	0.5	4534	2862	3692	1.29
poly(Fuc)$_{100}$	100/1	1	45425	27928	32676	1.17
poly(GlcNAc)$_{10}$	10/1	1	5179	3765	5158	1.37
poly(GlcNAc)$_{100}$	100/1	1.5	51097	38497	50431	1.31
poly(GalNAc)$_{10}$	10/1	0.5	5179	3998	5558	1.39
poly(GalNAc)$_{100}$	100/1	1	51097	37977	50510	1.33

[a]Theoretical molecular weights were calculated based on the catalyst-to-monomer ratio assuming full conversion. [b]Determined from GPC in THF utilizing a differential refractometer and a multiangle light scattering detector.

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7	Experiment	1D
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9	Receiver Gain	60
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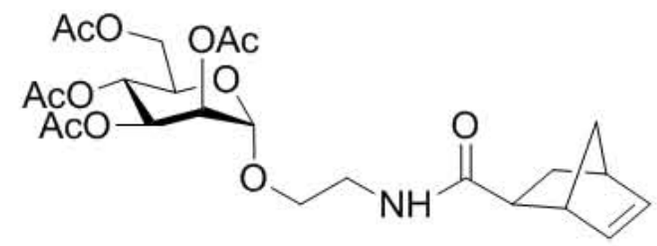
16	Nucleus	1H
17	Acquired Size	15133
18	Spectral Size	65536



^{1}H-NMR spectrum of NB-mannose 6

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5	Pulse Sequence	s2pul
6	Experiment	1D
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8	Receiver Gain	60
9	Relaxation Delay	1.0000
10	Pulse Width	0.0000
11	Acquisition Date	2010-03-03T20:48:04
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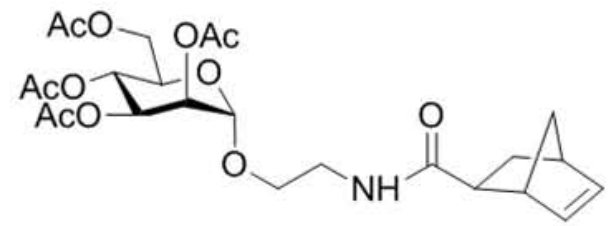
14	Spectral Width	31421.8
15	Lowest Frequency	-1884.1
16	Nucleus	13C
17	Acquired Size	40863
18	Spectral Size	131072



^{13}C-NMR spectrum of NB-mannose 6

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5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Number of Scans	30
9	Receiver Gain	46
10	Pulse Width	0.0000
11	Acquisition Date	2010-11-10T13:59:29
12	Modification Date	2010-11-10T17:05:38
13	Spectrometer Frequency	599.72
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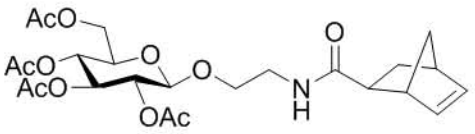
15	Lowest Frequency	-1001.3
16	Nucleus	1H
17	Acquired Size	15136
18	Spectral Size	65536



^{1}H-NMR spectrum of NB-glucose 11

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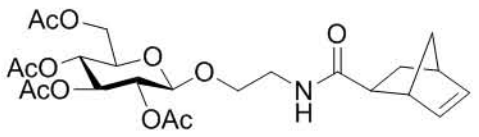
15	Lowest Frequency	-1884.1
16	Nucleus	13C
17	Acquired Size	40863
18	Spectral Size	131072



^{13}C-NMR spectrum of NB-glucose 11

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8	Experiment	1D
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10	Number of Scans	16
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19	Acquired Size	32768
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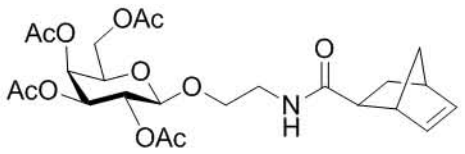

^{1}H-NMR spectrum of NB-galactose 16

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6	Temperature	298.1
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8	Experiment	1D
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11	Receiver Gain	197
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13	Pulse Width	10.0000
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17	Lowest Frequency	-2311.3
18	Nucleus	13C
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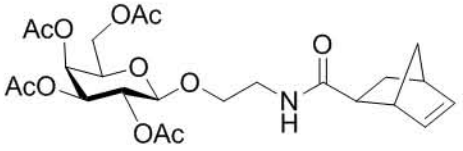

^{13}C-NMR spectrum of NB-galactose 16

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8	Experiment	1D
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11	Receiver Gain	32
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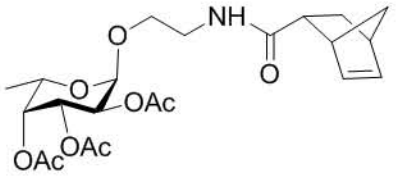

