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# Differential O-3/O-4 regioselectivity in the glycosylation of α and β anomers of 6-O-substituted *N*-dimethylmaleoyl-protected D-glucosamine acceptors

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**Abstract**—An assessment of the relative O-3/O-4 reactivities of both methyl α- and β-D-glycosides of *N*-dimethylmaleoyl (DMM) D-glucosamine acceptors protected at O-6 with benzoyl (Bz), benzyl (Bn), and *tert*-butyldiphenylsilyl (TBDPS) groups is presented using per-O-benzoylated β-D-galactofuranosyl and per-O-acetylated α-D-galactopyranosyl trichloroacetimidates as glycosyl donors. Using the former donor, the α anomer of the 6-O-benzoylated compound gave exclusive substitution at O-3, whereas the other two compounds with α-configuration kept this site as preferential. The β anomer of the 6-O-benzoylated compound gave the same amounts of reaction products on O-3 and O-4, whereas the other β analogs carried a more reactive O-4. The same reactions were carried out using as donor the less-reactive per-O-acetylated α-D-galactopyranosyl trichloroacetimidate. Although the same trend was found to occur, the O-4 was always relatively more reactive with the pyranosyl donor than with the furanosyl donor, when keeping the remaining factors constant. Furthermore, the β anomers of the acceptor gave almost exclusive substitution at O-4. These observations confirm and extend the utility of these 'matching' donor and acceptor reactivities.


*Keywords:* Glucosamine acceptors; *N*-Dimethylmaleoyl group; Galactofuranosyl donor; Galactopyranosyl donor; Regioselectivity

## 1. Introduction

The literature has provided many examples of selective glycosylation at O-4 of β-D-glucosamine derivatives having only the O-3 and O-4 positions free. This reaction suggested a higher reactivity for O-4, and this strategy was sometimes employed to introduce a second glycosyl donor on the less-reactive O-3 position. In 1998, Ellervik and Magnusson published a critical analysis[1] of previous publications where regioselective galactosylation of 6-O,N-protected glucosamine derivatives had been attempted showing that mixtures of 1→3- and 1→4-linked disaccharides were actually obtained in most of the reported cases. For instance, they showed that β-D-galactosylation of the glycosyl acceptors **1a** and **1b** with the disarmed[†] glycosyl donor **2a** gave exclusively the 1→4 disaccharides **3a** and **3b** in excellent yield.

In clear contrast, α-L-fucosylation of **1b** with the armed donor **4a**, under the same reaction conditions gave, in good yield, a 3.6:1 mixture of 1→3 and 1→4 disaccharides **5a** and **6a**. As occurred with donor **2a**, the disarmed donor **4b** reacted with **1b** with total

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† For the principle of armed–disarmed glycosyl donor, see the review by Fraser-Reid et al.[2]

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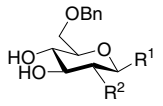
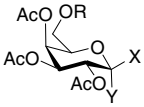
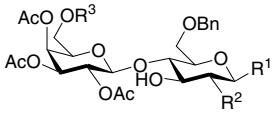


**1a**, $R^1 = O(CH_2)_2SiMe_3$; $R^2$ = NPhth
**1b**, $R^1 = OC_6H_4OMe$; $R^2$ = NTCP
**1c**, $R^1$ = SPh; $R^2$ = NTCP
**1d**, $R^1$ = OTDS; $R^2$ = NTCP

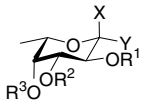


**2a**, R = Bn; X = SPh; Y = H
**2b**, R = Ac; X = H; Y = $OC(NH)CCl_3$
**2c**, R = Ac; X = OMe; Y = H

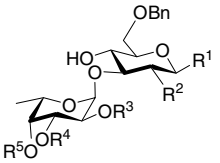


**3a**, $R^1 = O(CH_2)_2SiMe_3$; $R^2$ = NPhth; $R^3$ = Bn
**3b**, $R^1 = OC_6H_4OMe$; $R^2$ = NTCP; $R^3$ = Bn
**3c**, $R^1$ = SPh; $R^2$ = NTCP; $R^3$ = Ac
**3d**, $R^1$ = OTDS; $R^2$ = NTCP; $R^3$ = Ac

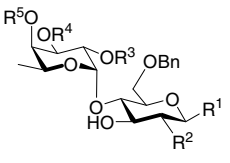
TDS = thexyldimethylsilyl; TCP = tetrachlorophtaloyl



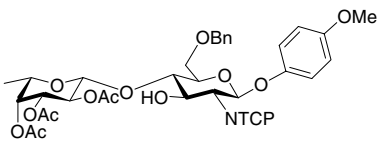
**4a**, X = H; Y = SPh; $R^1 = R^2 = R^3$ = Bn
**4b**, X = H; Y = SPh; $R^1 = R^2 = R^3$ = Ac
**4c**, X = $OC(NH)CCl_3$; Y = H; $R^1$ = Bn; $R^2 = R^3$ = Ac



**5a**, $R^1 = OC_6H_4OMe$; $R^2$ = NTCP; $R^3 = R^4 = R^5$ = Bn
**5b**, $R^1 = OC_6H_4OMe$; $R^2$ = NTCP; $R^3 = R^4 = R^5$ = Ac
**5c**, $R^1$ = SPh; $R^2$ = NTCP; $R^3$ = Bn; $R^4 = R^5$ = Ac
**5d**, $R^1$ = OTDS; $R^2$ = NTCP; $R^3$ = Bn; $R^4 = R^5$ = Ac



**6a**, $R^1 = OC_6H_4OMe$; $R^2$ = NTCP; $R^3 = R^4 = R^5$ = Bn
**6b**, $R^1 = OC_6H_4OMe$; $R^2$ = NTCP; $R^3 = R^4 = R^5$ = Ac
**6c**, $R^1$ = SPh; $R^2$ = NTCP; $R^3$ = Bn; $R^4 = R^5$ = Ac
**6d**, $R^1$ = OTDS; $R^2$ = NTCP; $R^3$ = Bn; $R^4 = R^5$ = Ac



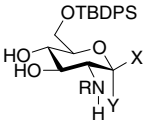
**7**

regioselectivity giving a mixture of 1→4 disaccharides **7** and **6b** (the β/α stereoselectivity was 2:1).

On the basis of these observations, Ellervik and Magnusson developed an efficient sequential double-glycosylation procedure (first at O-4 and then at O-3) for the synthesis of $Le^x$ trisaccharide and $sLe^x$ tetrasaccharide that avoids (at least in part) protecting group manipulations. Simultaneously, Schmidt and co-workers developed a similar approach for the synthesis of $Le^x$, and $Le^a$ building blocks and the $Le^x$ pentasaccharide.[3] They also found that, by β-D-galactosylation of acceptors **1c** and **1d** with the disarmed donor **2b**, the 1→4 disaccharides **3c** and **3d** were exclusively obtained in excellent yield. In addition, α-L-fucosylation of acceptors **1c** and **1d** with the armed donor **4c** again gave mixtures of disaccharides **5c** and **6c**, and **5d** and **6d**, respectively, in which the 1→3-linked disaccharides **5c** and **5d** were (as observed by Ellervik and Magnusson) the major products. Interestingly, the different regioselectivities in β-D-galactosylation versus α-L-fucosylation of acceptors **1a**, **1b**, **1c**, and **1d** are examples of 'match–mismatch' regioselectivity.[‡]

Later on, a series of publications appeared in the literature reporting that the O-4 of β-D-glucosamine acceptors carrying a variety of protecting groups at N-2 and O-6 was preferentially (if not exclusively) glycosylated under different reaction conditions.[5]

[‡] For an extension of the concept of 'match–mismatch', originally suggested by Paulsen[4] referring to the yield in the reaction of one donor/acceptor combination versus another, to the issue of regioselectivity, see Fraser-Reid et al.[2]

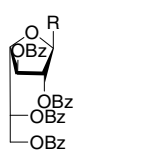


**8a**, R = Ac; X = OAll; Y = H
**8b**, R = Troc; X = H; Y = OAll

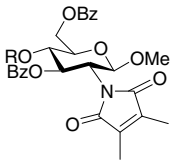
As further examples of 'match–mismatch' regioselectivity, it is remarkable that the β-D-glucosamine acceptor **8a**, carrying the bulky *tert*-butyldiphenylsilyl (TBDPS) group at O-6, was glycosylated at O-4 with total regioselectivity when coupled with the disarmed donor **2b**.[5c] However, when the α-D-glucosamine diol derivative **8b** was glycosylated with **2b** or **4c** in a perchloric acid–silica promoted coupling, O-3 reacted exclusively, independently of the nature (armed or disarmed) of the glycosyl donor.[5p]

In a view that the regioselective glycosylation at O-4 or O-3 constitutes an efficient and convenient strategy for the synthesis of biologically important compounds derived from D-glucosamine, we decided, as a continuation of our study on the reactivity of N-protected glucosaminyl acceptors,[6] to systematically examine the influence of the configuration of the anomeric carbon and the effect of the O-6 protecting group on the relative reactivities of both free hydroxyl groups.[7] The benzoyl, benzyl, and TBDPS groups, usually employed in carbohydrate chemistry, were used at O-6 of *N*-dimethylmaleimido (DMM) 3,4-diol derivatives in reaction with two donors, the furanosyl and pyranosyl trichloroacetimidates **9a**[8,9] and **2b**,[10] of different reactivity,[11] as a contribution to understand the relevance of the glycosyl

donor to the regioselectivity of these glycosylation reactions.[12]



**9a**, R = OC(NH)CCl$_3$
**9b**, R = OMe



**10a**, R = H
**10b**, R = β-D-Gal*f*
**10c**, R = β-D-Gal*p*

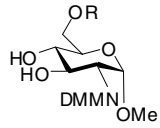
Upon activation of these donors, neighboring-group participation of the acyl group at O-2 ensures a β-selective coupling that leads to a simpler product analysis. Donor **9a** was also chosen because of the recent discovery of furanoside components in a wide variety of natural products of biological significance.[8,9,13,14] For instance, oligosaccharides derived from *N*-acetyl-D-glucosamine carrying D-galactopyranosyl and D-galactofuranosyl units have been shown to be components of the mucin of *Trypanosoma cruzi*.[15]

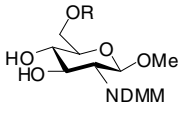
The advantages of the DMM group are well known: it is easily introduced, it is stable enough under a variety of reaction conditions used in carbohydrate chemistry, it is readily transformed into the *N*-acetyl derivative, etc.[16] In addition, the trichloroacetimidate-promoted glycosylations are widely used in the synthesis of oligosaccharides.[17]

## 2. Results and discussion

Initially, we confirmed that **9a** is indeed more reactive than **2b** through competitive glycosylation experiments. First, donors **9a** and **2b** were coupled separately with methanol, and the resulting methyl glycosides **9b** and **2c** were analyzed by $^1$H NMR spectroscopy. When an equimolecular mixture of both donors was allowed to compete for 1 equiv of methanol, a 2.8:1 mixture of **9b** and **2c** was obtained on the basis of the integration of the methoxyl group signals in the $^1$H NMR spectrum of the crude reaction mixture. In addition, when the known acceptor **10a**, carrying the *N*-dimethylmaleimido group, was allowed to react with an equimolecular mixture of both glycosyl donors, a 1.6:1 mixture of disaccharides **10b** and **10c** was obtained, indicating again that the furanosyl donor was preferred for coupling.

In order to investigate the effects of the factors mentioned above on the outcome of the regioselectivity, the reactivities of acceptors **11a–c** and **12a–c** were examined when coupled, under identical reaction conditions, with limiting amounts of the trichloroacetimidate donors **9a** and **2b**.





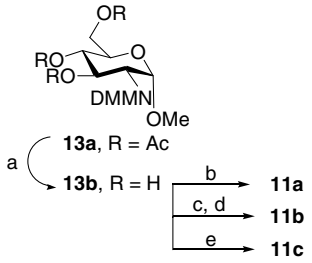
**11a**, R = Bz
**11b**, R = Bn
**11c**, R = TBDPS

**12a**, R = Bz
**12b**, R = Bn
**12c**, R = TBDPS

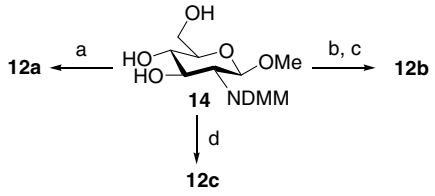
Acceptors **11a–c** were prepared from methyl 2-amino-2-deoxy-α-D-glucopyranoside,[18,19] which, upon treatment with dimethylmaleic anhydride, followed by acetic anhydride in pyridine,[16] afforded triacetate **13a**, easily purified by column chromatography. After deacetylation and subsequent regioselective benzoylation of triol **13b**, **11a** was obtained in 74% yield, whereas 4,6-*O*-benzylidene protection of **13b**, followed by reductive opening of the benzylidene group, afforded **11b** in 72% yield. In turn, selective silylation of the 6-OH of **13b** gave **11c** in 90% yield (Scheme 1).

Acceptors **12a–c** were prepared from the known compound **14**.[16,20] Regioselective benzoylation afforded **12a** in 55% yield. Alternatively, 4,6-*O*-benzylidene protection, followed by reductive opening of the benzylidene group, afforded **12b** in 73% yield. Finally, selective silylation of **14** gave **12c** in 73% yield (Scheme 2).

With these synthesized acceptors in hand, we performed a number of coupling experiments. Each glucosaminyl diol was first coupled with 1.1 equiv of the galactofuranosyl imidate **9a**, under activation with trimethylsilyl triflate (TMSOTf) at −25 °C. In most of the examples studied, the crude reaction mixtures were then analyzed by TLC and $^1$H NMR spectroscopy to establish the isomeric ratios. The results were confirmed by isolation of the disaccharides or their corresponding acetates by column chromatography. The results are shown in Table 1. When the α-anomeric diol **11a** was glycosylated, the only compound obtained was the 1→3-linked disaccharide **15a** in 68% yield. The corresponding 1→4-linked compound was not detected by



**Scheme 1.** Reagents and conditions: (a) MeONa, MeOH, rt; (b) benzoyl chloride, Py, −20 °C; (c) benzaldehyde dimethyl acetal, CSA, DMF; (d) $BH_3{\cdot}N(CH_3)_3$, $BF_3{\cdot}OEt_2$, $CH_3CN$; (e) TBDPSCl, imidazole, DMF, rt.



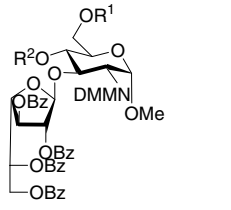

**Scheme 2.** Reagents and conditions: (a) benzoyl chloride, Py, −40 °C; (b) benzaldehyde dimethyl acetal, CSA, DMF; (c) $BH_3{\cdot}N(CH_3)_2$, $BF_3{\cdot}OEt_2$, $CH_3CN$; (d) TBDPSCl, imidazole, DMF, rt.

TLC or $^1$H NMR spectroscopy. By contrast, the glycosylation of diols **11b** and **11c** gave mixtures of regioisomers **15c** and **16a** (3.2:1) and **15e** and **16c** (5:1), respectively.

