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Synthesis of β-(1→6)-branched (1→3)-glucododecaose and -glucopentadecaose with alternate β- and α-bonds in the backbone

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Abstract

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)]-α-D-Glc*p*-(1→3)}$_{2-3}$-*β*-D-Glc*p*-(1→3)-[β-D-Glc*p*-(1→6)]-β-D-Glc*p* were synthesized as their methoxyphenyl glycosides in a concise way with a trisaccharide as the building block.

Keywords: Oligosaccharide; Synthesis; Glucose

1. Introduction

In continuation of our research on developing new immunopotentiating reagents, we have synthesized the heptasaccharide[1] repeating unit of lentinan and its anologues,[2] and the pentasaccharide fragments[3] of *Epicoccum nigrum* Ehrenb. ex Schlecht. It was interesting to find that not only the heptasaccharide shows strong antitumor activity as we expected. But also 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*-(1→6)]-D-Glc*p*, has good immunoregulating activity.[2] Bioassays showed that in combination with the chemotherapeutic agent, cyclophosphamide (CPA), the glucohexaose at a dose of 0.5–1 mg/kg substantially increased the inhibition of S_{180} for CPA, but decreased the toxicity caused by CPA. It was noted that this hexasaccharide was not fully β-linked like the repeating unit of lentinan[4] but contained one α-linkage between the two trisaccharide moieties. For a detailed study on the mechanism of action of the glucose hexasaccharide, a variety of model compounds was needed. We present herein the syntheses of a glucododecaose consisting four trisaccharide units and a glucopentadecaose containing five trisaccharide units.

2. Results and discussion

As shown in Scheme 1, coupling[5] of the trisaccharide donor **1**[2] with the trisaccharide acceptor **2**, which was obtained by condensation of **1** with 4-methoxyphenol, followed by deallylation, afforded the hexasaccharide **3** with an α-linkage[6] between the two trisaccharide moieties (68.2%), the same as that reported for the coupling of two trisaccharides with similar structures.[2] Deallylation of **3** with $PdCl_2$[7] in MeOH smoothly gave the hexasaccharide acceptor **4** (85.2%). Condensation of **1** with **4** furnished the nonasaccharide **5** (60.7%), and subsequent deallylation gave the nonasaccharide acceptor **6** (81.1%). Coupling of **7**[8] with **6** yielded the dodecasaccharide **8** (54.2%), and subsequent deacylation gave the target dodecaoside **9** (86.3%). The ^1H and ^{13}C NMR spectra of **9** showed all of the characteristic signals such as δ 5.19 with $J_{1,2}$ 3.2 Hz for **3** α-H-1, δ 4.68–4.10 with $J_{1,2}$ 8.0 Hz for **9** β-H-1, δ 103.5, 101.9, and 101.8 for **3** α-C-1, and δ 105.5 and 105.2 for **9** β-C-1. The pentadecasaccharide **13** was obtained by the same reaction sequence, i.e., condensation of **1** with **6** gave **10** (48.1%), deallylation of **10** afforded **11** (80.3%), subsequent condensation of **11** with **7** furnished **12** (42.7%),

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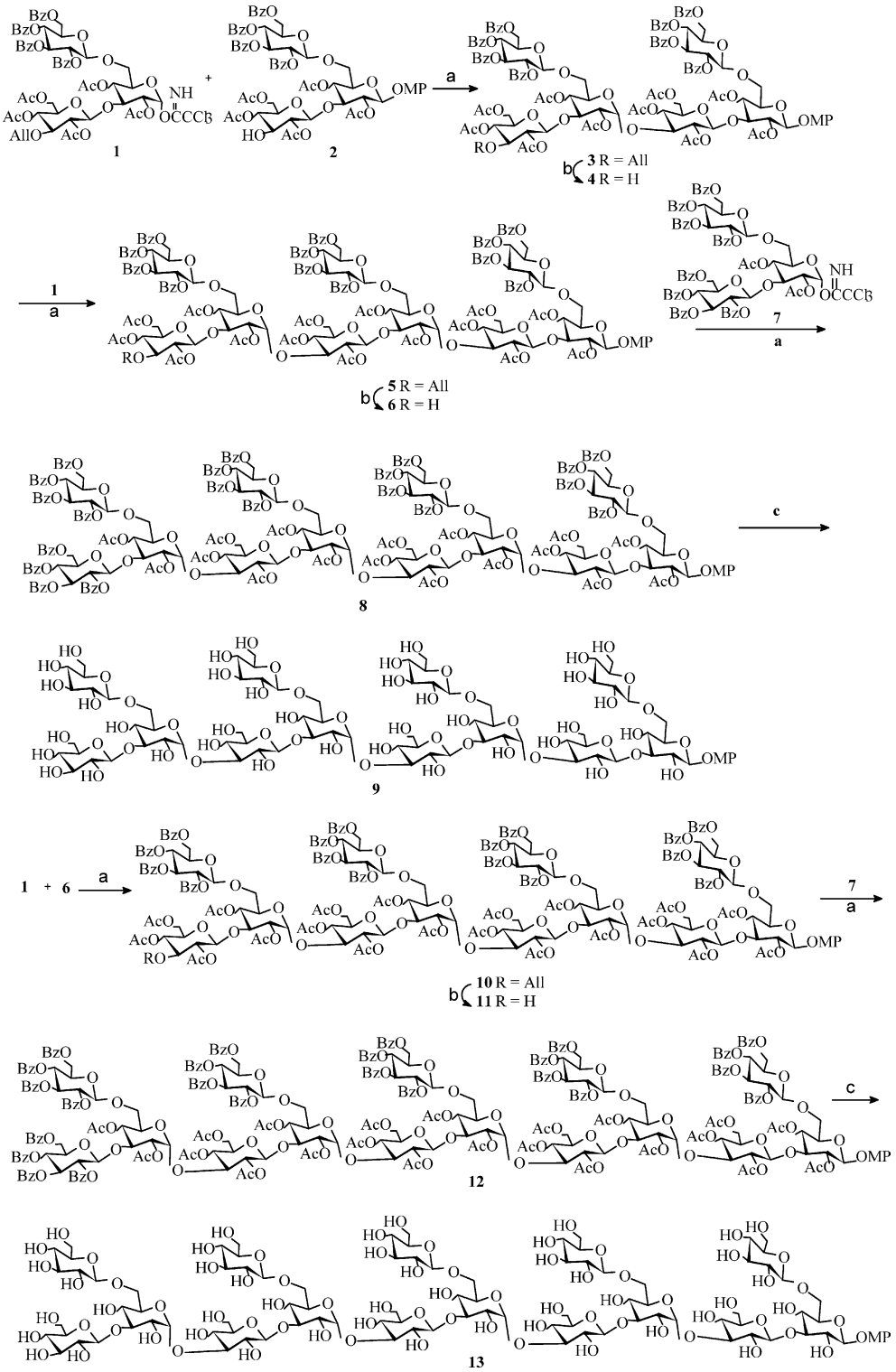


Scheme 1. Reagents and conditions: (a) TMSOTf, CH_2Cl_2, −20 °C to rt, 3–5 h; (b) $PdCl_2$ in CH_2Cl_2–CH_3OH, rt, 3 h; (c) satd NH_3–MeOH, rt, 7 d.

and finally deprotection (85.8%) yielded the target pentadecasaccharide. The ^1H and ^{13}C NMR spectra of **13** showed characteristic signals such as δ 5.29 with $J_{1,2}$ 3.2 Hz for **4** α-H-1, δ 5.04–4.10 with $J_{1,2}$ 7.8 Hz for **11** β-H-1, δ 103.4, 101.8, and 101.7 for **4** α-C-1, and δ 105.4 and 105.2 for **11** β-C-1. Bioactivity testing of **9** and **13** is in progress, and the results will be reported in due course.

