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Highly efficient synthesis of alternate α- and β-(1 → 3)-linked glucose hepta- and octasaccharides

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Abstract

Two heptasaccharides α-D-Glc*p*-(1 → 3)-β-D-Glc*p*-(1 → 3)-α-D-Glc*p*-(1 → 3)-β-D-Glc*p*-(1 → 3)-α-D-Glc*p*-(1 → 3)-β-D-Glc*p*-(1 → 3)-β-D-Glc*p*-1-OMP and β-D-Glc*p*-(1 → 3)-α-D-Glc*p*-(1 → 3)-β-D-Glc*p*-(1 → 3)-α-D-Glc*p*-(1 → 3)-β-D-Glc*p*-(1 → 3)-α-D-Glc*p*-(1 → 3)-β-D-Glc*p* 1-OMP, and two octasaccharides α-D-Glc*p*-(1 → 3)-β-D-Glc*p*-(1 → 3)-α-D-Glc*p*-(1 → 3)-β-D-Glc*p*-(1 → 3)-α-D-Glc*p*-(1 → 3)-β-D-Glc*p*-(1 → 3)-α-D-Glc*p*-(1 → 3)-β-D-Glc*p*-1-OMP and β-D-Glc*p*-(1 → 3)-α-D-Glc*p*-(1 → 3)-β-D-Glc*p*-(1 → 3)-α-D-Glc*p*-(1 → 3)-β-D-Glc*p*-(1 → 3)-α-D-Glc*p*-(1 → 3)-β-D-Glc*p*-(1 → 3)-β-D-Glc*p* 1-OMP were synthesized in a stereospecific way by remote control.

Keywords: Oligosaccharide; Glucose; Stereoselective synthesis

1. Introduction

β-D-(1 → 3)-Linked glucans are widely distributed in some biologically important natural products, such as *Ganoderma lucidum*, *Schizophyllum commune* and *Lentinus edodes*.[1] α-(1 → 3)-Linked glucans are found from some fungi such as *Cryphonectrini parasitica* and *Ganoderma lucidum*.[2] Although these glucans have high molecular weight, their active fragments are usually oligosaccharides with DP 6–7.[3] In order to investigate the relationship between structure and function of these oligosaccharides, a series of model compounds including artificially designed structures, are needed. The β-(1 → 3)-linked glucose oligosaccharides have been obtained by synthesis[4a] and from degradation of curdlan,[4b] and the bioactivity of sulfated oligosaccharides has been tested.[4b,4c] The synthesis of an α-(1 → 3)-linked glucose polysaccharide[5a] has been reported, and the bioactivity of a sulfated α-(1 → 3)-linked glucan as a potential antitumor agent has also been evaluated.[5b] Glucans with alternate α- and β-(1 → 3) linkages are novel molecules that will be useful in conformation and bioactivity studies. Our previous communications[6] disclosed a new method for construction of glucose oligosaccharides with alternate α- and β-(1 → 3) linkages by remote stereocontrol. We present herein the synthesis of glucose hepta- and octasaccharides with alternate α- and β-, or alternate β- and α-(1 → 3) linkages.

2. Results and discussion

Our previous report revealed that in (1 → 3)-glucosylation the glycosyl bond originally present in either donor or acceptor control the stereoselectivity of the forthcoming bond, i.e., the newly formed glycosidic linkage has the opposite anomeric configuration of that of either the donor or acceptor in spite of the presence of a C-2 ester capable of neighboring group participation. Thus, condensation of an α-(1 → 3)-linked disaccharide donor with an α-(1 → 3)-linked disaccharide acceptor readily affords a β-linked tetrasaccharide. Meanwhile, coupling of a β-(1 → 3)-linked disaccharide donor with a β-(1 → 3)-linked disaccharide acceptor, gives an α-linked tetrasaccharide. Based on the previously reported method, a glucose heptasaccharide with alternate α- and β-(1 → 3) linkages was prepared as outlined in Scheme 1. Condensation of 2,4,6-tri-*O*-acetyl-3-*O*-allyl-α-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl trichloroacetimi-

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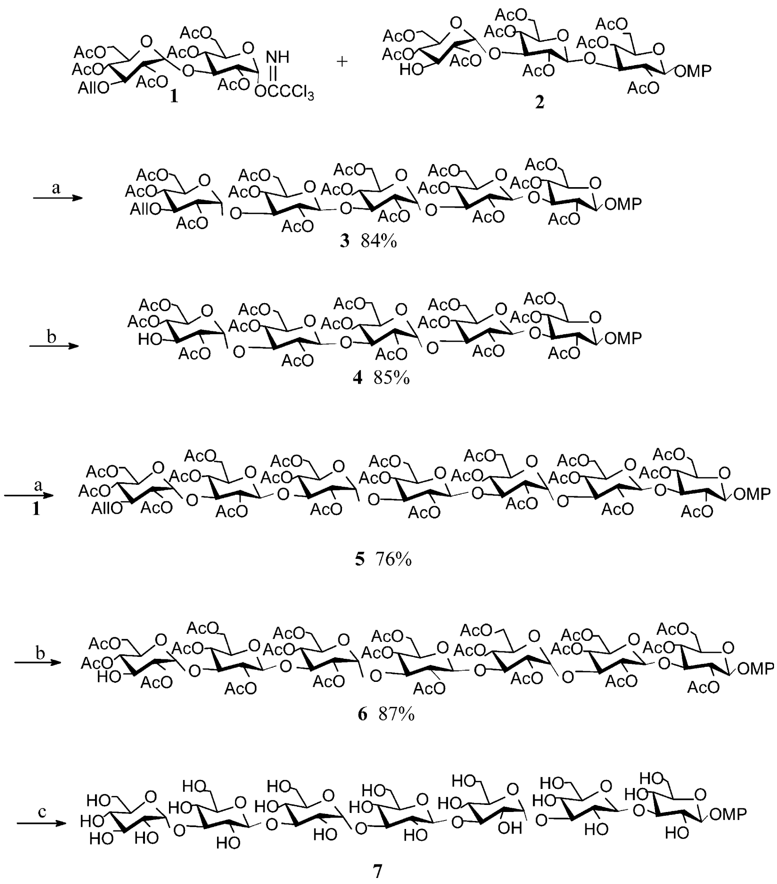
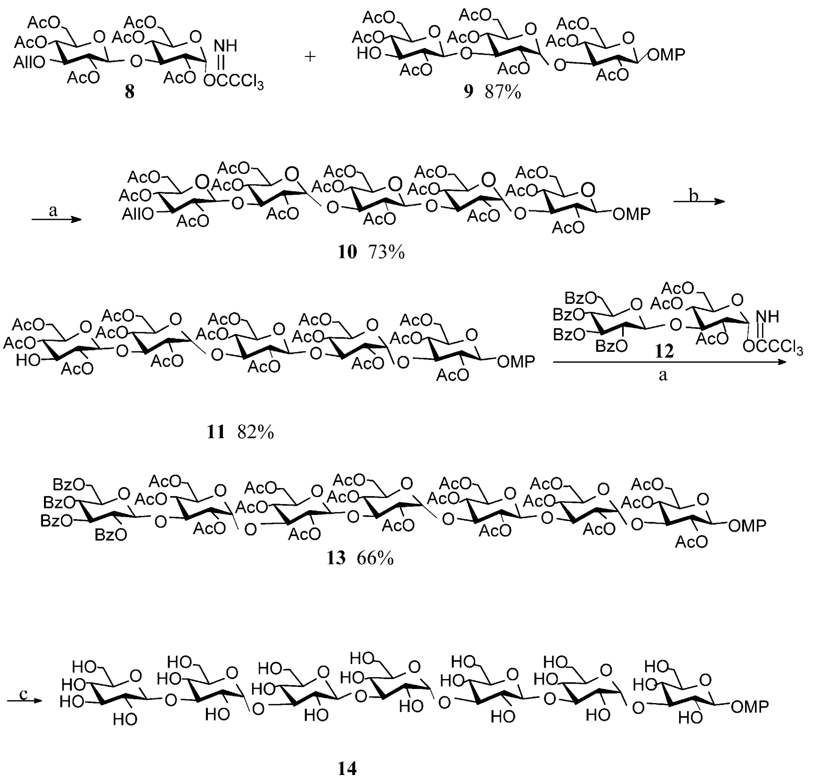


Scheme 1. Reagents and conditions: (a) TMSOTf, CH_2Cl_2, −20 °C to rt. (b) $PdCl_2$, MeOH, rt, 3 h. (c) Satd NH_3–MeOH, rt, 7 days.

