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Synthesis of five nona-β-(1→6)-D-glucosamines with various patterns of N-acetylation corresponding to the fragments of exopolysaccharide of *Staphylococcus aureus*

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ABSTRACT

A series of five 3-acetamidopropyl β-glycosides of nona-β-(1→6)-glucosamines containing two *N*-acetylglucosamine residues separated by a different number of glucosamine units with free amino groups have been synthesized using a convergent blockwise approach. Oxazoline glycosylation was used to introduce *N*-acetylglucosamine residues. These nonasaccharides are structurally related to the poly-*N*-acetylglucosamine (PNAG) extracellular polysaccharide of *Staphylococcus aureus* and can be used as models for biochemical and immunological studies.

1. Introduction

Poly-β-(1→6)-*N*-acetylglucosamine (PNAG) is a surface capsular polysaccharide that also mediates intercellular adherence of cells of *Staphylococcus aureus*.[1] PNAG is also produced by *Staphylococcus epidermidis*,[2] *Escherichia coli*,[3] *Yersinia pestis*,[4] *Bordetella pertussis*,[5] *Acinetobacter baumannii*[6], and others.[7] This antigen has good potential for use as an effective immunotherapeutic agent, but elicitation of protective antibodies depends on the degree of N-acetylation of the immunogens used.[8] However, finding the optimal glycoform needed for eliciting high titers of protective antibody is a difficult and empiric task. When PNAG is isolated from bacterial sources, a heterogeneous mixture of poly- and oligo-saccharides with different immunological activities is obtained. Protective antibodies are elicited when a de-N-acetylated form of PNAG (dPNAG, <30% of acetylated amino groups) is used in conjugate vaccines.[7] Preparation of dPNAG from native PNAG is imprecise and, therefore, synthetic oligoglucosamines with glucosamine units bearing acetylated and free amino groups in defined positions are needed to determine the structure of optimal epitopes needed to induce protective antibodies.

Previously we have described the synthesis of spacer-armed oligo-β-(1→6)-glucosamines consisting of 5, 7, 9, and 11 glucosamine residues and a series of corresponding per-N-acetylated derivatives.[9] Penta- and nonasaccharides were further conjugated to a carrier protein that was used for animal immunizations.[7] In contrast to the conjugates of the fully N-acetylated ligands, the oligoglucosamine conjugates elicited high titers of the antibody that bound both native, highly acetylated PNAG and poorly acetylated dPNAG and were able to protect mice from skin abscesses caused by *S. aureus* challenge.[7]

A series of oligo-β-(1→6)-*N*-acetylglucosamines containing 3–5 monosaccharide residues were synthesized by Nitz et al. using an acid reversion reaction of *N*-acetylglucosamine in HF·pyridine.[10] These oligosaccharides were further conjugated to bovine serum albumin and resultant glycoconjugates were proposed as potential vaccines against PNAG producing bacterial strains but no results of biological experiments have been reported so far.

In order to ascertain, if a combination of glucosamine and *N*-acetylglucosamine residues may form a protective epitope, a series of five nonasaccharides **1–5** (Fig. 1) containing two N-acetylated units separated by 1–5 glucosamine residues have been prepared. The degree of N-acetylation in this case is about 20% and theoretically these synthetic nonasaccharides may represent specific fragments of dPNAG.

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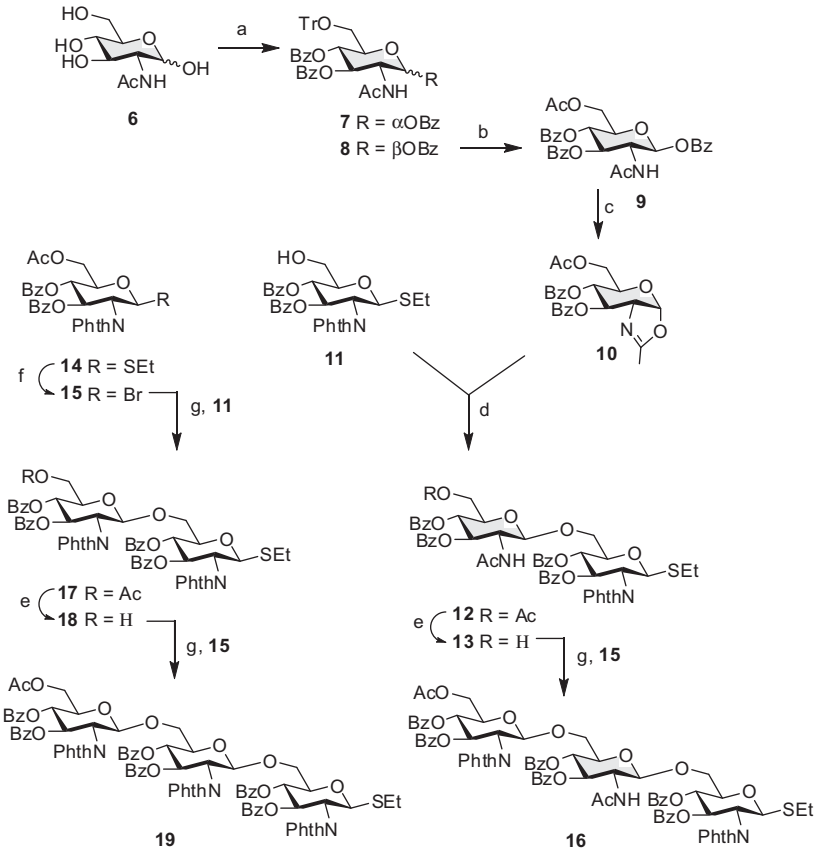
Figure 1. Target selectively N-acetylated nonasaccharides. Dashed lines show the retrosynthetic disconnections of the nonasaccharide structures.

2. Results and discussion

The key step in the synthesis of nonasaccharides **1**–**5** was the choice of a precursor for *N*-acetylglucosamine units ('pre-NAc-block'). One of the possible solutions was the use of a synthetic block with N-protecting groups which could be selectively removed in the presence of two other N-protections: one in the monosaccharide unit which is a precursor of the glucosamine unit ('pre-NH_2-block') and another N-protecting group in the spacer arm for possible conjugation to different carriers. Based on the successful synthesis of the homo-oligosaccharide ligands,[7,9] we planned to use *N*-phthaloyl groups for pre-NH_2-blocks and *N*-benzyloxycarbonyl group for the spacer derived from 3-aminopropanol. Therefore, the pre-NAc-block had to be readily available, effective as a β-stereoselective glycosyl donor, and easily convertible to the corresponding *N*-acetyl derivative. To meet these requirements, the derivative of *N*-acetylglucosamine itself was chosen as the pre-NAc-block. The main advantage of this approach was the possibility of avoiding the steps of selective deprotection and further N-acetylation.

The pre-NAc-block was prepared as follows. *N*-Acetylglucosamine **6** was successively tritylated and benzoylated with benzoyl chloride to give a mixture of α- and β-benozoates **7** and **8** in a ratio of ~2:1 (Scheme 1). Since only β-isomer is suitable for further conversion to oxazoline, we tried to improve the conditions of the benzoylation reaction to maximize the formation of **8**. A two-step benzoylation reaction, viz. first with benzoic anhydride and then with benzoyl chloride, was more effective in forming β-benzoate (α:β—1:3.5) and also avoided production of the undesirable N-benzoylation product. Compound **8** was isolated from the anomeric mixture and subjected to detritylation–acetylation by acetolysis in the presence of $BF_3{\cdot}Et_2O$ to form compound **9**. Reaction of **9** with $FeCl_3$ resulted in the formation of oxazoline **10** in a yield of 75% (30% overall from **6**).

