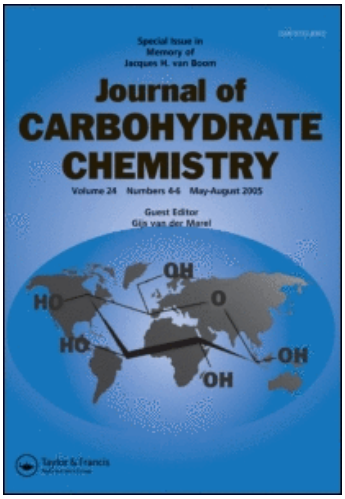

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Regioselective Glycodesilylation of Silylated Glycosides as a Useful Tool for the Preparation of Oligosaccharides

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REGIOSELECTIVE GLYCODESILYLATION OF SILYLATED GLYCOSIDES AS A USEFUL TOOL FOR THE PREPARATION OF OLIGOSACCHARIDES

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ABSTRACT

A series of fully or partially protected alkyl and aryl 4,6-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-D-glycopyranosides and 1-thio-β-D-glucopyranosides, respectively, were glycosylated by acetylated α-D-glucopyranosyl-, galactopyranosyl- and cellobiosyl fluoride under Lewis acid-catalysis to give the corresponding β-(1→6)-linked di- and trisaccharides, respectively, in moderate to high yield. With benzylated glucopyranosyl fluoride, anomeric mixtures of disaccharides were obtained depending on the solvent that was used for the glycosylation step. The initially formed oligosaccharides having a 1-fluoro-1,1,3,3-tetraisopropyl-1,3-disiloxane-3-yl substituent at position 4 were converted by treatment with tetrabutylammonium fluoride into the corresponding 4-OH compounds which are suitable as glycosyl acceptors for further extension of the sugar chain. Selective glycodesilylation of methyl 2-*O*-benzoyl-6-*O*-dimethylthexylsilyl-3,4-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-α-D-glucopyranoside at position 6 without affecting positions 3 and 4 was possible under similar conditions. 4,6-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-protected D-glycopyranosyl donors (fluoride, chloride, trichloroacetimidate and ethyl 1-thio-glycoside) of glucose and mannose were also prepared and used for the construction of the corresponding silylated disaccharides. Regioselective ring opening of the silylated glycosides by pyridine-polyhydrogen fluoride gave useful glycosyl acceptors that were subsequently coupled with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl trichloroacetimidate.

INTRODUCTION

The 1,1,3,3-tetraisopropyl-1,3-disiloxanediyl (TIPS) group, introduced by Markiewicz,[1,2] has found considerable applications as a temporary protective group in synthetic carbohydrate chemistry. The TIPS group can be selectively introduced to the 3,5-position of pentofuranose derivatives[1,3-5] and to the 4,6-position[5-8] or twice to the 2,3- and 4,6-position[9] of hexopyranosides leaving other hydroxyls free for further modifications. Under acidic conditions the 4,6-protected glycosides of glucose and mannose can be rearranged in high yield to the corresponding 3,4-TIPS protected glycosides.[5-8] Furthermore, the conversion of the TIPS group into other functional groups is also possible. For example, diastereomeric 4,6-*O*-(1-methoxycarbonyl)ethylidene substituents are easily generated from TIPS protected glycosides.[10]

Recently, we found that TIPS-protected methyl α-D-glucopyranosides were regioselectively glycosylated at one of the two silylated hydroxyls when treated with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl fluoride under Lewis acid-catalysis. Thus, the 4,6-TIPS-protected glucoside afforded exclusively the corresponding gentiobioside *via* regioselective glycodesilylation at position 6 leaving a 1-fluoro-1,1,3,3-tetraisopropyl-1,3-disiloxan-3-yl substituent at *O*-4 of the disaccharide. In contrast, the 3,4- and 2,3-TIPS-protected counterparts, respectively gave both laminaribiose derivatives.[11] The latter regioselective glycosylation procedure was recently adopted for a novel synthetic strategy for the convenient preparation of di- and trisaccharide fragments related to glycolipids of *Mycobacterium smegmatis*.[12] Here, we now present further applications of that glycodesilylation protocol in detail. Special attention was paid to the construction of various β-(1→6)-linked oligosaccharides, the combination of the TIPS group with other functionalities and the preparation and use of TIPS-protected glycosyl donors.

RESULTS AND DISCUSSION

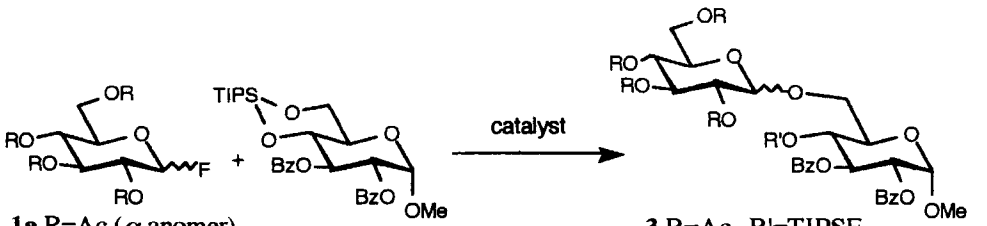
Previously, we found that $BF_3 \cdot Et_2O$ was the most effective catalyst for the glycodesilylation of methyl 2,3-di-*O*-benzoyl-4,6-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-α-D-glucopyranoside (**2**) with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl fluoride (**1a**), to give the methyl gentiobioside **3** (Table 1).[11] $BF_3 \cdot Et_2O$ has also been used for similar glycosylations of other silyl ethers with peracylated glycosyl fluorides.[13-15] Titanium tetrafluoride, introduced by Thiem et al.[16] as an effective and convenient catalyst for glycodesilylation reactions, gave significantly longer reaction times and lower yields of **3** in our case, probably due to its low solubility in dichloromethane. With the perbenzylated β-D-glucopyranosyl fluoride **1b** as glucosyl donor anomeric mixtures of (1→6)-linked disaccharides were obtained in general. For the determination of

Table 1. Reaction of D-glucopyranosyl fluorides **1a** and **1b** (1 equiv.) with methyl 2,3-di-*O*-benzoyl-4,6-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-α-D-glucopyranoside[11] **2** (1 equiv.) under Lewis acid-catalysis in different solvents to give disaccharides **3** and **4**.

Donor	Catalyst	Amount	Solvent	Conditions[a]	Yield	α:β-Ratio[b]
1a	$Et_2O{\cdot}BF_3$	10 mol-%	CH_2Cl_2	24h, rt	71% **3**[c]	0:100
1a[d]	TiF_4	10 mol-%	CH_2Cl_2	48h, rt	45% **3**	0:100
1b	$Et_2O{\cdot}BF_3$	40 mol-%	CH_2Cl_2	24h, rt	67% **4**	66:34
1b	$Et_2O{\cdot}BF_3$	40 mol-%	Et_2O	48h, rt	20% **4**	70:30
1b	TMSOTf	10 mol-%	CH_2Cl_2	15h, rt	62% **4**	71:29
1b	TMSOTf	10 mol-%	Et_2O	20h, rt	54% **4**	90:10
1b	TMSOTf	10 mol-%	H_3CCN	16h, rt	52% **4**	20:80
1b	Tf_2O	10 mol-%	Et_2O	10h 0 °C	decomp.	-
1b	TiF_4	10 mol-%	Et_2O	48h, rt	no reaction	-

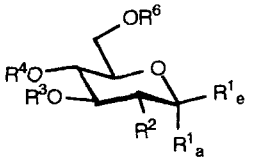
a. Reactions were performed until complete consumption (TLC) of **2**; rt = room temp.
b. Determined by HPLC. c. According to ref. 11. d. 1.1 equiv. of **1a**.

the α/β-ratio of the partially benzylated products we desilylated the initially formed reaction products with Bu_4NF in THF and measured the anomeric ratio of the thus formed 4-OH intermediates **4** by HPLC. As was expected from previous findings,[13,16,17] the solvent had a strong effect on the stereoselective outcome of the coupling reaction (Table 1). A high α-content of compounds **4** was obtained when the reaction was performed in diethyl ether with trimethylsilyl trifluoromethanesulfonate (TMSOTf) as the catalyst, whereas in acetonitrile the β-(1→6)-linked product predominated. Other Lewis acids ($BF_3{\cdot}Et_2O$ and TiF_4) were less reactive in combination with **1b** or resulted in decomposition of the acceptor **2**, as was observed for triflic anhydride (Tf_2O). The latter was recently found to be a superior catalyst for the α-selective coupling of the fluoride **1b** to an alcohol.[18]

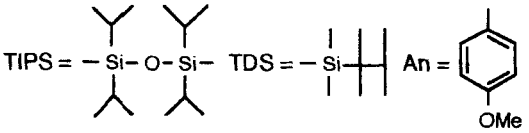


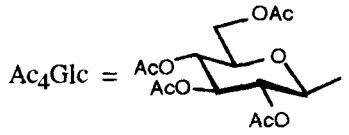
All 4,6-TIPS-protected gluco- and mannopyranosides used here were prepared from the corresponding free glycosides *via* reaction of the latter with 1,3-dichloro-1,1,3,3-tetraisopropyl-1,3-disiloxane[19] and imidazole followed by benzoylation of the TIPS protected intermediates as described previously[10,11] for compounds **2**, **5**, **7**, **14**, **21**, and

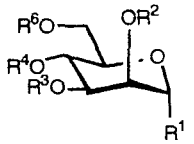
24. Thus, *p*-methoxyphenyl (**9**), and methyl 3-*O*-benzyl-β-D-glucopyranoside (**18**) afforded the corresponding 4,6-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-β-D-glucopyranosides **10** (77%) and **19** (74%), respectively. For the conversion **9**→**10** a small amount of the fully protected glucoside **10'** (14%) was isolated. Benzoylation of **10** with benzoyl bromide that was necessary[11] in order to benzoylate the sterically hindered position 3, and of **19** with benzoyl chloride gave then compounds **11** (100%) and **20** (77%). Selective monobenzoylation[11] at position 2 was performed with benzoyl chloride on 4,6-TIPS protected methyl β-D-glucopyranoside **12** and benzyl α-D-mannopyranoside **22**, to give alcohols **13** (83%) and **23** (93%), respectively. Methyl 3,4-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-α-D-glucopyranoside[11] (**15**) was silylated at position 6 with the chlorodimethylthexylsilane/imidazole-reagent[20] to give crude **16**, the benzoylation of which afforded glucoside **17** in 52% overall yield.



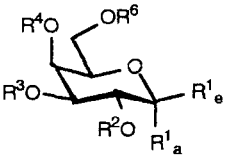
	R^1_e	R^1_a	R^2	R^3	R^4	R^6
1c	F	H	OAc	Ac	Ac_4Glc	Ac
5	SPh	H	OBz	Bz	TIPS	
6	SPh	H	OAc	Ac	Ac	Ac
7	SEt	H	OBz	Bz	TIPS	
8	SEt	H	OAc	Ac	Ac	Ac
9	OAn	H	OH	H	H	H
10	OAn	H	OH	H	TIPS	
10'	OAn	H	TIPS		TIPS	
11	OAn	H	OBz	Bz	TIPS	
12	OMe	H	OH	H	TIPS	
13	OMe	H	OBz	H	TIPS	
14	OMe	H	OBz	Bz	TIPS	
15	H	OMe	OH	TIPS		H
16	H	OMe	OH	TIPS		OTDS
17	H	OMe	OBz	TIPS		OTDS
18	OMe	H	OH	Bn	H	H
19	OMe	H	OH	Bn	TIPS	
20	OMe	H	OBz	Bn	TIPS	
21	H	OBn	NHAc	Bz	TIPS	





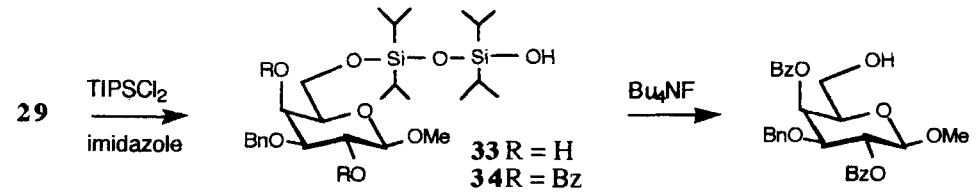


	R^1	R^2	R^3	R^4	R^6
22	OBn	H	H	TIPS	
23	OBn	Bz	H	TIPS	
24	OBn	Bz	Bz	TIPS	



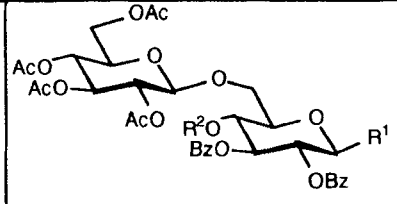
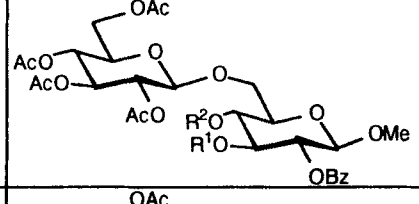
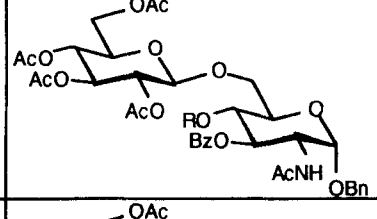
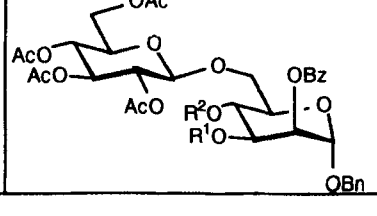
	R^1_e	R^1_a	R^2	R^3	R^4	R^6
1d	H	F	Ac	Ac	Ac	Ac
25	H	OMe	Bz	Bz	TIPS	
26	OMe	H	H	Bn	H	H
27	OMe	H	H	Bn	TIPS	
28	OMe	H	Bz	Bn	TIPS	
29	OBn	H	H	H	H	H
30	OBn	H	H	Bz	H	H
31	OBn	H	H	Bz	TIPS	
32	OBn	H	Bz	Bz	TIPS	

