# Potential Anticancer Drugs, 4[‡]

# Glycosyl Glycerol Derivatives as Drug Carrier System. Stereoselective Synthesis of Epoxyalkyl *N*-Acyl-β-D-glucopyranosides and Their Reactivity with Nucleophiles

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The synthesis of alkenyl 2-acylamino-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranosides from *N*-acetyl-D-glucosamine is described. The oxidation of alkenyl glycosides with *m*-CPBA gives the corresponding oxiranes in good yields, and with high stereoselectivity. Analogues of glycosyl glycerol derivatives, which can be used as drug carriers, were obtained by various ring-opening reactions with different nitrogen, sulfur, and carbon nucleophiles.

## Introduction

In a strategy to obtain new highly selective drugs against carcinoma cells in rapid growth, which have a great demand for primary metabolites such as carbohydrates, the latter are used as antitumor agent carrier.[2−4] In previous papers,[1,5,6] we described the synthesis of compounds with potential antitumour activity, in which the alkylating moiety − chlorambucil or cyclophosphamide (widely used clinically in the treatment of different types of cancer[7,8]) − was linked at C-2 and/or C-3 of the pyranose ring of 2-amino sugars in the *gluco*, *allo*, and *altro* configuration, and 2,3-diamino glucoses, obtained from saturated 2-nitrosugar derivatives.[9]

It is known that in certain cancer cells, the activity of extracellular β-*N*-acetylglucosaminidase is increased to a level several-fold that in normal cells.[10] We therefore considered the preparation of substances in which the anticancer agent is bound to a sugar carrier by the aglycone, so as to achieve a more active selectivity.

In the present paper, we describe the synthesis of sugar derivatives with structures related to glycosyl glycerols, modified with groups that allow binding to the active agent. Such compounds can act as drug carriers. We have obtained compounds with different hydrophilic-lipophilic balance by introduction of lipophilic moieties as amide on the sugar ring, or by modifying the aglycone. In this case, the polymethylenic chain acts as spacer between the sugar and the anchor point of the drug. The modified chiral glycerol moiety present in these molecules is therefore similar to that found in the glycolipids and glycosphingolipids forming the cell membranes.[11]

The glycosyl glycerol analogues reported in this paper were obtained from alkenyl glycopyranosides by stereoselective oxidation to oxirane with *m*-chloroperoxybenzoic acid (*m*-CPBA) and subsequent regiospecific opening with various nucleophiles. Published antecedents on the oxidation of allyl glycosides are scarce, and refer mostly to allyl glycosides of sugars.[12,13] Even fewer are those referring to the epoxidation of allyl glycosides derived from *N*-acetylglucosamine. Peter[14] describes the synthesis of 2,3-epoxypropyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside, with yields of 71% and diastereomeric excesses of 68%, from the corresponding allyl glycopyranoside. In this paper, we report the epoxidation of allyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside with *m*-CPBA, obtaining only one stereoisomer.

## Results and Discussion

The synthesis of the alkenyl glycopyranoside derivatives (**2**, **3**, **5**−**7**) to be used as substrates in the formation of the corresponding oxiranes is shown in Scheme 1. The preparation of 10-undecenyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (**3**) was carried out using the procedure described previously for alkyl glucopyranosides,[5,6,15] from **1**[16] via the undecenyl tetra-acetylated intermediate[17] (not isolated, but characterized by mass spectrometry). The reaction of **2**[18] with potassium hydroxide in ethanol, and subsequent treatment of the amine intermediate[18b] with acyl chloride/pyridine gave compounds **4** and **5**, which were transformed into **6** and **7** by deacylation with sodium methoxide in methanol. All compounds were obtained in good yield, and the proposed structures confirmed by elemental analyses and MS and NMR spectroscopic data. In order to assign the signals in the spectra, DEPT, COSY, and $^{1}H$-$^{13}C$-COSY experiments were performed in some cases.

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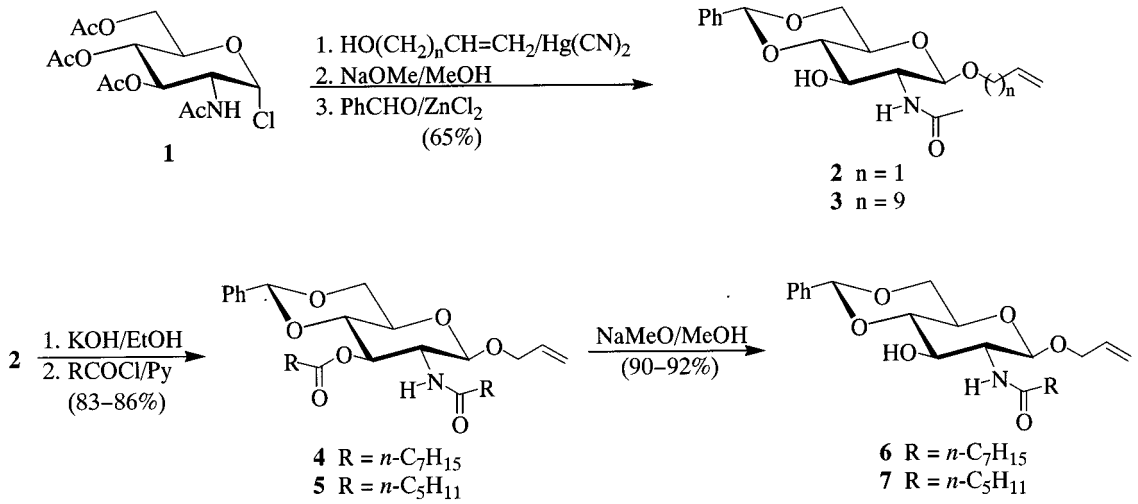
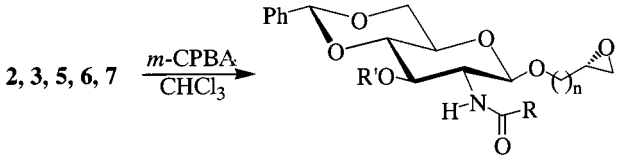



Scheme 1

The reaction of **2**, **3** and **5**−**7** with *m*-CPBA in chloroform at room temperature gave the corresponding oxiranes **8**−**12** in good yield (Scheme 2). The $^1$H NMR spectra of these compounds showed three characteristic signals for the oxirane system; a multiplet at δ = 3.0, corresponding to 2′-CH, and a triplet at δ = 2.7 and a double of doublets at δ = 2.6, corresponding to 3′-$CH_2$ for compounds **8** and **10**−**12**. In the $^1$H spectrum of **9**, these signals showed an upfield chemical shift in 0.1−0.2 ppm. The $^{13}$C NMR spectra showed signals corresponding to the oxirane ring at δ ≈ 50 for 2′-CH and at δ ≈ 45 for 3′-$CH_2$. The experimental section describes the best conditions for obtaining compounds **8**−**12** in the highest yields (overnight, room temperature). The NMR analysis of the reaction mixture indicated the presence of these compounds (**8** and **10**−**12**) and their minor stereoisomers (< 5%) [$^1$H NMR: δ = 3.88 (dd, $^3J$ = 2.5 Hz, $J_{gem}$ = 12.0 Hz, $OCH_AH_BR$), 4.54 (d, $J_{1,2}$ = 8.4 Hz, H-1). − $^{13}$C NMR: δ = 70.0 ($OCH_2R$), 101.6 (C-1), for minor stereoisomer of **8**. $^1$H-$^{13}$C-COSY experiments confirmed these assignments]. After purification, only the mayor stereoisomer was isolated in good yield. On the other hand, when the reaction was carried out at −5 °C, the NMR analysis of the reaction mixture showed only signals for one compound (**8** and **10**−**12**), although longer reaction times were necessary and lower yields were obtained. The antecedents of epoxidation of allyl glycosides of peracetylated sugars show that this reaction takes place with very little or no diastereoselectivity.[12] At the same time, when the reaction is carried out on substrates with an unprotected OH on C-2, the diastereomeric excess is considerable (80%), the major part having the *R*-configuration. This suggests the formation of a hydrogen bond between the OH group and the peroxyacid, preferentially stabilizing the transition state related to the electrophilic addition to the *Re*-face of the double bond.[13] In the case of peracetylated glucosamine derivatives, the NH may play a similar role, which could explain the diastereomeric excess observed (68%); again the major isomer has the *R*-configuration on the oxirane ring.[14] In our case, the presence of 2-NHAc, and the fact that the benzylidene group provides great rigidity to the molecule, results in a single stereoisomer (at −5 °C), to which we accordingly assign the *R*-configuration. In the synthesis of **9**, we obtained both possible stereoisomers, since the sugar is very far from the stereogenic centre formed in the reaction, and the signals of the NMR spectra coincide with those of the two isomers.