^{1}H-NMR spectrum of NB-fucose 20

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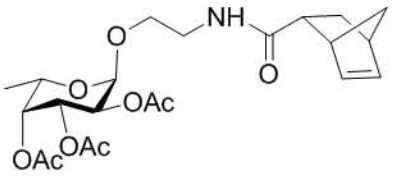
19	Acquired Size	32768
20	Spectral Size	65536



^{13}C-NMR spectrum of NB-fucose 20

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11	Receiver Gain	32
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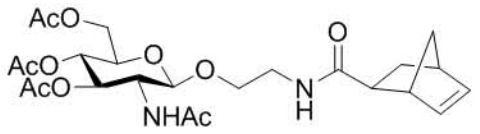

^{1}H-NMR spectrum of NB-GlcNAc 25

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10	Pulse Width	0.0000
11	Acquisition Date	2010-03-08T11:52:32
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14	Spectral Width	31421.8
15	Lowest Frequency	-1884.1
16	Nucleus	13C
17	Acquired Size	40863
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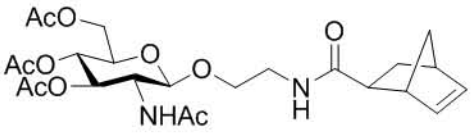

^{13}C-NMR spectrum of NB-GlcNAc 25

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10	Number of Scans	16
11	Receiver Gain	32
12	Relaxation Delay	1.0000
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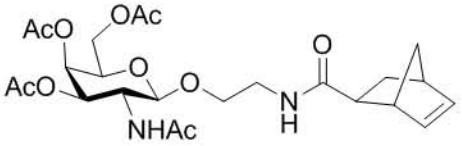
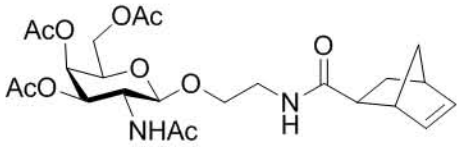
20	Spectral Size	65536



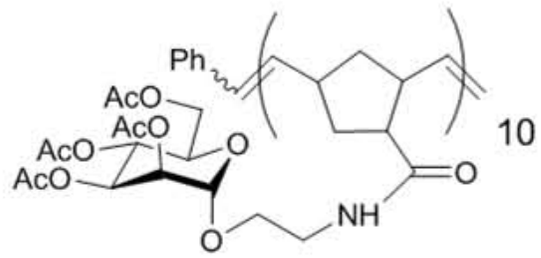
^{1}H-NMR spectrum of NB-GalNAc 31

Parameter	Value
1 Data File Name	F:/ NMR/ galNAc/ c13-nb-GalNAC-08292012/ 1/ fid
2 Title	c13-nb-GalNAC-08292012.1.fid
3 Origin	Bruker BioSpin GmbH
4 Spectrometer	spect
5 Solvent	CDCl3
6 Temperature	298.1
7 Pulse Sequence	zgpg30
8 Experiment	1D
9 Probe	5 mm CPPBBO BB-1H/ 19F/ D Z-GRD Z122624/ 0008
10 Number of Scans	176
11 Receiver Gain	197
12 Relaxation Delay	2.0000
13 Pulse Width	10.0000
14 Modification Date	2012-08-29T23:26:54
15 Spectrometer Frequency	125.71
16 Spectral Width	29761.9
17 Lowest Frequency	-2311.3
18 Nucleus	13C
19 Acquired Size	32768
20 Spectral Size	65536



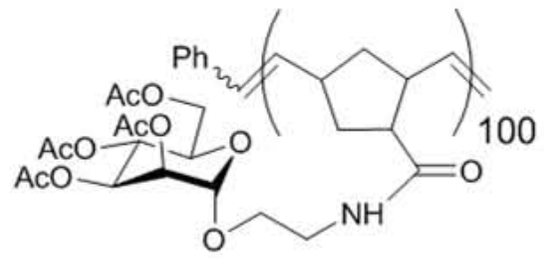
^{13}C-NMR spectrum of NB-GalNAc 31

	Parameter	Value
1	Data File Name	F:/ NMR/ mannose/ nb-mannoside10merpure-04162009.fid/ fid
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcx
9	Number of Scans	24
10	Receiver Gain	56
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.8920
14	Acquisition Date	2009-04-16T18:47:29
15	Spectrometer Frequency	599.72
16	Spectral Width	8000.0
17	Lowest Frequency	-1001.3
18	Nucleus	1H
19	Acquired Size	15136
20	Spectral Size	65536



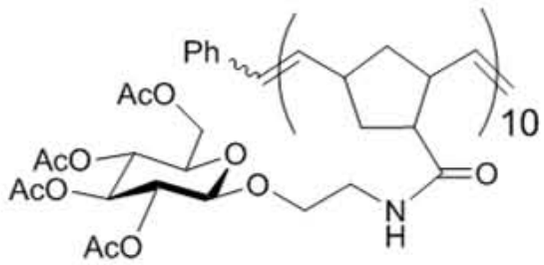
^{1}H-NMR spectrum of prot-poly(Man)$_{10}$

