The Dimethylmaleoyl Group as Amino Protective Group – Application to the Synthesis of Glucosamine-Containing Oligosaccharides

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Glucosamine was readily transformed into *N*-dimethylmaleoyl (DMM) protected derivative **1** which furnished trichloroacetimidate **4** as glycosyl donor. Reaction with various acceptors (**5a–g**) in the presence of TMSOTf as the catalyst afforded the corresponding β-glycosides **6a–g** generally in high yields. Cleavage of the DMM group was readily accomplished by treatment with aqueous NaOH and then with HCl (pH 5). Starting from **1** also DMM group containing glycosyl acceptors **9** and **14a–c** were synthesized. They furnished with trichloroacetimidates **12** and **4** as glycosyl donors β(1–4)- and β(1–3)-linked disaccharides **13** and **15a–c**, respectively. From **18** as galactosyl donor and **14a** as acceptor β(1–3)-linked disaccharide **19** was obtained in high yield, which is a versatile building block for the important Galβ(1–3)GlcNAc unit. **19** was transformed into trichloroacetimidate **21**; glycosylation with **5e** as acceptor gave trisaccharide **22** which furnished on partial deprotection Galβ(1–3)GlcNAcβ(1–4)Glc derivative **24**. Thus, the wide applicability of DMM as amino protective group in oligosaccharide synthesis is exhibited.

An important constituent of various glyconjugates is D-glucosamine which is mainly found as an *N*-acetyl derivative in β-glycosidic linkage[1]. Glycoside bond formation with donors derived from *N*-acetylglucosamine (GlcNAc) occurs generally by neighboring group participation to give a 1,3-oxazolinium intermediate[2], which exhibits only weak glycosyl donor properties. Therefore, various alternatives have been investigated having, for instance, a phthalimido[1][2], a tetrachlorophthalimido[3][4] a dithiasuccinylimido[5], an *N,N*-diacetylamino[6], a trichloroacetylamino[7], or a trichloroethoxycarbonylamino group[8][9] in the 2-position, thus supporting formation of the β anomer. Due to strong electron withdrawing character of the *N* substituents, these glucosamine derivatives also exhibit increased glycosyl donor properties. Also the 2-azido group has gained wide use in this regard[1][2][10][11][12]. However, all these groups also exhibit some disadvantages which have been recently discussed in detail[3][9]. Therefore, we investigated the dimethylmaleoyl (DMM) group[13] which to the best of our knowledge has not been used for the protection of amino groups in sugars[14]. The reported ease of introduction and also ease of cleavage under weakly aqueous basic and then acidic conditions[13] made it an interesting protective group for aminosugars because all the other beneficial properties of electron-withdrawing protective groups should be also found: high glycosyl donor properties, neighboring group participation to enforce β linkage, stability to acid and non nucleophilic bases and thus compatibility with an array of different functional groups and protective groups. Additionally, the cyclic DMM group is symmetric, thus easing structural assignments by NMR also in the case of hindered rotation of the DMM group. Our studies concentrated on glucosamine, which was investigated as *N*-DMM-protected glycosyl donor and glycosyl acceptor in situations typically found in oligosaccharide synthesis[15].

N-DMM-Protected Glucosamine as Glycosyl Donor

Treatment of glucosamine hydrochloride first with base and then with dimethylmaleic anhydride (DMMA)[16] led to *N*-acylation; upon treatment with acetic anhydride in pyridine *N*-DMM-protected tetra-*O*-acetylglucosamine **1** (Scheme 1) was obtained as starting material for the following investigations; only the β isomer was found.

The 1-*O*-acetyl group could be readily removed by treatment with hydrazinium acetate to afford compound **2**. Reaction with *tert*-butyldimethylsilyl chloride (TBDMS-Cl) in the presence of imidazole gave exclusively β-1-*O*-TBDMS protected compound **3**. Reaction of **2** with trichloroacetonitrile in the presence of 1,8-diaza[5.4.0]bicycloundec-7-ene (DBU) afforded β-trichloroacetimidate **4**, which was used as glycosyl donor with various acceptors (**5a−g**)[17]. Under standard conditions, i.e. activation of **4** with 0.01 equivalents of trimethylsilyl trifluoromethanesulfonate (TMSOTf) as the catalyst, generally high yields of glycosides **6a−g** were obtained (Table 1); in all cases only the β products were found; even the low reactive 4-hydroxy group of glu-

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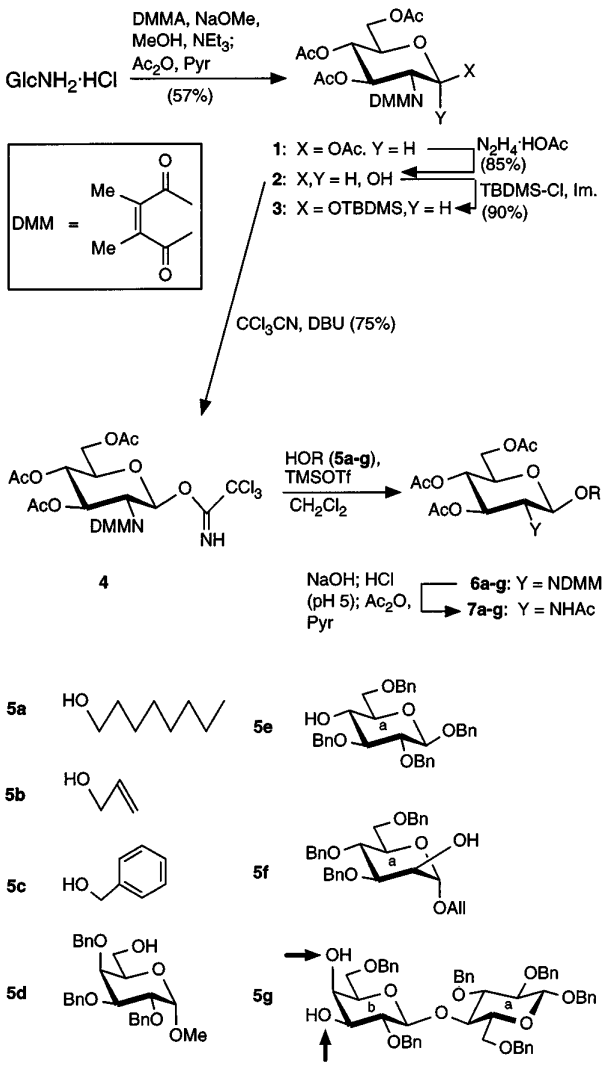
Scheme 1



cose derivative **5e** and the axial 2-hydroxy group of mannose derivative **5f** gave satisfactory yields. 3b,4b-*O*-Unprotected lactose derivative **5g** as acceptor led to particularly high glycosylation yields and, unexpectedly, 4b attack was preferentially observed [**6g**-(3b)/**6g**-(4b) = 1:2].

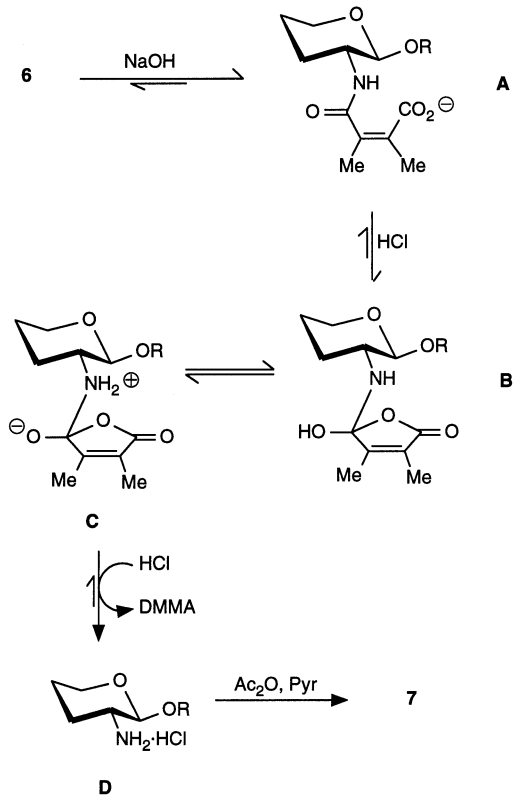
Table 1. Results of the transformation of **4** and **5a–g** into **6a–g** and **6a–g** into **7a–g**

5 HOR	**6** Yield [%]	**7** Yield [%]
a	88[a]	40[c], 64[d]
b	85[a]	23[c]
c	88[a]	71[c]
d	77[a]	65[c]
e	78[a]	65[c], 97[d], 89[e]
f	53[a]	68[c]
g	94[b] (**3b**/**4b**, 1:2)	74[c], 74[d]

[a] Reaction at room temp. – [b] –30°C. – [c] Method A. – [d] Method B. – [e] Method C.

Transformation of the *N*-DMM protected compounds **6a–g** into the corresponding *N*-acetyl derivatives **7a–g** could be carried out under the above described standard conditions: treatment with sodium hydroxide and then with hydrochloric acid at pH = 5 and finally acetylation with acetic anhydride in pyridine led to the desired products (Table 1, Method A)[18][19]. Only the yield for allyl glycoside **7b** was low; this could be due to interaction of the neighboring allyl group with the DMM cleavage process which is outlined in Scheme 2[13]: hydroxide reaction leads to ring-open intermediate **A** which in the presence of acid is in equilibrium with butenolide **B**; protonation of the basic nitrogen atom of the amide acetal moiety (→ **C**) leads to generation of DMMA and free amine hydrochloride **D** which is then transformed into the *N*-acetyl derivative.

Scheme 2



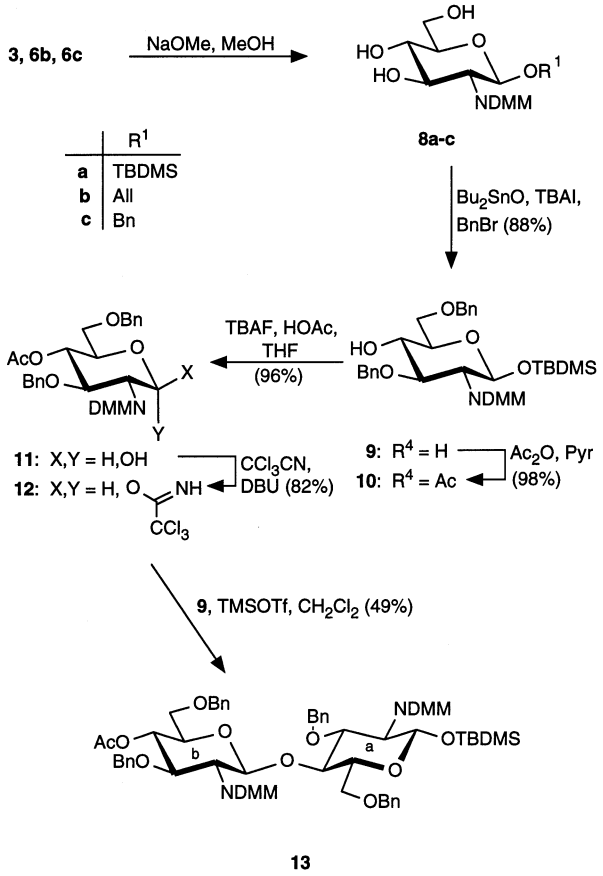
Addition of acetyl chloride under Schotten-Baumann conditions to **A** should shift the equilibrating reactions to the desired products. This was investigated for **6a, 6e** and **6g**-(4b) (Method B) and at least for the **6a**→**7a** and **6e**→**7e** transformation the yield could be increased. Also addition of amine should scavenge liberated DMMA (Method C) and thus increase the DMM deprotection yield; this could be shown for the **6e**→**7e** transformation.

N-DMM-Protected Glucosamine as Glycosyl Acceptor

Compounds **3**, **6b**, and **6c** could be readily transformed into glycosyl acceptors. Treatment with NaOMe in MeOH gave 3,4,6-*O*-unprotected derivatives **8a, 8b**, and **8c** (Scheme 3a). Treatment of **8a** with dibutyltin oxide and then with benzyl bromide in the presence of tetrabutylammonium

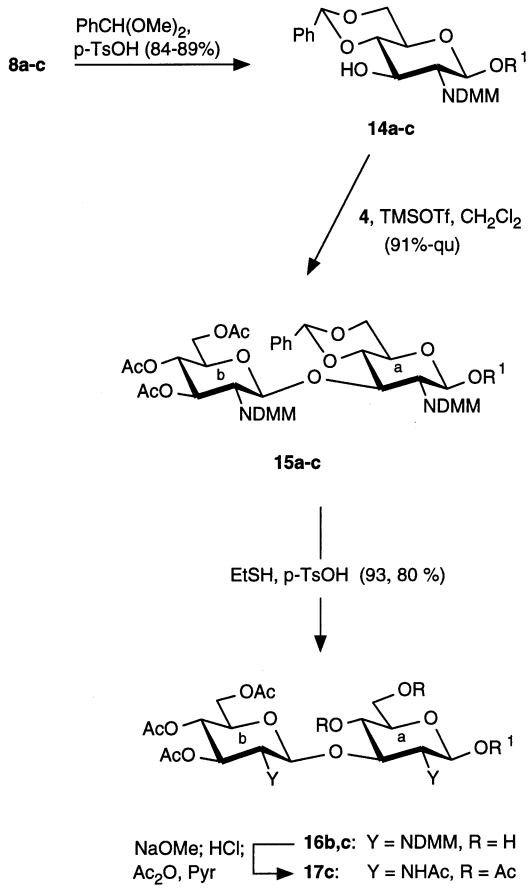
iodide (TBAI)[20] furnished highly regioselectively 3,6-di-*O*-benzyl derivative **9,** which is a very useful glycosyl acceptor. Reaction of **9** with acetic anhydride/pyridine afforded 4-*O*-acetyl derivative **10**; cleavage of the TBDMS group with TBAF in the presence of acetic acid gave 1-*O*-unprotected derivative **11,** which on treatment with CCl_3CN in the presence of DBU afforded trichloroacetimidate **12** (α/β = 1:3) a versatile glycosyl donor for β(1−4)connections with a glucosamine residue. Thus, reaction of acceptor **9** with donor **12** in the presence of TMSOTf as catalyst afforded β(1−4)-connected disaccharide **13** which was structurally assigned by NMR (^{1}H NMR: $J_{1a,2a}$ = 8.2 Hz; $J_{1b,2b}$ = 8.4 Hz).

Scheme 3a



Reaction of **8a−c** with benzaldehyde dimethylacetal in the presence of *p*-toluenesulfonic acid (*p*-TsOH) as catalyst afforded regioselectively 4,6-*O*-benzylidene derivatives **14a−c** as 3-*O*-unprotected glycosyl acceptors. Their reaction with glycosyl donor **4** furnished β(1−3)-linked disaccharides **15a−c** in very high yields. The benzylidene group in **15b,c** was removed on treatment with *p*-TsOH in the presence of ethanethiol as the nucleophile[21], thus affording 4a,6a-*O*-unprotected derivatives **16b,c**, which are again useful glycosyl acceptors for the synthesis of branched oligosaccharides. Removal of the two DMM groups, for instance in **16c**, could be carried out under standard conditions affording after treatment with acetic anhydride/pyridine GlcNAcβ(1−3)GlcNAc derivative **17c** (^{1}H NMR: $J_{1a,2a}$ = 8.1; $J_{1b,2b}$ = 8.2 Hz).