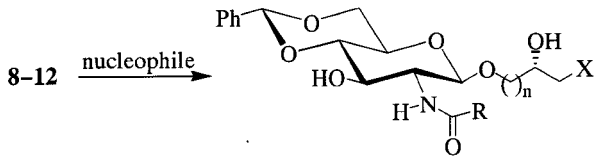

| | n | R | R' | Yield |
|---|---|---|---|---|
| **8** | 1 | $CH_3$ | H | 77% |
| **9**[a] | 9 | $CH_3$ | H | 85% |
| **10** | 1 | *n*-$C_7H_{15}$ | H | 80% |
| **11** | 1 | *n*-$C_5H_{11}$ | H | 76% |
| **12** | 1 | *n*-$C_5H_{11}$ | *n*-$C_5H_{11}CO$ | 74% |

[a] two isomers.

Scheme 2

We also studied the ring-opening reactions of oxiranes **8**−**12** with different nitrogen, sulfur, and carbon nucleophiles (Scheme 3). The reaction was carried out under different conditions[19−23] depending on the nature of the nucleophile, but in all cases the oxirane ring reacted regiospecifically via the least-substituted carbon, yielding a single compound. The $^{13}$C NMR spectra showed the characteristic signals corresponding to $CH_2X$ at δ = 58−59 (X = $NR_2$), at δ = 53−56 (X = $N_3$), at δ = 32−36 (X = SR) or at 22 (X = CN), and they did not show the corresponding signals for either CHX or $CH_2OH$. Besides this, the $^1$H NMR (500 MHz) for **13** showed signals for one compound (COSY and $^1$H-$^{13}$C-COSY experiments were performed). Compounds **13**−**22** are being used as starting material in

other projects in our group. Transformation of the azido and cyano functions to amine leads to molecules appropriately functionalized for binding to alkylating agents (chlorambucil, cyclophosphamide) as prodrugs, in which the modified sugar acts as labile modulator. Moreover, in compounds **13**−**16, 21**, and **22**, the aglycone is a chiral moiety of aminoglycerol substituted on one of the carbon ends that can be separated chemically or enzymatically from the sugar.



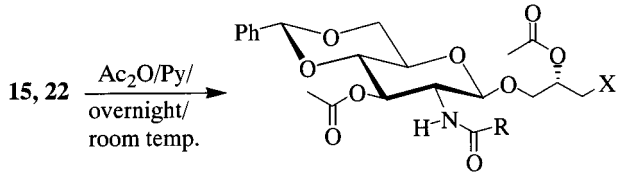

| | n | R | X | Yield | React. cond.[a] | Ref. |
|---|---|---|---|---|---|---|
| **13** | 1 | $CH_3$ | N | 90% | A | [19] |
| **14** | 1 | $CH_3$ | N N$(CH_2)_2OH$ | 78% | A | [19] |
| **15** | 1 | $CH_3$ | $HN(CH_2)_3CH_3$ | 95% | B | [20] |
| **16** | 1 | $CH_3$ | $N_3$ | 76% | C | [21] |
| **17** | 1 | $CH_3$ | SPh | 66% | D | [22] |
| **18** | 1 | $CH_3$ | $SC(CH_3)_3$ | 62% | E | [22] |
| **19**[b] | 9 | $CH_3$ | $N_3$ | 88% | C | [21] |
| **20**[b] | 9 | $CH_3$ | CN | 64% | F | [23] |
| **21** | 1 | $n$-$C_7H_{15}$ | $N_3$ | 90% | C | [21] |
| **22** | 1 | $n$-$C_5H_{11}$ | CN | 75% | F | [23] |

[a] A: $R_2NH/CH_3CN/LiClO_4$/overnight/room temp.
B: $RNH_2$/overnight/room temp.
C: $NaN_3/CH_3CN/LiClO_4$/overnight/80 °C.
D: $PhSH/Et_3N$/MeOH/overnight/room temp.
E: *t*-BuSH/KOH/MeOH/ overnight/room temp.
F: KCN/MeOH/24–36 h/room temp.
[b] two isomers.

Scheme 3

Compounds **15** and **22** were acetylated in the usual manner with acetic anhydride/pyridine, to give **23**−**24** (Scheme 4), which present a triplet at δ ≈ 5.2 for H-3 and a multiplet at δ ≈ 5.0 for 2′-C*H*OAc in the $^1H$ spectra. Compound **23** showed signals at δ ≈ 170 and at δ = 20−23 for the four acetyl groups in $^{13}C$ NMR. Compounds **24** showed characteristic signals at the same chemical shifts for three acyl groups.

In conclusion, we present a stereoselective procedure for the synthesis of oxirane derived from allyl glycopyranosides, with good yields, in which the *N*-acylglucosamine moiety acts as a good chiral adjutant. The functionalized *N*-acylglucopyranoside derivatives on the aglycone have the structure of chiral glycosyl glycerol analogues and may be used as drug carriers.




| | R | X | Yield |
|---|---|---|---|
| **23** | $CH_3$ | N O | 97% |
| **24** | $n$-$C_5H_{11}$ | CN | 89% |

Scheme 4

## Experimental Section

**General:** Compounds were evaporated under reduced pressure. − Preparative chromatography was performed on Silica Gel 60 (E. Merck). − Kieselgel 60 $F_{254}$ (E. Merck) was used for TLC. − Melting points are uncorrected. − Optical rotations were obtained on a Bellingham + Stanley Ltd P-20 polarimeter at 25 °C. − Infrared (IR) spectra were obtained on a Jasco FT/IR-410 spectrophotometer. − CI mass spectra were recorded on a Micromass AUTOSPECQ mass spectrometer at 150 eV. − FAB mass spectra were recorded on a Kratos MS-80-RFA using a thioglycerol matrix. − NMR spectra were recorded at 25 °C on a Bruker AC-200 spectrometer at 200 MHz for $^1H$ and 50 MHz for $^{13}C$, and on a Bruker AMX-500 spectrometer at 500 MHz for $^1H$ and 125 MHz for $^{13}C$. The chemical shifts are reported in ppm on the δ scale relative to TMS.

**10-Undecenyl 2-Acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (3):** A solution of 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl chloride[16] (**1**) (18.3 g, 50 mmol) in dry nitromethane (40 mL) was added dropwise, with exclusion of moisture, to a stirred mixture of 10-undecen-1-ol in anhydrous toluene (40 mL), containing 4-Å molecular sieves (30 g) and mercury(II) cyanide (12.5 g). The mixture was stirred overnight at room temperature. When TLC showed that all of the chloride had reacted, the mixture was diluted with ethyl acetate and filtered through a pad (12 cm diameter × 1 cm height) of alumina. The organic layer was washed with an aqueous saturated solution of sodium bicarbonate and water, then dried with $Na_2SO_4$ and concentrated. Suspension of the residue with stirring in hexane for 1 h gave a solid that was filtered off and washed with hexane {FAB-MS: *m*/*z* (%) = 531 (100) [$M^+$ + 23]}. To a solution of the solid in methanol (200 mL) was added a solution of sodium methoxide (4.0 mmol) in methanol (20 mL). After 30 min at room temperature, the mixture was neutralised by addition of Dowex 50 resin ($H^+$ form), filtered, and evaporated. The solid obtained was dissolved in benzaldehyde (100 mL), and zinc chloride (5 g) was added. The mixture was stirred overnight and then poured into hexane/water (1:1) (500 mL) with stirring. The precipitate was filtered off, washed with water and with hexane, and then recrystallized from ethanol: yield 15.0 g (65%), m.p. 235−237 °C. − $[\alpha]_D^{25}$ = −60.8 (*c* = 1.2, DMF). − IR (KBr): $\tilde{\nu}$ = 3434, 3271, 1628, 1560, 1375, 1101 $cm^{-1}$. − CI-MS:

*m*/*z* (%) = 462 (100) [M$^+$ + 1]. − $^1$H NMR (200 MHz, [D$_6$]DMSO): δ = 1.1−1.5 [m, 14 H, (CH$_2$)$_7$], 1.80 (s, 3 H, CH$_3$), 2.00 (m, 2 H, C*H*$_2$CH=CH$_2$), 4.18 (dd, $J_{5,6e}$ = 4.6 Hz, $J_{6a,6e}$ = 10.3 Hz, 1 H, H-6$_e$), 4.45 (d, $J_{1,2}$ = 8.0 Hz, 1 H, H-1), 4.95 (m, 2 H, CH=C*H*$_2$), 5.26 (d, $J_{3,OH}$ = 5.2 Hz, 1 H, OH), 5.58 (s, 1 H, PhC*H*), 5.80 (m, 1 H, C*H*=CH$_2$), 7.3−7.5 (m, 5 H, Ph), 7.81 (d, $J_{2,NH}$ = 8.6 Hz, 1 H, NH). − $^{13}$C NMR (50 MHz, [D$_6$]DMSO): δ = 23.0 (CH$_3$), 25.3, 28.3, 28.5, 28.7, 28.8, 29.1, 33.2 [(CH$_2$)$_8$], 56.2 (C-2), 65.9 (C-5), 67.9 (C-6), 68.7 (OCH$_2$R), 70.4 (C-3), 81.3 (C-4), 100.7 (Ph*C*H), 101.6 (C-1), 114.6 (CH=*C*H$_2$), 126.3, 128.0, 128.8, 137.8 (Ph), 138.8 (*C*H=CH$_2$), 169.0 (C=O). − $C_{26}H_{39}NO_6$ (461.61): calcd. C 67.65, H 8.52, N 3.03; found C 67.38, H 8.29, N 3.03.

