Studies on the Synthesis of Di- and Trisaccharide Analogues of Moenomycin A. Modifications in Unit E and in the Lipid Part

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Routes allowing the synthesis of moenomycin analogues with one modified sugar component and with new lipid parts were developed (see **10c**, **12c**, **16b**, and **20b** in *Schemes 2–4*). It is anticipated that such analogues will be useful for studying the mode of action of the moenomycin-type transglycosylase inhibitors in detail and for preparing analogues with improved pharmacokinetic properties.

Introduction. – The objectives of the studies described in this and the preceding communication [1] were twofold, *i.e.*, to prepare oligosaccharide analogues of moenomycin A with new lipid chains and to develop routes to oligosaccharide (preferably trisaccharide) analogues of moenomycin A (**1**) containing a substituent at C(6) of unit E (see formula **2**) with orthogonal reactivity to all other functional groups present in the molecule.

According to structure-activity-relationship (SAR) studies [2], the antibiotic activity of the moenomycins relies on two features, *i*) anchoring of the antibiotics to the cytoplasmic membrane *via* the lipid part and *ii*) highly selective binding *via* the C–E–F trisaccharide part[1]) (see **1** and **2**) to the glycosyl donor binding site of the enzyme that is responsible for the formation of the sugar strands in peptidoglycan biosynthesis[2]). Although membrane anchoring of the moenomycins [3] is essential for antibiotic activity to be exposed, the structural features of the lipid part that are mandatory to assist the proper interaction of the antibiotic with the membrane-bound enzyme are largely unexplored. With one exception, namely hydrogenation, all modifications of the lipid part of moenomycin caused a dramatic loss of antibiotic activity [3][4]. The prerequisite for the chemical synthesis of lipid-modified moenomycin analogues, *i.e.*, sufficiently convenient access to 2-*O*-alkylated glyceric acid building blocks, has been satisfied only recently [5]. The second objective is based on the SAR result that the 6-OH groups of units C and E are dispensable as far as antibiotic activity is concerned (see dotted arrows in **2**) [2]. Thus, moenomycin analogues with suitable substituents at the 6-position of unit C and/or unit E should allow the study of the mode of action of the moenomycin-type transglycosylase inhibitors in more detail [6] and the preparation of analogues with improved pharmacokinetics.

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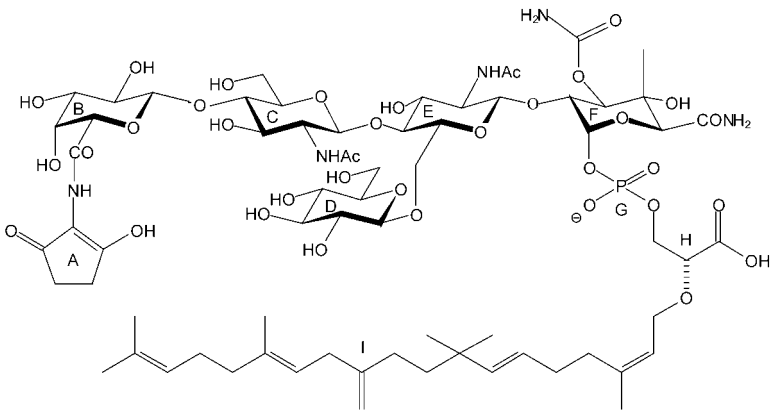
[1]) The different building blocks of the compounds discussed in this paper are indexed exactly as in moenomycin (**1**).

[2]) For a discussion of the SARs and the proposed mode of action, see preceding communication [1].



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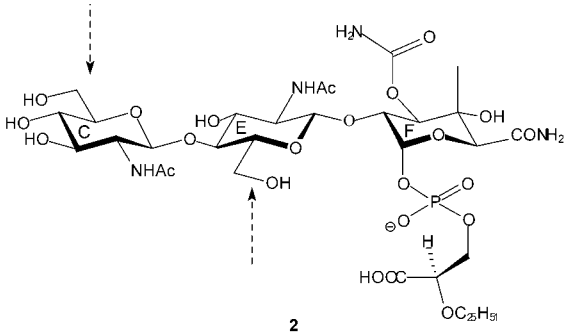

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Results. – *Synthesis of the Carbohydrate Part of a Moenomycin Trisaccharide Analogue. Koeller* and *Wong* [7] have reported that coupling of 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl trichloroacetimidate (**3a**) with (*tert*-butyl)dimethylsilyl 6-*O*-[(*tert*-butyl)diphenylsilyl]-2-deoxy-2-{[(2,2,2-trichloroethoxy)carbonyl]amino}-β-D-glucopyranoside (**4**) in CH_2Cl_2 solution with Me_3SiOTf as promoter afforded the $1\rightarrow4$-linked disaccharide (50%, after deacetylation) (Troc = (2,2,2-trichloroethoxy)carbonyl). The $1\rightarrow3$-linked disaccharide was only a minor product (8%). When we treated the related D-*gluco*-configurated donor **3b** with the same acceptor **4** in CH_2Cl_2 using Me_3SiOTf as promoter, the $1\rightarrow3$-linked disaccharide **5a** was obtained as the main product (76%) accompanied by small amounts of trisaccharide **5b** (8%) (*Scheme 1*)[3]). The desired $1\rightarrow4$ disaccharide was not detected. When the reaction was performed in Et_2O solution, disaccharide **5a** (46%) and trisaccharide **5b** (29%) were obtained. The structure of **5a** was confirmed by analyzing the NMR spectra of **5c**, which was obtained from **5a** by acetylation.

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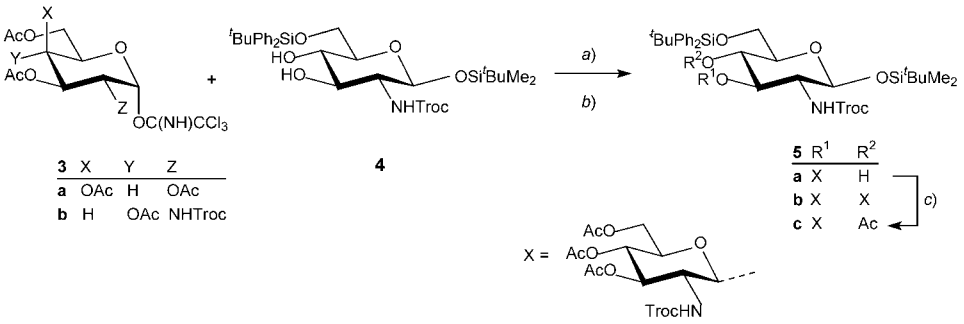
[3]) For a discussion of the influence of the configuration at C(4) on substiution reactions at the anomeric center, see [8].

Scheme 1

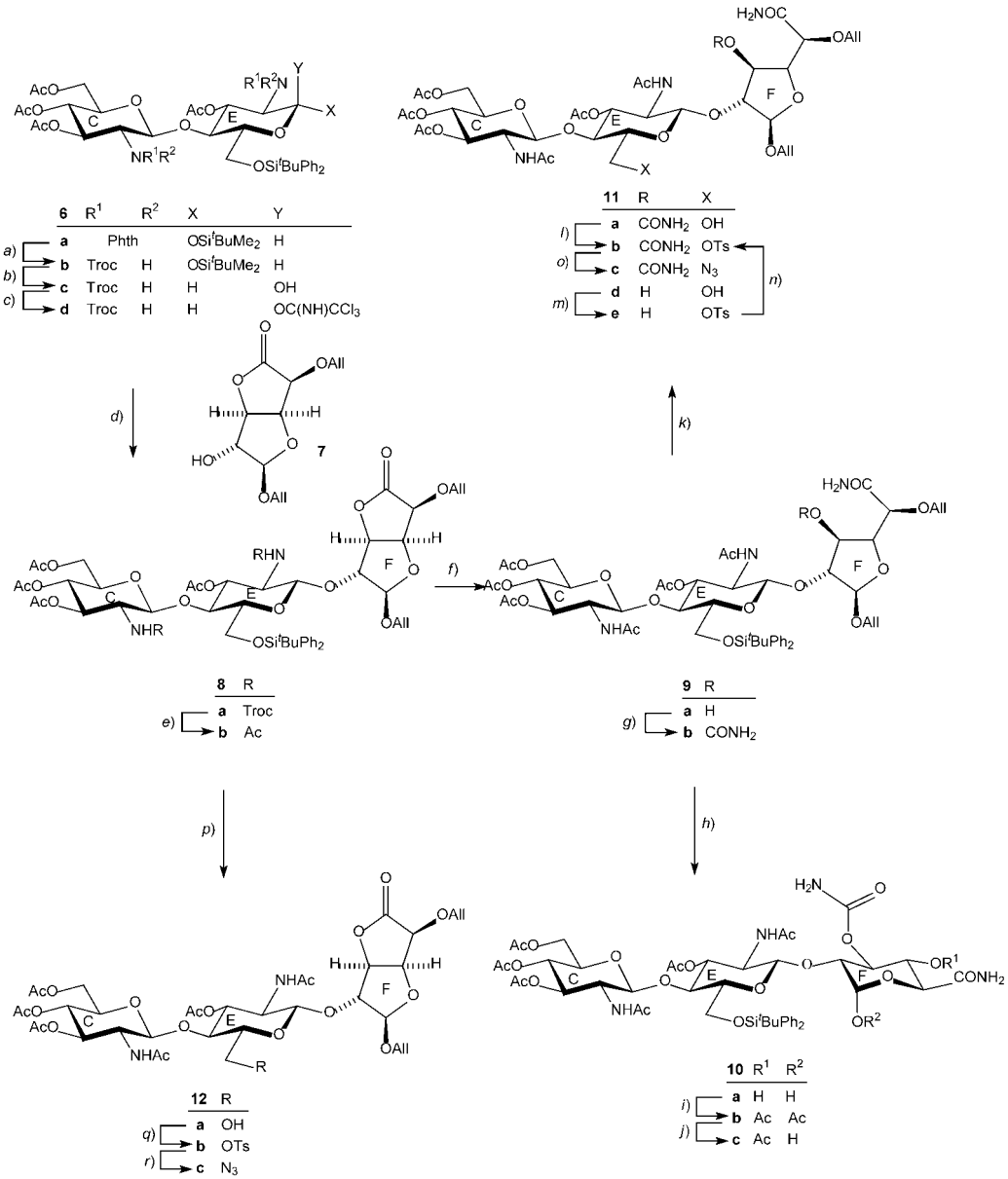


a) **3b** + **4**, 4-Å molecular sieves, CH_2Cl_2, Me_3SiOTf, 0°; 76% of **5a**, 8% of **5b**. *b*) Conditions *a*, Et_2O instead of CH_2Cl_2; 46% of **5a**, 29% of **5b**. *c*) Ac_2O, pyridine, 20°; 87%.

In view of the above results, we based our further synthetic efforts on to the C–E–F trisaccharide precursor **6a** of moenomycin analogues, the synthesis of which was discussed in the preceding communication [1]. As described, removal of the *N*-phthaloyl (PhthN) protecting group in the aminosugar moieties in later stages of the trisaccharide synthesis turned out to be incompatible with the urethane function at C(3) of unit F. Thus, in a new attempt, we replaced the *N*-phthaloyl groups in an early phase of the synthesis by *N*-(2,2,2-trichloroethoxy)carbonyl (TrocN) groups, which we expected to be easily convertible to *N*-Ac groups under mild conditions [9a] (see also [9b]). To this end, **6a** was treated with ethane-1,2-diamine in BuOH (*Scheme 2*). Subsequent *N*-(trichloroethoxy)carbonylation followed by reacetylation furnished **6b**. Selective desilylation at the anomeric position with I_2/MeOH [10], CF_3COOH [11], AcOH [11], KF [12] or Bu_4NF [11] failed [13]. Fortunately, selective removal of the ^{t}BuMe$_2$Si group with $[PdCl_2(MeCN)_2]$, a reagent known to leave ^{t}BuPh$_2$Si ethers intact [14], yielded compound **6c** (55%). The ^{1}H- and ^{13}C-NMR spectra of the desilylation product (H–C(1^E) at $\delta = 5.29$, $J(1E,2E) = 3.6$ Hz; C(1^E) at δ 92.22) indicated the presence of only the α-D-anomer. Treatment of **6c** with Cl_3CCN and Cs_2CO_3 furnished the disaccharide donor **6d** (88%) which was coupled with the ring-F acceptor building block **7**, which is more reactive than previously employed ring-F acceptor units [1]. When the reaction was performed in $ClCH_2CH_2Cl$ solution with Me_3SiOTf as promotor, trisaccharide **8a** was obtained in 55% yield. Performing the reaction in other solvents (MeCN, CH_2Cl_2, THF, and Et_2O) resulted in lower yields [13].

