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Synthesis of β-D-glucose oligosaccharides from *Phytophthora parasitica*

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Abstract

The glucohexaose, 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*-(1→3)-D-Glc*p*, was synthesized as its allyl glycoside via 3+3 strategy. The trisaccharide donor, 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl trichloroacetimidate (**11**), was obtained by 3-selective coupling of isopropyl 4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (**2**) with 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranosyl trichloroacetimidate (**6**), followed by hydrolysis, acetylation, dethiolation, and trichloroacetimidation. Meanwhile, the trisaccharide acceptor, allyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2-*O*-acetyl-β-D-glucopyranosyl-(1→3)-4,6-di-*O*-acetyl-2-*O*-benzoyl-α-D-glucopyranoside (**14**), was prepared by coupling of allyl 4,6-di-*O*-acetyl-2-*O*-benzoyl-α-D-glucopyranoside (**12**) with **6**, followed by debenzylidenation. Condensation of **14** with **11**, followed by deacylation, gave the target hexaoside. A β-(1→3)-linked tetrasaccharide **29** was also synthesized with methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranoside (**25**) as the acceptor and acylated β-(1→3)-linked disaccharide **21** as the donor.

Keywords: β-D-Glucans; Trichloroacetimidates; Regio- and stereoselective synthesis

1. Introduction

Glucans consisting of (1→3)-β-D linkages with various (1→6)-β-D-linked mono-, di-, and trisaccharide branches having 0, 1, or 2 (1→3)-linked β-D-glucose resides (Fig. 1), have been found in fruiting bodies and culture broths of fungi such as *Phytophthora parasitica*,[1] *Sclerotium glucanicum*,[2] *Auricularia auricula-judae*,[3] *Pullularia pullulans*,[4] *Pleurotus ostreatus*,[5] *Cordyceps ophioglossoides*,[6] and *Ganoderma applanaum*.[7] Since these glucans show antitumor activity, chemists are interested in synthesizing the minimum active unit of the natural polysaccharides to investigate their structure–activity relationships.[8–11] Some linear and branched glucans have been synthesized by different methods[8–12]; now we report the stereoselective synthesis of the allyl glycoside, of β-D-Glcp-(1→3)-[β-D-Glcp-(1→3)-β-D-Glcp-(1→3)-β-D-Glcp-(1→6)]-β-D-Glcp-(1→3)-D-Glcp, with benzylidenated glucose derivatives as the key intermediates.

2. Results and discussion

Retrosynthetic analysis reveals that the best way to synthesize the target hexaose is to first prepare two β-(1→3)-linked trisaccharide fragments, then connect them at the C-6 of the glucose residue of the trisaccharide backbone. For achieving the formation of β-glucosidic linkages, the use of a C-2 ester in the donor capable of neighboring group participation is necessary. However, our previous studies[13] indicated that in (1→3)-

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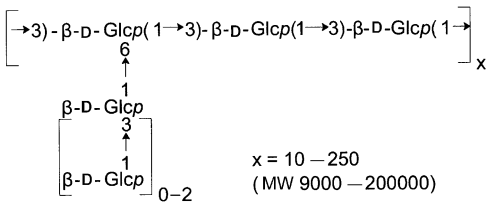


Fig. 1. Polysaccharide structure of *P. parasitica*.

glucosylation the glycosyl bond originally present in either donor or acceptor controlled the stereoselectivity of the forthcoming bond, i.e., the newly formed glycosidic linkage had the opposite anomeric configuration of that of either the donor or acceptor. With β-(1→3)-linked disaccharides as the acceptor and an acylated glucosyl trichloroacetimidate as the donor, or with a β-(1→3)-linked acylated disaccharide trichloroacetimidate as the donor and a glucoside as the acceptor, α-linked trisaccharides are always obtained in spite of the C-2 neighboring group participation. However, some reports[9,11] revealed that with 4,6-*O*-benzylidenated glucose derivatives as either donor or acceptor, β-linked oligosaccharides are readily obtained. Thus, in the present research, the benzylidenated glucose derivatives were applied as the key intermediates. As outlined in Scheme 1, isopropyl 4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (**2**),[8] obtained from 4,6-*O*-benzylidenation of isopropyl 1-thio-β-D-glucopyranoside, was used as the starting material. Coupling of **2** with the donor **1** selectively afforded β-(1→3)-linked disaccharide **3**. Acetylation of **3** gave **4** and the 2D ^{1}H NMR spectrum of **4** clearly showed H-2 at δ 5.59 with $J_{1,2}$ 7.8, $J_{2,3}$ 9.9 Hz, confirming the regioselectivity of the glycosylation. Due to the instability of the *O*-benzylidene group of **4** under the coupling conditions used for the thioglycoside donor, transformation of **4** to the corresponding trichloroacetimidate donor **6** was carried out. It was reported[14] that transformation of thioglycosides to the corresponding hemiacetals was achieved by treating the thioglycosides with water, *N*-bromosuccinimide (NBS) and catalytic TMSOTf in acetone. It was found, in our research, that treatment of **4** with *N*-iodosuccinimide (NIS) and catalytic TMSOTf in reagent grade dichloromethane without addition of water gave better results, smoothly affording the hemiacetal **5** (85%). Subsequent trichloroacetimidation[15] of **5** furnished the disaccharide donor **6** (89%). Condensation of **6** with the acceptor **2** again selectively offered β-(1→3)-linked trisaccharide **7** (83%). The 3-O-selective glycosylation was confirmed by debenzylidenation and followed by acetylation to give **9** whose ^{1}H NMR spectrum showed H-2 at δ 4.85 with $J_{1,2}$ 9.9, $J_{2,3}$ 9.6 Hz. Reiteration of the dethioisopropylation and trichloroacetimidation yielded the trisaccharide donor **11** (81% for two steps), suitable for construction of the side chain. The trisaccharide backbone was also similarly prepared. Thus, coupling of **6** with allyl 4,6-*O*-acetyl-2-*O*-benzoyl-α-D-glucopyranoside (**12**)[9] furnished β-(1→3)-linked trisaccharide **13** (86%). Debenzylidenation of **13** afforded the trisaccharide acceptor **14** (87%). Condensation of **14** with **11** selectively gave the (1→6)-linked hexasaccharide **15** (64%), and subsequent deacylation yielded the target hexasaccharide **16** (96%). The ^{1}H and ^{13}C NMR spectra of **16** showed characteristic signals such as at δ 4.86 (1 H, $J_{1,2}$ 3.6 Hz, α-H-1), 4.71 (1 H, $J_{1,2}$ 7.6 Hz, β-H-1), 4.69, 4.69, 4.60, 4.41 (4 H, $J_{1,2}$ 8.0 Hz, β-H-1), 102.9, 102.9, 102.8, 102.7, 102.6 ($J_{C\text{-}1,H\text{-}1}$ 163.2, 163.2, 165.1, 164.5, 164.3, 5 β-C-1), 97.2 ($J_{C\text{-}1,H\text{-}1}$ 171.6 Hz, α-C-1). The ^{13}C NMR data of C-3 also indicated selective C-6 glycosylation of **14** with **11**; otherwise, if C-4 were glycosylated, one more signal at δ 82–84 would appear.

