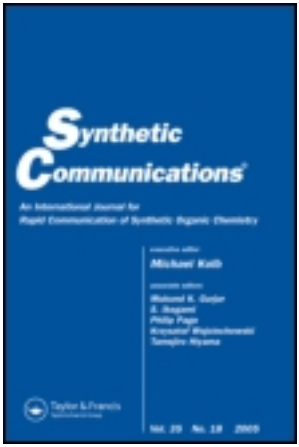

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Facile Syntheses of the Trisaccharide Acceptors—The Key Intermediates for Assembling the Elicitor Hexasaccharide

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FACILE SYNTHESES OF THE TRISACCHARIDE ACCEPTORS —THE KEY INTERMEDIATES FOR ASSEMBLING THE ELICITOR HEXASACCHARIDE

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Abstract: A facile synthesis of trisaccharide **7**, the key intermediate for assembling phytoalexin glucohexatose elicitor, was achieved *via* orthoester formation-rearrangement from stepwise coupling of 1,2-*O*-ethylidene-α-D-glucopyranose (**2**) with 2,3,4-tri-*O*-acetyl-6-*O*-chloroacetyl-α-D-glucopyranosyl bromide at 6-position and with acetobromoglucose at 3-position respectively. Similar strategy was used for the synthesis of **14**.

The hexasaccharide Gluβ1→6(Gluβ1→3)Gluβ1→6Gluβ1→6(Gluβ1→3)Glu has been well known as the basic structure for phytoalexin elicitor activity.[1] It has similar action as the corresponding heptasaccharide which is effective in very low doses—approximately 0.1 pmol per cotyledon[2a] and gives a half-maximal activity at a concentration of 10 nM.[2b] So far most of the methods for the synthesis of the elicitor oligosaccharides have involved the use of rare and expensive reagents, multifunctional groups protection, and lengthy route of chemical modifications.[3]

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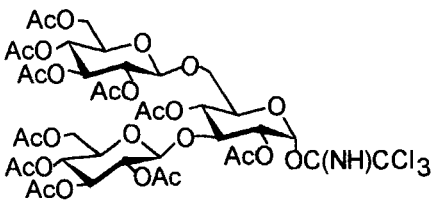
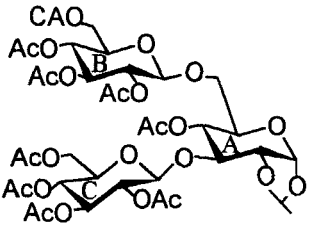
Scheme 1



