Pergamon

Tetrahedron 55 (1999) 687–698

TETRAHEDRON

Synthetic Studies of Moenomycin A Disaccharide Analogues. Protection of the Anomeric Centre with Long-Chain Protective Groups

Dirk Weigelt[a], Ralf Krähmer[a], Kathrin Brüschke[a], Lothar Hennig[a], Matthias Findeisen[a], Dietrich Müller[b], Peter Welzel[a*]

[a] Fakultät für Chemie und Mineralogie der Universität Leipzig, Talstr. 35, D-04103 Leipzig (Germany)

[b] Fakultät für Chemie der Ruhr-Universität, D-44780 Bochum (Germany)

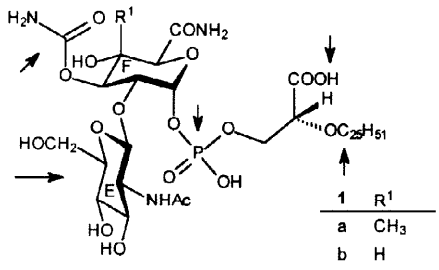
Received 4 October 1998; accepted 6 November 1998

Abstract - Two new C_9 protecting groups for the anomeric position of carbohydrates are reported. Methods both for their introduction and removal are described. The C_9-protected compounds are much less polar than the corresponding allyl protected analogues. The new protecting group chemistry has been used to prepare compound **17** *en route* to a disaccharide analogue of the antibiotic moenomycin A.

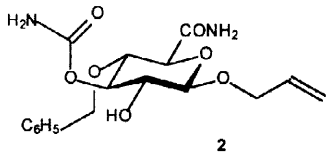
Key words: Carbohydrates, protecting groups, antibiotics

Introduction

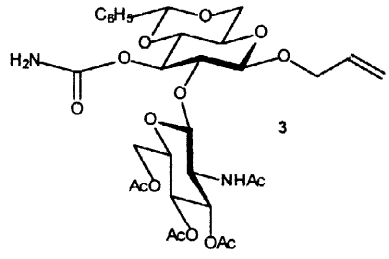
The moenomycin-type antibiotics inhibit the enzyme that catalyzes the so-called transglycosylation step in peptidoglycan biosynthesis. Di- and trisaccharide analogues obtained both by degradation of the naturally occurring antibiotics and by synthesis have contributed to a great extend to the understanding of structure-activity relationships in this class of compounds and have lead to a first mechanistic picture of the mode of action.[1]



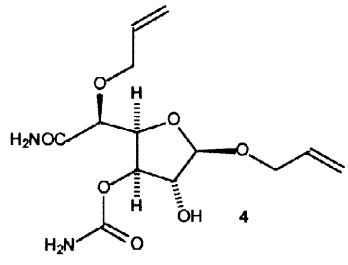
At least in the van Heijenoort *in-vitro* test system disaccharide analogue **1a** caused full inhibition of the enzyme at a concentration of 1 μg/ml (10^{-6} mol/l).[2] Arrows in formula **1a** indicate modifications that lead to inactive compounds.[3] However, until now the importance of the methyl group at C-4 of the moenuroncic acid moiety (F in formula **1**) for the transglycosylase inhibition potency remained unknown. Several attempts that have been undertaken to synthesize compound **1b** and to study its activity in the test system failed.[4,5] The main reason for this lack of success was the low solubility of the anticipated synthetic intermediates **2**, **3**, and **4** in suitable solvents which prevented their use in subsequent transformations.



2



3



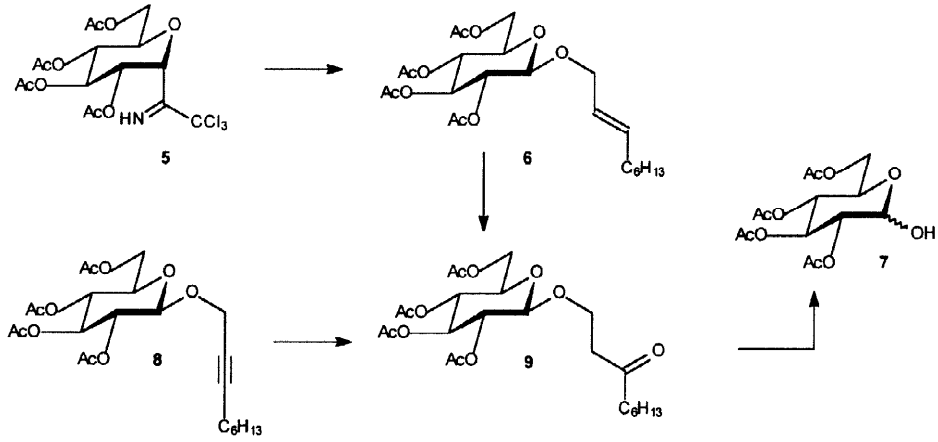
4

0040-4020/99/$ - see front matter
PII: S0040-4020(98)01062-X

This troublesome behaviour is probably caused by the amide and urethane functions in **2**, **3**, and **4**. We have now examined a number of options to overcome the disappointing limitations brought about by the solubility behaviour of compounds **2**, **3**, and **4**. One idea was to use for the anomeric position of unit F instead of the allyl protecting group a more lipophilic one. This structural change was hoped to render the synthetic intermediates less polar and, furthermore, would allow to purify them by reversed-phase chromatography. We decided to replace the allyl protecting group by an appropriate C_9 residue.

Model experiments

The nonenyl glycoside **6** was prepared using the Schmidt procedure (74%).[6] **8** was simply obtained from pentaacetyl-D-glucose on BF_3•OEt_2-mediated reaction[7] with 2-nonyn-1-ol[8] in 69% yield.

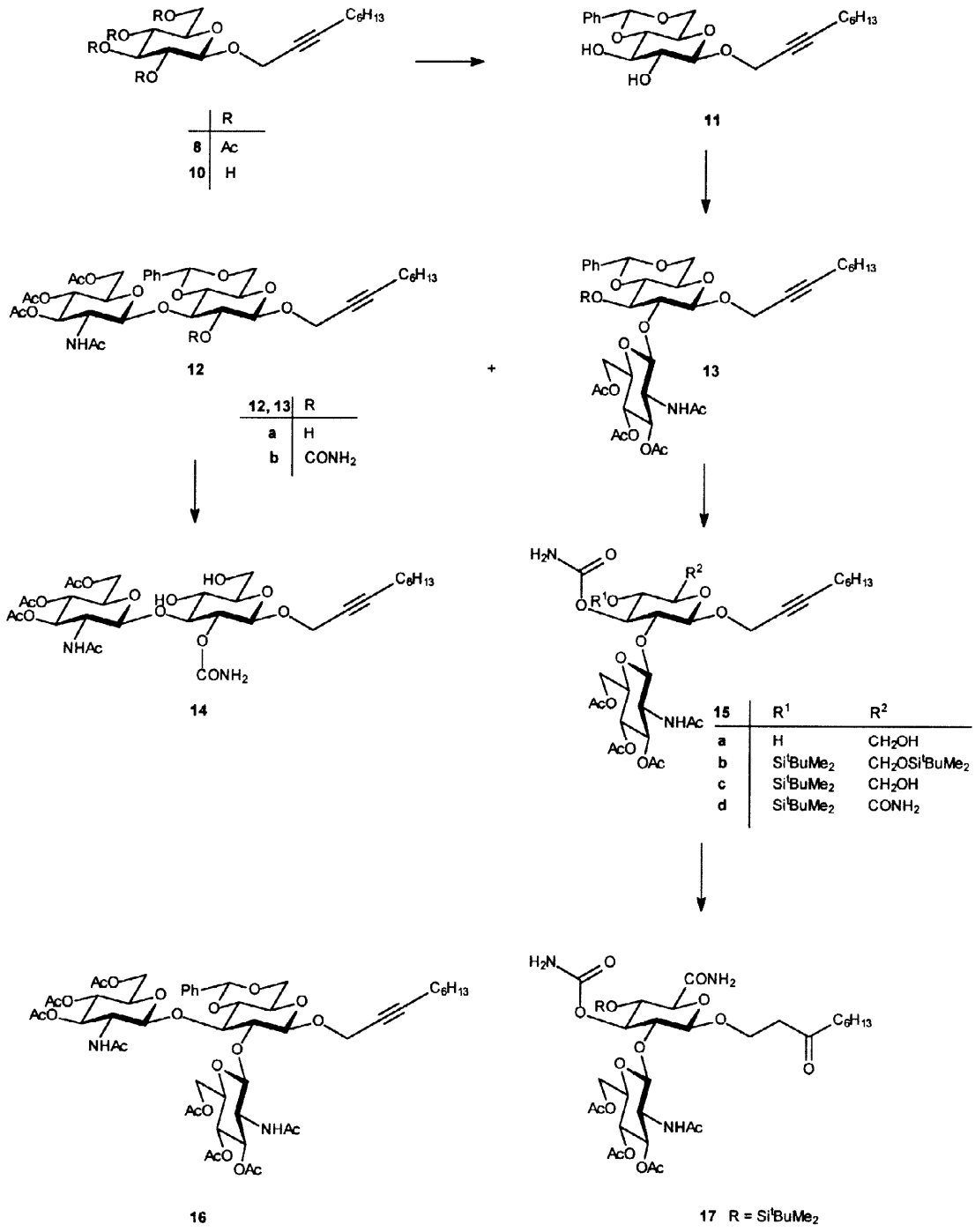


Removal of the C_9 protective groups was achieved via ß-alkoxy ketone **9**. Treatment of **6** with $PdCl_2$ (3 equiv) in 6:1 DMF-water furnished **9** in 97% yield. Only a trace of the isomeric α-alkoxy-ketone (formula not shown) could be detected. Water addition to **8** was accomplished by treatment with 5 mol% Hg^{2+} (from $HgSO_4$)[9] in 5:1 methanol-water and gave **9** in 69 % yield along with 3% of the isomeric ketone and 15 % of the target compound **7**. Finally, eliminative deprotection of **9** occurred on reaction with DBU (5 equiv, CH_2Cl_2, 20°C, 30 min)[10] and gave **7** in 82% yield. This part of the work was reported in preliminary form.[11] In a recent publication Mereyala and Gurrrala used the same type of chemistry to prepare simple propargyl and allyl glycosides.[12]

