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

*D. V. Yashunsky, Yu. E. Tsvetkov, and N. E. Nifantiev**

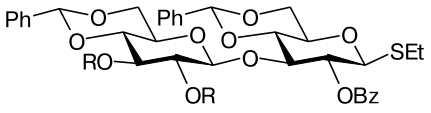
N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (499) 135 8784. E-mail: nen@ioc.ac.ru

The synthesis of branched β-(1→3)-glucooligosaccharides bearing a β-D-glucose residue at position 6 of one of the monosaccharides of the linear chain at a different distances from the reducing end was described.

Key words: β-(1→3)-D-glucans, branched oligosaccharides, aminopropyl glycosides, synthesis.

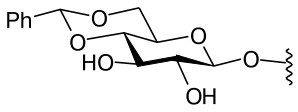
β-(1→3)-D-Glucans are a group of natural polysaccharides comprising D-glucose residues linked between each other by β-(1→3)-glycoside bonds. The β-(1→3)-linked main chain of these polysaccharides is frequently modified by the glucose β-(1→6)- or β-(1→4)-branches. β-(1→3)-D-Glucans are important structural elements of cell walls or reserve polysaccharides of bacteria, fungi, including yeast, algae, and higher plants.[1]

Earlier, we have synthesized linear β-(1→3)-linked glucooligosaccharides containing from 3 to 13 carbohydrate residues in the chain.[2] A key moment in this synthesis was the use as synthetic blocks of disaccharide donors of the type **I** and 2,3-diol acceptors of the type **II**, in which the hydroxy groups at atoms C(4) and C(6) of the glucose residues were protected by a benzylidene group. The presence of a bulky carbohydrate substituents at the anomeric position of terminal glucose residues in the type **II** acceptors and the presence at position 2 of donor **I** of O-benzoyl group provided the high regio- and stereoselectivity of the process of assembly of the β-(1→3)-glucan linear chain. Alternative approaches to the synthesis of linear β-(1→3)-glucooligosaccharides are considered in our recent review.[3]



I

R = Ac or ClAc



II

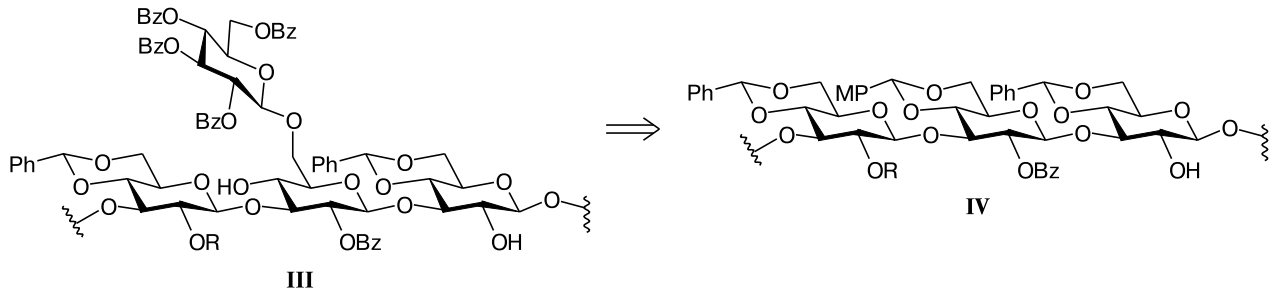
In the present work, we describe the synthesis of some 3-aminopropyl glycosides of β-(1→3)-D-glucooligosaccharides with branches of β-D-glucose residues at position 6 of the glucose of the linear chain. These oligosaccharides are intended to be used in the preparation of immunogens by the conjugation with carrier proteins, covering antigens for IEA, components of diagnosticums for the detection of fungal infections,[4] labeled molecular probes, and other biomolecular systems[5] necessary for the studies of the influence of branching on the immunobiological properties of β-(1→3)-D-glucans.

1,3-Diol *p*-methoxybenzylidene derivatives are considerably less stable under acidic conditions as compared to unsubstituted benzylidene analogues. The use of different hydrolytic stabilities makes it possible to plan the synthesis of branched oligosaccharides of the type **III** base on the retro synthetic Scheme 1, where in the intermediate compound **IV** a 4,6-*O*-*p*-methoxybenzylidene group is used as temporary protection in the glucose residue, which subsequently will bear branching at atom O(6). The synthesis of branched trisaccharides is given in Scheme 2.

To synthesize a branched trisaccharide **10**, a known tetraol **4** (see Ref. 6) was converted to 4,6-*O*-*p*-methoxybenzylidene derivative **5**, the glycosylation of which with known[7] thioglycoside **2** and subsequent acetylation led to the formation of disaccharide **7**. Note that the first attempts to prepare the disaccharide with the selectively removable 4,6-*O*-acetal protection in the glucose residue A at the reducing end *via* the reaction of benzoylated thioglycoside **1** (see Ref. 8) and diol **3** (see Ref. 6) were unsuccessful; this resulted in the formation of a mixture of more than four products. A low-field shift of the signal for H(2) in the ^{1}H NMR spectra on going from the monohydroxy derivative **6** to acetate **7** (δ 3.49 → 4.87) unambiguously confirmed the presence of the acetyl group at

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2922—2931, December, 2015.

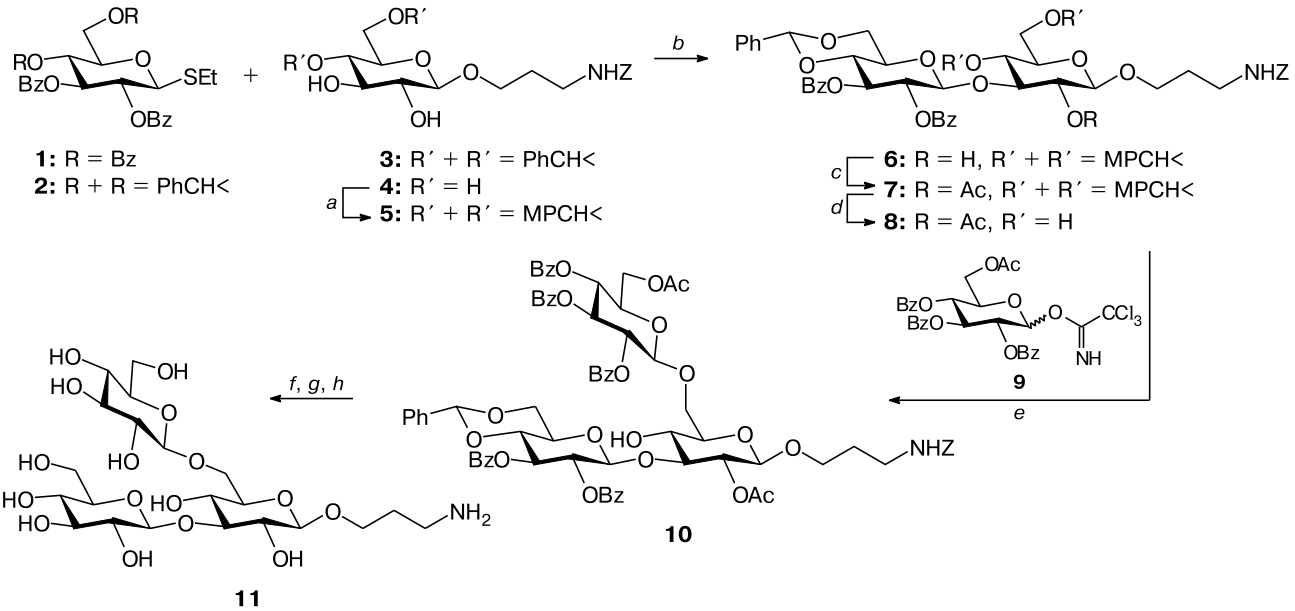
Scheme 1



III **IV**

MP = *p*-$MeOC_6H_4$

Scheme 2



1: R = Bz
2: R + R = PhCH<
3: R′ + R′ = PhCH<
4: R′ = H
5: R′ + R′ = MPCH<
6: R = H, R′ + R′ = MPCH<
7: R = Ac, R′ + R′ = MPCH<
8: R = Ac, R′ = H
9
10
11

Z = BnOC(O), MP = *p*-$MeOC_6H_4$

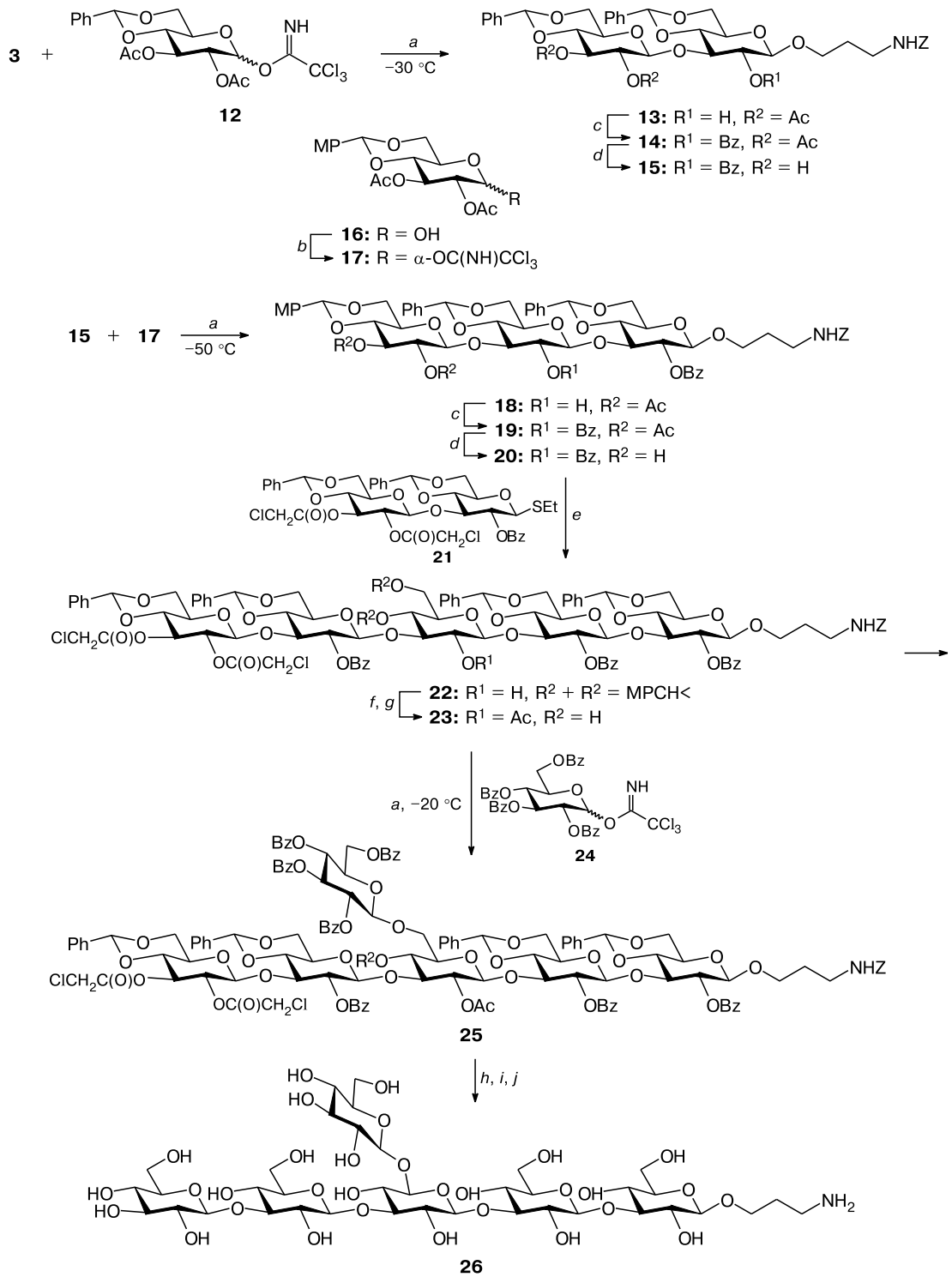
Reagents, reaction conditions, and yields: (*a*) *p*-$MeOC_6H_4CH(OMe)_2$—CSA, MeCN, 20 °C, 74% yield; (*b*) NIS, AgOTf, molecular sieves AW-300, CH_2Cl_2, 20 °C, 50% yield; (*c*) Ac_2O—Py, 20 °C, 93% yield; (*d*) $Ce(NO_3)_3 \cdot 6H_2O$, MeCN, 20 °C, 73% yield; (*e*) TMSOTf, CH_2Cl_2, 20 °C, 82% yield; (*f*) 1 *M* HCl, $CHCl_3$—MeOH, 40—45 °C; (*g*) MONa, MeOH, then NaOH, aqueous MeOH, 40—45 °C; (*h*) H_2, $Pd(OH)_2$/C, aqueous MeOH, 20 °C, 98% yield calculated on three steps.

atom O(2) and, consequently, the (1→3)-glycoside bond. The β-configuration of the newly formed glycoside bond was inferred from the spin-spin coupling constant value $J_{1,2}$ = 6.6 Hz of the glucose residue B.