Donor

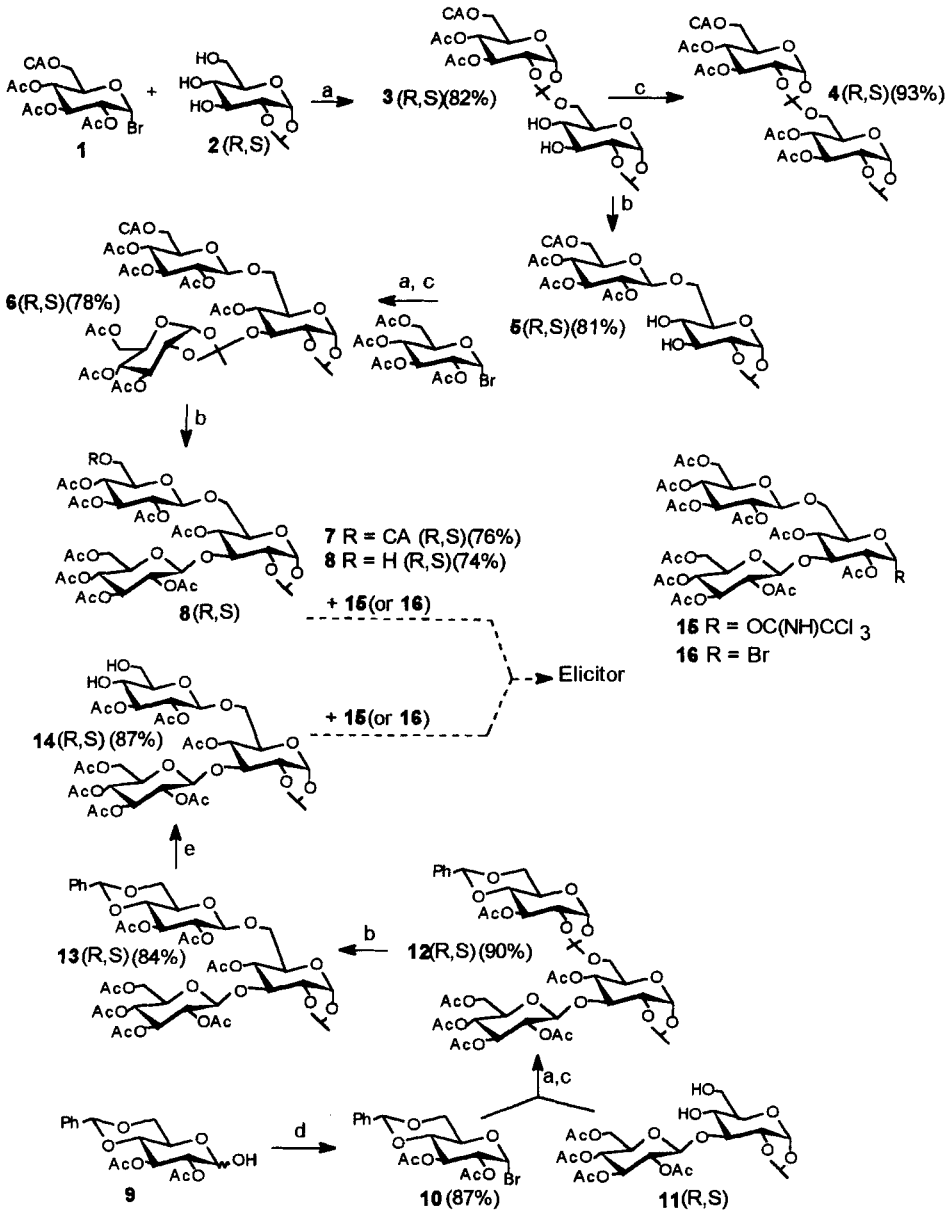


Acceptor

In the synthesis of elicitor hexasaccharide, the trisaccharide acceptor needs to have structurally different B and C unit enabling to make a free hydroxyl group at the C-6 of B unit. In our previous research,[4] the phytoalexin elicitor hexasaccharide was synthesized convergently through building two trisaccharide blocks as glycosylation donor and acceptor respectively (Scheme 1). Recently we developed a new and effective strategy for highly regio- and stereoselective synthesis of oligosaccharides using un- or less-protected sugar acceptors and *O*-acetylglycosyl bromides as raw materials through orthoester formation-rearrangement.[5] However, it was found that the reaction with unprotected methyl glucoside as the acceptor was rather slow and difficult to be monitored due to the poor solubility of the acceptor in the reaction media. Glucose 1,2-*O*-ethylidenate (**2**) is a readily available material with better solubility and it was used as the glycosyl acceptor in the present study for the synthesis of the trisaccharide acceptor **7** bearing 6-*O*-chloroacetyl (CA) at the B unit, and another trisaccharide acceptor **13** bearing 4,6-*O*-benzylidene at the B unit through orthoester formation-rearrangement.

