Blockwise synthesis of a pentasaccharide structurally related to the mannan fragment from the *Candida albicans* cell wall corresponding to the antigenic factor 6

*A. A. Karelin,[a] Yu. E. Tsvetkov,[a] E. Paulovičová,[b] L. Paulovičová,[b] and N. E. Nifantiev[a]**

[a]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
[b]Institute of Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia

A spacer-armed pentasaccharide structurally related to a fragment of the mannan from the cell wall of the fungus *Candida albicans* and corresponding to the antigenic factor 6 has been synthesized. This compound, comprising two α-(1→2)- and three β-(1→2)-linked mannose residues, was prepared by glycosylation of a selectively protected α-(1→2)-dimannoside bearing an aglycone spacer and a free OH group at atom C(2′) with a β-(1→2)-trimannoside glycosyl donor. The successful synthesis evidences that large β-(1→2)-oligomannoside donor blocks can be used for the preparation of oligosaccharides including extended sequences of repeating β-(1→2)-linked mannose residues.

Key words: *Candida albicans*, mannan, β-oligomannosides, antigenic factor 6, blockwise synthesis, β-mannosylation.

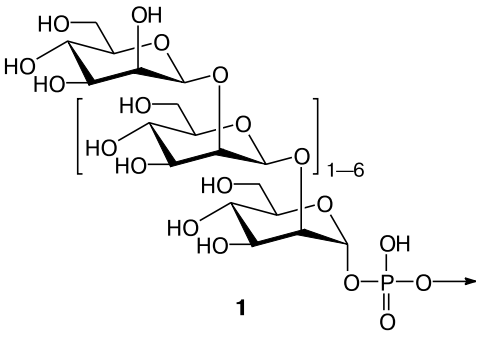
The present work is a continuation of our studies on the synthesis[1—4] and immunological properties[5—9] of oligosaccharides related to fragments of the mannan from the cell wall of the fungi of the genus *Candida*. The yeast-like fungi *Candida albicans* are part of the microflora of the skin, mucous membranes, and the gastrointestinal tract of healthy human, however, in people with weakened immune systems, they can cause superficial and deep candidiasis.[10] The cell wall of the fungi of the genus *Candida* is first to be involved in the interaction with the host organism and is responsible for the antigenic reaction, adhesion, and cell-cell interactions.[11]

Mannan is the major surface polysaccharide antigen of the cell wall of *Candida*, which is a carbohydrate part of the mannoprotein with a comb-like structure.[12] Mannan is based on the α-(1→6)-linked main chain, with relatively short side oligomannoside chains attached to the separate mannose residues through the α-(1→2)-bonds. These chains can contain α-(1→2)-, α-(1→3)-, α-(1→6)-, and β-(1→2)-linked mannose residues. These are the mannan side chains which in the first place determine the antigenic specificity of the fungi of the genus *Candida*.

The β-(1→2)-linked mannose residues are part of the composition of two types of antigenic structures of mannan from *Candida*. In the first case, the β-(1→2)-oligomannoside containing from two to seven mannose residues, is bonded by its reducing end to the side chain through a phosphate group[12] (structure **1**). This structural type is called as an acid-labile β-(1→2)-oligomannoside and corresponds to the antigenic factor 5 (see Ref. 13). In the second case, the short (1—4 residues) β-(1→2)-linked oligomannosides is bonded by a glycoside bond to α-(1→2)-oligomannoside chains at atom O(2) of the terminal mannose unit[14] (structure **2**). This type of β-(1→2)-oligomannoside is called an acid-stable and corresponds to the antigenic factor 6 (see Ref. 13). The acid-labile β-(1→2)-oligomannoside chains are a component of the mannan of the serotypes related to serogroups A and B, whereas the acid-stable β-(1→2)-oligomannoside is an antigen specific for serotypes of serogroup A.

Apart from *Candida albicans* serogroup A, the oligosaccharide structure of type **2** corresponding to the antigenic factor 6 were found in mannans of other *Candida* species (for example, in *C. tropicalis*, *C. glabrata*, *C. stellatoidea*, *C. lusitaniae*, and *C. kefyr*[15]). β-(1→2)-Oligomannoside chains of mannan play an important role in pathogenesis of candidiasis. Thus, it was found that they were involved in the first stage of development of an infectious process, namely, the adhesion of *Candida* to the cells of a host organism.[16] Animal models were used to demonstrate that the antibodies specific to β-(1→2)-oligomannosides possess protective properties against different types of

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2942—2948, December, 2015.



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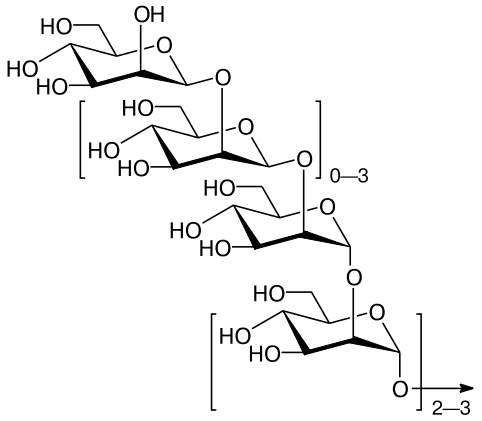

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candidiasis,[17–19] whereas the immunization with the conjugate of synthetic β-(1→2)-trimannoside with the *C. albicans* cell wall peptide protects from infection with a lethal dose of a live fungal culture.[20,21]