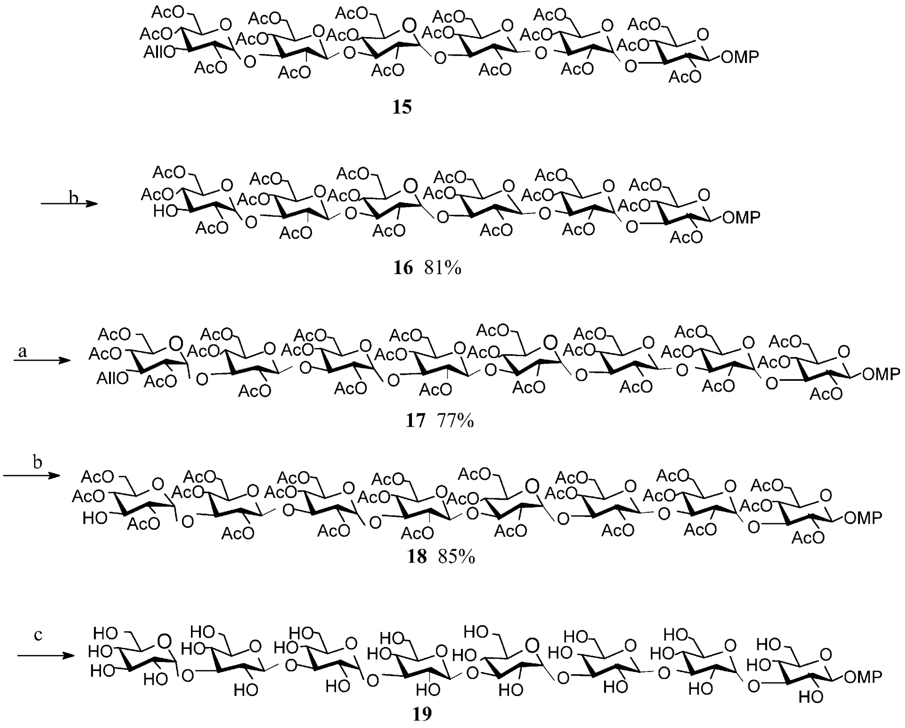
date (**1**)[6b] with the trisaccharide acceptor **2**, obtained by deallylation of 4-methoxyphenyl 2,4,6-tri-*O*-acetyl-3-*O*-allyl-α-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranoside,[6b] stereospecifically gave a β-linked pentasaccharide **3** in high yield (84%). Deallylation of **3** with $PdCl_2$ in methanol was carried out smoothly affording the pentasaccharide acceptor **4** (85%). Coupling of the donor **1** with the acceptor **4** yielded a β-linked heptasaccharide **5** in satisfactory yield (76%). Deallylation of **5** furnished **6** (87%) and subsequent deacetyaltion in saturated ammonia–methanol solution quantitatively gave the glucoheptaose **7** with alternate α- and β-(1 → 3) linkages. The ^1H and ^{13}C NMR spectra of **7** showed all of the characteristic signals such as δ 5.24, 5.24 and 5.21 ($J_{1,2}$ 3.2 or 4.0 Hz) for H-1 (α), and δ 4.88, 4.69, 4.67 and 4.61 ($J_{1,2}$ 7.6 Hz) for H-1 (β), and δ 101.21, 101.08 and 101.08 for C-1(α), and δ 104.97, 104.97, 104.97 and 103.15 for C-1(β).

Scheme 2 shows the synthesis of the frame-shifted heptasaccharide **14** with alternate β- and α-(1 → 3) linkages. In this synthesis, a β-(1 → 3)-linked disaccharide trichloroacetimidate **8**[6b] was used as the glycosyl donor, and a trisaccharide **9** was used as the acceptor, which was prepared by condensation of 2,4,6-tri-*O*-acetyl-3-*O*-allyl-β-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl trichloroacetimidate (**8**)[6b] with 4-methoxyphenyl 2,4,6-tri-*O*-acetyl-β-D-glucopyranoside, followed by deallylation. Again, α-linked pentasaccharide **10** was obtained stereospecifically in good yield (73%) in spite of the presence of the C-2 ester group in the donor. Deallylation of **10** (82%), followed by reaction with the disaccharide donor **12**,[6a] also gave the α-linked heptasaccharide **13** (66%), and subsequent deacylation afforded the target glucoheptaose with alternate β- and α-(1 → 3)-bonds.

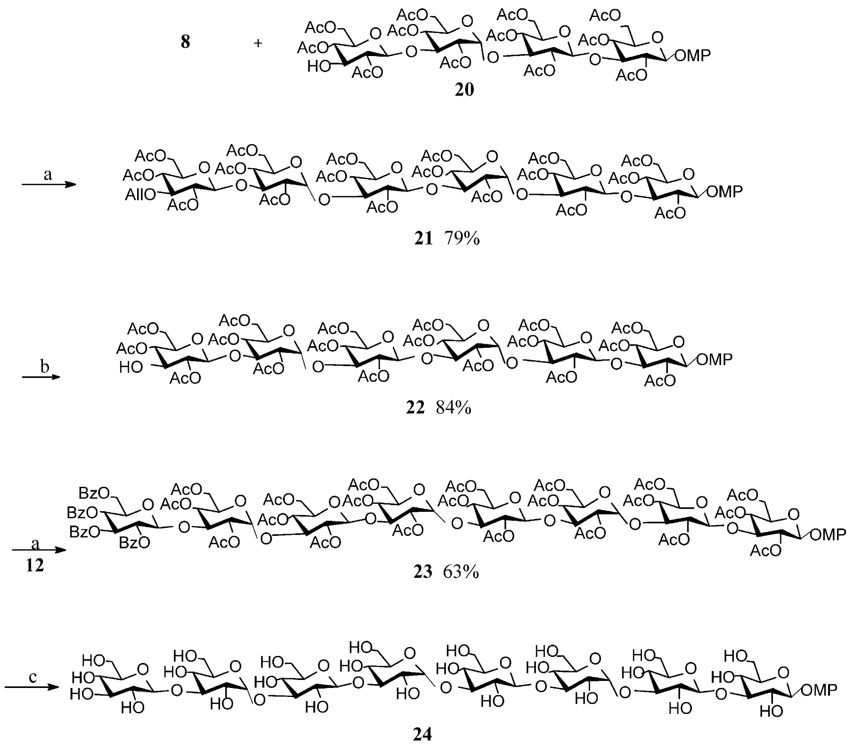
Syntheses of the glucooctaose **19** with alternate α- and β-(1 → 3)-bonds and the glucooctaose **24** with alternate β- and α-(1 → 3)-bonds are shown in Schemes 3 and 4, respectively. For the former, alternately α- and β-(1 → 3)-linked hexasaccharide (**15**)[6b] was deallylated to give the acceptor **16** (81%). Coupling of **16** with **1** stereospecifically furnished β-linked octasaccharide **17** (77%). Deallylation to give **18** (85%), followed by deacetylation, yielded the target glucooctaose **19**. For the latter, condensation of **8** with the alternate β- and α-(1 → 3)-linked glucotetraose acceptor, which was prepared from deallylation of the corresponding glucotetraose,[6b] afforded the alternate β- and α-(1 → 3)-linked glucohexaose **21** (79%). Deallylation, followed by coupling with the disaccharide donor **12**, and subsequent deacylation



Scheme 2. Reagents and conditions: (a) TMSOTf, CH_2Cl_2, −20 °C to rt. (b) $PdCl_2$, MeOH, rt, 3 h. (c) Satd NH_3–MeOH, rt, 7 days.