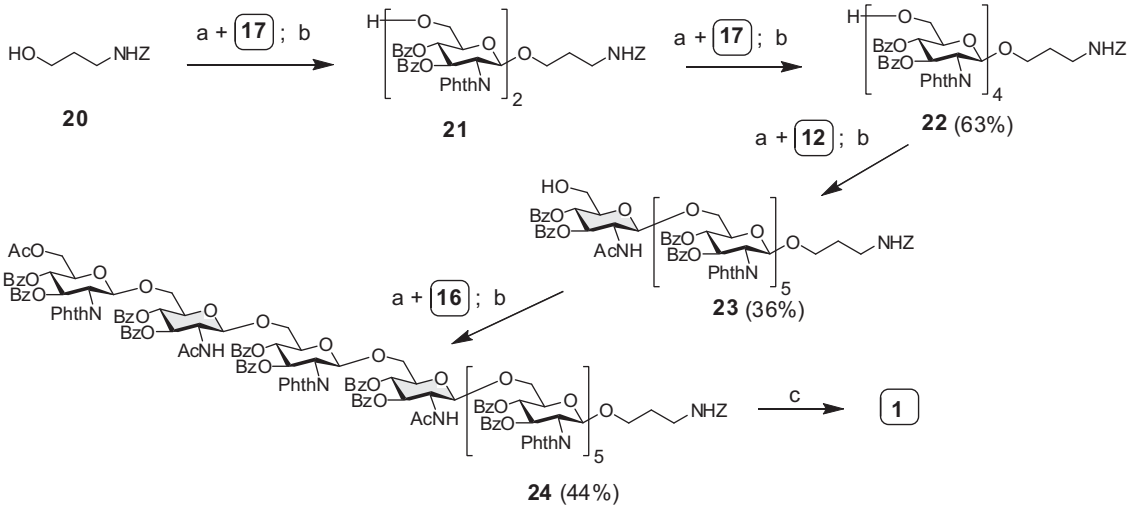
It is known that glycosylation with oxazolines usually proceeds with moderate yields but is relatively more efficient in the case of primary hydroxyl groups including 6-OH groups of hexopyranoses.[11] Nevertheless, we planned the synthetic schemes in such a way as to avoid glycosylations with oxazolines for the assembly of large oligosaccharide blocks. Thus, oxazoline **10** was used as the glycosyl donor only in the reaction with monosaccharide acceptor **11**.[9,12] This reaction proceeded in the presence of TfOH in dichloroethane at 50 °C and furnished disaccharide **12** with two different N-substituents ('mixed' disaccharide) in 79% yield. Disaccharide acceptor **13** obtained after selective deacetylation of **12** was glycosylated with bromide **15** prepared from thioglycoside **14**[9] to form the mixed trisaccharide **16** (91%). In our synthetic scheme mixed disaccharide **12** and trisaccharide **16** were used to introduce *N*-acetylglucosamine fragments onto the growing oligosaccharide chain. Previously a combination of glycosyl bromides and thioglycosides proved to be effective for the synthesis of homo-oligosaccharides.[9] Bromide **15**[9] also reacted with glycosyl acceptor **11** to



Scheme 1. Synthesis of oxazoline block **10** and key trisaccharides **16** and **19**. Reagents: (a) (1) TrCl, Py, rt; (2) Bz_2O, Py, 60 °C; (3) BzCl, Py; (b) $BF_3{\cdot}Et_2O$, Ac_2O; (c) $FeCl_3$, CH_2Cl_2; (d) TfOH, $Cl_2CH_2CH_2Cl_2$, MS AW300, 50 °C; (e) AcCl, MeOH, CH_2Cl_2; (f) Br_2, CH_2Cl_2; (g) $HgBr_2$, $Hg(CN)_2$, CH_3CN.

furnish disaccharide **17**. Deacetylation of **17** resulted in the formation of the 6-hydroxy derivative **18** and its further glycosylation afforded the trisaccharide block **19** in 66% yield.

The convergent schemes using the minimal number of synthetic blocks were developed for the assembly of the target nonasaccharides (Scheme 2). The size of blocks in each case was chosen in such a way as to provide an opportunity for isolation of the products by gel-permeation chromatography after each glycosylation step. Gel-permeation chromatography on the hydrophobic BioBeads gel is a useful alternative for isolation and purification of glycosylation products when the product and the starting compounds are hardly separable by conventional silica gel column chromatography. There are two prerequisites for the successful use of this method: the product and the starting compounds must differ strong enough in their molecular masses (hence the choice of the synthetic blocks for the assembly of oligosaccharides) and must

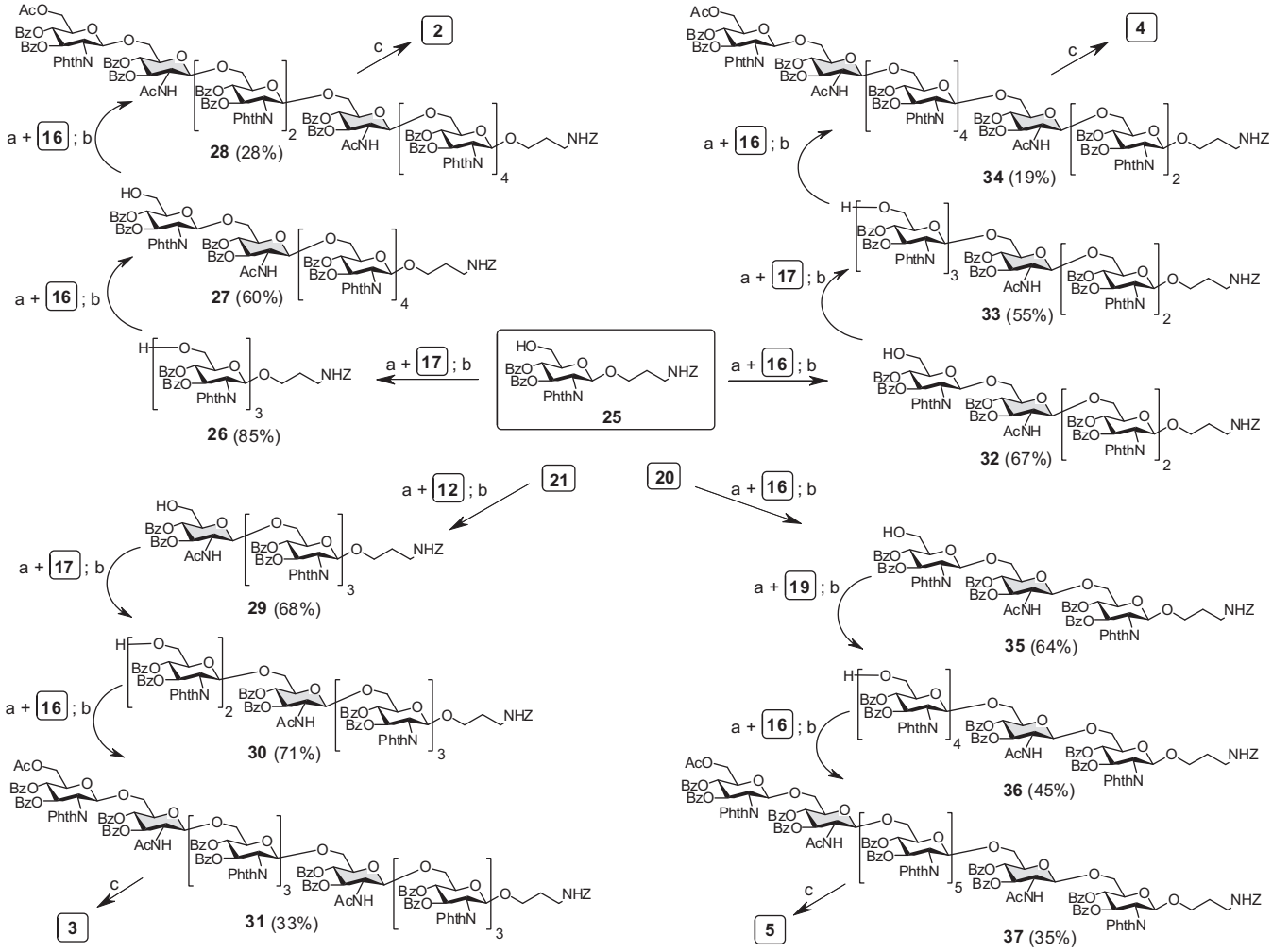


Scheme 2. Synthesis of nonasaccharide **24**. Reagents: (a) NIS, TfOH, MS 4 Å, CH_2Cl_2; (b) AcCl, MeOH, CH_2Cl_2; (c) (1) H_2 $Pd(OH)_2$/C, MeOH–THF–H_2O; (2) Ac_2O, Py; (3) $N_2H_4{\cdot}H_2O$, EtOH.

be soluble in toluene, the solvent of choice for this type of chromatography. Thus, the final step involved a glycosylation '3+6' using mixed trisaccharide block **16**. This block was also used in earlier stages for the assembly of some of the nonasaccharides. The synthesis of nonasaccharide **1** is described here in detail as an example, the other four nonasaccharides were synthesized analogously using respective building blocks depicted in Scheme 3. Glycosylation of 3-(benzyloxycarbonylamino)propanol **20** with disaccharide thioglycoside **17**[9] and subsequent removal of the *O*-acetyl group from the non-reducing glucosamine furnished the known spacer-armed disaccharide **21**. The same reaction sequence was used to obtain tetrasaccharide **22** in 63% yield. Further glycosylation with mixed disaccharide **12** and deacetylation afforded hexasaccharide **23** (36%). The final reaction of **23** with mixed trisaccharide **16** resulted in the formation of nonasaccharide **24** in only 40% yield. Unfortunately, all the reactions involving mixed blocks bearing *N*-acetylglucosamine residues were less effective (yields 20–50%) than corresponding glycosylations with homo-oligosaccharide blocks containing only *N*-phthaloyl protecting groups (60–90%).[9] All low-yield glycosylation reactions were accompanied by extensive decomposition of a glycosyl donor with the formation of a range of unidentified products, whereas an unreacted glycosyl acceptor could be recovered from the reaction mixture. This is in accordance with general observations of other examples of glycosylation involving *N*-acetylglucosamine blocks.[13–15] Lower yields in the case of N-acetylated oligosaccharide blocks are attributed to some specific intermolecular interactions of an unidentified nature.

