Synthesis of a Core Trisaccharide as a Versatile Building Block for N-Glycans and Glycoconjugates

Carlo Unverzagt*[a, b]

Dedicated to Professor Lutz Tietze on the occasion of his 60th birthday

Abstract: N-Linked oligosaccharides from glycoproteins (N-glycans) can be conveniently assembled with a building block approach. A protected form of the core trisaccharide (β-mannosyl chitobiose) was identified as a key building block. The chitobiose part of the core trisaccharide was built from a glycosyl fluoride, which served as a precursor for the reducing GlcNAc azide and the inner GlcNAc moiety. β-Mannosylation was accomplished at the trisaccharide stage by intramolecular inversion of a β-glucosyl chitobiose. The benzylidene protection of the β-mannoside and the azido group at the reducing end of the core trisaccharide allow modular synthesis of N-glycans and their glycoconjugates.

Keywords: β-mannosides · carbohydrates · glycosylation · glycoproteins · oligosaccharide

Introduction

Asparagine-linked oligosaccharides (N-glycans) are a common feature of eucaryotic proteins that are surface bound or secreted.[1] The biological properties of glycoproteins are influenced by the structure of their oligosaccharides. Despite a wide knowledge of structural details of N-glycans little is known about detailed structure – activity relationships of entire glycoproteins.[2] One of the few glycoproteins studied thoroughly is recombinant human erythropoietin (EPO), used in the treatment of cancer and kidney patients. The serum halflife of EPO and its modification (NESP) can be tuned by the extent of N-glycosylation.[3]

A combinatorial biochemical machinery is installing N-glycans as a posttranslational modification leading to a large variety of possible oligosaccharide structures. The resulting glycoproteins are therefore heterogeneous mixtures of individual glycoforms. The diversity of natural N-glycans is thus impairing the isolation of these compounds from glycoproteins.[4–6] Therefore, the synthesis of N-glycans has been used to overcome the shortage of material for biological studies. While only few groups pioneered the chemical synthesis of N-glycans,[7–9] the last decade has seen considerable increase in activity.[10–15] Up to now several strategies have been developed leading to complete N-glycans or partial structures.[16] The key challenges of the syntheses have been the construction of the β-mannoside[17] followed by the incorporation of terminal sialic acid and the deprotection of the final products. Besides the chemical approaches the core trisaccharide has also been synthesized by enzymatic methods.[18]

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Results and Discussion

The total synthesis of N-glycans and their derivatives can be facilitated by combining chemical and enzymatic approaches.[19] Our initial goal in N-glycan synthesis was the heptasaccharide – asparagine conjugate **1**,[20] which can serve both as a building block for glycopeptides[21] and as an acceptor for enzymatic elongation of the sugar chains.[19] Retrosynthetic analysis of **1** (Scheme 1) suggested a division into building blocks of general applicability.[22] A protected core trisaccharide was desired which would permit good coupling to various building blocks for the antennae and allow the convenient construction of glycoconjugates through an amino function at the reducing end. Furthermore, the protected core trisaccharide should be available in amounts over 10 g on a typical laboratory scale to yield sufficient quantities of N-glycans after deprotection. The building block meeting these requirements was found in trisaccharide **2** (see Scheme 1). An optimized approach to this versatile compound is described in the following.

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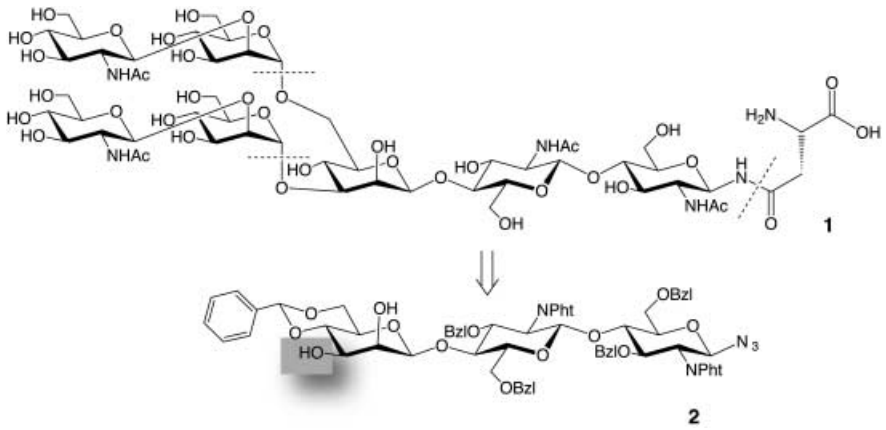


Scheme 1. Retrosynthetic analysis of the heptasaccharide-asparagine **1** suggests the disconnection to the core trisaccharide **2** as the key building block for N-glycans.

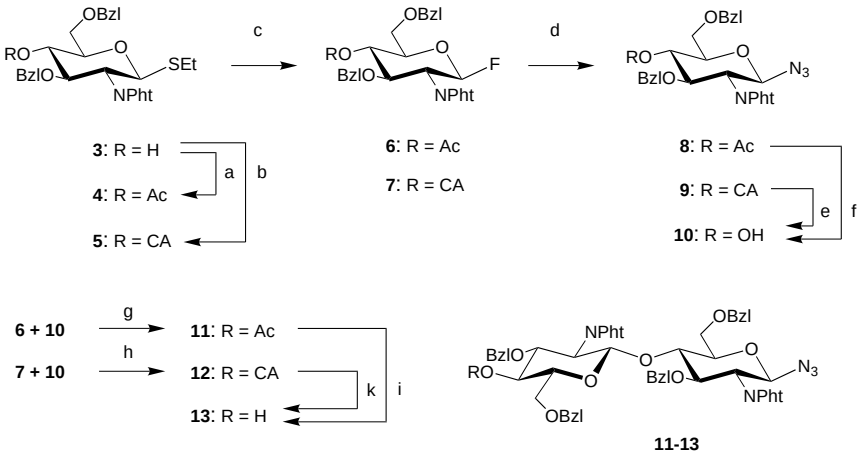
Synthesis of chitobiosylazide: The early introduction of an azido functionality[23, 24] at the reducing end of the core trisaccharide **2** is advantageous because this moiety remains neutral under most reaction conditions applied in carbohydrate chemistry. Glycosyl azides can also be converted into glycosyl donors after derivatization.[25, 26] The stable azido group at the anomeric center protects the labile amino function required for the attachment of aspartic acid[27] or spacers. Glycosyl azides are obtained from the corresponding fluorides[28] in high yield. The latter can be generated conveniently from thioglycosides.[29, 30]

The starting material for the intermediate chitobiosyl azide **13** (Scheme 2) was the thioglycoside **3**,[31, 32] a useful intermediate, which is accessible on a 100 g scale in a five-step sequence starting from glucosamine hydrochloride. First, the hydroxyl group was acetylated and the resulting thioglycoside **4** was converted to fluoride **6** with *N*-bromosuccinimide (NBS) and HF/pyridine according to Nicolaou.[29] When activated with $BF_3 \cdot Et_2O$ the fluoride[28] **6** readily reacted with trimethylsilylazide to give the β-azide **8**. The deacetylation using potassium methoxide in dioxane/methanol 1:1 proceeded slowly and gave only 67% yield. A nearly identical R_f value of compounds **8** and **10** required monitoring of the reaction by ^{1}H NMR spectroscopy. The cleavage appears to be sterically hindered[33] and led to phthalimido ring opening during the prolonged reaction time. Similar difficulties occurred for the deacetylations at the di- and trisaccharide stage, which suggested the synthesis of an alternative set of building blocks carrying chloroacetyl groups. After introduction of the chloroacetyl moiety[34] (**5**) the following transformations to fluoride **7** and azide **9** proceeded analogously in yields over 90%. With a base lability increased by three orders of magnitude,[35] a dechloroacetylation occurs much faster than the cleavage of the corresponding acetate. The improved cleavage conditions permitted the deprotection of compound **9** to furnish the acceptor **10** in 92% yield.

Acceptor **10** was treated with the glycosylfluorides **6** and **7** activated by $BF_3 \cdot Et_2O$ to give the chitobiosyl azides **11** and **12** in good yields. In the following deacylation step the chloroacetyl moiety could be readily removed. Compound **13** is equipped with a combination of protective groups suitable for the construction of the β-mannoside. The neighboring benzyl groups increase the reactivity[36] of the OH-4″ group; the phthalimido groups are known to be inert during nucleophilic substitutions and glycosylation reactions.

Synthesis of β-mannosides: The β-mannosidic linkage[17] was established following a procedure introduced by Kunz.[32, 37, 38] This method is based on the intramolecular inversion of 4,6-benzylidenated β-glucosides, which excludes unwanted anomeric or epimeric side products. For the synthesis of N-glycans with title compound **2** it was highly advantageous that the β-mannosyl moiety was not blocked by permanent protective groups, for example benzyl ethers, but could be easily debenzylidenated at the desired time under mild conditions.[32]

To introduce the β-glucosyl moiety the Kunz group used a glucosyl bromide,[32] which gave also orthoesters under glycosylation conditions. Therefore, we converted peracetylated 3-phenylcarbamoyl glucose **14**[32] to the anomeric fluoride **15** by reaction with HF/pyridine (Scheme 3).[39] Elongation of the chitobiosyl acceptor **13** with the donor **15** under $BF_3 \cdot Et_2O$ activation yielded 85% of the



Scheme 2. a) Ac_2O/pyridine (quant.); b) chloroacetic anhydride/pyridine, CH_2Cl_2 (93%); c) HF/pyridine, NBS, CH_2Cl_2 (93% **6**), (96% **7**); d) TMS-N_3, $BF_3 \cdot OEt_2$, CH_2Cl_2 (91% **8**), (92% **9**); e) MeOH, dioxane, NaOMe (67%); f) K_2CO_3, MeOH, CH_2Cl_2 (92%); g) $BF_3 \cdot OEt_2$, CH_2Cl_2 (83%); h) $BF_3 \cdot OEt_2$, CH_2Cl_2 (86%); i) K_2CO_3, MeOH, dioxane (79%); k) K_2CO_3, MeOH, CH_2Cl_2 (94%).

