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Synthesis of divalent β-(1→6)-branched (1→3)-glucohexaose and trivalent β-(1→6)-branched (1→3)-glucotriose

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Abstract—Hexaose, β-D-Glc*p*-(1→3)-[β-D-Glc*p*-(1→6)]-α-D-Glc*p*-(1→3)-β-D-Glc*p*-(1→3)-[β-D-Glc*p*-(1→6)]-β-D-Glc*p*, based dimers were synthesized by twofold glycosidation of the hexaosyl trichloroacetimidate with hexylene 1,6-diol, diethylene glycol and triethylene glycol, respectively. Meanwhile, a triose, β-1D-Glc*p*-(1→3)-[β-D-Glc*p*-(1→6)]-β-D-Glc*p*, based trimer was obtained by glycosidation of the triosyl trichloroacetimidate with a glycerol-derived triol scaffold.

Keywords: Oligosaccharide; Dendrimer; Glucose

1. Introduction

A glucohexaose, β-D-Glc*p*-(1→3)-[β-D-Glc*p*-(1→6)]-α-D-Glc*p*-(1→3)-β-D-Glc*p*-(1→3)-[β-D-Glc*p*-(16)]-D-Glc*p*,[1] has been proved to have good immunoregulating activity. In combination with the chemotherapeutic agent cyclophosphamide (CPA), the glucohexaose at a dose of 0.5–1 mg/kg substantially increased the inhibition of Sarcoma 180 for CPA, but decreased the toxicity caused by CPA.[1] A study on the stimulatory effect on mouse spleen showed that the hexaose has similar or better stimulatory effect compared to lentinan.[2]

It is well known[3,4] that most saccharide ligands bind to their protein receptors only weakly, seldom showing association constants beyond 10^6 M. Clearly, the effective in vivo control of events mediated by protein–carbohydrate binding requires significantly greater affinity. Against this backdrop, the development of tight-binding ligands for carbohydrate-binding proteins continues apace throughout the carbohydrate chemistry and biology community. A wide range of multivalent saccharide ligands have been reported.[5–8] Most fit into a relatively small number of conceptual frameworks, specifically dendritic ligands, polymeric ligands constructed on either peptide or acrylamide backbones and liposomes or other multivalent presentations created by self assembly of amphiphilic carbohydrates. We present herein the syntheses of the glucohexaose-based dimers **6**, **9** and **10** by glycosidation of the hexaosyl trichloroacetimidate with hexylene 1,6-diol, diethylene glycol and triethylene glycol, respectively, and the synthesis of glucotriose, β-D-Glc*p*-(1→3)-[β-D-Glc*p*-(1→6)]-D-Glc*p*, based glycocluster **16** by glycosidation of the triosyl trichloroacetimidate with a glycerol-derived triol scaffold. Among these compounds, **6** contained a relatively hydrophobic spacer, while **9** and **10** had relatively hydrophilic spacers. From the studies on their activity, we can observe the influence of spacers. Besides, since we have not, thus far, obtained a definite conclusion regarding the size of the active fragment, dendrimer **16** was synthesized for testing whether the trisaccharide was the possible minimum active moiety.

2. Results and discussion

As shown in Scheme 1, hexasaccharide donor **1**[9] was coupled with excess hexylene glycol gave monoglycosidated