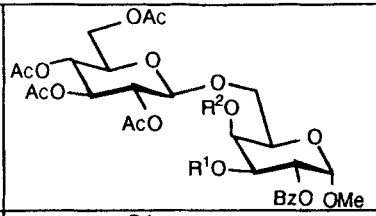
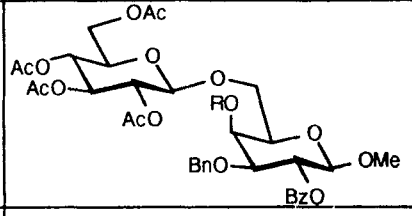
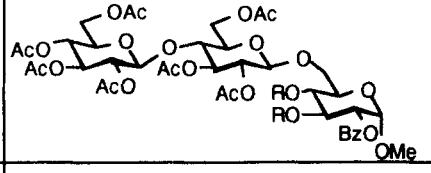
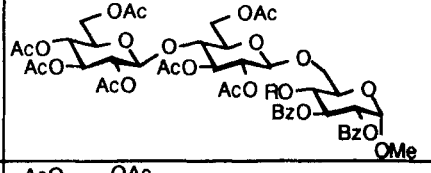
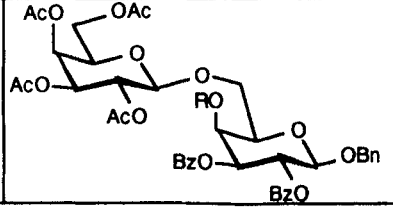
In the D-*galacto* series, we previously encountered some difficulties with silylations of methyl α-D-galactopyranoside.[10] The $TIPSCl_2$-imidazole-reagent was rather ineffective and harsher conditions ($TIPSCl_2$-AgOTf) had to be applied in order to get acceptable yields of the 4,6-TIPS-protected galactoside **25**. Since the hydroxyl at position 3 of galactosides is very reactive (*e.g.*, selective benzylation *via* stannylene derivatives[21] and direct benzoylation[22] of 3-OH in galactosides is described) we concluded that the initial reaction of $TIPSCl_2$ with 3-OH rather than 6-OH in methyl galactosides might be responsible for the poor yield of the desired 4,6-*O*-protected derivative. Therefore, we treated methyl 3-*O*-benzyl-β-D-galactopyranoside[21] **26** with $TIPSCl_2$ and imidazole in DMF. TLC revealed the formation of two products the faster moving of which was identified as compound **27** isolated in 44% yield. The slower moving product gave NMR data and elemental analyses which were consistent with compound **33**. The structure of **33** was proven by its subsequent benzoylation to give **34**, the acid-catalyzed desilylation of which afforded the known methyl 2,4-di-*O*-benzoyl-3-*O*-benzyl-β-D-galactopyranoside.[23] The formation of **33** could be suppressed by silylation of compound **26** with $TIPSCl_2$ in pyridine followed by benzoylation of intermediate **27** to give the desired galactoside **28** in 81% yield. Similarly, benzyl β-D-galactopyranoside was benzoylated at position 3 *via* the corresponding stannylene derivative[24] to give **30** (57%). Protection of the latter with $TIPSCl_2$ in pyridine gave first crude **31** that afforded compound **32** upon benzoylation in 94% overall yield.



The thus prepared TIPS-protected glycosides were then reacted with peracetylated glycosyl fluorides **1a,c** and **1d** under $BF_3{\cdot}Et_2O$-catalysis and the results are summarized in Table 2. In all cases (entries 1-13) the primary addition products of the glycosyl fluorides to the 6-positions of the acceptors were obtained in moderate to excellent yield. As was expected from the results of Table 1 the formed di- and trisaccharides were all β-(1→6)-linked. In cases where the yields of the oligosaccharides were less than 70% (entries 1,3-6 and 13) TLC revealed the presence of hydrolysis products due to the cleavage of the initially formed 4-*O*-(1-fluoro-1,1,3,3-tetraisopropyl-1,3-disiloxane-3-yl) substituent. These di- and trisaccharide alcohols were also conveniently obtained by fluorodesilylation of the isolated primary addition products with Bu_4NF.

Table 2. BF_3-Catalyzed glycodesilylation of various TIPS-protected glycosides with glycopyranosyl fluorides **1a**, **1c**, and **1d** at room temp, and subsequent derivatisation of the formed products.

Entry	Glycosyl Donor	Glycosyl Acceptor	Reaction Conditions BF_3·OEt_2	Time	Product	Substituents[a], Derivatisation[b]	Yield
1	**1a**	**5**	10 mol-%	20h		A → **35** R^1=SPh, R^2=TIPSF	63%
						A → **36** R^1=SPh, R^2=H	84%
2	**1a**	**7**	30 mol-%	62h		**37** R^1=SEt, R^2=TIPSF	70%
3	**1a**	**11**	10 mol-%	14h	+ 11% **6** (entry 1) + 10% **8** (entry 2)	A → **38** R^1=OAn, R^2=TIPSF	68%
						A → **39** R^1=OAn, R^2=H	77%
4	**1a**	**13**	20 mol-%	48h		A → **40** R^1=Bn, R^2=TIPSF	66%
						A → **41** R^1=Bn, R^2=H	88%
5	**1a**	**20**	10 mol-%	24h		A → **42** R^1=H, R^2=TIPSF	59%
						A → **43** R^1=R^2=H	99%
6	**1a**	**21**	100 mol-%	3days		A → **44** R=TIPSF	60%
						A → **45** R=H	96%
7	**1a**	**23**	10 mol-%	24h		A → **46** R^1=Bz, R^2=TIPSF	93%
						A → **47** R^1=Bz, R^2=H	76%
8	**1a**	**24**	10 mol-%	24h		A → **48** R^1=H, R^2=TIPSF	85%
						A → **49** R^1=R^2=H	87%

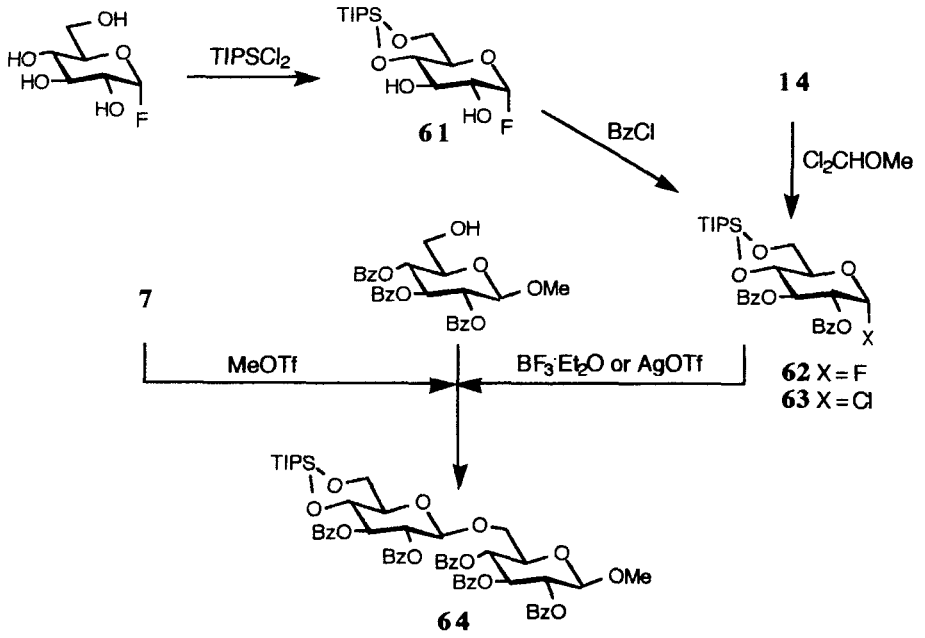
9	**1a**	**25**	15 mol-%	6h		A **50** R^1=Bz, R^2=TIPSF A → **51** R^1, R^2 = Bz, H B → **52** R^1=R^2=Bz	93% 97% 83%
10	**1a**	**28**	10 mol-%	3days		**53** R=TIPSF **54** R=H	20% 22%
11	**1c**	**17**	14 mol-%	2.5h		C **55** R=TIPS C → **56** R=H	61% 98%
12	**1c**	**2**	10 mol-%	24h		A **57** R=TIPSF A → **58** R=H	74% 95%
13	**1d**	**32**	200 mol%	0.5h		D **59** R=TIPSF D → **60** R=Bz	53% 85%

a. An = *p*-OMePh; TIPSF = -Si(*i*-Pr)$_2$-O-Si(*i*-Pr)$_2$F. b. A: $Bu_4NF{\cdot}3\ H_2O$; B: BzCl/pyridine; C: Pyridine $(HF)_x$; D: 1) A, 2) B.

For the conversions **5**→**35** and **7**→**37**, respectively, the transglycosylation products **6** and **8** were isolated as by-products of the glycodesilylation reaction. The partially benzoylated glycosides **13** and **23** were also smoothly glycodesilylated at positions 6, without any formation of β-(1→3)-linked products, to give gentiobioside **42** (entry 5) and disaccharide **48** (entry 8), respectively. Obviously, the bulky 4,6-TIPS group prevents position 3 from being glycosylated. The difficult accessibility of position 3 in 4,6-TIPS protected glycosides by electrophiles is well known.[5,7,10,11,25,26] The products **42** and **48** were subsequently converted to the diols **43** (99%) and **49** (87%), respectively, which are useful derivatives for further modifications of positions 3 and 4. Although the methyl 3-*O*-benzyl-β-D-glucopyranoside **20** afforded the gentiobioside **40** in moderate yield from fluoride **1a** (entry 4), difficulties were encountered during the corresponding glycosylation of methyl 3-*O*-benzyl-β-D-galactopyranoside **28** (entry 10). Only a small amount of the addition product **53** could be isolated since the fluorinated TIPS-residue at the axial position 4 of the galactose unit was too labile under the reaction conditions applied here. Thus, mixtures of compound **53** and of the corresponding desilylated product **54** were obtained that were rather difficult to purify by chromatography. We therefore recommend preparation of compound **53** by a two step procedure (see below) which gave better overall yields. When the disaccharide **50** (entry 9) was desilylated a mixture of the 2,3- and 2,4-di-*O*-benzoyl derivatives **51** were obtained by fluoride-catalyzed benzoyl-migration. Therefore, compounds **51** were benzoylated to give the fully blocked disaccharide **52**. Similarly, the β-(1→6)-linked digalactoside **59** (entry 13) was directly converted into compound **60**. Selective glycodesilylation of a dimethylthexylsilyl group in the presence of a 3,4-TIPS group is also possible as outlined in entry 11. The trisaccharide **55** thus obtained from cellobiosyl fluoride **1c** and acceptor **17** may serve on its part as a glycosyl acceptor since regioselective glycodesilylation at position 3 of 3,4-TIPS-protected α-D-glucose derivatives should be possible.[11] Unfortunately, we have not been able to open the 3,4-linked silyl ether ring in compound **55** regioselectively with pyridine-polyhydrogen fluoride as was possible for the corresponding 4,6-TIPS derivatives **24** and **28** (see below). In summary, we think that the regioselective glycodesilylation protocol outlined for the examples in Table 2, in combination with the subsequent formation of di- and trisaccharide alcohols as glycosyl acceptors might serve as a useful strategy for the effective construction of higher oligosaccharides.

