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Synthesis of Multiantennary Complex Type *N*-Glycans by Use of Modular Building Blocks

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In memory of Professor Peter Welzel

Abstract: A modular set of oligosaccharide building blocks was developed for the synthesis of multiantennary *N*-glycans of the complex type, which are commonly found on glycoproteins. The donor building blocks were laid out for the elongation of a core trisaccharide acceptor (β-mannosyl chitobiose) conveniently protected with a single benzylidene moiety at the β-mannoside. Through two consecutive regio- and stereoselective couplings the donors gave *N*-glycans with three to five antennae in high yields. Due to the consistent protection group pattern of the donors the deprotection of the final products can be performed by using a general reaction sequence.

Keywords: carbohydrates · glycoproteins · glycosylation · oligosaccharides · regioselectivity

Introduction

The rapidly growing demand for recombinant therapeutic glycoproteins[1] has improved the analytical tools[2–4] capable of determining the vast number of structures of *N*-glycans present in biological material. At the same time glycobiologists have revealed more details about the interplay of protein *N*-glycosylation[5] with cellular functions. Due to the microheterogeneity of *N*-glycoproteins only a few of these oligosaccharides can be isolated from natural sources[6,7] in more than analytical amounts and thus the biological roles of *N*-glycans remain difficult to elucidate.[8] These circumstances have stimulated the chemical synthesis of *N*-glycans as a method to provide sufficient quantities for biological testing by using classical approaches[9] or miniaturized methods.[10] Seminal work utilizing chemically synthesized multiantennary fragments of *N*-glycans has revealed a multivalency effect for the asialoglycoprotein receptor, which also shows preferences for certain types of branched *N*-glycans.[11] In order to keep up with the growing number of identified *N*-glycans[2] and the demand for *N*-glycans on glycoarrays[12] we have developed a versatile set of building blocks that allow the synthesis of the most frequent core structures of complex type *N*-glycans.[13] Based on the pioneering work of Ogawa[14] and Paulsen[15] we have established a robust and general method for the double regio- and stereoselective glycosylation[16] of differently functionalized core trisaccharides,[17,18] each equipped with a benzylidene protected β-mannose as a key component. After optimizing this approach for biantennary *N*-glycans[19] the building blocks were modified for the convergent synthesis of multiantennary *N*-glycans[20] with up to five branches.[13] Several groups have developed a variety of additional strategies for the chemical synthesis of *N*-glycans, which can be conducted in solution[21–30] or on solid phase.[31–33]

Results and Discussion

Based on the concept of modularizing the building blocks for the antennae of branched *N*-glycans a robust and scalable synthesis for the donors **C**, **D** and **E** was developed (Scheme 1). A seamless compatibility of these branched oligosaccharide donors with the double regio- and stereoselective glycosylation approach for biantennary *N*-glycans was attempted. The flexible use of key intermediates should thus be provided and the chemical synthesis of the most frequent patterns of branched *N*-glycans of the complex type should

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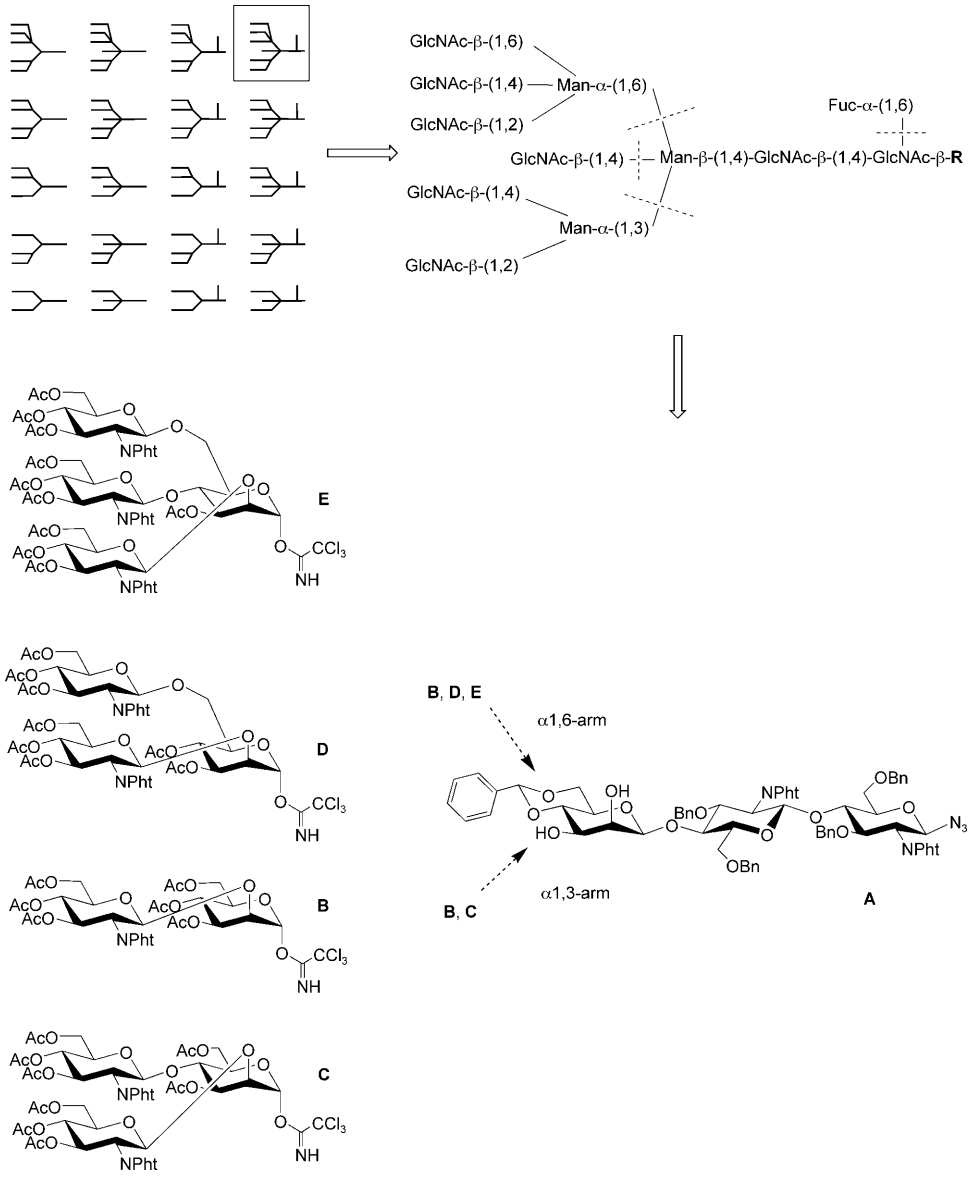


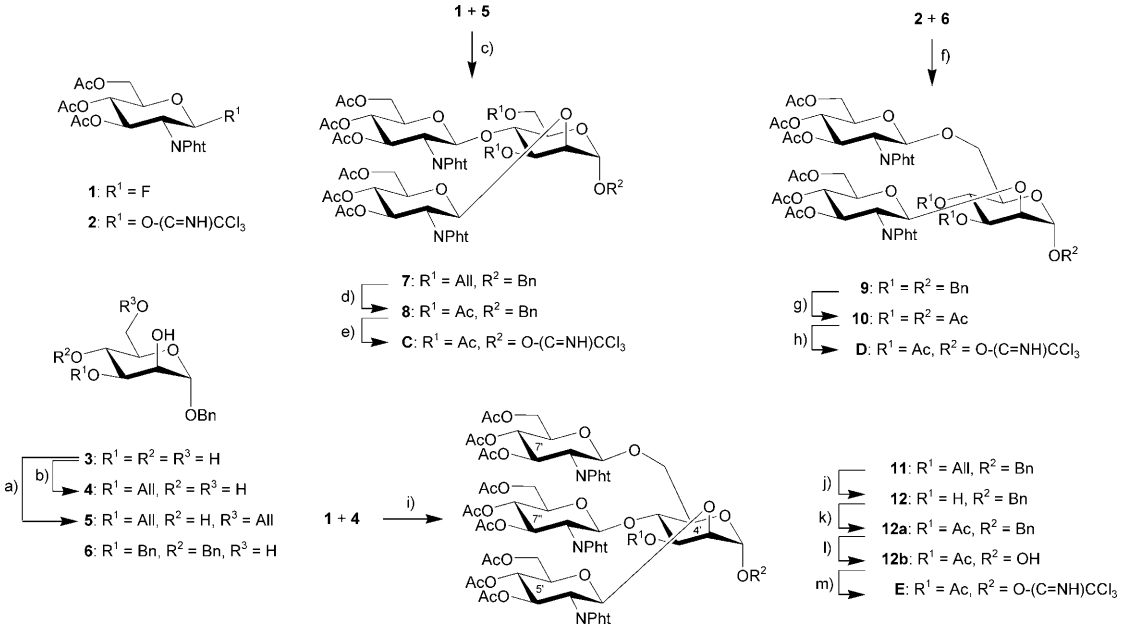
Scheme 1. Flexible chemical synthesis of multiantennary complex type *N*-glycans can be accomplished by using the modular set of oligosaccharide donors **B**–**E**. These building blocks react with the core trisaccharide **A** in a double regio- and stereoselective coupling procedure. The cartoon represents the most frequent complex type *N*-glycans found in vertebrates and a retrosynthetic disconnection of the penta-antennary structure highlighted in a box.

be facilitated. The antennae of these synthetic *N*-glycans generally terminate with GlcNAc residues, which can be liberated by chemical deprotection and elongated by enzymatic glycosylation reactions by using glycosyltransferases.[34] At the reducing end the synthetic *N*-glycans carry an azido group, which allows rapid conjugation to peptides[35] or linkers.[36]

Synthesis of the branched donors C, D and E: When planning the synthesis of the three branched donors **C**, **D** and **E** we aimed on maintaining the favorable reactivity and selectivity found for the elongation of core trisaccharide **A** with donor **B**.[19,37] It was assumed that the desired properties could be transferred to the building blocks **C**, **D** and **E** by adopting the protecting group pattern of **B** and the anomeric activation by using trichloroacetimidates.[38] The general use of acetyl or phthalimido groups in these compounds should ultimately facilitate global deprotection of the final *N*-glycans. Since the regioselective protection required benzyl groups or other ethers in the mannosyl part of the donors, which might lead to β-linked side products in the following glycosylations,[14] these ethers were generally replaced by acetates in the donors **C**, **D** and **E** (Scheme 1).

The synthesis of the 2,4-branched donor **C** commenced with the diallylated acceptor **5** (Scheme 2), which was initially obtained by regioselective tributylstannylation as described.[39] However, due to the large number of side products and the toxic properties of the volatile reagent bistributyltin oxide an alternative procedure was sought. A solution was found in a synthesis through dibutylstannylene acetals[40] and by employing the far less toxic polymeric dibutyltin oxide in conjunction with CsF,[41] which increases the yield in the subsequent alkylation step. This approach showed the desired 3,6-regioselectivity and furnished the diallylated mannoside **5** in 58% yield. A first attempt to glycosylate the acceptor **5** by using the trichloroacetimidate **2**[38] under activation with $BF_3{\cdot}OEt_2$ gave the trisaccharide **7** in 35% yield whereas activation with TMS-triflate at −40°C raised the yield to 75%. A further increase was achieved with the β-fluoride **1**[42] to give the trisaccharide **7** in 81% yield.

Subsequently, trisaccharide **7** was deallylated with $PdCl_2$ in acetic acid at 70°C. When attempting to acetylate the intermediate 3,6-diol with a 2:1 mixture of pyridine and acetic anhydride, it was found that only the primary OH-6 reacted, even when higher temperatures (80°C) were applied. However, after adding DMAP[43] the very unreactive OH-3 group was slowly acetylated. The resulting trisaccharide **8**



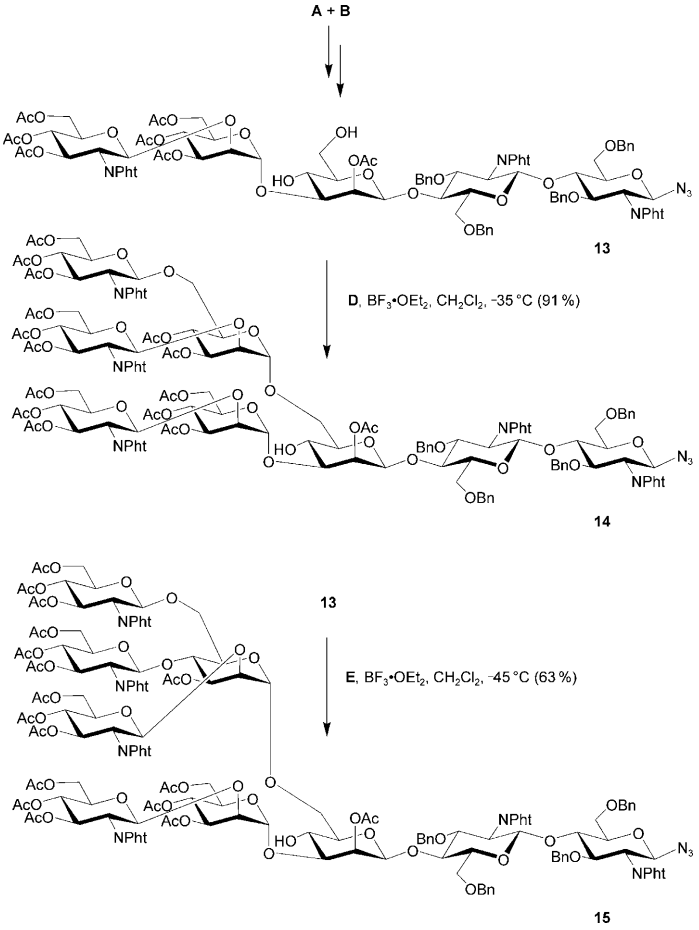
Scheme 2. a) 1) Bu_2SnO, MeOH; 2) AllBr, CsF, DMF; 1)–2) 58%; b) 1) Bu_2SnO, MeOH; 2) AllBr, CsF, DMF; 1)–2) 69%; c) **1+5**, $BF_3{\cdot}OEt_2$, CH_2Cl_2, 81%; d) 1) AcOH (95%), $PdCl_2$, NaOAc, 70°C; 2) Ac_2O, pyridine, DMAP; 1)–2) 71%; e) 1) Pd/C, MeOH, AcOH; 2) trichloroacetonitrile, DBU, CH_2Cl_2; 1)–2) 80%; f) **2+6**, $BF_3{\cdot}OEt_2$, CH_2Cl_2, −20°C, 53%; g) 1) Pd/C, MeOH, AcOH; 2) Ac_2O, pyridine; 1)–2) 70%; h) 1) hydrazine acetate, DMF; 2) trichloroacetonitrile, DBU, CH_2Cl_2; 1)–2) 68%; i) **1+4**, $BF_3{\cdot}OEt_2$, CH_2Cl_2, −10°C, 89%; j) $PdCl_2$, MeOH, 77%; k) Ac_2O, pyridine, DMAP, 81%; l) PdO/H_2O, MeOH, AcOH, 82%; m) trichloroacetonitrile, DBU, CH_2Cl_2, 85%.

was debenzylated by catalytic hydrogenation, which gave higher yields than the procedure with anhydrous $FeCl_3$.[44] Finally, the hemiacetal was converted to the imidate and trisaccharide donor **C** was isolated in 80% yield over two steps.

The synthesis of the 2,6-branched donor **D** was carried out in analogy to the route described by Arnarp et al. by using the benzylated acceptor **6**.[45] Surprisingly, when attempting the double glycosylation of **6** with the fluoride **1** about 10–20% of an α configured side product were obtained, which could not be separated by flash chromatography. However, coupling of the trichloroacetimidate **2** by using borontrifluoride etherate at −20°C gave the desired trisaccharide **9** in 53% yield without this side reaction. On a small scale the yield was raised to 60% by keeping the reaction temperature between −40 and −50°C. The trisaccharide **9** was debenzylated by catalytic hydrogenation and acetylated. Acetate **10** was selectively deprotected at the reducing end and converted to the trisaccharide imidate **D**.