As shown in scheme 2, coupling[5] of 2,3,4-tri-*O*-acetyl-6-*O*-chloroacetyl-α-D-glucopyranosyl bromide **1** (1.1 equiv) with 1,2-*O*-ethylidene-α-D-glucopyranose **2** (1 equiv) promoted by AgOTf (1.1 equiv)/lutidine (1.2 equiv) in anhydrous CH_2Cl_2 furnished 1,6-linked disaccharide orthoester (*exo*) **3** (R,S, 82%) after column

Scheme 2



Conditions and reagents: a. AgOTf (1 equiv), 2,4-lutidine (1.2 equiv), anhyd CH_2Cl_2, M.S.(4 Å), RT, N_2, 3 h. b. TMSOTf (0.1 equiv), anhyd CH_2Cl_2, M.S.(4 Å), -30 °C, N_2, 40 min. c. Ac_2O/pyridine (dry), CH_2Cl_2. d. Br_2 (3 equiv), Ph_3P (1.5-2 equiv.), and pyridine (dry, 0.25 equiv) in anhyd. CH_2Cl_2, RT, 2 h. e. 80% aq.$CHCl_2COOH$/AcOH, 4/50, RT, 3 h.

chromatography with petroleum ether/ethyl acetate (1/1.5) as the eluent. Similar preparation of the disaccharide orthoester from **2** and acetobromoglucose did not give very good regioselectivity perhaps due to the higher reactivity of the latter. Acetylation of **3** (giving **4**) confirmed the 6-*O*-glycosylation as indicated from its 2-D ^{1}H NMR showing H-6 at δ 3.62 (dd), 3.57 (dd) and H-3 at δ 5.22 (t), H-4 at δ 4.95 (dd) respectively. Rearrangement of **3** with a catalytic amount of TMSOTf in anhydrous CH_2Cl_2 yielded disaccharide **5** (R,S) in a good yield (81%). Glycosylation of **5** with acetobromoglucose under the same condition as described for the preparation of **3** followed by acetylation in anhydrous CH_2Cl_2 gave the 3-linked trisaccharide orthoester (*exo*) **6** in a yield of 78% (two steps) after purification by column chromatography. Trisaccharide **7** was obtained also in a satisfactory yield (76%) by isomerization with a catalytic amount of TMSOTf (0.1 equiv) and **7** gave physical data and ^{1}H NMR spectrum the same as reported[4] for the same compound prepared in another way.

An alternative trisaccharide acceptor **13** was also effectively synthesized similarly as shown in Scheme 2. Thus bromination of 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-α,β-D-glucopyranose (**9**)[6,7] with bromine-triphenyl phosphine gave 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranosyl bromide (**10**) in a satisfactory yield (87%). We found that the use of bromine-triphenyl phosphine instead of bromine-triphenyl phosphite[8] made more easily the bromination of sugar derivatives with C-1 free hydroxyl group. The disaccharide acceptor **11** was prepared readily from condensation of acetobromoglucose with 4,6-*O*-benzylidene-1,2-*O*-ethylidene-α-D-glucopyranose followed by debenzylidenation.[4] Coupling[5] of **10** with **11** followed by acetylation yielded the desired 6-linked trisaccharide orthoester (*exo*) **12** as the sole product in a very high yield (90%). Rearrangement[5] of **12** with a catalytic amount of TMSOTf (0.1 equiv) readily yielded trisaccharide **13** also in a high yield (84%). The benzylidene group was stable in both the orthoester formation and

rearrangement. The trisaccharide **13** was a key intermediate for the elicitor synthesis as its debenzylidenation with 80% dichloroacetic acid in acetic acid furnished trisaccharide acceptor **14** (R,S, 87%) having $4_B,6_B$-free hydroxyl groups, while selective coupling of **14** with the trisaccharide donor can afford the desired hexasaccharide.

In summary, here we present an effective method for the synthesis of 3,6-branched trisaccharides, the key intermediates for assembling the phytoalexin hexasaccharide, with naked glucose 1,2-O-ethylidenate and *O*-acetylglycosyl bromide or 4,6-*O*-benzylidenated glucosyl bromide as the starting materials by selective glycosylation *via* orthoester formation-rearrangement. In addition, the bromination of sugar derivatives bearing acidic labile groups with bromine-triphenyl phosphine as the reagents was achieved. As many naturally bioactive structures contain 1→6 and 1→3 glycosidic linkages, the presented strategy will be useful for the synthesis of complex oligosaccharides.