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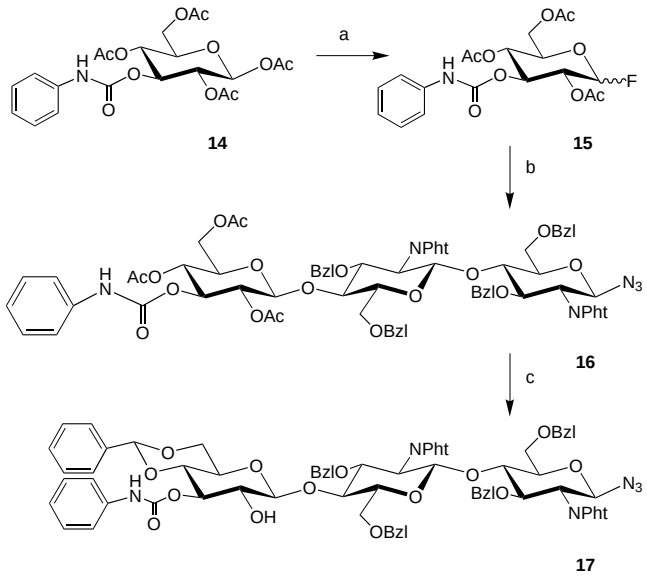


Scheme 3. a) HF/pyridine (56%); b) **13**, $BF_3 \cdot OEt_2$, CH_2Cl_2 (85%); c) 1) K_2CO_3, MeOH, dioxane, 2) benzaldehyde dimethylacetal, *p*-TosOH, CH_3CN (44% over two steps).

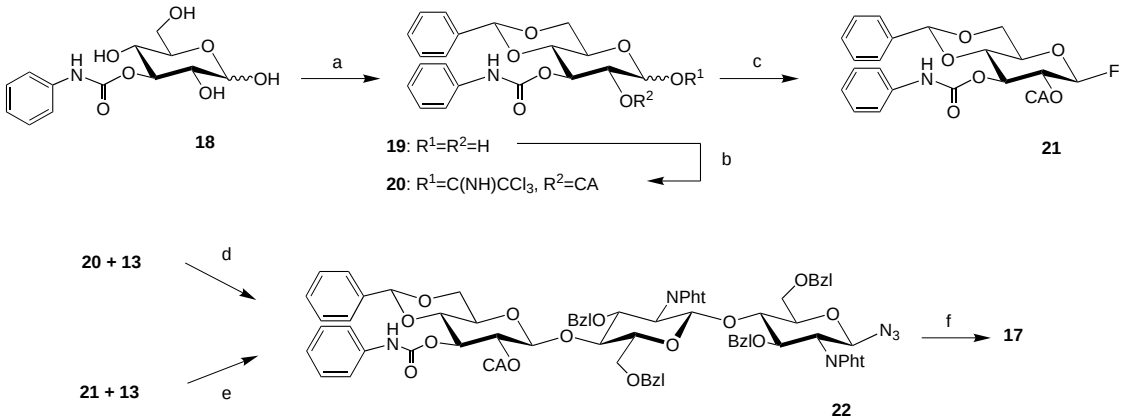
β-gluco configured trisaccharide **16**. Prior to the inversion of the β-glucoside to the β-mannoside the 2-OH″ group had to be selectively activated. Removal of the acetates and regioselective benzylidenation of the intermediate triol gave the trisaccharide **17**. This compound was suitably functionalized for the ensuing inversion sequence to the β-mannoside.

Unfortunately, compound **17** was obtained in only 44% yield after the two-step reaction. The main reason was again a difficult removal of acetyl groups, in particular of the sterically hindered 2″-acetate.[40] It is known that the deprotection of esters in the vicinity of sterically demanding residues is impaired. During the prolonged reaction times (1.5 d) the base labile phthalimido groups were also cleaved.

To circumvent these difficulties the novel β-glucosyl donor **20** (Scheme 4) was constructed, which was already equipped with a benzylidene acetal and carried an easily removable chloroacetyl group[41] in position 2. Thus, the critical change of protective groups at the trisaccharide stage was avoided. In contrast to 3-phenylcarbamoyl β-glucosides, the free 3-phenylcarbamoyl glucose **18** could not be acetalized selectively with benzaldehyde dimethylacetal. However, the traditional procedure with benzaldehyde in the presence of zinc chloride avoided the overreaction and gave the crystalline benzylidene acetal **19**. After chloroacetylation the anomeric center was liberated chemoselectively with hydrazine acetate and converted to the trichloroacetimidate **20** according to Schmidt.[42] The imidate **20** could be converted to the β-fluoride **21**, which was formed stereoselectively through neighboring-group participation.

Initial experiments to glycosylate the chitobiosyl azide **13** with the imidate **20** showed only little conversion when $BF_3 \cdot Et_2O$ was employed. Use of trimethylsilyl triflate[42] (TMSOTf) gave the β-glucoside **22** in 62% yield. The quality of the reagent was crucial for the success of the reaction. Only freshly opened trimethylsilyl triflate could suppress orthoester formation, which suggests that the deactivating 2-chloroacetyl moiety allows for the reaction to proceed via an intermediate orthoester. Furthermore, the yields were lowered by trimethylsilylation of the acceptor **13**, which was desilylated and recycled after large-scale reactions. These problems were avoided using the fluoride **21** as a donor. The glucosyl fluoride could be activated with $BF_3 \cdot Et_2O$ and did not show formation of the orthoester. From compounds **21** and **13** the chloroacetylated trisaccharide **22** was obtained in 45% yield, which was conveniently deacylated (**17**) by mild base treatment. For the removal of the chloroacetyl moiety alternative methods[43] are known, however, the rapid and easily adjustable procedure favored the use of potassium carbonate in methanol/dichloromethane.

The conversion of the β-*gluco* configured trisaccharide **17** to the β-mannoside **2** was achieved by a four-step procedure. This reaction sequence was previously established for mono- or disaccharides[32] and was successfully applied to the trisaccharide **17**. First, the 2″-OH function was converted to a good leaving group with trifluoromethanesulfonic acid anhydride and pyridine (Scheme 5). The intermediate triflate **17a** was substituted by an intramolecular nucleophilic attack of the neighboring carbonyl group of the phenylcarbamoyl moiety. This was achieved by warming a solution of the triflate in DMF/pyridine to 65 °C. The initially formed β-*manno* configured iminocarbonate **17b** was unstable and was con-



Scheme 4. a) Benzaldehyde, $ZnCl_2$ (34%); b) 1) chloroacetic anhydride/pyridine, CH_2Cl_2, 2) hydrazine acetate, DMF; 3) trichloroacetonitrile, DBU, CH_2Cl_2 (over three steps 55%); c) HF/pyridine, CH_2Cl_2 (91%); d) TMSOTf, CH_2Cl_2 (62%); e) $BF_3 \cdot OEt_2$, CH_2Cl_2 (45%); f) K_2CO_3, MeOH/CH_2Cl_2 (89%).

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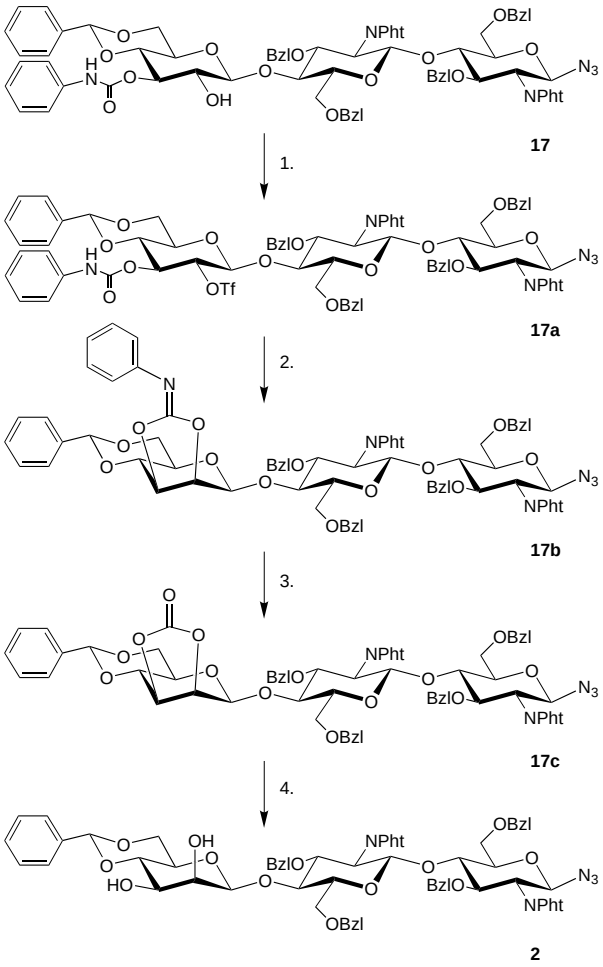

Scheme 5. 1) Tf_2O, pyridine, CH_2Cl_2; 2) DMF, pyridine, 65 °C; 3) AcOH, dioxane, water; 4) NaOMe, MeOH, CH_2Cl_2 (overall yield 70 %).

verted to the carbonate **17c** by mild acid hydrolysis. Deprotection of the carbonate **17c** by methanolysis gave the desired core trisaccharide **2** in 70 % yield over the reaction sequence.[22] The inversion at C-2″ was conducted as a one-pot reaction and every step was monitored by TLC. NMR spectroscopy confirmed the newly formed β-mannosidic linkage via the C-1″/H-1″ coupling constant of 163.3 Hz[44, 45] determined from an HMQC spectrum without decoupling.[46]

Following this approach the protected core trisaccharide **2** was obtained in overall amounts of more than 10 g. This building block has proven to be a key compound in the synthesis of several families of natural N-glycans[15, 47] with different substitution patterns.