In the synthesis of the dodecasaccharide **8**, another strategy with coupling of two hexasaccharides was also

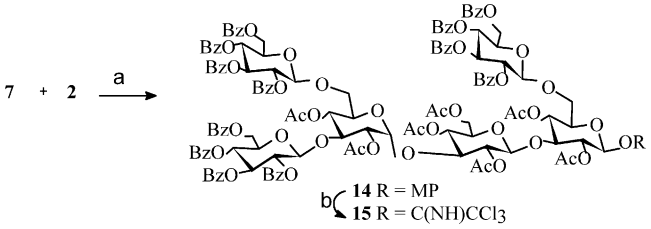
tried. Thus, the coupling of **7** with **2** gave the hexasaccharide **14**, and subsequent oxidative cleavage of the methoxyphenyl group with CAN, followed by trichloroacetimidation, gave the hexasaccharide donor **15** (72.5%) (Scheme 2). Coupling of **4** with **15** was carried out as a parallel experiment with the condensation of **1** and **6**, but no expected coupling product was obtained except the decomposed byproduct of the donor. This indicated that the hexasaccharide donor and the hexasaccharide acceptor may be not matched, while the trisaccharide donor and the hexa-, nano-, or dodecasaccharide acceptor were matched.

In summary, an efficient method for the construction of β-(1→6)-branched (1→3)-linked glucododecaose and glucopentadecaose with alternate β- and α-linkages in the backbone was achieved using trisaccharide as the building block. This method should be suitable for synthesis of high oligosaccharides of similar structure.

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. ^{1}H, ^{13}C, and 2D 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 δ-units (ppm) downfield from the Me_4Si absorption. Mass spectra were 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.



Scheme 2. Reagents and conditions: (a) TMSOTf, CH_2Cl_2, −20 °C to rt, 3–5 h; (b) i. CAN in MeCN–H_2O, rt, 3 h; ii. CH_2Cl_2, CCl_3CN, K_2CO_3, rt, 10 h.

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 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. 4-Methoxyphenyl 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** (10 g, 8.38 mmol) and 4-methoxyphenol (1.0 g, 0.926 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (150 mL). TMSOTf (100 μL, 0.870 mmol) was added dropwise at −20 °C with nitrogen 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 2:1 petroleum ether–EtOAc as the eluent gave 4-methoxyphenyl 2,4,6-tri-*O*-acetyl-3-*O*-allyl-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 (8.38 g, 78.4%) as a foamy solid: $[\alpha]_D$ +23.8° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.04–7.27 (m, 20 H, 4 Bz–*H*), 6.92–6.83 (dd, 4 H, MPC_6H_4–), 5.82 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.76–5.68 (m, 1 H, CH_2=C*H*–CH_2O), 5.64 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.49 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.18 (m, 1 H, CH_2=$CHCH_2O$), 5.14–5.04 (m, 2 H), 5.00 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 4.99 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.88 (dd, 1 H, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 4.75 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.74 (m, 1 H), 4.61 (dd, $J_{5,6}$ 2.7 Hz, $J_{6,6}$ 12.1 Hz, H-6), 4.49 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.47–4.45 (m, 1 H), 4.28 (dd, $J_{5,6}$ 4.7 Hz, $J_{6,6}$ 12.1 Hz, H-6), 4.04–4.00 (m, 4 H), 3.90–3.75 (m, 7 H), 3.57–3.53 (m, 2 H), 2.15, 2.10, 2.08, 2.06, 1.90 (s, 15 H, 5 CH_3 CO); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.5, 169.4, 169.1, 168.6, 166.0, (5 C, 5 CH_3CO), 165.6, 165.1, 155.6, 150.9 (4 C, 4 *C*OPh), 101.0, 100.4, 99.8 (C-1^{I-III}), 79.7, 78.2, 74.4, 72.9, 72.7, 72.3, 72.2, 71.9, 69.4, 69.1, 68.6, 67.9, 62.9, 62.0, 55.6 (C-2, 3, 4, 5, 6^{I-III}), 20.8, 20.7, 20.6, 20.3. Anal. Calcd for $C_{66}H_{68}O_{26}$: C, 62.07; H, 5.33. Found: C, 62.25; H, 5.24.

The resultant trisaccharide was dissolved in MeOH (100 mL), and then $PdCl_2$ (350 mg) was added. After stirring for 3 h at room temperature (rt), TLC (1.5:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was filtered, the solution was concentrated to dryness, and the resultant residue was purified by flash chromatography (1.5:1 petroleum

ether–EtOAc) to give **2** (7.04 g, 86.7%) as a foamy solid: $[\alpha]_D$ +20.4° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.04–7.28 (m, 20 H, 4 Bz–*H*), 6.90–6.85(dd, 4 H, MPC_6H_4–), 5.81 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.64 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.48 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.12 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 4.99 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.91 (m, 1 H), 4.75 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.72–4.65 (m, 3 H), 4.61 (dd, $J_{5,6}$ 2.7 Hz, $J_{6,6}$ 12.1 Hz, H-6), 4.50 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.47–4.42 (m, 1 H), 4.28 (dd, $J_{5,6}$ 4.7 Hz, $J_{6,6}$ 12.1 Hz, H-6), 4.04–3.99 (m, 2 H), 3.89–3.77 (m, 7 H), 3.62–3.58 (m, 2 H), 2.17, 2.12, 2.08, 2.05, 1.97 (s, 15 H, 5 C*H*$_3$CO); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.1, 170.4, 169.4, 168.5, 166.0 (5 C, 5 CH_3CO), 165.6, 165.1, 155.6, 150.9 (4 C, 4 *C*OPh), 100.8, 100.4, 99.8 (C-1^{I-III}), 78.7, 74.3, 74.0, 73.8, 72.9, 72.6, 72.2, 71.8, 71.6, 70.4, 69.4, 68.5, 67.8, 62.9, 61.8, 55.6 (C-2, 3, 4, 5, 6^{I-III}), 20.8, 20.7, 20.5, 20.3. Anal. Calcd for $C_{63}H_{64}O_{26}$: C, 61.17; H, 5.18. Found: C, 61.46; H, 5.26.

