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Synthesis of two heptasaccharide analogues of the lentinan repeating unit

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Abstract

β-D-Glc*p*-(1→3)-β-D-Glc*p*-(1→3)-β-D-Glc*p*-(1→3)-β-D-Glc*p*-(1→3)-[β-D-Glc*p*-(1→3)-β-D-Glc*p*-(1→6)]-β-D-Glc*p* (**18**) and the allyl glycoside of β-D-Glc*p*-(1→3)-[β-D-Glc*p*-(1→6)]-β-D-Glc*p*-(1→3)-β-D-Glc*p*-(1→3)-β-D-Glc*p*-(1→3)[-β-D-Glc*p*-(1→6)]-α-D-Glc*p* (**29**) were synthesized as the analogues of the lentinan repeating heptaose by building the pentasaccharide backbones first, followed by attaching the side chains. 4,6-*O*-Benzylidenated mono-**13** or disaccharide **8** were used as the acceptor to ensure the β linkage in the synthesis of **18**, while 4,6-*O*-benzylidenated disaccharides **21** and **23** were used as the donor and acceptor, respectively, to ensure the β linkage in the synthesis of **29**.
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Keywords: Oligosaccharide; Glucose; Synthesis

1. Introduction

Obtained from *Lentinus edodes*, an edible mushroom popular in East Asia, lentinan is a glucan that is well known as an antitumor agent[1] and immunostimulant in Japan and China. In a very small dosage, lentinan has marked antitumor effects in syngeneic and autochtonous hosts. Clinically, lentinan has proved effective with chemotherapeutic agents for patients with recurrent gastric and colorectal cancer.[2] Some physicochemical and immunopharmacological investigations have shown that the antitumor activity of these glucans may be related to the triplet–helix structures of the β-(1→3)-linked backbone chains,[3a,3b] and some biological aspects of these β-glucans have been reported.[3c,3d,3e] It was also reported that only higher molecular-weight fractions ($M_W > 16{,}000$) obtained from partial hydrolysis of lentinan with formic acid showed antitumor activity.[4] We hypothesize that the activity of lentinan is dependent upon its basic structural oligosaccharide unit rather than its macroscopic morphology. The major structure of lentinan consists of a glucoheptaose repeating unit[3] as shown in Fig. 1. Its synthesis has been reported by our group.[5]

Bioassay showed that at a dose of 5 mg/kg, the synthetic allyl glucoheptaoside inhibited U_{14} tumor effectively (58.4%).[6] Encouraged by the bioassay results, we are trying to synthesize more structurally diverse 3,6-branched glucans and investigate structure–activity relationships. We present herein the syntheses of a glucoheptaose **18** consisting of a β-(1→3)-linked pentaose backbone with a β-(1→3)-linked biose side chain attached at C-6 of the backbone, and a glucoheptaose **29** consisting of the same pentaose backbone with glucosyl side chains linked at C-6 and C-6‴of the backbone.

2. Results and discussion

Scheme 1 shows the synthesis of the glucoheptaose **18**. 1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose (**1**) was used as the starting material. Allylation of **1** gave **2**, subsequent hydrolysis in 80% HOAc–H_2O removed the two isopropylidene groups resulting in ring expansion at the same time. Benzoylation of the hemiacetal with benzoyl chloride in pyridine, followed by 1-O-selective debenzoylation and trichloroacetimidation,[7] afforded

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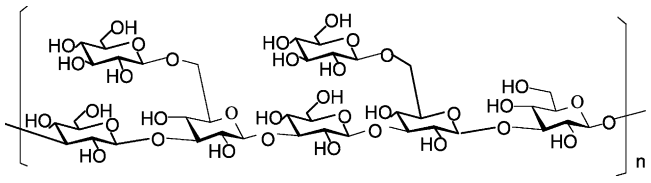


Fig. 1. Structure of lentinan.

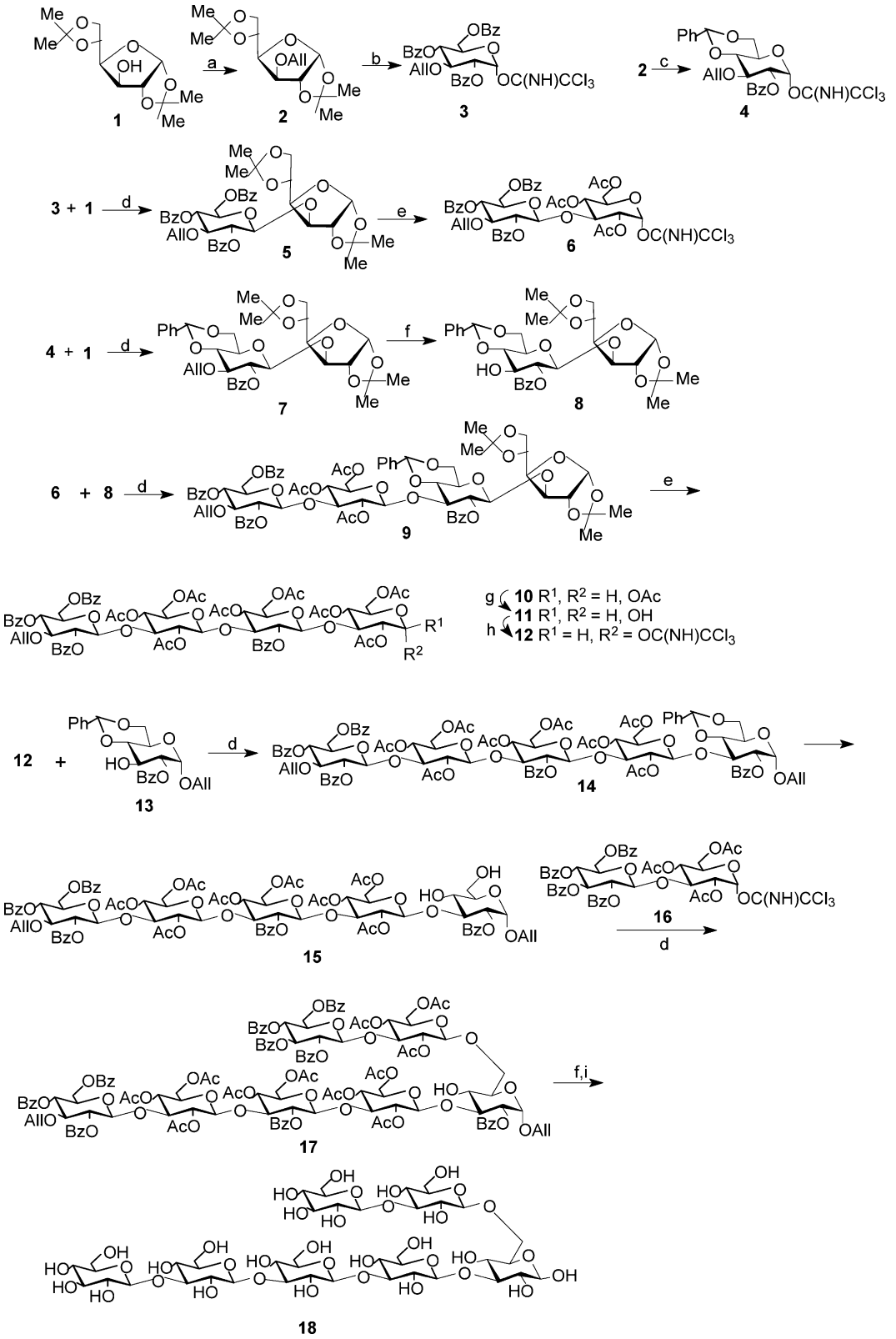
one donor **3**. Meanwhile, **2** was transformed to another donor **4** through hydrolysis, 4,6-O-benzylidenation, benzoylation, 1-O-selective debenzoylation, and trichloroacetimidation. The two donors **3** and **4** were key synthons in the present research, since the required disaccharide building blocks and related tetrasaccharide were readily obtained from them. Thus, condensation of **3** with **1** gave the β-(1→3)-linked disaccahride **5**, and subsequent hydrolysis, acetylation, selective 1-O-deacetylation, and trichloroacetimidation afforded the disaccharide donor **6**. Meanwhile, coupling of **4** with **1** furnished the β-(1→3)-linked disaccharide **7**, whose deallylation gave the disaccharide acceptor **8**. Coupling of **8** with **6** gained the β-(1→3)-linked tetrasaccharide **9** in good yield (85.5%), and no α-linked product was detected. The benzylidene group in **8** played an important role leading the coupling to β linkage. Otherwise, if acetylated or benzoylated disaccharide acceptors were used to couple with acylated disaccharide donors, α-linked products were always obtained.[8] The tetrasaccharide **9** was transformed to the tetrasaccharide donor **12** by hydrolysis, acetylation, selective 1-O-deacetylation, and trichloroacetimidation. An attempt to couple **12** with **1** or **8** was not successful, giving a poor yield. However, condensation of **12** with allyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**13**)[5] gave the required β-linked pentasaccharide in good yield (85.5%). Debenzylidenation of **14** went smoothly to afford the pentasaccharide acceptor **15**, and subsequent selective C-6 glycosylation of **15** with the disaccharide donor **16** yielded protected heptasaccharide **17**. Finally, deallylation and deacylation of **17** furnished the target heptasaccharide **18**. Compound **18** was characterized by ^{1}H and ^{13}C NMR spectrometry showing signals at δ 4.73–4.66 with $J_{1,2}$ 7.8–8.0 Hz for seven β H-1, and δ 102.4, 102.4, 102.3, 102.3, 102.2, 102.2, 102.1 for seven β C-1. The signal at δ 67.7 for C-6 proved the 6-glycosylation of **15**. The lack of signals in the region of δ 76–82 also confirmed the selective 6-glycosylation; otherwise, if C-4 were glycosylated, a signal at δ ~80 ppm would have appeared.