Conversion of the TrocNH groups in **8a** to AcNH functions was achieved on reaction with activated Zn dust [7] or with Zn–Cu complex [15] in Ac_2O and furnished compound **8b** in 63% yield. Treatment of **8b** with saturated NH_3 in THF/MeOH 9:1 opened the lactone ring to give uronamide **9a** (81%). The carbamoyl group was then introduced on reaction of the free OH group with trichloroacetyl isocyanate and subsequent reductive removal of the trichloroacetyl group from the trichloroacetyl urethane to give compound **9b** [16]. By means of the *Nakayama* method [17], the two allyl groups of **9b** were removed with $[Pd(PPh_3)_4]$ in degassed AcOH to furnish compound **10a** (94%). The ^{1}H- and ^{13}C-NMR spectra of **10a** (H–C(1^F) at δ 6.05, $J(1F,2F) = 2.9$ Hz; C(1^F) at δ 93.77) indicated that the anomeric equilibrium was

Scheme 2



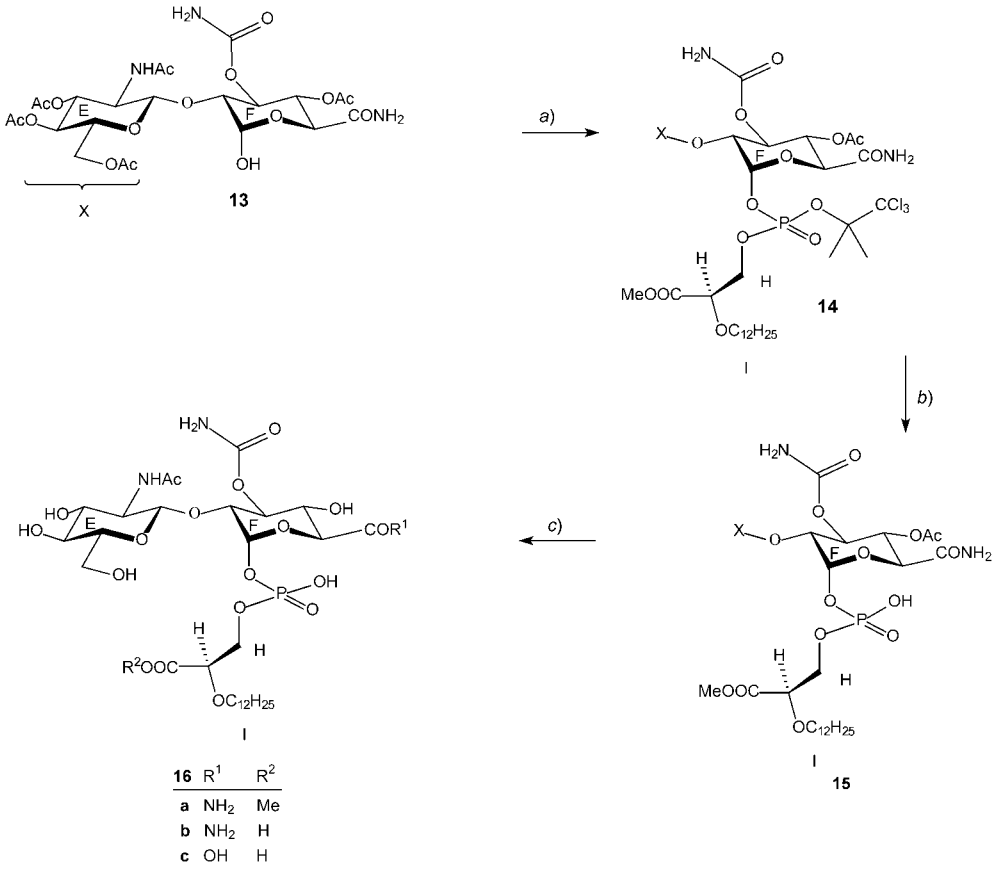
a) 1. BuOH, $H_2N(CH_2)_2NH_2$, 90°; 2. TrocCl, MeOH/H_2O, 20°; 3. Ac_2O, pyridine, 20°; 77%. *b*) $[PdCl_2(MeCN)_2]$, Me_2CO, 20°; 55%. *c*) Cl_3CCN, 4-Å molecular sieves, CH_2Cl_2, Cs_2CO_3, 20°, 88%. *d*) **6d** + **7**, 4-Å molecular sieves, $(ClCH_2)_2$, Me_3SiOTf, −30°; 55%. *e*) Zn, Ac_2O, 20°; 63%. *f*) **8b**, NH_3, THF/MeOH, 0°; 81% of **9a**. *g*) 1. Cl_3CONCO, CH_2Cl_2, 20°; 2. Zn, Me_3OH, 20°; 96% of **9b**. *h*) **9b**, $[Pd(PPh_3)_4]$, AcOH, 20°; 94% of **10a**. *i*) Ac_2O, pyridine, 20°; 93% of **10b**. *j*) $H_2NNH_2 \cdot AcOH$, DMF, 20°; 67% of **10c**. *k*) **9b**, Bu_4NF, THF, 20°; 15% of **11a**; or **9a**, Bu_4NF, THF, 20°; 64% of **11d**. *l*) TsCl, pyridine, DMAP, 20°; 15% of **11b**. *m*) TsCl, CH_2Cl_2/pyridine, DMAP, 20°; 40% of **11e**. *n*) Conditions *g*; 48% of **11b**. *o*) NaN_3, DMF, 85°; 34% of **11c**. *p*) **8b**, conditions *k*; 43% of **12a**. *q*) Conditions *l*; 52% of **12b**. *r*) Conditions *o*; 14% of **12c**.

practically exclusively in favor of the α-D isomer. For the construction of the phosphoric acid diester, the 4^F-OH group had to be protected. Thus, acetylation of **10a** yielded **10b** (H–C(1^F) at δ 6.35, J(1F,2F) = 3.0 Hz; C(1^F) at δ 90.46). Finally, selective removal of the anomeric acetyl group from **10b** with hydrazinium acetate in DMF [18] yielded compound **10c**. Again, only the α-D isomer was present (H–C(1^F) at δ 6.01, J(1F,2F) = 3.1 Hz; C(1^F) at δ 92.90).

Synthesis of a Moenomycin-Type Trisaccharide with a 6-Azido-6-deoxy Unit E. Desilylation of **9b** with Bu_4NF [14] yielded compound **11a** (*Scheme 2*). It turned out to be difficult to remove Bu_4NF chromatographically (FC (silica gel) or ion exchange (*Dowex 50 W X2*, H^+ form)) or by extraction of **11a** from the saturated NaCl solution with AcOEt/BuOH 4 : 1 [20]. In the latter case, the amount of isolated **11a** was low. Tosylation of **11a** with TsCl and *N*,*N*-dimethylpyridin-4-amine (DMAP) in pyridine furnished compound **11b** in low yield because the carbamoyl group was unstable under the reaction conditions. All of the problems mentioned could be avoided by unproblematic desilylation of **9a** with Bu_4NF to give **11d**; Bu_4NF could be removed by column chromatography. Selective tosylation of **11d** with TsCl and pyridine furnished compound **11e** in 40% yield. The carbamoyl group was then introduced as described above to give compound **11b** (48%). Nucleophilic substitution with NaN_3 in DMF [21] converted **11b** into **11c**. The progress of the reaction had to be controlled carefully by TLC since, at longer reaction times, the carbamoyl group was also removed. Similarly, lactone **8b** was converted into the 6^E-azido-6^E-deoxytrisaccharide **12c**: Desilylation of **8b** to give **12a** had also to be controlled carefully by TLC since the lactone did not withstand long reaction times. Tosylation of **12a** with TsCl and pyridine furnished compound **12b**. The reaction of **12b** with NaN_3 in DMF gave **12c**. At long reaction times, also opening of the lactone was observed [13]. Trisaccharides **10c** and **12c** should be very useful intermediates for moenomycin analogues, provided that the yields can be improved. From the azido group, an amino function can be released, *i.e.*, an anchor for conjugation reactions. Likewise, the azido group should allow the conjugation of reporter groups *via* a Cu^I-mediated 1,3-dipolar cycloaddition with suitable alkyne-containing reagents [22] or by a *Staudinger* ligation [23].

Synthesis of a Moenomycin A Disaccharide Analogue. For the construction of the phosphoric acid diester grouping, we used the phosphite methodology [24] as adapted to the synthesis of moenomycin analogues [25]. Thus, the 2,2,2-trichloro-1,1-dimethylethyl phosphorodichloridite [26] was converted to the corresponding bis[triazolide], which in turn was treated with disaccharide **13** [2] (*Scheme 3*). The reaction product was allowed to react with methyl 2-*O*-dodecylglycerate [5] (added in three portions within 2 h) to furnish the corresponding phosphorous acid triester, which, in turn, was oxidized with bis(trimethylsilyl) peroxide [27–29] to give **14** in 59% yield from which 33% could be isolated as a single P-diastereoisomer. Removal of the P-protecting group was achieved under the *Imai* conditions with freshly prepared Zn–Cu couple in pyridine [30]; pentane-2,4-dione was added to chelate the produced zinc cations and maintain the surface of the metal in a clean state. The ratio of the two products, **15** with five acetyl groups (66%) and a second product (22%) with four acetyl groups, was determined by ^{1}H-NMR. The ester-protecting groups of **15** were removed by hydrolysis with 0.3M aqueous LiOH in MeOH/H_2O 2 : 1, the solution of **15** in MeOH/H_2O and the aqueous LiOH solution being carefully degassed by sonication under Ar. The product

Scheme 3



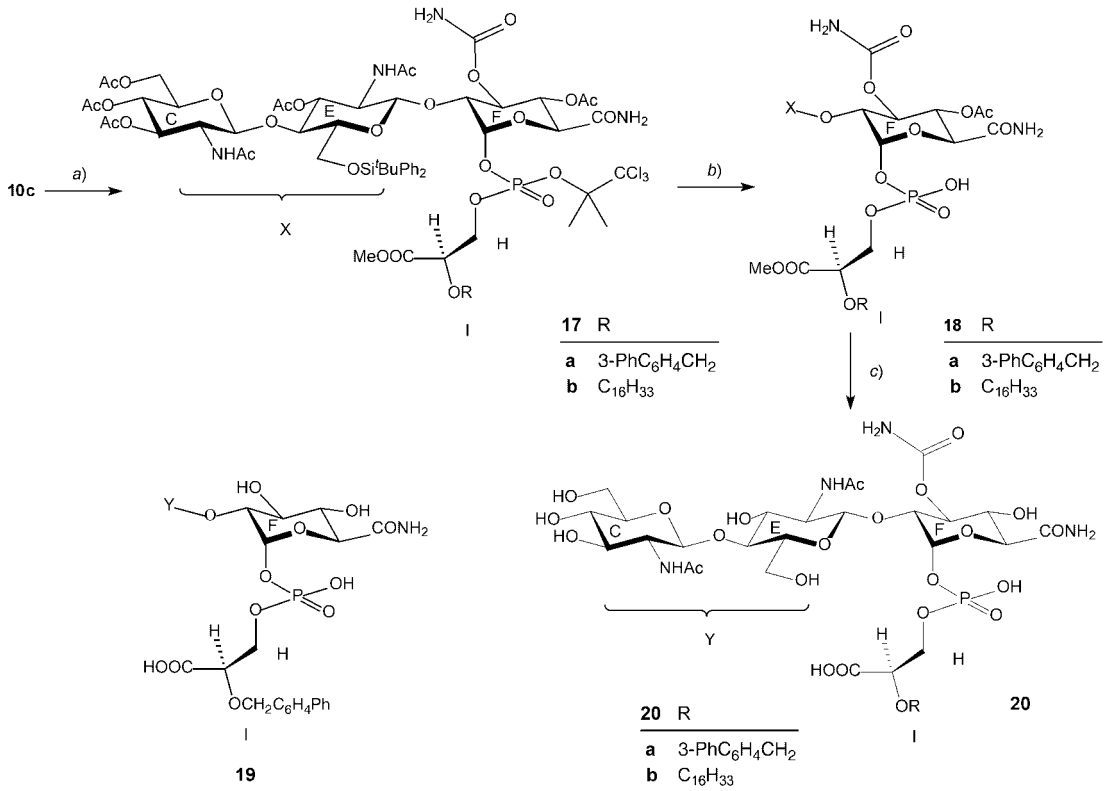
a) 1. 1*H*-1,2,4-triazole, $Cl_3CC(Me)_2OPCl_2$, CH_2Cl_2/pyridine, 0°; 2. **13**, 0°; 3. (*R*)-$MeO_2CCH(C_{12}H_{25}O)CH_2OH$, 0°; 4. $(Me_3SiO)_2$, 0° → 20°; 59% of **14**. *b*) Zn–Cu, pyridine, pentane-2,4-dione, 20°; 66% of **15**. *c*) LiOH, $MeOH/H_2O$, 20°; 30% of **15b**.

mixture consisted of the uronamide **16b** (the target compound of the synthesis, 30%), the less-polar **16a** (8%), and the more polar uronic acid **16c** (8%). The ^{1}H-NMR and the mass spectra of the hydrolysis product **16b** were in accord with the shown structure.

Synthesis of a Moenomycin A Trisaccharide Analogue. By means of the methods described above, the two triesters **17a** and **17b** were prepared each as a mixture of two P-diastereoisomers from **10c** and the 2-*O*-hexadecyl [31] and 2-*O*-([1,1′-biphenyl]-3-ylmethyl) [5] derivatives of methyl glycerate (*Scheme 4*). In the case of **17a**, we succeeded to separate the P-stereoisomers. Removal of the trichloroethyl-1,1-dimethyl protecting group from **17a** under the *Imai* conditions [30] gave a mixture of two compounds (87%) from which the desired compound **18a** was isolated and characterized by ^{1}H-NMR and MS; the second compound, most likely, again arose from the loss of an acetyl group. For the next step, the mixture was used without separation.

Under identical conditions, **17b** was converted to **18b**, which was used for the next step without purification. The final deprotection steps turned out to be unexpectedly unreliable. From **18a** and **18b**, the ^{t}BuPh$_2$Si group had to be removed under carefully controlled conditions with Bu$_4$NF in THF. Too long reaction times or an excess of Bu$_4$NF caused loss of the carbamoyl group. Finally, the ester groups were hydrolyzed with 0.3M aqueous LiOH in MeOH/H$_2$O 2:1. Again, all solutions were carefully degassed under Ar. From **18a**, only a mixture of two products was obtained, the target compound **20a** and the slightly less polar by-product **19** [13]. When **18b** was submitted to the same conditions, **20b** was formed. Here the formation of a by-product could be avoided.