	Parameter	Value
1	Data File Name	F:/ NMR/ mannose/ nb-man100mer-3-tlc-02202011.fid/ fid
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcx
9	Number of Scans	28
10	Receiver Gain	40
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.8920
14	Acquisition Date	2011-02-25T14:56:48
15	Spectrometer Frequency	599.72
16	Spectral Width	8000.0
17	Lowest Frequency	-1001.3
18	Nucleus	1H
19	Acquired Size	15136
20	Spectral Size	65536



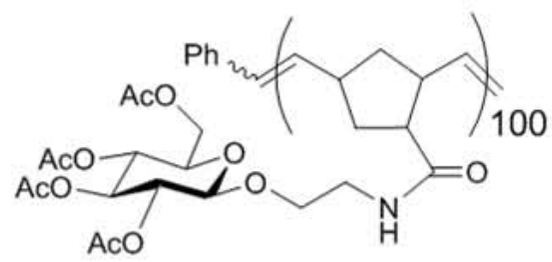
^{1}H-NMR spectrum of prot-poly(Man)$_{100}$

	Parameter	Value
1	Data File Name	D:/ Dropbox/ RESEARCH/ NMR/ NMR Varian 500 600/ 600/ glucose/ nb-glucose10mer-2-tlc-02212011.fid/ fid
2	Origin	Varian
3	Solvent	CDCl3
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Number of Scans	26
8	Receiver Gain	34
9	Relaxation Delay	1.0000
10	Pulse Width	0.0000
11	Acquisition Date	2011-02-25T15:10:51
12	Modification Date	2011-02-25T18:14:34
13	Spectrometer Frequency	599.72
14	Spectral Width	8000.0
15	Lowest Frequency	-1001.3
16	Nucleus	1H
17	Acquired Size	15136
18	Spectral Size	65536



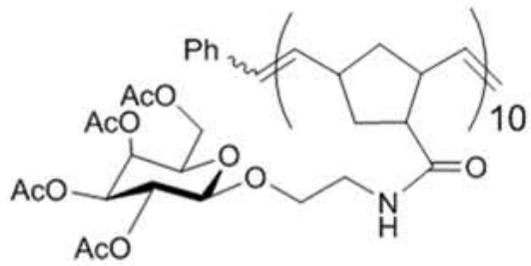
^{1}H-NMR spectrum of prot-poly(Glc)$_{10}$

	parameters	value
1	Data File Name	I:/ NMR/ glucose/ nb-glucose100mer04162010.fid/ fid
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Probe	HCN
8	Number of Scans	16
9	Receiver Gain	38
10	Reluxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	1.8920
13	Acquisition Date	2010-04-16T15:41:28
14	Spectrometer Frequency	599.72
15	Spectral Width	8000.0
16	Lowest Frequency	-1001.3
17	Nucleus	1H
18	Acquired Size	15136
19	Spectral Size	65536



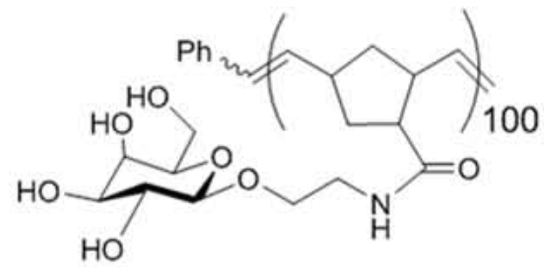
^{1}H NMR spectra of prot-poly(Glc)$_{100}$

	Parameter	Value
1	Data File Name	F:/ NMR/ galactose/ nb-galactose-10mer-09092010.fid/ fid
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcx
9	Number of Scans	1
10	Receiver Gain	34
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.8920
14	Acquisition Date	2010-09-09T21:19:26
15	Spectrometer Frequency	599.72
16	Spectral Width	8000.0
17	Lowest Frequency	-1001.3
18	Nucleus	1H
19	Acquired Size	15136
20	Spectral Size	65536



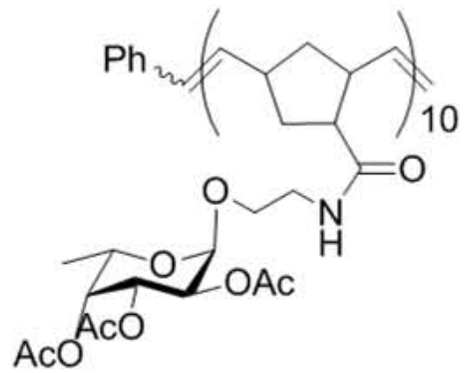
^{1}H-NMR spectrum of prot-poly(Gal)$_{10}$

