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Syntheses of L-glucosamine donors for 1,2-*trans*-glycosylation reactions

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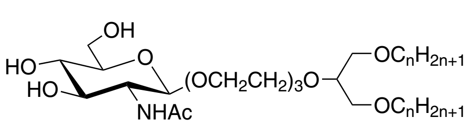
Abstract—Two new L-glucosamine donors, that is pent-4-enyl 3,4,6-tri-*O*-acetyl-2-allyloxycarbonylamino-2-deoxy-β-L-glucopyranoside **16** and ethyl 3,4,6-tri-*O*-acetyl-2-allyloxycarbonylamino-2-deoxy-1-thio-β-L-glucopyranoside **21** were prepared in 12 steps from L-arabinose. The reaction pathway uses 3,4,6-tri-*O*-acetyl-L-glucal **5**, and then 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-α-L-mannopyranosyl azide **8** as intermediates. The latter, together with donors **16** and **21**, were used for preparing L-glucosamine neoglycolipids.

1. Introduction

Chiral discrimination in self-organized supramolecular systems is of major importance in understanding the building of biological assemblies, such as cell membranes. Amongst such assemblies, monolayers constitute a very simple 2D cell membrane model that was studied in detail.[1] In these simple systems, the chirality of the molecules can induce the formation of chiral anisotropic domains that can be displayed in the π-A isotherm or directly visualized in the condensed phase by Brewster angle microscopy (BAM)[2] or fluorescence microscopy,[3] for example. The chiral discrimination can manifest itself in two ways: either the chiral molecules have a higher affinity for themselves than for the enantiomer, thus forming aggregates in the condensed phase (homochiral discrimination), or the chiral molecules have a higher affinity for their enantiomers (heterochiral discrimination). In the latter case, the racemic mixture displays lower surface areas than the pure enantiomers at any surface pressures. Many amphiphilic molecules able to form such assemblies have been studied, most of which bear one stereogenic center only. In the field of glycolipids, in which the hydrophilic head contains several stereogenic centers, mostly aldonamides were studied. Thus, it was demonstrated that epimers could behave quite differently, *N*-dodecyl gluconamide exhibiting an heterochiral preference whereas *N*-dodecyl mannonamide exhibited an homochiral preference.[4]

In the field of our research devoted to the use of *N*-acetyl-D-glucosaminyl neoglycolipids **I** in the formation of stable monolayers, able to strongly embed immunoglobulins in an oriented position, we were surprised by such a stability.[5] Amongst the hypotheses put forward to explain this phenomenon, a carbohydrate–carbohydrate recognition between the glycolipid head and the glycan fraction of the immunoglobulin could be responsible for the interaction. The assembly was modeled and shown to be compatible with the hypothesis.[6] Consequently, we decided to build monolayers with molecules of opposite chirality, that is *N*-acetyl-L-glucosamine neoglycolipids **II**, in order to check the stability of embeddement of immunuglobulins in the



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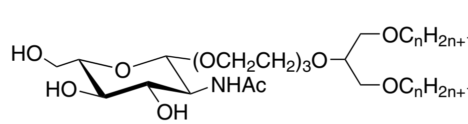

II

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latter and also to study the chiral discrimination between both enantiomers of the glycolipid. Herein, we report the synthesis of such neoglycolipids.

2. Results and discussion

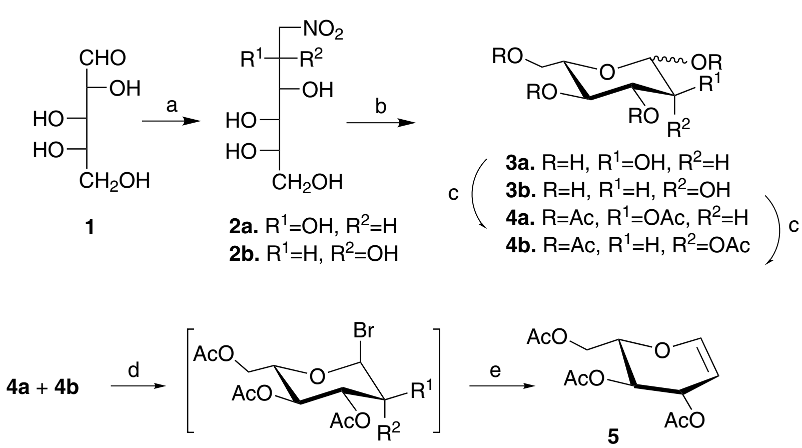
Due to the low occurrence of the L-enantiomer (only found as *N*-methyl derivatives in streptomycines[7]) compared with the D-enantiomer found in many natural compounds and biopolymers such as glycoproteins or chitins,[8] very few syntheses of L-glucosamine derivatives have been reported in the literature. Formerly, L-arabinose and hydrogen cyanide were used to prepare a 2-alkylamino-2-deoxy-L-glucononitrile, which was further transformed into *N*-alkyl-L-glucosamine by controlled hydrogenation.[9–12] In 1989, Leblanc et al.[13] reported the [4+2] cycloaddition of dibenzyl azodicarboxylate and glycals. Thus methyl 2-acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-β-L-glucopyranoside was prepared from a furanic L-glycal, thus avoiding the use of hydrogen cyanide. Azidonitration of tri-*O*-acetyl-L-glucal was reported to afford a mixture of separable 2-azido-2-deoxy-L-*manno* and -L-*gluco* epimers, each obtained in 38% yield;[14] the latter could be subsequently transformed into *N*-acetyl derivatives. In 2000, Sasaki et al.[15] reported an eight step synthesis of a 3-*O*-*tert*-butylsilyl derivative of L-glucosamine from 2,3-*O*-isopropylidene-L-glyceraldehyde and (*R*)-2-*tert*-butyloxycarbonylamino-3-phenylsulfonyl-1-propanol. More recently, using the 'mirror-image carbohydrate' concept,[16] Boulineau and Wei[17,18] reported the synthesis of non-natural enantiomers of lactosamine and a trisaccharide blood group. The key step was the iodosulfonamidation of L-glucal, followed by glycosylation using Danishefsky's procedure.[19,20]

We decided to explore a new strategy to prepare L-glucosamine glycosylation donors by simple methods that could be scaled up. Thus, the condensation of L-arabinose **1** with nitromethane, in the presence of sodium methylate[21] afforded a mixture of 1-deoxy-1-nitro-L-glucitol **2a** and 1-deoxy-1-nitro-L-mannitol **2b**. The acidic treatment (Nef reaction) of the mixture **2a/2b** gave rise to a mixture of L-glucose and L-mannose **3a/3b**, which was acetylated to **4a/4b**. Treatment of the mixture with hydrobromic acid, followed by zinc reduction, afforded 3,4,6-tri-*O*-acetyl-L-glucal **5** in 88% from **4a/4b** (Scheme 1).

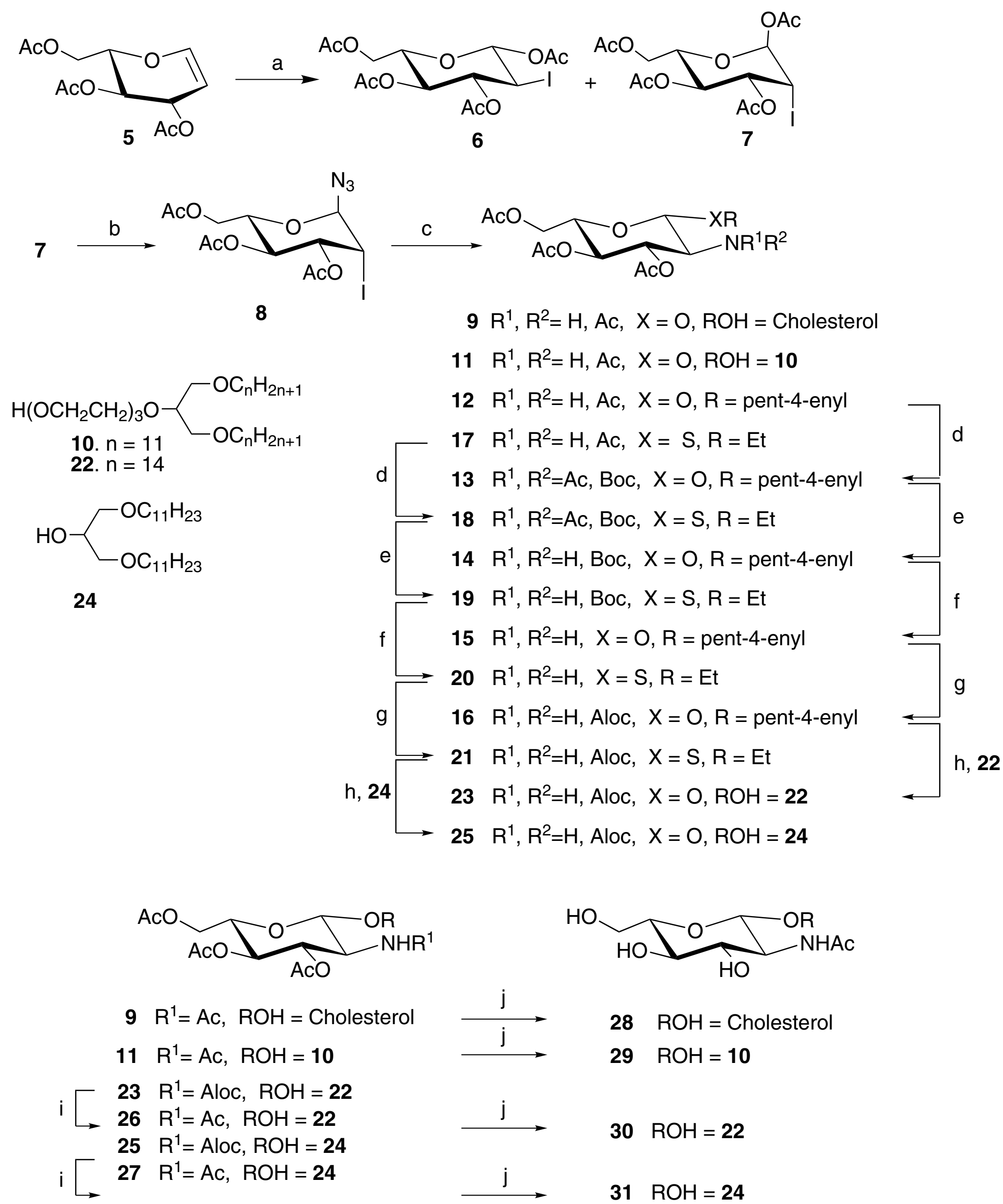
The iodoacetoxylation[22] of **5** (I_2, $Cu(OAc)_2$, AcOH, 80 °C) afforded 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-iodo-β-L-glucopyranose **6** and 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-iodo-α-L-mannopyranose **7** in 11% and 79% yields, after purification. Iodoacetate **7** was then converted to the 2-iodoglycosyl azide **8** ($TMSN_3$, TMSOTf, CH_2Cl_2) in 94% yield, by the methodology that we have already reported in the D-series.[23] The latter was used as glycosylation donor, using the procedure described previously (PPh_3, CH_2Cl_2),[24] with cholesterol or 10-undecyloxymethyl-3,6,9,12-tetraoxatricosanol **10**[25] as acceptors to afford 2-acetamido-2-deoxy L-glycosides **9** and **11** in 62% and 51% yields, respectively. Nevertheless, this procedure is only efficient with reactive acceptors, as mentioned previously in the D-series. Therefore, we were searching for more efficient glycosylation donors of L-glucosamine from intermediate **8**.

Several D-glucosamine donors for 1,2-*trans*-glycosylation have been reviewed in the literature,[26–28] which could be extended to L-glucosamine donors. We experienced 2-alkoxycarbonylamino derivatives, previously used in our laboratory, since they allow the use of a large variety of anomeric leaving groups and constitute as versatile derivatives for further transformations on the amino function. A pentenyl glycoside donor[29,30] was prepared by the reaction of **8** with pent-4-en-1-ol in the presence of PPh_3, as reported previously, to afford **12** in 71% yield (Scheme 2).

