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SYNTHETIC STUDIES

# Synthesis of *N*-Acetyllactosamine-Containing Oligosaccharides, Galectin Ligands

**V. V. Severov, I. M. Belyanchikov, G. V. Pazynina, and N. V. Bovin[1]**

*Shemyakin–Ovchinnikov Institute of Bioorganic Chemistry, Russian Academy of Sciences, ul. Miklukho-Maklaya 16/10, Moscow, 117997 Russia*

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**Abstract**—The following spacered oligosaccharides were synthesized: GlcNAcβ1-3Galβ1-4GlcNAcβ-sp, GlcNAcβ1-6Galβ1-4GlcNAcβ-sp, GlcNAcβ1-3(GlcNAcβ1-6)Galβ1-4GlcNAcβ-sp, Galβ1-4GlcNAcβ1-3Galβ1-4GlcNAcβ-sp, Galβ1-4GlcNAcβ1-6Galβ1-4GlcNAcβ-sp, Galβ1-4GlcNAcβ1-3(Galβ1-4GlcNAcβ1-6)Galβ1-4GlcNAcβ-sp, GlcNAcβ1-3(Galβ1-4GlcNAcβ1-6)Galβ1-4GlcNAcβ-sp, and Galβ1-4GlcNAcβ1-3(GlcNAcβ1-6)Galβ1-4GlcNAcβ-sp (sp = $O(CH_2)_2NH_2$). They represent *N*-acetyllactosamines substituted with *N*-acetylglycosamine or *N*-acetyllalctosamine residue at O3, O6, or at both positions of galactose. Glycosylation was achieved by coupling with *N*-trichloroethoxycarbonyl-protected glucosamine bromide in the presence of silver triflate.

*Key words: oligo-N-acetyllactosamines, oligosaccharide synthesis*

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## INTRODUCTION

Oligolactosamine and poly(lactosamine) fragments are the characteristic elements of architecture of complex *N*-chains of glycoproteins.[2] The specific interaction with proteins of galectin family is one of the functions of oligolactosamines [2]. The carbohydrate specificity was determined only for several galectins of the family consisting of 14 proteins. Even those galectins (first of all, galectin-1 and -3) that have been investigated better than others require additional studies, as there is no total consensus on their carbohydrate specificity in the studies reported. The further studies of galectins require new molecular tools, such as glycoconjugates that are usually synthesized from oligosaccharides. We describe in this work the synthesis of a series of linear and branched oligolactosamines, which are used in the studies of galectins in the form of individual soluble proteins and also as constituents of normal and transformed cells [3].

GlcNAcβ1-3Galβ1-4GlcNAcβ-sp, (**I**)

GlcNAcβ1-6Galβ1-4GlcNAcβ-sp, (**II**)

GlcNAcβ1-6
GlcNAcβ1-3 Galβ1-4GlcNAcβ-sp, (**III**)

Galβ1-4GlcNAcβ1-6
GlcNAcβ1-3 Galβ1-4GlcNAcβ-sp, (**IV**)

GlcNAcβ1-6
Galβ1-4GlcNAcβ1-3 Galβ1-4GlcNAcβ-sp, (**V**)

Galβ1-4GlcNAcβ1-3Galβ1-4GlcNAcβ-sp, (**VI**)

Galβ1-4GlcNAcβ1-6Galβ1-4GlcNAcβ-sp, (**VII**)

Galβ1-4GlcNAcβ1-6
Galβ1-4GlcNAcβ1-3 Galβ1-4GlcNAcβ-sp, (**VIII**)

sp = $O(CH_2)_2NH_2$.

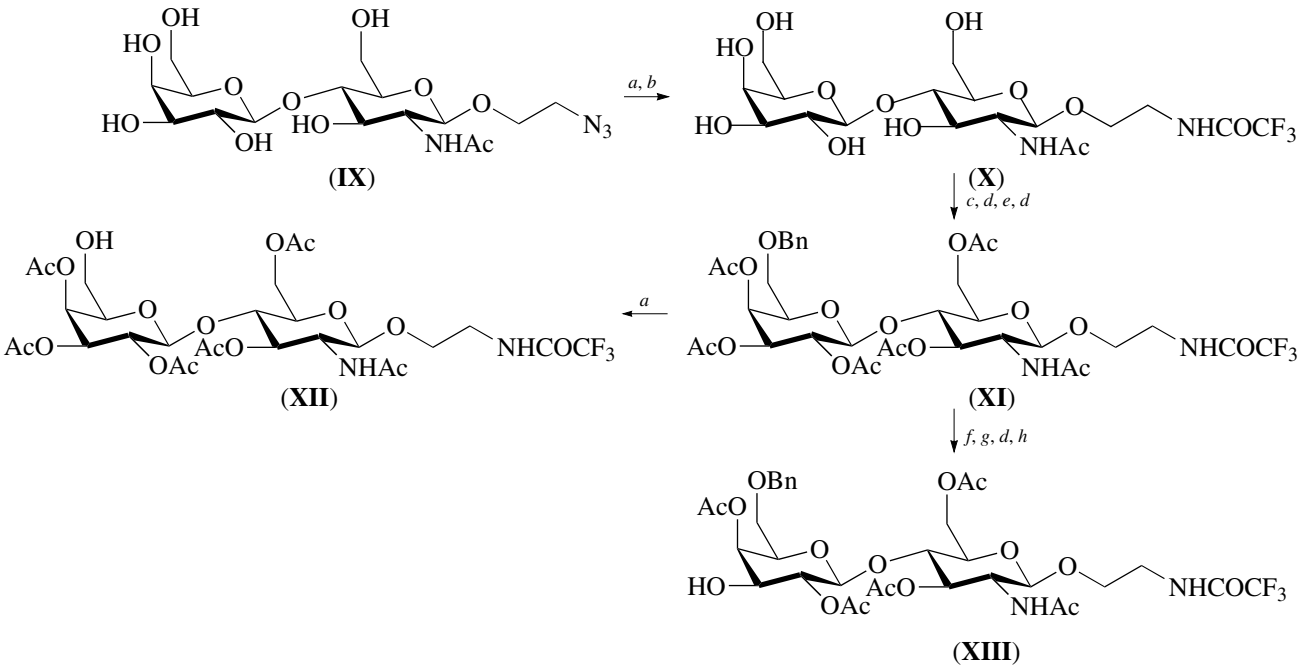
## RESULTS AND DISCUSSION

The goal of this study is the synthesis of oligosaccharides: two linear oligolactosamines (**VI**) and (**VII**), branched trilactosamine (**VIII**), and also their agalacto analogues (**I**)–(**V**). Glycosylation with *N*-Troc derivative of lactosamine or glucosamine by the Koenigs–Knorr method that allows the reaction to proceed stereospecifically and in a high yield [4] is a key stage in the synthesis. It should also be noted that the transformation of the TrocNH-fragment to the AcNH moiety does not involve other protective groups [4]. The use of these donors in the Koenigs–Knorr reaction has already been approved in the synthesis of another series of oligosaccharides, the fragments of glycoprotein *O*-chains [5, 6].

2-Azidoethyl-spacered lactosamine (**IX**) [7] was used as the starting compound for the construction of

[1] Corresponding author; phone: +7(495) 330-7138; fax: +7(495) 330-5592; e-mail: bovin@carbohydrate.ru.

[2] Abbreviations: AgOTf, silver triflate; Bn, benzyl; LacNAc, *N*-acetyllactosamine; TMM, tetramethylurea; and Troc, 2,2,2-trichloroethoxycarbonyl.



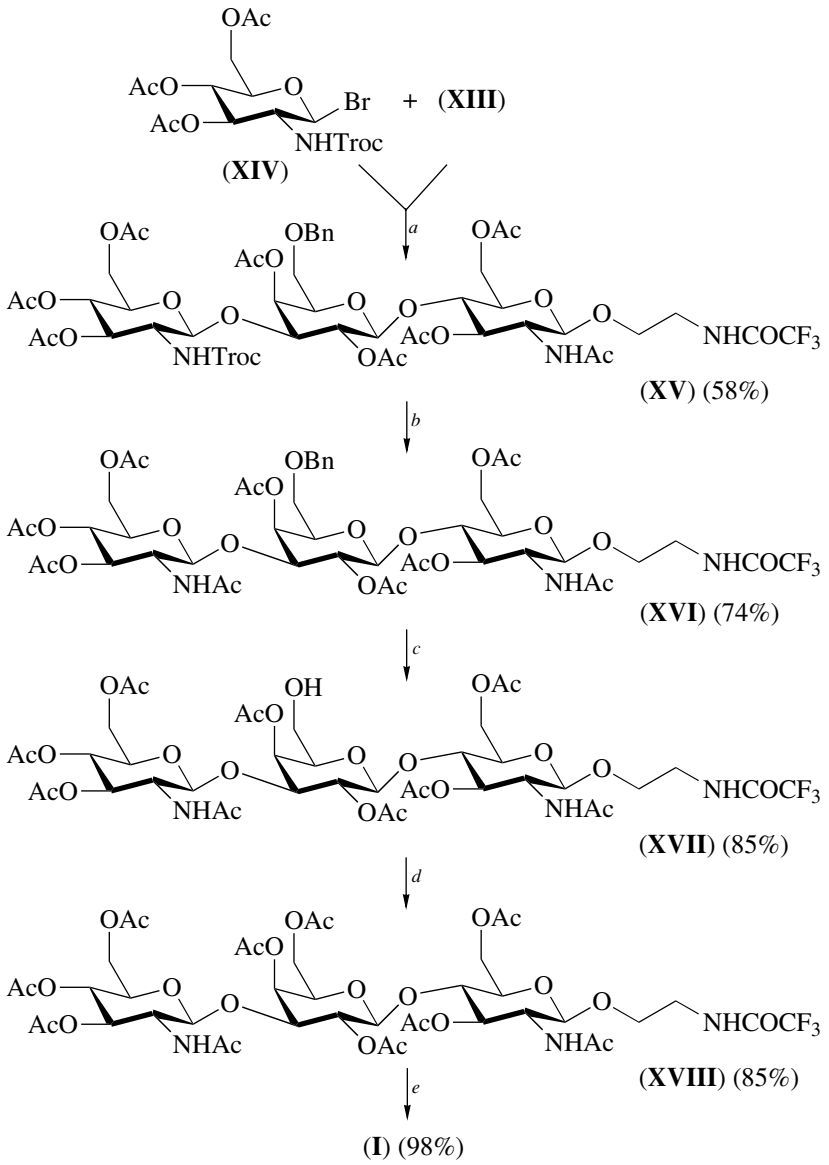

**Scheme 1.** Reagents: *a*: 10% Pd/C, $H_2$; *b*: $CF_3COOCH_3$, $NEt_3$, MeOH; *c*: $PhCH(OCH_3)_2$, TsOH, MeCN; *d*: $Ac_2O$/Py; *e*: $NaCNBH_3$, $HCl/Et_2O$; *f*: MeONa/MeOH; *g*: $CH_3C(OEt)_3$, TsOH, MeCN; *h*: 80% AcOH.

the core part of oligosaccharides (Scheme 1). Hydrogenation of the azide group resulted in an amine, which was protected with the *N*-trifluoroacetyl group by the treatment with methyl trifluoroacetate in methanol [8]. The substitution of 2-trifluoroacetamidoethyl spacer for the azidoethyl moiety was executed at the initial step of the synthesis, because the 2-trifluoroacetamidoethyl protective group is stable in the further synthetic procedures, particularly, at hydrogenolysis and, at the same time, can be quantitatively removed at the final step by an aqueous base.

Of two possible strategies for the creation of branching at the galactose residue, we have chosen the approach that included glycosylation of lactosamine first at position 3 of the galactose residue and then at position 6, because the primary hydroxy group is more reactive than the secondary hydroxy and its effective glycosylation is possible in the presence of the bulky substituent already introduced in position 3.

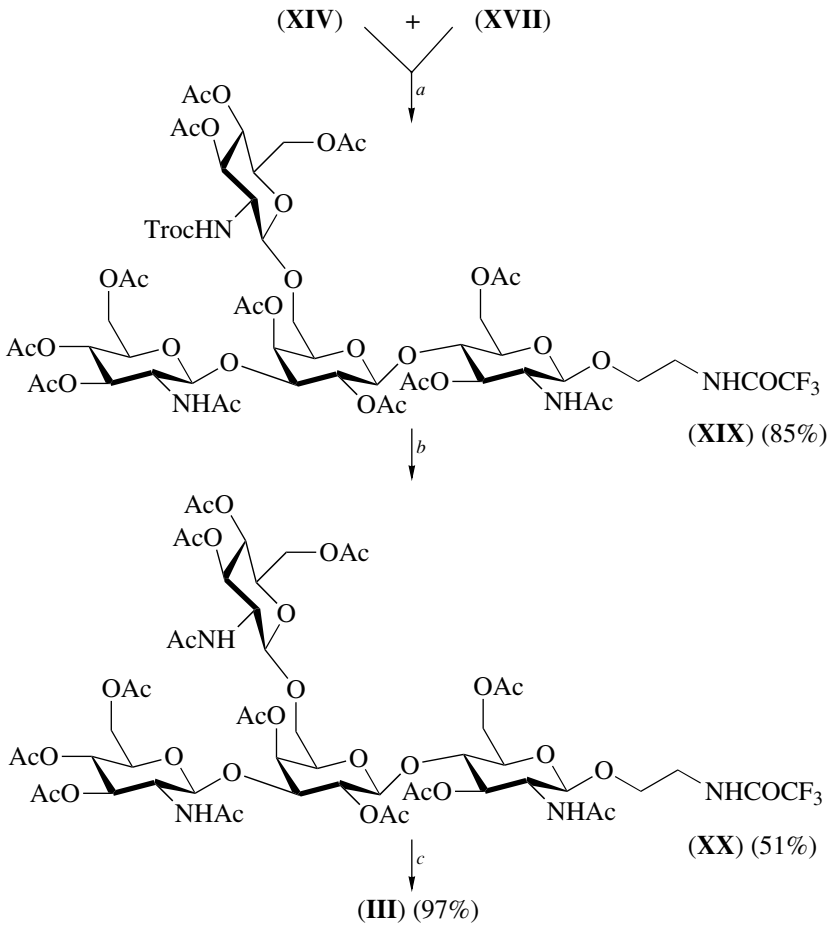
The benzyl group obtained from 4,6-*O*-benzylidene derivative was chosen for the selective protection of hydroxyl at C6 of galactose residue. The benzylidene protective group was introduced into lactosamine (**X**) by treatment with dimethoxytoluene in the presence of *p*-toluenesulfonic acid. The resulting benzylidene derivative was acetylated with acetic anhydride in pyridine without additional purification; the total yield after the two steps was 87%. The use of sodium cyanoborohydride [9] allowed a selective opening of the benzylidene cycle and, thus, the obtaining of the necessary derivative with the benzyl protective group at C6. Acetylation and chromatographic isolation led to (**XI**) in 84% yield. A comparison of the $^1H$ NMR spectrum of product (**XI**) with that of its benzylidene precursor proved the opening of the benzylidene acetal with the formation of 6-*O*-benzyl ether. The signal of the proton at C4 of galactose was shifted downfield (δ 5.460 ppm in lactosamine (**XI**) and 4.369 ppm in the benzylidene derivative), whereas the signals of H6' and H6" were shifted upfield (δ 3.521 and 3.437 ppm) as compared to those at δ 4.068 and 4.301 ppm in the benzylidene precursor. Furthermore, the signals of benzyl protons (δ 4.533 and 4.425 ppm) in the form of two doublets with the coupling constant $J_{hem}$ 11.7 Hz were observed.

