Synthesis of an Asparagine-Linked Heptasaccharide − Basic Structure of *N*-Glycans

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Galβ(1–4)GlcNAcβ(1–2)Manα(1–3)[Manα(1–6)]Manβ(1–4)-GlcNAcβ(1–4)GlcNAcβ(1–N)Asn (**1**) was disconnected into building blocks **2**–**6**. *N*-Dimethylmaleoyl (DMM) protected glucosamine **3** was readily obtained from glucosamine. Transformation of **3** into 4-*O*-unprotected glucosamine derivatives **9**, **14**, and **18** furnished the intermediates required for the incorporation of the three differently linked glucosamine residues. Thus, disaccharide **20** was obtained from acceptor **9** and glucosyl donor **19** and converted into protected Manβ(1–4)GlcNAc disaccharide donor **5** by inversion of the configuration at C-2 of the glucose residue. Glycosylation of acceptor **18** with known galactosyl donor **26** afforded protected lactosamine donor **6**. The synthesis of asparagine building block **2** and of mannosyl donor **4** has already been reported. With building blocks **2**–**6** in hand, the synthesis of **1** was accomplished. Glycosylation of acceptor **14** with donor **5** gave trisaccharide **29** which was transformed into acceptor **30**. Treatment of **30** with glycosyl donor **4** provided tetrasaccharide intermediate **31**. Its transformation into 2d-*O*-unprotected acceptor **33** and then reaction with disaccharide donor **6** furnished hexasaccharide **34**. Removal of the 4c,6c-*O*-benzylidene group gave 4c,6c-*O*-unprotected acceptor **35** which, on glycosylation with donor **4**, led to heptasaccharide **36**. Replacement of the *N*-DMM groups by *N*-acetyl groups and removal of all *O*-acyl groups, followed by transformation of the C-1a azido group into an amino group, and attachment of asparagine building block **2** led to the desired heptasaccharide β-linked to asparagine **39**. Hydrogenolysis of all *O*-benzyl groups afforded target molecule **1**.

Introduction

Most cell surface proteins and proteins present in blood serum of vertebrates are *N*- and/or *O*-glycosylated; the derived glycoproteins often appear in various glycoforms, thus constituting natural product libraries.[1,2] In order to investigate the biological function of the various oligosaccharide residues, the *N*-glycans in particular gained wide interest.[3,4] The required structurally defined *N*-glycans should be accessible by chemical[5−12] or chemoenzymatic[13−15] synthesis as shown by several groups.

We have developed over the years efficient syntheses of mono-, di- and trisaccharide building blocks which are also useful in *N*-glycan synthesis,[12,17] as also shown in related approaches.[10,14] Therefore, a versatile strategy for the eventual construction of all complex-type, including bisected-type oligosaccharides, required for *N*-glycopeptide synthesis was initiated.[12,18] Here it was applied to the asparagine-linked heptasaccharide **1**, consisting of the pentasaccharide core structure abcdg and of one *N*-acetyllactosamine residue (cf. Scheme 1); full details of the synthesis are reported. Our strategy was based on a flexible protecting group pattern, which included the dimethylmaleoyl (DMM) group as an amino protecting group,[19] and on *O*-glycosyl trichloroacetimidates as powerful glycosyl donors.[17] Bond disconnections 1−4 (Scheme 1) lead to the required building blocks **2**−**6**. They should allow for the generation of **1** as well as for the attachment of other antennae and also of different antennae at the 2-hydroxy groups of the two α-linked mannose residues; also either an *N*-acetylglucosamine or a fucosyl α(1−6)-*N*-acetylglucosamine residue can be attached with a β(1−4)-linkage at the reducing end. With an *N*-linkage to asparagine, these compounds can be directly employed for *N*-glycopeptide synthesis.[20] The required building block **2**[21] with an activated carboxylate side chain as well as the mannose building block **4**[22] are readily available following literature procedures.

Results and Discussion

The *N*-acetylglucosamine (GlcNAc) residue is contained in three different positions (a, b, e) each in a 1- and 4-linkage. These linkages can be accommodated by building block **3** which was readily obtained from known precursor **7**[19a] (Scheme 2). Silylation of **7** with thexyldimethylsilyl chloride (TDS-Cl) in the presence of imidazole gave **8**, which afforded the desired intermediate **3** on *O*-deacetylation under Zemplén conditions.[23] Regioselective *O*-benzylation of **3** with benzyl bromide in the presence of dibutyltin oxide in toluene[19a,24] afforded 3,6-di-*O*-benzyl derivative **9** in high yield, which is ideal for the incorporation of GlcNAc residue b. In order to allow for convenient ligation of the asparagine residue at position a, compound **9** was transformed under standard conditions into azido derivative **14** by means of 4-*O*-acetylation (→ **10**), 1-*O*-desilylation (→ **11**), and then transformation with DAST as fluorinating agent into fluoride **12**. Treatment of **12** with trimethylsilyl azide in the presence of $BF_3{\cdot}OEt_2$ as catalyst[25] gave 1-azido derivative **13** as the pure β-anomer (^{1}H NMR: $J_{1,2}$ = 9.4 Hz), which on 4-*O*-deacetylation furnished the desired compound **14**.

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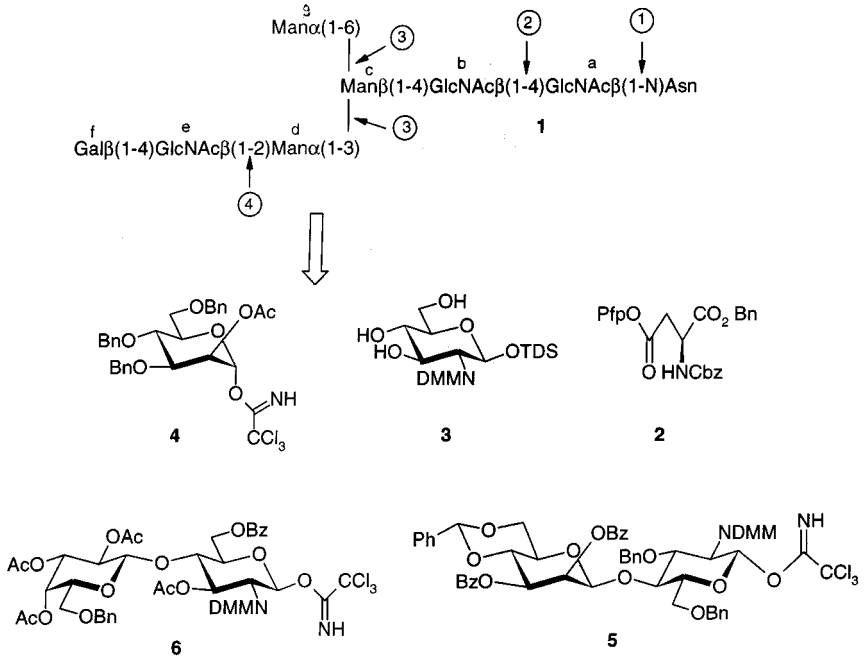
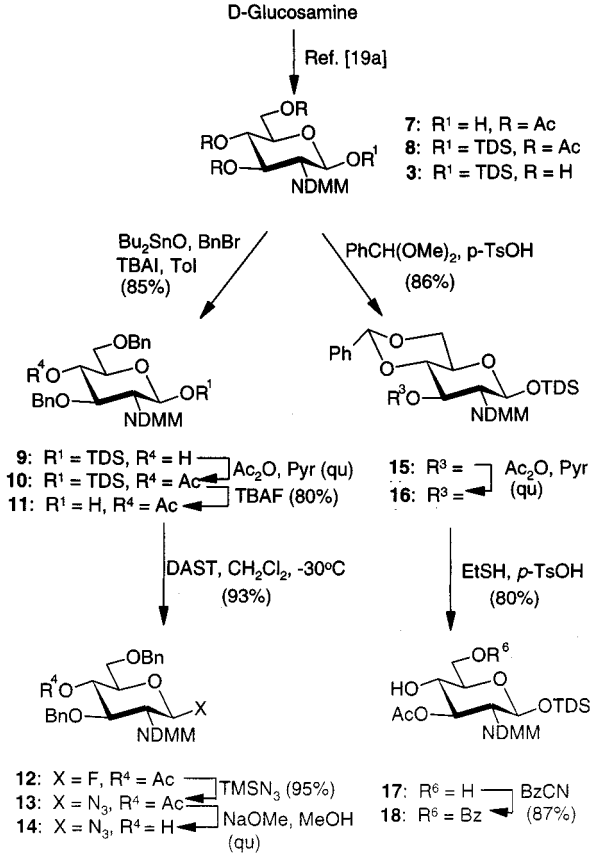


Scheme 1. Structure of target molecule **1** and its retrosynthesis leading to building blocks **2**–**6**

Although **9** would also be an ideal building block for the incorporation of GlcNAc residue e, instead building block **18** was envisaged, in order to gain both further versatility in this approach and reaction control in the glycosylation step. To this end, 3,4,6-*O*-unprotected **3** was transformed into 4,6-*O*-benzylidene derivative **15**; ensuing 3-*O*-acetylation (→ **16**), acid-catalyzed de-*O*-benzylidenation (→ **17**), and then 6-*O*-selective benzoylation with benzoyl cyanide in the presence of triethylamine as base in propionitrile as solvent at −60 °C afforded **18** in high overall yield.

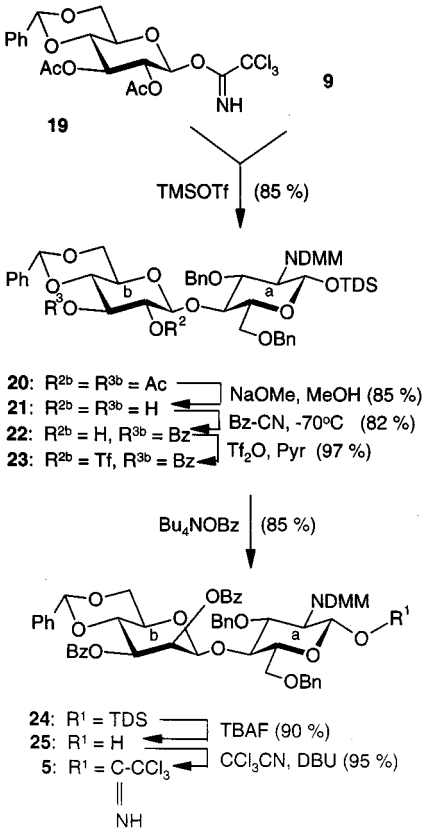
For the β-mannopyranosidic linkage between sugar residues c and b in **1**, which is required for the construction of building block **5**, transformation of a β-linked glucopyranosyl to a β-mannopyranosyl residue was envisaged, for which various modifications have already been reported (Scheme 3).[8,11,12,20,26–28] To this end, acceptor **9** was glucosylated with known glucosyl donor **19**[12] in the presence of trimethylsilyl trifluoromethanesulfonate (TMSOTf) as catalyst, furnishing the desired β-linked disaccharide **20** in high yield (^{1}H NMR: $J_{1,2}$ = 7.9 Hz, 1b-H). De-*O*-acetylation (→ **21**) and regioselective 3b-*O*-benzoylation, as described above, afforded **22**, which was converted with Tf_2O in the presence of pyridine into triflate **23**. Reaction of **23** with tetrabutylammonium benzoate in acetonitrile gave the desired disaccharide **24** (^{1}H NMR: $J_{1,2}$ = 1 Hz, 1b-H) in very high overall yield. 1-*O*-Desilylation with TBAF (→ **25**) and then trichloroacetimidate formation with trichloroacetonitrile in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) afforded building block **5**; only the β-isomer was obtained (^{1}H NMR: $J_{1,2}$ = 9.1 Hz, 1a-H).

The lactosamine building block **6** was readily obtained from **18** as acceptor and known galactosyl donor **26** (Scheme 4);[29] glycosylation in the presence of TMSOTf as catalyst afforded the desired β-linked disaccharide **27** (^{1}H NMR: $J_{1,2}$ = 7.8 Hz, 1b-H) (Scheme 4). Again 1-*O*-desilylation (→ **28**) and trichloroacetimidate formation under standard conditions afforded **6** in high overall yield.

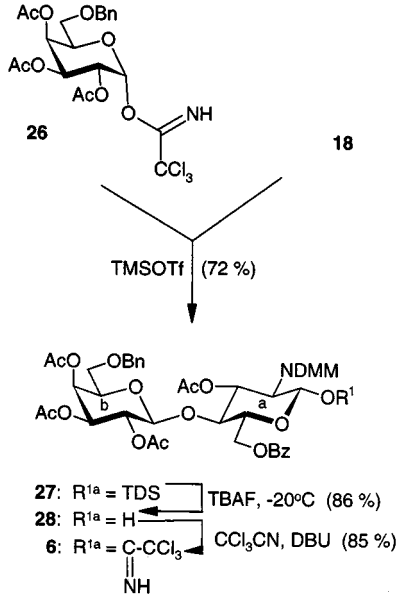


Scheme 2. Synthesis of the required *N*-acetylglucosamine building blocks **9**, **14**, and **18** derived from **3**

For the final ligation of the building blocks **2**–**6**, acceptor **14** was firstly glycosylated with donor **5** in the pres-



Scheme 3. Synthesis of disaccharide building block **5**



Scheme 4. Synthesis of disaccharide building block **6**

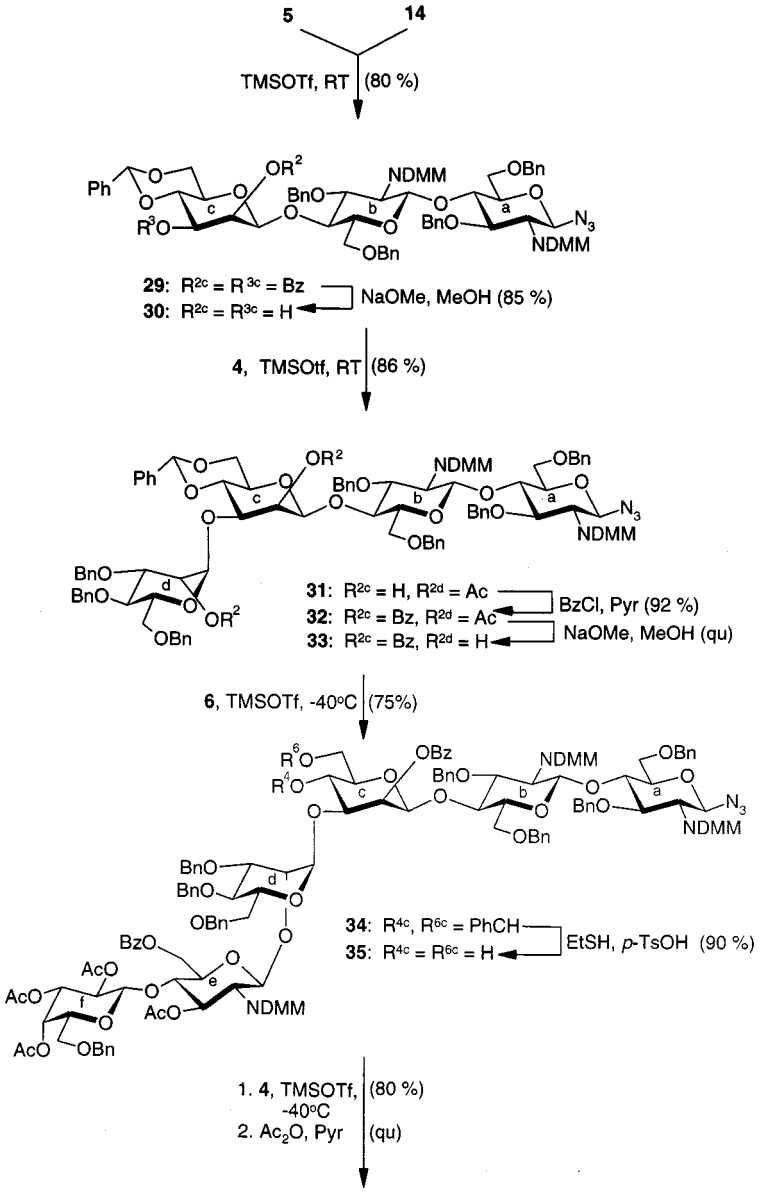
ence of TMSOTf as catalyst at room temperature affording trisaccharide **29** (^{1}H NMR: $J_{1,2}$ = 8.5 Hz, 1b-H) in 80% yield (Scheme 5). Debenzoylation with NaOMe in methanol furnished 2c,3c-*O*-unprotected acceptor **30**. Regioselective 3c-*O*-mannosylation of **30**, with **4** as glycosyl donor, provided tetrasaccharide **31** in high yield. The α-linkage of residue d was derived from the NMR spectroscopic data ($J_{1,2}$ < 1 Hz, 1d-H; δ = 98.7, C-1d). 2c-*O*-Benzoylation of **31** with benzoyl chloride in pyridine gave **32** from which the 2d-*O*-acetyl group could be selectively removed by treatment with NaOMe in MeOH/dichloromethane at room temperature, thus providing acceptor **33**. Glycosylation of **33** with donor **6** in the presence of TMSOTf as catalyst afforded hexasaccharide **34** in 75% yield. The β-linkage could be derived from the NMR-spectroscopic data ($J_{1,2}$ = 8.5 Hz, 1e-H). Removal of the 4c,6c-*O*-benzylidene group in **34** with ethanethiol as nucleophile in the presence of *p*-toluenesulfonic acid (*p*TsOH) as catalyst[30] afforded glycosyl acceptor **35**. Glycosylation with donor **4**, again in the presence of TMSOTf as catalyst, furnished the desired heptasaccharide **36** in 80% yield. The NMR-spectroscopic data for the mannosyl residue g are in the expected range for α-linkages (^{1}H: δ = 4.83, $J_{1,2}$ < 1 Hz, 1g-H; ^{13}C: δ = 98.5, C-1g). In order to confirm the structural assignments, C,H coupling constants were obtained for all anomeric positions with the help of HMQC experiments; they were found to be in the expected range: $^1J_{C,H}$ 163.94 Hz (1a-H, β), 168.49 Hz (1b-H, β), 161.2 Hz (1c-H, β), 170.39 Hz (1d-H, α), 164.84 Hz (1e-H, β), 161.2 Hz (1f-H, β), 172.13 Hz (1g-H, α). The three DMM protecting groups in **36** could be removed by sodium hydroxide followed by mild acid treatment, as previously described,[19] thus affording after *N*,*O*-acetylation with acetic anhydride in pyridine, compound **37** in 74% yield. The *O*-acetyl and *O*-benzoyl protecting groups could be removed with lithium hydroxide in MeOH (→ **38**). Transformation of the azido group into the amino group by treatment of **38** with propanedithiol as reducing agent[31] in the presence of Hünig's base and then amide bond formation with asparagine derivative **2**[21] and *N*-hydroxybenzotriazole (HOBT)/Hünig's base as promoter afforded compound **39**. The β-linkage of the asparagine residue could be derived from the NMR-spectroscopic data ($J_{1,2}$ = 9.4 Hz for 1a-H). Hydrogenation of **39** with Pearlman's catalyst in MeOH/water furnished target molecule **1** in good yield. The structural assignment was confirmed by the ^{1}H-NMR-spectroscopic data of the anomeric protons.

