# New Diacylamino Protecting Groups for Glucosamine

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*Dedicated to Professor András Liptak on the occasion of his 70th birthday*

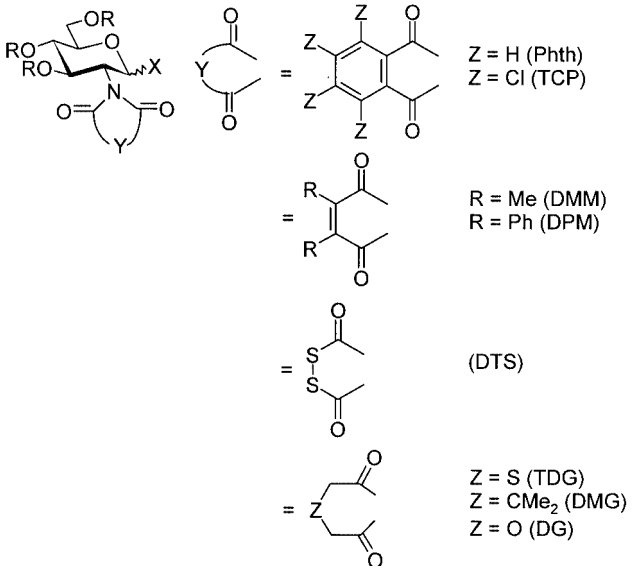
**Keywords:** Carbohydrates / Protecting groups / Amino sugars / Glycosylation / Trichloroacetimidates

Glucosamine was transformed into *N*-diphenylmaleoyl (DPM), *N*-(3,3-dimethylglutaryl) (DMG), and *N*-diglycolyl (DG) derivatives which furnished *O*-acetyl-protected *O*-glycosyl trichloroacetimidates **3**, **12**, and **20**, respectively, as glycosyl donors. Their reactions with various acceptors **4** in the presence of TMSOTf as catalyst afforded the corresponding β-glycosides **5a–c**, **13a–e**, and **21a**,**d**,**f**,**g** generally in high yields. Investigations into the cleavage of the *N*-protecting groups led to good results for the DPM and DG groups. 3-*O*-Unprotected glucosamine derivative **24** with *N*-DG protection also served well as an acceptor, as shown in its reaction with galactosyl donor **25** which led to disaccharide **26** in very high yield.



## Introduction

An important constituent of glycoconjugates is D-glucosamine which is mainly found as an *N*-acetyl derivative in β-glycosidic linkages.[1,2] Glycoside bond formation with donors derived from *N*-acetylglucosamine (GlcNAc) generally occurs by neighbouring-group participation to give a 1,3-oxazolinium intermediate,[3,4] that is, a cyclic imidate, that exhibits only weak glycosyl donor properties. In addition, *O*-glycosylation of acetamido groups, that is, intermolecular imidate formation, has also been observed as a side-reaction.[5] Therefore, the replacement of the *N*-acetyl group by strongly electron-withdrawing groups, such as the trifluoroacetyl, trichloroacetyl,[6,7] and trichloroethoxycarbonyl groups,[8–12] respectively, have been investigated in order to avoid the formation of stable cyclic imidate intermediates which impede glycoside bond formation. However, similar to the *N*-acetyl group, the structural assignment of these groups by NMR spectroscopy can be hampered when rotation around the amidic CN bond is hindered. Hence, $C_2$-symmetric *N*,*N*-diacyl compounds should be ideal amino-protecting groups, for example, two noncyclic *N*-acyl groups[13] or cyclic *N*,*N*-diacyl groups such as phthaloyl (Phth),[1–4] tetrachlorophthaloyl (TCP),[14,15] dithiasuccinyl (DTS),[16] dimethylmaleoyl (DMM),[17] and thiodiglycolyl (TDG) groups.[18] Indeed, formation of stable imidate intermediates and difficulties in structural assignment can be avoided by using such protecting groups (Scheme 1).




Scheme 1. Diacylamino protecting groups.

In addition, owing to the strong electron-withdrawing character of the nitrogen substituents, these glucosamine derivatives also exhibit increased glycosylic donor properties. The 2-azido group has also gained widespread use in this regard[1–4,19–21] because, particularly in combination with the nitrile effect, high β-selectivities can also be obtained.[1,22] However, all these groups also exhibit some disadvantages which have been discussed in detail previously.[12,14] Therefore, we have turned our attention to the use of diphenylmaleoyl (DPM), 3,3-dimethylglutaryl (DMG), and diglycolyl (DG) groups as amino protecting

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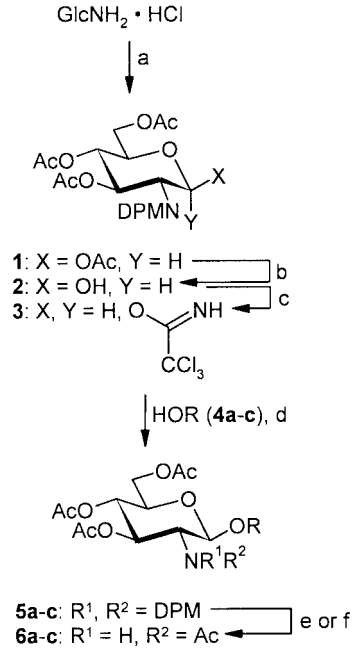
groups (Scheme 1) because it was hoped that even better properties than those found for the DMM group would be found; this group also proved to be successful in several complex oligosaccharide solid-support syntheses.[23,24]

## Results and Discussion

### The DPM Group

The fluorescent DPM group was investigated because it was expected that mild conditions would be sufficient for its attachment and cleavage, as observed for the DMM group; in addition, the presence and absence of this group can be readily monitored by fluorescence spectroscopy. Zehavi[25] used this group in 1976 as a protecting group for amino functions in sugars and steroids. Glycosylation reactions were studied with only methanol as an acceptor and deprotection was effected by ethanolic hydrazine. The *N*-DPM-protected per-*O*-acetyl glucosamine **1** was readily obtained from glucosamine by treatment with DPM anhydride (DPMA) and acetic anhydride in pyridine (Scheme 2). Chemoselective 1-*O*-deacetylation with hydrazinium acetate in DMF (→ **2**) and then reaction with trichloroacetonitrile in the presence of DBU as base afforded the desired trichloroacetimidate **3** as glucosyl donor.




Scheme 2. Synthesis and reactions of DPM-protected glycosyl donor **3**. Reagents and conditions: (a) NaOMe, MeOH; DPMA, $Ac_2O$, Pyr (35%); (b) $N_2H_4$·HOAc (94%); (c) $CCl_3CN$, DBU (63%); (d) TMSOTf (0.01 equiv.), $CH_2Cl_2$ (**5a**: 68%; **5b**: 68%; **5c**: 68%); (e) $N_2H_4$·$H_2O$, EtOH, reflux; $Ac_2O$, Pyr (**6a**: 68%; **6b**: 90%; **6c**: 63%); (f) NaOH, dioxane/$H_2O$; HCl (pH 5.0); $Ac_2O$, Pyr (**6c**: 22%).

The glycosylation of known 6-*O*-, 3-*O*-, and 4-*O*-unprotected sugars **4a**,[26] **4b**,[27] and **4c**[28] as acceptors (Figure 1) with **3** as donor in the presence of TMSOTf as catalyst in dichloromethane led exclusively to β-linked glycosides **5a**–**c** in satisfactory yields. Owing to the fluorescent properties of the products, monitoring of the reaction by TLC was convenient. The DPM group in **5a**–**c** could readily be removed with hydrazine hydrate in refluxing ethanol and subsequent *N*,*O*-acetylation in acetic anhydride/pyridine gave the known target molecules **6a**,[12] **6b**,[17] and **6c**.[29] However, the much milder ring-opening of the diphenylmaleimido ring with NaOH followed by removal of DPMA by treatment with acid at pH ≈ 5, a method that works very well with the DMM group,[17] gave only modest results; for instance, with compound **5c**, compound **6c** was obtained in only 22% yield. Hence, the two methyl groups in the DMM moiety seem to support ring–chain tautomerism in favour of the amide hemiacetal required for acid-supported DMMA cleavage more strongly than the two phenyl groups in the DPM moiety. Therefore, besides the fluorescent properties, the DPM group exhibits no advantages over the DMM group in terms of the ease of attachment, glycosylation yields, or ease of cleavage.

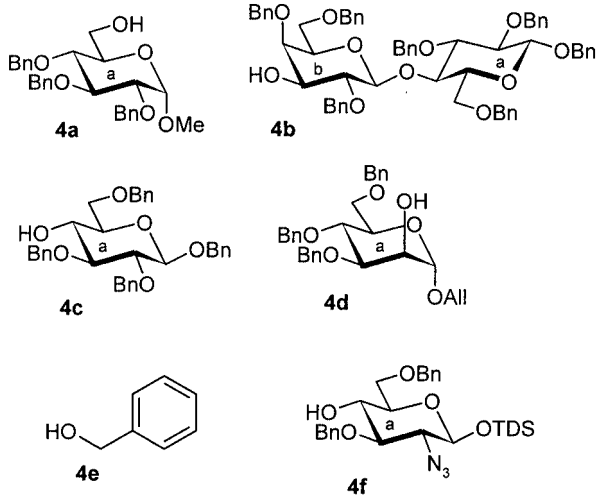
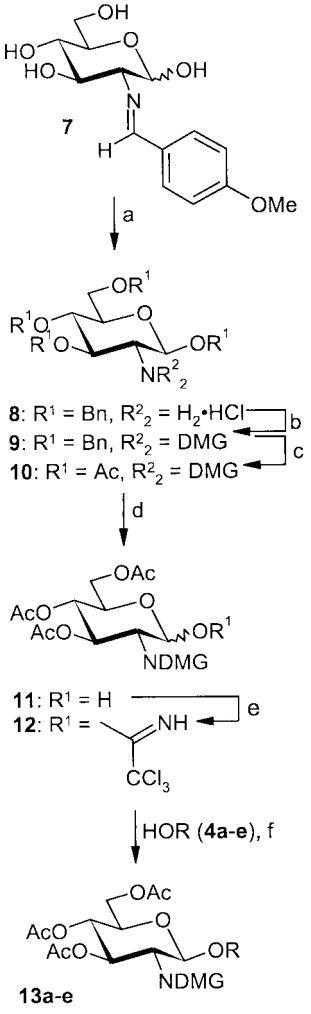



Figure 1. HOR acceptors used in reactions with glycosyl donors **3**, **12**, and **20**.

### The DMG Group

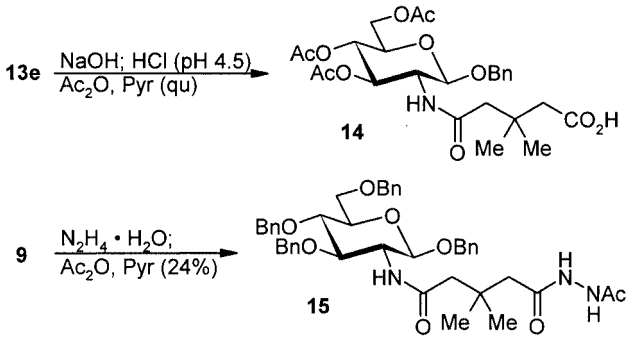
Amino protecting groups derived from glutaric acid have been employed in neither oligosaccharide nor peptide synthesis. 3,3-Dialkylglutaryl derivatives should be reasonable derivatives because one of the carbonyl groups provides anchimeric assistance for the β-glycosidic linkage and, similar to the DMM group, convenient cleavage by base and then acid treatment should be supported by the geminal dialkyl effect[30] of the two alkyl substituents at the 3-position. Therefore, commercially available 3,3-dimethylglutaric (DMG) anhydride was chosen although attachment of this group to glucosamine turned out to be more difficult than the attachment of DPM. Good results were obtained in the reaction of *N*-(4-methoxybenzylidene)glucosamine (**7**)[31] with benzyl bromide and sodium hydride in DMF followed by hydrolytic removal of the *N*-protecting group to afford the known amino derivative **8** (Scheme 3).[32]




Scheme 3. Synthesis and reactions of DMG-protected glycosyl donor **12**. Reagents and conditions: (a) NaH, BnBr, DMF (82%); 5 N HCl, $Me_2CO$; (b) DMGA, $Ac_2O$, Pyr (quant.); (c) Pd/C, $H_2$; $Ac_2O$, Pyr (98%); (d) $N_2H_4$·HOAc (99%); (e) $CCl_3CN$, DBU (80%); (f) TMSOTf (0.01 equiv.), $CH_2Cl_2$ (**13a**: 90%; **13b**: 96%; **13c**: 81%; **13d**: 92%; **13e**: 93%).