For tetrasaccharide donor **E** the 3-*O*-allylated benzylmannoside **4** was chosen as an acceptor. Compound **4** can be isolated as a side product (23%) in the improved synthesis of **5** as shown above. By modifying the procedure this approach might also be useful to obtain **4** as the major product. This was achieved by selectively activating **3**[46] by using only one equivalent of dibutyltin oxide[47] followed by addition of allylbromide and CsF in DMF, which resulted in a yield of 69% of the 3-*O*-monoallylated acceptor **4**. A threefold glycosylation of the triol **4** was attempted by treatment with the fluoride donor **1**. After optimizing the conditions it was found that the use of six equivalents of the donor **1** at −10°C gave the tetrasaccharide **11** in 89% yield. Removal of the allyl group was either carried out by using $PdCl_2$ in the presence of NaOAc in acetic acid (73% yield) or in anhydrous methanol at ambient temperature (77% yield) to furnish compound **12**. The latter conditions appear more robust and less prone to side reactions. In analogy to the synthesis of **8**, the tetrasaccharide **12** also required the addition of DMAP to achieve complete acetylation; this indicates a similarly low accessibility of OH-3. The fully protected compound **12a** was debenzylated and the resulting hemiacetal was converted to the tetrasaccharide imidate **E**.

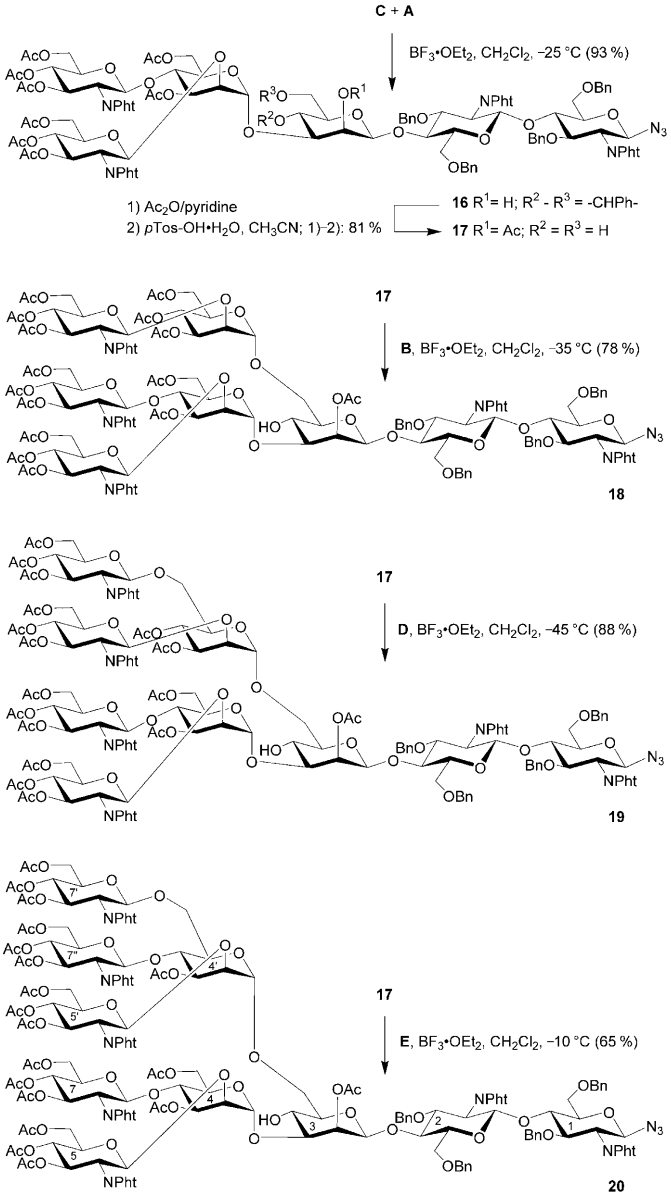
Regioselective glycosylations leading to *N*-glycans: With the donors **C**, **D** and **E** in hand the glycosylation of the core trisaccharide **A** and its coupling products was investigated. Starting with the building blocks **A** and **B** the pentasaccharide diol **13** was obtained after $BF_3{\cdot}OEt_2$ mediated coupling followed by acetylation and removal of the benzylidene acetal.[19,48] Acceptor **13** was employed in a coupling reaction with the branched donor **D** (Scheme 3). As desired a regio- and stereoselective glycosylation occurred at the primary OH-6^3 to furnish the triantennary octasaccharide *N*-glycan **14** in 91% yield. The initially reported yield[20] of 76% was improved by increasing the concentration and raising the starting temperature. Double glycosylation[19] was not found under these conditions. The resulting downfield shift for the ^{13}C NMR signal of C-6^3 (60.4 ppm for **13** vs. 66.3 ppm for **14**) indicated glycosylation at OH-6^3. The newly formed α-mannosidic linkage was confirmed after determination of $J_{C\text{-}1,H\text{-}1}$ for C-$1^{4'}$ with a value of 176.2 Hz, which is typical for α-mannosides.



Scheme 3. The linear pentasaccharide acceptor **13** can be converted to tri- or tetra-antennary *N*-glycans by regioselective coupling with donors **D** or **E**.

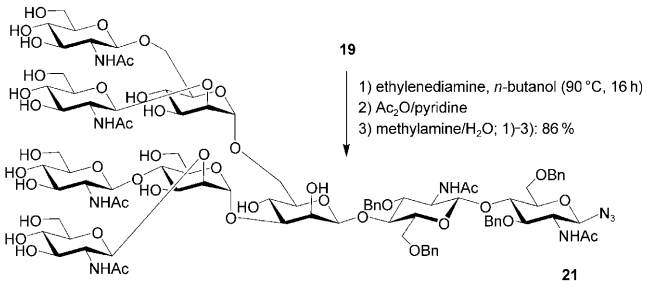
We were pleased to see that even the bulky 2,4,6-substituted tetrasaccharide donor **E** reacted with the pentasaccharide acceptor **13** selectively to give the tetra-antennary nonasaccharide **15** in 63% yield under nonoptimized conditions.

The incorporation of a branched α1,3-arm was achieved by treating donor **C** with the core trisaccharide **A** (Scheme 4). This glycosylation also proceeded regio- and stereoselectively ($J_{C\text{-}1,H\text{-}1}=172.7$ Hz for C-1[4]) and gave hexasaccharide **16** in high yield (93%). After acetylation of the OH-2[3] group the product was debenzylidenated to give hexasaccharide diol **17** in 81% over two steps. It is worth mentioning that the debenzylidenation reaction leading to the branched hexasaccharide **17** should be conducted under less acidic conditions compared to the analogous procedure for the linear derivative **13**, otherwise an unwanted deacetylation occurs. Glycosylation of **17** was investigated with the three donors **B**, **D** and **E**. Selective coupling of the linear donor **B** with the branched hexasaccharide diol **17** gave the desired α1,6-linked octasaccharide **18** in 78% yield. When using the branched donor **D** the tetra-antennary nonasaccharide **19** was obtained in similar yield (88%). Regio- and stereoselectivity were excellent in both cases and no signs of steric hindrance were found in these couplings. However, when using the tribranched donor **E** the initial yields of **20** were quite low (≈30%). Thus, the conditions were systematically optimized and it was found that higher yields could be obtained by increasing the amounts of donor **E** and activator (BF_3). The reaction showed temperature dependency with an optimum at −10 °C, which provided the penta-antennary decasaccharide **20** in 65% yield. Relative to the less branched donors **B** and **D** the tetrasaccharide donor **E** gave lower yields in the coupling with the hexasaccharide acceptor **17** even after optimization. This indicates steric hindrance for donor **E** due to the high degree of branching in conjunction with the three sterically demanding peripheral phthalimido groups.[13]



Scheme 4. The branched hexasaccharide intermediate **17** can be converted to tri-, tetra- or penta-antennary *N*-glycans by regioselective coupling with donors **B**, **D** or **E**.

Deprotection of the synthetic multiantennary *N*-glycans is achieved readily in a one-pot procedure.[34,48] Concomitant deacetylation and dephthaloylation can be carried out by heating the protected *N*-glycans with ethylenediamine in *n*-butanol.[49] Under these conditions the anomeric azide remains unaffected. Global acetylation and O-deacetylation by using aqueous methylamine gives the deprotected *N*-glycans. For the tetra-antennary nonasaccharide **19** this three-step procedure was conducted in a one-pot manner followed by a simple workup by using solid phase extraction on a C18 SepPak (Waters) cartridge to furnish compound **21** in 86% yield (Scheme 5). The selective removal of benzyl groups in the presence of an anomeric azide is not straightforward. Preferably after reduction of the anomeric azide to an amine a spacer is attached and the benzyl groups can be removed subsequently by catalytic hydrogenation. The *N*-glycan spacer conjugates thus obtained, were used as acceptors for enzymatic elongation and for the synthesis of neoglycoproteins.[34]



Scheme 5. One-pot deprotection of the tetra-antennary *N*-glycan **19**.

Conclusions

In summary we have developed a modular set of building blocks that can be used in a generally applicable double regio- and stereoselective glycosylation approach for multiantennary *N*-glycans from two to five antennae. The yields of the convergent glycosylation reactions were high and in all cases only the formation of desired stereo- and regioisomers was found. In the case of the tri- and tetra-antennary products the glycosylation reactions were free of steric hindrance. This demonstrates a high compatibility of the donors with the corresponding acceptors. These donors were successfully applied in the synthesis of other multiantennary *N*-glycans bearing additional core substituents.[13,50] After one-pot deprotection the *N*-glycans can be further modified and incorporated into neoglycoproteins.[39]

Experimental Section

General methods: Solvents were dried according to standard methods. Molecular sieves were activated prior to use by being heated under high vacuum. Optical rotations were measured on a Perkin–Elmer 241 polarimeter at 589 nm. NMR spectra were recorded on Bruker AC 250, Avance 360, AMX 500 and DMX 500 instruments. Coupling constants are reported in Hz. For mass spectra a Varian CH5 instrument was used in the fast atom bombardment mode (FAB) with an *m*-nitrobenzylalcohol matrix (NBA). ESI-TOF mass spectra were recorded on a Micromass LCT instrument coupled to an Agilent 1100 HPLC. Flash chromatography was performed on silica gel 60 (230–400 mesh; Merck, Darmstadt, Germany). The reactions were monitored by thin layer chromatography on coated aluminum plates (silica gel 60 GF_{254}; Merck, Darmstadt, Germany). Spots were detected by UV-light or by charring with a 1:1 mixture of H_2SO_4 (2N) and resorcine monomethylether (0.2%) in ethanol.

Benzyl 3-*O*-allyl-α-D-mannopyranoside (4) A mixture of benzylmannoside **3** (200 mg, 0.74 mmol) and dibutyltin oxide (184 mg, 0.74 mmol) was stirred under reflux in absolute methanol (4 mL) for 4 h resulting in a clear solution. The solvent was evaporated in vacuo followed by addition of caesium fluoride (169 mg, 1.3 mmol) to the solid remainder, which was dried under high vacuum for 16 h. The mixture was suspended in dry dimethylformamide (1 mL) and allyl bromide (0.33 mL, 3.75 mmol) was added at 0°C and the solution was vigorously stirred at room temperature for 22 h. The reaction was quenched by addition of ethyl acetate (2.4 mL) and water (40 μL). After filtration over Celite the solution was concentrated in vacuo and purified by flash chromatography (hexane/acetone, 1.5:1) to afford **4** (158 mg, 68.8%); $R_f = 0.10$ (hexane/acetone 1.2:1); $[\alpha]_D^{23} = +108.0$ ($c = 0.8$, CH_2Cl_2); ^{1}H NMR (360 MHz, [D$_6$]DMSO): $\delta = 7.47$–7.20 (m, 5H, Ph), 5.90 (m, 1H, =CH−), 5.28 (dd, $J_{trans} = 17.4$ Hz, $J_{gem} = 1.8$ Hz, 1H, H_2C=*trans*), 5.09 (dd, $J_{cis} = 10.4$ Hz, $J_{gem} = 1.6$ Hz, 1H, H_2C=*cis*), 4.91 (d, $J_{OH,4} = 6.1$ Hz, 1H, OH-4), 4.79 (d, $J_{OH,2} = 4.9$ Hz, 1H, OH-2), 4.70 (d, $J_{1,2} = 1.3$ Hz, 1H, H-1), 4.65 (d, $J_{gem} = 11.8$ Hz, 1H, CH_2O-Bn), 4.56 (t, $J_{OH,6} = 6.3$ Hz, 1H, OH-6), 4.42 (d, $J_{gem} = 11.8$ Hz, 1H, CH_2O-Bn), 4.09–4.03 (m, 2H, CH_2O-All), 3.82 (m, $J_{1,2} < 1$ Hz, $J_{2,3} < 1$ Hz, 1H, H-2), 3.86 (m, 1H, H-6a), 3.52–3.33 (m, 4H, H-4, H-6b, H-5, H-3); ^{13}C NMR (90 MHz, [D$_6$]DMSO): $\delta = 137.8$ (C-i Ar), 136.1 (=CH−), 128.3, 127.9, 127.6 (C-Ar), 115.9 (=CH_2), 99.0 (C-1), 79.0 (C-3), 74.4 (C-5), 70.3 (CH_2O-All), 67.5 (CH_2O), 67.1 (C-2), 66.2 (C-4), 61.2 (C-6); ESI-MS: *m/z* calcd for $C_{16}H_{22}O_6$: 310.14; found 333.5 $[M+Na]^+$.

Benzyl 3,6-di-*O*-allyl-α-D-mannopyranoside (5): A mixture of benzylmannoside **3** (12.4 g, 45.9 mmol) and dibutyltin oxide (34.3 g, 137.7 mmol) was stirred under reflux in absolute methanol (300 mL) for 4 h resulting in a clear solution. The solvent was evaporated and dried under high vacuum for 16 h. Cesium fluoride (20.9 g, 137.7 mmol) and dry dimethylformamide (200 mL) were added to the remainder. The suspension was stirred at 0°C for 10 min and allyl bromide (40 mL, 459 mmol) was added and vigorously stirred at room temperature for 4 days. The reaction was quenched by addition of ethyl acetate (480 mL) and water (8 mL). After filtration over Celite the solution was concentrated in vacuo and purified by flash chromatography (cyclohexane/acetone 5:1) to afford **5** (9.3 g, 57.9%). $R_f = 0.65$ (hexane/acetone 1:1).

