Tetrahedron: *Asymmetry* 19 (2008) 1494–1503

Contents lists available at ScienceDirect

Tetrahedron: *Asymmetry*

journal homepage: www.elsevier.com/locate/tetasy

Comparative investigations on the regioselective mannosylation of 2,3,4-triols of mannose

Piotr Cmoch [a,b], Zbigniew Pakulski [a,*]

[a] *Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warszawa, Poland*
[b] *Pharmaceutical Research Institute, Rydygiera 8, 01-793 Warszawa, Poland*

ARTICLE INFO

Article history:
Received 12 May 2008
Accepted 29 May 2008
Available online 24 June 2008

ABSTRACT

Regioselective glycosylation of 2,3,4-unprotected benzyl α-D-mannopyranoside and allyl α- and -β-D-mannopyranosides has been investigated. The configuration at the anomeric centre influences the outcome of the reaction. Possible role of hydrogen-bonding network in glycosylation of the above triols used as glycosidic acceptors is discussed.

1. Introduction

A practical, chemical synthesis of oligosaccharides is commonly recognized as a difficult task. The control of the regiochemistry is usually complicated by the necessity of using a protection–deprotection strategy for differentiation of hydroxyl groups of similar reactivity which makes the synthetic scheme lengthly, laborious and time consuming.[1] Such difficulties can be avoided by regioselective glycosylation of non-protected or partially-protected glycosyl acceptors. However, despite its potential importance, regioselective glycosylation of glycosyl acceptors having polyol fragments remains almost unexplored. This results, most probably, from serious difficulties which may appear during purification, separation and identification of the final products. To date, only very few examples of regioselective glycosylation of non-protected glycosyl acceptors have been reported.[2] Similarly, saccharide triols were only occasionally used as acceptors.[3] Reports on the combinatorial synthesis of oligosaccharide libraries with the use of non-protected glycosyl acceptors were also published.[4] By comparison, regioselective glycosylation of sugar diols[5,6] as well as in situ Sn-promoted[7] or arylboronic derivative[8] glycosylation were studied intensively.

In this context, we turned our attention to regioselective glycosylation of unprotected non-reducing glycosyl acceptors. Such a methodology reduces the number of necessary steps and simplifies the synthetic scheme. Herein, we report regioselective mannosylation of 2,3,4-triols of allyl and benzyl mannosides.

2. Results and discussion

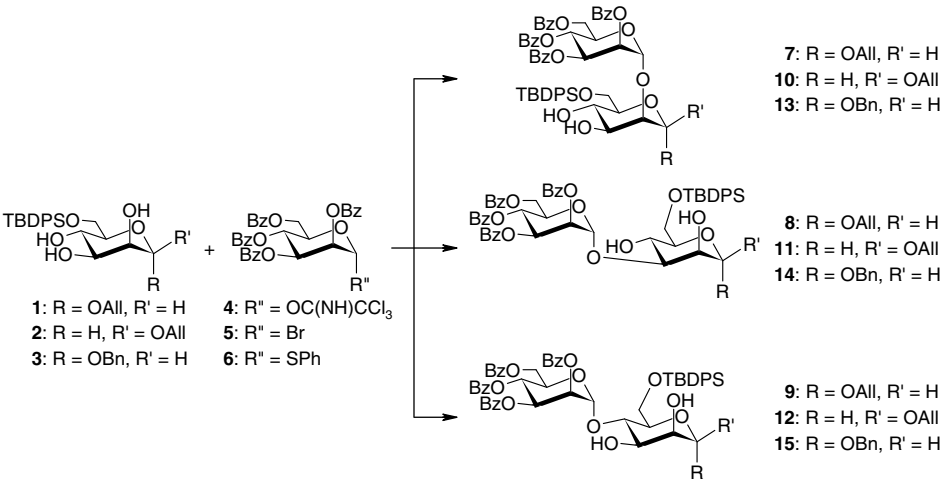
To elucidate the relationship between the regioselectivity, the structure of the glycosyl donor, structure of glycosyl acceptor, and the reaction conditions we examined the glycosylation of the allyl (both α- and β-anomers) and benzyl α-D-mannosides **1**–**3**, respectively, in which the most reactive primary hydroxyl group at the *C*-6 position was protected as a *tert*-butyldiphenylsilyl ether. This trick simplifies the identification of the products and prevents the formation of undesired trisaccharides. As glycosyl donors compounds **4**–**6** have been chosen. Glycosylation of triol acceptors **1**–**3** with glycosyl donors **4**–**6** provided the expected disaccharides **7**–**15** (Scheme 1).

2.1. Glycosylation of allyl 6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside 1

Initially, the glycosylation of allyl 6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside **1** according to a number of commonly used glycosylation methods, was tested, and the results are summarized in Table 1. Surprisingly, reactions employing phenyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-α-D-mannopyranoside[9] **6** as a glycosyl donor completely failed and did not lead to the desired products, irrespective of the reaction conditions and the promoters used. In most cases, unchanged starting materials were isolated. Application of Schmidt's trichloroacetimidate glycosylation methodology employing the donor **4** gave a mixture of expected disaccharides **7**–**9**. The regioselectivity of the glycosylation reaction depended mostly on the solvent. In dichloromethane, the (1→3)-linked isomer was obtained as the sole product in good yield (56% for TMSOTf as catalyst and 70% for $BF_3{\cdot}OEt_2$). Both regioselectivity and yield were lower in acetonitrile, although the (1→3)-linked isomer predominated strongly. The chemical yield was much

* Corresponding author.
E-mail address: pakul@icho.edu.pl (Z. Pakulski).

0957-4166/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetasy.2008.05.032



Scheme 1.

Table 1
Glycosylation of allyl 6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside **1**

Donor	Catalyst	Solvent	Temp (°C)	Time	Regioselectivity[a]			Yield[a] (%)
					7	**8**	**9**	
4	TMSOTf	DCM	−40	40 min	0	100	0	56
4	TMSOTf	MeCN	−40	30 min	1	92	7	10
4[b]	TMSOTf	MeCN	−40	30 min	4	78	18	52
4	TMSOTf	DMF	−40 to 20	2 h		No reaction		–
4	$BF_3{\cdot}OEt_2$	DCM	−40	40 min	0	100	0	70
4	$BF_3{\cdot}OEt_2$	DMF	−40	2 h		No reaction		–
4	TMSOTf	[bmim]PF_6/DCM	20	30 min	3	77	20	16
4	TMSOTf	[eoemim]PF_6/DCM	20	30 min		No reaction		–
4	TMSOTf	[bmim]dca	20			No reaction		–
4	TMSOTf	[bmim]NTf_2	20	30 min	13	53	34	45
5	AgOTf/TMU	DCM	20	24 h	3	79	18	85
5	$Hg(CN)_2/HgBr_2$	MeCN	20	48 h	15	71	14	61
6	NIS/TMSOTf	DCM	−40	2 h		Decomposition		–
6	MeOTf	DCM	0 to 20	4 d		No reaction		–
6	DMTST	DCM	20	24 h		No reaction		–
6	NIS/TfOH	DCE/diethyl ether	−30 to 20	48 h		No reaction		–
4[c]	TMSOTf	DCM	−40	1 h	53	43	4	9
5[c]	AgOTf/TMU	DCM	20	48 h	Traces	88	11	32
6[c]	DMTST	DCM	20	24 h		No reaction		–

[a] Determined by HPLC with 250-4 LiChrospher 100 RP-18 (5 μm) column; eluent MeCN–H_2O 96:4; flow 0.6 mL/min.
[b] A solution of **4** was added dropwise to a reaction mixture.
[c] Stannylene acetals of **1** were used as acceptors.

better when a solution of donor **4** was added dropwise to the reaction mixture but at the cost of regioselectivity. No products were obtained in DMF, even at room temperature. Reactions with mannopyranosyl bromide **5**[10] were highly efficient; chemical yields were good to excellent, although the regioselectivity was lower than in the previous cases.

Ionic liquids are known as good solvents for glycosylation.[11] However, the poor solubility of the acceptor **1** limited the reaction scope. The highest solubility of **1** was observed in 1-butyl-3-methylimidazolium dicyanamide ([bmim]dca), but in this solvent, the reaction did not take place. A slightly lower solubility of **1** was also observed in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim]NTf_2) but its glycosylation with **4** afforded the expected disaccharides **7**–**9** in good yield. Regioselectivity was, however, poor; only a slight preference for the (1→3)-linked product **8** was observed, and significant amounts of the (1→4)-linked product **9** were obtained. Complete dissolution of **1** in 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6) was not possible; thus a small amount of dichloromethane was added as a cosolvent. However, in this case the yield (16%) as well as regioselectivity was low. Similar transformations performed in a mixture of 1-ethoxyethyl-3-methylimidazolium hexafluorophosphate ([eomim]PF_6) and dichloromethane did not afford any product.

Finally, we tried the application of stannylene acetals[7] prepared in situ by treatment of mannoside **1** with dibutyltin oxide followed by glycosylation with donors **4**–**6**. Glycosylation of stannylene acetal of **1** with trichloroacetimidate **4** proceeded with low regioselectivity and chemical yield but, interestingly, with a slight preference for the (1→2)-linked product **7**. Using the donor **5** allowed us to obtain a mixture of (1→3)- and (1→4)-linked disaccharides in acceptable yield. Donor **6** was not reactive under the reaction conditions.

2.2. Glycosylation of allyl 6-*O*-*tert*-butyldiphenylsilyl-β-D-mannopyranoside *2*

In most cases, glycosylation of α-D-mannoside **1** strongly preferred the (1→3)-linked product **8**; additionally significant amounts of (1→4)-linked disaccharide **9** were detected, whereas

Table 2
Glycosylation of allyl 6-*O*-*tert*-butyldiphenylsilyl-β-D-mannopyranoside **2**

Donor	Catalyst	Solvent	Temp (°C)	Time	Regioselectivity[a]			Yield[a] (%)
					10	**11**	**12**	
4	TMSOTf	DCM	−40	1 h	32	38	30	35
4	$BF_3{\cdot}OEt_2$	DCM	−40	1 h	47	53	–	46
4	TMSOTf	MeCN	−40	1 h	30	62	8	24
4	TMSOTf	[bmim]PF_6/DCM	20	30 min		No reaction		–
4	TMSOTf	[bmim]NTf_2	20	30 min	30	60	10	27
4	TMSOTf	[eoemim]PF_6/DCM	20	30 min		No reaction		–
5	AgOTf/TMU	DCM	20	24 h	28	48	24	68

[a] Determined by HPLC with 250-4 LiChrospher 100 RP-18 (5 μm) column; eluent MeCN–H_2O 96:4; flow 0.6 mL/min.

the (1→2)-linked derivative **7** was observed only in minute quantities. By comparison, the regioselectivity of the glycosylation of β-D-mannoside **2** was completely different (Table 2). In all the cases studied, a strong preference for (1→2)- and (1→3)-linked compounds (**10** and **11**, respectively) was observed, whereas (1→4)-linked isomer **12** was usually detected in much lower yield. An almost equimolar amount of **10** and **11** was obtained in good yield during the glycosylation of mannoside **2** with trichloroacetimidate **4** in the presence of $BF_3{\cdot}OEt_2$; the (1→4)-linked isomer **12** was not detected in this case. In the presence of TMSOTf in dichloromethane solution, all possible isomers **10**–**12** were obtained in similar proportions; a noticeable preference for the (1→3)-linked product **11** was observed in acetonitrile. The best chemical yield was obtained for glycosylation of **2** with mannosyl bromide **5** but the regioselectivity was low.

2.3. Glycosylation of benzyl 6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside 3

Results of glycosylation of benzyl 6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside[12] **3** with donors **4**–**6** are summarized in Table 3. In almost all cases studied, the strong preference for the formation of (1→3)-linked product **14** was noted. Glycosylation of mannoside **3** with trichloroacetimidate **4** in dichloromethane solution in the presence of TMSOTf afforded (1→3)-linked disaccharide **14** exclusively. Here, the ionic liquids were very promising solvents for the glycosylation; chemical yields were high, (1→3)-linked product **14** predominated strongly and only traces of (1→2)-linked derivative **15** was detected. Almost equimolar amounts of (1→3)- and (1→4)-linked products were obtained in good yield (39%) during the glycosylation of stannylene acetal of **3** with imidate **4** in the presence of the TMSOTf; (1→2)-linked isomer was not found.

