Selective Silylation of β-D-Galactosides. A New Approach to the Synthesis of (1→6)-β-D-Galactopyranooligosaccharides†

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A simple and convenient synthesis of β-D-galactopyranose derivatives selectively modified at C-1 and C-6 is described. A key feature is the selective protection of the 6-OH group of methyl-, allyl-, and (*p*-nitrophenyl)-β-D-galactopyranosides using *tert*-butyldiphenylsilyl chloride, yielding silyl ethers **4–6**. After protection of the remaining hydroxyl groups with acetyl, benzoyl, or *p*-phenylbenzoyl functions, the glycosidic methyl group can be easily split by 1,1-dichloromethyl methyl ether (DCMME) to give galactosyl chlorides **17–19**, retaining the temporary protection at C-6. When benzoates or *p*-phenylbenzoates are used as permanent protection, the *tert*-butyldiphenylsilyl group (such as in compounds **8–11**) can be selectively removed to give 6-OH galactosides **13–16**. Some of these were coupled with tetraacetyl- or tetrabenzoylgalactosyl bromide to yield disaccharides **20–23**. Compounds **21** and **22** could be reacted with DCMME to give digalactosyl chlorides **24** and **25**. These are useful glycosyl donors for further chain expansion. The coupling of chloride **18** or **19** with nucleophile **14** or **15** under silver triflate/*sym*-collidine mediated conditions afforded disaccharides **26** and **27** bearing silyl protecting groups at C-6. The latter can be selectively removed, resulting in nucleophiles **28** and **29**, which can be coupled with tetraacetylgalactosyl bromide (to give trisaccharide **30**) or with chloride **18** to yield trisaccharide **31**. The latter one has again a *tert*-butyldiphenylsilyl function at C″-6, allowing further expansion of the chain from the nonreducing end. The structures of mono-, di-, and trisaccharides were confirmed by ^1H and ^{13}C NMR spectra.

Introduction

The increasing awareness of the biological significance of oligosaccharide-containing natural products has stimulated remarkable progress in carbohydrate synthesis in the past decade. However, present methodology in this field still leaves room for improvement. The problem of regioselective modification of sugar derivatives is particularly challenging, often due to the unique stereochemistry of each sugar. Monoclonal IgA's, having β-(1→6)-D-galactopyranan specificity, are of continuing interest in our laboratory.[1] We have, therefore, concentrated our efforts on the synthesis of intermediate units suitable for the construction of β-(1→6)-D-galactooligosaccharides. The axial 4-OH group in the galactopyranosyl intermediates has been problematic for selective protection/deprotection and coupling procedures involving the (nearby) 6-OH, frequently resulting in migrations and rearrangements between these two positions.[2] Usual strategies for the selective modification of O-6 in D-galactopyranose involve (1) temporary protection of the primary 6-OH as a trityl ether, (2) selective de-O-tritylation after blocking of the remaining hydroxyl groups, and finally (3) protection of the 6-OH by a suitably removable group such as chloroacetyl,[3] bromoacetyl,[4] or benzyl, which are stable under subsequent coupling conditions.

Herein we describe a simple synthesis (Scheme I) of β-D-galactopyranose derivatives selectively modified at C-1 and C-6 and their application to the construction of β-(1→6)-D-galactooligosaccharides.

Results and Discussion

The wide use of silyl ethers as selective protecting groups for hydroxyl functions[5] prompted us to examine some of these in the selective modification of the primary hydroxyl group in D-galactopyranose derivatives. As the most promising for our purpose we have chosen the widely used *tert*-butyldimethylsilyl[6] (TBDMS) and *tert*-butyldiphenylsilyl[7] (TBDPS) functions. Both silyl chlorides (TBDMS-Cl and TBDPS-Cl) were capable of the selective silylation of methyl β-D-galactopyranoside to give the 6-*O*-silyl derivatives in satisfactory yields (74% and 76%, respectively) provided reactions were performed in DMF with silver nitrate as a catalyst.[8] Of the two, the *tert*-butyldiphenylsilyl derivative was more suitable for our synthesis, due to its greater stability.

Thus, we prepared several 6-*O*-(*tert*-butyldiphenylsilyl)-β-D-galactosides (**4–6**) and protected the remaining hydroxyl groups with acetyl, benzoyl, or *p*-phenylbenzoyl ester functions (**7–11**). Methyl glycosides **7–9** are pivotal, as they could be easily converted to the corresponding chlorides with 1,1-dichloromethyl methyl ether (DCMME) in chloroform and zinc chloride as catalyst[9] under conditions retaining the *tert*-butyldiphenylsilyl ether. The bifunctional intermediates **17–19** thus obtained are extremely versatile in that they contain a reactive center (the chloride), allowing the compound to be a glycosyl donor, in addition to a group at O-6, whose eventual removal makes that hydroxyl available for subsequent nucleophilic coupling (chain extension).

For the selective deprotection of the 6-hydroxyl group, we examined several different reagents and procedures. The widely used tetra-*n*-butylammonium fluoride[7,10] when reacted with derivatives **7–11** gave complicated mixtures attributable to extensive acyl migration.[7,11,12] In our hands, some other reagents also were unsuitable, including tris-

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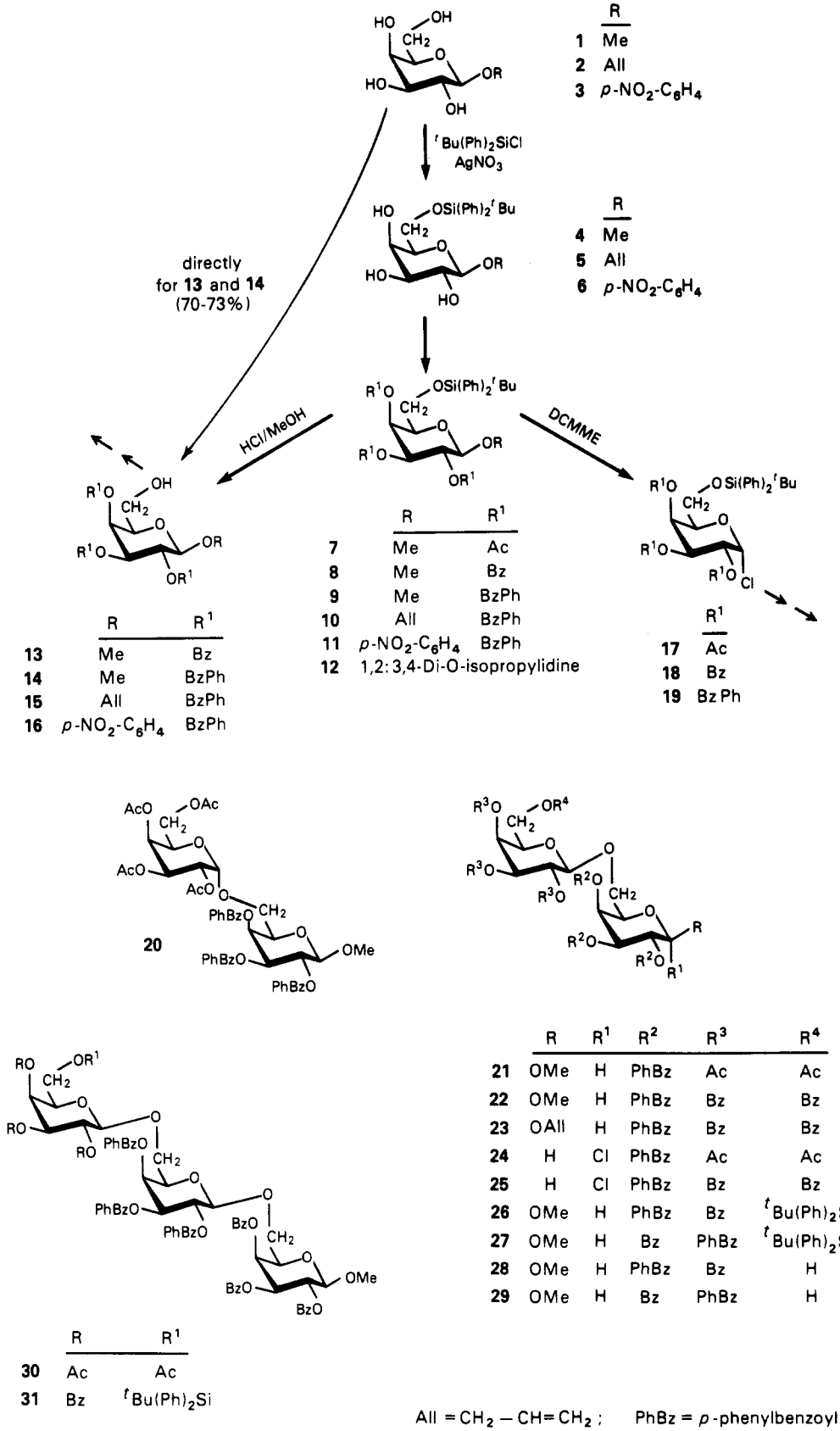
Scheme I