Scheme 4



a) 1. 1*H*-1,2,4-Triazole, $Cl_3CC(Me)_2OPCl_2$, CH_2Cl_2/pyridine, 0°; 2. **12c**, 0°; 3. (*R*)-$MeO_2CCH(3\text{-}PhC_6H_4CH_2O)$-$CH_2OH$ or (*R*)-$MeO_2CCH(C_{16}H_{33}O)CH_2OH$, 0°; 4. $(Me_3SiO)_2$, 0° → 20°; 68% of **17a** or 17% of **17b**, resp. *b*) Zn–Cu, pyridine, pentane-2,4-dione, 20°; 87% of **18a**. *c*) LiOH, MeOH/H$_2$O, 20°; 67% of **20a**/**19** [13] or 49% of **20b** (over steps *b* and *c*, resp.).

The structural assignment of **20b** is based on NMR and MS evidence. In the ^{1}H-NMR spectra, the signals of H–C(1^F) (br. *s* at δ 5.92), H–C(3^F) (*t* at δ 5.07), H–C(5^F) (*d* at δ 4.32), H–C(4^F) (*t* at δ 3.71), and H–C(2^F) (hidden in a *m* at δ 3.66–3.56) were unequivocally identified by ^{1}H,^{1}H-COSY. In addition, ESI-MS displayed

the correct molecular ion at 1033.44931 ($[M-H]^-$; calc. 1033.44869). Unfortunately, we could not find the ^{13}C-NMR signal of the carbamoyl group at *ca.* δ 156, probably due to the lack of an *Overhauser* effect.

In conclusion, methods are now at hand for the synthesis of moenomycin analogues with modified units E (at position 6) and with modified lipid parts. They should be useful for *i*) studying the transglycosylation reaction and the mode of action of the moenomycins in more detail and *ii*) to prepare moenomycin-type transglycosylase inhibitors with improved (pharmacokinetic) properties.

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Experimental Part

General. See [6].

Disaccharide Formation from **3b** *and* **4**. *a) In* CH_2Cl_2. A mixture of **3b** (100.0 mg, 0.16 mmol), **4** (100.0 mg, 0.14 mmol), 4-Å molecular sieves (200.8 mg), and dry CH_2Cl_2 (5.0 ml) was stirred for 1 h at 20° and then cooled to 0°. Me_3SiOTf (6.0 µl) was then injected, and the mixture was stirred at 0° for 1 h. After quenching with Et_3N (20 µl), the mixture was filtered and the filter cake washed with CH_2Cl_2. The combined filtrate and washings were washed with sat. $NaHCO_3$ soln. and H_2O. The org. phase was dried and evaporated. Purification by FC (petroleum ether/AcOEt 2:1) furnished **5a** (125.1 mg, 76%) and **5b** (18.0 mg, 8%) besides 12.2 mg of recovered **4**.

b) *In* Et_2O. As described above, with **3b** (100.0 mg, 0.16 mmol), **4** (100.0 mg, 0.14 mmol), 4-Å molecular sieves (200.7 mg), and dry Et_2O (5.0 ml) instead of CH_2Cl_2: **5a** (76.2 mg, 46%) and **5b** (66.0 mg, 29%).

*(*tert*-Butyl)dimethylsilyl 6*-O-*[(*tert*-Butyl)diphenylsilyl]-2-deoxy-3*-O-*{3,4,6-tri*-O-*acetyl-2-deoxy-2-{[(2,2,2-trichloroethoxy)carbonyl]amino}-β*-D-*glucopyranosyl}-2-{[(2,2,2-trichloroethoxy)carbonyl]amino}-β*-D-*glucopyranoside* (**5a**): R_f (petroleum ether/AcOEt 1:1): 0.68. ^{1}H-NMR (300 MHz, $CDCl_3$; signals that could be assigned): 7.75–7.70, 7.42–7.36 (2*m*, 10 arom. H); 2.06, 2.06, 2.01 (3*s*, 3 MeCO); 1.08 (*s*, Me_3C (^{t}BuPh$_2$Si)); 0.94 (*s*, Me_3C (^{t}BuMe$_2$Si)); 0.20, 0.16 (2 *s*, 2 Me).

*(*tert*-Butyl)dimethylsilyl 6*-O-*[(*tert*-Butyl)diphenylsilyl]-2-deoxy-3,4-bis*-O-*{3,4,6-tri*-O-*acetyl-2-deoxy-2-{[(2,2,2-trichloroethoxy)carbonyl]amino}-β*-D-*glucopyranosyl}-2-{[(2,2,2-trichloroethoxy)carbonyl]amino}-β*-D-*glucopyranoside* (**5b**): R_f (petroleum ether/AcOEt 1:1): 0.61. ^{1}H-NMR (300 MHz, $CDCl_3$; signals that could be assigned): 7.82–7.43 (*m*, 10 arom. H); 2.19, 2.13, 2.07, 2.05, 2.01, 1.99 (6*s*, 6 MeCO); 1.17 (*s*, Me_3C (^{t}BuPh$_2$Si)); 0.96 (*s*, Me_3C (^{t}BuMe$_2$Si)); 0.19, 0.15 (2*s*, 2 Me). ESI-MS ($C_{61}H_{82}Cl_9N_3O_{25}Si_2$ (1632.58, 1627.20)): 1628.22709 ($[M+H]^+$; calc. 1628.20425).

*(*tert*-Butyl)dimethylsilyl 4*-O-*Acetyl-6*-O-*[(*tert*-butyl)diphenylsilyl]-2-deoxy-3*-O-*{3,4,6-tri*-O-*acetyl-2-deoxy-2-{[(2,2,2-trichloroethoxy)carbonyl]amino}-β*-D-*glucopyranosyl}-2-{[(2,2,2-trichloroethoxy)carbonyl]amino}-β*-D-*glucopyranoside* (**5c**). To a soln. of **5a** (100.0 mg, 0.086 mmol) in pyridine (0.50 ml), Ac_2O (0.20 ml) and DMAP (8.0 mg, 0.066 mmol) were added. After stirring for 2 h at 20°, the mixture was evaporated. Purification by FC (petroleum ether/AcOEt 2:1) furnished **5c** (90.1 mg, 87%). R_f (petroleum ether/AcOEt 1:1): 0.70. ^{1}H-NMR (^{1}H,^{1}H-COSY; 600 MHz, $CDCl_3$): 7.71–7.36 (*m*, 10 arom. H), 5.67 (br. *s*, N*H*Troc); 5.25–5.11 (*m*, H–C(1^C), H–C(3^C), N*H*Troc); 5.01 (*t*, H–C(4^C)); 4.97 (*t*, H–C(4^E)); 4.83–4.65 (*m*, H–C(1^E), 2 CCl_3CH_2); 4.53–4.45 (*m*, H–C(3^E)); 4.22 (*dd*, H_a–C(6^C)); 4.14 (*d*, H_b–C(6^C)); 3.70–3.57 (*m*, H–C(2^C), H–C(5^E), H–C(5^C), CH_2(6^E)); 3.07–3.00 (*m*, H–C(2^E)); 2.09, 2.01, 2.00, 1.86 (4*s*, 4 MeCO); 1.04 (*s*, Me_3C (^{t}BuPH$_2$Si)); 0.91 (*s*, Me_3 (^{t}BuMe$_2$Si)); 0.15, 0.12 (2*s*, 2 Me); J(2E,3E) = 9.6, J(3E,4E) = 9.6, J(4E,5E) = 9.6, J(3C,4C) = 9.6, J(4C,5C) = 9.6, J(5C,6aC) = 3.9, J(6C,6bC) = 12.6. ^{13}C-NMR (^{13}C,^{1}H-COSY, 75.5 MHz, $CDCl_3$): 170.78, 170.50, 170.03, 169.53 (4 Me*C*O); 153.91 (2 CCl_3CH_2OCO); 135.76, 135.67, 133.21, 133.19, 129.84, 129.81, 127.84, 127.79 (arom. C); 100.10 (C(1^E)); 95.52 (2 *C*Cl_3CH_2OCO); 94.25 (C(1^C)); 77.84 (C(3^E)); 75.02 (C(3^C)); 74.80, 74.62 (2 CCl_3CH_2O); 72.14 (C(5^E)); 72.02 (C(5^C)); 68.49 (C(4^E)); 68.47 (C(4^C)); 63.16 (C(6^C)); 61.94 (C(6^E)); 60.72 (C(2^E)); 56.49 (C(2^C)); 26.84 (*Me*$_3$C (^{t}BuPh$_2$Si)); 25.77 (*Me*$_3$C (^{t}BuMe$_2$Si)); 20.86, 20.73, 20.70, 20.68 (4 *Me*CO); 19.26 (Me_3C (^{t}BuPh$_2$Si)); 18.06 (Me_3C (^{t}BuMe$_2$Si)); –4.11, –5.18 (2 Me). ESI-MS ($C_{48}H_{66}Cl_6N_2O_{17}Si_2$ (1211.94, 1208.20)): 1231.19438 ($[M+Na]^+$; calc. 1231.19210).

*(*tert*-Butyl)dimethylsilyl 3*-O-*Acetyl-6*-O-*[(*tert*-butyl)diphenylsilyl]-2-deoxy-4*-O-*{3,4,6-tri*-O-*acetyl-2-deoxy-2-{[(2,2,2-trichloroethoxy)carbonyl]amino}-β*-D-*glucopyranosyl}-2-{[(2,2,2-trichloroethoxy)carbonyl]ami-*

*no}-β-*D*-glucopyranoside* (**6b**). To a soln. of **6a** (1.09 g, 0.89 mmol) in BuOH (32 ml) ethane-1,2-diamine (8.0 ml) was added. The soln. was stirred at 90° for 12 h. After evaporation, the residue was dissolved in MeOH/H_2O 5:1 (12 ml), then $NaHCO_3$ (600.0 mg) was added. TrocCl (2.0 ml, 13.9 mmol) was added dropwise at 20°, and the mixture was stirred for 1 h. The soln. was neutralized with 1M HCl (2.0 ml) and evaporated. The residue was dissolved in pyridine (5.0 ml), Ac_2O (3.0 ml) was added, then the mixture was stirred at 20° overnight. The solvents were removed by azeotropic evaporation with toluene. Purification by FC (petroleum ether/AcOEt 2:1) afforded **6b** (830.2 mg, 77%). R_f (petroleum ether/AcOEt 1:1): 0.65. $[\alpha]_D^{26} = -6$ ($c = 1.0$, $CHCl_3$). ^{1}H-NMR (^{1}H,^{1}H-COSY; 600 MHz, $CDCl_3$): 7.78–7.28 (*m,* 10 arom. H); 5.66 (*d*, N*H*Troc); 5.06 (*t,* H–C(3^E)); 4.84 (*t,* H–C(4^C)); 4.78, 4.62 (*AB*, CCl_3CH_2OCO); 4.68 (*d,* H–C(1^E)); 4.67 (*t,* H–C(3^C)); 4.36 (*dd*, H_a–C(6^C)); 4.64, 4.37 (*AB*, CCl_3CH_2OCO); 4.18 (*d,* H–C(1^C)); 4.06 (*t,* H–C(4^E)); 4.00 (br. *d*, H_b–C(6^C)); 3.99 (br. *d*, H_a–C(6^E)); 3.75–3.71 (*m,* H–C(2^E)); 3.60 (br. *d*, H_b–C(6^E)); 3.54–3.47 (*m,* H–C(2^C)); 3.43–3.40 (*m,* H–C(5^C)); 3.34 (br. *d*, H–C(5^E)); 2.07, 2.05, 2.04, 1.95, (4*s,* 4 MeCO); 1.16 (*s,* Me_3C (^{t}BuPh$_2$Si)); 0.93 (*s,* Me_3C (^{t}BuMe$_2$Si)); 0.20, −0.14 (2*s,* 2 Me); J(1E,2E) = 8.0, J(2E,3E) = 9.7, J(3E,4E) = 9.7, J(4E,5E) = 9.7, J(5E,6bE) = J(5E,6bE) = small, J(6aE,6bE) = 10.3, J(1C,2C) = 7.2, J(2C,3C) = 9.5, J(3C,4C) = 9.5, J(4C,5C) = 9.5, J(5C,6aC) = 4.8, J(6aC,6bC) = 12.3, $2J_{(AB)}$ = 12.3, J(H,NHTroc) = 7.8. ^{13}C-NMR (^{13}C,^{1}H-COSY, 75.5 MHz, $CDCl_3$): 171.46, 170.73, 170.34, 169.74 (4 Me*C*O), 154.82, 153.87 (2 CCl_3CH_2OCO), 136.17, 135.98, 133.53, 132.17, 131.00, 130.41, 128.99, 128.16 (arom. C); 100.26 (C(1^C)); 97.00 (C(1^E)); 95.81, 95.67 (2 *C*Cl_3CH_2OCO); 75.01 (C(5^E)); 74.86, 74.50 (2 CCl_3CH_2OCO); 73.95 (C(4^E)); 72.73 (C(3^E)); 72.61 (C(3^C)); 71.51 (C(5^C)); 68.75 (C(4^C)); 62.03 (C(6^C)); 61.48 (C(6^E)); 58.16 (C(2^E)); 56.16 (C(2^C)); 27.18 (*Me*$_3$C (^{t}BuPH$_2$Si)); 25.89 (*Me*$_3$C (^{t}BuMe$_2$Si)); 21.04, 20.92, 20.92, 20.79 (4 *Me*CO); 19.35 (Me_3C (^{t}BuPH$_2$Si)); 18.29 (Me_3C (^{t}BuMe$_2$Si)); −4.07, −4.79 (2 Me). ESI-MS ($C_{48}H_{66}Cl_6N_2O_{17}Si_2$ (1211.94, 1208.20)): 1209.20683 ([*M* + H]$^+$; calc. 1209.21016).