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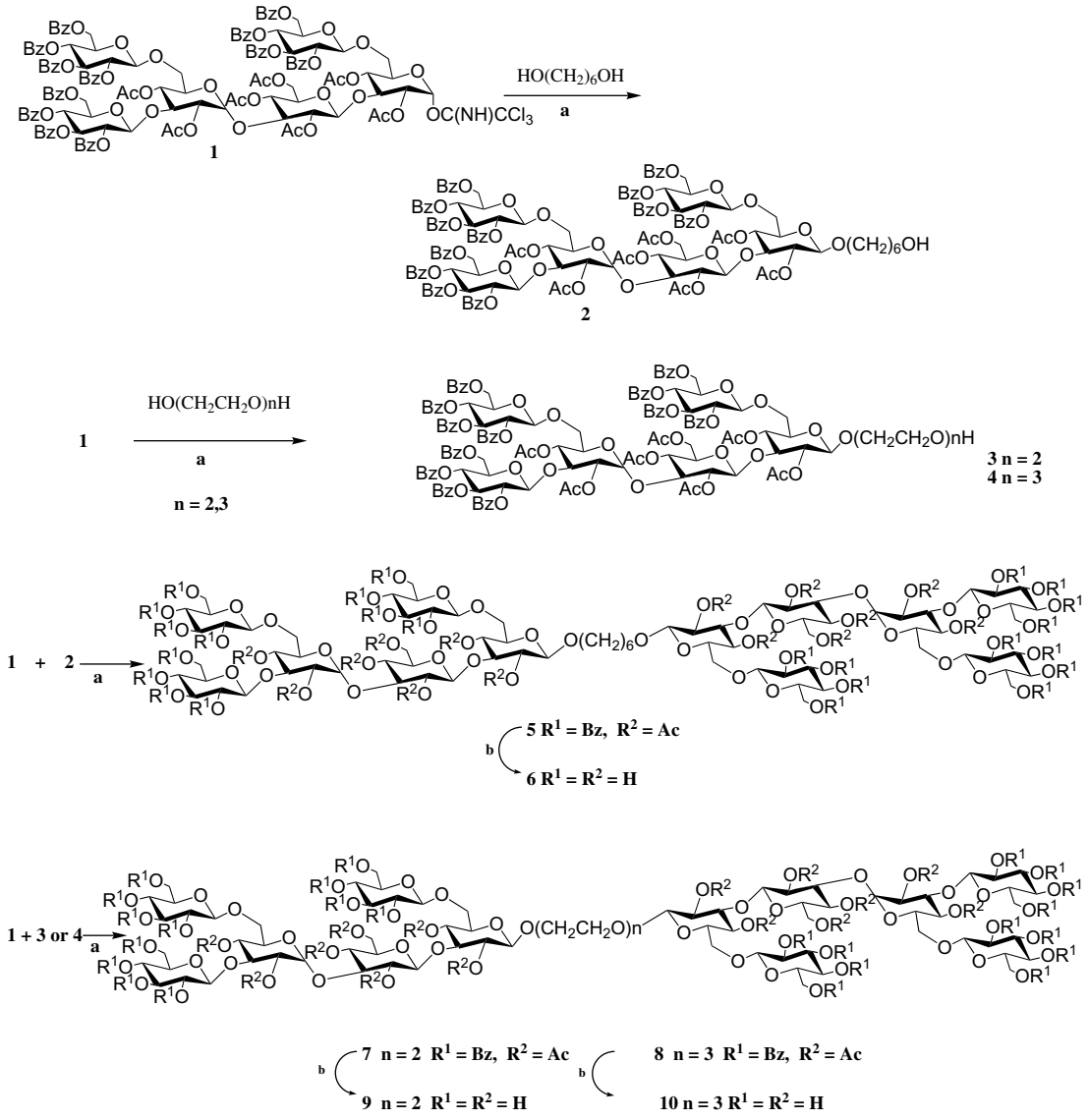
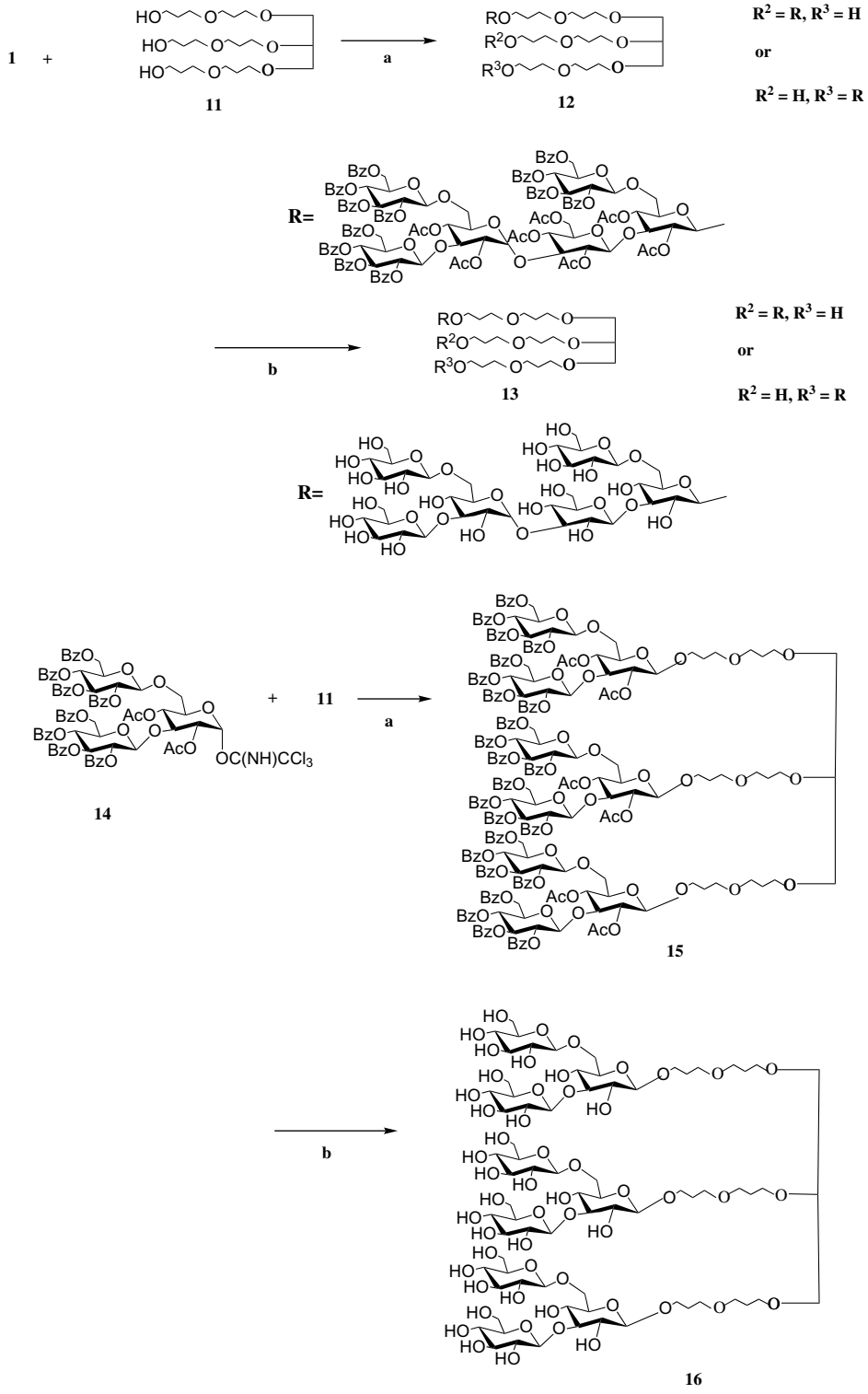


Scheme 1. Reagents and conditions: (a) TMSOTf (0.01–0.05 equiv), CH_2Cl_2, −20 to 0 °C, 2–4 h; (b) satd NH_3–MeOH, rt, a week.

compound **2** in good yield (89.7%). Subsequent condensation of **2** with **1** afforded diglycosidated compound **5** in satisfactory yield (80.3%). A trial for completion of the glycosidation with one coupling reaction, that is, coupling of two equivalents hexaosyl donors with one equivalent of hexylene glycol, was also carried out giving hardly any separated product. Similarly, diethylene and triethylene glycol linked hexaose dimers were also obtained with two steps. Thus, glycosidations of **1** with excess diethylene glycol and triethylene glycol were successfully performed producing **3** (90.2%) and **4** (88.2%), respectively. Subsequent condensation of **3** and **4** with **1** furnished the dimers **7** (76.5%) and **8** (68.8%), respectively. Deacylation of **5**, **7** and **8** in ammonium-saturated methanol gave the dimers **6**, **9** and **10**, respectively.

