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Synthesis of two isomeric pentasaccharides, the possible repeating unit of the β-glucan from the micro fungus *Epicoccum nigrum* Ehrenb. ex Schlecht

Ying Zeng, Wenhui Zhang, Jun Ning,* Fanzuo Kong*

Research Center for Eco-Environmental Sciences, Academia Sinica, PO Box 2871, Beijing 100085, China

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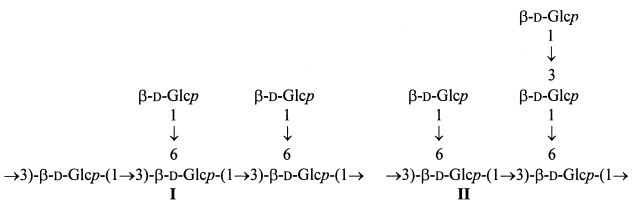
Abstract

Two isomeric pentasaccharides, β-D-Glc*p*-(1→3)-[β-D-Glc*p*-(1→6)]-β-D-Glc*p*-(1→3)-[β-D-Glc*p*-(1→6)]-β-D-Glc*p* (**I**) and β-D-Glc*p*-(1→6)-β-D-Glc*p*-(1→3)-[β-D-Glc*p*-(1→3)-β-D-Glc*p*-(1→6)]-β-D-Glc*p* (**II**), the possible repeating unit of the β-glucan from the micro fungus *Epicoccum nigrum* Ehrenb. ex Schlecht, were synthesized as their 4-methoxyphenyl glycosides in a regio- and stereoselective manner. The pentasaccharide **I** was obtained from 3-*O*-selective glycosylation of 4-methoxyphenyl 4,6-*O*-benzylidene-β-D-glucopyranoside (**12**) with 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 trichloroacetimidate (**6**) followed by acetylation, debenzylidenation, and 6-*O*-selective glucosylation with 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl trichloroacetimidate (**1**), and then by deprotection. The pentasaccharide **II** was obtained from 3-*O*-selective coupling of **12** with 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,4-di-*O*-acetyl-3-*O*-allyl-α-D-glucopyranosyl trichloroacetimidate (**10**) followed by acetylation, debenzylidenation, and 6-*O*-selective glycosylation with 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl trichloroacetimidate (**11**), and finally by deprotection.

Keywords: Glucose oligosaccharides; Trichloroacetimidates; Regio- and stereoselective synthesis

1. Introduction

β-(1→3)-Linked glucans occur in a variety of biologically important natural products with antitumor activities, such as schizophyllan, scleroglucan and lentinan.[1] A highly side-chain/branched (1→3;1→6)-β-glucan, epiglucan, was obtained from the micro fungus *Epicoccum nigrum* Ehrenb. ex Schlecht. Structural analysis[2] of the epiglucan revealed that it has a β-(1→3)-linked backbone with β-(1→6)-linked branches at frequencies greater than the homologous scleroglucan and schizophyllan. Two pentasaccharide structures **I** and **II** were supposed to be the possible repeating unit of the epiglucan. As a part of our ongoing research on the structure–antitumor function relationship for glucan, we needed to prepare a series of β-(1→3)-linked glucan with different β-(1→6)-side chains. The structures **I** and **II** are interested in terms of their side chain position and length. We present herein an unambiguous synthesis of the two isomeric pentasaccharides.



2. Results and discussion

For the synthesis of the target pentasaccharides, some di- and trisaccharide intermediates were prepared

* Corresponding authors. Tel.: 86-10-62936613; fax: 86-10-62923563

E-mail address: fzkong@mail.rcees.ac.cn (F. Kong).