2.4. Discussion

The practical usefulness of the proposed strategy is limited by the possibility of isolating the pure isomers. As we have found, there is a considerable difference in polarity between the (1→3)-linked isomer and (1→2)/(1→4)-linked compounds. The first one shows relatively low polarity and may be easily separated from the others, highly polar isomers by column chromatography. Separation of (1→2)- and (1→4)-linked compounds is usually not trivial. However, careful selection of substrates and reaction conditions may selectively provide, except the usually preferred (1→3)-derivative, the (1→2)- or (1→4)-linked products (Tables 1–3).

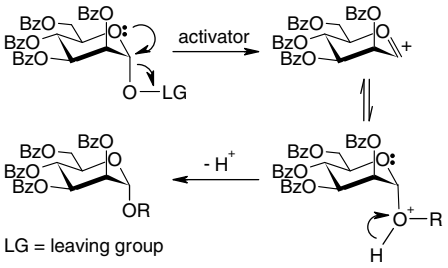
The observed significant differences between the reactivity of 2,3,4-triols having an α- or β-configuration at the anomeric centre is difficult to explain. The strong preference for the formation of (1→3)-linked disaccharides from allyl and benzyl α-mannosides **1** and **3** is in accordance with previous literature evidence.[2] However, formation of a large amount of (1→2)-linked product from allyl β-mannoside **2** was completely unexpected. The results reported in this article suggest that an intramolecular hydrogen-bonding network[13] may play a significant role in the formation of the glycosidic bond.[14]

It is known that the formation of the glycosidic bond proceeds via a nucleophilic substitution at the electron-deficient anomeric carbon (Scheme 2).[15] The hydroxyl groups involved in the hydrogen bond acting as hydrogen donors have increased electron density at the oxygen atom which makes this atom a more reactive nucleophile. As a result, this hydroxyl group should be more reactive in formation of the glycosidic linkage. In the case of β-anomer **2**, the hydroxyl group at the *C*-2 position may be included into three, theoretically possible, hydrogen bonds (Fig. 1, structures **2a**–**2a″**). Its nucleophilicity should be increased by comparison

Table 3
Glycosylation of benzyl 6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside **3**

Donor	Catal.	Solvent	Temp (°C)	Time	Regioselectivity[a]			Yield[a] (%)
					13	**14**	**15**	
4	TMSOTf	DCM	−40	1 h	0	100	0	34
4	$BF_3{\cdot}OEt_2$	DCM	−40	1 h	11	83	6	29
4	TMSOTf	MeCN	−40	1 h	12	75	13	23
4	TMSOTf	[bmim]PF_6/DCM	20	30 min	0	85	15	69
4	TMSOTf	[bmim]NTf_2	20	30 min	2	97	1	46
4	TMSOTf	[eoemim]PF_6/DCM	20	30 min	0	86	14	68
4	TMSOTf	[eoemim]dca/DCM	20	30 min		No reaction		–
5	AgOTf/TMU	DCM	20	24 h	4	71	25	59
5	$Hg(CN)_2/HgBr_2$	MeCN	20	24 h	18	61	21	22
6	NIS/TMSOTf	DCM	20	6 d		No reaction		–
4[b]	TMSOTf	DCM	0	1 h	–	47	53	39
5[b]	AgOTf/TMU	DCM	20	24 h	1	84	15	35

[a] Determined by HPLC with 250-4 LiChrospher 100 RP-18 (5 μm) column; eluent MeCN–H_2O 96:4; flow 0.6 mL/min.
[b] Stannylene acetals of **3** were used as acceptors.



Scheme 2.

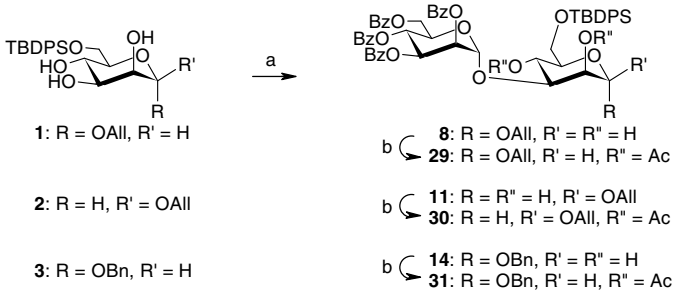
with α-anomer, in which only two hydrogen bonds may be considered (Fig. 1, structures **1a**–**1a′**). On the other hand, reactivity of the hydroxyl groups located at the *C*-3 and *C*-4 centres should not be changed. Therefore, a higher preference for the formation of (1→2)-linked compound may be noted for the β-acceptor. At the moment, this is only a plausible suggestion which needs further study.

2.5. Synthesis of the reference disaccharides 7–15

Determination of the composition of the reaction mixture was performed by HPLC chromatography. For reliable peak recognition, samples of reference compounds having independently confirmed structures were needed. Therefore, we decided to prepare analytical samples of disaccharides **7**–**15** by classical method to obtain compounds with a well-defined structure in pure form.

Glycosylation of allyl α-D-mannoside **17** bearing the free –OH group at the *C*-2 position with trichloroacetimidate **4** proceeded smoothly in the presence of TMSOTf under the standard conditions and yielded compound **18**. The butane 3,4-bisacetal protecting group was removed by acidic hydrolysis, which provided disaccharide **7** fully characterized further as diacetate **19**. A similar reaction sequence was employed in the synthesis of its benzyl congeners **13** and **23** (Scheme 3).

Attempts to prepare the β-anomer **10** by the same method failed due to high stability of the bisacetal protection. Compound



Scheme 5. Reagents: (a) **4**, TMSOTf, 4 Å, DCM; (b) Ac_2O, pyridine.

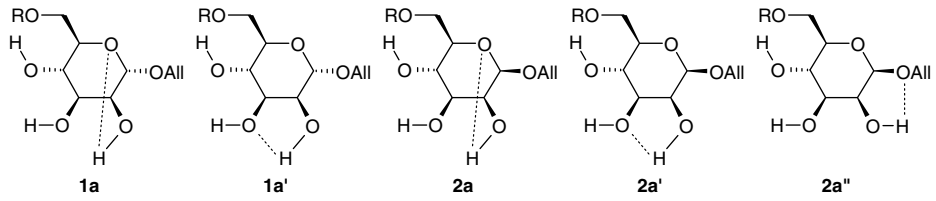
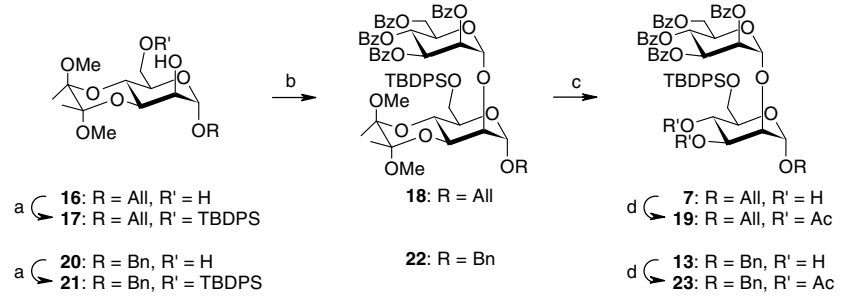
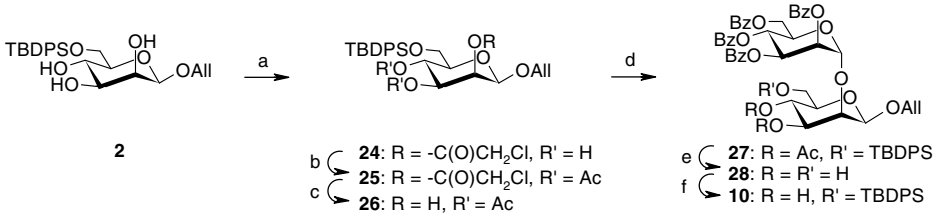


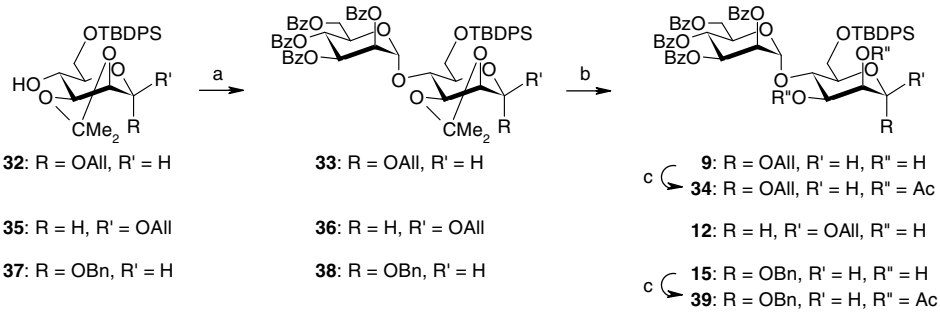
Figure 1.



Scheme 3. Reagents and conditions: (a) TBDPSCl, imidazole, DMF; (b) **4**, TMSOTf, 4 Å, DCM; (c) 90% CF_3CO_2H, DCM; (d) Ac_2O, pyridine.



Scheme 4. Reagents and conditions: (a) trimethyl orthochloroacetate, *p*-TsOH, MeCN then 90% CF_3CO_2H; (b) Ac_2O, pyridine; (c) thiourea, 2,4-lutidine, DCM, MeOH; (d) **4**, TMSOTf, 4 Å, DCM; (e) HCl in MeOH. (f) TBDPSCl, imidazole, DMF.



Scheme 6. Reagents: (a) **4**, TMSOTf, 4 Å, DCM; (b) *p*-TsOH, EtOAc, MeOH; (c) Ac_2O, pyridine.

10 was prepared by the treatment of mannoside **2** with trimethyl orthochloroacetate followed by the regioselective opening of the orthochloroacetate ring to form chloroacetate **24**, acetylation to form **25**, selective hydrolysis of chloroacetate group to form **26** and glycosylation of **26** with **4** under the standard conditions to form **27**. Both acetate and silyl groups were then removed simultaneously by treatment with methanolic HCl to yield **28** and final introduction of *tert*-butyldiphenylsilyl ether protection at the *O*-6 position afforded the required disaccharide **10** (Scheme 4).

(1→3)-Linked disaccharides **8**, **11** and **14** were prepared by the direct glycosylation of mannosides **1**–**3** with trichloroacetimidate **4** under the standard conditions. Products **8**, **11** and **14** were isolated by column chromatography and characterized as diacetates **29**–**31** (Scheme 5). The ^{1}H NMR spectra of diacetates **29**–**31** showed the *H*-2 and *H*-4 resonances of the central mannose residues being deshielded by ca. 1.0–1.6 ppm with respect to those of *H*-3. The ^{13}C NMR spectra of **29**–**31** indicated characteristic deshielding effects of the *C*-3 resonances. These observations clearly proved that the glycosidic linkages were at the *O*-3 position of the mannose ring.

Glycosylation of allyl α-D-mannoside **32** bearing a free –OH group at the *C*-4 position with trichloroacetimidate **4** took place smoothly by treatment with TMSOTf under standard conditions and yielded compound **33**. The isopropylidene protecting group was removed by acidic hydrolysis to give disaccharide **9**, fully characterized as diacetate **34**. A similar reaction sequence was employed in the synthesis of its β-allyl and benzyl congeners **12** and **15** (Scheme 6).

3. Conclusions

In conclusion, we have performed a systematic study on the regioselective glycosylation of mannoside 2,3,4-triol acceptors. Although some of the glycosyl couplings described in this paper proceeded only in moderate yields, this protocol is very competitive with the 'clasical' methods and allows us to avoid sequential protection–deprotection steps.This method may be used as a simple, fast and efficient procedure for the preparation of some particular disaccharides.

4. Experimental

4.1. General methods

Silica gel HF-254 and Silica Gel 230–400 mesh (E. Merck) were used for TLC and column chromatography, respectively. ^{1}H and ^{13}C NMR spectra were recorded at 303 K with a Bruker Avance DRX-500 spectrometer (500 MHz and 125 MHz, respectively) or with a Varian Mercury 400BB spectrometer (400 MHz and 100 MHz, respectively) for solutions in $CDCl_3$. An internal TMS was used as the ^{1}H and ^{13}C NMR chemical shift standard. Signals of the aromatic groups observed for the typical values were omitted for simplicity. High resolution mass spectra (HRMS) were acquired with a MARINER mass spectrometer. Optical rotations were measured with a JASCO P-1020 or with a JASCO P-2000 automatic polarimeters. Configurational assignments were based on the NMR measurements including DEPT and two-dimensional techniques, including *gradient-selected* COSY, as well as ^{1}H–^{13}C gradient selected HSQC (g-Heteronuclear Single Quantum Correlation; C, H correlation via double INEPT transfer in the phase sensitive mode).

