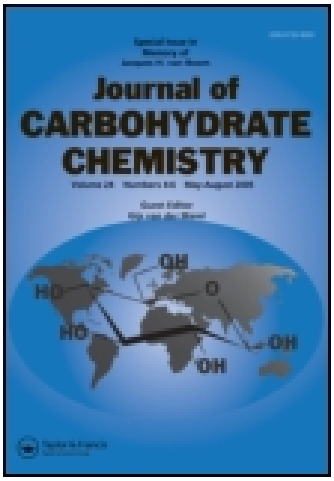

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Unexpected Products in the $LiAlH_4/AlCl_3$-Reduction of 3-O-Substituted and N-Benzyloxycarbonyl-Protected 4,6-O-[2-Methoxybenzylidene]-α-D-Glucosamine Derivatives

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UNEXPECTED PRODUCTS IN THE $LiAlH_4/AlCl_3$ - REDUCTION OF 3-*O*-SUBSTITUTED AND *N*-BENZYLOXYCARBONYL-PROTECTED 4,6-*O*-[2-METHOXYBENZYLIDENE]-α-D-GLUCOSAMINE DERIVATIVES

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ABSTRACT

The reductive cleavage of benzyl 2-benzyloxycarbonylamino-2-deoxy-4,6-*O*-(2-methoxybenzylidene)-α-D-glucopyranoside **2** with $LiAlH_4$-$AlCl_3$ gave the corresponding 4-*O*-(2-methoxybenzyl) ether along with the 6-*O*-ether as expected. When, however, the 3-hydroxyl group was substituted, acetal cleavage was not the main reaction path. With a 3-*O*-allyl or a 3-*O*-methyl group, the unsymmetrical urea derivatives **8** resulted together with the formamido and *N*-methylamino derivatives **9** and **10**, respectively, and no acetal cleavage was observed. Substitution at *O*-3 with a benzyl group allowed the formation of a small amount of 4-*O*-ether along with the formamido and *N*-methylamino derivatives with intact 2-methoxybenzylidene group.

INTRODUCTION

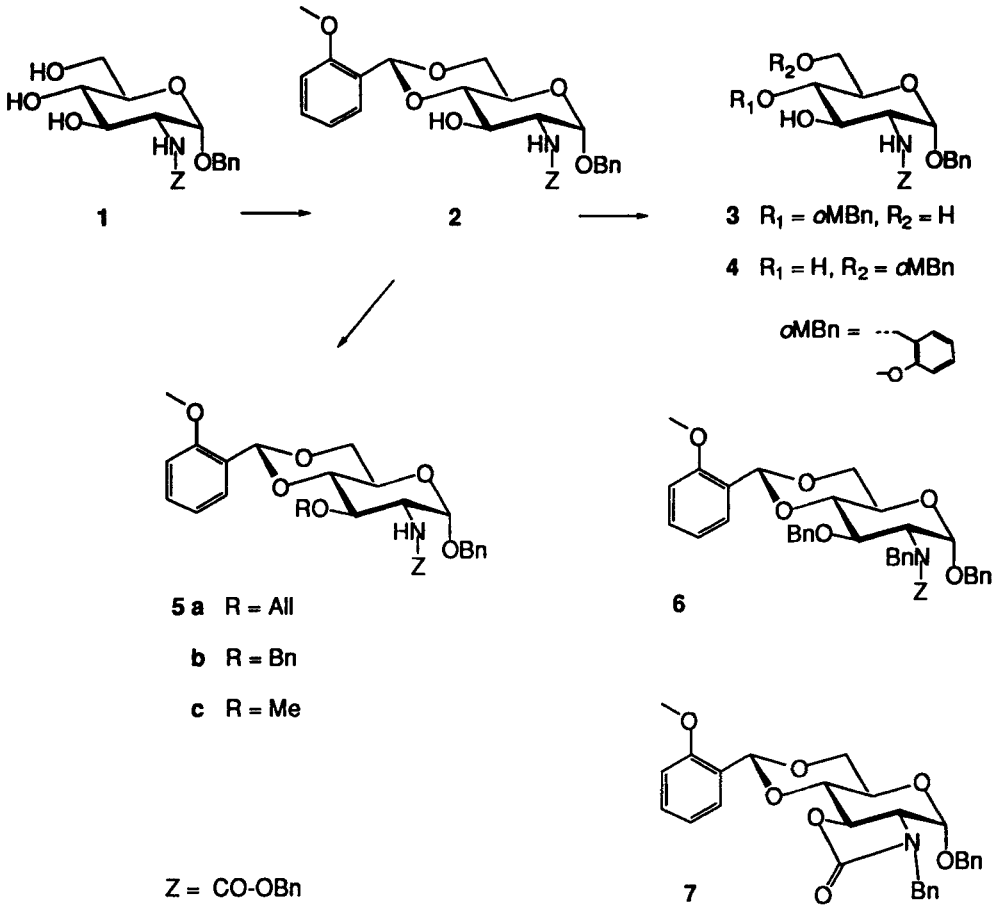
Cyclic acetals are among the most frequently used protective groups in carbohydrate chemistry, and of particular advantage are the various possible follow-up transformations such as the regioselective reductive opening.[3] Depending on the choice of reagent, e.g. a 4,6-cyclic acetal of a hexopyranose

derivative can be opened to afford a primary 6-*O*-ether group[4] or a secondary 4-*O*-ether.[5] For the latter reaction type mainly the lithium aluminum hydride/ aluminum trichloride reagent system has been used. Thus, 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosides gave the 4-*O*-benzyl ether upon treatment with $LiAlH_4$/ $AlCl_3$ exclusively and in good yields.[6] For the stereoselectivity of this reaction, the steric influence of the substituent in 3-position seems to be very important. Lack of this substituent decreased the yield of reduction product as well as the regioselectivity: the analogous reaction of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside furnished the 4-*O*- and 6-*O*-benzyl derivatives in a 3:2 ratio in moderate yields (36 - 45 %).[5,7] With the introduction of an electron-donating methoxy group on the benzylidene acetal the reactivity could be increased to nearly double the yield, but the 3:2 regioselectivity was maintained.[7]

The acetal opening with $LiAlH_4$/ $AlCl_3$ is compatible with a number of other protective groups, and, in particular, *O*-benzyl and *O*-allyl[8,9] ethers and the benzyloxycarbonylamino group in glucosamine derivatives[10] have not been affected. We now describe here our unexpected findings on the action of the $LiAlH_4/AlCl_3$ system on some benzyloxycarbonyl("Z")-protected 4,6-*O*-(2-methoxybenzylidene)-glucosamine derivatives.

