Supporting Information

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SI Text

Methods. ***Synthesis of polymers A and B.*** The lactose trichloroacetimidate donor was coupled with monoallylated hexa(ethylene glycol) in the presence of boron trifluoride etherate to provide lactoside **1**. The deacetylation of **5** under Zemplen conditions gave heptaol **2**. The compound **2** was then galactosylated enzymatically by using α-(1,4)-galactosyltransferase/UDP-4′-Gal-epimerase to provide target compound **3**. The hydrolysis of amide group of **4** (1) under basic conditions provided target compound **5**. Copolymerization of the equimolar mixture of **3** and **5** with acrylamide afforded polymer **A**.

The known lactoside **6** (1) was deacetylated under Zemplen conditions to provide glycoside **7**. The **7** was galactosylated enzymatically using α-(1,4)-galactosyltransferase/UDP-4′-Gal-epimerase to provide trisaccharide **8**. The hydrolysis of amide group of **8** under basic conditions afforded target compound **9**. Copolymerization of **9** with acrylamide afforded polymer **B**.

Synthesis of (S)-PolyBAIT and (R)-PolyBAIT. Fig. S2 delineates synthesis of (*S*)-PolyBAIT. Installation of a cyclic pyruvate function into the glucose moiety was achieved via the synthesis of the known 1,2-*O*-cyanoethylidene derivative of glucose followed by the treatment with alkaline methanol to generate a 1,2-cyclic pyruvate methyl ester **10** (2). Selective installation of benzylidene followed by acetylation of the remaining hydroxyl groups gave compound **11**. Reductive opening of benzylidene ring in **11** afforded the glycosyl acceptor **12**. Glycosylation of **12** with galactose trichloroacetimidate **13** yielded disaccharide **14**. Removal of the benzyl group by hydrogenolysis provided disaccharide **15** with free alcohol at the C-6 position in glucose moiety, which was activated as *p*-nitrophenylcarbonate **16** followed by the installation of the linker moiety containing a terminal double bond. The resulting lactose derivative **18** was deacetylated and converted into a P^k-trisaccharide derivative **20** by enzymatic glycosylation using a fusion enzyme UDP-Gal/Glc epimerase/(1–4)-α-D-galactosyl transferase and UDP-glucose. Radical copolymerization of the obtained monomer **20** with acrylamide completed the synthesis of the polymer-based heterobifunctional inhibitor (*S*)-PolyBAIT.

For the preparation of the (*R*)-stereoisomer, we used an alternative approach involving derivatization of disaccharide lactose (Fig. S3). Cyanoethylidene derivative **21** was converted into a 1,2-cyclic pyruvate methyl ester **22** by using MeONa. Deprotection and subsequent benzylidenation of the resulting disaccharide **23** yielded compound **24**, which allowed for selective 6-OH protection using TBDPSCl followed by the protection of the remaining hydroxyl groups as acetate esters to give compound **25**. The selective removal of TBDPS by HF-Py treatment gave alcohol **26**. Activation of the resulting hydroxyl group as a *p*-nitrophenyl carbonate allowed for the addition of the amine **17** to give **27**. Removal of bezylidene group yielded compound **28**, which was deacetylated and enzymatically glycosylated by using the fusion enzyme UDP-Gal/Glc epimerase/(1–4)-α-D-galactosyl transferase and UDP-glucose to give the trisaccharide **30**. Radical copolymerization of **30** with acrylamide yielded the target (*R*)-PolyBAIT.

Experimental. ***General methods.*** Optical rotations were measured on a PerkinElmer 241 polarimeter in a 10-cm cell at ambient temperature. Analytical TLC was performed on silica gel 60-F_{254} (Merck) with detection by quenching of fluorescence and/or by charring with 10% H_2SO_4 in ethanol solution followed by heating at 180 °C. Column chromatography was performed on silica gel 60 (40–60 μm; Merck), and solvents were used as supplied. ^{1}H-NMR spectra were recorded at 400, 500, or 600 MHz (Varian) in $CDCl_3$ (referenced to residual $CHCl_3$ at δ_H 7.24 ppm) or in D_2O (referenced to external acetone at δ_H 2.225 ppm). *J* values are given in Hertz. All commercial reagents were used as supplied.

3,6,9,12,15,18-Hexa-oxa-henicos-20-enyl 2,3,6-tri-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-β-D-glucopyranoside (1). The lactose 2,3,6,2′,3′,4′,6′-hexaacetate (1–*O*)-trichloroacetimidate (1.8 g, 2.3 mmol, as α/β 9:1 mixture), monoallyl hexa(ethylene glycol) (0.64 g, 2.0 mmol) and activated 4-Å molecular sieves (1.5 g) were stirred for 1 h in dry dichloromethane (20 ml). Then the mixture was cooled down to 0°C and $BF_3{\cdot}Et_2O$ (0.3 ml) was added dropwise. After TLC indicated the reaction to be completed, it was neutralized with Et_3N, filtered through Celite, and concentrated. Chromatography of the residue on the silica gel provided the title compound **1** (1.3 g, 71% yield). ^{1}H-NMR ($CDCl_3$): δ_H 5.89 (m, 1 H, allyl), 5.32 (dd, 1 H, J 1.0 Hz, 3.5 Hz, H-4′), 5.27 (m, 1 H, allyl), 5.23 (m, 1 H, allyl), 5.15 (m, 2 H, H-3 and allyl), 5.08 (dd, 1 H, J 8.0 Hz, 10.5 Hz, H-2′), 4.93 (dd, 1 H, J 3.5 Hz, 10.5 Hz, H-3′), 4.86 (dd, 1 H, J 8.0 Hz, 9.5 Hz, H-2), 4.53 (d, 1 H, J 7.5 Hz, H-1), 4.46 (m, 2 H, H-1′ and H-6a), 4.07 (m, 2 H, H-6b and H-6a′), 4.00 (m, 2 H, allyl), 3.84 (m, 2 H, H-5′), 3.77 (t, 1 H, J 9.5 Hz, H-4), 3.69 (m, 1 H, H-6b′), 3.57–3.65 (m, 15 H), 2.13 (s, 3 H, OAc), 2.10 (s, 3 H, OAc), 2.04 (s, 3 H, OAc), 2.02 (s, 3 H, OAc), 2.02 (s, 3 H, OAc), 2.01 (s, 3 H, OAc), 1.94 (s, 3 H, OAc). ESI-HRMS *m/z* 963.36814 ($[M+Na]^+$, $C_{41}H_{64}O_{24}Na^+$ requires 963.36798).

3,6,9,12,15,18-Hexa-oxa-henicos-20-enyl-O-(β-D-galactopyranosyl)-β-D-glucopyranoside (2). The lactoside **1** (1.3 g, 1.4 mmol) was dissolved in dry MeOH (20 ml) and MeONa (3 ml, 0.5 M) was added. The mixture was stirred overnight and then neutralized with Amberlite H^+, filtered and concentrated to provide title compound **2** (0.8 g, 90% yield). ^{1}H-NMR (D_2O): δ_H 5.95 (m, 1 H, allyl), 5.33 (m, 1 H, allyl), 5.26 (m, 1 H, allyl), 4.50 (d, 1 H, J 7.8 Hz, H-1′), 4.44 (d, 1 H, J 7.8 Hz, H-1), 4.06 (m, 3 H, allyl), 3.97 (m, 1 H), 3.92 (m, 1 H), 3.58–3.84 (m, 31 H), 3.53 (m, 1 H, H-2), 3.33 (m, 1 H, H-2′). ESI-HRMS *m/z* 669.29389 ($[M+Na]^+$, $C_{27}H_{50}O_{17}Na^+$ requires 669.29402).

3,6,9,12,15,18-Hexa-oxa-henicos-20-enyl 4-O-[4-O-(α-D-galactopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside (3). The lactoside **2** (0.11 g, 0.17 mmol) was dissolved in 4 ml of H_2O, Hepes buffer [1.25 ml, 1.6 M, 10 mM $MnCl_2$, bovine serum albumine (BSA, 0.8 mg/ml), pH 8], DTT solution (100 mM, 0.32 ml) and alkaline phosphatase (63 μl). To the mixture UDP-Glc (0.13 g) was added, followed by α- (1, 4)-galactosyltransferase/UDP-4′-Gal-epimerase (0.625 ml). The reaction was incubated at 37°C overnight and then chromatographed on C_{18} to afford title compound **3** (0.1 g, 75% yield). ^{1}H-NMR (D_2O): δ_H 5.95 (m, 1 H, allyl), 5.34 (m, 1 H, allyl), 5.27 (m, 1 H, allyl), 4.94 (d, 1 H, J 3.6 Hz, H-1"), 4.51 (d, 1 H, J 8.4 Hz, H-1′), 4.51 (d, 1 H, J 7.8 Hz, H-1), 4.35 (m, 1 H), 3.56–4.07 (m, 42 H), 3.33 (t, 1 H, J 8.4 Hz, H-2′). ESI-HRMS *m/z* 831.34649 ($[M+Na]^+$, $C_{33}H_{60}O_{22}Na^+$ requires 831.34685).

25-[(cis)-2-Hydroxycarbonyl-2-methyl-[1,3]dioxane-5-yloxy]-24-(R,S)-hydroxy-4,7,10,13,16,19,22-hepta-oxa-pentadecos-1-ene (5). To a solution of **4** (125 mg, 0.214 mmol) in methanol (4.5 ml), 4 M aqueous NaOH (268 μl) was added. The reaction mixture was stirred at 80°C overnight. On the following day, additional 4 M NaOH (134 μl) was added and the mixture was left at 80°C overnight. On the following day, NMR and TLC confirmed that the hydrolysis of the amide was complete. The mixture was diluted with methanol

and deionized with Dowex H^+ resin, filtered and concentrated. The dry residue was dissolved in water and freeze-dried to provide the title product as a syrup (97 mg; 84%). ^{1}H-NMR (D_2O) δ: 5.99–5.92 (m, 1 H, HC = CH_2), 5.36–5.26 (m, 2 H, HC = CH_2), 4.18 (dd, 2 H, J 4.7 Hz, J 11.4 Hz, H-4e, H-6e), 4.07 (d, 2 H, J 5.9 Hz, CH_2-CH = CH_2), 3.94–3.92 (m, 1 H, CH), 3.74–3.65 (m, 26 H, H-5, OCH_2), 3.70–3.60 (m, 5 H, H-4a, H-6a, OCH_2), 1.50 (s, 3 H, CH_3). Electrospray ionization HRMS, calcd for $C_{24}H_{44}O_{13}Na$ (M+Na): *m/z* 563.26741, found: *m/z* 563.26776.

24-(R,S)-[4-O-(β-D-Galactopyranosyl)-β-D-glucopyranosyloxy]-25-[(cis)-2-dimethylaminocarbonyl-2-methyl-[1,3]dioxane-5-yloxy]-4,7,10,13,16,19,22-hepta-oxa-pentacos-1-ene (7). The compound **6** (0.33 g, 0.3 mmol) was dissolved in dry MeOH (10 ml) and MeONa (1 ml of 0.5 M solution) was added. After stirring overnight at room temperature the mixture was neutralized with Amberlite (H^+) resin, filtered, concentrated and dried in vacuum to afford title compound **7** (0.24 g, 98% yield). ^{1}H-NMR (D_2O): δ_H 5.94 (m, 1 H, allyl), 5.34 (m, 1 H, allyl), 5.27 (m, 1 H, allyl), 4.60 (m, 1 H, H-1′), 4.44 (m, 1 H, H-1), 4.20 (m, 2 H), 4.07 (m, 3 H, allyl), 3.96 (m, 1 H), 3.92 (m, 1 H, H-4′), 3.61–3.82 (m, 39 H, OMe), 3.53 (m, 4 H), 3.31 (m, 1 H, H-2′), 3.26 (s, 3 H, NMe), 3.00 (s, 3 H, NMe), 1.52 (m, 3 H, C-Me). ESI-HRMS *m/z* 914.42097 ($[M+Na]^+$, $C_{38}H_{69}NO_{22}Na^+$ requires 914.42035).

