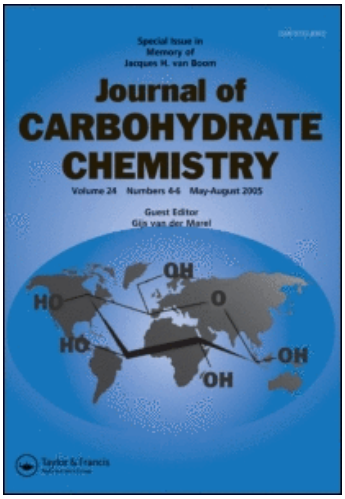

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SILYL GROUP MIGRATION IN 1-*O*-SILYL PROTECTED SUGARS - CONVENIENT SYNTHESIS OF 2-*O*-UNPROTECTED SUGARS

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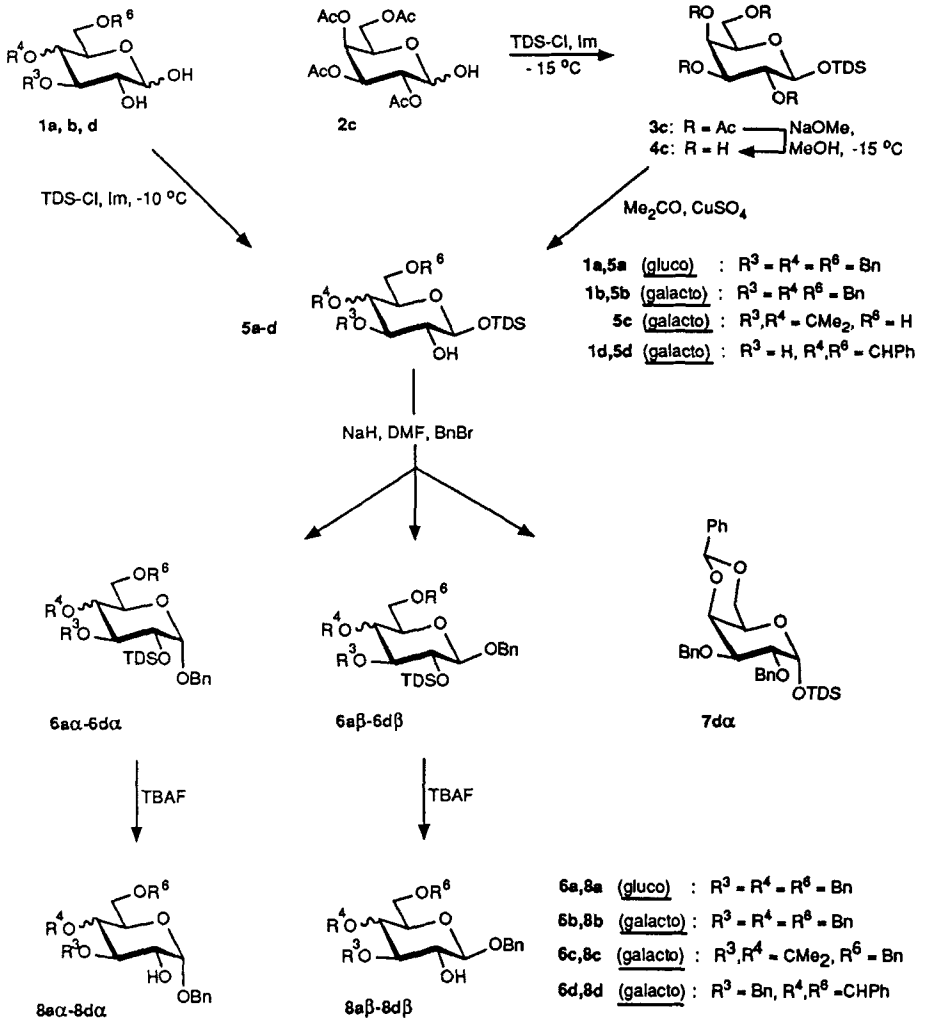
ABSTRACT

Reaction of 2-*O*-unprotected 1-*O*-silyl-protected D-glucose and D-galactose derivatives **5a-d** with benzyl bromide in the presence of sodium hydride as the base afforded 1-*O*-benzyl 2-*O*-silyl derivatives **6a**α/β - **6d**α/β. Thus, prior to anomeric *O*-benzylation, *trans*-1,2-silyl group migration takes place. Ensuing removal of the 2-*O*-silyl group furnishes 2-*O*-unprotected compounds **8a**α/β - **8d**α/β, which are useful building blocks. More prone to 1-*O*-silyl group migration is mannose as shown for derivatives of 4,6-*O*-benzylidene-D-mannose **9**. *Cis*-1,2- and *cis*-2,3-silyl group migrations affording compounds **15** and **13** were already observed on deacetylation of the thexyldimethylsilyl 2,3-di-*O*-acetyl derivative **12**β under Zemplén conditions.

INTRODUCTION

Base promoted *O*-silyl group migration in *cis*- and *trans*-1,2-diol systems have been already observed.[1,2] In the course of investigations on *O*-deacylation and regioselective *O*-benzylation reactions of 1-*O*-silyl protected sugars, we encountered interesting silyl group migrations away from the anomeric center. These reactions have to be considered not only as possible side reactions, but they also provide valuable partially *O*-unprotected sugars, as will be shown below.



Scheme 1

RESULTS AND DISCUSSION

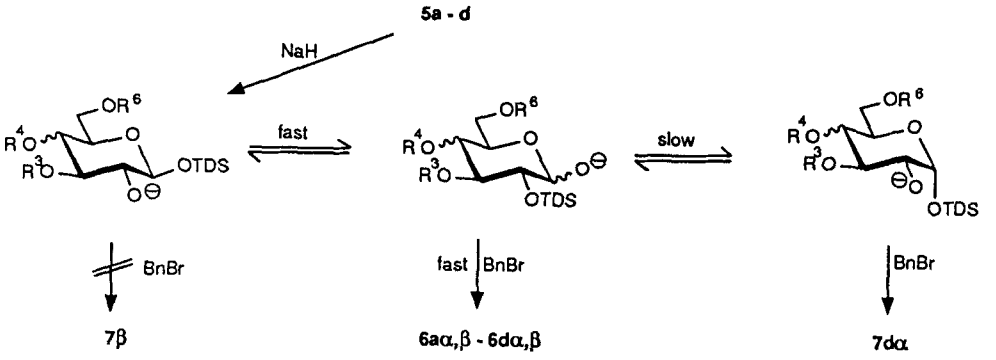
The migration of 1-*O*-silyl groups can be particularly well demonstrated for 3,4,6-tri-*O*-benzylglucose (**1a**)[3] and -galactose (**1b**)[4] (Scheme 1). Regioselective 1-*O*-silylation of **1a,b** can be readily performed with thexyldimethylsilyl chloride (TDS-Cl) in the presence of imidazole at -10 °C, thus providing selectively the β-derivatives **5a** and **5b**, respectively, as derived from their ^{1}H NMR data, also by adding CCl_3CO-NCO to the $CDCl_3$ solution.