Synthesis of the E-F part of 1b

The value of the new method was tested in the synthesis of disaccharide **17**. **8** was converted to **11** via **10** by (i) Zemplén hydrolysis[13] and (ii) acetal formation with $PhCH(OCH_3)_2$ in DMF[14] (89% overall yield). For the introduction of unit E the oxazoline method was used.[15,16] A mixture of the two isomers **12a** and **13a** was formed alongside with small amounts of trisaccharide **16**. Whereas **12a** and **13a** could not be separated at this stage, **16** was removed by reversed-phase chromatography demonstrating one of the hoped for merits of the new protecting group. **12a** and **13a** were jointly converted to urethanes **12b** and **13b** by treatment with (i) trichloroacetyl isocyanate and (ii) zinc dust in methanol.[17] In the reaction of **12a** and **13a** with trichloroacetyl isocyanate the advantages provided by the new protective group were again obvious. Whereas in related cases for solubility reasons the diol substrates first had to be converted to the corresponding tributylstannyl ether[15] in the present case the reaction could nicely be directly performed in methylene chloride solution. After acid hydrolysis (2:1 ethanol-water, cation exchange resin[18]) from the mixture of **12b** and **13b** the desired 1→2-linked disaccharide **15a** (31% overall yield) and the corresponding 1→3 isomer **14** (48% overall yield) were obtained. Chromatographic separation could easily be performed at this stage. The two

free OH groups in **15a** were silylated (^{t}BuMe$_2$SiCl, imidazole, DMF[19]) in quantitaive yield and the silyl ether in the 6-position was selectively cleaved by acid hydrolysis (1:1:3 THF-water-acetic acid, 20°C, 20 h, 86%).[20] Two-stage oxidation with (i) *o*-iodoxybenzoic acid in DMSO[21], (ii) $NaClO_2$[22] and subsequent amide formation using Staab's procedure[23] provided **15d** in 62% overall yield.[24] Then, water addition to **15d** as described above furnished **17** in 58% yield. In preliminary experiments it was found that the protecting group could be removed under the conditions reported above but the reaction was much more complicated than in the model case, presumably due to the presence of the uronamide function.[25] At this time another and more efficient synthetic approach to compound **1b** could be completed (see the accompanying paper) and we stopped, therefore, experiments aimed at optimising the deprotection of **17**.



In any case, the new protective groups can readily be introduced and their removal has been achieved in the model series with reasonable yields. Furthermore, in keeping with our expectations all compounds encountered in the present work were nicely soluble in CH_2Cl_2[26] in contrast to their allyl analogues investigated previously. The lipophilic anker has been demonstrated to be useful for reversed-phase separations.

EXPERIMENTAL

General

Organic solvent evaporations were performed *in vacuo* at 40 °C using a rotatory evaporator, water was removed by lyophilization (Leybold-Heraeus GT2 or Christ Alpha 1-2). Solvents were purified by standard procedures. If necessary, solvents were degassed by sonication (Bandelin, Sonorex Super RK 106).- O_2- or moisture-sensitive reactions were performed in oven-dried glassware under a positive pressure of argon. Liquids and solutions were transferred by syringe. Small-scale reactions were performed in Wheaton serum bottles sealed with aluminium caps with open top Teflon-faced septum (Aldrich).- The instrumentation used was: NMR: Gemini 200 and Gemini 2000 (Varian, ^{1}H NMR 200 MHz, ^{13}C NMR 50.3 MHz), Gemini 300 (Varian, ^{1}H NMR 300 MHz, ^{13}C NMR 75.5 MHz, Unity 400 (Varian, ^{1}H NMR 400 MHz, ^{13}C NMR 100.6 MHz), chemical shifts are given in δ values; IR Specord M80 grating spectrophotometer (Carl Zeiss Jena) and FT-IR spectrometer ATI Mattson, Genesis series; FAB MS: VG AUTOSPEC (matrix: lactic acid or 3-nitrobenzyl alcohol), two molecular masses are always communicated, the first was calculated using the International Atomic Masses, the second refers to ^{12}C, ^{1}H, ^{16}O, ^{14}N, (mono-isotopic masses), carbon and proton numbering in the subunits (see NMR data) as well as naming of the MS fragments follows the moenomycin nomenclature[3] (see formula); analytical TLC: Merck precoated silica gel 60 F_{254} plates (0.2 mm), spots were identified under a UV lamp (λ = 254 nm and λ = 366 nm) and by dipping into a 2.22 mol/L H_2SO_4 solution containing $Ce(SO_4)_2x4H_2O$ (10.0 g/L) and $H_3[PO_4(Mo_3O_9)_4]xH_2O$ (25.0 g/L)[27] and subsequent heating at 140°C, flash chromatography (FC)[28]: silica gel (ICN Biomedical Silica 32-63 μm), Optima pump (Model 10007); medium-pressure liquid chromatography (MPLC): silica gel 20-40 μm (Merck), 35-70 μm (Amicon) or 50 μm (Fa. Grace), the samples were applied to a precolumn (3-5 g Kieselgel, 63-100 μm) and eluted at 1-2·10^5 Pa using a dosage pump (Promint Dosiertechnik, Heidelberg or Kronlab Chromatographie und Labortechnik, Sinsheim).

(E)-2-Nonen-1-yl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (6)

Freshly distilled $BF_3{\cdot}Et_2O$ (29 μL, 0.23 mmol) was added to a cooled (-78°C) solution of (2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-trichloroacetimidate (1.12 g, 2.27 mmol) in dry CH_2Cl_2 (15 mL). After 10 min (E)-2-nonen-1-ol (0.38 mL, 2.3 mmol) was added and the mixture was stirred at -78°C for 3 h. Then the solution was allowed to warm to -10°C and was stirred at this temperature for 20 h. $NaHCO_3$ (200 mg) was added and the mixture was stirred for 30 min. After filtration the solvent was evaporated. The residue was purified by LC (hexanes-ethyl acetate 4:1) to give **6** (1.05 g, 2.21 mmol, 97 %).- ^{1}H NMR (400 MHz, $CDCl_3$): *Unit F:* 1-H^F d 4.54; 2-H^F dd 4.98; 3-H^F dd 5.18; 4-H^F dd 5.06; 5-H^F ddd 3.67; 6-H^F dd 4.14; 6-H'^{F} dd 4.24; $J_{1,2}$ = 8.0 Hz; $J_{2,3}$ = 9.5 Hz; $J_{3,4}$ = 9.5 Hz; $J_{4,5}$ = 10.0 Hz; $J_{5,6}$ = 5.5 Hz; $J_{5,6'}$ = 2.5 Hz; $J_{6,6'}$ = 12.5 Hz; *nonenyl group:* 1'-H ddd 4.04; 1'-H' ddd 4.26; 2'-H m 5.41-5.48; 3'-H m 5.64-5.72; CH_2-4' m 1.98-2.07; CH_2-5', CH_2-6', CH_2-7', CH_2-8' m 1.23-1.38; CH_3-9' t 0.87; $J_{1,1'}$ = 12.5 Hz; $J_{1,2}$ = 7.0 Hz; $J_{1',2}$ = 5.5 Hz; $J_{1,3}$ = $J_{1',3}$ = 1.0 Hz; $J_{8,9}$ = 7.0 Hz; *acetyl groups:* 4*s 1.99, 2.01, 2.04, 2.07. - ^{13}C NMR (100.6 MHz, $CDCl_3$, APT): δ = 13.62 (C-9'); 20.12, 20.15, 20.21, 20.26 ($CO\underline{C}H_3$); 22.15 (C-8'); 28.08, 28.40, 28.54 (C-7', C-6', C-5'); 31.83 (C-4'); 61.59 (C-6); 68.08, 70.92, 71.33, 72.54 (C-5, C-4, C-3, C-2); 69.56 (C-1'); 98.75 (C-1); 124.35 (C-2'); 135.26 (C-3'); 168.89, 168.98, 169.88, 170.24 ($\underline{C}OCH_3$).- $C_{23}H_{36}O_{10}$ (472.53, 472.23).- FAB MS: m/z 495.3 ([M+Na]$^+$), 331.2 ([f]$^+$).

2-Nonyn-1-yl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (8)

β-D-Glucose pentaacetate (1.00 g, 2.6 mmol) was dissolved in CH_2Cl_2 (8 mL). $BF_3{\cdot}OEt_2$ (640 μL, 5.1 mmol) and 20 min later 2-nonyn-1-ol (430 μL, 2.6 mmol) were added. After 4.5 h the solution was diluted with

ethyl acetate (4 mL) and after 30 min with another portion of ethyl acetate (30 mL). After washing this solution with aqueous $NaHCO_3$ solution (3 times with 8 mL) and solvent evaporation a yellow oil was obtained (1.34 g). LC (hexanes-ethyl acetate 3:1) gave **8** (844 mg, 69 %). - ^{1}H NMR (400 MHz, $CDCl_3$, COSY): *Unit F:* 1-H^F d 4.77; 2-H^F dd 4.99; 3-H^F dd 5.23; 4-H^F dd 5.08; 5-H^F ddd 3.70; 6-H^F dd 4.13; 6-H'^F dd 4.27; $J_{1,2}$ = 8.0 Hz; $J_{2,3}$= 9.6 Hz; $J_{3,4}$ = 9.4 Hz; $J_{4,5}$ = 10.0 Hz; $J_{5,6}$ = 2.4 Hz; $J_{5,6'}$ = 4.6 Hz; $J_{6,6'}$ = 12.3 Hz; *nonynyl group:* CH_2-1' t 4.33; CH_2-4' m 2.18-2.23; CH_2-5' m 1.46-1.54; CH_2-6' m 1.35-1.42; CH_2-7', CH_2-8' m 1.24-1.33; CH_3-9' t 0.89; $J_{1\text{-}4}$ = 2.1 Hz; $J_{8\text{-}9}$ = 6.8 Hz; *acetyl groups:* 4*s 1.99, 2.01, 2.04, 2.07. - ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 13.59 (C-9'); 18.27 (C-4'); 20.12, 20.15, 20.23, 20.25 ($CO\underline{C}H_3$); 22.09 (C-8'); 28.07 (2*) (C-5', C-6'); 30.85 (C-7'); 56.20 (C-1'); 61.39 (C-6^F); 67.98, 70.65, 71.40, 72.48 (C-2^F, C-3^F, C-4^F, C-5^F); 73.85 (C-2'); 87.81 (C-3'); 97.52 (C-1^F); 168.98, 169.86, 170.23 ($\underline{C}OCH_3$). - $C_{23}H_{34}O_{10}$ (470.52, 470.22). - FAB MS: m/z 493.1 ($[M+Na]^+$), 331.0 ($[f]^+$).

Water addition to 8

8 (100 mg, 0.21 mmol) was dissolved in methanol (1.0 mL) and a suspension of $HgSO_4$ (3 mg, 10 μmol) in water (0.2 mL) was added. After 22 h the resulting gel was dissolved in CH_2Cl_2 (15 mL), the solution was washed with water (5 mL) and evaporated. FC (hexanes-ethyl acetate 2:1) of the raw material (88 mg) provided **9** (71.9 mg, 69 %), the isomeric α-alkoxy ketone (formula not shown, 3.3 mg, 3 %) and **7** (11.0 mg, 15 %).