24-(R,S)-[4-O-(4-O-(α-D-Galactopyranosyl)-β-D-galactopyranosyl)-β-D-glucopyranosyloxy]-25-[(cis)-2-dimethylaminocarbonyl-2-methyl-[1,3]dioxane-5-yloxy]-4,7,10,13,16,19,22-hepta-oxa-pentacos-1-ene (8). The lactoside **7** (0.24 g, 0.27 mmol) was dissolved in 8 ml of H_2O, Hepes buffer[2.5 ml, 1.6 M, 10 mM $MnCl_2$, bovine serum albumine (BSA, 0.8 mg/ml), pH 8], DTT solution (100 mM, 0.63 ml) and alkaline phosphatase (125 μl). To the mixture UDP-Glc (0.25 g) was added, followed by α- (1, 4)-galactosyltransferase/ UDP-4′-Gal-epimerase (1.25 ml). The reaction was incubated at 37°C overnight and then chromatographed on C_{18} to afford title compound **8** (0.22 g, 78% yield). ^{1}H-NMR (D_2O): δ_H 5.94 (m, 1 H, allyl), 5.34 (m, 1 H, allyl), 5.27 (m, 1 H, allyl), 4.94 (d, 1 H, J 3.6 Hz, H-1"), 4.60 (m, 1 H, H-1′), 4.50 (m, 1 H, H-1), 4.34 (t, 1 H, J 6.0 Hz, H-5"), 4.20 (m, 2 H), 3.49–4.08 (m, 57 H), 3.31 (m, 1 H, H-2′), 3.26 (s, 3 H, NMe), 3.00 (s, 3 H, NMe), 1.52 (m, 3 H, C-Me). ESI-HRMS *m/z* 1076.47343 ($[M+Na]^+$, $C_{44}H_{79}NO_{27}Na^+$ requires 1076.47317).

24-(R,S)-[4-O-(4-O-(α-D-Galactopyranosyl)-β-D-galactopyranosyl)-β-D-glucopyranosyloxy]-25-[(cis)-2-carboxyl-2-methyl-[1,3]dioxane-5-yloxy]-4,7,10,13,16,19,22-hepta-oxa-pentacos-1-ene (9). A solution of **8** (0.15 g, 0.14 mmol) and NaOH (5 equiv.) was stirred 3 days at 80°C and the progress was followed by NMR, the mixture was neutralized with Amberlite H^+ resin, filtered and concentrated to give title compound **9** (0.14 g, 96% yield). ^{1}H-NMR (D_2O): δ_H 5.95 (m, 1 H, allyl), 5.34 (m, 1 H, allyl), 5.27 (m, 1 H, allyl), 4.94 (m, 1 H, H-1"), 4.60 (d, 1 H, J 7.8 Hz, H-1′), 4.50 (m, 1 H, H-1), 4.34 (t, 1 H, J 6.0 Hz, H-5"), 4.20 (m, 2 H), 3.55–4.09 (m, 57 H), 3.31 (m, 1 H, H-2′), 1.50 (m, 3 H, C-Me). ESI-HRMS *m/z* 1049.42593 ($[M+Na]^+$, $C_{42}H_{74}O_{28}Na^+$ requires 1049.42588).

Preparation of Heterobifunctional Polymers. ***Polymer A.*** To a solution of acrylamide (17.1 mg, 0.25 mmol), monomer **3** (81 mg, 0.1 mmol) and monomer **5** (54 mg, 0.1 mmol) in degassed water (1 ml) a solution of sodium persulfate (1 mg) in of water (10 μl) was added. The solution was spurged with argon and TEMED (12 μl) was added. The mixture was incubated for 16 h then dialyzed and freezed dried to give 13 mg of **A**. NMR indicates ≈4.9% incorporation of each ligand.

Polymer B. To a solution of acrylamide (34.2 mg, 0.5 mmol) and monomer **3** (103 mg, 0.1 mmol) in degassed water (1 ml) a solution of sodium persulfate (1 mg) in of water (10 μl) was added. The solution was spurged with argon and TEMED (12 μl) was added. The mixture was incubated for 16 h then dialyzed and freeze-dried to give 24 mg of **B**. NMR indicates ≈2.6% of sugar monomer incorporation of the ligand.

3-O-Acetyl-4,6-O-benzylidene-1,2-O-[(S)-1-(methoxycarbonyl)ethylidene]-α-D-glucopyranoside (11). To a solution of dry 1,2-*O*-[(*S*)-1-(methoxycarbonyl)ethylidene]-α-D-glucopyranoside **10** (4.62 g, 15.1 mmol) in MeCN (30 ml) $PhCH(OMe)_2$ (2.27 ml, 1 eq) was added followed by CSA (100 mg). After 30 min Py-Ac_2O (1:1 vol/vol, 10 ml) was added and the mixture was stirred for 3 h at RT. The reaction was quenched by addition of MeOH, concentrated and co-evaporated twice with toluene. Chromatography of the residue on silica gel (hexane/ethyl acetate (30–40%)) gave the title product (3.19 g, 54%), $[\alpha]_D$+23 °(*c* 1.2, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ_H 7.5–7.35 (m, 5 H, arom.), 5.84 (d, 1 H, $J_{1,2}$ 5.1 Hz, H-1), 5.53 (s, 1 H, C*H*Ph), 5.24 (dd, 1 H, $J_{2,3}$ 3.4 Hz, $J_{3,4}$ 8.3 Hz, H-3), 4.41 (dd, 1 H, $J_{5,6a}$ 5.1 Hz, $J_{6a,6b}$ 10.5 Hz, H-6a), 4.32 (dd, 1 H, H-2), 3.94 (dd, 1 H, $J_{6b,5}$ 5.2 Hz, H-6b), 3.77–3.70 (m, 5 H, H-4, H-5, CH_3), 2.126 (s, 3 H, OAc), 1.767 (s, 3 H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 169.79 (C = O), 169.48 (C = O), 136.80 (C arom.), 129.17 (CH arom.), 128.28 (CH arom.), 126.14 (CH arom.), 104.03 (C pyruvate), 101.59 (CH benzylidene), 98.84 (C-1), 77.68, 77.15, 73.07, 68.84 (C-6), 62.34, 52.69 (OCH_3), 22.39 (CH_3), 20.98 (CH_3). Electrospray ionization MS *m/z* 419.13136 ($[M+Na]^+$, $C_{19}H_{24}O_9Na^+$ requires 419.13125). Anal. Calcd for $C_{19}H_{24}O_9$: C, 57.86; H, 5.62. Found: C, 57.84; H, 5.59.

3-O-Acetyl-6-O-benzyl-1,2-O-[(S)-1-(methoxycarbonyl)ethylidene]-α-D-glucopyranoside (12). To a suspension of benzylidene derivative **11** (1.6 g, 4 mmol) and molecular sieves (4 Å, 1 g) in dry THF (30 ml) $NaCNBH_3$ (3.8 g, 60 mmol) was added followed by HCl-ether solution (2 M, ≈10 ml) until gas stopped to evolve. The mixture was neutralized by saturated aq. $NaHCO_3$, filtered through celite, concentrated, then taken up in DCM, washed with water and concentrated. Chromatography of the residue on silica gel (hexane/ethyl acetate = 1:1) gave the title compound **12** (1.16 g, 73%), $[\alpha]_D$+13 °(*c* 0.9, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ_H 7.28–7.25 (m, 5 H, arom.), 5.82 (d, 1 H, $J_{1,2}$ 5.1 Hz, H-1), 5.04 (t, 1 H, $J_{2,3}$≈$J_{3,4}$ = 3.4 Hz, H-3), 4.63 (d, 1 H, J_{gem} 12.2 Hz, CH_2), 4.58 (d, 1 H, CH_2), 4.39 (m, 1 H, H-2), 3.84 (m, 1 H, H-5), 3.79–3.75 (m, 5 H, H-4, H-6a, CH_3), 3.72 (dd, 1 H, $J_{5,6b}$ 3.8 Hz, $J_{6a,6b}$ 10.4 Hz, H-6b), 2.78 (s, 1 H, OH), 2.11 (s, 3 H, OAc), 1.75 (s, 3 H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 170.72 (C = O), 169.42 (C = O), 137.74 (C arom.), 128.43 (CH arom.), 127.77 (CH arom.), 104.87 (C pyruvate), 98.,07 (C-1), 74.82, 74.51, 73.67 (CH_2-Bn), 70.22, 69.62 (C-6), 69.23, 52.68 (OCH_3), 21.69 (CH_3), 20.88 (CH_3). Electrospray ionization MS *m/z* 417.11580 ($[M+Na]^+$, $C_{19}H_{22}O_9Na^+$ requires 417.11560). Anal. Calcd for $C_{19}H_{22}O_9$: C, 57.57; H, 6.10. Found: C, 57.42; H, 6.01.

3-O-Acetyl-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-6-O-benzyl-1,2-O-[(S)-1-(methoxycarbonyl)ethylidene]-α-D-glucopyranoside (14). Tetra-*O*-acetyl-galactopyranose (1-*O*)-trichloroacetimidate **13** (3.83 g, 7.77 mmol) and glycosyl acceptor **12** (2.77 g, 7 mmol) were combined, dried and dissolved in DCM (30 ml), then molec. sieves (4 Å, 1 g) were added. After 30 min TMSOTf (100 μl) was added. After 1 h the mixture was quenched with Py and concentrated. Chromatography of the residue on silica gel (hexane/ethyl acetate = 1:1) gave **14** (2.66 g, 52%), $[\alpha]_D$ +4 °(*c* 2.6, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ_H 7.40–7.30 (m, 5 H, arom.), 5.80 (d, 1 H, $J_{1,2}$ 5.2 Hz, H-1), 5.44 (dd, 1 H, $J_{2,3}$ 2.2 Hz, $J_{3,4}$ 2.7 Hz, H-3), 5.34 (dd, 1 H, $J_{3',4'}$ 3.5 Hz, $J_{4',5'}$ 1.0 Hz, H-4′), 5.12 (dd, 1 H, $J_{2',3'}$ 7.9 Hz, $J_{3',4'}$ 10.4 Hz, H-2′), 4.92 (dd, 1 H, H-3′), 4.70 (d, 1 H, J_{gem} 12.2 Hz, Bn), 4.50 (d, 1 H, Bn), 4.43 (d, 1 H, H-1′), 4.32 (m, 1 H, H-2), 4.13–4.09 (m, 2 H, H-6′a, H-6′b), 3.87–3.78 (m, 3 H, H-4, H-5, H-5′), 3.76 (s, 3 H, CH_3), 3.67 (dd, 1 H, $J_{5,6a}$ 2.2 Hz, $J_{6a,6b}$ 10.9 Hz, H-6a), 3.59 (dd, 1 H, $J_{5,6b}$ 3.4 Hz, H-6b), 2.16, 2.08, 2.03, 1.97, 1.92 (5s, 15 H, OAc), 1.73 (s, 3 H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 170.35 (C = O), 170.29 (C = O), 170.07 (C = O), 169.42 (C = O), 169.11 (C = O), 169.06(C = O), 137.82 (C arom.), 128.54 (CH arom.), 127.96 (CH arom.), 105.38 (C-pyruvate), 102.13 (C-1′), 98.08 (C-1), 76.10, 74.09, 73.60 (*C*H_2-Ph), 70.88, 70.69, 70.43, 68.90, 68.81, 68.33 (C-6′), 66.87, 61.03 (C-6), 52.65 (OCH_3), 21.26 (CH_3), 20.88 (CH_3), 20.69

(CH_3), 20.65 (CH_3), 20.62 (CH_3), 20.57 (CH_3). Electrospray ionization MS *m/z* 749.22665 ($[M+Na]^+$, $C_{33}H_{42}O_{18}Na^+$ requires 749.22634). Anal. Calcd for $C_{33}H_{42}O_{18}$: C, 54.54; H, 5.83;. Found: C, 54.23; H, 5.73.