Compound (**XI**) was deacetylated by Zemplen in 86% yield. Introduction of the 3',4'-orthoester protective group [10] with triethyl orthoacetate in the presence of *p*-toluenesulfonic acid in acetonitrile followed by acetylation and opening of the orthoester cycle with acetic acid permitted the obtaining of derivative (**XIII**) in 70% yield. The presence of free OH group at C3 of the galactose residue is indicated by an upfield shift of the signal of H3 (δ 3.810 ppm, $J_{3,OH}$ 6.1 Hz) as compared to that in (**XI**) acetylated at C3 of galactose (δ 4.985 ppm). The lactosamine derivative with the free OH group in position 4 of galactose (δ 4.147 ppm, H4) and acetyl group at C3 (δ 4.896 ppm, H3), which was apparently generated upon the chromatography on silica gel due to migration of the acetyl group (it was not observed in the reaction mixture according to TLC), was the main by-product of this transformation. The proportion of the 4-OH derivative can be decreased by the addition of 0.5% of pyridine in the eluent for chromatography.




**Scheme 2.** Reagents: *a*: AgOTf, TMM, molecular sieves 4Å, $CH_2Cl_2$; *b*: Zn, AcOH; *c*: 10% Pd/C, $H_2$; *d*: $Ac_2O$/Py; *e*: MeONa/MeOH, then NaOH, $H_2O$.

Oligosaccharides (**I**), (**III**), and (**IV**) with the GlcNAcβ(1-3')LacNAc fragment were obtained from (**XIII**) by its glycosylation with the bromide of glucosamine Troc derivative (**XIV**), which was synthesized from the corresponding peracetate by treatment with hydrogen bromide in acetic acid (Scheme 2). Glycosylation was carried out in dichloromethane in the presence of AgOTf, TMM, and molecular sieves 4 Å. The yield of trisaccharide (**XV**) was 58%, 38% of the starting disaccharide (**XIII**) being recovered. Note that this result was obtained using twofold excess of donor (**XIV**) relative to acceptor (**XIII**). In the case of (**XIV**) : (**XIII**) ratio equal 1.5, the yield of (**XV**) was 46%. Glycosylation of the corresponding 3,4-diol resulted in the mixture of mono- (1–3 and 1–4) and diadducts with yield of the target isomer (**XV**) of approximately 30% after acetylation and 50% recovery of disaccharide (**XIII**) in the form of 3-acetate. The use of the trichloroacetimidate of Troc-protected glucosamine as the glycosyl donor instead of bromide (**XIV**) also did not give the expected result: the yield of compound (**XV**) was 38%. Thus, the target product was obtained in the highest yield upon glycosylation of glycosyl acceptor (**XIII**) bearing one OH group with glycosyl bromide (**XIV**) using AgOTf as the promoter. The presence of glycosyl substituent at C3 of the Gal residue was confirmed by the position of the signal of H3b in the spectrum of (**XV**) (δ 3.935 ppm) as compared with the derivatives bearing OAc group in this position (δ ~ 5.0 ppm), e.g., δ 4.985 ppm in (**XI**). The configuration of the ter-



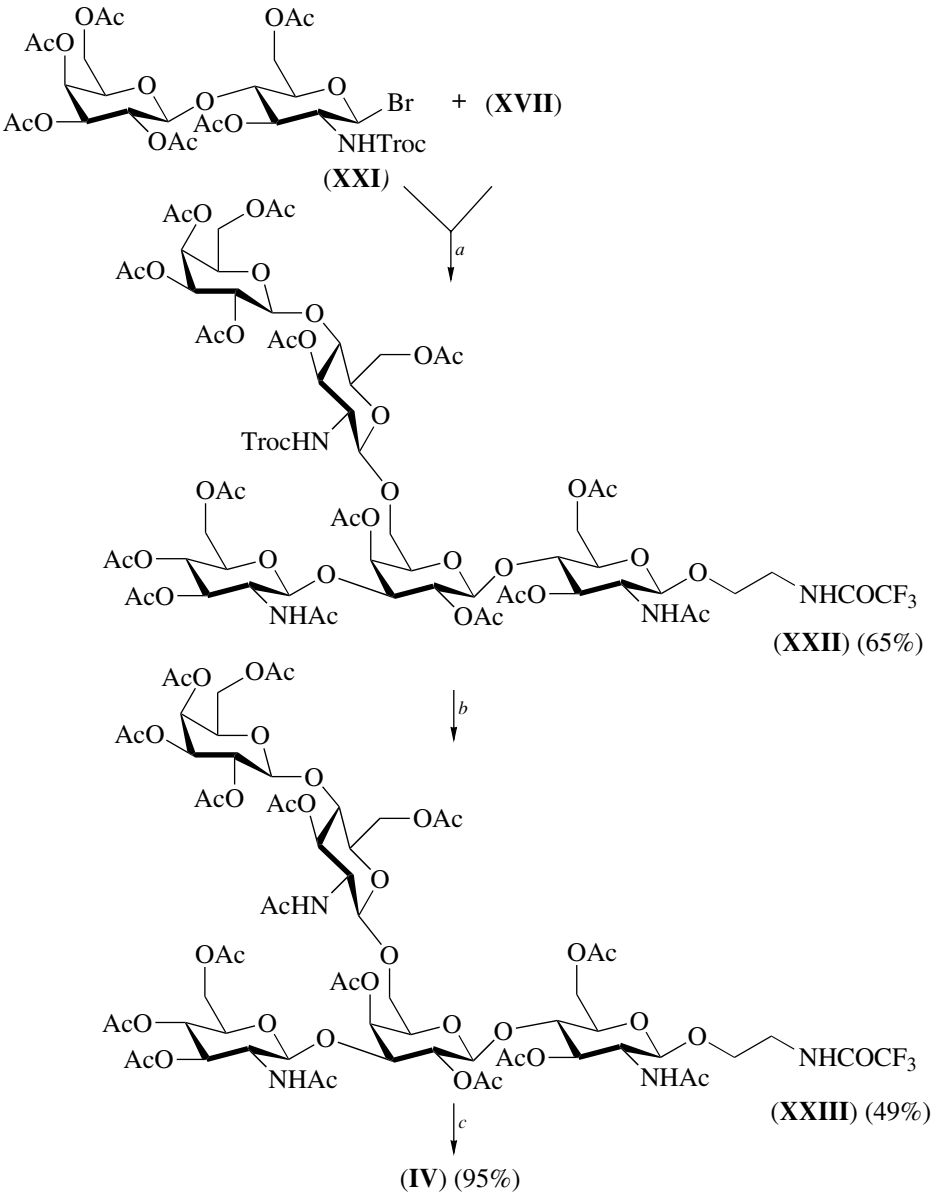

**Scheme 3.** Reagents: *a*: AgOTf, TMM, molecular sieves 4Å, $CH_2Cl_2$; *b*: Zn, AcOH; *c*: MeONa/MeOH, then NaOH, $H_2O$.

minal glucosamine unit was confirmed by the value of coupling constant $J_{1c,2c}$ 8.3 Hz. The presence of Troc moiety in the resulting compound was confirmed by two doublets (δ 4.975 and 4.506 ppm, $J_{hem}$ 12.5 Hz). Glycosylation was hereinafter achieved according to a similar method varying the excess of a glycosyl donor within the range of 1.5–2 in dependence on the expected activity of glycosyl acceptor.

Despite of the literature data [11] on the stability of the Troc protective group under the conditions of hydrogenolysis in neutral medium, our attempt to remove the benzyl protective group in (**XV**) in the presence of palladium on carbon resulted in a multicomponent mixture. Therefore, we first substituted *N*-acetyl protection for the *N*-Troc protective group by the treatment of (**XV**) with zinc in acetic acid–acetic anhydride to get product (**XVI**) in 74% yield. Its $^1$H NMR spectrum exhibited no doublets of Troc group; instead, nine singlets of acetyl groups were present [one more than in lactosamine (**XV**)]. The subsequent hydrogenolysis of benzyl derivative (**XVI**) resulted in the formation of (**XVII**), containing one OH group at C6 of galactose unit, in 85% yield. We also isolated from the reaction mixture a product of migration of acetyl group from C4 to C6 of the galactose fragment (~10%) (the value of the chemical shift of H4 in the product of migration was 4.343 ppm, whereas that of trisaccharide (**XVII**) was 5.488 ppm). The amount of the migration product increased with the time of hydrogenolysis and chromatographic purification.

Acetylation of (**XVII**) resulted in peracetate (**XVIII**) in 85% yield. The necessity of this step is substantiated by the facts that oligosaccharides in the form of peracetates are convenient for additional chromatographic purification and their $^1$H NMR spectra are more informative than those of partially protected carbohydrates. The subsequent deacetylation of peracetate (**XVIII**) and removal of the *N*-trifluoroacetyl protective group resulted in the target trisaccharide (**I**) in 98% yield.

Glycosylation of trisaccharide (**XVII**) with the glycosyl bromide of Troc derivative of glucosamine (**XIV**) (Scheme 3) and lactosamine (**XXI**) (Scheme 4) resulted in tetrasaccharide (**XIX**) (in 85% yield) and in pentasaccaride (**XXII**) (in 65% yield), respectively. Compound (**XIX**) that appeared to be homogeneous according to TLC contained in fact ~20% of impurity according to $^1$H NMR spectroscopy. In this and subsequent



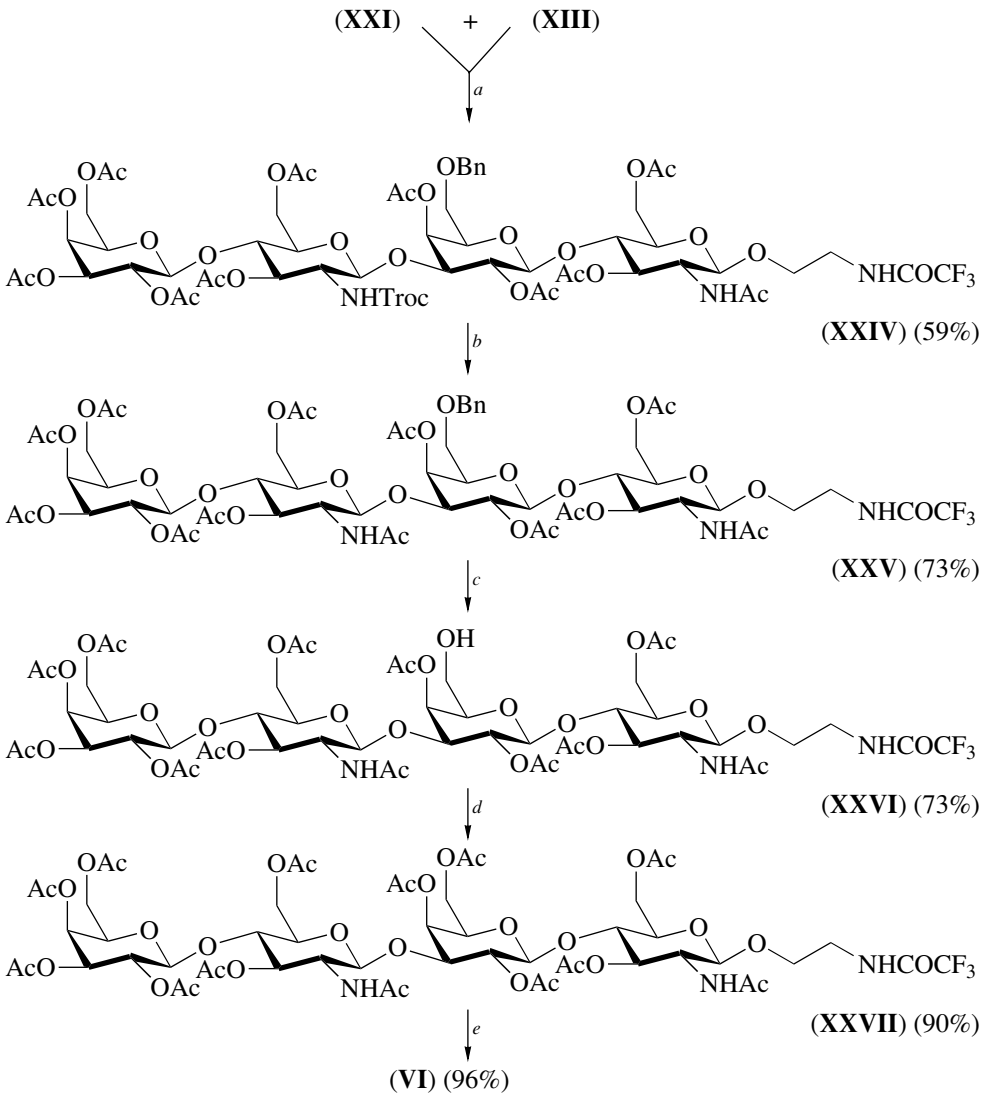

**Scheme 4.** Reagents: *a*: AgOTf, TMM, molecular sieves 4Å, $CH_2Cl_2$; *b*: Zn, AcOH; *c*: MeONa/MeOH, then NaOH, $H_2O$.

cases, the total assigning of the signals in the $^1$H NMR spectra of oligosaccharide Troc-derivatives was not achieved, since these compounds usually contained impurities (mainly α-anomers) and, furthermore, the spectra of *N*-acetyl derivatives are easier to interpret. Then, the *N*-acetyl protective group was substituted for Troc by treatment with zinc in acetic acid–acetic anhydride to give peracetates (**XX**) and (**XXIII**) in 51 and 59% yields, respectively.

Deacetylation and removal of *N*-trifluoroacetyl protective group resulted in the target compounds (**III**) and (**IV**) in 97 and 95% yields, respectively.

Oligosaccharides (**V**), (**VI**), and (**VIII**) containing the LacNAcβ(1–3')LacNAc fragment were obtained as follows. Compound (**XIII**) was glycosylated with the glycosyl bromide of lactosamine Troc derivative (**XXI**) (Scheme 5) to give tetrasaccharide (**XXIV**) in 59% yield. The subsequent substitution of the *N*-acetyl protective group for Troc moiety resulted in (**XXV**) in 73% yield. Its $^1$H NMR spectrum corresponded to the structure expected: the four H1 signals were characterized by the coupling constants $J_{1,2}$ of 7.8–8.3 Hz, the formation of the GlcN(1-3)Gal links was confirmed by the position of H3 (δ 3.67–3.83 ppm) in the glycosylated galactose residue (see above).

Compound (**XXV**) was hydrogenolyzed to (**XXVI**) with a free OH group at C6 of the internal galactose residue in 73% yield, which was proved by the $^1$H NMR spectroscopy: the signals of H6' and H6"[a5] are shifted




**Scheme 5.** Reagents: *a*: AgOTf, TMM, molecular sieves 4Å, $CH_2Cl_2$; *b*: Zn, AcOH; *c*: 10% Pd/C, $H_2$; *d*: $Ac_2O$/Py; *e*: MeONa/MeOH, then NaOH, $H_2O$.