3.3. 4-Methoxyphenyl 3-*O*-allyl-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-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** (7.9 g, 6.62 mmol) and **2** (6.8 g, 5.50 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (200 mL). TMSOTf (100 μL, 0.87 mmol) was added dropwise at −20 °C with nitrogen 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 1.5:1 petroleum ether–EtOAc as the eluent gave the hexasaccharide **3** (8.96 g, 68.2%) as a foamy solid: $[\alpha]_D$ +16.3° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.16–7.21 (m, 40 H, 8 Bz–*H*), 6.96–6.82 (dd, 4 H, MPC_6H_4–), 5.89 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.83 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.80–5.68 (m, 1 H, CH_2=C*H*–CH_2O), 5.65 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.61 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.50 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.55–5.49 (m, 5 H), 5.49 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.19–5.12 (m, 3 H), 5.03 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 5.01–4.95 (m, 2 H), 4.90 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 4.86 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.83–4.72 (m, 4 H), 4.62 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.61–4.56 (m, 3 H), 4.48 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.46–4.39 (m, 3 H), 4.23–4.11 (m, 5 H), 4.30–4.3.98 (m, 4 H), 3.90–3.81 (m, 6 H), 3.80 (s, 3 H, C*H*$_3$O), 3.77–3.72 (m, 1 H), 3.62–3.52 (m, 2 H), 3.50–3.42 (m, 2 H), 2.43, 2.11, 2.10, 2.09, 2.07, 2.04, 1.99, 1.98, 1.97, 1.95 (s, 30 H, 10 C*H*$_3$CO); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.6, 170.5, 170.4, 169.5, 169.4, 169.3, 169.3, 169.2, 168.8, 168.6 (10 C, 10 *C*OCH_3), 166.0, 166.0, 165.6, 165.6, 165.4, 165.1, 165.1, 165.1 (8 C, 8 *C*OPh), 101.5, 100.8, 100.6, 100.4, 99.8 (5 β-C-1), 93.3 (α-C-1), 79.9, 78.1, 74.9, 74.4, 72.9, 72.6, 72.5, 72.4, 72.3, 72.2, 72.1, 72.0, 71.9, 71.0, 69.7, 69.5, 69.1, 68.6, 68.4, 67.8, 67.6, 62.9, 62.4, 62.0, 61.3, 60.3, 55.6 (C-2, 3, 4, 5, 6^{I-VI}), 21.2, 20.7, 20.6, 20.5, 20.5, 20.4, 20.4. Anal. Calcd for $C_{122}H_{124}O_{50}$: C, 61.31; H, 5.19. Found: C, 61.59; H, 5.02.

3.4. 4-Methoxyphenyl 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-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)

To a solution of **3** (8.7 g, 3.64 mmol) in MeOH (100 mL) was added $PdCl_2$ (250 mg). After stirring the mixture for 3 h at rt, TLC (1:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was filtered, the solution was concentrated to dryness, and the resultant residue was purified by flash chromatography (1:1 petroleum ether–EtOAc) to give **4** (7.28 g, 85.2%) as a foamy solid: $[\alpha]_D$ +24.5° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.03–7.24 (m, 40 H, 8 Bz–*H*), 6.94–6.90 (dd, 4 H, MPC_6H_4–), 5.88 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.82 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.65 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.62 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.49 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.39 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.16 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.02 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.99 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 4.89 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 4.85 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.78 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.77–4.72 (m, 4 H), 4.68–4.63 (m, 5 H), 4.61 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.48 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.48–4.42 (m, 3 H), 4.30 (dd, 1 H, $J_{5,6}$ 5.1 Hz, $J_{6,6}$ 12.4 Hz, H-6), 4.19 (dd, 1 H, $J_{5,6}$ 4.2 Hz, $J_{6,6}$ 12.4 Hz, H-6), 4.14–4.09 (m, 3 H), 4.01–3.98 (m, 2 H), 3.92–3.83 (m, 7 H), 3.80 (s, 3 H, C*H*$_3$O), 3.78–3.74 (m, 1 H), 3.61–3.57 (m, 3 H), 3.47–3.42 (m, 1 H), 2.41, 2.11, 2.10, 2.09, 2.08, 2.06, 2.00, 1.99, 1.98, 1.98 (s, 30 H, 10 C*H*$_3$CO); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.5, 170.5, 170.4, 170.4, 169.6, 169.4, 169.3, 169.3, 169.2, 168.8 (10 C, 10 *C*OCH_3), 166.0, 166.0, 165.6, 165.6, 165.5, 165.1, 165.1, 165.1 (8 C, 8 *C*OPh), 101.5, 100.6, 100.4, 100.4, 99.8 (5 β-C-1), 93.4 (α-C-1), 78.1, 75.1, 74.4, 74.4, 74.0, 72.9, 72.6, 72.5, 72.4, 72.3, 72.2, 72.1, 71.9, 71.8, 71.6, 71.1, 70.6, 70.6, 69.6, 69.5, 69.1, 68.6, 68.3, 67.8, 67.7, 62.9, 62.4, 61.9, 61.4, 55.9 (C-2, 3, 4, 5, 6^{I-VI}), 21.2, 20.9, 20.7, 20.6, 20.5, 20.5, 20.4, 20.4. Anal. Calcd for $C_{119}H_{120}O_{50}$: C, 60.82; H, 5.11. Found: C, 60.53; H, 5.01.

3.5. 4-Methoxyphenyl 3-*O*-allyl-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-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-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** (4.3 g, 3.60 mmol) and **4** (7.0 g, 2.98 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (150 mL). TMSOTf (150 μL, 1.31 mmol) was added dropwise at −20 °C with nitrogen 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** (6.33 g, 60.7%) as a syrup: $[\alpha]_D$ +23.5° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.02–7.26 (m, 60 H, 12 Bz–*H*), 6.95–6.84 (dd, 4 H, MPC_6H_4–), 5.90 (dd, 1 H, $J_{3,4}=J_{4,5}=9.7$ Hz, H-4), 5.89 (dd, 1 H, $J_{3,4}=J_{4,5}=9.7$ Hz, H-4), 5.82 (dd, 1 H, $J_{3,4}=J_{4,5}=9.7$ Hz, H-4), 5.80–5.68 (m, 1 H, CH_2=C*H*–CH_2O), 5.64 (dd, 1 H, $J_{2,3}=J_{3,4}=9.7$ Hz, H-3), 5.61 (dd, 1 H, $J_{2,3}=J_{3,4}=9.7$ Hz, H-3), 5.59 (dd, 1 H, $J_{2,3}=J_{3,4}=9.7$ Hz, H-3), 5.50 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.45 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.40 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.22–5.14 (m, 2 H), 5.12–5.06 (m, 1 H, CH_2=C*H*–CH_2O), 5.01 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 5.00 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.98 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 4.96 (dd, 1 H, $J_{3,4}=J_{4,5}=$ 9.7 Hz, H-4), 4.95 (dd, 1 H, $J_{3,4}=J_{4,5}=9.7$ Hz, H-4), 4.84 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.80 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.78 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.76–4.72 (m, 4 H), 4.70–4.68 (m, 2 H), 4.64 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.63–4.59 (m, 5 H), 4.58 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.52–4.45 (m, 3 H), 4.44 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.20 (dd, 1 H, $J_{5,6}$ 4.7 Hz, $J_{6,6}$ 12.4 Hz, H-6), 4.18 (dd, 1 H, $J_{5,6}$ 5.1 Hz, $J_{6,6}$ 12.4 Hz, H-6), 4.15–4.08 (m, 3 H), 4.04–3.82 (m, 14 H), 3.81(s, 3 H, CH_3O), 3.80–3.74 (m, 2 H), 3.62 (m, 1 H, H-5), 3.54 (m, 1 H, H-5), 3.49–3.41 (m, 3 H), 2.43, 2.32, 2.12, 2.11, 2.09, 2.08, 2.08, 2.06, 2.00, 2.00, 1.99, 1.95, 1.95, 1.93, 1.88 (s, 45 H, 15 CH_3CO); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.8, 170.6, 170.5, 170.4, 170.4, 169.8, 169.5, 169.5, 169.4, 169.3, 169.2, 169.2, 168.9, 168.8, 168.6 (15 C, 15 *C*OCH$_3$), 166.0, 166.0, 166.0, 165.6, 165.6, 165.6, 165.5, 165.1, 165.1, 165.1, 165.1 (12 C, 12 *C*OPh), 101.6, 101.5, 100.6, 100.6, 100.4, 100.1, 99.8 (7 β-C-1), 93.8, 93.5 (2 α-C-1), 80.0, 78.1, 75.5, 74.9, 74.4, 74.1, 73.6, 72.9, 72.6, 72.5, 72.4, 72.2, 72.2, 72.1, 72.0, 71.9, 71.6, 71.6, 70.8, 70.5, 69.8, 69.7, 69.5, 69.2, 69.1, 69.0, 68.6, 68.3, 67.9, 67.6, 62.9, 62.8, 62.4, 62.0, 61.5, 61.3, 60.3, 55.6 (C-2, 3, 4, 5, 6), 21.2, 20.8, 20.7, 20.6, 20.4, 20.2. Anal. Calcd for $C_{178}H_{180}O_{74}$: C, 61.03; H, 5.14. Found: C, 61.31; H, 5.03.