EXPERIMENTAL

Melting points were determined with a 'Mel-Temp' apparatus. Optical rotations were determined at 20 °C with a Perkin-Elmer Model 241-MC automatic polarimeter. ^{1}H NMR spectra were recorded with Varian XL-200 or XL-400 spectrometer for solutions in $CDCl_3$. Chemical shifts are given in ppm downfield from internal Me_4Si. TLC was performed on silica gels G and HF, with detection either by charring with 30% (v/v) H_2SO_4 and MeOH or by UV light. Column chromatography was conducted on columns (16 × 240 mm, 18 × 300 mm) of silica gel (100-200 mesh). Solutions were concentrated at <60 °C under diminished pressure. All of the described orthoesters and the oligosaccharides containing 1,2-*O*-ethylidenated sugar residues were obtained as R,S mixtures which were used directly in the next reaction.

Intensive purification of the mixtures usually gave one isomer (R or S), which was subjected to NMR spectrometry analysis, but isomerization occurred upon a long term standing or during NMR determination.

3,4-Di-*O*-acetyl-6-*O*-chloroacetyl-α-D-glucopyranose 1,2-(1,2-*O*-Ethylidene-α-D-glucopyranos)-6-yl Orthoacetate (3). To a stirred solution of 2,3,4-tri-*O*-acetyl-6-*O*-chloroacetyl-α-D-glucopyranosyl bromide[9] (488 mg, 1.1 mmol), and 2,4-lutidine (140 μL, 1.2 mmol), 1,2-*O*-ethylidene(R,S)-α-D-glucopyranose **2** (206 mg, 1 mmol) and 4 Å molecular sieves (0.5 g) in anhydrous dichloromethane (20 mL) under nitrogen atmosphere was added silver triflate (283 mg, 1.1 mmol) in a dark room, and the reaction was carried out at room temperature and monitored by TLC (1:1.5 petroleum ether/ethyl acetate). After completion of the reaction, the mixture was partitioned between dichloromethane and water, the organic phase was washed with sat. aq. $NaHCO_3$, 10% $Na_2S_2O_3$, and concentrated, dried, then subjected to column chromatography with 1:1.5 petroleum ether/ethyl acetate as the eluent, giving the disaccharide orthoester **3** in a good yield (R,S, 467 mg, 82%, based on acceptor **2**); $[\alpha]_D^{20}$ +21.4° (R, *c* 1.0, $CHCl_3$); ^{1}H NMR: δ (R) 5.74 (d, 1 H, $J_{1',2'}$ 5.2 Hz, H-1'), 5.55 (d, 1 H, $J_{1,2}$ 5.1 Hz, H-1), 5.19 (t, 1 H, J 2.7 Hz, H-3'), 5.13 (q, 1 H, J 4.8 Hz, CH_3CH), 4.90 (dd, 1 H, $J_{3',4'}$ 2.7 Hz, $J_{4',5'}$ 8.9 Hz, H-4'), 4.42-4.40 (m, 1 H, H-2'), 4.32-4.30 (m, 2 H, H-6'), 4.13 (s, 2 H, $ClCH_2CO$), 4.04 (t, 1 H, J 5.1 Hz, H-2), 4.00-3.90 (m, 2 H, H-3, 4), 3.88-3.85 (m, 1 H, H-5'), 3.76 (d, 2 H, $J_{5,6}$ 3.2 Hz, H-6), 3.66-3.62 (m, 1 H, H-5), 2.12, 2.10 (2 s, 6 H, 2 CH_3CO), 1.74 (s, 3 H, CH_3CO_3), 1.48 (d, 3 H, J 4.8 Hz, CH_3CH)

Anal. Calcd for $C_{22}H_{31}O_{15}Cl$: C, 46.28; H, 5.47. Found: C, 46.41; H, 5.77.