In order to further demonstrate the flexibility of that approach we also explored the potential of TIPS-protected glycosyl donors. The possibility to glycosylate a TIPS-protected glycosyl acceptor using glucosyl fluoride **1a** *without* affecting the TIPS group (Table 2, entry 11) prompted us to prepare the fluoride **62**. It is easily accessible from α-D-glucopyranosyl fluoride *via* protection with the $TIPSCl_2$-imidazole-reagent affording first

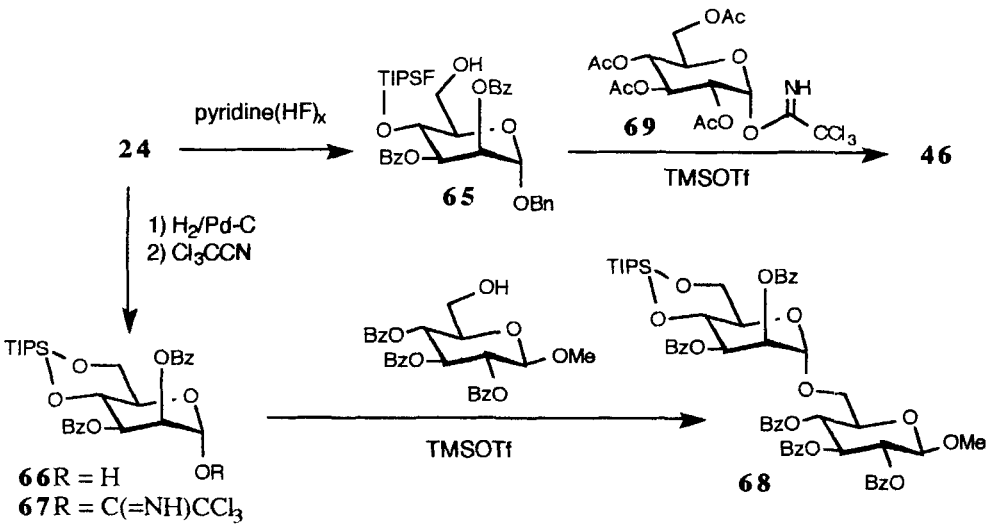
61 (78%) followed by benzoylation of the latter with benzoyl bromide to give **62** (88%). Under Lewis acid-catalysis, fluoride **62** reacted smoothly with methyl 2,3,4-tri-*O*-benzoyl-β-D-glucopyranoside to give the TIPS protected methyl β-D-gentiobioside **64** in 84% yield. A molar amount of Et_3N was added to the glycosylation mixture in order to neutralize the formed HF, as was previously recommended by Kunz et al.[14] Similarly, the TIPS protected glucosyl chloride **63**, obtained from methyl glucoside **14** and dichloromethyl methyl ether[27] in 90% yield, as well as the 1-thioglucoside **7** afforded **64** from the former glucosyl acceptor under promotion by silver- and methyl trifluoromethanesulfonate, respectively.



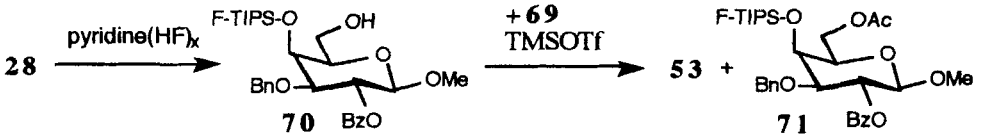
Furthermore, TIPS protected glucosyl trichloroacetimidates are also suitable as efficient glycosyl donors. For example, the aglycon of benzyl α-D-mannopyranoside **24** was first hydrogenolized affording **66** (95%) which was subsequently reacted with trichloroacetonitrile to give crystalline **67** (89%). The latter imidate afforded the disaccharide **68** (83%) upon Lewis acid-catalyzed reaction with methyl 2,3,4-tri-*O*-benzoyl-β-D-glucopyranoside. No cleavage of the TIPS groups could be detected.

When treated with pyridine-polyhydrogen fluoride in dichloromethane, compound **24** was selectively converted into the glycosyl acceptor **65** (97%). A similar regioselective ring opening of the TIPS group in benzyl 3-*O*-acetyl-2-*O*-allyl-4,6-*O*-(1,1,3,3-

tetraisopropyl-1,3-disiloxane-1,3-diyl)-β-D-glucopyranoside by acidic hydrolysis with aqueous hydrochloric acid has been previously described.[7] The use of HF under nonaqueous conditions is however recommended since the reaction proceeded almost instantaneously and a fluorosilane substituent was formed rather than a more reactive silanol residue. The usefulness of acceptor **65** was demonstrated by its glycosylation with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl trichloroacetimidate (**69**) to give the disaccharide **46** (78%) which was further converted to the alcohol **47** (Table 2, entry 7).



Methyl galactoside **28** that could not be efficiently glycosylated by fluoride **1a** (see Table 2, entry 10) was also transformed in the same way into alcohol **70** (85%). The latter was coupled with **69** to give compound **53** (70%) and then the alcohol **54** (77%) upon fluoride-catalyzed desilylation. A small amount of the transesterification product[28] **71** (17%) was formed as a by-product of the conversion **70**→**53**. Attempts to open the 3,4-*O*-TIPS ring of the trisaccharide **55** (Table 2, entry 11) by pyridine-polyhydrogen fluoride were, however, unsuccessful. Only complete protodesilylation was observed, affording diol **56** as the sole product.



CONCLUSION

The regioselective glycosylation of 4,6-*O*-TIPS protected glycopyranosides with glycosyl fluorides (glycodesilylation) can serve as a useful tool for the preparation of highly functionalized β-(1→6)-linked oligosaccharides. Furthermore, the possibility to prepare TIPS protected glycosyl donors such as halides, trichloroacetimidates and 1-thio-glycosides in high yield and their use in "classical" glycosylation reactions provide further extensions of this method. Also various alcohols are easily available *via* regioselective opening of the TIPS ring and can be used as glycosyl acceptors. Further extensions of this approach to 3,4- and 2,3-*O*-TIPS-protected glycosides are now under investigation.

EXPERIMENTAL

General Methods. NMR data (Table 3) were extracted from spectra measured in solutions of $CDCl_3$ (with TMS as an internal standard) at 25 °C with a Bruker AC 250F spectrometer. Proton-signal assignments were made by first order analysis of the spectra. Of the two magnetically non-equivalent geminal protons at C-6, the one resonating at lower field was designated 6-Ha and the one resonating at higher field was designated 6-Hb. Carbon-signal assignments were made by mutual comparison of the spectra and by comparison with spectra of related compounds. Data in the first, second and third row, when present, refer to the first, second and third sugar residue beginning at the residue bearing the aglycon. Optical rotations were measured at 25 °C with a Perkin-Elmer automatic polarimeter, Model 241. Melting points were measured with a Büchi apparatus, Model SMP-20. Thin-layer chromatographies (TLC) were performed on precoated plastic sheets, Polygram SIL UV_{254}, 40 x 80 mm (Macherey-Nagel) using appropriately adjusted mixtures of carbon tetrachloride-acetone for the developing. Detection was effected with UV light, where applicable and by charring with 5% sulfuric acid in ethanol. HPLC analysis of compounds **4** was performed with a LDC/Milton Roy system by elution of 0.6 mg samples from a Nucleosil 100-5 column (Macherey-Nagel) using ethyl acetate/*n*-hexane (20:80) as solvent at a flow rate of 2 mL/min and detection of the products at 257 nm. Preparative chromatographies were performed by elution from columns of Silica Gel 60 (Merck) using carbon tetrachloride-acetone mixtures as solvent. Solutions in organic solvents were dried with anhydrous sodium sulfate, and concentrated at 2 kPa, ≤40 °C.

Methyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2,3-di-*O*-benzoyl-4-*O*-(1-fluoro-1,1,3,3-tetraisopropyl-1,3-disiloxane-3-yl)-α-D-glucopyranoside (3). A mixture of **1a** (0.35 g, 1.0 mmol), **2**[11] (0.65 mmol) and TiF_4 (12.4 mg, 0.1 mmol) in dichloromethane (20 mL) was stirred at room temp. until TLC

Table 3. NMR data in $CDCl_3$: chemical shifts δ [ppm]; coupling constants J [Hz]

Comp.	H-1 ($J_{1,2}$)	H-2 ($J_{2,3}$)	H-3 ($J_{3,4}$)	H-4 ($J_{4,5}$)	H-5 ($J_{5,6a}$)	H-6a ($J_{5,6b}$)	H-6b ($J_{6a,6b}$)	Subst.[a]	C-1	C-2	C-3	C-4	C-5	C-6	Subst.[a]
10	4.75d	3.71-3.58m	3.71-3.58m	3.90t	3.27bd	4.11dd	3.96dd	3.76s, Me	102.2	69.0	76.1	76.7	73.7	60.9	55.6, Me
	(7.4)	(-)	(9.0)	(9.0)	(2.0)	(1.4)	(-12.5)								
10'	4.74d	3.75bt	3.80t	3.96t	3.24bd	4.14dd	4.02dd	3.75s, Me							
	(7.3)	(8.2)	(9.0)	(9.0)	(2.0)	(1.2)	(-12.5)								
11	5.13d	5.56dd	5.73t	4.35t	3.55bd	4.21dd	4.12dd	3.73s, Me	101.1	72.3	75.3	77.5	67.8	60.9	55.6, Me
	(7.9)	(9.7)	(9.6)	(9.3)	(2.0)	(<1.0)	(-12.6)								
13	4.50d	5.05dd	3.84t	3.95t	3.27bd	4.13dd	4.02dd	3.50s, Me	102.2	74.6	76.5[b]	75.7[b]	69.4	60.7	57.0, Me
	(7.8)	(9.1)	(9.1)	(9.0)	(2.0)	(1.2)	(-12.5)								
17	4.93d	5.03dd	4.21dd	3.69-3.61m	3.69-3.61m	3.95dd	3.69-3.61m	3.38s, Me	97.1	72.6	73.7[b]	74.3	73.5[b]	62.6	55.6, Me
	(3.8)	(9.6)	(7.7)	(-)	(1.4)	(-)	(-11.2)								
23	5.08d	5.49dd	3.63bd	4.31t	4.24bd	4.17dd	3.91dd	4.71d, 4.54d	97.8	70.7	72.9[b]	67.6	73.1[b]	60.8	69.5, Bn
	(1.3)	(3.2)	(9.3)	(9.3)	(1.8)	(1.2)	(-12.6)	(-11.9), Bn							
27	4.13d	3.88dd	3.33dd	4.25bd	3.48-3.44m	3.84-3.80m	3.84-3.80m	4.77d, 4.63d[c]	104.3	70.4	80.5	74.1	65.5	59.4	72.5, Bn
	(7.7)	(9.8)	(3.8)	(<1.0)	(-)	(-)	(-)	3.51s, Me							56.9, Me
28	4.43d	5.57dd	3.60-3.51m	4.35bd	3.60-3.51m	3.90dd	3.83dd	4.63d, 4.55d[d]	102.1	71.0	78.6	74.1	65.5	59.4	72.0, Bn
	(8.0)	(10.1)	(-)	(<1.0)	(3.0)	(4.4)	(-10.3)	3.42s, Me							55.8, Me
30[e]	4.50d	3.98dd	4.96dd	4.17bd	3.65bt	3.82dd	3.75dd	4.97d, 4.70d	105.4	71.5	79.4	69.3	77.9	63.6	73.2, Bn
	(7.8)	(10.2)	(3.2)	(<1.0)	(6.9)	(5.3)	(-11.2)	(-11.8), Bn							
32	4.69d	5.85dd	5.22dd	4.59bd	3.77bdd	3.94bd	3.94bd	4.90d, 4.66d	99.6	69.5	74.0[b]	74.6	66.6[b]	59.2	70.0, Bn
	(7.9)	(10.6)	(3.2)	(<1.0)	(-)	(-)	(-)	(-12.6), Bn							
33	4.16d	3.79dd	3.41dd	4.12bs	3.46-3.43m	4.04dd	3.92dd	4.75d, 4.72d[f]	104.0	71.1	80.6	74.8	65.7	61.3	71.9, Bn
	(7.7)	(9.4)	(3.3)	(<1.0)	(7.0)	(5.4)	(-10.0)	3.54s, Me							56.9, Me
34	4.50d	5.49dd	3.77dd	5.91bd	3.83-3.73m	3.96dd	3.86dd	4.73d, 4.55d[g]	102.4	71.4	76.3	74.3	66.2	60.9	70.7, Bn
	(8.0)	(10.0)	(3.3)	(<1.0)	(6.3)	(6.9)	(-10.0)	3.51s, Me							56.9, Me
35	5.00d	5.13t	5.33t	4.02bt	4.29-4.22m	4.27dd	4.13dd		86.4	71.0	76.7	70.0	80.6	68.2	
	(10.0)	(9.9)	(9.9)	(9.0)	(6.3)	(2.3)	(-12.4)								
	4.65d	5.05dd	5.64t	5.19t	3.63ddd	3.89-3.73m	3.89-3.73m		101.0	71.3	73.1	69.8	71.8	61.7	
	(7.9)	(9.4)	(9.2)	(9.2)	(2.2)	(5.9)	(-)								
36	4.93d	5.18t	5.42t	3.85-3.75m	4.67-4.20m	4.25dd	4.18dd		86.3	70.0	78.1	68.9	79.5	68.3	
	(9.8)	(9.8)	(9.9)	(-)	(4.5)	(2.6)	(-12.5)								
	4.67d	5.05dd	5.38t	5.21t	3.70ddd	3.91dd	3.85-3.75m		101.0	71.2	72.8	70.0	72.0	61.8	
	(7.9)	(9.4)	(9.2)	(9.4)	(5.5)	(2.6)	(-11.3)								
37	4.74d	5.03dd	5.29t	4.00t	4.34-4.22m	4.34-4.22m	4.13dd	2.77-2.69m,	83.5	71.3	76.8	70.2	80.6	68.3	
	(10.0)	(9.8)	(9.8)	(9.8)	(-)	(2.2)	(-12.1)	1.27t, EtS							
	4.66d	5.06dd	5.63t	5.17t	3.78-3.68m	3.78-3.68m	3.78-3.68m		101.0	71.3	73.0	69.8	71.9	61.8	
	(7.9)	(9.3)	(9.2)	(9.3)	(-)	(-)	(-)								
38	5.17d	5.53dd	5.67dd	4.08bt	4.35-4.24m	4.35-4.24m	3.94-3.79m	3.77s, Me	100.1	72.1	74.5	75.4	73.0	68.2	55.6, Me
	(8.0)	(9.8)	(9.0)	(9.0)	(-)	(-)	(-)								
	4.69d	5.06dd	5.14t	5.07t	4.88bt	4.13-4.08m	3.94-3.79		100.7	71.3	73.0	69.9	71.8	61.6	
	(7.8)	(9.5)	(9.8)	(9.9)	(-)	(-)	(-)								