Wacker-type oxidation of 6

6 (50 mg, 105 μmol) was dissolved in a mixture of DMF (1.8 mL) and water (0.3 mL). The solution was heated to 45°C and $PdCl_2$ (3 portions of 18.6 mg, 105 μmol each) was added over a period of 24 h. After further stirring at 45°C for 24 h water (10 mL) was added and the resulting mixture was lyophilized. The residue was dissolved in methanol. After addition through a bed of kieselguhr the solvent was evaporated and the kieselguhr used was extracted for 18 h with CH_2Cl_2 using a Soxhlet apparatus. After evaporation and FC (hexanes-ethyl acetate 2.5:1) **9** (51 mg, 97 %) was obtained containing a trace of the isomeric α-alkoxy ketone.

3-Oxononan-1-yl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (9)

^{1}H NMR (400 MHz, $CDCl_3$): *Unit F:* 1-H^F d 4.59; 2-H^F dd 4.91; 3-H^F dd 5.17; 4-H^F dd 5.04; 5-H^F ddd 3.66; 6-H^F dd 4.11; 6-H'^F dd 4.24; $J_{1,2}$ = 8.1 Hz; $J_{2,3}$ = 9.5 Hz; $J_{3,4}$ = 9.5 Hz; $J_{4,5}$ = 9.9 Hz; $J_{5,6}$ = 2.5 Hz; $J_{5,6'}$ = 4.6 Hz; $J_{6,6'}$ = 12.3 Hz; *3-oxononan-1-yl group:* 1'-H ddd 3.83; 1'-H' ddd 4.01; 2'-H ddd 2.55; 2'-H' ddd 2.73; CH_2-4' m 2.35-2.40; CH_2-5', CH_2-6', CH_2-7', CH_2-8' 2*m 1.21-1.30, 1.48-1.55; CH_3-9' t 0.86; $J_{1,1'}$ = 9.8 Hz; $J_{1,2}$ = 5.4 Hz; $J_{1,2'}$ = 8.2 Hz; $J_{1',2}$ = 5.4 Hz; $J_{1',2'}$ = 5.7 Hz; $J_{2,2'}$ = 17.1 Hz; $J_{8,9}$ = 6.9 Hz; *acetyl groups:* 4*s 1.97, 2.00, 2.00, 2.06. - ^{13}C NMR (50.3 MHz, $CDCl_3$, APT): δ = 14.46 (C-9'); 21.05 (3* ?); 21.18 ($CO\underline{C}H_3$); 22.92, 23.97 (C-5', C-8'); 29.28, 32.03 (C-6', C-7'); 42.69, 44.06 (C-2', C-4'); 62.35, 65.66, 68.86, 71.62, 72.26, 73.21 (C-2^F, C-3^F, C-4^F, C-5^F, C-6^F, C-1'); 101.60 (C-1^F); 169.82, 169.87, 170.65, 171.09 ($\underline{C}OCH_3$); 209.14 (C-3').- $C_{23}H_{36}O_{11}$ (488.53, 488.23).- FAB MS: m/z 511.2 ($[M+Na]^+$), 489.2 ($[M+H]^+$), 487.2 ($[M+H\text{-}H_2]^+$), 331.1 ($[f]^+$).

2-Oxononan-1-yl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (formula not shown)

^{1}H NMR (200 MHz, $CDCl_3$, COSY (400 MHz)): *Unit F:* 1-H^F d 5.76; 2-H^F, 3-H^F, 4-H^F m 5.05-5.34; 5-H^F ddd 3.86; 6-H^F dd 4.13; 6-H'^F dd 4.30; $J_{1,2}$ = 8.1 Hz; $J_{4,5}$ = 9.7 Hz; $J_{5,6}$ = 2.2 Hz; $J_{5,6'}$ = 4.4 Hz; $J_{6,6'}$ = 12.4 Hz; *2-oxononan-1-yl group:* CH_2-1' AB,t 3.46, 3.55; CH_2-3' t 2.49; CH_2-4', CH_2-5', CH_2-6', CH_2-7', CH_2-8' m 1.25-1.35, CH_3-9' t 0.89; $^2J_1$ = 15.8 Hz; $J_{1\text{-}3}$ = 7.3 Hz; $J_{8\text{-}9}$ = 7.0 Hz; *acetyl groups:* 3*s 2.02, 2.04, 2.09. - APT (50.3 MHz, $CDCl_3$): δ = 13.52 (CH_3-9'); 20.09 (3*), 20.22 ($CO\underline{C}H_3$); 21.96, 22.93 (CH_2-4', CH_2-8'); 28.88, 29.16, 31.04 (CH_2-5', CH_2-6', CH_2-7'); 42.88 (CH_2-3'); 48.33 (CH_2-1'); 60.99 (CH_2-6^F); 67.35, 69.37, 72.14, 72.44 (CH-2^F, CH-3^F, CH-4^F, CH-5^F); 91.73 (CH-1^F); 164.91 (not assigned); 169.01, 169.11, 169.65, 170.19 ($\underline{C}OCH_3$); 201.23: (C-2'). - $C_{23}H_{36}O_{11}$ (488.53, 488.23). - FAB MS: m/z 331.1 ($[f]^+$)

Deprotection of 9

DBU (70 μL, 0.48 mmol) was added to a solution of **9** (44.2 mg, 91 μmol) in CH_2Cl_2 (0.4 mL) and the mixture was stirred for 30 min at 20°C. The solution was diluted with CH_2Cl_2 (15 mL), washed with aqueous NH_4Cl, dried over Na_2SO_4 and evaporated. The resulting brown oil was purified by FC (hexanes-ethyl acetate 2:1) to furnish **7** (24.5 mg, 82 %) and an unknown compound (3.7 mg). 2.3 mg of **9** were recovered.

2-Nonyn-1-yl β-D-glucopyranoside (10)

A solution of $LiOH·H_2O$ (154 mg,3.67 mmol) in water (25 mL) was added to glucoside **8** (431 mg, 0.92 mmol) in THF (25 mL) and the mixture was stirred for 3 h at 20°C. Then cation exchange resin was added. 30 min later the resin was filtered off, washed with methanol and the combined filtrates were evaporated. LC (hexanes-$CHCl_3$-ethanol 5:1:1) yielded **10** (211 mg, 76 %) as a colorless oil. - ^{1}H NMR (400 MHz, pyridine-d_5, COSY): *Unit F:* 1-H^F d 5.04; 2-H^F dd 4.00; 3-H^F, 4-H^F m 4.15-4.25; 5-H^F ddd 3.89; 6-H^F dd 4.32; 6-H'^F dd 4.46; $J_{1,2}$ = 7.7 Hz; $J_{2,3}$ = 8.5 Hz; $J_{4,5}$ = 9.1 Hz; $J_{5,6}$ = 5.3 Hz; $J_{5,6'}$ = 2.2 Hz; $J_{6,6'}$ = 11.9 Hz; *nonynyl group:* CH_2-1' AB,t 4.61, 4.71; CH_2-4' m 2.13-2.18; CH_2-5' m 1.35-1.42; CH_2-6' m 1.22-1.31; CH_2-7', CH_2-8' m 1.05-1.20; CH_3-9' t 0.78; $^2J_1$ = 15.0 Hz; $J_{1\text{-}4}$ = 2.1 Hz; $J_{8\text{-}9}$ = 7.0 Hz; *OH:* s,b 6.80. - ^{13}C NMR (100.6 MHz, pyridine-d_5, APT): δ = 14.04 (CH_3-9'); 18.77 (CH_2-4'); 22.57 (CH_2-8'); 28.55, 28.66 (CH_2-5', CH_2-6'); 31.33 (CH_2-7'); 56.63 (CH_2-1'); 62.51 (CH_2-6^F); 71.37, 74.80, 78.31, 78.34 (CH-2^F, CH-3^F, CH-4^F, CH-5^F); 76.58 (C-2'); 87.17 (C-3'); 102.51 (CH-1^F). - $C_{15}H_{26}O_6$ (302.37, 302.17). - FAB MS: m/z 325.1 ($[M+Na]^+$), 303 ($[M+H]^+$), 185.1 ($[f+Na-H]^+$).

2-Nonyn-1-yl 4,6-*O*-benzylidene-β-D-glucopyranoside (11) from 8

Sodium methoxide (10 mg, 0.19 mmol) in methanol (1.0 mL) was added in 2 portions to a solution of **8** (654 mg, 1.39 mmol) in methanol (5.0 mL) over a period of 2 h. After 2 h the solvent was evaporated and the residue was redissolved in DMF (5 mL). $PhCH(OMe)_2$ (380 μL, 2.53 mmol) and *p*-$TsOH·H_2O$ (60 mg, 0.32 mmol) were added. The reaction flask was attached to a rotatory evaporator and the rotating flask was kept at ca. 4 hPa and 45°C for 2 h. Solvent was removed after that time and the residue was dried in vacuo. The resulting yellow solid (730 mg) was purified by FC (hexanes-ethyl acetate 1:1) to provide **11** (468 mg, 86 % based on **8**) as a white solid.- ^{1}H NMR (400 MHz, $CDCl_3$, COSY): *Unit F:* 1-H^F d 4.55; 2-H^F dd 3.46; 3-H^F dd 3.77; 4-H^F dd 3.48; 5-H^F ddd 3.40; 6-$H_{ax}{}^F$ dd 3.71; 6-$H_{eq}{}^F$ dd 4.28; $J_{1,2}$ = 7.9 Hz; $J_{2,3}$= 9.1 Hz; $J_{3,4}$ = 9.1 Hz; $J_{4,5}$ = 9.5 Hz; $J_{5,6ax}$ = 10.0 Hz; $J_{5,6eq}$ = 5.0 Hz; $J_{6ax,6eq}$ = 10.3 Hz; *nonynyl group:* CH_2-1' AB,t 4.30, 4.37; CH_2-4' m 2.15-2.20; CH_2-5' m 1.42-1.50; CH_2-6' m 1.29-1.47; CH_2-7', CH_2-8' m 1.19-1.29; CH_3-9' t 0.84; $^2J_1$ = 15.4 Hz; $J_{1\text{-}4}$ = 2.1 Hz; $J_{8\text{-}9}$ = 6.9 Hz; *benzylidene acetal:* CH^{benzal} s 5.47; Ph 2*m 7.29-7.32, 7.42-7.45; *OH protons*: s,b 2.96. - ^{13}C NMR (100.6 MHz, $CDCl_3$, APT): δ = 14.05 (CH_3-9'); 18.75 (CH_2-4'); 22.53 (CH_2-8'); 28.44, 28.54 (CH_2-5', CH_2-6'); 31.28 (CH_2-7'); 57.09 (CH_2-1'); 66.41, 73.10, 74.27, 80.48 (CH-2^F, CH-3^F, CH-4^F, CH-5^F); 68.61 (CH_2-6^F); 74.48 (C-2'); 88.53 (C-3'); 100.74, 101.92 (CH-1^F, CH^{benzal}); 126.31, 128.34 ($CH_{arom}{}^o$, $CH_{arom}{}^m$); 129.28 ($CH_{arom}{}^p$); 136.95 ($C_{arom}{}^i$). - $C_{22}H_{30}O_6$ (390.48, 390.20). - FAB MS: m/z 391.1 ($[M+H]^+$), 251.0 ($[f]^+$).

