Synthesis of 2-aminoethyl glycosides of chitooligosaccharides*

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2-Aminoethyl glycosides of chitotriose, chitopentaose, and chitoheptaose were synthesized. The successive extension of the oligosaccharide chain by two monosaccharide residues was carried out using a monosaccharide acceptor and a disaccharide donor, in which amino groups were protected by phthaloyl groups, benzyl moieties were used as a permanent protection for the hydroxy groups at C(3) and C(6), and acetyl or chloroacetyl groups were employed as a temporary protection for the hydroxy group at C(4).

Key words: chitin, chitooligosaccharides, 2-aminoethyl glycosides, blockwise synthesis.

Chitin is a polysaccharide composed of β-(1→4)-linked *N*-acetylglucosamine units. This polysaccharide together with cellulose are the most abundant natural organic compounds. Chitin is an essential structural element of the exoskeleton of insects and crustaceans and a major constituent of the cell wall of fungi,[1] including such clinically important pathogenic fungi as *Candida albicans* and *Aspergillus fumigatus*.[2] A contact of a pathogen with the immune system of the host organism produces an immune response to surface polysaccharide antigens of the fungal cell wall, such as mannan, α- and β-(1→3)-glucans, galactomannans, and chitin. The detection of antibodies specific for fungal surface polysaccharide antigens, including chitin, in the blood serum can be used for the diagnosis of fungal infections.[3] The reliable antibody detection requires samples of the corresponding polysaccharide antigens, which were isolated from natural sources, or their oligosaccharide fragments, which can be prepared *via* a synthetic route.

The present work was performed as a part of research on the synthesis of oligosaccharide derivatives representing distinct structural fragments of surface polysaccharide antigens of pathogenic fungi.[4—9] The aim of this study is to prepare 2-aminoethyl glycosides of chitooligosaccharides — β-(1→4)-linked oligo-*N*-acetylglucosamines containing three, five, and seven monosaccharide residues. Such compounds are intended for use in the development of enzyme immunoassay test systems (including those based on chip technologies[10]) for the detection of polysaccharide mycoantigens and homologous antibodies, as well as of glycoconjugate molecular systems[11] for use as immunogens to induce specific antichitin antibodies.

Examples of the synthesis of rather large chitooligosaccharides or their analogs with unacetylated amino groups containing four to twelve monosaccharides were described in the literature[12—15] and have been recently summarized in the review.[16] These methods of synthesis differ from each other in the type of *N*-protecting groups used (phthaloyl,[12,13] dimethylmaleoyl,[14] or trichloroacetyl[15]), as well as in the nature (thioglycoside,[13,15] glycosyl fluoride,[13] or trichloroacetimidate[12,14]) and the size (from mono-[15] to tetrasaccharides[12]) of glycosyl donors, which were employed for the extension of the oligosaccharide chain. In the present study, we report the blockwise synthesis of 2-aminoethyl glycosides of chitotriose, chitopentaose, and chitoheptaose based on the extension of the oligosaccharide chain of a disaccharide glycosyl donor containing *N*-phthaloyl protecting groups.

Results and Discussion

In order to synthesize the target compounds, we initially intended (Scheme 1) to use thioglycoside donor **3**, in which the hydroxy groups at C(3) and C(6) are protected by permanent benzyl groups, while the hydroxy group at C(4) is protected by the temporary acetyl group.

However, the orthogonal glycosylation of thioglycoside **2** (see Ref. 17) with trichloroacetimidate **1** (see Ref. 18) in the presence of TMSOTf or $BF_3 \cdot Et_2O$ afforded desired disaccharide **3** (see Ref. 19) in yields of not higher than 25—30%. This synthesis gave thioglycoside **4** as the major product, which was generated *via* intermolecular transfer of the ethylthio group from acceptor **2** to activated donor **1** (the transfer of alkyl- and arylthio groups in glycosylation reactions was considered in detail in the review[20]).

* Dedicated to Academician of the Russian Academy of Sciences N. S. Zefirov on the occasion of his 80th birthday.

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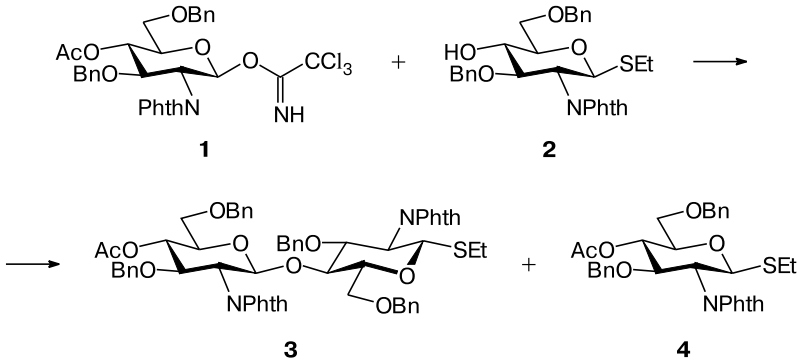
Scheme 1



Reagents and conditions: TMSOTf, CH_2Cl_2, –25 °C or $BF_3 \cdot Et_2O$, CH_2Cl_2, –40 °C.

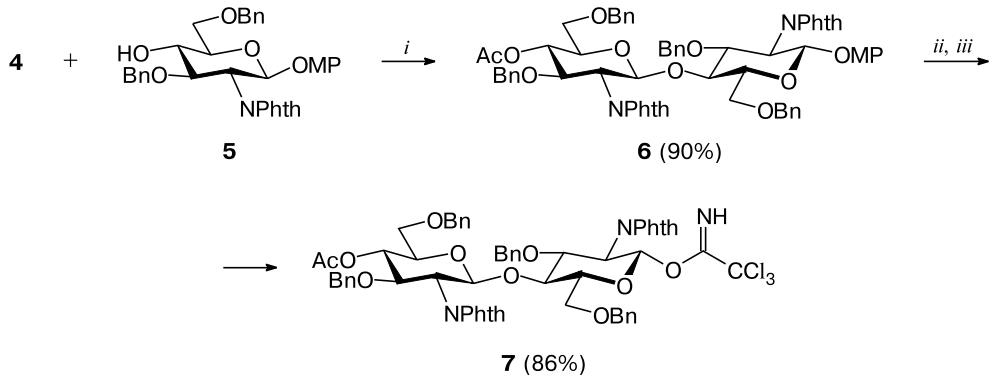
Therefore, we synthesized the disaccharide glycosyl donor by the glycosylation reaction of *p*-methoxyphenyl glycoside **5** (see Ref. 21) with thioglycoside **4**,[22] which produced known disaccharide **6**. Earlier, this disaccharide has been synthesized[12] by the reaction of imidate **1** with acceptor **5**. Then compound **6** was transformed into imidate **7** using the described sequence of transformations (Scheme 2), involving the removal of the anomeric *p*-methoxyphenyl group followed by the reaction of the hemiacetal that formed with trichloroacetonitrile.[12]

Since it was necessary to synthesize the target chitooligosaccharides in the form of 2-aminoethyl glycosides, we employed 2-azidoethyl glycoside **10** as the glycosyl acceptor that served as the starting point for the extension of the polysaccharide chain (see Schemes 3 and 4). The azide group is stable under the conditions of removal of the *N*-phthaloyl group. This ensures the differentiation between the amino groups in the glucosamine residues and the aglycone.

The glycosylation of 2-chloroethanol with thioglycoside **8** (see Ref. 17) (Scheme 3) gave 2-chloroethyl glycoside **9**. The latter was transformed into 2-azidoethyl glycoside **10** by the replacement of the chlorine atom with the azide group. The reductive cleavage of the benzylidene ring in compound **10** under the conditions described earlier[23] afforded target acceptor **11**.

Then we proceeded to extend the oligoglucosamine chain. The glycosylation of derivative **11** with imidate **7** in the presence of TMSOTf gave trisaccharide **12** in good yield (Scheme 4). The spin-spin coupling constant $J_{1,2} = 7.9$ Hz of the glucosamine residue B (the notation of monosaccharide residues is given in Scheme 4) in the ^{1}H NMR spectrum confirms the β configuration of the glycosidic bond that formed. The removal of the acetyl group in trisaccharide **12** with sodium methoxide in methanol[12] was rather inefficient due, apparently, to the competitive cleavage of the phthalimide ring.[24] Therefore, compound **12** was deacetylated with hydrogen chloride in

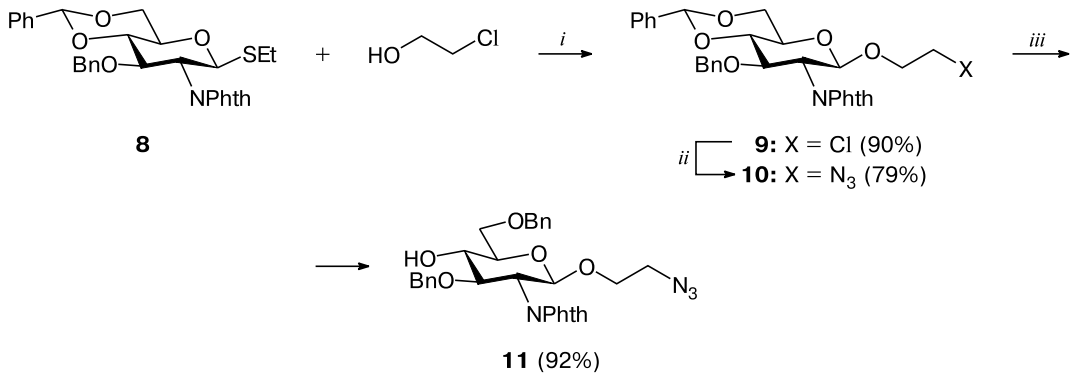
Scheme 2



MP is 4-$MeOC_6H_4$.