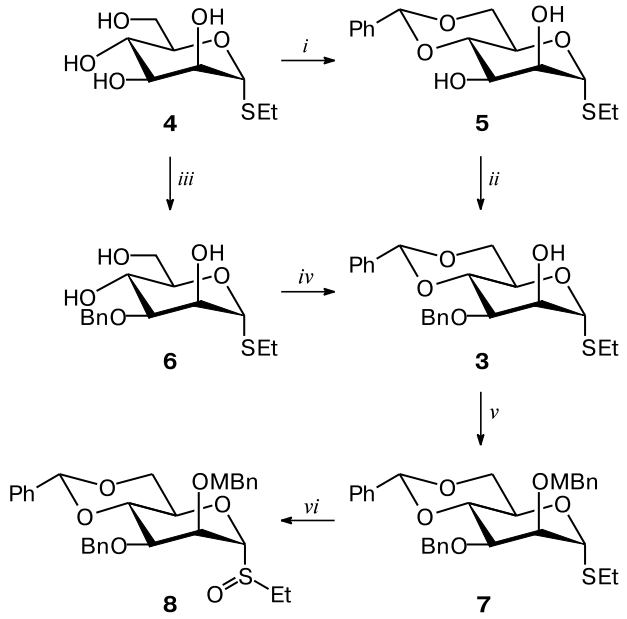
There are literature reports on the synthesis of oligosaccharides of type **2**, in which from one to three β-(1→2)-linked mannose residues are attached to the only α-linked mannose residue[22–25] or to α-(1→2)-mannobioside.[26,27] The main problem, which was necessary to solve in the process of their synthesis, was β-mannosylation, which is regarded as one of the most challenging cases of glycosylation.[28] At the present time, there are known two general approaches to the solution of the problem of stereoselective β-mannosylation. The first method is indirect and based on the initial β-glucosylation and subsequent inversion of configuration of atom C(2) in the glucose residue in the reaction product. This approach was used to obtain a number of β-(1→2)-oligomannosides,[29,30] including those corresponding to the antigenic factor 6 (see Refs 22 and 26). The second approach is based on the direct β-mannosylation with conformationally rigid 4,6-*O*-benzylidene-protected mannosyl donors,[31–33] usually thioglycosides or glycosyl sulfoxides. Though the mechanism of β-stereocontrol in this type of glycosylation reactions is still in dispute (*cf.* Ref. 33 and Ref. 34), this approach was successfully used for the preparation of both homo-β-(1→2)-octamannoside[35,36] and the structures of type **2** (see Refs 23, 24, and 27). In contrast to the first approach, which allows the building up a β-(1→2)-oligomannoside chain by only one monosaccharide unit, the case of the direct β-mannosylation also permits more efficient blockwise method of assembly of β-(1→2)-oligomannosides. Separate examples when the blockwise method uses β-(1→2)-dimannoside donor blocks are described in the literature.[23,24]

In the present work, we describe a blockwise synthesis of a pentamannoside corresponding to the antigenic factor 6 and containing three β- and two α-linked mannose residues, using direct β-mannosylation. One of the purposes of this work is to study a possibility of using donor blocks for the preparation of β-(1→2)-oligomannosides, which are larger than the dimannosides mentioned above.

Results and Discussion

Known thiomannoside **3** was used as the starting compound for the assembly of a trimannoside glycosyl donor block. It was obtained in two steps from free thioglycoside **4** (see Ref. 37) through the initial setting of the 4,6-*O*-benzylidene group[37] and subsequent regioselective 3-*O*-benzylation of derivative **5** through the intermediate 2,3-dibutylstannylene derivative[38] (Scheme 1).

Scheme 1



MBn = *n*-$CH_3OC_6H_4CH_2$

Reagents, conditions, and yields: *i*. PhCHO, HCOOH, 49% yield (see Ref. 37); *ii*. 1) Bu_2SnO, MeOH, reflux; 2) BnBr, DMF, 110 °C, 80% yield (see Ref. 38); *iii*. 1) Bu_2SnO, MeOH, reflux; 2) BnBr, CsF, DMF, 20 °C, 74% yield; *iv*. $PhCH(OMe)_2$, CSA, MeCN, 84% yield; *v*. MBnCl, NaH, Bu_4NI, DMF, 75% yield (see Ref. 36); *vi*. *m*-CPBA, CH_2Cl_2, −78 → −20 °C, 84% yield (see Ref. 36).

The main disadvantage of this method for the preparation of compound **3** is the low yield of 4,6-monoacetal **5** because of the competitive formation of a 2,3 : 4,6-bisacetal. As a result, the total yield of the conversion **4** → **5** → **3** is below 40%. We used a reversed sequence of the introduction of protecting groups into thioglycoside **4**. Regioselective benzylation of compound **4** through a dibutylstannylene derivative led to 3-benzyl ether **6** in 74% yield. Further introduction of 4,6-*O*-benzylidene group into compound **6** because of the impossibility to form 2,3-acetal proceeded without complications and led to derivative **3** in 84% yield (the overall yield for the conversion **4** → **6** → **3** was 62%). The conversion of compound **3** to *p*-methoxybenzyl ether **7** and its oxidation to sulfoxide **8**, which was further used as a glycosyl donor in the assembly of β-(1→2)-trimannoside, was carried out according to the procedure described earlier.[36]

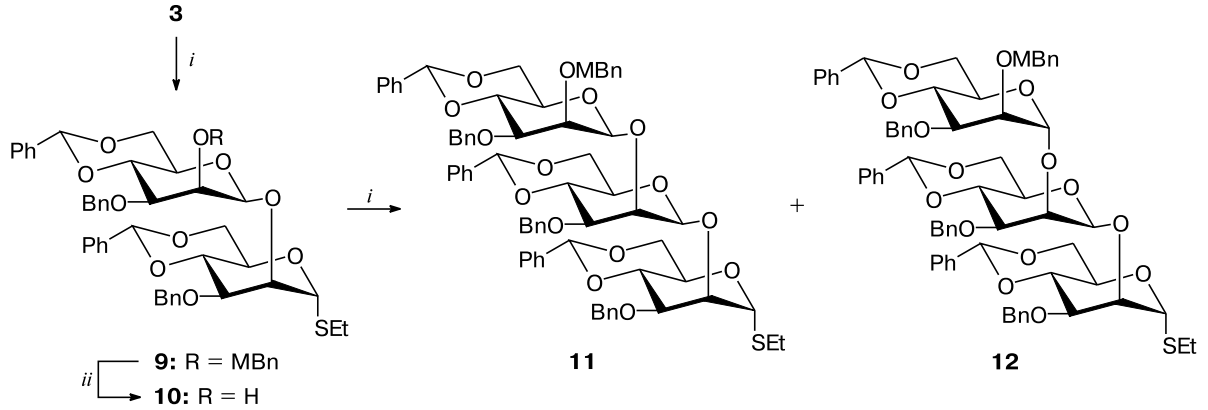
Glycosylation of derivative **3** with sulfoxide **8** was effected under conditions of a pre-activation of the donor upon treatment with Tf_2O in the presence of 2,6-di-*tert*-butylpyridine (DTBP) with subsequent addition of acceptor **3** (Scheme 2). It is believed[33] that the preactivation of the donor results in the formation of a covalent α-mannosyl triflate, the further S_N2-like reaction of which with glycosyl acceptor secures the high β-selectivity of glycosylation.