**Allyl 3-*O*-Acyl-2-acylamino-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (4, 5):** A solution of allyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (**2**)[18] (5.60 g, 16.0 mmol) in a hot mixture of potassium hydroxide (30 g) and 96% ethanol (100 mL) was heated under reflux for 6 h. The hot solution was poured carefully into hot water (800 mL). After being cooled to room temperature, the precipitate was kept overnight at −10 °C. The solid was filtered off, washed with water, and dried {CI-MS: *m*/*z* (%) = 308 (100) [M$^+$ + 1]}. A solution of the solid in anhydrous pyridine (60 mL) was cooled to 0 °C, and acyl chloride (35.2 mmol) was added with stirring. The mixture was stirred overnight at room temperature. The solution was poured into ice−water, and the precipitate was filtered, washed with water, dried, and then recrystallized from 96% ethanol.

**Allyl 4,6-*O*-Benzylidene-2-deoxy-2-octanamido-3-*O*-octanoyl-β-D-glucopyranoside (4):** Yield 7.4 g (83%), m.p. 186−188 °C. − $[\alpha]_D^{25}$ = −61.0 (*c* = 0.9, CH$_2$Cl$_2$). − IR (KBr): ṽ = 3280, 1745, 1660, 1545, 1380, 1185, 1100 cm$^{-1}$. − FAB-MS: *m*/*z* (%) = 582 (100) [M$^+$ + 23]. − $^1$H NMR (200 MHz, [D$_6$]DMSO): δ = 0.5−0.9 (m, 6 H, 2 CH$_3$), 1.0−1.6 [m, 20 H, 10 (CH$_2$)], 1.97 (t, *J* = 6.8 Hz, 2 H, CH$_2$CON), 2.20 (m, 2 H, CH$_2$COO), 3.45 (m, 1 H, H-5), 3.6−3.8 (m, 3 H, H-2, H-4, H-6$_a$), 4.01 (m, 1 H, OC*H*$_A$H$_B$R), 4.15−4.30 (m, 2 H, H-6$_e$, OCH$_A$*H*$_B$R), 4.65 (d, $J_{1,2}$ = 7.8 Hz, 1 H, H-1), 5.0−5.3 (m, 3 H, H-3, CH=C*H*$_2$), 5.80 (m, 1 H, C*H*=CH$_2$), 5.62 (s, 1 H, PhC*H*), 7.3−7.4 (m, 5 H, Ph), 7.87 (d, $J_{2,NH}$ = 8.3 Hz, 1 H, NH). − $^{13}$C NMR (50 MHz, [D$_6$]DMSO): δ = 13.7, 13.9 (2 CH$_3$), 22.0, 22.1, 24.5, 25.2, 28.2, 28.4, 28.5, 31.0, 31.1, 33.5, 35.6 [12 (CH$_2$)], 53.3 (C-2), 65.8 (C-5), 67.6 (C-6), 69.3 (OCH$_2$R), 71.5 (C-3), 78.2 (C-4), 100.1 (Ph*C*H), 101.7 (C-1), 116.3 (CH=*C*H$_2$), 126.0, 128.0, 128.8, 137.4 (Ph), 134.3 (*C*H=CH$_2$), 172.0, 172.2 (2 C=O). − $C_{32}H_{49}NO_7$ (559.75): calcd. C 68.66, H 8.82, N 2.50; found C 68.49, H 8.47, N 2.68.

**Allyl 4,6-*O*-Benzylidene-2-deoxy-2-hexanamido-3-*O*-hexanoyl-β-D-glucopyranoside (5):** Yield 6.9 g (86%), m.p. 190−192 °C. − $[\alpha]_D^{25}$ = −65.0 (*c* = 0.8, DMF). − IR (KBr): ṽ = 3282, 1740, 1658, 1550, 1377, 1181, 1099 cm$^{-1}$. − CI-MS: *m*/*z* (%) = 504 (100) [M$^+$ + 1]. − $^1$H NMR (200 MHz, CDCl$_3$): δ = 0.7−0.9 (m, 6 H, 2 CH$_3$), 1.1−1.7 [m, 12 H, 6 (CH$_2$)], 2.10 (t, *J* = 7.5 Hz, 2 H, CH$_2$CON), 2.33 (t, *J* = 7.3 Hz, 2 H, CH$_2$COO), 3.6−3.8 (m, 4 H, H-4, H-5, H-6$_a$, OC*H*$_A$H$_B$R), 4.1−4.3 (m, 3 H, H-2, H-6$_e$, OCH$_A$*H*$_B$R), 4.40 (d, $J_{1,2}$ = 8.4 Hz, 1 H, H-1), 5.10 (m, 2 H, CH=C*H*$_2$), 5.31 (t, $J_{2,3}$ = $J_{3,4}$ = 9.7 Hz, 1 H, H-3), 5.47 (s, 1 H, PhC*H*), 5.75 (m, 1 H, C*H*=CH$_2$), 6.24 (d, $J_{2,NH}$ = 9.5 Hz, 1 H, NH), 7.2−7.4 (m, 5 H, Ph). − $^{13}$C NMR (50 MHz, CDCl$_3$): δ = 13.8, 13.9 (2 CH$_3$), 22.2, 22.3, 24.6, 25.4, 31.0, 31.3, 34.1, 36.7 [8 (CH$_2$)], 53.6 (C-2), 65.9 (C-5), 68.5 (C-6), 70.0 (OCH$_2$R), 72.0 (C-3), 78.8 (C-4), 101.0 (Ph*C*H), 101.5 (C-1), 117.0 (CH=*C*H$_2$), 125.8, 128.1, 128.9, 137.1 (Ph), 133.5 (*C*H=CH$_2$), 173.2, 174.4 (2 C=O). − $C_{28}H_{41}NO_7$ (503.64): calcd. C 66.78, H 8.21, N 2.78; found C 66.55, H 8.37, N 2.83.

**Allyl 2-Acylamino-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (6, 7):** To a solution of allyl 3-*O*-acyl-2-acylamino-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (**4**, **5**) (12.0 mmol) in methanol (60 mL) was added a solution of sodium methoxide (1.2 mmol) in methanol (10 mL). After 30 min at room temperature, the mixture was neutralised by addition of Dowex 50 resin (H$^+$ form), filtered, and evaporated to dryness. The solid obtained was recrystallized from 96% ethanol.

**Allyl 4,6-*O*-Benzylidene-2-deoxy-2-octanamido-β-D-glucopyranoside (6):** Yield 4.8 g (92%), m.p. 226−228 °C. − $[\alpha]_D^{25}$ = −93.2 (*c* = 0.7, CH$_2$Cl$_2$). − IR (KBr): ṽ = 3485, 3272, 1650, 1546, 1385, 1108 cm$^{-1}$. − CI-MS: *m*/*z* (%) = 434 (20) [M$^+$ + 1]. − $^1$H NMR (200 MHz, [D$_6$]DMSO): δ = 0.85 (t, *J* = 6.2 Hz, 3 H, CH$_3$), 1.1−1.6 [m, 10 H, (CH$_2$)$_5$], 2.05 (t, *J* = 7.2 Hz, 2 H, CH$_2$CON), 3.78 (t, $J_{5,6a}$ = $J_{6a,6e}$ = 10.0 Hz, 1 H, H-6$_a$), 3.95 (m, 1 H, OC*H*$_A$H$_B$R), 4.1−4.2 (m, 2 H, H-6$_e$, OCH$_A$*H*$_B$R), 4.51 (d, $J_{1,2}$ = 7.8 Hz, 1 H, H-1), 5.20 (m, 2 H, CH=C*H*$_2$), 5.25 (d, $J_{3,OH}$ = 5.4 Hz, 1 H, OH), 5.59 (s, 1 H, PhC*H*), 5.80 (m, 1 H, C*H*=CH$_2$), 7.3−7.5 (m, 5 H, Ph), 7.75 (d, $J_{2,NH}$ = 8.3 Hz, 1 H, NH). − $^{13}$C NMR (50 MHz, [D$_6$]DMSO): δ = 14.0 (CH$_3$), 22.1, 25.4, 28.6, 31.2, 33.5, 35.9 [(CH$_2$)$_6$], 56.0 (C-2), 65.0 (C-5), 67.9 (C-6), 69.1 (OCH$_2$R), 70.3 (C-3), 81.3 (C-4), 100.7 (Ph*C*H), 101.2 (C-1), 116.1 (CH=*C*H$_2$), 126.4, 128.0, 128.8, 137.8 (Ph), 134.5 (*C*H=CH$_2$), 172.0 (C=O). − $C_{24}H_{35}NO_6$ (433.55): calcd. C 66.49, H 8.14, N 3.23; found C 66.33, H 8.14, N 3.07.

