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Temporary Carbohydrate Diol Protection with Ester Groups – Orthogonality under Solid-Phase Oligosaccharide Synthesis Conditions[‡]

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For regioselective deprotection studies under SPOS conditions the glucosamine derivatives **4ab/4ba**, **4ac/4ca** and **4ad/4da** – with Fmoc/PA, Fmoc/Lev or Fmoc/Alloc, respectively, as temporary ester protecting groups at 3-*O* and 4-*O* – were prepared. Fmoc cleavage with triethylamine in **4ab** or **4ba** led to PA migration, so the Fmoc/PA pair does not permit regioselective access to the vicinal hydroxy groups. Under the same reaction conditions no Lev migration in **4ac/4ca** or Alloc migration in **4ad/4da** was observed. Lev removal with hydrazinium acetate in **4ac/4ca** and Alloc removal with Pd^0 and dimedone as nucleophile in **4ad/4da** was also not accompanied by Fmoc migration, so the Fmoc/Lev pair and the Fmoc/Alloc pair can be successfully employed for regioselective access to the 3-hydroxy or the 4-hydroxy group, respectively. However, Fmoc cleavage with piperidine in **4ac/4ca** led to Lev migration, and the use of a basic nucleophile for Alloc cleavage also led to Fmoc migration in **4ad**. 4-*O*-Fmoc protection was also combined with Nap ether protection in **4ea**. These two groups could be readily and regioselectively removed, thus providing another useful pair for temporary protection of vicinal diols.

Introduction

Oligosaccharides play important roles in various biological processes, so general interest in these compounds, particularly as constituents of glycoconjugates, has greatly increased in recent years.[1–4] As a consequence, oligosaccharide synthesis has become an important issue.[5–10] In addition, successful solid-phase oligosaccharide syntheses (SPOS) have been developed,[11,12] complemented by methods to avoid undesired byproducts in the synthesis of the target molecules.[13–16] With our ester-based SPOS design[17] very good results have been obtained.[6,17,18] To cope with complex oligosaccharide synthesis, besides the linker-spacer system corresponding to a temporary protecting group that is orthogonal to all other protecting groups, three types of building blocks are required: for controlled chain extension, branching and termination. A study on the orthogonality of temporarily ester-group-protected diols required for the synthesis of branched oligosaccharides, and for diols in general, is reported.

Results and Discussion

The ester-based SPOS methodology, very successfully applied to the synthesis of branched *N*-glycans[17] (Scheme 1, **A**), involves: (i) different types of esters as temporary protecting groups [that is, the benzoate group as a linker and for chain termination and the Fmoc and PA (phenoxyacetyl) groups as temporary protecting groups for chain extension and 3-*O*,6-*O*-branching at the mannosyl residue c, respectively] that can be chemoselectively cleaved, (ii) the benzyl group for permanent *O*-protection and for the spacer between the anomeric centre at the reducing end sugar, thus providing a structurally defined target molecule after final product cleavage from the resin, (iii) *O*-glycosyl trichloroacetimidates [for chain extension, branching or termination as powerful glycosyl donors, which can be readily activated by catalytic amounts of (Lewis) acid], and (iv) benzoic acid residues on the Merrifield resin for the linkage of the hydroxymethylbenzyl spacer.

Application of this methodology to the synthesis of Lewis X (Le^x) and Lewis A (Le^a) oligosaccharides and gangliosides (Scheme 1, **B**–**D**) requires 3-*O*,4-*O*-branching at the *N*-acetylglucosamine and galactose residues, respectively. However, cleavage of one of the temporary ester protecting groups may be accompanied by migration of the remaining temporary ester protecting group to the liberated vicinal hydroxy group. A detailed investigation of the orthogonality, including the desirable regioselectivity of temporary ester protecting groups under SPOS conditions, was therefore undertaken in order to identify a suit-

[‡] Fmoc- and Alloc-*O*-protection leads to diesters of carbonic acid. Hence, the use of the term "ester groups" for *O*-acylated and *O*-alkoxycarbonylated hydroxy groups seems to be reasonable.

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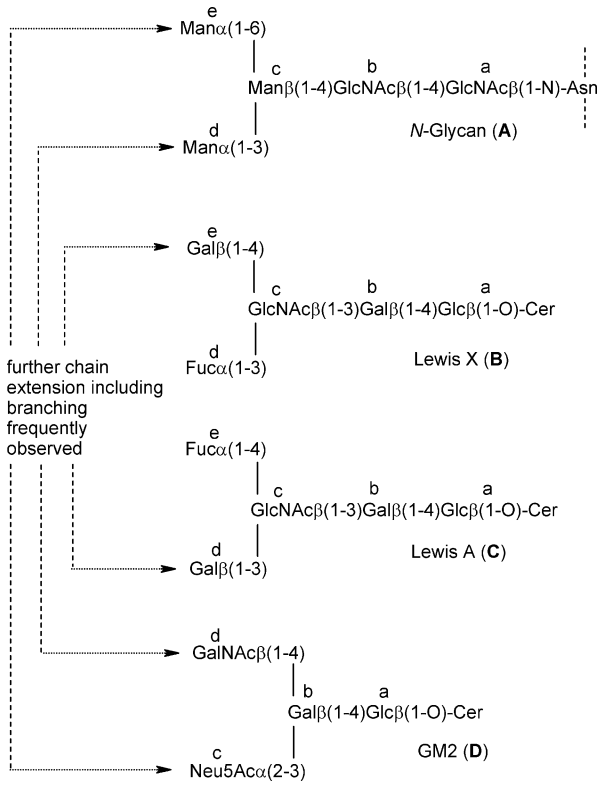
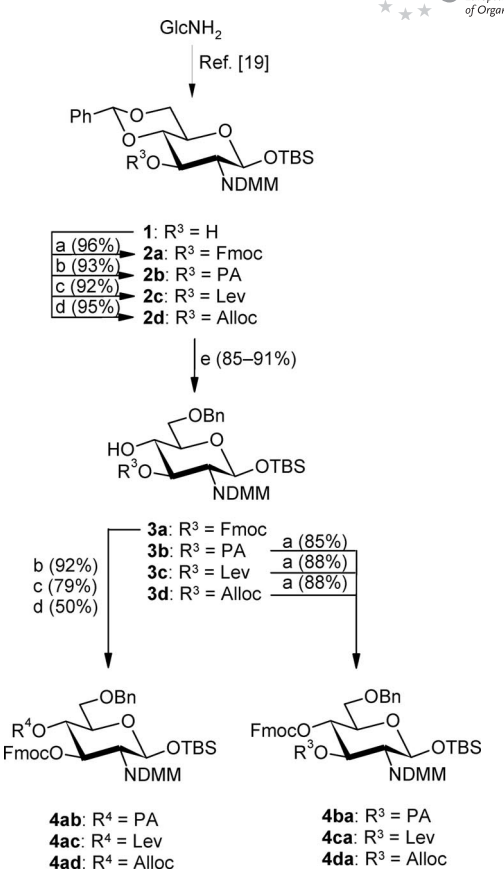


Scheme 1. Typical branched oligosaccharides.



Scheme 2. Synthesis of glucosamine derivatives with temporary protection at 3-*O* and 4-*O*. Reagents and conditions: (a) Fmoc-Cl, pyridine, DMAP, 0 °C; (b) PA-Cl, pyridine, 0 °C; (c) Lev-OH, DCC, DMAP, CH_2Cl_2, room temp.; (d) Alloc-Cl, CH_2Cl_2/pyridine, –10 °C; (e) Et_3SiH, trifluoroacetic anhydride (TFAA), trifluoroacetic acid (TFA), 0 °C → room temp.

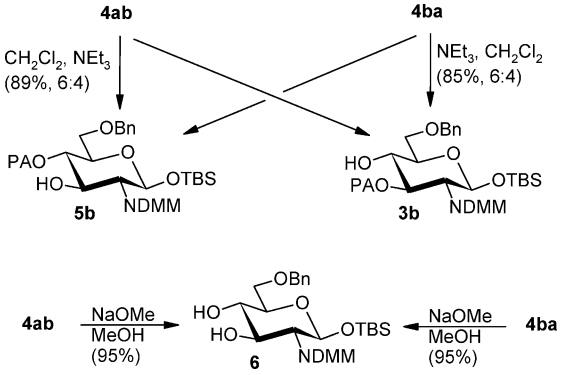
able system for the precise synthesis of branched oligosaccharides. Because *N*-acetylglucosamine is frequently found at the branching points of oligosaccharides (see Lewis antigens in Scheme 1), glucosamine derivatives with temporary ester protecting groups at 3-*O* and 4-*O* were selected for these studies.

To this end, glucosamine was transformed into the 3-*O*-unprotected derivative **1** (Scheme 2) according to reported procedures.[19] As temporary ester protecting groups at 3-*O*, 9-fluorenylmethoxycarbonyl (Fmoc), phenoxyacetyl (PA), levulinoyl (Lev) and allyloxycarbonyl (Alloc) were introduced, affording compounds **2a**, **2b**, **2c**[20] and **2d**. Selective cleavage of these groups can be performed as follows: Fmoc is cleaved with triethylamine, PA is removed with sodium methoxide in methanol, Lev is removed with hydrazinium acetate, and Alloc is cleaved with Pd^0 in the presence of a nucleophile. PA cleavage conditions will not affect *O*-benzoyl groups, but they will affect *O*-Fmoc, *O*-Lev and *O*-Alloc groups, so the presence of an *O*-PA group limits the cleavage sequence.

Reductive opening of the benzylidene acetal groups in compounds **2a**–**2d** with triethylsilane in the presence of trifluoroacetic anhydride[21] afforded the 4-*O*-unprotected 6-*O*-benzylated derivatives **3a**, **3b**, **3c**[20] and **3d**, which were employed for the generation of three pairs with regioisomeric 3-*O*,4-*O*-protection. In previous work, the Fmoc group had turned out to be ideally suited as a temporary protecting group in SPOS, so in **3a** this group was complemented by the PA, Lev and Alloc groups at 4-O, thus leading to compounds **4ab**, **4ac** and **4ad**. Correspondingly, introduction of the Fmoc group at 4-*O* in **3b**, **3c** and **3d** led to **4ba**, **4ca** and **4da**. In this way, **4ab** and **4ba** had Fmoc/PA protection at 3-*O* and 4-*O*, **4ac** and **4ca** had Fmoc/Lev protection, and **4ad** and **4da** had Fmoc/Alloc protection. The Fmoc/PA pair (**4ab**/**4ba**) and the Fmoc/Lev pair (**4ac**/**4ca**) were selected because these groups had previously been employed in SPOS for the synthesis of other branched oligosaccharides.[17,18,22] The particularly mild cleavage conditions for the Fmoc and Alloc groups, which should be totally orthogonal, were the reason for investigating the **4ad**/**4da** pair.

