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Synthesis of an α-linked dimer of the trisaccharide repeating unit of the exopolysaccharide produced by *Pediococcus damnosus* 2.6

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Abstract—A hexasaccharide, β-D-Glc*p*-(1→3)-[β-D-Glc*p*-(1→2)]-α-D-Glc*p*-(1→3)-β-D-Glc*p*-(1→3)-[β-D-Glc*p*-(1→2)]-D-Glc*p*, the α-linked dimer of the trisaccharide repeating unit of the exopolysaccharide produced by *Pediococcus damnosus* 2.6, was synthesized as its methyl glycoside. Condensation of fully benzoylated α-D-glucopyranosyl trichloroacetimidate (**1**) with isopropyl 4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (**2**) selectively furnished (1→3)-linked disaccharide **3**, and subsequent 2-O-acetylation, desulfation, and trichloroacetimidate formation afforded the disaccharide donor **6**. Meanwhile, selective 3-O-coupling of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (**8**) with 3-*O*-allyl-2,4,6-tri-*O*-benzoyl-α-D-glucopyranosyl trichloroacetimidate (**7**), followed by coupling with **1** gave the trisaccharide **10**. Removal of the benzylidene group of **10**, benzoylation, and deallylation produced the trisaccharide acceptor **12**. Condensation of **12** with **6** yielded a pentasaccharide mixture **13** with β and α isomers in a ratio of 2:1. Removal of the benzylidene group of **13**, followed by benzoylation gave the pentasaccharide mixture **14**. Selective 2‴-deacetylation of the isolated β-linked **14**β with MeCOCl/MeOH/CH_2Cl_2 did not give the expected pentasaccharide acceptor, and serious decomposition occurred, indicating a large steric hindrance at C-2‴. Alternatively, 2,3-di-O-glycosylation of allyl 4,6-*O*-benzylidene-β-D-glucopyranoside (**21**) with **1** gave **22**, then deallylation and trichloroacetimidate formation afforded the trisaccharide donor **24**. Condensation of **12** with **24** furnished only the α-linked hexasaccharide **25**, and its deprotection gave the free hexaoside **27**.

Keywords: Glucan; Trichloroacetimidates; Synthesis

1. Introduction

It has been reported that the polysaccharide produced by strains of lactic acid bacteria is related to the alteration in ciders described as "oily" or "ropy".[1] Such is also known to occur in wines.[2] The exopolysaccharide produced by a ropy strain of *Pediococcus damnosus* 2.6 was reported to consist of β-(1→2)-branched β-(1→3)-linked glucan with the trisaccharide repeating unit structure as shown below.[3]

→3)-β-D-Glc*p*-(1→3)-β-D-Glc*p*-(1→
↑2
β-D-Glc*p*-1

Our group has been engaged in studies on the structure–bioactivity relationships of oligosaccharides for years. We have synthesized a series of bioactive glucans, such as the phytoalexin hexaose[4] with a β-(1→6)-linked backbone and β-(1→3)-linked side chains, the heptaose repeating unit of letinan[5] and its analogues[6] with a β-(1→3)-linked backbone and β-(1→6)-linked side chains, or with alternate β- and α-(1→3)-linked backbone and β-(1→6)-linked side chains. We present herein an effective synthesis of glucohexaoside corresponding to the dimer of the trisaccharide repeating unit of the exopolysaccharide produced by *P. damnosus* 2.6.

2. Results and discussion

In our synthesis, 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl trichloroacetimidate (**1**),[7] isopropyl 4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (**2**),[8,9] 3-*O*-allyl-2,4,