Selective removal of the *p*-methoxybenzylidene group upon treatment with cerium nitrate hexahydrate in acetonitrile led to diol **8**. Selective glycosylation of the latter with known trichloroacetimidate donor **9** (see Ref. 9) regioselectively led to the preparation of protected branched trisaccharide **10**. The presence of the (1→6)-glycoside bond in trisaccharide **10** followed from the low-field position of the signal for C(6) atom (δ 69.3) of the glucose residue A as compared to the position of the signal for C(6) (δ 62.3) in the glucose residue A in disaccharide **8**. The removal of the acetal, acyl, and benzyloxycarbonyl protecting groups sequentially by acid hydrolysis, treatment with alkali, and hydrogenolysis in the presence of a palladium catalyst led to the preparation of the target trisaccharide **11**.

The next purpose of the present work was the synthesis of branched hexasaccharides (Schemes 3 and 4). Disaccharide **14** obtained by glycosylation of diol **3** (see Ref. 6) with trichloroacetimidate **12** (see Ref. 10) with subsequent benzoylation of the free hydroxy group in glycosylation product **13** was converted to diol **15** by selective removal of the *O*-acetyl group in the presence of *O*-benzoyl group by a short-time treatment with a large excess of hydrazine hydrate in 92% yield. Glycosylation of diol **15**

Scheme 3



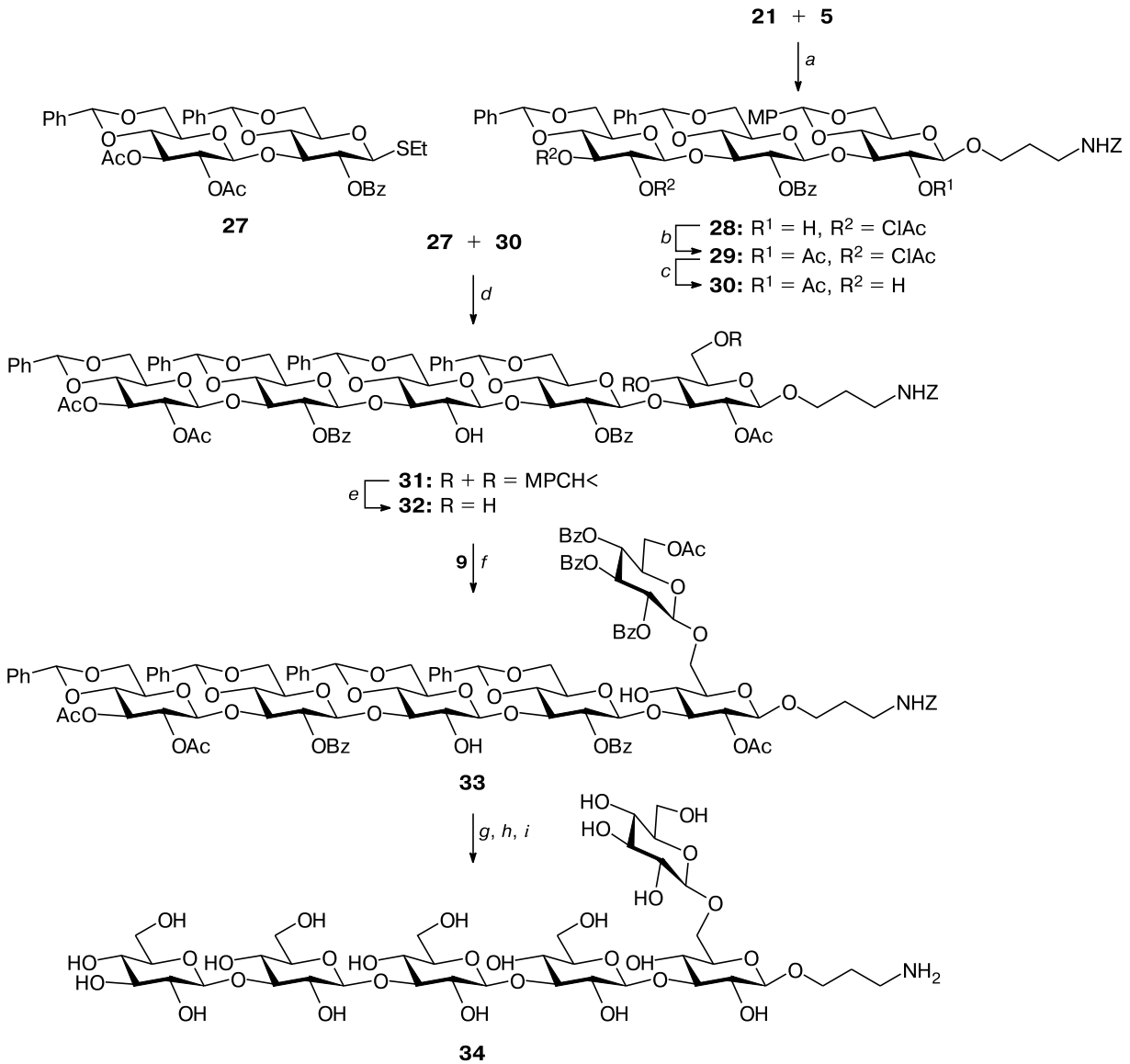
Reagents and reaction conditions: (*a*) TMSOTf, CH_2Cl_2, −30 °C, 52% yield for **13**, 86% for **18**, 65% for **25**; (*b*) $Cl_3CCN—Cs_2CO_3$, CH_2Cl_2, 20 °C, 89% yield; (*c*) BzCl, pyridine, DMAP, 20 °C, 89% yield for **14**, 100% for **19**; (*d*) $H_2NNH_2 \cdot H_2O$, $CH_2Cl_2—MeOH$, 20 °C, 92% yield for **15**, 78% for **20**; (*e*) NIS, TfOH, molecular sieves AW-300, CH_2Cl_2, −30 °C → −10 °C, 80% yield; (*f*) $CH_3C(O)Cl$, 2,4,6-collidine, CH_2Cl_2, 20 °C; (*g*) TsOH · Py, 95% aqueous MeCN, 20 °C, 43% yield on two steps; (*h*) 1 *M* HCl, $CHCl_3—MeOH$, 40—45 °C; (*i*) MeONa, MeOH, then NaOH, aqueous MeOH, 40—45 °C; (*j*) H_2, $Pd(OH)_2/C$, aqueous MeOH, 20 °C, 87% yield calculated on three steps.

with trichloroacetimidate **17** (obtained from known[11] hemiacetal **16**) with subsequent benzoylation of the OH group in the product **18** led to the preparation of trisaccharide **19**. Selective *O*-deacetylation of **19** under conditions similar to those in deacetylation of **14** led to the formation of diol **20** in 78% yield. The acceptor **20** obtained was involved in the reaction of (1→3)-glycosylation with disaccharide donor **21** (see Ref. 2) with subsequent acetylation of the free hydroxy group in the product **22**. The presence in tri- and pentasaccharide **19** and **22** of β-(1→3)-glycoside bonds was inferred from the ^{1}H NMR spectra, as this was described above for acetate **7**.

In the derivative obtained after acetylation of pentasaccharide **22**, the *p*-methoxybenzylidene group was selectively removed upon treatment with TsOH · Py with the formation of 4,6-diol **23**. Selective glycosylation of primary hydroxy group in compound **23** with trichloroacetimidate **24** (see Ref. 12) led to the protected branched hexasaccharide **25**. Removal of acetal, acyl, and benzyloxycarbonyl protecting groups using a sequence of the reactions similar to those described for trisaccharide **10** gave the target hexasaccharide **26**.

The synthesis of isomeric branched hexasaccharide **34** (Scheme 4) was carried out according to a similar scheme,

Scheme 4



Reagents and reaction conditions: (*a*) NIS, AgOTf, molecular sieves AW-300, CH_2Cl_2. 20 °C, 74% yield in the mixture with 2-*O*-isomer; (*b*) Ac_2O—Py, 20 °C; (*c*) thiourea, 2,4,6-collidine, EtOH—EtOAC (1 : 1), 80 °C, 61% yield on two steps; (*d*) NIS, TfOH, molecular sieves AW-300, CH_2Cl_2. −30 °C → −10 °C, 78% yield; (*e*) $Ce(NO_3)_3 \cdot 6H_2O$, MeCN, 20 °C, 60% yield; (*f*) TMSOTf, CH_2Cl_2, −30 °C, 70% yield; (*g*) 1 *M* HCl, $CHCl_3$—MeOH, 40—45 °C; (*h*) MeONa, MeOH, then NaOH, aqueous MeOH, 40—45 °C; (*i*) H_2, $Pd(OH)_2$/C, aqueous MeOH, 20 °C, 79% yield calculated on three steps.

starting from diol **5** already used earlier (Scheme 2). Its glycosylation with disaccharide donor **21** and acetylation of the free OH group at atom C(2) in the glycosylation product **28** led to trisaccharide **29**. Selective removal of the chloroacetyl protecting groups upon treatment with thiourea gave 2,3-diol **30**. Then, diol **30** was involved in the glycosylation reaction with disaccharide thioglycoside **27** (see Ref. 2). In the pentasaccharide **31** obtained, the *p*-methoxybenzylidene group was selectively removed upon treatment with cerium nitrate hexahydrate in acetonitrile, which resulted in the obtaining of triol **32**. Selective glycosylation of the latter at the primary hydroxy group with trichloroacetimidate **9** led to the preparation of protected branched hexasaccharide **33**. Removal of acetal, acyl, and benzyloxycarbonyl protecting groups, using a standard sequence of reactions led to the target hexasaccharide **34**.

The successful syntheses of 6-branched β-(1→3)-glucooligosaccharides described in the present work demonstrate that the glucosyl donors bearing selectively removable 4,6-*O*-*p*-methoxybenzylidene protecting group can be efficiently used for the introduction in the oligosaccharide chain of glucose residues, which will subsequently bear branching at position 6.