4.2. Allyl 6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside 1

To a solution of allyl α-D-mannopyranoside[2g] (2.20 g, 10 mmol) and imidazole (1.2 g, 17.5 mmol) in DMF (20 mL) cooled to 0 °C, *tert*-butylchlorodiphenylsilane (TBDPSCl, 3.2 g, 11.5 mmol) in DMF (5 mL) was added slowly. The mixture was stirred at room temperature for 24 h, solvents were evaporated under diminished pressure and the residue was purified by column chromatography (9:1 hexane–EtOAc→5:3:1 hexane–EtOAc–MeOH) to afford 4.31 g (94%) of the title compound as a thick syrup. $[\alpha]_D^{20} = <1$ (*c* 0.6, $CHCl_3$). ^{1}H NMR δ: 5.86 (m, 1H, CH=), 5.25 (m, 1H, =C*H*H), 5.18 (m, 1H, =CH*H*), 4.84 (s, 1H, H-1), 4.12 (m, 1H, OCH), 3.81–3.95 (m, 6H), 3.67 (m, 1H, H-5), 1.07 (s, 9H, *t*Bu). ^{13}C NMR δ: 117.5 (OCH_2), 98.6 (C-1), 71.7, 70.6, 70.5, 70.4, 67.9 (=CH_2), 65.2 (C-6), 26.8 (*t*Bu), 19.2 (SiC). HRMS-ESI calcd for $C_{25}H_{34}NaO_6Si$ $(M+Na)^+$: 481.2017, found: 481.2034. Anal. Calcd for $C_{25}H_{34}O_6Si{\cdot}0.5H_2O$: C, 64.21; H, 7.54, Found: C, 64.47; H, 7.63.

4.3. Allyl 6-*O*-*tert*-butyldiphenylsilyl-β-D-mannopyranoside 2

Allyl β-D-mannopyranoside[2g] was converted into the title compound using the procedure described for **1** to yield **2** (86%) as a thick syrup. $[\alpha]_D^{20} = -49.5$ (*c* 0.6, $CHCl_3$). ^{1}H NMR δ: 5.91 (m, 1H, CH=), 5.27 (m, 1H, =C*H*H), 5.21 (m, 1H, =CH*H*), 4.53 (d, 1H, $J_{1,2}$ 1.1 Hz, H-1), 4.36 (m, 1H, OC*H*H), 4.11 (m, 1H, OCH*H*), 4.00 (dd, 1H, $J_{2,3}$ 3.4 Hz, H-2), 3.96 (dd, 1H, $J_{6,5}$ 4.9, $J_{6,6'}$ 10.7 Hz, H-6), 3.93 (dd, 1H, $J_{6',5}$ 5.3 Hz, H-6′), 3.81 (t, 1H, $J_{4,3} = J_{4,5} = 9.3$ Hz, H-4), 3.53 (dd, 1H, H-3), 3.33 (m, 1H, H-5), 1.06 (s, 9H, *t*Bu). ^{13}C NMR δ: 118.1 (CH_2), 98.3 (C-1), 74.8, 74.4, 70.5, 70.1, 69.7 (CH_2), 64.8 (C-6), 26.7 (*t*Bu), 19.2 (SiC). HRMS-ESI calcd for $C_{25}H_{34}NaO_6Si$ $(M+Na)^+$: 481.2017, found: 481.2041. Anal. Calcd for $C_{25}H_{34}O_6Si{\cdot}0.5H_2O$: C, 64.21; H, 7.54, Found: C, 64.36; H, 7.51.

4.4. (2′*S*,3′*S*)-Allyl 3,4-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside 17

(2′*S*,3′*S*)-Allyl 3,4-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-α-D-mannopyranoside[16] **16** was converted into the title compound using the procedure described for **1** to yield **17** (65%) as a thick syrup. $[\alpha]_D^{20} = +118.0$ (*c* 0.5, $CHCl_3$). ^{1}H NMR δ: 5.89 (m, 1H, CH=), 5.25 (m, 1H, =C*H*H), 5.18 (m, 1H, =CH*H*), 4.90 (d, 1H, $J_{1,2}$

1.4 Hz, H-1), 4.18 (m, 1H, OC*H*H), 4.05 (m, 2H), 3.99 (m, 1H, OC*H*H), 3.84–3.95 (m, 4H), 3.28 (s, 3H, OCH_3), 3.14 (s, 3H, OCH_3), 1.31 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 1.04 (s, 9H, *t*Bu). ^{13}C NMR δ: 117.7 (CH_2=), 100.3 (C-2′), 99.8 (C-3′), 98.7 (C-1), 71.7, 69.8, 68.5, 67.7 (OCH_2), 63.0, 62.4 (C-6), 48.1 (OCH_3), 47.9 (OCH_3), 26.7 (*t*Bu), 19.3 (C–Si), 17.8 (CH_3), 17.7 (CH_3). HRMS-ESI calcd for $C_{31}H_{44}NaO_8Si$ $[M+Na]^+$: 595.2698, found: 595.2724.

4.5. (2′*S*,3′*S*)-Benzyl 3,4-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-α-D-mannopyranoside 20

To a solution of benzyl α-D-mannopyranoside[17] (2.70 g, 10 mmol) in methanol (30 mL) trimethyl orthoformate (5.5 mL, 50 mmol), 2,3-butanedione (1.3 mL, 15 mmol), and camphorsulfonic acid (250 mg) were added and the mixture was refluxed for 19 h under an argon atmosphere, cooled to room temperature and neutralized by the addition of triethylamine (1 mL). Solvents were evaporated under diminished pressure and the residue was purified by column chromatography (7:3 hexane–EtOAc→5:3:0.5 hexane–EtOAc–MeOH) to afford 2.33 g (61%) of the title compound as a foam. $[\alpha]_D^{20} = +202.8$ (*c* 0.5, $CHCl_3$); ^1H NMR δ: 4.93 (d, 1H, $J_{1,2}$ 1.4 Hz, H-1), 4.70 and 4.51 (ABq, 2H, *J* 11.8 Hz, OCH_2), 4.12 (dd, 1H, $J_{6,5}$ 9.4, $J_{6,6'}$ 10.3 Hz, H-6), 4.05 (dd, 1H, $J_{6',5}$ 3.1 Hz, H-6′), 3.96 (m, 1H), 3.81 (m, 3H), 3.27 (s, 3H, OCH_3), 3.26 (s, 3H, OCH_3), 1.32 (s, 3H, CH_3), 1.29 (s, 3H, CH_3). ^{13}C NMR δ: 100.3 (C-2′), 99.9 (C-3′), 99.3 (C-1), 70.7, 69.8, 69.4 (OCH_2), 68.1, 63.0, 61.3 (C-6), 48.1 (OCH_3), 47.9 (OCH_3), 17.8 (CH_3), 17.7 (CH_3). HRMS-ESI calcd for $C_{19}H_{28}NaO_8$ $[M+Na]^+$: 407.1676, found: 407.1695.

4.6. (2′*S*,3′*S*)-Benzyl 3,4-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside 21

Compound **20** was converted into the title compound using the procedure described for **1** to yield **21** (89%) as a foam. $[\alpha]_D^{20} = +124.7$ (*c* 0.7, $CHCl_3$). ^1H NMR δ: 4.91 (d, 1H, $J_{1,2}$ 1.3 Hz, H-1), 4.71 and 4.51 (ABq, 2H, *J* 11.9 Hz, OCH_2), 4.05 (m, 2H), 3.92 (m, 4H), 3.27 (s, 3H, CH_3), 3.15 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 1.06 (s, 9H, 3 × CH_3). ^{13}C NMR δ: 100.2 (C-2′), 99.8 (C-3′), 98.6 (C-1), 71.8, 69.8, 68.7 (OCH_2), 68.5, 63.1, 62.4 (C-6), 48.1 (OCH_3), 47.9 (OCH_3), 26.8 (*t*Bu), 19.3 (SiC), 17.8 (CH_3), 17.7 (CH_3). HRMS-ESI calcd for $C_{35}H_{46}NaO_8Si$ $[M+Na]^+$: 645.2854, found: 645.2857. Anal. Calcd for $C_{35}H_{46}O_8Si{\cdot}H_2O$: C, 65.60; H, 7.55. Found: C, 65.56; H, 7.49.

4.7. Allyl 3,4-di-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-2-*O*-chloroacetyl-β-D-mannopyranoside 25

To a stirred solution of **2** (700 mg, 1.53 mM) in acetonitrile (30 mL) trimethyl orthochloroacetate (0.43 mL, 3.2 mM) and *p*-TsOH (30 mg) were added. After 15 min, the solvents were evaporated under diminished pressure, the residue was dissolved in acetonitrile (25 mL), aqueous trifluoroacetic acid (90%, 0.5 mL) was added, the mixture was stirred at room temperature for 3 h and concentrated. The residue (crude **24**) was acetylated under the standard conditions (pyridine, acetic anhydride) for 2 h. Solvents were evaporated under diminished pressure and the residue was purified by column chromatography (20:1→5:1 hexane–EtOAc) to afford 500 mg (53%) of **25** as an oil; $[\alpha]_D^{20} = -18.8$ (*c* 0.43 $CHCl_3$). ^1H NMR δ: 5.89 (m, 1H, CH=), 5.51 (dd, 1H, $J_{2,1}$ 0.9, $J_{2,3}$ 3.2 Hz, H-2), 5.21–5.34 (m, 3H, H-4, =CH_2), 5.07 (dd, 1H, $J_{3,4}$ 10.1 Hz, H-3), 4.70 (d, 1H, H-1), 4.35 (m, 1H, OCH*H*), 4.18 (ABq, 2H, *J* 15.3 Hz, CH_2Cl), 4.12 (m, 1H, OC*H*H), 3.81 (dd, 1H, $J_{6,5}$ 5.3, $J_{6,6'}$ 11.5 Hz, H-6), 3.73 (dd, 1H, $J_{6',5}$ 2.2 Hz, H-6′), 3.50 (m, 1H, H-5), 2.00 (s, 3H, CH_3), 1.91 (s, 3H, CH_3), 1.06 (*t*Bu). ^{13}C NMR δ: 170.1 (C=O), 169.3 (C=O), 167.1 (C=O), 118.3 (CH_2), 96.5 (C-1), 75.2, 71.2, 71.0, 69.8 (CH_2), 65.9, 62.7 (CH_2), 40.8 (CH_2), 26.6 (*t*Bu), 20.6 (CH_3), 19.2 (C). HRMS-ESI calcd for $C_{31}H_{39}ClNaO_9Si$ $[M+Na]^+$: 641.1944, found: 641.1957. Anal. Calcd for $C_{31}H_{39}ClO_9Si$: C, 60.13; H, 6.35; Cl, 5.73. Found: C, 59.96; H, 6.53; Cl, 5.79.

4.8. Allyl 3,4-di-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-β-D-mannopyranoside 26

A mixture of **25** (336 mg, 0.54 mM), thiourea (100 mg) and 2,4-lutidine (0.06 mL) in dichloromethane (3 mL) and MeOH (15 mL) was stirred at 50 °C for 48 h, evaporated under diminished pressure and purified by column chromatography (5:1→7:3 hexane–EtOAc) to afford 200 mg (55%) of **26** as a foam. $[\alpha]_D^{20} = -20.6$ (*c* 0.5, $CHCl_3$). ^1H NMR δ: 5.93 (m, 1H, CH=), 5.37 (t, 1H, $J_{4,3} = J_{4,5} = 9.9$ Hz, H-4), 5.30 (m, 1H, =C*H*H), 5.25 (m, 1H, =CH*H*), 4.96 (dd, 1H, $J_{3,2}$ 3.1 Hz, H-3), 4.63 (d, 1H, $J_{1,2}$ 1.0 Hz, H-1), 4.40 (m, 1H, OCH*H*), 4.16 (m, 1H, OC*H*H), 4.12 (dd, 1H, H-2), 3.79 (dd, 1H, $J_{6,5}$ 5.7, $J_{6,6'}$ 11.6 Hz, H-6), 3.72 (dd, 1H, $J_{6',5}$ 2.4 Hz, H-6′), 3.49 (m, 1H, H-5), 2.09 (s, 3H, CH_3), 1.90 (s, 3H, CH_3), 1.06 (*t*Bu). ^{13}C NMR δ: 170.5 (C=O), 169.3 (C=O), 118.3 (CH_2), 97.7 (C-1), 75.1, 73.4, 69.7 (CH_2), 69.3, 66.2, 62.9 (CH_2), 26.6 (*t*Bu), 20.9 (CH_3), 20.6 (CH_3), 19.2 (C). HRMS-ESI calcd for $C_{29}H_{38}NaO_8Si$ $[M+Na]^+$: 565.2228, found: 565.2212.