Benzyl *O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-*O*-[(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)]-3,6-di-*O*-allyl-α-D-mannopyranoside (7): A suspension of acceptor **5** (5.25 g, 15 mmol), fluoride **1** (20.1 g, 46 mmol) and ground molecular sieves 4 Å (21 g) in absolute CH_2Cl_2 (215 mL) was stirred at ambient temperature for 30 min. Boron trifluoride ethyl etherate (1.0 mL, 8 mmol) was added over a period of 5 min. After 3 h (TLC: hexane/acetone 1:2) the mixture was filtered over Celite, washed with CH_2Cl_2 and extracted with dilute $KHCO_3$. The organic phase was dried over $MgSO_4$, concentrated and purified by flash chromatography (hexane/acetone, 1.7:1) to afford **7** (14.3 g, 80.6%); $R_f = 0.32$ (hexane/acetone 2:1); $[\alpha]_D^{23} = +33.8$ ($c = 1$, CH_2Cl_2); ^{1}H NMR (250 MHz, [D$_6$]DMSO): $\delta = 8.0$–7.6 (m, 8H, Pht), 7.35–7.15 (m, 5H, Ar), 6.0–5.84 (m, 1H, =CH−), 5.60 (dd, $J_{2,3} = 10.8$ Hz, $J_{3,4} = 9.2$ Hz, 1H, H-3′), 5.57 (dd, $J_{2,3} = 10.6$ Hz, $J_{3,4} = 9.2$ Hz, 1H, H-3″), 5.50 (d, $J_{1,2} = 8.5$ Hz, 1H, H-1″), 5.45 (d, $J_{1,2} = 8.5$ Hz, 1H, H-1′), 5.22 (m, 1H, H_2C=*trans*), 5.17–5.07 (m, 2H, =CH−, H_2C=*cis*), 5.01 (dd, $J_{4,5} = 8.5$ Hz, 1H, H-4′), 4.97 (dd, $J_{4,5} = 8.6$ Hz, 1H, H-4″), 4.81 (m, 1H, H_2C=*cis*), 4.67 (m, 1H, H_2C=*trans*), 4.52 (d, $J_{1,2} = 1.7$ Hz, 1H, H-1), 4.38 (d, $J_{gem} = 11.6$ Hz, 1H, CH_2O), 4.26–3.85 (m, 12H, CH_2O, H-2, H-2′, H-2″, H-5′, H-5″, H-6a,b′, H-6a,b″), 3.61 (dd, $J_{2,3} = 3.2$ Hz, $J_{3,4} = 7.9$ Hz, 1H, H-3), 3.34 (m, 1H, H-4), 3.26 (m, 1H, H-5), 2.91 (m, 2H, CH_2O), 2.80 (dd, $J_{gem} = 10.7$ Hz, $J_{vic} < 1.0$ Hz, 1H, H-6a), 2.49 (m, 1H, H-6b), 2.09,

2.04, 2.00, 1.99, 1.79, 1.76 (6s, 18H, OAc); ^{13}C NMR (62.5 MHz, [D$_6$]DMSO): δ = 169.9, 169.5, 169.2, 167.3 (C=O), 136.8 (C-i Ar), 135.5 (=CH−), 134.9 (C-4/5 Pht), 134.2 (=CH−), 130.6 (C-1/2 Pht), 128.2, 127.8, 127.6 (C-Ar), 123.5 (C-3/6 Pht), 116.2, 115.7 (CH_2=), 97.2 (C-1″), 96.0 (C-1), 95.8 (C-1′), 75.6 (C-3), 74.1 (C-4), 72.4 (C-2), 70.8 (C-5′, C-5″), 70.4 (CH_2O-All), 69.9 (C-5, C-3′, C-3″), 68.8 (CH_2O-All), 68.6 (CH_2O-Bn, C-4′), 68.2 (C-4″), 67.7 (C-6), 61.8 (C-6′), 61.5 (C-6″), 54.7 (C-2″), 53.8 (C-2′), 20.3, 20.03, 19.95 (OAc); FAB-MS (NBA): *m/z* calcd for $C_{59}H_{64}N_2O_{24}$: 1184.4; found 1191.4 $[M+Li]^+$, 1207.6 $[M+Na]^+$; elemental analysis calcd (%) for $C_{59}H_{64}N_2O_{24}$ (1185.15): C 59.79, H 5.44, N 2.36; found: C 59.79, H 5.44, N 2.36.

Benzyl *O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-*O*-[(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)]-3,6-di-*O*-acetyl-α-D-mannopyranoside (8): Palladium chloride (2.8 g, 15.8 mmol) and sodium acetate (2.8 g, 34 mmol) were added to a solution of trisaccharide **7** (8.0 g, 6.75 mmol) in acetic acid (530 mL, 95%). The reaction was stirred for 2.5 h at 70 °C. Subsequently, the precipitate was filtered off and the solvents were removed on a rotary evaporator. The remainder was dissolved in CH_2Cl_2 (300 mL) and extracted with water (2×) and dilute $KHCO_3$. The organic phase was dried over $MgSO_4$ and concentrated. Pyridine (50 mL), acetic anhydride (25 mL) and *p*-dimethylaminopyridine (DMAP, 1 g) were added to the residue. After 24 h the mixture was concentrated, dissolved in CH_2Cl_2 (300 mL) and extracted with dilute HCl (3×) and dilute $KHCO_3$. The organic phase was dried over $MgSO_4$, concentrated and purified by flash chromatography (hexane/ethyl acetate 1:2) to afford **8** (5.73 g, 71.4%). R_f diol = 0.21 (hexane/acetone 1:1); R_f acetate = 0.30 (hexane/acetone 1:1); $[\alpha]_D^{23}$ = +15.6 (c = 1, CH_2Cl_2); ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 7.95–7.63 (m, 8H, Pht), 7.35–7.15 (m, 5H, Ar), 5.63 (dd, $J_{2,3}$ = 10.5 Hz, 1H, H-3″), 5.60 (dd, $J_{2,3}$ = 10.8 Hz, 1H, H-3′), 5.40 (d, $J_{1,2}$ = 8.4 Hz, 1H, H-1″), 5.35 (d, $J_{1,2}$ = 8.5 Hz, 1H, H-1′), 4.98 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, 1H, H-4′), 4.96 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, 1H, H-4″), 4.81 (dd, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 9.3 Hz, 1H, H-3), 4.37 (d, J_{gem} = 11.4 Hz, 1H, CH_2O), 4.33 (d, $J_{1,2}$ < 1.0 Hz, 1H, H-1), 4.24–4.18 (m, 3H, CH_2O, H-6a′, H-6a″), 4.08–4.03 (m, 3H, H-2, H-2′, H-5″), 4.0–3.94 (m, 3H, H-2″, H-5′, H-6b′), 3.84 (dd, J_{gem} = 10.8 Hz, J_{vic} < 1.0 Hz, 1H, H-6b″), 3.69–3.62 (m, 2H, H-4, H-6a), 3.41 (m, 1H, H-5), 3.06 (dd, J_{gem} = 11.8 Hz, J_{vic} = 3.7 Hz, 1H, H-6b), 2.04, 2.02, 2.00, 1.98, 1.97, 1.77, 1.73, 1.48 (8s, 24H, OAc); ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 170.0, 169.5, 169.2, 169.0, 167.2 (C=O), 136.6 (C-i Ar), 135.1, 134.8 (C-4/5 Pht), 130.4 (C-1/2 Pht), 123.7, 123.3 (C-3/6 Pht), 96.77 (C-1″), 96.42 (C-1′), 96.35 (C-1), 73.6 (C-2), 72.3 (C-4), 70.8 (C-5′), 70.6 (C-5″), 70.4 (C-3), 69.8 (C-3′), 69.7 (C-3″), 69.0 (CH_2O), 68.6 (C-4′), 68.2 (C-4″), 67.5 (C-5), 61.9 (C-6′), 61.7 (C-6″), 61.6 (C-6), 54.6 (C-2″), 53.8 (C-2′), 20.5, 20.41, 20.36, 20.1, 20.0, 19.6 (OAc); ESI-MS: *m/z* calcd for $C_{57}H_{60}N_2O_{28}$: 1188.34; found 1211.81 $[M+Na]^+$; elemental analysis calcd (%) for $C_{57}H_{60}N_2O_{28}$ (1189.1): C 57.58, H 5.09, N 2.36; found: C 57.37, H 5.13, N 2.13.

***O*-{*O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-*O*-[(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)]-3,6-di-*O*-acetyl-α-D-mannopyranosyl}-trichloroacetimidate (C)**: Trisaccharide **8** (5.3 g, 4.8 mmol) was dissolved in methanol (70 mL). After addition of acetic acid (7 mL) and Pd/C (10%, 5 g) the suspension was stirred under a hydrogen atmosphere. After complete reaction (TLC: hexane/acetone 1:1) the catalyst was filtered off and the solvents were evaporated. The remainder was taken up in CH_2Cl_2 (300 mL), extracted with dilute $KHCO_3$, dried over $MgSO_4$ and concentrated. The hemiacetal was dissolved in absolute CH_2Cl_2 (50 mL) cooled to 0 °C and treated with trichloroacetonitrile (4 mL, 39.9 mmol) and 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU, 280 μL, 1.9 mmol). Upon disappearance of the hemiacetal (TLC: hexane/acetone 1:1) the solution was evaporated and the residue was purified by flash chromatography (hexane/acetone 1:1) to afford **C** (4.76 g, 79.8%). R_f hemiacetal = 0.23 (hexane/acetone 2:1); R_f imidate = 0.31 (hexane/acetone 2:1); $[\alpha]_D^{23}$ = +22.6 (c = 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 9.87 (s, 1H, NH), 7.92–7.68 (m, 8H, Pht), 5.70 (d, $J_{1,2}$ < 1.0 Hz, 1H, H-1), 5.63 (dd, $J_{2,3}$ = 10.7 Hz, 1H, H-3″), 5.61 (dd, $J_{2,3}$ = 10.9 Hz, 1H, H-3′), 5.48 (d, $J_{1,2}$ = 7.7 Hz, 1H, H-1′), 5.46 (d, $J_{1,2}$ = 8.3 Hz, 1H, H-1″), 5.01 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, 1H, H-4′), 4.98 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, 1H, H-4″), 4.94 (dd, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 9.3 Hz, 1H, H-3), 4.3–4.2 (m, 3H, H-2, H-6a′, H-6a″), 4.13–4.08 (m, 2H, H-2′, H-5″), 4.0–3.94 (m, 3H, H-2″, H-5′, H-6b′), 3.84 (dd, J_{gem} = 12.0 Hz, J_{vic} < 1.0 Hz, 1H, H-6b″), 3.79 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, 1H, H-4), 3.72 (dd, J_{gem} = 11.5 Hz, J_{vic} < 1.0 Hz, 1H, H-6a), 3.62 (m, 1H, H-5), 3.16 (m, 1H, H-6b), 2.04, 2.03, 2.00, 1.98, 1.97, 1.77, 1.73, 1.44 (8s, 24H, OAc); ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 170.13, 170.09, 169.7, 169.6, 169.4, 169.2, 168.9, 167.5 (C=O), 156.8 (C=NH), 135.2, 134.9 (C-4/5 Pht), 130.4 (C-1/2 Pht), 123.8, 123.5 (C-3/6 Pht), 96.9 (C-1″), 96.5 (C-1′), 93.5 (C-1), 90.0 (CCl_3), 72.3 (C-2), 71.9 (C-4), 71.0 (C-5′), 70.8 (C-5″), 69.9 (C-3′, C-5), 69.7 (C-3, C-3″), 68.4 (C-4′), 68.3 (C-4″), 61.8 (C-6″), 61.7 (C-6′), 61.2 (C-6), 54.5 (C-2″), 53.8 (C-2′), 20.44, 20.40, 20.1, 20.0, 19.5 (OAc); ESI-MS: *m/z* calcd for $C_{52}H_{54}Cl_3N_3O_{26}$: 1241.21; found 1264.13 $[M+Na]^+$.

Benzyl *O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-*O*-[(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→6)]-3,4-di-*O*-benzyl-α-D-mannopyranoside (9): A suspension of diol **6** (3.68 g, 8.2 mmol), imidate **2** (19.8 g, 34.2 mmol) and ground molecular sieves 4 Å (10 g) in absolute CH_2Cl_2 (150 mL) was stirred for 60 min at −20 °C. Boron trifluoride ethyl etherate (1.0 mL, 8 mmol) was added over 5 min. After 2 h (TLC: hexane/ethyl acetate 1:2) the reaction was quenched with triethylamine (1.0 mL). The solids were filtered over Celite and washed with CH_2Cl_2. The organic phase was washed with dilute $KHCO_3$, dried over $MgSO_4$ and concentrated. The remainder was purified by flash chromatography (hexane/ethyl acetate, 0.75:1) to afford **9** (5.58 g, 53.2%). R_f = 0.45 (hexane/ethyl acetate 1:2); $[\alpha]_D^{23}$ = +5.7 (c = 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 7.9–7.6 (m, 8H, Pht), 7.3–6.95 (m, 15H, Ar), 5.68 (dd, $J_{2,3}$ = 10.3 Hz, 1H, H-3′), 5.61 (dd, $J_{2,3}$ = 10.3 Hz, 1H, H-3″), 5.40 (d, $J_{1,2}$ = 8.5 Hz, 1H, H-1′), 5.01 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.7 Hz, 1H, H-4′), 4.93 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.7 Hz, 1H, H-4″), 4.87 (d, $J_{1,2}$ = 8.3 Hz, 1H, H-1″), 4.55 (d, J_{gem} = 11.4 Hz, 1H, CH_2O), 4.54 (d, J_{gem} = 11.0 Hz, 1H, CH_2O), 4.42 (d, $J_{1,2}$ < 1 Hz, 1H, H-1), 4.33 (d, J_{gem} = 11.3 Hz, 1H, CH_2O), 4.23–4.18 (m, 3H, CH_2O, H-6a′, H-6a″), 4.15–4.07 (m, 3H, H-2, H-2′, H-6b′), 4.03–3.98 (m, 3H, CH_2O, H-5′, H-6b″), 3.94 (dd, 1H, H-2″), 3.85 (m, 1H, H-5″), 3.72 (d, J_{gem} = 11.3 Hz, 1H, CH_2O), 3.55 (m, 2H, H-3, H-6a), 3.28 (m, 1H, H-5), 3.03 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.8 Hz, 1H, H-4), 2.45 (m, 1H, H-6b), 2.01, 2.00, 1.98, 1.95, 1.81, 1.77 (6s, 18H, OAc); ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 170.0, 169.6, 169.3, 167.1 (C=O), 138.1, 137.9, 136.5 (C-i Ar), 134.9 (C-4/5 Pht), 130.4 (C-1/2 Pht), 128.2–127.3 (C-Ar), 123.4 (C-3/6 Pht), 97.6 (C-1″), 95.4 (C-1′), 95.2 (C-1), 77.4 (C-3), 73.8 (C-4, CH_2O), 72.1 (C-2), 71.0 (C-5′), 70.9 (C-5″), 70.5 (C-5), 69.8 (C-3′, C-3″), 69.6 (CH_2O), 69.3 (C-6), 68.6 (C-4′), 68.6 (C-4″), 67.7 (CH_2O), 61.8 (C-6′), 61.6 (C-6″), 54.1 (C-2″), 54.0 (C-2′), 20.44, 20.40, 20.16, 20.06 (OAc); ESI-MS: *m/z* calcd for $C_{67}H_{68}N_2O_{24}$: 1284.42; found 1307.65 $[M+Na]^+$; elemental analysis calcd (%) for $C_{67}H_{68}N_2O_{24}$ (1285.27): C 62.61, H 5.33, N 2.18; found: C 62.69, H 5.40, N 2.01.