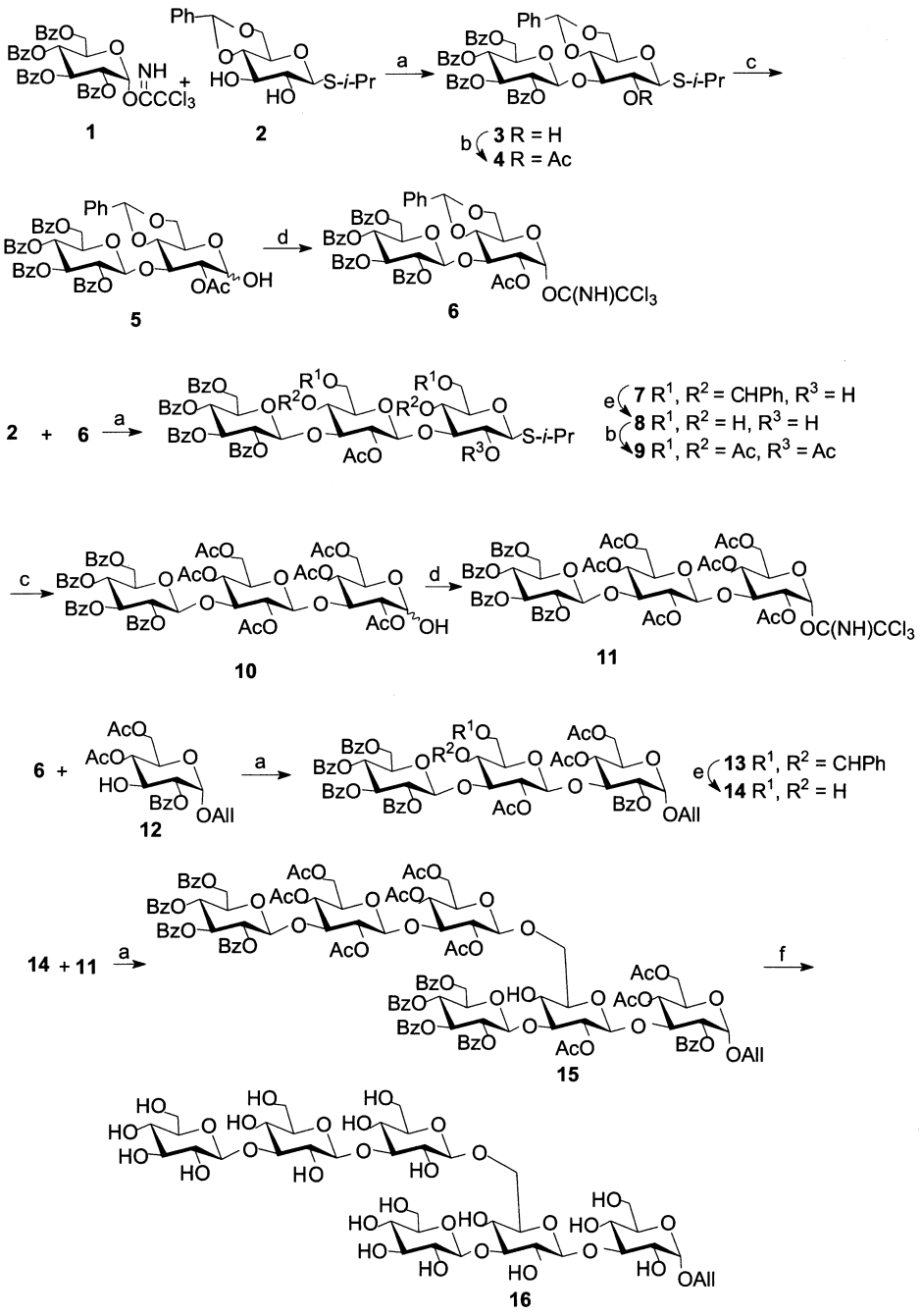
For investigation of the conditions necessary for glucose β-(1→3) linkage formation and preparation of more complex glucans, coupling of the β-(1→3)-linked disaccharide donor **21** with the β-(1→3)-linked disaccharide acceptor **25** bearing a 4,6-*O*-benzylidene group at the nonreducing end was carried out giving β-(1→3)-linked tetrasaccharide **26** (60%). This is different from the coupling that gives completely α-linked tetrasaccharide[13b] with acylated β-(1→3)-linked disaccharides as the donors and acylated β-(1→3)-linked disaccharides as the acceptors, indicating the important role of the 4,6-*O*-benzylidene group in control of the stereoselectivity of glycosylation (Scheme 2).

In summary, a convergent synthesis of glucose hexasaccharide containing a β-(1→3)-linked backbone with a β-(1→6)-linked trisaccharide branch having 2 (1→3)-linked β-D-glucose residues was achieved. The method is simple and practical, and it should be possible to apply the process to large-scale synthesis.

3. Experimental

3.1. General methods

Optical rotations were determined at 25 °C with a Perkin–Elmer Model 241-Mc automatic polarimeter. ^{1}H, ^{13}C NMR and ^{1}H–^{1}H, ^{1}H–^{13}C COSY spectra were recorded with Bruker ARX 400 spectrometers (400 MHz for ^{1}H, 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, 18 × 300, 35 × 400 mm) of silica gel (100–200 mesh) with EtOAc–petroleum ether (60–90 °C) as the eluent. Solutions were concentrated at <60 °C under reduced pressure.