Scheme 3. Reagents and conditions: (a) TMSOTf, CH_2Cl_2, −20 °C to rt. (b) $PdCl_2$, MeOH, rt, 3 h. (c) Satd NH_3–MeOH, rt, 7 days.



Scheme 4. Reagents and conditions: (a) TMSOTf, CH_2Cl_2, −20 °C to rt. (b) $PdCl_2$, MeOH, rt, 3 h. (c) Satd NH_3–MeOH, rt, 7 days.

gave the target glucooctaose **24** with alternate β- and α-(1 → 3)-bonds.

For investigation of the antiviral activities, **7** and **14** were sulfated. The biological evaluations of all of the hepta- and octaoses are in progress.

In summary, alternate α- and β-(1 → 3)-linked and β- and α-(1 → 3)-linked glucoheptaoses and glucooctaoses were readily synthesized in a stereospecific manner by remote stereocontrol. Owing to the use of acyl groups in the syntheses, the procedure was significantly simplified, and large-scale preparations of higher oligosaccharides should be possible.

3. Experimental

3.1. General methods

Melting points were determined with a 'Mel-Temp' apparatus. Optical rotations were determined with a Perkin–Elmer model 241-MC automatic polarimeter for solutions in a 1-dm, jacketed cell. ^1H NMR, ^{13}C NMR, and 2D NMR spectra were recorded with Varian XL-400 spectrometers, for solutions in $CDCl_3$ or in D_2O as indicated. Chemical shifts are expressed in δ (ppm) downfield from the Me_4Si absorption. Mass spectra were recorded with a VG PLATFORM mass spectrometer using the ESI mode. Thin-layer chromatography (TLC) was performed on silica gel HF with detection by charring with 30% (v/v) sulfuric acid in MeOH or by UV detection. Column chromatography was conducted by elution of a column (8 × 100, 16 × 240, 18 × 300, 35 × 400 mm) of silica gel (100–200 mesh) with EtOAc–petroleum ether (bp 60–90 °C) as the eluent. Analytical LC was performed with a Gilson HPLC consisting of a pump (model 306), stainless steel column packed with silica gel (Spherisorb SiO_2, 10 × 300 or 4.6 × 250 mm), differential refractometer (132-RI Detector), UV–Vis detector (model 118). EtOAc–petroleum ether (bp 60–90 °C) was used as the eluent at a flow rate of 1–4 mL/min. Solutions were concentrated at a temperature < 60 °C under diminished pressure.

3.2. General procedure for deallylation[7] to prepare acceptors

To a solution of 3-*O*-allylated oligosaccharide [**3**, **5**, **10**, **15**, **17** or **21** (0.387–0.124 mmol)] in MeOH was added $PdCl_2$ (60–20 mg). After stirring for several h at room temperature (rt), TLC indicated that the reaction was complete. The mixture was filtered, and the combined filtrate and washings were concentrated to dryness. The resultant residue was purified by flash chromatography to give products [**4**, **6**, **11**, **16**, **18** or **22** (81–87%)], respectively.

3.3. General procedure for the glycosidation[8]

The mixture of donor (**1**, **8** or **12**) and acceptor (**2**, **4**, **9**, **11**, **16**, **20** or **22**) 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 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, gave the corresponding products (**3**, **5**, **10**, **13**, **17**, **21** or **23**).

3.4. General procedure for the deacylation

The oligosaccharides (**6**, **13**, **18** or **23**) was added to a saturated 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 products as a white amorphous powder (**7**, **14**, **19** or **24**), respectively.

3.5. General procedure for sulfation[4c]

The free oligosaccharide (**7** or **14**) was dissolved in pyridine at 85 °C, and SO_3–pyridine complex (500 mg) was added, with subsequent stirring for 90 min. After cooling at rt, the solution was adjusted with satd $Ba(OH)_2$ to pH 8.0 in an ice bath. The $BaSO_4$ was separated by centrifugation, and water was evaporated off. The residue was passed through a Na^+ type ion-exchange resin column. The product was precipitated with acetone.

3.6. 4-Methoxyphenyl 2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranoside (2)

Deallylation of 4-methoxyphenyl 2,4,6-tri-*O*-acetyl-3-*O*-allyl-α-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranoside (400 mg, 0.387 mmol) gave acceptor **2** (324 mg, 84%): $[\alpha]_D$ −24.5° (*c* 1.5, $HCCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.93–6.80 (dd, 4 H, $-C_6H_4-$), 5.23 (d, 1 H, *J* 3.6 Hz, α H-1), 5.20 (dd, 1 H, *J* 9.2 Hz), 5.18 (dd, 1 H, *J* 9.6 Hz), 5.00 (d, 1 H, *J* 9.6 Hz), 4.97 (dd, 1 H, *J* 9.6 Hz), 4.91 (dd, 1 H, *J* 9.6 Hz), 4.81 (d, 1 H, *J* 8.0 Hz, β H-1), 4.61 (dd, 1 H, $J_{1,2}$ 3.6, $J_{3,4}$ 9.6 Hz, H-2″), 4.49 (d, 1 H, *J* 8.0 Hz, β H-1), 4.31–4.25 (m, 2 H), 4.20–3.90 (m, 7 H), 3.84 (dd, 1 H, *J* 9.6 Hz), 3.81–3.77 (m, 4 H, CH_3O), 3.57–3.55 (m, 1 H), 2.15, 2.12, 2.10, 2.10, 2.09, 2.07, 2.07, 2.06, 2.05 (9 CH_3CO). Anal. Calcd for $C_{43}H_{56}O_{26}$: C, 52.23; H, 5.71. Found: C, 52.34; H, 5.74.