The unreactive acetamido function of **12** was then activated via a 2-amino-2-deoxy intermediate **15** by the following pathway: treatment with *tert*-butyl pyrocarbonate in the presence of DMAP in THF[31] afforded the *N*-acetyl, *N*-*tert*-butoxycarbonyl compound **13** (93%) as a mixture of two rotamers.[32] Then de-O,N-acetylation and re-O-acetylation afforded the NHBoc derivative **14** (92%), which was deprotected quantitatively to give the free amino derivative **15** using trifluoroacetic acid. The latter can then be activated in several manners; we chose the reaction of allylchloroformate under biphasic conditions ($CHCl_3/H_2O$), in



Scheme 1. Reagents and conditions: (a) $MeNO_2$, MeONa, MeOH, 50%; (b) H_2SO_4, then Dowex $[H]^+$, 78%; (c) Ac_2O, pyridine, 74%; (d) 33% HBr in AcOH, Ac_2O, 100%; (e) Zn powder, $CuSO_4$, AcONa, 60% aq AcOH, 88%.



Scheme 2. Reagents and conditions: (a) I_2, $Cu(OAc)_2$, AcOH, 80 °C (11% **6**, 79% **7**); (b) $TMSN_3$, TMSOTf, CH_2Cl_2, 94%; (c) (I) ROH or EtSH, PPh_3, CH_2Cl_2, (II) Dowex 2X8 [OH^-], EtOH, (III) MeONa (cat.), MeOH, (IV) Ac_2O, pyridine (62% **9**, 51% **11**, 71% **12**, 43% **17**); (d) Boc_2O, DMAP (cat.), THF, 80 °C (93% **13**, 90% **18**); (e) (I) MeONa (cat.), MeOH, (II) Ac_2O, pyridine (92% **14**, 90% **19**); (f) TFA, CH_2Cl_2 (100% **15** and **20**); (g) AllOCOCl, $NaHCO_3$, $CHCl_3$, H_2O (90% **16**, 95% **21**); (h) ROH, NIS, TMSOTf, CH_2Cl_2, −20 °C; (i) (I) $Pd(PPh_3)_4$, $CH_2(COOEt)_2$, THF; (II) Ac_2O, pyridine (77% **26**, 81% **27**); (j) MeONa (cat.), MeOH, 93–95%.

the presence of $NaHCO_3$, which afforded donor **16** in 90% yield, that is 72% overall yield from compound **12**. The same reaction pathway was applied to prepare a thioalkyl glycosyl donor.[33] The Staudinger reaction of **8** and ethanethiol affording **17** was accompanied by several by-products (43% yield only). Further transformations of *N*-acetyl derivative **17** to *N*-Boc derivative **19**, then to the free amino compound **20**, and finally to ethyl 3,4,6-tri-*O*-acetyl-2-allyloxycarbonylamino-2-deoxy-1-thio-β-L-glucopyranoside **21** were realized, as previously, in 73% overall yield.

It should be noted that a shorter route to compounds **16** and **21** was also explored, that is saponification of compounds **12** and **17** to (thio)alkyl 2-amino-2-deoxy-L-glucosides, followed by N-carbamoylation, then O-acetylation. Despite its simplicity, this reaction pathway afforded several by-products, which were difficult to separate from the expected intermediates. Therefore, the four step reactions from **12** and **17** to **16** and **21**, respectively, were preferred to the latter.

Glycosylation reactions from L-donors **16** and **21**, as well as their D-enantiomers, and two acceptor alcohols (10-tetradecyloxymethyl-3,6,9,12-tetraoxahexacosanol[34] **22** and 1,3-bis(undecyloxy)propan-2-ol[25] **24**) were then realized under the usual conditions, in order to demonstrate the feasibility of this method. Thus, glycoside **23** (81% yield) was obtained via reaction of **16** with **22** in the presence of stoichiometric amounts of *N*-iodosuccinimide and trimethylsilyl triflate, whereas glycoside **25** (76% yield) was obtained by reaction of **21** with **24** under the same conditions. The enantiomeric glycoside of **25** (**25-D**) was also prepared in 74% yield, by reaction of the enantiomeric donor of **16** (**16-D**) and acceptor alcohol **24**, under the same conditions.

Glycosides **9**, **11**, **23**, **25**, and **25-D** were fully deprotected affording products **28**–**31** and **31-D** in good yields.

3. Conclusion

The reaction pathway depicted herein allowed us to prepare the expected 2-acetamido-2-deoxy-β-L-glucopyranosyl neoglycolipids in reasonable yields, without using toxic derivatives, such as hydrogen cyanide. The glycosylations with donors **16** and **21** were shown to be of great synthetic interest, as previously demonstrated for their D-counterparts. They can be used for the preparation of other unnatural derivatives of L-glucosamine. The study of chiral discrimination in the monolayers of **I** and **II** is now under investigation and the results will be reported in due course.

4. Experimental

4.1. General methods

Pyridine was dried by boiling with CaH_2 prior to distillation. Dichloromethane was washed twice with water, dried with $CaCl_2$, and distilled from CaH_2. Methanol was distilled from magnesium. Tetrahydrofuran was distilled from sodium-benzophenone. Pyridine, THF, and CH_2Cl_2 were stored over 4 Å molecular sieves and MeOH over 3 Å molecular sieves. Melting points were determined on a Büchi apparatus and are uncorrected. Thin layer chromatography was performed on aluminum sheets coated with Silica gel 60 F_{254} (E. Merck). Compounds were visualized by spraying the TLC plates with dilute 15% aq H_2SO_4, followed by charring at 150 °C for a few minutes. Column chromatography was performed on Silica-gel Geduran Si 60 (Merck). Optical rotations were recorded on a Perkin Elmer 241 polarimeter in a 1 dm cell at 21 °C. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AC-200 spectrometer working at 200 and 50 MHz, respectively, with Me_4Si as internal standard. Elemental analyses were performed by the 'Laboratoire Central d'Analyses du CNRS' (Vernaison, France).

4.2. Mixture of L-glucose 3a and L-mannose 3b

To a suspension of L-arabinose **1** (20.0 g, 133 mmol) in a mixture of anhydrous MeOH (40 mL) and nitromethane (72 mL) was added a solution of MeONa (10.0 g, 185 mmol) in dry MeOH (120 mL). The suspension was stirred for 48 h, then filtered, and the filter cake washed exhaustively with cold MeOH (200 mL), and then Et_2O (20 mL). After dissolving the solid in H_2O (75 mL), the solution was eluted with water through a column of Dowex 50WX4 [H^+] resin. After concentration, the residue was co-evaporated twice from EtOH (2 × 100 mL), and crystallized on standing overnight at −15 °C in absolute EtOH (75 mL). Filtration afforded a mixture of 1-deoxy-1-nitro-L-glucitol **2a** and 1-deoxy-1-nitro-L-mannitol **2b** (14.0 g, 50%). Compound **2a**: ^{13}C NMR (D_2O): δ 78.8 (C-1), 71.5 (C-5), 71.1 (C-4), 70.7 (C-2), 70.4 (C-3), 63.2 (C-6). Compound **2b**: ^{13}C NMR (D_2O): δ 79.7 (C-1), 70.7 (C-5), 70.5 (C-3), 69.4 (C-4), 69.0 (C-2), 63.7 (C-6).

A solution of nitrosugars **2a**/**2b** (14.0 g, 66.3 mmol) in 2 M NaOH (42.1 mL, 84.2 mmol) was added dropwise to a stirred solution of 7.3 M H_2SO_4 (46.6 mL, 0.68 mol). After 30 min, the solution was diluted with water (400 mL), then neutralized with warm aq $Ba(OH)_2$. After centrifugation and addition of a slight excess of aq $Ba(OAc)_2$ to the supernatant, the solution was filtered through Celite, concentrated to 200 mL, and deionized on a column of Dowex 50WX4 [H^+]. The L-glucose/L-mannose mixture **3a**/**3b** was obtained as a white powder after evaporation and co-evaporation from absolute EtOH (2 × 100 mL) and was pure enough for the next step (9.3 g, 78%). Compound **3aα**: ^{13}C NMR (D_2O): δ 92.5 (C-1), 73.2 (C-3), 71.9, 71.8 (C-2, C-5), 70.1 (C-4), 61.1 (C-6). Compound **3aβ**: ^{13}C NMR (D_2O): δ 96.3 (C-1), 76.3, 76.2 (C-3, C-5), 74.6 (C-2), 70.0 (C-4), 61.2 (C-6). Compound **3bα**: ^{13}C NMR (D_2O): δ 94.5 (C-1), 72.8 (C-5), 71.1 (C-2), 70.7 (C-3), 67.3 (C-4), 61.4 (C-6). Compound **3bβ**: ^{13}C NMR (D_2O): δ 94.1 (C-1), 76.6 (C-5), 73.5 (C-3), 71.6 (C-2), 67.1 (C-4), 61.4 (C-6).

4.3. Mixture of 1,2,3,4,6-penta-*O*-acetyl-L-glucopyranose 4a and L-mannopyranose 4b

The mixture **3a**/**3b** (6.0 g, 33.3 mmol) was added at 0 °C to a stirred solution of pyridine (60 mL) and acetic anhydride (50 mL). The solution was allowed to reach room temperature and stirring was maintained for 16 h. After concentration, the residue was dissolved in CH_2Cl_2 (150 mL) and the organic solution was washed with 10% aq HCl (25 mL), then with satd aq $NaHCO_3$ (250 mL) and finally with water. After drying and evaporation, the product was purified by column chromatography (4:5 EtOAc–petroleum ether) to afford the expected mixture **4a**/**4b** as an oily material (9.6 g, 74%). $R_f = 0.72$ (EtOAc–petroleum ether 1:1); ^{1}H NMR ($CDCl_3$): δ 6.31 (d, 0.32 H, $J = 3.6$ Hz, H-$1_{\alpha\text{-glc}}$), 6.08 (d, 0.25H, $J = 1.6$ Hz, H-$1_{\alpha\text{-man}}$), 5.86 (br s, 0.15H, H-$1_{\beta\text{-man}}$), 5.71 (d, 0.27H, $J = 7.8$ Hz, H-$1_{\beta\text{-glc}}$), 5.50–5.05 (m, 3H, H-2, H-3, H-4), 4.35–4.01 (m, 2H, H-6a, H-6b), 3.87–3.72 (m, 1H, H-5), 2.17–2.00 (m, 15H, 5CH_3COO). Compound **4aα**: ^{13}C NMR ($CDCl_3$): δ 88.9 (C-1), 69.7 (C-3, C-5), 69.1 (C-2), 67.8 (C-4), 61.4 (C-6). Compound **4aβ**: ^{13}C NMR ($CDCl_3$): δ 91.6 (C-1), 72.6, 72.5 (C-3, C-5), 69.7 (C-2), 67.7 (C-4), 61.4 (C-6). Compound **4bα**: ^{13}C NMR ($CDCl_3$): δ 90.5 (C-1), 70.3 (C-5), 68.7 (C-2), 68.2 (C-3), 65.4 (C-4), 62.0 (C-6). Compound **4bβ**: ^{13}C NMR ($CDCl_3$): δ 90.3 (C-1), 73.0 (C-5), 69.7 (C-4), 68.1 (C-2), 65.4 (C-3), 62.0 (C-6).