Acetyl *O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-*O*-[(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→6)]-3,4-di-*O*-acetyl-α-D-mannopyranose (10): Trisaccharide **9** (4.5 g, 3.5 mmol) was dissolved in methanol (100 mL). After addition of acetic acid (1.0 mL) and Pd/C (10%, 5 g) the mixture was stirred under a hydrogen atmosphere. After complete reaction (TLC: hexane/acetone 1:1) the catalyst was filtered off and the solvents were removed in vacuum. The remainder was treated with pyridine (10 mL) and acetic anhydride (5 mL) and concentrated in vacuum after 2 h. The residue was codistilled with toluene and purified by flash chromatography (hexane/acetone 1:1) to afford **10** (2.78 g, 69.6%). R_f = 0.13 (hexane/acetone 1:1); $[\alpha]_D^{23}$ = −0.4 (c = 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 7.95–7.77 (m, 8H, Pht), 5.64 (dd, $J_{2,3}$ = 10.5 Hz, 1H, H-3′), 5.50–5.46 (m, 2H, H-1, H-3″), 5.42 (d, $J_{1,2}$ = 8.5 Hz, 1H, H-1′), 5.06 (d, $J_{1,2}$ = 8.5 Hz, 1H, H-1″), 4.99 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, 1H, H-4′), 4.91 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.7 Hz, 1H, H-4″), 4.77 (dd, $J_{2,3}$ = 2.9 Hz, $J_{3,4}$ = 9.8 Hz, 1H, H-3), 4.68 (dd, $J_{4,5}$ = 10.0 Hz, 1H, H-4), 4.22–4.17 (m, 2H, H-6a′, H-6a″), 4.13–4.08 (m, 2H, H-2, H-2′), 4.00–3.96 (m, 3H, H-5′, H-6b′, H-6b″), 3.89 (dd, $J_{2,3}$ = 10.4 Hz, 1H, H-2″), 3.83 (m, 1H, H-5″), 3.58 (m, 1H, H-5), 3.40 (dd, J_{gem} = 10.1 Hz, J_{vic} < 1.0 Hz, 1H, H-6a), 2.91 (dd, J_{vic} = 5.9 Hz, 1H, H-6b), 2.05, 2.00, 1.98, 1.89, 1.88, 1.82, 1.80, 1.77 (8s, 27H, OAc); ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 170.0, 169.6, 169.3, 169.2, 168.9, 167.8, 167.1 (C=O), 134.8 (C-4/5 Pht), 130.7 (C-1/2 Pht), 123.6 (C-3/6 Pht), 97.6 (C-1″), 95.9 (C-1′), 89.8 ($J_{C\text{-}1,H\text{-}1}$ = 177.6 Hz from a coupled HMQC spectrum, C-1α), 72.4 (C-2), 71.02 (C-5′), 70.95 (C-5″), 70.90 (C-5), 70.1 (C-3″), 69.8 (C-3′), 69.0 (C-3), 68.6 (C-4′), 68.4 (C-4″, C-6), 61.6 (C-6′, C-6″), 53.8 (C-

2′, C-2″), 20.5, 20.4, 20.3, 20.1, 20.0 (OAc); elemental analysis calcd (%) for $C_{52}H_{56}N_2O_{27}$ (1141.01): C 54.74, H 4.95, N 2.46; found: C 54.47, H 5.04, N 2.49.

O-{O-(3,4,6-Tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-O-[(3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→6)]-3,4-di-O-acetyl-α-D-mannopyranosyl}-trichloroacetimidate (D): Hydrazine acetate (400 mg) was added to a solution of trisaccharide **10** (2.61 g, 2.29 mmol) in DMF (10 mL). After complete reaction (TLC: hexane/acetone 1:1) acetone (2 mL) was added and the volatiles were distilled off. The remainder was taken up in CH_2Cl_2 (200 mL) and washed with dilute HCl and $KHCO_3$. The organic phase was dried over $MgSO_4$ and concentrated. Subsequently, the hemiacetal was dissolved in absolute CH_2Cl_2 (20 mL) and trichloroacetonitrile (3 mL, 29.9 mmol) and DBU (150 μL, 1 mmol) were added at 0 °C. After complete reaction (TLC: hexane/acetone 1:1) the mixture was concentrated and purified by flash chromatography (hexane/acetone 1:1) to afford **D** (1.94 g, 68.2 %). R_f hemiacetal = 0.27 (hexane/acetone 1:1); R_f imidate = 0.35 (hexane/acetone 1:1); $[\alpha]_D^{23} = -8.9$ ($c = 1$, methanol); ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 9.5$ (s, 1H, NH), 7.97–7.77 (m, 8H, Pht), 5.71 (d, $J_{1,2} <$ 1.0 Hz, 1H, H-1), 5.65 (dd, $J_{2,3} = 10.7$ Hz, $J_{3,4} = 9.2$ Hz, 1H, H-3′), 5.46 (m, 2H, H-1′, H-3″), 5.42 (d, $J_{1,2} = 8.5$ Hz, 1H, H-1′), 5.01 (m, 2H, H-1″, H-4′), 4.90 (dd, $J_{3,4} = J_{4,5} = 9.6$ Hz, 1H, H-4″), 4.84 (dd, $J_{2,3} = 2.9$ Hz, $J_{3,4} =$ 10.1 Hz, 1H, H-3), 4.75 (dd, $J_{4,5} = 9.9$ Hz, 1H, H-4), 4.23 (m, 1H, H-2), 4.22–4.17 (m, 2H, H-6a′, H-6a″), 4.13 (dd, 1H, H-2′), 4.04–3.95 (m, 3H, H-5′, H-6b′, H-6b″), 3.87 (dd, $J_{1,2} = 8.6$ Hz, $J_{2,3} = 10.2$ Hz, 1H, H-2″), 3.81 (m, 1H, H-5″), 3.63 (m, 1H, H-5), 3.43 (dd, $J_{gem} = 11.3$ Hz, $J_{vic} = 2.1$ Hz, 1H, H-6a), 2.88 (dd, $J_{vic} = 6.3$ Hz, 1H, H-6b), 2.04, 2.00, 1.98, 1.89, 1.87, 1.80, 1.76 (7s, 24H, OAc); ^{13}C NMR (125 MHz, [D$_6$]DMSO): $\delta = 170.0$, 169.6, 169.24, 169.17, 169.1, 166.9 (C=O), 156.6 (C=NH), 134.8 (C-4/5) Pht, 130.6 (C-1/2) Pht, 123.5 (C-3/6) Pht, 97.8 (C-1″), 95.9 (C-1′), 93.2 (C-1), 89.8 (CCl_3), 71.7 (C-2), 71.5 (C-5), 71.0 (C-5′), 70.9 (C-5″), 70.0 (C-3″), 69.7 (C-3′), 68.8 (C-6), 68.7 (C-3), 68.5 (C-4′), 68.4 (C-4″), 61.6 (C-6′, C-6″), 53.7 (C-2′), 53.6 (C-2″), 20.4, 20.3, 20.23, 20.16, 20.08, 19.98 (OAc); elemental analysis calcd (%) for $C_{52}H_{54}Cl_3N_3O_{26}$ (1243.36): C 50.23, H 4.38, N 3.38; found: C 49.86, H 4.38, N 3.46.

Benzyl O-[(3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)]-O-[(3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)]-O-[(3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→6)]-3-O-allyl-α-D-mannopyranoside (11): A suspension of triol **4** (118 mg, 0.38 mmol), fluoride **1** (1.0 g, 2.29 mmol) and ground molecular sieves 4 Å (1.2 g) in absolute CH_2Cl_2 (2.4 mL) was stirred at ambient temperature and at −10 °C for 30 min at each temperature. Boron trifluoride ethyl etherate (48 μL, 0.38 mmol, 1.0 equiv) was added over 5 min. After 4.5 h at −10 °C (TLC: hexane/ethyl acetate 1:2) the reaction was diluted with CH_2Cl_2 and the solids were filtered over Celite. The organic phase was extracted with dilute $KHCO_3$, dried over $MgSO_4$ and concentrated. The remainder was purified by flash chromatography (hexane/acetone, 1.5:1) to afford **11** (529 mg, 88.8 %). $R_f = 0.20$ (hexane/acetone, 1.2:1); $[\alpha]_D^{23} = -83.7$ ($c = 0.5$, CH_2Cl_2); ^{1}H NMR (360 MHz, [D$_6$]DMSO): $\delta = 8.10$–6.90 (m, 17H, Pht, Ar), 5.81 (m, 1H, =CH−), 5.65–5.45 (m, 3H, H-3^5, H-3$^{7''}$, H-3^7), 5.40 (d, $J_{1,2} = 8.4$ Hz, 1H, H-1$^{7''}$), 5.30 (d, $J_{1,2} = 8.4$ Hz, 1H, H-1^5), 5.11 (m, 1H, =CH$_2$ *trans*), 5.04–4.91 (m, 3H, H-4^5, H-4$^{7''}$, =CH$_2$ *trans*), 4.85 (dd, $J_{3,4} = 9.6$ Hz, $J_{4,5} = 10.4$ Hz, 1H, H-4^7), 4.67 (d, $J_{1,2} = 5.7$ Hz, 1H, H-1^7), 4.30 (d, $J_{1,2} = 1.5$ Hz, 1H, H-1^4), 4.22–3.81 (m, 16H, H-6a$^{7''}$, H-6a^5, H-6a^7, H-2$^{7''}$, H-6b^5, H-2^5, H-6b$^{7''}$, H-5^5, H-6b^7, H-5$^{7''}$, H-2$^{7'}$, H-2^4, H-6a^4, CH$_2$O-All, CH$_2$O-Bn), 3.76 (d, $J_{gem} =$ 11.2 Hz, 1H, CH$_2$O-Bn), 3.56–3.43 (m, 2H, H-3^4, H-5^7), 3.37 (dd, $J_{3,4} =$ 9.2 Hz, $J_{4,5} = 9.3$ Hz, 1H, H-4$^{4''}$), 3.21 (dd, $J_{gem} = 10.5$ Hz, 1H, H-6b^4), 3.04 (m, 1H, H-5^4), 2.09–1.65 (9s, 27H, OAc); ^{13}C NMR (90 MHz, [D$_6$]DMSO): $\delta = 170.1$, 169.9 (C=O), 136.5 (−CH=), 135.2, 135.1, 135.0 (C-4/5 Pht), 131.6, 130.9, 130.4 (C-i Ph), 128.7–127.6 (C-Ar), 123.8, 123.5, 123.0 (C-1/2 Pht), 123.7, 123.5, 123.1 (C-3/6 Pht), 116.5 (=CH$_2$), 98.1 (C-1^7), 96.6 (C-1$^{7''}$), 95.0 (C-1^5), 94.9 (C-1^4), 75.4 (C-3^4), 74.3 (C-5^4), 72.1 (C-2^4), 70.7 (C-5^5), 70.6 (C-5^7), 70.6 (C-5$^{7''}$), 69.6 (C-4^4), 69.6 (C-3^7), 69.5 (C-3$^{7''}$), 69.4 (C-3^5), 69.4 (C-6^4), 69.3 (CH$_2$O-All), 68.2 (C-4^7), 68.2 (C-4$^{7''}$), 68.1 (C-4^5), 67.6 (CH$_2$O-Bn), 61.4 (C-6^5), 61.4 (C-6^7), 61.4 (C-6$^{7''}$), 54.1 (C-2^7), 53.8 (C-2^5), 53.7 (C-2$^{7''}$), 20.4–20.0 (OAc); ESI-MS: *m/z* calcd for $C_{76}H_{79}N_3O_{33}$: 1561.46; found 1584.51 $[M+Na]^+$.

Benzyl O-[(3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)]-O-[(3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)]-O-[(3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→6)]-α-D-mannopyranoside (12): a) Sodium acetate (531 mg, 6.4 mmol) and palladium chloride (345 mg, 1.92 mmol) were added under an argon atmosphere to a solution of tetrasaccharide **11** (2.0 g, 1.28 mmol) in acetic acid (100 mL, 95 %). The suspension was stirred at 80 °C until the reaction was completed (TLC: hexane/acetone, 1.2:1). Subsequently, the precipitate was filtered off and the solvents were removed on a rotary evaporator. The remainder was taken up in water/dichloromethane and extracted with dilute $KHCO_3$ and water. The organic phase was dried over $MgSO_4$ and concentrated. The remainder was purified by flash chromatography (cyclohexane/ethyl acetate 1:1.2) to afford **12** (1.41 g, 72.5 %). $R_f = 0.09$ (cyclohexane/ethyl acetate 1:1.5); $[\alpha]_D^{23} = +12.9$ ($c = 0.4$, CH_2Cl_2).

b) Tetrasaccharide **11** (100 mg, 64 μmol) was dissolved in absolute methanol (1.5 mL) under an argon atmosphere. Subsequently anhydrous palladium chloride (55.3 mg, 0.31 mmol) was added and the suspension was stirred for 60 min (TLC: cyclohexane/ethyl acetate 1:2). The solids were removed by filtration over Celite and the filtrate was concentrated to dryness. The remainder was dissolved in dichloromethane and extracted with brine and $KHCO_3$ (2 M). After being dried over $MgSO_4$ the organic phase was concentrated. The remainder was purified by flash chromatography (cyclohexane/ethyl acetate 1:1) to afford **12** (75 mg, 77.0 %). $R_f =$ 0.27 (cyclohexane/ethyl acetate 1:2); ^{1}H NMR (360 MHz, [D$_6$]DMSO): $\delta = 8.00$–6.80 (m, 17H, Pht, Ar), 5.63–5.52 (m, 2H, H-3^5, H-3$^{7''}$), 5.48 (dd, $J_{2,3} = 10.1$ Hz, $J_{3,4} = 9.7$ Hz, 1H, H-3^7), 5.33–5.31 (m, 2H, H-1^5, H-1$^{7''}$), 4.95–4.88 (m, 2H, H-4^7, H-4^5), 4.82 (dd, $J_{2,3} = J_{3,4} = 9.7$ Hz, 1H, H-4$^{7''}$), 4.64 (d, $J_{1,2} = 9.2$ Hz, 1H, H-1^7), 4.42 (d, $J_{OH,3} = 8.2$ Hz, 1H, OH-3^4), 4.36 (d, $J_{1,2} < 1$ Hz, 1H, H-1^4), 4.27–4.17 (m, 2H, H-6a$^{7''}$, H-6a^5), 4.12–3.79 (m, 10H, H-2^5, H-2^7, H-2$^{7''}$, H-5^5, H-5$^{7''}$, CH$_2$O, H-6b^5, H-6a,b^7, H-6b$^{7''}$), 3.72–3.48 (m, 3H, H-2^4, H-3^4, CH$_2$O), 3.44–3.21 (m, 3H, H-5^7, H-5^4, H-6a^4), 2.97 (dd, $J_{3,4} = J_{4,5} = 8.8$ Hz, 1H, H-4^4), 2.13 (m, 1H, H-6b^4), 2.10–1.70 (9s, 27H, OAc); ^{13}C NMR (90 MHz, [D$_6$]DMSO): $\delta = 170.0$–166.9 (C=O), 136.6 (C-i Ph), 135.1 (C-4/5 Pht), 129.5 (C-1/2 Pht), 128.1–127.0 (C-Ar), 123.7, 123.5, 123.1 (C-3/6 Pht), 98.3 (C-1^7), 95.9 (C-1$^{7''}$), 95.1 (C-1^5), 94.7 (C-1^4), 76.1 (C-4^4), 75.7 (C-2^4), 70.7 (C-5^5), 70.6 (C-5$^{7''}$), 70.4 (C-5^7), 69.9 (C-5^4), 69.6 (C-3^5, C-3$^{7''}$), 69.5 (C-6^4, C-3^7), 68.2 (C-4^7, C-4^5, C-4$^{7''}$), 67.4 (CH$_2$O-Bn), 67.1 (C-3^4), 61.4 (C-6^7), 61.3 (C-6$^{7''}$), 61.2 (C-6^5), 53.9 (C-2$^{7''}$), 53.7 (C-2^7, C-2^5), 20.4–20.0 (OAc); ESI-MS: *m/z* calcd for $C_{73}H_{75}N_3O_{33}$: 1521.43; found 1544.51 $[M+Na]^+$.