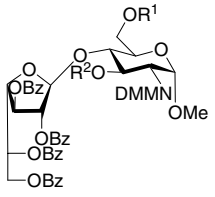
The assignment of the regioisomeric structures was readily accomplished by acylating the disaccharide in question and determining the chemical shift of the newly downfield-shifted proton.

For example, in **15a**, **15c**, and **15e**, acetylation gave rise to signals at $\delta_H$ 5.24 (**15b**), 5.13 (**15d**), and 5.02 (**15f**), respectively, assignable to the glucosamine H-4, whereas acetates **16b** and **16d** gave rise to a multiplet at $\delta_H$ 6.41–6.33 and a double of doublet at $\delta_H$ 6.37 as expected for the H-3 of a glucosamine moiety.

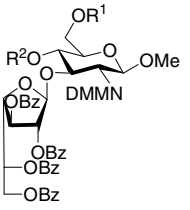
When the β-D-glucosaminyl acceptors **12a**–**c** were coupled with **9a**, mixtures of 1→3- and 1→4-linked disaccharides **17a** and **18a** (1:1) and **17c** and **18c** (1:2.9) and **17e** and **18e** (1:2.2), respectively, were obtained (Table 1). Again, the analysis of the $^1$H NMR spectra of acetates **17b** ($\delta_H$ 5.22, H-4), **17d** ($\delta_H$ 5.08,



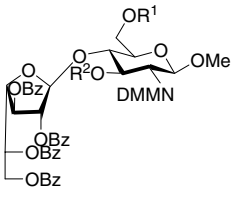

**15a**, $R^1$ = Bz; $R^2$ = H
**15b**, $R^1$ = Bz; $R^2$ = Ac
**15c**, $R^1$ = Bn; $R^2$ = H
**15d**, $R^1$ = Bn; $R^2$ = Ac
**15e**, $R^1$ = TBDPS; $R^2$ = H
**15f**, $R^1$ = TBDPS; $R^2$ = Ac




**16a**, $R^1$ = Bn; $R^2$ = H
**16b**, $R^1$ = Bn; $R^2$ = Ac
**16c**, $R^1$ = TBDPS; $R^2$ = H
**16d**, $R^1$ = TBDPS; $R^2$ = Ac

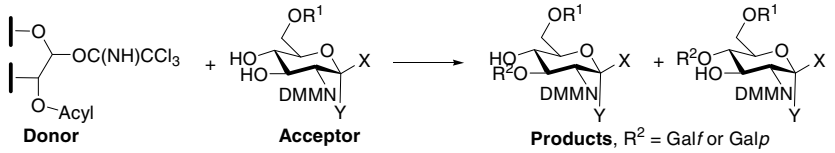



**17a**, $R^1$ = Bz; $R^2$ = H
**17b**, $R^1$ = Bz; $R^2$ = Ac
**17c**, $R^1$ = Bn; $R^2$ = H
**17d**, $R^1$ = Bn; $R^2$ = Ac
**17e**, $R^1$ = TBDPS; $R^2$ = H
**17f**, $R^1$ = TBDPS; $R^2$ = Ac




**18a**, $R^1$ = Bz; $R^2$ = H
**18b**, $R^1$ = Bz; $R^2$ = Ac
**18c**, $R^1$ = Bn; $R^2$ = H
**18d**, $R^1$ = Bn; $R^2$ = Ac
**18e**, $R^1$ = TBDPS; $R^2$ = H
**18f**, $R^1$ = TBDPS; $R^2$ = Ac

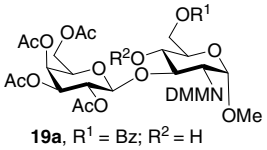
**Table 1.** Ratios and yields of 3- and 4-linked disaccharides obtained after reaction of donors **9a** and **2b** with α- and β-glycosyl acceptors



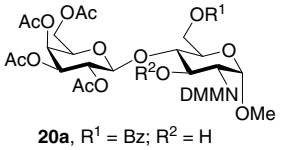

| Entry | Donor | Acceptor | Products | Ratio (1→3):(1→4) | Yields (%) |
|---|---|---|---|---|---|
| i | **9a** (furanosyl) | **11a**, $R^1$ = Bz, Y = OMe, X = H | Only **15a** | 1:0 | 68 |
| ii | **9a** (furanosyl) | **11b**, $R^1$ = Bn, Y = OMe, X = H | **15c** + **16a** | 3.2:1 | 71 |
| iii | **9a** (furanosyl) | **11c**, $R^1$ = TBDPS, Y = OMe, X = H | **15e** + **16c** | 5:1 | 73 |
| iv | **2b** (pyranosyl) | **11a**, $R^1$ = Bz, Y = OMe, X = H | **19a** + **20a** | 2:1[a] | 91 |
| v | **2b** (pyranosyl) | **11b**, $R^1$ = Bn, Y = OMe, X = H | **19c** + **20c** | 1:1 | 56 |
| vi[b] | **2b** (pyranosyl) | **11c**, $R^1$ = TBDPS, Y = OMe, X = H | **19e** + **20e** | 1.6:1 | 50 |
| vii | **9a** (furanosyl) | **12a**, $R^1$ = Bz, Y = H, X = OMe | **17a** + **18a** | 1:1 | 75 |
| viii | **9a** (furanosyl) | **12b**, $R^1$ = Bn, Y = H, X = OMe | **17c** + **18c** | 1:2.9 | 71 |
| ix | **9a** (furanosyl) | **12c**, $R^1$ = TBDPS, Y = H, X = OMe | **17e** + **18e** | 1:2.2 | 87 |
| x | **2b** (pyranosyl) | **12a**, $R^1$ = Bz, Y = H, X = OMe | **22a** + **23a** | 1:13[c] | 74 |
| xi | **2b** (pyranosyl) | **12b**, $R^1$ = Bn, Y = H, X = OMe | Only **23c** | 0:1 | 88 |
| xii | **2b** (pyranosyl) | **12c**, $R^1$ = TBDPS, Y = H, X = OMe | Only **23e** | 0:1 | 88 |

[a] This ratio was determined by $^1$H NMR spectroscopy. The ratio determined by isolation of acetates **19b** and **20b** was 2.3:1.
[b] An inseparable mixture of disaccharides **19e** and **20e** together with trisaccharide **21** (28%) and unreacted **11a** (9.6%) was obtained. The ratio of regioisomeric disaccharides was determined as their corresponding acetates **19f** and **20f**.
[c] This ratio was determined by $^1$H NMR spectroscopy. The minor disaccharide was better purified as its acetate **22b**.

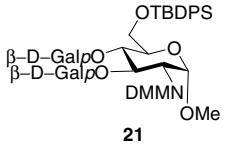
H-4), **17f** ($\delta_H$ 5.08, H-4), **18b** ($\delta_H$ 5.70, H-3), **18d** ($\delta_H$ 5.65, H-3), and **18f** ($\delta_H$ 5.68, H-3) was used to assign their regioisomeric structures. As expected, all disaccharides obtained in this part of the study were shown to be β-linked, on the basis of the small coupling constant of the galactofuranose anomeric proton ($J_{1',2'} < 1$ Hz) and by the characteristic C-1′ $^{13}$C NMR chemical shift.[8]



**19a**, $R^1$ = Bz; $R^2$ = H
**19b**, $R^1$ = Bz; $R^2$ = Ac
**19c**, $R^1$ = Bn; $R^2$ = H
**19d**, $R^1$ = Bn; $R^2$ = Ac
**19e**, $R^1$ = TBDPS; $R^2$ = H
**19f**, $R^1$ = TBDPS; $R^2$ = Ac

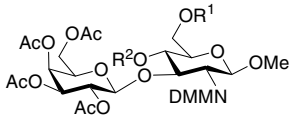


**20a**, $R^1$ = Bz; $R^2$ = H
**20b**, $R^1$ = Bz; $R^2$ = Ac
**20c**, $R^1$ = Bn; $R^2$ = H
**20d**, $R^1$ = Bn; $R^2$ = Ac
**20e**, $R^1$ = TBDPS; $R^2$ = H
**20f**, $R^1$ = TBDPS; $R^2$ = Ac

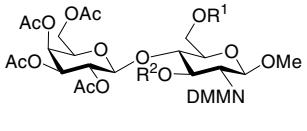


**21**

The regioselectivity of glycosylation of acceptors **11a**–**12c** in couplings with the less-reactive glycosyl donor**2b** was also analyzed. The α-anomeric diols **11a** and **11b** afforded mixtures of 1→3- and 1→4-linked disaccharides **19a** and **20a** (2:1) and **19c** and **20c** (1:1), respectively, whereas acceptor **11c** gave an inseparable mixture of disaccharides **19e** and **20e** (50%), trisaccharide **21** (28%), and unreacted acceptor **11c** (9.6%). The disaccharides were isolated as their corresponding acetates **19f** and **20f** in a 1.6:1 ratio. The spectra of the corresponding acetates **19b** ($\delta_H$ 5.11, H-4), **19d** ($\delta_H$ 5.01, H-4), **19f** ($\delta_H$ 4.89, H-4), **20b** ($\delta_H$ 6.27, H-3), **20d** ($\delta_H$ 6.21, H-3), and **20f** ($\delta_H$ 6.25, H-3) were used to assign their regioisomeric structures. By contrast, the β-D-glucosaminyl acceptors **12a**–**c** were preferentially glycosylated at O-4 giving a 1:13 mixture of **22a** and **23a**, and exclusively **23c** and **23e**, respectively (Table 1). As usual, the analysis of the $^1$H NMR spectra of the acetates **22b** ($\delta_H$ 5.09, H-4), **23b** ($\delta_H$ 5.60, H-3), **23d** ($\delta_H$ 5.50, H-3), and **23f** ($\delta_H$ 5.55, H-3) was used to assign their regioisomeric structures. On the basis of the value of the $J_{1',2'}$ (ca. 7.9 Hz), all disaccharides obtained were shown to contain the β-D-galactopyranosyl moiety.



**22a**, $R^1$ = Bz; $R^2$ = H
**22b**, $R^1$ = Bz; $R^2$ = Ac



**23a**, $R^1$ = Bz; $R^2$ = H
**23b**, $R^1$ = Bz; $R^2$ = Ac
**23c**, $R^1$ = Bn; $R^2$ = H
**23d**, $R^1$ = Bn; $R^2$ = Ac
**23e**, $R^1$ = TBDPS; $R^2$ = H
**23f**, $R^1$ = TBDPS; $R^2$ = Ac

As shown in Table 1, the evaluation of the influence of the configuration at the anomeric carbons on the regioselective glycosylation of the anomeric glucosaminyl diols **11a**–**11c** and **12a**–**12c** with donors **9a** and **2b** showed qualitatively different results. In the α anomers **11a**–**11c**, as was previously observed in acylation[15] and tosylation[21] reactions of 6-O-protected 2-amino-2-deoxy-α-D-glucopyranosides, the O-3 was preferentially glycosylated, whereas in the β anomers **12a**–**12c**, the preference was, as it had been reported,[1,3,5] at O-4. However, and due to the influence of the 6-O-protecting groups, some variations in the regioselectivity outcome were observed. In addition, the reactivity of the disarmed donors (**9a** or **2b**) also plays a role in the regioselectivity of these reactions.

A clear preference for the glycosylation at O-3 was observed when the more reactive galactofuranosyl donor **9a** was used in reactions with the α acceptors **11a**–**11c**. The glycosylation of **11a** carrying the electron-withdrawing 6-*O*-benzoyl group represents an excellent example of 'match' regioselectivity since the 1→3-linked disaccharide **15a** was exclusively observed. With **11b**, protected with the electron-donating benzyl group at O-6, and **11c** carrying the bulky TBDPS group, mixtures of disaccharides were obtained; however, the preference for the 1→3-linked compounds was still being observed. It is worthwhile mentioning that the related acceptor **8b** was reported to have total regioselectivity for O-3, although under quite different reaction conditions.[5p] With the β acceptors **12b** and **12c**, preference for O-4 was observed—more marked with **12b**—whereas no regioselectivity was observed with **12a**.

When the α acceptors **11a**–**11c** were glycosylated with the less-reactive galactopyranosyl donor **2b**, regioselectivity was poor with **11a** and was not detected with **11b**. With **11c** a completely different result was obtained in comparison with the related acceptor **8b**.[5p] Under our reaction conditions, **11c** was the only acceptor that afforded an appreciable amount of a trisaccharide (**21**) and further, the ratio of 1→3 and 1→4 disaccharides was only 1.6:1. By contrast, the glycosylation of the β acceptors **12a**–**12c** showed preference for the O-4. The galactosylation of acceptor **12a** gave a 1:13 mixture of 1→3 and 1→4 disaccharides, whereas **12b** and **12c**, with the electron-donating benzyl group and the bulky TBDPS group at O-6, respectively, afforded exclusively the 1→4 disaccharides **23c** and **23e**. These galactosylations also constitute excellent examples of 'match' regioselectivity.

The influence of the reactivity of glycosyl donors in glycosylation reactions has been fully analyzed, and many publications have appeared in the literature. Among them, the work of Koeller and Wong[22] showed systematic studies of the reactivity of a large number of thioglycosides with the idea of developing a programmable one-pot oligosaccharide synthesis. It is also

remarkable that more recently, Fraser-Reid and coworkers have shown that the nature (armed or disarmed) of the glycosyl donor has a great influence on the regioselectivity of glycosylation reactions.[12] These observations were the basis for the development of the new concept for 'matching' donors with acceptors called 'reciprocal donor acceptor selectivity'.[23] In connection with glycosylations of 3,4-diols derived from D-glucosamine, Ellervick and Magnusson[1] and Schmidt and coworkers[3] had also observed that, for glycosylations with the disarmed donor **2a** or **2b**, the 1→4-linked disaccharides were obtained, whereas glycosylations with the armed donors **4a** or **4c** afforded mainly the 1→3-linked compounds. Interestingly, we have observed that of both disarmed donors analyzed in this study, the furanosyl donor (**9a**) showed preference for the O-3 of the α acceptors (**11a**–**c**) and the pyranosyl donor (**2b**), as had been previously observed,[1,3,5] for the O-4 of the β acceptors (**12a**–**c**), respectively. In any case, it can be observed that in the α acceptors the relative reactivity at O-3 is higher than at O-4 and more marked with the furanosyl donor than with the less-reactive pyranosyl one. Furthermore, the reactivity increases when the substituent at O-6 changes from Bn to TBDPS to Bz. On the other hand, the β anomers show a relatively higher reactivity at O-4, which is clearly evident with the less-reactive pyranosyl donor (Table 1). Although a rationalization for these regioselectivities awaits further insight, our observations confirm and extend the utility of these 'matching' donor and acceptor reactivities.