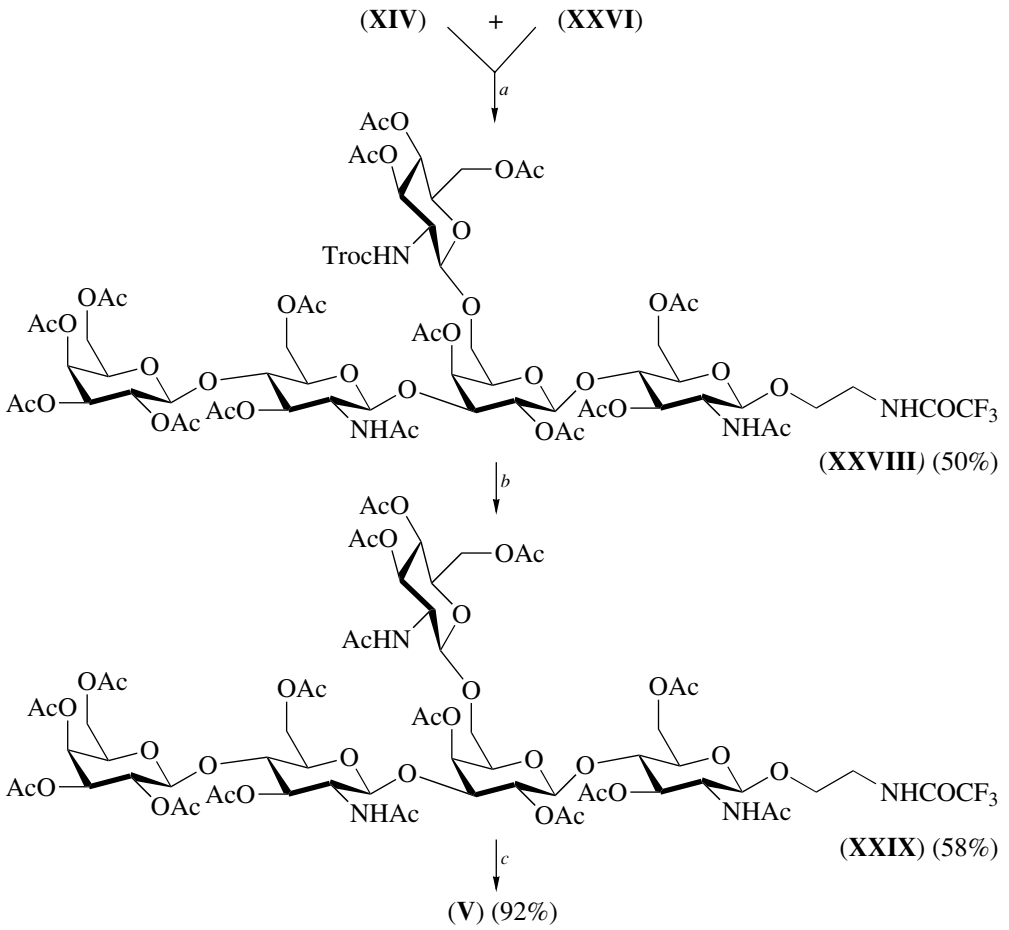
downfield (δ 3.55–3.77 ppm) as compared to those of the benzyl derivative (**XXV**) (δ 3.43–3.51 ppm).

Acetylation of (**XXVI**) gave peracetate (**XXVII**) in 90% yield. The subsequent deacetylation and removal of *N*-trifluoroacetyl protective group resulted in tetrasaccharide (**VI**) in 96% yield.

Glycosylation of (**XXVI**) with the glycosyl bromide of Troc derivative of glucosamine (**XIV**) (Scheme 6) and lactosamine (**XXI**) (Scheme 7) afforded pentasaccaride (**XXVIII**) in 50% yield and hexasaccharide (**XXX**) in 53% yield, respectively. The subsequent substitution of *N*-acetyl protective group for the Troc protective group resulted in peracetate (**XXIX**) in 58% yield and peracetate (**XXXI**) in 46% yield, respectively. Deacetylation of peracetates and removal of *N*-trifluoroacetyl protective group resulted in the target oligosaccharides (**V**) and (**VIII**) in 92 and 93% yield, respectively.

To obtain lactosamine derivatives (**II**) and (**VII**) nonsubstituted in position-3 of the galactose unit, lactosamine derivative (**XI**) was hydrogenolyzed to disaccharide (**XII**) (see Scheme 1) with OH group at C6 of the terminal galactose unit (H4, δ 5.557; H6', δ 3.799; and H6", δ 3.655 ppm) in 69% yield. The lactosamine derivative with OH group at C4 of the galactose residue (H4, δ 4.152 ppm, H6' and H6", δ 4.399 ppm) was obtained as a by-product in 14% yield.

Glycosylation of lactosamine derivative (**XII**) with glycosyl bromide (**XIV**) resulted in compound (**XXXII**) in 79% yield (the purity was ~80% according to $^1$H NMR spectroscopy) (Scheme 8). Glycosylation of compound (**XII**) with glycosyl bromide (**XXI**) resulted in (**XXXIV**) in 61% yield (Scheme 9). The fur-




**Scheme 6.** Reagents: *a*: AgOTf, TMM, molecular sieves 4Å, $CH_2Cl_2$; *b*: Zn, AcOH; *c*: MeONa/MeOH, then NaOH, $H_2O$.

ther substitution of the *N*-acetyl protective group for the Troc moiety resulted in peracetates (**XXXIII**) and (**XXXV**) in 59 and 68% yield, respectively. Deacetylation of peracetates and removal of the *N*-trifluoroacetyl protective group gave the target oligosaccharides (**II**) and (**VII**) in 99 and 95% yield, respectively.

The structures of the compounds were confirmed by mass spectrometry and $^1$H NMR spectroscopy. The total assignment of the signals for the peracetates of all oligosaccharides synthesized was achieved by 2D-$^1$H, $^1$H-COSY experiments.

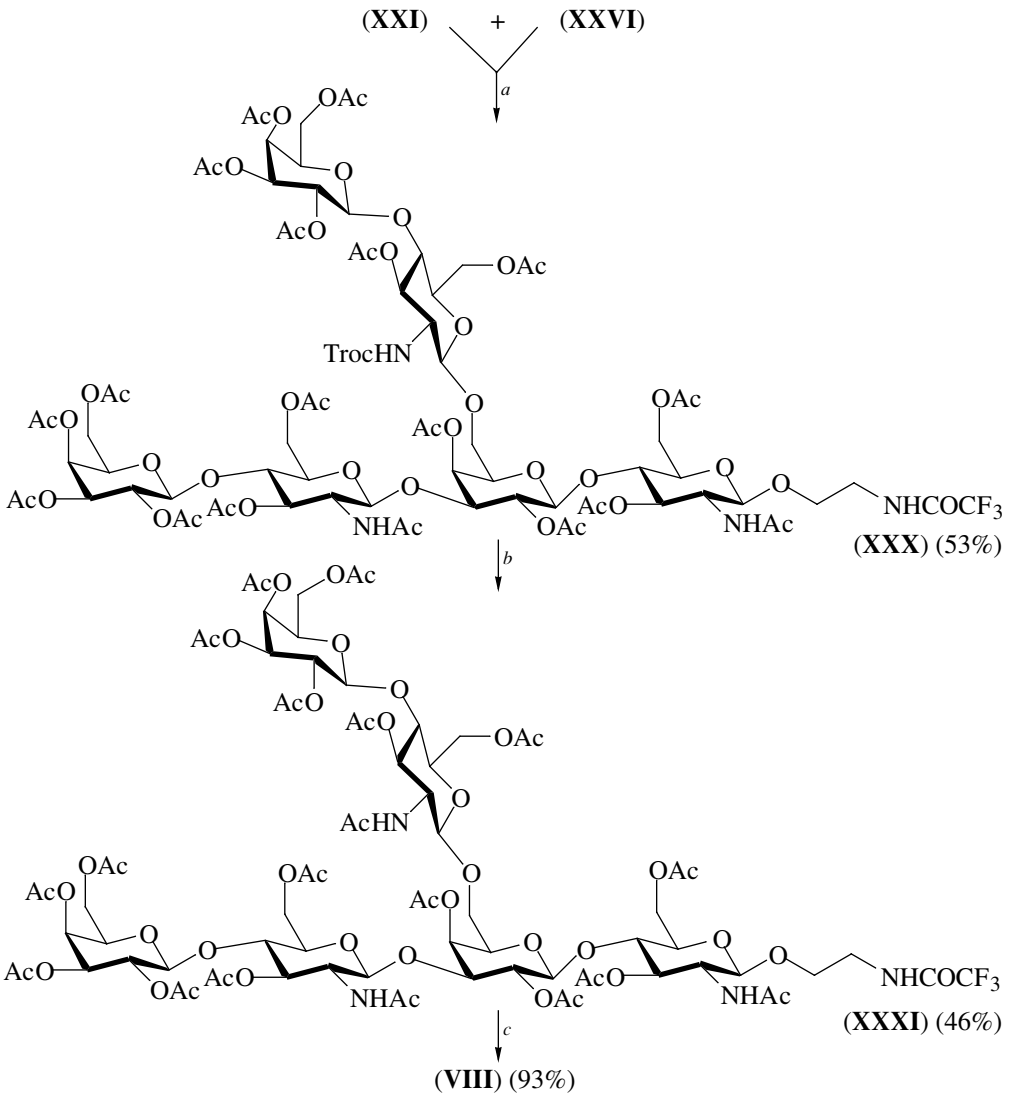
We should note that the glycosylation was not β-stereospecific. Glycosylation of the hydroxy group at C6 of the galactose residue of lactosamine (**XII**) with glucosamine (**XIV**) resulted in the formation of 18% of α-anomer, whereas the use of lactosamine (**XXI**) as the glycosyl donor gave 7% of the α-anomer. Glycosylation of the hydroxyl group at C3 of lactosamine (**XIII**) with glucosamine (**XIV**) yielded 5% of α-anomer. In other cases, α-anomers were generated in the amounts not exceeding 2%. The separation of the anomer mixture was more effective after the substitution of the *N*-acetyl protective group for the Troc protective group. Also note that low yields of the target products of glycosylation are due to a low conversion degree rather than side processes taking place (taking into account the recovery of glycosyl acceptors, the yields exceed 80%).

The strategy of block synthesis used in this study is one of the most convenient approaches to the synthesis of complex oligosaccharides. This approach is especially effective for the synthesis of a series of structures containing an identical fragment. As compared to the strategy of sequential chain lengthening, this method allows obtaining the same oligosaccharides in a lesser number of synthetic steps [12].

Thus, glycosylation with lactosamine block (**XXI**) is a convenient method for the synthesis of oligolactosamines. Synthesis of some linear lactosamines is reported in [13–16]. We have herein demonstrated that this approach also gives good results for the synthesis of the branched oligolactosamine chains.

## EXPERIMENTAL

Values of optical rotation were measured on a Jasco DIP-360 digital polarimeter at 25°C. $^1$H NMR spectra were registered on a Bruker WM spectrometer (500 MHz) at 25°C. Values of chemical shifts (δ, ppm)

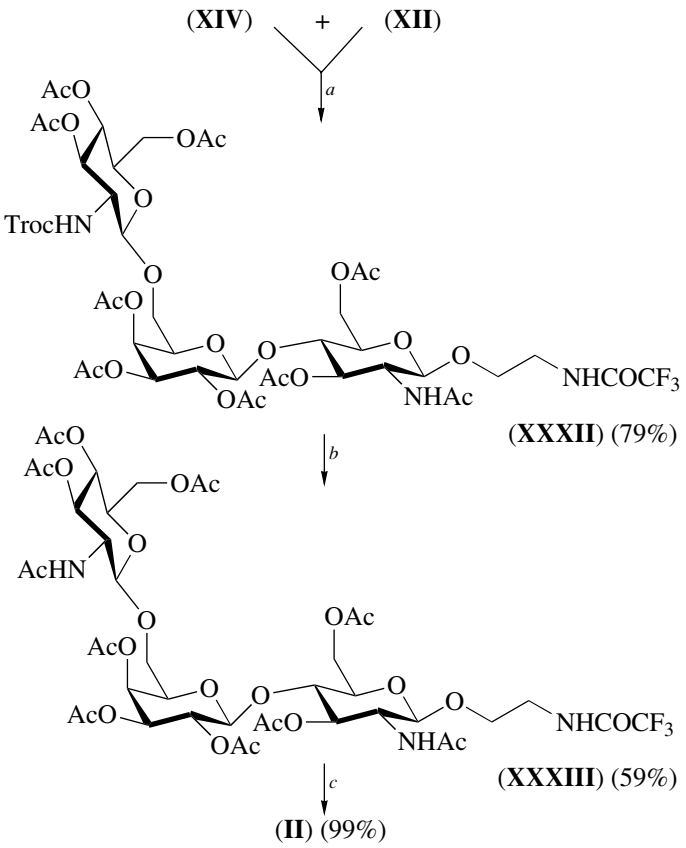



**Scheme 7.** Reagents: *a*: AgOTf, TMM, molecular sieves 4Å, $CH_2Cl_2$; *b*: Zn, AcOH; *c*: MeONa/MeOH, then NaOH, $H_2O$.

are given using residual signals of solvents: $D_2O$ (δ 4.750), $CDCl_3$ (δ 7.270), or DMSO-$d_6$ (δ 2.500) as internal standards; values of coupling constants are given in Hz. Signals in $^1H$ NMR spectra were assigned using the technique of the suppression of spin coupling (double resonance) and 2D-$^1H$,$^1H$-COSY experiments. Mass spectra were registered on a Vision-2000 (Thermo Bioanalysis, UK) MALDI TOF mass spectrometer using dihydroxybenzoic acid as a matrix. TLC was carried out on silica gel 60 precoated plates (Merck, Germany). The spots were visualized by spraying with 5% aqueous orthophosphoric acid and subsequent heating at 150°C in the case of carbohydrates or by soaking in a ninhydrin solution (3 g/l in 30 : 1 butanol–acetic acid) in the case of amines. Column chromatography was carried out on silica gel 60 (0.040–0.063 μm, Merck, Germany) and gel chromatography, on Sephadex LH-20 (Pharmacia, Sweden). Solvents were removed in a vacuum at 30–40°C. Solvents for glycoside synthesis were dried by distillation from drying agents and stored over molecular sieves. Solid reagents were dried for 2 h in a vacuum (0.1 mm Hg) at 20–40°C.

Deacetylation was executed according to Zemplen in anhydrous methanol by addition of 2 M sodium methylate in methanol up to pH 8–9 to a solution of acetylated compound. After the reaction was over, $Na^+$ ions were removed with cation exchange resin Dowex 50X-400 ($H^+$ form, Acros, Belgium); the solution was evaporated in a vacuum.

**Glycosyl bromide (XIV).** Acetyl bromide (0.256 ml, 3.2 mmol) was added to a solution of peracetylated Troc derivative of glucosamine (0.21 mmol) in anhydrous dichloromethane (2 ml) and acetic acid (0.5 ml), the mixture was cooled to 0°C, and methanol (0.128 ml, 3.2 mmol) was added. The reaction mixture




**Scheme 8.** Reagents: *a*: AgOTf, TMM, molecular sieves 4Å, $CH_2Cl_2$; *b*: Zn, AcOH, *c*: MeONa/MeOH, then NaOH, $H_2O$.

was kept for 1 h at room temperature and poured on crashed ice. The organic layer was diluted with chloroform; subsequently washed with water, saturated sodium bicarbonate, and water; filtered through a cotton layer; concentrated in a vacuum; and coevaporated with toluene. The residue was used for glycosylation without additional purification on the same day.

**Glycosyl bromide (XXI).** Bromine (18 μl, 0.37 mmol) was added to a solution of thioglycoside of peracetylated Troc derivative of lactosamine (270 mg, 0.332 mmol) in anhydrous dichloromethane (10 ml) cooled to 0°C. The reaction mixture was kept for 1 h at 0°C, concentrated, coevaporated with toluene, and used without additional purification on the same day, considering the yield to be quantitative; $R_f$ 0.60 (10 : 1 chloroform–isopropanol).