The conditions employed for the cleavage of the Fmoc, PA and Lev groups followed reported work on SPOS on Merrifield resins.[11,17,18] Firstly, Fmoc cleavage with triethylamine (100 equiv.) in dichloromethane as solvent was investigated in the presence of the 4-*O*-PA group in **4ab** (Scheme 3). However, beside the desired 3-*O*-unprotected **5b**, PA migration to 3-*O*, affording compound **3b** (**5b**/**3b** = 40:60), was also observed. Similar results were obtained when starting from **4ba** (**5b**/**3b** = 60:40) and also when pure **3b** was investigated: under these reaction conditions, **5b**/**3b** were again obtained in a 40:60 ratio. Not unexpectedly, se-

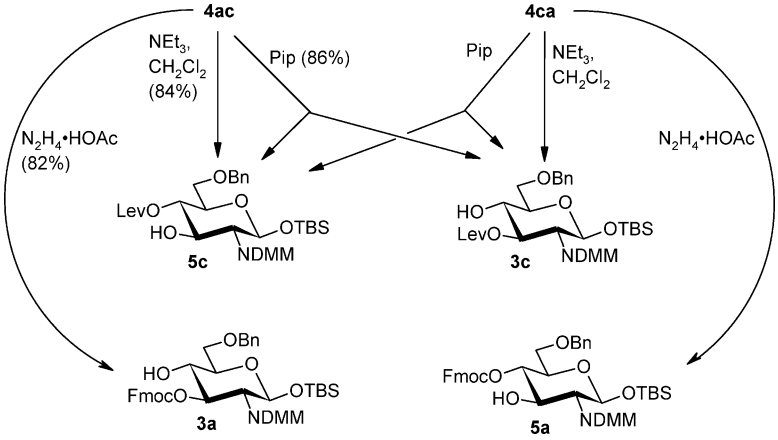
lective cleavage of the PA group in **4ab** or **4ba** with NaOMe in MeOH (0.5 equiv.) was also not possible: both groups were removed to afford the 3-*O*,4-*O*-unprotected compound **6**. Hence, in contrast with observations made for Fmoc and PA in remote positions,[17] these groups cannot be employed as temporary protecting groups in vicinal positions.



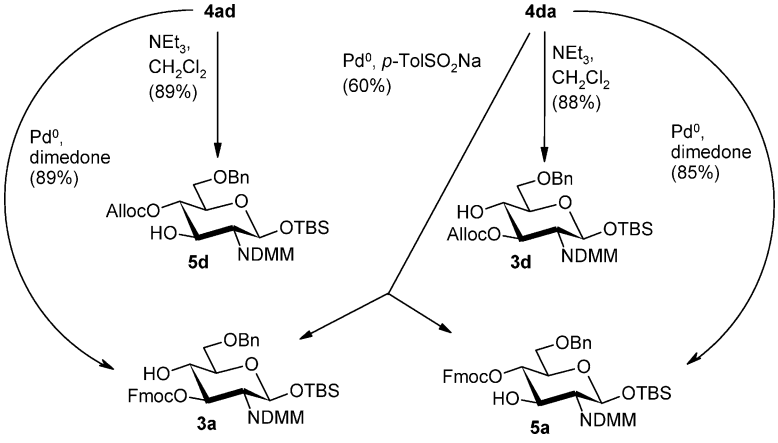
Scheme 3. Cleavage of the temporary Fmoc and PA protecting groups in **4ab** and **4ba**.

Investigation of Fmoc cleavage with triethylamine in the presence of the Lev group in **4ac/4ca** under SPOS conditions afforded the desired 4-*O*-Lev-protected **5c** and the 3-*O*-Lev-protected compound **3c**, respectively, both practically exclusively (Scheme 4). The other way around, initial Lev cleavage in **4ac** and **4ca** with hydrazinium acetate also selectively afforded the desired 3-*O*-Fmoc protected **3a** or the 4-*O*-Fmoc protected **5a**, respectively. Previous work by Boons et al.[22] could thus be confirmed. Hence, under these cleavage conditions, Fmoc and Lev are orthogonal protecting groups for vicinal hydroxy groups. Some Lev migration was observed when Fmoc cleavage was performed with piperidine (100 equiv.), however, with compounds **5c**/**3c** being obtained in a 82:18 ratio when starting from **4ac** and in a 7:93 ratio when starting from **4ca**. Previous SPOS with a building block structurally closely related to **4ac**[18] might hence have led to some regioisomeric glycosylation product under the applied piperidine cleavage conditions.

In our SPOS experiments, complete removal of hydrazinium acetate from the resin before the next glycosylation step had turned out to be difficult,[23] so the Fmoc/Alloc pair in **4ad/4da** was investigated for temporary protection of the vicinal 3-*O*,4-*O*-hydroxy groups. Gratifyingly, treatment of **4ad** and **4da** with triethylamine in dichloromethane led practically exclusively to 3-*O*-unprotected **5d** or to 4-*O*-unprotected **3d**, respectively (Scheme 5). Similarly, treatment of **4ad** and **4da** with tetrakis(triphenylphosphane)palladium



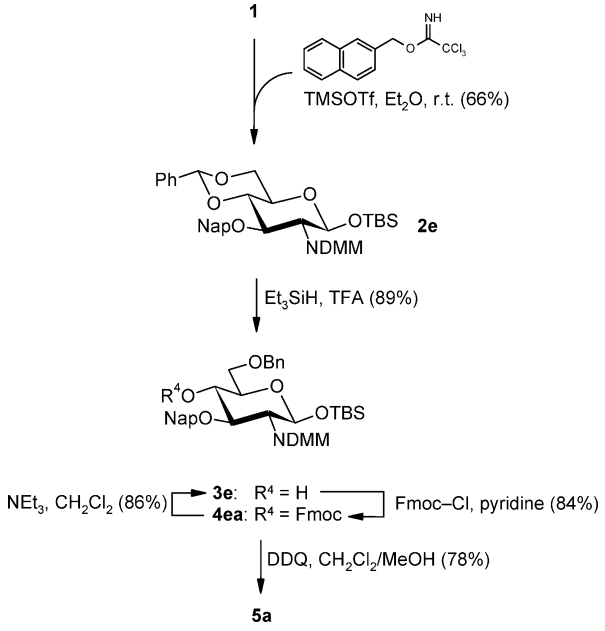
Scheme 4. Cleavage of the temporary Fmoc and Lev protecting groups in **4ac** and **4ca**.



Scheme 5. Cleavage of the temporary Fmoc and Alloc protecting groups in **4ad** and **4da**.

(Pd^0) as catalyst and excess dimedone as nucleophile in THF[24] exclusively furnished 4-*O*-unprotected **3a** and 3-*O*-unprotected **5a**, respectively. When the quite basic sodium *p*-toluenesulfinate was employed as nucleophile in this reaction, however (starting from **4da**, for instance), **3a** and **5a** were obtained in a 45:55 ratio, pointing to Fmoc migration under these conditions. Preliminary SPOS studies showed that the Fmoc/Alloc pair is highly useful for temporary protection in order to access branched oligosaccharides.[25]

To provide further options in orthogonal protection of vicinal hydroxy groups, a combination of the Fmoc group with the 2-naphthylmethyl (Nap) group ether-linked to the 3-*O*-position was also investigated (Scheme 6). To this end, the 3-*O*-Nap-protected compound **2e** was prepared from **1** and *O*-naphthylmethyl trichloroacetimidate[26] and, after reductive benzylidene cleavage (→ **3e**) and 4-*O*-Fmoc protection, afforded the desired starting material **4ea**. Gratifyingly, selective removal of the two groups – either Fmoc with triethylamine to afford 4-*O*-unprotected **3e** exclusively or Nap with DDQ to afford **5a** exclusively – offered a further useful alternative for temporary protection of vicinal hydroxy groups.



Scheme 6. Synthesis of the glucosamine derivative **4ea** and cleavage of the temporary Fmoc and Nap protecting groups.

Conclusions

The compound pairs **4ab/4ba**, **4ac/4ca** and **4ad/4da**, with temporary ester protecting groups at vicinal 3-*O* and 4-*O* for the regiocontrolled synthesis of branched oligosaccharides together with *tert*-butyldimethylsilyl (TBS) groups at their anomeric hydroxy groups for eventual transformation of these intermediates into glycosyl donors, were investigated under SPOS cleavage conditions. The Fmoc/PA pair (**4ab/4ba**) did not comply with the stability requirements, and the Fmoc/Lev pair (**4ac/4ca**) also required cleavage conditions that limit its use for the temporary protection of vicinal hydroxy groups in SPOS. Excellent results were obtained for the Fmoc/Alloc pair (**4ad/4da**), which could be orthogonally cleaved under mild conditions independent of the position and the sequence. Not surprisingly, the same results were obtained for Fmoc cleavage in combination with the ether-linked Nap group (**4ea**). Regiocontrolled synthesis of branched oligosaccharides is now being carried out with these systems.

Experimental Section

General: Solvents were purified by standard procedures. NMR spectra were recorded at 22 °C with a Bruker 400 spectrometer; tetramethylsilane (TMS) or the resonance of the undeuterated solvent were used as internal standards (solvent $CDCl_3$, δ = 7.24 ppm). Mass spectra were recorded with a Bruker ESI-MS mass spectrometer. Thin-layer chromatography was performed on Merck silica gel (60 F_{254}) plastic plates; compounds were visualized by treatment with a solution of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (20 g) and $Ce(SO_4)_2$ (0.4 g) in sulfuric acid (10%, 400 mL) and then by heating to 120 °C. Flash chromatography was performed on MN Silica gel 60 (230–400 mesh) at a pressure of 0.2 bar. Optical rotations were measured at 22 °C with a Büchi Polar-Monitor using sodium D line light.

A. General Procedure for 9-Fluorenylmethoxycarbonylation: FmocCl (1.2 mmol), followed by DMAP (0.01 mmol), were added at 0 °C to a solution of the compound (1 mmol) in dry pyridine (10 mL), and the resulting reaction mixture was allowed to warm to room temperature and stirred for 2–4 h. The reaction mixture was quenched by addition of excess methanol (1 mL) and concentrated under reduced pressure to give a residue.

B. General Procedure for Phenoxyacetylation: Phenoxyacetyl chloride (PACl, 1.2 mmol) was added dropwise at 0 °C to a solution of the compound (1 mmol) in dry pyridine (10 mL), and the resulting reaction mixture was stirred for 30 min at the same temperature. The reaction mixture was quenched by addition of excess methanol (1 mL) and concentrated under reduced pressure to give a residue.

C. General Procedure for the Reductive Opening of the 4,6-*O*-Benzylidene Ring: Triethylsilane (5.0 mmol), followed by trifluoroacetic anhydride (3.0 mmol), were added at 0 °C to a solution of the compound (1 mmol) in dry CH_2Cl_2 (10 mL). TFA (5.0 mmol) was added dropwise over a period of 10 min, and the reaction mixture was allowed to warm to room temperature and stirred for 2–4 h. The reaction mixture was quenched by dropwise addition of cold saturated $NaHCO_3$ and extracted with CH_2Cl_2 (15 mL × 3). The organic layer was washed with water (10 mL × 3), dried with anhydrous $MgSO_4$ and concentrated under reduced pressure to give a residue.