## 3. Experimental

Melting points were determined on an Electrothermal 9100 apparatus and are uncorrected. The $^1$H and $^{13}$C NMR spectra were recorded on Bruker AC 200 and Bruker Avance 300 spectrometers for $CDCl_3$ solutions with $Me_4Si$ as internal standard. For the 2D and COSY experiments, Bruker standard software was employed. Mass spectra were measured using MALDI-TOF HRMS and HRFABMS at the UCR Mass Spectrometry Facility (Department of Chemistry, University of California Riverside, USA) and Kent Mass Spectrometry (Kent, UK). Optical rotations were measured with a Jasco DIP-1000 polarimeter. Column chromatography was performed on Silica Gel 60 H, slurry packed, run under low pressure of nitrogen and employing increasing amounts of EtOAc in hexane as solvent (except where noted). Analytical TLC was carried out using Kieselgel GF254 (E. Merck) with a thickness of 0.20 mm. The homogeneity of all disaccharides prior to the high-resolution mass spectral determination was carefully verified by TLC. Reactions were routinely run under a dry nitrogen atmosphere with magnetic stirring. All chemicals were used as purchased or purified according to standard procedures.

### 3.1. Competition experiments

**3.1.1. Competitive experiment of reactivity of donors 9a and 2b with methanol.** A suspension of donors **9a**[8,9] and **2b**[10] (0.11 mmol), anhyd MeOH (0.1 mmol), activated 4 Å molecular sieves (30 mg) in anhyd $CH_2Cl_2$ (7 mL), and $CH_3CN$ (190 μL) was stirred at room temperature. After 40 min, the mixture was cooled to −30 °C, TMSOTf (0.33 mmol) was slowly added, and stirring was continued for 30 min. The mixture was then neutralized by addition of solid $NaHCO_3$ (190 mg) and filtered through a silica gel pad with copious washings with EtOAc. The filtrate was dried ($Na_2SO_4$) and evaporated. The ratio of **9b**:**2c** was 2.8:1 by integration of the signals at $\delta$ 3.49 (s, 3H, $OCH_3$) in **9b** and $\delta$ 3.53 (s, 3H, $OCH_3$) in **2c** in the $^1$H NMR spectrum of the crude reaction mixture.

**3.1.1.1. Data for 9b.** $R_f$ 0.71 (7:3 hexane–EtOAc); $^1$H NMR (300 MHz): $\delta$ 8.15–7.85, 7.60–7.20 (m, 20H, ArH), 6.11–6.05 (m, 1H, H-5), 5.64 (ddd, 1H, $J_{3,1}$ 0.6, $J_{3,2}$ 1.3, $J_{3,4}$ 5.4 Hz, H-3), 5.47 (dd, 1H, $J_{2,1}$ 0.4 Hz, H-2), 5.22 (br s, 1H, H-1), 4.80 (dd, 1H, $J_{6a,5}$ 4.8, $J_{6a,6b}$ 11.7 Hz, H-6a), 4.75 (dd, 1H, $J_{6b,5}$ 6.6 Hz, H-6b), 4.67 (dd, 1H, $J_{4,5}$ 3.5 Hz, H-4), 3.49 (s, 3H, $OCH_3$); $^{13}$C NMR (50 MHz): $\delta$ 165.98–165.34 (CO), 134.36–128.25 (C-Ar), 106.76 (C-1), 82.04 (C-4), 81.05 (C-2), 77.53 (C-3), 70.21 (C-5), 63.37 (C-6), 54.85 ($OCH_3$).

**3.1.1.2. Data for 2c.** $R_f$ 0.23 (7:3 hexane–EtOAc); $^1$H NMR (300 MHz): $\delta$ 5.39 (dd, 1H, $J_{4,5}$ 1.1, $J_{4,3}$ 3.3 Hz, H-4), 5.20 (dd, 1H, $J_{2,1}$ 8.0, $J_{2,3}$ 10.5 Hz, H-2), 5.02 (dd, 1H, H-3), 4.40 (d, 1H, H-1), 4.21 (dd, 1H, $J_{6a,5}$ 6.6, $J_{6a,6b}$ 11.2 Hz, H-6a), 4.14 (dd, 1H, $J_{6b,5}$ 6.9 Hz, H-6b), 3.91 (ddd with appearance of dt, 1H, H-5), 3.52 (s, 3H, $OCH_3$), 2.15, 2.07, 2.06, 1.99 (4s, 12H, $COCH_3$); $^{13}$C NMR (75 MHz): $\delta$ 170.31–169.40 (CO), 101.98 (C-1), 70.87 (C-5), 70.53 (C-3), 68.71 (C-2), 66.96 (C-4), 61.17 (C-6), 56.87 ($OCH_3$), 26.68–20.46 ($COCH_3 \times 4$).

**3.1.2. Competitive glycosylation experiment of donors 9a and 2b with acceptor 10a.** A suspension of acceptor **10a**[6] (0.1 mmol), donors **9a**,[8,9] and **2b**[10] (0.1 mmol), activated 4 Å molecular sieves (146 mg) in anhyd $CH_2Cl_2$ (3.9 mL), and $CH_3CN$ (126 μL) was stirred at room temperature. After 40 min, the mixture was cooled to −30 °C, TMSOTf (0.4 mmol) was slowly added, and stirring was continued for 3 h. The mixture was then neutralized by addition of solid $NaHCO_3$ (400 mg) and filtered through a silica gel pad with copious washings with EtOAc. The filtrate was dried ($Na_2SO_4$) and evaporated. The ratio of **10b**:**10c** was 1.6:1 by integra-

tion of the signals at 3.47 (s, 3H, $OCH_3$) in **10b** and 3.44 (s, 3H, $OCH_3$) in **10c** in the $^1H$ NMR spectrum of the crude reaction mixture.

**3.1.2.1. Disaccharide 10b.** Spectral data were identical to those described in Ref. 6.

**3.1.2.2. Disaccharide 10c.** $[\alpha]_D^{27}$ +26.1 (*c* 1.02, $CHCl_3$); $R_f$ 0.02 ($(iPr)_2O$); $^1H$ NMR (300 MHz): $\delta$ 8.15–7.90, 7.55–7.35 (m, 10H, ArH), 5.91 (dd, 1H, $J_{3,4}$ 8.5, $J_{3,2}$ 10.6 Hz, H-3), 5.24 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 5.14–5.09 (m, 1H, H-4′), 5.08 (dd, 1H, $J_{2',1'}$ 7.9, $J_{2',3'}$ 10.2 Hz, H-2′), 4.79 (dd, 1H, $J_{3',4'}$ 3.5 Hz, H-3′), 4.77 (dd, 1H, $J_{6a,5}$ 1.5, $J_{6a,6b}$ 12.1 Hz, H-6a), 4.56 (d, 1H, H-1′), 4.42 (dd, 1H, $J_{6b,5}$ 4.8 Hz, H-6b), 4.17 (dd, 1H, H-2), 4.08 (dd, 1H, $J_{4,5}$ 10.0 Hz, H-4), 4.02–3.93 (m, 1H, H-5), 3.51 (dd, 1H, $J_{6'a,5'}$ 7.8, $J_{6'a,6'b}$ 10.5 Hz, H-6′a), 3.44 (s, 3H, $OCH_3$), 3.40 (d, 1H, $J_{6'a,5'}$ 10.5 Hz, H-6′a), 3.38–3.33 (m, 1H, H-5′), 2.00, 1.98, 1.93, 1.91 (4s, 12H, $CO\mathit{CH}_3 \times 4$), 1.88 (br s, 6H, $C\mathit{CH}_3 \times 2$); $^{13}C$ NMR (75 MHz): $\delta$ 169.97–164.91 (CO), 133.28, 129.55–128.38 (C-Ar, C × 2), 100.65 (C-1′), 99.00 (C-1), 77.10 (C-4), 72.58 (C-5), 71.47 (C-3), 70.82 (C-3′), 70.37 (C-5′), 69.09 (C-2′), 66.18 (C-4′), 62.64 (C-6), 59.90 (C-6′), 56.86 ($OCH_3$), 54.54 (C-2), 20.50–20.39 ($CO\mathit{CH}_3 \times 4$), 8.62 ($C\mathit{CH}_3$).

### 3.2. General procedure for glycosylation and acetylation reactions

A suspension of acceptor **11a**, **11b**, **11c**, **12a**, **12b**, or **12c** (0.1 mmol), donor **9a**[8,9] or **2b**[10] (0.11 mmol), activated 4 Å molecular sieves (106 mg) in anhyd $CH_2Cl_2$ (4.9 mL) and $CH_3CN$ (133 μL) was stirred at room temperature. After 40 min, the mixture was cooled to −25 °C, TMSOTf (0.21 mmol) was slowly added, and stirring was continued for 30 min. The mixture was then neutralized by addition of solid $NaHCO_3$ (188 mg) and filtered through a silica gel pad with copious washings with EtOAc. The filtrate was dried ($Na_2SO_4$) and evaporated. The residue was chromatographed to give the products, except where noted otherwise. The glycosylation of acceptors **11c** and **12c** was performed under the same reaction conditions except that 0.037 mmol of TMSOTf was used as a promoter. The acetylations were carried out under standard conditions: pyridine, DMAP, $Ac_2O$, room temperature, overnight. All disaccharides were characterized as their corresponding acetates. In the $^1H$ NMR data of the disaccharides and their corresponding acetates listed below, the carbinolic and the 'new' signals upon acylation are shown in italics.

**3.2.1. Methyl 6-*O*-benzoyl-2-deoxy-2-dimethylmaleimido-α-D-glucopyranoside (11a).** Starting with methyl 2-deoxy-2-methoxycarbonylamido-α-D-glucopyranoside[18] and following the procedure described by Bauer and coworkers,[19] methyl 2-amino-2-deoxy-α-D-glucopyranoside was obtained and used in the next step without further purification. A MeOH solution of this product was treated with dimethylmaleic anhydride (281 mg, 2.21 mmol) and stirred for 20 min. $Et_3N$ (471 μL, 3.34 mmol) was added, and the reaction mixture was again treated with dimethylmaleic anhydride (281 mg, 2.21 mmol). The reaction mixture was warmed to 60 °C with stirring for 5.15 h, then dried well in vacuo. The residue from the last step was treated with pyridine (9 mL), $Ac_2O$ (4.3 mL) and stirred at room temperature. After 22 h water was added, and the reaction mixture was stirred for 10 min and extracted with $Et_2O$. The organic layer was washed with satd aq $NaHCO_3$, dried ($Na_2SO_4$), and evaporated. The residue was recrystallized (EtOAc, $(iPr)_2O$) to give pure **13a** (1.04 g, 66%) as a solid: mp 196.3–196.8 °C; $^1H$ NMR (200 MHz): $\delta$ 6.39 (dd, 1H, $J_{3,4}$ 9.1, $J_{3,2}$ 11.5 Hz, H-3), 5.01 (dd with appearance of t, 1H, $J_{4,5}$ 9.5 Hz, H-4), 4.73 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 4.43–4.30 (m, 1H, H-6a), 4.33 (dd, 1H, H-2), 4.17–4.03 (m, 2H, H-5, H-6b), 3.33 (s, 3H, $OCH_3$), 2.10, 2.02, 1.96, 1.90 (4s, 15H, $CO\mathit{CH}_3 \times 3$, $C\mathit{CH}_3 \times 2$); $^{13}C$ NMR (50 MHz): $\delta$ 170.98–169.16 (CO), 137.10 (C × 2), 98.19 (C-1), 69.84, 67.24, 67.18 (C-3, C-4, C-5), 61.81 (C-6), 55.22 ($OCH_3$), 53.30 (C-2), 20.49 ($CO\mathit{CH}_3 \times 3$), 8.60 ($C\mathit{CH}_3 \times 2$). HRCIMS: calcd for $C_{19}H_{25}NO_{10}$ $[M+NH_4]^+$, *m*/*z* 445.1817; found, *m*/*z* 445.1833.

A mixture of triacetate **13a** (462 mg, 1.08 mmol), anhyd MeOH (10.5 mL), and NaOMe (0.169 M, 650 μL) was stirred at room temperature. After 1 h, the solution was neutralized with Amberlite IR-120 ($H^+$) resin, filtered, and evaporated. The residue was chromatographed (9:1 EtOAc–MeOH) to yield **13b** (299 mg, 92%) as a foamy solid. To a stirred solution of triol **13b** (131 mg, 0.44 mmol) in anhyd pyridine (3.2 mL) at −40 °C was added dropwise freshly distilled benzoyl chloride (157 μL, 1.35 mmol). After 2 h at −20 °C the reaction mixture was allowed to warm to room temperature. After 3 h, water was added, and the mixture was stirred for 10 min and then extracted with EtOAc. The organic layer was washed with 1 N HCl, satd aq $NaHCO_3$ and brine, dried ($Na_2SO_4$), and evaporated. The residue was chromatographed to give **11a** (131 mg, 74%) as a solid: mp 196.6–198.0 °C; $[\alpha]_D^{32}$ +99.9 (*c* 1.02, MeOH); $R_f$ 0.09 (1:1 hexane–EtOAc); $^1H$ NMR (200 MHz): $\delta$ 8.08 (d, 2H, *J* 7.1 Hz, ArH), 7.70–7.40 (m, 3H, ArH), 5.02 (dd, 1H, $J_{3,4}$ 9.0, $J_{3,2}$ 11.2 Hz, H-3), 4.80 (d, 1H, $J_{1,2}$ 3.4 Hz, H-1), 4.80 (dd, 1H, $J_{6a,5}$ 4.5, $J_{6a,6b}$ 12.2 Hz, H-6a), 4.52 (dd, 1H, $J_{6b,5}$ 2.1 Hz, H-6b), 4.01–3.94 (m, 1H, H-5), 3.98 (dd, 1H, H-2), 3.50 (dd with appearance of t, 1H, $J_{4,5}$ 9.4 Hz, H-4), 3.33 (s, 3H, $OCH_3$), 1.96 (s, 6H, $C\mathit{CH}_3 \times 2$); $^{13}C$ NMR (50 MHz): $\delta$ 172.20, 167.06 (CO), 137.16 (C × 2), 133.17, 129.71–128.32 (C-Ar), 98.32 (C-1), 71.14 (C-4), 70.00 (C-5), 67.24 (C-3), 63.62 (C-6), 56.29 (C-2),

55.23 ($OCH_3$), 8.66 ($CCH_3 \times 2$). HRCIMS: calcd for $C_{20}H_{23}NO_8$ $[M+H]^+$, *m/z* 406.1496; found, *m/z* 406.1503.

**3.2.2. Methyl 6-*O*-benzyl-2-deoxy-2-dimethylmaleimido-α-D-glucopyranoside (11b).** To a stirred solution of **13b** (109 mg, 0.36 mmol) in anhyd DMF (1.8 mL) was added benzaldehyde dimethyl acetal (112 μL, 0.20 mmol) and a catalytic amount of camphorsulfonic acid. The mixture was stirred overnight at room temperature, then neutralized with solid $Na_2CO_3$ and diluted with EtOAc. The organic layer was washed with brine, dried ($Na_2SO_4$), and evaporated. The residue was chromatographed to yield the 4,6-*O*-benzylidene acetal (84 mg, 59%), as a foamy solid. $^1$H NMR (200 MHz): $\delta$ 7.55–7.27 (m, 5H, ArH), 5.57 (s, 1H, *CH*Ph), 5.25 (dd, 1H, $J_{3,4}$ 9.4, $J_{3,2}$ 10.8 Hz, H-3), 4.75 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 4.29 (dd, 1H, $J_{6a,5}$ 4.3, $J_{6a,6b}$ 9.7 Hz, H-6a), 4.10 (dd, 1H, H-2), 3.99–3.87 (m, 1H, H-5), 3.79 (dd, 1H, $J_{6b,5}$ 1.9 Hz, H-6b), 3.54 (dd with appearance of t, $J_{4,5}$ 9.2 Hz, H-4), 3.33 (s, 3H, $OCH_3$), 1.96 (s, 6H, $CCH_3 \times 2$); $^{13}$C NMR (50 MHz): $\delta$ 171.90 ($CO \times 2$), 137.12 ($C \times 2$), 129.13–126.27 (C-Ar), 101.87 (*CH*Ph), 99.05 (C-1), 82.44 (C-4), 68.78 (C-6), 64.65 (C-3), 62.50 (C-5), 56.38 (C-2), 56.36 ($OCH_3$), 8.65 ($CCH_3 \times 2$).