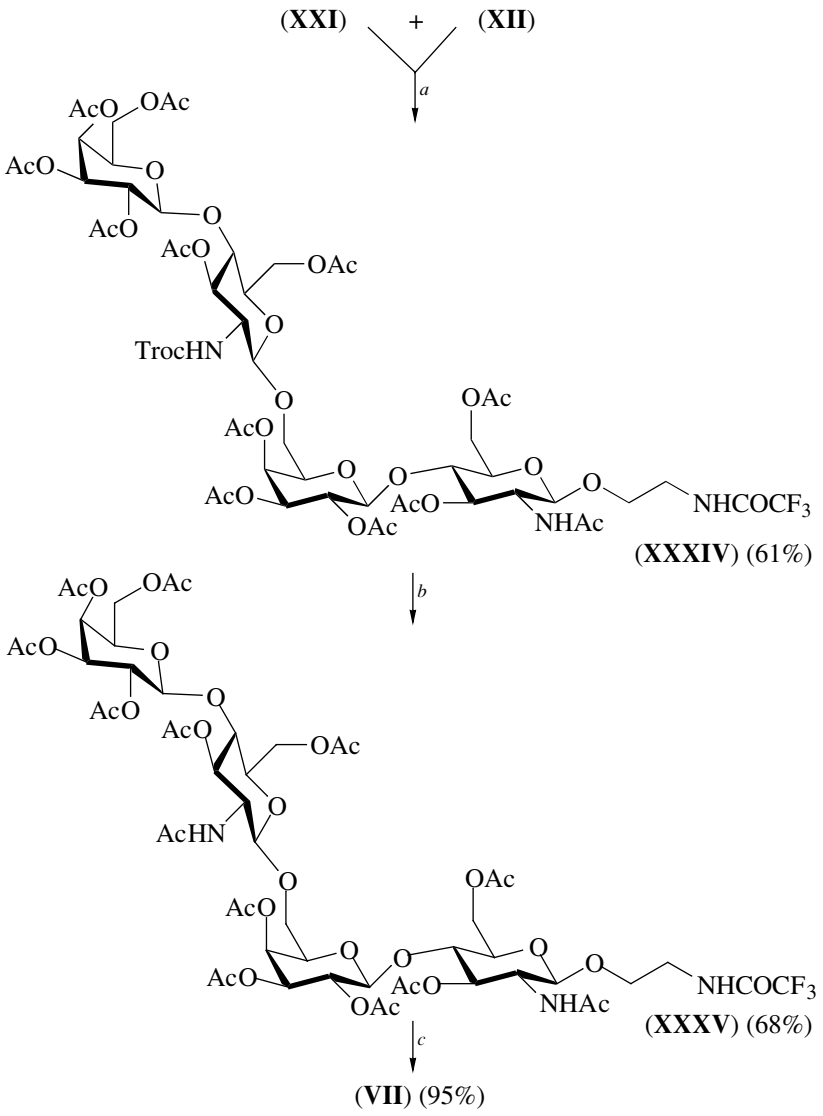
**A general glycosylation procedure.** A mixture of a glycosyl acceptor (0.1 mmol), AgOTf (0.15 mmol), TMM (0.15 mmol), and freshly calcined molecular sieves 4Å (300 mg) in anhydrous dichloromethane (5 ml) was stirred for 30 min at room temperature in the dark. Additional portion of molecular sieves 4Å (100 mg) was added and a solution of a glycosyl bromide (0.15 mmol) in anhydrous dichloromethane (2 ml) was added. The mixture was stirred for 15–20 h and filtered, the filtrate was concentrated in a vacuum, and the product was isolated by column chromatography on silica gel.

**Acetylation** was carried out by treatment with 2 : 1 pyridine–acetic anhydride at 20°C for 12–24 h. After the reaction was over, the reagents were removed by coevaporation with toluene.

**Hydrogenolysis** was achieved in methanol or 1 : 1 methanol–water at atmospheric pressure for 1–3 h in the presence of 10% Pd/C (Merck, Germany). The catalyst was taken at a catalyst–substrate mass ratio of 2 : 1.

**Removal of Troc group and *N*-acetylation.** Freshly activated zinc powder (4 g) and then thriethylamine (0.5 ml) were added to a solution of a Troc derivative (0.5 mmol) in acetic acid (40 ml) and acetic anhydride (2 ml). The reaction mixture was stirred for 20–30 h and filtered, the solvents were removed, and the residue was chromatographed on a Sephadex LH-20 column (elution with 1 : 1 chloroform–methanol).

**Deacetylation with simultaneous removal of the *N*-trifluoroacetyl protective group.** Sodium methylate (50 μl of 2 M solution in methanol) was added to a solution of a peracetate (0.05 mmol) in anhydrous methanol (2 ml). The solution was kept for 1 h and concentrated in a vacuum. Water (2 ml) was added, and the mixture was kept for 3 h and then applied onto a column with cation exchange resin Dowex 50 ($H^+$). The




**Scheme 9.** Reagents: *a*: AgOTf, TMM, molecular sieves 4Å, $CH_2Cl_2$; *b*: Zn, AcOH; *c*: MeONa/MeOH, then NaOH, $H_2O$.

target compound was eluted with 1 M ammonia, the eluate was concentrated in a vacuum, and the residue was lyophilized.

**2-Trifluoroacetamidoethyl 2-acetamido-2-deoxy-4-*O*-(β-*D*-galactopyranosyl)-β-*D*-glucopyranoside (X).** A solution of azide (**IX**) (4.82 g, 10.65 mmol) in 1 : 1 methanol–water (150 ml) was subjected to hydrogenolysis over 10% Pd/C (2.4 g) for 1.5 h. The reaction mixture was then filtered; the cation exchange resin Dowex 50 ($H^+$) (35 ml) was added to the filtrate. Then the resin was filtered off and washed with 1 : 1 methanol–water (4 × 20 ml). The product was eluted with 1 M ammonia, and the eluate was concentrated in a vacuum to give 3.77 g (8.84 mmol, 83%) of 2-aminoethyl derivative of *N*-acetyllactosamine; $R_f$ 0.60 (3 : 1 : 1 : 1 ethanol–water–pyridine–acetic acid). The resulting product was dissolved in anhydrous methanol (150 ml), methyl trifluoroacetate (6 ml) and thriethylamine (2 ml) were added, and the mixture was stirred for 2.5 h until the negative test for amine. The reaction mixture was diluted with anhydrous methanol (50 ml) and quenched with Dowex 50 ($H^+$) up to the neutral reaction of medium. The solution was filtered and then concentrated in a vacuum. The residue was purified by gel filtration on Sephadex LH-20 (elution with 0.5% aqueous acetic acid) to give 3.91 (85%) of (**X**) (85%), $R_f$ 0.89 (3 : 1 : 1 : 1 ethanol–water–pyridine–acetic acid); $R_f$ 0.40 (2 : 3 : 1 isopropanol–ethanol–water); $[\alpha]_D$ –15.8 (*c* 1, water); MS, *m/z*: 545 (522 + 23) $M^+ + Na^+$.

**2-Trifluoroacetamidoethyl 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-(2,3,4-tri-*O*-acetyl-6-*O*-benzyl-β-*D*-galactopyranosyl)-β-*D*-glucopyranoside (XI).** α,α-Dimethoxytoluene (2.2 ml, 12 mmol) and *p*-toluenesulfonic acid (0.63 g) (to pH 2–3) were added to a solution of disaccharide (**X**) (3.91 g, 7.48 mmol) in anhydrous acetonitrile (200 ml). A gradual precipita-

tion of the product was observed. After 24 h, the reaction mixture was quenched with pyridine, concentrated, and coevaporated with toluene. The dry residue was acetylated with 2 : 1 pyridine–acetic anhydride (45 ml). Chromatography on silica gel (elution with 4 : 2 : 1 hexane–chloroform–isopropanol) resulted in 5.08 g (87%) of 2-trifluoroacetamidoethyl 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-(2,3-di-*O*-acetyl-4,6-*O*-benzylidene-β-*D*-galactopyranosyl)-β-*D*-glucopyranoside; $R_f$ 0.21 (4 : 2 : 1 hexane–chloroform–isopropanol); $^1$H NMR ($CDCl_3$): 1.952, 2.051, 2.054, 2.099, and 2.120 (5 × 3 H, 5 s, 5 Ac), 3.414–3.584 (4 H, m, C$H_2$N, H5a, H5b), 3.686 (1 H, m, OC*H*), 3.797 (1 H, dd ≈ t, $J_{3,4}$ 8.8, $J_{4,5}$ 9.1, H4a), 3.824 (1 H, m, OC*H*), 4.068 (1 H, dd, $J_{5,6'}$ 1.5, $J_{6',6''}$ 12.7, H6'b), 4.082–4.159 (2 H, m, H6'a, H2a), 4.301 (1 H, dd, $J_{5,6''}$ 1.5, $J_{6',6''}$ 12.5, H6"b), 4.369 (1 H, dd ≈ d, $J_{3,4}$ 3.4, $J_{4,5}$ < 1, H4b), 4.433 (1 H, d, $J_{1,2}$ 8.1, H1a), 4.501 (1 H, d, $J_{1,2}$ 7.8, H1b), 4.546 (1 H, dd, $J_{5,6''}$ 2.0, $J_{6',6''}$ 11.9, H6"a), 4.914 (1 H, dd, $J_{2,3}$ 10.4, $J_{3,4}$ 3.4, H3b), 5.093 (1 H, dd, $J_{2,3}$ 10.3, $J_{3,4}$ 8.8, H3a), 5.234 (1 H, dd, $J_{1,2}$ 7.8, $J_{2,3}$ 10.4, H2b), 5.495 (1 H, s, PhC*H*), 6.291 (1 H, d, $J_{2,NH}$ 9.1, N*H*Ac), 7.179(1 H, m, N*H*COC$F_3$), 7.376–7.389 (3 H, m, Ph), 7.442–7.461 (2 H, m, Ph).

A mixture of the resulting disaccharide (4.67 g, 6 mmol) and freshly calcined molecular sieves 3Å (12 g) in anhydrous THF (100 ml) was stirred for 30 min. Then sodium cyanoborohydride (3.77 g, 60 mmol) was added portionwise, the saturated HCl in anhydrous $Et_2O$ was added dropwise for 1 h (up to pH 2–3), and the mixture was stirred for 3 h. The reaction mixture was quenched with thriethylamine and filtered, the precipitate was washed with chloroform, and the combined filtrate was concentrated in a vacuum. The dry residue was dissolved in chloroform (300 ml), washed with water (2 × 300 ml), dried with sodium sulfate, and concentrated. The resulting product was acetylated with 2 : 1 with pyridine–acetic anhydride (45 ml). Chromatography on silica gel (elution with 5–10 % isopropanol in chloroform) resulted in 0.64 g (8%) of the starting benzylidene derivative and 4.13 g (84%) of benzyl derivative (**XI**) (84%). $R_f$ 0.26 (4 : 2 : 1 hexane–chloroform–isopropanol); $^1$H NMR ($CDCl_3$): 1.962, 1.975, 2.018, 2.055 (×2), and 2.100 (6 × 3 H, 6 s, 6 Ac), 3.437 (1 H, dd, $J_{5,6'}$ 7.1, $J_{6',6''}$ 9.3, H6'b), 3.439–3.491 (1 H, m, CHN), 3.521 (1 H, dd, $J_{5,6''}$ 5.6, $J_{6',6''}$ 9.3, H6"b), 3.595–3.655 (2 H, m, C*H*N, H5a), 3.733 (1 H, m, OC*H*), 3.779–3.821 (2 H, m, H4a, H5b), 3.877 (1 H, m, OC*H*), 4.038 (1 H, ddd, $J_{1,2}$ 8.1, $J_{2,3}$ 9.8, $J_{2,NH}$ 8.8, H2a), 4.099 (1 H, dd, $J_{5,6'}$ 5.1, $J_{6',6''}$ 12.0, H6'a), 4.408 (1 H, d, $J_{1,2}$ 7.8, H1b), 4.425 and 4.553 (2 × 1 H, 2 d, $J_{AB}$ 11.9, C$H_2$Ph), 4.498 (1 H, d, $J_{1,2}$ 8.1, H1a), 4.501 (1 H, dd, $J_{5,6''}$ 2.7, $J_{6',6''}$ 11.9, H6"a), 4.985 (1 H, dd, $J_{2,3}$ 10.3, $J_{3,4}$ 3.4, H3b), 5.036 (1 H, dd, $J_{2,3}$ 9.8, $J_{3,4}$ 8.3, H3a), 5.095 (1 H, dd, $J_{1,2}$ 7.8, $J_{2,3}$ 10.3, H2b), 5.460 (1 H, dd ≈d, $J_{3,4}$ 3,4, $J_{4,5}$ < 1, H4b), 5.701 (1 H, d, $J_{2,NH}$ 8.8, N*H*Ac), 7.136 (1 H, m, N*H*COC$F_3$), 7.255–7.360 (5 H, m, Ph).

**2-Trifluoroacetamidoethyl 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-(2,4-di-*O*-acetyl-6-*O*-benzyl-β-*D*-galactopyranosyl)-β-*D*-glucopyranoside (XIII).** Lactosamine derivative (**XI**) (4.13 g, 5 mmol) was deacetylated by Zemplen. Anhydrous acetonitrile (100 ml), triethyl orthoacetate (1.2 ml, 6.5 mmol), and *p*-toluenesulfonic acid (150 mg) were added to the deacetylation product. The mixture was stirred for 1 h at room temperature (the mixture becomes homogenous after 10 min) and quenched with pyridine. The solution was concentrated, the resulting orthoacetate was acetylated with 2 : 1 pyridine–acetic anhydride (30 ml), and the resulting compound was treated with 80% aqueous acetic acid (10 ml). After 4 h, the solution was concentrated in a vacuum. Chromatography on silica gel (elution with 10–20% isopropanol in chloroform) resulted in 2.34 g (70%) of the product of the orthoacetate opening (**XIII**); $R_f$ 0.29 (10 : 1 chloroform–methanol); $[\alpha]_D$ –17.8 (*c* 1, $CHCl_3$); MS, *m/z*: 802 (780 + 23) $M^+$ + $Na^+$; $^1$H NMR ($CDCl_3$): 1.959, 2.012, 2.096, 2.102, and 2.131 (5 × 3 H, 5 s, 5 Ac), 2.537 (1 H, d, $J_{3,OH}$ 6.1, 3-OH), 3.42–3.50 (1 H, m, C*H*N), 3.472 (1 H, dd, $J_{5,6'}$ 6.7, $J_{6',6''}$ 9.5, H6'b), 3.524 (1 H, dd, $J_{5,6''}$ 5.9, $J_{6',6''}$ 9.5, H6"b), 3.59–3.67 (2 H, m, C*H*N, H5a), 3.71–3.84 (4 H, m, H5b, OC*H*, H4a, H3b), 3.881 (1 H, m, OC*H*), 4.040 (1 H, ddd, $J_{1,2}$ 7.8, $J_{2,3}$ 10.0, $J_{2,NH}$ 9.0, H2a), 4.141 (1 H, dd, $J_{5,6'}$ 5.4, $J_{6',6''}$ 12.0, H6'a), 4.414 (1 H, d, $J_{1,2}$ 7.8, H1a), 4.435 (1 H, d, $J_{1,2}$ 8.1, H1b), 4.454 and 4.522 (2 × 1 H, 2 d, $J_{AB}$ 11.7, C$H_2$Ph), 4.501 (1 H, dd, $J_{5,6''}$ 2.2, $J_{6',6''}$ 11.7, H6"a), 4.872 (1 H, dd, $J_{1,2}$ 8.1, $J_{2,3}$ 9.8, H2b), 5.036 (1 H, dd, $J_{2,3}$ 10.0, $J_{3,4}$ 8.8, H3a), 5.383 (1 H, dd ≈ d, $J_{3,4}$ 3.7, $J_{4,5}$ < 1, H4b), 5.755 (1 H, d, $J_{2,NH}$ 9.0, N*H*Ac), 7.192 (1 H, m, N*H*COC$F_3$), 7.29–7.39 (5 H, m, Ph).