Scheme 2 shows the synthesis of another glucoheptaose **29**. First, a β-(1→3)-linked disaccharide **19** was obtained by coupling of perbenzoylated glucosyl trichloroacetimidate with the acceptor **13**. Owing to the use of benzylidenated acceptor, no α-linked product was detected. Deallylation of **19** with $PdCl_2$ in 90% acetic acid containing sodium acetate smoothly furnished the hemiacetal **20**, and subsequent trichloroacetimidation afforded the disaccharide **21**. Meanwhile, the trisaccharide acceptor **25** was obtained by coupling 4,6-di-*O*-acetyl-2-*O*-benzoyl-3-*O*-chloroacetyl-α-D-glucopyranosyl trichloroacetimidate (**22**)[5] with the disaccharide acceptor **23**, followed by dechloroacetylation with thiourea. The benzylidene group in **23**, played a key role leading the coupling to β linkage, although it was at the reducing end of the disaccharide acceptor. Here, a remote control of the benzylidene group for the stereoselective glucosylation was shown, as it was known[8] that α linkage was always obtained when the benzylidene group was replaced with acyl groups for the similar couplings. Condensation of **25** with **21** was carried out readily giving β-linked pentasaccharide **26**, and the β-stereoselectivity of this reaction was also controlled by the benzylidene group in the donor **21** and also maybe in the acceptor **25**. Otherwise, if benzylidene groups were replaced by acyl groups, α-linked pentasaccharides would be the products.[8] Removal of the benzylidene groups with toluenesulfonic acid in acetonitrile–ethylene glycol (75%), followed by coupling with perbenzoylated glucosyl trichloroacetimidate gave the 6-, 6‴-branched heptaoside **28** (68%). Finally, deacylation of **28** in ammonia-saturated methanol yielded the target compound. The ^{1}H and ^{13}C NMR spectra showed all of the characteristic signals, such as at δ 4.98 with $J_{1,2}$ 3.6 Hz for α H-1, 4.76, 4.76, 4.75, 4.53, 4.50, and 4.50 with J 8.0 Hz for β H-1, δ 102.6, 102.5, 102.5, 102.3, 102.3, 102.3 for β C-1, and 97.03 for α C-1. The four glycosylated C-3 signals at δ 84.53, 83.94, 83.80, 81.89 also confirmed the selective 6-glycosylation of **27**; otherwise, if C-4 were glycosylated, additional signals at δ ~80 would have appeared.

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 and ^{13}C NMR spectra were recorded with Varian XL-400 spectrometers, for solutions in $CDCl_3$ or in D_2O as indicated. Individual resonances could not be identified with the specific sugar residues. Chemical shifts are expressed in 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, 16 × 240, 18 × 300, 35 × 400 mm) of silica gel (100–200



Scheme 1. (a) AllBr, DMF; (b) i. 80% HOAc, reflux, 3–4 h; ii. BzCl–pyridine; iii. NH_3–toluene–MeOH, rt, ~10 h; iv. K_2CO_3, Cl_3CCN, CH_2Cl_2, rt, overnight; (c) i. 80% HOAc, reflux, 3–4 h; ii. TsOH, DMF, $HC(OEt)_3$; iii. BzCl–pyridine; iv. NH_3–toluene–MeOH, rt, ~10 h; v. K_2CO_3, Cl_3CCN, CH_2Cl_2, rt, overnight; (d) TMSOTf, CH_2Cl_2, −20 °C to rt, 3 h; (e) i. 80% HOAc, reflux, 3–4 h; ii. Ac_2O–pyridine; iii. NH_3–toluene–MeOH, rt, 40 min; iv. K_2CO_3, Cl_3CCN, CH_2Cl_2, rt, overnight; (f) $PdCl_2$, MeOH, rt, 4 h; (g) NH_3–toluene–MeOH, rt, 40 min; (h) CCl_3CN, DBU, CH_2Cl_2 8 h; (i) saturated NH_3–MeOH, rt, 72 h.

mesh) with EtOAc–petroleum ether (bp 60–90 °C) as the eluent. Analytical LC was performed with a Gilson high performance ion chromatography (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. 3-*O*-Allyl-2,4,6-tri-*O*-benzoyl-α-D-glucopyranosyl trichloroacetimidate (3)

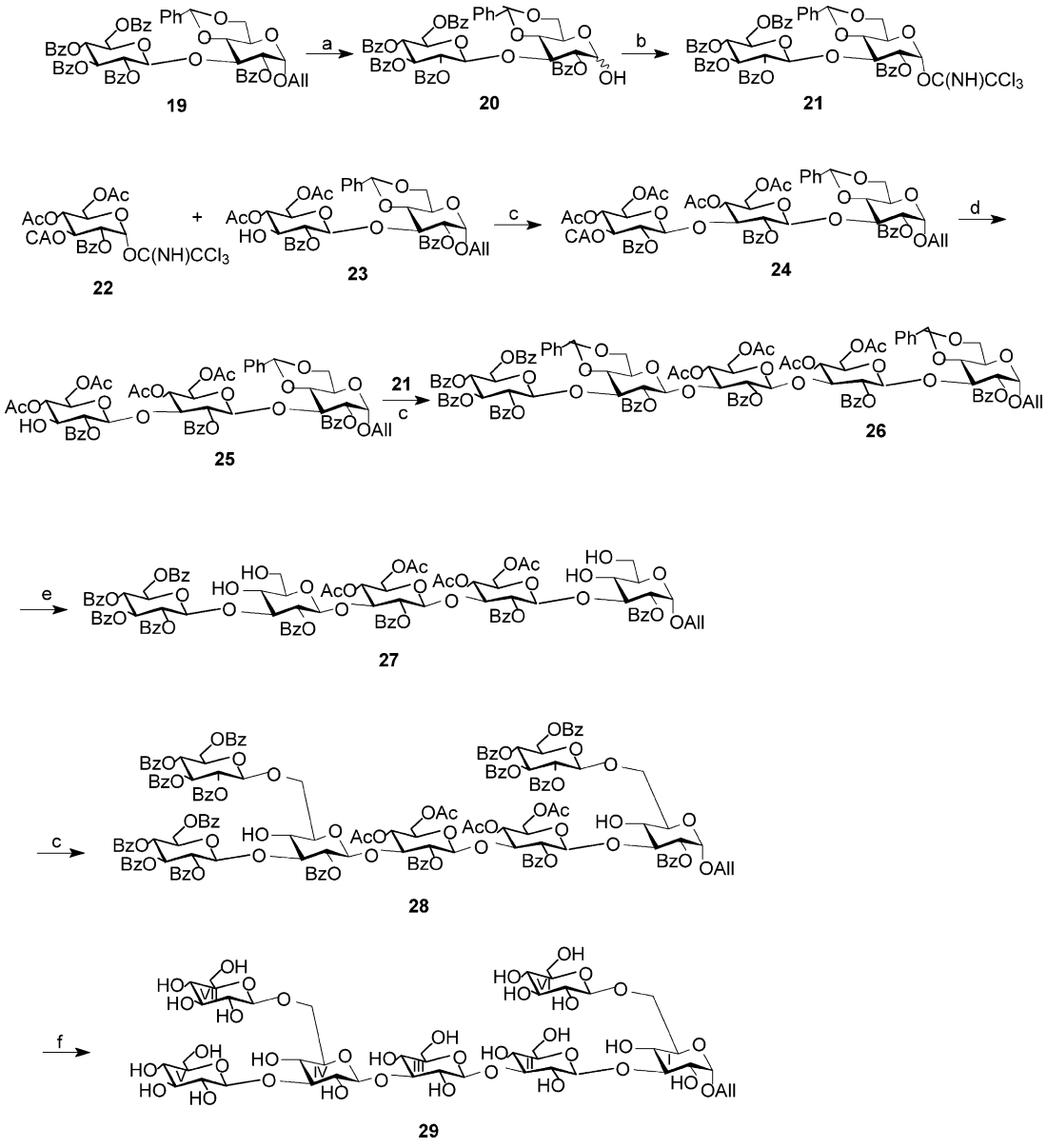
3-*O*-Allyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**2**) (6.5 g, 0.02 mol) was added to 80% HOAc–H_2O (150 mL). The reaction mixture was refluxed for 3–4 h, at the end of which time TLC (1:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was concentrated, the residue was dissolved in Py, and BzCl (20 mL) was added. The reaction mixture was stirred for 10 h, at the end of which time TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was concentrated, and the residue was dissolved in 100:30 satd NH_3–toluene–MeOH (130 mL). The reaction mixture was stirred for 10 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The crude 3-*O*-allyl-2,4,6-tri-*O*-benzoyl-D-glucopyranose (5.3 g, 10 mmol) thus obtained was dissolved in CH_2Cl_2 (50 mL), then CCl_3CN (1.0 mL, 20 mmol) and K_2CO_3 (2.0 g, 15.0 mmol) were added. The reaction mixture was stirred for 10 h, at the end of which time TLC (3:1 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 (3:1 petroleum ether–EtOAc) to give **3** (5.60 g, 82.1%) as a syrup: $[\alpha]_D$ +11° (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 1 H, CNHCCl$_3$), 8.11–7.35 (m, 15 H, Ph*H*), 6.73 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 5.70–5.57 (m, 1 H, CH_2=C*H*–CH_2), 5.64 (dd, 1 H, $J_{4,5} = J_{3,4} = 9.2$ Hz, H-4), 5.47 (dd, 1 H, $J_{2,3}$ 9.4 Hz, H-2), 5.11–4.96 (m, 2 H, CH_2=CH–CH_2), 4.64–4.13 (m, 6 H). Anal. Calcd for $C_{32}H_{28}Cl_3NO_9$: C, 56.72; H, 4.14. Found: C, 56.80; H, 4.10.