We also tried to vary the conditions such as dilution of the reaction mixtures and the use of acetonitrile as a solvent for NIS/TfOH-promoted glycosylation, but in all cases we failed to improve the yields of the reactions with *N*-acetylglucosamine oligosaccharides. Total deprotection of **24** with the formation of **1** was achieved as described before for homo-oligosaccharides.[9] Benzyloxycarbonyl group in the spacer-arm was selectively removed to liberate an amino group which may be used at this step for the introduction of an appropriate linker for the conjugation.[7] But currently, these molecules were needed in a non-conjugated form, and, therefore, the amino group in the aminopropyl moiety was acetylated. Further one-step removal of all *O*-acyl and *N*-phthaloyl groups by hydrazinolysis in boiling ethanol afforded nonasaccharide **1**. The synthesis of nonasaccharides **2–5** was accomplished similarly by combining mono- and oligosaccharide blocks **12**, **16**, **17**, **19**, and **25** in the proper order according to the reaction sequences shown in Scheme 3.

The NMR characterization of all final and intermediate products was complicated due to close chemical nature of these compounds. The presence of a large number of uniform monosaccharide units made it difficult to attribute signals in NMR spectra to a certain residue for oligomers longer than a trisaccharide. Therefore, NMR



Scheme 3. Synthesis of nonasaccharides **2–5**. Reagents: (a) NIS, TfOH, MS 4 Å, CH_2Cl_2; (b) AcCl, MeOH, CH_2Cl_2; (c) (1) H_2, $Pd(OH)_2$/C, MeOH–THF–H_2O; (2) Ac_2O, Py; (3) $N_2H_4 \cdot H_2O$, EtOH.

data of the higher oligosaccharides were only used to establish the length of the oligosaccharide (by comparison of integral intensities of relevant groups of signals) and the number of GlcNAc units. Deprotected oligosaccharides **1–5** were also characterized by high resolution mass-spectrometry.

3. Experimental

3.1. General methods

NMR spectra were recorded on Bruker DRX-500 and Bruker AM-300 instruments. Spectra of protected oligosaccharides were measured for solutions in $CDCl_3$, and ^1H NMR chemical shifts were referenced to a residual solvent signal. NMR spectra of free oligosaccharides were measured for solutions in D_2O. Optical rotation values were measured on a JASCO DIP-360 polarimeter at 22 ± 2 °C. TLC was performed on Silica Gel 60 F_{254} plates (E. Merck), and visualization was accomplished using UV light or by charring with 10% H_3PO_4 in ethanol. Column chromatography was carried out on Silica Gel 60 (40–63 μm, E. Merck). Gel-permeation chromatography of protected oligosaccharides was performed on columns with Bio-Beads SX-3 (15 × 500 mm) or Bio-Beads SX-1 (20 × 600 mm) (Bio-Rad Laboratories) in toluene. Gel-permeation chromatography of free oligosaccharides was performed on a column with TSK HW-40 (S) (25 × 400 mm) in 0.1 M AcOH. HRESIMS spectra were obtained on Finnigan LTQ FT (Thermo Scientific) and MicrOTOF II (Bruker Daltonics) instruments. All reactions involving air- or moisture-sensitive reagents were carried out using dry solvents under dry argon.

3.2. General procedure for selective deacetylation in the presence of benzoyl groups

A solution of a 6-*O*-acetyl derivative (1 mmol) in CH_2Cl_2 (6 mL) was diluted with absolute MeOH (20 mL) and then AcCl (0.2 mL) was added under cooling in an ice-bath. The mixture was kept for 16 h at rt and then concentrated. The residue was purified by flash chromatography on silica gel (EtOAc–toluene) to give the product with a free terminal 6-OH group.

3.3. General procedure for NIS-TfOH-catalyzed glycosylation

A solution of an ethyl thioglycoside (0.1 mmol) and a glycosyl acceptor (0.09 mmol) in freshly distilled anhydrous CH_2Cl_2 (1 mL) containing 4 Å MS (130 mg) was stirred at rt under argon for 1 h and then cooled to −20 °C. NIS (0.2 mmol) and TfOH (0.04 mmol) were successively added and the resulting mixture was stirred for an additional 30 min at −20 °C. The reaction was quenched with a drop of pyridine, allowed to attain rt, diluted with CH_2Cl_2, and filtered through Celite. The filtrate was washed with 1 M $Na_2S_2O_3$, then with water, dried with Na_2SO_4, and concentrated. The residue was purified by gel chromatography either on the Bio-Beads SX-1 (hexa- and nonasaccharides) or on the Bio-Beads SX-3 (lower oligosaccharides) column in toluene.

3.4. General procedure for total deprotection of oligoglucosamines

A protected oligosaccharide (0.01 mmol) was dissolved in a mixture of MeOH–THF (1:1.5 mL) and $Pd(OH)_2/C$ (50 mg) was added. The resulting mixture was stirred under an H_2 atmosphere (1 atm) overnight, then filtered through Celite and the filtrate was concentrated. The product of hydrogenolysis was dissolved in pyridine (0.5 mL) and treated with Ac_2O (0.2 mL) and the resulting mixture was kept for 1 h at rt, and concentrated. The residue was dissolved in EtOH (10 mL) and $N_2H_4{\cdot}H_2O$ (1 mL) was added. The mixture was heated under reflux for 3 h, then concentrated and co-concentrated several times with toluene under diminished pressure. The residue was purified on the TSK HW-40S column in 0.1 M AcOH to give a pure oligo-β-(1→6)-glucosamine.

3.5. 2-Methyl-(6-*O*-acetyl-3,4-di-*O*-benzoyl-1,2-dideoxy-α-D-glucopyrano)-[2,1-*d*]-2-oxazoline (10)

Trityl chloride (16.4 g, 58.7 mmol) was added to a suspension of *N*-acetylglucosamine **6** (10 g, 45.2 mmol) in pyridine (200 mL) and the mixture was stirred for 7 h at ∼60 °C. Then benzoic anhydride (24.5 g, 108 mmol) was added and the resulting mixture was stirred for 3 days at ∼60 °C. Then the reaction mixture was cooled to 0 °C and benzoyl chloride (23.7 mL, 203.4 mmol) was added dropwise. After being kept at rt for 48 h, the mixture was cooled to 0 °C and MeOH (100 mL) was added. The resulting solution was concentrated, co-evaporated with toluene, dissolved in $CHCl_3$, and washed successively with 5% H_2SO_4, water, and saturated $NaHCO_3$. The organic layer was concentrated and the residue purified by silica gel column chromatography (toluene–acetone, 9:1) to give β-isomer **8** (15 g, 43%), α-isomer **7** (2.4 g, 6%), and a mixture **7**+**8** (7.4 g, 21%).

Compound **7**. ^1H NMR ($CDCl_3$): δ 8.25–7.00 (m, 30H, Ar), 6.70 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 6.05 (m, 1H, NH), 5.91 (t, 1H, $J_{3,4}$ 9.6 Hz, H-4), 5.51 (t, 1H, $J_{3,2}$ 10.3 Hz, H-3), 4.80 (dd, 1H, H-2), 4.22 (m, 1H, H-5), 3.39 (dd, 1H, $J_{5,6a}$ 4.2 Hz, $J_{6a,6b}$ 10.7 Hz, H-6a), 3.13 (dd, 1H, $J_{6b,5}$ 4.0 Hz, H-6b), 1.85 (s, 3H, CH_3CON); ^{13}C NMR ($CDCl_3$): δ 170.27, 167.16 (C═O), 144.09–127.05 (Ar), 91.70 (C-1), 74.90 (C-5), 73.50 (C-3), 70.59 (C-4), 62.13 (C-6), 53.43 (C-2), 23.10 (*C*H_3CON).

Compound **8**. ^1H NMR ($CDCl_3$): δ 6.05 (d, 1H, $J_{1,2}$ 8.7 Hz, H-1), 5.94 (d, 1H, $J_{NH,2}$ 7.4 Hz, NH), 5.80 (t, 1H, $J_{3,4}$ 9.6 Hz, H-4), 5.52 (t, 1H, $J_{3,2}$ 10.1 Hz, H-3), 4.83 (dd, 1H, H-2), 3.90 (m, 1H, H-5), 3.43 (dd, 1H, $J_{6a,5}$ 2.5 Hz, $J_{6a,6b}$ 8.3 Hz, H-6a), 3.20 (dd, 1H, $J_{6b,5}$ 4.2 Hz, H-6b), 1.79 (s, 3H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 170.21, 164.55 (C═O), 143.33–125.14 (Ar), 93.70 (C-1), 74.90 (C-5), 73.42 (C-3), 68.52 (C-4), 61.93 (C-6), 53.32 (C-2), 23.03 (*C*H_3CON).