The glycosylation gave β-dimannoside **9** in 59% yield. The β-configuration of the newly formed glycoside bond was confirmed by a high-field position of the signal for atom H(5) in the mannose residue at the nonreducing end (δ 3.37)[33] in the ^{1}H NMR spectrum. The removal of the *p*-methoxybenzyl group in compound **9** upon treatment with DDQ gave disaccharide glycosyl acceptor **10** in high yield. The glycosylation of compound **10** with sulfoxide **8** proceeded less efficiently and led to β-(1→2)-trimannoside **11** in 40% yield. Apart from that, the α-linked product **12** was isolated in 16% yield. The configuration of the newly formed glycoside bond in trimannosides **11** and **12** was also inferred from the signal positions for atom H(5) in the terminal mannose residues in the ^{1}H NMR spectra. Thus, in the case of β-anomer **11**, the signal for atom H(5) resonated at δ 3.49, whereas in α-anomer it was found in the group of signals at δ ~4.35.

The synthesis was finalized by the condensation of β-(1→2)-trimannoside donor **11** with disaccharide acceptor **13** described by us earlier.[1] There are contradictory literature data on the influence of mannosylation conditions on its stereochemical result, especially concerning the order of mixing the reagents. In the works,[31–33] it was shown that the high β-selectivity of mannosylation can be reached by a preliminary low-temperature activation of the mannosyl donor with subsequent addition of an acceptor. At the same time, in the work[34] it was demonstrated that 4,6-benzylidene-protected mannosyl trichloroacetimidate secured the β-selectivity of mannosylation without preliminary activation, which turned out to be virtually the same as that observed with its preactivation. Taking into account the latter result, the glycosylation of acceptor **13** with thioglycoside **11** was carried out without preliminary activation of the donor, *i.e.*, by the addition of a catalytic amount of TfOH to a mixture of compounds **11**, **13**, and NIS (Scheme 3).

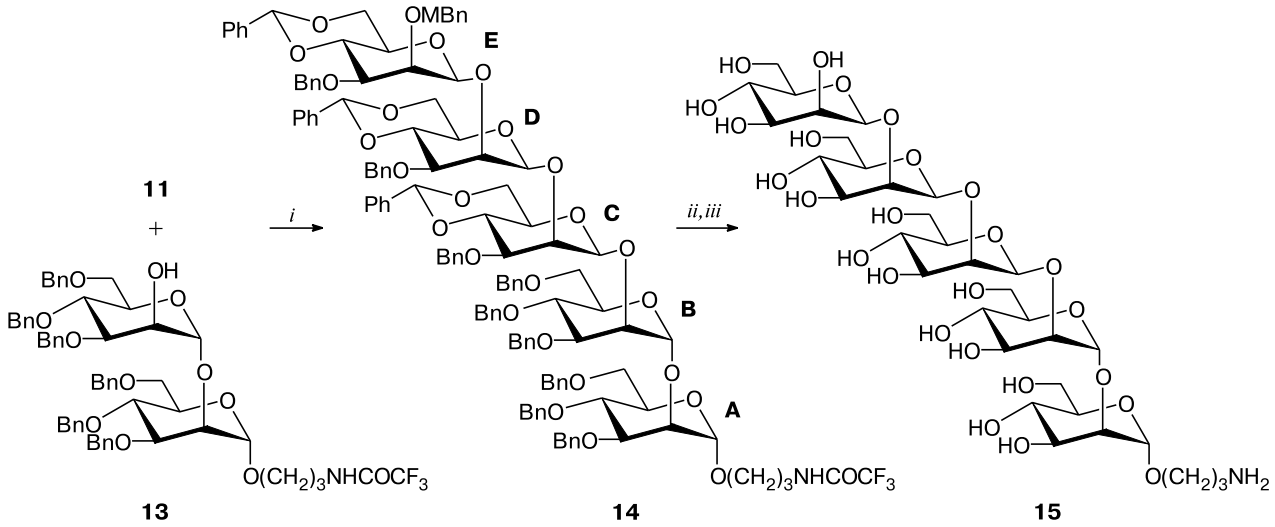
The β-mannosylation product, pentasaccharide **14**, was obtained in 41% yield. The β-configuration of the newly formed glycoside bond was inferred from the high-field position of the signal for atom H(5) of the mannose residue C (δ 2.77) in the ^{1}H NMR spectrum of pentasaccharide **14**. This means that even without preliminary activation of the donor, the glycosylation with trisaccharide **11** leads to the β-linked mannoside. This result also confirms a possibility of using β-(1→2)-oligomannosyl donor blocks (larger than dimannoside units) for the

Scheme 2



Reagents, conditions, and yields: *i*. 1) Tf_2O, DTBP, MS 4 Å, CH_2Cl_2, −80 °C; 2) **8**, CH_2Cl_2, −80 → +10 °C, 59% yield for **9**, 40% yield for **11**; *ii*. DDQ, $CHCl_3$—water, 91% yield.

Scheme 3



Reagents, conditions, and yields: *i*. NIS, TfOH, MS 4 Å, CH_2Cl_2, $-40 \rightarrow -10$ °C, 41% yield; *ii*. H_2, $Pd(OH)_2/C$, MeOH—EtOAc, 20 °C; *iii*. aqueous NaOH, 47% yield.

preparation of oligosaccharides containing large enough β-(1→2)-oligomannoside sequences.

The benzyl and the benzylidene groups in protected pentasaccharide **14** were removed by catalytic hydrogenolysis, the *N*-trifluoroacetyl group was removed by alkaline hydrolysis. The thus obtained free pentamannoside 3-aminopropylglycoside (**15**) will be used further for the preparation of immunogens by the conjugation with protein carriers, coating antigens for enzyme-linked immunosorbent assay labeled molecular probes, and other biomolecular systems.[39]

Experimental

All the reactions were carried out in the solvents purified according to the standard procedures. The reagents TfOH, Tf_2O, NIS (Acros), and DTBP (Aldrich) were used without additional purification. Thin-layer chromatography was carried out 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 carried out on a column with a TSK HW-40(S) gal (1.5×90 cm) in 0.1 *M* acetic acid, the eluate was analyzed using a Knauer K-2401 flow refractometer. Optical rotation was measured on a JASCO P-2000 digital polarimeter (Japan) at ~20 °C in methanol or chloroform (in the case of protected derivatives) and in water (in case of free oligosaccharide).