Conversion of 11 to a mixture of 12a and 13a, and 16

11 (12.86 g, 32.9 mmol) was dissolved in CH_2Cl_2 (40 mL). At 60°C solutions of camphorsulfonic acid (0.75 g, 3.3 mmol) in CH_2Cl_2 (4.5 mL) and subsequently of 2-methyl-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-α-D-glucopyrano)[2,1-d]oxazoline[29] (5 portions, total 12.65 g, 38.2 mmol) in CH_2Cl_2 (26 mL) were added over a period of 6.5 h. Triethylamine (1.0 mL) addition, solvent evaporation and FC (gradient hexanes-ethyl acetate-methanol 6:2:1 → pure ethyl acetate) gave a mixture of the isomeric disaccharides **13a** and **12a** and trisaccharide **16** (total 23.97 g). 0.39 g of **11** were recovered.- From such a mixture (410 mg) by reversed-phase MPLC (RP-18, methanol-water 65:35) pure **16** (9 mg) and a mixture containing only **12a** and **13a** (110 mg) was obtained. For characterization **12a** and **13a** could be enriched by FC (toluene-pyridine 10:1).

2-Nonyn-1-yl 2-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranoside (13a)

^{1}H NMR (400 MHz, $CDCl_3$, COSY, from a 3:1 mixture of **13a** and **12a**): *Unit F:* 1-H^F d 4.56; 2-H^F dd 3.37; 3-H^F dd 3.81; 4-H^F dd 3.47; 5-H^F m 3.31-3.38; 6-$H_{ax}{}^F$ m 3.66-3.72; 6-$H_{eq}{}^F$ m 4.22-4.28; $J_{1,2}$ = 7.7 Hz; $J_{2,3}$ = 8.5 Hz; $J_{3,4}$ = 9.4 Hz; $J_{4,5}$ = 9.1 Hz; *unit E:* 1-H^E d 4.76; 2-H^E ddd 3.95; 3-H^E, 4-H^E m 5.02-5.11; 5-H^E m 3.66-3.72; 6-H^E ca. 4.21; 6-H'^{E} m 4.22-4.28; $J_{1,2}$ = 8.4 Hz; $J_{2,NH}$ = 8.4 Hz; $J_{2,3}$ = 10.4 Hz; $J_{5,6}$ = 3.3 Hz; *nonynyl group:* CH_2-1' AB,t 4.24, 4.41; CH_2-4' m 2.11-2.18; CH_2-5' m 1.39-1.48; CH_2-6' m 1.27-1.35; CH_2-7', CH_2-8' m 1.17-1.27; CH_3-9' t 0.83; $^2J_1$ = 14.5 Hz; $J_{1,4}$ = 2.1 Hz; $J_{8,9}$ = 6.9 Hz; *acetyl groups:* 4*s 1.89, 1.96, 1.97, 2.02; *OH*: 3^F-OH s 3.48; *NH*: 2^E-NHAc d 5.77; *benzylidene acetal:* H^{benzal} s 5.45; Ph 2*m 7.26-7.29, 7.39-7.43. - ^{13}C NMR (100.6 MHz, $CDCl_3$, APT): δ = 13.65 (CH_3-9'); 18.33 (CH_2-4'); 20.19, 20.27, 20.34, 23.11 (CO<u>C</u>H_3); 22.13 (CH_2-8'); 28.07, 28.21 (CH_2-5', CH_2-6'); 30.90 (CH_2-7'); 54.63 (CH-2^E); 57.48 (CH_2-1'); 61.49 (CH_2-6^E); 65.80, 67.54, 71.59, 71.70, 72.07, 79.31, 83.20 (CH-2^F, CH-3^F, CH-4^F, CH-5^F, CH-3^E, CH-4^E, CH-5^E); 68.18 (CH_2-6^F); 74.33 (C-2'); 87.77 (C-3'); 100.41, 101.42, 101.57 (CH-1^F, CH-1^E, CH^{benzal}); 125.95, 127.86 ($CH_{arom}{}^o$, $CH_{arom}{}^m$); 128.78 ($CH_{arom}{}^p$); 136.57 ($C_{arom}{}^i$); 168.88, 170.38, 171.06, 171.52 (<u>C</u>OCH$_3$). - $C_{36}H_{49}NO_{14}$ (719.78, 719.32).

2-Nonyn-1-yl 3-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranoside (12a)

^{1}H NMR (400 MHz, $CDCl_3$, COSY, from a 2.5:1 mixture of **12a** and **13a**): *Unit F:* 1-H^F d 4.55; 2-H^F m 3.46-3.54; 3-H^F m 3.67-3.81; 4-H^F dd 3.58; 5-H^F m 3.32-3.40; 6-$H_{ax}{}^F$ m 3.67-3.81; 6-$H_{eq}{}^F$ dd 4.26; $J_{1,2}$ = 7.9 Hz; $J_{2,OH}$ = 1.9 Hz; $J_{3,4}$ = 9.4 Hz; $J_{4,5}$ = 9.4 Hz; $J_{5,6eq}$ = 5.0 Hz; $J_{6ax,6eq}$ = 10.4 Hz; *unit E:* 1-H^E d 4.89; 2-H^E m 3.67-3.81; 3-H^E dd 5.20; 4-H^E dd 4.99; 5-H^E m 3.46-3.54; 6-H^E dd 3.86; 6-H'^{E} dd 4.07; $J_{1,2}$ = 8.4 Hz; $J_{2,NH}$ = 8.2 Hz; $J_{2,3}$ = 10.3 Hz; $J_{3,4}$ = 9.5 Hz; $J_{4,5}$ = 9.9 Hz; $J_{5,6}$ = 2.4 Hz; $J_{5,6'}$ = 4.4 Hz; $J_{6,6'}$ = 12.3 Hz; *nonynyl group:* CH_2-1' AB,t 4.30, 4.36; CH_2-4' m 2.11-2.19; CH_2-5' m 1.38-1.49; CH_2-6' m 1.26-1.35; CH_2-7', CH_2-8' m 1.16-1.26; CH_3-9' t 0.83; $^2J_1$ = 15.2 Hz; $J_{1,4}$ = 2.1 Hz; $J_{8,9}$ = 6.9 Hz; *acetyl groups:* 4*s 1.76, 1.92, 1.93, 1.93; *OH*: 2^F-OH d 3.14; *NH*: 2^E-NHAc d 5.75; *benzylidene acetal:* H^{benzal} s 5.45; Ph 2*m 7.25-7.28, 7.38-7.42. - ^{13}C NMR (100.6 MHz, $CDCl_3$, APT): δ = 13.65 (CH_3-9'); 18.37 (CH_2-4'); 20.19, 20.26, 20.34, 22.89 (CO<u>C</u>H_3); 22.13 (CH_2-8'); 28.07, 28.14 (CH_2-5', CH_2-6'); 30.89 (CH_2-7'); 54.72 (CH-2^E); 56.66 (CH_2-1'); 61.47 (CH_2-6^E); 66.26, 67.92, 71.52, 72.00, 73.19, 78.43, 81.31 (CH-2^F, CH-3^F, CH-4^F, CH-5^F, CH-3^E, CH-4^E, CH-5^E); 68.20 (CH_2-6^F); 74.04 (C-2'); 88.09 (C-3'); 100.25, 100.66, 101.01 (CH-1^F, CH-1^E, CH^{benzal}); 125.71, 127.87 ($CH_{arom}{}^o$, $CH_{arom}{}^m$); 128.88 ($CH_{arom}{}^p$); 136.76 ($C_{arom}{}^i$); 169.00, 170.38, 170.51, 170.77 (<u>C</u>OCH$_3$). - $C_{36}H_{49}NO_{14}$ (719.78, 719.32).

2-Nonyn-1-yl 2,3-di-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-4,6-*O*-benzylidene-β-D-glucopyranoside (16)

^{1}H NMR (400 MHz, $CDCl_3$, COSY): *Unit F:* 1-H^F d 4.56; 2-H^F dd 3.52; 3-H^F dd 3.84; 4-H^F dd 3.63; 5-H^F m 3.29-3.37; 6-$H_{ax}{}^F$ dd 3.67; 6-$H_{eq}{}^F$ m 4.18-4.26; $J_{1,2}$ = 7.7 Hz; $J_{2,3}$ = 8.9 Hz; $J_{3,4}$ = 9.1 Hz; $J_{4,5}$ = 9.5 Hz; $J_{5,6ax}$ = 10.4 Hz; $J_{6ax,6eq'}$ = 10.4 Hz; *unit E:* 1-H^E d 5.08; 2-H^E m 3.25-3.33; 3-H^E dd 5.33; 4-H^E dd 4.89; 5-H^E ddd 3.16; 6-H^E m 3.52-3.62; 6-H'^{E} dd 3.84; $J_{1,2}$ = 8.5 Hz; $J_{2,NH}$ = 8.2 Hz; $J_{2,3}$ = 10.1 Hz; $J_{3,4}$ = 9.6 Hz; $J_{4,5}$ = 9.9 Hz; $J_{5,6}$ = 2.4 Hz; $J_{5,6'}$ = 3.4 Hz; $J_{6,6'}$ = 12.4 Hz; *unit D:* 1-H^D d 5.11; 2-H^D m 3.52-3.62; 3-H^D dd 5.29; 4-H^D dd 5.00; 5-H^D ddd 3.75; 6-H^D, 6-H'^{D} m 4.15-4.25; $J_{1,2}$ = 8.7 Hz; $J_{2,NH}$ = 8.9 Hz; $J_{2,3}$ = 10.4 Hz; $J_{3,4}$ = 9.6 Hz; $J_{4,5}$ = 9.9 Hz; $J_{5,6}$ = 3.8 Hz; $J_{5,6'}$ = 2.6 Hz; *nonynyl group:* CH_2-1' AB,t 4.17, 4.41; CH_2-4' m 2.11-2.17; CH_2-5' m 1.40-1.49; CH_2-6' m 1.25-1.34; CH_2-7', CH_2-8' m 1.17-1.25; CH_3-9' t 0.83; $^2J_1$ = 14.4 Hz; $J_{1,4}$ = 2.0 Hz; $J_{8,9}$ = 6.9 Hz; *acetyl groups:* 8*s 1.88, 1.91, 1.92, 1.94, 1.95, 1.96, 1.97, 2.01; *NH's:* 2^D-NHAc d 6.23; 2^E-NHAc d 6.49; *benzylidene acetal:* H^{benzal} s 5.42; Ph 2*m 7.32-7.35, 7.36-7.40. - ^{13}C NMR (100.6 MHz, $CDCl_3$, APT): δ = 13.63 (CH_3-9'); 18.35 (CH_2-4'); 20.15, 20.18, 20.22, 20.28, 23.01, 23.04 (CO<u>C</u>H_3); 22.11 (CH_2-8'); 28.07, 28.23 (CH_2-5', CH_2-6'); 30.88 (CH_2-7'); 55.11, 55.73 (CH-2^E, CH-2^D); 57.39 (CH_2-1'); 61.16, 61.62 (CH_2-6^E, CH_2-6^D); 65.22, 68.02 (2*), 71.24, 71.35, 71.39, 71.83, 79.60, 79.86, 80.07 (CH-2^F, CH-3^F, CH-4^F, CH-5^F, CH-3^E, CH-4^E, CH-5^E, CH-3^D, CH-4^D, CH-5^D); 68.27 (CH_2-6^F); 74.15 (C-2'); 87.92 (C-3'); 99.41, 99.63, 100.61, 101.60 (CH-1^F, CH-1^E, CH-1^D, CH^{benzal}); 125.77, 128.12 ($CH_{arom}{}^o$, $CH_{arom}{}^m$); 129.19 ($CH_{arom}{}^p$); 136.50 ($C_{arom}{}^i$); 169.15, 170.16, 170.23, 170.30,