3.7. 4-Methoxyphenyl 2,4,6-tri-*O*-acetyl-3-*O*-allyl-α-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranoside (3)

Donor **1** (245 mg, 0.314 mmol) was coupled with acceptor **2** (310 mg, 0.314 mmol) to give **3** (420 mg, 84%): $[\alpha]_D$ −17.3°(*c* 1.5, H CCl_3); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92–6.79 (dd, 4 H, $-C_6H_4-$), 5.80–5.74 (m, 1 H, $-CH=$), 5.22–4.98 (m, 12 H), 4.81 (d, 1 H, *J* 8.0 Hz, β H-1), 4.71–4.57 (m, 2 H), 4.49 (d, 1 H, *J* 8.0 Hz, β H-1), 4.45 (d, 1 H, *J* 8.0 Hz, β H-1), 4.29–3.82 (m, 18 H), 3.79–3.77 (m, 4 H, CH_3O), 3.68 (dd, 1 H, *J* 9.2 Hz), 3.58–3.53 (m, 2 H), 2.15, 2.14, 2.11, 2.10, 2.08, 2.07, 2.07, 2.07, 2.07, 2.05, 2.04, 2.03, 2.02, 1.97 (15 CH_3CO some signals overlapped); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.54, 170.52, 170.50, 170.39, 170.30, 169.35, 169.11, 169.09, 168.91, 168.85, 168.62, 168.59, 166.99 (15 CH_3*C*O some signals overlapped), 155.65, 150.85, 134.20, 118.38, 116.64, 114.46 (*C*H_2=*C*H–CH_2–, MeO*Ph*), 100.67 (β C-1), 100.58 (β C-1), 100.04 (β C-1), 95.87 (α C-1), 94.91 (α C-1), 78.21, 75.91, 74.93, 74.89, 73.84, 73.03, 72.68, 72.31, 71.92, 71.72, 71.56, 71.13, 70.49, 69.71, 69.18, 68.31, 68.13, 67.83, 67.38, 62.13, 61.44, 55.55, 51.98, 20.88, 20.85, 20.76, 20.69, 20.66, 20.64, 20.58, 20.56, 2.50, 20.45, 20.34 (some signals overlapped). Anal. Calcd for $C_{70}H_{92}O_{42}$: C, 52.37; H, 5.78. Found: C, 52.28; H, 5.71.

3.8. 4-Methoxyphenyl 2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranoside (4)

Deallylation of **3** (400 mg, 0.25 mmol) gave acceptor **4** (330 mg, 85%): $[\alpha]_D$ −10.8° (*c* 1.5, $HCCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92–6.79 (dd, 4 H, $-C_6H_4-$), 5.20 (d, 1 H, *J* 4.0 Hz, α H-1), 5.19 (dd, 1 H, *J* 8.0 Hz), 5.16–4.87 (m, 8 H), 4.84 (d, 1 H, *J* 8.0 Hz, β H-1), 4.71–4.59 (m, 2 H), 4.49 (d, 1 H, *J* 8.0 Hz, β H-1), 4.46 (d, 1 H, *J* 8.0 Hz, β H-1), 4.32–3.87 (m, 17 H), 3.79–3.77 (m, 4 H, CH_3O), 3.58–3.53 (m, 2 H), 2.15, 2.14, 2.13, 2.11, 2.09, 2.08, 2.07, 2.05, 2.03, 2.02, 1.98 (15 CH_3CO some signals overlapped). Anal. Calcd for $C_{67}H_{88}O_{42}$: C, 51.41; H, 5.67. Found: C, 51.52; H, 5.56.

3.9. 4-Methoxyphenyl 2,4,6-tri-*O*-acetyl-3-*O*-allyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranoside (5)

Donor **1** (155 mg, 0.198 mmol) was coupled with acceptor **4** (310 mg, 0.198 mmol) to give **5** (328 mg, 76%): $[\alpha]_D$ −8.7° (*c* 1.5, H CCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.91–6.79 (dd, 4 H, $-C_6H_4-$), 5.80–5.73 (m, 1 H, $-CH=$), 5.21–4.93 (m, 16 H), 4.81 (d, 1 H, *J* 8.0 Hz, β H-1), 4.71–4.68 (m, 3 H), 4.50–4.43 (m, 3 H), 4.32–3.82 (m, 25 H), 3.81–3.71 (m, 4 H, CH_3O), 3.56 (dd, 1 H, *J* 9.0 Hz), 3.56–3.54 (m, 3 H), 2.15, 2.14, 2.14, 2.11, 2.10, 2.10, 2.10, 2.09, 2.09, 2.07, 2.07, 2.07, 2.06, 2.04, 2.04, 2.03, 2.02, 2.01, 2.01, 1.97, 1.96 (18 s, 18 CH_3CO); ^{13}C NMR (100 MHz, CDCl$_3$): δ 170.70, 170.68, 170.65, 170.50, 170.45, 169.53, 169.49, 169.24, 169.18, 169.05, 168.99, 16.875, 168.59 (18 CH_3CO, some signals overlapped), 155.67, 150.45, 134.38, 118.57, 116.78, 114.65 (CH_2=CH–CH_2–, MeO*Ph*), 100.82 (β C-1), 100.76 (β C-1), 100.65 (β C-1), 100.22 (β C-1), 96.01 (α C-1), 95.21 (α C-1), 95.06 (α C-1), 78.36, 76.11, 75.58, 75.09, 75.01, 74.93, 74.00, 73.18, 72.90, 72.46, 72.13, 71.87, 71.76, 71.49, 71.32, 70.73, 69.98, 69.37, 68.49, 68.36, 68.07, 68.01, 67.59, 62.33, 62.02, 61.67, 55.74, 21.01, 20.92, 20.82, 20.73, 20.66, 20.62, 20.52 (some signals overlapped). Anal. Calcd for $C_{94}H_{124}O_{58}$: C, 51.74; H, 5.73. Found: C, 51.62; H, 5.80.

3.10. 4-Methoxyphenyl 2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranoside (6)

Deallylation of **5** (300 mg, 0.138 mmol) gave **6** (256 mg, 87%): $[\alpha]_D$ −7.6° (*c* 1.5, H CCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.91–6.79 (dd, 4 H, $-C_6H_4-$), 5.20–4.89 (m, 14 H), 4.81 (d, 1 H, *J* 8.0 Hz, β H-1), 4.71–4.68 (m, 2 H), 4.62–4.59 (m, 1 H), 4.50–4.43 (m, 3 H), 4.30–3.79 (m, 23 H), 3.81–3.71 (m, 5 H, CH_3O), 3.57–3.55 (m, 3 H), 2.15, 2.14, 2.14, 2.12, 2.11,, 2.10, 2.09, 2.09, 2.09, 2.07, 2.07, 2.07, 2.06, 2.04, 2.04, 2.03, 2.02, 2.01, 2.01, 1.98, 1.95 (18 s, 18 CH_3CO). Anal. Calcd for $C_{91}H_{120}O_{58}$: C, 51.03; H, 5.65. Found: C, 50.93; H, 5.68.

3.11. 4-Methoxyphenyl α-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-α-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-α-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranoside (7)

Compound **7** (140 mg) was obtained by deacetylation of **6** (255 mg, 0.120 mmol): $[\alpha]_D$ −0.4°(*c* 1.0, H$_2$O); ^{1}H NMR (400 MHz, D$_2$O): δ 6.99–6.82 (dd, 4 H, $-C_6H_4-$), 5.24 (d, 2 H, *J* 3.2 Hz, 2α H-1), 5.21 (d, 1 H, *J* 4.0 Hz, α H-1), 4.88 (d, 1 H, *J* 7.6 Hz, β H-1), 4.69–4.66 (m, 2 H, 2 β H-1), 4.61 (d, 1 H, *J* 7.6 Hz, β H-1), 3.97–3.27 (m, 45 H); ^{13}C NMR (100 MHz, D$_2$O): δ 156.87, 153.00, 120.40, 117.16 (MeO*Ph*), 104.97 (β C-1), 104.97 (β C-1), 104.97 (β C-1), 103.15 (β C-1), 101.21 (α C-1), 101.08 (α C-1), 101.08 (α C-1), 86.36, 84.29, 84.06, 75.55, 75.31, 75.03, 74.83, 74.33, 73.85, 73.62, 73.30, 72.93, 72.39, 72.13, 72.07, 71.88, 71.68, 71.42, 71.22, 71.01, 70.80, 70.24, 70.09, 70.9, 70.63, 62.35, 57.90 (some signals overlapped). Anal. Calcd for $C_{49}H_{78}O_{37}$: C, 46.74; H, 6.24. Found: C, 46.92; H, 6.21.

