Carbohydrate Research 419 (2016) 1–10

Contents lists available at ScienceDirect

Carbohydrate Research

journal homepage: www.elsevier.com/locate/carres

Synthesis of 3-aminopropyl glycosides of linear β-(1→3)-D-glucooligosaccharides

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ARTICLE INFO

Article history:
Received 13 September 2015
Received in revised form 18 October 2015
Accepted 23 October 2015
Available online 30 October 2015

Keywords:
β-(1→3)-Glucooligosaccharides
β-Glucan
De-O-acetylation

ABSTRACT

3-Aminopropyl glycosides of a series of linear β-(1→3)-linked D-glucooligosaccharides containing from 3 to 13 monosaccharide units were efficiently prepared. The synthetic scheme featured highly regioselective glycosylation of 4,6-*O*-benzylidene-protected 2,3-diol glycosyl acceptors with a disaccharide thioglycoside donor bearing chloroacetyl groups at O-2′ and -3′ as a temporary protection of the diol system. Iteration of the deprotection and glycosylation steps afforded the series of the title oligoglucosides differing in length by two monosaccharide units. A novel procedure for selective removal of acetyl groups in the presence of benzoyl ones consisting in a brief treatment with a large excess of hydrazine hydrate has been proposed.

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1. Introduction

β-(1→3)-Glucans are widespread in Nature being essential constituents of the cell wall in fungi and yeasts[1,2] and a major storage polysaccharide in brown seaweeds.[3] Great interest in this type of polysaccharides relates to their immunostimulating properties, including antibacterial and antitumor activities.[4,5] On the other hand, the presence of highly conserved β-(1→3)-glucans in different pathogenic fungal species makes these glycopolymers a rational target for vaccine development. Conjugates of either laminaran,[6] an algal β-(1→3)-glucan, or linear synthetic oligoglucoside fragments[7–11] with carrier proteins were proved to be immunogenic and protective in mice against infections induced by *Candida albicans* and *Aspergillus fumigatus*.

Important biological properties of β-(1→3)-glucans stimulated considerable activity toward the synthesis of β-(1→3)-oligoglucosides, linear or containing sporadic β-(1→6)-branchings, of the strictly defined structure to reveal immunodominant fragments of the polysaccharides or those responsible for binding to receptors. Several syntheses of linear[8,9,12–20] and branched[17,18,21–23] oligomers having different anomeric functionalization of the monosaccharide at the reducing end have been published (for review, see Ref. 24).

The aim of this work was the synthesis of a series of linear β-(1→3)-oligoglucosides comprising 3–13 monosaccharide units as 3-aminopropyl glycosides for further preparation of conjugated vaccine candidates, as well as labeled oligosaccharides and other biomolecular systems[25] as model compounds to study biological activities of β-(1→3)-glucans.

2. Results and discussion

A common feature of most published syntheses of oligosaccharides related to β-(1→3)-glucans was the use of glycosyl acceptors having a single free OH group at C-3.[8,9,12–16,19–23] If both adjacent hydroxyl groups at C-2 and C-4 are protected by acyl groups, such glycosyl acceptors may have low reactivity[12] and, more critical, gave sometimes α-glycosides even upon glycosylation with glycosyl donors bearing a participating acyl group at O-2.[24–27] Therefore, glycosyl acceptors protected with 4,6-O-benzylidene and 2-O-acyl groups became more common for the synthesis of such oligosaccharides.[8,9,12–16,19–21,28] Another approach was based on regioselective 3-*O*-glycosylation of 4,6-*O*-benzylidene-protected glycosyl acceptors with a free 2-OH group.[17,18] The absence of an acyl protecting group at O-2 would minimize steric and electronic hindrances to 3-O-glycosylation that enables an efficient chain elongation. This is the approach that allowed the preparation of the longest synthetic β-(1→3)-oligoglucosides.[17,18]

Elongation of the oligosaccharide chain was carried out starting from the reducing end by attachment of mono-[14,19] or oligosaccharide[8,9,12–18,20] donor blocks followed by removal of a temporary protecting group at O-3. Reiteration of this glycosylation-deprotection sequence afforded a series of β-(1→3)-oligoglucosides differing in the length by one, two or more monosaccharide residues.

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http://dx.doi.org/10.1016/j.carres.2015.10.012
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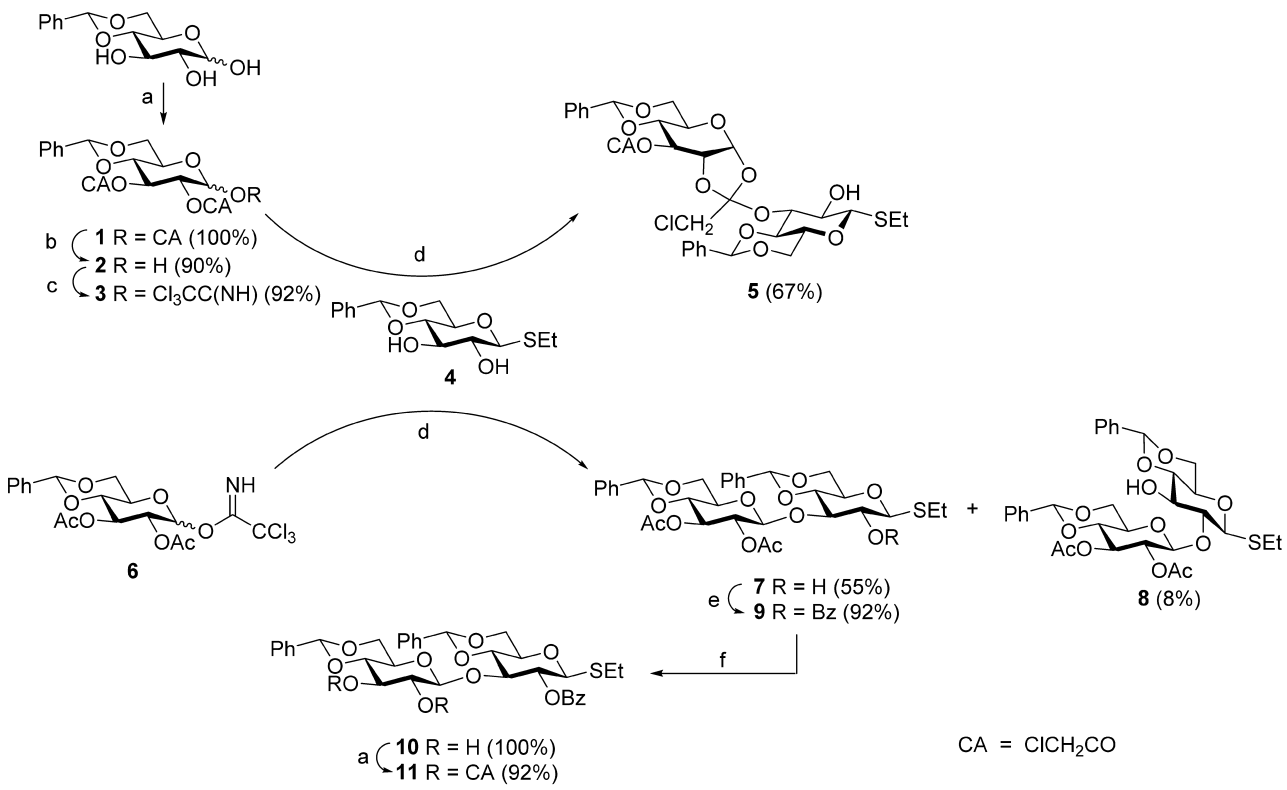


Scheme 1. Synthesis of disaccharide glycosyl donors **9** and **11**. Reagents and conditions: (a) chloroacetic anhydride, 2,4,6-collidine, CH_2Cl_2, rt; (b) H_2NNH_2·AcOH, DMF, rt; (c) Cl_3CCN, Cs_2CO_3, CH_2Cl_2, rt; (d) TMSOTf, CH_2Cl_2, –30 °C; (e) BzCl, pyridine, rt; (f) H_2NNH_2·H_2O, CH_2Cl_2—MeOH, rt.

In this work, we used regioselective 3-*O*-glycosylation of 4,6-*O*-benzylidene-protected 2,3-diol glycosyl acceptors by a disaccharide donor block for the chain elongation (Scheme 1). Chloroacetyl groups were applied as temporary protections of the hydroxyl groups at positions 2 and 3 of the glycosyl donor block.

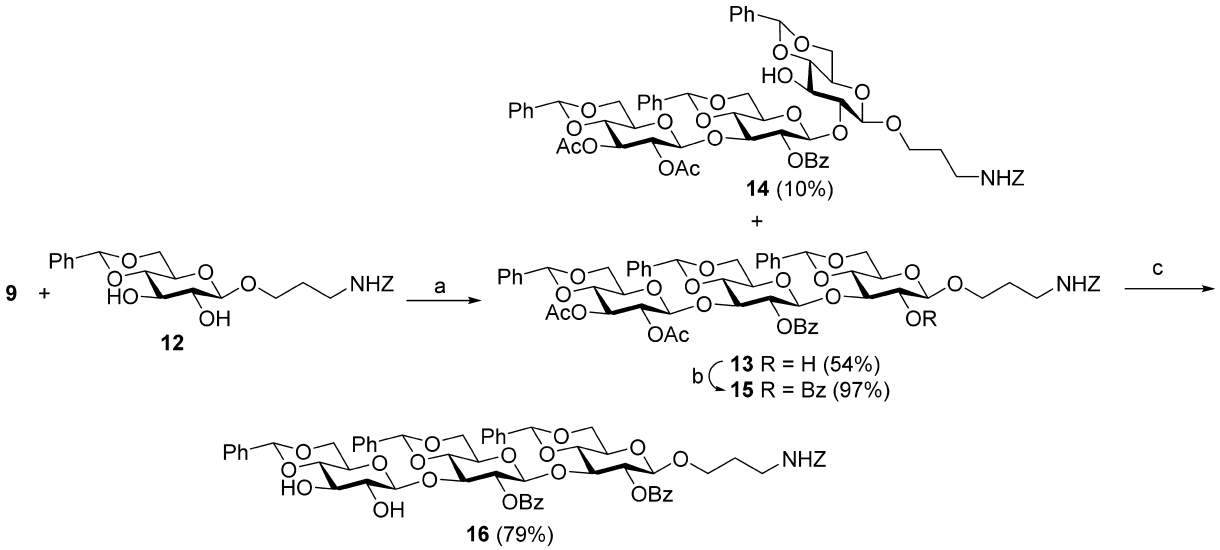
Disaccharide thioglycoside donors **9** and **11** were synthesized as shown in Scheme 1. First, an attempt to prepare a 2′,3′-di-*O*-chloroacetylated donor in a straightforward manner was undertaken. 4,6-*O*-Benzylidene-D-glucose was subjected to chloroacetylation and the anomeric chloroacetyl group in obtained tris(chloroacetate) **1** was selectively removed to afford hemiacetal **2**. The latter was converted into imidate **3**; however, its coupling with diol **4**[29] provided orthoester **5** instead of the expected glycoside. The chemical shifts of the signals for H-1 (δ 5.88) and H-2 (δ 4.44) and the coupling constants pattern ($J_{1,2}$ = 5.6 Hz, $J_{2,3}$ = 3.8 Hz) of the chloroacetylated glucose residue in the ^{1}H NMR spectrum of **5**, as well as the position of the signal for C-1 (δ 98.5) and the presence of the signal for quaternary orthoester carbon (δ 118.1) in the ^{13}C NMR spectrum were in good agreement with the orthoester structure.[30,31] The presence of a correlation peak between H-2 and the HO-proton of the thioglycoside residue in the COSY spectrum indicated that O-3 is involved in the orthoester formation.

Apparently, the electron-withdrawing chloromethyl group at C-2 of the dioxolane ring in **5** stabilizes the orthoester structure and prevents its isomerization to the corresponding glycoside. To overcome this problem, known 2,3-di-*O*-acetyl analog **6**[32] was examined in glycosylation of **4**; as a result, (1→3)-linked disaccharide **7** was obtained in acceptable yield (55%) along with (1→2)-regioisomer **8** (8%). The remaining 2-OH group in **7** was benzoylated to give disaccharide donor **9**. The low-field shift of the signal for H-2 (δ 3.55 → 5.32) in the ^{1}H NMR spectra upon transformation **7** → **9** indicated the presence of the (1→3)-glycoside bond.

