

113. Synthesis of Allosamidin

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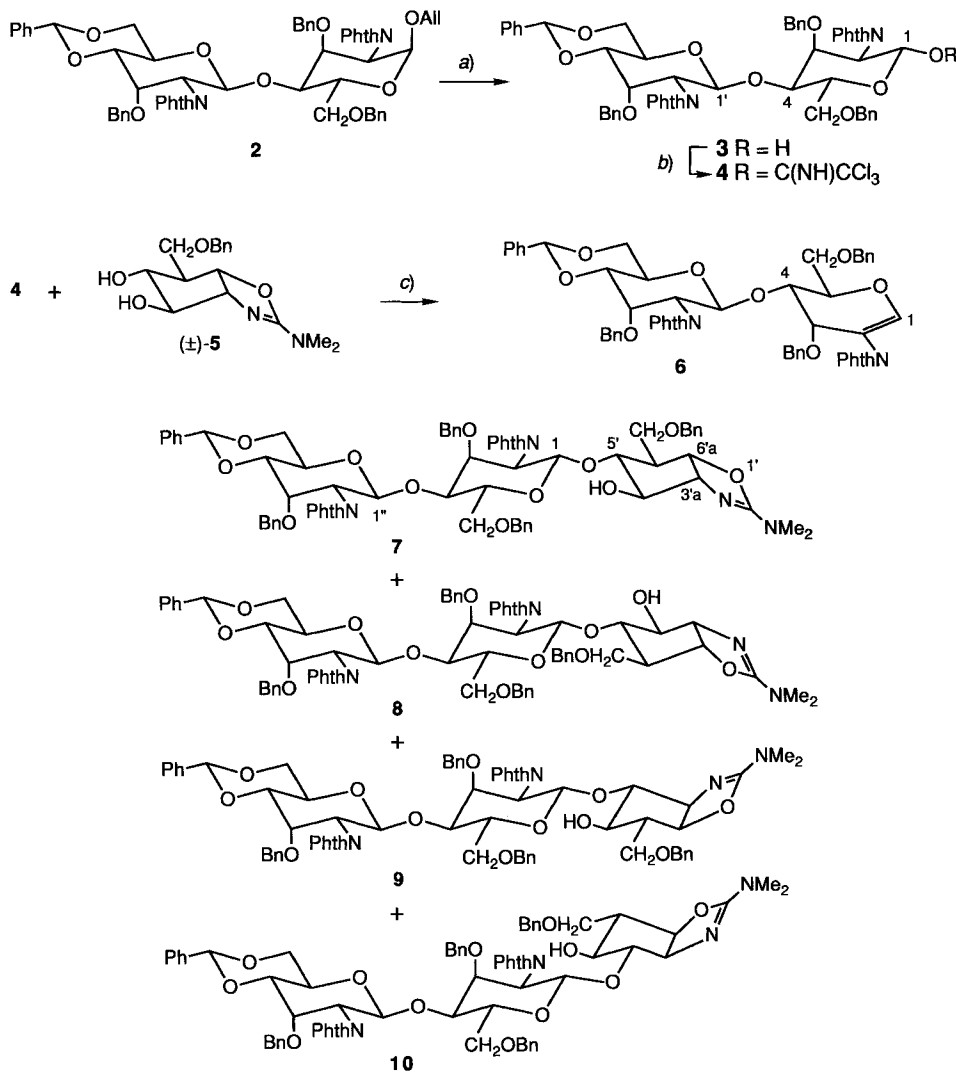
The previously prepared disaccharide **2** was deprotected ($\rightarrow$ **3**) and transformed into the trichloroacetimidate **4**. In the presence of Me_3SiOTf , **4** reacted regioselectively with the racemic allosamizoline benzyl ether **5**, to yield (61%) the pseudotrisaccharides **7–10** (44:40:9:7) and the elimination product **6** (*Scheme 1*). Selective dephthaloylation (MeNH_2 , MeOH) of **7** and **8**, followed by acetylation, gave **12** (73%) and **13** (74%), respectively (*Scheme 2*); harsher conditions ($\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$, EtOH , reflux), followed by acetylation, transformed **7** into **11**. Deacetylation of **11–13** yielded **14–16**, respectively. Allosamidin (**1**) was obtained in high yield by hydrogenation of **15** under acidic conditions (*Scheme 3*). Similarly, **16** and **14** were transformed into **17** and **18**, respectively. Preliminary data on the inhibition of endochitinases by **1** and **17** are reported.

Introduction. – In the preceding paper [1], we have described the synthesis of the protected disaccharide **2** (*Scheme 1*), corresponding to the disaccharide moiety of allosamidin (**1**), the first representative of a new class of endochitinase inhibitors. Here, we report on the synthesis of allosamidin and of two new analogues, **17** and **18** (see *Scheme 3*). The synthesis is based on the regioselective glycosidation of the partially protected racemate ($\pm$)-**5** [2], corresponding to allosamizoline, the aglycon of allosamidin.

Results and Discussion. – The best results in the glycosidation leading to **2** had been realized with the trichloroacetimidate method [3]. For this reason, we chose the trichloroacetimidate **4** (*Scheme 1*) as the glycosyl donor which was obtained in high yield from the allyl glycoside **2** after usual deprotection [4] ($\rightarrow$ **3**) and reaction with CCl_3CN and K_2CO_3 in CH_2Cl_2 . In keeping with previous results [1], we obtained exclusively the β -D-anomers of the hemiacetal **3** and the imidate **4**.

Glycosidation by **4** of the partially protected racemate ($\pm$)-**5** [2], promoted by Me_3SiOTf , afforded the four pseudotrisaccharides **7/8/9/10** in an overall yield of 61% and in a ratio of 44:40:9:7. No α -D-glycosides and only traces of pseudopentasaccharides were obtained. The main by-product was the aminoglycal **6**. Similar elimination products have been isolated in the synthesis of **2** [1]. The regioselectivity of the glycosidation (5:1) was as expected, favouring $\text{OH}-\text{C}(5')$, which possesses only one vicinal, electronegative substituent, while $\text{OH}-\text{C}(4')$ possesses two such neighbours. One of them is part of the dihydro-oxazole moiety, which may react with Me_3SiOTf , leading to a further decrease of electron density at $\text{OH}-\text{C}(4')$ and of its nucleophilic character. An attempt to increase the selectivity of the glycosidation by performing it at -30° only lowered the overall yield. Determination of the absolute configuration of the allosamizoline moiety of the pairs of diastereoisomers **7/8** and **9/10** was impossible at this stage and had to be derived from the conversion of **7** to **1**.

Scheme 1



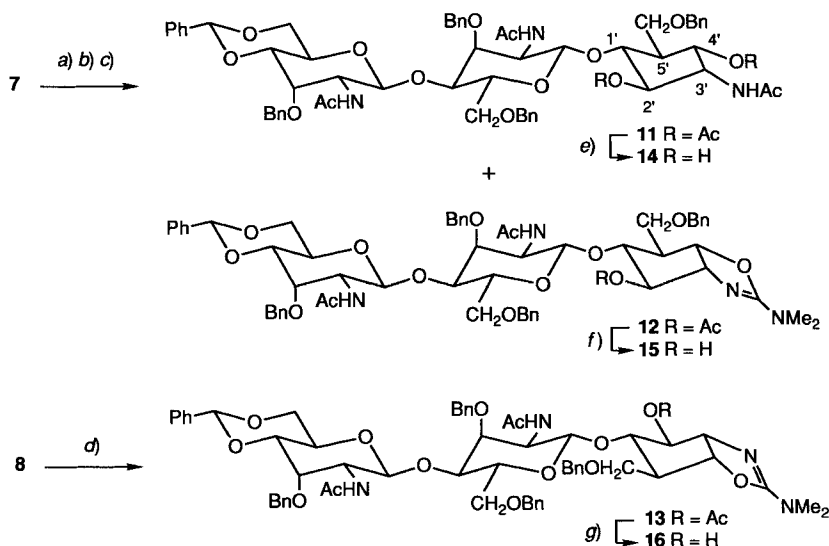
a) 1. (Cycloocta-1,5-diene)bis(methyldiphenylphosphine)iridium hexafluorophosphate, H₂, THF, 3 h, r.t.; 2. HgO, HgCl₂, acetone/H₂O 9:1, 1 h, r.t.; 75%. b) CCl₃CN, K₂CO₃, CH₂Cl₂, 16 h, r.t.; 90%. c) Me₃SiOTf, 4-Å molecular sieves, CH₂Cl₂, 20 min, 0°; 6, 17%; 7, 27%; 8, 24.5%; 9 and 10, 5.5 and 4.3% (or vice versa).

The OH group of the hemiacetal 3 absorbs at 3590 cm⁻¹. In the ¹H-NMR spectrum of 3, H-C(1) resonates at 6.20 ppm as a *dd* (*J*(1,2) = 8.6 Hz, *J*(1,OH-C(1)) = 5.3 Hz). The imino group of 4 is characterized by IR bands at 3330 cm⁻¹ (NH) and at 1675 cm⁻¹ (C=N). NH resonates at 8.66 and H-C(1) at 7.15 ppm (*d*, *J*(1,2) = 9.1 Hz). H-C(1) of 6 appears as a *s* at 6.59 ppm. The ¹³C-NMR spectrum of 6 is characterized by the downfield shift of C(1) (*d*, 145.6 ppm) and of C(2) (*s*, 107.8 ppm). The OH group of 7 and of 8 absorbs at 3480 and 3520 cm⁻¹, respectively. The NMR spectra of 7 and 8 both exhibit the characteristic signals of the aminocyclitol (±)-5: H-C(6'a) resonates at low field (4.64 ppm for 7, 4.66 ppm for 8) and is characterized by a large coupling constant with H-C(3'a)

($J(3'a,6'a) = 9.2$ Hz for **7** and **8**); H-C(5') resonates at high field (2.08 ppm for **7**, 2.13 ppm for **8**) as a *m*; the signals of Me₂N appear at 2.84 and 2.80 ppm for **7** and **8**, respectively; C(2') resonates at low field (161.4 ppm for **7**, 161.7 ppm for **8**). In the ¹H-NMR spectrum of **7**, H-C(1) resonates at 5.95 ppm as a *d* with $J(1,2) = 8.7$ Hz, typical for a 1,2-*trans*-configured glycosidic bond. OH-C(4') resonates at 4.54–4.49 ppm and H-C(4') at 3.87 ppm as a *m* which is transformed into a *dd* after exchange with D₂O. In the ¹H-NMR spectrum of **8**, the signal of H-C(1) is a *d* at 5.99 ppm ($J(1,2) = 8.7$ Hz). The signal of OH-C(4') appears at 4.51–4.44 ppm. It disappears upon addition of D₂O, and the signal of H-C(4') is simplified (*ddd* → *dd*). The chemical shifts of H-C(1), H-C(1'), H-C(3), and H-C(3') of **7** and **8** are in agreement with a conformation of the 2- and 2'-phthalimido group analogous as the one observed for the 2-phthalimido-β-D-allopyranosides [1]. Similarly to **2**, the 2 H-C(6) signals of **8** appear at high field (3.53 and 3.45 ppm). The shielding effect, which may be due to the 2'-phthalimido group, is even stronger for the 2 H-C(6) signals of **7** (3.35 and 3.19 ppm). This indicates a conformation of the disaccharide moiety of **7** and **8** which is similar to the one of **2** [1]. The signals for the 2 CH-C(6') are slightly shifted for **8** (3.64 and 3.48 ppm vs. 3.70 and 3.65 ppm in (±)-**5**) and more strongly shifted for **7** (3.41 and 3.33 ppm). An unambiguous determination of the conformation of the glycosidic bond between the disaccharide moiety and the allosamizoline moiety was, however, not possible, as these chemical-shift differences may be due to the 6-*O*-benzyl group, or to the 2-phthalimido group. For **7** and **8**, NOE's between H-C(1') and H-C(5') and between H-C(1') and H-C(4) (same intensity) confirm previous observations [1] and suggest that the torsion angles Ψ (H-C(1')-O-C(4)) and Ψ (H-C(4)-O-C(1')) of the glycosidic bond of the disaccharide moiety are *ca.* 0 and -30°, respectively. For both diastereoisomers, no NOE was observed between H-C(1) and any protons of the aminocyclitol moiety.