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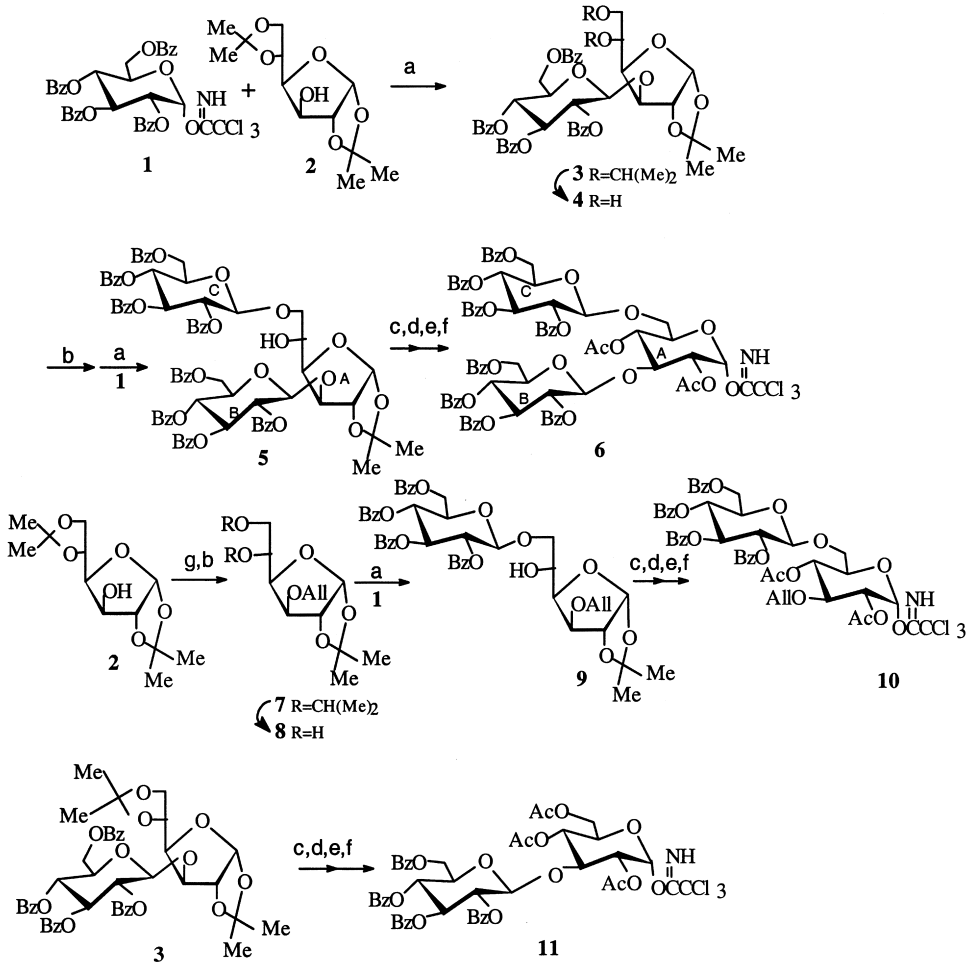
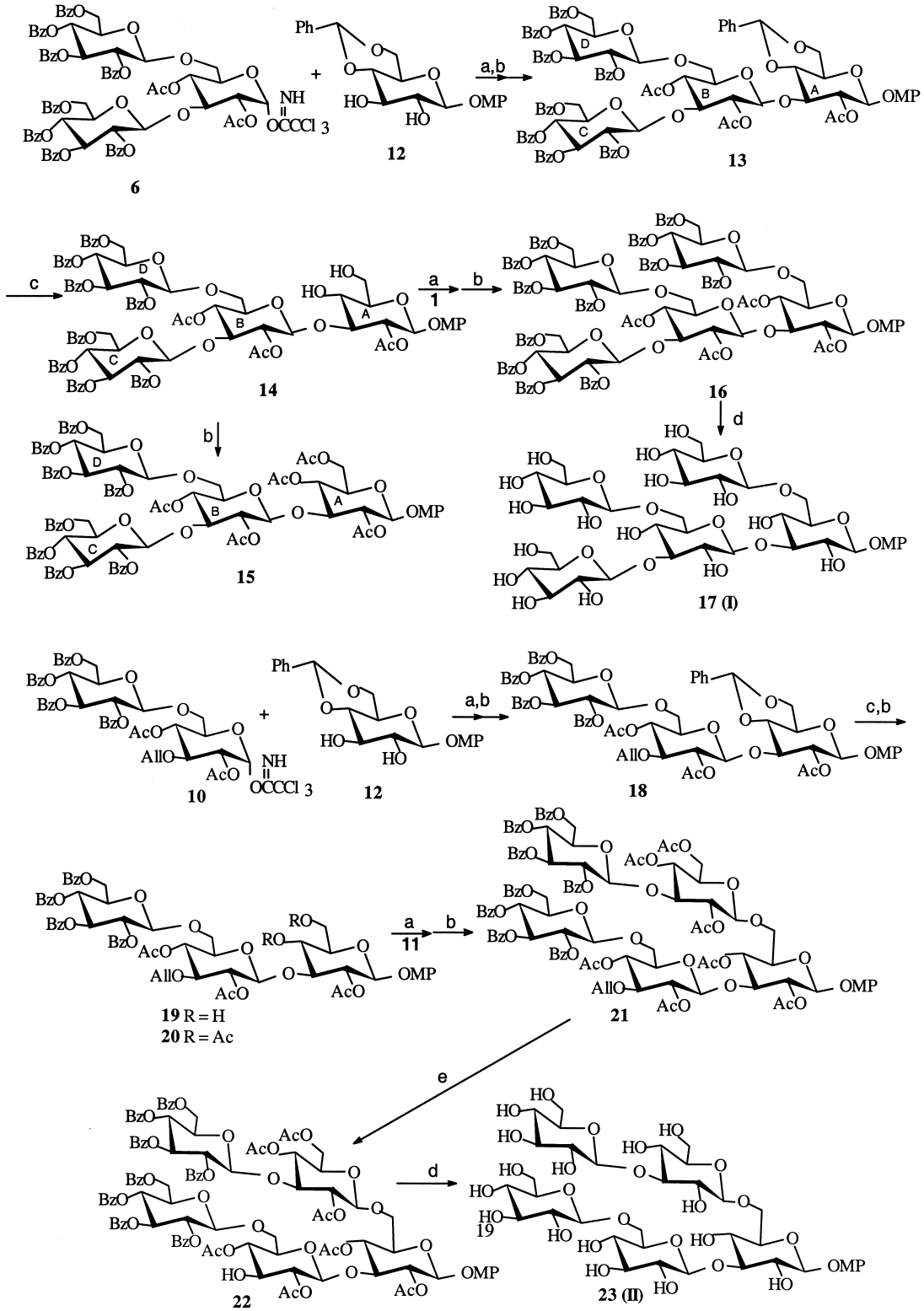
first. Coupling of 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl trichloroacetimidate[3] (**1**) with 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**2**) afforded the disaccharide **3** (Scheme 1). Selective removal of the 5,6-*O*-isopropylidene group gave crystalline **4**, and subsequent selective 6-*O*-glycosylation[4] of **4** with **1** gave the trisaccharide **5**. Removal of the 1,2-*O*-isopropylidene groups of furanose **5** was accompanied by ring expansion. Subsequent acetylation with acetic anhydride in pyridine, selective 1-*O*-deacetylation with ammonia in 3:1 THF–MeOH, and trichloroacetimidation in dichloromethane with trichloroacetonitrile in the presence of potassium carbonate gave the 3,6-branched trisaccharide donor **6**. The β-(1→6)-linked disaccharide **10** was obtained as follows: Allylation of **2** at *O*-3, selective removal of the 5,6-*O*-isopropylidene group, followed by selective 6-*O*-glucosylation with **1** gave **9**. Subsequent hydrolysis, acetylation, selective 1-*O*-deacetylation, and trichloroacetimidation furnished **10**. Another β-(1→3)-linked disaccharide donor **11** was prepared by hydrolysis of **3** in 80% HOAc under reflux, acetylation, selective 1-*O*-deacetylation, and trichloroacetimidation.

With the described di- and trisaccharide fragments in hand, the synthesis of the target pentasaccharides was readily achieved. In our previous work regarding the synthesis of glucoheptaose repeating unit of lentinan,[5] we reported that with 4,6-benzylidenated glucose derivative as either the donor or the acceptor, coupling reactions predominantly gave β-linked products. Thus, coupling of **12** with the trisaccharide donor **6**, followed by acetylation, selectively afforded β-(1→3)-linked tetrasaccharide **13** (Scheme 2). The ^{1}H NMR spectrum of **13** showed 4 H-1 at δ 4.96, 4.86, 4.72, and 4.41 ppm, respectively, with $J_{1,2}$ 8.0 Hz, indicating only β-linkage. Sequential irradiation of the 4 H-1 found the related signals of 4 H-2 at δ 5.45, 5.41, 5.27, and 4.84 ppm, respectively, and collapsed the H-2 signals from a triplet to a doublet. This confirmed the 3-*O*-selective glucosylation, since 2-*O*-selective glucosylation would



Scheme 1. Reagents and conditions: (a) TMSOTf, CH_2Cl_2, N_2, −20 °C to rt, 4 h; (b) 90% HOAc, 40 °C, 20 h; (c) 80% HOAc, reflux, 4 h; (d) Ac_2O–pyridine (dry), rt, 10 h; (e) THF–CH_3OH, 1.5N NH_3, rt, 1–2 h; (f) CCl_3CN, DBU, CH_2Cl_2 (dry), 10 h; (g) AllBr, DMF, NaH, 0 °C to rt, 4 h.