	Parameter	Value
1	Data File Name	F:/ nmr/ NMR with fixed fid/ galactose/ nb-galactose100mer-deprot-02072011.fid/ fid
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	D2O
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcx
9	Number of Scans	69
10	Receiver Gain	38
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.8920
14	Acquisition Date	2011-02-07T14:00:30
15	Spectrometer Frequency	599.72
16	Spectral Width	8000.0
17	Lowest Frequency	-1001.3
18	Nucleus	1H
19	Acquired Size	15136
20	Spectral Size	65536



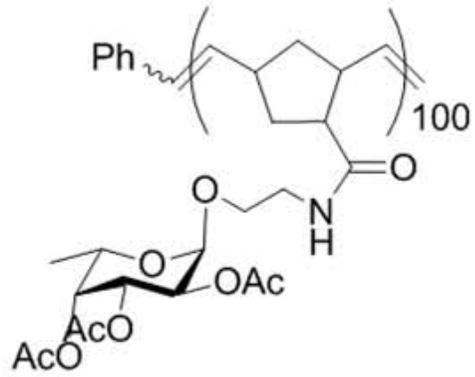
^{1}H-NMR spectrum of poly(Gal)$_{100}$

	Parameter	Value
1	Data File Name	F:/ fucose/ nb-l-fucose-10mer dry04162013/ 1/ fid
2	Title	nb-l-fucose-10mer dry04162013.1.fid
3	Origin	Bruker BioSpin GmbH
4	Spectrometer	spect
5	Solvent	CDCl3
6	Temperature	298.2
7	Pulse Sequence	zg30
8	Experiment	1D
9	Probe	5 mm CPPBBO BB-1H/ 19F/ D Z-GRD Z122624/ 0008
10	Number of Scans	16
11	Receiver Gain	32
12	Relaxation Delay	1.0000
13	Pulse Width	12.0000
14	Modification Date	2013-04-16T17:50:50
15	Spectrometer Frequency	499.89
16	Spectral Width	10000.0
17	Lowest Frequency	-1913.0
18	Nucleus	1H
19	Acquired Size	32768
20	Spectral Size	65536



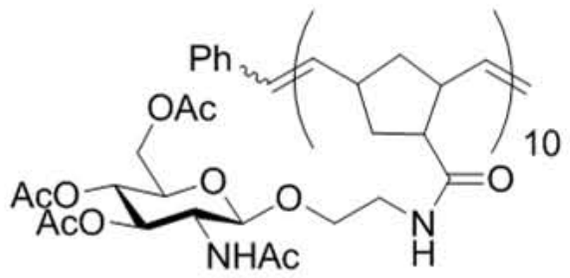
^{1}H-NMR spectrum of prot-poly(Fuc)$_{10}$

	Parameter	Value
1	Data File Name	F:/ fucose/ nb-l-fucose-100mer dry04162013/ 1/ fid
2	Title	nb-l-fucose-100mer dry04162013.1.fid
3	Origin	Bruker BioSpin GmbH
4	Spectrometer	spect
5	Solvent	CDCl3
6	Temperature	298.1
7	Pulse Sequence	zg30
8	Experiment	1D
9	Probe	5 mm CPPBBO BB-1H/ 19F/ D Z-GRD Z122624/ 0008
10	Number of Scans	16
11	Receiver Gain	32
12	Relaxation Delay	1.0000
13	Pulse Width	12.0000
14	Modification Date	2013-04-16T17:56:32
15	Spectrometer Frequency	499.89
16	Spectral Width	10000.0
17	Lowest Frequency	-1913.0
18	Nucleus	1H
19	Acquired Size	32768
20	Spectral Size	65536



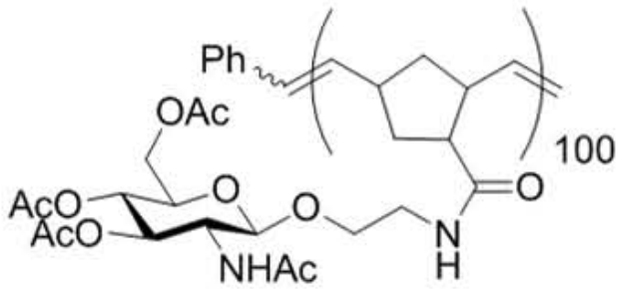
^{1}H-NMR spectrum of prot-poly(Fuc)$_{100}$

	Parameter	Value
1	Data File Name	C:/ Users/ Stella/ Dropbox/ RESEARCH/ NMR/ NMR Varian 500 600/ 600/ glcNAc/ nb-glcnac10mer-03192010.fid/ fid
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Number of Scans	29
9	Receiver Gain	40
10	Pulse Width	0.0000
11	Acquisition Date	2010-03-19T15:33:48
12	Modification Date	2010-03-19T19:40:48
13	Spectrometer Frequency	599.72
14	Spectral Width	8000.0
15	Lowest Frequency	-1001.3
16	Nucleus	1H
17	Acquired Size	15136
18	Spectral Size	65536