*3-*O*-Acetyl-6-*O*-[(*tert*-butyl)diphenylsilyl]-2-deoxy-4-*O*-{3,4,6-tri-*O*-acetyl-2-deoxy-2-{[(2,2,2-trichloroethoxy)carbonyl]amino}-β-*D*-glucopyranosyl}-2-{[(2,2,2-trichloroethoxy)carbonyl]amino}-α-*D*-glucopyranose* (**6c**). Bis(acetonitrile)dichloropalladium (130.0 mg, 0.50 mmol) was added to a foil-covered flask containing **6b** (1.20 g, 0.99 mmol) in acetone (20 ml). After stirring for 4 d at 20°, the mixture was evaporated and the residue purified by FC (petroleum ether/AcOEt 2:1): **6c** (600.2 mg, 55%). R_f (petroleum ether/AcOEt 1:1): 0.54. $[\alpha]_D^{26} = -33$ ($c = 1.0$, $CHCl_3$). ^{1}H-NMR (^{1}H,^{1}H-COSY; 300 MHz, $CDCl_3$): 7.78–7.21 (*m,* 10 arom. H); 5.71 (*t,* H–C(3^E)); 5.29 (*dd*, H–C(1^E)); 5.05, 4.54 (*AB*, CCl_3CH_2OCO); 4.91 (*t,* H–C(4^C)); 4.79 (*d,* OH–C(1)); 4.59 (*t,* H–C(3^C)); 4.61, 4.37 (*AB*, CCl_3CH_2OCO); 4.41 (*dd*, H_a–C(6^C)); 4.10 (*d,* H–C(1^C)); 4.09–3.96 (*m,* H–C(4^E), H–C(2^E), H_b–C(6^C)); 3.84–3.58 (*m,* CH_2(6^E), H–C(2^C), H–C(5^E)); 3.78–3.41 (*m,* H–C(5^C)); 2.06, 2.05, 2.04, 2.01 (4*s,* 4 MeCO); 1.14 (*s,* Me_3C); J(1E,2E) = 3.6, J(2E,3E) = 9.6, J(3E,4E) = 9.6, J(1C,2C) = 7.9, J(2C,3C) = 9.6, J(3C,4C) = 9.6, J(4C,5C) = 9.6, J(5C,6aC) = 4.1, J(6aC,6bC) = 12.6, J(H,OH) = 4.6, $2J_{Troc}$ = 12.1. ^{13}C-NMR (^{13}C,^{1}H-COSY; 75.5 MHz, $CDCl_3$): 170.82, 170.74, 170.72, 169.63 (4 Me_3CO); 155.77, 155.47 (2 CCl_3CH_2OCO); 136.12, 136.06, 133.60, 132.53, 130.88, 130.33, 128.96, 128.13 (arom. C)); 101.06 (C(1^C)); 96.31, 95.06 (2 *C*Cl_3CH_2OCO); 92.22 (C(1^E)); 74.90, 74.77 (2 CCl_3CH_2OCO); 74.77 (C(4^E)); 72.24 (C(3^C)); 71.41 (C(5^C)); 70.89 (C(3^E)); 70.39 (C(5^E)); 68.38 (C(4^C)); 61.81 (C(6^E)); 61.74 (C(6^C)); 56.16 (C(2^E)); 54.89 (C(2^C)); 27.23 (*Me*$_3$C); 21.10, 20.93, 20.93, 20.90 (4 *Me*CO); 19.44 (Me_3C). ESI-MS (acetone/H_2O/NH_4CO_3; $C_{42}H_{52}Cl_6N_2O_{17}Si$ (1097.68, 1094.12)): 1112.15218 ([*M* + NH_4]$^+$; calc. 1112.15094).

*3-*O*-Acetyl-6-*O*-[(*tert*-butyl)diphenylsilyl]-2-deoxy-4-*O*-{3,4,6-tri-*O*-acetyl-2-deoxy-2-{[(2,2,2-trichloroethoxy)carbonyl]amino}-β-*D*-glucopyranosyl}-2-{[(2,2,2-trichloroethoxy)carbonyl]amino}-1-*O*-(2,2,2-trichloro-1-iminoethyl)-α-*D*-glucopyranose* (**6d**). Trichloroacetonitrile (0.4 ml) and 4-Å molecular sieves (100 mg) were added to a soln. of **6c** (500 mg, 0.46 mmol) in dry CH_2Cl_2 (4.0 ml). The mixture was stirred for 1 h at 20°. Dry cesium carbonate (40.0 mg, 0.12 mmol) was then added and stirring continued for an additional 4.5 h. Et_3N (2.0 ml) was added and the mixture filtered through a short plug of silica gel. Evaporation and FC (petroleum ether/AcOEt 2:1) afforded **6d** (500 mg, 88%). R_f (petroleum ether/AcOEt 1:1): 0.58. $[\alpha]_D^{26} = +14$ ($c = 1.0$, $CHCl_3$). ^{1}H-NMR (^{1}H,^{1}H-COSY; 300 MHz, $CDCl_3$): 8.71 (*s,* C=NH); 7.77–7.43 (*m,* 10 arom. H); 6.47 (*d,* H–C(1^E)); 5.24 (*d,* NH); 5.23 (*dd*, H–C(3^E)); 4.90 (*t,* H–C(4^C)); 4.79 (*t,* H–C(3^C)); 4.72 (*s,* CCl_3CH_2OCO); 4.62, 4.48 (*AB*, CCl_3CH_2OCO); 4.37 (*dd*, H_a–C(6^C)); 4.36 (*d,* H–C(1^C)); 4.23–4.14 (*m,* H–C(2^E); H–C(4^E)); 3.99 (*dd*, H_b–C(6^C)); 3.95 (br. *d*, H_a–C(6^E)); 3.79–3.68 (*m,* H_b–C(6^E), H–C(5^E)); 3.55–3.40 (*m,* H–C(2^C), H–C(5^C)); 2.06, 2.06, 2.03, 1.98, (4*s,* 4 MeCO); 1.14 (*s,* Me_3C); J(1E,2E) = 3.6, J(2E,3E) = 10.2, J(3E,4E) = 9.3, J(5E,6aE) = small, J(6aE,6bE) = 12.9, J(1C,2C) = 8.1, J(2C,3C) = 9.6, J(3C,4C) = 9.6, J(4C,5C) = 9.6, J(5C,6aC) = 4.8, J(5C,6bC) = 1.3, J(6aC,6bC) = 12.6, J(H,NH) = 9.0, $^2J_{Troc}$ = 12.3. ^{13}C-NMR (^{13}C,^{1}H-COSY; 75.5 MHz, $CDCl_3$): 171.37, 170.70, 170.45, 169.77 (4 Me*C*O); 160.91 (C=NH); 154.60, 153.87 (2 CCl_3CH_2OCO); 136.15, 135.95, 133.43, 132.24, 130.92, 130.45, 128.85, 128.26 (arom. C); 100.27 (C(1^C)); 95.59, 95.19 (2 *C*Cl_3CH_2OCO); 95.19 (C(1^E)); 74.83 (C(NH)*C*Cl_3); 74.56 (2 CCl_3CH_2OCO); 73.67 (C(4^E)); 73.21 (C(5^C));

72.44 (C(3^C)); 71.66 (C(5^E)); 70.33 (C(3^E)); 68.63 (C(4^C)); 61.95 (C(6^C)); 61.14 (C(6^E)); 56.22 (C(2^E)); 54.52 (C(2^C)); 27.22 (*Me*$_3$C), 20.92–20.86 (4 *Me*CO); 19.53 (Me$_3$*C*). ESI-MS ($C_{44}H_{52}Cl_9N_3O_{17}Si$ (1242.07, 1237.03)), 1260.01042 ([*M* + Na]$^+$; calc. 1260.01533).

Prop-2-enyl O-*3,4,6-Tri*-O-*acetyl-2-deoxy-2-{[(2,2,2-trichloroethoxy)carbonyl]amino}-β*-D-*glucopyranosyl-(1 → 4)*-O-*3*-O-*acetyl-6*-O-*[(*tert*-*butyl)diphenylsilyl]-2-deoxy-2-{[(2,2,2-trichloroethoxy)carbonyl]amino}-β*-D-*glucopyranosyl-(1 → 2)-5*-O-*prop-2-enyl-β*-D-*glucofuranosidurono-6,3-lactone* (**8a**). A mixture of **6d** (200.0 mg, 0.16 mmol), **7** [1] (80.0 mg, 0.31 mmol), 4-Å molecular sieves (200.0 mg), and dry 1,2-dichloroethane (5.0 ml) was stirred for 1 h at 20° under Ar and then cooled to −30°. Me$_3$SiOTf (6 µl) was injected, and the mixture was stirred at −30° for 45 min (TLC (petroleum ether/AcOEt 2:1) monitoring). After quenching with Et$_3$N (20 µl), the mixture was filtered and the filter cake washed with CH_2Cl_2. The combined filtrate and washings were washed with sat. $NaHCO_3$ soln. and H_2O. The org. phase was dried (Na_2SO_4) and evaporated. Purification by FC (petroleum ether/AcOEt 2:1) furnished **8a** (118.0 mg, 55%). R_f (petroleum ether/AcOEt 1:1.5): 0.64. $[\alpha]_D^{26} = -4$ (*c* = 1.0, $CHCl_3$). ^{1}H-NMR (^{1}H,^{1}H-COSY; 400 MHz, $CDCl_3$): 7.74–7.41 (*m,* 10 arom. H); 6.07 (br. *s,* NH); 6.04–5.94, 5.86–5.76 (2 *m,* 2 CH$_2$=C*H*CH$_2$); 5.41–5.09 (*m,* 2 C*H*$_2$=CHCH$_2$); 5.30 (*s,* H–C(1^F)); 5.07 (*t,* H–C(3^E)); 4.93 (*t,* H–C(4^F)); 4.86 (*t,* H–C(4^C)); 4.84 (*d,* H–C(3^F)); 4.70 (*d,* H–C(1^E)); 4.81–4.48 (*m,* 2 CCl$_3$CH$_2$OCO, H–C(3^C)); 4.46 (*s,* H–C(2^F)); 4.33 (*d,* H–C(1^C)); 4.33–4.27 (*m,* H$_a$–C(6^C)); CH$_2$=CHC*H*$_2$, 1 H of CH$_2$=CHC*H*$_2$); 4.14 (*d,* H–C(5^F)); 4.09 (*t,* H–C(4^E)); 3.99 (*dd,* H$_b$–C(6^C)); 3.94 (br. *d,* H$_a$–C(6^E)); 3.87–3.82 (*m,* 1 H, CH$_2$=CHC*H*$_2$); 3.78–3.73 (*m,* H–C(2^E)); 3.68 (br. *d,* H$_b$–C(6^E)); 3.45–3.38 (*m,* H–C(2^C), H–C(5^C)); 3.28 (br. *d,* H–C(5^E)); 2.05, 2.04, 2.02, 1.99 (4*s,* 4 MeCO); 1.12 (*s,* Me$_3$C); *J*(3F,4F) = 4.6, *J*(4F,5F) = 6.7, *J*(1E,2E) = 7.8, *J*(2E,3E) = 9.2, *J*(3E,4E) = 9.2, *J*(4E,5E) = 9.2, *J*(6aE,6bE) = 11.6, *J*(1C,2C) = 7.8, *J*(3C,4C) = 9.5, *J*(4C,5C) = 9.5, *J*(5C,6bC) = 1.2, *J*(6aC,6bC) = 11.2. ^{13}C-NMR (^{13}C,^{1}H-COSY; 75.5 MHz, $CDCl_3$): 172.39, 171.32, 170.81, 170.52, 169.68 (4 Me*C*O, CO); 154.78, 153.87 (2 CCl$_3$CH$_2$O*C*O); 135.92, 135.74, 133.23, 132.07, 130.79, 130.35, 128.66, 128.15 (arom. C); 133.72, 133.69 (2 CH$_2$=*C*HCH$_2$); 119.07, 117.54 (*C*H$_2$=CHCH$_2$); 106.39 (C(1^F)); 101.00 (C(1^E)); 100.22 (C(1^C)); 95.87, 95.41 (2 *C*Cl$_3$CH$_2$OCO); 83.80 (C(2^F)); 81.71 (C(3^F)); 76.20 (C(4^F)); 75.09 (C(5^E)); 74.63 (C(4^C)); 74.45 (CCl$_3$*C*H$_2$OCO); 74.10 (C(5^F)); 73.45 (C(4^E)); 72.36 (C(3^E)); 72.05 (C(3^C)); 71.78 (CCl$_3$CH$_2$OCO); 71.59 (C(5^C)); 68.54 (2 CH$_2$=CH*C*H$_2$); 62.00 (C(6^C)); 61.37 (C(6^E)); 56.43 (C(2^C)); 55.76 (C(2^E)); 27.15 (*Me*$_3$C); 21.02, 20.82, 20.78, 20.73 (4 *Me*CO); 19.44 (Me$_3$*C*). ESI-MS ($C_{54}H_{66}Cl_6N_2O_{22}Si$ (1335.92, 1332.20)): 1355.18850 ([*M* + Na]$^+$; calc. 1355.19057).