Benzylation of these compounds with benzyl bromide in DMF and NaH as the base did not lead to the expected 2-*O*-benzyl derivatives, instead, about 1:1-mixtures of 2-*O*-silyl-protected benzyl α- and β-glycopyranosides **6a**α/β and **6b**α/β were obtained in high overall yields. Practically the same result was obtained for 1-*O*-TDS protected 3,4-*O*-isopropylidene-D-galactose **5c** which is readily available from known **2c**[5] via 1-*O*-silylation (→ **3c**), removal of the acetyl groups under Zemplén conditions[6] (NaOMe/MeOH) at -15 °C (→ **4c**) (thus preventing silyl group migration),[7] and then treatment with acetone in the presence of anhydrous $CuSO_4$. Treatment of **5c** with benzyl bromide in DMF and NaH as the base gave again via *trans*-(1→2)-*O*-silyl group migration and 1-*O*- and 6-*O*-benzylation compounds **6c**α,β (α:β ~ 1:1).

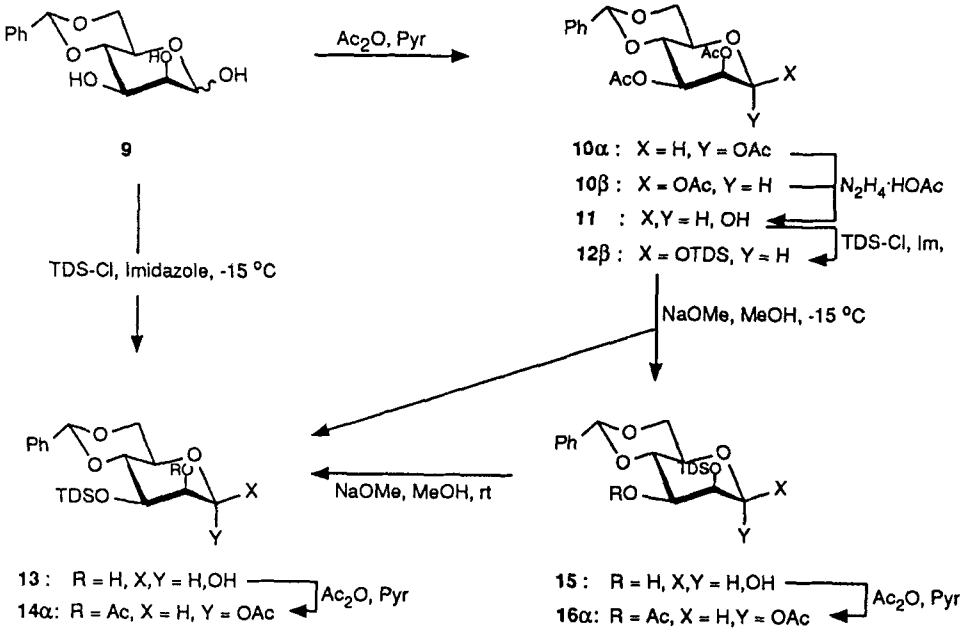
Besides 2,6-di-*O*-unprotected **5c**, also 2,3-di-*O*-unprotected **5d**, readily available from known **1d**[8] via direct 1-*O*-silylation was investigated in this reaction; again benzyl 3-*O*-benzyl-2-*O*-silyl derivatives **6d**α/β (61%, α:β = 1:3) were the main products; however, in addition 1-*O*-silyl 2,3-*O*-benzyl-α-D-galactopyranoside **7d**α was obtained as a reaction product (20%). Thus, fast *trans*-(1→2)-*O*-silyl group migration and then anomeric *O*-alkylation leading to benzyl α- and β-glycosides **6a**α,β - **6d**α,β (Scheme 2) are not the only alternatives. Additionally, either direct anomerisation of **5** or, as indicated in Scheme 2, reversible *cis*- and *trans*- (2→1)-*O*-silyl migration may take place. However, in none of the examples the expected direct 2-*O*-benzylation leading to compounds of type **7**β was found; and in 2,3-*O*-unprotected galactose derivative **5d** the unprotected 3-OH group did not participate in the silyl migration processes.

Compounds **6a-d** are interesting intermediates because 2-*O*-desilylation with tetra-*n*-butylammonium fluoride (TBAF) furnishes 2-*O*-unprotected derivatives **8a-d** in very high yields. For instance, compounds **8c** and **8d** are particularly valuable intermediates because they offer regioselective access to all other hydroxy groups. Additionally, the ^1H NMR data obtained for compounds **8a-d** ascertain the structural assignments of compounds **6a-d**.

Silyl group migration as investigated for derivatives of 4,6-*O*-benzylidene-D-mannose (**9**)[9] (Scheme 3) exhibited a very different picture; as *cis*-(1→2)-migrations they are obviously much faster. Thus, silylation of **9** with TDS-Cl in the presence of imidazole at -15 °C did not yield the expected 1-*O*-silyl-protected derivative, but instead directly the 3-*O*-silyl-derivative **13** was obtained. Therefore, via per-*O*-acetylation of **9** with acetic anhydride in pyridine (→ **10**α,β), selective 1-*O*-deacylation with hydrazinium acetate (→ **11**), and then silylation with TDS-Cl in the presence of imidazole at 0 °C the desired 1-*O*-silyl protected intermediate **12**β was synthesized. However, deacylation of **12**β under Zemplén conditions at -15 °C led already to silyl group migration affording 2-



Scheme 2



Scheme 3

O-silyl- and 3-*O*-silyl derivatives **15** and **13** in high overall yield (**15**: 34%, **13**: 53%). Further treatment of **15** with NaOMe/MeOH led to transformation into **13**, which is under these conditions obviously the thermodynamically most stable product. Therefore, in the formation of **13** from **9** the 1-*O*- and 2-*O*-silyl derivatives could well be transient intermediates. The structures of compounds **13** and **15** were assigned with the help of their acetylated compounds **14**α and **16**α, respectively.

GENERAL METHODS

Solvents were purified and dried in the usual way; the light petroleum ether used had boiling range 35-65 °C. Melting points were measured in a metal block and are uncorrected. Optical rotations were determined at 25 °C with a Perkin-Elmer 241/MS polarimeter. Flash chromatography was performed on silica gel (Baker, particle size 30-60 μm). Thin layer chromatography (TLC) was performed on silica gel precoated plates (Merck 60 F_{254}, 0.2 mm thickness), detection was achieved by treatment with a solution of 20 g of ammonium molybdate and 0.4 g of cerium (IV) sulfate in 400 mL of 10% sulfuric acid and heating at 120 °C. ^{1}H NMR Spectra were recorded with a Bruker AC 250 Cryospec instrument, using chloroform-d as solvent and tetramethylsilane as internal standard.

Thexyldimethylsilyl 2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranoside (3c). To a stirred solution of **2c**[5] (1 g, 2.8 mmol) and imidazole (0.47 g, 7 mmol) in dry dimethylformamide (3 mL) was added dimethylthexylsilyl chloride (0.68 mL, 3.4 mmol). After 2 h the mixture was diluted with water (10 mL) and extracted with ethyl acetate (20 mL). The organic layer was washed with satd. ammonium chloride solution and dried over calcium chloride. The solvent was removed *in vacuo* and the residue was purified by column chromatography (7:3 petroleum ether/ethyl acetate) to afford **3c** (1.09 g, 80%); $[\alpha]_D$ -2.4° (*c* 1, chloroform), TLC (1:1 petroleum ether/ethyl acetate): R_f 0.75, ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.12 and 0.14 (2s, 6H, $SiMe_2$), 0.81-0.85 (m, 12H, $CHMe_2$ and $SiCMe_2$), 1.57 (m, 1H, $CHMe_2$), 1.96, 2.01, 2.02, 2.14 (4s, 12H, 4 OAc), 3.87 (m, 1H, H-5), 4.03-4.18 (m, 2H, H-6, H-6'), 4.67 (d, $J_{1,2}$ = 7.6 Hz, 1H, H-1), 4.96 (dd, $J_{3,4}$ = 3.4 Hz, $J_{2,3}$ = 10.5 Hz, 1H, H-3), 5.14 (dd, $J_{1,2}$ = 7.6 Hz, $J_{2,3}$ = 10.5 Hz, 1H, H-2) 5.34 (dd, $J_{4,5}$ = 1.0 Hz, $J_{3,4}$ = 3.4 Hz, 1H, H-4).