For preparation of dendrimers, a core scaffold trialcohol **11** (Scheme 2) was obtained from glycerol by employing an iterative allylation–hydroboration strategy in satisfactory overall yield.[10] However, glycosidation of **1** with **11** only produced a diglycosylated mixture, and the triglycosylated cluster was not obtainable even repeating the coupling–separation process for five times. This indicated that clusters with a large oligosaccharide as the ligand were difficult to prepare if the scaffold did not have long enough spacers. In contrast, a triose-based glycocluster **16** was successfully obtained by repeated glycosylation of **11** with excess triosyl donor **14** followed by deprotection. Bioactivity evaluation of **6**, **9**, **10**, **13** and **16** is in progress, and the results will be reported in due course.



Scheme 2. Reagents and conditions: (a) TMSOTf (0.01–0.05 equiv), CH_2Cl_2, −20 to 0 °C, 2–4 h; (b) satd NH_3–MeOH, rt, a week.

3. Experimental

3.1. General methods

Melting points were determined with a 'Mel-Temp' apparatus. Optical rotations were determined with a Perkin–Elmer model 241-MC automatic polarimeter for solutions in a 1-dm, jacketed cell. ^1H NMR and ^{13}C NMR spectra were recorded with Varian XL-400 spectrometers, for solutions in $CDCl_3$ or in D_2O as indicated. Chemical shifts are expressed in ppm downfield from the internal Me_4Si absorption. Mass spectra

were measured using MALTI-TOF-MS with CCA as matrix or recorded with a VG PLATFORM mass spectrometer using the ESI mode. Thin-layer chromatography (TLC) was performed on silica gel HF with detection by charring with 30% (v/v) sulfuric acid in MeOH or by UV detection. Column chromatography was conducted by elution of a column (8 × 100 mm, 16 × 240 mm, 18 × 300 mm, 35 × 400 mm) of silica gel (100–200 mesh) with EtOAc–petroleum ether (bp 60–90 °C) as the eluent. Analytical LC was performed with a Gilson HPLC consisting of a pump (model 306), stainless steel column packed with silica gel (Spherisorb SiO_2, 10 × 300 mm or 4.6 × 250 mm), differential refractometer (132-RI Detector), UV–vis detector (model 118). EtOAc–petroleum ether (bp 60–90 °C) was used as the eluent at a flow rate of 1–4 mL/min. Solutions were concentrated at a temperature <60 °C under diminished pressure.

3.2. 6-Hydroxyhexyl 2,3,4,6-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-β-D-glucopyranoside (2)

Compound **1** (1 g, 0.373 mmol) and 1,6-hexanediol (400 mg, 3.39 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (20 mL). TMSOTf (15 μL, 0.132 mmol) was added dropwise at −20 °C with N_2 protection. The reaction mixture was stirred for 3 h, during which time the temperature was gradually raised to ambient temperature. Then the mixture was neutralized with Et_3N. Concentration of the reaction mixture, followed by purification on a silica gel column with 1:1 petroleum ether–EtOAc as the eluent gave the product **2** (881 mg, 89.7%) as a foamy solid: $[\alpha]_D$ +37.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03–7.27 (m, 60H, 12 Bz-*H*), 5.88 (dd, 1H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.86 (dd, 1H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.83 (dd, 1H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.76 (dd, 1H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.67 (dd, 1H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.54 (dd, 1H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.52 (dd, 1H, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.36 (dd, 1H, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.35 (dd, 1H, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 4.97 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.94 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.91 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 4.88 (dd, 1H, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 4.87 (dd, 1H, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 9.7 Hz, H-2), 4.79 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 4.75 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.71–4.64 (m, 4H), 4.59 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.50–4.46 (m, 3H), 4.30 (dd, 1H, $J_{5,6}$ 4.7 Hz, $J_{6,6}$ 12.4 Hz, H-6), 4.21 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.19–4.06 (m, 5H), 4.01–3.82 (m, 7H), 3.73–3.51 (m, 4H), 3.38–3.34 (m, 4H), 2.38, 2.05, 2.03, 1.97, 1.84, 1.78, 1.62 (s, 21H, 7 C*H*$_3$CO), 1.58–1.52 (m, 8H, –C*H*$_2$–); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.5, 170.1, 169.6, 169.5, 169.5, 169.3, 168.9 (7C, 7 *C*OCH$_3$), 166.1, 166.0, 166.0, 166.0, 165.9, 165.6, 165.6, 165.2, 165.2, 165.1, 165.0, 165.0 (12C, 12 *C*OPh), 101.3, 101.3, 101.1, 100.6, 100.4 (5β-C-1), 93.4 (α-C-1); Anal. Calcd for $C_{140}H_{136}O_{51}$: C, 63.82; H, 5.20. Found: C, 64.01; H, 5.12.