RESULTS AND DISCUSSION

For our investigations we have chosen to employ a 2-methoxybenzylidene acetal which would be expected to have, in a reduction with $LiAlH_4/AlCl_3$, an increased reactivity compared to the unsubstituted benzylidene acetal in analogy to previous findings.[7] Starting from the known benzyl 2-benzyloxycarbonylamino-2-deoxy-α-D-glucopyranoside (**1**) we have synthesized, using 2-methoxybenzaldehyde dimethyl acetal prepared in situ,[11] the 4,6-*O*-(2-methoxybenzylidene) acetal **2** in excellent yield (93 %). Reduction of **2** with $LiAlH_4/AlCl_3$ gave the 4-*O*-(2-methoxybenzyl)-ether **3** and the 6-*O*-(2-methoxybenzyl)-ether **4** in moderate yields of 24 % and 33 %, respectively. Notably, the low regioselectivity was inverted to an approximate 2:3 ratio of 4-



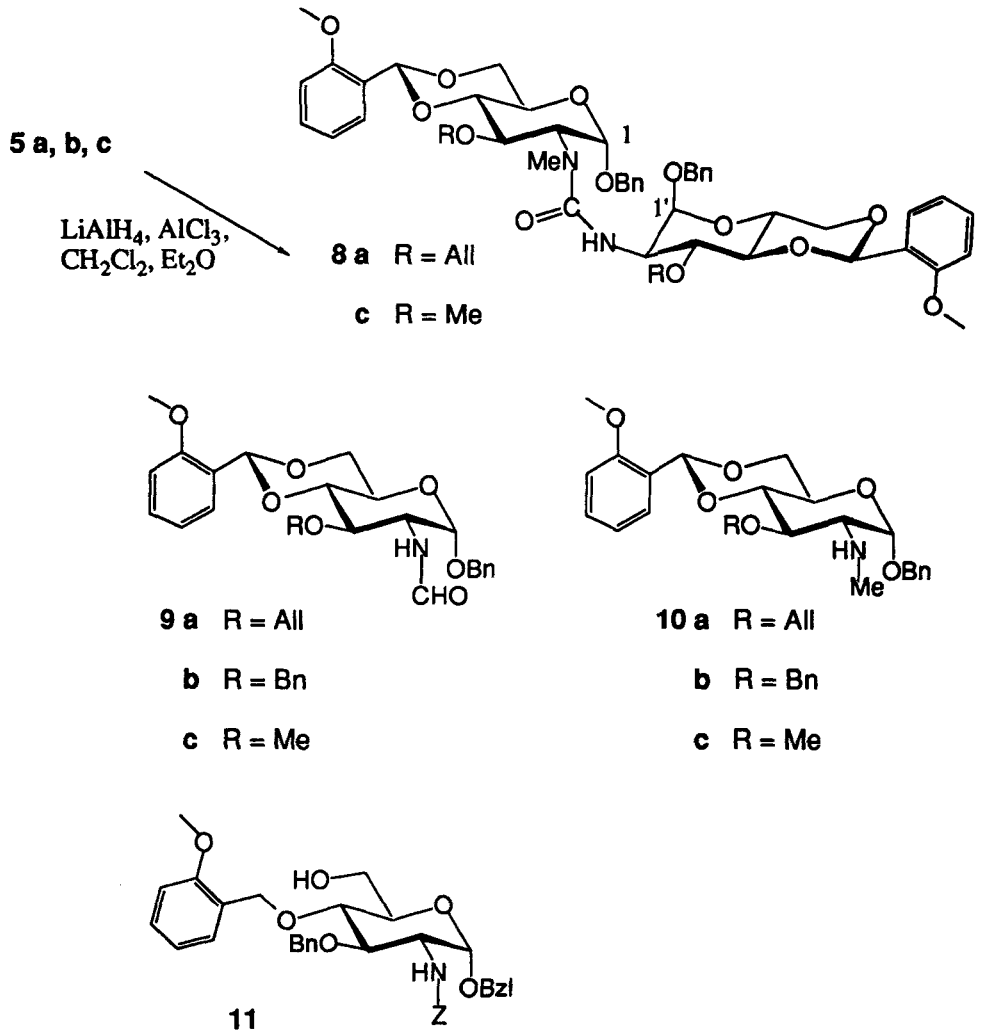
Scheme 1

to 6-substitution. Structural assignments were straightforward with the help of ^1H NMR spectroscopy which showed, in a spectrum recorded in deuterated dimethyl sulfoxide, the primary hydroxyl group of **3** as a triplet and the secondary ones of **4** as doublets.

With the goal to prepare an analogue of the 4-*O*-(2-methoxybenzyl)-ether **3** allylated in the 3-position we have allylated the acetal protected pyranoside **2**. Since with sodium hydride major side reactions were to be expected, the base of choice for alkylation was powdered potassium hydroxide in dioxane.[12] Under these conditions, reaction of **2** with allyl bromide furnished the allyl

ether **5a** as the sole product in excellent yield (91 %). Analogously, reaction of **2** with benzyl bromide gave **5b** in 74 % yield. In this case, as reported for the 4,6-*O*-benzylidene derivative,[12] a small amount (4 %) of additionally *N*-benzylated product **6** was formed as well as the cyclic carbamate **7** (16 %). The ^{1}H NMR spectrum of the latter by-product is characterized by a big geminal coupling constant (J_{gem} = 14.8 Hz) of the *N*-benzyl methylene group. The pyranose ring is flattened as indicated by a slightly smaller $J_{1,2}$ = 2.9 Hz and a bigger $J_{2,3}$ = 11.6 Hz. Reaction of **2** with methyl iodide afforded again only one product, the methyl ether **5c** which could be isolated by crystallization in 64 % yield.

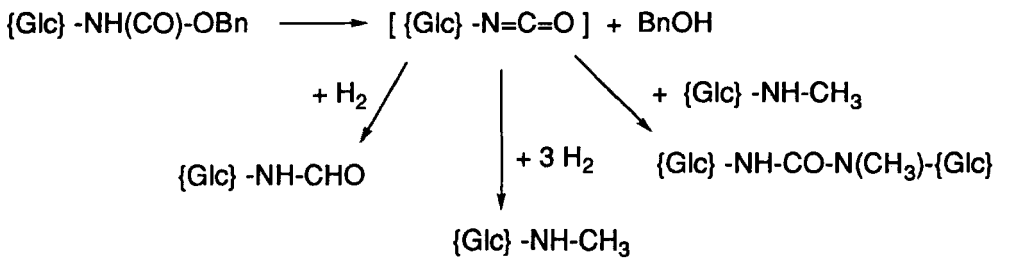
Treatment of the cyclic acetal compound **5a** with $LiAlH_4$/ $AlCl_3$ did not, contrary to our expectations, lead to the expected ether derivatives. Instead, three other products were formed. The major product, isolated in 21 % yield, was the unsymmetrical urea derivative **8a**. The structure of this unusual compound was supported by mass spectrometry (M = 894) and ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum displayed one NH-signal, one *N*-methyl peak, and two sets of similar pyranose protons. In deuterated chloroform as solvent, H-2 appeared as a very broad signal without any fine structure, and H-2 (δ = 4.59 ppm) and H-2' (δ = 4.22 ppm) were the protons with the biggest shift difference when comparing the two pyranose rings. Alternatively, the spectrum was recorded in deuterated dimethyl sulfoxide, where the H-2 signal was less broad and became sharper upon heating the sample to 50 °C. These findings may be regarded as an indication of hindered rotation around one or both of the urea C-N bonds.[13] The compound eluted second was the formamide **9a**, isolated in 6 %, which showed the presence of two rotamers in a 1:1 ratio in the ^{1}H NMR spectrum, one with a small formyl - NH coupling constant $J_{NH,CHO}$ = 1.0 Hz (the quasi *Z* derivative) and a second with a big coupling constant $J_{NH,CHO}$ = 11.8 Hz (the quasi *E* derivative). With a H,H-COSY spectrum the pyranose ring protons of both rotamers could be partially assigned. The third compound was the *N*-methylated derivative **10a** isolated in 4 % yield. In the spectra of all three products the characteristic acetal



Scheme 2

proton at 5.87-5.88 ppm was maintained and proved the existence of the acetal group.

To investigate whether an electronic effect such as the influence of the double bond π-system might be responsible for the changed course of the reaction we subjected the benzylated analogue **5b** to the same reducing reaction conditions. This time some of the expected acetal opening product



Scheme 3

benzyl 3-*O*-benzyl-2-benzyloxycarbonylamino-2-deoxy-4-*O*-[2-methoxy-benzyl]-α-D-glucopyranoside (**11**) could be isolated (15 %), but none of the product 2-methoxybenzylated in position 6; the structural assignment was again clear from the appearance of a triplet for the hydroxyl group in the ^{1}H NMR spectrum in deuterated dimethyl sulfoxide. In this reaction no urea type product could be detected, however, a small amount (4 %) of the formamide **9b** and the *N*-methylated compound **10b** (22 %) were isolated.