Sulfation of **7** (120 mg, 0.0985 mmol) gave sulfated oligosaccharide (170 mg): ^{1}H NMR (400 MHz, D$_2$O): δ 7.11–6.89 (dd, 4 H, $-C_6H_4-$), 5.66–5.63 (m, 3 H, 3 α H-1), 5.29 (d, 1 H, *J* 5.6 Hz, β H-1), 5.09–5.08 (m, 3 H, 3 β H-1), 4.87–4.13 (m, 42 H), 3.74 (s, 3 H, CH_3O); ^{13}C NMR (100 MHz, D$_2$O): δ 158.84, 154.86, 118.71, 115.23 (MeO*Ph*), 100.26 (β C-1), 99.80 (3 β C-1), 95.31 (α C-1), 95.20 (α C-1), 95.15 (α C-1), 78.59, 78.36, 78.04, 76.49, 76.36, 75.99, 75.31, 75.02, 74.81, 74.59, 74.35, 74.04, 73.29, 73.67, 68.91, 68.66, 68.37, 68.20, 67.87, 67.66, 66.63, 66.37, 56.08 (some signals overlapped). Anal. Found (Calcd): C, 14.10 (16.8); H, 2.38 (1.60); S, 16.63 (20.11). The degree of sulfation (ds) 2.2 (ds designate the number of sulfate groups per glucose residue).

3.12. 4-Methoxyphenyl 2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranoside (9)

Deallylation of 4-methoxyphenyl 2,4,6-tri-*O*-acetyl-3-*O*-allyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranoside (400 mg, 0.387 mmol) gave acceptor **9** (385 mg, 87%): $[\alpha]_D$ +5.7° (*c* 1.5, HCCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.93–6.80 (dd, 4 H, $-C_6H_4-$), 5.27 (dd, 1 H, *J* 9.2 Hz), 5.28 (dd, 1 H, *J* 9.6 Hz), 5.20 (d, 1 H, *J* 3.2 Hz, α H-1), 4.99 (dd, 1 H, *J* 9.6 Hz), 4.90 (dd, 1 H, *J* 9.6 Hz), 4.82 (d, 1 H, *J* 8.0 Hz, β H-1), 4.80 (dd, 1 H, $J_{1,2}$ 4.0, $J_{3,4}$ 9.6 Hz, H-2′), 4.71 (dd, 1 H, *J* 9.6 Hz), 4.58 (d, 1 H, *J* 8.0 Hz, β H-1), 4.41–4.21 (m, 2 H), 4.18–3.99 (m, 7 H), 3.77 (s, 3 H, CH_3O), 3.72–3.52 (m, 3 H), 2.20, 2.10, 2.10, 2.09, 2.09, 2.07, 2.06, 2.04, 2.02 (9 CH_3CO). Anal. Calcd for $C_{43}H_{56}O_{26}$: C, 52.23; H, 5.71. Found: C, 52.26; H, 5.74.

3.13. 4-Methoxyphenyl 2,4,6-tri-*O*-acetyl-3-*O*-allyl-β-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranoside (10)

Donor **8** (245 mg, 0.314 mmol) was coupled with acceptor **9** (360 mg, 0.314 mmol) to give **10** (426 mg, 73%): $[\alpha]_D$ +8.7° (*c* 1.0, $HCCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92–6.80 (dd, 4 H, $-C_6H_4-$), 5.76–5.69 (m, 1 H, $-CH=$), 5.26–4.93 (m, 11 H), 4.86 (dd, 1 H, *J* 9.2 Hz), 4.81 (d, 1 H, *J* 7.8 Hz, β H-1), 4.73–4.69 (m, 2 H), 4.51 (d, 1 H, *J* 8.2 Hz, β H-1), 4.48 (d, 1 H, *J* 8.2 Hz, β H-1) 4.31–3.85 (m, 18 H), 3.77 (s, 3 H, CH_3O), 3.69–3.48 (m, 4 H), 2.16, 2.16, 2.10, 2.09, 2.09, 2.06, 2.05, 2.04, 2.03, 2.00, 1.99, 1.97 (15 CH_3CO some signals overlapped); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.63, 170.54, 170.46, 170.40, 170.37, 170.26, 169.37, 169.15, 168.90, 168.81, 168.67, 168.43 (15 CH_3CO some signals overlapped), 155.76, 150.85, 134.03, 118.49, 116.75, 114.49 ($CH_2=CH-CH_2-$, MeO*Ph*), 100.78 (β C-1), 10047 (β C-1), 100.47 (β C-1), 9525 (α C-1), 95.10 (α C-1), 75.33, 75.10, 74.95, 74.80, 72.35, 72.23, 72.14, 72.05, 71.57, 71.44, 71.22, 70.37, 69.10, 67.93, 67.86, 67.49, 67.43, 61.78, 61.67, 61.43, 55.55, 20.84, 20.79, 20.69, 20.58, 20.47, 20.36 (some signals overlapped) Anal. Calcd for $C_{70}H_{92}O_{42}$: C, 52.37; H, 5.78. Found: C, 52.43; H, 5.81.

3.14. 4-Methoxyphenyl 2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranoside (11)

Deallylation of **10** (400 mg, 0.387 mmol) gave acceptor **11** (320 mg, 82%): $[\alpha]_D$ +11.3° (*c* 1.0, $HCCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.91–6.78 (dd, 4 H, $-C_6H_4-$), 5.24–4.87 (m, 10 H), 4.80 (d, 1 H, *J* 7.8 Hz, β H-1), 4.76–4.68 (m, 2 H), 4.50 (d, 2 H, *J* 8.2 Hz, 2 β H-1), 4.33–3.85 (m, 14 H), 3.77 (s, 3 H, CH_3O), 3.69–3.56 (m, 4 H), 2.15, 2.15, 2.08, 2.05, 2.04, 2.02, 2.01, 2.00, 1.96, 1.91 (15 CH_3CO some signals overlapped); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.59, 170.55, 170.48, 170.43, 170.38, 170.26, 169.38, 169.32, 169.08, 168.93, 168.83, 168.48 (15 CH_3CO some signals overlapped), 155.73, 150.83, 118.46, 114.47 (MeO*Ph*), 100.44 (3 β C-1), 95.26 (α C-1), 95.2 (α C-1), 75.64, 75.07, 75.03, 74.06, 74.02, 72.35, 72.19, 71.87, 71.69, 71.54, 71.50, 71.31, 70.49, 70.37, 70.25, 67.90, 67.41, 67.32, 61.74, 61.40, 20.88, 20.84, 20.78, 20.65, 20.60, 20.57, 20.52, 20.43, 20.35, 20.29 (some signals overlapped). Anal. Calcd for $C_{67}H_{88}O_{42}$: C, 51.41; H, 5.67. Found: C, 51.55; H, 5.86.