3-O-Acetyl-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-1,2-O-[(S)-1-(methoxycarbonyl)ethylidene]-α-D-glucopyranoside (15). To a solution of **14** (1.6 g, 2.2 mmol) in MeOH (10 ml) drop of water and $Pd(OH)_2$ (30 mg) were added. After 2 h of stirring under H_2 atmosphere the mixture was filtered via Millipore membrane filter, concentrated and chromatographed on silica gel (hexane/acetone = 1:1) to give **15** (1.0 g, 71%), $[\alpha]_D$+8 °(*c* 1.2, $CHCl_3$).^{1}H-NMR ($CDCl_3$): δ_H 5.76 (d, 1 H, $J_{1,2}$ 5.2 Hz, H-1), 5.51 (dd, 1 H, $J_{2,3}$ ~$J_{3,4}$ 2.3 Hz, H-3), 5.38 (dd, 1 H, $J_{3',4'}$ 3.5 Hz, $J_{4',5'}$ 0.9 Hz, H-4′), 5.18 (dd, 1 H, $J_{2',3'}$ 8.0 Hz, $J_{3',4'}$ 10.4 Hz, H-2′), 5.01 (dd, 1 H, H-3′), 4.64 (d, 1 H, H-1′), 4.33 (m, 1 H, H-2), 4.14–4.10 (m, 2 H, H-6′a, H-6′b), 3.93 (td, 1 H, $J_{4',5'}$ 0.9 Hz, $J_{5',6a'}$ ~$J_{5',6b'}$ 6.7 Hz, H-5′), 3.85–3.82 (m, 2 H, H-4, H-6a), 3.766 (s, 3 H, CH_3), 3.75 (m, 1 H, H-5), 3.61 (dd, 1 H, $J_{5,6b}$ 3.8 Hz, $J_{6a,6b}$ 12.0 Hz, H-6b), 2.16, 2.09, 2.06, 2.03, 1.98 (5s, 15 H, OAc), 1.74 (s, 3 H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 170.37 (C = O), 170.27 (C = O), 170.07 (C = O), 169.32 (C = O), 169.08 (C = O), 105.47 (C-pyruvate), 102.25 (C-1′), 97.78 (C-1), 76.49, 74.40, 70.93, 70.84. 70.36, 69.05, 68.98, 66.89, 61.80 (C-6′), 61.05 (C-6), 52.69 (OCH_3), 21.27 (CH_3), 20.86 (CH_3), 20.68 (CH_3), 20.64 (CH_3), 20.55 (CH_3). Electrospray ionization MS *m/z* 659.17920 ($[M+Na]^+$, $C_{26}H_{36}O_{18}Na^+$ requires 659.17939). Anal. Calcd for $C_{26}H_{36}O_{18}$: C, 49.06; H, 5.70. Found: C, 49.12; H, 5.70.

3-O-Acetyl-6-O-(4-nitrophenyl)-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-1,2-O-[(S)-1-(methoxycarbonyl)ethylidene]-α-D-glucopyranoside (16). To a solution of **15** (1 g, 1.57 mmol) and 4-nitrophenyl chloroformate (380 mg, 1.2 eq) in dry DCM (10 ml) Py (≈0.2 ml) was added. TLC (hexane/acetone = 1:1) shows complete conversion after 5 min. Water (0.2 ml) was added and the mixture was concentrated and chromatographed on silica gel in hexane/ethyl acetate = 1:1 to give **16** (1.2 g, 95%), $[\alpha]_D$+0.7 °(*c* 1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ_H 8.31–8.28 (m, 2 H, arom.), 7.42–7.39 (m, 2 H, arom.), 5.80 (d, 1 H, $J_{1,2}$ 5.1 Hz, H-1), 5.55 (dd, 1 H, $J_{2,3}$ 1.6 Hz, $J_{3,4}$ 2.5 Hz, H-3), 5.39 (dd, 1 H, $J_{3',4'}$ 3.5 Hz, $J_{4',5'}$ 1.1 Hz, H-4′), 5.21 (dd, 1 H, $J_{2',3'}$ 8.0 Hz, $J_{3',4'}$ 10.4 Hz, H-2′), 5.04 (dd, 1 H, H-3′), 4.70 (d, 1 H, H-1′), 4.51 (dd, 1 H, $J_{6a,5}$ 2.3 Hz, $J_{6a,6b}$ 11.7 Hz, H-6a), 4.39 (m, 1 H, H-2), 4.51 (dd, 1 H, $J_{6b,5}$ 5.7 Hz, H-6b), 4.17 (dd, 1 H, $J_{6'a,5}$ 6.5 Hz, $J_{6'a,6'b}$ 11.3 Hz, H-6a), 4.07 (m, 1 H, H-5), 3.93 (td, 1 H, $J_{4',5'}$ 1.1 Hz, $J_{5',6a'}$ ~$J_{5',6b'}$ 6.6 Hz, H-5′), 3.78 (m, 4 H, H-4, CH_3), 2.17, 2.12, 2.07, 2.05, 1.98 (5s, 15 H, OAc), 1.78 (s, 3 H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 170.35 (C = O), 170.21 (C = O), 170.05 (C = O), 169.38 (C = O), 169.09 (C = O), 169.03 (C = O), 155.33 (C-O of Ph), 152.28 (C = O of carbonate), 145.53 (*C*-NO_2 of Ph), 125.36 (CH of Ph), 121.71 (CH of Ph), 105.67 (C-pyruvate), 101.66 (C-1′), 97.65 (C-1), 77.26, 74.22, 71.00, 70.82. 69.71, 68.89, 67.76 (C-6), 66.85, 66.57, 61.18 (C-6′), 52.79 (OCH_3), 21.20 (CH_3), 20.84 (CH_3), 20.69 (CH_3), 20.67 (CH_3), 20.64 (CH_3), 20.54 (CH_3). Electrospray ionization MS *m/z* 824.18573 ($[M+Na]^+$, $C_{33}H_{39}NO_{22}Na^+$ requires 824.18559). Anal. Calcd for $C_{33}H_{39}NO_{22}$: C, 49.44; H, 4.90; N, 1.75. Found: C, 49.64; H, 4.88; N, 2.07.

2-(Pent-4-enyloxycarbamoyl)-ethylamine (17). To a solution of pent-4-enol-1 (0.97 g, 11.26 mmol) and 4-nitrophenyl chloroformate (2.3 g) in dry DCM (7 ml) Py (0.92 ml) was slowly added. After 30 min the resulting mixture was added to a solution of 1,2-diaminoethane (2 ml) in DCM (10 ml). After 20 min the mixture was washed with brine and the DCM fractions were concentrated. Chromatography of the residue on silica gel (DCM-MeOH = 1:1–0:1) gave the product **17** as a slightly yellow syrup (1.11 g; 57%). ^{1}H-NMR ($CDCl_3$): δ_H 5.88–5.74 (m, 1 H, CH = CH_2), 5.15–4.90 (m, 3 H, NH, CH = CH_2), 4.06 (t, 2 H, *J* 6.6 Hz, CH_2O), 3.21 (t, 2 H, *J* 6.0 Hz, CH_2NHCO), 2.81 (t, 2 H, CH_2NH_2), 2.16–2.06 (m, 2 H, CH_2CH = CH_2), 1.76–1.60 (m, 2 H, $CH_2CH_2CH_2$). ^{13}C-NMR ($CDCl_3$): δ 156.90 (C = O), 137.59 (*C*H = CH_2), 115.12 (CH = *C*H_2), 64.29 (CH_2O), 42.89 (CH_2N), 41.34 (CH_2N), 29.98 (CH_2), 28.24 (CH_2). Electrospray ionization MS *m/z* 173.12849 ($[M+H]^+$, $C_8H_{17}N_2O_2^+$ requires 173.12845).

3-O-Acetyl-6-O-(2,5-dinitra-7-oxa-6-oxo-dodec-11-enoyl)-1,2-O-[(S)-1-(methoxycarbonyl)ethylidene]-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-α-D-glucopyranose (18). To a solution of **17** (250 mg) in DCM a solution of **16** (884 mg, 1.1 mmol) was added followed by Et_3N (300 μl). After 1 h with occasional gentle heating below boiling point TLC (hexane/acetone = 1:1) indicated completion of the reaction. The mixture was concentrated and the residue was chromatographed on silica gel (hexane/acetone = 1:1) to give **18** (550 mg, 60%), $[\alpha]_D$+0.8 °(*c* 1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ_H 5.84–5.76 (m, 1 H, -*CH* = CH_2), 5.76 (d, 1 H, $J_{1,2}$ 5.2 Hz, H-1), 5.53 (dd, 1 H, $J_{2,3}$ 1.4 Hz, $J_{3,4}$ 2.3 Hz, H-3), 5.38 (dd, 1 H, $J_{3',4'}$ 3.5 Hz, $J_{4',5'}$ 0.9 Hz, H-4′), 5.23 (broad s, 1 H, NH), 5.18 (dd, 1 H, $J_{2',3'}$ 8.2 Hz, $J_{3',4'}$ 10.4 Hz, H-2′), 5.08–4.97 (m, 4 H, H-3′, NH, -CH = CH_2), 4.63 (d, 1 H, H-1′), 4.35 (m, 1 H, H-2), 4.22 (dd, 1 H, $J_{6a,5}$ 2.0 Hz, $J_{6a,6b}$ 11.6 Hz, H-6a), 4.18–4.09 (m, 3 H, H-6b, H-6′a, H-6′b), 4.07 (m, 2 H, CH_2), 3.95 (td, 1 H, $J_{4',5'}$ 1.0 Hz, $J_{5',6a'}$ ~$J_{5',6b'}$ = 7.3 Hz, H-5′), 3.90 (m, 1 H, H-5), 3.77 (s, 3 H, CH_3), 3.64 (d, 1 H, H-4), 3.32 (broad s, 4 H, CH_2N), 2.17, 2.10, 2.08, 2.03, 1.98 (5 s, 15 H, OAc), 2.14–2.10 (m, 2 H, CH_2), 1.75 (s, 3 H, CH_3), 1.74–1.68 (m, 2 H, CH_2). ^{13}C-NMR ($CDCl_3$): δ 170.37 (C = O), 170.28 (C = O), 170.07 (C = O), 169.49 (C = O), 169.25 (C = O), 169.01 (C = O), 157.03 (C = O), 156.27 (C = O), 137.53 (-*C*H = CH_2), 115.20 (-CH = *C*H_2), 105.64 (C-pyruvate), 102.37 (C-1′), 97.71 (C-1), 77.32, 73.93, 70.88, 70.79, 69.84, 68.89, 67.21, 66.87, 64.50 (CH_2), 64.12 (CH_2), 61.99 (CH_2), 52.69 (OCH_3), 41.31 (CH_2), 41.06 (CH_2), 30.00 (CH_2), 28.19 (CH_2), 21.15 (CH_3), 20.86 (CH_3), 20.70 (CH_3), 20.66 (CH_3), 20.55 (CH_3). Electrospray ionization MS *m/z* 857.27929 ($[M+Na]^+$, $C_{35}H_{50}N_2O_{21}Na^+$ requires 857.27983). Anal. Calcd for $C_{35}H_{50}N_2O_{21}$: C, 50.36; H, 6.04, N, 3.36. Found: C, 50.37; H, 6.15; N, 3.35.

