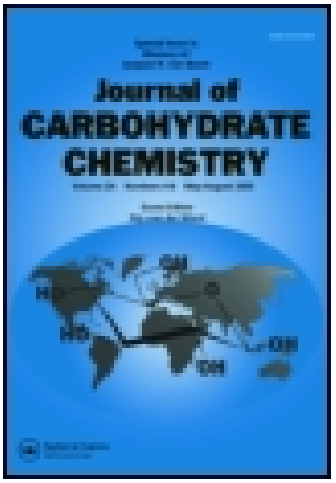

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Novel Selectivity in Carbohydrate Reactions Ii. Selective 6-O-Glycosylation of a Partially Protected Lactoside

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NOVEL SELECTIVITY IN CARBOHYDRATE REACTIONS II. SELECTIVE 6-*O*-GLYCOSYLATION OF A PARTIALLY PROTECTED LACTOSIDE[1,2]

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ABSTRACT

A novel regioselectivity was observed in the silver salt promoted glycosylation of 2-(trimethylsilyl)ethyl 3'-*O*-benzyl-β-D-lactoside using acetobromogalactose as the glycosyl donor. The resulting trisaccharide, obtained in 67% yield, was shown to have the newly formed β-glycosidic linkage at the *O*-6 position of the lactoside. This was confirmed by synthesis of the authentic product by an alternate route. The novel regioselectivity observed is attributed to the presence of the axially disposed 4'-OH group in the lactoside acceptor.

INTRODUCTION

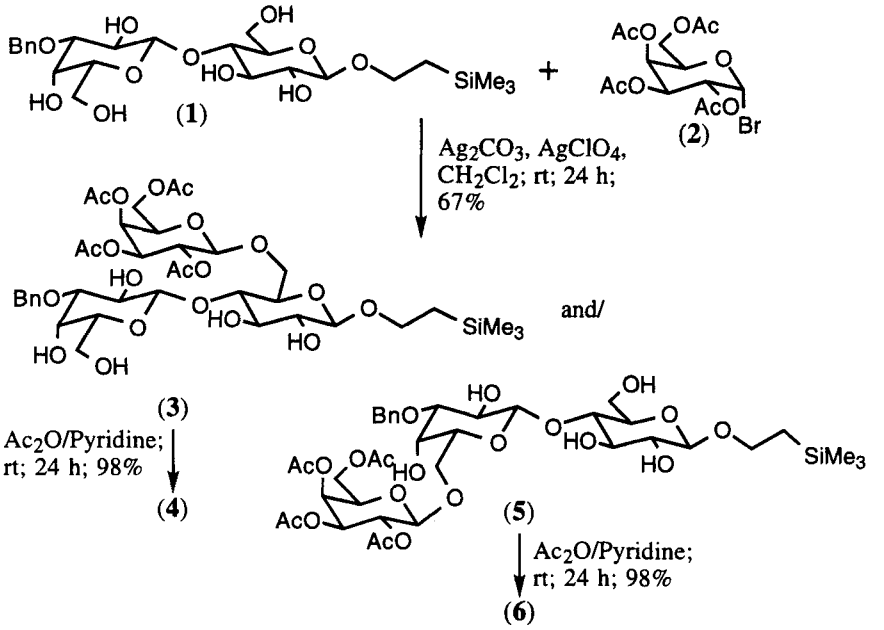
We have recently shown that in spite of its exceptionally high reactivity, as for example towards acylating agents, the secondary hydroxyl group at the C-3 position[4] and the remaining two secondary hydroxyl groups at C-2 and C-4 positions of 2-(trimethylsilyl)ethyl β-D-galactopyranoside can be differentiated from the primary hydroxyl group at the C-6 position and selective glycosylation at C-6 position of the molecule is possible when the glycosylation reaction is carried out under mild conditions.[5] In order to test the differential reactivity of two primary hydroxyl groups, a partially protected lactoside 2-(trimethylsilyl)ethyl 3'-*O*-benzyl-β-D-lactoside (**1**) was chosen as the substrate. Though the preferential reactivity of the hydroxyl groups at C-2, C-6 and C-6' positions of **1** towards benzoyl chloride in cold pyridine is well known[6] because of the axial orientation of the hydroxyl group at its C-4' position we felt that the primary hydroxyl group at C-6

might be more reactive to acetobromogalactose than the one at C-6'. The 3'-*O*-benzyl group improved the solubility of the lactoside in dichloromethane and allowed us to use it as an acceptor in glycosylation reactions.