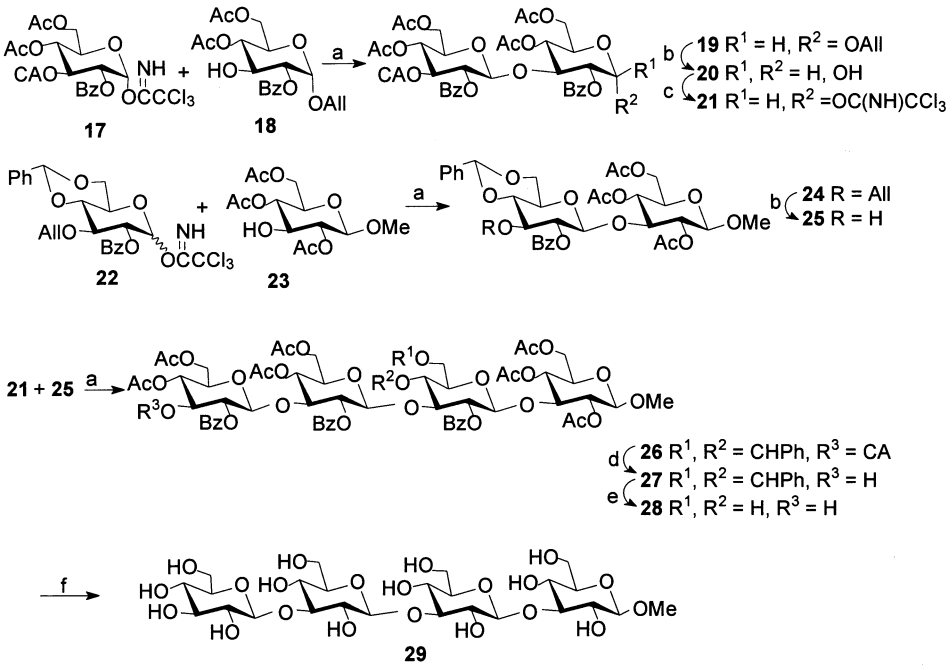
Scheme 1. Conditions and reagents for Scheme 1: (a) TMSOTf, CH_2Cl_2, −20 °C to rt; (b) Ac_2O, pyridine, rt, 12 h; (c) NIS, TMSOTf, CH_2Cl_2, 3 h; (d) CCl_3CN, CH_2Cl_2, DBU, rt; (e) 90% HOAc–H_2O, reflux, 3 h; (f) MeOH, NH_3, rt, 1 week.

3.2. General procedure for the glycosylations

The mixture of donor and acceptor was dried together under high vacuum for 2 h, then dissolved in anhyd CH_2Cl_2. MeSiOTf (0.05 equiv) was added drop-wise 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. The mixture was then neutralized with Et_3N. Concentration of the reaction mixture, followed by purification on a silica gel column, gave the desired products.

3.3. Isopropyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2-*O*-acetyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (4)

As described in the general procedure, **1** (4.09 g, 5.52 mmol) and **2** (1.72 g, 5.27 mmol) were coupled, and the product was purified by silica gel column chromatography with 3:1 petroleum ether–EtOAc as the eluent to give **3** (4.53 g, 95%). To a solution of **3** (4.41 g, 4.88 mmol) in Py (20 mL) was added Ac_2O (3 mL, 31.8 mmol), the reaction mixture was stirred for 4 h, at the



Scheme 2. Conditions and reagents for Scheme 2: (a) TMSOTf, CH_2Cl_2, −20 °C to rt; (b) $PdCl_2$, CH_2Cl_2, MeOH, rt; (c) CCl_3CN, CH_2Cl_2, DBU, rt; (d) thiourea, CH_2Cl_2, MeOH, reflux, 17 h. (e) 90% HOAc–H_2O, reflux, 3 h; (f) MeOH, NH_3, rt, 1 week.

end of which time the TLC (4:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was concentrated to dryness and then purified by column chromatography with 3:1 petroleum ether–EtOAc as the eluent to afford **4** (4.47 g, 96%): $[\alpha]_D$ + 34.7° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.03–7.25 (m, 25 H, 4 Bz-*H*, Ph-*H*), 6.17 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.9$ Hz, H-3′), 5.81 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.9$ Hz, H-4′), 5.80 (s, 1 H, PhC*H*), 5.59 (dd, 1 H, $J_{1,2}$ 7.8, $J_{2,3}$ 9.9 Hz, H-2′), 5.55 (dd, 1 H, $J_{1,2}$ 7.8, $J_{2,3}$ 9.9 Hz, H-2), 5.04 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1′), 4.62 (dd, 1 H, $J_{5',6'e}$ 2.7, $J_{6'e,\ 6'a}$ 12.1 Hz, H-6′e), 4.47 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 4.53–4.20 (m, 3 H, H-6′a, H-6e, H-6a), 4.03 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.9$ Hz, H-3), 3.84–3.44 (m, 3 H, H-4, 2 H-5), 3.10 (m, 1 H, C*H*$(CH_3)_2$), 2.23 (s, 3 H, *Me*CO), 1.55 (d, 6 H, CH(C*H*$_3)_2$). Anal. Calcd for $C_{52}H_{50}O_{15}S$: C, 65.95; H, 5.32. Found: C, 65.78; H, 5.29.