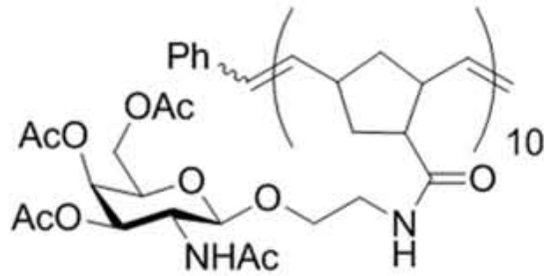
^{1}H-NMR spectrum of prot-poly(GlcNAc)$_{10}$

	Parameter	Value
1	Data File Name	F:/ nmr/ nb-glcnac100mer-06222010.fid/ fid
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	CDCl3
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcx2
9	Number of Scans	141
10	Receiver Gain	60
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.8920
14	Acquisition Date	2010-06-22T17:36:04
15	Spectrometer Frequency	499.90
16	Spectral Width	7998.4
17	Lowest Frequency	-999.9
18	Nucleus	1H
19	Acquired Size	15133
20	Spectral Size	65536



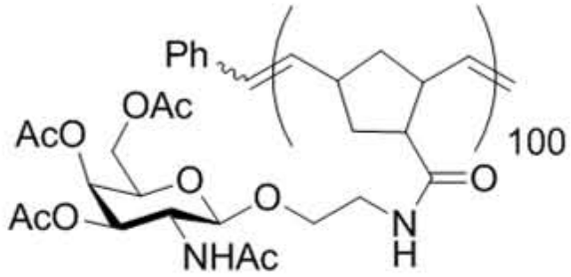
^{1}H NMR spectrum of prot-poly(GlcNAc)$_{100}$

	Parameter	Value
1	Data File Name	F:/ NMR/ galNAc/ nb-galnac-10mer-10042012/ 1/ fid
2	Title	nb-galnac-10mer-10042012.1.fid
3	Origin	Bruker BioSpin GmbH
4	Spectrometer	spect
5	Solvent	CDCl3
6	Temperature	298.2
7	Pulse Sequence	zg30
8	Experiment	1D
9	Probe	5 mm CPPBBO BB-1H/ 19F/ D Z-GRD Z122624/ 0008
10	Number of Scans	14
11	Receiver Gain	32
12	Relaxation Delay	1.0000
13	Pulse Width	12.0000
14	Modification Date	2012-10-04T11:50:54
15	Spectrometer Frequency	499.89
16	Spectral Width	15000.0
17	Lowest Frequency	-4413.0
18	Nucleus	1H
19	Acquired Size	32768
20	Spectral Size	65536



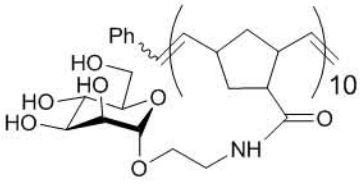
^{1}H-NMR spectrum of prot-poly(GalNAc)$_{10}$

	Parameter	Value
1	Data File Name	F:/ NMR/ galNAc/ nb-galnac-100mer-1-09032012/ 1/ fid
2	Title	NB-Galnac-100mer-1-09032012.1.fid
3	Origin	Bruker BioSpin GmbH
4	Spectrometer	spect
5	Solvent	CDCl3
6	Temperature	298.1
7	Pulse Sequence	zg30
8	Experiment	1D
9	Probe	5 mm CPPBBO BB-1H/ 19F/ D Z-GRD Z122624/ 0008
10	Number of Scans	16
11	Receiver Gain	32
12	Relaxation Delay	1.0000
13	Pulse Width	12.0000
14	Modification Date	2012-09-04T01:19:48
15	Spectrometer Frequency	499.89
16	Spectral Width	10000.0
17	Lowest Frequency	-1913.0
18	Nucleus	1H
19	Acquired Size	32768
20	Spectral Size	65536



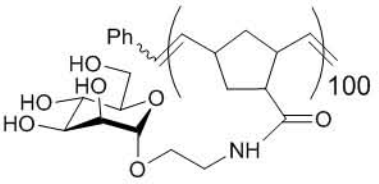
^{1}H-NMR spectrum of prot-poly(GalNAc)$_{100}$

	Parameter	Value
1	Data File Name	D:/ Dropbox/ RESEARCH/ NMR/ NMR Varian 500 600/ 600/ mannose/ others/ nb-man10mer-3-deprot-03072011.fid/ fid
2	Origin	Varian
3	Solvent	D2O
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Number of Scans	79
8	Receiver Gain	40
9	Relaxation Delay	1.0000
10	Pulse Width	0.0000
11	Acquisition Date	2011-03-07T15:33:12
12	Modification Date	2011-03-07T18:38:00
13	Spectrometer Frequency	599.72
14	Spectral Width	8000.0
15	Lowest Frequency	-1001.3
16	Nucleus	1H
17	Acquired Size	15136
18	Spectral Size	65536