Compound **8** (5 g, 6.4 mmol) was dissolved in Ac_2O (20 mL) and $BF_3{\cdot}Et_2O$ (2 mL, 15.6 mmol) was added at 0 °C, and the resultant mixture was kept at rt for 30 min. Then the reaction mixture was poured into ice-cold water and extracted with $CHCl_3$. The organic layer was washed with saturated $NaHCO_3$, concentrated, and co-evaporated with toluene. The residue was subjected to silica gel column chromatography (toluene–acetone 50:1→4:1) to give **9** (2.63 g, 71%). $[\alpha]_D$ −59 (*c* 1, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.24–7.10 (m, 15H, Ar), 6.03 (d, 1H, $J_{1,2}$ 8.7 Hz, H-1), 5.86 (d, 1H, $J_{NH,2}$ 9.3 Hz, NH), 5.65 (m, 2H, H-3, H-4), 4.76 (m, 1H, H-2), 4.40–4.20 (m, 2H, H-6a, H-6b), 4.18 (m, 1H, H-5), 2.10 (s, 3H, CH_3COO), 1.76 (s, 3H, CH_3CON); ^{13}C NMR ($CDCl_3$): δ 170.61, 170.17, 167.02, 165.22, 162.87, 162.22 (C═O), 133.91–128.26 (Ar), 93.58 (C-1), 73.12 (C-3, C-5), 68.64 (C-4), 62.19 (C-6), 53.33 (C-2), 23.20 (*C*H_3CON), 20.70 (*C*H_3COO).

To a solution of **9** (2.5 g, 4.3 mmol) in anhydrous CH_2Cl_2 (190 mL) was added $FeCl_3$ (2.5 g, 15.4 mmol), and the reaction mixture was stirred for 2 h at rt under argon, then washed with H_2O, and concentrated. The residue was purified by silica gel column chromatography (petroleum ether–acetone, gradient of acetone 0→30%) to provide compound **10** (1.48 g, 75%). $[\alpha]_D$ −49 (*c* 1, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 8.10–7.10 (m, 10H, Ar), 6.11 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1), 5.67 (m, 1H, H-3), 5.35 (d, 1H, $J_{4,5}$ 8.1 Hz, H-4), 4.38–4.31 (m, 2H, H-2, H-6a), 4.28 (dd, 1H, $J_{6b,5}$ 5.6 Hz, $J_{6b,6a}$ 12.1 Hz, H-6b), 3.84 (m, 1H, H-5) 2.12 (CH_3), 1.98 (CH_3COO); ^{13}C NMR ($CDCl_3$): δ 170.50 (C═O), 166.39 (*C*═N), 164.67 (C═O), 133.50, 130.27–126.97 (Ar), 99.55 (C-1), 69.92 (C-3), 68.38 (C-4), 68.16 (C-5), 64.57(C-2), 62.05 (C-6), 20.56 (*C*H_3COO). 13.89 (CH_3). Anal. Calcd for $C_{24}H_{23}NO_8$: C, 63.57; H, 5.11; N, 3.09. Found: C, 62.73; H, 5.11; N, 2.92.

3.6. Ethyl 2-acetamido-6-*O*-acetyl-3,4-di-*O*-benzoyl-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (12)

A solution of oxazoline **10** (0.43 g, 0.64 mmol) and acceptor **6** (0.36 g, 0.64 mmol) in anhydrous dichloroethane (10 mL) containing MS AW 300 (1 g) was stirred for 30 min at rt under argon, then TfOH (0.03 mL, 0.32 mmol) was added and the mixture was stirred and heated under reflux for 40 h. After cooling to rt, the reaction was quenched with pyridine (0.05 mL), diluted with $CHCl_3$, and filtered through Celite. The filtrate was washed with water and concentrated. The residue was purified by silica gel chromatography (gradient 0→40% of acetone in petroleum ether) to give disaccharide **12** (0.514 g, 79%). $[\alpha]_D$ −4 (*c* 1, $CHC1_3$). ^{1}H NMR ($CDCl_3$): δ 7.95–7.20 (m, 24H, Ar), 6.28 (t, 1H, $J_{3,2}$ 9.7 Hz, H-3^I), 6.10 (d, 1H, $J_{NH,2}$ 8.9 Hz, NH), 5.61–5.54 (m, 3H, H-1^I, H-3^{II}, H-4^I), 5.48 (t, 1H, $J_{3,4}$ 9.7 Hz, H-4^{II}), 4.67 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1^{II}), 4.61 (t, 1H, $J_{2,1}$ 10.4 Hz, H-2^I), 4.30 (dd, 1H, H-2^{II}), 4.24–4.13 (m, 3H, H-6a^I, H-6a^{II}, H-6b^{II}), 4.10 (m, 1H, H-5^I), 3.85 (m, 1H, H-5^{II}), 3.65 (dd, 1H, $J_{6b,5}$ 5.2 Hz, $J_{6b,6a}$ 11.63 Hz, H-6b^I), 2.85–2.65 (m, 2H, CH_3CH_2S), 1.95 (s, 3H, H1, CH_3COO), 1.97 (s, 3H, CH_3CON), 1.28 (t, 3H, CH_3CH_2S); ^{13}C NMR ($CDCl_3$): δ 170.63, 170.31, 167.93, 167.07, 165.71, 165.49 (C=O), 134.13–123.65 (Ar), 101.87 (C-1^{II}), 80.67 (C-1^I), 77.38 (C-5^I), 73.20 (C-3^{II}), 72.00 (C-5^{II}, C-3^I), 69.83 (C-4^I), 69.27(C-4^{II}), 68.29 (C-6^I), 62.42 (C-6^{II}), 54.30 (C-2^{II}), 53.59 (C-2^I), 23.44 (SCH_2CH_3), 23.18 (CH_3CON), 20.60 (CH_3COO), 14.94 (SCH_2CH_3). Anal. Calcd for $C_{54}H_{50}N_2O_{16}S$: C, 63.90; H, 4.96; N, 2.76. Found: C, 63.84; H, 5.03; N, 2.63.

3.7. Ethyl 6-*O*-acetyl-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-*O*-benzoyl-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-1-thio-2-phthalimido-β-D-glucopyranoside (16)

Disaccharide **12** (2.04 g, 2.01 mmol) was deacetylated as described in Section 3.2. The product was purified by flash-chromatography on silica gel (toluene–ethyl acetate, 2:1) to give disaccharide **13** (1.86 g, 95%). $[\alpha]_D$ −12 (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 8.00–7.05 (m, 24H, Ar), 6.27 (t, 1H, $J_{3,2}$ 9.7 Hz, H-3^I), 5.99 (d, 1H, $J_{NH,2}$ 8.9 Hz, NH), 5.66–5.58 (m, 3H, H-3^{II}, H-1^I, H-4^I), 5.31 (t, 1H, $J_{4,3}$ 9.6 Hz, H-4^{II}), 4.71 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1^{II}), 4.61 (t, 1H, $J_{2,1}$ 10.4 Hz, H-2^I), 4.26–4.18 (m, 2H, H-2^{II}, H-6a^I), 4.09 (m, 1H, H-5^I), 3.73–3.55 (m, 4H, H-6b^I, H-6a^{II}, H-5^{II}, H-6b^{II}), 2.72–2.61 (m, 2H, SCH_2CH_3), 1.92 (s, 3H, CH_3CON), 1.55 (br. s, 1H, OH), 1.25 (t, 3H, SCH_2CH_3); ^{13}C NMR ($CDCl_3$): δ 174.73, 170.23, 167.90, 166.51, 165.89, 165.51 (C=O), 134.22–123.61 (Ar), 101.39 (C-1^{II}), 80.80 (C-1^I), 76.70 (C-5^I), 74.68 (C-3^{II}), 73.15 (C-3^I), 72.08 (C-5^{II}), 70.02 (C-4^I), 69.43 (C-4^{II}), 67.63 (C-6^{II}), 61.36 (C-6^I), 54.20 (C-2^I), 53.65 (C-2^{II}), 23.45 (SCH_2CH_3), 23.14 (CH_3CON), 14.94 (SCH_2CH_3).