As several methods of selective removal of acetyl groups in the presence of benzoyl ones are known,[33–37] we attempted initially to apply donor **9** for elongation of the oligoglucoside chain (Scheme 2). NIS-TfOH-promoted coupling of *N*-Z-protected 3-aminopropyl glucoside **12**[38] with disaccharide **9** displayed almost the same regioselectivity as the coupling **4** + **6** and resulted in the formation of necessary (1→3)-linked product **13** (54%) and its positional isomer **14** (10%); subsequent benzoylation of **13** afforded dibenzoate **15**. A set of reagents and conditions for selective removal of the acetyl groups from **15** was examined; some of them (diluted MeONa in MeOH, DBU in benzene,[36] Et_3N in MeOH) exhibited poor chemoselectivity, others (magnesium methoxide[33] or hydrazine acetate[37] in MeOH) demonstrated too slow conversion of starting **15**.

We found that a brief treatment of **15** with a large excess of hydrazine hydrate (~50 equiv.)[a] in a mixture CH_2Cl_2—MeOH provided fast and selective removal of the acetyl groups in **15** and gave diol **16** in total yield of 79% after repeated treatment of recovered **15**. Although the yield of the conversion **15** → **16** was good enough, one could assume that accumulation of the 2-*O*-benzoyl groups upon elongation of the oligosaccharide chain would lead to decrease of chemoselectivity of deacetylation. To ensure a reliable transformation of oligosaccharides longer than the trisaccharide into corresponding glycosyl acceptors, we decided to revert to the use of chloroacetyl groups as the temporary protections of the 2,3-diol. To this aim, diacetate **9** was treated with hydrazine hydrate as described above to give diol **10** (Scheme 1) quantitatively after two runs of deacetylation; noticeably higher yield of this transformation as compared to deacetylation of **15**, containing two benzoyl groups, confirmed the assumption of lowering the chemoselectivity

[a] The best selectivity was achieved when a ratio substrate–reagent of ~1:50 and a reaction time of 25 min was employed. In a range of 1–15 equiv. of hydrazine hydrate, incomplete conversion (<50%) of **15** was observed, while an extension of reaction time within that range resulted in partial removal of the benzoyl group.



Scheme 2. Synthesis of trisaccharide acceptor **16**. Regents and conditions: (a) NIS, TfOH, mol. sieve AW-300, CH_2Cl_2, –30 °C; (b) BzCl, pyridine, rt; (c) $H_2NNH_2{\cdot}H_2O$, CH_2Cl_2—MeOH, rt.

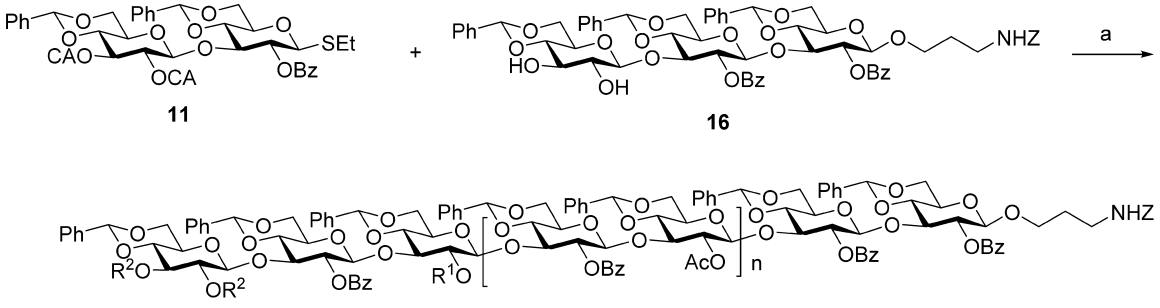
of deacetylation on accumulation of benzoyl groups in the molecule. Further reaction of **10** with chloroacetic anhydride in the presence of 2,4,6-collidine provided target glycosyl donor **11** in 92% yield.

NIS-TfOH-promoted glycosylation of acceptor **16** with **11** proceeded (1→3)-regiospecifically and provided pentasaccharide **17** in 91% yield (Scheme 3). The difference in the regioselectivity of glycosylation of thioglycoside **4** and alkyl glycoside **12**, on the one hand, and trisaccharide **16**, on the other, clearly indicated that a bulky sugar substituent at the anomeric position of the glycosyl acceptor exerts an effective regiocontrol of glycosylation. Acetylation of **17** followed by removal of the chloroacetyl groups produced pentasaccharide acceptor **18** in 86% yield. Further iteration of glycosylation and deprotection steps afforded a series of β-(1→3)-oligoglucosides **19**, **21**, **23**, and **25** in yields of 80–95% having an odd number of the monosaccharide units.

It should be noted that some internal glucose residues in pentasaccharide **17** and longer oligoglucosides had unusual for β-anomers $J_{1,2}$ coupling constant values (around 5 Hz). The same effect was observed by other authors[8,14,16] and ascribed to a distortion of the normal $^4C_1$ glucose ring conformation.[14,16]

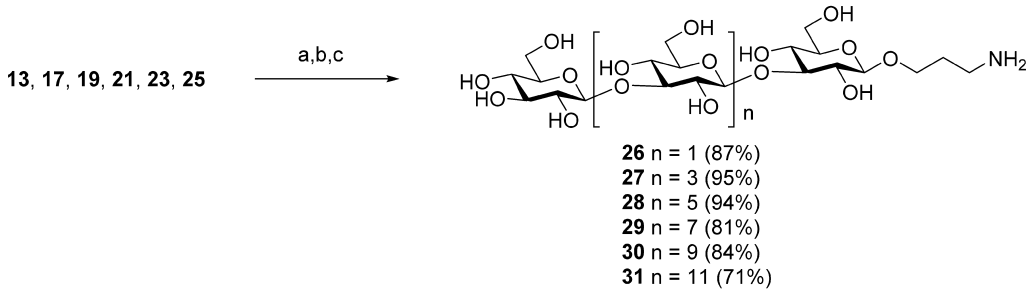
Transformation of protected oligomers into free 3-aminopropyl glycosides **26**–**31** was achieved by successive acidic removal of the benzylidene groups, basic deacylation and hydrogenolysis of the *N*-benzyloxycarbonyl group (Scheme 4).

The structure of oligomers **26**–**31** was confirmed by ^1H and ^{13}C NMR data. The spectra of synthesized compounds were very close



b,c → **17** R^1 = H, R^2 = CA, n = 0 (91%)
+**11**, a → **18** R^1 = Ac, R^2 = H, n = 0 (86%)
b,c → **19** R^1 = H, R^2 = CA, n = 1 (83%)
+**11**, a → **20** R^1 = Ac, R^2 = H, n = 1 (90%)
b,c → **21** R^1 = H, R^2 = CA, n = 2 (91%)
+**11**, a → **22** R^1 = Ac, R^2 = H, n = 2 (88%)
b,c → **23** R^1 = H, R^2 = CA, n = 3 (80%)
+**11**, a → **24** R^1 = Ac, R^2 = H, n = 3 (86%)
+**11**, a → **25** R^1 = H, R^2 = CA, n = 4 (95%)

Scheme 3. Synthesis of linear β-(1→3)-oligoglucosides by iterative glycosylation-deprotection. Reagents and conditions: (a) NIS, TfOH, mol. sieve AW-300, CH_2Cl_2. –30 °C → –10 °C; (b) AcCl, 2,4,6-collidine, CH_2Cl_2, rt; (c) thiourea, 2,4,6-collidine, EtOH—EtOAc (1:1), 80 °C.



Scheme 4. Preparation of free 3-aminopropyl oligoglucosides. Regents and conditions: (a) 1 M HCl, $CHCl_3$—MeOH, 40–45 °C; (b) MaONa, MeOH then NaOH, aq MeOH, 40–45 °C; (c) H_2, $Pd(OH)_2/C$, aq MeOH, rt.

Table 1
^{1}H NMR[a] data for linear oligosaccharides **26**–**31** (D_2O, 600 MHz, 308 K)

Residue[b]	H-1 ($J_{1,2}$)	H-2	H-3	H-4	H-5	H-6a	H-6b
G_m	4.76 (8.1)	3.38	3.53	3.43	3.50	3.93	3.73
G_{m-1}	4.78 (8.0)	3.57	3.79	3.52	3.52	3.93	3.75
G_2–G_{m-2}[c,d]	4.78 (8.0)	3.57	3.79	3.52	3.52	3.93	3.75
G_1	4.52 (8.1)	3.51	3.77	3.52	3.52	3.93	3.75

[a] Signals for the aglycon of compounds **26**–**31** (δ): 4.05, 3.83 (2 m, 2H $OCH_2CH_2CH_2NH_2$), 3.17 (t, 2H, J = 7.0 Hz, $OCH_2CH_2CH_2NH_2$) 2.02 (m, 2H, $OCH_2CH_2CH_2NH_2$).
[b] Glucose units in oligomers are numbered starting from the reducing end; m is the total number of monosaccharides in an oligoglucoside.
[c] The signals of all internal glucose residues.
[d] These residues are absent in the β-(1→3)-triglucoside **26**.

Table 2
^{13}C NMR[a] data for linear oligosaccharides **26**–**31** (D_2O, 150 MHz, 308 K)

Residue[b]	C-1	C-2	C-3	C-4	C-5	C-6
G_m	104.2	74.9	77.1	71.0	77.5	62.2
G_{m-1}	104.0	74.7	85.8	69.6	77.0	62.2
G_2–G_{m-2}	104.0	74.7	85.7	69.6	77.0	62.2
G_1	103.4	74.2	85.9	69.6	77.0	62.2

[a] Signals for the aglycon of compounds **26**–**31** (δ): 69.3 ($OCH_2CH_2CH_2NH_2$), 39.0 ($OCH_2CH_2CH_2NH_2$); 28.1 ($OCH_2CH_2CH_2NH_2$).
[b] See footnotes b–d to Table 1.

to each other in terms of chemical shifts of signals and coupling constant values and differed in the relative intensity of signals belonging to the internal and terminal monosaccharides. Generalized ^{1}H and ^{13}C NMR data are given in Tables 1 and 2. Coupling constant values $J_{1,2}$ of signals for H-1 and chemical shifts of signals for C-1 in ^{1}H and ^{13}C NMR spectra of **26**–**31** clearly indicated that all glucose units had β-configuration. Low-field position of all signals for C-3 (except those of monosaccharides at the nonreducing end) showed all glucose units to be glycosylated at the position 3 (for more detailed discussion of the NMR data of oligomers **26**–**31** with regard to their conformational analysis see Ref. 39).

3. Conclusion

In conclusion, a series of 3-aminopropyl glycosides of linear β-(1→3)-oligoglucosides comprising 3–13 glucose residues have been efficiently synthesized by highly regioselective glycosylation of 2,3-diol glycosyl acceptors. This representative set of oligoglucosides will allow examination of the effect of the oligosaccharide length on the protective properties of corresponding conjugates with a carrier protein against fungal infections as well as on the effectiveness of binding to β-(1→3)-glucan receptors.