Experimental

All the reactions were carried out in the solvents purified according to the standard procedures. Thin-layer chromatography was performed on Kieselgel 60 F^{254} plates with silica gel (Merck), compounds were visualized under UV light or by spraying with a solution of orcinol (180 mg of orcinol in a mixture of water (85 mL), 85% aqueous orthophosphoric acid (10 mL), and 95% aqueous ethanol (5 mL)) with subsequent heating at ~150 °C. Column chromatography was carried out on Silica gel 60 (40—63 μm, Merck), gel-chromatography of free oligosaccharides was performed on column with a TSK HW-40(S) gel (1.5×90 cm) in 0.1 *M* acetic acid; the eluate was analyzed using a Knauer K-2401 differential refractometer. Optical rotation was measured on a JASCO P-2000 digital polarimeter (Japan) at room temperature in chloroform in the case of protected derivatives and in water in the case of free oligosaccharides.

NMR spectra were recorded at 25 °C on a Bruker Avance 600 spectrometer in deuterochloroform ($CDCl_3$, δ_H 7.27, δ_C 77.0) or deuteroacetone (acetone-d_6, δ_H 2.05, δ_C 29.9) in the case of protected derivatives. Spectra of unprotected oligosaccharides were recorded in heavy water (D_2O), using acetone (δ_H 2.225, δ_C 31.45) as an internal standard. Signals were assigned using procedures of 2D correlation spectroscopy COSY and HSQC. In the description of NMR spectra, the monosaccharide moieties starting from the reducing end of the oligosaccharide are designated in Latin letters (A, B, C, *etc.*). The glucose residue attached at position 6 of the main chain glucose residue is designated in Latin letter F.

Electrospray ionization (ESI) high resolution mass spectra were recorded on a Bruker micrOTOF II instrument.

Glycosylation reaction was carried out in anhydrous solvent. Powdered molecular sieves before use in the reaction were activated for 2 h at 180 °C *in vacuo*, using an oil pump. .

3-(Benzyloxycarbonylamino)propyl 4,6-*O*-(4-methoxybenzylidene)-β-D-glucopyranoside (5). A mixture of tetraol **4** (670 mg, 1.8 mmol), *p*-methoxybenzaldehyde dimethyl acetal (0.5 mL, 2.7 mmol, 1.5 equiv.), and CSA (50 mg) in acetonitrile (7 mL) was heated at 50 °C with stirring for 1 h. The mixture was neutralized by the addition of triethylamine (0.05 mL) and concentrated dry *in vacuo*, the residue was purified on silica gel in the gradient acetone—dichloromethane, (5→30%) to obtain diol **5** (650 mg, 74%), an amorphous powder; R_f 0.5 ($CHCl_3$: MeOH, 9 : 1); $[\alpha]_D^{22}$ −28 (*c* 1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$), δ: 1.60—1.80 (m, 2 H, $NHCH_2C\underline{H}_2CH_2O$); 3.25 and 3.52 (both m, 1 H each, $NHC\underline{H}_2CH_2CH_2O$); 3.42 (dt, 1 H, $H_A(5)$, $J_{5,6a}$ = 4.9 Hz, $J_{5,6b} = J_{5,4}$ = 10.3 Hz); 3.47—3.53 (m, 2 H, $H_A(2)$ and $H_A(3)$); 3.62 and 3.96 (both m, 1 H each, $NHCH_2CH_2C\underline{H}_2O$); 3.74 (t, 1 H, $H_A(6b)$, $J_{6a,6b}$ = = 10.3 Hz); 3.80 (m, 4 H, OMe and $H_A(4)$); 4.30 (dd, 1 H, $H_A(6a)$); 4.35 (d, 1 H, $H_A(1)$, $J_{1,2}$ = 7.7 Hz); 5.20 (s, 2 H, $PhC\underline{H}_2O$); 5.25 (m, 1 H, NH); 5.48 (s, 1 H, PhC<u>H</u>); 7.30—8.10 (m, 9 H, Ph). ^{13}C NMR (150 MHz, $CDCl_3$), δ: 29.7 ($NHCH_2\underline{C}H_2CH_2O$); 37.7 ($NH\underline{C}H_2CH_2CH_2O$); 55.3 (OMe); 66.4 ($C_A(5)$); 66.8 ($Ph\underline{C}H_2O$); 67.3 ($NHCH_2CH_2\underline{C}H_2O$); 68.6 ($C_A(6)$); 73.4 ($C_A(4)$); 74.6 ($C_A(2)$); 80.4 ($C_A(3)$); 101.8 (Ph<u>C</u>H); 103.3 ($C_A(1)$); 127.6—136.5 (Ph); 160.2 (O<u>C</u>ONH). Found, *m/z*: 512.1882 $[M + Na]^+$. $C_{25}H_{31}NNaO_9$. Calculated: 512.1891.

3-(Benzyloxycarbonylamino)propyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-4,6-*O*-(4-methoxybenzylidene)-β-D-glucopyranoside (6). A mixture of donor **2** (190 mg, 0.365 mmol, 1.1 equiv.), diol **5** (163 mg, 0.322 mmol), molecular sieves AW-300 (2.5 g) in dichloromethane (2.5 mL) was stirred at 20 °C for 30 min, then *N*-iodosuccinimide (115 mg, 0.51 mmol, 1.4 equiv.) and silver triflate (12 mg, 0.045 mmol, 12 mol.%) were added. The reaction mixture was stirred at 20 °C for 30 min, then a saturated solution of sodium hydrogen carbonate (2 mL) and 1 *M* aqueous solution of sodium thiosulfate (2 mL) were added. The mixture was filtered through a layer of celite (eluting with dichloromethane), the layers formed were separated, the organic layer was dried by filtration through a purified cotton and concentrated *in vacuo*. The residue was separated on silica gel in the gradient ethyl acetate—toluene, (10→30%) to obtain disaccharide **6** (158 mg, 50%), an amorphous powder; R_f 0.34 (toluene : AcOEt, 2 : 1); $[\alpha]_D^{22}$ −45 (*c* 1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$), δ; characteristic signals: 1.65—1.85 (m, 2 H, $NHCH_2C\underline{H}_2CH_2O$); 3.20 and 3.49 (both m, 1 H each, $NHC\underline{H}_2CH_2CH_2O$); 3.28 (br.s, 1 H, OH); 3.47 (t, 1 H, $H_A(2)$, $J_{2,1} = J_{2,3}$ = 8.3 Hz); 3.76 (s, 3 H, OMe); 4.07 (t, 1 H, $H_B(4)$, $J_{3,4} = J_{4,5}$ = 9.4 Hz); 4.29 (d, 1 H, $H_A(1)$, $J_{1,2}$ = 7.9 Hz); 5.10 (s, 2 H, $PhC\underline{H}_2O$); 5.12 (m, 1 H, NH); 5.27 (d, 1 H, $H_B(1)$, $J_{1,2}$ = 6.6 Hz); 5.32 (s, 1 H, PhC<u>H</u>); 5.48 (t, 1 H, $H_B(2)$, $J_{2,1} = J_{2,3}$ = 7.3 Hz); 5.51(s, 1 H, PhC<u>H</u>); 5.72 (t, 1 H, $H_B(3)$, $J_{2,3} = J_{3,4}$ = 8.7 Hz); 6.85—8.05 (m, 24 H, Ph). ^{13}C NMR (150 MHz, $CDCl_3$), δ; characteristic signals: 29.5 ($NHCH_2\underline{C}H_2CH_2O$); 37.7 ($NH\underline{C}H_2CH_2CH_2O$); 55.2 (OMe); 66.7 ($Ph\underline{C}H_2O$); 72.3 ($C_B(3)$); 73.4 ($C_B(2)$); 78.3 ($C_B(4)$); 101.1 ($C_B(1)$); 101.2 and 101.5 (Ph<u>C</u>H); 103.2 ($C_A(1)$); 125.2—136.9 (Ph); 160.2 (O<u>C</u>ONH); 165.5 and 165.7 (2 Ph<u>C</u>O). Found, *m/z*: 970.3252 $[M + Na]^+$. $C_{52}H_{53}NNaO_{16}$. Calculated: 970.3257.

3-(Benzyloxycarbonylamino)propyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2-*O*-acetyl-β-D-glucopyranoside (8). A solution of disaccharide **6** (217 mg, 0.229 mmol), acetic anhydride (0.5 mL), and DMAP (5 mg) in pyridine (2 mL) was stirred at 20 °C for 1 h. Excessive Ac_2O was decomposed by the addition of methanol (1 mL). The mixture was diluted with dichloromethane, washed with 1 *M* aqueous solution of HCl, water, and saturated solution of sodium hydrogen carbonate, the organic layer was dried by filtration through

a purified cotton and concentrated *in vacuo*. The residue (disaccharide **7**, 211 mg, 93%) was dissolved in acetonitrile (2 mL) and treated with cerium nitrate hexahydrate (1 g, 2.3 mmol, 11 equiv.) at 20 °C for 1 h. The mixture was diluted with dichloromethane, washed with water, dried by filtration through a purified cotton and concentrated *in vacuo*. The residue was separated on silica gel in the gradient acetone—toluene, (10→25%) to obtain diol **8** (135 mg, 73%); an amorphous powder; R_f 0.41 (toluene : acetone, 2 : 1); $[\alpha]_D^{22}$ −27 (*c* 1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$), δ: 1.48 (s, 3 H, Ac); 1.60—1.75 (m, 2 H, $NHCH_2C\underline{H}_2CH_2O$); 2.82 (m, 1 H, OH); 3.15 and 3.23 (both m, 1 H each, $NHC\underline{H}_2CH_2CH_2O$); 3.39 (m, 1 H, $H_A(4)$); 3.52 and 3.80 (both m, 1 H each, $NHCH_2CH_2C\underline{H}_2O$); 3.62 (m, 1 H, $H_A(5)$); 3.70 (t, 1 H, $H_A(3)$, $J_{2,3} = J_{3,4} = 9.1$ Hz); 3.78—3.82 (m, 2 H, $H_B(5)$ and $H_A(6a)$); 3.87 (t, 1 H, $H_B(6a)$, $J_{5,6} = J_{6,6} = 10.1$ Hz); 3.92 (m, 1 H, $H_A(6b)$); 3.97 (t, 1 H, $H_B(4)$, $J_{3,4} = J_{4,5} = 9.4$ Hz); 4.36 (d, 1 H, $H_A(1)$, $J_{1,2} = 8.0$ Hz); 4.45 (dd, 1 H, $H_B(6b)$, $J_{5,6} = 4.6$ Hz); 4.86 (t, 1 H, $H_A(2)$); 4.90 (d, 1 H, $H_B(1)$, $J_{1,2} = 7.8$ Hz); 5.08 (s, 2 H, $PhC\underline{H}_2O$); 5.17 (m, 1 H, NH); 5.50 (t, 1 H, $H_B(2)$, $J_{2,1} = J_{2,3} = 8.9$ Hz); 5.52 (s, 1 H, $PhC\underline{H}$); 5.83 (t, 1 H, $H_B(3)$); 6.87—8.10 (m, 20 H, Ph). ^{13}C NMR (150 MHz, $CDCl_3$), δ: 20.7 ($\underline{C}H_3CO$); 29.7 ($NHCH_2\underline{C}H_2CH_2O$); 37.9 ($NH\underline{C}H_2CH_2CH_2O$); 62.2 ($C_A(6)$); 66.7 (3 C, $Ph\underline{C}H_2O$, $NHCH_2CH_2\underline{C}H_2O$, and $C_B(5)$); 68.2 ($C_B(6)$); 71.5 ($C_B(3)$); 71.8 ($C_A(2)$); 72.2 ($C_B(2)$); 75.7 ($C_A(4)$); 78.2 ($C_B(4)$); 85.1 ($C_A(3)$); 100.6 ($C_A(1)$); 101.6 ($Ph\underline{C}H$); 102.1 ($C_B(1)$); 126.5—136.9 (Ph); 160.5 ($O\underline{C}ONH$); 165.4 and 165.8 (2 $Ph\underline{C}O$); 170.1 ($CH_3\underline{C}O$). Found, *m/z*: 894.2942 $[M + Na]^+$. $C_{46}H_{49}NO_{16}$. Calculated: 894.2944.