**2-Trifluoroacetamidoethyl 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-[2,4-di-*O*-acetyl-6-*O*-benzyl-3-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamido)-β-*D*-glucopyranosyl)-β-*D*-galactopyranosyl]-β-*D*-glucopyranoside (XV).** Glycosylation of lactosamine derivative (**XIII**) (390 mg, 0.5 mmol) with glycosyl bromide (**XIV**) resulted in 522 mg (1.0 mmol) of the corresponding peracetate. Chromatography on silica gel (elution with 3–10% isopropanol in chloroform) gave 150 mg (38%) of the starting disaccharide (**XIII**) and 360 mg (58%) of trisaccharide (**XV**); $R_f$ 0.29 (10 % isopropanol in chloroform); $^1$H NMR (DMSO-$d_6$): 1.730, 1.872, 1.881, 1.956, 1.969, 1.997, 2.011, and 2.050 (8 × 3 H, 8 s, 8 Ac), 3.913 (1 H, m, H5b), 3.935 (1 H, dd, $J_{2,3}$ 10.5, $J_{3,4}$ 3.4, H3b), 4.010 (1 H, dd, $J_{5,6'}$ 2.2, $J_{6',6''}$ 12.0, H6'a), 4.026–4.070 (2 H, m, H6'c, H6"c), 4.297 (1 H, dd, $J_{5,6''}$ 1.0, $J_{6',6''}$ 12.0, H6"a), 4.426 and 4.464 (2 × 1 H, 2 d, $J_{AB}$ 12.0, C$H_2$Ph), 4.490 (1 H, d, $J_{1,2}$ 7.8, H1b), 4.506 and 4.975 (2 × 1 H, 2 d, $J_{AB}$ 12.5, C$H_2$CC$l_3$), 4.546 (1 H, d, $J_{1,2}$ 8.6, H1a), 4.662 (1 H, d, $J_{1,2}$ 8.3, H1c), 4.750 (1 H, dd, $J_{1,2}$ 7.8, $J_{2,3}$ 10.5, H2b), 4.796 (1 H, dd ≈t, $J_{3,4}$ 9.8, $J_{4,5}$ 9.3, H4c), 4.908 (1 H, dd, $J_{2,3}$ 8.3, $J_{3,4}$ 10.0, H3a), 5.092 (1 H, dd ≈ t, $J_{2,3}$ 10.0, $J_{3,4}$ 9.8, H3c), 5.340 (1 H, dd ≈ d, $J_{3,4}$ 3.4, $J_{4,5}$ < 1, H4b), 7.268–7.381 (5 H, m, Ph), 7.794 (1 H, d, $J_{2,NH}$ 9.0,

N*H*Ac), 7.822 (1 H, d, $J_{2,NH}$ 9.3, N*H*Troc), 9.292 (1 H, m, N*H*COCF$_3$).

**2-Trifluoroacetamidoethyl 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-[2,4-*O*-acetyl-6-*O*-benzyl-3-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-glucopyranosyl)-β-*D*-galactopyranosyl]-β-*D*-glucopyranoside (XVI).** The treatment of Troc derivative (**XV**) (517 mg, 0.416 mmol) with zinc in acetic acid and subsequent purification by chromatography on silica gel (elution with 5–10% methanol in chloroform) resulted in 343 mg (74%) of *N*-acetyl derivative (**XVI**) (74%), $R_f$ 0.31 (10% isopropanol in ethyl acetate); $^1$H NMR (CDCl$_3$): 1.903, 1.957, 2.006, 2.016, 2.023, 2.067, 2.078, and 2.095 (×2) (9 × 3 H, 9c, 9Ac), 3.360 (1 H, ddd, $J_{1,2}$ 8.1, $J_{2,3}$ 10.5, $J_{2,NH}$ 7.8, H2c), 3.483 (2 H, m, H6'b, H6"b), 3.578–3.751 (6 H, m, C*H*$_2$N, OC*H*, H5a, H5b, H5c), 3.774 (1 H, dd ≈ t, $J_{3,4} \approx J_{4,5} \approx 8.6$, H4a), 3.828 (1 H, dd, $J_{2,3}$ 10.0, $J_{3,4}$ 3.7, H3b), 3.879 (1 H, m, OC*H*), 4.045 (1 H, ddd, $J_{1,2}$ 7.8, $J_{2,3}$ 9.3, $J_{2,NH}$ 9.0, H2a), 4.096–4.143 (2 H, m, H6'a, H6'c), 4.295 (1 H, dd, $J_{5,6"}$ 2.6, $J_{6',6"}$ 12.4, H6"c), 4.378 (1 H, d, $J_{1,2}$ 8.1, H1b), 4.397 (1 H, d, $J_{1,2}$ 7.8, H1a), 4.458 (1 H, dd, $J_{5,6"}$ 2.7, $J_{6',6"}$ 12.0, H6"a), 4.473 and 4.507 (2 × 1 H, 2 d, $J_{AB}$ 11.7, C*H*$_2$Ph), 4.990–5.058 (4 H, m, H1c, H2b, H3a, H4c), 5.414 (1 H, dd ≈ d, $J_{3,4}$ 3.7, $J_{4,5} < 1$, H4b), 5.454 (1 H, dd, $J_{2,3}$ 10.5, $J_{3,4}$ 9.5, H3c), 5.485 (1 H, d, $J_{2,NH}$ 7.8, N*H*Ac-c), 5.806 (1 H, d, $J_{2,NH}$ 9.0, N*H*Ac-a), 7.225 (1 H, m, N*H*COCF$_3$), 7.339 (5 H, m, Ph).

**2-Trifluoroacetamidoethyl 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-[2,4-di-*O*-acetyl-3-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-glucopyranosyl)-β-*D*-galactopyranosyl]-β-*D*-glucopyranoside (XVII).** Hydrogenolysis of 6'-*O*-benzyl derivative (**XVI**) (333 mg, 0.3 mmol) and subsequent chromatography on silica gel (elution with 7% methanol in chloroform) resulted in 260 mg (85%) of trisaccharide (**XVII**); $R_f$ 0.21 (10% isopropanol in ethyl acetate); MS, *m/z*: 1043 (1019 + 23) $M^+ + Na^+$; $^1$H NMR (3 : 1 CDCl$_3$–CD$_3$OD): 2.026, 2.067, 2.149, 2.167, 2.186, 2.233, 2.244, 2.267, and 2.271 (9 × 3 H, 9 s, 9 Ac), 3.56–3.67 (4 H, m, C*H*$_2$N, H2c, H6'b), 3.69–3.83 (3 H, m, H6"b, H5a, H5b), 3.804 (1 H, m, OC*H*), 3.851 (1 H, ddd, $J_{4,5}$ 10.0, $J_{5,6'}$ 2.4, $J_{5,6"}$ 4.2, H5c), 3.932 (1 H, dd ≈ t, $J_{3,4}$ 8.7, $J_{4,5}$ 9.3, H4a), 3.973 (1 H, dd, $J_{2,3}$ 10.0, $J_{3,4}$ 3.4, H3b), 4.010 (1 H, m, OC*H*), 4.086 (1 H, ddd, $J_{1,2}$ 8.1, $J_{2,3}$ 10.3, $J_{2,NH}$ 9.0, H2a), 4.256 (1 H, dd, $J_{5,6'}$ 5.6, $J_{6',6"}$ 12.0, H6'a), 3.955 (1 H, dd, $J_{5,6'}$ 4.2, $J_{6',6"}$ 12.3, H6'c), 4.381 (1 H, dd, $J_{5,6"}$ 2.4, $J_{6',6"}$ 12.3, H6"c), 4.563 (1 H, d, $J_{1,2}$ 7.8, H1b), 4.576 (1 H, d, $J_{1,2}$ 8.1, H1a), 4.602 (1 H, dd, $J_{5,6"}$ 2.3, $J_{6',6"}$ 12.0, H6"a), 5.086 (1 H, d, $J_{1,2}$ 8.3, H1c), 5.10–5.18 (3 H, m, H4c, H2b, H3a), 5.488 (1 H, dd ≈ d, $J_{3,4}$ 3.4, $J_{4,5} < 1$, H4b), 5.510 (1 H, dd, $J_{2,3}$ 10.5, $J_{3,4}$ 9.3, H3c).

**2-Trifluoroacetamidoethyl 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-[2,4,6-tri-*O*-acetyl-3-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-glucopyranosyl)-β-*D*-galactopyranosyl]-β-*D*-glucopyranoside (XVIII).** Acetylation of trisaccharide (**XVII**) (87 mg, 0.085 mmol) and subsequent chromatography on silica gel (elution with 10% isopropanol in ethyl acetate) resulted in 77 mg (85%) of peracetate (**XVIII**); $R_f$ 0.35 (9 : 1 ethyl acetate–isopropanol); $[\alpha]_D$ +15.1 (*c* 1, chloroform); MS, *m/z*: 1084 (1061 + 23) $M^+ + Na^+$; $^1$H NMR (CDCl$_3$): 1.907, 1.962, 2.020, 2.028, 2.076, 2.101 (×2), 2.115, 2.119, and 2.125 (10 × 3 H, 10 s, 10 Ac), 3.315 (1 H, dd, $J_{1,2}$ 8.1, $J_{2,NH}$ 7.8, $J_{2,3}$ 10.5, H2c), 3.491 (1 H, m, C*H*N), 3.609 (2 H, m, C*H*N, H5a), 3.677 (1 H, m, H5c), 3.740 (1 H, dd ≈ t, $J_{3,4}$ 8.4, $J_{4,5}$ 8.8, H4a), 3.749 (1 H, m, OC*H*), 3.801 (1 H, ddd ≈t, H5b), 3.815 (1 H, dd, $J_{3,4}$ 3.5, $J_{2,3}$ 9.9, H3b), 3.893 (1 H, m, OC*H*), 4.036 (1 H, ddd, H2a), 4.065 (3 H, m, H6"c, H6'b, H6"b), 4.121 (1 H, dd, $J_{6',6"}$ 11.9, $J_{5,6"}$ 5.2, H6"a), 4.393 (2 H, m, H1b, $J_{1,2}$ 7.9, H6'c), 4.444 (1 H, d, $J_{1,2}$ 7.8, H1a), 4.484 (1 H, dd, $J_{6',6"}$ 11.0, $J_{5,6'}$ 2.2, H6'a), 5.013 (1 H, dd, $J_{1,2}$ 7.9, $J_{2,3}$ 9.9, H2b), 5.030 (1 H, dd, $J_{2,3}$ 9.9, $J_{3,4}$ 8.4, H3a), 5.032 (1 H, d, $J_{1,2}$ 7.9, H1c), 5.054 (1 H, dd ≈ t, $J_{3,4}$ 9.3, $J_{4,5}$ 10.1, H4c), 5.360 (1 H, dd ≈ d, $J_{3,4}$ 3.5, $J_{4,5} < 1$, H4b), 5.473 (1 H, dd, $J_{2,3}$ 10.5, $J_{3,4}$ 9.3, H3a), 5.510 (1 H, d, $J_{2,NH}$ 7.8, N*H*Ac-c), 5.849 (1 H, d, $J_{2,NH}$ 8.7, N*H*Ac-a), 7.207 (1 H, m, N*H*COCF$_3$).

**2-Aminoethyl 2-acetamido-2-deoxy4-*O*-[3-*O*-(2-acetamido-2-deoxy-β-*D*-glucopyranosyl)-β-*D*-galactopyranosyl]-β-*D*-glucopyranoside (I).** De-*O*-acetylation and removal of the *N*-trifluoroacetamide protective group in derivative (**XVIII**) (71 mg, 0.067 mmol) resulted in 41.3 mg (98%) of trisaccharide (**I**); $R_f$ 0.56 (4 : 1 : 1 : 1 ethanol–water–pyridine–acetic acid); $[\alpha]_D$ –15.1 (*c* 0.5, water); MS, *m/z*: 652 (629 + 23) $M^+ + Na^+$; $^1$H NMR (D$_2$O): 2.052 and 2.062 (2 × 3 H, 2 s, 2 Ac), 3.238 (2 H, m, C*H*$_2$N), 3.42–3.51 (2 H, m), 3.55–3.66 (3 H, m), 3.69–3.83 (9 H, m), 3.854 (1 H, dd, $J_{6',6"}$ 12.2, $J_{5,6"}$ 5.2, H6"a), 3.911 (2 H, m, OC*H*, H6'c), 4.010 (1 H, dd, $J_{6',6"}$ 12.2, $J_{5,6'}$ 2.0, H6'a), 4.073 (1 H, m, OC*H*), 4.168 (1 H, dd, $J_{3,4}$ 3.2, $J_{4,5} < 1$, H4b), 4.478 (1 H, d, $J_{1,2}$ 8.0, H1b), 4.594 (1 H, d, $J_{1,2}$ 8.3, H1a), 4.701 (1 H, d, $J_{1,2}$ 8.4, H1c).

**2-Trifluoroacetamidoethyl 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-{2,4-*O*-acetyl-3-*O*-[2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-glucopyranosyl]-6-*O*-[2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-glucopyranosyl]-β-*D*β-*D*-glucopyranoside (XX).** Glycosylation of trisaccharide (**XVII**) (177 mg, 0.174 mmol) with glycosyl bromide (**XIV**) obtained from the corresponding peracetate (136 mg, 0.261 mmol) and subsequent chromatography on silica gel (elution with 7% isopropanol in ethyl acetate) yielded 219 mg (85%) of tetrasaccharide (**XIX**), $R_f$ 0.44 (10% isopropanol in ethyl acetate). The substance that seemed to be individual according to TLC appeared to contain about 20% of impurity according to $^1$H NMR spectroscopy. The treatment of Troc derivative (**XIX**) with zinc in acetic acid and three chromatographic purifications on silica gel (elution with 7% methanol in chloroform, 6 : 1 ethyl acetate–isopropanol, and then 8 : 1 chloroform–isopropanol) yielded 100 mg (51%) of peracetylated tetrasaccharide (**XX**); $R_f$ 0.25 (6 : 1 ethyl acetate–isopropanol); $^1$H NMR (3 : 1 CDCl$_3$–CD$_3$OD): 2.019, 2.070, 2.077,

2.145, 2.164 (×2), 2.180, 2.186, 2.231 (×2), 2.245, 2.255, and 2.266 (13 × 3 H, 13 s, 13 Ac), 3.55–3.69 (2 H, m, C$H_2$N), 3.605 (1 H, dd, $J_{1,2}$ 8.3, $J_{2,3}$ 10.5, H2c), 3.682 (1 H, dd, $J_{6',6''}$ 10.5, $J_{5,6''}$ 7.0, H6"b), 3.767 (1 H, m, H5a), 3.79–3.85 (2 H, m, OC*H*, H5c), 3.813 (1 H, dd, $J_{1,2}$ 8.3, $J_{2,3}$ 10.7, H2d), 3.86–3.93 (3 H, m, H4a, H5b, H5d), 3.938 (1 H, dd, $J_{6',6''}$ 10.5, $J_{5,6'}$ 4.6, H6'b), 3.975 (1 H, dd, $J_{3,2}$ 10.0, $J_{3,4}$ 3.7, H3b), 4.018 (1 H, m, OC*H*), 4.077 (1 H, dd, $J_{1,2}$ 8.3, $J_{2,3}$ 10.0, H2a), 4.279 (2 H, m, H6"a, H6"c), 4.322 (1 H, dd, $J_{6',6''}$ 12.2, $J_{5,6''}$ 2.2, H6"d), 4.410 (1 H, dd, $J_{6',6''}$ 12.2, $J_{5,6'}$ 4.7, H6'd), 4.422 (1 H, dd, $J_{6',6''}$ 12.2, $J_{5,6'}$ 2.4, H6'c), 4.534 (1 H, d, $J_{1,2}$ 7.8, H1b), 4.575 (1 H, dd, $J_{6',6''}$ 12.0, $J_{5,6'}$ 2.0, H6'a), 4.590 (1 H, d, $J_{1,2}$ 8.3, H1a), 4.952 (1 H, d, $J_{1,2}$ 8.3, H1d), 5.041 (1 H, d, $J_{1,2}$ 8.3, H1c), 5.094 (1 H, dd, $J_{1,2}$ 7.8, $J_{2,3}$ 10.0, H2b), 5.13–5.20 (3 H, m, H3a, H4c, H4d), 5.471 (1 H, dd, $J_{3,4}$ 3.7, $J_{4,5}$ < 1, H4b), 5.498 (1 H, dd, $J_{2,3}$ 10.7, $J_{3,4}$ 9.5, H3d), 5.521 (1 H, dd, $J_{2,3}$ 10.5, $J_{3,4}$ 9.3, H3c).