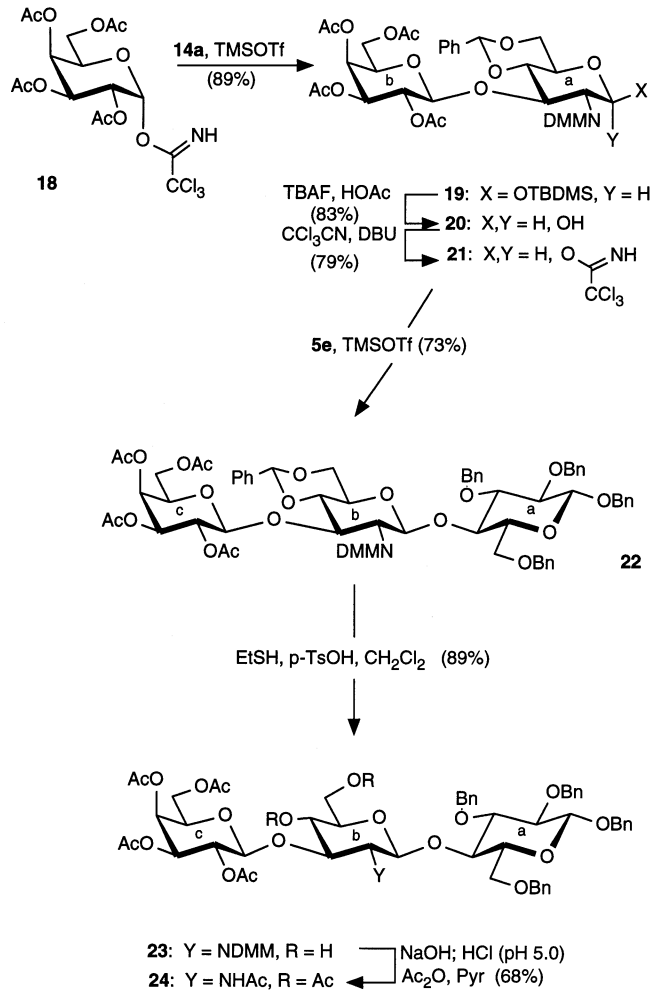
Scheme 3b



Also the frequently occurring Galβ(1−3)GlcNAc disaccharide moiety could be readily synthesized with the help of known galactosyl donor **18** (Scheme 4)[22]; reaction with **14a** as acceptor gave in the presence of TMSOTf as catalyst the desired β(1−3)-linked disaccharide **19** in very good yield (^{1}H NMR: $J_{1a,2a}$ = 8.1, $J_{1b,2b}$ = 8.0 Hz). 1-*O*-Desilylation with TBAF in the presence of acetic acid led to 1-*O*-unprotected compound **20**, which on treatment with CCl_3CN/DBU furnished trichloroacetimidate **21** (α/β = 1:4). Reaction of **21** with 4-*O*-unprotected glucose derivative **5e** as acceptor in the presence of TMSOTf as catalyst gave exclusively β(1−4)-linkage, affording trisaccharide **22** (^{1}H NMR: $J_{1a,2a}$ = 8.5; $J_{1b,2b}$ = 7.7; $J_{1c,2c}$ = 7.9 Hz). Debenzylidenation with *p*-TsOH as catalyst in the presence of ethanethiol as nucleophile[21] gave 4b,6b-*O*-unprotected derivative **23**; then the DMM group was replaced by the *N*-acetyl group under standard conditions to afford trisaccharide **24** in good yield.

In conclusion, DMM-protected glucosamine could be transformed into various glycosyl donors and glycosyl acceptors, thus withstanding different acidic and basic conditions. Glycosylation reactions with DMM-protected donors and acceptors furnished in the presence of TMSOTf as the catalyst the desired glycosidic bonds generally in high yields. Also cleavage of the DMM group under standard conditions worked reliably and in good yields. Hence, the DMM group is a very useful alternative to the above men-

Scheme 4



tioned amino protective groups in oligosaccharide synthesis.

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Experimental Section

Solvents were purified in the usual way. Melting points are uncorrected. − TLC was performed on plastic plates Silica Gel 60 F_{254} (E. Merck, layer thickness 0.2 mm). The detection was achieved by treatment with a solution of 20 g ammonium molybdate and 0.4 g cerium(IV) sulfate in 400 ml 10% H_2SO_4 or with 15% H_2SO_4, and heating at 150°C. − Flash chromatography was carried out on silica gel (Baker, 30−60 μm). − Medium pressure liquid chromatography (MPLC): LiChroprep Si 60 (Merck; ∅ 15−25 μm), detection by differential refractometer. − Optical rotations were determined at room temp. with a Perkin-Elmer 241/MC polarimeter (1 dm cell). − NMR spectra were recorded with Bruker AC 250 and 600 DRX instruments, using tetramethylsilane as internal standard. − MS spectra were recorded with MALDI-Kompakt (Kratos), EI and FAB with Finnigen MAT 312/AMD.

1,3,4,6-Tetra-O-acetyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (**1**): D-Glucosamine hydrochloride (3.0 g, 13.91 mmol) was added to a sodium ethoxide solution (1.0 M, 13.92 ml, 13.92 mmol). After 10 min, the mixture was treated with dimethylmaleic anhydride (0.88 g, 6.97 mmol) and stirred for 20 min. Triethylamine (1.4 ml, 13.91 mmol) was added and the reaction mixture was again treated with dimethylmaleic anhydride (0.88 g, 6.97 mmol). The reaction mixture was warmed to 60°C with stirring for 1.5 h then dried well in vacuo. The residue from the last step was treated with pyridine (28 ml), acetic anhydride (14 ml) and stirred at room temp. After 20 h the reaction mixture was evaporated and the residue poured on ice, extracted with chloroform (3 × 100 ml), washed with aqueous hydrochloric acid (3%, 100 ml), saturated sodium bicarbonate solution (100 ml), distilled water (3 × 100 ml), dried by anhydrous sodium sulfate, and coevaporated with toluene in vacuo. The residue was purified by flash chromatography (*n*-hexane/ethyl acetate, 1:1) to yield **1** (3.64 g, 57%) as a white powder. − TLC (*n*-hexane/ethyl acetate, 1:1): R_f = 0.39; m.p. 109−110°C. − $[\alpha]_D$ = +40 (*c* = 1.0, chloroform). − ^{1}H NMR (250 MHz , $CDCl_3$): δ = 2.10 , 2.05 , 2.03, 1.96, 1.92 (5 s, 18 H, 2 CH_3, 4 $COCH_3$), 3.95 (2 m, 1 H, 5-H), 4.11 (dd, J_{gem} = 12.5, $J_{5,6}$ = 2.5 Hz, 1 H, 6-H), 4.20 (dd, $J_{1,2}$ = 8.9, $J_{2,3}$ = 10.4 Hz,1 H, 2-H), 4.34 (dd, J_{gem} = 12.5, $J_{5,6'}$ = 4.4 Hz, 1 H, 6′-H), 5.10 (dd, $J_{3,4}$ = 9.2, $J_{4,5}$ = 10.0 Hz, 1 H, 4-H), 5.70 (dd, $J_{2,3}$ = 10.4, $J_{3,4}$ = 9.2 Hz, 1 H, 3-H), 6.35 (d, $J_{1,2}$ = 8.9 Hz, 1 H, 1-H). − MALDI-MS (positive mode, DHB/THF matrix); *m/z*: 478 [MNa^+], 494 [MK^+]. − $C_{20}H_{25}NO_{11}$ (455.4): calcd. C 52.74, H 5.53, N, 3.07; found C 52.26, H 5.52, N 2.86.

3,4,6-Tri-O-acetyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranose (**2**): A solution of **1** (3.2 g, 7 mmol) and hydrazinum acetate (0.74 g, 8.0 mmol) in DMF (11 ml) was stirred at room temp. After 1 h the reaction mixture was diluted with ethyl acetate (40 ml) and washed with ice-cold saturated sodium bicarbonate solution (5 × 100 ml). The organic layer was separated, dried by anhydrous magnesium sulfate, filtered and coevaporated with toluene in vacuo. The residue was purified by flash chromatography (*n*-hexane/ethyl acetate, 1:1) to yield **2** (2.47 g, 85%) as white crystals. − TLC (*n*-hexane/ethyl acetate, 1:1): R_f = 0.2; m.p. = 140−141°C. − $[\alpha]_D$ = +54.3 (*c* = 1.0, chloroform). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.08, 2.00, 1.93, 1.90 (4 s, 15 H, 2 CH_3, 3 $COCH_3$), 3.23 (d, $J_{1,OH}$ = 7.4 Hz , 1 H, OH), 3.85 (2 m, 1 H, 5-H), 3.99 (dd, $J_{1,2}$ = 8.3, $J_{2,3}$ = 10.7 Hz, 1 H, 2-H), 4.14 (dd, J_{gem} = 12.3, $J_{5,6}$ = 2.3 Hz , 1 H, 6-H), 4.25 (dd, J_{gem} = 12.3, $J_{5,6'}$ = 4.7 Hz, 1 H, 6′-H), 5.09 (dd, $J_{3,4}$ = 9.1, $J_{4,5}$ = 10.1 Hz, 1 H, 4-H), 5.44 (dd, $J_{1,2}$ = 8.3, $J_{1,OH}$ = 7.4 Hz, 1 H, 1-H), 5.66 (dd, $J_{2,3}$ = 10.7, $J_{3,4}$ = 9.1 Hz, 1 H, 3-H). − MALDI-MS (positive mode-DHB/Matrix); *m/z*: 436 [MNa^+], 452 [MK^+]. − $C_{18}H_{23}NO_{10}$ (413.4): calcd. C 52.29, H 5.60, N 3.38; found C 52.92, H 5.80, N 3.43.

tert-Butyldimethylsilyl 3,4,6-Tri-O-acetyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (**3**): To a solution of **2** (1.04 g, 3.38 mmol) and imidazole (0.46 g, 6.76 mmol) in dry dichloromethane (10 ml) was added *tert*-butylchlorodimethylsilane (0.61 g, 4.0 mmol). After stirring at room temp for 1 h the reaction mixture was diluted with water (100 ml), then extracted with dichloromethane (3 × 30 ml), dried with anhydrous magnesium sulfate, and evaporated in vacuo. The residue was purified by flash chromatography (*n*-hexane/ethyl acetate, 2:1) to yield **3** (1.18 g, 90%) as white crystals. − TLC (petroleum ether/ethyl acetate, 1:1): R_f = 0.6; m.p. 126−127°C. − $[\alpha]_D$ = +9.6 (*c* = 1.0, chloroform). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = −0.02 (s, 3 H, $SiCH_3$), 0.03 (s, 3 H, $SiCH_3$), 0.74 [s, 9 H, $SiC(CH_3)_3$], 1.90, 1.91, 1.99, 2.05 (4 s, 15 H, 2 CH_3, 3 CH_3CO), 3.78 (m, 1 H, 5-H), 3.98 (dd, $J_{1,2}$ = 8.1, $J_{2,3}$ = 10.8 Hz, 1 H, 2-H), 4.10 (dd, J_{gem} = 12.1, $J_{5,6}$ = 2.5 Hz, 1 H, 6-H), 4.20 (dd, J_{gem} = 12.1, $J_{5,6'}$ = 5.8 Hz, 1 H, 6′-H), 5.03 (dd, $J_{3,4}$ = 9.0, $J_{4,5}$ = 10.2 Hz, 1 H, 4-H), 5.35 (d, $J_{1,2}$ = 8.1 Hz, 1 H,

1-H), 5.64 (dd, $J_{2,3}$ = 10.8, $J_{3,4}$ = 9.0 Hz, 1 H, 3-H). − MALDI-MS (positive mode, DHB/THF matrix); *m/z*: 549 [MNa^+], 566 [MK^+]. − $C_{24}H_{37}NO_{10}Si$ (527.6): calcd. C 54.62, H 7.06, N 2.65; found C 54.58, H 6.77, N 2.65.

O-[3,4,6-Tri-O-acetyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl] Trichloroacetimidate (**4**): A mixture of **2** (1.0 g, 2.4 mmol), trichloroacetonitrile (1.48 ml, 14.5 mmol), and 1,8-diazabicyclo[5,4,0]undec-7-ene (0.05 ml, 0.3 mmol) in dry dichloromethane (7 ml) was stirred at room temp. for 5 h and then concentrated in vacuo. The residue was purified by flash chromatography (*n*-hexane/ethyl acetate, 1:1 + 1% triethylamine) to yield **4** (0.98 g, 75%) as a fluorescent foam. − TLC (*n*-hexane/ethyl acetate, 1:1): R_f = 0.4. − $[\alpha]_D$ = +31.5 (*c* = 1.0, chloroform). − ^{1}H NMR (250 MHz , $CDCl_3$): δ = 1.92, 1.94, 2.04, 2.11 (4 s, 15 H, 2 CH_3, 3 $COCH_3$), 4.00 (2 m, 1 H, 5-H), 4.17 (dd, J_{gem} = 12.5, $J_{5,6}$ = 2.2 Hz, 1 H, 6-H), 4.43−4.33 (m, 2 H, 2-H, 6′-H), 5.22 (dd, $J_{3,4}$ = 9.1, $J_{4,5}$ = 10.1 Hz, 1 H, 4-H), 5.74 (dd, $J_{2,3}$ = 10.1, $J_{3,4}$ = 9.1 Hz, 1 H, 3-H), 6.46 (d, $J_{1,2}$ = 8.9 Hz, 1 H, 1-H), 8.67 (s, 1 H, NH). − FAB-MS (positive mode, NBOH/NaI-matrix); *m/z*: 579/581/583 [MNa^+], 396 [556 − OC(=NH)CCl_3^+]. − $C_{20}H_{23}Cl_3N_2O_{10}$ (557.8): calcd. C 43.06, H 4.15, N 5.02; found C 42.59, H 4.20, N 4.88.

General Procedure for the Synthesis of Compounds **6a−g**: A solution of **4** (0.15 g, 0.258 mmol) and **5a−g**[17] (0.21 mmol) in dry dichloromethane (1 ml) was stirred under nitrogen for 10 min. TMSOTf (0.01 M in dichloromethane, 0.27 ml) was added dropwise. After 3 h the reaction mixture was neutralized with triethylamine and dried in vacuo.

n-Octyl 3,4,6-Tri-O-acetyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (**6a**): The residue was purified by flash chromatography (*n*-hexane/ethyl acetate, 2:1) to yield **6a** (0.097 g, 88%) as white and fine crystals. − TLC (*n*-hexane/ethyl acetate, 2:1): R_f = 0.3, m.p. 137−138°C. − $[\alpha]_D$ = +2.0 (*c* = 1.0, chloroform). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.88 (dd, *J* = 6.5, *J* = 7.0 Hz, 3 H, CH_3), 1.19−1.47 [m, 10 H, -$(CH_2)_5$-], 1.43−1.50 (m, 2 H, CH_2), 1.93, 1.96, 2.03, 2.10 (4 s, 15 H, 2 CH_3, 3 $COCH_3$), 3.43 (m, 1 H, 5-H), 3.77−3.84 (m, 2 H, -OCH_2-), 4.07 (dd, $J_{1,2}$ = 8.5, $J_{2,3}$ = 10.7 Hz, 1 H, 2-H), 4.14 (dd, J_{gem} = 12.3, $J_{5,6}$ = 2.4 Hz, 1 H, 6-H), 4.31 (dd, J_{gem} = 12.3, $J_{5,6'}$ = 4.6 Hz, 1 H, 6′-H), 5.12 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.1 Hz, 1 H, 4-H), 5.2 (d, $J_{1,2}$ = 8.5 Hz, 1 H, 1-H), 5.62 (dd, $J_{2,3}$ = 10.7, $J_{3,4}$ = 9.1 Hz, 1 H, 3-H). − EI-MS (positive mode); *m/z*: 525 [M^+], 43 [CH_3CO^+]. − $C_{26}H_{39}NO_{10}$ (525.6): calcd. C 59.41, H 7.47, N 2.66; found C 59.54, H 7.58, N 2.97.

Allyl 3,4,6-Tri-O-acetyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (**6b**)**:** The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 1.5:1) to yield **6b** (0.8 g, 85%) as a white foam. − TLC (petroleum ether/ethyl acetate, 1.5:1): R_f = 0.26. − $[\alpha]_D$ = +3.8 (*c* = 0.65, chloroform). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.92, 1.95, 2.02, 2.10 (4 s, 15 H, 2 CH_3, 3 CH_3CO), 3.79 (m, 1 H, 5-H), 4.00−4.34 (m, 5 H, 2-H, 6-H, 6′-H, $CH_2CH{=}CH_2$), 5.08−5.21 (m, 3 H, $CH_2CH{=}CH_2$, 4-H), 5.25 (d, $J_{1,2}$ = 8.5 Hz, 1 H, 1-H), 5.62 (dd, $J_{2,3}$ = 10.6, $J_{3,4}$ = 9.1 Hz, 1 H, 3-H), 5.75 (m, 1 H, $CH_2CH{=}CH_2$). − MALDI-MS (positive mode, DHB/THF matrix); *m/z*: 478 [MNa^+], 494 [MK^+]. − $C_{21}H_{27}NO_{10}$ (453.4): calcd. C 55.62, H 6.00, N 3.08; found C 55.69, H 6.03, N 2.57.