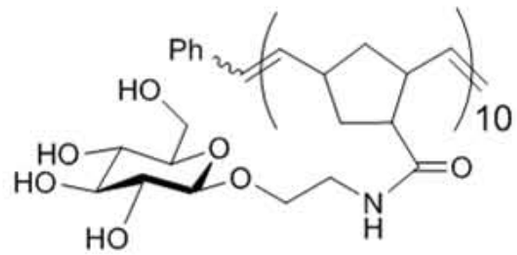
^{1}H-NMR spectrum of poly(Man)$_{10}$

	Parameter	Value
1	Data File Name	D:/ Dropbox/ RESEARCH/ NMR/ NMR Varian 500 600/ 600/ mannose/ nb-man100mer-3-deprot-03102011.fid/ fid
2	Origin	Varian
3	Solvent	D2O
4	Temperature	25.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Number of Scans	64
8	Receiver Gain	40
9	Relaxation Delay	1.0000
10	Pulse Width	0.0000
11	Acquisition Date	2011-03-10T15:33:37
12	Modification Date	2011-03-10T18:39:00
13	Spectrometer Frequency	599.72
14	Spectral Width	8000.0
15	Lowest Frequency	-1001.3
16	Nucleus	1H
17	Acquired Size	15136
18	Spectral Size	65536



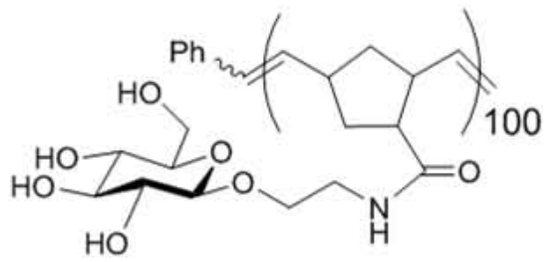
^{1}H-NMR spectrum of poly(Man)$_{100}$

	Parameter	Value
1	Data File Name	C:/ Users/ Stella/ Dropbox/ RESEARCH/ NMR/ NMR Varian 500 600/ 600/ glucose/ nb-glucose10mer-deprot-03092011.fid/ fid
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	D2O
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Number of Scans	53
9	Receiver Gain	38
10	Pulse Width	0.0000
11	Acquisition Date	2011-03-10T11:53:12
12	Modification Date	2011-03-10T14:57:10
13	Spectrometer Frequency	599.72
14	Spectral Width	8000.0
15	Lowest Frequency	-1001.3
16	Nucleus	1H
17	Acquired Size	15136
18	Spectral Size	65536



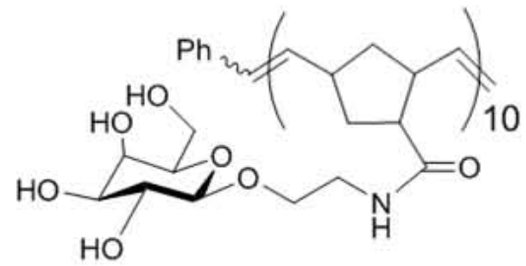
^{1}H-NMR spectrum of poly(Glc)$_{10}$

	parameters	value
1	Data File Name	J:/ nmr/ deprotectedNB-glucose 100mer-09172012/ 1/ fid
2	Origin	Bruker BioSpin GmbH
3	Spectrometer	spect
4	Solvent	D20
5	Temperature	298.1
6	Pulse Sequence	zg30
7	Experiment	1D
8	Probe	5 mm CPPBBO BB-1H/ 19F/ D Z-GRD Z122624/ 0008
9	Number of Scans	241
10	Receiver Gain	32
11	Relaxation Delay	1.0000
12	Pulse Width	12.0000
13	Acquisition Time	3.2768
14	Acquisition Date	2012-09-17T14:13:00
15	Spectrometer Frequency	499.89
16	Spectral Width	10000.0
17	Lowest Frequency	-1913.0
18	Nucleus	1H
19	Acquired Size	32768
20	Spectral Size	65536