4. Experimental

4.1. General methods

NMR spectra were recorded on Bruker AMX-400, Bruker DRX-500, and Bruker Avance 600 instruments. The spectra of protected carbohydrate derivatives were measured for solutions in $CDCl_3$ or acetone-d_6, and ^{1}H NMR chemical shifts were referenced to the corresponding solvent residual signals (δ_H 7.27 and 2.05 respectively). ^{13}C chemical shifts were referenced to the central resonance of $CDCl_3$ (δ_C 77.0) and acetone-d_6 (δ_C 29.9). NMR spectra of free oligosaccharides were measured for solutions in D_2O using acetone (δ_H 2.225, δ_C 31.45) as an internal standard. Signal assignment was made using COSY, TOCSY, and HSQC experiments. Monosaccharide residues in oligosaccharides are numbered by Arabic numerals starting from the reducing end. HRMS (ESI) were obtained on a MicrOTOF II (Bruker Daltonics) instrument. Optical rotations were measured using a JASCO DIP-360 polarimeter at 18–22 °C in solvents specified. Melting points were determined using a Koffler apparatus. TLC was performed on Silica Gel 60 F254 plates (E. Merck), and visualization was accomplished using UV light or by charring at ~150 °C with 10% (v/v) H_3PO_4 in ethanol or Mostain reagent (ceric sulfate (1% w/v) and ammonium molybdate (2.5% w/v) in 10% (v/v) aqueous H_2SO_4). Column chromatography was carried out on Silica gel 60 (40–63 μm, E. Merck). Gel-permeation chromatography of free oligosaccharides was carried out on a TSK HW-40(S) column (2 × 80 cm) in 0.1 M AcOH. Refractive Index Detector K-2401 (Knauer) was used to monitor gel-permeation chromatography. All air- or moisture-sensitive reactions were carried out using dry solvents under dry argon. Chemicals were purchased from Acros, Fluka, or Aldrich and used without further purification.

4.2. 4,6-O-Benzylidene-1,2,3-tri-O-chloroacetyl-D-glucopyranose (*1*)

Chloroacetic anhydride (578 mg, 3.38 mmol) was added to a stirred solution of 4,6-*O*-benzylidene-D-glucopyranose (200 mg, 0.75 mmol) and 2,4,6-collidine (0.60 mL, 4.50 mmol) in dry CH_2Cl_2 (5 mL). The mixture was stirred at rt for 3 h, quenched with methanol (0.5 mL) and stirring was continued for additional 30 min. The mixture was diluted with CH_2Cl_2, washed with aq 1 M HCl, water, satd aq $NaHCO_3$, dried and concentrated to give crude **1** (375 mg, 100%), which was used in the next step without purification. A small portion of crude **1** was purified by column chromatography (95:5 toluene–EtOAc) to provide pure **1** as a semicrystalline mixture of α- and β-anomers in a ratio of ~2:3. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.71 (m, 0.6H, H-5β), 3.75–3.83 (m, 2H, H-4αβ, H-6aαβ), 4.01, 4.02, 4.04, 4.09, 4.17 (5 s, 6H, 3 $ClCH_2$α, 3 $ClCH_2$β), 4.06 (m, 0.4H, H-5α), 4.34 (dd, 0.4H, $J_{6b,5}$ = 4.9 Hz, $J_{6b,6a}$ = 10.4 Hz, H-6bα), 4.41 (dd, 0.6H, $J_{6b,5}$ = 4.6 Hz, $J_{6b,6a}$ = 10.2 Hz, H-6bβ), 5.21–5.26 (m, 1H, H-2α, H-2β), 5.45 (t, 0.6H, J = 9.4 Hz, H-3β), 5.51 (s, 0.6H, PhC*H*β), 5.53 (s, 0.4H,

PhC*H*α), 5.65 (t, 0.4 H, *J* = 9.9 Hz, H-3α), 5.88 (d, 0.6H, $J_{1,2}$ = 8.1 Hz, H-1β), 6.41 (d, 0.4H, $J_{1,2}$ = 3.8 Hz, H-1α), 7.32–7.46 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 40.2, 40.3, 40.5 (3 $ClCH_2$), 65.4 (C-5α), 67.3 (C-5β), 68.2 (C-6β), 68.3 (C-6α), 70.3 (C-3α), 71.1 (C-2α), 72.4 (C-2β), 73.1 (C-3β), 77.6 (C-4β), 78.0 (C-4α), 91.0 (C-1α), 93.0 (C-1β), 101.9 (PhCHαβ), 126.2, 128.4, 129.5, 136.4 (Ph), 165.5, 165.8, 166.3, 166.5, 166.7 ($ClCH_2CO$). HRMS (ESI): calcd. for $C_{19}H_{19}Cl_3O_9$ $[M + Na]^+$ 518.9987; found 518.9975.

4.3. 4,6-O-Benzylidene-2,3-di-O-chloroacetyl-D-glucopyranose (2)

Hydrazine acetate (48 mg, 0.52 mmol) was added to a solution of **1** (200 mg, 0.40 mmol) in anhydrous DMF (5 mL). The mixture was stirred at rt for 1 h, diluted with EtOAc, washed with aq 1 M HCl, water, satd aq $NaHCO_3$, dried and concentrated. The residue was purified by silica gel column chromatography (85:15 toluene–EtOAc) to give syrupy hemiacetal **2** (152 mg, 90%) as a mixture of α- and β-anomers in a ratio of about 5:3. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.90 (d, 1H, $J_{1,OH}$ = 3.7 Hz, OHα), 3.26 (d, 0.6H, $J_{1,OH}$ = 8.0 Hz, OHβ), 3.52 (m, 0.6H, H-5β), 3.62–3.77 (m, 3.2H, H-4αβ, H-6aαβ), 3.97, 4.02, 4.03 (3 s, 6.4H, 2 $ClCH_2$α, 2 $ClCH_2$β), 4.13 (m, 1H, H-5α), 4,24 (dd, 1H, $J_{6b,5}$ = 5.0 Hz, $J_{6b,6a}$ = 10.2 Hz, H-6bα), 4.32 (dd, 0.6H, $J_{6b,5}$ = 4.9 Hz, $J_{6b,6a}$ = 10.5 Hz, H-6bβ), 4.82 (t, 0.6H, *J* = 7.9 Hz, H-1β), 4.90–4.96 (m, 1.6H, H-2αβ), 5.37 (t, 0.6H, *J* = 9.5 Hz, H-3β), 5.43–5.45 (m, 2.6H, H-1α, PhC*H*αβ), 5.64 (t, 1H, *J* = 9.8 Hz, H-3α), 7.28–7.39 (m, 8H, Ph). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 40.5, 40.6, 40.8 (2 $ClCH_2$), 62.5 (C-5α), 66.7 (C-5β), 68.5 (C-6β), 68.8 (C-6α), 70.6 (C-3α), 72.9 (C-3β), 73.2 (C-2α), 75.3 (C-2β), 78.2 (C-4β), 78.8 (C-4α), 90.8 (C-1α), 95.6 (C-1β), 101.8 (PhCHαβ), 126.2, 128.4, 129.3, 136.5, 136.7 (Ph), 166.6, 166.8, 167.0, 167.3 ($ClCH_2CO$). HRMS (ESI): calcd. for $C_{17}H_{18}Cl_2O_8$ $[M + Na]^+$ 443.0271; found 443.0268.

4.4. 4,6-O-Benzylidene-2,3-di-O-chloroacetyl-D-glucopyranosyl trichloroacetimidate (3)

Trichloroacetonitrile (0.5 mL) and Cs_2CO_3 (50 mg) were added to a solution of **2** (152 mg, 0.36 mmol) in dichloromethane (5 mL), the mixture was stirred at rt for 30 min, diluted with toluene, and filtered through a pad of silica gel (toluene → 95:5 toluene–EtOAc) to give trichloroacetimidate **3** (187 mg, 92%) as a syrupy anomeric mixture; α:β-ratio ~1:1. ^{1}H NMR (C_6D_6, 600 MHz): δ 3.05 (m, 1H, H-5β), 3.19–3.52 (m, 12H, H-4αβ, H-6aαβ, 2 $ClCH_2$αβ), 3.95 (dd, 1H, $J_{6b,5}$ = 4.9 Hz, $J_{6b,6a}$ = 10.3 Hz, H-6bβ), 4.05 (dd, 1H, $J_{6b,5}$ = 5.0 Hz, $J_{6b,6a}$ = 10.5 Hz, H-6bα), 4.22 (m, 1H, H-5α), 5.07 (s, 1H, PhC*H*), 5.19 (dd, 1H, $J_{2,3}$ = 9.9 Hz, H-2α), 5.22 (s, 1H, PhC*H*), 5.39 (t, 1H, *J* = 9.8 Hz, H-3β), 5.42 (t, 1H, *J* = 9.1 Hz, H-2β), 5.87 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1β), 5.98 (t, 1H, *J* = 9.9 Hz, H-3α), 6.70 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1α), 7.00–7.57 (m, 10H, Phαβ), 8.42, 8.59 (2 s, each 1H, NHαβ). ^{13}C NMR (C_6D_6, 150 MHz): δ 40.3, 40.4, 40.5, 40.6 (2 $ClCH_2$), 66.0 (C-5α), 67.2 (C-5β), 68.5 (C-6β), 68.6 (C-6α), 70.9 (C-3α), 72.3 (C-2α), 73.0 (C-2β), 73.5 (C-3β), 77.9 (C-4β), 78.4 (C-4α), 93.9 (C-1α), 96.0 (C-1β), 102.2, 102.5 (PhCHαβ), 127.0, 128.2, 128.4, 129.7, 129.8, 137.5, 137.6 (Ph), 161.2, 161.4 (C = NH), 166.4, 166.7, 166.8, 167.0 ($ClCH_2CO$). HRMS (ESI): calcd. for $C_{19}H_{18}Cl_5NO_8$ $[M + Na]^+$ 585.9367; found 585.9364.

4.5. 4,6-O-Benzylidene-3-O-chloroacetyl-1,2-O-[1-(ethyl 4,6-O-benzylidene-1-thio-β-D-glucopyranoside-3-O-yl)-2-chloroethylidene]-α-D-glucopyranose (5)

A mixture of thioglycoside **4** (61 mg, 0.194 mmol, 1.1 eq.), trichloroacetimidate **3** (100 mg, 0.177 mmol) and MS 4 Å (150 mg) in dry CH_2Cl_2 (2 mL) was stirred at rt for 30 min. Then the mixture was cooled to –30 °C, and a solution of TMSOTf in dry CH_2Cl_2 (0.1 mL, prepared by dissolving 34 μL of TMSOTf in 1 mL of dry CH_2Cl_2, 0.018 mmol) was added. After being stirred for 30 min at –30 °C, the reaction mixture was neutralized with triethylamine, filtered through a pad of Celite and concentrated. The residue was purified by silica gel column chromatography (1:1 hexane–EtOAc) to give orthoester **5** (85 mg, 67%) as a syrup. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.35 (t, 3H, *J* = 7.4 Hz, C*H*$_3$CH$_2$S), 2.55 (s, 1H, OH), 2.79 (m, 2H, CH$_3$C*H*$_2$S), 3.49 (t, 1H, *J* = 9.6 Hz, H-2^1), 3.52 (m, 1H, H-5^1), 3.58 (t, 1H, *J* = 9.4 Hz, H-4^1), 3.66 (t, 1H, *J* = 9.5 Hz, H-4^2), 3.67 (t, 1H, *J* = 10.8 Hz, H-6^{1}a), 3.76 (t, 1H, *J* = 10.2 Hz, H-6^{2}a), 3.88 and 3.95 (2 d, each 1H, J_{gem} = 12.3 Hz, $ClCH_2$), 4.03–4.10 (m, 3H, H-3^1, $ClCH_2$), 4.14 (m, 1H, H-5^2), 4.37 (dd, 1H, $J_{6b,5}$ = 4.7 Hz, $J_{6b,6a}$ = 10.5 Hz, H-6^{2}b), 4.40 (dd, 1H, $J_{6b,5}$ = 5.2 Hz, $J_{6b,6a}$ = 10.5 Hz, H-6^{1}b), 4.43–4.47 (m, 2H, H-1^1, H-2^2), 5.50, 5.51 (2 s, 2H, 2 PhC*H*), 5.54 (dd, 1H, $J_{2,3}$ = 3.8 Hz, $J_{3,4}$ = 9.1 Hz, H-3^2), 5.88 (d, 1H, $J_{1,2}$ = 5.6 Hz, H-1^2), 7.35–7.50 (m, 10H, 2 Ph). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 15.4 (*C*H$_3$CH$_2$S), 24.8 (CH$_3$*C*H$_2$S), 40.7, 44.1 (2 $ClCH_2$), 62.6 (C-5′), 68.5 (C-6′), 68.6 (C-6), 71.0 (C-5), 72.5 (C-2), 75.0 (C-3′), 75.5 (C-2′), 76.5 (C-4′), 76.8 (C-3), 79.5 (C-4), 87.3 (C-1), 98.5 (C-1′), 101.5, 102.0 (2 PhC*H*), 118.1 (orthoester C), 126.1–136.8 (2 Ph), 166.1 ($ClCH_2CO$). HRMS (ESI): calcd. for $C_{32}H_{36}Cl_2O_{12}S$ $[M + Na]^+$ 737.1197; found 737.1188.