**2-Aminoethyl 2-acetamido-2-deoxy-4-*O*-{3-*O*-[2-acetamido-2-deoxy-β-*D*-glucopyranosyl]-6-*O*-[2-acetamido-2-deoxy-β-*D*-glucopyranosyl]-β-*D*-galactopyranosyl}-β-*D*-glucopyranoside (III).** De-*O*-acetylation and removal of the *N*-trifluoroacetyl protective group from oligosaccharide (**XX**) (100 mg, 0.074 mmol) yielded 60 mg (97%) of tetrasaccharide (**III**); $R_f$ 0.57 (3 1 : 1 : 1 ethanol–water–pyridine–acetic acid); $[\alpha]_D$ –16.0 (*c* 0.5, water); MS, *m*/*z*: 855 (832 + 23) $M^+ + Na^+$; $^1$H NMR ($D_2O$): 2.050 and 2.073 (×2) (3 × 3 H, 3c, 3Ac), 3.243 (2 H, m, C$H_2$N), 3.42–3.51 (4 H, m), 3.53–3.65 (4 H, m), 3.66–4.02 (16 H, m), 4.079 (1 H, m, OC*H*), 4.158 (1 H, dd, $J_{3,4}$ 3.2, $J_{4,5}$ < 1, H4b), 4.471 (1 H, d, $J_{1,2}$ 7.8, H1b), 4.598 (2 H, d, $J_{1,2}$ 8.4, H1a, H1c), 4.696 (1 H, d, $J_{1,2}$ 8.5, H1d).

**2-Trifluoroacetamidoethyl 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-{2,4-di-*O*-acetyl-3-*O*-[2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-glucopyranosyl]-6-*O*-[3,6-di-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamido)-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-β-*D*-glucopyranosyl]-β-*D*-galactopyranosyl}-β-*D*-glucopyranoside (XXII).** Glycosylation of trisaccharide (**XVII**) (222 mg, 0.218 mmol) with glycosyl bromide (**XXI**) obtained from the corresponding thioglycoside (270 mg, 0.332 mmol) and subsequent chromatography on silica gel (elution with 5–15% isopropanol in chloroform) resulted in 57 mg (26%) of a mixture of starting glycosyl acceptor (**XVII**) with its isomer (the product of migration of the OAc group from C4 to C6 of the galactose unit) and 250 mg (65%) of pentasaccaride (**XXII**); $R_f$ 0.37 (10% isopropanol in ethyl acetate).

**2-Trifluoroacetamidoethyl 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-{2,4-di-*O*-acetyl-3-*O*-[2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-glucopyranosyl]-6-*O*-[2-acetamido-3,6-di-*O*-acetyl-2-deoxy-44-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-β-*D*-glucopyranosyl]-β-*D*-galactopyranosyl}-β-*D*-glucopyranoside (XXIII).** The treatment of Troc derivative (**XXII**) with zinc in acetic acid and subsequent chromatography on silica gel (twofold elution with 10–20% isopropanol in chloroform and then with 15% isopropanol in ethyl acetate) yielded 124 mg (49%) of peracetate (**XXIII**); $R_f$ 0.17 (10% isopropanol in ethyl acetate); $^1$H NMR (3 : 1 $CDCl_3$–$CD_3OD$): 2.024, 2.072, 2.086, 2.126, 2.148, 2.168, 2.183, 2.218 (×2), 2.221, 2.230, 2.233, 2.253, 2.266, 2.276, and 2.300 (16 × 3 H, 16 s, 16 Ac), 3.57–3.70 (4 H, m, $J_{1,2}$ 8.3, $J_{2,3}$ 10.5, C$H_2$N, H6"b, H2c), 3.75–3.98 (10 H, m), 3.995 (1 H, dd, $J_{2,3}$ 10.0, $J_{3,4}$ 3.4, H3b), 4.024 (1 H, m, OC*H*), 4.057 (1 H, dd, $J_{1,2}$ 8.3, $J_{2,3}$ 10.0, H2a), 4.115 (1 H, t, H5a), 4.23–4.33 (5 H, m), 4.532 (1 H, d, $J_{1,2}$ 8.1, H1b), 4.575 (1 H, dd, $J_{6',6''}$ 12.2, $J_{5,6'}$ 2.0, H6'a), 4.608 (1 H, d, $J_{1,2}$ 8.1, H1a), 4.727 (1 H, dd, $J_{6',6''}$ 11.7, $J_{5,6'}$ 2.0, H6'd), 4.744 (1 H, d, $J_{1,2}$ 7.8, H1c), 4.757 (1 H, d, $J_{1,2}$ 8.1, H1d), 5.043 (1 H, d, $J_{1,2}$ 8.1, H1c), 5.096 (1 H, dd, $J_{1,2}$ 8.1, $J_{2,3}$ 10.0, H2b), 5.153 (1 H, dd, $J_{3,4}$ 9.3, $J_{4,5}$ 9.8, H4c), 5.157 (1 H, dd, $J_{2,3}$ 10.5, $J_{3,4}$ 3.0, H3e), 5.193 (1 H, dd, $J_{2,3}$ 10.0, $J_{3,4}$ 9.1, H3b), 5.235 (1 H, dd, $J_{1,2}$ 7.8, $J_{2,3}$ 10.5, H2a), 5.324 (1 H, dd, $J_{2,3}$ 10.0, $J_{3,4}$ 9.1, H3d), 5.485 (1 H, dd, $J_{3,4}$ 3.4, $J_{4,5}$ < 1, H4b), 5.497 (1 H, dd, $J_{2,3}$ 10.5, $J_{3,4}$ 9.3, H3c), 5.514 (1 H, dd, $J_{3,4}$ 3.0, $J_{4,5}$ < 1, H4a).

**2-Aminoethyl 2-acetamido-2-deoxy-4-*O*-{3-*O*-[2-acetamido-2-deoxy-β-*D*-glucopyranosyl]-6-*O*-[2-acetamido-2-deoxy-4-*O*-(β-*D*-galactopyranosyl)-β-*D*-glucopyranosyl]-β-*D*-galactopyranosyl}-β-*D*-glucopyranoside (IV).** De-*O*-acetylation and removal of the *N*-trifluoroacetamide protective group from peracetate (**XXIII**) (124 mg, 0.076 mmol) yielded 71.4 mg (95%) of pentasaccharide (**IV**); $R_f$ 0.54 (3 : 1 : 1 :1 ethanol–water–pyridine–acetic acid); $[\alpha]_D$ –11.8 (*c* 1, water); MS, *m*/*z*: 1018 (995 + 23) $M^+ + Na^+$; $^1$H NMR ($D_2O$): 2.043 and 2.063 (×2) (3 × 3 H, 3c, 3Ac), 3.235 (2 H, m, C$H_2$N), 3.42–3.46 (2 H, m), 3.53–3.64 (5 H, m), 3.66–4.02 (23 H, m), 4.073 (1 H, m, OC*H*), 4.153 (1 H, dd, $J_{3,4}$ 3.4, $J_{4,5}$ < 1, H4b), 4.466 (1 H, d, $J_{1,2}$ 7.8, H1b), 4.475 (1 H, d, $J_{1,2}$ 7.8, H1e), 4.589 (1 H, d, $J_{1,2}$ 8.2, H1a), 4.656 (1 H, d, $J_{1,2}$ 7.5, H1d), 4.690 (1 H, d, $J_{1,2}$ 8.4, H1c).

**2-Trifluoroacetamidoethyl 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-{2,4-di-*O*-acetyl-6-O-benzyl-3-*O*-[3,6-di-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamido)-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-β-*D*-glucopyranosyl]-β-*D*-galactopyranosyl}-β-*D*-glucopyranoside (XXIV).** Glycosylation of lactosamine derivative (**XIII**) (516 mg, 0.66 mmol) with glycosyl bromide (**XXI**) obtained from the corresponding thioglycoside (1.073 g, 1.32 mmol) and two subsequent chromatographic purifications on silica gel (elution with 6–8% isopropanol in chloroform and 1–10 % isopropanol in chloroform) yielded 119 mg (23%) of the starting disaccharide (**XIII**), 48 mg (9%) of its isomer (the product of migration of OAc group from C4 to C3 of the galactose unit) and 601 mg (59%) of tetrasaccharide (**XXIV**); $R_f$ 0.44 (10% isopropanol in chloroform).

**2-Trifluoroacetamidoethyl 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-{2,4-di-*O*-acetyl-6-*O*-benzyl-3-*O*-[2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-β-*D*-glucopyranosyl]-β-*D*-galactopyranosyl}-β-*D*-glucopyranoside (XXV).** The treatment of Troc derivative (**XXIV**) (601 mg, 0.39 mmol) with zinc in acetic acid and three subsequent chromatographic purifications on silica gel (elution with 9% isopropanol in chloroform, and then twice with 10 : 1 ethyl acetate–isopropanol) yielded 401.6 mg (73%) of tetrasaccharide (**XXV**); $R_f$ 0.45 (9 : 1 ethyl acetate–isopropanol); MS, *m/z*: 1420 (1397 + 23) $M^+ + Na^+$; $^1$H NMR ($CDCl_3$): 1.907, 1.955, 1.977, 2.004, 2.055, 2.066, 2.073, 2.080, 2.083, 2.092, 2.095, and 2.154 (12 × 3 H, 12 s, 12 Ac), 3.43–3.51 (3 H, m, C*H*N, H6'b, H6"b), 3.537 (1 H, m, H5c), 3.618 (3 H, m, C*H*N, H2c, H5a), 3.67–3.83 (5 H, m, OC*H*, H3b, H5b, H4a, H4c), 3.880 (2 H, m, OC*H*, H5d), 4.019 (1 H, dd, $J_{6',6"}$ 11.9, $J_{5,6"}$ 3.8, H6"c), 4.043 (1 H, m, H2a), 4.103 (2 H, m, H6'd, H6"d), 4.131 (1 H, dd, $J_{6',6"}$ 11.5, $J_{5,6"}$ 6.6, H6"a), 4.369 (1 H, d, $J_{1,2}$ 7.9, H1b), 4.392 (1 H, d, $J_{1,2}$ 7.6, H1a), 4.460 (1 H, dd, $J_{6',6"}$ 11.5, $J_{5,6'}$ 2.3, H6'a), 4.474 and 4.519 (2 × 1 H, 2 d, $J_{AB}$ 11.6, C$H_2$Ph), 4.536 (1 H, d, $J_{1,2}$ 7.8, H1d), 4.677 (1 H, d, $J_{1,2}$ 7.5, H1c), 4.687 (1 H, dd, $J_{6',6"}$ 11.9, $J_{5,6'}$ 2.2, H6'c), 4.985 (1 H, dd, $J_{2,3}$ 10.5, $J_{3,4}$ 3.4, H3d), 5.004 (1 H, dd, $J_{1,2}$ 7.9, $J_{2,3}$ 10.1, H2b), 5.010 (1 H, dd, $J_{2,3}$ 9.6, $J_{3,4}$ 8.2, H3a), 5.118 (1 H, dd, $J_{1,2}$ 7.8, $J_{2,3}$ 10.5, H2d), 5.165 (1 H, dd, $J_{2,3}$ 9.8, $J_{3,4}$ 8.8, H3c), 5.361 (1 H, dd, $J_{3,4}$ 3.4, $J_{4,5} < 1$, H4b), 5.394 (1 H, dd, H4d), 5.400 (1 H, d, $J_{2,NH}$ 8.7, N*H*Ac-c), 5.777 (1 H, d, $J_{2,NH}$ 8.8, N*H*Ac-a), 7.230 (1 H, m, N*H*COC$F_3$), 7.331 (5 H, m, Ph).

**2-Trifluoroacetamidoethyl) 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-{2,4-di-*O*-acetyl-3-*O*-[2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-β-*D*-glucopyranosyl]-β-*D*-galactopyranosyl}-β-*D*-glucopyranoside (XXVI).** Hydrogenolysis of (**XXV**) (372 mg, 0.266 mmol) and the subsequent chromatographic purification of product on silica gel (elution with 9% isopropanol in chloroform containing 0.5% pyridine and then with 9 : 1 ethyl acetate–isopropanol containing 0.5% pyridine) yielded 255 mg (73%) of the corresponding 6b-OH derivative (**XXVI**); $R_f$ 0.36 (5 : 1 chloroform–isopropanol); $^1$H NMR (3 : 1 $CDCl_3$–$CD_3OD$): 2.023, 2.066, 2.118, 2.185, 2.197, 2.205, 2.213, 2.229, 2.259, 2.265, 2.294, and 2.296 (112 × 3 H, 12 s, 12 Ac), 3.55–3.77 (8 H, m, C$H_2$N, H6'b, H6"b, H5b, H5a, H5c, H2c), 3.803 (1 H, m, OC*H*), 3.918 (3 H, m, H3b, H4a, H4c), 4.009 (1 H, m, OC*H*), 4.088 (2 H, m, $J_{1,2}$ 8.3, $J_{2,3}$ 10.3, H2a, H5d), 4.149 (1 H, dd, $J_{6',6"}$ 11.9, $J_{5,6"}$ 3.9, H6"c), 4.256 (3 H, m, H6'a, H6'd, H6"d), 4.549 (1 H, d, $J_{1,2}$ 7.9, H1b), 4.571 (1 H, d, $J_{1,2}$ 8.3, H1a), 4.593 (1 H, dd, $J_{6',6"}$ 11.9, $J_{5,6"}$ 2.0, H6"a), 4.721 (1 H, d, $J_{1,2}$ 7.8, H1d), 4.778 (1 H, dd, $J_{6',6"}$ 11.9, $J_{5,6'}$ 2.0, H6'c), 4.854 (1 H, d, $J_{1,2}$ 8.1, H1c), 5.101 (1 H, dd, $J_{1,2}$ 7.9, $J_{2,3}$ 9.9, H2b), 5.140 (1 H, dd, $J_{3,4}$ 3.4, $J_{2,3}$ 10.5, H3d), 5.152 (1 H, dd, $J_{2,3}$ 10.3, $J_{3,4}$ 8.8, H3a), 5.219 (1 H, dd, $J_{1,2}$ 7.8, $J_{2,3}$ 10.5, H2d), 5.307 (1 H, dd, $J_{2,3}$ 10.3, $J_{3,4}$ 8.9, H3c), 5.477 (1 H, dd ≈ d, $J_{3,4}$ 3.4, $J_{4,5} < 1$, H4b), 5.499 (1 H, dd ≈ d, $J_{3,4}$ 3.2, $J_{4,5} < 1$, H4d).