Prop-2-enyl O-*3,4,6-Tri*-O-*acetyl-2-(acetylamino)-2-deoxy-β*-D-*glucopyranosyl-(1 → 4)*-O-*3*-O-*acetyl-2-(acetylamino)-6*-O-*[(*tert*-*butyl)diphenylsilyl]-2-deoxy-β*-D-*glucopyranosyl-(1 → 2)-5*-O-*prop-2-enyl-β*-D-*glucofuranosidurono-6,3-lactone* (**8b**). Activated Zn dust (4.5 g) was added to a soln. of **8a** (300.0 mg, 0.23 mmol) in Ac_2O (4.5 ml). The mixture was stirred for 24 h at 20°. The mixture was filtered through a plug of *Celite*, eluting with AcOEt and MeOH. Evaporation and FC (AcOEt) furnished **8b** (150.0 mg, 63%). R_f (CH_2Cl_2/MeOH 10:1): 0.58. $[\alpha]_D^{26} = -25$ (*c* = 1.0, $CHCl_3$). ^{1}H-NMR (^{1}H,^{1}H-COSY; 300 MHz, $CDCl_3$): 7.74–7.41 (*m,* 10 arom. H); 6.65 (br. *s,* NH); 6.01–5.92, 5.81–5.71 (2 *m,* 2 CH$_2$=C*H*CH$_2$); 5.39–5.25, 5.15–5.04 (*m,* 2 C*H*$_2$=CHCH$_2$); 5.23 (*s,* H–C(1^F)); 4.97 (*t,* H–C(3^C)); 4.96 (*t,* H–C(3^E)); 4.94 (*dd,* H–C(4^F)); 4.90 (*t,* H–C(4^C)); 4.84 (*d,* H–C(3^F)); 4.64 (*d,* H–C(1^C)); 4.48 (*d,* H–C(1^E)); 4.35 (*s,* H–C(2^F)); 4.34–4.23 (*m,* H$_a$–C(6^C), CH$_2$=CHC*H*$_2$, 1 H of CH$_2$=CHC*H*$_2$); 4.17 (*d,* H–C(5^F)); 4.08 (*t,* H–C(4^E)); 4.04–3.97 (*m,* H–C(2^C)); 3.98 (br. *d,* H$_b$–C(6^C)); 3.91 (*dd,* H$_a$–C(6^E)); 3.82–3.78 (*m,* 1 H, CH$_2$=CHC*H*$_2$); 3.75–3.66 (*m,* H–C(2^E)); 3.59 (*dd,* H$_b$–C(6^E)); 3.46–3.42 (*m,* H–C(5^C)); 3.37–3.33 (*m,* H–C(5^E)); 2.03, 2.00, 1.98, 1.96, 1.95, 1.52 (6*s,* 6 MeCO); 1.09 (*s,* *Me*$_3$C); *J*(3F,4F) = 5.0, *J*(4F,5F) = 6.7, *J*(1E,2E) = 8.1, *J*(2E,3E) = 9.2, *J*(3E,4E) = 9.2, *J*(4E,5E) = 9.2, *J*(5E,6aE) = 1.2, *J*(5E,6bE) = 1.0, *J*(6aE,6bE) = 12.3, *J*(1C,2C) = 7.8, *J*(2C,3C) = 9.5, *J*(3C,4C) = 9.5, *J*(4C,5C) = 9.5, *J*(6aC,6bC) = 12.3. ^{13}C-NMR (^{13}C,^{1}H-COSY; 75.5 MHz, $CDCl_3$): 172.97, 171.10, 170.96, 170.72, 170.72, 170.30, 169.74 (6 Me*C*O, CO); 136.07, 135.91, 133.78, 132.30, 130.66, 130.34, 128.55, 128.21 (arom. C); 133.78, 133.74 (2 CH$_2$=*C*HCH$_2$); 119.11, 117.65 (2 *C*H$_2$=CHCH$_2$); 106.30 (C(1^F)); 101.06 (C(1^C)); 100.51 (C(1^E)); 84.17 (C(2^F)); 81.93 (C(3^F)); 76.32 (C(4^F)); 75.56 (C(5^E)); 74.29 (C(5^F)); 73.47 (C(4^E)); 72.70 (C(3^C)); 72.41 (C(3^E)); 71.81 (CH$_2$=CH*C*H$_2$); 71.74 (C(5^C)); 68.63 (CH$_2$=CH*C*H$_2$); 68.50 (C(4^C)); 62.08 (C(6^C)); 61.68 (C(6^E)); 54.83 (C(2^E)); 53.38 (C(2^C)); 27.30 (*Me*$_3$C); 23.46, 23.19, 20.89, 20.89, 20.89, 20.89 (6 MeCO); 19.51 (Me$_3$*C*). ESI-MS ($C_{52}H_{68}N_2O_{20}Si$ (1069.20, 1068.41)): 1091.40550 ([*M* + Na]$^+$; calc. 1091.40327), 1069.42372 ([*M* + H]$^+$; calc. 1069.42127).

Prop-2-enyl O-*3,4,6-Tri*-O-*acetyl-2-(acetylamino)-2-deoxy-β*-D-*glucopyranosyl-(1 → 4)*-O-*3*-O-*acetyl-2-(acetylamino)-6*-O-*[(*tert*-*butyl)diphenylsilyl]-2-deoxy-β*-D-*glucopyranosyl-(1 → 2)-5*-O-*prop-2-enyl-β*-D-*glucofuranosiduronamide* (**9a**). Compound **8b** (100.0 mg, 0.94 mmol) was added to a sat. NH_3 soln. in THF/MeOH 9:1 (10.0 ml) at 0°, and the mixture was stirred at 0° for 3 h (TLC ($CHCl_3$/MeOH 10:1) monitoring). Evaporation and FC ($CHCl_3$/MeOH 20:1) furnished **9a** (82.2 mg, 81%). R_f (CH_2Cl_2/MeOH 10:1): 0.40. $[\alpha]_D^{26} = -30$ (*c* = 1.0, $CHCl_3$). ^{1}H-NMR (^{1}H,^{1}H-COSY; 400 MHz, $CDCl_3$): 7.70–7.36 (*m,* 10 arom. H); 6.73, 5.99 (2 br. *s,*

$CONH_2$); 6.31 (br. *d*, N*H*Ac); 5.90–5.75 (*m*, 2 CH_2=C*H*CH_2, N*H*Ac); 5.27–5.04 (*m*, 2 CH_2=CHCH_2); 5.06 (*s*, H–C(1^F)); 4.93 (*t*, H–C(3^E)); 4.90 (*t*, H–C(4^C)); 4.81 (*t*, H–C(3^C)); 4.69 (*d*, N*H*Ac); 4.50 (*d*, H–C(1^E)); 4.43 (*dd*, H–C(4^F)); 4.39 (*d*, H–C(1^C)); 4.23 (*dd*, H_a–C(6^C)); 4.18 (*d*, H–C(5^F)); 4.18–4.07 (*m*, H–C(2^F), H–C(3^F), CH_2=CHCH_2, 1 H of CH_2=CHCH_2); 4.06–3.99 (*m*, H–C(4^E), H–C(2^E)); 3.94 (*dd*, H_b–C(6^C)); 3.89–3.84 (*m*, H_a–C(6^E), 1 H of CH_2=CHCH_2); 3.79 (*t*, H–C(2^C)); 3.53 (*dd*, H_b–C(6^E)); 3.40–3.34 (*m*, H–C(5^C)); 3.33–3.28 (*m*, H–C(5^E)); 1.99, 1.96, 1.94, 1.93, 1.90, 1.46 (6*s*, 6 MeCO); 1.05 (*s*, Me_3C); *J*(3F,4F) = 4.2, *J*(4F,5F) = 3.6, *J*(1E,2E) = 8.0, *J*(2E,3E) = 9.6, *J*(3E,4E) = 9.6, *J*(5E,6bE) = 1.9, *J*(6aE,6bE) = 11.4, *J*(1C,2C) = 8.4, *J*(2C,3C) = 9.6, *J*(3C,4C) = 9.6, *J*(4C,5C) = 9.6, *J*(5C,6aC) = 4.9, *J*(5C,6bC) = 1.9, *J*(6aC,6bC) = 12.4. ^{13}C-NMR (^{13}C,^{1}H-COSY; 50 MHz, $CDCl_3$): 173.68, 171.17, 170.95, 170.66, 169.93, 169.50 (6 Me_3CO); 135.99, 135.72, 133.60, 132.05, 130.51, 130.12, 128.46, 128.05 (arom. C); 134.12, 133.70 (2 CH_2=*C*HCH_2); 118.60, 117.09 (2 *C*H_2=CHCH_2); 106.00 (C(1^F)); 100.57 (C(1^C)); 100.51 (C(1^E)); 86.37 (C(2^F)); 82.46 (C(4^F)); 78.82 (C(5^F)); 75.17 (C(5^E)); 74.61 (C(3^F)); 73.76 (C(4^E)); 73.32 (CH_2=CH*C*H_2); 72.92 (C(3^E)); 72.69 (C(3^C)); 71.68 (C(5^C)); 68.88 (CH_2=CH*C*H_2); 68.24 (C(4^C)); 61.92 (C(6^C)); 61.49 (C(6^E)); 54.23 (C(2^C)); 53.40 (C(2^E)); 27.17 (Me_3C); 23.22, 22.95, 20.86, 20.73, 20.73, 20.73 (6 *Me*CO); 19.35 (Me_3*C*). ESI-MS ($C_{52}H_{71}N_3O_{20}Si$ (1086.23, 1085.44)): 1086.44615 ([*M* + H]$^+$; calc. 1086.44782).

Prop-2-enyl O-*3,4,6-Tri*-O-*acetyl-2-(acetylamino)-2-deoxy-β*-D-*glucopyranosyl-(1 → 4)*-O-*3*-O-*acetyl-2-(acetylamino)-6*-O-*[(*tert*-butyl)diphenylsilyl]-2-deoxy-β*-D-*glucopyranosyl-(1 → 2)-3*-O-*(aminocarbornyl)-5*-O-*prop-2-enyl-β*-D-*glucofuranosiduronamide* (**9b**). To a soln. of **9a** (100.0 mg, 0.092 mmol) in dry CH_2Cl_2 (0.5 ml), trichloroacetyl isocyanate (25 µl, 0.20 mmol) was added, and the mixture was stirred at 20° for 1 h. Excess reagent was destroyed by addition of MeOH (0.2 ml), and stirring was continued at 0° for 10 min. After evaporation, the residue was redissolved in MeOH (5.0 ml), Zn dust (100.0 mg) was added, and the mixture was stirred at 20° for 3 h. Filtration, washing the solid with MeOH, evaporation of the combined liquid phases, and purification by FC ($CHCl_3$/MeOH 15:1) furnished **9b** (100.2 mg, 96%). R_f (CH_2Cl_2/MeOH 10:1): 0.37. ^{1}H-NMR (^{1}H,^{1}H-COSY; 300 MHz; $CDCl_3$): 7.71–7.36 (*m*, 10 arom. H); 6.87 (*d*, N*H*Ac); 6.54, 6.33 (2 br. *s*, $CONH_2$); 5.91–5.74 (*m*, 2 CH_2=C*H*CH_2); 5.23–5.02 (*m*, H–C(3^F), 2 CH_2=CHCH_2); 5.02 (*d*, H–C(1^F)); 4.88 (*t*, H–C(4^C)); 4.87 (*t*, H–C(3^E)); 4.76 (*t*, H–C(3^C)); 4.54–4.48 (*m*, H–C(4^F)); 4.50 (*d*, H–C(1^E)); 4.38 (*d*, H–C(1^C)); 4.33 (*dd*, H–C(2^F)); 4.26 (*dd*, H_a–C(6^C)); 4.20–4.00 (*m*, H–C(2^E), H–C(4^E), 1 CH_2=CHCH_2, 1 H of CH_2=CHC*H*); 4.01 (*d*, H–C(5^F)); 3.96–3.89 (*m*, H_b–C(6^C); 1 H of CH_2=CHCH_2); 3.87 (br. *d*, H_a–C(6^E)); 3.83–3.76 (*m*, H–C(2^C)); 3.47 (br. *d*, H_b–C(6^E)); 3.39–3.34 (*m*, H–C(5^C)); 3.32–3.28 (*m*, H–C(5^E)); 1.99, 1.96, 1.95, 1.91, 1.84, 1.41 (6*s*, 6 MeCO); 1.05 (*s*, Me_3C); *J*(1F,2F) = 2.8, *J*(2F,3F) = 3.0, *J*(4F,5F) = 5.3, *J*(1E,2E) = 8.4, *J*(2E,3E) = 9.6, *J*(3E,4E) = 9.6, *J*(5E,6aE), *J*(5E,6bE) = small, *J*(6aE,6bE) = 12.4, *J*(1C,2C) = 8.4, *J*(2C,3C) = 9.6, *J*(3C,4C) = 9.6, *J*(4C,5C) = 9.6, *J*(5C,6aC) = 4.6, *J*(6aC,6bC) = 11.0, *J*(H,NH) = 9.5. ^{13}C-NMR (^{13}C,^{1}H-COSY; 75.5 MHz, $CDCl_3$): 173.62, 171.51, 171.08, 171.06, 170.82, 170.25, 169.67 (6 Me*C*O, $CONH_2$); 156.23 ($OCONH_2$); 136.21, 135.90, 133.95, 132.05, 130.78, 130.32, 128.73, 128.29 (arom. C); 134.41, 134.28 (2 CH_2=*C*HCH_2); 118.61, 117.25 (2 *C*H_2=CHCH_2); 106.66 (C(1^F)); 100.96 (C(1^E)); 100.52 (C(1^C)); 85.37 (C(2^F)); 79.80 (C(4^F)); 79.11 (C(5^F)); 76.00 (C(3^F)); 75.09 (C(5^E)); 74.14 (C(4^E)); 73.67 (C(3^E)); 73.54 (C(3^C)); 72.97 (C(5^C)); 71.80, 69.89 (2 CH_2=CH*C*H_2); 68.29 (C(4^C)); 61.98 (C(6^C)); 61.45 (C(6^E)); 54.09 (C(2^C)); 53.68 (C(2^E)); 27.33 (*Me*$_3$C); 23.35, 23.10, 21.02, 20.94, 20.90, 20.85 (6 *Me*CO); 19.49 (Me_3*C*). ESI-MS ($C_{53}H_{72}N_4O_{21}Si$ (1129.25, 1128.45)): 1129.45364 ([*M* + H]$^+$; calc. 1129.45311).