NMR spectra of protected derivatives were recorded on a Bruker Avance 600 spectrometer in $CDCl_3$ at 25 °C. The signal of residual nondeuterated $CHCl_3$ (δ_H 7.27) were used as an internal standard for ^1H NMR spectra, the signal of $CDCl_3$ (δ_C 77.0) was a reference for ^{13}C NMR spectra. Spectra of unprotected oligosaccharides were recorded in heavy water (D_2O), using acetone as an internal standard (δ_H 2.225, δ_C 31.45). The signals were assigned using procedures of 2D correlation spectroscopy COSY, TOCSY, ROESY, 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.*) (see Scheme 3).

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

Glycosylation reactions were carried out in anhydrous solvents under dry argon. Molecular sieves before use in the reaction were activated for 2 h at 180 °C *in vacuo*, using an oil pump.

Ethyl 3-*O*-benzyl-1-thio-α-D-mannopyranoside (6). The reagent Bu_2SnO (1.25 g, 5.0 mmol) was added to a solution of thioglycoside **4** (1.15 g, 5.13 mmol) in anhydrous MeOH (20 mL). The reaction mixture was refluxed until a homogeneous solution was formed (~3 h). Then the solvent was evaporated, the residue was dried *in vacuo*, using an oil pump. Cesium fluoride (935 mg, 6.16 mmol) and benzyl bromide (0.673 mL, 5.64 mmol) were added to a solution of the product obtained in anhydrous DMF (20 mL). The reaction mixture was stirred for 16 h at ~20 °C, then filtered through a layer of silica gel, which was washed with ethyl acetate. The filtrate was concentrated and then twice coconcentrated with toluene. The residue was dried *in vacuo*, using an oil pump. 3-Benzyl ether **6** (1.17 g, 74%) was isolated by column chromatography in ethyl acetate, colorless syrup, $[\alpha]_D$ +114.4 (*c* 1, CH_3OH). ^1H NMR (600 MHz, $CDCl_3$), δ: 7.43—7.27 (m, 5 H, Ph); 5.25 (d, 1 H, H(1), $J_{1,2}$ = 1.5 Hz); 4.71 (d, 1 H, PhC$\underline{H}_2$, J = 11.8 Hz); 4.64 (d, 1 H, PhC$\underline{H}_2$); 4.04 (dd, 1 H, H(2), $J_{2,3}$ = 3.2 Hz); 3.92 (m, 1 H, H(5)); 3.84—3.79 (m, 2 H, H(4), H(6a)); 3.74 (dd, 1 H, H(6b), $J_{5,6}$ = 5.7 Hz, $J_{6a,6b}$ = 11.9 Hz); 3.56 (dd, 1 H, H(3), $J_{3,4}$ = 9.3 Hz); 2.66 (m, 1 H, SC$\underline{H}_2CH_3$); 2.58 (m, 1 H, SC$\underline{H}_2CH_3$); 1.27 (t, 3 H, $SCH_2C\underline{H}_3$, J = 7.4 Hz). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 129.4, 129.3, 128.8 (Ph);

86.1 (C(1)); 80.9 (C(3)); 75.1 (C(5)); 72.8 (PhCH$_2$); 70.9 (C(2)); 68.1 (C(4)); 62.9 (C(6)); 25.9 (SCH$_2$CH$_3$); 15.4 (SCH$_2$CH$_3$). Found: *m/z* 353.0818 [M + K]$^+$. $C_{15}H_{22}O_4KS$. Calculated: 353.0820.

Ethyl 3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (3). Benzaldehyde dimethyl acetal (0.29 mL, 1.9 mmol) and CSA (40 mg) were added to a solution of thioglycoside **6** (400 mg, 1.27 mmol) in anhydrous acetonitrile (5 mL). The mixture was allowed to stand at ~20 °C until the full conversion of the starting compound **6**, then triethylamine (0.1 mL) was added, the solvent was evaporated. Compound **3** was isolated (427 mg, 84%) by column chromatography (toluene—ethyl acetate, 20 : 1) as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.51—7.46, 7.40—7.28 (both m, 10 H, 2 Ph); 5.61 (s, 1 H, PhCH); 5.36 (s, 1 H, H(1)); 4.85 (d, 1 H, PhCH$_2$, J = 11.7 Hz); 4.69 (d, 1 H, PhCH$_2$, J = 11.8 Hz); 4.26—4.20 (m, 2 H, H(5), H(6a)); 4.14 (t, 1 H, H(4), J = 9.3 Hz); 4.10 (d, 1 H, H(2), $J_{2,3}$ = 3.1 Hz); 3.92—3.85 (m, 2 H, H(3), H(6b)); 2.69—2.52 (m, 2 H, SCH$_2$CH$_3$); 1.28 (t, 3 H, SCH$_2$CH$_3$, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 137.5, 137.7, 128.9, 128.5, 128.2, 128.0, 127.8, 126.0 (Ph); 101.6 (PhCH); 84.1 (C(1)); 79.1 (C(4)); 75.8 (C(3)); 73.1 (ArCH$_2$); 71.4 (C(2)); 68.6 (C(6)); 63.8 (C(5)); 24.9 (SCH$_2$CH$_3$); 14.8 (SCH$_2$CH$_3$). According to the NMR spectral data, the product obtained was identical to derivative **3** described in the work.[38]