**2-Trifluoroacetamidoethyl 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-{2,4,6-tri-*O*-acetyl-3-*O*-[2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-β-*D*-glucopyranosyl]-β-*D*-galactopyranosyl}-β-*D*-glucopyranoside (XXVII).** Acetylation of tetrasaccharide (**XXVI**) (42 mg, 0.032 mmol) and the subsequent chromatography on silica gel (7 : 1 chloroform–isopropanol) yielded 39 mg (90%) of peracetate (**XXVII**); $R_f$ 0.35 (7 : 1 chloroform–isopropanol); $[\alpha]_D$ +4.73 (*c* 1, chloroform); MS, *m/z*: 1372 (1349 + 23) $M^+ + Na^+$; $^1$H NMR ($CDCl_3$): 1.903, 1.960, 1.978, 2.052, 2.072 (×3), 2.087, 2.114, 2.122, 2.124, 2.154, and 2.157 (13 × 3 H, 13 s, 13 Ac), 3.44–3.66 (5 H, m, C$H_2$N, H5a, H5c, H2c), 3.738 (1 H, dd ≈ t, $J_{3,4}$ 8.4, $J_{4,5}$ 8.8, H4a), 3.745 (1 H, m, OC*H*), 3.759 (1 H, dd, $J_{2,3}$ 10.1, $J_{3,4}$ 3.5, H3b), 3.802 (1 H, ddd ≈ t, H5b), 3.807 (1 H, dd ≈ t, $J_{3,4}$ 8.8, $J_{4,5}$ 9.4, H4c), 3.883 (2 H, m, H5d, OC*H*), 3.985 (1 H, dd, $J_{6',6"}$ 11.9, $J_{5,6"}$ 3.3, H6"c), 4.035 (1 H, ddd, $J_{1,2}$ 7.9, $J_{2,NH}$ 8.8, $J_{2,3}$ 9.7, H2a), 4.04–4.16 (5 H, m, H6"a, H6'b, H6"b, H6'd, H6"d), 4.383 (1 H, d, $J_{1,2}$ 7.9, H1b), 4.439 (1 H, d, $J_{1,2}$ 7.9, H1a), 4.474 (1 H, dd, $J_{6',6"}$ 11.9, $J_{5,6'}$ 2.3, H6'a), 4.555 (1 H, d, $J_{1,2}$ 7.9, H1d), 4.693 (1 H, d, $J_{1,2}$ 7.7, H1c), 4.781 (1 H, dd, $J_{6',6"}$ 11.9, $J_{5,6'}$ 2.3, H6'c), 4.992 (1 H, dd, $J_{1,2}$ 7.9, $J_{2,3}$ 10.1, H2b), 4.993 (1 H, dd, $J_{2,3}$ 10.5, $J_{3,4}$ 3.5, H3d), 5.024 (1 H, dd, $J_{2,3}$ 9.7, $J_{3,4}$ 8.4, H3a), 5.118 (1 H, dd, $J_{1,2}$ 7.9, $J_{2,3}$ 10.5, H2d), 5.192 (1 H, dd, $J_{2,3}$ 10.1, $J_{3,4}$ 8.8, H3c), 5.335 (1 H, dd ≈ d, $J_{3,4}$ 3.5, $J_{4,5} < 1$, H4b), 5.361 (1 H, dd ≈ d, $J_{3,4}$ 3.5, $J_{4,5} < 1$, H4d), 5.417 (1 H, d, $J_{2,NH}$ 8.4, N*H*Ac-c), 5.831 (1 H, d, $J_{2,NH}$ 8.8, N*H*Ac-a), 7.204 (1 H, m, N*H*COC$F_3$).

**2-Aminoethyl 2-acetamido-2-deoxy-4-*O*-{3-*O*-[2-acetamido-2-deoxy-4-*O*-(β-*D*-galactopyranosyl)-β-*D*-glucopyranosyl]-β-*D*-galactopyranosyl}-β-*D*-glucopyranoside (VI).** De-*O*-acetylation and removal of the *N*-trifluoroacetamide protective group from (**XXVII**) (98 mg, 0.073 mmol) resulted in 55 mg (96%) of tetrasaccharide (**VI**), $R_f$ 0.46 (4 : 1 : 1 : 1 ethanol–water–pyridine–acetic acid), $[\alpha]_D$ –8.67 (*c* 0.5, water). MS, *m/z*: 1948 (1925 + 23) $M^+ + Na^+$; $^1$H NMR ($D_2O$): 2.051 and 2.064 (2 × 3 H, 2 s, 2 Ac), 3.240 (2 H, m, C$H_2$N), 3.559 (1 H, dd, $J_{1,2}$ 7.9, $J_{2,3}$ 9.8, H2d), 3.607 (1 H, dd, $J_{1,2}$ 7.9, $J_{2,3}$ 9.8, H2b), 3.58–3.66 (2 H, m), 3.687 (1 H, dd, $J_{2,3}$ 9.8, $J_{3,4}$ 3.4, H3d), 3.70–3.83 (13 H, m), 3.83–3.89 (2 H, m), 3.914 (1 H, m, OC*H*), 3.946 (1 H, dd, $J_{3,4}$ 3.4, $J_{4,5} < 1$, H4d), 3.972 (1 H, dd, $J_{6',6"}$ 12.2, $J_{5,6'}$ 2.0, H6'c), 4.012 (1 H, dd, $J_{6',6"}$ 12.1, $J_{5,6'}$ 1.7, H6'a), 4.076 (1 H, m, OC*H*), 4.173 (1 H, dd, $J_{3,4}$ 3.4, $J_{4,5} < 1$, H4b), 4.480 and 4.500 (2 H, 2 d, $J_{1,2}$ 7.8, H1b and H1d), 4.596 (1 H, d, $J_{1,2}$ 8.2, H1a), 4.724 (1 H, d, $J_{1,2}$ 8.4, H1c).

**2-Trifluoroacetamidoethyl 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-{2,4-di-*O*-acetyl-3-*O*-[2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-β-*D*-glucopyranosyl]-6-*O*-[2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-**

***D*-glucopyranosyl]-β-*D*-galactopyranosyl}-β-*D*-glucopyranoside (XXIX).** Glycosylation of tetrasaccharide (**XXVI**) (142 mg, 0.109 mmol) with glycosyl bromide (**XIV**) prepared from the corresponding peracetate (114 mg, 0.217 mmol) and subsequent isolation by chromatography on silica gel (10 : 1chloroform–isopropanol) yielded 35 mg (24%) of the starting (**XXVI**) and 96 mg (50% or 65% taking into account the recovery of the starting compound) of a mixture of the products with the same chromatographic mobility, $R_f$ 0.45 (10 : 1 ethyl acetate–isopropanol). According to $^1$H NMR, pentasaccharide (**XXVIII**) was the main component of the mixture. The resulting mixture was treated with zinc in acetic acid and separated by repeated chromatography on silica gel (elution with 17% isopropanol in chloroform and with 12% isopropanol in chloroform) to give 51.4 mg (58%) of peracetate (**XXIX**); $R_f$ 0.27 (7 : 1 ethyl acetate–isopropanol); $[\alpha]_D$ +9.8 (*c* 1, chloroform); MS, *m/z*: 1660 (1637 + 23) $M^+ + Na^+$; $^1$H NMR (3 : 1 $CDCl_3$–$CD_3OD$): 2.020, 2.072, 2.081, 2.121, 2.170, 2.185, 2.187, 2.199, 2.209, 2.216, 2.227, 2.230, 2.246, 2.269, 2.299, and 2.320 (16 × 3 H, 16 s, 16 Ac), 3.56–3.66 (2 H, m, C*H*$_2$N), 3.66–3.84 (7 H, m, OC*H*, H2c, H2e, H5a, H5c, H6'b, H6"b), 3.85–3.97 (5 H, m, H3b, H4a, H4c, H5e, H5b), 4.020 (1 H, m, OC*H*), 4.077 (1 H, dd, $J_{1,2}$ 7.9, $J_{2,3}$ 9.8, H2a), 4.095 (1 H, ddd ≈ t, $J_{4,5} < 1$, $J_{5,6'} \approx J_{5,6"} \approx 6.0$, H5d), 4.154 (1 H, dd, $J_{6',6"}$ 11.9, $J_{5,6"}$ 3.8, H6"c), 4.260 (2 H, m, H6'd and H6"d), 4.282 (1 H, dd, $J_{6',6"}$ 12.1, $J_{5,6"}$ 5.5, H6"a), 4.412 (1 H, dd, $J_{6',6"}$ 12.3, $J_{5,6'}$ 4.7, H6'e), 4.528 (1 H, d, $J_{1,2}$ 8.1, H1b), 4.574 (1 H, dd, $J_{6',6"}$ 12.0, $J_{5,6'}$ 2.0, H6'a), 4.595 (1 H, d, $J_{1,2}$ 7.9, H1a), 4.735 (1 H, d, $J_{1,2}$ 7.7, H1d), 4.825 (2 H, m, $J_{1,2}$ 8.1, H6'c, H1c), 4.981 (1 H, d, $J_{1,2}$ 8.3, H1e), 5.072 (1 H, dd, $J_{1,2}$ 8.1, $J_{2,3}$ 10.0, H2b), 5.152 (1 H, dd, $J_{2,3}$ 10.5, $J_{3,4}$ 3.5, H3d), 5.172 (2 H, dd ≈ t, $J_{2,3} \approx J_{3,4} \approx J_{4,5} \approx 9.5$, H3a, H4e), 5.223 (1 H, dd, $J_{2,3}$ 10.1, $J_{3,4}$ 9.0, H3c), 5.465 (1 H, dd ≈ d, $J_{3,4}$ 3.4, $J_{4,5} < 1$, H4b), 5.501 (1 H, dd ≈ d, $J_{3,4}$ 3.5, $J_{4,5} < 1$, H4d), 5.564 (1 H, dd, $J_{2,3}$ 10.1, $J_{3,4}$ 9.5, H3e).

**2-Aminoethyl 2-acetamido-2-deoxy-4-*O*-{3-*O*-[2-acetamido-2-deoxy-4-O-(β-*D*-galactopyranosyl)-β-*D*-glucopyranosyl]-6-*O*-[2-acetamido-2-deoxy-β-*D*-glucopyranosyl]-β-*D*-galactopyranosyl}-β-*D*-glucopyranoside (V).** De-*O*-acetylation and removal of the *N*-trifluoroacetamide protective group from (**XXIX**) (50.4 mg, 0.031 mmol) yielded 28.1 mg (92%) of pentasaccaride (**V**); $R_f$ 0.44 (4 : 1 : 1 : 1 ethanol–water–pyridine–acetic acid); $[\alpha]_D$ –12.5 (*c* 0.5, water); MS, *m/z*: 1017 (994 + 23) $M^+ + Na^+$; $^1$H NMR ($D_2O$): 2.047 and 2.073 (×2) (3 × 3 H, 3c, 3Ac), 3.242 (2 H, m, C*H*$_2$N), 3.461 (2 H, m), 3.53–3.65 (5 H, m), 3.66–3.89 (18 H, m), 3.89–4.03 (6 H, m), 4.078 (1 H, m, OC*H*), 4.162 (1 H, dd, $J_{3,4}$ 3.1, $J_{4,5} < 1$, H4b), 4.470 (1 H, d, $J_{1,2}$ 7.9, H1b), 4.495 (1 H, d, $J_{1,2}$ 7.7, H1d), 4.596 (2 H, 2 d, $J_{1,2}$ 8.4, H1a and H1e), 4.716 (1 H, d, $J_{1,2}$ 8.3, H1c).

**2-Trifluoroacetamidoethyl 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-{2,4-di-*O*-acetyl-3-*O*-[2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-β-*D*-glucopyranosyl]-6-*O*-[2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-β-*D*-glucopyranosyl]-β-*D*-galactopyranosyl}-β-*D*-glucopyranoside (XXXI).** Glycosylation of tetrasaccharide (**XXVI**) (148 mg, 0.113 mmol) with glycosyl bromide (**XXI**) prepared from the corresponding thioglycoside (139 mg, 0.171 mmol) and repeated chromatographic purification on silica gel (10 : 1 chloroform–isopropanol) yielded 39 mg (26%) of the starting (**XXVI**) and 122.6 mg (53%) of the target (**XXX**); $R_f$ 0.22 (10 : 1 chloroform–methanol). Troc derivative (**XXX**) was treated with zinc in acetic acid and subjected to five subsequent chromatographic purifications on silica gel (elution with 9% isopropanol in ethyl acetate, twice with 10% isopropanol in ethyl acetate, and twice with 17% isopropanol in chloroform) to give 53 mg (46%) of peracetate (**XXXI**); $R_f$ 0.30 (7 : 1 ethyl acetate–isopropanol); $[\alpha]_D$ –6.4 (*c* 1, chloroform); MS, *m/z*: 1947 (1924 + 23) $M^+ + Na^+$; $^1$H NMR ($CDCl_3$): 1.912, 1.963, 1.971, 1.977, 1.986, 2.052, 2.063 (×4), 2.082, 2.085, 2.089, 2.100, 2.108, 2.143, 2.153, 2.158, and 2.161 (19 × 3 H, 19 s, 19 Ac), 3.48–3.76 (10 H, m), 3.806 (4 H, m, H2e, H4e, H3b, H4c), 3.84–3.94 (4 H, m, OC*H*, H4a, H5d, H5f), 4.003 (1 H, dd, $J_{6',6"}$ 11.9, $J_{5,6"}$ 3.1, H6"c), 4.009 (1 H, ddd, H2a), 4.05–4.23 (6 H, m, H6"a, H6"e, H6'd, H6"d, H6'f, H6"f), 4.378 (1 H, d, $J_{1,2}$ 8.2, H1b), 4.449 (1 H, dd, $J_{6',6"}$ 11.9, $J_{5,6'}$ 2.2, H6'a), 4.530 (1 H, d, $J_{1,2}$ 7.9, H1a), 4.537 (2 H, 2 d, $J_{1,2}$ 7.9, H1d and H1f), 4.594 (1 H, dd, $J_{6',6"}$ 12.0, $J_{5,6'}$ 2.6, H6'e), 4.665 (1 H, d, $J_{1,2}$ 7.9, H1c), 4.700 (1 H, dd, $J_{5,6'}$ 1.8, $J_{6',6"}$ 12.0, H6'c), 4.738 (1 H, d, $J_{1,2}$ 7.0, H1e), 4.958 (1 H, dd, $J_{1,2}$ 7.9, $J_{2,3}$ 9.7, H2b), 4.983 and 5.005 (2 × 1 H, 2 dd, $J_{2,3}$ 11.0, $J_{3,4}$ 3.4, H3d and H3f), 5.115 (2 H, 2 dd, H2d and H2f), 5.158 (2 H, 2dd ≈ t, H3a and H3c), 5.218 (1 H, dd ≈ t, $J_{3,4}$ 8.3, $J_{2,3}$ 8.8, H3e), 5.299 (1 H, dd ≈ d, $J_{3,4}$ 3.4, $J_{4,5} < 1$, H4b), 5.358 and 5.377 (2 × 1 H, 2 dd ≈ d, $J_{3,4}$ 3.4, $J_{4,5} < 1$, H4d and H4f), 5.407 (1 H, d, $J_{2,NH}$ 8.6, N*H*Ac-c), 6.281 (1 H, d, $J_{2,NH}$ 8.8, N*H*Ac-e), 6.324 (1 H, d, $J_{2,NH}$ 8.6, N*H*Ac-a), 7.335 (1 H, m, N*H*$COCF_3$).