A solution of bromide **15**[8] (200 mg, 0.33 mmol) in anhydrous CH_3CN (2 mL) was added to a solution of glycosyl acceptor **13** (215 mg, 0.22 mmol), $Hg(CN)_2$ (84 mg, 0.33 mmol), $HgBr_2$ (32 mg, 0.4 mmol) in anhydrous CH_3CN (5 mL) at rt under argon. The mixture was stirred for 45 min, diluted with $CHCl_3$, washed with a mixture of saturated $NaHCO_3$ and 1 M KBr, and the organic layer was concentrated. Product **16** (305 mg, 91%) was isolated by gel chromatography (BioBeads SX-3) in toluene. $[\alpha]_D$ +1.5 (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 8.00–7.05 (m, 38H, Ar), 6.30–6.13 (m, 3H, H-3^I, NH, H-3^{III}), 5.51–5.42 (m, 2H, H-4^{III}, H-3^{II}), 5.20 (t, 1H, $J_{4,3}$ 9.6 Hz, H-4^{II}), 5.15–5.07 (m, 3H, H-4^I, H-1^{III}, H-1^I), 4.51 (t, 1H, $J_{2,1}$ 10.4 Hz, H-2^I), 4.49–4.42 (m, 2H, H-2^{III}, H-1^{II}), 4.29–4.22 (m, 2H, H-2^{II}, H-6a^{III}), 4.17 (dd, 1H, $J_{6b,5}$ 2.6 Hz, $J_{6b,6a}$ 12.2 Hz, H-6b^{III}), 4.08–4.02 (m, 2H, H-5^{III}, H-6a^I), 3.97–3.87 (m, 2H, H-5^I, H-6a^{II}), 3.38–3.20 (m, 2H, H-5^{II}, H-6b^{II}), 3.50 (dd, 1H, $J_{6b,5}$ 3.4 Hz, H-6b^I), 2.90–2.65 (m, 2H, CH_3CH_2S), 2.00 (s, 3H, CH_3COO), 1.95 (s, 3H, CH_3CON), 1.25 (t, 3H, SCH_2CH_3); ^{13}C NMR ($CDCl_3$): δ 167.05, 166.47, 165.85, 165.54, 165.49, 165.16 (C=O), 134.1–123.46 (Ar), 101.87 (C-1^{II}), 97.91 (C-1^{III}), 80.40 (C-1^I), 77.14 (C-5^I), 74.01 (C-5^{II}), 73.43 (C-3^{II}), 72.22 (C-3^I), 71.93 (C-5^{III}), 71.00 (C-3^{III}), 69.85 (C-4^{II}), 69.68 (C-4^I, C-4^{III}), 68.02 (C-6^{II}, C-6^I), 62.38 (C-6^{III}), 54.75 (C-2^I), 54.12 (C-2^{II}), 53.49 (C-2^{III}), 23.10 (CH_3CON), 20.56 (CH_3COO), 14.83 (SCH_2CH_3). HRESIMS: found *m/z* 1514.4237 $[M+H]^+$; calcd for $C_{82}H_{72}N_3O_{24}S$ 1514.4221.

3.8. 3-(Benzyloxycarbonylamino)propyl 3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (22)

Glycosyl acceptor **21** (210 mg, 0.168 mmol), obtained in the reaction of disaccharide **17** and compound **20** as described before,[12] was glycosylated with donor **17** (204 mg, 0.185 mmol) followed by *O*-deacetylation as described in Sections 3.3 and 3.2 to give tetrasaccharide **22** (215 mg, 63% over two stages). Selected ^{1}H NMR data ($CDCl_3$): δ 8.00–7.05 (m, 61H, Ar), 6.25 (t, 1H, $J_{3,2}$ 9.7 Hz, H-3^{IV}), 6.20–6.05 (m, 3H, 3 H-3), 5.63 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1^{IV}), 5.04 (s, 2H, CH_2Ph), 3.08 (m, 2H, $OCH_2CH_2CH_2N$), 1.80 (br s, 1H, OH), 1.61 (m, 2H, $OCH_2CH_2CH_2N$); Selected ^{13}C NMR data ($CDCl_3$): δ 97.99 (C-1), 97.74 (C-1), 97.44 (2 C-1), 61.26 (C-6^{IV}), 54.75 (2C-2), 54.63 (2 C-2), 38.02 ($CH_2CH_2CH_2N$), 29.45 ($CH_2CH_2CH_2N$). HRESIMS: found *m/z* 1146.8011 $[M+2Na]^{2+}$; calcd for $C_{125}H_{101}N_5Na_2O_{36}$ 1146.8005.

3.9. 3-Acetamidopropyl 2-amino-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-2-amino-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-2-amino-2-deoxy-β-D-glucopyranosyl-(1→6)-2-amino-2-deoxy-β-D-glucopyranosyl-(1→6)-2-amino-2-deoxy-β-D-glucopyranosyl-(1→6)-2-amino-2-deoxy-β-D-glucopyranoside (1)

Hexasaccharide **23** was prepared by the reaction of glycosyl donor **12** (66 mg, 0.065 mmol) with glycosyl acceptor **22** (130 mg, 0.06 mmol) as described in Section 3.3. The reaction was performed twice, after the first run, unreacted acceptor **22** was recovered and subjected to the same glycosylation. Deacetylation of the product as described in Section 3.2 afforded hexasaccharide **23** (67 mg, total yield 36%). Selected ^{1}H NMR data ($CDCl_3$): δ 6.72 (d, 1H, $J_{NH,2}$ 8.9 Hz, NH), 5.99 (t, 1H, *J* 9.9 Hz, H-3^{VI}), 5.62 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1^I), 5.24 (t, 1H, *J* 8.4 Hz, H-4^{VI}), 5.04 (s, 2H, CH_2Ph), 3.03 (m, 2H, $OCH_2CH_2CH_2N$), 1.75 (s, 3H, CH_3CON). Selected ^{13}C NMR data ($CDCl_3$): δ 101.68 (C-1^{VI}), 98.27 (C-1), 97.95 (C-1), 97.61 (C-1), 97.53 (C-1), 97.03 (C-1), 62.7 (C-6 ^{VI}), 55.32 (5C-2), 54.67 (C-2), 38.02 ($CH_2CH_2CH_2N$), 29.45 ($CH_2CH_2CH_2N$) 22.42 (CH_3CON).

Glycosyl acceptor **23** (65 mg, 0.021 mmol) was glycosylated with donor **16** (38 mg, 0.025 mmol) as described in Section 3.3 to give nonasaccharide **24** (42 mg, 44%). $[\alpha]_D$ +19.5 (*c* 1, $CHCl_3$). Selected ^{1}H NMR data ($CDCl_3$): δ 6.49 (d, 1H, $J_{NH,2}$ 8.9 Hz, NH), 6.39 (d, 1H, $J_{NH,2}$ 8.9 Hz, NH), 6.27 (t, 1H, $J_{3,4}$ 9.6 Hz, H-3), 6.21–6.05 (m, 8H), 5.68 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 5.01 (s, 2H, CH_2Ph), 3.01 (m, 2H, $OCH_2CH_2CH_2N$), 1.92–1.89 (3s, 9H, CH_3COO, $2CH_3CON$). Selected ^{13}C NMR data ($CDCl_3$): δ 101.90 (2C-1), 98.13 (C-1), 97.91 (3C-1), 97.73 (2C-1), 97.39 (C-1), 62.39 (C-6 ^{IX}), 54.64 (7C-2), 54.08 (2C-2), 38.02 ($CH_2CH_2CH_2N$), 29.41 ($CH_2CH_2CH_2N$) 23.04 ($2CH_3CON$), 20.50 (CH_3COO).

Compound **24** (42 mg, 0.009 mmol) was deprotected as described in Section 3.4 to give **1** (10 mg, 65%). ^{1}H NMR (D_2O): δ 4.70–4.83 (m, 7H, 7H-1), 4.57 (m, 2H, 2H-1), 4.31–4.18 (m, 8H), 3.98–3.85 (m, 9H), 3.85–3.60 (m, 24H), 3.60–3.49 (m, 10H), 3.49–3.40 (m, 3H), 3.35–3.29 (m, 1H), 3.27–3.19 (m, 1H), 3.10–2.98 (m, 7H, 7H-2), 2.09 (s, 6H, 2CH_3CON), 1.99 (s, 3H, CH_3CON), 1.94 (s, 21H, CH_3COOH), 1.87–1.81 (m, 2H, OCH$_2$CH_2CH$_2$N). ^{13}C NMR (D_2O): 103.02 (2C-1), 101.22 (2C-1), 101.01 (2C-1), 100.88 (C-1), 100.60 (C-1), 100.47 (C-1), 77.46, 77.06, 76.15, 75.98, 75.60, 74.77, 73.59, 73.50, 73.27, 70.93, 70.84, 69.62, 69.18, 61.62 (C-6^{IX}), 56.93 (7C-2), 56.61 (2C-2), 37.35 (CH$_2$CH$_2$CH$_2$N), 29.70 (CH$_2$CH$_2$CH$_2$N), 24.19, 23.55, 23.19 (3CH_3CON). HRESIMS: found *m/z* 1650.721 [M+H]$^+$; calcd for $C_{63}H_{115}N_{10}O_{40}$ 1650.719.