Prop-2-enyl O-*3,4,6-Tri*-O-*acetyl-2-(acetylamino)-2-deoxy-β*-D-*glucopyranosyl-(1 → 4)*-O-*3*-O-*acetyl-2-(acetylamino)-2-deoxy-β*-D-*glucopyranosyl-(1 → 2)-3*-O-*(aminocarbonyl)-5*-O-*prop-2-enyl-β*-D-*glucofuranosiduronamide* (**11a**). To a soln. of **9b** (100 mg, 0.089 mmol) in THF (2 ml), 1M Bu_4NF in THF (30 µl) was added, and the mixture was stirred at 20° for 3 h. Evaporation and FC ($CHCl_3$/MeOH 10:1) furnished impure **11a** (70 mg). To remove Bu_4NF from **11a**, it was extracted with AcOEt/BuOH 4:1 from a sat. NaCl soln. Subsequently ammonium salts were removed by passing a MeOH soln. through an ion-exchange column (*Dowex 50 W X2*, H^+ form): **11a** (12 mg, 15%). R_f (CH_2Cl_2/MeOH 10:1.5): 0.28. ^{1}H-NMR (400 MHz, $CDCl_3$; signals that could be assigned): 5.87–5.78 (*m*, 2 CH_2=C*H*CH_2); 4.94 (*s*, H–C(1^F)); 4.59, 4.57 (2*d*, H–C(1^C), H–C(1^E)); 2.00, 1.95, 1.93, 1.92, 1.85, 1.84 (6*s*, 6 MeCO); *J*(1C,2C) = 8.4, *J*(1C,2C) = 8.4. 13C-NMR (75.5 MHz, CD_3OD/$CDCl_3$ 1:1): 172.50, 172.24, 171.61, 171.45, 171.37, 170.47 (6 Me*C*O); 134.26, 133.95 (2 CH_2=*C*HCH_2); 118.57, 117.71 (2 *C*H_2=CHCH_2); 107.04 (C(1^F)); 101.39, 100.77 (C(1^E), C(1^C)); 85.39, 80.21, 75.76, 75.54, 75.48, 73.77, 73.29, 72.50, 71.86, 69.72, 68.82, 62.30, 60.15, 54.64, 53.81 (C(2^E), C(2^C)); 22.77, 22.77, 20.85, 20.79, 20.74, 20.67 (6 *Me*CO). ESI-MS ($C_{37}H_{54}N_4O_{21}$ (890.85, 890.33)): 913.31712 ([*M* + Na]$^+$; calc. 913.31728), 891.33680 ([*M* + H]$^+$; calc. 891.33533).

Prop-2-enyl O-*3,4,6-Tri*-O-*acetyl-2-(acetylamino)-2-deoxy-β*-D-*glucopyranosyl-(1 → 4)*-O-*3*-O-*acetyl-2-(acetylamino)-2-deoxy-6*-O-*tosyl-β*-D-*glucopyranosyl-(1 → 2)-3*-O-*(aminocarbonyl)-5*-O-*prop-2-enyl-β*-D-*glucofuranosiduronamide* (**11b**). a) To a soln. of **11a** (70 mg, 0.079 mmol) in dry pyridine (2 ml), TsCl (30 mg,

0.16 mmol) and DMAP (7 mg) were added. The mixture was stirred at 20° overnight. The solvent was evaporated and the residue purified by FC ($CHCl_3$/MeOH 15:1): **11b** (12 mg, 14.6%).

b) To a soln. of **11e** (7 mg, 0.007 mmol) in dry CH_2Cl_2 (0.5 ml), trichloroacetyl isocyanate (1.5 µl, 12.5 µmol) was added, and the mixture was stirred at 20° for 1 h. Excess reagent was destroyed by addition of MeOH (0.2 ml), and stirring was continued at 0° for 10 min. After evaporation, the residue was dissolved in MeOH (5 ml), Zn dust (20 mg) was added, and the mixture was stirred at 20° for 3 h. Filtration, washing the solid with MeOH, evaporation of the combined liquid phases, and purification by FC ($CHCl_3$/MeOH 15:1) furnished **11b** (3.5 mg, 48%). R_f (CH_2Cl_2/MeOH 10:1.5): 0.65. ^{1}H-NMR (300 MHz, $CDCl_3$; signals that could be assigned): 7.78, 7.38 (2*d*, 4 arom. H); 5.89–5.76 (*m*, 2 CH_2=C*H*CH_2); 5.35–4.96 (*m*, 2 CH_2=C*H*CH_2, H–C(3^E), H–C(3^C), H–C(3^F), H–C(4^C)); 5.01 (*s*, H–C(1^F)); 4.58, 4.56 (2*d*, H–C(1^C), H–C(1^E)); 2.45 (*s*, Me); 2.05, 1.99, 1.99, 1.98, 1.93, 1.88 (6*s*, 6 MeCO); *J*(1C,2C) = 8.4, *J*(1E,2E) = 8.4.

Prop-2-enyl O-*3,4,6-Tri*-O-*acetyl-2-(acetylamino)-2-deoxy-β*-D-*glucopyranosyl-(1 → 4)*-O-*3*-O-*acetyl-2-(acetylamino)-6-azido-2,6-dideoxy-β*-D-*glucopyranosyl-(1 → 2)-3*-O-*(aminocarbonyl)-5*-O-*β*-D-*glucofuranosiduronamide* (**11c**). To a soln. of **11b** (10 mg, 0.01 mmol) in dry DMF (0.5 ml), NaN_3 (5 mg, 0.077 mmol) was added. The mixture was stirred at 85° for 3 h. The mixture was filtered and washed with MeOH. The combined filtrate and washings were evaporated. The residue was purified by FC ($CHCl_3$/MeOH 15:1): **11c** (3 mg, 34%) and recovered **11b** (2 mg). R_f (CH_2Cl_2/MeOH 10:1.5): 0.62. ^{1}H-NMR (300 MHz, (D_5)pyridine; signals that could be assigned): 9.48, 9.24 (2*d*, 2 N*H*Ac); 5.54 (*s*, H–C(1^F)); 2.24, 2.12, 2.08, 2.01, 1.99, 1.99 (6*s*, 6 MeCO); *J*(H,NH) = 8.7. ^{13}C-NMR (75.5 MHz, (D_5)pyridine): 169.49, 169.21, 169.13, 169.04, 168.39 (6 Me*C*O); 155.25 (NH_2*C*OO); 133.10, 131.80 (2 CH_2=*C*HCH$_2$); 117.62, 115.60 (2 *C*H$_2$=CHCH$_2$); 106.29 (C(1^F)); 99.88, 99.68 (C(1^C), C(1^E)); 85.21 (C(2^F)); 78.31, 75.50, 73.65, 73.34, 72.39, 71.30, 70.64, 70.58, 68.02, 67.89, 66.61, 60.75, 54.87, 53.36 (C(2^C), C(2^E)); 49.49 (C(6^E)); 21.77, 21.77, 21.57, 19.50, 19.13, 19.06 (6 *Me*CO). ESI-MS ($C_{37}H_{53}N_7O_{20}$ (915.86, 915.33)): inconclusive.

Prop-2-enyl O-*3,4,6-Tri*-O-*acetyl-2-(acetylamino)-2-deoxy-β*-D-*glucopyranosyl-(1 → 4)*-O-*3*-O-*acetyl-2-(acetylamino)-2-deoxy-β*-D-*glucopyranosyl-(1 → 2)-5*-O-*prop-2-enyl-β*-D-*glucofuranosiduronamide* (**11d**). To a soln. of **9a** (30 mg, 0.028 mmol) in THF (3 ml), 1M Bu_4NF in THF (0.07 ml) was added dropwise. The mixture was stirred at 20° for 40 min and then evaporated. The residue was purified by FC ($CHCl_3$/MeOH 20:1): **11d** (15 mg, 64%). R_f (CH_2Cl_2/MeOH 10:1.7): 0.52. ^{1}H-NMR (^{1}H,^{1}H-COSY; 400 MHz, $CDCl_3$): 5.93–5.87, 5.78–5.72 (2*m*, 2 CH_2=C*H*CH_2), 5.32–5.08 (*m*, C*H*$_2$=CHCH$_2$); 5.20 (*s*, H–C(1^F)); 5.07 (*t*, H–C(3^C)); 4.93 (*t*, H–C(4^C), H–C(3^E)); 4.84 (*dd*, H–C(4^F)); 4.77 (*d*, H–C(3^F)); 4.54, 4.53 (2*d*, H–C(1^C), H–C(1^E)); 4.30 (*dd*, H_a–C(6^C)); 4.25–4.23 (*m*, H–C(2^F), 1 H of CH_2=CHC*H*$_2$); 4.20–4.17 (*m*, 1 H, CH_2=CHC*H*$_2$); 4.14 (*d*, H–C(5^F)); 3.94 (*dd*, H_b–C(6^C)); 3.84–3.77 (*m*, H–C(2^C), H–C(2^E), H–C(4^E)); 3.72 (*dd*, H_a–C(6^E)); 3.63–3.56 (*m*, H–C(5^C), H_b–C(6^E), CH_2=CHC*H*$_2$); 3.33–3.28 (*m*, H–C(5^E)); 2.00, 1.95, 1.93, 1.92, 1.85, 1.85 (6*s*, 6 MeCO); *J*(3F,4F) = 5.2, *J*(4F,5F) = 6.8, *J*(1E,2E) = 8.3, *J*(2E,3E) = 9.9, *J*(3E,4E) = 9.9, *J*(6aE,6bE) = 12.0, *J*(1C,2C) = 8.3, *J*(2C,3C) = 9.9, *J*(3C,4C) = 9.9, *J*(4C,5C) = 9.9, *J*(5C,6aC) = 4.2, *J*(5C,6bC) = 1.2, *J*(6aC,6bC) = 12.0. ESI-MS ($C_{36}H_{53}N_3O_{20}$ (847.82, 847.32)): inconclusive.

Prop-2-enyl O-*3,4,6-Tri*-O-*acetyl-2-(acetylamino)-2-deoxy-β*-D-*glucopyranosyl)-(1 → 4)*-O-*3*-O-*acetyl-2-(acetylamino)-2-deoxy-6*-O-*tosyl-β*-D-*glucopyranosyl-(1 → 2)-5*-O-*prop-2-enyl-β*-D-*glucofuranosiduronamide* (**11e**). To a soln. of **11d** (15 mg, 0.018 mmol) and DMAP (3 mg) in pyridine/CH_2Cl_2 1:1 (1 ml), TsCl (45 mg, 0.24 mmol) was added in three portions within 4 h. Then the mixture was stirred at 20° overnight and evaporated. The residue was purified by FC ($CHCl_3$/MeOH 15:1): **11e** (7 mg, 40%). R_f (CH_2Cl_2/MeOH 10:1.5): 0.76. ^{1}H-NMR (300 MHz, $CDCl_3$; signals that could be assigned): 7.80, 7.41 (2*d*, 4 arom. H); 6.03–5.89, 5.87–5.71 (2*m*, 2 CH_2=C*H*CH_2); 4.69, 4.61 (2*d*, H–C(1^C), H–C(1^E)); 2.47 (*s*, Me); 2.08, 2.03, 2.02, 2.02, 1.97, 1.96 (6*s*, 6 MeCO); *J*(1C,2C) = 7.5, *J*(1C,2C) = 7.5. ESI-MS ($C_{43}H_{59}N_3O_{22}S$ (1002.01, 1001.33)): inconclusive.

Prop-2-enyl O-*3,4,6-Tri*-O-*acetyl-2-(acetylamino)-2-deoxy-β*-D-*glucopyranosyl-(1 → 4)*-O-*3*-O-*acetyl-2-(acetylamino)-2-deoxy-β*-D-*glucopyranosyl-(1 → 2)-5*-O-*prop-2-enyl-β*-D-*glucofuranosidurono-6,3-lactone* (**12a**). As described for **11d**, with **8b** (80 mg, 0.075 mmol), THF (3 ml), and 1M Bu_4NF (0.4 ml) (1 h): **12a** (28 mg, 43%). R_f (CH_2Cl_2/MeOH 10:1): 0.30. ^{1}H-NMR (200 MHz, $CDCl_3$; signals that could be assigned): 6.08–5.63 (*m*, 2 CH_2=C*H*CH_2); 2.07, 2.05, 2.02, 2.01, 1.96, 1.96 (6*s*, 6 MeCO). ESI-MS ($C_{36}H_{50}N_2O_{20}$ (830.79, 830.30)): 853.28580 ([*M* + Na]$^+$; calc. 853.28549), 831.30374 ([*M* + H]$^+$; calc. 831.30291).

Prop-2-enyl O-*3,4,6-Tri*-O-*acetyl-2-(acetylamino)-2-deoxy-β*-D-*glucopyranosyl-(1 → 4)*-O-*3*-O-*acetyl-2-(acetylamino)-2-deoxy-6*-O-*tosyl-β*-D-*glucopyranosyl-(1 → 2)-5*-O-*prop-2-enyl-β*-D-*glucofuranosidurono-6,3-lactone* (**12b**). As described for **11b** (*a*)), with **12a** (28 mg, 0.032 mmol), pyridine (2 ml), TsCl (30 mg, 0.16 mmol), and DMAP (3 mg): **12b** (17 mg, 52%). R_f (CH_2Cl_2/MeOH 10:1): 0.34. ^{1}H-NMR (300 MHz, $CDCl_3$; signals that could be assigned): 7.80, 7.41 (2*d*, 4 arom. H); 6.03–5.60 (*m*, 2 CH_2=C*H*CH_2); 2.47 (*s*, Me); 2.05, 1.99, 1.99, 1.98, 1.93, 1.88 (6*s*, 6 MeCO).