3.3. 3-*O*-Allyl-2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranosyl trichloroacetimidate (4)

3-*O*-Allyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**2**) (13.0 g, 40 mmol) was added to 80% HOAc–H_2O (300 mL). The reaction mixture was refluxed for 3–4 h, at the end of which time TLC (1:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was concentrated, the residue was dissolved in DMF (140 mL), and PhCHO (50 mL, 0.12 mol), *p*-TsOH (1.6 g) and $HC(OEt)_3$ (30 mL) were added. The reaction mixture was stirred for 10 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was concentrated, the residue was dissolved in pyridine (100 mL), and BzCl (40 mL) was added. The reaction mixture was stirred for 10 h, at the end of which time TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was concentrated and the residue was dissolved in satd 200:60 NH_3–toluene–MeOH (260 mL). The reaction mixture was stirred for 10 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The crude 3-*O*-allyl-2-*O*-benzoyl-4,6-*O*-benzylidene-D-glucopyranose (8.30 g, 20.2 mmol) was dissolved in CH_2Cl_2 (50 mL), then CCl_3CN (2.0 mL, 40 mmol) and K_2CO_3 (4.0 g, 30.0 mmol) were added. The reaction mixture was stirred for 10 h, at the end of which time TLC (3:1 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 (3:1 petroleum ether–EtOAc) to give **4** (9.6 g, 87.1%) as a syrup: $[\alpha]_D$ +25° (*c* 1. 0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 1 H, CN*H*CCl$_3$), 8.09–7.40 (m, 10 H, Ph*H*), 6.67 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 5.87–5.84 (m, 1 H, CH_2=C*H*–CH_2), 5.66 (s, 1 H, PhC*H*), 5.38 (dd, 1 H, $J_{2,3}$ 9.6 Hz, H-2), 5.28–5.20 (m, 1 H, CH_2=CH–CH_2), 5.13–5.09 (m, 1 H, CH_2=CH–CH_2O), 4.47–3.81(m, 7 H, H-3, H-4, H-5, H-6, H-6′, CH_2=CH–CH_2). Anal. Calcd for $C_{25}H_{24}Cl_3NO_7$: C, 53.86; H, 4.31. Found: C, 53.98; H, 4.19.

3.4. 3-*O*-Allyl-2,4,6-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (5)

3-*O*-Allyl-2,4,6-tri-*O*-benzoyl-β-D-glucopyranosyl trichloroacetimidate (**3**) (7.0 g, 10.3 mmol) and 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**1**) (2.95 g, 11.3 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (50.0 mL). Me_3SiOTf (20.0 μL, 0.174 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 of the product on a silica gel column with 3:1 petroleum ether–EtOAc as the eluent gave **5** (6.77 g, 85.3%) as a syrup: $[\alpha]_D$ +15° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.09–7.38 (m, 15 H, 3 Ph*H*), 5.60–5.52 (m, 1 H, CH_2=C*H*CH$_2$), 5.52 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.3$ Hz, H-4′), 5.45 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 5.30 (dd, 1 H, $J_{1,2}$ 7.8 Hz, $J_{2,3}$ 9.2 Hz, H-2′), 5.10–4.91 (m, 2 H, CH_2=CHCH$_2$), 4.80 (d, 1 H, H-1′), 4.60 (dd, 1 H, $J_{5,6}$ 5.1, $J_{6,6'}$ 12.0 Hz, H-6′) 4.45–3.93 (m, 11 H), 1.40, 1.35, 1.23, 1.11 (4 s, 12 H, CH_3).



Scheme 2. $PdCl_2$, HOAc–NaOAc, rt, overnight; (b) CCl_3CN, DBU, CH_2Cl_2, 2 h; (c) TMSOTf, CH_2Cl_2, −10 °C, 2–4 h; (d) thiurea, CH_2Cl_2–MeOH, reflux, overnight; (e) *p*-TsOH·H_2O, ethylene glycol, CH_3CN, rt, overnight; (f) saturated NH_3–MeOH, rt, 72 h.

Anal. Calcd for $C_{42}H_{46}O_{14}$: C, 65.12; H, 5.94. Found: C, 65.30; H, 5.90.

3.5. 3-*O*-Allyl-2,4,6-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl trichloroacetimidate (6)

Compound **5** (4.35 g, 9.5 mmol) was added to 80% HOAc–H_2O (100 mL). The reaction mixture was refluxed for 3–4 h, then concentrated to dryness. The residue was dissolved in pyridine (50 mL), and then Ac_2O (30 mL) was added. After stirring the mixture at rt for 12 h, TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was concentrated, and the residue was dissolved in 80:30 satd NH_3–toluene–MeOH (110 mL). The reaction mixture was stirred for 40 min, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was concentrated to dryness. The residue was dissolved in CH_2Cl_2 (60 mL), and CCl_3CN (1.0 mL, 10 mmol) and K_2CO_3 (2.0 g, 15.0 mmol) were added. The reaction mixture was stirred for 10 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. Concentration of the reaction mixture, followed by purification on a silica gel column with 2:1

petroleum ether–EtOAc as the eluent, furnished the disaccharide donor **6** (3.10 g, 42% for four steps) as a syrup: $[\alpha]_D$ +55° (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 1 H, CN*H*CCl_3), 8.04–7.40 (m, 15 H, Ph*H*), 6.42 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 5.60–5.51 (m, 1 H, CH_2=C*H*–CH_2), 5.46 (dd, 1 H, $J_{4,5} = J_{3,4} = 9.6$ Hz, H-4′), 5.20 (dd, 1 H, $J_{2,3}$ 9.6 Hz, H-2′), 5.16 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.6$ Hz, H-4), 5.03–4.89 (m, 2 H, CH_2=CH–CH_2), 4.90 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1′), 4.88 (dd, 1 H, $J_{2,3}$ 9.6 Hz, H-2), 4.64–4.04 (m, 10 H), 2.05, 1.98, 1.85 (3 s, 9 H, C*H*$_3$CO). Anal. Calcd for $C_{44}H_{44}Cl_3NO_{17}$: C, 54.72; H, 4.56. Found: C, 54.88; H, 4.59.