Scheme 2. Reagents and conditions: (a) TMSOTf, CH_2Cl_2, N_2, -20 °C to rt, 4 h; (b) Ac_2O–pyridine (dry), rt, 10 h; (c) CH_3OH, CH_3COCl (0.3%, v/v), rt, 2 h; (d) NH_3, CH_3OH; (e) $PdCl_2$, CH_3OH, 4 h.

give H-2_a at $\delta < 4.2$ ppm. Debenzylidenation of **13** gave the tetrasaccharide **14**, whose characterization was carried out through its acetylated derivative **15**. Selective 6-*O*-glucosylation of the tetrasaccharide acceptor **14** with the donor **1** furnished the pentasaccharide **16**, and finally, deacylation of **16** in ammonia-saturated

methanol gave the 4-methoxyphenyl pentaoside **17**. The ^{13}C NMR of **17** showed 5 anomeric carbons at δ 105.23, 105.23, 105.04, 105.04, and 103.36 ppm, indicating all of the linkages in **17** are β. Another pentasaccharide **23**, corresponding to structure **II** was synthesized in a similar way. Thus, the β-(1→6)-linked disaccharide donor **10** was selectively coupled with the acceptor **12**, and subsequent acetylation gave the trisaccharide **18**. The regioselective glycosylation was also confirmed by ^1H NMR spectroscopy. Sequential irradiation of the 3 H-1 at δ 5.01, 4.78, and 4.45 ppm identified the related signals of 3 H-2 at δ 5.66, 5.35, and 4.80 ppm, respectively. Debenzylidenation of **18**, followed by selective glycosylation with the disaccharide donor **11**, and then acetylation, afforded the pentasaccharide **21** in satisfactory yield. Removal of the allyl group with $PdCl_2$ in methanol[6] gave **22**, and deacylation of **22** in ammonia-saturated methanol furnished the target pentaoside **23**. Again, the ^{13}C NMR spectrum of **23** showed 5 anomeric carbons at δ 105.39, 105.35, 105.20, 104.75, and 103.32 ppm, indicating only β-linkages in **23**.

The bioassay of **17** and **23** is in progress and the results will be reported in due course.

3. Experimental

General methods.—Optical rotations were determined at 25 °C with a Perkin–Elmer model 241-Mc automatic polarimeter. ^1H NMR, ^{13}C NMR and ^1H–^{13}C COSY spectra were recorded with Bruker ARX 400 spectrometers (400 MHz for ^1H, 100 MHz for ^{13}C) at 25 °C for solutions in $CDCl_3$ or D_2O as indicated. Mass spectra were recorded with a VG PLATFORM mass spectrometer using the ESI mode. Thin-layer chromatography (TLC) was performed on silica gel HF_{254} with detection by charring with 30% (v/v) H_2SO_4 in MeOH or in some cases by a UV lamp. Column chromatography was conducted by elution of a column (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. Solutions were concentrated at < 60 °C under reduced pressure.

2,3,4,6-Tetra-O-*benzoyl*-β-D-*glucopyranosyl*-(1→3)-*1,2:5,6-di*-O-*isopropylidene*-α-D-*glucofuranose* (**3**).—2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl trichloroacetimidate **1** (3.0 g, 4.0 mmol) and 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose **2** (1.04 g, 4.0 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (20 mL). TMSOTf (30 μL) 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 4:1 petroleum ether–EtOAc as the eluent, gave the product **3** (2.91 g, 87%) as a syrup: $[\alpha]_D$ +25.0° (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.02–7.34 (m, 20 H, 4 Bz*H*), 5.92 (dd, 1 H, $J_{3',4'} = J_{4',5'} = 9.8$ Hz, H-4′), 5.85 (d, 1 H, $J_{1,2}$ 3.0 Hz, H-1), 5.69 (dd, 1 H, $J_{3',4'} = J_{2',3'} = 9.8$ Hz, H-3′), 5.55 (dd, 1 H, $J_{1',2'}$ 8.0 Hz, $J_{2',3'}$ 9.6 Hz, H-2′), 4.95 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1′), 4.68 (dd, 1 H, $J_{6'^a,6'^b}$ 12.4 Hz, $J_{5',6'^a}$ 3.2 Hz, H-6′^{a}), 4.51 (d, 1 H, $J_{1,2}$ 3.0 Hz, H-2), 4.48 (dd, 1 H, $J_{6'^a,6'^b}$ 12.4 Hz, $J_{5',6'^b}$ 3.2 Hz, H-6′^{b}), 4.12–3.86 (m, 7 H), 1.45, 1.37, 1.31, 1.28 (4 s, 4 C*H*$_3$). Anal. Calcd for $C_{46}H_{46}O_{15}$: C, 65.87; H, 5.49. Found: C, 65.61; H, 5.53.

2,3,4,6-Tetra-O-*benzoyl*-β-D-*glucopyranosyl*-(1→3)-[*2,3,4,6-tetra*-O-*benzoyl*-β-D-*glucopyranosyl*-(1→6)]-*1,2*-O-*isopropylidene*-α-D-*glucofuranose* (**5**).—To a solution of 90% HOAc (20 mL) was added **3** (1.00 g, 1.20 mmol), and the mixture was stirred at 40 °C overnight, then concentrated to dryness. The residue was passed through a short silica gel column (1:1 petroleum ether–EtOAc) to give **4** (880 mg, 93%) as crystals (mp 144–146 °C). Compound **5** was prepared by coupling of **1** (750 mg, 1.0 mmol) with **4** (800 mg, 1.0 mmol) under the same conditions as described for the synthesis of **3** by coupling of **1** with **2**. 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 **5** (980 mg, 71%) as a syrup: $[\alpha]_D$ +42.3° (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.02–7.34 (m, 40 H, 8 BzH), 5.91 (dd, 1 H, $J_{3^c,4^c} = J_{4^c,5^c} = 9.6$ Hz, H-4^c), 5.87 (d, 1 H, $J_{1^a,2^a}$ 3.0 Hz, H-1^a), 5.83 (dd, 1 H, $J_{4^b,5^b} = J_{3^b,4^b} = 9.6$ Hz, H-4^b), 5.63 (m, 2 H, H-3^b, H-3^c), 5.48 (dd, 1 H, $J_{1^c,2^c}$ 8.0 Hz, $J_{2^c,3^c}$ 9.6 Hz, H-2^c), 5.43 (dd, 1 H, $J_{1^b,2^b}$ 8.0 Hz, $J_{2^b,3^b}$ 9.6 Hz, H-2^b), 5.03 (d, 1 H, $J_{1^c,2^c}$ 8.0 Hz, H-1^c), 4.94 (d, 1 H, $J_{1^b,2^b}$ 8.0 Hz, H-1^b), 4.68 (m, 2 H), 4.45 (d, 1 H, $J_{1^a,2^a}$ 3.0 Hz, H-2^a), 4.48–3.86 (m, 9 H), 1.37, 1.28 (2 s, 2 CH_3). Anal. Calcd for $C_{77}H_{68}O_{24}$: C, 67.15; H, 4.94. Found: C, 67.38; H, 4.98.