Then reaction with DMGA in pyridine/acetic anhydride furnished the desired *N*-DMG-protected glucosamine **9**. Hydrogenolytic *O*-debenzylation and *O*-acetylation led to per-*O*-acetyl derivative **10**. Selective removal of the 1-*O*-acetyl group with hydrazinium acetate (→ **11**) and base-catalyzed reaction with trichloroacetonitrile led to trichloroacetimidate **12**. Glycosylation of acceptors **4a**–**e**[27–29,33] with **12** under standard conditions, that is, trimethylsilyl trifluoromethanesulfonate catalysis in dichloromethane, afforded the desired β-glycosides in almost quantitative yields (Scheme 4), thus illustrating the power of this glycosyl donor. However, unexpectedly, the cleavage of the DMG group turned out to be very difficult; neither hydrazine in ethanol nor base and ensuing acid treatment was successful. For instance, the reaction of **13e** with base and ensuing acid treatment led only to ring-opening, which, after acetylation, afforded compound **14** as the product (Scheme 4). Even heating of *O*-benzyl-protected **9** with hydrazine hydrate afforded only the ring-opened product, which, after acetylation, yielded compound **15**. Hence, anchimeric assistance of the DMG group in the glycosylation step seems to be optimal, however the cleavage reaction needs to be improved.




Scheme 4. Cleavage reactions of **9** and **13e**.

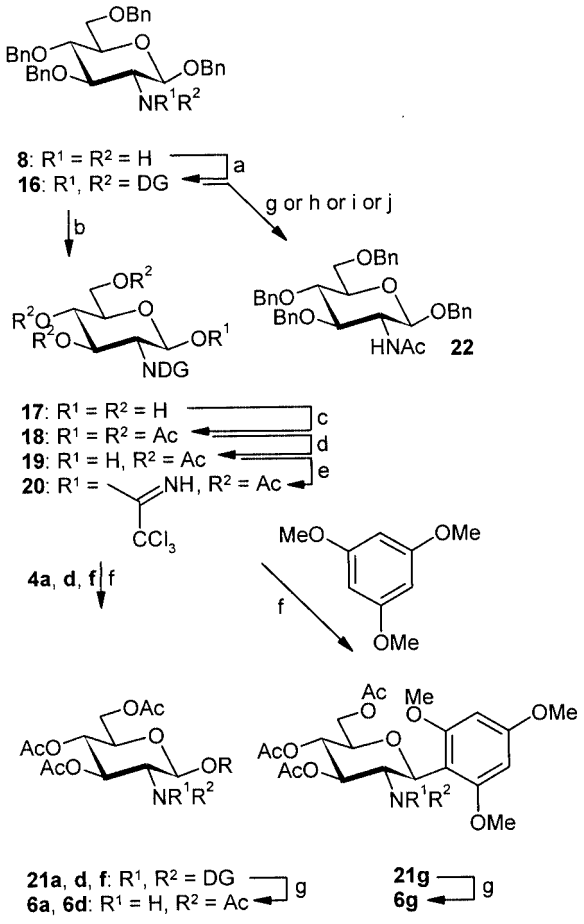
## The DG Group

In order to maintain the excellent anchimeric assistance of a six-membered cyclic imido group at the 2-position of amino sugars in glycosylation reactions yet improve its cleavability, the dimethylmethylene group in DMG was replaced by an electron-withdrawing oxygen atom to give the diglycolyl (DG) group as the amino protecting group. Clearly, the TDG group is closely related to the DG group, however, it lacks the electron-withdrawing effect of the oxygen atom and the presence of the sulfur atom often interferes with oxidative or hydrogenolytic removal of protecting groups, thus limiting the versatility of this group. The DG group was readily attached starting from **8** or its hydrochloride. Heating with diglycolyl anhydride (DGA) in acetic anhydride/pyridine afforded *N*-DG-protected derivative **16** (Scheme 5).

Hydrogenolytic *O*-debenzylation (→ **17**), *O*-acetylation (→ **18**), selective 1-*O*-deacetylation, and then treatment with trichloroacetonitrile in the presence of DBU as base afforded the desired trichloroacetimidate **20** in high overall yield. Glycosylation of acceptors **4a**,[26] **4d**,[33] and **4f**[34] with **20** under standard conditions furnished very good glycosylation results and only the β-anomers **21a**, **21d**, and **21f** were obtained, thus illustrating the excellent anchimeric assistance provided by the DG group. Similarly, with 1,3,5-trimethoxybenzene as acceptor *C*-glycoside **21g** was obtained in very good yield. Deprotection of intermediate **16** with KOH in refluxing ethanol, NaOBu in butyl alcohol, hydrazine hydrate, and hydrazine in refluxing ethanol followed by *N*-acetylation afforded *N*-acetyl-protected derivative **22**[35,36] in 82, 69, 38, and 3% yields, respectively. Hence, deprotection of **21a**, **21d**, and **21g** was carried out using the first method, providing, after acetylation, target molecules **6a**,[12] **6d**,[17] and **6g**[37] in very good yields.

This success encouraged us to investigate the acceptor properties of a DG-containing acceptor. Because the hydroxy group next to the DG-protected amino group is par-

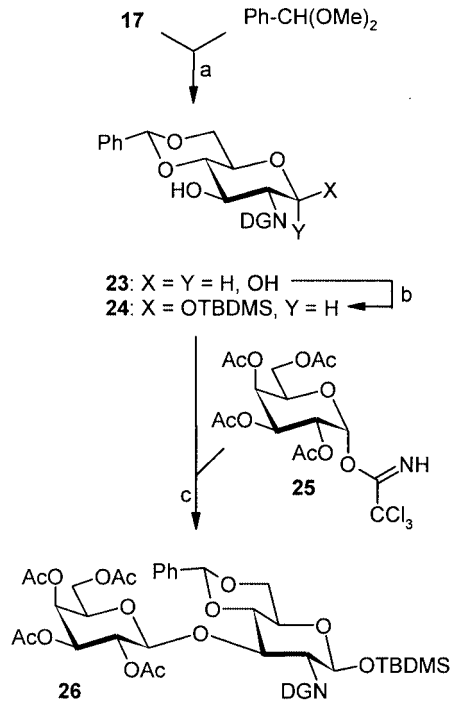



Scheme 5. Synthesis and reactions of DG-protected glycosyl donor **20**. Reagents and conditions: (a) DGA, Pyr, $Ac_2O$ (quant.); (b) Pd/C, $H_2$ (quant.); (c) $Ac_2O$, Pyr (98%); (d) $N_2H_4$·HOAc (77%); (e) $CCl_3CN$, DBU (80%); (f) TMSOTf (0.01 equiv.), $CH_2Cl_2$ (**21a**: quant.; **21d**: 94%; **21f**: 86%; **21g**: 86%); (g) KOH, EtOH, reflux; $Ac_2O$, Pyr (**6a**: 83%; **6d**: 83%; **6g**: 76%; **22**: 82%); (h) NaOBu, BuOH, reflux; $Ac_2O$, Pyr (69%); (i) $N_2H_4$·$H_2O$, reflux; $Ac_2O$, Pyr (38%); (j) $N_2H_4$·$H_2O$, EtOH, reflux; $Ac_2O$, Pyr (3%).

ticularly affected by its proximity to the diacyl moiety, intermediate **17** was transformed into 3-*O*-unprotected acceptor **24** by treatment with benzylidene acetal in the presence of *p*-toluenesulfonic acid as catalyst (→ **23**) followed by anomeric *O*-silylation with *tert*-butyldimethylsilyl (TBDMS) chloride and imidazole to furnish only the β-isomer **24** (Scheme 6). Reaction of **24** with known galactosyl donor **25**[38,39] afforded under standard conditions the isolactosamine derivative **26** in excellent yield. Thus the versatility of the DG protecting group has been further established.

## Conclusions

In conclusion, the use of DPM, DMG, and DG as amino protecting groups of glucosamine gave varying results. In contrast to the dimethylmaleoyl (DMM) group, the fluorescent DPM group did not undergo either base- or mild acid-catalyzed cleavage in good yield. The excellent glycosylation yields observed for the DMG group were also obtained




Scheme 6. Reaction of galactosyl donor **25** with acceptor **24**. Reagents and conditions: (a) $PhCH(OMe)_2$, *p*TsOH, $CH_3CN$/DMF (55%); (b) TBDMS-Cl, imidazole, $CH_2Cl_2$ (79%); (c) TMSOTf (0.01 equiv.), $CH_2Cl_2$, room temp. (91%).

with the DG group, which could also be removed under basic conditions in high yields. In addition, the DG group is compatible with glycosylation at a vicinal hydroxy group which functions as an accepting group in glycosylation reactions. Hence, the DG group is at least as competitive as or even superior to the standard anchimerically assisting amino protecting groups.

## Experimental Section

**General Remarks:** Solvents were purified in the usual way. Melting points were determined with a Gallenkamp apparatus, values were not corrected. TLC was performed on plastic plates coated with Silica Gel 60 $F_{254}$ (E. Merck, layer thickness = 0.2 mm). Detection was achieved by treatment with a solution of ammonium molybdate (20 g) and cerium(IV) sulfate (0.4 g) in 10% $H_2SO_4$ (400 mL) 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; Korngröße 15–25 μm) and detection was carried out with a differential refractometer. Optical rotations were determined at 20 °C 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 the internal standard. The $^1H$ NMR spectral assignments were based on chemical shift correlation (DQF COSY) and rotating frame nuclear Overhauser effect spectroscopy (ROESY). The $^{13}C$ NMR spectral assignments were based on carbon–proton shift-correlation heteronuclear multiple quantum coherence (HMQC). MS spectra were recorded with a MALDI-Kompakt (Kratos) spectrometer. Microanalyses were performed at the Microanalysis unit at the Fachbereich Chemie, Universität Konstanz.

**1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-diphenylmaleimido-β-D-glucopyranose (1):** D-glucosamine hydrochloride (1.0 g, 4.63 mmol) was stirred at room temp. with a solution of NaOMe (1.0 M, 4.63 mL) for 10 min and then treated with diphenylmaleic anhydride (0.58 g, 2.315 mmol). After 20 min the reaction mixture was treated with triethylamine (0.5 mL, 4.96 mmol) and again with diphenylmaleic anhydride (0.58 g, 2.315 mmol), then warmed to 60 °C for 75 min. The solvent was evaporated in vacuo and the residue dried well. The residue was stirred with pyridine/acetic anhydride (2:1, 30 mL) at room temp., then coevaporated with toluene in vacuo after 20 h, and purified by flash chromatography (petroleum ether/ethyl acetate, 2.5:1) to yield **1** (0.930 g, 35%) as a fluorescent yellow foam. TLC (petroleum ether/ethyl acetate, 2.5:1): $R_f$ = 0.2. $[\alpha]_D$ = +24.9 ($c$ = 1.05, $CHCl_3$). $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.94, 2.05, 2.10, 2.12 (4 s, 12 H, 4 $CH_3CO$), 3.99 (m, 1 H, 5-H), 4.14 (dd, $J_{6,6'}$ = 12.5, $J_{5,6}$ = 1.9 Hz, 1 H, 6-H), 4.38 (dd, $J_{6,6'}$ = 12.5, $J_{5,6'}$ = 4.4 Hz, 1 H, 6′-H), 4.41 (dd, $J_{1,2}$ = 8.9, $J_{2,3}$ = 10.3 Hz, 1 H, 2-H), 5.23 (dd, $J_{3,4}$ = 9.3, $J_{4,5}$ = 9.8 Hz, 1 H, 4-H), 5.84 (dd, $J_{2,3}$ = 10.3, $J_{3,4}$ = 9.3 Hz, 1 H, 3-H), 6.47 (d, $J_{1,2}$ = 8.9 Hz, 1 H, 1-H), 7.32–7.48 (m, 10 H, 2 Ph) ppm. MALDI MS (positive ion mode, DHB–THF matrix): $m/z$ = 601.8 $[M + Na]^+$, 617.7 $[M + K]^+$. $C_{30}H_{29}NO_{11}$ (579.6): C 62.17, H 5.04, N 2.41; found C 61.73, H 5.09, N 2.43.

**3,4,6-Tri-*O*-acetyl-2-deoxy-2-diphenylmaleimido-β-D-glucopyranose (2):** A mixture of **1** (0.879 g, 1.5 mmol) and hydrazine acetate (0.17 g, 1.8 mmol) in dry DMF (3 mL) was stirred at room temp. After 2 h the mixture was diluted with ethyl acetate (50 mL) and treated with saturated $NaHCO_3$ solution (3 mL). The organic layer was separated and the aqueous layer extracted with ethyl acetate (10 mL); the combined organic layers were dried with $MgSO_4$, filtered, and the solvents evaporated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 3:2) to yield **2** (0.773 g, 94%) as a yellow fluorescent foam. TLC (petroleum ether/ethyl acetate, 3:2): $R_f$ = 0.19. $[\alpha]_D$ = +69.0 ($c$ = 0.2, $CHCl_3$). $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.94, 2.04, 2.05 (3 s, 9 H, 3 $CH_3CO$), 3.58 (br. s, 1 H, OH), 3.88 (m, 1 H, 5-H), 4.10–4.31 (m, 3 H, 6′-H, 2-H, 6-H), 5.19 (dd, $J_{3,4}$ = 9.2, $J_{4,5}$ = 9.8 Hz, 1 H, 4-H), 5.57 (d, $J_{1,2}$ = 8.3 Hz, 1 H, 1-H), 5.79 (dd, $J_{2,3}$ = 10.6, $J_{3,4}$ = 9.2 Hz, 1 H, 3-H), 7.31–7.47 (m, 10 H, 2 Ph) ppm. MALDI MS (positive ion mode, DHB–THF matrix): $m/z$ = 559.8 $[M + Na]^+$, 575.8 $[M + K]^+$. $C_{28}H_{27}NO_{10}$ (537.5): C 62.56, H 5.06; N 2.60; found C 62.12, H 5.21, N 2.61.