3.6. 4-Methoxyphenyl 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-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-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 (6)

To a solution of **5** (6 g, 1.71 mmol) in MeOH (100 mL) was added $PdCl_2$ (200 mg). After stirring the mixture for 3 h at rt, TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was filtered, the solution was concentrated to dryness, and the resultant residue was purified by flash chromatography (2:1 petroleum ether–EtOAc) to give **6** (4.80 g, 81.1%) as a foamy solid: $[\alpha]_D$ +30.6° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.02–7.26 (m, 60 H, 12 Bz–*H*), 6.96–6.84 (dd, 4 H, MPC_6H_4–), 5.91 (dd, 1 H, $J_{3,4}=J_{4,5}=9.7$ Hz, H-4), 5.89 (dd, 1 H, $J_{3,4}=J_{4,5}=9.7$ Hz, H-4), 5.82 (dd, 1 H, $J_{3,4}=J_{4,5}=9.7$ Hz, H-4), 5.67 (dd, 1 H, $J_{2,3}=J_{3,4}=9.7$ Hz, H-3), 5.62 (dd, 1 H, $J_{2,3}=J_{3,4}=$ 9.7 Hz, H-3), 5.59 (dd, 1 H, $J_{2,3}=J_{3,4}=9.7$ Hz, H-3), 5.49 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.41 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.39 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.19 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.03 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 5.01 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.98 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 4.96 (dd, 1 H, $J_{3,4}=J_{4,5}=9.7$ Hz, H-4), 4.94 (dd, 1 H, $J_{3,4}=J_{4,5}=9.7$ Hz, H-4), 4.84 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.81 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.79 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.77–4.72 (m, 6 H), 4.68–4.62 (m, 2 H), 4.62 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.59 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.58–4.53 (m, 4 H), 4.52–4.45 (m, 3 H), 4.44 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.27 (dd, 1 H, $J_{5,6}$ 4.7 Hz, $J_{6,6}$ 12.4 Hz, H-6), 4.17 (dd, 1 H, $J_{5,6}$ 5.1 Hz, $J_{6,6}$ 12.4 Hz, H-6), 4.15–4.08 (m, 5 H), 4.05–3.84 (m, 12 H), 3.81 (s, 3 H, CH_3O), 3.80–3.74 (m, 2 H), 3.62–3.55 (m, 3 H), 3.47–3.42 (m, 3 H), 2.43, 2.31, 2.11, 2.09, 2.09, 2.08, 2.08, 2.03, 2.00, 2.00, 1.99, 1.99, 1.95, 1.94, 1.88 (s, 45 H, 15 CH_3CO); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.8, 170.7, 170.6, 170.6, 170.4, 170.4, 170.3, 169.7, 169.5, 169.4, 169.3, 169.3, 169.2, 169.0, 168.8 (15 C, 15 *C*OCH$_3$), 166.0, 166.0, 166.0, 165.9, 165.6, 165.6, 165.5, 165.1, 165.1, 165.1, 165.1 (12 C, 12 *C*OPh), 101.6, 101.4, 100.7, 100.4, 100.3, 100.1, 99.8 (7 β-C-1), 93.9, 93.5 (2 α-C-1), 78.1, 75.1, 74.9, 74.4, 74.1, 74.1, 73.6, 72.9, 72.6, 72.2, 72.4, 72.2, 72.2, 72.1, 72.0, 71.9, 71.6, 71.6, 70.8, 70.5, 69.8, 69.7, 69.5, 69.2, 69.1, 69.0, 68.6, 68.3, 67.9, 67.6, 62.9, 62.8, 62.4, 62.0, 61.8, 61.5, 61.3, 55.6 (C-2, 3, 4, 5, 6), 21.3, 21.2, 20.8, 20.7, 20.6, 20.4, 20.3. Anal. Calcd for $C_{175}H_{176}O_{74}$: C, 60.69; H, 5.09. Found: C, 61.01; H, 5.16.