Next, we studied the behaviour of the 3-*O*-methylated analogue **5c** to obtain an impression on the steric influence of the 3-*O*-substituent. Surprisingly, again no products from an acetal opening reaction were observed. Instead, as in the case of the 3-*O*-allylated derivative, three products were formed, which were the unsymmetrical urea derivative **8c** isolated in 17 % yield, the formamido derivative **9c** (14 %), and *N*-methylamino derivative **10c** as the major product (25 %). The comparison of results obtained with the 3-*O*-benzyl and the less bulky 3-*O*-methyl and 3-*O*-allyl substituent suggests that it is not the steric demand of the substituent in 3-position which is responsible for the unexpected course of reaction.

To account for the three new products formed in the $LiAlH_4/AlCl_3$ reaction a possible assumption is that a 2-isocyanate derivative was produced as an intermediate by elimination of benzyl alcohol (cf. Scheme 3). Hydrogen transfer would then under the reaction conditions lead to the formamide **9** and the *N*-methylamino derivative **10**.[14] A trapping of the isocyanate with

the *N*-methylamino derivative, which has the more basic nitrogen than the formamide, would lead to the unsymmetrical urea derivative **8**.

An analogous reaction of 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-isocyanato-β-D-glucose with 1,3,4,6-tetra-*O*-acetyl-β-D-glucosamine has been described to give a corresponding symmetrical urea derivative.[15,16] Symmetrical urea derivatives were also obtained as by-products in the activation of glucosamine derivatives with *N,N*-carbonyldiimidazole.[17] Unsymmetrical bis-glycosyl urea derivatives of the type reported here have, to the best of our knowledge, not been reported yet. They may be viewed as new disaccharide mimetics with an alternative interglycosidic linkage.

EXPERIMENTAL

General Procedures. Solvents and reagents were bought from Fluka. Evaporation: *in vacuo*, conducted with a Büchi rotary evaporator. TLC: precoated silica gel 60F-254 plates (Merck), detection by UV light (254 nm) and spraying with a 10% soln of concd sulfuric acid in methanol followed by heating. Specific rotations: Perkin-Elmer Polarimeter 241, measured at 20 °C. MS: API III Sciex, Perkin Elmer (ionspray); MS 9 updated with Finnigan ZAB console, data system SS 200, VG Altrichem (EI, 70 eV). ^{1}H NMR: Bruker AC-250 (250 MHz) or Bruker AM-400 (400 MHz) with Aspect 3000, ARX-400 with ASPECT station 1, standard Bruker pulse programs were applied; chemical shifts in ppm relative to tetramethylsilane as internal standard; in some cases not all assignments are proven but made in analogy.

Benzyl 2-Benzyloxycarbonylamino-2-deoxy-4,6-*O*-(*R*)-(2-methoxybenzylidene)-α-D-glucopyranoside (2). To a soln of 2-methoxybenzaldehyde (4.05 g, 29.8 mmol) in MeOH (6 mL) containing camphor sulfonic acid (CSA) (58 mg, 0.25 mmol) was added trimethyl orthoformate (3.3 mL, 29.8 mmol), and the mixture was stirred under argon at rt for 6 h to allow for the formation of 2-methoxybenzaldehyde dimethyl acetal.[11] This reagent was added to a soln of **1** (10.0 g, 24.8 mmol) in anhydrous DMF (40 mL). The mixture was heated to 85 °C under reduced pressure (ca. 250 mbar) on the

evaporator to remove the methanol formed. After 3 h the reaction was stopped by addition of triethylamine. DMF was co-evaporated with toluene. The residue was purified by chromatography on silica gel using hexane/ ethyl acetate 2:1 as eluent to give colourless crystalline **2** (12.0 g, 93%): $[\alpha]_D$ +108.5 ° (*c* 0.2, dioxane); MS (ionspray): *m/z* 544 (20 %, $[M + Na]^+$), 539 (40 %, $[M + NH_4]^+$), 522 (50 %, $[M + H]^+$), 414 (100 %, $[M + H - PhCH_2OH]^+$); ^1H NMR (250 MHz, $CDCl_3$) δ 7.59 (dd, 1H, aromat), 7.35 - 7.28 (m, 11H, aromat), 6.97 (dd ~ t, 1H, aromat), 6.88 (d, 1H, aromat), 5.94 (s, 1H, CHPh), 5.14, 5.08 (2 d, 2H, J_{gem} = 12.5 Hz, Z-CH_2Ph), 5.11 (br d, 1H, NH), 4.95 (d, 1H, $J_{1,2}$ = 3.0 Hz, H-1), 4.73, 4.49 (2 d, 2H, J_{gem} = 11.8 Hz, CH_2Ph), 4.21 (dd, 1H, $J_{5,6a}$ = 3.9 Hz, $J_{6a,6b}$ = 9.3 Hz, H-6a), 3.98 (ddd ~ dt, 1H, H-2), 3.96 - 3.73 (m, 3H, H-3, H-5, H-6b), 3.83 (s, 3H, OMe), 3.63 (dd ~ t, 1H, H-4), 2.60 (br s, 1H, OH).

Anal. Calcd for $C_{29}H_{31}NO_8$ (521.56): C, 66.78; H, 5.99; N, 2.69. Found: C, 66.79; H, 6.08; N, 2.60.

Benzyl 2-(Benzyloxycarbonylamino)-2-deoxy-4-*O*-(2-methoxybenzyl)-α-D-glucopyranoside (3) and **Benzyl 2-(Benzyloxycarbonylamino)-2-deoxy-6-*O*-(2-methoxybenzyl)-α-D-glucopyranoside (4)**. To a stirred suspension of lithium aluminum hydride (640 mg, 16.9 mmol) in abs dichloromethane (80 mL) and diethyl ether (80 mL) under an argon atmosphere was added the acetal **2** (5.5 g, 10.5 mmol) and a soln of aluminum trichloride (2.25 g, 16.9 mmol) in diethyl ether (160 mL). The reaction mixture was stirred under reflux for 20 h. Cold water was added, and the mixture was filtered through a small pad of filter aid. The organic phase was separated, and the aqueous phase was extracted three times with dichloromethane. The organic phases were washed with water, dried over magnesium sulfate, filtered, and concentrated. The crude product was purified by column chromatography on silica gel using ethyl acetate/ hexane 3:1 as eluent to recover some unreacted **2** (1.26 g, 23 %) and to obtain **3** (1.31 g, 24%) and **4** (1.84 g, 33%) as colourless solids.

Data for **3**: $[\alpha]_D$ +114 ° (*c* 0.2, dioxane); MS (ionspray): *m/z* 546 (35 %, $[M + Na]^+$), 541 (25 %, $[M + NH_4]^+$), 524 (100 %, $[M + H]^+$), 416 (75 %, $[M + H -$

$PhCH_2OH]^+$); ^1H NMR (400 MHz, Me_2SO-d_6) δ 7.37 - 7.22 (m, 13H, aromat, NH), 6.97 - 6.90 (m, 2H, aromat), 5.05, 5.01 (2 d, 2H, $J_{gem} \approx 12$ Hz, Z-CH_2Ph), 4.95 (d, 1H, $J_{3,3\text{-OH}} = 6.9$ Hz, 3-OH), 4.88, 4.58 (2 d, 2H, $J_{gem} = 12.4$ Hz, 4-OCH_2Ph), 4.80 (d, 1H, $J_{1,2} = 3.5$ Hz, H-1), 4.67, 4.44 (2 d, 2H, $J_{gem} = 12.6$ Hz, 1-OCH_2Ph), 4.65 (d, 1H, $J_{6,6\text{-OH}} = 5.6$ Hz, 6-OH), 3.77 (s, 3H, OMe), 3.74 (ddd, 1H, $J_{2,3} = 10.2$ Hz, $J_{3,4} = 8.3$ Hz, H-3), 3.61 (ddd ~ dt, 1H, $J_{5,6a} = 4.2$ Hz, $J_{6a,6b} = 9.5$ Hz, H-6a), 3.53 - 3.48 (m, 2H, H-5, H-6b), 3.50 (ddd, 1H, $J_{2,2\text{-NH}} = 8.0$ Hz, H-2), 3.33 (dd ~ t, 1H, $J_{4,5} \approx 9.7$ Hz, H-4).