Benzyl 3,4,6-Tri-O-acetyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (**6c**): The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 3:1) to yield **6c** (0.098 g, 88%) as a white foam. − TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.1. − $[\alpha]_D$ = −44.6 (*c* = 0.15, chloroform). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.86, 1.88, 1.99, 2.09 (4 s, 15 H, 2 CH_3, 3 CH_3CO), 3.76, 3.80 (2 m, 1 H, 5-H), 4.06−4.17 (m, 2 H, 2-H, 6-H), 4.29 (dd, J_{gem} = 10.3, $J_{5,6'}$ = 4.6 Hz, 1 H, 6′-H), 4.49 (d, J_{gem} = 12.2 Hz, 1 H, C*H*HPh), 4.83 (d, J_{gem} = 12.2 Hz, 1 H, CH*H*Ph), 5.10 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.1 Hz, 1 H, 4-H), 5.20 (d, $J_{1,2}$ = 8.5 Hz, 1 H, 1-H), 5.59 (dd, $J_{2,3}$ = 10.6, $J_{3,4}$ = 9.1 Hz, 1 H, 3-H), 7.14, 7.22 (2 m, 5 H, Ph). − MALDI-MS (positive mode, DHB/THF matrix); *m/z*: 526 [MNa^+]. − $C_{25}H_{29}NO_{10}$ (503.5): calcd. C 59.63, H 5.80, N 2.78; found C 58.96, H 5.91, N 2.62.

Methyl O-(3,4,6-Tri-O-acetyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-α-D-galactopyranoside (**6d**): The residue was purified by flash chromatography (*n*-pentane/ethyl acetate, 2:1) to give **6d** (0.137 g, 77%) as a colorless oil. − TLC (petroleum ether/ethyl acetate, 2:1): R_f = 0.37. − $[\alpha]_D$ = +10.8 (*c* = 0.44, chloroform). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.88, 1.98, 2.02 (3 s, 15 H, 2 CH_3, 3 $COCH_3$), 3.20 (s, 3 H, -OCH_3), 3.49 (dd, J_{gem} = 8.9, $J_{5,6}$ = 6.2 Hz, 1 H, 6a-H), 3.72 (m, 1 H, 5a-H), 3.74 (m, 2 H, 4a-H, 6′a-H), 3.75 (m, 1 H, 5b-H), 3.83 (dd, $J_{2,3}$ = 10.0, $J_{3,4}$ = 3.9 Hz, 1 H, 3a-H), 3.94 (dd, $J_{1,2}$ = 3.9 Hz, $J_{2,3}$ = 10.0, 1 H, 2a-H), 4.02 (dd, $J_{1,2}$ = 8.5, $J_{2,3}$ = 10.6 Hz, 1 H, 2b-H), 4.05 (dd, J_{gem} = 12.3, $J_{5,6}$ = 2.0 Hz, 1 H, 6b-H), 4.26 (dd, J_{gem} = 12.3, $J_{5,6'}$ = 4.3, 1 H, 6′b-H), 4.53 (d, $J_{1,2}$ = 3.9 Hz, 1 H, 1a-H), 4.54, 4.88 (2 d, J_{gem} = 11.2 Hz, 2 H, CH_2Ph), 4.63, 4.78 (2 d, J_{gem} = 11.2 Hz, 2 H, CH_2Ph), 4.68, 4.86 (2 d, J_{gem} = 11.8 Hz, 2 H, CH_2Ph), 5.07 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.2 Hz, 1 H, 4b-H), 5.13 (d, $J_{1,2}$ = 8.5 Hz, 1 H, 1b-H), 5.59 (dd, $J_{2,3}$ = 10.6, $J_{3,4}$ = 9.2 Hz, 1 H, 3b-H), 7.24−7.35 (m, 15 H, 3 Ph). − ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 8.74 (2 CH_3-C), 20.5, 20.61, 20.69 (3 *C*H_3CO-C), 54.50 (2b-C), 55.01 (-OCH_3-C), 61.89 (6b-C), 68.81 (4b-C), 69.02 (5a-C), 69.15 (6a-C), 70.75 (3b-C), 71.66 (5b-C), 73.29, 73.54, 74.65 (3 *C*H_2Ph-C), 75.22 (4a-C), 76.25(2a-C), 78.89 (3a-C), 98.33 (1b-C), 98.65 (1a-C), 127.44−138.67 (3 Ph-C), 169.48, 170.11, 170.67 (3 CH_3*C*O-C). − MALDI-MS (positive mode, DHB/THF matrix); *m/z*: 882 [MNa^+], 898 [MK^+]. − $C_{46}H_{53}NO_{15}$ H_2O (877.9): calcd. C 62.92, H 6.08, N 1.59; found C 62.87, H 5.97, N 1.58.

Benzyl O-(3,4,6-Tri-O-acetyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (**6e**): The residue was purified by flash chromatography (*n*-hexane/ethyl acetate, 2:1) to yield **6e** (0.15 g, 78%) as an oil which crystallizes on standing. − TLC (petroleum ether/ethyl acetate, 1:1): R_f = 0.57, m.p. 90−92°C. − $[\alpha]_D$ = −4.7 (*c* = 1.0, chloroform). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.86, 1.88, 1.94, 1.95 (4 s, 15 H, 2 CH_3, 3 CH_3CO), 3.28−3.33 (m, 2 H, 5a-H, 5b-H), 3.46−3.51 (m, 2 H, 2a-H, 6a-H), 3.58−3.61 (m, 2 H, 3a-H, 6′a-H), 3.75−3.77 (m, 1 H, 6b-H), 3.95−4.02 (m, 3 H, 4a-H, 2b-H, 6′b-H), 4.42 (d, $J_{1,2}$ = 7.7 Hz, 1 H, 1a-H), 4.56, 4.57 (2 d, J_{gem} = 12.0 Hz, 2 H, CH_2Ph), 4.62, 4.86 (2 d, J_{gem} = 10.9 Hz, 2 H, CH_2Ph), 4.61 (d, J_{gem} = 12.0 Hz, 1 H, C*H*HPh), 4.86−4.93 (m, 3 H, 1.5 CH_2Ph), 5.03 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.8 Hz, 1 H, 4b-H), 5.49 (d, $J_{1,2}$ = 8.4 Hz, 1 H, 1b-H), 5.51 (dd, $J_{2,3}$ = 10.3, $J_{3,4}$ = 9.8 Hz, 1 H, 3b-H), 7.22−7.35 (m, 20 H, 4 Ph). − ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 8.71 (2 CH_3-C), 20.46, 20.57, 20.65 (3 *C*H_3CO-C), 55.23 (2b-C), 61.46 (6b-C), 68.30 (6a-C), 68.45 (4b-C), 70.87, 73.22, 74.38, 74.48 (4 *C*H_2Ph-C), 70.91 (3b-C), 71.52 (5a-C), 74.78 (5b-C), 75.71 (4a-C), 81.96 (2a-C), 82.84 (3a-C), 97.31 (1b-C), 102.30 (1a-C), 126.76−139.16 (4 Ph-C), 169.39, 170.12, 170.65 (3 CH_3*C*O-C). − MALDI-MS (positive mode, DHB/THF matrix); *m/z*: 957 [MNa^+]. − $C_{52}H_{57}NO_{15}$ (936.0): calcd. C 66.72, H 6.13, N 1.49; found C 66.57, H 6.18, N 1.39.

Allyl O-(3,4,6-Tri-O-acetyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranoside (**6f**): The residue was purified by flash chromatography (*n*-hexane/ethyl acetate, 2:1) to yield **6f** (0.1 g, 53%) as a white foam. − TLC

(petroleum ether/ethyl acetate, 2:1): R_f = 0.57. − $[\alpha]_D$ = +35.4 (*c* = 0.5, chloroform). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.82, 1.91, 2.00, 2.02 (4 s, 15 H, 2 CH_3, 3 CH_3CO), 3.37 (dd, J_{gem} = 10.8 Hz, $J_{5,6}$ = 6.5, 1 H, 6a-H), 3.56 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, 1 H, 4a-H), 3.59 (dd, J_{gem} = 10.8, $J_{5,6'}$ = 1.1 Hz, 1 H, 6′a-H), 3.68 (m, 1 H, 5a-H), 3.80 (m, 1 H, 5b-H), 3.87 (m, 2 H, C*H*HCH=CH_2, 3a-H), 4.07−4.10 (m, 2 H, 2a-H, CH*H*CH=CH_2)$_2$], 4.16 (dd, J_{gem} = 12.2, $J_{5,6}$ = 2.0 Hz, 1 H, 6b-H), 4.20−4.25 (m, 2 H, 2b-H, 6′b-H), 4.40, 4.81 (2 d, 2 H, J_{gem} = 10.8 Hz, CH_2Ph), 4.43 (m, 2 H, CH_2Ph), 4.50, 4.75 (2 d, 2 H, J_{gem} = 11.3 Hz, CH_2Ph), 4.58 (d, 1 H, $J_{1,2}$ = 1.2 Hz, 1a-H), 5.11 (dd, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, 4b-H), 5.17 (m, 2 H, CH_2CH=CH_2), 5.30 (d, 1 H, $J_{1,2}$ = 8.5 Hz, 1b-H), 5.64 (dd, 1 H, $J_{2,3}$ = 10.6, $J_{3,4}$ = 9.6 Hz, 3b-H), 5.84 (m, 1 H, CH_2C*H*=C*H*$_2$), 7.13−7.35 (m, 15 H, 3Ph). − ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 8.65 (2 CH_3-C), 20.57, 20.63, 20.72 (3 C*H*$_3$CO-C), 54.29 (2b-C), 62.40 (6b-C), 68.04 (CH_2CH=CH_2-C), 69.06 (4b-C), 69.86 (6a-C), 70.76 (3b-C), 71.11 (CH_2Ph-C), 71.45 (5a-C), 71.99 (5b-C), 72.87 (CH_2Ph-C), 74.17 (2a-C), 74.53 (4a-C), 75.00 (CH_2Ph-C), 78.10 (3a-C), 96.38 (1a-C), 97.07 (1b-C), 117.54 (CH_2CH=CH_2-C), 127.46−128.34 (3 Ph-C), 133.54 (CH_2C*H*=CH_2-C), 138.34 (3 Ph-C), 169.46, 170.21, 170.67 (3 CH_3C*O*-C). − MALDI-MS (positive mode, DHB/THF matrix); *m/z*: 909 [MNa^+]. − $C_{48}H_{55}NO_{15}$ (885.9): calcd. C 65.07, H 6.25, N 1.58; found C 64.32, H 6.46, N 1.56.

*Benzyl 3,4,6-Tri-O-acetyl-2-deoxy-2-dimethylmaleimido-β-*D*-glucopyranosyl-(1→4)-(2,6-di-O-benzyl-β-*D*-galactopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-*D*-glucopyranoside* **6g-**(4b) *and Benzyl 3,4,6-Tri-O-acetyl-2-deoxy-2-dimethylmaleimido-β-*D*-glucopyranosyl-(1→3)-(2,6-di-O-benzyl-β-*D*-galactopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-*D*-glucopyranoside* **6g-**(3b)**:** The residue was purified first by flash chromatography (petroleum ether/ethyl acetate, 4:3) to yield **6g-**(4b) (0.173 g, 63%) as a colorless oil. − TLC (petroleum ether/ethyl acetate, 4:3): R_f = 0.18. − $[\alpha]_D$ = +1.6 (*c* = 1.0, chloroform). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.84, 1.88, 1.99, 2.03 (4 s, 15 H, 2 CH_3, 3 CH_3CO), 3.10 (dd, $J_{1,2}$ = 7.9, $J_{2,3}$ = 9.5 Hz, 1 H, 2b-H), 3.35−3.45 (m, 6 H, 5a-H, 5b-H, 6a-H, 6b-H, 3b-H, 2a-H), 3.55 (dd, $J_{2,3}$ = $J_{3,4}$ = 9.0 Hz, 1 H, 3a-H), 3.69 (m, 2 H, 6′a-H, 6′b-H), 3.74 (m, 1 H, 5c-H), 3.94 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.0 Hz, 1 H, 4a-H), 4.00 (m, 2 H, 4b-H, 6c-H), 4.12 (dd, $J_{1,2}$ = 8.4, $J_{2,3}$ = 10.5 Hz, 1 H, 2c-H), 4.27 (d, 2 H, 6′c-H, C*H*HPh), 4.34 (d, $J_{1,2}$ = 7.9 Hz, 1 H, 1b-H), 4.45 (d, $J_{1,2}$ = 7.8 Hz, 1 H, 1a-H), 4.30−5.00 (m, 11 H, 5.5 CH_2Ph), 5.12 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.2 Hz, 1 H, 4c-H), 5.39 (d, $J_{1,2}$ = 8.4 Hz, 1 H, 1c-H), 5.75 (dd, $J_{2,3}$ = 10.5, $J_{3,4}$ = 9.2 Hz, 1 H, 3c-H), 7.22−7.31 (m, 30 H, 6 Ph). − ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 8.73 (2 CH_3-C), 20.57, 20.63, 20.66 (3 C*H*$_3$CO-C), 54.72 (2c-C), 61.85 (6c-C), 68.24, 68.59 (6a-C, 6b-C), 68.91 (4c-C), 70.64 (3c-C), 70.91 (CH_2Ph-C), 71.35 (5c-C), 73.14, 73.25 (2 CH_2Ph-C), 73.31 (3b-C), 73.45 (5b-C), 75.08, 75.16, 75.38, 75.64 (3 CH_2Ph-C, 5a-C), 75.83 (4b-C), 76.57 (4a-C), 81.32 (2b-C), 81.70 (2a-C), 82.65 (3a-C), 99.25 (1c-C), 102.04 (1b-C), 102.49 (1a-C), 127.11−128.80, 137.54−139.05 (6 Ph-C), 169.55−170.55 (3 CH_3C*O*-C). − MALDI-MS (positive mode, DHB/THF matrix); *m/z*: 1300 [MNa^+]. − $C_{72}H_{79}NO_{20}$ (1278.3): C 67.64, H 6.22, N 1.09; found C 67.03, H 6.20, N 0.99. The other fractions from the previous chromatography were dried in vacuo and separated by MPLC (petroleum ether/ethyl acetate, 2:1) to yield **6g-**(3b) (0.087 g, 31%) as a colorless oil. − TLC (petroleum ether/ethyl acetate, 2:1):R_f = 0.38. − $[\alpha]_D$ = +8.45 (*c* = 1.06, chloroform). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.88, 2.02, 2.17, (3 s, 15 H, 2 CH_3, 3 CH_3CO), 2.67 (br.s, 1 H, OH), 3.11 (m, 1 H, 5a-H), 3.39 (m, 1 H, 5b-H), 3.41 (m, 1 H, 2a-H), 3.46−3.47 (m, 5 H, 3b-H, 3a-H, 2b-H, 6a-H, 6b-H), 3.60 (dd, J_{gem} = 11.0, $J_{5,6'}$ = 4.2 Hz, 1 H, 6′a-H), 3.71 (dd, J_{gem} = 9.7, $J_{5,6'}$ = 7.2 Hz, 1 H, 6′b-H), 3.84 (m, 1 H, 5c-H), 3.91 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.2 Hz, 1 H, 4a-H), 4.03 (br.s, 1 H, 4b-H), 4.15−4.17 (m, 3 H, 2c-H, 6c-H, 6′c-H), 4.30 (br.s, J_{gem} = 12.2 Hz, 1 H, C*H*HPh), 4.33 (d, J_{gem} = 12.0 Hz, 1 H, C*H*HPh), 4.37 (d, $J_{1,2}$ = 7.6 Hz, 1 H, 1a-H), 4.40 (d, $J_{1,2}$ = 7.1 Hz, 1 H, 1b-H), 4.44−4.94 (m, 10 H, 5 CH_2Ph), 5.07 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.1 Hz, 1 H, 4c-H), 5.44 (d, $J_{1,2}$ = 8.5 Hz, 1 H, 1c-H), 5.56 (dd, $J_{2,3}$ = 10.6, $J_{3,4}$ = 9.1 Hz, 1 H, 3c-H), 7.08−7.32 (m, 30 H, 6 Ph). − ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 8.41 (2 CH_3-C), 20.41, 20.58, 30.92 (3 C*H*$_3$CO-C), 54.41 (2c-C), 62.02 (6c-C), 67.28 (4b-C), 68.04 (6a-C), 68.39 (6b-C), 68.74 (4c-C), 70.70 (3c-C), 70.89 (CH_2Ph-C), 71.96 (5c-C), 72.52 (5b-C), 73.11, 73.42 (3 CH_2Ph-C), 74.85 (5a-C), 74.96, 75.36 (2 CH_2Ph-C), 76.17 (4a-C), 77.90 (2b-C), 81.81 (2a-C), 82.91 (3b-C), 84.43 (3a-C), 98.68 (1c-C), 101.99 (1b-C), 102.44 (1a-C), 128.08−139.04 (6 Ph-C), 169.39, 170.06, 170.69 (3 CH_3C*O*-C). − MALDI-MS (positive mode, DHB/THF matrix); *m/z*: 1302 [MNa^+]. − $C_{72}H_{79}NO_{20}$ (1278.4): calcd. C 67.64, H 6.22, N 1.09; found C 67.75, H 6.50, N 1.07.