3.3. 2-(2-Hydroxyethoxy)ethyl 2,3,4,6-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-β-D-glucopyranoside (3)

Compound **1** (1.00 g, 0.373 mmol) and diethylene glycol (370 mg, 3.49 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (20 mL). TMSOTf (15 μL, 0.132 mmol) was added dropwise at −20 °C with N_2 protection. The reaction mixture was stirred for 3 h, during which time the temperature was gradually raised to ambient temperature. Then the mixture was neutralized with Et_3N. Concentration of the reaction mixture, followed by purification on a silica gel column with 1:1 petroleum ether–EtOAc as the eluent gave the product **3** (823 mg, 90.2%) as a foamy solid: $[\alpha]_D$ +40.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.05–7.26 (m, 60H, 12 Bz-*H*), 5.91 (dd, 1H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.86 (dd, 1H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.85 (dd, 1H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.76 (dd, 1H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.68 (dd, 1H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.53 (dd, 1H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.52 (dd, 1H, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.37 (dd, 1H, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.35 (dd, 1H, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 4.98 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.93 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.91 (dd, 1H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 4.90 (dd, 1H, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 4.87 (dd, 1H, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 9.7 Hz, H-2), 4.80 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 4.77 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.74–4.63 (m, 4H), 4.59 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.56 (dd, 1H, $J_{5,6}$ 4.7 Hz, $J_{6,6}$ 12.4 Hz, H-6), 4.50–4.46 (m, 3H), 4.40 (dd, 1H, $J_{5,6}$ 4.7 Hz, $J_{6,6}$ 12.4 Hz, H-6), 4.32 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.28 (dd, 1H, $J_{5,6}$ 4.7 Hz, $J_{6,6}$ 12.4 Hz, H-6), 4.20–4.06 (m, 5H), 3.96–3.88 (m, 5H), 3.85–3.80 (m, 4H), 3.70–3.59 (m, 6H), 3.40–3.36 (m, 1H), 3.18–3.13 (m, 1H), 2.38, 2.05, 2.03, 1.97, 1.84, 1.79, 1.61 (s, 21H, 7 C*H*$_3$CO); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.6, 170.1, 169.6, 169.4, 169.4, 169.3, 169.2 (7C, 7 *C*OCH$_3$), 166.1, 166.0, 166.0, 166.0, 165.8, 165.8, 165.6, 165.6, 165.4, 165.2, 165.1, 165.0 (12C, 12 *C*OPh), 101.3, 101.3, 101.1, 100.7, 100.4 (5β-C-1), 93.0 (α-C-1); Anal. Calcd for $C_{138}H_{132}O_{52}$: C, 63.21; H, 5.04. Found: C, 63.42; H, 4.99.

3.4. 2-[2-(2-Hydroxyethoxy)ethoxy]ethyl 2,3,4,6-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-β-D-glucopyranoside (4)

Compound **1** (1.00 g, 0.373 mmol) and triethylene glycol (500 mg, 3.33 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (20 mL). TMSOTf (15 μL, 0.132 mmol) was added dropwise at −20 °C with N_2 protection. The reaction mixture was stirred for 3 h, during which time the temperature was gradually raised to ambient temperature. Then the mixture was neutralized with Et_3N. Concentration of the reaction mixture, followed by purification on a silica gel column with 1:1 petroleum ether–EtOAc as the eluent gave the product **2** (877 mg, 88.2%) as a foamy solid: $[\alpha]_D$ +43.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03–7.26 (m, 60H, 12 Bz-*H*), 5.90 (dd, 1H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.86 (dd, 1H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.84 (dd, 1H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.75 (dd, 1H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.67 (dd, 1H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.53 (dd, 1H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.51 (dd, 1H, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.37 (dd, 1H, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.35 (dd, 1H, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 4.97 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.93 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.91 (dd, 1H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 4.90 (dd, 1H, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 4.86 (dd, 1H, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 9.7 Hz, H-2), 4.80 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 4.75 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.73–4.60 (m, 4H), 4.59 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.57 (dd, 1H, $J_{5,6}$ 4.7 Hz, $J_{6,6}$ 12.4 Hz, H-6), 4.50–4.45 (m, 3H), 4.33 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.28 (dd, 1H, $J_{5,6}$ 4.7 Hz, $J_{6,6}$ 12.4 Hz, H-6), 4.21–4.08 (m, 5H), 4.02–3.79 (m, 5H), 3.71–3.58 (m, 7H), 3.55–3.54 (m, 6H), 3.43–3.29 (m, 4H), 2.36, 2.04, 2.02, 1.96, 1.84, 1.77, 1.63 (s, 21H, 7 CH_3CO); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.5, 170.1, 169.6, 169.5, 169.5, 169.4, 169.1 (7 C, 7 *C*OCH$_3$), 166.1, 166.0, 166.0, 165.8, 165.8, 165.6, 165.6, 165.3, 165.2, 165.1, 165.0, 164.9 (12C, 12 *C*OPh), 101.4, 101.3, 101.3, 100.6, 100.3 (5β-C-1), 93.1 (α-C-1); Anal. Calcd for $C_{140}H_{136}O_{53}$: C, 63.06; H, 5.11. Found: C, 63.25; H, 5.06.