Reagents, conditions, and yields: *i*. NIS, TfOH, 4 Å molecular sieves, CH_2Cl_2, –20 °C; *ii*. $(NH_4)_2Ce(NO_3)_6$, acetonitrile—toluene—water (4 : 1 : 1), 0 °C, yield 90%; *iii*. CCl_3CN, DBU, –20 °C, yield 96%.

Scheme 3



Reagents and conditions: *i*. NIS, TfOH, 4 Å molecular sieves, CH_2Cl_2, –20 °C; *ii*. NaN_3, DMF, 60 °C; *iii*. $H_3B \cdot NMe_3$, $AlCl_3$, H_2O, THF.

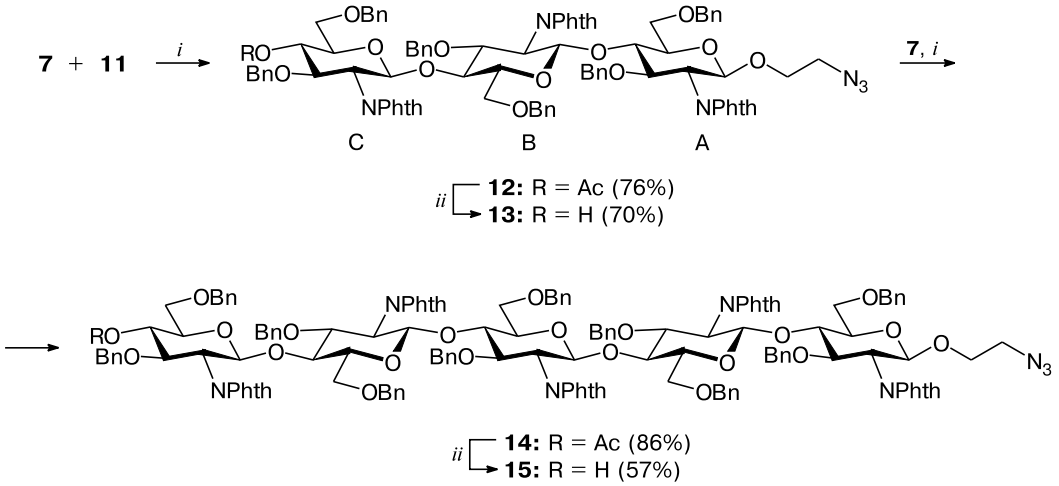
a methanol—CH_2Cl_2 mixture. The reaction proceeded slowly (the complete conversion of the starting acetate was achieved in five—six days) and afforded trisaccharide glycosyl acceptor **13** in moderate yield (70%). The further glycosylation of glycosyl acceptor **13** with imidate **7** produced pentasaccharide **14** (86%), which was also subjected to acidic deacetylation to form pentasaccharide acceptor **15**; however, the latter was obtained in a moderate yield (57%).

Because of the long reaction time of acidic deacetylation, which is inconvenient from a preparative point of view, and a low yield of pentasaccharide glycosyl acceptor **15**, we used the chloroacetyl group instead of the acetyl group as a temporary protection of the hydroxy group at C(4). For this purpose, glycosyl acceptor **5** was introduced into the glycosylation reaction with thioglycoside **16**,[25] giving disaccharide **17** (Scheme 5), and the latter was transformed into imidate **18** by means of the conventional removal of the *p*-methoxyphenyl group and the reaction with trichloroacetonitrile in the presence of a base.

The glycosylation of trisaccharide acceptor **13** with imidate **18** in the presence of TMSOTf produced pentasaccharide **19**. The removal of the chloroacetyl group in **19** by the treatment with thiourea proceeded much faster than the removal of the acetyl group in acetylated analog **14** (8—10 h *versus* 6 days) and gave product **15** in higher yield. The final step of the extension of the oligosaccharide chain *via* the glycosylation of pentasaccharide **15** with imidate **18** afforded heptasaccharide **20** in 68% yield.

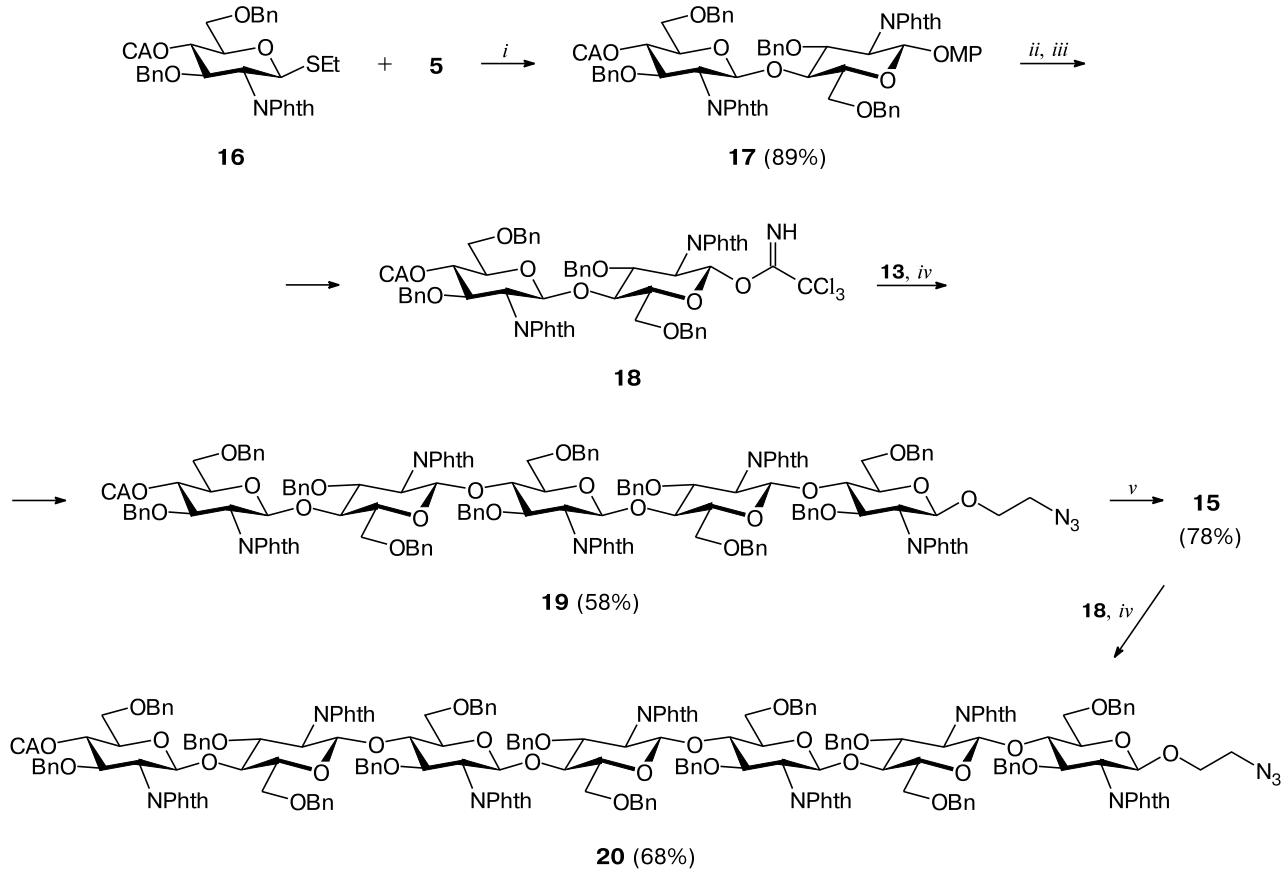
The protecting groups in oligomers **13**, **14**, and **20** were removed by means of the reaction sequence presented in Scheme 6. The *N*-phthaloyl protecting groups were

Scheme 4



Reagents and conditions: *i*. TMSOTf, 4 Å molecular sieves, CH_2Cl_2, –40 °C; *ii*. HCl, CH_2Cl_2, MeOH.

Scheme 5



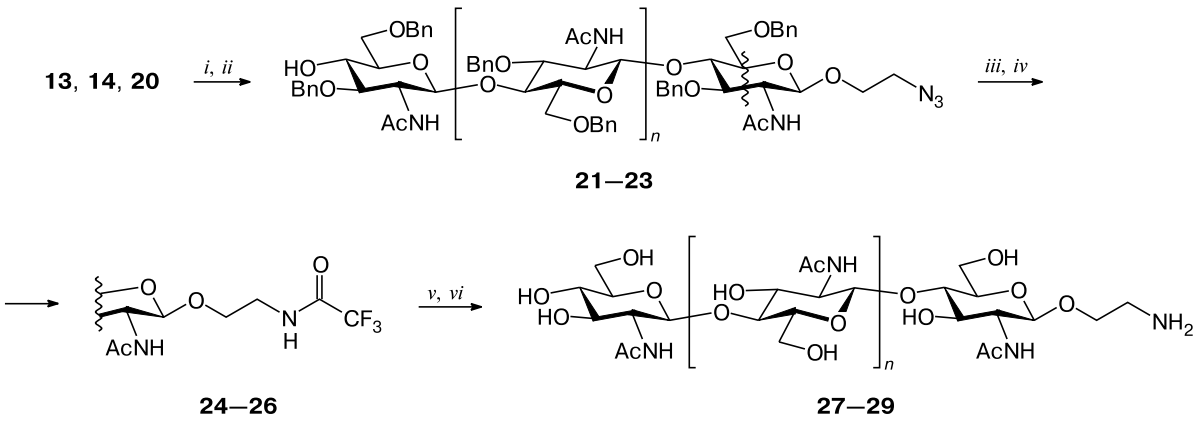
CA is $ClCH_2C(O)$.