**2-Aminoethyl 2-acetamido-2-deoxy-4-*O*-{3-*O*-[2-acetamido-2-deoxy-4-*O*-(β-*D*-galactopyranosyl)-β-*D*-glucopyranosyl]-6-*O*-[2-acetamido-2-deoxy-4-*O*-(β-*D*-galactopyranosyl)-β-*D*-glucopyranosyl]-β-*D*-galactopyranosyl}-β-*D*-glucopyranoside (VIII).** De-*O*-acetylation and the removal of *N*-trifluoroacetamide protective group from (**XXXI**) (53 mg, 0.028 mmol) yielded 29.4 mg (93%) of hexasaccharide (**VIII**); $R_f$ 0.39 (4 : 1 : 1 : 1 ethanol–water–pyridine–acetic acid); $[\alpha]_D$ +7.15 (*c* 0.5, water); MS, *m/z*: 1179 (1156 + 23) $M^+ + Na^+$; $^1$H NMR ($D_2O$): 2.046 and 2.069 (×2) (3 × 3 H, 3c, 3Ac), 3.241 (2 H, m, C*H*$_2$N), 3.52–3.69 (6 H, m), 3.66–3.89 (24 H, m), 3.90–4.03 (7 H, m), 4.079 (1 H, m, OC*H*), 4.165 (1 H, dd, $J_{3,4}$ 2.4, $J_{4,5} < 1$, H4b), 4.484 (3 H, m, H1b, H1d, and H1f), 4.594 (1 H, d, H1a, $J_{1,2}$ 8.3), 4.641 (1 H, d, $J_{1,2}$ 7.2, H1e), 4.716 (1 H, d, $J_{1,2}$ 8.3, H1c).

**2-Trifluoroacetamidoethyl 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-(2,3,4-tri-*O*-acetyl-β-*D*-galactopyranosyl)-β-*D*-glucopyranoside (XII).** Hydrogenolysis

of lactosamine derivative (**XI**) (975 mg, 1.13 mmol) and the subsequent chromatography on silica gel (elution with 7–15% isopropanol in chloroform containing 0.5% pyridine) yielded 572 mg (69%) of 6b-OH derivative (**XII**); $R_f$ 0.45 (10% isopropanol in ethyl acetate); $[\alpha]_D$ –17.4 (*c* 1, 3 : 1 $CHCl_3$–$CH_3OH$); MS, *m/z*: 754 (732 + 23) $M^+ + Na^+$; $^1$H NMR (3 : 1 $CDCl_3$–$CD_3OD$): 2.074, 2.120, 2.211, 2.220, 2.269, and 2.292 (6 × 3 H, 6 s, 6 Ac), 3.55–3.69 (3 H, m, C$H_2$N, 3.655, $J_{6',6''}$ 11.1, $J_{5,6'}$ 6.4, H6'b), 3.74–3.84 (3 H, m, OC*H*, H5a, 3.799, dd, $J_{6',6''}$ 11.1, $J_{5,6''}$ 6.6, H6"b), 3.871 (1 H, m, H5b), 3.970 (1 H, dd, $J_{3,4}$ 8.8, $J_{4,5}$ 9.5, H4a), 4.014 (1 H, m, OC*H*), 4.095 (1 H, dd, $J_{1,2}$ 8.3, $J_{2,3}$ 10.3, H2a), 4.248 (1 H, dd, $J_{6',6''}$ 12.0, $J_{5,6'}$ 5.4, H6'a), 4.589 (1 H, d, $J_{1,2}$ 8.3, H1a), 4.639 (1 H, dd, $J_{6',6''}$ 12.0, $J_{5,6''}$ 2.1, H6"a), 4.689 (1 H, d, $J_{1,2}$ 7.8, H1b), 5.144 (1 H, dd, $J_{3,4}$ 3.2, $J_{2,3}$ 10.3, H3b), 5.173 (1 H, dd, $J_{2,3}$ 10.3, $J_{3,4}$ 8.8, H3a), 5.211 (1 H, dd, $J_{1,2}$ 7.8, $J_{2,3}$ 10.3, H2b), 5.557 (1 H, dd, $J_{3,4}$ 3.2, $J_{4,5} < 1$, H4b).

**2-Trifluoroacetamidoethyl 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-[2,3,4-tri-*O*-acetyl-6-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-glucopyranosyl)-β-*D*-galactopyranosyl]-β-*D*-glucopyranoside (XXXIII).** Glycosylation of disaccharide (**XII**) (250 mg, 0.342 mmol) with glycosyl bromide (**XIV**) prepared from the corresponding peracetate (267 mg, 0.512 mmol) and subsequent chromatography on silica gel (elution with 5–10% isopropanol in chloroform) yielded 37 mg (15%) of the mixture of the starting (**XII**), its isomer (the product of migration of the OAc group from C6 to C4 of the galactose unit), and 323 mg (79%) of the mixture of the products with the same chromatographic mobility, $R_f$ 0.30 (10% isopropanol in chloroform). According to $^1$H NMR data, trisaccharide (**XXXII**) was the main component. The resulting mixture was treated with zinc in acetic acid. Four chromatographic purifications on silica gel (elution with 8–15% isopropanol in chloroform and with 8% isopropanol in ethyl acetate) yielded 160 mg (59%) of peracetate (**XXXIII**); $R_f$ 0.34 (10% isopropanol in ethyl acetate); $^1$H NMR (3 : 1 $CDCl_3$–$CD_3OD$): 2.073, 2.077, 2.104, 2.166, 2.180, 2.207, 2.211, 2.249, and 2.275 (×2) (10 × 3 H, 10c, 10Ac), 3.56–3.69 (2 H, m, C$H_2$N), 3.770 (1 H, dd, $J_{1,2}$ 8.3, $J_{2,3}$ 10.5, H2c), 3.75–3.79 (1 H, m, H5a), 3.814 (1 H, m, OC*H*), 3.85–3.91 (3 H, m, H5, H6'b and H6"b), 3.933 (1 H, dd, $J_{3,4}$ 8.8, $J_{4,5}$ 9.5, H4a), 3.99–4.05 (2 H, m, OC*H*, H5b), 4.081 (1 H, dd, $J_{1,2}$ 8.3, $J_{2,3}$ 10.3, H2a), 4.260 (1 H, dd, $J_{6',6''}$ 11.7, $J_{5,6'}$ 5.6, H6'a), 4.298 (1 H, dd, $J_{6',6''}$ 12.5, $J_{5,6''}$ 2.2, H6"c), 4.412 (1 H, dd, $J_{6',6''}$ 12.5, $J_{5,6'}$ 4.7, H6'c), 4.606 (1 H, d, $J_{1,2}$ 8.3, H1a), 4.628 (1 H, dd, $J_{6',6''}$ 11.7, $J_{5,6''}$ 2.2, H6"a), 4.703 (1 H, d, $J_{1,2}$ 7.8, H1b), 4.980 (1 H, d, $J_{1,2}$ 8.3, H1C), 5.066 (1 H, dd, $J_{2,3}$ 10.3, $J_{3,4}$ 3.4, H3b), 5.155 (1 H, dd ≈ t, $J_{3,4} \approx J_{4,5} \approx 9.3$, H4c), 5.191 (1 H, dd, $J_{1,2}$ 7.8, $J_{2,3}$ 10.3, H2b), 5.213 (1 H, dd, $J_{2,3}$ 10.3, $J_{3,4}$ 8.8, H3a), 5.488 (1 H, dd, $J_{2,3}$ 10.5, $J_{3,4}$ 9.3, H3C), 5.511 (1 H, dd, $J_{3,4}$ 3.4, $J_{4,5} < 1$, H4b).

**2-Aminoethyl 2-acetamido-2-deoxy-4-*O*-[6-*O*-(2-acetamido-2-deoxy-β-*D*-glucopyranosyl)-β-*D*-galactopyranosyl]-β-*D*-glucopyranoside (II).** De-*O*-acetylation and removal of the *N*-trifluoroacetamide protective group from (**XXXIII**) (153 mg, 0.144 mmol) yielded 90 mg (99%) of trisaccharide (**II**); $R_f$ 0.61 (3 : 1 : 1 : 1 ethanol–water–pyridine–acetic acid); $[\alpha]_D$ –32.5 (*c* 1, water); MS, *m/z*: 652 (629 + 23) $M^+ + Na^+$; $^1$H NMR ($D_2O$): 2.069 (×2) (2 × 3 H, 2 s, 2 Ac), 3.238 (2 H, m, C$H_2$N), 3.42–3.49 (2 H, m, H4c), 3.544 (1 H, dd, $J_{1,2}$ 7.8, $J_{2,3}$ 10.0, H2b), 3.560 (1 H, dd, $J_{2,3}$ 10.4, $J_{3,4}$ 8.4, H3c), 3.629 (1 H, m, H5a), 3.666 (1 H, dd, $J_{2,3}$ 10.0, $J_{3,4}$ 3.3, H3b), 3.689 (1 H, dd, $J_{3,4}$ 8.2, $J_{4,5}$ 9.7, H4a), 3.699 (1 H, dd, $J_{1,2}$ 8.4, $J_{2,3}$ 10.4, H2c), 3.738 (1 H, dd, $J_{2,3}$ 10.2, $J_{3,4}$ 8.2, H3a), 3.74–3.78 (1 H, m, H5c), 3.817 (1 H, dd, $J_{1,2}$ 8.4, $J_{2,3}$ 10.2, H2a), 3.82–4.02 (9 H, m), 4.074 (1 H, m, OC*H*), 4.477 (1 H, d, $J_{1,2}$ 7.8, H1b), 4.595 (2 H, d, $J_{1,2}$ 8.4, H1a, H1c).

**2-Trifluoroacetamidoethyl 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-{2,3,4-tri-*O*-acetyl-6-*O*-[2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-β-*D*-glucopyranosyl]-β-*D*-galactopyranosyl}-β-*D*-glucopyranoside (XXXV).** Glycosylation of disaccharide (**XII**) (210 mg, 0.287 mmol) with glycosyl bromide (**XXI**) obtained from the corresponding thioglycoside (301 ;mg, 0.370 mmol) and the subsequent chromatography on silica gel (elution with 5–10 % isopropanol in chloroform) yielded 63 mg (30%) of the starting (**XII**) and 258 mg (61%) of tetrasaccharide (**XXXIV**), $R_f$ 0.27 (10% isopropanol in chloroform). The treatment of Troc derivative (**XXXIV**) with zinc in acetic acid and four subsequent chromatographic purifications on silica gel (elution with 5–7% isopropanol in ethyl acetate) yielded 159 mg (68%) of *N*-acetyl derivative (**XXXV**) (68%), $R_f$ 0.48 (10% isopropanol in ethyl acetate); $[\alpha]_D$ –7.2 (*c* 1, chloroform); MS, *m/z*: 1372 (1349 + 23) $M^+ + Na^+$; $^1$H NMR ($CDCl_3$): 1.961, 1.964, 1.975, 1.981, 2.053, 2.064, 2.065, 2.089, 2.095, 2.114, 2.135, 2.143, and 2.157 (13 × 3 H, 13 s, 13 Ac), 3.47–3.64 (2 H, m, C$H_2$N), 3.64–3.77 (5 H, m, OC*H*, H6'b, H6"b, H5a, H5c), 3.794 (1 H, dd ≈ t, $J_{3,4} \approx J_{4,5} \approx 8.1$, H4c), 3.843 (1 H, ddd ≈ t, $J_{4,5} < 1$, $J_{5,6'} \approx J_{5,6''} \approx 5.6$, H5b), 3.865–3.946 (4 H, m, OC*H*, H2c, H5d, H4a), 4.015 (1 H, ddd, $J_{2,NH}$ 8.8, $J_{1,2}$ 8.1, $J_{2,3}$ 8.7, H2a), 4.111 (2 H, m, H6'd and H6"d), 4.177 (2 H, m, H6"a and H6"c), 4.491 (5 H, m, H1a, H1b, H1d, H6'a, H6'c), 4.671 (1 H, d, $J_{1,2}$ 7.0, H1c), 4.985 (1 H, dd, $J_{2,3}$ 10.4, $J_{3,4}$ 3.4, H3b), 5.000 (1 H, dd, $J_{2,3}$ 10.4, $J_{3,4}$ 3.4, H3d), 5.078 (1 H, dd, $J_{1,2}$ 7.8, $J_{2,3}$ 10.4, H2b), 5.112 (1 H, dd, $J_{1,2}$ 7.8, $J_{2,3}$ 10.4, H2d), 5.141 (1 H, dd ≈ t, $J_{3,4}$ 8.1, $J_{2,3}$ 8.8, H3c), 5.170 (1 H, dd ≈ t, $J_{2,3} \approx J_{3,4} \approx 9.0$, H3a), 5.361 (1 H, dd ≈ d, $J_{3,4}$ 3.4, $J_{4,5} < 1$, H4b), 5.373 (1 H, dd ≈ d, $J_{3,4}$ 3.4, $J_{4,5} < 1$, H4d), 6.046 (1 H, d, $J_{2,NH}$ 9.0, N*H*Ac-c), 6.236 (1 H, d, $J_{2,NH}$ 8.8, N*H*Ac-a), 7.371 (1 H, m, N*H*COC$F_3$).

**2-Aminoethyl 2-acetamido-2-deoxy-4-*O*-{6-*O*-[2-acetamido-2-deoxy-4-*O*-(β-*D*-galactopyranosyl)-β-*D*-glucopyranosyl]-β-*D*-galactopyranosyl}-β-*D*-glucopyranoside (VII).** De-*O*-acetylation and removal of *N*-trifluoroacetamide protective group from peracetate (**XXXV**) (262 mg, 0.194 mmol) yielded 146 mg (95%)

of tetrasaccharide (**VII**); $R_f$ 0.59 (3 : 1 : 1 : 1 ethanol–water–pyridine–acetic acid); $[\alpha]_D$ –23.9 (*c* 0.5, water); MS, *m/z*: 814 (791 + 23) $M^+ + Na^+$; $^1H$ NMR ($D_2O$): 2.071 and 2.076 (2 × 3 H, 2 s, 2 Ac), 3.246 (2 H, m, C$H_2$N), 3.557 (2 H, m, H2b and H2d), 3.59–3.94 (18 H, m), 3.934 and 3.946 (2 H, 2 dd, $J_{3,4}$ 3.4, $J_{4,5} < 1$, H4b and H4d), 3.96–4.03 (3 H, m), 4.082 (1 H, m, OC*H*), 4.486 (2 H, 2 d, $J_{1,2}$ 7.9, H1b and H1d), 4.601 (1 H, d, $J_{1,2}$ 8.2, H1a), 4.645 (1 H, d, $J_{1,2}$ 7.2, H1c).

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