6-O-(2,5-Dinitra-7-oxa-6-oxo-dodec-11-enoyl)-1,2-O-[(S)-1-(carboxy)ethylidene]-4-O-(β-D-galactopyranosyl)-α-D-glucopyranose (19). The protected derivative **18** (0.53 g, 0.63 mmol) was dissolved in dry MeOH (3.5 ml) and NaOMe (1 M, 0.64 ml) in MeOH was added. The mixture was stirred at room temperature for 2 h then concentrated and the resulting solid was dissolved in water (3 ml). After 1 h the hydrolysis of the methyl ester was complete. The solution was neutralized with acetic acid, concentrated used directly in the next step. A small sample was purified by HPLC chromatography on C-18 in water-MeOH containing 1% AcOH, $[\alpha]_D$+19 °(*c* 1, H_2O). ^{1}H NMR (D_2O) δ: 5.90 (m,1 H, C*H* = CH_2), 5.62 (d, 1 H, $J_{1,2}$ 4.9 Hz, H-1), 5.10–5.01 (m, 2 H, CH = CH_2), 4.44 (d, 1 H, $J_{1',2'}$ 7.8 Hz, H-1′), 4.41–4.34 (m, 2 H, H-3, H-6a), 4.23 (dd, 1 H, $J_{5,6b}$ 5.3 Hz, $J_{6a,6b}$ 12.0 Hz, H-6b), 4.18 (m, 1 H, H-2), 4.08–4.01 (m, 3 H, H-5, OCH_2), 3.92 (d, 1 H, $J_{3',4'}$ 3.4 Hz, H-4′), 3.83–3.74 (m, 3 H, H-4, H-6′a, H-6′b), 3.69 (m, 1 H, H-5′), 3.64 (dd, 1 H, $J_{2',3'}$ 9.9 Hz, H-3′), 3.55 (m, 1 H, H-2′), 3.24 (s, 4 H, NCH_2), 2.12 (m, 2 H, CH_2), 1.72 (m, 2 H, CH_2), 1.64 (s, 3 H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 181.28 (C = O), 159.23 (C = O), 158.41 (C = O), 138.85 (-CH = CH_2), 115.26 (-CH = *C*H_2), 107.36 (C-pyruvate), 105.15 (C-1′), 96.74 (C-1), 78.53, 75.61, 75.37, 72.84, 71.04, 69.54, 68.87, 68.52, 65.29 (CH_2), 64.34 (CH_2), 61.33 (CH_2), 40.56 (CH_2), 40.35 (CH_2), 29.66 (CH_2), 27.75 (CH_2), 21.76 (CH_3). Electrospray ionization MS *m/z* 609.21365 ($[M]^-$), $C_{24}H_{37}N_2O_{16}^-$ requires 609.21376). Anal. Calcd for $C_{24}H_{38}N_2O_{16}$: C, 47.21; H, 6.27; N, 4.59. Found: C, 46.67; H, 6.23; N, 4.57.

6-O-(2,5-Dinitra-7-oxa-6-oxo-dodec-11-enoyl)-1,2-O-[(S)-1-(carboxy)ethylidene]-4-O-[4-O-(α-D-galactopyranosyl)-β-D-galactopyranosyl]-α-D-glucopyranose (20). Deprotected lactose derivative **19** was dissolved in water (7.14 ml) followed by the addition of Hepes buffer[3 ml, 1.6 M, 10 mM $MnCl_2$, bovine serum albumine (BSA, 0.8 mg/ml), pH 8], alkaline phosphatase (54 μl) and UDP-glucose (0.58 g; 1.5 eq.). α- (1, 4)-Galactosyltransferase/UDP-

4′-Gal-epimerase (0.7 ml) was added to the reaction mixture and it was incubated at 37°C. After 18 h NMR indicated that the reaction was complete. The reaction mixture was concentrated. The residue was treated with methanol, the solid precipitate was filtered off and rinsed with methanol. The combined methanol solution fractions were concentrated and chromatographed on silica gel (DCM-MeOH (4% of AcOH) = 6:4 - 4:5). The product was dissolved in water, filtered through 0.2 μm membrane and freeze-dried to give white powder **20** (394 mg; 80%), $[\alpha]_D$+61 °(*c* 1, H_2O). ^{1}H-NMR (D_2O): δ_H 5.90 (m, 1 H, C*H* = CH_2), 5.73 (d, 1 H, $J_{1,2}$ 4.9 Hz, H-1), 5.10–5.02 (m, 2 H, CH = CH_2), 4.94 (d, 1 H, $J_{1'',2''}$ 4.1 Hz, H-1″), 4.51 (d, 1 H, $J_{1',2'}$ 7.7 Hz, H-1′), 4.42–4.36 (m, 3 H, H-3, H-6a, H-5″), 4.31 (t, 1 H, $J_{2,3}$ 4.0 Hz, H-2), 4.24 (dd, 1 H, $J_{5,6b}$ 5.4 Hz, $J_{6a,6b}$ 12.0 Hz, H-6b), 4.07 (t, 2 H, *J* 6.5 Hz, OCH_2), 4.04–4.01 (m, 3 H, H-4′, H-4″, H-5), 3.94–3.90 (m, 2 H, H-5′, H-3″), 3.86–3.68 (m, 7 H, H-4, H-3′, H-6a′, H-6b′, H-2″, H-6a″, H-6b″), 3.58 (dd, 1 H, $J_{2',3'}$ 10.3 Hz, H-2′), 3.24 (bs, 4 H, NCH_2), 2.14 (m, 2 H, CH_2), 1.73 (m, 5 H, CH_2, CH_3), 1.65 (s, 3 H, CH_3). ^{13}C-NMR (D_2O): δ 174.53 (C = O), 159.85 (C = O), 159.00 (C = O), 139.44 (-CH = CH_2), 115.84 (-CH = CH_2), 106.71 (C-pyruvate), 106.10 (C-1″), 101.13 (C-1′), 97.82 (C-1), 79.44, 77.89, 76.38, 76.10, 73.01, 71.62, 70.06, 69.87, 69.60, 69.30, 65.90 (CH_2), 64.99 (CH_2), 61.39 (CH_2), 61.12 (CH_2), 41.15 (CH_2), 40.96 (CH_2), 30.26 (CH_2), 28.36 (CH_2), 21.85 (CH_3). Electrospray ionization MS *m*/*z* 795.26438 ($[M+Na]^+$), $C_{30}H_{48}N_2O_{21}Na^+$ requires 795.26418. Anal. Calcd for $C_{30}H_{47}N_2NaO_{21}$: C, 45.34; H, 5.96; N, 3.53. Found: C, 45.38; H, 6.11; N, 3.80.

(S)-PolyBAIT. The solution of **20** (471 mg; 0.61 mmol) and acrylamide (264 mg; 3.7 mmol) in Tris buffer (0.2 M, pH 9; 7.32 ml) was sparged with argon, then a solution of ammonium persulfate (7.43 mg) in Tris buffer (74.3 μl) was added and sparged with argon. TEMED (37.15 μl) was added to the reaction mixture and it was vortexed briefly then left at room temperature overnight. The mixture was diluted with ethanol (40 ml). The precipitate was collected, washed with ethanol, taken up in water and dialyzed 4 times against deionized water (2 L). The dialyzed solution of the polymer was filtered through 0.2 μm membrane and freeze-dried to provide the product as a white powder (390 mg). The ethanol solution containing unreacted substrate **20** was concentrated and then **20** was purified by chromatography on silica gel as described above.

4-O-(2′,3′,4′,6′-Tetra-O-acetyl-β-D-galactopyranosyl)-3,6-di-O-acetyl-1,2-O-[(R)-1-(methoxycarbonyl)ethylidene]-α-D-glucopyranose (22). To a solution of 4-*O*-(2′,3′,4′,6′-Tetra-*O*-acetyl-β-D-galactopyranosyl)-3,6-di-*O*-acetyl-1,2-*O*-[(*R*)-1-(cyano)ethylidene]-α-D-glucopyranose **21** (2.56 g, 3.97 mmol) in dry CH_3OH (120 ml) CH_3ONa (1 N, 3 ml) was added. The mixture was stirred overnight till TLC indicated maximum product formation then glacial AcOH (150 ml) was added to convert the imidate intermediate into the methyl ester. When NMR showed completion of product formation, the mixture was concentrated. To the residue Ac_2O-Py (1:1, 20 ml) was added. When reaction was complete, the mixture was concentrated and co-evaporated with toluene to remove pyridine. The residue was dissolved in EtOAc, washed with $NaHCO_3$, brine, filtered and concentrated to give **22** (2.607 g, 97%), $[\alpha]_D$+16 °(*c* 0.9, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ_H 5.63 (d, 1 H, $J_{1,2}$ 4.7 Hz, H-1), 5.52 (t, 1 H, $J_{2,3} = J_{3,4}$ = 3.2 Hz, H-3), 5.38 (dd, 1 H, $J_{3',4'}$ 3.4 Hz, $J_{4',5'}$ 0.9 Hz, H-4′), 5.18 (dd, 1 H, $J_{2',3'}$ 10.3 Hz, $J_{1',2'}$ 7.9 Hz, H-2′), 5.00 (dd, 1 H, H-3′), 4.65 (d, 1 H, H-1′), 4.34 (dd, 1 H, $J_{6a,6b}$ 11.9 Hz, $J_{5,6a}$ 2.1 Hz, H-6a), 4.29 (ddd, 1 H, $J_{4,5}$ 9.7 Hz, $J_{5,6b}$ 5.2 Hz, H-5), 4.24 (t, 1 H, H-2), 4.16–4.08 (m, 3 H, H-6a′, 6b′, 6b,), 3.99 (td, 1H, $J_{5',6'a} = J_{5',6'a}$ = 7.3 Hz, H-5′), 3.85 (s, 3 H, -OCH_3), 3.71 (dd, 1 H, H-4), 2.16 (s, 3 H, OAc), 2.12 (s, 3 H, OAc), 2.11 (s, 3 H, OAc), 2.07 (s, 3 H, OAc), 2.04 (s, 3 H, OAc), 1.97 (s, 3 H, OAc), 1.55 (s, 3 H, CH_3). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.60 (C = O), 170.34 (C = O), 170.29 (C = O), 170.11 (C = O), 169.32 (C = O), 169.12 (C = O), 168.51 (C = O), 106.05 (C pyruvate), 101.39 (C-1′), 96.83 (C-1), 76.61, 74.17, 71.00, 70.64, 70.58, 68.79, 67.52, 66.82, 63.18 (CH_2), 60.85 (CH_2), 53.06 (OCH_3), 22.76 (CH_3), 20.87 (CH_3), 20.85 (CH_3), 20.70 (CH_3), 20.66 (CH_3), 20.63 (CH_3), 20.55 (CH_3). Electrospray ionization MS *m*/*z* 701.18995 ($[M+Na]^+$, $C_{28}H_{38}O_{19}Na^+$ requires 701.18995). Anal. Calcd: C, 49.56; H, 5.64. Found: C, 49.73; H, 5.70.

