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A Double Regio- and Stereoselective Glycosylation Strategy for the Synthesis of N-Glycans

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Dedicated to Professor Peter Welzel on the occasion of his 70th birthday

Abstract: A building block approach for biantennary N-linked oligosaccharides from glycoproteins (N-glycans) has been developed. Starting from a core trisaccharide (β-mannosyl chitobiose) containing a benzylidene-protected β-mannoside, the attachment of the disaccharide building blocks for the antennae can be performed in a double regio- and stereoselective manner. A short synthesis of a GlcNPhtβ1,2Man donor was developed. The benzylidene acetal moiety, as a minimal protection of the β-mannoside, allows selective α-glycosylation at OH-3 of the 2,3-diol with GlcNβ1,2Man trichloroacetimidate donors. Subsequent debenzylidenation leads to a 4,6-diol, which can be selectively extended at OH-6. Overreaction at OH-4 was generally low when phthalimido-protected donors were used. This general strategy represents a modular synthesis of N-glycans and their glycoconjugates.

Keywords: carbohydrates · glycoproteins · glycosylation · oligosaccharides · regioselectivity

Introduction

The chemical synthesis of N-glycans has received considerable attention in recent years, driven by the rapidly growing field of glycobiology, in which N-glycosylation is one of the key modifications of eukaryotic secretory proteins. It is now widely accepted that glycosylation influences the physical and biological properties of glycoproteins.[1] Analysis of N-glycans from glycoproteins reveals a high degree of heterogeneity,[2] resulting in tedious and low-yielding routes when it is attempted to isolate these oligosaccharides from natural sources.[3] In order to improve this situation we have developed a synthetic alternative, planned on the basis of the seminal developments of Ogawa[4] and Paulsen,[5] involving a set of modular building blocks.[6] Key to this endeavor was the finding of a double regio- and stereoselective glycosylation sequence.[7,8] In recent years several groups have developed additional chemical routes for the synthesis of N-glycans, employing a variety of disconnection points and chemistries in solution and on the solid phase.[9–17]

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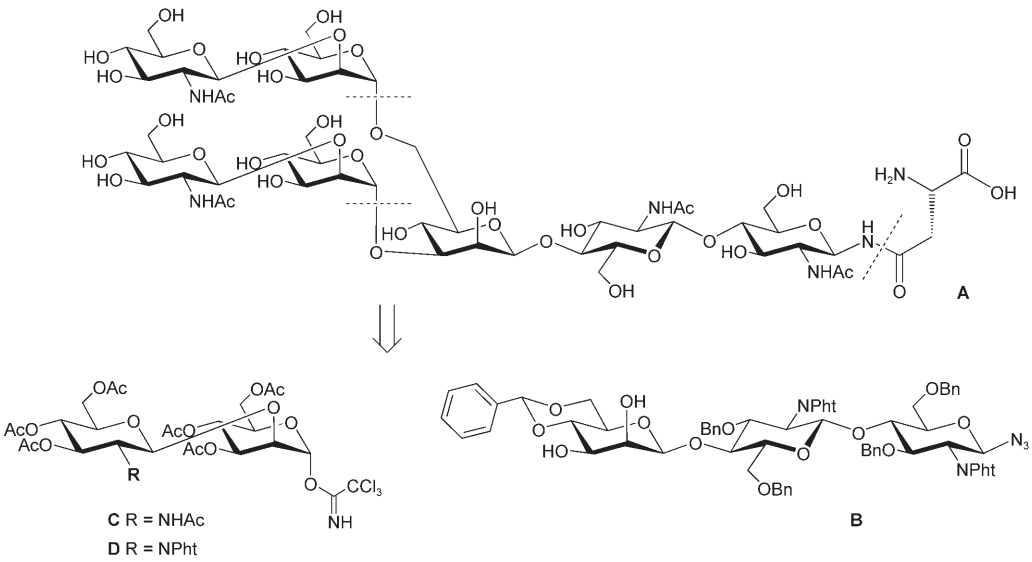
Results

The initial goal for developing a chemical synthesis of N-glycans was the biantennary heptasaccharide asparagine (**A**; Scheme 1),[8] which can serve as an acceptor for enzymatic elongation[18] and as a building block for glycopeptide synthesis.[19,20] Retrosynthetic disconnection suggested a core trisaccharide **B** bearing an anomeric azide[21] for conjugation to asparagine or a linker. The introduction of the antennae was initially planned through the trichloroacetimidate-activated disaccharide building block **C**.[22]

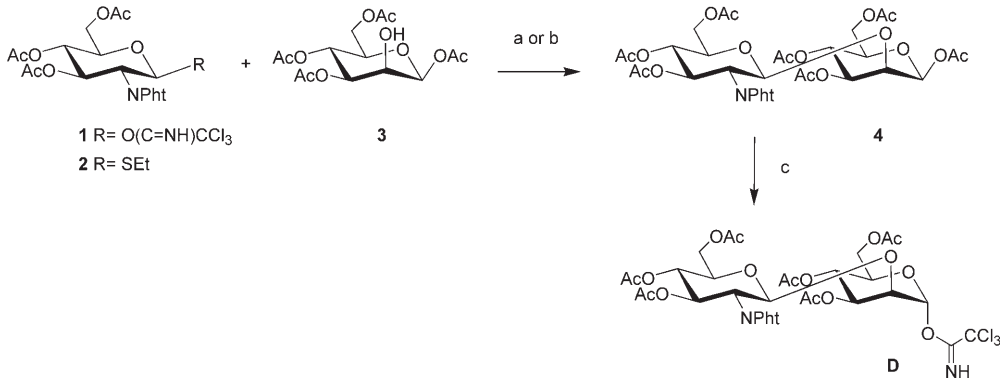
Synthesis of GlcNAcβ(1,2)Man imidates: The route to compound **C** was analogous to that described by Paulsen,[22] with the exception that the mannosyl acceptor benzyl 3,4,6-tri-*O*-benzyl-D-mannoside[23,24] was employed instead of the corresponding allyl glycoside, thus shortening the overall synthesis by two steps. Despite acceptable yields in the individual steps leading to imidate **C** the synthesis was lengthy and not appropriate for larger scale. In particular, the replacement of the benzyl groups by acetates was laborious, and a shorter approach was investigated. We reasoned that tetraacetyl-



Scheme 1. Retrosynthesis of biantennary N-glycan-Asn **A** into suitably protected di- and trisaccharide building blocks **B**–**D**. Ac = acetyl, Pht = phthalimido, Bn = benzyl.

mannose **3** (Scheme 2) should serve as an acceptor.[25] The crystalline compound **3** can be produced in a one-pot manner as described by Helferich,[26,27] but yields and reproducibility were better through the isomerization of the isolated ethyl orthoester.[28] Glycosylation of tetraacetylmannose **3** with the imidate **1**[29] gave the disaccharide **4** in a yield of 39%. The yields were optimized by lowering the temperature and employing molecular sieves as beads (58%). A further improvement was achieved when thioglycoside **2** was allowed to react with **3**, giving **4** in 95% yield. Disaccharide **4** was selectively deprotected with hydrazine acetate and converted into the desired donor **D** by treatment with trichloroacetonitrile in the presence of DBU. This route was used to generate donor **D** on a 20 g scale within a short time.

Pentasaccharide syntheses: With the donors **C** and **D** to hand, the glycosylation of core trisaccharide **B** was investigated. As a result of β-mannoside formation by the intramolecular inversion method developed by Kunz,[30] the acceptor **B**[31] carries two neighboring OH groups. In the case of a corresponding disaccharide, a strategy to protect the axial OH-2 group selectively through the regioselective isomerization of an intermediate orthoester was devised.[32] We suspected that this step might be avoidable through exploitation of the different reactivities of the axial and equatorial OH groups. To test this hypothesis, donor **C** (known to give only α-linked products[5]) was treated directly with trisaccharide diol **B**. The resulting pentasaccharide **5** was isolated in a yield of 62%, and the newly formed linkage was confirmed as an α-mannoside ($J_{C\text{-}1,H\text{-}1} = 177.3$ Hz, C-1^{4}α). Only the O-3^3-linked natural isomer was obtained, as was confirmed by a COSY cross-peak of the OH signal to H-2^3 and by the ^{13}C signal for C-3^3 shifting from 69.9 to 79.1 ppm, due to glycosylation. No other isomers were found.



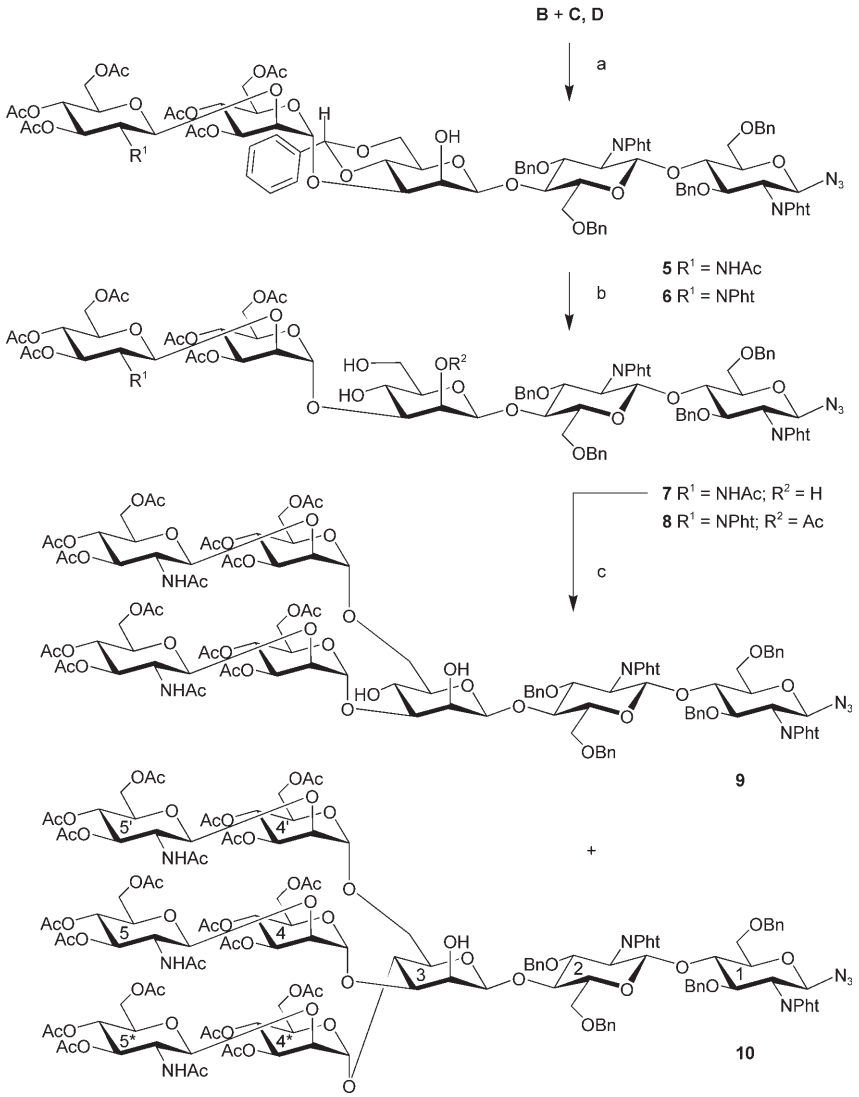
Scheme 2. a) **1**, $BF_3{\cdot}OEt_2$, CH_2Cl_2, −50 °C, MS (4 Å, beads), 58%; b) **2**, NIS, TfOH, CH_2Cl_2, −45 °C, MS (4 Å), 95%; c) 1) hydrazine acetate, DMF; 2) Cl_3CCN, DBU, CH_2Cl_2, 0 °C, [1)–2) 78%]. MS = molecular sieves, TfOH = trifluoromethanesulfonic acid, NIS = *N*-iodosuccinimide, DMF = *N*,*N*-dimethylformamide, DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.