Anal. Calcd for $C_{29}H_{33}NO_8$ (523.58): C, 66.53; H, 6.35; N, 2.68. Found: C, 66.16; H, 6.35; N, 2.64.

Data for **4**: $[\alpha]_D$ +101.5 ° (*c* 0.2, dioxane); MS (ionspray): *m/z* 546 (60 %, $[M + Na]^+$), 541 (30 %, $[M + NH_4]^+$), 524 (100 %, $[M + H]^+$), 416 (75 %, $[M + H - PhCH_2OH]^+$); ^1H NMR (400 MHz, Me_2SO-d_6) δ 7.37 - 7.25 (m, 13H, aromat, NH), 6.99 - 6.92 (m, 2H, aromat), 5.13 (d, 1H, $J_{4,4\text{-OH}} = 5.9$ Hz, 4-OH), 5.05 (s, 2H, Z-CH_2Ph), 4.81 (d, 1H, J = 5.8 Hz, 3-OH), 4.80 (d, 1H, $J_{1,2} = 3.5$ Hz, H-1), 4.66, 4.44 (2 d, 2H, $J_{gem} = 12.5$ Hz, 1-OCH_2Ph), 4.52 (s, 2H, 6-OCH_2Ph), 3.77 (s, 3H, OMe), 3.73 (dd, 1H, $J_{5,6a} = 1.0$ Hz, $J_{6a,6b} = 9.2$ Hz, H-6a), 3.67 - 3.59 (m, 2H, H-5, H-6b), 3.55 (ddd, 1H, $J_{3,4} = 8.5$ Hz, H-3), 3.44 (ddd, 1H, $J_{2,3} = 10.7$ Hz, $J_{2,2\text{-NH}} = 8.0$ Hz, H-2), 3.20 (ddd ~ dt, 1H, $J_{4,5} = 9.4$ Hz, H-4).

Anal. Calcd for $C_{29}H_{33}NO_8$ (523.58): C, 66.53; H, 6.35; N, 2.68. Found: C, 66.49; H, 6.48; N, 2.66.

Benzyl 3-*O*-allyl-2-benzyloxycarbonylamino-2-deoxy-4,6-*O*-(*R*)-(2-methoxybenzylidene)-α-D-glucopyranoside (5a). To a soln of acetal **2** (5.01 g, 9.61 mmol) in dry dioxane (24 mL) was added allyl bromide (8.1 mL, 96.1 mmol) and powdered potassium hydroxide (1.44 g) under argon, and the mixture was refluxed for 16 h. Then the reaction mixture was cooled, poured into water, and extracted with dichloromethane. The organic phases were washed twice with water, dried over magnesium sulfate, filtered, and concentrated to give a crude product which was crystallized from dichloromethane/methanol to furnish colourless crystals of **5a** (4.95 g, 91 %): mp 166 - 167 °C; $[\alpha]_D$ +105 ° (*c* 0.2, dioxane); MS (ionspray) *m/z* 584 (25 %, $[M+Na]^+$), 579 (35 %, [M +

$NH_4]^+$), 562.3 (100 %, $[M + H]^+$); ^1H NMR ($CDCl_3$, 250 MHz) δ 7.59 (dd, 1H, aromat), 7.35 - 7.25 (m, 11H, aromat), 6.97 (~t, 1H, aromat), 6.88 (~d, 1H, aromat), 5.87 (s, 1H, CHPh), 5.75 (dddd ~ ddt, 1H, allyl), 5.16 (dddd ~ dq, 1H, $J_{trans} \approx 16$ Hz, allyl), 5.16, 5.06 (2 d, 2H, $J_{gem} = 12.0$ Hz, Z-CH_2Ph), 5.04 (dddd ~ d, 1H, $J_{cis} \approx 11$ Hz, allyl), 5.02 (d, 1H, $J_{2,2\text{-NH}} = 8.0$ Hz, NH), 4.95 (d, 1H, $J_{1,2} = 3.2$ Hz, H-1), 4.72, 4.48 (2 d, 2H, $J_{gem} = 11.7$ Hz, 1-OCH_2Ph), 4.32 (dddd ~ ddt, 1H, $J_{gem} = 13.2$ Hz, allyl), 4.20 (dd, 1H, $J_{5,6eq} = 4.2$ Hz, $J_{6eq,6ax} = 9.5$ Hz, H-6eq), 4.01 (dddd ~ ddt, 1H, allyl), 3.98 (ddd ~ dt, 1H, H-2), 3.88 (ddd ~ dt, 1H, $J_{5,6ax} = 10.0$ Hz, H-5), 3.84 (s, 3H, CH_3), 3.77 (dd ~ t, 1H, H-6ax), 3.68, 3.65 (2 dd ~ t, 2H, H-3, H-4).

Anal. Calcd for $C_{32}H_{35}NO_8$ (561.63): C, 68.43; H, 6.28; N, 2.49. Found: C, 68.30; H, 6.28; N, 2.65.

Benzyl 3-*O*- Benzyl - 2 - benzyloxycarbonylamino - 2-deoxy-4,6-*O* - (*R*) -[2-methoxybenzylidene]-α-D-glucopyranoside (5b). A soln of acetal **2** (1.02 g, 1.95 mmol) in dry dioxane (5 mL) was refluxed for 4.5 h under stirring and argon atmosphere in the presence of benzyl bromide (2.4 mL, 20.19 mmol) and powdered potassium hydroxide (0.29 g). Then the reaction mixture was cooled, poured into water, and extracted with dichloromethane. The organic phases were washed twice with water, dried over magnesium sulfate, filtered, and co-evaporated repeatedly with toluene to remove benzyl bromide. The crude product was purified by column chromatography on silica gel using hexane/ethyl acetate 3:1 as eluents to obtain a small amount of benzyl 3-*O*-benzyl-2- (*N*-benzyl-*N*-benzyloxycarbonylamino) -2-deoxy-4,6-*O*- (*R*) -(2-methoxybenzylidene)-α-D-glucopyranoside (**6**, 54 mg, 4 %) followed by **5b** (880 mg, 74 %) and benzyl 2-[(*N*-benzyl)amino]-2*N*:3-*O*-carbonyl-2-deoxy-4,6-*O*-(*R*)-[2-methoxybenzylidene]-α-D-glucopyranoside (**7**, 197 mg, 16 %).