4-O-(β-D-Galactopyranosyl)-1,2-O-[(R)-1-(methoxycarbonyl)ethylidene]-α-D -glucopyranose (23). To a solution of **22** (2.555 g, 3.77 mmol) in dry CH_3OH (60 ml) CH_3ONa (1N, 3 ml) was then added. The reaction was allowed to proceed at room temperature overnight until completion as indicated by TLC. Reaction mixture was then neutralized using Dowex 50W (H^+) resin to pH 7, filtered, concentrated and purified by column chromatography on silica gel (20% MeOH in DCM) to give **23** (1.198 g, 75%), $[\alpha]_D$+55 °(*c* 1, H_2O). ^{1}H NMR (600 MHz, D_2O): δ_H 5.80 (d, 1 H, $J_{1,2}$ 4.8 Hz, H-1), 4.45 (d, 1 H, $J_{1',2'}$ 7.8 Hz, H-1′), 4.40 (t, 1 H, $J_{2,3}$ 4.8 Hz, H-2), 4.12 (t, 1 H, $J_{3,4}$ 5.2 Hz, H-3), 3.92 (d, 1 H, $J_{3',4'}$ 3.4 Hz, H-4′), 3.88–3.69 (m, 10 H, H-4, H-5, H-6a, H-6b, H-5′, H-6a′, H-6b′, OCH_3), 3.65 (dd, 1 H, $J_{2',3'}$ 10.0 Hz, H-3′), 3.54 (dd, 1 H, H-2′). ^{13}C-NMR (125 MHz, D_2O): δ 171.69 (C = O), 106.20 (C pyruvate), 171.69 (C = O), 104.58 (C-1′), 98.14 (C-1), 77.64, 77.57, 75.95, 73.24, 72.80, 71.59, 71.17, 69.29, 61.78 (CH_2), 61.14 (CH_2), 54.27 (OCH_3), 23.48 (CH_3). Electrospray ionization MS *m*/*z* 449.12663 ($[M+Na]^+$, $C_{16}H_{26}O_{13}Na^+$ requires 449.12656). Anal. Calcd for $C_{16}H_{26}O_{13}$+0.5 H_2O: C, 44.14; H, 6.25. Found: C, 44.35; H, 6.23.

4-O-(4′,6′-O-Benzylidene-β-D-galactopyranosyl)-1,2-O-[(R)-1-(methoxycarbonyl)ethylidene]-α-D-glucopyranose (24). To a solution of **23** (1.198 g, 2.81 mmol) in dry CH_3CN (60 ml) α,α-dimethoxytoluene (1.1 eq, 464 μl) and CSA (50 mg) were added. The reaction proceeded for 2 h until TLC analysis showed reaction is complete. The reaction mixture was then neutralized with a small amount of Et_3N, concentrated and purified by column chromatography on silica gel (5% MeOH in CH_2Cl_2) to give **24** (1.068 g, 74%), $[\alpha]_D$+46 °(*c* 0.8, $CHCl_3$). ^{1}H NMR (600 MHz, CD_3OD): δ_H 7.54 (m, 2 H, arom.), 7.35 (m, 3 H, arom), 5.67 (d, 1 H, $J_{1,2}$ 4.7 Hz, H-1), 5.62 (s, 1 H, CH of benzylidene), 4.49 (d, 1 H, $J_{1',2'}$ 7.3 Hz, H-1′), 4.21 (m, 2 H, H-4′, 6a′), 4.15 (m, 2 H, H-6b′, H-2), 4.00 (dd, 1 H, $J_{2,3}$ 5.6 Hz, $J_{3,4}$ 7.8 Hz, H-3), 3.94 (dd, 1 H, $J_{5,6a}$ 3.5 Hz, $J_{6a,6b}$ 12.1 Hz, H-6a), 3.88 (ddd, 1 H, $J_{5,6b}$ 2.4 Hz, $J_{4,5}$ 9.7 Hz, H-5), 3.81 (dd, 1 H, H-6b), 3.77 (s, 3 H, OCH_3), 3.65 (m, 4 H, H-2′, H-3′, H-5′, H-4), 1.53 (s, 3 H, CH_3). ^{13}C-NMR (125 MHz, CD_3OD): δ 171.71 (C = O), 139.53 (C-arom.), 129.90 (CH-arom.), 129.05 (CH-arom.), 127.51 (CH-arom.), 105.84 (C-pyruvate), 105.10 (CH of benzylidene), 102.32 (C-1′), 99.73 (C-1), 80.12, 78.47, 77.42, 73.70, 73.57, 73.47, 71.87, 70.26 (CH_2), 68.30, 61.66 (CH_2), 53.26 (OCH_3), 24.29 (CH_3). Electrospray ionization MS *m*/*z* 537.15801 ($[M+Na]^+$, $C_{23}H_{30}O_{13}Na^+$ requires 537.15786). Anal. Calcd for $C_{23}H_{30}O_{13}$+0.5 H_2O: C, 52.77; H, 5.97. Found: C, 52.72; H, 5.89.

4-O-(2′,3′-Di-O-Acetyl-4′,6′-O-benzylidene-β-D-galactopyranosyl)-3-O-acetyl-6-O-(tert-butyldiphenylsilyl)-1,2-O-[(R)-1-(methoxycarbonyl)ethylidene]-α-D-glucopyranose (25). To a solution of **24** (994 mg, 1.93 mmol) in dry CH_2Cl_2 (30 ml) Et_3N (1.2 eq, 323 μl) and DMAP (0.04 eq, 10 mg) was added. *t*-butyldiphenylsilylchloride (1.2 eq, 500 μl) was then added dropwise over 4 h. After a further 12 h another 1 equivalent of TBDPSCl was added and the reaction was allowed to proceed for another 24 h with occasional heating. After this time the reaction mixture was acetylated with 1:1 pyridine/acetic anhydride (40 ml each) and placed on rotovap to remove CH_2Cl_2. Upon completion of acetylation the mixture was concentrated and the residue was purified on silica gel in hexane/EtOAc (1:1) to give **25** (817 mg, 48%), $[\alpha]_D$+69 °(*c* 1.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.72 (m, 4 H, arom.), 7.42 (m, 11 H, arom), 5.74 (d, 1 H, $J_{1,2}$ 4.9 Hz, H-1), 5.46 (s, 1 H, CH of benzylidene), 5.34 (dd, 1 H, $J_{2,3}$ 6.2 Hz, $J_{3,4}$ 8.4 Hz, H-3), 5.24 (dd, 1 H, $J_{1',2'}$ 8.1 Hz, $J_{2',3'}$ 10.4 Hz, H-2′), 4.82 (dd, 1 H, $J_{2',3'}$

3.7 Hz, H-3′), 4.79 (d, 1 H, H-1′), 4.32–4.27 (m, 3 H, H-4′, H-6a′, H-2), 4.07 (t, 1 H, $J_{4,5}$ 8.4, H-4), 4.03–3.96 (m, 4 H, H-6b′, H-5, H-6a, H-6b), 3.86 (s, 3 H, OCH_3), 3.32 (m, 1 H, H-5′), 2.09 (s, 3 H, OAc), 2.07 (s, 3 H, OAc), 2.05 (s, 3 H, OAc), 1.83 (s, 3 H, Me), 1.09 (s, 9 H, *t*-Bu); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 170.57 (C = O), 169.86 (C = O), 169.52 (C = O), 168.49 (C = O), 137.41 (C arom.), 135.77 (CH arom.), 135.38 (CH arom.), 133.49 (C arom.), 132.35 (C arom.), 129.79 (CH arom.), 129.75 (CH arom.), 128.99 (CH arom.), 128.10 (CH arom.), 127.76 (CH arom.), 127.64 (CH arom.), 126.34 (CH arom.), 104.51 (C-pyruvate), 101.13 (CH-benzylidene), 100.20 (C-1′), 98.55 (C-1), 76.03, 73.24, 72.76, 72.32, 72.16, 71.72, 68.91, 68.59 (CH_2), 66.11, 61.37 (CH_2), 52.96 (CH_3), 26.79 (CH_3), 20.86 (CH_3), 20.78 (CH_3), 20.50 (CH_3), 19.42 (C of *t*-Bu). Electrospray ionization MS *m/z* 901.30795 ($[M+Na]^+$, $C_{45}H_{54}SiO_{16}Na^+$ requires 901.30734). Anal. Calcd: C, 61.49; H, 6.19. Found: C, 61.48; H, 6.34.

4-O-(2′,3′-Di-O-acetyl-4′,6′-O-benzylidene-β-D-galactopyranosyl)-3-O-acetyl-1,2-O-[(R)-1-(methoxycarbonyl)ethylidene]-α-D-glucopyranose (26). To a solution of **25** (763 mg, 0.87 mmol) in dry THF (10 ml) and placed in polypropylene container. HF-pyridine (2 eq, 60 μl) was added at room temperature and the reaction was monitored by TLC for 120 min and showed no progress. Another 8 equivalents of HF-pyridine were added and allowed to react overnight until completion. The mixture was washed with sat. $NaHCO_3$, brine, dried with Na_2SO_4, filtered and concentrated. The residue was then purified on silica gel (40% acetone in hexane) to give **26** (505 mg, 91%), [α]D+73 °(*c* 2.2, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.49 (m, 2 H, arom.), 7.38 (m, 3 H, arom.), 5.66 (d, 1 H, $J_{1,2}$ 4.9 Hz, H-1), 5.48 (s, 1 H, CH of benzylidene), 5.39 (dd, 1 H, $J_{2,3}$ 4.9 Hz, $J_{3,4}$ 6.2 Hz, H-3), 5.31 (dd, 1 H, $J_{1',2'}$ 7.9 Hz, $J_{2',3'}$ 10.4 Hz, H-2′), 4.95 (dd, 1 H, $J_{3',4'}$ 3.7 Hz, H-3′), 4.71 (d, 1 H, H-1′), 4.34 (d, 1 H, H-4′), 4.29 (dd, 1 H, $J_{6a',5'}$ 1.5 Hz, $J_{6'a,6'b}$ 12.4 Hz, H-6a′), 4.25 (t, 1 H, H-2), 4.08–4.03 (m, 2 H, H-6b′, H-5), 3.93–3.76 (m, 3 H, H-4, H-6a, H-6b), 3.87 (s, 3 H, OCH_3), 3.55 (m, 1 H, H-5′), 2.09 (s, 3 H, OAc), 2.07 (s, 3 H, OAc), 2.06 (s, 3 H, OAc), 1.57 (s, 3 H, CH_3). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 170.75 (C = O), 169.72 (C = O), 169.14 (C = O), 169.00 (C = O), 137.46 (C arom.), 129.09 (CH arom.), 128.20 (CH arom.), 126.40 (CH arom.), 105.17 (C pyruvate), 101.18 (C of benzylidene), 100.72 (C-1′), 97.79 (C-1), 75.63, 73.91, 73.34, 72.16, 71.61, 71.14, 68.88, 68.74 (CH_2), 66.36, 60.77 (CH_2), 53.09 (OCH_3), 23.49 (CH_3), 20.92 (CH_3), 20.86 (CH_3), 20.75 (CH_3). Electrospray ionization MS *m/z* 663.18945 ($[M+Na]^+$, $C_{29}H_{36}O_{16}Na^+$ requires 663.18956).