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 trichloroacetimidate* (**6**).—A solution of **5** (950 mg, 0.69 mmol) in 80% HOAc (50 mL) was heated under reflux for 4 h, then concentrated to dryness. The residue was dissolved in pyridine (10 mL), and then Ac_2O (2 mL) was added. After stirring the mixture at rt for 12 h, TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. To the reaction mixture was added water (10 mL), and the mixture was stirred for 0.5 h, then washed with dil HCl, and extracted with CH_2Cl_2. The organic phase was dried over anhyd Na_2SO_4, then

concentrated to dryness. The resultant crude product was dissolved in a 1 M solution of NH_3 in 3:1 THF–MeOH (20 mL), and the mixture was stirred at rt until TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The solution was concentrated and the residue was purified by column chromatography with 2:1 petroleum ether–EtOAc as the eluent to give 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,β-D-glucopyranose (560 mg, 57% for three steps) as a syrup. A mixture of the hemiacetal (560 mg, 0.40 mmol), CCl_3CN (1.0 mL, 5 mmol), and 1,8-diazabicyclo[5.4.0]undecene (DBU, 0.10 mL) in dry CH_2Cl_2 (20 mL) was stirred for 3 h and then concentrated. The residue was purified by flash chromatography (2:1 petroleum ether–EtOAc) to give **6** (510 mg, 82%) as a syrup: $[\alpha]_D$ +79.2° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (s, 1 H, NH), 7.91–7.27 (m, 40 H, 8 BzH), 6.21 (d, 1 H, $J_{1^a,2^a}$ 3.6 Hz, H-1^a), 5.92 (dd, 1 H, $J_{3^c,4^c} = J_{4^c,5^c} = 9.6$ Hz, H-4^c), 5.85 (dd, 1 H, $J_{4^b,5^b} = J_{3^b,4^b} = 9.6$ Hz, H-4^b), 5.64 (dd, 1 H, $J_{3^c,4^c} = J_{2^c,3^c} = 9.6$ Hz, H-3^c), 5.62 (dd, 1 H, $J_{3^b,4^b} = J_{2^b,3^b} = 9.6$ Hz, H-3^b), 5.49 (dd, 1 H, $J_{1^c,2^c}$ 8.0 Hz, $J_{2^c,3^c}$ 9.6 Hz, H-2^c), 5.43 (dd, 1 H, $J_{1^b,2^b}$ 8.0 Hz, $J_{2^b,3^b}$ 9.6 Hz, H-2^b), 4.98 (d, 1 H, $J_{1^c,2^c}$ 8.0 Hz, H-1^c), 4.96 (d, 1 H, $J_{1^a,2^a}$ 8.0 Hz, H-1^b), 4.86 (dd, 1 H, $J_{3^a,4^a} = J_{5^a,4^a} = 9.6$ Hz, H-4^a), 4.65–4.40 (m, 4 H), 4.22–3.67 (m, 7 H), 1.94, 1.79 (2 s, 2 CH_3CO). Anal. Calcd for $C_{80}H_{68}Cl_3NO_{26}$: C, 61.36; H, 4.35. Found: C, 61.05; H, 4.32.

2,3,4,6-Tetra-O-*benzoyl-β*-D-*glucopyranosyl-(1→6)-3*-O-*allyl-1,2*-O-*isopropylidene-α*-D-*glucofuranose* (**9**). —To a solution of **2** (13 g, 50 mmol) in dry DMF (50 mL), AllBr (4.4 mL, 1.01 equiv) and NaH (4.0 g, 49%) were added under cooling with an ice bath. The mixture was stirred for 2 h at rt, then diluted with CH_2Cl_2 and washed 3–4 times with H_2O. The organic phase was dried over anhyd Na_2SO_4, then concentrated to dryness. The resultant crude product was dissolved in 90% HOAc (100 mL), and the mixture was stirred overnight at 40 °C and then concentrated. The residue was purified by flash chromatography (2:1 petroleum ether–EtOAc) to give **8** (9.5 g, 73% for two steps) as a syrup. The donor **1** (1.5 g, 2 mmol) and acceptor **8** (520 mg, 2 mmol) were coupled under the same conditions as described for the synthesis of **3** by coupling of **1** with **2**. 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 **9** (1.25 g, 76%) as a syrup: $[\alpha]_D$ +35.1° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05–7.34 (m, 20 H, 4 Bz*H*), 5.94 (dd, 1 H, $J_{3',4'} = J_{4',5'} = 9.8$ Hz, H-4′), 5.88 (m, 1 H, –C*H*=), 5.84 (d, 1 H, $J_{1,2}$ 3.0 Hz, H-1), 5.71 (dd, 1 H, $J_{3',4'} = J_{2',3'} = 9.8$ Hz, H-3′), 5.54 (dd, 1 H, $J_{1',2'}$ 8.0 Hz, $J_{2',3'}$ 9.6 Hz, H-2′), 5.28–5.14 (m, 2 H, CH_2=), 4.94 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1′), 4.67 (dd, 1 H, $J_{6'^a,6'^b}$ 12.4 Hz, $J_{5',6'^a}$ 3.2 Hz, H-6′^{a}), 4.50 (d, 1 H, $J_{1,2}$ 3.0 Hz, H-2), 4.48 (dd, 1 H, $J_{6'^a,6'^b}$ 12.4 Hz, $J_{6'^a,6'^b}$ 3.2 Hz, H-6′^{b}), 4.12–3.86 (m, 7 H), 1.39, 1.28 (2 s, 2 CH_3). Anal. Calcd for $C_{46}H_{46}O_{15}$: C, 65.87; H, 5.49. Found: C, 65.71; H, 5.43.

2,3,4,6-Tetra-O-*benzoyl-β*-D-*glucopyranosyl-(1→6)-2,4-di*-O-*acetyl-3*-O-*allyl-α*-D-*glucopyranosyl trichloroacetimidate* (**10**).—A solution of **9** (1.20 g, 1.43 mmol) in 80% HOAc (50 mL) was heated under reflux for 4 h, then concentrated to dryness. The residue was dissolved in pyridine (10 mL), and then Ac_2O (1 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 reaction mixture was diluted with water, and extracted with CH_2Cl, washed with 1N HCl, water, and satd aq $NaHCO_3$. The organic phase was dried over anhyd Na_2SO_4, then concentrated to dryness. The resultant crude product was dissolved in a 1 M solution of NH_3 in MeOH (20 mL), and the mixture was stirred at rt until TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The solution was concentrated, and the residue was purified by column chromatography with 2:1 petroleum ether–EtOAc as the eluent to give 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,4-di-*O*-acetyl-α,β-D-glucopyranose as a syrup (830 mg, 64% for three steps). A mixture of the product, CCl_3CN (2.0 mL, 10 mmol), and DBU (0.20 mL, 1.50 mmol) in dry CH_2Cl_2 (20 mL) was stirred for 3 h and then concentrated. The residue was purified by flash chromatography (3:1 petroleum ether–EtOAc) to give **10** (840 mg, 87%) as a syrup: $[\alpha]_D$ +45.4° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (s, 1 H, N*H*), 8.06–7.29 (m, 20 H, 4 Bz*H*), 6.31 (d, 1 H, $J_{1,2}$ 3.2 Hz, H-1), 5.94 (dd, 1 H, $J_{3',4'} = J_{4',5'} = 9.6$ Hz, H-4′), 5.85 (m, 1 H, –C*H*=), 5.70 (dd, 1 H, $J_{3',4'} = J_{2',3'} = 9.8$ Hz, H-3′), 5.54 (dd, 1 H, $J_{1',2'}$ 8.0 Hz, $J_{2',3'}$ 9.6 Hz, H-2′), 5.29–5.18 (m, 2 H, CH_2=), 5.04 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1′), 4.88 (dd, 1 H, $J_{3,4} = J_{5,4} = 9.8$ Hz, H-4), 4.86 (dd, 1 H, $J_{6'^a,6'^b}$ 10.4 Hz, $J_{5',6'^a}$ 3.0 Hz, H-6′^{a}), 4.67 (dd, 1 H, $J_{6'^a,6'^b}$ 10.4 Hz, $J_{5',6'^b}$ 3.2 Hz, H-6′^{b}), 4.50 (dd, 1 H, $J_{1,2}$ 3.0 Hz, $J_{2,3}$ 9.6 Hz, H-2), 4.24–3.86 (m, 7 H), 2.04, 1.81 (2 s, 2 CH_3CO). Anal. Calcd for $C_{49}H_{46}Cl_3NO_{17}$: C, 57.28; H, 4.48. Found: C, 57.41; H, 4.41.