We were pleased to see that the glycosylation of the vicinal *cis*-diol **B** proceeded in a highly regio- and stereoselective manner. Two factors may be relevant for this outcome: 1) the reactivities of equatorial OH groups in glycosylation reactions are usually higher than those of axial OH groups (this is exploited in reactions of galactose derivatives with unprotected OH-3 and OH-4 groups, in which cases glycosylation preferentially occurs at the equatorial OH-3 functions[33–35]), and 2) in diol **B** the β-mannosidic linkage, in conjunction with the two benzyl protecting groups of the neighboring GlcNAc^2, may additionally shield the less reactive OH-2 group. A selective glycosylation of vicinal diols at OH-3 has been demonstrated in the case of benzylidene-protected glucosides.[36]

When the phthalimido-protected donor **D** was treated with trisaccharide **B**, only the α1,3-linked pentasaccharide **6** was isolated, in a yield of 84% (Scheme 3). In order to investigate the reactivity of the remaining OH-2^3 group in the pentasaccharides **5** and **6**, the glycosylation of **B** was carried out with four equivalents of the donors **C** or **D** at −20°C. In both cases only the corresponding pentasaccharides **5** or **6** were found in the crude reaction mixtures, according to LC-MS analysis, indicating that no double glycosylation had occurred. In the case of the LEC14 glycan, however, it had been possible to glycosylate the axial OH-2^3 group of **6** with a glucosamine derivative, though this required different activation and more stringent conditions.[37]

For further elongation at OH-6^3 the benzylidene acetal of pentasaccharide **5** was removed by heating in 80% acetic acid (70% yield of **7**). The yields were not very reproducible, and occasional loss of acetates was observed by LC-MS. Debenzylidenation was more reliably carried out by acetylation of **6**, followed by treatment with *p*-toluenesulfonic acid hydrate in acetonitrile (84% yield of **8** over both steps). The addition of water in this deprotection procedure did not improve the yields, with an increase in polar side products instead being observed.

Heptasaccharide syntheses: We assumed that the elongation of the pentasaccharide acceptor **7** with donor **C** should selectively provide the desired α-1,6-linked heptasaccharide **9**. Unexpectedly, though, the reaction proceeded sluggishly and showed only low levels of conversion of acceptor **7**. Various conditions were tested in order to increase the conversion rate, but this led only to inconsistent results with no overall improvement. In one experiment two products were obtained: the heptasaccharide **9** (19%) and a nonasaccharide product **10** (16%), in which an additional disaccharide unit was connected to O-4 of the central β-mannoside. The structures of **9** and **10** were unambiguously confirmed by 2D-NMR spectroscopy. Heptasaccharide **9** shows an α-linked Man$^{4'}$-moiety ($J_{C\text{-}1,H\text{-}1}$ = 172.1 Hz, C-1$^{4'}\alpha$) attached to O-6^3 of the β-mannoside, as indicated by a doublet for OH-4^3 and a low-field shift from 61.2 to 67.8 ppm for C-6^3. For

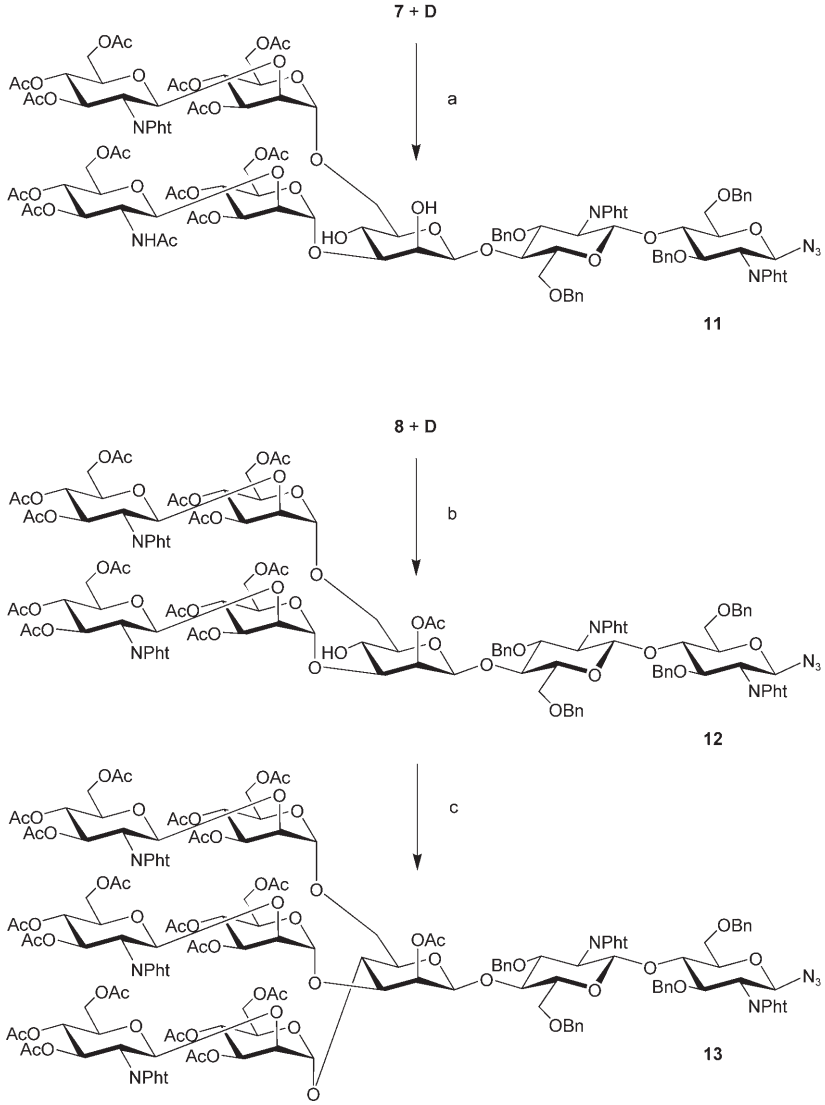


Scheme 3. a) **B+C**, $BF_3{\cdot}OEt_2$, CH_2Cl_2, −10°C, MS (4 Å), 62% yield of **5**; **B+D**, $BF_3{\cdot}OEt_2$, CH_2Cl_2, −20°C, MS (4 Å), 84% yield of **6**; b) **5**, AcOH (80%), 70°C, 70% yield of **7**; **6**, 1) Ac_2O, pyridine; 2) *p*-toluenesulfonic acid·H_2O, CH_3CN, [1)–2) 84% yield of **8**]; c) **7+C**, $BF_3{\cdot}OEt_2$, CH_2Cl_2, MS (4 Å), 19% yield of **9**, 16% yield of **10**.

nonasaccharide **10** the low-field shift of C-4^3 from 67.9 to 77.3 ppm confirmed that the additional glycosylation had occurred at the equatorial OH-4 group. In order to facilitate selective glycosylation at OH-6^3 of the pentasaccharides **7** and **8**, other donor/acceptor combinations were investigated. Glycosylation of the relatively unreactive donor **C** with the phthalimido-protected acceptor **8** showed an increased conversion of the acceptor (data not shown).

A significant improvement was found when the phthalimido-protected donor **D** was treated under diluted conditions with acceptor **7** carrying an acetamido group, which led to the heptasaccharide **11** in 57% yield (Scheme 4). When these reaction conditions were applied to the coupling of the phthalimido-protected building blocks **D** and **8** the heptasaccharide **12** was obtained in 73% yield. Careful analysis of the crude reaction mixture by LC-MS revealed only a minor amount of nonasaccharide **13**. Thus, conditions allowing for the regio- and stereoselective glycosylation of the primary OH groups in pentasaccharide 4,6-diols had been found.

To investigate the propensity of the remaining OH-4^3 group of the biantennary heptasaccharide **12** to serve as an acceptor for **D** the conditions for the regioselective glycosylation of **8** were systematically varied (Table 1). Variations of temperature and concentration of the reactants or the addition of excess trichloroacetamide had little effect on the product distribution, and similar fractions (2–5%) of **13** were detected by LC-MS analysis (Table 1). Only when the isolated heptasaccharide **12** was used as an acceptor conversions corresponding to 10–23% of nonasaccharide **13** were obtained, depending on the concentration of the reaction mixture (Table 2). The reactivity of the OH-4^3 group of the phthalimido-protected heptasaccharide product **12** is therefore very low under the reaction conditions generally employed for regioselective glycosylation with donor **D**, preventing further reaction to nonasaccharide **13**. The novel nonasaccharides **10** and **13** represent non-natural N-glycan homologues that are only accessible by this chemical glycosylation pathway.