Benzyl O-[(3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)]-O-[(3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)]-O-[(3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→6)]-3-O-acetyl-α-D-mannopyranoside (12a): Tetrasaccharide **12** (1.06 g, 0.7 mmol) was dissolved in pyridine (10.0 mL) and acetic anhydride (5.0 mL) at 0 °C. DMAP (150 mg, 1.2 mmol) was added and the mixture was stirred for 2 days at ambient temperature. The solvents were removed and the remainder was codistilled with toluene (3×). The residue was taken up in CH_2Cl_2 and extracted with dilute HCl, dilute $KHCO_3$ and water. The organic phase was dried over $MgSO_4$ and concentrated. The remainder was purified by flash chromatography (hexane/acetone, 1.1:1) to afford **12a** (881 mg, 81.0 %); $R_f = 0.30$ (hexane/acetone 1.1:1); $[\alpha]_D^{23} = +3.1$ ($c = 0.4$, CH_2Cl_2); ^{1}H NMR (360 MHz, [D$_6$]DMSO): $\delta = 8.20$–6.90 (m, 17H, Pht, Ar), 5.65–5.50 (m, 2H, H-3^5, H-3$^{7''}$), 5.43 (dd, $J_{2,3} = 9.9$ Hz, $J_{3,4} = 11.1$ Hz, 1H, H-3^7), 5.30–5.25 (m, 2H, H-1^5, H-1$^{7''}$), 4.97–4.91 (m, 2H, H-4^5, H-4$^{7''}$), 4.79–4.73 (m, 2H, H-4^7, H-3^4), 4.64 (d, $J_{1,2} = 8.4$ Hz, 1H, H-1^7), 4.30–3.70 (m, 15H, H-1^4, H-6a^7, H-6a$^{7''}$, CH$_2$O-Bn, H-6a^5, H-5^5, H-2$^{7''}$, H-6b$^{7''}$, H-2^5, H-5$^{7''}$, H-2^4, H-6b^5, CH$_2$O-Bn, H-2^7, H-6b^7), 3.94 (dd, $J_{4,5} = 9.3$ Hz, $J_{5,6} = 10.2$ Hz, 1H, H-5^4), 3.27–3.18 (m, 2H, H-4^4, H-6a^4), 3.08 (dd, $J_{4,5} = 7.4$ Hz, $J_{5,6} = 9.6$ Hz, 1H, H-5^7), 2.46 (m, 1H, H-6b^4), 2.30–1.60 (10s, 30H, OAc); ^{13}C NMR (90 MHz, [D$_6$]DMSO): $\delta = 170.0$, 169.5, 169.2 (C=O), 136.2 (C-i Ph), 135.2, 135.0, 134.8 (C-4/5 Pht), 130.4 (C-1/2 Pht), 128.2–127.7 (C-Ar), 123.9, 123.5, 123.3 (C-3/6 Pht), 98.4 (C-1^7), 96.3 C-1^5), 95.3 (C-1$^{7''}$), 94.7 (C-1^4), 73.0 (C-2^4), 72.6 (C-4^4), 70.6 (C-5$^{7''}$), 70.5 (C-5^5), 70.4 (C-5^7), 69.6 (C-5^4), 69.5 (C-3^4), 69.5 (C-6^4), 69.5 (C-3$^{7''}$), 69.5 (C-3^5), 69.4 (C-3^7), 68.2 (C-4$^{7''}$), 68.2 (C-4^7), 68.1 (C-4^5), 67.6 (CH$_2$O-Bn), 61.5 (C-6^5), 61.4 (C-6^7), 61.3 (C-

6‴), 54.2 (C-2$^{5'}$), 53.6 (C-2$^{7'}$), 53.7 (C-2$^{7''}$), 20.4–19.9 (OAc); ESI-MS: *m/z* calcd for $C_{75}H_{77}N_3O_{34}$: 1563.44; found 1586.54 $[M+Na]^+$.

***O*-{*O*-[(3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)]-*O*-[(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)]-*O*-[(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→6)]-3-*O*-acetyl-α-D-mannopyranosyl}-trichloroacetimidate (E)**: Tetrasaccharide **12a** (100 mg, 63.9 μmol) was dissolved in methanol (10.8 mL). Acetic acid (1.2 mL) and palladium oxide hydrate (222 mg) were added and the suspension was stirred under a hydrogen atmosphere. After complete reaction (TLC: CH_2Cl_2/methanol, 10:1) the catalyst was filtered off and washed with methanol (3×). After removal of the volatiles the remainder was purified by flash chromatography (hexane/acetone 1.2:1) to afford the hemiacetal **12b** (77 mg, 81.7%). R_f = 0.22 (CH_2Cl_2/methanol, 20:1); ESI-MS: *m/z* calcd for $C_{68}H_{71}N_3O_{34}$: 1473.39; found 1496.1 $[M+Na]^+$.

Hemiacetal **12b** (4.60 g, 3.12 mmol) and trichloroacetonitrile (11.9 mL, 117 mmol) were dissolved in CH_2Cl_2 (250 mL) and stirred for 30 min at 0°C. The reaction was started by addition of DBU (441 μL, 2.95 mmol). After complete reaction (TLC: CH_2Cl_2/methanol, 20:1) the volatiles were removed at ambient temperature. The remainder was dried in high vacuum and purified by flash chromatography (hexane/acetone, 1.2:1) to afford **E** (4.3 g, 85.3%). R_f = 0.35 (CH_2Cl_2/methanol 20:1); $[\alpha]_D^{23}$ = +15.4 (*c* = 0.4, CH_2Cl_2); ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 9.50 (s, 1H, NH), 8.20–7.55 (m, 12H, Pht), 5.67 (d, $J_{1,2}$ < 1 Hz, 1H, H-1$^{4'}$), 5.62 (dd, $J_{2,3}$ = 9.9 Hz, $J_{3,4}$ = 8.8 Hz, 1H, H-3$^{5'}$), 5.49–5.38 (m, 3H, H-3$^{7''}$, H-3$^{7'}$, H-1$^{5'}$), 5.30 (d, $J_{1,2}$ = 8.4 Hz, 1H, H-1$^{7''}$), 4.99–4.94 (m, 3H, H-4$^{5'}$, H-4$^{7''}$, H-3$^{4'}$), 4,77 (dd, $J_{3,4}$ = 10.0 Hz, $J_{4,5}$ = 9.4 Hz, 1H, H-4$^{7'}$), 4.72 (d, $J_{1,2}$ = 8.0 Hz, 1H, H-1$^{7'}$), 4.28–4.23 (m, 3H, H-6a$^{7''}$, H-6a$^{7'}$, H-6a$^{5'}$), 4.08–3.90 (m, 7H, H-2$^{4'}$, H-2$^{5'}$, H-6b$^{5'}$, H-2$^{7''}$, H-5$^{5'}$, H-5$^{7''}$, H-6b$^{7'}$), 3.88 (dd, J_{gem} = 12.0 Hz, 1H, H-6b$^{7''}$), 3.78 (dd, $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 9.5 Hz, 1H, H-2$^{7'}$), 3.67 (dd, $J_{4,5}$ = 9.4 Hz, $J_{5,6}$ = 8.5 Hz, 1H, H-5$^{4'}$), 3.40 (dd, $J_{3,4}$ = 8.8 Hz, $J_{4,5}$ = 9.4 Hz, 1H, H-4$^{4'}$), 3.18 (dd, J_{gem} = 11.2 Hz, 1H, H-6a$^{4'}$), 3.15 (dd, $J_{4,5}$ = 9.4 Hz, $J_{5,6}$ = 10.0 Hz, 1H, H-5$^{7'}$), 2.61 (dd, J_{gem} = 11.2 Hz, $J_{5,6}$ = 9.4 Hz, 1H, H-6b$^{4'}$), 2.07–1.70 (10s, 30H, OAc); ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 170.0, 169.6, 169.2, 167.1, 166.9 (C=O), 135.1, 134.8 (C-4/5 Pht), 130.4 (C-1/2 Pht), 123.7, 123.3 (C-3/6 Pht), 98.7 (C-1$^{7'}$), 96.6 (C-1$^{7''}$), 95.8 (C-1$^{5'}$), 93.2 (C-1$^{4'}$), 72.3 (C-4$^{4'}$, C-5$^{4'}$), 71.5 (C-5$^{4'}$), 70.9 (C-5$^{5'}$), 70.5 (C-5$^{7''}$), 70.4 (C-5$^{7'}$), 69.6 (C-3$^{7''}$), 69.4 (C-6$^{4'}$, C-3$^{5'}$), 69.3 (C-3$^{7'}$), 68.9 (C-3$^{4'}$), 68.1 (C-4$^{5'}$), 68.0 (C-4$^{7''}$), 67.7 (C-4$^{7''}$), 61.4 (C-6$^{7'}$), 61.2 (C-6$^{5'}$), 60.9 (C-6$^{7''}$), 54.1 (C-2$^{7''}$), 53.4 (C-2$^{5'}$), 53.2 (C-2$^{7'}$), 20.00, 19.7 (OAc); ESI-MS: *m/z* calcd for $C_{70}H_{71}Cl_3N_4O_{34}$: 1616.30; found 1639.41 $[M+Na]^+$.

***O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl)-(1→3)-*O*-{3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-*O*-[(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→6)]-*O*-(3,4-di-*O*-acetyl-α-D-mannopyranosyl)-(1→6)}-*O*-(2-*O*-acetyl-β-D-mannopyranosyl)-(1→4)-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl azide (14)**: A suspension of pentasaccharide **13** (661 mg, 349 μmol), donor **D** (650 mg, 523 μmol) and ground molecular sieves 4 Å (1 g) in absolute CH_2Cl_2 (65 mL) was stirred for 30 min at −35°C. Boron trifluoride ethyl etherate (17 μL, 138 μmol) was added over 5 min. The reaction was carried out over 4 h (TLC: cyclohexane/acetone, 1.5:1) and gradually warmed to +1°C. Subsequently, the solids were removed by filtration over Celite and washed with CH_2Cl_2. After removal of the solvent the remainder was purified by flash chromatography (cyclohexane/acetone 1.6:1) to afford **14** (940 mg, 90.6%). R_f = 0.26 (cyclohexane/acetone, 1.6:1); $[\alpha]_D^{23}$ = −13.3 (*c* = 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 8.02–7.60 (m, 20H, Pht) 7.30–6.72 (m, 20H, Ar), 5.71 (dd, $J_{2,3}$ = $J_{3,4}$ = 10.0 Hz, 1H, H-3^5), 5.43 (m, 2H, H-3$^{5'}$, H-3^7), 5.40–5.35 (m, 2H, H-1^5, OH-4^3), 5.25 (d, $J_{1,2}$ = 9.5 Hz, 1H, H-1^1), 5.14 (d, $J_{1,2}$ = 8.0 Hz, 1H, H-1^2), 5.11 (d, $J_{1,2}$ = 8.2 Hz, 1H, H-1$^{5'}$), 5.08–5.02 (m, 2H, H-2^3, H-4^5), 4.98 (dd, $J_{3,4}$ = $J_{4,5}$ = 10.1 Hz, 1H, H-4^4), 4.93 (d, $J_{1,2}$ = 8.3 Hz, 1H, H-1$^{7'}$), 4.90–4.78 (m, 5H, H-1^4, H-3$^{4'}$, H-4$^{5'}$, H-4$^{7'}$, CH$_2$O), 4.76 (dd, $J_{2,3}$ = 2.4 Hz, 1H, H-3^4), 4.69 (dd, $J_{3,4}$ = $J_{4,5}$ = 10.2 Hz, 1H, H-4$^{4'}$), 4.54 (d, $J_{1,2}$ < 1.0 Hz, 1H, H-1^3), 4.52–4.42 (m, 3H, CH$_2$O), 4.38 (d, J_{gem} = 12.9 Hz, 1H, CH$_2$O), 4.33–4.17 (m, 8H, CH$_2$O, H-1$^{4'}$, H-2^4, H-2^5, H-6a^5, H-6a$^{7'}$), 4.07–3.84 (m, 11H, H-2^2, H-2$^{4'}$, H-2$^{5'}$, H-3^1, H-3^2, H-4^1, H-4^2, H-5^5, H-6b^5, H-6a$^{5'}$, H-6b$^{7'}$), 3.83–3.60 (m, 8H, H-2^1, H-2$^{7'}$, H-5^4, H-5$^{4'}$, H-6a^2, H-6a,b^4, H-6b$^{5'}$), 3.58–3.52 (m, 2H, H-5^1, H-5$^{7'}$), 3.50–3.43 (m, 2H, H-6b^2, H-6a$^{4'}$), 3.39–3.34 (m, 2H, H-3^3, H-6a^1), 3.33–3.16 (m, 5H, H-4^3, H-5^2, H-5$^{5'}$, H-6b^1, H-6a^3), 2.99–2.88 (m, 3H, H-5^3, H-6b^3, H-6b$^{4'}$), 2.02, 2.01, 2.00, 1.99, 1.98, 1.96, 1.94, 1.91, 1.89, 1.80, 1.78, 1.76, 1.75, 1.69 (14s, 45H, OAc); ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 170.0, 169.9, 169.8, 169.5, 169.2, 169.1, 169.0, 167.6, 167.1 (C=O), 138.2, 138.1, 138.0, 137.95 (C-i Ar), 134.8, 134.7 (C-4/5 Pht), 130.8, 130.6, 130.5 (C-1/2 Pht), 128.1–127.0 (C-Ar), 123.6, 123.4 (C-3/6 Pht), 97.7 ($J_{C\text{-}1,H\text{-}1}$ = 176.2 Hz from a coupled HMQC spectrum, C-1^{4}α), 97.6 (C-1^7), 96.9 (C-1^3), 96.64 ($J_{C\text{-}1,H\text{-}1}$ = 176.2 Hz from a coupled HMQC spectrum, C-1$^{4'}$α), 96.62 (C-1^2), 96.0 (C-1^5), 95.9 (C-1$^{5'}$), 84.7 (C-1^1), 77.3 (C-4^2), 76.6 (C-3^1), 76.3 (C-3^3), 75.6 (C-3^2, C-5^1), 75.2 (C-4^1), 74.2 (C-5^2), 74.1 (C-5^3), 73.8 (CH$_2$O), 73.30 (C-2^4), 73.29 (C-2$^{4'}$), 73.28, 72.3, 71.6 (CH$_2$O), 71.0 (C-5^5), 70.8 (C-5$^{7'}$), 70.6 (C-5$^{5'}$), 70.3 (C-2^3), 70.0 (C-3$^{7''}$), 69.8 (C-3$^{5'}$), 69.6 (C-3^5), 69.5 (C-3^4), 69.0 (C-3^4), 68.6 (C-4^5), 68.5 (C-5^4), 68.3 (C-4^7), 68.2 (C-4$^{5'}$), 68.1 (C-5^4), 68.0 (C-6^4), 67.6 (C-6^2), 67.4 (C-6^1), 66.3 (C-6^3), 66.1 (C-4^3), 64.8 (C-4$^{4'}$), 64.7 (C-4^4), 61.9 (C-6^5), 61.8 (C-6^4), 61.5 (C-6^7), 61.3 (C-6$^{5'}$), 55.8 (C-2^2), 54.6 (C-2^1), 53.9 (C-2$^{7'}$), 53.7 (C-2^5, C-2$^{5'}$), 20.5, 20.3, 20.1, 20.0, 19.9 (OAc); FAB-MS (NBA): *m/z* calcd for $C_{146}H_{150}N_8O_{60}$: 2974.9; found 2976 $[M+H]^+$; elemental analysis calcd (%) for $C_{146}H_{150}N_8O_{60}$ (2976.81): C 58.91, H 5.08, N 3.76; found: C 58.59, H 5.08, N 3.70.