3.4. 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1 → 3)-2-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranosyl trichloroacetimidate (6)

NIS (1.16 g, 5.04 mmol) was added to a solution of **4** (4.01 g, 4.20 mmol) in CH_2Cl_2. MeSiOTf (38 μL, 0.22 mmol) was added drop-wise 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 **5** (3.17 g, 85%). To a solution of **5** (3.00 g, 3.38 mmol) in dry CH_2Cl_2 was added trichloroacetonitrile (2 mL, 9.4 mmol) and DBU (0.2 mL, 1.61 mmol). The mixture was stirred for 3 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The reaction mixture was concentrated, and the crude product was then purified by flash chromatography with 2:1 petroleum ether–EtOAc as the eluent to afford the donor **6** (3.06 g, 89%) as a foamy solid: $[\alpha]_D$ +55.7° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.56 (s, 1 H, CN*H*CCl_3), 7.96–7.25 (m, 25 H, 4 Bz-*H*, Ph-*H*), 6.41 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 5.84 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.6$ Hz, H-4′), 5.67 (dd, 1 H, $J_{2,3} = J_{3,4} = 9.6$ Hz, H-3′), 5.63 (s, 1 H, PhC*H*), 5.52 (dd, 1 H, $J_{1,2}$ 7.9, $J_{3,4}$ 9.6 Hz, H-2′), 5.13 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1′), 5.00 (dd, 1 H, $J_{1,2}$ 3.8, $J_{2,3}$ 9.6 Hz, H-2), 4.46 (dd, 1 H, $J_{5,6'e}$ 3.4, $J_{6'e,\ 6'a}$ 12.1 Hz, H-6′e), 4.35–4.25 (m, 3 H, H-6′a, H-6e, H-6a), 4.03–3.87 (m, 3 H, H-3, H-5, H-5′), 3.79 (dd, 1 H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4), 1.67 (s, 3 H, *Me*CO). Anal. Calcd for $C_{51}H_{44}Cl_3NO_{16}$: C, 59.28; H, 4.29. Found: C, 59.04; H, 4.26.

3.5. Isopropyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-1-thio-β-D-glucopyranoside (9)

Donor **6** (2.23 g, 2.14 mmol) was coupled with acceptor **2** (607 mg, 1.86 mmol) as described in the general procedure, and the product was purified by chromatography with 2:1 petroleum ether–EtOAc as the eluent to

give **7** (2.14 g, 83%). Compound **7** (1.89 g, 1.57 mmol) was added to 90% HOAc–H_2O (100 mL), the mixture was refluxed for 2 h, then concentrated, and the residue was co-evaporated with toluene (10 mL) for three times. The residue was dried under high vacuum for 2 h, then dissolved in Py (10 mL), and Ac_2O (2 mL, 21.2 mmol) was added. The mixture was stirred at room temperature (rt) for 3 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) suggested that the reaction was finished. The mixture was concentrated and purified by chromatography with 2:1 petroleum ether–EtOAc as the eluent to afford compound **9** as a foamy solid (1.35 g, 72% for two steps): $[\alpha]_D$ −20.1° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.02–7.25 (m, 20 H, 4 Bz-*H*), 5.89 (dd, 1 H, $J_{3,4}=J_{4,5}=9.7$ Hz, H-4″), 5.68 (dd, 1 H, $J_{2,3}=J_{3,4}=9.7$ Hz, H-3″), 5.41 (dd, 1 H, $J_{1,2}$ 7.9, $J_{2,3}$ 9.7 Hz, H-2″), 5.01 (dd, 1 H, $J_{3,4}=J_{4,5}=9.6$ Hz, H-4′), 4.90–4.78 (m, 4 H, H-1″, H-2′, H-2, H-4), 4.59 (dd, 1 H, $J_{5'',6''e}$ 3.6, $J_{6''e,6''a}$ 12.6 Hz, H-6″e), 4.53 (dd, 1 H, $J_{5'',6''a}$ 4.6, $J_{6''e,6''a}$ 12.6 Hz, H-6″a), 4.42 (d, 1 H, $J_{1,2}$ 9.9 Hz, H-1′), 4.40 (d, 1 H, $J_{1,2}$ 9.9 Hz, H-1), 4.29 (dd, 1 H, $J_{5',6'a}$ 4.3, $J_{6'e,\ 6'a}$ 12.3 Hz, H-6′a), 4.16–4.10 (m, 3 H, H-5″, H-6′e, H-6a), 4.01 (dd, 1 H, $J_{5,6a}$ 2.4, $J_{6e,6a}$ 12.3 Hz, H-6′a), 3.89 (dd, 1 H, $J_{2,3}=J_{3,4}=9.6$ Hz, H-3′), 3.85 (dd, 1 H, $J_{2,3}=J_{3,4}=9.6$ Hz, H-3), 3.65–3.52 (m, 2 H, H-5, H-5′), 3.11 (m, 1 H, C*H*$(CH_3)_2$), 2.12, 2.06, 2.03, 1.99, 1.95, 1.89 (6 s, 18 H, 6 *Me*CO), 1.55 (d, 6 H, CH(C*H*$_3)_2$). Anal. Calcd for $C_{61}H_{66}O_{25}S$: C, 59.51; H, 5.40. Found: C, 59.52; H, 5.39.

3.6. 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl trichloroacetimidate (11)

The solution of **9** (1.12 g, 0.94 mmol) and NIS (0.26 g, 1.23 mmol) in CH_2Cl_2 was cooled to −20 °C, then MeSiOTf (2 μL, 0.10 mmol) was added drop-wise with nitrogen protection. The solution was stirred for 3 h, during which time the temperature of the reaction mixture was gradually raised to ambient temperature. The mixture was neutralized with Et_3N. Concentration of the reaction mixture, followed by purification of the crude product on a silica gel column with 2:1 petroleum ether–EtOAc as the eluent gave **10** as a syrup. A mixture of **10**, trichloroacetonitrile (1 mL, 4.69 mmol), and DBU (0.1 mL, 0.81 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 donor **11** as a foamy solid (998 mg, 81% for two steps from **9** through **11**): $[\alpha]_D$ +6.4° (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.68 (s, 1 H, CN*H*CCl_3), 8.02–7.25 (m, 20 H, 4 Bz-*H*), 6.42 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 5.90 (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″), 5.38 (dd, 1 H, $J_{1,2}$ 7.9, $J_{2,3}$ 9.8 Hz, H-2″), 5.02–4.81 (m, 5 H, H-1″, H-2′, H-2, H-4′, H-4), 4.56 (m 2 H, 2 H-6″), 4.46 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1′), 4.25 (dd, 1 H, $J_{5',6'e}$ 6.5, $J_{6'e,6'a}$ 12.3 Hz, H-6′e), 4.16–4.04 (m, 5 H, H-5′, H-5″, H-6′a, H-6e, H-6a), 3.91 (dd, 1 H, $J_{2,3}=J_{3,4}=9.4$ Hz, H-3), 3.68 (ddd, 1 H, $J_{4,5}$ 9.7, $J_{5,6e}$ 5.8, $J_{5,6a}$ 5.7 Hz, H-5), 2.09, 2.06, 2.05, 2.00, 1.97, 1.82 (s, 3 H, *Me*CO). Anal. Calcd for $C_{60}H_{60}Cl_3NO_{26}$: C, 54.70; H, 4.59. Found: C, 54.48; H, 4.55.