39	5.15d	5.65dd	5.48bt	3.95-3.84m	3.95-3.48m	4.24dd	4.15dd	3.76s, Me	100.5	71.1[b]	74.2	76.0	68.5	68.3	55.6, Me
	(7.8)	(9.8)	(9.6)	(-)	(2.4)	(4.6)	(-12.3)								
	4.71d	5.05dd	5.09t	5.20t	3.66ddd	3.95-3.84m	3.95-3.84m		100.7	71.2[b]	72.8	70.1	71.9	61.8	
	(7.8)	(9.7)	(9.7)	(9.3)	(-)	(-)	(-)								
40	4.47d	5.23dd	3.75t	3.78-3.64m	3.78-3.64m	4.33-4.25m	4.11dd	4.72d, 4.59d	101.0	71.5	82.9	76.7	74.2	69.9	74.4, Bn
	(7.8)	(9.0)	(9.0)	(-)	(-)	(2.1)	(-12.5)	(-11.1), Bn							
	4.67d	5.03dd	5.25t	5.16t	3.78-3.64m	4.33-4.25mm	3.78-3.64m	3.47 s, Me	101.7	71.3	73.0	68.3	71.8	61.8	56.9, Me
	(8.0)	(9.3)	(9.5)	(9.6)	(-)	(-)	(-)								
41	4.44d	5.09bt	3.68-3.64m	3.68-3.64m	3.72ddd	4.28dd	4.16dd	4.73d, 4.63d	100.8	71.0	82.3	74.7	72.7	68.8	74.6, Bn
	(7.9)	(9.5)	(-)	(-)	(4.7)	(2.5)	(-12.6)	(-11.5), Bn							
	4.68d	5.03dd	5.21t	5.21t	3.57-3.48m	3.81dd	3.68-3.64m	3.46s, Me	102.0	71.1	73.4	68.3	71.9	61.8	56.6, Me
	(7.9)	(9.4)	(9.3)	(9.3)	(6.1)	(-)	(-11.2)								
42	4.46d	5.03dd	3.79-3.68m	3.79-3.68m	3.79-3.68m	4.26dd	4.16dd	3.51s, Me	101.0	75.9	73.0	76.3	74.5	69.3	56.9, Me
	(7.9)	(9.0)	(-)	(-)	(4.3)	(2.4)	(-12.3)								
	4.69d	5.01dd	5.20t	5.11t	3.62bd	3.79-3.68m	3.79-3.68m		101.6	71.4	73.0	71.4	71.9	61.9	
	(7.9)	(9.1)	(9.1)	(9.1)	(1.4)	(-)	(-10.9)								
43	4.46d	5.01dd	3.62-3.52m	3.62-3.52m	4.28-4.23m	4.26dd	3.78-3.69m	3.49s, Me	101.0	74.7	74.4	75.5	71.5	69.1	57.0, Me
	(7.9)	(9.5)	(-)	(-)	(4.0)	(-)	(-12.5)								
	4.68d	5.03dd	5.22t	5.09t	3.78-3.69m	4.16dd	3.84dd		101.8	71.1	72.7	68.3	71.9	61.7	
	(7.9)	(9.4)	(9.4)	(9.6)	(2.0)	(5.6)	(-11.2)								
44	4.86d	4.37ddt	5.49dd	4.30-4.12m	4.10-3.76m	4.10-3.76m	3.74-3.70m	4.79d, 4.46d	96.6	52.4	72.1	69.2	74.4	68.8	69.8, Bn
	(3.6)	(10.7)	(9.3)	(9.3)	(-)	(-)	(-)	(-12.0), Bn							
	4.64d	5.10dd	5.24t	5.10t	3.74-3.70m	4.30-4.12m	4.30-4.12m	5.78d, NH	101.3	71.3	72.9	68.3	71.8	61.8	
	(7.7)	(9.5)	(9.3)	(9.5)	(-)	(-)	(-)	(9.6)							
45	4.91d	4.43dt	5.32dd	4.17t	3.94ddd	3.83dd	3.77-3.70m	4.75d, 4.48d	96.4	51.5	71.3	69.4	75.1	68.6	69.5, Bn
	(3.6)	(10.6)	(9.2)	(9.6)	(5.4)	(2.0)	(-10.8)	(-11.9), Bn							
	4.66d	5.06dd	5.23t	5.08t	3.77-3.70m	4.24dd	4.18dd	5.88d, NH	101.0	71.1	72.7	68.3	71.9	61.8	
	(7.9)	(9.2)	(9.4)	(9.5)	(4.7)	(2.1)	(-12.4)	(9.6)							
46	5.06d	5.64dd	5.59dd	4.17t	3.75ddd	4.29-4.14m	4.29-4.15m	4.78d, 4.58d	96.8	70.5	73.2	66.9	71.9	69.0	69.4, Bn
	(1.6)	(3.5)	(9.5)	(9.5)	(2.7)	(4.3)	(-)	(-11.9), Bn							
	4.67d	5.13dd	5.25t	5.11t	4.01ddd	4.29-4.15m	3.90dd		101.3	71.2	72.8	68.4	71.9	61.8	
	(7.9)	(9.3)	(9.4)	(9.4)	(2.1)	(5.3)	(-10.1)								
47	4.97d	5.67dd	5.63dd	4.34bt	3.72ddd	4.28-4.18m	4.10dd	4.84d, 4.58d	95.9	70.4	72.9	67.1	72.7	68.4	70.4, Bn
	(1.4)	(3.5)	(8.8)	(8.8)	(2.4)	(4.1)	(-12.3)	(-11.9), Bn							
	4.67d	5.15dd	5.26t	5.14t	4.28-4.18m	4.28-4.18m	3.81dd		101.4	71.4	72.9	68.4	71.8	61.8	
	(7.7)	(9.5)	(9.3)	(9.5)	(-)	(-)	(-10.5)								
48	4.98d	5.40dd	3.97t	3.75-3.66m	4.33bd	4.24dd	4.10dd	4.76d, 4.49d	96.2	70.5	73.0[b]	71.4	72.4	68.7	69.7, Bn
	(1.5)	(3.5)	(9.5)	(9.6)	(4.4)	(2.4)	(-12.2)	(-12.9), Bn							
	4.65d	5.10dd	5.23t	5.11t	3.75-3.66m	4.14-4.08m	3.97dd		101.1	70.6	72.9[b]	68.4	71.8	62.0	
	(7.8)	(9.2)	(9.3)	(9.6)	(-)	(-)	(-)								

(*continued*)

Table 3. Continued

49	5.00d (1.6)	5.38dd (3.4)	3.90-3.79m (-)	4.16bt (9.9)	3.73ddd (4.5)	4.26dd (2.3)	4.15dd (-12.4)	4.72d, 4.52d (-11.8), Bn	97.0	69.3	72.4[b]	69.1	70.5	68.7	69.6, Bn
	4.64d (7.7)	5.09dd (9.7)	5.24t (9.4)	5.10t (9.7)	3.90-3.79m (-)	4.19-4.11m (-)	3.90-3.79m (-)		101.0	71.1	72.7[b]	68.4	71.9	61.8	
50	5.11d (3.3)	5.72dd (10.8)	5.64dd (2.5)	4.55bd (<1.0)	4.17bdd (2.8)	4.02dd (8.5)	3.85dd (-10.8)	3.41s, Me	97.4	68.7	70.5	70.5	71.8	70.3	55.2, Me
	4.62d (8.0)	5.04dd (9.4)	5.24t (9.3)	5.13t (9.3)	3.72ddd (4.3)	4.31dd (2.1)	4.12dd (-12.4)		101.4	71.3[b]	72.8	68.3	71.2[b]	61.8	
52	5.27d (3.6)	5.64dd (10.3)	5.93dd (3.4)	5.89bd (<1.0)	4.46bdd (3.7)	3.98dd (8.0)	3.77dd (-10.8)	3.46s, Me	97.4	68.2[b]	68.4[b]	69.4	69.7	68.9	55.5, Me
	4.58d (7.8)	5.01dd (9.6)	5.06t (9.5)	5.20t (9.4)	3.69ddd (4.8)	4.21dd (2.3)	4.05dd (-12.3)		101.0	71.8	72.7	68.3[b]	71.2	61.8	
53	4.29d (7.7)	5.45dd (9.7)	3.44dd (2.7)	4.18bd (<1.0)	3.52bdd (3.0)	3.93dd (7.9)	3.80dd (-11.0)	4.42d, 4.41d (-11.8), Bn	101.4	73.0	79.0	75.4	68.5	70.4	72.9, Bn
	4.44d (8.0)	4.91dd (9.3)	5.10t (9.3)	5.00t (9.6)	3.60ddd (4.4)	4.19dd (2.1)	4.01dd (-12.3)	3.35s, Me	102.1	72.0[b]	71.5[b]	49.2	71.3[b]	62.0	56.2, Me
54	4.37d (8.0)	5.43dd (9.6)	3.67dd (3.3)	4.04bd (<1.0)	3.67-3.60m (4.2)	4.10dd (7.4)	3.96dd (-11.1)	4.67d, 4.52d (-12.2), Bn	101.1	71.9	78.0	73.9	66.2	69.1	72.8, Bn
	4.67d (8.0)	5.02dd (9.4)	5.21t (9.4)	5.09t (9.6)	3.73ddd (4.7)	4.27dd (3.3)	4.16dd (-12.4)	3.46s, Me	101.9	71.0	71.4[b]	68.3	71.3[b]	61.9	56.6, Me
55	4.90d (3.9)	5.03dd (9.8)	3.67bt (9.8)	3.46bt (9.5)	3.90-3.82m (8.2)	4.19dd (8.2)	3.57dd (-10.0)	3.36s, Me	97.1	72.7	74.2	74.0	72.0	68.9	55.1, Me
	4.52d (7.8)	4.93dd (9.1)	5.18t (9.1)	3.81bt (9.1)	4.15-4.08m (4.0)	4.50dd (-)	4.15-4.08m (-10.2)		100.9[b]	71.7	73.2	76.7	71.7	62.2	
	4.66d (7.7)	4.95dd (9.3)	5.16t (9.3)	5.06t (9.8)	3.70-3.63m (4.4)	4.37dd (2.1)	4.04dd (-12.5)		100.7[b]	71.2	73.0	67.9	71.7	61.6	
56	4.98d (3.5)	4.98-4.89m (9.1)	3.79bt (9.1)	3.79bt (9.1)	3.86-3.79m (-)	4.14-4.02m (-)	3.69-3.60m (-)	3.36s, Me	97.2	72.4	73.7	71.8	71.3	68.8	55.3, Me
	4.53d (7.9)	4.98-4.89m (9.3)	5.20t (9.3)	4.14-4.02m (-)	4.14-4.02m (-)	4.60dd (3.8)	3.55dd (-10.0)		100.8	72.0	72.9	76.3	71.6	61.6	
	4.63d (7.8)	4.98-4.89m (9.2)	5.16t (9.2)	5.07t (9.4)	3.69-3.60m (4.3)	4.38dd (-)	4.14-4.02m (-12.6)		100.8	70.0	72.9	67.8	71.4	61.6	
57	5.11d (3.8)	4.99dd (9.1)	5.88t (9.1)	3.82t (9.4)	4.07-3.97m (4.8)	4.11dd (3.4)	3.72dd (-12.0)	3.39s, Me	96.5	72.5[b]	72.6[b]	72.0	73.0	70.0	55.2, Me
	4.52d (7.9)	4.96dd (9.3)	4.78t (9.2)	3.98t (9.4)	4.21bd (4.4)	4.38dd (-)	4.07-3.97m (-12.5)		100.9	71.6	71.6	77.2	72.7[b]	62.0[h]	
	4.62d (7.8)	4.94dd (9.0)	5.19t (9.1)	4.97t (9.3)	3.69-3.48m (-)	4.49bd (-)	4.07-3.97m (-)		101.3	70.3	73.0	67.8	71.6	61.6[h]	