Dephtaloylation of **7** and **8** was the critical step in the sequence of deprotection and *N*-acetylation, as mild conditions were necessary to avoid concomitant hydrolysis of the dihydro-oxazole group. Moreover, the progression of the reaction was difficult to follow, as the intermediates, the side products, and the desired diamines had similar *R_f* values. In a first attempt, **7** was treated for 4 h with excess NH₂NH₂ · H₂O in refluxing EtOH [5] and then acetylated. This gave the triacetamide **11** (Scheme 2) in 61%. Using only 2 equiv. of

Scheme 2

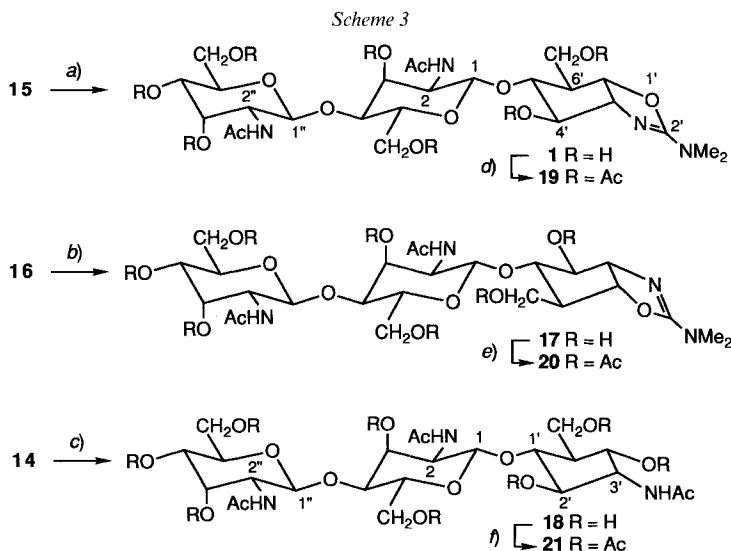


a) 1. NH₂NH₂ · H₂O, EtOH, 4 h, reflux; 2. pyridine, Ac₂O, 4-(Me₂N)C₅H₄N, 10 h, r.t.; **11**, 61%. b) 1. NH₂NH₂ · H₂O, EtOH, 45 min, reflux; 2. pyridine, Ac₂O, 4-(Me₂N)C₅H₄N, 10 h, r.t.; **11**, 12%; **12**, 17%. c) 1. 40% aq. MeNH₂, MeOH, 48 h, r.t.; 2. pyridine, Ac₂O, 4-(Me₂N)C₅H₄N, 10 h, r.t.; **12**, 73%. d) As c); **13**, 74%. e) NaOMe, MeOH, 10 h, r.t., 97%. f) NaOMe, MeOH, 5 h, r.t., 96%. g) NaOMe, MeOH, 5 h, r.t., 93%.

$\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$ and shortening the reaction time to 45 min, led, after acetylation, in low yields to the diacetamide **12** and to **11**. The use of hydrazine acetate [6] gave complex mixtures. Treatment of **7** with BuNH_2 in refluxing MeOH [7], followed by acetylation, yielded inseparable mixtures of the desired **12** and *N*-butylphthalamide derivatives. The desired bis-acetamide **12** was finally obtained (73 %) by effecting the dephthaloylation with aq. MeNH_2 in EtOH [8], followed by acetylation. The diastereoisomer **8** was treated similarly to yield 74 % of **13**. Deacetylation under *Zemplén* conditions of **11**, **12**, and **13** gave **14**, **15**, and **16**, respectively, in high yields.

The IR spectra of **11**–**13** show the disappearance of the strong phthalimido band at 1720 cm^{-1} . In the ^1H -NMR spectrum of **11**, $\text{NH}-\text{C}(3')$ appears at 6.01 ppm ($J(\text{NH}, 3') = 8.8\text{ Hz}$), while $\text{NH}-\text{C}(2'')$ and $\text{NH}-\text{C}(2)$ resonate at 5.82 and 5.51 ppm. The $\text{H}-\text{C}(4')$ signal appears at 5.33 ppm (shifted upfield by 1.3 ppm as compared to $\text{H}-\text{C}(3'a)$ of **7**). The 5 Ac groups give rise to *s* at 2.05, 1.99, 1.96, 1.62, and 1.55 ppm. In the ^{13}C -NMR, there are 5*s* in the typical $\text{C}=\text{O}$ region, and 5*q* between 23 and 20.8 ppm, characteristic for *MeCO*. The ^1H -NMR spectra of **12** and **13** exhibit the typical signal of Me_2N (2.90 ppm for **12** and 2.89 ppm for **13**), the high-field resonance of $\text{H}-\text{C}(4')$ (5.26 ppm for **12** and 5.10 ppm for **13**) confirming the regioselectivity of the glycosidation, and 3*s* for the Ac groups. The $\text{C}(2')$ signals of **12** and **13** appear as *s* at 161.7 and 161.9 ppm, respectively, and $(\text{CH}_3)_2\text{N}$ resonates at 37.6 (**12**) and 37.5 ppm (**13**).

Hydrogenolysis of **15** under acidic conditions yielded allosamidin (**1**) (*Scheme 3*) in 95 % yield. Similarly, **16** was deprotected to give the diastereoisomer **17**. Hydrogenolysis of **14**, albeit more sluggish, afforded **18**, equally in high yield. The spectroscopic data of the synthetic allosamidin (**1**) were in agreement with the one reported by *Sakuda et al.* [9] and could not be distinguished from those of an authentic sample¹⁾. Allosamidin (**1**) and the two analogues **17** and **18** were peracetylated to **19**, **20**, and **21**, respectively. The



a) H_2 (7 bar), 10% Pd/C , MeOH/AcOH 9:1, 36 h, r.t.; 95%. b) As a); 95%. c) H_2 (7 bar), 10% Pd/C , MeOH/AcOH 9:1, 72 h, r.t.; 92%. d) Pyridine, Ac_2O , $4-(\text{Me}_2\text{N})\text{C}_3\text{H}_4\text{N}$, 14 h, r.t.; 97%. e) As d); 96%. f) As d); 97%.

¹⁾ We thank *Lilly Research Laboratories, Eli Lilly & Co.*, Indianapolis, Indiana 46285, USA, for providing an authentic sample of allosamidin.

spectroscopic data of **19** could again not be distinguished from those of a similarly prepared acetate of authentic allosamidin. The ^1H -NMR data of **1**, **17**, and **18** are collected and assigned in *Table 1*, the ^1H -NMR data of their peracetates **19–21** in *Table 2*, and the ^{13}C -NMR data of **1** and **17–21** in *Table 3*.

Table 1. ^1H -NMR ($\text{D}_2\text{O}/0.3\% \text{CD}_3\text{CO}_2\text{D}$) Data for **1**, **17**, and **18**. δ in ppm, J in Hz.

	1	17	18
H–C(6'a) ^a or –C(4') ^b	5.44 (<i>dd</i> , $J = 5, 9$)	5.45 (<i>dd</i> , $J = 5, 9$)	4.02 (<i>dd</i> , $J = 3, 6$)
H–C(3'a) ^a or –C(3') ^b	4.44 (<i>dd</i> , $J = 4, 9$)	4.42 (<i>dd</i> , $J = 4, 9$)	3.94 (<i>dd</i> , $J = 6, 10$)
H–C(4') ^a or –C(2') ^b	4.35 (<i>dd</i> , $J = 4, 6$)	4.2 (<i>dd</i> , $J = 4, 6$)	4.17 (<i>dd</i> , $J = 7, 10$)
H–C(5') ^a or –C(1') ^b	3.94 (<i>dd</i> , $J = 6, 7$)	4.07 (<i>dd</i> , $J = 6, 7$)	3.79 (<i>dd</i> , $J = 6, 7$)
H–C(6') ^a or –C(5') ^b	2.61 (<i>m</i>)	2.65 (<i>m</i>)	2.01 (<i>m</i>)
CH–C(6') ^a or –C(5') ^b	3.87 (<i>dd</i> , $J = 5, 12$); 3.74 (<i>dd</i> , $J = 7, 12$)	3.94 (<i>dd</i> , $J = 5, 12$); 3.82 (<i>dd</i> , $J = 7, 12$)	3.75 (<i>dd</i> , $J = 5, 12$); 3.69 (<i>dd</i> , $J = 6, 12$)
Me ₂ N	3.15, 3.14 (2 <i>s</i>)	3.15, 3.13 (2 <i>s</i>)	–
H–C(1)	4.85 (<i>d</i> , $J = 9$)	4.85 (<i>d</i> , $J = 9$)	4.86 (<i>d</i> , $J = 9$)
H–C(2)	3.91 (<i>dd</i> , $J = 3, 9$)	3.87 (<i>dd</i> , $J = 3, 9$)	3.95 (<i>dd</i> , $J = 3, 9$)
H–C(3)	4.41 (<i>t</i> , $J = 3$)	4.41 (<i>t</i> , $J = 3$)	4.42 (<i>t</i> , $J = 3$)
H–C(4)	3.79 (<i>dd</i> , $J = 3, 10$)	3.80 (<i>dd</i> , $J = 3, 10$)	3.80 (<i>dd</i> , $J = 3, 10$)
H–C(5)	3.96 (<i>ddd</i> , $J = 2, 7, 10$)	3.91 (<i>ddd</i> , $J = 2, 6, 10$)	3.93 (<i>ddd</i> , $J = 2, 7, 10$)
H–C(6)	3.88 (<i>dd</i> , $J = 2, 12$), 3.68 (<i>dd</i> , $J = 7, 12$)	3.86 (<i>dd</i> , $J = 2, 12$), 3.69 (<i>dd</i> , $J = 6, 12$)	3.85 (<i>dd</i> , $J = 2, 12$), 3.67 (<i>dd</i> , $J = 7, 12$)
H–C(1'')	4.87 (<i>d</i> , $J = 9$)	4.92 (<i>d</i> , $J = 9$)	4.85 (<i>d</i> , $J = 9$)
H–C(2'')	3.95 (<i>dd</i> , $J = 3, 9$)	3.95 (<i>dd</i> , $J = 3, 9$)	3.93 (<i>dd</i> , $J = 3, 9$)
H–C(3'')	4.12 (<i>t</i> , $J = 3$)	4.11 (<i>t</i> , $J = 3$)	4.10 (<i>t</i> , $J = 3$)
H–C(4'')	3.75 (<i>dd</i> , $J = 3, 10$)	3.75 (<i>dd</i> , $J = 3, 10$)	3.74 (<i>dd</i> , $J = 3, 10$)
H–C(5'')	3.83 (<i>ddd</i> , $J = 2, 5, 10$)	3.83 (<i>ddd</i> , $J = 2, 5, 10$)	3.83 (<i>ddd</i> , $J = 2, 5, 10$)
H–C(6'')	3.92 (<i>dd</i> , $J = 2, 12$), 3.80 (<i>dd</i> , $J = 5, 12$)	3.92 (<i>dd</i> , $J = 2, 12$), 3.79 (<i>dd</i> , $J = 5, 12$)	3.91 (<i>dd</i> , $J = 2, 12$), 3.79 (<i>dd</i> , $J = 5, 12$)
Ac	2.15, 2.13 (2 <i>s</i>)	2.13, 2.11 (2 <i>s</i>)	2.12 (<i>s</i>); 2.10 (2 <i>s</i>)

^a) For **1** and **17**. ^b) For **18**.

Table 2. ^1H -NMR (CDCl_3) Data for **19–21**. δ in ppm, J in Hz.