Experimental Section

General methods: Solvents were dried according to standard methods. Melting points were determined on a Büchi apparatus and are uncorrected. Optical rotations were measured on a Perkin–Elmer 241 polarimeter at 589 nm. NMR spectra were recorded on Bruker AC 250 and AMX 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 a thioglycerine/HOAc (MB) or a *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). The reactions were monitored by thin-layer chromatography on coated aluminum plates (silica gel 60 GF_{254}, Merck Darmstadt). Spots were detected by UV light or by charring with a 1:1 mixture of 2 N H_2SO_4 and 0.2 % resorcine monomethyl ether in ethanol.

Ethyl 4-*O*-acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (4): Compound **3**[31, 32] (13.31 g, 24.9 mmol) was dissolved in pyridine (20 mL) and acetic anhydride (10 mL). After 20 h at ambient temperature the reaction mixture was concentrated and codistilled three times with toluene (50 mL). The residue was dried in high vacuo to yield **4** (14.35 g, quant.). $[\alpha]_D^{23} = +77.5^\circ$ ($c = 1.0$ in CH_2Cl_2); $R_f = 0.34$ (hexane/acetone 2:1); ^{1}H NMR (250 MHz, [D$_6$]DMSO): $\delta = 7.87-7.79$ (m, 4H, Pht), 7.25 (m, 5H, Ph), 6.92 (m, 5H, Ph), 5.30 (d, $J_{1,2} = 10.4$ Hz, 1H, H-1β), 5.00 (dd, $J_{4,5} = 9.8$ Hz, 1H, H-4), 4.56–4.44 (m, 3H, CH_2O), 4.35 (dd, $J_{3,4} = 8.1$ Hz, 1H, H-3), 4.26 (d, $J_{gem} = 12.2$ Hz, 1H, CH_2O), 4.05 (dd, $J_{2,3} = 10.4$ Hz, 1H, H-2), 3.90–3.83 (m, 1H, H-5), 3.59–3.47 (m, 2H, H-6a,b), 2.57 (m, 2H, SCH_2), 2.02 (s, 3H, OAc), 1.09 (t, $J = 7.4$ Hz, CH_3); ^{13}C NMR (62.5 MHz, [D$_6$]DMSO): $\delta = 168.8$ (C=O Ac), 166.9, 166.5 (C=O, Pht), 137.6, 136.9 (C-*i* Ph), 134.3 (C-4/5 Pht), 130.1 (C-1/2 Pht), 127.6, 127.4, 127.0, 126.8 (C-Ar), 122.9 (C-3/6 Pht), 80.0 (C-1), 77.1 (C-3), 76.1 (C-5), 73.0, 71.08 (CH_2O), 70.9 (C-4), 68.2 (C-6), 53.9 (C-2), 23.4 (CH_2), 20.7 (OAc), 15.0 (CH_3); elemental analysis calcd (%) for $C_{32}H_{33}NO_7S$ (575.68): C 66.77, H 5.78, N 2.43; found: C 66.69, H 5.56, N 2.57.

4-*O*-Acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosylfluoride (6): Thioglycoside **4** (12.6 g, 21.9 mmol) was dissolved in dichloromethane (130 mL) and cooled to 0 °C. *N*-Bromosuccinimide (5.83 g, 32.7 mmol) was added to the stirred solution followed by HF/pyridine complex (12.6 mL). The reaction was complete after 10 min (TLC: hexane/acetone 1.5:1). Subsequently, dichloromethane (130 mL) was added and the reaction mixture was extracted in a Teflon separatory funnel with water, aq HCl (3 ×) and aq Na_2CO_3. The organic phase was dried ($MgSO_4$), concentrated and purified by flash chromatography (hexane/acetone 2:1) to yield **6** (10.83 g, 92.7 %). The product was recrystallized from acetone/hexane. M.p. 100 °C; $R_f = 0.45$ (hexane/acetone 1.5:1); $[\alpha]_D^{23} = +76.4^\circ$ ($c = 0.5$ in CH_2Cl_2); ^{1}H NMR (250 MHz, [D$_6$]DMSO): $\delta = 7.88$ (m, 4H, Pht), 7.35 (m, 5H, Ph), 6.93 (m, 5H, Ph), 5.93 (dd, $J_{1,2} = 8.0$, $J_{1,F} = 53.6$ Hz, 1H, H-1β), 5.10 (dd, $J_{4,5} = 9.5$ Hz, 1H, H-4), 4.57–4.44 (m, 3H, CH_2O), 4.39 (dd, $J_{2,3} = J_{3,4} = 9.9$ Hz, 1H, H-3), 4.27 (d, $J_{gem} = 12.0$ Hz, 1H, CH_2O), 4.14 (m, 1H, H-2), 4.04 (m, 1H, H-5), 3.58 (m, 2H, H-6a,b), 2.05 (s, 3H, OAc); ^{13}C NMR (62.5 MHz, [D$_6$]DMSO): $\delta = 169.2$, 167.2 (C=O), 137.9, 137.3 (C-*i* Ph), 134.9 (C-4/5 Pht), 130.5 (C-1/2 Pht), 128.2–127.5 (C-Ar), 123.5 (C-3/6 Pht), 104.0 (d, $J_{C\text{-}1,F} = 212.3$ Hz, C-1), 75.9 (d, $J_{C\text{-}3,F} = 9.7$ Hz, C-3), 73.4 (CH_2O), 72.5 (C-5), 72.4 (CH_2O), 70.7 (C-4), 68.1 (C-6), 55.1 (d, $J_{C\text{-}2,F} = 21.8$ Hz, C-2), 20.6 (OAc); elemental analysis calcd (%) for $C_{30}H_{28}FNO_7$ (533.55): C 67.53, H 5.29, N 2.63; found: C 67.62, H 5.48, N 2.52.

4-*O*-Acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosylazide (8): Trimethylsilylazide (2.35 mL, 17.7 mmol) was added to a stirred solution of fluoride **6** (4 g, 7.5 mmol) in dry dichloromethane (70 mL). The reaction was initiated with $BF_3 \cdot OEt_2$ (300 μL, 2.4 mmol). After complete reaction (TLC: hexane/acetone 1.5:1) dichloromethane was added followed by extraction with dilute K_2CO_3. The organic phase was dried ($MgSO_4$), evaporated and purified by flash chromatography (hexane/acetone 2:1) to afford **8** (3.81 g, 91.3 %). $[\alpha]_D^{23} = +49.5^\circ$ ($c = 0.5$ in dichloromethane); $R_f = 0.48$ (hexane/acetone 1.5:1); ^{1}H NMR (250 MHz, [D$_6$]DMSO): $\delta = 7.9-7.7$ (m, 4H, Pht), 7.4–7.25 (m, 5H, Ph), 6.94 (m, 5H, Ph), 5.54 (d, $J_{1,2} = 9.5$ Hz, 1H, H-1β), 5.04 (dd, $J_{3,4} = J_{4,5} = 9.5$ Hz, 1H, H-4), 4.57–4.47 (m, 3H, CH_2O), 4.37 (dd, $J_{2,3} = 10.1$ Hz, 1H, H-3), 4.26 (d, $J_{gem} = 12.0$ Hz, 1H, CH_2O), 3.98 (m, 1H, H-5), 3.94 (dd, 1H, H-2), 3.6–3.5 (m, 2H, H-6a,b), 2.03 (s, 3H, OAc); ^{13}C NMR (125 MHz, [D$_6$]DMSO): $\delta = 169.3$, 167.0 broad (C=O), 138.1, 137.4 (C-*i* Ph), 134.9 (C-4/5 Pht), 130.6 (C-1/2 Pht), 128.2, 127.9, 127.6, 127.50, 127.47, 127.42 (C-Ar), 123.5 (C-3/6 Pht), 85.0 (C-1), 76.4 (C-3), 74.6 (C-5), 73.5 (CH_2O), 71.1 (C-4), 72.4 (CH_2O), 71.1 (C-4), 68.3 (C-6), 54.6 (C-2), 20.7 (OAc); elemental analysis calcd (%) for $C_{30}H_{28}N_4O_7$ (556.57): C 64.74, H 5.07, N 10.07; found: C 64.71, H 5.00, N 10.00.

3,6-Di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosylazide (10): *a) Starting from **8***: NaOMe (100 mg) was added to a stirred solution of acetate **8** (3.7 g, 6.65 mmol) in dioxane/methanol 1:1 (40 mL). The course of the reaction was monitored by ^{1}H NMR spectroscopy following the disappearance of the signal of the acetyl group. Two further portions of sodium methylate (100 mg each) were added after 30 min intervals. After

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complete reaction the solution was neutralized with the acidic ion exchange resin Amberlyst 15 H^+, filtered and concentrated. The residue was purified by flash chromatography (hexane/acetone 2.2:1) and gave **10** (2.3 g, 67.2 %).

b) Starting from ***9***: K_2CO_3 (200 mg) was added to a stirred solution of chloroacetate **9** (12.0 g, 20.3 mmol) in methanol/dichloromethane 1:2 (120 mL). After complete reaction (TLC: hexane/ethyl acetate 1.5:1) the solution was filtered, neutralized with acidic acid and concentrated. The residue was purified by flash chromatography (hexane/ethyl acetate 5:3) and gave **10** (9.6 g, 91.9 %). $[\alpha]_D^{23} = +17.2^\circ$ ($c = 0.5$ in CH_2Cl_2); $R_f = 0.45$ (hexane/ethyl acetate 1.5:1); ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 7.9 - 7.7$ (m, 4H, Pht), 7.4 – 7.33 (m, 5H, Ph), 6.93 – 6.86 (m, 5H, Ph), 5.74 (d, $J_{4,OH} =$ 7.2 Hz, 1H, OH-4), 5.42 (d, $J_{1,2} = 9.5$ Hz, 1H, H-1β), 4.78 (d, $J_{gem} = 12.2$ Hz, 1H, CH_2O), 5.58 (s, 2H, CH_2O), 4.42 (d, $J_{gem} = 12.2$ Hz, 1H, CH_2O), 4.14 (dd, $J_{3,4} = J_{2,3} = 9.6$ Hz, 1H, H-3), 3.86 – 3.82 (m, 2H, H-6a, H-2), 3.75 – 3.68 (m, 2H, H-6b, H-5), 3.54 (ddd, $J_{4,5} = 8.5$ Hz, 1H, H-4); ^{13}C NMR (125 MHz, [D$_6$]DMSO): $\delta = 167.3$ (C=O), 138.4, 138.1 (C-*i* Ph), 134.7 (C-4/5 Pht), 130.6 (C-1/2 Pht), 128.2 – 127.1 (C-Ar), 123.5 (C-3/6 Pht), 84.9 (C-1), 78.3 (C-3), 77.8 (C-5), 73.6, 72.3 (CH_2O), 71.1 (C-4), 68.9 (C-6), 54.6 (C-2); elemental analysis calcd (%) for $C_{28}H_{26}N_4O_6$ (514.53): C 65.36, H 5.09, N 10.89; found: C 65.45, H 5.33, N 10.78.