3.7. Allyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2-*O*-acetyl-β-D-glucopyranosyl-(1→3)-4,6-di-*O*-acetyl-2-*O*-benzoyl-α-D-glucopyranoside (14)

Donor **6** (2.30 g, 2.21 mmol) was coupled with acceptor **12** (783 mg, 1.92 mmol), and the product was purified by chromatography with 3:2 petroleum ether–EtOAc as the eluent to give **13** as a syrup (2.08 g, 86%). Compound **13** (1.98 g, 1.57 mmol) was added to 90% HOAc–H_2O (100 mL), and the mixture was refluxed for 2 h, then concentrated to dryness, and the resultant residue was co-evaporated with toluene (10 mL) for three times. The residue was purified by chromatography with 1:1 petroleum ether–EtOAc as the eluent to give **14** (1.63 g, 87%): $[\alpha]_D$ +41.8° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.10–7.22 (m, 25 H, 5 Bz-*H*), 5.84 (dd, 1 H, $J_{3,4}=J_{4,5}=9.8$ Hz, H-4″), 5.80 (m, 1 H, CH_2–C*H*=CH_2), 5.55 (dd, 1 H, $J_{2,3}=J_{3,4}=9.8$ Hz, H-3″), 5.46 (dd, 1 H, $J_{1,2}$ 7.9, $J_{2,3}$ 9.8 Hz, H-2″), 5.22 (dd, 1 H, *J* 1.3, 17.2 Hz, CH_2–CH=CH_2), 5.12 (dd, 1 H, *J* 1.3, 10.2 Hz, CH_2–CH=CH_2), 5.06 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.97 (dd, 1 H, $J_{1,2}$ 3.7, $J_{2,3}$ 9.9 Hz, H-2), 4.88 (dd, 1 H, $J_{3,4}=J_{4,5}=9.8$ Hz, H-4), 4.79–4.75 (m, 2 H, H-2′, H-6″e), 4.63 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1″), 4.51 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1′), 4.35–4.31 (m, 2 H, H-4′, H-6a″), 4.18–3.91 (m, 7 H, 2 CH_2–CH=CH_2, H-5″, H-6′e, H-6′a, H-6e, H-6a), 3.68 (ddd, 1 H, $J_{4,5}$ 9.8 Hz, $J_{5,6e}$ 4.8, $J_{5,6a}$ 4.6 Hz, H-5′), 3.48 (dd, 1 H, $J_{2,3}=J_{3,4}=9.3$ Hz, H-3), 3.37–3.32 (m, 2 H, H-3′, H-5), 2.09, 2.03, 1.03 (3 s, 9 H, 3 *Me*CO). Anal. Calcd for $C_{62}H_{62}O_{24}$: C, 62.52; H, 5.25. Found: C, 62.45; H, 5.23.

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

Donor **11** (421 mg, 0.32 mmol) and acceptor **14** (331 mg, 0.28 mmol) were coupled as described in the general procedure, and the product was purified by chromatography with 1:1 petroleum ether–EtOAc as the eluent to furnish **15** (420 mg, 64%): $[\alpha]_D$ +1.3° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.10–7.23 (m, 45 H, 9 Bz-*H*), 5.92 (dd, 1 H, $J_{3,4}=J_{4,5}=9.7$ Hz, H-4), 5.85 (dd, 1 H, $J_{3,4}=J_{4,5}=9.8$ Hz, H-4), 5.80 (m, 1 H, CH_2–C*H*=CH_2), 5.72 (dd, 1 H, $J_{2,3}=J_{3,4}=9.6$ Hz, H-3), 5.54 (dd, 1 H, $J_{2,3}=$

$J_{3,4}$ = 9.8 Hz, H-3), 5.47–5.42 (m, 2 H, 2 H-2), 5.22 (dd, 1 H, *J* 1.2, 17.2 Hz, CH_2–CH=CH_2), 5.12 (dd, 1 H, *J* 1.2, 10.4 Hz, CH_2–CH=CH_2), 5.07 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 5.03 (d, 1 H, $J_{1,2}$ 9.4 Hz, H-1), 4.97–4.78 (m, 6 H, 4 H-1, H-2, H-4), 4.68–4.54 (m, 5 H, 3 H-2, H-4, H-6), 4.44–4.31 (m, 4 H, H-4, 3 H-6), 4.22–3.89 (m, 14 H, H-4, 2 CH_2–CH=CH_2, 3 H-5, 8 H-6), 3.73–3.24 (m, 7 H, 4 H-3, 3 H-5), 2.16, 2.09, 2.06, 2.04, 2.00, 1.98, 1.95, 1.90 1.03 (9 s, 27 H, 9 *Me*CO); ^{13}C NMR (100 MHz, $CDCl_3$), δ 170.8, 170.8, 170.7, 169.9, 169.2, 169.0, 168.6, 168.3, 168.3 (9 C, 9 Me*C*O), 166.2, 166.1, 165.9, 165.8, 165.6, 165.3, 165.3, 164.9 (9 C, 9 Ph*C*O), 133.8–133.2, 130.2–128.2 (9 *Ph*CO, –CH_2–*C*H=CH_2), 118.3 (1 C, –CH_2–CH=*C*H_2), 101.8, 101.8, 101.6, 101.1, 100.9, 95.1 (6 C-1, $J_{C\text{-}1,H\text{-}1}$ = 161.1, 161.1, 167.5, 163.6, 168.0, 177.4 Hz), 86.4, 79.2, 78.5, 77.2, 76.5, 74.4, 73.1–71.3, 69.6–67.6, 63.8, 60.8 (C-2–6, –*C*H_2–CH=CH_2), 22.7, 22.7,22.7, 20.6, 20.6, 20.6, 20.2, 20.2 (9 C, 9 *Me*CO). Anal. Calcd for $C_{120}H_{120}O_{49}$: C, 61.43; H, 5.16. Found: C, 61.45; H, 5.15.