To a solution of the 4,6-*O*-benzylidene acetal (142 mg, 0.37 mmol) and $BH_3{\cdot}N(CH_3)_3$ (52 mg, 0.74 mmol) in $CH_3CN$ (3.7 mL) in an ice-water bath was added dropwise $BF_3{\cdot}OEt_2$ (92 μL, 0.84 mmol). After 1 h at this temperature, the solution was stirred at room temperature for an additional 0.5 h (TLC). $NaHCO_3$ (54 mg) was then added, and the solution was evaporated to dryness. The crude product in $CH_2Cl_2$ was washed with brine, dried ($Na_2SO_4$), and evaporated. The residue was chromatographed to yield **11b** (103 mg, 72%), as a foamy solid: $[\alpha]_D^{31}$ +136.1 (*c* 0.97, MeOH); $R_f$ 0.32 (1:1 hexane–EtOAc); $^1$H NMR (300 MHz): $\delta$ 7.45–7.26 (m, 5H, ArH), 4.94 (dd, 1H, $J_{3,4}$ 9.0, $J_{3,2}$ 11.1 Hz, H-3), 4.74 (d, 1H, $J_{1,2}$ 3.3 Hz, H-1), 4.64 (d, 1H, *J* 12.3 Hz, $CH_2$Ph), 4.59 (d, 1H, $CH_2$Ph), 3.99 (dd, 1H, H-2), 3.85–3.75 (m, 3H, H-5, H-6a, H-6b), 3.57 (dd with appearance of t, $J_{4,5}$ 9.3 Hz, H-4), 3.29 (s, 3H, $OCH_3$), 1.93 (s, 6H, $CCH_3 \times 2$); $^{13}$C NMR (50 MHz): $\delta$ 172.39 ($CO \times 2$), 137.26 ($C \times 2$), 128.46–127.50 (C-Ar), 98.39 (C-1), 73.68 ($CH_2$Ph), 72.46 (C-4), 70.20 (C-5), 69.82 (C-6), 67.68 (C-3), 56.64 (C-2), 55.34 ($OCH_3$), 8.78 ($CCH_3 \times 2$). HRFABMS: calcd for $C_{20}H_{25}NO_7$ $[M+Na]^+$, *m/z* 414.1529; found, *m/z* 414.1544.

**3.2.3. Methyl 6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-2-dimethylmaleimido-α-D-glucopyranoside (11c).** To a stirred solution of triol **13b** (250 mg, 0.81 mmol) in anhyd DMF (2.6 mL) at room temperature were added imidazole (142 mg, 2.08 mmol) and *tert*-butylchlorodiphenylsilane (294 μL, 1.21 mmol). After 2 h $CH_2Cl_2$ (43 mL) was added. The organic layer was washed with water, dried ($Na_2SO_4$), and evaporated. The residue was chromatographed ($CH_2Cl_2$–MeOH) to give **11c** (405 mg, 90%) as a foamy solid: $[\alpha]_D^{31}$ +106.6 (*c* 1.02, $CHCl_3$); $R_f$ 0.22 (7:3 hexane–EtOAc); $^1$H NMR (300 MHz): $\delta$ 7.75–7.65, 7.45–7.30 (m, 5H, ArH), 4.96 (dd, 1H, $J_{3,4}$ 9.4, $J_{3,2}$ 10.8 Hz, H-3), 4.72 (d, 1H, $J_{1,2}$ 3.4 Hz, H-1), 3.97 (dd, 1H, H-2), 4.01–3.85 (m, 2H, H-6a, H-6b), 3.80–3.69 (m, 1H, H-5), 3.56 (dd with appearance of t, 1H, $J_{4,5}$ 9.2 Hz, H-4), 3.26 (s, 3H, $OCH_3$), 1.94 (s, 6H, $CCH_3 \times 2$), 1.06 (s, 9H, $C(CH_3)_3$); $^{13}$C NMR (75 MHz): $\delta$ 172.20 (CO), 137.05 ($C \times 2$), 135.49, 132.99–132.96, 129.63, 127.60 (C-Ar), 98.12 (C-1), 72.85 (C-4), 71.06 (C-5), 67.48 (C-3), 64.34 (C-6), 56.35 (C-2), 54.96 ($OCH_3$), 26.66 (C ($CH_3$)$_3$), 19.09 ($C(CH_3)_3$), 8.61 ($CCH_3 \times 2$). HRFABMS: calcd for $C_{29}H_{37}NO_7Si$ $[M+Na]^+$, *m/z* 562.2237; found, *m/z* 562.2244.

**3.2.4. Methyl 6-*O*-benzoyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (12a).** To a stirred solution of triol **14**[16,20] (490 mg, 1.63 mmol) in anhyd pyridine (6 mL) at −40 °C was added dropwise freshly distilled benzoyl chloride (242 μL, 2.1 mmol). After 2 h at this temperature, the reaction mixture was allowed to warm to room temperature. After 15 h, water was added, and the mixture was stirred for 10 min and then extracted with $CH_2Cl_2$. The organic layer was washed with 1 N HCl, satd aq $NaHCO_3$ and brine, dried ($Na_2SO_4$), and evaporated. The residue was chromatographed to give **12a** (280.9 mg, 55%): $[\alpha]_D^{20}$ −17.2 (*c* 1.02, MeOH); $R_f$ 0.12 (1:1 hexane–EtOAc); $^1$H NMR (200 MHz): $\delta$ 8.12–8.02, 7.65–7.37 (m, 5H, ArH), 5.02 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 4.84 (dd, 1H, $J_{6a,5}$ 3.9, $J_{6a,6b}$ 12.2 Hz, H-6a), 4.53 (dd, 1H, $J_{6b,5}$ 2.1 Hz, H-6b), 4.23 (dd, 1H, $J_{3,4}$ 8.6, $J_{3,2}$ 10.7 Hz, H-3), 3.89 (dd, 1H, H-2), 3.73–3.61 (m, 1H, H-5), 3.46 (dd with appearance of t, 1H, $J_{4,5}$ 9.2 Hz, H-4), 3.44 (s, 3H, $OCH_3$), 1.95 (s, 6H, $CCH_3 \times 2$); $^{13}$C NMR (50 MHz): $\delta$ 171.94, 167.14 (CO), 137.17 ($C \times 2$), 133.19, 129.72–128.28 (C-Ar), 99.22 (C-1), 73.86 (C-5), 71.48 (C-4), 71.40 (C-3), 63.65 (C-6), 56.59 ($OCH_3$), 55.89 (C-2), 8.60 ($CCH_3 \times 2$). HRFABMS: calcd for $C_{20}H_{23}NO_8$ $[M+Na]^+$, *m/z* 428.1321; found, *m/z* 428.1322.

**3.2.5. Methyl 6-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (12b).** To a stirred solution of **14**[16,20] (107 mg, 0.36 mmol) in anhyd DMF (1.8 mL) were added benzaldehyde dimethyl acetal (109 μL, 0.19 mmol) and a catalytic amount of camphorsulfonic acid, and the mixture was stirred overnight at room temperature. The reaction mixture was neutralized with solid $Na_2CO_3$ and diluted with EtOAc. The organic layer was washed with brine, dried ($Na_2SO_4$), and evaporated. The residue was chromatographed to yield the 4,6-*O*-benzylidene acetal (116.9 mg, 85%), as a foamy solid:

$^1$H NMR (200 MHz): $\delta$ 7.52–7.32 (m, 5H, ArH), 5.55 (s, 1H, *CH*Ph), 5.03 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 4.46 (dd, 1H, $J_{3,4}$ 8.8, $J_{3,2}$ 10.5 Hz, H-3), 4.37 (dd, 1H, $J_{6a,5}$ 4.3, $J_{6a,6b}$ 10.9 Hz, H-6a), 3.98 (dd, 1H, H-2), 3.83 (dd with appearance of t, 1H, $J_{4,5}$ 9.9 Hz, H-4), 3.61–3.51 (m, 2H, H-5, H-6b), 3.44 (s, 3H, $OCH_3$), 1.96 (s, 6H, C*CH*$_3$ × 2); $^{13}$C NMR (50 MHz): $\delta$ 171.61 (CO × 2), 137.02 (C × 2), 136.85, 128.96–126.07 (C-Ar), 101.51 (*CH*Ph), 99.65 (C-1), 81.88 (C-4), 68.27 (C-3), 68.36 (C-6), 65.81 (C-5), 56.64 ($OCH_3$), 56.10 (C-2), 8.48 (C*CH*$_3$ × 2).

To a solution of the 4,6-*O*-benzylidene acetal (420 mg, 1.08 mmol) and $BH_3{\cdot}N(CH_3)_3$ (154 mg, 2.2 mmol) in $CH_3CN$ (11 mL) in an ice-water bath was added dropwise $BF_3{\cdot}OEt_2$ (272 μL, 2.5 mmol). After 1 h at this temperature, the solution was stirred at room temperature for an additional 0.5 h (TLC). $NaHCO_3$ (154 mg) was then added, and the solution was evaporated to dryness. The crude product in $CH_2Cl_2$ was washed with brine, dried ($Na_2SO_4$), and evaporated. The residue was chromatographed to yield **12b** (308 mg, 73%), as a foamy solid: $[\alpha]_D^{28}$ −13.2 (*c* 1.03, MeOH); $R_f$ 0.08 (1:1 hexane–EtOAc); $^1$H NMR (300 MHz): $\delta$ 7.34 (br s, 5H, ArH), 4.98 (d, 1H, $J_{1,2}$ 8.2 Hz, H-1), 4.65 (d, 1H, *J* 12.0 Hz, *CH*$_2$Ph), 4.57 (d, 1H, *CH*$_2$Ph), 4.24–4.09 (m, 1H, H-3), 3.89 (dd, 1H, $J_{2,3}$ 10.9 Hz, H-2), 3.82–3.77 (m, 2H, H-6a, H-6b), 3.62–3.52 (m, 2H, H-4, H-5), 3.41 (s, 3H, $OCH_3$), 3.00 (br s, 1H, OH), 2.32 (br s, 1H, OH), 1.96 (s, 6H, C*CH*$_3$ × 2); $^{13}$C NMR (75 MHz): $\delta$ 171.94 (CO × 2), 137.69 (C-Ar), 137.11 (C × 2), 128.29–127.60 (C-Ar), 99.09 (C-1), 74.10 (C-4*), 73.51 (*CH*$_2$Ph), 73.17 (C-5*), 71.65 (C-3), 70.00 (C-6), 56.41 ($OCH_3$), 55.87 (C-2), 8.55 (C*CH*$_3$ × 2). HRFABMS: calcd for $C_{20}H_{25}NO_7$ $[M+Na]^+$, *m*/*z* 414.1529; found, *m*/*z* 414.1532.

### 3.2.6. Methyl 6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (12c).

To a stirred solution of triol **14** (171 mg, 0.57 mmol) in anhyd DMF (1.8 mL) at room temperature were added imidazole (97 mg, 1.42 mmol) and *tert*-butylchlorodiphenylsilane (201 μL, 0.83 mmol). After 2 h $CH_2Cl_2$ (32 mL) was added. The organic layer was washed with water, dried ($Na_2SO_4$), and evaporated. The residue was chromatographed ($CH_2Cl_2$–MeOH) to give **12c** (224 mg, 73%) as a foamy solid: $[\alpha]_D^{31}$ −23.6 (*c* 1.02, $CHCl_3$); $R_f$ 0.27 (1:1 hexane–EtOAc); $^1$H NMR (300 MHz): $\delta$ 7.80–7.65, 7.55–7.45 (m, 10H, ArH), 4.96 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 4.18 (dd, 1H, $J_{3,4}$ 8.5, $J_{3,2}$ 10.4 Hz, H-3), 3.96 (d, 2H, $J_{6,5}$ 4.7 Hz, H-6a, H-6b), 3.86 (dd, 1H, H-2), 3.66–3.45 (m, 3H, H-4, H-5, OH), 3.58–3.50 (m, 1H, H-5), 3.39 (s, 3H, $OCH_3$), 1.97 (s, 6H, C*CH*$_3$ × 2), 1.08 (s, 9H, C (*CH*$_3$)$_3$); $^{13}$C NMR (75 MHz): $\delta$ 171.92 (CO), 137.17–132.53 (C × 2, C-Ar), 129.82–127.71 (C-Ar), 98.97 (C-1), 74.22 (C-4*), 74.09 (C-5*), 71.78 (C-3), 64.92 (C-6), 56.32 ($OCH_3$), 55.75 (C-2), 26.68 (C (*CH*$_3$)$_3$), 19.07 (*C*(CH$_3$)$_3$), 8.68 (C*CH*$_3$ × 2). HRFABMS: calcd for $C_{29}H_{37}NO_7Si$ $[M+Na]^+$, *m*/*z* 562.2237; found, *m*/*z* 562.2239.

### 3.2.7. Methyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→3)-4-*O*-acetyl-6-*O*-benzoyl-2-deoxy-2-dimethylmaleimido-α-D-glucopyranoside (15b)

**3.2.7.1. Disaccharide 15a.** 68%; $[\alpha]_D^{23}$ +64.3 (*c* 0.91, $CHCl_3$); $R_f$ 0.17 (7:3 hexane–EtOAc); $^1$H NMR (300 MHz): $\delta$ 8.15–7.75, 7.60–7.25 (m, 25H, ArH), 5.98–5.91 (m, 1H, H-5′), 5.60 (dd, 1H, $J_{3',2'}$ 2.3, $J_{3',4'}$ 5.1 Hz, H-3′), 5.46 (br s, 1H, H-1′), 5.40 (dd, 1H, $J_{2',1'}$ 1.4 Hz, H-2′), 5.10 (dd, 1H, $J_{3,4}$ 8.6, $J_{3,2}$ 11.2 Hz, H-3), 4.87 (dd with appearance of t, 1H, $J_{4',5'}$ 5.1 Hz, H-4′), 4.77 (dd, 1H, $J_{6'a,5'}$ 4.9, $J_{6'a,6'b}$ 11.8 Hz, H-6′a), 4.71 (d, 1H, $J_{1,2}$ 3.3 Hz, H-1), 4.64–4.58 (m, 2H, H-6a, H-6′b), 4.51 (dd, 1H, $J_{6b,5}$ 5.7, $J_{6b,6a}$ 11.9 Hz, H-6b), 4.24 (dd, 1H, H-2), 4.21 (br s, 1H, OH), 4.04–3.95 (m, 1H, H-5), *3.66–3.56* (*m*, *1H*, *H-4*), 3.32 (s, 3H, $OCH_3$), 1.85 (br s, 6H, C*CH*$_3$ × 2); $^{13}$C NMR (75 MHz): $\delta$ 166.24–164.72 (CO), 133.50–132.82 (C × 2, C-Ar), 129.60–128.24 (C-Ar), 107.48 (C-1′), 98.35 (C-1), 81.70 (C-2′), 81.19 (C-4′), 78.61 (C-3), 77.29 (C-3′), 70.45 (C-4, C-5′), 69.73 (C-5), 63.70 (C-6), 63.62 (C-6′), 55.03 ($OCH_3$), 54.27 (C-2), 8.57 (C*CH*$_3$ × 2).