171.05, 171.23 ($\underline{C}OCH_3$). - $C_{50}H_{68}N_2O_{22}$ (1049.09, 1048.43). - FAB MS: m/z 1071.1 ($[M+Na]^+$), 1049.2 ($[M+H]^+$), 330.0 ($[e]^+$) bzw. ($[d]^+$).

2-Nonyn-1-yl 2-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-4,6-*O*-benzylidene-3-*O*-carbamoyl-β-D-glucopyranoside (13b)

A 2:1 mixture of **13a** and **12a** (25.6 mg, 36 μmol) was dissolved in CH_2Cl_2 (1.0 mL) and the solution was cooled to -7°C. Trichloroacetyl isocyanate (7 μL, 59 μmol) was added. After 1 h the reaction was quenched with methanol (0.1 mL) and the solvents were evaporated in a stream of argon. The residue was redissolved in methanol (5.0 mL), zinc powder (35 mg, 0.54 mmol) was added and the mixture was stirred for 16 h at 20°C. Solids were removed by filtration and carefully washed with methanol and CH_2Cl_2. The combined organic solutions were evaporated. FC ($CHCl_3$-methanol 20:1) gave a 2:1 mixture of **13b** and **12b** (24.3 mg, 90 %).- ^{1}H NMR (400 MHz, $CDCl_3$, COSY of **13b**, obtained from the mixture): *Unit F:* 1-H^F ca. 4.72; 2-H^F m 3.69-3.76; 3-H^F dd 4.95; 4-H^F dd 3.73; 5-H^F ddd 3.49; 6-$H_{ax}{}^F$ dd 3.66; 6-$H_{eq}{}^F$ m 4.23-4.31; $J_{2,3}$ = 7.0 Hz; $J_{3,4}$ = 9.6 Hz; $J_{4,5}$ = 9.7 Hz; $J_{5,6ax}$ = 10.1 Hz; $J_{5,6eq}$ = 5.1 Hz; $J_{6ax,6eq}$ = 10.3 Hz; *unit E:* 1-H^E d 4.87; 2-H^E ddd 3.83; 3-H^E dd 5.18; 4-H^E dd 5.02; 5-H^E m 3.62-3.69; 6-H^E, 6-H'^E m 4.23-4.31; $J_{1,2}$ = 8.7 Hz; $J_{2,NH}$ = 8.7 Hz; $J_{2,3}$ = 10.4 Hz; $J_{3,4}$ = 9.4 Hz; $J_{4,5}$ = 9.8 Hz; *nonynyl group:* CH_2-1' AB,t 4.26, 4.26; CH_2-4' m 2.12-2.18; CH_2-5' m 1.39-1.48; CH_2-6' m 1.26-1.35; CH_2-7', CH_2-8' m 1.17-1.26; CH_3-9' t 0.83; $^2J_1$ = 14.9 Hz; $J_{1,4}$ = 2.1 Hz; $J_{8,9}$ = 6.9 Hz; *acetyl groups:* 4*s 1.89, 1.94, 1.96, 2.02; *NH's:* 3^F-$OCONH_2$ s,b 4.83; 2^E-NHAc d 5.93; *benzylidene acetal:* H^{benzal} s 5.41; Ph 2*m 7.25-7.29, 7.35-7.39. - ^{13}C NMR (75 MHz, pyridine-d_5): δ = 14.66 (C-9'); 19.35 (C-4'); 20.99, 21.08, 21.12 ($CO\underline{C}H_3$); 23.22, 23.95 (C-8', $CO\underline{C}H_3$); 29.24 (2*) (C-5', C-6'); 31.94 (C-7'); 56.02, 57.19 (C-2^E, C-1'); 62.98 (C-6^E); 66.00, 69.95, 70.12 (2*), 72.80, 74.12, 74.55, 79.54, 80.06 (C-2^F, C-3^F, C-4^F, C-5^F, C-6^F, C-3^E, C-4^E, C-5^E, C-2'); 88.41 (C-3'); 100.60, 101.11, 102.20 (C-1^F, C-1^E, C^{benzal}); 127.40, 128.92 ($C_{arom}{}^o$, $C_{arom}{}^m$); 129.68 ($C_{arom}{}^p$); 138.77 ($C_{arom}{}^i$); 158.15 (3^F-$OCONH_2$); 170.29, 171.08, 171.33 ($\underline{C}OCH_3$). - $C_{37}H_{50}N_2O_{15}$ (762.81, 762.32).

2-Nonyn-1-yl 3-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-4,6-*O*-benzylidene-2-*O*-carbamoyl-β-D-glucopyranoside (12b)

A 4:1 mixture of **12a** and **13a** was converted into a 4:1 mixture of **12b** and **13b** as described above.- ^{1}H NMR (400 MHz, $CDCl_3$, COSY of **12b**, obtained from the mixture): *Unit F:* 1-H^F, 2-H^F m 4.78-4.75; 3-H^F dd 3.95; 4-H^F dd 3.65; 5-H^F ddd 3.39; 6-$H_{ax}{}^F$ dd 3.71; 6-$H_{eq}{}^F$ m 4.23-4.30; $J_{2,3}$ = 7.5 Hz; $J_{3,4}$ = 8.9 Hz; $J_{4,5}$ = 9.7 Hz; $J_{5,6ax}$ = 9.7 Hz; $J_{5,6eq}$ = 5.0 Hz; $J_{6ax,6eq}$ = 10.3 Hz; *unit E:* 1-H^E d 4.86; 2-H^E m 3.63-3.75; 3-H^E dd 5.26; 4-H^E dd 4.98; 5-H^E ddd 3.53; 6-H^E dd 3.92; 6-H'^E dd 4.08; $J_{1,2}$ = 8.4 Hz; $J_{2,NH}$ = 8.4 Hz; $J_{2,3}$ = 10.4 Hz; $J_{3,4}$ = 9.4 Hz; $J_{4,5}$ = 9.9 Hz; $J_{5,6}$ = 2.7 Hz; $J_{5,6'}$ = 4.0 Hz; $J_{6,6'}$ = 12.2 Hz; *nonynyl group:* CH_2-1' t 4.27; CH_2-4' m 2.11-2.18; CH_2-5' m 1.39-1.48; CH_2-6' m 1.26-1.35; CH_2-7', CH_2-8' m 1.17-1.26; CH_3-9' t 0.83; $J_{1,4}$ = 2.0 Hz; $J_{8,9}$ = 6.9 Hz; *acetyl groups:* 4*s 1.85, 1.90, 1.92, 1.93; *NH's:* 2^F-$OCONH_2$ s,b 4.94; 2^E-NHAc d 5.92; *benzylidene acetal:* H^{benzal} s 5.45; Ph m 7.24-7.28, 7.37-7.42. - ^{13}C NMR (50 MHz, pyridine-d_5): δ = 14.61 (C-9'); 19.36 (C-4'); 20.93, 21.04, 21.11 ($CO\underline{C}H_3$); 23.17, 23.82 (C-8', $CO\underline{C}H_3$); 29.17 (2*) (C-5', C-6'); 31.89 (C-7'); 56.20, 57.10 (C-2^E, C-1'); 63.06 (C-6^E); 67.12, 69.49, 70.09 (2* ?), 72.62, 73.95, 74.66, 79.97, 80.34 (C-2^F, C-3^F, C-4^F, C-5^F, C-6^F, C-3^E, C-4^E, C-5^E, C-2'); 88.55 (C-3'); 100.19, 101.60, 101.94 (C-1^F, C-1^E, C^{benzal}); 127.37, 128.88 ($C_{arom}{}^o$, $C_{arom}{}^m$); 129.68 ($C_{arom}{}^p$); 138.94 ($C_{arom}{}^i$); 157.56 (2^F-$OCONH_2$); 170.25, 171.05 (2*), 171.38 ($\underline{C}OCH_3$). - $C_{37}H_{50}N_2O_{15}$ (762.81, 762.32).

Conversion of the mixture of 12a, 13a and 16 into 15a, 14 and 2-nonyn-1-yl 2,3-di-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-β-D-glucopyranoside (formula not shown)

A sample of the original glycosidation mixture obtained from **11** (vide supra) (2.39 g, max. 3.32 mmol) was dissolved in CH_2Cl_2 (60 mL) and cooled to -7°C. Trichloroacetyl isocyanate (430 μL, 3.63 mmol) was added. After 2.5 h methanol (1.0 mL) was added and the mixture left for 30 min. Solvents were evaporated and the residue redissolved in methanol (80 mL). Zinc powder (2.2 g, 35 mmol) was added and the mixture was stirred overnight. Solids were removed by filtration and after drying extracted with CH_2Cl_2 in a Soxhlet apparatus. The organic combined solutions were evaporated and redissolved in ethanol (80 mL). Then Dowex 50 (H^+, 4.4 g) and water (40 mL) were added and the flask was sealed. For 1 h the mixture was

heated to 100°C, alternatively for 48 h at 60°C. Then, the resin was filtered off and washed with methanol. The combined solutions were evaporated. FC ($CHCl_3$-methanol 15:1) provided **15a** (0.70 g, 31 %, based on **11**), **14** (1.07 g, 48 %, based on **11**) and 2-nonyn-1-yl 2,3-di-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-β-D-glucopyranoside (formula not shown, 258 mg, **8 %, based on 11**).