4.4. 3,4,6-Tri-*O*-acetyl-1,5-anhydro-2-deoxy-L-*arabino*-hex-1-enitol 5

A mixture of **4a/4b** (9.2 g, 23.5 mmol) was dissolved in AcOH (15 mL) and Ac_2O (3 mL), then 33% HBr in acetic acid (25 mL) was added at room temperature. After 16 h, the solution was cooled to 0 °C, neutralized with anhydrous AcONa (10.0 g, 121.9 mmol) and then added to a mixture of $CuSO_4{\cdot}5H_2O$ (1.55 g, 6.2 mmol), zinc powder (37.8 g, 578 mmol), and $AcONa{\cdot}3H_2O$ (47.3 g, 347.5 mmol) in water (50 mL) and AcOH (75 mL). After vigourous stirring for 1.5 h at room temperature, the mixture was filtered and the filter cake was washed with EtOAc (150 mL), and then H_2O (150 mL). The aq filtrate was extracted with EtOAc (2 × 75 mL) and the combined organic phases were washed with satd aq $NaHCO_3$ until neutral. After drying over Na_2SO_4 and concentration, the residue was purified by flash column chromatography (1:4 EtOAc–petroleum ether, 0.5% NEt_3) to afford the expected compound **5** as a colorless oil (5.6 g, 88%). $[\alpha]_D = +22.0$ (*c* 1.2, $CHCl_3$) [D-enantiomer: lit.[35] $[\alpha]_D = -22$ (*c* 2.1, $CHCl_3$)]; ^1H NMR ($CDCl_3$) δ 6.47 (dd, 1H, *J* = 6.1, 1.0 Hz, H-1), 5.30 (m, 1H, H-3), 5.22 (dd, 1H, *J* = 5.8, 7.2 Hz, H-4), 4.85 (dd, 1H, *J* = 6.1, 3.2 Hz, H-2), 4.42 (dd, 1H, *J* = 5.3, 11.8 Hz, H-6a), 4.26 (ddd, 1H, *J* = 7.2, 5.4, 2.7 Hz, H-5), 4.20 (dd, 1H, *J* = 2.7, 11.8 Hz, H-6b), 2.10, 2.08, 2.05 (3s, 9H, 3CH_3COO).

4.5. 1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-iodo-β-L-glucopyranose 6 and 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-iodo-α-L-mannopyranose 7

A mixture of **5** (5.45 g, 20.00 mmol), $Cu(OAc)_2{\cdot}H_2O$ (4.39 g, 22.00 mmol), and iodine (6.09 g, 24.00 mmol) in AcOH (120 mL) was stirred for 4 h at 80 °C. The mixture was cooled to room temperature and concentrated under reduced pressure. The residue was diluted with EtOAc (250 mL) and the solution neutralized with satd aq $NaHCO_3$, then treated with satd aq $Na_2S_2O_3$ (50 mL) and finally with water (50 mL). The organic solution was dried (Na_2SO_4), concentrated, and purified by flash column chromatography (1:2 EtOAc–petroleum ether) affording compounds **6** (1.01 g, 11%) and **7** (7.24 g, 79%).

Compound **6**: white solid; mp 108 °C; $[\alpha]_D = -64.5$ (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.87 (d, 1H, *J* = 9.6 Hz, H-1), 5.35 (dd, 1H, *J* = 11.1, 9.0 Hz, H-3), 5.01 (dd, 1H, *J* = 9.0, 10.1 Hz, H-4), 4.33 (dd, 1H, *J* = 4.4, 12.5 Hz, H-6a), 4.08 (dd, 1H, *J* = 2.2, 12.5 Hz, H-6b), 3.98 (dd, 1H, *J* = 9.6, 11.1 Hz, H-2), 3.89 (ddd, 1H, *J* = 10.1, 4.4, 2.2 Hz, H-5), 2.17, 2.09, 2.05, 2.02 (4s, 12H, 4CH_3COO); ^{13}C NMR ($CDCl_3$): δ 170.4, 169.4, 169.4, 168.4 (CH_3*C*OO), 93.8 (C-1), 75.1 (C-5), 72.9 (C-3), 68.5 (C-4), 61.5 (C-6), 25.9 (C-2), 20.7, 20.7, 20.7, 20.5 (*C*H_3COO). Anal. Calcd for $C_{14}H_{19}IO_9$ (458.192): C, 36.69; H, 4.18. Found: C, 36.89; H, 4.28.

Compound **7**: syrup; $[\alpha]_D = -15.0$ (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 6.40 (d, 1H, *J* = 1.4 Hz, H-1), 5.46 (dd, 1H, *J* = 9.1, 9.8 Hz, H-4), 4.59 (dd, 1H, *J* = 4.4, 9.1 Hz, H-3), 4.53 (dd, 1H, *J* = 1.4, 4.4 Hz, H-2), 4.24 (dd, 1H, *J* = 4.6, 12.4 Hz, H-6a), 4.15 (dd, 1H, *J* = 2.4, 12.4 Hz, H-6b), 4.12 (ddd, 1H, *J* = 9.8, 4.4, 2.4 Hz, H-5), 2.17, 2.12, 2.11, 2.07 (4s, 12H, CH_3COO); ^{13}C NMR ($CDCl_3$): δ 170.5, 169.8, 169.3, 168.1 (CH_3*C*OO), 94.6 (C-1), 71.4 (C-5), 68.6 (C-3), 67.0 (C-4), 61.8 (C-6), 27.3 (C-2), 20.8, 20.8, 20.7, 20.6 (*C*H_3COO). Anal. Calcd for $C_{14}H_{19}IO_9$ (458.192): C, 36.69; H, 4.18. Found: C, 37.01; H, 4.21.

4.6. 3,4,6-Tri-*O*-acetyl-2-deoxy-2-iodo-α-L-mannopyranosyl azide 8

Trimethylsilyl trifluoromethanesulfonate (0.360 mL, 1.86 mmol) was added under argon to a solution of compound **7** (5.50 g, 12.00 mmol) and Me_3SiN_3 (3.0 mL, 22.40 mmol) in dry CH_2Cl_2 (25 mL). The mixture was stirred for 24 h, diluted with CH_2Cl_2 (100 mL), and neutralized by the addition of an excess of satd aq $NaHCO_3$ and stirring for 2 h. The aqueous solution was extracted with CH_2Cl_2 (2 × 60 mL) and the combined organic phases were dried over Na_2SO_4, concentrated under reduced pressure, and purified by column chromatography (1:1 EtOAc–petroleum ether).

Compound **8** was obtained as a syrup (4.98 g, 94%); $[\alpha]_D = -81.8$ (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.71 (d, 1H, *J* = 1.2 Hz, H-1), 5.36 (dd, 1H, *J* = 8.6, 9.5 Hz, H-4), 4.52 (dd, 1H, *J* = 4.3, 8.6 Hz, H-3), 4.48 (dd, 1H, *J* = 1.2, 4.3 Hz, H-2), 4.26 (dd, 1H, *J* = 4.9, 12.4 Hz, H-6a), 4.22–4.18 (m, 2H, H-5, H-6b), 2.13, 2.10, 2.07 (3s, 9H, 3CH_3COO); ^{13}C NMR ($CDCl_3$): δ 170.5, 169.6, 169.3 (CH_3*C*OO), 91.0 (C-1), 71.4 (C-5), 68.6 (C-3), 67.1 (C-4), 61.8 (C-6), 28.0 (C-2), 20.9, 20.7, 20.6 (*C*H_3COO). Anal. Calcd for $C_{12}H_{16}IN_3O_7$ (441.169): C, 32.67; H, 3.66; N, 9.52. Found: C, 32.73; H, 3.66; N, 9.18.

4.7. Cholesteryl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-L-glucopyranoside 9

A solution of L-glycosyl donor **8** (0.180 g, 0.41 mmol) and cholesterol (0.174 g, 0.45 mmol) in CH_2Cl_2 (3 mL) was cooled to 10 °C before the addition of PPh_3 (0.118 g, 0.45 mmol). The mixture was allowed to reach room temperature and stirring was maintained overnight. After concentration, the residue was dissolved in the minimum amount of EtOH and was then applied at the top of a column of Dowex 2X8 [OH^-]. After elution with EtOH and concentration, the residue was treated overnight by a catalytic amount of MeONa in MeOH (5 mL). The alcoholic solution was concentrated under diminished pressure and the residue acetylated overnight in a 2:1 pyridine–Ac_2O mixture (5 mL). The solution was then concentrated and purified by column chromatography (EtOAc). Compound **9** was recrystallized from absolute EtOH and obtained as a white crystalline material (0.180 g, 62%). Mp 227 °C; R_f 0.62 (EtOAc); $[\alpha]_D = -14.1$ (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.56 (d, 1H, *J* = 8.5 Hz, N*H*), 5.43 (dd, 1H, *J* = 10.1, 9.4 Hz, H-3), 5.37 (m, 1H, H-6_{Chol}), 5.05 (dd, 1H, *J* = 9.4, 9.9 Hz, H-4), 4.90 (d, 1H, *J* = 8.2 Hz, H-1), 4.28 (dd, 1H, *J* = 4.7, 12.1 Hz, H-6a), 4.12 (dd, 1H, *J* = 1.9, 12.1 Hz, H-6b), 3.73 (ddd, 1H, *J* = 9.9, 4.7, 1.9 Hz, H-5), 3.64 (ddd, 1H, *J* = 8.2, 10.1, 8.5 Hz, H-2), 3.50–3.48 (m, 1H, H-3_{Chol}), 2.09, 2.06, 2.03, 1.96 (4s, 12H, 4CH_3CO), 3.38–0.68 (m, 43H, H cholesterol); ^{13}C

NMR ($CDCl_3$): δ 170.7, 170.7, 170.4, 169.5 (CH_3CO), 140.5 (C-5_{chol}), 122.1 (C-6_{chol}), 99.3 (C-1), 79.9 (C-3_{chol}), 72.3 (C-3), 71.5 (C-5), 69.1 (C-4), 62.5 (C-6), 56.8 (C-14_{chol}), 56.2 (C-17_{chol}), 55.4 (C-2), 50.2 (C-9_{chol}), 42.3 (C-13_{chol}), 40.1 (C-12_{chol}), 39.8 (C-24_{chol}), 39.5 (C-4_{chol}), 37.1 (C-1_{chol}), 36.6 (C-10_{chol}), 36.2 (C-22_{chol}), 35.8 (C-20_{chol}), 31.9 (C-7_{chol}), 31.8 (C-8_{chol}), 28.2 (C-2_{chol}), 28.0 (C-16_{chol}), 28.0 (C-25_{chol}), 24.3 (C-15_{chol}), 23.8 (C-23_{chol}), 22.3 (C-27_{chol}), 22.8 (C-26_{chol}), 22.6 (CH_3CON), 21.1 (C-11_{chol}), 20.8, 20.8, 20.7 (CH_3COO), 19.4 (C-19_{chol}), 18.8 (C-21_{chol}), 11.9 (C-18_{chol}). Anal. Calcd for $C_{41}H_{65}NO_9$ (715.937): C, 68.78; H, 9.15; N, 1.96. Found: C, 68.72; H, 9.15; N, 1.93.

4.8. 10-Undecyloxymethyl-3,6,9,12-tetraoxatricosyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-L-glucopyranoside 11

A solution of donor **8** (0.267 g, 0.605 mmol) and 10-undecyloxymethyl-3,6,9,12-tetraoxatricosanol **10**[25] (0.311 g, 0.584 mmol) in CH_2Cl_2 (10 mL) was cooled to 10 °C before the addition of PPh_3 (0.174 g, 0.665 mmol). The mixture was stirred for 16 h at room temperature before further addition of donor **8** (0.040 g, 0.091 mmol) and PPh_3 (0.025 g, 0.095 mmol) at 10 °C and subsequent stirring at room temperature for 16 h. After concentration, the residue was purified by column chromatography using first EtOAc, then 2:1 EtOAc–EtOH as the eluents to isolate the aminophosphonium salt as a yellow amorphous solid. ^1H NMR ($CDCl_3$): δ 7.87–7.41 (m, 15H, $3C_6H_5$), 5.86 (dd, 1H, $J = 9.5$, 9.3 Hz, H-3), 5.70 (d, 1H, $J = 8.1$ Hz, H-1), 4.79 (dd, 1H, $J = 9.3$, 9.7 Hz, H-4), 4.23 (dd, 1H, $J = 4.9$, 12.5 Hz, H-6a), 4.00 (dd, 1H, $J = 1.8$, 12.5 Hz, H-6b), 3.95 (ddd, $J = 9.7$, 4.9, 1.8 Hz, 1H, H-5), 3.70–3.00 (m, 22H, H-2, $OCH(CH_2OCH_2C_{10}H_{21})_2$-$(OCH_2CH_2)_3$), 2.00, 1.96 (2s, 6H, $2CH_3COO$), 1.60–1.40 (m, 7H, CH_3COO, $2OCH_2CH_2C_9H_{19}$), 1.35–1.20 (m, 32H, $16CH_2$ alkyl chains), 0.86 (t, 6H, $J = 6.4$ Hz, $2CH_3$ alkyl chains).