All = $CH_2-CH=CH_2$; PhBz = *p*-phenylbenzoyl;

(dialkylamino)sulfonium difluorotrimethylsiliconate $[(C_2H_5)_2N]_3S^+(CH_3)_3SiF_2^-$,[13] *N*-bromosuccinimide in CCl_4 or DMSO,[14] trimethylsilyl iodide, aluminum chloride in CH_3NO_2, or 10% palladium on charcoal (Aldrich). The only method that we found to be effective for selective de-O-*tert*-butyldiphenylsilylation of galactopyranose de-

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Table I. ^{1}H NMR Chemical Shifts (δ, in $CDCl_3$)[a]

compd	H-1	H-2	H-3	H-4	H-5	H-6,6a	t-BuSi or (OH)	CH_3O or (AllO)	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$
4[c]	4.07 d	3.61 dd	3.50 dd	3.92 bd	3.46 m	3.86 m	1.03 s	3.44 s	7.6	9.8	3.2	b
5[c]	4.21 d	3.66 dd	3.51 dd	3.90 db	3.46 bt	3.85 bd	1.04 s	(4.06, 4.28, 5.10, 5.23, 5.89)	7.6	9.8	3.1	b
6[c]	4.96 d	3.97 m	3.68 dd	4.13 bd	3.72 bt	3.97 m	1.07 s		7.5	9.7	3.4	b
7	4.38 d	5.18 dd	5.10 dd	5.58 bd	3.77 m	3.77 m	1.05 s	3.48 s	7.8	10.5	3.5	b
8	4.67 d	5.71 dd	5.62 dd	6.04 bd	4.07 m	3.85 m	1.00 s	3.53 s	7.9	10.2	3.2	b
9	4.75 d	5.83 dd	5.70 dd	6.13 bd	4.15 bt	3.58 bd	1.03 s	3.58 s	7.7	10.5	3.2	b
10	4.86 d	5.83 dd	5.69 dd	6.10 bd	4.11 bt	3.90 bd	1.03 s	(4.17, 4.40, 5.15, 5.26, 5.80)	7.8	10.5	3.4	b
11	5.55 d	6.14 m	5.83 dd	6.14 m	4.36 bt	3.97 bd	1.07 s		7.8	10.2	3.4	b
12	5.51 d	4.29 dd	4.61 dd	4.35 dd	3.87 m	3.87 m	1.07 s		4.9	2.2	8.1	1.2
13	4.76 d	5.85 dd	5.64 dd	5.88 bd	4.08 bt	3.86 m 3.70 m	(2.95 bt)	3.57 s	7.8	10.2	3.4	b
14	4.79 d	5.91 dd	5.66 dd	5.88 bd	4.08 bt	3.89 m 3.70 m	(2.70 bt)	3.62 s	7.7	10.6	3.4	b
15	4.93 d	5.97 dd	5.67 dd	5.90 bd	4.08 bt	3.89 m 3.74 m	(2.74 bt)	(4.25, 4.45, 5.19, 5.31, 5.87)	7.8	10.3	3.4	b
16	5.70 d	6.30 dd	6.15 dd	6.26 bd	4.58 bt	4.00 m 3.86 m	(3.24 bt)		7.8	10.3	3.2	b
17	6.32 d	5.20 dd	5.43 dd	5.63 bd	4.38 bt	3.67 m	1.03 s		3.9	10.8	3.2	b
18	6.59 d	5.74 dd	6.07 dd	6.17 bd	4.67 bt	3.81 bd	1.01 s		3.9	10.5	3.1	b
19	6.64 d	5.82 dd	6.14 dd	6.22 bd	4.72 bt	3.86 bd	1.04 s		3.7	10.8	2.5	b

[a] Multiplicities: s, singlet; d, doublet; t, triplet; m, multiplet; b, broadening. [b] $J < 1$ Hz. [c] $CDCl_3 + D_2O$.

rivatives **8–11** employs a solution of 3% hydrogen chloride[7] in methanol/ethyl ether (1:1, v/v), prepared freshly from acetyl chloride and methanol (see the Experimental Section). Under these conditions, cleavage of silyl groups occurred smoothly at room temperature, and 6-hydroxygalactopyranosides **13–16** were obtained in good yields (88–89%). This procedure is not suitable when acetyl groups are present but works well when benzoyl or *p*-phenylbenzoyl functions are employed as protecting groups elsewhere in the molecule. The latter migrates less readily than acetyl or benzoyl groups (Hammett constant for *p*-phenyl, $\sigma = -0.01$),[15] and these derivatives frequently gave crystalline and/or more easily separable (chromatography) mixtures than the other esters studied.

The combination of *tert*-butyldiphenylsilyl and benzoyl or *p*-phenylbenzoyl protecting groups together with the use of hydrogen chloride for O-6 deprotection resulted in the development of an easy and efficient procedure for the preparation of nucleophiles **13** and **14** from methyl β-galactoside **1** in 70% and 73% yields, respectively (Scheme I) without separation of intermediate products (see the Experimental Section).

The coupling of either of these nucleophiles (**13** or **14**) with the chloride **18** or **19** using silver triflate/*sym*-collidine mediated conditions[16] yielded disaccharides **26** and **27**, bearing a temporary blocking group at C′-6. The removal of the *tert*-butyldiphenylsilyl group (see the Experimental Section) yielded the disaccharide nucleophiles **28** and **29**. These could in turn be coupled with different glycosyl donors such as 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl bromide or chloride **18** to give trisaccharides **30** and **31**, respectively. Trisaccharide **31** bears a *tert*-butyldiphenylsilyl group at C″-6, which allows for further expansion of the chain if desired.