RESULTS AND DISCUSSION

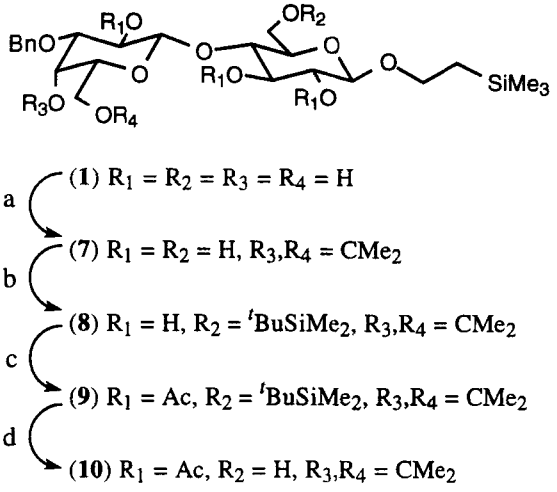
When a mixture of 2-(trimethylsilyl)ethyl 3'-*O*-benzyl-β-D-lactoside (**1**), acetobromogalactose (**2**) (1.5 mol equiv) and silver carbonate in dichloromethane was stirred at room temperature [conditions analogous to the selective 6-*O*-glycosylation of 2-(trimethylsilyl)ethyl β-D-galactopyranoside with **2**[5]] almost no reaction could be detected by TLC for several hours. However, when the reaction was repeated in the presence of silver perchlorate, a product with a greater R_F value than that of **1** started to emerge. The concentration of this compound in the reaction mixture increased with time matching the progressive disappearence of **1** and **2**. After 24 h at room temperature the product was isolated in 67% yield following work up and purification of the product mixture by chromatography. The ^1H NMR spectrum of this product in deuteriochloroform revealed the presence of three axially placed anomeric protons (δ 4.26, 4.28 and 4.64 ppm, 3d, $J_{1,2}$ = 7.8 Hz, 7.8 Hz and 8.0 Hz, respectively) consistent with a trisaccharide having three 1,2-*trans* linkages. Signals in the region of δ 1.90-2.20 in the spectrum showed the presence of four acetyl groups in the compound as expected for the addition of one tetra-*O*-acetyl galactosyl residue to the lactoside acceptor **1**. Other signals in the ^1H NMR spectrum were also consistent with the addition of a single tetra-*O*-acetyl-β-D-galactosyl residue to the acceptor **1**. Characteristic signals in the ^{13}C NMR spectrum [δ 20.57, 20.63, 20.72 and 20.84 ppm, 4 x $OCOCH_3$; 101.12, 101.87 and 103.76 ppm, three 1,2-*trans* linked anomeric carbons and 169.37, 170.07, 170.23 and 170.49 ppm, 4 x OCOMe] confirmed the above conclusion. The IR spectrum of the compound showed strong hydroxyl group absorption (ν_{max} approximately 3450 cm^{-1}) in accordance with a partially protected polyhydroxylic compound. Moreover on acetylation of the above product using acetic anhydride in pyridine, the hydroxyl-absorption band disappeared from the IR spectrum. The NMR spectra obtained for the acetylated product were consistent with a trisaccharide structure (see Experimental).

Although there are two primary hydroxyl groups present in the partially protected lactoside **1**, we argued that the axial hydroxyl at the 4'-position may impart some steric retardation on the reactivity of the 6'-OH group as it competes with the 6-OH group for the glycosyl residue derived from **2**. In such an event the expected product should have structure **3** and the acetylation product derived from it should be of structure **4** (see Scheme 1). As the unambiguous differentiation of structures **3** and **4** from the corresponding