The latter was dissolved in the minimum amount of EtOH and was applied at the top of a column of Dowex 2X8 [OH^-]. After elution with EtOH and concentration, the residue was treated overnight by a catalytic amount of MeONa in MeOH (5 mL), then concentrated and acetylated overnight in a 2:1 pyridine–Ac_2O mixture (15 mL). After evaporation under diminished pressure, the mixture was purified by column chromatography (EtOAc, then 4:1 EtOAc–EtOH); a second purification was necessary for the elimination of remaining traces of PPh_3O (7:4 Me_2CO–petroleum ether). Pure product **11** was obtained as a waxy material (0.255 g, 51%). R_f 0.58 (3:2 Me_2CO–petroleum ether); $[\alpha]_D = +14.5$ (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 6.75 (d, 1H, $J = 9.3$ Hz, NH), 5.15–5.05 (m, 2H, H-3, H-4), 4.80 (d, 1H, $J = 8.6$ Hz, H-1), 4.26 (dd, 1H, $J = 4.4$, 12.2 Hz, H-6a), 4.16 (dd, 1H, $J = 1.9$, 12.1 Hz, H-6b), 4.16–4.08 (m, 1H, H-5), 3.94–3.42 (m, 22H, H-2, $OCH(CH_2OCH_2C_{10}H_{21})_2(OCH_2CH_2)_3$), 2.08, 2.01, 2.00, 1.96 (4s, 12H, $4CH_3CO$), 1.60–1.40 (m, 4H, $2OCH_2CH_2C_9H_{19}$), 1.35–1.20 (m, 32H, $16CH_2$ alkyl chains), 0.86 (t, 6H, $J = 6.5$ Hz, $2CH_3$ alkyl chains). ^{13}C NMR ($CDCl_3$): δ 170.7, 170.7, 170.4, 169.5 (CH_3CO), 101.7 (C-1), 78.3 ($HC(CH_2OC_{11}H_{23})_2$), 73.3 (C-3), 71.6 (C-5), 71.5, 71.4, 70.6, 69.7, 68.6 ($C(CH_2OCH_2$-$C_{10}H_{21})_2(OCH_2CH_2)_3$), 68.7 (C-4), 62.2 (C-6), 53.8 (C-2), 31.8, 29.5, 29.4, 29.3, 26.1, 22.3 (CH_2 alkyl chains), 22.9 (CH_3CON), 20.6, 20.5, 20.5 (CH_3COO), 14.0 (CH_3 alkyl chains). Anal. Calcd for $C_{45}H_{83}NO_{14}$ (862.121): C, 62.69; H, 9.70; N, 1.62. Found: C, 62.41; H, 9.61; N, 1.40.

4.9. Pent-4-enyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-L-glucopyranoside 12

A solution of donor **8** (4.10 g, 9.30 mmol) and pent-4-en-1-ol (1.45 mL, 14.04 mmol, 1.51 equiv) in CH_2Cl_2 (10 mL) was cooled to 10 °C before the dropwise addition of a solution of PPh_3 (3.15 g, 12.00 mmol) in CH_2Cl_2 (8 mL). The mixture was stirred overnight at room temperature, concentrated under diminished pressure, and then purified on a short column of silica-gel, using first EtOAc, then 4:1 EtOAc–EtOH as the eluents. The salt was a yellow amorphous solid. R_f 0.50–0.65 (4:1 EtOAc–EtOH); ^1H NMR ($CDCl_3$): δ 7.98–7.47 (m, 15H, $3C_6H_5$), 5.88 (dd, 1H, $J = 9.6$, 9.2 Hz, H-3), 5.69 (m, CH=), 5.68 (d, 1H, $J = 8.0$ Hz, H-1), 4.98–4.89 (m, 2H, CH_2=), 4.81 (dd, 1H, $J = 9.2$, 9.9 Hz, H-4), 4.27 (dd, 1H, $J = 5.2$, 12.2 Hz, H-6a), 4.00 (dd, 1H, $J = 1.8$, 12.2 Hz, H-6b), 3.95 (ddd, 1H, $J = 9.9$, 5.2, 1.8 Hz, H-5), 3.76 (m, 1H, $1/2OCH_2$), 3.51 (m, 1H, $1/2OCH_2$), 3.02 (ddd, 1H, $J = 8.0$, 9.6, 21.3, H-2), 2.01, 1.98 (2s, 6H, $2CH_3COO$), 2.05–1.80 (m, 2H, $CH_2CH{=}CH_2$), 1.58 (s, 3H, CH_3COO), 1.40–1.05 (m, 2H, OCH_2CH_2).

The latter was dissolved in the minimum amount of EtOH and then applied at the top of a column of Dowex 2X8 [OH^-]. After elution with EtOH and concentration, the residue was treated overnight by a catalytic amount of MeONa in MeOH (25 mL). After evaporation, water (50 mL) was added to the mixture, which was acidified to pH 4 with 3 M HCl and extracted with CH_2Cl_2 (5 × 10 mL). The aqueous layer was neutralized with solid $NaHCO_3$ and concentrated. The residue was co-evaporated twice from EtOH and acetylated overnight in a 3:2 pyridine–Ac_2O mixture (50 mL). The solution was concentrated and the residue was purified by column chromatography (EtOAc, then 6:1 EtOAc–EtOH). Glycoside **12** was obtained as a white solid (2.75 g, 71%). Mp 120–122 °C (EtOH); $[\alpha]_D = +15.3$ (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.80 (m, 1H, CH=), 5.71 (d, 1H, $J = 8.7$ Hz, NH), 5.31 (dd, 1H, $J = 10.4$, 9.4 Hz, H-3), 5.06 (dd, 1H, $J = 9.4$, 9.8 Hz, H-4), 5.04–4.94 (m, 2H, =CH_2), 4.66 (d, 1H, $J = 8.3$ Hz, H-1), 4.26 (dd, 1H, $J = 4.7$, 12.2 Hz, H-6a), 4.12 (dd, 1H, $J = 2.4$, 12.2, H-6b), 3.86 (ddd, 1H, $J = 6.7$, 6.7, 9.6 Hz, $1/2OCH_2$), 3.83 (ddd, 1H, $J = 8.3$, 10.4, 8.7 Hz, H-2), 3.71 (ddd, 1H, $J = 9.8$, 4.7, 2.4 Hz, H-5), 3.49 (ddd, 1H, $J = 6.7$, 6.7, 9.6 Hz, $1/2OCH_2$), 2.15–2.08 (m, 2H, CH_2–$CH{=}CH_2$), 2.07, 2.02, 2.01, 1.94 (4s, 12H, $4CH_3CO$), 1.70–1.62 (m, 2H, OCH_2CH_2); ^{13}C NMR ($CDCl_3$): δ 170.7, 170.7, 170.4, 169.4 (CH_3CO), 137.9 (CH=), 115.0 (=CH_2), 100.7 (C-1), 72.5 (C-3), 71.6 (C-5), 69.1 (OCH_2), 69.0 (C-4), 62.3 (C-6), 54.6 (C-2), 28.9, 28.6 ($OCH_2CH_2CH_2$), 23.2 (CH_3CON), 20.7, 20.7, 20.6 (CH_3COO). Anal. Calcd for $C_{19}H_{29}NO_9$ (415.429): C, 54.94; H, 7.04; N, 3.37. Found: C, 55.30; H, 7.05; N, 3.32.

4.9.1. Pent-4-enyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside 12-D. Obtained in 71% yield as described above from 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-α-D-mannopyranosyl azide (**8-D**). Product **12-D** was a white solid; mp 121–123 °C (EtOH) [lit.[36] mp 122–124 °C (EtOH)]; $[\alpha]_D = -15.0$ (*c* 1.0, $CHCl_3$) {lit.[37] $[\alpha]_D = -15.0$ (*c* 1.1, $CHCl_3$)}.

4.10. Pent-4-enyl *N*-acetyl-3,4,6-tri-*O*-acetyl-*N*-*tert*-butoxycarbonylamino-2-deoxy-β-L-glucopyranoside 13

A mixture of glycoside **12** (2.54 g, 6.11 mmol), Boc_2O (4.00 g, 18.33 mmol), and DMAP (0.225 g, 1.84 mmol) in dry THF (20 mL) was refluxed for 5 h under argon. After concentration, the residue was purified by column chromatography using first 1:2 EtOAc–petroleum ether, then 1:1 EtOAc–petroleum ether as the eluents. Pure compound **13** was obtained as an oily material (2.93 g, 93%). $[\alpha]_D = +20.3$ (*c* 1.0, $CHCl_3$); R_f 0.83 (1:1 EtOAc–petroleum ether). ^{1}H and ^{13}C NMR spectra showed two rotamers around the amide bond leading to a broad ^{1}H NMR spectrum. ^{1}H NMR ($CDCl_3$): δ 5.82–5.66 (m, 2H, H-3, C*H*=), 5.32 (d, 0.4H, *J* = 8.0 Hz, H-1_{min}), 5.13–4.93 (m, 3.6H, H-1_{maj}, H-4, CH_2=), 4.87 (dd, 0.6H, *J* = 8.0, 10.4 Hz, H-2_{maj}), 4.35–4.07 (m, 2.4H, H-2_{min}, H-6a, H-6b), 3.85 (ddd, 1H, *J* = 10.4, 6.3, 6.3 Hz, 1/2OCH_2), 3.72–3.62 (m, 1H, H-5), 3.45 (ddd, 1H, *J* = 10.4, 6.3, 6.3 Hz, 1/2OCH_2), 2.41 (s, 1.2H, CH_3CON), 2.34 (s, 1.8H, CH_3CON), 2.25–2.05 (m, 2H, CH_2–CH=CH_2), 2.08 (s, 3H, CH_3COO), 2.04 (s, 1.2H, CH_3COO minor rotamer), 2.01 (s, 3H, CH_3COO), 1.98 (s, 1.8H, CH_3COO major rotamer), 1.75–1.60 (m, 2H, OCH_2CH_2), 1.58 (s, 3.6H, (CH_3)$_3$C minor rotamer), 1.51 (s, 5.4H, (CH_3)$_3$C major rotamer); ^{13}C NMR, minor rotamer ($CDCl_3$): δ 172.9 (CH_3*C*ON), 170.7, 170.6, 169.6 (CH_3*C*OO), 152.0 (N*C*OO), 137.8 (*C*H=), 115.0 (*C*H_2=), 100.2 (C-1), 84.5 (*C*(CH_3)$_3$), 71.6, 71.2 (C-3, C-5), 69.6 (C-4), 69.1 (O*C*H_2), 62.2 (C-6), 56.7 (C-2), 29.8, 28.6 (OCH_2*C*H_2*C*H_2), 28.0 (C(*C*H_3)$_3$), 26.8 (*C*H_3CON), 20.8, 20.7, 20.6 (*C*H_3COO). ^{13}C NMR, major rotamer ($CDCl_3$): δ 174.0 (CH_3*C*ON), 170.7, 170.6, 169.6 (CH_3*C*OO), 153.4 (N*C*OO), 137.8 (*C*H=), 115.0 (*C*H_2=), 99.5 (C-1), 83.9 (*C*(CH_3)$_3$), 71.4, 70.6 (C-3, C-5), 69.6 (C-4), 69.2 (O*C*H_2), 62.2 (C-6), 61.6 (C-2), 29.8, 28.6 (OCH_2*C*H_2*C*H_2), 27.9 (C(*C*H_3)$_3$), 27.2 (*C*H_3CON), 20.8, 20.7, 20.6 (*C*H_3COO). Anal. Calcd for $C_{24}H_{37}NO_{11}$ (515.543): C, 55.91; H, 7.43; N, 2.72. Found: C, 55.64; H, 7.43; N, 2.54.

4.10.1. Pent-4-enyl *N*-acetyl-3,4,6-tri-*O*-acetyl-*N*-*tert*-butoxycarbonylamino-2-deoxy-β-D-glucopyranoside 13-D. Obtained in 95% as described above from the acetamido derivative **12-D**. $[\alpha]_D = -20.2$ (*c* 1.0, $CHCl_3$); R_f 0.83 (1:1 EtOAc–petroleum ether); ^{1}H and ^{13}C NMR spectra were identical with those of compound **13**. Anal. Calcd for $C_{24}H_{37}NO_{11}$ (515.543): C, 55.91; H, 7.43; N, 2.72. Found: C, 55.83; H, 7.24; N, 2.71.