Experimental Section

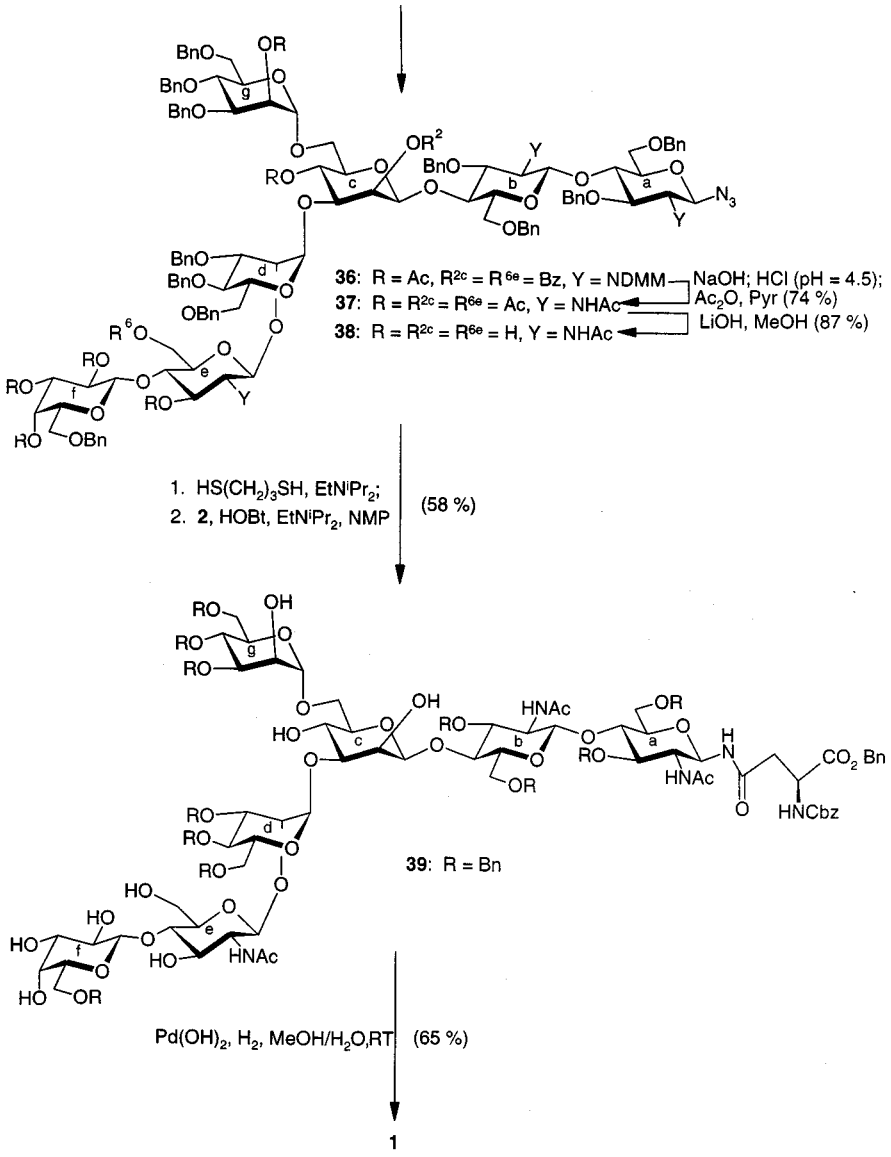
Solvents were purified in the usual way. − Melting points are uncorrected. − TLC was performed on plastic plates coated with silica gel 60 F_{254} and on HPTL plates with NH_2 F_{254} S (E. Merck, layer thickness 0.2 mm). − Detection was achieved by treatment with a solution of ammonium molybdate (20 g) and cerium(IV) sulfate (0.4 g) in H_2SO_4 (10%, 400 mL), or with H_2SO_4 (15%), and heating at 150 °C. Flash chromatography was carried out on silica gel (Baker, 30−60 μm) and Lichroprep NH_2, particle size 40−63 μm. − Medium-pressure liquid chromatography (MPLC): LiChroprep Si 60 (Merck: mesh size 15−25 μm), detection by a differential refractometer. − Optical rotations were determined at 21 °C with a Perkin−Elmer 241/MC polarimeter (1-dm cell). − NMR spectra were recorded with Bruker AC 250 and 600 DRX instruments, with tetramethylsilane as internal standard. The assignment of ^{1}H NMR

spectra was based on chemical shift correlation (DQF COSY) and Rotating Frame Nuclear Overhauser Effect Spectroscopy (ROESY). − The assignment of ^{13}C NMR spectra was based on Carbon-Proton Shift-Correlation Heteronuclear Multiple Quantum Coherence (HMQC). − MS spectra were recorded with a MALDI-Kompakt (Kratos) and FAB with a Finningan MAT 312/AMD mass spectrometer. Microanalyses were performed in the Microanalysis Unit at the Fakultät für Chemie, Universität Konstanz.

Dimethyl(thexyl)silyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (8): To a solution of **7**[19a] (9.00 g, 21.9 mmol) and imidazole (3.00 g, 43.8 mmol) in dry dichloromethane (100 mL) was added chlorodimethyl(thexyl)silane (5.1 mL, 26.3 mmol) and stirred at room temp. for 16 h. The reaction mixture was diluted with dichloromethane (200 mL), poured into water (300 mL) and separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 300 mL), the combined organic layers were dried with magnesium sulfate and concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 3:1) to give **3** (10.6 g, 87%) as a white powder. − TLC (petroleum ether/ethyl acetate, 2:1): R_f = 0.51. − $[\alpha]_D^{20}$ = −15.1 (*c* = 1.0, $CHCl_3$). − ^1H NMR (250 MHz, $CDCl_3$): δ = 0.03 [2 s, 6 H, $Si(CH_3)_2$], 0.7 (m, 12 H, 4 CH_3), 1.48 [m, 1 H, $CH(CH_3)_2$], 1.90 (s, 6 H, 2 CH_3), 1.92 (s, 3 H, $COCH_3$), 2.00 (s, 3 H, $COCH_3$), 2.03 (s, 3 H, $COCH_3$), 3.82 (dd, $^3J_{5,4}$ = 10.1 Hz, $^3J_{5,6}$ = 5.8 Hz, $^3J_{5,6'}$ = 2.6 Hz, 1 H, 5-H), 4.03 (dd, $^3J_{2,3}$ = 10.8 Hz, $^3J_{2,1}$ = 8.0 Hz, 1 H, 2-H), 4.14 (dd, ^2J = 12.0 Hz, $^3J_{6',5}$ = 2.6 Hz, 1 H, 6′-H), 4.23 (dd, ^2J = 12.0 Hz, $^3J_{6,5}$ = 5.8 Hz, 1 H, 6-H), 5.07 (dd, $^3J_{4,5}$ = 10.1 Hz, $^3J_{4,3}$ = 9.0 Hz, 1 H, 4-H), 5.39 (d, $^3J_{1,2}$ = 8.0 Hz, 1 H, 1-H), 5.67 (dd, $^3J_{3,2}$ = 10.8 Hz, $^3J_{3,4}$ = 9.0 Hz, 1 H, 3-H). − $C_{26}H_{40}NO_{10}Si$ (554.7): calcd. C 56.30, H 7.26, N 2.52; found C 56.00, H 7.07, N 2.54.



Scheme 5. Synthesis of **1** from building blocks **2**, **4**, **5**, **6** and **14**, which is obtained from **3**



Scheme 5. *(Continued)*

Dimethyl(thexyl)silyl 2-Deoxy-2-dimethylmaleimido-β-D-glucopyranoside (3): A solution of **8** (9.0 g, 16.3 mmol) in dry methanol (60 mL) was treated with a catalytic amount of sodium methoxide (0.1 M, 1.8 mL) and stirred at room temp. After 4 h, the solution was neutralized with ion-exchange resin (Amberlite IR-120 H^+), the resin filtered off and the filtrate concentrated in vacuo. The residue was crystallized from petroleum ether/ethyl acetate to give **3** (6.9 g, 98%) as white crystals. − TLC (toluene/acetone, 5:3): R_f = 0.44. − M.p. 164.5−165.7 °C. − $[\alpha]_D^{20}$ = −22.1 (c = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.03 [2 s, 6 H, $Si(CH_3)_2$], 0.7 (m_c, 12 H, 4 CH_3), 1.48 [m_c, 1 H, C*H*$(CH_3)_2$], 1.91 (s, 6 H, 2 CH_3), 3.39−3.58 (m, 3 H, 4-H, 5-H, 6′-H), 3.74 (dd, $^3J_{2,3}$ = 10.9 Hz, $^3J_{2,1}$ = 8.0 Hz, 1 H, 2-H), 3.82 (dd, ^2J = 3.3 Hz, $^3J_{6,5}$ = 1.0 Hz, 1 H, 6-H), 4.15 (dd, $^3J_{3,2}$ = 10.9 Hz, $^3J_{3,4}$ = 8.6 Hz, 1 H, 3-H), 5.21 (d, $^3J_{1,2}$ = 8.0 Hz, 1 H, 1-H). − $C_{20}H_{35}NO_7Si$ (429.6): calcd. C 55.91, H 8.21, N 3.26; found C 55.71, H 8.11, N 3.22.

Dimethyl(thexyl)silyl 3,6-Di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (9): A suspension of **3** (6.5 g, 15.2 mmol) and dibutyltin oxide (8.3 g, 33.4 mmol) in toluene (150 mL) was heated at reflux (Dean-Stark apparatus) overnight with azeotropic removal of water. The reaction mixture was cooled below boiling and treated with tetrabutylammonium iodide (12.3 g, 33.4 mmol) and benzyl bromide (4 mL, 33.4 mmol) and then gently heated at reflux for 3 h. The solution was cooled to room temp., the precipitate was filtered and the filtrate concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 4:1) to give **9** (7.87 g, 85%) as a yellow oil. − TLC (petroleum ether/ethyl acetate, 2:1): R_f = 0.57. − $[\alpha]_D^{20}$ = +22.6 (c = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.03 [2 s, 6 H, $Si(CH_3)_2$], 0.7 (m_c, 12 H, 4 CH_3), 1.48 [m_c, 1 H, $CH(CH_3)_2$], 1.82 (br. s, 6 H, 2 CH_3), 2.88 (d, ^2J = 2.6 Hz, 1 H, OH), 3.55 (ddd, $^3J_{5,6}$ = 9.6 Hz, $^3J_{5,6'}$ = 9.4 Hz, $^3J_{5,4}$ = 4.5 Hz, 1 H, 5-H), 3.70−3.80 (m, 3 H, 4-H, 6-H, 6′-H), 3.85 (dd, $^3J_{2,3}$ = 10.9 Hz, $^3J_{2,1}$ = 8.1 Hz,

1 H, 2-H), 4.09 (dd, $^3J_{3,2}$ = 10.9 Hz, $^3J_{3,4}$ = 8.3 Hz, 1 H, 3-H), 4.50 (d, ^2J = 12.4 Hz, 1 H, C*H*Ph), 4.57 (2d, 2 H, CH_2Ph), 4.73 (d, ^2J = 12.4 Hz, 1 H, C*H*Ph), 5.16 (d, $^3J_{1,2}$ = 8.1 Hz, 1 H, 1-H), 7.11−7.32 (m, 10 H, 2 Ph). − $C_{34}H_{47}NO_7Si$ (609.8): calcd. C 66.96, H 7.76, N 2.29; found C 66.95, H 7.73, N 2.24.

Dimethyl(thexyl)silyl 4-*O*-Acetyl-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (6): Compound **9** (3.4 g, 5.57 mmol) was treated with pyridine (30 mL) and acetic anydride (15 mL) and stirred at room temp. After 2 h, the mixture was concentrated in vacuo by co-distillation with toluene/ethanol and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 3:1) to give **10** (3.58 g, 98%) as a yellow oil. −TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.50. − $[\alpha]_D^{20}$ = +33.4 (c = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.03 [2 s, 6 H, $Si(CH_3)_2$], 0.7 (m_c, 12 H, 4 CH_3), 1.48 [m_c, 1 H, C$H(CH_3)_2$], 1.83 (br. s, 6 H, 2 CH_3), 1.92 (s, 3 H, $COCH_3$), 3.56 (dd, $^3J_{6,5}$ = $^3J_{6',5}$ = 4.6 Hz, 2 H, 6-H, 6′-H), 3.69 (ddd, $^3J_{5,4}$ = 9.8 Hz, $^3J_{5,6}$ = $^3J_{5,6'}$ = 4.6 Hz, 1 H, 5-H), 3.96 (dd, $^3J_{2,3}$ = 10.9 Hz, $^3J_{2,1}$ = 8.0 Hz, 1 H, 2-H), 4.29 (dd, $^3J_{3,2}$ = 10.9 Hz, $^3J_{3,4}$ = 9.1 Hz, 1 H, 3-H), 4.33 (d, ^2J = 12.1 Hz, 1 H, C*H*Ph), 4.53 (2d, 2 H, CH_2Ph), 4.60 (d, ^2J = 12.1 Hz, 1 H, C*H*Ph), 5.05 (dd, ^3J = 9.8 Hz, $^3J_{4,3}$ = 9.1 Hz, 1 H, 4-H), 5.19 (d, $^2J_{1,2}$ = 8.0 Hz, 1 H, 1-H), 7.03−7.36 (m, 10 H, 2 Ph). − $C_{36}H_{49}NO_8$ (651.9): calcd. C 66.33, H 7.57, N 2.14; found C 66.36, H 7.54, N 1.85.

4-*O*-Acetyl-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranose (11): To a solution of **10** (2.9 g, 4.45 mmol) in dry THF (30 mL) was added dropwise TBAF (2 mL of a 1 M solution in THF, 6.68 mmol) at −50 °C; the temperature was kept at −20 °C and the mixture was stirred for 3 h. Acetic acid (127 μL, 2.25 mmol) was added at −20 °C, the mixture was kept at room temp. and the reaction mixture was poured onto ice/water (150 mL) and extracted with ethyl acetate (5 × 200 mL). The combined organic layers were dried with magnesium sulfate and concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 1:1) to give **11** (1.81 g, 80%) as a white solid. − TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.16. − M.p. 132−134 °C. − $[\alpha]_D^{20}$ = +29.1 (c = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.82 (br. s, 6 H, 2 CH_3), 3.01 (d, ^2J = 7.9 Hz, 1 H, OH), 3.54 (d, $^3J_{6,5}$ = 4.9 Hz, 1 H, 6-H), 3.55 (d, $^3J_{6',5}$ = 4.2 Hz, 1 H, 6′-H), 3.74 (ddd, $^3J_{5,4}$ = 9.8 Hz, $^3J_{5,6}$ = 4.9 Hz, $^3J_{5,6'}$ = 4.2 Hz, 1 H, 5-H), 3.94 (dd, $^3J_{2,3}$ = 10.8 Hz, $^3J_{2,1}$ = 8.2 Hz, 1 H, 2-H), 4.37 (dd, $^3J_{3,2}$ = 10.8 Hz, $^3J_{3,4}$ = 9.1 Hz, 1 H, 3-H), 4.33 (d, ^2J = 12.1 Hz, 1 H, C*H*Ph), 4.54 (s, 2 H, CH_2Ph), 4.62 (d, ^2J = 12.1 Hz, 1 H, C*H*Ph), 5.09 (dd, $^3J_{4,5}$ = 9.8 Hz, $^3J_{4,3}$ = 9.1 Hz, 1 H, 4-H), 5.18 (dd, $^3J_{1,2}$ = 8.2 Hz, $^3J_{1,OH}$ = 7.9 Hz, 1 H, 1-H), 7.04−7.48 (m, 10 H, 2 Ph). $C_{28}H_{31}NO_8$ (509.6): calcd. C 66.01, H 6.09, N 2.75; found C 66.07, H 6.11, N 2.37.

4-*O*-Acetyl-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl Fluoride (12): A solution of **11** (1.3 g, 2.55 mmol) in dry CH_2Cl_2 (20 mL) was cooled to −30 °C and DAST (401.2 μL, 3.06 mmol) was rapidly added. The mixture was kept at room temp. and the reaction mixture was stirred for 20 min. The solution was then poured into ice-cold saturated sodium bicarbonate solution (20 mL) and separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL), the combined organic layers were dried with magnesium sulfate and concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 2:1) to afford **12** (1.21 g, 93%) as a yellow oil. − TLC (petroleum ether/ethyl acetate, 2:1): R_f = 0.38. − $[\alpha]_D^{20}$ = +69.8 (c = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.82 (s, 6 H, 2 CH_3), 1.92 (s, 3 H, $COCH_3$), 3.58 (d, $^3J_{6,5}$ = $^3J_{6',5}$ = 4.3 Hz, 2 H, 6-H, 6′-H), 3.80 (ddd, $^3J_{5,4}$ = 9.0 Hz, $^3J_{5,6}$ = $^3J_{5,6'}$ = 4.3 Hz, 1 H, 5-H), 4.12 (ddd, $^3J_{2,F}$ = 18.8 Hz, $^3J_{2,3}$ = 10.8 Hz, $^3J_{2,1}$ = 7.8 Hz, 1 H, 2-H), 4.32 (dd, $^3J_{3,2}$ = 10.8 Hz, $^3J_{3,4}$ = 9.8 Hz, 1 H, 3-H), 4.31 (d, ^2J = 12.2 Hz, 1 H, C*H*Ph), 4.55 (s, 2 H, CH_2Ph), 4.64 (d, ^2J = 12.2 Hz, 1 H, C*H*Ph), 5.14 (dd, $^3J_{4,3}$ = 9.8 Hz, $^3J_{4,5}$ = 9.0 Hz, 1 H, 4-H), 5.70 (dd, $^3J_{1,F}$ = 53.0 Hz, $^3J_{1,2}$ = 7.8 Hz, 1 H, 1-H), 7.03−7.32 (m, 10 H, 2 Ph). − $C_{28}H_{30}NO_7F$ (511.5): calcd. C 65.74, H 5.91, N 2.73; found C 65.62, H 5.82, N 2.43.