2-Nonyn-1-yl 2-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-3-*O*-carbamoyl-β-D-glucopyranoside (15a)

^{1}H NMR (400 MHz, pyridine-d_5, COSY): *Unit F:* 1-H^F d 5.08; 2-H^F dd 4.26; 3-H^F dd 5.65; 4-H^F dd 4.34; 5-H^F ddd 3.88; 6-H^F, 6-H'^F m 4.30-4.43; $J_{1,2}$ = 7.4 Hz; $J_{2,3}$ = 8.6 Hz; $J_{3,4}$ = 9.0 Hz; $J_{4,5}$ = 9.7 Hz; $J_{5,6}$ = 4.2 Hz; $J_{5,6'}$ = 2.2 Hz; *unit E:* 1-H^E d 5.74; 2-H^E m 4.37-4.45; 3-H^E dd 5.89; 4-H^E dd 5.48; 5-H^E m 3.98-4.04; 6-H^E dd 4.51; 6-H'^E m 4.57-4.64; $J_{1,2}$ = 8.6 Hz; $J_{2,NH}$ = 8.6 Hz; $J_{2,3}$ = 10.1 Hz; $J_{3,4}$ = 9.7 Hz; $J_{4,5}$ = 9.5 Hz; $J_{5,6}$ = 2.4 Hz; $J_{6,6'}$ = 12.1 Hz; *nonynyl group:* CH_2-1' AB,t 4.60, 4.70; CH_2-4' m 2.13-2.19; CH_2-5' m 1.36-1.44; CH_2-6' m 1.22-1.32; CH_2-7', CH_2-8' m 1.12-1.22; CH_3-9' t 0.83; $^2J_1$ = 14.7 Hz; $J_{1,4} \approx 2.0$ Hz; $J_{8,9}$ = 7.0 Hz; *acetyl groups:* 4*s 2.00, 2.01, 2.09, 2.18; *NH's:* 3^F-$OCONH_2$ s,b 7.58; 2^E-NHAc d 8.83. - ^{13}C NMR (50 MHz, pyridine-d_5): δ = 14.32 (C-9'); 18.97 (C-4'); 20.66, 20.75, 20.83 ($CO\underline{C}H_3$); 22.84, 23.49 (C-8', $CO\underline{C}H_3$); 28.81, 28.87 (C-5', C-6'); 31.58 (C-7'); 55.99, 57.22 (C-2^E, C-1'); 61.93, 62.76 (C-6^F, C-6^E); 69.59, 69.68, 72.40, 73.92, 76.43, 78.06, 78.84, 80.26, 87.65 (C-2^F, C-3^F, C-4^F, C-5^F, C-3^E, C-4^E, C-5^E, C-2', C-3'); 101.18, 101.30 (C-1^F, C-1^E); 158.87 (3^F-$OCONH_2$); 169.73, 170.76 (2*), 171.26 ($\underline{C}OCH_3$). - $C_{30}H_{46}N_2O_{15}$ (674.70, 674.29).- FAB MS: m/z 1371.7 ([2M+Na]$^+$), 1349.7 ([2M+H]$^+$), 697.2 ([M+Na]$^+$), 675.2 ([M+H]$^+$), 330.1 ([e]$^+$).

2-Nonyn-1-yl 3-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-2-*O*-carbamoyl-β-D-glucopyranoside (14)

^{1}H NMR (400 MHz, pyridine-d_5, COSY): *Unit F:* 1-H^F d 5.16; 2-H^F dd 5.51; 3-H^F dd 4.26; 4-H^F dd,b 4.09; 5-H^F ddd 3.84; 6-H^F m 4.19-4.25; 6-H'^F m,b 4.38-4.43; $J_{1,2}$ = 8.1 Hz; $J_{2,3}$ = 8.8 Hz; $J_{3,4}$ = 8.8 Hz; $J_{4,5}$ = 9.4 Hz; $J_{5,6}$ = 5.3 Hz; $J_{5,6'}$ = 1.8 Hz; *unit E:* 1-H^E d 5.63; 2-H^E m 4.12-4.20; 3-H^E dd 6.05; 4-H^E dd 5.36; 5-H^E ddd 4.02; 6-H^E dd 4.31; 6-H'^E dd 4.47; $J_{1,2}$ = 8.4 Hz; $J_{2,NH}$ = 8.2 Hz; $J_{2,3}$ = 9.9 Hz; $J_{3,4}$ = 9.7 Hz; $J_{4,5}$ = 9.7 Hz; $J_{5,6}$ = 2.4 Hz; $J_{5,6'}$ = 5.7 Hz; $J_{6,6'}$ = 12.1 Hz; *nonynyl group:* CH_2-1' s 4.59, $w_{½} \approx 5$ Hz; CH_2-4' m 2.09-2.15; CH_2-5' m 1.33-1.41; CH_2-6' m 1.20-1.28; CH_2-7', CH_2-8' m 1.07-1.20; CH_3-9' t 0.80; $J_{8,9}$ = 7.1 Hz; *acetyl groups:* 4*s 1.98, 2.02, 2.04, 2.22; *OH's:* OH 2*s,b 5.85, 6.51; *NH's*: 2^F-$OCONH_2$ s,b 7.61; 2^E-NHAc d 8.78. - ^{13}C NMR (50 MHz, pyridine-d_5): δ = 14.46 (C-9'); 19.21 (C-4'); 20.76, 20.82, 20.90 ($CO\underline{C}H_3$); 23.01, 23.71 (C-8', $CO\underline{C}H_3$); 29.00, 29.05 (C-5', C-6'); 31.73 (C-7'); 56.15, 56.77 (C-2^E, C-1'); 62.46, 62.91 (C-6^F, C-6^E); 69.98, 70.08, 72.29, 73.26, 73.91, 76.37, 78.35, 85.99, 87.99 (C-2^F, C-3^F, C-4^F, C-5^F, C-3^E, C-4^E, C-5^E, C-2', C-3'); 99.99, 101.79 (C-1^F, C-1^E); 157.57 (2^F-$OCONH_2$); 170.16, 170.77, 171.39 ($\underline{C}OCH_3$). - $C_{30}H_{46}N_2O_{15}$ (674.70, 674.29). - FAB MS: m/z 1371.6 ([2M+Na]$^+$), 1349.7 ([2M+H]$^+$), 697.3 ([M+Na]$^+$), 675.3 ([M+H]$^+$), 535.1 ([f]$^+$), 330.1 ([e]$^+$).

2-Nonyn-1-yl 2,3-di-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-β-D-glucopyranoside (formula not shown)

^{1}H NMR (400 MHz, $CDCl_3$, COSY): *Unit F:* 1-H^F d 4.61; 2-H^F m 3.43-3.50; 3-H^F dd 3.59; 4-H^F m 3.43-3.50; 5-H^F m 3.22-3.28; 6-H^F m 3.67-3.73; 6-H'^F m 3.74-3.81; $J_{1,2}$ = 7.8 Hz; *unit E:* 1-H^E d 5.15; 2-H^E ddd,b 5.38; 3-H^E dd 5.55; 4-H^E dd 4.88; 5-H^E m 3.79-3.91; 6-H^E ,6-H'^E m 4.02-4.17; $J_{1,2}$ = 8.4 Hz; $J_{2,NH} \approx 8.4$ Hz; $J_{2,3}$ = 10.3 Hz; $J_{3,4}$ = 9.4 Hz; $J_{4,5}$ = 10.0 Hz; *unit D:* 1-H^D d 5.00; 2-H^D m 3.79-3.91; 3-H^D dd 5.04; 4-H^D dd 4.97; 5-H^D m 3.67-3.73; 6-H^D, 6-H'^D m 4.02-4.17; $J_{1,2}$ = 8.4 Hz; $J_{2,3}$ = 10.2 Hz; $J_{3,4}$ = 9.5 Hz; $J_{4,5}$ = 9.4 Hz; *nonynyl group:* CH_2-1' AB,t 4.28-4.40; CH_2-4' m 2.12-2.18; CH_2-5' m 1.39-1.49; CH_2-6' m 1.25-1.34; CH_2-7', CH_2-8' m 1.17-1.25; CH_3-9' t 0.83; $^2J_1$ = 14.9 Hz; $J_{4,5}$ = 2.0 Hz; $J_{8,9}$ = 6.9 Hz; *acetyl groups:* 8*s 1.93, 1.96, 1.96, 1.97, 1.97, 1.98, 2.01, 2.03; *OH's*: OH m 6.19-6.35, s,b 6.71; *NH's*: 2^D-NHAc m 6.19-6.28; 2^E-NHAc m 7.09-7.15. - APT (100.6 MHz, $CDCl_3$): δ = 14.02 (CH_3-9'); 18.74 (CH_2-4'); 20.62, 20.69, 23.39 ($CO\underline{C}H_3$); 22.50 (CH_2-8'); 28.51, 28.64 (CH_2-5', CH_2-6'); 31.27 (CH_2-7'); 54.81, 55.75 (CH-2^E, CH-2^D); 57.16 (CH_2-1'); 62.08, 62.23, 62.54 (CH_2-6^F, CH_2-6^E, CH_2-6^D); 68.28, 69.20, 69.83, 71.53, 71.80 ,72.09, 72.74, 75.17, 78.72, 85.94 (CH-2^F, CH-3^F, CH-4^F, CH-5^F, CH-3^E, CH-4^E, CH-5^E, CH-3^D, CH-

4^D, CH-5^D); 74.80 (C-2'); 88.41 (C-3'); 99.15, 99.66, 100.87 (CH-1^F, CH-1^E, CH-1^D); 169.39, 169.73, 170.27, 170.55 (2*), 170.95, 171.42, 171.75 ($\underline{C}OCH_3$). - $C_{43}H_{64}N_2O_{22}$ (960.98, 960.40). - FAB MS: m/z 983.4 ($[M+Na]^+$), 961.4 ($[M+H]^+$), 330.1 ($[e]^+$) bzw. ($[d]^+$).