2,3,4,6-Tetra-O-*benzoyl-β*-D-*glucopyranosyl-(1→3)-2,4,6-tri*-O-*acetyl-α*-D-*glucopyranosyl trichloroacetimidate* (**11**).—A solution of **3** (900 mg, 1.07 mmol) in 80% HOAc (20 mL) was heated under reflux for 4 h, then concentrated to dryness. The residue was dissolved in pyridine (10 mL), and then Ac_2O (1 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 reaction mixture was diluted with water (10 mL), then extracted with CH_2Cl_2 and

washed with dil HCl. The organic phase was combined, dried, and concentrated. The resultant crude product was dissolved in a 1 M solution of NH_3 in MeOH (20 mL), and the mixture was stirred at rt until TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The solution was concentrated, and the residue was purified on a silica gel column with 2:1 petroleum ether–EtOAc to give 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2,4-di-*O*-acetyl-α,β-D-glucopyranose as a syrup (675 mg, 71% for three steps). A mixture of the hemiacetal, CCl_3CN (1.5 mL, 7.5 mmol), and DBU (0.15 mL, 1.20 mmol) in dry CH_2Cl_2 (20 mL) was stirred for 3 h and then concentrated. The residue was purified by flash chromatography (2:1 petroleum ether–EtOAc) to give **11** (600 mg) as a syrup: $[\alpha]_D$ +21.3° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (s, 1 H, N*H*), 8.06–7.27 (m, 20 H, 4 Bz*H*), 6.44 (d, 1 H, $J_{1,2}$ 3.2 Hz, H-1), 5.95 (dd, 1 H, $J_{3',4'} = J_{4',5'} = 9.6$ Hz, H-4′), 5.74 (dd, 1 H, $J_{3',4'} = J_{2',3'} = 9.8$ Hz, H-3′), 5.46 (dd, 1 H, $J_{1',2'} = J_{2',3'} = 8.8$ Hz, H-2′), 5.19 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4), 5.03 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1′), 4.86 (dd, 1 H, $J_{6'}{}^{a},{}_{6'}{}^{b}$ 10.4 Hz, $J_{5',6'}{}^{a}$ 3.0 Hz, H-6′^{a}), 4.69 (dd, 1 H, $J_{6'}{}^{a},{}_{6'}{}^{b}$ 10.4 Hz, $J_{5',6'}{}^{b}$ 3.2 Hz, H-6′^{b}), 4.48 (dd, 1 H, $J_{1,2}$ 3.0 Hz, $J_{2,3}$ 9.6 Hz, H-2), 4.24–4.07 (m, 5 H), 2.08, 1.99, 1.81 (3 s, 3 C*H*$_3$CO). Anal. Calcd for $C_{48}H_{44}Cl_3NO_{18}$: C, 56.00; H, 4.08. Found: C, 55.83; H, 4.03.

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-β*-D-*glucopyranosyl-(1→3)-2*-O-*acetyl-4,6*-O-*benzylidene-β*-D-*glucopyranoside* (**13**).—Compound **13** was prepared by coupling of **6** (800 mg, 0.51 mmol) with **12**[5] (190 mg, 0.51 mmol) under the same conditions as described for the synthesis of **3** by coupling of **1** with **2**. Concentration of the reaction mixture, followed by purification on a silica gel column with 3:1 petroleum ether–EtOAc as the eluent, gave a tetrasaccharide (607 mg, 67%). The tetrasaccharide was quantitatively acetylated in pyridine (10 mL) with Ac_2O (2 mL), then concentrated to dryness. The residue was purified by flash chromatography (2:1 petroleum ether–EtOAc) to give **13** (592 mg, 95%) as a syrup: $[\alpha]_D$ +45.1° (*c* 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01–7.32 (m, 45 H, 9 PhH), 6.95–6.82 (dd, 4 H, –C_6H_4–), 5.88 (dd, 1 H, $J_3{}^{d},{}_4{}^{d} = J_4{}^{d},{}_5{}^{d} = 9.6$ Hz, H-4^d), 5.86 (dd, 1 H, $J_4{}^{c},{}_5{}^{c} = J_3{}^{c},{}_4{}^{c} = 9.6$ Hz, H-4^c), 5.66 (dd, 1 H, $J_3{}^{d},{}_4{}^{d} = J_4{}^{d},{}_5{}^{d} = 9.6$ Hz, H-3^d), 5.65 (dd, 1 H, $J_3{}^{c},{}_4{}^{c} = J_2{}^{c},{}_3{}^{c} = 9.6$ Hz, H-3^c), 5.51 (s, 1 H, PhCH), 5.45 (dd, 1 H, $J_1{}^{d},{}_2{}^{d}$ 8.0 Hz, $J_2{}^{d},{}_3{}^{d}$ 9.6 Hz, H-2^d), 5.41 (dd, 1 H, $J_1{}^{c},{}_2{}^{c}$ 8.0 Hz, $J_2{}^{c},{}_3{}^{c}$ 9.6 Hz, H-2^c), 5.27 (dd, 1 H, $J_1{}^{a},{}_2{}^{a}$ 8.0 Hz, $J_2{}^{a},{}_3{}^{a}$ 9.6 Hz, H-2^a), 4.96 (d, 1 H, $J_1{}^{d},{}_2{}^{d}$ 8.0 Hz, H-1^d), 4.86 (d, 1 H, $J_1{}^{a},{}_2{}^{a}$ 8.0 Hz, H-1^a), 4.84 (dd, 1 H, $J_1{}^{b},{}_2{}^{b} = J_2{}^{b},{}_3{}^{b} = 9.2$ Hz, H-2^b), 4.79 (m, 2 H), 4.72 (d, 1 H, $J_1{}^{c},{}_2{}^{c}$ 8.0 Hz, H-1^c), 4.68–4.48 (m, 4 H, 2 H-6^a, 2 H-6^d), 4.41 (d, 1 H, $J_1{}^{b},{}_2{}^{b}$ 8.0 Hz, H-1^b), 4.18–3.82 (m, 8 H), 3.81 (s, 3 H, CH_3O), 3.67–3.63 (m, 2 H), 2.03, 1.94, 1.79 (3 s, 3 CH_3CO). Anal. Calcd for $C_{100}H_{90}O_{33}$: C, 66.01; H, 4.95. Found: C, 66.07; H, 4.91.