3.6. 3-*O*-Allyl-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (7)

Donor **4** (5.74 g, 10.3 mmol) and acceptor **1** (2.99 g, 11.4 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (50.0 mL). Me_3SiOTf (20.0 μL, 0.174 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 3:1 petroleum ether–EtOAc as the eluent gave the product **7** (6.02 g, 92.1%) as a syrup: $[\alpha]_D$ +24.0° (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.10–7.37 (m, 10 H, 2 Ph*H*), 5.78–5.69 (m, 1 H, CH_2=C*H*CH_2), 5.60 (s, 1 H, PhC*H*), 5.44 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 5.20 (dd, 1 H, $J_{1,2}$ 7.4, $J_{2,3}$ 8.1 Hz, H-2′), 5.20–5.04 (m, 2 H, C*H*$_2$=CHCH_2), 4.76 (d, 1 H, H-1′), 4.39–3.51 (m, 13 H), 1.42 (2 s, 6 H, C*H*$_3$), 1.35 (s, 3 H, C*H*$_3$), 1.11 (s, 3 H, C*H*$_3$). Anal. Calcd for $C_{35}H_{42}O_{12}$: C, 64.22; H, 6.42. Found: C, 64.37; H, 6.57.

3.7. 2-*O*-Benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (8)

To a soln of compound **7** (5.45 g, 8.33 mmol) in MeOH (20 mL) was added $PdCl_2$ (450 mg, 2.55 mmol). After stirring the mixture for 4 h at rt, TLC (1:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was filtered and the soln was concentrated to dryness. The resultant residue was purified by flash chromatography (1:1 petroleum ether–EtOAc) to give **8** (3.68 g, 78.5%): $[\alpha]_D$ +29° (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.09–7.38 (m, 10 H, 2 Ph*H*), 5.59 (s, 1 H, PhC*H*), 5.44 (d, 1 H, $J_{1,2}$ 3.6, H-1), 5.16 (dd, 1 H, $J_{2,3} = J_{1,2} = 7.8$ Hz, H-2′), 4.81 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1′), 4.40–3.55 (m, 12 H), 1.43 (s, 3 H, C*H*$_3$), 1.42 (s, 3 H, C*H*$_3$), 1.34 (s, 3 H, C*H*$_3$), 1.14 (s, 3 H, C*H*$_3$). Anal. Calcd for $C_{32}H_{38}O_{12}$: C, 67.84; H, 6.71. Found: C, 67.66; H, 6.78.

3.8. 3-*O*-Allyl-2,4,6-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (9)

Donor **6** (3.08 g, 3.20 mmol) and acceptor **8** (1.95 g, 3.44 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (30.0 mL). Me_3SiOTf (20.0 μL, 0.174 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 2:1 petroleum ether–EtOAc as the eluent, gave the product **9** (3.85 g, 85.5%) as a syrup: $[\alpha]_D$ +46° (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.04–7.30 (m, 25 H, 5 Ph*H*), 5.56–5.50 (m, 1 H, CH_2=C*H*CH_2), 5.51 (s, 1 H, PhC*H*), 5.45 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.6$ Hz, H-4‴), 5.42 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 5.13 (dd, 1 H, $J_{1,2}$ 7.8, $J_{2,3}$ 8.6 Hz, H-2‴), 5.07 (dd, 1 H, $J_{1,2} = 7.9$, $J_{2,3} = 8.8$ Hz, H-2′), 5.00–4.96 (m, 1 H, CH_2=C*H*CH_2), 4.96 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.6$ Hz, H-4″), 4.90 (dd, 1 H, $J_{1,2}$ 6.1, $J_{2,3}$ 9.0 Hz, H-2″), 4.90–4.87 (m, 1 H, C*H*$_2$=CHCH_2), 4.80 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1‴), 4.70 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1′), 4.58 (d, 1 H, $J_{1,2}$ 6.1 Hz, H-1″), 4.52–3.45 (m, 21 H), 1.89, 1.85, 1.79 (3 s, 9 H, C*H*$_3$CO), 1.44, 1.43, 1.33, 1.15 (4 s, 12 H, 4 C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 169.2, 168.4, (3 C, 3 CH_3CO–), 166.2, 165.0, 164.9, 164.6, (4 C, 4 *C*OPh), 117.5(*C*H_2=CH–CH_2) 112.0, 108.3 (2 C, 2 *C*(CH_3)), 104.9, 100.6, 99.6, 98.2 (4 C, 4 C-1), 101.1 (1 C, Ph*C*H), 82.1, 80.5, 79.6. 79.3, 78.0, 77.9, 73.9, 73.7, 73.1, 72.5, 72.0, 71.8, 71.1, 68.7, 68.5, 66.6, 66.4, 63.3, 62.3 (C-2–6), 26.9, 26.7, 26.0, 25.4, 20.7, 20.6. Anal. Calcd for $C_{74}H_{80}O_{28}$: C, 62.71; H, 5.65. Found: C, 62.97; H, 5.75.

3.9. 3-*O*-Allyl-2,4,6-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-acetyl-β-D-glucopyranosyl-(1→3)-1,2,4,6-tetra-*O*-acetyl-D-glucopyranose (10)

A mixture of **9** (3.55 g, 2.5 mmol) and 80% HOAc–H_2O (80 mL) was refluxed for 3–4 h, then concentrated to dryness. The residue was dissolved in pyridine (50 mL), and Ac_2O (15 mL, 0.16 mol) was added. After stirring the mixture at rt for 12 h, TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The reaction mixture was concentrated to dryness, and the residue was purified by flash column chromatography on a silica gel column (1:1 petroleum ether–EtOAc) to give compound **10** (3.22 g, 89.8% for two steps) as an anomeric mixture that was used for further reaction. Pure α-anomer was isolated as a foamy solid: $[\alpha]_D$ +48° (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.98–7.40 (m, 20 H, 4 Ph*H*), 6.16 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1),

5.58–5.46 (m, 1H, CH_2=C*H*–CH_2), 5.41 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.6$ Hz, H-4‴), 5.12 (dd, 1 H, $J_{1,2}$ 8.0, $J_{2,3}$ 9.6 Hz, H-2‴), 5.07–4.70 (m, 8 H, CH_2=CH–CH_2, H-2, H-2′, H-2″, H-4, H-4′, H-4″), 4.64 (d,1 H, $J_{1,2}$ 8.0 Hz, H-1‴), 4.49 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1′), 4.37 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1″), 4.50–4.38 (m, 18 H,), 2.12, 2.06, 2.06, 2.04, 2.03, 2.01, 1.94, 1.82, 1.81 (9 s, 27 H, 9 C*H*$_3$CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 170.7, 170.7, 169.2, 169.1, 169.0, 168.8, 168.7, 168.4, (9 C, 9 CH_3*C*O–), 166.2, 166.0, 165.0, 164.6 (4 C, 4 *C*OPh), 117.5 (*C*H_2=CH–CH_2), 101.0, 100.8, 100.6, 89.2 (4 C, 4 C-1), 79.6, 78.3, 77.7, 77.5, 75.3, 74.5, 73.6, 73.2, 72.2, 72.1, 72.0, 71.7, 71.6, 71.0, 70.0, 68.7, 68.4, 67.5, 63.3, 62.2, 62.2, 61.9, 60.4, 21.1, 20.9, 20.8, 20.6. Anal. Calcd for $C_{73}H_{80}O_{34}$: C, 58.40; H, 5.33. Found: C, 58.66; H, 5.45.

3.10. 3-*O*-Allyl-2,4,6-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-D-glucopyranose (11)

Compound **10** (3.08 g, 2.14 mmol) was dissolved in 60:20 satd NH_3–toluene–MeOH (80 mL). The reaction mixture was stirred for 40 min, at the end of which time TLC (1:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was concentrated to dryness. Purification by silica gel column chromatography (1:2 petroleum ether–EtOAc) gave **11** as an anomeric mixture (1.80 g, 60.2%) that was used for further reaction. Pure α-anomer was isolated as a foamy solid: $[\alpha]_D$ +54° (*c* 1.0, $CHCl_3$); δ 7.80–7.40 (m, 20 H, 4 Ph*H*), 5.50 (m, 1 H, CH_2=C*H*–CH_2), 5.42 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.6$ Hz, H-4‴), 5.30 (d, 1 H, $J_{1,2} = 3.2$ Hz, H-1), 5.10 (dd, 1 H, $J_{1,2}$ 8.2, $J_{2,3}$ 8.8 Hz, H-2‴), 5.03–4.55 (m, 8 H, CH_2=CH–CH_2, H-2, H-2′, H-2″, H-4, H-4′, H-4″), 4.65 (d,1 H, $J_{1,2}$ 8.0 Hz, H-1‴), 4.44 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1′), 4.40 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1″), 4.48–3.52 (m, 19 H, CH_2=CH–C*H*$_2$, 4 H-3, 4 H-5, 8 H-6, –OH), 2.06, 2.05, 2.04, 2.03, 2.01, 1.95, 1.88, 1.84 (8 s, 24 H, 8 C*H*$_3$CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 170.6, 170.6, 169.3, 169.2, 169.1, 169.0, 168.3 (8 C, 8 CH_3*C*O–), 166.1, 164.9, 164.8, 164.3 (4 C, 4 *C*OPh), 133.9 (CH_2=*C*H–CH_2), 117.5 (*C*H_2=CH–CH_2), 101.0, 100.7, 100.6, 89.6 (4 C, 4 C-1), 79.5, 78.6, 77.6, 75.1, 74.4, 73.3, 73.1, 72.0, 71.9, 71.8, 71.7, 71.4, 71.0, 68.3, 68.1, 67.9, 67.1, 63.1, 62.2, 62.0, 60.4 (C-2–6), 20.8, 20.7, 20.6, 20.5, 20.4, 20.4, 20.3. Anal. Calcd for $C_{71}H_{78}O_{33}$: C, 58.44; H, 5.35. Found: C, 58.33; H, 5.44.