3-(Benzyloxycarbonylamino)propyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2-*O*-acetyl-β-D-glucopyranoside (10). Trimethylsilyl triflate (0.7 μL, 3 mol.%) was added to a mixture of donor **9** (90 mg, 0.133 mmol, 1.92 equiv.), diol **8** (60 mg, 0.069 mmol) in dichloromethane (2 mL) at 20 °C. The reaction mixture was stirred at 20 °C for 5 min, neutralized by the addition of triethylamine (0.05 mL), and concentrated *in vacuo*. The resulting mixture was separated on silica gel in the gradient ethyl acetate—toluene (15→30%) to obtain trisaccharide **10** (78 mg, 82%); an amorphous powder; R_f 0.31 (toluene : EA, 2 : 1); $[\alpha]_D^{22}$ −39 (*c* 1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$), δ: 1.40—1.50 (m, 2 H, $NHCH_2C\underline{H}_2CH_2O$); 1.42 and 2.05 (both s, 3 H each, 2 Ac); 2.95—3.15 (m, 3 H, $NHC\underline{H}_2CH_2$-CH_2O and $NHCH_2CH_2C\underline{H}HO$); 3.21 (m, 1 H, $H_B(5)$); 3.40—3.60 (m, 4 H, $NHCH_2CH_2C\underline{H}HO$, $H_A(3)$, $H_A(4)$ and $H_A(5)$); 3.73—3.77 (m, 2 H, $H_F(5)$ and $H_A(6a)$); 3.87 (t, 1 H, $H_B(6a)$, $J_{5,6} = J_{6,6} = 10.1$ Hz); 3.96 (t, 1 H, $H_B(4)$, $J_{4,5} = J_{3,4} =$ $= 9.5$ Hz); 4.17 (d, 1 H, $H_A(1)$, $J_{1,2} = 7.9$ Hz); 4.25—4.37 (m, 3 H, $H_A(6b)$, $H_F(6a)$ and $H_F(6b)$); 4.45 (dd, 1 H, $H_B(6b)$, $J_{5,6} = 4.7$ Hz, $J_{6,6} = 10.2$ Hz); 4.70 (dd, 1 H, $H_A(2)$, $J_{2,3} = 9.3$ Hz); 4.83 (d, 1 H, $H_F(1)$, $J_{1,2} = 7.8$ Hz); 4.90 (d, 1 H, $H_B(1)$, $J_{1,2} =$ $= 7.8$ Hz); 5.05—5.18 (m, 3 H, $PhC\underline{H}_2O$ and NH); 5.45—5.62 (m, 4 H, $H_B(2)$, $H_F(2)$, $H_F(4)$ and $PhC\underline{H}$); 5.80—5.87 (m, 2 H, $H_B(3)$ and $H_F(3)$); 7.26—7.97 (m, 35 H, Ph). ^{13}C NMR (150 MHz, $CDCl_3$), δ: 20.0 and 20.7 (2 $\underline{C}H_3CO$); 29.2 ($NHCH_2\underline{C}H_2CH_2O$); 37.9 ($NH\underline{C}H_2CH_2CH_2O$); 62.4 ($C_F(6)$); 66.2 ($NHCH_2CH_2\underline{C}H_2O$); 66.3 ($Ph\underline{C}H_2O$); 66.8 ($C_A(5)$); 68.1 ($C_B(6)$); 68.7 ($C_A(6)$); 68.8 ($C_B(5)$); 69.3 ($C_F(4)$); 71.3 ($C_A(2)$); 71.7 ($C_B(2)$ and $C_F(3)$); 72.0 ($C_F(5)$); 72.2 ($C_F(2)$); 72.8 ($C_B(3)$); 74.9 ($C_A(4)$); 78.2 ($C_B(4)$); 85.0 ($C_A(3)$); 100.4 ($C_A(1)$); 101.2 ($C_B(1)$); 101.6 ($Ph\underline{C}H$); 102.1 ($C_F(1)$); 126.1—136.9 (Ph); 156.3 ($O\underline{C}ONH$); 164.9, 165.0, 165.1, 165.6 and 165.7 (5 $Ph\underline{C}O$); 168.6 and 170.6 (2 $CH_3\underline{C}O$). Found, *m/z*: 1410.4359 $[M + Na]^+$. $C_{75}H_{73}NNaO_{25}$. Calculated: M + Na = 1410.4364.

3-(Benzyloxycarbonylamino)propyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-β-D-glucopyranoside (13). Trimethylsilyl triflate (0.02 mL, 0.1 mmol, 10 mol.%) was added to a stirred solution of trichloroacetimidate **12** (546 mg, 1.1 mmol, 1.1 equiv.) and diol **3** (460 mg, 1 mmol) in dichloromethane (15 mL) at −30 °C. The reaction mixture was stirred at −30 °C for 10 min, neutralized by the addition of triethylamine (0.05 mL) and concentrated *in vacuo*. The resulting mixture was separated on silica gel in the gradient ethyl acetate—dichloromethane (0→10%) to obtain disaccharide **13** (413 mg, 52%), an amorphous powder; R_f 0.22 (toluene : EA, 2 : 1); $[\alpha]_D^{22}$ −50 (*c* 1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$), δ; characteristic signals: 1.86 (m, 2 H, $NHCH_2C\underline{H}_2CH_2O$); 2.08, 2.10 (both s, 3 H each, 2 $\underline{C}H_3CO$); 3.30 (m, 1 H, $NHCH\underline{H}CH_2CH_2O$); 4.36—4.40 (m, 2 H, $H_A(1)$, $H_A(6b)$); 4.95 (d, 1 H, $H_B(1)$, $J_{1,2} = 6.7$ Hz); 5.06—5.20 (m, 4 H, $H_B(2)$, $PhC\underline{H}_2$, NH); 5.33 (t, 1 H, $H_B(3)$, $J = 8.8$ Hz); 5.41 and 5.57 (both s, 1 H each, 2 $PhC\underline{H}$); 7.30—7.60 (m, 15 H, 3 Ph). ^{13}C NMR (150 MHz, $CDCl_3$), δ: 20.8 (2 C, 2 $\underline{C}H_3CO$); 29.7 ($NHCH_2\underline{C}H_2CH_2O$); 37.7 ($NH\underline{C}H_2CH_2CH_2O$); 66.3, 66.5 ($C_A(5)$, $C_B(5)$); 66.8 ($Ph\underline{C}H_2$); 67.5 ($NHCH_2CH_2\underline{C}H_2O$); 68.6 (2C, $C_A(6)$, $C_B(6)$); 71.9 ($C_B(3)$); 72.9 ($C_B(2)$); 73.9 ($C_A(2)$); 78.2 ($C_B(4)$); 79.3 ($C_A(4)$); 82.2 ($C_A(3)$); 101.3, 101.4 (2 $Ph\underline{C}H$); 102.1 ($C_B(1)$); 103.4 ($C_A(1)$); 126.0—137.2 (3 Ph); 156.8 (OCONH); 170.0, 170.1 (2 $CH_3\underline{C}O$). Found, *m/z*: 816.2839 $[M + Na]^+$. $C_{41}H_{47}NNaO_{15}$. Calculated: 816.2838.

3-(Benzyloxycarbonylamino)propyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (14). Benzoyl chloride (0.2 mL, 1.72 mmol, 3.4 equiv.) and dimethylaminopyridine (10 mg) were added to a solution of disaccharide **13** (400 mg, 0.505 mmol) in pyridine (2 mL) and the mixture was stirred at 20 °C for 20 h. Excessive BzCl was decomposed by the addition of water (0.2 mL), the mixture was diluted with dichloromethane and sequentially washed with 1 *M* aqueous solution of HCl, water, and a saturated solution of sodium hydrogen carbonate. Organic layer was dried by filtration through a purified cotton and concentrated *in vacuo*. The residue was purified on silica gel in the gradient ethyl acetate—dichloromethane (0→8%) to obtain disaccharide **14** (408 mg, 89%), an amorphous powder; R_f 0.47 (toluene : AcOEt, 2 : 1); $[\alpha]_D^{22}$ −35 (*c* 1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$), δ: 1.70 (m, 2 H, $NHCH_2C\underline{H}_2CH_2O$); 1.93 (s, 6 H, 2 CH_3CO); 3.10 and 3.15 (both m, 1 H each, $NHC\underline{H}_2$-CH_2CH_2O); 3.38 (m, $H_B(5)$); 3.47—3.52 (m, 2 H, $H_A(5)$, $NHCH_2CH_2C\underline{H}HO$); 3.64 (t, 1 H, $H_B(6a)$, $J = 9.7$ Hz); 3.66 (t, 1 H, $H_B(4)$, $J = 10.3$ Hz); 3.74 (t, 1 H, $H_A(4)$, $J = 9.3$ Hz); 3.80 (t, 1 H, $H_A(6a)$, $J = 10.3$ Hz); 3.88 (m, 1 H, $NHCH_2CH_2CH\underline{H}O$); 4.13 (t, 1 H, $H_A(3)$, $J = 9.0$ Hz); 4.21 (dd, 1 H, $H_B(6b)$, $J_{6b,5} = 4.9$ Hz, $J_{6a,6b} = 10.4$ Hz); 4.35 (dd, 1 H, $H_A(6b)$, $J_{6b,5} = 4.8$ Hz, $J_{6a,6b} = 10.5$ Hz); 4.58 (d, 1 H, $H_A(1)$, $J_{1,2} = 7.7$ Hz); 4.72 (d, 1 H, $H_B(1)$, $J_{1,2} = 7.6$ Hz); 4.94 (m, 1 H, NH); 4.95 (t, 1H, $H_B(2)$, $J = 8.3$ Hz); 5.04 (s, 2 H, $PhC\underline{H}_2$); 5.07 (t, 1 H, $H_B(3)$, $J = 9.1$ Hz); 5.27 (t, 1 H, $H_A(2)$, $J = 8.3$ Hz); 5.36 and 5.55 (both s, 1 H each, 2 $PhC\underline{H}$); 7.30—8.05 (m, 20 H, 4 Ph). ^{13}C NMR (150 MHz, $CDCl_3$), δ: 20.1, 20.7 (2 $\underline{C}H_3CO$); 29.4 ($NHCH_2\underline{C}H_2CH_2O$); 66.1 ($C_B(5)$); 66.4 ($C_A(5)$); 67.6 ($NHCH_2CH_2\underline{C}H_2O$); 68.5 (2C, $C_A(6)$, $C_B(6)$); 71.9 ($C_B(3)$); 72.0 ($C_B(2)$); 73.6 ($C_A(2)$); 78.1 ($C_B(4)$); 78.6 ($C_A(3)$); 78.7 ($C_A(4)$); 101.0 ($C_B(1)$); 101.1, 101.3 (2 $Ph\underline{C}H$); 101.5 ($C_A(1)$); 126.0—137.1 (4 Ph); 156.4 (OCONH); 165.0 ($Ph\underline{C}O$); 169.5,

170.0 (2 $CH_3\underline{C}O$). Found, *m/z*: 920.3134 $[M + Na]^+$. $C_{48}H_{51}NaO_{16}$. Calculated: 920.3100.