The coupling of nucleophile **14** or **15** with 2,3,4,6-tetra-*O*-acetyl- or benzoyl-α-D-galactopyranosyl bromide in the presence of mercuric cyanide and mercuric bromide, or under silver triflate/*sym*-collidine mediated conditions, yielded disaccharides **20–23**. Oxidation of the glycosidic allyl function of **23** can yield the corresponding epoxypropyl glycoside.[2,17] Cleavage of the glycosidic methyl group with DCMME gave either the disaccaride chloride **24** or **25** in good yields (74–82%). In the last case we found that strictly anhydrous conditions (argon) and the use of the optimal ratio of reagents diminished the formation of side products resulting from cleavage of intersaccharide linkages to less than 5%.

In conclusion: the combination of 6-*O*-*tert*-butyldiphenylsilyl and glycosidic methyl groups as temporary protecting groups and *p*-phenylbenzoyl or benzoyl as persistent blocking groups proved to be amenable for expansion of the chain from both reducing and nonreducing ends. Therefore, derivatives **8–11** serve as easily accessible and convenient intermediates for the synthesis of β-(1→6)-D-galactooligosaccharides. In addition, disaccharide nucleophiles (such as **28** and **29**) and glycosyl donors (such as **24** and **25**) can serve as useful units for the synthesis of higher β-D-galactooligosaccharides in either stepwise or blockwise approaches.

Proton spectra of all the new compounds presented in this paper were interpreted by first-order analysis, or when necessary, by homonuclear selective decoupling. Carbon signals were assigned by comparison with signals of similar compounds[2,17] or when possible by two-dimensional ^{1}H–^{13}C shift-correlation spectra.

Experimental Section

Melting points are uncorrected. NMR spectra (^{1}H and ^{13}C) were recorded with Varian FX 300 or JEOL FX 100 spectrometers of $CDCl_3$ solutions, with Me_4Si as the internal standard. Optical rotations were measured with a Perkin-Elmer 241 MC automatic polarimeter. TLC was carried out on silica gel GHLF (Analtech), and flash chromatography was performed with columns of silica gel 60 (Merck, 230–400 or >400 mesh) with the following eluting solvents: A, *n*-hexane/ethyl acetate; B, *n*-hexane/acetone; C, carbon tetrachloride/acetone; D, toluene/acetone.

All reactions were performed under argon in dry solvents. Nonaqueous solutions obtained during workup procedures were dried over magnesium sulfate and concentrated under reduced pressure at ≤40 °C.

Methyl 6-*O*-(*tert*-Butyldiphenylsilyl)-β-D-galactopyranoside (4). Galactoside **1** (5.83 g, 30 mmol)[18] was dissolved in *N*,*N*-dimethylformamide (65 mL). *tert*-Butyldiphenylsilyl chloride (5.8 mL, 23 mmol; Fluka) followed by silver nitrate (7.1

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(18) Sigma, crystallized from anhydrous MeOH.

Table II. ^{13}C NMR Chemical Shifts (δ, in $CDCl_3$)

carbon, atom	compound															
	4	5	6	7[a]	8	9[a]	10	11	12	13	14[a]	15	16	17[a]	18	19
C-1	104.1	102.0	100.3	102.1	102.4	102.4	100.3	99.3	96.4	102.5	102.5	100.5	98.9	91.5	91.9	92.0
C-2	71.2	71.3	71.7	69.2	70.1	70.0	70.1	69.6	70.7[b]	70.0	70.0	70.0	69.5	67.4	68.3	68.3
C-3	73.6	73.8	73.6	71.3	72.0	72.0	72.2	71.8	71.0	72.0	72.0	72.0	72.1	68.2	69.2	69.2
C-4	68.8	68.9	68.9	67.0	68.0	67.9	68.1	67.9	70.8[b]	69.0	69.0	69.1	68.5	67.0	68.0	68.1
C-5	74.9	75.0	75.2	73.2	74.0	73.8	74.0	75.1	68.4	74.1	74.0	74.1	74.7	71.6	72.2	72.3
C-6	63.0	63.0	63.5	61.1	61.5	61.4	61.6	62.0	62.7	60.6	60.6	60.7	60.3	60.6	60.9	60.9
CSi	19.2	19.2	19.3	19.0	19.0	19.0	19.1	19.1	19.3					19.0	19.0	19.0
CH_3O or (CH_2=$CHCH_2O$)	56.9	(70.0)		56.9	57.0	57.1	(70.0)			57.2	57.3	(70.4)				

[a] Recorded with JEOL FX 100 at 25 MHz. [b] Based on comparison with other compounds.

g, 22 mmol) was added, and the mixture was stirred at room temperature for 1 day. More *tert*-butyldiphenylsilyl chloride (5.8 mL) and silver nitrate (7.1 g) were added, and stirring was continued for another day [TLC, solvents A (2:7) and C (9:1)]. The mixture was filtered, and the precipitate was washed with chloroform. Combined filtrates were concentrated, diluted with chloroform, washed with water, dried, and concentrated. Product **4** (9.9 g, 76%) was isolated by column chromatography [solvent A (1:1–1:3)] as a white jellylike substance, which crystallized after a few weeks: mp 92–93 °C; $[\alpha]_D$ −19.05° (*c* 0.4, $CHCl_3$); NMR data (^1H and ^{13}C) given in Tables I and II. Anal. Calcd for $C_{23}H_{32}O_6Si$: C, 63.86; H, 7.46. Found: C, 63.90; H, 7.50.

Allyl 6-*O*-(*tert*-Butyldiphenylsilyl)-β-D-galactopyranoside (5). This was obtained from galactoside **2** (4.6 g, 10 mmol)[19] according to the procedure described above for the preparation of **4** [TLC, solvent C (3:2)]. Column chromatography [solvent C (2:1)] gave **5**: 3.4 g (74%); $[\alpha]_D$ −23.04° (*c* 1, $CHCl_3$); NMR data (^1H and ^{13}C) given in Tables I and II. Anal. Calcd for $C_{25}H_{34}O_6Si$: C, 65.47; H, 7.47. Found: C, 65.59; H, 7.49.

***p*-Nitrophenyl 6-*O*-(*tert*-Butyldiphenylsilyl)-β-D-galactopyranoside (6).** Treatment of **3** (3.0 g, 10 mmol) according to the procedure described for the preparation of **4** [TLC, solvent C (3:2)] followed by column chromatography [solvent C (2:1)] gave **6**: 4.05 g (75%), mp 215–216 °C; $[\alpha]_D$ −83.49° (*c* 0.7, THF); NMR data (^1H and ^{13}C) given in Tables I and II. Anal. Calcd for $C_{28}H_{33}NO_8Si$: C, 62.32; H, 6.16; N, 2.60. Found: C, 62.02; H, 6.44; N, 2.45.