3.5. Hexyl-1,6-diyl bis{2,3,4,6-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-β-D-glucopyranoside} (5)

Compound **1** (610 mg, 0.227 mmol) and **2** (500 mg, 0.190 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (30 mL). TMSOTf (20 μL, 0.176 mmol) was added dropwise at −20 °C with N_2 protection. The reaction mixture was stirred for 3 h, during which time the temperature was gradually raised to ambient temperature. Then the mixture was neutralized with Et_3N. Concentration of the reaction mixture, followed by purification on a silica gel column with 1:1.5 petroleum ether–EtOAc as the eluent gave the product **5** (786 mg, 80.3%) as a foamy solid: $[\alpha]_D$ +63.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.01–7.25 (m, 60H, 12 Bz-*H*), 6.11 (dd, 1H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.87 (dd, 1H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.85 (dd, 1H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.74 (dd, 1H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.70 (dd, 1H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.56 (dd, 1H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.53 (dd, 1H, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.37 (dd, 1H, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.32 (dd, 1H, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 4.99 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.95 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.90 (dd, 1H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 4.88 (dd, 1H, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 4.86 (dd, 1H, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 9.7 Hz, H-2), 4.80 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 4.76 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.71–4.64 (m, 4H), 4.57 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.49–4.38 (m, 5H), 4.30 (dd, 1H, $J_{5,6}$ 4.7 Hz, $J_{6,6}$ 12.4 Hz, H-6), 4.26 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.19–4.06 (m, 6H), 4.01–3.82 (m, 5H), 3.78–3.51 (m, 4H), 3.39–3.32 (m, 3H), 2.32, 2.04, 2.02, 1.96, 1.83, 1.75, 1.62 (s, 21H, 7 CH_3CO), 1.32–1.25 (m, 4H, –CH_2–); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.6, 170.1, 169.7, 169.6, 169.6, 169.3, 169.3 (7C, 7 *C*OCH$_3$), 166.0, 166.0, 165.9, 165.9, 165.8, 165.6, 165.2, 165.2, 165.2, 165.0, 165.0, 165.0 (12C, 12 *C*OPh), 101.4, 101.3, 101.0, 100.1, 100.4 (5β-C-1), 93.6 (α-C-1); ESIMS for $C_{274}H_{258}O_{100}$ (5152): 5173 $[M+Na]^+$. Anal. Calcd for $C_{274}H_{258}O_{100}$: C, 63.89; H, 5.05. Found: C, 64.08; H, 5.12.

3.6. Hexyl-1,6-diyl bis{β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→6)]-α-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→6)]-β-D-glucopyranoside} (6)

Compound **5** (500 mg, 0.097 mmol) was dissolved in a satd solution of NH_3 in MeOH (15 mL). After a week at rt, the reaction mixture was concentrated and the residue was purified by chromatography on Sephadex LH-20 (MeOH) to afford **6** (174 mg, 87.2%) as a foamy solid: $[\alpha]_D$ +14.6 (*c* 1.0, H_2O); ^{1}H NMR (D_2O, 400 MHz): δ 5.20 (d, 1H, *J* 3.2 Hz, H-1), 4.66 (d, 1H, *J* 8.0 Hz, H-1), 4.64 (d, 1H, *J* 8.0 Hz, H-1), 4.40 (d, 1H, *J* 8.0 Hz, H-1), 4.38 (d, 1H, *J* 8.0 Hz, H-1), 4.36 (d, 1H, *J* 8.0 Hz, H-1), 4.12–4.00 (m, 4H), 3.83–3.78 (m, 8H), 3.62–3.53 (m, 11H), 3.40–3.15 (m, 17H), 1.58–1.52 (m, 4H, –CH_2–); ^{13}C NMR (D_2O, 100 MHz): δ 102.8, 102.8, 102.7, 102.7, 101.9 (5β-C-1), 99.1 (α-C-1). Anal. Calcd for $C_{78}H_{134}O_{62}$: C, 45.39; H, 6.50. Found: C, 45.54 H, 6.44.

3.7. 3-Oxapent-1,5-diyl bis{2,3,4,6-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-β-D-glucopyranoside} (7)

Compound **1** (613mg, 0.229mmol) and **3** (500mg, 0.191mmol) were dried together under high vacuum for 2h, then dissolved in anhyd CH_2Cl_2 (30mL). TMSOTf (25μL, 0.220mmol) was added dropwise at −20°C with N_2 protection. The reaction mixture was stirred for 3h, during which time the temperature was gradually raised to ambient temperature. Then the mixture was neutralized with Et_3N. Concentration of the reaction mixture, followed by purification on a silica gel column with 1:1.5 petroleum ether–EtOAc as the eluent gave the product **7** (751mg, 76.5%) as a foamy solid: $[\alpha]_D$ +35.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400MHz): δ 8.01–7.25 (m, 60H, 12 Bz-*H*), 5.97 (dd, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.7Hz, H-4), 5.86 (dd, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.7Hz, H-4), 5.85 (dd, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.7Hz, H-4), 5.73 (dd, 1H, $J_{2,3}$ = $J_{3,4}$ = 9.7Hz, H-3), 5.70 (dd, 1H, $J_{2,3}$ = $J_{3,4}$ = 9.7Hz, H-3), 5.57 (dd, 1H, $J_{2,3}$ = $J_{3,4}$ = 9.7Hz, H-3), 5.55 (dd, 1H, $J_{1,2}$ 7.9Hz, $J_{2,3}$ 9.7Hz, H-2), 5.38 (dd, 1H, $J_{1,2}$ 7.9Hz, $J_{2,3}$ 9.7Hz, H-2), 5.34 (dd, 1H, $J_{1,2}$ 7.9Hz, $J_{2,3}$ 9.7Hz, H-2), 4.93 (d, 1H, $J_{1,2}$ 7.9Hz, H-1), 4.92 (d, 1H, $J_{1,2}$ 7.9Hz, H-1), 4.90 (dd, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.7Hz, H-4), 4.88 (dd, 1H, $J_{1,2}$ 7.9Hz, $J_{2,3}$ 9.7Hz, H-2), 4.86 (dd, 1H, $J_{1,2}$ 3.6Hz, $J_{2,3}$ 9.7Hz, H-2), 4.81 (d, 1H, $J_{1,2}$ 3.6Hz, H-1), 4.78 (d, 1H, $J_{1,2}$ 7.9Hz, H-1), 4.76–4.68 (m, 4H), 4.58 (d, 1H, $J_{1,2}$ 7.9Hz, H-1), 4.56 (dd, 1H, $J_{5,6}$ 4.7Hz, $J_{6,6}$ 12.4Hz, H-6), 4.50–4.46 (m, 4H), 4.32 (d, 1H, $J_{1,2}$ 7.9Hz, H-1), 4.28 (dd, 1H, $J_{5,6}$ 4.7Hz, $J_{6,6}$ 12.4Hz, H-6), 4.19–4.09 (m, 5H), 3.96–3.75 (m, 6H), 3.85–3.80 (m, 4H), 3.70–3.59 (m, 5H), 3.38–3.30 (m, 5H), 2.30, 2.05, 2.03, 1.98, 1.96, 1.83, 1.76 (s, 21H, 7 CH_3CO); ^{13}C NMR ($CDCl_3$, 100MHz): δ 170.6, 170.1, 169.6, 169.6, 169.4, 169.4, 168.8 (7C, 7 *C*OCH$_3$), 166.1, 166.0, 166.0, 165.9, 165.7, 165.6, 165.5, 165.2, 165.2, 165.2, 165.0, 165.0 (12C, 12 *C*OPh), 101.4, 101.2, 101.0, 100.0, 100.0 (5β-C-1), 93.2 (α-C-1); ESIMS for $C_{272}H_{254}O_{101}$ (5141): 5163 $[M+Na]^+$. Anal. Calcd for $C_{272}H_{254}O_{101}$: C, 63.58; H, 4.95. Found: C, 63.31; H, 5.04.