Anal. Calcd for $C_{22}H_{35}O_{10}Si$: C, 53.89; H, 7.75. Found: C, 53.91; H, 7.71.

Thexyldimethylsilyl β-D-Galactopyranoside (4c). To a cooled (-15 °C) solution of **3c** (43 g, 80 mmol) in dry methanol (325 mL) was added sodium methoxide (1 M in dry methanol, 8.7 mL) and the mixture was stirred for 12 h. The mixture was then neutralized with ion-exchange resin Amberlite IR 120 (+), filtered and concentrated *in vacuo*. The resulting residue was purified by flash chromatography (3:7 toluene/acetone) to yield **4c** (25.5 g, 91%); mp 105 °C; $[\alpha]_D$ -2.4 ° (*c* 1, chloroform), TLC (3:7 toluene/acetone): R_f 0.30, ^{1}H NMR (250 MHz, DMSO-d_6): δ 0.09 and 0.10 (2s, 6H, $SiMe_2$), 0.75-0.81 (m, 12H, $CHMe_2$ and $SiCMe_2$), 1.6 (m, 1H, $CHMe_2$), 3.14-3.63 (m, 6H, H-2, H-3, H-4, H-5, H-6, H-6'), 4.29 (d, $J_{1,2}$ = 6.8 Hz, 1H, H-1), 4.30 (d, J 4.4 Hz, 1H, OH), 4.46 (t, J = 5.5 Hz, 1H, OH-6), 4.56 (d, J = 5.3 Hz, 1H, OH), 4.59 (d, J = 4.8 Hz, 1H, OH).

Anal. Calcd for $C_{14}H_{30}O_6Si$: C, 52.19; H, 9.31. Found: C, 51.98; H, 9.14.

Preparation of the Silyl Glycosides 5a,b,d: General Procedure. To a cooled (-10 °C) solution of **1** (2 mmol) and imidazole (272 mg, 4 mmol) in dry dichloromethane (**1a,1b**) or dimethylformamide (**1d**) (5 mL) was added dimethylthexylsilyl chloride (0.44 mL, 2.2 mmol). The mixture was warmed up to room temperature and stirred for 2 h. The solvent was removed *in vacuo* and the residue was purified by flash chromatography to afford **5**. Starting material, eluent used for the flash chromatography, yields and physical data are as follows:

Thexyldimethylsilyl 3,4,6-Tri-*O*-benzyl-β-D-glucopyranoside (5a). From **1a**[3] (780 mg, 1.73 mmol); eluted with 8:1 petroleum ether/ethyl acetate; yield : 930 mg, 91%; $[\alpha]_D$ +15.1 ° (*c* 1, chloroform), TLC (6:1 petroleum ether/ethyl acetate): R_f 0.41, ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.12 (s, 6H, Si*Me*$_2$), 0.85 (s, 6H, SiC*Me*$_2$), 0.88 (d, J = 6.8 Hz, 6H, CH*Me*$_2$), 1.60 (m, J = 6.8 Hz, C*H*Me$_2$), 2.27 (bs, 1H, OH), 3.4-3.7 (m, 6H, H-2, H-3, H-4, H-5, H-6, H-6'), 4.48 (d, $J_{1,2}$ = 7.3 Hz, 1H, H-1), 4.49-4.96 (m, 6H, 3 PhC*H*$_2$), 7.0-7.4 (m, 15H, arom.).

Anal. Calcd for $C_{35}H_{48}O_6Si$: C, 70.91; H, 8.10. Found: C, 71.01; H, 8.10.

Thexyldimethylsilyl 3,4,6-Tri-*O*-benzyl-β-D-galactopyranoside (5b). From **1b**[4] (820 mg, 1.82 mmol); eluted with 8:1 petroleum ether/ethyl acetate; yield: 971 mg, 90%; $[\alpha]_D$ +32.3 ° (*c* 1, chloroform), TLC (6:1 petroleum ether/ethyl acetate): R_f 0.39, ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.16 and 0.17 (2s, 6H, Si*Me*$_2$), 0.85-0.90 (m, 12H, CH*Me*$_2$ and SiC*Me*$_2$), 1.64 (m, J = 6.9 Hz, C*H*Me$_2$), 2.24 (bs, 1H, OH), 3.42 (dd, $J_{3,4}$ = 2.9 Hz, $J_{2,3}$ = 9.8 Hz, 1H, H-3), 3.55-3.64 (m, 3H, H-5, H-6, H-6'), 3.87 (dd, $J_{1,2}$ = 7.4 Hz, $J_{2,3}$ = 9.8 Hz, 1H, H-2), 3.90 (br.d, $J_{3,4}$ = 2.9 Hz, 1H, H-4), 4.46 (d, $J_{1,2}$ = 7.4 Hz, 1H, H-1), 4.42 and 4.48 (2d, J = 11.7 Hz, 2H, PhC*H*$_2$), 4.70 (s, 2H, PhC*H*$_2$), 4.61 and 4.90 (2d, J = 11.6 Hz, 2H, PhC*H*$_2$), 7.2-7.4 (m, 15H arom.).

Anal. Calcd for $C_{35}H_{48}O_6Si$: C, 70.91; H, 8.16. Found: C, 70.72; H, 8.21.

Thexyldimethylsilyl 4,6-*O*-Benzylidene-β-D-galactopyranoside (5d). From **1d**[8] (500 mg, 1.86 mmol); eluted with 6:1 petroleum ether/ethyl acetate; Yield: 520 mg, 70%; $[\alpha]_D$ +30.8 ° (*c* 1, chloroform), TLC (4:1 petroleum ether/ethyl acetate): R_f 0.39, ^{1}H NMR (250 MHz, $CDCl_3$): 0.04 and 0.10 (2s, 6H, SiMe$_2$), 0.85-0.89 (m, 12H, CH*Me*$_2$ and SiC*Me*$_2$), 1.61 (m, J = 6.8 Hz, C*H*Me$_2$), 3.44 (m, 1H, H-5), 3.6-3.7 (m, 2H, H-2 and H-3), 4.04 (dd, $J_{5,6'}$ = 1.9 Hz, J_{gem} = 12.4 Hz, 1H, H-6'), 4.17 (m, 1H, H-4), 4.26 (dd, $J_{5,6}$ = 1.5 Hz, J_{gem} = 12.4 Hz, 1H, H-6), 4.52 (d, $J_{1,2}$ = 7.4 Hz, 1H, H-1), 5.52 (s, 1H, PhC*H*), 7.3-7.5 (m, 15H, arom.).

Anal. Calcd for $C_{21}H_{34}O_6Si$: C, 61.43; H, 8.35. Found: C, 61.22; H, 8.23.