Ethyl 3,6-di-*O*-benzyl-4-*O*-chloroacetyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (5): Compound **3**[31, 32] (97 g, 181.8 mmol) and pyridine (100 mL) were dissolved in dichloromethane (500 mL) and cooled to 0 °C. Chloroacetic acid anhydride (45 g, 263.2 mmol) was added and the reaction was maintained at 0 °C until the starting material was consumed (TLC: hexane/ethyl acetate 1:1). Subsequently, the solution was diluted with dichloromethane (500 mL) and extracted with dilute K_2CO_3, dilute HCl (3 ×) and dilute K_2CO_3. The organic phase was dried ($MgSO_4$), concentrated and purified by flash chromatography (hexane/acetone 2:1) to give **5** (103.4 g, 93.2 %). $[\alpha]_D^{23} = +50.9^\circ$ ($c = 1$ in dichloromethane); $R_f = 0.66$ (hexane/EtOAc 1:1); ^{1}H NMR (250 MHz, [D$_6$]DMSO): $\delta = 7.9 - 7.7$ (m, 4H, Pht), 7.34 (m, 5H, Ph), 6.92 (m, 5H, Ph), 5.30 (d, $J_{1,2} = 10.4$ Hz, 1H, H-1β), 5.10 (dd, $J_{4,5} = 9.5$ Hz, 1H, H-4), 4.6 – 4.35 (m, 6H, CH_2O, CH_2Cl, H-3), 4.26 (d, $J_{gem} = 12.2$ Hz, 1H, CH_2O), 4.07 (dd, $J_{2,3} = 10.3$ Hz, 1H, H-2), 3.92 (m, 1H, H-5), 3.58 (m, 2H, H-6a,b), 2.68 – 2.47 (m, 2H, SCH_2), 1.09 (t, $J = 7.4$ Hz, CH_3); ^{13}C NMR (62.5 MHz, [D$_6$]DMSO): $\delta = 167.4$, 167.0, 166.4 (C=O), 138.4, 137.4 (C-*i* Ph), 134.9 (C-4/5 Pht), 130.6 (C-1/2 Pht), 128.2 – 127.4 (C-Ar), 123.5 (C-3/6 Pht), 80.5 (C-1), 77.5 (C-3), 76.3 (C-5), 73.7 (CH_2O), 74.1 (C-4), 72.5 (CH_2O), 68.5 (C-6), 54.4 (C-2), 41.0 (CH_2Cl), 23.5 (CH_2), 15.1 (CH_3); elemental analysis calcd (%) for $C_{32}H_{32}ClNO_7S$ (610.12): C 63.0, H 5.29, N 2.30; found: C 62.85, H 5.48, N 2.07.

3,6-Di-*O*-benzyl-4-*O*-chloroacetyl-2-deoxy-2-phthalimido-β-D-glucopyranosylfluoride (7): Thioglycoside **5** (112.0 g, 183.6 mmol) was dissolved in dichloromethane (800 mL) and cooled to 0 °C. *N*-Bromosuccinimide (42.5 g, 239.8 mmol) was added to the stirred solution followed by HF/pyridine complex (20 mL). The reaction was complete after 20 min (TLC: hexane/acetone 1.5:1). Subsequently, the reaction mixture was transferred to a Teflon separatory funnel and extracted with a mixture of water and ice (2 ×), dilute HCl (3 ×) and aq Na_2CO_3. The organic phase was dried ($MgSO_4$), concentrated and purified by flash chromatography (hexane/ethyl acetate 2:1) to yield **7** (99.6 g, 95.5 %). The product was recrystallized from acetone/hexane. M.p. 115 °C; $[\alpha]_D^{23} = +75.4^\circ$ ($c = 1$ in CH_2Cl_2); $R_f =$ 0.33 (hexane/acetone 2:1); ^{1}H NMR (250 MHz, [D$_6$]DMSO): $\delta = 7.85$ (m, 4H, Pht), 7.35 (m, 5H, Ph), 6.93 (m, 5H, Ph), 5.96 (dd, $J_{1,2} = 7.8$, $J_{1,F} =$ 53.4 Hz, 1H, H-1β), 5.22 (dd, $J_{3,4} = J_{4,5} = 9.4$ Hz, 1H, H-4), 4.6 – 4.4 (m, 6H, CH_2O, CH_2Cl, H-3), 4.27 (d, $J_{gem} = 12.0$ Hz, 1H, CH_2O), 4.2 (m, 1H, H-2), 4.13 (m, 1H, H-5), 3.64 (m, 2H, H-6a,b); ^{13}C NMR (62.5 MHz, [D$_6$]DMSO): $\delta = 167.2$, 166.4 (C=O, Ac, Pht), 137.9, 137.2 (C-*i* Ph), 134.9 (C-4/5 Pht), 130.5 (C-1/2 Pht), 128.2, 127.9, 127.6, 127.5 (C-Ar), 123.6 (C-3/6 Pht), 104.5 (d, $J_{C\text{-}1,F} = 212.4$ Hz, C-1), 75.3 (d, $J_{C\text{-}3,F} = 9.7$ Hz, C-3), 73.6 (CH_2O), 72.5 (CH_2O), 72.3 (C-4), 72.2 (C-5), 68.0 (C-6), 55.1 (d, $J_{C\text{-}2,F} =$ 22.0 Hz, C-2), 40.9 (CH_2Cl); elemental analysis calcd (%) for $C_{30}H_{27}ClFNO_7 \times H_2O$ (586.01): C 61.49, H 4.99, N 2.39; found: C 61.82, H 4.94, N 2.66.

3,6-Di-*O*-benzyl-4-*O*-chloroacetyl-2-deoxy-2-phthalimido-β-D-glucopyranosylazide (9): TMS-N_3 (20 mL, 150.6 mmol) followed by $BF_3 \cdot OEt_2$ (2 mL, 16.3 mmol) was added to a stirred suspension of fluoride **7** (40.0 g, 70.4 mmol) and ground molecular sieves 4 Å (20 g) in dry dichloromethane (400 mL). After complete reaction (TLC: hexane/acetone 2:1) the mixture was diluted with dichloromethane and filtered. The organic phase was washed with aq K_2CO_3, dried ($MgSO_4$) and concentrated. The residue was purified by flash chromatography (hexane/acetone 2:1) to yield **9** (38.2 g, 91.8 %). Crystals were obtained by trituration of the product with methanol. M.p. 86 – 91 °C; $[\alpha]_D^{23} = +45.0^\circ$ ($c = 0.5$ in dichloromethane); $R_f = 0.37$ (hexane/acetone 2:1); ^{1}H NMR (250 MHz, [D$_6$]DMSO): $\delta = 7.85$ (m, 4H, Pht), 7.35 (m, 5H, Ph), 6.92 (m, 5H, Ph), 5.57 (d, $J_{1,2} = 9.4$ Hz, 1H, H-1β), 5.15 (dd, $J_{4,5} = 9.5$ Hz, 1H, H-4), 4.6 – 4.4 (m, 6H, CH_2O, CH_2Cl, H-3), 4.25 (d, $J_{gem} = 12.0$ Hz, 1H, CH_2O), 4.03 (m, 1H, H-5), 3.97 (dd, $J_{2,3} =$ 10.6 Hz, 1H, H-2), 3.63 (m, 2H, H-6a,b); ^{13}C NMR (62.5 MHz, [D$_6$]DMSO): $\delta = 167.2$, 166.4 (C=O, ClAc, Pht), 138.0, 137.3 (C-*i* Ph), 134.9 (C-4/5 Pht), 130.5 (C-1/2 Pht), 128.2, 127.9, 127.5 (C-Ar), 123.5 (C-3/6 Pht), 84.9 (C-1), 76.2 (C-3), 74.3 (C-5), 73.6 (CH_2O), 72.6 (C-4), 72.4 (CH_2O), 68.0 (C-6), 54.5 (C-2), 40.9 (CH_2Cl); ESI-MS: *m*/*z*: calcd for $C_{30}H_{27}ClN_4O_7$: 590.16; found: 613.26 $[M+Na]^+$.