3.8. 3,6-Dioxaoct-1,8-diyl bis{2,3,4,6-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-β-D-glucopyranoside} (8)

Compound **1** (600mg, 0.224mmol) and **4** (500mg, 0.188mmol) were dried together under high vacuum for 2h, then dissolved in anhyd CH_2Cl_2 (30mL). TMSOTf (30μL, 0.264mmol) was added dropwise at −20°C with N_2 protection. The reaction mixture was stirred for 3h, during which time the temperature was gradually raised to ambient temperature. Then the mixture was neutralized with Et_3N. Concentration of the reaction mixture, followed by purification on a silica gel column with 1:1.5 petroleum ether–EtOAc as the eluent gave the product **8** (670mg, 68.8%) as a foamy solid: $[\alpha]_D$ +42.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.95–7.24 (m, 60H, 12 Bz-*H*), 5.93 (dd, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.7Hz, H-4), 5.87 (dd, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.7Hz, H-4), 5.84 (dd, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.7Hz, H-4), 5.74 (dd, 1H, $J_{2,3}$ = $J_{3,4}$ = 9.7Hz, H-3), 5.67 (dd, 1H, $J_{2,3}$ = $J_{3,4}$ = 9.7Hz, H-3), 5.56 (dd, 1H, $J_{2,3}$ = $J_{3,4}$ = 9.7Hz, H-3), 5.53 (dd, 1H, $J_{1,2}$ 7.9Hz, $J_{2,3}$ 9.7Hz, H-2), 5.37 (dd, 1H, $J_{1,2}$ 7.9Hz, $J_{2,3}$ 9.7Hz, H-2), 5.35 (dd, 1H, $J_{1,2}$ 7.9Hz, $J_{2,3}$ 9.7Hz, H-2), 4.96 (d, 1H, $J_{1,2}$ 7.9Hz, H-1), 4.93 (d, 1H, $J_{1,2}$ 7.9Hz, H-1), 4.90 (dd, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.7Hz, H-4), 4.88 (dd, 1H, $J_{1,2}$ 7.9Hz, $J_{2,3}$ 9.7Hz, H-2), 4.86 (dd, 1H, $J_{1,2}$ 3.6Hz, $J_{2,3}$ 9.7Hz, H-2), 4.81 (d, 1H, $J_{1,2}$ 3.6Hz, H-1), 4.76 (d, 1H, $J_{1,2}$ 7.9Hz, H-1), 4.72–4.55 (m, 5H), 4.54 (d, 1H, $J_{1,2}$ 7.9Hz, H-1), 4.50–4.45 (m, 3H), 4. 29 (d, 1H, $J_{1,2}$ 7.9Hz, H-1), 4.26 (dd, 1H, $J_{5,6}$ 4.7Hz, $J_{6,6}$ 12.4Hz, H-6), 4.19–4.09 (m, 5H), 4.02–3.84 (m, 6H), 3.78–3.72 (m, 4H), 3.68–3.50 (m, 6H), 3.42–3.35 (m, 4H), 2.34, 2.05, 2.02, 1.96, 1.83, 1.77, 1.66 (s, 21H, 7 CH_3CO); ^{13}C NMR ($CDCl_3$, 100MHz): δ 170.5, 170.1, 169.6, 169.5, 169.5, 169.4, 168.9 (7C, 7 *C*OCH$_3$), 166.1, 166.0, 166.0, 165.8, 165.7, 165.6, 165.5, 165.2, 165.2, 165.1, 165.0, 165.0 (12C, 12 *C*OPh), 101.3, 101.2, 101.1, 100.6, 100.4 (5β-C-1), 93.4 (α-C-1); ESIMS for $C_{274}H_{258}O_{102}$ (5184): 5206 $[M+Na]^+$. Anal. Calcd for $C_{274}H_{258}O_{102}$: C, 63.50; H, 5.02. Found: C, 63.32; H, 5.10.