D. General Procedure for Fmoc Removal: Triethylamine (10 mmol) or piperidine (10 or 17.5 mmol) was added to a solution of the compound (0.1 mmol) in CH_2Cl_2 (10 mL), and the resulting reaction mixture was stirred at room temp. for 40 min to 3 h. Volatiles were removed under reduced pressure, and the residue was purified by column chromatography.

***tert*-Butyldimethylsilyl 4,6-*O*-Benzylidene-2-deoxy-2-dimethylmaleimido-3-*O*-(9-fluorenylmethoxycarbonyl)-β-D-glucopyranoside (2a):** The residue obtained from **1** after General Procedure A was purified by column chromatography (petroleum ether/ethyl acetate, 9:1) to give **2a** (7.0 g, 96%) as a colourless foam. R_f = 0.45 (petroleum ether/ethyl acetate, 8:2). $[\alpha]_D^{22}$ = +15.3 (c = 1.0, $CHCl_3$). ^1H NMR

(400 MHz, $CDCl_3$): δ = 7.74 (d, J = 7.7 Hz, 2 H, Ar-*H*), 7.54 (d, J = 7.5 Hz, 1 H, Ar-*H*), 7.46–7.52 (m, 3 H, Ar-*H*), 7.31–7.42 (m, 5 H, Ar-*H*), 7.29 (dt, J = 7.2, 1.0 Hz, 1 H, Ar-*H*), 7.22 (dt, J = 7.3, 1.0 Hz, 1 H, Ar-*H*), 5.61 (dd, J = 10.4, 9.6 Hz, 1 H, 3-H), 5.44 (s, 1 H, PhC*H*), 5.38 (d, J = 8.0 Hz, 1 H, 1-*H*), 4.25 (dd, J = 10.8, 5.1 Hz, 1 H, 6-*H*b), 4.12–4.15 (m, 2 H, Fmoc-CH_2), 4.09 (dd, J = 10.5, 8.0 Hz, 1 H, 2-*H*), 4.03 (t, J = 7.6 Hz, 1 H, Fmoc-C*H*), 3.75 (dd, J = 10.3, 3.6 Hz, 1 H, 4-*H*), 3.72 (dd, J = 10.2, 4.0 Hz, 1 H, 6-*H*a), 3.61 (ddd, J = 14.3, 9.6, 4.5 Hz, 1 H, 5-*H*), 1.74 (s, 6 H, DMM-CH_3), 0.70 [s, 9 H, SiC(CH_3)$_3$], 0.00 (s, 3 H, SiCH_3), –0.09 (s, 3 H, SiCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.5 (*C*O), 143.3, 143.2, 141.2, 141.1, 137.4, 137.0, 129.2, 128.3, 127.9, 127.8, 127.4, 127.3, 126.4, 125.3, 125.2, 120.0, (Ar-*C*), 101.7 (Ph*C*H), 93.9 (*C*-1), 79.5 (*C*-4), 74.4, 73.7 (*C*-3), 70.3 (Fmoc-*C*H_2), 68.7 (*C*-6), 66.2 (*C*-5), 57.3 (*C*-2), 46.5 (Fmoc-*C*H), 25.4 [C(*C*H_3)$_3$], 17.6 [*C*(CH$_3$)$_3$], 8.7 (DMM-*C*H_3), –4.1, –5.5 (2× Si*C*H_3) ppm. ESI-HRMS (positive mode): calcd. for $[C_{40}H_{45}NO_9Si+Na]^+$ 734.2756; found 734.2739. $C_{40}H_{45}NO_9Si$ (711.87): calcd. C 67.49, H 6.37, N 1.97; found C 67.26, H 6.12, N 1.87.

***tert*-Butyldimethylsilyl 4,6-*O*-Benzylidene-2-deoxy-2-dimethylmaleimido-3-*O*-phenoxyacetyl-β-D-glucopyranoside (2b):** The residue obtained from **1** after General Procedure B was purified by column chromatography (petroleum ether/ethyl acetate, 9:1) to give **2b** (5.70 g, 93%) as a white foam. R_f = 0.55 (petroleum ether/ethyl acetate, 8:2). $[\alpha]_D^{22}$ = –13.9 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.35 (m, 2 H, Ar-*H*), 7.33–7.28 (m, 3 H, Ar-*H*), 7.05 (t, J = 7.6 Hz, 2 H, Ar-*H*), 6.84 (t, J = 7.3 Hz, 1 H, Ar-*H*), 6.70 (d, J = 8.4 Hz, 2 H, Ar-*H*), 5.83 (dd, J = 9.6 Hz, 1 H, 3-*H*), 5.41 (s, 1 H, C*H*Ph), 5.40 (d, J = 8.1 Hz, 1 H, 1-*H*), 4.48 (ABq, J = 17.0 Hz, 2 H, –CH_2OPh), 4.28 (dd, J = 10.6, 4.5 Hz, 1 H, 6-*H*b), 4.00 (dd, J = 10.3, 8.1 Hz, 1 H, 2-*H*), 3.76 (t, J = 10.0 Hz, 1 H, 6-*H*a), 3.71–3.59 (m, 2 H, 4-*H*/5-*H*), 1.85 (s, 6 H, DMM-CH_3), 0.71 [s, 9 H, –SiC(CH_3)$_3$], 0.00 (s, 3 H, SiCH_3), –0.09 (s, 3 H, SiCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 168.5 (*C*O), 157.8 (O*C*O), 137.1, 129.7, 129.4, 128.5, 126.5, 121.8, 114.7 (Ar-*C*), 101.9 (Ph*C*H), 94.0 (*C*-1), 79.6 (*C*-4), 70.9 (*C*-3), 68.9 (*C*-6), 66.3 (*C*-5), 65.0 (PhO*C*H$_2$), 57.3 (*C*-2), 25.5 [SiC(*C*H$_3$)$_3$], 17.8 [Si*C*(CH$_3$)$_3$], 8.9 (DMM-*C*H_3), –4.0, –5.5 (2× Si*C*H_3) ppm. ESI-HRMS (positive mode): calcd. for $[C_{33}H_{41}NO_9Si+Na]^+$ 646.2443; found 746.2404.

***tert*-Butyldimethylsilyl 3-*O*-Allyloxycarbonyl-4,6-*O*-benzylidene-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (2d):** AllocCl (1.06 mL, 12.44 mmol) was added at –10 °C to a solution of compound **1** (1.74 g, 3.55 mmol) in CH_2Cl_2/pyridine (3:2, 35 mL) over a period of 10 min, and the resulting reaction mixture was stirred at the same temperature for 1 h. The reaction mixture was quenched by addition of excess MeOH (5 mL) and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate, 9:1) to give **2d** (1.94 g, 95%) as a syrup. R_f = 0.60 (petroleum ether/ethyl acetate, 7:3). $[\alpha]_D^{22}$ = –36.5 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.34 (m, 2 H, Ar-*H*) 7.31–7.23 (m, 3 H, Ar-*H*), 5.77–5.66 (m, 1 H, –C*H*=CH$_2$), 5.56 (dd, J = 10.6, 9.2 Hz, 1 H, 3-*H*), 5.44 (s, 1 H, C*H*Ph), 5.36 (d, J = 7.8 Hz, 1 H, 1-*H*), 5.15 (dd, J = 17.2, 1.3 Hz, 1 H, –OCH$_2$CH=CH_2), 5.07 (dd, J = 10.9, 1.3 Hz, 1 H, –OCH$_2$CH=CH_2), 4.48–4.37 (m, 2 H, OCH_2CH=CH$_2$), 4.26 (dd, J = 10.5, 5.1 Hz, 1 H, 6-*H*a), 4.02 (dd, J = 10.3, 7.8 Hz, 1 H, 2-*H*), 3.74 (t, J = 10.0 Hz, 1 H, 6-*H*a), 3.69 (t, J = 9.3 Hz, 1 H, 4-*H*), 3.60 (ddd, J = 9.5, 5.4, 4.6 Hz, 1 H, 5-*H*), 1.88 (s, 6 H, DMM-CH_3), 0.71 [s, 9 H, Si(CH_3)$_3$], 0.00 (s, 3 H, SiCH_3), –0.08 (s, 3 H, SiCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.3 (O*C*O), 137.1, 131.4 (O*C*H$_2$CH=CH$_2$), 129.2, 128.3, 126.4 (Ar-*C*), 118.6 (CH=*C*H$_2$), 101.7 (*C*HPh), 93.9 (*C*-1), 79.5 (*C*-4), 73.6 (*C*-3), 68.8, 68.6 (*C*-6/O*C*H$_2$CH=), 66.2 (*C*-5), 57.2 (*C*-2), 25.4 [SiC(*C*H$_3$)$_3$], 17.7 [Si*C*(CH$_3$)$_3$], 8.8 (DMM-*C*H$_3$), –4.1, –5.5 (2× Si*C*H$_3$) ppm. ESI-HRMS (positive mode): calcd. for $[C_{29}H_{39}NO_9Si+Na]^+$ 596.2286; found 596.2273. $C_{29}H_{39}NO_9Si$ (573.71): calcd. C 60.71, H 6.85, N 2.44; found C 60.61, H 7.05, N 2.34.

***tert*-Butyldimethylsilyl 6-*O*-Benzyl-2-deoxy-2-dimethylmaleimido-3-*O*-(9-fluorenylmethoxycarbonyl)-β-D-glucopyranoside (3a):** The residue obtained from **2a** after General Procedure C was purified by column chromatography (petroleum ether/ethyl acetate, 8:2) to give **3a** (6.40 g, 91%) as a foam. R_f = 0.41 (petroleum ether/ethyl acetate, 7:3). $[\alpha]_D^{22}$ = +36.3 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (d, J = 7.1 Hz, 2 H, Ar-*H*), 7.46 (d, J = 7.1 Hz, 1 H, Ar-*H*), 7.40 (d, J = 7.5 Hz, 1 H, Ar-*H*), 7.32–7.14 (m, 9 H, Ar-*H*), 5.44 (dd, J = 11.1, 9.1 Hz, 1 H, 3-H), 5.32 (d, J = 8.1 Hz, 1 H, 1-H), 4.51 (ABq, J = 12.4 Hz, 2 H, OCH_2Ph), 4.22–4.12 (m, 2 H, Fmoc-CH_2), 4.05 (t, J = 7.6 Hz, 1 H, Fmoc-C*H*), 3.99 (dd, J = 10.8, 8.0 Hz, 1 H, 2-H), 3.75 (t, J = 9.3 Hz, 1 H, 4-H), 3.72 (d, J = 4.5 Hz, 2 H, 6a,b-H), 3.65 (dt, J = 9.9, 4.5 Hz, 1 H, 5-H), 3.13–2.89 (br. s, 1 H, O*H*), 1.74 (s, 6 H, 2× CH_3), 0.69 [s, 9 H, SiC-(CH_3)$_3$], 0.00 (s, 3 H, SiCH_3), –0.10 (s, 3 H, SiCH_3) ppm. ^{13}C NMR (101 MHz, CDCl3): δ = 155.5 (*C*O), 143.4, 143.2, 141.3, 141.3, 137.9, 137.5, 128.6, 128.4, 128.0, 128.0, 127.9, 127.8, 127.4, 125.4, 125.4, 120.1 (Ar-*C*), 93.3 (*C*-1), 77.3 (*C*-3), 74.3 (*C*-5), 73.8 (O*C*H$_2$Ph), 71.7 (*C*-4), 70.5, 70.4 (*C*-6, Fmoc-*C*H$_2$), 56.6 (*C*-2), 46.6 (Fmoc-*C*H), 25.5 [SiC(*C*H$_3$)$_3$], 17.7 [Si*C*(CH$_3$)$_3$], 8.8 (DMM-*C*H$_3$), –4.0, –5.5 (2× Si*C*H$_3$) ppm. ESI-HRMS (positive mode): calcd. for $[C_{40}H_{47}NO_9Si+Na]^+$ 736.2912; found 736.2896. $C_{40}H_{47}NO_9Si$ (713.89): calcd. C 67.30, H 6.64, N 1.96; found C 66.39, H 7.00, N 1.69.