4-*O*-Acetyl-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl Azide (13): A solution of **12** (1.2 g, 2.42 mmol) and $TMSN_3$ (617 μL, 4.7 mmol) in dry dichloromethane (18 mL) was stirred under nitrogen at room temp. for 5 min. and then $Et_2O{\cdot}BF_3$ (15 μL, 0.12 mmol) was added dropwise. After stirring for 1 h, the solution was neutralized with triethylamine and concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 5:2) to afford **13** (1.22 g, 95%) as a yellow oil. TLC (petroleum ether/ethyl acetate, 2:1): R_f = 0.57. − $[\alpha]_D^{20}$ = +30.7 (c = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.81 (br. s, 6 H, 2 CH_3), 1.94 (s, 3 H, $COCH_3$), 3.59 (d, $^3J_{6,5}$ = $^3J_{6',5}$ = 4.7 Hz, 2 H, 6-H, 6′-H), 3.78 (ddd, $^3J_{5,4}$ = 9.9 Hz, $^3J_{5,6}$ = $^3J_{5,6'}$ = 4.7 Hz, 1 H, 5-H), 3.94 (dd, $^3J_{2,3}$ = 10.8 Hz, $^3J_{2,1}$ = 9.4 Hz, 1 H, 2-H), 4.29 (d, ^2J = 12.2 Hz, 1 H, C*H*Ph), 4.30 (dd, $^3J_{3,2}$ = 10.8 Hz, $^3J_{3,4}$ = 9.2 Hz, 1 H, 3-H), 4.55 (s, 2 H, CH_2Ph), 4.62 (d, ^2J = 12.2 Hz, 1 H, C*H*Ph), 5.09 (dd, $^3J_{4,5}$ = 9.9 Hz, $^3J_{4,3}$ = 9.2 Hz, 1 H, 4-H), 5.19 (d, $^3J_{1,2}$ = 9.4 Hz, 1 H, 1-H), 7.05−7.38 (m, 10 H, 2 Ph). − $C_{28}H_{30}N_4O_7$ (534.6): calcd. C 62.91, H 5.65, N 10.48; found C 62.74, H 5.78, N 10.33.

3,6-Di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl Azide (14): A solution of **13** (1.2 g, 2.2 mmol) in dry methanol (15 mL) was treated with a catalytic amount of sodium methoxide (0.1 M, 800 μL) and stirred at room temp. After 3 h, the solution was neutralized with ion-exchange resin (Amberlite IR-120 H^+), the resin filtered off and the filtrate concentrated in vacuo. Flash chromatography of the residue (petroleum ether/ethyl acetate, 2:1) gave a yellow oil which was lyophilized from dioxane to afford **14** (1.05 g, quant.) as a white powder. TLC (toluene/ethyl acetate, 4:1): R_f = 0.47. − $[\alpha]_D^{20}$ = +15.5 (c = 1.0, $CHCl_3$). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.83−1.93 (m, 6 H, 2 CH_3), 2.87 (br. s, 1 H, OH), 3.65 (ddd, $^3J_{5,4}$ = 9.6 Hz, $^3J_{5,6}$ = $^3J_{5,6'}$ = 4.6 Hz, 1 H, 5-H), 3.74−3.78 (m, 2 H, 4-H, 6′-H), 3.80 (dd, ^2J = 10.4 Hz, $^3J_{6,5}$ = 4.6 Hz, 1 H, 6-H), 3.84 (dd, $^3J_{2,3}$ = $^3J_{2,1}$ = 9.4 Hz, 1 H, 2-H), 4.10 (dd, $^3J_{3,4}$ = 10.4 Hz, $^3J_{3,2}$ = 9.4 Hz, 1 H, 3-H), 4.48 (d, ^2J = 12.4 Hz, 1 H, C*H*Ph), 4.60 (dd, ^2J = 12.0 Hz, 2 H, CH_2Ph), 4.75 (d, ^2J = 12.4 Hz, 1 H, C*H*Ph), 5.17 (d, $^3J_{1,2}$ = 9.4 Hz, 1 H, 1-H), 7.15−7.35 (m, 10 H, 2 Ph). − ^{13}C NMR (600 MHz, $CDCl_3$): δ = 54.4 (C-2), 69.8 (C-6), 73.3 (C-4), 75.8 (C-5), 78.8 (C-3), 85.5 (C-1). $C_{26}H_{28}N_4O_6$ (492.5): calcd. C 63.40, H 5.73, N 11.39; found C 63.51, H 5.94, N 11.31.

Dimethyl(thexyl)silyl 4,6-*O*-Benzylidene-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (15): To a solution of **3** (702.2 mg, 1.63 mmol) in dry acetonitrile (10 mL) were added benzaldehyde dimethylacetal (344 μL, 2.3 mmol) and *p*TsOH (6.2 mg, 0.03 mmol). After stirring at room temp. for 16 h, the solution was neutralized with triethylamine and concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 3:1) to give **15** (7.4 g, 86%) as a white foam. − TLC (petroleum ether/ethyl acetate, 2:1): R_f = 0.83. − $[\alpha]_D^{20}$ = −39.5 (c = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.03 [2 s, 6 H, $Si(CH_3)_2$], 0.7 (m_c, 12 H, 4 CH_3), 1.48 [m_c, 1 H, C$H(CH_3)_2$], 1.92 (s, 6 H, 2 CH_3), 3.53−3.58 (m, 2 H, 6-H, 6′-H), 3.66 (dd, $^3J_{4,5}$ = 10.6 Hz, $^3J_{4,3}$ = 9.7 Hz, 1 H, 4-H), 3.95 (dd, $^3J_{2,3}$ = 10.6 Hz, $^3J_{2,1}$ = 8.0 Hz, 1 H, 2-H), 4.29 (ddd, $^3J_{5,4}$ = 10.6 Hz, $^3J_{5,6}$ = 6.1 Hz, $^3J_{5,6'}$ = 4.3 Hz, 1 H, 5-H), 4.47 (dd, $^3J_{3,2}$ = 10.6 Hz, $^3J_{3,4}$ = 9.7 Hz,

1 H, 3-H), 5.29 (d, $^3J_{1,2}$ = 8.0 Hz, 1 H, 1-H), 5.51 (s, 1 H, C*H*Ph), 7.31−7.51 (m, 5 H, Ph). − $C_{27}H_{39}NO_7Si{\cdot}0.5\ H_2O$ (526.7): calcd. C 61.57, H 7.65, N 2.65; found C 61.10, H 7.63, N 2.26.

Dimethyl(thexyl)silyl 3-*O*-Acetyl-4,6-*O*-benzylidene-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (16): Compound **15** (703 mg, 1.35 mmol) was treated with acetic anhydride (2.5 mL) in pyridine (5 mL) and stirred at room temp. After 1 h, the mixture was concentrated in vacuo by co-distillation with toluene/ethanol and the residue purified by flash chromatography (petroleum ether/ethyl acetate, 4:1) to afford **16** (755.5 mg, quant.) as a white foam. − TLC (petroleum ether/ethyl acetate, 4:1): R_f = 0.33. − $[\alpha]_D^{20}$ = −42.8 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.03 [2 s, 6 H, $Si(CH_3)_2$], 0.7 (m_c, 12 H, 4 CH_3), 1.48 [m_c, 1 H, C*H*$(CH_3)_2$], 1.92 (s, 6 H, 2 CH_3), 2.02 (s, 3 H, $COCH_3$), 3.62−3.73 (m, 2 H, 6-H, 6′-H), 3.81 (dd, $^3J_{4,5}$ = 10.2 Hz, $^3J_{4,3}$ = 9.7 Hz, 1 H, 4-H), 3.97 (dd, $^3J_{2,3}$ = 10.6 Hz, $^3J_{2,1}$ = 8.0 Hz, 1 H, 2-H), 4.30 (ddd, $^3J_{5,4}$ = 10.2 Hz, $^3J_{5,6}$ = $^3J_{5,6'}$ = 4.2 Hz, 1 H, 5-H), 5.46 (d, $^3J_{1,2}$ = 8.0 Hz, 1 H, 1-H), 5.48 (s, 1 H, C*H*Ph), 5.70 (dd, $^3J_{3,2}$ = 10.6 Hz, $^3J_{3,4}$ = 9.7 Hz, 1 H, 3-H), 7.31−7.51 (m, 5 H, Ph). − $C_{29}H_{41}NO_8$ Si (559.7): calcd. C 62.23, H 7.38, N 2.50; found C 62.24, H 7.45, N 2.15.

Dimethyl(thexyl)silyl 3-*O*-Acetyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (17): A solution of **16** (751 mg, 1.34 mmol) in dry dichloromethane (5 mL) was treated with ethanethiol (596 μL, 8.06 mmol) and *p*TsOH (51.0 mg, 0.27 mmol) and then stirred at room temp. After 2 h, the solution was neutralized with triethylamine and the solvent evaporated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 1:1) to give **17** (534.5 mg, 86%) as a white foam. − TLC (petroleum ether/ethyl acetate, 2:3): R_f = 0.28. − $[\alpha]_D^{20}$ = −21.1 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.03 [2 s, 6 H, $Si(CH_3)_2$], 0.7 (m_c, 12 H, 4 CH_3), 1.48 [m_c, 1 H, C*H*$(CH_3)_2$], 1.92 (s, 6 H, 2 CH_3), 2.02 (s, 3 H, $COCH_3$), 2.88 (d, *J* = 5.0 Hz, 1 H, OH), 3.53−3.85 (m, 5 H, 4-H, 5-H, 6-H, 6′-H, OH), 3.91 (dd, $^3J_{2,3}$ = 10.8 Hz, $^3J_{2,1}$ = 8.1 Hz, 1 H, 2-H), 5.40 (d, $^3J_{1,2}$ = 8.1 Hz, 1 H, 1-H), 5.49 (dd, $^3J_{3,2}$ = 10.8 Hz, $^3J_{3,4}$ = 8.7 Hz, 1 H, 3-H). − $C_{22}H_{37}NO_8$ Si (471.6): calcd. C 56.03, H 7.90, N 2.96; found C 56.25, H 7.97, N 2.66.

Dimethyl(thexyl)silyl 3-*O*-Acetyl-6-*O*-benzoyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (18): Compound **17** (529.4 mg, 1.13 mmol) was dissolved in dry propionitrile (19 mL) and triethylamine (4.5 mL, 1.13 mmol) was added. The mixture was cooled to −60 °C and a solution of benzoyl cyanide (162.4 mg, 1.23 mmol) in dry propionitrile (8.5 mL) was added dropwise under nitrogen. After 90 min, the mixture was kept at room temp. and the solution carefully concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 2:1) to afford **14** (551 mg, 87%) as a white foam. − TLC (petroleum ether/ethyl acetate, 1:1): R_f = 0.50. − $[\alpha]_D^{20}$ = −7.3 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.03 (2 s, 6 H, $Si(CH_3)_2$), 0.7 (m_c, 12 H, 4 CH_3), 1.48 [m_c, 1 H, $CH(CH_3)_2$], 1.92 (s, 6 H, 2 CH_3), 2.00 (s, 3 H, $COCH_3$), 3.01 (d, ^2J = 5.2 Hz, 1 H, 4-OH), 3.62 (ddd, $^3J_{4,5}$ = 9.9 Hz, $^3J_{4,3}$ = 8.8 Hz, $^3J_{4,OH}$ = 5.2 Hz, 1 H, 4-H), 3.79 (ddd, $^3J_{5,4}$ = 9.9 Hz, $^3J_{5,6}$ = 4.1 Hz, $^3J_{5,6'}$ = 3.0 Hz, 1 H, 5-H), 3.94 (dd, $^3J_{2,3}$ = 10.8 Hz, $^3J_{2,1}$ = 8.1 Hz, 1 H, 2-H), 4.61−4.63 (m, 2 H, 6-H, 6′-H), 5.39 (d, $^3J_{1,2}$ = 8.1 Hz, 1 H, 1-H), 5.52 (dd, $^3J_{3,2}$ = 10.8 Hz, $^3J_{3,4}$ = 8.8 Hz, 1 H, 3-H), 7.39−7.50 (m, 2 H, H_m-PhCO), 7.53−7.62 (m, 1 H, H_p-PhCO), 8.03−8.10 (2 H, H_o-PhCO). − $C_{29}H_{41}NO_9$ Si (575.7): calcd. C 60.50, H 7.17, N 2.43; found C 60.45, H 7.09, N 2.03.

Dimethyl(thexyl)silyl O-(2,3-Di-O-acetyl-4,6-O-benzylidene-β-D-glucopyranosyl)-(1→4)-3,6-di-O-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (20): To a stirred mixture of **5** (9.7 g, 15.93 mmol) and **19**[12] (8.7 g, 17.53 mmol) in dry dichloromethane (22 mL) TMSOTf (143 μL, 0.80 mmol) was added dropwise under nitrogen at room temp. After 30 min, the solution was neutralized with triethylamine and concentrated in vacuo. The residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to afford **20** (12.78 g, 85%) as a white foam. − TLC (petroleum ether/ethyl acetate, 2:1): R_f = 0.58. − $[\alpha]_D^{20}$ = +4.4 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.03 [2 s, 6 H, $Si(CH_3)_2$], 0.7 (m_c, 12 H, 4 CH_3), 1.48 [m_c, 1 H, $CH(CH_3)_2$], 1.80 (br. s, 6 H, 2 CH_3), 2.00 (s, 3 H, $COCH_3$), 2.03 (s, 3 H, $COCH_3$), 3.30 (ddd, $^3J_{5,6}$ = 9.7 Hz, $^3J_{5,6'}$ = 9.5 Hz, $^3J_{5,4}$ = 4.7 Hz, 1 H, 5b-H), 3.43−3.81 (m, 5 H, 5a-H, 6a-H, 6′a-H, 6′b-H, 6b-H), 3.82 (dd, $^3J_{2,3}$ = 10.4 Hz, $^3J_{2,1}$ = 8.1 Hz, 1 H, 2a-H), 4.00 (dd, $^3J_{4,5}$ = 9.4 Hz, $^3J_{4,3}$ = 8.5 Hz, 1 H, 4a-H), 4.10 (dd, $^3J_{3,2}$ = 10.4 Hz, $^3J_{3,4}$ = 8.5 Hz, 1 H, 3a-H), 4.20 (dd, $^3J_{4,3}$ = 10.0 Hz, $^3J_{4,5}$ = 4.7 Hz, 1 H, 4b-H), 4.42 (d, ^2J = 12.4 Hz, 1 H, CHPh), 4.55 (d, ^2J = 12.2 Hz, 1 H, CHPh), 4.74 (d, ^2J = 7.9 Hz, 1 H, 1b-H), 4.77 (d, ^2J = 12.2 Hz, 1 H, CHPh), 4.78 (dd, ^2J = 12.4 Hz, 1 H, CHPh), 4.90 (dd, $^3J_{2,3}$ = 9.3 Hz, $^3J_{2,1}$ = 7.9 Hz, 1 H, 2b-H), 5.10 (d, $^3J_{1,2}$ = 8.1 Hz, 1 H, 1a-H), 5.20 (dd, $^3J_{3,2}$ = 10.0 Hz, $^3J_{3,4}$ = 9.3 Hz, 1 H, 3b-H), 5.41 (s, 1 H, HCPh), 7.10−7.48 (m, 15 H, 3 Ph). − $C_{51}H_{65}NO_{14}Si$ (944.1): calcd. C 64.87, H 6.93, N 1.48; found C 64.79, H 6.88, N 1.22.

Dimethyl(thexyl)silyl *O*-(4,6-*O*-Benzylidene-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (21): A solution of **20** (10.9 g, 11.3 mmol) in dry methanol (50 mL) was treated with a catalytic amount of sodium methoxide (0.1 M, 2.3 mL) and stirred at room temp. After 8 h, the solution was neutralized with ion-exchange resin (Amberlite IR-120 H^+), the resin filtered off and the filtrate concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 2:1) to give **21** (8.3 g, 85%) as a white foam. − TLC (petroleum ether/ethyl acetate, 2:1): R_f = 0.32. − $[\alpha]_D^{20}$ = +32.4 (*c* = 1.08, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.03 [2 s, 6 H, $Si(CH_3)_2$], 0.7 (m_c, 12 H, 4 CH_3), 1.48 [m_c, 1 H, C*H*$(CH_3)_2$], 1.80 (s, 6 H, 2 CH_3), 3.22 (ddd, $^3J_{5,6}$ = 9.7 Hz, $^3J_{5,6'}$ = 9.5 Hz, $^3J_{5,4}$ = 4.9 Hz, 1 H, 5b-H), 3.41−3.60 (m, 3 H, 5a-H, 6′b-H, 6b-H), 3.68−3.75 (m, 2 H, 6a-H, 6′a-H), 3.90 (dd, $^3J_{2,3}$ = 10.7 Hz, $^3J_{2,1}$ = 8.1 Hz, 1 H, 2a-H), 3.98−4.11 (m, 4 H, 4a-H, 2b-H, 3b-H, 4b-H), 4. 26 (dd, $^3J_{3,2}$ = 10.7 Hz, $^3J_{3,4}$ = 8.7 Hz, 1 H, 3a-H), 4.42 (d, ^2J = 12.4 Hz, 1 H, C*H*Ph), 4.63 (d, ^2J = 12.2 Hz, 1 H, C*H*Ph), 4.73 (d, $^3J_{1,2}$ = 7.8 Hz, 1 H, 1b-H), 4.74 (s, 2 H, CH_2Ph), 4.75 (d, ^2J = 12.2 Hz, 1 H, C*H*Ph), 4.81 (d, ^2J = 12.4 Hz, 1 H, C*H*Ph), 5.13 (d, $^3J_{1,2}$ = 8.1, 1 H, 1a-H), 5.45 (s, 1 H, *H*CPh), 7.12−7.47 (m, 15 H, 3 Ph). − $C_{47}H_{61}NO_{12}Si{\cdot}0.5\ H_2O$ (869.1): calcd. C 64.95, H 7.13, N 1.61; found C 64.98, H 7.10, N 1.27.