Data for **5b**: mp 173 - 174 °C; $[\alpha]_D$ +99.5 ° (*c* 0.2, dioxane); MS (EI) *m/z* 611 (3 %, $[M]^+$), 91 (100 %, $[Bn]^+$); ^1H NMR ($CDCl_3$, 250 MHz) δ 7.63 (dd, 1H, aromat), 7.34 - 7.21 (m, 16H, aromat), 7.00 (ddd ~ dt, 1H, aromat), 6.90 (dd ~ d, 1H, aromat), 5.90 (s, 1H, CHPh), 5.14, 5.06 (2 d, 2H, $J_{gem} = 12.2$ Hz, Z-CH_2Ph), 4.95 (d, 1H, H-1), 4.92 (d, 1H, NH), 4.85, 4.59 (2 d, 2H, $J_{gem} = 11.9$ Hz, 3-OCH_2Ph), 4.71, 4.48 (2 d, 2H, $J_{gem} = 11.8$ Hz, 1-OCH_2Ph), 4.21 (dd, 1H, $J_{5,6eq} = 3.9$ Hz, $J_{6eq,6ax}$

= 9.3 Hz, H-6eq), 4.05 (ddd ~ dt, 1H, $J_{1,2}$ = 3.7, H-2), 3.90 (ddd ~ dt, 1H, H-5), 3.83 (s, 3H, CH_3), 3.79 (dd ~ t, 1H, H-6ax), 3.75, 3.72 (dd ~ t, 1H, H-3, H-4).

Anal. Calcd for $C_{36}H_{37}NO_8$ (611.69): C, 70.69; H, 6.10; N, 2.29. Found: C, 70.67; H, 6.04; N, 2.40.

Data for **6**: $[\alpha]_D$ +106 ° (*c* 0.2, dioxane); MS (ionspray) *m/z* 724 (30 %, $[M + Na]^+$), 719 (20 %, $[M + NH_4]^+$), 702 (100 %, $[M + H]^+$), 594 (65 %, $[M + H - BnOH]^+$); ^1H NMR ($CDCl_3$, 250 MHz) δ 7.60 (dd, 1H, aromat), 7.35 - 6.86 (m, 23H, aromat), 5.89 (s, 1H, OCHO), 3.79 (s, 3H, CH_3).

Anal. Calcd for $C_{43}H_{43}NO_8$ (701.82): C, 73.59; H, 6.18; N, 2.00. Found: C, 73.43; H, 6.22; N, 2.08.

Data for **7**: Colourless crystals, mp 157 - 158 °C; $[\alpha]_D$ +81.5 ° (*c* 0.2, dioxane); MS (ionspray) *m/z* 526 (35 %, $[M + Na]^+$), 521 (50 %, $[M + NH_4]^+$), 504 (100 %, $[M + H]^+$); ^1H NMR ($CDCl_3$, 400 MHz; H,H-COSY) δ 7.59 (dd, 1H, aromat), 7.46 - 7.26 (m, 10H, aromat), 7.09 - 7.08 (m, 2H, aromat), 6.96 (t, 1H, aromat), 6.87 (d, 1H, aromat), 5.91 (s, 1H, CHPh), 4.81 (d, 1H, $J_{1,2}$ = 2.9 Hz, H-1), 4.73 (dd, 1H, $J_{3,4}$ = 10.0 Hz, H-3), 4.66, 4.30 (2d, 2H, J_{gem} = 12.0 Hz, 1-OCH_2Ph), 4.54, 4.06 (2d, 2H, J_{gem} = 14.8 Hz, N-CH_2Ph), 4.14 (dd, 1H, H-6eq), 3.96 (dd, 1H, H-4), 3.84 (ddd ~ dt, 1H, H-5), 3.81 (s, 3H, OCH_3), 3.79 (dd ~ t, 1H, H-6ax), 3.27 (dd, 1H, $J_{2,3}$ = 11.6 Hz, H-2).

Anal. Calcd for $C_{29}H_{29}NO_7$ (503.55): C, 69.17; H, 5.81; N, 2.78. Found: C, 69.04; H, 5.87; N, 2.84.

Benzyl 3-*O*-methyl-2-benzyloxycarbonylamino-2-deoxy-4,6-*O*-(*R*)-[2-methoxybenzylidene]-α-D-glucopyranoside (5c). To a solution of acetal **2** (5.0 g, 9.58 mmol) in dry dioxane (20 mL) and of methyl iodide (6.0 mL, 95.8 mmol) was added powdered potassium hydroxide (1.43 g), and the suspension was refluxed for 2.5 h with stirring under an argon atmosphere. The reaction mixture was cooled, poured into cold water, and extracted with dichloromethane. The organic phases were washed twice with water, dried over magnesium sulfate, filtered, and concentrated. The crystalline residue was crystallized from dichloromethane and methanol to obtain colorless

crystals of **5c** (3.29 g, 64 %): mp 154-159 °C; $[\alpha]_D$ +111 ° (*c* 0.2, dioxane); MS (ionspray) *m/z* 553 (44 %, $[M + NH_4]^+$), 536 (100 %, $[M + H]^+$), 428 (56 %, $[M + H - BnOH]^+$); ^1H NMR ($CDCl_3$, 250 MHz) δ 7.59 (dd, 1H, aromat), 7.41 - 7.29 (m, 11H, aromat), 6.96 (t, 1H, aromat), 6.88 (d, 1H, aromat), 5.88 (s, 1H, CHPh), 5.15, 5.08 (2 d, 2H, J_{gem} = 12.0 Hz, Z-CH_2Ph), 5.01 (d, 1H, $J_{2,2\text{-NH}}$ = 9.2 Hz, NH), 4.96 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 4.72, 4.48 (2 d, 2H, J_{gem} = 11.6 Hz, 1-OCH_2Ph), 4.21 (dd, 1H, $J_{5,6eq}$ = 4.0 Hz, $J_{6eq,6ax}$ = 9.5 Hz, H-6eq), 3.96 (ddd ~ dt, 1H, $J_{2,3}$ = 9.6 Hz, H-2), 3.89 (ddd ~ dt, 1H, $J_{4,5} \approx$ 8.7 Hz, H-5), 3.84 (s, 3H, Ph-OCH_3), 3.72 (dd ~ dt, 1H, $J_{5,6ax}$ = 10.0 Hz, H-6ax), 3.69, 3.52 (dd ~ t, 1H, H-3, H-4), 3.48 (s, 3H, 3-OCH_3).

Anal. Calcd for $C_{30}H_{33}NO_8$ (535.59): C, 67.28; H, 6.21; N, 2.62. Found: C, 67.55; H, 6.26; N, 2.50.

1*N*,1'*N*-bis-[Benzyl 3-*O*-Allyl-2-deoxy-4,6-*O*-(*R*)-(2-methoxybenzylidene)-α-D-glucopyranoside-2-yl]-1-methylurea (8a), Benzyl 3-*O*-Allyl-2-deoxy-2-formamido-4,6-*O*-(*R*)-[2-methoxybenzylidene]-α-D-glucopyranoside (9a), and **Benzyl 3-*O*-Allyl-2-deoxy-4,6-*O*-(*R*)-[2-methoxybenzyl]-2-methylamino-α-D-glucopyranoside (10a)**. To a stirred suspension of lithium aluminum hydride (67.6 mg, 1.78 mmol) in distilled dichloromethane (10 mL) and diethyl ether (10 mL) under an argon atmosphere was added the acetal **5a** (1.0 g, 1.78 mmol) and a soln of aluminum trichloride (237 mg, 1.78 mmol) in diethyl ether (20 mL). The reaction mixture was stirred under reflux at 59 °C for 1 d. After addition of cold water, the organic phase was separated. The aqueous phase was extracted three times with dichloromethane, and the organic phases were washed with water twice, dried over magnesium sulfate, filtered, and concentrated. The crude product contained three different compounds which were purified by column chromatography on silica gel using hexane/ethyl acetate 1:1 as eluents to recover unreacted **5a** (290 mg, 29 %) and to obtain pure **8a** (171 mg, 21.4 %), **9a** (50 mg, 6.2 %), and **10a** (31 mg, 3.9 %).