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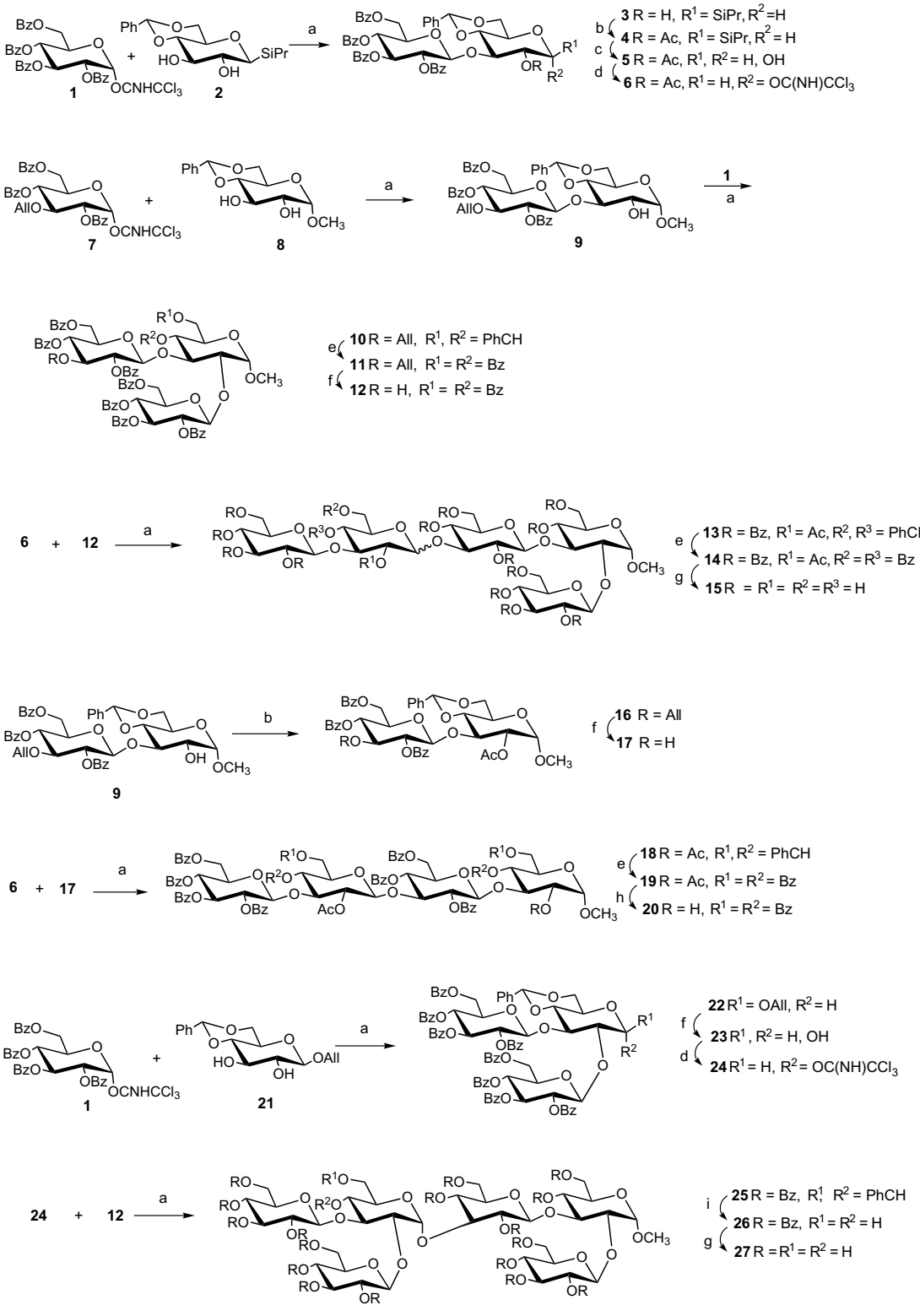
6-tri-*O*-benzoyl-α-D-glucopyranosyl trichloroacetimidate (**7**),[10] methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (**8**),[10] and allyl 4,6-*O*-benzylidene-β-D-glucopyranoside (**21**)[10] were used as the key synthons (Scheme 1). Condensation of **2** with **1** selectively gave a (1→3)-linked disaccharide **3** (95%), and subsequent 2-O-acetylation



Scheme 1. Reagents and conditions: (a) TMSOTf, CH_2Cl_2, −20 °C to rt; (b) Ac_2O, pyridine, rt, 4 h; (c) NIS, TMSOTf, CH_2Cl_2, 3 h; (d) CCl_3CN, CH_2Cl_2, DBU, rt; (e) i. 90% HOAc–H_2O, reflux, 2 h; ii. BzCl, pyridine, rt, 6 h; (f) $PdCl_2$, CH_2Cl_2, MeOH, rt; (g) MeOH, NH_3, rt, a week; (h) 7:50:50 MeCOCl–CH_3OH–CH_2Cl_2, rt, 72 h; (i) 90% HOAc–H_2O, reflux, 2 h.

with acetic anhydride in pyridine, 1-desulfation with NIS in dichloromethane, and trichloroacetimidate formation with trichloroacetonitrile in the presence of base afforded the disaccharide donor **6**.[11] Meanwhile, selective 3-O-coupling[10] (57%) of **8** with **7**, followed by coupling with **1**, furnished the trisaccharide **10** (82%). Hydrolysis to cleave the *O*-benzylidene group of **10**, benzoylation with benzoyl chloride in pyridine, and subsequent deallyl-ation with $PdCl_2$ in methanol gave the trisaccharide acceptor **12**. Then coupling of **12** with the disaccharide donor **6** produced a mixture (69%) of **13** consisting of a β-linked pentasaccharide and an α-linked pentasacchar- ide in a ratio of 2:1. Subsequent removal of the *O*-benz-ylidene groups of **13** and benzoylation yielded the pentasaccharide mixture **14**. The two isomers **14**β and **14**α were well separated by column chromatography. Methanolysis for selective removal of 2‴-O-acetyl of **14**β with 7:50:50 MeCOCl–MeOH–CH_2Cl_2 (v/v/v) did not occur even if the reaction time was prolonged for three days. This indicated that there was a serious steric hindrance at C-2‴ of **14**β. In contrast, to that which we reported[12] previously, selective removal of the 2-O-acetyl group of β-(1→6)-linked galactan was carried out smoothly in high yields. Deprotection of **14**β and **14**α by ammonia in methanol gave the free pentaosides **15**β and **15**α, respectively.