3-(Benzyloxycarbonylamino)propyl 4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (15). Hydrazine hydrate (1 mL, 20.6 mmol, 100 equiv.) was added to a solution of diacetate **14** (390 mg, 0.21 mmol) in dichloromethane (3 mL) and methanol (6 mL). The mixture of was allowed to stand at 20 °C for 20 min, diluted with dichloromethane, and sequentially washed with 1 *M* aqueous solution of HCl, water, and a saturated solution of sodium hydrogen carbonate. Organic layer was dried by filtration through a purified cotton and concentrated *in vacuo*. The residue was purified on silica gel in the gradient acetone—dichloromethane (0→15%) to obtain the starting diacetate **14** (156 mg, 40%) and diol **15** (210 mg, 57%). Recovered diacetate **14** was treated with hydrazine hydrate under conditions described above, that additionally gave 115 mg of diol **15**. A total yield of diol **15** was 325 mg (92%), an amorphous powder; R_f 0.38 (toluene : acetone, 2 : 1); $[\alpha]_D^{22}$ −43 (*c* 1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$), δ: 1.75 (m, 2 H, $NHCH_2C\underline{H}_2CH_2O$); 2.56 and 2.93 (both br.s, 2 H each, 2 OH); 3.16 and 3.22 (both m, 1 H each, $NHC\underline{H}_2CH_2CH_2O$); 3.33 (m, 1 H, $H_B(5)$); 3.47—3.51 (m, 3 H, $H_B(2)$, $H_B(4)$, $H_B(6a)$); 3.57—3.61 (m, 2 H, $H_A(5)$, $NHCH_2$-$CH_2C\underline{H}HO$); 3.65 (t, 1 H, $H_B(3)$, J = 9.2 Hz); 3.83 (t, 1 H, $H_A(4)$, J = 9.3 Hz); 3.85 (t, 1 H, $H_A(6a)$, J = 10.3 Hz); 3.90—3.94 (m, 2 H, $H_B(6b)$, $NHCH_2CH_2C\underline{H}HO$); 4.20 (t, 1 H, $H_A(3)$, J = 9.0 Hz); 4.42 (dd, 1 H, $H_A(6b)$, $J_{6b,5}$ = 4.6 Hz, $J_{6a,6b}$ = = 10.5 Hz); 5.51 (d, 1 H, $H_B(1)$, $J_{1,2}$ = 7.5 Hz); 4.73 (d, 1 H, $H_A(1)$, $J_{1,2}$ = 7.6 Hz); 4.92 (br.s, 1 H, NH); 5.08 (s, 2 H, $PhC\underline{H}_2$); 5.33 (t, 1 H, $H_A(2)$, J = 8.1 Hz); 5.45, 5.62 (both s, 1 H each, 2 $PhC\underline{H}$); 7.30—8.10 (m, 20 H, 4 Ph). ^{13}C NMR (150 MHz, $CDCl_3$), δ: 29.6 ($NHCH_2\underline{C}H_2CH_2O$); 38.1 ($NH\underline{C}H_2CH_2CH_2O$); 66.4 ($C_B(5)$); 66.5 ($C_A(5)$); 66.6 ($Ph\underline{C}H_2$); 67.8 ($NHCH_2CH_2\underline{C}H_2O$); 68.4 ($C_B(6)$); 68.6 ($C_A(6)$); 72.8 ($C_B(3)$); 73.4 ($C_A(2)$); 73.5 ($C_B(2)$); 78.2 ($C_A(3)$); 79.0 ($C_A(4)$); 80.3 ($C_B(4)$); 101.5 ($C_A(1)$); 101.6, 101.8 (2 $Ph\underline{C}H$); 102.9 ($C_B(1)$); 126.1—136.9 (4 Ph); 156.4 (OCONH); 165.7 ($Ph\underline{C}O$). Found, *m/z*: 814.3029 $[M + Na]^+$. $C_{44}H_{47}NNaO_{14}$. Calculated: 814.3069.

2,3-Di-*O*-acetyl 4,6-*O*-(4-methoxybenzylidene)-β-D-glucopyranosyltrichloroacetimidate (17). Trichloroacetonitrile (1 mL) and cesium carbonate (50 mg) was added to a solution of hemiacetal **16** (768 mg, 2 mmol) in dichloromethane (10 mL). The mixture of was stirred at 20 °C for 1 h, diluted with toluene, and filtered through a layer of silica gel, eluting product **17** with a mixture of ethyl acetate—toluene (1 : 10). The yield of trichloroacetimidate **17** was 936 mg (89%), an amorphous powder; R_f 0.47 (toluene : AcOEt, 2 : 1). The product was used immediately. ^{1}H NMR (600 MHz, $CDCl_3$), δ: 2.05 and 2.10 (both s, OAc); 3.77 (t, 1 H, $H_A(4)$, J = 9.8 Hz); 3.79 (t, 1 H, $H_A(6a)$, J = 10.6 Hz); 3.83 (s, 3 H, OMe); 4.14 (dt, 1 H, $H_A(5)$, $J_{5,6a}$ = = 10.4 Hz, $J_{5,6b}$ = 4.9 Hz); 4.37 (dd, 1 H, $H_A(6b)$); 5.18 (dd, 1 H, $H_A(2)$, $J_{2,1}$ = 3.8 Hz, $J_{2,3}$ = 9.9 Hz); 5.52 (s, 1 H, $PhC\underline{H}$); 5.70 (t, 1 H, $H_A(3)$); 6.57 (d, 1 H, $H_A(1)$); 6.91 and 7.40 (both d, 4 H, $MeOC_6\underline{H}_4$); 8.70 (s, 1 H, NH). ^{13}C NMR (150 MHz, $CDCl_3$), δ: 20.4 and 20.8 (2 $\underline{C}H_3CO$); 55.3 (OMe); 65.1 ($C_A(6)$); 68.4, 68.8 and 70.4 ($C_A(2)$, $C_A(3)$, $C_A(5)$); 78.6 ($C_A(4)$); 93.6 ($C_A(1)$); 101.6 ($Ph\underline{C}H$); 113.6, 127.4, 129.1 and 160.2 (Ph); 161.2 (C=NH); 169.6 and 170.0 (2 $CH_3\underline{C}O$).

3-(Benzyloxycarbonylamino)propyl 2,3-di-*O*-acetyl-4,6-*O*-(4-methoxybenzylidene)-β-D-glucopyranosyl-(1→3)-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (18). Trimethylsilyl triflate (15 μL, 0.075 mmol) was added to a solution of diol **15** (249 mg, 0.307 mmol) and imidate **17** (218 mg, 0.414 mmol, 1.35 equiv.) in dichloromethane at −50 °C. The mixture of was stirred at this temperature for 20 min, neutralized by the addition of triethylamine (0.05 mL), and concentrated *in vacuo*. The residue was purified on silica gel in the gradient acetone—dichloromethane (0→7%) to obtain trisaccharide **18** (310 mg, 86%): an amorphous powder; R_f 0.28 (toluene : AcOEt, 2 : 1); $[\alpha]_D^{22}$ −51 (*c* 1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$), δ; characteristic signals: 1.66—1.74 (m, 5 H, CH_3CO, $NHCH_2C\underline{H}_2CH_2O$); 2.63 (br.s, 1 H, OH); 3.15 (m, 2 H, $NHC\underline{H}_2CH_2CH_2O$); 3.79 (s, 3 H, CH_3O); 4.18 (t, 1 H, $H_A(3)$, J = 8.8 Hz); 4.48 (d, 1 H, $H_B(1)$, $J_{1,2}$ = 7.5 Hz); 4.68 (d, 1 H, $H_A(1)$, $J_{1,2}$ = 7.6 Hz); 4.75 (d, 1 H, $H_C(1)$, $J_{1,2}$ = 7.4 Hz); 4.93 (m, 2 H, $H_C(2)$, NH); 5.08 (s, 2 H, $PhC\underline{H}_2$); 5.19 (t, 1 H, $H_C(3)$, J = 9.1 Hz); 5.30, 5.45, and 5.60 (all s, 1 H each, 2 $PhC\underline{H}$ and $MeOC_6H_4C\underline{H}$); 5.32 (t, 1 H, $H_A(2)$, J = 8.1 Hz); 6.70—8.10 (m, 24 H, 4 Ph, $MeOC_6\underline{H}_4$). ^{13}C NMR (150 MHz, $CDCl_3$), δ; characteristic signals: 20.4 and 20.8 (2 $\underline{C}H_3CO$); 29.7 ($NHCH_2\underline{C}H_2CH_2O$); 38.1 ($NH$-$\underline{C}H_2CH_2CH_2O$); 55.3 ($CH_3O$); 67.7 ($NHCH_2CH_2\underline{C}H_2O$); 71.9 ($C_C(3)$); 72.8 ($C_C(2)$); 73.5 ($C_A(2)$); 81.2 ($C_B(3)$); 101.3 (3 C, 2 $Ph\underline{C}H$ and $MeOC_6H_4\underline{C}H$); 101.5 ($C_A(1)$); 101.7 ($C_C(1)$); 103.5 ($C_B(1)$); 126.0—137.1 (4 Ph, $MeO\underline{C}_6H_4CH$); 156.4 (OCONH); 165.7 ($Ph\underline{C}O$); 169.8 and 170.0 (2 $CH_3\underline{C}O$). Found, *m/z*: 1178.4197 $[M + Na]^+$. $C_{62}H_{67}NNaO_{22}$. Calculated: 1178.4227.

3-(Benzyloxycarbonylamino)propyl 2,3-di-*O*-acetyl-4,6-*O*-(4-methoxybenzylidene)-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). Trisaccharide **18** (336 mg, 0.286 mmol) was benzoylated under conditions described for disaccharide **14** to obtain trisaccharide **19** (365 mg, 100%) as an amorphous powder, R_f 0.47 (toluene : acetone, 2 : 1); $[\alpha]_D^{22}$ −33 (*c* 1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$), δ; characteristic signals: 1.59 (m, 2 H, $NHCH_2C\underline{H}_2CH_2O$); 1.72 and 1.89 (both s, 3 H each, 2 CH_3CO); 3.10 (m, 2 H, $NHC\underline{H}_2CH_2CH_2O$); 3.72 (s, 3 H, CH_3O); 3.95 (dd, $H_A(3)$, $J_{2,3}$ = 7.0 Hz, $J_{3,4}$ = 8.6 Hz); 4.52 (d, 1 H, $H_A(1)$, $J_{1,2}$ = 7.2 Hz); 4.65 (d, 1 H, $H_C(1)$, $J_{1,2}$ = 7.6 Hz); 4.87 (d, 1 H, $H_B(1)$, $J_{1,2}$ = = 7.0 Hz); 4.88 (t, 1 H, $H_C(2)$, J = 7.6 Hz); 5.00 (m, 3 H, $PhC\underline{H}_2$ and $H_B(2)$); 5.07 (br.t, 1 H, NH); 5.11, 5.27, and 5.53 (all s, 1 H each, 2 $PhC\underline{H}$, $MeOC_6H_4C\underline{H}$); 5.15 (m, 2 H, $H_A(2)$ and $H_C(3)$); 6.75—7.80 (m, 29 H, 5 Ph, $MeOC_6\underline{H}_4$). ^{13}C NMR (150 MHz, $CDCl_3$), δ; characteristic signals: 20.2, 20.6 (2 $\underline{C}H_3CO$); 29.4 ($NHCH_2\underline{C}H_2CH_2O$); 37.9 ($NH\underline{C}H_2CH_2$-$CH_2O$); 55.2 ($CH_3O$); 65.9, 66.0, 66.4 ($C_A(5)$, $C_B(5)$ and $C_C(5)$); 66.3 ($Ph\underline{C}H_2$); 67.2 ($NHCH_2CH_2\underline{C}H_2O$); 68.4, 68.5 and 68.7 ($C_A(6)$, $C_B(6)$ and $C_C(6)$); 99.1 ($C_B(1)$); 100.3 ($C_C(1)$); 100.7, 101.2, 101.5 (2 $Ph\underline{C}H$, $MeOC_6H_4\underline{C}H$); 101.1 ($C_A(1)$); 122.9—137.2 (5 Ph, $MeO\underline{C}_6H_4CH$); 156.4 (OCONH); 164.4, 164.6 (2 $Ph\underline{C}O$); 169.5, 169.9 (2 $CH_3\underline{C}O$). Found, *m/z*: 1282.4461 $[M + Na]^+$. $C_{69}H_{71}NNaO_{23}$. Calculated: 1282.4490.