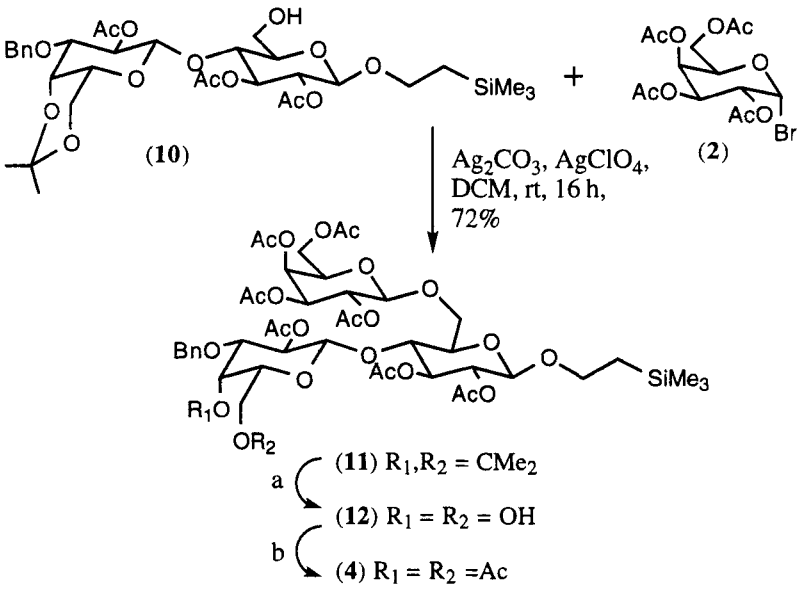
Scheme 1

isomeric structures **5** and **6** was difficult by simple NMR spectroscopy, the trisaccharide derivative **4** was synthesized following a standard protocol as depicted in Schemes 2 and 3. The 6'- and the 4'-OHs of the 3'-*O*-benzyl lactoside **1** were first protected by treatment with 2,2-dimethoxypropane in cold dimethylformamide containing *p*-toluenesufonic acid to give the known isopropylidene derivative **7**.[7] Compound **7** was then converted to **9** by a one-pot, two step procedure involving selective protection of the 6-OH as a silyl ether derivative followed by acetylation of the secondary hydroxyl groups at the C-2, C-3 and C-2' positions by addition of acetic anhydride to the reaction mixture. Treatment of **9** with tetrabutylammonium fluoride[8] gave **10** as crystals (Scheme 2). The NMR spectra obtained for this compound were in accordance with structure **10** (see Experimental). Glycosylation of **10** with acetobromogalactose (**2**) was then carried out under standard Koenigs-Knorr conditions in the presence of silver carbonate and silver perchlorate in anhydrous dichloromethane (Scheme 3). The isopropylidene group in the trisaccharide was then hydrolysed with aqueous acetic acid to give a diol which, when treated with acetic anhydride in pyridine, gave a nonaacetate derivative identical in all respects to **4** obtained directly from **3**. In conclusion glycosylation of partially protected lactoside derivative **1** with acetobromogalactose (**2**) by Koenigs-Knorr method results in a highly regioselective



a 2,2-dimethoxypropane, *p*-toluenesulphonic acid/DMF at 5 °C, 1.5 h, 85%; b ^{t}BuSiMe$_2$Cl/pyridine, 0-10 °C, 8 h; c Ac_2O/pyridine, rt, 16 h, 92% for two steps; d tetrabutylammonium fluoride/THF, 5 °C 15 min, 93%

Scheme 2



a 90% aqueous AcOH, rt, 12 h; b Ac_2O/pyridine, rt, 24 h, 98% for two steps

Scheme 3

reaction leading to the formation of the trisaccharide **3** in high yield; the reduced reactivity of 6'-OH as compared with 6-OH is attributable to steric factors.

EXPERIMENTAL

General Procedures. TLC was carried out with 0.2 mm Merck precoated silica gel 60 aluminium sheets. Compounds were revealed by dipping in an ethanolic solution of sulfuric acid (5% v/v) and heating. Column chromatography was carried out with Merck silica gel G-60 (70-230 mesh) and Aldrich solvents were used as purchased. Hexane refers to *n*-hexane. Melting points were determined using a Yanagimoto micro melting point apparatus and are uncorrected. Specific rotations were determined using a Perkin Elmer 243 automatic polarimeter at 22 °C for solutions in dichloromethane. IR spectra were recorded on a JASCO IR-1 spectrophotometer. ^{1}H NMR spectra were recorded at 200 MHz/500 MHz on a Brucker AM-200/AMX-500 spectrophotometer, respectively, in deuteriochloroform. Chemical shifts are expressed relative to that of the residual proton (δ 7.25 ppm) in the deuterated solvent. ^{13}C NMR spectra were recorded at 50 or 125 MHz at 27 °C using δ_C 77.0 ppm for the central line of CD triplet as reference. Assignments of resonances are based on published data and have not been confirmed by 2D NMR. DCM and rt refer to dichloromethane and room temperature (22-25 °C) respectively.