Since the selective removal of the C‴-O-acetyl group of **14**β was not successful, an alternative route was tested. This route consisted of first constructing the β-(1→3)-linked tetrasaccharide with free 2- and 2‴-free hydroxyl groups, then attaching the β-(1→2)-linked side chains. Thus, acetylation of the disaccharide **9**, followed by deallylation, produced the disaccharide acceptor **17**, and subsequent coupling with the disaccharide donor **6** gave β-linked tetrasaccharide **18** (67%). It seemed that the use of a benzylidenated donor and acceptor in the coupling was very helpful for obtaining the β-linkage, since the coupling of the similar donor and acceptor with the benzoyl groups instead of the *O*-benzylidene groups furnished an α-linkage.[13] Removal of the benzylidene groups of **18** and subsequent benzoylation were carried out smoothly giving the tetrasaccharide **19**. However, selective removal of 2- and 2‴-O-acetyl groups with 7:50:50 MeCOCl–MeOH–CH_2Cl_2 (v/v/v) again was troublesome, as 2-O-deacetylated tetrasaccharide **20** was obtained as the only product, which also revealed a serious steric hindrance at the C-2‴. The existence of C‴-2-OAc in **20** was proved by a single irradiation of H-1 at δ 4.80 whereby a collapse of a doublet of doublets at δ 3.62 to a doublet occurred, indicating C-2-O-deacetylation.

For obtaining the dimer of the trisaccharide repeating unit, a strategy of 3 + 3 was tried. Thus, coupling of **21** with **1** (2.4 equiv) gave trisaccharide **22**, and subsequent deallylation, and trichloroacetimidate formation afforded the trisaccharide donor **24**. Condensation of the trisaccharide acceptor **12** with the donor **24** produced a sole α-linked hexasaccharide **25** (79%), and no β-form was detected. Deprotection of **25** by conventional methods gave the free hexaoside **27**.

In summary, a special strategy suitable for the preparation of the dimer of the trisaccharide repeating unit of the exopolysaccharide produced by *P. damnosus* 2.6 was described. The unusual difficulty in selective removal of 2‴-O-acetyl groups of the β-(1→3)-linked glucopyranosyl tetrasaccharide was an indication of a serious steric hindrance at the C-2‴.

3. Experimental

3.1. General methods

Optical rotations were determined at 25 °C with a Perkin–Elmer Model 241-Mc automatic polarimeter. ^{1}H NMR, ^{13}C NMR spectra were recorded with a Bruker ARX 400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C) at 25 °C for solutions in $CDCl_3$ or D_2O as indicated. Individual resonances could not be identified with the specific sugar residues using 1D techniques. 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 (8 × 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.

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. TMSOTf (0.05 equiv) was added dropwise at −20 °C with nitrogen protection. The reaction mixture was stirred for 3 h, during which time the temperature was gradually raised to ambient temperature. Then the mixture was neutralized with Et_3N. Concentration of the reaction mixture, followed by purification on a silica gel column, gave the desired products.

3.3. 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranosyl trichloroacetimidate (6)

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 pyridine (20 mL) was added Ac_2O (3 mL, 31.8 mmol), the reaction mixture was stirred for 4 h, at the 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%). NIS (1.16 g, 5.04 mmol) was added to a solution of **4** (4.01 g, 4.20 mmol) in CH_2Cl_2. TMSOTf (38 μL, 0.22 mmol) was added dropwise at −20 °C with nitrogen protection. The reaction mixture was stirred for 3 h, during which time the temperature was gradually raised to ambient temperature. Then the mixture was neutralized with Et_3N. Concentration of the reaction mixture, followed by purification on a silica gel column chromatography 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 the reaction was complete. The reaction mixture was concentrated and 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. The physical data were identical with those reported in lit.[11]

3.4. Methyl 3-*O*-allyl-2,4,6-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-α-D-glucopyranoside (9)

Donor **7** (4.88 g, 7.09 mmol) was coupled with acceptor **8** (2 g, 7.09 mmol) as described in the general procedure, and the product was purified by chromatography with 3:1 petroleum ether–EtOAc as the eluent to give **9** as a foamy solid (3.2 g, 57%): $[\alpha]_D$ +7.1 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.08–7.24 (m, 15H, 3P*h*), 5.58 (m, 1H, CH_2–C*H*=CH_2), 5.55 (dd, 1H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 5.53 (s, 1H, PhC*H*), 5.35 (dd, 1H, $J_{1,2} = 7.6$ Hz, $J_{2,3} = 8.8$ Hz, H-2), 5.02 (d, 1H, $J_{1,2} = 7.6$ Hz, H-1), 5.02–4.87 (m, 2H, CH_2–CH=CH_2), 4.69 (d, 1H, $J_{1,2} = 4.0$ Hz, H-1), 4.46 (dd, 1H, $J_{5,6} = 3.6$ Hz, $J_{6,6} = 12$ Hz, H-6), 4.25–4.21 (m, 2H), 4.04 (m, 2H, CH_2–CH=CH_2), 4.00–3.91 (m, 2H), 3.81–3.64 (m, 4H), 3.59 (dd, 1H, $J_{2,3} = J_{3,4} = 8.8$ Hz, H-3), 3.37 (s, 3H, OCH_3). Anal. Calcd for $C_{44}H_{44}O_{14}$: C, 66.32; H, 5.57. Found: C, 66.40; H, 5.51.