4.11. Pent-4-enyl 3,4,6-tri-*O*-acetyl-2-*tert*-butoxycarbonylamino-2-deoxy-β-L-glucopyranoside 14

Compound **12** (2.85 g, 5.53 mmol) in MeOH (50 mL) was stirred for 6 h in the presence of a catalytic amount of sodium. After concentration, the product was acetylated overnight in a 2:3 Ac_2O–pyridine mixture (30 mL). The solution was concentrated under diminished pressure and the residue was co-evaporated from toluene (2 × 15 mL). The product was purified by column chromatography (1:1 EtOAc–petroleum ether) and recrystallized from absolute EtOH (2.41 g, 92%). Mp 150 °C (EtOH); $[\alpha]_D = +1.9$ (*c* 1.6, $CHCl_3$); R_f 0.70 (EtOAc–petroleum ether 1:1); ^{1}H NMR ($CDCl_3$): δ 5.76 (m, 1H, C*H*=), 5.25 (dd, 1H, *J* = 11.1, 8.0 Hz, H-3), 5.04–4.91 (m, 2H, CH_2=), 4.90 (dd, 1H, *J* = 8.0, 9.9 Hz, H-4), 4.73–4.56 (m, 2H, H-1, N*H*), 4.24 (dd, 1H, *J* = 4.9, 12.2 Hz, H-6a), 4.08 (dd, 1H, *J* = 2.3, 12.2 Hz, H-6b), 3.86 (ddd, 1H, *J* = 9.6, 6.3, 6.3 Hz, 1/2OCH_2), 3.65 (ddd, 1H, *J* = 9.9, 4.9, 2.3 Hz, H-5), 3.48 (ddd, 1H, *J* = 6.6, 11.1, 8.6 Hz, H-2), 3.47 (ddd, 1H, *J* = 9.6, 6.3, 6.3 Hz, 1/2OCH_2), 2.15–2.05 (m, 2H, CH_2CH=CH_2), 2.04, 2.00, 1.98 (3s, 9H, 3CH_3COO), 1.73–1.60 (m, 2H, OCH_2CH_2), 1.39 (s, 9H, (CH_3)$_3$C); ^{13}C NMR ($CDCl_3$): δ 170.7, 170.5, 169.5 (CH_3*C*OO), 155.1 (NH*C*OO), 137.9 (*C*H=), 115.0 (*C*H_2=), 101.2 (C-1), 79.9 (*C*(CH_3)$_3$), 72.4 (C-3), 71.7 (C-5), 69.3 (O*C*H_2), 69.0 (C-4), 62.3 (C-6), 55.9 (C-2), 29.9, 28.7 (OCH_2*C*H_2*C*H_2), 28.3 (C(*C*H_3)$_3$), 20.7, 20.7, 20.6 (*C*H_3COO). Anal. Calcd for $C_{22}H_{35}NO_{10}$ (473.507): C, 55.80; H, 7.45; N, 2.96. Found: C, 56.08; H, 7.31; N, 2.70.

4.11.1. Pent-4-enyl 3,4,6-tri-*O*-acetyl-2-butoxycarbonylamino-2-deoxy-β-D-glucopyranoside 14-D. Obtained in 88% as described above from **13-D**. Mp 150 °C (EtOH); $[\alpha]_D = -2.5$ (*c* 1.5, $CHCl_3$); R_f 0.70 (1:1 EtOAc–petroleum ether); ^{1}H and ^{13}C NMR spectra were identical with those of compound **14**. Anal. Calcd for $C_{22}H_{35}NO_{10}$ (473.507): C, 55.80; H, 7.45; N, 2.96. Found: C, 55.32; H, 7.50; N, 2.79.

4.12. Pent-4-enyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-L-glucopyranoside 15

A solution of glycoside **14** (2.36 g, 4.98 mmol) and trifluoroacetic acid (2 mL) in CH_2Cl_2 (5 mL) was stirred overnight at room temperature. After concentration and co-evaporation from toluene (2 × 10 mL), the residue was dissolved in CH_2Cl_2 (50 mL). Then, the organic solution was washed with satd aq $NaHCO_3$ (10 mL) and dried over Na_2SO_4 before evaporation to afford compound **15** in pure form as an amorphous solid (1.86 g, 100%). $[\alpha]_D = -5.1$ (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.82 (dddd, 1H, *J* = 6.6, 6.6, 10.3, 16.9 Hz, C*H*=), 5.08–4.93 (m, 4H, H-3, H-4, CH_2=), 4.30 (dd, 1H, *J* = 4.8, 12.2 Hz, H-6a), 4.24 (d, 1H, *J* = 8.0 Hz, H-1), 4.11 (dd, 1H, *J* = 2.3, 12.2 Hz, H-6b), 3.94 (ddd, 1H, *J* = 6.3, 6.3, 9.6 Hz, 1/2OCH_2), 3.68 (ddd, 1H, *J* = 9.2, 4.8, 2.3 Hz, H-5), 3.54 (ddd, 1H, *J* = 6.3, 6.3, 9.6 Hz, 1/2OCH_2), 2.94 (dd, 1H, *J* = 8.0, 9.9 Hz, H-2), 2.20–2.09 (m, 2H, CH_2CH=CH_2), 2.09, 2.08, 2.03 (3s, 9H, 3CH_3COO), 1.81–1.67 (m, 2H, OCH_2CH_2), 1.50–1.37 (m, 2H, NH_2); ^{13}C NMR ($CDCl_3$): δ 170.7, 170.6, 169.7 (CH_3*C*OO), 137.8 (*C*H=), 115.1 (*C*H_2=), 104.1 (C-1), 75.4 (C-3), 71.8 (C-5), 69.6 (O*C*H_2), 69.0 (C-4), 62.3 (C-6), 55.9 (C-2), 30.1, 28.7 (OCH_2*C*H_2*C*H_2), 20.8, 20.7, 20.7 (*C*H_3COO). Anal. Calcd for $C_{17}H_{27}NO_8$ (373.393): C, 54.68; H, 7.29; N, 3.75. Found: C, 54.93; H, 7.38; N, 3.69.

4.12.1. Pent-4-enyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranoside 15-D. Obtained in 95% as described above from **14-D**. $[\alpha]_D = +4.8$ (*c* 1.0, $CHCl_3$); R_f 0.30–0.35 (CH_2Cl_2–MeOH, 1:1), {lit.[38] $[\alpha]_D = +5.4$ (*c* 1.1, $CHCl_3$)}.

4.13. Pent-4-enyl 3,4,6-tri-*O*-acetyl-2-allyloxycarbonyl-amino-2-deoxy-β-L-glucopyranoside 16

Pentenyl glycoside **15** (1.86 g, 4.98 mmol) was dissolved in $CHCl_3$ (40 mL) before subsequent additions of a solution of $NaHCO_3$ (0.836 g, 9.96 mmol) in H_2O (20 mL) and allyl chloroformate (0.637 mL, 7.20 mmol). The mixture was stirred for 6 h; the aqueous phase was extracted with $CHCl_3$ (2 × 20 mL) and the combined organic extracts washed once with water, dried, and concentrated under diminished pressure. The residue was purified by column chromatography (1:1 EtOAc–petroleum ether). Product **16** was obtained as a solid and recrystallized from absolute EtOH (2.05 g, 90%). Mp 94–95 °C (EtOH); $[\alpha]_D = -1.0$ (*c* 5.0, $CHCl_3$); R_f 0.60 (EtOAc–petroleum ether 1:1); ^1H NMR ($CDCl_3$): δ 6.00–5.69 (m, 2H, 2C*H*=), 5.33–4.94 (m, 6H, 2CH_2=, H-3, H-4), 4.86 (d, 1H, *J* = 6.5 Hz, N*H*), 4.64–4.52 (m, 3H, H-1, allyl CH_2), 4.24 (dd, 1H, *J* = 4.7, 12.2 Hz, H-6a), 4.12 (dd, 1H, *J* = 2.1, 12.2 Hz, H-6b), 3.90 (ddd, 1H, *J* = 6.2, 6.2, 9.4 Hz, pent. 1/2OCH_2), 3.69 (ddd, 1H, *J* = 9.3, 4.7, 2.1 Hz, H-5), 3.65–3.44 (m, 2H, H-4, pent. 1/2OCH_2), 2.15–2.05 (m, 2H, pent. CH_2CH=CH_2), 2.09, 2.04, 2.03 (3s, 9H, 3CH_3COO), 1.75–1.60 (m, 2H, OCH_2CH_2); ^{13}C NMR ($CDCl_3$): δ 170.7, 170.7, 169.5 (CH_3*C*OO), 155.7 (NH*C*OO), 137.9 (pent. *C*H=), 132.7 (allyl *C*H=), 117.7 (allyl *C*H_2=), 115.0 (pent. *C*H_2=), 101.2 (C-1), 72.3 (C-3), 71.7 (C-5), 69.4 (pent. O*C*H_2), 68.9 (C-4), 65.7 (allyl O*C*H_2), 62.3 (C-6), 56.1 (C-2), 29.9, 28.6 ($OCH_2CH_2CH_2$), 20.8, 20.7, 20.7 (*C*H_3COO). Anal. Calcd for $C_{21}H_{31}NO_{10}$ (457.465): C, 55.13; H, 6.83; N, 3.06. Found: C, 54.89; H, 6.82; N, 2.78.

4.13.1. Pent-4-enyl 3,4,6-tri-*O*-acetyl-2-allyloxycarbonyl-amino-2-deoxy-β-D-glucopyranoside 16-D. Obtained in 95% as described above from **15-D**. Mp 95–96 °C (EtOH); $[\alpha]_D = +1.2$ (*c* 1.0, $CHCl_3$) {lit.[39] $[\alpha]_D = +0.4$ (*c* 1.1, $CHCl_3$)}; R_f 0.60 (1:1 EtOAc–petroleum ether).

4.14. Ethyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-1-thio-β-L-glucopyranoside 17

Ethanethiol (3.15 mL, 42.5 mmol) was added at 0 °C to a solution of donor **8** (3.70 g, 8.40 mmol) in CH_2Cl_2 (25 mL). A solution of PPh_3 (2.42 g, 1.1 equiv) in CH_2Cl_2 (10 mL) was then added dropwise and the mixture stirred overnight at room temperature, before evaporation. The aminophosphonium salt was transformed as described above for compound **12** and crude product **17** was purified by column chromatography (EtOAc). Glycoside **17** was obtained as a white solid (1.41 g, 43%). Mp 190–192 °C (EtOH); $[\alpha]_D = +42.8$ (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.58 (d, 1H, *J* = 9.5 Hz, N*H*), 5.19 (dd, 1H, *J* = 9.9, 8.9 Hz, H-3), 5.10 (dd, 1H, *J* = 8.9, 9.9 Hz, H-4), 4.60 (d, 1H, *J* = 10.3 Hz, H-1), 4.25 (dd, 1H, *J* = 4.9, 12.4 Hz, H-6a), 4.13 (dd, 1H, *J* = 2.4, 12.4 Hz, H-6b), 4.10 (ddd, 1H, *J* = 10.3, 9.9, 9.5 Hz, H-2), 3.71 (ddd, 1H, *J* = 9.9, 4.9, 2.4 Hz, H-5), 2.79–2.67 (m, 2H, SCH_2CH_3), 2.08, 2.04, 2.04, 1.96 (4s, 12H, 4CH_3CO), 1.25 (t, 3H, *J* = 7.4 Hz, SCH_2CH_3); ^{13}C NMR ($CDCl_3$): δ 170.9, 170.8, 170.4, 169.4 (CH_3*C*O), 84.3 (C-1), 75.7 (C-3), 73.9 (C-5), 68.7 (C-4), 62.5 (C-6), 53.2 (C-2), 24.2 (S*C*H_2CH_3), 23.2 (*C*H_3CON), 20.8, 20.7, 20.6 (*C*H_3COO), 14.9 (SCH_2*C*H_3). Anal. Calcd for $C_{16}H_{25}NO_8S$ (391.431): C, 49.09; H, 6.44; N, 3.58. Found: C, 48.78; H, 6.42; N, 3.50.