**3.2.7.2. Acetate 15b.** $[\alpha]_D^{29}$ +105.0 (*c* 1.03, $CHCl_3$); $R_f$ 0.28 (7:3 hexane–EtOAc, two developments); $^1$H NMR (300 MHz): *δ 5.24* (*dd with appearance of t*, *1H*, $J_{4,5}$ *9.7 Hz*, *H-4*); HRMALDI-TOF MS: calcd for $C_{56}H_{51}NO_{18}$ $[M+Na]^+$, *m*/*z* 1048.3004; found, *m*/*z* 1048.3005.

### 3.2.8. Methyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→3)-4-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-dimethylmaleimido-α-D-glucopyranoside (15d) and methyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→4)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-dimethylmaleimido-α-D-glucopyranoside (16b)

**3.2.8.1. Disaccharide 15c.** 54%; $[\alpha]_D^{24}$ +70.6 (*c* 1.04, $CHCl_3$); $R_f$ 0.18 (7:3 hexane–EtOAc); $^1$H NMR (300 MHz): $\delta$ 8.15–7.75, 7.60–7.20 (m, 25H, ArH), 6.00–5.90 (m, 1H, H-5′), 5.60 (dd, 1H, $J_{3',2'}$ 2.1, $J_{3',4'}$ 5.6 Hz, H-3′), 5.45 (br s, 1H, H-1′), 5.37 (dd, 1H, $J_{2',1'}$ 1.2 Hz, H-2′), 5.06 (dd, 1H, $J_{3,4}$ 8.5, $J_{3,2}$ 11.1 Hz, H-3), 4.85 (dd, 1H, $J_{4',5'}$ 4.4 Hz, H-4′), 4.77 (dd, 1H, $J_{6'a,5'}$ 4.8, $J_{6'a,6'b}$ 11.9 Hz, H-6′a), 4.72 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 4.64 (dd, 1H, $J_{6'b,5'}$ 6.4 Hz, H-6′b), 4.61 (s, 2H, *CH*$_2$Ph), 4.22 (dd, 1H, H-2), 4.04 (d, 1H, $J_{OH,4}$ 1.5 Hz, OH), 3.88–3.79 (m, 1H, H-5), 3.76 (dd, 1H, $J_{6a,5}$ 2.2, $J_{6a,6b}$ 10.7 Hz, H-6a), 3.70 (dd, 1H, $J_{6b,5}$ 5.0 Hz, H-6b), *3.61* (*ddd*, *1H*, $J_{4,5}$ *9.0 Hz*, *H-4*), 3.31 (s, 3H, $OCH_3$), 1.86 (br s, 6H, C*CH*$_3$ × 2); $^{13}$C NMR (75 MHz): $\delta$ 165.73–164.63 (CO), 138.15 (C × 2), 133.42–132.93, 129.88–127.33 (C-Ar), 107.33 (C-1′), 98.35 (C-1), 81.60 (C-2′), 81.16 (C-4′), 78.69 (C-3),

77.18 (C-3′), 73.31 ($CH_2$Ph), 70.81 (C-5), 70.32 (C-5′*), 70.18 (C-4*), 69.00 (C-6), 62.65 (C-6′), 54.96 ($OCH_3$), 54.31 (C-2), 8.50 (C$CH_3 \times 2$).

**3.2.8.2. Acetate 15d.** $[\alpha]_D^{27}$ +73.5 (*c* 0.86, $CHCl_3$); $R_f$ 0.21 (($i$Pr)$_2$O); $^1$H NMR (300 MHz): *δ 5.13* (*dd with appearance of t*, *1H*, *$J_{4,5}$ 9.4 Hz*, *H-4*); HRFABMS: calcd for $C_{56}H_{53}NO_{17}$ $[M+Na]^+$, *m*/*z* 1034.3211; found, *m*/*z* 1034.3218.

**3.2.8.3. Disaccharide 16a.** 17%; $[\alpha]_D^{27}$ +57.9 (*c* 1.03, $CHCl_3$); $R_f$ 0.14 (7:3 hexane–EtOAc); $^1$H NMR (300 MHz): *δ* 8.15–7.85, 7.65–7.10 (m, 25H, ArH), 6.00–5.92 (m, 1H, H-5′), 5.67 (dd, 1H, $J_{3',2'}$ 1.4, $J_{3',4'}$ 5.6 Hz, H-3′), 5.45 (d, 1H, H-2′), 5.41 (s, 1H, H-1′), *5.17–5.08* (*m*, *1H*, *H-3*), 4.94 (dd, 1H, $J_{4',5'}$ 3.8 Hz, H-4′), 4.77–4.71 (m, 2H, H-6′a, H-6′b), 4.75 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 4.58 (br s, 2H, $CH_2$Ph), 4.10 (dd, 1H, $J_{2,3}$ 11.2 Hz, H-2), 3.98–3.91 (m, 2H, H-6a, H-6b), 3.88–3.74 (m, 2H, H-4, H-5), 3.34 (s, 3H, $OCH_3$), 1.98 (s, 6H, C$CH_3 \times 2$); $^{13}$C NMR (75 MHz): *δ* 171.89, 166.04–165.41 (CO), 137.91 (C-Ar), 136.99 (C × 2), 133.44–132.90, 129.88–127.47 (C-Ar), 106.93 (C-1′), 98.55 (C-1), 82.27 (C-2′), 81.43 (C-4′), 79.23 (C-4), 77.20 (C-3′), 73.17 ($CH_2$Ph), 70.21 (C-5′), 69.78 (C-5), 68.16 (C-6), 65.93 (C-3), 63.19 (C-6′), 56.30 (C-2), 55.31 ($OCH_3$), 8.66 (C$CH_3 \times 2$).

**3.2.8.4. Acetate 16b.** $[\alpha]_D^{21}$ +55.8 (*c* 0.50, $CHCl_3$); $R_f$ 0.33 (($i$Pr)$_2$O); $^1$H NMR (300 MHz): *δ 6.41–6.33* (*m*, *1H*, *H-3*); HRFABMS: calcd for $C_{56}H_{53}NO_{17}$ $[M+Na]^+$, *m*/*z* 1034.3211; found, *m*/*z* 1034.3188.

### 3.2.9. Methyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→3)-4-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-2-dimethylmaleimido-α-D-glucopyranoside (15f) and methyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→4)-3-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-2-dimethylmaleimido-α-D-glucopyranoside (16d)

**3.2.9.1. Disaccharide 15e.** 61%; $[\alpha]_D^{25}$ +62.9 (*c* 1.02, $CHCl_3$); $R_f$ 0.56 (1:1 hexane–EtOAc); $^1$H NMR (300 MHz): *δ* 8.15–8.05, 8.00–7.65, 7.60–7.25 (m, 30H, ArH), 5.97–5.89 (m, 1H, H-5′), 5.59 (dd, 1H, $J_{3',2'}$ 2.1, $J_{3',4'}$ 5.3 Hz, H-3′), 5.44 (br s, 1H, H-1′), 5.37 (dd, 1H, $J_{2',1'}$ 1.1 Hz, H-2′), 5.06 (dd, 1H, $J_{3,4}$ 8.4, $J_{3,2}$ 11.2 Hz, H-3), 4.82 (dd, 1H, $J_{4',5'}$ 4.5 Hz, H-4′), 4.73 (dd, 1H, $J_{6'a,5'}$ 4.6, $J_{6'a,6'b}$ 12.0 Hz, H-6′a), 4.72 (d, 1H, $J_{1,2}$ 3.3 Hz, H-1), 4.64 (dd, 1H, $J_{6'b,5'}$ 6.4 Hz, H-6′b), 4.20 (dd, 1H, H-2), 4.00 (d, 1H, $J_{6a,5}$ 8.9 Hz, H-6a), 3.93 (d, 1H, $J_{OH,4}$ 1.5 Hz, OH), 3.87–3.75 (m, 1H, H-5), 3.81 (d, 1H, H-6b), *3.49* (*dd with appearance of t*, *1H*,*H-4*), 3.33 (s, 3H, $OCH_3$), 1.88 (br s, 6H, C$CH_3 \times 2$), 1.06 (s, 9H, C ($CH_3$)$_3$); $^{13}$C NMR (75 MHz): *δ* 165.73–164.70 (CO), 135.54–132.91 (C × 2, C-Ar), 129.92–127.47 (C-Ar), 107.24 (C-1′), 98.14 (C-1), 81.68 (C-2′), 81.08 (C-4′), 78.71 (C-3), 77.23 (C-3′), 72.31 (C-5), 70.42 (C-4, C-5′), 63.46 (C-6), 62.63 (C-6′), 54.78 ($OCH_3$), 54.46 (C-2), 26.63 (C($CH_3$)$_3$), 19.15 ($C$(CH$_3$)$_3$), 8.57 (C$CH_3 \times 2$).

**3.2.9.2. Acetate 15f.** $[\alpha]_D^{30}$ +70.5 (*c* 1.02, $CHCl_3$); $R_f$ 0.49 (($i$Pr)$_2$O, two developments); $^1$H NMR (300 MHz): *δ 5.02* (*dd*,*1H*, *$J_{4,5}$ 9.8 Hz*, *H-4*); HRFABMS: calcd for $C_{65}H_{65}NO_{17}Si$ $[M+Na]^+$, *m*/*z* 1182.3919; found, *m*/*z* 1182.3900.

**3.2.9.3. Disaccharide 16c.** 12%; $[\alpha]_D^{28}$ +46.8 (*c* 1.01, $CHCl_3$); $R_f$ 0.47 (1:1 hexane–EtOAc); $^1$H NMR (300 MHz): *δ* 8.12–7.20 (m, 30H, ArH), 6.00–5.90 (m, 1H, H-5′), 5.66 (d, 1H, $J_{3',4'}$ 4.8 Hz, H-3′), 5.58 (s, 1H, H-1′), 5.40 (s 1H, H-2′), *5.12* (*dd with appearance of br t*, *1H*, *$J_{3,4}$ 8.5 Hz*, *H-3*), 4.93 (dd with appearance of t, 1H, $J_{4',5'}$ 4.7 Hz, H-4′), 4.70 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 4.80–4.65 (m, 2H, H-6′a, H-6′b), 4.15–4.00 (m, 2H, H-2, H-6a), 3.97–3.78 (m, 3H, H-4, H-5, H-6b), 3.26 (s, 3H, $OCH_3$), 1.97 (s, 6H, C$CH_3 \times 2$), 0.99 (s, 9H, C ($CH_3$)$_3$); $^{13}$C NMR (75 MHz): *δ* 172.08–165.29 (CO), 137.12–133.00 (C × 2, C-Ar), 130.01–127.46 (C-Ar), 106.88 (C-1′), 98.38 (C-1), 82.37 (C-2′), 81.84 (C-4′), 78.90 (C-4), 77.22 (C-3′), 71.11 (C-5), 70.39 (C-5′), 66.07 (C-3), 63.37 (C-6′), 62.87 (C-6), 56.63 (C-2), 55.20 ($OCH_3$), 26.77 (C($CH_3$)$_3$), 19.35 ($C$(CH$_3$)$_3$), 8.80 (C$CH_3 \times 2$).

**3.2.9.4. Acetate 16d.** $[\alpha]_D^{29}$ +47.9 (*c* 0.76, $CHCl_3$); $R_f$ 0.43 (($i$Pr)$_2$O, three developments); $^1$H NMR (300 MHz): *δ 6.37* (*dd*,*1H*, *$J_{3,4}$ 8.6*, *$J_{3,2}$ 11.3 Hz*, *H-3*); HRFABMS: calcd for $C_{65}H_{65}NO_{17}Si$ $[M+Na]^+$, *m*/*z* 1182.3919; found, *m*/*z* 1182.3945.

### 3.2.10. Methyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→3)-4-*O*-acetyl-6-*O*-benzoyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (17b) and methyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→4)-3-*O*-acetyl-6-*O*-benzoyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (18b)

**3.2.10.1. Disaccharide 17a.** 37%; $[\alpha]_D^{25}$ +30.1 (*c* 0.99, $CHCl_3$); $R_f$ 0.18 (7:3 hexane–EtOAc); $^1$H NMR (300 MHz): *δ* 8.10–7.90, 7.80–7.70, 7.60–7.20 (m, 25H, ArH), 5.98–5.90 (m, 1H, H-5′), 5.64 (dd, 1H, $J_{3',2'}$ 1.9, $J_{3',4'}$ 5.5 Hz, H-3′), 5.26 (dd, 1H, $J_{2',1'}$ 1.0 Hz, H-2′), 5.21 (s, 1H, H-1′), 4.93 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1), 4.86 (dd with appearance of t, 1H, $J_{4',5'}$ 4.7 Hz, H-4′), 4.77 (dd, 1H, $J_{6'a,5'}$ 5.1, $J_{6'a,6'b}$ 11.9 Hz, H-6′a), 4.69–4.58 (m, 2H, H-6a, H-6′b), 4.50 (dd, 1H, $J_{6b,5}$ 5.5, $J_{6b,6a}$ 11.9 Hz, H-6b), 4.34 (dd, 1H, $J_{3,4}$ 8.1, $J_{3,2}$ 10.8 Hz, H-3), 4.09 (dd, 1H, H-2), 3.94 (d, 1H, $J_{OH,4}$ 1.7 Hz, OH), 3.77–3.69 (m, 1H, H-5), *3.64* (*ddd with appearance of dt*, *1H*, *$J_{4,5}$ 8.9 Hz*, *H-4*), 3.42 (s, 3H, $OCH_3$), 1.90 (s, 6H, C$CH_3 \times 2$); $^{13}$C NMR (75 MHz): *δ* 166.32–164.96 (CO), 137.21 (C × 2), 133.52–132.85, 129.88–128.35 (C-Ar), 107.96 (C-1′), 99.19 (C-1), 82.21 (C-2′, C-3), 81.35

(C-4′), 76.73 (C-3′), 73.71 (C-5), 70.34 (C-5′), 70.26 (C-4), 63.68 (C-6*), 62.58 (C-6′*), 56.50 ($OCH_3$), 54.44 (C-2), 8.59 ($CCH_3 \times 2$).

**3.2.10.2. Acetate 17b.** $[\alpha]_D^{24}$ +32.2 (*c* 1.03, $CHCl_3$); $R_f$ 0.64 (7:3 hexane–EtOAc, two developments); $^1H$ NMR (300 MHz): *δ 5.22* (*dd*,*1H*, *J4,3 9.0*, *J4,5 9.8 Hz*, *H-4*); HRMALDI-TOF MS: calcd for $C_{56}H_{51}NO_{18}$ $[M+Na]^+$, *m*/*z* 1048.3004; found, *m*/*z* 1048.2958.