Thexyldimethylsilyl 3,4-*O*-Isopropylidene-β-D-galactopyranoside (5c). To a suspension of **4c** (24.5 g, 76 mmol) in dry acetone (2.4 L) was added anhydrous copper

(II) sulfate (224 g, 1.40 mmol) and the mixture was stirred vigorously for 30 h. The mixture was then filtered through Celite, washed with more acetone and concentrated *in vacuo*. The resulting residue was purified by flash chromatography (1:1 petroleum ether/ethyl acetate) to yield **5c** (19.4 g, 71%); mp 98-100 °C; $[\alpha]_D$ +27.3 ° (*c* 1, chloroform), TLC (1:1 petroleum ether/ethyl acetate): R_f 0.32, ^1H NMR (250 MHz, $CDCl_3$): δ 0.15 and 0.17 (2s, 6H, Si*Me*$_2$), 0.85-0.90 (m, 12H, CH*Me*$_2$ and SiC*Me*$_2$), 1.32 and 1.51 (2s, 6H, Ipn), 1.64 (m, 1H, C*H*Me$_2$), 1.99 (m, 1H, OH-6), 2.19 (d, $J_{2,OH}$ = 2.9 Hz, 1H, OH-2), 3.46 (dt, $J_{2,OH}$ = 2.9 Hz, $J_{1,2}$ = 7.8 Hz, 1H, H-2), 3.73-4.14 (m, 5H, H-3, H-4, H-5, H-6, H-6'), 4.39 (d, $J_{1,2}$ = 7.8 Hz, 1H, H-1).

Anal. Calcd for $C_{17}H_{34}O_6Si$: C, 56.37; H, 9.39. Found: C, 56.09; H, 9.24.

Synthesis of Benzyl Glycosides 6a-d: General Procedure. To a cooled (0 °C) solution of **5a-d** and benzyl bromide (2 equiv) in dry dimethylformamide was added sodium hydride (1.5 equiv) while stirring. The mixture was allowed to reach room temperature and stirred until TLC indicated total consumption of the starting material (2-4 h). After addition of methanol, the mixture was poured on ice-water and extracted with ethyl acetate. The organic layer was dried over magnesium sulfate, filtered, and concentrated *in vacuo*. The residue was purified by flash chromatography affording compounds **6a-d**. In cases **a** and **b**, separation of anomeric mixtures was not possible at this step. In case **c**, this was carried out by MPLC. Compound **7d**α was also obtained when starting from compound **2d**. Starting material, eluent used for the chromatographic separations, yields and physical data are as follows:

Benzyl 3,4,6-Tri-*O*-benzyl-2-*O*-thexyldimethylsilyl-α- and -β-D-gluco-pyranoside (6aα/β). From **5a** (300 mg, 0.51 mmol); eluted with 12:1 petroleum ether/ethyl acetate; yield: 325 mg, 94%, TLC (8:1 petroleum ether/ethyl acetate): R_f 0.63, ^1H NMR (250 MHz, $CDCl_3$): δ 0.03 and 0.04, 0.06, 0.08 (s, 6H, Si*Me*$_2$α and β), 0.77-0.87 (m, 12H, CH*Me*$_2$ and SiC*Me*$_2$), 1.60 (m, J = 6.8 Hz, C*H*Me$_2$), 3.41-3.95 (m, 6H, H-2, H-3, H-4, H-5, H-6, H-6'), 4.31 (d, $J_{1,2}$ = 7.4 Hz, H-1β), 4.87 (d, $J_{1,2}$ = 2.4 Hz, H-1α), 4.40-4.95 (m, 8H, 4 PhC*H*$_2$), 7.0-7.4 (m, 20H, Ph).

Anal. Calcd for $C_{42}H_{54}O_6Si{\cdot}H_2O$: C, 71.96; H, 8.05. Found: C, 72.18, H, 7.94.

Benzyl 3,4,6-Tri-*O*-benzyl-2-*O*-thexyldimethylsilyl-α- and -β-galacto-pyranoside (6bα/β). From **5b** (300 mg, 0.51 mmol); eluted with 12:1 petroleum ether/ethyl acetate; yield: 332 mg, 96%, TLC (6:1 petroleum ether/ethyl acetate): R_f 0.56, ^1H NMR (250 MHz, $CDCl_3$): δ 0.04-0.06 (m, 6H, Si*Me*$_2$α and β), 0.77-0.86 (m, 12H, CH*Me*$_2$ and SiC*Me*$_2$), 1.62 (m, J = 6.9 Hz, C*H*Me$_2$), 3.31-4.27 (m, 6H, H-2, H-3, H-4, H-5, H-6, H-6'), 4.27 (d, $J_{1,2}$ = 7.4 Hz, H-1β), 4.86 (d, $J_{1,2}$ = 3.6 Hz, H-1α), 4.39-4.93 (m, 8H, 4 PhC*H*$_2$), 7.2-7.4 (m, 20H, Ph).

Anal. Calcd for $C_{42}H_{54}O_6Si$: C, 73.86; H, 7.97. Found: C, 74.15; H, 7.96.

Benzyl 6-*O*-Benzyl-3,4-*O*-isopropylidene-2-*O*-thexyldimethylsilyl-α-D-galactopyranoside (6cα) and Benzyl 6-*O*-Benzyl-3,4-*O*-isopropylidene-2-*O*-thexyldimethylsilyl-β-D-galactopyranoside (6cβ). From **5c** (19 g, 53 mmol); eluted with 95:5 petroleum ether/ethyl acetate; yield 22.3 g, 78% of **6cα/6cβ** (1:1 mixture). This mixture was further separated by MPLC (9:1) petroleum ether/ethyl acetate. Eluted first **6cα**; $[\alpha]_D$ +14.4 ° (*c* 1, chloroform), TLC (95:5 petroleum ether/ethyl acetate): R_f 0.38, ^1H NMR (250 MHz, $CDCl_3$): δ -0.02 and 0.11 (2s, 6H, Si*Me*$_2$), 0.81-0.86 (m, 12H, CH*Me*$_2$ and SiC*Me*$_2$), 1.31 and 1.47 (2s, 6H, Ipn), 1.58 (m, 1H, C*H*Me$_2$), 3.71-4.28 (m, 6H, H-2, H-3, H-4, H-5, H-6, H-6'), 4.55-4.66 (2d, J = 12.1 Hz, 2H, PhC*H*$_2$), 4.50 and 4.72 (2d, J = 11.9 Hz, 2H, PhC*H*$_2$), 4.76 (d, $J_{1,2}$ = 3.5 Hz, 1H, H-1), 7.2-7.4 (m, 10H, arom.).

Anal. Calcd for $C_{31}H_{46}O_6Si$: C, 68.65; H, 8.48. Found: C, 68.24; H, 8.21.