Scheme 4. a) **7+D**, $BF_3{\cdot}OEt_2$, CH_2Cl_2, −25°C, MS (4 Å), 57%; b) **8+D**, $BF_3{\cdot}OEt_2$, CH_2Cl_2, −45°C, MS (4 Å), 73%; c) **12+D**, $BF_3{\cdot}OEt_2$, CH_2Cl_2, −20°C, MS (4 Å).

The pentasaccharide acceptors **7** and **8** differ only in the acetate at O-2^3 and the phthalimido group of the glucosamine[5] residue in the α1,3-arm. Regioselective α-glycosylation of **7** and **8** with the disaccharide donors **C** and **D**, containing either an acetamido or a phthalimido group at their peripheral glucosamines, influenced the efficiency of the reactions considerably. In particular, the presence of acetamido groups caused lower yields and in some cases facilitated additional glycosylation. It can be assumed that the differences in reactivity of the differently N-protected acceptors are caused by a combination of steric and electronic effects. For the synthesis of N-glycans branching at O-3^3 and O-6^3 of the central β-mannoside by the double regio- and stereoselective glycosylation approach outlined in this paper the general use of phthalimido groups is recommended, as higher yields are obtained and side reactions are mini-

Table 1. Formation of nonasaccharide **13** as a side product during the extension of pentasaccharide **8** to heptasaccharide **12** (Scheme 4).

Entry	*c* **8** [μmol mL^{-1}]	Equiv of **D**[a]	*T* [°C]	Equiv of Cl_3CONH_2[b]	**13**[c] [%]	**12**[c] [%]
1	37.7	2.1	−20	–	≈3	≈65
2	34.9	2.0	−10	5	≈2	≈61
3	34.9	2.0	−10	10	≈2	≈55
4	12.6	3.4	−20	–	≈5	≈63
5	12.6	3.1	−10	–	≈5	≈59
6	12.6	2.1	−10	–	≈3	≈65

[a] Relative to **8**. [b] Trichloroacetamide was added to the mixture before activation. [c] Yields were calculated from the integrals of the UV peaks at 255 nm.

Table 2. Formation of nonasaccharide **13** during coupling of heptasaccharide **12** with donor **D**.

Entry	*c* **12** [μmol mL^{-1}]	Equiv of donor **D**[a]	**13**[b] [%]
1	33.47	2.1	≈23
2	6.60	2.2	≈10
3	3.96	2.0	≈10

[a] Relative to acceptor **12**. [b] Yields were calculated from the integrals of the UV peaks at 255 nm.

mized. The finding that phthalimido groups in distant glucosamine residues can influence the reactivities of OH groups in glycosylation reactions of N-glycans is in accordance with the protecting-group-dependent reactivity observed for bulky donors in the synthesis of highly branched N-glycans.[38]

Conclusions

In summary, we have developed a double regio- and stereoselective glycosylation protocol for N-glycans, allowing selective reactions at any OH group in the central β-mannoside through the use of a single benzylidene protection group. Yields were generally improved and side reactions minimized through the use of phthalimido-protected donors and acceptors. These building blocks gave only the desired α-linked products and can be employed in a modular fashion.[6] The N-glycans thus obtained were deprotected for subsequent incorporation into glycopeptides[18,19] or neoglycoproteins.[39]

Experimental Section

General methods: Solvents were dried by standard methods. Molecular sieves were activated prior to use by heating 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, 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 *m*-nitrobenzyl alcohol (NBA) matrix. 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 aluminium plates (silica gel 60 GF_{254}, Merck Darmstadt). Spots were detected under UV light or by charring with a 1:1 mixture of 2 N H_2SO_4 and 0.2% resorcine monomethyl ether in ethanol.

Acetyl *O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-acetyl-β-D-mannopyranoside (4): A mixture of mannoside **3** (14.4 g, 41.3 mmol), imidate **1** (36 g, 62.1 mmol), and molecular sieves (4 Å, 20 g beads) in freshly distilled CH_2Cl_2 (400 mL) was stirred at −50 °C for 20 min. Boron trifluoride ethyl etherate (720 μL, 5.8 mmol) was slowly added over 5 minutes, and the solution was allowed to warm up to −20 °C within 3 h (TLC: hexane/acetone 1.5:1). The suspension was filtered over celite, and the filtrate was washed with $KHCO_3$ (2 M). The organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (hexane/ethyl acetate 1:1.25) to afford **4** (18.5 g, 58.4%). R_f = 0.51 (hexane/ethyl acetate 1:2); $[\alpha]_D^{23} = -42.3$ (c = 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 7.9–7.8 (m, 4H; Pht), 5.95 (dd, $J_{2,3}$ = 10.5 Hz, 1H; H-3′), 5.76 (d, $J_{1,2}$ < 1 Hz, 1H; H-1), 5.25 (d, $J_{1,2}$ = 8.4 Hz, 1H; H-1′), 5.00 (dd, $J_{4,5} = J_{3,4}$ = 9.6 Hz, 1H; H-4′), 4.94 (m, 2H; H-3, H-4), 4.25 (dd, $J_{1,2}$, $J_{2,3}$ < 1 Hz, 1H; H-2), 4.24 (m, 1H; H-6a′), 4.17 (dd, 1H; H-2′), 4.00 (m, 1H; H-5′), 3.93 (m, 1H; H-6b′), 3.80 (dd, J_{gem} = 12.4 Hz, J_{vic} = 5.3 Hz, 1H; H-6a), 3.75–3.70 (m, 2H; H-5, H-6b), 2.03, 2.02, 2.00, 1.98, 1.97, 1.96, 1.82 ppm (7×s, 21H; OAc); ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 170.1, 169.9, 169.7, 169.5, 169.3, 169.2, 168.5, 167.4, 167.1 (C=O), 134.7 (C-4/5 Pht), 130.9 (C-1/2 Pht), 123.3, 123.1 (C-3/6 Pht), 97.5 (C-1′), 90.3 ($J_{C\text{-}1,H\text{-}1}$ = 164.4 Hz from a coupled ^{13}C spectrum; C-1β), 72.7 (C-2), 71.3 (C-5), 71.1 (C-3), 70.4 (C-5′), 69.2 (C-3′), 68.9 (C-4′), 64.6 (C-4), 61.9 (C-6), (C-6′), 54.0 (C-2′), 20.5, 20.3, 20.2, 20.1 ppm (OAc); ESI-MS: *m*/*z*: calcd for $C_{34}H_{39}NO_{19}$: 765.21; found: 788.23 [*M*+Na]$^+$; elemental analysis calcd (%) for $C_{34}H_{39}NO_{19}$ (765.68): C 53.33, H 5.13, N 1.83; found: C 53.42, H 5.22, N 1.94.

*From thioglycoside **2***: NIS (26.2 g, 0.12 mol) was added to a suspension of thioglycoside **2** (22.3 g, 46.51 mmol), acceptor **3** (25.2 g, 72.35 mmol), and ground molecular sieves (4 Å, 30 g) in freshly distilled CH_2Cl_2 (1 L). The mixture was cooled to −45 °C and after 20 min of stirring, TfOH (0.60 mL, 6.88 mmol) was added dropwise over 5 minutes. The reaction mixture was allowed to warm up to room temperature over 2 h (TLC: cyclohexane/ethyl acetate 1:1.5) and was filtered over celite. The filtrate was washed with $KHCO_3$ (2 M, 2×) and $Na_2S_2O_3$ (10%, 1×). The organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by silica gel flash chromatography (cyclohexane/ethyl acetate 7:8→4:6→5:7) to afford **4** (33.90 g, 95%). R_f = 0.25 (cyclohexane/ethyl acetate 1:1.5).

***O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl trichloroacetimidate (D)**: A mixture of **4** (18.5 g, 24.16 mmol) and hydrazine acetate (3 g) was stirred in DMF (65 mL). Upon completion (TLC: hexane/ethyl acetate 1:2) the reaction mixture was quenched with acetone (15 mL) and concentrated under high vacuum. The residue was diluted with CH_2Cl_2 (800 mL), washed with HCl (1 M, 200 mL) and $KHCO_3$ (10%, 200 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The hemiacetal was dissolved in freshly distilled CH_2Cl_2 (400 mL) and cooled to 0 °C, followed by the addition of trichloroacetonitrile (24 mL, 239 mmol) and DBU (900 μL, 6 mmol). After disappearance of the starting material (TLC: hexane/ethyl acetate 1:2), the reaction mixture was concentrated in vacuo and purified by flash chromatography (hexane/ethyl acetate 1:1) to afford imidate **D** (16.3 g, 77.7%). R_f hemiacetal = 0.44 (hexane/ethyl acetate 1:2), R_f imidate **D** = 0.58 (hexane/ethyl acetate 1:2); $[\alpha]_D^{23} = +1.7$ (c = 1.5, CH_2Cl_2); ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 10.0 (s, 1H; NH), 7.9 (m, 4H; Pht), 5.84 (d, $J_{1,2}$ < 1 Hz, 1H; H-1), 5.68 (dd, $J_{2,3} = J_{3,4}$ = 10.0 Hz, 1H; H-3′), 5.55 (d, $J_{1,2}$ = 8.3 Hz, 1H; H-1′), 5.04 (m, 2H; H-4, H-4′), 4.96 (dd, $J_{1,2}$ = 3.1 Hz, 1H; H-3), 4.38 (dd, 1H; H-2), 4.23 (dd, J_{gem} = 12.4, J_{vic} = 5.4 Hz, 1H; H-6a′), 4.18 (dd, 1H; H-2′), 4.02 (m, 2H; H-5′, H-6b′), 3.80 (m, 1H; H-5), 3.69 (dd, J_{gem} = 12.6 Hz, J_{vic} = 4.6 Hz, 1H; H-6a), 3.60 (dd, J_{vic} < 1 Hz, 1H; H-6b), 2.03, 2.0, 1.98, 1.97, 1.87, 1.80 ppm (6×s, 18H; OAc); ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 170.1, 169.7, 169.6, 169.2, 168.0–167.0 (broad C=O), 156.7 (C=N), 134.9 (C-4/5 Pht), 130.6 (C-1/2 Pht), 123.5 (C-3/6 Pht), 96.1 (C-1′), 93.3 ($J_{C\text{-}1,H\text{-}1}$ = 183.1 Hz from a cou-

pled HMQC spectrum, C-1α), 90.0 (CCl_3), 72.2 (C-2), 71.0 (C-5′), 70.1 (C-5), 69.8 (C-3′), 68.9 (C-3), 68.6 (C-4′), 64.1 (C-4), 61.7 (C-6′), 61.5 (C-6), 53.8 (C-2′), 20.42, 20.38, 20.33, 20.1 ppm (OAc); ESI-MS: *m/z*: calcd for $C_{34}H_{37}Cl_3N_2O_{18}$: 866.11; found: 889.28 $[M+Na]^+$; elemental analysis calcd (%) for $C_{34}H_{37}Cl_3N_2O_{18}$ (868.03): C 47.05, H 4.30, N 3.23; found: C 47.19, H 4.30, N 3.49.