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-β*-D-*glucopyranosyl-(1→3)-2,4,6-tri*-O-*acetyl-β*-D-*glucopyranoside* (**15**).—To a solution of **13** (900 mg, 0.50 mmol) in MeOH (50 mL) was added AcCl (0.3 mL). The solution was stoppered in a flask and stirred at rt for 1 h, at the end of which time TLC (1:1 petroleum ether–EtOAc) showed that the starting material had disappeared. The solution was neutralized with Et_3N, then concentrated to dryness. The residue was purified by flash chromatography (2:1 petroleum ether–EtOAc) to give **14** (750 mg, 83%) as a syrup. Compound **14** (50 mg, 0.29 mmol) was dissolved in pyridine (2 mL) and Ac_2O (0.1 mL) was added. After stirring the mixture at rt for 12 h, TLC (1:1 petroleum ether–EtOAc) showed that the reaction was complete. The residue was purified by flash chromatography (2:1 petroleum ether–EtOAc) to give **15** (45 mg, 90%) as a syrup: $[\alpha]_D$ +39.1° (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98–7.35 (m, 40 H, 8 PhH), 6.95–6.80 (dd, 4 H, –C_6H_4–), 5.86 (dd, 1 H, $J_3{}^{d},{}_4{}^{d} = J_4{}^{d},{}_5{}^{d} = 9.6$ Hz, H-4^d), 5.84 (dd, 1 H, $J_4{}^{c},{}_5{}^{c} = J_3{}^{c},{}_4{}^{c} = 9.6$ Hz, H-4^c), 5.69 (dd, 1 H, $J_3{}^{d},{}_4{}^{d} = J_2{}^{d},{}_3{}^{d} = 9.6$ Hz, H-3^d), 5.67 (dd, 1 H, $J_3{}^{c},{}_4{}^{c} = J_2{}^{c},{}_3{}^{c} = 9.6$ Hz, H-3^c), 5.49 (dd, 1 H, $J_1{}^{d},{}_2{}^{d}$ 8.0 Hz, $J_2{}^{d},{}_3{}^{d}$ 9.6 Hz, H-2^d), 5.39 (dd, 1 H, $J_1{}^{c},{}_2{}^{c}$ 8.0 Hz, $J_2{}^{c},{}_3{}^{c}$ 9.6 Hz, H-2^c), 5.14 (d, 1 H, $J_1{}^{d},{}_2{}^{d}$ 8.0 Hz, H-1^d), 5.12 (dd, 1 H, $J_1{}^{a},{}_2{}^{a}$ 8.0 Hz, $J_2{}^{a},{}_3{}^{a}$ 9.6 Hz, H-2^a), 4.94 (dd, 1 H, $J_4{}^{b},{}_5{}^{b} = J_3{}^{b},{}_4{}^{b} = 9.6$ Hz, H-4^b), 4.86 (d, 1 H, $J_1{}^{c},{}_2{}^{c}$ 8.0 Hz, H-1^c), 4.82 (d, 1 H, $J_1{}^{a},{}_2{}^{a}$ 8.0 Hz, H-1^a), 4.70 (m, 2 H, H-4^a, H-2^b), 4.68–4.48 (m, 4 H, 2 H-6^a, 2 H-6^d), 4.33 (d, 1 H, $J_1{}^{b},{}_2{}^{b}$ 8.4 Hz, H-1^b), 4.22–4.3.81 (m, 7 H), 3.81 (s, 3 H, CH_3O), 3.67–3.63 (m, 3 H), 2.03, 1.94, 1.79 (5 CH_3CO). Anal. Calcd for $C_{97}H_{90}O_{35}$: C, 64.17; H, 4.96. Found: C, 63.91; H, 4.92.

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-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* (**16**).—The acceptor **14** (220 mg, 0.13 mmol) and donor **1** (100 mg, 0.13 mmol) were dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2 (20 mL). TMSOTf (15 μL) was added dropwise at −20 °C with N_2 protection. The reaction mixture was stirred for 3 h, during which time the reaction mixture 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. To the solution of the product in pyridine (20

mL), Ac_2O (1 mL, 10 mmol) was added dropwise, and the mixture was stirred overnight at rt. TLC (1.5:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was diluted with CH_2Cl_2, washed with 1N HCl, water, and then with satd aq $NaHCO_3$. The organic layers were combined, dried, and concentrated. Purification by column chromatography (2:1 petroleum ether–EtOAc) gave **16** (220 mg, 74% for two steps) as a syrup: $[\alpha]_D$ +43.1° (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.08–7.32 (m, 60 H, 12 BzH), 6.81 (dd, 4 H, $-C_6H_4-$), 5.85 (dd, 1 H, *J* 9.6 Hz), 5.84 (dd, 1 H, *J* 9.6 Hz), 5.76 (dd, 1 H, *J* 9.6 Hz), 5.66–5.62 (m, 3 H), 5.49 (dd, 1 H, *J* 9.2 Hz), 5.47 (dd, 1 H, *J* 9.6 Hz), 5.37 (dd, 1 H, *J* 9.6 Hz), 4.96 (d, 1 H, *J* 8.0 Hz, βH-1), 4.91 (dd, 1 H, *J* 9.6 Hz), 4.89 (d, 1 H, *J* 8.0 Hz, βH-1), 4.82 (dd, 1 H, *J* 8.0 Hz, βH-1), 4.63–4.55 (m, 6 H), 4.52–4.47 (m, 4 H), 4.43 (d, 1 H, *J* 8.0 Hz, βH-1), 4.16–4.09 (m, 2 H), 3.97–3.94 (m, 1 H), 3.88–3.80 (m, 3 H), 3.76 (s, 3 H, CH_3O), 3.67–3.62 (m, 2 H), 3.57–3.51 (m, 2 H), 3.49–3.42 (m, 1 H), 2.04, 1.86, 1.86, 1.66 (4 CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.53, 169.10, 168.76, 168.20 (4 CH_3CO), 166.02, 165.97, 165.93, 165.76, 165.64, 165.57, 165.17, 165.15, 165.09, 165.04, 164.98, 164.75 (12 C_6H_5CO), 155.84, 151.27, 133.61, 133.44, 133.40, 133.34, 133.31, 133.21, 133.18, 133.15, 133.08, 132.85, 118.07, 116.41, 101.14, 100.35, 100.35, 99.83, 99.47 (5 C-1), 73.85. 73.54, 73.01, 72.77, 72.77, 72.57, 72.35, 72.38, 72.15, 71.86, 71.86, 71.76, 71.45, 69.44, 69.40, 69.33, 68.85, 68.26, 67.67, 62.67, 55.53, 20.96, 20.82, 20.75, 20.40. Anal. Calcd for $C_{129}H_{114}O_{43}$: C, 65.87; H, 4.85. Found: C, 65.88; H, 4.82. Anal. Calcd for $C_{129}H_{114}O_{43}$: C, 65.87; H, 4.85. Found: C, 65.79; H, 4.87.