***O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-diphenylmaleimido-D-glucopyranosyl) Trichloroacetimidate (3):** A mixture of **2** (0.66 g, 1.13 mmol) and trichloroacetonitrile (0.8 mL, 7.9 mmol) in dry dichloromethane (3 mL) was stirred at room temp. while DBU (0.14 mL, 0.93 mmol) was added dropwise. After 4 h the solvent was evaporated in vacuo and the residue purified by flash chromatography (petroleum ether/ethyl acetate, 1:1 + 1% $Et_3N$) to yield **3** (0.496 g, 63%) as a fluorescent green foam in an α/β ratio of 1:8. TLC (petroleum ether/ethyl acetate, 1:1 + 1% $Et_3N$): $R_f$ = 0.73 (α-form), 0.64 (β-form). $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.94–2.13 (sev. s, 9 H, 3 $CH_3CO$), 4.01–4.49 (m, 3 H, 6′-H, 6-H, 5-H), 4.57 (dd, $J_{1,2}$ = 8.9 Hz, $J_{2,3}$ = 10.7 Hz, 0.89 H, 2β-H), 4.73 (dd, $J_{1,2}$ = 3.7, $J_{2,3}$ = 11.5 Hz, 0.11 H, 2α-H), 5.15–5.37 (m, 1 H, 4-H), 5.79–5.94 (m, 1 H, 3-H), 6.42 (d, $J_{1,2}$ = 3.7 Hz, 0.11 H, 1α-H), 6.52 (d, $J_{1,2}$ = 8.9 Hz, 0.89 H, 1β-H), 7.26–7.47 (m, 10 H, 2 Ph) ppm. $C_{30}H_{27}Cl_3N_2O_{10}$ (681.9): C 52.84, H 3.99; N. 4.10; found C 53.03, H 4.22, N 4.30.

**General Procedure for the Synthesis of Compounds 5a–c:** A solution of **3** (0.3 g, 0.44 mmol) and **4a**,[26] **4b**,[27] or **4c**[28] (0.36 mmol) in dry dichloromethane (2 mL) was stirred at room temp. under argon while TMSOTf (0.01 M in $CH_2Cl_2$, 0.45 mL) was added dropwise. After 2 h the mixture was neutralized with $Et_3N$ and the solvents evaporated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 2.5:1) and then with MPLC under the same conditions to afford compounds **5a–c** (68%) as a fluorescent foam.

**Methyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-diphenylmaleimido-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (5a):** TLC (petroleum ether/ethyl acetate, 2.5:1): $R_f$ = 0.1. $[\alpha]_D$ = +26.0 ($c$ = 0.4, $CHCl_3$). $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ = 1.92, 2.03, 2.07 (3 s, 9 H, 3 $CH_3CO$), 3.27 (s, 3 H, $OCH_3$), 3.37 (dd, $J_{3,4}$ = 9.2, $J_{4,5}$ = 9.5 Hz, 1 H, 4a-H), 3.46 (dd, $J_{1,2}$ = 3.2, $J_{2,3}$ = 9.6 Hz, 1 H, 2a-H), 3.66 (dd, $J_{gem}$ = 10.3, $J_{5,6}$ = 4.4 Hz, 1 H, 6a-H), 3.72 (m, 1 H, 5a-H), 3.82 (m, 1 H, 5b-H), 3.92 (dd, $J_{2,3}$ = 9.6, $J_{3,4}$ = 9.2 Hz, 1 H, 3a-H), 4.10 (dd, $J_{6,6'}$ = 10.3, $J_{5,6'}$ < 1 Hz, 1 H, 6′a-H), 4.16 (dd, $J_{6,6'}$ = 12.1, $J_{5,6}$ < 1 Hz, 1 H, 6b-H), 4.31–4.34 (m, 2 H, 2b-H, 6′b-H), 4.52 (d, $J_{1,2}$ = 2.3 Hz, 1 H, 1a-H), 4.33, 4.66 (2 d, $J_{gem}$ = 10.5 Hz, 2 H, C$H_2$Ph), 4.59, 4.73 (2 d, $J_{gem}$ = 12 Hz, 2 H, C$H_2$Ph), 4.71, 4.92 (2 d, $J_{gem}$ = 10.5 Hz, 2 H, C$H_2$Ph), 5.18 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, 1 H, 4b-H), 5.35 (d, $J_{1,2}$ = 8.4 Hz, 1 H, 1b-H), 5.76 (dd, $J_{2,3}$ = 10.1, $J_{3,4}$ = 9.6 Hz, 1 H, 3b-H), 7.02–7.30 (m, 25 H, 5 Ph) ppm. $^{13}C$ NMR (150.9 MHz, $CDCl_3$): $\delta$ = 20.54, 20.64, 20.75 (3 $CH_3CO$), 54.81 (C-2b), 55.06 ($OCH_3$), 62.03 (C-6b), 68.50 (C-6a), 68.82 (C-4b), 69.24 (C-5a), 70.72 (C-3b), 71.86 (C-5b), 73.40, 74.89, 75.58 (3 $CH_2$Ph), 77.66 (C-4a), 81.84 (C-3a), 97.83 (C-2a), 97.97 (C-1a), 98.42 (C-1b), 127.43–138.73 (5 Ph), 169.42, 170.34, 170.72 (5 CO) ppm. MALDI MS (positive ion mode, DHB/THF matrix): $m/z$ = 1006.2 $[M + K]^+$. $C_{56}H_{57}NO_{15}$ (984.1): C 68.33, H 5.84, N 1.42; found C 67.68, H 6.00, N 1.52.

**Benzyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-diphenylmaleimido-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (5b):** TLC (petroleum ether/ethyl acetate, 2.5:1): $R_f$ = 0.25. $[\alpha]_D$ = –16.6 ($c$ = 0.3, $CHCl_3$). $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ = 1.91, 1.97, 2.05 (3 s, 9 H, 3 $CH_3CO$), 2.80 (m, 1 H, 5a-H), 3.34–3.38 (m, 5 H, 2a-H, 6a-H, 6b-H, 5b-H, 3a-H), 3.50–3.53 (m, 2 H, 6′a-H, 6′b-H), 3.60–3.61 (m, 2 H, 2b-H, 3b-H), 3.82 (m, 1 H, 5c-H), 3.88 (dd, $J_{3,4}$ = 9.0, $J_{4,5}$ = 9.3 Hz, 1 H, 4a-H), 3.98 (dd, $J_{3,4}$ = $J_{4,5}$ < 1.0 Hz, 1 H, 4b-H), 4.19–4.36 (m, 8 H, 6′c-H, 6c-H, 1a-H, 1b-H, 2c-H, 1.5 C$H_2$Ph), 4.43 (d, $J_{gem}$ = 11.7 Hz, 1 H, 0.5 C$H_2$Ph), 4.48 (d, $J_{gem}$ = 12.1 Hz, 1 H, 0.5 C$H_2$Ph), 4.52–4.58 (m, 4 H, 2 C$H_2$Ph), 4.69 (d, $J_{gem}$ = 10.8 Hz, 1 H, 0.5 C$H_2$Ph), 4.84–4.90 (m, 3 H, 1.5 C$H_2$Ph), 5.00 (d, $J_{gem}$ = 11.4 Hz, 1 H, 0.5 C$H_2$Ph), 5.15 (dd, $J_{3,4}$ = 9.3, $J_{4,5}$ = 9.8 Hz, 1 H, 4c-H), 5.60 (d, $J_{1,2}$ = 8.3 Hz, 1 H, 1c-H), 5.80 (dd, $J_{2,3}$ = 10.3, $J_{3,4}$ = 9.3 Hz, 1 H, 3c-H), 7.05–7.32 (m, 45 H, 9 Ph) ppm. $^{13}C$ NMR (150.9 MHz, $CDCl_3$): $\delta$ = 20.49, 20.57, 20.65 (3 $CH_3CO$), 55.46 (C-2c), 62.09 (C-6c), 68.01 (C-6a, C-6b), 68.90 (C-4c), 70.61 (C-3c), 70.81 ($CH_2$Ph), 71.58 (C-5c), 72.59–76.79 (C-5a, C-5b, 6 $CH_2$Ph), 77.00 (C-4a), 77.21 (C-4b), 78.83 (C-2b), 81.65 (C-2a), 82.54 (C-3b), 82.85 (C-3a), 99.32 (C-1c), 102.10 (C-1b), 102.39 (C-1a), 127.14–139.26 (9 Ph) ppm. MALDI MS (positive ion mode, DHB/THF matrix): $m/z$ = 1514.1 $[M + Na]^+$, 1527.5 $[M + K]^+$. $C_{89}H_{89}NO_{20}$ (1492.8): C 71.60, H 6.02, N 0.93; found C 70.97, H 6.04, N 1.06.

**Benzyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-diphenylmaleimido-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-β-*O*-glucopyranoside (5c):** TLC (petroleum ether/ethyl acetate, 2.5:1): $R_f$ = 0.19. $[\alpha]_D$ = +30.4 ($c$ = 0.25, $CHCl_3$). $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ = 1.90, 1.96–1.98 (3 s, 9 H, 3 $CH_3CO$), 3.35–3.39 (m, 2 H, 5a-H, 5b-H), 3.47 (dd, $J_{1,2}$ = 7.8, $J_{2,3}$ = 8.4 Hz, 1 H, 2a-H), 3.53 (dd, $J_{6,6'}$ = 11.2, $J_{5,6}$ = 4.3 Hz, 1 H, 6a-H), 3.57 (dd, $J_{6,6'}$ = 12.3, $J_{5,6}$ = 1,4 Hz, 1 H, 6b-H), 3.61–3.65 (m, 2 H, 6′a-H, 3a-H), 4.00 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.1 Hz, 1 H, 4a-

H), 4.02 (dd, $J_{6,6'}$ = 12.3, $J_{5,6'}$ = 3.7 Hz, 1 H, 6′b-H), 4.19 (dd, $J_{1,2}$ = 8.4, $J_{2,3}$ = 10.4 Hz, 1 H, 2b-H), 4.43 (d, $J_{1,2}$ = 7.8 Hz, 1 H, 1a-H), 4.45, 4.52 (2 d, $J_{gem}$ = 12.1 Hz, 2 H, C$H_2$Ph), 4.60 (d, $J_{gem}$ = 11.6 Hz, 1 H, 0.5 C$H_2$Ph), 4.61 (d, $J_{gem}$ = 10.4 Hz, 1 H, 0.5 C$H_2$Ph), 4.85–4.91 (m, 3 H, 1.5 C$H_2$Ph), 4.95 (d, $J_{gem}$ = 11.8 Hz, 1 H, 0.5 C$H_2$Ph), 5.11 (dd, $J_{3,4}$ = 9.5, $J_{4,5}$ = 9.7 Hz, 1 H, 4b-H), 5.60 (d, $J_{1,2}$ = 8.4 Hz, 1 H, 1b-H), 5.66 (dd, $J_{2,3}$ = 10.4, $J_{3,4}$ = 9.5 Hz, 1 H, 3b-H), 7.19–7.44 (m, 30 H, 6 Ph) ppm. $^{13}$C NMR (150.9 MHz, $CDCl_3$): $\delta$ = 20.49, 20.59, 20.68 (3 $C$H$_3$CO), 55.63 (C-2b), 61.40 (C-6b), 67.91 (C-6a), 68.31 (C-4b), 70.81 ($C$H$_2$Ph), 70.88 (C-3b), 71.64 (C-5b), 72.93 ($C$H$_2$Ph), 74.43 (C-5a), 74.79 (2 $C$H$_2$Ph), 76.11 (C-4a), 81.96 (C-2a), 82.91 (C-3a), 97.64 (C-1b), 102.26 (C-1a), 126.68–139.17 (6 Ph), 169.37, 170.29, 170.67 (5 CO) ppm. MALDI MS (positive ion mode, DHB/THF matrix): $m/z$ = 1081.8 $[M + K]^+$. $C_{62}H_{61}NO_{15}$ (1060.2): C 70.23, H 5.81, N 1.32; found C 69.77, H 5.87, N 1.33.