3,4-Di-*O*-acetyl-6-*O*-chloroacetyl-α-D-glucopyranose 1,2-(3,4-Di-*O*-acetyl-1,2-*O*-ethylidene-α-D-glucopyranos)-6-yl Orthoacetate (4). To a solution of **3** (100 mg, 0.18 mmol) in anhydrous dichloromethane (5 mL) and pyridine (5 mL), was added Ac_2O dropwise and the mixture was stirred at room temperature for 3 h,

at the end of which time the reaction was complete as indicated by TLC (2/1 petroleum ether/ethyl acetate). Ice water was added, and the mixture was diluted with CH_2Cl_2. The organic layers were combined, dried, and concentrated to give **4** (R,S, 110 mg, 93%) as a syrup. $[\alpha]_D^{20}$ +39.7° (S, *c* 1.0, $CHCl_3$); ^{1}H NMR: δ (S) 5.73 (d, 1 H, $J_{1',2'}$ 5.2 Hz, H-1'), 5.61 (q, 1 H, J 4.9 Hz, CH_3CH), 5.60 (d, 1 H, $J_{1,2}$ 4.7 Hz, H-1), 5.22 (t, 1 H, J 5.7 Hz, H-3), 5.17 (t, 1 H, J 2.7 Hz, H-3'), 4.95 (dd, 1 H, $J_{3,4}$ 5.7 Hz, $J_{4,5}$ 9.4 Hz, H-4), 4.89 (dd, 1 H, $J_{3',4'}$ 2.7 Hz, $J_{4',5'}$ 8.9 Hz, H-4'), 4.33-4.30 (m, 3 H, H-2', 6'), 4.22 (dd, 1 H, $J_{1,2}$ 4.7 Hz, $J_{2,3}$ 5.7 Hz, H-2), 4.11 (s, 2 H, $ClCH_2CO$), 3.95-3.88 (m, 2 H, H-5, 5'), 3.62 (dd, 1 H, $J_{5,6a}$ 2.8 Hz, $J_{6a,6b}$ 10.5 Hz, H-6_a), 3.57 (dd, 1 H, $J_{5,6b}$ 4.6 Hz, $J_{6a,6b}$ 10.5 Hz, H-6_b), 2.12, 2.10, 2.09, 2.06 (4s, 12 H, 4 CH_3CO), 1.70 (s, 3 H, CH_3CO_3), 1.33 (d, 3 H, J 4.9 Hz, CH_3CH).

6-*O*-(2,3,4-Tri-*O*-acetyl-6-*O*-chloroacetyl-β-D-glucopyranosyl)-1,2-*O*-ethylidene-α-D-glucopyranose (5). To a stirred solution of sugar-sugar orthoester **3** (365 mg, 0.64 mmol) and 4 Å molecular sieves (0.5 g) in anhydrous dichloromethane (10 mL) was added TMSOTf (12 μL, 0.1 equiv) under nitrogen atmosphere at -30°C, and the reaction was monitored by TLC (1:1.5 petroleum ether/ethyl acetate). After completion of the reaction, triethyl amine (20 μL) was added to the mixture. The mixture was filtered, and the filtrate was washed with CH_2Cl_2. The combined solution was washed with N HCl (10 mL), sat. aq. $NaHCO_3$ (10 mL), and brine (2×10 mL), then dried over anhydrous Na_2SO_4, concentrated. The residue was subjected to column chromatography with 1:1 petroleum ether/ethyl acetate as the eluent, giving the product **5** (R,S, 296 mg, 81%); $[\alpha]_D^{20}$ +19.5° (R, *c* 0.6, $CHCl_3$); ^{1}H NMR: δ (R) 5.59 (d, 1 H, $J_{1,2}$ 5.1 Hz, H-1), 5.23 (t, 1 H, J 9.4 Hz, H-3'), 5.16-5.07 (m, 2 H, H-4',$CHCH_3$), 5.02 (dd, 1 H, $J_{1',2'}$ 7.8 Hz, $J_{2',3'}$ 9.4 Hz, H-2'), 4.63 (d, 1 H, $J_{1',2'}$ 7.8 Hz, H-1'), 4.33-4.30 (m, 1 H, H-6'), 4.15 (s, 2 H, $ClCH_2CO$), 4.16-3.68 (m, 8 H, H-2, 3, 4, 5, 5', 6, 6'), 2.08, 2.05, 2.02 (3 s, 9 H, CH_3CO), 1.49 (d, 3 H, J 4.8 Hz, $CHCH_3$).