4-O-(2′,3′-Di-O-acetyl-4′,6′-O-benzylidene-β-D-galactopyranosyl)-3-O-acetyl-6-O-(2,5-dinitra-7-oxa-6-oxo-dodec-11-enoyl)-1,2-O-[(R)-1-(methoxycarbonyl)ethylidene]-α-D-glucopyranose (27). Alcohol **26** (427 mg, 0.67mmol) was combined with *p*-nitrophenyl chloroformate (1.2eq, 161 mg) and dissolved in dry CH_2Cl_2 (10 ml). Pyridine (0.1 ml) was added, and the reaction was monitored by TLC. After 10 min the reaction was shown to be complete. The reaction mixture was concentrated with no heating after which the residue was again dissolved in a minimum of CH_2Cl_2 and the 4-nitra-6-oxa-5-oxo-dec-10-en-1-amine (≈0.460 g, 4 eq, 2.67 mmol) was added followed by Et_3N (0.64 ml). The reaction proceeded for 1 h at room temperature until reaction was shown to be complete. The mixture was concentrated and purified on silica gel [toluene/acetone (3:1) → toluene/acetone (1:1)] to give **27** (378 mg, 65%), [α]D+50 °(*c* 1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.51–7.49 (m, 2 H, arom.), 7.40–7.34 (m, 3 H, arom.), 5.81 (tdd, *J* 16.9 Hz, *J* 10.3 Hz, *J* 6.6 Hz, CH = CH_2), 5.63 (d, 1 H, $J_{1,2}$ 4.8 Hz, H-1), 5.49–5.46 (m, 2 H, CH of benzylidene, H-3), 5.31 (dd, 1 H, $J_{1',2'}$ 8.2 Hz, $J_{2',3'}$ 10.2 Hz, H-2′), 5.23 (broad s, 1 H, NH), 5.14 (broad s, 1 H, NH), 5.06–4.98 (m, 2 H, CH = CH_2), 4.94 (dd, 1 H, $J_{3',4'}$ 3.6 Hz, H-3′), 4.63 (d, 1 H, H-1′), 4.38 (broad d, 1 H, H-6a), 4.34 (d, 1 H, H-4′), 4.30 (dd, 1 H, $J_{6'a,5'}$ 1.3 Hz, $J_{6'a,6'b}$ 12.1 Hz, H-6a′), 4.26–4.22 (m, 2 H, H-2, H-5), 4.18 (dd, 1 H, $J_{6'b,5'}$ 5.4 Hz, $J_{6'a,6'b}$ 11.6 Hz, H-6b), 4.08–4.03 (m, 3 H, H-6′b, CH_2O), 3.86 (s, 3 H, OCH_3), 3.72 (dd, 1 H, H-4), 3.58 (m, 1 H, H-5′), 3.33–3.23 (m, 4 H, CH_2N), 2.14–2.10 (m, 2 H, CH_2), 2.09 (s, 3 H, OAc), 2.08 (s, 3 H, OAc), 2.05 (s, 3 H, OAc), 1.74–1.69 (m, 2 H, CH_2), 1.55 (s, 3 H, CH_3). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 170.77 (C = O), 169.48 (C = O), 169.22 (C = O), 168.96 (C = O), 157.11 (NHC = O), 156.29 (NHC = O), 137.56 (*C*H = CH_2), 137.48 (C arom.), 129.11 (CH arom.), 128.20 (CH arom.), 126.42 (CH arom.), 115.21 (CH = *C*H_2), 105.61 (C pyruvate), 101.12 (C of benzylidene, C-1′), 97.43 (C-1), 75.61, 75.02, 73.31, 72.14, 71.12, 69.00, 68.75, 68.69 (CH_2), 66.42, 64.45 (CH_2), 63.62 (CH_2), 53.11 (OCH_3), 41.36 (CH_2), 41.00 (CH_2), 29.98 (CH_2), 28.22 (CH_2), 23.25 (CH_3), 20.89 (CH_3), 20.86 (CH_3), 20.71 (CH_3). Electrospray ionization MS *m/z* 861.29070 ($[M+Na]^+$, $C_{38}H_{50}N_2O_{19}Na^+$ requires 861.29000). Anal. Calcd: C, 54.41; H, 6.01; N, 3.26. Found: C, 54.62; H, 6.13; N, 3.25.

4-O-(2′,3′-Di-O-acetyl-β-D-galactopyranosyl)-3-O-acetyl-6-O-(2,5-dinitra-7-oxa-6-oxo-dodec-11-enoyl)-1,2-O-[(R)-1-(methoxycarbonyl)ethylidene]-α-D -glucopyranose (28). Compound **27** (337 mg, 0.402mmol) was dissolved in 80% aq. CH_3COOH (25 ml) and heated to 80°C for 1 h until reaction was shown to be complete by TLC (1:1 toluene/acetone). The mixture was then coevaporated with toluene and a small amount of H_2O to remove AcOH and the residue was purified on a short silica gel column (toluene - acetone) to give **28** (235 mg, 78%), [α]D+18 °(*c* 1.2, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 5.80 (m, C*H* = CH_2), 5.66 (d, 1 H, $J_{1,2}$ 4.8 Hz, H-1), 5.60 (broad s, 1 H, H-3), 5.34 (broad s, 1 H, NH), 5.28 (dd, 1 H, $J_{1',2'}$ 8.0 Hz, $J_{2',3'}$ 10.3 Hz, H-2′), 5.22 (m, 1 H, NH), 5.06–4.97 (m, 2 H, CH = CH_2), 4.92 (dd, 1 H, $J_{3',4'}$ 3.1 Hz, H-3′), 4.63 (d, 1 H, H-1′), 4.39 (broad d, 1 H, H-6a), 4.24 (m, 1 H, H-2), 4.20–4.14 (m, 1 H, H-5), 4.11–4.04 (m, 2 H, H-6b, H-4′), 3.98–3.92 (m, 1 H, H-6a′), 3.85 (s, 3 H, OCH_3), 3.80–3.75 (m, 1 H, H-6′b), 3.66–3.60 (m, 2 H, H-4, 6′-OH), 3.34–3.36 (m, 5 H, H-5′, CH_2N), 3.15 (broad s, 1 H, 4′-OH), 2.14–2.10 (m, 2 H, CH_2), 2.12 (s, 3 H, OAc), 2.08 (s, 3 H, OAc), 2.07 (s, 3 H, OAc), 1.74–1.69 (m, 2 H, CH_2), 1.54 (s, 3 H, CH_3). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 170.30 (C = O), 169.91 (C = O), 169.59 (C = O), 168.45 (C = O), 157.08 (NHC = O), 156.42 (NHC = O), 137.57 (*C*H = CH_2), 115.18 (CH = *C*H_2), 106.50 (C pyruvate), 101.70 (C-1′), 96.82 (C-1), 76.16, 74.78, 73.57, 73.42, 70.28, 69.17, 68.58, 68.25, 64.44 (CH_2), 64.24 (CH_2), 62.90 (CH_2), 53.13 (OCH_3), 41.24 (CH_2), 40.91 (CH_2), 29.96 (CH_2), 28.20 (CH_2), 22.82 (CH_3), 20.97 (CH_3), 20.84 (CH_3), 20.63 (CH_3). Electrospray ionization MS *m/z* 773.25846 ($[M+Na]^+$, $C_{31}H_{46}N_2O_{19}Na^+$ requires 773.25870). Anal. Calcd for $C_{31}H_{46}N_2O_{19}$: C, 49.60; H, 6.18; N, 3.73. Found: C, 49.52; H, 6.41; N, 3.44.

4-O-(β-D-Galactopyranosyl)-6-O-(2,5-dinitra-7-oxa-6-oxo-dodec-11-enoyl)-1,2-O-[(R)-1-(carboxy)ethylidene]-α-D-glucopyranose (29). To a solution of **28** (212 mg, 0.282 mmol) in dry CH_3OH (10 ml) to which CH_3ONa (2 eq, 1.13 ml) was added and allowed to react overnight at room temperature until reaction complete as shown on TLC. The mixture was then concentrated to remove formed MeOH after which H_2O (10 ml) was added to convert methoxy ester into carboxylic acid. After 2 h analysis of TLC showed hydrolysis to be complete. The mixture was neutralized with Dowex 50W (H^+) resin, filtered, concentrated and freeze dried to give **29** (162 mg, 94% yield), $[\alpha]_D$+27 °(*c* 0.8 H_2O). ^{1}H NMR (D_2O) δ: 5.90 (m,1 H, C*H* = CH_2), 5.70 (d, 1 H, $J_{1,2}$ 4.7 Hz, H-1), 5.11–5.01 (m, 2 H, CH = CH_2), 4.40 (d, 1 H, $J_{1',2'}$ 7.8 Hz, H-1′), 4.38–4.35 (m, 2 H, H-2, H-6a), 4.25 (dd, 1 H, $J_{5,6b}$ 4.8 Hz, $J_{6a,6b}$ 12.1 Hz, H-6b), 4.19 (t, 1 H, $J_{3,4} \approx J_{3,4}$ = 6.3 Hz, H-3), 4.10–4.05 (m, 2 H, OCH_2), 4.02–3.98 (m, 1 H, H-5), 3.91 (d, 1 H, $J_{3',4'}$ 3.4 Hz, H-4′), 3.80 (dd, 1 H, $J_{5',6'a}$ 8.1 Hz, $J_{6'a,6'b}$ 11.7 Hz, H-6′a), 3.77–3.74 (m, 1 H, H-4), 3.74 (dd, 1 H, $J_{5',6'b}$ 4.1 Hz, H-6′b), 3.68 (dd, 1 H, H-5′), 3.62 (dd, 1 H, $J_{2',3'}$ 9.9 Hz, H-3′), 3.53 (dd, 1 H, H-2′), 3.24 (s, 4 H, NCH_2), 2.18–2.10 (m, 2 H, CH_2), 1.78–1.70 (m, 2 H, CH_2), 1.54 (s, 3 H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 176.99 (C = O), 159.84 (C = O), 158.99 (C = O), 139.45 (-*C*H = CH_2),

115.82 (-CH = CH_2), 108.63 (C-pyruvate), 104.91 (C-1′), 97.54 (C-1), 78.43, 77.01, 76.24, 73.39, 71.66, 71.19, 70.09, 69.52, 65.90 (CH_2), 64.54 (CH_2), 62.00 (CH_2), 41.10 (CH_2), 30.25 (CH_2), 30.22 (CH_2), 24.06 (CH_3). Electrospray ionization MS *m/z* 633.21194 ($[M+Na]^+$, $C_{24}H_{38}N_2O_{16}Na^+$ requires 633.21136).