4.9. Allyl 6-*O*-*tert*-butyldiphenylsilyl-2,3-*O*-isopropylidene-α-D-mannopyranoside 32

To a solution of **1** (530 mg, 1.15 mmol) in dimethoxypropane (10 mL) camphorsulfonic acid (30 mg) was added and the mixture was stirred at room temperature for 18 h. The catalyst was neutralized by the addition of 25% aq NH_3 (0.5 mL) and solvents were evaporated under diminished pressure. Column chromatography of the residue (9:1→7:3 hexane–EtOAc) gave 546 mg (95%) of the title compound as a colourless oil. $[\alpha]_D^{20} = +2.6$ (*c* 0.4, $CHCl_3$). ^1H NMR δ: 5.88 (m, 1H, CH=), 5.26 (m, 1H, =C*H*H), 5.19 (m, 1H, =CH*H*), 5.04 (s, 1H, H-1), 4.16 (m, 2H), 4.11 (t, 1H, $J_{4,3} = J_{4,5} = 7.2$ Hz, H-4), 3.97 (m, 1H, OCH), 3.90 (m, 2H), 3.79 (m, 1H), 3.67 (m, 1H), 1.50 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.06 (s, 9H, *t*Bu). ^{13}C NMR δ: 117.9 (OCH_2), 109.5 (CMe_2), 96.2 (C-1), 78.2, 75.4, 70.8, 69.5, 67.9 (=CH_2), 64.6 (C-6), 27.9 (CH_3), 26.8 (*t*Bu), 26.1 (CH_3), 19.2 (SiC). HRMS-ESI calcd for $C_{28}H_{38}NaO_6Si$ $[M+Na]^+$: 521.2330, found: 521.2333. Anal. Calcd for $C_{28}H_{38}O_6Si$: C, 67.44; H, 7.68. Found: C, 67.47; H, 7.46.

4.10. Allyl 6-*O*-*tert*-butyldiphenylsilyl-2,3-*O*-isopropylidene-β-D-mannopyranoside 35

Compound **2** was converted into the title compound using the procedure described for **32** to yield **35** (84%) as an oil. $[\alpha]_D^{20} = -54.1$ (*c* 0.3, $CHCl_3$). ^1H NMR δ: 5.89 (m, 1H, CH=), 5.25 (m, 1H, =C*H*H), 5.19 (m, 1H, =CH*H*), 4.78 (d, 1H, $J_{1,2}$ 2.4 Hz, H-1), 4.35 (m, 1H, OCH*H*), 4.24 (dd, 1H, $J_{2,3}$ 6.1 Hz, H-2), 4.12 (m, 2H, H-3, OC*H*H), 3.99 (m, 1H, H-5), 3.91 (m, 2H, H-6, H-6′), 3.38 (m, 1H, H-4), 1.56 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.06 (s, 9H, *t*Bu). ^{13}C NMR δ: 118.2 (CH_2), 110.9 (C), 96.8 (C-1), 79.7, 74.2, 73.7, 71.9, 69.9 (CH_2), 65.4 (CH_2), 27.7 (CH_3), 26.8 (*t*Bu), 26.2 (CH_3), 19.1 (C). HRMS-ESI calcd for $C_{28}H_{38}NaO_6Si$ $[M+Na]^+$: 521.2330, found: 521.2312. Anal. Calcd for $C_{28}H_{38}O_6Si$: C, 67.44; H, 7.68. Found: C, 67.25; H, 7.56.

4.11. General procedure for the glycosylation reaction

A solution of trichloroacetimidate **4**[2e] (1.1 mmol) and a suitable acceptor (1.0 mmol) in dichloromethane (25 mL) solution was stirred for 1 h at room temperature over molecular sieves (4 Å, 800 mg, finely ground), then cooled to −40 °C and TMSOTf (50 μL) was added. After 30 min, the reaction was quenched with

Et_3N (0.2 mL), and the solvents were evaporated under diminished pressure. Column chromatography (9:1→5:1 hexane–EtOAc) of the residue gave the disaccharide.

4.11.1. Allyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-6-*O*-*tert*-butyldiphenylsilyl-3,4-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-α-D-mannopyranoside 18

Yield 83%, as a foam. $[\alpha]_D^{20} = +7.0$ (*c* 0.4, $CHCl_3$). ^1H NMR δ: 6.08 (t, 1H, $J_{4,3} = J_{4,5} = 10.0$ Hz, H-4′), 5.97 (dd, 1H, $J_{2,1}$ 1.6, $J_{2,3}$ 3.2 Hz, H-2′), 5.95 (dd, 1H, H-3′), 5.89 (m, 1H, CH=), 5.46 (d, 1H, H-1′), 5.26 (m, 1H, =C*H*H), 5.18 (m, 1H, =CH*H*), 5.00 (br s, 1H, H-1), 4.74 (dd, 1H, $J_{6,5}$ 2.4, $J_{6,6'}$ 12.0 Hz, H-6′), 4.55 (m, 1H, H-5′), 4.48 (dd, 1H, $J_{6',5}$ 4.4 Hz, H-6′), 4.21 (m, 2H, $J_{4,3} = J_{4,5}$ =10.1 Hz, H-4, OC*H*H), 4.11 (dd, 1H, $J_{3,2}$ 2.7 Hz, H-3), 4.07 (m, 1H, H-2), 4.01 (m, 2H, H-6, 6), 3.97 (m, 1H, OC*H*H), 3.91 (m, 1H, H-5), 3.26 (s, 3H, CH_3), 3.23 (s, 3H, CH_3), 1.23 (s, 6H, 2 × CH_3), 1.12 (s, 9H, *t*Bu). ^{13}C NMR δ: 166.2 (C=O), 165.5 (C=O), 164.9 (C=O), 164.8 (C=O), 117.6 (=CH_2), 100.1 (C), 99.6 (C), 99.4 (C-1′), 98.3 (C-1), 76.7 (C-2), 72.6 (C-5), 70.2 (C-2′), 70.1 (C-3′), 69.2 (C-5′), 68.8 (C-3), 67.7 (OCH_2), 67.2 (C-4′), 63.4 (C-4), 63.0 (C-6′), 62.7 (C-6), 48.0 (CH_3), 47.9 (CH_3), 26.9 (*Me*$_3$C), 19.4 (CSi), 17.6 (CH_3), 17.5 (CH_3). HRMS-ESI calcd for $C_{65}H_{70}NaO_{17}Si$ $[M+Na]^+$: 1173.4275, found: 1173.4277. Anal. Calcd for $C_{65}H_{70}O_{17}Si{\cdot}H_2O$: C, 66.76; H, 6.21. Found: C, 66.96; H, 6.02.

4.11.2. Benzyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-6-*O*-*tert*-butyldiphenylsilyl-3,4-*O*-(2′,3′-dimethoxybutane-2′,3′-diyl)-α-D-mannopyranoside 22

Yield 53%, as a foam. $[\alpha]_D^{20} = +14.7$ (*c* 0.4, $CHCl_3$). ^1H NMR δ: 6.08 (t, 1H, $J_{4,3} = J_{4,5} = 10.0$ Hz, H-4′), 5.97 (dd, 1H, $J_{2,1}$ 1.0, $J_{2,3}$ 3.3 Hz, H-2′), 5.93 (dd, 1H, H-3′), 5.45 (d, 1H, H-1′), 5.03 (s, 1H, H-1), 4.77 and 4.48 (ABq, 2H, *J* 11.7 Hz, OCH), 4.67 (dd, 1H, $J_{6,5}$ 2.4, $J_{6,6'}$ 12.0 Hz, H-6′), 4.48 (m, 1H, H-5′), 4.44 (dd, 1H, $J_{6',5}$ 4.1 Hz, H-6′), 4.22 (t, 1H, $J_{4,3} = J_{4,5} = 9.8$ Hz, H-4), 4.11 (m, 2H, H-2,3), 4.02 (m, 2H, H-6, 6), 3.96 (m, 1H, H-5), 3.26 (s, 3H, CH_3), 3.21 (s, 3H, CH_3), 1.23 (s, 3H, CH_3), 1.22 (s, 3H, CH_3), 1.13 (*t*Bu). ^{13}C NMR δ: 166.2 (C=O), 165.5 (C=O), 164.9 (C=O), 164.8 (C=O), 100.1 (C), 99.6 (C), 99.4 (C-1), 98.4 (C-1), 76.6, 72.7, 70.2, 70.1, 69.1, 68.9, 68.8 (OCH_2), 67.1, 63.4, 62.9 (C-6), 62.7 (C-6), 48.1 (OCH_3), 47.9 (OCH_3), 26.9 (*t*Bu), 19.4 (CSi), 17.6 (CH_3), 17.5 (CH_3). HRMS-ESI calcd for $C_{69}H_{72}NaO_{17}Si$ $[M+Na]^+$: 1223.4431, found: 1223.4413. Anal. Calcd for $C_{69}H_{72}O_{17}Si{\cdot}2H_2O$: C, 66.97; H, 6.19. Found: C, 67.19; H, 5.73.

4.11.3. Allyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-3,4-di-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-β-D-mannopyranoside 27

Yield 87%, as a foam. $[\alpha]_D^{20} = -37.0$ (*c* 0.5, $CHCl_3$). ^1H NMR δ: 6.21 (t, 1H, $J_{4,3} = J_{4,5} = 10.2$ Hz, H-4′), 5.98 (dd, 1H, $J_{3,2}$ 3.3 Hz, H-3′), 5.92 (m, 1H, =CH), 5.75 (dd, 1H, $J_{2,1}$ 1.8 Hz, H-2′), 5.20–5.36 (m, 4H, $J_{4,3} = J_{4,5} = 9.8$ Hz, H-1′, H-4, =CH_2), 5.08 (dd, 1H, $J_{3,2}$ 3.1 Hz, H-3), 5.01 (m, 1H, H-5′), 4.64 (2H, $J_{6,5}$ 2.5 Hz, H-1, H-6′), 4.44 (m, 1H, OC*H*H), 4.38 (dd, 1H, $J_{6,5}$ 2.8, $J_{6,6'}$ 12.3 Hz, H-6′), 4.22 (dd, 1H, H-2), 4.15 (m, 1H, OCH*H*), 3.97 (dd, 1H, $J_{6,5}$ 6.6, $J_{6,6'}$ 11.5 Hz, H-6), 3.78 (dd, 1H, $J_{6,5}$ 2.3 Hz, H-6), 3.54 (m, 1H, H-5), 2.13 (s, 3H, CH_3), 1.86 (s, 3H, CH_3), 1.10 (*t*Bu). ^{13}C NMR δ: 170.6 (C=O), 169.4 (C=O), 166.2 (C=O), 165.5 (C=O), 165.2 (C=O), 165.0 (C=O), 118.8 (=CH_2), 98.7 (C-1′), 98.2 (C-1), 75.8 (C-2 or C-5), 75.7 (C-2 or C-5), 72.9 (C-3), 70.9 (C-2′), 70.3 (CH_2), 69.9 (C-3′), 68.6 (C-5′), 67.3 (C-4′), 66.9 (C-4), 63.5 (C-6), 62.6 (C-6′), 26.8 (*t*Bu), 20.7 (CH_3), 20.6 (CH_3), 19.2 (C). HRMS-ESI calcd for $C_{63}H_{64}NaO_{17}Si$ $[M+Na]^+$: 1143.3805, found: 1143.3763.

4.11.4. Allyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→3)-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside 8

Yield 56%, as a foam. $[\alpha]_D^{20} = -17.7$ (*c* 0.6, $CHCl_3$). ^1H NMR δ: 6.06 (t, 1H, $J_{4,3} = J_{4,5} = 10.1$ Hz, H-4′), 5.95 (dd, 1H, $J_{3,2}$ 3.3 Hz, H-3′), 5.84 (dd, 1H, $J_{1,2}$ 1.8 Hz, H-2′), 5.80 (m, 1H, CH=), 5.47 (d, 1H, H-1′), 5.22 (m, 1H, =C*H*H), 5.15 (m, 1H, =CH*H*), 4.75 (d, 1H, $J_{1,2}$ 1.6 Hz, H-1), 4.71 (m, 2H, H-5′,6′), 4.53 (dd, 1H, $J_{6',5}$ 5.2, $J_{6,6'}$ 12.3 Hz, H-6′), 4.15 (dd, 1H, $J_{2,3}$ 3.1 Hz, H-2), 4.08 (m, 2H, $J_{4,3} = J_{4,5} = 9.3$ Hz, H-4, OC*H*H), 4.03 (dd, 1H, H-3), 3.95 (m, 2H, H-6,6), 3.90 (m, 1H, OCH*H*), 3.70 (m, 1H, H-5), 1.09 (*t*Bu). ^{13}C NMR δ: 166.3 (C=O), 165.7 (C=O), 165.5 (C=O), 165.3 (C=O), 117.7 (OCH_2), 99.6 (C-1′), 98.6 (C-1), 80.7 (C-3), 71.7 (C-5), 70.4 (C-2,2′), 70.2 (C-3′), 69.3 (C-5′), 68.1 (C-4), 68.0 (=CH_2), 67.1 (C-4′), 64.5 (C-6), 63.3 (C-6′), 26.9 (*t*Bu), 19.2 (SiC). HRMS-ESI calcd for $C_{59}H_{60}NaO_{15}Si$ $(M+Na)^+$: 1059.3594, found: 1059.3599. Anal. Calcd for $C_{59}H_{60}O_{15}Si$: C, 68.32; H, 5.83. Found: C, 68.08; H, 5.90.