General Procedure for the Synthesis of Compounds **7a−g**. − *Method A:* A mixture of **6a−g** (0.1 mmol) and sodium hydroxide (0.1 g, 2.5 mmol) in a dioxane/water mixture (4:1, 5 ml) was stirred at room temp. After 24 h the pH was adjusted at 5 by N HCl and the solution was stirred and monitored by TLC (ethyl acetate and different amounts of methanol); intermediate **A** did not migrate; acid addition led to a higher moving spot (**B** or **C**) which resulted in lower moving **D**. After 24−48 h the solution was neutralized with potassium carbonate and dried well in vacuo. The residue was treated with pyridine (10 ml), acetic anhydride (5 ml), and stirred at room temp. After 19 h the solution was coevaporated with toluene in vacuo. The residue was dissolved in chloroform (50 ml) and washed successively with hydrochloric acid (3%, 50 ml), water (100 ml), saturated sodium bicarbonate solution (50 ml), water (100 ml), dried over $MgSO_4$ (anhydrous), and coevaporated with toluene in vacuo.

*n-Octyl 2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-*D*-glucopyranoside* (**7a**)[19a]: *Method A*: The residue was purified by flash chromatography (toluene/acetone, 2:1) to yield **7a** (0.02 g, 40%) as a white powder. − TLC (toluene/acetone, 2:1): R_f = 0.52, m.p. 110−111°C. − $[\alpha]_D$ = −37.0 (*c* = 0.1, chloroform). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.88 (dd, *J* = 6.4, *J* = 6.8 Hz, 3 H, CH_3), 1.29 [m, 10 H, -$(CH_2)_5$-], 1.55 (b, 2 H, -CH_2-), 1.94, 2.03, 2,08 (3 s, 12 H , 4 $COCH_3$), 3.47 (m, 1 H, 2-H), 3.67, 3.74 (2 m, 1 H, 5-H), 3.81−3.9 (m, 2 H, -OCH_2-), 4.09−4.16 (dd, J_{gem} = 12.2, $J_{5,6}$ = 2.5 Hz, 1 H, 6-H), 4.24−4.31(dd, J_{gem} = 12.2 , $J_{5,6'}$ = 2.7 Hz, 1 H, 6′H), 4.69 (d, $J_{1,2}$ = 8.3 Hz, 1 H, 1-H), 5.07 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.3 Hz, 1 H, 4-H), 5.32 (dd, $J_{2,3}$ = 10.5, $J_{3,4}$ = 9.3 Hz, 1 H, 3-H), 5.52 (d, $J_{2,NH}$ = 8.6 Hz, 1 H, NH). − MALDI-MS (positive mode-DHB/THF matrix); *m/z*: 483 [MNa^+], 499 [MK^+]. − $C_{22}H_{37}NO_9$ (459.5): calcd. C 57.49, H 8.12, N 3.04; found C 57.00, H 7.68, N 2.87.

Method B: Compound **6a** (0.212 g, 0.4 mmol) was treated with NaOH and HCl as described in Method A. The solution was cooled in an ice salt bath, made alkaline with a sodium hydroxide solution (0.1 M), and treated with acetyl chloride (0.055 g, 0.7 mmol, 0.5 ml); after 30 min the pH was adjusted to 5 with 1 N HCl and left for 1 d. Acetylation was performed as described before to yield **7a** (0.12 g, 64%).

*Allyl 2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-*β-D*-glucopyranoside* (**7b**)[19b]. − *Method A:* The residue was purified by flash chromatography (toluene/acetone, 2:1) to yield **7b** (0.009 g, 23%) as a white powder. − TLC (toluene/acetone, 2:1): R_f = 0.25; m.p. 158°C. − $[\alpha]_D$ = −6.0 (*c* = 0.55, chloroform). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.93, 2.0, 2.01, 2.07 (4 s, 12 H, 4 $COCH_3$), 3.66 (m, 1 H, 5-H), 3.83 (ddd, $J_{1,2}$ = 8.3, $J_{2,3}$ = 10.6, $J_{2,NH}$ = 8.8 Hz,

1 H, 2-H), 4.02−4.36 (m, 5 H, 4-H, 6-H, 6′-H, C*H*$_2$CH=CH$_2$), 4.69 (d, $J_{1,2}$ = 8.3 Hz, 1 H, 1-H), 5.06 (dd, $J_{2,3}$ = $J_{3,4}$ = 9.7 Hz, 1 H, 3-H), 5.24 (m, 2 H, CH$_2$CH=C*H*$_2$), 5.43 (br.d, 1 H, $J_{2,NH}$ = 8.8 Hz, NH), 5.85 (m, 1 H, CH$_2$C*H*=CH$_2$). − MALDI-MS (positive mode, DHB/THF matrix); *m/z*: 412 [MNa$^+$]. − $C_{17}H_{25}NO_9$ (387.4): calcd. C 52.70, H 6.50, N 3.61; found C 53.37, H 6.64, N 3.46.

Benzyl 2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-*glucopyranoside* (**7c**)[19b]. − *Method A:* The residue was purified by flash chromatography (toluene/acetone, 4:1) to yield **7c** (0.0315 g, 71%) as a white powder. − TLC (toluene/acetone, 4:1). R_f = 0.12; m.p. 154°C. − [α]$_D$ = −36.6 (*c* = 0.75, chloroform). − ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.89, 1.99, 2.09 (3 s, 12 H, 4 CH$_3$CO), 3.64 (m, 1 H, 5-H), 3.95 (ddd, $J_{1,2}$ = 8.3, $J_{2,3}$ = 10.2, $J_{2,NH}$ = 8.9 Hz, 1 H, 2-H), 4.14 (dd, J_{gem} = 12.2, $J_{5,6}$ = 2.5 Hz, 1 H, 6-H), 4.26 (dd, J_{gem} = 12.2, $J_{5,6'}$ = 4.7 Hz, 1 H, 6′-H), 4.58 (d, J_{gem} = 12.2 Hz, 1 H, C*H*HPh), 4.6 (d, $J_{1,2}$ = 8.3 Hz, 1 H, 1-H), 4.88 (d, J_{gem} = 12.2 Hz, 1 H, CH*H*Ph), 5.07 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.3 Hz, 1 H, 4-H), 5.18 (dd, $J_{2,3}$ = 10.2, $J_{3,4}$ = 9.3 Hz, 1 H, 3-H), 5.32 (d, $J_{2,NH}$ = 8.9 Hz, 1 H, NH), 7.31 (m, 5 H, Ph). − MALDI-MS (positive mode, DHB/THF matrix); *m/z*: 460 [MNa$^+$]. − $C_{21}H_{27}NO_9$ (437.5): calcd. C 57.65, H 6.22, N 3.20; found C 58.24, H, 6.35, N 2.78.

Methyl O-(2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-α-D-galactopyranoside (**7d**): *Method A:* The residue was purified by flash chromatography (toluene/acetone, 2:1) to yield **7d** (0.048 g, 57%) as a white powder. − TLC (toluene/acetone, 2:1): R_f = 0.32, m.p. 154°C. − [α]$_D$ = −1.2 (*c* = 1.0, chloroform). − ^{1}H NMR (600 MHz, CDCl$_3$ + DMSO, 1 drop): δ = 1.81, 1.94, 1.95 (3 s, 12 H, 4 CH$_3$CO), 3.28 (s, 3 H,-OCH$_3$), 3.52 (dd, J_{gem} = 9.5, $J_{5,6}$ = 6.8 Hz, 1 H, 6a-H), 3.58 (m, 1 H, 5b-H), 3.74−3.79 (m, 3 H, 5a-H, 4a-H, 6′a-H), 3.85 (dd, $J_{2,3}$ = 10.0, $J_{3,4}$ = 2.3 Hz, 1 H, 3a-H), 3.90−3.94 (m, 2 H, 2a-H, 2b-H), 3.99 (dd, J_{gem} = 12.3, $J_{5,6}$ = 4.0 Hz, 1 H, 6b-H), 4.15 (dd, J_{gem} = 12.3, $J_{5,6'}$ = 4.1 Hz, 1 H, 6′b-H), 4.47 (d, $J_{1,2}$ = 8.3 Hz, 1 H, 1b-H), 4.53, 4.86 (2 d, J_{gem} = 11.2 Hz, 2 H, C*H*$_2$Ph), 4.57 (d, $J_{1,2}$ = 3.5 Hz, 1 H, 1a-H), 4.61, 4.66 (2 d, J_{gem} = 12.1 Hz, 2 H, C*H*$_2$Ph), 4.75, 4.77 (2 d, J_{gem} = 11.1 Hz, 2 H, C*H*$_2$Ph), 4.98 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.7, 1 H, 4b-H), 5.08 (dd, $J_{2,3}$ = 10.1, $J_{3,4}$ = 9.7 Hz, 1 H, 3b-H), 6.1 (d, $J_{2,NH}$ = 8.9 Hz, 1 H, NH), 7.19−7.3 (m, 15 H, 3 Ph). − ^{13}C NMR(150.9 MHz, CDCl$_3$): δ = 20.62, 20.71, 29.68 (4 *C*H$_3$CO-C), 54.35 (2b-C), 55.27 (-OCH$_3$-C), 61.97 (6b-C), 68.31 (4b-C), 69.47 (5a-C), 69.55 (6a-C), 71.86 (5b-C), 72.66 (3b-C), 73.43, 73.58, 74.69 (3 *C*H$_2$Ph-C), 75.39 (4a-C), 76.28 (2a-C), 78.89 (3a-C), 98.76 (1a-C), 101.42 (1b-C), 127.53−128.4 (3 Ph-C), 138.43, 138.48, 138.68 (3 Ph-C), 169.32, 170.68,171.1 (4 CH$_3$*C*O-C). − MALDI-MS (positive mode, DHB/THF matrix); *m/z*: 815 [MNa$^+$], 831 [MK$^+$]. − $C_{42}H_{51}NO_{14}$ (793.8): calcd. C 63.54, H 6.47, N 1.76; found C 63.55, H 6.37, N 1.64.

Benzyl O-(2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-*glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D*-glucopyranoside (**7e**)[19c]: *Method A:* The residue was purified by flash chromatography (toluene/acetone, 2:1) to yield **7e** (0.06 g, 65%) as a white foam. − TLC(toluene/acetone, 4:1): R_f = 0.29. − [α]$_D$ = −53.0 (*c* = 0.1, chloroform). − ^{1}H NMR (600 MHz, CDCl$_3$): δ = 1.7, 1.89, 1.93, 1.97 (4 s, 12 H, 4 CH$_3$CO), 3.35(m, 1 H, 5a-H), 3.38 (m, 1 H, 5b-H), 3.44 (dd, $J_{1,2}$ = 7.7, $J_{2,3}$ = 8.9 Hz, 1 H, 2a-H), 3.54 (dd, $J_{2,3}$ = $J_{3,4}$ = 8.9 Hz, 1 H, 3a-H), 3.65 (m, 2 H, 6a-H, 6′a-H), 3.81 (dd, J_{gem} = 12.3, $J_{5,6}$ = 2.0 Hz, 1 H, 6b-H), 3.85 (m, 1 H, 2b-H), 3.88 (m, 1 H, 4a-H), 4.05 (dd, J_{gem} = 12.3, $J_{5,6'}$ = 4.2 Hz, 1 H, 6′b-H), 4.44 (d, $J_{1,2}$ = 7.7 Hz, 1 H, 1a-H), 4.45, 4.81 (2 d, J_{gem} = 12.2 Hz, 2 H, C*H*$_2$Ph), 4.63, 4.83 (2 d, J_{gem} = 11.4 Hz, 2 H, C*H*$_2$Ph), 4.63, 4.92 (2 d, J_{gem} = 11.4 Hz, 2 H, C*H*$_2$Ph), 4.74, 4.94 (2 d, J_{gem} = 11.6 Hz, 2 H, C*H*$_2$Ph), 4.55 (d, $J_{1,2}$ = 8.4 Hz, 1 H, 1b-H), 4.82 (d, $J_{2,NH}$ = 1.9 Hz, 1 H, NH), 4.90 (m, 1 H, 3b-H), 4.95 (m, 1 H, 4b-H), 7.19−7.41 (m, 20 H, 4 Ph). − ^{13}C NMR (150.9 MHz, CDCl$_3$): δ = 20.61, 23.14 (4 *C*H$_3$CO-C), 54.58 (2b-C), 61.76 (6b-C), 68.06 (6a-C), 68.3 (4b-C), 71.13, 73.88, 74.8, 74.9 (4 *C*H$_2$Ph-C), 71.51 (5b-C), 72.94 (3b-C), 74.21 (5a-C), 77.47 (4a-C), 81.77 (2a-C), 82.72 (3a-C), 100.51 (1b-C), 102.52 (1a-C), 127.01−139.29 (4 Ph-C), 169.83 (4 CH$_3$*C*O-C). − FAB-MS (positive mode, NBOH/NaI matrix); *m/z*: 870 [MH$^+$], 892 [MNa$^+$], 1002 [MCs$^+$]. − $C_{48}H_{55}NO_{14}$ (869.9): C 66.26, H 6.37, N 1.61; found C 66.14; H 6.71, N 1.53.

Method C: Compound **6e** (0.119 g, 0.127 mmol) was treated with sodium hydroxide as described in method A. After 24 h the reaction mixture was treated with ethylamine (0.013 g, 0.3 mmol, 0.02 ml) and the pH was adjusted to 5 by *N*-hydrochloric acid. After 48 h the reaction mixture was neutralized with ethanolamine and dried well in vacuo. The residue was acetylated and purified as described before in method A to yield **7e** (0.098 g, 89%).

Allyl O-(2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl)-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranoside (**7f**)[19d]: *Method A:* The residue was purified by flash chromatography (toluene/acetone, 2:1) to yield **7f** (0.063 g, 68%) as a white powder. − TLC (toluene/acetone, 4:1): R_f = 0.34; m.p. 149−150°C. − [α]$_D$ = +24.5 (*c* = 0.2, chloroform). − ^{1}H NMR (600 MHz, CDCl$_3$): δ = 1.74, 1.98, 1.99, 2.01 (4 s, 12 H, 4 CH$_3$CO), 3.27 (m, 1 H, 2b-H), 3.64 (m, 1 H, 6a-H), 3.7 (m, 1 H, 5a-H), 3.73 (m, 1 H, 6′a-H), 3.76 (m, 1 H, 5b-H), 3.91 (m, 1 H, C*H*HCH=CH$_2$), 3.94 (m, 1 H, 3a-H), 3.95 (m, 1 H, 4a-H), 4.13 (m, 2 H, CH*H*CH=CH, 6b-H), 4.14 (m, 1 H, 2a-H), 4.24 (dd, J_{gem} = 12.2, $J_{5,6'}$ = 4.8 Hz, 1 H, 6′b-H), 4.46, 4.52 (2 d, J_{gem} = 12.2 Hz, 2 H, C*H*$_2$Ph), 4.51, 4.89 (2 d, J_{gem} = 11.6 Hz, 2 H, C*H*$_2$Ph), 4.57, 4.75 (2 d, J_{gem} = 11.2 Hz, 2 H, C*H*$_2$Ph), 4.77 (br.s, 1 H, 1a-H), 4.98 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.8 Hz, 1 H, 4b-H), 5.14−5.16 (d, 2 H, 1b-H, CH$_2$CH=C*H*H), 5.21 (d, J_{gem} = 13.5 Hz, 1 H, CH$_2$CH=CH*H*), 5.51 (d, $J_{2,NH}$ = 6.9 Hz, 1 H, NH), 5.72 (dd, $J_{2,3}$ = $J_{3,4}$ = 9.8 Hz, 1 H, 3b-H), 5.84 (m, 1 H, CH$_2$C*H*=CH$_2$), 7.2−7.37 (m, 15 H, 3 Ph). − ^{13}C NMR (150.9 MHz, CDCl$_3$): δ = 20.66, 20.7, 23.23 (4 *C*H$_3$CO-C), 56.35 (2b-C), 62.47 (6b-C), 68.21 (*C*H$_2$CH=CH$_2$-C), 69.23 (6a-C, 4b-C), 71.05 (3b-C), 71.44 (*C*H$_2$Ph-C), 71.67 (5a-C), 71.74 (5b-C), 73.23 (*C*H$_2$Ph-C), 73.54 (2a-C), 74.23 (4a-C), 75.16 (*C*H$_2$Ph-C), 78.21 (3a-C), 96.67 (1a-C), 97.63 (1b-C), 117.34 (CH$_2$CH=*C*H$_2$-C), 127.54−128.39 (3 Ph-C), 133.59 (CH$_2$*C*H=CH$_2$-C), 138.1, 138.35, 138.46 (3 Ph-C), 169.63, 170.12, 170.63, 171.32 (4 CH$_3$*C*O-C). − MALDI-MS (positive mode, DHB/THF matrix); *m/z*: 840 [MNa$^+$]. − $C_{44}H_{53}NO_{14}$ (819.9): calcd. C 64.45, H 6.51, N 1.70; found C 64.21, H 6.12, N 1.24.