**Allyl 4,6-*O*-Benzylidene-2-deoxy-2-hexanamido-β-D-glucopyranoside (7):** Yield 4.4 g (90%), m.p. 244−246 °C. − $[\alpha]_D^{25}$ = −59.4 (*c* = 1.6, DMF). − IR (KBr): ṽ = 3485, 3276, 1650, 1548, 1380, 1107 cm$^{-1}$. − CI-MS: *m*/*z* (%) = 406 (100) [M$^+$ + 1]. − $^1$H NMR (200 MHz, [D$_6$]DMSO): δ = 0.84 (t, *J* = 6.6 Hz, 3 H, CH$_3$), 1.2−1.6 [m, 6 H, (CH$_2$)$_3$], 2.05 (t, *J* = 7.2 Hz, 2 H, CH$_2$CON), 3.73 (t, $J_{5,6a}$ = $J_{6a,6e}$ = 9.9 Hz, 1 H, H-6$_a$), 3.95 (m, 1 H, OC*H*$_A$H$_B$R), 4.2−4.3 (m, 2 H, H-6$_e$, OCH$_A$*H*$_B$R), 4.50 (d, $J_{1,2}$ = 7.9 Hz, 1 H, H-1), 5.20 (m, 2 H, CH=C*H*$_2$), 5.59 (s, 1 H, PhC*H*), 5.81 (m, 1 H, C*H*=CH$_2$), 7.3−7.5 (m, 5 H, Ph), 7.76 (d, $J_{2,NH}$ = 8.3 Hz, 1 H, NH). − $^{13}$C NMR (50 MHz, [D$_6$]DMSO): δ = 14.0 (CH$_3$), 22.0, 25.0, 30.8, 35.9 [(CH$_2$)$_4$], 56.0 (C-2), 66.0 (C-5), 67.9 (C-6), 69.1 (OCH$_2$R), 70.3 (C-3), 81.4 (C-4), 100.7 (Ph*C*H), 101.2 (C-1), 116.2 (CH=*C*H$_2$), 126.4, 128.0, 128.9, 137.8 (Ph), 134.5 (*C*H=CH$_2$), 172.2 (C=O). − $C_{22}H_{31}NO_6$ (405.50): calcd. C 65.16, H 7.71, N 3.45; found C 65.20, H 7.82, N 3.54.

**Oxidation of Alkenyl Glycosides with *m*-Chloroperoxybenzoic Acid**

**(ω−1),ω-Epoxyalkyl 2-Acylamino-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (8−12):** To a solution of (ω−1)-alkenyl 2-acylamino-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (**2**, **3**, **5**−**7**) (8.0 mmol) in chloroform (400 mL), solid sodium sulfate (8.0 g) and *m*-chloroperoxybenzoic acid (Aldrich 57−86%) (12.0 g) were added, and the suspension was stirred overnight at room temperature. It was diluted with dichloromethane, and filtered. The filtrate was washed successively with 5% aqueous solution of sodium hydroxide and with water, then dried (Na$_2$SO$_4$), and evaporated to dryness. The product obtained was purified by recrystallization, giving **8**−**12**.

**(*R*)-2,3-Epoxypropyl 2-Acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (8):** Recrystallized from methanol yielding 2.25 g (77%), m.p. 266−268 °C. − $[\alpha]_D^{25}$ = −83.5 (*c* = 0.7, DMF). − IR (KBr): ṽ = 3340, 3302, 1660, 1556, 1373, 1092 cm$^{-1}$. − FAB-MS: *m*/*z* (%) = 388 (100) [M$^+$ + 23]. − $^1$H NMR (500 MHz,

[D$_6$]DMSO): δ = 1.82 (s, 3 H, CH$_3$), 2.56 (dd, $J_{trans}$ = 2.7 Hz, $J_{gem}$ = 5.2 Hz, 1 H, CH$_{cis}$*H*$_{trans}$ oxirane), 2.70 (dd, $J_{cis}$ = 4.5 Hz, $J_{gem}$ = 5.2 Hz, 1 H, C*H*$_{cis}$H$_{trans}$ oxirane), 3.05 (m, 1 H, CH oxirane), 3.33 (dt, $J_{4,5}$ = $J_{5,6a}$ = 9.7 Hz, $J_{5,6e}$ = 4.9 Hz, 1 H, H-5), 3.43 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, 1 H, H-4), 3.52 (q, $J_{1,2}$ = $J_{2,3}$ = $J_{2,NH}$ = 8.8 Hz, 1 H, H-2), 3.55−3.65 (m, 2 H, H-3, OC*H*$_A$H$_B$R), 3.69−3.75 (m, 2 H, H-6$_a$, OCH$_A$*H*$_B$R), 4.18 (dd, $J_{5,6e}$ = 4.9 Hz, $J_{6a,6e}$ = 10.0 Hz, 1 H, H-6$_e$), 4.51 (d, $J_{1,2}$ = 8.6 Hz, 1 H, H-1), 5.22 (d, $J_{3,OH}$ = 5.5 Hz, 1 H, OH), 5.59 (s, 1 H, PhC*H*), 7.3−7.5 (m, 5 H, Ph), 7.79 (d, $J_{2,NH}$ = 8.8 Hz, 1 H, NH). − $^{13}$C NMR (125 MHz, [D$_6$]DMSO): δ = 23.1 (CH$_3$), 43.6 (CH$_2$ oxirane), 50.0 (CH oxirane), 56.2 (C-2), 66.0 (C-5), 67.9 (C-6), 69.6 (OCH$_2$R), 70.4 (C-3), 81.2 (C-4), 100.7 (Ph*C*H), 101.8 (C-1), 126.4, 128.0, 128.9, 137.8 (Ph), 169.2 (C=O). − C$_{18}$H$_{23}$NO$_7$ (365.39): calcd. C 59.17, H 6.35, N 3.83; found C 58.90, H 6.34, N 3.72.

**10,11-Epoxyundecyl 2-Acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (9):** Recrystallized from ethanol yielding 3.24 g (85%), m.p. 226−228 °C. − $[\alpha]_D^{25}$ = −59.5 (*c* = 1.3, DMF). − IR (KBr): ṽ = 3436, 3273, 1628, 1560, 1375, 1102 cm$^{-1}$. − FAB-MS: *m*/*z* (%) = 500 (100) [M$^+$ + 23]. − $^1$H NMR (500 MHz, [D$_6$]DMSO): δ = 1.2−1.5 [m, 16 H, (CH$_2$)$_8$], 1.80 (s, 3 H, CH$_3$), 2.40 (dd, $J_{trans}$ = 2.7 Hz, $J_{gem}$ = 5.2 Hz, 1 H, CH$_{cis}$*H*$_{trans}$ oxirane), 2.64 (t, $J_{cis}$ = $J_{gem}$ = 4.8 Hz, 1 H, C*H*$_{cis}$H$_{trans}$ oxirane), 2.84 (m, 1 H, CH oxirane), 3.48 (q, $J_{1,2}$ = $J_{2,3}$ = $J_{2,NH}$ = 9.0 Hz, 1 H, H-2), 3.59 (td, $J_{3,OH}$ = 5.6 Hz, $J_{2,3}$ = $J_{3,4}$ = 9.4 Hz, 1 H, H-3), 4.18 (dd, $J_{5,6e}$ = 5.0 Hz, $J_{6a,6e}$ = 10.2 Hz, 1 H, H-6$_e$), 4.45 (d, $J_{1,2}$ = 8.6 Hz, 1 H, H-1), 5.26 (d, $J_{3,OH}$ = 5.6 Hz, 1 H, OH), 5.58 (s, 1 H, PhC*H*), 7.3−7.5 (m, 5 H, Ph), 7.80 (d, $J_{2,NH}$ = 9.0 Hz, 1 H, NH). − $^{13}$C NMR (125 MHz, [D$_6$]DMSO): δ = 23.0 (CH$_3$), 25.4, 25.6, 28.8, 28.9, 29.0, 29.1, 31.9 [(CH$_2$)$_8$], 46.1 (CH$_2$ oxirane), 51.1 (CH oxirane), 56.2 (C-2), 66.0 (C-5), 67.9 (C-6), 68.7 (OCH$_2$R), 70.4 (C-3), 81.4 (C-4), 100.7 (Ph*C*H), 101.6 (C-1), 126.4, 128.0, 128.8, 137.8 (Ph), 169.0 (C=O). − C$_{26}$H$_{39}$NO$_7$ (477.61): calcd. C 65.39, H 8.23, N 2.93; found C 65.26, H 8.02, N 2.87.