6-*O*-(*tert*-Butyldiphenylsilyl)-1,2:3,4-di-*O*-isopropylidene-β-D-galactopyranose (12): obtained from 1,2:3,4-di-*O*-isopropylidene-β-D-galactopyranose (2.6 g, 10 mmol) according to the procedure described for the preparation of **4** [TLC, solvent B (6:1)]. Chromatography [solvent B (8:1)] gave **12**: 4.5 g (91%); $[\alpha]_D$ −48.92° (*c* 1.4, $CHCl_3$); NMR data (^1H and ^{13}C) given in Tables I and II. Anal. Calcd for $C_{28}H_{38}O_6Si$: C, 67.44; H, 7.68. Found: C, 67.55; H, 7.75.

Methyl 2,3,4-Tri-*O*-acetyl-6-*O*-(*tert*-butyldiphenylsilyl)-β-D-galactopyranoside (7). Silyl derivative **4** (3.4 g, 7.9 mmol) was dissolved in a mixture of pyridine (15 mL) and acetic anhydride (10 mL). A catalytic amount of 4-(dimethylamino)-pyridine was added, and after being stirred for 1 h [TLC, solvent A (3:2)] at room temperature, the mixture was coevaporated with toluene to dryness. Column chromatography [solvent A (3:1)] gave **7**: 4.16 g (94%); NMR data (^1H and ^{13}C) given in Tables I and II. Anal. Calcd for $C_{29}H_{38}O_9Si$: C, 62.34; H, 6.86. Found: C, 62.12; H, 6.90.

General Procedure for Benzoylation. Galactoside **4**, **5**, or **6** (5 mmol) was dissolved in dichloromethane[20] (15 mL) containing *sym*-collidine (2.6 mL, 20 mmol), and benzoyl chloride (2.1 mL, 18 mmol) or phenylbenzoyl chloride (3.9 g, 18 mmol) was added in portions. A catalytic amount of 4-(dimethylamino)pyridine was added, and the mixture was stirred overnight at room temperature. The reaction was quenched by addition of ice–water, and the organic layer was extracted with dichloromethane. The extract was washed with water and aqueous sodium bicarbonate, dried, and concentrated. The crystalline residue could be purified by recrystallization from ethanol or by chromatography. Thus compounds **8–11** were obtained (see below). NMR data (^1H and ^{13}C) for all obtained products (**8–11**) are given in Tables I and II.

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(*tert*-butyldiphenylsilyl)-β-D-galactopyranoside (8): 3.4 g (92%); mp 193–194 °C; $[\alpha]_D$ +114.55° (*c* 0.9, $CHCl_3$); TLC, solvent B (3:1); column chromatography, solvent B (5:1). Anal. Calcd. for $C_{44}H_{44}O_9Si$: C, 70.94; H, 5.95. Found: C, 71.18; H, 6.06.

Methyl 6-*O*-(*tert*-butyldiphenylsilyl)-2,3,4-tris-*O*-(*p*-phenylbenzoyl)-β-D-galactopyranoside (9): 4.5 g (93%); mp 117 °C; (with gassing); $[\alpha]_D$ +325.23° (*c* 1.2, $CHCl_3$); TLC, solvent B (3:1) or C (9:1) and C (15:1); column chromatography, solvent B (6:1) or C (30:1). Anal. Calcd for $C_{62}H_{56}O_9Si$: C, 76.52; H, 5.80. Found: C, 76.67; H, 6.12.

Allyl 6-*O*-(*tert*-butyldiphenylsilyl)-2,3,4-tris-*O*-(*p*-phenylbenzoyl)-β-D-galactopyranoside (10): 4.5 g (90%); mp 106–108 °C; $[\alpha]_D$ +333.65 (*c* 1.1, $CHCl_3$); TLC, solvent B (4:1); column chromatography, solvent B (5:1). Anal. Calcd for $C_{64}H_{58}O_9Si$: C, 76.93; H, 5.85. Found: C, 77.06; H, 5.95.

***p*-Nitrophenyl 6-*O*-(*tert*-butyldiphenylsilyl)-2,3,4-tris-*O*-(*p*-phenylbenzoyl)-β-D-galactopyranoside (11)**: 4.9 g (91%); mp 126 °C; (with gassing); $[\alpha]_D$ +291.40 (*c* 1.1, $CHCl_3$); TLC, solvent C (15:1); column chromatography, solvent C (30:1). Anal. Calcd for $C_{67}H_{57}NO_{11}Si$: C, 74.49; H, 5.32; N, 1.30. Found: C, 74.58; H, 5.53; N, 1.25.

General Procedure for the Selective De-O-silylation of Monosaccharides. Acetyl chloride (4 mL) was added dropwise to methanol (100 mL), and the hydrogen chloride solution obtained was cooled to 20 °C. A solution of the silyl derivative **8–11**, (3 mmol) in ethyl ether (100 mL) was added, and the mixture was stirred at room temperature overnight [TLC, solvent B (5:2)]. The reaction mixture was neutralized with Amberlite IR-45 (OH^-), concentrated, and purified by chromatography [solvent B (4:1)]. Thus, compounds **13–16** were obtained (see below). NMR data (^1H and ^{13}C) for the products are given in Tables I and II.

Methyl 2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (13): 1.37 g (88%); mp 157–158 °C (lit.[21] mp 152 °C).

Methyl 2,3,4-tris-*O*-(*p*-phenylbenzoyl)-β-D-galactopyranoside (14): 1.96 g (89%); mp 130–132 °C; $[\alpha]_D$ +471.78° (*c* 0.9, $CHCl_3$). Anal. Calcd for $C_{46}H_{38}O_9$: C, 75.19; H, 5.21. Found: C, 75.41; H, 5.41.

Allyl 2,3,4-tris-*O*-(*p*-phenylbenzoyl)-β-D-galactopyranoside (15): 2.0 g (88%); mp 113 °C (with gassing), $[\alpha]_D$ +445.75° (*c* 1.3, $CHCl_3$). Anal. Calcd for $C_{48}H_{40}O_9$: C, 75.77; H, 5.30. Found: C, 75.63; H, 5.34.

***p*-Nitrophenyl 2,3,4-tris-*O*-(*p*-phenylbenzoyl)-β-D-galactopyranoside (16)**: 2.3 g (89%); $[\alpha]_D$ +355.65° (*c* 1.6, $CHCl_3$). Anal. Calcd for $C_{51}H_{39}NO_{11}$: C, 72.76; H, 4.67; N 1.66. Found: C, 72.70; H, 4.75; N, 1.60.

Direct Preparation of 13 and 14 from Galactoside 1 without Isolation of Intermediates. Galactoside **1** (9.71 g, 0.05 M)[18] was silylated according to the procedure described for the preparation of **4**. Crude product was directly benzoylated or *p*-phenylbenzoylated as described. The resulting crystalline mass was de-O-silylated without further purification according to the general procedure described. The product was purified by chromatography [solvent B (4:1)] to give methyl 2,3,4-tri-*O*-

(19) Allyl β-D-galactopyranoside (**2**) was obtained from 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide by coupling with allyl alcohol in the presence of mercuric cyanide/mercuric bromide[2] followed by de-O-acetylation with sodium methanolate: Zemplén, G. *Ber. Dtsch. Chem. Ges.* **1927**, *60*, 1555.

(20) Yields are equally good if pyridine is used as a solvent instead of a dichloromethane/collidine mixture.