3.5. Methyl 3-*O*-allyl-2,4,6-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→2)]-4,6-*O*-benzylidene-α-D-glucopyranoside (10)

Donor **1** (3.57 g, 4.82 mmol) was coupled with acceptor **9** (3.2 g, 4.02 mmol) as described in the general procedure, and the product was purified by chromatography with 3:1 petroleum ether–EtOAc as the eluent to give **10** as a foamy solid (4.5 g, 82%): $[\alpha]_D$ +16.4 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.37–7.11 (m, 40H, 8P*h*), 5.85 (dd, 1H, $J_{3,4} = J_{4,5} = 10$ Hz, H-4), 5.61–5.51 (m, 3H, CH_2–C*H*=CH_2, H-4, H-2), 5.50 (s, 1H, PhC*H*), 5.31 (dd, 1H, $J_{1,2} = 7.6$ Hz, $J_{2,3} = 9.6$ Hz, H-2), 5.26 (dd, 1H, $J_{2,3} = J_{3,4} = 9.6$ Hz, H-3), 5.02–4.86 (m, 2H, CH_2–CH=CH_2), 4.72 (d, 1H, $J_{1,2} = 4.0$ Hz, H-1), 4.57 (d, 1H, $J_{1,2} = 7.6$ Hz, H-1), 4.51–4.44 (m, 2H), 4.27–4.12 (m, 5H), 3.92–3.89 (m, 2H), 3.74 (dd, 1H, $J_{5,6} = 4.8$ Hz, $J_{6,6} = 12$ Hz, H-6), 3.66–3.59 (m, 2H), 3.42 (dd, 1H), 3.31 (s, 3H, OCH_3), 3.15 (dd, 1H), 3.03–3.01 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 164.9, 164.8, 164.8, 164.8, 164.7, 164.7 (7C, 7Ph*C*O), 100.9, 100.7, 100.0 (2β-C-1, Ph*C*H), 99.3 (α-C-1). Anal. Calcd for $C_{78}H_{70}O_{23}$: C, 68.11; H, 5.13. Found: C, 68.29; H, 5.21.

3.6. Methyl 2,4,6-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→2)]-4,6-di-*O*-benzoyl-α-D-glucopyranoside (12)

Compound **10** (4.0 g, 2.9 mmol) was added to 90% HOAc–H_2O (100 mL), the mixture was refluxed for 2 h, then concentrated, and co-evaporated with toluene (10 mL) three times. The residue was dried under high vacuum for 2 h, then dissolved in pyridine (20 mL), and benzoyl chloride (0.82 mL, 5.8 mmol) was added. The reaction mixture was stirred at rt for 6 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) suggested that the reaction was finished. Excess benzoyl chloride was destroyed by the addition of MeOH. The mixture was concentrated and purified by chromatography with 3:1 petroleum ether–EtOAc as the eluent to afford compound **11** as a foamy solid (3.2 g, 74% for two steps). To a solution of **11** (3.2 g, 2.1 mmol) in CH_2Cl_2 (10 mL) and CH_3OH (40 mL) was added $PdCl_2$ (100 mg, 0.56 mmol), the reaction mixture 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 2:1 petroleum ether–EtOAc as the eluent to give **12** (2.67 g, 86%) as a foamy solid: $[\alpha]_D$ +11.8 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.40–7.17 (m, 45H, 9P*h*), 5.98 (dd, 1H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4), 5.69 (dd, 1H, $J_{1,2} = 7.6$ Hz, $J_{2,3} = 10.4$ Hz, H-2), 5.64 (dd, 1H, $J_{3,4} = J_{4,5} = 9.6$ Hz, H-4), 5.20 (dd, 1H, $J_{2,3} = J_{3,4} = 10$ Hz, H-3), 5.00 (dd, 1H, $J_{1,2} = 8.0$ Hz, $J_{2,3} = 10$ Hz, H-2), 4.91 (d, 1H, $J_{1,2} = 3.6$ Hz, H-1), 4.75 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.67 (dd, 1H, $J_{2,3} = J_{3,4} = 9.6$ Hz, H-4), 4.55 (dd, 1H, $J_{5,6} = 5.8$ Hz, $J_{6,6} = 12$ Hz, H-6), 4.51 (d, 1H, $J_{1,2} = 7.6$ Hz, H-1), 4.43 (dd, 1H, $J_{5,6} = 5.8$ Hz, $J_{6,6} = 12$ Hz, H-6), 4.34 (dd, 1H), 4.31–4.25 (m, 3H), 3.95 (dd, 1H, $J_{5,6} = 5.8$ Hz, $J_{6,6} = 12$ Hz, H-6), 3.94–3.68 (m, 2H), 3.41 (s, 3H, OCH_3), 3.28 (m, 1H), 2.99 (m, 1H), 2.81 (dd, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 166.2, 165.0, 164.9, 164.8, 164.8, 164.8, 164.7, 164.7 (9C, 9Ph*C*O), 100.9, 100.8, 100.0 (2β-C-1, Ph*C*H), 99.2

(α-C-1). Anal. Calcd for $C_{82}H_{70}O_{25}$: C, 67.67; H, 4.85. Found: C, 67.49; H, 4.93.