Anal. Calcd for $C_{22}H_{31}O_{15}Cl$: C, 46.28; H, 5.47. Found: C, 46.12; H, 5.21.

3,4,6-Tri-*O*-acetyl-α-D-glucopyranose 1,2-{6-*O*-(2,3,4-Tri-*O*-acetyl-6-*O*-chloroacetyl-β-D-glucopyranosyl)-4-*O*-acetyl-1,2-*O*-ethylidene-α-D-glucopyranos}-3-yl Orthoacetate (6). As described for the preparation of **3** and **4**, coupling of acetobromoglucose (158 mg, 0.39 mmol) with **3** (200 mg 0.35 mmol) followed by acetylation afforded **6** in a high yield (R,S, 256 mg, 78%, two steps). $[\alpha]_D^{20}$ +28.5° (R, *c* 1.6, $CHCl_3$); ^1H NMR: δ (R) 5.70 (d, 1 H, $J_{1C,2C}$ 5.2 Hz, H-1_C), 5.50 (d, 1 H, $J_{1,2}$ 4.9 Hz, H-1_A), 5.30-4.93 (m, 6 H, H-2_B, 3_C, 3_B,4_A, 4_B, CH_3CH), 4.92 (dd, 1 H, $J_{3C,4C}$ 2.7 Hz, $J_{4C,5C}$ 9.6 Hz, H-4_C), 4.82 (d, 1 H, $J_{1B,2B}$ 8.0 Hz, H-1_B), 4.40-3.60 (m, 12 H, H-2_A, 2_C, 3_A, 5_A, 5_C, 5_B, 6_A, 6_C, 6_B), 4.14 (s, 2 H, $ClCH_2CO$), 2.17-1.98 (m, 21 H, 7 CH_3CO), 1.88 (s, 3 H, CH_3CO_3), 1.48 (d, 3 H, J 4.9 Hz, $CHCH_3$).

Anal. Calcd for $C_{38}H_{51}O_{25}Cl$: C, 48.39; H, 5.45. Found: C, 48.17; H, 5.26.

4-*O*-Acetyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-6-*O*-(2,3,4-tri-*O*-acetyl-6-*O*-chloroacetyl-β-D-glucopyranosyl)-1,2-*O*-(R,S)ethylidene-α-D-glucopyranose (7). As described for the preparation of **5**, isomerization of compound **6** (200 mg, 0.21 mmol) with a catalytic amount of TMSOTf (0.1 equiv) furnished the trisaccharide **7** (R,S, 152 mg) also in a satisfactory yield (76%) and gave physical data the same as reported[4] for the same compound prepared in another way.

2,3-Di-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranosyl bromide (10). To a solution of **9**[6,7] (304 mg, 0.86 mmol), pyridine (90 μL) in 6 mL anhydrous dichloromethane, Br_2 (120 μL, 2.58 mmol) in anhydrous dichloromethane (2mL) and Ph_3P (338 mg, 1.5 mmol) was added at 0°C, then the reaction solution was allowed to regain room temperature. The solution was stirred for 5 h, at the end of which time TLC (petroleum ether/ethyl acetate, 2:1) showed the completion of the reaction. The reaction was quenched with 9 mL aq. 10% Na_2CO_3 and poured into ice-cold water, extracted with dichloromethane (3 × 25mL). The organic layer was washed with 5% $CuSO_4$ (10 mL), and brine (3×10 mL), dried over Na_2SO_4, concentrated to a

syrup, which was subjected to column chromatography with 1:1 petroleum ether/ethyl acetate as the eluent. Compound **10** was obtained as an amorphous solid (310 mg, 87%); The physical data and ^{1}H NMR spectrum of compound **10** was identical to that reported in lit.[8]