**(*R*)-2,3-Epoxypropyl 4,6-*O*-Benzylidene-2-deoxy-2-octanamido-β-D-glucopyranoside (10):** Recrystallized from ethanol yielding 3.02 g (80%), m.p. 220−222 °C. − $[\alpha]_D^{25}$ = −103.2 (*c* = 0.5, CH$_2$Cl$_2$). − IR (KBr): ṽ = 3448, 3280, 1650, 1551, 1382, 1100 cm$^{-1}$. − FAB-MS: *m*/*z* (%) = 472 (100) [M$^+$ + 23]. − $^1$H NMR (200 MHz, [D$_6$]DMSO): δ = 0.85 (t, *J* = 6.7 Hz, 3 H, CH$_3$), 1.1−1.6 [m, 10 H, (CH$_2$)$_5$], 2.06 (t, *J* = 7.5 Hz, 2 H, CH$_2$CON), 2.55 (dd, $J_{trans}$ = 2.7 Hz, $J_{gem}$ = 5.2 Hz, 1 H, CH$_{cis}$*H*$_{trans}$ oxirane), 2.69 (t, $J_{cis}$ = $J_{gem}$ = 5.2 Hz, 1 H, C*H*$_{cis}$H$_{trans}$ oxirane), 3.07 (m, 1 H, CH oxirane), 4.18 (dd, $J_{5,6e}$ = 4.7 Hz, $J_{6a,6e}$ = 10.2 Hz, 1 H, H-6$_e$), 4.51 (d, $J_{1,2}$ = 8.0 Hz, 1 H, H-1), 5.25 (d, $J_{3,OH}$ = 5.4 Hz, 1 H, OH), 5.59 (s, 1 H, PhC*H*), 7.3−7.5 (m, 5 H, Ph), 7.74 (d, $J_{2,NH}$ = 8.4 Hz, 1 H, NH). − $^{13}$C NMR (50 MHz, [D$_6$]DMSO): δ = 14.0 (CH$_3$), 22.1, 25.3, 28.5, 31.2, 35.8 [(CH$_2$)$_6$], 43.4 (CH$_2$ oxirane), 49.9 (CH oxirane), 56.0 (C-2), 66.0 (C-5), 67.8 (C-6), 69.5 (OCH$_2$R), 70.3 (C-3), 81.3 (C-4), 100.6 (Ph*C*H), 101.8 (C-1), 126.3, 128.0, 128.8, 137.7 (Ph), 172.2 (C=O). − C$_{24}$H$_{35}$NO$_7$ (449.55): calcd. C 64.12, H 7.85, N 3.12; found C 63.86, H 7.64, N 3.16.

**(*R*)-2,3-Epoxypropyl 4,6-*O*-Benzylidene-2-deoxy-2-hexanamido-β-D-glucopyranoside (11):** Recrystallized from ethanol yielding 2.56 g (76%), m.p. 233−235 °C. − $[\alpha]_D^{25}$ = −44.3 (*c* = 1.0, DMF). − IR (KBr): ṽ = 3450, 3285, 1650, 1547, 1380, 1102 cm$^{-1}$. − CI-MS: *m*/*z* (%) = 422 (100) [M$^+$ + 1]. − $^1$H NMR (200 MHz, [D$_6$]DMSO): δ = 0.85 (t, *J* = 6.6 Hz, 3 H, CH$_3$), 1.2−1.5 [m, 6 H, (CH$_2$)$_3$], 2.06 (t, *J* = 7.4 Hz, 2 H, CH$_2$CON), 2.54 (dd, $J_{trans}$ = 2.6 Hz, $J_{gem}$ = 5.1 Hz, 1 H, CH$_{cis}$*H*$_{trans}$ oxirane), 2.69 (t, $J_{cis}$ = $J_{gem}$ = 5.0 Hz, 1 H, C*H*$_{cis}$H$_{trans}$ oxirane), 3.02 (m, 1 H, CH oxirane), 4.19 (dd, $J_{5,6e}$ = 4.6 Hz, $J_{6a,6e}$ = 10.1 Hz, 1 H, H-6$_e$), 4.52 (d, $J_{1,2}$ = 7.9 Hz, 1 H, H-1), 5.26 (d, $J_{3,OH}$ = 5.3 Hz, 1 H, OH), 5.59 (s, 1 H, PhC*H*), 7.3−7.5 (m, 5 H, Ph), 7.76 (d, $J_{2,NH}$ = 8.4 Hz, 1 H, NH). − $^{13}$C NMR (50 MHz, [D$_6$]DMSO): δ = 13.9 (CH$_3$), 22.0, 25.0, 30.8, 35.8 [(CH$_2$)$_4$], 43.5 (CH$_2$ oxirane), 50.0 (CH oxirane), 56.0 (C-2), 66.0 (C-5), 67.8 (C-6), 69.6 (OCH$_2$R), 70.3 (C-3), 81.3 (C-4), 100.7 (Ph*C*H), 101.8 (C-1), 126.4, 128.0, 128.9, 137.8 (Ph), 172.2 (C=O). − C$_{22}$H$_{31}$NO$_7$ (421.50): calcd. C 62.69, H 7.41, N 3.32; found C 62.78, H 7.35, N 3.21.

**(*R*)-2,3-Epoxypropyl 4,6-*O*-Benzylidene-2-deoxy-2-hexanamido-3-*O*-hexanoyl-β-D-glucopyranoside (12):** Recrystallized from ethanol yielding 3.07 g (74%), m.p. 190−192 °C. − $[\alpha]_D^{25}$ = −46.5 (*c* = 1.7, DMF). − IR (KBr): ṽ = 3282, 1742, 1656, 1550, 1378, 1181, 1100 cm$^{-1}$. − CI-MS: *m*/*z* (%) = 520 (100) [M$^+$ + 1]. − $^1$H NMR (200 MHz, CDCl$_3$): δ = 0.7−0.9 (m, 6 H, 2 CH$_3$), 1.1−1.7 [m, 12 H, 6 (CH$_2$)], 2.13 (t, *J* = 7.6 Hz, 2 H, CH$_2$CON), 2.32 (t, *J* = 7.5 Hz, 2 H, CH$_2$COO), 2.60 (dd, $J_{trans}$ = 2.7 Hz, $J_{gem}$ = 5.3 Hz, 1 H, CH$_{cis}$*H*$_{trans}$ oxirane), 2.68 (t, $J_{cis}$ = $J_{gem}$ = 5.2 Hz, 1 H, C*H*$_{cis}$H$_{trans}$ oxirane), 3.00 (m, 1 H, CH oxirane), 3.4−3.8 (m, 5 H, H-4, H-5, H-6$_a$, OCH$_2$R), 4.1−4.4 (m, 3 H, H-1, H-2, H-6$_e$), 5.26 (t, $J_{2,3}$ = $J_{3,4}$ = 9.8 Hz, 1 H, H-3), 5.47 (s, 1 H, PhC*H*), 6.15 (d, $J_{2,NH}$ = 9.4 Hz, 1 H, NH), 7.2−7.5 (m, 5 H, Ph). − $^{13}$C NMR (50 MHz, CDCl$_3$): δ = 13.8, 13.9 (2 CH$_3$), 22.2, 22.3, 24.6, 25.2, 31.0, 31.3, 34.1, 36.7 [8 (CH$_2$)], 44.0 (CH$_2$ oxirane), 50.2 (CH oxirane), 53.7 (C-2), 66.1 (C-5), 68.1 (OCH$_2$R), 68.5 (C-6), 71.8 (C-3), 78.7 (C-4), 101.0 (Ph*C*H), 102.6 (C-1), 125.9, 128.2, 128.9, 137.0 (Ph), 173.2, 174.3 (2 C=O). − C$_{28}$H$_{41}$NO$_8$ (519.64): cald. C 64.72, H 7.95, N 2.70; found C 64.41, H 7.69, N 2.76.

**Ring-Opening Nucleophilic Reactions**

**(*R*)-3-Dialkylamino-2-hydroxypropyl 2-Acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (13, 14):** To a solution of (*R*)-2,3-epoxypropyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (**8**) (0.73 g, 2.0 mmol) in acetonitrile (50 mL), was added lithium perchlorate (0.42 g, 4.0 mmol) and secondary amine (4.0 mmol). The mixture was kept overnight at room temperature. Dichloromethane was added, and the solution was washed with water, dried (Na$_2$SO$_4$), and evaporated to dryness.

**(*R*)-2-Hydroxy-3-(1-pyrrolidyl)propyl 2-Acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (13):** Recrystallized from ethanol yielding 0.78 g (90%), m.p. 250−252 °C. − $[\alpha]_D^{25}$ = −81.5 (*c* = 0.5, DMF). − IR (KBr): ṽ = 3300b, 1658, 1551, 1378, 1089 cm$^{-1}$. − CI-MS: *m*/*z* (%) = 437 (100) [M$^+$ + 1]. − $^1$H NMR (500 MHz, [D$_6$]DMSO): δ = 1.65 (m, 4 H, 2 CH$_2$ β pyrrolidine), 1.81 (s, 3 H, CH$_3$), 2.31 (dd, $^3J$ = 7.0 Hz, $J_{gem}$ = 12.3 Hz, 1 H, C*H*$_A$H$_B$N), 2.44 (m, 5 H, CH$_A$*H*$_B$N, 2 CH$_2$ α pyrrolidine), 3.31 (dt, $J_{4,5}$ = $J_{5,6a}$ = 9.8 Hz, $J_{5,6e}$ = 4.9 Hz, 1 H, H-5), 3.36 (dd, $^3J$ = 5.5 Hz, $J_{gem}$ = 9.7 Hz, 1 H, OC*H*$_A$H$_B$R), 3.41 (t, $J_{3,4}$ = $J_{4,5}$ = 9.4 Hz, 1 H, H-4), 3.50 (m, 1 H, H-2), 3.57−3.65 (m, 3 H, H-3, C*H*OH, OCH$_A$*H*$_B$R), 3.71 (t, $J_{5,6a}$ = $J_{6a,6e}$ = 10.2 Hz, 1 H, H-6$_a$), 4.19 (dd, $J_{5,6e}$ = 5.0 Hz, $J_{6a,6e}$ = 10.2 Hz, 1 H, H-6$_e$), 4.40 (br. s, 1 H, OH), 4.49 (d, $J_{1,2}$ = 8.3 Hz, 1 H, H-1), 5.25 (br. s, 1 H, OH), 5.58 (s, 1 H, PhC*H*), 7.35−7.45 (m, 5 H, Ph), 7.80 (d, $J_{2,NH}$ = 8.9 Hz, 1 H, NH). − $^{13}$C NMR (125 MHz, [D$_6$]DMSO): δ = 23.1 (CH$_3$), 23.2 (2 CH$_2$ β pyrrolidine), 54.2 (2 CH$_2$ α pyrrolidine), 56.2 (C-2), 59.0 (CH$_2$N), 66.0 (C-5), 67.9 (C-6), 68.2 (CHOH), 70.4 (C-3), 72.2 (OCH$_2$R), 81.3 (C-4), 100.7 (Ph*C*H), 102.1 (C-1), 126.4, 128.1, 128.9, 137.8 (Ph), 169.2 (C=O). − C$_{22}$H$_{32}$N$_2$O$_7$ (436.51): calcd. C 60.54, H 7.39, N 6.42; found C 60.46, H 7.35, N 6.40.