***O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl)-(1→3)-*O*-{3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-*O*-[3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)]-*O*-[3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)]-*O*-(3-*O*-acetyl-α-D-mannopyranosyl)-(1→6)}-*O*-(2-*O*-acetyl-β-D-mannopyranosyl)-(1→4)-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosylazide (15)**: Pentasaccharide **13** (200 mg, 105 μmol), donor **E** (540 mg, 334 μmol) and ground molecular sieves 4 Å (800 mg) in absolute CH_2Cl_2 (30 mL) were stirred for 30 min at −45°C. Boron trifluoride ethyl etherate (4 μL, 32.5 μmol) was added over 5 min. The reaction was carried out for 3 h (TLC: hexane/acetone 1:1) and gradually warmed to −5°C. Subsequently, the solids were removed by filtration over Celite and washed with CH_2Cl_2. After removal of the solvent the remainder was purified by flash chromatography (cyclohexane/acetone 1.2:1) to afford **15** (224 mg, 63.3%). R_f = 0.29 (cyclohexane/acetone 1:1); $[\alpha]_D^{23}$ = −25.1 (*c* = 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 8.04–7.40 (m, 24H, Pht), 7.30–6.70 (m, 20H, Ar), 5.67 (dd, $J_{2,3}$ = 10.4 Hz, $J_{3,4}$ = 12.2 Hz, 1H, H-3$^{7''}$), 5.60 (d, $J_{4,OH}$ = 3.7 Hz, 1H, OH-4^3), 5.51 (dd, $J_{2,3}$ = 10.4 Hz, $J_{3,4}$ = 11.0 Hz, 1H, H-3^5), 5.44–2.91 (m, 69H, H-1$^{7''}$, H-3$^{5'}$, H-1^5, H-1^1, H-3$^{7'}$, H-1^2, H-4$^{7''}$, H-4^5, H-4^3, H-4$^{5'}$, CH$_2$O, H-3^4, H-1^4, H-4$^{7'}$, H-3^3, H-1^3, H-1$^{7'}$, CH$_2$O, CH$_2$O, CH$_2$O, CH$_2$O, H-1$^{5'}$, CH$_2$O, H-2^3, CH$_2$O, CH$_2$O, H-6a$^{7''}$, H-6a$^{7'}$, H-6a^5, H-2$^{7''}$, H-2$^{4'}$, H-3^1, H-1$^{4'}$, H-4^1, H-5^5, H-2^2, H-6b$^{7''}$, H-2^5, H-6b$^{7'}$, H-5$^{7''}$, H-3^2, H-5^3, H-2$^{7'}$, H-6a$^{5'}$, H-6b^5, H-2^1, H-2$^{5'}$, H-6a,b^3, H-6a^2, H-4$^{4'}$, H-2^4, H-5^1, H-6a,b^4, H-6b^2, H-6b$^{5'}$, H-6a^1, H-5^4, H-3$^{4'}$, H-6a$^{4'}$, H-4^2, H-6b^1, H-5$^{5'}$, H-5^2, H-4^4, H-5$^{4'}$, H-6b$^{4'}$, H-5$^{7'}$), 2.08–1.67 (17s, 51H, OAc); ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 170.1–167.2 (C=O), 138.1, 138.0, 137.9 (C-i Ar), 135.0, 134.9, 134.7 (C-4/5 Pht), 130.8, 130.7, 130.6, 130.5 (C-1/2 Pht), 128.3–127.1 (C-Ar), 123.6, 123.5, 123.4 (C-3/6 Pht), 97.84 (C-1^3), 97.80 (C-1^4), 97.7 (C-1$^{5'}$), 96.9 (C-1^5), 96.5 (C-1$^{4'}$), 96.0 (C-1^2), 95.6 (C-1^7), 95.5 (C-1$^{7'}$), 84.6 (C-1^1), 78.3 (C-3^2), 76.2 (C-3^4), 75.8 (C-3^1), 75.3 (C-5^1), 74.7 (C-4^1), 73.8 (C-4^2), 73.4 (CH$_2$O), 73.3 (C-5$^{4'}$), 72.9 (C-4^4), 72.9 (CH$_2$O), 72.8 (C-2^4), 72.6 (C-2^3), 72.0, 71.4 (CH$_2$O), 70.7 (C-5$^{7''}$), 70.5 (C-2$^{4'}$), 70.41 (C-5^5), 70.40 (C-5$^{5'}$), 70.1 (C-3^4), 69.6 (C-3^5), 69.5 (C-6^4), 69.5 (C-3$^{7''}$), 69.4 (C-3$^{5'}$), 69.1 (C-3$^{7'}$), 68.9 (C-3^3), 68.7 (C-5^4), 68.3 (C-4$^{7''}$), 68.1 (C-5$^{7'}$), 68.0 (C-5^2), 67.9 (C-4^5), 67.89 (C-4$^{5'}$), 67.8 (C-5^3), 67.7 (C-4$^{7'}$), 67.4 (C-6^2), 67.2 (C-6^1), 65.7 (C-6$^{4'}$), 64.7 (C-4$^{4'}$), 64.4 (C-4^3), 61.6 (C-6$^{7''}$), 61.5 (C-6^3, C-6^5), 61.1 (C-6$^{7'}$), 60.8 (C-6$^{5'}$), 55.8 (C-2^2), 54.3 (C-2^5), 54.2 (C-2^1), 53.7 (C-2$^{5'}$), 53.4 (C-2$^{7'}$), 53.39 (C-2$^{7''}$), 20.4, 20.2, 20.1, 20.0, 19.8 (OAc); ESI-MS: *m/z* calcd for $C_{164}H_{167}N_9O_{68}$: 3349.99; found 3350.73 $[M+H]^+$.

***O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-*O*-[(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)]-*O*-(3,6-di-*O*-acetyl-α-D-mannopyranosyl)-(1→3)-*O*-(4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1→4)-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosylazide (16)**: A suspension of trisaccharide **A** (558 mg,

451 μmol), imidate **C** (840 mg, 676 μmol) and ground molecular sieves 4 Å (1.3 g) in absolute CH_2Cl_2 (10 mL) was stirred for 30 min at −25 °C. Boron trifluoride ethyl etherate (10 μL, 81 μmol) was added over 5 min and the solution was stirred continuously for 1 h (TLC: hexane/acetone 1:1). The solids were removed by filtration over Celite and washed with CH_2Cl_2. After concentration the remainder was purified by flash chromatography (hexane/acetone, 1.2:1) to afford **16** (975 mg, 93.2 %). R_f = 0.24 (hexane/acetone 2:1); $[\alpha]_D^{23}$ = −16.0 (c = 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 8.0–6.8 (m, 41H, Pht, Ar), 5.62 (dd, $J_{2,3}$ = 10.5 Hz, $J_{3,4}$ = 9.5 Hz, 1H, H-3^7), 5.61 (s, 1H, =C*H*-Ph), 5.43 (dd, $J_{2,3}$ = $J_{3,4}$ = 9.8 Hz, 1H, H-3^5), 5.42 (d, $J_{1,2}$ = 8.9 Hz, 1H, H-1$^7\beta$), 5.29 (d, $J_{1,2}$ = 9.5 Hz, 1H, H-1$^1\beta$), 5.23 (d, $J_{1,2}$ = 8.8 Hz, 1H, H-1$^2\beta$), 5.22 (d, $J_{2,OH}$ = 3.7 Hz, 1H, OH-2^3), 5.0–4.95 (m, 2H, H-4^7, H-3^4), 4.89 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.4 Hz, 1H, H-4^5), 4.85 (d, $J_{1,2}$ = 8.7 Hz, 1H, H-1$^5\beta$), 4.83 (d, J_{gem} = 11.8 Hz, 1H, CH_2O), 4.78 (d, J_{gem} = 11.8 Hz, 1H, CH_2O), 4.63 (d, $J_{1,2}$ < 1.0 Hz, 1H, H-1^4), 4.54 (d, J_{gem} = 11.8 Hz, 1H, CH_2O), 4.49 (d, J_{gem} = 11.8 Hz, 1H, CH_2O), 4.45–4.36 (m, 5H, H-1^3, CH_2O), 4.24 (dd, J_{gem} = 12.1 Hz, J_{vic} = 4.2 Hz, 1H, H-6a^7), 4.17–4.06 (m, 9H, H-3^2, H-4^1, H-3^1, H-5^7, H-2^5, H-2^7, H-2^2, H-6a^5, H-6a^3), 4.03–3.72 (m, 9H, H-4^2, H-4^3, H-2^4, H-6b^7, H-2^1, H-5^4, H-6a^4, H-6b^5, H-6a^2), 3.68–3.61 (m, 3H, H-2^3, H-4^4, H-5^1), 3.57–3.44 (m, 4H, H-6b^2, H-6b^3, H-6a^1, H-3^3), 3.38–3.30 (m, 2H, H-6b^1, H-5^2), 3.1–3.0 (m, 2H, H-5^3, H-6b^4), 2.27 (m, 1H, H-5^5), 2.04, 2.02, 2.0, 1.98, 1.97, 1.77, 1.73, 1.51 (8s, 24H, OAc); ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 170.1, 169.9, 169.62, 169.57, 169.3, 169.2, 168.8, 167.4, 167.1 (C=O), 138.3, 138.1, 138.0, 137.8 (C-i Ar), 135.1, 134.8 (C-4/5 Pht), 130.7, 130.6, 130.4 (C-1/2 Pht), 128.3–126.6 (C-Ar), 123.4 (C-3/6 Pht), 101.2 (=*C*H-Ph), 99.6 (C-1$^3\beta$), 97.8 ($J_{C\text{-}1,H\text{-}1}$ = 172.7 from a coupled HMQC spectrum, C-1$^4\alpha$), 97.0 (C-1$^7\beta$), 96.5 (C-1$^2\beta$), 95.8 (C-1$^5\beta$), 84.9 (C-1$^1\beta$), 78.0 (C-3^3), 77.2 (C-4^3), 76.9 (C-4^2), 76.2 (C-3^1), 75.8 (C-3^2), 75.7 (C-5^1), 75.0 (C-4^1), 74.5 (C-5^2), 73.8, 73.6 (CH_2O), 72.9 (C-2^4), 72.4 (C-4^4), 72.3, 71.6 (CH_2O), 70.8 (C-5^5), 70.6 (C-5^7), 70.2 (C-3^4), 69.8 (C-2^3, C-3^5, C-3^7), 68.2 (C-4^5, C-4^7), 67.8 (C-6^3), 67.7 (C-6^2), 67.6 (C-6^1), 67.4 (C-5^4), 66.1 (C-5^3), 61.8 (C-6^7), 61.7 (C-6^4), 61.3 (C-6^5), 56.0 (C-2^2), 54.6 (C-2^1, C-2^7), 53.7 (C-2^5), 20.6, 20.4, 20.0, 19.9, 19.0 (OAc); ESI-MS: m/z calcd for $C_{119}H_{117}N_7O_{42}$: 2315.72; found 2334.66 $[M+H_3O]^+$.

***O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-*O*-[(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)]-*O*-(3,6-di-*O*-acetyl-α-D-mannopyranosyl)-(1→3)-*O*-(2-*O*-acetyl-β-D-mannopyranosyl)-(1→4)-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosylazide (17)**: Hexasaccharide **16** (1288 mg, 556 μmol) was dissolved in pyridine (10 mL) and acetic anhydride (5 mL). The mixture was concentrated after 16 h and codistilled (3×) with toluene. The acetylated hexasaccharide was taken up in acetonitrile (200 mL) and a solution containing *p*-toluenesulfonic acid (2 g) in acetonitrile (20 mL) was added. After 1 h (TLC: hexane/acetone 1:1) the reaction was neutralized with pyridine and evaporated to dryness. The residue was dissolved in CH_2Cl_2 (500 mL) and extracted with water, dilute $KHCO_3$ and water. The organic phase was dried over $MgSO_4$, concentrated and purified by flash chromatography (hexane/acetone, 1.1:1) to afford **17** (1020 mg, 80.8 %). R_f = 0.23 (hexane/acetone 1:1); $[\alpha]_D^{23}$ = +2.0 (c = 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 7.95–7.63 (m, 16H, Pht), 7.35–6.72 (m, 20H, Ar), 5.63 (dd, $J_{2,3}$ = 10.4 Hz, 1H, H-3^7), 5.59 (dd, $J_{2,3}$ = 10.2 Hz, 1H, H-3^5), 5.43 (d, $J_{1,2}$ = 8.3 Hz, 1H, H-1^7), 5.42 (d, $J_{OH,4}$ = 5.6 Hz, 1H, OH-4^3), 5.28 (d, $J_{1,2}$ = 9.8 Hz, 1H, H-1^1), 5.25 (d, $J_{1,2}$ = 9.9 Hz, 1H, H-1^5), 5.20 (d, $J_{1,2}$ = 8.8 Hz, 1H, H-1^2), 5.08 (dd, $J_{1,2}$, $J_{2,3}$ < 1.0 Hz, 1H, H-2^3), 4.99 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.2 Hz, 1H, H-4^7), 4.97 (dd, $J_{3,4}$ = $J_{4,5}$ = 9.3 Hz, 1H, H-4^5), 4.89 (d, J_{gem} = 11.9 Hz, 1H, CH_2O), 4.80 (d, $J_{1,2}$ < 1.0 Hz, 1H, H-1^4), 4.79 (d, J_{gem} = 11.3 Hz, 1H, CH_2O), 4.71 (m, 1H, H-3^4), 4.61 (d, $J_{1,2}$ < 1.0 Hz, 1H, H-1^3), 4.48 (s, 2H, CH_2O), 4.62 (t, $J_{6,OH}$ = 5.2 Hz, 1H, OH-6^3), 4.40 (s, 2H, CH_2O), 4.37 (d, J_{gem} = 12.7 Hz, 1H, CH_2O), 4.29 (d, J_{gem} = 11.9 Hz, 1H, CH_2O), 4.22–3.90 (m, 14H, H-2^2, H-2^4, H-2^5, H-2^7, H-3^1, H-3^2, H-4^1, H-4^2, H-5^7, H-6a^4, H-6a,b^5, H-6a,b^7), 3.85 (m, 1H, H-5^5), 3.8–3.3 (m, 13H, H-2^1, H-3^3, H-4^3, H-4^4, H-5^1, H-5^4, H-6a,b^1, H-6a,b^2, H-6a,b^3, H-6b^4), 3.24 (m, 1H, H-5^2), 3.03 (m, 1H, H-5^3), 2.02, 1.97, 1.75, 1.74, 1.66, 1.60 (6s, 27H, OAc); ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 170.1, 170.0, 169.9, 169.6, 169.4, 169.2, 167.4, 167.1 (C=O), 138.4, 138.1, 137.9 (C-i Ar), 135.1, 134.8 (C-4/5 Pht), 130.6, 130.5 (C-1/2 Pht), 128.2–127.1 (C-Ar), 123.8, 123.4 (C-3/6 Pht), 97.4 (C-1^4), 97.0 (C-1^3), 96.5 (C-1^2), 96.2 (C-1^5), 95.1 (C-1^7), 84.8 (C-1^1), 76.6 (C-3^2), 76.5 (C-5^3), 76.3 (C-4^2), 76.20 (C-3^1), 76.16 (C-3^3), 75.7 (C-5^1), 75.0 (C-4^1), 74.3 (C-5^2), 73.8, 73.7 (CH_2O), 72.4 (C-2^4), 72.1, 71.7 (CH_2O), 71.6 (C-4^4), 70.9 (C-5^5), 70.5 (C-2^3), 70.4 (C-5^7), 69.9 (C-3^7), 69.8 (C-3^5), 68.7 (C-3^4), 68.5 (C-4^5), 68.2 (C-4^7), 67.7 (C-5^4), 67.63 (C-6^1), 67.60 (C-6^2), 66.8 (C-4^3), 61.9 (C-6^5, C-6^4), 61.5 (C-6^7), 60.4 (C-6^3), 55.9 (C-2^2), 54.6 (C-2^1), 54.5 (C-2^7), 53.7 (C-2^5), 20.4, 20.1, 20.04, 20.00, 19.7 (OAc); ESI-MS: m/z calcd for $C_{114}H_{115}N_7O_{43}$: 2269.70; found 2288.94 $[M+H_3O]^+$.