Ethyl [3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-(*p*-methoxybenzyl)-β-D-mannopyranosyl]-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (9). Molecular sieves 4 Å (300 mg) and DTBP (0.18 mL, 0.815 mmol) were added to a solution of sulfoxide **8** (228 mg, 0.424 mmol) in CH_2Cl_2 (2 mL). The resulting mixture was stirred for 30 min at ~20 °C, then cooled to −80 °C, followed by the addition of Tf_2O (69 μL, 0.51 mmol). After 5 min, a solution of thioglycoside **3** (131 mg, 0.326 mmol) in CH_2Cl_2 (1 mL) was added dropwise to the reaction mixture. The mixture was stirred for 1 h at −80 °C, then the temperature was gradually elevated to +10 °C over 1 h. The reaction mixture was neutralized with triethylamine (0.3 mL), diluted with chloroform, and filtered through a layer celite. The celite was washed with chloroform, the combined filtrates were washed with water and concentrated. Disaccharide **9** (159 mg, 59%) was isolated by column chromatography (toluene—ethyl acetate, 20 : 1) as a colorless syrup, $[\alpha]_D$ −27.9 (*c* 1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$), δ: 7.55—7.28 (m, 22 H, 4 Ph, *p*-CH$_3$OC$_6$H$_4$); 6.88—6.84 (m, 2 H, *p*-CH$_3$OC$_6$H$_4$); 5.65 (s, 1 H, PhCH); 5.54 (s, 1 H, PhCH); 5.36 (s, 1 H, H(1)$_A$); 5.02 (d, 1 H, ArCH$_2$, J = 11.8 Hz); 4.95 (d, 1 H, ArCH$_2$, J = 11.8 Hz); 4.80 (d, 1 H, ArCH$_2$, J = 12.0 Hz); 4.77—4.73 (m, 2 H, ArCH$_2$); 4.69 (s, 1 H, H(1)$_B$); 4.66 (d, 1 H, ArCH$_2$, J = 12.5 Hz); 4.39 (d, 1 H, H(2)$_A$, $J_{2,3}$ = 3.1 Hz); 4.32—4.24 (m, 4 H, H(4)$_B$, H(5)$_A$, H(6a)$_A$, H(6a)$_B$); 4.17 (t, 1 H, H(4)$_A$, J = 9.8 Hz); 4.04 (d, 1 H, H(2)$_B$, $J_{2,3}$ = 3.1 Hz); 3.97 (dd, 1 H, H(3)$_A$, $J_{2,3}$ = 3.1 Hz, $J_{3,4}$ = 9.8 Hz); 3.91 (t, 1 H, H(6b)$_B$, J = 10.2 Hz); 3.83 (t, 1 H, H(6b)$_A$, J = 11.6 Hz); 3.78 (s, 3 H, OCH$_3$); 3.65 (dd, 1 H, H(3)$_B$, $J_{2,3}$ = 3.1 Hz, $J_{3,4}$ = 9.8 Hz); 3.37 (m, 1 H, H(5)$_B$); 2.67 (m, 2 H, SCH$_2$CH$_3$); 1.31 (t, 3 H, SCH$_2$CH$_3$, J = 7.4 Hz). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 159.2, 138.6, 138.4, 137.5, 130.6, 130.2, 128.9—126.1, 113.6 (Ar); 101.7 (PhCH); 101.4 (PhCH); 99.9 (C(1)$_B$); 82.7 (C(1)$_A$); 78.9 (C(4)$_A$); 78.5 (C(4)$_B$); 77.7 (C(3)$_B$); 76.2 (C(2)$_A$); 75.6 (C(2)$_B$); 74.5 (C(3)$_A$); 74.2 (ArCH$_2$); 72.3 (ArCH$_2$); 71.4 (ArCH$_2$); 68.7 (C(6)$_A$); 68.5 (C(6)$_B$); 67.8 (C(5)$_B$); 64.7 (C(5)$_A$); 55.2 (OCH$_3$); 25.6 (SCH$_2$CH$_3$); 15.0 (SCH$_2$CH$_3$). Found: *m/z* 863.3457 [M + H]$^+$. $C_{50}H_{54}O_{11}S$. Calculated: 863.3460.

Ethyl (3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (10). Water (0.2 mL) and DDQ (46 mg, 0.2 mmol) were added to a solution of dimannoside **9** (145 mg, 0.168 mmol) in chloroform (2 mL). The reaction mixture was stirred for 1.5 h, then diluted with chloroform, washed with saturated aqueous $NaHCO_3$, and concentrated. Derivative **10** (114 mg, 91%) was isolated by column chromatography (toluene—ethyl acetate, 10 : 1 → 6 : 1) as a colorless syrup, $[\alpha]_D$ +5.4 (*c* 1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$), δ: 7.55—7.28 (m, 20 H, 4 Ph); 5.58 (s, 1 H, PhCH); 5.51 (s, 1 H, PhCH); 5.35 (s, 1 H, H(1)$_A$); 4.89 (d, 1 H, PhCH$_2$, J = 12.2 Hz); 4.83—4.78 (m, 3 H, H(1)$_B$, 2 PhCH$_2$); 4.76 (d, 1 H, PhCH$_2$, J = 11.8 Hz); 4.50 (d, 1 H, H(2)$_A$, $J_{2,3}$ = 3.2 Hz); 4.35—4.29 (m, 2 H, H(4)$_B$, H(6b)); 4.25—4.17 (m, 4 H, H(2)$_B$, H(4)$_A$, H(5)$_A$, H(6a)$_A$); 3.97 (dd, 1 H, H(3)$_A$, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 8.6 Hz); 3.84—3.78 (m, 2 H, H(6b)$_A$, H(6b)$_B$); 3.74 (dd, 1 H, H(3)$_B$, $J_{2,3}$ = 3.9 Hz, $J_{3,4}$ = 9.0 Hz); 3.45 (m, 1 H, H(5)$_B$); 2.65 (m, 2 H, SCH$_2$CH$_3$); 1.32 (t, 3 H, SCH$_2$CH$_3$, J = 7.4 Hz). ^{13}C NMR (150 MHz, $CDCl_3$), δ: 138.2, 138.1, 137.6, 137.5, 128.9—127.7, 126.1 (Ar); 101.5 (PhCH); 101.4 (PhCH); 97.6 (C(1)$_B$); 83.0 (C(1)$_A$); 78.9 (C(4)$_A$); 78.6 (C(4)$_B$); 76.3 (C(3)$_B$); 74.8 (C(3)$_A$); 74.6 (C(2)$_A$); 72.6 (PhCH$_2$); 72.4 (PhCH$_2$); 69.6 (C(2)$_B$); 68.7 (C(6)$_A$); 68.5 (C(6)$_B$); 66.9 (C(5)$_B$); 64.5 (C(5)$_A$); 25.5 (SCH$_2$CH$_3$); 15.0 (SCH$_2$CH$_3$). Found: *m/z* 760.3146 [M + NH$_4$]$^+$. $C_{42}H_{50}O_{10}NS$. Calculated: 760.3150.

Ethyl [3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-(*p*-methoxybenzyl)-β-D-mannopyranosyl]-(1→2)-(3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (11) and ethyl [3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-(*p*-methoxybenzyl)-α-D-mannopyranosyl]-(1→2)-(3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (12). Molecular sieves 4 Å (150 mg) and DTBP (80 μL, 0.36 mmol) were added to a solution of sulfoxide **8** (96 mg, 0.18 mmol) in CH_2Cl_2 (1 mL). The resulting mixture was stirred for 30 min at ~20 °C, then cooled to −80 °C, followed by the addition of Tf_2O (30 μL, 0.22 mmol). The reaction mixture was stirred for 5 min, then a solution of dimannoside **10** (95 mg, 0.13 mmol) in CH_2Cl_2 (1.5 mL) was added dropwise, the stirring was continued for 40 min at −80 °C. Then, the temperature of the reaction mixture was gradually increased to +10 °C over ~1 h, and the reaction was stopped by the addition of triethylamine (0.2 mL). This mixture was diluted with chloroform, filtered through a layer of celite, the celite was washed with chloroform. The combined filtrates were washed with water and concentrated. β-Product **11** (61 mg, 40%) and a-product **12** (24 mg, 16%) were isolated by column chromatography (toluene—ethyl acetate, 15 : 1 → 10 : 1).