	19	20	21
H–C(6'a) ^a or –C(4') ^b	4.76 (<i>dd</i> , $J = 6, 9$)	4.82 (<i>dd</i> , $J = 5, 9$)	4.96 (<i>dd</i> , $J = 3, 6$)
H–C(3'a) ^a or –C(3') ^b	4.27 (<i>dd</i> , $J = 4, 9$)	4.39 (<i>dd</i> , $J = 3, 9$)	4.37 (<i>td</i> , $J = 6, 9$)
H–C(4') ^a or –C(2') ^b	5.23 (<i>dd</i> , $J = 4, 7$)	5.18 (<i>dd</i> , $J = 3, 5$)	5.38 (<i>dd</i> , $J = 7, 9$)
H–C(5') ^a or –C(1') ^b	3.81 (<i>dd</i> , $J = 7, 9$)	4.03–3.94 (<i>m</i>)	3.82 (<i>t</i> , $J = 7$)
H–C(6') ^a or –C(5') ^b	2.5 (<i>m</i>)	2.54 (<i>m</i>)	2.28 (<i>m</i>)
CH–(6') ^a or –C(5') ^b	4.41 (<i>dd</i> , $J = 5, 12$); 4.23–4.17 (<i>m</i>)	4.26 (<i>dd</i> , $J = 5, 12$); 4.19–4.05 (<i>m</i>)	4.42 (<i>dd</i> , $J = 5, 11$); 4.23–4.07 (<i>m</i>)
NH–C(3')	–	–	5.96 (<i>d</i> , $J = 9$)
Me ₂ N	2.92 (<i>s</i>)	2.91 (<i>s</i>)	–
H–C(1)	4.75 (<i>d</i> , $J = 8$)	4.66 (<i>d</i> , $J = 9$)	4.62 (<i>d</i> , $J = 8$)
H–C(2)	4.09–4.01 (<i>m</i>)	3.89 (<i>td</i> , $J = 8, 3$)	4.23–4.07 (<i>m</i>)
H–C(3)	5.65 (<i>t</i> , $J = 3$)	5.77 (<i>t</i> , $J = 3$)	5.63 (<i>br. s</i>)
H–C(4)	3.62 (<i>dd</i> , $J = 3, 8$)	3.53 (<i>dd</i> , $J = 3, 10$)	3.59 (<i>dd</i> , $J = 3, 9$)
H–C(5)	3.99–3.92 (<i>m</i>)	3.86 (<i>td</i> , $J = 3, 10$)	3.89 (<i>td</i> , $J = 3, 9$)
H–C(6)	4.58 (<i>dd</i> , $J = 4, 12$); 4.09–4.01 (<i>m</i>)	4.62 (<i>dd</i> , $J = 3, 12$); 4.03–3.94 (<i>m</i>)	4.66 (<i>dd</i> , $J = 3, 12$); 3.99–3.94 (<i>m</i>)

Table 2 (cont.)

	19	20	21
NH–C(2)	6.35 (<i>d</i> , <i>J</i> = 8)	6.80 (<i>d</i> , <i>J</i> = 7)	6.14 (<i>d</i> , <i>J</i> = 9)
H–C(1'')	4.53 (<i>d</i> , <i>J</i> = 9)	4.56 (<i>d</i> , <i>J</i> = 9)	4.51 (<i>d</i> , <i>J</i> = 8)
H–C(2'')	4.23–4.17 (<i>m</i>)	3.95 (<i>dd</i> , <i>J</i> = 3, 9)	4.23–4.07 (<i>m</i>)
H–C(3'')	5.53 (<i>t</i> , <i>J</i> = 3)	5.62 (<i>t</i> , <i>J</i> = 3)	5.53 (<i>t</i> , <i>J</i> = 3)
H–C(4'')	4.85 (<i>dd</i> , <i>J</i> = 3, 10)	4.84 (<i>dd</i> , <i>J</i> = 3, 10)	4.87 (<i>dd</i> , <i>J</i> = 3, 10)
H–C(5'')	3.99–3.92 (<i>m</i>)	4.03–3.94 (<i>m</i>)	3.99–3.94 (<i>m</i>)
H–C(6'')	4.13 (<i>dd</i> , <i>J</i> = 5, 12); 4.09–4.01 (<i>m</i>)	4.19–4.05 (<i>m</i>); 4.19–4.05 (<i>m</i>)	4.23–4.07 (<i>m</i>); 4.23–4.07 (<i>m</i>)
NH–C(2'')	6.27 (<i>d</i> , <i>J</i> = 9)	6.33 (<i>d</i> , <i>J</i> = 9)	6.29 (<i>d</i> , <i>J</i> = 8)
Ac	2.18, 2.15, 2.12, 2.11, 2.09, 2.07, 1.97, 1.96, 1.93 (9s)	2.17, 2.15, 2.11, 2.10, 2.09, 2.07, 1.96, 1.95, 1.91 (9s)	2.18, 2.17, 2.15, 2.11, 2.10, 2.09 (6 H), 1.98, 1.97 (6 H), 1.96 (9s)

a) For **19** and **20**. b) For **21**.Table 3. ¹³C-NMR Assignments of **1** and **17–21**. δ in ppm.

	1 ^{c)}	17 ^{c)}	18 ^{c)}	19 ^{d)}	20 ^{d)}	21 ^{d)}
C(6'a ^{a)} or C(4' ^{b)})	87.7 (<i>d</i>)	88.5 (<i>d</i>)	69.9 (<i>d</i>)	80.3 (<i>d</i>)	81.8 (<i>d</i>)	72.6 (<i>d</i>)
C(3'a ^{a)} or C(3' ^{b)})	65.1 (<i>d</i>)	65.5 (<i>d</i>)	56.7 (<i>d</i>)	71.5 (<i>d</i>)	71.9 (<i>d</i>)	59.2 (<i>d</i>)
C(4' ^{a)} or C(2' ^{b)})	81.3 (<i>d</i>)	81.9 (<i>d</i>)	78.2 (<i>d</i>)	81.7 (<i>d</i>)	84.9 (<i>d</i>)	78.2 (<i>d</i>)
C(5' ^{a)} or C(1' ^{b)})	85.9 (<i>d</i>)	84.5 (<i>d</i>)	85.3 (<i>d</i>)	81.1 (<i>d</i>)	80.9 (<i>d</i>)	80.8 (<i>d</i>)
C(6' ^{a)} or C(5' ^{b)})	52.3 (<i>d</i>)	52.0 (<i>d</i>)	52.8 (<i>d</i>)	48.9 (<i>d</i>)	48.8 (<i>d</i>)	48.8 (<i>d</i>)
CH ₂ –C(6' ^a) or –C(5' ^{b)})	60.1 (<i>t</i>)	60.1 (<i>t</i>)	61.7 (<i>t</i>)	61.1 (<i>t</i>)	61.5 (<i>t</i>)	62.4 (<i>t</i>)
C(2'') ^{a)}	161.4 (<i>s</i>)	161.5 (<i>s</i>)	–	161.8 (<i>s</i>)	161.7 (<i>s</i>)	–
Me ₂ N	38.4, 38.2 (2 <i>q</i>)	38.6, 38.4 (2 <i>q</i>)	–	37.7 (2 <i>q</i>)	37.8 (2 <i>q</i>)	–
C(1)	100.7 (<i>d</i>)	100.4 (<i>d</i>)	100.2 (<i>d</i>)	97.7 (<i>d</i>)	97.6 (<i>d</i>)	99.9 (<i>d</i>)
C(2)	53.4 (<i>d</i>)	53.5 (<i>d</i>)	53.4 (<i>d</i>)	51.4 (<i>d</i>)	52.1 (<i>d</i>)	50.9 (<i>d</i>)
C(3)	69.8 (<i>d</i>)	69.9 (<i>d</i>)	69.8 (<i>d</i>)	69.3 (<i>d</i>)	69.7 (<i>d</i>)	69.8 (<i>d</i>)
C(4)	77.7 (<i>d</i>)	77.5 (<i>d</i>)	75.8 (<i>d</i>)	74.2 (<i>d</i>)	74.3 (<i>d</i>)	73.9 (<i>d</i>)
C(5)	73.4 (<i>d</i>)	73.6 (<i>d</i>)	73.3 (<i>d</i>)	71.9 (<i>d</i>)	71.7 (<i>d</i>)	72.2 (<i>d</i>)
C(6)	61.8 (<i>t</i>)	61.8 (<i>t</i>)	61.8 (<i>t</i>)	62.6 (<i>t</i>)	62.5 (<i>t</i>)	62.4 (<i>t</i>)
C(1'')	101.4 (<i>d</i>)	101.4 (<i>d</i>)	101.4 (<i>d</i>)	100.1 (<i>d</i>)	99.9 (<i>d</i>)	100.2 (<i>d</i>)
C(2'')	53.7 (<i>d</i>)	53.8 (<i>d</i>)	53.7 (<i>d</i>)	50.7 (<i>d</i>)	50.9 (<i>d</i>)	50.7 (<i>d</i>)
C(3'')	70.9 (<i>d</i>)	71.0 (<i>d</i>)	70.9 (<i>d</i>)	70.0 (<i>d</i>)	70.0 (<i>d</i>)	69.9 (<i>d</i>)
C(4'')	67.2 (<i>d</i>)	67.3 (<i>d</i>)	67.2 (<i>d</i>)	66.5 (<i>d</i>)	66.5 (<i>d</i>)	66.5 (<i>d</i>)
C(5'')	74.4 (<i>d</i>)	74.4 (<i>d</i>)	74.4 (<i>d</i>)	70.1 (<i>d</i>)	70.2 (<i>d</i>)	70.1 (<i>d</i>)
C(6'')	61.8 (<i>t</i>)	61.8 (<i>t</i>)	61.7 (<i>t</i>)	62.6 (<i>t</i>)	62.0 (<i>t</i>)	62.2 (<i>t</i>)
MeCO	174.8 174.6 (2 <i>s</i>)	174.9, 174.7 (2 <i>s</i>)	175.1, 174.8, 174.6 (3 <i>s</i>)	171.5, 171.1, 171.0, 170.2, 170.0, 169.8, 169.6, 169.2, 169.1 (9 <i>s</i>)	^{c)}	^{c)}
MeCO	22.8 (<i>q</i>)	23.0, 22.9 (2 <i>q</i>)	22.9, 22.8, 22.7 (3 <i>q</i>)	23.0, 22.9, 21.2, 21.1, 21.0, 20.9, 20.8, 20.7, 20.5 (9 <i>q</i>)	23.0 (2 <i>q</i>); 21.1–20.5 (several <i>q</i>)	23.0 (2 <i>q</i>); 21.1–20.5 (several <i>q</i>)

a) For **1**, **17**, **19**, and **20**. b) For **18** and **21**. c) In D₂O/0.3% CD₃CO₂. d) In CDCl₃. e) Not measured.

Allosamidin (**1**) inhibited *Artemia salina* endochitinase to 84% (0.25 μM final conc.) and the *Streptomyces* enzyme to about the same extent as determined by Koga *et al.* [10]. The diastereoisomer **17** inhibited *Artemia salina* endochitinase to 62% (0.25 μM final conc.), but had no effect on the *Streptomyces* enzyme [11].

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Experimental Part

General. See [1]. TLC: imidate **4** was detected by spraying the plates with a 2% 4-(4-nitrobenzyl)pyridine soln. in acetone and heating at 100° [12]. ¹H-NMR Spectra: in D₂O, DHO (δ 4.8 ppm) as internal standard; in ambiguous cases, assignments by selective homonuclear decoupling experiments, 1D-TOCSY [13], or ¹H,¹H-TOCSY (¹H, 400 or 600 MHz) with various mixing times; coupling constants *J*(H,H) of **1**, **17**, and **18** from *J*-resolved 2D spectra. ¹³C-NMR Spectra: in D₂O, dioxane (δ 67.4 ppm) as external reference; assignments by ¹H,¹³C-HMQC spectra (¹H, 400 or 600 MHz) [14]. Mass spectra: FAB on a Varian-711 spectrometer, ESI (electrospray ionization [15]) on a Finnigan MAT TSQ 700 spectrometer.