**Deprotection of the DPM Group. Method A:** Compounds **5** (0.06 mmol) dissolved in dry ethanol (5 mL) were treated with hydrazine hydrate (0.3 mL, 6.1 mmol, 0.309 g) and refluxed overnight. The mixture was coevaporated with toluene in vacuo and the dry residue was treated with pyridine (Pyr)/$Ac_2O$, (2:1, 6 mL). This mixture was stirred at room temp. for 6 h and then coevaporated with toluene in vacuo. The residue was purified by flash chromatography to give compounds **6b** (90%), **6a** (68%), and **6c** (63%). The physical data obtained for these compounds are identical to those given in the literature.[12,17,29]

**Method B:** Compound **5c** (0.176 g, 0.17 mmol) in a dioxane/water mixture (5:1, 6 mL) was stirred with NaOH (0.2 g) at room temp. After 24 h the pH was adjusted to and kept at 5 by the addition of 1 N HCl while stirring. After 24 h the mixture was made basic with ethanolamine and the solvents evaporated in vacuo. The residue was treated with Pyr/$Ac_2O$, (2:1, 12 mL) and stirred overnight and then coevaporated with toluene in vacuo. The residue was purified by flash chromatography (2:1 toluene/acetone) to yield **6c** (31.0 mg, 22%). The data obtained for **6c** are identical to those of an authentic sample prepared in a previous work.[17]

**2-Amino-1,3,4,6-tetra-*O*-benzyl-2-deoxy-β-D-glucose Hydrochloride (8):** A mixture of **7**[31] (44.22 g, 148.7 mmol) and benzyl bromide (81.8 mL, 689.15 mmol, 117.87 g) in dry DMF (300 mL) was stirred vigorously in an ice/salt bath while NaH (95% in oil, 17.7 g, 737.2 mmol) was added in 17 portions. The mixture was then allowed to reach room temp. overnight. Ethyl acetate (100 mL) was added dropwise while stirring and then the solvent was evaporated in vacuo. The residue was taken up in ethyl acetate (900 mL) and water (100 mL), the organic layer was separated, dried with $MgSO_4$, and the solvents evaporated in vacuo. Flash chromatography of the residue on alumina (150 g) (petroleum ether/ethyl acetate, 4:1, plus 1% $Et_3N$) afforded the β-tetra-*O*-benzyl derivative (97.0 g, quant.) as a yellow oil. TLC on alumina (petroleum ether/ethyl acetate, 4:1, plus 1% $Et_3N$): $R_f$ = 0.75. The product from the last step was dissolved in acetone (200 mL), treated with HCl (5 N, 31.2 mL), refluxed for 20 min, and then refrigerated after having cooled to room temp. The white mass was broken, filtered at a vacuum pump, washed with acetone, and recrystallized from aqueous ethanol to yield **8**[32] (69.6 g, 82%) as white crystals, which were immediately used in the next step.

**1,3,4,6-Tetra-*O*-benzyl-2-deoxy-2-(3,3-dimethylglutarimido)-β-D-glucopyranoside (9):** Crystalline **8** (3.0 g, 5.2 mmol) suspended in dichloromethane (50 mL) was neutralized by shaking with a solution of sodium acetate (3.0 g, 36.5 mmol) in water (30 mL). The organic layer was separated, dried with $MgSO_4$, and the solvents evaporated in vacuo. The residue was taken up in pyridine (10 mL) and stirred with 3,3-dimethylglutaric anhydride (0.9 g, 6.3 mmol) at room temp. $Et_3N$ (1.0 mL) was added after 2 h and the solution was warmed at 80 °C for 30 min, acetic anhydride (1 mL) was then added, and the mixture was stirred at this temperature overnight. The mixture was coevaporated with toluene in vacuo and the residue purified by flash chromatography (petroleum ether/ethyl acetate, 4:1) to yield **9** (3.4 g, quant.) as a colourless oil. TLC (petroleum ether/ethyl acetate, 4:1): $R_f$ = 0.2. $[\alpha]_D$ = + 1.46 ($c$ = 1.05, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 0.76, 0.83 (2 s, 6 H, 2 $CH_3$), 1.74 (d, $J_{gem}$ = 16.8 Hz, 1 H, 0.5 -$CH_2$-), 2.07 (m, 2 H, -$CH_2$-), 2.34 (d, $J_{gem}$ = 18.5 Hz, 1 H, 0.5 -$CH_2$-), 3.61 (m, 1 H, 5-H), 3.74 (dd, $J_{3,4}$ = 8.5, $J_{4,5}$ = 9.5 Hz, 1 H, 4-H), 4.42–4.46 (m, 2 H, 6′-H, 6-H), 4.42–4.46 (m, 3 H, 2 C$H_2$Ph, 3-H), 4.58, 4.66 (2 d, $J_{gem}$ = 12.2 Hz, 2 H, C$H_2$Ph), 4.60 (d, $J_{gem}$ = 11.5 Hz, 1 H, 0.5 C$H_2$Ph), 4.79–4.87 (m, 4 H, 1.5 C$H_2$Ph, 2-H), 5.27 (d, $J_{1,2}$ = 8.2 Hz, 1 H, 1-H), 7.21–7.38 (m, 20 H, 4 Ph) ppm. $^{13}$C NMR (150.9 MHz, $CDCl_3$): $\delta$ = 25.86, 28.60 (2 $CH_3$), 46.65 (2 -$CH_2$-), 56.02 (C-2), 68.81 (C-6), 70.80 ($C$H$_2$Ph), 73.47 ($C$H$_2$Ph), 74.57, 74.79, 75.08 (2 $C$H$_2$Ph, C-5), 79.77 (C-3), 80.21 (C-4), 98.17 (C-1), 127.47–128.45, 137.37–139.01 (4 Ph), 172.18, 172.84 (2 CO) ppm. MALDI MS (positive ion mode, DHB/THF matrix): $m/z$ = 684.2 $[M + Na]^+$, 700.1 $[M + K]^+$. $C_{41}H_{45}NO_7$ (663.9): C 74.17, H 6.84, N 2.11; found C 73.80, H 6.77, N 2.23.

**1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-(3,3-dimethylglutarimido)-β-D-glucopyranose (10):** A solution of **9** (3.4 g, 5.12 mmol) in dry methanol (30 mL) was stirred under hydrogen in the presence of Pd/C (10%, 0.6 g). After 24 h the reaction mixture was filtered through Celite, washed with aqueous methanol (1:1, 50 mL), evaporated in vacuo, and dried well. The residue was stirred with pyridine (20 mL) and acetic anhydride (10 mL) overnight then coevaporated with toluene in vacuo and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 2:1) to yield **10** (2.364 g, 98%) as a white powder. TLC (petroleum ether/ethyl acetate, 2:1): $R_f$ = 0.13; m.p. 139–140 °C. $[\alpha]_D$ = +16.9 ($c$ = 0.95, $CHCl_3$). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.01, 1.06 (2 s, 2 $CH_3$), 1.95, 2.03, 2.03, 2.10 (4 s, 12 H, 4 C$H_3$CO), 2.37–2.57 (m, 4 H, 2 -C$H_2$-), 3.92–3.99 (2 m, 1 H, 5-H), 4.10 (dd, $J_{6,6'}$ = 12.5, $J_{5,6}$ = 2.2 Hz, 1 H, 6-H), 4.32 (dd, $J_{6,6'}$ = 12.5, $J_{5,6}$ = 4.5 Hz, 1 H, 6′-H), 5.01 (dd, $J_{1,2}$ = 8.6, $J_{2,3}$ = 10.4 Hz, 1 H, 2-H), 5.17 (m, $J_{3,4}$ = 8.9, $J_{4,5}$ = 10.2 Hz, 1 H, 4-H), 5.87 (dd, $J_{2,3}$ = 10.4, $J_{3,4}$ = 8.9 Hz, 1 H, 3-H), 6.53 (d, $J_{1,2}$ = 8.6 Hz, 1 H, 1-H) ppm. MALDI MS (positive ion mode, DHB/THF matrix): $m/z$ = 494.7 $[M + Na]^+$, 510.8 $[M + K]^+$. $C_{21}H_{29}NO_{11}$ (471.5): C 53.48, H 6.21, N 2.97; found C 53.16, H 6.06, N 2.94.

**3,4,6-Tri-*O*-acetyl-2-deoxy-2-(3,3-dimethylglutarimido)-β-D-glucopyranose (11):** A solution of **10** (0.937 g, 1.98 mmol) in dry DMF (6 mL) was stirred at room temp. with hydrazine acetate (0.2 g, 2.17 mmol). After 2 h the reaction mixture was diluted with ethyl acetate (50 mL) and then washed with saturated $NaHCO_3$ (15 mL) and water (2×20 mL). The combined aqueous layer was extracted with ethyl acetate (2×25 mL) and the combined organic layer was dried with $MgSO_4$ and the solvents evaporated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 1:1) to yield **11** (0.848 g, 99%) as an amorphous mass. TLC (petroleum/ethyl acetate, 1:1.5): $R_f$ = 0.21. $[\alpha]_D$ = +5.6 ($c$ = 1.5, $CHCl_3$) $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.05, 1.09 (2 s, 6 H, 2 $CH_3$), 1.94, 2.02, 2.11 (3 s, 9 H, 3 $CH_3$CO), 2.41–2.61 (m, 4 H, 2-$CH_2$-), 3.51 (d, $J_{1,OH}$ = 8.2 Hz, 1 H, OH), 3.82–3.89 (2 m, 1 H, 5-H), 4.11 (m, 1 H, 6-H), 4.27 (dd, $J_{6,6'}$ = 12.3, $J_{5,6}$ = 4.6 Hz, 1 H, 6′-H), 4.79 (dd, $J_{1,2}$ = 8.2, $J_{2,3}$ = 10.6 Hz, 1 H, 2-H), 5.13 (dd, $J_{3,4}$ = 8.9, $J_{4,5}$ = 10.2 Hz, 1 H, 4-H), 5.59 (dd, $J_{1,2}$ = $J_{1,OH}$ = 8.2 Hz, 1 H, 1-H), 5.86 (dd, $J_{2,3}$ = 10.6, $J_{3,4}$ = 8.9 Hz, 1 H, 3-H) ppm. MALDI MS (positive ion mode, DHB/THF matrix): $m/z$ = 452.0

$[M + Na]^+$, 468.0 $[M + K]^+$. $C_{19}H_{27}NO_{10}$ (429.5): C 53.13, H 6.34, N 3.26; found C 52.99, H 6.52, N 3.13.

***O*-[3,4,6-Tri-*O*-acetyl-2-deoxy-2-(3,3-dimetylglutarimido)-D-glucopyranosyl] Trichloroacetimidate (12):** A mixture of **11** (1.0 g, 2.3 mmol) and tricloroacetonitrile (1.5 mL, 15.0 mmol, 2.16 g) in dry dichloromethane (5 mL) was treated with DBU (0.1 mL, 0.66 mmol) and stirred at room temp. overnight. The reaction mixture was evaporated in vacuo and the residue purified by flash chromatography (petroleum ether/ethyl acetate, 1:1 + 2% $Et_3N$) to yield **12** (1.077 g, 80%) as a faint yellow foam in an α/β ratio of 1:2.3. TLC (petroleum ether/ethyl acetate, 1:1 + 2% $Et_3N$): $R_f$ = 0.47 (α-form), 0.42 (β-form). $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.02, 1.12 (2 s, 6 H, 2 $CH_3$), 1.96, 2.03, 2.10 (3 s, 9 H, 3 $CH_3CO$), 2.30, 2.59 (m, 4 H, 2 -$CH_2$-), 3.95–4.40 (m, 3 H, 5-H, 6′-H, 6-H), 5.06–5.26 (m, 2 H, 2-H, 4-H), 5.42 (dd, $J_{2,3}$ = 7.2, $J_{3,4}$ = 6.0 Hz, 0.3 H, 3α-H), 5.75 (d, $J_{1,2}$ = 5.6 Hz, 0.3 H, 1α-H), 5.93 (dd, $J_{2,3}$ = 10.5, $J_{3,4}$ = 8.8 Hz, 0.7 H, 3β-H), 6.69 (d, $J_{1,2}$ = 8.5 Hz, 0.7 H, 1β-H), 8.67 (s, 1 H, NH) ppm. $C_{21}H_{27}Cl_3N_2O_{10}$ (573.8).

**General Procedure for the Synthesis of Compounds 13a–e:** A mixture of **12** (0.63 mmol) and the appropriate acceptor **4a**–**e**[27–29] (0.42 mmol) in dry dichloromethane (1 mL) was stirred under argon at room temp. while TMSOTf (0.01 M in $CH_2Cl_2$, 0.65 mL) was added dropwise. After 75 min the mixture was neutralized with $Et_3N$ and the solvents evaporated in vacuo.

**Methyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-(3,3-dimethylglutarimido)-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (13a):** The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 1.5:1) to afford **13a** (90%) as a white foam. TLC (petroleum ether/ethyl acetate, 1.5:1): $R_f$ = 0.16. $[\alpha]_D$ = +6.5 ($c$ = 1.1, $CHCl_3$). $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ = 0.93, 0.98 (2 s, 6 H, $CH_3$), 1.92, 2.01, 2.03 (3 s, 9 H, 3 $CH_3CO$), 2.30, 2.40 (2 d, 2 H, $J_{gem}$ = 17.0 Hz, -$CH_2$-), 2.36 (m, 2 H, -$CH_2$-), 3.28 (dd, $J_{3,4}$ = 9.2, $J_{4,5}$ = 9.5 Hz, 1 H, 4a-H), 3.31 (s, 3 H, -$OCH_3$), 3.44 (dd, $J_{1,2}$ = 3.7, $J_{2,3}$ = 9.6 Hz, 1 H, 2a-H), 3.55 (dd, $J_{5,6}$ = 6.0, $J_{6,6'}$ = 10.5 Hz, 1 H, 6a-H), 3.76 (m, 2 H, 5a-H, 5b-H), 3.95 (dd, $J_{2,3}$ = 9.6, $J_{3,4}$ = 9.2 Hz, 1 H, 3a-H), 3.98 (dd, $J_{5,6'}$ = 1.1, $J_{gem}$ = 10.5 Hz, 1 H, 6′a-H), 4.10 (dd, $J_{5,6}$ = 1.9, $J_{6,6'}$ = 12.1 Hz, 1 H, 6b-H), 4.25 (dd, $J_{5,6'}$ = 4.6, $J_{6,6'}$ = 12.1 Hz, 1 H, 6′b-H), 4.47 (d, $J_{1,2}$ = 3.7 Hz, 1 H, 1a-H), 4.48 (2 d, $J_{gem}$ = 10.8 Hz, 2 H, C$H_2$Ph), 4.63 (d, $J_{gem}$ = 12.1 Hz, 1 H, 0.5 C$H_2$Ph), 4.76 (m, 2 H, C$H_2$Ph), 4.91 (dd, $J_{1,2}$ = 8.2, $J_{2,3}$ = 10.5 Hz, 1 H, 2b-H), 4.96 (d, $J_{gem}$ = 10.8 Hz, 1 H, 0.5 C$H_2$Ph), 5.11 (dd, $J_{3,4}$ = 9.0, $J_{4,5}$ = 9.8 Hz, 1 H, 4b-H), 5.40 (d, $J_{1,2}$ = 8.2 Hz, 1 H, 1b-H), 5.78 (dd, $J_{2,3}$ = 10.5, $J_{3,4}$ = 9.0 Hz, 1 H, 3b-H), 7.25–7.34 (m, 15 H, 3 Ph) ppm. $^{13}C$ NMR (600 MHz, $CDCl_3$): $\delta$ = 20.67, 20.73 (2 $CH_3$), 27.22, 27.60, 28.78 (3 $CH_3CO$), 46.18, 46.85 (2 -$CH_2$-), 54.71 (C-2b), 55.11 (-$OCH_3$), 62.14 (C-6b), 68.45 (C-6a), 69.36 (C-5b), 69.42 (C-4b), 70.72 (C-3b), 71.66 (C-5a), 73.29, 74.68, 75.70 (3 $CH_2$Ph), 78.05 (C-4a), 81.76 (C-3a), 97.66 (C-1a), 97.80 (C-2a), 98.82 (C-1b), 127.62–137.98 (3 Ph-C) ppm. MALDI MS (positive ion mode, DHB/THF matrix): $m/z$ = 898.3 $[M + Na]^+$. $C_{47}H_{57}NO_{15}$ (876.0): C 64.43, H 6.57, N 1.59; found C 63.93, H 6.87, N 1.68.

**Benzyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-(3,3-dimethylglutarimido)-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (13b):** The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 1:2) to yield **13b** (96%) as a white foam. TLC (petroleum ether/ethyl acetate, 2:1): $R_f$ = 0.16. $[\alpha]_D$ = –9.0 ($c$ = 0.2, $CHCl_3$). $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ = 0.68, 0.82 (2 s, 6 H, 2 $CH_3$), 1.78, 2.17 (2 d, $J_{gem}$ = 17.2 Hz, 2 H, -$CH_2$-), 1.89, 1.95, 2.01 (3 s, 9 H, 3 $CH_3CO$), 1.97, 2.26 (2 d, $J_{gem}$ = 16.4 Hz, 2 H, -$CH_2$-), 3.14 (m, 1 H, 5a-H), 3.39–3.62 (m, 8 H, 6′b-H, 5b-H, 2a-H, 3a-H, 6b-H, 6a-H, 2b-H, 3b-H), 3.66 (dd, $J_{6,6'}$ = 10.8, $J_{5,6'}$ = 3.7 Hz, 1 H, 6′a-H), 3.79 (m, 1 H, 5c-H), 3.96–3.98 (m, 2 H, 4a-H, 4b-H), 4.17 (dd, $J_{6,6'}$ = 10.7, $J_{5,6}$ < 1 Hz, 1 H, 6c-H), 4.22–4.24 (m, 2 H, 6′c-H, C$H_2$Ph), 4.34 (d, $J_{gem}$ = 12.1 Hz, 1 H, 0.5 C$H_2$Ph), 4.35 (d, $J_{gem}$ = 11.7 Hz, 1 H, 0.5 C$H_2$Ph), 4.39–4.40 (m, 2 H, 1a-H, 1b-H), 4.49 (d, $J_{gem}$ = 11.6 Hz, 1 H, 0.5 C$H_2$Ph), 4.54 (2 d, $J_{gem}$ = 12.9 Hz, 1 H, 0.5 C$H_2$Ph), 4.56 (d, $J_{gem}$ = 12.8 Hz, 1 H, 0.5 C$H_2$Ph), 4.59 (d, $J_{gem}$ = 12.1 Hz, 1 H, 0.5 C$H_2$Ph), 4.65 (d, $J_{gem}$ = 10.5 Hz, 1 H, 0.5 C$H_2$Ph), 4.71 (d, $J_{gem}$ = 10.9 Hz, 1 H, 0.5 C$H_2$Ph), 4.74 (d, $J_{gem}$ = 12.1 Hz, 1 H, 0.5 C$H_2$Ph), 4.87–4.90 (m, 2 H, $CH_2$Ph), 4.93–4.98 (m, 3 H, C$H_2$Ph, 2c-H), 5.07 (dd, $J_{3,4}$ = 8.9, $J_{4,5}$ = 9.8 Hz, 1 H, 4c-H), 5.65 (d, $J_{1,2}$ = 8.0 Hz, 1 H, 1c-H), 5.86 (dd, $J_{2,3}$ = 10.4, $J_{3,4}$ = 8.9 Hz, 1 H, 3c-H), 7.10–7.34 (m, 35 H, 7 Ph) ppm. $^{13}C$ NMR (150.9 MHz, $CDCl_3$): $\delta$ = 20.56, 20.67 (2 $CH_3$), 26.15, 28.12, 28.42 (3 $CH_3CO$), 45.79, 46.20 (2 -$CH_2$-), 55.11 (C-2c), 62.13 (C-6c), 67.90 (C-6a), 69.82 (C-4c, C-6b), 70.37 (C-3c), 70.85 ($CH_2$Ph), 71.31 (C-5c), 73.00 (C-5b), 73.13, 73.93, 74.73 (3 $CH_2$Ph), 74.90 (C-5a), 75.02, 75.38, 75.93 (3 $CH_2$Ph), 76.10 (C-4a, C-4b), 79.14 (C-2b), 80.99 (C-3b), 81.63 (C-2a), 82.89 (C-3a), 99.45 (C-1c), 102.48 (C-1a, C-1b), 126.37 (7 Ph), 169.68, 170.17 (5 CO) ppm. MALDI MS (positive ion mode, DHB/THF matrix): $m/z$ = 1404.7 $[M + Na]^+$, 1420.4 $[M + K]^+$. $C_{80}H_{89}NO_{20}$ (1384.7): C 69.38, H 6.49, N 1.01; found C 68.99, H 6.19, N 1.07.

**Benzyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-(3,3-dimethylglutarimido)-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (13c):** The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 2:1) to afford **13c** (81%) as a white foam. TLC (petroleum ether/ethyl acetate, 2:1): $R_f$ = 0.16. $[\alpha]_D$ = –11.3 ($c$ = 0.65, $CHCl_3$). $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ = 0.91, 0.99 (2 s, 6 H, 2 $CH_3$), 1.91, 1.95, 1.97 (3 s, 9 H, 3 $CH_3CO$), 2.36–2.43 (m, 3 H, 1.5 -$CH_2$-), 2.52 (d, $J_{gem}$ = 16.6 Hz, 1 H, 0.5 -$CH_2$-), 3.28 (m, 1 H, 5a-H), 3.34 (m, 1 H, 5b-H), 3.47 (dd, $J_{1,2}$ = 7.7, $J_{2,3}$ = 8.7 Hz, 1 H, 2a-H), 3.56 (dd, $J_{2,3}$ = 8.7, $J_{3,4}$ = 8.9 Hz, 1 H, 3a-H), 3.62 (dd, $J_{5,6}$ = 3.8, $J_{6,6'}$ = 10.8 Hz, 1 H, 6a-H), 3.69 (dd, $J_{5,6'}$ < 1.0, $J_{6,6'}$ = 10.8 Hz, 1 H, 6′a-H), 3.82 (dd, $J_{5,6}$ = 1.7, $J_{6,6'}$ = 12.4 Hz, 1 H, 6b-H), 4.04 (dd, $J_{5,6}$ = 4.0, $J_{6,6'}$ = 12.4 Hz, 1 H, 6′b-H), 4.08 (dd, $J_{3,4}$ = 8.9, $J_{4,5}$ = 9.2 Hz, 1 H, 4a-H), 4.43 (d, $J_{1,2}$ = 7.7 Hz, 1 H, 1a-H), 4.63–4.66 (m, 2 H, C$H_2$Ph), 4.61, 4.69 (2 d, 2 H, C$H_2$Ph), 4.79 (d, $J_{gem}$ = 11.5 Hz, 1 H, 0.5 C$H_2$Ph), 4.83–4.96 (m, 4 H, 1.5 C$H_2$Ph, 2b-H), 5.05 (dd, $J_{3,4}$ = 8.9, $J_{4,5}$ = 9.9 Hz, 1 H, 4b-H), 5.58 (d, $J_{1,2}$ = 8.1 Hz, 1 H, 1b-H), 5.73 (dd, $J_{2,3}$ = 10.6, $J_{3,4}$ = 8.9 Hz, 1 H, 3b-H), 7.21–7.39 (m, 20 H, 4 Ph) ppm. $^{13}C$ NMR (150.9 MHz, $CDCl_3$): $\delta$ = 20.64, 20.70 (2 $CH_3$), 27.07, 27.54, 27.87 (3 $CH_3CO$), 46.06, 46.82 (2 -$CH_2$-), 55.40 (C-2b), 61.66 (C-6b), 68.37 (C-6a), 69.23 (C-4b), 70.69 (C-3b), 70.95 ($CH_2$Ph), 71.44 (C-5b), 73.33 ($CH_2$Ph), 74.69 (C-4a), 74.87 (C-5a, 2 $CH_2$Ph), 81.76 (C-2a), 82.17 (C-3a), 97.17 (C-1b), 102.44 (C-1a), 127.28–138.34 (4 Ph), 172.89 (5 CO) ppm. MALDI MS (positive ion mode, DHB/THF matrix): $m/z$ = 974.0 $[M + Na]^+$. $C_{53}H_{61}NO_{15}$ (952.1): C 66.85, H 6.47, N 1.47; found C 66.51, H 6.47, N 1.55.

**Allyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-(3,3-dimethylgluarimido)-β-D-glucopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (13d):** The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 2:1) to afford **13d** (92%) as a white foam. TLC (petroleum ether/ethyl acetate, 2:1): $R_f$ = 0.15. $[\alpha]_D$ = +6.0 ($c$ = 0.3, $CHCl_3$). $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ = 0.91, 0.96 (2 s, 6 H, 2 $CH_3$), 1.93, 2.02 (2 s, 9 H, 3 $CH_3CO$), 2.18 (d, $J_{gem}$ = 16.3 Hz, 1 H, 0.5 -$CH_2$-), 2.42 (d, $J_{gem}$ = 16.6 Hz, 1 H, 0.5 -$CH_2$-), 2.49 (m, 2 H, -$CH_2$-), 3.57 (dd, $J_{6,6'}$ = 10.5, $J_{5,6}$ = 4.5 Hz, 1 H, 6a-H), 3.64 (dd, $J_{6,6'}$ = 10.5, $J_{5,6'}$ < 1.0 Hz, 1 H, 6′a-H), 3.71 (m, 2 H, 4a-H, 5a-H), 3.82 (m, 1 H, 5b-H), 3.87–3.95 (m, 2 H, -C$H$H-CH=$CH_2$, 3a-H), 4.12–4.14 (m, 2 H, -CH$H$-CH=$CH_2$, 2a-H), 4.18 (dd, $J_{6,6'}$ = 10.7, $J_{5,6}$ < 1.0 Hz, 1 H, 6b-H), 4.25 (dd, $J_{6,6'}$ = 10.7, $J_{5,6'}$ =

5.1 Hz, 1 H, 6′b-H), 4.42, 4.87 (d, $J_{gem}$ = 10.7 Hz, 2 H, C$H_2$Ph), 4.45–4.51 (m, 3 H, 1.5 C$H_2$Ph), 4.61 (d, $J_{1,2}$ < 1.0 Hz, 1 H, 1a-H), 4.79 (d, $J_{gem}$ = 11.3 Hz, 1 H, 0.5 C$H_2$Ph), 5.01 (dd, $J_{1,2}$ = 8.2, $J_{2,3}$ = 10.4 Hz, 1 H, 2b-H), 5.13 (dd, $J_{3,4}$ = 9.3, $J_{4,5}$ = 9.6 Hz, 1 H, 4b-H), 5.20 (m, 2 H, -$CH_2$-CH=C$H_2$), 5.47 (d, $J_{1,2}$ = 8.2 Hz, 1 H, 1b-H), 5.84–5.87 (m, 1 H, -$CH_2$-C$H$=$CH_2$), 5.86 (dd, $J_{2,3}$ = 10.4, $J_{3,4}$ = 9.3 Hz, 1 H, 3b-H), 7.16–7.39 (m, 15 H, 3 Ph) ppm. $^{13}$C NMR (150.9 MHz, $CDCl_3$): $\delta$ = 20.65, 20.73 (2 $CH_3$), 26.40, 28.58 (3 $CH_3$CO), 45.87, 46.92 (2 -$CH_2$-), 54.55 (C-2b), 62.53 (C-6b), 68.07 (-$CH_2$-CH=$CH_2$), 69.60 (C-4b), 70.48 (C-3b), 69.51 (C-6a), 70.78 (C$H_2$Ph), 71.10 (C-5a), 71.93 (C-5b), 73.10 (C$H_2$Ph), 73.93 (C-2a), 74.07 (C-4a), 75.08 (C$H_2$Ph), 78.09 (C-3a), 82.00 (-$CH_2$-CH=C$H_2$), 96.76 (C-1a), 97.72 (C-1b), 117.57–138.42 (3 Ph, $CH_2$C$H$=$CH_2$), 169.51–173.42 (5 CO) ppm. MALDI MS (positive ion mode, DHB/THF matrix): $m/z$ = 923.5 [M + Na]$^+$, 939.5 [M + K]$^+$. $C_{49}H_{59}NO_{15}$ (902.1): C 65.23, H 6.60, N 1.55; found C 65.21, H 6.58, N 1.53.

**Benzyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-(3,3-dimethylglutarimido)-β-D-glucopyranoside (13e):** The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 1.5:1) to yield **13e** (0.254 g, 93%) as a colourless oil. TLC (petroleum ether/ethyl acetate, 1:1): $R_f$ = 0.36. $[\alpha]_D$ = –19.0 ($c$ = 0.55, $CHCl_3$). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 0.91, 0.98 (2 s, 6 H, 2 $CH_3$), 1.92, 2.02, 2.12 (3 s, 9 H, 3 C$H_3$CO), 2.23–2.47 (m, 4 H, 2 -$CH_2$-), 3.38, 3.77 (2 m, 1 H, 5-H), 4.16 (dd, $J_{6,6'}$ = 12.3, $J_{5,6}$ = 2.2 Hz, 1 H, 6-H), 4.30 (dd, $J_{6,6'}$ = 12.3, $J_{5,6'}$ = 4.6 Hz, 1 H, 6′-H), 4.48, 4.85 (2 d, $J_{gem}$ = 11.8 Hz, 2 H, C$H_2$Ph), 4.92 (dd, $J_{1,2}$ = 8.2, $J_{2,3}$ = 10.6 Hz, 1 H, 2-H), 5.15 (dd, $J_{3,4}$ = 8.8, $J_{4,5}$ = 10.1 Hz, 1 H, 4-H), 5.47 (d, $J_{1,2}$ = 8.2 Hz, 1 H, 1-H), 5.79 (dd, $J_{2,3}$ = 10.6, $J_{3,4}$ = 8.8 Hz, 1 H, 3-H), 7.20–7.32 (m, 5 H, Ph) ppm. MALDI MS (positive ion mode, DHB/THF matrix): $m/z$ = 543.3 [M + Na]$^+$. $C_{26}H_{33}NO_{10}$ (519.6): C 60.09, H 6.41, N 2.69; found C 59.58, H 6.41, N 2.76.

**Benzyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-(3,3-dimethylglutaramido)-β-D-glucopyranoside (14):** Compound **13e** (0.225 g, 0.433 mmol) and NaOH (0.25 g, 6.2 mmol) in MeOH/dioxane/water (1:1:1, 6 mL) was stirred at room temp. overnight and then warmed to 60 °C. After 5 h the pH of the mixture was adjusted to 4.5 by the addition of 2 N HCl and maintained at this pH for 24 h. The mixture was then neutralized with $K_2CO_3$ and dried in vacuo. The residue was treated with Pyr/$Ac_2O$, (2:1, 12 mL), stirred for 14 h, and then coevaporated with toluene in vacuo. The residue was purified by flash chromatography (toluene/acetone, 2.5:1) to afford **14** (quant.) as a yellow oil. TLC (toluene/acetone, 2.5:1): $R_f$ = 0.2. $[\alpha]_D$ = –45.0 ($c$ = 0.4, $CHCl_3$). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 0.99, 1.01 (2 s, 6 H, 2 $CH_3$), 2.01, 2.02, 2.11 (3 s, 9 H, 3 $CH_3$CO), 2.20–2.36 (m, 2 H, 2 -$CH_2$-), 3.70 (m, 1 H, 5-H), 4.00 (m, 1 H, 2-H), 4.18 (m, 1 H, 6-H), 4.29 (dd, $J_{5,6'}$ = 4.8, $J_{6,6'}$ = 12.3 Hz, 1 H, 6′-H), 4.72 (d, $J_{1,2}$ = 8.3 Hz, 1 H, 1-H), 4.56, 4.90 (2 d, $J_{gem}$ = 11.7 Hz, 2 H, $CH_2$Ph), 5.09 (dd, $J_{3,4}$ = 9.3, $J_{4,5}$ = 9.8 Hz, 1 H, 4-H), 5.30 (dd, $J_{2,3}$ = 10.6, $J_{3,4}$ = 9.3 Hz, 1 H, 3-H), 6.43 (br. d, $J_{2,NH}$ = 8.4 Hz, 1 H, NH), 7.25–7.36 (m, 5 H, Ph) ppm. $C_{26}H_{35}NO_{11}$ (537.6): C 58.08, H 6.57, N 2.60; found C 57.91, H 6.88, N 2.70.

**Benzyl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-($N^3$-acetyl-3,3-dimethylhydrazidoglutaramido)-β-D-glucopyranoside (15):** A mixture of **3** (0.23 g, 0.34 mmol) and hydrazine hydrate (6 mL) was refluxed overnight and then cooled to room temp. The mixture was diluted with dichloromethane (50 mL), washed with water (3 × 10 mL), dried with $MgSO_4$, and coevaporated in vacuo. The residue was stirred with Pyr/$Ac_2O$, (2:1, 12 mL) for 2 h, then evaporated with toluene in vacuo, and purified by flash chromatography (toluene/acetone, 2:1) to yield **15** (63.0 mg, 24%) as an amorphous white mass. TLC (toluene/acetone, 2:1): $R_f$ = 0.22. $[\alpha]_D$ = –9.0 ($c$ = 1.1, $CHCl_3$). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.04, 1.05 (2 s, 6 H, 2 $CH_3$), 1.84–2.35 (m, 7 H, 2 -$CH_2$-, $CH_3$CO), 3.46–4.95 (m, 15 H), 7.12–7.36 (m, 21 H, 4 Ph, NH), 7.62 (br. s, 1 H, NH), 8.98 (br. s, 1 H, NH) ppm. MALDI MS (positive ion mode, DHB/THF matrix): $m/z$ = 758.5 [M + Na]$^+$, 774.5 [M + K]$^+$. $C_{43}H_{51}N_3O_8$ (738.0): C 69.97, H 6.97, N 5.69; found C 69.64, H 6.86, N 5.56.

**Benzyl 3,4,6-Tri-*O*-benzyl-2-deoxy-2-diglycolylimido-β-D-glucopyranoside (16):** Crystalline **8** (4.20 g, 7.28 mmol) suspended in dichloromethane (75 mL) was neutralized by shaking with saturated $Na_2CO_3$ solution (15 mL). The organic layer was separated, dried with $MgSO_4$, and the solvent evaporated in vacuo. The residue was stirred with diglycolic anhydride (1.13 g, 9.7 mmol) in pyridine (10 mL) at room temp. $Et_3N$ (0.5 mL) was added after 1 h and the solution heated at 80 °C for 30 min. Acetic anhydride (0.5 mL) was then added and heating was continued for a further 6 h. The mixture was coevaporated with toluene in vacuo and the residue purified by flash chromatography (petroleum ether/ethyl acetate, 4:1) to yield **16** (4.64 g, quant.) as a colourless oil which solidified in the form of an amorphous mass upon standing. TLC (petroleum ether/ethyl acetate, 4:1): $R_f$ = 0.22. $[\alpha]_D$ = +4.2 ($c$ = 0.35, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 3.50 (d, $J_{gem}$ = 18.5 Hz, 1 H, -$CH_2$-), 3.58 (m, 1 H, 5-H), 3.75–3.81 (m, 4 H, 0.5 -$CH_2$-, 6′-H, 6-H, 4-H), 3.91, 4.19 (2 d, $J_{gem}$ = 16.2 Hz, 2 H, -$CH_2$-), 4.37 (m, 1 H, 3-H), 4.41–4.51 (m, 2 H, C$H_2$Ph), 4.57–4.63 (m, 2 H, C$H_2$Ph), 4.66–4.69 (m, 2 H, 0.5 C$H_2$Ph, 2-H), 4.81–4.84 (m, 3 H, 1.5 $CH_2$Ph), 5.12 (d, $J_{1,2}$ = 8.3 Hz, 1 H, 1-H), 7.20–7.37 (m, 20 H, 4 Ph) ppm. $^{13}$C NMR (150.9 MHz, $CDCl_3$): $\delta$ = 55.87 (C-2), 67.25, 67.55 (2 -$CH_2$-), 68.63 (C-6), 70.68, 73.47, 74.70, 74.83 (4 C$H_2$Ph), 74.96 (C-5), 78.94 (C-3), 80.06 (C-4), 97.17 (C-1), 127.58–138.59 (4 Ph) ppm. MALDI MS (positive ion mode, DHB/THF matrix): $m/z$ = 659.4 [M + Na]$^+$, 675.3 [M + K]$^+$. $C_{38}H_{39}NO_8$ (637.8): C 71.55, H 6.17, N 2.19; found C 71.16, H 6.27, N 2.22.

**1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-diglycolylimido-β-D-glucopyranose (18):** A solution of **16** (4.28 g, 6.71 mmol) in dry methanol (30 mL) was stirred under hydrogen in the presence of Pd/C (10%, 0.78 g). After 24 h the reaction mixture was filtered through Celite, washed with aqueous methanol (1:1, 50 mL), evaporated in vacuo, and dried to give **17** (quant.) as a white powder. Compound **17** was stirred overnight with pyridine (20 mL) and acetic anhydride (10 mL), and then coevaporated with toluene in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 1:1) to yield **18** (2.93 g, 98%) as a colourless foam. TLC (petroleum ether/ethyl acetate, 1:1): $R_f$ = 0.21. $[\alpha]_D$ = +6.6 ($c$ = 0.15, $CHCl_3$). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.98, 2.05, 2.08, 2.11 (4 s, 12 H, 4 $CH_3$CO), 3.93–3.99 (2 m, 1 H, 5-H), 4.11 (dd, $J_{6,6'}$ = 12.5, $J_{5,6}$ = 2.1 Hz, 1 H, 6-H), 4.27–4.40 (m, 5 H, 2 -$CH_2$-, 6′-H), 4.88 (dd, $J_{1,2}$ = 8.6, $J_{2,3}$ = 10.3 Hz, 1 H, 2-H), 5.20 (dd, $J_{3,4}$ = 9.0, $J_{4,5}$ = 10.2 Hz, 1 H, 4-H), 5.82 (dd, $J_{2,3}$ = 10.3, $J_{3,4}$ = 9.0 Hz, 1 H, 3-H), 6.52 (d, $J_{1,2}$ = 8.6 Hz, 1 H, 1-H) ppm. MALDI MS (positive ion mode, DHB/THF matrix): $m/z$ = 468.0 [M + Na]$^+$, 483.9 [M + K]$^+$. $C_{18}H_{23}NO_{12}$ (445.4): C 48.53, H 5.21, N 3.14; found C 48.36, H 5.29, N 3.09.

**3,4,6-Tri-*O*-acetyl-2-deoxy-2-diglycolylimido-β-D-glucopyranose (19):** A solution of **18** (7.0 g, 15.7 mmol) in dry DMF (15 mL) was stirred at room temp. with hydrazine acetate (1.55 g, 16.8 mmol). After 1.5 h the reaction mixture was diluted with ethyl acetate (200 mL) and washed with HCl (5%, 3 × 20 mL), $H_2O$ (20 mL), and saturated $NaHCO_3$ (20 mL). The organic layer was dried with $MgSO_4$ and the solvents evaporated in vacuo. The residue was purified by flash chromatography (toluene/acetone, 3:1) to yield **19** (4.88 g, 77%) as an amorphous mass. TLC (toluene/acetone, 3:1): $R_f$ = 0.27. $[\alpha]_D$ = +14.1 ($c$ = 0.6, $CHCl_3$). $^1$H NMR (250 MHz,

$CDCl_3$): $\delta$ = 1.05, 1.09 (2 s, 6 H, 2 $CH_3$), 1.98, 2.04, 2.11 (3 s, 9 H, 3 $CH_3CO$), 3.58 (br. s, 1 H, OH), 3.86 (m, 1 H, 5-H), 4.11–4.42 (m, 6 H, 2 -$CH_2$-, 6′-H, 6-H), 4.68 (dd, $J_{1,2}$ = 8.2, $J_{2,3}$ = 10.6 Hz, 1 H, 2-H), 5.16 (dd, $J_{3,4}$ = 8.9, $J_{4,5}$ = 10.2 Hz, 1 H, 4-H), 5.64 (dd, $J_{1,2}$ = 8.2 Hz, 1 H, 1-H), 5.76 (dd, $J_{2,3}$ = 10.6, $J_{3,4}$ = 8.9 Hz, 1 H, 3-H) ppm. MALDI MS (positive ion mode, DHB/THF matrix): *m*/*z* = 426.0 $[M + Na]^+$, 441.9 $[M + K]^+$. $C_{16}H_{21}NO_{11}$ (403.4): C 47.63, H 5.25, N 3.47; found C 47.55, H 5.33, N 3.40.