Benzyl O-2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl-(1→4)-(2,6-di-O-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside **7g-**(4b)[19e]: *Method A, B:* The residue was purified by flash chromatography (ethyl acetate/petroleum ether, 1.5:1) to yield **7g-**(4b) (0.092 g, 74%) as a colorless oil. − TLC (ethyl acetate/petroleum ether, 1.5:1). R_f = 0.25. − [α]$_D$ = +9.58 (*c* = 0.73, chloroform). − ^{1}H NMR (600 MHz, CDCl$_3$): δ = 1.79, 1.99, 2.01, 2.04, 2.1 (5 s, 15 H, 5 CH$_3$CO), 3.35 (m, 1 H, 2c-H), 3.38 (m, 1 H, 5a-H), 3.44−3.48 (m, 3 H, 6b-H, 5b-H, 2a-H), 3.55 (dd, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.1 Hz, 1 H, 2b-H), 3.58 (dd, $J_{2,3}$ = $J_{3,4}$ = 9.5 Hz, 1 H, 3a-H), 3.64 (m, 1 H, 5c-H), 3.67 (dd, J_{gem} = 8.6, $J_{5,6'}$ = 5.5 Hz, 1 H, 6′b-H), 3.75 (m, 2 H, 6a-H, 6′a-H), 3.99 (dd, J_{gem} = 10.7, $J_{5,6}$ = 1.6 Hz, 1 H, 6c-H), 4.02 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, 1 H, 4a-H), 4.12 (dd, $J_{3,4}$ = $J_{4,5}$ = 2.7 Hz, 1 H, 4b-H), 4.22 (dd, J_{gem} = 12.7, $J_{5,6'}$ = 4.6 Hz, 1 H, 6′c-H), 4.31 (d, J_{gem} = 12.1 Hz, 1 H, C*H*HPh), 4.38 (d, J_{gem} = 12.1 Hz, 1 H,

CH*H*Ph), 4.43 (d, J_{gem} = 12.2 Hz, 1 H, C*H*HPh), 4.49 (d, $J_{1,2}$ = 7.7 Hz, 1 H, 1a-H), 4.52 (d, $J_{1,2}$ = 8.0 Hz, 1 H, 1b-H), 4.54 (d, J_{gem} = 11.8 Hz, 1 H, CH*H*Ph), 4.58 (d, J_{gem} = 12.2 Hz, 1 H, CH*H*Ph), 4.66 (d, J_{gem} = 12.1 Hz, 1 H, C*H*HPh), 4.73−4.76 (m, 3 H, 1.5 CH_2Ph), 4.87 (dd, $J_{2,3}$ = 10.1, $J_{3,4}$ = 2.7 Hz, 1 H, 3b-H), 4.89 (d, J_{gem} = 10.9 Hz, 1 H, CH*H*Ph), 4.93−4.95 (m, 2 H, 1c-H, CH*H*Ph), 5.01 (d, J_{gem} = 10.3 Hz, 1 H, CH*H*Ph), 5.05 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.8 Hz, 1 H, 4c-H), 5.33 (d, $J_{2,NH}$ = 7.5 Hz, 1 H, NH), 5.58 (dd, $J_{2,3}$ = 10.2, $J_{3,4}$ = 9.8 Hz, 1 H, 3c-H), 7.22−7.36 (m, 30 H, 6 Ph). − ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 22.02 , 22.38, 24.72 (5 *C*H_3 CO-C), 57.9 (2c-C), 63.22 (6c-C), 69.51 (6a-C), 69.91 (6b-C), 69.99 (4c-C), 72.28 (*C*H_2Ph-C), 72.74 (3c-C), 72.89 (5c-C), 74.43 (*C*H_2Ph-C), 74.59 (*C*H_2Ph-C), 74.65 (5b-C), 75.2 (4b-C), 76.29 (3b-C, *C*H_2Ph-C), 76.41 (5a-C), 76.49 (*C*H_2Ph-C), 76.73 (*C*H_2Ph-C), 77.67 (4a-C), 79.47 (2b-C), 83.05 (2a-C), 84.16 (3a-C), 101.18 (1c-C), 103.71 (1b-C), 103.85 (1a-C), 128.59−140.48 (6 Ph-C), 170.95−171.89 (5 CH_3*C*O-C). − FAB-MS (positive mode, NBOH/NaI matrix); *m/z*: 1277 [MNa^+], 1293 [MK^+], 1428 [MNaI]Na^+. − $C_{70}H_{79}NO_{20}$ (1254.3): calcd. C 67.02, H 6.34, N 1.11; found C 66.90, H 6.15, N 0.91.

General Procedure for the Synthesis of Compounds **8a−c**: A mixture of **3**, **6b**, or **6c** (1.94 mmol), dry methanol (19 ml) and sodium methoxide solution (0.169 M, 1.15 ml) was stirred at room temp. After 75 min the solution was neutralized with Amberlite IR 120 (H^+) resin. The solution was filtered and dried in vacuo.

tert-Butyldimethylsilyl 2-Deoxy-2-dimethylmaleimido-β-D-glucopyranoside (**8a**)**:** The residue was purified by flash chromatography (toluene/acetone, 5:3.5) to yield **8a** (0.748 g, 96%) as white crystals. − TLC (toluene/acetone, 5:3.5): R_f = 0.3; m.p. 164−166°C. − $[\alpha]_D$ = −20.4 (*c* = 0.5, chloroform). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = −0.03 (s, 3 H, $SiCH_3$), 0.03 (s, 3 H, $SiCH_3$), 0.75 [s, 9 H, $SiC(CH_3)_3$], 1.93 (s, 6 H, 2 CH_3), 3.43−4.26 (m, 6 H, 2-H, 3-H, 4-H, 5-H, 6-H, 6′-H), 5.24 (d, $J_{1,2}$ = 8.0 Hz, 1 H, 1-H). − MALDI-MS (positive mode, DHB/THF matrix); *m/z*: 424 [MNa^+], 439 [MK^+]. − $C_{18}H_{31}NO_7Si$ (401.5): calcd. C 53.83, H 7.78, N 3.48; found C 53.62, H 7.15, N 3.32.

Allyl 2-Deoxy-2-dimethylmaleimido-β-D-glucopyranoside (**8b**): The residue was purified by flash chromatography (toluene/acetone, 1:1) to yield **8b** (0.612 g, 96%) as a white foam. − TLC (toluene/acetone, 1:1): R_f = 0.21. − $[\alpha]_D$ = −7.4 (*c* = 1.05, chloroform). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.93, (s, 6 H, 2 CH_3), 3.20 (br.s, 3 H, 3 OH), 3.4 (m, 1 H, 5-H), 3.63 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.2 Hz, 1 H, 4-H), 3.84 (m, 3 H, 2-H, CH_2CH=CH_2), 3.99 (dd, J_{gem} = 12.9, $J_{5,6}$ = 6.0 Hz, 1 H, 6-H), 4.11 (m, 1 H, 3-H), 4.23 (dd, J_{gem} = 12.9, $J_{5,6'}$ = 4.8 HZ, 1 H, 6′-H), 5.06 (d, $J_{1,2}$ = 8.4 Hz, 1 H, 1-H), 5.1 (m, 2 H, CH_2CH=CH_2), 5.72 (m, 1 H, CH_2C*H*=CH_2). − MALDI-MS (positive mode, DHB/THF matrix); *m/z*: 349 [MNa^+]. − $C_{15}H_{21}NO_7$0.25 H_2O (331.8): calcd. C 54.28, H 6.53, N 4.22; found C 53.92, H 6.71, N 4.23.

Benzyl 2-Deoxy-2-dimethylmaleimido-β-D-glucopyranoside (**8c**): The residue was purified by flash chromatography (toluene/acetone, 1:1) to yield **8c** (0.73 g, quantitative) as white crystals. − TLC (toluene/acetone, 1:1): R_f = 0.19, m.p. 129°C. − $[\alpha]_D$ = −26.0 (*c* = 0.65, chloroform). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.86 (s, 6 H, 2 CH_3), 2.73 (br.s, 3 H, 3 OH), 3.42 (m, 1 H, 5-H), 3.61 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.2 Hz, 1 H, 4-H), 3.80−3.93 (m, 3 H, 3-H, 6-H, 6′-H), 4.14 (dd, $J_{1,2}$ = 8.4, $J_{2,3}$ = 10.8 Hz, 1 H, 2-H), 4.49 (d, J_{gem} = 12.3 Hz, 1 H, C*H*HPh), 4.78 (d, J_{gem} = 12.3 Hz, 1 H, CH*H*Ph), 5.07 (d, $J_{1,2}$ = 8.4 Hz, 1 H, 1-H), 7.11−7.24 (m, 5 H, Ph). − MALDI-MS (positive mode, DHB/THF matrix); *m/z*: 403 [MNa^+]. − $C_{19}H_{23}NO_7$ (377.4): calcd. C 60.46, H 6.14, N 3.71; found C 60.34, H 5.80, N 3.67.

tert-Butyldimethylsilyl 3,6-Di-O-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (**9**): A suspension of **8a** (1.79 g, 4.45 mmol) and dibutyltin oxide (2.44 g, 9.89 mmol) in toluene (40 ml) was heated under reflux (dean-Stark apparatus). After 12.5 h tetrabutylammonium iodide (3.62 g, 9.8 mmol) and benzyl bromide (1.677 g, 9.8 mmol, 1.16 ml) were added and the mixture was gently refluxed. After 3 h the reaction mixture was cooled, filtered and evaporated in vacuo. The residue was dissolved in ethyl acetate, filtered and evaporated in vacuo. The residue was purified by flash chromatography and if necessary by MPLC (petroleum ether/ethyl acetate, 4:1) to yield **9** (2.29 g, 88%) as white needles. − TLC (petroleum ether/ethyl acetate, 4:1): R_f = 0.2, m.p. 66−69°C. − $[\alpha]_D$ = +25.74 (*c* = 1.29, chloroform). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = −0.08 (s, 3 H, $SiCH_3$), 0.01 (s, 3 H, $SiCH_3$), 0.72 [s, 9 H, $SiC(CH_3)_3$], 1.81 (br.s, 6 H, 2 CH_3), 2.84 (br.s, 1 H, OH), 3.57 (m, 1 H, 5-H), 3.68−3.78 (m, 3 H, 4-H, 6-H, 6′-H), 3.85 (dd, $J_{1,2}$ = 8.1, $J_{2,3}$ = 10.8 Hz, 1 H, 2-H), 4.11 (dd, $J_{2,3}$ = 10.8, $J_{3,4}$ = 8.5 Hz,3-H), 4.48−4.76 (m, 4 H, 2 CH_2Ph), 5.15 (d, $J_{1,2}$ = 8.1 Hz, 1 H, 1-H), 7.13−7.35 (m, 10 H, 2 Ph). − MALDI-MS (positive mode,DHB/THF matrix); *m/z*: 604 [MNa^+]. − $C_{32}H_{43}NO_7Si$ (581.7): calcd. C 66.06, H 7.44, N 2.40; found C 65.66, H 7.72, N 2.32.

tert-Butyldimethylsilyl 4-O-Acetyl-3,6-di-O-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (**10**): A mixture of **9** (1.11 g, 1.9 mmol), pyridine (20 ml) and acetic anhydride (10 ml) was stirred at room temp. After 12 h the reaction mixture was worked up as described for **7a−g**. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 6:1) to yield **10** (1.17 g, 98%) as a colorless oil. − TLC (*n*-hexane/ethyl acetate, 5:1): R_f = 0.3. − $[\alpha]_D$ = +45.1 (*c* = 0.45, chloroform). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = −0.06 (s, 3 H, $SiCH_3$), 0.04 (s, 3 H, $SiCH_3$), 0.72 [s, 9 H, $SiC(CH_3)_3$], 1.79 (br.s, 6 H, 2 CH_3), 1.92 (s, 3 H, CH_3CO), 3.55 (br.d, 2 H, 6-H, 6′-H), 3.68 (m, 1 H, 5-H), 3.95 (dd, $J_{1,2}$ = 8.1, $J_{2,3}$ = 10.9 Hz, 1 H, 2-H), 4.25−4.35 (m, 2 H, 3-H, C*H*HPh), 4.51−4.61 (m, 3 H, 1.5 CH_2Ph), 5.04 (dd, $J_{3,4}$ = 9.1, $J_{4,5}$ = 9.8 Hz, 1 H, 4-H), 5.16 (d, $J_{1,2}$ = 8.1 Hz, 1 H, 1-H), 7.07−7.32 (m, 10 H, 2 Ph). − MALDI-MS (positive mode, DHB/THF matrix); *m/z*: 646 [MNa^+], 664 [MK^+]. − $C_{34}H_{45}NO_8Si$ (623.8): calcd. C 65.46, H 7.27, N 2.24; found C 65.66, H 7.30, N 2.32.

O-[4-O-Acetyl-3,6-di-O-benzyl-2-deoxy-2-dimethylmaleimido-α/β-D-glucopyranosyl] Trichloroacetimidate (**12**): To a solution of **10** (0.28 g, 0.448 mmol) in dry THF (5 ml) in an ice-salt bath was added glacial acetic acid (26.0 µl, 0.45 mmol) and TBAF (0.1 M, 0.45 ml, 0.45 mmol) under stirring. After 1 h the solution was treated with a saturated sodium chloride solution (5 ml) and extracted with dichloromethane (3 × 10 ml). The organic layer was separated, dried with anhydrous magnesium sulfate, and evaporated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 1:1) to yield **11** (0.22 g, 96%) as a white needles. − A mixture of **11** (0.913 g, 1.79 mmol), trichloroacetonitrile (1.1 ml, 15.3 mmol), and 1,8-diazabicyclo[5,4,0]undec-7-ene (0.04 ml, 0.24 mmol) in dry dichloromethane (5 ml) was stirred at room temp. for 4 h and then concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 2:1 +1% triethylamine) to yield **12** (0.969 g, 82%) as a pale yellow foam in the ratio of a:b = 1:3. − TLC (petroleum ether/ethyl acetate, 2:1 + 1% triethylamine): R_f = 0.5 (β-form) and R_f = 0.39 (α-form). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.79 (s, 6 H, 2 CH_3), 1.93 (s, 3 H, $COCH_3$), 3.57−3.63 (m,, 2 H, 6-H, 6′-H), 3.88 (m, 1 H, 5-H), 4.27−4.67 (m, 6 H, 2 CH_2Ph, 2-H, 3-H), 5.19 (dd, $J_{3,4}$ = $J_{4,5}$ = 8.8 Hz, 1 H, 4-H), 6.26 (d, $J_{1,2}$ = 8.5 Hz, 0.75 H, 1_β-H), 6.25 (d, $J_{1,2}$ = 3.5 Hz, 0.25 H, 1_α-H), 7.09−7.33 (m,

10 H, 2 Ph), 8.59 (s, 1 H, NH). − FAB-MS (positive mode, NBOH/NaI matrix); *m/z*: 675/677/679 [MNa^+]. − $C_{30}H_{31}N_2O_8Cl_3$ (653.9): calcd. C 55.09, H 4.77, N 4.28; found C 54.67, H 4.85, N 4.30.