***O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-*O*-[(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)]-*O*-(3,6-di-*O*-acetyl-α-D-mannopyranosyl)-(1→3)-*O*-[(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl)-(1→6)]-*O*-(2-*O*-acetyl-β-D-mannopyranosyl)-(1→4)-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosylazide (18)**: A suspension of hexasaccharide **17** (600 mg, 264 μmol), imidate **B** (342 mg, 394 μmol) and ground molecular sieves 4 Å (900 mg) in absolute CH_2Cl_2 (60 mL) was stirred for 30 min at −35 °C. Boron trifluoride ethyl etherate (12 μL, 98 μmol) was added over 5 min and the reaction was allowed to gradually warm up to +5 °C over a period of 3 h (TLC: cyclohexane/acetone 1:1). Subsequently, the solids were removed by filtration over Celite and washed with CH_2Cl_2. After concentration the remainder was purified by flash chromatography (cyclohexane/acetone, 1.4:1) to afford **18** (614 mg, 78.1 %). R_f = 0.3 (cyclohexane/acetone 1:1); $[\alpha]_D^{23}$ = +4.0 (c = 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 7.95–7.66 (m, 20H, Pht), 7.30–6.72 (m, 20H, Ar), 5.63–5.55 (m, 3H, H-3^5, H-3$^{5'}$, H-3^7), 5.53 (d, $J_{OH,4}$ = 4.6 Hz, 1H, OH-4^3), 5.43 (d, $J_{1,2}$ = 8.1 Hz, 1H, H-1^7), 5.30–5.24 (m, 3H, H-1^1, H-1^5, H-1$^{5'}$), 5.14 (d, $J_{1,2}$ = 8.0 Hz, 1H, H-1^2), 5.07 (dd, $J_{1,2}$, $J_{2,3}$ < 1.0 Hz, 1H, H-2^3), 5.02–4.90 (m, 5H, H-3$^{4'}$, H-4$^{4'}$, H-4^5, H-4$^{5'}$, H-4^7), 4.85 (d, J_{gem} = 12.4 Hz, 1H, CH_2O), 4.74 (d, $J_{1,2}$ < 1.0 Hz, 1H, H-1^4), 4.71 (m, 1H, H-3^4), 4.62 (d, J_{gem} = 12.4 Hz, 1H, CH_2O), 4.57 (d, $J_{1,2}$ < 1.0 Hz, 1H, H-1^3), 4.47, 4.41 (2d, J_{gem} = 12.2 Hz, 2H, CH_2O), 4.39–4.29 (m, 5H, CH_2O, H-1$^{4'}$), 4.22–3.85 (m, 18H, H-2^2, H-2^4, H-2$^{4'}$, H-2^5, H-2$^{5'}$, H-2^7, H-3^1, H-3^2, H-4^1, H-4^2, H-5^5, H-5^7, H-6a^4, H-6a,b^5, H-6a$^{5'}$, H-6a,b^7), 3.8–3.7 (m, 4H, H-2^1, H-4^4, H-5^4, H-6b$^{5'}$), 3.65–3.36 (m, 13H, H-3^3, H-4^3, H-5^1, H-5$^{4'}$, H-5$^{5'}$, H-6a^1, H-6a,b^2, H-6a,b^3, H-6b^4, H-6a,b$^{4'}$), 3.32–3.19 (m, 3H, H-5^2, H-5^3, H-6b^1), 2.025, 2.021, 1.99, 1.98, 1.97, 1.93, 1.81, 1.78, 1.77, 1.74, 1.70, 1.64 (12s, 45H, OAc); ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 170.1, 170.05, 169.9, 169.8, 169.6, 169.4, 169.2, 169.1, 167.9, 167.1 (C=O), 138.1, 138.0 (C-i Ar), 135.1, 134.9 (C-4/5 Pht), 130.7, 130.6, 130.5 (C-1/2 Pht), 128.2–127.0 (C-Ar), 123.8, 123.4 (C-3/6 Pht), 97.7 ($J_{C\text{-}1,H\text{-}1}$ = 177.6 Hz from a coupled HMQC spectrum, C-1$^4\alpha$), 97.1 ($J_{C\text{-}1,H\text{-}1}$ = 177.6 Hz from a coupled HMQC spectrum, C-1$^{4'}\alpha$), 96.8 (C-1^2), 96.7 (C-1^3), 96.4 (C-1$^{5'}$), 96.2 (C-1^5), 95.3 (C-1^7), 84.8 (C-1^1), 76.7 (C-3^1, C-4^2), 76.0 (C-3^3), 75.8 (C-3^2), 75.7 (C-5^1), 75.3 (C-4^1), 74.3 (C-5^2), 74.2 (C-5^3), 73.9 (CH_2O), 73.8 (C-2$^{4'}$), 73.6 (C-2^4), 73.5, 72.3 (CH_2O), 71.7 (C-4^4), 71.6 (CH_2O), 71.0 (C-5^5), 70.7 (C-5$^{5'}$), 70.5 (C-5^7), 70.4 (C-2^3), 69.9 (C-3^7, C-3$^{5'}$), 69.7 (C-3^5, C-3$^{4'}$), 68.7 (C-3^4), 68.5 (C-4^5), 68.4 (C-4$^{5'}$), 68.2 (C-4^7), 67.8 (C-5^4), 67.53 (C-6^2, C-5$^{4'}$), 67.48 (C-6^1), 67.3 (C-6^3), 67.1 (C-4^3), 64.3 (C-4$^{4'}$), 61.9 (C-6^5, C-6^4), 61.6 (C-6$^{4'}$), 61.4 (C-6$^{5'}$, C-6^7), 55.7 (C-2^2), 54.6 (C-2^1), 54.5 (C-2^7), 53.8 (C-2$^{5'}$), 53.7 (C-2^5), 20.5, 20.4, 20.3, 20.25, 20.18, 20.1, 20.0, 19.8 (OAc); ESI-MS: m/z calcd for $C_{146}H_{150}N_8O_{60}$: 2974.9; found 2997.9 $[M+Na]^+$.

***O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-*O*-[3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)]-*O*-(3,6-di-*O*-acetyl-α-D-mannopyranosyl)-(1→3)-*O*-{3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-*O*-[(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→6)]-*O*-(3,4-di-*O*-acetyl-α-D-mannopyranosyl)-(1→6)}-*O*-(2-*O*-acetyl-β-D-mannopyranosyl)-(1→4)-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosylazide (19)**: A suspension of hexasaccharide acceptor **17** (721 mg, 320 μmol), imidate **D** (590 mg, 261 μmol) and ground molecular sieves 4 Å (530 mg) in absolute CH_2Cl_2 (55 mL) was stirred for 30 min at −45 °C. Boron trifluoride ethyl etherate (16 μL, 130 μmol) was added over 5 min. The reaction was carried out for 3 h (cyclohexane/acetone, 1.5:1) and gradually warmed to −5 °C. Subsequently, the solids were removed by filtration over Celite and washed with CH_2Cl_2. After removal of the solvent the remainder was purified by flash chromatography (cyclohexane/acetone, 1.7:1) to afford **19** (932 mg, 87.6 %). R_f = 0.19 (cyclohexane/acetone, 1.5:1); $[\alpha]_D^{23}$ = −2.1 (c = 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 8.04–7.60 (m,

24H, Pht), 7.30–6.70 (m, 20H, Ar), 5.64 (m, 1H, H-3^5), 5.62 (m, 1H, H-3^7), 5.48–5.39 (m, 3H, H-1^7, H-3$^{5'}$, H-3$^{7'}$), 5.31 (d, $J_{1,2}$=8.5 Hz, 1H, H-1^5), 5.29 (d, $J_{OH,4}$=5.2 Hz, 1H, OH-4^3), 5.25 (d, $J_{1,2}$=9.5 Hz, 1H, H-1^1), 5.18–5.12 (m, 2H, H-1^2, H-1$^{5'}$), 5.04–4.97 (m, 3H, H-2^3, H-4^5, H-4^7), 4.94 (d, $J_{1,2}$=8.2 Hz, 1H, H-1^7), 4.89 (dd, $J_{3,4}$=$J_{4,5}$=9.5 Hz, 1H, H-4$^{5'}$), 4.85–4.80 (m, 3H, H-4$^{7'}$, H-3$^{4'}$, CH$_2$O), 4.76–4.70 (m, 3H, H-1^4, H-3^4, H-4$^{4'}$), 4.50–4.42 (m, 3H, H-1^3, CH$_2$O), 4.39 (d, J_{gem}=12.2 Hz, 1H, CH$_2$O), 4.37–3.82 (m, 25H, CH$_2$O, H-1$^{4'}$, H-2^2, H-2^4, H-2$^{4'}$, H-2^5, H-2$^{5'}$, H-2^7, H-3^1, H-3^2, H-4^1, H-4^2, H-5^5, H-5^7, H-6a^4, H-6a,b^5, H-6a$^{5'}$, H-6a,b^7, H-6a,b$^{7'}$), 3.80–3.62 (m, 6H, H-2^1, H-2$^{7'}$, H-4^4, H-5^4, H-5$^{4'}$, H-6b$^{5'}$), 3.59 (m, 1H, H-6a^2), 3.57–3.50 (m, 2H, H-5^1, H-5$^{7'}$), 3.48–3.36 (m, 4H, H-6a^1, H-6b^2, H-6b^4, H-6a$^{4'}$), 3.30–3.17 (m, 6H, H-3^3, H-4^3, H-5^2, H-5$^{5'}$, H-6b^1, H-6a^3), 3.04–2.94 (m, 2H, H-6b^3, H-6b$^{4'}$), 2.90 (m, 1H, H-5^3), 2.02, 2.015, 2.01, 2.0, 1.98, 1.96, 1.92, 1.78, 1.77, 1.76, 1.75, 1.74, 1.73, 1.68, 1.63 (15s, 51H, OAc); ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ=170.1–167.2 (C=O), 138.3, 138.1, 138.0 (C-i Ar), 135.1, 134.9, 134.6 (C-4/5 Pht), 130.9, 130.7, 130.6, 130.5 (C-1/2 Pht), 128.2–127.0 (C-Ar), 123.8, 123.7, 123.4 (C-3/6 Pht), 97.9 ($J_{C-1,H-1}$=180.0 Hz from a coupled HMQC spectrum, C-1^{4}α), 97.7 (C-1$^{7'}$), 96.70 (C-1^2, $J_{C-1,H-1}$=162.7 Hz from a coupled HMQC spectrum, C-1^{3}β), 96.65 ($J_{C-1,H-1}$=172.6 Hz from a coupled HMQC spectrum, C-1$^{4'}$α), 96.2 (C-1^5), 96.0 (C-1$^{5'}$), 95.3 (C-1^7), 84.7 (C-1^1), 77.0 (C-4^2), 76.8 (C-3^1), 76.6 (C-3^3), 75.7 (C-5^1), 75.5 (C-3^2), 75.3 (C-4^1), 74.3 (C-5^3), 74.2 (C-5^2), 73.9 (CH$_2$O), 73.4 (C-2^4), 73.3 (C-2$^{4'}$), 73.2, 72.3 (CH$_2$O), 71.6 (CH$_2$O, C-4^4), 71.0 (C-5^5), 70.8 (C-5^7), 70.7 (C-5$^{5'}$), 70.5 (C-5^7), 70.3 (C-2^3), 70.1 (C-3$^{7'}$), 69.9 (C-3$^{5'}$, C-3^7), 69.8 (C-3^5), 69.6 (C-3$^{4'}$), 68.8 (C-3^4), 68.6 (C-4^5), 68.5 (C-5$^{4'}$), 68.4 (C-4$^{7'}$), 68.3 (C-4$^{5'}$), 68.2 (C-4^7), 67.9 (C-5^4, C-6$^{4'}$), 67.4 (C-6^1, C-6^2), 66.5 (C-6^3), 66.2 (C-4^3), 64.8 (C-4$^{4'}$), 61.9 (C-6^4, C-6^5), 61.5 (C-6$^{7'}$), 61.4 (C-6$^{5'}$, C-6^7), 55.8 (C-2^2), 54.6 (C-2^1), 54.5 (C-2^7), 53.9 (C-2$^{7'}$), 53.8 (C-2^5, C-2$^{5'}$), 20.4, 20.2, 20.1, 20.0, 19.8 (OAc); ESI-MS: *m/z* calcd for $C_{164}H_{167}N_9O_{68}$: 3349.99; found 3372.5 $[M+Na]^+$.

***O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-*O*-[3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)]-*O*-(3,6-di-*O*-acetyl-α-D-mannopyranosyl)-(1→3)-*O*-{3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-*O*-[3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)]-*O*-[3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)]-*O*-(3-*O*-acetyl-α-D-mannopyranosyl)-(1→6)}-*O*-(2-*O*-acetyl-β-D-mannopyranosyl)-(1→4)-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosylazide (20)**: Hexasaccharide **17** (200 mg, 88 μmol), donor **E** (428 mg, 264 μmol) and ground molecular sieves 4 Å (600 mg) in absolute CH_2Cl_2 (32 mL) were stirred for 30 min at 0 °C. The suspension was cooled to −10 °C and boron trifluoride ethyl etherate (5.8 μL, 47 μmol) was added over 5 min. The reaction was stirred at −10 °C (TLC: hexane/acetone 1:1). After a further 3 h boron trifluoride ethyl etherate (2.5 μL, 20.3 μmol) was added and 1 h later boron trifluoride ethyl etherate (2.5 μL, 20.3 μmol) and donor **E** (100 mg, 62 μmol) were added. The reaction was continued for 1 h and the solids were removed by filtration over Celite and washed with CH_2Cl_2. After removal of the solvent the remainder was purified by flash chromatography (cyclohexane/ethyl acetate 1:2) to afford **20** (213 mg, 64.9%). R_f=0.07 (cyclohexane/ethyl acetate 1:2); $[\alpha]_D^{23}$=+0.2 (c=0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ=8.04–7.40 (m, 28H, Pht), 7.30–6.65 (m, 20H, Ar), 5.67–3.00 (m, 75H, H-3^7, H-3^5, H-3$^{7''}$, H-1^7, H-3$^{5'}$, H-1^5, H-1$^{7''}$, H-1^1, H-3$^{7'}$, H-1^2, OH-4^3, H-4^5, H-4$^{7''}$, H-2^3, H-4^7, CH$_2$O, H-4$^{5'}$, H-3$^{4'}$, H-4$^{7'}$, H-3^4, H-1^4, H-1$^{7'}$, H-1^3, CH$_2$O, CH$_2$O, H-1$^{5'}$, CH$_2$O, CH$_2$O, CH$_2$O, H-2^4, CH$_2$O, CH$_2$O, H-6a^5, H-6a$^{7'}$, H-6a$^{7''}$, H-6a^7, H-6a$^{4'}$, H-5$^{7''}$, H-2^5, H-3^1, H-6b^7, H-4^1, H-2^7, H-2^2, H-1$^{4'}$, H-5^7, H-2$^{7''}$, H-6b^5, H-6a^4, H-5^5, H-2$^{5'}$, H-2$^{7'}$, H-3^2, H-6a$^{5'}$, H-6b$^{7''}$, H-6b$^{7'}$, H-2^1, H-4^4, H-5^4, H-2$^{4'}$, H-6a^2, H-4^3, H-5^1, H-6b$^{5'}$, H-6b^2, H-6b^4, H-6a^1, H-5$^{4'}$, H-6a^3, H-6b^1, H-5$^{5'}$, H-4^2, H-3^3, H-5^2, H-4$^{4'}$), 2.72 (m, 1H, H-5^3), 2.55 (m, 1H, H-6b^3), 2.28–2.20 (m, 2H, H-6b$^{4'}$, H-5$^{7'}$), 2.18–1.68 (19s, 57H, OAc); ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ=170.1–167.2 (C=O), 138.80, 138.75, 138.72 (C-i Ar), 135.8, 135.6, 135.5 (C-4/5 Pht), 131.5, 131.3, 131.26, 131.1 (C-1/2 Pht), 129.1–127.8 (C-Ar), 124.5, 124.4, 124.2 (C-3/6 Pht), 97.8 (C-1$^{5'}$), 97.7 (C-1^4), 97.6 (C-1^3), 96.8 (C-1$^{7''}$), 96.5 (C-1$^{4'}$), 96.0 (C-1^2), 95.6 (C-1^5), 95.5 (C-1^7), 94.9 (C-1^7), 84.4 (C-1^1), 78.3 (C-3^2), 76.7 (C-3^3), 75.8 (C-3^1), 75.3 (C-5^1), 74.6 (C-4^1), 73.6 (C-4^2), 73.4 (CH$_2$O), 73.3 (C-5^3), 72.9 (C-4$^{4'}$), 72.7 (CH$_2$O), 72.6 (C-2^4), 72.04 (C-2^4), 72.03 (CH$_2$O), 71.4 (C-4^4, CH$_2$O), 70.6 (C-5^5), 70.5 (C-5^7), 70.4 (C-5$^{5'}$), 70.3 (C-2^3), 70.13 (C-5$^{7''}$), 70.10 (C-6$^{4'}$), 69.9 (C-3$^{4'}$), 69.58 (C-3$^{7''}$), 69.56 (C-3^7), 69.55 (C-3^5), 69.5 (C-3$^{5'}$), 69.1 (C-3$^{7'}$), 68.7 (C-5$^{4'}$), 68.5 (C-3^4), 68.2 (C-5^2), 68.2 (C-5$^{7'}$), 68.1 (C-4^5), 67.9 (C-4$^{5'}$), 67.9 (C-4^7), 67.8 (C-4$^{7''}$), 67.6 (C-4$^{7'}$), 67.56 (C-5^4), 67.3 (C-6^2), 67.2 (C-6^1), 65.6 (C-6^3), 64.6 (C-4^3), 61.8 (C-6^4), 61.5 (C-6^5), 61.45 (C-6$^{7''}$), 61.11 (C-6^7), 61.10 (C-6$^{7'}$), 60.7 (C-6$^{5'}$), 55.8 (C-2^2), 54.3 (C-2$^{7''}$, C-2^1), 54.2 (C-2^7), 53.6 (C-2$^{5'}$), 53.4 (C-2^5, C-2$^{7''}$), 21.5–19.7 (OAc); ESI-MS: *m/z* calcd for $C_{182}H_{184}N_{10}O_{76}$: 3725.08; found 3748.10 $[M+Na]^+$.