**Trichloroacetimidate 20:** A mixture of **19** (0.77 g, 1.9 mmol) and trichloroacetonitrile (1.5 mL, 15.0 mmol, 2.16 g) in dry dichloromethane (7.0 mL) was treated with DBU (0.1 mL, 0.66 mmol) and stirred at room temp. overnight. The solvent was evaporated in vacuo and the residue purified by flash chromatography (petroleum ether/ethyl acetate, 1:2 + 1% $Et_3N$) to yield **20** (0.843 g, 80%) as a pale yellow foam. TLC (petroleum ether/ethyl acetate, 1:2 + 1% $Et_3N$): $R_f$ = 0.53. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.99, 2.06, 2.11 (3 s, 9 H, 3 $CH_3CO$), 4.02 (m, 1 H, 5-H), 4.11–4.39 (m, 6 H, 2 -$CH_2$-,6′-H, 6-H), 5.05 (dd, $J_{1,2}$ = 8.7, $J_{2,3}$ = 10.5 Hz, 1 H, 2-H), 5.27 (dd, $J_{3,4}$ = 8.9, $J_{4,5}$ = 10.2 Hz, 1 H, 4-H), 5.84 (dd, $J_{2,3}$ = 10.5, $J_{3,4}$ = 8.9 Hz, 1 H, 3-H), 6.64 (d, $J_{1,2}$ = 8.7 Hz, 1 H, 1-H), 8.74 (s, 1 H, NH) ppm. $C_{18}H_{21}Cl_3N_2O_{11}$ (547.8).

**General Procedure for the Synthesis of Compounds 21a,d,f,g:** A mixture of **20** (0.53 mmol) and the appropriate acceptor (**4a**,[26] **4d**,[33] and **4f**[34]) or 1,3,5-trimethoxybenzene (0.348 mmol) in dry dichloromethane (1 mL) was stirred under argon at room temp. while TMSOTf (0.01 M in $CH_2Cl_2$, 0.53 mL) was added dropwise. After 2 h the mixture was neutralized with $Et_3N$ and the solvents evaporated in vacuo.

**Methyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-diglycolylimido-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (21a):** The residue was purified by flash chromatography or MPLC (petroleum ether/ethyl acetate, 1.5:1) to afford **21a** (quant.) as a colourless foam. TLC (petroleum ether/ethyl acetate, 1.5:1): $R_f$ = 0.12. $[\alpha]_D$ = +2.8 (*c* = 0.25, $CHCl_3$). $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ = 0.93, 0.98 (2 s, 6 H, $CH_3$), 1.94, 2.02, 2.06 (3 s, 9 H, 3 $CH_3CO$), 3.33 (s, 3 H, -$OCH_3$), 3.37 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, 1 H, 4a-H), 3.50 (dd, $J_{1,2}$ = 3.4, $J_{2,3}$ = 9.6 Hz, 1 H, 2a-H), 3.68 (dd, $J_{5,6}$ = 1.1, $J_{6,6'}$ = 10.5 Hz, 1 H, 6a-H), 3.74–3.79 (m, 2 H, 5b-H, 5a-H), 3.94–3.97 (m, 2 H, 3a-H, 0.5 -$CH_2$-), 4.06 (dd, $J_{5,6'}$ < 1.0, $J_{6,6'}$ = 10.5 Hz, 1 H, 6′a-H), 4.12–4.21 (m, 4 H, 1.5 -$CH_2$-, 6b-H), 4.27 (dd, $J_{5,6'}$ = 4.7, $J_{6,6'}$ = 12.2 Hz, 1 H, 6′b-H), 4.43 (d, $J_{gem}$ = 10.7, 1 H, 0.5 C$H_2$Ph), 4.55 (d, $J_{1,2}$ = 3.4 Hz, 1 H, 1a-H), 4.63 (d, $J_{gem}$ = 12.1 Hz, 1 H, 0.5 C$H_2$Ph), 4.76–4.82 (m, 4 H, 2b-H, 1.5 C$H_2$Ph), 4.95 (d, $J_{gem}$ = 10.8 Hz, 1 H, 0.5 C$H_2$Ph), 5.16 (dd, $J_{3,4}$ = 9.1, $J_{4,5}$ = 9.7 Hz, 1 H, 4b-H), 5.44 (d, $J_{1,2}$ = 8.3 Hz, 1 H, 1b-H), 5.68 (dd, $J_{2,3}$ = 10.3, $J_{3,4}$ = 9.1 Hz, 1 H, 3b-H), 7.24–7.35 (m, 15 H, 3 Ph) ppm. $^{13}C$ NMR (600 MHz, $CDCl_3$): $\delta$ = 20.51, 20.63, 20.74 (3 *C*$H_3CO$), 54.94 (C-2b), 55.14 (-$OCH_3$), 62.04 (C-6b), 67.98, 67.31 (2 -$CH_2$-), 69.49 (C-6a), 68.80 (C-4b), 69.17 (C-5a), 70.74 (C-3b), 71.76 (C-5b), 73.39, 74.81, 75.82 (3 *C*$H_2$Ph), 77.69 (C-4a), 81.82 (C-3a), 97.75 (C-2a), 97.99 (C-1a), 98.45 (C-1b), 127.61–138.57 (3 Ph), 169.13, 169.30, 169.96, 170.72, 170.86 (5 CO) ppm. MALDI MS (positive ion mode, DHB/THF matrix): *m*/*z* = 870.1 $[M + Na]^+$, 886.0 $[M + K]^+$. $C_{44}H_{51}NO_{16}$ (850.0): C 62.17, H 6.06, N 1.64; found C 61.71, H 6.04, N 1.64.

**Allyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-diglycolylimido-β-D-glucopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (21d):** The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 2:1) to afford **21d** (94%) as a colourless foam. TLC (petroleum ether/ethyl acetate, 2:1): $R_f$ = 0.17. $[\alpha]_D$ = +6.0 (*c* = 0.2, $CHCl_3$). $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ = 1.96, 2.03, 2.04 (3 s, 9 H, 3 $CH_3CO$), 3.62–3.73 (m, 4 H, 4a-H, 5a-H, 6′a-H, 6a-H), 3.82 (m, 1 H, 5b-H), 4.33–4.88 (m, 10 H, 2 -$CH_2$-, 6′b-H, 6b-H, 2a-H, -C$H_2$-CH=$CH_2$, 3a-H), 4.43–4.46 (d, 2 H, C$H_2$Ph), 4.52–4.54 (m, 2 H, C$H_2$Ph), 4.59 (d, $J_{1,2}$ < 1.0 Hz, 1 H, 1a-H), 4.75 (d, $J_{gem}$ = 11.3 Hz, 1 H, 0.5 C$H_2$Ph), 4.88 (d, $J_{gem}$ = 10.4 Hz, 1 H, 0.5 C$H_2$Ph), 4.90 (dd, $J_{1,2}$ = 8.3, $J_{2,3}$ = 10.8 Hz, 1 H, 2b-H), 5.15 (dd, $J_{3,4}$ = 9.0, $J_{4,5}$ = 9.6 Hz, 1 H, 4b-H), 5.17–5.24 (m, 2 H, -$CH_2$-CH=C$H_2$), 5.46 (d, $J_{1,2}$ = 8.3 Hz, 1 H, 1b-H), 5.77 (dd, $J_{2,3}$ = 10.8, $J_{3,4}$ = 9.0 Hz, 1 H, 3b-H), 5.84 (m, 1 H, -$CH_2$-C*H*=$CH_2$), 7.18–7.39 (m, 15 H, 3 Ph) ppm. $^{13}C$ NMR (150.9 MHz, $CDCl_3$): $\delta$ = 20.55, 20.65, 20.73 (3 *C*$H_3CO$), 54.26 (C-2b), 62.40 (C-6b), 67.08 (-*C*$H_2$-CH=$CH_2$), 68.07, 68.10 (2 -$CH_2$-), 69.18 (C-6a), 69.26 (C-4b), 70.11 (C-3b), 70.96 (*C*$H_2$Ph), 71.13 (C-5a), 72.09 (C-5b), 73.23 (*C*$H_2$Ph), 73.98 (C-4a), 74.02 (C-2a), 75.16 (*C*$H_2$Ph), 78.02 (C-3a), 81.80 (-$CH_2$CH=$CH_2$), 96.40 (C-1a), 97.07 (C-1b), 117.61–138.42 (3 Ph, -$CH_2$-*C*H=$CH_2$), 168.90, 169.41, 170.48, 170.70, 170.83 (5 CO) ppm. MALDI MS (positive ion mode, DHB/THF matrix): *m*/*z* = 896.1 $[M + Na]^+$, 912.1 $[M + K]^+$. $C_{46}H_{53}NO_{16}$ (876.0): C 63.06, H 6.11, N 1.59; found C 62.84, H 6.15, N 1.61.

**Thexyldimethylsilyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-diglycolylimido-β-D-glucopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (21f):** The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 2:1) to afford **21f** (86%) as a colourless foam. TLC (petroleum ether/ethyl acetate, 2:1): $R_f$ = 0.16. $[\alpha]_D$ = +12.0 (*c* = 0.15, $CHCl_3$). $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ = 0.05–0.08 [2 s 6 H, $Si(CH_3)_2$], 0.66, 0.67, 0.70, 0.72 (4 s, 12 H, 4 $CH_3$), 1.45 (m, 1 H, CH), 1.94, 1.95, 1.96, 1.99 (4 s, 12 H, 4 $CH_3CO$), 3.44 (m, 1 H, 5a-H), 3.51 (m, 1 H, 5b-H), 3.56 (dd, $J_{6,6'}$ = 11.6, $J_{5,6}$ = 3.3 Hz, 1 H, 6a-H), 3.61 (dd, $J_{6,6'}$ = 11.6, $J_{5,6'}$ = 1.1 Hz, 1 H, 6′a-H), 3.85 (dd, $J_{1,2}$ = 10.7 Hz, 1 H, 2a-H), 3.90 (dd, $J_{6,6'}$ = 12.3, $J_{5,6}$ = 2.0 Hz, 1 H, 6b-H), 4.04–4.08 (m, 2 H, 0.5 -$CH_2$-, 4a-H), 4.13–4.17 (m, 2 H, 6′b-H, 3a-H), 4.23–4.26 (m, 2 H, -$CH_2$-), 4.33 (d, $J_{gem}$ = 16.4 Hz, 1 H, 0.5 -$CH_2$-), 4.60–4.67 (2 d, $J_{gem}$ = 11.4 Hz, 2 H, C$H_2$Ph), 4.74 (dd, $J_{1,2}$ = 8.2, $J_{2,3}$ = 10.5 Hz, 1 H, 2b-H), 4.43, 4.83 (2 d, $J_{gem}$ = 12.7 Hz, 2 H, C$H_2$Ph), 5.09 (d, $J_{1,2}$ = 8.2 Hz, 1 H, 1a-H), 5.10 (dd, $J_{3,4}$ = 8.9, $J_{4,5}$ = 10.0 Hz, 1 H, 4b-H), 5.61 (d, $J_{1,2}$ = 8.2 Hz, 1 H, 1b-H), 5.67 (dd, $J_{2,3}$ = 10.5, $J_{3,4}$ = 8.9 Hz, 1 H, 3b-H), 7.14–7.39 (m, 10 H, 2 Ph) ppm. $^{13}C$ NMR (150.9 MHz, $CDCl_3$): $\delta$ = –3.89, –1.91 $[Si(CH_3)_2]$, 3.16 (SiC), 8.14 (C-thexyl), 18.37–20.66 (4 $CH_3$, 3 *C*$H_3CO$), 24.49 (CH), 33.94 (2 $CH_3$), 55.59 (C-2b), 57.52 (C-2a), 61.60 (C-6b), 67.41, 68.05 (2 -$CH_2$-), 68.23 (C-6a), 68.65 (C-4b), 70.56 (C-3b), 71.41 (C-5b), 73.46, 73.80 (2 *C*$H_2$Ph), 74.76 (C-5a), 76.60 (C-4a), 77.59 (C-3a), 93.29 (C-1a), 97.54 (C-1b), 122.13–139.10 (2 Ph), 169.37, 169.57, 170.09, 170.66, 170.72 (5 CO) ppm. MALDI MS (positive ion mode, DHB/THF matrix): *m*/*z* = 936.0 $[M + Na]^+$, 952.0 $[M + K]^+$. $C_{44}H_{62}N_4O_{15}Si$ (913.2): C 57.86, H 6.63, N 6.13; found C 57.45, H 6.71, N 6.11.