Reagents, conditions, and yields: *i*. NIS, TfOH, 4 Å molecular sieves, CH_2Cl_2, −20 °C; *ii*. $(NH_4)_2Ce(NO_3)_6$, 90% aqueous MeCN, yield 61%; *iii*. CCl_3CN, DBU, CH_2Cl_2, −20 °C, yield 85%; *iv*. TMSOTf, 4 Å molecular sieves, CH_2Cl_2, −40 °C; *v*. $(H_2N)_2CS$, 2,4,6-collidine, EtOH—AcOEt (1 : 1), 70—80 °C.

removed by the treatment with hydrazine hydrate, and the resulting oligosaccharides containing free amino groups were treated with acetic anhydride in methanol to obtain *N*-acetylated oligosaccharides **21**—**23**. Attempts to simultaneously reduce the azide group and remove the benzyl groups by the Pd-catalyzed hydrogenation gave rise to complex mixtures consiting, apparently, of partially benzylated amino derivatives. We failed to convert these compounds into the corresponding free oligosaccharides even during a longer reaction time. This result is evidently attributed to the ability of amines to inhibit *O*-debenzylation.[26] Therefore, the reduction of the azide group and the debenzylation were performed sequentially, using the temporary protection of the amine that formed with the trifluoroacetyl group. Earlier,[27—29] we have employed a similar approach.

The azide group was reduced under the conditions, which we have proposed recently,[30] including the treatment with 1,4-dithiothreitol (DTT) in aqueous acetonitrile in the presence of a base. The most efficient reduction was observed in trisaccharide **21**, the reduction was less efficient in pentasaccharide **22**, whereas the reaction with heptasaccharide **23** was not completed under these conditions even in the presence of a large excess of the reagent during a long reaction time. The azide group in **23** was more efficiently reduced by the treatment with triphenylphosphine in aqueous THF[31] or anhydrous $SnCl_2$ and with thiophenol in acetonitrile.[32] 2-Aminoethyl glycosides that formed were subjected to *N*-trifluoroacetylation to obtain derivatives **24**—**26**. The removal of the benzyl groups in compounds **24**—**26** by catalytic hydrogenolysis afforded target chitooligosaccharides **27**—**29**. It should be noted that the efficiency of the above-described six-step reaction sequence, which was employed to remove the protecting groups and convert the azide group into amine, substantially decreased with increasing length of the oligosaccharide chain. Thus, the transformations of protected oligomers **13** and **14** to free 2-aminoethyl glycosides **27** and **28**

Scheme 6



Reagents and conditions: *i*. $H_2NNH_2 \cdot H_2O$, EtOH, reflux; *ii*. Ac_2O, MeOH; *iii*. DTT, Pr^i_2NH, 75% aqueous MeCN or Ph_3P, 90% aqueous THF, 60 °C, or $SnCl_2$, PhSH, Et_3N, MeCN; *iv*. CF_3COOEt, Et_3N, MeOH; *v*. H_2, Pd/C, MeOH; *vi*. 1 *M* aqueous NaOH, aqueous MeOH.

proceeded in satisfactory overall yields (37 and 22%, respectively). By contrast, the reaction of heptasaccharide **20** gave product **29** in a total yield of only 3.4%, the main loss being in the step of the catalytic debenzylation of intermediate **26**.

The structures of oligomers **27—29** were confirmed by ^1H and ^{13}C NMR spectroscopic data, which are in good agreement with the NMR spectra of chitooligosaccharides published earlier.[33,34] The results of application of the newly synthesized ligands in the synthesis of glycoconjugates and biochemical investigations will be described elsewhere.

Experimental

All reactions were performed in solvents purified by standard procedures; TfOH, TMSOTf, NIS, DBU, and trichloroacetonitrile (Acros) were used as purchased. Thin layer chromatography was performed on Kieselgel 60 F254 silica gel plates (Merck). The spots of compounds were visualized using UV radiation and by spraying with an orcinol solution (180 mg of orcinol in a mixture of 85 mL of water, 10 mL of orthophosphoric acid, and 5 mL of ethanol) followed by heating at ~150 °C. Column chromatography was carried out on silica gel 60 (40—63 μm, Merck). Gel chromatography of protected oligosaccharides was performed using Bio-Beads S-X1 and Bio Beads S-X3 (Bio Rad) in toluene. Gel chromatography of free oligosaccharides was carried out on a Fractogel TSK HW-40(S) column (1.5×90 cm) in 0.1 *M* acetic acid; the eluate was analyzed using a Knauer K-2401 differential flow refractometer. The optical rotation was measured using a JASCO P-2000 digital polarimeter (Japan) at room temperature (20—25 °C) in chloroform in the case of protected derivatives or in water in the case of free oligosaccharides.

The NMR spectra were recorded at 25 °C on Bruker AMX-400 and Bruker Avance 600 instruments in deuterochloroform ($CDCl_3$) in the case of protected derivatives. The ^1H NMR spectra were measured using signals of residual undeuterated $CHCl_3$ (δ_H 7.27) as the internal standard; the ^{13}C NMR spectra, using the signal of $CDCl_3$ (δ_C 77.0). The spectra of unprotected oligosaccharides were recorded in heavy water (D_2O) with acetone (δ_H 2.225, δ_C 31.45) as the internal standard. The assignment of the signals was made by means of 2D correlation techniques (COSY, TOCSY, and HSQC). In the description of the NMR spectra, monosaccharide residues are denoted with Latin letters (A, B, C, *etc*.) beginning with the reducing end of an oligosaccharide (see Scheme 4).

High-resolution mass spectra were recorded on a Bruker micrOTOF II instrument.

Glycosylation reactions were performed in anhydrous solvents under a dry argon atmosphere. Prior to the reaction, molecular sieves were activated for 2 h at 180 °C using a vacuum oil pump.

***p*-Methoxyphenyl 4-*O*-acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (6).** Molecular sieves 4 Å (0.4 mg) were added to a solution of thioglycoside **4** (217 mg, 0.38 mmol) and glycosyl acceptor **5** (160 mg, 0.27 mmol) in dichloromethane (4 mL). The mixture was stirred for 1.5 h and then cooled to −20 °C, after which NIS (122 mg, 0.54 mmol) was added, the mixture was stirred for 10 min, and TfOH (11.3 μL, 0.11 mmol) was added. The mixture was stirred for 20 min at −20 °C, triethylamine (50 μL) was added, and the mixture was diluted with dichloromethane (30 mL) and filtered through celite. The precipitate was washed with dichloromethane (20 mL). The combined filtrates were washed with a 1 *M* aqueous $Na_2S_2O_3$ solution and a saturated aqueous $NaHCO_3$ solution, dried with Na_2SO_4, and concentrated. The residue was chromatographed on silica gel (toluene—acetone, 6 : 1) to isolate disaccharide **6** in a yield of 270 mg (90%). ^1H NMR (600 MHz, $CDCl_3$), δ, characteristic signals): 5.47 (d, 1 H, $H_A(1)$, $J_{1,2}$ = 8.4 Hz); 5.36 (d, 1 H, $H_B(1)$, $J_{1,2}$ = 8.3 Hz); 5.18 (t, 1 H, $H_B(4)$, J = 9.4 Hz); 3.66 (s, 3 H, CH_3O); 1.94 (s, 3 H, $OCOCH_3$) (*cf*. Refs 12, 35). ^{13}C NMR (150 MHz, $CDCl_3$), δ: 169.6 ($CH_3\underline{C}O$); 167.5 (Ar$\underline{C}$ON); 155.3,

150.9, 138.5—137.8, 134.1—133.6, 131.7, 129.0—127.0, 123.7, 123.3, 118.6, 114.2 (Ar); 97.5 (C_A(1)); 97.2 (C_B(1)); 76.9 (C_B(3)); 76.8 (C_A(3)); 76.3 (C_A(4)); 74.7 (C_A(4)); 74.5, 73.9, 73.6 (3 Ph$\underline{C}H_2$); 73.5 (C_B(5)); 72.7 (C_B(4), Ph$\underline{C}H_2$); 69.5 (C_B(6)); 68.0 (C_A(6)); 56.2 (C_B(2)); 55.6 (C_A(2)); 55.5 (CH_3O); 20.9 ($\underline{C}H_3CO$).