2-(Trimethylsilyl)ethyl 3'-*O*-Benzyl-β-D-lactoside (1). This compound[7] was prepared from 2-(trimethylsilyl)ethyl β-D-lactoside by the stannylene acetal mediated regioselective 3'-*O*-benzylation by the method reported previously.[7]

2-(Trimethylsilyl)ethyl 6-*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-4-*O*-(3-*O*-benzyl-β-D-galactopyranosyl)-β-D-glucopyranoside (3) from (1). A mixture of **1** (533 mg, 1 mmol), silver carbonate (414 mg, 1.5 mmol), silver perchlorate (207 mg, 1 mmol) and powdered molecular sieves (4Å, 1 g) in dry dichloromethane (17 mL) was stirred at ambient temperature for about 8 h in the dark. Acetobromogalactose **2** (617 mg, 1.5 mmol) was then added to the mixture and stirring was continued for 24 h at room temperature. TLC (DCM:MeOH, 10:0.75) at this stage showed nearly complete disappearence of **2**. The reaction mixture was then filtered through a Celite bed and the residue was washed with dichloromethane. The combined filtrate was then concentrated under reduced pressure and the product was isolated by chromatography on a column of silica gel using DCM:MeOH, 100:1.5 and 100:4 as successive eluents. While the unreacted acetobromogalactose and any byproducts of the reaction were eluted with the former eluent, the latter gave the desired product, after lyophilization from dioxan, as a white powder (578 mg, 67%); $[\alpha]_D$ -4.3° (*c* 0.6); ^{1}H NMR δ 0.01 (s, 9H, Si(C*H*$_3$)$_3$), 0.90-1.10 (m, 2H, C*H*$_2$SiMe$_3$), 1.97, 2.04, 2.12 (3s, 12H, OAc), 3.40 (dd,

1H, $J_{3',4'}$ = 3.3 Hz and $J_{2',3'}$ = 10.1 Hz, H-3'), 4.26, 4.28, 4.64 (3d, 3H, $J_{1,2}$ = 7.8 Hz, 7.8 Hz and 8.0 Hz respectively, H-1, H-1' and H-1"), 4.69, 4.74 (2d, 2H, 11.8 Hz each, CH_2Ph), 4.95 (dd, 1H, $J_{3",4"}$ = 3.3 Hz and $J_{2",3"}$ = 10.4 Hz, H-3"), 5.20 (dd, 1H, $J_{1",2"}$ = 8.0 Hz and $J_{2",3"}$ = 10.4 Hz, H-2"), 5.37.(near d, 1H, $J_{3",4"}$ = 2.6 Hz, H-4") and 7.30-7.42 (m, 5H, C_6H_5);^{13}C NMR δ -1.38 [3C, Si(CH_3)3], 18.27 (1C, CH_2SiMe_3), 20.57, 20.63, 20.72, 20.89 (4C, 4 x OCOCH_3), 61.29, 62.12, 67.51, 68.28, 72.28 (5C, C-6, C-6', C-6", CH_2Ph and O$CH_2CH_2SiMe_3$), 66.76, 67.08, 68.72, 70.57, 70.74, 70.93, 73.23, 74.20, 74.72, 75.12, 80.46, 81.76 (12C, secondary ring carbons except the anomeric carbons), 101.12, 101.87, 103.7 (3C, C-1, C-1', C-1"), 127.98 (x 2), 128.22, 128.68 (x 2), 137.49 (6C, C_6H_5), 169.37, 170.07, 170.23, and 170.49 (4C, 4 x OCOMe).

Anal. Calcd for $C_{38}H_{58}O_{20}Si$ (862.948): C, 52.89, H, 6.78. Found: C, 52.80, H, 6.69.