Data for **8a**: Colourless crystals, mp 176-177 °C; $[\alpha]_D$ +146.5 ° (*c* 0.2, dioxane); MS (ionspray) *m/z* 895 (100 %, $[M + H]^+$); ^1H NMR ($CDCl_3$, 400 MHz; H,H-COSY) δ 7.59 (2 dd, 2H, aromat), 7.36 - 7.29 (m, 12H, aromat),

6.97 (t, 2H, aromat), 6.89 (d, 2H, aromat), 5.884, 5.880 (2 s, 2H, CHPh), 5.80, 5.76 (2 dddd ~ ddt, 2H, allyl), 5.21, 5.15 (2 dddd ~ dq, 2H, allyl), 5.02, 4.99 (2 dddd ~ dq, 2H, allyl), 5.00 (2d, 2H, J ≈ 3.5 Hz, H-1, H-1'), 4.75 (br s, 1H, NH), 4.70, 4.69, 4.47, 4.44 (4d, 4H, J_{gem} = 11.7 Hz, 2 CH_2Ph), 4.59 (very br d, 1H, H-2), 4.35, 4.32 (2 dddd ~ ddt, 2H, allyl), 4.22 (ddd, 1H, $J_{2',3'}$ = 9.8 Hz, H-2'), 4.22, 4.20 (2 dd, 2H, H-6eq, H-6eq'), 4.04 (2 dddd ~ ddt, 2H, allyl), 4.01 (dd ~ br t, 1H, H-3), 3.91, 3.88 (2 ddd ~ dt, 2H, H-5, H-5'), 3.84 (s, 6H, OCH_3), 3.84 - 3.68 (m, 5H, H-3', H-4, H-4', H-6ax, H-6ax'), 2.89 (s, 3H, NCH_3); ^1H NMR (Me_2SO-d_6, 400 MHz; H,H-COSY, 323 K) δ 7.45 (m_c, 2H, aromat), 7.38 - 7.27 (m, 12H, aromat), 7.01 (d, 2H, aromat), 6.95 (t, 2H, aromat), 5.99 (d, 1H, $J_{2',2'\text{-NH}}$ = 8.3 Hz, NH), 5.86, 5.84 (2 s, 2H, CHPh), 5.77, 5.76 (2 dddd ~ ddt, 2H, allyl), 5.12, 5.08 (2 dddd ~ dq, 2H, allyl), 4.93 (dddd ~ dq, 2H, allyl), 4.88 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 4.86 (d, 1H, $J_{1',2'}$ = 3.7 Hz, H-1'), 4.70, 4.45 (2d, 2H, J_{gem} = 12.1 Hz, CH_2Ph), 4.69, 4.47 (2d, 2H, J_{gem} = 12.3 Hz, CH_2Ph), 4.36 (broadened dd, 1H, $J_{2,3}$ = 10.4 Hz, H-2), 4.20, 4.11 (2 dddd ~ ddt, 1H, allyl), 4.20, 4.03 (2 dddd ~ ddt, 1H, allyl), 4.11, 4.03 (2 dddd ~ ddt, 2H, allyl), 4.13 (2 dd ~ d, 2H, H-6eq, H-6eq'), 3.98 (m_c, 1H, H-3), 3.93 (ddd, 1H, H-2'), 3.80 (s, 6H, CH_3), 3.82 - 3.61 (m, 7H, H-3', H-4, H-4', H-5, H-5', H-6ax, H-6ax'), 2.89 (s, 3H, NCH_3).

Anal. Calcd for $C_{50}H_{58}N_2O_{13}$ (895.01): C, 67.10; H, 6.53; N, 3.13. Found: C, 67.13; H, 6.49; N, 3.22.

Data for **9a**: Colourless crystals, mp 193 - 196 °C; $[\alpha]_D$ +115.5 ° (*c* 0.2, dioxane); MS (ionspray) *m/z* 478 (18 %, $[M+Na]^+$), 473 (38 %, $[M + NH_4]^+$), 456 (100 %, $[M + H]^+$), 348 (75 %, $[M + H - BnOH]^+$); ^1H NMR ($CDCl_3$, 400 MHz; H,H-COSY) δ 8.21 (d, 0.5H, $J_{NH,CHO}$ = 1.0 Hz, CHO_I), 8.07 (d, 0.5H, $J_{NH,CHO}$ = 11.8 Hz, CHO_{II}), 7.59, 7.58 (2 dd, 1H, aromat), 7.42 - 7.31 (m, 6H, aromat), 6.98, 6.97 (2 ddd ~ dt, 1H, aromat), 6.90, 6.92 (2 d, 1H, aromat), 5.88, 5.87 (2 s, 1H, CHPh), 5.87 - 5.76 (m, 1H, H-allyl), 5.70 (dd ~ t, 0.5H, NH_{II}), 5.69 (dd ~ d, 0.5H, NH_I), 5.21, 5.16, 5.11, 5.09 (4 dddd ~ dq, 2H, allyl), 4.98 (d, 0.5H, $J_{1,2}$ = 3.8 Hz, $H\text{-}1_I$), 4.95 (d, 0.5H, $J_{1,2}$ = 3.8 Hz, $H\text{-}1_{II}$), 4.74, 4.73, 4.52, 4.48 (4 d, 2H, J_{gem} = 11.6 Hz, CH_2Ph), 4.36 (ddd ~ dt, 0.5H, $H\text{-}2_I$), 4.35, 4.32 (2 dddd ~ ddt, 1H, allyl), 4.22 (dd, 1H, $J_{5,6eq}$ = 4.8 Hz, $J_{6eq,6ax}$ = 10.1 Hz, H-6eq), 4.04, 4.03 (2 dddd ~ ddt, 1H,

allyl), 3.93 - 3.87 (m, 1H, H-5), 3.845, 3.840 (2 s, 3H, CH_3), 3.79 (dd ~ t, 1H, H-6ax), 3.72, 3.63 (2 m_c, 4H, (H-3/H-4)$_I$, (H-3/H-4)$_{II}$), 3.48 (m_c, 0.5H, H-2$_{II}$).

Anal. Calcd for $C_{25}H_{29}NO_7$ (455.51): C, 65.92; H, 6.42; N, 3.08. Found: C, 65.84; H, 6.51; N, 3.16.

Data for **10a**: Colourless solid, $[\alpha]_D$ +100 ° (*c* 0.2, dioxane); MS (ionspray) *m/z* 442 (100 %, $[M + H]^+$); ^{1}H NMR ($CDCl_3$, 400 MHz; H,H-COSY) δ 7.60 (m_c, 1H, aromat), 7.42 - 7.30 (m, 5H, aromat), 6.98 (dd ~ t, 1H, aromat), 6.88 (d, 1H, aromat), 5.90 (m_c, 1H, allyl), 5.87 (s, 1H, CHPh), 5.19, 5.09 (2 dddd ~ dq, 2H, allyl), 4.96 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 4.75, 4.57 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.38 (dddd ~ ddt, 1H, allyl), 4.18 (dd, 1H, $J_{5,6eq}$ = 4.8 Hz, $J_{6eq,6ax}$ = 10.0 Hz, H-6eq), 4.12 (dddd ~ ddt, 1H, allyl), 3.88 (ddd ~ dt, 1H, H-5), 3.84 (s, 3H, OCH_3), 3.76 (dd ~ t, 1H, $J_{3,4}$ = 8.9 Hz, H-3), 3.75 (dd ~t, 1H, $J_{5,6ax}$ = 10.4 Hz, H-6ax), 3.65 (dd ~ t, 1H, $J_{4,5}$ = 9.5 Hz, H-4), 2.71 (ddd ~ dd, 1H, $J_{2,3}$ = 9.8 Hz, H-2), 2.37 (s, 3H, NCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz; H,C-COSY) δ 134.97 (-CH=), 129.86 - 126.52 (aromat), 116.56 (=CH_2), 110.31 (aromat), 96.74 (CHPh), 96.54 (C-1), 83.24 (C-4), 77.37 (C-3), 73.36 (OCH_2-,allyl), 69.15 (CH_2Ph), 69.03 (C-6), 62.98 (C-2), 62.64 (C-5), 55.27 (OCH_3), 34.02 (NCH_3).