3.7. 4-Methoxyphenyl 2,3,4,6-tetra-*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-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-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 **7** (700 mg, 0.447 mmol) and **6** (1.20 g, 0.347 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (30 mL). TMSOTf (40 μL, 0.352 mmol) was added dropwise at −20 °C with nitrogen 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 **8** (915 mg, 54.2%) as a syrup: $[\alpha]_D$ +32.4° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.17–7.17 (m, 100 H, 20 Bz–*H*), 6.96–6.84 (dd, 4 H, $-C_6H_4-$), 5.92 (dd, 1 H, $J_{3,4}=J_{4,5}=9.7$ Hz, H-4), 5.91 (dd, 1 H, $J_{3,4}=J_{4,5}=9.7$ Hz, H-4), 5.89 (dd, 1 H, $J_{3,4}=J_{4,5}=9.7$ Hz, H-4), 5.88 (dd, 1 H, $J_{3,4}=J_{4,5}=9.7$ Hz, H-4), 5.83 (dd, 1 H, $J_{3,4}=J_{4,5}=9.7$ Hz, H-4), 5.75 (dd, 1 H, $J_{2,3}=J_{3,4}=9.7$ Hz, H-3), 5.65–5.58 (m, 4 H), 5.50 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.42–5.36 (m, 4 H), 5.22 (dd, 1 H, $J_{2,3}=J_{3,4}=9.7$ Hz, H-3), 5.08 (dd, 1 H, $J_{2,3}=J_{3,4}=9.7$ Hz, H-3), 5.03 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.98 (dd, 1 H, $J_{3,4}=J_{4,5}=9.7$ Hz, H-4), 4.94 (d, 2 H, $J_{1,2}$ 7.9 Hz, 2 H-1), 4.85–4.82 (m, 6 H), 4.82 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.82–4.78 (m, 3 H), 4.76 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.75 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.64 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.62 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.62–4.55 (m, 7 H), 4.53 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.52–4.45 (m, 7 H), 4.31 (dd, $J_{5,6}$ 3.1 Hz, $J_{6,6}$ 10.2 Hz, H-6), 4.25–4.14 (m, 7 H), 4.06–3.88 (m, 15 H), 3.81 (s, 3 H, CH_3O), 3.80–3.72 (m, 5 H), 3.65 (m, 1 H), 3.50–3.41 (m, 4 H), 2.44, 2.32, 2.29, 2.12, 2.09, 2.06, 2.04, 2.01, 1.97, 1.96, 1.95, 1.91, 1.90, 1.85, 1.81, 1.77, 1.74 (s, 51 H, 17 CH_3CO); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.8, 170.6, 170.6, 170.6, 170.6, 170.4, 169.9, 169.5, 169.5, 169.4, 169.4, 169.3, 169.2, 169.2, 169.0, 169.0, 168.8 (17 C, 17 $COCH_3$), 166.0, 166.0, 165.9, 165.9, 165.9, 165.8, 165.6, 165.6, 165.6, 165.6, 165.5, 165.1, 165.1, 165.1, 165.1, 165.0, 165.0, 165.0, 164.9, 164.9 (20 C, 20 *C*OPh), 101.6, 101.5, 101.2, 100.9, 100.7, 100.4, 100.2, 100.0, 99.9, (9 C-1 for β bonds, $J_{C-H}=163.0–164.8$ Hz), 94.2, 93.6, 93.5 (3 C-1 for α bond, $J_{C-H}=172.0–174.6$ Hz), 78.3, 74.4, 74.4, 74.2, 73.6, 73.3, 73.1, 72.9, 72.7, 72.6, 72.6, 72.6, 72.5, 72.4, 72.3, 72.2, 72.2, 72.2, 72.1, 72.0, 71.9, 71.9, 71.7, 71.7, 71.6, 71.1, 70.6, 70.5, 69.8, 69.5, 69.5, 69.5, 69.1, 69.1, 69.0, 68.7, 68.6, 68.5, 68.4, 68.3, 68.2, 67.9, 67.8, 67.6, 67.5, 67.4, 63.2, 63.1, 63.1, 62.9, 62.9, 62.8, 62.7, 62.5, 62.4, 61.6, 61.5, 61.5, 60.3, 55.6 (C-2, 3, 4, 5, 6), 21.3, 20.9, 20.9, 20.8, 20.8, 20.7, 20.7, 20.6, 20.6, 20.6, 20.4, 20.4, 20.3, 14.1. Anal. Calcd for $C_{253}H_{242}O_{99}$: C, 62.44; H, 4.98. Found: C, 62.69; H, 5.08.

3.8. 4-Methoxyphenyl 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)]-α-D-glucopyranosyl-(1→3)-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 **8** (800 mg, 0.164 mmol) was dissolved in a satd solution of NH_3 in MeOH (10 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 **9** (293 mg, 86.3%) as a foamy solid: $[\alpha]_D$ +22.1° (*c* 1.0, H_2O); ^1H NMR (D_2O, 400 MHz): δ 7.01–6.84 (dd, 4 H, MPC_6H_4-), 5.19 (d, 3 H, *J* 3.2 Hz, 3 H-1), 4.68 (d, 1 H, *J* 8.0 Hz, H-1), 4.64 (d, 1 H, *J* 8.0 Hz, H-1), 4.61 (d, 1 H, *J* 8.0 Hz, H-1), 4.58 (d, 1 H, *J* 8.0 Hz, H-1), 4.37 (d, 1 H, *J* 8.0 Hz, H-1), 4.35 (d, 1 H, *J* 8.0 Hz, H-1), 4.33 (d, 1 H, *J* 8.0 Hz, H-1), 4.11–4.00 (m, 8 H), 3.83–3.71 (m, 17 H), 3.68 (s, 3 H, CH_3O), 3.67–3.49 (m, 23 H), 3.38–3.12 (m, 26 H); ^{13}C NMR (D_2O, 100 MHz): δ 105.5, 105.5, 105.5, 105.5, 105.5, 105.5, 105.5, 105.5, 105.2 (9 C-1 for β bonds, $J_{C-H}=163.0, 164.3$ Hz), 103.5, 101.9, 101.8 (3 C-1 for α bond, $J_{C-H}=174.1$ Hz) 78.6, 78.5, 78.5, 78.5, 78.3, 78.3, 78.3, 78.3, 77.8, 76.2, 75.8, 75.8, 75.8, 75.3, 74.9, 74.9, 73.9, 73.9, 73.5, 73.5, 72.5, 72.5, 72.3, 72.3, 72.3, 72.3, 71.1, 71.0, 70.6, 70.5, 70.5, 70.4, 70.4, 63.4, 63.4, 63.4, 63.2, 63.2, 58.5, 58.5 (C-2, 3, 4, 5, 6). Anal. Calcd for $C_{79}H_{128}O_{62}$: C, 45.84; H, 6.19. Found: C, 46.03; H, 6.28. ESIMS for $C_{79}H_{128}O_{62}$ (2068): 2091.5 $[M+Na]^+$.

3.9. 4-Methoxyphenyl 3-*O*-allyl-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-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-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-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 (10)

Compound **1** (1.34 g, 1.12 mmol) and **6** (3.0 g, 0.867 mmol) were dried together under high vacuum for 2 h,