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-acetyl-6-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-4-*O*-(2,4,6-tri-*O*-acetyl-3-*O*-benzyl-β-D-galactopyranosyl)-β-D-glucopyranoside (4). **3** (100 mg) was dissolved in anhydrous pyridine (1 mL). Acetic anhydride (0.5 mL) was added to it and the resultant solution was gently stirred for 24 h at room temperature. It was then cooled in an ice bath and the excess of acetic anhydride was destroyed by addition of anhydrous methanol with stirring for a few minutes. The reaction mixture was then concentrated to dryness by repeated coevaporation with toluene and the product was obtained as a white powder after filtration through a short column of silica gel and lyophilization from dioxan (122 mg, 98%); $[\alpha]_D$ +11.7° (*c* 0.6); ^{1}H NMR δ -0.01 [s, 9H, Si(CH_3)3], 0.85-1.02 (m, 2H, CH_2SiMe_3), 1.97, 1.99, 2.00, 2.04, 2.08, 2.13, 2.14 (7s, 27H, OAc; 3.47 (dd, 1H, $J_{3',4'}$ = 3.3 Hz and $J_{2',3'}$ = 10.0 Hz, H-3'), 4.33, 4.41, 4.59 (3d, 3H, $J_{1,2}$ = 7.9 Hz each, H-1, H-1' and H-1"), 4.34, 4.66 (2d, 2H, 12.2 Hz each, CH_2Ph), 4.82 (dd, 1H, $J_{1,2}$ = 8.0 Hz and $J_{2,3}$ = 9.5 Hz, H-2), 4.93 (dd, 1H, $J_{3",4"}$ = 3.3 Hz and $J_{2",3"}$ = 10.4 Hz, H-3"), 5.00 (dd, 1H, $J_{1',2'}$ = 8.1 Hz, $J_{2',3'}$ = 10.0 Hz, H-2'), 5.14 (t, 1H, $J_{3,4}$ = 9.9 Hz, H-3), 5.17 (dd, 1H, $J_{1",2"}$ = 8.0 Hz and $J_{2",3"}$ = 10.4 Hz, H-2"), 5.37, 5.46 (2 near d, 2H, $J_{3"/3',4"/4'}$ = 2.6 Hz, and 3.3 Hz respectively, H-4" and H-4') and 7.18-7.34 (m, 5H, C_6H_5); ^{13}C NMR δ -1.37 [3C, Si(CH_3)3], 17.85 (1C, CH_2SiMe_3), 61.10, 61.58, 67.46 (x 2), 71.25 (5C, C-6, C-6', C-6", CH_2Ph and O$CH_2CH_2SiMe_3$), 65.43, 66.93, 68.87, 70.69, 70.84 (x 4), 71.78, 72.97, 74.88, 76.13 (12C, secondary ring carbons except the anomeric carbons), 99.98, 100.89, 101.38 (3C, C-1, C-1', C-1"), 127.81 (x 2), 127.89, 128.40 (x 2), 137.38 (6C, C_6H_5) and 168.99, 169.07, 169.55, 169.80, 170.02, 170.15, 170.27 (x 2), 170.44 (9C, 9 x OCOMe).

Anal. Calcd for $C_{48}H_{68}O_{25}Si$ (1073.133): C, 53.72, H, 6.39. Found: C, 53.77, H, 6.50.

2-(Trimethylsilyl)ethyl 3'-*O*-Benzyl-4',6'-*O*-isopropylidene-β-D-lactoside (7). This compound[7] was prepared from **1** by treatment with 2,2-dimethoxypropane as per the method reported previously.[7]