**3.2.10.3. Disaccharide 18a.** 38%; $[\alpha]_D^{22}$ +4.2 (*c* 1.01, $CHCl_3$); $R_f$ 0.10 (7:3 hexane–EtOAc); $^1H$ NMR (300 MHz): *δ* 8.10–7.90, 7.75–7.10 (m, 25H, ArH), 5.98–5.90 (m, 1H, H-5′), 5.67 (dd, 1H, $J_{3',2'}$ 1.6, $J_{3',4'}$ 5.4 Hz, H-3′), 5.47 (d, 1H, H-2′), 5.42 (s, 1H, H-1′), 5.06 (d, 1H, $J_{1,2}$ 8.7 Hz, H-1), 4.85 (dd, 1H, $J_{4',5'}$ 4.1 Hz, H-4′), 4.82–4.68 (m, 3H, H-6a, H-6′a, H-6b), 4.64 (dd, 1H, $J_{6'b,5'}$ 6.1, $J_{6'b,6'a}$12.0 Hz, H-6′b), *4.42–4.32* (*m*, *1H*, *H-3*), 3.99 (dd, 1H, $J_{2,3}$ 10.6 Hz, H-2), 3.93–3.85 (m, 1H, H-5), 3.84–3.74 (m, 2H, H-4, OH), 3.43 (s, 3H, $OCH_3$), 1.97 (s, 6H, $CCH_3 \times 2$); $^{13}C$ NMR (75 MHz): *δ* 171.73, 165.95–165.31 (CO), 137.10 (C × 2), 133.46–132.74, 129.80–128.21 (C-Ar), 108.04 (C-1′), 99.18 (C-1), 82.46 (C-2′), 81.78 (C-4′), 81.29 (C-4), 76.95 (C-3′), 72.37 (C-5), 70.22 (C-5′), 70.07 (C-3), 62.96 (C-6*), 62.82 (C-6′*), 56.55 ($OCH_3$), 55.88 (C-2), 8.65 ($CCH_3 \times 2$).

**3.2.10.4. Acetate 18b.** $[\alpha]_D^{20}$ +7.7 (*c* 0.97, $CHCl_3$); $R_f$ 0.24 (7:3 hexane–EtOAc, two developments); $^1H$ NMR (300 MHz): *δ 5.70* (*dd*, *1H*, *J3,4 8.5*, *J3,2 10.6 Hz*, *H-3*); HRMALDI-TOF MS: calcd for $C_{56}H_{51}NO_{18}$ $[M+Na]^+$, *m*/*z* 1048.3004; found, *m*/*z* 1048.2954.

### 3.2.11. Methyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→3)-4-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (17d) and methyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→4)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (18d)

**3.2.11.1. Disaccharide 17c.** 18%; $[\alpha]_D^{22}$ +28.1 (*c* 0.64, $CHCl_3$); $R_f$ 0.27 (7:3 hexane–EtOAc); $^1H$ NMR (300 MHz): *δ* 8.10–7.70, 7.60–7.20 (m, 25H, ArH), 6.00–5.92 (m, 1H, H-5′), 5.63 (dd, 1H, $J_{3',2'}$ 1.8, $J_{3',4'}$ 5.3 Hz, H-3′), 5.24 (m, 1H, H-2′), 5.20 (s, 1H, H-1′), 4.90 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1), 4.84 (dd, 1H, $J_{4',5'}$ 4.1 Hz, H-4′), 4.76 (dd, 1H, $J_{6'a,5'}$ 4.8, $J_{6'a,6'b}$ 11.7 Hz, H-6′a), 4.64 (dd, 1H, $J_{6'b,5'}$ 6.2 Hz, H-6′b), 4.61 (s, 2H, $CH_2$Ph), 4.35–4.27 (m, 1H, H-3), 4.07 (dd, 1H, $J_{2,3}$ 10.7 Hz, H-2), 3.85–3.77 (m, 2H, H-6a, OH), 3.71–3.63 (m, 1H, H-6b), *3.61–3.56* (*m*, *2H*, *H-4*, *H-5*), 3.45 (s, 3H, $OCH_3$), 1.91 (br s, 6H, $CCH_3 \times 2$); $^{13}C$ NMR (75 MHz): *δ* 166.02–165.12 (CO), 138.28 (C × 2), 133.69–126.50 (C-Ar), 107.96 (C-1′), 99.27 (C-1), 82.41 (C-3*), 82.33 (C-2′*), 81.50 (C-4′), 76.85 (C-3′), 75.18 (C-4), 73.56 ($CH_2$Ph), 70.75 (C-5), 70.30 (C-5′), 69.58 (C-6), 62.88 (C-6′), 56.70 ($OCH_3$), 54.63 (C-2), 8.82 ($CCH_3 \times 2$).

**3.2.11.2. Acetate 17d.** $[\alpha]_D^{32}$ +33.2 (*c* 0.65, $CHCl_3$); $R_f$ 0.55 ($(iPr)_2O$); $^1H$ NMR (300 MHz): *δ 5.08* (*with appearance of t*, *1H*, *J4,3* ≈ *J4,5 9.7 Hz*, *H-4*); HRFABMS: calcd for $C_{56}H_{53}NO_{17}$ $[M+Na]^+$, *m*/*z* 1034.3211; found, *m*/*z* 1034.3218.

**3.2.11.3. Disaccharide 18c.** 53%; $[\alpha]_D^{20}$ −11.6 (*c* 1.00, $CHCl_3$); $R_f$ 0.21 (7:3 hexane–EtOAc); $^1H$ NMR (300 MHz): *δ* 8.10–7.70, 7.60–7.10 (m, 25H, ArH), 5.98–5.91 (m, 1H, H-5′), 5.64 (dd, 1H, $J_{3',2'}$ 1.4, $J_{3',4'}$ 5.3 Hz, H-3′), 5.42 (d, 1H, H-2′), 5.39 (s, 1H, H-1′), 5.00 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1), 4.87 (dd, 1H, $J_{4',5'}$ 3.8 Hz, H-4′), 4.75–4.68 (m, 2H, H-6′a, H-6′b), 4.59 (d, 1H, *J* 12.9 Hz, $CH_2$Ph), 4.55 (d, 1H, $CH_2$Ph), *4.33–4.22* (*m*, *1H*, *H-3*), 3.96 (dd, 1H, $J_{2,3}$ 10.9 Hz, H-2), 3.90 (dd, 1H, $J_{6a,5}$ 3.6, $J_{6a,6b}$ 11.0 Hz, H-6a), 3.83 (dd, 1H, $J_{6b,5}$ 1.5 Hz, H-6b), 3.78 (dd, 1H, $J_{4,3}$ 8.5, $J_{4,5}$ 9.7 Hz, H-4), 3.70–3.62 (m, 1H, H-5), 3.54–3.50 (m, 1H, OH), 3.45 (s, 3H, $OCH_3$), 1.97 (s, 6H, $CCH_3 \times 2$); $^{13}C$ NMR (75 MHz): *δ* 171.78, 166.11–165.34 (CO), 137.98 (C × 2), 137.05–127.22 (C-Ar), 107.10 (C-1′), 99.08 (C-1), 82.06 (C-2′), 81.57 (C-4′), 79.66 (C-4), 77.18 (C-3′), 74.29 (C-5), 73.04 ($CH_2$Ph), 70.30 (C-3), 70.09 (C-5′), 68.13 (C-6), 63.11 (C-6′), 56.47 (C-2), 56.18 ($OCH_3$), 8.65 ($CCH_3 \times 2$).

**3.2.11.4. Acetate 18d.** $[\alpha]_D^{33}$ +0.5 (*c* 0.73, $CHCl_3$); $R_f$ 0.42 (7:3 hexane–EtOAc, two developments); $^1H$ NMR (300 MHz): *δ 5.65* (*dd*, *1H*, *J3,4 8.8*, *J3,2 10.6 Hz*, *H-3*); HRFABMS: calcd for $C_{56}H_{53}NO_{17}$ $[M+Na]^+$, *m*/*z* 1034.3211; found, *m*/*z* 1034.3219.

### 3.2.12. Methyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→3)-4-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (17f) and methyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→4)-3-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (18f)

**3.2.12.1. Disaccharide 17e.** 27%; $[\alpha]_D^{30}$ +29.6 (*c* 1.01, $CHCl_3$); $R_f$ 0.56 (1:1 hexane–EtOAc); $^1H$ NMR (300 MHz): *δ* 8.15–7.90, 7.95–7.65, 7.60–7.20 (m, 30H, ArH), 5.98–5.90 (m, 1H, H-5′), 5.63 (br d, 1H, $J_{3',4'}$ 5.6 Hz, H-3′), 5.26 (br s, 1H, H-2′), 5.20 (s, 1H, H-1′), 4.91 (d, 1H, $J_{1,2}$ 8.8 Hz, H-1), 4.83 (dd with appearance of t, 1H, $J_{4',5'}$ 4.7 Hz, H-4′), 4.74 (dd, 1H, $J_{6'a,5'}$ 4.4, $J_{6'a,6'b}$ 12.0 Hz, H-6′a), 4.64 (dd, 1H, $J_{6'b,5'}$ 6.3 Hz, H-6′b), 4.32 (dd, 1H, $J_{3,4}$ 7.0, $J_{3,2}$ 10.3 Hz, H-3), 4.11–3.98 (m, 2H, H-2, H-6a), 3.84 (dd, 1H, $J_{6b,5}$ 5.1, $J_{6b,6a}$ 11.0 Hz, H-6b), 3.69 (br s, 1H, OH), *3.60–3.51* (*m*, *2H*, *H-4*, *H-5*), 3.46 (s, 3H, $OCH_3$), 1.91 (br s, 6H, $CCH_3 \times 2$), 1.06 (s, 9H, C $(CH_3)_3$); $^{13}C$ NMR (75 MHz): *δ* 165.81–164.95 (CO), 135.57–133.00 (C × 2, C-Ar), 129.90–127.52 (C-Ar), 107.75 (C-1′),

99.00 (C-1), 82.34 (C-3), 82.19 (C-2′), 81.24 (C-4′), 77.10 (C-3′), 76.74 (C-4*), 70.52 (C-5*), 70.26 (C-5′), 63.59 (C-6), 62.73 (C-6′), 56.32 ($OCH_3$), 54.62 (C-2), 26.62 (C($CH_3$)$_3$), 19.16 ($C(CH_3)_3$), 8.63 ($CCH_3 \times 2$).

**3.2.12.2. Acetate 17f.** $[\alpha]_D^{28}$ +36.9 (*c* 1.05, $CHCl_3$); $R_f$ 0.56 ((*i*Pr)$_2$O, two developments); $^1$H NMR (300 MHz): *δ 5.08* (*dd*, *1H*, *$J_{4,3}$ 9.0*, *$J_{4,5}$ 9.8 Hz*, *H-4*); HRFABMS: calcd for $C_{65}H_{65}NO_{17}Si$ $[M+Na]^+$, *m/z* 1182.3919; found, *m/z* 1182.3888.

**3.2.12.3. Disaccharide 18e.** 60%; $[\alpha]_D^{32}$ −4.1 (*c* 0.99, $CHCl_3$); $R_f$ 0.47 (1:1 hexane–EtOAc); $^1$H NMR (300 MHz): *δ* 8.10–7.95, 7.85–7.70, 7.65–7.20 (m, 30H, ArH), 6.00–5.93 (m, 1H, H-5′), 5.66 (dd, 1H, $J_{3',2'}$ 1.0, $J_{3',4'}$ 5.4 Hz, H-3′), 5.62 (s, 1H, H-1′), 5.46 (d, 1H, H-2′), 5.00 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1), 4.90 (dd, 1H, $J_{4',5'}$ 5.1 Hz, H-4′), 4.78 (dd, 1H, $J_{6'a,5'}$ 4.2, $J_{6'a,6'b}$ 12.2 Hz, H-6′a), 4.71 (dd, 1H, $J_{6'b,5'}$ 6.3 Hz, H-6′b), *4.38–4.27* (*m*, *1H*, *H-3*), 4.08 (dd, 1H, $J_{6a,5}$ 2.9, $J_{6a,6b}$ 11.7 Hz, H-6a), 4.03–3.90 (m, 3H, H-2, H-4, H-6b), 3.58–3.50 (m, 1H, H-5), 3.46 (d, 1H, $J_{OH,3}$ 4.7 Hz, OH), 3.42 (s, 3H, $OCH_3$), 1.99 (s, 6H, $CCH_3 \times 2$), 0.99 (s, 9H, C($CH_3$)$_3$); $^{13}$C NMR (75 MHz): *δ* 171.85–165.15 (CO), 137.08–132.96 (C × 2, C-Ar), 129.84–127.34 (C-Ar), 107.01 (C-1′), 98.79 (C-1), 82.05 (C-2′), 81.89 (C-4′), 78.84 (C-4), 77.45 (C-3′), 75.04 (C-5), 70.29 (C-3), 70.20 (C-5′), 63.13 (C-6′), 62.44 (C-6), 56.46 (C-2), 56.11 ($OCH_3$), 26.58 (C($CH_3$)$_3$), 19.16 ($C(CH_3)_3$), 8.70 ($CCH_3 \times 2$).

**3.2.12.4. Acetate 18f.** $[\alpha]_D^{30}$ −8.5 (*c* 1.01, $CHCl_3$); $R_f$ 0.34 ((*i*Pr)$_2$O, two developments); $^1$H NMR (300 MHz): *δ 5.68* (*dd*, *1H*, *$J_{3,4}$ 9.0*, *$J_{3,2}$ 10.3 Hz*, *H-3*); HRFABMS: calcd for $C_{65}H_{65}NO_{17}Si$ $[M+Na]^+$, *m/z* 1182.3919; found, *m/z* 1182.3934.

**3.2.13. Methyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→3)-4-*O*-acetyl-6-*O*-benzoyl-2-deoxy-2-dimethylmaleimido-α-D-glucopyranoside (19b) and methyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-3-*O*-acetyl-6-*O*-benzoyl-2-deoxy-2-dimethylmaleimido-α-D-glucopyranoside (20b).** In spite of the fact that by column chromatography of the crude reaction mixture disaccharides **19a** and **20a** could not be separated efficiently, using the data from the $^1$H NMR spectroscopy of the pure fractions, a 2:1 ratio of regioisomeric disaccharides was established for the mixture. On the other hand, chromatography of the corresponding acetates allowed the isolation of acetates **19b** (48.1%) and **20b** (20.8%) that were fully characterized.