Azide 5: A mixture of acceptor **B** (500 mg, 404 μmol), donor **C** (500 mg, 642 μmol), and ground molecular sieves (4 Å, 1.5 g) in freshly distilled CH_2Cl_2 (15 mL) was stirred at −10 °C for 30 minutes. Boron trifluoride ethyl etherate (50 μL, 407 μmol) was slowly added over 5 minutes. After 2 h (TLC: hexane/acetone 1:1) the suspension was filtered over celite and the filtrate was washed with $KHCO_3$ (2 M). The organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (hexane/acetone 1:1) to afford **5** (465 mg, 62.0 %). R_f = 0.28 (hexane/acetone 1:1); $[\alpha]_D^{23} = -4.0$ (c = 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 8.0–7.73 (m, 9H; NH, Pht), 7.50–7.23 (m, 15H; Ar), 6.97–6.77 (m, 10H; Ar), 5.63 (s, 1H; =C*H*–Ph), 5.29 (d, $J_{2,OH}$ = 5.8 Hz, 1H; OH-2^3), 5.28 (d, $J_{1,2}$ = 9.1 Hz, 1H; H-1^{1}β), 5.25 (d, $J_{1,2}$ = 8.4 Hz, 1H; H-1^{2}β), 5.08 (d, $J_{1,2}$ < 1.0 Hz, 1H; H-1^4), 5.06–5.02 (m, 2H; H-3^4, H-4^4), 4.96 (dd, $J_{2,3} = J_{3,4}$ = 10.0 Hz, 1H; H-3^5), 4.83 (d, J_{gem} = 11.8 Hz, 1H; CH_2O), 4.82 (d, J_{gem} = 11.4 Hz, 1H; CH_2O), 4.75 (dd, $J_{2,3} = J_{3,4}$ = 10.0 Hz, 1H; H-4^5), 4.68 (d, $J_{1,2}$ < 1.0 Hz, 1H; H-1^3), 4.62 (d, J_{gem} = 12.1 Hz, 1H; CH_2O), 4.57 (d, J_{gem} = 12.1 Hz, 1H; CH_2O), 4.44–4.38 (m, 4H; CH_2O), 4.39 (d, $J_{1,2}$ = 8.5 Hz, 1H; H-1^{5}β), 4.23–4.18 (m, 2H; H-3^2, H-5^4), 4.14–3.92 (m, 11H; H-2^2, H-2^3, H-2^4, H-3^1, H-4^1, H-4^2, H-4^3, H-6a^3, H-6a,b^4, H-6a^5), 3.82–3.77 (m, 3H; H-2^1, H-6a^2, H-6b^5), 3.73–3.70 (m, 2H; H-2^5, H-3^3), 3.68–3.58 (m, 3H; H-5^1, H-6b^2, H-6b^3), 3.50 (dd, J_{gem} = 11.6, J_{vic} < 1.0 Hz, 1H; H-6a^1), 3.42–3.35 (m, 2H; H-5^2, H-6b^1), 3.17 (m, 1H; H-5^3), 2.99 (m, 1H; H-5^5), 2.00, 1.99, 1.94, 1.93, 1.89, (5×s, 18H; OAc), 1.73 ppm (s, 3H; NAc); ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 170.1, 169.9, 169.73, 169.68, 169.5, 169.3, 167.1 (C=O), 138.4, 138.3, 138.1, 137.9, 137.8 (C-*i* Ar), 134.8 (C-4/5 Pht), 130.8, 130.6 (C-1/2 Pht), 128.3–126.3 (C-Ar), 123.4 (C-3/6 Pht), 100.8 (=*C*H–Ph), 99.7 ($J_{C\text{-}1,H\text{-}1}$ = 163.6 Hz from a coupled HMQC spectrum, C-1^{3}β), 99.6 ($J_{C\text{-}1,H\text{-}1}$ = 166.0 Hz, C-1^{5}β), 98.8 ($J_{C\text{-}1,H\text{-}1}$ = 177.7 Hz, C-1^{4}α), 96.5 ($J_{C\text{-}1,H\text{-}1}$ = 172.1 Hz, C-1^{2}β), 84.9 ($J_{C\text{-}1,H\text{-}1}$ = 170.2 Hz, C-1^{1}β), 79.1 (C-3^3), 77.0 (C-4^2), 76.8 (C-4^3), 76.2 (C-3^1), 76.0 (C-3^2), 75.7 (C-5^1), 75.0 (C-4^1), 74.7 (C-5^2), 74.0 (C-2^4), 73.74, 73.66, 72.3 (CH_2O), 71.9 (C-3^5), 71.6 (CH_2O), 70.9 (C-5^5), 70.1 (C-2^3), 69.6 (C-3^4), 68.5 (C-4^5), 68.1 (C-5^4), 67.9 (C-6^2), 67.8 (C-6^3), 67.5 (C-6^1), 66.5 (C-5^3), 65.4 (C-4^4), 62.1 (C-6^4), 61.7 (C-6^5), 56.0 (C-2^2), 54.6 (C-2^1), 52.7 (C-2^5), 22.4 (NAc), 20.41, 20.35 ppm (OAc); ESI-MS: *m/z*: calcd for $C_{95}H_{100}N_6O_{33}$: 1852.6; found: 1853.6 $[M+H]^+$; FAB-MS (NBA): 1854 $[M+H]^+$.

Azide 6: A mixture of **B** (3.0 g, 2.43 mmol), **D** (4.21 g, 4.85 mmol), and ground molecular sieves (4 Å, 5 g) in freshly distilled CH_2Cl_2 (70 mL) was stirred at −20 °C for 30 minutes. Boron trifluoride ethyl etherate (150 μL, 1.2 mmol) was slowly added over 5 min. After 1.5 h (TLC: hexane/acetone 1.5:1) the suspension was filtered over celite, and the filtrate was washed with $KHCO_3$ (2 M). The organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (hexane/acetone 1.4:1) to afford **6** (3.97 g, 84.2 %). R_f = 0.1 (hexane/acetone 1.5:1); $[\alpha]_D^{23} = -23.7$ (c = 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 8.0–7.73 (m, 12H; Pht), 7.60–7.22 (m, 15H; Ar), 6.96–6.75 (m, 10H; Ar), 5.63 (s, 1H; =C*H*–Ph), 5.53 (dd, $J_{2,3} = J_{3,4}$ = 10.0 Hz, 1H; H-3^5), 5.29 (d, $J_{1,2}$ = 9.5 Hz, 1H; H-1^{1}β), 5.25 (d, $J_{1,2}$ = 8.4 Hz, 1H; H-1^{2}β), 5.22 (d, $J_{2,OH}$ = 4.4 Hz, 1H; OH-2^3), 5.03 (dd, $J_{2,3}$ = 3.0, $J_{3,4}$ = 9.9 Hz, 1H; H-3^4), 4.95 (d, $J_{1,2}$ = 8.4 Hz, 1H; H-1^{5}β), 4.9–4.8 (m, 5H; H-1^4, H-3^4, H-4^4, CH_2O), 4.60–4.52 (m, 3H; H-1^3, CH_2O), 4.43–4.36 (m, 4H; CH_2O), 4.3–3.92 (m, 10H; H-3^1, H-4^1, H-2^2, H-3^2, H-4^2, H-6a^3, H-2^4, H-5^4, H-2^5, H-6a^5), 3.90 (dd, $J_{2,3} = J_{3,4}$ = 9.5 Hz, 1H; H-4^3), 3.82–3.70 (m, 4H; H-2^1, H-6a^2, H-2^3, H-6b^5), 3.64–3.53 (m, 6H; H-5^1, H-6b^2, H-3^3, H-6b^3, H-6a,b^4), 3.49 (dd, J_{gem} = 11.0, J_{vic} < 1.0 Hz, 1H; H-6a^1), 3.40–3.33 (m, 2H; H-6b^1, H-5^2), 3.13 (m, 1H; H-5^3), 2.66 (m, 1H; H-5^5), 2.04, 1.98, 1.95, 1.90, 1.81, 1.80 ppm (6×s, 18H; OAc); ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 169.9, 169.8, 169.7, 169.2, 168.1, 167.4, 167.2 (C=O), 138.4, 138.2, 138.1, 138.0, 137.8 (C-i Ar), 134.9 (C-4/5 Pht), 130.8, 130.6 (C-1/2 Pht), 128.3–126.6 (C-Ar), 123.4 (C-3/6 Pht), 101.1 (=*C*H–Ph), 99.7 (C-1^{3}β), 97.6 (C-1^{4}α), 96.6 (C-1^{2}β), 95.5 (C-1^{5}β), 84.9 (C-1^{1}β), 77.9 (C-3^3), 77.3 (C-4^3), 77.1 (C-4^2), 76.2 (C-3^1), 75.9 (C-3^2), 75.7 (C-5^1), 75.1 (C-4^1), 74.6 (C-5^2), 73.8, 73.6 (CH_2O), 73.0 (C-2^4), 72.4, 71.6 (CH_2O), 70.9 (C-5^5), 69.9 (C-2^3), 69.5 (C-3^5), 69.1 (C-3^4), 68.3 (C-4^5), 67.8 (C-6^2, C-6^3), 67.7 (C-5^4), 67.6 (C-6^1), 66.2 (C-5^3), 65.2 (C-4^4), 62.1 (C-6^4), 61.2 (C-6^5), 56.0 (C-2^2), 54.7 (C-2^1), 53.7 (C-2^5), 20.4, 20.3, 20.1 ppm (OAc); ESI-MS: *m/z*: calcd for $C_{101}H_{100}N_6O_{34}$: 1940.6; found: 1959.4 $[M+H_3O]^+$; FAB-MS (NBA): 1964 $[M+Na]^+$; elemental analysis calcd (%) for $C_{101}H_{100}N_6O_{34}$ (1941.92): C 62.47, H 5.19, N 4.33; found: C 62.11, H 5.11, N 4.62.