4.6. Ethyl 2,3-di-O-acetyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-4,6-O-benzylidene-1-thio-β-D-glucopyranoside (7) and ethyl 2,3-di-O-acetyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→2)-4,6-O-benzylidene-1-thio-β-D-glucopyranoside (8)

Trimethylsilyl triflate (50 μL, 0.26 mmol) was added to a stirred solution of imidate **6** (4.30 g, 8.66 mmol) and diol **4** (4.20 g, 13.46 mmol) in dichloromethane (70 mL) at –30 °C, the resulting mixture was stirred at this temperature for 10 min, and quenched with triethylamine. The solvent was evaporated and the residue was subjected to silica gel column chromatography (toluene → 93:7 toluene–acetone) to provide starting diol **4** (1.45 g, 35%) and disaccharides **7** (3.07 g, 55%), and **8** (446 mg, 8%).

Compound **7**, crystalline solid, mp 214–215 °C (EtOAc–hexane), $[\alpha]_D$ –84 (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.31 (t, 3H, *J* = 7.3 Hz, C*H*$_3$CH$_2$S), 2.04, 2.05 (2 s, each 3H, 2 CH$_3$CO), 2.68 (br. s, 1H, OH), 2.75 (m, 2H, CH$_3$C*H*$_2$S), 3.43 (m, 1H, H-5^2), 3.49 (m, 1H, H-5^1), 3.43 (br. t, 1H, *J* = 9.1 Hz, H-2^1), 3.65 (t, 1H, *J* = 9.7 Hz, H-4^1), 3.70 (t, 1H, *J* = 10.3 Hz, H-6^{2}a), 3.74 (t, 1H, *J* = 10.3 Hz, H-4^2), 3.77 (t, 1H, *J* = 10.4 Hz, H-6^{1}a), 3.83 (t, 1H, *J* = 8.9 Hz, H-3^1), 4.12 (dd, 1H, $J_{6b,5}$ = 5.0 Hz, $J_{6b,6a}$ = 10.5 Hz, H-6^{2}b), 4.35 (dd, 1H, $J_{6b,5}$ = 4.9 Hz, $J_{6b,6a}$ = 10.5 Hz, H-6^{1}b), 4.45 (d, 1H, $J_{1,2}$ = 7.5 Hz, H-1^1), 4.94 (d, 1H, $J_{1,2}$ = 7.5 Hz, H-1^2), 5.05 (t, 1H, *J* = 8.1 Hz, H-2^2), 5.28 (t, 1H, *J* = 9.1 Hz, H-3^2), 5.35, 5.55 (2 s, each 1H, 2 PhC*H*), 7.30–7.50 (m, 10H, 2 Ph). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 15.2 (*C*H$_3$CH$_2$S), 20.7, 20.8 (2 *C*H$_3$CO), 24.6 (CH$_3$*C*H$_2$S), 66.3 (C-5′), 68.4 (C-6′), 68.5 (C-6), 70.8 (C-5), 71.8 (C-3′), 72.5 (C-2), 73.0 (C-2′), 78.0 (C-4′), 79.4 (C-4), 82.3 (C-3), 86.5 (C-1), 101.3, 101.4 (2 PhC*H*), 101.7 (C-1′), 125.9–137.0 (2 Ph), 170.0, 170.1 (2 CH$_3$*C*O). HRMS (ESI): calcd. for $C_{32}H_{38}O_{12}S$ $[M + Na]^+$ 669.1976; found 669.1965.

Compound **8**, crystalline solid, mp 172–174 °C (EtOAc–hexane), $[\alpha]_D$ –91 (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.21 (t, 3H, *J* = 7.3 Hz, C*H*$_3$CH$_2$S), 1.96, 1.99 (2 s, each 3H, 2 CH$_3$CO), 2.59–2.72 (m, 3H, CH$_3$C*H*$_2$S, OH), 3.36 (m, 1 H, H-5^1), 3.43 (t, 1H, *J* = 9.3 Hz, H-4^1), 3.47 (m, 1H, H-5^2), 3.62 (t, 1H, *J* = 8.5 Hz, H-2^1), 3.65 (t, 1H, *J* = 10.2 Hz, H-6^{2}a), 3.71 (1 H, t, *J* = 9.7 Hz, H-4^2), 3.74–3.82 (m, 2H, H-3^1, H-6^{1}a), 4.22–4.32 (m, 2H, H-6^{1}b, 6^{2}b), 4.42 (d, 1H, $J_{1,2}$ = 9.6 Hz, H-1^1), 4.97 (dd, 1H, $J_{2,3}$ = 8.8 Hz, H-2^2), 5.07 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1^2), 5.25 (t, 1H, *J* = 9.3 Hz, H-3^2), 5.42, 5.45 (2 s, each 1H, 2 PhC*H*), 7.25–7.42 (m, 10H, 2 Ph). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.8 (*C*H$_3$CH$_2$S), 20.8, 20.9 (2 *C*H$_3$CO), 24.5 (CH$_3$*C*H$_2$S), 66.4 (C-5^2), 68.6 (C-6^2), 68.7 (C-6^1), 70.1 (C-5^1), 72.1 (C-3^2), 73.0 (C-2^2), 75.4 (C-3^1), 78.2 (C-4^2), 79.9 (C-2^1), 80.4 (C-4^1), 84.1 (C-1^1), 101.1 (C-1^2), 101.6, 102.0 (2 PhC*H*), 126.1–136.9 (2 Ph), 169.9, 170.2 (2 CH$_3$*C*O). HRMS (ESI): calcd. for $C_{32}H_{38}O_{12}S$ $[M + Na]^+$ 669.1976; found 669.1971.

*4.7. Ethyl 2,3-di-O-acetyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-O-benzylidene-1-thio-β-D-glucopyranoside (**9**)*

Benzoyl chloride (1.2 mL, 10.3 mmol) and DMAP (100 mg) were added to a solution of **7** (3.00 g, 4.64 mmol) in pyridine (20 mL) and the mixture was stirred for 20 h at rt. Water (1 mL) was added and stirring was continued for 30 min. The mixture was diluted with CH_2Cl_2, washed successively with aq 1 M HCl, water, and satd aq $NaHCO_3$, dried and concentrated. The residue was crystallized from ethanol to give **9** (3.20 g, 92%) as white crystals, mp 207–208 °C, $[\alpha]_D$ –69 (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): 1.20 (t, 3H, *J* = 7.5 Hz, C*H*$_3$CH$_2$S), 1.73, 1.94 (2 s, each 3H, 2 CH_3CO), 2.70 (m, 2H, CH_3C*H*$_2$S), 3.37 (m, 1H, H-5^2), 3.55 (m, 1H, H-5^1), 3.64 (t, 1H, *J* = 9.5 Hz, H-4^2), 3.66 (t, 1H, *J* = 10.0 Hz, H-6^{2}a), 3.74 (t, 1H, *J* = 9.4 Hz, H-4^1), 3.80 (t, 1H, *J* = 10.3 Hz, H-6^{1}a), 4.16 (t, 1H, *J* = 9.1 Hz, H-3^1), 4.20 (dd, 1H, $J_{6b,5}$ = 5.0 Hz, $J_{6b,6a}$ = 10.5 Hz, H-6^{2}b), 4.38 (dd, 1H, $J_{6b,5}$ = 4.9 Hz, $J_{6b,6a}$ = 10.5 Hz, H-6^{1}b), 4.59 (d, 1H, $J_{1,2}$ = 10.0 Hz, H-1^1), 4.72 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1^2), 4.96 (t, 1H, *J* = 8.8 Hz, H-2^2), 5.04 (t, 1H, *J* = 9.2 Hz, H-3^2), 5.32 (t, 1H, *J* = 9.4 Hz, H-2^1), 5.35, 5.57 (2 s, each 1H, 2 PhC*H*), 7.30–8.06 (m, 15H, 3 Ph). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 14.7 (*C*H$_3$CH$_2$S), 20.1, 20.7 (2 *C*H$_3$CO), 23.4 (CH$_3$CH$_2$S), 66.1 (C-5^2), 68.5 (2C, C-6^1, 6^2), 71.1 (C-5^1), 71.9, 71.95, 72.0 (C-2^1, 2^2, 3^2), 78.1 (C-4^2), 78.8 (C-4^1), 79.7 (C-3^1), 84.3 (C-1^1), 100.9 (C-1^2), 101.1, 101.3 (2 PhC*H*), 126.0–137.1 (3 Ph), 164.9 (Ph*C*O), 169.6, 170.0 (2 CH$_3$*C*O). HRMS (ESI): calcd. for $C_{39}H_{42}O_{13}S$ $[M + Na]^+$ 773.2238; found 773.2216.

*4.8. Ethyl 4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-O-benzylidene-1-thio-β-D-glucopyranoside (**10**)*

Hydrazine hydrate (4.7 mL, 97 mmol) was added to a solution of **9** (1.42 g, 1.89 mmol) in CH_2Cl_2 (14 mL) and MeOH (28 mL). The mixture was stirred for 25 min, diluted with water (150 mL), and extracted with CH_2Cl_2 (3 × 50 mL). The combined extracts were washed with brine, dried, and concentrated. Column chromatography of the residue (CH_2Cl_2 → 95:5 CH_2Cl_2–acetone) afforded starting **9** (120 mg, 8.5%) and diol **10** (1.15 g, 91.5%). Treatment of recovered **9** as described above provided more **10** (110 mg); total yield of diol **10** made up 1.26 g (100%), amorphous solid, $[\alpha]_D$ –54 (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.26 (t, 3H, *J* = 7.4 Hz, C*H*$_3$CH$_2$S), 2.53 (s, 1H, OH-3^2), 2.76 (m, 2H, CH_3C*H*$_2$S), 2.90 (d, 1H, $J_{OH,2}$ = 2.4 Hz, OH-2^2), 3.30 (m, 1H, H-5^2), 3.44–3.48 (m, 3H, H-2^2, 4^2, 6^{2}a), 3.58–3.65 (m, 2H, H-3^2, 5^1), 3.81 (t, 1H, *J* = 9.6 Hz, H-4^1), 3.83–3.87 (m, 2H, H-6^{1}a, 6^{2}b), 4.21 (t, 1H, *J* = 9.0 Hz, H-3^1), 4.43 (dd, 1H, $J_{6b,5}$ = 5.1 Hz, $J_{6b,6a}$ = 10.5 Hz, H-6^{1}b), 4.47 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1^2), 4.73 (d, 1H, $J_{1,2}$ = 10.2 Hz, H-1^1), 5.37 (t, 1H, *J* = 9.3 Hz, H-2^1), 5.43, 5.63 (2 s, each 1H, 2 PhC*H*), 7.32–8.08 (m, 15H, 3 Ph). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 14.8 (*C*H$_3$CH$_2$S), 24.1 (CH$_3$CH$_2$S), 66.6 (C-5^2), 68.4 (C-6^2), 68.5 (C-6^1), 70.9 (C-5^1), 71.9 (C-2^1), 72.8 (C-3^2), 73.4 (C-2^2), 79.1 (C-4^1), 79.3 (C-3^1), 80.2 (C-4^2), 84.3 (C-1^1), 101.6, 101.8 (2 PhCH), 103.0 (C-1^2), 126.1–136.9 (3 Ph), 156.8 (Ph*C*O). HRMS (ESI): calcd. for $C_{35}H_{38}O_{11}S$ $[M + K]^+$ 705.1766; found 705.1778.