3-(Benzyloxycarbonylamino)propyl 4,6-*O*-(4-methoxybenzylidene)-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 (20). Trisaccharide **19** (350 mg, 0.273 mmol) was treated with hydrazine hydrate (0.7 mL, 12.9 mmol) in dichloromethane (2 mL) and methanol (4 mL) at 20 °C for 15 min as described in the preparation of compound **15**. After repeating deacetylation procedure twice, diol **20** (255 mg, 78%) was obtained as an amorphous powder; R_f 0.38 (toluene : acetone, 2 : 1); $[\alpha]_D^{22}$ −21 (*c* 1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$), δ; characteristic signals: 1.57 (m, 2 H, $NHCH_2C\underline{H}_2CH_2O$); 3.01 (m, 2 H, $NHC\underline{H}_2CH_2CH_2O$); 3.71

(s, 3 H, CH_3O); 3.99 (t, 1 H, $H_B(3)$, J = 8.2 Hz); 4.39 (d, 1 H, $H_C(1)$, $J_{1,2}$ = 7.6 Hz); 4.54 (d, 1 H, $H_A(1)$, $J_{1,2}$ = 7.0 Hz); 4.96 (d, 1 H, $H_B(1)$, $J_{1,2}$ = 6.6 Hz); 5.00 (s, 2 H, PhC$\underline{H}_2$); 5.08 (br.t, 1 H, NH); 5.18 (t, 1 H, $H_A(2)$, J = 7.7 Hz); 5.22 (t, 1 H, $H_B(2)$, J = 7.4 Hz); 5.27, 5.30 and 5.50 (all s, 1 H each, 2 PhC$\underline{H}$, $MeOC_6H_4C\underline{H}$); 6.75—7.80 (m, 29 H, 5 Ph, $MeOC_6\underline{H}_4$). ^{13}C NMR (150 MHz, $CDCl_3$), δ; characteristic signals: 29.4 ($NHCH_2\underline{C}H_2CH_2O$); 37.9 ($NH\underline{C}H_2CH_2CH_2O$); 55.2 ($CH_3O$); 66.0, 66.2, 66.3 and 66.5 ($C_A(5)$, $C_B(5)$, $C_C(5)$, Ph$\underline{C}H_2$); 67.1 ($NHCH_2CH_2\underline{C}H_2O$); 68.3, 68.5 and 68.7 ($C_A(6)$, $C_B(6)$, $C_C(6)$); 100.1 ($C_B(1)$); 100.9 ($C_A(1)$); 101.1, 101.5 and 101.6 (2 Ph$\underline{C}$H, $MeOC_6H_4\underline{C}$H); 102.8 ($C_C(1)$); 122.9—137.0 (5 Ph, $MeO\underline{C}_6H_4$-CH); 156.4 (OCONH); 164.7 and 165.1 (2 Ph$\underline{C}$O). Found, *m/z*: 1198.4266 $[M + Na]_+$. $C_{65}H_{67}NO_{21}$. Calculated: 1198.4278.

3-(Benzyloxycarbonylamino)propyl 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*-(4-methoxybenzylidene)-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). A mixture of thioglycoside **21** (198 mg, 0.241 mmol 1.2 equiv.), diol **20** (240 mg, 0.201 mmol), and molecular sieves AW-300 (0.9 g) in dichloromethane (5 mL) was stirred at 20 °C for 30 min, cooled to −30 °C. After addition of *N*-iodosuccinimide (120 mg, 0.533 mmol, 2.2 equiv.), the mixture was stirred at −30 °C for another 30 min, followed by the addition of a solution of trifluoromethanesulfonic acid in acetonitrile (2 μL, 9 mol.%). The reaction mixture was stirred for 2 h, the temperature was gradually increased from −30 °C to −10 °C, a saturated solution of sodium hydrogen carbonate (2 mL) and 1 *M* aqueous solution of sodium thiosulfate (2 mL) were added. The mixture was filtered through a layer of celite, a solid precipitate was washed with dichloromethane, the organic layer was dried by filtration through a purified cotton and concentrated *in vacuo*. The residue was separated on silica gel in the gradient acetone—toluene (0→9%) to obtain pentasaccharide **22** (315 mg, 80%) as an amorphous powder; R_f 0.59 (toluene : AcOEt, 2 : 1); $[\alpha]_D^{22}$ −19 (*c* 1, $CHCl_3$). ^{1}H NMR (600 MHz, acetone-d_6), δ: characteristic signals: 1.60 (m, 2 H, $NHCH_2C\underline{H}_2CH_2O$); 3.01 (m, 2 H, $NHC\underline{H}_2CH_2CH_2O$); 3.62 (s, 3 H, CH_3O); 4.48 (d, 1 H, H(1), J = 7.5 Hz); 4.77 (d, 1 H, H(1), J = = 7.4 Hz); 4.82, 5.33, 5.50, 5.59 and 5.71 (all s, 1 H each, 4 PhC$\underline{H}$, $MeOC_6H_4C\underline{H}$); 4.97—5.08 (m, 6 H, Ph$C\underline{H}_2$, H(1), 3 H(2)); 5.15—5.21 (m, 3 H, 2 H(1) and H(2)); 5.37 (t, 1 H, $H_E(3)$, J = = 9.5 Hz); 6.03 (br.t, 1 H, NH); 6.82—8.07 (m, 44 H, 8 Ph, $MeOC_6\underline{H}_4$). ^{13}C NMR (150 MHz, acetone-d_6), δ; characteristic signals: 30.8 ($NHCH_2\underline{C}H_2CH_2O$); 38.6 ($NH\underline{C}H_2CH_2CH_2O$); 41.5, 41.7 (2 CH_2Cl); 55.5 (CH_3O); 99.1 (C(1)); 100.2 (C(1)); 101.3 (2C, C(1), Ph$\underline{C}$H); 102.1 (2 C, 2 Ph$\underline{C}$H); 102.3 (2 C, C(1), Ph$\underline{C}$H); 102.4 (C(1)); 102.6 (Ph$\underline{C}$H); 126.2—139.1 (8 Ph, $MeO\underline{C}_6H_4CH$); 157.1 (OCONH); 165.5, 166.2, 166.9 and 167.5 ($ClCH_2\underline{C}O$, Ph$\underline{C}$O). Found, *m/z*: 1976.5494 $[M + Na]^+$. $C_{102}H_{101}Cl_2NNaO_{34}$. Calculated: 1976.5474.

3-(Benzyloxycarbonylamino)propyl 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)-2-*O*-acetyl-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). Acetyl chloride (0.12 mL, 1.7 mmol) was added to a solution of pentasaccharide **22** (303 mg, 0.155 mmol) and 2,4,6-collidine (0.5 mL, 3.76 mmol) in dichloromethane (4 mL) and the reaction mixture was stirred at 20 h for 20 °C. The mixture was diluted with dichloromethane and sequentially washed with 1 *M* aqueous solution of HCl, water, and a saturated solution of sodium hydrogen carbonate. The organic layer was dried by filtration through a purified cotton and concentrated *in vacuo*. The residue was dissolved in aqueous 95% acetonitrile (5 mL), followed by the addition of pyridinium tosylate (730 mg). The mixture was allowed to stand for 18 h at 20 °C and concentrated *in vacuo*. The residue was diluted with dichloromethane, washed with a saturated solution of sodium hydrogen carbonate, the organic layer was dried by filtration through a purified cotton and concentrated *in vacuo*. The residue was separated on silica gel in the gradient acetone—toluene (5→15%) to obtain unreacted acetylated pentasaccharide **22** (41 mg, 13%) and diol **23** (124 mg, 43%) as an amorphous powder; R_f 0.59 (toluene : acetone, 2 : 1); $[\alpha]_D^{22}$ −31 (*c* 1, $CHCl_3$). ^{1}H NMR (600 MHz, acetone-d_6), δ; characteristic signals: 1.37 (s, 3 H, Ac); 1.60 (m, 2 H, $NHCH_2C\underline{H}_2CH_2O$); 3.10 (m, 2 H, $NHC\underline{H}_2CH_2CH_2O$); 4.53 (d, 1 H, H(1), J = 8.0 Hz); 4.77 (m, 2 H, 2 H(1)); 4.98—5.02 (m, 4 H, Ph$C\underline{H}_2$O and 2 H(1)); 5.33, 5.57 and 5.66 (2) (all s, 4 H, 4 PhC$\underline{H}$); 6.03 (m, 1 H, NH); 7.30—8.10 (m, 40 H, 8 Ph). ^{13}C NMR (150 MHz, acetone-d_6), δ; characteristic signals: 20.5 (Ac); 30.7 ($NHCH_2\underline{C}H_2CH_2O$); 38.6 ($NH\underline{C}H_2CH_2CH_2O$); 41.1 and 41.3 (2 $ClCH_2$); 100.4, 101.0, 101.2, 102.1 and 102.2 (5 C(1)); 101.3(3) and 102.0 (4 Ph$\underline{C}$H); 127.2—139.0 (Ph); 157.1 (OCONH); 165.4, 165.5 and 166.0 (3 Ph$\underline{C}$O); 167.0 and 167.2 (2 $ClCH_2\underline{C}O$); 169.0 ($CH_3\underline{C}O$). Found, *m/z*: 1900.5179 $[M + Na]^+$. $C_{96}H_{97}Cl_2NNaO_{34}$. Calculated: 1900.5161.

3-(Benzyloxycarbonylamino)propyl 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)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2-*O*-acetyl-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). A solution of trimethylsilyl triflate (3.3 μL, 0.017 mmol, 25 mol.%) in dichloromethane (0.33 mL) to a stirred mixture of trichloroacetimidate **24** (50 mg, 0.067 mmol, 1.5 equiv.), diol **23** (82 mg, 0.044 mmol), and molecular sieves 4 Å (80 mg) in dichloromethane (3.5 mL) at 20 °C. The reaction mixture was stirred for at 20 °C for 1 h, neutralized by the addition of triethylamine (0.05 mL), filtered through celite, and concentrated *in vacuo*. The resulting mixture was separated on silica gel in the gradient ethyl acetate—toluene (5→15%) to obtain **25** (70 mg, 65%) as an amorphous powder; R_f 0.41 (toluene : AcOEt, 2 : 1); $[\alpha]_D^{21}$ −35 (*c* 1, $CHCl_3$). ^{1}H NMR (600 MHz, acetone-d_6), δ; characteristic signals: 1.55 (m, 2 H, $NHCH_2C\underline{H}_2CH_2O$); 2.28 (s, 3 H, Ac); 2.98 (m, 2 H, $NHC\underline{H}_2CH_2CH_2O$); 4.41 (d, 1 H, H(1), J = 8.0 Hz); 4.62 (d, 1 H, H(1), J = 7.8 Hz); 4.75 (d, 1 H, H(1), J = 7.8 Hz); 4.94—5.00 (m, 4 H, Ph$C\underline{H}_2$O and 2 H(1)); 5.15 (d, 1 H, H(1), J = 8.0 Hz); 5.37, 5.56, 5.63, and 5.64 (all s, 4 H, 4 PhC$\underline{H}$); 5.52 (dd, 1 H, H(2), J = 8.2 Hz, J = 9.7 Hz); 5.76 (t, 1 H, H(4), J = 9.6 Hz); 5.97 (t, 1 H, H(3), J = 9.6 Hz); 6.04 (m, 1 H, NH); 7.10—8.10 (m, 60 H, 12 Ph). ^{13}C NMR (150 MHz, acetone-d_6), δ; characteristic signals: 20.3 (Ac); 30.6 ($NHCH_2\underline{C}H_2CH_2O$); 38.5 ($NH\underline{C}H_2CH_2CH_2O$); 41.1 and 41.3 (2 $ClCH_2$); 70.5 (C(4)); 73.1 (C(2)); 74.3 (C(3)); 100.4, 100.8, 101.2, 101.7, 102.2 and 102.3 (6 C(1)); 101.5, 101.6, 101.9, and 102.2 (4 Ph$\underline{C}$H); 126.2—139.0 (Ph); 157.1 (OCONH); 165.1, 165.5, 165.8, 165.9, 166.1, 166.4, and 166.5 (7 Ph$\underline{C}$O); 167.0 and 167.2 (2 $ClCH_2\underline{C}O$); 168.6 ($CH_3\underline{C}O$). Found, *m/z*: 2473.7169 $[M + NH_4]^+$. $C_{130}H_{124}Cl_2N_2O_{43}$. Calculated: 2473.7184.