(21) Szabó, P.; Szabó, L. *J. Chem. Soc.* **1960**, 3762–3768.

benzoyl-β-D-galactopyranoside [13; 18.1 g (70%)] or methyl 2,3,4-tris-O-(p-phenylbenzoyl)-β-D-galactopyranoside [14; 26.8 g (73%)].

General Procedure for the Preparation of Chlorides. Methyl galactoside 7–9, 21, or 22 (1 mmol) was dissolved in chloroform (7 mL), and dichloromethyl methyl ether (2 mL) was added followed by freshly fused zinc chloride (catalytic amount) while stirring at room temperature. The mixture was heated on an oil bath (55 °C) until TLC showed only traces of the starting material (1–6 h). The reaction mixture was cooled, filtered through a small amount of Celite, diluted with dichloromethane, washed with diluted aqueous sodium bicarbonate, dried, concentrated, and purified by chromatography to give the following compounds.

2,3,4-Tri-O-acetyl-6-O-(*tert*-butyldiphenylsilyl)-α-D-galactopyranosyl chloride (17): 0.45 g (79%); $[\alpha]_D$ +94.36° (*c* 0.8, $CHCl_3$); TLC, solvent A (3:1); chromatography, solvent A (4:1); ^1H and ^{13}C NMR data given in Table I and II. Anal. Calcd for $C_{28}H_{35}ClO_8Si$: C, 59.72; H, 6.27. Found: C, 59.67; H, 6.30.

2,3,4-Tri-O-benzoyl-6-O-(*tert*-butyldiphenylsilyl)-α-D-galactopyranosyl chloride (18): 0.64 g (86%); mp 134–135 °C; $[\alpha]_D$ +131.77° (*c* 1.3, $CHCl_3$); TLC, solvent B (3:1); chromatography, solvent A (6:1); ^1H and ^{13}C NMR data given in Tables I and II. Anal. Calcd for $C_{43}H_{41}ClO_8Si$: C, 68.92; H, 5.52. Found: C, 69.01; H, 5.58.

2,3,4-Tris-O-(p-phenylbenzoyl)-6-O-(*tert*-butyldiphenylsilyl)-α-D-galactopyranosyl chloride (19): 0.85 g (87%); $[\alpha]_D$ +319.56° (*c* 1.1, $CHCl_3$); TLC, solvent B (3:1); chromatography, solvent A (6:1); ^1H and ^{13}C NMR spectra given in Tables I and II. Anal. Calcd for $C_{61}H_{53}ClO_8Si$: C, 74.94; H, 5.46. Found: C, 74.85; H, 5.54.

O-(2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl)-(1→6)-2,3,4-tris-O-(p-phenylbenzoyl)-α-D-galactopyranosyl chloride (24): 0.79 g (74%); $[\alpha]_D$ +334.06° (*c* 1.4, $CHCl_3$); TLC, solvent B (6:1); chromatography, solvent C (9:1); ^1H NMR δ 6.69 (d, 1 H, $J_{1,2}$ = 3.9 Hz, H-1), 6.03–6.08 (m, 2 H, H-3,4), 5.87 (dd, 1 H, $J_{1,2}$ = 3.9 Hz, $J_{2,3}$ = 10.1 Hz, H-2), 5.37 (br d, 1 H, $J_{3',4'}$ = 3.5 Hz, H-4′), 5.23 (dd, 1 H, $J_{1',2'}$ = 7.8 Hz, $J_{2',3'}$ = 10.5 Hz, H-2′), 5.04 (dd, 1 H, $J_{3',4'}$ = 3.5 Hz, $J_{2',3'}$ = 10.5 Hz, H-3′), 4.82 (m, 1 H, H-5), 4.58 (d, 1 H, $J_{1'2'}$ = 7.8 Hz, H-1′), 4.02–4.08 (m, 3 H, H-6,6′,6a′), 3.85–3.91 (m, 2 H, H-6a,5′), 1.98–2.14 (4 s, 12 H, 4 OAc); ^{13}C NMR δ 101.2 (C-1′), 91.5 (C-1), 71.6 (C-5), 70.8 (C-3′), 70.7 (C-5′), 68.8 (C-2), 68.4 (C-4,2′), 68.0 (C-3), 67.1 (C-6), 66.8 (C-4′), 61.0 (C-6′), 20.5-20.7 ($COCH_3$). Anal. Calcd for $C_{59}H_{53}ClO_{17}$: C, 66.26; H, 5.00. Found: C, 66.03; H, 4.80.

O-(2,3,4,6-Tetra-O-benzoyl-β-D-galactopyranosyl)-(1→6)-2,3,4-tris-O-(p-phenylbenzoyl)-α-D-galactopyranosyl chloride (25): 1.07 g (82%); $[\alpha]_D$ +303.2° (*c* 1.1, $CHCl_3$); TLC, solvent C (9:1); chromatography, solvent C (20:1); ^1H NMR δ 6.46 (d, 1 H, $J_{1,2}$ = 3.9 Hz, H-1), 6.05 (m, 1 H, H-4), 6.02 (m, 1 H, H-3), 5.95 (br d, 1 H, $J_{3',4'}$ = 3.4 Hz, H-4′), 5.76 - 5.83 (m, 2 H, H-2,2′), 5.59 (dd, 1 H, $J_{3',4'}$ = 3.4 Hz, $J_{2',3'}$ = 10.8 Hz, H-3′), 4.93 (d, $J_{1',2'}$ = 7.8 Hz, H-1′), 4.81 (m, 1 H, H-5), 4.44 (dd, 1 H, $J_{5'6'}$ = 9.3 Hz, H-6′), 4.17–4.29 (m, 3 H, H-6,5′,6a′), 3.95 (dd, 1 H, $J_{5,6a}$ = 7.3 Hz, $J_{6,6a}$ = 10.8 Hz, H-6a); ^{13}C NMR δ 101.3 (C-1′), 91.3 (C-1), 71.6 (2 C), 71.3 (C-5,3′,5′), 69.6, 68.9, 68.4, 67.9 (2 C), 67.1 (C-2,3,4,6,2′,4′), 61.7 (C-6′). Anal. Calcd for $C_{79}H_{61}ClO_{17}$: C, 72.00; H, 4.67; Cl, 2.69. Found: C, 71.85; H, 4.63; Cl, 2.90.