2-Azidoethyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside (10). 2-Chloroethanol (47 μL, 0.7 mmol) and 4 Å molecular sieves (200 mg) were added to a solution of compound **8** (150 mg, 0.28 mmol) in dichloromethane (2 mL). The mixture was stirred at room temperature for 1 h and cooled to −20 °C. Then NIS (126 mg, 0.56 mmol) was added, the mixture was stirred for 30 min, and TfOH (15 μL, 0.17 mmol) was added. The reaction mixture was stirred for 45 min at −20 °C, after which triethylamine (50 μL) was added. The mixture was diluted with dichloromethane (20 mL) and filtered through celite. The precipitate was washed with dichloromethane (30 mL). The filtrate was washed with a 1 *M* aqueous $Na_2S_2O_3$ solution and a saturated aqueous $NaHCO_3$ solution, dried with Na_2SO_4, and concentrated. The residue was chromatographed on silica gel (toluene—AcOEt, 95 : 5) to obtain chloroethyl glycoside **9** in a yield of 150 mg (90%). Sodium azide (165 mg, 2.5 mmol) was added to a solution of derivative **9** in DMF (5 mL). The mixture was vigorously stirred for 19 h at 60 °C, cooled, diluted with water (20 mL), and extracted with ethyl acetate (3×20 mL). The combined extracts were washed with water and a saturated aqueous NaCl solution, dried with Na_2SO_4, and concentrated. The silica gel column chromatography (toluene—AcOEt, 95 : 5) of the residue gave azidoethyl glycoside **10** in a yield of 118 mg (79%), $[\alpha]_D$ +34.4 (*c* 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.66—6.79 (m, 14 H, Phth, 2 Ph); 5.55 (s, 1 H, C$\underline{H}$Ph); 5.21 (d, 1 H, H(1), $J_{1,2}$ = 8.5 Hz); 4.72 (d, 1 H, C$\underline{H}_2$Ph, *J* = 12.3 Hz); 4.42 (d, 1 H, C$\underline{H}_2$Ph); 4.37—4.30 (m, 2 H, H(3), H(6a)); 4.18 (dd, 1 H, H(2), $J_{2,3}$ = 10.4 Hz); 3.86 (m, 1 H, OC$\underline{H}_2CH_2N_3$); 3.78 (t, 1 H, H(6b), *J* = 10.2 Hz); 3.75 (t, 1 H, H(4), *J* = 9.1 Hz); 3.56 (m, 1 H, H(5)); 3.52 (m, 1 H, OC$\underline{H}_2CH_2N_3$); 3.23 (m, 1 H, $OCH_2C\underline{H}_2N_3$); 3.08 (m, 1 H, $OCH_2C\underline{H}_2N_3$). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 133.8, 129.1—127.5, 123.3 (Ar); 101.4 ($\underline{C}$HPh); 99.1 (C(1)); 83.1 (C(4)); 74.7 (C(3)); 74.2, ($\underline{C}H_2$Ph); 68.8 (C(6)); 68.5 ($O\underline{C}H_2CH_2N_3$); 66.3 (C(5)); 55.7 (C(2)); 50.5 ($CH_2\underline{C}H_2N_3$). MS (ESI), *m/z*: 579.1842 $[M + Na]^+$. Calculated for $C_{30}H_{28}N_4NaO_7$: 579.1850.

2-Azidoethyl 3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (11). To a solution of compound **10** (98 mg, 0.163 mmol) in THF (3 mL), $BH_3 \cdot NMe_3$ (48 mg, 0.65 mmol) was added. The mixture was cooled to 0 °C, and then $AlCl_3$ (130 mg, 0.98 mmol) was added. The mixture was allowed to warm to room temperature (~25 °C), water (6 μL) was added, and the mixture was stirred for 16 h and then cooled to 0 °C. Water (1.5 mL) and 1 *M* HCl (1.5 mL) were added to the mixture, and the resulting mixture was extracted with AcOEt (3×20 mL). The combined extracts were washed with water and a saturated aqueous NaCl solution, dried with Na_2SO_4, and concentrated. The silica gel column chromatography (toluene—AcOEt, 95 : 5) gave glucopyranoside **11** in a yield of 84 mg (92%), $[\alpha]_D$ +26.1 (*c* 1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$), δ: 7.66—6.89 (m, 14 H, Phth, 2 Ph); 5.17 (d, 1 H, H(1), $J_{1,2}$ = 8.1 Hz); 4.66 (d, 1 H, C$\underline{H}_2$Ph, *J* = 12.3 Hz); 4.58 (d, 1 H, C$\underline{H}_2$Ph, *J* = 12.0 Hz); 4.51 (d, 1 H, C$\underline{H}_2$Ph); 4.47 (d, 1 H, C$\underline{H}_2$Ph); 4.14 (m, 2 H, H(2), H(3)); 3.85 (m, 1 H, OC$\underline{H}_2CH_2N_3$); 3.80—3.68 (m, 3 H, H(4), 2 H(6)); 3.58 (m, 1 H, H(5)); 3.50 (m, 1 H, OC$\underline{H}_2CH_2N_3$); 3.25, 3.05 (both m, 2 H, $OCH_2C\underline{H}_2N_3$). ^{13}C NMR (150 MHz, $CDCl_3$), δ: 168.3 (Ar$\underline{C}$ON); 138.2, 137.7, 133.8, 129.1—127.5, 123.3 (Ar); 98.5 (C(1)); 78.8 (C(3)); 74.4 ($\underline{C}H_2$Ph); 74.1 (C(5)); 74.0 (C(4)); 73.8 ($\underline{C}H_2$Ph); 70.7 (C(6)); 68.2 ($\underline{C}H_2CH_2N_3$); 55.4 (C(2)); 50.5 ($CH_2\underline{C}H_2N_3$). MS (ESI), *m/z*: 576.2457 $[M + NH_4]^+$. Calculated for $C_{30}H_{38}N_6NaO_7$: 576. 2443.

2-Azidoethyl 4-*O*-acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (12). A mixture of imidate **7** (218 mg, 0.19 mmol) and glycosyl acceptor **11** (89 mg, 0.16 mmol) was once coevaporated with anhydrous toluene, dried using a vacuum oil pump for 2 h, and dissolved in dichloromethane (3 mL). Then 4 Å molecular sieves (200 mg) were added. The mixture was stirred for 1 h at room temperature and cooled to −40 °C, after which TMSOTf (6 μL, 0.03 mmol) was added. The mixture was stirred for 30 min at −40 °C, diluted with dichloromethane (40 mL), and filtered through celite. The precipitate was washed on a filter with dichloromethane (20 mL). The combined filtrates were washed with a saturated aqueous $NaHCO_3$ solution, dried with Na_2SO_4, and concentrated. The silica gel column chromatography (toluene—AcOEt, 4 : 1) gave trisaccharide **12** in a yield of 188 mg (76%) as a white foam, $[\alpha]_D$ +35.5 (*c* 1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$), δ: 7.77—6.68 (m, 42 H, 3 Phth, 6 Ph); 5.33 (d, 1 H, H_C(1), $J_{1,2}$ = 8.3 Hz); 5.16 (t, 1 H, H_C(4), *J* = 9.3 Hz); 5.12 (d, 1 H, H_B(1), $J_{1,2}$ = 7.9 Hz); 5.00 (m, 1 H, H_A(1)); 4.90 (d, 1 H, C$\underline{H}_2$Ph, *J* = 12.5 Hz); 4.76 (d, 1 H, C$\underline{H}_2$Ph, *J* = 13.0 Hz); 4.61 (d, 1 H, C$\underline{H}_2$Ph, *J* = 11.9 Hz); 4.56 (d, 1 H, C$\underline{H}_2$Ph, *J* = 12.2 Hz); 4.51—4.44 (m, 4 H, H_C(3), C$\underline{H}_2$Ph); 4.41—4.36 (m, 4 H, C$\underline{H}_2$Ph); 4.33 (d, 1 H, C$\underline{H}_2$Ph, *J* = 12.0 Hz); 4.29 (dd, 1 H, H_C(2), $J_{1,2}$ = 10.7 Hz); 4.23—4.13 (m, 3 H, H_B(4), H_B(3), H_B(2)); 4.10—4.04 (m, 3 H, H_A(4), H_A(3), H_A(2)); 3.80 (m, 1 H, OC$\underline{H}_2CH_2N_3$); 3.54 (m, 2 H, H_C(5), H_C(6a)); 3.48 (br.d, H_A(6a), $J_{6a,6b}$ = 10.7 Hz); 3.44 (m, 2 H, H_C(6b), OC$\underline{H}_2CH_2N_3$); 3.39 (br.d, H_B(6a), $J_{6a,6b}$ = 10.7 Hz); 3.35 (dd, 1 H, H_A(6b), $J_{6b,5}$ = 4.1 Hz); 3.28 (m, 1 H, H_A(5)); 3.25 (m, 1 H, $OCH_2C\underline{H}_2N_3$); 3.15 (dd, 1 H, H_B(6b), $J_{6b,5}$ = 3.1 Hz); 3.04 (m, 1 H, $OCH_2C\underline{H}_2N_3$); 2.93 (m, 1 H, H_B(5)); 1.91 (s, 3 H, $OCOCH_3$). ^{13}C NMR (150 MHz, $CDCl_3$), δ: 169.7 ($CH_3\underline{C}O$); 168.2, 167.5 (Ar$\underline{C}$ON); 138.7—137.7, 134.0—133.4, 129.0—127.7, 123.5—123.0 (Ar); 98.2 (C_A(1)); 97.1 (C_C(1)); 96.7 (C_B(1)); 76.9 (C_C(3)); 76.8 (C_B(3)); 76.62 (C_A(3)); 76.0 (C_B(4)); 75.5 (C_A(4)); 74.60 (2 C, $\underline{C}H_2$Ph, C_A(5)); 74.37 (2 C, $\underline{C}H_2$Ph, C_B(5)); 73.9 ($\underline{C}H_2$Ph); 73.5 ($\underline{C}H_2$Ph); 73.1 (C_C(5)); 72.7 (C_C(4)); 72.6 ($\underline{C}H_2$Ph); 72.3 ($\underline{C}H_2$Ph); 69.5 (C_C(6)); 68.1 (C_B(6)); 67.9 ($O\underline{C}H_2CH_2N_3$); 67.0 (C_A(6)); 56.6 (C_B(2)); 56.2 (C_C(2)); 55.5 (C_A(2)); 50.3 ($CH_2\underline{C}H_2N_3$). MS (ESI), *m/z*: 1565.5476 $[M + Na]^+$. Calculated for $C_{88}H_{82}N_6NaO_{20}$: 1565.5483.