**2,4,6-Trimethoxyphenyl 3,4,6-Tri-*O*-acetyl-1,2-dideoxy-2-diglycolylimido-β-D-glucopyranoside (21g):** The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 1.5:1) to yield **21g** (86%) as a colourless foam. TLC (petroleum ether/ethyl acetate, 1.5:1): $R_f$ = 0.2. $[\alpha]_D$ = –21.2 (*c* = 0.25, $CHCl_3$). $^1H$ NMR (600 MHz, $CDCl_3$): $\delta$ = 1.97, 2.06, 2.07 (3 s, 9 H, 3 $CH_3CO$), 3.74, 3.77, 3.83 (3 s, 9 H, 3 $OCH_3$), 3.90 (m, 1 H, 5-H), 4.01–4.19 (m, 5 H, 6-H, 2 -$CH_2$-), 4.29 (dd, $J_{6,6'}$ = 12.3, $J_{5,6'}$ = 4.4 Hz, 1 H, 6′-H), 5.27 (dd, $J_{3,4}$ = 9.4, $J_{4,5}$ = 9.7 Hz, 1 H, 4-H), 5.70 (dd, $J_{1,2}$ = 10.4, $J_{2,3}$ = 10.3 Hz, 1 H, 2-H), 5.87 (d, $J_{1,2}$ = 10.4 Hz, 1 H, 1-H), 5.98 (dd, $J_{2,3}$ = 10.3, $J_{3,4}$ = 9.4 Hz, 1 H, 3-H), 6.02, 6.07 (2 d, *J* = 2.1 Hz, 2 H, Ar) ppm. $^{13}C$ NMR (150.9 MHz, $CDCl_3$): $\delta$ = 20.72, 20.76, 20.82 (3 *C*$H_3CO$), 52.67 (C-2), 55.19, 55.78, 56.02 (3 $OCH_3$), 62.65 (C-6), 67.29, 68.11 (2 -$CH_2$-), 69.48 (C-4), 69.65 (C-1), 72.40 (C-3), 75.68 (C-5), 90.39, 91.70 (2 C-Ar), 104.45 (C-Ar), 159.70–170.89 (5 CO, 3 C-Ar) ppm. MALDI MS (positive ion mode, DHB/THF

matrix): *m*/*z* = 575.9 [M + Na]$^+$, 591.9 [M + K]$^+$. $C_{25}H_{31}NO_{13}$ (553.9): C 54.23, H 5.65, N 2.53; found C 53.92, H 5.85; N 2.64.

**General Procedure for the Synthesis of Compounds 6a,[12] 6d,[17] 6g,[37] and 22.**[35,36] **Method A:** A mixture of the appropriate glycoside **16** or **21a**, **21d**, and **21f** (0.17 mmol) and KOH (1.2 g) in EtOH (96% v/v, 5 mL) was refluxed for 4 h and then the solvent was evaporated until dryness in vacuo. The residue was stirred with pyridine (12 mL) in an ice/water bath and then treated with $Ac_2O$ (6 mL). The cooling bath was removed after 2 h and the mixture stirred at room temp. overnight and then coevaporated with toluene in vacuo. The residue was taken up in $H_2O$ (20 mL) and dichloromethane (100 mL), the organic layer was separated, dried with $MgSO_4$, and the solvents evaporated in vacuo. The physical data obtained for **6a**[12] and **6d**[17] are identical to those given in the literature.

**2,4,6-Trimethoxyphenyl 2-Acetamido-3,4,6-tri-*O*-acetyl-1,2-dideoxy-β-D-glucopyranoside (6g):** The residue was purified by flash chromatography (toluene/acetone, 1.5:1) to yield **6g**[37] (76%) as a yellowish foam. TLC (toluene/acetone, 1.5:1): $R_f$ = 0.26. $^1$H NMR (600 MHz, [D$_6$]DMSO, 100 °C): $\delta$ = 1.53, 1.91, 1.97, 1.98 (4 s, 12 H, 4 $CH_3CO$), 3.70 (m, 1 H, 5-H), 3.75 (br. s, 9 H, 3 $OCH_3$), 4.06 (m, 2 H, 6′-H, 6-H), 4.70 (m, 1 H, 2-H), 4.88 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, 1 H, 4-H), 4.96 (d, $J_{1,2}$ = 10.3 Hz, 1 H, 1-H), 5.19 (dd, $J_{2,3}$ = $J_{3,4}$ = 9.6 Hz, 1 H, 3-H), 6.17 (s, 2 H, Ar), 7.12 (d, $J_{2,NH}$ = 6.9 Hz, 1 H, NH) ppm. $^{13}$C NMR (150.9 MHz, $CDCl_3$): $\delta$ = 19.74, 21.84 (4 *C*H$_3$CO), 50.46 (C-2), 54.71, 55.88 (3 $OCH_3$), 62.27 (C-6), 69.43 (C-4), 71.55 (C-1), 74.55 (C-3, C-5), 92.04 (Ar) ppm.

**Benzyl 2-Acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucose (22):** The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 1:1) to yield **22**[36] (94 mg, 82%) as amorphous mass. TLC (petroleum ether/ethyl acetate, 1:1): $R_f$ = 0.31. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.81 (s, 3 H, $CH_3CO$), 3.53–3.80 (m, 5 H), 4.04 (dd, *J* = 8.5, 10.0 Hz, 1 H), 4.55–4.85 (m, 8 H, 3.5 C*H*$_2$Ph, 1-H), 4.89 (d, $J_{gem}$ = 11.5 Hz, 1 H, CH*H*Ph), 5.53 (d, $J_{8,6}$ = Hz, 1 H, NH), 7.18–7.38 (m, 20 H, 4 Ph) ppm. MALDI MS (positive ion mode, DHB/THF matrix): *m*/*z* = 582.3 [*M* + H]$^+$, 604.2 [*M* + Na]$^+$ , 620.2 [*M* + K]$^+$. $C_{36}H_{39}NO_6$ (581.76).

**Method B:** Compound **16** (0.268 g, 0.42 mmol) in NaOBu (1.0 M, 10 mL) was gently refluxed for 20 h. The reaction mixture was then treated with Pyr/$Ac_2O$ and worked up as described in method A. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 1:1) to yield **22** (0.169 g, 69%).

**Method C:** A mixture of **16** (0.22 g, 0.34 mmol) and hydrazine hydrate (3 mL) was heated at 120–130 °C for 14 h and then stirred with Pyr (16 mL) and $Ac_2O$ (12 mL) in an ice bath. After 1 h the mixture was diluted with ethyl acetate (20 mL), filtered at a vacuum pump, and coevaporated with toluene in vacuo. The residue was taken up in ethyl acetate (100 mL), washed with 5% HCl (5 × 20 mL), $H_2O$ (20 mL), and sat. $Na_2CO_3$ (20 mL), dried with $MgSO_4$, evaporated in vacuo, and purified as described before to yield **22** (76.0 mg, 38%).

**Method D:** A mixture of **16** (0.174 g, 0.27 mmol) and hydrazine hydrate (0.5 mL, 10.2 mmol) in dry EtOH (5 mL) was refluxed overnight, then evaporated in vacuo, and dried well. The residue was treated with $Ac_2O$/Pyr and purified as described in method B to yield **22** (6.0 mg, 3%).

***tert*-Butyldimethylsilyl 4,6-Di-*O*-benzylidene-2-deoxy-2-diglycolylimido-β-D-glucopyranoside (24):** A mixture of **17** (0.626 g, 2.2 mmol), benzaldehyde dimethylacetal (0.7 mL, 4.6 mmol), and *p*TsOH (0.04 g, 0.2 mmol) in a mixture of $CH_3CN$/DMF (2:1, 15 mL) was stirred at room temp. overnight. The mixture was neutralized with $Et_3N$, the solvent evaporated in vacuo, and the residue purified by flash chromatography (toluene/acetone, 3:1) to yield **23** (0.458 g, 55%) as colourless foam. TLC (toluene/acetone, 3:1): $R_f$ = 0.24. Compound **23** was stirred with TBDMS-Cl (0.18 g, 1.2 mmol) and imidazole (0.17 g, 2.5 mmol) in dry dichloromethane (5 mL) at room temp. After 75 min the mixture was diluted with $H_2O$ (10 mL) and dichloromethane (50 mL), then the organic layer was separated, dried with $MgSO_4$, and the solvent evaporated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 2:1) to yield **24** (0.475 g, 79%) as a colourless amorphous mass. TLC (petroleum ether/ethyl acetate, 2:1): $R_f$ = 0.18. $[a]_D$ = –4.5 (*c* = 0.3, $CHCl_3$). $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 0.02, 0.07 [2 s, 6 H, Si(CH$_3$)$_3$], 0.82 [s, 9 H, C(CH$_3$)$_3$], 2.64 (br. s, 1 H, OH), 3.51, 3.77 (2 m, 3 H, 4-H, 6-H, 5-H), 4.20–4.36 (m, 5 H, 2 -C*H*$_2$-, 6′-H), 4.55–4.64 (m, 2 H, 2-H, 3-H), 5.45 (d, $J_{1,2}$ = 7.2 Hz, 1 H, 1-H), 5.51 (s, 1 H, C*H*Ph), 7.32–7.48 (m, 5 H, Ph) ppm. MALDI MS (positive ion mode, DHB/THF matrix): *m*/*z* = 502.5 [M + Na]$^+$, 516.6 [M + K]$^+$. $C_{23}H_{33}NO_8Si$ (479.7): C 57.58, H 6.94, N 2.92; found C 57.11, H 7.17; N 2.91.

***tert*-Butyldimethylsilyl 2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1→3)-4,6-di-*O*-benzylidene-2-deoxy-2-diglycolylimido-β-D-glucopyranoside (26):** A mixture of **25**[38,39] (0.3 g, 0.6 mmol) and **24** (0.2 g, 0.41 mmol) in dry dichloromethane (1 mL) was stirred under argon at room temp. while TMSOTf (0.01 M in $CH_2Cl_2$, 0.6 mL) was added dropwise. After 45 min the mixture was neutralized with $Et_3N$ and the solvent evaporated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 2:1) and then stirred with Pyr (4 mL) and $Ac_2O$ (2 mL). After 4 h the mixture was coevaporated with toluene in vacuo and the residue was purified by MPLC (petroleum ether/ethyl acetate, 2:1) to yield **26** (0.308 g, 91%) as a colourless foam. TLC (petroleum ether/ethyl acetate, 2:1): $R_f$ = 0.18. $[a]_D$ = –4.8 (*c* = 1.85, $CHCl_3$). $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 0.03, 0.08 [2 s, 6 H, Si(CH$_3$)$_2$], 0.84 [s, 9 H, SiC(C*H*$_3$)$_3$], 1.93, 1.94, 1.99, 2.12 (4 s, 12 H, 4 $CH_3CO$), 3.43 (m, 1 H, 5b-H), 3.58 (m, 1 H, 5a-H), 3.81–3.88 (m, 3 H, 6b-H, 6a-H, 4a-H), 4.03 (dd, $J_{6,6'}$ = 11.0, $J_{5,6'}$ = 8.0 Hz, 1 H, 6′b-H), 4.28–4.31 (m, 2 H, 0.5 -CH$_2$-, 6′a-H), 4.36 (m, 2 H, -CH$_2$-), 4.47 (d, $J_{gem}$ = 16.1 Hz, 1 H, 0.5 -CH$_2$-), 4.65 (d, $J_{1,2}$ = 7.9 Hz, 1 H, 1b-H), 4.72–4.73 (m, 2 H, 2a-H, 3a-H), 4.85 (dd, $J_{2,3}$ = 10.2, $J_{3,4}$ = 3.0 Hz, 1 H, 3b-H), 4.98 (dd, $J_{1,2}$ = 7.3, $J_{2,3}$ = 10.2 Hz, 1 H, 2b-H), 5.23 (d, $J_{3,4}$ = $J_{4,5}$ = 3.0 Hz, 1 H, 3b-H), 5.36 (d, $J_{1,2}$ = 7.3 Hz, 1 H, 1a-H), 5.53 (s, 1 H, C*H*Ph), 7.38–7.47 (m, 5 H, Ph) ppm. $^{13}$C NMR (600 MHz, $CDCl_3$): $\delta$ = –5.47, –4.22 [Si(CH$_3$)$_2$], 17.62 (Si-C), 20.54, 20.57, 20.70, 20.80 (4 *C*H$_3$CO), 25.39 [C(*C*H$_3$)$_3$], 57.17 (C-2a), 60.97 (C-6b), 66.28 (C-5a), 66.60 (C-4b), 67.48, 68.15 (2 -*C*H$_2$-), 68.83 (C-6a), 69.84 (C-2b), 70.23 (C-5b), 70.93 (C-3b), 75.11 (C-3a), 81.90 (C-4a), 93.39 (C-1a), 100.07 (C-1b), 101.63 (C*H*Ph), 126.00, 128.46, 129.40, 136.99 (Ph), 169.54, 170.02, 170.09, 170.32 (6 CO) ppm. FAB MS (positive ion mode, NBOH/NaI matrix): *m*/*z* = 832.0 [M + Na]$^+$. $C_{37}H_{51}NO_{17}Si$ (810.0): C 54.86, H 6.35, N 1.72; found C 55.01, H 6.39; N 1.77.

## Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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Received: February 9, 2005
Published Online: August 26, 2005

  