3.11. 3-*O*-Allyl-2,4,6-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl trichloroacetimidate (12)

Compound **11** (1.66 g, 1.20 mmol) was dissolved in CH_2Cl_2 (30 mL), then CCl_3CN (0.4 mL, 6.2 mmol) and DBU (60 μL, 0.5 mmol) were added. The reaction mixture was stirred for 2 h, at the end of which time TLC (1:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was concentrated and the residue was purified by flash chromatography (1:1 petroleum ether–EtOAc) to give **12** (1.74 g, 80.1%) as a syrup: $[\alpha]_D$ +40° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (s, 1 H, CN*H*CCl_3), 7.80–7.38 (m, 20 H, 4 Ph*H*), 6.40 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 5.55–5.46 (m, 1 H, CH_2=C*H*–CH_2), 5.43 (dd, 1 H, $J_{4,5} = J_{3,4} = 9.6$ Hz, H-4‴), 5.09 (dd, 1 H, $J_{2,3}$ 9.4 Hz, H-2‴), 5.09 (dd, 1 H, $J_{4,5} = J_{3,4} = 9.6$ Hz, H-4″), 5.03 (dd, 1 H, $J_{1,2}$ 7.8, $J_{2,3}$ 9.1 Hz, H-2′), 4.98–4.88 (m, 2 H, CH_2=CH–CH_2), 4.92–4.73 (m, 2 H, H-2, H-4), 4.80 (dd, 1 H, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 9.6 Hz, H-2), 4.67 (d, 1 H, H-1‴), 4.48 (d, 1 H, H-1′), 4.40 (d, 1 H, H-1″), 4.52-3.50 (m, 18 H), 2.07, 2.06, 2.05, 2.02, 1.96, 1.83, 1.82, 1.80 (8 s, 24 H, 8 C*H*$_3$CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 170.5, 170.4, 169.1, 169.0, 169.0, 168.9, 168.3 (8 C, 8 CH_3*C*O–), 166.0, 164.8, 164.8, 164.2 (4 C, 4 *C*OPh), 133.9 (CH_2=*C*H–CH_2), 117.4 (*C*H_2=CH–CH_2), 101.0, 100.6, 100.6, 92.8 (4 C, 4 C-1), 90.7 (–CCl_3), 79.4, 78.3, 77.5., 77.2, 74.3, 73.4, 73.1, 72.0, 71.9, 71.8, 71.7, 71.6, 71.0, 70.0, 68.5, 68.1, 67.0, 63.1, 62.1, 61.7, 20.6, 20.4, 20.4, 20.3, 20.2. Anal. Calcd for $C_{73}H_{78}Cl_3NO_{33}$: C, 54.65; H, 4.87. Found: C, 54.82; H, 4.90.

3.12. Allyl 3-*O*-allyl-2,4,6-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside (14)

Compound **12** (870 mg, 0.57 mmol) and **13** (270 mg, 0.65 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (30.0 mL). Me_3SiOTf (10.0 μL, 0.087 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 2:1 petroleum ether–EtOAc as the eluent gave the product **14** (850 mg, 85.5%) as a syrup: $[\alpha]_D$ +62° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60–7.32 (m, 30 H, 6 Ph*H*), 5.82–5.74 (m, 1 H, CH_2=C*H*–CH_2), 5.54–5.44 (m, 1 H, CH_2=C*H*–CH_2), 5.50 (s, 1 H,

PhC*H*), 5.42 (dd, 1 H, $J_{4,5} = J_{3,4} = 9.4$ Hz, H-4^{V}), 5.25–5.09 (m, 2 H, CH_2=CH–CH$_2$), 5.10 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 5.07 (dd, 1 H, $J_{2,3}$ 9.6, $J_{1,2}$ 7.8 Hz, H-2^{V}), 4.98–4.70 (m, 9 H, CH_2=CH–CH$_2$, H-2^{I-IV}, H-4^{II-IV}), 4.59 (d, 1 H, $J_{1,2}$ 7.8Hz, H-1^{V}), 4.42 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1^{II}), 4.34 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1^{III}), 4.30 (d, 1 H, $J_{1,2}$ 6.0 Hz, H-1^{I}), 4.50–3.46 (m, 25 H), 2.04, 2.04, 2.03, 1.94, 1.94, 1.91, 1.81, 1.80 (8 s, 24 H, 8 CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 170.8, 170.7, 169.2, 169.1, 168.4, 168.2, 168.1 (8 C, 8 CH_3CO–), 166.2, 165.7, 165.0, 164.7 (4 C, 4 *C*OPh), 137.3, 134.0 (2 C, CH_2=*C*H–CH$_2$), 118.2, 117.5 (2 C, CH_2=*C*H–CH$_2$), 101.2 (–*C*HPh), 101.0, 100.7, 100.6, 99.9 (4 C, β C-1), 95.8 (1 C, α C-1), 79.6, 79.1, 78.3, 77.4, 74.8, 74.1, 74.0, 73.5, 73.2, 72.5, 72.0, 71.7, 71.0, 68.9, 68.5, 68.3, 63.2, 62.8, 62.6, 62.1, 62.0, 61.9 (C-2–6), 20.8, 20.6. Anal. Calcd for $C_{94}H_{100}O_{39}$: C, 60.91; H, 5.40. Found: C, 61.18; H, 5.44.

3.13. Allyl 3-*O*-allyl-2,4,6-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-α-D-glucopyranoside (15)

To a soln of 90% HOAc (30 mL) was added **14** (800 mg, 0.45 mmol), and the mixture was stirred at 40 °C overnight, then concentrated to dryness. The residue was passed through a short silica column (1:2 petroleum ether–EtOAc) to give **15** (720 mg, 93%) as a foamy solid: $[\alpha]_D$ +67° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04–7.39 (m, 25 H, 5 Ph*H*), 5.81–5.74 (m, 1 H, CH$_2$–C*H*=CH$_2$), 5.54–5.43 (m, 1 H, CH$_2$–C*H*=CH$_2$), 5.42 (dd, 1 H, $J_{4,5} = J_{3,4} = 9.4$ Hz, H-4^{V}), 5.25–4.84 (m, 4 H, CH$_2$CH=CH_2), 5.08 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 5.08–4.70 (m, 8 H), 4.66 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1^{V}), 4.52 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1^{III}), 4.48 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1^{IV}), 4.42 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1^{II}), 4.50–3.36 (m, 27 H), 2.08, 2.06, 2.05, 2.04, 2.01, 1.92, 1.82, 1.79 (8 s, 24 H, CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 170.7, 169.2, 169.1, 169.0, 168.4, 168.2, 168.1 (8 C, 8 CH_3CO), 166.2, 165.5, 165.0, 165.0, 164.4 (5 C, 5 *C*OPh), 134.7, 133.6 (2 C, CH_2=*C*H–CH$_2$), 118.0, 117.5 (2 C, *C*H$_2$=CH–CH$_2$), 101.1, 101.0, 100.7, 99.8 (4 C, β C-1), 95.0 (1 C, α C-1), 82.3, 79.6, 78.3, 77.8, 73.9, 73.5, 73.2, 73.1, 72.8, 72.4, 72.0, 72.0, 71.8, 71.1, 71.0, 69.6, 68.6, 68.5, 63.4, 63.3, 63.2, 63.2, 62.8, 62.4, 62.1, 62.0, 60.5 (C-2–6), 20.8, 20.6, 20.5, 20.0. Anal. Calcd for $C_{87}H_{96}O_{39}$: C, 59.18; H, 5.44. Found: C, 59.36; H, 5.57.