then dissolved in anhyd CH_2Cl_2 (50 mL). TMSOTf (100 μL, 0.870 mmol) was added dropwise at −20 °C with nitrogen protection. The reaction mixture was stirred for 3 h, during which time the temperature was gradually raised to ambient temperature. Then he 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 the product **10** (1.92 g, 48.1%) as a syrup: $[\alpha]_D$ +28.6° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.12–7.24 (m, 90 H, 16 Bz–*H*), 6.94–6.85 (dd, 4 H, MPC_6H_4–), 5.92 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.90 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.87 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.82 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.79–5.68 (m, 1 H, CH_2=C*H*–CH_2O), 5.64 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.63 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.60 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.59 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.49 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.43 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.40 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.39 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.24–5.14 (m, 3 H), 5.12–5.06 (m, 1 H, CH_2=C*H*–CH_2O), 5.04 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.00 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.95 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.98 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 4.96 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 4.95 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 4.83 (d, 2 H, $J_{1,2}$ 3.6 Hz, 2 H-1), 4.81 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.79 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.76 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.76–4.72 (m, 6 H), 4.64 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.60 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.59–4.55 (m, 6 H), 4.52 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.49–4.45 (m, 6 H), 4.44 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.21 (dd, 1 H, $J_{5,6}$ 4.7 Hz, $J_{6,6}$ 12.4 Hz, H-6), 4.19 (dd, 1 H, $J_{5,6}$ 5.1 Hz, $J_{6,6}$ 12.4 Hz, H-6), 4.15–4.10 (m, 6 H), 4.02–3.88 (m, 13 H), 3.81 (s, 3 H, CH_3O), 3.80–3.74 (m, 7 H), 3.65–3.40 (m, 7 H), 2.43, 2.34, 2.31, 2.11, 2.09, 2.08, 2.08, 2.06, 2.06, 2.05, 2.00, 1.97, 1.96, 1.95, 1.94, 1.94, 1.90, 1.89, 1.81, 1.78 (s, 60 H, 20 CH_3CO); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.1, 171.0, 170.8, 170.8, 170.8, 170.6, 170.5, 170.4, 170.4, 170.0, 169.7, 169.5, 169.5, 169.4, 169.7, 169.2, 169.2, 168.9, 168.9, 168.9 (20 C, 20 $COCH_3$), 166.2, 166.2, 166.1, 166.1, 166.0, 165.8, 165.6, 165.6, 165.6, 165.5, 165.2, 165.2, 165.1, 165.1, 165.0, 165.0 (16 C, 16 *C*OPh), 101.8, 101.6, 101.5, 100.9, 100.5, 100.4, 100.3, 100.1, 99.8 (9 β-C-1), 94.5, 94.1, 93.6 (3 α-C-1), 78.5, 75.8, 75.4, 75.3, 75.0, 74.9, 74.4, 74.1, 73.6, 72.9, 72.6, 72.6, 72.6, 72.5, 72.4, 72.4, 72.4, 72.2, 72.2, 72.1, 72.0, 71.9, 71.8, 71.8, 71.6, 71.6, 70.8, 70.5, 69.8, 69.7, 69.5, 69.3, 69.3, 69.2, 69.1, 69.0, 68.4, 68.4, 68.1, 68.1, 68.1, 67.9, 67.7, 62.9, 62.9, 62.5, 62.1, 61.5, 61.5, 60.6, 55.8 (C-2, 3, 4, 5, 6), 29.8, 21.5, 21.0, 20.8, 20.6, 20.6, 20.4, 20.2. Anal. Calcd for $C_{234}H_{236}O_{98}$: C, 60.88; H, 5.12. Found: C, 61.05; H, 5.22.

3.10. 4-Methoxyphenyl 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-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-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-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 (11)

To a solution of **10** (1.8 g, 0.390 mmol) in MeOH (30 mL) was added $PdCl_2$ (100 mg). After stirring for 3 h at rt, TLC (1:2 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was filtered, the solution was concentrated to dryness, and the resultant residue was purified by flash chromatography (1:2 petroleum ether–EtOAc) to give **11** (1.43 g, 80.3%) as a foamy solid: $[\alpha]_D$ +20.2° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.09–7.26 (m, 90 H, 16 Bz–*H*), 6.95–6.84 (dd, 4 H, MPC_6H_4–), 5.90 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.89 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.87 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.82 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.65 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.62 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.61 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.60 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.50 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.45 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.42 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.40 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.24–5.14 (m, 3 H), 5.02 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 4.96 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.92 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.85 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.82 (d, 2 H, $J_{1,2}$ 3.6 Hz, 2 H-1), 4.78 (d, 1 H, $J_{1,2}$7.9 Hz, H-1), 4.76 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.76–4.72 (m, 6 H), 4.66 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.61 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.59–4.56 (m, 6 H), 4.55 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.52–4.48 (m, 10 H), 4.46 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.23 (dd, 1 H, $J_{5,6}$ 4.7 Hz, $J_{6,6}$ 12.4 Hz, H-6), 4.21 (dd, 1 H, $J_{5,6}$ 5.1 Hz, $J_{6,6}$ 12.4 Hz, H-6), 4.15–4.10 (m, 6 H), 4.02–3.88 (m, 10 H), 3.81 (s, 3 H, CH_3O), 3.80–3.74 (m, 6 H), 3.65–3.40 (m, 7 H), 2.43, 2.34, 2.31, 2.11, 2.09, 2.08, 2.08, 2.06, 2.06, 2.05, 2.00, 1.97, 1.96, 1.95, 1.94, 1.94, 1.90, 1.89, 1.81, 1.78 (s, 60 H, 20 CH_3CO); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.1, 171.0, 170.8, 170.8, 170.8, 170.6, 170.5, 170.4, 170.4, 170.0, 169.7, 169.5, 169.5, 169.4, 169.7, 169.2, 169.2, 168.9, 168.9, 168.9 (20 C, 20 $COCH_3$), 166.2, 166.2, 166.1, 166.1, 166.0, 165.8, 165.6, 165.6, 165.6, 165.5, 165.2,

165.2, 165.1, 165.1, 165.0, 165.0 (16 C, 16 *C*OPh), 101.8, 101.6, 101.5, 100.9, 100.5, 100.4, 100.3, 100.1, 99.8 (9 β-C-1), 94.5, 94.1, 93.6 (3 α-C-1), 78.5, 75.8, 75.4, 75.3, 75.0, 74.9, 74.4, 74.1, 73.6, 72.9, 72.6, 72.6, 72.6, 72.5, 72.4, 72.4, 72.4, 72.2, 72.2, 72.1, 72.0, 71.9, 71.8, 71.8, 71.6, 71.6, 70.8, 70.5, 69.8, 69.7, 69.5, 69.3, 69.3, 69.2, 69.1, 69.0, 68.4, 68.4, 68.1, 68.1, 68.1, 67.9, 67.7, 62.9, 62.9, 62.5, 62.1, 61.5, 61.5, 60.6, 55.8 (C-2, 3, 4, 5, 6), 29.8, 21.5, 21.0, 20.8, 20.6, 20.6, 20.4, 20.2. Anal. Calcd for $C_{231}H_{232}O_{98}$: C, 66.54; H, 5.16. Found: C, 66.82; H, 5.23.

3.11. 4-Methoxyphenyl 2,3,4,6-tetra-*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-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-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-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 (12)