Dimethyl(thexyl)silyl *O*-(3-*O*-Benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→4)−3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (22): Compound **21** (5.2 g, 6.05 mmol) was dissolved in a mixture of dry acetonitrile/dichloromethane/triethylamine (2:2:1, 50 mL) and the mixture was cooled to −70 °C. A solution of benzoyl cyanide (872.7 mg, 6.65 mmol) in dry dichloromethane (1 mL) was slowly added dropwise under nitrogen. After 2 h, the mixture was kept at room temp., washed with saturated aqueous sodium bicarbonate solution (50 mL) and separated. The aqueous layer was extracted with dichloromethane (3 × 100 mL), the combined organic layers were dried with magnesium sulfate and the solvent evaporated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 3:1) to afford **22** (4.8 g, 82%) as a white foam. − TLC (petroleum ether/ethyl acetate, 2:1): R_f = 0.8. − $[\alpha]_D^{20}$ = −20.9 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR

(250 MHz, $CDCl_3$): δ = 0.03 [2 s, 6 H, $Si(CH_3)_2$], 0.7 (m_c, 12 H, 4 CH_3), 1.48 [m_c, 1 H, C*H*$(CH_3)_2$], 1.80 (s, 6 H, 2 CH_3), 3.31 (ddd, $^3J_{5,6}$ = 10.5 Hz, $^3J_{5,6'}$ = 9.7 Hz, $^3J_{5,4}$ = 4.9 Hz, 1 H, 5b-H), 3.51−3.74 (m, 5 H, 4a-H, 5a-H, 2b-H, 4b-H, 6′b-H), 3.89 (dd, $^3J_{2,3}$ = 10.7 Hz, $^3J_{2,1}$ = 8.1 Hz, 1 H, 2a-H), 3.98 (dd, ^2J = 11.6 Hz, $^3J_{6,5}$ = 3.2 Hz, 1 H, 6a-H), 4.04 (d, ^2J = 11.6 Hz, 1 H, 6′a-H), 4.13 (dd, $^3J_{6,5}$ = 10.5 Hz, ^2J = 4.9 Hz, 1 H, 6b-H), 4.23 (dd, $^3J_{3,2}$ = 10.7 Hz, $^3J_{3,4}$ = 8.6 Hz, 1 H, 3a-H), 4.42 (d, ^2J = 12.5 Hz, 1 H, C*H*Ph), 4.57 (d, ^2J = 12.2 Hz, 1 H, C*H*Ph), 4.72 (d, ^2J = 12.5 Hz, 1 H, C*H*Ph), 4.76 (d, $^3J_{1,2}$ = 8.1 Hz, 1 H, 1b-H), 4.80 (d, ^2J = 12.2 Hz, 1 H, C*H*Ph), 5.11 (d, $^3J_{1,2}$ = 8.1, 1 H, 1a-H), 5.35 (dd, $^3J_{3,2}$ = $^3J_{3,4}$ = 9.4 Hz, 1 H, 3b-H), 5.41 (s, 1 H, *H*CPh), 7.09−7.58 (m, 18 H, 3 Ph, 2 H_m-PhCO, H_p-PhCO), 8.06 (2 H, H_o-PhCO). − $C_{54}H_{65}NO_{13}Si$ (964.2): calcd. C 67.26, H 6.80, N 1.45; found C 67.34, H 7.08, N 1.49.

Dimethyl(thexyl)silyl *O*-(3-*O*-Benzoyl-4,6-*O*-benzylidene-2-*O*-trifluoromethanesulfonyl-β-D-glucopyranosyl)-(1→4)−3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-gluco-pyranoside (23): To a solution of **22** (4.2 g, 4.36 mmol) in dry dichloromethane (43 mL) was added dry pyridine (8 mL). The solution was then cooled to −15 °C. Trifluoromethanesulfonic anhydride (2.8 mL, 17.44 mmol) was slowly added dropwise and the reaction mixture was stirred for 5 h under nitrogen at −15 °C. The solution was diluted with dichloromethane (60 mL) and carefully treated with saturated aqueous sodium bicarbonate solution (50 mL). The aqueous layer was extracted with dichloromethane (3 × 60 mL) and the combined organic layers were dried with magnesium sulfate and concentrated in vacuo to give **23** (4.16 g, 97%) as a light pink foam. The compound **23** was used in the next step without further purification. − TLC (petroleum ether/ethyl acetate, 5:1): R_f = 0.64. − $[\alpha]_D^{20}$ = +23 (c = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.03 [2 s, 6 H, $Si(CH_3)_2$], 0.7 (m_c, 12 H, 4 CH_3), 1.48 [m_c, 1 H, C*H*$(CH_3)_2$], 1.70−1.88 (br. s, 6 H, 2 CH_3), 3.45−3.68 (m, 5 H, 5a-H, 6′a-H, 5b-H, 6′b-H, 6b-H), 3.83−3.90 (m, 2 H, 2a-H, 6a-H), 4.09 (dd, $^3J_{4,5}$ = 10.4 Hz, $^3J_{4,3}$ = 8.7 Hz, 1 H, 4a-H), 4.19 (dd, $^3J_{3,2}$ = 9.4 Hz, $^3J_{3,4}$ = 8.7 Hz, 1 H, 3a-H), 4.28 (dd, $^3J_{4,5}$ = 10.5 Hz, $^3J_{4,3}$ = 5.8 Hz, 1 H, 4b-H), 4.43 (d, ^2J = 12.1 Hz, 1 H, C*H*Ph), 4.45 (d, ^2J = 12.2 Hz, 1 H, C*H*Ph), 4.66−4.75 [m, 3 H, H,H-COSY: 4.70 (d, $^3J_{1,2}$ = 7.1 Hz, 1b-H), 4.72 (dd, $^3J_{3,2}$ = 9.4 Hz, $J_{3,4}$ = 5.8 Hz, 3b-H), 4.73 (d, ^2J = 12.1 Hz, C*H*Ph)], 4.82 (d, ^2J = 12.1 Hz, 1 H, C*H*Ph), 5.15 (d, $^3J_{1,2}$ = 8.0 Hz, 1 H, 1a-H), 5.36 (s, 1 H, *H*CPh), 5.53 (dd, $^3J_{2,3}$ = 9.4 Hz, $^3J_{2,1}$ = 7.1 Hz, 1 H, 2b-H), 7.09−7.58 (m, 18 H, 3 Ph, 2 H_m-PhCO, H_p-PhCO), 8.06 (2 H, H_o-PhCO). − $C_{55}H_{64}NO_{15}SiF_3S$ (1096.2): calcd. C 60.26, H 5.88, N 1.27; found C 60.60, H 6.03, N 1.25.

Dimethyl(thexyl)silyl *O*-(2,3-Di-*O*-benzoyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1→4)−3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (24): 23 (4.6 g, 4.19 mmol) was dissolved in dry acetonitrile (60 mL) and treated with tetrabutylammonium benzoate (5.3 g, 14.7 mmol). The reaction mixture was stirred overnight at room temp. and the solvent was then evaporated in vacuo. Flash chromatography (toluene/ethyl acetate, 20:1) of the residue gave compound **24** (3.8 g, 85%) as a white foam. − TLC (petroleum ether/ethyl acetate, 5:1): R_f = 0.54. − $[\alpha]_D^{20}$ = −32.1 (c = 1.2, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.03 [2 s, 6 H, $Si(CH_3)_2$], 0.7 (m_c, 12 H, 4 CH_3), 1.48 [m_c, 1 H, C*H*$(CH_3)_2$], 1.62−1.82 (m, 6 H, 2 CH_3), 3.37−3.47 (m, 2 H, 6′a-H, 5b-H), 3.67−3.86 (m, 4 H, 2a-H, 5a-H, 6a-H, 6′b-H), 3.95 (dd, $^3J_{4,5}$ = 10.6 Hz, $^3J_{4,3}$ = 8.4 Hz, 1 H, 4a-H), 4.09−4.18 (m, 2 H, 4b-H, 6b-H), 4.29−4.37 (m, 2 H, 3a-H, C*H*Ph), 4.66 (d, ^2J = 12.1 Hz, 1 H, C*H*Ph), 4.77 (d, ^2J = 12.1 Hz, 1 H, C*H*Ph), 4.81 (d, ^2J = 12.5 Hz, 1 H, C*H*Ph), 5.02 (d, $^3J_{1,2}$ = 1.0 Hz, 1 H, 1b-H), 5.07 (d, $^3J_{1,2}$ = 7.9 Hz, 1 H, 1a-H), 5.40 (dd, $^3J_{3,4}$ = 10.2 Hz, $^3J_{3,2}$ = 3.4 Hz, 1 H, 3b-H), 5.55 (s, 1 H, C*H*Ph), 5.84 (dd, $^3J_{2,3}$ = 3.4 Hz, $^3J_{2,1}$ = 1.0 Hz, 1 H, 2b-H), 6.90 (dd, $J_{p,m}$ = 8.0 Hz, $J_{p,o}$ = 1.1 Hz, 2 H, H_p-PhCO), 7.05−7.60 (m, 19 H, 3 Ph, 4 H_m-PhCO), 7.88 (dd, $J_{o,m}$ = 8.1 Hz, $J_{o,p}$ = 1.1 Hz, 2 H, H_o-PhCO), 8.08 (2 H, H_o-PhCO). − $C_{61}H_{69}NO_{14}Si{\cdot}0.5\ H_2O$ (1077.3): calcd. C 68.00, H 6.54, N 1.30; found C 67.95, H 6.51, N 1.22.

***O*-(2,3-Di-*O*-benzoyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1→4)−3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-gluco-pyranose (25):** To a solution of compound **24** (3.7 g, 3.46 mmol) in dry THF (30 mL) was added dropwise tetrabutylammonium fluoride (2 mL of a 1 M solution in THF, 6.92 mmol) under nitrogen at −20 °C. After stirring for 2 h, acetic acid (198 μL, 3.46 mmol) was added, the mixture was raised to room temp. and the solvent was evaporated in vacuo. The residue was dissolved in ethyl acetate (50 mL), the mixture was poured onto ice/water (40 mL) and separated. The aqueous layer was extracted with ethyl acetate (4 × 50 mL), the combined organic solutions were dried with magnesium sulfate and concentrated in vacuo. Flash chromatography (petroleum ether/ethyl acetate, 3:2) of the residue gave **25** (2.9 g, 90%) as a white foam. − TLC (petroleum ether/ethyl acetate, 3:2): R_f = 0.31. − $[\alpha]_D^{20}$ = −50.5 (c = 1.47, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.62−1.82 (br. s, 6 H, 2 CH_3), 2.95−3.10 (br. s, 1 H, OH), 3.32 (ddd, $^3J_{5,4}$ = 10.0 Hz, $^3J_{5,6'}$ = 9.8 Hz, $^3J_{5,6}$ = 5.0 Hz, 1 H, 5b-H), 3.53 (d, ^2J = 9.3 Hz, 1 H, 6a-H), 3.75−3.84 (m, 4 H, 2a-H, 5a-H, 6′a-H, 6′b-H), 4.01−4.18 (m, 3 H, 3a-H, 4a-H, 4b-H), 4.26 (d, ^2J = 12.4 Hz, 1 H, CHPh), 4.35 (dd, ^2J = 10.2 Hz, $^3J_{6,5}$ = 5.0 Hz, 1 H, 6b-H), 4.53 (d, ^2J = 12.0 Hz, 1 H, CHPh), 4.80 (d, ^2J = 12.4 Hz, 1 H, CHPh), 4.85 (d, ^2J = 12.0 Hz, 1 H, CHPh), 4.88 (d,$^3J_{1,2}$ = 1.0 Hz, 1 H, 1b-H), 5.08 (d, $^2J_{1,2}$ = 8.3 Hz, 1 H, 1a-H), 5.31 (dd, $^3J_{3,4}$ = 10.2 Hz, $^3J_{3,2}$ = 3.3 Hz, 1 H, 3b-H), 5.55 (s, 1 H, CHPh), 5.78 (dd, $^3J_{2,3}$ = 3.3 Hz, $^3J_{2,1}$ = 1.0 Hz, 1 H, 2b-H), 6.90 (dd, $J_{p,m}$ = 8.0 Hz, $J_{p,o}$ = 1.1 Hz, 2 H, H_p-PhCO), 7.10−7.60 (m, 19 H, 3 Ph, 4 H_m-PhCO), 7.88 (2 H, H_o-PhCO), 8.08 (dd, $J_{o,m}$ = 8.1 Hz, $J_{o,p}$ = 1.1 Hz, 2 H, H_o-PhCO). − $C_{61}H_{69}NO_{14}{\cdot}H_2O$ (944.0): calcd. C 67.44, H 5.65, N 1.48; found C 67.57, H 5.64, N 1.23.

***O*-(2,3-Di-*O*-benzoyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1→4)−3,6-di-*O*-benzyl-2-deoxy-2-dimethylmaleimido-β-D-gluco-pyranosyl trichloroacetimidate (5):** A mixture of **25** (2.3 g, 2.5 mmol), trichloroacetonitrile (2.5 mL, 24.9 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (7.5 μL, 0.05 mmol) in dry dichloromethane (15 mL) was stirred under nitrogen at room temp. After 1 h, the reaction mixture was concentrated in vacuo and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 1:1 + 1% Et_3N) to give **5** (2.5 g, 95%) as a white foam. − TLC (petroleum ether/ethyl acetate, 1:2): R_f = 0.63. − $[\alpha]_D^{20}$ = −26.5 (c = 1.0, $CHCl_3$). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.69 (s, 6 H, 2 CH_3), 3.33 (ddd, $^3J_{5,6'}$ = 9.8 Hz, $^3J_{5,6}$ = 9.7 Hz, $^3J_{5,4}$ = 4.9 Hz, 1 H, 5b-H), 3.64 −3.84 (m, 4 H, 5a-H, 6a-H, 6′a-H, 6b-H), 4.06−4.30 (m, 6 H, 2a-H, 3a-H, 4a-H, 4b-H, 6′b-H, C*H*Ph), 4.54 (d, ^2J = 12.0 Hz, 1 H, C*H*Ph), 4.78 (d, ^2J = 12.0 Hz, 1 H, C*H*Ph), 4.84 (d, ^2J = 12.5 Hz, 1 H, C*H*Ph), 4.92 (d, $^3J_{1,2}$ < 1.0 Hz, 1 H, 1b-H), 5.32 (dd, $^3J_{3,4}$ = 10.2 Hz, $^3J_{3,2}$ = 3.5 Hz, 1 H, 3b-H), 5.53 (s, 1 H, C*H*Ph), 5.80 (dd, $^3J_{2,3}$ = 3.5 Hz, $^3J_{2,1}$ < 1.0 Hz, 1 H, 2b-H), 6.13 (d, $^3J_{1,2}$ = 9.1 Hz, 1 H, 1a-H), 6.88 (dd, $J_{m,o}$ = 8.1 Hz, $J_{m,p}$ = 2.0 Hz, 2 H, H_m-PhCO), 7.09−7.44 (m, 19 H, 3 Ph, 4 H_m-PhCO), 7.84 (dd, $J_{o,m}$ = 8.1 Hz, $J_{o,p}$ = 1.1 Hz, 2 H, H_o-PhCO), 8.03 (2 H, H_o-PhCO), 8.51 (s, 1 H, NH). − ^{13}C NMR (600 MHz, $CDCl_3$): δ = 54.3 (C-2a), 66.9 (C-5b), 67.8 (C-6a), 68.6 (C-6b), 70.1 (C-2b), 70.7 (C-3b), 75.2 (C-5a), 76.4 (C-4b), 76.6 (C-3a), 78.2 (C-4a), 94.1 (C-1a), 98.8 (C-1b), 101.7 (H*C*Ph), 136.9 (O*C*Ph). −

$C_{53}H_{51}N_2O_{14}Cl_3$ (1046.2): calcd. C 60.84, H 4.91, N 2.67; found C 60.27, H 5.07, N 2.74.

Dimethyl(thexyl)silyl *O*-(2,3,4-Tri-*O*-acetyl-6-*O*-benzyl-β-D-galactopyranosyl)-(1→4)−3-*O*-acetyl-6-*O*-benzoyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranoside (27): A solution of 18 (4.6 g, 8.0 mmol) and **26**[29] (7.3 g, 13.6 mmol) in dry dichloromethane (20 mL) was stirred in the presence of molecular sieves (4 Å) under nitrogen at room temp. for 5 min, TMSOTf (72.3, μL, 0.4 mmol) was then added dropwise. After 1 h, the reaction mixture was neutralized with triethylamine and concentrated in vacuo. Flash chromatography (petroleum ether/ethyl acetate, 2:1) of the residue gave compound **27** (5.49 g, 72%) as a white foam. − TLC (petroleum ether/ethyl acetate, 5:2): R_f = 0.18. − $[\alpha]_D^{20}$ = +33.8 (*c* = 0.2, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.03 [2 s, 6 H, $Si(CH_3)_2$], 0.7 (m_c, 12 H, 4 CH_3), 1.48 [m_c, 1 H, C*H*$(CH_3)_2$], 1.92 (s, 6 H, 2 CH_3), 1.93 (s, 3 H, $COCH_3$), 2.02 (s, 3 H, $COCH_3$), 2.05 (s, 3 H, $COCH_3$), 3.42−3.44 (m, 2 H, 4a-H, 5a-H), 3.72 (ddd, $^3J_{5,6}$ = 7.4 Hz, $^3J_{5,6'}$ = 5.6 Hz, $^3J_{5,4}$ = 1.0 Hz, 1 H, 5b-H), 3.80−3.87 (m, 2 H, 6b-H, 6′b-H), 3.92 (dd, $^2J_{2,3}$ = 10.7 Hz, $^2J_{2,1}$ = 8.0 Hz, 1 H, 2a-H), 4.34 (dd, ^2J = 11.3 Hz, $^3J_{6,5}$ = 4.3 Hz, 1 H, 6a-H), 4.43 (d, ^2J = 12.0 Hz, 1 H, C*H*Ph), 4.51 (d, ^2J = 12.0 Hz, 1 H, C*H*Ph), 4.54 (d, $^3J_{1,2}$ = 7.8 Hz, 1 H, 1b-H), 4.68 (dd, ^2J = 11.3 Hz, $^3J_{6,5}$ = 1.2 Hz, 1 H, 6′a-H), 4.92 (dd, $^3J_{3,2}$ = 10.3 Hz, $^3J_{3,4}$ = 3.3 Hz, 1 H, 3b-H), 5.10 (dd, $^3J_{2,3}$ = 10.3 Hz, $^3J_{2,1}$ = 7.8 Hz, 1 H, 2b-H), 5.41 (dd, $^3J_{4,3}$ = 3.3 Hz, $^3J_{4,5}$ = 1.0 Hz, 1 H, 4b-H), 5.42 (d, $^3J_{1,2}$ = 8.0 Hz, 1 H, 1a-H), 5.64 (dd, $^3J_{3,2}$ = 10.7 Hz, $^3J_{3,4}$ = 8.2 Hz, 1 H, 3a-H), 7.22−7.63 (m, 8 H, 1 Ph, 2 H_m-PhCO, H_p-PhCO), 8.03 (2 H, H_o-PhCO). − MS (MALDI, positive mode, matrix: DHB): *m*/*z* = 977 $[M + Na]^+$, 993 $[M + K]^+$. − $C_{48}H_{63}NO_{17}Si$ (953.1): calcd. C 60.48, H 6.61, N 1.46; found C 60.57, H 6.54, N 1.27.