3.14. Allyl 3-*O*-allyl-2,4,6-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-di-*O*-acetyl-β-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→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→6)]-2-*O*-benzoyl-α-D-glucopyranoside (17)

Compounds **15** (470 mg, 0.28 mmol) and **16** (340 mg, 0.33 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (30.0 mL). Me_3SiOTf (10.0 μL, 0.087 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 of the product on a silica gel column with 2:1 petroleum ether–EtOAc as the eluent gave **17** (220 mg, 65.5%) as a syrup: $[\alpha]_D$ +75° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03–7.38 (m, 45 H, 9 Ph*H*), 5.91 (dd, 1 H, $J_{4,5} = J_{3,4} = 9.6$ Hz, H-4), 5.73–5.62 (m, 1 H, CH$_2$C*H*=CH$_2$), 5.54–5.45 (m, 1 H, CH$_2$C*H*=CH$_2$), 5.66 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.4$ Hz, H-3), 5.53 (dd, 1 H, $J_{1,2} = J_{2,3} = 9.4$ Hz), 5.20–4.76 (m, 17 H), 4.97 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1), 4.57–3.21 (m, 30 H), 4.56 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1), 4.46 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 4.41 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.36 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1), 4.34 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.29 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 2.05, 2.05, 2.04, 2.03, 2.00, 1.94, 1.90, 1.88, 1.85, 1.83, 1.79 (11 s, 33 H, 11 CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 171.1, 170.8, 170.8, 170.7, 169.2, 169.1, 169.0, 168.4, 168.2, 168.1 (11 C, 11 CH_3CO), 166.2, 166.1, 165.5, 165.3, 165.1, 165.0, 164.9, 164.9, 164.3 (9 C, 9 *C*OPh), 134.7, 133.6 (2 C, CH_2=*C*H–CH$_2$), 118.0, 117.5 (2 C, *C*H$_2$=CH–CH$_2$), 101.6, 101.3, 101.1, 101.1, 100.7, 100.2 (6 C, β C-1), 94.4 (1 C, α C-1), 82.3, 79.6, 78.3, 77.8, 73.9, 73.5, 73.2, 73.1, 72.8, 72.4, 72.0, 72.0, 71.8, 71.1, 71.0, 69.6, 68.6, 68.5, 63.4, 63.3, 63.2, 63.2, 62.8, 62.4, 62.1, 62.0, 60.5 (C-2–6), 20.8, 20.7, 20.7, 20.6, 20.6, 20.5, 20.0. Anal. Calcd for $C_{133}H_{138}O_{56}$: C, 60.68; H, 5.25. Found: C, 60.44; H, 5.35.

3.15. β-D-Glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→6)]-β-D-glucopyranose (18)

To a soln of **17** (192 mg, 0.15 mmol) in MeOH (20 mL) was added $PdCl_2$ (100 mg, 0.64 mmol). After stirring the mixture for 6 h at rt, TLC (1:2 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was filtered, the soln was concentrated to dryness, and the resultant residue was dissolved in a satd soln 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 **18** (52 mg, 66.3% for two steps) as a foamy solid: $[\alpha]_D$ −1.3° (*c* 1.0, H_2O); ^1H NMR (400 MHz, D_2O): δ 4.73 (d, 1 H, *J* 7.8 Hz, H-1), 4.72–4.69 (m, 5 H, H-1), 4.66 (d, 1 H, *J* 8.0 Hz, H-1), 3.87–3.30 (m, 42 H); ^{13}C NMR: δ 102.4, 102.4, 102.3, 102.3, 102.2, 102.2, 102.1 (7 C-1), 84.2, 84.1, 83.9, 83.7, 75.6, 75.2, 75.2, 73.1, 72.9, 72.8, 72.4, 69.2, 67.7, 60.4, 60.3, 60.2, (C-2–6). Anal. Calcd for $C_{42}H_{72}O_{36}$: C, 43.75; H, 6.25. Found: C, 43.56, H, 6.14.

3.16. Allyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside (19)

To a soln of compounds **13** (1.0 g, 2.43 mmol) and 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl trichloroacetimidate (2.1 g, 2.80 mmol) in CH_2Cl_2 (30 mL) was added 4A molecular sieves (1.0 g). The mixture was stirred and cooled to −10 °C under N_2 protection, and Me_3SiOTf (50 μL, 0.28 mmol) was added. Stirring was continued at the low temperature for 1 h, at the end of which time TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. Et_3N was added to quench the reaction, the mixture was filtered, and the filter cake was washed with CH_2Cl_2. The combined filtrate and washings were washed with satd aq $NaHCO_3$ and water, then dried and concentrated. Purification by column chromatography with 3:1 petroleum ether–EtOAc as the eluent afforded compound **19** (2.2 g, 91%) as a syrup: $[\alpha]_D^{20}$ +22.2° (*c*, 1.5, $CHCl_3$); ^1H NMR δ: 7.96–7.06 (m, 30 H, 5 Bz–*H*, Ph–*H*), 5.78 (dd, 1 H, $J_{2,3}=J_{3,4}=9.6$ Hz, H-3′), 5.77–5.67 (m, 1 H, CH_2=C*H*–CH_2), 5.64 (dd, 1 H, $J_{3,4}=J_{4,5}=9.6$ Hz, H-4′), 5.64 (s, 1 H, PhC*H*), 5.52 (dd, 1 H, $J_{1,2}$ 8.0, $J_{2,3}$ 9.6 Hz, H-2′), 5.21–5.05 (m, 2 H, CH_2=CH–CH_2), 5.15 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1′), 5.13 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 5.05 (dd, 1 H, $J_{1,2}$ 3.6, $J_{2,3}$ 9.8 Hz, H-2), 4.54 (dd, 1 H, $J_{5,6a}$ 3.6, $J_{6a,6b}$ 12.0 Hz, H-6′a), 4.50 (dd, 1 H, $J_{2,3}=J_{3,4}=9.8$ Hz, H-3), 4.39 (dd, 1 H, $J_{5,6b}$ 4.9, $J_{6a,6b}$ 12.0 Hz, H-6′b), 4.28 (dd, 1 H, $J_{5,6a}$ 4.6, $J_{6a,6b}$ 10.2 Hz, H-6a), 4.15-3.78 (m, 6 H, CH_2=CH–CH_2, H-4, 5, 5′, 6b). Anal. Calcd for $C_{57}H_{50}O_{16}$: C, 69.08; H, 5.09. Found: C, 69.16; H, 5.23.

3.17. 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-D-glucopyranose (20)

To a soln of sodium acetate (670 mg, 8.17 mmol) and $PdCl_2$ (750 mg, 4.23 mmol) in AcOH (90%, 10 mL) was added compound **19** (2.1 g, 2.12 mmol). The mixture was stirred at rt overnight under N_2 protection. TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was filtered, and the filter cake was washed with CH_2Cl_2. The organic phase was washed with satd aq $NaHCO_3$ and water, then dried and concentrated. Purification by column chromatography with 2:1 petroleum ether–EtOAc as the eluent afforded compound **20** (1.6 g, 79%) as a syrup: $[\alpha]_D^{20}$ +30.6° (*c*, 1.5, $CHCl_3$); ^1H NMR δ: 7.96–7.05 (m, 30 H, 5 Bz–*H*, Ph–*H*), 5.78 (dd, 1 H, $J_{2,3}=J_{3,4}=9.6$ Hz, H-3′), 5.63 (dd, 1 H, $J_{3,4}=J_{4,5}=9.6$ Hz, H-4′), 5.62 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 5.62 (s, 1 H, PhC*H*), 5.52 (dd, 1 H, $J_{1,2}$ 8.0, $J_{2,3}$ 9.6 Hz, H-2′), 5.15 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1′), 5.03 (dd, 1 H, $J_{1,2}$ 3.6, $J_{2,3}$ 9.8 Hz, H-2), 4.55–3.77 (m, 8 H, H-3, 4, 5, 5′, 6, 6′). Anal. Calcd for $C_{54}H_{46}O_{16}$: C, 68.20; H, 4.88. Found: C, 68.36; H, 4.94.