Eluted second **6cβ**; $[\alpha]_D$ -23.3 ° (*c* 1 chloroform), TLC (95:5 petroleum ether/ethyl acetate): R_f 0.33, ^1H NMR (250 MHz, $CDCl_3$): δ 0.04 and 0.12 (2s, 6H, Si*Me*$_2$), 0.81-0.86 (m, 12H, CH*Me*$_2$ and SiC*Me*$_2$), 1.26 and 1.48 (2s, 6H, Ipn), 1.56 (m, 1H, C*H*Me$_2$), 3.57 (dd, $J_{1,2}$ = 7.6 Hz, $J_{2,3}$ = 6.7 Hz, 1H, H-2), 3.73-4.14 (m, 5H, H-3, H-4, H-5, H-6, H-6'), 4.21 (d, $J_{1,2}$ = 7.6 Hz, 1H, H-1), 4.56 and 4.65 (2d, J = 12.0 Hz, 2H, PhC*H*$_2$), 4.58 and 4.87 (2d, J = 11.7 Hz, 2H, PhC*H*$_2$), 7.2-7.4 (m, 10H, arom.).

Anal. Calcd for $C_{31}H_{46}O_6Si$: C, 68.65; H, 8.48. Found: C, 68.72; H, 8.34.

Benzyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-thexyldimethylsilyl-α-D-galactopyranoside (6dα), Thexyldimethylsilyl 2,3-di-*O*-Benzyl-4,6-*O*-benzylidene-α-D-galactopyranoside (7dα) and Benzyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-thexyldimethylsilyl-β-D-galactopyranoside (6dβ). From **5d** (650 mg, 1.58 mmol); eluted with 10:1 petroleum ether/ethyl acetate. Eluted first **6dα**; yield: 150 mg, 16%; $[\alpha]_D$ +90.5 ° (*c* 1, chloroform), TLC (8:1 petroleum ether/ethyl acetate): R_f 0.46, ^1H NMR (250 MHz, $CDCl_3$): δ 0.14 and 0.15 (2s, 6H, Si*Me*$_2$), 0.85-0.89 (m, 12H, CH*Me*$_2$ and SiC*Me*$_2$), 1.66 (m, J = 6.8 Hz, C*H*Me$_2$), 3.58 (bs, 1H, H-5), 3.81 (dd, $J_{3,4}$ = 3.6 Hz, $J_{2,3}$ = 9.8 Hz, 1H, H-3), 3.95 (dd, $J_{5,6'}$ = 1.5 Hz, J_{gem} = 12.5 Hz, 1H, H-6'), 4.05 (br.d, $J_{3,4}$ = 3.6 Hz, 1H, H-4), 4.13 (dd, $J_{5,6}$ = 1.3 Hz, J_{gem} = 12.5 Hz, 1H, H-6), 4.20 (dd, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 9.8 Hz, 1H, H-2), 4.58 and 4.63 (2d, J = 12.5 Hz, 2H, PhC*H*$_2$), 4.47 and 4.71 (2d, J = 12.0 Hz, 2 H, PhC*H*$_2$), 4.89 (d, $J_{1,2}$ = 3.6 Hz, 1H, H-1), 5.48 (s, 1H, PhC*H*), 7.2-7.6 (m, 15H, arom.).

Anal. Calcd for $C_{35}H_{46}O_6Si \cdot 1/2\ H_2O$: C, 70.08; H, 7.90. Found: C, 70.18; H, 7.76.

Eluted second **7dα**; yield: 187 mg, 20%; $[\alpha]_D$ +42.0 ° (*c* 1, chloroform), TLC (8:1 petroleum ether/ethyl acetate): R_f 0.41, ^1H NMR (250 MHz, $CDCl_3$): δ 0.02 and

0.07 (2s, 6H, SiMe_2), 0.80-0.87 (m, 12H, CHMe_2 and SiCMe_2), 1.62 (m, J = 6.9 Hz, C*H*Me_2), 3.57 (bs, 1H, H-5), 3.83 (dd, $J_{3,4}$ = 3.5 Hz, $J_{2,3}$ = 9.8 Hz, 1H, H-3), 3.94 (dd, $J_{5,6'}$ = 1.7 Hz, J_{gem} = 11.3 Hz, 1H, H-6'), 4.09 (br.d, J = 3.2 Hz, 1H, H-4), 4.15 (dd, $J_{5,6}$ = 1.3 Hz, J_{gem} = 11.3 Hz, 1H, H-6), 4.23 (dd, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 9.8 Hz, 1H, H-2), 4.57 and 4.62 (2d, J = 12.0 Hz, 2H, PhCH_2), 4.62 and 4.72 (2d, J = 12.0 Hz, 2H, PhCH_2), 4.95 (d, $J_{1,2}$ = 3.6 Hz, 1H, H-1), 5.41 (s, 1 H, PhC*H*), 7.2-7.6 (m, 15H, arom.).

Anal. Calcd for $C_{35}H_{46}O_6Si$: C, 71.15; H, 7.84. Found: C, 71.10; H, 7.92.

Eluted third **6d**β; yield: 420 mg, 45%; $[\alpha]_D$ +5.1 ° (*c* 1, chloroform), TLC (8:1 petroleum ether/ethyl acetate): R_f 0.31, ^{1}H NMR (250 MHz, $CDCl_3$): 0.05 and 0.08 (2s, 6H, $SiMe_2$), 0.78 and 0.79 (2s, 6H, $SiCMe_2$), 0.82 (d, J = 6.8 Hz, 6H, CHMe_2), 1.60 (m, J = 6.9 Hz, C*H*Me_2), 3.26 (bs, 1H, H-5), 3.36 (dd, $J_{3,4}$ = 3.7 Hz, $J_{2,3}$ = 9.2 Hz, 1H, H-3), 3.92 (dd, $J_{1,2}$ = 7.6 Hz, $J_{2,3}$ = 9.2 Hz, 1H, H-2), 3.95-4.00 (m, 2H, H-4, H-6'), 4.29 (d, $J_{1,2}$ = 7.6 Hz, 1H, H-1), 4.30 (dd, $J_{5,6}$ = 1.3 Hz, J_{gem} = 11.5 Hz, 1H, H-6), 4.60 and 4.68 (2d, J = 12.2 Hz, 2H, PhCH_2), 4.55 and 4.92 (2d, J = 11.6 Hz, 2H, PhCH_2), 5.38 (s, 1H, PhC*H*), 7.2-7.6 (m, 15H, arom.).

Anal. Calcd for $C_{35}H_{46}O_6Si$: C, 71.15; H, 7.84. Found: C, 71.22; H, 7.79.

Hydrolysis of Silyl Ethers 6a-d to Alcohols 8a-d: General Procedure. To a solution of silyl ether **6** (1 mmol) in dry tetrahydrofuran (15 mL) was added tetrabutylammonium fluoride (1.1 M solution in dry tetrahydrofuran, 1 mL) at 0 °C. After 1 h, the mixture was allowed to reach room temperature and stirred until TLC indicated total consumption of the starting material (4-12 h). The solution was then diluted with diethyl ether (50 mL) and washed with satd. ammonium chloride solution (20 mL). The organic layer was dried (magnesium sulfate) and concentrated *in vacuo*, and the residue purified by flash chromatography. For the case **a**, **b**, and **d**, the starting material used was the mixture of anomers obtained from the benzylation reaction. Starting material, eluent used for the flash chromatography, yield, and physical data are as follows:

Benzyl 3,4,6-Tri-*O*-benzyl-β-D-glucopyranoside (8aβ) and Benzyl 3,4,6-Tri-*O*-benzyl-α-D-glucopyranoside (8aα). From **6a**β; eluted with 4:1 petroleum ether/ethyl acetate; eluted first **8a**β (281 mg, 52%); $[\alpha]_D$ -18.9 ° (*c* 1, chloroform), TLC (3:1 petroleum ether/ethyl acetate): R_f 0.43, ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.33 (bs, 1H, OH), 3.49-3.79 (m, 6H, H-2, H-3, H-4, H-5, H-6, H-6'), 4.36 (d, $J_{1,2}$ = 7.2 Hz, 1H, H-1), 4.51-4.98 (m, 8H, 4 PhCH_2), 7.1-7.4 (m, 20H, Ph).