2-(Trimethylsilyl)ethyl 2,3,2'-Tri-*O*-acetyl-3'-*O*-benzyl-4',6'-*O*-isopropylidene-6-*O*-*tert*-butyldimethylsilyl-β-D-lactoside (9). To a solution of **7** (1.145 g, 2 mmol) in dry pyridine (20 mL) cooled in an ice-bath was added *tert*-butyldimethylsilyl chloride (362 mg, 2.4 mmol). The reaction mixture was stirred for about 8 h during which time the temperature was allowed to slowly rise to about 10 °C. TLC (ethyl acetate) of the reaction mixture at this time revealed complete disappearence of **7**. The reaction mixture was then again cooled to ice-bath temperature, acetic anhydride (10 mL) was added to it, and the reaction mixture was stirred for about 16 h during which the temperature of the bath was allowed to warm to about 20 °C. TLC (ethyl acetate:hexane, 1:1) then showed complete disappearence of **8**. Concentration of the reaction mixture by repeated coevaporation with toluene gave a syrup which on purification by chromatography on a silica gel column (eluent, ethyl acetate:hexane, 1:3 and 2:3 successively) followed by lyophilization from dioxan gave a white powder (1.5 g, 92%) ; $[\alpha]_D$ +9.4° (*c* 0.7); ^{1}H NMR δ -0.02, 0.02, 0.04 [3s, 15H, Si(C*H*3)3, Si(C*H*3)2], 0.82-0.93 (m, 2H, C*H*2SiMe3), 0.85 [s, 9H, C(C*H*3)3], 1.36, 1.42 [2s, 6H, C(C*H*3)2], 1.99, 2.00, 2.09 (3s, 9H, Ac), 3.25, 3.29 (2t, 2H, H-5 and H-5'), 3.34, dd, 1H, $J_{3',4'}$ = 3.4 Hz and $J_{2',3'}$ = 10.0 Hz, H-3'), 3.51, 3.87 (2m, 2H, OC*H*2CH2SiMe3), 3.77 (t, 1H, $J_{3,4} = J_{4,5}$ = 9.6 Hz, H-4), 3.83, 3.95 (d, 2H and m, 2H, H-6 and H-6'), 4.09 (d, $J_{3',4'}$ = 3.2 Hz, H-4'), 4.40, 4.46 (2d, 2H, $J_{1,2}$ = 8.0 Hz each, H-1 and H-1'), 4.51, 4.61 (2d, 2H, 12.6 Hz each, C*H*2Ph), 4.83 (dd, 1H $J_{1,2}$ = 8.0 Hz and $J_{2,3}$ = 9.8 Hz, H-2), 5.11 (t, 1H, $J_{3,4}$ = 9.6 Hz, H-3), 5.14 (dd, 1H, $J_{1',2'}$ = 8.0 Hz and $J_{2',3'}$ = 10.0 Hz, H-2') and 7.22-7.35 (m, 5H, C6*H*5); ^{13}C NMR δ –5.50, –5.10, -1.43 [5C, Si(*C*H3)3, Si(*C*H3)2], 17.93 (1C, *C*H2SiMe3), 18.31, 29.13 [2C, C(*C*H3)2], 25.83 [3C, C(*C*H3)3], 20.62, 20.82, 20.93 (3C, 3 x OCO*C*H3), 60.87, 62.36, 66.49, 70.78 (4C, C-6, C-6', *C*H2Ph and O*C*H2CH2SiMe3), 65.67, 66.33, 70.27, 71.70, 72.64, 74.62, 75.35 and 77.58 (8C, secondary ring carbons except the anomeric carbons), 98.72 (1C, *C*Me2), 99.94, 100.57 (2C, C-1 and C-1'), 127.56 (x 2), 127.72, 128.34 (x 2), 138.00 (6C, *C*6H5) and 168.79, 169.73, 170.48 (3C, 3 x O*C*OMe).

Anal. Calcd for C39H64O14Si2 (813.099): C, 57.61, H, 7.93. Found: C, 57.72, H, 7.80.

2-(Trimethylsilyl)ethyl 2,3,2'-Tri-*O*-acetyl-3'-*O*-benzyl-4',6'-*O*-isopropylidene-β-D-lactoside (10). Tetrabutylammonium fluoride (2.25 mL of a 1 M solution in tetrahydrofuran, 2.25 mmol) was added to a solution of **9** (1.22 g, 1.5 mmol) in tetrahydrofuran (12 mL) held at 5 °C in a cooling bath and the solution was then stirred