3.18. 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranosyl trichloroacetimidate (21)

To a soln of compound **20** (1.5 g, 1.58 mmol) in dry CH_2Cl_2 (25 mL) were added CCl_3CN (0.5 mL, 5.0 mmol) and DBU (40 μL). The mixture was stirred at rt for 2 h, at the end of which time TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was concentrated, and the residue thus obtained was subjected to column chromatography with 3:1 petroleum ether–EtOAc as the eluent. Compound **21** was obtained as a syrup (1.40 g, 81%): $[\alpha]_D^{20}$ +39.9° (*c*, 1.0, $CHCl_3$); ^1H NMR δ: 8.49 (s, 1 H, CN*H*CCl_3), 7.96–7.08 (m, 30 H, 5 Bz–*H*, Ph–*H*), 6.52 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 5.78 (dd, 1 H, $J_{2,3}=J_{3,4}$ 9.6 Hz, H-3′), 5.67 (s, 1 H, PhC*H*), 5.62 (dd, 1 H, $J_{3,4}=J_{4,5}=9.6$ Hz, H-4′), 5.52 (dd, 1 H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 9.6 Hz, H-2′), 5.32 (dd, 1 H, $J_{1,2}$ 3.6, $J_{2,3}$ 9.6 Hz, H-2), 5.14 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1′), 4.57 (dd, 1 H, $J_{5,6a}$ 3.6, $J_{6a,6b}$ 12.0 Hz, H-6′a), 4.50 (dd, 1 H, $J_{2,3}=J_{3,4}$ 9.6 Hz, H-3), 4.38–4.34 (m, 2 H, H-6a, 6′b), 4.11–4.05 (m, 2 H, H-5, 5′), 3.96 (dd, 1 H, $J_{3,4}=J_{4,5}=9.6$ Hz, H-4), 3.84 (dd, 1 H, $J_{5,6b}$ 10.3, $J_{6a,6b}$ 10.3 Hz, H-6b). Anal. Calcd for $C_{56}H_{46}Cl_3NO_{16}$: C, 61.13; H, 5.25. Found: C, 61.26; H, 5.33.

3.19. Allyl 4,6-di-*O*-acetyl-2-*O*-benzoyl-3-*O*-chloroacetyl-β-D-glucopyranosyl-(1→3)-4,6-di-*O*-acetyl-2-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside (24)

To a soln of compounds **23** (240 mg, 0.58 mmol) and **22** (500 mg, 0.53 mmol) in CH_2Cl_2 (20 mL) was added 4A molecular sieves (0.5 g). The mixture was stirred and cooled to −10 °C under N_2 protection, and Me_3SiOTf (10 μL, 0.056 mmol) was added. Stirring was continued at the low temperature for 2 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. Et_3N was added to quench the reaction, the mixture was filtered, and the filter cake was washed with CH_2Cl_2. The combined filtrate and washings were washed with satd aq $NaHCO_3$ and water, then dried and concentrated. Purification of the product by

column chromatography with 2:1 petroleum ether–EtOAc as the eluent afforded compound **24** (500 mg, 79%) as a syrup: $[\alpha]_D^{20}+36.0^\circ$ (*c*, 0.5, $CHCl_3$); ^1H NMR δ: 7.80–7.17 (m, 40 H, 7 Bz–*H*, Ph–*H*), 5.73–5.63 (m, 1 H, CH_2=C*H*–CH_2), 5.52 (s, 1 H, PhC*H*), 5.17–5.02 (m, 8 H, CH_2=CH–CH_2, H-1, 2′, 2″, 3″, 4′, 4″), 4.81, 4.61 (2 d, 2 H, $J_{1,2}$ 8.0 Hz, H-1′, 1″), 4.79 (dd, 1 H, $J_{1,2}$ 3.9, $J_{2,3}$ 9.6 Hz, H-2), 4.40–3.59 (m, 14 H, CH_2=CH–C*H*$_2$, H-3, 3′, 4, 5, 5′, 5″, 6, 6′, 6″), 3.78, 3.71 (ABq, 2 H, *J* 14.8 Hz, ClC*H*$_2$CO), 2.04, 1.99, 1.98, 1.97 (4 s, 12 H, 4 C*H*$_3$CO). Anal. Calcd for $C_{59}H_{61}ClO_{24}$: C, 59.57; H, 5.17. Found: C, 59.44; H, 5.07.

3.20. Allyl 4,6-di-*O*-acetyl-2-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-4,6-di-*O*-acetyl-2-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside (25)

Compound **24** (450 mg, 0.38 mmol) was dissolved in mixed solvents of CH_2Cl_2 (4 mL) and MeOH (6 mL). To the soln were added thiourea (145 mg, 1.91 mmol) and 2,4-lutidine (42 μL, 0.38 mmol), and the reaction mixture was boiled under reflux for 16 h, at the end of which time TLC (1.5:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was concentrated and extracted with CH_2Cl_2, the organic phase was washed sequentially with N HCl, satd aq $NaHCO_3$, and water, then dried and concentrated. Purification by column chromatography with 2:1 petroleum ether–EtOAc as the eluent afforded **25** (360 mg, 84%) as a syrup: $[\alpha]_D^{20}$ +35.3° (*c*, 0.7, $CHCl_3$); ^1H NMR δ: 7.82–7.20 (m, 40 H, 7 Bz–*H*, Ph–*H*), 5.76–5.66 (m, 1 H, CH_2=C*H*–CH_2), 5.54 (s, 1 H, PhC*H*), 5.21–4.85 (m, 7 H, C*H*$_2$=CH–CH_2, H-2, 2′, 2″, 4′, 4″), 5.08 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.84, 4.59 (2 d, 2 H, $J_{1,2}$ 8.0 Hz, H-1′, 1″), 4.40–3.47 (m, 15 H, CH_2=CH–C*H*$_2$, H-3, 3′, 3″, 4, 5, 5′, 5″, 6, 6′, 6″), 2.05, 2.04, 1.99, 1.98 (4 s, 12 H, 4 C*H*$_3$CO). Anal. Calcd for $C_{57}H_{60}O_{23}$: C, 61.50; H, 5.43. Found: C, 61.76; H, 5.48.

3.21. Allyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-4,6-di-*O*-acetyl-2-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-4,6-di-*O*-acetyl-2-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside (26)

To a soln of compounds **25** (300 mg, 0.27 mmol) and **21** (350 mg, 0.32 mmol) in CH_2Cl_2 (15 mL) was added 4A molecular sieves (0.5 g). The mixture was stirred and cooled to −10 °C under N_2 protection, and Me_3SiOTf (7.5 μL, 0.041 mmol) was added. Stirring was continued at −10 °C for 4 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. Et_3N was added to quench the reaction, the mixture was filtered, and the filter cake was washed with CH_2Cl_2. The combined filtrate and washings were washed with satd aq $NaHCO_3$ and water, then dried and concentrated. Purification by column chromatography with 2:1 petroleum ether–EtOAc as the eluent afforded compound **26** (400 mg, 73.6%) as a syrup: $[\alpha]_D^{20}$ +16.6° (*c*, 1.2, $CHCl_3$); ^1H NMR δ: 7.90–7.09 (m, 50 H, 8 Bz–*H*, 2 Ph–*H*), 5.73–5.63 (m, 1 H, CH_2=C*H*–CH_2), 5.54–5.50 (m, 2 H, H-3^V, 4^V), 5.52, 5.48 (2 s, 2 H, 2 PhC*H*), 5.32 (dd, 1 H, $J_{2,3}$ 9.6, $J_{1,2}$ 8.0 Hz, H-2^V), 5.15–4.80 (m, 7 H, C*H*$_2$=CH–CH_2–, H-2^{II-IV}, 4^{II,III}), 5.02 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.75, 4.74, 4.45, 4.45 (4 d, 4 H, *J* = 8.0 Hz, H-1^{II-V}), 4.69 (dd, 1 H, $J_{1,2}$ 3.6, $J_{2,,3}$ 9.6 Hz, H-2^I), 4.39–3.24 (m, 23 H, CH_2=CH–C*H*$_2$, H-3^{I-IV}, 4^{I,IV}, 5^{I-V}, 6^{I-V}), 2.02, 1.94, 1.92, 1.89 (4 s, 12 H, 4 C*H*$_3$CO). Anal. Calcd for $C_{111}H_{104}O_{38}$: C, 65.16; H, 5.12. Found: C, 65.06; H, 4.98.