4.11.5. Allyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→3)-6-*O*-*tert*-butyldiphenylsilyl-β-D-mannopyranoside 11

Yield 35%, as a foam. $[\alpha]_D^{20} = -31.0$ (*c* 0.6, $CHCl_3$). ^1H NMR δ: 6.12 (t, 1H, $J_{4,3} = J_{4,5} = 10.1$ Hz, H-4′), 5.98 (dd, 1H, $J_{3,2}$ 3.3 Hz, H-3′), 5.88 (m, 1H, CH=), 5.85 (dd, 1H, $J_{2,1}$ 1.8 Hz, H-2′), 5.41 (d, 1H, H-1′), 5.27 (m, 1H, =C*H*H), 5.21 (m, 1H, =CH*H*), 4.84 (m, 1H, H-5′), 4.71 (dd, 1H, $J_{6,5}$ 2.5, $J_{6,6'}$ 12.2 Hz, H-6′), 4.49 (m, 2H, $J_{6,5}$ 4.5, H-1,6′), 4.33 (m, 1H, OC*H*H), 4.24 (d, 1H, $J_{2,3}$ 2.8 Hz, H-2), 4.12 (m, 2H, H-4, OCH*H*), 3.98 (m, 2H, H-6,6), 3.66 (dd, 1H, $J_{3,4}$ 9.3 Hz, H-3), 3.35 (m, 1H, H-5), 1.09 (s, 9H, *t*Bu). ^{13}C NMR δ: 166.3 (C=O), 165.6 (C=O), 165.5 (C=O), 165.4 (C=O), 118.1 (OCH_2), 99.8 (C-1′), 98.0 (C-1), 83.6 (C-3), 75.4 (C-5), 70.8 (C-2), 70.4 (C-2′), 70.3 (C-3′), 69.6 (=CH_2), 69.3 (C-5′), 67.5 (C-4), 66.9 (C-4′), 64.4 (C-6), 63.1 (C-6′), 26.8 (*t*Bu), 19.2 (SiC). HRMS-ESI calcd for $C_{59}H_{60}NaO_{15}Si$ $(M+Na)^+$: 1059.3594, found: 1059.3624. Anal. Calcd for $C_{59}H_{60}O_{15}Si$: C, 68.32; H, 5.83. Found: C, 68.02; H, 5.85.

4.11.6. Benzyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→3)-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside 14

Yield 34%, as a foam. $[\alpha]_D^{20} = -10.4$ (*c* 0.6, $CHCl_3$). ^1H NMR δ: 6.07 (t, 1H, $J_{3,2} = J_{3,4} = 10.0$ Hz, H-4′), 5.95 (dd, 1H, $J_{3,2}$ 3.3 Hz, H-3′), 5.85 (dd, 1H, $J_{2,1}$ 1.8 Hz, H-2′), 5.47 (d, 1H, H-1′), 4.78 (d, 1H, $J_{1,2}$ 1.5 Hz, H-1), 4.72 (m, 2H), 4.63 and 4.42 (ABq, 2H, *J* 11.9 Hz, OCH_2), 4.52 (dd, 1H, *J* 4.8 and 12.0 Hz), 4.18 (m, 1H), 4.09 (m, 2H), 3.96 (m, 2H), 3.73 (m, 1H), 1.10 (s, 9H, *t*-Bu). ^{13}C NMR δ: 166.3 (C=O), 165.7 (C=O), 165.5 (C=O), 165.4 (C=O), 99.6 (C-1), 98.6 (C-1), 80.9 (C-3), 72.0, 70.4, 70.2, 69.3, 68.9 (OCH_2), 67.9, 67.1, 64.5 (C-6), 63.3 (C-6), 26.9 (3 × CH_3), 19.2 (SiC). HRMS-ESI calcd for $C_{63}H_{62}O_{15}NaSi$ $[M+Na]^+$: 1109.3750, Found: 1109.3733. Anal. Calcd for $C_{63}H_{62}O_{15}Si$: C, 69.60; H, 5.75. Found: C, 69.43; H, 5.97.

4.11.7. Allyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→4)-6-*O*-*tert*-butyldiphenylsilyl-2,3-*O*-isopropylidene-α-D-mannopyranoside 33

Yield 86%, as a foam. $[\alpha]_D^{20} = -3.5$ (*c* 0.25, $CHCl_3$). ^1H NMR δ: 6.12 (t, 1H, $J_{4,3} = J_{4,5} = 10.1$ Hz, H-4′), 5.90 (m, 1H, *H*C=), 5.79 (m, 2H, $J_{3,2}$ 3.2 Hz, H-2′,3′), 5.64 (br s, 1H, H-1′), 5.29 and 5.22 (2m, 2H, =CH_2), 5.12 (br s, 1H, H-1), 4.40 (m, 2H), 4.20 (m, 4H), 4.03 (m, 4H), 3.84 (m, 1H), 1.52 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.10 (s, 9H, 3 × CH_3). ^{13}C NMR δ: 166.0 (C=O), 165.5 (C=O), 165.3 (C=O), 165.2 (C=O), 117.9 (=CH_2), 109.8 (*C*Me$_2$), 96.2 (C-1), 95.9 (C-1), 78.2, 76.0, 73.0, 70.5, 70.1, 69.4, 68.8, 67.7 (OCH_2), 66.5, 63.3 (C-6), 62.6 (C-6), 27.9 (CH_3), 27.0 (3 × CH_3), 26.3 (CH_3), 19.4 (SiC). HRMS-ESI calcd for $C_{62}H_{64}NaO_{15}Si$ $[M+Na]^+$: 1099.3907, found: 1099.3914.

4.11.8. Allyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→4)-6-*O*-*tert*-butyldiphenylsilyl-2,3-*O*-isopropylidene-β-D-mannopyranoside 36

Yield 94%, as a foam. $[\alpha]_D^{20} = -30.3$ (*c* 0.4, $CHCl_3$). ^1H NMR δ: 6.12 (t, 1H, $J_{4,3} = J_{4,5} = 10.1$ Hz, H-4′), 5.96 (m, 1H, =CH), 5.81 (dd, 1H, $J_{3,2}$ 3.2 Hz, H-3′), 5.75 (dd, 1H, $J_{2,1}$ 2.0 Hz, H-2′), 5.61 (d, 1H, H-1′), 5.28 (m, 2H, =CH_2), 4.85 (d, 1H, $J_{1,2}$ 1.9 Hz, H-1), 4.45 (m, 1H, OC*H*H), 4.40 (dd, 1H, $J_{6,5}$ 2.2, $J_{6,6'}$ 12.3 Hz, H-6′), 4.35 (m, $J_{3,4} \cong 6.1$ Hz, 1H,

H-3), 4.29 (dd, 1H, $J_{2,3}$ 5.8 Hz, H-2), 4.22 (m, 2H, H-5′, OCH*H*), 4.15 (m, 2H, H-4, H-6′), 4.08 (m, 2H, H-6, H-6), 3.55 (m, 1H, H-5), 1.55 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.10 (s, 9H, *t*Bu). ^{13}C NMR δ: 166.0 (C=O), 165.5 (C=O), 165.3 (C=O), 165.3 (C=O), 118.6 (CH_2), 111.3 (C), 96.9 (C-1), 96.2 (C-1), 79.4, 75.0, 74.7, 73.3, 70.5, 70.1 (CH_2), 70.0, 69.6, 66.4, 63.8 (CH_2), 62.5 (CH_2), 27.7 (CH_3), 26.9 (*t*Bu), 26.2 (CH_3), 19.4 (C). HRMS-ESI calcd for $C_{62}H_{64}NaO_{15}Si$ $[M+Na]^+$: 1099.3907, found: 1099.3904. Anal. Calcd for $C_{62}H_{64}O_{15}Si\cdot 3H_2O$: C, 65.82; H, 6.24. Found: C, 65.74; H, 5.79.

4.11.9. Benzyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→4)-6-*O*-*tert*-butyldiphenylsilyl-2,3-*O*-isopropylidene-α-D-mannopyranoside 38

Starting from benzyl 6-*O*-*tert*-butyldiphenylsilyl-2,3-*O*-isopropylidene-α-D-mannopyranoside[12] **37**, the title compound was obtained as a foam in 82% yield. $[\alpha]_D^{20}$ = +11.6 (*c* 0.3, $CHCl_3$). ^{1}H NMR δ: 6.11 (t, 1H, $J_{4,3} = J_{4,5}$ = 10.1 Hz, H-4′), 5.81 (dd, 1H, $J_{3,2}$ 3.2 Hz, H-3′), 5.77 (m, 1H, H-2′), 5.64 (d, 1H, $J_{1,2}$ 1.6 Hz, H-1′), 5.14 (br s, 1H, H-1), 4.72 and 4.52 (ABq, 2H, *J* 11.8 Hz, OCH_2), 4.40 (m, 2H, H-3′, 6), 4.23 (m, 1H, H-5′), 4.20 (d, 1H, $J_{2,3}$ 5.7 Hz, H-2), 4.14 (dd, 1H, $J_{6,5}$ 3.6, $J_{6,6'}$ 12.3 Hz, H-6′), 4.03–4.09 (m, 3H, H-4, 6, 6), 3.90 (m, 1H, H-5), 1.51 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.11 (s, 9H, 3 × CH_3). ^{13}C NMR δ: 166.0 (C=O), 165.5 (C=O), 165.3 (C=O), 165.2 (C=O), 109.8 (*C*Me$_2$), 96.2 (C-1′), 95.8 (C-1), 78.2 (C-3), 76.0 (C-2), 73.1 (C-4), 70.4 (C-2′), 70.1 (C-3′), 69.4 (C-5′), 68.9 (C-5), 68.6 (OCH_2), 66.5 (C-4′), 63.5 (C-6), 62.5 (C-6′), 27.9 (CH_3), 27.0 (3 × CH_3), 26.3 (CH_3), 19.4 (SiC). HRMS-ESI calcd for $C_{66}H_{66}NaO_{15}Si$ $[M+Na]^+$: 1149.4063, found: 1149.4057. Anal. Calcd for $C_{66}H_{66}O_{15}Si\cdot 3H_2O$: C, 67.10; H, 6.14. Found: C, 66.91; H, 5.83.

4.12. Allyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside 7

To a solution of **18** (194 mg, 0.17 mM) in dichloromethane (2 mL) was added 90% aqueous trifluoroacetic acid (1 mL) and the whole mixture was stirred for 5 min. Solvents were evaporated under diminished pressure and the residue was immediately purified by column chromatography (5:1→7:3 hexane–EtOAc, then 5:3:0.2 hexane–EtOAc–MeOH) to afford **7** as a foam (100 mg, 58%). $[\alpha]_D^{20} = -19.6$ (*c* 0.3, $CHCl_3$). ^{1}H NMR δ: 6.09 (t, 1H, $J_{4,3} = J_{4,5}$ = 10.1 Hz, H-4′), 5.87 (dd, 1H, $J_{2,1}$ 1.7, $J_{2,3}$ 3.3 Hz, H-2′), 5.83 (dd, 1H, H-3′), 5.80 (m, 1H, CH=), 5.36 (d, 1H, H-1′), 5.21 (m, 1H, =C*H*H), 5.16 (m, 1H, =CH*H*), 5.11 (br s, 1H, H-1), 4.66 (dd, 1H, $J_{6,5}$ 2.3, $J_{6,6'}$ 12.2 Hz, H-6′), 4.59 (m, 1H, H-5′), 4.49 (dd, 1H, $J_{6',5}$ 4.6 Hz, H-6′), 4.06 (m, 5H, H-2, 3, 4, 6, OC*H*H), 3.80 (m, 1H, OC*H*H), 3.71 (m, 1H, H-5), 1.10 (s, 9H, *t*Bu). ^{13}C NMR δ: 166.2 (C=O), 165.5 (C=O), 165.5 (C=O), 165.2 (C=O), 117.3 (=CH_2), 100.3 (C-1′), 97.7 (C-1), 80.4, 71.9, 71.4, 70.3, 70.1, 69.7, 69.5, 67.9 (OCH_2), 66.6, 64.7 (C-6), 62.9 (C-6), 26.9 (*t*Bu), 19.2 (CSi). HRMS-ESI calcd for $C_{59}H_{60}NaO_{15}Si$ $[M+Na]^+$: 1059.3594, found: 1059.3646. Anal. Calcd for $C_{59}H_{60}O_{15}Si$: C, 68.32; H, 5.83. Found: C, 68.19; H, 5.84.