*4.9. Ethyl 4,6-O-benzylidene-2,3-di-O-chloroacetyl-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-O-benzylidene-1-thio-β-D-glucopyranoside (**11**)*

Chloroacetic anhydride (845 mg, 4.95 mmol) was added to a solution of diol **10** (1.10 g, 1.65 mmol) and 2,4,6-collidine (0.88 mL, 6.6 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred for 2 h at rt, then MeOH (1 mL) was added and stirring was continued for next 30 min. After dilution with CH_2Cl_2, the mixture was successively washed with aq 1 M HCl, water, satd aq $NaHCO_3$, dried and concentrated. The residue was recrystallized from ethanol to afford **11** (1.24 g, 92%), mp 178–179 °C, $[\alpha]_D$ –57 (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.32 (t, 3H, *J* = 7.3 Hz, C*H*$_3$CH$_2$S), 2.74 (m, 2H, CH_3C*H*$_2$S), 3.44 (m, 1H, H-5^2), 3.60 (m, 1H, H-5^1), 3.70–3.75 (m, 3H, H-4^2, 6^{2}a, ClCHb*Ha*), 3.78 (t, 1H, *J* = 9.4 Hz, H-4^1), 3.84 (t, 1H, *J* = 10.3 Hz, H-6^{1}a), 3.99 (s, 2H, $ClCH_2$), 4.01 (d, 1H, *J* = 14.9 Hz, ClC*Hb*Ha), 4.22 (t, 1H, *J* = 9.1 Hz, H-3^1), 4.30 (dd, 1H, $J_{6b,5}$ = 4.9 Hz, $J_{6b,6a}$ = 10.5 Hz, H-6^{2}b), 4.42 (dd, 1H, $J_{6b,5}$ = 4.8 Hz, $J_{6b,6a}$ = 10.5 Hz, H-6^{1}b), 4.64 (d, 1H, $J_{1,2}$ = 10.1 Hz, H-1^1), 4.78 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1^2), 5.09 (t, 1H, *J* = 8.4 Hz, H-2^2), 5.16 (t, 1H, *J* = 9.3 Hz, H-3^2), 5.35 (t, 1H, *J* = 9.3 Hz, H-2^1), 5.42, 5.61 (2 s, each 1H, 2 PhC*H*), 7.33–8.11 (m, 15H, 3 Ph). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 14.7 (*C*H$_3$CH$_2$S), 24.0 (CH$_3$CH$_2$S), 40.2, 40.4 (2 $ClCH_2$), 66.2 (C-5^2), 68.4 (C-6^2), 68.5 (C-6^1), 71.1 (C-5^1), 72.2 (C-2^1), 73.2, (C-2^2), 73.3 (C-3^2), 77.9 (C-4^1), 78.6 (C-4^2), 79.8 (C-3^1), 84.2 (C-1^1), 100.5 (C-1^2), 101.1, 101.5 (2 PhCH), 126.0–137.1 (3 Ph), 165.2 (Ph*C*O), 166.5, 166.6 (2 $ClCH_2$*C*O). HRMS (ESI): calcd. for $C_{39}H_{40}Cl_2O_{13}S$ $[M + Na]^+$ 841.1459; found 841.1459.

*4.10. 3-Benzyloxycarbonylaminopropyl 2,3-di-O-acetyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-4,6-O-benzylidene-β-D-glucopyranoside (**13**) and 3-benzyloxycarbonylaminopropyl 2,3-di-O-acetyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→2)-4,6-O-benzylidene-β-D-glucopyranoside (**14**)*

A mixture of diol **12** (1.16 g, 2.53 mmol), thioglycoside **9** (1.88 g, 2.50 mmol) and mol. sieve AW-300 (3.7 g) in CH_2Cl_2 (40 mL) was stirred for 30 min at rt and then cooled to –30 °C. NIS (650 mg, 2.89 mmol) was added, stirring was continued for 30 min at –30 °C, and a solution of TfOH (50 μL, 0.56 mmol) in CH_2Cl_2 (1 mL) was added. The mixture was stirred for additional 30 min, quenched by adding satd aq $NaHCO_3$ and aq 1 M $Na_2S_2O_3$ and filtered through a layer of Celite. The solids were washed with CH_2Cl_2, the combined filtrates were allowed to separate, and the organic layer was dried and concentrated. Column chromatography of the residue (toluene → 95:5 toluene–EtOAc) provided (1→3)-trisaccharide **13** (1.56 g, 54%), and (1→2)-trisaccharide **14** (287 mg, 10%).

(1→3)-Trisaccharide **13**: amorphous solid, $[\alpha]_D$ –34 (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.75 (m, 2H, NHCH$_2$C*H*$_2$CH$_2$O), 1.83, 2.00 (2 s, each 3H, CH_3CO), 3.22 (m, 1H, NHC*Ha*HbCH$_2$CH$_2$O), 3.39–3.48 (m, 4H, NHCHa*Hb*CH$_2$CH$_2$O, H-2^1, 5^1, 5^3), 3.53 (m, 1H, NHCH$_2$CH$_2$C*Ha*HbO), 3.58 (m, 1H, H-5^2), 3.61 (t, 1H, *J* = 9.4 Hz, H-4^1), 3.70 (t, 2H, *J* = 10.0 Hz, H-4^3, 6^{3}a), 3.73 (t, 1H, *J* = 10.6 Hz, H-6^{2}a), 3.77 (t, 1H, *J* = 10.4 Hz, H-6^{1}a), 3.85 (t, 1H, *J* = 9.0 Hz, H-3^1), 3.92 (m, 1H, NHCH$_2$CH$_2$CHa*Hb*O), 3.96 (t, 1H, *J* = 9.4 Hz, H-4^2), 4.13 (t, 1H, *J* = 7.9 Hz, H-3^2), 4.21 (dd, 1H, $J_{6b,5}$ = 4.6 Hz, $J_{6b,6a}$ = 10.3 Hz, H-6^{2}b), 4.24 (dd, 1H, $J_{6b,5}$ = 5.0 Hz, $J_{6b,6a}$ = 10.5 Hz, H-6^{3}b), 4.28 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1^1), 4.33 (dd, 1H, $J_{6b,5}$ = 4.8 Hz, $J_{6b,6a}$ = 10.5 Hz, H-6^{2}b), 4.86 (d, 1H, $J_{1,2}$ = 7.5 Hz, H-1^3), 5.02 (t, 1H, *J* = 9.0 Hz, H-2^3), 5.04 (br. t, 1H, NH), 5.11 (s, 2H, PhC*H*$_2$), 5.16 (t, 1H, *J* = 9.2 Hz, H-3^3), 5.17 (d, 1H, $J_{1,2}$ = 6.1 Hz, H-1^2), 5.27, 5.40, 5.56 (3 s, each 1H, 3 PhC*H*), 5.31 (t, 1H, *J* = 6.7 Hz, H-2^2), 7.30–8.09 (m, 25H, 5 Ph). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 20.5, 20.6 (2 *C*H$_3$CO), 29.4 (NHCH$_2$CH$_2$CH$_2$O), 38.1 (NHCH$_2$CH$_2$CH$_2$O), 66.1 (C-5^2), 66.2 (C-5^3), 66.5 (C-5^1), 66.8 (PhCH$_2$), 67.3 (NHCH$_2$CH$_2$C*H*$_2$O), 68.5, 68.6, 68.8 (C-6^1, 6^2, 6^3), 72.1 (C-3^3), 72.2 (C-2^3), 74.4 (C-2^2), 74.5 (C-2^1), 78.2 (C-4^3), 78.3 (C-4^2), 78.7 (C-3^2), 79.2 (C-4^1), 79.8 (C-3^1), 100.5 (C-1^3), 100.9 (2C, C-1^2, PhCH), 101.4, 101.5 (2 PhCH), 103.2 (C-1^1), 156.5 (OCONH), 165.3 (Ph*C*O), 169.6, 170.0 (2 CH$_3$*C*O). HRMS (ESI): calcd. for $C_{61}H_{65}NO_{21}$ $[M + Na]^+$ 1170.3941; found 1170.3901.

(1→2)-Trisaccharide **14**: amorphous solid, $[\alpha]_D$ –38 (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.74 (s, 3H, CH_3CO), 1.82 (m, 2H, NHCH$_2$C*H*$_2$CH$_2$O), 1.96 (s, 3H, CH_3CO), 3.30–3.36 (m, 3H, NHC*H*$_2$CH$_2$CH$_2$O, H-5^1), 3.37–3.44 (m, 2H, H-4^1, 5^3), 3.52–3.58 (m, 2H, H-2^1, 5^2), 3.63–3.72 (m, 5H, H-3^1, 4^3, 6^{1}a, 6^{3}a, NHCH$_2$CH$_2$C*Ha*HbO), 3.78–3.85 (m, 2H, H-4^2, 6^{2}a), 3.93 (m, 1H, NHCH$_2$CH$_2$CHa*Hb*O), 4.18 (t, 1H, *J* = 8.8 Hz, H-3^2), 4.20 (dd, 1H, $J_{6b,5}$ = 4.8 Hz, $J_{6b,6a}$ = 10.3 Hz, H-6^{3}b), 4.29 (dd, 1H, $J_{6b,5}$ = 5.0 Hz, $J_{6b,6a}$ = 10.6 Hz, H-6^{1}b), 4.33 (dd, 1H, $J_{6b,5}$ = 4.6 Hz, $J_{6b,6a}$ = 10.2 Hz, H-6^{2}b), 4.41 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1^1), 4.77 (d, 1H, $J_{1,2}$ = 7.5 Hz, H-1^3), 4.98 (t, 1H, *J* = 8.4 Hz, H-2^3), 5.09 (t,

1H, J = 9.3 Hz, H-3^3), 5.12 (m, 2H H-1^2, PhC*Ha*Hb), 5.21 (d, 1H, J = 12.3 Hz, PhCHa*Hb*), 5.33 (t, 1H, J = 8.0 Hz, H-2^2), 5.36, 5.40, 5.44 (3 s, each 1H, 3 PhC*H*), 5.45 (br. t, 1H, NH), 7.30–8.07 (m, 25H, 5 Ph). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 20.1, 20.7 (2 *C*H_3CO), 28.9 (NHCH$_2$*C*H$_2$CH$_2$O), 38.1 (NHCH$_2$CH$_2$*C*H$_2$O), 65.8 (C-5^1), 66.1 (C-5^3), 66.5 (2C, C-5^2, PhCH_2), 68.1 (NHCH$_2$CH$_2$*C*H$_2$O), 68.4 (C-6^2), 68.5 (2C, C-6^1, 6^3), 72.0 (C-3^3), 72.1 (C-2^3), 73.7 (C-3^1), 74.2 (C-2^2), 78.1 (C-4^3), 78.4 (C-4^2), 78.7 (C-3^2), 80.2 (C-4^1), 81.1 (C-2^1), 100.9 (C-1^3), 101.1, 101.4 (2 PhCH), 101.7 (C-1^2), 101.9 (2C, C-1^1, PhCH), 126.0–137.2 (5 Ph), 156.6 (OCONH), 165.3 (Ph*C*O), 169.5, 170.0 (2 CH$_3$*C*O). HRMS (ESI): calcd. for $C_{61}H_{65}NO_{21}$ [M + Na]$^+$ 1170.3941; found 1170.3937.