Anal. Calcd for $C_{25}H_{31}NO_6$ (441.52): C, 68.01; H, 7.08; N, 3.17. Found: C, 67.89; H, 7.11; N, 3.17.

Benzyl 3-*O*-Benzyl-2-benzyloxycarbonylamino-2-deoxy-4-*O*-[2-methoxybenzyl]-α-D-glucopyranoside (11), Benzyl 3-*O*-Benzyl-2-deoxy-2-formamido-4,6-*O*-(*R*)-[2-methoxybenzylidene]-α-D-glucopyranoside (9b) and **Benzyl 3-*O*-benzyl-2-deoxy-2-methylamino-4,6-*O*-(*R*)-[2-methoxybenzylidene]-α-D-glucopyranoside (10b)**. To a stirred suspension of lithium aluminum hydride (58 mg, 1.52 mmol) in distilled dichloromethane (10 mL) and diethyl ether (10 mL) under an argon atmosphere was added the acetal **5b** (930 mg, 1.52 mmol) and a soln of aluminum trichloride (203 mg, 1.52 mmol) in diethyl ether (20 mL). The reaction mixture was stirred under reflux at 53 °C for 1 d. After addition of cold water the reaction mixture was worked up as described above. The crude product contained three different compounds which were purified by column chromatography on silica gel using hexane/

ethyl acetate 3:2 and 1:1 as eluents to recover unreacted **5b** (195 mg, 21 %) and to obtain **11** (136 mg, 14.6 %), **9b** (30 mg, 3.9 %), and **10c** (162 mg, 21.7 %).

Data for **11**: Colourless crystals, mp 150 - 152 °C; $[\alpha]_D$ +88.5 ° (*c* 0.2, dioxane); MS (ionspray) *m/z* 636 (14 %, $[M+Na]^+$), 631 (100 %, $[M + NH_4]^+$), 614 (33 %, $[M + H]^+$); ^1H NMR ($CDCl_3$, 250 MHz) δ 7.32 - 7.26 (m, 17H, aromat), 6.90 - 6.80 (m, 2H, aromat), 5.12, 5.04 (2 d, 2H, J = 12.2 Hz, Z-CH_2Ph), 4.89 (d, 1H, H-1), 4.89, 4.88, 4.72, 4.67 (4 d, 4H, CH_2Ph), 4.83 (d, 1H, NH), 4.66, 4.43 (2 d, 2H, J_{gem} = 11.6 Hz, CH_2Ph), 3.99 (ddd ~ dt, 1H, $J_{1,2}$ = 3.4 Hz, H-2), 3.82 (s, 3H, CH_3), 3.79 - 3.58 (m, 5H, H-3, H-4, H-5, 2 H-6); ^1H NMR (Me_2SO-d_6, 400 MHz; H,H-COSY) δ 7.65 (d, 1H, $J_{2,2\text{-NH}}$ = 9.1 Hz, NH), 7.43 (d, 2H, aromat), 7.36 - 7.17 (m, 16H, aromat), 6.97 (d, 1H, aromat), 6.92 (t, 1H, aromat), 5.09, 5.01 (2d, 2H, J_{gem} = 12.7 Hz, Z-CH_2Ph), 4.81 (d, 1H, H-1), 4.79, 4.61 (2d, 2H, J_{gem} = 11.6 Hz, CH_2Ph), 4.75, 4.68 (2d, 2H, J_{gem} = 10.8 Hz, CH_2Ph), 4.73 (dd ~ t, 1H, $J_{6,6\text{-OH}}$ = 5.6 Hz, 6-OH), 4.70, 4.48 (2d, 2H, J_{gem} = 12.4 Hz, CH_2Ph), 3.78 (dd, 1H, $J_{2,3}$ = 10.5 Hz, $J_{3,4}$ = 8.6 Hz, H-3), 3.74 (s, 3H, CH_3), 3.67 (ddd ~ dt, 1H, $J_{1,2}$ = 3.6 Hz, H-2), 3.66 (dd, 1H, H-6a), 3.61 - 3.54 (m, 2H, H-5, H-6), 3.49 (dd ~ t, 1H, $J_{4,5}$ = 9.2 Hz, H-4).

Anal. Calcd for $C_{36}H_{39}NO_8$ (613.71): C, 70.46; H, 6.41; N, 2.28. Found: C, 70.40; H, 6.35; N, 2.40.

Data for **9b**: Colourless crystals, mp 188 - 190 °C; $[\alpha]_D$ +93.9 ° (*c* 0.15, dioxane); MS (ionspray) *m/z* 523 (34 % $[M + NH_4]^+$), 506 (75 %, $[M + H]^+$); ^1H NMR ($CDCl_3$, 400 MHz; H,H-COSY, data for rotamers I and II) δ 8.12 (d, 0.5H, $J_{NH,CHO} \leq 1$ Hz, CHO_I), 8.07 (d, 0.5H, $J_{NH,CHO}$ = 11.8 Hz, CHO_{II}), 7.65 - 7.61 (m, 1H, aromat), 7.38 - 7.24 (m, 11H, aromat), 7.00 (t, 1H, aromat), 6.91, 6.89 (2 d, 1H, aromat), 5.91 (s, 1H, CHPh), 5.70 (dd ~ t, 0.5H, $J_{2,2\text{-NH}}$ = 10.2 Hz, NH_{II}), 5.52 (dd ~ d, 0.5H, $J_{2,2\text{-NH}}$ = 9.4 Hz, NH_I), 4.95 (d, 0.5H, $J_{1,2}$ = 3.6 Hz, H-1_I), 4.94 (d, 0.5H, $J_{1,2}$ = 3.4 Hz, H-1_{II}), 4.88, 4.58 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.84, 4.58 (2 d, 2H, J_{gem} = 10.9 Hz, CH_2Ph), 4.74, 4.72, 4.52, 4.46 (4 d, 4H, J_{gem} ≈ 11.6 Hz, CH_2Ph), 4.39 (ddd ~ dt, 0.5H, $J_{2,3}$ = 9.6 Hz, H-2_I), 4.24, 4.23 (2 dd, 1H, H-$6eq_{I+II}$), 3.92, 3,89 (2 ddd ~ dt, 1H, H-5_{I+II}), 3.85, 3.83 (2 s, 3H, $CH_{3\,I+II}$), 3.88 - 3.68 (m, 3H, H-3, H-4, H-6ax), 3.57 - 3.49 (m_c, 0.5H, H-2_{II}).

Anal. Calcd for $C_{29}H_{31}NO_7$ (505.57): C, 68.90; H, 6.18; N, 2.77. Found: C, 68.81; H, 6.21; N, 2.79.

Data for **10b**: Colourless solid, $[\alpha]_D$ +90 ° (*c* 0.2, dioxane); MS (ionspray) *m/z* 492 (100 %, $[M + H]^+$); ^1H NMR ($CDCl_3$, 400 MHz; H,H-COSY) δ 7.63 (dd, 1H, aromat), 7.40 - 7.25 (m, H, aromat), 6.99 (dd ~ t, 1H, aromat), 6.89 (d, 1H, aromat), 5.90 (s, 1H, CHPh), 4.96 (d, 1H, H-1), 4.94, 4.64 (2 d, 2H, J_{gem} = 11.1 Hz, CH_2Ph), 4.76, 4.59 (2 d, 2H, J_{gem} = 12.0 Hz, CH_2Ph), 4.20 (dd, 1H, $J_{5,6eq}$ = 4.9 Hz, $J_{6eq,6ax}$ = 10.1 Hz, H-6eq), 3.91 (ddd ~ dt, 1H, H-5), 3.89 (dd ~ t, 1H, $J_{3,4}$ = 9.0 Hz, H-3), 3.83 (s, 3H, CH_3), 3.77 (dd ~ t, 1H, $J_{5,6ax}$ = 10.3 Hz, H-6), 3.73 (dd ~t, 1H, $J_{4,5}$ = 9.5 Hz, H-4), 2.75 (dd, 1H, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 9.8 Hz, H-2), 2.36 (s, 3H, NCH_3).