3.7. Methyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→2)]-4,6-di-*O*-benzoyl-α-D-glucopyranoside (14β) and methyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzoyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→2)]-4,6-di-*O*-benzoyl-α-D-glucopyranoside (14α)

Donor **6** (1.07 g, 1.03 mmol) and acceptor **12** (1 g, 0.69 mmol) were coupled as described in the general procedure, and the product was purified by chromatography with 1.5:1 petroleum ether–EtOAc as the eluent to furnish **13** (1.10 g, 69%). Compound **13** (1.10 g, 0.47 mmol) was added to 90% HOAc–H_2O (50 mL), the mixture was refluxed for 2 h, then concentrated, and co-evaporated with toluene (10 mL) three times. The residue was dried under high vacuum for 2 h, then dissolved in pyridine (10 mL), and benzoyl chloride (0.13 mL, 0.94 mmol) was added. The reaction mixture was stirred at rt for 6 h, at the end of which time TLC (1:1 petroleum ether–EtOAc) suggested that the reaction was finished, then excess benzoyl chloride was destroyed by MeOH. The mixture was concentrated and purified by chromatography with 1:1 petroleum ether–EtOAc as the eluent to afford compounds **14**β (547 mg, 47%) and **14**α (274 mg, 24%) as foamy solids: **14**β: $[\alpha]_D$ +4.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.12–7.03 (m, 75H, 15P*h*), 5.85 (dd, 1H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4), 5.69 (dd, 1H, $J_{3,4} = J_{4,5} = 9.6$ Hz, H-4), 5.55–5.47 (m, 3H), 5.41 (dd, 1H, $J_{1,2} = 8.0$ Hz, $J_{2,3} = 10$ Hz, H-2), 5.16 (dd, 1H, $J_{2,3} = J_{3,4} = 9.6$ Hz, H-3), 4.79 (d, 1H, $J_{1,2} = 3.6$ Hz, α-H-1), 4.77–4.67 (m, 3H), 4.52 (d, 1H, $J_{1,2} = 7.6$ Hz, H-1), 4.50 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.46–4.38 (m, 5H), 4.31–4.07 (m, 8H), 3.91 (m, 1H), 3.71–3.65 (m, 3H), 3.63 (dd, 1H, $J_{2,3} = J_{3,4} = 9.2$ Hz, H-3), 3.52–3.48 (m, 2H), 3.38 (s, 3H, OCH_3), 3.22 (dd, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.1 (1C, 1Me*C*O), 168.8, 166.2, 166.1, 166.0, 166.0, 166.0, 165.9, 165.6, 165.0, 165.0, 164.9, 164.9, 164.5, 164.3, 163.7 (15C, 15Ph*C*O), 101.8, 100.9, 100.7, 99.6 (4β-C-1), 99.2 (α-C-1). Anal. Calcd for $C_{138}H_{116}O_{42}$: C, 67.75; H, 4.78. Found: C, 67.51; H, 4.81. Compound **14**α: $[\alpha]_D$ −11.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.37–7.26 (m, 75H, 15P*h*), 5.94 (dd, 1H, $J_{3,4} = J_{4,5} = 9.6$ Hz, H-4), 5.82 (dd, 1H, $J_{3,4} = J_{4,5} = 10$ Hz, H-4), 5.63 (dd, 1H, $J_{3,4} = J_{4,5} = 9.6$ Hz, H-4), 5.56 (dd, 1H, $J_{2,3} = J_{3,4} = 9.2$ Hz, H-3), 5.53 (dd, 1H, $J_{1,2} = 8.0$ Hz, $J_{2,3} = 10$ Hz, H-2), 5.46 (dd, 1H, $J_{1,2} = 8.0$ Hz, $J_{2,3} = 10$ Hz, H-2), 5.24 (dd, 1H, $J_{2,3} = J_{3,4} = 9.2$ Hz, H-3), 5.12 (dd, 1H, $J_{1,2} = 8.0$ Hz, $J_{2,3} = 9.2$ Hz, H-2), 4.83 (d, 1H, $J_{1,2} = 4.0$ Hz, α-H-1), 4.80 (d, 1H, $J_{1,2} = 3.2$ Hz, α-H-1), 4.82–4.75 (m, 2H), 4.46–4.38 (m, 5H), 4.62–4.41 (m, 7H), 4.39 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.31–4.14 (m, 5H), 4.13 (d, 1H, $J_{1,2} = 7.2$ Hz, H-1), 3.81 (m, 2H), 3.65–3.62 (m, 3H), 3.41–3.39 (m, 3H), 3.38 (s, 3H, OCH_3), 3.17 (dd, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9 (1C, 1Me*C*O), 167.9, 167.2, 166.1, 166.0, 166.0, 165.8, 165.7, 165.7, 165.0, 165.0, 164.9, 164.9, 164.7, 164.6, 164.4 (15C, 15Ph*C*O), 101.4, 100.9, 99.9 (3β-C-1), 99.2, 96.6 (2α-C-1). Anal. Calcd for $C_{138}H_{116}O_{42}$: C, 67.75; H, 4.78. Found: C, 67.57; H, 4.70.