6-O-(2,5-Dinitra-7-oxa-6-oxo-dodec-11-enoyl)-1,2-O-[(R)-1-(carboxy)ethylidene]-4-O-[4-O-(α-D-galactopyranosyl)-β-D-galactopyranosyl]-α-D-glucopyranose (30). DTT solution (199 μl; 64 mg/ml H_2O) was mixed with fused enzyme and left at room temperature for 15 min. Meantime **29** (142 mg; 0.233 mmol) was dissolved in degassed water (2.6 ml) and the solution was neutralized with aqueous $NaHCO_3$, then Hepes Buffer [1.25 ml, 1.6 M, 10 mM $MnCl_2$, bovine serum albumine (BSA, 0.8 mg/ml), pH 8] (0.796 ml) was added and the mixture was sparged with argon. Alkaline phosphatase (19.8 μl) was added to the solution followed by UDP-glucose (214 mg; 0.349 mmol) and the mixture was sparged with argon. Finally DTT-enzyme solution was added to the reaction mixture and it was left at 37°C for 30 min. and then at room temperature overnight. After 18 h it was checked by TLC and NMR that the reaction was complete. The mixture was treated with Dowex H^+ (≈600 mg), filtered and concentrated. The solid residue was treated with methanol. Insoluble solid was filtered off and the filtrate as chromatographed on silica gel using dichloromethane-methanol-acetic acid (30:20:1). Pure title product **30** was separated; it was concentrated dissolved in water filtered through Milipore membrane 0.45 μm and freeze-dried to provide pure product as a white foam-powder (115 mg) and a fraction containing some impurity which was purified further on HPLC providing an additional amount (14 mg) of the product (total yield 72%), $[\alpha]_D$+68 °(*c* 1, H_2O). ^{1}H MNR (D_2O): δ 5.90 (m, 1 H, C*H* = CH_2), 5.70 (d, 1 H, $J_{1,2}$ 4.7 Hz, H-1), 5.08(m, 1 H, CH = C*H*$_2$), 5.02 (m, 1 H, CH = C*H*$_2$), 4.94 (d, 1H, $J_{1'',2''}$ 3.9 Hz, H-1″), 4.77 (d, 1 H, $J_{1',2'}$ 7.7 Hz, H-1′), 4.42–4.34 (m, 3 H, H-2, H-6a, H-5″), 4.28–4.22 (m, 2 H, H-3, H-6b), 4.08–4.06 (m, 2 H, OCH_2), 4.04–4.02 (m, 2 H, H-4′, H-4″), 4.00–3.96 (m, 1 H, H-5), 3.93–3.80 (m, 7 H, H-4, H-3′, H-6′a, H-6′b, H-2″, H-6″a, H-6″b), 3.59 (dd, 1 H, $J_{2,3}$ 10.1 Hz, H-2), 3.24 (broad s, 4 H, NCH_2), 2.15–2.10 (2 H, CH_2), 1.74–1.68 (m, 2 H, CH_2), 1.54 (s, 3 H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 174.14 (C = O), 159.86 (C = O), 158.96 (C = O), 139.46 (-CH = CH_2), 115.83 (-CH = *C*H_2), 107.45 (C-pyruvate), 105.38 (C-1″), 101.21 (C-1′), 97.77 (C-1), 78.63, 78.06, 77.13, 76.32, 72.97, 71.65, 71.62, 70.70, 70.50, 70.04, 69.86, 69.58, 65.91 (CH_2), 64.59 (CH_2), 61.39 (CH_2), 61.15 (CH_2), 41.12 (CH_2), 40.97 (CH_2), 30.27 (CH_2), 28.37 (CH_2), 23.60 (CH_3). Electrospray ionization MS *m/z* 771.26795 ($[M]^-$), $C_{30}H_{47}N_2O_{21}^-$ requires 771.26768.

(R)-PolyBAIT. Compound **30** (105 mg; 0.136 mmol) and acrylamide (58 mg; 0.817 mmol) were dissolved in degassed Tris buffer (0.2 M, 1.634 ml; pH 9) and sparged with argon. Then ammonium persulfate (1.63 mg) in Tris buffer (16.3 μl) was added and the mixture was sparged with argon. Finally TEMED (8.17 μl) was added and the reaction mixture was spinned on Vortex for few seconds then left at room tempetature overnight. After 19 h ethanol was added to the solution (≈8 ml). Precipitated polymer was separated, dissolved in water and dialyzed against deionized water for 2 days. Then the solution filtered through membrane and freeze-dried to provide the target polymer as a white solid (81.4 mg). Ethanolic solution was concentrated and purified on C-18 Sep-Pak cartridge using water-methanol containing 0.5% of acetic acid. After concentration and freeze drying pure unreacted substrate **30** was recovered (40 mg).

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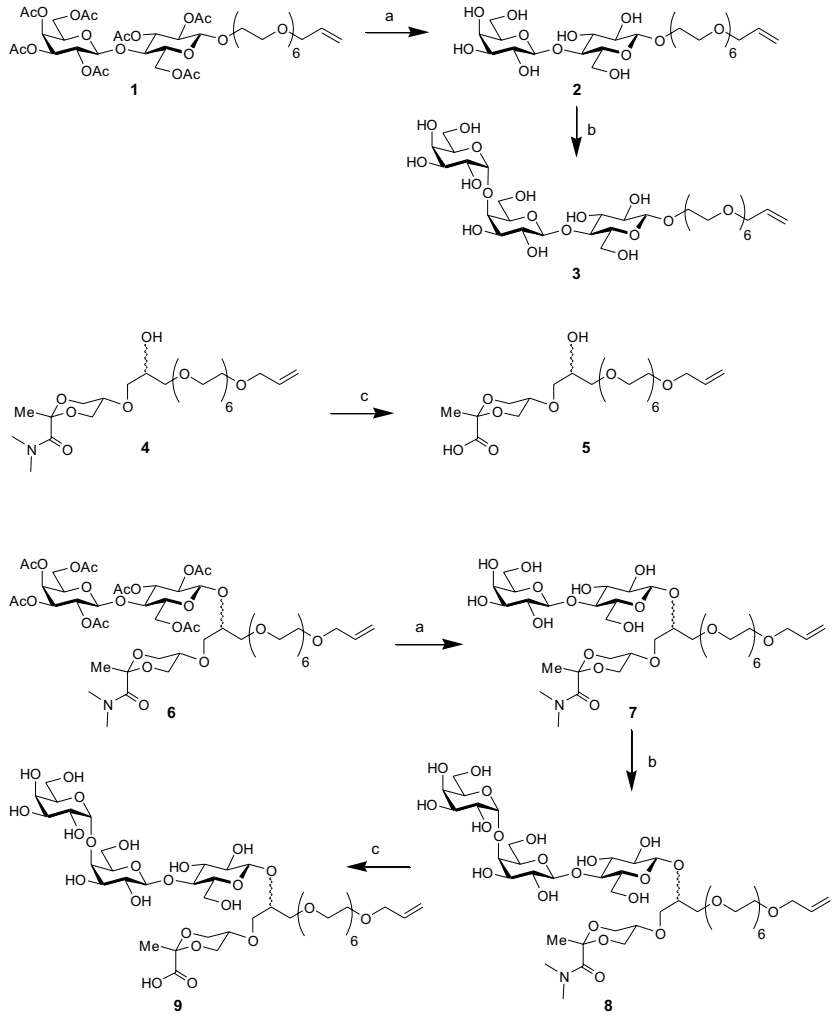

Fig. S1. Synthesis of ligands for preparation of polymers A and B. Conditions: (a) MeOH-MeONa; (b) UDP-Glc, α- (1, 4)-galactosyltransferase/UDP-4′-Gal/Glc-epimerase, 37°C; (c) aq. NaOH, 80°C.

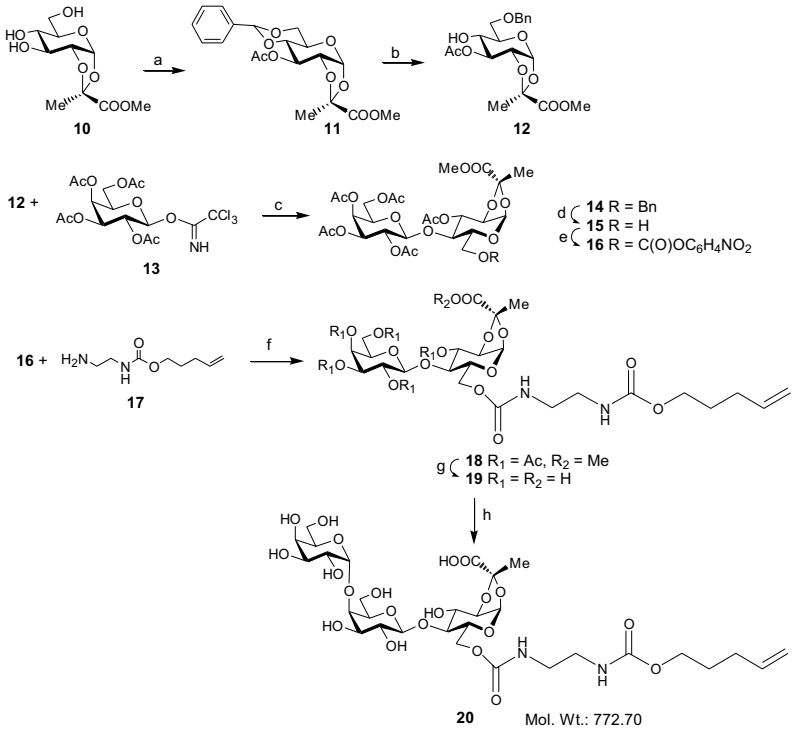

Fig. S2. Synthesis of the ligand for preparation of (*S*)-PolyBAIT. Conditions: (a) 1. $PhCH(OMe)_2$, CSA, MeCN; 2. Ac_2O, Py; (b) $NaCNBH_3$, THF, HCl/Et_2O; (c) TMSOTf; (d) H_2-$Pd(OH)_2$; (e) 4-$NO_2C_6H_4OC(O)Cl$, Py, DCM; (f) Et_3N, DCM; (g) MeONa-MeOH; (h) UDP-Glc, α- (1, 4)-galactosyltransferase/UDP-4′-Gal/Glc-epimerase, 37°C.

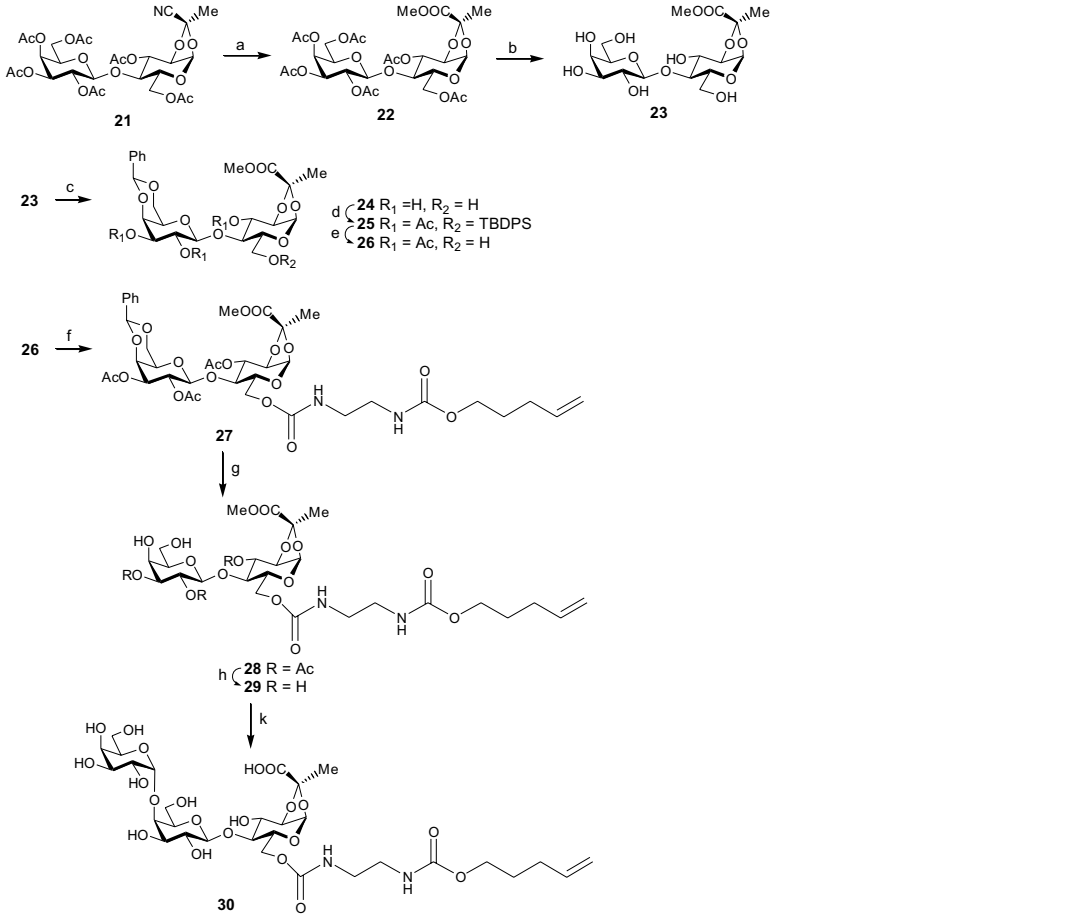

Fig. S3. Synthesis of the ligand for preparation of (*R*)-PolyBAIT. Conditions: (a) 1. MeOH-MeONa, 2. AcOH, 3. Ac_2O-Py; (b) MeOH-MeONa; (c) 1. $PhCH(OMe)_2$, CSA, MeCN; (d) 1. TBDPSCl, Et_3N, DMAP, 2. Ac_2O, Py; (e) HF-Py; (f) 1. 4-$NO_2C_6H_4OC(O)Cl$, Py, DCM, 2. 17, Et_3N; (g) 80% AcOH, 80°C; (h) MeONa-MeOH; (k) UDP-Glc, α- (1, 4)-galactosyltransferase/UDP-4′-Gal/Glc-epimerase, 37°C.