3-(Benzyloxycarbonylamino)propyl 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)-2-*O*-acetyl-4,6-*O*-(4-methoxybenzylidene)-β-D-glucopyranoside (30). A mixture of

donor **21** (180 mg, 0.22 mmol 1.08 equiv.), diol acceptor **5** (100 mg, 0.203 mmol), and molecular sieves AW-300 (2.5 g) in dichloromethane (3 mL) was stirred at 20 °C for 30 min, then *N*-iodosuccinimide (120 mg, 0.533 mmol, 2.4 equiv.) and a solution of silver triflate (5 mg, 9 mol.%) in acetonitrile (0.2 mL) were added. The reaction mixture was stirred for 10 min at 20 °C, after addition of a saturated solution of sodium hydrogen carbonate (2 mL) and 1 *M* aqueous solution of sodium thiosulfate (2 mL), the mixture was filtered through a layer of celite, a solid precipitate was washed with dichloromethane, the organic layer was dried by filtration through a purified cotton and concentrated *in vacuo*. The residue was separated on silica gel in the gradient acetone—toluene (0→9%) to obtain trisaccharide **28** (188 mg, 74%) as a mixture with 2-*O*-isomer. The mixture of trisaccharides (187 mg, 0.15 mmol) was dissolved in dichloromethane (2 mL), to which 2,4,6-collidine (0.4 mL, 3 mmol) and acetyl chloride (0.1 mL, 1.4 mmol) were added and the reaction mixture was stirred for 20 h at 20 °C. Then, the mixture was diluted with dichloromethane, sequentially washed with 1 *M* aqueous solution of HCl, water, and a saturated solution of sodium hydrogen carbonate. The organic layer was dried by filtration through a purified cotton and concentrated *in vacuo*. The residue (compound **29** as a mixture with 2-*O*-isomer) was dissolved in a mixture of ethyl acetate (4 mL) and ethanol (4 mL), 2,4,6-collidine (0.2 mL, 1.5 mmol) and thiourea (100 mg, 1.3 mmol) were added. The resulting mixture was stirred for 4 h at 80 °C, cooled, and concentrated *in vacuo*. A solution of the residue in dichloromethane was washed with 1 *M* aqueous solution of HCl, water, and a saturated solution of sodium hydrogen carbonate. The organic layer was dried by filtration through a purified cotton, concentrated *in vacuo* and the residue was purified on silica gel in the ethyl acetate—dichloromethane (1 : 3) solvent system to obtain **30** (104 mg, 61%) as an amorphous powder; R_f 0.31 (CH_2Cl_2 : AcOEt, 3 : 2); $[\alpha]_D^{21}$ −23 (*c* 1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$), δ; characteristic signals: 1.70 (m, 2 H, NHC$\underline{H}_2$C$\underline{H}_2$CH$_2$O); 1.89 (s, 3 H, Ac); 3.12 and 3.22 (both m, 1 H each, NHC$\underline{H}_2$-CH$_2$CH$_2$O); 3.74 (s, 3 H, CH$_3$O); 3.98 (t, 1 H, H_B(3), J = 8.7 Hz); 4.08 (t, 1 H, H_B(4), J = 8.5 Hz); 4.40 (d, 1 H, H_A(1), $J_{1,2}$ = 7.4 Hz); 4.49 (d, 1 H, H_C(1), $J_{1,2}$ = 7.6 Hz); 4.97 (t, 1 H, H_A(2), J = 7.9 Hz); 5.02 (d, 1 H, H_B(1), $J_{1,2}$ = 6.2 Hz); 5.05 (br.t, 1 H, NH); 5.10 (s, 2 H, PhC$\underline{H}_2$); 5.23 (t, 1 H, H_B(2), J = 6.4 Hz); 5.25, 5.42, and 5.50 (all s, 1 H each, 2 PhC$\underline{H}$, MeOC$_6$H$_4$C$\underline{H}$); 6.90—8.05 (m, 24 H, 4 Ph, MeOC$_6\underline{H}_4$). ^{13}C NMR (150 MHz, $CDCl_3$), δ; characteristic signals: 20.5 (C$\underline{H}_3$CO); 29.4 (NHCH$_2$C$\underline{H}_2$-CH$_2$O); 38.2 (NC$\underline{H}_2$CH$_2$CH$_2$O); 55.2 (CH$_3$O); 65.9, 66.2, 66.5 and 66.6 (C_A(5), C_B(5), C_C(5), PhC$\underline{H}_2$); 67.1 (NHCH$_2$CH$_2$-C$\underline{H}_2$O); 68.3, 68.6 and 68.7 (C_A(6), C_B(6), C_C(6)); 79.7 (C_A(2)); 80.2 (C_B(2)); 99.8 (C_B(1)); 100.8 (C_A(1)); 101.2, 101.8 and 101.9 (2 PhC$\underline{H}$, MeOC$_6$H$_4$C$\underline{H}$); 102.6 (C_C(1)); 125.4—137.0 (Ph); 156.4 (OCONH); 165.3 (PhC$\underline{O}$); 169.4 (CH$_3$C$\underline{O}$). Found, *m/z*: 1158.3922 $[M + N]^+$. $C_{60}H_{65}NNaO_{21}$. Calculated: 1158.3941.

3-(Benzyloxycarbonylamino)propyl 4,6-*O*-benzylidene-2,3-di-*O*-acetyl-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-β-D-glucopyranoside (32). A mixture of donor **27** (75 mg, 0.1 mmol 1.1 equiv.), diol acceptor **30** (103 mg, 0.091 mmol), molecular sieves AW-300 (1.5 g) in dichloromethane (1.5 mL) was stirred for 30 min at 20 °C, cooled to −30 °C, followed by the addition of *N*-iodosuccinimide (60 mg, 0.267 mmol, 2.7 equiv.). After stirring for 30 min at −30 °C, a solution of trifluoromethanesulfonic acid (2 μL, 9 mol.%) in acetonitrile was added. The reaction mixture was stirred for 2 h, gradually increasing temperature from −30 to −10 °C. After addition of a saturated solution of sodium hydrogen carbonate (2 mL) and 1 *M* aqueous solution of sodium thiosulfate (2 mL), the mixture was filtered through a layer of celite and washed with dichloromethane, the organic layer was separated, dried by filtration through a purified cotton, and concentrated *in vacuo*. The residue was separated on silica gel in the gradient ethyl acetate—toluene (0→30%) to obtain pentasaccharide **31** (130 mg, 78%) with admixtures of the corresponding ortho ester and hemiacetal from the disaccharide donor. This mixture was involved in the next step without additional purification. A solution of pentasaccharide **31** (130 mg, 0.071 mmol) in acetonitrile (2 mL) was treated with cerium nitrate hexahydrate (0.7 g, 1.6 mmol, 23 equiv.) at 20 °C for 40 min. The mixture was diluted with dichloromethane, washed with water, dried by filtration through a purified cotton, and concentrated *in vacuo*. The residue was separated on silica gel in the gradient acetone—toluene (20→25%) to obtain triol **32** (73 mg, 60%) as an amorphous powder; R_f 0.50 (toluene : acetone, 3 : 2); $[\alpha]_D^{22}$ −36 (*c* 1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$), δ; characteristic signals: 1.58, 1.89, and 2.02 (all s, 3 H each, 3 Ac); 1.70 (m, 2 H, NHCH$_2$C$\underline{H}_2$CH$_2$O); 3.20 (m, 2 H, NHC$\underline{H}_2$CH$_2$CH$_2$O); 4.34 (d, 1 H, H(1), J = 8.0 Hz); 4.42 (d, 1 H, H(1), J = 7.9 Hz); 4.81 (d, 1 H, H(1), J = 7.6 Hz); 4.88 (d, 1 H, H(1), J = 7.7 Hz); 5.00, 5.39, 5.43, and 5.52 (all s, 4 H, 4 PhC$\underline{H}$); 5.03 (m, 1 H, NH); 5.08 (br.s, 2 H, PhC$\underline{H}_2$O); 7.25—8.05 (m, 35 H, 7 Ph). ^{13}C NMR (150 MHz, $CDCl_3$), δ; characteristic signals: 20.2, 20.4, and 20.7 (3 Ac); 29.6 (NH-CH$_2$C$\underline{H}_2$CH$_2$O); 37.9 (NHC$\underline{H}_2$CH$_2$CH$_2$O); 62.3 (C_A(6)); 99.6, 100.2, 100.6, 100.8, 101.3, 101.4, 101.5(2), and 102.6 (5 C(1) and 4 PhC$\underline{H}$); 125.9—137.2 (Ph); 156.5 (OCONH); 165.0 and 165.1 (2 PhC$\underline{O}$)); 168.9, 169.5, and 170.0 (3 CH$_3$C$\underline{O}$). Found, *m/z*: 1728.5674 $[M + Na]_+$. $C_{89}H_9NNaO_{33}$. Calculated: 1728.5679.

3-(Benzyloxycarbonylamino)propyl 4,6-*O*-benzylidene-2,3-di-*O*-acetyl-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)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2-*O*-acetyl-β-D-glucopyranoside (33). A solution of trimethylsilyl triflate (3 μL, 0.015 mmol, 36 mol.%) in dichloromethane (0.15 mL) to a stirred mixture of trichloroacetimidate **9** (30 mg, 0.043 mmol, 1.2 equiv.), triol **32** (61 mg, 0.036 mmol), and molecular sieves 4 Å (130 mg) in dichloromethane (1.3 mL) at 0 °C. The reaction mixture was stirred for 1 h at 0 °C, neutralized by the addition of triethylamine (0.05 mL), filtered through celite, and concentrated *in vacuo*. The resulting mixture was subjected to chromatography on silica gel in the gradient acetone—toluene (5→15%) to obtain **33** (56 mg, 70%) as an amorphous powder; R_f 0.44 (toluene : acetone, 3 : 1); $[\alpha]_D^{21}$ −42 (*c* 1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$), δ; characteristic signals: 1.52, 1.86, 1.98, and 2.03 (all s, 3 H each, 4 Ac); 1.45 (m, 2 H, NHCH$_2$C$\underline{H}_2$CH$_2$O); 3.00 (m, 2 H, NHC$\underline{H}_2$CH$_2$CH$_2$O); 4.38 (d, 1 H, H(1), J = 8.0 Hz); 4.65 (d, 1 H, H(1), J = 8.2 Hz); 4.67 (d, 1 H, H(1), J = 8.1 Hz); 4.86 (d, 1 H, H(1), J = 7.5 Hz); 4.95 (m, 1 H, H(1)); 4.98, 5.37, 5.42, and 5.53 (all s, 4 H, 4 PhC$\underline{H}$); 5.81 (t, 1 H, H(3), J = 10.3 Hz); 7.15—8.02 (m, 50 H, 12 Ph). ^{13}C NMR (150 MHz, $CDCl_3$), δ; characteristic signals: 20.2, 20.5, 20.6, and 20.7 (4 Ac); 29.6 (NHCH$_2$C$\underline{H}_2$CH$_2$O); 37.9 (NHC$\underline{H}_2$CH$_2$CH$_2$O); 62.4 (C_F(6)); 99.7, 100.3, 100.4, 100.6, 101.2, 101.4, 101.5(3), 102.7 (6 C(1) and 4 PhC$\underline{H}$); 126.0—137.3 (Ph); 156.3 (OCONH); 164.9, 165.0, 165.1(2), and 165.7 (5 PhC$\underline{O}$); 168.8, 169.5, 170.0, and 170.6

(4 $CH_3\underline{C}O$). Found, *m/z*: 2244.7098 $[M + N]^+$. $C_{118}H_{119}NNaO_{42}$. Calculated: 2244.7099.