3.8. Methyl β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→2)]-α-D-glucopyranoside (15β) and methyl β-D-glucopyranosyl-(1→3)-α-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→2)]-α-D-glucopyranoside (15α)

Compound **14**β (300 mg, 0.12 mmol) was dissolved in satd NH_3–MeOH (50 mL). After one week at rt, the reaction mixture was concentrated, and the residue was purified on a BioGel P2 column with MeOH–water as the eluent to afford **15**β (98 mg, 95%) as an amorphous solid: $[\alpha]_D$ −3.4 (*c* 1.0, H_2O); ^{1}H NMR (400 MHz, D_2O): δ 4.95 (1H, $J_{1,2} = 3.6$ Hz, H-1), 4.81 (1H, $J_{1,2} = 7.6$ Hz, H-1), 4.73 (1H, $J_{1,2} = 8.0$ Hz, H-1), 4.69 (1H, $J_{1,2} = 8.0$ Hz, H-1), 4.65 (1H, $J_{1,2} = 8.0$ Hz, H-1); ^{13}C NMR (100 MHz, D_2O): δ 103.4, 102.8, 102.6, 102.2 (4β-C-1), 98.8 (α-C-1). Anal. Calcd for $C_{31}H_{54}O_{26}$: C, 44.38; H, 6.46. Found: C, 44.17; H, 6.33. Compound **15** (93 mg, 91%) was obtained using the same procedure as described in the preparation of **15**β: $[\alpha]_D$ +1.6 (*c* 1.0, H_2O); ^{1}H NMR (400 MHz, D_2O): δ 5.27 (1H, $J_{1,2} = 3.6$ Hz, H-1), 4.93 (1H, $J_{1,2} = 3.6$ Hz, H-1), 4.85 (1H, $J_{1,2} = 8.0$ Hz, H-1), 4.75 (1H, $J_{1,2} = 8.0$ Hz, H-1), 4.53 (1H, $J_{1,2} = 8.0$ Hz, H-1); ^{13}C NMR (100 MHz, D_2O): δ 103.4, 102.8, 102.5 (3β-C-1), 99.4, 98.9 (2α-C-1). Anal. Calcd for $C_{31}H_{54}O_{26}$: C, 44.38; H, 6.46. Found: C, 44.45; H, 6.31.

3.9. Methyl 2,4,6-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranoside (17)

To a solution of **9** (2.0 g, 2.5 mmol) in pyridine (20 mL) was added Ac_2O (1 mL, 10.1 mmol), and the reaction mixture was stirred for 4 h, at the end of which time the TLC (2:1 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 **16** (2.0 g, 96%). To a solution of **16** (2.0 g, 2.4 mmol) in CH_2Cl_2 (10 mL) and CH_3OH

(30 mL) was added $PdCl_2$ (100 mg, 0.56 mmol). The reaction mixture was stirred at rt until TLC (2:1 petroleum ether–EtOAc) suggested that the reaction was complete. The mixture was then 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 **17** (1.65 g, 87%) as a foamy solid: $[\alpha]_D$ +8.6 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.03–7.25 (m, 15H, 3P*h*), 5.58 (s, 1H, PhC*H*), 5.38 (dd, 1H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4), 5.18 (dd, 1H, $J_{1,2} = 8.0$ Hz, $J_{2,3} = 8.8$ Hz, H-2), 5.00 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.87 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.78 (dd, 1H, $J_{1,2} = 4.0$ Hz, $J_{2,3} = 9.6$ Hz, H-2), 4.46 (dd, 1H, $J_{5,6} = 3.2$ Hz, $J_{6,6} = 12$ Hz, H-6), 4.33–4.21 (m, 3H), 4.02 (dd, 1H, $J_{2,3} = J_{3,4} = 8.8$ Hz, H-3), 3.84–3.71 (m, 4H), 3.47 (s, 3H, OCH_3), 2.01 (s, 3H, *Me*CO). Anal. Calcd for $C_{43}H_{42}O_{15}$: C, 64.66; H, 5.30. Found: C, 64.58; H, 5.39.

3.10. Methyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranoside (18)

Donor **6** (832 mg, 0.81 mmol) was coupled with acceptor **17** (500 mg, 0.62 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 **18** (706 mg, 67%) as a foamy solid: ^1H NMR ($CDCl_3$): δ 7.93–7.20 (m, 35H, 7P*h*), 5.71 (dd, 1H, $J_{3,4} = J_{4,5} = 9.6$ Hz, H-4), 5.56 (s, 1H, PhC*H*), 5.53 (dd, 1H, $J_{2,3} = J_{3,4} = 9.6$ Hz, H-3), 5.33 (dd, 1H, $J_{1,2} = 7.8$ Hz, $J_{2,3} = 9.6$ Hz, H-2), 5.24 (s, 1H, PhC*H*), 5.19 (m, 2H), 4.82 (d, 1H, $J_{1,2} = 4.0$ Hz, H-1), 4.81–4.79 (m, 2H), 4.72 (dd, 1H, $J_{1,2} = 3.6$ Hz, $J_{2,3} = 9.6$ Hz, H-2), 4.69 (d, 1H, $J_{1,2} = 7.8$ Hz, H-1), 4.45 (d, 1H, $J_{1,2} = 7.6$ Hz, H-1), 4.38 (dd, 1H, $J_{5,6} = 4.8$ Hz, $J_{6,6} = 12$ Hz, H-6), 4.29 (dd, 1H, $J_{5,6} = 3.6$ Hz, $J_{6,6} = 12$ Hz, H-6), 4.25–4.10 (m, 5H), 3.84–3.65 (m, 6H), 3.65 (dd, 1H), 3.45 (dd, 1H), 3.29 (s, 3H, OCH_3), 3.18 (m, 1H), 2.80 (dd, 1H), 1.75 (s, 3H, *Me*CO), 1.54 (s, 3H, COCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 168.7 (2C, 2Me*C*O), 166.2, 166.0, 165.9, 165.0, 164.9, 164.7, 164.5 (7C, 7Ph*C*O), 101.6, 101.4, 101.3, 100.7, 100.7 (3β-C-1, 2Ph*C*H), 97.2 (α-C-1). Anal. Calcd for $C_{92}H_{84}O_{30}$: C, 66.18; H, 5.07. Found: C, 66.47; H, 5.19.