2-Nonyn-1-yl 2-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-4,6-di-*O*-*tert.*-butyldimethylsilyl-3-*O*-carbamoyl-β-D-glucopyranoside (15b)

A solution of **15a** (100 mg, 0.15 mmol), imidazole (66 mg, 0.97 mmol) and ^{t}BuMe$_2$SiCl (110 mg, 0.73 mmol) in DMF (1.6 mL) was stirred for 4 days at 40°C. Methanol (0.5 mL) and then $CHCl_3$-ethanol 3:2 (15 mL) were added. The solution was washed with water (10 mL) and evaporated. FC ($CHCl_3$-methanol 50:1) furnished pure **15b** (115 mg, 85 %) and a fraction of **15b** (22.7 mg, ca. 15 %) containing traces of two unknown compounds.- ^{1}H NMR (300 MHz, $CDCl_3$, COSY): *Unit F:* 1-H^F d 4.66; 2-H^F dd 3.55; 3-H^F dd 4.82; 4-H^F m 3.68-3.83; 5-H^F ddd 3.27; 6-H^F, 6-H'^{F} m 3.68-3.83; $J_{1,2}$ = 6.9 Hz; $J_{2,3}$ = 8.4 Hz; $J_{3,4}$ = 8.9 Hz; *unit E:* 1-H^E d 4.95; 2-H^E m 3.68-3.83; 3-H^E dd 5.37; 4-H^E dd 5.08; 5-H^E m 3.68-3.83; 6-H^E dd 4.17; 6-H'^{E} dd 4.32; $J_{1,2}$ = 8.5 Hz; $J_{2,NH}$ = 8.2 Hz; $J_{5,6}$ = 4.1 Hz; $J_{5,6'}$ = 3.0 Hz; $J_{6,6'}$ = 12.4 Hz; *nonynyl group:* CH_2-1' m 4.25-4.42; CH_2-4' m 2.16-2.24; CH_2-5' m 1.44-1.53; CH_2-6', CH_2-7', CH_2-8' m 1.15-1.42; CH_3-9' m 0.90; *acetyl groups:* 4*s 1.96, 2.02, 2.02, 2.09; *NH's*: 3^F-$OCONH_2$ s,b 4.87; 2^E-NHAc d 5.88; *silyl groups:* $Si(CH_3)_2$ 3*s 0.07, 0.08 (2*), 0.10; $SiC(CH_3)_3$ 2*s 0.86, 0.90.[1] - APT (75 MHz, $CDCl_3$): δ = -5.34, -4.97, -4.83, -4.53 (2 * $Si(CH_3)_2$); 14.05 (CH_3-9'); 17.99, 18.42, 18.78 (2 * $Si\underline{C}(CH_3)_3$, CH_2-4'); 20.67, 20.73, 20.77 ($CO\underline{C}H_3$); 22.55 (CH_2-8'); 23.42 ($CO\underline{C}H_3$); 25.74, 25.95 (2 * $SiC(\underline{C}H_3)_3$); 28.56, 28.62 (CH_2-5', CH_2-6'); 31.32 (CH_2-7'); 55.03 (CH-2^E); 56.15 (CH_2-1'); 61.61, 61.94 (CH_2-6^F, CH_2-6^E); 68.37, 68.72. 71.73, 72.62, 76.38, 78.30, 78.36 (CH-2^F, CH-3^F, CH-4^F, CH-5^F, CH-3^E, CH-4^E, CH-5^E); 74.90 (C-2'); 87.77 (C-3'); 99.01, 99.49 (CH-1^F, CH-1^E); 156.51 (3^F-$OCONH_2$); 169.44, 170.65, 170.69, 170.77 ($\underline{C}OCH_3$).- $C_{42}H_{74}N_2O_{15}Si_2$ (903.22, 902.46). - FAB MS: m/z 925.4 ($[M+Na]^+$), 845.4 ($[M+H-HC(CH_3)_3]^+$), 330.1 ($[e]^+$).

2-Nonyn-1-yl 2-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-4-*O*-*tert.*-butyldimethylsilyl-3-*O*-carbamoyl-β-D-glucopyranoside (15c)

A mixture of **15b** (127 mg, 0.14 mmol) in THF (1.2 mL), water (1.2 mL), and acetic acid (3.6 mL) was stirred at 20°C for 20 h. CH_2Cl_2 (25 mL)was added and the solution was washed with water (10 mL) and evaporated. Acetic acid was removed by codistillation with toluene. FC ($CHCl_3$-methanol 50:1) furnished **15c** (95.2 mg, 86 %). - ^{1}H NMR (400 MHz, pyridine-d_5, COSY): *Unit F:* 1-H^F d 5.15; 2-H^F dd 4.29; 3-H^F dd 5.49; 4-H^F m 4.42-4.49; 5-H^F m 3.71-3.77; 6-H^F dd 4.07; 6-H'^{F} d,b 4.16; $J_{1,2}$ = 6.2 Hz; $J_{2,3}$ = 7.3 Hz; $J_{3,4}$ = 8.0 Hz; $J_{5,6}$ = 3.4 Hz; $J_{6,6'}$ = 12.1 Hz; *unit E:* 1-H^E d 5.77; 2-H^E m 4.36-4.46; 3-H^E dd 5.88; 4-H^E dd 5.48; 5-H^E m 3.97-4.02; 6-H^E m 4.44-4.49; 6-H'^{E} dd 4.58; $J_{1,2}$ = 8.4 Hz; $J_{2,3}$ = 10.4 Hz; $J_{3,4}$ = 9.8 Hz ; $J_{4,5}$ = 9.7 Hz; $J_{5,6'}$ = 4.1 Hz; $J_{6,6'}$ = 12.2 Hz; *nonynyl group:* CH_2-1' m 4.62-4.67; CH_2-4' m 2.14-2.20; CH_2-5' m 1.37-1.46; CH_2-6', CH_2-7', CH_2-8' m 1.13-1.32; CH_3-9' t 0.84; $J_{8,9}$ = 7.1 Hz; *acetyl groups:* 4*s 2.00, 2.01, 2.07, 2.18; *NH's*: 3^F-$OCONH_2$ s 7.61; 2^E-NHAc 8.71; *silyl group:* $Si(CH_3)_2$ 2*s 0.32, 0.34; $SiC(CH_3)_3$ s 1.01. - ^{13}C NMR (50 MHz, $CDCl_3$, APT): δ = -4.35, -3.98 ($Si(CH_3)_2$); 14.50 (CH_3-9'); 18.36, 19.21 ($Si\underline{C}(CH_3)_3$, CH_2-4'); 21.09, 21.16, 21.23 ($CO\underline{C}H_3$); 22.98 (CH_2-8'); 23.85 ($CO\underline{C}H_3$); 26.15 ($SiC(\underline{C}H_3)_3$); 28.97, 29.08 (CH_2-6', CH_2-7'); 31.75 (CH_2-5'); 55.36 (CH-2^E); 57.91 (CH_2-1'); 61.76, 62.50 (CH_2-6^F, CH_2-6^E); 68.93, 69.07, 72.26, 73.18, 76.45, 78.32, 79.33 (CH-2^F, CH-3^F, CH-4^F, CH-5^F, CH-3^E, CH-4^E, CH-5^E); 75.52 (C-2'); 88.47 (C-3'); 100.50, 100.75 (CH-1^F, CH-1^E); 156.95 (3^F-$OCONH_2$); 169.85, 171.18, 171.37 ($\underline{C}OCH_3$). - $C_{36}H_{60}N_2O_{15}Si$ (788.96, 788.38). - FAB MS: m/z 811.5 ($[M+Na]^+$), 789.5 ($[M+H]^+$), 330.1 ($[e]^+$).

2-Nonyn-1-yl 2-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-4-*O*-*tert.*-butyldimethylsilyl-3-*O*-carbamoyl-β-D-glucopyranosiduronic acid (formula not shown)

A solution of **15c** (0.84 g, 1.07 mmol) in DMSO (3.0 mL) was added to *o*-iodoxy benzoic acid (IBX, 1.05 g, 3.75 mmol) dissolved in DMSO (4.0 mL). The mixture was left at 20°C for 24 h. Water (5 mL) was added whereupon a suspension resulted. CH_2Cl_2 (180 mL) and water (70 mL) were added. The phases were separated after shaking in a separatory funnel. The organic layer was clear and was evaporated. To this raw

[1] The 9'-CH_3 signal was presumably hidden by the $SiCH_3$ signals.

material *tert.*-butanol (50 mL) and 2-methyl-2-butene (10 mL) were added. Over a period of 1.5 h a solution of $NaClO_2$ (480 mg, 5.3 mmol) and $NaH_2PO_4 \cdot H_2O$ (960 mg) in water (7.5 mL) was added. After 1.5 h the yellow solution was evaporated. Water (60 mL) was added to the residue. After acidifying the resulting suspension with aqueous HCl (5 %) it was extracted 4 times with $CHCl_3$-ethanol 3:2 (total 300 mL). The combined organic layers were evaporated and the raw uronic acid (1.10 g) was obtained as a yellow oil. - ^{13}C NMR (50 MHz, pyridine-d_5): δ = -4.23, -3.74 ($Si(CH_3)_2$); 14.46 (C-9'); 18.58, 19.13 ($SiC(CH_3)_3$, C-4'); 20.78, 20.89, 23.00, 23.68 (C-8', $COCH_3$); 26.28 ($SiC(CH_3)_3$); 29.02 (2*) (C-5', C-6'); 31.72 (C-7'); 41.38, 42.74 (DMSO); 55.90, 56.68 (C-2^E, C-1'); 62.78 (C-6^E); 69.91, 71.82, 72.57, 73.95, 76.14, 76.77, 77.64, 79.60 (C-2^F, C-3^F, C-4^F, C-5^F, C-3^E, C-4^E, C-5^E, C-2'); 88.28 (C-3'); 99.72, 100.85 (C-1^F, C-1^E); 124.08, 128.54, 131.42, 132.59, 136.09, 141.74 (IBX); 157.81 (3^F-$OCONH_2$); 170.05, 170.83 (2*), 171.01, 172.30 (C-6^F, $COCH_3$). - $C_{36}H_{58}N_2O_{16}Si$ (802.95, 802.36). - FAB MS: m/z 825.3 ($[M+Na]^+$), 330.1 ($[e]^+$).