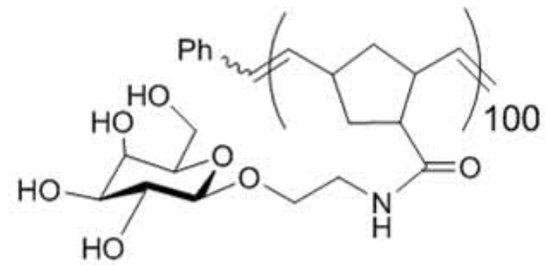
^{1}H NMR spectra of poly(Glc)$_{100}$

	Parameter	Value
1	Data File Name	C:/ Users/ Stella/ Dropbox/ RESEARCH/ NMR/ NMR Varian 500 600/ 600/ galactose/ nb-galactose-deprot-10mer 01292011.fid/ fid
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	D2O
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Number of Scans	53
9	Receiver Gain	34
10	Pulse Width	0.0000
11	Acquisition Date	2011-01-31T12:19:18
12	Modification Date	2011-01-31T15:23:54
13	Spectrometer Frequency	599.72
14	Spectral Width	8000.0
15	Lowest Frequency	-1001.3
16	Nucleus	1H
17	Acquired Size	15136
18	Spectral Size	65536



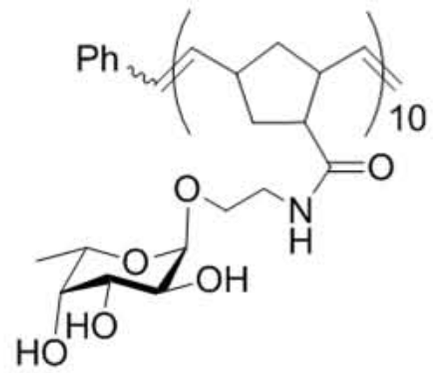
^{1}H-NMR spectrum of poly(Gal)$_{10}$

	Parameter	Value
1	Data File Name	F:/ nmr/ NMR with fixed fid/ galactose/ nb-galactose100mer-deprot-02072011.fid/ fid
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	D2O
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcx
9	Number of Scans	69
10	Receiver Gain	38
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.8920
14	Acquisition Date	2011-02-07T14:00:30
15	Spectrometer Frequency	599.72
16	Spectral Width	8000.0
17	Lowest Frequency	-1001.3
18	Nucleus	1H
19	Acquired Size	15136
20	Spectral Size	65536



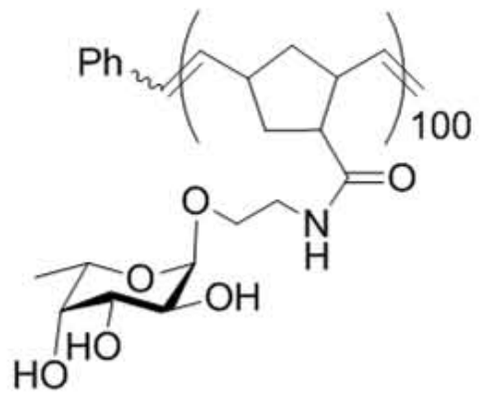
^{1}H-NMR spectrum of poly(Gal)$_{100}$

	Parameter	Value
1	Data File Name	F:/ fucose/ fucose-10mer/ 1/ fid
2	Title	fucose-10mer.1.fid
3	Origin	Bruker BioSpin GmbH
4	Spectrometer	spect
5	Solvent	D2O
6	Temperature	308.2
7	Pulse Sequence	zg30
8	Experiment	1D
9	Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z116098/ 0058
10	Number of Scans	164
11	Receiver Gain	32
12	Relaxation Delay	1.0000
13	Pulse Width	10.1000
14	Modification Date	2013-05-04T14:50:28
15	Spectrometer Frequency	399.83
16	Spectral Width	8223.7
17	Lowest Frequency	-1603.6
18	Nucleus	1H
19	Acquired Size	32768
20	Spectral Size	65536



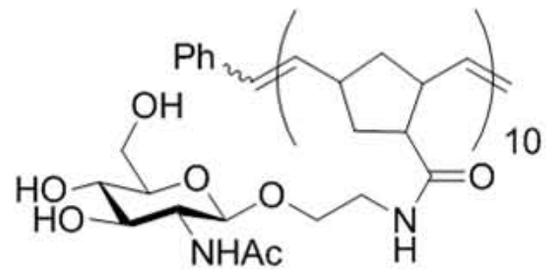
^{1}H-NMR spectrum of poly(Fuc)$_{10}$

	Parameter	Value
1	Data File Name	F:/ fucose/ fucose-100mer/ 1/ fid
2	Title	fucose-100mer.1.fid
3	Origin	Bruker BioSpin GmbH
4	Spectrometer	spect
5	Solvent	D2O
6	Temperature	308.2
7	Pulse Sequence	zg30
8	Experiment	1D
9	Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z116098/ 0058
10	Number of Scans	340
11	Receiver Gain	59
12	Relaxation Delay	1.0000
13	Pulse Width	10.1000
14	Modification Date	2013-05-04T15:46:20
15	Spectrometer Frequency	399.83
16	Spectral Width	8223.7
17	Lowest Frequency	-1602.6
18	Nucleus	1H
19	Acquired Size	32768
20	Spectral Size	65536