3.10. 3-(Benzyloxycarbonylamino)propyl 3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-*O*-benzoyl-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (27)

Glycosyl donor **16**[8] (90 mg, 0.066 mmol) was allowed to react with acceptor **26**[8] (74 mg, 0.045 mmol) as described in Section 3.3 with further deacetylation as described in Section 3.2 to give hexasaccharide **27** (81 mg, 60%). $[\alpha]_D$ +10.5 (*c* 1, $CHCl_3$). Selected ^{1}H NMR data ($CDCl_3$): δ 6.42 (d, 1H $J_{NH,2}$ 8.7 Hz, NH), 6.27–6.05 (m, 5H, 5H-3), 5.63 (d, 1H, $J_{1,2}$ 8.2 Hz, H-1), 5.58 (t, 1H, $J_{3,4}$ 10.0 Hz, H-3^V), 5.51–5.08 (m, 10H, 4H-1, 6H-4), 5.01 (s, 2H, CH_2Ph), 4.53 (d, $J_{1,2}$ 8.3 Hz, H-1^V), 4.50–4.39 (m, 3H, 3H-2), 4.34 (dd, 1H, $J_{2,1}$ 8.6 Hz, $J_{2,3}$ 10.5 Hz, H-2), 4.25 (dd, 1H, $J_{2,1}$ 8.5 Hz, $J_{2,3}$ 10.6 Hz, H-2), 4.16 (m, 1H, H-2^V), 3.43 (m, 1H, OCH_2CH$_2$CH$_2$N), 3.01 (m, 2H, OCH$_2$CH$_2$CH_2N), 1.91 (s, 3H, CH_3CON), 1.55 (m, 2H, OCH$_2$CH_2CH$_2$N). Selected ^{13}C NMR data ($CDCl_3$): δ 101.66 (C-1^V), 98.20 (C-1), 98.04 (C-1), 97.89 (C-1), 97.42 (2 C-1), 61.14 (C-6^{VI}), 54.79 (4C-2), 54.58 (2C-2), 38.09 (CH$_2$CH$_2$CH$_2$N), 29.47 (CH$_2$CH$_2$CH$_2$N) 23.72 (*C*H$_3$CON). HRESIMS: found *m/z* 1575.9728 [M+2NH$_4$]$^{2+}$; calcd for $C_{173}H_{149}N_9O_{50}$ 1575.9691.

3.11. 3-(Benzyloxycarbonylamino)propyl-6-*O*-acetyl-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-*O*-benzoyl-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-*O*-benzoyl-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (28)

Glycosyl acceptor **27** (90 mg, 0.029 mmol) was allowed to react with donor **16** (52.5 mg, 0.035 mmol) as described in Section 3.3 to give nonasaccharide **28** (36.5 mg, 28%). $[\alpha]_D$ +17 (*c* 1, $CHCl_3$). Selected ^{1}H NMR data ($CDCl_3$): δ 6.41 (d, 1H, $J_{NH,2}$ 8.9 Hz, NH), 6.38 (d, 1H, $J_{NH,2}$ 8.7 Hz, NH), 6.26 (m, 1H, H-3), 6.20–6.02 (m, 6H, 6H-3), 5.65 (d, 1H, $J_{1,2}$ 8.2 Hz, H-1), 5.57–5.48 (m, 2H, 2H-3), 4.98 (s, 2H, CH_2Ph), 3.00 (m, 2H, OCH$_2$CH$_2$CH_2N), 1.95 (s, 3H, CH_3CON), 1.90 (s, 3H, CH_3COO), 1.88 (s, 3H, CH_3CON), 1.52 (m, 2H, OCH$_2$CH_2CH$_2$N); Selected ^{13}C NMR data ($CDCl_3$): δ 102.09 (C-1), 101.79 (C-1), 98.19 (C-1), 97.98 (3C-1), 97.95 (2C-1), 97.48 (C-1), 62.43 (C-6^{IX}), 54.89 (C-2), 54.75 (C-2), 54.65 (C-2), 54.43 (C-2), 54.03 (C-2), 53.85 (C-2), 53.38 (C-2), 53.15 (2C-2), 38.09 (CH$_2$CH$_2$CH$_2$N), 29.45 (CH$_2$CH$_2$CH$_2$N) 23.02 (2 *C*H$_3$CON), 20.06 (*C*H$_3$COO). HRESIMS: found *m/z* 2301.6700 [M+2NH$_4$]$^{2+}$; calcd for $C_{253}H_{214}N_{12}O_{74}$ 2301.6670.

3.12. 3-Acetamidopropyl 2-amino-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-2-amino-2-deoxy-β-D-glucopyranosyl-(1→6)-2-amino-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-2-amino-2-deoxy-β-D-glucopyranosyl-(1→6)-2-amino-2-deoxy-β-D-glucopyranosyl-(1→6)-2-amino-2-deoxy-β-D-glucopyranosyl-(1→6)-2-amino-2-deoxy-β-D-glucopyranoside (2)

Compound **28** (60 mg, 0.013 mmol) was deprotected as described in Section 3.4 to give **2** (12 mg, 57%). ^{1}H NMR (D_2O): δ 4.80–4.68 (m, 7H, 7H-1), 4.59–4.51 (m, 2H, 2H-1), 4.28–4.16 (m, 7H), 3.98–3.81 (m, 8H), 3.80–3.57 (m, 18H), 3.56–3.42 (m, 9H), 3.42–3.37 (m, 2H), 3.33–3.25 (m, 1H), 3.16–3.25 (m, 1H), 2.93–3.09 (m, 7H, 7H-2), 2.07 (s, 6H, 2CH_3CON), 1.97 (s, 3H, CH_3CON), 1.90 (s, 21H, CH_3COOH), 1.77–1.84 (m, 2H, OCH$_2$CH_2CH$_2$N); ^{13}C NMR (D_2O): 102.95 (2C-1), 100.71 (4C-1), 100.40 (2C-1), 100.25 (C-1), 77.33, 76.05, 75.83, 75.46, 74.63, 73.24, 73.06, 70.72, 69.49, 69.04, 61.47 (C-6^{IX}), 56.76 (7C-2), 56.49 (2C-2), 37.22 (CH$_2$CH$_2$CH$_2$N), 29.56 (CH$_2$CH$_2$CH$_2$N), 24.04, 23.43, 23.06 (3CH_3CON). HRESIMS: found *m/z* 1650.720 [M+H]$^+$; calcd for $C_{63}H_{115}N_{10}O_{40}$ 1650.719.3

3.13. 3-(Benzyloxycarbonylamino)propyl 3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-*O*-benzoyl-2-deoxy-2-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (30)

Tetrasaccharide **29** was prepared by the reaction of glycosyl acceptor **21** (90 mg, 0.02 mmol) with glycosyl donor **12** (120. mg, 0.118 mmol) as described in Section 3.3 and subsequent deacetylation as described in Section 3.2 (170 mg, 68% over two stages). Selected ^{1}H NMR data ($CDCl_3$): δ 6.51 (d, 1H, $J_{NH,2}$ 9.8 Hz, NH), 6.21–6.08 (m, 3H, 3 H-3), 5.79 (t, 1H, *J* 10.0 Hz, H-3^{IV}), 5.70–5.29 (m, 7H, 3H-1, 4H-4), 5.01 (s, 2H, CH_2Ph), 4.91 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1^{IV}), 3.02 (m, 2H, OCH$_2$CH$_2$CH_2N), 1.80 (s, 3H, CH_3CON). Selected ^{13}C NMR data ($CDCl_3$): δ 100.87 (C-1^{IV}), 98.53 (C-1), 98.13 (C-1), 97.72 (C-1), 61.55 (C-6^{IV}), 54.85 (2C-2), 54.75 (C-2), 54.23 (C-2), 38.00 (CH$_2$CH$_2$CH$_2$N), 29.62 (CH$_2$CH$_2$CH$_2$N), 23.21 (*C*H$_3$CON).

Hexasaccharide **30** was prepared by the reaction of glycosyl acceptor **29** (150 mg, 0.071 mmol) with donor **17** (86 mg, 0.078 mmol) as described in Section 3.3 with subsequent deacetylation as described in Section 3.2 (160 mg, 71% over two stages). Selected ^{1}H NMR data ($CDCl_3$): δ 6.51 (d, 1H, $J_{NH,2}$ 9.8 Hz, NH), 6.28–6.06 (m, 5H, 5H-3), 5.63–5.56 (m, 4H, 3H-1, H-3^{IV}), 5.48 (d, $J_{1,2}$ 8.34 Hz, H-1), 5.04 (s, 2H, CH_2Ph), 4.56 (d, $J_{1,2}$ 8.3 Hz, H-1^{IV}), 4.24 (m, 1H, H-2^{IV}), 3.50 (m, 1H, OCH_2CH$_2$CH$_2$N), 3.09 (m, 2H, OCH$_2$CH$_2$CH_2N), 1.98 (s, 3H, CH_3CON), 1.52 (m, 2H, OCH$_2$CH_2CH$_2$N); Selected ^{13}C NMR data ($CDCl_3$): δ 101.70 (C-1^{IV}), 97.98 (C-1), 97.87 (2C-1), 97.65 (C-1), 97.61 (C-1), 61.35 (C-6^{VI}), 54.78 (2C-2), 54.69 (2C-2), 54.64 (C-2), 54.28 (C-2), 38.08 (CH$_2$CH$_2$CH$_2$N), 29.51 (CH$_2$CH$_2$CH$_2$N) 23.17 (CH_3CON). HRESIMS: found *m/z* 3138.8556 [M+Na]$^+$; calcd for $C_{173}H_{141}N_7NaO_{50}$ 3138.8598.