Compound **11**, a colorless syrup, $[\alpha]_D$ −56.1 (*c* 1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$), δ: 7.57—7.19 (m, 32 H, 6 Ph, *p*-CH$_3$OC$_6$H$_4$); 6.81—6.77 (m, 2 H, *p*-CH$_3$OC$_6$H$_4$); 5.65 (s, 1 H, PhCH); 5.59 (s, 1 H, PhCH); 5.46 (s, 1 H, PhCH); 5.39 (s, 1 H, H(1)$_A$); 5.18 (s, 1 H, H(1)$_C$); 4.93 (d, 1 H, PhCH$_2$, J = 12.0 Hz); 4.90 (d, 1 H, PhCH$_2$, J = 12.8 Hz)); 4.84 (d, 1 H, PhCH$_2$, J = 12.6 Hz)); 4.74 (s, 1 H, H(1)$_B$); 4.71 (d, 1 H, PhCH$_2$, J = 12.0 Hz)); 4.69 (d, 1 H, PhCH$_2$, J = 12.0 Hz)); 4.63 (d, 1 H, PhCH$_2$, J = 12.2 Hz); 4.50 (d, 1 H, PhCH$_2$, J = 11.6 Hz); 4.47—4.43 (m, 4 H, H(2)$_A$, H(2)$_B$, H(2)$_C$, PhCH$_2$); 4.42—4.37 (m, 2 H, H(6a)$_B$, H(6a)$_C$); 4.31—4.24 (m, 3 H, H(4)$_C$, H(5)$_A$, H(6a)$_A$); 4.14 (t, 1 H, H(4)$_B$, J = 9.5 Hz); 4.05—3.96 (m, 3 H, H(3)$_A$,

$H(4)_A$, $H(6b)_C$); 3.85—3.79 (m, 2 H, $H(6b)_A$, $H(6b)_B$); 3.73 (dd, 1 H, $H(3)_B$, $J_{2,3}$ = 2.9 Hz, $J_{3,4}$ = 9.8 Hz); 3.68 (s, 3 H, OCH_3); 3.59 (dd, 1 H, $H(3)_C$, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 9.3 Hz); 3.49 (m, 1 H, $H(5)_C$); 3.43 (m, 1 H, $H(5)_B$); 2.69 (m, 2 H, $SC\underline{H}_2CH_3$); 1.43 (t, 3 H, $SCH_2C\underline{H}_3$, J = 7.4 Hz). ^{13}C NMR (150 MHz, $CDCl_3$), δ: 158.8, 138.6, 138.7, 138.2, 137.6, 137.4, 137.1, 131.5, 129.6—126.1, 125.3, 126.0, 113.4 (Ar); 103.0 ($C(1)_C$); 102.1 (Ph$\underline{C}$H); 101.7 (Ph$\underline{C}$H); 100.3 (Ph$\underline{C}$H); 98.7 ($C(1)_B$); 82.1 ($C(1)_A$); 79.3 ($C(3)_C$); 79.2 ($C(4)_A$); 78.3 ($C(4)_B$); 78.2 ($C(4)_C$); 76.2 (C(2)); 75.8 ($C(3)_B$); 75.7 (C(2)); 75.1 (C(2)); 74.8 ($C(3)_A$); 74.5 (Ph$\underline{C}H_2$); 72.2 (Ph$\underline{C}H_2$); 71.7 (Ph$\underline{C}H_2$); 71.1 (Ph$\underline{C}H_2$); 68.8 (2C, $C(6)_B$, $C(6)_C$); 68.7 ($C(6)_A$); 68.0 ($C(5)_C$); 67.9 ($C(5)_B$); 64.4 ($C(5)_A$); 55.1 (OCH_3); 25.6 ($S\underline{C}H_2CH_3$); 14.9 ($SCH_2\underline{C}H_3$). Found: *m/z* 1225.4584 $[M + Na]^+$. $C_{70}H_{74}O_{16}NaS$. Calculated: 1225.4590.