Prop-2-enyl O-*3,4,6-Tri*-O-*acetyl-2-(acetylamino)-2-deoxy-β*-D-*glucopyranosyl-(1 → 4)*-O-*3*-O-*acetyl-2-(acetylamino)-6-azido-2,6-dideoxy-β*-D-*glucopyranosyl-(1 → 2)-5*-O-*prop-2-enyl-β*-D-*glucofuranosidurono-6,3-lactone* (**12c**). As described for **11c**, with **12b** (17 mg, 0.017 mmol), DMF (1 ml), and NaN_3 (11 mg, 0.17 mmol): **12c** (2 mg, 14%). R_f (CH_2Cl_2/MeOH 10:1): 0.32. ^{1}H-NMR (300 MHz, (D_5)pyridine; signals that could be assigned): 6.05–5.85 (*m*, 2 CH_2=C*H*CH_2); 2.12, 2.11, 2.08, 2.06, 1.99, 1.99 (6*s*, 6 MeCO). ^{13}C-NMR (75.5 MHz, (D_5)pyridine; signals that could be assigned): 119.89, 118.37 (*C*H_2=CHCH_2), 105.93 (C(1^F)); 85.51 (C(2^F)); 55.44, 55.40 (C(2^E), C(2^C)); 50.79 (C(6^E)). ESI-MS ($C_{36}H_{49}N_5O_{19}$ (855.81, 855.30)): inconclusive.

O-*3,4,6-Tri*-O-*acetyl-2-(acetylamino)-2-deoxy-β*-D-*glucopyranosyl-(1 → 4)*-O-*3*-O-*acetyl-2-(acetylamino)-6*-O-*[(*tert*-butyl)diphenylsilyl]-2-deoxy-β*-D-*glucopyranosyl-(1 → 2)-3*-O-*(aminocarbonyl)-α*-D-*glucopyranuronamide* (**10a**). A mixture of **9b** (78.0 mg, 0.069 mmol) and [Pd(PPh_3)$_4$] (90.0 mg, 0.078 mmol) in degassed AcOH (1 ml) was stirred under Ar at 20° for 5 h. The solvent was removed by azeotropic evaporation with toluene. The residue was taken up in H_2O and washed repeatedly with $CHCl_3$, then H_2O was removed by lyophilization. The product was further purified by washing it with toluene/$CHCl_3$/MeOH 10:10:3: **10a** (68.1 mg, 94%). $[\alpha]_D^{26} = +12$ ($c = 1.0$, $CHCl_3$). R_f (CH_2Cl_2/MeOH 3:1): 0.47. ^{1}H-NMR (^{1}H,^{1}H-COSY; 600 MHz, (D_5)pyridine): 8.74 (overlapped by solvent, N*H*Ac), 8.53, 8.32 (2 br. *s*, NH_2); 8.04 (*d*, N*H*Ac); 7.99–7.35 (*m*, NH_2, arom. H); 6.31 (*t*, H–C(3^F)); 6.10 (*t*, H–C(4^C)); 6.05 (*d*, H–C(1^F)); 5.86 (*t*, H–C(3^E)); 5.59 (*d*, H–C(1^C)); 5.41 (*t*, H–C(3^C)); 5.35 (*d*, H–C(1^E)); 5.23 (*d*, H–C(5^F)); 4.71 (*dd*, H_a–C(6^C)); 4.55–4.49 (*m*, H–C(2^E), H–C(4^E), H–C(4^F)); 4.29 (*dd*, H–C(2^F)); 4.26 (br. *d*, H_b–C(6^C)); 4.21 (*dd*, H_a–C(6^E)); 4.15 (br. *d*, H_b–C(6^E)); 4.00–3.94 (*m*, H–C(2^C), H–C(5^C)); 3.71–3.66 (*m*, H–C(5^E)); 2.22, 2.16, 2.03, 2.02, 2.00, 1.99 (6*s*, 6 MeCO); 1.12 (*s*, Me_3C); J(1F,2F) = 2.9, J(2F,3F) = 9.8, J(3F,4F) = 9.8, J(4F,5F) = 9.8, J(1E,2E) = 8.1, J(2E,3E) = 9.3, J(3E,4E) = 9.3, J(5E,6aE) = 4.2, J(6aE,6bE) = 11.0, J(1C,2C) = 8.2, J(2C,3C) = 9.9, J(3C,4C) = 9.9, J(4C,5C) = 9.9, J(5C,6aC) = 4.2, J(6aC,6bC) = 12.0, J(H,NH) = 8.8. ^{13}C-NMR (^{13}C,^{1}H-COSY; 75.5 MHz, (D_5)pyridine): 174.13, 171.22, 170.77, 170.70, 170.62, 170.13 (6 Me*C*O); 158.89 (O*C*ONH_2); 136.50, 136.39, 134.58, 134.44, 130.92, 130.83, 128.67, 128.60 (arom. C); 103.04 (C(1^E)); 99.49 (C(1^C)); 93.77 (C(1^F)); 79.24 (C(2^F)); 76.79 (C(5^E)); 75.93 (C(3^F)); 74.80 (C(3^E)); 74.13 (C(4^F)); 73.07 (C(4^E)); 72.66 (C(4^C)); 72.23 (C(5^F)); 72.23 (C(5^C)); 69.12 (C(3^C)); 63.50 (C(6^E)); 62.45 (C(6^C)); 56.98 (C(2^E)); 55.28 (C(2^C)); 27.25 (*Me*$_3$C); 23.65, 23.37, 21.27, 20.81, 20.81, 20.72 (6 *Me*CO); 19.81 (Me$_3$*C*). ESI-MS ($C_{47}H_{64}N_4O_{21}Si$ (1049.12, 1048.38)): 1071.37479 ([M + Na]$^+$; calc. 1071.37245).

O-*3,4,6-Tri*-O-*acetyl-2-(acetylamino)-2-deoxy-β*-D-*glucopyranosyl)-(1 → 4)*-O-*3*-O-*acetyl-2-(acetylamino)-6*-O-*[(*tert*-butyl)diphenylsilyl]-2-deoxy-β*-D-*glucopyranosyl-(1 → 2)-1,4-di*-O-*acetyl-3*-O-*(aminocarbonyl)-α*-D-*glucopyranuronamide* (**10b**). Ac_2O (1.3 ml) was added to a soln. of **10a** (68.0 mg, 0.065 mmol) in pyridine (2.0 ml), and the mixture was stirred at 20° for 2 h. The solvents were removed by azeotropic evaporation with toluene. The crude product was purified by FC ($CHCl_3$/MeOH 15:1): **10b** (68.2 mg, 93%). R_f (CH_2Cl_2/MeOH 8:1): 0.36. $[\alpha]_D^{26} = -15$ ($c = 1.0$, $CHCl_3$). ^{1}H-NMR (^{1}H,^{1}H-COSY; 600 MHz, $CDCl_3$): 7.78–7.48 (*m*, 10 arom. H); 6.35 (*d*, H–C(1^F)); 6.33 (br. *s*, N*H*Ac); 6.19 (br. *s*, 1 H, NH_2); 5.26 (*t*, H–C(3^F)); 5.14 (*t*, H–C(4^F)); 4.99 (*t*, H–C(3^E)); 4.93 (*t*, H–C(4^C)); 4.79 (*t*, H–C(3^C)); 4.60 (*d*, H–C(1^C)); 4.29–4.26 (*m*, H–C(1^E), H_a–C(6^C)); 4.24 (*d*, H–C(5^F)); 4.10–4.07 (*m*, H–C(4^E), H–C(2^E)); 3.97 (br. *d*, H_b–C(6^C)); 3.93–3.86 (*m*, H–C(2^F), H_a–C(6^E)); 3.83–3.78 (*m*, H–C(2^C)); 3.58 (br. *d*, H_b–C(6^E)); 3.43–3.40 (*m*, H–C(5^E)); 3.36–3.34 (*m*, H–C(5^C)); 2.16, 2.06, 2.06, 2.04, 2.01, 2.01, 1.98, 1.62 (8*s*, 8 MeCO); 1.14 (*s*, Me_3C); J(1F,2F) = 3.0, J(2F,3F) = 9.7, J(3F,4F) = 9.7, J(4F,5F) = 9.7, J(2E,3E) = 9.3, J(3E,4E) = 9.3, J(6aE,6bE) = 10.2, J(1C,2C) = 6.8, J(2C,3C) = 9.7, J(3C,4C) = 9.7, J(4C,5C) = 9.7, J(6aC,6bC) = 11.0. ^{13}C-NMR (^{13}C,^{1}H-COSY; 50 MHz, $CDCl_3$): 170.96, 170.86, 170.59, 170.59, 170.44, 169.39, 169.21, 168.94 (8 Me*C*O); 156.14 (O*C*ONH_2); 135.95, 135.78, 133.50, 132.16, 130.66, 130.37, 128.53, 128.16 (arom. C); 102.64 (C(1^E)); 100.48 (C(1^C)); 90.46 (C(1^F)); 75.88 (C(5^E)); 75.70 (C(2^F)); 73.37 (C(4^E)); 73.12 (C(3^E)); 72.52 (C(3^C)); 72.05 (C(3^F)); 71.62 (C(5^C)); 70.22 (C(5^F)); 69.95 (C(4^F)); 68.09 (C(4^C)); 61.80 (C(6^E); C(6^C)); 54.09 (C(2^C)); 53.09 (C(2^E)); 27.16 (*Me*$_3$C); 23.25, 23.06, 20.90, 20.85, 20.85, 20.85, 20.85, 20.85 (8 *Me*CO); 19.42 (Me$_3$*C*). ESI-MS ($C_{51}H_{68}N_4O_{23}Si$ (1133.20, 1132.40)): 1155.39492 ([M + Na]$^+$; calc. 1155.39358), 1133.41461 ([M + H]$^+$; calc. 1133.41164).

O-*3,4,6-Tri*-O-*acetyl-2-(acetylamino)-2-deoxy-β*-D-*glucopyranosyl-(1 → 4)*-O-*3*-O-*acetyl-2-(acetylamino)-6*-O-*[(*tert*-butyl)diphenylsilyl]-2-deoxy-β*-D-*glucopyranosyl-(1 → 2)-4*-O-*acetyl-3*-O-*(aminocarbonyl)-α*-D-*glucopyranuronamide* (**10c**). A mixture of **10b** (68.0 mg, 0.060 mmol), hydrazinium acetate (11.0 mg, 0.12 mmol), and DMF (0.8 ml) was stirred at 20° for 40 min. After addition of H_2O, usual workup ($CHCl_3$) and FC ($CHCl_3$/MeOH 15:1) gave **10c** (44.1 mg, 67%) besides recovered **10b** (8.0 mg). R_f (CH_2Cl_2/MeOH 8:1): 0.32. $[\alpha]_D^{26} = -3$ ($c = 1.0$, $CHCl_3$). ^{1}H-NMR (^{1}H,^{1}H-COSY; 600 MHz, (D_5)pyridine): 8.77 (*d*, N*H*Ac); 8.38 (br. *s*, 1 H, NH_2); 8.12 (*d*, N*H*Ac); 8.00 (br. *s*, 1 H, NH_2); 7.97–7.42 (*m*, 10 arom. H); 7.75 (br. *s*, NH_2); 6.32 (*t*, H–C(3^F)); 6.09 (*t*, H–C(4^C)); 6.01 (*d*, H–C(1^F)); 5.94 (*t*, H–C(4^F)); 5.88 (*t*, H–C(3^E)); 5.57 (*d*, H–C(1^C)); 5.40 (*t*, H–C(3^C)); 5.31 (*d*, H–C(1^E)); 5.23 (*d*, H–C(5^F)); 4.71 (*dd*, H_a–C(6^C)); 4.50 (*t*, H–C(4^E)); 4.47–4.42 (*m*, H–C(2^E));

4.27–4.25 (*m*, H–C(2^F), H$_b$–C(6^C)); 4.21 (*dd*, H$_a$–C(6^E)); 4.17 (*dd*, H$_b$–C(6^E)); 3.98–3.91 (*m*, H–C(5^C), H–C(2^C)); 3.72–3.70 (*m*, H–C(5^E)); 2.20, 2.15, 2.11, 2.02, 2.01, 2.01, 2.00 (7*s*, 7 MeCO); 1.11 (*s*, Me$_3$C); *J*(1F,2F) = 3.1, *J*(2F,3F) = 9.8, *J*(3F,4F) = 9.8, *J*(4F,5F) = 9.8, *J*(1E,2E) = 8.3, *J*(2E,3E) = 9.0, *J*(3E,4E) = 9.0, *J*(4E,5E) = 9.0, *J*(5E,6aE) = 4.4, *J*(5E,6bE) = 1.0, *J*(6aE,6bE) = 12.4, *J*(1C,2C) = 8.2, *J*(2C,3C) = 9.9, *J*(3C,4C) = 9.9, *J*(4C,5C) = 9.9, *J*(5C,6aC) = 4.7, *J*(5C,6bC) = 2.1, *J*(6aC,6bC) = 12.0, *J*(H,NH) = 8.7. ^{13}C-NMR (^{13}C,^{1}H-COSY; 75.5 MHz, (D$_5$)pyridine): 170.93, 170.57, 170.18, 170.13, 170.06, 170.02, 169.66, 169.47 (7 Me*C*O, CONH$_2$); 157.19 (OCONH$_2$); 135.87, 135.43, 133.75, 133.03, 129.97, 128.06, 127.97 (arom. C); 102.15 (C(1^E)); 99.09 (C(1^C)); 92.90 (C(1^F)); 78.16 (C(2^F)); 76.25 (C(5^E)); 73.72 (C(4^E)); 73.58 (C(3^E)); 72.52 (C(3^F)); 71.92 (C(4^C)); 71.70 (C(5^C)); 71.47 (C(4^F)); 69.23 (C(3^C)); 69.12 (C(5^F)); 62.88 (C(6^E)); 61.82 (C(6^C)); 56.42 (C(2^E)); 54.95 (C(2^C)); 26.63 (*Me*$_3$C); 22.97, 22.74, 20.70, 20.65, 20.21, 20.15, 20.15 (7 *Me*CO); 19.23 (Me$_3$*C*). ESI-MS ($C_{49}H_{66}N_4O_{22}Si$ (1091.16, 1090.39)): (1091.40136 [*M* + H]$^+$; calc. 1091.40107).