4.15. Ethyl *N*-acetyl-3,4,6-tri-*O*-acetyl-2-*tert*-butoxycar-bonylamino-2-deoxy-1-thio-β-L-glucopyranoside 18

A mixture of thioglycoside **17** (1.076 g, 2.75 mmol), Boc_2O (1.44 g, 6.87 mmol), and DMAP (0.030 g) in dry THF (6 mL) was refluxed for 3 h under argon. Concentration of the solution gave a residue, which was purified by column chromatography (1:1 EtOAc–petroleum ether) to afford pure derivative **18** as an oil (1.22 g, 90%). $[\alpha]_D = +5.7$ (*c* 1.0, $CHCl_3$); R_f 0.80 (EtOAc–petroleum ether 1:1). ^1H and ^{13}C NMR spectra showed two rotamers around the amide bond. Major rotamer, ^1H NMR ($CDCl_3$): δ 5.82 (dd, 1H, *J* = 9.9, 9.0 Hz, H-3), 5.53 (d, 1H, *J* = 10.1 Hz, H-1), 5.07 (dd, 1H, *J* = 9.0, 9.9 Hz, H-4), 4.27 (dd, 1H, *J* = 10.1, 9.9 Hz, H-2), 4.29–4.05 (m, 2H, H-6a, H-6b), 3.78 (ddd, 1H, *J* = 9.9, 5.1, 2.2 Hz, H-5), 2.71–2.57 (m, 2H, SCH_2), 2.36 (s, 3H, CH_3CON), 2.09–1.96 (m, 9H, 3CH_3COO), 1.54 (s, 9H, $(CH_3)_3$C), 1.26 (t, 3H, *J* = 7.4 Hz, SCH_2CH_3); ^{13}C NMR ($CDCl_3$): δ 173.0 (CH_3*C*ON), 170.4, 170.0, 169.2 (CH_3*C*OO), 151.6 (N*C*OO), 84.6 (*C*$(CH_3)_3$), 83.2 (C-1), 75.8 (C-3), 71.8 (C-5), 69.5 (C-4), 62.3 (C-6), 55.6 (C-2), 28.0 ($C(CH_3)_3$), 26.7 (*C*H_3CON), 24.1 (S*C*H_2CH_3), 20.6, 20.5, 20.4 (*C*H_3COO), 15.0 (SCH_2*C*H_3). Minor rotamer, ^1H NMR ($CDCl_3$): δ 5.72 (dd, 1H, *J* = 10.2, 9.0 Hz, H-3), 5.27 (d, 1H, *J* = 10.2 Hz, H-1), 5.11 (dd, 1H, *J* = 9.0, 9.9 Hz, H-4), 4.94 (dd, 1H, *J* = 10.2, 10.2 Hz, H-2), 4.29–4.05 (m, 2H, H-6a, H-6b), 3.71 (ddd, 1H, *J* = 9.9, 5.1, 2.1 Hz, H-5), 2.71–2.62 (m, 2H, SCH_2CH_3), 2.44 (s, 3H, CH_3CON), 2.09–1.96 (m, 9H, 3CH_3COO), 1.59 (s, 9H, $(CH_3)_3$C), 1.26 (t, 3H, *J* = 7.4 Hz, SCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 173.6 (CH_3*C*ON), 170.0, 169.8, 169.5 (CH_3*C*OO), 153.0 (N*C*OO), 84.2 (*C*$(CH_3)_3$), 82.6 (C-1), 75.5 (C-3), 71.3 (C-5), 69.5 (C-4), 62.4 (C-6), 60.4 (C-2), 27.8 ($C(CH_3)_3$), 26.7 (*C*H_3CON), 24.9 (S*C*H_2CH_3), 20.6, 20.5, 20.4 (*C*H_3COO), 15.1 (SCH_2*C*H_3). Anal. Calcd for $C_{21}H_{33}NO_{10}S$ (491.545): C, 51.31; H, 6.77; N, 2.85. Found: C, 51.39; H, 6.80; N, 2.84.

4.15.1. Ethyl *N*-acetyl-3,4,6-tri-*O*-acetyl-2-*tert*-butoxy-carbonylamino-2-deoxy-1-thio-β-D-glucopyranoside 18-D. Obtained in 95% yield as described for **17** from ethyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-1-thio-β-D-gluco-pyranoside **17-D**.[40] Compound **18-D** was obtained as an oil. $[\alpha]_D = -6.2$ (*c* 1.0, $CHCl_3$); R_f 0.80 (EtOAc–petroleum ether 1:1); ^1H and ^{13}C NMR spectra were identical with those of compound **18**. Anal. Calcd for $C_{21}H_{33}NO_{10}S$ (491.545): C, 51.31; H, 6.77; N, 2.85. Found: C, 51.27; H, 6.63; N, 2.97.

4.16. Ethyl 3,4,6-tri-*O*-acetyl-2-*tert*-butoxycarbonylamino-2-deoxy-1-thio-β-L-glucopyranoside 19

Compound **18** (1.20 g, 2.44 mmol) in MeOH (15 mL) was stirred for 6 h in the presence of a catalytic amount of sodium. After concentration, the product was acetylated overnight in a 3:4 Ac_2O–pyridine mixture (30 mL). The solution was concentrated under diminished pressure and the residue co-evaporated from toluene (2 × 15 mL). The product was purified by column chromatography (2:1 EtOAc–petroleum ether), recrystallized from absolute EtOH, and obtained as a white solid (0.980 g, 90%). Mp 149–150 °C (EtOH); $[\alpha]_D = +22.9$ (*c* 1.6, $CHCl_3$); R_f 0.80 (EtOAc–petroleum ether 2:1); ^1H NMR (CD_3COCD_3): δ 6.15 (d, 1H, *J* = 9.5 Hz, N*H*), 5.21 (dd, 1H, *J* = 10.0, 9.4 Hz, H-3), 4.98 (dd, 1H, *J* = 9.4, 10.0 Hz, H-4), 4.84 (dd, 1H, *J* = 10.4 Hz, H-1), 4.24 (d, 1H, *J* = 5.3, 12.2 Hz, H-6a), 4.09 (dd, 1H, *J* = 2.4, 12.2 Hz, H-6b), 3.81 (ddd, 1H, *J* = 10.0, 5.3, 2.4 Hz, H-5), 3.76 (ddd, 1H, *J* = 10.4, 10.0, 9.5 Hz, H-2), 2.77–2.67 (m, 2H, SCH_2CH_3), 2.02, 1.99, 1.95 (3s, 9H, $3CH_3COO$), 1.40 (s, 9H, $(CH_3)_3C$), 1.25 (t, 3H, *J* = 7.4 Hz, SCH_2CH_3); ^{13}C NMR ($CDCl_3$): δ 170.7, 170.6, 169.4 (CH_3COO), 155.0 (NHCOO), 84.6 (C-1), 80.0 ($C(CH_3)_3$), 75.8 (C-3), 73.8 (C-5), 68.8 (C-4), 62.5 (C-6), 54.6 (C-2), 28.3 ($C(CH_3)_3$), 24.2 (SCH_2CH_3), 20.7, 20.7, 20.6 (CH_3COO), 14.9 (SCH_2CH_3). Anal. Calcd for $C_{19}H_{31}NO_9S$ (449.509): C, 50.76; H, 6.95; N, 3.12. Found: C, 50.36; H, 6.89; N, 3.00.

4.16.1. Ethyl 3,4,6-tri-*O*-acetyl-2-*tert*-butoxycarbonylamino-2-deoxy-1-thio-β-D-glucopyranoside 19-D. Obtained in 93% yield from **18-D** as described for **19**. Compound **19-D** was a crystalline solid. Mp 151–152 °C (EtOH); $[\alpha]_D = -23.0$ (*c* 1.0, $CHCl_3$); R_f 0.80 (EtOAc–petroleum ether 1:1); ^1H and ^{13}C NMR spectra were identical with those of compound **19**. Anal. Calcd for $C_{19}H_{31}NO_9S$ (449.509): C, 50.76; H, 6.95; N, 3.12. Found: C, 50.36; H, 6.99; N, 3.14.

4.17. Ethyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-1-thio-β-L-glucopyranoside 20

A mixture of glycoside **19** (0.820 g, 1.82 mmol) and trifluoroacetic acid (2 mL) in CH_2Cl_2 (4 mL) was stirred overnight at room temperature, then concentrated under diminished pressure, and co-evaporated from toluene (2 × 15 mL). The residue was diluted in CH_2Cl_2 (40 mL) and the organic solution was washed with satd aq $NaHCO_3$ (15 mL), then with water (10 mL) and dried over Na_2SO_4. Concentration afforded the amino derivative **20**, which was used without purification in the next step (0.604 g, 95%). R_f 0.30 (CH_2Cl_2–MeOH, 20:1); $[\alpha]_D = +22.0$ (*c* 1.0, $CHCl_3$); ^1H NMR (CD_3Cl_3): δ 5.08–4.95 (m, 2H, H-3, H-4), 4.37 (d, 1H, *J* = 10.0 Hz, H-1), 4.27 (d, 1H, *J* = 5.0, 12.3 Hz, H-6a), 4.11 (dd, 1H, *J* = 1.8, 12.3 Hz, H-6b), 3.77–3.64 (m, 1H, H-5), 3.02–2.93 (m, 1H, H-2), 2.75 (q, 2H, *J* = 7.4 Hz, SCH_2CH_3), 2.09, 2.08, 2.03 (3s, 9H, $3CH_3COO$), 1.33 (t, 3H, *J* = 7.4 Hz, SCH_2CH_3); ^{13}C NMR ($CDCl_3$): δ 170.6, 170.6, 169.7 (CH_3COO), 87.6 (C-1), 76.6 (C-3), 75.7 (C-5), 68.8 (C-4), 62.5 (C-6), 55.3 (C-2), 24.6 (SCH_2CH_3), 20.8, 20.7, 20.6 (CH_3COO), 15.2 (SCH_2CH_3).

4.17.1. Ethyl 3,4,6-tri-*O*-acetyl-2-amino-deoxy-1-thio-β-D-glucopyranoside 20-D. Obtained in 95% yield from **19-D** as described for **20**. Compound **20-D** was used without purification in the next step. R_f 0.30 (CH_2Cl_2–MeOH 20:1); $[\alpha]_D = -21.7$ (*c* 1.0, $CHCl_3$).

4.18. Ethyl 3,4,6-tri-*O*-acetyl-2-allyloxycarbonylamino-2-deoxy-1-thio-β-L-glucopyranoside 21

Compound **20** (0.600 g, 1.72 mmol) was dissolved in $CHCl_3$ (15 mL) before subsequent additions of a solution of $NaHCO_3$ (0.288 g, 3.44 mmol) in H_2O (15 mL) and allyl chloroformate (0.218 mL, 2.04 mmol). The mixture was stirred for 4 h; the aqueous phase was extracted with $CHCl_3$ (2 × 15 mL) and the combined organic extracts dried and concentrated under reduced pressure. The residue was purified by column chromatography (1:1 EtOAc–petroleum ether). Product **21** was obtained as a white solid (0.706 g, 95%). Mp 129–131 °C (EtOH); $[\alpha]_D = +18.5$ (*c* 1.0, $CHCl_3$); R_f 0.66 (1:1 EtOAc–petroleum ether); ^1H NMR ($CDCl_3$): δ 5.90 (m, 1H, C*H*=), 5.34–5.19 (m, 3H, CH_2=, H-3), 5.07 (dd, 1H, *J* = 9.5, 9.6 Hz, H-4), 4.88 (d, 1H, *J* = 8.2 Hz, N*H*), 4.65–4.56 (m, 3H, H-1, allyl CH_2), 4.26 (dd, 1H, *J* = 5.0, 12.3 Hz, H-6a), 4.13 (dd, 1H, *J* = 2.4, 12.3 Hz, H-6b), 3.76 (ddd, 1H, *J* = 10.4, 10.0, 8.2 Hz, H-2), 3.70 (ddd, 1H, *J* = 9.6, 5.0, 2.4 Hz, H-5), 2.74 (q, 2H, *J* = 7.5 Hz, SCH_2CH_3), 2.08, 2.04, 2.03 (3s, 9 H, $3CH_3COO$), 1.28 (t, 3H, *J* = 7.5 Hz, CH_3CH_2S); ^{13}C NMR ($CDCl_3$): δ 170.7, 170.7, 169.5 (CH_3COO), 155.7 (NHCOO), 132.7 (CH=), 117.5 (CH_2=), 84.5 (C-1), 75.7 (C-3), 73.7 (C-5), 68.8 (C-4), 65.8 (allyl CH_2), 62.5 (C-6), 55.0 (C-2), 24.3 (SCH_2CH_3), 20.7, 20.7, 20.6 (CH_3COO), 14.9 (SCH_2CH_3). Anal. Calcd for $C_{18}H_{27}NO_9S$ (433.467): C, 49.87; H, 6.28; N, 3.23. Found: C, 49.88; H, 6.03; N, 3.21.