***O*-(2,3,4-Tri-*O*-acetyl-6-*O*-benzyl-β-D-galactopyranosyl)-(1→4)−3-*O*-acetyl-6-*O*-benzoyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranose (28):** To a solution of **27** (7.00 g, 7.34 mmol) in dry THF (40 mL) was added dropwise tetrabutylammonium fluoride (5.3 mL of a 1 M solution in THF, 18.3 mmol) at −50 °C; the temperature was kept at −20 °C and the reaction mixture stirred for 3 h. Acetic acid (630 μL, 11.01 mmol) was added at −20 °C, the mixture was warmed to room temp. and the solvent was evaporated in vacuo. The residue was dissolved in ethyl acetate (50 mL), poured into water (50 mL) and separated. The aqueous layer was extracted with ethyl acetate (6 × 50 mL) and the combined organic layers were dried with magnesium sulfate and concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 1:1) to afford **28** (5.4 g, 86%) as a white foam. − TLC (petroleum ether/ethyl acetate, 1:1): R_f = 0.37. − $[\alpha]_D^{20}$ = +22.2 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.90 (s, 6 H, 2 CH_3), 1.93 (s, 6 H, 2 $COCH_3$), 2.05 (s, 3 H, $COCH_3$), 3.20 (br. s, 1 H, OH), 3.42−3.44 (m, 2 H, 4a-H, 5a-H), 3.90−3.93 (m, 2 H, 2a-H, 6b-H), 3.98 (dd, ^2J = 10.7 Hz, $^3J_{6',5}$ = 1.9 Hz, 1 H, 6′b-H), 4.35 (d, ^2J = 11.9 Hz, 1 H, 6a-H), 4.37 (d, ^2J = 12.0 Hz, 1 H, C*H*Ph), 4.50 (d, ^2J = 12.0 Hz, 1 H, C*H*Ph), 4. 56 (d, $^3J_{1,2}$ = 7.8 Hz, 1 H, 1b-H), 4.72 (dd, ^2J = 11.9 Hz, $^3J_{6,5}$ = 1.5 Hz, 1 H, 6′a-H), 4.89 (dd, $^3J_{3,2}$ = 10.4 Hz, $^3J_{3,4}$ = 3.3 Hz, 1 H, 3b-H), 5.09 (dd, $^3J_{2,3}$ = 10.4 Hz, $^3J_{2,1}$ = 7.8 Hz, 1 H, 2b-H), 5.39 (dd, $^3J_{4,3}$ = 3.3 Hz, $^3J_{4,5}$ = 1.2 Hz, 1 H, 4b-H), 5.49 (d, $^3J_{1,2}$ = 8.0 Hz, 1 H, 1a-H), 5.65 (dd, $^3J_{3,2}$ = 10.5 Hz, $^3J_{3,4}$ = 8.4 Hz, 1 H, 3a-H), 7.21−7.28 (m, 5 H, Ph), 7.48 (d, $J_{m,o}$ = $J_{m,p}$ = 10.6 Hz, 2 H, H_m-PhCO), 7.60 (1 H, H_p-PhCO), 8.03 (2 H, H_o-PhCO). − $C_{40}H_{45}NO_{17}\cdot 0.25\ H_2O$ (815.5): calcd. C 58.85, H 5.64, N 1.71; found C 58.80, H 5.50, N 1.52.

***O*-(2,3,4-Tri-*O*-acetyl-6-*O*-benzyl-β-D-galactopyranosyl)-(1→4)−3-*O*-acetyl-6-*O*-benzoyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl Trichloroacetimidate (6):** A mixture of **28** (3.5 g, 4.31 mmol), trichloroacetonitrile (4.3 mL, 43.1 mmol) and DBU (13 μL, 0.09 mmol) in dry dichloromethane (40 mL) was stirred at room temp. for 1 h and then concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 2:1 + 1% Et_3N) to give **6** (3.5 g, 85%) as a white foam. −TLC (petroleum ether/ethyl acetate, 2:1): R_f = 0.36. − $[\alpha]_D^{20}$ = +16.6 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.91 (s, 3 H, $COCH_3$), 1.92 (s, 12 H, 2 CH_3, 2 $COCH_3$), 2.02 (s, 3 H, $COCH_3$), 3.38−3.45 (m, 2 H, 4a-H, 5a-H), 3.69 (ddd, $^3J_{5,6}$ = 5.9 Hz, $^3J_{5,6'}$ = 5.3 Hz, $^3J_{5,4}$ = 1.0 Hz, 1 H, 5b-H), 4.04 (d, $^3J_{6,5}$ = 5.9 Hz, 1 H, 6b-H), 4.06 (d, $^3J_{6',5}$ = 5.3 Hz, 1 H, 6′b-H), 4.33 (dd, $^3J_{2,3}$ = 10.5 Hz, $^3J_{2,1}$ = 8.9 Hz, 1 H, 2a-H), 4.37 (d, ^2J = 12.8 Hz, 1 H, C*H*Ph), 4.39 (d, ^2J = 11.9 Hz, 1 H, 6a-H), 4.51 (d, ^2J = 12.8 Hz, 1 H, C*H*Ph), 4. 55 (d, $^3J_{1,2}$ = 7.8 Hz, 1 H, 1b-H), 4.73 (d, ^2J = 11.9 Hz, 1 H, 6′a-H), 4.87 (dd, $^3J_{3,2}$ = 10.4 Hz, $^3J_{3,4}$ = 3.4 Hz, 1 H, 3b-H), 5.11 (dd, $^3J_{2,3}$ = 10.4 Hz, $^3J_{2,1}$ = 7.8 Hz, 1 H, 2b-H), 5.39 (dd, $^3J_{4,3}$ = 3.4 Hz, $^3J_{4,5}$ = 1.0 Hz, 1 H, 4b-H), 5.73 (dd, $^3J_{3,2}$ = 10.5 Hz, $^3J_{3,4}$ = 8.4 Hz, 1 H, 3a-H), 6.49 (d, $^3J_{1,2}$ = 8.9 Hz, 1 H, 1a-H), 7.21−7.38 (m, 5 H, Ph), 7.48 (H_m-PhCO), 7.60 (1 H, H_p-PhCO), 8.03 (d, $J_{o,m}$ = 7.8 Hz, 2 H, H_o-PhCO), 8.65 (s, 1 H, NH). − $C_{42}H_{45}Cl_3N_2O_{17}\cdot 0.5\ H_2O$ (964.2): calcd. C 52.27, H 4.77, N 2.68; found C 52.19, H 4.81, N 2.68.

***O*-(2,3-Di-*O*-benzoyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1→4)−(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-glucopyranosyl Azide (29):** A solution of **14** (1.3 g, 2.65 mmol) and **5** (3.41 g, 3.2 mmol) in dry dichloromethane (13 mL) was stirred in the presence of molecular sieves (4 Å) under nitrogen at room temp. for 5 min. TMSOTf (5 μL, 0.026 mmol) was slowly added dropwise and the reaction mixture was stirred for 30 min. The solution was neutralized with triethylamine, filtered and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 5:2) to afford **29** (2.9 g, 80%) as a white foam. − TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.18. − $[\alpha]_D^{20}$ = −16.3 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.65−1.85 (m, 12 H, 4 CH_3), 3.02 (dd, $^3J_{5,4}$ = 9.8 Hz, $^3J_{5,6}$ = $^3J_{5,6'}$ = 1.0 Hz, 1 H, 5b-H), 3.31−3.35 (m, 3 H, 5a-H, 6a-H, 5c-H), 3.54−3.61 (m, 2 H, 6′a-H, 6b-H), 3.69 (dd, ^2J = 10.5 Hz, $^3J_{5,6}$ = 10.3 Hz, 1 H, 6c-H), 3.80−3.99 (m, 4 H, 2a-H, 3a-H, 2b-H, 3b-H), 4.07−4.13 (m, 3 H, 4a-H, 4b-H, 4c-H), 4.24 (d, ^2J = 12.4 Hz, 1 H, C*H*Ph), 4.28 (dd, ^2J = 10.5 Hz, $^3J_{6,5}$ = 4.9 Hz, 1 H, 6′c-H), 4.39 (d, ^2J = 12.8 Hz, 1 H, C*H*Ph), 4.45 (2d, 2 H, CH_2Ph), 4.50 (d, ^2J = 12.0 Hz, 1 H, C*H*Ph), 4.55 (d, ^2J = 12.0 Hz, 1 H, C*H*Ph), 4.85 (d, ^2J = 12.4 Hz, 1 H, C*H*Ph), 4.87 (d, ^2J = 12.8 Hz, 1 H, C*H*Ph), 4.96 (d, $^3J_{1,2}$ = 1.1 Hz, 1 H, 1c-H), 4.98 (d, $^3J_{1,2}$ = 8.5 Hz, 1 H, 1b-H), 5.00 (d, $^3J_{1,2}$ = 9.4 Hz, 1 H, 1a-H), 5.34 (dd, $^3J_{3,4}$ = 10.2 Hz, $^3J_{3,2}$ = 3.4 Hz, 1 H, 3c-H), 5.50 (s, 1 H, *H*CPh), 5.81 (dd, $^3J_{2,3}$ = 3.4 Hz, $^3J_{2,1}$ = 1.1 Hz, 1 H, 2c-H), 6.90 (2 H, H_m-PhCO), 7.11−7.38 (m, 31 H, 5 Ph, 4 H_m-PhCO, 2 H_p − PhCO), 7.89 (2 H, H_o-PhCO), 8.04 (2 H, H_o-PhCO). − ^{13}C NMR (600 MHz, $CDCl_3$): δ = 54.9 (C-2a), 56.2 (C-2b), 66.9 (C-5b), 67.5 (C-6b), 67.7 (C-6a), 68.7 (C-6c), 70.1 (C-2c), 70.8 (C-3c), 74.1 (C-5b), 74.8 (C-4a), 76.4 (C-4c), 76.8 (4a-C, 3b-C), 77.0 (C-3a), 78.6 (C-4b), 85.6 (C-1a), 96.8 (C-1b), 98.6 (C-1c), 101.7 (H*C*Ph), 136.9 (O*C*Ph). − $C_{79}H_{77}N_5O_{19}$ (1400.5): calcd. C 67.75, H 5.54, N 5.00; found C 67.57, H 5.62, N 4.70.

***O*-(4,6-*O*-Benzylidene-β-D-mannopyranosyl)-(1→4)−(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-glucopyranosyl**

Azide (30): A solution of **29** (1.9 g, 1.35 mmol) in a mixture of dry methanol/dichloromethane (6:1, 28 mL) was treated with a catalytic amount of sodium methoxide (0.2 M, 2 mL) and stirred at room temp. After 8 h, the solution was neutralized with ion-exchange resin (Amberlite IR-120 H^+), the resin was filtered off and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 1:1) to give **30** (1.37 g, 85%) as a white foam. − TLC (petroleum ether/ethyl acetate, 3:2): R_f = 0.16. − $[\alpha]_D^{20}$ = +26.4 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.68−1.82 (m, 12 H, 4 CH_3), 2.50 (br. s, 1 H, OH), 2.57 (br. s, 1 H, OH), 3.04 (ddd, $^3J_{5,4}$ = 9.8 Hz, $^3J_{5,6}$ = 9.9 Hz, $^3J_{5,6'}$ = 5.0 Hz, 1 H, 5c-H), 3.18 (d, $^3J_{5,4}$ = 10.1 Hz, 1 H, 5b-H), 3.33−3.35 (m, 2 H, 5a-H, 6a-H), 3.45 (dd, ^2J = $^3J_{6,5}$ = 9.9 Hz, 1 H, 6c-H), 3.50−3.56 (m, 4 H, 6′a-H, 6b-H, 6′b-H, 3c-H), 3.68 (dd, $^3J_{4,5}$ = 9.8 Hz, $^3J_{4,3}$ = 9.9 Hz, 1 H, 4c-H), 3.77 (dd, $^3J_{2,1}$ = 9.4 Hz, $^3J_{2,3}$ = 9.3 Hz, 1 H, 2a-H), 3.84 (dd, $^3J_{2,3}$ = 3.6 Hz, $^3J_{2,1}$ = 1.0 Hz, 1 H, 2c-H), 3.91 (dd, $^3J_{2,3}$ = 8.5 Hz, $^3J_{2,1}$ = 8.4 Hz, 1 H, 2b-H), 3.95−4.01 (m, 2 H, 3a-H, 4b-H), 4.05 (dd, ^2J = 9.9 Hz, $^3J_{6',5}$ = 5.0 Hz, 1 H, 6′c-H), 4.10 (dd, $^3J_{4,3}$ = 8.4 Hz, $^3J_{4,5}$ = 8.3 Hz, 1 H, 4a-H), 4.15 (dd, $^3J_{3,2}$ = 8.5 Hz, $^3J_{3,4}$ = 8.3 Hz, 1 H, 3b-H), 4.31 (d, ^2J = 12.0 Hz, 1 H, C*H*Ph), 4.35 (d, ^2J = 12.5 Hz, 1 H, C*H*Ph), 4.36 (d, ^2J = 12.1 Hz, 1 H, C*H*Ph), 4.47−4.53 (m, 3 H, 3 C*H*Ph), 4.64 (d, $^3J_{1,2}$ = 1.0 Hz, 1 H, 1c-H), 4.78 (d, ^2J = 12.0 Hz, 1 H, C*H*Ph), 4.80 (d, ^2J = 12.5 Hz, 1 H, C*H*Ph), 4.98 (d, $^3J_{1,2}$ = 9.4 Hz, 1 H, 1a-H), 5.04 (d, $^3J_{1,2}$ = 8.4 Hz, 1 H, 1b-H), 5.38 (s, 1 H, *H*CPh), 6.99−7.38 (m, 25 H, 5 Ph). − ^{13}C NMR (600 MHz, $CDCl_3$): δ = 55.0 (C-2a), 56.3 (C-2b), 66.6 (C-5c), 67.7 (C-6b, C-6a), 68.4 (C-6c), 70.8 (C-2c, C-3c), 74.3 (C-5b), 74.8 (C-4a), 76.8 (C-5a), 77.0 (C-3a), 78.2 (C-3b), 78.5 (C-4b, C-4c), 85.8 (C-1a), 97.1 (C-1b), 100.3 (C-1c), 102.1 (H*C*Ph). − MS (MALDI, positive mode, matrix: DHB); *m*/*z*: 1187 [M − N_2 + Na]$^+$, 1215 [M + Na]$^+$ $C_{65}H_{69}N_5O_{17}$·0.5 H_2O (1201.3): calcd. C 64.98, H 5.87, N 5.82; found C 64.97, H 5.92, N 5.54.

***O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-(4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1→4)−(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-glucopyranosyl Azide (31):** A mixture of **30** (2.8 g, 2.35 mmol), **4**[22] (1.8 g, 2.82 mmol) and molecular sieves (4 Å) in dry CH_2Cl_2/Et_2O (1:1, 20 mL) was cooled to −40 °C. TMSOTf (21.2 μL, 0.12 mmol) was slowly added dropwise and the reaction mixture was stirred under nitrogen. After 1 h, the solution was neutralized with triethylamine, filtered and the filtrate was concentrated in vacuo. Flash chromatography (petroleum ether/ethyl acetate, 2:1) of the residue gave the compound **31** (3.4 g, 86%) as a white foam. − TLC (petroleum ether/ethyl acetate, 3:2): R_f = 0.68. − $[\alpha]_D^{20}$ = +8.9 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.36−1.82 (m, 12 H, 4 CH_3), 2.03 (s, 3 H, $COCH_3$), 2.88 (br. s, 1 H, OH), 3.02 (ddd, $^3J_{5,4}$ = 10.4 Hz, $^3J_{5,6}$ = $^3J_{5,6'}$ = 5.2 Hz, 1 H, 5c-H), 3.12 (d, $^3J_{5,4}$ = 9.7 Hz, 1 H, 5b-H), 3.33−3.35 (m, 2 H, 5a-H, 6a-H), 3.42−3.43 (m, 2 H, 6b-H, 6c-H), 3.54 (s, 1 H, 6′b-H), 3.55 (s, 1 H, 6′a-H), 3.58 (dd, $^3J_{3,4}$ = 9.7 Hz, $^3J_{3,2}$ = 2.7 Hz, 1 H, 3c-H), 3.64 (d, ^2J = 5.5 Hz, 2 H, 6d-H, 6′d-H), 3.68 (dd, $^3J_{4,3}$ = $^3J_{4,5}$ = 9.3 Hz, 1 H, 4d-H), 3.75 (dd, $^3J_{2,3}$ = $^3J_{2,1}$ = 9.4 Hz, 1 H, 2a-H), 3.86−3.88 (m, 2 H, 2b-H, 4c-H), 3.93−3.97 (m, 4 H, 3a-H, 4b-H, 2c-H, 3d-H), 4.00−4.03 (m, 2 H, 6′c-H, 5d-H), 4.07−4.09 (m, 2 H, 4a-H, 3b-H), 4.29 (d, ^2J = 12.2 Hz, 1 H, C*H*Ph), 4.32 (d, ^2J = 12.0 Hz, 1 H, C*H*Ph), 4.34 (d, ^2J = 11.2 Hz, 1 H, C*H*Ph), 4.39 (d, ^2J = 10.8 Hz, 1 H, C*H*Ph), 4.41 (d, ^2J = 11.9 Hz, 1 H, C*H*Ph), 4.43 (d, ^2J = 10.8 Hz, 1 H, C*H*Ph), 4.44 (d, ^2J = 12.2 Hz, 1 H, C*H*Ph), 4.50 (d, ^2J = 10.8 Hz, 1 H, C*H*Ph), 4.52 (d, ^2J = 10.8 Hz, 1 H, C*H*Ph), 4.53 (br. s, 1 H, 1c-H), 4.54 (d, ^2J = 10.8 Hz, 1 H, C*H*Ph), 4.61 (d, ^2J = 11.2 Hz, 1H C*H*Ph), 4.77−4.80 (m, 3 H, 3 C*H*Ph), 4.97 (d, $^2J_{1,2}$ = 9.4 Hz, 1 H, 1a-H), 5.03 (d, $^3J_{1,2}$ = 8.5 Hz, 1 H, 1b-H), 5.04 (d, $^3J_{1,2}$ < 1.0 Hz, 1 H, 1d-H), 5.37 (s, 1 H, *H*CPh), 5.41 (d, $^3J_{2,1}$ < 1.0 Hz, 1 H, 2d-H), 6.98−7.27 (m, 40 H, 8 Ph). − ^{13}C NMR (600 MHz, $CDCl_3$): δ = 55.0 (C-2a), 56.2 (C-2b), 66.7 (C-5c), 67.6 (C-6a), 67.7 (C-6b), 68.3 (C-6c), 68.5 (C-2d), 69.2 (C-6d), 70.6 (C-2c), 71.8 (C-5d), 74.4 (C-5b, C-4d), 75.0 (C-4a), 76.8 (C-5a), 76.9 (C-3a), 77.0 (C-3c), 77.1 (C-4c), 77.7 (C-3b), 77.8 (C-3d), 78.6 (C-4b), 85.6 (C-1a), 97.0 (C-1b), 98.7 (C-1d), 100.5 (C-1c), 101.3 (H*C*Ph). − $C_{94}H_{99}N_5O_{23}$·H_2O (1684.8): calcd.: C 67.01, H 6.04, N 4.15; found C 66.78, H 5.92, N 3.96.