**3.2.13.1. Disaccharide 19a.** 61%; $[\alpha]_D^{26}$ +69.1 (*c* 1.05, $CHCl_3$); $R_f$ 0.14 (1:1 hexane–EtOAc); $^1$H NMR (300 MHz): *δ* 8.10–8.00, 7.65–7.42 (m, 5H, ArH), 5.35 (dd, 1H, $J_{4',5'}$ 0.9, $J_{4',3'}$ 3.4 Hz, H-4′), 5.16 (dd, 1H, $J_{2',1'}$ 8.1, $J_{2',3'}$ 10.4 Hz, H-2′), 5.07 (dd, 1H, $J_{3,4}$ 8.4, $J_{3,2}$ 11.1 Hz, H-3), 4.97 (dd, 1H, H-3′), 4.71–4.63 (m, 1H, H-6a), 4.66 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 4.65 (d, 1H, H-1′), 4.57 (dd, 1H, $J_{6b,5}$ 5.1, $J_{6b,6a}$ 12.0 Hz, H-6b), 4.24–4.10 (m, 4H, H-2, H-6′a, H-6′b, OH), 4.09–4.01 (m, 1H, H-5′), 4.01–3.93 (m, 1H, H-5), *3.66* (*dd with appearance of t*, *1H*, *$J_{4,5}$ 9.1 Hz*, *H-4*), 3.31 (s, 3H, $OCH_3$), 2.14, 2.08, 1.94, 1.74 (4s, 12H, $COCH_3 \times 4$), 2.01, 1.96 (2br s, 6H, $CCH_3 \times 2$); $^{13}$C NMR (75 MHz): *δ* 171.62–166.24 (CO), 132.87 (C-Ar, C × 2), 129.56–128.25 (C-Ar), 99.94 (C-1′), 98.25 (C-1), 78.74 (C-3), 71.16 (C-5′), 70.67 (C-3′), 69.56 (C-4, C-5), 68.65 (C-2′), 66.90 (C-4′), 63.51 (C-6), 61.36 (C-6′), 55.11 ($OCH_3$), 54.34 (C-2), 20.44–19.85 ($COCH_3 \times 4$), 8.79, 8.64 ($CCH_3$).

**3.2.13.2. Acetate 19b.** $[\alpha]_D^{26}$ +56.4 (*c* 0.97, $CHCl_3$); $R_f$ 0.17 (1:1 hexane–EtOAc); $^1$H NMR (300 MHz): *δ 5.11* (*dd with appearance of t*, *1H*, *$J_{4,5}$ 9.4 Hz*, *H-4*); HRFABMS: calcd for $C_{36}H_{43}NO_{18}$ $[M+Na]^+$, *m/z* 800.2378; found, *m/z* 800.2385.

**3.2.13.3. Disaccharide 20a.** 30%; $[\alpha]_D^{32}$ +65.3 (*c* 0.86, $CHCl_3$); $R_f$ 0.17 (1:1 hexane–EtOAc); $^1$H NMR (300 MHz): *δ* 8.10–8.00, 7.65–7.42 (m, 5H, ArH), 5.36 (br d, 1H, $J_{4',3'}$ 3.0 Hz, H-4′), 5.25 (dd, 1H, $J_{2',1'}$ 8.0, $J_{2',3'}$ 10.4 Hz, H-2′), *5.13* (*ddd*, *1H*, *$J_{3,OH}$ 1.6*, *$J_{3,4}$* 8.2, *$J_{3,2}$ 10.6 Hz*, *H-3*), 4.96 (dd, 1H, H-3′), 4.69 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 4.60 (d, 1H, H-1′), 4.56 (dd, 1H, $J_{6a,5}$ 1.8, $J_{6a,6b}$ 12.0 Hz, H-6a), 4.36 (dd, 1H, $J_{6b,5}$ 4.9 Hz, H-6b), 4.17–4.00 (m, 5H, H-2, H-5, H-6′a, H-6′b, OH), 3.99–3.92 (m, 1H, H-5′), 3.58 (dd, 1H, $J_{4,3} \approx J_{4,5}$ 9.8 Hz, H-4), 3.33 (s, 3H, $OCH_3$), 2.17, 2.08, 1.97, 1.96 (4s, 12H, $COCH_3 \times 4$), 1.95 (s, 6H, $CCH_3 \times 2$); $^{13}$C NMR (75 MHz): *δ* 171.68–166.10 (CO), 136.99 (C × 2, C-Ar), 133.22–128.47 (C-Ar), 101.69 (C-1′), 98.31 (C-1), 83.21 (C-4), 71.07 (C-5′), 70.83 (C-3′), 68.74 (C-2′), 67.47 (C-5), 66.64 (C-4′), 65.51 (C-3), 62.95 (C-6), 61.50 (C-6′), 55.31 ($OCH_3$), 55.22 (C-2), 20.50–20.23 ($COCH_3 \times 4$), 8.64 ($CCH_3 \times 2$).

**3.2.13.4. Acetate 20b.** $[\alpha]_D^{28}$ +78.1 (*c* 0.62, $CHCl_3$); $R_f$ 0.10 (1:1 hexane–EtOAc); $^1$H NMR (300 MHz): *δ 6.27* (*dd, 1H, $J_{3,4}$ 9.0, $J_{3,2}$ 11.4 Hz, H-3*); HRFABMS: calcd for $C_{36}H_{43}NO_{18}$ $[M+Na]^+$, *m/z* 800.2378; found, *m/z* 800.2393.

**3.2.14. Methyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→3)-4-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-dimethylmaleimido-α-D-glucopyranoside (19d) and methyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-dimethylmaleimido-α-D-glucopyranoside (20d).** Since the mixture of disaccharides could not be separated by column chromatography, the crude reaction product was acetylated. On the basis of the analysis of the $^1$H NMR spectrum of the mixture, a 1:1 mixture of acetates was detected. Column chroma-

tography afforded acetates **19d** and **20d** allowing their full characterization.

**3.2.14.1. Acetate 19d.** 27.3%; $[\alpha]_D^{31}$ +70.9 (*c* 1.01, $CHCl_3$); $R_f$ 0.38 (3:7 hexane–EtOAc); $^1H$ NMR (300 MHz): $\delta$ 7.40–7.28 (m, 5H, ArH), 5.29 (dd, 1H, $J_{4',5'}$ 1.0, $J_{4',3'}$ 3.4 Hz, H-4′), 5.15 (dd, 1H, $J_{3,4}$ 8.8, $J_{3,2}$ 10.9 Hz, H-3), *5.01* (*dd*, *1H*, $J_{4,5}$ *10.3 Hz*, *H-4*), 4.94 (dd, 1H, $J_{2',1'}$ 7.8, $J_{2',3'}$ 10.4 Hz, H-2′), 4.85 (dd, 1H, H-3′), 4.63 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1), 4.56 (d, 1H, *J* 12.0 Hz, $CH_2$Ph), 4.52 (d, 1H, $CH_2$Ph), 4.45 (d, 1H, H-1′), 4.24 (dd, 1H, H-2), 4.12–4.06 (m, 2H, H-6′a, H-6′b), 4.01–3.92 (m, 1H, H-5), 3.87–3.80 (m, 1H, H-5′), 3.57–3.52 (m, 2H, H-6a, H-6b), 3.32 (s, 3H, $OCH_3$), 2.13, 2.06, 1.97, 1.93, 1.80 (5s, 15H, CO$CH_3 \times 5$), 2.02, 1.98 (2br s, 6H, C$CH_3 \times 2$); $^{13}C$ NMR (75 MHz): $\delta$ 170.15–168.61 (CO), 138.63–135.89 (C-Ar, C × 2), 128.17–127.49 (C-Ar), 99.32 (C-1′), 98.49 (C-1), 73.37 ($CH_2$Ph), 72.82 (C-3), 70.85 (C-3′), 70.32 (C-5′), 69.89 (C-4), 69.03 (C-2′), 68.76 (C-5, C-6), 66.77 (C-4′), 60.73 (C-6′), 55.19 ($OCH_3$), 55.00 (C-2), 20.71–20.21 (CO$CH_3 \times 5$), 8.80, 8.67 (C$CH_3$); HRFABMS: calcd for $C_{36}H_{45}NO_{17}$ $[M+Na]^+$, *m*/*z* 786.2585; found, *m*/*z* 786.2606.

**3.2.14.2. Acetate 20d.** 28.9%; $[\alpha]_D^{30}$ +77.0 (*c* 1.02, $CHCl_3$); $R_f$ 0.30 (3:7 hexane–EtOAc); $^1H$ NMR (300 MHz): $\delta$ 7.46–7.31 (m, 5H, ArH), *6.21* (*dd*, *1H*, $J_{3,4}$ *8.5*, $J_{3,2}$ *11.4 Hz*, *H-3*), 5.25 (dd, 1H, $J_{4',5'}$ 0.9, $J_{4',3'}$ 3.5 Hz, H-4′), 4.98 (dd, 1H, $J_{2',1'}$ 7.9, $J_{2',3'}$ 10.3 Hz, H-2′), 4.82 (d, 1H, *J* 12.0 Hz, $CH_2$Ph), 4.76 (dd, 1H, H-3′), 4.70 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1), 4.46 (d, 1H, $CH_2$Ph), 4.39 (d, 1H, H-1′), 4.34 (dd, 1H, H-2), 4.05 (d, 2H, $J_{6',5'}$ 6.8 Hz, H-6′a, H-6′b), 3.98–3.78 (m, 3H, H-4, H-5, H-6a), 3.67 (dd, 1H, $J_{6b,5}$ 1.2, $J_{6b,6a}$ 10.6 Hz, H-6b), 3.59 (ddd with appearance of dt, 1H, H-5′), 3.30 (s, 3H, $OCH_3$), 2.12, 2.07, 1.954, 1.95, 1.91 (5s, 15H, CO$CH_3 \times 5$), 1.94 (s, 6H, C$CH_3 \times 2$); $^{13}C$ NMR (75 MHz): $\delta$ 170.20–168.38 (CO), 137.37, 137.02 (C-Ar, C × 2), 128.57–128.09 (C-Ar), 99.82 (C-1′), 98.58 (C-1), 75.57 (C-4), 73.59 ($CH_2$Ph), 70.96 (C-3′), 70.34 (C-5′), 69.70 (C-5), 69.12 (C-2′), 67.12 (C-3, C-6), 66.77 (C-4′), 60.87 (C-6′), 55.20 ($OCH_3$), 53.39 (C-2), 20.84–20.38 (CO$CH_3 \times 5$), 8.67 (C$CH_3 \times 2$); HRFABMS: calcd for $C_{36}H_{45}NO_{17}$ $[M+Na]^+$, *m*/*z* 786.2585; found, *m*/*z* 786.2613.

**3.2.15. Methyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→3)-4-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-2-dimethylmaleimido-α-D-glucopyranoside (19f), methyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-3-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-2-dimethylmaleimido-α-D-glucopyranoside (20f) and methyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)]-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-2-dimethylmaleimido-α-D-glucopyranoside (21).** Column chromatography of the crude reaction mixture afforded a mixture of disaccharides **19e** and **20e** (50%), trisaccharide **21** (28%) and unreacted acceptor **11c** (9.6%). The inseparable mixture of disaccharides was acetylated, and the acetates **19f** and **20f** were isolated and fully characterized.

**3.2.15.1. Acetate 19f.** 49.8%; $[\alpha]_D^{29}$ +52.1 (*c* 1.04, $CHCl_3$); $R_f$ 0.34 (1:1 hexane–EtOAc, two developments); $^1H$ NMR (300 MHz): $\delta$ 7.75–7.60, 7.50–7.35 (m, 10H, ArH), 5.29 (dd, 1H, $J_{4',5'}$ 0.8, $J_{4',3'}$ 3.2 Hz, H-4′), 5.13 (dd, 1H, $J_{3,4}$ 9.0, $J_{3,2}$ 11.0 Hz, H-3), 4.93 (dd, 1H, $J_{2',1'}$ 7.7, $J_{2',3'}$ 10.6 Hz, H-2′), *4.89* (*dd*, *1H*, $J_{4,5}$ *10.0 Hz*, *H-4*), 4.84 (dd, 1H, H-3′), 4.63 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1), 4.45 (d, 1H, H-1′), 4.21 (dd, 1H, H-2), 4.12–4.02 (m, 2H, H-6′a, H-6′b), 3.96–3.87 (m, 1H, H-5), 3.87–3.79 (m, 1H, H-5′), 3.74 (dd, 1H, $J_{6a,5}$ 6.2, $J_{6a,6b}$ 11.1 Hz, H-6a), 3.66 (dd, 1H, $J_{6b,5}$ 2.2 Hz, H-6b), 3.33 (s, 3H, $OCH_3$), 2.11, 2.06, 1.92, 1.87, 1.79 (5s, 15H, CO$CH_3 \times 5$), 2.02, 1.98 (2s, 6H, C$CH_3 \times 2$), 1.04 (s, 9H, C $(CH_3)_3$); $^{13}C$ NMR (75 MHz): $\delta$ 172.18–168.67 (CO), 135.54–133.12 (C × 2, C-Ar), 129.54–127.55 (C-Ar), 99.38 (C-1′), 98.33 (C-1), 73.09 (C-3), 70.91 (C-3′), 70.72 (C-5), 70.32 (C-5′), 69.73 (C-4), 69.08 (C-2′), 66.80 (C-4′), 63.19 (C-6), 60.79 (C-6′), 55.14 (C-2), 55.07 ($OCH_3$), 26.60 (C$(CH_3)_3$), 20.65–20.26 (CO$CH_3$), 19.04 ($C(CH_3)_3$), 8.86, 8.72 (C$CH_3$); HRFABMS: calcd for $C_{45}H_{57}NO_{17}Si$ $[M+Na]^+$, *m*/*z* 934.3293; found, *m*/*z* 934.3274.

**3.2.15.2. Acetate 20f.** 30.5%; $[\alpha]_D^{31}$ +69.3 (*c* 1.01, $CHCl_3$); $R_f$ 0.25 (1:1 hexane–EtOAc); $^1H$ NMR (300 MHz): $\delta$ 7.82–7.68, 7.50–7.35 (m, 10H, ArH), *6.25* (*dd*, *1H*, $J_{3,4}$ *9.5*, $J_{3,2}$ *11.4 Hz*, *H-3*), 5.29 (dd, 1H, $J_{4',5'}$ 0.9, $J_{4',3'}$ 3.1 Hz, H-4′), 5.07 (dd, 1H, $J_{2',1'}$ 8.0, $J_{2',3'}$ 10.2 Hz, H-2′), 4.87 (dd, 1H, H-3′), 4.81 (d, 1H, H-1′), 4.71 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 4.34 (dd, 1H, H-2), 4.16–4.05 (m, 3H, H-4, H-6′a, H-6′b), 3.98 (dd, 1H, $J_{6a,5}$ 2.3, $J_{6a,6b}$ 11.8 Hz, H-6a), 3.90 (dd, 1H, $J_{6b,5}$ 1.1 Hz, H-6b), 3.80–3.67 (m, 2H, H-5′, H-5), 3.24 (s, 3H, $OCH_3$), 2.14, 2.06, 1.98, 1.96, 1.82 (5s, 15H, CO$CH_3 \times 5$), 1.96 (s, 6H, C$CH_3 \times 2$), 1.11 (s, 9H, C $(CH_3)_3$); $^{13}C$ NMR (75 MHz): $\delta$ 170.23–168.50 (CO), 137.08–135.31 (C × 2, C-Ar), 133.37–127.56 (C-Ar), 99.85 (C-1′), 98.46 (C-1), 75.32 (C-4), 71.14 (C-3′), 70.62 (C-5*), 70.54 (C-5′*), 69.32 (C-2′), 67.24 (C-3), 66.90 (C-4′), 61.15 (C-6*), 61.04 (C-6′*), 54.98 ($OCH_3$), 53.64 (C-2), 26.76 (C $(CH_3)_3$), 20.95–20.42 (CO$CH_3$), 19.35 ($C(CH_3)_3$), 8.76 (C$CH_3 \times 2$); HRFABMS: calcd for $C_{45}H_{57}NO_{17}Si$ $[M+Na]^+$, *m*/*z* 934.3293; found, *m*/*z* 934.3310.