***O*-(4-*O*-Acetyl-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 (11)**: A suspension of azide **10** (3.0 g, 5.8 mmol), fluoride **6** (3.9 g, 7.3 mmol) and ground molecular sieves 4 Å (7 g) in dry dichloromethane (70 mL) was stirred for 30 min at room temperature. $BF_3 \cdot OEt_2$ (150 µL, 1.2 mmol) was added and the reaction was allowed to proceed for 1 h (TLC: hexane/acetone 1.5:1). The suspension was filtered over Celite, washed with dichloromethane followed by extraction with aq Na_2CO_3. The organic phase was dried ($MgSO_4$), concentrated and the residue was purified by flash chromatography (hexane/acetone 2.3:1) to give **11** (5.0 g, 83.4 %). $[\alpha]_D^{23} = +26.5^\circ$ ($c = 0.5$ in CH_2Cl_2); $R_f = 0.42$ (hexane/acetone 1.5:1); ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 8.0 - 7.7$ (m, 8H, Pht), 7.4 – 7.2 (m, 10H, Ph), 6.95 – 6.80 (m, 10H, Ph), 5.31 (d, $J_{1,2} = 7.2$ Hz, 1H, H-1′β), 5.29 (d, $J_{1,2} = 9.0$ Hz, 1H, H-1β), 5.01 (dd, $J_{3,4} = J_{4,5} = 9.5$ Hz, 1H, H-4′), 4.81 (d, $J_{gem} = 12.3$ Hz, 1H, CH_2O), 4.54 – 4.36 (m, 7H, CH_2O, H-3′), 4.26 (d, $J_{gem} = 12.0$ Hz, 1H, CH_2O), 4.12 – 4.07 (m, 3H, H-2′, H-3, H-4), 3.80 (dd, $J_{2,3} = 10.6$ Hz, 1H, H-2), 3.62 – 3.54 (m, 3H, H-5, H-5′, H-6a′), 3.49 (d, $J_{gem} = 10.9$ Hz, 1H, H-6a), 3.41 (dd, $J_{vic} = 5.5$, $J_{gem} = 11.2$ Hz, 1H, H-6b′), 3.37 (dd, $J_{vic} = 3.8$ Hz, 1H, H-6b), 2.03 (OAc); ^{13}C NMR (125 MHz, [D$_6$]DMSO): $\delta = 169.4$, 167.1 (C=O), 138.2, 138.0, 137.9, 137.4 (C-*i* Ph), 134.9, 134.8 (C-4/5 Pht), 130.6 (C-1/2 Pht), 128.2 – 127.0 (C-Ar), 123.5 (C-3/6 Pht), 96.4 (C-1′), 84.8 (C-1), 76.3 (C-3′), 76.1 (C-3), 75.6 (C-5), 75.1 (C-4), 73.7, 73.5 (CH_2O), 73.0 (C-5′), 72.5, 71.7 (CH_2O), 71.5 (C-4′), 68.3 (C-6′), 67.6 (C-6), 55.7 (C-2′), 54.6 (C-2), 20.6 (OAc); elemental analysis calcd (%) for $C_{58}H_{53}N_5O_{13} \times 0.5\,H_2O$ (1028.08): C 67.17, H 5.25, N 6.75; found: C 67.07, H 5.07, N 6.42.

***O*-(3,6-Di-*O*-benzyl-4-*O*-chloroacetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1 → 4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosylazide (12)**: A suspension of azide **10** (13.0 g, 25.3 mmol), fluoride **7** (17.0 g, 29.9 mmol) and ground molecular sieves 4 Å (22 g) in dry dichloromethane (350 mL) was stirred for 30 min at room temperature. $BF_3 \cdot OEt_2$ (1.46 mL, 11.9 mmol) was added and the reaction was allowed to proceed for 1 h (TLC: hexane/acetone 1.5:1). The suspension was filtered over Celite, washed with dichloromethane followed by extraction with aq Na_2CO_3. The organic phase was dried ($MgSO_4$), concentrated and the residue was purified by flash chromatography (hexane/acetone 2:1) furnishing **12** (23.12 g, 86.1 %). $[\alpha]_D^{23} = +17.6^\circ$ ($c = 0.5$ in dichloromethane); $R_f = 0.36$ (hexane/acetone 1.5:1); ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta =$ 7.9 – 7.7 (m, 8H, Pht), 7.4 – 7.2 (m, 10H, Ph), 6.92 – 6.79 (m, 10H, Ph), 5.31 (d, $J_{1,2} = 7.9$ Hz, 1H, H-1′β), 5.29 (d, $J_{1,2} = 9.2$ Hz, 1H, H-1β), 5.12 (dd, $J_{3,4} =$ $J_{4,5} = 9.4$ Hz, 1H, H-4′), 4.81 (d, $J_{gem} = 12.3$ Hz, 1H, CH_2O), 4.56 (d, $J_{gem} =$ 12.0 Hz, 1H, CH_2O), 4.50 (d, $J_{gem} = 12.0$ Hz, 1H, CH_2O), 4.44 – 4.38 (m, 7H, CH_2O, CH_2Cl, H-3′), 4.26 (d, $J_{gem} = 12.1$ Hz, 1H, CH_2O), 4.16 – 4.05 (m, 3H, H-2′, H-3, H-4), 3.81 (dd, $J_{2,3} = 10.5$ Hz, 1H, H-2), 3.63 – 3.55 (m, 3H, H-5, H-5′, H-6a′), 3.49 (d, $J_{gem} = 10.8$ Hz, 1H, H-6a), 3.45 (dd, $J_{vic} = 5.0$, $J_{gem} = 11.1$ Hz, 1H, H-6b′), 3.37 (dd, $J_{vic} = 3.7$ Hz, 1H, H-6b); ^{13}C NMR (125 MHz, [D$_6$]DMSO): $\delta = 168.1$, 167.1, 166.5 (C=O), 138.3, 138.1, 138.0, 137.4 (C-*i* Ph), 134.9, 134.8 (C-4/5 Pht), 130.6 (C-1/2 Pht), 128.3 – 127.0 (C-Ar), 123.6, 123.4 (C-3/6 Pht), 96.5 (C-1′), 84.8 (C-1), 76.2 (C-3′, C-3′), 75.6 (C-5), 75.2 (C-4), 73.8, 73.7 (CH_2O), 73.1 (C-4′), 72.7 (C-5′), 72.6, 71.7 (CH_2O), 68.1 (C-6′), 67.6 (C-6), 55.8 (C-2′), 54.6 (C-2), 41.0 (CH_2Cl); elemental analysis calcd (%) for $C_{58}H_{52}ClN_5O_{13}$ (1062.53): C 65.56, H 4.93, N 6.59; found: C 65.39, H 4.89, N 6.50.

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 (13)**: *a) Starting from* ***11: Disaccharide **11** (4.1 g, 3.99 mmol) was dissolved in dioxane/methanol 1:1 (80 mL) and stirred for 36 h at +4 °C with

potassium carbonate (350 mg). The suspension was filtered, neutralized with acetic acid and concentrated. The residue was purified by flash chromatography (hexane/acetone 2:1) and gave title compound **13** (3.1 g, 78.7 %).

b) *Starting from **12***: Disaccharide **12** (14.0 g, 13.2 mmol) was dissolved in methanol/dichloromethane 1:2 (120 mL) and stirred with potassium carbonate (30 mg). After complete reaction (TLC: hexane/acetone 1.5:1) the suspension was filtered, neutralized with acetic acid and concentrated. The residue was purified by flash chromatography (hexane/acetone 1.5:1) and yielded **13** (12.2 g, 93.7 %). $[\alpha]_D^{23} = -3.3^\circ$ ($c = 0.5$ in CH_2Cl_2); $R_f = 0.22$ (hexane/acetone 1.5:1); ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 7.95-7.7$ (m, 8H, Pht), 7.4–7.2 (m, 10H, Ph), 6.95–6.80 (m, 10H, Ph), 5.63 (d, $J_{4,OH} = 7.2$ Hz, 1H, OH-4), 5.29 (d, $J_{1,2} = 9.1$ Hz, 1H, H-1β), 5.27 (d, $J_{1,2} = 7.1$ Hz, 1H, H-1′β), 4.82 (d, $J_{gem} = 12.2$ Hz, 1H, CH_2O), 4.77 (d, $J_{gem} = 12.2$ Hz, 1H, CH_2O), 4.60 (d, $J_{gem} = 12.4$ Hz, 1H, CH_2O), 4.48 (d, $J_{gem} = 12.4$ Hz, 1H, CH_2O), 4.45–4.38 (m, 4H, CH_2O), 4.15 (dd, $J_{3,4} = 8.4$ Hz, 1H, H-3′), 3.98 (dd, $J_{2,3} = 10.5$ Hz, 1H, H-2′), 3.85–3.80 (m, 2H, H-2, H-6a′), 3.60 (m, 1H, H-5), 3.56–3.48 (m, 3H, H-6b′, H-4′, H-6a), 3.43 (m, 1H, H-5′), 3.37 (dd, $J_{vic} = 3.6$, $J_{gem} = 11.3$ Hz, 1H, H-6b); ^{13}C NMR (125 MHz, [D$_6$]DMSO): $\delta =$ 168.2, 167.1 (C=O), 138.8, 138.3, 138.1, 138.0 (C-*i* Ph), 134.8 (C-4/5 Pht), 130.8, 130.6 (C-1/2 Pht), 128.2–127.0 (C-Ar), 123.4 (C-3/6 Pht), 96.5 (C-1′), 84.9 (C-1), 78.4 (C-3′), 76.1 (C-3, C-5′), 75.8 (C-5), 74.8 (C-4), 73.6, 72.4, 71.71 (CH_2O), 71.65 (C-4′), 68.9 (C-6′), 67.5 (C-6), 55.9 (C-2′), 54.6 (C-2); elemental analysis calcd (%) for $C_{56}H_{51}N_5O_{12}$ (986.05): C 68.21, H 5.21, N 7.10; found: C 68.09, H 5.15, N 7.02.