3.11. Methyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2-*O*-acetyl-4,6-di-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-4,6-di-*O*-benzoyl-α-D-glucopyranoside (20)

Compound **18** (700 mg, 0.42 mmol) was added to 90% HOAc–H_2O (30 mL), the mixture was refluxed for 2 h, then concentrated, and co-evaporated with toluene (5 mL) three times. The residue was dried under high vacuum for 2 h, then dissolved in pyridine (10 mL), and benzoyl chloride (0.12 mL, 0.84 mmol) was added. The reaction mixture was stirred at rt for 6 h, at the end of which time TLC (1:1 petroleum ether–EtOAc) suggested that the reaction was finished. Excess benzoyl chloride was destroyed by the addition of MeOH. The mixture was concentrated and purified by chromatography with 1:1 petroleum ether–EtOAc as the eluent to afford compound **19** (547 mg, 73% for two steps) as a foamy solid. To a solution of **19** (500 mg, 0.28 mmol) in CH_3OH (50 mL)–CH_2Cl_2 (50 mL) was added CH_3COCl (7 mL), and the mixture was stirred at rt for 72 h, at the end of which time TLC (1:1 petroleum ether–EtOAc) indicated that the reaction was complete, then neutralized with Et_3N. The reaction mixture was concentrated, then the residue was passed through a silica gel column with 2:1 petroleum ether–EtOAc as the eluent to give **20** (356 g, 73%) as a syrup: $[\alpha]_D$ +25.2 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.09–7.17 (m, 55H, 11 P*h*), 5.71 (dd, 1H, $J_{3,4} = J_{4,5} = 9.6$ Hz, H-4), 5.28–5.17 (m, 4H), 5.10–5.03 (m, 2H), 5.01 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.83 (dd, 1H, $J_{3,4} = J_{4,5} = 8.8$ Hz, H-4), 4.80 (d, 1H, $J_{1,2} = 3.6$ Hz, H-1), 4.70 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.54 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.47 (dd, 1H, $J_{5,6} = 2.4$ Hz, $J_{6,6} = 12$ Hz, H-6), 4.35 (dd, 1H), 4.25 (dd, 1H), 4.15–4.3.89 (m, 9H), 3.76–3.63 (m, 3H), 3.62 (dd, 1H, $J_{1,2} = 3.6$ Hz, $J_{2,3} = 9.2$ Hz, H-2), 3.43 (s, 3H, OCH_3), 1.84 (s, 3H, *Me*CO); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, (1C, 1Me*C*O), 166.0, 165.8, 165.8, 165.7, 165.6, 164.9, 164.9, 164.8, 164.6, 164.6, 164.2 (11C, 11Ph*C*O), 101.0, 101.0, 100.6 (3β-C-1), 96.2 (α-C-1). Anal. Calcd for $C_{104}H_{90}O_{33}$: C, 66.87; H, 4.86. Found: C, 66.65; H, 4.99.

3.12. Allyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→2)]-4,6-*O*-benzylidene-β-D-glucopyranoside (22)

Compound **22** (2.25 g, 95%) was obtained by coupling the donor **1** (3.0 g, 4.05 mmol) with the acceptor **21** (0.5 g, 1.62 mmol) as described in the general procedure: $[\alpha]_D$ 5.4 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.25–7.21 (m, 45H, 9P*h*), 5.82 (dd, 1H, $J_{3,4} = J_{4,5} = 9.6$ Hz, H-4), 5.80–5.77 (m, 2H), 5.57–5.52 (m, 3H), 5.50 (s, 1H, PhC*H*), 5.41 (dd, 1H), 5.28–5.00 (m, 2H, CH_2–CH=CH_2), 4.84 (d, 1H, $J_{1,2} = 7.6$ Hz, H-1), 4.76 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.48 (d, 1H, $J_{1,2} = 7.2$ Hz, H-1), 4.26–4.19 (m, 6H), 4.12–3.96 (m, 2H), 3.84 (dd, 1H), 3.82 (dd, 1H), 3.62 (dd, 1H), 3.34 (m, 1H), 2.75–2.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 165.0, 164.8, 164.8, 164.8, 164.7, 164.7, 164.6 (8C, 8Ph*C*O), 100.9, 100.8, 100.6, 100.3 (3β-C-1, Ph*C*H). Anal. Calcd for $C_{84}H_{72}O_{24}$: C, 68.85; H, 4.95. Found: C, 68.70; H, 4.87.