Anal. Calcd for $C_{29}H_{33}NO_6$ (491.58): C, 70.86; H, 6.77; N, 2.85. Found: C, 70.61; H, 6.79; N, 2.93.

1*N*,1'*N*-bis-[Benzyl 3-*O*-Methyl-2-deoxy-4,6-*O*-(*R*)-(2-methoxybenzylidene)-α-D-glucopyranoside-2-yl]-1-methylurea (8c), Benzyl 2-deoxy-2-formamido-4,6-*O*-(*R*)-[2-methoxybenzylidene]-3-*O*-methyl-α-D-glucopyranoside (9c), and **Benzyl 2-deoxy-4,6-*O*-(*R*)-[2-methoxybenzylidene]-3-*O*-methyl-2-methylamino-α-D-glucopyranoside (10c)**. To a stirred suspension of lithium aluminum hydride (69 mg, 1.83 mmol) in distilled dichloromethane (10 mL) and diethyl ether (10 mL) under an argon atmosphere was added the acetal **5c** (980 mg, 1.83 mmol) and a soln of aluminum trichloride (244 mg, 1.83 mmol) in diethyl ether (20 mL). The reaction mixture was stirred under reflux at 60 °C for 1 d. After addition of cold water and phase separation, the aqueous phase was extracted three times with dichloromethane. The organic phases were washed twice, dried over magnesium sulfate, filtered, and concentrated. The crude product was purified by column chromatography on silica gel using hexane/acetone 1:1 as eluent to obtain unreacted **5c** (104 mg, 11 %) and **8c** (255 mg, 16.5 %), **9c** (109 mg, 13.9 %), and **10c** (189 mg, 24.9 %).

Data for **8c**: Colourless crystals, mp 160-161; $[\alpha]_D$ +139.5 ° (*c* 0.2, dioxane); MS (ionspray) *m/z* 865 (12 %, $[M + Na]^+$), 843 (100 %, $[M + H]^+$); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.61 - 7.58 (m, 2H, aromat), 7.36 - 7.29 (m, 12H, aromat), 6.96 (dd ~ t, 2H, aromat), 6.88 (d, 2H, aromat), 5.90 (s, 2H, CHPh), 5.01, 5.00 (2d,

2H, H-1, H-1'), 4.77 (br s, 1H, NH), 4.71, 4.47, 4.70, 4.46 (4 d, 4H, J_{gem} = 11.5 Hz, CH_2Ph), 4.59 (br, 1H, H-2), 4.22 (dd, 2H, $J_{5,6eq}$ = 4.6 Hz, $J_{6eq,6ax}$ = 10.0 Hz, H-6eq, H-6eq'), 4.18 (ddd, 1H, $J_{1',2'}$ = 3.8 Hz, $J_{2',3'}$ = 10.2 Hz, $J_{2',2'\text{-NH}}$ = 10.2 Hz, H-2'), 3.95 - 3.88 (m, 3H, H-5, H-5', H-3), 3.85, 3.84 (2s, 6H, OCH_3), 3.84 - 3.58 (m, 5H, H-3', H-4, H-4', H-6ax, H-6ax'), 2.92 (s, 3H, NCH_3).

Anal. Calcd for $C_{46}H_{54}N_2O_{13}$ (842.94): C, 65.55; H, 6.46; N, 3.32. Found: C, 65.55; H, 6.52; N, 3.28.

Data for **9c**: Colourless crystals, mp 192 - 193 °C; $[\alpha]_D$ +108.5 ° (*c* 0.2, dioxane); MS (ionspray) *m/z* 447 (27 %, $[M + NH_4]^+$), 430 (100 %, $[M + H]^+$); ^1H NMR ($CDCl_3$, 400 MHz) δ 8.21 (d, 0.5H, $J_{NH,CHO}$ = 0.9 Hz, CHO_I), 8.05 (d, 0.5H, $J_{NH,CHO}$ = 11.8 Hz, CHO_{II}), 7.60 - 7.58 (m, 1H, aromat), 7.42 - 7.30 (m, 6H, aromat), 6.98, 6.97 (2 ddd ~ dt, 1H, aromat), 6.88 (d, 1H, aromat), 5.89, 5.88 (2 s, 1H, OCHPh), 5.74 (dd ~ br d, 0.5H, NH_I), 5.73 (dd ~ t, 0.5H, NH_{II}), 4.97 (d, 0.5H, $J_{1,2}$ = 3.8 Hz, H-1_I), 4.94 (d, 0.5H, $J_{1,2}$ = 3.4 Hz, H-1_{II}), 4.74, 4.74, 4.51, 4.48 (4d, 4H, J_{gem} = 11.3 Hz, CH_2Ph), 4.34 (ddd ~ dt, 0.5H, H-2_I), 4.22, 4.21 (2 dd, 1H, $J_{5,6eq}$ = 4.7 Hz, $J_{6eq,6ax}$ = 10.1 Hz, H-6eq), 3.91, 3.90 (2 ddd ~ dt, 1H, H-5), 3.85, 3.84 (2 s, 3H, $PhOCH_3$), 3.80 (dd ~ t, 1H, H-6ax), 3.73, 3.60, 3.59, 3.47 (4 dd ~ t, 2H), 3.51, 3.49 (2 s, 3H, OCH_3), 3.47 - 3.40 (m, 0.5H, H-2_{II}).

Anal. Calcd for $C_{23}H_{27}NO_7$ (429.47): C, 64.32; H, 6.34; N, 3.26. Found: C, 64.12; H, 6.36; N, 3.32.

Data for **10c**: Colourless solid, $[\alpha]_D$ +106 ° (*c* 0.1, dioxane); MS (ionspray) *m/z* 416 (100 %, $[M + H]^+$); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.61 (dd, 1H, aromat), 7.39 - 7.30 (m, 6H, aromat), 6.97 (dd ~ t, 1H, aromat), 6.88 (d, 1H, aromat), 5.87 (s, 1H, OCHPh), 4.97 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 4.75, 4.56 (2 d, 2H, J_{gem} = 11.9 Hz, CH_2Ph), 4.19 (dd, 1H, $J_{5,6eq}$ = 4.8 Hz, $J_{6eq,6ax}$ = 10.0 Hz, H-6eq), 3.88 (ddd ~ dt, 1H, $J_{4,5}$ = 9.0 Hz, H-5), 3.84 (s, 3H, OCH_3), 3.75 (dd ~t, 1H, $J_{5,6ax}$ = 10.4 Hz, H-6ax), 3.63 (dd ~ t, 1H, H-4), 3.56 (dd ~ t, 1H, $J_{3,4}$ = 8.9 Hz, H-3), 3.56 (s, 3H, OCH_3), 2.65 (dd, 1H, $J_{2,3}$ = 9.6 Hz, H-2), 2.36 (s, 3H, NCH_3).

Anal. Calcd for $C_{23}H_{29}NO_6$ (415.49): C, 66.49; H, 7.04; N, 3.37. Found: C, 66.21; H, 7.04; N, 3.35.

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