***O*-(2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1→4)−(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-glucopyranosyl Azide (32):** Compound **31** (2.36 g, 1.40 mmol) was treated with benzoyl chloride (325.7 μL, 2.80 mmol) in pyridine (25 mL) and the solution was stirred overnight at room temp. The mixture was concentrated in vacuo by co-distillation with toluene/ethanol and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 4:1) to afford **32** (2.28 g, 92%) as a white foam. − TLC (petroleum ether/ethyl acetate, 2:1): R_f = 0.45. − $[\alpha]_D^{20}$ = −19.7 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.57−1.77 (m, 12 H, 4 CH_3), 1.94 (s, 3 H, $COCH_3$), 3.00 (d, $^3J_{5,4}$ = 9.8 Hz, 1 H, 5b-H), 3.05 (ddd, $^3J_{5,6}$ = 11.2 Hz, $^3J_{5,6'}$ = $^3J_{5,4}$ = 8.0 Hz, 1 H, 5c-H), 3.25 (dd, ^2J = 11.1 Hz, $^3J_{6,5}$ = 3.5 Hz, 1 H, 6a-H), 3.28 (dd, $^3J_{5,4}$ = 10.1 Hz, $^3J_{5,6}$ = 3.5 Hz, 1 H, 5a-H), 3.47 (d, ^2J = 11.1 Hz, 1 H, 6′a-H), 3.49 (d, ^2J = 12.8 Hz, 2 H, 6b-H, 6′b-H), 3.56 (dd, ^2J = $^3J_{6,5}$ = 11.2 Hz, 1 H, 6c-H), 3.60−3.63 (m, 2 H, 3d-H, 6d-H), 3.69−3.79 (m, 4 H, 2a-H, 2b-H, 4d-H, 6′d-H), 3.84−3.90 (m, 5 H, 3a-H, 3b-H, 3c-H, 4c-H, 5d-H), 3.98−4.00 (m, 2 H, 4a-H, 4b-H), 4.01 (d, ^2J = 13.0 Hz, 1 H, C*H*Ph), 4.13 (d, ^2J = 12.7 Hz, 1 H, C*H*Ph), 4.14 (dd, ^2J = 11.2 Hz, $^3J_{6,5}$ = 8.0 Hz, 1 H, 6′c-H), 4.27 (d, ^2J = 13.0 Hz, 2 H, 2 C*H*Ph), 4.30 (d, ^2J = 12.7 Hz, 1 H, C*H*Ph), 4.37 (d, ^2J = 11.9 Hz, 1 H, C*H*Ph), 4.41 (d, ^2J = 11.9 Hz, 1 H, C*H*Ph), 4.42 (s, 2 H, CH_2Ph), 4.44 (d, ^2J = 11.9 Hz, 1 H, C*H*Ph), 4.57 (d, ^2J = 11.9 Hz, 1 H, C*H*Ph), 4.69 (d, $^3J_{1,2}$ < 1.0 Hz, 1 H, 1c-H), 4.70 (d, ^2J = 9.7 Hz, 1 H, C*H*Ph), 4.73 (d, ^2J = 12.4 Hz, 1 H, C*H*Ph), 4.75 (d, ^2J = 12.4 Hz, 1 H, C*H*Ph), 4.91 (d, $^3J_{1,2}$ = 7.9 Hz, 1 H, 1b-H), 4.92 (d, $^3J_{1,2}$ = 9.3 Hz, 1 H, 1a-H), 5.13 (s, 1 H, 1d-H), 5.19 (br. s, 1 H, 2d-H), 5.44 (s, 1 H, *H*CPh), 5.53 (dd, $^3J_{2,3}$ = 1.9 Hz, $^3J_{2,1}$ < 1.0 Hz, 1 H, 2c-H), 6.81 (d, $J_{m,o}$ = $J_{m,p}$ = 8.3 Hz, 2 H, H_m-PhCO), 6.95−7.22 (m, 41 H, 8 Ph, H_p-PhCO), 8.03 (d, $J_{o,m}$ = 8.3 Hz, 2 H, H_o-PhCO). − ^{13}C NMR (600 MHz, $CDCl_3$): δ = 55.4 (C-2a), 56.6 (C-2b), 66.8 (C-5c), 68.0 (C-6b), 68.1 (C-6a), 68.9 (C-6c), 69.0 (C-2d), 69.3 (C-6d), 71.6 (C-2c), 72.4 (C-5d), 73.2 (C-3c), 74.3 (C-4d), 74.6 (C-5b), 75.3 (C-4a), 77.2 (C-5a), 77.4 (C-3b), 77.5 (C-3a), 78.3 (C-3d), 78.8 (C-4b), 79.6 (C-4c), 86.1 (C-1a), 97.3 (C-1b), 98.8 (C-1d), 99.4 (C-1c), 101.6 (H*C*Ph). − $C_{101}H_{103}N_5O_{24}$ (1770.9): calcd. C 68.50, H 5.86, N 3.95; found C 68.54, H 5.52, N 4.08.

***O*-(3,4,6-Tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1→4)−(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-glucopyranosyl Azide (33):** A solution of **32** (804.7 mg, 0.45 mmol) in a mixture of dry methanol/dichloromethane (5:1, 6 mL) was treated with a catalytic amount of sodium methoxide (0.2 M, 500 μL) and stirred at room temp. After 7 h, the solution was neutralized with ion-exchange resin (Amberlite IR-120 H^+), the resin was filtered off and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 3:1) to give **33** (778 mg, quant.) as a white foam. − TLC (petroleum ether/ethyl acetate,

3:2): R_f = 0.57. − $[\alpha]_D^{20}$ = −5.5 (*c* = 3.8, $CHCl_3$). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.51−1.79 (m, 12 H, 4 CH_3), 3.02 (d, $^3J_{5,4}$ = 9.7 Hz, 1 H, 5b-H), 3.06 (ddd, $^3J_{5,6}$ = 11.2 Hz, $^3J_{5,6'}$ = $^3J_{5,4}$ = 4.1 Hz, 1 H, 5c-H), 3.27 (dd, ^2J = 11.1 Hz, $^3J_{5,6}$ = 3.4 Hz, 1 H, 6a-H), 3.30 (ddd, $^3J_{5,4}$ = 10.1 Hz, $^3J_{5,6}$ = $^3J_{5,6'}$ = 3.4 Hz, 1 H, 5a-H), 3.49−3.52 (m, 3 H, 6′a-H, 6b-H, 6′b-H), 3.55−3.58 (m, 2 H, 6c-H, 3d-H), 3.67 (d, ^2J = 8.4 Hz, 1 H, 6d-H), 3.68 (dd, ^2J = 8.4 Hz, $^3J_{6',5}$ = 4.1 Hz, 1 H, 6′d-H), 3.74−3.76 (m, 3 H, 2a-H, 2d-H, 4d-H), 3.81−3.83 (m, 2 H, 2b-H, 4c-H), 3.85 (dd, $^3J_{3,2}$ = $^3J_{3,4}$ = 8.5 Hz, 1 H, 3b-H), 3.90−3.93 (m, 3 H, 3a-H, 3c-H, 5d-H), 3.99−4.01 (m, 2 H, 4a-H, 4b-H), 4.13 (d, ^2J = 12.5 Hz, 1 H, C*H*Ph), 4.16 (dd, ^2J = 12.2 Hz, $^3J_{6',5}$ = 4.1 Hz, 1 H, 6′c-H), 4.28 (d, ^2J = 11.5 Hz, 1 H, C*H*Ph), 4.29 (d, ^2J = 11.5 Hz, 1 H, C*H*Ph), 4.31 (d, ^2J = 11.7 Hz, 2 H, CH_2Ph), 4.43−4.46 (m, 5 H, CH_2Ph, 3 C*H*Ph), 4.58 (d, ^2J = 12.3 Hz, 1 H, C*H*Ph), 4.71 (d, ^2J = 12.8 Hz, 1 H, C*H*Ph), 4.73 (br. s, 1 H, 1c-H), 4.74 (d, ^2J = 12.5 Hz, 1 H, C*H*Ph), 4.80 (d, ^2J = 12.8 Hz, 1 H, C*H*Ph), 4.93 (d, $^2J_{1,2}$ = 8.0 Hz, 1 H, 1b-H), 4.94 (d, $^3J_{1,2}$ = 9.4 Hz, 1 H, 1a-H), 5.13 (d, $^3J_{1,2}$ < 1.0 Hz, 1 H, 1d-H), 5.42 (s, 1 H, *H*CPh), 5.56 (d, $^3J_{2,3}$ = 2.9 Hz, 1 H, 2c-H), 6.82−7.32 (m, 43 H, 8 Ph, 2 H_m-PhCO, H_p-PhCO), 8.02 (2 H, H_o-PhCO). − ^{13}C NMR (600 MHz, $CDCl_3$): δ = 55.4 (C-2a), 56.7 (C-2b), 66.9 (C-5c), 68.0 (C-6b), 68.1 (C-6a), 68.8 (C-2d), 69.0 (C-6c), 69.3 (C-6d), 71.9 (C-2c), 72.1 (C-5d), 73.6 (C-3c), 74.3 (C-4d), 74.6 (C-5b), 75.4 (C-4a), 77.2 (C-5a), 77.4 (C-3b), 77.5 (C-3a), 78.8 (C-4b), 79.6 (C-4c), 80.1 (C-3d), 86.0 (C-1a), 97.3 (C-1b), 99.4 (C-1c), 100.5 (C-1d), 102.0 (H*C*Ph). − MS (MALDI, positive mode, matrix: DHB); *m*/*z*: 1723 [M − N_2 + Na]$^+$, 1751 [M + Na]$^+$. − $C_{99}H_{101}N_5O_{23}$·H_2O (1746.9): calcd.: C 68.06, H 5.94, N 4.00; found C 68.26, H 5.90, N 3.76.

***O*-(2,3,4-Tri-*O*-acetyl-6-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-(3-*O*-acetyl-6-*O*-benzoyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-(2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1→4)−(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-glucopyranosyl Azide (34):** A solution of **33** (303.8 mg, 0.17 mmol) and **6** (252 mg, 0.26 mmol) in dry dichloromethane (1.8 mL) was cooled to −20 °C and stirred in the presence of 4 Å molecular sieves under nitrogen for 10 min. TMSOTf (0.1 M in CH_2Cl_2, 3.2 μL) was slowly added dropwise and the reaction mixture was stirred for 20 min. A solution of the trichloroacetimidate (50.1 mg, 0.05 mmol) in dry CH_2Cl_2 (300 μL) was added dropwise under nitrogen and after stirring for 1 h at −20 °C, the reaction mixture was neutralized with triethylamine, the mixture was warmed to room temp. and the solvent was evaporated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 2:1) to afford **34** (331 mg, 75%) as a white foam. − TLC (petroleum ether/ethyl acetate, 1:1): R_f = 0.70. − $[\alpha]_D^{20}$ = −38.2 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.69−2.00 (m, 18 H, 6 CH_3), 2.04 (s, 6 H, 2 $COCH_3$), 2.14 (s, 3 H, $COCH_3$), 2.16 (s, 3 H, $COCH_3$), 2.88 (ddd, $^3J_{5,4}$ = 9.5 Hz, $^3J_{5,6'}$ = $^3J_{5,6}$ = 4.7 Hz, 1 H, 5c-H), 3.15 (d, $^3J_{5,4}$ = 9.7 Hz, 1 H, 5b-H), 3.34 (dd, ^2J = 10.7 Hz, $^3J_{6,5}$ = 3.8 Hz, 1 H, 6d-H), 3.42−3.48 (m, 4 H, 5a-H, 6a-H, 4d-H, 6f-H), 3.56−3.60 (m, 6 H, 6′a-H, 6b-H, 6c-H, 3d-H, 5e-H, 6′f-H), 3.65 (d, ^2J = 8.8 Hz, 1 H, 6′b-H), 3.69 (d, ^2J = 10.7 Hz, 1 H, 6′d-H), 3.73−3.78 (m, 3 H, 4c-H, 4e-H, 5f-H), 3.82 (dd, $^3J_{3,4}$ = 9.5 Hz, $^3J_{3,2}$ = 2.5 Hz, 1 H, 3c-H), 3.91 (dd, $^3J_{2,1}$ = $^3J_{2,3}$ = 9.5 Hz, 1 H, 2a-H), 3.94−4.03 (m, 5 H, 2b-H, 3b-H, 2d-H, 6e-H, C*H*Ph), 4.06−4.11 (m, 4 H, 3a-H, 4b-H, 5d-H, 2e-H), 4.16−4.18 (m, 2 H, 4a-H, C*H*Ph), 4.24 (dd, ^2J = 9.7 Hz, $^3J_{6',5}$ = 4.8 Hz, 1 H, 6′c-H), 4.29 (d, ^2J = 12.3 Hz, 1 H, C*H*Ph), 4.34 (d, ^2J = 11.3 Hz, 1 H, C*H*Ph), 4.44 (d, ^2J = 9.7 Hz, 1 H, 6e-H), 4.47−4.51 [m, 5 H, 2 C*H*Ph, CH_2Ph, H,H-COSY: 4.50 (d, $^3J_{1,2}$ = 8.0 Hz, 1f-H)], 4.56 (s, 1 H, 1c-H), 4.60 (s, 4 H, 2 CH_2Ph), 4.64 (d, ^2J = 12.0 Hz, 1 H, C*H*Ph), 4.82 (d, ^2J = 11.3 Hz, 1 H, C*H*Ph), 4.91 (d, ^2J = 12.5 Hz, 1 H, C*H*Ph), 4.93 (dd, $^3J_{3,2}$ = 8.4 Hz, $^3J_{3,4}$ = 2.7 Hz 1 H, 3f-H), 4.97 (d, $^3J_{1,2}$ = 8.5 Hz, 1 H, 1e-H), 5.01 (d, ^2J = 12.5 Hz, 1 H, C*H*Ph), 5.09 (d, $^3J_{1,2}$ = 7.8 Hz, 1 H, 1b-H), 5.11 (d, $^3J_{1,2}$ < 1.0 Hz, 1 H, 1d-H), 5.12 (d, $^3J_{1,2}$ = 9.5 Hz, 1 H, 1a-H), 5.20 (d, $^3J_{2,3}$ = 8.4 Hz, $^3J_{2,1}$ = 8.0 Hz, 1 H, 2f-H), 5.35 (s, 1 H, *H*CPh), 5.43 (dd, $^3J_{3,2}$ = $^3J_{3,4}$ = 8.7 Hz, 1 H, 3e-H), 5.49 (d, $^3J_{4,3}$ = 2.7 Hz, 1 H, 4f-H), 5.57 (d, $^3J_{2,3}$ = 2.5 Hz, 1 H, 2c-H), 6.93−7.67 (m, 51 H, 9 Ph, 4 H_m-PhCO, 2 H_p-PhCO), 8.03 (2 H, H_o-PhCO), 8.12 (2 H, H_o-PhCO). − ^{13}C NMR (600 MHz, $CDCl_3$): δ = 54.8 (C-2e), 55.3 (C-2a), 56.6 (C-2b), 62.4 (C-6e), 66.3 (C-5c), 67.2 (C-6f), 67.5 (C-4f), 68.0 (C-6a, C-6b), 69.1 (C-6c), 69.9 (C-2f), 70.7 (C-6d), 71.5 (C-5d, C-3e), 71.7 (C-2c), 71.8 (C-3f), 72.1 (C-2d), 72.2 (C-5f), 73.7 (C-5a), 74.4 (C-5b-), 74.6 (C-3c), 75.6 (C-4a), 77.0 (C-3b), 77.1 (C-4e, C-4d), 77.6 (C-3a), 77.9 (C-3d), 78.2 (C-4b), 79.5 (C-4c), 86.0 (C-1a), 95.4 (C-1e), 97.5 (C-1b), 97.7 (C-1d), 98.9 (C-1c), 101.4 (C-1f), 102.5 (H*C*Ph). − MS (MALDI, positive mode, matrix: DHB); *m*/*z*: 2513 [M − N_2+ Na]$^+$, 2545 [M + Na]$^+$. − $C_{139}H_{144}N_6O_{39}$·0.5 H_2O (2531.5): calcd.: C 65.95, H 5.77, N 3.31; found C 66.09, H 5.88, N 2.81.

***O*-(2,3,4-Tri-*O*-acetyl-6-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-(3-*O*-acetyl-6-*O*-benzoyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-(2-*O*-benzoyl-β-D-mannopyranosyl)-(1→4)−(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-glucopyranosyl Azide (35):** A solution of **34** (300 mg, 0.12 mmol) in dry dichloromethane (3 mL) was treated with ethanethiol (53.2 μL, 0.72 mmol) and *p*TsOH (4.6 mg, 0.02 mmol) and stirred at room temp. After 2 h, the solution was neutralized with triethylamine and concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 1:1) to give **35** (262.9 mg, 90%) as a white foam. − TLC (petroleum ether/ethyl acetate, 1:1): R_f = 0.15. − $[\alpha]_D^{20}$ = +4.6 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.79−1.84 (m, 18 H, 6 CH_3), 1.85 (s, 3 H, $COCH_3$), 1.96 (s, 3 H, $COCH_3$), 2.04 (s, 3 H, $COCH_3$), 2.14 (s, 3 H, $COCH_3$), 2.83 (dd, ^2J = $^3J_{5,6}$ = 9.4 Hz, 1 H, 6d-H), 3.07 (d, $^3J_{5,4}$ = 9.9 Hz, 1 H, 5b-H), 3.19 (m_c, 1 H, 5c-H), 3.27−3.30 (m, 2 H, 6a-H, 4d-H), 3.35−3.37 (m, 2 H, 5a-H, 6f-H), 3.46 (dd, ^2J = 8.7 Hz, $^3J_{6,5}$ = 4.4 Hz, 1 H, 6′f-H), 3.51−3.57 (m, 6 H, 6′a-H, 6b-H, 6′b-H, 6′d-H, 4e-H, 5e-H), 3.67 (m_c, 1 H, 5f-H), 3.68 (d, ^2J = 9.5 Hz, 1 H, 6c-H), 3.78−3.92 (m, 9 H, 2a-H, 2b-H, 3b-H, 3c-H, 6′c-H, 2d-H, 3d-H, 5d-H, 2e-H), 3.97−3.99 (m, 2 H, 3a-H, 4b-H), 4.03 (d, ^2J = 12.6 Hz, 1 H, C*H*Ph), 4.04−4.06 (m, 2 H, 4a-H, 6e-H), 4.16 (dd, $^3J_{4,5}$ = 9.9 Hz, $^3J_{4,3}$ = 4.9 Hz, 1 H, 4c-H), 4.24 (d, ^2J = 11.4 Hz, 1 H, C*H*Ph), 4.29 (d, ^2J = 5.5 Hz, 1 H, 6′e-H), 4.32 (d, ^2J = 12.6 Hz, 1 H, C*H*Ph), 4.34 (d, ^2J = 13.0 Hz, 1 H, C*H*Ph), 4.36 (d, $^3J_{1,2}$ = 8.0 Hz, 1 H, 1f-H), 4.37 (s, 2 H, CH_2Ph), 4.40 (d, ^2J = 11.2 Hz, 1 H, C*H*Ph), 4.42 (d, ^2J = 12.1 Hz, 1 H, C*H*Ph), 4.47 (d, ^2J = 8.0 Hz, 1 H, C*H*Ph), 4.49 (s, 2 H, CH_2Ph), 4.50 (s, 2 H, CH_2Ph), 4.53 (d, ^2J = 11.2 Hz, 1 H, C*H*Ph), 4.71−4.75 [m, 4 H, CH_2Ph, H,H-COSY: 4.71 (d, $^3J_{1,2}$ < 1.0 Hz, 1c-H), 4.72 (d, $^3J_{1,2}$ = 7.6 Hz, 1e-H)], 4.86 (m_c, 1 H, 3f-H), 4.87 (d, ^2J = 13.0 Hz, 1 H, C*H*Ph), 4.97 (d, $^3J_{1,2}$ = 8.2 Hz, 1 H, 1b-H), 5.01 (d, $^3J_{1,2}$ = 9.7 Hz, 1 H, 1a-H), 5.09 (dd, $^3J_{2,3}$ = 8.4 Hz, $^2J_{2,1}$ = 8.0 Hz, 1 H, 2f-H), 5.15 (dd, $^3J_{3,2}$ = $^3J_{3,4}$ = 8.7 Hz, 1 H, 3e-H), 5.30 (s, 1 H, 1d-H), 5.40 (d, $^3J_{4,3}$ = 3.0 Hz, 1 H, 4f-H), 5.56 (dd, $^3J_{2,3}$ = 3.2 Hz, $^3J_{2,1}$ < 1.0 Hz, 1 H, 2c-H), 6.67 (d, $J_{p,m}$ = 7.3 Hz, 2 H, H_p − PhCO), 7.05−7.50 (m, 44 H, 8 Ph, 4 H_m-PhCO), 8.03 (2 H, H_o-PhCO), 8.41 (2 H, H_o-PhCO). − ^{13}C NMR (600 MHz, $CDCl_3$): δ = 54.1 (C-2e), 55.0 (C-2a), 56.2 (C-2b), 62.6 (C-6e), 63.0 (C-6c), 64.5 (C-4c), 66.8 (C-6f), 67.1 (C-4f), 67.5 (C-6b), 67.7 (C-6a), 69.5 (C-2f), 70.1 (C-6d), 70.6 (C-3e), 70.7 (C-5d), 71.4 (C-3f), 71.8 (C-5f), 72.5