Compound **12**, a colorless syrup, $[\alpha]_D$ −7.9 (*c* 1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$), δ: 7.59—7.19 (m, 32 H, 6 Ph, *p*-$CH_3OC_6\underline{H}_4$); 6.82—6.79 (m, 2 H, *p*-$CH_3OC_6\underline{H}_4$); 5.69 (s, 1 H, PhC$\underline{H}$); 5.63 (s, 1 H, PhC$\underline{H}$); 5.60 (s, 1 H, $H(1)_C$); 5.39 (s, 1 H, $H(1)_A$); 5.36 (s, 1 H, PhC$\underline{H}$); 4.88 (d, 1 H, PhC$\underline{H}_2$, J = 11.8 Hz); 4.78—4.73 (m, 2 H, 2 PhC$\underline{H}_2$); 4.69 (d, 1 H, PhC$\underline{H}_2$, J = 12.4 Hz); 4.66 (s, 1 H, $H(1)_B$); 4.55 (s, 2 H, 2 PhC$\underline{H}_2$); 4.46 (dd, $H(6a)_C$, $J_{5,6}$ = 4.9 Hz, $J_{6a,6b}$ = 10.0 Hz); 4.42 (d, 1 H, PhC$\underline{H}_2$, J = 11.9 Hz); 4.38 (d, 1 H, $H(2)_B$, J = 1.6 Hz); 4.37—4.33 (m, 2 H, $H(2)_A$, $H(5)_C$); 4.31—4.25 (m, $H(4)_C$, $H(6a)_B$); 4.25—4.15 (m, 3 H, $H(3)_C$, $H(4)_A$, $H(5)_A$); 4.09 (t, $H(4)_B$, J = 9.5 Hz); 4.05—4.02 (m, 2 H, $H(2)_C$, $H(6a)_A$); 3.95—3.87 (m, 3 H, $H(3)_A$, $H(6b)_A$, $H(6b)_C$); 3.78—3.73 (m, 5 H, $H(3)_B$, $H(6b)_B$, OCH_3); 3.39 (m, 1 H, $H(5)_B$); 2.70—2.58 (m, 2 H, $SC\underline{H}_2CH_3$); 1.32 (t, 3 H, $SCH_2C\underline{H}_3$, J = 7.4 Hz). ^{13}C NMR (150 MHz, $CDCl_3$, δ: 159.1, 139.1, 138.9, 137.9, 137.6, 137.5, 137.4, 130.4, 129.7—127.1, 126.1, 126.0, 125.9, 113.6 (Ar); 101.6 (Ph$\underline{C}$H); 101.5 (Ph$\underline{C}$H); 100.6 (Ph$\underline{C}$H); 99.3 ($C(1)_C$); 99.2 ($C(1)_B$); 83.1 ($C(1)_A$); 79.6 ($C(4)_C$); 79.0 ($C(3)_B$); 78.9 ($C(4)_B$); 77.6 ($C(4)_A$); 76.8 ($C(2)_A$); 76.7 ($C(2)_C$); 76.4 ($C(3)_C$); 74.5 ($C(3)_A$); 73.5 (Ph$\underline{C}H_2$); 73.4 (Ph$\underline{C}H_2$); 72.9 ($C(2)_B$); 72.7 (Ph$\underline{C}H_2$); 70.8 (Ph$\underline{C}H_2$); 68.7 ($C(6)_C$); 68.4 ($C(6)_B$); 67.8 ($C(6)_A$); 67.6 ($C(5)_B$); 64.7 ($C(5)_A$); 64.4 ($C(5)_C$); 55.2 (OCH_3); 25.3 ($S\underline{C}H_2CH_3$); 14.9 ($SCH_2\underline{C}H_3$). Found: *m/z* 1241.4325 $[M + K]^+$. $C_{70}H_{74}O_{16}KS$. Calculated: 1241.4329.

3-Trifluoroacetamidopropyl [3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-(*p*-methoxybenzyl)-β-D-mannopyranosyl]-(1→2)-(3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1→2)-(3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (14). Molecular sieves 4 Å (125 mg) were added to a solution of thioglycoside **11** (55 mg, 0.046 mmol) and acceptor **13** (39 mg, 0.034 mmol) in CH_2Cl_2 (2.5 mL). The mixture was stirred for 30 min at ~20 °C and cooled to −10 °C, followed by the addition of NIS (20 mg, 0.094 mmol) and stirring for another 10 min. Then, the temperature was reduced to −40 °C and TfOH (3 μL, 0.034 μmol) was added. The temperature of the reaction mixture was gradually elevated to −10 °C over 40 min. The stirring was continued at this temperature until the reagents were completely consumed (TLC monitoring). The reaction was stopped by addition of triethylamine (0.1 mL), the mixture was diluted with chloroform and filtered through a layer of celite, the celite was washed with chloroform, the combined filtrates were washed with 1 *M* aqueous $Na_2S_2O_3$, the organic layer was concentrated. Pentasaccharide **14** (30 mg, 41%) was isolated by column chromatography (toluene—ethyl acetate, 6 : 1) as a colorless syrup, $[\alpha]_D$ −60.9 (*c* 1, $CHCl_3$). ^{1}H NMR (600 MHz, D_2O), δ: 7.54—6.94 (m, 62 H, 12 Ph, *p*-$CH_3OC_6\underline{H}_4$); 6.82 (br.s, 1 H, N$\underline{H}$); 6.73—6.59 (m, 2 H, *p*-$CH_3OC_6\underline{H}_4$); 5.60 (s, 1 H, PhC$\underline{H}$); 5.44 (s, 1 H, PhC$\underline{H}$); 5.40 (s, 1 H, PhC$\underline{H}$); 5.27 (s, 1 H, $H(1)_D$); 5.13 (d, $H(1)_B$, $J_{1,2}$ = 1.8 Hz); 5.06 (s, 1 H, $H(1)_E$); 4.93 (d, 1 H, $PhCH_2$, J = 12.1 Hz); 4.84 (d, 1 H, PhC$\underline{H}_2$, J = 10.9 Hz); 4.78 (d, $H(1)_A$, $J_{1,2}$ = 1.1 Hz); 4.77—4.66 (m, 4 H, PhC$\underline{H}_2$); 4.64—4.45, (m, 9 H, $H(2)_E$, 8 PhC$\underline{H}_2$); 4.45—4.33 (m, 6 H, $H(2)_C$, $H(2)_D$, $H(6a)_D$, 3 PhC$\underline{H}_2$); 4.32—4.22 (m, 3 H, $H(2)_B$, $H(6a)_E$, PhC$\underline{H}_2$); 4.22—4.09 (m, 3 H, $H(1)_C$, $H(4)_E$, $H(6a)_C$); 4.08—4.00 (m, 2 H, $H(2)_A$, $H(4)_D$); 3.93 (t, 1 H, $H(6b)_E$, $J_{5,6}$ = $J_{6a,6b}$ = 10.3 Hz); 3.89—3.62 (m, 13 H, $H(3)_A$, $H(3)_B$, $H(4)_A$, $H(4)_B$, $H(4)_C$, $H(5)_A$, $H(5)_B$, $H(6a)_A$, $H(6a)_B$, $H(6b)_A$, $H(6b)_C$, $H(6b)_D$, $OC\underline{H}_2CH_2CH_2N$); 3.62—3.50 (m, 6 H, $H(3)_D$, $H(3)_E$, $H(6b)_B$, $OC\underline{H}_3$); 3.50—3.43 (m, 2 H, $H(5)_D$, $OCH_2CH_2C\underline{H}_2N$); 3.43—3.32 (m, 2 H, $H(5)_E$, $OC\underline{H}_2CH_2CH_2N$); 3.32—3.24 (m, 2 H, $H(3)_C$, $OCH_2CH_2C\underline{H}_2N$); 2.76 (m, 1 H, $H(5)_C$); 1.78 (m, 2 H, $OCH_2C\underline{H}_2CH_2N$). ^{13}C NMR (150 MHz, D_2O, δ: 158.8, 156.9, 138.8—137.3, 131.7, 129.9—127.1, 126.3, 113.5 (Ar); 103.7 ($C(1)_E$); 102.2 (Ph$\underline{C}$H); 101.4 ($C(1)_D$); 101.4 (Ph$\underline{C}$H); 99.2 ($C(1)_A$); 99.1 ($C(1)_C$); 98.7 ($C(1)_B$); 80.5 ($C(3)_A$); 79.4 ($C(3)_E$); 78.7 ($C(4)_C$); 78.5 ($C(4)_D$); 78.4 ($C(4)_E$); 77.9 ($C(3)_B$); 77.2 ($C(3)_D$); 76.7 ($C(2)_D$); 75.7 (2 C, $C(2)_E$, $C(3)_C$); 75.2 (2 C, Ph$\underline{C}H_2$); 75.0 ($C(4)_A$); 74.8 ($C(4)_B$); 74.5 ($C(2)_A$); 74.4 (Ph$\underline{C}H_2$); 73.8 (Ph$\underline{C}H_2$); 73.6 (Ph$\underline{C}H_2$); 73.4 (Ph$\underline{C}H_2$); 72.9 ($C(2)_C$); 72.4 ($C(5)_A$); 72.2 (Ph$\underline{C}H_2$); 71.7 ($C(2)_B$); 71.5 ($C(5)_B$); 71.2 (Ph$\underline{C}H_2$); 70.7 (Ph$\underline{C}H_2$); 70.6 (Ph$\underline{C}H_2$); 69.3 ($C(6)_A$); 68.7 (2 C, $C(6)_D$, $C(6)_E$); 68.6 (2 C, $C(6)_B$, $C(6)_C$); 67.9 (2 C, $C(5)_D$, $C(5)_E$); 67.1 ($C(5)_C$); 66.1 ($O\underline{C}H_2CH_2CH_2N$); 55.1 ($O\underline{C}H_3$); 38.2 ($OCH_2CH_2\underline{C}H_2N$); 28.3 ($OCH_2\underline{C}H_2CH_2N$). Found: *m/z* 2214.8503 $[M + K]^+$. $C_{127}H_{133}F_3KNO_{28}$. Calculated: 2214.8520.