3.22. Allyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-4,6-di-*O*-acetyl-2-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-4,6-di-*O*-acetyl-2-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-α-D-glucopyranoside (27)

To a soln of compounds **26** (350 mg, 0.171 mmol) and ethylene glycol (0.1 mL, 1.80 mmol) in CH_3CN (5 mL) was added *p*-$TsOH\cdot H_2O$ (10 mg). The mixture was stirred at rt overnight. TLC (1:2 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was neutralized with Et_3N, concentrated and extracted with CH_2Cl_2. The organic phase was washed with water, then dried and concentrated. Purification by column chromatography with 1:3 petroleum ether–EtOAc as the eluent afforded compound **27** (240 mg, 75%) as a syrup: $[\alpha]_D^{20}$ +18.9° (*c*, 0.8, $CHCl_3$); ^1H NMR δ: 8.09–7.01 (m, 40 H, 8 Bz–*H*), 5.73–5.63 (m, 1 H, CH_2=C*H*–CH_2–), 5.67 (dd, 1 H, $J_{2,3}=J_{3,4}=9.8$ Hz, H-3^V), 5.52 (dd, 1 H, $J_{3,4}=J_{4,5}=9.8$ Hz, H-4^V), 5.38 (dd, 1 H, $J_{1,2}$ 8.0, $J_{2,3}$ 9.8 Hz, H-2^V), 5.16–5.01 (m, 2 H, C*H*$_2$=CH–CH_2), 5.00 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.97–4.73 (m, 5 H, H-2^{II-IV}, 4^{II,III}), 4.71 (dd, 1 H, $J_{1,2}$ 3.6, $J_{2,3}$ 9.6 Hz, H-2^I), 4.62, 4.61, 4.49, 4.36 (4 d, 4 H, $J_{1,2}$ 8.0 Hz, H-1^{II-V}), 4.35–3.19 (m, 23 H, CH_2=CH–C*H*$_2$–, H-3^{I-IV}, 4^{I,IV}, 5^{I-V}, 6^{I-V}), 2.07, 2.06, 1.96, 1.81 (4 s, 12 H, 4 C*H*$_3$CO). Anal. Calcd for $C_{97}H_{96}O_{38}$: C, 62.31; H, 5.17. Found: C, 62.45; H, 5.24.

3.23. Allyl 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-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-4,6-di-*O*-acetyl-2-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-4,6-di-*O*-acetyl-2-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2-*O*-benzoyl-α-D-glucopyranoside (28)

To a soln of compounds **27** (200 mg, 0.107 mmol) and 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl trichloro-

acetimidate (200 mg, 0.266 mmol) in CH_2Cl_2 (15 mL) was added 4A molecular sieves (0.3 g). The mixture was stirred and cooled to -10 °C under N_2 protection, and Me_3SiOTf (7.5 μL, 0.041 mmol) was added. Stirring was continued at -10 °C for 4 h, at the end of which time TLC (1:1 petroleum ether–EtOAc) indicated that the reaction was complete. Et_3N was added to quench the reaction, the mixture was filtered, and the filter cake was washed with CH_2Cl_2. The combined filtrate and washings were washed with satd aq $NaHCO_3$ and water, then dried and concentrated. Purification by column chromatography with 1:1 petroleum ether–EtOAc as the eluent afforded compound **28** (220 mg, 68%) as a syrup: $[\alpha]_D^{20}$ +4.8° (*c*, 0.5, $CHCl_3$); ^{1}H NMR δ: 8.10–7.00 (m, 80 H, 16 Bz–*H*), 5.94, 5.92, 5.77 (dd, 3 H, $J_{2,3} = J_{3,4} =$ 9.6 Hz, H-3), 5.68, 5.61, 5.55 (dd, 3 H, $J_{3,4} = J_{4,5} = 9.6$ Hz, H-4), 5.54, 5.48, 5.34 (dd, $J_{1,2}$ 8.0, $J_{2,3}$ 9.6 Hz, H-2), 5.53-5.43 (m, 1 H, CH_2=C*H*–CH_2), 5.01–4.24 (m, 15 H, CH_2=CH–CH_2, H-1^{I-VII}, 2^{I-IV}, 4^{II,III}), 4.23–3.11 (m, 29 H, CH_2=CH–CH_2, H-3^{I-IV}, 4^{I,IV}, 5^{I-VII}, 6^{I-VII}), 2.03, 2.01, 1.94, 1.78 (4 s, 12 H, 4 CH_3CO). ^{13}C NMR δ: 170.58, 170.58, 169.26, 169.15 (4 s, 4 C, 4 CH_3*C*O), 166.12, 166.06, 165.92, 165.74, 165.74, 165.53, 165.23, 165.15, 165.11, 165.06, 164.90, 164.84, 164.72, 163.72, 163.57, 163.41 (16 s, 16 C, 16 Bz*C*O), 117.30 (s, 1 C, *C*H_2=CH–CH_2), 101.99, 101.59, 101.34, 101.19, 100.79, 100.59, 94.27 (7 s, 7 C, C-1^{I-VII}), 85.42, 84.52, 83.42, 82.30 (4 s, 4 C, C-3^{I-IV}), 63.10, 63.09, 62.66, 62.15, 61.98 (5 s, 5 C, C-6$^{II,III,V-VII}$), 22.66, 20.68, 20.64, 20.40 (4 s, 4 C, 4 *C*H_3CO). Anal. Calcd for $C_{165}H_{148}O_{56}$: C, 65.47; H, 4.93. Found: C, 65.66; H, 5.01.

3.24. Allyl β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→6)]-β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→6)]-α-D-glucopyranoside (29)

A satd soln of NH_3 in MeOH (5 mL) was added to a soln of compound **28** (180 mg, 0.059 μmol) in MeOH (4 mL). After 48 h at rt, the reaction mixture was concentrated, and the residue was purified by Sephadex LH-20 chromatography (MeOH) to afford **29** (70 mg, 98%): $[\alpha]_D^{20}$ +4.3° (*c*, 1.0, H_2O); ^{1}H NMR δ: 6.06–5.96 (m, 1 H, CH_2=C*H*–CH_2–), 5.42–5.37 (m, 2 H, CH_2= CH–CH_2–), 4.98 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1^I), 4.76, 4.76, 4.75, 4.53, 4.50, 4.50 (6 d, 6 H, *J* 8.0 Hz, H-1^{II-VII}), 4.29–3.30 (m, 44 H, CH_2=CH–CH_2, H-2^{I-VII}, 3^{I-VII}, 4^{I-VII}, 5^{I-VII}, 6^{I-VII}). ^{13}C NMR δ: 133.2 (s, 1 C, CH_2= *C*H–CH_2), 118.1 (s, 1 C, *C*H_2=CH–CH_2), 102.6, 102.5, 102.5, 102.3, 102.3, 102.3 (6 s, 6 C, C-1^{II-VII}), 97.03 (s, 1 C, C-1^I), 84.53, 83.94, 83.80, 81.89 (4 s, 4 C, C-3^{I-IV}), 60.53, 60.48, 60.48, 60.44, 60.44 (5 s, 5 C, C-6$^{II,III,V-VII}$). Anal. Calcd for $C_{45}H_{76}O_{36}$: C, 45.30; H, 6.42. Found: C, 45.16; H, 6.24.

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References

1. Chihara, G.; Maeda, Y.; Hamuro, J.; Sasaki, T.; Fukuoka, F. *Nature* **1969**, *222*, 687–688.
2. Oka, M.; Hazama, S.; Suzuki, M.; Wang, F.; Wadamori, K.; Lizuka, N.; Takeda, S.; Akitomi, Y.; Ohba, Y.; Kajiwara, K.; Suga, T.; Suzuki, T. *Int. J. Immunopharmacol.* **1996**, *18*, 211–216.
3. (a) Norisue, T.; Yanaki, T.; Fujita, H. *J. Polym. Sci.* **1980**, *18*, 547–552;
   (b) Kojima, T.; Tabata, K.; Itoh, W.; Yanaki, T. *Agric. Biol. Chem.* **1986**, *50*, 231–238;
   (c) Brown, G. D.; Gordon, S. *Nature* **2001**, *413*, 36–37;
   (d) Willment, J. A.; Gordon, S.; Brown, G. D. *J. Biol. Chem.* **2001**, *276*, 43818–43823;
   (e) Mueller, A.; Raptis, J.; Rice, P. J.; Kalbfleisch, J. H.; Stout, R. D.; Ensley, H. E.; Browder, W.; Williams, D. L. *Glycobiology* **2000**, *10*, 339–346.
4. Saito, H.; Ohki, T.; Takasuka, N.; Sasaki, T. *Carbohydr. Res.* **1977**, *58*, 293–305.
5. Yang, G.; Kong, F. *Synlett* **2000**, 1423–1426.
6. Ning, J.; Zhang, W.; Yi, Y.; Yang, G.; Wu, Z.; Yi, J.; Kong, F. *Bioorg. Biomed. Chem.* **2003**, *11*, 2193–2203.
7. Schmidt, R. R.; Kinzy, W. *Adv. Carbohydr. Chem. Biochem.* **1994**, *50*, 21–125.
8. (a) Zeng, Y.; Ning, J.; Kong, F. *Tetrahedron Lett.* **2002**, 3729–3733;
   (b) Zeng, Y.; Ning, J.; Kong, F. *Carbohydr. Res.* **2003**, *338*, 307–311.