4.11. 3-Benzyloxycarbonylaminopropyl 2,3-di-O-acetyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranoside (**15**)

Trisaccharide **13** was benzoylated as described for **9** to provide trisaccharide **15** (97%), amorphous solid, [α]$_D$ –33 (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.66 (m, 2H, NHCH$_2$*CH$_2$*CH$_2$O), 1.80, 1.96 (2 s, each 3H, 2 CH$_3$CO), 3.09 (m, 2H, NHC*H$_2$*CH$_2$CH$_2$O), 3.35 (m, 1H, H-5^3), 3.43 (m, 1H, NHCH$_2$CH$_2$C*Ha*HbO), 3.48 (m, 1H, H-5^2), 3.57 (m, 1H, H-5^1), 3.62–3.69 (m, 3H, H-4^3, 6^{2}a, 6^{3}a), 3.78–3.89 (m, 4H, H-4^1, 4^2, 6^{1}a, NHCH$_2$CH$_2$CHa*Hb*O), 4.01 (t, 1H, J = 7.5 Hz, H-3^2), 4.18–4.22 (m, 3H, H-3^1, 6^{2}b, 6^{3}b), 4.37 (dd, 1H, $J_{6b,5}$ = 4.8 Hz, $J_{6b,6a}$ = 10.2 Hz, H-6^{1}b), 4.57 (d, 1H, $J_{1,2}$ = 7.2 Hz, H-1^1), 4.72 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1^3), 4.88–4.96 (m, 3H, H-1^2, 2^3, NH), 5.04–5.08 (m, 3H, H-3^3, PhCH_2), 5.17 (s, 1H, PhC*H*), 5.18–5.23 (m, 2H, H-2^1, 2^2), 5.37, 5.59 (2 s, each 1H, 2 PhC*H*), 7.30–7.85 (m, 30 H, 6 Ph). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 20.2, 20.7 (2 *C*H_3CO), 29.4 (NHCH$_2$*C*H$_2$CH$_2$O), 38.0 (NH*C*H$_2$CH$_2$CH$_2$O), 66.0 (C-5^2), 66.1 (C-5^3), 66.4 (Ph*C*H$_2$), 66.5 (C-5^1), 67.2 (NHCH$_2$CH$_2$*C*H$_2$O), 68.5, 68.6 (C-6^2, 6^3), 68.7 (C-6^1), 71.9 (2C, C-2^3, 3^3), 73.8 (2C, C-2^2, 2^3), 77.0 (C-3^1), 78.1 (C-4^2), 78.2 (C-4^3), 78.4 (C-3^2), 79.0 (C-4^1), 99.9 (C-1^2), 100.3 (C-1^3), 100.8 (Ph*C*H), 101.2 (C-1^1), 101.3, 101.6 (2 Ph*C*H), 126.0–137.2 (6 Ph), 156.4 (OCONH), 164.5, 164.8 (2 Ph*C*O), 169.6, 170.0 (2 CH$_3$*C*O). HRMS (ESI): calcd. for $C_{68}H_{69}NO_{22}$ [M + Na]$^+$ 1274.4203; found 1274.4210.

4.12. 3-Benzyloxycarbonylaminopropyl 4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranoside (**16**)

Hydrazine hydrate (2.6 mL, 54 mmol) was added to a solution of **15** (1.55 g, 1.24 mmol) in CH_2Cl_2 (8 mL) and MeOH (16 mL) at rt. After being stirred for 25 min, the mixture was diluted with water (100 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The combined extracts were washed with brine, dried, and concentrated. Column chromatography of the residue CH_2Cl_2 → 85:15 CH_2Cl_2–acetone gave unreacted **15** (200 mg, 13%) and diol **16** (1.03 g, 71%). Repeated deacetylation of recovered **15** provided an additional portion of **16** (110 mg). Total yield of **16** made up 1.14 g (79%), amorphous solid, [α]$_D$ –21 (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 600 MHz, selected data): δ 1.64 (m, 2H NHCH$_2$*CH$_2$*CH$_2$O), 3.08, 3.12 (2 m, 2H, NHC*H$_2$*CH$_2$CH$_2$O), 3.26 (m, 1H, H-5^3), 3.38–3.52 (m, 4H, H-2^3, 4^3, 6^{3}a, NHCH$_2$CH$_2$C*Ha*HbO), 3.48 (m, 1H, H-5^1), 3.59–3.65 (m, 2H, H-3^3, H-5^2), 3.68 (t, 1H, J = 10.2 Hz, H-6^{1}a), 3.79–3.88 (m, 3H, H-6^{2}a, 6^{3}b, NHCH$_2$CH$_2$CHa*Hb*O), 3.86 (t, 1H, J = 9.1 Hz, H-4^1), 3.91 (t, 1H, J = 9.2 Hz, H-4^2), 4.04 (t, 1H, J = 8.1 Hz, H-3^1), 4.18–4.22 (m, 2H, H-3^2, 6^{1}b), 4.39 (dd, 1H, $J_{6b,5}$ = 4.7 Hz, $J_{6b,6a}$ = 10.5 Hz, H-6^{2}b), 4.44 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1^3), 4.62 (d, 1H, $J_{1,2}$ = 7.0 Hz, H-1^1), 4.97 (br. t, 1H, NH), 5.03 (d, 1H, $J_{1,2}$ = 6.6 Hz, H-1^2), 5.07 (s, 2H, PhCH_2), 5.23–5.27 (m, 2H, H-2^1, 2^2), 5.35, 5.41, 5.58 (3 s, each 1H, PhC*H*), 7.30–8.89 (m, 30H, 6 Ph). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 29.4 (NHCH$_2$*C*H$_2$CH$_2$O), 38.0 (NH*C*H$_2$CH$_2$CH$_2$O), 65.9 (C-5^1), 66.2 (C-5^2), 66.4 (C-5^3), 66.6 (Ph*C*H$_2$), 67.2 (NHCH$_2$CH$_2$*C*H$_2$O), 68.3 (C-6^3), 68.6 (C-6^1), 68.8 (C-6^2), 72.7 (C-3^3), 73.5 (2C), 73.6 (C-2^1, 2^2, 2^3), 77.9 (C-3^2), 78.2 (C-3^1), 78.5 (C-4^1), 79.3 (C-4^2), 80.2 (C-4^3), 100.0 (C-1^2), 100.9 (C-1^1), 101.3, 101.7, 101.8 (3 Ph*C*H), 102.5 (C-1^3), 126.0–137.0 (6 Ph), 156.4 (OCONH), 164.9, 165.3 (2 Ph*C*O). HRMS (ESI): calcd. for $C_{64}H_{65}NO_{20}$ [M + Na]$^+$ 1190.3992; found 1190.4002.

4.13. General procedure A. Elongation of the oligosaccharide chain by glycosylation of diol acceptors with donor **11**

A mixture of donor **11** (1.05–1.15 equiv.), a diol acceptor and mol. sieve AW-300 (1.5 g/mmol) in CH_2Cl_2 (15 mL/mmol) was stirred at rt for 30 min and cooled to –30 °C. NIS (1.5 equiv. relative to **11**) was added and the resulting mixture was stirred for additional 30 min at the same temperature. Then a solution of TfOH (7 molar %) in CH_2Cl_2 was added at –30 °C, and stirring was continued for next 2 h, while the temperature was gradually increased to –10 °C. The reaction mixture was quenched with satd aq $NaHCO_3$ and aq 1 M $Na_2S_2O_3$ and filtered through a Celite layer. The solids were washed with CH_2Cl_2, the organic layer from the combined filtrates was separated, dried, and concentrated. The residue was purified by silica gel column chromatography (9:1 toluene–EtOAc → 85:15 toluene–EtOAc) to provide a glycosylation product.

4.14. 3-Benzyloxycarbonylaminopropyl 4,6-O-benzylidene-2,3-di-O-chloroacetyl-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranoside (**17**)

Pentasaccharide **17** was prepared by glycosylation of diol **16** with **11** according to the general procedure A in 91% yield, amorphous powder, [α]$_D$ –23 (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 600 MHz, selected data): δ 1.68 (m, 2H, NHCH$_2$*CH$_2$*CH$_2$O), 2.90 (br. s, 1H, OH), 3.09, 3.12 (2 m, 2H, NHC*H$_2$*CH$_2$CH$_2$O), 3.33 (br. t, J = 8.5 Hz, H-2^3), 3.99, 4.07 (2 d, each 1H, J = 15.9 Hz, ClCH$_2$), 4.09 (s, 2H, ClCH$_2$), 4.36 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1^3), 4.61 (d, 1H, $J_{1,2}$ = 7.2 Hz, H-1), 4.72 (s, 1H, Ph*C*H), 5.00 (d, 1H, $J_{1,2}$ = 6.9 Hz, H-1), 5.07 (d, 1H, $J_{1,2}$ = 4.8 Hz, H-1), 5.08 (s, 2H, PhCH_2), 5.09 (d, 1H, $J_{1,2}$ = 7.4 Hz, H-1), 5.16 (t, 2H, J = 8.6 Hz, 2 H-2), 5.26 (t, 1H, J = 7.7 Hz, H-2), 5.32 (s, 1H, Ph*C*H), 5.40 (t, 1H, J = 9.5 Hz, H-3^5), 5.43, 5.48, 5.58 (3 s, each 1H, 3 Ph*C*H), 7.18–8.09 (m, 45H, 9 Ph). ^{13}C NMR ($CDCl_3$, 150 MHz, selected data): δ 29.4 (NHCH$_2$*C*H$_2$CH$_2$O), 38.0 (NH*C*H$_2$CH$_2$CH$_2$O), 40.6, 40.8 (2 ClCH$_2$), 66.4 (Ph*C*H$_2$), 98.5 (C-1), 99.2 (C-1), 100.2 (C-1), 100.4 (Ph*C*H), 101.1 (C-1), 101.3, 101.6, 101.7, 101.8 (4 Ph*C*H), 102.0 (C-1^3), 126.0–137.3 (9 Ph), 156.4 (OCONH), 164.9, 165.0, 165.3, 166.2, 166.7 (3 Ph*C*O, 2 ClCH$_2$*C*O). HRMS (ESI): calcd. for $C_{101}H_{99}Cl_2NO_{33}$ [M + Na]$^+$ 1946.5369; found 1946.5369.

4.15. 3-Benzyloxycarbonylaminopropyl 4,6-O-benzylidene-2,3-di-O-chloroacetyl-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-acetyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranoside (**19**)

Heptasaccharide **19** (83%) was synthesized from donor **11** and acceptor **18** according to the general procedure A, amorphous solid, [α]$_D$ –20 (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 600 MHz, selected data): δ 1.73 (m, 2H, NHCH$_2$*CH$_2$*CH$_2$O), 1.83 (s, 3H, CH$_3$CO), 2.98 (br. s, 1H, OH), 3.09 (m, 2H, NHC*H$_2$*CH$_2$CH$_2$O), 4.43 (d, 1H, $J_{1,2}$ = 9.2 Hz, H-1^5), 4.58 (d, 1H, $J_{1,2}$ = 8.1 Hz, H-1), 4.67 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1), 4.88 (d, 1H, $J_{1,2}$ = 8.4 Hz, H-1^7), 4.90 (s, 1H, Ph*C*H), 4.93 (d, 1H, $J_{1,2}$ = 7.2 Hz, H-1), 4.99 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1), 5.02 (s, 1H, Ph*C*H), 5.07 (s, 2H, PhCH_2), 5.11 (s, 1H, Ph*C*H), 5.12 (d, 1H, $J_{1,2}$ = 7.4 Hz, H-1), 5.23 (s, 1H, Ph*C*H), 5.31 (t, 1H, J = 9.4 Hz, H-3^7), 5.46, 5.48, 5.61 (3 Ph*C*H), 7.18–8.10 (m, 60H, 12 Ph). ^{13}C NMR ($CDCl_3$, 150 MHz, selected data): δ 20.5 (*C*H$_3$CO), 29.5

(NHCH$_2$CH$_2$CH$_2$O), 38.0 (NHCH$_2$CH$_2$CH$_2$O), 40.5, 40.6 (2 ClCH$_2$), 66.4 (PhCH$_2$), 98.8, 99.0, 99.2, 99.5 (2C) (5 C-1), 100.5, 101.0, 101.1 (3 PhCH), 101.3 (C-1), 101.5, 101.6 (2C), 101.7 (4 PhCH), 102.2 (C-1[5]), 164.5, 164.7, 165.2, 165.3, 166.3, 166.7 (4 PhCO, 2 ClCH$_2$CO), 169.4 (CH$_3$CO). HRMS (ESI): calcd. for $C_{136}H_{133}Cl_2NO_{45}$ [M + Na]$^+$ 2592.7419; found 2592.7467.