3.9. Allyl β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→6)]-β-D-glucopyranosyl-(1→3)-α-D-glucopyranoside (16)

Compound **15** (320 mg, 0.14 mmol) was dissolved in a satd solution of NH_3 in MeOH (10 mL). After 2 weeks at rt, the reaction mixture was concentrated, and the residue was purified on a Bio-Gel P2 column with MeOH–water as the eluent to afford **16** (138 mg, 96%) as a pulverous crystalloid: $[\alpha]_D$ +36.6° (*c* 1.0, H_2O); ^{1}H NMR (400 MHz, D_2O): δ 5.86 (m, 1 H, CH_2–C*H*=CH_2), 5.25 (dd, 1 H, *J* 1.4, 17.2 Hz, CH_2–CH=C*H*$_2$), 5.15 (dd, 1 H, *J* 1.4, 10.2 Hz, CH_2–CH=C*H*$_2$), 4.86 (1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.71 (1 H, $J_{1,2}$ 7.6 Hz, H-1), 4.69 (1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.69 (1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.60 (1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.41 (1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.11–3.22 (m, 38 H, H-2–6, CH_2–CH=CH_2); ^{13}C NMR (100 MHz, D_2O): δ 132.7 (1 C, CH_2–CH=*C*H_2), 118.4 (1 C, CH_2–*C*H=CH_2), 102.9, 102.9, 102.8, 102.7, 102.6, 97.2 (6 C-1, $J_{C\text{-}1,H\text{-}1}$ = 163.2, 163.2, 165.1, 164.5, 164.3, 171.6 Hz), 84.3, 84.3, 84.1, 83.3, 76.1, 75.7, 75.6, 74.5, 74.1, 73.5, 73.3, 73.2, 73.1, 72.2, 71.7, 70.9, 70.7, 69.6, 69.0, 68.9, 68.5, 68.2, 67.8 (C-2–6, *C*H_2–CH=CH_2, some signals overlapped). Anal. Calcd for $C_{39}H_{66}O_{31}$: C, 45.44; H, 6.45. Found: C, 45.30; H, 6.41.

3.10. 4,6-Di-*O*-acetyl-2-*O*-benzoyl-3-*O*-chloroacetyl-β-D-glucopyranosyl-(1→3)-4,6-di-*O*-acetyl-2-*O*-benzoyl-α-D-glucopyranosyl trichloroacetimidate (21)

Donor **17** (1.17 g, 1.98 mmol) and acceptor **18** (739 mg, 1.81 mmol) were coupled as described in the general procedure. Purification of the product by chromatography with 3:1 petroleum ether–EtOAc as the eluent afforded **19** (1.37 g, 91%). To a solution of **19** in CH_2Cl_2 (60 mL) and CH_3OH (30 mL) was added $PdCl_2$ (50 mg, 0.28 mmol), and the reaction mixture was stirred at rt until TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. Then the mixture was filtered, the solution was concentrated to dryness, and the residue was purified by flash chromatography with 3:2 petroleum ether–EtOAc as the eluent to give **20** as a foamy solid. A mixture of **20**, trichloroacetonitrile (1.0 mL, 4.95 mmol) and DBU (0.1 mL, 0.65 mmol) in dry CH_2Cl_2 (20 mL) was stirred for 3 h and then concentrated. The residue was purified by flash chromatography with 2:1 petroleum ether–EtOAc as the eluent to give **21** as a syrup (1.23 g, 80% for two steps): $[\alpha]_D$ + 58.6° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.55 (s, 1 H, CN*H*CCl_3), 7.81–7.13 (m, 10 H, 2 Bz-*H*), 6.56 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 5.31 (dd, 1 H, $J_{1,2} = J_{2,3}$ = 9.5 Hz, H-2′), 5.24–5.12 (m, 4 H, H-2, H-3′, H-4, H-4′), 4.88 (d, 1 H, $J_{1,2}$ 9.5 Hz, H-1′), 4.44 (dd, 1 H, $J_{5,6'e}$ 4.6, $J_{6'e,6'a}$ 12.5 Hz, H-6′e), 4.39 (dd, 1 H, $J_{2,3} = J_{3,4}$ = 9.6 Hz, H-3), 4.30–4.09 (m, 5 H, H-6′a, H-6e, H-6a, H-5, H-5′), 3.95, 3.77 (ABq, *J* 14.8 Hz, 2 H, ClCH_2CO), 2.10 (s, 3 H, *Me*CO), 2.08 (s, 3 H, *Me*CO), 2.08 (s, 3 H, *Me*CO), 2.02 (s, 3 H, *Me*CO). Anal. Calcd for $C_{38}H_{39}Cl_4NO_{18}$: C, 48.58; H, 4.18. Found: C, 48.43; H, 4.13.

3.11. 3-*O*-Allyl-2-*O*-benzoyl-4,6-*O*-benzylidene-D-glucopyranosyl trichloroacetimidate (22)

3-*O*-Allyl-D-glucopyranose[16] (3.85 g, 17.5 mmol) was dissolved in DMF (50 mL), and then benzaldehyde (2.35 mL, 19.3 mmol), triethyl orthoformate (3.0 mL, 18.0 mmol) and toluenesulfonic acid (0.22 g, 1.16 mmol) were added. The reaction mixture was stirred overnight at rt, and then quenched with Et_3N. The solution was concentrated, and the residue was purified by chromatography (1:1 petroleum ether–EtOAc) to give 3-*O*-allyl-4,6-*O*-benzylidene-D-glucopyranose. The hemiacetal was dissolved in Py (20 mL), and benzoyl chloride (2 mL, 17.1 mmol) was added drop-wise. After 4 h at 20 °C, excess benzoyl chloride was destroyed with MeOH, and the reaction mixture was concentrated. The residue was taken up in CH_2Cl_2, washed with 0.2 M HCl, 10% $NaHCO_3$ and H_2O, and then concentrated. Crude 3-*O*-allyl-1,2-*O*-benzoyl-4,6-*O*-benzylidene-D-glucopyranose thus obtained was redissolved in a satd solution of NH_3 in 3:1 toluene–MeOH (200 mL) and stirred at rt until TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. The solution was concentrated, and the residue was purified by chromatography with 3:1 petroleum ether–EtOAc as the eluent to give 3-*O*-allyl-2-*O*-benzoyl-4,6-*O*-benzylidene-D-glucopyranose. A mixture of the hemiacetal, trichlorocetonitrile (3.2 mL, 15.0 mmol) and DBU (0.25 mL, 2.02 mmol) in dry CH_2Cl_2 (40 mL) was stirred at rt for 3 h and then concentrated. The residue was purified