tert-Butyldimethylsilyl (4-O-Acetyl-3,6-di-O-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→4)-3,6-di-O-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (**13**): A solution of **12** (0.2 g, 0.305 mmol) and **9** (0.14g, 0.24 mmol) in dry dichloromethane (2 ml) was stirred under nitrogen at room temp. for 10 min. TMSOTf (0.01 M in dichloromethane, 0.27 ml) was added dropwise. After 3 h the reaction mixture was neutralized with triethylamine and dried in vacuo. The residue was purified by preparative thin layer chromatography (petroleum ether/ethyl acetate, 3:1, 30 mg/plate) to yield **13** (0.121 g, 49%) as a white foam. − TLC (petroleum ether/ethyl acetate, 3.5:1): R_f = 0.37. − $[\alpha]_D$ = +29.6 (*c* = 1, chloroform). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = −0.15 (s, 3 H, $SiCH_3$), −0.03 (s, 3 H, $SiCH_3$), 0.69 [s, 9 H, $SiC(CH_3)_3$], 1.74−1.85 (m, 12 H, 4 CH_3), 1.89 (s, 3 H, CH_3CO), 3.31−3.33 (br.d, 2 H, 5a-H, 6a-H), 3.41 (dd, J_{gem} = 10.7, $J_{5,6}$ = 5.0 Hz, 1 H, 6b-H), 3.45 (bd, 1 H, 6′a-H), 3.48−3.55 (m, 2 H, 5b-H, 6′b-H), 3.82 (dd, $J_{1,2}$ = 8.2, $J_{2,3}$ = 10.2 Hz, 1 H, 2a-H), 3.98−4.06 (m, 3 H, 2b-H, 3a-H, 4a-H), 4.28−4.32 (m, 3 H, CH_2Ph, 3b-H), 4.39−4.83 (m, 6 H, 3 CH_2Ph), 5.03 (d, $J_{1,2}$ = 8.2 Hz, 1 H, 1a-H), 5.07 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.4 Hz, 1 H, 4b-H), 5.14 (d, $J_{1,2}$ = 8.4 Hz, 1 H, 1b-H), 7.07−7.31 (m, 20 H, 4 Ph). − ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = −5.64 ($SiCH_3$-C), −4.28 ($SiCH_3$-C), 8.45 (4 CH_3-C), 20.87 (CH_3CO-C), 25.32 [$SiC(CH_3)_3$-C], 55.93 (2b-C), 57.64 (2a-C), 68.02 (6a-C), 69.47 (6b-C), 72.51 (4b-C), 72.8−74.18 (4 CH_2Ph-C, 5b-C), 74.6 (5a-C), 76.33 (4a-C), 76.79 (3a-C), 77.35 (3b-C), 93.27 (1a-C), 97.29 (1b-C), 126.87−139.18 (4 Ph-C), 169.63 (CH_3CO-C). − FAB-MS (positive mode, NBOH/NaI matrix); *m/z*: 1095 [MNa^+]. − $C_{60}H_{72}N_2O_{14}Si$ (1073.3): calcd. C 67.13, H 6.76, N 2.61; found C 67.56 H 7.05 , N 2.67 .

General Procedure for the Synthesis of Compounds **14a−c**: To a solution of **8a−c** (1.82 mmol) in dry acetonitrile (8 ml) was added benzaldehyde dimethylacetal (0.32 g, 2.1 mmol, 0.32 ml) p-TsOH (0.028g, 0.14 mmol) and the solution was stirred. After 17 h the solution was neutralized with triethylamine and evaporated in vacuo.

tert-Butyldimethylsilyl 4,6-O-Benzylidene-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (**14a**): The residue was purified by flash chromatography (*n*-hexane/ethyl acetate, 3:1) to yield **14a** (0.8g, 89%) as a white foam. − TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.34. − $[\alpha]_D$ = -32.2 (c = 0.45, chloroform). − ^{1}H NMR (250 MHz,$CDCl_3$):δ = −0.02 (s, 3 H, $SiCH_3$), 0.05 (s, 3 H, $SiCH_3$), 0.77 [s, 9 H, $SiC(CH_3)_3$], 1.95, (s, 6 H, 2 CH_3), 3.55−3.6 (m, 2 H, 4-H, 5-H), 3.81 (dd, J_{gem} = 10.1 Hz, 1 H, 6-H), 3.96 (dd, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.6 Hz, 1 H, 2-H), 4.31 (dd, J_{gem} = 10.1 Hz, 1 H, 6′-H), 4.52 (dd, $J_{2,3}$ = 10.6, $J_{3,4}$ = 8.7 Hz, 1 H, 3-H), 5.3 (d, $J_{1,2}$ = 8.0 Hz, 1 H, 1-H), 5.53 (s, 1 H, C*H*Ph), 7.35−7.5 (2 m, 5 H, Ph). − EI-MS (positive mode); *m/z*: 488 [M − 1^+]. − $C_{25}H_{35}NO_7Si$ (489.6): calcd. C 61.32, H 7.20, N 2.86; found C 61.45, H 7.10, N 2.82.

Allyl 4,6-O-Benzylidene-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (**14b**): The residue was purified by flash chromatography (petroleum ether/ethyl actate, 2.5:1) to yield **14b** (0.659 g, 87%) as a colorless oil. − TLC (petroleum ether/ethyl acetate, 2.5:1): R_f = 0.25. − $[\alpha]_D$ = −12.8 (*c* = 1.35, chloroform). − ^{1} H NMR (250 MHz, $CDCl_3$): δ = 1.95 (s, 6 H, 2 CH_3), 3.49−3.58 (m, 2 H, 4-H, 5-H), 3.73−3.82 (m, 1 H, 6-H), 3.97−4.09 (m, 2 H, 2-H, C*H*HCH=CH_2), 4.22−4.31 (m, 1 H, CH*H*CH=CH_2), 4.34 (dd,J_{gem} = 9.8, $J_{5,6'}$ = 3.9 Hz, 1 H, 6′-H), 4.47 (dd, 1 H, 3-H), 5.15 (m, 3 H, 1-H, CH_2CH=CH_2), 5.53 (s, 1 H, C*H*Ph), 5.75 (m, 1 H, CH_2CH=CH_2), 7.36, 7.45 (2 m, 5 H, Ph). − MALDI-MS (positive mode, DHB/THF matrix); *m/z*: 439 [MNa^+]. − $C_{22}H_{25}NO_7$ (415.4): calcd. C 63.60, H 6.06, N 3.37; found C 63.39, H 6.10, N 3.38.

Benzyl 4,6-O-Benzylidene-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (**14c**): The residue was purified by flash chromatography (petroleum ether/ethyl actate, 3:1) to yield **14c** (0.715 g, 84%) as a white foam. − TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.14. − $[\alpha]_D$ = −110.5 (*c* = 0.2, chloroform). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.88 (s, 6 H, 2 CH_3), 2.28 (br.s, 1 H, OH), 3.54−3.59 (m, 2 H, 4-H, 5-H), 3.82 (m, 1 H, 6-H), 4.04 (dd, $J_{1,2}$ = 8.5, $J_{2,3}$ = 10.4 Hz, 1 H, 2-H), 3.35−4.52 (m, 3 H, 3-H, 6′-H, C*H*HPh), 4.84 (d, J_{gem} = 12.4 Hz, 1 H, CH*H*Ph), 5.11 (d, $J_{1,2}$ = 8.5 Hz, 1 H, 1-H), 5.54 (s, 1 H, C*H*Ph), 7.12−7.48 (m, 10 H, 2 Ph). − MALDI-MS (positive mode, DHB/THF matrix); *m/z*: 688 [MNa^+]. − $C_{26}H_{27}NO_7$ (465.5): calcd. C 67.08, H 5.84, N 3.00; found C 66.92, H 5.67, N 2.89.

General Procedure for the Synthesis of **15a−c**: A solution of **4** (0.5 g, 0.89 mmol) and **14a−c** (0.74 mmol) in dry dichloromethane (2 ml) was stirred under nitrogen at −30°C for 10 min. TMSOTf (0.01 M in dichloromethane, 0.97 ml) was added dropwise. After 45 min the reaction mixture was neutralized with triethylamine and dried in vacuo.

tert-Butyldimethylsilyl O-(3,4,6-Tri-O-acetyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→3)-4,6-O-benzylidene-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (**15a**): The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 3:2) to yield **15a** (0.65 g, quantitative) as a white foam. − TLC (petroleum ether/ethyl acetate, 3:2): R_f = 0.26. − $[\alpha]_D$ = −29.3 (*c* = 0.6, chloroform). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = −0.11 (s, 3 H, $SiCH_3$), −0.02 (s, 3 H, $SiCH_3$), 0.71 [s, 9 H, $SiC(CH_3)_3$], 1.81, 1.87, 1.92, 1.94, 1.98 (5 s, 21 H, 4 CH_3, 3 CH_3CO), 3.47 (m, 1 H, 5b-H), 3.51 (m, 1 H, 5a-H), 3.59 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.3 Hz, 1 H, 4a-H), 3.76 (dd, J_{gem} = $J_{5,6}$ = 10.2 Hz, 1 H, 6a-H), 3.87 (dd, $J_{1,2}$ = 8.1, $J_{2,3}$ = 10.4 Hz, 1 H, 2a-H), 3.92 (dd, J_{gem} = 12.2, $J_{5,6}$ = 1.6 Hz, 1 H, 6b-H), 3.96 (dd, $J_{1,2}$ = 8.4, $J_{2,3}$ = 10.4 Hz, 1 H, 2b-H), 4.08 (dd, J_{gem} = 12.2, $J_{5,6}$ = 4.0 Hz, 1 H, 6′b-H), 4.22 (dd, J_{gem} = 10.2, $J_{5,6}$ = 4.8 Hz, 1 H, 6′a-H), 4.71 (dd, $J_{2,3}$ = 10.4, $J_{3,4}$ = 9.3 Hz, 1 H, 3a-H), 5.02 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.3 Hz, 1 H, 4b-H), 5.05 (d, $J_{1,2}$ = 8.1 Hz, 1 H, 1a-H), 5.17 (d, $J_{1,2}$ = 8.4 Hz, 1 H, 1b-H). 5.38 (dd, $J_{2,3}$ = 10.4, $J_{3,4}$ = 9.3 Hz, 1 H, 3b-H), 5.5 (s, 1 H, C*H*Ph), 7.23, 7.48 (m, 5 H, Ph). − ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = −5.74 ($SiCH_3$-C), −4.2 ($SiCH_3$-C), 8.82 (4 CH_3-C), 17.46 [$SiC(CH_3)_3$-C], 20.41, 20.56, 20.74 (3 CH_3CO-C), 25.23 [$SiC(CH_3)_3$-C], 54.53 (2b-C), 57.82 (2a-C), 61.68 (6b-C), 66.5 (5a-C), 68.58 (4b-C), 68.69 (6a-C), 70.93 (3b-C), 71.57 (5b-C), 73.68 (3a-C), 80.12 (4a-C), 93.98 (1a-C), 96.94 (1b-C), 101.24 (CHPh-C), 126.17−137.32 (Ph-C), 169.34, 170.16, 170.68 (3 CH_3CO-C, 4 CO-C). − FAB-MS (positive mode, NBOH/NaI matrix); *m/z*: 907 [MNa^+]. − $C_{43}H_{56}N_2O_{16}Si$ (885.0): calcd. C 58.35, H 6.37, N 3.16; found C 58.68, H 6.13, N 3.08.

Allyl O-(3,4,6-Tri-O-acetyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→3)-4,6-O-benzylidene-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (**15b**): The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 1:1) to yield **15b** (0.89 g, 91%) as a white foam. − TLC (petroleum ether/ethyl acetate, 1:1): R_f = 0.23. − $[\alpha]_D$ = −155.0 (*c* = 0.06, chloroform). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.82, 1.88, 1.92, 1.96, 1.99 (5 s, 21 H, 4 CH_3, 3 CH_3CO), 3.45 (m, 1 H, 5b-H), 3.51 (m, 1 H, 5a-H), 3.61 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.4 Hz, 1 H, 4a-H), 3.77 (dd, J_{gem} = $J_{5,6}$ = 10.4 Hz, 1 H, 6a-H), 3.9 (m, 1 H, C*H*HCH=CH_2), 3.92 (m, 1 H, 6b-H), 3.97 (m, 2 H, 2a-H, 2b-H), 4.07 (dd, J_{gem} = 12.6,

$J_{5,6'}$ = 4.2 Hz, 1 H, 6′b-H), 4.18 (dd, J_{gem} = 13.2, J_{vic} = 3.6 Hz, 1 H, CH*H*CH=CH_2), 4.28 (dd, J_{gem} = 10.4, $J_{5,6'}$ = 4.7 Hz, 1 H, 6′a-H), 4.71 (dd, $J_{2,3}$ = $J_{3,4}$ = 9.4 Hz, 1 H, 3a-H), 4.86 (d, $J_{1,2}$ = 8.4 Hz, 1 H, 1a-H), 5.02 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, 1 H, 4b-H), 5.08 (m, 2 H, CH_2CH=C*H*$_2$), 5.17 (d, $J_{1,2}$ = 8.4 Hz, 1 H, 1b-H), 5.39 (dd, $J_{2,3}$ = 10.0, $J_{3,4}$ = 9.5 Hz, 1 H, 3b-H), 5.52 (s, 1 H, C*H*Ph), 5.65 (m, 1 H, CH_2C*H*=CH_2), 7.34, 7.47 (2 m, 5 H, Ph). − ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 54.80 (2a-C, 2b-C), 61.40 (6b-C), 66.30 (5a-C), 68.50 (6a-C, 4b-C), 69.90 (*C*H_2CH=CH_2-C), 70.80 (3b-C), 71.50 (5b-C), 73.60 (3a-C), 79.90 (4a-C), 96.90 (1b-C), 98.00 (1a-C), 101.40 (*C*HPh-C). − FAB-MS (positive mode, NBOH/NaI matrix); *m/z*: 833 [MNa^+], 983 [MNaI]Na^+. − $C_{40}H_{46}N_2O_{16}$ (810.8): calcd. C 59.25, H 5.71, N 3.45; found C 59.48, H 5.56, N 2.88.

Benzyl O-(3,4,6-Tri-O-acetyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→3)-4,6-O-benzylidene-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (**15c**): The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 1.5:1) to yield **15c** (0.92 g, quantitative) as a white foam. − TLC (petroleum ether/ethyl acetate, 1.5:1): R_f = 0.12. − $[\alpha]_D$ = -21.3 (*c* = 0.65, chloroform). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.81, 1.85, 1.86, 1.91, 1.97 (5 s, 21 H, 4 CH_3, 3 CH_3CO), 3.44 (m, 1 H, 5b-H), 3.51 (m, 1 H, 5a-H), 3.61 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.2 Hz, 1 H, 4a-H), 3.79 (dd, J_{gem} = $J_{5,6}$ = 10.2 Hz, 1 H, 6a-H), 3.91(dd, J_{gem} = 12.2, $J_{5,6}$ = 1.9 Hz, 1 H, 6b-H), 3.95−4.08 (m, 2 H, 2a-H, 2b-H), 4.08 (dd, J_{gem} = 12.2, $J_{5,6'}$ = 4.1 Hz, 1 H, 6′b-H), 4.32 (dd, J_{gem} = 10.2, $J_{5,6'}$ = 4.8 Hz, 1 H, 6′a-H), 4.40 (d, J_{gem} = 12.4 Hz, 1 H, C*H*HPh), 4.68 (dd, $J_{2,3}$ = 10.0, $J_{3,4}$ = 9.2 Hz, 1 H, 3a-H), 4.74 (d, J_{gem} = 12.4 Hz, 1 H, CH*H*Ph), 4.84 (d, $J_{1,2}$ = 8.5 Hz, 1 H, 1a-H), 5.00 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.2 Hz, 1 H, 4b-H), 5.11 (d, $J_{1,2}$ = 8.4 Hz, 1 H, 1b-H), 5.37 (dd, $J_{2,3}$ = 10.4 , $J_{3,4}$ = 9.2 Hz, 1 H, 3b-H), 5.52 (s, 1 H, C*H*Ph), 7.06, 7.47 (4 m, 10 H, 2 Ph). − ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 8.79 (4 CH_3-C), 20.39, 20.54, 20.72 (3 *C*H_3CO-C), 54.40 (2b-C), 55.60 (2a-C), 61.60 (6b-C), 66.20 (5a-C), 68.56 (6a-C), 68.62 (4b-C), 70.83 (3b-C), 71.01 (*C*H_2Ph-C), 71.56 (5b-C), 73.68 (3a-C), 79.82 (4a-C), 96.89 (1b-C), 97.89 (1a-C), 101.19 (*C*HPh-C), 126.12−137.23 (2 Ph-C), 169.32, 170.13, 170.76 (3 CH_3*C*O-C, 4 CO-C). − FAB-MS (positive mode, NBOH/NaI matrix); *m/z*: 883 [MNa^+], 1033 [MNaI]Na^+. − $C_{44}H_{48}N_2O_{16}$ (860.8): calcd. C 61.38, H 5.62, N 3.25; found C 61.09, H 5.58, N 3.27.