Methyl O-(2,3,4,6-Tetra-O-acetyl-α-D-galactopyranosyl)-(1→6)-2,3,4-tris-O-(p-phenylbenzoyl)-β-D-galactopyranoside (20) and Methyl O-(2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl)-(1→6)-2,3,4-tris-O-(p-phenylbenzoyl)-β-D-galactopyranoside (21). 2,3,4,6-Tetra-O-acetyl-α-D-galactopyranosyl bromide (0.617 g, 1.5 mmol) was added to a mixture of nucleophile 14 (0.735 g, 1 mmol), mercuric cyanide (0.19 g, 0.75 mmol), mercuric bromide (0.02 g), and Drierite (1 g) in benzene (8 mL) at room temperature, and the suspension was stirred overnight [TLC, solvent B (2:1) or C (6:1)]. The mixture was filtered, and solids were washed with dichloromethane. The combined filtrates were washed with an aqueous solution of potassium bromide, dried, and concentrated. Chromatography [solvent C (9:1)] first gave **20**: 0.04 g (4%); $[\alpha]_D$ +358.47° (*c* 1.5, $CHCl_3$); ^1H NMR δ 5.99 (br d, 1 H, $J_{3,4}$ = 3.2 Hz, H-4), 5.84 (dd, 1 H, $J_{1,2}$ = 7.8 Hz, $J_{2,3}$ = 10.3 Hz, H-2), 5.63 (dd, 1 H, $J_{3,4}$ = 3.2 Hz, $J_{2,3}$ = 10.3 Hz, H-3), 5.50 (br d, 1 H, $J_{3',4'}$ ~ 3 Hz, H-4′), 5.38 (dd, 1 H, $J_{1',2'}$ = 3.5 Hz, $J_{2',3'}$ = 10.3 Hz, H-2′), 5.20 (dd, 1 H, $J_{3',4'}$ = 3.2 Hz, $J_{2',3'}$ = 10.3 Hz, H-3′), 4.96 (d, 1 H, $J_{1',2'}$ = 3.5 Hz, H-1′), 4.80 (d, 1 H, $J_{1,2}$ = 7.8 Hz, H-1), 3.88–4.38 (m, 6 H, H-5,6,6a,5′6′,6a′), 3.65 (s, 3 H, OCH_3), 1.98–2.21 (12 H, 4 OAc); ^{13}C NMR δ 102.5 (C-1), 96.7 (C-1′), 72.1, 71.9 (C-3,5), 69.7 (C-2), 68.1, 68.0, 67.6, 67.4 (C-4,2′,3′,4′), 66.6 (C-5′), 65.9 (C-6), 61.7 (C-6′), 57.3 (OCH_3), 20.6 ($COCH_3$).

Eluted next was **21**: 0.92 g (86%); $[\alpha]_D$ +314.76° (*c* 1, $CHCl_3$); TLC, solvent B (2:1) or C (6:1); chromatography, solvent C (9:1); ^1H NMR δ 5.91 (br d, 1 H, $J_{3,4}$ ~ 3 Hz, H-4), 5.84 (dd, 1 H, $J_{1,2}$ = 7.8 Hz, $J_{2,3}$ = 10.2 Hz, H-2), 5.63 (dd, 1 H, $J_{3,4}$ = 3.2 Hz, $J_{2,3}$ = 10.2 Hz, H-3), 5.41 (br d, 1 H, $J_{3',4'}$ ~ 3 Hz, H-4′), 5.25 (dd, 1 H, $J_{1',2'}$ = 7.8 Hz, $J_{2',3'}$ = 10.2 Hz, H-2′), 5.02 (dd, 1 H, $J_{3',4'}$ = 3.2 Hz, H-3′), 4.77 (d, 1 H, $J_{1,2}$ = 7.8 Hz, H-1), 4.59 (d, 1 H, $J_{1',2'}$ = 7.8 Hz, H-1′), 3.82–4.27 (m, 6 H, H-5,6,6a,5′,6′,6a′), 3.66 (s, 3 H, OCH_3), 1.97–2.20 (12 H, 4 OAc); ^{13}C NMR δ 102.3 (C-1), 100.9 (C-1′), 73.0 (C-5), 71.7 (C-3), 70.8, 70.7 (C-3′,5′), 69.6 (C-2), 68.6 (C-4,2′), 67.7 (C-6), 66.9 (C-4′), 61.1 (C-6′), 57.2 (OCH_3), 20.5 ($COCH_3$). Anal. Calcd for $C_{60}H_{56}O_{18}$: C, 67.66; H, 5.30. Found: C, 67.75; H, 5.32.

Methyl O-(2,3,4,6-Tetra-O-benzoyl-β-D-galactopyranosyl)-2,3,4-tris-O-(p-phenylbenzoyl)-β-D-galactopyranoside (22). 2,3,4,6-Tetra-O-benzoyl-α-D-galactopyranosyl bromide (5.3 g, 8 mmol) was added to a mixture of nucleophile 14 (4.4 g, 6 mmol), mercuric cyanide (1.14 g, 4.5 mmol), mercuric bromide (0.1 g), and Drierite (8 g) in benzene (20 mL) at room temperature, and the suspension was stirred for 2 days [TLC, solvent C (9:1)]. The mixture was then worked up as described for the preparation of **21**. Chromatography [solvent C (20:1)] gave one major product **22**: 7.2 g, (91%); mp 165–167 °C; $[\alpha]_D$ +318.46° (*c* 1.2, $CHCl_3$); ^1H NMR δ 5.94 and 5.98 (2 br d, 2 × 1 H, $J_{3,4}$ = $J_{3',4'}$ = 2.9 Hz, H-4,4′), 5.74–5.87 (m, 2 H, H-2,2′), 5.56–5.64 (m, 2 H, H-3,3′), 4.95 (d, 1 H, $J_{1',2'}$ = 7.8 Hz, H-1′), 4.61 (d, 1 H, $J_{1,2}$ = 8.3 Hz, H-1), 4.23–4.55 (m, 6 H, H-5,6,6a,5′6′,6a′), 3.26 (s, 3 H, OCH_3); ^{13}C NMR δ 102.2 (C-1), 101.3 (C-1′), 73.2 (C-5), 71.8, 71.6, 71.3 (C-3,3′5′), 69.8 (2 C, C-2,2′), 68.8, 68.1 (C-4,6,4′), 61.9 (C-6′), 56.8 (OCH_3). Anal. Calcd for $C_{80}H_{64}O_{18}$: C, 73.16; H, 4.91. Found: C, 72.94; H, 5.01.

Allyl O-(2,3,4,6-Tetra-O-benzoyl-β-D-galactopyranosyl)-(1→6)-2,3,4-tris-O-(p-phenylbenzoyl)-β-D-galactopyranoside (23). Nucleophile **15** (0.122 g, 0.16 mmol) and 2,3,4,6-tetra-O-benzoyl-α-D-galactopyranosyl bromide (0.125 g, 0.18 mmol) were dissolved in toluene/nitromethane (1:1, v/v, 1 mL), and the solution was cooled to −10 °C. A solution of silver triflate (0.0488 g, 0.19 mmol) and *sym*-collidine (20 μL, 0.15 mmol) in toluene/nitromethane (0.5 mL) was added dropwise with stirring, and the mixture was allowed to warmup to room temperature. After being stirred overnight [TLC, solvent C (9:1)] at room temperature, the mixture was neutralized with pyridine and filtered through Celite. The filtrate was diluted with dichloromethane, washed with water, aqueous sodium thiosulfate, and again water, dried, and concentrated. Chromatography [solvent C (15:1)] gave **23**: 0.178 g (83%); mp 228–229 °C; $[\alpha]_D$ +317.98° (*c* 0.9, $CHCl_3$); ^1H NMR δ 5.97, 5.93 (2 br d, 2 × 1 H, $J_{3,4}$ = $J_{3',4'}$ = 3.5 Hz, H-4,4′), 5.77–5.85 (m, 2 H, H-2,2′), 5.55–5.70 (m, 3 H, H-3,3′, $OCH_2CH{=}CH_2$), 5.07–5.19 (m, 2 H, $OCH_2CH{=}CH_2$), 4.93 (d, 1 H, $J_{1',2'}$ = 8.7 Hz, H-1′), 4.76 (m, 1 H, $J_{1,2}$ = 8.6 Hz, H-1), 3.84–4.54 (m, 8 H, H-5,6,6a,5′,6′,6a′, $OCH_2CH{=}CH_2$); ^{13}C NMR δ 117.6 ($OCH_2CH{=}CH_2$), 101.3 (C-1), 99.9 (C-1′), 73.2 (C-5), 71.8, 71.6, 71.3 (C-3,3′,5′), 69.8, 69.7, 69.6 (C-2,2′, $OCH_2CH{=}CH_2$), 68.8, 68.3, 68.0 (C-4,6,4′), 61.8 (C-6′). Anal. Calcd for $C_{82}H_{66}O_{18}$: C, 73.53; H, 4.97. Found: C, 73.27; H, 5.11.