2,4,6-Tri-*O*-acetyl-3-*O*-(*N*-phenylcarbamoyl)-α-D-glucopyranosylfluoride (15): Acetate **14**[32] (11.0 g, 23.5 mmol) was dissolved in HF/pyridine (20 mL). After 20 h at ambient temperature the mixture was added to dichloromethane (200 mL) and ice (200 mL) in a Teflon separatory funnel. The organic phase was extracted with aq HCl (3×), aq K_2CO_3 and dried ($MgSO_4$). After removal of the solvent the residue was purified by flash chromatography (hexane/acetone 2.5:1) and furnished fluoride **15** (5.6 g, 55.7 %). $[\alpha]_D^{23} = +57.6^\circ$ ($c = 1$ in dichloromethane); $R_f = 0.38$ (hexane/acetone 1.5:1); ^{1}H NMR (250 MHz, [D$_6$]DMSO): $\delta = 9.8$ (s, 1H, NH), 7.5–7.0 (m, 5H, Ph), 5.94 (dd, $J_{1,F} = 52.9$, $J_{1,2} = 2.5$ Hz, 1H, H-1α), 5.32 (dd, $J_{2,3} = J_{3,4} = 9.9$ Hz, 1H, H-3), 5.15 (dd, $J_{4,5} = 8.8$ Hz, 1H, H-4), 5.06 (ddd, $J_{2,F} = 24.8$ Hz, 1H, H-2), 4.28–4.2 (m, 2H, H-5, H-6a), 4.10 (dd, $J_{gem} = 14.4$, $J_{vic} = 4.5$ Hz, 1H, H-6b), 2.04, 1.98 (2s, 9H, OAc); ^{13}C NMR (125 MHz, [D$_6$]DMSO): $\delta = 169.9$, 169.4, 169.1 (C=O), 152.3 (C=O urethane), 138.6 (C-*i* Ph), 128.7, 122.8, 118.4 (C-Ar), 104.0 (d, $J_{C\text{-}1,F} = 226.4$ Hz, C-1), 69.7 (C-5), 69.4 (d, $J_{C\text{-}2,F} = 24.2$ Hz, C-2), 69.3 (C-3), 67.2 (C-4), 61.4 (C-6), 20.4, 20.2 (OAc); elemental analysis calcd (%) for $C_{19}H_{22}FNO_9$ (427.38): C 53.4, H 5.19, N 3.28; found: C 53.51, H 5.10, N 3.44.

***O*-(2,4,6-Tri-*O*-acetyl-3-*O*-(*N*-phenylcarbamoyl)-β-D-glucopyranosyl)-(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)**: Disaccharide **13** (2.9 g, 2.9 mmol), fluoride **15** (1.95 g, 4.6 mmol) and ground molecular sieves 4 Å (3.4 g) in dry dichloromethane (50 mL) were stirred for 30 min at room temperature. $BF_3 \cdot OEt_2$ (500 μL, 4.1 mmol) was added and the reaction was allowed to proceed for 7 h (TLC: hexane/acetone 1.5:1). The suspension was filtered over Celite, washed with dichloromethane followed by extraction with aq Na_2CO_3. The organic phase was dried ($MgSO_4$), concentrated and the residue was purified by flash chromatography (hexane/acetone 2:1) to yield trisaccharide **16** (3.5 g, 85.4 %). $[\alpha]_D^{23} = -7.5^\circ$ ($c = 0.5$ in dichloromethane); $R_f = 0.28$ (hexane/acetone 1.5:1); ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 9.7$ (s, 1H, NH), 7.9–7.65 (m, 8H, Pht), 7.50–7.20 (m, 20H, Ar), 7.02–6.8 (m, 10H, Ar), 5.28 (d, $J_{1,2} = 9.5$ Hz, 1H, H-1β), 5.27 (m, 1H, H-3″), 5.25 (d, $J_{1,2} = 8.5$ Hz, 1H, H-1′β), 4.95 (dd, $J_{3,4} = J_{4,5} = 9.6$ Hz, 1H, H-4″), 4.90–4.86 (m, 2H, H-1″, H-2″), 4.83–4.78 (m, 2H, CH_2O), 4.63 (d, $J_{gem} = 12.3$ Hz, 1H, CH_2O), 4.57 (d, $J_{gem} = 12.3$ Hz, 1H, CH_2O), 4.41 (m, 3H, CH_2O), 4.31 (d, $J_{gem} = 12.3$ Hz, 1H, CH_2O), 4.20–4.06 (m, 4H, H-3′, H-3, H-4, H-6a″), 4.03 (dd, $J_{2,3} = 10.5$ Hz, 1H, H-2′), 3.94–3.89 (m, H-4′, H-5″, H-6b″), 3.83–3.78 (m, 2H, H-2, H-6a′), 3.61–3.58 (m, 2H, H-5, H-6b′), 3.50 (dd, $J_{vic} < 1.0$, $J_{gem} = 11.6$ Hz, 1H, H-6a), 3.4–3.3 (m, 2H, H-5, H-6b); ^{13}C NMR (125 MHz, [D$_6$]DMSO): $\delta = 169.8$, 169.2, 168.9, 168.1, 167.1 (C=O), 152.42 (C=O urethane), 138.7, 138.31, 138.25, 138.1, 138.0 (C-*i* Ar), 134.8 (C-4/5 Pht), 130.6 (C-1/2 Pht), 128.8, 128.3, 128.2, 127.8, 127.7, 127.5, 127.4, 127.2, 127.0 (C-Ar), 123.5 (C-3/6 Pht), 122.8, 118.5 (C-Ar), 99.8 (C-1″), 96.3 (C-1′), 84.9 (C-1), 78.4 (C-4′), 76.8 (C-3′), 76.1 (C-3), 75.6 (C-5), 75.0 (C-4), 74.7 (C-5′), 73.8, 73.7 (CH_2O), 72.4 (CH_2O, C-3″), 71.7 (CH_2O), 71.5 (C-2″), 70.6 (C-5″), 68.4 (C-4″), 67.6 (C-6), 67.5 (C-6′), 61.7 (C-6″), 55.8 (C-2′), 54.7 (C-2), 20.4, 20.3 (OAc); elemental analysis calcd (%) for $C_{75}H_{72}N_6O_{21}$ (1393.42): C 64.65, H 5.21, N 6.03; found: C 64.81, H 5.24, N 5.66.

4,6-*O*-Benzylidene-3-*O*-(*N*-phenylcarbamoyl)-D-glucopyranoside (19): Compound **18**[32] (101 g, 337 mmol) and anhydrous zinc chloride (25 g) were suspended in benzaldehyde (270 mL) and stirred for 3 d at ambient temperature (TLC: hexane/acetone 1:1). The reaction was added to ethyl acetate/water 1:1 (1.6 L). After thorough extraction a first fraction of product crystallized. The crystals were filtered off and washed with water and diethyl ether. The organic phase was dried ($MgSO_4$) and diluted with hexane. A second crop of crystalline product was filtered off and washed with water and diethyl ether. The fractions of crystalline **19** were combined (45 g, 34.4 %). M.p. 179 °C; $[\alpha]_D^{23} = +2.2^\circ$ (1, MeOH/DMF 5:1); $R_f = 0.42$ (hexane/acetone 1:1); in DMSO compound **19** was present as a mixture of anomers (α:β = 2:1); α-anomer: ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 9.61$ (s, 1H, NH), 7.5–7.2 (m, 9H, Ph), 6.95 (m, 1H, Ph), 6.88 (d, $J_{1,OH} = 4.8$ Hz, 1H, OH-1), 5.59 (s, 1H, =C*H*-Ph), 5.15 (dd, $J_{2,3} = J_{3,4} = 9.7$ Hz, 1H, H-3), 5.08 (dd, $J_{1,2} = 3.6$ Hz, 1H, H-1α), 5.02 (d, $J_{2,OH} = 7.7$ Hz, 1H, OH-2), 4.16 (dd, $J_{gem} = 10.2$, $J_{vic} = 4.5$ Hz, 1H, H-6a), 3.93 (m, 1H, H-5), 3.74 (dd, $J_{vic} = 10.2$ Hz, 1H, H-6b), 3.62 (m, 1H, H-4), 3.55 (m, 1H, H-2); β-anomer: ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 9.63$ (s, 1H, NH), 7.5–7.2 (m, 9H, Ph), 7.07 (d, $J_{1,OH} = 6.5$ Hz, 1H, OH-1), 6.95 (m, 1H, Ph), 5.60 (s, 1H, =C*H*-Ph), 5.48 (d, $J_{2,OH} = 5.7$ Hz, 1H, OH-2), 4.99 (dd, $J_{2,3} = J_{3,4} = 9.5$ Hz, 1H, H-3), 4.63 (dd, $J_{1,2} = 7.5$ Hz, 1H, H-1β), 4.22 (dd, $J_{gem} = 10.2$ Hz, $J_{vic} = 5.0$ Hz, 1H, H-6a), 3.74 (dd, $J_{vic} = 10.2$ Hz, 1H, H-6b), 3.64 (m, 1H, H-4), 3.53 (m, 1H, H-5), 3.28 (m, 1H, H-5); ^{13}C NMR (125 MHz, [D$_6$]DMSO): $\delta = 153.1$ (C=O urethane), 139.2–118.1 (C-Ar), 100.5 (=*C*H-Phα), 100.3 (=*C*H-Phβ), 97.7 (C-1β), 93.3 (C-1α), 79.1 (C-4α), 78.6 (C-4β), 74.3 (C-3β), 73.7 (C-2β), 72.1 (C-3α), 70.9 (C-2α), 68.2 (C-6α), 67.9 (C-6β), 65.5 (C-5β), 62.1 (C-5α); FAB-MS (MB): *m*/*z*: calcd for $C_{20}H_{21}NO_7$: 387.1; found: 388 $[M+H]^+$.