Anal. Calcd for $C_{34}H_{36}O_6$: C, 75.53; H, 6.71. Found: C, 75.41; H, 6.73.

Eluted second **8a**α (249 mg, 46%); $[\alpha]_D$ +97.5 ° (*c* 1, chloroform), TLC (3:1 petroleum ether/ethyl acetate): R_f 0.27, ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.09 (d, $J_{2,OH}$ =

8.9 Hz, OH), 3.59-3.85 (m, 6H, H-2, H-3, H-4, H-5, H-6, H-6'), 4.45-4.92 (m, 8H, 4 PhCH_2), 5.03 (d, $J_{1,2}$ = 3.3 Hz, 1 H, H-1), 7.1-7.4 (m, 20H, Ph).

Anal. Calcd for $C_{34}H_{36}O_6$: C, 75.53; H, 6.71. Found: C, 75.40; H, 6.76.

Benzyl 3,4,6-Tri-*O*-benzyl-β-D-galactopyranoside (8bβ) and Benzyl 3,4,6-Tri-*O*-benzyl-α-D-galactopyranoside (8bα). From **6bα/β**; eluted with 5:1 petroleum ether/ethyl acetate; eluted first **8bβ** (243 mg, 45%); $[\alpha]_D$ -33.1 ° (*c* 1, chloroform), TLC (3:1 petroleum ether-ethyl acetate): R_f 0.50, ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.35 (d, $J_{2,OH}$ = 2.0 Hz, 1H, OH), 3.42 (dd, $J_{3,4}$ = 2.8 Hz, $J_{2,3}$ = 9.7 Hz, 1H, H-3), 3.46-3.66 (m, 3 H, H-5, H-6, H-6'), 3.92 (br.d, J = 2.6 Hz, 1H, H-4), 4.02 (ddd, $J_{2,OH}$ = 2.0 Hz, $J_{1,2}$ = 7.7 Hz, $J_{2,3}$ = 9.7 Hz, 1H, H-2), 4.33 (d, $J_{1,2}$ = 7.7 Hz, H-1), 4.41-4.95 (m, 8H, 4 PhCH_2), 7.2-7.4 (m, 20H, Ph).

Eluted second **8bα** (270 mg, 50%); $[\alpha]_D$ +66.6 ° (*c* 1, chloroform), TLC (3:1 petroleum ether/ethyl acetate): R_f 0.47, ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.13 (d, $J_{2,OH}$ = 8.0 Hz, 1H, OH), 3.50 (dd, $J_{5,6'}$ = 5.9 Hz, J_{gem} = 9.3 Hz, 1H, H-6'), 3.59 (dd, $J_{5,6}$ = 7.4 Hz, J_{gem} = 9.3 Hz, 1H, H-6), 3.73 (dd, $J_{3,4}$ = 2.7 Hz, $J_{2,3}$ = 10.0 Hz, 1H, H-3), 3.93-4.00 (m, 2H, H-4, H-5), 4.19 (ddd, $J_{1,2}$ = 4.0 Hz, $J_{2,OH}$ = 8.0 Hz, $J_{2,3}$ = 10.0 Hz, 1H, H-2), 4.39-4.92 (m, 8H, 4 PhCH_2), 5.05 (d, $J_{1,2}$ = 4.0 Hz, H-1), 7.2-7.4 (m, 20H, Ph).

Anal. Calcd for $C_{34}H_{36}O_6$: C, 75.53; H, 6.71. Found: C, 75.39; H, 6.71.

Benzyl 6-*O*-Benzyl-3,4-*O*-isopropylidene-α-D-galactopyranoside (8cα) and Benzyl 6-*O*-Benzyl-3,4-*O*-isopropylidene-β-D-galactopyranoside (8cβ). From **6cα/β** (10.0 g, 18 mmol); eluted with 55:45 petroleum ether/ethyl acetate. Eluted first **8cα** (3.30 g, 42%); $[\alpha]_D$ +16.4 ° (*c* 1, chloroform), TLC (1:1 petroleum ether/ethyl acetate): R_f 0.53, ^{1}H NMR (250 MHz, $CDCl_3$): 1.39 and 1.48 (2s, 6H, Ipn), 2.29 (d, $J_{2,OH}$ = 7.5 Hz, 1H, OH), 3.70 (dd, $J_{5,6'}$ = 6.9 Hz, J_{gem} = 10.2 Hz, 1H, H-6'), 3.75 (dd, $J_{5,6}$ = 7.8 Hz, J_{gem} = 10.2 Hz, 1H, H-6), 3.83 (m, 1H, H-2), 4.19-4.28 (m, 3H, H-3, H-4, H-5), 4.54 and 4.64 (2d, J = 12.1 Hz, 2H, PhCH_2), 4.55 and 4.82 (2d, J = 11.6 Hz, 2H, PhCH_2), 4.97 (d, $J_{1,2}$ = 3.9 Hz, 1H, H-1), 7.2-7.4 (m, 10H, arom.).

Anal. Calcd for $C_{23}H_{28}O_6$: C, 69.03; H, 6.99. Found: C, 69.00; H, 7.01.

Eluted second **8cβ** (3.32 g, 42%); $[\alpha]_D$ -27.2 ° (*c* 1, chloroform), TLC (1:1 petroleum ether/ethyl acetate): R_f 0.40, ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.33 and 1.50 (2s, 6H, Ipn), 2.40 (d, $J_{2,OH}$ = 2.3 Hz, 1H, OH), 3.60 (ddd, $J_{2,OH}$ = 2.3 Hz, $J_{2,3}$ = 7.3 Hz, $J_{1,2}$ = 8.3 Hz, 1H, H-2), 3.82 (m, 2H, H-3, H-6, H-6'), 3.95 (m, 1H, H-5), 4.03 (dd, $J_{3,4}$ = 5.5 Hz, $J_{2,3}$ = 7.3 Hz, 1H, H-3), 4.14 (dd, $J_{4,5}$ = 2.1 Hz, $J_{3,4}$ = 5.5 Hz, 1H, H-4), 4.24 (d, $J_{1,2}$ = 8.3 Hz, 1H, H-1), 4.57 and 4.66 (2d, J = 12.0 Hz, 2H, PhCH_2), 4.59 and 4.93 (2d, J = 11.6 Hz, 2H, PhCH_2), 7.2-7.4 (m, 10H, arom.).

Anal. Calcd for $C_{23}H_{28}O_6$: C, 69.03; H, 6.99. Found: C, 68.85; H, 6.99.