for about 15 min. TLC (ethyl acetate:hexane, 1:1) showed complete conversion of **9** to a slower moving compound. The reaction mixture was then concentrated to a thick syrup under reduced pressure and chromatographed on a column of silica gel (eluent, EtOAc:Hexane, 2:3 and 1:1 successively) to yield **10** as fine crystals (975 mg, 93%); mp, 78-80 °C; $[\alpha]_D$ +1.0° (*c* 1.0); ^{1}H NMR δ -0.02 [s, 9H, Si(C*H*3)3], 0.80-1.02 (m, 2H, C*H*2SiMe3), 1.35, 1.42 [2s, 6H, C(C*H*3)2], 2.00, 2.01, 2.02 (3s, 3H, Ac), 3.41 (dd, 1H, $J_{3',4'}$ = 3.3 Hz and $J_{2',3'}$ = 10.0 Hz, H-3') 3.50, 3.92 (2m, 2H, OC*H*2CH2SiMe3), 4.06 (near d, 1H, $J_{3',4'}$ = 3.1 Hz, H-4'), 4.39, 4.48 (2d, 2H, $J_{1,2}$ = 8.0 Hz each, H-1 and H-1'), 4.51, 4.60 (2d, 2H, C*H*2Ph), 4.83 (dd, 1H, $J_{1,2}$ = 8.0 Hz and $J_{2,3}$ = 9.8 Hz, H-2), 5.14 (dd, 1H, $J_{1',2'}$ = 8.0 Hz and $J_{2',3'}$ = 10.0 Hz, H-2'), 5.16 (t, 1H, $J_{3,4}$ = 9.6 Hz, H-3) and 7.22-7.38 (m, 5H, C6*H*5); ^{13}C NMR δ -1.46 [3C, Si(*C*H3)3], 17.95 (1C, *C*H2SiMe3), 18.33, 29.09 [2C, C(*C*H3)2], 20.56, 20.74, 20.86 (3C, 3 x OCO*C*H3), 60.34, 62.31, 67.65, 70.94 (4C, C-6, C-6', *C*H2Ph and OCH2CH2SiMe3), 65.64, 66.32, 70.52, 71.68, 72.63, 74.42, 74.95,77.42 (8C, secondary ring carbons except the anomeric carbons), 98.77 (1C, *C*Me2), 100.31, 100.76 (2C, C-1 and C-1'), 127.53 (x 2), 127.76, 128.37 (x 2), 137.90 (6C, *C*6H5) and 168.96, 169.92, 170.25 (3C, 3 x *C*OMe).

Anal. Calcd for C33H50O14Si (698.835.948): C, 56.72, H, 7.21. Found: C, 56.83, H, 7.30.

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-acetyl-6-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-4-*O*-(2-*O*-acetyl-3-*O*-benzyl-4,6-*O*-isopropylidene-β-D-galactopyranosyl)-β-D-glucopyranoside (11). Condensation of **10** (699 mg, 1 mmol) and **2** (617 mg, 1.5 mmol) to give **11** was carried out as described for the preparation of **3** from **1** and **2** above. Ethyl acetate-hexane, 1:1 was used as eluent for the chromatographic purification of the crude product obtained. After lyophilization from dioxan, **11** was obtained as a white powder (741 mg, 72%); $[\alpha]_D$ +10.3° (*c* 0.6); ^{1}H NMR δ -0.04 [s, 9H, Si(C*H*3)3], 0.78-1.01 (m, 2H, C*H*2SiMe3) 1.33, 1.39 [2s, 6H, C(C*H*3)2], 1.93, 1.97, 2.01, 2.04, 2.10 (5s, 21H, OAc), 3.39 (dd, 1H, $J_{3',4'}$ = 3.5 Hz and $J_{2',3'}$ = 10.1 Hz, H-3'; 4.22, 4.38, 4.59 (3d, 3H, $J_{1,2}$ = 7.9-8.0 Hz each, H-1 and H-1' and H-1"), 4.48, 4.59 (2d, 2H, 12.7 Hz each, C*H*2Ph), 4.80 (dd, 1H, $J_{1,2}$ = 8.0 Hz and $J_{2,3}$ = 9.7 Hz, H-2), 4.92 (dd, 1H, $J_{3",4"}$ = 3.4 Hz and $J_{2",3"}$ = 10.4 Hz, H-3"), 5.10 (t, 1H, $J_{3,4}$ = 9.5 Hz, H-3), 5.13 (dd, 2H, $J_{1',2'}$ = $J_{1",2"}$ = 8.0 Hz and $J_{2',3'}$ = $J_{2",3"}$ = 10.1 Hz, H-2' and H-2") 5.34 (near d, 1H, $J_{3",4"}$ = 2.7 Hz, H-4") and 7.18-7.32 (m, 5H, C6*H*5); ^{13}C NMR δ -1.48 [3C, Si(*C*H3)3], 17.74 (1C, *C*H2SiMe3), 18.75, 29.02 [2C, C(*C*H3)2], 20.46 (x 2), 20.54, 20.56, 20.65 (x 2), 20.81 (7C, 7 x OCO*C*H3), 61.07, 62.20, 67.33, 67.65, 70.68 (5C, C-6, C-6', C-6", *C*H2Ph and OCH2CH2SiMe3), 65.43, 66.31, 66.84, 68.82, 70.37, 70.68, 70.74, 71.51, 72.43, 75.04, 75.75 and 77.11 (12C,