3-*O*-Acetyl-4,6-*O*-benzylidene-α-D-glucopyranose 1,2-{3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-4-*O*-acetyl-1,2-*O*-(R,S)ethylidene-α-D-glucopyranos}-6-yl orthoacetate (12). To a stirred mixture of **11**[4] (322 mg, 0.6 mmol), **10** (240 mg, 0.62 mmol), 2,4-lutidine (78 μL, 0.68 mmol), and 4 Å molecular sieves (0.5 g) in anhydrous CH_2Cl_2 (10 mL) was added silver triflate (160 mg, 0.62 mmol) under nitrogen atmosphere in a dark room, and the reaction was carried out at room temperature, and monitored by TLC (1/1.5 petroleum ether/ethyl acetate). After completion of the reaction, the mixture was partitioned between CH_2Cl_2 (15 mL) and brine (15 mL), the organic phase was washed with aq. 10% $Na_2S_2O_3$ (10 mL) and brine (2×10 mL), dried over Na_2SO_4, then concentrated under reduced pressure. The residual oil was purified by column chromatography with 1/1.5 petroleum ether/ethyl acetate as the eluent giving the orthoester (R,S) which was acetylated with Ac_2O/pyridine quantitatively yielded compound **12** (R,S, 490 mg, 90% in two steps) as a syrup after purification by column chromatography. $[\alpha]_D^{20}$ +30.1° (S, *c* 1.0, $CHCl_3$); ^{1}H NMR: δ (S) 7.50-7.31 (m, 5 H, Ph-H), 5.79 (d, 1 H, $J_{1B,2B}$ 5.3 Hz, H-1_B), 5.60 (d, 1 H, $J_{1,2}$ 4.5 Hz, H-1_A), 5.53 (q, 1 H, J 4.9 Hz, CH_3CH), 5.52 (s, 1 H, PhC*H*=), 5.23-5.18 (m, 2 H, H-3_A, 3_B), 5.08, 5.06, 5.04, 4.95 (4 t, J 9.2 Hz, H-2_C, 3_C, 4_A, 4_C), 4.79 (d, 1 H, J 7.9 Hz, H-1_C), 4.39 (dd, 1 H, $J_{5,6a}$ 5.0 Hz, $J_{6a,6b}$ 10.5 Hz, H-6_{Aa}), 4.30-3.59 (m, 12 H, H-2_A, 2_B, 3_A, 4_B, 5_A, 5_C, 5_B, 6_{Ab}, 6_C, 6_B), 2.13, 2.08, 2.06, 2.06, 2.01, 2.00 (6 s, 18 H, 6 CH_3CO), 1.71 (s, 3 H, CH_3CO_3), 1.36 (d, 3 H, J 4.9 Hz, CH_3CH).

Anal. Calcd for $C_{41}H_{52}O_{23}$: C, 53.95; H, 5.74. Found: C, 54.11; H, 5.55.