3.14. 3-(Benzyloxycarbonylamino)propyl 6-*O*-acetyl-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-*O*-benzoyl-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-*O*-benzoyl-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (31)

Glycosyl acceptor **30** (52 mg, 0.018 mmol) was allowed to react with donor **16** (40 mg, 0.022 mmol) as described in Section 3.3 to give nonasaccharide **31** (25 mg, 33%). $[\alpha]_D$ +20 (*c*1, $CHCl_3$). Selected ^{1}H NMR data ($CDCl_3$): δ 6.43 (d, 1H, $J_{NH,2}$ 8.8 Hz, NH), 6.38 (d, 1H, $J_{NH,2}$ 8.8 Hz, NH), 6.28–6.02 (m, 7H, 7H-3), 5.65 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1), 5.62 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1), 5.00 (s, 2H, CH_2Ph), 3.04 (m, 2H, $OCH_2CH_2CH_2N$), 1.98 (s, 3H, CH_3CON), 1.90 (s, 3H, CH_3CON), 1.88 (s, 3H, CH_3COO), 1.52 (m, 2H, $OCH_2CH_2CH_2N$); Selected ^{13}C NMR data ($CDCl_3$): δ 102.02 (C-1), 101.79 (C-1), 98.16 (2C-1), 98.09 (C-1) 97.92 (2C-1), 97.54 (C-1), 97.27 (C-1), 62.41 (C-6^{IX}), 54.69 (4C-2), 54.61 (2C-2), 54.23 (2C-2), 54.07 (C-2), 38.00 ($CH_2CH_2CH_2N$), 29.46 ($CH_2CH_2CH_2N$), 23.11 (2CH_3CON), 20.08 (CH_3COO). HRESIMS: found *m/z* 2301.6615 $[M+2NH_4]^{2+}$; $C_{253}H_{214}N_{12}O_{74}$ 2301.6670.

3.15. 3-Acetamidopropyl 2-amino-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-2-amino-2-deoxy-β-D-glucopyranosyl-(1→6)-2-amino-2-deoxy-β-D-glucopyranosyl-(1→6)-2-amino-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-2-amino-2-deoxy-β-D-glucopyranosyl-(1→6)-2-amino-2-deoxy-β-D-glucopyranosyl-(1→6)-2-amino-2-deoxy-β-D-glucopyranoside (3)

Compound **31** (21 mg, 0.005 mmol) was deprotected as described in Section 3.4 to give **3** (5.5 mg, 66%). ^{1}H NMR (D_2O): δ 4.81–4.66 (m, 7H, 7H-1), 4.61–4.56 (m, 2H, 2H-1), 4.33–4.21 (m, 8H), 4.01–3.86 (m, 9H), 3.84–3.62 (m, 25H), 3.62–3.49 (m, 10H), 3.49–3.41 (m, 2H), 3.38–3.22 (m, 2H), 2.96–3.10 (m, 7H, 7H-2), 2.10 (s, 6H, 2CH_3CON), 2.01 (s, 3H, CH_3CON), 1.96 (s, 21H, CH_3COOH), 1.85 (m, 2H, $OCH_2CH_2CH_2N$); ^{13}C NMR (D_2O): 103.33 (C-1), 103.21 (C-1), 101.72 (3C-1), 101.57 (C-1), 101.42 (C-1), 101.16 (C-1), 100.93 (C-1), 77.71, 76.43, 76.24, 76.04, 75.88, 75.04, 74.98, 74.19, 74.05, 73.94, 73.75, 71.21, 71.14, 71.03, 70.05, 69.93, 69.72, 69.42, 61.91 (C-6^{IX}), 57.25 (7C-2), 56.88 (2C-2), 37.63 ($CH_2CH_2CH_2N$), 29.95 ($CH_2CH_2CH_2N$), 24.57, 23.82, 23.46 (3CH_3CON). HRESIMS: found *m/z* 1650.720 $[M+H]^+$; calcd for $C_{63}H_{115}N_{10}O_{40}$ 1650.719.

3.16. 3-(Benzyloxycarbonylamino)propyl 3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-*O*-benzoyl-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (32)

Tetrasaccharide **32** was prepared by the reaction of glycosyl acceptor **25** (159 mg, 0.225 mmol) with donor **16** (367. mg, 0.242 mmol) as described in Section 3.3 with subsequent deacetylation as described in Section 3.2 (300 mg, 67% for two stages). Selected ^{1}H NMR data ($CDCl_3$): δ 6.34 (d, 1H, $J_{NH,2}$ 8.8 Hz, NH), 6.23–6.15 (m, 3H, 3 H-3), 5.63–5.22 (m, 8H, 3H-1, 4 H-4, H-3^{III}), 5.16 (m, 1H, $OCH_2CH_2CH_2NH$), 5.02 (s, 2H, CH_2Ph), 4.53–4.41 (m, 3H, 2 H-2, H-1^{III}), 3.02 (m, 2H, $OCH_2CH_2CH_2N$), 1.95 (s, 3H, CH_3CON); Selected ^{13}C NMR data ($CDCl_3$): δ 101.62 (C-1^{III}), 98.14 (2C-1), 97.50 (C-1), 61.15 (C-6^{IV}), 54.85 (C-2), 54.75 (C-2), 54.67 (C-2), 54.47 (C-2), 38.05 ($CH_2CH_2CH_2N$), 29.52 ($CH_2CH_2CH_2N$), 23.23 (CH_3CON). HRESIMS: found *m/z* 2118.6233 $[M+H]^+$; $C_{117}H_{100}N_5O_{34}$ 2118.6244.

3.17. 3-(Benzyloxycarbonylamino)propyl 6-*O*-acetyl-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-*O*-benzoyl-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-*O*-benzoyl-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (34)

Hexasaccharide **33** was prepared by the reaction of glycosyl acceptor **32** (213 mg, 0.09 mmol) with donor **17** (142 mg, 0.122 mmol) as described in Section 3.3 with subsequent deacetylation as described in Section 3.2 (138 mg, 55% for two stages). Selected ^{1}H NMR data ($CDCl_3$): δ 6.55 (d, 1H, $J_{NH,2}$ 8.9 Hz, NH), 6.28–6.16 (m, 5H, 5 H-3), 5.04 (s, 2H, CH_2Ph), 4.58–4.40 (m, 3H, 2H-2, H-1^{III}), 4.37–4.21 (m, 3H, 3H-2), 3.10 (m, 2H, $OCH_2CH_2CH_2N$), 1.90 (s, 3H, $NCOCH_3$), 1.50 (m, 2H, $OCH_2CH_2CH_2N$); Selected ^{13}C NMR data ($CDCl_3$):101.91 (C-1^{III}), 98.06 (2C-1), 97.90 (2C-1), 97.28 (C-1), 61.18 (C-6^{VI}), 54.77 (4C-2), 54.42 (C-2), 54.03 (C-2), 38.00 ($CH_2CH_2CH_2N$), 29.36 ($CH_2CH_2CH_2N$), 23,18 (CH_3CON).

The reaction of glycosyl acceptor **33** (138 mg, 0.044 mmol) with glycosyl donor **16** (80.5 mg, 0.053 mmol) as described in Section 3.3 afforded nonasaccharide **34** (25.6 mg, 19%). $[\alpha]_D$ +18.6 (*c* 1, $CHC1_3$). Selected ^{1}H NMR data ($CDCl_3$): δ 6.42 (d, 1H, $J_{NH,2}$ 8.8 Hz, NH), 6.31 (d, 1H, $J_{NH,2}$ 8.8 Hz, NH), 6.28–6.02 (m, 7H, 7H-3), 5.65 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1), 5.62 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1), 5.00 (s, 2H, CH_2Ph), 3.04 (m, 2H, $OCH_2CH_2CH_2N$), 2.00 (s, 3H, CH_3CON), 1.83 (s, 3H, CH_3CON), 1.80 (s, 3H, CH_3COO), 1.52 (m, 2H, $OCH_2CH_2CH_2N$); Selected ^{13}C NMR data ($CDCl_3$): δ 101.92 (C-1^{II}, C-1^{VII}), 98.16 (3C-1), 97.92 (2C-1), 97.54, (2C-1), 62.50 (C-6^{IX}), 54.78 (7C-2), 54.46 (2C-2), 38.02 ($CH_2CH_2CH_2N$), 29.47 ($CH_2CH_2CH_2N$) 22.97 (2 CH_3CON), 21.32 (CH_3COO). HRESIMS: found *m/z* 2301.6628 $[M+2NH_4]^{2+}$; $C_{253}H_{214}N_{12}O_{74}$ 2301.6670.