Azide 7: Compound **5** (190 mg, 102 μmol) was dissolved in acetic acid (80 %, 5 mL), and the system was stirred for 90 minutes at 70 °C (TLC: hexane/acetone 1:1.5). The reaction mixture was concentrated in vacuo and co-distilled with toluene (2×5 mL). The residue was purified by flash chromatography (hexane/acetone 1:1.3) to afford **7** (127 mg, 70.2 %). R_f = 0.3 (hexane/acetone 1:1.5); $[\alpha]_D^{23} = +7.1$ (c = 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 7.95–7.69 (m, 9H; NH, Pht), 7.38–7.22 (m, 10H; Ar), 6.97–6.77 (m, 10H; Ar), 5.28 (d, $J_{1,2}$ = 9.5 Hz, 1H; H-1^{1}β), 5.23 (d, $J_{1,2}$ = 8.2 Hz, 1H; H-1^{2}β), 5.20 (d, $J_{4,OH}$ = 4.3 Hz, 1H; OH-4^3), 5.11 (d, $J_{1,2}$ < 1.0 Hz, 1H; H-1^4), 5.06–5.00 (m, 3H; H-3^4, H-4^4, H-3^5), 4.90–4.80 (m, 3H; CH_2O, H-4^5), 4.78 (d, $J_{2,OH}$ = 5.1 Hz, 1H; OH-2^3), 4.58–4.52 (m, 4H; CH_2O, H-1^3, H-1^5), 4.48 (d, J_{gem} = 12.4 Hz, 1H; CH_2O), 4.42–4.37 (m, 3H; CH_2O), 4.25–3.72 (m, 12H; H-2^2, H-2^4, H-3^1, H-3^2, H-4^1, H-4^2, H-5^4, H-6a,b^4, H-6a,b^5, OH-6^3), 3.85–3.77 (m, 4H; H-2^1, H-2^3, H-2^5, H-6a^2), 3.75–3.63 (m, 2H, H-5^5, H-6a^3), 3.62–3.55 (m, 3H; H-4^3, H-5^1, H-6b^2), 3.51–3.45 (m, 2H; H-6a^1, H-6b^3), 3.40–3.30 (m, 3H; H-3^3, H-5^2, H-6b^1), 3.06 (m, 1H; H-5^3), 2.01, 1.972, 1.967, 1.93, (4×s, 18H; OAc), 1.74 ppm (s, 3H; NAc); ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 170.1, 169.7, 169.5, 169.3, 169.2, 167.1 (C=O), 138.7, 138.2, 138.0 (C-*i* Ar), 134.8 (C-4/5 Pht), 130.8, 130.6 (C-1/2 Pht), 128.3–126.8 (C-Ar), 123.4 (C-3/6 Pht), 100.8 (=*C*H–Ph), 99.9 (C-1^5), 99.5 (C-1^4), 99.4 (C-1^3), 96.6 (C-1^2), 84.8 (C-1^1), 82.7 (C-3^3), 77.1 (C-5^3), 76.9 (C-4^2), 76.4 (C-3^2), 76.2 (C-3^1), 75.7 (C-5^1), 75.0 (C-4^1), 74.8 (C-5^2), 74.2 (C-2^4), 73.8, 73.7, 72.4 (CH_2O), 72.2 (C-3^5), 71.6 (CH_2O), 70.8 (C-5^5), 69.8 (C-3^4), 69.7 (C-2^3), 68.6 (C-4^5), 67.9 (C-4^4, C-6^2), 67.6 (C-6^1), 65.5 (C-4^4), 65.3 (C-4^3), 62.2 (C-6^4), 62.0 (C-6^5), 61.2 (C-6^3), 56.0 (C-2^2), 54.6 (C-2^1), 52.5 (C-2^5), 22.5 (NAc), 20.5, 20.4 ppm (OAc); ESI-MS: *m/z*: calcd for $C_{88}H_{96}N_6O_{33}$: 1764.6; found: 1765.7 $[M+H]^+$; FAB-MS (NBA): 1766 $[M+H]^+$.

Azide 8: Compound **6** (3.9 g, 2 mmol) was suspended in pyridine/acetic anhydride (15 mL, 2:1), and the system was stirred for 16 h at room temperature. The solution was concentrated in vacuo, and the residue was co-distilled with toluene (3×15 mL). The acetylated pentasaccharide was dissolved in acetonitrile (40 mL) and treated with a solution of *p*-toluenesulfonic acid monohydrate (1 g) in acetonitrile (40 mL). After 2 h the reaction mixture was neutralized with pyridine and concentrated in vacuo. The residue was diluted with CH_2Cl_2 (300 mL), washed with HCl (1 M, 3×) and $KHCO_3$ (2 M), dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (hexane/acetone 1.5:1) to afford **8** (3.18 g, 83.5 %). R_f = 0.33 (hexane/acetone 2:1); $[\alpha]_D^{23} = -11.6$ (c = 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 7.93–7.73 (m, 12H; Pht), 7.30–7.10 (m, 10H; Ar), 6.96–6.76 (m, 10H; Ar), 5.67 (dd, $J_{2,3}$ = 10.5 Hz, $J_{3,4}$ = 9.3 Hz, 1H; H-3^5), 5.45 (d, $J_{4,OH}$ = 5.7 Hz, 1H; OH-4^3), 5.32 (d, $J_{1,2}$ = 8.5 Hz, 1H; H-1^{5}β), 5.27 (d, $J_{1,2}$ = 9.5 Hz, 1H; H-1^{1}β), 5.20 (d, $J_{1,2}$ = 8.4 Hz, 1H; H-1^{2}β), 5.14 (dd, $J_{2,3}$ = 3.0 Hz, $J_{1,2}$ < 1.0 Hz; H-2^3), 5.03 (dd, $J_{3,4} = J_{4,5}$ = 9.6 Hz, 1H; H-4^5), 4.97 (dd, $J_{3,4} = J_{4,5}$ = 10.2 Hz, 1H; H-4^4), 4.91 (d, $J_{1,2}$ < 1.0 Hz, 1H; H-1^4), 4.90 (d, J_{gem} = 12.0 Hz, 1H; CH_2O), 4.78 (d, J_{gem} = 12.3 Hz, 1H; CH_2O), 4.75 (dd, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 10.4 Hz, 1H; H-3^4), 4.70 (d, $J_{1,2}$ < 1.0 Hz, 1H; H-1^3), 4.50 (2×d, J_{gem} = 12.3 Hz, 2H; CH_2O), 4.45 (t, $J_{6,OH}$ = 5.3 Hz, 1H; OH-6^3), 4.39–4.35 (m, 3H; CH_2O), 4.30 (d, J_{gem} = 12.0 Hz, 1H; CH_2O), 4.27–4.20 (m, 2H; H-2^4, H-6a^5), 4.16 (dd, 1H; H-2^5), 4.13 (dd, $J_{2,3}$ = 10.4 Hz, $J_{3,4}$ = 8.8 Hz, 1H; H-3^2), 4.10–3.94 (m, 5H; H-3^1, H-4^1, H-2^2, H-4^2, H-6b^5), 3.90 (m, 1H; H-5^5), 3.82–3.75 (m, 2H; H-5^4, H-2^1), 3.73–3.63 (m, 4H; H-6a^2, H-6a^3, H-6a,b^4), 3.60–3.44 (m, 6H; H-5^1, H-6a^1, H-6b^2, H-3^3, H-4^3, H-6b^3), 3.37 (m, 1H; H-6b^1), 3.27 (m, 1H; H-5^2), 3.08 (m, 1H; H-5^3), 2.04, 1.99, 1.98, 1.94, 1.93, 1.88, 1.79 ppm (7×s, 21H; OAc); ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 170.0, 169.82, 169.77, 169.65, 169.53, 169.21, 169.14, 168.0, 167.3, 167.0 (C=O), 138.3, 138.1, 138.0, 137.9 (C-*i* Ar), 134.7 (C-4/5 Pht), 130.5 (C-1/2 Pht), 128.2–126.2 (C-Ar), 123.4 (C-3/6 Pht), 97.5 (C-1^{4}α), 97.1 (C-1^{3}β), 96.4 (C-1^{2}β), 96.0 (C-1^{5}β), 84.8 (C-1^{1}β), 76.6 (C-3^2), 76.53 (C-4^2), 76.45 (C-5^3), 76.2 (C-3^1), 75.9 (C-3^3), 75.6 (C-5^1), 75.0 (C-4^1), 74.3 (C-5^2), 73.8, 73.7 (CH_2O), 73.4 (C-2^4), 72.1, 71.7

(CH_2O), 71.0 (C-5^5), 70.5 (C-2^3), 69.7 (C-3^5), 69.1 (C-3^4), 68.6 (C-4^5), 68.0 (C-4^4), 67.7 (C-6^2), 67.6 (C-6^1), 66.8 (C-4^3), 64.6 (C-4^4), 61.8 (C-6^5), 61.7 (C-6^4), 60.4 (C-6^3), 55.9 (C-2^2), 54.6 (C-2^1), 53.6 (C-2^5), 20.5, 20.3, 20.1, 20.0 ppm (OAc); ESI-MS: *m/z*: calcd for $C_{96}H_{98}N_6O_{35}$: 1894.61; found: 1914.16 $[M+H_3O]^+$; FAB-MS (NBA): 1913 $[M+H_3O]^+$; elemental analysis calcd (%) for $C_{96}H_{98}N_6O_{35}$ (1895.85): C 60.82, H 5.21, N 4.43; found: C 60.78, H 5.27, N 4.42.