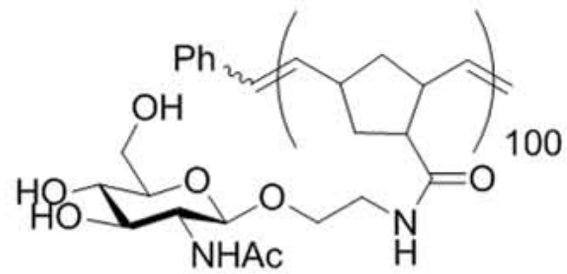
^{1}H-NMR spectrum of poly(Fuc)$_{100}$

	Parameter	Value
1	Data File Name	F:/ NMR/ glcNAc/ nb-glcnac10mer-2-deprot-12102010.fid/ fid
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	D2O
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Experiment	1D
8	Probe	hcx
9	Number of Scans	48
10	Receiver Gain	40
11	Relaxation Delay	1.0000
12	Pulse Width	0.0000
13	Acquisition Time	1.8920
14	Acquisition Date	2010-12-11T17:26:54
15	Spectrometer Frequency	599.72
16	Spectral Width	8000.0
17	Lowest Frequency	-1001.3
18	Nucleus	1H
19	Acquired Size	15136
20	Spectral Size	65536



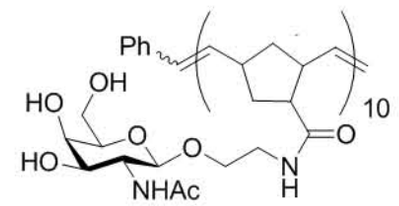
^{1}H-NMR spectrum of poly(GlcNAc)$_{10}$

Parameters	value
1 Data File Name	I:/ NMR/ glcNAc/ deprot_nb-glcnac-100mer-12062010.fid/ fid
2 Origin	Varian
3 Spectrometer	inova
4 Solvent	D20
5 Temperature	25.0
6 Pulse Sequence	s2pul
7 Probe	hcx
8 Number of Scans	100
9 Receiver Gain	28
10 Relaxation Delay	1.0000
11 Pulse Width	0.0000
12 Acquisition Time	1.8920
13 Acquisition Date	2010-12-06T13:17:09
14 Spectrometer Frequency	599.72
15 Spectral Width	8000.0
16 Lowest Frequency	-1001.3
17 Nucleus	1H
18 Acquired Size	15136
19 Spectral Size	65536



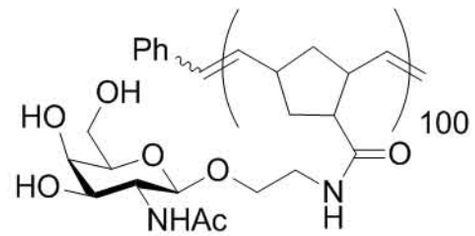
^{1}H NMR spectra of poly(GlcNAc)$_{100}$

	Parameter	Value
1	Data File Name	F:/ NMR/ galNAc/ deprot-nb-galnac-10mer-10042012/ 1/ fid
2	Title	deprot-nb-galnac-10mer-10042012.1.fid
3	Origin	Bruker BioSpin GmbH
4	Spectrometer	spect
5	Solvent	D2O
6	Temperature	298.1
7	Pulse Sequence	zg30
8	Experiment	1D
9	Probe	5 mm CPPBBO BB-1H/ 19F/ D Z-GRD Z122624/ 0008
10	Number of Scans	100
11	Receiver Gain	32
12	Relaxation Delay	1.0000
13	Pulse Width	12.0000
14	Modification Date	2012-10-05T11:45:02
15	Spectrometer Frequency	499.89
16	Spectral Width	10000.0
17	Lowest Frequency	-1913.0
18	Nucleus	1H
19	Acquired Size	32768
20	Spectral Size	65536



^{1}H-NMR spectrum of poly(GalNAc)$_{10}$

	Parameter	Value
1	Data File Name	F:/ NMR/ galNAc/ deacetyl-NB-GalNAc100mer-1-09062012/ 1/ fid
2	Title	deacetyl-NB-GalNAc100mer-1-09062012.1.fid
3	Origin	Bruker BioSpin GmbH
4	Spectrometer	spect
5	Solvent	D2O
6	Temperature	298.1
7	Pulse Sequence	zg30
8	Experiment	1D
9	Probe	5 mm CPPBBO BB-1H/ 19F/ D Z-GRD Z122624/ 0008
10	Number of Scans	52
11	Receiver Gain	32
12	Relaxation Delay	1.0000
13	Pulse Width	12.0000
14	Modification Date	2012-09-06T17:22:54
15	Spectrometer Frequency	499.89
16	Spectral Width	10000.0
17	Lowest Frequency	-1913.0
18	Nucleus	1H
19	Acquired Size	32768
20	Spectral Size	65536



^{1}H-NMR spectrum of poly(GalNAc)$_{100}$