Removal of protecting groups in β-(1→3)-glucooligosaccharides (general procedure). A protected oligosaccharide (50—60 mg) was dissolved in a mixture of chloroform—methanol—1 *M* HCl (5 : 5 : 1) (5 mL) and the solution was heated at 40—45 °C until the TLC monitoring in the chloroform—methanol solvent system (9 : 1) showed the absence in the reaction mixture of the products with $R_f > 0$ (4—6 h). Anion-exchange resin Amberlyst A-26 (HCO_3^--form) was added to the mixture to make it neutral, ion-exchange resin was filtered off, washed with a mixture of chloroform—methanol (1 : 1) (20 mL) on the filter. The combined filtrates were concentrated and the residue was dried *in vacuo*. The product obtained was diluted with methanol (5 mL) and 1 *M* sodium methoxide (0.5 mL). The mixture was stirred at 40—45 °C for 4—5 h, then water was added until a homogeneous solution was formed (1—2 mL), and the solution was heated for another 6—16 h. Then, cationite Amberlite IR-120 (H^+-form) was added to make it neutral, then anionite Amberlyst A-26 (HCO_3^--form) (1—2 mL) was added to the mixture. The resins were filtered off, washed with 50% aqueous methanol on the filter, and the combined filtrates were concentrated. The residue was dissolved in 50% aqueous methanol (3 mL), followed by the addition of 1 *M* HCl (50 μL) and $Pd(OH)_2/C$ (25—35 mg), and the resulting mixture was stirred in hydrogen atmosphere at room temperature and normal pressure until the TLC monitoring (chloroform—methanol—water, 10 : 10 : 3) showed the disappearance from the reaction mixture of the products with $R_f > 0$ (2—4 h). The catalyst was removed by filtration through a layer of celite and washed with aqueous methanol, the combined filtrates were concentrated. The residue was subjected to gel-chromatography on a column with TSK HW-40(S) in 0.1 *M* aqueous acetic acid, using a refractometric detector to analyze the eluate. The oligosaccharide fraction was lyophilized to obtain 3-aminopropyl glycoside of branched β-glucan as a salt with acetic acid, a white amorphous powder, 79—98% yield.

3-Aminopropyl β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→6)]-β-D-glucopyranoside (11). Trisaccharide **11** was obtained from protected trisaccharide **10** according to the general procedure in 98% yield, an amorphous powder; $[\alpha]_D^{22}$ −36 (*c* 1, H_2O). ^1H NMR (600 MHz, D_2O), δ; characteristic signals: 2.02 (m, 2 H, $H_2NCH_2C\underline{H}_2CH_2O$); 3.18 (t, 2 H, $NHC\underline{H}_2CH_2CH_2O$, $J = 6.9$ Hz); 3.83 and 4.07 (both m, 1 H each, $NHCH_2CH_2C\underline{H}_2O$); 3.89 and 4.23 (both m, 1 H each, $H_F(6a)$ and $H_F(6a)$); 4.51 (d, 1 H, $H_A(1)$, $J_{1,2} = 8.0$ Hz); 4.53 (d, 1 H, $H_F(1)$, $J_{1,2} = 8.1$ Hz); 4.75 (d, 1 H, $H_B(1)$, $J_{1,2} = 7.9$ Hz). ^{13}C NMR (150 MHz, D_2O), δ; characteristic signals: 27.9 ($H_2NCH_2\underline{C}H_2CH_2O$); 38.8 ($H_2N\underline{C}H_2CH_2CH_2O$); 61.9 and 62.0 ($C_B(6)$ and $C_F(6)$); 69.0 ($C_A(6)$); 69.2 ($H_2NCH_2CH_2\underline{C}H_2O$); 70.2 85.4 ($C_A(3)$); 103.3, 104.0 and 104.1 ($C_A(1)$, $C_B(1)$ and $C_F(1)$). Found, *m/z*: 562.2340 $[M + H]^+$. $C_{21}H_{40}NO_{16}$. Calculated: 562.2342.

3-Aminopropyl β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→6)]-β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-β-D-glucopyranoside (26). Hexasaccharide **26** was obtained from protected hexasaccharide **25** according to the general procedure in 87% yield, an amorphous powder. ^1H NMR (600 MHz, D_2O), δ; characteristic signals: 2.03 (m, 2 H, $H_2NCH_2C\underline{H}_2CH_2O$); 3.18 (t, 2 H, $NHC\underline{H}_2CH_2CH_2O$, $J = 7.0$ Hz); 3.33 (t, 1 H, $H_F(2)$, $J = 9.2$ Hz); 3.38 (t, 1 H, $H_E(2)$, $J = 9.2$ Hz); 3.92 and 4.07 (both m, 1 H each, $NHCH_2CH_2C\underline{H}_2O$); 4.52 (d, 1 H, $H_A(1)$, $J_{1,2} = 8.7$ Hz); 4.55 (d, 1 H, $H_F(1)$, $J_{1,2} = 8.4$ Hz); 4.76 (d, 1 H, $H_E(1)$, $J_{1,2} = 7.6$ Hz); 4.78 (d, 1 H, $H_C(1)$, $J_{1,2} = 7.7$ Hz); 4.79 (d, 1 H, $H_B(1)$, $J_{1,2} = 8.2$ Hz); 4.82 (d, 1 H, $H_D(1)$, $J_{1,2} = 8.0$ Hz). ^{13}C NMR (150 MHz, D_2O), δ; characteristic signals: 28.1 ($H_2NCH_2\underline{C}H_2CH_2O$); 39.0 ($H_2N\underline{C}H_2CH_2CH_2O$); 62.2 (5 C(6)); 69.3 ($H_2NCH_2CH_2\underline{C}H_2O$); 70.2 ($C_C(6)$); 85.4, 85.8, 85.9, 86.3 ($C_A(3)$, $C_B(3)$, $C_C(3)$ and $C_D(3)$); 103.4 ($C_A(1)$); 103.9 ($C_B(1)$ and $C_D(1)$); 104.0 ($C_C(1)$); 104.2 ($C_E(1)$ and $C_F(1)$). Found, *m/z*: 1048.3934 $[M + H]^+$. $C_{39}H_{70}NO_{31}$. Calculated: 1048.3926.

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→6)]-β-D-glucopyranoside (34). Hexasaccharide **34** was obtained from protected hexasaccharide **33** according to the general procedure in 79% yield, an amorphous powder; $[\alpha]_D^{22}$ −38 (*c* 1, H_2O). ^1H NMR (600 MHz, D_2O), δ; characteristic signals: 2.02 (m, 2 H, $H_2NCH_2C\underline{H}_2CH_2O$); 3.18 (t, 2 H, $NHC\underline{H}_2CH_2CH_2O$, $J = 7.0$ Hz); 3.32 (t, 1 H, $H_F(2)$, $J = 8.8$ Hz); 3.82 and 4.05 (both m, 1 H each, $NHCH_2CH_2C\underline{H}_2O$); 3.89 (dd, 1 H, $H_A(6a)$, $J_{5,6} = 5.6$ Hz, $J_{6,6} = 11.0$ Hz); 4.23 (d, 1 H, $H_A(6b)$, $J_{6,6} = 11.0$ Hz); 4.51 (d, 1 H, $H_F(1)$, $J_{1,2} = 8.2$ Hz); 4.53 (d, 1 H, $H_A(1)$, $J_{1,2} =$ = 8.4 Hz); 4.75—4.82 (m, 4 H, $H_B(1)$, $H_C(1)$, $H_D(1)$ and $H_E(1)$). ^{13}C NMR (150 MHz, D_2O, δ; characteristic signals: 27.9 ($H_2NCH_2\underline{C}H_2CH_2O$); 38.8 ($H_2N\underline{C}H_2CH_2CH_2O$); 61.9 (5×C(6)); 69.3 ($H_2NCH_2CH_2\underline{C}H_2O$); 69.8 ($C_C(6)$); 103.3 ($C_A(1)$); 103.7(3) and 104.0 ($C_B(1)$, ($C_C(1)$, $C_D(1)$ and $C_E(1)$); 104.1 ($C_F(1)$). Found, *m/z*: 1048.3913 $[M + H]^+$. $C_{39}H_{70}NO_{31}$. Calculated: 1048.3926.

References

1. *Chemistry, Biochemistry and Biology of (1→3)-β-Glucans and Related Polysaccharides*, Eds A. Bacic, G. B. Fincher, B. A. Stone, Academic Press, Elsevier, Amsterdam, 2009, 677 pp.
2. D. V. Yashunsky, Y. E. Tsvetkov, A. A. Grachev, A. O. Chizhov, N. E. Nifantiev, *Carbohydr. Res.*, 2016, **419**, 8.
3. Y. E. Tsvetkov, E. A. Khatuntseva, D. V. Yashunsky, N. E. Nifantiev, *Russ. Chem. Bull.* (*Int. Ed.*), 2015, **64**, 990 [*Izv. Akad. Nauk*, *Ser. Khim.*, 2015, 990].
4. E. Paulovičová, H. Bujdáková, J. Chupáčová, L. Paulovičová, P. Kertys, M. Hrubiŝko, *FEMS Yeast Res.*, 2015, **15**, DOI: 10.1093/femsyr/fou001.
5. V. P. Ananikov, E. A. Khokhlova, M. P. Egorov, A. M. Sakharov, S. G. Zlotin, A. V. Kucherov, L. M. Kustov, M. L. Gening, N. E. Nifantiev, *Mendeleev Commun.*, 2015 **25**, 75.
6. Y. Wang, Q. Yan, J. Wu, L.-H. Zhang, X.-S. Ye, *Tetrahedron*, 2005, **61**, 4313.
7. P. J. Garegg, I. Kvarnstroem, A. Niklasson, G. Niklasson, S. C. T. Svensson, *J. Carbohydr. Chem.*, 1993, **12**, 933.
8. F. Dasgupta, P. J. Garegg, *Acta Chem. Scand.*, 1989, **43**, 471.
9. J. Ning, Y. Yi, F. Kong, *Tetrahedron Lett.*, 2002, **43**, 5545.
10. A. Fürstner, T. Müller, *J. Am. Chem. Soc.*, 1999, **121**, 7814.
11. A. Fürstner, K. Radkowski, J. Grabowski, C. Wirtz, R. Mynott, *J. Org. Chem.*, 2000, **65**, 8758.
12. I. A. Ivanova, A.J. Ross, M. A. J. Ferguson, A. V. Nikolaev, *J. Chem. Soc.*, *Perkin Trans. 1*, 1999, 1743.

Received October 2, 2015;
in revised form November 10, 2015