Heptasaccharide 9 and nonasaccharide 10: A mixture of **7** (120 mg, 66 μmol), **C** (100 mg, 128 μmol), and ground molecular sieves (4 Å, 300 mg) in freshly distilled CH_2Cl_2 (2 mL) was stirred at room temperature for 30 minutes. Boron trifluoride ethyl etherate (10 μL, 81 μmol) was slowly added over 5 minutes. After 3 h the suspension was filtered over celite, and the filtrate was washed with $KHCO_3$ (2 M). The organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (hexane/ethyl acetate/methanol 33:100:1→20:100:1) to afford heptasaccharide **9** (31.4 mg, 19.4 %), nonasaccharide **10** (32 mg, 15.7 %), and recovered acceptor **7** (66 mg, 55 %).

Compound ***9***: R_f=0.21 (ethyl acetate/methanol 100:1); $[\alpha]_D^{23}$=+2.1 (*c*= 0.1, CH_2Cl_2); ^{1}H NMR (360 MHz, [D$_6$]DMSO): δ=7.96 (d, $J_{2,NH}$=9.5 Hz, 1H; NH^5), 7.91–7.61 (m, 9H; NH$^{5'}$, Pht), 7.38–7.16 (m, 10H; Ar), 7.01–6.65 (m, 10H; Ar), 5.41 (d, $J_{4,OH}$=3.6 Hz, 1H; OH-4^3), 5.28 (d, $J_{1,2}$= 9.7 Hz, 1H; H-1^1), 5.16 (d, $J_{1,2}$=9.2 Hz, 1H; H-1^2), 5.13–4.74 (m, 12H; H-4$^{4'}$, H-1^4, H-3^5, H-4^4, H-3^4, OH-2^3, H-3$^{4'}$, H-3$^{5'}$, H-1$^{4'}$, H-4^5, CH_2O, H-4$^{5'}$), 4.74 (d, J_{gem}=12.7 Hz, 1H; CH_2O), 4.63–4.51 (m, 5H; CH_2O, H-1^5, CH_2O, H-1^3, CH_2O), 4.47 (d, $J_{1,2}$=9.4 Hz, 1H; H-1$^{5'}$), 4.41–4.26 (m, 4H; CH_2O, CH_2O, CH_2O, H-2^4), 4.22–3.89 (m, 15H; H-5^4, H-6a^5, H-3^2, H-3^1, H-4^1, H-2$^{4'}$, H-6a^4, H-6a$^{5'}$, H-6a$^{4'}$, H-2^2, H-4^2, H-6b^4, H-6b$^{4'}$, H-6b^5, H-5$^{4'}$), 3.88–3.65 (m, 10H; H-2^3, H-2^5, H-2^1, H-2$^{5'}$, H-6a^2, H-6b$^{5'}$, H-5^3, H-5^5, H-6a^3, H-6b^3), 3.61–3.21 (m, 8H; H-5^1, H-5$^{5'}$, H-4^3, H-6b^2, H-6a^1, H-5^2, H-3^3, H-6b^1), 2.06–1.84 (m, 36H; OAc), 1.75 (s, 3H; NAc), 1.70 ppm (s, 3H; NAc); ^{13}C NMR (90 MHz, [D$_6$]DMSO): δ=169.8, 169.5, 169.4, 167.5, 167.4 (C=O), 138.2, 138.1 (C-*i* Ar), 134.9, 134.8 (C-4/5 Pht), 130.9, 130.8, 130.6 (C-1/2 Pht), 128.6, 128.2, 127.7, 127.4, 127.3, 127.0, 126.7 (C-Ar), 123.4, 123.3 (C-3/6 Pht), 99.9 (C-1$^{5'}$), 99.6 (C-1^5), 99.4 (C-1^4), 98.3 (C-1^3), 96.7 (C-1$^{4'}$), 96.7 (C-1^2), 84.4 (C-1^1), 82.6 (C-3^3), 76.4 (C-3^1), 76.3 (C-4^2), 75.3 (C-5^1), 75.2 (C-3^2), 74.9 (C-4^1), 74.6 (C-5^2), 74.5 (C-2$^{4'}$), 73.8 (C-2^4), 73.6 (CH_2O), 72.9 (CH_2O), 72.2 (CH_2O), 72.0 (C-3$^{5'}$), 71.9 (C-3^5), 71.2 (CH_2O), 70.5 (C-5^3), 70.5 (C-5^5), 70.3 (C-5$^{5'}$), 69.8 (C-3$^{4'}$), 69.5 (C-3^4), 69.1 (C-2^3), 68.4 (C-4^5), 68.1 (C-4$^{5'}$), 67.9 (C-4^3), 67.8 (C-6^2), 67.7 (C-4^4), 67.5 (C-5$^{4'}$), 67.4 (C-6^3), 67.2 (C-6^1), 65.2 (C-4^4), 64.5 (C-4$^{4'}$), 62.0 (C-6^4), 61.9 (C-6$^{4'}$), 61.8 (C-6^5), 61.4 (C-6$^{5'}$), 55.6 (C-2^2), 54.3 (C-2^1), 52.3 (C-2^5), 52.1 (C-2$^{5'}$), 20.5, 20.4, 20.3, 20.2 ppm (NAc, OAc); ESI-MS: *m/z*: calcd for $C_{114}H_{131}N_7O_{49}$: 2381.8; found: 2405.3 $[M+Na]^+$, 2421.3 $[M+K]^+$.

Compound ***10***: R_f=0.11 (ethyl acetate/methanol 100:1); $[\alpha]_D^{23}$=+0.8 (*c*= 0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ=7.95–7.63 (m, 10H; NH^5, NH^{5*}, Pht), 7.40–6.68 (m, 21H; NH$^{5'}$, Ar), 5.30 (m, 2H; H-1^1, OH-2^3), 5.18–5.05 (m, 6H; H-1^2, H-1^4, H-3$^{4'}$, H-4^4, H-4$^{4'}$, H-4^{4*}), 5.03–4.85 (m, 10H; H-1$^{4'}$, H-1^{4*}, H-3^4, H-3^{4*}, H-3^5, H-3$^{5'}$, H-3^{5*}, CH_2O, H-4^5, H-4^{5*}), 4.80 (dd, $J_{3,4}$=$J_{4,5}$=9.6 Hz, 1H; H-4$^{5'}$), 4.74 (d, J_{gem}=13.4 Hz, 1H; CH_2O), 4.68 (d, $J_{1,2}$=8.4 Hz, 1H; H-1^5), 4.64 (d, J_{gem}=13.4 Hz, 1H; CH_2O), 4.61–4.55 (m, 4H; CH_2O, H-1^3, H-6a^4), 4.47 (d, $J_{1,2}$=8.2 Hz, 1H; H-1$^{5'}$), 4.40–4.31 (m, 5H; H-1^{5*}, H-5^4, CH_2O), 4.30–4.20 (m, 4H; H-3^2, H-6a^4, H-6a^5, H-6a^{5*}), 4.20–3.60 (m, 29H; H-2^1, H-2^2, H-2^3, H-2^4, H-2$^{4'}$, H-2^{4*}, H-2^5, H-2$^{5'}$, H-2^{5*}, H-3^1, H-4^1, H-4^2, H-4^3, H-5$^{4'}$, H-5^{4*}, H-5^5, H-5$^{5'}$, H-5^{5*}, H-6a^2, H-6a,b^3, H-6b^4, H-6a,b$^{4'}$, H-6b^{4*}, H-6b^5, H-6a,b$^{5'}$, H-6b^{5*}), 3.59–3.52 (m, 3H; H-3^3, H-5^1, H-6b^2), 3.47–3.36 (m, 3H; H-5^2, H-5^3, H-6a^1), 3.26 (m, 1H; H-6b^1), 2.18–1.64 ppm (m, 63H; OAc, NAc); ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ=170.1, 170.0, 169.8, 169.4, 169.1, 169.0, 167.0 (C=O), 138.9, 138.3, 138.2 (C-*i* Ar), 134.8, 134.7 (C-4/5 Pht), 130.8, 130.6 (C-1/2 Pht), 128.2–126.6 (C-Ar), 123.4 (C-3/6 Pht), 102.5 (C-1^{5*}), 101.0 (C-1^5), 100.0 (C-1$^{5'}$, C-1^{4*}), 99.7 (C-1^4), 97.9 (C-1^3), 97.4 (C-1$^{4'}$), 97.0 (C-1^2), 84.8 (C-1^1), 82.7 (C-3^3), 77.3 (C-4^3), 77.0 (C-2^{4*}), 76.8 (C-4^2, C-3^1), 75.8 (C-2^4), 75.6 (C-5^1), 75.4 (C-3^2), 75.2 (C-4^1), 74.7 (C-5^2), 74.5 (C-5^3, C-2$^{4'}$), 74.2, 73.3 (CH_2O), 72.4 (CH_2O, C-3^5, C-3^{5*}), 71.8 (C-3$^{5'}$), 71.3 (CH_2O), 70.6 (C-5^5, C-5$^{5'}$, C-5^{5*}), 70.1 (C-3$^{4'}$), 69.9 (C-3^4), 69.6 (C-3^{4*}), 69.3 (C-2^3), 68.3 (C-4$^{5'}$), 68.1 (C-4^4), 68.0 (C-4^5, C-6^2, C-5^{4*}), 67.9 (C-5$^{4'}$), 67.8 (C-4^{5*}, C-6^3), 67.4 (C-6^1), 65.1 (C-4^4), 64.9 (C-4^{4*}), 64.8 (C-4$^{4'}$), 62.1 (C-6$^{4'}$), 61.9 (C-6^4), 61.7 (C-6$^{5'}$), 61.5 (C-6^5), 61.2 (C-6^{5*}), 60.8 (C-6^{4*}), 55.6 (C-2^2), 54.7 (C-2^1), 52.6 (C-2^5), 52.5 (C-2$^{5'}$), 52.4 (C-2^{5*}), 22.3, 22.2 (NAc), 20.6, 20.5, 20.4, 20.0 ppm (OAc); FAB-MS (NBA): *m/z*: calcd for $C_{140}H_{166}N_8O_{65}$: 2999.0; found: 3001.1 $[M+H]^+$, 3023.8 $[M+Na]^+$.