2-Azidoethyl 3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (13). A solution of HCl in methanol, which was prepared by mixing acetyl chloride (0.1 mL) and methanol (2.3 mL) at 0 °C, was added to a solution of trisaccharide **12** (76 mg, 0.05 mmol) in dichloromethane (1.5 mL) at ~20 °C. The mixture was allowed to stand for 5 days at room temperature (~25 °C), volatile components were evaporated, and HCl was removed by coevaporation with toluene. The silica gel column chromatography (toluene—AcOEt, 4 : 1) gave compound **13** in a yield of 52 mg (70%), $[\alpha]_D$ 0 (*c* 0.6, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.85—6.57 (m, 42 H, 3 Phth, 6 Ph); 5.21 (d, 1 H, H_C(1), $J_{1,2}$ = 8.4 Hz); 5.02 (m, 1 H, H_B(1));

4.90 (m, 1 H, $H_A(1)$); 4.76—4.68 (m, 3 H, $C\underline{H}_2Ph$); 4.50—4.27 (m, 9 H, $C\underline{H}_2Ph$); 4.18 (dd, 1 H, $H_C(3)$, $J_{3,4}$ = 8.4 Hz, $J_{3,2}$ = = 10.6 Hz); 4.14—3.95 (m, 5 H, $H_C(2)$, $H_B(2)$, $H_A(2)$, $H_A(3)$, $H_B(3)$); 3.74—3.67 (m, 2 H, $OC\underline{H}_2CH_2N_3$, $H_C(4)$); 3.59 (dd, 1 H, $H_C(6a)$, $J_{6a,5}$ = 4.4 Hz, $J_{6a,6b}$ = 10.0 Hz); 3.45—3.23 (m, 6 H, $H_A(6a)$, $H_A(6b)$, $H_C(6b)$, $H_C(5)$, $H_B(6a)$, $OC\underline{H}_2CH_2N_3$); 3.19—3.08 (m, 3 H, $H_A(5)$, $H_B(6b)$, $OCH_2C\underline{H}_2N_3$); 2.83 (m, 1 H, $H_B(5)$). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 168.3, 167.6 (Ar$\underline{C}$ON); 138.9—137.6, 134.0—131.9, 129.1—126.8, 123.6—123.1 (Ar); 98.3 ($C_A(1)$); 97.0 ($C_C(C)$); 96.8 ($C_B(1)$); 76.8 (2 C, $C_C(3)$, $C_B(3)$); 75.6 (3 C, $C_A(4)$, $C_B(4)$, $C_C(4)$); 74.7 ($C_A(5)$); 74.5, 74.4 (4 C, 3 $\underline{C}H_2Ph$, $C_B(5)$); 73.8 ($C_C(5)$); 72.7 (2 C, 2 $\underline{C}H_2Ph$); 72.4 ($\underline{C}H_2Ph$); 71.2 ($C_C(6)$); 68.2 ($C_A(6)$); 68.0 ($O\underline{C}H_2CH_2N_3$); 67.3 ($C_B(6)$); 56.7 ($C_B(2)$), 56.2 ($C_C(2)$); 55.6 ($C_A(2)$); 50.4 ($OCH_2\underline{C}H_2N_3$). MS (ESI), *m/z*: 1523.5370 $[M + Na]^+$. Calculated for $C_{86}H_{80}N_6NaO_{19}$: 1523.5373.

2-Azidoethyl 4-*O*-acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (14). A mixture of imidate **7** (45 mg, 0.04 mmol) and glycosyl acceptor **13** (50 mg, 0.03 mmol) was once coevaporated with anhydrous toluene, dried using a vacuum oil pump for 2 h, and dissolved in dichloromethane (1 mL). Then 4 Å molecular sieves (100 mg) were added. The mixture was stirred for 1 h at room temperature and then cooled to −40 °C, after which TMSOTf (1.3 μL, 0.007 mmol) was added. The mixture was stirred for 30 min at −40 °C, diluted with dichloromethane (40 mL), and filtered through a layer of celite. The precipitate was washed on a filter with dichloromethane (20 mL). The combined filtrates were washed with a saturated aqueous $NaHCO_3$ solution, dried with Na_2SO_4, and concentrated. Pentasaccharide **14** was isolated in a yield of 70 mg (86%) by silica gel column chromatography of the residue (toluene—AcOEt, 9 : 1). ^1H NMR (600 MHz, $CDCl_3$), δ: 7.88—6.65 (m, 70 H, 10 Ph, 5 Phth); 5.31 (d, 1 H, $H_E(1)$, $J_{1,2}$ = 8.3 Hz); 5.14 (t, 1 H, $H_E(4)$, J = 9.3 Hz); 5.08 (d, 1 H, H(1), $J_{1,2}$ = 8.2 Hz); 5.06—5.03 (m, 2 H, 2 H(1)); 4.98 (m, 1 H, H(1)); 4.61—4.25 (m, 22 H, 10 $C\underline{H}_2Ph$, $H_E(2)$, $H_E(3)$); 4.21—4.03 (m, 12 H, $H_A(2,3,4)$, $H_B(2,3,4)$, $H_C(2,3,4)$, $H_D(2,3,4)$); 3.78 (m, 1 H, $OC\underline{H}_2CH_2N_3$); 3.54—3.50 (m, 2 H, $H_E(5)$, H(6)); 3.45—3.40 (m, 3 H, 2 H(6), $OC\underline{H}_2CH_2N_3$); 3.36—3.29 (m, 3 H, 3 H(6)); 3.25—3.20 (m, 2 H, $H_A(5)$, $OCH_2C\underline{H}_2N_3$); 3.11 (dd, 1 H, H(6), $J_{6,5}$ = 2.7 Hz, $J_{6a,6b}$ = 10.9 Hz); 3.06—3.00 (m, 3 H, H(6), $OCH_2C\underline{H}_2N_3$); 2.87—2.80 (m, 3 H, $H_B(5)$, $H_C(5)$, $H_D(5)$); 1.90 (s, 3 H, $OCOCH_3$). ^{13}C NMR (150 MHz, $CDCl_3$), δ: 169.6 ($CH_3\underline{C}O$); 168.1, 168.0, 167.5 (Ar$\underline{C}$ON); 138.7—123.1 (Ar); 98.3 (C(1)); 97.0 ($C_E(1)$); 96.72 (C(1)); 96.66 (C(1)); 95.6 (C(1)); 77.2—76.6 (4 C, $C_A(3)$, $C_B(3)$, $C_C(3)$, $C_D(3)$); 75.9—75.2 (4 C, $C_A(4)$, $C_B(4)$, $C_C(4)$, $C_D(4)$); 74.6—74.1 (7 $\underline{C}H_2Ph$, $C_E(3)$, 4 C(5)); 73.1 ($C_E(5)$); 72.8 ($C_E(4)$); 72.6—72.2 (3 $\underline{C}H_2Ph$); 69.4—67.0 (5 C(6), $O\underline{C}H_2CH_2N_3$); 56.6—55.4 (5 C(2)); 50.23 ($CH_2\underline{C}H_2N_3$); 20.8 ($OCO\underline{C}H_3$). MS (ESI), *m/z*: 1265.4410 $[M + 2 Na]^{2+}$. Calculated for $C_{144}H_{132}N_8NaO_{32}$: 1265.4366.