*4.16. 3-Benzyloxycarbonylaminopropyl 4,6-*O*-benzylidene-2,3-di-*O*-chloroacetyl-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**21**)*

Nonasaccharide **21** (91%) was obtained from donor **11** and acceptor **20** according to the general procedure A, amorphous solid, $[\alpha]_D$ –21 (*c* 1, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 600 MHz, selected data): δ 1.65 (m, 2H, NHCH$_2$C*H*$_2$CH$_2$O), 1.79, 1.81 (2 s, each 3H, 2 CH$_3$CO), 2.94 (br. s, 1H, OH), 3.10 (m, 2H, NHC*H*$_2$CH$_2$CH$_2$O), 4.41 (d, 1H, $J_{1,2}$ = 8.5 Hz, H-1), 4.57 (d, 1H, $J_{1,2}$ = 8.2 Hz, H-1), 4.61 (d, 1H, $J_{1,2}$ = 6.9 Hz, H-1), 4.70 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1), 4.78 (t, 1H, $J_{1,2}$ = 6.7 Hz, H-2), 4.80–4.85 (m, 4H, PhC*H*, 2 H-1, H-2), 4.89 (t, 1H, *J* = 6.9 Hz, H-2), 4.92–4.97 (m, 2H, PhC*H*, H-1), 4.99–5.03 (m, 3H, H-1, 2 H-2), 5.03–5.07 (m, 4H, PhC*H*$_2$, 2 PhC*H*), 5.09–5.16 (m, 3H, H-1, H-2, PhC*H*), 5.22 (t, 1H, *J* = 8.1 Hz, H-2), 5.24 (s, 1H, PhC*H*), 5.32 (t, 1H, *J* = 8.0 Hz, H-3[9]), 5.45, 5.46, 6.63 (3 s, each 1H, 3 PhC*H*), 7.15–8.10 (m, 75H, 15 Ph). ^{13}C NMR (CDCl$_3$, 150 MHz, selected data): δ 20.5, 20.6 (2 *C*H$_3$CO), 29.4 (NHCH$_2$*C*H$_2$CH$_2$O), 37.9 (NHCH$_2$CH$_2$CH$_2$O), 40.5, 40.6 (2 ClCH$_2$), 66.4 (PhCH$_2$), 98.1, 98.4, 98.6, 98.9, 99.0, 99.4 (2C), 101.2, 102.1 (9 C-1), 100.4, 101.0, 101.1 (2C), 101.3, 101.4, 101.5, 101.6 (2C) (9 PhCH), 156.3 (OCONH), 164.5, 164.7, 165.2, 165.3, 166.3, 166.6, 166.7 (5 PhCO, 2 ClCH$_2$CO), 168.9, 169.3 (2 CH$_3$CO). HRMS (ESI): calcd. for $C_{171}H_{167}Cl_2NO_{57}$ [M + Na]$^+$ 3238.9469; found 3238.9473.

*4.17. 3-Benzyloxycarbonylaminopropyl 4,6-*O*-benzylidene-2,3-di-*O*-chloroacetyl-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**23**)*

Undecasaccharide **23** was synthesized by glycosylation of acceptor **22** with donor **11** according to the general procedure A in 80% yield, amorphous solid, $[\alpha]_D$ –18 (*c* 1, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 600 MHz, selected data): δ 1.70 (m, 2H, NHCH$_2$C*H*$_2$CH$_2$O), 1.79, 1.80, 1.83 (3 s, each 3H, 3 CH$_3$CO), 2.93 (br. s, 1H, OH), 3.10 (m, 2H, NHC*H*$_2$CH$_2$CH$_2$O), 4.43 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.59 (d, 1H, $J_{1,2}$ = 7.2 Hz, H-1), 4.63 (d, 1H, $J_{1,2}$ = 5.5 Hz, H-1), 4.68 (d, 1H, $J_{1,2}$ = 5.2 Hz, H-1), 4.72 (d, 1H, $J_{1,2}$ = 5.9 Hz, H-1), 4.79–4.93 (m, 12H, 3 H-1, 6 H-2, 2 PhC*H*, NH), 4.97, 5.04, 5.10, 5.15, 5.18, 5.27, 5.47, 5.48, 5.64 (9 s, 9H, 9 PhC*H*), 4.99 (d, 1H, $J_{1,2}$ = 6.7 Hz, H-1), 5.01–5.07 (m, 2H, H-1, H-2), 5.08 (s, 2H, PhC*H*$_2$), 5.12–5.18 (m, 3H, H-1, 2 H-2), 5.23 (t, 1H, *J* = 7.9 Hz, H-2), 5.35 (t, 1H, *J* = 9.4 Hz, H-3[11]), 7.18–8.08 (m, 90H, 18 Ph). ^{13}C NMR (CDCl$_3$, 150 MHz, selected data): δ 20.4, 20.6, 20.7 (3 *C*H$_3$CO), 29.6 (NHCH$_2$*C*H$_2$CH$_2$O), 38.0 (NHCH$_2$CH$_2$CH$_2$O), 40.5, 40.7 (2 ClCH$_2$), 66.4 (PhCH$_2$), 97.9, 98.1, 98.4, 98.5, 98.6, 98.8, 99.0, 99.3, 99.4, 101.2, 102.1 (11 C-1), 100.5, 100.9 (2C), 101.2 (C2), 101.3, 101.4 (2C), 101.6 (2C), 101.7 (11 PhCH). HRMS (ESI): calcd. for $C_{206}H_{201}Cl_2NO_{69}$ [M + 2 NH$_4$]$^{2+}$ 1949.1152; found 1949.1156.

*4.18. 3-Benzyloxycarbonylaminopropyl 4,6-*O*-benzylidene-2,3-di-*O*-chloroacetyl-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**25**)*

Tridecasaccharide **25** was obtained in 95% yield by coupling of acceptor **24** with donor **11** according to the general procedure A, amorphous powder, $[\alpha]_D$ –17 (*c* 1, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 600 MHz, selected data): δ 1.68 (m, 2H, NHCH$_2$C*H*$_2$CH$_2$O), 1.80 (s, 6H, 2 CH$_3$CO), 1.81, 1.83 (2 s, each 3H, 2 CH$_3$CO), 2.94 (br. s, 1H, OH), 3.10 (m, 2H, NHC*H*$_2$CH$_2$CH$_2$O), 4.44 (d, $J_{1,2}$ = 8.2 Hz, H-1), 4.59 (d, $J_{1,2}$ = 7.1 Hz, H-1), 4.63 (d, $J_{1,2}$ = 5.1 Hz, H-1), 4.66–4.69 (m, 2H, 2 H-1), 4.72 (d, $J_{1,2}$ = 5.8 Hz, H-1), 4.79–4.84 (m, 2H, H-1, H-2), 4.83–4.94 (m, 12H, 3 H-1, 6 H-2, 3 PhC*H*), 4.96, 5.10, 5.19, 5.21, 5.27, 5.47, 5.48, 5.64 (8 s, 8H, 8 PhC*H*), 4.99 (d, $J_{1,2}$ = 6.2 Hz, H-1), 5.02–5.07 (m, 4H, H-1, 2 H-2, PhC*H*), 5.08 (s, 2H, PhC*H*$_2$), 5.12–5.17 (m, 3H, H-1, H-2, PhC*H*), 5.24 (t, 1H, *J* = 7.8 Hz, H-2), 5.35 (t, 1H, *J* = 9.3 Hz, H-3[13]), 7.15–8.10 (m, 105H, 21 Ph). ^{13}C NMR (CDCl$_3$, 150 MHz, selected data): δ 20.5 (2C), 20.6 (2C), (4 *C*H$_3$CO), 29.5 (NHCH$_2$CH$_2$CH$_2$O), 38.0 (NHCH$_2$CH$_2$CH$_2$O), 40.5, 40.7 (2 ClCH$_2$), 66.4 (PhCH$_2$), 67.4 (NHCH$_2$CH$_2$*C*H$_2$O), 97.9 (2C), 98.4 (3C), 98.6, 98.9, 99.1, 99.5 (3C), 101.2, 102.2 (13 C-1), 100.5, 101.0 (2C), 101.2 (3C), 101.3, 101.4 (4C), 101.6, 101.7 (2C) (13 PhCH), 156.4 (OCONH), 164.5 (2C), 164.8 (3C), 165.3 (2C), 166.2, 166.6 (7 PhCO, 2 ClCH$_2$CO), 168.9, 169.0 (2C), 169.3 (4 CH$_3$CO). HRMS (ESI): calcd. for $C_{241}H_{235}Cl_2NO_{81}$ [M + 2 NH$_4$]$^{2+}$ 2272.2177; found 2272.2277.

4.19. General procedure B. Conversion of oligosaccharides obtained by General procedure A into new diol acceptors

Acetyl chloride (8 equiv.) was added to a solution of an oligosaccharide, obtained by general procedure A, and 2,4,6-collidine (15 equiv.) in CH$_2$Cl$_2$ (15 mL/mmol) and the mixture was stirred at rt for 20 h. MeOH (50 equiv.) was added and stirring was continued for next 30 min. The mixture was diluted with CH$_2$Cl$_2$, successively washed with aq 1 M HCl, water, satd aq NaHCO$_3$, dried, and concentrated. 2,4,6-Collidine (9 equiv.) and thiourea (17 equiv.) were added to a solution of the acetylated product in EtOAc (20 mL/mmol) and ethanol (20 mL/mmol), the resulting mixture was stirred at 80 °C for 12 h, cooled to rt, and concentrated. A solution of the residue in CH$_2$Cl$_2$ (100 mL) was washed with aq 1 M HCl, water, satd aq NaHCO$_3$, dried, and the solvent was evaporated. The residue was purified by silica gel column chromatography (toluene → 85:15 toluene–acetone) to provide a diol acceptor.

*4.20. 3-Benzyloxycarbonylaminopropyl 4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**18**)*

Diol **18** was obtained from **17** according to the general procedure B in 86% yield, amorphous solid, $[\alpha]_D$ –24 (*c* 1, CHCl$_3$). ^{1}H NMR

($CDCl_3$, 600 MHz, selected data): δ 1.67 (m, 2H, $NHCH_2CH_2CH_2O$), 1.82 (s, 3H, CH_3CO), 3.10 (m, 2H, $NHCH_2CH_2CH_2O$), 4.57 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1[5]), 4.59 (d, 1H, $J_{1,2}$ = 7.5 Hz, H-1), 4.69 (d, 1H, $J_{1,2}$ = 5.4 Hz, H-1), 4.86 (t, 1H, J = 5.4 Hz, H-2), 4.88 (d, 1H, $J_{1,2}$ = 6.5 Hz, H-1), 4.92 (br. t, 1H, NH), 4.96 (s, 1H, PhC*H*), 4.97 (t, 1H, J = 6.8 Hz, H-2), 5.08 (s, 2H, $PhCH_2$), 5.10 (s, 1H, PhC*H*), 5.23 (t, 1H, J = 8.0 Hz, H-2), 5.29 (t, 1H, J = 6.5 Hz, H-2), 5.32, 5.47, 5.64 (3 s, each 1H, 3 PhC*H*), 7.18–8.10 (m, 45H, 9 Ph). ^{13}C NMR ($CDCl_3$, 150 MHz, selected data): δ 20.5 (CH_3CO), 29.4 ($NHCH_2CH_2CH_2O$), 38.0 ($NHCH_2CH_2CH_2O$), 66.4 ($PhCH_2$), 67.3 ($NHCH_2CH_2CH_2O$), 98.5 (2C), 99.5, 101.2, 102.5 (5 C-1), 101.2, 101.3, 101.4, 101.7, 101.9 (5 PhCH), 125.3–137.3 (9 Ph), 156.4 (OCONH), 164.5, 164.7, 165.5 (3 PhCO), 169.3 (CH_3CO). HRMS (ESI): calcd. for $C_{99}H_{99}NO_{32}$ $[M + Na]^+$ 1836.6042; found 1836.6089.