Azide 11: A mixture of **7** (60 mg, 34 μmol), **D** (33 mg, 38 μmol), and ground molecular sieves (4 Å, 100 mg) in freshly distilled CH_2Cl_2 (10 mL) was stirred at −40 °C for 30 min. Boron trifluoride ethyl etherate (50 μL, 407 μmol) was slowly added over 5 min, and the solution was allowed to warm up to −25 °C within 1 h. After disappearance of the donor (TLC: hexane/ethyl acetate 1:3) the suspension was filtered over celite, and the filtrate was washed with $KHCO_3$ (2 M). The organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (hexane/ethyl acetate/methanol 20:100:1) to afford **11** (48 mg, 57.2 %). R_f=0.23 (hexane/ethyl acetate/methanol 20:100:1); $[\alpha]_D^{23}$=−2.4 (*c*=0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ=7.92 (d, $J_{2,NH}$=9.3 Hz, 1H; NH), 7.90–7.62 (m, 12H; Pht), 7.36–7.19 (m, 10H; Ar), 6.92–6.65 (m, 10H; Ar), 5.59 (dd, $J_{2,3}$=10.5 Hz, $J_{3,4}$=9.5 Hz, 1H; H-3$^{5'}$), 5.38 (d, $J_{1,2}$=8.5 Hz, 1H; H-1^{5}β), 5.34 (d, $J_{OH,4}$=4.1 Hz, 1H; OH-4^3), 5.28 (d, $J_{1,2}$=9.5 Hz, 1H; H-1^{1}β), 5.16 (d, $J_{1,2}$=8.4 Hz, 1H; H-1^{2}β), 5.08 (d, $J_{1,2}$<1.0 Hz, 1H; H-1^4), 5.07–4.83 (m, 9H; H-3^4, H-3$^{4'}$, H-3^5, H-4^4, H-4$^{4'}$, H-4^5, H-4$^{5'}$, CH_2O, OH-2^3), 4.65 (d, J_{gem}=13.0 Hz, 1H; CH_2O), 4.58 (d, $J_{1,2}$=8.5 Hz, 1H; H-1^{5}β), 4.56–4.48 (m, 4H; H-1^3, CH_2O), 4.39 (d, $J_{1,2}$<1.0 Hz, 1H; H-1$^{4'}$), 4.35–4.26 (m, 3H; CH_2O), 4.25 (m, 1H; H-2^4), 4.18–3.92 (m, 13H; H-2^2, H-2$^{4'}$, H-2$^{5'}$, H-3^1, H-3^2, H-4^1, H-4^2, H-5^4, H-6ab^4, H-6ab^5, H-6a$^{5'}$), 3.85–3.70 (m, 8H; H-2^1, H-2^3, H-2^5, H-5$^{4'}$, H-5^5, H-5$^{5'}$, H-6a^2, H-6b$^{5'}$), 3.62–3.56 (m, 2H; H-6a$^{4'}$, H-5^1), 3.55–3.21 (m, 10H; H-3^3, H-4^3, H-5^2, H-5^3, H-6ab^1, H-6b^2, H-6ab^3, H-6b$^{4'}$), 2.01, 2.00, 1.98, 1.97, 1.96, 1.94, 1.93 (7×s, 27H; OAc), 1.79, 1.78, 1.77, 1.75 ppm (4×s, 12H; NAc, OAc); ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ=170.1, 170.0, 169.8, 169.5, 169.4, 169.3, 169.2, 167.8, 167.1 (C=O), 138.5, 138.2, 138.1 (C-*i* Ar), 134.8, 134.7 (C-4/5 Pht), 130.8, 130.5 (C-1/2 Pht), 128.2–126.7 (C-Ar), 123.4 (C-3/6 Pht), 99.9 ($J_{C-1,H-1}$=162.7 Hz from a coupled HMQC spectrum, C-1^{5}β), 99.6 ($J_{C-1,H-1}$=175.6 Hz from a coupled HMQC spectrum, C-1^{4}α), 98.7 ($J_{C-1,H-1}$=158.4 Hz from a coupled HMQC spectrum, C-1^{3}β), 96.9 ($J_{C-1,H-1}$=165.7 Hz from a coupled HMQC spectrum, C-1^{2}β and $J_{C-1,H-1}$=172.1 Hz from a coupled HMQC spectrum, C-1$^{4'}$α), 95.9 ($J_{C-1,H-1}$=167.4 Hz from a coupled HMQC spectrum, C-1$^{5'}$β), 84.8 ($J_{C-1,H-1}$=167.0 Hz from a coupled HMQC spectrum, C-1^{1}β), 76.8 (C-3^1), 76.6 (C-4^2), 75.6 (C-5^1), 75.5 (C-3^2), 75.2 (C-4^1), 74.8 (C-5^2), 74.7 (C-5^3), 74.2 (C-2^4), 73.9 (CH_2O), 73.6 (C-2$^{4'}$), 73.2, 72.5 (CH_2O), 72.2 (C-3^5), 71.4 (CH_2O), 70.8 (C-5^5, C-5$^{5'}$), 69.8 (C-3^3, C-3^4, C-3$^{4'}$, C-3$^{5'}$), 69.4 (C-2^3), 68.6 (C-4^5), 68.5 (C-4$^{5'}$), 68.0 (C-6^2), 67.9 (C-4^4), 67.8 (C-6^3), 67.4 (C-5^4, C-6^1), 65.5 (C-4^4, C-4^3), 64.5 (C-4$^{4'}$), 62.3 (C-6^4), 62.0 (C-6^5), 61.8 (C-6$^{4'}$), 61.5 (C-6$^{5'}$), 55.8 (C-2^2), 54.6 (C-2^1), 53.8 (C-2$^{5'}$), 52.6 (C-2^5), 22.6 (NAc), 20.6, 20.5, 20.4, 20.3, 20.1 ppm (OAc); FAB-MS (NBA): *m/z*: calcd for $C_{120}H_{131}N_7O_{50}$: 2469.8; found: 2495 $[M+Na]^+$.

Azide 12: A mixture of **8** (900 mg, 475 μmol), **D** (620 mg, 712 μmol), and ground molecular sieves (4 Å, 1.5 g) in freshly distilled CH_2Cl_2 (120 mL) was stirred at −45 °C for 30 min. Boron trifluoride ethyl etherate (33 μL, 268 μmol) was slowly added over 5 minutes. After 2 h (TLC: hexane/acetone 1:1) the suspension was filtered over celite and the filtrate was washed with $KHCO_3$ (2 M). The organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (hexane/acetone 1.2:1→1.1:1) to afford **12** (905 mg, 73.3 %); R_f=0.25 (hexane/acetone 1:1); $[\alpha]_D^{23}$=−7.5 (*c*=0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ=7.97–7.73 (m, 16H; Pht), 7.30–7.10 (m, 10H; Ar), 6.90–6.70 (m, 10H; Ar), 5.69 (dd, $J_{2,3}$=10.5, $J_{3,4}$=9.5 Hz, 1H; H-3^5), 5.60–5.45 (m, 2H; H-3$^{5'}$, OH-4^3), 5.32 (d, $J_{1,2}$=8.5 Hz, 1H; H-1^{5}β), 5.28–5.23 (m, 2H; H-1^{1}β, H-1^{5}β), 5.16–5.12 (m, 2H; H-1^2, H-2^3), 5.03 (dd, $J_{3,4}$=$J_{4,5}$=9.5 Hz, 1H; H-4^5), 5.00–4.90 (m, 4H; H-3$^{4'}$, H-4^4, H-4$^{4'}$, H-4$^{5'}$), 4.87–4.82 (m, 2H; H-1^4, CH_2O), 4.73 (dd, $J_{2,3}$=2.8, $J_{3,4}$= 10.4 Hz, 1H; H-3^4), 4.66–4.61 (m, 2H; H-1^3, CH_2O), 4.47 (2×d, J_{gem}= 12.1 Hz, 2H; CH_2O), 4.40 (d, J_{gem}=12.6 Hz, 1H; CH_2O), 4.37 (d, $J_{1,2}$< 1.0 Hz, 1H; H-1$^{4'}$), 4.35–4.29 (m, 3H; CH_2O), 4.28–4.21 (m, 2H; H-2^4, H-6a^5), 4.17 (dd, 1H; H-2^5), 4.12–3.87 (m, 10H; 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$^{5'}$), 3.81 (m, 1H; H-5^4), 3.78–3.43 (m, 14H; H-2^1, H-3^3, H-4^3, H-5^1, H-5$^{4'}$, H-5$^{5'}$, H-6a,b^2, H-6a,b^3, H-6a,b^4, H-6a$^{4'}$, H-6b$^{5'}$), 3.41–3.37 (m, 2H; H-6a^1, H-6b$^{4'}$), 3.27–3.22 (m, 3H; H-5^2, H-5^3, H-6b^1), 2.07, 2.03, 1.994, 1.987, 1.975, 1.970, 1.93, 1.92, 1.90, 1.82,