***tert*-Butyldimethylsilyl 6-*O*-Benzyl-2-deoxy-2-dimethylmaleimido-3-*O*-phenoxyacetyl-β-D-glucopyranoside (3b):** The residue obtained from **2b** after General Procedure C was purified by column chromatography (petroleum ether/ethyl acetate, 9:1) to give **3b** (2.45 g, 85%) as a viscous liquid. R_f = 0.66 (petroleum ether/ethyl acetate, 7:3). $[\alpha]_D^{22}$ = –3.75 (c = 0.8, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.14 (m, 5 H, Ar-*H*), 7.10 (t, J = 8.0 Hz, 2 H, Ar-*H*), 6.82 (t, J = 7.3 Hz, 1 H, Ar-*H*), 6.68 (d, J = 8.0 Hz, 2 H, Ar-*H*), 5.67 (dd, J = 10.8, 8.3 Hz, 1 H, 3-*H*), 5.35 (d, J = 8.0 Hz, 1 H, 1-*H*), 4.49 (s, 2 H, OCH_2Ph) 4.43 (ABq, J = 16.2 Hz, 2 H, PhOCH_2), 3.89 (dd, J = 10.9, 8.0 Hz, 1 H, 2-*H*), 3.75–3.52 (m, 4 H, 4-*H*/5-*H*/6-*H*ab), 3.35–3.01 (br. s, 1 H, O*H*), 1.75 (s, 6 H, DMM-CH_3), 0.68 [s, 9 H, –SiC(CH_3)$_3$], –0.00 (s, 3 H, SiCH_3), –0.10 (s, 3 H, SiCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.5 (*C*O), 157.7 (*C*O), 138.1, 129.6, 128.5, 127.7, 127.6, 121.7, 114.6 (Ar-*C*), 93.1 (*C*-1), 74.8 (*C*-4/*C*-5), 74.4 (*C*-3), 73.6 (O*C*H$_2$Ph), 71.0 (*C*-4/*C*-5), 70.0 (*C*-6), 64.9 (PhO*C*H$_2$), 56.6 (*C*-2), 25.4 [SiC(*C*H$_3$)$_3$], 17.6 [Si*C*(CH$_3$)$_3$], 8.7 (DMM-*C*H$_3$), –4.1, –5.6 (2× Si*C*H$_3$) ppm. ESI-HRMS (positive mode): calcd. for $[C_{33}H_{43}NO_9Si+Na]^+$ 648.2599; found 648.2590.

***tert*-Butyldimethylsilyl 3-*O*-Allyloxycarbonyl-6-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (3d):** The residue obtained from **2d** after General Procedure C was purified by column chromatography (petroleum ether/ethyl acetate, 8:2) to give **3d** (1.7 g, 88%) as a viscous syrup. R_f = 0.43 (petroleum ether/ethyl acetate, 7:3). $[\alpha]_D^{22}$ = –6.0 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.15 (m, 5 H, Ar-*H*) 5.79–5.67 (m, 1 H, C*H*=CH$_2$), 5.37 (dd, J = 11.1, 8.3 Hz, 1 H, 3-*H*), 5.31 (d, J = 8.1 Hz, 1 H, 1-*H*), 5.17 (dd, J = 17.3, 1.1 Hz, 1 H, –OCH_2CH=), 5.10 (dd, J = 10.5, 1.1 Hz, 1 H, –OCH_2CH=), 4.52 (ABq, J = 12.3 Hz, 2 H, OCH_2Ph), 4.48–4.38 (m, 2 H, OCH_2CH=), 3.92 (dd, J = 11.0, 8.1 Hz, 1 H, 2-*H*), 3.74–3.60 (m, 4 H, 4-*H*/5-*H*/6-*Ha*,b), 3.21–2.83 (br. s, 1 H, O*H*), 1.84 (s, 6 H, DMM-CH_3), 0.69 [s, 9 H,

SiC(CH_3)$_3$], 0.00 (s, 3 H, SiCH_3), –0.09 (s, 3 H, SiCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 155.2 (O*C*O), 138.0, 131.4 (*C*H=CH_2), 128.5, 127.8, 127.7 (Ar-*C*), 118.8 (CH=*C*H_2), 93.2 (*C*-1), 77.2 (*C*-3), 74.4 (*C*-5), 73.7 (O*C*H_2Ph), 71.4 (*C*-4), 70.2 (*C*-6), 68.8 (-O*C*H_2CH=), 56.5 (*C*-2), 25.4 [C(*C*H_3)$_3$], 17.7 [*C*(CH$_3$)$_3$], 8.7 (DMM-*C*H$_3$), –4.1, –5.5 (2× Si*C*H$_3$) ppm. ESI-HRMS (positive mode): calcd. for [$C_{29}H_{41}NO_9Si$+Na]$^+$ 598.2443; found 598.2468. $C_{29}H_{41}NO_9Si$ (575.72): calcd. C 60.50, H 7.18, N 2.43; found C 59.79, H 7.34, N 2.18.

***tert*-Butyldimethylsilyl 6-*O*-Benzyl-2-deoxy-2-dimethylmaleimido-3-*O*-(9-fluorenylmethoxycarbonyl)-4-*O*-phenoxyacetyl-β-D-glucopyranoside (4ab):** The residue obtained from **3a** after General Procedure B was purified by column chromatography (petroleum ether/ethyl acetate, 9:1) to give **4ab** (0.219 g, 92%) as a foam. R_f = 0.52 (petroleum ether/ethyl acetate, 8:2). $[\alpha]_D^{22}$ = +32.3 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 3.6 Hz, 1 H, Ar-*H*), 7.58 (d, *J* = 3.4 Hz, 1 H, Ar-*H*), 7.40 (d, *J* = 7.6 Hz, 1 H, Ar-*H*), 7.35 (d, *J* = 7.5 Hz, 1 H, Ar-*H*), 7.27–7.08 (9 H, Ar-*H*), 7.08–7.02 (m, 2 H, Ar-*H*), 6.82–6.76 (m, 1 H, Ar-*H*), 6.69–6.63 (m, 2 H, Ar-*H*), 5.54 (dd, *J* = 10.9, 9.1 Hz, 1 H, 3-*H*), 5.29 (d, *J* = 8.0 Hz, 1 H, 1-*H*), 5.24 (dd, *J* = 9.8, 9.3 Hz, 1 H, 4-*H*), 4.38 (ABq, *J* = 12.0 Hz, 2 H, OCH_2Ph), 4.30 (ABq, *J* = 16.1 Hz, 2 H, PhOCH_2), 4.10 (dd, *J* = 9.3, 8.0 Hz, 1 H, 2-*H*), 4.08–4.02 (m, 2 H, Fmoc-CH_2), 3.98 (t, *J* = 7.7 Hz, 1 H, Fmoc-C*H*), 3.71 (dt, *J* = 9.9, 4.2 Hz, 1 H, 5-*H*), 3.46 (m, 2 H, 6-*H*a,b), 1.72 (s, 6 H, DMM-CH_3), 0.68 [s, 9 H, SiC(CH_3)$_3$], –0.00 (s, 3 H, SiCH_3), –0.10 (s, 3 H, SiCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.4, 167.9 (2× *C*O), 157.6 (O*C*O), 154.5, 143.2, 143.1, 141.2, 141.2, 137.8, 137.5, 129.6, 128.4, 127.9, 127.9, 127.8, 127.8, 127.3, 125.3, 125.2, 121.8, 120.0, 114.6 (Ar-*C*), 93.3 (*C*-1), 74.6 (*C*-3), 73.6 (O*C*H_2Ph), 72.7 (*C*-5), 71.1 (*C*-4), 70.5 (Fmoc-*C*H_2), 69.3 (*C*-6), 65.0 (PhO*C*H_2), 56.6 (*C*-2), 46.4 (Fmoc-*C*H), 25.4 [SiC(*C*H_3)$_3$], 17.6 [Si*C*(CH$_3$)$_3$], 8.7 (DMM-*C*H$_3$), –4.1 (Si*C*H$_3$), –5.5 (Si*C*H$_3$) ppm. ESI-HRMS (positive mode): calcd. for [$C_{48}H_{53}NO_{11}Si$+Na]$^+$ 870.3280; found 870.3256.

***tert*-Butyldimethylsilyl 6-*O*-Benzyl-2-deoxy-2-dimethylmaleimido-3-*O*-(9-fluorenylmethoxycarbonyl)-4-*O*-levulinoyl-β-D-glucopyranoside (4ac):** DCC (0.274 g, 1.33 mmol), followed by a catalytic amount of DMAP, was added to a solution of compound **3a** (0.19 g, 2.04 mmol) and levulinic acid (271 μL, 2.66 mmol) in CH_2Cl_2 (3 mL) at room temperature, and the mixture was stirred for 1 h. The milky reaction mixture was concentrated under reduced pressure to give a residue. Column chromatography of the residue afforded **4ac** (0.17 g, 79%) as a viscous liquid. R_f = 0.43 (petroleum ether/ethyl acetate, 7:3). $[\alpha]_D^{22}$ = +38.3 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 7.5 Hz, 2 H, Ar-*H*), 7.53 (dd, *J* = 7.2, 3.9 Hz, 2 H, Ar-*H*), 7.31 (m, 9 H, Ar-*H*), 5.62 (dd, *J* = 10.5, 9.4 Hz, 1 H, 3-*H*), 5.38 (d, *J* = 8.0 Hz, 1 H, 1-*H*), 5.21 (t, *J* = 9.6 Hz, 1 H, 4-*H*), 4.56 (s, 2 H, OCH_2Ph), 4.32–4.12 (m, 4 H, Fmoc-CH_2, 2-*H*, Fmoc-C*H*), 3.87–3.77 (m, 1 H, 5-*H*), 3.62 (m, 2 H, 6-*H*ab), 2.56 (t, *J* = 6.4 Hz, 2 H, CH_2), 2.40 (t, *J* = 6.3 Hz, 2 H, CH_2), 2.02 (s, 3 H, COCH_3), 1.85 (s, 6 H, DMM-CH_3), 0.77 [s, 9 H, SiC(CH_3)$_3$], 0.10 (s, 3 H, SiCH_3), –0.00 (s, 3 H, SiCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 206.1 (*C*OCH_3), 171.5 (*C*O), 154.6 (O*C*O), 143.5, 143.3, 141.3, 138.2, 137.5, 128.4, 128.0, 127.9, 127.8, 127.7, 127.4, 127.4, 125.5, 120.1 (Ar-*C*), 93.3 (*C*-1), 74.8 (*C*-3), 73.6 (O*C*H_2Ph), 73.4 (*C*-5), 70.5 (Fmoc-*C*H_2), 70.3 (*C*-4), 69.4 (*C*-6), 56.7 (*C*-2), 46.5 (Fmoc-*C*H), 37.8 (*C*H_2), 29.7 (CO*C*H_3), 28.0 (*C*H_2), 25.5 [SiC(*C*H_3)$_3$], 17.7 [Si*C*(CH$_3$)$_3$], 8.8 (DMM-*C*H$_3$), –4.0, –5.5 (2× Si*C*H$_3$) ppm. ESI-HRMS (positive mode): calcd. for [$C_{45}H_{53}NO_{11}Si$+Na]$^+$ 834.3280; found 834.3260.