***O*-(2-Acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-*O*-[2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)]-*O*-α-D-mannopyranosyl-(1→3)-*O*-{2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-*O*-[(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→6)]-*O*-α-D-mannopyranosyl-(1→6)}-*O*-β-D-mannopyranosyl-(1→4)-*O*-(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-glucopyranosylazide (21)**: Nonasaccharide **19** (900 mg, 0.27 mmol) was dissolved in *n*-butanol (90 mL) and ethylenediamine (27.5 mL) and stirred at 90 °C for 16 h (TLC: isopropanol/1 M ammonium acetate 2:1). The volatiles were distilled off and the remainder was dried in vacuo until the weight remained constant. Subsequently, pyridine (90 mL) and acetic anhydride (45 mL) were added. After 16 h (TLC: CH_2Cl_2/methanol, 10:1) the mixture was concentrated and codistilled with toluene (3×). The remainder was dried in high vacuum and methylamine (90 mL, 40% in H_2O) was added. After stirring for 2 h at ambient temperature (TLC: isopropanol/1 M ammonium acetate 2:1) the solution was evaporated and dried in high vacuum. The remainder was dissolved in water (50 mL) and passed in portions of 10 mL over three connected SepPak cartridges (Waters). Elution of each batch was performed with water (30 mL) followed by acetonitrile/water (10 mL each, ratios 1:19, 1:9 and 1:6.6). The product was eluted with acetonitrile/water (30 mL, 4:1) and lyophilized yielding **21** (485.2 mg, 85.7%). R_f amine=0.55 (isopropanol/1 M ammoniumacetate 2:1); R_f peracetate=0.60 (CH_2Cl_2/methanol, 10:1); R_f **21**=0.67 (isopropanol/1 M ammoniumacetate 2:1); $[\alpha]_D^{23}$=−23.8 (0.4, H_2O); ^{1}H NMR (500 MHz, D_2O [D$_6$]DMSO as internal standard): δ=7.41–6.89 (m, 20H, Ar), 4.98 (d, $J_{1,2}$<1.0 Hz, 1H, H-1^4), 4.78–2.95 (m, 69H, CH$_2$O, CH$_2$O, H-1$^{4'}$, CH$_2$O, CH$_2$O, H-1^1, CH$_2$O, H-1^3, H-1^5, H-1^7, CH$_2$O, H-1$^{7'}$, CH$_2$O, CH$_2$O, H-1^2, H-1$^{5'}$, H-2^4, H-6a$^{4'}$, H-3^4, H-2^3, H-6a^7, H-6a^3, H-6a$^{7''}$, H-4^2, H-6a^5, H-4^1, H-4^3, H-2$^{4'}$, H-5^4, H-6a^4, H-6a^1, H-6b^7, H-2^1, H-2^7, H-2^2, H-6b$^{7'}$, H-3$^{4'}$, H-6b^5, H-2^5, H-4^4, H-2$^{7''}$, H-6a^2, H-5$^{4'}$, H-6a,b$^{5'}$, H-6b^1, H-3^1, H-6b^3, H-6b^4, H-5^1, H-3^5, H-3^2, H-3^7, H-3$^{7''}$, H-6b$^{4'}$, H-3^3, H-6b^2, H-2$^{5'}$, H-5^7, H-3$^{5'}$, H-4^7, H-4^5, H-5^5, H-4$^{7''}$, H-4$^{5'}$, H-5$^{7''}$, H-4$^{4'}$, H-5^3, H-5^2), 2.88 (dd, $J_{4,5}$=7.9 Hz, 1H, H-5$^{5'}$), 2.09–1.38 (6s, 18H, NAc); ^{13}C NMR (125 MHz, D_2O [D$_6$]DMSO as internal standard): δ=174.9, 174.7, 174.6, 174.4, 174.1 (C=O), 138.3, 138.1, 137.4, 137.2 (C-i Ar), 129.2–128.1 (C-Ar), 101.9 (C-1^7), 101.8 (C-1$^{7'}$), 100.7 (C-1^2), 100.5 (C-1^3), 100.2 (C-1^5), 99.9 (C-1$^{5'}$), 99. 5 (C-1^4), 97.0 (C-1$^{4'}$), 88.8 (C-1^1), 81.0 (C-3^3), 80.4 (C-3^1), 80.3 (C-3^2), 78.3 (C-4^4), 77.6 (C-4^2), 76.9 (C-2$^{4'}$), 76.5 (C-2^4), 76.3 (C-5^1), 76.21 (C-5^7), 76.16 (C-5^5), 76.1 (C-5$^{7'}$), 75.8 (C-5$^{5'}$), 75.4 (C-4^1), 74.6 (C-5^3), 74.12, 74.06, (CH$_2$O), 74.03 (C-3$^{7'}$), 73.98 (C-5^2), 73.91 (C-3^5), 73.7 (C-3^7), 73.32 (CH$_2$O), 73.29 (C-3$^{5'}$), 73.23 (CH$_2$O), 72.1 (C-5^4), 71.8 (C-5$^{4'}$), 70.7 (C-2^3), 70.3 (C-4$^{7'}$), 70.2 (C-4^5), 70.10 (C-4^7), 70.06 (C-6$^{4'}$), 69.89 (C-3$^{4'}$), 69.88 (C-4$^{5'}$), 68.4 (C-3^4), 68.3 (C-6^2), 68.0 (C-6^1), 67.7 (C-4$^{4'}$), 65.8 (C-4^3), 65.6 (C-6^3), 61.4 (C-6^4), 61.1 (C-6^5), 61.0 (C-6$^{7'}$), 60.9 (C-6^7), 60.5 (C-6$^{5'}$), 55.9 (C-2^7, C-2$^{7'}$, C-2$^{5'}$), 55.7 (C-2^5), 55.2 (C-2^2), 53.9 (C-2^1), 20.4, 20.2, 20.1, 20.0, 19.8 (NAc); ESI-MS: *m/z* calcd for $C_{94}H_{133}N_9O_{45}$: 2107.84; found 2130.8 $[M+Na]^+$.

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[1] S. Dübel, *Appl. Microbiol. Biotechnol.* **2007**, *74*, 723.
[2] M. P. Campbell, L. Royle, C. M. Radcliffe, R. A. Dwek, P. M. Rudd, *Bioinformatics* **2008**, *24*, 1214.

[3] H. Shimaoka, H. Kuramoto, J. Furukawa, Y. Miura, M. Kurogochi, Y. Kita, H. Hinou, Y. Shinohara, S. Nishimura, *Chem. Eur. J.* **2007**, *13*, 1664.
[4] K. T. Pilobello, L. K. Mahal, *Methods Mol. Biol.* **2008**, *385*, 193.
[5] Y. G. Kim, D. S. Shin, Y. H. Yang, G. C. Gil, C. G. Park, Y. Mimura, D. K. Cooper, P. M. Rudd, R. A. Dwek, Y. S. Lee, B. G. Kim, *Chem. Biol.* **2008**, *15*, 215.
[6] K. G. Rice, *Anal. Biochem.* **2000**, *283*, 10.
[7] Y. Kajihara, Y. Suzuki, K. Sasaki, L. R. Juneja, *Methods Enzymol.* **2003**, *362*, 44.
[8] T. Schallus, C. Jaeckh, K. Feher, A. S. Palma, Y. Liu, J. C. Simpson, M. Mackeen, G. Stier, T. J. Gibson, T. Feizi, T. Pieler, C. Muhle-Goll, *Mol. Biol. Cell* **2008**, *19*, 3404.
[9] S. André, T. Kozar, R. Schuberth, C. Unverzagt, S. Kojima, H. J. Gabius, *Biochemistry* **2007**, *46*, 6984.
[10] E. W. Adams, D. M. Ratner, H. R. Bokesch, J. B. McMahon, B. R. O'Keefe, P. H. Seeberger, *Chem. Biol.* **2004**, *11*, 875.
[11] Y. C. Lee, R. R. Townsend, M. R. Hardy, J. Lonngren, J. Arnarp, M. Haraldsson, H. Lönn, *J. Biol. Chem.* **1983**, *258*, 199.
[12] V. I. Dyukova, N. V. Shilova, O. E. Galanina, A. Y. Rubina, N. V. Bovin, *Biochim. Biophys. Acta* **2006**, *1760*, 603.
[13] S. Eller, R. Schuberth, G. Gundel, J. Seifert, C. Unverzagt, *Angew. Chem.* **2007**, *119*, 4251; *Angew. Chem. Int. Ed.* **2007**, *46*, 4173.
[14] T. Ogawa, M. Sugimoto, T. Kitajima, K. K. Sadozai, T. Nukada, *Tetrahedron Lett.* **1986**, *27*, 5739.
[15] H. Paulsen, M. Heume, H. Nürnberger, *Carbohydr. Res.* **1990**, *200*, 127.
[16] C. Unverzagt, *Angew. Chem.* **1994**, *106*, 1170; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1102.
[17] J. Seifert, C. Unverzagt, *Tetrahedron Lett.* **1996**, *37*, 6527.
[18] G. Wang, W. Zhang, Z. Lu, P. Wang, X. Zhang, Y. Li, *J. Org. Chem.* **2009**, *74*, 2508.
[19] C. Unverzagt, S. Eller, S. Mezzato, R. Schuberth, *Chem. Eur. J.* **2008**, *14*, 1304.
[20] C. Unverzagt, *Angew. Chem.* **1997**, *109*, 2078; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1989.
[21] W. Günther, H. Kunz, *Carbohydr. Res.* **1992**, *228*, 217.
[22] J. G. M. van der Ven, J. Kerekgyarto, J. P. Kamerling, A. Liptak, J. F. G. Vliegenthart, *Carbohydr. Res.* **1994**, *264*, 45.
[23] H. Paulsen, B. Helpap, *Carbohydr. Res.* **1992**, *216*, 289.
[24] G. M. Watt, G. J. Boons, *Carbohydr. Res.* **2004**, *339*, 181.
[25] V. Y. Dudkin, J. S. Miller, S. J. Danishefsky, *J. Am. Chem. Soc.* **2004**, *126*, 736.
[26] Y. Ito, S. Hagihara, I. Matsuo, K. Totani, *Curr. Opin. Struct. Biol.* **2005**, *15*, 481.
[27] B. Li, H. Song, S. Hauser, L.-X. Wang, *Org. Lett.* **2006**, *8*, 3081.
[28] T. W. Rising, C. D. Heidecke, J. W. Moir, Z. Ling, A. J. Fairbanks, *Chem. Eur. J.* **2008**, *14*, 6444.
[29] B. Sun, B. Srinivasan, X. Huang, *Chem. Eur. J.* **2008**, *14*, 7072.
[30] S. Serna, B. Kardak, N.-C. Reichardt, M. Martin-Lomas, *Tetrahedron: Asymmetry* **2009**, *20*, 851.
[31] D. M. Ratner, E. R. Swanson, P. H. Seeberger, *Org. Lett.* **2003**, *5*, 4717.
[32] S. Jonke, K. G. Liu, R. R. Schmidt, *Chem. Eur. J.* **2006**, *12*, 1274.
[33] K. Tanaka, Y. Fujii, H. Tokimoto, Y. Mori, S. Tanaka, G. M. Bao, E. R. Siwu, A. Nakayabu, K. Fukase, *Chem. Asian J.* **2009**, *4*, 574.
[34] S. Andre, S. Kojima, G. Gundel, R. Russwurm, X. Schratt, C. Unverzagt, H. J. Gabius, *Biochim. Biophys. Acta Gen. Subj.* **2006**, *1760*, 768.
[35] C. Unverzagt, *Tetrahedron Lett.* **1997**, *38*, 5627.
[36] S. André, C. Unverzagt, S. Kojima, X. Dong, C. Fink, K. Kayser, H.-J. Gabius, *Bioconjugate Chem.* **1997**, *8*, 845.
[37] C. Unverzagt, *Angew. Chem.* **1996**, *108*, 2507; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2350.
[38] R. R. Schmidt, W. Kinzy, *Adv. Carbohydr. Chem. Biochem.* **1994**, *50*, 21.
[39] J. Arnarp, J. Lönngren, *Acta Chem. Scand. B* **1978**, *32*, 696.
[40] S. David, S. Hanessian, *Tetrahedron* **1985**, *41*, 643.
[41] J. Arukwe, *Acta Chem. Scand.* **1998**, *52*, 819.
[42] C. Unverzagt, H. Kunz, *J. Prakt. Chem./Chem.-Ztg.* **1992**, *334*, 570.
[43] W. Steglich, G. Hoefle, *Angew. Chem.* **1969**, *81*, 1001; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 981.
[44] R. Rodebaugh, J. S. Debenham, B. Fraser-Reid, *Tetrahedron Lett.* **1996**, *37*, 5477.
[45] J. Arnarp, M. Haraldsson, J. Lönngren, *Carbohydr. Res.* **1981**, *97*, 307.
[46] J. Alais, A. Veyrieres, *J. Chem. Soc. Perkin Trans. 1* **1981**, 377.
[47] V. K. Srivastava, C. Schuerch, *Tetrahedron Lett.* **1979**, *20*, 3269.
[48] C. Unverzagt, *Carbohydr. Res.* **1997**, *305*, 423.
[49] O. Kanie, S. C. Crawley, M. M. Palcic, O. Hindsgaul, *Carbohydr. Res.* **1993**, *243*, 139.
[50] H. Weiss, C. Unverzagt, *Angew. Chem.* **2003**, *115*, 4389; *Angew. Chem. Int. Ed.* **2003**, *42*, 4261.

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