**(*R*)-2-Hydroxy-3-{1-[4-(2-hydroxyethyl)piperazyl]}propyl 2-Acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (14):** Column-chromatography using dichloromethane-methanol (5:2) as eluent yielded 0.77 g (78%), m.p. 99−101 °C. − $[\alpha]_D^{25}$ = −41.0 (*c* =

2.1, DMF). − CI-MS: *m*/*z* (%) = 496 (52) [M$^+$ + 1]. − $^1$H NMR (200 MHz, [D$_6$]DMSO, D$_2$O): δ = 1.83 (s, 3 H, CH$_3$), 4.18 (dd, $J_{5,6e}$ = 4.8 Hz, $J_{6a,6e}$ = 10.1 Hz, 1 H, H-6$_e$), 4.48 (d, $J_{1,2}$ = 8.2 Hz, 1 H, H-1), 5.59 (s, 1 H, PhC*H*), 7.3−7.5 (m, 5 H, Ph). − $^{13}$C NMR (50 MHz, [D$_6$]DMSO): δ = 23.2 (CH$_3$), 45.0, 53.3, 53.6, 58.4, 58.5, 60.4, 61.1 [7 (CH$_2$) hydroxyethylpiperazine], 56.2 (C-2), 66.0 (C-5), 67.0 (CHOH), 67.9 (C-6), 70.4 (C-3), 72.1 (OCH$_2$R), 81.3 (C-4), 100.7 (Ph*C*H), 102.1 (C-1), 126.4, 128.1, 128.9, 137.8 (Ph), 169.0 (C=O). − C$_{24}$H$_{37}$N$_3$O$_8$ (495.58): cald. C 58.17, H 7.53, N 8.48; found C 57.88, H 7.40, N 8.36.

**(*R*)-3-(1-Butyl)amino-2-hydroxypropyl 2-Acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (15):** A solution of (*R*)-2,3-epoxypropyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (**8**) (1.28 g, 3.5 mmol) in *n*-butylamine (18 mL) was stirred overnight at room temperature. The solution was evaporated to dryness and purified by column chromatography using dichloromethane/methanol (1:1) mixture as solvent, to give compound **15**: yield 1.45 g (95%), m.p. 238−240 °C. − $[\alpha]_D^{25}$ = −110.6 (*c* = 0.6, DMF). − IR (KBr): ν̃ = 3350b, 1655, 1545, 1381, 1092 cm$^{-1}$. − FAB-MS: *m*/*z* (%) = 461 (100) [M$^+$ + 23]. − $^1$H NMR (200 MHz, [D$_6$]DMSO, D$_2$O, 80 °C): δ = 0.89 (t, 3 H, *J* = 6.8 Hz, CH$_3$), 1.85 (s, 3 H, CH$_3$CON), 4.19 (dd, $J_{5,6e}$ = 4.8 Hz, $J_{6a,6e}$ = 10.3 Hz, 1 H, H-6$_e$), 4.56 (d, $J_{1,2}$ = 8.1 Hz, 1 H, H-1), 5.55 (s, 1 H, PhC*H*), 7.3−7.5 (m, 5 H, Ph). − $^{13}$C NMR (50 MHz, [D$_6$]DMSO): δ = 14.1 (CH$_3$), 20.0, 29.2 (HNCH$_2$*C*H$_2$*C*H$_2$), 23.2 (*C*H$_3$CON), 55.2 (HN*C*H$_2$CH$_2$CH$_2$), 56.2 (C-2), 57.8 (HOCH*C*H$_2$NH), 66.0 (C-5), 67.1 (HO*C*HCH$_2$NH), 68.0 (C-6), 70.5 (C-3), 71.7 (OCH$_2$R), 81.4 (C-4), 100.8 (Ph*C*H), 102.0 (C-1), 126.5, 128.2, 129.0, 137.4 (Ph), 169.7 (C=O). − C$_{22}$H$_{34}$N$_2$O$_7$ (438.53): calcd. C 60.26, H 7.82, N 6.39; found C 60.10, H 7.88, N 6.32.

**ω-Azido-(ω−1)-hydroxyalkyl 2-Acylamino-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (16, 19, 21):** To a solution of (ω−1),ω-epoxyalkyl 2-acylamino-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (**8**−**10**) (3.5 mmol) in acetonitrile (35 mL), lithium perchlorate (0.75 g, 7.0 mmol) and sodium azide (0.91 g, 14.0 mmol) were added. The mixture was heated overnight at 80 °C, with stirring. It was then left to cool to room temperature and poured into ice water. The precipitate obtained was filtered off and dried.

**(*R*)-3-Azido-2-hydroxypropyl 2-Acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (16):** Recrystallized from ethanol yielding 1.08 g (76%), m.p. 230−232 °C. − $[\alpha]_D^{25}$ = −23.5 (*c* = 0.5, DMF). − IR (KBr): ν̃ = 3420, 3288, 2100, 1655, 1560, 1375, 1091 cm$^{-1}$. − FAB-MS: *m*/*z* (%) = 431 (100) [M$^+$ + 23]. − $^1$H NMR (200 MHz, [D$_6$]DMSO): δ = 1.81 (s, 3 H, CH$_3$), 4.19 (dd, $J_{5,6e}$ = 4.5 Hz, $J_{6a,6e}$ = 10.3 Hz, 1 H, H-6$_e$), 4.44 (d, $J_{1,2}$ = 7.9 Hz, 1 H, H-1), 5.28 (m, 2 H, 2 OH), 5.59 (s, 1 H, PhC*H*), 7.3−7.5 (m, 5 H, Ph), 7.82 (d, $J_{2,NH}$ = 8.4 Hz, 1 H, NH). − $^{13}$C NMR (50 MHz, [D$_6$]DMSO): δ = 23.1 (CH$_3$), 53.2 (CH$_2$N$_3$), 56.1 (C-2), 65.9 (C-5), 67.8 (C-6), 68.6 (CHOH), 70.3 (C-3), 70.4 (OCH$_2$R), 81.2 (C-4), 100.7 (Ph*C*H), 102.2 (C-1), 126.4, 128.1, 128.9, 137.7 (Ph), 169.3 (C=O). − C$_{18}$H$_{24}$N$_4$O$_7$ (408.42): calcd. C 52.94, H 5.92, N 13.72; found C 53.21, H 6.22, N 13.40.

**11-Azido-10-hydroxyundecyl 2-Acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (19):** Recrystallized from ethanol yielding 1.60 g (88%), m.p. 198−200 °C. − $[\alpha]_D^{25}$ = −68.6 (*c* = 0.6, DMF). − IR (KBr): ν̃ = 3430, 3290, 2102, 1658, 1559, 1372, 1090 cm$^{-1}$. − FAB-MS: *m*/*z* (%) = 543 (100) [M$^+$ + 23]. − $^1$H NMR (200 MHz, [D$_6$]DMSO): δ = 1.1−1.5 [m, 16 H, (CH$_2$)$_8$], 1.79 (s, 3 H, CH$_3$), 4.18 (dd, $J_{5,6e}$ = 4.6 Hz, $J_{6a,6e}$ = 10.3 Hz, 1 H, H-6$_e$), 4.44 (d, $J_{1,2}$ = 8.0 Hz, 1 H, H-1), 4.97 (d, *J* = 5.4 Hz, 1 H, CHO*H*), 5.25 (d, $J_{3,OH}$ = 5.0 Hz, 1 H, OH-3), 5.58 (s, 1 H, PhC*H*), 7.3−7.5 (m, 5 H, Ph), 7.79 (d, $J_{2,NH}$ = 8.5 Hz, 1 H, NH). − $^{13}$C NMR (50 MHz, [D$_6$]DMSO): δ = 23.0 (CH$_3$), 25.0, 25.3, 28.8, 29.0, 29.1, 34.2 [(CH$_2$)$_8$], 56.1 (CH$_2$N$_3$), 56.2 (C-2), 65.9 (C-5), 67.9 (C-6), 68.7 (OCH$_2$R), 69.6 (CHOH), 70.4 (C-3), 81.3 (C-4), 100.6 (Ph*C*H), 101.6 (C-1), 126.3, 128.0, 128.8, 137.8 (Ph), 169.0 (C=O). − C$_{26}$H$_{40}$N$_4$O$_7$ (520.63): cald. C 59.98, H 7.74, N 10.76; found C 59.99, H 7.46, N 10.51.