58	5.17d	5.20dd	5.72dd	3.80bt	3.96-3.76m	4.38dd	3.96-3.76m	3.41s, Me	96.9	71.8	72.3[b]	71.3	73.9	68.4	55.3, Me
	(3.6)	(10.1)	(9.1)	(9.6)	(4.1)	(-)	(-12.0)								
	4.53d	4.98dd	5.07t	4.12t	4.37-4.31m	4.56dd	3.96-3.76m		100.7[h]	71.3	72.8	76.3	72.7[b]	61.6[i]	
	(8.0)	(9.0)	(9.0)	(9.3)	(1.7)	(-)	(-12.3)								
	4.65d	5.21dd	5.12t	4.93t	3.71-3.62m	4.38dd	4.04dd		100.8[h]	70.7	69.7	67.7	71.5	61.5[i]	
	(7.9)	(9.4)	(9.4)	(9.0)	(4.1)	(1.9)	(-12.2)								
59	4.59d	5.26dd	5.03dd	4.48bd	4.23-3.84m	4.23-3.84m	4.23-3.84m	4.92d, 4.74d	99.5	69.4	74.6[b]	69.0	74.9[b]	69.8	69.8, Bn
	(7.9)	(10.5)	(3.4)	(<1.0)	(-)	(-)	(-)	(-12.7), Bn							
	4.69d	5.85dd	5.20dd	5.40bd	4.23-3.84m	4.23-3.84m	4.23-3.84m		101.6	69.4	70.9	67.0	70.7	61.1	
	(7.8)	(10.4)	(2.3)	(<1.0)	(-)	(-)	(-)								
60	4.57d	5.26dd	5.02dd	4.09bd	4.11-4.03m	4.11-4.03m	3.90bt	4.98d, 4.77d	99.5	69.7	73.1	68.7	71.1	68.0	70.4, Bn
	(7.9)	(10.4)	(3.4)	(<1.0)	(-)	(-)	(-)	(-12.5), Bn							
	4.79d	5.85dd	5.49dd	5.39bd	4.11-4.03m	4.11-4.03m	3.86dd		101.0	68.0	70.9[b]	67.0	70.8[b]	61.2	
	(7.9)	(10.4)	(3.4)	(<1.0)	(-)	(7.6)	(-10.6)								
61	5.66dd[j]	3.57ddd[k]	3.72bt	3.80t	3.86-3.81m	4.09dd	3.92dd		107.3[i]	72.3[k]	73.8		68.6	74.7[l]	60.3
	(2.9)	(9.4)	(9.3)	(9.0)	(1.9)	(1.2)	(-12.9)								
62	5.88dd[m]	5.12ddd[n]	5.91t	4.23t	3.94bt	4.13dd	3.94bt		104.4[m]	73.5[n]	71.9	67.0	72.0[o]	60.3	
	(2.8)	(10.1)	(9.8)	(9.5)	(2.1)	(9.5)	(-13.0)								
63	6.51d	5.25dd	6.05t	4.32t	4.13bt	4.22dd	4.01bd		91.4	72.3[b]	72.0[b]	75.5	66.9	60.3	
	(4.0)	(10.0)	(9.7)	(9.5)	(2.0)	(9.6)	(-12.3)								
64	4.83d	5.32dd	5.79t	5.27t	4.02bd	4.14dd	3.78dd	3.10s, Me	101.8[b]	69.9	72.9	74.0	71.8	68.8	56.7, Me
	(7.9)	(9.7)	(9.6)	(9.6)	(1.9)	(8.6)	(-11.8)								
	4.46d	5.34dd	5.67t	4.24t	3.44bd	4.08dd	3.93dd		101.6[b]	67.8	75.2	76.9	72.5	60.7	
	(7.9)	(9.7)	(9.5)	(9.3)	(1.5)	(1.3)	(-10.6)								
65	5.05d	5.69-5.62m	5.69-5.62m	4.61t	3.95-3.85m	3.95-3.85m	3.95-3.85m	4.82d, 4.64d	96.8	70.5	73.5[b]	66.3	73.1[b]	61.7	69.6, Bn
	(1.0)	(3.3)	(9.0)	(9.0)	(-)	(-)	(-)	(-12.1), Bn							
66	5.45d	5.64dd	5.79dd	4.63t	4.08bd	4.25dd	3.96bd	3.53bd, OH	92.9	71.4	73.2	64.9	72.0	61.0	
	(1.5)	(3.3)	(9.8)	(9.5)	(1.8)	(<1.0)	(-12.5)	(3.8)							
67	6.48d	5.82dd	5.79dd	4.72t	4.00bd	4.23dd	4.04bd		95.7	69.1	76.1	64.3	71.5	60.6	
	(1.0)	(3.4)	(9.4)	(9.5)	(2.1)	(<1.0)	(-12.8)								
68	4.78d	5.52dd	5.92t	5.47t	4.19-3.89m	4.19-3.89m	4.19-3.89m	3.61s, Me	102.0	70.7	73.0[b]	73.1[b]	71.9	66.3	57.4, Me
	(7.9)	(9.8)	(9.6)	(9.7)	(-)	(-)	(-)								
	5.01d	5.58dd	5.71dd	4.61t	4.19-3.89m	4.19-3.89m	3.67bd		97.7	69.9	73.1[b]	64.8	72.2	60.8	
	(1.1)	(3.5)	(9.8)	(9.6)	(-)	(-)	(-)								
70	4.47d	5.61dd	3.58dd	4.38bd	3.49-3.60m	3.95bdd	3.85-3.72m	4.46d, 4.52d[p]	102.1	71.1	79.2	76.0	68.2	62.2	72.6, Bn
	(7.9)	(9.8)	(2.6)	(<1.0)	(7.6)	(-)	(-11.1)	3.47s, Me							55.9, Me
71	4.45d	5.59dd	3.59dd	4.40bd	3.70bt	4.38bd	4.32dd	4.65d, 4.55d[q]	101.8	70.9	78.9	73.4	68.5	63.9	72.7, Bn
	(7.5)	(9.5)	(2.7)	(<1.0)	(<1.0)	(5.1)	(-11.5)	3.46s, Me							55.8, Me

a. Bn = CH_2Ph, Me = CH_3. b. Attributions may be inverted. c. CH_2Ph (J = -12.0 Hz). d. CH_2Ph (J = -12.2 Hz). e. In d_6-acetone. f. CH_2Ph (J = -12.0 Hz); 4.34bs, SiOH. g. CH_2Ph (J = -12.9 Hz); 4.29bs, SiOH. h,i. Attributions may be inverted. j. $J_{H,F}$ = 53.8 Hz, $J_{C,F}$ = 224.0 Hz. k. $J_{H,F}$ = 25.1 Hz, $J_{C,F}$ = 25.5 Hz. l. $J_{C,F}$ = 2.9 Hz. m. $J_{H,F}$ = 53.7 Hz, $J_{C,F}$ = 228.0 Hz. n. $J_{H,F}$ = 24.2 Hz, $J_{C,F}$ = 26.3 Hz. o. $J_{C,F}$ = 5.9 Hz. p. CH_2Ph (J = -11.8 Hz). q. CH_2Ph (J = -11.8 Hz).

revealed complete consumption of **2** (48 h). The mixture was washed with aqueous $NaHCO_3$ solution and concentrated. Chromatography of the residue gave **3** (0.45 g, 45%) as a colorless foam: $[\alpha]_D$ +70.0° (*c* 0.3, chloroform), ref. 11: $[\alpha]_D$ +70.4° (*c* 0.3, chloroform).

Methyl *O*-(2,3,4,6-Tetra-*O*-benzyl-D-glucopyranosyl)-(1→6)-2,3-di-*O*-benzoyl-α-D-glucopyranoside (4). a) A mixture of **1b**[29] (0.77 g, 1.2 mmol), **2** (0.71 g, 1.3 mmol) and $BF_3 \cdot Et_2O$ (60 µL, 0.5 mmol) in dichloromethane (10 mL) was stirred at room temp. until TLC revealed complete consumption of **2** (24 h). The mixture was washed with aqueous $NaHCO_3$ solution and concentrated. $Bu_4NF \cdot 3\ H_2O$ (0.35 g, 1.0 mmol) was added to a solution of the residue in THF (20 mL), the mixture was stirred at room temp. for 0.5 h and concentrated. Chromatography of the residue gave **4** (0.74 g, 67%) as a colorless foam: α:β = 66:34 (HPLC); ^1H NMR δ (significant peaks) **4β**: 5.11 (bd, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 4.57 (d, 1 H, $J_{1,2}$ = 7.9 Hz, H-1'); **4α**: 5.11 (bd, 2 H, $J_{1,2}$ = 3.6 Hz, H-1,1'); ^{13}C NMR δ (significant peaks) **4β**: 103.7 (C-1'), 97.8 (C-1), 84.7 (C-3'), 55.4 (OMe); **4α**: 96.8, 96.9 (C-1,1'), 82.0 (C-3'), 55.3 (OMe).

Anal. Calcd for $C_{55}H_{56}O_{13}$: C, 71.41; H, 6.10. Found: C, 71.12; H, 6.09.

b) *General Procedure*: A solution of **1b** (271.3 mg, 0.5 mmol), **2** (322.5 mg, 0.5 mmol) and catalyst (10-40 mol-%) in the appropriate solvent (10 mL) was treated as described above to give compounds **4** the anomeric ratio of which was determined by HPLC (see Table 1).

***p*-Methoxyphenyl 4,6-*O*-(1,1,3,3-Tetraisopropyl-1,3-disiloxane-1,3-diyl)-β-D-glucopyranoside (10) and *p*-Methoxyphenyl 2,3:4,6-Bis-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-β-D-glucopyranoside (10').** 1,3-Dichloro-1,1,3,3-tetraisopropyl-1,3-disiloxane[19] (1.74 g, 5.5 mmol) was added dropwise at room temp. to a solution of *p*-methoxyphenyl β-D-glucopyranoside[30] **9** (1.43 g, 5.0 mmol) and imidazole (1.50 g, 22.0 mmol) in DMF (10 mL). The mixture was stirred for 1 h, diluted with water (200 mL) and extracted with dichloromethane. The organic layers were washed with aqueous $NaHCO_3$-solution and concentrated. Chromatography of the residue gave first **10'** (0.56 g, 14%) as colorless crystals: mp 103-105 °C with softening at 95 °C (from methanol); $[\alpha]_D$ -41.9° (*c* 0.7, chloroform).

Anal. Calcd for $C_{37}H_{70}O_9Si_2$: C, 57.62; H, 9.15. Found: C, 57.87; H, 9.15.

Eluted next was **10** (2.04 g, 77%) as colorless crystals: mp 104-108 °C (from acetone/*n*-hexane); $[\alpha]_D$ -74.9° (*c* 0.7, chloroform).

Anal. Calcd for $C_{25}H_{44}O_8Si_2$: C, 56.78; H, 8.39. Found: C, 56.93; H, 8.42.

***p*-Methoxyphenyl 2,3-Di-*O*-benzoyl-4,6-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-β-D-glucopyranoside (11).** Benzoyl bromide (1.85 g, 10.0 mmol) was added to a solution of **10** (1.0 g, 1.9 mmol) in pyridine (30 mL), the

resulting yellow suspension was stirred at room temp. for 24 h and at 60 °C for 5 h. Water (5 mL) was added to the mixture and stirring was continued for 0.5 h. The mixture was diluted with water (200 mL), extracted with dichloromethane and the organic layers were washed with aqueous HCl and $NaHCO_3$ solution. Concentration and chromatography of the residue gave **11** (1.4 g, 100%) as a colorless foam: $[\alpha]_D$ +40.8° (*c* 0.7, chloroform).

Anal. Calcd for $C_{39}H_{52}O_{10}Si_2$: C, 63.56; H, 7.11. Found: C, 63.70; H, 7.16.

Methyl 2-*O*-Benzoyl-4,6-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-β-D-glucopyranoside (13). Benzoyl chloride (1.03 g, 7.3 mmol) was added to a solution of **12**[10] (1.31 g, 3.0 mmol) in pyridine (6 mL) and the mixture was stirred at room temp. for 20 min. Workup as described for the preparation of **11** gave **13** (1.13 g, 70%) as colorless crystals: mp 104-105 °C (from acetone/*n*-hexane); $[\alpha]_D$ -25.6° (*c* 1.0, chloroform).

Anal. Calcd for $C_{26}H_{43}O_8Si_2$: C, 57.85; H, 8.03. Found: C, 57.57; H, 8.09.