3-Aminopropyl β-D-mannopyranosyl-(1→2)-β-D-mannopyranosyl-(1→2)-β-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranoside, acetate (15). A 20% $Pd(OH)_2$/C (30 mg) was added to a solution of protected pentamannoside **14** (30 mg, 0.014 mmol) in a mixture of methanol (1 mL) and ethyl acetate (1 mL). The mixture obtained was stirred in the hydrogen atmosphere for 3 days. Then, the reaction mixture was diluted with methanol, the catalyst was filtered through celite, thoroughly washed with aqueous methanol (1 : 1). The combined filtrates were concentrated, NaOH (3 mg, 0.078 mmol) was added to a solution of the residue in water (1 mL), after 3 h the solution was neutralized with acetic acid and concentrated. The product was isolated by gel-chromatography as an acetate and lyophilized from water to obtain pentasaccharide **15** (6 mg, 47%), $[\alpha]_D$ −16.5 (*c* 0.4, water). ^{1}H NMR (600 MHz, D_2O), δ: 5.13 (s, 1 H, $H(1)_B$); 5.06 (s, 1 H, $H(1)_A$); 4.92 (s, 2 H, $H(1)_D$, $H(1)_E$); 4.84 (s, 1 H, $H(1)_C$); 4.40 (d, 1 H, $H(2)_D$, $J_{2,3}$ = 2.7 Hz); 4.27 (br.s, 1 H, $H(2)_B$); 4.24 (d, 1 H, $H(2)_C$, $J_{2,3}$ = 3.1 Hz); 4.14 (d, 1 H, $H(2)_E$, $J_{2,3}$ = 2.8 Hz); 3.99 (br.s, 1 H, $H(2)_A$); 3.94—3.82 (m, 8 H, $H(3)_A$, $H(3)_B$, $H(6a)_A$, $H(6a)_B$, $H(6a)_C$, $H(6a)_D$, $H(6a)_E$, $OC\underline{H}_2CH_2CH_2N$); 3.77—3.64 (m, 8 H, $H(3)_C$, $H(4)_A$, $H(5)_B$, $H(6b)_A$, $H(6b)_B$, $H(6b)_C$, $H(6b)_D$, $H(6b)_E$); 3.63—3.54 (m, 7 H, $H(3)_D$, $H(3)_E$, $H(4)_B$, $H(4)_D$, $H(4)_E$, $H(5)_A$, $OC\underline{H}_2CH_2CH_2N$); 3.50 (t, 1 H, $H(4)_C$, J = 9.7 Hz); 3.41—3.33 (m, 3 H, $H(5)_C$, $H(5)_D$, $H(5)_E$); 3.12 (m, 2 H, $OCH_2CH_2C\underline{H}_2N$); 1.98 (m, 2 H, $OCH_2C\underline{H}_2CH_2N$); 1.90 (s, 3 H, CH_3COO^-). ^{13}C NMR (150 MHz, D_2O), δ: 102.5, 102.2 (2 C, $C(1)_E$, $C(1)_D$); 101.5 ($C(1)_B$); 100.4 ($C(1)_C$); 99.5 ($C(1)_A$); 80.6 ($C(2)_C$); 79.9 ($C(2)_A$); 79.6 ($C(2)_D$); 79.3 ($C(2)_B$); 77.6 ($C(5)_D$); 77.4 (2 C, $C(5)_C$, $C(5)_E$); 74.5 ($C(5)_B$); 74.2 ($C(3)_E$); 74.1 ($C(3)_D$); 73.5 ($C(5)_A$); 73.1 ($C(3)_C$); 71.6 ($C(2)_E$); 71.4 ($C(3)_B$); 70.5 ($C(3)_A$); 68.7 ($C(4)_E$); 68.4

($C(4)_C$); 68.2 (2 C, $C(4)_A$, $C(4)_D$); 68.0 ($C(4)_B$); 66.2 ($O\underline{C}H_2CH_2CH_2N$); 62.4, 62.2, 62.1, 61.9 (5 C, $C(6)_A$, $C(6)_B$, $C(6)_C$, $C(6)_D$, $C(6)_E$); 38.7 ($OCH_2\underline{C}H_2CH_2N$); 27.9 ($OCH_2\underline{C}H_2CH_2N$); 24.6 ($\underline{C}H_3COO^-$). Found: *m/z* 886.3384 $[M + H]^+$. $C_{33}H_{60}NO_{26}$. Calculated: 886.3398.

This work was financially supported by the Russian Science Foundation (Project No. 14-50-00126).

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Received August 20, 2015;
in revised form October 9, 2015