(C-2c), 73.4 (C-2d), 74.0 (C-5b, C-4d), 75.0 (C-4a), 75.5 (C-5c), 76.8 (C-3b, C-5a), 77.1 (C-4b, C-3d), 77.4 (C-4c), 78.6 (C-3a), 79.5 (C-3c), 85.7 (C-1a), 93.1 (C-1d), 95.9 (C-1e), 96.8 (C-1b), 98.5 (C-1c), 101.3 (C-1f). − MS (FAB, positive mode, $CHCl_3$/NBA + NaI); *m/z*; 2430 $[M - N_2 + Na]^+$, 2458 $[M + Na]^+$2475 $[M + K]^+$, 2610 $[M + Na + NaI]^+$. − $C_{132}H_{140}N_6O_{39}\cdot 2\ H_2O$ (2470.6): calcd.: C 64.17, H 5.87, N 3.40; found C 64.06, H 5.83, N 2.86.

***O*-(2,3,4-Tri-*O*-acetyl-6-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-(3-*O*-acetyl-6-*O*-benzoyl-2-deoxy-2-dimethylmaleimido-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-[(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)]-(4-*O*-acetyl-2-*O*-benzoyl-β-D-mannopyranosyl)-(1→4)−(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-glucopyranosyl Azide (36):** A mixture of **35** (270 mg, 0.11 mmol), **4**[22] (84 mg, 0.13 mmol) and molecular sieves (4 Å) in dry dichloromethane (2 mL) was cooled to −40 °C. TMSOTf (0.1 M in CH_2Cl_2, 10 μL) was slowly added dropwise under nitrogen and the reaction mixture was stirred for 20 min. A solution of the trichloroacetimidate (21.0 mg, 0.03 mmol) in dry CH_2Cl_2 (200 μL) was added dropwise at −40 °C and after stirring for 1 h [TLC (petroleum ether/ethyl acetate, 1:1): R_f = 0.45], the mixture was neutralized with triethylamine. The mixture was warmed to room temp. and the solvent evaporated in vacuo. Flash chromatography (petroleum ether/ethyl acetate, 1:1) of the residue gave the heptasaccharide (218.5 mg, 80%) as a white foam. The heptasaccharide (218.5 mg, 0.08 mmol) was treated with acetic anhydride (1 mL) in pyridine (2 mL) and the reaction mixture was stirred overnight at room temp. The mixture was concentrated in vacuo by co-distillation with toluene/ethanol and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 3:2) to afford **36** (238 mg, quant.) as a white foam. − TLC (petroleum ether/ethyl acetate, 3:2): R_f = 0.39. − $[\alpha]_D^{20}$ = +8.2 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.55−1.80 (m, 18 H, 6 CH_3), 1.88 (s, 3 H, $COCH_3$), 1.94 (s, 6 H, 2 $COCH_3$), 2.00 (s, 6 H, 2 $COCH_3$), 2.19 (s, 3 H, $COCH_3$), 3.04 (d, $^3J_{5,4}$ = 9.9 Hz, 1 H, 5b-H), 3.13 (d, $^3J_{5,4}$ = 10.2 Hz, 1 H, 5c-H), 3.25−3.37 (m, 4 H, 5a-H, 6a-H, 6d-H, 6f-H), 3.42−3.58 (m, 7 H, 6′a-H, 6b-H, 6′b-H, 3d-H, 4d-H, 6′d-H, 6′f-H), 3.66−4.03 (m, 21 H, 2a-H, 3a-H, 4a-H, 2b-H, 3b-H, 4b-H, 3c-H, 6c-H, 6′c-H, 2d-H, 5d-H, 4e-H, 5e-H, 5f-H, 3g-H, 4g-H, 5g-H, 6g-H, 6′g-H, CH_2Ph), 4.14 (dd, $^3J_{2,3}$ = $^3J_{2,1}$ = 8.5 Hz, 1 H, 2e-H), 4.24 (d, ^2J = 12.3 Hz, 1 H, C*H*Ph), 4.27−4.40 (m, 9 H, 6e-H, 4 CH_2Ph), 4.46−4.51 (m, 9 H, C*H*Ph, 4 CH_2Ph), 4.54 (d, $^3J_{1,2}$ = 7.9 Hz, 1 H, 1f-H), 4.59 (d, ^2J = 12.4 Hz, 1 H, 6′e-H), 4.63 (d, ^2J = 11.0 Hz, 1 H, C*H*Ph), 4.70 (br. s, 1 H, 1c-H), 4.74−4.83 [m, 6 H, 2 CH_2Ph, H,H-COSY: 4.76 (d, $^3J_{1,2}$ < 1.0 Hz, 1d-H), 4.83 (d, $^3J_{1,2}$ < 1.0 Hz, 1g-H)], 4.88 (dd, $^3J_{3,2}$ = 10.5 Hz, $^3J_{3,4}$ = 2.4 Hz, 1 H, 3f-H), 4.94 (d, $^3J_{1,2}$ = 7.8 Hz, 1 H, 1b-H), 4.99 (d, $^3J_{1,2}$ = 9.6 Hz, 1 H, 1a-H), 5.08 (dd, $^3J_{2,3}$ = 10.5 Hz, $^3J_{2,1}$ = 7.9 Hz, 1 H, 2f-H), 5.26 (d, $^3J_{1,2}$ = 8.5 Hz, 1 H, 1e-H), 5.30 (dd, $^3J_{4,3}$ = $^3J_{4,5}$ = 10.2 Hz, 1 H, 4c-H), 5.34 (d, $^3J_{2,1}$ < 1.0 Hz, 1 H, 2g-H), 5.40 (d, $^3J_{4,3}$ = 2.4 Hz, 1 H, 4f-H), 5.55 (dd, $^3J_{3,2}$ = 8.5 Hz, $^3J_{3,4}$ = 8.4 Hz, 1 H, 3e-H), 5.56 (br. s, 1 H, 2c-H), 6.75−7.34 (m, 61 H, 11 Ph, 2 H_p -PhCO, 4 H_m-PhCO), 7.80 (2 H, H_o-PhCO), 8.05 (2 H, H_o-PhCO). − ^{13}C NMR (600 MHz, $CDCl_3$): δ = 54.9 (C-2e), 55.3 (C-2a), 56.5 (C-2b), 63.3 (C-6e), 66.7 (C-6c), 67.0 (C-6f), 67.4 (C-4f), 67.9 (C-5b, C-6a), 68.7 (C-2g), 69.1 (C-6g), 69.5 (C-4c), 69.8 (C-2f), 70.2 (C-6d), 71.5 (C-3f), 71.6 (C-2c), 72.3 (C-3e, C-5g), 72.4 (C-5d, C-5f), 72.7 (C-5c), 73.3 (C-5e), 73.5 (C-2d), 73.6 (C-4d), 74.4 (C-4g), 74.6 (C-5b), 75.3 (C-4a), 75.5 (C-3c), 76.9 (C-3b), 77.1 (C-5a), 77.3 (C-4e), 77.4 (C-3a), 77.7 (C-3d), 78.9 (C-3g), 79.0 (C-4b), 85.9 (C-1a), 96.8 (C-1e), 97.3 (C-1b), 98.5 (C-1g, C-1d), 99.0 (C-1c), 101.5 (C-1f). − MS (FAB, positive mode, $CHCl_3$/NBA + NaI); *m/z*: 2591 $[M - N_2 + Na]^+$, 2619 $[M + Na]^+ - C_{165}H_{172}N_6O_{46}\cdot 2\ H_2O$ (3011.2): calcd.: C 65.81, H 5.89, N 2.79; found C 65.75, H 6.28, N 2.29.

***O*-(2,3,4-Tri-*O*-acetyl-6-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-(2-acetamido-3-*O*-acetyl-6-*O*-benzoyl-2-deoxy-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-[(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)]-(2,4-di-*O*-acetyl-β-D-mannopyranosyl)-(1→4)−(2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranosyl Azide (37):** A mixture of **36** (194 mg, 0.06 mmol) and sodium hydroxide (104.3 mg, 2.6 mmol) in a mixture of dioxane/water (4:1, 10 mL) was stirred overnight at room temp. A solution of HCl (1 M, 4 mL) was slowly added dropwise until pH = 4.5 was reached; the reaction mixture was stirred and the pH constantly checked by a pH-meter. After 5 d [TLC (ethyl acetate/methanol, 5:1): R_f = 0.29], the mixture was neutralized with a solution of NaOH (1 M), ethanolamine (11.7 μL, 0.19 mmol) was added and the solvent was evaporated in vacuo. The residue was lyophilized from dioxane/water and used in the next step without further purification. The residue was dissolved in pyridine (5 mL), treated with acetic anhydride (2.5 mL) and the mixture was stirred at room temp. for 12 h. The solvent was evaporated in vacuo by co-distillation with toluene/ethanol and the residue purified by flash chromatography (toluene/acetone, 3:2) to afford **37** (121 mg, 74%) as a white foam. − TLC (toluene/acetone, 2:1): R_f = 0.20. − $[\alpha]_D^{20}$ = −17.5 (*c* = 0.52, $CHCl_3$). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.53 (s, 3 H, NHAc), 1.67 (s, 3 H, NHAc), 1.75 (s, 3 H, NHAc), 1.84 (s, 3 H, $COCH_3$), 1.94 (s, 3 H, $COCH_3$), 1.96 (s, 3 H, $COCH_3$), 1.98 (s, 3 H, $COCH_3$), 2.03 (s, 6 H, 2 $COCH_3$), 2.09 (s, 3 H, $COCH_3$), 3.11 (d, $^3J_{5,4}$ = 9.9 Hz, 1 H, 5b-H), 3.20 (dd, $^3J_{3,4}$ = $^3J_{3,2}$ = 9.0 Hz, 1 H, 3b-H), 3.27−3.28 [m, 2 H, 5c-H, H,H-COSY: 3.28 (dd, $^3J_{2,3}$ = 9.3 Hz, $^3J_{2,1}$ = 8.0 Hz, 2e-H)], 3.40 (dd, ^2J = $^3J_{6,5}$ = 7.5 Hz, 1 H, 6f-H), 3.44 (m_c, 1 H, 5e-H), 3.49 (dd, ^2J = 7.5 Hz, $^3J_{6',5}$ = 6.0 Hz, 1 H, 6′f-H), 3.55−3.67 [m, 14 H, 3a-H, 4a-H, 6a-H, 6′a-H, 6b-H, 6′b-H, 6c-H, 3d-H, 4d-H, 6d-H, 6′d-H, 4e-H, 6g-H, H,H-COSY: 3.56 (dd, $^3J_{2,3}$ = 9.0 Hz, $^3J_{2,1}$ = 8.2 Hz, 2b-H)], 3.74−3.76 (m, 4 H, 6′c-H, 5f-H, 5g-H, 6′g-H), 3.83−3.93 [m, 7 H, 5a-H, 3c-H, 2d-H, 5d-H, 3g-H, 4g-H, H,H-COSY: 3.87 (ddd, $^2J_{2,1}$ = $^2J_{2,3}$ = 9.7 Hz, J_{NH} = 8.4 Hz, 2a-H)], 4.00−4.01 (m, 2 H, 4b-H, 6e-H), 4.15 (d, $^3J_{1,2}$ = 8.2 Hz, 1 H, 1b-H), 4.30−4.45 [m, 17 H, NH_b, C*H*Ph, 5 CH_2Ph, H,H-COSY: 4.31 (d, ^2J = 12.8 Hz, C*H*Ph), 4.32 (d, ^2J = 10.7 Hz, C*H*Ph), 4.35 (d, ^2J = 12.2 Hz, 6′e-H), 4.43 (d, $^3J_{1,2}$ = 7.5 Hz, 1f-H), 4.44 [d, ^2J = 11.9 Hz, C*H*Ph)], 4.49 (d, ^2J = 12.5 Hz, 1 H, C*H*Ph), 4.50 (d, ^2J = 6.8 Hz, 1 H, C*H*Ph), 4.51 (d, ^2J = 6.8 Hz, 1 H, C*H*Ph), 4.52 (d, ^2J = 12.3 Hz, 1 H, C*H*Ph), 4.53 (d, ^2J = 10.8 Hz, 1 H, C*H*Ph), 4.62 (s, 2 H, CH_2Ph), 4.70−4.71 [m, 2 H, H,H-COSY: 4.70 (d, $^3J_{1,2}$ < 1.0 Hz, 1c-H), 4.71 (d, $^3J_{1,2}$ = 9.7 Hz, 1a-H)], 4.79 (d, ^2J = 12.5 Hz, 1 H, C*H*Ph), 4.86 (s, 1 H, 1g-H), 4.89 (d, $^3J_{1,2}$ = 1.9 Hz, 1 H, 1d-H), 4.94−4.95 [m, 2 H, H,H-COSY: 4.94 (d, $^3J_{1,2}$ = 8.0 Hz, 1e-H, 4.95 (dd, $^3J_{3,2}$ = 8.3 Hz, $^3J_{3,4}$ = 2.6 Hz, 3f-H)], 5.06 (dd, $^3J_{2,3}$ = 8.3 Hz, $^2J_{2,1}$ = 7.5 Hz, 1 H, 2f-H), 5.29 (dd, $^3J_{4,3}$ = $^3J_{4,5}$ = 9.8 Hz, 1 H, 4c-H), 5.36 (s, 1 H, 2g-H), 5.43 (d, $^3J_{4,3}$ = 2.6 Hz, 1 H, 4f-H), 5.46 (dd, $^3J_{3,4}$ = $^3J_{3,2}$ = 9.3 Hz, 1 H, 3e-H), 5.60 (dd, $^3J_{2,3}$ = 2.4 Hz, $^3J_{2,1}$ < 1.0 Hz, 1 H, 2c-H), 5.64 (br. s, 1 H, NH_e), 6.20 (d, J_{NH} = 8.4 Hz, 1 H, NH_a), 6.91 (d, $J_{p,m}$ = 7.3 Hz, 1 H, H_p − PhCO), 7.14 −7.35 (m, 57 H, 11 Ph, 2 H_m-PhCO), 8.05 (2 H, H_o-PhCO). − ^{13}C NMR (600 MHz, $CDCl_3$): δ = 51.5 (C-2a), 54.9 (C-2b), 55.8 (C-2e), 62.6 (C-6e), 66.4 (C-6c), 66.8 (C-6f), 67.1 (C-4f), 68.2 (C-6b), 68.5 (C-2g), 68.7 (C-6g), 68.8 (C-6a), 69.0 (C-4c), 69.3 (C-6d), 69.4 (C-2f), 71.1 (C-3f), 71.3 (C-3e), 71.4 (C-2), 71.8 (C-5g), 72.0 (C-5f), 72.1 (C-5d), 72.3 (C-5e), 72.4 (C-5c), 73.2 (C-5a), 74.2 (C-2d, C-4g), 74.3 (C-5b), 75.5 (C-3c), 76.2 (C-4a, C-4d), 76.5 (C-4e), 77.3

(C-4b), 77.4 (C-3d), 77.6 (C-3a), 77.8 (C-3b), 78.4 (C-3g), 88.2 (C-1a), 97.6 (C-1e), 97.9 (C-1g), 98.2 (C-1c), 98.9 (C-1d), 99.8 (C-1b), 101.0 (C-1f). − MS (FAB, positive mode, $CHCl_3$/NBA + NaI); *m/z*; 2687 $[M - N_2 + Na]^+$, 2713 $[M + Na]^+$2729 $[M + K]^+$, 2864 $[M + NaI + Na]^+$. − $C_{146}H_{164}N_6O_{43}$·2.5 H_2O (2736.0): calcd.: C 64.09, H 6.22, N 3.07; found C 64.10, H 6.26, N 2.76.