4-Methoxyphenyl β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→6)]-β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→6)]-β-D-glucopyranoside (**17**). —Compound **16** (200 mg, 0.085 mmol) was added to an NH_3-satd MeOH solution (40 mL). After a week at rt, the reaction mixture was concentrated, and the residue was purified by chromatography on Sephadex LH-20 (column 2.0 × 30 cm, flow 5 mL/min, about 300 mL MeOH) to afford the product **17** (75 mg, 95%) as a white amorphous powder: $[\alpha]_D$ +24.2° (*c* 5.0, $HOCH_3$); ^1H NMR (400 MHz, D_2O): δ 6.80 (dd, 4 H, $-C_6H_4-$), 4.93 (d, 1 H, *J* 7.6 Hz, H-1),), 4.74 (d, 1 H, *J* 7.6 Hz, H-1), 4.63 (d, 1 H, *J* 8.0 Hz, H-1), 4.41 (d, 1 H, *J* 7.6 Hz, H-1), 4.35 (d, 1 H, *J* 7.6 Hz, H-1), 4.09 (m, 2 H), 3.82–3.22 (m, 31 H); ^{13}C NMR (100 MHz, D_2O): δ 157.33, 153.21, 120.92, 117.63, 105.23, 105.23, 105.04, 105.04, 103.36 (5 C-1), 87.45, 86.92 (2 C-3), 78.48, 78.32, 78.22, 78.17, 77.45, 77.02, 75.98, 75.85, 75.66, 75.50, 74.85, 72.16, 71.23, 70.76, 70.69, 70.55, 63.31, 63.31, 63.31, 58.42. Anal. Calcd for $C_{37}H_{58}O_{27}$: C, 47.53; H, 6.21. Found: C, 47.68; H, 6.12.

4-Methoxyphenyl 2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl-(1→6)-2,4-di-O-acetyl-3-O-allyl-β-D-glucopyranosyl-(1→3)-2-O-acetyl-4,6-O-benzylidene-β-D-glucopyranoside (**18**).—Compound **18** was prepared by coupling of **10** (800 mg, 0.78 mmol) with **12** (210 mg, 0.78 mmol) under the same conditions as described for the synthesis of **3** by coupling of **1** with **2**. 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. Acetylation in pyridine (10 mL) with Ac_2O (1 mL), and concentration, then purification of the residue by flash chromatography (2:1 petroleum ether–EtOAc) gave **18** (950 mg, 67% for two steps) as a syrup: $[\alpha]_D$ +17.0° (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.90–7.32 (m, 25 H, 5 PhH), 6.95–6.82 (dd, 4 H, $-C_6H_4-$), 5.88 (dd, 1 H, $J_{4'',5''} = J_{3'',4''} = 9.6$ Hz, H-4″), 5.70–5.68 (m, 2 H, –CH=, H-3″), 5.66 (dd, 1 H, $J_{2'',3''} = J_{1'',2''} =$ 9.6 Hz, H-2″), 5.46 (s, 1 H, pHCH), 5.35 (dd, 1 H, $J_{2,3} = J_{1,2} = 9.6$ Hz, H-2), 5.16–5.07 (m, 2 H, $=CH_2$), 5.01 (d, 1 H, $J_{1'',2''}$ 8.0 Hz, H-1″), 4.87 (dd, 1 H, $J_{3',4'}$ 8.0 Hz, $J_{4',5'}$ 9.6 Hz, H-4′), 4.80 (dd, 1 H, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 9.6 Hz, H-2′), 4.78 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.62 (m, 1 H, H-6″^{a}), 4.54 (m, 1 H, H-6″^{b}), 4.45 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1′), 4.24–4.16 (m, 2 H), 3.97–3.82 (m, 4 H), 3.81 (s, 3 H, CH_3O), 3.73–3.56 (m, 3 H), 3.49–3.44 (m, 3 H), 1.96, 1.80, 1.75 (3 s, 3 CH_3CO). Anal. Calcd for $C_{69}H_{68}O_{24}$: C, 64.69; H, 5.31. Found: C, 64.71; H, 5.28.

4-Methoxyphenyl 2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl-(1→6)-2,4-di-O-acetyl-3-O-allyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-O-acetyl-β-D-glucopyranoside (**20**).—Compound **19** (220 mg, 84%) was prepared by debenzylidenation of **18** (280 mg, 0.22 mmol) under the same conditions as described for the preparation of **14** with AcCl in MeOH. For the convenience of identification, **19** (50 mg) was acetylated with Ac_2O in pyridine to give **20** (45 mg, 92%) as a syrup: $[\alpha]_D$ +27.6° (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.06–7.29 (m, 20 H, 4 BzH), 6.92–6.83 (dd, 4 H, $-C_6H_4-$), 5.92 (dd, 1 H, $J_{3'',4''} = J_{4'',5''} = 9.6$ Hz, H-4″), 5.80 (m, 1 H, –CH=), 5.70 (t, 1 H, $J_{3'',4''} = J_{2'',3''} = 9.8$ Hz, H-3″), 5.50 (dd, 1 H, $J_{1'',2''}$ 8.0 Hz, $J_{2'',3''}$ 9.6 Hz, H-2″), 5.27–5.16 (m, 2 H, $CH_2=$), 5.08 (d, 1 H, $J_{1'',2''}$ 8.0 Hz, H-1″), 5.01 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4), 4.88 (dd, 1 H, $J_{1,2} = J_{2,3} = 9.8$ Hz, H-2), 4.83 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.81 (m, 2 H, H-4′, H-2′), 4.72 (dd, 1 H, $J_{6'^a,6'^b}$ 10.4 Hz, $J_{5',6'}$ 3.0 Hz, H-6′^{a}), 4.64 (dd, 1 H, $J_{6'^a,6'^b}$ 10.4 Hz, $J_{5',6'}$ 3.2 Hz, H-6′^{b}), 4.47 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1′), 4.14–3.88 (m, 5 H), 3.82 (s, 3 H, CH_3O), 3.78–3.42 (m, 6 H), 2.09, 2.07, 2.04, 1.92, 1.81 (5 s, 5 CH_3CO). Anal. Calcd for $C_{66}H_{68}O_{26}$: C, 62.07; H, 5.33. Found: C, 62.32; H, 5.37.