Benzyl 3-*O*-Benzyl-4,6-*O*-benzylidene-α-D-galactopyranoside (8dα). From **6dα**; eluted with 3:2 petroleum ether/ethyl acetate; yield 439 mg, 98%; $[\alpha]_D$ +108.8 ° (*c* 1, chloroform), TLC (3:2 petroleum ether/ethyl acetate): R_f 0.27, ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.43 (d, $J_{2,OH}$ = 7.4 Hz, 1H, OH), 3.68 (bs, 1H, H-5), 3.84 (dd, $J_{3,4}$ = 3.6 Hz, $J_{2,3}$ = 9.9 Hz, 1H, H-3), 4.02 (dd, $J_{5,6'}$ = 1.8 Hz, J_{gem} = 12.6 Hz, 1H, H-6'), 4.16-4.25 (m, 2H, H-2, H-6), 4.29 (dd, $J_{4,5}$ = 0.8 Hz, $J_{3,4}$ = 3.6 Hz, 1H, H-4), 4.54 and 4.68 (2d, J = 11.8 Hz, 2H, PhC*H*$_2$), 4.56 and 4.68 (2d, J = 12.3 Hz, 2H, PhC*H*$_2$), 5.05 (d, $J_{1,2}$ = 3.5 Hz, 1H, H-1), 5.55 (s, 1H, PhC*H*), 7.2-7.6 (m, 15H, arom.).

Anal. Calcd for $C_{27}H_{28}O_6 \cdot 1/2\ H_2O$: C, 70.88; H, 6.39. Found: C, 71.00; H, 6.27.

Benzyl 3-*O*-Benzyl-4,6-*O*-benzylidene-β-D-galactopyranoside (8dβ). From **6dβ**; eluted with 3:2 petroleum ether/ethyl acetate; yield 426 mg, 95%; $[\alpha]_D$ -2.8 ° (*c* 1, chloroform), TLC (3:2 petroleum ether/ethyl acetate): R_f 0.28, ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.45 (bs, 1H, OH), 3.36 (bs, 1H, H-5), 3.48 (dd, $J_{3,4}$ = 3.6 Hz, $J_{2,3}$ = 9.6 Hz, 1H, H-3), 4.01-4.14 (m, 3H, H-4, H-2, H-6'), 4.35 (dd, $J_{5,6}$ = 1.4 Hz, J_{gem} = 13.6 Hz, 1H, H-6), 4.39 (d, $J_{1,2}$ = 7.7 Hz, 1H, H-1), 4.75 (s, 2H, PhC*H*$_2$), 4.65 and 4.98 (2d, J = 11.9 Hz, 2H, PhC*H*$_2$), 5.47 (s, 1H, PhC*H*), 7.2-7.6 (m, 15H, arom.).

Anal. Calcd for $C_{27}H_{28}O_6 \cdot H_2O$: C, 69.51; H, 6.48. Found: C, 69.71; H, 6.39.

1,2,3-Tri-*O*-acetyl-4,6-*O*-benzylidene-α- and -β-D-mannopyranose (10α and 10β). Compound **9**[9] (1 g, 3.74 mmol) was solved in an 1:1 mixture of pyridine and acetic anhydride (10 mL) and stirred for 12 h at room temperature. The solvents were evaporated *in vacuo* and coevaporated three times with toluene. The residue was purified by flash chromatography (4:1 toluene/ethyl acetate). Eluted first **10α** (0.13 g, 9%); $[\alpha]_D$ +32.4 (*c* 1, chloroform), TLC (2:1 petroleum ether/ethyl acetate): R_f 0.47, ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.04 and 2.18 (2s, 9H, 3 OAc), 3.81 (t, J = 10.2 Hz, 1H, H-6ax), 3.98 (dt, J = 3.8 Hz, J = 10.0 Hz, 1H, H-5), 4.08 (dd, J = 10.0 Hz, 1H, H-4), 4.29 (dd, J = 4.5 Hz, J = 10.5 Hz, 1H, H-6*eq*), 5.33 (dd, $J_{1,2}$ = 1.7 Hz, $J_{2,3}$ = 3.6 Hz, 1H, H-2), 5.41 (dd, $J_{2,3}$ = 3.6 Hz, $J_{3,4}$ = 10.0 Hz, 1H, H-3), 5.57 (s, 1H, PhC*H*), 6.00 (d, $J_{1,2}$ = 1.7 Hz, 1H, H-1), 7.30-7.50 (m, 5H, arom.).

Eluted second **10β** (1.3 g, 88%); $[\alpha]_D$ -31.8 (*c* 1, chloroform), TLC (2:1 petroleum ether/ethyl acetate): R_f 0.39, ^{1}H NMR (250 MHz, $CDCl_3$): 2.01, 2.08 and 2.20 (3s, 9H, 3 OAc), 3.63 (dt, J = 4.8 Hz, J = 10.0 Hz, 1 H, H-5), 3.86 (t, J = 10.1 Hz, 1H, H-6ax), 4.04 (t, J = 10.0 Hz, 1H, H-4), 4.36 (dd, J = 4.8 Hz, J = 10.2 Hz, 1H, H-6*eq*), 5.20 (dd, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 10.2 Hz, 1H, H-3), 5.53-5.57 (m, 2H, H-2 and PhC*H*), 5.91 (d, $J_{1,2}$ = 1.3 Hz, 1H, H-1), 7.24-7.45 (m, 5H, arom.).

Anal. Calcd for $C_{19}H_{22}O_9$: C, 57.86; H, 5.62. Found: C, 57.90; H, 5.66

2,3-Di-*O*-acetyl-4,6-*O*-benzylidene-α/β-D-mannopyranose (11). To a solution of **10**α/β (α:β = 1:10, 1.47 g, 3.74 mmol) in dry dimethylformamide (10 mL) was added hydrazinium acetate (0.41 g, 4.48 mmol) and the mixture was stirred for 1 h at 50 °C. The mixture was cooled to room temperature, diluted with water (100 mL) and extracted with ethyl acetate (3 x 100 mL). The organic layer was dried (sodium sulfate), concentrated *in vacuo*, and the resulting residue was purified by flash chromatography (3:1 toluene/ethyl acetate) to yield **11** (935 mg, 71%): $[\alpha]_D$ -21.5 (*c* 1, chloroform), TLC (1:1 petroleum ether/ethyl acetate): R_f 0.51, ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.13 and 2.21 (2s, 6H, 2 OAc), 3.39 (d, $J_{1,OH}$ = 3 Hz, 1H, OH-1), 3.50-4.50 (m, 4 H, H-4, H-5, H-6*eq*, H-6*ax*), 5.13 (bs, 1H, H-1), 5.35 (dd, J = 1.6 Hz, $J_{2,3}$ = 3.4 Hz, 1H, H-2), 5.45 (dd, $J_{2,3}$ = 3.4 Hz, $J_{3,4}$ = 10.1 Hz, 1H, H-3), 5.54 and 5.56 (2s, 1H, PhC*H*α and β), 7.30-7.52 (m, 5H, arom.).

Anal. Calcd for $C_{17}H_{20}O_8$: C, 57.95; H, 6.12. Found: C, 57.98; H, 5.82.