2-Azidoethyl 3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (15). ***A.*** A solution of HCl in methanol, which was prepared by mixing acetyl chloride (50 μL) and methanol (1 mL) at 0 °C, was added to a solution of pentasaccharide **14** (41 mg, 0.012 mmol) in dichloromethane (1 mL) at ~25 °C. The resulting solution was allowed to stand for 6 days at room temperature (~25 °C), volatile components were evaporated, and HCl was removed by coevaporation with toluene. The silica gel column chromatography (toluene—AcOEt, 4 : 1) gave monohydroxy derivative **15** in a yield of 23 mg (57%), $[\alpha]_D$ +10.7 (*c* 1, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$), δ: 7.85—6.65 (m, 70 H, 5 Phth, 10 Ph); 5.26 (d, 1 H, Hz, $H_E(1)$, $J_{1,2}$ = 8.4 Hz); 5.06 (d, 1 H, H(1), $J_{1,2}$ = 7.7 Hz); 5.03 (m, 2 H, 2 H(1)); 4.95 (m, 1 H, H(1)); 4.82—4.69 (m, 5 H, $C\underline{H}_2Ph$); 4.52—4.33 (m, 15 H, $C\underline{H}_2Ph$); 4.26—4.22 (m, 2 H, $H_E(3)$, H(4)); 4.19—3.98 (m, 12 H, $H_A(2,3)$, $H_B(2,3)$, $H_C(2,3)$, $H_D(2,3)$, $H_E(2)$, 3 H(4)); 3.81—3.76 (m, 2 H, $H_E(4)$, $OC\underline{H}_2CH_2N_3$); 3.65 (dd, 1 H, H(6), $J_{6,5}$ = 4.1 Hz, $J_{6a,6b}$ = 9.8 Hz); 3.47 (dd, 1 H, H(6), $J_{6,5}$ = 6.2 Hz, $J_{6a,6b}$ = 9.8 Hz); 3.43—3.27 (m, 7 H, $H_E(5)$, 5 H(6), $OC\underline{H}_2CH_2N_3$); 3.24—3.19 (m, 2 H, H(5), $OCH_2C\underline{H}_2N_3$); 3.13 (dd, 1 H, H(6), $J_{6,5}$ = 2.9 Hz, $J_{6a,6b}$ = 10.7 Hz); 3.05—2.98 (m, 3 H, 2 H(6), $OCH_2C\underline{H}_2N_3$); 2.85—2.78 (m, 3 H, 3 H(5)). ^{13}C NMR (150 MHz, $CDCl_3$), δ: 168.1, 167.6 (Ar$\underline{C}$ON); 138.8—121.7 (Ar); 98.1 (C(1)); 96.8, 96.7, 96.6, 95.6 (4 C(1)); 78.4 ($C_E(3)$); 77.2—76.7 (4 C(3)); 75.6—75.3 (5 C(4)); 74.6—74.2 (6 $\underline{C}H_2Ph$, 4 C(5)); 73.7 ($\underline{C}H_2Ph$); 72.6—72.2 (3 $\underline{C}H_2Ph$, $C_E(5)$); 71.1 (C(6)); 68.1 (C(6)); 67.9 ($O\underline{C}H_2CH_2N_3$); 67.1 (3 C(6)); 56.6, 56.1, 55.4 (5 C(2)); 50.3 ($CH_2\underline{C}H_2N_3$). MS (ESI), *m/z*: 1239.4741 $[M + 2 NH_4]^{2+}$. Calculated for $C_{142}H_{138}N_{10}O_{31}$: 1239.4759.

B. 2,4,6-Collidine (47 μL, 0.35 mmol) and thiourea (12 mg, 0.16 mmol) were added to a solution of compound **19** (81 mg, 0.032 mmol) in a mixture of EtOH (1 mL) and AcOEt (1 mL). The mixture was stirred for 9 h at 75—80 °C, cooled, and concentrated. The residue was dissolved in dichloromethane (50 mL). The resulting solution was washed with 1 *M* HCl and water, dried with Na_2SO_4, and concentrated. The silica gel column chromatography gave 61 mg (78%) of compound **15**, which was identical, according to the ^1H and ^{13}C NMR spectra, to the sample synthesized by the method ***A***.

4-Methoxyphenyl 3,6-di-*O*-benzyl-4-*O*-chloroacetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (17). A mixture of thioglycoside **16** (225 mg, 0.37 mmol) and glycosyl acceptor **5** (162 mg, 0.27 mmol) was once coevaporated with anhydrous toluene, dried using a vacuum oil pump for 2 h, and dissolved in dichloromethane (5 mL). Then 4 Å molecular sieves (500 mg) were added. The mixture was stirred for 1 h at room temperature and cooled to −20 °C, after which NIS (140 mg, 0.62 mmol) was added. The mixture was stirred for 10 min, TfOH (11 μL, 0.124 mmol) was added, and the mixture was stirred for 20 min at −20 °C. Then the reaction was terminated by adding Et_3N (20 μL). The mixture was diluted with dichloromethane (20 mL) and filtered through celite. The precipitate was washed on a filter with dichloromethane (30 mL). The combined filtrates were washed with a 1 *M* aqueous $Na_2S_2O_3$ solution and water, dried with Na_2SO_4, and concentrated. The gel chromatography of the residue using Bio Beads S-X3 gave disaccharide **17** in a yield of 275 mg (89%), $[\alpha]_D$ +25.1 (*c* 0.3, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$), δ: 7.73—6.56 (m, 32 H, 2 Phth, 4 CH_2Ph, 4-$MeOC_6H_4$); 5.46 (d, 1 H, $H_A(1)$, $J_{1,2}$ = 8.5 Hz); 5.34 (d, 1 H, $H_B(1)$, $J_{1,2}$ = 8.4 Hz); 5.22 (t, 1 H, $H_B(4)$, J = 9.3 Hz); 4.83 (d, 1 H, $C\underline{H}_2Ph$, J = 12.3 Hz); 4.59 (d, 1 H, $C\underline{H}_2Ph$, J = 12.2 Hz);

4.55—4.51 (m, 3 H, $H_B(3)$, $C\underline{H}_2Ph$); 4.48—4.41 (m, 5 H, $C\underline{H}_2Ph$); 4.39—4.36 (m, 2 H, $H_A(2)$, $C\underline{H}_2Ph$); 4.32 (dd, 1 H, $H_B(2)$, $J_{2,3}$ = 10.6 Hz); 4.27—4.22 (m, 1 H, $H_A(3)$, $H_A(4)$); 3.74, 3.71 (both d, 2 H, CH_2Cl, J = 14.7 Hz); 3.67 (s, 3 H, CH_3O); 3.58—3.49 (m, 4 H, $H_B(5)$, $H_A(6a)$, 2 $H_B(6)$); 3.46—3.42 (m, 2 H, $H_A(6b)$, $H_A(5)$). ^{13}C NMR (150 MHz, $CDCl_3$), δ: 167.8 (Ar$\underline{C}$ON); 166.1 ($ClCH_2\underline{C}O$); 155.4, 150.9, 137.8—114.2 (Ar); 97.5 ($C_A(1)$); 97.2 ($C_B(1)$); 76.7 ($C_A(3)$); 76.5 ($C_B(3)$); 76.3 ($C_A(4)$); 74.7 ($C_B(4)$); 74.60 ($C_B(5)$); 74.5 ($\underline{C}H_2Ph$); 74.2, 73.6, 72.7 (3 $\underline{C}H_2Ph$); 72.4 ($C_A(5)$); 69.6 ($C_B(6)$); 67.9 ($C_A(6)$); 56.2 ($C_A(2)$); 55.6 ($C_B(2)$); 55.5 (CH_3O); 40.6 (CH_2Cl). MS (ESI), m/z: 1165.3474 $[M + Na]^+$. Calculated for $C_{65}H_{59}ClN_2NaO_{15}$: 1165.3496.

3,6-Di-*O*-benzyl-4-*O*-chloroacetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl trichloroacetimidate (18). Ammonium cerium nitrate (576 mg, 1.05 mmol) was added to a solution of disaccharide **17** (243 mg, 0.21 mmol) in 90% aqueous acetonitrile (2 mL) at 0 °C. The reaction mixture was stirred for 2 h, diluted with AcOEt (50 mL), washed with water and a saturated aqueous NaCl solution, dried with Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography (toluene—AcOEt, 4 : 1) to obtain hemiacetal in a yield of 134 mg (61%). Trichloroacetonitrile (82 μL, 0.8 mmol) was added to a solution of this product (110 mg, 0.106 mmol) in dichloromethane (1 mL), the mixture was cooled to −20 °C, and then DBU (0.7 μL, 0.005 mmol) was added. The mixture was stirred for 2 h at −20 °C and concentrated. The residue was chromatographed on a silica gel column (toluene—AcOEt, 96 : 4) to obtain imidate **18** in a yield of 105 mg (85%), $[\alpha]_D$ +48.0 (*c* 0.6, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$), δ: 8.34 (s, 1 H, NH); 7.83—6.71 (m, 28 H, 2 Phth, 4 Ph); 6.16 (d, 1 H, $H_A(1)$, $J_{1,2}$ = = 8.8 Hz); 5.27 (d, 1 H, $H_B(1)$, $J_{1,2}$ = 8.3 Hz); 5.14 (m, 1 H, $H_B(4)$); 4.77 (d, 1 H, $C\underline{H}_2Ph$, J = 12.5 Hz); 4.54—4.15 (m, 12 H, $C\underline{H}_2Ph$, $H_A(2)$, $H_B(2)$, $H_A(3)$, $H_B(3)$, $H_A(4)$); 3.63 (s, 2 H, CH_2Cl); 3.55—3.32 (m, 6 H, $H_A(5)$, $H_B(5)$, 2 $H_A(6)$, 2 $H_B(6)$). ^{13}C NMR (150 MHz, $CDCl_3$), δ: 167.5 (Ar$\underline{C}$ON); 166.2 (O$\underline{C}$OCH_2Cl); 160.9 (O$\underline{C}$(=NH)CCl_3); 138.5—123.4 (Ar); 97.0 ($C_B(1)$); 94.1 ($C_A(1)$); 76.4, 75.5 (3 C); 74.8, 74.6, 74.3, 73.7, 72.8, 72.6 (4 $\underline{C}H_2Ph$, $C_A(3)$, $C_B(3)$, $C_A(4)$, $C_B(4)$, $C_A(5)$, $C_B(5)$); 69.7, 67.8 ($C_A(6)$, $C_B(6)$); 56.3, 54.6 ($C_A(2)$, $C_B(2)$); 40.7 (OCO$\underline{C}H_2Cl$). MS (ESI), m/z: 1202.2160 $[M + Na]^+$. Calculated for $C_{60}H_{53}Cl_4N_3NaO_{14}$: 1202.2174.