Compound **7** (500 mg, 0.319 mmol) and **11** (1.2 g, 0.262 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (30 mL). TMSOTf (30 μL, 0.265 mmol) was added dropwise at −20 °C with nitrogen 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 1:2.5 petroleum ether–EtOAc as the eluent gave the product **12** (668 mg, 42.7%) as a syrup: $[\alpha]_D$ +30.6° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.17–7.17 (m, 120 H, 24 Bz–*H*), 6.96–6.83 (dd, 4 H, MPC_6H_4–), 5.93–5.84 (m, 5 H), 5.84 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.82 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.74 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.66–5.57 (m, 7 H), 5.50 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.8 Hz, H-2), 5.42–5.32 (m, 6 H), 5.20 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.08 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.00 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.98 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 4.95 (d, 3 H, $J_{1,2}$ 7.9 Hz, 3 H-1), 4.89–4.84 (m, 3 H), 4.83 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.82 (d, 2 H, $J_{1,2}$ 3.6 Hz, H-1), 4.82–4.76 (m, 15 H), 4.76 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.75 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.64 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.62 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.62–4.56 (m, 15 H), 4.55 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.54–4.42 (m, 10 H), 4.30 (dd, $J_{5,6}$ 3.1 Hz, $J_{6,6}$ 10.2 Hz, H-6), 4.25–4.13 (m, 15 H), 3.81 (s, 3 H, CH_3O), 3.80–3.72 (m, 6 H), 3.62 (m, 1 H), 3.50–3.41 (m, 6 H), 2.43, 2.33, 2.32, 2.27, 2.11, 2.09, 2.05, 2.05, 2.04, 2.00, 1.95, 1.95, 1.90, 1.90, 1.90, 1.89, 1.84, 1.81, 1.80, 1.76, 1.74, 1.73 (s, 66 H, 22 CH_3CO); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.9, 170.7, 170.7, 170.7, 170.6, 170.6, 170.5, 170.4, 170.0, 169.5, 169.5, 169.4, 169.4, 169.3, 169.3, 169.2, 169.2, 169.1, 169.1, 169.0, 169.0, 168.8 (22 C, 22 *C*OCH$_3$), 166.1, 166.0, 166.0, 166.0, 166.0, 166.0, 166.0, 165.9, 165.9, 165.9, 165.8, 165.8, 165.6, 165.6, 165.6, 165.6, 165.5, 165.1, 165.1, 165.1, 165.1, 165.0, 165.0, 165.0, 164.9, 164.9 (24 C, 24 *C*OPh), 101.6, 101.5, 101.4, 101.2, 100.9, 100.7, 100.6, 100.4, 100.2, 100.0, 99.8 (11 C-1 for β bonds, $J_{C-H} = 163.0–164.8$ Hz), 94.2, 94.2, 93.7, 93.5 (4 C-1 for α bond, $J_{C-H} = 172.0–174.6$ Hz), 78.6, 74.4, 74.4, 74.2, 74.2, 73.6, 73.2, 73.2, 72.9, 72.7, 72.6, 72.6, 72.6, 72.5, 72.4, 72.3, 72.2, 72.2, 72.2, 72.1, 72.1, 72.0, 71.9, 71.9, 71.7, 71.7, 71.6, 71.1, 71.0, 71.0, 71.0, 70.6, 70.5, 69.8, 69.5, 69.5, 69.5, 69.4, 69.4, 69.1, 69.1, 69.0, 68.7, 68.6, 68.5, 68.4, 68.3, 68.2, 67.9, 67.8, 67.6, 67.5, 67.4, 63.2, 63.1, 63.1, 63.0, 62.9, 62.9, 62.8, 62.8, 62.7, 62.5, 62.4, 61.8, 61.6, 61.5, 61.5, 60.3, 55.6 (C-2, 3, 4, 5, 6), 29.6, 21.3, 20.9, 20.9, 20.8, 20.8, 20.7, 20.7, 20.6, 20.6, 20.6, 20.4, 20.4, 20.4, 20.3, 14.1. Anal. Calcd for $C_{309}H_{298}O_{123}$: C, 62.07; H, 4.99. Found: C, 62.31; H, 5.16.

3.12. 4-Methoxyphenyl 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)]-α-D-glucopyranosyl-(1→3)-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)]-α-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→6)]-β-D-glucopyranoside (13)

Compound **12** (500 mg, 0.084 mmol) was dissolved in a satd solution of NH_3 in MeOH (10 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** (184 mg, 85.8%) as a foamy solid: $[\alpha]_D$ +26.2° (*c* 1.0, H_2O): δ 7.11–6.94 (dd, 4 H, MPC_6H_4–), 5.29 (d, 4 H, *J* 3.2 Hz, 4 H-1), 5.04 (d, 1 H, *J* 7.8 Hz, H-1), 4.69 (d, 5 H, *J* 7.8 Hz, 5 H-1), 4.45 (d, 4 H, *J* 7.8 Hz, 4 H-1), 4.21–4.18 (m, 10 H), 3.94–3.80 (m, 22 H), 3.78 (s, 3 H, CH_3O), 3.77–3.52 (m, 26 H), 3.45–3.22 (m, 33 H); ^{13}C NMR (D_2O, 100 MHz): δ 105.4, 105.4, 105.4, 105.4, 105.4, 105.4, 105.4, 105.4, 105.4, 105.4, 105.2, (11 C-1 for β bonds, $J_{C-H} = 163.0$, 164.3 Hz), 103.4, 101.8, 101.7, 101.7 (4 C-1 for α bond, $J_{C-H} = 174.1$ Hz), 85.6, 85.3, 84.5, 78.6, 78.6, 78.5, 78.5, 78.5, 78.2, 78.2, 78.2, 78.2, 77.7, 76.1, 75.8, 75.8, 75.8, 75.8, 75.3, 74.8, 74.8, 74.8, 74.8, 73.8, 73.8, 73.8, 73.4,

73.4, 72.5, 72.5, 72.5, 72.2, 72.2, 72.2, 72.2, 72.2, 71.0, 71.0, 70.6, 70.5, 70.5, 70.4, 70.4, 70.3, 70.3, 63.4, 63.4, 63.4, 63.4, 63.2, 63.2, 58.5 (C-2, 3, 4, 5, 6), 32.8, 32.8, 32.5. Anal. Calcd for $C_{97}H_{158}O_{77}$: C, 45.58; H, 6.19. Found: C, 45.76; H, 6.28. ESIMS for $C_{97}H_{158}O_{77}$ (2554): 2577.0 $[M+Na]^+$.

3.13. 4-Methoxyphenyl 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 (14)

Compound **7** (450 mg, 0.287 mmol) and **2** (300 mg, 0.243 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (10 mL). TMSOTf (15 μL, 0.132 mmol) was added dropwise at −20 °C with nitrogen 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 **14** (471 mg, 73.4%) as a foamy solid: $[\alpha]_D$ +18.9° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.12–7.26 (m, 60 H, 12 Bz–*H*), 6.98–6.85 (dd, 4 H, MPC$_6$*H*$_4$–), 5.91 (dd, 1 H, $J_{3,4}=J_{4,5}=9.7$ Hz, H-4), 5.89 (dd, 1 H, $J_{3,4}=J_{4,5}=9.7$ Hz, H-4), 5.82 (dd, 1 H, $J_{3,4}=J_{4,5}=9.7$ Hz, H-4), 5.67 (dd, 1 H, $J_{2,3}=J_{3,4}=$ 9.7 Hz, H-3), 5.62 (dd, 1 H, $J_{2,3}=J_{3,4}=9.7$ Hz, H-3), 5.59 (dd, 1 H, $J_{2,3}=J_{3,4}=9.7$ Hz, H-3), 5.49 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.41 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.39 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.03 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.98 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 4.96 (dd, 1 H, $J_{3,4}=J_{4,5}=9.7$ Hz, H-4), 4.95 (dd, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 9.7 Hz, H-2), 4.93 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.85 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.66 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.58–4.53 (m, 5 H), 4.52–4.45 (m, 5 H), 4.41 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.38 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.32 (dd, 1 H, $J_{5,6}$ 4.7 Hz, $J_{6,6}$ 12.4 Hz, H-6), 4.18–4.03 (m, 6 H), 4.05–3.84 (m, 5 H), 3.81(s, 3 H, C*H*$_3$O), 3.60–3.56 (m, 1 H), 3.42–3.40 (m, 1 H), 2.39, 2.10, 2.00, 1.99, 1.85, 1.82, 1.62 (s, 21 H, 7 C*H*$_3$CO); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.4, 170.1, 169.6, 169.4, 169.4, 169.3, 168.7 (7 C, 7 *C*OCH$_3$), 166.0, 166.0, 165.9, 165.9, 165.8, 165.6, 165.6, 165.5, 165.1, 165.1, 164.9, 164.9 (12 C, 12 *C*OPh), 101.4, 101.1, 100.6, 100.4, 99.8 (5 β-C-1), 93.0 (α-C-1), 78.4, 75.5, 74.5, 73.1, 72.9, 72.9, 72.7, 72.6, 72.4, 72.2, 72.1, 72.1, 72.0, 71.9, 71.6, 71.1, 71.0, 70.4, 69.5, 69.5, 69.5, 69.3, 68.8, 68.6, 68.2, 67.9, 67.8, 62.9, 62.6, 62.4, 61.4, 55.6 (C-2, 3, 4, 5, 6), 29.6, 21.2, 20.7, 20.6, 20.5, 20.5, 20.4. Anal. Calcd for $C_{141}H_{130}O_{51}$: C, 64.14; H, 4.93. Found: C, 64.34; H, 5.02.