3.15. 4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranoside (13)

Donor **12** (200 mg, 0.191 mmol) was coupled with acceptor **11** (300 mg, 0.191 mmol) to give **13** (335 mg, 66%): $[\alpha]_D$ +5.7° (*c* 1.0, CCl_3H); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87–7.34 (m, 20 H, 4 *Ph*CO), 6.91–6.18 (dd, 4 H, $-C_6H_4-$), 5.90 (dd, 1 H, *J* 9.6 Hz), 5.70 (dd, 1 H, *J* 9.6 Hz), 5.36 (dd, 1 H, *J* 9.6 Hz), 5.26–4.87 (m, 14 H), 4.80 (d, 1 H, *J* 8.0 Hz, β H-1), 4.72–4.69 (m, 3 H), 4.57–4.41 (m, 4 H), 4.30–3.82 (m, 20 H), 3.79–3.77 (m, 4 H, CH_3O), 3.70–3.48 (m, 3 H), 2.16, 2.12, 2.09, 2.08, 2.04, 2.01, 1.96, 1.93, 1.88, 1.85 (18 CH_3CO some signals overlapped); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.51, 170.47, 170.43, 170.40, 170.26, 169.99, 169.37, 169.25, 169.06, 168.93, 168.82, 168.67, 168.47 (18 CH_3CO some signals overlapped), 165.96, 165.79, 164.91 (4 Ph*C*O some signals overlapped), 155.54, 150.87, 118.47, 114.47 (MeO*Ph*), 101.09 (β C-1), 100.44 (3 β C-1), 95.33 (α C-1), 95.23 (α C-1), 95.03 (α C-1), 76.33, 75.39, 5.07, 74.93, 74.82, 74.45, 73.08, 72.72, 72.34, 71.92, 71.88, 71.61, 71.55, 71.48, 71.30, 70.37, 70.29, 69.71, 69.16, 68.42, 67.91, 67.86, 67.40, 67.32, 62.55, 61.75, 61.39, 55.53, 21.04, 20.84, 20.79, 20.70, 20.65, 20.57, 20.52, 20.46, 20.39, 20.35 (some signals overlapped). Anal. Calcd for $C_{113}H_{130}O_{59}$: C, 55.80; H, 5.39. Found: C, 55.97; H, 5.31.

3.16. 4-Methoxyphenyl β-D-glucopyranosyl-(1 → 3)-α-D-glucopyranosyl-(1 → 3)-β-D-glucopyranosyl-(1 → 3)-α-D-glucopyranosyl-(1 → 3)-β-D-glucopyranosyl-(1 → 3)-α-D-glucopyranosyl-(1 → 3)-β-D-glucopyranoside (14)

Compound **14** (140 mg) was obtained by deacylation of **13** (335 mg, 0.125 mmol): $[\alpha]_D$ −2.6° (*c* 0.5, H_2O); ^{1}H NMR (400 MHz, D_2O): δ 6.96–6.78 (dd, 4 H, $-C_6H_4-$), 5.23 (s, 3 H, 3 α H-1), 4.83 (d, 1 H, *J* 8.0 Hz, β H-1), 4.61–4.55 (m, 3 H, 3 β H-1), 3.96–3.23 (m, 45 H); ^{13}C NMR (100 MHz, D_2O): δ 156.79, 153.18, 120.38, 117.11 (MeO*Ph*), 104.96 (β C-1), 104.96 (β C-1), 104.93 (β C-1), 103.52 (β C-1), 101.15 (α C-1), 101.15 (α C-1), 101.07 (α C-1), 78.04, 77.97, 77.70, 75.52, 74.29, 73.78, 73.59, 73.28, 72.10, 71.95, 71.65, 69.89, 62.78, 62.60, 62.48, 62.33, 57.86 (some signals overlapped). Anal. Calcd for $C_{49}H_{78}O_{37}$: C, 46.74; H, 6.24. Found: C, 46.87; H, 6.26.

Sulfation of **14** (120 mg, 0.0985 mmol) gave sulfated oligosaccharide (167 mg): ^{1}H NMR (400 MHz, D_2O): δ 7.09–6.93 (dd, 4 H, $-C_6H_4-$), 5.72 (s, 1 H, α H-1), 5.65 (s, 1 H, α H-1), 5.60 (s, 1 H, α H-1), 5.42 (d, 1 H, *J* 5.6

Hz, β H-1), 5.12–5.06 (m, 3 H, 3 β H-1), 4.74–4.08 (m, 42 H), 3.75 (s, 3 H, CH_3O); ^{13}C NMR (100 MHz, D_2O): *δ* 157.49, 153.46, 118.22, 114.55 (MeO*Ph*), 101.68 (β C-1), 101.58 (β C-1), 100.98 (β C-1), 100.98 (β C-1), 96.65 (α C-1), 96.19 (α C-1), 95.74 (α C-1), 80.22, 79.98, 79.50, 79.10, 78.88, 78.47, 77.64, 77.47, 77.23, 76.89, 76.72, 75.41, 71.63, 71.31, 70.76, 70.35, 69.33, 58.79 (some signals overlapped). Anal. Found (Calcd): C, 13.57 (16.8); H, 2.29 (1.60); S, 15.36 (20.11), ds: 2.1.

3.17. 4-Methoxyphenyl 2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranoside (16)

Deallylation of 4-methoxyphenyl 2,4,6-tri-*O*-acetyl-3-allyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranoside **15** (400 mg, 0.211 mmol) gave acceptor **16** (315 mg, 81%): $[\alpha]_D$ + 57.7° (*c* 1.4, $CHCl_3$); ^1H NMR ($CDCl_3$): *δ* 6.92–6.77 (dd, 4 H, $-C_6H_4-$), 5.33–4.91 (m, 12 H, 3 α-H-1), 4.83 (d, 1 H, *J* 8.0 Hz, β H-1), 4.79–4.61 (m, 3 H), 4.52 (d, 1 H, *J* 8.4 Hz, β H-1), 4.46 (d, 1 H, *J* 8.4 Hz, β H-1), 4.37–3.93 (m, 18 H), 3.90–3.76 (m, 7 H, CH_3O), 3.71–3.55 (m, 4 H), 2.15, 2.14, 2.10, 2.09, 2.07, 2.07, 2.06, 2.04, 2.03, 2.02, 1.97, 1.96 (54 H, 18 CH_3CO). Anal. Calcd for $C_{79}H_{104}O_{50}$: C, 51.19; H, 5.66. Found: C, 51.38; H, 5.84.

3.18. 4-Methoxyphenyl 2,4,6-tri-*O*-acetyl-3-*O*-allyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranoside (17)

Donor **1** (126 mg, 0.162 mmol) was coupled with acceptor **16** (300 mg, 0.162 mmol) to give **17** (335 mg, 66%): $[\alpha]_D$ +45.7° (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): *δ* 6.93–6.80 (dd, 4 H, $-C_6H_4-$), 5.76–5.69 (m, 1 H, $-CH=$), 5.24–4.93 (m, 18 H), 4.81 (d, 1 H, *J* 8.0 Hz, β H-1), 4.76–4.67 (m, 4 H), 4.51 (d, 1 H, *J* 8.0 Hz, β H-1), 4.47–4.44 (m, 2 H), 4.32–3.87 (m, 38 H), 3.77 (s, 3 H, CH_3O), 3.69–3.51 (m, 6 H), 2.15, 2.15, 2.13, 2.10, 2.08, 2.05, 2.04, 2.02, 2.01, 1.98, 1.97, 2.00, 1.96, 1.93 (72 H, 24 CH_3CO some signals overlapped); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 170.67, 170.57, 170.49, 170.36, 170.31, 169.93, 169.66, 169.55, 169.41, 169.38, 169.26, 169.15, 169.10, 168.95, 168.92, 168.85, 168.60, 168.48 (24 CH_3CO some signals overlapped), 155.73, 150.83, 130.07, 118.48, 116.69, 114.46 ($CH_2=CH-CH_2-$, MeO*Ph*), 100.46 (4 β C-1), 95.84 (α C-1), 95.22 (α C-1), 95.02 (α C-1), 95.02 (α C-1), 76.05, 75.90, 75.40, 75.24, 75.06, 74.96, 74.76, 73.87, 73.01, 72.26, 71.87, 71.63, 71.52, 71.27, 70.26, 69.67, 69.05, 68.27, 67.84, 67.57, 67.32, 61.42, 61.39, 61.32, 20.88, 20.82, 20.70, 20.48, 20.38 (some signals overlapped). Anal. Calcd for $C_{106}H_{140}O_{66}$: C, 51.54; H, 5.71. Found: C, 51.42; H, 5.57.