by flash chromatography (3:1 petroleum ether–EtOAc) to give **22** as an anomeric mixture (4.07 g, 42% for four steps): ^{1}H NMR ($CDCl_3$): δ 8.70 (s, 1 H, CN*H*CCl$_3$), 8.59 (s, 1 H, CN*H*CCl$_3$), 8.09–7.40 (m, 20 H, 2 Bz-*H*, 2 Ph-*H*), 6.66 (d, 1 H, $J_{1,2}$ 3.6 Hz, α-H-1), 6.10 (d, 1 H, $J_{1,2}$ 7.8 Hz, β-H-1), 5.86 (m, 1 H, CH$_2$–C*H*=CH$_2$), 5.82 (m, 1 H, CH$_2$–C*H*=CH$_2$), 5.66 (s, 1 H, PhC*H*), 5.62 (s, 1 H, PhC*H*), 5.57 (dd, 1 H, $J_{1,2}=J_{2,3}=7.8$ Hz, H-2), 5.39 (dd, 1 H, $J_{1,2}$ 3.6, $J_{2,3}$ 9.6 Hz, H-2), 5.28–5.06 (m, 4 H, 2 CH$_2$–CH=C*H*$_2$), 4.46–3.81 (m, 12 H, 2 H-3, 2 H-4, 2 H-5, 4 H-6, 2 C*H*$_2$–CH=CH$_2$). Anal. Calcd for $C_{25}H_{24}Cl_3NO_7$: C, 53.93; H, 4.34. Found: C, 53.85; H, 4.24.

3.12. Methyl 2,4,6-tri-*O*-acetyl-β-D-glucopyranoside (23)

1,2,4,6-Tetra-*O*-acetyl-3-*O*-allyl-D-glucopyranose (8.00 g, 20.6 mmol)[16] was dissolved in a satd solution of NH_3 in 3:1 toluene–MeOH (100 mL), and the mixture was stirred at rt until TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. The solution was concentrated and purified by chromatography with 3:1 petroleum ether–EtOAc as the eluent to give 2,4,6-tri-*O*-acetyl-3-*O*-allyl-D-glucopyranose. A mixture of 2,4,6-tri-*O*-acetyl-3-*O*-allyl-D-glucopyranose, trichloroacetonitrile (5.6 mL, 26.2 mmol) and DBU (0.5 mL, 4.04 mmol) in dry CH_2Cl_2 (60 mL) was stirred at rt for 3 h and then concentrated. The residue was purified by flash chromatography (2:1 petroleum ether–EtOAc) to give the donor, 2,4,6-tri-*O*-acetyl-3-*O*-allyl-α-D-glucopyranosyl trichloroacetimidate (6.36 g, 63% for two steps). The donor (6.4 g, 11.5 mmol) was coupled with MeOH (5 mL) as described in the general procedure, and the product was purified by flash chromatography (3:1 petroleum ether–EtOAc) to give methyl 2,4,6-tri-*O*-acetyl-3-*O*-allyl-β-D-glucopyranoside. To a solution of the methyl glucoside in 60 mL CH_2Cl_2 and 30 mL CH_3OH was added $PdCl_2$ (100 mg, 0.56 mmol), and the reaction mixture was stirred at rt until TLC (2:1 petroleum ether–EtOAc) suggested the reaction was complete. Then the mixture was filtered, the solution was concentrated to dryness, and the residue was purified by flash chromatography (3:2 petroleum ether–EtOAc) to give **23** (2.64 g, 62% for two steps) as a foamy solid: $[\alpha]_D$ +45.2° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 4.96 (dd, 1 H, $J_{3,4}=J_{4,5}=9.7$ Hz, H-4), 4.85 (dd, 1 H, $J_{1,2}$ 7.8, $J_{2,3}$ 9.6 Hz, H-2), 4.37 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 4.29 (dd, 1 H, $J_{5,6'e}$ 4.8 Hz, $J_{6'e,6'a}$ 12.3 Hz, H-6′e), 4.16 (dd, 1 H, $J_{5,6'a}$ 4.8, $J_{6'e,6'a}$ 12.2 Hz, H-6′e), 4.11 (dd, 1 H, $J_{2,3}=J_{3,4}=9.7$ Hz, H-3), 3.72 (ddd, 1 H, $J_{4,5}$ 9.7, $J_{5,6'e}$ 4.8, $J_{5,6'a}$ 3.4 Hz, H-5), 3.51 (s, 3 H, OCH_3). Anal. Calcd for $C_{13}H_{20}O_9$: C, 48.75; H, 6.29. Found: C, 48.64; H, 6.20.