4.13. Benzyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside 13

Compound **22** (258 mg, 0.21 mM) was converted into the title compound using the procedure described for **7** to yield **13** (147 mg, 63%) as a foam. $[\alpha]_D^{20} = -9.4$ (*c* 0.3, $CHCl_3$). ^{1}H NMR δ: 6.08 (t, 1H, $J_{4,3} = J_{4,5}$ = 10.0 Hz, H-4′), 5.88 (dd, 1H, H-2′), 5.84 (dd, 1H, $J_{3,2}$ 3.2 Hz, H-3′), 5.37 (d, 1H, H-1′), 5.16 (br s, 1H, H-1), 4.64 and 4.33 (ABq, 2H, *J* 11.8 Hz, OCH_2), 4.54 (m, 2H, H-5′, 6′), 4.46 (dd, 1H, $J_{6,5}$ 4.6, $J_{6,6'}$ 12.3 Hz, H-6′), 4.09 (m, 4H, H-2, 3, 4, 6), 4.01 (dd, 1H, $J_{6,5}$ 5.1, $J_{6,6'}$ 10.8 Hz, H-6), 3.78 (m, 1H, H-5), 1.12 (s, 9H, *t*Bu). ^{13}C NMR δ: 166.1 (C=O), 165.5 (C=O), 165.4 (C=O), 165.2 (C=O), 100.3 (C-1), 97.7 (C-1), 80.4, 72.2, 71.5, 70.3, 70.1, 69.6, 69.4, 68.9 (OCH_2), 66.6, 64.7 (C-6), 62.9 (C-6), 26.9 (*t*Bu), 19.3 (CSi). HRMS-ESI calcd for $C_{63}H_{62}NaO_{15}Si$ $[M+Na]^+$: 1109.3750, found: 1109.3733. Anal. Calcd for $C_{63}H_{62}O_{15}Si$: C, 69.60; H, 5.75. Found: C, 69.38; H, 5.71.

4.14. Allyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-β-D-mannopyranoside 28

To a stirred solution of **27** (188 mg, 0.17 mM) in MeOH (10 mL) a mixture of MeOH (5 mL) and acetyl chloride (0.1 mL) was added. Stirring was continued for 20 h, the solvents were evaporated under diminished pressure with the aid of toluene and the residue was purified by column chromatography (7:3 hexane–EtOAc, then 5:3:0.5 hexane–EtOAc–MeOH) to yield **28** (93 mg, 70%) as a foam. $[\alpha]_D^{20} = -46.3$ (*c* 0.3, $CHCl_3$). ^{1}H NMR δ: 6.16 (t, 1H, $J_{4,3} = J_{4,5}$ = 10.2 Hz, H-4′), 5.99 (dd, 1H, $J_{3,2}$ 3.3 Hz, H-3′), 5.94 (dd, 1H, $J_{2,1}$ 1.7 Hz, H-2′), 5.90 (m, 1H, =CH), 5.49 (d, 1H, H-1′), 5.31 (m, 1H, =C*H*H), 5.17 (m, 1H, =CH*H*), 5.02 (m, 1H, H-5′), 4.65 (dd, 1H, $J_{6,5}$ 2.7, $J_{6,6'}$ 12.3 Hz, H-6′), 4.61 (br s, 1H, H-1), 4.41 (m, 1H, OC*H*H), 4.37 (dd, 1H, $J_{6,5}$ 3.1 Hz, H-6′), 4.22 (d, 1H, H-2), 4.11 (m, 2H, H-4, OCH*H*), 4.04 (m, 2H, H-6, H-6), 3.74 (dd, 1H, $J_{3,2}$ 3.0, $J_{3,4}$ 9.5 Hz, H-3), 3.36 (m, 1H, H-5). ^{13}C NMR δ: 166.3 (C=O), 166.1 (C=O), 165.6 (C=O), 165.4 (C=O), 118.2 (CH_2), 99.2 (C-1), 98.9 (C-1), 76.2, 74.6, 70.9, 70.5 (CH_2), 70.4, 68.5, 68.3, 66.7, 62.7 (CH_2), 62.4 (CH_2). HRMS-ESI calcd for $C_{43}H_{42}NaO_{15}$ $[M+Na]^+$: 821.2416, found: 821.2435.

4.15. Allyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-6-*O*-*tert*-butyldiphenylsilyl-β-D-mannopyranoside 10

Compound **28** (172 mg, 0.22 mM) was converted into disaccharide **10** using the procedure described for **1** to yield **10** (154 mg, 70%) as a foam. $[\alpha]_D^{20} = -30.7$ (*c* 0.3, $CHCl_3$). ^{1}H NMR δ: 6.16 (t, 1H, $J_{4,3} = J_{4,5}$ = 10.1 Hz, H-4′), 5.90 (m, 3H, H-2′, H-3′, =CH), 5.46 (d, 1H, $J_{1,2}$ 1.6 Hz, H-1′), 5.28 (m, 1H, =C*H*H), 5.16 (m, 1H, =CH*H*), 4.98 (m, 1H, H-5′), 4.66 (dd, 1H, $J_{6,5}$ 2.7, $J_{6,6'}$ 12.3 Hz, H-6′), 4.55 (br d, 1H, $J_{1,2}$ < 1 Hz, H-1), 4.37 (m, 2H, $J_{6,5}$ 3.1 Hz, H-6′, OC*H*H), 4.20 (br d, 1H, H-2), 4.05 (m, 4H, H-4, H-6, H-6, OCH*H*), 3.71 (dd, 1H, $J_{3,2}$ 3.0, $J_{3,4}$ 9.4 Hz, H-3), 3.37 (m, 1H, H-5), 1.11 (s, 9H, *t*Bu). ^{13}C NMR δ: 166.3 (C=O), 165.4 (2 × C=O), 165.3 (C=O), 118.2 (CH_2), 99.0 (C-1′), 98.8 (C-1), 76.2 (C-2), 74.8 (C-3), 74.5 (C-5), 71.0 (C-4), 70.6 (C-3′), 70.3 (C-2′), 70.2 (CH_2), 68.4 (C-5′), 66.8 (C-4′), 65.8 (C-6), 62.7 (C-6′), 26.8 (*t*Bu), 19.2 (C). HRMS-ESI calcd for $C_{59}H_{60}NaO_{15}Si$ $[M+Na]^+$: 1059.3594, found: 1059.3559. Anal. Calcd for $C_{59}H_{60}O_{15}Si$: C, 68.32; H, 5.83, Found: C, 68.16; H, 5.85.

4.16. Allyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→4)-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside 9

To a solution of **33** (160 mg, 0.15 mM) in EtOAc (3 mL) and MeOH (3 mL) was added solution of *p*-toluenesulfonic acid (80 mg) in EtOAc (1 mL) and MeOH (1 mL), and stirred at room temperature for 2.5 h. Then Et_3N (0.5 mL) was added, solvents were evaporated under diminished pressure, and the residue was purified by column chromatography (7:3 hexane–EtOAc, then 5:3:0.5 hexane–EtOAc–MeOH) to afford **9** (64 mg, 42%) as a foam. $[\alpha]_D^{20} = +10.9$ (*c* 0.3, $CHCl_3$). ^{1}H NMR δ: 6.10 (t, 1H, $J_{4,3} = J_{4,5}$ = 10.0 Hz, H-4′), 5.93 (m, 1H, =CH), 5.82 (m, 2H, H-2′, 3′), 5.58 (d, 1H, $J_{1,2}$ 1.6 Hz, H-1′), 5.32 (m, 1H, =C*H*H), 5.23 (m, 1H, =CH*H*), 4.92 (d, 1H, $J_{1,2}$ 1.2 Hz, H-1), 3.83–4.29 (m, 11H, other protons), 1.07 (s, 9H, *t*Bu). ^{13}C NMR δ: 166.0 (C=O), 165.8 (C=O), 165.5 (C=O), 165.3 (C=O), 117.8 (=CH), 98.7 (C-1), 98.2 (C-1), 75.9, 71.9, 71.5, 71.5, 70.6, 70.1, 69.8, 67.9 (OCH_2), 66.3, 63.6 (C-6), 62.4 (C-6), 26.8 (*t*Bu), 19.3 (SiC). HRMS-ESI calcd for

$C_{59}H_{60}NaO_{15}Si$ $[M+Na]^+$: 1059.3600, found: 1059.3599. Anal. Calcd for $C_{59}H_{60}O_{15}Si$: C, 68.32; H, 5.83. Found: C, 68.11; H, 5.97.

4.17. Allyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→4)-6-*O*-*tert*-butyldiphenylsilyl-β-D-mannopyranoside 12

Compound **36** (168 mg, 0.15 mM) was converted into the title compound using the procedure described for **9** to yield **12** (96 mg, 59%) as a foam. $[\alpha]_D^{20} = -29.7$ (*c* 0.35, $CHCl_3$). ^1H NMR δ: 6.10 (t, 1H, $J_{4,3} = J_{4,5} = 10.1$ Hz, H-4′), 5.96 (m, 1H, =CH), 5.86 (dd, 1H, $J_{3,2}$ 3.2 Hz, H-3′), 5.83 (dd, 1H, Hz, H-2′), 5.72 (d, 1H, $J_{1,2}$ 1.5 Hz, H-1′), 5.32 (m, 1H, =C*H*H), 5.25 (m, 1H, =CH*H*), 4.60 (br s, 1H, H-1), 4.42 (m, 1H, OC*H*H), 4.35 (dd, 1H, $J_{6,5}$ 2.2, $J_{6,6'}$ 12.3 Hz, H-6′), 4.24 (m, 1H, H-5′), 4.16 (m, 2H, H-6′, OCH*H*), 4.09 (m, 2H, H-6, H-6), 4.03 (m, 2H, H-4, H-2), 3.82 (m, 1H, H-3), 3.46 (m, 1H, H-5), 1.08 (s, 9H, *t*Bu). ^{13}C NMR δ: 166.0 (C=O), 165.6 (C=O), 165.3 (C=O), 165.3 (C=O), 118.2 (CH_2), 98.3 (C-1), 98.2 (C-1), 75.3, 75.0, 74.6, 71.2, 70.6, 70.0, 69.7, 69.6 (CH_2), 66.5, 63.5 (CH_2), 62.5 (CH_2), 26.8 (*t*Bu), 19.3 (C). HRMS-ESI calcd for $C_{59}H_{60}NaO_{15}Si$ $[M+Na]^+$: 1059.3594, found: 1059.3590. Anal. Calcd for $C_{59}H_{60}O_{15}Si$: C, 68.32; H, 5.83. Found: C, 68.34; H, 5.92.

4.18. Benzyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→4)-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside 15

Compound **38** (158 mg, 0.14 mM) was converted into the title compound using the procedure described for **9** to yield **15** (77 mg, 51%) as a foam. $[\alpha]_D^{20} = +19.7$ (*c* 0.3, $CHCl_3$). ^1H NMR δ: 6.11 (t, 1H, $J_{4,3} = J_{4,5} = 9.9$ Hz, H-4′), 5.84 (m, 2H, H-2′, 3′), 5.58 (d, 1H, $J_{1,2}$ 1.6 Hz, H-1′), 4.96 (d, 1H, $J_{1,2}$ 1.3 Hz, H-1), 4.79 and 4.56 (ABq, 2H, *J* 11.9 Hz, OCH_2), 4.30 (dd, 1H, $J_{6,5}$ 2.4, $J_{6,6'}$ 12.3 Hz, H-6′), 4.20 (m, 2H, $J_{3,2}$ 3.5, $J_{3,4}$ 8.8 Hz, H-3, 5′), 4.13 (dd, 1H, $J_{6',5}$ 3.4 Hz, H-6′), 4.07 (dd, 1H, $J_{6,5}$ 5.5, $J_{6,6'}$ 11.2 Hz, H-6), 4.04 (dd, 1H, $J_{6',5}$ 2.1 Hz, H-6), 3.98 (m, 2H, H-2, 4), 3.92 (m, 1H, H-5), 1.09 (s, 9H, $3 \times CH_3$). ^{13}C NMR δ: 166.0 (C=O), 165.8 (C=O), 165.5 (C=O), 165.3 (C=O), 98.8 (C-1), 98.0 (C-1), 76.0, 71.9, 71.6, 71.5, 70.6, 70.1, 69.8, 68.7 (OCH_2), 66.3, 63.6 (C-6), 62.4 (C-6), 26.8 (*t*Bu), 19.3 (SiC). HRMS-ESI calcd for $C_{63}H_{62}NaO_{15}Si$ $[M+Na]^+$: 1109.3750, found: 1109.3772. Anal. Calcd for $C_{63}H_{62}O_{15}Si{\cdot}H_2O$: C, 68.46; H, 5.84. Found: C, 68.93; H, 5.95.