3.9. 3-Oxapent-1,5-diyl bis{β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→6)]-α-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→6)]-β-D-glucopyranoside} (9)

Compound **7** (500mg, 0.097mmol) was dissolved in a satd solution of NH_3 in MeOH (20mL). After a week at rt, the reaction mixture was concentrated, and the residue was purified by chromatography on Sephadex LH-20 (MeOH) to afford **9** (175mg, 88.2%) as a foamy solid: $[\alpha]_D$ +32.7 (*c* 1.0, H_2O); ^{1}H NMR (D_2O, 400MHz): δ 5.20 (d, 1H, *J* 3.2Hz, H-1), 4.62 (d, 1H, *J* 8.0Hz, H-1), 4.60 (d, 1H, *J* 8.0Hz, H-1), 4.41 (d, 1H, *J* 8.0Hz, H-1), 4.39 (d, 1H, *J* 8.0Hz, H-1), 4.36 (d, 1H, *J* 8.0Hz, H-1), 4.12–3.98 (m, 5H), 3.92–3.78 (m, 8H), 3.65–3.51 (m, 14H), 3.40–3.15 (m, 17H); ^{13}C NMR (D_2O, 100MHz): δ 102.9, 102.8, 102.7, 102.7, 102.1 (5β-C-1), 99.1 (α-C-1). Anal. Calcd for $C_{76}H_{130}O_{63}$: C, 44.49; H, 6.34. Found: C, 44.65; H, 6.28.

3.10. 3,6-Dioxaoct-1,8-diyl bis{β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→6)]-α-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→6)]-β-D-glucopyranoside} (10)

Compound **8** (500 mg, 0.096 mmol) was dissolved in a satd solution of NH_3 in MeOH (20 mL). After a week at rt, the reaction mixture was concentrated, and the residue was purified by chromatography on Sephadex LH-20 (MeOH) to afford **10** (174 mg, 84.6%) as a foamy solid: $[\alpha]_D$ +29.6 (*c* 1.0, H_2O); ^1H NMR (D_2O, 400 MHz): δ 5.20 (d, 1H, *J* 3.2 Hz, H-1), 4.66 (d, 1H, *J* 8.0 Hz, H-1), 4.62 (d, 1H, *J* 8.0 Hz, H-1), 4.39 (d, 1H, *J* 8.0 Hz, H-1), 4.38 (d, 1H, *J* 8.0 Hz, H-1), 4.37 (d, 1H, *J* 8.0 Hz, H-1), 4.16–3.98 (m, 5H), 3.82–3.72 (m, 10H), 3.63–3.49 (m, 17H), 3.45–3.15 (m, 16H); ^{13}C NMR (D_2O, 100 MHz): δ 102.9, 102.8, 102.8, 102.7, 102.1 (5β-C-1), 99.1 (α-C-1). Anal. Calcd for $C_{78}H_{134}O_{64}$: C, 44.70; H, 6.40. Found: C, 45.56 H, 6.33.

3.11. 1,2,3-Tris-*O*-[2-(2-Hydroxyethoxy)ethyl]glycerol (11)

To a solution of glycerol (5.0 g, 54.3 mmol) in dry DMF (50 mL), AllBr (17.3 mL, 196 mmol) and NaH (13.9 g, 49% in oil, 285 mmol) were added under cooling with an ice bath. The mixture was stirred for 2 h at rt, at the end of which time TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was poured to water and extracted with CH_2Cl_2. The organic phase was concentrated, and the residue was purified on a silica gel column with 1:1.5 petroleum ether–EtOAc as the eluent to give a syrupy product (10.6 g, 92.5%). Then the product (500 mg, 2.36 mmol) was dissolved in dry THF (20 mL) and stirred. A solution of 9-BBN in THF (0.5 M, 28.4 mL, 14.2 mmol) was added dropwise. The reaction mixture was heated under reflux for 2 h, and excess of 9-BBN was then destroyed by dropwise addition of water at 0 °C. The hydroboration mixture was oxidized by treatment with 3 M aq NaOH (28.4 mL) and 30% H_2O_2 solution (28.4 mL) at 0 °C, followed by stirring overnight at rt. The mixture was saturated with K_2CO_3 and extracted with THF. The organic phase was concentrated, and the residue was purified by a silica gel column with 1:3 petroleum ether–EtOAc to yield a trialcohol (511 mg, 82.3%). The allylation–hydroboration process was repeated on the trialcohol to give compound **11** (600 mg, 53.4% overall): ^1H NMR ($CDCl_3$, 400 MHz): δ 3.83–3.79 (m, 6H), 1.90–1.85 (m, 16H), 1.67–1.55 (m, 13H), 1.49–1.44 (m, 6H). Anal. Calcd for $C_{21}H_{44}O_9$: C, 57.27; H, 10.00. Found: C, 57.46; H, 10.06.

3.12. Diglycosylated mixture 12

Compound **1** (2.51 g, 0.940 mmol) and **11** (80 mg, 0.182 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (50 mL). TMSOTf (50 μL, 0.440 mmol) was added dropwise at −20 °C with N_2 protection. The reaction mixture was stirred for 3 h, during which time the temperature was gradually raised to ambient temperature. Then the mixture was neutralized with Et_3N. Concentration of the reaction mixture, followed by purification on a silica gel column with 1:2 petroleum ether–EtOAc as the eluent gave a product (500 mg). With the product as the starting acceptor and **1** as the donor, reiteration of the coupling–separation process for four times produced the mixture **12** (400 mg, 40.2%): $[\alpha]_D$ +45.2 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.02–7.26 (m, 60H, 12 Bz-*H*), 5.88 (dd, 1H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.86 (dd, 1H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.85 (dd, 1H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.74 (dd, 1H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.67 (dd, 1H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.60 (dd, 1H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.54 (dd, 1H, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.37 (dd, 1H, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.35 (dd, 1H, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 4.93 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.90 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.86 (dd, 1H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 4.85 (dd, 1H, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 4.82 (dd, 1H, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 9.7 Hz, H-2), 4.81 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 4.77 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.73–4.56 (m, 5H), 4.55 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.50–4.42 (m, 4H), 4.30 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.27 (dd, 1H, $J_{5,6}$ 4.7 Hz, $J_{6,6}$ 12.4 Hz, H-6), 4.19–4.09 (m, 4H), 4.04–3.81 (m, 6H), 3.78–3.59 (m, 7H), 3.68–3.50 (m, 6H), 3.42–3.35 (m, 5H), 2.05, 2.02, 1.99, 1.96, 1.84, 1.79, 1.68 (s, 21H, 7 CH_3CO), 1.66–1.46 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.5, 170.1, 169.6, 169.5, 169.4, 169.4, 168.7 (7 C, 7 *C*OCH$_3$), 166.1, 166.0, 165.8, 165.7, 165.6, 165.6, 165.2, 165.2, 165.2, 165.0, 165.0, 165.0 (12C, 12 *C*OPh), 101.8, 101.4, 101.1, 100.6, 99.5 (5β-C-1), 93.4 (α-C-1); ESIMS for $C_{289}H_{288}O_{107}$ (5471): 5492 $[M+Na]^+$. Anal. Calcd for $C_{289}H_{288}O_{107}$: C, 63.42; H, 5.27. Found: C, 63.22; H, 5.20.