**(*R*)-3-Azido-2-hydroxypropyl 4,6-*O*-Benzylidene-2-deoxy-2-octanamido-β-D-glucopyranoside (21):** Column-chromatography using dichloromethane-methanol (75:1) as eluent yielded 1.55 g (90%), m.p. 230−232 °C. − $[\alpha]_D^{25}$ = −26.2 (*c* = 0.6, DMF). − IR (KBr): ν̃ = 3420sh, 3290, 2105, 1655, 1544, 1379, 1088 cm$^{-1}$. − FAB-MS: *m*/*z* (%) = 515 (100) [M$^+$ + 23]. − $^1$H NMR (200 MHz, [D$_6$]DMSO): δ = 0.87 (t, *J* 6.7 Hz, 3 H, CH$_3$), 1.1−1.6 [m, 10 H, (CH$_2$)$_5$], 2.02 (t, *J* = 7.5 Hz, 2 H, CH$_2$CON), 4.19 (dd, $J_{5,6e}$ = 4.6 Hz, $J_{6a,6e}$ = 10.3 Hz, 1 H, H-6$_e$), 4.44 (d, $J_{1,2}$ = 7.9 Hz, 1 H, H-1), 5.25 (m, 2 H, 2 OH), 5.59 (s, 1 H, PhC*H*), 7.3−7.5 (m, 5 H, Ph), 7.73 (d, $J_{2,NH}$ = 8.4 Hz, 1 H, NH). − $^{13}$C NMR (50 MHz, [D$_6$]DMSO): δ = 14.0 (CH$_3$), 22.1, 25.3, 28.6, 28.7, 31.2, 35.8 [(CH$_2$)$_6$], 53.3 (CH$_2$N$_3$), 55.9 (C-2), 66.0 (C-5), 67.8 (C-6), 67.8 (OCH$_2$R), 68.6 (CHOH), 70.3 (C-3), 81.2 (C-4), 100.6 (Ph*C*H), 102.2 (C-1), 126.4, 128.0, 128.9, 137.7 (Ph), 172.2 (C=O). − C$_{24}$H$_{36}$N$_4$O$_7$ (492.58) calcd. C 58.52, H 7.37, N 11.37; found C 58.81, H 7.16, N 11.21.

**(*S*)-1-Alkylthio-2-hydroxyprop-3-yl 2-Acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranosides 17−18:** To a solution of (*R*)-2,3-epoxypropyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (**8**) (0.73 g, 2.0 mmol) in methanol (50 mL), a solution of thiophenol (0.4 mL, 4.0 mmol) and triethylamine (0.6 mL, 4.0 mmol), or *tert*-butanethiol (0.45 mL, 4.0 mmol) and solid potassium hydroxide (0.11 g, 2.0 mmol) in methanol (10 mL) was added, and the mixture stirred overnight at room temperature. The solvent was evaporated in vacuo and the solid dissolved in dichloromethane. The solution was washed successively with 5% aqueous solution of sodium hydroxide and with water, dried (Na$_2$SO$_4$), and evaporated to dryness.

**(*S*)-2-Hydroxy-1-phenylthioprop-3-yl 2-Acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (17):** Column chromatography using dichloromethane/methanol (40:1) as eluent yielded 0.63 g (66%), m.p. 224−226 °C. − $[\alpha]_D^{25}$ = −47.5 (*c* = 0.4, DMF). − IR (KBr): ν̃ = 3435, 3288, 1655, 1556, 1374, 1093 cm$^{-1}$. − CI-MS: *m*/*z* (%) = 476 (10) [M$^+$ + 1]. − $^1$H NMR (200 MHz, [D$_6$]DMSO): δ = 1.75 (s, 3 H, CH$_3$), 2.83 (dd, $^3J$ = 7.2 Hz, $J_{gem}$ = 13.1 Hz, 1 H, C$H_A$H$_B$SPh), 3.15 (dd, $^3J$ = 3.8 Hz, $J_{gem}$ = 13.1 Hz, 1 H, CH$_A$$H_B$SPh), 4.18 (dd, $J_{5,6e}$ = 4.4 Hz, $J_{6a,6e}$ = 9.8 Hz, 1 H, H-6$_e$), 4.49 (d, $J_{1,2}$ = 7.8 Hz, 1 H, H-1), 5.11 (d, *J* = 5.1 Hz, 1 H, OH), 5.28 (d, *J* = 5.0 Hz, 1 H, OH), 5.59 (s, 1 H, PhC*H*), 7.1−7.5 (m, 10 H, 2 Ph), 7.83 (d, $J_{2,NH}$ = 8.4 Hz, 1 H, NH). − $^{13}$C NMR (50 MHz, [D$_6$]DMSO): δ = 23.0 (CH$_3$), 36.3 (*C*H$_2$SPh), 56.1 (C-2), 66.0 (C-5), 67.8 (C-6), 67.9 (CHOH), 70.4 (C-3), 72.2 (OCH$_2$R), 81.2 (C-4), 100.7 (Ph*C*H), 102.2 (C-1), 125.2, 126.4, 127.4, 128.0, 128.9, 129.0, 136.9, 137.7 (2 Ph), 169.2 (C=O). − C$_{24}$H$_{29}$NO$_7$S (475.56): calcd. C 60.62, H 6.15, N 2.95, S 6.74; found C 60.32, H 6.11, N 3.01, S 6.47.

**(*S*)-1-*tert*-Butylthio-2-hydroxyprop-3-yl 2-Acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (18):** Recrystallized from diethyl ether yielding 0.56 g (62%), m.p. 196−198 °C. − $[\alpha]_D^{25}$ = −55.0 (*c* = 1.0, DMF). − IR (KBr): ν̃ = 3445, 3300, 1658, 1552, 1374, 1092 cm$^{-1}$. − CI-MS: *m*/*z* (%) = 456 (5) [M$^+$ + 1]. − $^1$H NMR (200 MHz, [D$_6$]DMSO): δ = 1.24 [s, 9 H, C(CH$_3$)$_3$], 1.81 (s, 3 H, CH$_3$CON), 2.3−2.7 (m, CH$_2$S), 4.19 (dd, $J_{5,6e}$ = 4.4 Hz, $J_{6a,6e}$ =

10.5 Hz, 1 H, H-6$_e$), 4.46 (d, $J_{1,2}$ = 7.8 Hz, 1 H, H-1), 4.85 (d, $J$ = 5.0 Hz, 1 H, OH), 5.29 (d, $J$ = 4.7 Hz, 1 H, OH), 5.59 (s, 1 H, PhC*H*), 7.3−7.5 (m, 5 H, Ph), 7.84 (d, $J_{2,NH}$ = 8.2 Hz, 1 H, NH). − $^{13}$C NMR (50 MHz, [D$_6$]DMSO): δ = 23.1 (*C*H$_3$CON), 30.8 [SC(*C*H$_3$)$_3$], 32.2 (CH$_2$S), 41.5 [S*C*(CH$_3$)$_3$], 56.1 (C-2), 66.0 (C-5), 67.9 (C-6), 69.5 (CHOH), 70.4 (C-3), 72.5 (OCH$_2$R), 81.3 (C-4), 100.7 (Ph*C*H), 102.1 (C-1), 126.4, 128.1, 128.9, 137.8 (Ph), 169.2 (C=O). − $C_{22}H_{33}NO_7S$ (455.57): calcd. C 58.00, H 7.30, N 3.07, S 7.04; found C 57.77, H 7.09, N 3.11, S 7.18.

**ω-Cyano-(ω−1)-hydroxyalkyl 2-Acylamino-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (20, 22):** A solution of (ω−1),ω-epoxyalkyl 2-acylamino-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (**9**, **11**, **12**). (2.0 mmol) and potassium cyanide (1.04 g, 16.0 mmol) in methanol (40 mL) was stirred for 24−36 hours at room temperature. The solvent was evaporated in vacuo and the solid dissolved in dichloromethane. The solution was washed with water, dried (Na$_2$SO$_4$), evaporated to dryness, and recrystallized from ethanol, yielding white solids.