3.19. 4-Methoxyphenyl 2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranoside (18)

Deallylation of **17** (310 mg, 0.126 mmol) gave **18** (260 mg, 85%): $[\alpha]_D$ +62.3° (*c* 0.8, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): *δ* 6.91–6.79 (dd, 4 H, $-C_6H_4-$), 5.27–5.08 (m, 9 H), 4.98–4.89 (m, 7 H), 4.81 (d, 1 H, *J* 8.0 Hz, β H-1), 4.77–4.69 (m, 3 H), 4.62–4.59 (m, 4 H, CH_3O), 3.71–3.64 (m, 1 H), 3.62–3.54 (m, 3 H), 2.17, 2.15, 2.14, 2.12, 2.10, 2.09, 2.08, 2.07, 2.05, 2.04, 2.03, 2.02, 2.01, 1.98, 1.97, 1.96 (24 CH_3CO some signals overlapped). Anal. Calcd for $C_{103}H_{136}O_{66}$: C, 50.91; H, 5.64. Found: C, 50.89; H, 5.69.

3.20. 4-Methoxyphenyl α-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-α-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-α-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-α-D-glucopyranosyl-(1→3)-β-D-glucopyranoside (19)

Compound **19** (142 mg) was obtained by deacylation of **18** (260 mg, 0.107 mmol): $[\alpha]_D$ +15.7° (*c* 1.5, H_2O); ^1H NMR (400 MHz, D_2O): *δ* 6.99–6.83 (dd, 4 H, $-C_6H_4-$), 5.26–5.24 (m, 3 H, 3 α H-1), 5.22 (d, 1 H, *J* 3.6 Hz, α H-1), 4.88 (d, 1 H, *J* 8.0 Hz, β H-1), 4.64–4.60 (m, 3 H, 3 β H-1), 3.97–3.31 (m, 45 H); ^{13}C NMR (100 MHz, D_2O): *δ* 157.41, 153.60, 120.95, 117.71 (MeO*Ph*), 105.51 (3 β C-1), 104.06 (β C-1), 101.75 (α C-1), 101.69 (α C-1), 101.63 (α C-1), 101.63 (α C-1), 84.81, 84.57, 78.39, 78.28, 76.11, 75.86, 75.57, 74.87, 74.37, 74.16, 73.86, 73.40, 72.67, 71.97, 70.43, 63.16, 63.03, 62.88, 58.46 (some signals overlapped). Anal. Calcd for $C_{55}H_{88}O_{42}$: C, 46.48; H, 6.24. Found: C, 46.35; H, 6.26.

3.21. 4-Methoxyphenyl 2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranoside (20)

Deallylation of 4-methoxyphenyl 2,4,6-tri-*O*-acetyl-3-*O*-allyl-β-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranoside (450 mg, 0.342 mmol) gave acceptor **20** (350 mg, 80%): $[\alpha]_D$ −7.35° (*c* 0.5, $\mathrm{CHCl_3}$); ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 6.91–6.78 (dd, 4 H, $-\mathrm{C_6}H_4-$), 5.22–4.96 (m, 6 H), 4.87 (dd, 1 H, *J* 9.6 Hz), 4.81 (d, 1 H, *J* 8.0 Hz, β H-1), 4.76–4.69 (m, 2 H), 4.52 (d, 1 H, *J* 8.0 Hz, β H-1), 4.49 (d, 1 H, *J* 8.0 Hz, β H-1), 4.35–4.29 (m, 2 H), 4.18–3.90 (m, 10 H), 3.79–3.77 (m, 4 H, $\mathrm{CH_3O}$), 3.70–3.55 (m, 3 H), 2.15, 2.13, 2.10, 2.09, 2.07, 2.06, 2.06, 2.04, 2.03, 2.01, 2.01, 1.99, 1.96 (12 $\mathrm{C}H_3\mathrm{CO}$ some signals overlapped); ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 170.59, 170.45, 169.30, 169.10, 168.62 (12 $\mathrm{CH_3}C\mathrm{O}$ some signals overlapped), 155.65, 150.83, 118.35, 114.43 (MeO*Ph*), 100.68 (β C-1), 100.39 (β C-1), 100.01 (β C-1), 95.12 (α C-1), 78.16, 75.16, 75.11, 74.09, 72.66, 72.16, 71.78, 71.70, 71.53, 71.10, 70.47, 68.67, 67.81, 67.25, 62.13, 61.76, 61.45, 61.30, 60.29, 55.54, 20.90, 20.74, 20.65, 20.57, 20.45, 20.32 (some signals overlapped). Anal. Calcd for $\mathrm{C_{55}H_{72}O_{34}}$: C, 51.72; H, 5.68. Found: C, 51.66; H, 5.71.

3.22. 4-Methoxyphenyl 2,4,6-tri-*O*-acetyl-3-*O*-allyl-β-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranoside (21)

Donor **8** (200 mg, 0.258 mmol) was coupled with acceptor **20** (330 mg, 0.258 mmol) to give **21** (387 mg, 79%): $[\alpha]_D$ −5.23° (*c* 1.0, $\mathrm{CHCl_3}$); ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 6.93–6.79 (dd, 4 H, $-\mathrm{C_6}H_4-$), 5.76–5.69 (m, 1 H, $-\mathrm{C}H=$), 5.21–4.83 (m, 15 H), 4.82 (d, 1 H, *J* 8.0 Hz, β H-1), 4.73–4.68 (m, 2 H), 4.51–4.47 (m, 2 H), 4.37–3.85 (m, 21 H), 3.79–3.77 (m, 4 H, $\mathrm{C}H_3\mathrm{O}$), 3.61–3.49 (m, 4 H), 2.19, 2.18, 2.16, 2.14, 2.12, 2.10, 2.09, 2.08, 2.07, 2.05, 2.04, 2.03, 2.02, 1.98, 1.97, 1.96 (18 $\mathrm{C}H_3\mathrm{CO}$ some signals overlapped); ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 170.67, 170.57, 170.39, 170.35, 169.33, 169.18, 169.13, 168.84, 168.62 (18 $\mathrm{CH_3}C\mathrm{O}$ some signals overlapped), 155.64, 150.83, 134.02, 118.35, 116.84, 114.42 ($C\mathrm{H_2}{=}C\mathrm{H{-}CH_2}-$, MeO*Ph*), 100.77 (β C-1), 100.65 (β C-1), 100.48 (β C-1), 100.02 (β C-1), 95.12 (α C-1), 94.90 (α C-1), 79.90, 78.17, 75.33, 74.95, 74.61, 72.26, 72.00, 71.88, 71.68, 71.52, 71.07, 70.43, 69.05, 68.08, 67.82, 67.77, 67.36, 67.26, 62.10, 61.88, 61.38, 55.55, 20.88, 20.67, 2.59, 20.49, 20.48, 20.38 (some signals overlapped). Anal. Calcd for $\mathrm{C_{82}H_{108}O_{50}}$: C, 52.01; H, 5.75. Found: C, 51.87; H, 5.74.