3.13. Diglycosylated mixture 13

Compound **12** (300 mg, 0.055 mmol) was dissolved in a satd solution of NH_3 in MeOH (15 mL). After a week at rt, the reaction mixture was concentrated, and the residue was purified by chromatography on Sephadex LH-20 (MeOH) to afford **13** (111 mg, 84.6%) as a foamy solid: $[\alpha]_D$ +29.6 (*c* 1.0, H_2O); ^1H NMR (D_2O, 400 MHz): δ 5.26 (d, 1H, *J* 3.2 Hz, H-1), 4.67 (d, 1H, *J* 8.0 Hz, H-1), 4.65 (d, 1H, *J* 8.0 Hz, H-1), 4.48 (d, 1H, *J* 8.0 Hz, H-1), 4.46 (d, 1H, *J* 8.0 Hz, H-1), 4.43 (d, 1H, *J* 8.0 Hz, H-1), 4.16–4.02 (m, 5H), 3.88–3.82 (m, 10H), 3.80–3.52 (m, 16H), 3.52–3.12 (m, 23H), 1.93–1.62 (m, 4H); ^{13}C NMR (D_2O, 100 MHz): δ 102.8, 102.8, 102.8, 102.7, 102.7 (5β-C-1), 99.1 (α-C-1). Anal. Calcd for $C_{93}H_{164}O_{69}$: C, 46.81; H, 6.88. Found: C, 47.04 H, 6.76.

3.14. Triose-based glycocluster 15

Compound **14** (1.18 g, 0.752 mmol) and **11** (50 mg, 0.188 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (30 mL). TMSOTf (50 μL, 0.440 mmol) was added dropwise at −20 °C with N_2 protection. The reaction mixture was stirred for 3 h, during which time the temperature was gradually raised to ambient temperature. Then the mixture was neutralized with Et_3N. Concentration of the reaction mixture, followed by purification on a silica gel column with 1:1.5 petroleum ether–EtOAc as the eluent gave a product (300 mg). Mass spectrometry of the product indicated incomplete glycosylation. Thus, with the product as the starting acceptor, reiteration of the coupling–separation process for three times produced the product **15** (456 mg, 52.2%) as a foamy solid: $[\alpha]_D$ +35.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.17–7.26 (m, 40H, 8 Bz-*H*), 5.88 (dd, 1H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.85 (dd, 1H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.68 (dd, 1H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.65 (dd, 1H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.49 (dd, 1H, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.37 (dd, 1H, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.00 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.97 (d, 1H, $J = 7.9$ Hz, H-1), 4.85 (dd, 1H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 4.74 (d, 1H, $J = 7.9$ Hz, H-1), 4.67–4.60 (m, 3H), 4.52–4.41 (m, 3H), 4.19–4.05 (m, 6H), 4.01–3.83 (m, 4H), 3.48–3.22 (m, 4H) 2.04, 1.89 (s, 6H, 2 C*H*$_3$CO) 1.69–1.51 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.4, 169.6 (2C, 2 *C*OCH$_3$), 166.1, 165.7, 165.6, 165.6, 165.2, 165.1, 165.0, 165.0 (8C, 8 *C*OPh), 101.8, 101.4, 100.6, (3β-C-1); ESIMS for $C_{255}H_{242}O_{84}$ (4649): 4670 $[M+Na]^+$. Anal. Calcd for $C_{245}H_{242}O_{84}$: C, 64.96 H, 5.35. Found: C, 64.72 H, 5.45.

3.15. Triose-based glycocluster 16

Compound **15** (400 mg, 0.086 mmol) was dissolved in a satd solution of NH_3 in MeOH (15 mL). After a week at rt, the reaction mixture was concentrated, and the residue was purified by chromatography on Sephadex LH-20 (MeOH) to afford **16** (126 mg, 82.6%) as a foamy solid: $[\alpha]_D$ +36.2 (*c* 1.0, H_2O); ^{1}H NMR (D_2O, 400 MHz): δ 4.62 (d, 1H, *J* 8.0 Hz, H-1), 4.50 (d, 1H, *J* 8.0 Hz, H-1), 4.46 (d, 1H, *J* 8.0 Hz, H-1), 4.15–4.04 (m, 4H), 3.92–3.76 (m, 5H), 3.62–3.55 (m, 6H), 3.46–3.20 (m, 12H) 1.93–1.61 (m, 4H); ^{13}C NMR (D_2O, 100 MHz): δ 101.8, 100.5, 97.0 (3β-C-1). Anal. Calcd for $C_{75}H_{134}O_{54}$: C, 47.67; H, 7.15. Found: C, 47.84 H, 7.31.

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