4.19. General procedure for acetylation

An analytical sample of disaccharide (20–30 mg) was dissolved in pyridine (2 mL) and acetic anhydride (1 mL) was added. The mixture was kept overnight at room temperature, then solvents were evaporated under diminished pressure and the residue was purified by column chromatography (5:3:0.2 hexane–EtOAc–MeOH).

4.19.1. Allyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-3,4-di-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside 19

As a foam. $[\alpha]_D^{20} = -23.2$ (*c* 0.5, chloroform). ^1H NMR δ: 6.12 (t, 1H, $J_{4,3} = J_{4,5} = 10.1$ Hz, H-4′), 5.93 (dd, 1H, $J_{3,2}$ 3.3 Hz, H-3′), 5.86 (m, 1H, =CH), 5.74 (dd, 1H, $J_{2,1}$ 1.9Hz, H-2′), 5.36 (dd, 1H, $J_{3,2}$ 3.3, $J_{3,4}$ 9.5 Hz, H-3), 5.32 (t, 1H, $J_{4,3} = J_{4,5} = 9.4$ Hz, H-4), 5.27 (m, 1H, =C*H*H), 5.20 (m, 2H, H-1′, =CH*H*), 5.07 (d, 1H, $J_{1,2}$ 1.9 Hz, H-1), 4.67 (dd, 1H, $J_{6,5}$ 2.5, $J_{6,6'}$ 12.1 Hz, H-6′), 4.58 (m, 1H, H-5′), 4.50 (dd, 1H, $J_{6',5}$ 4.7 Hz, H-6′), 4.23 (m, 1H, OC*H*H), 4.18 (dd, 1H, H-2), 3.92 (m, 3H, H-5, 6, OC*H*H), 3.75 (m, 1H, H-6), 2.14 (s, 3H, CH_3), 1.86 (s, 3H, CH_3), 1.11 (s, 9H, $3 \times CH_3$). ^{13}C NMR δ: 170.6 (C=O), 169.3 (C=O), 166.1 (C=O), 165.6 (C=O), 165.2 (C=O), 165.0 (C=O), 117.7 (=CH_2), 99.6 (C-1′), 97.4 (C-1), 77.4 (C-2), 71.8 (C-5), 70.6 (C-3), 70.5 (C-2′), 69.5 and 69.5 (C-3′, 5′), 68.0 (OCH_2), 67.1 (C-4), 67.0 (C-4′), 63.5 (C-6), 62.9 (C-6′), 26.8 (*t*Bu), 20.8 (CH_3), 20.6 (CH_3), 19.2 (CSi). Anal. Calcd for $C_{63}H_{64}O_{17}Si{\cdot}H_2O$: C, 66.42; H, 5.84. Found: C, 66.69; H, 5.61.

4.19.2. Benzyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-3,4-di-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside 23

As a foam. $[\alpha]_D^{20} = -5.2$ (*c* 0.4, chloroform). ^1H NMR δ: 6.14 (t, 1H, $J_{4,3} = J_{4,5} = 10.1$ Hz, H-4′), 5.94 (dd, 1H, $J_{3,2}$ 3.3 Hz, H-3′), 5.76 (dd, 1H, $J_{2,1}$ 1.8 Hz, H-2′), 5.41 (dd, 1H, $J_{3,2}$ 3.3, $J_{3,4}$ 9.3 Hz, H-3), 5.37 (t, 1H, $J_{4,3} = J_{4,5} = 9.3$ Hz, H-4), 5.23 (d, 1H, H-1′), 5.12 (d, 1H, H-1), 4.82 and 4.48 (ABq, 2H, *J* 11.9 Hz, OCH_2), 4.53 (m, 2H, H-5′, 6′), 4.43 (m, 1H, H-6′), 4.25 (dd, 1H, H-2), 3.98 (m, 2H, H-5, 6), 3.80 (m, 1H, H-6), 2.18 (s, 3H, CH_3), 1.91 (s, 3H, CH_3), 1.15 (*t*Bu). ^{13}C NMR δ: 170.5 (C=O), 169.3 (C=O), 166.1 (C=O), 165.5 (C=O), 165.2 (C=O), 165.0 (C=O), 99.5 (C-1′), 97.2 (C-1), 77.3 (C-2), 71.9 (C-5), 70.6 (C-3), 70.5 (C-2′), 69.5 (C-3′), 69.4 (C-5′), 68.9 (OCH_2), 67.1 (C-4), 66.9 (C-4′), 63.5 (C-6), 62.7 (C-6′), 26.8 (*t*Bu), 20.8 (CH_3), 20.6 (CH_3), 19.2 (SiC). Anal. Calcd for $C_{67}H_{66}O_{17}Si{\cdot}H_2O$: C, 67.66; H, 5.76. Found: C, 67.94; H, 5.56.

4.19.3. Allyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→3)-2,4-di-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside 29

As a foam. $[\alpha]_D^{20} = -7.4$ (*c*, 2.85, $CHCl_3$). ^1H NMR δ: 6.12 (t, 1H, $J_{4,3} = J_{4,5} = 10.1$ Hz, H-4′), 5.83 (m, 1H, CH=), 5.78 (dd, 1H, $J_{3,2}$ 3.2 Hz, H-3′), 5.44 (dd, 1H, $J_{2,1}$ 1.9 Hz, H-2′), 5.40 (dd, 1H, $J_{2,3}$ 3.4, $J_{2,1}$ 1.6 Hz, H-2), 5.37 (t, 1H, $J_{4,3} = J_{4,5} = 9.9$ Hz, H-4), 5.28 (d, 1H, H-1′), 5.25 (m, 1H, =C*H*H), 5.19 (m, 1H, =CH*H*), 4.89 (d, 1H, H-1), 4.66 (dd, 1H, $J_{6,5}$ 2.3, $J_{6,6'}$ 12.2 Hz, H-6′), 4.57 (m, 1H, H-5′), 4.49 (dd, 1H, $J_{6,5}$ 3.9 Hz, H-6′), 4.32 (dd, 1H, H-3), 4.19 (m, 1H, OC*H*H), 4.00 (m, 1H, OCH*H*), 3.80 (m, 2H, H-5,5), 3.68 (m, 1H, H-6), 2.30 (s, 3H, Ac), 2.03 (s, 3H, Ac), 1.08 (s, 9H, Me_3C). ^{13}C NMR δ: 170.6 (C=O), 169.9 (C=O), 166.2 (C=O), 165.5 (C=O), 165.3 (C=O), 165.2 (C=O), 118.1 (=CH_2), 98.8 (C-1′), 96.1 (C-1), 75.1 (C-3), 72.0 (C-5), 71.2 (C-2), 70.8 (C-2′), 69.5 (C-5′), 69.3 (C-3′), 68.2 (C-4), 68.0 (OCH_2), 66.6 (C-4′), 63.1 (C-6), 62.7 (C-6′), 26.7 (Me_3C), 21.0 (Ac), 20.6 (Ac), 19.2 (CMe_3). HRMS-ESI calcd for $C_{63}H_{64}NaO_{17}Si$ $(M+Na)^+$: 1143.3805, found: 1143.3824.

4.19.4. Allyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→3)-2,4-di-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-β-D-mannopyranoside 30

As a foam. $[\alpha]_D^{20} = -31.9$ (*c* 1.8, $CHCl_3$). ^1H NMR δ: 6.14 (t, 1H, $J_{4,3} = J_{4,5} = 10.1$ Hz, H-4′), 5.91 (m, 1H, CH=), 5.76 (dd, 1H, $J_{3,2}$ 3.2 Hz, H-3′), 5.59 (br d, 1H, $J_{2,3}$ 3.3 Hz, H-2), 5.41 (dd, 1H, $J_{2,1}$ 1.8 Hz, H-2′), 5.34 (t, 1H, $J_{4,3} = J_{4,5} = 9.9$ Hz, H-4), 5.30 (m, 1H, =C*H*H), 5.25 (d, 1H, H-1′), 5.22 (m, 1H, =CH*H*), 4.75 (dd, 1H, $J_{6,5}$ 2.3, $J_{6,6'}$ 12.3 Hz, H-6′), 4.69 (m, 1H, H-5′), 4.59 (br s, 1H, H-1), 4.48 (dd, 1H, $J_{6,5}$ 3.8 Hz, H-6′), 4.38 (m, 1H, OCH), 4.11 (m, 1H, OCH), 3.99 (dd, 1H, H-3), 3.86 (dd, 1H, $J_{6,5}$ 6.1, $J_{6,6'}$ 11.6 Hz, H-6), 3.71 (dd, 1H, $J_{6,5}$ 2.3 Hz, H-6), 3.39 (m, 1H, H-5), 2.35 (s, 3H, Ac), 2.03 (s, 3H, Ac), 1.08 (s, 9H, Me_3C). ^{13}C NMR δ: 171.0 (C=O), 169.8 (C=O), 166.1 (C=O), 165.5 (C=O), 165.3 (C=O), 165.2 (C=O), 117.9 (=CH_2), 98.7 (C-1′), 97.2 (C-1), 76.5 (C-3), 75.5 (C-5), 70.8 (C-2′), 70.6 (C-2), 69.8 (OCH_2), 69.6 (C-5′), 69.2 (C-3′), 68.5 (C-4), 66.5 (C-4′), 63.1 (C-6), 62.5 (C-6′), 26.7 (Me_3C), 21.1 (Ac), 20.6 (Ac), 19.2 (CSi). HRMS-ESI calcd for $C_{63}H_{64}NaO_{17}Si$ $(M+Na)^+$: 1143.3805, found: 1143.3843. Anal. Calcd for $C_{63}H_{64}O_{17}Si{\cdot}3H_2O$: C, 64.38; H, 6.00. Found: C, 64.36; H, 5.54.

4.19.5. Benzyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→3)-2,4-di-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside 31

As a foam. $[\alpha]_D^{20} = -3.0$ (*c* 0.6, $CHCl_3$). ^1H NMR δ: 6.14 (t, 1H, $J_{4,3} = J_{4,5} = 10.1$ Hz, H-4′), 5.78 (dd, 1H, $J_{3,2}$ 3.2 Hz, H-3′), 5.44 (m,

2H, H-2, 2′), 5.42 (t, 1H, $J_{4,3} = J_{4,5} = 9.8$ Hz, H-4), 5.29 (d, 1H, $J_{1,2}$ 1.7 Hz, H-1′), 4.92 (d, 1H, $J_{1,2}$ 1.6 Hz, H-1), 4.73 and 4.53 (ABq, 2H, J 11.9 Hz, OCH_2), 4.66 (dd, 1H, $J_{6,5}$ 2.4, $J_{6,6'}$ 12.3 Hz, H-6′), 4.58 (m, 1H, H-5′), 4.50 (dd, 1H, $J_{6',5}$ 3.7 Hz, H-6′), 4.36 (dd, 1H, $J_{3,2}$ 3.4 Hz, H-3), 3.83 (m, 2H, H-5,6), 3.68 (m, 1H, H-6), 2.29 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 1.10 (s, 9H, $3 \times CH_3$). ^{13}C NMR δ: 170.6 (C=O), 170.0 (C=O), 166.2 (C=O), 165.5 (C=O), 165.3 (C=O), 165.3 (C=O), 98.8 (C-1′), 96.1 (C-1), 75.2 (C-3), 72.1 (C-5), 71.1 (C-2 or C-2′), 70.8 (C-2 or C-2′), 69.5 (C-5′), 69.3 (C-3′), 68.8 (OCH_2), 68.1 (C-4), 66.5 (C-4′), 63.0 (C-6), 62.6 (C-6′), 26.8 ($3 \times CH_3$), 21.0 (CH_3), 20.7 (CH_3), 19.2 (SiC). HRMS-ESI calcd for $C_{67}H_{66}NaO_{17}Si$ $[M+Na]^+$: 1193.3962, found: 1193.3973. Anal. Calcd for $C_{67}H_{66}O_{17}Si{\cdot}3H_2O$: C, 65.67; H, 5.92. Found: C, 65.81; H, 5.49.