3,6-Di-O-benzyl-4-O-(3-O-benzyl-4,6-O-benzylidene-2-deoxy-2-phthalimido- β -D-allopyranosyl)-2-deoxy-2-phthalimido- β -D-allopyranose (3). [Ir(cycloocta-1,5-diene)(PMePh₂)₂PF₆ (0.1 equiv.) was added under N₂ to a stirred soln. of **2** (3.618 g, 3.62 mmol) in dry THF (500 ml). The orange soln. was degassed and left under H₂ until the colour turned yellow (*ca.* 1 min). The soln. was then degassed again and left under N₂ for 3 h. Evaporation gave a foam which was dissolved in acetone (360 ml) and H₂O (40 ml). HgO (1.49 g, 6.88 mmol) and HgCl₂ (1.67 g, 6.14 mmol) were added. The mixture was stirred for 1 h and then filtered through *Celite*. The acetone was evaporated to give a suspension which was extracted with AcOEt. The org. layer was washed with sat. aq. KI soln. (2 $\times$) and H₂O, dried, and evaporated. FC (toluene/AcOEt 3:1) afforded **3** (2.61 g, 75%). White foam. *R*_f(toluene/AcOEt 4:1) 0.16. $[\alpha]_D^{25} = -127.8$ (*c* = 0.8, CHCl₃). IR (CHCl₃): 3590w, 3570w (sh), 3090w (sh), 3060w (sh), 3040w, 3000w, 1755m, 1720m (sh), 1710s, 1685w (sh), 1610w, 1490w, 1465w (sh), 1450w, 1380s, 1360m (sh), 1310m, 1260w, 1160m (sh), 1135m, 1005s (sh), 1075s (br.), 1040s, 1025s, 1010s (sh), 970m (sh), 915w, 895w, 860w. ¹H-NMR (400 MHz, CDCl₃): 7.78–7.63 (*m*, 8 arom. H); 7.53–7.50 (*m*, 2 arom. H); 7.43–7.38 (*m*, 3 arom. H); 7.29–7.19 (*m*, 5 arom. H); 7.09–7.06 (*m*, 4 arom. H); 6.99–6.76 (*m*, 5 arom. H); 6.27 (*d*, *J* = 8.5, H–C(1')); 6.20 (*dd*, *J* = 8.6, 5.3, with D₂O *d*, *J* = 8.6, H–C(1)); 5.56 (*s*, PhCH); 4.85 (*d*, *J* = 12.2, PhCH); 4.65 (*d*, *J* = 11.9, PhCH); 4.54–4.47 (*m*, 2 PhCH, H_{eq}–C(6')); 4.38 (*d*, *J* = 11.7, PhCH); 4.34 (*t*, *J* = 2.6, H–C(3')); 4.32 (*ddd* (= '*td*'), *J* = 10.0, 5.1, H–C(5')); 4.21–4.12 (*m*, PhCH, H–C(3), H–C(5), H–C(2')); 3.96 (*dd*, *J* = 10.0, 2.5, H–C(4)); 3.92 (*dd*, *J* = 8.7, 2.6, H–C(2)); 3.84 (*dd*, *J* = 9.4, 2.3, H–C(4)); 3.81 (*t*, *J* = 10.0, H_{ax}–C(6')); 3.55 (*dd*, *J* = 10.5, 6.6, H–C(6)); 3.49 (*dd*, *J* = 10.5, 2.0, H–C(6)); 3.26 (*d*, *J* = 5.3, exchange with D₂O, OH–C(1)). ¹³C-NMR (50 MHz, CDCl₃): 167.9 (*s*, 2 CO); 167.7 (*s*, CO); 167.5 (*s*, CO); 138.2 (*s*); 137.9 (*s*); 137.4 (*s*); 137.3 (*s*); 134.0 (*d*); 133.7 (*d*); 133.4 (*d*); 132.2 (*s*); 131.7 (*s*); 131 (*s*); 129.1–122.9 (*m*, arom. C); 102 (*d*, PhCH); 98.0 (*d*, C(1')); 90.4 (*d*, C(1)); 79.9 (*d*, C(4)); 76.8 (*d*); 76.5 (*d*); 74.1 (*d*, *t*, 2 C); 74.0 (*t*, PhCH₂); 72.9 (*t*, PhCH₂); 72.4 (*d*, C(5)); 70 (*t*, C(6)); 69.1 (*t*, C(6')); 64 (*d*, C(5')); 57.8 (*d*, C(2)); 56.8 (*d*, C(2)). Anal. calc. for C₅₆H₅₀N₂O₁₃ (959.017): C 70.14, H 5.26, N 2.92; found: C 70.36, H 4.99, N 2.82.

3,6-Di-O-benzyl-4-O-(3-O-benzyl-4,6-O-benzylidene-2-deoxy-2-phthalimido- β -D-allopyranosyl)-2-deoxy-2-phthalimido- β -D-allopyranosyl Trichloroacetimidate (4). CCl₃CN (1.37 ml, 13.61 mmol) and powdered anh. K₂CO₃ (1.81 g, 13.1 mmol) were added to a stirred soln. of **3** (2.61 g, 2.72 mmol) in CH₂Cl₂ (80 ml). After 16 h, the mixture was filtered through *Celite* and the filtrate evaporated. FC (AcOEt/hexane 2:5) gave **4** (2.7 g, 90%). Colourless oil. *R*_f(AcOEt/hexane 1:2) 0.22. IR (CHCl₃): 3330w, 3090w (sh), 3060w (sh), 3000w, 2920w, 2855w, 1775w, 1720m (sh), 1710s, 1675m, 1650w (sh), 1645w (sh), 1635w (sh), 1605w, 1585w, 1555w, 1490w, 1465w (sh), 1450w, 1380m, 1360m (sh), 1310m, 1260w, 1160m (sh), 1130m, 1095s (sh), 1065s (br.), 1040s (sh), 1000m (sh), 965m (sh), 910w, 890w, 870w, 830w. ¹H-NMR (400 MHz, CDCl₃): 8.66 (*s*, NH); 7.79–7.63 (*m*, 8 arom. H); 7.55–7.50 (*m*, 2 arom. H); 7.43–7.38 (*m*, 3 arom. H); 7.29–7.19 (*m*, 5 arom. H); 7.15 (*d*, *J* = 9.1, H–C(1)); 7.12–7.04 (*m*, 4 arom. H); 6.92–6.80 (*m*, 6 arom. H); 6.32 (*d*, *J* = 8.4, H–C(1')); 5.58 (*s*, PhCH); 4.87 (*d*, *J* = 12.1, PhCH); 4.70 (*d*, *J* = 11.9, PhCH); 4.57–4.49 (*m*, 3 PhCH, H_{eq}–C(6')); 4.41 (*dd* (= '*t*'), *J* $\approx$ 2.6, H–C(3')); 4.39 (*d*, *J* = 11.9, PhCH); 4.32 (*ddd* (= '*td*'), *J* = 10.1, 5.1, PhCH, H–C(5)); 4.28 (*dd*, *J* = 9.1, 2.6, H–C(2)); 4.28–4.24 (*m*, H–C(2'), H–C(5')); 4.21

(*dd* (= 't'), $J = 2.6$, H-C(3)); 4.19–4.16 (*m*, H-C(2'), H-C(4)); 3.86 (*dd*, $J = 9.6$, 2.3, H-C(4')); 3.83 (*t*, $J = 10.3$, H_{ax}-C(6')); 3.60 (*m*, 2 H-C(6)).

Glycosidation of (±)-5 by 4. A mixture of (±)-5 (586 mg, 1.9 mmol), **4** (2.1 g, 1.9 mmol), and 4-Å molecular sieves (500 mg) in CH₂Cl₂ (30 ml) was stirred at r.t. for 20 min. The suspension was cooled to 0° and treated with a soln. of Me₃Si-OTf (345 µl, 1.9 mmol) in CH₂Cl₂ (1 ml). After stirring for 20 min at 0°, TLC showed that **4** had disappeared. After addition of Et₃N (0.9 ml), the mixture was left for 10 min, filtered through *Celite*, and evaporated. The residue was dissolved in a minimum of CHCl₃ and adsorbed on silica gel. FC (CHCl₃/MeOH 99:1→90:10) gave **6** (304 mg, 17%), partially purified mixtures **9/7** (436 mg), **7/10** (458 mg), **10/8** (629 mg), and unreacted (±)-5 (70 mg, 12%). MPLC (CHCl₃/MeOH 97:3) of the mixtures of pseudotrisaccharides, yielded **9** (135 mg, 5.7%), **7** (640 mg, 27%), **10** (102 mg, 4.3%), and **8** (576 mg, 24.3%).

1,5-Anhydro-3,6-di-O-benzyl-4-O-(3-O-benzyl-4,6-O-benzylidene-2-deoxy-2-phthalimido-β-D-allopyranosyl)-2-deoxy-2-phthalimido-D-ribo-hex-1-enitol (6). R_f (toluene/AcOEt 10:1) 0.18. $[\alpha]_D^{25} = -28.4$ ($c = 0.8$, CHCl₃). IR (CHCl₃): 3080w (sh), 3060w (sh), 3000w, 2920w, 2860w, 1755w, 1715s, 1665w (sh), 1650w (sh), 1640w, 1600w, 1575w (sh), 1490w, 1465w (sh), 1450w, 1375m (br.), 1360m (sh), 1320w (sh), 1305w, 1280w, 1160w (sh), 1135m (sh), 1100s, 1075s (br.), 1035m, 1025m, 1000m, 965w (sh), 910w, 895w, 870w, 840w. ¹H-NMR (400 MHz, CDCl₃): 7.80–7.67 (*m*, 9 arom. H); 7.55–7.52 (*m*, 2 arom. H); 7.44–7.38 (*m*, 3 arom. H); 7.29–7.19 (*m*, 4 arom. H); 7.11–7.06 (*m*, 4 arom. H); 6.91–6.83 (*m*, 5 arom. H); 6.74–6.70 (*m*, 1 arom. H); 6.59 (*s*, H-C(1)); 6.36 (*d*, $J = 8.4$, H-C(1')); 5.60 (*s*, PhCH); 4.87 (*d*, $J = 12.1$, PhCH); 4.65 (*d*, $J = 12.5$, PhCH); 4.56–4.49 (*m*, 3 PhCH, H_{eq}-C(6')); 4.47 (*d*, $J = 11.8$, PhCH); 4.39–4.36 (*m*, 2 H); 4.33 (*td*, $J = 9.9$, 5.0, H-C(5')); 4.24–4.20 (*m*, 3 H); 3.89 (*dd*, $J = 9.4$, 2.2, H-C(4')); 3.86 (*t*, $J = 10.2$, H_{ax}-C(6')); 3.65 (*dd*, $J = 10.3$, 5.3, H-C(6)); 3.58 (*dd*, $J = 10.3$, 1.8, H-C(6)). ¹³C-NMR (50 MHz, CDCl₃): 167.6 (*s*, CO); 167.4 (*s*, CO); 167.2 (*s*, 2 CO); 145.6 (*d*, C(1)); 139.6 (*s*); 139.0 (*s*); 138.6 (*s*); 137.3 (*s*); 134–124 (*m*, arom. C); 107.8 (*s*, C(2)); 101.9 (*d*, PhCH); 97.9 (*d*, C(1')); 79.8 (*d*, C(4')); 75.3 (*d*); 74.1 (*d*, C(3')); 74 (*t*, PhCH₂); 73.1 (*t*, PhCH₂); 72.8 (*t*, PhCH₂); 72.7 (*d*); 70.6 (*d*, C(5)); 69.0, 68.9 (2 *t*, C(6), C(6')); 64.0 (*d*, C(5')); 56.7 (*d*, C(2')). Anal. calc. for C₅₆H₄₈N₂O₁₂ (941.002): C 71.48, H 5.14, N 2.98; found: C 71.27, H 5.26, N 2.99.