3.13. Methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranoside (25)

Compound **24** (2.52 g, 85%) was obtained by coupling of the donor **22** (2.77 g, 4.98 mmol) with the acceptor **23** (1.33 g, 4.16 mmol) as described in the general procedure. A mixture of **24** (2.42 g, 3.39 mmol), $PdCl_2$ (50 mg, 0.28 mmol), CH_2Cl_2 (60 mL), and CH_3OH (30 mL) was stirred at rt until TLC (2:1 petroleum ether–EtOAc) suggested that the reaction was complete. Then the mixture was filtered, the solution was concentrated to dryness, and the residue was purified by flash chromatography with 3:1 petroleum ether–EtOAc as the eluent to give **25** (2.10 g, 92%): $[\alpha]_D$ −35.4° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.00–7.26 (m, 10 H, Bz-*H*, Ph-*H*), 5.56 (s, 1 H, PhC*H*), 5.04 (dd, 1 H, $J_{3,4}=J_{4,5}=8.8$ Hz, H-4), 5.02 (dd, 1 H, $J_{1,2}$ 7.4, $J_{2,3}$ 9.4 Hz, H-2′), 4.90 (dd, 1 H, $J_{1,2}$ 7.8, $J_{2,3}$ 8.8 Hz, H-2), 4.81 (d, 1 H, $J_{1,2}$ 7.4 Hz, H-1′), 4.37 (dd, 1 H, $J_{5,6'e}$ 4.8, $J_{6'e,6'a}$ 10.2 Hz, H-6′e), 4.28 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 4.30–4.09 (m, 2 H, H-6′a, H-6e), 4.01 (dd, 1 H, $J_{2,3}=J_{3,4}=9.4$ Hz, H-3′), 4.96 (dd, 1 H, $J_{2,3}=J_{3,4}=8.8$ Hz, H-3), 3.75 (dd, 1 H, $J_{3,4}=J_{4,5}=9.4$ Hz, H-4′), 3.68–3.49 (m, 3 H, H-5, H-5′, H-6a), 3.38 (s, 1 H, C*H*$_3$O), 2.07 (s, 3 H, *Me*CO), 2.04 (s, 3 H, *Me*CO), 1.91 (s, 3 H, *Me*CO). Anal. Calcd for $C_{33}H_{38}O_{15}$: C, 58.75; H, 5.64. Found: C, 58.63; H, 5.57.

3.14. Methyl 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-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranoside (26)

Coupling of the donor **21** (1.05 g, 1.12 mmol) with the acceptor **25** (0.69 g, 1.02 mmol), followed by purification on a silica gel column with 1:1 petroleum ether–EtOAc as the eluent gave **26** as a foamy solid (888 mg, 60%): $[\alpha]_D$ −13.4° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.06–7.26 (m, 20 H, 3 Bz-*H*, Ph-*H*), 5.48 (s, 1 H, PhC*H*), 5.32 (dd, 1 H, $J_{1,2}$ 7.7, $J_{2,3}$ 9.6 Hz, H-2), 5.13–5.06 (m, 4 H, 3 H-2, H-3), 4.97 (dd, 1 H, $J_{3,4}=J_{4,5}=9.5$ Hz, H-4), 4.92 (dd, 1 H, $J_{3,4}=J_{4,5}=9.2$ Hz, H-4), 4.88 (dd, 1 H, $J_{3,4}=J_{4,5}=9.6$ Hz, H-4), 4.69 (d, 1 H, $J_{1,2}$ 8.9 Hz, H-1), 4.68 (d, 1 H, $J_{1,2}$ 7.4 Hz, H-1), 4.66 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1), 4.35 (dd, 1 H, $J_{5,6e}$ 5.6, $J_{6e,6a}$ 13.9 Hz, H-6e), 4.34 (dd, 1 H, $J_{5,6e}$ 5.3, $J_{6e,6a}$ 10.1 Hz, H-6e), 4.18 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1), 4.22–3.97 (m, 7 H, H-3, 6 H-6), 3.92 (dd, 1 H, $J_{2,3}=J_{3,4}=9.1$ Hz, H-3), 3.84 (dd, 1 H, $J_{2,3}=J_{3,4}=8.9$ Hz, H-3), 3.78, 3.72 (ABq, 2 H, *J* 15.2 Hz, ClC*H*$_2$CO), 3.64 (dd, 1 H, $J_{3,4}=J_{4,5}=9.1$ Hz, H-4), 3.61–3.35 (m, 4 H, 4 H-5), 3.30 (s, 3 H, C*H*$_3$O), 2.05 (s, 3 H, *Me*CO), 2.02 (s, 3 H, *Me*CO), 1.97 (s, 3 H, *Me*CO), 1.96 (s, 3 H, *Me*CO), 1.95 (s, 3 H, *Me*CO), 1.94 (s, 3 H, *Me*CO), 1.79 (s, 3 H, *Me*CO). Anal. Calcd for

$C_{69}H_{75}ClO_{32}$: C, 57.08; H, 5.21. Found: C, 57.10; H, 5.19.

3.15. Methyl β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranoside (29)

Thiourea (150 mg, 1.97 mmol) was added to a solution (50 mL) of **26** (520 mg, 0.36 mmol) in 1:2 MeOH and CH_2Cl_2, then the reaction mixture was refluxed for 17 h, at the end of which time TLC (2:3 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was concentrated to 1/5 of the original volume, diluted with CH_2Cl_2, washed with satd aq $NaHCO_3$ and water, and the organic phase was dried and concentrated. Purification by column chromatography with 1:1 petroleum ether–EtOAc as the eluent afforded **27** (420 mg, 85%). Compound **27** (380 mg, 0.28 mmol) was added to 90% HOAc–H_2O (20 mL), and the mixture was refluxed for 2 h, then concentrated, and co-evaporated with toluene (10 mL) for three times. Purification by column chromatography with 2:3 petroleum ether–EtOAc as the eluent gave compound **28** (312 mg, 88%), which was dissolved in a satd solution of NH_3 in MeOH (10 mL). After 2 weeks at rt, the reaction mixture was concentrated, and the residue was purified on a Bio-Gel P2 column with MeOH–water as the eluent to afford **29** (86.7 mg, 94%) as a pulverous crystalloid: $[\alpha]_D$ −2.6° (*c* 1.0, H_2O); ^1H NMR (400 MHz, D_2O): 4.69 (1 H, $J_{1,2}$ 8.4 Hz, H-1), 4.67 (1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.65 (1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.31 (1 H, $J_{1,2}$ 8.0 Hz, H-1), 3.85–3.24 (m, 27 H, H-2–6, OCH_3); ^{13}C NMR (100 MHz, D_2O): δ 103.0, 102.8, 102.6, 102.5 (4 C-1, $J_{C\text{-}1,H\text{-}1} = 165.1$, 164.7, 165.3, 164.8 Hz), 84.5, 84.3, 84.1, 76.0, 75.6, 75.5, 73.5, 73.3, 73.2, 72.8, 69.6, 68.2, 68.1, 68.9, 60.7, 57.2 (C-2–6, O*C*H_3, some signals overlapped). Anal. Calcd for $C_{25}H_{44}O_{21}$: C, 44.12; H, 6.52. Found: C, 43.98; H, 6.48.

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