Methyl O-[6-O-(*tert*-Butyldiphenylsilyl)-2,3,4-tris-O-(p-phenylbenzoyl)-β-D-galactopyranosyl]-(1→6)-2,3,4-tri-O-benzoyl-β-D-galactopyranoside (27). A solution of chloride **19** (2.24 g, 2.3 mmol), nucleophile **13** (1.01 g, 2 mmol), and *sym*-collidine (0.29 mL, 2.2 mmol) in dichloromethane (15 mL) was added dropwise to a suspension of silver triflate (0.64 g, 2.5 mmol) in dichloromethane (10 mL) at −10 °C. The reaction mixture was allowed to warmup to +10°C and after 20 min [TLC, solvent D (29:1)] was neutralized with *sym*-collidine and worked up as described for the preparation of **23**. Chromatography [solvent D (50:1)] gave **27**: 2.36 g (81%); mp 137–138 °C; $[\alpha]_D$ +268.3° (*c* 1.3, $CHCl_3$); ^1H NMR δ 6.06 (br d, 1 H, $J_{3',4'}$ ~ 3.5 Hz, H-4′), 5.85 (br d, 1 H, $J_{3,4}$ ~ 3.5 Hz, H-4), 5.74 (dd, 1 H, $J_{2',3'}$ = 10.1 Hz, $J_{1',2'}$ = 7.8 Hz, H-2′), 5.64–5.68 (m, 2 H, H-2,3′), 5.50 (dd, 1 H, $J_{2,3}$ = 11.1 Hz, $J_{3,4}$ = 3.5 Hz, H-3), 4.86 (d, 1 H, $J_{1',2'}$ = 7.8 Hz,

H-1′), 4.54 (d, 1 H, $J_{1,2}$ = 7.8 Hz, H-1), 3.64–4.15 (m, 6 H, H-5,6,6a,5′,6′,6a′), 3.24 (s, 3 H, OCH_3), 0.95 (s, 9 H, *t*-BuSi); ^{13}C NMR δ 102.2 (C-1), 101.2 (C-1′), 73.7, 73.1 (C-5,5′), 71.9, 71.7 (C-3,3′), 70.2, 69.8 (C-2,2′), 68.6, 67.7 (2 C) (C-4,6,4′), 60.8 (C-6′), 56.8 (OCH_3), 26.7 [$C(CH_3)_3$], 18.9 [$C(CH_3)_3$]. Anal. Calcd for $C_{89}H_{78}O_{17}Si$: C, 73.84; H, 5.43. Found: C, 73.89; H, 5.46.

Methyl *O*-[6-*O*-(*tert*-Butyldiphenylsilyl)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl]-(1→6)-2,3,4-tris-*O*-(*p*-phenylbenzoyl)-β-D-galactopyranoside (26). Chloride **18** (0.9 g, 1.2 mmol) and nucleophile **14** (0.74 g, 1 mmol) were reacted in the presence of silver triflate (0.36 g, 1.4 mmol) and *sym*-collidine (0.016 mL, 0.12 mmol) as described for the preparation of **27**. Chromatography [solvent A (3:1)] gave **26**: 1.15 g (79%); mp 177–178 °C; $[\alpha]_D$ +287.6° (*c* 1, $CHCl_3$); ^1H NMR δ 6.03 (br d, 1 H, $J_{3',4'} \sim$ 3.6 Hz, H-4′), 5.86 (br d, 1 H, $J_{3,4} \sim$ 3.5 Hz, H-4), 5.69–5.75 (m, 2 H, H-2,2′), 5.61 (dd, 1 H, $J_{2',3'}$ = 11.0 Hz, $J_{3',4'}$ = 3.6 Hz, H-3′), 5.53 (dd, 1 H, $J_{2,3}$ = 10.1 Hz, $J_{3,4}$ = 3.5 Hz, H-3), 4.84 (d, 1 H, $J_{1',2'}$ = 7.8 Hz, H-1′), H-1 (d, 1 H, $J_{1,2}$ = 7.8 Hz, H-1), 3.72–4.13 (m, 6 H, H-5,6,6a,5′,6′,6a′), 3.22 (s, 3 H, OCH_3), 0.94 (s, 9 H, *t*-BuSi); ^{13}C NMR δ 102.2 (C-1), 101.3 (C-1′), 73.7, 73.4 (C-5,5′), 71.9, 71.8 (C-3,3′), 70.1, 69.9 (C-2,2′), 68.8, 68.1, 67.7 (C-4,6,4′), 61.0 (C-6′), 56.8 (OCH_3), 26.6 [$C(CH_3)_3$], 18.9 [$C(CH_3)_3$]. Anal. Calcd for $C_{89}H_{78}O_{17}Si$: C, 73.84; H, 5.43. Found: C, 73.62, H, 5.47.

Methyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→6)-*O*-[2,3,4-tris-*O*-(*p*-phenylbenzoyl)-β-D-galactopyranosyl]-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (30). 2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranosyl bromide (0.12 g, 0.3 mmol) and nucleophile **29** (0.24 g, 0.2 mmol) were reacted in the presence of silver triflate (0.09 g, 0.35 mmol) and *sym*-collidine (0.04 mL, 0.32 mmol) as described for the preparation of **27** [TLC, solvent D (7:1)]. Chromatography [solvent D (9:1)] gave **30**: 0.23 g (74%), mp 154–155 °C; $[\alpha]_D$ +235.7° (*c* 1, $CHCl_3$); ^1H NMR δ 5.96, 5.90 (2 br d, 2 × 1 H, $J_{3,4} = J_{3',4'} \sim$ 3.4 Hz, H-4,4′), 5.82, 5.72 (2 dd, 2 × 1 H, $J_{1,2} = J_{1',2'}$ = 7.8 Hz, $J_{2,3} = J_{2',3'}$ = 10.3 Hz, H-2,2′), 5.54–5.62 (m, 2 H, H-3,3′), 5.34 (br d, 1 H, $J_{3'',4''} \sim$ 3.4 Hz, H-4″), 5.16 (dd, 1 H, $J_{2'',3''}$ = 10.5 Hz, $J_{1'',2''}$ = 7.8 Hz, H-2″), 4.97 (dd, 1 H, $J_{2'',3''}$ = 10.5 Hz, $J_{3'',4''}$ = 3.4 Hz, H-3″), 4.90 (d, 1 H, $J_{1',2'}$ = 7.8 Hz, H-1′), 4.61 (d, 1 H, $J_{1,2}$ = 7.8 Hz, H-1), 4.32 (d, 1 H, $J_{1'',2''}$ = 7.8 Hz, H-1″), 3.60–4.25 (m, 9 H, H-5,6,6a,5′,6′,6a′,5″,6″,6a″), 3.29 (s, 3 H, OCH_3), 2.12, 2.03, 1.97, 1.93 (4 OAc); ^{13}C NMR 102.2 (C-1), 101.1, 100.6 (C-1′,1″), 72.9, 72.5 (C-5,5′), 71.8 (2 C, C-3,3′), 70.9, 70.7 (C-3″,5″), 69.9 (2 C, C-2,2′), 68.6 (2 C, C-4,2″), 68.2, 67.6, 66.9, 66.7 (C-6,4′,6′,4″), 61.1 (C-6″), 56.8 (OCH_3), 20.5–20.7 ($COCH_3$). Anal. Calcd for $C_{87}H_{78}O_{26}$: C, 67.87; H, 5.11. Found: C, 67.75; H, 5.14.