Methyl 2-*O*-Benzoyl-6-*O*-dimethylthexylsilyl-3,4-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-α-D-glucopyranoside (17). Chlorodimethylthexylsilane[31] (0.39 g, 2.2 mmol) was added dropwise at 0 °C to a solution of **15**[11] (0.87 g, 2.0 mmol) and imidazole (0.27 g, 4.0 mmol) in DMF (10 mL) and the mixture was stirred at room temp. for 1 h. Water (200 mL) was added, the mixture was extracted with dichloromethane and the combined organic layers were washed with aqueous $NaHCO_3$ solution. Concentration and filtration of the residue with ethyl acetate/*n*-hexane (1:5) over a short column of silica gel gave crude **16** (0.7 g, 60%) as a viscous oil. Benzoyl chloride (2.26 g, 16.0 mmol) in pyridine (10 mL) was added to crude **16** and the mixture was stirred at room temp. for 16 h. Workup as described for the preparation of **11** gave **17** (0.71 g, 52%) as a colorless oil: $[\alpha]_D$ +88.3° (*c* 0.6, chloroform).

Anal. Calcd for $C_{34}H_{62}O_8Si_3$: C, 59.78; H, 9.15. Found: C, 59.84; H, 9.30.

Methyl 2-*O*-Benzoyl-3-*O*-benzyl-4,6-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-β-D-glucopyranoside (20). A solution of 1,3-dichloro-1,1,3,3-tetraisopropyl-1,3-disiloxane (1.12 g, 3.5 mmol) in dichloromethane (2 mL) was added dropwise at 0 °C to a solution of **18**[32] (0.9 g, 3.2 mmol) and imidazole (0.96 g, 14.1 mmol) in DMF (20 mL) and the mixture was stirred at room temp. for 1 h. Workup as described for the preparation of **10** gave crude **19** (1.24 g, 74%) as a viscous oil. Benzoyl chloride (2.26 g, 16.0 mmol) was added to a solution of crude **19** in pyridine (50 mL) and the mixture was stirred for 2 h. Workup as described for the preparation of **11** gave **20** (1.12 g, 55%) as a colorless foam: $[\alpha]_D$ +28.0° (*c* 0.6, chloroform).

Anal. Calcd for $C_{33}H_{50}O_8Si_2$: C, 62.82; H, 8.00. Found: C, 62.73; H, 8.10.

Benzyl 2-*O*-Benzoyl-4,6-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-α-D-mannopyranoside (23). Benzoyl chloride (0.7 g, 5.0 mmol) was

added to a solution of **22**[10] (1.44 g, 2.8 mmol) in pyridine (20 mL) and the mixture was stirred at room temp. for 2 h. Workup as described for the preparation of **11** (without chromatography) afforded material which was crystallized from *n*-hexane to give **23** (1.6 g, 93%): mp 116 °C; $[\alpha]_D$ +3.5° (*c* 0.2, chloroform).

Anal. Calcd for $C_{32}H_{48}O_8Si_2$: C, 62.30; H, 7.84. Found: C, 62.16; H, 8.06.

Methyl 3-*O*-Benzyl-4,6-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-β-D-galactopyranoside (27) and Methyl 3-*O*-Benzyl-6-*O*-(1-hydroxy-1,1,3,3-tetraisopropyl-1,3-disiloxane-3-yl)-β-D-galactopyranoside (33). A solution of 1,3-dichloro-1,1,3,3-tetraisopropyl-1,3-disiloxane (0.87 g, 2.25 mmol) in dichloromethane (5 mL) was added dropwise at 0 °C to a solution of **26**[21] (0.71 g, 2.5 mmol) and imidazole (1.25 g, 11.0 mmol) in DMF (10 mL) and the mixture was stirred at room temp. for 1 h. Workup as described for the preparation of **10** and chromatography gave first **27** (0.55 g, 44%) as colorless crystals: mp 73-75 °C (*n*-hexane); $[\alpha]_D$ +34.0° (*c* 0.5, chloroform).

Anal. Calcd for $C_{26}H_{46}O_7Si_2$: C, 59.28; H, 8.80. Found: C, 59.53; H, 8.90.

Eluted next was **33** (0.5 g, 42%) as colorless crystals: mp 46 °C (*n*-hexane); $[\alpha]_D$ -8.0° (*c* 1.2, chloroform).

Anal. Calcd for $C_{26}H_{48}O_8Si_2$: C, 57.32; H, 8.88. Found: C, 57.29; H, 9.07.

Methyl 2-*O*-Benzoyl-3-*O*-benzyl-4,6-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-β-D-galactopyranoside (28). A solution of 1,3-dichloro-1,1,3,3-tetraisopropyl-1,3-disiloxane (0.87 g, 2.25 mmol) in dichloromethane (2 mL) was added dropwise at 0 °C to a solution of **26** (0.71 g, 2.5 mmol) in pyridine (5 mL), the mixture was stirred at room temp. for 12 h, diluted with water (200 mL) and extracted with dichloromethane. The organic layers were washed with aqueous HCl and $NaHCO_3$ solution and concentrated to give crude **27** (1.19 g, 90%) as a semicrystalline material. Benzoyl chloride (3.0 g, 21.2 mmol) was added to a solution of crude **27** in pyridine (20 mL) and the mixture was stirred at room temp. for 5 h. Workup as described for the preparation of **11** gave **28** (1.28 g, 81%) as a viscous oil: $[\alpha]_D$ +32.8° (*c* 0.2, chloroform).

Anal. Calcd for $C_{33}H_{50}O_8Si_2$: C, 62.82; H, 7.99. Found: C, 63.03; H, 7.88.

Benzyl 3-*O*-Benzoyl-β-D-galactopyranoside (30). A suspension of **29**[33] (1.35 g, 5.0 mmol) and dibutyltin oxide (1.25 g, 5.0 mmol) in methanol (20 mL) was refluxed until a clearing of the solution (2 h). The solvent was evaporated, the residue resuspended in dioxane (20 mL) and benzoyl chloride (0.78 g, 5.5 mmol) was added. The resulting solution was stirred at room temp. for 2 h and concentrated. Chromatography of the residue gave **30** (1.07 g, 57%) as a colorless foam: $[\alpha]_D$ +27.5° (*c* 0.5, methanol).

Anal. Calcd for $C_{20}H_{22}O_7 \cdot 0.5\ H_2O$: C, 62.66; H, 6.05. Found: C, 62.66; H, 5.94.

Benzyl 2,3-Di-*O*-benzoyl-4,6-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-β-D-galactopyranoside (32). A solution of 1,3-dichloro-1,1,3,3-tetraisopropyl-1,3-disiloxane (1.01 g, 2.6 mmol) in dichloromethane (5 mL) was added dropwise at 0 °C to a solution of **30** (1.0 g, 2.6 mmol) in pyridine (10 mL) and the mixture was stirred at room temp. for 10 h. Workup as described for the preparation of **10** (without chromatography) gave crude **31** (1.55 g, 97%) as a viscous oil. Benzoyl chloride (2.26 g, 16.0 mmol) was added to a solution of crude **31** in pyridine (20 mL) and the mixture was stirred for 3 h. Workup as described for the preparation of **11** gave **32** (1.77 g, 94%) as a highly viscous oil: $[\alpha]_D$ +23.0° (*c* 0.3, chloroform).

Anal. Calcd for $C_{39}H_{52}O_9Si_2$: C, 64.97; H, 7.27. Found: C, 64.56; H, 7.32.

Methyl 2,4-Di-*O*-benzoyl-3-*O*-benzyl-6-*O*-(1-hydroxy-1,1,3,3-tetraisopropyl-1,3-disiloxane-3-yl)-β-D-galactopyranoside (34) and its Desilylation. a) Benzoyl chloride (3.0 g, 21.2 mmol) was added to a solution of **33** (0.45 g, 0.83 mmol) in pyridine (10 mL) and the mixture was stirred at room temp. for 2 h. Workup as described for the preparation of **11** gave **34** (0.62 g, 99%) as a colorless foam: $[\alpha]_D$ +77.1° (*c* 1.2, chloroform).

Anal. Calcd for $C_{40}H_{56}O_{10}Si_2$: C, 63.80; H, 7.50. Found: C, 63.64; H, 7.45.

b) $BF_3 \cdot Et_2O$ (0.5 mL) was added to a solution of **34** (0.53 g, 0.7 mmol) in methanol (10 mL) and the mixture was stirred at room temp. until TLC revealed complete conversion of the starting material into a single slower moving product (12 h). Dichloromethane (80 mL) was added and the resulting solution was washed with aqueous $NaHCO_3$ solution. Concentration and chromatography of the residue gave methyl 2,4-di-*O*-benzoyl-3-*O*-benzyl-β-D-galactopyranoside (0.3 g, 87%) as a colorless foam: $[\alpha]_D$ +142° (*c* 1.1, chloroform), $[\alpha]_D$ +147° (*c* 1.4, chloroform).[23]

Phenyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (6) and Phenyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2,3-di-*O*-benzoyl-4-*O*-(1-fluoro-1,1,3,3-tetraisopropyl-1,3-disiloxane-3-yl)-1-thio-β-D-glucopyranoside (35). $BF_3 \cdot Et_2O$ (12 μL, 0.1 mmol) was added to a solution of **1a** (0.42 g, 1.2 mmol) and **5**[10] (0.72 g, 1.0 mmol) in dichloromethane (10 mL) and the mixture was stirred at room temp. until TLC revealed the complete consumption of **5** (20 h). Workup as described for the preparation of compound **3** and chromatography gave first **35** (0.68 g, 63%) as a colorless foam: $[\alpha]_D$ +60.9° (*c* 0.6, chloroform).

Anal. Calcd for $C_{52}H_{69}FO_{17}SSi_2$: C, 58.19; H, 6.48; S, 2.99. Found: C, 57.77; H, 6.38; S, 2.75.

Eluted next was **6** (50 mg, 11%) as colorless crystals: mp 114 °C (*n*-hexane), mp[34] 117-118 °C.

Phenyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2,3-di-*O*-benzoyl-1-thio-β-D-glucopyranoside (36). $Bu_4NF{\cdot}3\ H_2O$ (15 mg, 0.05 mmol) was added to a solution of **35** (0.11 g, 0.1 mmol) in THF (5 mL) and the solution was stirred until TLC showed the complete conversion of the starting material into a single slower moving product (5 min). Concentration and chromatography of the residue gave **36** (62 mg, 84%) as a colorless foam: $[\alpha]_D$ +30.9° (*c* 0.1, chloroform).

Anal. Calcd for $C_{40}H_{42}O_{16}S$: C, 59.25; H, 5.22. Found: C, 59.27; H, 5.24.

Ethyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (8) and Ethyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2,3-di-*O*-benzoyl-4-*O*-(1-fluoro-1,1,3,3-tetraisopropyl-1,3-disiloxane-3-yl)-1-thio-β-D-glucopyranoside (37). $BF_3{\cdot}Et_2O$ (86 μL, 0.72 mmol) was added to a solution of **1a** (0.84 g, 2.4 mmol) and **7**[10] (1.61 g, 2.39 mmol) in dichloromethane (20 mL) and the mixture was stirred at room temp. until TLC revealed the complete consumption of **7** (62 h). Workup as described for the preparation of compound **3** and chromatography gave first **37** (1.71 g, 70%) as a colorless foam: $[\alpha]_D$ +27.6° (*c* 0.5, chloroform).

Anal. Calcd for $C_{48}H_{69}FO_{17}SSi_2$: C, 56.23; H, 6.78. Found: C, 56.28; H, 6.71.

Eluted next was **8** (94 mg, 10%) as colorless crystals: mp 78 °C (*n*-hexane), mp[35] 78.5-79.5 °C.

***p*-Methoxyphenyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2,3-di-*O*-benzoyl-4-*O*-(1-fluoro-1,1,3,3-tetraisopropyl-1,3-disiloxane-3-yl)-β-D-glucopyranoside (38).** A solution of $BF_3{\cdot}Et_2O$ (6 μL, 0.05 mmol), **1a** (175 mg, 0.5 mmol) and **11** (310 mg, 0.42 mmol) in dichloromethane (5 mL) was processed for 14 h as described for the preparation of compound **35** to give **38** (310 mg, 68%) as a colorless foam: $[\alpha]_D$ +48.1° (*c* 0.8, chloroform).

Anal. Calcd for $C_{53}H_{71}FO_{19}Si_2$: C, 58.55; H, 6.58. Found: C, 58.00; H, 6.57.

***p*-Methoxyphenyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2,3-di-*O*-benzoyl-β-D-glucopyranoside (39).** A solution of $Bu_4NF{\cdot}3\ H_2O$ (0.1 g, 0.32 mmol) and **38** (0.21 g, 0.19 mmol) in THF (20 mL) was processed as described for the preparation of compound **36** to give **39** (0.12 g, 77%) as colorless crystals: mp 90 °C (*n*-hexane); $[\alpha]_D$ +34.6° (*c* 0.3, chloroform).

Anal. Calcd for $C_{41}H_{44}O_{18}$: C, 59.70; H, 5.38. Found: C, 59.67; H, 5.39.

Methyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2-*O*-benzoyl-3-*O*-benzyl-4-*O*-(1-fluoro-1,1,3,3-tetraisopropyl-1,3-disiloxane-3-yl)-β-D-glucopyranoside (40). A solution of $BF_3{\cdot}Et_2O$ (40 μL, 0.3 mmol), **1a** (0.53 g, 1.5 mmol) and **20** (0.88 g, 1.4 mmol) in dichloromethane (20 mL) was processed for 48

h as described for the preparation of compound **35** to give **40** (0.9 g, 66%) as a colorless foam: $[\alpha]_D$ +15.9° (*c* 0.3, chloroform).

Anal. Calcd for $C_{47}H_{69}FO_{17}Si_2$: C, 57.53; H, 7.09. Found: C, 57.78; H, 7.04.

Methyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2-*O*-benzoyl-3-*O*-benzyl-β-D-glucopyranoside (41). A solution of $Bu_4NF{\cdot}3\ H_2O$ (0.1 g, 0.32 mmol) and **40** (0.26 g, 0.27 mmol) in THF (5 mL) was processed as described for the preparation of compound **36** to give **41** (0.17 g, 88%) as a colorless foam: $[\alpha]_D$ -9.1° (*c* 0.2, chloroform).

Anal. Calcd for $C_{35}H_{42}O_{16}$: C, 58.49; H, 5.89. Found: C, 58.69; H, 5.90.

Methyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2-*O*-benzoyl-4-*O*-(1-fluoro-1,1,3,3-tetraisopropyl-1,3-disiloxane-3-yl)-β-D-glucopyranoside (42). A solution of $BF_3{\cdot}Et_2O$ (36 μL, 0.3 mmol), **1a** (1.05 g, 3.0 mmol) and **13** (1.61 g, 2.85 mmol) in dichloromethane (20 mL) was processed for 24 h as described for the preparation of compound **35** to give **42** (1.51 g, 59%) as a colorless foam: $[\alpha]_D$ -7.9° (*c* 0.8, chloroform).

Anal. Calcd for $C_{40}H_{63}FO_{17}Si_2$: C, 53.92; H, 7.13. Found: C, 54.15; H, 7.20.

Methyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2-*O*-benzoyl-β-D-glucopyranoside (43). A solution of $Bu_4NF{\cdot}3\ H_2O$ (0.13 g, 0.4 mmol) and **42** (0.36 g, 0.4 mmol) in THF (10 mL) was processed as described for the preparation of compound **36** to give **43** (0.25 g, 99%) as a colorless foam: $[\alpha]_D$ -30.9° (*c* 0.3, chloroform).

Anal. Calcd for $C_{28}H_{36}O_{16}$: C, 53.50; H, 5.77. Found: C, 53.34; H, 5.83.

Benzyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2-acetamido-3-*O*-benzoyl-2-deoxy-4-*O*-(1-fluoro-1,1,3,3-tetraisopropyl-1,3-disiloxane-3-yl)-α-D-glucopyranoside (44). A solution of $BF_3{\cdot}Et_2O$ (6 μL, 0.05 mmol), **1a** (175 mg, 0.5 mmol) and **21**[10] (329 mg, 1.4 mmol) in dichloromethane (10 mL) was processed for 3 days as described for the preparation of compound **35** to give **44** (0.3 g, 60%) as a colorless foam: $[\alpha]_D$ +56.7° (*c* 1.3, chloroform).

Anal. Calcd for $C_{48}H_{70}FNO_{17}Si_2$: C, 57.18; H, 6.99; N, 1.39. Found: C, 57.02; H, 7.13; N, 1.51.

Benzyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2-acetamido-3-*O*-benzoyl-2-deoxy-α-D-glucopyranoside (45). A solution of $Bu_4NF{\cdot}3\ H_2O$ (0.1 g, 0.32 mmol) and **44** (0.21 g, 0.21 mmol) in THF (5 mL) was processed as described for the preparation of compound **36** to give **45** (0.15 g, 96%) as a colorless foam: $[\alpha]_D$ +49.6° (*c* 0.8, chloroform).

Anal. Calcd for $C_{36}H_{43}NO_{16}$: C, 57.98; H, 5.81; N, 1.88. Found: C, 57.54; H, 5.85; N, 1.71.

Benzyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2,3-di-*O*-benzoyl-4-*O*-(1-fluoro-1,1,3,3-tetraisopropyl-1,3-disiloxane-3-yl)-α-D-mannopyranoside (46). a) A solution of $BF_3 \cdot Et_2O$ (6 μL, 0.05 mmol), **1a** (175 mg, 0.5 mmol) and **24**[10] (360.5 mg, 0.5 mmol) in dichloromethane (10 mL) was processed for 24 h as described for the preparation of compound **35** to give **46** (500 mg, 93%) as colorless crystals: mp 115 °C (*n*-hexane); $[\alpha]_D$ -20.5° (*c* 0.2, chloroform).

Anal. Calcd for $C_{53}H_{71}FO_{18}Si_2$: C, 59.42; H, 6.68. Found: C, 59.25; H, 6.66.

b) A solution of **69**[36] (246.3 mg, 0.5 mmol) in dichloromethane (1 mL) was added at -20 °C to a solution of **65** (300 mg, 0.4 mmol, see below) and trimethylsilyl trifluoromethanesulfonate (6.6 μL, 0.04 mmol) in dichloromethane (2 mL) and the mixture was stirred at -20 °C for 0.5 h. The solution was washed with aqueous $NaHCO_3$ solution and concentrated. Chromatography of the residue gave **46** (334 mg, 78%).

Benzyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2,3-di-*O*-benzoyl-α-D-mannopyranoside (47). A solution of $Bu_4NF \cdot 3\ H_2O$ (0.15 g, 0.48 mmol) and **46** (0.54 g, 0.5 mmol) in THF (10 mL) was processed as described for the preparation of compound **36** to give **47** (0.31 g, 76%) as a colorless foam: $[\alpha]_D$ -23.2° (*c* 0.2, chloroform).

Anal. Calcd for $C_{41}H_{44}O_{17}$: C, 60.98; H, 5.48. Found: C, 60.99; H, 5.58.

Benzyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2-*O*-benzoyl-4-*O*-(1-fluoro-1,1,3,3-tetraisopropyl-1,3-disiloxane-3-yl)-α-D-mannopyranoside (48). A solution of $BF_3 \cdot Et_2O$ (6 μL, 0.05 mmol), **1a** (175 mg, 0.5 mmol) and **23** (308.5 mg, 0.5 mmol) in dichloromethane (10 mL) was processed for 24 h as described for the preparation of compound **35** to give **48** (410 mg, 85%) as a colorless foam: $[\alpha]_D$ +13.3° (*c* 0.2, chloroform).

Anal. Calcd for $C_{46}H_{67}FO_{17}Si_2$: C, 57.12; H, 6.98. Found: C, 57.14; H, 7.01.

Benzyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2-*O*-benzoyl-α-D-mannopyranoside (49). A solution of $Bu_4NF \cdot 3\ H_2O$ (0.15 g, 0.48 mmol) and **48** (0.8 g, 0.83 mmol) in THF (20 mL) was processed as described for the preparation of compound **36** to give **49** (0.51 g, 87%) as a colorless foam: $[\alpha]_D$ 0.0°, $[\alpha]_{365}$ +13.6° (*c* 1.0, chloroform).

Anal. Calcd for $C_{34}H_{40}O_{16}$: C, 57.95; H, 5.72. Found: C, 57.95; H, 5.86.

Methyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2,3-di-*O*-benzoyl-4-*O*-(1-fluoro-1,1,3,3-tetraisopropyl-1,3-disiloxane-3-yl)-α-D-galactopyranoside (50). A solution of $BF_3 \cdot Et_2O$ (10 μL, 0.08 mmol), **1a** (0.21 g, 0.6 mmol) and **25**[10] (0.35 g, 0.58 mmol) in dichloromethane (5 mL) was processed for 6 h as described for the preparation of compound **35** to give **50** (0.45 g, 93%) as a colorless foam: $[\alpha]_D$ +58.9° (*c* 0.4, chloroform).

Anal. Calcd for $C_{47}H_{67}FO_{18}Si_2$: C, 56.72; H, 6.78. Found: C, 56.44; H, 6.82.

Methyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2,3-di-*O*-benzoyl-α-D-galactopyranoside and Methyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2,4-di-*O*-benzoyl-α-D-galactopyranoside (51). A solution of $Bu_4NF{\cdot}3\ H_2O$ (0.1 g, 0.32 mmol) and **50** (0.28 g, 0.28 mmol) in THF (10 mL) was processed as described for the preparation of compound **36** to give **51** (0.2 g, 97%) as an unseparated 1:2 mixture of the 3- and 4-*O*-benzoylated derivative: ^1H NMR δ (significant peaks): **51** (3-*O*-benzoate) 4.54 (d, 1H, $J_{1,2}$ = 7.9 Hz, H-1'), 4.35 (bs, 1H, H-4), 3.40 (s, 3H, OMe); **51** (4-*O*-benzoate) 4.64 (d, 1H, $J_{1,2}$ = 7.9 Hz, H-1'), 5.66 (bd, 1H, H-4), 3.41 (s, 3H, OMe); ^{13}C NMR δ (significant peaks): **51** (3-*O*-benzoate) 100.9 (C-1'), 97.3 (C-1); **51** (4-*O*-benzoate) 101.0 (C-1'), 97.4 (C-1).

Anal. Calcd for $C_{35}H_{40}O_{17}$: C, 57.38; H, 5.50. Found: C, 57.20; H, 5.57.

Methyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-galactopyranoside (52). Benzoyl chloride (0.7 g, 4.9 mmol) was added to a solution of **51** (165 mg, 0.23 mmol) in pyridine (10 mL) and the mixture was stirred at room temp. for 4 h. Workup as described for the preparation of **11** gave **52** (160 mg, 83%) as a colorless foam: $[\alpha]_D$ +133.5° (*c* 0.4, chloroform).

Anal. Calcd for $C_{42}H_{44}O_{18}$: C, 60.28; H, 5.30. Found: C, 60.04; H, 5.20.

Methyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2-*O*-benzoyl-3-*O*-benzyl-4-*O*-(1-fluoro-1,1,3,3-tetraisopropyl-1,3-disiloxane-3-yl)-β-D-galactopyranoside (53), Methyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2-*O*-benzoyl-3-*O*-benzyl-β-D-galactopyranoside (54) and Methyl 6-*O*-Acetyl-2-*O*-benzoyl-3-*O*-benzyl-4-*O*-(1-fluoro-1,1,3,3-tetraisopropyl-1,3-disiloxane-3-yl)-β-D-galactopyranoside (71). a) A solution of $BF_3{\cdot}Et_2O$ (6 μL, 0.05 mmol), **1a** (125 mg, 0.5 mmol) and **28** (315.5 mg, 0.5 mmol) in dichloromethane (5 mL) was processed for 3 days as described for the preparation of compound **35**. Chromatography gave first **53** (98.1 mg, 20%) as a colorless foam: $[\alpha]_D$ +13.0° (*c* 0.2, chloroform).

Anal. Calcd for $C_{47}H_{69}FO_{17}Si_2$: C, 57.53; H, 7.09. Found: C, 57.22; H, 7.09.

Eluted next was **54** (79.1 mg, 22%) as a colorless foam: $[\alpha]_D$ -4.2° (*c* 0.2, chloroform).

Anal. Calcd for $C_{35}H_{42}O_{16}$: C, 58.49; H, 5.89. Found: C, 58.45; H, 5.93.

b) A solution of **69**[32] (0.34 g, 0.69 mmol) in dichloromethane (2 mL) was added at -20 °C to a solution of **70** (0.42 g, 0.65 mmol, see below) and trimethylsilyl trifluoromethanesulfonate (10 μL, 0.07 mmol) in dichloromethane (8 mL) and the mixture was stirred at -20 °C for 0.5 h. The solution was neutralized with pyridine and worked up

as described for the preparation of compound **46** (b). Chromatography gave first **71** (77.2 mg, 17%) as a colorless oil: $[\alpha]_D$ +30.3° (*c* 0.3, chloroform).

Anal. Calcd for $C_{35}H_{53}FO_9Si_2$: C, 60.66; H, 7.71. Found: C, 60.86; H, 7.75.

Eluted next was compound **53** (0.45 g, 70%).

c) A solution of $Bu_4NF{\cdot}3\ H_2O$ (94.6 mg, 0.3 mmol) and **53** (258 mg, 0.26 mmol) in THF (2 mL) was processed as described for the preparation of compound **36** to give compound **54** (143.7 mg, 77%).

Methyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2-*O*-benzoyl-3,4-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-α-D-glucopyranoside (55). A solution of $BF_3{\cdot}Et_2O$ (12 μL, 0.1 mmol), **1c** (0.51 g, 0.8 mmol) and **17** (0.49 g, 0.72 mmol) in dichloromethane (10 mL) was processed for 2.5 h as described for the preparation of compound **35** to give **55** (0.51 g, 61%) as a colorless foam: $[\alpha]_D$ +37.7° (*c* 0.3, chloroform).