2-Azidoethyl 3,6-di-*O*-benzyl-4-*O*-chloroacetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (19). A mixture of imidate **18** (95 mg, 0.084 mmol) and glycosyl acceptor **13** (105 mg, 0.07 mmol) was once coevaporated with anhydrous toluene, dried using a vacuum oil pump for 2 h, and dissolved in dichloromethane (2 mL). Then 4 Å molecular sieves (200 mg) were added. The mixture was stirred for 1 h at room temperature and cooled to −40 °C, after which TMSOTf (2.6 μL, 0.014 mmol) was added. The mixture was stirred for 30 min at −40 °C, diluted with dichloromethane (30 mL), and filtered through celite. The precipitate was washed with dichloromethane (20 mL). The combined filtrates were washed with a saturated $NaHCO_3$ solution, dried with Na_2SO_4, and concentrated. The gel permeation chromatography of the residue using Bio Beads S-X3 gave pentasaccharide **19** in a yield of 103 mg (58%), $[\alpha]_D$ +21.5 (*c* 1, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$), δ: 7.74—6.69 (m, 70 H, 5 Phth, 10 Ph); 5.33 (d, 1 H, $H_E(1)$, $J_{1,2}$ = = 8.1 Hz); 5.22 (t, 1 H, $H_E(4)$, J = 8.7 Hz); 5.11 (d, 1 H, H(1), $J_{1,2}$ = 8.0 Hz); 5.07 (m, 2 H, 2 H(1)); 4.98 (m, 1 H, H(1)); 4.89—4.74 (m, 4 H, $C\underline{H}_2Ph$); 4.59—4.33 (m, 16 H, H(3), H(4), $C\underline{H}_2Ph$); 4.30—4.25 (m, 3 H, $H_E(2)$, $C\underline{H}_2Ph$); 4.22—4.16 (m, 4 H, 2 H(2), H(3), H(4)); 4.15—4.08 (m, 8 H, 2 H(2), 3 H(3), 3 H(4)); 3.81 (m, 1 H, O$C\underline{H}_2CH_2N_3$); 3.69 (br.s, 2 H, CH_2Cl); 3.54—3.20 (m, 10 H, O$C\underline{H}_2CH_2N_3$, 2 H(5), 3 H(6), $OCH_2C\underline{H}_2N_3$). ^{13}C NMR (150 MHz, $CDCl_3$), δ: 168.1, 167.9, 167.5 (Ar$\underline{C}$ON); 166.0 (O$\underline{C}$OCH_2Cl); 133.8—123.0 (Ar); 98.1 ($C_E(1)$); 97.0, 96.6, 96.55, 96.5 (4 C(1)); 76.8, 76.6 (4 C(3)); 75.9—75.2 (4 C(4)); 74.8—74.1 (7 $\underline{C}H_2Ph$ $C_E(3)$, 4 C(5)); 73.5—72.1 (3 $\underline{C}H_2Ph$, $C_E(4)$, $C_E(5)$); 69.6—67.0 (5 C(6), O$\underline{C}H_2CH_2N_3$); 56.6—55.4 (5 C(2)); 50.2 ($CH_2\underline{C}H_2N_3$); 40.5 (CH_2Cl). MS (ESI), m/z: 1277.4610 $[M + 2\ NH_4]^{2+}$. Calculated for $C_{144}H_{139}ClN_{10}O_{32}$: 1277.4617.

2-Azidoethyl 3,6-di-*O*-benzyl-4-*O*-chloroacetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (20). Heptasaccharide **20** was synthesized from donor **18** (22 mg, (0.019 mmol) and glycosyl acceptor **15** (38 mg, 0.016 mmol) as described above for compound **19**. The product was isolated by gel permeation chromatography using Bio Beads S-X1 in toluene, the yield was 37 mg (68%), $[\alpha]_D$ +19.4 (*c* 1, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$), δ: 7.74—6.64 (m, 98 H, 7 Phth, 14 Ph); 5.29 (d, 1 H, $H_G(1)$, $J_{1,2}$ = 8.4 Hz); 5.19 (t, 1 H, $H_G(4)$, J = 8.9 Hz); 5.06 (d, 1 H, H(1), $J_{1,2}$ = 8.1 Hz); 5.03—4.98 (m, 4 H, 4 H(1)); 4.96 (d, 1 H, H(1), $J_{1,2}$ = 8.4 Hz); 4.85 (d, 1 H, $C\underline{H}_2Ph$, J = 12.5 Hz); 4.79—4.69 (m, 6 H, $C\underline{H}_2Ph$); 4.57—4.08 (m, 27 H, $H_G(3)$, $C\underline{H}_2Ph$, $H_G(2)$, H(2), H(3), H(4)); 4.07—3.98 (m, 16 H, 5 H(2), 5 H(3), 6 H(4)); 3.80—3.76 (m, 1 H, $C\underline{H}_2CH_2N_3$); 3.67 (br.s, 2 H, CH_2Cl); 3.47—3.38 (m, 4 H, O$C\underline{H}_2CH_2N_3$, 2 H(6), H(5)); 3.34—3.21 (m, 8 H, $OCH_2C\underline{H}_2N_3$, 6 H(6), H(5)); 3.08 (br.d, 1 H, H(6), J = 11.0 Hz); 3.02—2.97 (m, 5 H, $CH_2C\underline{H}_2N_3$, 4 H(6)); 2.83—2.72 (m, 5 H, 5 H(5)). ^{13}C NMR (150 MHz, $CDCl_3$), δ: 168.1, 167.9, 167.5 (Ar$\underline{C}$ON); 166.1 (O$\underline{C}$OCH_2Cl); 138.8—123.0 (Ar); 98.1 ($C_G(1)$); 97.0, 96.6 (2 C(1)); 96.5 (4 C(1)); 77.0—74.9 (7 C(3), 7 C(4)); 74.6—72.1 (14 $\underline{C}H_2Ph$, 6 C(5)); 69.7—67.0 (7 C(6), O$\underline{C}H_2CH_2N_3$); 56.8—55.4 (7 C(2)); 50.4 ($OCH_2\underline{C}H_2N_3$); 40.6 (CH_2Cl). MS (ESI), m/z: 1748.6256 $[M + 2\ NH_4]^{2+}$. Calculated for $C_{200}H_{189}ClN_{12}O_{44}$: 1748.6299.

2-Aminoethyl 2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (27). Hydrazine hydrate (0.5 mL) was added to a solution of trisaccharide **13** (73 mg, 0.049 mmol) in EtOH (5 mL). The resulting mixture was refluxed for 3 h and then cooled. The solvent was evaporated, and the residue was dried using a vacuum oil pump for 2 h. Then Ac_2O (0.3 mL) was added to a solution of the residue in methanol (5 mL), the mixture was allowed to stand for 20 min, the solvent was evaporated, and the residue was chromatographed on a silica gel column (chloroform—methanol, 95 : 5) to obtain *N*-acetylated trisaccharide **21** (55 mg). Then DTT (20 mg, 0.13 mmol) and diisopropylamine (5.3 μL, 0.044 mmol) were added to a solution of this product in aqueous acetonitrile (3 : 1,

1.2 mL). The resulting solution was allowed to stand for 24 h at room temperature (~25 °C). The solvent was evaporated, water was removed by coevaporation with toluene, the residue was dissolved in methanol (2 mL), and then one drop of triethylamine and CF_3COOEt (22 μL, 0.22 mmol) were added. After 2.5 h, the mixture was coevaporated with toluene and the residue was chromatographed on a silica gel column (toluene—acetone gradient, from 4 : 1 to 1 : 1) to obtain 2-trifluoroacetamidoethyl glycoside **24** (33 mg). The latter was dissolved in methanol (1.5 mL), 10% Pd/C (20 mg) was added, and the mixture was stirred under a hydrogen atmosphere for 2.5 h. The catalyst was filtered off through celite and washed with 80% aqueous methanol (20 mL). The combined filtrates were concentrated, the residue was dissolved in 80% aqueous methanol (1 mL), and then 1 *M* NaOH was added to pH ~10. After 2 h, AcOH was added until the mixture was neutral, the solvent was evaporated, and the residue was chromatographed using Fractogel TSK HW-40. After freeze-drying from water, trisaccharide **27** was obtained in a yield of 12.4 mg (37% overall yield for six steps), $[\alpha]_D$ −21.2 (*c* 0.7, H_2O). ^{1}H NMR (600 MHz, D_2O), δ: 4.57 (d, 2 H, 2 H(1), $J_{1,2}$ = 8.3 Hz); 4.54 (d, 1 H, H(1), $J_{1,2}$ = 8.3 Hz); 4.03 (m, 1 H, $OC\underline{H}_2CH_2NH_2$); 3.92—3.82 (m, 4 H, 3 H(6a), $OC\underline{H}_2CH_2NH_2$); 3.78—3.59 (m, 10 H, 3 H(2), 3 H(6b), 2 H(3), 2 H(4)); 3.57—3.45 (m, 5 H, H(3), H(4), 3 H(5)); 3.25—3.15 (m, 2 H, $CH_2C\underline{H}_2NH_2$); 2.05 (s, 6 H, 2 CH_3CO); 2.03 (s, 3 H, CH_3CO); 1.92 (s, 1 H, ~0.3 CH_3COO^-). ^{13}C NMR (150 MHz, D_2O), δ: 176.1, 175.8 ($NH\underline{C}OCH_3$); 102.7, 102.5, 102.1 (3 C(1)); 80.5, 80.4 (2 C(4)); 77.1, 75.7 (3 C(5)); 74.7, 73.5, 73.4 (3 C(3)); 70.9 (C_C(4)); 67.0 ($O\underline{C}H_2CH_2NH_2$); 61.8, 61.2 (3 C(6)); 56.8, 56.2, 56.0 (3 C(2)); 40.6 ($OCH_2\underline{C}H_2NH_2$); 23.4, 23.3 ($CO\underline{C}H_3$). MS (ESI), *m/z*: 693.2794 $[M + Na]^+$. Calculated for $C_{26}H_{46}N_4NaO_{16}$: 693.2801.