3.23. 4-Methoxyphenyl 2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranoside (22)

Deallylation of **21** (350 mg, 0.184 mmol) gave acceptor **22** (285 mg, 84%): $[\alpha]_D$ −18.5° (*c* 1.5, $\mathrm{CHCl_3}$); ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 6.92–6.80 (dd, 4 H, $-\mathrm{C_6}H_4-$), 5.21–4.89 (m, 11 H), 4.82 (d, 1 H, *J* 8.0 Hz, β H-1), 4.79–4.69 (m, 3 H), 4.53–4.49 (m, 3 H), 4.39–3.85 (m, 29 H), 3.79–3.76 (m, 4 H, $\mathrm{CH_3O}$), 3.63–3.59 (m, 4 H), 2.19, 2.18, 2.15, 2.14, 2.12, 2.10, 2.09, 2.08, 2.07, 2.05, 2.04, 2.03, 2.02, 2.00, 1.99, 1.98 (18 $\mathrm{CH_3CO}$ some signals overlapped). Anal. Calcd for $\mathrm{C_{79}H_{104}O_{50}}$: C, 51.19; H, 5.66. Found: C, 51.30; H, 5.61.

3.24. 4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1 → 3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranoside (23)

Donor **12** (145 mg, 0.14 mmol) was coupled with acceptor **22** (260 mg, 0.14 mmol) to give **23** (240 mg, 63%): $[\alpha]_D$ −17.9° (*c* 1.0, $\mathrm{CHCl_3}$); ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$): δ 8.05–7.25 (m, 20 H, 4 PhCO), 6.90–6.77 (dd, 4 H, $-\mathrm{C_6}H_4-$), 5.86 (dd, 1 H, *J* 9.6 Hz), 5.69 (dd, 1 H, *J* 9.6 Hz), 5.35 (dd, 1 H, *J* 9.6 Hz), 5.21–4.87 (m, 12 H), 4.80 (d, 2 H, *J* 8.0 Hz, 2β H-1), 4.71–4.67 (m, 3 H), 4.51–4.41 (m, 4 H), 4.31–3.87 (m, 25 H), 3.79–3.69 (m, 5 H, $\mathrm{CH_3O}$), 3.67–3.50 (m, 3 H), 2.14, 2.13, 2.12, 2.09, 2.08, 2.07, 2.06, 2.05, 2.04, 2.03, 2.01, 1.98, 1.96, 1.93, 1.88, 1.85 (63 H, 21 $\mathrm{C}H_3\mathrm{CO}$ some signals overlapped); ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$): δ 170.51, 170.47, 170.43, 170.40, 170.26, 169.99, 169.37, 169.25, 169.06, 168.93, 168.82, 168.67, 168.47 (21 $\mathrm{CH_3}C\mathrm{O}$ some signals overlapped), 165.96, 165.79, 164.9 (4 PhCO some signals overlapped), 155.54, 150.87, 118.47, 114.47 (MeO*Ph*), 101.09 (β C-1), 100.44 (4 β C-1), 95.33 (α C-1), 95.23 (α C-1), 95.03 (α C-1), 76.33, 75.39, 5.07, 74.93, 74.82, 74.45, 73.08, 72.72, 72.34, 71.92, 71.88, 71.61, 71.55, 71.48, 71.30, 70.37, 70.29, 69.71, 69.16, 68.42, 67.91, 67.86, 67.40, 67.32, 62.55, 61.75, 61.39, 55.53, 21.04, 20.84, 20.79, 20.70, 20.65, 20.57, 20.52, 20.46, 20.39, 20.35 (some signals overlapped). Anal. Calcd for

$C_{125}H_{146}O_{67}$: C, 55.19; H, 5.41. Found: C, 55.10; H, 5.37.

3.25. 4-Methoxyphenyl β-D-glucopyranosyl-(1 → 3)-α-D-glucopyranosyl-(1 → 3)-β-D-glucopyranosyl-(1 → 3)-α-D-glucopyranosyl-(1 → 3)-β-D-glucopyranosyl-(1 → 3)-α-D-glucopyranosyl-(1 → 3)-β-D-glucopyranosyl-(1 → 3)-β-D-glucopyranoside (24)

Compound **24** (120 mg) was obtained by deacylation of **23** (240 mg, 0.088 mmol): $[\alpha]_D$ −8.3°(*c* 1.5, H_2O); ^1H NMR (400 MHz, D_2O): δ 7.06–6.89 (dd, 4 H, $-C_6H_4-$), 5.30 (s, 3 H, 3 α H-1), 4.98 (d, 1 H, *J* 7.6 Hz, β H-1), 4.76–4.69 (m, 4 H, 4 β H-1), 4.03–3.29 (m, 45 H); ^{13}C NMR (100 MHz, D_2O): δ 157.56, 153.64, 121.14, 117.98 (MeO*Ph*), 105.58 (4 β C-1), 103.74 (β C-1), 101.77 (3 α C-1), 87.16, 85.02, 78.72, 78.38, 76.28, 75.51, 75.04, 74.38, 74.01, 72.78, 72.41, 70.83, 70.69, 63.54, 63.40, 63.19, 58.83 (some signals overlapped). Anal. Calcd for $C_{55}H_{88}O_{42}$: C, 46.48; H, 6.24. Found: C, 46.60; H, 6.22.

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References

1. Sasaki, T.; Takasuka, N. *Carbohydr. Res.* **1976**, *47*, 99–105.
2. (a) Molinaro, A.; Lanzetta, R.; Mancino, A.; Evidente, A.; Rosa, M. D.; Ianaro, A. *Carbohydr. Res.* **2000**, *329*, 441–445;
   (b) Bao, X.; Liu, C.; Fang, J.; Li, X. *Carbohydr. Res.* **2001**, *336*, 127–133.
3. (a) Sharp, J. K.; Valent, B.; Albersheim, P. *J. Biol. Chem.* **1984**, *259*, 11312–11317;
   (b) Ning, J.; Zhang, W.; Yi, Y.; Yang, G.; Wu, Z.; Yi, J.; Kong, F. *Bioorg. Med. Chem.* **2003**, *11*, 2193–2203.
4. (a) Takeo, K.; Maki, K.; Wada, Y.; Kitamura, S. *Carbohydr. Res.* **1993**, *245*, 81–96;
   (b) Katsuraya, K.; Shoji, T.; Inazawa, K.; Nakashima, H.; Yamamoto, N.; Uryu, T. *Macromolecules* **1994**, *27*, 6695–6699;
   (c) Katsuraya, K.; Ikusima, N.; Takahashi, N.; Shoji, T.; Nakashima, H.; Yamamoto, N.; Yoshida, T.; Uryu, T. *Carbohydr. Res.* **1994**, *260*, 51–61.
5. (a) Good, F.; Schuerch, C. *Macromolecules* **1985**, *18*, 595–598;
   (b) Zhang, P.; Cheung, P. C. K. *Biosci. Biotechnol. Biochem.* **2002**, *66*, 1052–1056.
6. (a) Zeng, Y.; Ning, J.; Kong, F. *Tetrahedron Lett.* **2002**, 43, 3279–3233.;
   (b) Zeng, Y.; Ning, J.; Kong, F. *Carbohydr. Res.* **2003**, *338*, 307–311.
7. Ogawa, T.; Yamamoto, H. *Carbohydr. Res.* **1985**, *137*, 79–88.
8. Schmidt, R. R.; Kinzy, W. *Adv. Carbohydr. Chem. Biochem.* **1994**, *50*, 21–125.