secondary ring carbons except the anomeric carbons), 98.75 (1C, *C*Me2), 100.00, 100.64, 101.29 (3C, C-1, C-1'and C-1"), 127.46 (x 2), 127.71, 128.31 (x 2), 137.82 (6C, C_6H_5) and 168.99 (x 2), 169.51, 169.93, 170.08, 170.13 and 170.22 (7C, 7 x O*C*OMe).

Anal. Calcd for $C_{47}H_{68}O_{23}Si$ (1029.124): C, 54.85, H, 6.66. Found: C, 54.92, H, 6.74.

2-(Trimethylsilyl)ethyl 2,3-Di-*O*-acetyl-6-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-4-*O*-(2,4,6-tri-*O*-acetyl-3-*O*-benzyl-β-D-galactopyranosyl)-β-D-glucopyranoside (4) from (11). A solution of **11** (250 mg) in aqueous acetic acid (5 mL, 90%, v/v) was gently stirred at room temperature for 12 h, concentrated to dryness under reduced pressure by repeated coevaporation with toluene, and then lyophilized from dioxan to yield **12** as a white powder in quantitative yield; $[\alpha]_D$ +5.4° (*c* 0.6); ^{1}H NMR δ -0.02 [s, 9H, Si(C*H*3)3], 0.82-1.01 (m, 2H, C*H*2SiMe3) 1.95, 1.98, 1.99, 2.00, 2.02, 2.03, 2.12 (7s, 21H, OAc), 3.43 (dd, 1H, $J_{3',4'}$ = 3.3 Hz and $J_{2',3'}$ = 9.8 Hz, H-3'), 4.02 (d, 1H, $J_{3',4'}$ = 2.9 Hz, H-4'), 4.13 (d, 2H, H-6"a, H-6"b), 4.33, 4.42, 4.58 (3d, 3H, $J_{1,2}$ = 7.9-8.0 Hz each, H-1 and H-1' and H-1"), 4.46, 4.65 (2d, 2H, 12.2 Hz each, C*H*2Ph), 4.81 (dd, 1H, $J_{1,2}$ = 8.0 Hz and $J_{2,3}$ = 9.4 Hz, H-2), 4.94 (dd, 1H, $J_{3",4"}$ = 3.4 Hz and $J_{2",3"}$ = 10.4 Hz, H-3"), 5.06 (dd, 1H, $J_{1',2'}$ = 8.0 Hz and $J_{2',3'}$ = 9.8 Hz, H-2'), 5.13 (t, 1H, $J_{3,4}$ = 9.4 Hz, H-3), 5.16 (dd, 1H, $J_{1",2"}$ = 8.0 Hz and $J_{2",3"}$ = 10.4 Hz, H-2"), 5.36 (near d, 1H, $J_{3",4"}$ = 2.6 Hz, H-4") and 7.22-7.38 (m, 5H, C_6H_5).

Anal. Calcd for $C_{44}H_{64}O_{23}Si$ (989.059): C, 53.43, H, 6.52. Found: C, 53.69, H, 6.71.

Compound **12** thus obtained was then acetylated using acetic anhydride in pyridine by the procedure described under the preparation of **4** from **3** above. The product obtained was homogeneous with **4** in all respects.

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