General Procedure for the Synthesis of Compounds **16b−c:** A solution of **15b,c** (0.29 mmol) in dry dichloromethane (3 ml) was treated with ethanethiol (0.126 g, 2.02 mmol, 0.15 ml) and *p*-TsOH (0.012 g, 0.063 mmol) and stirred at room temp. After 16 h the solution was neutralized with triethylamine and coevaporated with toluene in vacuo.

Allyl O-(3,4,6-Tri-O-acetyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→3)-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (**16b**): The residue was purified by flash chromatography (ethyl acetate/petroleum ether, 2:1) to yield **16b** (0.195 g, 93%) as a colorless oil. − TLC (ethyl acetate/petroleum ether, 2:1): R_f = 0.24. − $[\alpha]_D$ = −31.6 (*c* = 0.55, chloroform). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.84, 1.88, 1.94, 1.98, 2.09 (5 s, 21 H, 4 CH_3, 3 CH_3CO), 3.42 (m, 1 H, 5a-H), 3.48 (dd, $J_{3,4}$ = 8.3, $J_{4,5}$ = 9.5 Hz, 1 H, 4a-H), 3.76 (dd, J_{gem} = 11.8, $J_{5,6}$ = 5.3 Hz, 1 H, 6a-H), 3.79 (m, 1 H, 5b-H), 3.83 (dd, $J_{1,2}$ = 8.5, $J_{2,3}$ = 10.5 Hz, 1 H, 2a-H), 3.91 (m, 2 H, 6′a-H, C*H*HCH=CH_2), 4.01 (dd, $J_{1,2}$ = 8.3, $J_{2,3}$ = 10.5 Hz, 1 H, 2b-H), 4.16 (m, 1 H, CH*H*CH=CH_2), 4.18 (m, 2 H, 6b-H, 6′b-H), 4.43 (dd, $J_{2,3}$ = 10.5, $J_{3,4}$ = 8.3 Hz, 1 H, 3a-H), 4.79 (d, $J_{1,2}$ = 8.5 Hz, 1 H, 1a-H), 5.02 (m, 1 H, 4b-H), 5.05 (m, 2 H, CH_2CH=C*H*$_2$), 5.07 (d, $J_{1,2}$ = 8.3 Hz, 1 H, 1b-H), 5.42 (dd, $J_{2,3}$ = 10.5, $J_{3,4}$ = 9.2 Hz, 1 H, 3b-H), 5.64 (m, 1 H, CH_2C*H*=CH_2). − ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 8.84 (4 CH_3-C), 20.35, 20.53, 20.62 (3 *C*H_3CO-C), 54.3 (2b-C), 54.9 (2a-C), 61.6 (6b-C), 62.9 (6a-C), 68.6 (4b-C), 69.8 (*C*H_2CH=CH_2 -C), 70.38 (3b-C), 70.5 (4a-C), 71.96 (5b-C), 75.3 (5a-C), 79.96 (3a-C), 97.5 (1a-C), 97.73 (1b-C), 117.12 (CH_2CH=*C*H_2-C), 133.512 (CH_2*C*H=CH_2-C), 137.32 (DMM-C), 169.27, 170.60 (3 CH_3*C*O-C, 4 CO-C). − FAB-MS (positive mode, NBOH/NaI matrix); *m/z*: 745 [MNa^+], 895 [MNaI]Na^+. − $C_{33}H_{42}N_2O_{16}$ (722.7): calcd. C 54.84, H 5.85, N 3.87; found C 54.92, H 6.04, N 3.74.

Benzyl O-(3,4,6-Tri-O-acetyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→3)-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (**16c**): The residue was purified by flash chromatography (ethyl acetate/petroleum ether, 1.5:1) to yield **16c** (0.182 g, 80%) as a colorless oil. − TLC (ethyl acetate/petroleum ether, 1.5:1): R_f = 0.1. − $[\alpha]_D$ = −23.7 (*c* = 0.4, chloroform). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.83, 1.86, 1.97, 2.08 (4 s, 21 H, 4 CH_3, 3 CH_3CO), 3.40 (m, 1 H, 5a-H), 3.47 (dd, *J* = 8.4, *J* = 9.5 Hz, 1 H, 4a-H), 3.62 (br.s, 2 H, 2 OH), 3.76 (m, 2 H, 6a-H, 5b-H), 3.84 (dd, $J_{1,2}$ = 8.5, $J_{2,3}$ = 10.5 Hz, 1 H, 2a-H), 3.92 (dd, J_{gem} = 11.8, $J_{5,6}$ = 3.4 Hz, 1 H, 6′a-H), 3.99 (dd, $J_{1,2}$ = 8.4, $J_{2,3}$ = 10.6 Hz, 1 H, 2b-H), 4.15 (m, 1 H, 6b-H, 6′b-H), 4.40 (m, 1 H, 3a-H), 4.41 (d, J_{gem} = 12.4 Hz, 1 H, C*H*HPh), 4.70 (d, J_{gem} = 12.4 Hz, 1 H, CH*H*Ph), 4.78 (d, $J_{1,2}$ = 8.5 Hz, 1 H, 1a-H), 5.00 (m, 1 H, 4b-H), 5.01 (d, $J_{1,2}$ = 8.4 Hz, 1 H, 1b-H), 5.39 (dd, $J_{2,3}$ = 10.6, $J_{3,4}$ = 9.2 Hz, 1 H, 3b-H), 7.06, 7.22 (2 m, 5 H, Ph). − ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 11.9 (4 CH_3-C), 23.45, 23.62, 23.71 (3 *C*H_3CO-C), 57.33 (2b-C), 58.1 (2a-C), 64.71 (6b-C), 66.03 (6a-C), 71.67 (4b-C), 73.44 (3b-C), 73.55 (4a-C), 74.15 (*C*H_2Ph-C), 75.03 (5b-C), 78.41 (5a-C), 82.98 (3a-C), 100.55 (1a-C), 100.79 (1b-C), 130.89−140.29 (Ph-C), 172.36−173.69 (3 CH_3*C*O-C, 4 CO-C). − MALDI-MS (positive mode, DHB/THF matrix); *m/z*: 796 [MNa^+]. − $C_{37}H_{43}N_2O_{16}$ (772.7): calcd. C 57.54, H 5.73, N 3.62; found C 57.40, H 5.58, N 3.56.

Benzyl O-(2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucoranospyyl)-(1→3)-2-acetamido-2-deoxy-4,6-di-O-acetyl-β-D-glucopyranoside (**17c**): A mixture of **16c** (0.09 g, 0.11 mmol), sodium hydroxide (0.2 g, 5.0 mmol) in a dioxan/water mixture (3:1, 8 ml) was stirred at room temp. After 48 h the pH of the solution was adjusted at 5 by N HCl. After 48 h the solution was neutralized with potassium carbonate and dried well in vacuo. The residue was acetylated and worked up as descriebed for **7a−g.** The residue was purified by MPLC (toluene/acetone, 1:1) to yield **17c** (0.057g, 67%) as an amorphous mass. − TLC (toluene/acetone, 1:1): R_f = 0.12. − $[\alpha]_D$ = −9.5 (*c* = 0.2, chloroform). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.88−2.09 (5 s, 21 H, 7 CH_3CO), 3.29−3.33 (m, 1 H, 2a-H), 3.39−3.43 (m, 1 H, 2b-H), 3.63 (m, 1 H, 5b-H), 3.71 (m, 1 H, 5a-H), 4.08 (dd, J_{gem} = 12.2, $J_{5,6}$ = 1.4 Hz, 1 H, 6b-H), 4.12 (dd, J_{gem} = 12.1, $J_{5,6}$ = 1.7 Hz, 1 H, 6a-H), 4.25−4.30 (m, 2 H, 6′b-H, 6′a-H), 4.46 (dd, $J_{2,3}$ = $J_{3,4}$ = 9.6 Hz, 1 H, 3a-H), 4.55 (d, J_{gem} = 11.7 Hz, 1 H, C*H*HPh), 4.84 (d, J_{gem} = 11.7 Hz, 1 H, CH*H*Ph), 4.94 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, 1 H, 4a-H), 4.96 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.7 Hz, 1 H, 4b-H), 5.01 (d, $J_{1,2}$ = 8.1 Hz, 1 H, 1b-H), 5.10 (d, $J_{1,2}$ = 8.1 Hz, 1 H, 1a-H), 5.40 (dd, $J_{2,3}$ = 10.0 , $J_{3,4}$ = 9.7 Hz, 1 H, 3b-H), 5.72 (d, $J_{2,NH}$ = 7.7 Hz, 1 H, 2b-NH), 5.83 (d, $J_{2,NH}$ = 6.8 Hz, 1 H, 2a-NH). − ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 20.62, 20.83, 23.37, 23.7 (7 *C*H_3CO-C), 55.90 (2b-C), 57.69 (2a-C), 61.86 (6b-C), 62.38 (6a-C), 68.12 (4a-C), 68.68 (4b-C), 71.52 (5a-C), 71.52−71.85 (3b-C, 5b-C, *C*H_2Ph-C), 76.35 (3a-C), 97.9 (1b-C), 98.69 (1a-C), 128.0−136.87 (Ph-C), 169.54−171.30 (7 CH_3*C*O-C). − FAB-MS (positive mode, NBOH/NaI matrix); *m/z*: 747 [MNa^+], 897 [MNaI]Na^+. − $C_{33}H_{44}N_2O_{16}$ (724.7): calcd. C 54.68, H 6.11, N 3.86. found C 55.20, H 6.48, N 3.60.

tert-Butyldimethylsilyl O-(2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl)-(1→3)-4,6-O-benzylidene-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (**19**): A solution of **14a** (0.5 g, 1.02 mmol) and **18**[22] (0.55 g, 1.1 mmol) in dry dichloromethane (3 ml) was stirred under nitrogen at room temp. for 10 min while TMSOTf (0.01 M in dichloromethane, 1.2 ml) was added dropwise. After 45 min the reaction mixture was neutralized with triethylamine and dried in vacuo. The residue was purified by flash chromatography (*n*-hexane/ethyl acetate, 2:1) to yield **19** (0.75 g, 89%) as an oil which solidifies on standing. − TLC (petroleum ether/ethyl acetate, 2:1): R_f = 0.24, m.p. 127−129°C. − $[\alpha]_D$ = -12.2 (*c* = 0.5, chloroform). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = −0.07 (s, 3 H, $SiCH_3$), 0.02 (s, 3 H, $SiCH_3$), 0.73 [s, 9 H, $SiC(CH_3)_3$], 1.85, 1.90, 1.91, 1.95, 2.07, 2.14 (6 s, 18 H, 2 CH_3, 4 CH_3CO), 3.51 (m, 1 H, 5b-H), 3.51 (m, 1 H, 5a-H), 3.73 (m, $J_{3,4} = J_{4,5}$ = 9.1 Hz, 1 H, 4a-H), 3.80 (dd, $J_{gem} = J_{5,6}$ = 10.3 Hz, 1 H, 6a-H), 3.84 (dd, J_{gem} = 11.0, $J_{5,6}$ = 5.6 Hz, 1 H, 6b-H), 3.99 (dd, $J_{1,2}$ = 8.1, $J_{2,3}$ = 10.5 Hz, 1 H, 2a-H), 4.03 (dd, J_{gem} = 11.0, $J_{5,6}$ = 8.2 Hz, 1 H, 6′b-H), 4.27 (dd, J_{gem} = 10.3, $J_{5,6'}$ = 4.8 Hz, 1 H, 6′a-H), 4.52 (d, $J_{1,2}$ = 8.0 Hz, 1 H, 1b-H). 4.57 (dd, $J_{2,3}$ = 10.5, $J_{3,4}$ = 9.1 Hz, 1 H, 3a-H), 4.82 (dd, $J_{2,3}$ = 10.3, $J_{3,4}$ = 3.4 Hz, 1 H, 3b-H), 5.02 (dd, $J_{1,2}$ = 8.0, $J_{2,3}$ = 10.3 Hz, 1 H, 2b-H), 5.17 (d, $J_{1,2}$ = 8.1 Hz, 1 H, 1a-H), 5.21 (d, $J_{3,4}$ = 3.4 Hz, 1 H, 4b-H), 5.52 (s, 1 H, C*H*Ph), 7.34−7.46 (m, 5 H, Ph). − ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = −5.64 ($SiCH_3$-C), −4.24 ($SiCH_3$-C), 8.68 (2 CH_3-C), 20.5−20.64 (4 *C*H_3CO-C), 25.26 [$SiC(CH_3)_3$-C], 57.39 (2b-C), 60.89 (6a-C), 66.39 (5b-C), 66.71 (4a-C), 68.74 (6b-C), 69.36 (2a-C), 70.29 (5a-C), 71.05 (3a-C), 75.47 (3b-C), 81.05 (4b-C), 93.85 (1b-C), 100.38 (1a-C), 101.37 (*C*HPh-C), 126.02−129.21 (Ph-C), 137.13 (Ph-C), 169.65, 169.07, 170.31 (4 CH_3CO-C, 2 CO-C). − MALDI-MS (positive mode, DHB/THF matrix); *m/z*: 842 [MNa^+]. − $C_{39}H_{53}NO_{16}Si$ (819.9): calcd. C 57.12, H 6.51, N 1.70; found C 56.74, H 6.69, N 1.71.

O-[(2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl)-(1→3)-4,6-O-benzylidene-2-deoxy-2-dimethylmaleimido-α/β-D-glucopyranosyl] Trichloroacetimidate (**21**): A solution of **19** (0.554 g, 0.67 mmol) in dry THF (3 ml) was desilylated and worked up as described for **11**. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 1:1) to yield **20** (0.396 g, 83%) as a colorless oil. A solution of the afore-mentioned oil (0.384 g, 0.54 mmol) in dry dichloromethane (2 ml) was transformed into the trichloroacetimidate as described for **4**. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 1:1 + 1% triethylamine) to yield **21** (0.368 g, 79%) as a pale yellow foam in the ratio of α/β = 1:4. − TLC (petroleum ether/ethyl acetate, 1:1 + 1% triethylamine): R_f = 0.38. − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.86, 1.90, 1.93, 1.95, 2.08, 2.09 (6 s, 18 H, 2 CH_3, 4 CH_3CO), 3.54−5.57 (m, 14 H), 6.17 (d, $J_{1,2}$ = 3.9 Hz, 0.2 H, $1a_\alpha$-H), 6.26 (d, $J_{1,2}$ = 8.9 Hz, 0.8 H, $1a_\beta$-H), 7.36−7.48 (m, 5 H, Ph), 8.35 (s, 0.2 H, NH_α), 8.61 (s, 0.8 H, NH_β). − FAB-MS (positive mode, NBOH/NaI matrix); *m/z*: 873 [MNa^+], 1023 [MNaI]Na^+. − $C_{35}H_{39}N_2O_{16}Cl_3$ (850.0): calcd. C 49.45, H 4.62, N 3.29; found C 49.10, H 4.83, N 3.37.