***tert*-Butyldimethylsilyl 4-*O*-Allyloxycarbonyl-6-*O*-benzyl-2-deoxy-2-dimethylmaleimido-3-*O*-(9-fluorenylmethoxycarbonyl)-β-D-glucopyranoside (4ad):** (Alloc)$_2$O (116 μL, 0.70 mmol) was added to a solution of compound **3a** (0.05 g, 0.07 mmol) in CH_2Cl_2/pyridine (2:1, 3 mL), and the resulting reaction mixture was stirred at room temperature for 16 h. The reaction mixture was quenched with excess methanol (1 mL) and concentrated under reduced pressure to give a viscous mass. Column purification afforded **4ad** (0.028 g, 50%) as a foam, together with the starting material **3a** (0.013 g, 26%). R_f = 0.45 (petroleum ether/ethyl acetate, 8:2). $[\alpha]_D^{22}$ = +34.0 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76–7.69 (d, *J* = 7.4 Hz, 2 H, Ar-*H*), 7.56–7.48 (t, *J* = 8.4 Hz, 2 H, Ar-*H*), 7.38 (t, *J* = 7.4 Hz, 2 H, Ar-*H*), 7.35–7.23 (m, 7 H, Ar-*H*), 5.78–5.67 (m, 1 H, CH_2=C*H*–CH_2), 5.65 (dd, *J* = 10.8, 9.1 Hz, 1 H, 3-*H*), 5.38 (d, *J* = 8.0 Hz, 1 H, 1-*H*), 5.17 (dd, *J* = 17.2, 1.4 Hz, 1 H, OC*H*H–CH=), 5.09 (dd, *J* = 10.4, 1.2 Hz, 1 H, OCH*H*–CH=), 5.06 (dd, *J* = 9.8, 9.4 Hz, 1 H, 4-*H*), 4.57 (ABq, *J* = 12.1 Hz, 2 H, OCH_2Ph), 4.45 (d, *J* = 5.7 Hz, 2 H, OCH_2–CH=), 4.28–4.19 (m, 2 H, Fmoc-CH_2), 4.18 (*J* = 10.8, 8.0 Hz, 1 H, 2-*H*), 4.13 (t, *J* = 7.3 Hz, 1 H, Fmoc-C*H*), 3.86 (dt, *J* = 10.1, 4.4 Hz, 1 H, 5-*H*), 3.67 (d, *J* = 4.3 Hz, 2 H, 6-*H*ab), 1.84 (br. s, 6 H, DMM-CH_3), 0.77 [s, 9 H, SiC(CH_3)$_3$], 0.09 (s, 3 H, SiCH_3), –0.01 (s, 3 H, SiCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.6, 154.2 (2× O*C*O), 143.5, 143.3, 141.3, 138.1, 137.6, 131.3 (H*C*=CH_2), 128.5, 128.1, 128.0, 127.8, 127.7, 127.5, 127.5, 125.5, 125.5, 120.1 (Ar-*C*), 119.1 (HC=*C*H_2), 93.4 (*C*-1), 74.8 (*C*-3), 74.3 (*C*-4), 73.7 (O*C*H_2Ph), 73.1 (*C*-5), 70.6 (Fmoc-*C*H_2), 69.4 (*C*-6), 69.1 (O*C*H_2–CH=CH_2), 56.7 (*C*-2), 46.6 (Fmoc-*C*H), 25.5 [SiC(*C*H_3)$_3$], 17.8 [Si*C*(CH$_3$)$_3$], 8.8 (DMM-*C*H$_3$), –4.0, –5.4 (2× Si*C*H$_3$) ppm. ESI-MS (positive mode): calcd. for [$C_{44}H_{51}NO_{11}Si$+Na]$^+$ 820.3124; found 820.3115.

***tert*-Butyldimethylsilyl 6-*O*-Benzyl-2-deoxy-2-dimethylmaleimido-4-*O*-(9-fluorenylmethoxycarbonyl)-3-*O*-phenoxyacetyl-β-D-glucopyranoside (4ba):** The residue obtained from **3b** after General Procedure A was purified by column chromatography (petroleum ether/ethyl acetate, 9:1) to give **4ba** (5.10 g, 85%) as a white foam. R_f = 0.45 (petroleum ether/ethyl acetate, 8:2). $[\alpha]_D^{22}$ = +17.0 (*c* = 0.8, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (t, *J* = 6.7 Hz, 2 H, Ar-*H*), 7.46–7.39 (m, 2 H, Ar-*H*), 7.33–7.09 (m, 9 H, Ar-*H*), 7.05 (t, *J* = 7.9 Hz, 2 H, Ar-*H*), 6.79 (t, *J* = 7.3 Hz, 1 H, Ar-*H*), 6.64 (d, *J* = 8.3 Hz, 2 H, Ar-*H*), 5.79 (dd, *J* = 9.5, 9.1 Hz, 1 H, 3-*H*), 5.33 (d, *J* = 8.0 Hz, 1 H, 1-*H*), 4.91 (t, *J* = 9.5 Hz, 1 H, 4-*H*), 4.46 (ABq, *J* = 12.1 Hz, 2 H, OCH_2Ph), 4.35 (ABq, *J* = 16.8 Hz, 2 H, PhOCH_2), 4.22–4.11 (m, 2 H, Fmoc-CH_2), 4.04 (t, *J* = 7.8 Hz, 1 H, Fmoc-C*H*), 3.98 (*J* = 10.8, 8.0 Hz, 1 H, 2-*H*), 3.80 (dt, *J* = 10.1, 4.0 Hz, 1 H, 5-*H*), 3.56 (d, *J* = 4.0 Hz, 2 H, 6-*H*ab), 1.81 (s, 6 H, DMM-CH_3), 0.68 [s, 9 H, –SiC(CH_3)$_3$], –0.00 (s, 3 H, –SiCH_3), –0.10 (s, 3 H, –SiCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.5 (*C*O), 168.5 (*C*O), 157.7 (O*C*O), 154.4, 143.3, 143.3, 141.5, 141.4, 138.1, 129.6, 128.5, 128.1, 127.8, 127.7, 127.5, 127.4, 125.3, 121.9, 120.3, 120.2, 114.7 (Ar-*C*), 93.4 (*C*-1), 74.2 (*C*-4), 73.7 (O*C*H_2Ph), 73.1 (*C*-5), 72.1 (*C*-3), 70.5 (Fmoc-*C*H_2), 69.3 (*C*-6), 65.0 (PhO*C*H_2), 56.8 (*C*-2), 46.7 (Fmoc-*C*H), 25.5 [SiC(*C*H_3)$_3$], 17.8 [Si*C*(CH$_3$)$_3$], 8.9 (DMM-*C*H$_3$), –4.0, –5.4 (2× Si*C*H$_3$) ppm. ESI-HRMS (positive mode): calcd. for [$C_{48}H_{53}NO_{11}Si$+Na]$^+$ 870.3280; found 870.3248.

***tert*-Butyldimethylsilyl 6-*O*-Benzyl-2-deoxy-2-dimethylmaleimido-4-*O*-(9-fluorenylmethoxycarbonyl)-3-*O*-levulinoyl-β-D-glucopyranoside (4ca):** The residue obtained from **3c** after General Procedure A was purified by column chromatography (petroleum ether/ethyl acetate, 7:3) to afford **4ca** (1.21 g, 88%) as a foam. R_f = 0.35 (petroleum ether/ethyl acetate, 7:3). $[\alpha]_D^{22}$ = –2.6 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 7.6 Hz, 2 H, Ar-*H*), 7.56 (dd, *J* = 10.8, 7.5 Hz, 2 H, Ar-*H*), 7.39 (dt, *J* = 7.4, 3.4 Hz, 2 H, Ar-

H), 7.35–7.19 (m, 7 H, Ar-*H*), 5.83 (dd, *J* = 10.8, 9.2 Hz, 1 H, 3-*H*), 5.41 (d, *J* = 8.1 Hz, 1 H, 1-*H*), 4.97 (t, *J* = 9.6 Hz, 1 H, 4-*H*), 4.56 (ABq, *J* = 12.1 Hz, 2 H, OCH_2Ph), 4.38 (dd, *J* = 9.4, 6.9 Hz, 1 H, Fmoc-CH*H*), 4.23 (dd, *J* = 9.3, 7.6 Hz, 1 H, Fmoc-CH*H*), 4.19 (t, *J* = 7.5 Hz, 1 H, Fmoc-C*H*), 4.03 (dd, *J* = 10.9, 8.1 Hz, 1 H, 2-*H*), 3.88 (dt, *J* = 10.1, 4.0 Hz, 1 H, 5-*H*), 3.66 (d, *J* = 4.0 Hz, 2 H, 6-*H*a,b), 2.60–2.45 (m, 2 H, CH_2), 2.41–2.26 (m, 2 H, CH_2), 1.98 (s, 3 H, COCH_3), 1.95 (s, 6 H, DMM-CH_3), 0.77 [s, 9 H, SiC(CH_3)$_3$], 0.09 (s, 3 H, SiCH_3), –0.00 (s, 3 H, SiCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 205.9 (CH_3*C*O), 171.8 (*C*O), 154.4 (O*C*O), 143.5, 141.4, 141.4, 138.2, 137.5, 128.5, 128.1, 128.1, 127.8, 127.7, 127.4, 125.5, 125.4, 120.2, 120.2 (Ar-*C*), 93.5 (*C*-1), 74.3 (*C*-4), 73.71 (O*C*H_2Ph), 73.2 (*C*-5), 70.8 (*C*-3), 70.5 (Fmoc-CH_2), 69.3 (*C*-6), 56.6 (*C*-2), 46.7 (Fmoc-*C*H), 37.8 (CH_2), 29.6 (CH_2), 28.1 (CO*C*H_3), 25.5 [SiC(*C*H_3)$_3$], 17.8 [Si*C*(CH$_3$)$_3$], 8.9 (DMM-*C*H_3), –4.0, –5.4 (2× Si*C*H_3) ppm. ESI-HRMS (positive mode): calcd. for [$C_{45}H_{53}NO_{11}Si$+Na]$^+$ 834.3280; found 834.3255.