3.13. 2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→2)]-4,6-*O*-benzylidene-α-D-glucopyranosyl trichloroacetimidate (24)

A mixture of **22** (2.25 g, 1.53 mmol), $PdCl_2$ (90 mg, 0.50 mmol), CH_2Cl_2 (50 mL), and CH_3OH (10 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 2:1 petroleum ether–EtOAc as the eluent to give **23** (1.61 g, 74%). To a solution of **23** (1.61 g, 1.13 mmol) in dry CH_2Cl_2 was added trichloroacetonitrile (0.23 mL, 2.26 mmol) and DBU (0.1 mL, 0.8 mmol). The mixture was stirred for 3 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated the reaction was complete. The reaction mixture was concentrated and then purified by flash chromatography with 2:1 petroleum ether–EtOAc as the eluent to afford the donor **24** (1.50 g, 83%) as a foamy solid: $[\alpha]_D$ −3.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.35–7.23 (m, 40H, 8P*h*), 6.45 (d, 1H, $J_{1,2}$ = 4.0 Hz, H-1), 6.03 (dd, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, H-4), 5.81–5.77 (m, 2H), 5.67 (dd, 1H, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 9.6 Hz, H-2), 5.65 (s, 1H, PhC*H*), 5.62–5.51 (m, 2H), 5.41 (dd, 1H), 4.73 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.50 (d, 1H, $J_{1,2}$ = 7.2 Hz, H-1), 4.28–4.17 (m, 6H), 4.10–3.95 (m, 2H), 3.83 (dd, 1H), 3.82 (dd, 1H), 3.65 (dd, 1H), 3.35 (m, 1H), 2.76–2.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 165.4, 164.9, 164.8, 164.8, 164.6, 164.5, 164.5, (8C, 8Ph*C*O), 101.2, 101.0, 100.7, 100.2 (3β-C-1, Ph*C*H). Anal. Calcd for $C_{83}H_{68}Cl_3NO_{24}$: C, 63.51; H, 4.37. Found: C, 63.77; H, 4.42.

3.14. Methyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→2)]-4,6-*O*-benzylidene-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→2)]-4,6-di-*O*-benzoyl-α-D-glucopyranoside (25)

Compound **25** (2.25 g, 95%) was obtained by coupling the donor **24** (500 mg, 0.31 mmol) with the acceptor **12** (375 mg, 0.25 mmol) as described in the general procedure: $[\alpha]_D$ −2.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.13–7.25 (m, 85H, 17P*h*), 6.01 (dd, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, H-4), 5.81 (dd, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, H-4), 5.62–5.50 (m, 5H), 5.48 (dd, 1H, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 10 Hz, H-2), 5.33–5.21 (m, 3H), 5.15 (s, 1H, PhC*H*), 5.02 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 4.85 (dd, 1H), 4.80 (d, 1H, $J_{1,2}$ = 4.0 Hz, H-1), 4.64 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1), 4.52–4.39 (m, 5H), 4.34–4.27 (m, 3H), 4.22–4.00 (m, 4H), 3.75–3.48 (m, 8H), 3.23 (dd, 1H, $J_{5,6}$ = 4.0 Hz, $J_{6,6}$ = 11.6 Hz, H-6), 3.08 (dd, 1H), 3.06–3.26 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 166.0, 166.0, 165.9, 165.9, 165.9, 165.6, 165.4, 165.2, 165.1, 165.0, 165.0, 165.0, 164.8, 164.5, 164.5, 164.0 (17C, 17Ph*C*O), 101.0, 101.0, 100.0, 99.7, 99.7 (4β-C-1, Ph*C*H), 99.4, 97.8 (2α-C-1). Anal. Calcd for $C_{163}H_{136}O_{48}$: C, 68.39; H, 4.79. Found: C, 68.09; H, 4.64.

3.15. Methyl β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→2)]-α-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→2)]-α-D-glucopyranoside (27)

Compound **25** (500 mg, 0.17 mmol) was added to 90% HOAc–H_2O (30 mL), the mixture was refluxed for 2 h, then concentrated, and co-evaporated with toluene (10 mL) three times, and purified by chromatography with 1:1 petroleum ether–EtOAc as the eluent to afford compound **26** (373 mg, 77%) as a foamy solid. Compound **26** (300 mg, 0.11 mmol) was dissolved in satd NH_3–MeOH (50 mL). After one week at rt, the reaction mixture was concentrated, and the residue was purified on a BioGel P2 column with MeOH–water as the eluent to afford **27** (99 mg, 91%) as an amorphous solid: $[\alpha]_D$ +26.6 (*c* 1.0, H_2O); ^{1}H NMR (400 MHz, D_2O): δ 5.58 (1H, $J_{1,2}$ = 3.6 Hz, H-1), 4.97 (1H, $J_{1,2}$ = 4.0 Hz, H-1), 4.83 (1H, $J_{1,2}$ = 7.6 Hz, H-1), 4.74 (1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.69 (1H, $J_{1,2}$ = 7.6 Hz, H-1), 4.65 (1H, $J_{1,2}$ = 7.6 Hz, H-1); ^{13}C NMR (100 MHz, D_2O): δ 103.6, 103.4, 103.4, 102.4 (4β-C-1), 99.2, 98.1 (2α-C-1). Anal. Calcd for $C_{37}H_{64}O_{31}$: C, 44.22; H, 6.42. Found: C, 44.03; H, 6.58.

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