4.19.6. Allyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→4)-2,3-di-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside 34

As a foam. $[\alpha]_D^{20} = +8.0$ (c 0.4, chloroform). ^{1}H NMR δ: 6.12 (t, 1H, $J_{4,3} = J_{4,5} = 10.2$ Hz, H-4′), 5.94 (m, 1H, =CH), 5.78 (dd, 1H, $J_{3,2}$ 3.2 Hz, H-3′), 5.61 (dd, 1H, H-2′), 5.48 (dd, 1H, $J_{3,2}$ 3.3, $J_{3,4}$ 9.9 Hz, H-3), 5.42 (d, 1H, $J_{1,2}$ 1.8 Hz, H-1′), 5.34 (m, 2H, H-2, =C*H*H), 5.25 (m, 1H, =CH*H*), 4.89 (d, 1H, $J_{1,2}$ 1.5 Hz, H-1), 4.31 (m, 2H, H-4, 6′), 4.21 (m, 2H, H-5′, OC*H*H), 4.16 (dd, 1H, $J_{6,5}$ 4.6, $J_{6,6'}$ 11.3 Hz, H-6), 4.02 (m, 3H, H-6, 6′, OCH*H*), 3.92 (m, 1H, H-5), 2.15 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 1.09 (s, 9H, *t*Bu). ^{13}C NMR δ: 170.3 (C=O), 170.0 (C=O), 165.9 (C=O), 165.3 (C=O), 165.3 (C=O), 165.2 (C=O), 118.2 (=CH_2), 99.5 (C-1′), 96.2 (C-1), 73.9 (C-4), 72.1 (C-5), 71.6 (C-3), 70.5 (C-2′), 70.1 (C-2), 69.9 (C-5′), 69.6 (C-3′), 68.2 (OCH_2), 66.2 (C-4′), 63.1 (C-6), 62.2 (C-6′), 26.8 (*t*Bu), 20.9 (CH_3), 20.8 (CH_3), 19.3 (CSi). Anal. Calcd for $C_{63}H_{64}O_{17}Si{\cdot}H_2O$: C, 66.42; H, 5.84. Found: C, 66.85; H, 5.80.

4.19.7. Benzyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→4)-2,3-di-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside 39

As a foam. $[\alpha]_D^{20} = +16.7$ (c 0.4, chloroform). ^{1}H NMR δ: 6.12 (t, 1H, $J_{4,3} = J_{4,5} = 10.1$ Hz, H-4′), 5.78 (dd, 1H, $J_{3,2}$ 3.2 Hz, H-3′), 5.62 (m, 1H, H-2′), 5.51 (dd, 1H, $J_{3,2}$ 3.3, $J_{3,4}$ 9.9 Hz, H-3), 5.41 (d, 1H, $J_{1,2}$ 1.9 Hz, H-1′), 5.39 (dd, 1H, $J_{2,1}$ 1.8 Hz, H-2), 4.88 (d, 1H, H-1), 4.75 and 4.57 (ABq, 2H, J 12.0 Hz, OCH_2Ph), 4.32 (m, 2H, H-4, 6′), 4.20 (m, 1H, H-5′), 4.16 (dd, 1H, $J_{6,5}$ 4.7, $J_{6,6'}$ 11.3 Hz, H-6), 4.00 (m, 2H, H-6, 6′), 3.93 (m, 1H, H-5), 2.15 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 1.10 (*t*Bu). ^{13}C NMR δ: 170.3 (C=O), 170.0 (C=O), 165.9 (C=O), 165.3 (C=O), 165.2 ($2 \times$ C=O), 99.5 (C-1′), 96.1 (C-1), 73.9 (C-4), 72.2 (C-5), 71.6 (C-3), 70.5 (C-2′), 70.0 (C-2), 69.9 (C-5′), 69.6 (C-3′), 68.9 (OCH_2Ph), 66.2 (C-4′), 63.0 (C-6′), 62.2 (C-6), 26.8 (*t*Bu), 20.9 (CH_3), 20.8 (CH_3), 19.3 (SiC). Anal. Calcd for $C_{67}H_{66}O_{17}Si{\cdot}H_2O$: C, 67.66; H, 5.76. Found: C, 67.87; H, 5.72.

Acknowledgement

This work was financed by the Grant No. PBZ-KBN-126/T09/07 from the Ministry of Science and Higher Education, Poland.

References

1. (a) Davis, B. G. *J. Chem. Soc., Perkin Trans. 1* **2000**, 2137–2160; (b) Nicolaou, K. C.; Mitchell, H. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 1576–1624.
2. (a) Kaur, K. J.; Hindsgaul, O. *Glycoconjugate J.* **1991**, *8*, 90–94; (b) Kartha, R. K. P.; Kiso, M.; Hasegawa, A.; Jennings, H. J. *J. Chem. Soc., Perkin Trans. 1* **1995**, 3023–3026; (c) Roy, R.; Page, D.; Figueroa-Perez, S.; Verez-Bencomo, V. *Glycoconjugate J.* **1998**, *15*, 251–263; (d) Figueroa-Perez, S.; Verez-Bencomo, V. *J. Carbohydr. Chem.* **1998**, *17*, 851–868; (e) Becker, B.; Furneaux, R. H.; Reck, F.; Zubkov, O. A. *Carbohydr. Res.* **1999**, *315*, 148–158; (f) Tanaka, H.; Nishida, Y.; Kobayashi, K. *J. Carbohydr. Chem.* **2000**, *19*, 413–418; (g) Utille, J.-P.; Priem, B. *Carbohydr. Res.* **2000**, *329*, 431–439; (h) Zhu, Y.; Kong, F. *Synlett* **2000**, 663–667; (i) Zhu, Y.; Kong, F. *Carbohydr. Res.* **2001**, *332*, 1–21; (j) Furneaux, R. H.; Pakulski, Z.; Tyler, P. C. *Can. J. Chem.* **2002**, *80*, 964–972; (k) Tarling, C. A.; Withers, S. G. *Carbohydr. Res.* **2004**, *339*, 2487–2497; (l) Pakulski, Z. *Polish J. Chem.* **2005**, *79*, 361–367; (m) Cmoch, P.; Pakulski, Z.; Swaczynová, J.; Strnad, M. *Carbohydr. Res.* **2008**, *343*, 995–1003.
3. (a) Lin, C.-C.; Shimazaki, M.; Heck, M.-P.; Aoki, S.; Wang, R.; Kimura, T.; Ritzèn, H.; Takayama, S.; Wu, S.-H.; Weitz-Schmidt, G.; Wong, C.-H. *J. Am. Chem. Soc.* **1996**, *118*, 6826–6840; (b) López, J. C.; Agocs, A.; Uriel, C.; Gómez, A. M.; Fraser-Reid, B. *Chem. Commun.* **2005**, 5088–5090.
4. (a) Kanie, O.; Baressi, F.; Ding, Y.; Labbe, J.; Otter, A.; Forsberg, L. S.; Ernst, B.; Hindsgaul, O. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2720–2722; (b) Ding, Y.; Labbe, J.; Kanie, O.; Hindsgaul, O. *Bioorg. Med. Chem* **1996**, *4*, 683–692; (c) Arya, P.; Ben, R. N. *Angew. Chem., Int. Ed.* **1997**, *36*, 1280–1282; (d) Yu, B.; Li, B.; Xing, G.; Hui, Y. *J. Comb. Chem.* **2001**, *3*, 404–406; (e) Steinmann, A.; Thimm, J.; Thiem, J. *Eur. J. Org. Chem.* **2007**, 5506–5513.
5. Fraser-Reid, B.; López, J. C.; Gómez, A. M.; Uriel, C. *Eur. J.Org. Chem.* **2004**, 1387–1395.
6. For some recent papers, see: (a) Matsuo, I.; Isomura, M.; Miyazaki, T.; Sakakibara, T.; Ajisaka, K. *Carbohydr. Res.* **1998**, *305*, 401–413; (b) Fraser-Reid, B.; López, J. C.; Radhakrishnan, K. V.; Mach, M.; Schlueter, U.; Gómez, A. M.; Uriel, C. *J. Am. Chem. Soc.* **2002**, *124*, 3198–3199; (c) Zeng, Y.; Kong, F. *Carbohydr. Res.* **2003**, *338*, 843–849; (d) Smiljanic, N.; Halila, S.; Moreau, V.; Djedaïni-Pilard, F. *Tetrahedron Lett.* **2003**, *44*, 8999–9002; (e) Uriel, C.; Gómez, A. M.; López, J. C.; Fraser-Reid, B. *Synlett* **2003**, 2203–2207; (f) Jayaprakash, K. N.; Fraser-Reid, B. *Org. Lett.* **2004**, *6*, 4211–4214; (g) Uriel, C.; Agocs, A.; Gómez, A. M.; López, J. C.; Fraser-Reid, B. *Org. Lett.* **2005**, *7*, 4899–4902; (h) Cid, M. B.; Valverde, S.; López, J. C.; Gómez, A. M.; García, M. *Synlett* **2005**, 1095–1100; (i) Rising, T. W. D. F.; Heidecke, C. D.; Fairbanks, A. J. *Synlett* **2007**, 1421–1425.
7. (a) Cruzado, C.; Bernabe, M.; Martin-Lomas, M. *Carbohydr. Res.* **1990**, *203*, 296–301; (b) Garegg, P. J.; Maloisel, J.-L.; Oscarson, S. *Synthesis* **1995**, 409–414; (c) Nicolaou, K. C.; van Delft, F. L.; Conley, S. R.; Mitchell, H. J.; Jin, Z.; Rodríguez, R. M. *J. Am. Chem. Soc.* **1997**, *119*, 9057–9058; (d) Kaji, E.; Harita, N. *Tetrahedron Lett.* **2000**, *41*, 53–56; (e) Kaji, E.; Shibayama, K.; In, K. *Tetrahedron Lett.* **2003**, *44*, 4881–4885.
8. (a) Oshima, K.; Aoyama, Y. *J. Am. Chem. Soc.* **1999**, *121*, 2315–2316; (b) Oshima, K.; Yamauchi, T.; Shimomura, M.; Miyauchi, S.; Aoyama, Y. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1319–1324.
9. Arjona, O.; de Dios, A.; Montero, C.; Plumet, J. *Tetrahedron* **1995**, *51*, 9191–9200.
10. Ness, R. K.; Fletcher, H. G.; Hudson, C. S. *J. Am. Chem. Soc.* **1950**, *72*, 2200–2205.
11. (a) Pakulski, Z. *Synthesis* **2003**, 2074–2078; (b) Sasaki, K.; Nagai, H.; Matsumura, S.; Toshima, K. *Tetrahedron Lett.* **2003**, *44*, 5605–5608; (c) Poletti, L.; Rencurosi, A.; Lay, L.; Russo, G. *Synlett* **2003**, 2297–2300; (d) Sasaki, K.; Matsumura, S.; Toshima, K. *Tetrahedron Lett.* **2004**, *45*, 7043–7047; (e) Rencurosi, A.; Lay, L.; Russo, G.; Caneva, E.; Poletti, L. *J. Org. Chem.* **2005**, *70*, 7765–7768; (f) Zhang, J.; Ragauskas, A. *Beilstein J. Org. Chem.* **2006**, *2*:12 doi:10.1186/1860-5397-2-12.; (g) Park, T.-J.; Weïwer, M.; Yuan, X.; Baytas, S. N.; Munoz, E. M.; Murugesan, S.; Linhardt, R. J. *Carbohydr. Res.* **2007**, *342*, 614–620.
12. Bashyal, B. P.; Fleet, G. W. J.; Gough, M. J.; Smith, P. W. *Tetrahedron* **1987**, *43*, 3083–3093.
13. Kurahashi, T.; Mizutani, T.; Yoshida, J. *J. Chem. Soc., Perkin Trans. 1* **1999**, 465–473.
14. (a) Whitfield, D. M.; Douglas, S. P.; Tang, T.-H.; Csizmadia, I. G.; Pang, H. Y. S.; Moolten, F. L.; Krepinsky, J. J. *Can. J. Chem.* **1994**, *72*, 2225–2238; (b) Bozó, E.; Vasella, A. *Helv. Chim. Acta* **1994**, *77*, 745–753.
15. Garegg, P. J. *Adv. Carbohydr. Chem. Biochem.* **2004**, *59*, 69–134.
16. Marwood, R. D.; Riley, A. M.; Jenkins, D. J.; Potter, B. V. L. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1935–1947.
17. Dziewiszek, K.; Zamojski, A. *Carbohydr. Res.* **1986**, *150*, 163–171.