**11-Cyano-10-hydroxypropyl 2-Acetamino-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (20):** Yield 0.65 g (64%), m.p. 199−201 °C. − $[\alpha]_D^{25}$ = −49.5 (*c* = 1.8, DMF). − IR (KBr): $\tilde{\nu}$ = 3430, 3290, 2251, 1657, 1553, 1375, 1096 cm$^{-1}$. − FAB-MS: *m*/*z* (%) = 527 (100) [M$^+$ + 23]. − $^1$H NMR (200 MHz, [D$_6$]DMSO): δ = 1.2−1.5 [m, 16 H, (CH$_2$)$_8$], 1.80 (s, 3 H, CH$_3$), 2.50 (m, CH$_2$C≡N), 4.18 (dd, $J_{5,6e}$ = 4.4 Hz, $J_{6a,6e}$ = 10.2 Hz, 1 H, H-6$_e$), 4.44 (d, $J_{1,2}$ = 8.0 Hz, 1 H, H-1), 5.18 (d, $J_{H,OH}$ = 5.2 Hz, 1 H, OH), 5.26 (d, $J_{H,OH}$ = 5.1 Hz, 1 H, OH), 5.58 (s, 1 H, PhC*H*), 7.3−7.5 (m, 5 H, Ph), 7.80 (d, $J_{2,NH}$ = 8.5 Hz, 1 H, NH). − $^{13}$C NMR (50 MHz, [D$_6$]DMSO): δ = 23.0 (CH$_3$), 25.0, 25.4, 25.5, 28.8, 28.9, 29.0, 36.2 [9 (CH$_2$)], 56.2 (C-2), 65.9 (C-5), 66.0 (CHOH), 67.9 (C-6), 68.7 (OCH$_2$R), 70.4 (C-3), 81.3 (C-4), 100.7 (Ph*C*H), 101.6 (C-1), 119.1 (C≡N), 126.4, 128.0, 128.9, 137.8 (Ph), 169.0 (C=O). − $C_{27}H_{40}N_2O_7$ (504.63): calcd. C 64.26, H 7.99, N 5.55; found C 64.30, H 7.97, N 5.23.

**(*R*)-3-Cyano-2-hydroxypropyl 4,6-*O*-Benzylidene-2-deoxy-2-hexanamido-β-D-glucopyranoside (22):** Yield 0.67 g (75%) from **11**, 0.55 g (61%) from **12**, m.p. 223−225 °C. − $[\alpha]_D^{25}$ = −30.1 (*c* = 0.7, DMF). − IR (KBr): $\tilde{\nu}$ = 3450b, 3294, 2253, 1651, 1547, 1378, 1098 cm$^{-1}$. − CI-MS: *m*/*z* (%) = 449 (78) [M$^+$ + 1]. − $^1$H NMR (200 MHz, [D$_6$]DMSO): δ = 0.86 (t, $J$ = 6.7 Hz, 3 H, CH$_3$), 1.2−1.5 [m, 6 H, (CH$_2$)$_3$], 2.08 (s, 2 H, CH$_2$CON), 2.48 (m, C*H*$_A$H$_B$C≡N), 2.63 (dd, $^3J$ = 3.9 Hz, $J_{gem}$ = 10.7 Hz, 1 H, CH$_A$*H*$_B$C≡N), 4.20 (dd, $J_{5,6e}$ = 4.2 Hz, $J_{6a,6e}$ = 10.1 Hz, 1 H, H-6$_e$), 4.47 (d, $J_{1,2}$ = 7.8 Hz, 1 H, H-1), 5.28 (d, $J_{H,OH}$ = 5.1 Hz, 1 H, OH), 5.50 (d, $J_{H,OH}$ = 4.8 Hz, 1 H, OH), 5.60 (s, 1 H, PhC*H*), 7.3−7.5 (m, 5 H, Ph), 7.78 (d, $J_{2,NH}$ = 8.2 Hz, 1 H, NH). − $^{13}$C NMR (50 MHz, [D$_6$]DMSO): δ = 13.9 (CH$_3$), 22.3 (*C*H$_2$C≡N), 22.0, 24.9, 30.9, 35.8 [(CH$_2$)$_4$], 55.9 (C-2), 65.1 (CHOH), 66.0 (C-5), 67.8 (C-6), 70.3 (C-3), 71.2 (OCH$_2$R), 81.2 (C-4), 100.7 (Ph*C*H), 102.1 (C-1), 118.6 (C≡N), 126.4, 128.0, 128.9, 137.7 (Ph), 172.4 (C=O). − $C_{23}H_{32}N_2O_7$ (448.52): calcd. C 61.59, H 7.19, N 6.25; found C 61.63, H 7.22, N 5.97.

**Acetyl Derivatives from 15 and 22:** An aliquot of compounds **15** and **22** (0.75 mmol) was acetylated in the usual way with acetic anhydride/pyridine (1:1) (10 mL). The reaction mixture was kept overnight at room temperature and then poured into ice water. The precipitate obtained was isolated by filtration and recrystallized from ethanol/water, giving compounds **23** and **24** as white solids.

**(*R*)-2-Acetoxy-3-[(*N*-1-butyl)acetamido]propyl 2-Acetamido-3-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (23):** Yield 0.41 g (97%), m.p. 168−170 °C. − $[\alpha]_D^{25}$ = −38.7 (*c* = 0.9, DMF). − FAB-MS: *m*/*z* (%) = 587 (100) [M$^+$ + 23]. − $^1$H NMR (200 MHz, [D$_6$]DMSO, 60 °C): δ = 0.89 (t, $J$ = 7.0 Hz, 3 H, CH$_3$), 1.76, 1.96, 1.98, 1.99 (4 s, 12 H, CH$_3$CO), 4.24 (dd, $J_{5,6e}$ = 5.0 Hz, $J_{6a,6e}$ = 10.2 Hz, 1 H, H-6$_e$), 4.70 (d, $J_{1,2}$ = 8.3 Hz, 1 H, H-1), 5.05 (m, 1 H, C*H*OAc), 5.16 (t, $J_{2,3}$ = $J_{3,4}$ = 9.8 Hz, 1 H, H-3), 5.61 (s, 1 H, PhC*H*), 7.3−7.4 (m, 5 H, Ph), 7.72 (d, $J_{2,NH}$ = 9.2 Hz, 1 H, NH). − $^{13}$C NMR (50 MHz, [D$_6$]DMSO): δ = 13.7 (CH$_3$), 20.5, 20.7, 21.3, 22.7 (4 *C*H$_3$CO), 19.2, 19.9, 29.0, 30.4 (AcNCH$_2$*C*H$_2$*C*H$_2$), 44.8, 45.3 (AcN*C*H$_2$CH$_2$CH$_2$), 47.5, 48.8 (AcOCH*C*H$_2$NAc), 53.6 (C-2), 65.7 (C-5), 67.6 (C-6), 70.0, 70.2 (*C*HOAc), 71.6 (C-3), 78.0 (C-4), 100.2 (Ph*C*H), 101.5, 101.7 (C-1), 126.1, 128.1, 128.9, 137.3 (Ph), 169.2, 169.7, 169.9, 170.0 (4 C=O). − $C_{28}H_{40}N_2O_{10}$ (564.64): calcd. C 59.56, H 7.14, N 4.96; found C 59.23, H 6.96, N 4.72.

**(*R*)-2-Acetoxy-3-cyanopropyl 3-*O*-Acetyl-4,6-*O*-benzylidene-2-deoxy-2-hexanamido-β-D-glucopyranoside (24):** Yield 0.35 g (89%), m.p. 195−197 °C. − $[\alpha]_D^{25}$ = −28.0 (*c* = 1.0, DMF). − IR (KBr): $\tilde{\nu}$ = 3460b, 3287, 2253, 1746, 1655, 1545, 1374, 1239, 1101 cm$^{-1}$. − FAB-MS: *m*/*z* (%) = 555 (100) [M$^+$ + 23]. − $^1$H NMR (200 MHz, [D$_6$]DMSO): δ = 0.84 (t, $J$ 6.8 Hz, 3 H, CH$_3$), 1.1−1.5 [m, 6 H, (CH$_2$)$_3$], 1.95−2.05 (m, 8 H, 2 CH$_3$CO$_2$, CH$_2$CON), 2.83 (m, 2 H, CH$_2$C≡N), 3.4−3.9 (m, 6 H, H-2, H-4, H-5, H-6$_a$, OCH$_2$R), 4.23 (dd, $J_{5,6e}$ = 4.9 Hz, $J_{6a,6e}$ = 10.1 Hz, 1 H, H-6$_e$), 4.66 (d, $J_{1,2}$ = 8.4 Hz, 1 H, H-1), 5.02 (m, 1 H, C*H*OAc), 5.15 (d, $J_{2,3}$ = $J_{3,4}$ = 9.9 Hz, 1 H, H-3), 5.62 (s, 1 H, PhC*H*), 7.36 (s, 5 H, Ph), 7.90 (d, $J_{2,NH}$ = 9.2 Hz, 1 H, NH). − $^{13}$C NMR (50 MHz, [D$_6$]DMSO) δ = 13.8 (CH$_3$), 19.2 (*C*H$_2$C≡N), 20.6, 20.7 (2 *C*H$_3$CO$_2$), 21.9, 24.9, 30.7, 35.6 [(CH$_2$)$_4$], 53.3 (C-2), 65.8 (C-5), 67.4 (CHOH), 67.6 (C-6), 68.4 (OCH$_2$R), 71.5 (C-3), 78.0 (C-4), 100.3 (Ph*C*H), 101.5 (C-1), 117.5 (C≡N), 126.1, 128.2, 129.0, 137.3 (Ph), 169.5, 169.6, 172.3 (3 C=O). − $C_{27}H_{36}N_2O_9$ (532.60): calcd. C 60.89, H 6.81, N 5.26; found C 61.00, H 6.69, N 5.37.

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