(3aR,4R,5R,6S,6aS)-6-[(Benzyloxy)methyl]-2-(dimethylamino)-3a,5,6,6a-tetrahydro-4-hydroxy-4H-cyclopentoxazol-5-yl 3,6-Di-O-benzyl-4-O-(3-O-benzyl-4,6-O-benzylidene-2-deoxy-2-phthalimido-β-D-allopyranosyl)-2-deoxy-2-phthalimido-β-D-allopyranoside (7). R_f (CHCl₃/MeOH 92.5:7.5) 0.37. $[\alpha]_D^{25} = -89$ ($c = 0.6$, CHCl₃). IR (CHCl₃): 3480w (br.), 3090w, 3070w, 3040w, 3000w, 2920w, 2860w, 1775m, 1715s, 1685w (sh), 1655m (sh), 1650m, 1620w, 1495w, 1470w, 1455w, 1385s, 1365m (sh), 1320w, 1160m, 1135m, 1105s, 1085s, 1075s, 1040s, 1025s, 1015s (sh), 1005m (sh), 970m, 890w, 870w. ¹H-NMR (400 MHz, CDCl₃): 7.74–7.59 (*m*, 8 arom. H); 7.52–7.49 (*m*, 2 arom. H); 7.43–7.38 (*m*, 3 arom. H); 7.31–7.18 (*m*, 8 arom. H); 7.09–7.04 (*m*, 6 arom. H); 6.92–6.84 (*m*, 5 arom. H); 6.81–6.77 (*m*, 1 arom. H); 6.24 (*d*, $J = 8.6$, H-C(1'')); 5.95 (*d*, $J = 8.7$, H-C(1)); 5.55 (*s*, PhCH); 4.84 (*d*, $J = 12.2$, PhCH); 4.65 (*d*, $J = 11.7$, PhCH); 4.64 (*dd*, $J = 9.2$, 6.5, H-C(6'a)); 4.54–4.49 (*m*, exchange with D₂O (1 H), PhCH, H_{eq}-C(6')), OH-C(4'); 4.46 (*d*, $J = 12.2$, PhCH); 4.37–4.31 (*m*, 2 PhCH, H-C(5'), H-C(3)); 4.29–4.21 (*m*, H-C(5), PhCH); 4.19 (*t*, $J = 2.5$, H-C(3'')); 4.09 (*dd*, $J = 8.6$, 2.9, H-C(2'')); 4.04 (*dd*, $J = 9.2$, 5.8, H-C(3'a)); 4.03 (*d*, $J = 12.3$, PhCH); 3.98 (*dd*, $J = 8.7$, 2.7, H-C(2)); 3.87 (*m*, with D₂O *dd*, $J = 7.4$, 5.6, H-C(4')); 3.83–3.77 (*m*, H_{ax}-C(6'), H-C(4), H-C(4'')); 3.69 (*dd*, $J = 10.7$, 7.4, H-C(5'')); 3.41 (*dd* (= 't'), $J = 9.6$, CH-C(6'')); 3.35 (*dd*, $J = 11.6$, 3.5, H-C(6)); 3.33 (*dd*, $J = 9.7$, 2.4, CH-C(6'')); 3.19 (*dd*, $J = 11.6$, 5.6, H-C(6)); 2.84 (*s*, Me₂N); 2.08 (*m*, H-C(6')). ¹³C-NMR (50 MHz, CDCl₃): 167.8 (*s*, CO); 167.5 (*s*, CO); 167.4 (*s*, CO); 167.3 (*s*, CO); 161.4 (*s*, C(2'')); 138.8–122.6 (several *d* and *s*, arom. C); 101.8 (*d*, PhCH); 98.4 (*d*, C(1'')); 96.7 (*d*, C(1)); 85.4 (*d*, C(5'')); 84.2 (*d*, C(4'')); 80.6 (*d*, C(6'a)); 79.6 (*d*, C(4'')); 78.4 (*d*, C(4)); 76.1 (*d*, C(3)); 74.0 (*t*, PhCH₂); 73.8 (*t*, *d*, PhCH₂, C(3'')); 72.9 (*t*, PhCH₂); 72.7 (*d*, C(3'a)); 72.6 (*t*, PhCH₂); 71.4 (*d*, C(5)); 69.8 (*t*, C(6)); 68.9 (*t*, C(6'')); 68.0 (*t*, CH₂-C(6'')); 63.9 (*d*, C(5'')); 56.6 (*d*, C(2'')); 56.4 (*d*, C(2)); 49.2 (*d*, C(6'')); 37.5 (*q*, Me₂N). ESI-MS: 1248 ($[M + 1]^+$).

(3aS,4S,5S,6R,6aR)-6-[(Benzyloxy)methyl]-2-(dimethylamino)-3a,5,6,6a-tetrahydro-4-hydroxy-4H-cyclopentoxazol-5-yl 3,6-Di-O-benzyl-4-O-(3-O-benzyl-4,6-O-benzylidene-2-deoxy-2-phthalimido-β-D-allopyranosyl)-2-deoxy-2-phthalimido-β-D-allopyranoside (8). R_f (CHCl₃/MeOH 92.5:7.5) 0.3. $[\alpha]_D^{25} = -73.8$ ($c = 0.8$, CHCl₃). IR (CHCl₃): 3540w (sh), 3520w (br.), 3090w, 3070w, 3040w, 3000w, 2920m, 2870w, 1775w, 1715s, 1685w (sh), 1655m (sh), 1650m, 1620w (sh), 1495w, 1465w, 1450w, 1380s, 1365m (sh), 1310w, 1260m, 1160m, 1135m (sh), 1105s, 1085s, 1040s, 1025s, 1015s (sh), 970m, 915w, 890w, 870w. ¹H-NMR (400 MHz, CDCl₃): 7.77–7.60 (*m*, 8 arom. H); 7.53–7.51 (*m*, 2 arom. H); 7.42–7.38 (*m*, 3 arom. H); 7.30–7.20 (*m*, 9 arom. H); 7.1–7.03 (*m*, 5 arom. H); 6.91–6.83 (*m*, 5 arom. H); 6.78–6.74 (*m*, 1 arom. H); 6.25 (*d*, $J = 8.5$, H-C(1'')); 5.99 (*d*, $J = 8.7$, H-C(1)); 5.56 (*s*, PhCH); 4.85 (*d*, $J = 12.1$, PhCH); 4.66 (*dd*, $J = 9.2$, 6.0, H-C(6'a)); 4.61 (*d*, $J = 12.0$, PhCH); 4.51–4.44 (*m*, exchange with D₂O (1 H), 3 PhCH, H_{eq}-C(6'), OH-C(4')); 4.37–4.31 (*AB*, 2 PhCH); 4.28 (*ddd* (= 'td'), $J = 10.1$, 5.3, H-C(5'')); 4.26 (*t*, $J = 2.6$, H-C(3)); 4.22 (*d*, $J = 11.7$, PhCH); 4.18 (*t*, $J = 2.6$, H-C(3'')); 4.13 (*dd*, $J = 8.5$, 2.7, H-C(2'')); 4.09 (*dd*, $J = 8.6$, 2.9, H-C(2'')); 4.04 (*dd*, $J = 9.2$, 5.8, H-C(3'a)); 4.03 (*d*, $J = 12.3$, PhCH); 3.98 (*dd*, $J = 8.7$, 2.7, H-C(2)); 3.87 (*m*, with D₂O *dd*, $J = 7.4$, 5.6, H-C(4'')); 3.83–3.77 (*m*, H_{ax}-C(6'), H-C(4), H-C(4'')); 3.69 (*dd*, $J = 10.7$, 7.4, H-C(5'')); 3.41 (*dd* (= 't'), $J = 9.6$, CH-C(6'')); 3.35 (*dd*, $J = 11.6$, 3.5, H-C(6)); 3.33 (*dd*, $J = 9.7$, 2.4, CH-C(6'')); 3.19 (*dd*, $J = 11.6$, 5.6, H-C(6)); 2.84 (*s*, Me₂N); 2.08 (*m*, H-C(6')). ¹³C-NMR (50 MHz, CDCl₃): 167.8 (*s*, CO); 167.5 (*s*, CO); 167.4 (*s*, CO); 167.3 (*s*, CO); 161.4 (*s*, C(2'')); 138.8–122.6 (several *d* and *s*, arom. C); 101.8 (*d*, PhCH); 98.4 (*d*, C(1'')); 96.7 (*d*, C(1)); 85.4 (*d*, C(5'')); 84.2 (*d*, C(4'')); 80.6 (*d*, C(6'a)); 79.6 (*d*, C(4'')); 78.4 (*d*, C(4)); 76.1 (*d*, C(3)); 74.0 (*t*, PhCH₂); 73.8 (*t*, *d*, PhCH₂, C(3'')); 72.9 (*t*, PhCH₂); 72.7 (*d*, C(3'a)); 72.6 (*t*, PhCH₂); 71.4 (*d*, C(5)); 69.8 (*t*, C(6)); 68.9 (*t*, C(6'')); 68.0 (*t*, CH₂-C(6'')); 63.9 (*d*, C(5'')); 56.6 (*d*, C(2'')); 56.4 (*d*, C(2)); 49.2 (*d*, C(6'')); 37.5 (*q*, Me₂N).

4.06 (*dd*, $J = 10.0, 2.5$, H-C(4)); 4.01 (*dd*, $J = 9.2, 5.8$, H-C(3'a)); 3.98 (*ddd*, $J = 10.0, 5.0, 1.8$, H-C(5)); 3.94 (*dd*, $J = 8.7, 2.7$, H-C(2)); 3.88 (*dd*, $J = 10.1, 7.6$, H-C(5')); 3.84 (*m*, H-C(4'')); 3.80 (*t*, $J = 10.3$, H-C(6'')); 3.69 (*m*, with D₂O *dd*, $J = 7.5, 5.8$, H-C(4')); 3.64 (*dd*, $J = 9.8, 3.3$, CH-C(6')); 3.53 (*dd*, $J = 10.6, 5$, H-C(6)); 3.48 (*dd*, $J = 9.8, 5.6$, CH-C(6')); 3.45 (*dd*, $J = 10.6, 1.8$, H-C(6)); 2.80 (*s*, Me₂N); 2.13 (*m*, H-C(6')). ¹³C-NMR (50 MHz, CDCl₃): 168.1 (*s*, CO); 167.8 (*s*, CO); 167.7 (*s*, CO); 167.4 (*s*, CO); 161.7 (*s*, C(2'')); 138.5–122.3 (several *d* and *s*, arom. C); 102.1 (*d*, PhCH); 97.7 (*d*, C(1'')); 95.7 (*d*, C(1)); 84.2 (*d*, C(5'')); 82 (*d*, C(4'')); 81.9 (*d*, C(6'a)); 80.0 (*d*, C(4'')); 76.6 (*d*, C(4)); 75.8 (*d*, C(3)); 74.2 (2*t*, 1*d*, 2 PhCH₂, C(3'')); 72.9 (*t*, PhCH₂); 72.7 (*t*, PhCH₂); 72.2 (*d*, C(3'a)); 71.9 (*d*, C(5)); 69.6 (*t*, C(6)); 69.1 (*t*, C(6'')); 68.0 (*t*, CH₂-C(6'')); 64.0 (*d*, C(5'')); 56.9 (*d*, C(2'')); 56.6 (*d*, C(2)); 49.1 (*d*, C(6'')); 37.6 (2*q*, Me₂N). ESI-MS: 1248 ([*M* + 1]⁺). FAB-MS: 1248 (100, [*M* + 1]⁺), 1249 (89, [*M* + 2]⁺).

(3*aR**,4*S**,5*S**,6*S**,6*aR**)-6-[(Benzlyoxy)methyl]-2-(dimethylamino)-3*a*,5,6,6*a*-tetrahydro-5-hydroxy-4-H-cyclopentoxazol-4-yl 3,6-Di-O-benzyl-4-O-(3-O-benzyl-4,6-O-benzylidene-2-deoxy-2-phthalimido-β-D-allopyranosyl)-2-deoxy-2-phthalimido-β-D-allopyranoside (**9**). *R*_f (CHCl₃/MeOH 92.5:7.5) 0.40. ¹H-NMR (400 MHz, CDCl₃): 7.79–7.64 (*m*, 8 arom. H); 7.53–7.51 (*m*, 2 arom. H); 7.43–7.37 (*m*, 3 arom. H); 7.30–7.20 (*m*, 8 arom. H); 7.18–7.15 (*m*, 2 arom. H); 7.11–7.03 (*m*, 4 arom. H); 6.93–6.84 (*m*, 5 arom. H); 6.80–6.84 (*m*, 1 arom. H); 6.27 (*d*, $J = 8.5$, H-C(1'')); 5.99 (*d*, $J = 8.6$, H-C(1)); 5.56 (*s*, PhCH); 4.96 (*dd*, $J = 2.9, 7.9$, H-C(6'a)); 4.86 (*d*, $J = 12.2$, PhCH); 4.63 (*d*, $J = 11.9$, PhCH); 4.52–4.48 (*m*, 3 PhCH, H_{eq}-C(6'')); 4.45–4.38 (*m*, H-C(3'a), H-C(4'')); 4.31 (*d*, $J = 11.7$, PhCH); 4.30 (*m*, H-C(5'')); 4.28 (*dd* (= 't'), $J = 2.5$, H-C(3)); 4.25 (*m*, 2 PhCH); 4.19 (*dd* (= 't'), $J = 2.5$, H-C(3'')); 4.13 (*dd*, $J = 8.5, 2.9$, H-C(2'')); 4.14 (*m*, exchange with D₂O (1 H), H-C(5), OH-C(5'')); 4 (*dd*, $J = 9.9, 2.4$, H-C(4)); 3.94 (*dd*, $J = 8.6, 2.5$, H-C(2)); 3.84 (*dd*, $J = 9.7, 2.3$, H-C(4'')); 3.83–3.78 (*m*, H-C(6''), H-C(5'')); 3.60–3.54 (*m*, 2 H-C(6)); 3.38 (*dd*, $J = 9.5, 4.1$, CH-C(6'')); 3.29 (*dd* (= 't'), $J = 8.9$, CH-C(6'')); 2.88 (*s*, Me₂N); 2.38 (*m*, H-C(6')).