2-Nonyn-1-yl 2-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-4-*O*-*tert.*-butyldimethylsilyl-3-*O*-carbamoyl-β-D-glucopyranosiduronic amide (15d)

To a solution of the raw acid described above in CH_2Cl_2 (8.0 mL) a solution of *N,N'*-carbonyl diimidazole (CDI, 600 mg, 3.70 mmol) in CH_2Cl_2 (6.0 mL) was added over a period of 3 h. The mixture was then left at 20°C for 1 h. After cooling to 0°C ammonia was bubbled through the solution for 15 min and the mixture was then left at 0°C for 30 min. Solvent evaporation and FC ($CHCl_3$-methanol 50:1) furnished **15d** (527 mg, 62 % based on **15c**).- ^1H NMR (400 MHz, pyridine-d_5, COSY): *Unit F:* 1-H^F d 5.30; 2-H^F dd 4.37; 3-H^F dd 5.53; 4-H^F dd 4.74; 5-H^F d 4.48; $J_{1,2}$ = 5.6 Hz; $J_{2,3}$ = 6.3 Hz; $J_{3,4}$ = 7.9 Hz; $J_{4,5}$ = 9.1 Hz; *unit E:* 1-H^E d 5.73; 2-H^E m 4.38-4.47; 3-H^E dd 5.87; 4-H^E dd 5.47; 5-H^E m 3.97-4.02; 6-H^E m 4.38-4.47; 6-H'^E dd 4.57; $J_{1,2}$ = 8.4 Hz; $J_{2,NH}$ = 8.7 Hz; $J_{2,3}$ = 9.9 Hz; $J_{3,4}$ = 9.6 Hz; $J_{4,5}$ = 9.7 Hz; $J_{5,6'}$ = 4.1 Hz; $J_{6,6'}$ = 12.2 Hz; *nonynyl group:* CH_2-1' m 4.68-4.72; CH_2-4' m 2.12-2.17; CH_2-5' m 1.34-1.43; CH_2-6', CH_2-7', CH_2-8' m 1.12-1.30; CH_3-9' t 0.83; $J_{8,9}$ = 6.9 Hz; *acetyl groups:* 4*s 2.00, 2.01, 2.06, 2.17; *NH's*: 3^F-$OCONH_2$ s 7.71; $CONH_2$-6^F 2*s,b 8.37, 8.37; 2^E-NHAc d 8.84; *silyl group:* $Si(CH_3)_2$ 2*s 0.33, 0.34; $SiC(CH_3)_3$ s 1.02. - ^{13}C NMR (100 MHz, pyridine-d_5, APT, CH COSY): δ = -4.16, -3.92 ($Si(CH_3)_2$); 14.64 (CH_3-9'); 18.81, 19.32 ($SiC(CH_3)_3$, CH_2-4'); 20.96, 21.07, 21.12 ($COCH_3$); 23.18 (CH_2-8'); 23.85 ($COCH_3$); 26.58 ($SiC(CH_3)_3$); 29.22 (2*) (CH_2-5', CH_2-6'); 31.92 (CH_2-7'); 56.11 (CH-2^E); 57.26 (CH_2-1'); 63.03 (CH_2-6^E); 70.02 (CH-4^E); 71.86 (CH-4^F); 72.74 (CH-5^E); 74.24 (CH-3^E); 76.55 (C-2'); 77.70 (CH-5^F); 78.00 (CH-3^F); 80.50 (CH-2^F); 88.34 (C-3'); 100.47 (CH-1^F); 101.65 (CH-1^E); 157.99 (3^F-$OCONH_2$); 170.27, 171.06, 171.31, 171.37 (C-6^F, $COCH_3$). - $C_{36}H_{59}N_3O_{15}Si$ (801.96, 801.37). - FAB MS: m/z 824.3 ($[M+Na]^+$), 802.3 ($[M+H]^+$), 744.2 ($[M+H-HC(CH_3)_3]^+$), 662.2 ($[f]^+$), 330.1 ($[e]^+$)

3-Oxononan-1-yl 2-*O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-4-*O*-*tert.*-butyldimethylsilyl-3-*O*-carbamoyl-β-D-glucopyranosiduronic amide (17)

15d (50 mg, 62 μmol) was converted into **17** as described for conversion **8** → **9**. FC ($CHCl_3$-MeOH 50:1) provided **17** (29.4 mg, 58 %). - ^1H NMR (400 MHz, pyridine-d_5, COSY): *Unit F:* 1-H^F 4.96; 2-H^F dd 4.27; 3-H^F dd 5.52; 4-H^F dd 4.63; 5-H^F d 4.40; $J_{1,2}$ = 6.3 Hz; $J_{2,3}$ = 7.3 Hz; $J_{3,4}$ = 8.4 Hz; $J_{4,5}$ = 8.9 Hz; *unit E:* 1-H^E d 5.59; 2-H^E m 4.40-4.49; 3-H^E dd 5.80; 4-H^E dd 5.46; 5-H^E ddd 3.93; 6-H^E dd 4.40; 6-H'^E dd 4.58; $J_{1,2}$ = 8.4 Hz; $J_{2,NH}$ = 8.7 Hz; $J_{2,3}$ = 10.2 Hz; $J_{3,4}$ = 9.6 Hz; $J_{4,5}$ = 9.6 Hz; $J_{5,6}$ = 2.7 Hz; $J_{5,6'}$ = 4.4 Hz; $J_{6,6'}$ = 12.1 Hz; *3-oxononan-1-yl group*: 1'-H m 3.97-4.03; 1'-H' m 4.27-4.35; CH_2-2' dt 2.83; CH_2-4' dt 2.45; CH_2-5' m 1.51-1.62; CH_2-6', CH_2-7', CH_2-8' m 1.17-1.25; CH_3-9' t 0.82; $J_{1,2'}$ = 6.3 Hz; $J_{2,4}$ 1.9 Hz; $J_{4,5} \approx$ 7.0 Hz; $J_{8,9}$ = 6.9 Hz; *acetyl groups:* 4*s 1.99, 2.01, 2.07, 2.18; *NH's:* 3^F-$OCONH_2$ s 7.70; $CONH_2$-6^F 2*s,b 8.36, 8.45; 2^E-NHAc d 8.60; *silyl group:* $Si(CH_3)_2$ 2*s 0.36, 0.37; $SiC(CH_3)_3$ s 1.03. - APT (100 MHz, pyridine-d_5): δ = -6.45, -6.26 ($Si(CH_3)_2$); 12.28 (CH_3-9'); 16.48 ($SiC(CH_3)_3$); 18.58, 18.69, 18.79 ($COCH_3$); 20.82, 21.90 (CH_2-5', CH_2-8'); 21.46 ($COCH_3$); 24.24 ($SiC(CH_3)_3$); 27.19, 29.99 (CH_2-6', CH_2-7'); 41.20 (2*) (CH_2-2', CH_2-4'); 53.74 (CH-2^E); 60.79, 63.05 (CH_2-6^E, CH_2-1'); 67.67, 69.73, 70.41, 71.93, 75.58 (2*), 77.49 (CH-2^F, CH-3^F, CH-4^F, CH-5^F, CH-3^E, CH-4^E, CH-5^E); 99.18, 100.18 (CH-1^F, CH-1^E); 155.71 (3^F-$OCONH_2$); 167.95, 168.74, 168.80, 168.90, 169.06 (C-6^F, $COCH_3$); 206.93 (C-3'). - $C_{36}H_{61}N_3O_{16}Si$ (819.98, 819.38). - FAB MS: m/z 842.4 ($[M+Na]^+$), 820.4 ($[M+H]^+$), 762.3 ($[M+H-HC(CH_3)_3]^+$), 330.1 ($[e]^+$).

Acknowledgements - Financial support by the Deutsche Forschungsgemeinschaft Innovationskolleg „Chemisches Signal und biologische Antwort"), the Fonds der Chemischen Industrie, and the Freistaat Sachsen (Graduiertenstipendium to D.W.) is gratefully acknowledged.

REFERENCES AND NOTES

1 Ritzeler, O.; Hennig, L.; Findeisen, M.; Welzel, P.; Müller, D.; Markus, A.; Lemoine, G.; Lampilas, M.; van Heijenoort, J. *Tetrahedron* **1997**, *53*, 1675-1694, and references therein.

2 Van Heijenoort, J.; van Heijenoort, Y.; Welzel, P. in „Antibiotic Inhibition of Bacterial Cell Surface Assembly and Function", eds. Actor P.; Daneo-Moore, L.; Higgins, M.L.; Salton, M.R.J.; Shockman, G.D., American Society for Microbiology, Washington 1988, p.549-557.

3 Fehlhaber, H.-W.; Girg, M.; Seibert, G.; Hobert, K.; Welzel, P.; van Heijenoort, Y.; van Heijenoort, J. *Tetrahedron* **1990**, *46*, 1557-1568, and references therein.

4 Heuer, M.; Hohgardt, K.; Heinemann, F.; Kühne, H.; Dietrich, W.; Grzelak, D.; Müller, D.; Welzel, P.; Markus, A.; van Heijenoort, Y.; van Heijenoort, J. *Tetrahedron* **1994**, *50*, 2029-2046

5 Heuer, M. *Dissertation*, Bochum **1993**.

6 Schmidt, R.R.; Stumpp, M. *Liebigs Ann.Chem.* **1983**, 1249-1254

7 Takano, T.; Nakatsubo, F.; Murakami, K. *Carbohydr. Res.* **1990**, *203*, 341-342.

8 Kitching, W.; Lewis, J. A.; Perkins, M. V.; Drew, R.; Moore, C. J.; Schurig, V.; König, W. A.; Francke, W. *J. Org. Chem.* **1989**, *54*, 3893-3902

9 Schick, H.; Pogoda, B.; Schwarz, S. *Z. Chem.* **1982**, *22*, 185.

10 The concentration was about 0.2 M.

11 Weigelt, D.; Kraehmer, R.; Welzel, P. *Tetrahedron Lett.* **1996**, *37*, 367-370.

12 Mereyala, H.B.; Gurrala, S.R. *Carbohydr. Res.* **1998**, *307*, 351-354.

13 Zemplén, G.; Pacsu, E. *Ber. Dtsch. Chem. Ges.* **1929**, *62*, 1613-1614.

14 Evans, M.E. *Carbohydr. Res.* **1972**, *21*, 473-475.

15 See, Möller, U.; Hobert, K.; Donnerstag, A.; Wagner, P.; Müller, D.; Fehlhaber, H.-W.; Markus, A.; Welzel, P. *Tetrahedron* **1993**, *49*, 1635-1648 , and references therein.

16 Review: Banoub, J.; Boullanger, P.; Lafont, D. *Chem. Rev.* **1992**, *92*, 1167-1195.

17 For leading references, see Möller et al., ref.[13]

18 Peters, U.; Bankova, W.; Welzel, P. *Tetrahedron* **1987**, *43*, 3803-3816.

19 Halmos, T.; Montserret, R.; Filippi, J.; Antonakis, K. *Carbohydr. Res.* **1987**, *170*, 57-69.

20 Corey, E.J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190-6191.

21 Frigerio, M.; Santagostino, M. *Tetrahedron Lett.* **1994**, *35*, 8019-8022.

22 Bal, B.S.; Childers, Jr., W.E.; Pinnick, H.W. *Tetrahedron* **1981**, *37*, 2091-2096.

23 We used a protocol published by Jansen, R.; Schummer, D.; Irschik, H.; Höfle, G. *Liebigs Ann. Chem.* **1990**, 975-988, see also Heuer et al.[4]

24 Attempts to perform the oxidation with a free 4-OH group or a 4-O-acetyl protecting group met with no success. Rather than yielding the desired compound an elimination reaction took place leading to hex-4-ene-pyranoside derivatives: Weigelt, D., *Dissertation*, Leipzig 1996.

25 Brüschke, K., *Diploma Thesis*, Leipzig 1997.

26 In the case of diol **11a** some methanol had to be added.

27 Kritchevsky, D.; Kirk, M.R.; *Arch.Biochem.Biophys.* **1952**, *35*, 346-351.

28 Still, W.C., Kahn, M.; Mitra, A. *J.Org.Chem.* **1978**, *43*, 2923-2925.

29 Nakabayashi, S.; Warren, C.D.; Jeanloz, R.W. *Carbohydr. Res.* **1986**, *150*, C7-C10.