4-Methoxyphenyl 2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl-(1→6)-2,4-di-O-acetyl-3-O-allyl-β-D-gluco-

pyranosyl-(1→3)-[2,3,4,6-tetra-O-*benzoyl-β*-D-*gluco-pyranosyl-(1→3)-2,4,6-tri*-O-*acetyl-β*-D-*glucopyranosyl-(1→6)]-2,4-di*-O-*acetyl-β*-D-*glucopyranoside* (**21**).—Compound **19** (180 mg, 0.15 mmol) and donor **11** (150 mg, 0.15 mmol) were dried together under high vacuum for 4 h, then dissolved in anhyd CH_2Cl_2 (20 mL). TMSOTf (60 μL) was added dropwise at −20 °C with N_2 protection. The reaction mixture was stirred for 3 h, during which time the reaction mixture 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. To a solution of the product in pyridine (10 mL), Ac_2O (0.1 mL, 1 mmol) was added dropwise, and the mixture was stirred overnight at rt. TLC (1.5:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was diluted with CH_2Cl_2, washed with 1N HCl, water, and satd aq $NaHCO_3$. The organic layers were combined, dried, and concentrated. Purification by column chromatography (1:1 petroleum ether–EtOAc) gave **21** (220 mg, 69% for two steps) as a foamy solid: $[\alpha]_D$ +32.5° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90–7.32 (m, 40 H, 8 BzH), 6.95–6.82 (dd, 4 H, $-C_6H_4-$), 5.92 (dd, 1 H, *J* 9.6 Hz), 5.89 (dd, 1 H, *J* 9.6 Hz), 5.72–5.60 (m, 3 H), 5.50 (dd, 1 H, *J* 9.6 Hz), 5.47 (dd, 1 H, *J* 9.6 Hz), 5.15–4.90 (m, 7 H), 4.73 (d, 1 H, *J* 8.0 Hz, βH-1), 4.71 (d, 1 H, *J* 8.0 Hz, βH-1), 4.68–4.59 (m, 3 H), 4.56–4.43 (m, 3 H), 4.42 (d, 1 H, *J* 8.0 Hz, βH-1), 4.34 (d, 1 H, *J* 8.0 Hz, βH-1), 4.26–4.05 (m, 6 H), 4.01–3.87 (m, 3 H), 3.85–3.71 (m, 4 H), 3.67 (m, 1 H), 3.60–3.54 (m, 2 H), 3.49–3.44 (m, 2 H), 3.42 (m, 1 H), 2.10, 2.05, 2.04, 1.96, 1.94, 1.80, 1.60 (7 s, 7 CH_3CO). Anal. Calcd for $C_{110}H_{108}O_{42}$: C, 62.86; H, 5.14. Found: C, 63.01; H, 5.10.

4-Methoxyphenyl 2,3,4,6-tetra-O-*benzoyl-β*-D-*gluco-pyranosyl-(1→6)-2,4-di*-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)]-2,4-di*-O-*acetyl-β*-D-*glucopyranoside* (**22**).—To a solution of **21** (220 mg) in MeOH (10 mL) was added $PdCl_2$ (15 mg). After stirred for 3 h at rt, TLC (3:2 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 (2:1 petroleum ether–EtOAc) to give **22** (180 mg, 84%) as a syrup: $[\alpha]_D$ +46.1° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90–7.32 (m, 40 H, 8 BzH), 6.95–6.82 (dd, 4 H, $-C_6H_4-$), 5.92 (dd 1 H, *J* 9.6 Hz), 5.89 (dd, 1 H, *J* 9.6 Hz), 5.72–5.60 (m, 3 H), 5.50 (dd, 1 H, *J* 9.6 Hz), 5.47 (dd, 1 H, *J* 9.6 Hz), 5.15–4.90 (m, 7 H), 4.73 (d, 1 H, *J* 8.0 Hz, βH-1), 4.71 (d, 1 H, *J* 8.0 Hz, βH-1), 4.68–4.59 (m, 3 H), 4.56–4.43 (m, 3 H), 4.42 (d, 1 H, *J* 8.0 Hz, βH-1), 4.34 (d, 1 H, *J* 8.0 Hz, βH-1), 4.26–4.05 (m, 3 H), 4.01–3.87 (m, 3 H), 3.85–3.71 (m, 2 H), 3.67 (m, 1 H), 3.60–3.54 (m, 2 H), 3.49–3.44 (m, 2 H), 3.42 (m, 1 H), 2.10, 2.05, 2.04, 1.96, 1.94, 1.80, 1.60 (7 s, 7 CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.65, 170.36, 169.49, 169.49, 169.20, 168.67, 168.05 (7 CH_3CO), 165.99, 165.99, 165.93, 165.66, 165.34, 165.14, 165.14, 164.83 (8 C_6H_5CO), 155.21, 151.32, 133.61, 133.44, 133.40, 133.34, 133.31, 133.21, 133.18, 133.15, 133.08, 132.85, 117.74, 114.67, 101.04, 100.60, 100.49, 100.22, 99.60 (5 C-1), 78.56, 78.39, 73.99, 73.49, 73.21, 72.85, 72.63, 72.36, 72.12, 71.90, 71.52, 71.23, 69.52, 69.34, 68.52, 67.10, 67.68, 67.43, 20.96, 20.75, 20.68, 20.54, 20.52, 20.46, 20.37. Anal. Calcd for $C_{107}H_{104}O_{42}$: C, 62.33; H, 5.05. Found: C, 62.15; H, 4.99.

4-Methoxyphenyl β-D-*glucopyranosyl-(1→6)-β*-D-*glucopyranosyl-(1→3)-[β*-D-*glucopyranosyl-(1→3)-β*-D-*glucopyranosyl-(1→6)]-β*-D-*glucopyranoside* (**23**).—Compound **22** (180 mg, 1.07 mmol) was added to a satd solution of NH_3 in MeOH (40 mL). After a week at rt, the reaction mixture was concentrated, and the residue was purified by chromatography on a Sephadex LH-20 (column 2.0 × 30 cm, flow 5 mL/min, about 300 mL MeOH) to afford the pentasaccharidic **23** (76 mg, 93%) as a white amorphous powder: $[\alpha]_D$ +47.5° (*c* 3.3, CH_3OH); ^{1}H NMR (400 MHz, $HOCH_3$): δ 6.92–6.83 (dd, 4 H, $-C_6H_4-$), 4.97 (d, 1 H, *J* 8.0 Hz, H-1), 4.65 (d, 1 H, *J* 7.8 Hz, H-1), 4.60 (d, 1 H, *J* 7.6 Hz, H-1), 4.41 (d, 1 H, *J* 7.6 Hz, H-1), 4.40 (d, 1 H, *J* 8.0 Hz, H-1), 4.10 (m, 2 H), 3.83–3.22 (m, 31 H); ^{13}C NMR (100 MHz, D_2O): δ 157.19, 154.23, 121.01, 117.71, 105.39, 105.35, 105.20, 104.75, 103.32 (5 C-1), 87.54, 87.54 (2 C-3), 78.53, 78.37, 78.20, 78.15, 78.06, 77.98, 77.60, 77.39, 76.01, 75.88, 75.71, 75.23, 74.85, 72.21, 72.15, 72.09, 71.27, 70.76, 70.65, 63.34, 63.34, 63.25, 58.52. Anal. Calcd for $C_{37}H_{58}O_{27}$: C, 47.53; H, 6.21. Found: C, 47.72; H, 6.16.

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