4,6-*O*-Benzylidene-2-*O*-chloroacetyl-3-*O*-(*N*-phenylcarbamoyl)-D-glucopyranosyltrichloroacetimidate (20): Benzylidene acetal **19** (11.4 g, 29.4 mmol) and pyridine (20 mL) were dissolved in dichloromethane (100 mL) and cooled to 0 °C. Chloroacetic acid anhydride (15 g, 87.7 mmol) was added and the reaction was allowed to proceed at 0 °C until the starting material disappeared (TLC: hexane/acetone 1.5:1). The solution was diluted with dichloromethane (200 mL) and extracted with aq K_2CO_3, aq HCl (3×) and aq K_2CO_3. After drying ($MgSO_4$) the solvent was evaporated. The residue (14.6 g) was dissolved in DMF (21 mL) and hydrazine acetate (2.4 g) was added. After complete reaction (TLC: hexane/acetone 1.5:1) the mixture was diluted with dichloromethane (400 mL) and extracted with water (2×) and aq $KHCO_3$. The organic phase was dried ($MgSO_4$) and concentrated. Subsequently, the hemiacetal was dissolved in dry dichloromethane (100 mL) and cooled to 0 °C. Trichloroacetonitrile (8 mL, 54 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (775 μL, 7.7 mmol) were added. Upon complete consumption of the starting material (TLC: hexane/acetone 1.5:1) the solution was evaporated to dryness and the residue was purified by flash chromatography (hexane/acetone 2:1) to give the imidate **20** (9.77 g, 54.6 %). R_f bischloroacetate = 0.44 (hexane/acetone 1.5:1); R_f hemiacetal = 0.33 (hexane/acetone 1.5:1); R_f imidate = 0.47 (hexane/acetone 1.5:1); ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 9.97$ (s, 1H, C=NH), 9.78 (s, 1H, NH urethane), 7.49–6.96 (m, 10H, Ph), 6.53 (d, $J_{1,2} = 3.6$ Hz, 1H, H-1α), 5.71 (s, 1H, =C*H*-Ph), 5.49(dd, $J_{2,3} = J_{3,4} = 9.8$ Hz, 1H, H-3), 5.30 (dd, 1H, H-2), 4.42–4.27 (m, 3H, CH_2Cl, H-6a), 4.11 (dd, $J_{4,5} = 9.6$ Hz, 1H, H-4), 4.01 (m, 1H, H-5), 3.89 (dd, $J_{gem} = J_{vic} = 10.2$ Hz, H-6b); ^{13}C NMR (125 MHz, [D$_6$]DMSO): $\delta = 166.3$ (C=O), 158.0 (C=N), 152.3 (C=O urethane), 138.7–118.4 (C-Ar), 100.6 (=*C*H-Ph), 92.5 (C-1α), 77.2 (C-4), 71.4 (C-2), 68.8 (C-3), 67.2 (C-6), 65.3 (C-5), 40.5 (CH_2Cl); FAB-MS (MB): *m*/*z*: calcd for $C_{24}H_{22}Cl_4N_2O_8$: 606.0; found: 607 $[M+H]^+$.

4,6-*O*-Benzylidene-2-*O*-chloroacetyl-3-*O*-(*N*-phenylcarbamoyl)-β-D-glucopyranosylfluoride (21): Imidate **20** (2 g, 21.9 mmol) was dissolved in dry dichloromethane (30 mL) in a polyethylene container and cooled to 0 °C. To the stirred solution was added HF/pyridine complex (420 μL). The reaction was complete after 5 min (TLC: hexane/acetone 2:1). Subsequently, the biphasic reaction was diluted with dichloromethane (130 mL), transferred to a Teflon separaratory funnel and neutralized with cold aq $KHCO_3$. The organic phase was extracted with aq HCl (3×) and aq $KHCO_3$. After concentration the residue was purified by flash chromatography (hexane/acetone 2:1) to yield the fluoride **21** (1.4 g, 91.4 %).

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$[\alpha]_D^{23} = -32.2^\circ$ ($c = 1$ in dichloromethane); $R_f = 0.44$ (hexane/acetone 2:1); ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 9.80$ (s, 1H, NH), 7.45–6.96 (m, 10H, Ph), 5.79 (dd, $J_{1,2} = 6.5$, $J_{1,F} = 53.7$ Hz, 1H, H-1β), 5.68 (s, 1H, =C*H*-Ph), 5.38 (dd, $J_{2,3} = J_{3,4} = 8.9$ Hz, 1H, H-3), 5.09 (m, 1H, H-2), 4.51, 4.41 (2d, $J_{gem} = 15.3$ Hz, 1H, CH_2Cl), 4.34 (dd, $J_{gem} = 9.9$, $J_{vic} = 4.5$ Hz, 1H, H-6a), 4.03 (dd, $J_{4,5} = 9.4$ Hz, 1H, H-4), 3.97 (m, 1H, H-5), (dd, $J_{gem} = 9.9$, $J_{vic} = 10.1$ Hz, 1H, H-6b); ^{13}C NMR (125 MHz, [D$_6$]DMSO): $\delta = 152.3$ (C=O urethane), 138.6, 136.9 (C-*i* Ph), 129.4–118.5 (C-Ar), 106.3 (d, $J_{C\text{-}1,F} = 214.1$ Hz, C-1), 100.5 (=*C*H-Ph), 79.9 (C-4), 73.4 (d, $J_{C\text{-}2,F} = 25.4$ Hz, C-2), 70.8 (d, $J_{C\text{-}3,F} = 9.5$ Hz, C-3), 67.2 (C-6), 65.1 (C-5), 40.6 (CH_2Cl); FAB-MS (MB): m/z: calcd for $C_{22}H_{21}ClFNO_7$: 665.1; found: 666 $[M+H]^+$.

O*-(4,6-*O*-Benzylidene-2-*O*-chloroacetyl-3-*O*-(*N*-phenylcarbamoyl)-β-D-glucopyranosyl)-(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 (22)**: *a) Starting from **21: Disaccharide **13** (85 mg, 86 μmol), fluoride **21** (120 mg, 258 μmol) and ground molecular sieves 4 Å (320 mg) were suspended in dry dichloromethane (3 mL) and stirred for 30 min at 0 °C. $BF_3 \cdot OEt_2$ (40 μL, 326 μmol) was added and the reaction was allowed to proceed at ambient temperature for 24 h (TLC: hexane/acetone 1.5:1). Subsequently, the suspension was filtered over celite, washed with dichloromethane and extracted with aq K_2CO_3. The organic phase was dried ($MgSO_4$), concentrated and the residue was purified by flash chromatography (hexane/acetone 2:1) to furnish the title trisaccharide **22** (56 mg, 45.5%).

*b) Starting from **20***: Disaccharide **14** (5.8 g, 5.9 mmol), imidate **20** (6.65 g, 10.9 mmol) and ground molecular sieves 4 Å (18 g) were suspended in dry dichloromethane (50 mL) and stirred for 20 min at 0 °C. Trifluoromethanesulfonic acid trimethylsilylester (600 μL, 3.2 mmol) was added and the reaction was monitored for 3 h (TLC: hexane/acetone 1.5:1). Subsequently, the solids were filtered off over Celite, washed with dichloromethane and the organic phase was extracted with dilute K_2CO_3. The dried solution ($MgSO_4$) was concentrated and the residue was purified by flash chromatography (hexane/acetone 2:1) to give trisaccharide **22** (5.26 g, 62.4%). $[\alpha]_D^{23} = -14.1^\circ$ ($c = 0.5$ in dichloromethane); $R_f = 0.33$ (hexane/acetone 1.5:1); ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 9.71$ (s, 1H, NH), 7.95–7.65 (m, 8H, Pht), 7.50–7.20 (m, 20H, Ar), 7.00–6.78 (m, 10H, Ar), 5.61 (s, 1H, =C*H*-Ph), 5.30–5.24 (m, 3H, H-1, H-1′, H-3″), 4.95 (m, 2H, H-1″, H-2″), 4.83 (d, $J_{gem} = 12.4$ Hz, 1H, CH_2O), 4.79 (d, $J_{gem} = 11.9$ Hz, 1H, CH_2O), 4.63 (d, $J_{gem} = 11.6$ Hz, 1H, CH_2O), 4.58 (d, $J_{gem} = 12.2$ Hz, 1H, CH_2O), 4.43–4.37 (m, 4H, CH_2O), 4.32 (m, 2H, CH_2Cl), 4.20 (dd, $J_{2,3} = J_{3,4} = 9.8$ Hz, 1H, H-3′), 4.15 (dd, $J_{vic} = 4.7$ Hz, $J_{gem} = 9.8$ Hz, 1H, H-6a″), 4.12–4.08 (m, 2H, H-3, H-4), 4.03 (m, 1H, H-2′), 3.98 (dd, $J_{4,5} = 8.4$ Hz, 1H, H-4′), 3.84–3.80 (m, 3H, H-2, H-4″, H-6a′), 3.68–3.60 (m, 3H, H5, H-6b′, H-6b″), 3.54 (m, 1H, H-5″), 3.49 (dd, $J_{vic} < 1.0$, $J_{gem} = 10.8$ Hz, 1H, H-6a), 3.41 (m, 1H, H-5′), 3.36 (dd, $J_{vic} = 3.1$ Hz, 1H, H-6b); ^{13}C NMR (62.5 MHz, [D$_6$]DMSO): $\delta = 167.1$, 166.1 (C=O), 152.5 (C=O urethane), 138.7, 138.3, 138.0, 137.0 (C-*i* Ar), 134.8 (C-4/5 Pht), 130.6 (C-1/2 Pht), 129.0–126.1 (C-Ar), 123.4 (C-3/6 Pht), 122.3, 118.6 (C-Ar), 100.4 (=*C*H-Ph), 99.6 (C-1″), 96.4 (C-1′), 84.8 (C-1), 77.6 (C-4″, C-4′), 76.5 (C-3′), 76.2 (C-3), 75.7 (C-5), 75.1 (C-4), 74.5 (C-5′), 74.2 (C-2″), 73.9 (CH_2O), 73.7 (CH_2O), 72.3 (CH_2O), 71.7 (C-2″, CH_2O), 67.6 (C-6, C-6′), 67.4 (C-6″), 65.5 (C-5″), 55.8 (C-2′), 54.6 (C-2), 40.6 (CH_2Cl); ESI-MS: m/z: calcd for $C_{78}H_{71}ClN_6O_{19}$: 1430.45; found: 1453.50 $[M+Na]^+$.