Anal. Calcd for $C_{52}H_{78}O_{25}Si_2$: C, 53.87; H, 6.78. Found: C, 53.88; H, 6.89.

Methyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2-*O*-benzoyl-α-D-glucopyranoside (56). Pyridine-polyhydrogen fluoride (50 μL, 1.8 mmol) was added to a solution of **55** (230 mg, 0.2 mmol) in dichloromethane (5 mL) and the mixture was stirred at room temp. until TLC revealed the complete conversion of the starting material into a single slower moving product (24 h). Workup as described for the preparation of compound **35** (without chromatography) gave a material which was crystallized from ethyl acetate/*n*-hexane to give **56** (180 mg, 98%): mp 211 °C; $[\alpha]_D$ +14.7° (*c* 0.2, chloroform).

Anal. Calcd for $C_{40}H_{52}O_{24}$: C, 52.40; H, 5.72. Found: C, 52.32; H, 5.69.

Methyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2,3-di-*O*-benzoyl-4-*O*-(1-fluoro-1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-α-D-glucopyranoside (57). A solution of $BF_3{\cdot}Et_2O$ (3 μL, 0.025 mmol), **1c** (190 mg, 0.3 mmol) and **2**[11] (161 mg, 0.25 mmol) in dichloromethane (2.5 mL) was processed for 24 h as described for the preparation of compound **35** to give **57** (236.7 mg, 74%) as a colorless foam: $[\alpha]_D$ +35.1° (*c* 0.7, chloroform).

Anal. Calcd for $C_{59}H_{83}FO_{26}Si_2$: C, 55.51; H, 6.52. Found: C, 55.27; H, 6.57.

Methyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl)-(1→6)-2,3-di-*O*-benzoyl-α-D-gluco-pyranoside (58). A solution of $Bu_4NF{\cdot}3\ H_2O$ (0.01 g, 0.03 mmol) and **57** (180 mg, 0.14 mmol) in THF (5 mL) was processed as described for the preparation of

compound **36** to give **58** (135 mg, 95%) as a colorless foam: $[\alpha]_D$ +44.8° (*c* 0.6, chloroform).

Anal. Calcd for $C_{47}H_{56}O_{25}$: C, 55.29; H, 5.53. Found: C, 55.55; H, 5.51.

Benzyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→6)-2,3-di-*O*-benzoyl-4-*O*-(1-fluoro-1,1,3,3-tetraisopropyl-1,3-disiloxane-3-yl)-β-D-galactopyranoside (59). A solution of $BF_3{\cdot}Et_2O$ (123 μL, 1.0 mmol), **1d** (0.2 g, 0.57 mmol) and **32** (0.41 g, 0.57 mmol) in dichloromethane (4 mL) was processed for 0.5 h as described for the preparation of compound **35** to give **59** (0.32 g, 53%) as a colorless foam: $[\alpha]_D$ +2.7° (*c* 0.4, chloroform).

Anal. Calcd for $C_{53}H_{71}FO_{18}Si_2$: C, 59.42; H, 6.68. Found: C, 59.29; H, 6.62.

Benzyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside (60). A solution of $Bu_4NF{\cdot}3\ H_2O$ (0.01 g, 0.03 mmol) and **59** (242 mg, 0.27 mmol) in THF (5 mL) was processed as described for the preparation of compound **36** to give material that was treated with benzoyl chloride (1.2 g, 8.5 mmol) in pyridine (4 mL) for 2 h at room temp. Water (100 mL) was added to the solution and the resulting mixture was extracted with dichloromethane. The combined organic layers were washed with aqueous HCl and $NaHCO_3$ solution, concentrated, and the residue was chromatographed to give **60** (176.2 mg, 85%) as a colorless foam: $[\alpha]_D$ +79.4° (*c* 0.5, chloroform).

Anal. Calcd for $C_{48}H_{48}O_{18}$: C, 63.15; H, 5.30. Found: C, 62.94; H, 5.35.

4,6-*O*-(1,1,3,3-Tetraisopropyl-1,3-disiloxane-1,3-diyl)-α-D-glucopyranosyl Fluoride (61). A solution of 1,3-dichloro-1,1,3,3-tetraisopropyl-1,3-disiloxane (3.47 g, 11.0 mmol) in dichloromethane (10 mL) was added dropwise at 0 °C to a solution of α-D-glucopyranosyl fluoride (1.82 g, 10.0 mmol) and imidazole (3.0 g, 44.0 mmol) in DMF (20 mL) and the mixture was stirred at room temp. for 0.5 h. Workup as described for the preparation of **10** gave **61** (3.26 g, 78%) as a viscous oil: $[\alpha]_D$ +57.0° (*c* 0.2, chloroform).

Anal. Calcd for $C_{18}H_{37}FO_6Si_2$: C, 50.93; H, 8.78. Found: C, 50.82; H, 8.73.

2,3-Di-*O*-benzoyl-4,6-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-α-D-glucopyranosyl Fluoride (62). Benzoyl bromide (1.67 g, 9.0 mmol) was added to a solution of **61** (1.14 g, 2.7 mmol) in pyridine (20 mL) and the mixture was stirred at room temp. for 1 h and at 60 °C for 5 h. Workup as described for the preparation of **11** gave **62** (1.50 g, 88%) as a colorless foam: $[\alpha]_D$ +76.7° (*c* 0.5, chloroform).

Anal. Calcd for $C_{32}H_{45}FO_8Si_2$: C, 60.73; H, 7.17. Found: C, 60.66; H, 7.26.

2,3-Di-*O*-benzoyl-4,6-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-α-D-glucopyranosyl Chloride (63). A suspension of **14**[10] (129.0 mg, 0.2 mmol) and a catalytic amount of $ZnCl_2$ (ca. 5 mg) in 4:1 chloroform/dichloromethyl methyl

ether (2 mL) was stirred at 40–45 °C until TLC revealed complete conversion of the starting material into a single faster moving product (3 h). Concentration and chromatography of the residue gave **63** (117.6 mg, 90%) as a viscous oil: $[\alpha]_D$ +127.3° (*c* 0.4, chloroform).

Anal. Calcd for $C_{32}H_{45}ClO_8Si_2$: C, 59.19; H, 6.99; Cl, 5.46. Found: C, 59.38; H, 7.08; Cl, 5.72.

Methyl *O*-[2,3-Di-*O*-benzoyl-4,6-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-β-D-glucopyranosyl]-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranoside (64). a) A suspension of **7**[10] (86.5 mg, 0.13 mmol), methyl 2,3,4-tri-*O*-benzoyl-β-D-glucopyranoside (70.9 mg, 0.14 mmol), methyl trifluoromethanesulfonate (55 μL, 0.5 mmol) and molecular sieves (3 Å, 0.1 g) in dichloromethane (2 mL) was stirred at room temp. until TLC revealed complete consumption of the starting materials (4 h). The mixture was neutralized by addition of Et_3N (0.5 mL), diluted with dichloromethane and washed with aqueous $NaHCO_3$ solution. Concentration and chromatography of the residue gave **64** (111.7 mg, 77%) as colorless crystals: mp 205 °C (*n*-hexane); $[\alpha]_D$ +3.9° (*c* 0.5, chloroform).

Anal. Calcd for $C_{60}H_{70}O_{17}Si_2$: C, 64.38; H, 6.30. Found: C, 64.32; H, 6.33.

b) $BF_3{\cdot}Et_2O$ (395 μL, 3.16 mmol) was added to a solution of **62** (1.0 g, 1.58 mmol), methyl 2,3,4-tri-*O*-benzoyl-β-D-glucopyranoside (0.81 g, 1.6 mmol) and Et_3N (224 μL, 1.6 mmol) in dichloromethane (10 mL) and the resulting yellow mixture was stirred at room temp. until TLC revealed complete consumption of the starting materials (20 min). The solution was washed with aqueous $NaHCO_3$ solution and concentrated. Chromatography of the residue gave **64** (1.49 g, 84%).

c) A solution of **63** (97.0 mg, 0.15 mmol) and methyl 2,3,4-tri-*O*-benzoyl-β-D-glucopyranoside (101.3 mg, 0.2 mmol) in dichloromethane (5 mL) was added at room temp. to a suspension of silver trifluoromethanesulfonate (128.5 mg, 0.5 mmol) and molecular sieves (3 Å, 0.1 g) in dichloromethane (5 mL), the mixture was stirred for 10 min and filtered. The filtrate was washed with aqueous $Na_2S_2O_3$ and $NaHCO_3$ solution and concentrated. Chromatography of the residue gave **64** (111.0 mg, 66%).

Benzyl 2,3-Di-*O*-benzoyl-4-*O*-(1-fluoro-1,1,3,3-tetraisopropyl-1,3-disiloxane-3-yl)-α-D-mannopyranoside (65). Pyridine-polyhydrogen fluoride (100 μL, 3.5 mmol) was added to a solution of **24**[10] (360.5 mg, 0.5 mmol) in dichloromethane (10 mL) and the mixture was stirred at room temp. until TLC revealed the complete conversion of the starting material into a single slower moving product (5 min). Workup as described for the preparation of compound **35** gave **65** (359 mg, 97%) as a colorless oil: $[\alpha]_D$ -26.6° (*c* 0.5, chloroform).

Anal. Calcd for $C_{39}H_{53}FO_9Si_2$: C, 63.21; H, 7.21. Found: C, 63.07; H, 7.20.

2,3-Di-*O*-benzoyl-4,6-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-α-D-mannopyranose (66). A suspension of **24**[10] (1.44 g, 2.0 mmol) and Pd

(10% on charcoal, 2 g) in ethyl acetate (20 mL) was treated with H_2 at atmospheric pressure until TLC revealed complete conversion of the starting material into a single slower moving product (18 h). Filtration of the mixture, concentration of the filtrate and crystallization of the residue from *n*-hexane gave **66** (1.2 g, 95%): mp 164 °C; $[\alpha]_D$ -97.9° (*c* 0.2, pyridine, after 1 h at room temp.).

Anal. Calcd for $C_{32}H_{46}O_9Si_2$: C, 60.92; H, 7.35. Found: C, 60.68; H, 7.30.

2,3-Di-*O*-benzoyl-4,6-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-α-D-mannopyranosyl Trichloroacetimidate (67). A suspension of **66** (0.69 g, 1.1 mmol), trichloroacetonitrile (2 mL) and K_2CO_3 (2 g, 14.5 mmol)) in dichloromethane was stirred at room temp. until TLC revealed the complete conversion of the starting material into a single faster moving product (4 h). Filtration of the mixture, concentration of the filtrate and crystallization of the residue from *n*-hexane gave **67** (0.76 g, 89%): mp 147 °C; $[\alpha]_D$ -59.6° (*c* 0.6, chloroform).

Anal. Calcd for $C_{34}H_{46}Cl_3NO_9Si_2$: C, 52.67; H, 5.98; Cl, 13.72; N, 1.81. Found: C, 52.56; H, 5.98; Cl, 13.83; N, 1.73.

Methyl *O*-[2,3-Di-*O*-benzoyl-4,6-*O*-(1,1,3,3-tetraisopropyl-1,3-disiloxane-1,3-diyl)-α-D-mannopyranosyl]-(1→6)-2,3,4-tri-*O*-benzoyl-β-D-glucopyranoside (68). A solution of **67** (310 mg, 0.4 mmol) in dichloromethane (1 mL) was added at -20 °C to a solution of methyl 2,3,4-tri-*O*-benzoyl-β-D-glucopyranoside (253 mg, 0.5 mmol) and trimethylsilyl trifluoromethanesulfonate (6.6 µL, 0.04 mmol) in dichloromethane (5 mL) and the mixture was stirred at -20 °C for 20 min. Workup as described for the preparation of compound **46** (b) gave **68** (370 mg, 83%) as a colorless foam: $[\alpha]_D$ -28.4° (*c* 1.5, chloroform).

Anal. Calcd for $C_{60}H_{70}O_{17}Si_2$: C, 64.38; H, 6.30. Found: C, 64.58; H, 6.17.

Methyl 2-*O*-Benzoyl-3-*O*-benzyl-4-*O*-(1-fluoro-1,1,3,3-tetraisopropyl-1,3-disiloxane-3-yl)-β-D-galactopyranoside (70). Pyridine-polyhydrogen fluoride (100 µL, 3.5 mmol) was added to a solution of **28** (315.5 mg, 0.5 mmol) in dichloromethane (10 mL) and the mixture was stirred at room temp. until TLC revealed the complete conversion of the starting material into a single slower moving product (5 min). Workup as described for the preparation of compound **35** gave **70** (277.2 mg, 85%) as a colorless oil: $[\alpha]_D$ +22.7° (*c* 0.1, chloroform).

Anal. Calcd for $C_{33}H_{51}FO_8Si_2$: C, 60.89; H, 7.90. Found: C, 60.89; H, 7.80.

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