Thexyldimethylsilyl 2,3-di-*O*-Acetyl-4,6-*O*-benzylidene-β-D-mannopyranose (12β). To a stirred solution of **11** (840 mg, 2.39 mmol) and imidazole (243 mg, 3.6 mmol) in dry dimethylformamide (10 mL) was added dimethylthexylsilyl chloride (0.56 mL, 2.87 mmol) at 0 °C and the mixture was stirred for 12 h. The mixture was then poured on ice-water (100 mL) and extracted with ethyl acetate (3 x 50 mL). The organic layer was dried (sodium sulfate), concentrated *in vacuo*, and the resulting residue was purified by flash chromatography (10:1 toluene/ethyl acetate) to yield **12**β (1.16 g, 98%); $[\alpha]_D$ -41.2 (*c* 1, chloroform), TLC (3:1 petroleum ether/ethyl acetate): R_f 0.70, ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.12 and 0.15 (2s, 6H, $SiMe_2$), 0.80-0.85 (m, 12H, $CHMe_2$ and $SiCMe_2$), 1.58 (m, 1H, $CHMe_2$), 1.98 and 2.17 (2s, 6H, 2 OAc), 3.49 (dt, J = 4.8 Hz, J = 10.4 Hz, 1H, H-5), 3.89 (t, J = 10.4 Hz, 1H, H-6*ax*), 4.02 (t, J = 10.4 Hz, 1H, H-4), 4.28 (dd, J = 4.9 Hz, J = 10.5 Hz, 1H, H-6*eq*), 4.97 (d, $J_{1,2}$ = 1.2 Hz, 1H, H-1), 5.15 (dd, $J_{2,3}$ = 3.4 Hz, $J_{3,4}$ = 10.4 Hz, 1H, H-3), 5.43 (dd, $J_{1,2}$ = 1.2 Hz, $J_{2,3}$ = 3.4 Hz, 1H, H-2), 5.53 (s, 1H, PhC*H*), 7.25-7.50 (m, 5H, arom.).

Anal. Calcd for $C_{25}H_{38}O_8Si$: C, 60.65; H, 7.69. Found: C, 60.31; H, 7.73.

4,6-*O*-Benzylidene-3-*O*-thexyldimethylsilyl-α/β-D-mannopyranose (13). To a stirred solution of **9** (630 mg, 2.35 mmol) and imidazole (242 mg, 353 mmol) in dry dimethylformamide (10 mL) was added dimethylthexylsilyl chloride (0.48 mL, 2.47 mmol) at -15 °C under a nitrogen atmosphere. After 20 h, the mixture was diluted with water (50 mL) and extracted with ethyl acetate (3 x 30 mL). The organic layer was dried (sodium sulfate), concentrated *in vacuo*, and the residue was purified by flash chromatography (4:1 toluene/ethyl acetate) to yield **13** (693 mg, 72%); $[\alpha]_D$ -14.8 (*c* 1, chloroform), TLC (2:1 petroleum ether/ethyl acetate): R_f 0.55, ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.08 and 0.12 (2s, 6H, $SiMe_2$), 0.75-0.95 (m, 12H, $CHMe_2$ and $SiCMe_2$), 1.60

(m, 1H, C*H*Me$_2$), 2.86 (bs, 1H, OH-2), 3.20 (d, $J_{1,OH}$ = 1 Hz, 1H, OH-1), 3.28-4.36 (m, 6H, H-2, H-3, H-4, H-5, H-6, H-6'), 5.27 (bs, 1H, H-1), 5.50 and 5.52 (2s, 1H, PhC*H*α and β), 7.4-7.6 (m, 5H, arom.).

Anal. Calcd for $C_{21}H_{34}O_6Si$: C, 61.43; H, 8.35. Found: C, 61.43; H, 8.40.

1,2-Di-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-thexyldimethylsilyl-α-D-mannopyranose (14). ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.07 and 0.10 (2s, 6H, SiMe$_2$), 0.70-0.90 (m, 12H, CH*Me*$_2$ and SiCMe$_2$), 1.61 (m, 1H, C*H*Me$_2$), 2.12 and 2.13 (2s, 6H, 2 OAc), 3.74-3.95 (m, 3H, H-4, H-5, H-6*ax*), 4.19 (dd, $J_{2,3}$ = 3.8 Hz, $J_{3,4}$ = 10.1 Hz, 1H, H-3), 4.26 (dd, $J_{5,6}$ = 3.2 Hz, J_{gem} = 9.4 Hz, 1H, H-6*eq*), 5.15 (dd, $J_{1,2}$ = 1.7 Hz, $J_{2,3}$ = 3.8 Hz, 1H, H-2), 5.58 (s, 1H, PhC*H*), 5.88 (d, $J_{1,2}$ = 1.7 Hz, 1H, H-1), 7.30-7.55 (m, 5H, arom.).

Anal. Cald for $C_{25}H_{38}O_8Si$: C, 60.65; H, 7.90. Found: C, 60.44; H, 7.71.

4,6-*O*-Benzylidene-2-*O*-thexyldimethylsilyl-α,β-D-mannopyranose (15). To a solution of **12**β (283 mg, 0.58 mmol) in dry methanol (10 mL) was added sodium methoxide (0.1 M in dry methanol, 0.1 mL) and the mixture was stirred for 12 h at -15 °C. The mixture was then neutralized with ion-exchange resin Amberlite IR 120 (H^+), filtered and concentrated *in vacuo*. The resulting residue was purified by flash chromatography (5:1 toluene/acetone). Eluted first **15** (80 mg, 34%); $[\alpha]_D$ -25.8 (*c* 1, chloroform), TLC (2:1 petroleum ether/ethyl acetate): R_f 0.55, ^{1}H NMR (250 MHz, $CDCl_3$): 0.13 and 0.17 (2s, 6H, Si*Me*$_2$), 0.85-0.95 (m, 12H, CH*Me*$_2$ and SiC*Me*$_2$), 1.65 (m, 1H, C*H*Me$_2$), 2.10 (d, $J_{3,OH}$ = 8.3 Hz, 1H, OH-3), 2.77 (d, $J_{1,OH}$ = 1.8 Hz, 1H, OH-1), 3.30-3.83 (m, 3H, H-3, H-6*ax*), 3.94-4.33 (m, 3H, H-2, H-5, H-6*eq*), 5.09 (d, J = 2.7 Hz, 1H, H-1), 5.52 and 5.54 (2s, 1H, PhC*H*α and β), 7.4-7.6 (m, 5H, arom.).

Anal. Calcd for $C_{21}H_{34}O_6Si$: C, 61.43; H, 8.35. Found: C, 61.35; H, 8.34.

Eluted second **13** (125 mg, 53%), identical with the product described above.

1,3-Di-*O*-acetyl-4,6-*O*-benzylidene-2-*O*-thexyldimethylsilyl-α-D-mannopyranose (16). $[\alpha]_D$ -9.4 (*c* 1, chloroform), ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.09 and 0.12 (2s, 6H, Si*Me*$_2$), 0.80-1.00 (m, 12H, CH*Me*$_2$ and SiC*Me*$_2$), 1.65 (m, 1H, C*H*Me$_2$), 2.07 and 2.17 (2s, 6H, 2 OAc), 3.75 (dd, $J_{5,6}$ = 3.2 Hz, J_{gem} = 10.2 Hz, 1H, H-6*ax*), 3.94 (m, 1H, H-5), 4.07-4.15 (m, 2H, H-2, H-4), 4.26 (dd, $J_{5,6}$ = 4.6 Hz, J_{gem} = 10.2 Hz, 1H, H-6*eq*), 5.24 (dd, $J_{2,3}$ = 3.1 Hz, $J_{3,4}$ = 10.1 Hz, 1H, H-3), 5.54 (s, 1H, PhC*H*), 5.89 (d, $J_{1,2}$ = 1.8 Hz, 1H, H-1), 7.3-7.5 (m, 5H, arom.).

Anal. Calcd for $C_{25}H_{38}O_8Si$: C, 60.65; H 7.90. Found: C, 60.96; H, 7.85.

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