***tert*-Butyldimethylsilyl 3-*O*-Allyloxycarbonyl-6-*O*-benzyl-2-deoxy-2-dimethylmaleimido-4-*O*-(9-fluorenylmethoxycarbonyl)-β-D-glucopyranoside (4da):** The residue obtained from **3d** after General Procedure A was purified by column chromatography (petroleum ether/ethyl acetate, 9:1) to give **4da** (0.304 g, 88%) as a foam. R_f = 0.48 (petroleum ether/ethyl acetate, 8:2). $[\alpha]_D^{22}$ = –3.7 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 7.6 Hz, 2 H, Ar-*H*), 7.44 (dd, *J* = 12.0, 7.5 Hz, 2 H, Ar-*H*), 7.28 (d, *J* = 1.8 Hz, 2 H, Ar-*H*), 7.24–7.13 (m, 6 H, Ar-*H*), 7.11 (d, *J* = 9.9 Hz, 1 H, Ar-*H*), 5.62–5.51 (m, 1 H, *H*C=CH$_2$), 5.57 (dd, *J* = 10.9, 9.1 Hz, 1 H, 3-*H*), 5.30 (d, *J* = 8.0 Hz, 1 H, 1-*H*), 4.99 (dd, *J* = 17.3, 1.4 Hz, 1 H, HC=CH_2), 4.93 (t, *J* = 9.6 Hz, 1 H, 4-*H*), 4.90 (dd, *J* = 10.4, 1.2 Hz, 1 H, HC=CH_2), 4.44 (ABq, *J* = 12.1 Hz, 2 H, OCH_2Ph), 4.34 (dd, *J* = 13.2, 5.6, = Hz, 1 HCHCH*H*O–), 4.30–4.22 (m, 2 H, =CHCH*H*O–/Fmoc-CH*H*), 4.10 (dd, *J* = 9.9, 7.5 Hz, 1 H, Fmoc-C*H*H), 4.04 (t, *J* = 7.5 Hz, 1 H, Fmoc-C*H*), 4.03 (dd, *J* = 10.8, 8.0 Hz, 1 H, 2-*H*), 3.80 (dt, *J* = 9.9, 4.2 Hz, 1 H, 5-*H*), 3.57 (d, *J* = 4.2 Hz, 2 H, 6-*H*ab), 1.83 (s, 6 H, DMM-CH_3), 0.68 [s, 9 H, SiC(CH_3)$_3$], –0.00 (s, 3 H, SiCH_3), –0.09 (s, 3 H, SiCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.4, 154.3 (2× O*C*O), 143.4, 143.2, 141.3, 138.0, 137.49, 131.3 (H*C*=CH$_2$), 128.4, 128.0, 127.7, 127.6, 127.3, 127.3, 125.3, 125.3, 120.1, 120.1 (Ar-*C*), 118.5 (HC=*C*H$_2$), 93.3 (*C*-1), 74.7 (*C*-3), 74.3 (*C*-4), 73.6 (O*C*H$_2$Ph), 72.9 (*C*-5), 70.4 (Fmoc-*C*H$_2$), 69.3 (*C*-6), 68.7 (O*C*H$_2$CH=CH$_2$), 56.6 (*C*-2), 46.7 (Fmoc-*C*H), 25.4 [C(*C*H$_3$)$_3$], 17.7 [*C*(CH$_3$)$_3$], 8.8 (DMM-*C*H$_3$), –4.1, –5.5 (2× Si*C*H$_3$) ppm. ESI-MS (positive mode): calcd. for [$C_{44}H_{51}NO_{11}Si$+Na]$^+$ 820.3124; found 820.3091. $C_{44}H_{51}NO_{11}Si$ (797.96): calcd. C 66.23, H 6.44, N 1.76; found C 65.80, H 6.25, N 1.76.

***tert*-Butyldimethylsilyl 6-*O*-Benzyl-2-deoxy-2-dimethylmaleimido-4-*O*-phenoxyacetyl-β-D-glucopyranoside (5b) and *tert*-Butyldimethylsilyl 6-*O*-Benzyl-2-deoxy-2-dimethylmaleimido-3-*O*-phenoxyacetyl-β-D-glucopyranoside (3b):** The regioisomeric mixture obtained from **4ab** after General Procedure D was separated by column chromatography. Initial elution with petroleum ether/ethyl acetate (9:1) afforded **5b** (684 mg, 53%) as a viscous liquid. The physical and analytical data were found to be the same as given above. Further elution with petroleum ether/ethyl acetate (8.5:1.5) afforded **3b** (458 mg, 36%) as a viscous liquid. R_f = 0.55 (petroleum ether/ethyl acetate, 7:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24–7.11 (m, 7 H, Ar-*H*), 6.87 (t, *J* = 7.4 Hz, 1 H, Ar-*H*), 6.75 (d, *J* = 8.0 Hz, 2 H, Ar-*H*), 5.16 (d, *J* = 8.0 Hz, 1 H, 1-*H*), 4.98 (t, *J* = 9.5 Hz, 1 H, 4-*H*), 4.42 (ABq, *J* = 16.2 Hz, 2 H, PhOCH_2), 4.39 (ABq, *J* = 12.0 Hz, 2 H, OCH_2Ph), 4.29 (dd, *J* = 10.4, 9.5 Hz, 1 H, 3-*H*), 3.88 (dd, *J* = 11.0, 8.1 Hz, 1 H, 2-*H*), 3.67–3.60 (m, 1 H, 5-*H*), 3.48–3.38 (m, 2 H, 6-*H*ab), 3.01–2.68 (br. s, 1 H, O*H*), 1.81 (s, 6 H, DMM-CH_3), 0.69 [s, 9 H, SiC(CH_3)$_3$], –0.00 (s, 3 H, SiCH_3), –0.09 (s, 3 H, SiCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.1, 169.0 (2× *C*O), 157.7 (O*C*O), 138.0, 137.3, 129.6, 128.4, 127.8, 127.7, 121.8, 114.6 (Ar-*C*), 93.5 (*C*-1), 74.0 (*C*-4), 73.4 (O*C*H_2Ph), 72.9 (*C*-5), 69.8 (*C*-3), 69.4 (*C*-6), 65.1 (PhO*C*H$_2$), 59.0 (*C*-2), 25.4 [SiC-(*C*H$_3$)$_3$], 17.6 [Si*C*(CH$_3$)$_3$], 8.7 (DMM-C*H*$_3$), –4.1, –5.5 (2× Si*C*H$_3$) ppm. ESI-HRMS (positive mode): calcd. for [$C_{33}H_{43}NO_9Si$+Na]$^+$ 648.2599; found 648.2577.

***tert*-Butyldimethylsilyl 6-*O*-Benzyl-2-deoxy-2-dimethylmaleimido-3-*O*-phenoxyacetyl-β-D-glucopyranoside (3b) and *tert*-Butyldimethylsilyl 6-*O*-Benzyl-2-deoxy-2-dimethylmaleimido-4-*O*-phenoxyacetyl-β-D-glucopyranoside (5b):** The regioisomeric mixture obtained from **4ba** after General Procedure D was purified by column chromatography to give **3b/5b** = 60:40 (0.34 g, 85%). The physical and analytical data were found to be the same as given above.

***tert*-Butyldimethylsilyl 6-*O*-Benzyl-2-deoxy-2-dimethylmaleimido-3-*O*-phenoxyacetyl-β-D-glucopyranoside (3b) and *tert*-Butyldimethylsilyl 6-*O*-Benzyl-2-deoxy-2-dimethylmaleimido-4-*O*-phenoxyacetyl-β-D-glucopyranoside (5b):** The regioisomeric mixture obtained from pure **3b** after General Procedure D indicated **3b/5b** = 60:40 by ^{1}H NMR of the crude reaction mixture.

***tert*-Butyldimethylsilyl 6-*O*-Benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (6):** NaOMe/MeOH (1 M, 118 μL) was added to a solution of compound **4ab** or **4ba** (0.20 g, 0.236 mmol) in CH_2Cl_2/MeOH (24 mL, 4:1), and the resulting reaction mixture was stirred at room temp. for 2 h. The reaction mixture was neutralized with IRA-120 and filtered through a plug of cotton. All washings were concentrated under reduced pressure to give a residue, and the residue was purified by column chromatography to give **6** (0.11 g, 95%), as a viscous liquid. R_f = 0.33 (petroleum ether/ethyl acetate, 1:1). $[\alpha]_D^{22}$ = –21.43 (*c* = 0.7, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.18 (m, 5 H, Ar-*H*), 5.16 (d, *J* = 8.0 Hz, 1 H, 1-*H*), 4.54 (ABq, *J* = 12.1 Hz, 2 H, OCH_2Ph), 4.14 (dd, *J* = 10.6, 8.1 Hz, 1 H, 3-*H*), 3.77 (dd, *J* = 10.1, 8.1 Hz, 1 H, 2-*H*), 3.73–3.65 (m, 2 H, 6-*H*ab), 3.55–3.38 (m, 3 H, 4-*H*/5-*H*/O*H*), 3.16–2.93 (br. s, 1 H, O*H*), 1.87 (s, 6 H, DMM-CH_3), 0.70 [s, 9 H, SiC(CH_3)$_3$], –0.00 (s, 3 H, SiCH_3), –0.08 (s, 3 H, SiCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.3 (*C*O), 138.0, 137.4, 128.7, 128.0, 127.9 (Ar-*C*), 93.6 (*C*-1), 74.1, 74.0 (*C*-4/*C*-5), 73.9 (O*C*H$_2$Ph), 71.7 (*C*-3), 70.7 (*C*-6), 58.4 (*C*-2), 25.5 [SiC(*C*H$_3$)$_3$], 17.8 [Si*C*(CH$_3$)$_3$], 8.8 (DMM-*C*H$_3$), –4.0, –5.4 (2× Si*C*H$_3$) ppm. ESI-HRMS (positive mode): calcd. for [$C_{25}H_{37}NO_7Si$+Na]$^+$ 514.2232; found 514.2214.