1.80, 1.79 ppm (12×s, 39H; OAc); ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 170.0, 169.8, 169.6, 169.4, 169.22, 169.14, 169.07, 168.0, 167.8, 167.1 (C=O), 138.2, 138.09, 138.06, 137.97 (C-*i* Ar), 134.8, 134.7 (C-4/5 Pht), 130.6, 130.5 (C-1/2 Pht), 128.1–127.0 (C-Ar), 123.4 (C-3/6 Pht), 97.7 ($J_{C\text{-}1,H\text{-}1}$ = 175.1 Hz from a coupled HMQC spectrum, C-1$^{4'}\alpha$), 97.1 ($J_{C\text{-}1,H\text{-}1}$ = 172.6 Hz from a coupled HMQC spectrum, C-1$^{4}\alpha$), 96.8 ($J_{C\text{-}1,H\text{-}1}$ = 162.8 Hz from a coupled HMQC spectrum, C-1$^{3}\beta$), 96.7 ($J_{C\text{-}1,H\text{-}1}$ = 170.2 Hz from a coupled HMQC spectrum, C-1$^{2}\beta$), 96.1 ($J_{C\text{-}1,H\text{-}1}$ = 167.7 Hz from a coupled HMQC spectrum, C-1$^{5}\beta$ and $J_{C\text{-}1,H\text{-}1}$ = 167.7 Hz from a coupled HMQC spectrum, C-1$^{5'}\beta$), 84.7 ($J_{C\text{-}1,H\text{-}1}$ = 167.7 Hz from a coupled HMQC spectrum, C-1$^{1}\beta$), 77.0 (C-4^{2}), 76.6 (C-3^{1}), 75.7 (C-3^{2}, C-3^{3}), 75.6 (C-5^{1}), 75.2 (C-4^{1}), 74.3 (C-5^{2}), 74.1 (C-5^{3}), 73.9 (CH$_2$O), 73.7 (CH$_2$O), 73.8 (C-2$^{4'}$), 73.5 (CH$_2$O, C-2^{4}), 72.3, 71.6 (CH$_2$O), 71.0 (C-5^{5}), 70.7 (C-5$^{5'}$), 70.4 (C-2^{3}), 69.7 (C-3$^{4'}$, C-3^{5}, C-3$^{5'}$), 69.0 (C-3^{4}), 68.6 (C-4^{5}), 68.3 (C-4$^{5'}$), 68.1 (C-4^{4}), 67.7 (C-6^{2}), 67.5 (C-5$^{4'}$, C-6^{1}), 67.2 (C-6^{3}), 66.9 (C-4^{3}), 64.6 (C-4^{4}), 64.3 (C-4$^{4'}$), 61.8 (C-6^{5}), 61.7 (C-6^{4}), 61.6 (C-6$^{4'}$), 61.4 (C-6$^{5'}$), 55.7 (C-2^{2}), 54.5 (C-2^{1}), 53.8 (C-2$^{5'}$), 53.7 (C-2^{5}), 20.5, 20.4, 20.33, 20.29, 20.25, 20.19, 20.1, 20.0 ppm (OAc); ESI-MS: *m*/*z*: calcd for $C_{128}H_{133}N_7O_{52}$: 2559.8; found: 2623.4 [*M*+Na]$^+$; FAB-MS (NBA): 2623.3 [*M*+Na]$^+$; elemental analysis calcd (%) for $C_{128}H_{133}N_7O_{52}$ (2601.47): C 59.10, H 5.15, N 3.77; found: C 59.20, H 5.38, N 3.51.

Azide 13

Starting from heptasaccharide ***12***: A mixture of donor **D** (23 mg, 26.5 μmol), acceptor **12** (32 mg, 12.3 μmol), and ground molecular sieves (4 Å, 55 mg) in freshly distilled CH_2Cl_2 (for concentrations see Table 2) was stirred at −20 °C for 20 minutes. Boron trifluoride ethyl etherate (3.25 μL, 6.63 μmol in 35 μL CH_2Cl_2) was slowly added over 10 minutes, and the solution was allowed to reach room temperature. After 21 h the reaction mixture was checked by TLC (TLC: CH_2Cl_2/MeOH 50:1; hexane/acetone 1:1) and LC-MS (Table 2). Analytical HPLC conditions for LC-MS; column: YMC-Pack Pro C4 S-3 mm (50×2.1 mm); solvent system: eluent A, water (0.1 % formic acid); eluent B, acetonitrile (0.1 % formic acid), linear gradient: 50 % B for 5 minutes, 50–95 % B for 25 minutes, flow rate: 200 mL min^{-1}, diode array UV detection: 215–275 nm. To obtain a pure sample of **13**, the products of several reactions were combined and purified by flash chromatography (hexane/acetone 1.2:1→1.1:1). R_f = 0.20 (hexane/acetone 1:1); $[\alpha]_D^{23} = -6.1$ (c = 1.4, CH_2Cl_2); ^{1}H NMR (360 MHz, [D$_6$]DMSO): δ = 7.98–7.54 (m, 20H; Pht), 7.45–7.16 (m, 10H; Ar), 6.94–6.49 (m, 10H; Ar), 7.74–7.64 (m, 2H; H-3^{5*}, H-3^{5}), 5.58–5.40 (m, 3H; H-1^{5*}, H-3$^{5'}$, H-1^{5}), 5.29 (d, $J_{1,2}$ = 9.5 Hz, 1H; H-1^{1}), 5.21–4.78 (m, 13H; H-1$^{5'}$, H-1^{2}, H-4^{5}, H-4^{4}, H-4^{4*}, H-4^{5*}, H-2^{3}, H-4$^{4'}$, H-3^{4*}, H-4$^{5'}$, CH$_2$O, H-3$^{4'}$, H-3^{4}), 4.68–4.45 (m, 6H; CH$_2$O, H-1^{3}, CH$_2$O, H-1^{4}, CH$_2$O, H-1$^{4'}$), 4.39–4.15 (m, 10H; H-6a^{5*}, CH$_2$O, H-1^{4*}, CH$_2$O, CH$_2$O, H-2^{5}, H-2^{5*}, H-6a^{5}, H-2^{4}), 4.14–3.93 (m, 14H; H-2$^{4'}$, H-3^{1}, H-2^{4*}, H-2$^{5'}$, H-6b^{5*}, H-3^{2}, H-5^{5*}, H-6b^{5}, H-2^{2}, H-5^{5}, H-4^{1}, H-4^{2}, H-5$^{5'}$, H-3^{3}), 3.92–3.51 (m, 16H; H-4^{3}, H-6a^{2}, H-2^{1}, H-6a$^{4'}$, H-6a^{4}, H-6a^{3}, H-6b^{3}, H-6b$^{4'}$, H-6b^{4}, H-6a$^{5'}$, H-5$^{4'}$, H-5^{4}, H-5^{4*}, H-6a^{4*}, H-5^{1}, H-6b^{2}), 3.49–3.20 (m, 6H; H-6b$^{5'}$, H-6b^{4*}, H-6a^{1}, H-5^{3}, H-5^{2}, H-6b^{1}), 2.14–1.72 ppm (m, 57H; OAc); ^{13}C NMR (90 MHz, [D$_6$]DMSO): δ = 170.0, 169.9, 169.6, 169.5, 169.1, 169.0, 168.7, 167.8, 167.1 (C=O), 138.3, 138.1, 138.0, 137.8 (C-*i*, Ar), 135.0, 134.7 (C-4/5 Pht), 130.7, 130.5 (C-1/2 Pht), 128.2, 127.9, 127.8, 127.6, 127.3, 127.2, 127.1, 127.0 (C-Ar), 123.4 (C-3/6 Pht), 98.6 ($^1J_{C\text{-}1,H\text{-}1}$ = 174.3 Hz from a coupled HSQC spectrum, C-1$^{4}\alpha$), 98.3 ($^1J_{C\text{-}1,H\text{-}1}$ = 177.3 Hz from a coupled HSQC spectrum; C-1$^{4'}\alpha$), 96.9 ($^1J_{C\text{-}1,H\text{-}1}$ = 174.3 Hz from a coupled HSQC spectrum; C-1$^{4*}\alpha$), 96.5 ($^1J_{C\text{-}1,H\text{-}1}$ = 165.1 Hz from a coupled HSQC spectrum; C-1$^{3}\beta$), 96.5 ($^1J_{C\text{-}1,H\text{-}1}$ = 165.3 Hz from a coupled HSQC spectrum; C-1$^{2}\beta$), 96.2 ($^1J_{C\text{-}1,H\text{-}1}$ = 166.2 Hz from a coupled HSQC spectrum; C-1$^{5*}\beta$), 95.8 ($^1J_{C\text{-}1,H\text{-}1}$ = 166.2 Hz from a coupled HSQC spectrum; C-1$^{5}\beta$), 95.8 ($^1J_{C\text{-}1,H\text{-}1}$ = 168.2 Hz from a coupled HSQC spectrum; C-1$^{5'}\beta$), 84.4 ($^1J_{C\text{-}1,H\text{-}1}$ = 167.5 Hz from a coupled HSQC spectrum; C-1$^{1}\beta$), 77.3 (C-4^{3}), 76.4 (C-3^{1}), 75.4 (C-3^{2}), 75.4 (C-3^{3}), 75.4 (C-4^{2}), 75.4 (C-5^{1}), 75.0 (C-4^{1}), 74.1 (C-5^{3}), 74.1 (C-5^{2}), 73.6 (CH$_2$O), 73.5 (C-2^{4}), 73.5 (C-2$^{4'}$), 73.3 (C-2^{4*}), 73.3 (CH$_2$O), 72.1 (CH$_2$O), 71.4 (CH$_2$O), 70.9 (C-5$^{5'}$), 70.9 (C-5^{5}), 70.9 (C-5^{5*}), 69.4 (C-3^{5}), 69.4 (C-3^{5*}), 69.4 (C-3$^{5'}$), 69.4 (C-2^{3}), 69.4 (C-3^{4*}), 68.9 (C-3^{4}), 68.0 (C-4^{5}), 68.0 (C-4^{5*}), 68.0 (C-4$^{5'}$), 68.0 (C-5$^{4'}$), 68.0 (C-6^{3}), 67.6 (C-6^{2}), 67.6 (C-5^{4}), 67.6 (C-5^{4*}), 67.1 (C-6^{1}), 65.4 (C-3$^{4'}$), 63.9 (C-4^{4}), 63.9 (C-4$^{4'}$), 63.9 (C-4^{4*}), 61.6 (C-6^{4}), 61.2 (C-6$^{4'}$), 61.2 (C-6^{4*}), 61.2 (C-6^{5}), 61.2 (C-6^{5*}), 60.8 (C-6$^{5'}$), 55.3 (C-2^{2}), 54.3 (C-2^{1}), 53.6 (C-2^{5*}), 53.6 (C-2$^{5'}$), 53.6 (C-2^{5}), 20.5, 19.9 ppm (OAc); ESI-MS: *m*/*z*: calcd for $C_{160}H_{168}N_8O_{69}$: 3305.0; found: 3300.7 [*M*+Na-N$_2$]$^+$, 3324.5 [*M*+H$_3$O]$^+$, 3328.3 [*M*+Na]$^+$.

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