**3.2.15.3. Trisaccharide 21.** 28%; $[\alpha]_D^{28}$ +39.3 (*c* 1.04, $CHCl_3$); $R_f$ 0.19 (1:1 hexane–EtOAc); $^1H$ NMR (300 MHz): $\delta$ 7.80–7.70, 7.50–7.25 (m, 10H, ArH), 5.34 (d, 1H, $J_{3'',4''}$ 3.1 Hz, H-4″), 5.30 (d, 1H, $J_{3',4'}$ 3.2 Hz, H-4′), 5.16 (dd, 1H, $J_{3,2}$ 9.3, $J_{3,4}$ 10.6 Hz,

H-3), 5.09 (dd, 1H, $J_{2'',1''}$ 8.1, $J_{2'',3''}$ 10.5 Hz, H-2″), 5.00 (dd, 1H, $J_{2',1'}$ 7.9, $J_{2',3'}$ 10.5 Hz, H-2′), 4.92 (dd, 1H, H-3′), 4.86 (dd, 1H, H-3″), 4.85 (d, 1H, H-1″), 4.58 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1), 4.51 (d, 1H, H-1′), 4.31 (dd, 1H, $J_{6'a,5'}$ 1.9, $J_{6'a,6'b}$ 11.0 Hz, H-6′a), 4.35–4.25 (m, 1H, H-6″a), 4.24–4.09 (m, 3H, H-2, H-6′b, H-6″b), 3.98 (dd with appearance of t, 1H, $J_{4,5}$ 9.5 Hz, H-4), 4.03–3.77 (m, 4H, H-5′, H-5″, H-6a, H-6b), 3.72–3.64 (m, 1H, H-5), 3.21 (s, 3H, $OCH_3$), 2.14, 2.05, 2.04, 1.99, 1.92, 1.88, 1.85 (7s, 24H, $CO\mathit{CH}_3\times 8$), 1.97 (s, 6H, $C\mathit{CH}_3\times 2$), 1.10 (s, 9H, $C(\mathit{CH}_3)_3$); $^{13}C$ NMR (75 MHz): $\delta$ 170.39–168.80 (CO), 135.92–132.77 ($C\times 2$, C-Ar), 129.91–127.62 (C-Ar), 99.32 (C-1″), 98.75 (C-1′), 98.62 (C-1), 74.52 (C-4), 71.94 (C-3), 71.19 (C-3′*), 71.12 (C-3″*), 70.65 (C-5), 70.46 (C-5′, C-5″), 69.13 (C-2′, C-2″), 67.41 (C-4′, C-4″), 61.79 (C-6′*, C-6″*), 61.37 (C-6*), 55.80 (C-2), 55.11 ($OCH_3$), 26.87 (C $(\mathit{CH}_3)_3$), 20.62–20.53 ($CO\mathit{CH}_3\times 8$), 19.40 ($\mathit{C}(CH_3)_3$), 8.88 ($C\mathit{CH}_3\times 2$); HRFABMS: calcd for $C_{57}H_{73}NO_{25}Si$ $[M+Na]^+$, *m*/*z* 1222.4138; found, *m*/*z* 1222.4108.

**3.2.16. Methyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→3)-4-*O*-acetyl-6-*O*-benzoyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (22b) and methyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-3-*O*-acetyl-6-*O*-benzoyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (23b).** The analysis of the $^1H$ NMR of the crude reaction product allowed the identification of two disaccharides in a 13:1 ratio. The major one (**23a**) was readily isolated and as usual characterized as its acetate (**23b**). However, the minor disaccharide was better purified as its acetate (**22b**) and fully characterized. The ratio of acetates is coincident with the ratio obtained by $^1H$ NMR spectroscopy.

**3.2.16.1. Acetate 22b.** $[\alpha]_D^{32}$ +6.8 (*c* 0.38, $CHCl_3$); $R_f$ 0.37 (3:7 hexane–EtOAc); $^1H$ NMR (300 MHz): $\delta$ 8.11–8.04, 7.62–7.35 (m, 5H, ArH), 5.29 (br d, 1H, $J_{4',3'}$ 3.2 Hz, H-4′), *5.09* (*dd with appearance of t*, *1H*, $J_{4,3}\approx J_{4,5}$ *9.5 Hz*, *H-4*), 4.95 (dd, 1H, $J_{2',1'}$ 7.5, $J_{2',3'}$ 10.4 Hz, H-2′), 4.90–4.82 (m, 1H, H-3′), 4.85 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1), 4.65–4.51 (m, 2H, H-3, H-6a), 4.36 (dd, 1H, $J_{6b,5}$ 5.3, $J_{6b,6a}$ 12.0 Hz, H-6b), 4.20 (d, 1H, H-1′), 4.15–4.07 (m, 2H, H-6′a, H-6′b), 4.06 (dd, 1H, $J_{2,3}$ 10.5 Hz, H-2), 3.95–3.83 (m, 1H, H-5), 3.81–3.73 (m, 1H, H-5′), 3.39 (s, 3H, $OCH_3$), 2.12, 2.06, 2.05, 1.95, 1.94 (5s, 15H, $CO\mathit{CH}_3\times 5$), 2.02 (s, 6H, $C\mathit{CH}_3\times 2$); $^{13}C$ NMR (75 MHz): $\delta$ 170.19–166.18 (CO), 137.50 ($C\times 2$), 133.03–128.31 (C-Ar), 100.23 (C-1′), 98.89 (C-1), 74.95 (C-3), 71.80 (C-5), 70.75 (C-3′), 70.43 (C-5′), 69.64 (C-4), 68.97 (C-2′), 66.63 (C-4′), 63.01 (C-6), 60.58 (C-6′), 56.52 ($OCH_3$), 55.20 (C-2), 20.70–20.41 ($CO\mathit{CH}_3\times 5$), 8.86 ($C\mathit{CH}_3\times 2$); HRFABMS: calcd for $C_{36}H_{43}NO_{18}$ $[M+Na]^+$, *m*/*z* 800.2378; found, *m*/*z* 800.2393.

**3.2.16.2. Disaccharide 23a.** 68.3%; $[\alpha]_D^{28}$ +10.6 (*c* 1.02, $CHCl_3$); $R_f$ 0.22 (1:1 hexane–EtOAc); $^1H$ NMR (300 MHz): $\delta$ 8.09–8.02, 7.66–7.45 (m, 5H, ArH), 5.35 (br d, 1H, $J_{4',3'}$ 2.9 Hz, H-4′), 5.25 (dd, 1H, $J_{2',1'}$ 8.1, $J_{2',3'}$ 10.4 Hz, H-2′), 5.07 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1), 4.94 (dd, 1H, H-3′), 4.60 (dd, 1H, $J_{6a,5}$ 1.8, $J_{6a,6b}$ 11.7 Hz, H-6a), 4.58 (d, 1H, H-1′), *4.37–4.24* (*m*, *2H*, *H-3*, *OH*), 4.32 (dd, 1H, $J_{6b,5}$ 4.9 Hz, H-6b), 4.14–4.06 (m, 2H, H-6′a, H-6′b), 4.05–3.90 (m, 1H, H-5′), 3.95 (dd, 1H, $J_{2,3}$ 10.9 Hz, H-2), 3.87–3.79 (m, 1H, H-5), 3.65 (dd, 1H, $J_{4,3}$ 8.4, $J_{4,5}$ 9.5 Hz, H-4), 3.44 (s, 3H, $OCH_3$), 2.14, 2.08, 1.98, 1.956 (4s, 12H, $CO\mathit{CH}_3\times 4$) 1.96 (s, 6H, $C\mathit{CH}_3\times 2$); $^{13}C$ NMR (75 MHz): $\delta$ 171.62–166.03 (CO), 137.08 ($C\times 2$, C-Ar), 133.20–128.41 (C-Ar), 101.86 (C-1′), 99.11 (C-1), 83.32 (C-4), 71.80 (C-5), 71.16 (C-5′), 70.70 (C-3′), 69.85 (C-3), 68.50 (C-2′), 66.58 (C-4′), 62.92 (C-6), 61.49 (C-6′), 56.61 ($OCH_3$), 55.33 (C-2), 20.45–20.11 ($CO\mathit{CH}_3\times 4$), 8.59 ($C\mathit{CH}_3\times 2$).

**3.2.16.3. Acetate 23b.** $[\alpha]_D^{29}$ +5.4 (*c* 1.04, $CHCl_3$); $R_f$ 0.43 (3:7 hexane–EtOAc); $^1H$ NMR (300 MHz): $\delta$ *5.60* (*dd*, *1H*, $J_{3,4}$ *8.5*, $J_{3,2}$ *10.6 Hz*, *H-3*); HRFABMS: calcd for $C_{36}H_{43}NO_{18}$ $[M+Na]^+$, *m*/*z* 800.2378; found, *m*/*z* 800.2353.

**3.2.17. Methyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-3-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (23d)**

**3.2.17.1. Disaccharide 23c.** 88%; $[\alpha]_D^{30}$ +9.3 (*c* 1.02, $CHCl_3$); $R_f$ 0.25 (1:1 hexane–EtOAc); $^1H$ NMR (300 MHz): $\delta$ 7.45–7.35 (m, 5H, ArH), 5.33 (dd, 1H, $J_{4',5'}$ 0.9, $J_{4',3'}$ 3.5 Hz, H-4′), 5.17 (dd, 1H, $J_{2',1'}$ 7.9, $J_{2',3'}$ 10.6 Hz, H-2′), 4.96 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1), 4.92 (dd, 1H, H-3′), 4.75 (d, 1H, *J* 12.0 Hz, $CH_2Ph$), 4.52 (d, 1H, $CH_2Ph$), 4.45 (d, 1H, H-1′), *4.24* (*dd*, *1H*, $J_{3,4}$ *8.1*, $J_{3,2}$ *10.7 Hz*, *H-3*), 4.10 (dd, 1H, $J_{6'a,5'}$ 7.0, $J_{6'a,6'b}$ 13.5 Hz, H-6′a), 4.08 (d, 1H, $J_{6'b,5'}$ 6.2 Hz, H-6′b), 3.92 (dd, 1H, H-2), 3.94–3.86 (m, 2H, H-5′, OH), 3.77–3.63 (m, 2H, H-6a, H6b), 3.68 (dd with appearance of t, $J_{4,5}$ 8.2 Hz, H-4), 3.61–3.54 (m, 1H, H-5), 3.44 (s, 3H, $OCH_3$), 2.13, 2.01, 2.00, 1.98 (4s, 12H, $CO\mathit{CH}_3\times 4$), 1.96 (s, 6H, $C\mathit{CH}_3\times 2$); $^{13}C$ NMR (75 MHz): $\delta$ 171.76–169.08 (CO), 138.06 (C-Ar), 137.15 ($C\times 2$), 128.51–127.82 (C-Ar), 101.38 (C-1′), 99.23 (C-1), 81.80 (C-4), 74.05 (C-5), 73.62 ($CH_2Ph$), 71.10 (C-5′), 70.72 (C-3′), 69.64 (C-3), 68.70 (C-2′), 67.84 (C-6), 66.83 (C-4′), 61.38 (C-6′), 56.62 ($OCH_3$), 55.63 (C-2), 20.64–20.37 ($CO\mathit{CH}_3\times 4$), 8.70 ($C\mathit{CH}_3\times 2$).

**3.2.17.2. Acetate 23d.** $[\alpha]_D^{30}$ +4.8 (*c*1.05, $CHCl_3$); $R_f$ 0.19 (1:1 hexane–EtOAc, two developments); $^1H$ NMR (300 MHz): $\delta$ *5.50* (*dd*, *1H*, $J_{3,4}$ *9.1*, $J_{3,2}$ *10.6 Hz*, *H-3*); HRFABMS: calcd for $C_{36}H_{45}NO_{17}$ $[M+H]^+$, *m*/*z* 764.2766; found, *m*/*z* 764.2752.

### 3.2.18. Methyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-3-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (23f)

**3.2.18.1. Disaccharide 23e.** 88.3%; $[\alpha]_D^{32}$ +8.9 (*c* 1.04, $CHCl_3$); $R_f$ 0.38 (1:1 hexane–EtOAc); $^1$H NMR (300 MHz): *δ* 7.80–7.70, 7.43–7.35 (m, 10H, ArH), 5.35 (dd, 1H, $J_{5',4'}$ 1.0, $J_{3',4'}$ 3.4 Hz, H-4′), 5.20 (dd, 1H, $J_{2',1'}$ 8.0, $J_{2',3'}$ 10.2 Hz, H-2′), 4.964 (dd, 1H, H-3′), 4.962 (d, 1H, $J_{1,2}$ 8.6 Hz, H-1), 4.70 (d, 1H, H-1′), *4.30* (*dd*, *1H*, $J_{3,2}$ *8.4*, $J_{3,4}$ *10.9 Hz*, *H-3*), 4.15–4.08 (m, 2H, H-6′a, H-6′b), 4.00–3.78 (m, 4H, H-4, H-5′, H-6a, H-6b), 3.92 (dd, 1H, H-2), 3.72 (br s, 1H, OH), 3.54–3.46 (m, 1H, H-5), 3.42 (s, 3H, $OCH_3$), 2.13, 2.03, 1.98, 1.96, 1.69 (5s, 18H, $CO\mathit{CH}_3 \times 4$, $C\mathit{CH}_3 \times 2$), 1.09 (s, 9H, C $(\mathit{CH}_3)_3$); $^{13}$C NMR (75 MHz): *δ* 171.78–169.04 (CO), 137.17–132.62 (C × 2, C-Ar), 129.88–127.66 (C-Ar), 101.20 (C-1′), 98.88 (C-1), 80.93 (C-4), 74.56 (C-5), 71.24 (C-5′), 70.84 (C-3′), 69.42 (C-3), 68.79 (C-2′), 66.78 (C-4′), 61.78 (C-6), 61.22 (C-6′), 56.20 ($OCH_3$), 55.94 (C-2), 26.84 (C $(\mathit{CH}_3)_3$), 20.53–20.25 ($CO\mathit{CH}_3 \times 4$), 19.33 ($\mathit{C}(CH_3)_3$), 8.72 ($C\mathit{CH}_3 \times 2$).

**3.2.18.2. Acetate 23f.** $[\alpha]_D^{27}$ +3.6 (*c* 1.04, $CHCl_3$); $R_f$ 0.40 (1:1 hexane–EtOAc, two developments); $^1$H NMR (300 MHz): *δ 5.55* (*dd*, *1H*, $J_{3,2}$ *9.1*, $J_{3,4}$ *10.7 Hz*, *H-3*); HRFABMS: calcd for $C_{45}H_{57}NO_{17}Si$ $[M+Na]^+$, *m*/*z* 934.3293; found, *m*/*z* 934.3320.

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## Supplementary data

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