***tert*-Butyldimethylsilyl 6-*O*-Benzyl-2-deoxy-2-dimethylmaleimido-4-*O*-levulinoyl-β-D-glucopyranoside (5c) and *tert*-Butyldimethylsilyl 6-*O*-Benzyl-2-deoxy-2-dimethylmaleimido-3-*O*-levulinoyl-β-D-glucopyranoside (3c):** The residue obtained from **4ac** after General Procedure D (with piperidine) was purified by column chromatography to give **5c/3c** (82:18, 53 mg, 86%) as a thick liquid. The residue obtained from **4ac** after General Procedure D (with triethylamine) was purified by column chromatography to give **5c** (0.052 g, 84%) as a viscous liquid. R_f = 0.24 (petroleum ether/ethyl acetate, 1:1). $[\alpha]_D^{22}$ = +3.1 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.23 (m, 5 H, Ar-*H*), 5.24 (d, *J* = 8.1 Hz, 1 H, 1-*H*), 4.89 (t, *J* = 9.4 Hz, 1 H, 4-*H*), 4.53 (ABq, *J* = 12.4 Hz, 2 H, OCH_2Ph), 4.36 (t, *J* = 9.4 Hz, 1 H, 3-*H*), 3.91 (dd, *J* = 10.7, 8.2 Hz, 1 H, 2-*H*), 3.76–3.67 (m, 1 H, 5-*H*), 3.62–3.52 (m, 2 H, 6-*H*ab), 2.97–2.83 (br. s, 1 H, O*H*), 2.82–2.62 (m, 2 H, CH_2), 2.54–2.32 (m, 2 H, CH_2), 2.12 (s, 3 H, COCH_3), 1.92 (s, 6 H, DMM-CH_3), 0.75 [s, 9 H, SiC(CH_3)$_3$], 0.06 (s, 3 H, SiCH_3), –0.03 (s, 3 H, SiCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 207.6 (*C*OCH$_3$), 172.9, 172.1 (2× *C*O), 138.4, 137.3, 130.0, 128.5, 127.8, 127.7 (Ar-*C*), 93.6 (*C*-1),

73.7 (*C*-4), 73.6 (O*C*H$_2$Ph), 73.5 (*C*-5), 70.3 (*C*-3), 69.6 (*C*-6), 58.7 (*C*-2), 38.5 (*C*H$_2$), 29.9 (CO*C*H$_3$), 28.3 (*C*H$_2$), 25.6 [SiC(*C*H$_3$)$_3$], 17.8 [Si*C*(CH$_3$)$_3$], 8.9 (DMM-*C*H$_3$), –4.0, –5.4 (2× Si*C*H$_3$) ppm. ESI-HRMS (positive mode): calcd. for [C$_{30}$H$_{43}$NO$_9$Si+Na]$^+$ 612.2599; found 612.2579.

***tert*-Butyldimethylsilyl 6-*O*-Benzyl-2-deoxy-2-dimethylmaleimido-3-*O*-(9-fluorenylmethoxycarbonyl)-β-D-glucopyranoside (3a):** Hydrazine acetate (11 mg, 126 μmol) was added to a solution of **4ac** (85 mg, 105 μmol) in CH$_2$Cl$_2$/MeOH (9:1; 1 mL), and the resulting reaction mixture was stirred at room temp. for 25 min. Volatiles were removed under reduced pressure to give a viscous mass, which was purified by column chromatography to give **3a** (61 mg, 82%) as a foam. The physical and analytical data were found to be the same as given above.

***tert*-Butyldimethylsilyl 6-*O*-Benzyl-2-deoxy-2-dimethylmaleimido-3-*O*-levulinoyl-β-D-glucopyranoside (3c) and *tert*-Butyldimethylsilyl 6-*O*-Benzyl-2-deoxy-2-dimethylmaleimido-4-*O*-levulinoyl-β-D-glucopyranoside (5c):** The residue obtained from **4ca** after General Procedure D (with piperidine) indicated **3c/5c** = 93:7 by ^{1}H NMR of the crude reaction mixture. General procedure D (with triethylamine) indicated **3c/5c** (> 99:1) by ^{1}H NMR spectroscopy of the crude reaction mixture.

***tert*-Butyldimethylsilyl 6-*O*-Benzyl-2-deoxy-2-dimethylmaleimido-4-*O*-(9-fluorenylmethoxycarbonyl)-β-D-glucopyranoside (5a):** Hydrazine acetate (4.1 mg, 44.3 μmol) was added to a solution of **4ca** (30 mg, 36.9 μmol) in CH$_2$Cl$_2$/MeOH (9:1; 1 mL), and the resulting reaction mixture was stirred at room temp. for 16 h. Volatiles were removed under reduced pressure and co-evaporated with toluene (1 mL × 3) to give a viscous mass of **5a**, which was vacuum-dried for 3 h and confirmed by NMR spectroscopy.

***tert*-Butyldimethylsilyl 4-*O*-Allyloxycarbonyl-6-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (5d):** The residue obtained after General Procedure D was purified by column chromatography to give **5d** (18 mg, 89%) as a viscous liquid. R_f = 0.35 (petroleum ether/ethyl acetate, 7:3). $[\alpha]_D^{22}$ = –2.4 (*c* = 1.0, CHCl$_3$). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.37–7.25 (m, 5 H, Ar-*H*), 5.94–5.80 (m, 1 H, H*C*=CH$_2$), 5.33 (dd, *J* = 17.4, 1.4 Hz, 1 H, HC=C*H*$_2$), 5.26 (dd, *J* = 10.4, 1.1 Hz, 1 H, HC=C*H*$_2$), 5.25 (d, *J* = 8.0 Hz, 1 H, 1-*H*), 4.77 (t, *J* = 9.4 Hz, 1 H, 4-*H*), 4.59 (m, 4 H, OC*H*$_2$Ph, OC*H*$_2$CH=), 4.41 (dd, *J* = 10.9, 9.1 Hz, 1 H, 3-*H*), 3.94 (dd, *J* = 11.0, 8.0 Hz, 1 H, 2-*H*), 3.75 (dt, *J* = 9.9, 4.0 Hz, 1 H, 5-*H*), 3.67 (d, *J* = 4.0 Hz, 2 H, 6-*H*ab), 2.52–2.06 (br. s, 1 H, O*H*), 1.95 (s, 6 H, DMM-C*H*$_3$), 0.78 [s, 9 H, SiC(C*H*$_3$)$_3$], 0.09 (s, 3 H, SiC*H*$_3$), 0.00 (s, 3 H, SiC*H*$_3$) ppm. ^{13}C NMR (101 MHz, CDCl$_3$): δ = 172.1 (*C*O), 155.2 (O*C*O), 138.2, 137.4, 131.3 (H*C*=CH$_2$), 128.7, 128.5, 127.9, 127.7, 127.7 (Ar-*C*), 119.5 (H*C*=CH$_2$), 93.6 (*C*-1), 77.1 (*C*-4), 73.7 (O*C*H$_2$Ph), 73.3 (*C*-5), 70.3 (*C*-3), 69.3, 69.2 (O*C*H$_2$CH = / *C*-6), 59.0 (*C*-2), 25.5 [SiC(*C*H$_3$)$_3$], 17.8 [Si*C*(CH$_3$)$_3$], 8.9 (DMM-*C*H$_3$), –4.0, –5.4 (2× Si*C*H$_3$) ppm. ESI-HRMS (positive mode): calcd. for [C$_{29}$H$_{41}$NO$_9$Si+Na]$^+$ 598.2443; found 598.2427.

***tert*-Butyldimethylsilyl 6-*O*-Benzyl-2-deoxy-2-dimethylmaleimido-3-*O*-(9-fluorenylmethyoxycarbonyl)-β-D-glucopyranoside (3a):** Dimedone (107 mg, 762 μmol), followed by Pd(PPh$_3$)$_4$ (1.6 mg, 10 μmol), were added under a counter flow of Ar to a solution of **4ad** (80 mg, 100 μmol) in degassed THF (2 mL), and the resulting reaction mixture was stirred under Ar for 90 min. The reaction mixture was diluted with ethyl acetate and concentrated under reduced pressure to give a residue. Column chromatographic (petroleum ether/ethyl acetate, 8:2) purification of the residue afforded **3a** (64 mg, 89%) as a foam.

***tert*-Butyldimethylsilyl 3-*O*-Allyloxycarbonyl-6-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (3d):** The residue obtained after General Procedure D was purified by column chromatography to give **5a** (160 mg, 88%) as a viscous liquid. The physical and analytical data were found to be the same as given above.

***tert*-Butyldimethylsilyl 6-*O*-Benzyl-2-deoxy-2-dimethylmaleimido-4-*O*-(9-fluorenylmethoxycarbonyl)-β-D-glucopyranoside (5a):** Dimedone (0.133 g, 0.952 mmol), followed by Pd(PPh$_3$)$_4$ (2.0 mg, 0.0125 mmol), were added under a counter flow of Ar to a solution of **4da** (100 mg, 0.125 mmol) in degassed THF (3 mL), and the resulting reaction mixture was stirred under Ar for 30 min. The reaction mixture was diluted with ethyl acetate and concentrated under reduced pressure to give a residue. Column chromatographic purification of the residue afforded **5a** (76 mg, 85%) as a viscous liquid. R_f = 0.39 (petroleum ether/ethyl acetate, 7:3). $[\alpha]_D^{22}$ = +0.86 (*c* = 0.7, CHCl$_3$). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.76 (d, *J* = 7.5 Hz, 2 H, Ar-*H*), 7.56 (dd, *J* = 6.6, 6.1 Hz, 2 H, Ar-*H*), 7.40 (t, *J* = 7.3 Hz, 2 H, Ar-*H*), 7.34–7.18 (m, 7 H, Ar-*H*), 5.26 (d, *J* = 8.0 Hz, 1 H, 1-*H*), 4.78 (t, *J* = 9.4 Hz, 1 H, 4-*H*), 4.56 (ABq, *J* = 12.2 Hz, 2 H, OC*H*$_2$Ph), 4.45 (t, *J* = 10.1 Hz, 1 H, 3-*H*), 4.39 (dd, *J* = 10.4, 7.4 Hz, 1 H, Fmoc-CH*H*), 4.33 (dd, *J* = 10.4, 7.3 Hz, 1 H, Fmoc-CH*H*), 4.19 (app. t, *J* = 7.3 Hz, 1 H, Fmoc-C*H*), 3.94 (dd, *J* = 10.9, 8.1 Hz, 1 H, 2-*H*), 3.78 (dt, *J* = 9.8, 4.0 Hz, 1 H, 5-*H*), 3.66 (d, *J* = 4.0 Hz, 2 H, 6-*H*ab), 2.50–2.31 (br. s, 1 H, O*H*), 1.95 (s, 6 H, DMM-C*H*$_3$), 0.78 [s, 9 H, SiC(C*H*$_3$)$_3$], 0.09 (s, 3 H, SiC*H*$_3$), –0.00 (s, 3 H, SiC*H*$_3$) ppm. ^{13}C NMR (101 MHz, CDCl$_3$): δ = 172.1 (*C*O), 155.4 (O*C*O), 143.4, 143.4, 141.5, 141.5, 138.2, 137.4, 128.5, 128.1, 127.7, 127.7, 127.4, 127.4, 125.4, 125.3, 120.3 (Ar-*C*), 93.6 (*C*-1), 76.9 (*C*-4), 73.7 (O*C*H$_2$Ph), 73.3 (*C*-5), 70.5 (*C*-3), 70.3 (Fmoc-*C*H$_2$), 69.4 (*C*-6), 59.1 (*C*-2), 46.8 (Fmoc-*C*H), 25.5 [SiC(*C*H$_3$)$_3$], 17.8 [Si*C*(CH$_3$)$_3$], 8.9 (DMM-*C*H$_3$), –4.0, –5.4 (2× Si*C*H$_3$) ppm. ESI-HRMS (positive mode): calcd. for [C$_{40}$H$_{47}$NO$_9$Si+Na]$^+$ 736.2812; found 736.2868.