3-*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-6-*O*-(2,3-di-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-4-*O*-acetyl-1,2-*O*-(R,S)ethylidene-α-D-glucopyranose (13). To a stirred mixture of **12** (474 mg, 0.52 mmol) and 4 Å molecular sieves (0.5 g) in anhydrous CH_2Cl_2 (20 mL) was added TMSOTf (10 μL, 0.1 equiv) at -30 °C under nitrogen atmosphere, and the reaction was monitored by TLC (1/1.5 petroleum ether/ethyl acetate). After completion of the reaction, to the mixture was added triethylamine (10 μL), and the reaction was allowed to regain room temperature. The mixture was filtered and the filtrate was treated with aq. 5% AcOH (20 mL), satd. aq. Na_2CO_3 (20 mL), and brine (20 mL), dried, and concentrated. The residue was subjected to column chromatography with 1/1 petroleum ether/ethyl acetate as the eluent, giving product **13** (R,S, 398 mg) as a syrup in a yield of 84%. $[\alpha]_D^{20}$ +25.2° (R, *c* 1.5, $CHCl_3$); ^{1}H NMR: δ (R) 7.48-7.30 (m, 5 H, Ph-H), 5.54 (d, 1 H, $J_{1,2}$ 4.6 Hz, H-1_A), 5.49 (s, 1 H, PhC*H*=), 5.33, 5.22 (t, 2 H, J 9.5 Hz, H-3_C, 3_B), 5.07 (t, 1 H, J 9.5 Hz, H-4_A), 5.06 (q, 1 H, J 4.8 Hz, CH_3CH), 5.00-4.94 (m, 3 H, H-2_C, 2_B, 4_C), 4.79, 4.70 (2 d, J 8.0 Hz, 7.9 Hz, H-1_C, 1_B), 4.36 (dd, 1 H, $J_{5B,6Ba}$ 5.0 Hz, $J_{6Ba,6Bb}$ 10.5 Hz, H-6_{Ba}), 4.21 (d, 2 H, $J_{5C,6C}$ 3.2 Hz, H-6_C), 4.04-3.50 (m, 9 H, H-2_A, 3_A, 4_B, 5_A, 5_C, 5_B, 6_A, 6_{Bb}), 2.09, 2.07, 2.07, 2.04, 2.04, 2.02, 2.00 (7 s, 21 H, 7 CH_3CO), 1.47 (d, 3 H, J 4.8 Hz, CH_3CH).

Anal. Calcd for $C_{41}H_{52}O_{23}$: C, 53.95; H, 5.74. Found: C, 54.19; H, 5.91.

3-*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-6-*O*-(2,3-di-*O*-acetyl-β-D-glucopyranosyl)-4-*O*-acetyl-1,2-*O*-(R,S)ethylidene-α-D-glucopyranose (14). Compound **13** (360 mg, 0.39 mmol) was dissolved in AcOH (5 mL) and treated with 4/1 $Cl_2CHCOOH/H_2O$ (v/v) (0.4 mL) at room temperature for 6 h, at the end of which time TLC (1/2 petroleum ether/ethyl acetate) indicated that the reaction was complete. The reaction mixture was diluted with H_2O, extracted with CH_2Cl_2 (3 × 5 mL), and the organic phase was washed with satd. aq. Na_2CO_3 (3 × 5 mL) and brine (2×5 mL), dried, concentrated and subjected to column chromatography with 1/2

petroleum ether/ethyl acetate as the eluent, giving **14** (R,S) as a syrup (280 mg, 87%). ^{1}H NMR: δ (R/S, 1/1) 5.63 (d, 1/2 H, J 4.6 Hz, H-1_S), 5.55-5.50 (m, 1 H, 1/2 CH_3CH, 1/2 H-1_R), 4.81, 4.62 (2 d, 1 H, J 7.0 Hz, 1/2 H-1_{CR}, 1/2 H-1_{BR}), 4.79, 4.54 (2 d, 1 H, J 7.8 Hz, 1/2 H-1_{CS}, 1/2 H-1_{BS}), 2.10-2.00 (m, 21 H, 7 CH_3CO), 1.49 (d, 3/2 H, J 4.8 Hz, CH_3CH_R), 1.36 (d, 3/2 H, J 4.9 Hz, CH_3CH_S).

Anal. Calcd for $C_{34}H_{48}O_{23}$: C, 49.52; H, 5.87. Found: C, 49.35; H, 5.57.

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