(3*aS**,4*R**,5*R**,6*R**,6*aS**)-6-[(Benzlyoxy)methyl]-2-(dimethylamino)-3*a*,5,6,6*a*-tetrahydro-5-hydroxy-4-H-cyclopentoxazol-4-yl 3,6-Di-O-benzyl-4-O-(3-O-benzyl-4,6-O-benzylidene-2-deoxy-2-phthalimido-β-D-allopyranosyl)-2-deoxy-2-phthalimido-β-D-allopyranoside (**10**). *R*_f (CHCl₃/MeOH 92.5:7.5) 0.34. ¹H-NMR (400 MHz, CDCl₃): 7.78–7.57 (*m*, 8 arom. H); 7.52–7.49 (*m*, 2 arom. H); 7.43–7.38 (*m*, 3 arom. H); 7.31–7.14 (*m*, 10 arom. H); 7.09–7.05 (*m*, 5 arom. H); 6.92–6.84 (*m*, 4 arom. H); 6.81–6.77 (*m*, 1 arom. H); 6.25 (*d*, $J = 8.5$, H-C(1'')); 5.97 (*d*, $J = 8.7$, H-C(1)); 5.56 (*s*, PhCH); 4.99 (*dd*, $J = 8.7, 4.3$, H-C(6'a)); 4.84 (*d*, $J = 12.0$, PhCH); 4.62 (*d*, $J = 12.0$, PhCH); 4.48 (*d*, $J = 12.0$, PhCH); 4.48 (*d*, $J = 10.3, 5.1$, H_{eq}-C(6'')); 4.38 (*d*, $J = 12.2$, PhCH); 4.36–4.19 (*m*, 9 H); 4.14 (*dd*, $J = 8.5, 2.9$, H-C(2'')); 4.11–3.99 (*m*, exchange with D₂O (1 H), H-C(5'), H-C(5), OH-C(5'')); 3.93 (*dd*, $J = 5.7, 4.3$, H-C(4'')); 3.87 (*dd*, $J = 8.7, 2.7$, H-C(2)); 3.83 (*dd*, $J = 9.8, 2.4$, H-C(4'')); 3.80 (*t*, $J = 10.4$, H_{ax}-C(6'')); 3.57 (*m*, 2 CH-C(6'')); 3.51 (*dd*, $J = 10.5, 4.6$, H-C(6)); 3.43 (*br. d*, $J = 10.1$, H-C(6)); 2.9 (*s*, Me₂N); 2.61 (*m*, H-C(6')).

Deprotection of 7 and 8. a) A soln. of **7** (200 mg, 0.16 mmol) and NH₂NH₂·H₂O (2 ml) in EtOH (5 ml) was heated at 80° for 4 h. The mixture was evaporated, co-evaporated with toluene (3 × 20 ml), and dried under h.v. The residue was treated with pyridine (8 ml) and Ac₂O (4 ml) for 14 h under Ar at r.t., workup as usual and FC (CHCl₃/MeOH 99:1→95:5) yielded **11** (112 mg, 61 %). White foam.

b) A soln. of **7** (50 mg, 0.04 mmol) and NH₂NH₂·H₂O (3.8 μl, 0.08 mmol) in EtOH (2 ml) was kept for 45 min at 80°. Workup as described in a); treatment with pyridine (4 ml) and Ac₂O (1 ml) for 14 h, and FC (CHCl₃/MeOH 99:1→95:5) afforded **11** (5.5 mg, 12%) and **12** (7.6 mg, 17%) as a colourless oil.

c) A soln. of **7** (250 mg, 0.2 mmol) and 40 % aq. MeNH₂ soln. (5 ml) in EtOH (8 ml) was stirred at r.t. for 48 h. The mixture was evaporated, co-evaporated with toluene (2 × 30 ml), and dried under h.v. The residue was treated with pyridine (10 ml) and Ac₂O (5 ml) for 14 h under Ar. Workup as usual and FC (CHCl₃/MeOH 99:1→95:5) yielded **12** (163 mg, 73 %).

(1*R*,2*R*,3*S*,4*S*,5*S*)-3-Acetamido-2,4-diacetoxy-5-[(benzlyoxy)methyl]cyclopentyl 2-Acetamido-4-O-(2-acetamido-3-O-benzyl-4,6-O-benzylidene-2-deoxy-β-D-allopyranosyl)-3,6-di-O-benzyl-2-deoxy-β-D-allopyranoside (**11**). *R*_f (CHCl₃/MeOH 9:1) 0.49. [α]_D²⁵ = -60.6 (*c* = 0.4, CHCl₃). IR (CHCl₃): 3420*m*, 3350*w*, 3090*w*, 2860*w*, 1745*s*, 1720*m* (sh), 1665*s*, 1655*s* (sh), 1635*m* (sh), 1510*m* (sh), 1495*m*, 1450*m*, 1435*w*, 1420*w*, 1365*m*, 1325*w*, 1260*m* (sh), 1240*w*, 1160*m*, 1145*m* (sh), 1115*s*, 1090*s*, 1040*s*, 1025*s*, 1005*s* (sh), 960*w*, 940*w*, 910*w*, 880*w*. ¹H-NMR (400 MHz, CDCl₃): 7.52–7.47 (*m*, 2 arom. H); 7.42–7.24 (*m*, 23 arom. H); 6.01 (*d*, $J = 8.8$, NH-C(3'')); 5.82 (*d*, $J = 8.7$, NH-C(2'')); 5.54 (*s*, PhCH); 5.51 (*br. s*, NH-C(2)); 5.33 (*dd*, $J = 8.2, 5.5$, H-C(2'')); 4.97 (*d*, $J = 11.8$, PhCH); 4.91 (*dd*, $J = 5.8, 3.3$, H-C(4'')); 4.88 (*dd*, $J = 13.1$, PhCH); 4.76 (*dd*, $J = 8.4$, H-C(1'')); 4.74 (*d*, $J = 11.3$, PhCH); 4.60 (*d*, $J = 12.1$, PhCH); 4.55 (*d*, $J = 11.8$, PhCH); 4.54–4.40 (*m*, 3 PhCH, H-C(1), H-C(3'), H_{eq}-C(6'')); 4.19–4.12 (*m*, H-C(3), H-C(5'')); 4.08–4.02 (*m*, H-C(3''), H-C(2'')); 3.98 (*t*, $J = 5.3$, H-C(1'')); 3.91–3.84 (*m*, H-C(2), H-C(5)); 3.80 (*m*, H-C(4)); 3.79 (*t*, $J = 10.2$, H_{ax}-C(6'')); 3.73 (*dd*, $J = 9.5, 2.0$, H-C(4'')); 3.69 (*dd*, $J = 11.6, 3.0$, H-C(6)); 3.53–3.45 (*m*, H-C(6), 2 CH-C(5'')); 2.11 (*m*, H-C(5'')); 2.05 (*s*, Ac); 1.99 (*s*, Ac); 1.96 (*s*,

Ac); 1.62 (s, Ac); 1.55 (s, Ac). ^{13}C -NMR (50 MHz, CDCl_3): 170.4 (s, CO); 170.0 (s, CO); 169.9 (s, CO); 169.3 (s, CO); 169.2 (s, CO); 138.5 (s, arom. C); 138.1 (2s, arom. C); 137.7 (s, arom. C); 137.2 (s, arom. C); 129.1–126.1 (several *d*, arom. C); 102.4 (*d*, C(1'')); 102.0 (*d*, PhCH); 100.5 (*d*, C(1)); 82.3 (*d*, C(1')); 80.0 (*d*, C(4'')); 79.3 (*d*, C(2'')); 78.1 (*d*, C(4)); 76.8 (*d*, C(3'')); 75.1 (*d*, C(3)); 74.6 (*t*, PhCH_2); 74.2 (*t*, PhCH_2); 74.0 (*t*, PhCH_2); 73.7 (*d*, C(4'')); 73.1 (*t*, PhCH_2); 72.5 (*d*, C(5)); 69.1 (*t*, C(6'')); 68.7 (2*t*, C(6), $\text{CH}_2\text{--C}(5'')$); 63.8 (*d*, C(5'')); 53.6 (*d*, C(3'')); 52.7 (*d*, C(2'')); 51.4 (*d*, C(2)); 49.8 (*d*, C(5'')); 23.0 (*q*, Me); 22.8 (*q*, Me); 20.9 (*q*, Me); 20.8 (2 *q*, 2 Me). ESI-MS: 1145 ($[\text{M} + 1]^+$).

(3*a*S,4*R*,5*R*,6*S*,6*a*S)-4-Acetoxy-6-[(benzyloxy)methyl]-2-(dimethylamino)-3*a*,5,6,6*a*-tetrahydro-4*H*-cyclopentoxazol-5-yl 2-Acetamido-4-O-(2-acetamido-3-O-benzyl-4,6-O-benzylidene-2-deoxy- β -D-allopyranosyl)-3,6-di-O-benzyl-2-deoxy- β -D-allopyranoside (**12**). R_f ($\text{CHCl}_3/\text{MeOH}$ 92.5:7.5) 0.44. $[\alpha]_D^{25} = -50.5$ ($c = 1$, CHCl_3). IR (CHCl_3): 3420*w*, 3370*w*, 3090*w*, 3060*w*, 2980*w* (sh), 2950*w* (sh), 2920*m*, 2800*m*, 1730*m*, 1720*m*, 1650*s* (br.), 1635*m* (sh), 1510*w* (sh), 1490*m*, 1450*m*, 1410*w*, 1365*m*, 1315*w*, 1240*m* (br.), 1155*m*, 1115*s* (sh), 1080*s* (br.), 1040*s*, 1025*s*, 970*m*, 915*w*, 885*w*, 865*w*. ^1H -NMR (400 MHz, CDCl_3): 7.50–7.48 (*m*, 2 arom. H); 7.40–7.24 (*m*, 23 arom. H); 6.09–5.94 (br. *s*, NH–C(2)); 5.91 (*d*, $J = 8.5$, NH–C(2'')); 5.53 (*s*, PhCH); 5.26 (*m*, H–C(4'')); 4.98 (*d*, $J = 11.7$, PhCH); 4.9 (*dd*, $J = 8.2$, 4.1, H–C(6'a)); 4.87 (*d*, $J = 11.8$, PhCH); 4.75 (*d*, $J = 8.7$, H–C(1)); 4.72 (*d*, $J = 12.2$, PhCH); 4.59–4.43 (*m*, $\text{H}_{\text{eq}}\text{--C}(6'')$, H–C(1''), 5 PhCH); 4.26 (*dd*, $J = 8.3$, 2.6, H–C(3'a)); 4.13 (*ddd* ($=$ 'rd'), $J = 10.0$, 5.3, H–C(5'')); 4.11 (*m*, H–C(3)); 4.06–4.04 (*m*, H–C(3''), H–C(2)); 3.96–3.85 (*m*, H–C(5'), H–C(2''), H–C(4), H–C(5)); 3.78 (*t*, $J = 10.3$, $\text{H}_{\text{ax}}\text{--C}(6'')$); 3.74–3.71 (*m*, H–C(4''), H–C(6)); 3.62 (*dd*, $J = 11.3$, 2.5, H–C(6)); 3.50 (*d*, $J = 5.4$, 2 CH–C(6'')); 2.90 (*s*, Me_2N); 2.43 (*m*, H–C(6'')); 2.02 (*s*, Ac); 1.99 (*s*, Ac); 1.64 (*s*, Ac). ^{13}C -NMR (50 MHz, CDCl_3): 169.5 (s, CO); 169.4 (s, 2 CO); 161.7 (s, C(2'')); 138.6 (s, arom. C); 138.2 (s, arom. C); 138.1 (s, arom. C); 138.0 (s, arom. C); 137.3 (s, arom. C); 129.0–126.1 (several *d*, arom. C); 102.2 (*d*, C(1)); 102.0 (*d*, PhCH); 99.5 (*d*, C(1'')); 83.4 (*d*, C(4'')); 81.9 (*d*, C(5'')); 81.6 (*d*); 80.0 (*d*, C(4'')); 77.2 (*d*); 75.1 (*d*); 74.5 (*t*, PhCH_2); 73.9 (*t*, PhCH_2); 73.1 (2*t*, 1*d*); 72.6 (*d*); 69.3, 69.1 (*t*, C(6), C(6'')); 52.6 (*d*, C(2)); 51.6 (*d*, C(2'')); 50.0 (*d*, $\text{CH}_2\text{--C}(6'')$); 37.6 (*q*, Me_2N); 22.9 (*q*, Me); 22.8 (*q*, Me); 21.1 (*q*, Me).