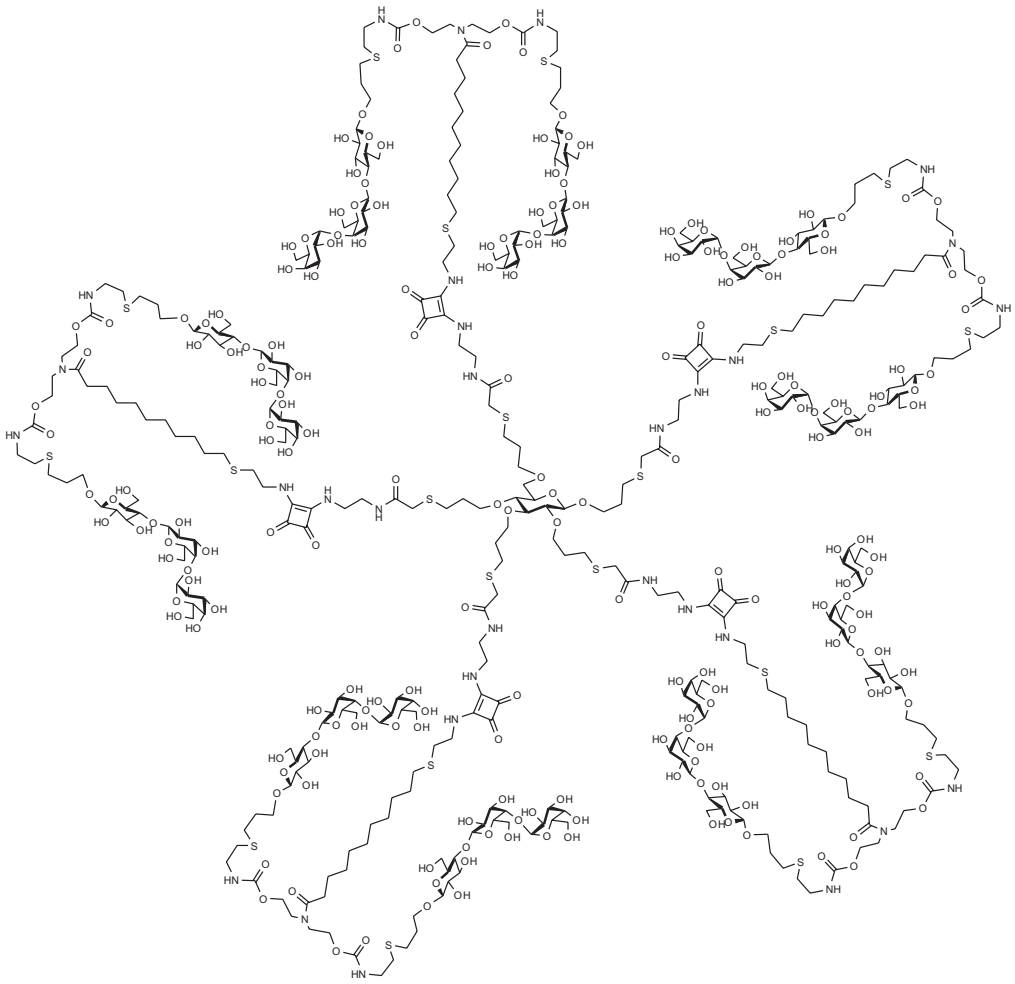

Fig. S4. Structure of the dendrimeric P^k-trisaccharide ligand, which is referred as STARFISH, used as a positive control in *in vitro* and *in vivo* biological tests.

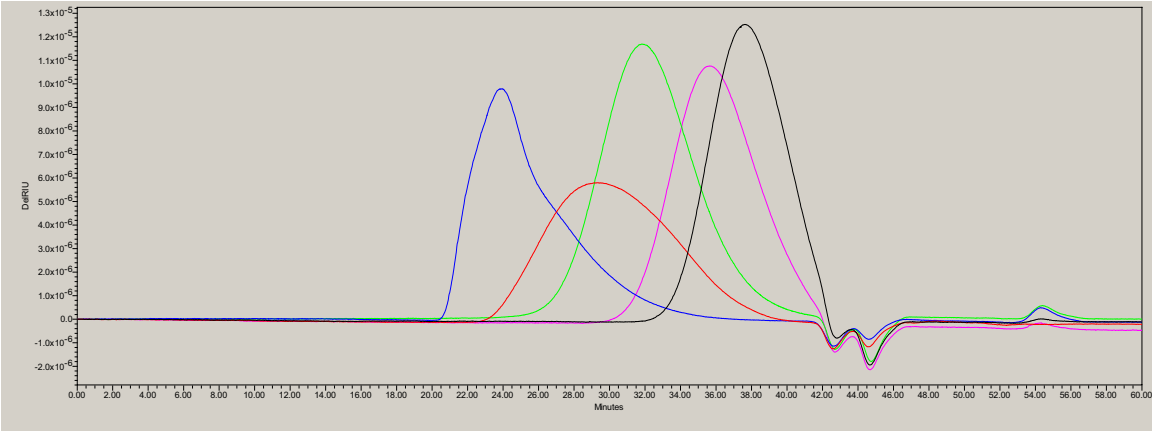

Fig. S5. Gel HPLC of polyacrylamide samples conducted on Ultrahydrogel 1000 in series with Ultrahydrogel 500 in PBS buffer (1-mg injections). Blue: 1,000-kDa standard polyacrylamide. Green: 65-kDa standard polyacrylamide, Magenta: 22-kDa standard polyacrylamide. Black: 12-kDa standard polyacrylamide. Red: (*S*)-PolyBAIT.

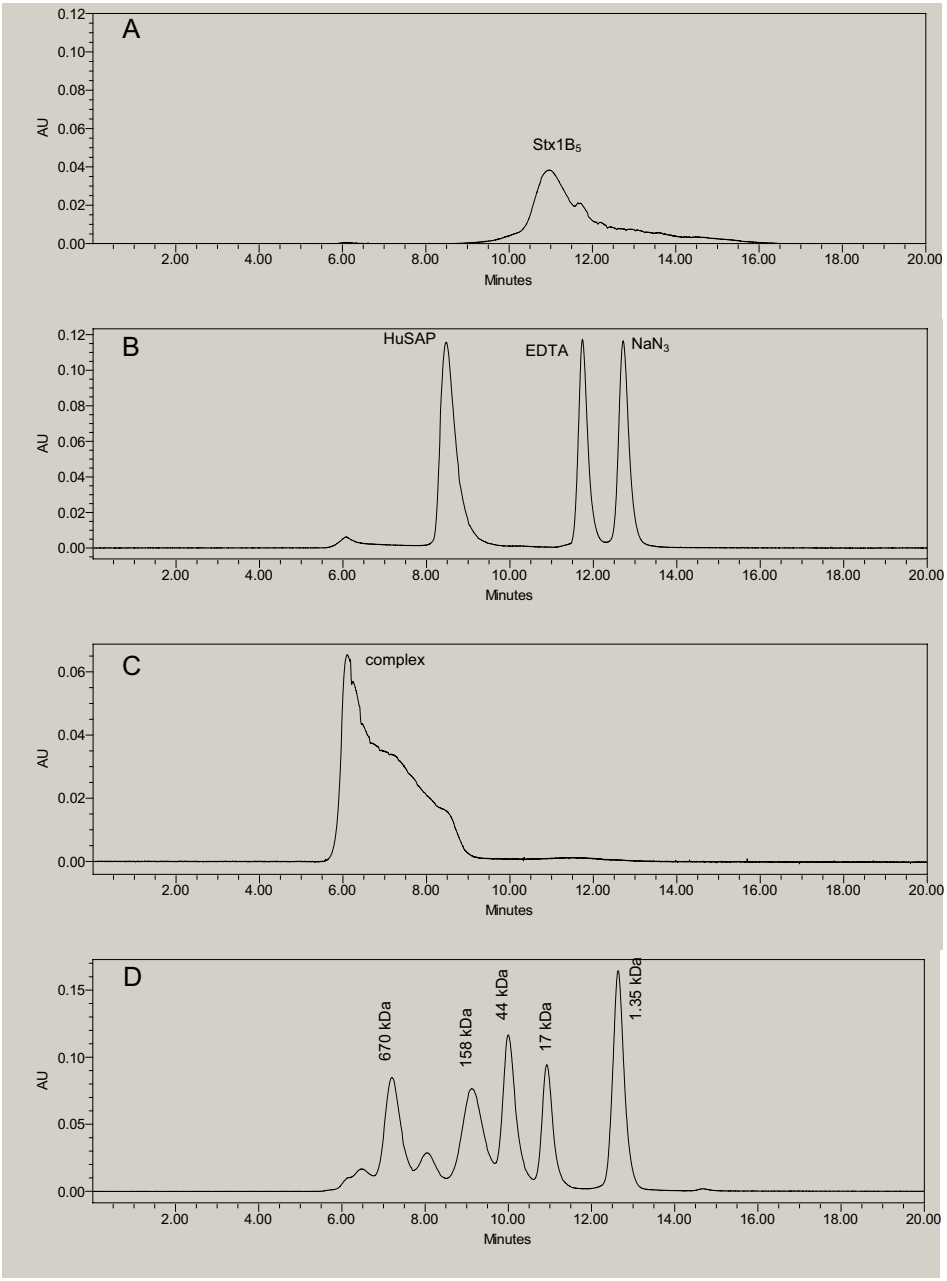

Fig. S6. GPC isolation of a ternary complex between SAP and Stx1 B_5-subunit mediated by (*S*)-PolyBAIT using Shodex KW-803 column. (*A*) Stx1 B_5-subunit in buffer 1. (*B*) HuSAP in buffer 1. (*C*) complex between HuSAP and Stx1B_5 mediated by (*S*)-PolyBAIT in buffer 2. (*D*). Standard protein mixture (Bio-Rad) in buffer 2.

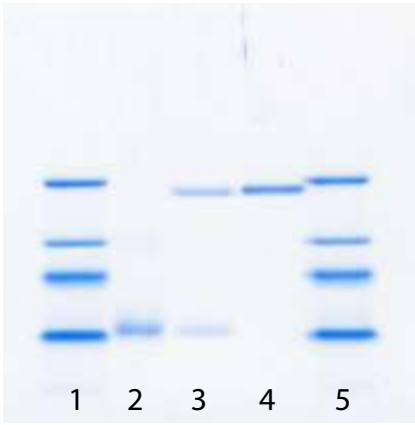

Fig. S7. SDS/PAGE shows the presence of both Stx1B and SAP in the fractions corresponding to the complex isolated by GPC. Line assignment: 2, $Stx1B_5$; 3, complex $HuSAP_5$-PolyBAIT-$Stx1B_5$; 4, HuSAP; 1 and 5, mixture of reference proteins.

Other Supporting Information Files

Appendix (PDF)