Benzyl O-[2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl)-(1→3)-4,6-O-benzylidene-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl]-(1→4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (**22**): A solution of **21** (0.25 g, 0.29 mmol) and **5e** (0.13 g, 0.24 mmol) in dry dichloromethane (2 ml) was stirred under nitrogen at room temp. for 10 min while TMSOTf (0.01 M in dichloromethane, 0.26 ml) was added dropwise. After 35 min the reaction mixture was neutralized with triethylamine and dried in vacuo. The residue was purified by flash chromatography (*n*-hexane/ethyl acetate, 3:2.5) to yield **22** (0.216 g, 73%) as a colorless oil. − TLC (petroleum ether/ethyl acetate, 3:2.5): R_f = 0.4. − $[\alpha]_D$ = −2.8 (*c* = 1.0, chloroform). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.84, 1.89, 1.91, 2.07 (4 s, 18 H, 2 CH_3, 4 CH_3CO), 3.21 (m, 1 H, 5b-H), 3.23 (m, 1 H, 5a-H), 3.39 (dd, J_{gem} = 10.4, $J_{5,6}$ = 4.1 Hz, 1 H, 6a-H), 3.41−3.45 (m, 3 H, 5c-H, 2a-H, 6b-H), 3.51 (dd, $J_{2,3} = J_{3,4}$ = 9.2 Hz, 1 H, 3a-H), 3.56 (dd, J_{gem} = 10.4, $J_{5,6'}$< 1 Hz, 1 H, 6′a-H), 3.63 (dd, $J_{3,4} = J_{4,5}$ = 9.1 Hz, 1 H, 4b-H), 3.83 (dd, J_{gem} = 11.0, $J_{5,6}$ = 5.5 Hz, 1 H, 6c-H), 3.93 (dd, $J_{3,4} = J_{4,5}$ = 9.2 Hz, 1 H, 4a-H), 3.98−4.03 (m, 3 H, 6′b-H, 2b-H, 6′c-H) 4.39 (d, $J_{1,2}$ = 7.7 Hz, 1 H, 1a-H), 4.48 (dd, $J_{2,3}$ = 10.1, $J_{3,4}$ = 9.1 Hz, 1 H, 3b-H), 4.52 (d, $J_{1,2}$ = 7.9 Hz, 1 H, 1c-H), 4.49−4.65 (m, 4 H, 2 CH_2Ph), 4.78 (dd, $J_{2,3}$ = 10.3, $J_{3,4}$ = 2.8 Hz, 1 H, 3c-H), 4.82−4.88 (m, 4 H, 2 CH_2Ph), 4.96 (dd, $J_{1,2}$ = 7.9, $J_{2,3}$ = 10.3 Hz, 1 H, 2c-H), 5.19 (d, $J_{3,4}$ = 2.8 Hz, 1 H, 4c-H), 5.21 (d, $J_{1,2}$ = 8.5 Hz, 1 H, 1b-H), 5.40 (s, 1 H, C*H*Ph),7.2−7.35 (m, 25 H, 5 Ph). − ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 8.81 (2 CH_3-C), 20.49, 20.56, 20.64 (4 *C*H_3CO-C), 55.78 (2b-C), 60.83 (6c-C), 65.84 (5b-C), 66.62 (4c-C), 68.23 (6a-C), 68.56 (6b-C), 69.39 (2c-C), 70.22 (5c-C), 70.92 (*C*H_2Ph-C), 71.02 (3c-C), 73.16 (*C*H_2Ph-C), 74.65 (5a-C), 74.82 (*C*H_2Ph-C), 74.95 (*C*H_2Ph-C), 75.38 (3b-C), 75.8 (4a-C), 80.97 (4b-C), 81.81 (2a-C), 82.76 (3a-C), 97.79 (1b-C), 100.05 (1c-C), 101.38 (*C*HPh-C), 102.33 (1a-C), 126.03−139.05 (5 Ph-C), 169.0−170.29 (4 CH_3CO-C). − FAB-MS (positive mode, NBOH/NaI matrix); *m/z*: 1251 [MNa^+], 1402 [MNaI] Na^+. − $C_{67}H_{73}NO_{21}$ (1228.3): calcd. C 65.51, H 5.99, N 1.14; found C 65.18, H 5.77, N 1.10.

Benzyl O-[2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl)-(1→3)-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl]-(1→4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (**23**): A solution of **22** (0.174 g, 0.141mmol) in dry dichloromethane (5 ml) was debenzylidenated and worked up as described for **16b,c.** The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 1:1) to yield **23** (0.144 g, 89%) as a white foam. − TLC (petroleum ether/ethyl acetate, 1:1): R_f = 0.23. − $[\alpha]_D$ = +1.15 (*c* = 0.26, chloroform). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.85, 1.91, 1.94, 2.04, 2.14, (5 s, 18 H, 2 CH_3, 4 CH_3CO), 3.2 (m, 1 H, 5b-H), 3.28 (m, 1 H, 5a-H), 3.36 (m, 2 H, 6b-H, 6a-H), 3.45 (m, 1 H, 4b-H), 3.46 (m, 1 H, 2a-H), 3.53 (dd, $J_{2,3} = J_{3,4}$ = 9.0 Hz, 1 H, 3a-H), 3.61 (dd, J_{gem} = 10.3 Hz, $J_{5,6}$ < 1 Hz, 1 H, 6′a-H), 3.67 (dd, J_{gem} = 11.9, $J_{5,6'}$ = 3.0 Hz, 1 H, 6′b-H), 3.84 (br.s, 2 H, 2 OH), 3.88 (dd, $J_{3,4} = J_{4,5}$ = 9.0 Hz, 1 H, 4a-H), 3.94 (m, 1 H, 2b-H), 3.95 (m,1 H, 5c-H), 4.11 (m, 2 H, 6c-H, 6′c-H), 4.29 (dd, $J_{2,3}$ = 10.1 , $J_{3,4}$ = 9.0 Hz, 1 H, 3b-H), 4.34 (d, $J_{1,2}$ = 8.0 Hz, 1 H, 1c-H), 4.42 (d, $J_{1,2}$ = 7.7 Hz, 1 H, 1a-H), 4.55−4.78 (m, 6 H, 3 CH_2Ph), 4.87−4.92 (m, 3 H, 3c-H, CH_2Ph)), 5.04 (d, $J_{1,2}$ = 8.4 Hz, 1 H, 1b-H), 5.14 (dd, $J_{1,2}$ = 8.0 , $J_{2,3}$ = 10.4 Hz, 1 H, 2c-H), 5.32 (d, $J_{3,4}$ = 5.4 Hz, 1 H, 4c-H), 7.25−7.36 (m, 20 H, 4 Ph). − FAB-MS (positive mode-NBOH/NaI matrix); *m/z*: 1162 [MNa^+], 1178 [MK^+], 1314 [MNaI]Na^+. − $C_{60}H_{69}NO_{21}$ (1140.2): calcd. C 63.20, H 6.10, N 1.22; found C 63.00, H 6.10, N 1.13.

Benzyl 2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl-(1→3)-(2-acetamido-4,6-di-O-acetyl-2-deoxy-β-D-glucopyranosyl)-(1→4)-2,3,6 -tri-O-benzyl-β-D-glucopyranoside (**24**): Compound **23** (0.122 mg, 0.107 μmol) was deprotected and worked up as described for **7a−g** by Method A. The residue was purified by MPLC (toluene/acetone, 3.5:1) to yield **24** (0.084 g, 68%) as a colorless oil. − TLC (toluene/acetone, 3.5:1): R_f = 0.24. − $[\alpha]_D$ = -11.6 (*c* = 0.5, chloroform). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.83, 1.91, 1.97, 2.00, 2.03, 2.08, 2.14 (7 s, 21 H, 7 CH_3CO), 3.35−3.48 (m, 4 H, 5a-H, 2b-H, 5b-H, 2a-H), 3.54 (dd, $J_{1,2} = J_{2,3}$ = 9.0 Hz, 1 H, 3a-H), 3.68 (br.s, 2 H, 6a-H, 6′a-H), 3.87 (m, 1 H, 6b-H), 3.88 (m, 1 H, 5c-H), 3.93 (dd, $J_{3,4} = J_{4,5}$ = 9.0 Hz, 1 H, 4a-H), 4.05−4.11 (m, 3 H, 6′b-H, 3b-H, 6c-H), 4.16 (dd, J_{gem} = 11.2, $J_{5,6'}$ = 6.5 Hz, 1 H, 6′c-H), 4.4 (d, $J_{1,2}$ = 7.7 Hz, 1 H, 1c-H), 4.47 (d, $J_{1,2}$ = 7.7 Hz, 1 H, 1a-H), 4.51 (d, J_{gem} = 12.0 Hz, 1 H, C*H*HPh), 4.64 (d, J_{gem} = 10.7

Hz, 1 H, C*H*HPh), 4.65 (d, J_{gem} = 12.0 Hz, 1 H, C*H*HPh), 4.73 (d, J_{gem} = 11.6 Hz, 1 H, C*H*HPh), 4.75 (d, $J_{1,2}$ = 8.3 Hz, 1 H, 1b-H), 4.79 (d, 2 H, 4b-H, CH*H*Ph), 4.83−4.84 (m, 2 H, NH, CH*H*Ph), 4.94−4.95 (m, 3 H, CH_2Ph, 3c-H), 5.01 (dd, $J_{1,2}$ = 7.7, $J_{2,3}$ = 10.2 Hz, 1 H, 2c-H), 5.35 (d, $J_{3,4}$ = $J_{4,5}$ = 2.8 Hz, 1 H, 4c-H), 7.19−7.45 (m, 20 H, 4 Ph). − ^{13}C NMR (150.9 MHz, $CDCl_3$): δ = 57.50 (2b-C), 61.60 (6c-C), 62.30 (6b-C), 67.10 (4c-C), 68.40 (6a-C), 69.40 (4b-C, 2c-C), 70.90 (5c-C), 71.20 (3c-C, CH_2Ph-C), 71.50 (5b-C), 73.80 (2 CH_2Ph-C), 74.60 (5a-C), 75.20 (CH_2Ph-C), 76.80 (4a-C), 77.20 (3b-C), 81.90 (2a-C), 83.20 (3a-C), 99.50 (1b-C), 100.90 (1c-C), 102.70 (1a-C). − FAB-MS (positive mode, NBOH/NaI matrix); *m/z*: 1158 [MH^+], 1180 [MNa^+], 1332 [MNaI]Na^+. − $C_{60}H_{71}NO_{22}$ (1158.2): calcd. C 62.21, H 6.17, N 1.20; found C 61.89, H 6.36, N 1.12.

[1] R. R. Schmidt, W. Kinzy, *Adv. Carbohydr. Chem. Biochem.* **1994**, *50*, 21−123. − H. G. Garg, K. von dem Bruch, H. Kunz, *ibid.* **1994**, *50*, 227−310; and refereces therein.

[2] R. U. Lemieux, T. Takeda, B. Y. Chung, *ACS Symp. Ser.* **1976**, *39*, 90−115. − J. Banoub, P. Boullanger, D. Lafont, *Chem. Rev.* **1992**, *92*, 1167−1195. − D. Lafont, P. Boullanger, *J. Carbohydr. Chem.* **1992**, *11*, 567−586; and references therein.

[3] J. S. Debenham, R. Madsen, C. Roberts, B. Fraser-Reid, *J. Am Chem. Soc.* **1995**, *117*, 3302−3303. − J. Debenham, R. Rodebough, B. Fraser-Reid, *Liebigs Ann.* **1997**, 791−802; and references therein.

[4] J. C. Castro-Palomino, R. R. Schmidt, *Tetrahedron Lett.* **1995**, *36*, 5343−5346. − L. Lay, L. Manzoni, R. R. Schmidt, manuscript in preparation.

[5] E. Meinjohanns, M. Meldal, H. Paulsen, K. Bock, *J. Chem. Soc., Perkin Trans. I* **1995**, 405−415. − K. J. Jensen, P. R. Hansen, D. Venugopal, G. Barany, *J. Am. Chem. Soc.* **1996**, *118*, 3148−3155.

[6] J. C. Castro-Palomino, R. R. Schmidt, *Tetrahedron Lett.* **1995**, *36*, 6871−6874.

[7] G. Blatter, J.-M. Beau, J. −C. Jacquinet, *Carbohydr. Res.* **1994**, *260*, 189−202. − A. Gerull, R. R. Schmidt, manuscript in preparation.

[8] M. Imoto, H. Yoshimura, T. Shimamoto, N. Skaguchi, S. Kusumoto, T. Shiba, *Bull Chem. Soc. Jpn.* **1987**, 2205−2214. − H. Paulsen, C. Krogmann, *Liebigs Ann. Chem.* **1989**, 1203−1213. − H. Paulsen B. Helpap, *Carbohydr. Res.* **1991**, *216*, 289−313. − U. Ellervik, G. Magnusson, *Carbohydr. Res.* **1996**, *280*, 251−260. − D. Qiu, R. R. Koganty, *Tetrahedron Lett.* **1997**, *38*, 45−48. − K. G. I. Nilsson, *Tetrahedron Lett.* **1997**, *38*, 135−136.

[9] W. Dullenkopf, J. C. Castro-Palomino, L. Manzoni, R. R. Schmidt, *Carbohydr. Res.* **1996**, *296*, 135−147. − L. Manzoni, L. Lay, R. R. Schmidt, *J. Carbohydr. Chem.*, in print.

[10] R. U. Lemieux, R. M. Ratcliffe, *Can. J. Chem.* **1979**, *54*, 1244−1251.

[11] R. R. Schmidt, *Angew. Chem.* **1986, 98**, 213−236; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 212−235. − H. Paulsen, *Angew. Chem.* **1982**, *94*, 184−201; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 155−173; *Chem. Soc. Rev.* **1984**, *15*.

[12] A. Toepfer, W. Kinzy, R. R. Schmidt, *Liebigs Ann. Chem.* **1994**, 449−464. − A. Toepfer, R. R. Schmidt, *Tetrahedron Lett.* **1992**, *33*, 5161−5164. − G. Hummel, R. R. Schmidt, *Tetrahedron Lett.* **1997**, *38*, 1173−1176; and references therein.

[13] H. B. F. Dixon, R. N. Perham, *Biochem. J.* **1968**, *109*, 312−314. − A. J. Kirby, P. W. Lancaster, *J. Chem. Soc., Perkin II Trans.* **1972**, 1206−1214. − A. J. Kirby, *Acc. Chem. Res.* **1997**, *30*, 290−296.

[14] For applications in proteins, see: F. Wieland, L. Renner, C. Vorfürth, F. Lynen, *Eur. J. Biochem.* **1979**, *94*, 189−197. − T. Hirano, T. Todoroki, S. Kato, H. Yamamoto, P. Caliceti, F. Veronese, H. Maeda, S. Ohashi, *J. Controlled Release* **1994**, *28*, 203−209 (*Chem. Abstr.* **1994**, *121*, 103050).

[15] This work is part of the Ph.D. Thesis of M. R. E. A. .

[16] DMMA is commercially available.

[17] For the preparation of the acceptor see: **5d** [17a] A. Liptak, I. Jodal, P. Nanasi, *Carbohydr. Res.* **1975**, *44*, 1−11. − **5e** [17b] J.-M. Petit, S.-C. Jaquinet, P. Sinaÿ, *Carbohydr. Res.* **1980**, *82*, 130−134. − **5f** [17c] T. Ogawa, T. Nukuda, *Carbohydr. Res.* **1985**, *136*, 135−152. − **5g** [17d] K. H. Jung, M. Hoch, R. R. Schmidt, *Liebigs Ann. Chem.* **1989**, 1099−1106. − U. Greilich, R. Brescello, K.-H. Jung, R. R. Schmidt, *Liebigs Ann.* **1996**, 663−672.

[18] Obviously, *O*-silyl protective groups are affected under these cleavage conditions.

[19] Some compounds are known: **7a** [19a] P. Boullanger, Y. Chevalier, M.-C. Croizier, D. Lafont, M.-R. Sancho, *Carbohydr. Res.* **1995**, *278*, 91−101. − **7b,c** [19b] C. G. Sowell, M. T. Livesay, D. A. Johnson, *Tetrahedron Lett.* **1996**, *37*, 609−610. − **7e** [19c] X. Qian, O. Hindsgaul, *Chem. Commun.* **1997**, 1059−1060. − **7f** [19d] H. Paulsen, B. Helpap, *Carbohydr. Res.* **1991**, *216*, 289−313. − **7g-4b**,**3b** [19e] H. Paulsen, D. Hadamczyk, W. Kutschker, A. Bünsch, *Liebigs Ann. Chem.* **1985**, 129−141.

[20] For previous applications of this procedure, see: S. Gomez-Bujedo, I. Robina, E. Lopez-Barba, J. Fuentes, *8th European Carbohydrate Symposium*, July 1995, Sevilla/Spain: Abstract A-57. − T. K. Park, I. J. Kim, S. Hu, M. T. Bilodeau, J. T. Randolph, O. Kwon, S. J. Danishefsky, *J. Am. Chem. Soc.* **1996**, *118*, 11488−11500. − M. Grathwohl, Diplomarbeit, Universität Konstanz, **1997**.

[21] D. R. Williams, S.-Y. Sit, *J. Am. Chem. Soc.* **1984**, *106*, 2949−2954.

[22] R. R. Schmidt, J. Michel, M. Roos, *Liebigs Ann. Chem.* **1984**, 1343−1357. − P. H. Amvam-Zollo, P. Sinaÿ, *Carbohydr. Res.* **1986**, *150*, 199−212.

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