3.14. 2,3,4,6-Tetra-*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-α-D-glucopyranosyl trichloroacetimidate (15)

Compound **14** (400 mg, 0.152 mmol) was dissolved 4:1 CH_3CN–H_2O (1 mL), and then $(NH_4)_2Ce(NO_3)_6$ (50 mg) was added. After stirring the mixture for 3 h at rt, TLC (1:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was filtered, the solution was concentrated to dryness, and the resultant residue was purified by flash chromatography (1.5:1 petroleum ether–EtOAc) to give the hexasaccharide hemiacetal (322 mg, 83.6%) as a syrup: $[\alpha]_D$ +17.6° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 8.06–7.25 (m, 60 H, 12 Bz–*H*), 5.93 (dd, 1 H, $J_{3,4}=J_{4,5}=9.7$ Hz, H-4), 5.91 (dd, 1 H, $J_{3,4}=J_{4,5}=9.7$ Hz, H-4), 5.85 (dd, 1 H, $J_{3,4}=J_{4,5}=9.7$ Hz, H-4), 5.77 (dd, 1 H, $J_{2,3}=J_{3,4}=$ 9.7 Hz, H-3), 5.73 (dd, 1 H, $J_{2,3}=J_{3,4}=9.7$ Hz, H-3), 5.51 (dd, 1 H, $J_{2,3}=J_{3,4}=9.7$ Hz, H-3), 5.47 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.36 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.34 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.01 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.97 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 4.95 (dd, 1 H, $J_{3,4}=J_{4,5}=9.7$ Hz, H-4), 4.94 (dd, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 9.7 Hz, H-2), 4.92 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.86 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.66 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.58–4.53 (m, 5 H), 4.52–4.45 (m, 4 H), 4.42 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.37 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.32 (dd, 1 H, $J_{5,6}$ 4.7 Hz, $J_{6,6}$ 12.4 Hz, H-6), 4.22–4.10 (m, 7 H), 4.08–4.00 (m, 1 H), 3.94–3.84 (m, 6 H), 3.71–3.56 (m, 2 H), 3.41–3.36 (m, 1 H), 2.39, 2.04, 2.02, 1.99, 1.87, 1.78, 1.62 (s, 21 H, 7 C*H*$_3$CO); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.5, 170.0, 169.8, 169.5, 169.5, 169.3, 169.1 (7 C, 7 *C*OCH$_3$), 166.2, 165.9, 165.9, 165.9, 165.7, 165.7, 165.5, 165.2, 165.1, 165.4, 164.9, 164.8 (12 C, 12 *C*OPh), 102.3, 101.4, 101.0, 100.3, 99.8, 93.0 (C-1), 75.2, 74.3, 73.2, 72.8, 72.8, 72.6, 72.5, 72.5, 72.2, 72.1, 72.1, 71.9, 71.9, 71.7, 71.5, 71.0, 70.5, 70.3, 69.5, 69.2, 68.8, 68.7, 68.2, 68.0, 62.7, 62.6, 62.5, 62.4, 61.5 (C-2, 3, 4, 5, 6), 29.6, 22.6, 21.4, 20.6, 20.6, 20.5, 20.4, 20.3. Anal. Calcd for $C_{134}H_{124}O_{50}$: C, 63.51; H, 4.90. Found: C, 63.80; H, 5.00.

The hemiacetal was dissolved in CH_2Cl_2 (10 mL), then CCl_3CN (0.05 mL, 1.0 mmol) and K_2CO_3 (500 mg, 3.5 mmol) was added. The reaction mixture was stirred for 10 h, at the end of which time TLC (1.5:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was filtered, and the filtrate was concentrated. The residue was purified by flash chromatography (1.5:1 petroleum ether–EtOAc) to give **15** (295 mg, 86.7%) as a foamy solid: $[\alpha]_D$ +26.9° (*c* 1.0, $CHCl_3$); ^1H

NMR ($CDCl_3$, 400 MHz): δ 8.44 (s, 1 H, C=N*H*), 8.05–7.27 (m, 60 H, 12 Bz–*H*), 6.32 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 5.92 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.90 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.87 (dd, 1 H, $J_{3,4} = J_{4,5} =$ 9.7 Hz, H-4), 5.83 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.78 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.65 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3), 5.50 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.37 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.40 (dd, $J_{1,2}$ 7.9 Hz, $J_{2,3}$ 9.7 Hz, H-2), 5.00 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.97 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 4.94 (dd, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 9.7 Hz, H-2), 4.92 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.86 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.57(d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.58–4.53 (m, 5 H), 4.52–4.45 (m, 4 H), 4.42 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.38 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.30 (dd, 1 H, $J_{5,6}$ 4.7 Hz, $J_{6,6}$ 12.4 Hz, H-6), 4.22–4.10 (m, 6 H), 3.96–3.75 (m, 6 H), 3.68–3.49 (m, 3 H), 3.43–3.37 (m, 2 H), 2.36, 2.04, 2.02, 2.00, 1.86, 1.82, 1.63 (s, 21 H, 7 C*H*$_3$CO); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.4, 170.0, 169.5, 169.5, 169.4, 169.3, 169.0 (7 C, 7 *C*OCH$_3$), 166.0, 165.9, 165.9, 165.7, 165.7, 165.5, 165.3, 165.2, 165.1, 165.0, 164.9, 164.9 (12 C, 12 *C*OPh), 101.3, 101.0, 100.9, 100.6 (4 β-C-1), 93.1, 92.8 (2 α-C-1), 76.1, 74.3, 73.1, 72.9, 72.7, 72.6, 72.3, 72.2, 72.1, 72.0, 71.9, 71.8, 71.6, 71.6, 71.5, 71.2, 70.9, 70.4, 69.7, 69.2, 68.9, 68.1, 68.1, 67.8, 67.6, 63.0, 62.5, 61.3, 60.3 (C-2, 3, 4, 5, 6), 29.6, 22.6, 20.9, 20.9, 20.7, 20.6, 20.5, 20.3. Anal. Calcd for $C_{136}H_{124}Cl_3NO_{50}$: C, 60.98; H, 4.63. Found: C, 61.23; H, 4.81.

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