4.18.1. Ethyl 3,4,6-tri-*O*-acetyl-2-allyloxycarbonylamino-2-deoxy-1-thio-β-D-glucopyranoside 21-D. Obtained in 90% yield from **20-D** as described for **21**. Compound **21-D** was recrystallized from absolute EtOH. Product **21** was obtained in 93% yield. R_f 0.66 (1:1 EtOAc–petroleum ether); mp 133–134 °C (EtOH); $[\alpha]_D = -18.0$ (*c* 1.0, $CHCl_3$). These data are in agreement with our preceding results.[41]

4.19. 10-Tetradecyloxymethyl-3,6,9,12-tetraoxahexacosyl 3,4,6-tri-*O*-acetyl-2-allyloxycarbonylamino-2-deoxy-β-L-glucopyranoside 23

Trimethylsilyl trifluoromethanesulfonate (0.092 mL, 0.476 mmol), was added at −20 °C under argon to a mixture of pentenyl glycoside **16** (0.210 g, 0.459 mmol), 10-tetradecyloxymethyl-3,6,9,12-tetraoxahexacosanol[34] **22** (0.297 g, 0.482 mmol), *N*-iodosuccinimide (0.115 g, 0.545 mmol), and crushed activated 4 Å molecular sieves (0.500 g) in dry alcohol-free CH_2Cl_2 (5 mL). The mixture was stirred for 16 h at −20 °C, and then neutralized with Et_3N (0.150 mL), filtered through Celite, and diluted with CH_2Cl_2 (50 mL). The organic solution was washed successively with aq $Na_2S_2O_3$, aq $NaHCO_3$ (15 mL), then with water (15 mL). After drying and evaporation under diminished pressure, the crude product was purified by column chromatography (3:2 EtOAc–petroleum ether) to afford compound **23** as an amorphous solid (0.373 g, 82%). R_f 0.60 (3:2 EtOAc–petroleum ether); $[\alpha]_D = +5.6$ (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 6.00–5.77 (m, 2H, C*H*=, N*H*), 5.33–5.16 (m, 2H, C*H*$_2$=), 5.12–5.06 (m, 1H, H-3), 5.05 (dd, 1H, $J = 9.2$, 9.5 Hz, H-4), 4.79 (d, 1H, $J = 8.3$ Hz, H-1), 4.60–4.54 (m, 2H, allyl C*H*$_2$), 4.28 (dd, 1H, $J = 4.6$, 12.2 Hz, H-6a), 4.16 (dd, 1H, $J = 2.2$, 12.2 Hz, H-6b), 3.95–3.40 (m, 23H, H-2, H-5, C*H*(C*H*$_2$OC*H*$_2$C$_{13}$H$_{27}$)$_2$(OC*H*$_2$C*H*$_2$)$_3$), 2.09, 2.02, 2.01 (3s, 9H, 3C*H*$_3$COO), 166–1.50 (m, 4H, 2OCH$_2$C*H*$_2$C$_{12}$H$_{25}$), 1.40–1.20 (m, 44H, 22C*H*$_2$ alkyl chains), 0.88 (t, 6H, $J = 6.3$ Hz, 2C*H*$_3$ alkyl chains); ^{13}C NMR (CDCl$_3$): δ 170.6, 170.5, 170.3 (CH$_3$*C*OO), 156.2 (NH*C*OO), 133.0 (*C*H=), 117.1 (*C*H$_2$=), 101.8 (C-1), 76.6 (*C*H(CH$_2$-OC$_{14}$H$_{29}$)$_2$), 73.0 (C-3), 71.7 (C-5), 71.6, 71.3, 70.6, 69.9, 68.9 (C(*C*H$_2$O*C*H$_2$C$_{13}$H$_{27}$)$_2$(O*C*H$_2$*C*H$_2$)$_3$), 68.6 (C-4), 65.4 (allyl *C*H$_2$), 62.2 (C-6), 55.9 (C-2), 31.9, 29.6, 29.5, 29.3, 26.1, 22.6 (*C*H$_2$ alkyl chains), 20.7, 20.6, 20.5 (*C*H$_3$COO), 14.1 (*C*H$_3$ alkyl chains). Anal. Calcd for $C_{53}H_{97}NO_{15}$ (988.34): C, 64.41; H, 9.89; N, 1.42. Found: C, 64.35; H, 9.78; N, 1.43.

4.20. 1,3-Bis(undecyloxy)prop-2-yl 3,4,6-tri-*O*-acetyl-2-allyloxycarbonylamino-2-deoxy-β-L-glucopyranoside 25

Trimethylsilyl trifluoromethanesulfonate (0.092 mL, 0.502 mmol), was added at −20 °C under argon to a mixture of thioethyl glycoside **21** (0.217 g, 0.50 mmol), 1,3-bis(undecyloxy)-propan-2-ol[25] **24** (0.200 g, 0.50 mmol), *N*-iodosuccinimide (0.124 g, 0.588 mmol), and crushed activated 4 Å molecular sieves (0.500 g) in dry alcohol-free CH$_2$Cl$_2$ (5 mL). The mixture was stirred for 16 h at −20 °C, then neutralized with Et$_3$N (0.150 mL), filtered through Celite, and diluted with CH$_2$Cl$_2$ (50 mL). The organic solution was washed successively with aq Na$_2$S$_2$O$_3$, aq NaHCO$_3$ (15 mL), then with water (15 mL). After drying and evaporation under diminished pressure, the crude product was purified by column chromatography (2:3 EtOAc–petroleum ether) to afford compound **25** as a solid (0.293 g, 76%). Mp 60–61 °C; R_f 0.75 (2:3 EtOAc–petroleum ether); $[\alpha]_D = -6.1$ (c 1.0, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ 5.86 (m, 1H, C*H*=), 5.32–5.10 (m, 4H, C*H*$_2$=, H-3, N*H*), 5.05 (dd, 1H, $J = 9.3$, 9.6 Hz, H-4), 4.78 (d, 1H, $J = 8.3$ Hz, H-1), 4.56–4.53 (m, 2H, allyl C*H*$_2$), 4.27 (dd, 1H, $J = 4.8$, 12.2 Hz, H-6a), 4.11 (dd, 1H, $J = 2.2$, 12.2 Hz, H-6b), 4.02–3.92 (m, 1H, C*H*(CH$_2$OCH$_2$C$_{11}$H$_{23}$)$_2$), 3.70–3.40 (m, 10H, H-2, H-5, CH(C*H*$_2$OC*H*$_2$C$_{10}$H$_{21}$)$_2$), 2.08, 2.03, 2.02 (3s, 9H, 3C*H*$_3$COO), 1.66–1.50 (m, 4H, 2OCH$_2$-C*H*$_2$C$_9$H$_{19}$), 1.40–1.20 (m, 32H, 16C*H*$_2$ alkyl chains), 0.88 (t, 6H, $J = 6.5$ Hz, 2C*H*$_3$ alkyl chains); ^{13}C NMR (CDCl$_3$): δ 170.5, 170.5, 169.4 (CH$_3$*C*OO), 155.9 (NH*C*OO), 132.8 (*C*H=), 117.3 (*C*H$_2$=), 101.4 (C-1), 78.4 (*C*H(CH$_2$OC$_{11}$H$_{23}$)$_2$), 73.0 (C-3), 71.9, 71.8, 71.7, 71.6 (CH(*C*H$_2$O*C*H$_2$C$_{10}$H$_{21}$)$_2$) 70.4 (C-5), 68.8 (C-4), 65.5 (allyl *C*H$_2$), 62.3 (C-6), 56.2 (C-2), 31.9, 29.6, 29.5, 29.3, 26.1, 26.1, 22.6 (*C*H$_2$ alkyl chains), 20.6, 20.6, 20.5 (*C*H$_3$COO), 14.1 (*C*H$_3$ alkyl chains). Anal. Calcd for $C_{41}H_{73}NO_{12}$ (772.00): C, 63.78; H, 9.53; N, 1.82. Found: C, 64.01; H, 9.76; N, 1.72.

4.20.1. 1,3-Bis(undecyloxy)prop-2-yl 3,4,6-tri-*O*-acetyl-2-allyloxycarbonylamino-2-deoxy-β-D-glucopyranoside 25-D.

Prepared as described above, from pentenyl glycoside **17** (0.229 g, 0.50 mmol) and 1,3-bis(undecyloxy)propan-2-ol[25] **24** (0.200 g, 0.50 mmol). Product **25-D** was obtained in 74% yield. Mp 60–61 °C; $[\alpha]_D = +6.5$ (c 1.0, CHCl$_3$); ^{1}H and ^{13}C NMR spectra were identical with those of compound **25**. Anal. Calcd for $C_{41}H_{73}NO_{12}$ (772.00): C, 63.78; H, 9.53; N, 1.82. Found: C, 63.55; H, 9.52; N, 1.79.

4.21. General procedure for the cleavage of the *N*-allyloxycarbonyl group of compounds 23, 25, and 25-D

Tris(dibenzylideneacetone)dipalladium (0.012 g, 0.0126 mmol) and PPh$_3$ (0.032 g, 0.122 mmol) were reacted for 10 min in dry oxygen-free THF (2 mL) under argon. The solution was added to a solution of *N*-allyloxycarbonyl derivative (0.35 mmol) and diethyl malonate (0.60 mL, 3.95 mmol) in dry THF and the mixture was stirred for 16 h under argon. After concentration, the residue was eluted on a short column of silica-gel to separate the free amino derivative, which was acetylated in a 2:1 pyridine–Ac$_2$O mixture (3 mL). The pure peracetylated derivatives were obtained after concentration and purification of the residue by column chromatography.

4.21.1. 10-Tetradecyloxymethyl-3,6,9,12-tetraoxahexacosyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-L-glucopyranoside 26.

Compound **26** was prepared from **23** as described above. The 2-amino intermediate was purified by column chromatography (1:2 acetone–petroleum ether, R_f 0.54); then, compound **26** was purified by column chromatography (1:10 EtOH–EtOAc) and obtained as an amorphous solid (77%). R_f 0.63 (1:10 EtOH–EtOAc); $[\alpha]_D = +13.5$ (c 1.0, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ 6.72 (d, 1H, $J = 9.4$ Hz, N*H*), 5.14–5.04 (m, 2H, H-3, H-4), 4.81 (dd, 1H, $J = 8.5$ Hz, H-1), 4.27 (dd, 1H, $J = 4.5$, 12.2 Hz, H-6a), 4.16 (m, 1H, OC*H*(CH$_2$OC$_{14}$H$_{29}$)$_2$), 4.13 (dd, 1H, $J = 2.0$, 12.2 Hz, H-6b), 3.88–3.40 (m, 22H, H-2, H-5, OCH(C*H*$_2$OC*H*$_2$C$_{13}$H$_{27}$)$_2$(OC*H*$_2$C*H*$_2$)$_3$), 2.09, 2.01, 2.01 (3s, 9H, 3C*H*$_3$COO), 1.97 (s, 3H, C*H*$_3$CON), 1.63–1.48 (m, 4H, 2OCH$_2$C*H*$_2$C$_{12}$H$_{25}$), 1.39–1.20 (m, 44H, 22C*H*$_2$ alkyl chains), 0.89 (t, 6H, $J = 6.3$ Hz, 2C*H*$_3$ alkyl chains); ^{13}C NMR (CDCl$_3$): δ 170.6, 170.6, 170.5, 169.2 (CH$_3$*C*O), 101.8 (C-1), 78.3 (*C*H(CH$_2$OC$_{14}$H$_{29}$)$_2$), 73.4 (C-3), 71.7 (C-5), 71.6, 70.6, 68.6 (CH(*C*H$_2$O*C*H$_2$C$_{13}$H$_{27}$)$_2$(O*C*H$_2$*C*H$_2$)$_3$), 68.7 (C-4), 62.2 (C-6), 53.8 (C-2), 31.9, 29.6, 29.5, 29.3, 29.1, 22.6 (*C*H$_2$ alkyl chains), 23.0 (*C*H$_3$CON), 20.7, 20.6, 20.5 (*C*H$_3$COO), 14.0 (*C*H$_3$ alkyl chains). Anal. Calcd for $C_{51}H_{95}NO_{14}$ (946.30): C, 64.73; H, 10.12; N, 1.48. Found: C, 64.49; H, 10.16; N, 1.38.