3.18. 3-Acetamidopropyl 2-amino-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-2-amino-2-deoxy-β-D-glucopyranosyl-(1→6)-2-amino-2-deoxy-β-D-glucopyranosyl-(1→6)-2-amino-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-2-amino-2-deoxy-β-D-glucopyranosyl-(1→6)-2-amino-2-deoxy-β-D-glucopyranoside (4)

Compound **34** (30 mg, 0.007 mmol) was deprotected as described in Section 3.4 to give **4** (8 mg, 75%). ^{1}H NMR (D_2O): δ 4.78–4.64 (m, 7H, 7H-1), 4.58–4.52 (m, 2H, 2 H-1), 4.30–4.16 (m, 7H), 3.97–3.83 (m, 8H), 3.80–3.34 (m, 36H), 3.33–3.17 (m, 2H), 3.10–2.92 (m, 7H, 7 H-2), 2.07 (s, 6H, 2CH_3CON), 1.98 (s, 3H, CH_3CON), 1.92 (s, 21H, CH_3COOH), 1.77 (m, 2H, $OCH_2CH_2CH_2N$). HRESIMS: found *m/z* 1650.719 $[M+H]^+$; calcd for $C_{63}H_{115}N_{10}O_{40}$ 1650.719.

3.19. 3-(Benzyloxycarbonylamino)propyl 3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-*O*-benzoyl-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (36)

Reaction of glycosyl acceptor **20** (250 mg, 0.165 mmol) with glycosyl donor **16** (31.5 mg, 0.15 mmol) according to general procedure 3.3 with subsequent deacetylation according to 3.2 afforded trisaccharide **35** (170 mg, 64% for two stages). $[\alpha]_D$ +1.5 (*c* 1, $CHC1_3$). ^{1}H NMR ($CDCl_3$): δ 8.25–7.00 (m, 43H, Ar), 6.25–6.15 (m, 2H, H-3^{I}, H-3^{III}), 6.11 (d, 1H, $J_{NH,2}$ 8.3 Hz, NH), 5.58–5.54 (m, 4H, 2 H-1, H-3^{II}, H-4), 5.34–5.21 (m, 5H, 2 H-4, N*H*Z), 5.10–4.97 (m, 2H, CH_2Ph), 4.59 (d, 1H, $J_{1,2}$ 8.2 Hz, H-1^{II}), 4.50 (dd, 1H, $J_{2,1}$ 9.0 Hz, $J_{2,3}$ 10.6 Hz, H-2), 4.30 (dd, 1H, $J_{2,1}$ 8.7 Hz, $J_{2,3}$ 10.5 Hz, H-2^{I}), 4.15–3.87 (m, 5H), 3.82–3.52 (m, 7H), 3.18 (m, 2H, $OCH_2CH_2CH_2N$), 1.88 (s, 3H, CH_3CON). Selected ^{13}C NMR data ($CDCl_3$): δ 101.16 (C-1^{II}), 97.98 (C-1), 97.47 (C-1), 74.18, 72.87 (C-5), 71.37, 70.81, 70.18 (C-3), 69.72, 69.67 (C-4), 68.02, 66.73 (C-6), 61.03 (C-6^{III}), 54.52 (3C-2), 37.75 ($CH_2CH_2CH_2N$), 29.54 ($CH_2CH_2CH_2N$), 23.06 (CH_3CON).

Hexasaccharide **36** was prepared by the reaction of glycosyl acceptor **35** (117 mg, 0.073 mmol) with donor **19** (138 mg, 0.08 mmol) as described in Section 3.3 with subsequent deacetylation as described in Section 3.2 (64 mg, 27% for two stages). After replacement of the solvent for the glycosylation reaction with CH_3CN (molecular sieves 3 Å were also used instead of MS 4 Å) the yield of the reaction rose to 45%. $[\alpha]_D$ +2 (*c* 1, $CHC1_3$). Selected ^{1}H NMR data ($CDCl_3$): δ 6.39 (d, 1H, $J_{NH,2}$ 8.7 Hz, NH), 6.28–6.16 (m, 2H, 2 H-3), 6.12–6.05 (m, 3H, 3 H-3), 5.59–5.32 (m, 8H, 5 H-1, H-3, 2H-4), 5.26–5.09 (m, 4H, 4H-4), 5.01 (s, 2H, CH_2Ph), 4.51–4.40 (m, 2H, H-2, H-1^{II}), 3.10 (m, 2H, $OCH_2CH_2CH_2N$), 1.90 (s, 3H, CH_3CON), 1.50 (m, 2H, $OCH_2CH_2CH_2N$). Selected ^{13}C NMR data ($CDCl_3$): δ 101.74 (C-1^{II}), 98.00 (C-1), 97.58 (3C-1), 97.27 (C-1), 61.20 (C-6^{VI}), 54.64 (2C-2), 54.55 (2C-2), 54.45 (C-2), 54.10 (C-2), 37.96 ($CH_2CH_2CH_2N$), 29.55 ($CH_2CH_2CH_2N$) 23.10 (CH_3CON). HRESIMS: found *m/z* 1575.9724 $[M+2NH_4]^{2+}$; calcd for $C_{173}H_{149}N_9O_{50}$ 1575.9691.

3.20. 3-(Benzyloxycarbonylamino)propyl 6-*O*-acetyl-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-*O*-benzoyl-2-deoxy-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-2-acetamido-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3,4-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (37)

Reaction of glycosyl acceptor **36** (85 mg, 0.027 mmol) with glycosyl donor **16** (54 mg, 0.035 mmol) as described in Section 3.3 yielded nonasaccharide **37** (43.7 mg, 35%). $[\alpha]_D$ +18 (*c* 1, $CHC1_3$). Selected ^{1}H NMR data ($CDCl_3$): δ 6.47 (d, 1H, $J_{NH,2}$ 8.7 Hz, NH), 6.35 (d, 1H, $J_{NH,2}$ 8.6 Hz, NH), 6.28–6.02 (m, 7H, 7H-3), 5.66–5.32 (m, 12H, 7H-1, 2H-3, 3H-4), 5.28–5.09 (m, 7H, 6H-4, N*H*Z), 4.98 (s, 2H, CH_2Ph), 3.10 (m, 2H, $OCH_2CH_2CH_2N$), 1.98 (s, 3H, CH_3CON), 1.92 (s, 3H, CH_3CON), 1.89 (s, 3H, CH_3COO). Selected ^{13}C NMR data ($CDCl_3$): 101.84 (C-1^{II}, C-1^{VIII}), 97.91 (2C-1), 97.82 (3C-1), 97.51 (C-1) 97.37 (C-1), 62.46 (C-6^{IX}), 54.78 (7C-2), 54.22 (2C-2), 38.01 ($CH_2CH_2CH_2N$), 29.33 ($CH_2CH_2CH_2N$), 23.09, 21.41 (2 CH_3CON), 20.53 (CH_3COO). HRESIMS: found *m/z* 2301.6736 $[M+2NH_4]^{2+}$; $C_{253}H_{206}N_{10}O_{74}$ 2301.6670.

3.21. 3-Acetamidopropyl 2-amino-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-2-amino-2-deoxy-β-D-glucopyranosyl-(1→6)-2-amino-2-deoxy-β-D-glucopyranosyl-(1→6)-2-amino-2-deoxy-β-D-glucopyranosyl-(1→6)-2-amino-2-deoxy-β-D-glucopyranosyl-(1→6)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-2-amino-2-deoxy-β-D-glucopyranoside (5)

Compound **37** (31 mg, 0.007 mmol) was deprotected as described in Section 3.4 to give **5** (9 mg, 83%). Selected ^{1}H NMR data (D_2O): δ 4.82–4.74 (m, 7H, 7H-1), 4.62–4.56 (m, 2H, 2H-1), 4.33–4.19 (m, 7H), 4.00–3.87 (m, 8H), 3.84–3.50 (m, 31H), 3.47–3.42 (m, 2H), 3.38–3.32 (m, 2H), 3.12–2.97 (m, 7H, 7H-2), 2.08 (s, 6H, 2CH_3CON), 2.01 (s, 3H, CH_3CON), 1.96 (s, 21H, CH_3COOH), 1.85 (m, 2H, $OCH_2CH_2CH_2N$); ^{13}C NMR (D_2O): 103.35 (C-1), 102.99 (C-1), 101.71 (2C-1), 101.56 (2C-1), 101.04 (2C-2), 100.55 (C-1), 77.71, 76.42, 76.28, 76.02, 75.87, 75.03, 74.92, 74.06, 73.83, 73.69, 71.14, 70.10, 69.92, 69.70, 69.09, 61.89 (C-6^{IX}), 57.22 (7C-2), 56.87 (2C-2), 37.63 ($CH_2CH_2CH_2N$), 29.85 ($CH_2CH_2CH_2N$), 24.50, 23.74, 23.44 (3CH_3CON). HRESIMS: found *m/z* 1650.719 $[M+H]^+$; calcd for $C_{63}H_{115}N_{10}O_{40}$: 1650.719.

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