Methyl *O*-[6-*O*-(*tert*-Butyldiphenylsilyl)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl]-(1→6)-*O*-[2,3,4-tris-*O*-(*p*-phenylbenzoyl)-β-D-galactopyranosyl]-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (31). Chloride **18** (0.26 g, 0.35 mmol) and nucleophile **29** (0.36 g, 0.3 mmol) were reacted in the presence of silver triflate (0.1 g, 0.39 mmol) and *sym*-collidine (0.045 mL, 0.34 mmol) as described for the preparation of **27** [TLC, solvent D (15:1)]. Chromatography [solvent D (20:1)] gave **31**: 0.48 g (83%); mp 236–237 °C; $[\alpha]_D$ +204.1° (*c* 1.2, $CHCl_3$); ^1H NMR 6.03 (br d, 1 H, H-4″), 5.90 (m, 2 H, H-4,4′), 5.52–5.75 (m, 6 H, H-2,3,2′3′2″,3″), 4.77 (d, 1 H, $J_{1',2''}$ = 7.8 Hz, H-1″), 4.57, 4.54 (2 d, 2 × 1 H, $J_{1,2} = J_{1',2'}$ = 7.8 Hz, H-1,1′), 3.48–4.11 (m, 9 H, H-5,6,6a,5′,6′,6a′,5″,6″,6a″), 3.31 (s, 3 H, OCH_3), 0.92 (s, 9 H, *t*-BuSi); ^{13}C NMR δ 102.3 (C-1), 100.9, 100.7 (C-1′,1″), 73.5, 72.8, 72.6 (C-5,5′,5″), 72.0, 71.9 (2 C, C-3,3′,3″), 70.2, 70.1, 69.9 (C-2,2′,2″), 68.5, 67.9, 67.6, 67.1 (C-4,6,4′,4″), 66.0 (C-6′), 60.5 (C-6″), 56.9 (OCH_3), 26.7 [$C(CH_3)_3$], 18.9 [$C(CH_3)_3$]. Anal. Calcd for $C_{116}H_{100}O_{25}Si$: C, 72.48; H, 5.24. Found: C, 72.38; H, 5.27.

Selective De-O-silylation of Disaccharides. General Procedure. Acetyl chloride (6.5 mL) was added dropwise to methanol (100 mL), and the solution obtained was cooled to room temperature. Disaccharide **26** or **27** (1.6 g, 1.1 mmol) in toluene (100 mL) was added and stirred at room temperature for ~20 h [TLC, solvent B (3:2)]. The reaction mixture was neutralized with Amberlite IR-45 (OH^-), concentrated, and purified by chromatography [solvent B (5:2)]. Thus were obtained the following compounds.

Methyl *O*-(2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→6)-2,3,4-tris-*O*-(*p*-phenylbenzoyl)-β-D-galactopyranoside (28): 1.09 g (82%); mp 152–153 °C; ^1H NMR δ 5.72–5.98 (m, 4 H, H-2,4,2′,4′), 5.54–5.60 (m, 2 H, H-3,3′), 4.86 (d, 1 H, $J_{1',2'}$ = 8.1 Hz, H-1′), 4.61 (d, 1 H, $J_{1,2}$ = 8.1 Hz, H-1), 3.51–4.18 (m, 6 H, H-5,6,6a,5′,6′,6a′), 3.32 (s, 3 H, OCH_3), 2.65 (br t, D_2O exchangeable, OH). Anal. Calcd for $C_{73}H_{60}O_{17}$: C, 72.50; H, 5.00. Found: C, 72.25; H, 4.92.

Methyl *O*-[2,3,4-tris-*O*-(*p*-phenylbenzoyl)-β-D-galactopyranosyl]-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (29): 1.11 g (83%); mp 153–154 °C; $[\alpha]_D$ +326.3° (*c* 1.3, $CHCl_3$); ^1H NMR δ 5.87–6.00 (m, 3 H, H-4,2′,4′), 5.56–5.73 (m, 3 H, H-2,3,3′), 4.94 (d, 1 H, $J_{1',2'}$ = 7.8 Hz, H-1′), 4.62 (d, 1 H, $J_{1,2}$ = 7.5 Hz, H-1), 3.52–4.21 (m, 6 H, H-5,6,6a,5′,6′,6a′), 3.33 (s, 3 H, OCH_3), 2.69 (br t, exchangeable with D_2O, OH); ^{13}C NMR δ 102.3 (C-1), 101.4 (C-1′), 74.2 (C-5′), 73.0 (C-5), 71.9, 71.8 (C-3,3′), 70.1, 69.8 (C-2,2′), 68.9, 68.6 (C-4,4′), 68.0 (C-6), 60.7 (C-6′), 56.9 (OCH_3). Anal. Calcd for $C_{73}H_{60}O_{17}$; C, 72.50; H, 5.00. Found: C, 72.20; H, 4.88.

Registry No. **1**, 1824-94-8; **2**, 2595-07-5; **3**, 3150-24-1; **4**, 110319-35-2; **5**, 110319-36-3; **6**, 110319-37-4; **7**, 110319-38-5; **8**, 110319-39-6; **9**, 110319-40-9; **10**, 110319-41-0; **11**, 110319-42-1; **12**, 110319-43-2; **13**, 53182-61-9; **14**, 110319-44-3; **15**, 110319-45-4; **16**, 110319-46-5; **17**, 110319-47-6; **18**, 110319-48-7; **19**, 110319-49-8; **20**, 110319-50-1; **21**, 110319-51-2; **22**, 110330-32-0; **23**, 110319-52-3; **24**, 110319-53-4; **25**, 110319-54-5; **26**, 110319-55-6; **27**, 110319-56-7; **28**, 110319-57-8; **29**, 110319-58-9; **30**, 110319-59-0; **31**, 110319-60-3; 1,2:3,4-di-*O*-isopropylidene-β-D-galactopyranose, 110319-61-4; 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide, 3068-32-4; 2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranosyl bromide, 61198-88-7.