(3*a*R,4*S*,5*S*,6*R*,6*a*R)-4-Acetoxy-6-[(benzyloxy)methyl]-2-(dimethylamino)-3*a*,5,6,6*a*-tetrahydro-4*H*-cyclopentoxazol-5-yl 2-Acetamido-4-O-(2-acetamido-3-O-benzyl-4,6-O-benzylidene-2-deoxy- β -D-allopyranosyl)-3,6-di-O-benzyl-2-deoxy- β -D-allopyranoside (**13**). Similarly as for the preparation of **11** from **7**, a soln. of **8** (310 mg, 0.249 mmol) in EtOH (8 ml) and 40% aq. MeNH_2 soln. (5 ml) was stirred at r.t. for 48 h. Evaporation, treatment of the residue with pyridine/Ac₂O 2:1 (6 ml), normal workup, and FC ($\text{CHCl}_3/\text{MeOH}$ 99:1 $\rightarrow$ 95:5) gave **13** (205 mg, 74%). Colourless oil. R_f ($\text{CHCl}_3/\text{MeOH}$ 92.5:7.5) 0.48. $[\alpha]_D^{25} = -69.6$ ($c = 0.8$, CHCl_3). IR (CHCl_3): 3410*w*, 3380*w* (br.), 2980*w*, 2920*m*, 2860*m*, 1725*m*, 1655*s*, 1645*s*, 1620*m* (sh), 1545*w*, 1530*w*, 1510*w*, 1495*w*, 1450*w*, 1410*w*, 1315*m*, 1245*w*, 1155*m* (sh), 1165*s*, 1080*s*, 1040*s*, 1025*s*, 970*m*, 950*w*, 910*w*, 885*w*. ^1H -NMR (400 MHz, CDCl_3): 7.50–7.47 (*m*, 2 arom. H); 7.39–7.20 (*m*, 23 arom. H); 6.28 (*d*, $J = 4.4$, NH–C(2)); 5.77 (*d*, $J = 8.6$, NH–C(2'')); 5.10 (*dd*, $J = 7.2$, 5.1, H–C(4'')); 4.98 (*d*, $J = 11.8$, PhCH); 4.87 (*d*, $J = 11.4$, PhCH); 4.82 (*dd*, $J = 9.1$, 6.4, H–C(6'a)); 4.75 (*d*, $J = 8.5$, H–C(1)); 4.54–4.46 (*m*, 7 H); 4.27 (*d*, $J = 11.9$, PhCH); 4.21 (br. *s*, H–C(3)); 4.18 (*dd*, $J = 9.1$, 5.1, H–C(3'a)); 4.15–4.1 (*m*, H–C(3''), H–C(5'')); 4.03 (*dd*, $J = 10.1$, 7.2, H–C(5'')); 4.02 (*m*, H–C(5)); 3.84–3.8 (*m*, 3 H); 3.75 (*t*, $J = 10.4$, $\text{H}_{\text{ax}}\text{--C}(6'')$); 3.72–3.64 (*m*, 3 H); 3.63 (*dd*, $J = 9.6$, 4.2, CH–C(6'')); 3.48 (br. *d*, $J = 11.3$, H–C(6)); 2.89 (*s*, Me_2N); 2.28 (*m*, H–C(6'')); 1.92 (*s*, Ac); 1.84 (*s*, Ac); 1.6 (*s*, Ac). ^{13}C -NMR (50 MHz, CDCl_3): 171.0 (s, CO); 170 (s, 2 CO); 161.9 (s, C(2'')); 138.8 (s, arom. C); 138.3 (s, arom. C); 138.1 (s, arom. C); 137.9 (s, arom. C); 137.2 (s, arom. C); 128.9–126.0 (several *d*, arom. C); 101.9 (2*d*, C(1), PhCH); 98.6 (*d*, C(1'')); 85.6 (*d*); 80.1 (*d*, C(4'')); 79.9 (*d*); 79.4 (*d*); 77.7 (*d*); 77.2 (*d*); 75.1 (*d*); 74.4 (*t*, PhCH_2); 73.8 (*t*, 2 PhCH_2); 72.9 (*t*, PhCH_2); 72.8 (*d*); 71.3 (*d*); 69.0 (*t*, C(6), C(6'')); 67.3 (*t*, $\text{CH}_2\text{--C}(6'')$); 63.6 (*d*); 52.7, 52.5 (2 *d*, C(2), C(2'')); 49.6 (*d*, C(6'')); 37.5 (*q*, Me_2N); 22.9 (*q*, Me); 22.7 (*q*, Me); 20.9 (*q*, Me).

(1*R*,2*R*,3*S*,4*S*,5*S*)-3-Acetamido-5-[(benzyloxy)methyl]-2,4-dihydroxycyclopentyl 2-Acetamido-4-O-(2-acetamido-3-O-benzyl-4,6-O-benzylidene-2-deoxy- β -D-allopyranosyl)-3,6-di-O-benzyl-2-deoxy- β -D-allopyranoside (**14**). A soln. of **11** (90 mg, 0.079 mmol) in MeOH (10 ml) was treated at r.t. with 1 mM NaOMe in MeOH (3 ml). After stirring 5 h and addition of Dowex-1 (H^+), filtration and evaporation left a residue which upon FC ($\text{CHCl}_3/\text{MeOH}$ 97:3) yielded **14** (80.8 mg, 97%). Colourless glass. R_f ($\text{CHCl}_3/\text{MeOH}$ 9:1) 0.33. IR (CHCl_3): 3595*w*, 3500*w* (sh), 3400*m*, 3350*w* (br.), 3090*w*, 3070*w*, 2995*w*, 2940*w*, 2870*m*, 1670*s*, 1655*s* (sh), 1610*w*, 1585*w*, 1545*w* (sh), 1510*m* (sh), 1500*m*, 1455*m*, 1370*m*, 1320*m*, 1165*m*, 1110*s*, 1090*s* (br.), 1040*s*, 1025*s*, 1010*s* (sh), 965*w*, 945*w*, 915*w*. ^1H -NMR (400 MHz, CDCl_3): 7.48–7.45 (*m*, 2 arom. H); 7.40–7.45 (*m*, 23 arom. H); 6.26 (*d*, $J = 4.5$, NH–C(3'')); 5.90 (*d*, $J = 9$, NH–C(2'')); 5.54–5.51 (br. *s*, NH–C(2)); 5.51 (*s*, PhCH); 4.97 (*d*, $J = 11.8$, PhCH); 4.92 (*d*, $J = 11.9$, PhCH); 4.70 (*d*, $J = 8.5$, H–C(1'')); 4.64 (*d*, $J = 12.2$, PhCH); 4.59 (*d*, $J = 12.0$, PhCH); 4.53 (*d*, $J = 11.8$, PhCH); 4.52 (*d*, $J = 12.3$, PhCH); 4.47 (*d*, $J = 8.3$, H–C(1)); 4.46 (*d*, $J = 12.2$, PhCH); 4.43 (*dd*, $J = 10.3$, 5.1, $\text{H}_{\text{eq}}\text{--C}(6'')$); 4.38 (*d*, $J = 12.3$, PhCH); 4.31 (br. *s*, exchange with D_2O , OH–C(2'')); 4.15–3.90 (*m*, 9 H); 3.76 (*t*, $J = 10.3$, $\text{H}_{\text{ax}}\text{--C}(6'')$); 3.72 (*dd*, $J = 9.8$, 2.1, H–C(4'')); 3.69 (*dd*, $J = 9.8$, 1.7, H–C(4)); 3.64–3.54 (*m*,

H–C(4'), 2 H–C(6)); 3.43 (*dd*, $J = 9.2, 5.2$, CH–C(5')); 3.36 (*dd*, $J = 9.2, 5.4$, CH–C(5')); 2.90 (*br. s*, exchange with D₂O, OH–C(4')); 2.06 (*m*, H–C(5')); 1.98 (*s*, Ac); 1.59 (*s*, Ac); 1.47 (*s*, Ac).

(3*a*S,4*R*,5*R*,6*S*,6*a*S)-6-[(Benzyloxy)methyl]-2-(dimethylamino)-3*a*,5,6,6*a*-tetrahydro-4-hydroxy-4*H*-cyclopentoxazol-5-yl 2-Acetamido-4-O-(2-acetamido-3-O-benzyl-4,6-O-benzylidene-2-deoxy-β-D-allopyranosyl)-3,6-di-O-benzyl-2-deoxy-β-D-allopyranoside (**15**). As described for **14**, with **12** (120 mg, 0.108 mmol) in MeOH (10 ml) and 1 mM NaOMe in MeOH (2 ml; 10 h). FC (CHCl₃/MeOH 98:2→95:5) yielded **15** (110 mg, 96%). Colourless glass. R_f (CHCl₃/MeOH 9:1) 0.35. $[\alpha]_D^{25} = -35$ ($c = 0.9$, CHCl₃). IR (CHCl₃): 3590*w*, 3540*w*, 3495*w*, 3430*m*, 2990*w*, 2970*w*, 2960*m*, 2950*m*, 2920*m*, 2875*m*, 1670*s* (*sh*), 1655*s*, 1510*w* (*sh*), 1495*m*, 1470*w*, 1450*w*, 1405*w*, 1365*m*, 1320*w*, 1310*w*, 1260*w*, 1160*m*, 1140*m* (*sh*), 1115*s* (*sh*), 1095*s* (*br.*), 1040*s*, 1025*s*, 970*m*, 940*w*, 915*w*, 885*w*, 860*w*. ¹H-NMR (400 MHz, CDCl₃): 7.50–7.47 (*m*, 2 arom. H); 7.42–7.2 (*m*, 22 arom. H); 7.17–7.13 (*m*, 1 arom. H); 5.61 (*d*, $J = 9.1$, NH–C(2'')); 5.52 (*s*, PhCH); 5.30 (*br. d*, $J = 8.2$, NH–C(2)); 5.00 (*d*, $J = 11.7$, PhCH); 4.95 (*d*, $J = 11.8$, PhCH); 4.78 (*dd*, $J = 9.2, 6.8$, H–C(6'a)); 4.70–4.61 (*m*, PhCH, H–C(1'')); 4.57 (*d*, $J = 11.8$, PhCH); 4.53 (*d*, $J = 11.7$, PhCH); 4.51 (*d*, $J = 12.3$, PhCH); 4.47 (*dd*, $J = 10.3, 5.1$, H_{eq}–C(6'')); 4.42 (*d*, $J = 8.3$, H–C(1)); 4.34 (*d*, $J = 12.7$, PhCH); 4.21 (*br. s*, exchange with D₂O, OH–C(4'')); 4.14–4.04 (*m*, 6 H); 3.98 (*dd* (= '*td*'), $J = 8.8, 2.6$, H–C(2)); 3.89 (*m*, after D₂O exchange *dd*, $J = 7.4, 5.9$, H–C(4'')); 3.75 (*t*, $J = 10.4$, H_{ax}–C(6'')); 3.71 (*dd*, $J = 9.5, 1.9$, H–C(4'')); 3.66 (*dd*, $J = 9.8, 2.1$, H–C(4)); 3.61–3.55 (*m*, H–C(5'), 2 H–C(6)); 3.53 (*dd*, $J = 9.4, 3.1$, CH–C(6'')); 3.36 (*dd*, $J = 3.4, 9.4$, CH–C(6'')); 2.87 (*s*, Me₂N); 2.19 (*m*, H–C(6'')); 1.53 (*s*, Ac); 1.43 (*s*, Ac). ¹³C-NMR (50 MHz, CDCl₃): 169.2 (*s*, CO); 169.1 (*s*, CO); 161.7 (*s*, C(2'')); 138.6 (*s*, arom. C); 138.5 (*s*, arom. C); 138.0 (*s*, arom. C); 137.7 (*s*, arom. C); 137.2 (*s*, arom. C); 129.2–126.1 (several *d*, arom. C); 102.4 (*d*, C(1'')); 102.1 (*d*, PhCH); 100.9 (*d*, C(1)); 85.7 (*d*, C(5'')); 84.0 (*d*, C(4'')); 80.1 (*d*, C(4'')); 79.8 (*d*, C(6'a)); 78.6 (*d*, C(4)); 77.3 (*d*); 75.3 (*d*); 74.7 (*t*, 2 PhCH₂); 74.1 (*t*, PhCH₂); 72.7 (*t*, PhCH₂); 72.2, 71.8 (2*d*, C(5), C(5'')); 69.3 (*t*, C(6)); 69.1 (*t*, C(6'')); 66.2 (*t*, CH₂–C(6'')); 63.8 (*d*, C(3'a)); 52.3 (*d*, C(2'')); 51.4 (*d*, C(2)); 49.4 (*d*, C(6'')); 37.7 (*q*, Me₂N); 22.8 (*q*, Me); 22.7 (*q*, Me).