***O*-(6-*O*-Benzyl-β-D-galactopyranosyl)-(1→4)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-[(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)]-(β-D-mannopyranosyl)-(1→4)-(2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranosyl Azide (38):** To a solution of **37** (130 mg, 0.05 mmol) in methanol (5 mL) was added an aqueous solution of LiOH (1 M, 1 mL) and the mixture was vigorously stirred at 50 °C. After 20 h, the solution was neutralized with ion-exchange resin (Amberlite IR 120 H^+form), the resin was filtered off and the filtrate was concentrated in vacuo. Flash chromatography (ethyl acetate/methanol, 8:1) of the residue gave **38** (97.5 mg, 87% as a white foam. − TLC (ethyl/acetate/methanol, 9:2): R_f = 0.48. − $[\alpha]_D^{20}$ = −27.5 (*c* = 0.2 MeOH). − ^{1}H NMR (600 MHz, MeOD(D_2O, 10:1): δ = 1.90 (s, 3 H, NHAc), 1.91 (s, 3 H, NHAc), 2.04 (s, 3 H, NHAc), 3.31 (d, $^3J_{5,4}$ = 10.0 Hz, 1 H, 5c-H), 3.35 (d, $^3J_{5,6}$ = 9.5 Hz, 1 H, 5b-H), 3.54−4.09 (m, 38 H, 2a-H, 3a-H, 4a-H, 5a-H, 6a-H, 6′a-H, 2b-H, 3b-H, 4b-H, 6b-H, 6′b-H, 3c-H, 4c-H, 6c-H, 6′c-H, 2d-H, 4d-H, 5d-H, 6d-H, 6′d-H, 2e-H, 3e-H, 4e-H, 5e-H, 6e-H, 6′e-H, 2f-H, 3f-H, 4f-H, 5f-H, 6f-H, 6′f-H, 2g-H, 3g-H, 4g-H, 5g-H, 6g-H, 6′g-H), 4.15 (dd, $^3J_{3,4}$ = 9−2 Hz, $^3J_{3,2}$ = 3.5 Hz, 1 H, 3d-H), 4.21 (dd, $^3J_{2,3}$ = 4.2 Hz, $^3J_{2,1}$ < 1.0 Hz, 1 H, 2c-H), 4.39 (d, ^2J = 12.1 Hz, 1 H, C*H*Ph), 4.40 (d, ^2J = 12.1 Hz, 1 H, C*H*Ph), 4.46 (d, ^2J = 12.4 Hz, 1 H, C*H*Ph), 4.48−4.50 (m, 2 H, 2d-H, C*H*Ph), 4.53−4.61 [m, 7 H, 2 CH_2Ph, H,H-COSY: 4.53 (d, $^3J_{1,2}$ = 7.5 Hz, 1f-H), 4.55 (d, ^2J = 12.9 Hz, C*H*Ph), 4.59 (d, ^2J = 10.0 Hz, C*H*Ph)], 4.63−4.73 [m, 12 H, 3 CH_2Ph, C*H*Ph, H,H-COSy: 4.66 (d, ^2J = 12.5 Hz, C*H*Ph), 4.67 (d, $^3J_{1,2}$ = 9.5 Hz, 1a-H), 4.69 (d, $^3J_{1,2}$ = 8.1 Hz, 1b-H), 4.70 (d, $^3J_{1,2}$ < 1.0 Hz, 1c-H), 4.73 (d, $^3J_{1,2}$ = 7.4 Hz, 1e-H)], 4.80 (dd, ^2J = 12.5 Hz, 2 H, CH_2Ph), 4.88 (d, $^3J_{1,2}$ = 1.1 Hz, 1 H, 1g-H), 5.07 (dd, ^2J = 10.9 Hz, 2 H, CH_2Ph), 5.21 (s, 1 H, 1d-H), 7.28−7.50 (m, 55 H, 11 Ph). − ^{13}C NMR (600 MHz, MeOD/D_2O, 10:1): δ = 53.3 (C-2a), 55.3 (C-2b), 55.6 (C-2e), 61.1 (C-6e), 66.1 (C-6c), 67.4 (C-2c), 68.1 (C-6f), 68.5 (C-6b), 68.8 (C-6g), 69.1 (C-4f), 69.4 (C-6d), 70.0 (C-6a), 70.5 (C-2g), 73.6 (C-2d), 74.8 (C-5b), 75.2 (C-5a), 75.3 (C-5c), 76.9 (C-4b), 77.2 (C-2f), 78.6 (C-3d), 79.9 (C-3g), 80.7 (C-3b), 81.0 (C-4d), 81.5 (C-3c), 88.7 (C-1a), 99.8 (C-1d), 100.1 (C-1g), 100.3 (C-1b), 100.7 (C-1e), 101.0 (C-1c), 104.3 (C-1f). − MS (FAB, positive mode, $CHCl_3$/NBA + NaI); *m/z*: 2288 $[M - N_2 + Na]^+$, 2315 $[M + Na]^+$, 2465 $[M + NaI + Na]^+$, 2617 $[M + 2NaI + Na]^+$. − $C_{125}H_{146}$, N_6O_{35}·7 H_2O (2418.6): calcd.: C 62.07, H 6.66, N 3.47; found C 62.01, H 673, N 202.

***N*-{(6-*O*-Benzyl-β-D-galactopyranosyl)-(1→4)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-[(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)]-(β-D-mannopyranosyl)-(1→4)−(2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1→4)-(2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)}*N*-benzyloxycarbonyl-L-asparagine Benzyl Ester (39):** To a mixture of **38** (30 mg, 0.013 mmol) and ethyldiisopropylamine (27.7 μL, 0.16 mmol) in dry methanol (1.3 mL), propanedithiol (65.4 μL, 0.65 mmol) was added dropwise under nitrogen and the solution was stirred at room temp. After 4 h [TLC (ethyl acetate/methanol, 3:1): R_f (amine, α) = 0.47; R_f (amine, β) = 0.35], the reaction mixture was concentrated and dried in vacuo to remove the majority of the reagents. The residue (β/α mixture: 95:5) was dissolved in *N*-methylpyrrolidone (200 μL) and treated with a solution of **2**[21] (44.2 mg, 0.08 mmol), ethyldiisopropylamine (27.2 μL, 0.15 mmol), and *N*-hydroxybenzotriazole (9.8 mg, 0.07 mmol) in *N*-methylpyrrolidone (300 μL). The mixture was stirred under nitrogen at room temp. After 5 h, the solvent was evaporated in vacuo and the residue was purified by LH-20 sephadex gel filtration chromatography (chloroform/methanol, 1:1; flow rate: 1mL/min). The fractions containing the compound were concentrated in vacuo and the residue was lyophilized from dioxane to afford **39** (19.6 mg, 58%) as a white powder. − TLC (ethyl acetate): R_f = 0.40. − $[\alpha]_D^{20}$ = −12.4 (*c* = 1.0, MeOH). − ^{1}H NMR (600 MHz, MeOD/$CDCl_3$, 1:1): δ = 1.73 (s, 3 H, NHAc), 1.79 (s, 3 H, NHAc), 1.90 (s, 3 H, NHAc), 2.73−2.75 (m, 2 H, βCH_a Asn, βCH_b Asn), 3.15−3.17 (m, 2 H, 5b-H, 5c-H), 3.40−3.41 (m, 2 H, 5a-H, 3c-H), 3.51−4.16 (m, 37 H, 2a-H, 3a-H, 4a-H, 6a-H, 6′a-H, 2b-H, 3b-H, 4b-H, 6b-H, 6′b-H, 2c-H, 4c-H, 6c-H, 6′c-H, 3d-H, 4d-H, 5d-H, 6d-H, 6′d-H, 2e-H, 3e-H, 4e-H, 5e-H, 6e-H, 6′e-H, 2f-H, 3f-H, 4f-H, 5f-H, 6f-H, 6′f-H, 2g-H, 3g-H, 4g-H, 5g-H, 6g-H, 6′g-H), 4.28 (d, $^3J_{2,1}$ < 1.0 Hz, 1 H, 2d-H), 4.38−4.45 [m, 9 H, 3 CH_2Ph, C*H*Ph, H,H-COSY: 4.39 (d, $^3J_{1,2}$ = 7.8 Hz, 1f-H), 4.41 (d, ^2J = 13.0 Hz, C*H*Ph)], 4.48−4.64 [m, 13 H, CH_2Ph, H,H-COSY: 4.48 (d, ^2J = 11.8 Hz, C*H*Ph), 4.53 (d, ^2J = 13.0 Hz, C*H*Ph), 4.57 (d, ^2J = 12.5 Hz, C*H*Ph), 4.59 (d, $^3J_{1,2}$ = 8.5 Hz, 1e-H), 4.63 (d, $^3J_{1,2}$ < 1.0 Hz, 1c-H), 4.64 (dd, $J_{\alpha,\beta a}$ = 7.2 Hz, $J_{\alpha,\beta b}$ = 4.5 Hz, αCH Asn), 4.67 (d, $^3J_{1,2}$ = 7.8 Hz, 1b-H)], 4.77 (d, ^2J = 11.2 Hz, 1 H, CHPh), 4.82 (d, ^2J = 12.2 Hz, 1 H, C*H*Ph), 4.83 (s, 1 H, 1g-H), 4.88 (d, $^3J_{1,2}$ = 9.4 Hz, 1 H, 1a-H), 4.99 (d, ^2J = 12.2 Hz, 1 H, C*H*Ph), 5.04 (d, ^2J = 11.9 Hz, 1 H, C*H*Ph), 5.05 (d, $^3J_{1,2}$ < 1.0 Hz, 1 H, 1d-H), 5.06 (d, ^2J = 11.9 Hz, 1 H, C*H*Ph Asn), 5.07 (d, ^2J = 8.9 Hz, 1 H, C*H*Ph Asn), 5.09 (d, ^2J = 8.9 Hz, 1 H, C*H*Ph Asn), 7.13−7.36 (m, 65 H, 13 Ph). − ^{13}C NMR (600 MHz, MeOD/$CDCl_3$, 1:1): δ = 79.1 (C-1a), 100.6 (C-1d, C-1g), 100.4 (C-1b), 100.6 (C-1e), 101.0 (C-1c), 104.6 (C-1f). − $C_{144}H_{165}N_5O_{40}$ (2605.9): MS (FAB, positive mode, $CHCl_3$/NBA + NaI); *m/z*: 2629 $[M + Na]^+$, 2643 $[M + K]^+$. MS (MALDI, positive mode, matrix: DHB); *m/z*: 2629 $[M + Na]^+$.

***N*-{(β-D-Galactopyranosyl)-(1→4)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-(α-D-mannopyranosyl)-(1→3)-[(α-D-mannopyranosyl)-(1→6)]-(β-D-mannopyranosyl)-(1→4)−(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→4)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)}L-asparagine (1):** To a solution of compound **39** (6 mg, 2.3 μmol) in a mixture of methanol/water (5:1, 1.2 mL) was added palladium hydroxide (3 mg) and the suspension was vigorously stirred under hydrogen at room temp. After 5 h, the mixture was filtered and the filtrate concentrated in vacuo. The residue was purified by P4 gel filtration chromatography (column: Pharmacia 16 mm × 40 cm; mobile phase: 0.03% NH_4HCO_3; flow rate: 1mL/min) and lyophilized from water to give the final compound **40** (2 mg, 65%) as a white powder. − TLC (*i*PrOH/NH_4OAc, 2:1): R_f = 0.15. − ^{1}H NMR (250 MHz, D_2O): δ = 1.81 (s, 3 H, NHAc), 1.91 (s, 6 H, 2 NHAc), 2.68 (dd, ^2J = 16.8 Hz, $^3J_{vic}$ = 2.5 Hz, 1 H, βCH_a Asn), 2.74 (dd, ^2J = 16.8 Hz, $^3J_{vic}$ = 8.0 Hz, 1 H, βCH_b Asn), 3.28 (m, 37 H), 3.80 (dd, $^3J_{2,3}$ = $^3J_{2,1}$ = 1.3 Hz, 1 H, 2d-H), 4.02 (dd, $^3J_{2,3}$ = 1.7 Hz, $^3J_{2,1}$ < 1.0 Hz, 1 H, 2c-H), 4.11 (d, $^3J_{2,1}$ < 1.0 Hz, 1 H, 2g-H), 4.31 (d, $^3J_{1,2}$ = 7.7 Hz, 1 H, 1f-H), 4.41−4.43 [m, 2 H, H,H-COSY: 4.41 (d, $^3J_{1,2}$ = 7.5 Hz, 1e-H), 4.42 (d, $^3J_{1,2}$ = 8.0 Hz, 1b-H)], 4.58 (d, $^3J_{1,2}$ < 1.0 Hz, 1 H, 1c-H), 4.73 (d, $^3J_{1,2}$ < 1.0 Hz, 1 H, 1g-H), 4.94 (d, $^3J_{1,2}$ = 9.5 Hz, 1 H, 1a-H), 5.01 (d, $^3J_{1,2}$ = 1.3 Hz, 1 H, 1d-H). − $C_{52}H_{87}N_5O_{38}$ (1390.5): MS (MALDI, positive mode, matrix: DHB); *m/z*: 1414 $[M + Na]^+$.

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[1] A. Varki, *Glycobiology* **1993**, *3*, 97−130; R. A. Dwek, *Chem. Rev.* **1996**, *96*, 683−720.
[2] B. G. Davis, *J. Chem. Soc., Perkin Trans. 1* **1999**, 3315−3237; C. D. Warren, H. G. Garg, in *Glycopeptides and Related Compounds* (Eds.: D. G. Large, C. D. Warren), Marcel Dekker Inc., New York, **1997**, pp. 1−22.
[3] E. G. Berger, E. Buddeecke, J. P. Kamerling, A. Kobata, J. C. Paulson, J. F. G. Vliegenthart, *Experientia* **1982**, *38*, 1129−1162; J. Montreuil, *Adv. Carbohydr. Chem. Biochem.* **1981**, *37*, 157−223.
[4] M. Takeuchi, N. Inoue, T. W. Strickland, M. Kobuta, M. Wada, R. Shimizu, S. Hoshi, H. Kozutsumi, H. Takasaki, A. Kobata, *Proc. Natl. Acad. Sci. USA* **1989**, *86*, 7819−7822.
[5] J. Arnarp, M. Haraldsen, J. Lönngren, *J. Chem. Soc., Perkin Trans. 1* **1982**, 18412−1844.
[6] T. Ogawa, M. Sugimoto, T. Kitajima, K. K. Sadozai, T. Nukada, *Tetrahedron Lett.* **1986**, *27*, 5739−5742; Y. Nakahara, S. Shibayama, Y. Nakahara, T. Ogawa, *Carbohydr. Res.* **1996**, *280*, 67−84.
[7] H. Paulsen, *Angew. Chem.* **1990**, *102*, 851−867; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 823−839; H. Paulsen, B. Helpap, *Carbohydr. Res.* **1991**, *216*, 289−313; G. Klich, H. Paulsen, B. Meyer, M. Meldal, K. Bock *Carbohydr. Res.* **1997**, *299*, 33−48.
[8] H. Kunz, W. Günther, *Angew. Chem.* **1988**, K100, 1118−1119, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1086−1087; H. Kunz, M. Schultz, in *Glycopeptides and Related Compounds* (Eds.: D. G. Large, C. D. Warren), Marcel Dekker Inc., New York, **1997**, pp. 23−78.
[9] J. Kerekgyarto, J. P. Kamerling, J. B. Bouwstra, J. F. G. Vliegenthart, A. Liptak, *Carbohydr. Res.* **1989**, *186*, 51−62.
[10] C. Unverzagt, *Angew. Chem.* **1994**, *106*, 1170−1173; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1102−1104.
[11] I. Matsuo, M. Isomura, R. Walton, K. Ajisaka, *Tetrahedron Lett.* **1996**, *37*, 8795−8798; and refences therein.
[12] S. Weiler, R. R. Schmidt, *XVIII Int. Cabohydr. Symp.*, Milano/Italy, July **1996**; Abstract BP 185; S. Weiler, Dissertation, University of Konstanz, **1998**; S. Weiler, R. R. Schmidt, *Tetrahedron Lett.* **1998**, *39*, 2299−2302.
[13] C.-H. Wong, R. L. Halcomb, Y. Ichikawa, T. Kajimoto, *Angew. Chem.* **1995**, *107*, 453−474; 569−593; *Angew. Int. Ed. Engl.* **1995**, *34*, 412−432; 521−546.
[14] C. Unverzagt, H. Kunz, J. C. Paulson, *J. Am. Chem. Soc.* **1990**, *112*, 9308−9309; C. Unverzagt, *Angew. Chem.* **1996**, *108*, 2507−2510; **1997**, *109*, 2078−2081; *Tetrahedron Lett.* **1997**, *38*, 5627−5630.
[15] K. Haneda, T. Inazu, K. Yamamoto, Y. Nakahara, A. Kobata, *Carbohydr. Res.* **1996**, *292*, 61−70; M. Mizuno, K. Haneda, R. Iguchi, I. Muramoto, T. Kawakami, S. Aimoto, K. Yamamoto, T. Inazu, *J. Am. Chem. Soc.* **1999**, *121,* 284−290.
[16] Y. Ichikawa, in *Glycopeptides and Related Compounds* (Eds.: G. D. Large, C. D. Warren), Marcel Dekker Inc., New York, **1997**, pp. 79−205.
[17] R. R. Schmidt, *Angew. Chem.* **1986**, *98*, 213−236; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 212−235; R. R. Schmidt, W. Kinzy, *Adv. Carbohydr. Chem. Biochem.* **1994**, *50*, 21−213.
[18] M. V. Chiesa, Dissertation, University of Konstanz, **2000**.
[19] [19a] M. R. E. Aly, J. C. Castro-Palomino, E. I. Ibrahim, E. H. El-Ashry, R. R. Schmidt, *Eur. J. Org. Chem.* **1998,** 2305−2316. – [19b] M. R. E. Aly, E. I. Ibrahim, E. H. El-Ashry, R. R. Schmidt, *Carbohydr. Res.* **1999**, *316*, 121−132. – [19c] M. R. E. Aly, E. I. Ibrahim, E. H. El-Ashry, R. R. Schmidt, *Eur. J. Org. Chem.* **2000**, 319−326.
[20] H. Kunz, *Angew. Chem.* **1987**, *99*, 297−311; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 294−308; M. Meldal, K. Bock, *Glycoconjugate J.* **1994**, *11*, 59−63.
[21] M. Green, J. Bermann, *Tetrahedron Lett.* **1990**, *31*, 5881−5882.
[22] F. Yamazaki, S. Sato, T. Nukuda, Y. Ito, T. Ogawa, *Carbohydr. Res.* **1990,** *201*, 31−50.
[23] G. Zemplén, *Ber. Dtsch. Chem. Ges.* **1927**, *60*, 1555−1564.
[24] 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**.
[25] C. Unverzagt, H. Kunz, *J. Prakt. Chem.* **1992**, *334*, 570−578.
[26] R. Albert, K. Dax, R. W. Link, A. E. Stütz, *Carbohydr. Res.* **1983**, *118*, C5−C6.
[27] J. Alais, S. David, *Carbohydr. Res.* **1990**, *201*, 69−77; S. David, A. Molleron, C. Dini, *Carbohydr. Res.* **1987**, *165*, C11.
[28] R. W. Binkley, *J. Carbohydr. Chem.* **1994**, *13*, 111−123.
[29] G. Hummel, R. R. Schmidt, *Tetrahedron Lett.* **1998**, *38*, 1173−1176; *Pol. J. Chem.* **1999**, *73*, 941−954 and references therein.
[30] D. R. Williams, S.-Y. Sit, *J. Am. Chem. Soc.* **1984**, *106*, 2949−2954; T. Eisele, R. R. Schmidt, *Liebigs Ann./Receuil* **1997**, 1303−1313.
[31] H. Baylony, D. N. Standring, J. R. Knowles, *Tetrahedron Lett.* **1978**, *18*, 3633−3634.

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