4.21.2. 1,3-Bis(undecyloxy)prop-2-yl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-L-glucopyranoside 27.

Compound **27** was prepared from **25** as described above. The 2-amino intermediate was purified by column chromatography (2:3 to 2:1 EtOAc–petroleum ether, R_f 0.80, 2:1 EtOAc–petroleum ether); then, compound **27** was purified by column chromatography (3:2 EtOAc–petroleum ether) and obtained as a solid (85%). Mp 93 °C (EtOH); R_f 0.50 (1:1 EtOAc–petroleum ether); $[\alpha]_D = -1.0$ (c 2.0, CHCl$_3$); ^{1}H NMR (CDCl$_3$): δ 5.77 (d, 1H, $J = 8.3$ Hz, N*H*), 5.25 (dd, 1H, $J = 10.3$, 9.5 Hz, H-3), 5.12 (dd, 1H, $J = 9.5$, 9.5 Hz, H-4), 4.89 (d, 1H, $J = 8.5$ Hz, H-1), 4.26 (dd, 1H, $J = 5.8$, 12.2 Hz, H-6a), 4.12 (dd, 1H, $J = 1.7$, 12.2 Hz, H-6b), 3.96–3.85 (m, 2H, OC*H*(CH$_2$OC$_{11}$H$_{23}$)$_2$, H-2), 3.70–3.34 (m, 9H, H-5, OCH(C*H*$_2$OC*H*$_2$C$_{10}$H$_{21}$)$_2$), 2.08, 2.02, 2.02 (3s, 9 H, $3CH_3COO$), 1.93 (s, 3H, CH_3CON), 1.62–1.48 (m, 4H, $2OCH_2CH_2C_9H_{19}$), 1.30–1.18 (m, 32H, $16CH_2$ alkyl chains), 0.88 (t, 6H, $J = 6.4$ Hz, $2CH_3$ alkyl chains); ^{13}C NMR ($CDCl_3$): δ 170.7, 170.6, 170.8, 169.3 (CH_3CO) 101.1 (C-1), 78.2 ($CH(CH_2OC_{11}H_{23})_2$), 73.0 (C-3), 71.8 (C-5), 71.9, 71.7, 71.6, 70.3 ($CH(CH_2OCH_2C_{10}H_{21})_2$), 68.7 (C-4), 62.3 (C-6), 54.8 (C-2), 31.9, 29.7, 29.6, 29.5, 29.3, 26.2, 26.1, 22.6 (CH_2 alkyl chains), 23.2 (CH_3CON), 20.7, 20.7, 20.6 (CH_3COO), 14.1 (CH_3 alkyl chains). Anal. Calcd for $C_{39}H_{71}NO_{11}$ (729.97): C, 64.17; H, 9.80; N, 1.92. Found: C, 64.34; H, 9.99; N, 1.82.

4.21.3. 1,3-Bis(undecyloxy)prop-2-yl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside 27-D. Compound **27-D** was synthesized from **25-D** as described for **27**. Product **27-D** was obtained in 81% yield. Mp 93–94 °C; $[\alpha]_D = +0.8$ (c 5.0, $CHCl_3$); ^1H and ^{13}C NMR spectra were identical to those of compound **27**. Anal. Calcd for $C_{39}H_{71}NO_{11}$ (729.97): C, 64.17; H, 9.80; N, 1.92. Found: C, 63.91; H, 9.64; N, 1.85.

4.22. General procedure for de-O-acetylation of compounds 9, 11, 26, 27, and 27-D

Compounds **9**, **11**, **26**, **27**, and **27-D** (0.25–0.35 mmol) were treated overnight in a CH_2Cl_2–MeOH mixture (1:1, 25 mL, compound **9**) or in pure MeOH (25 mL, compounds **11**, **26**, **27**, and **27-D**) containing a chip of sodium. Insoluble compound **28** was isolated by filtration and washing with cold MeOH. Pure products **29**, **30**, **31**, and **31-D** were obtained after neutralization of the solution with amberlyst IR 120 $[H^+]$, filtration, and concentration.

4.22.1. Cholesteryl 2-acetamido-2-deoxy-β-L-glucopyranoside 28. Obtained in 93% yield from **9**. Mp 235 °C (EtOH) (decomp); $[\alpha]_D = -4.3$ (c 0.6, 4:1 $CHCl_3$–MeOH); ^1H NMR (2:1 $CDCl_3$-CD_3OD): δ 5.28 (m, 1H, H-6_{Chol}), 4.58 (d, 1H, $J = 8.2$ Hz, H-1), 3.81 (dd, 1H, $J = 2.7$, 12.3 Hz, H-6a), 3.71 (dd, 1H, $J = 4.1$, 12.3 Hz, H-6b), 3.60–3.22 (m, 5H, H-2, H-3, H-4, H-5, H-3_{Chol}), 2.07 (s, 3H, CH_3CON), 2.28–0.68 (m, 43H, H cholesterol). Anal. Calcd for $C_{35}H_{59}NO_6{\cdot}2.5H_2O$ (634.89): C, 66.20; H, 10.16; N, 2.21. Found: C, 66.06; H, 9.86; N, 2.07.

4.22.2. 10-Undecyloxymethyl-3,6,9,12-tetraoxatricosyl 2-acetamido-2-deoxy-β-L-glucopyranoside (29). Compound **29** was obtained in 95% yield from **10** as an amorphous solid. $[\alpha]_D = +29.2$ (c 1.0, $CHCl_3$); ^1H NMR (CD_3OD): δ 4.48 (d, 1H, $J = 8.3$ Hz, H-1), 3.37–3.93 (m, 1H, $OCH(CH_2OC_{11}H_{23})_2$), 3.88 (dd, 1H, $J = 2.3$, 11.7 Hz, H-6a), 3.76–3.42 (m, 25H, H-2, H-3, H-4, H-5, H-6b, $OCH(CH_2OCH_2C_{10}H_{21})_2(OCH_2CH_2)_3$), 2.06 (s, 3H, CH_3CON), 1.60–1.52 (m, 4H, $2OCH_2CH_2C_9H_{19}$), 1.39–1.20 (m, 32H, $16CH_2$ alkyl chains), 0.90 (t, 6H, $J = 6.3$ Hz, $2CH_3$ alkyl chains); ^{13}C NMR (CD_3OD): δ 173.9 (CH_3CO), 103.0 (C-1), 79.8 ($CH(CH_2OC_{11}H_{23})_2$), 78.2 (C-3), 76.5 (C-5), 73.3 (C-4), 72.8, 72.1, 71.9, 70.9 ($CH(CH_2OCH_2C_{10}H_{21})_2(OCH_2\ CH_2)_3$), 63.0 (C-6), 57.6 (C-2), 33.4, 31.1, 31.0, 30.9, 30.8, 27.6, 24.0 (CH_2 alkyl chains), 23.4 (CH_3CON), 14.9 (CH_3 alkyl chains). Anal. Calcd for $C_{39}H_{77}NO_{11}$, H_2O (754.03): C, 62.12; H, 10.56; N, 1.86. Found: C, 62.09; H, 10.22; N, 1.82.

4.22.3. 10-Tetradecyloxymethyl-3,6,9,12-tetraoxahexacosyl 2-acetamido-2-deoxy-β-L-glucopyranoside 30. Compound **30** was obtained as an amorphous solid in 94% yield from **26** as described above. $[\alpha]_D = +26.0$ (c 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 4.62 (d, 1H, $J = 8.1$ Hz, H-1), 3.95–3.40 (m, 27H, $OCH(CH_2OCH_2C_{13}H_{27})_2(OCH_2CH_2)_3$, H-2, H-3, H-4, H-5, H-6a, H-6b), 2.07 (s, 3H, CH_3CON), 1.65–1.48 (m, 4H, $2OCH_2CH_2C_{12}H_{25}$), 1.39–1.20 (m, 44H, $22CH_2$ alkyl chains), 0.89 (t, 6H, $J = 6.3$ Hz, $2CH_3$ alkyl chains); ^{13}C NMR ($CDCl_3$): δ 172.7 (CH_3CO), 101.3 (C-1), 78.3 ($CH(CH_2OC_{14}H_{29})_2$), 75.9, 75.2 (C-3, C-5), 71.6, 71.3, 70.9, 69.4, 68.5 ($CH(CH_2OCH_2C_{13}H_{27})_2(OCH_2\ CH_2)_3$), 68.5 (C-4), 61.6 (C-6), 56.2 (C-2), 31.8, 29.6, 29.6, 29.5, 29.4, 29.3, 26.0, 22.6 (CH_2 alkyl chains), 22.8 (CH_3CON), 14.0 (CH_3 alkyl chains). Anal. Calcd for $C_{45}H_{89}NO_{11}$, H_2O (838.21): C, 64.48; H, 10.94; N, 1.67. Found: C, 64.25; H, 10.96; N, 1.58.

4.22.4. 1,3-Bis(undecyloxy)prop-2-yl 2-acetamido-2-deoxy-β-L-glucopyranoside 31. Compound **31** was obtained in 95% yield from **27** as described above. Mp 136–138 °C; $[\alpha]_D = +16.0$ (c 1.0, $CHCl_3$); ^1H NMR (2:1 $CDCl_3$-CD_3OD): δ 4.52 (d, 1H, $J = 7.3$ Hz, H-1), 3.88 (m, 1H, $OCH(CH_2OC_{11}H_{23})_2$), 3.79 (dd, 1H, $J = 2.3$, 12.2 Hz, H-6a), 3.67 (dd, 1H, $J = 4.8$, 12.2 Hz, H-6b), 3.60–3.22 (m, 16H, NH, H-2, H-3, H-4, H-5, 3OH, $OCH(CH_2OCH_2C_{10}H_{21})_2$), 1.93 (s, 3H, CH_3CON), 1.55–1.37 (m, 4H, $2OCH_2CH_2C_9H_{19}$), 1.30–1.18 (m, 32H, $16CH_2$ alkyl chains), 0.88 (t, 6H, $J = 6.5$ Hz, CH_3 alkyl chains); ^{13}C NMR (2:1 $CDCl_3$–CD_3OD): δ 172.8 (CH_3CON) 100.9 (C-1), 77.8 ($CH(CH_2OC_{11}H_{23})$), 75.9, 75.4 (C-3, C-5), 71.7, 71.1, 70.6 ($CH(CH_2OCH_2C_{10}H_{21})$), 70.7 (C-4), 61.6 (C-6), 57.2 (C-2), 31.8, 29.5, 29.3, 29.2, 29.3, 25.9, 26.1, 24.3, 22.5 (CH_2 alkyl chains), 22.7 (CH_3CON), 13.9 (CH_3 alkyl chains). Anal. Calcd for $C_{33}H_{65}NO_8$, H_2O (621.89): C, 63.73; H, 10.86; N, 2.25. Found: C, 63.70; H, 11.10; N, 2.26.

4.22.5. 1,3-Bis(undecyloxy)prop-2-yl 2-acetamido-2-deoxy-β-D-glucopyranoside 31-D. Compound **31-D** was obtained in 95% yield from **27-D** as described above. Mp 134–136 °C; $[\alpha]_D = -15.9$ (c 1.0, $CHCl_3$); ^1H and ^{13}C NMR spectra were identical with those of compound **31**. Anal. Calcd for $C_{33}H_{65}NO_8$, H_2O (621.89): C, 63.73; H, 10.86; N, 2.25. Found: C, 63.63; H, 10.94; N, 2.15.

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