***tert*-Butyldimethylsilyl 6-*O*-Benzyl-2-deoxy-2-dimethylmaleimido-4-*O*-(9-fluorenylmethoxycarbonyl)-β-D-glucopyranoside (5a) and *tert*-Butyldimethylsilyl 6-*O*-Benzyl-2-deoxy-2-dimethylmaleimido-3-*O*-(9-fluorenylmethoxycarbonyl)-β-D-glucopyranoside (3a):** *p*-TolSO$_2$Na (60 mg, 340 μmol) and Pd(PPh$_3$)$_4$ (5.4 mg, 34 μmol) were added under a counter flow of Ar to a solution of **4da** (274 mg, 340 μmol) in degassed and dry THF/MeOH (2:1; 3 mL). After 1 h, the pale yellow reaction mixture was diluted with ethyl acetate (5 mL), and volatiles were removed under reduced pressure to give a residue. Column chromatographic purification of the residue afforded **5a** (79 mg, 33%) and **3a** (65 mg, 27%) as foams.

***tert*-Butyldimethylsilyl 4,6-*O*-Benzylidene-2-deoxy-2-dimethylmaleimido-3-*O*-naphthylmethyl-β-D-glucopyranoside (2e):** TMSOTf (20 μL, 107 μmol) was added dropwise to a solution of compound **1** (5.22 g, 10.67 mmol) in diethyl ether (25 mL), and the mixture was stirred at room temp. for 10 min. NapOTCA (4.48 g, 14.94 mmol) in Et$_2$O (35 mL) was injected over a period of 30 min. Additional TMSOTf (20 μL, 107 μmol) was injected, and the mixture was stirred for 10 min. The reaction mixture was neutralized with triethylamine (1 mL) and concentrated under reduced pressure to give a residue. The residue was purified by column chromatography (petroleum ether/ethyl acetate, 9:1) to give **2e** (4.44 g, 66%) as a white solid. M.p. 148–149 °C; R_f = 0.66 (petroleum ether/ethyl acetate, 8:2). $[\alpha]_D^{22}$ = +59.6 (*c* = 1.0, CHCl$_3$). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.81–7.69 (m, 2 H, Ar-*H*), 7.66 (d, *J* = 8.4 Hz, 1 H, Ar-*H*), 7.57 (m, 3 H, Ar-*H*), 7.51–7.32 (m, 5 H, Ar-*H*), 7.28 (dd, *J* = 8.4, 1.4 Hz, 1 H, Ar-*H*), 5.62 (s, 1 H, C*H*Ph), 5.26 (d, *J* = 8.1 Hz, 1 H, 1-*H*), 5.00 (d, *J* = 12.8 Hz, 1 H, OC*H*Ar), 4.63 (d, *J* = 12.8 Hz, 1 H, OC*H*Ar), 4.40 (dd, *J* = 10.3, 9.0 Hz, 1 H, 3-*H*), 4.35 (dd, *J* = 10.4, 5.4 Hz, 1 H, 6-*H*a), 3.97 (dd, *J* = 10.4, 8.1 Hz, 1 H, 2-*H*), 3.84 (dd, *J* = 10.4, 9.8 Hz, 1 H, 6-*H*b), 3.79 (t, *J* = 9.0 Hz, 1 H, 4-

H), 3.62 (dt, *J* = 9.8, 4.9 Hz, 1 H, 5-*H*), 1.92–1.48 (s, 3 H, DMM-CH_3), 1.39–1.02 (s, 3 H, DMM-CH_3), 0.75 [s, 9 H, SiC(CH_3)$_3$], 0.04 (s, 3 H, SiCH_3), –0.08 (s, 3 H, SiCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.4 (*C*O), 137.6, 136.5, 136.1, 133.2, 132.9, 129.1, 128.3, 128.1, 127.9, 127.5, 127.3, 126.7, 126.2, 126.2, 126.0 (Ar-*C*), 101.4 (Ph*C*H), 94.0 (*C*-1), 83.0 (*C*-4), 75.5 (*C*-3), 74.5 (O*C*H_2Ar), 68.8 (*C*-6), 66.3 (*C*-5), 57.9 (*C*-2), 25.4 [SiC(*C*H_3)$_3$], 17.6 [Si*C*(CH$_3$)$_3$], 7.8 (DMM-*C*H_3), –4.2, –5.6 (2× Si*C*H_3) ppm. ESI-HRMS (positive mode): calcd. for [$C_{36}H_{43}NO_7Si$+Na]$^+$ 652.2701; found 652.2673.

***tert*-Butyldimethylsilyl 6-*O*-Benzyl-2-deoxy-2-dimethylmaleimido-3-*O*-naphthylmethyl-β-D-glucopyranoside (3e):** The residue obtained from **2e** after General Procedure C was purified by column chromatography (petroleum ether/ethyl acetate, 8:2) to afford **3e** (2.4 g, 89%) as a viscous syrup. R_f = 0.55 (petroleum ether/ethyl acetate, 7:3). $[\alpha]_D^{22}$ = +28.60 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (dd, *J* = 6.1, 2.9 Hz, 2 H, Ar-*H*), 7.76 (d, *J* = 8.4 Hz, 1 H, Ar-*H*), 7.68 (s, 1 H, Ar-*H*), 7.58–7.50 (m, 2 H, Ar-*H*), 7.48–7.36 (m, 6 H, Ar-*H*), 5.26 (d, *J* = 8.1 Hz, 1 H, 1-*H*), 5.11 (d, *J* = 12.8 Hz, 1 H, OC*H*Ar), 4.73 (d, *J* = 12.8 Hz, 1 H, OC*H*Ar), 4.70 (ABq, *J* = 11.8 Hz, 2 H, OCH_2Ph), 4.29 (dd, *J* = 10.8, 8.5 Hz, 1 H, 3-*H*), 3.96 (dd, *J* = 10.7, 8.1 Hz, 1 H, 2-*H*), 3.93–3.84 (m, 3 H, 4-*H*/6-*H*ab), 3.71 (dt, *J* = 9.7, 4.8 Hz, 1 H, 5-*H*), 3.36–3.23 (br. s, 1 H, O*H*), 1.82–1.55 (br. s, 3 H, DMM-CH_3), 1.45–1.15 (br. s, 3 H, DMM-CH_3), 0.80 [s, 9 H, SiC(CH_3)$_3$], 0.11 (s, 3 H, SiCH_3), –0.00 (s, 3 H, SiCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.1, 171.4 (2× *C*O), 137.9, 136.5, 133.3, 132.9, 129.2, 128.6, 128.4, 128.2, 128.1, 127.9, 127.8, 127.6, 126.9, 126.5, 126.3, 126.0, 125.4 (Ar-*C*), 93.6 (*C*-1), 80.0 (*C*-3), 74.9 (O*C*H_2Ph), 74.4 (*C*-4), 73.9 (s, *C*-5/O*C*H_2Ar), 70.9 (*C*-6), 57.5 (*C*-2), 25.4 [SiC(*C*H_3)$_3$], 17.7 [Si*C*(CH$_3$)$_3$], 8.4, 7.6 (DMM-*C*H_3), –4.1, –5.5 (2× Si*C*H_3) ppm. ESI-HRMS (positive mode): calcd. for [$C_{36}H_{45}NO_7Si$+Na]$^+$ 654.2858; found 654.2832.

***tert*-Butyldimethylsilyl 6-*O*-Benzyl-2-deoxy-2-dimethylmaleimido-4-*O*-(9-fluorenylmethoxycarbonyl)-3-*O*-naphthylmethyl-β-D-glucopyranoside (4ea):** The residue obtained from **3e** after General Procedure A was purified by column chromatography to give **4ea** (2.77 g, 84%) as a viscous oil. R_f = 0.50 (petroleum ether/ethyl acetate, 8:2). $[\alpha]_D^{22}$ = +52.8 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73–7.62 (m, 4 H, Ar-*H*), 7.60–7.45 (m, 4 H, Ar-*H*), 7.43–7.35 (m, 2 H, Ar-*H*), 7.34–7.14 (m, 10 H, Ar-*H*), 5.13 (d, *J* = 8.1 Hz, 1 H, 1-*H*), 4.95–4.87 (dd, *J* = 9.6, 9.4 Hz, 1 H, 4-*H*), 4.77 (d, *J* = 12.8 Hz, 1 H, OC*H*HAr), 4.50 (s, 2 H, OCH_2Ph), 4.40–4.26 (m, 4 H, Fmoc-CH_2/OCH*H*Ar/3-*H*), 4.09 (t, *J* = 7.0 Hz, 1 H, Fmoc-C*H*), 3.90 (dd, *J* = 10.8, 8.1 Hz, 1 H, 2-*H*), 3.75 (dt, *J* = 10.1, 4.0 Hz, 1 H, 5-*H*), 3.66–3.57 (m, 2 H, 6-*H*ab), 1.65–1.40 (br. s, 3 H, DMM-CH_3), 1.28–0.97 (br. s, 3 H, DMM-CH_3), 0.67 [s, 9 H, SiC(CH_3)$_3$], –0.00 (3 H, s SiCH_3), –0.13 (3 H, s SiCH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.5 (*C*O), 143.4, 143.2, 141.4, 141.4, 138.2, 136.5, 136.0, 133.1, 132.9, 128.4 (s), 128.1, 128.0, 128.0, 127.6 (s), 127.6, 127.5, 127.3, 127.2, 126.8, 126.5, 126.3, 126.1, 125.1, 125.1, 120.2 (Ar-*C*), 93.5 (*C*-1), 77.9 (*C*-3), 77.4 (*C*-4), 74.6 (O*C*H_2Ar), 73.6 (O*C*H_2Ph), 73.1 (*C*-5), 69.9 (s, Fmoc-*C*H_2/*C*-6), 57.6 (*C*-2), 46.8 (Fmoc-*C*H), 25.4 [SiC(*C*H_3)$_3$], 17.6 [Si*C*(CH$_3$)$_3$], 7.6 (DMM-*C*H_3), –4.1, –5.6 (2× Si*C*H_3) ppm. ESI-HRMS (positive mode): calcd. for [$C_{51}H_{55}NO_9Si$+Na]$^+$ 876.3538; found 876.3496.

***tert*-Butyldimethylsilyl 6-*O*-Benzyl-2-deoxy-2-dimethylmaleimido-4-*O*-(9-fluorenylmethoxycarbonyl)-β-D-glucopyranoside (5a):** DDQ (81 mg, 357 μmol) was added to a solution of **4ea** (100 mg, 119 μmol) in CH_2Cl_2/MeOH (4:1; 5 mL), and the resulting reaction mixture was stirred at room temp. for 2 h. The reaction mixture was diluted by addition of satd. $NaHCO_3$ (3 mL), and volatiles were removed under reduced pressure. The resulting solution was extracted with CH_2Cl_2 (5 mL × 3) and worked up. The residue was purified by column chromatography to give **5a** (65 mg, 78%) as a foam. The physical and analytical data were found to be the same as given above.

***tert*-Butyldimethylsilyl 6-*O*-Benzyl-2-deoxy-2-dimethylmaleimido-3-*O*-naphthylmethyl-β-D-glucopyranoside (3e):** The residue obtained after General Procedure D gave **2e** (75 mg, 86%) as a white solid. The physical and analytical data were the same as given above.

Supporting Information (see footnote on the first page of this article): NMR spectra for all new compounds.

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