(3*a*S,4*S*,5*S*,6*R*,6*a*R)-6-[(Benzyloxy)methyl]-2-(dimethylamino)-3*a*,5,6,6*a*-tetrahydro-4-hydroxy-4*H*-cyclopentoxazol-5-yl 2-Acetamido-4-O-(2-acetamido-3-O-benzyl-4,6-O-benzylidene-2-deoxy-β-D-allopyranosyl)-3,6-di-O-benzyl-2-deoxy-β-D-allopyranoside (**16**). As described for **14**, with **13** (135 mg, 0.121 mmol) in MeOH (10 ml) and 1 mM NaOMe in MeOH (2 ml; 10 h). FC (CHCl₃/MeOH 98:2→95:5) yielded **16** (121 mg, 93%). Colourless glass. R_f (CHCl₃/MeOH 9:1) 0.26. $[\alpha]_D^{25} = -64$ ($c = 0.7$, CHCl₃). IR (CHCl₃): 3680*w*, 3580*w*, 3490*w* (*sh*), 3430*w*, 3360*w* (*br.*), 3090*w*, 3070*w*, 2990*w*, 2920*m*, 2855*m*, 2800*w*, 1685*w* (*sh*), 1650*s* (*br.*), 1545*w*, 1530*w*, 1510*w* (*sh*), 1490*w*, 1450*w*, 1410*w*, 1360*m*, 1315*w*, 1155*m* (*sh*), 1115*m*, 1070*s*, 1040*s*, 1025*s*, 1010*m* (*sh*), 970*m*, 945*w*, 915*w*, 890*w*. ¹H-NMR (400 MHz, CDCl₃): 7.52–7.46 (*m*, 2 arom. H); 7.41–7.22 (*m*, 23 arom. H); 5.93–5.91 (*br. s*, NH); 5.76 (*d*, $J = 8.8$, NH–C(2'')); 5.53 (*s*, PhCH); 4.99 (*d*, $J = 11.7$, PhCH); 4.85 (*d*, $J = 12.4$, PhCH); 4.78–4.76 (*m*, 2 H); 4.75 (*dd*, $J = 9.1, 5.9$, H–C(6'a)); 4.69 (*d*, $J = 12.1$, PhCH); 4.56 (*d*, $J = 12.0$, PhCH); 4.54 (*d*, $J = 11.7$, PhCH); 4.50–4.43 (*m*, 3 H); 4.34 (*d*, $J = 12.1$, PhCH); 4.16–4.11 (*m*, 4 H, exchange with D₂O (1 H)); 4.08–3.95 (*m*, 3 H); 3.90 (*ddd* (= '*dt*'), $J = 8.9, 2.6$, H–C(5)); 3.87–3.81 (*m*, 3 H); 3.77 (*t*, $J = 10.4$, H_{ax}–C(6'')); 3.72 (*dd*, $J = 9.5, 3.3$, H–C(4'')); 3.67 (*dd*, $J = 9.5, 3.3$, H–C(6)); 3.63–3.58 (*m*, CH–C(6'), H–C(6)); 3.45 (*dd*, $J = 11.2, 1.4$, CH–C(6'')); 2.85 (*m*, Me₂N); 2.23 (*m*, H–C(6'')); 1.75 (*s*, Ac); 1.59 (*s*, Ac). ¹³C-NMR (50 MHz, CDCl₃): 169.4 (*s*, CO); 169.2 (*s*, CO); 161.8 (*s*, C(2'')); 138.8 (*s*, arom. C); 138.3 (*s*, arom. C); 138.1 (*s*, arom. C); 138 (*s*, arom. C); 137.2 (*s*, arom. C); 129–126 (several *d*, arom. C); 102.1 (*d*, C(1'')); 101.9 (*d*, PhCH); 100.1 (*d*, C(1)); 83.9 (*d*); 82.1 (*d*); 81.7 (*d*); 80.6 (*d*); 79.9 (*d*); 78.1 (*d*); 77.2 (*d*); 75.1 (*d*); 74.5 (*t*, PhCH₂); 73.8 (*t*, PhCH₂); 72.9 (*t*, 2 PhCH₂); 72.5 (*d*); 71.7 (*d*); 69.0 (*t*, C(6), C(6'')); 67.4 (*t*, CH₂–C(6'')); 63.7 (*d*, C(3'a)); 52.7, 52.4 (2*d*, C(2), C(2'')); 48.7 (*d*, C(6'')); 37.5 (2*q*, Me₂N); 23 (*q*, Me); 22.7 (*q*, Me).

(3*a*R,4*R*,5*R*,6*S*,6*a*S)-2-(Dimethylamino)-3*a*,5,6,6*a*-tetrahydro-4-hydroxy-6-(hydroxymethyl)-4*H*-cyclopentoxazol-5-yl 2-Acetamido-4-O-(2-acetamido-3-deoxy-β-D-allopyranosyl)-2-deoxy-β-D-allopyranoside (**1**). A mixture of **15** (45 mg, 0.042 mmol) and 10% Pd/C (80 mg) in MeOH/AcOH 9:1 (18 ml) was stirred for 36 h at r.t. under 7 bar of H₂. The solids were then removed by centrifugation (2000 r.p.m., 5 min), and the pellet was washed with MeOH/AcOH 9:1 (3 × 20 ml). The combined supernatants were collected and evaporated. The white solid residue was dissolved in a minimum of a 3% aq. AcOH soln. and chromatographed on *Sephadex G 10*: 1 (25 mg, 95%). White powder. R_f (AcOEt/pyridine/AcOH/H₂O 5:5:1:3) 0.40. $[\alpha]_D^{25} = -21.4$ ($c = 0.3$, H₂O). ¹H-NMR (600 MHz, D₂O/0.3% CD₃CO₂D²): Table 1. ¹³C-NMR (150 MHz, D₂O/0.3% CD₃CO₂D): Table 3. ESI-MS: 623 (100 [*M* + H]⁺).

(3*a*S,4*S*,5*S*,6*R*,6*a*R)-2-(Dimethylamino)-3*a*,5,6,6*a*-tetrahydro-4-hydroxy-6-(hydroxymethyl)-4*H*-cyclopentoxazol-5-yl 2-Acetamido-4-O-(2-acetamido-3-deoxy-β-D-allopyranosyl)-2-deoxy-β-D-allopyranoside (**17**). As de-

²) The values of the coupling constants of the signals between 3.95 and 3.65 ppm were determined from the *J*-resolved 2D spectra.

scribed for **1**, with 10% Pd/C (90 mg), 7 bar of H₂, **16** (72 mg, 0.067 mmol), and MeOH/AcOH 9:1 (18 ml): **17** (39.7 mg, 95%). White powder. *R*_f (AcOEt/pyridine/AcOH/H₂O 5:5:1:3) 0.40. $[\alpha]_D^{25} = -12.3$ (*c* = 0.26, H₂O). ¹H-NMR (600 MHz, D₂O/0.3% CD₃CO₂D₂): Table 1. ¹³C-NMR (50 MHz, D₂O/0.3% CD₃CO₂D): Table 3. ESI-MS: 623 (100, [M + H]⁺).

(1*R*,2*R*,3*S*,4*S*,5*S*)-3-*Acetamido-2,4-dihydroxy-5-(hydroxymethyl)cyclopentyl-2-Acetamido-4-O-(2-acetamido-2-deoxy-β-D-allopyranosyl)-2-deoxy-β-D-allopyranoside* (**18**). As described for **1**, with **14** (58 mg, 0.055 mmol), 10% Pd/C (80 mg), MeOH/AcOH 9:1 (18 ml), and 7 bar of H₂ (72 h): **18** (30.8 mg, 92%). White powder. *R*_f (CHCl₃/MeOH/H₂O/NH₃ 10:10:1.75:0.25) 0.2. $[\alpha]_D^{25} = -18.3$ (*c* = 0.5, 0.1M aq. AcOH). ¹H-NMR (600 MHz, D₂O/0.3% CD₃CO₂D): Table 1. ¹³C-NMR (50 MHz, D₂O/0.3% CD₃CO₂D): Table 3. ESI-MS: 612 (100, [M + H]⁺).

(3*aS*,4*R*,5*R*,6*S*,6*aS*)-4-*Acetoxy-6-(acetoxymethyl)-2-(dimethylamino)-3*a*,5,6,6*a*-tetrahydro-4*H*-cyclopent-oxazol-5-yl-2-Acetamido-4-O-(2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-allopyranosyl)-3,6-di-O-acetyl-2-deoxy-β-D-allopyranoside* (**19**). A soln. of **1** (9 mg, 0.014 mmol) and 4-(Me₂N)C₅H₄N (0.5 mg) in pyridine (2 ml) was cooled to 0°, treated with Ac₂O (1 ml), and stirred for 14 h at r.t. The solvents were co-evaporated with toluene (4 × 10 ml). FC (CHCl₃/MeOH 95:5) of the residue yielded **19** (12.7 mg, 97%). Oil. *R*_f (CHCl₃/MeOH 9:1) 0.23. $[\alpha]_D^{25} = -41.5$ (*c* = 0.2, CHCl₃). IR (CHCl₃): 3450w, 3390w, 1740s (br.), 1675m (sh), 1655s, 1550w, 1530w, 1415w, 1370m, 1280m (sh), 1240s, 1165m, 1125w, 1090m, 1040s, 975w, 950w. ¹H-NMR (600 MHz, CDCl₃): Table 2. ¹³C-NMR (150 MHz, CDCl₃): Table 3. ESI-MS: 623 (100, [M + H]⁺).

(3*aR*,4*S*,5*S*,6*R*,6*aR*)-4-*Acetoxy-6-(acetoxymethyl)-2-(dimethylamino)-3*a*,5,6,6*a*-tetrahydro-4*H*-cyclopent-oxazol-5-yl-2-Acetamido-4-O-(2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-allopyranosyl)-3,6-di-O-acetyl-2-deoxy-β-D-allopyranoside* (**20**). As described for **19**, with **17** (12 mg, 0.019 mmol), pyridine (2 ml), Ac₂O (1 ml), and 4-(Me₂N)C₅H₄N (0.5 mg): **20** (16.9 mg, 96%). Oil. *R*_f (CHCl₃/MeOH 9:1) 0.27. $[\alpha]_D^{25} = -55.4$ (*c* = 0.1, CHCl₃). IR (CHCl₃): 3450w, 3390w, 1740s (br.), 1675m (sh), 1655s, 1550w, 1530w, 1415w, 1370m, 1280m (sh), 1240s, 1165m, 1125w, 1090m, 1040s, 975w, 950w. ¹H-NMR (400 MHz, CDCl₃): Table 2. ¹³C-NMR (HMQC 100 MHz, CDCl₃): Table 3.

(1*R*,2*R*,3*S*,4*S*,5*S*)-3-*Acetamido-2,4-diacetoxy-5-(acetoxymethyl)cyclopentyl-2-Acetamido-4-O-(2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-allopyranosyl)-3,6-di-O-acetyl-2-deoxy-β-D-allopyranoside* (**21**). As described for **19**, with **18** (8 mg, 0.013 mmol), pyridine (2 ml), Ac₂O (1 ml), and 4-(Me₂N)C₅H₄N (0.5 mg): **21** (11.9 mg, 97%). Oil. *R*_f (CHCl₃/MeOH 9:1) 0.29. $[\alpha]_D^{25} = -36.7$ (*c* = 0.7, CHCl₃). IR (CHCl₃): 3440w, 3390w, 3040w, 2990w, 2980w, 2900w, 1735s (br.), 1685s (sh), 1675s, 1655m (sh), 1620w, 1565w, 1545w, 1525m (sh), 1510m, 1500m, 1475w, 1370s, 1270m, 1160s, 1130s (sh), 1090s, 1045s, 995m, 950m, 935w (sh), 900w. ¹H-NMR (400 MHz, CDCl₃): Table 2. ¹³C-NMR (HMQC 100 MHz, CDCl₃): Table 3. ESI-MS: 948 (50, [M + H]⁺), 970 (100, [M + Na]⁺), 986 (50, [M + K]⁺).

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