*4.21. 3-Benzyloxycarbonylaminopropyl 4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-acetyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-acetyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranoside (**20**)*

Diol **20** was prepared from **19** according to the general procedure B in 90% yield, amorphous solid, $[\alpha]_D$ –24 (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 600 MHz, selected data): δ 1.78 (m, 2H, $NHCH_2CH_2CH_2O$), 1.78, 1.81 (2 s, each 3H, 2 CH_3CO), 2.72 (br. s, 1H, OH), 3.09 (m, 2H, $NHCH_2CH_2CH_2O$), 3.14 (br. s, 1H, OH), 4.55 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1[7]), 4.58 (d, 1H, $J_{1,2}$ = 7.6 Hz, H-1), 4.62 (d, 1H, $J_{1,2}$ = 5.5 Hz, H-1), 4.74 (d, 1H, $J_{1,2}$ = 5.4 Hz, H-1), 4.79 (t, 1H, J = 5.5 Hz, H-2), 4.82–4.86 (m, 3H, H-1, H-2, PhC*H*), 4.87–4.92 (m, 3H, H-1, H-2, NH), 4.93 (s, 1H, PhC*H*), 4.98 (t, 1H, J = 6.9 Hz, H-2), 5.06–5.10 (m, 4H, H-1, $PhCH_2$, PhC*H*), 5.23 (t, 1H, J = 8.0 Hz, H-2), 5.29 (t, 1H, J = 6.7 Hz, H-2), 5.34, 5.46, 5.64 (3 s, each 1 H, 3 PhC*H*), 7.18–8.08 (m, 60H, 12 Ph). ^{13}C NMR ($CDCl_3$, 150 MHz, selected data): δ 20.5, 20.6 (2 CH_3CO), 29.4 ($NHCH_2CH_2CH_2O$), 37.9 ($NHCH_2CH_2CH_2O$), 66.4 ($PhCH_2$), 67.4 ($NHCH_2CH_2CH_2O$), 98.0, 98.3, 98.4 (2C), 101.1, 102.6 (6 C-1), 99.5, 101.0, 101.7, 101.8, (4 PhC*H*), 101.3 (4C, C-1, 3 PhCH), 126.1–137.3 (12 Ph), 156.4 (OCONH), 154.5, 164.7, 164.8, 165.5 (4 PhCO), 169.0, 169.3 (2 CH_3CO). HRMS (ESI): calcd. for $C_{134}H_{133}NO_{44}$ $[M + K]^+$ 2498.7832; found 2498.7800.

*4.22. 3-Benzyloxycarbonylaminopropyl 4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-acetyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-acetyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranoside (**22**)*

Diol **22** (88%) was synthesized from **21** according to the general procedure B, amorphous solid, $[\alpha]_D$ –25 (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 600 MHz, selected data): δ 1.67 (m, 2H, $NHCH_2CH_2CH_2O$), 1.81. 1.82, 1.84 (3 s, each 3H, 3 CH_3CO), 2.67 (br. s, 1H, OH), 2.09 (br. s, 1H, OH), 3.10 (m, 2H, $NHCH_2CH_2CH_2O$), 4.55 (d, 1H, $J_{1,2}$ = 7.9 Hz, H-1[9]), 4.59 (d, 1H, $J_{1,2}$ = 7.2 Hz, H-1), 4.63 (d, 1H, $J_{1,2}$ = 5.1 Hz, H-1), 4.69 (d, 1H, $J_{1,2}$ = 5.2 Hz, H-1), 4.75 (d, 1H, $J_{1,2}$ = 5.0 Hz, H-1), 4.80–4.93 (m, 11H, 3 H-1, 5 H-2, NH, 2 PhC*H*), 4.97 (s, 1H, PhC*H*), 5.00 (t, 1H, J = 7.0 Hz, H-2), 5.07–5.12 (m, 4H, H-1, PhC*H*, $PhCH_2$), 5.17, 5.19 (2 s, each 1H, 2 PhC*H*), 5.23 (t, 1H, J = 7.9 Hz, H-2), 5.31 (t, 1H, J = 6.8 Hz, H-2), 5.37, 5.46, 5.64 (3 s, each 1H, 3 PhC*H*), 7.18–8.13 (m, 75H, 15 Ph). ^{13}C NMR ($CDCl_3$, 150 MHz, selected data): δ 20.3, 20.5, 20.6 (3 CH_3CO), 29.4 ($NHCH_2CH_2CH_2O$), 38.2 ($NHCH_2CH_2CH_2O$), 66.4 ($PhCH_2$), 67.3 ($NHCH_2CH_2CH_2O$), 97.8, 98.0, 98.2 (2C), 98.3, 98.4, 99.4 (7 C-1), 101.0 (3C, 3 PhCH), 101.3 (2C, C-1, PhCH), 101.4 (3C, 3 PhCH), 101.7, 101.8 (2 PhCH), 102.5 (C-1[9]). HRMS (ESI): calcd. for $C_{169}H_{167}NO_{56}$ $[M + 2 NH_4]^{2+}$ 1571.0464; found 1571.0489.

*4.23. 3-Benzyloxycarbonylaminopropyl 4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-acetyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-acetyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-acetyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranosyl-(1→3)-2-O-benzoyl-4,6-O-benzylidene-β-D-glucopyranoside (**24**)*

Diol **24** was obtained from **23** according to the general procedure B in 86% yield, amorphous solid, $[\alpha]_D$ –19 (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 600 MHz, selected data): δ 1.67 (m, 2H, $NHCH_2CH_2CH_2O$), 1.79 (s, 6H, 2 CH_3CO), 1.81, 1.83 (2 s, each 3H, 2 CH_3CO), 3.11 (m, 2H, $NHCH_2CH_2CH_2O$), 4.55 (d, 1H, $J_{1,2}$ = 7.9 Hz, H-1[11]), 4.59 (d, 1H, $J_{1,2}$ = 7.3 Hz, H-1), 4.63 (d, 1H, $J_{1,2}$ = 5.4 Hz, H-1), 4.66–4.70 (m, 2H, 2 H-1), 4.75 (d, 1H, $J_{1,2}$ = 5.1 Hz, H-1), 4.79–4.93 (m, 14H, 4 H-1, 7 H-2, 3 PhC*H*, NH), 4.96 (s, 1H, PhC*H*), 5.01 (t, 1H, J = 7.0 Hz, H-2), 5.07–5.12 (m, 4H, H-1, PhC*H*, $PhCH_2$), 5.17, 5.19, 5.21 (3 s, each 1H, 3 PhC*H*), 5.23 (t, 1H, J = 8.0 Hz, H-2), 5.31 (t, 1H, J = 6.9 Hz, H-2), 5.37, 5.46, 5.64 (3 s, each 1H, 3 PhC*H*), 7.18–8.12 (m, 90H, 18 Ph). ^{13}C NMR ($CDCl_3$, 150 MHz, selected data): δ 20.6 (4C, 4 CH_3CO), 29.5 ($NHCH_2CH_2CH_2O$), 38.0 ($NHCH_2CH_2CH_2O$), 66.5 ($PhCH_2$), 67.4 ($NHCH_2CH_2CH_2O$), 97.8, 97.9, 98.1, 98.3 (3C), 98.4 (2C), 99.5 (9 C-1), 100.9, 101.0 (2C), 101.1 (4 PhCH), 101.3 (3C, C-1, 2 PhCH), 101.4 (2C), 101.5, 101.7, 101.8 (5 PhCH), 102.6 (C-1[11]), 126.1–137.2 (18 Ph), 156.4 (OCONH), 164.5, 164.8 (3C), 164.9, 165.6 (6 PhCO), 168.9, 169.0 (2C), 169.3 (4 CH_3CO). HRMS (ESI): calcd. for $C_{204}H_{201}NO_{68}$ $[M + 2 NH_4]^{2+}$ 1894.1489; found 1894.1480.

4.24. General procedure C. Preparation of unprotected oligoglucosides

A solution of a protected oligosaccharide (100–120 mg) in a 5:5:1 (v/v/v) mixture of $CHCl_3$—MeOH—aq 1 M HCl (10 mL) was heated at 40–45 °C until TLC (9:1 $CHCl_3$—MeOH) indicated disappearance of products with $R_f > 0$ (4–6 h). The mixture was made neutral with Amberlyst A-26 (HCO_3^-), the resin was filtered off and thoroughly washed with a 1:1 mixture $CHCl_3$—MeOH (50 mL), and the combined filtrates were taken to dryness. The residue was dissolved in MeOH (10 mL), 1 M sodium methoxide (1 mL) was added, and the mixture was heated at 40–45 °C with stirring for 4–5 h, then water (2–5 mL) was added until homogeneity, and stirring was continued for next 6–16 h. The mixture was made neutral with Amberlite IR-120 (H^+), then Amberlyst A-26 (HCO_3^-) (2–3 mL) was added. The resins were filtered off, thoroughly washed with aq 50% MeOH, and the combined filtrates were concentrated. The residue was dissolved in aq MeOH (the proportion of water was increased from 30 to 70% on increasing oligosaccharide length, while water was used for 13-mer), then $Pd(OH)_2$/C (50–70 mg) and 1 M HCl (50–70 μL) were added, and the resulting mixture was stirred at rt under a hydrogen atmosphere until TLC (10:10:3 $CHCl_3$—MeOH—water) showed the absence of substances with $R_f > 0$ (2–4 h). The catalyst was filtered off through a Celite layer, washed with aq MeOH, and the combined filtrates were taken to dryness. The residue was subjected to gel-permeation chromatography, appropriate fractions were collected and freeze-dried to provide a 3-aminopropyl β-(1→3)-oligoglucoside as amorphous fluffy solid.

*4.25. 3-Aminopropyl β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranoside (**26**)*

Trisaccharide **26** was prepared from protected precursor **13** according to the general procedure C in 87% yield, $[\alpha]_D$ –22 (*c* 1, water). ^{1}H and ^{13}C NMR data see Tables 1 and 2. HRMS (ESI): calcd. for $C_{21}H_{39}NO_{16}$ $[M+H]^+$ 562.2342; found 562.2344.

*4.26. 3-Aminopropyl β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranoside (**27**)*

Pentasaccharide **27** was obtained from protected pentamer **17** according to the general procedure C in 95% yield, $[\alpha]_D$ –23 (*c* 1, water). ^{1}H and ^{13}C NMR data see Tables 1 and 2. HRMS (ESI): calcd. for $C_{33}H_{59}NO_{26}$ $[M+H]^+$ 886.3398; found 886.3395.

*4.27. 3-Aminopropyl β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranoside (**28**)*

Heptasaccharide **28** was prepared from **19** according to the general procedure C in 94% yield, $[\alpha]_D$ –16 (*c* 1, water). ^{1}H and ^{13}C NMR data see Tables 1 and 2. HRMS (ESI): calcd. for $C_{45}H_{79}NO_{36}$ $[M+H]^+$ 1210.4455; found 1210.4438.

*4.28. 3-Aminopropyl β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranoside (**29**)*

Nonasaccharide **29** was obtained from **21** according to the general procedure C in 81% yield, $[\alpha]_D$ –16 (*c* 1, water). ^{1}H and ^{13}C NMR data see Tables 1 and 2. HRMS (ESI): calcd. for $C_{57}H_{99}NO_{46}$ $[M+H]^+$ 1534.5511; found 1534.5523.

*4.29. 3-Aminopropyl β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranoside (**30**)*

Undecasaccharide **30** was prepared from precursor **23** according to the general procedure C in 84% yield, $[\alpha]_D$ –17 (*c* 1, water). ^{1}H and ^{13}C NMR data see Tables 1 and 2. HRMS (ESI): calcd. for $C_{69}H_{119}NO_{56}$ $[M+H]^+$ 1858.6567; found 1858.6552.

*4.30. 3-Aminopropyl β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranoside (**31**)*

Tridecasaccharide **31** was prepared from precursor **25** according to the general procedure C in 71% yield, $[\alpha]_D$ –16 (*c* 1, water). ^{1}H and ^{13}C NMR data see Tables 1 and 2. HRMS (ESI): calcd. for $C_{81}H_{139}NO_{66}$ $[M+H]^+$ 2182.7624; found 2182.7606.

Acknowledgment

This work was supported by a grant from the Ministry of Education and Science of the Russian Federation (unique identification number RFMEF157914X0022).

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