O*-(4,6-*O*-Benzylidene-3-*O*-(*N*-phenylcarbamoyl)-β-D-glucopyranosyl)-(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)**: *a) Starting from **22: Trisaccharide **22** (14 g, 9.78 mmol) was dissolved in methanol/dichloromethane 1:2 (120 mL). To the stirred solution was added K_2CO_3 (300 mg). After complete deacylation (TLC: hexane/acetone 1.5:1) the solids were filtered off, followed by neutralization with acetic acid. The solution was concentrated and purified by flash chromatography (hexane/acetone 1.5:1) furnishing the trisaccharide **17** (11.82 g, 89.2%).

*b) Starting from **16***: Trisaccharide **16** (3.25 g, 2.3 mmol) was dissolved in dioxane/methanol 1:1 (80 mL) and cooled to 4 °C. K_2CO_3 (400 mg) was added and the suspension was stirred for 36 h. Subsequently, the solids were removed by filtration. The solution was neutralized with Amberlyst 15 ion-exchange resin (H^+) and concentrated. The residue was dissolved in acetonitrile (50 mL) and benzaldehyde dimethylacetal (10 mL) and *p*-toluenesulfonic acid (100 mg) were added. After 1 h the reaction was stopped with triethylamine (150 μL), concentrated and purified by flash chromatography (hexane/acetone 2.5:1) to give the trisaccharide **17** (1.395 g, 44.1%). $[\alpha]_D^{23} = -8.2^\circ$ ($c = 0.5$ in dichloromethane); $R_f = 0.28$ (hexane/acetone 1.5:1); ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 9.6$ (s, 1H, NH), 7.95–7.65 (m, 8H, Pht), 7.50–7.20 (m, 20H, Ar), 7.00–6.75 (m, 10H, Ar), 5.92 (d, $J_{2,OH} = 6.0$ Hz, 1H, OH-2″), 5.56 (s, 1H, =C*H*-Ph), 5.28 (d, $J_{1,2} = 9.2$ Hz, 1H, H-1β), 5.27 (d, $J_{1,2} = 8.3$ Hz, 1H, H-1′β), 5.01 (dd, $J_{2,3} = J_{3,4} = 9.5$ Hz, 1H, H-3″), 4.85 (d, $J_{gem} = 12.4$ Hz, 1H, CH_2O), 4.79 (d, $J_{gem} = 11.9$ Hz, 1H, CH_2O), 4.67 (d, $J_{1,2} = 6.9$ Hz, 1H, H-1″β), 4.65 (d, $J_{gem} = 11.6$ Hz, 1H, CH_2O), 4.55 (d, $J_{gem} = 12.2$ Hz, 1H, CH_2O), 4.42–4.34 (m, 4H, CH_2O), 4.27 (dd, $J_{2,3} = 10.4$, $J_{3,4} = 8.9$ Hz, 1H, H-3′), 4.14–3.96 (m, 6H, H-3, H-4, H-6a′, H-6a″, H-2′, H-4′), 3.89 (dd, $J_{vic} = 4.2$, $J_{gem} = 11.0$ Hz, 1H, H-6b′), 3.81 (dd, $J_{2,3} = 10.5$ Hz, 1H, H-2), 3.67–3.60 (m, 3H, H-4″, H-6b″, H-5), 3.54 (m, 1H, H-5′), 3.48 (dd, $J_{vic} < 1.0$, $J_{gem} = 10.6$ Hz, 1H, H-6a), 3.45–3.32 (m, 3H, H-2″, H-5″, H-6b); ^{13}C NMR (62.5 MHz, [D$_6$]DMSO): $\delta = 168.1$, 167.0 (C=O), 152.9 (C=O urethane), 139.1, 138.6, 138.1, 138.0, 137.9, 137.3 (C-*i* Ar), 134.8 (C-4/5 Pht), 130.6 (C-1/2 Pht), 128.7–126.1 (C-Ar), 123.4 (C-3/6 Pht), 122.3, 118.2 (C-Ar), 103.2 (C-1″), 100.2 (=*C*H-Ph), 96.5 (C-1′), 84.8 (C-1), 78.1 (C-4″), 77.9 (C-4′), 76.6 (C-3′), 76.2 (C-3), 75.7 (C-5), 75.0 (C-4), 74.7 (C-5′), 74.0 (C-3″), 73.7 (CH_2O), 72.7 (C-2″), 72.1, 71.6 (CH_2O), 67.5 (C-6), 67.5 (C-6′, C-6″), 65.7 (C-5″), 56.0 (C-2′), 54.6 (C-2); elemental analysis calcd (%) for $C_{76}H_{70}N_6O_{18}$ (1355.42): C 67.35, H 5.21, N 6.20; found: C 67.32, H 5.15, N 6.00.

***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 (2)**: Trisaccharide **17** (4.2 g, 3.1 mmol) and pyridine (2 mL) were dissolved in dry dichloromethane (150 mL). The stirred solution was cooled to −40 °C and trifluoromethanesulfonic acid anhydride (700 μL, 4.16 mmol) was added. Upon warming to 0 °C the reaction went to completion (TLC: hexane/acetone 1.5:1). The mixture was concentrated in a water bath at ambient temperature followed by evaporation to drynesss in high vacuo. Subsequently, dry DMF (20 mL) and pyridine (2 mL) were added prior to heating to 65 °C. After 2 h the reaction was complete (TLC: dichloromethane/methanol 50:1) and concentrated in high vacuo. The residue was dissolved in dichloromethane (250 mL) and extracted with aq K_2CO_3. The organic phase was dried ($MgSO_4$), concentrated to dryness and subsequently dissolved in a mixture of dioxane (20 mL), acetic acid (6 mL) and water (4 mL). After complete hydrolysis of the iminocarbonate (TLC: dichloromethane/methanol 50:1) the solvents were removed at ambient temperature in a rotary evaporator. The residue was taken up in dichloromethane (250 mL), extracted with aq HCl and aq K_2CO_3, dried ($MgSO_4$) and concentrated. The crude product (carbonate) was dissolved in dry dichloromethane (150 mL) and a freshly prepared solution (5 mL) of sodium (100 mg) in dry methanol (100 mL) was added. After complete reaction (TLC: hexane/acetone 1.5:1) the solution was neutralized with acetic acid, concentrated and purified by flash chromatography (hexane/acetone 1.5:1) to give trisaccharide **2** (2.69 g, 70.2%). $[\alpha]_D^{23} = -3.3^\circ$ ($c = 0.5$ in dichloromethane); R_f phenylurethane **17** = 0.28 (hexane/acetone 1.5:1); R_f triflate = 0.34 (hexane/acetone 1.5:1); R_f triflate **17a** = 0.67 (dichloromethane/methanol 50:1); R_f iminocarbonate **17b** = 0.62 (dichloromethane/methanol 50:1); R_f carbonate **17c** = 0.64 (dichloromethane/methanol 50:1); R_f carbonate **17c** = 0.29 (hexane/acetone 1.5:1); R_f diol **2** = 0.21 (hexane/acetone 1.5:1); ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 7.95–7.65$ (m, 8H, Pht), 7.41–7.22 (m, 15H, Ar), 6.96–6.75 (m, 10H, Ar), 5.51 (s, 1H, =C*H*-Ph), 5.28 (d, $J_{1,2} = 9.5$ Hz, 1H, H-1β), 5.25 (d, $J_{1,2} = 8.5$ Hz, 1H, H-1′β), 4.96 (d, $J_{2,OH} = 4.3$ Hz, 1H, OH-2″), 4.92 (d, $J_{3,OH} = 6.9$ Hz, 1H, OH-3″), 4.82 (d, $J_{gem} = 12.1$ Hz, 2H, CH_2O), 4.62 (d, $J_{1,2} < 1.0$ Hz, 1H, H-1″β), 4.60 (d, $J_{gem} = 12.2$ Hz, 1H, CH_2O), 4.55 (d, $J_{gem} = 12.2$ Hz, 1H, CH_2O), 4.43–4.37 (m, 4H, CH_2O), 4.21 (dd, $J_{2,3} = 10.4$, $J_{3,4} = 8.8$ Hz, 1H, H-3′), 4.14–3.96 (m, 5H, H-3, H-4, H-6a″, H-2′, H-4′), 3.80–3.76 (m, 3H, H-2, H-2″, H-6a′), 3.71 (dd, $J_{3,4} = J_{4,5} = 9.5$ Hz, 1H, H-4″), 3.66–3.47 (m, 5H, H-5, H-6a, H-6b′, H-3″, H-6b″), 3.41 (m, 1H, H-5′), 3.36 (m,1H, H-6b), 3.10 (m, 1H, H-5″); ^{13}C NMR (62.5 MHz, [D$_6$]DMSO): $\delta = 168.0$, 167.1, 167.0 (C=O), 138.4, 138.3, 138.1, 137.9 (C-*i* Ar), 134.8 (C-4/5 Pht), 130.7, 130.5 (C-1/2 Pht), 128.7–126.3 (C-Ar), 123.4 (C-3/6 Pht), 100.9 (=*C*H-Ph), 100.4 (C-1″β, $J_{C\text{-}1,H\text{-}1} = 158.6$ Hz from a coupled HMQC spectrum), 96.5 (C-1′β, $J_{C\text{-}1,H\text{-}1} = 169.0$ Hz see above), 84.8 (C-1β, $J_{C\text{-}1,H\text{-}1} = 166.9$ Hz see above), 78.3 (C-4″), 77.3 (C-4′), 76.2 (C-3), 76.0 (C-3′), 75.6 (C-5), 74.9 (C-4), 74.5 (C-5′), 73.7, 73.6, 72.1, 71.5 (CH_2O), 70.9 (C-2″),69.9 (C-3″), 67.8 (C-6′, C-6″), 67.5 (C-6), 66.8 (C-5″), 56.0 (C-2′), 54.7 (C-2); elemental analysis calcd (%) for $C_{69}H_{65}N_5O_{17}$ (1236.30): C 67.04, H 5.30, N 5.66; found: C 66.70, H 5.18, N 5.52. ESI-MS: m/z: calcd for $C_{69}H_{65}N_5O_{17}$: 1235.44); found: 1258.45 $[M+Na]^+$.

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