2-Aminoethyl 2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (28). Hydrazine hydrate (0.5 mL) was added to a solution of pentasaccharide **14** (82 mg, 0.033 mmol) in EtOH (5 mL). The mixture was refluxed for 12 h, the solvent was evaporated, and the residue was dried using a vacuum oil pump at 50 °C for 2 h. The product was dissolved in methanol (5 mL), Ac_2O (0.3 mL) was added, and the solution was allowed to stand for 1 h and then concentrated to dryness. The residue was chromatographed on a silica gel column (chloroform—methanol, 95 : 5) to obtain *N*-acetylated pentasaccharide **22** (50 mg). The product was dissolved in aqueous acetonitrile (3 : 1, 1.2 mL), DTT (11 mg, 0.072 mmol) and diisopropylamine (5 μL, 0.036 mmol) were added, and the solution was allowed to stand for 4 days at room temperature (~25 °C). The solvent was evaporated, water was removed by coevaporation with toluene, and the residue was dissolved in methanol (1 mL). Then one drop of triethylamine and CF_3COOEt (21 μL, 0.18 mmol) were added. After 3 h, the mixture was coevaporated with toluene, and the residue was chromatographed on a silica gel column (toluene—acetone, 2 : 1) to obtain trifluoroacetamidoethyl glycoside **25** (28 mg). The latter was dissolved in methanol (3 mL), 10% Pd/C (20 mg) was added, and the mixture was stirred under a hydrogen atmosphere for 5 h. The catalyst was filtered through celite and washed with 50% aqueous methanol (20 mL). The combined filtrates were concentrated, and then 1 *M* NaOH was added to a solution of the residue in water (1 mL) to pH ~10. The solution was allowed to stand for 3 h at room temperature, neutralized with AcOH, and concentrated. The residue was subjected to gel permeation chromatography on TSK HW-40, and the product was freeze-dried from water to obtain pentasaccharide **28** in a yield of 8 mg (22% overall yield for six steps), $[\alpha]_D$ −17.8 (*c* 0.5, H_2O). ^{1}H NMR (600 MHz, D_2O), δ: 4.61—4.57 (m, 4 H, 4 H(1)); 4.56 (d, 1 H, H(1), $J_{1,2}$ = 8.4 Hz); 4.06 (m, 1 H, $OC\underline{H}_2CH_2NH_2$); 3.95—3.84 (m, 6 H, 5 H(6a), $OC\underline{H}_2CH_2NH_2$); 3.80—3.62 (m, 18 H, 5 H(2), 5 H(6b), 4 H(3), 4 H(4)); 3.58—3.46 (m, 7 H, H(3), H(4), 5 H(5)); 3.27—3.17 (m, 2 H, $OCH_2C\underline{H}_2NH_2$); 2.08 (s, 3 H, CH_3CO); 2.07 (s, 9 H, 3 CH_3CO); 2.06 (s, 3 H, CH_3CO). ^{13}C NMR (150 MHz, D_2O), δ: 175.8 ($NH\underline{C}OCH_3$); 102.7, 102.5, 102.1 (5 C(1)); 80.3, 80.1 (4 C(4)); 77.1 (C_E(5)); 75.8, 75.7 (4 C(5)); 74.6 (C_E(3)); 73.5, 73.3, 73.2 (4 C(3)); 70.9 (C_E(4)); 67.0 ($O\underline{C}H_2CH_2NH_2$); 61.7, 61.1 (5 C(6)); 56.8, 56.3, 56.0 (5 C(2)) 40.6 ($CH_2\underline{C}H_2NH_2$); 23.3 ($CO\underline{C}H_3$). MS (ESI), *m/z*: 1099.4371 $[M + Na]^+$. Calculated for $C_{42}H_{72}N_6NaO_{26}$: 1099.4388.

2-Aminoethyl 2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (29). Hydrazine hydrate (0.5 mL) was added to a solution of heptasaccharide **20** (69 mg, 0.02 mmol) in EtOH (5 mL). The mixture was refluxed for 16 h, the solvent was evaporated, and the residue was dried using a vacuum oil pump at 50 °C for 2 h. The product was treated with a solution of Ac_2O (0.3 mL) in methanol (1 mL) for 1 h at room temperature. The mixture was concentrated and then subjected to silica gel column chromatography (chloroform—methanol, 97 : 3) to obtain 43 mg of *N*-acetylated heptasaccharide **23**. The further reduction of the azide group was performed by two methods.

Method ***A***. Triphenylphosphine (3.2 mg, 0.012 mmol) was added to a solution of 2-azidoethyl glycoside **23** (19.6 mg, 0.007 mmol) in 90% aqueous THF (0.5 mL). The mixture was stirred for 21 h at 60 °C. The solvent was evaporated, and the residue was chromatographed on a silica gel column (chloroform—methanol, from 97 : 3 to 1 : 1). The product was dissolved in methanol (0.5 mL) and treated with CF_3COOEt (0.1 mL) in the presence of one drop of triethylamine for 2 h. Trifluoroacetamidoethyl glycoside **26** (10.7 mg) was isolated by silica gel column chromatography (chloroform—methanol, 97 : 3).

Method ***B***. A solution (65 μL), which was prepared by mixing $SnCl_2$ (18.2 mg), thiophenol (39 μL), triethylamine (40 μL), and acetonitrile (0.6 mL), was added to a solution of 2-azidoethyl glycoside **23** (19.7 mg, 0.007 mmol) in acetonitrile (100 μL). The mixture was stirred for 16 h at room temperature (~25 °C), the solvent was evaporated, 2 *M* NaOH (3 mL) was added to the residue, and the resulting solution was extracted with dichloromethane (3×10 mL). The combined extracts were dried with Na_2SO_4 and concentrated. 2-Aminoethyl glycoside was subjected to trifluoroacetylation, and the product was isolated as described in the method ***A***. The yield of trifluoroacetamidoethyl glycoside **26** was 8.4 mg.

The products prepared by the methods ***A*** and ***B*** were subjected to hydrogenolysis in methanol (0.5 mL) in the presence of Pd/C (5 mg) for 24 h and then treated with 1 *M* NaOH, as described above for compound **28**. The product was isolated by gel chromatography on TSK HW-40. After freeze-drying from water, heptasaccharide **29** was obtained in yield of 1 mg (3.4%),

$[\alpha]_D$ −25.8 (*c* 0.08, H_2O). ^1H NMR (600 MHz, D_2O), δ: 4.61—4.57 (m, 6 H, 6 H(1)); 4.56 (d, 1 H, H(1), $J_{1,2}$ = 8.4 Hz); 4.04 (m, 1 H, $OC\underline{H}_2CH_2NH_2$); 3.95—3.83 (m, 8 H, 7 H(6a), $OC\underline{H}_2CH_2NH_2$); 3.80—3.61 (m, 26 H, 7 H(2), 6 H(3), 6 H(4), 7 H(6b)); 3.59—3.46 (m, 9 H, H(3), H(4), 7 H(5)); 3.18 (m, 2 H, $CH_2C\underline{H}_2NH_2$); 2.08 (s, 3 H, CH_3CO); 2.07 (s, 15 H, 5 CH_3CO); 2.06 (s, 3 H, CH_3CO); 1.92 (s, 1 H, ~0.3 CH_3COO^-). ^{13}C NMR (150 MHz, D_2O), δ: 175.8 ($NH\underline{C}OCH_3$); 102.7, 102.4, 102.1 (7 C(1)); 80.4, 80.2 (6 C(4)); 77.1 (C_G(5)); 75.7 (6 C(5)); 74.6 (C_G(3)); 73.5, 73.3 (6 C(3)); 70.9 (C_G(4)); 67.5 ($O\underline{C}H_2CH_2NH_2$); 61.8, 61.1 (7 C(6)); 56.8, 56.2, 56.0 (7 C(2)); 40.7 ($CH_2\underline{C}H_2NH_2$); 23.3 ($CO\underline{C}H_3$). MS (ESI), *m/z*: 1505.5968 $[M + Na]^+$. Calculated for $C_{58}H_{98}N_8NaO_{36}$: 1505.5976.

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