4-O-*Acetyl-3*-O-*(aminocarbonyl)-2*-O-*[3,4,6-tri*-O-*acetyl-2-(acetylamino)-2-deoxy-β*-D-*glucopyranosyl]-α*-D-*glucopyranuronamide 1-[(2*R*)-2-(Dodecyloxy)-3-methoxy-3-oxopropyl 2,2,2-Trichloro-1,1-dimethylethyl Phosphate]* (**14**). To a soln. of 1*H*-1,2,4-triazole (45 mg, 0.67 mmol, 4.8 equiv.) in CH_2Cl_2/pyridine 4:1 (1.5 ml), 2,2,2-trichloro-1,1-dimethylethyl phosphodichloridite (33 µl, 0.17 mmol, 1.2 equiv.) was added at 0°. This mixture was stirred at 0° under Ar for 30 min. A soln. of **13** (83 mg, 0.14 mmol) in 7:1 CH_2Cl_2/pyridine 7:1 (2.1 ml) was added, and the mixture was stirred for 3 h at 0°. After addition of (2*R*)-methyl 2-*O*-dodecylglycerate (48 mg, 0.21 mmol, 1.5 equiv.) in CH_2Cl_2/pyridine 7:1 (2.1 ml) in three portions within 2 h, the mixture was stirred for 1 h at 0°. Bis(trimethylsilyl) peroxide (58 µl, 0.28 mmol, 2.0 equiv.) was injected, and the mixture was stirred at 0° for 1 h, then at 20° for 15 h. The solvents were removed by azeotropic evaporation with toluene (25°, Ar stream). The residue was dissolved in CH_2Cl_2/MeOH and mixed with 'Kieselguhr' (500 mg), the mixture evaporated, the residue dried at 0.1 Torr, and the crude product transferred to the top of a FC column (silica gel (20 g), CH_2Cl_2/MeOH 10:1): pure P-diastereoisomer **14** (50 mg, 33%; containing some triazole (^{1}H-NMR)) and a mixture of two P-diastereoisomers (40 mg, 26%). **14**: R_f ($CHCl_3$/MeOH 9:1): 0.25. IR (film): 3369 (OH), 1747 (CO). ^{1}H-NMR (^{1}H,^{1}H-COSY; 300 MHz, (D$_5$)pyridine): 9.28 (*d*, N*H*Ac); 8.69 (*s*, CONH$_2$); 8.09 (*s*, CONH$_2$); 7.72 (*s*, H$_2$NCOO); 6.52 (*dd*, H–C(1^F)); 6.12 (*t*, H–C(3^E)); 5.98 (*t*, H–C(3^F)); 5.96 (*t*, H–C(4^F)); 5.55 (*d*, H–C(1^E)); 5.47 (*t*, H–C(4^E)); 5.00 (*m*, H–C(5^F), partly overlapped by H$_2$O); 4.80–4.39 (*m*, CH$_2$(3^H), CH$_2$(6^E), H–C(2^H)); 4.14–4.03 (*m*, H–C(2^F), H–C(2^E)); 4.10–4.00 (*m*, H–C(5^E)); 3.84–3.76 (*m*, H–C(1^I)); 3.76 (*s*, COOMe); 3.62–3.59 (*m*, H′–C(1^I)); 2.19, 2.16, 2.15, 2.07, 2.00 (5*s*, 7 Me); 1.70–1.62 (*m*, H–C(2^I)); 1.21 (*m*, CH$_2$(3^I) to CH$_2$ (11^I)); 0.85 (*t*, Me(12^I); *J*(1F,2F) = 3.6, *J*(1F,P) = 5.5, *J*(2F,3F) = 9.5, *J*(3F,4F) = 9.5, *J*(4F,5F) = 9.5, *J*(1E,2E) = 8.8, *J*(NH,2E) = 8.7, *J*(2E,3E) = 10.0, *J*(3E,4E) = 10.0, *J*(4E,5E) = 9.3 . ^{13}C-NMR (^{13}C,^{1}H-COSY; 75.5 MHz, (D$_5$)pyridine): 170.41, 170.06, 169.51, 169.02 (CO); 156.73 (H$_2$NCOO); 102.22 (C(1^E)); 97.28 (*d*, C(1^F)); 90.38 (*d*, Me$_2$*C*); 78.18 (C(2^F)); 77.97 (*d*, C(2^H)); 72.32 (C(3^E)); 71.59 (C(5^E)); 71.28 (C(5^F)); 70.76 (C(3^F)); 70.44 (C(4^F)); 69.86 (C(1^I)); 69.25 (C(4^E)); 68.07 (C(3^H)); 62.09 (C(6^E)); 55.33 (C(2^E)); 54.66 (no C,H correlation); 51.87 (COOMe); 31.73, 29.64, 29.52, 29.35, 29.21, 25.87 (C(2^I) to C(11^I)); 23.34, 22.90, 22.55, 20.48, 20.40, 20.20, 20.11 (7*s*, 7 MeCO); 13.90 (C(12^I)). ^{31}P-NMR (121.5 MHz, (D$_5$)pyridine): −9.41. FAB-MS ($C_{43}H_{69}Cl_3N_3O_{22}P$ (1117.36, 1115.32)): 1138.3 ([*M* + Na]$^+$), 1116.3 ([*M* + H]$^+$).

Second P-diastereoisomer: R_f ($CHCl_3$/MeOH 9:1): 0.20. ^{31}P-NMR (121.5 MHz, (D$_5$)pyridine): −7.84.

4-O-*Acetyl-3*-O-*(aminocarbonyl)-2*-O-*[3,4,6-tri*-O-*acetyl-2-(acetylamino)-2-deoxy-β*-D-*glucopyranosyl]-α*-D-*glucopyranuronamide 1-[(2*R*)-2-(Dodecyloxy)-3-methoxy-3-oxopropyl Hydrogen Phosphate]* (**15**)*/Partly Deacetylated Derivative 3:1.* To a soln. of **14** (90 mg, 0.08 mmol) in dry pyridine (3.5 ml), Zn–Cu couple (freshly prepared; 70 mg, 1.14 mmol) and pentane-2,4-dione (90 µl, 0.77 mmol) were added, and the mixture was stirred under Ar at 20° for 8 h. Excess Zn–Cu was removed by filtration and the residue washed with CH_2Cl_2 (3 × 10 ml), EtOH (3 × 10 ml), and MeOH (3 × 10 ml). After evaporation, the residue was taken up in H$_2$O/EtOH 8:1 (18 ml). *Dowex 50 W X2 /50-100* (H$^+$ form, 1.0 g) was added, and the mixture was stirred for 1 h. After filtration, the resin was washed with CH_2Cl_2 (3 × 10 ml), EtOH (3 × 10 ml), MeOH (3 × 10 ml), and MeOH/H$_2$O 1:1 (3 × 10 ml). The org. solvents were evaporated and the remaining aq. soln. was lyophilized. The crude product was dissolved in CH_2Cl_2/MeOH and mixed with 'Kieselguhr', the mixture evaporated, and the crude product transferred to the top of a FC column ($CHCl_3$/MeOH 4:1): **15**/compound with only 4 acetyl groups, ratio 3:1 (^{1}H-NMR; 50 mg, 66%). R_f ($CHCl_3$/MeOH 2:1): 0.10. ^{1}H-NMR (^{1}H,^{1}H-COSY; 300 MHz, (D$_5$)pyridine; **15**/partly deacetylated derivative): **15**: 9.23 (*d*, N*H*Ac); 8.51 (*s*, CONH$_2$); 8.37 (*s*, CONH$_2$); 6.54 (*m*, H–C(1^F)); 5.96 (*t*, H–C(3^E)); 5.93 (*t*, H–C(4^F)); 5.43 (*d*, H–C(1^E)); 5.36 (*t*, H–C(3^F)); 5.25 (*t*, H–C(4^E)); 5.07 (*d*, H–C(5^F)); 4.90–4.45 (*m*, H–C(5^E), CH$_2$(6^E), CH$_2$(3^H)); 4.37–4.25 (*m*, H–C(2^F)); 4.20–4.10 (*m*, H–C(2^F)); 4.08–3.96 (*m*, H–C(2^H)); 3.79–3.60 (*m*, overlapping COOMe, CH$_2$(1^I)); *J*(2F,3F) = 9.9, *J*(3F,4F) = 9.9, *J*(4F,5F) = 9.9, *J*(1E,2E) = 9.0, *J*(NH,2E) = 8.4, *J*(2E,3E) = 9.9, *J*(3E,4E) = 9.9, *J*(4E,5E) = 9.9, partly deacetylated derivative: 9.45 (*d*, N*H*Ac); 8.31 (*s*, CONH$_2$); 8.11 (*s*, CONH$_2$); 6.83 (*m*, H–C(1^F)); 5.99 (*t*,

H–C(3^{F})); 5.96 (*t,* H–C(4^{F})); 5.72 (*t,* H–C(3^{E})); 5.29 (*d,* H–C(5^{F})); 5.17 (*d,* H–C(1^{E})); 4.90–4.45 (*m,* H–C(5^{E}), CH$_2$(6^{E}), CH$_2$(3^{H})); 4.37–4.25 (*m,* H–C(2^{E})); 4.08–3.96 (*m,* H–C(2^{F}), H–C(2^{H})); 3.79–3.60 (*m,* overlapping COOMe, CH$_2$(1^{I})); **15**/partly deacetylated derivative: 7.32 (hidden by solvent peak, H$_2$NCOO); 3.67, 3.60 (2*s,* 2 COOMe); 2.24–1.93 (Me of units E and F); 1.64 (*m,* H–C(2^{I})); 1.19 (*m,* CH$_2$(3^{I}) to CH$_2$ (11^{I})); 0.84 (*t,* Me(12^{I})); *J*(2F,3F) = 9.9, *J*(3F,4F) = 9.9, *J*(4F,5F) = 9.9, *J*(1E,2E) = 9.0, *J*(NH,2E) = 8.7, *J*(2E,3E) = 9.9, *J*(3E,4E) = 9.9, *J*(4E,5E) = 9.9. ^{13}C-NMR (75.5 MHz, (D$_5$)pyridine; **15**/partly deacetylated derivative): 171.17, 170.99, 170.49, 170.44, 170.32, 170.15, 170.10, 169.98, 169.44, 169.30 (CO); 157.02, 156.95 (H$_2$NCOO); 102.68, 102.26 (C(1^{E})); 95.20, 95.12 (C(1^{F})); 79.11, 78.98 (C(2^{F}), C(2^{H})); 75.68 (C(1^{I})); 73.80 (C(3^{E})); 73.14 (C(3^{F})); 71.68, 71.61, 71.11, 70.69, 70.29, 69.51, 69.34 (C(5^{E}), C(3^{E}), C(5^{F}), C(4^{F})); 66.55–66.18 (C(3^{F}), C(1^{I}), C(4^{E}), C(3^{H})); 62.30, 61.25 (C(6^{E})); 54.81, 54.45 (C(2^{E})); 51.69, 51.56 (COO*Me*); 49.33, 31.77, 29.85, 29.59, 29.46, 29.26, 25.97, 23.03, 22.93, 22.59 (NHCO*Me*, CH$^{I}_{2}$); 20.63, 20.50, 20.26, 20.16 (Me of units E and F); 13.94 (C(12^{I})). ^{31}P-NMR (81.0 MHz, CD$_3$OD): –3.21. ESI-MS (**15**; C$_{39}$H$_{64}$N$_3$O$_{22}$P (957.91, 957.37)), 956.36551 ([*M* – H]$^-$; calc. 956.36463). ESI-MS (partly deacetylated derivative; C$_{37}$H$_{62}$N$_3$O$_{21}$P (915.88, 915.36)): 914.35518 ([*M* – H]$^-$; calc. 914.35352).

Deprotection of **15**. To a degassed soln. (Ar stream, sonication) of **15** (30 mg, 0.03 mmol) in MeOH/H$_2$O 2:1 (bidist.; 3.6 ml) at 0°, a degassed 0.3M aq. LiOH soln. (700 µl, 7.0 equiv.) was added. The mixture was stirred at 0° for 30 min, then at 20° for 2 h. The pH of the reaction was controlled with pH paper. The reaction was stopped by addition of *Dowex 50 W X2* (H$^+$ form, 0.5 g). Stirring at 20° was continued for 10 min. After filtration, the resin was washed with MeOH/H$_2$O 2:1 then with H$_2$O. The combined filtrates were evaporated, and the remaining aq. soln. was lyophilized. The crude products TLC (CHCl$_3$/MeOH/H$_2$O 18:13:2.7) were purified by FC (silica gel, CHCl$_3$/MeOH/H$_2$O 18:13:2.7): **16b** (7.0 mg, 30%), **16c** (2.0 mg, 8%), and a less-polar product, probably methyl ester **16a** (2.0 mg, 8%).

*2-*O*-[2-(Acetylamino)-2-deoxy-β-*D*-glucopyranosyl]-3-*O*-(aminocarbonyl)-α-*D*-glucopyranuronamide 1-[(2*R*)-2-(Dodecyloxy)-3-methoxy-3-oxopropyl Hydrogen Phosphate]* (**16a**): R_f (CHCl$_3$/MeOH/H$_2$O 18:13:2.7): 0.38. ^{1}H-NMR: uninformative. ^{31}P-NMR (81.0 MHz, D$_2$O): 14.50. ESI-MS (C$_{31}$H$_{56}$N$_3$O$_{18}$P (789.76, 789.33)): 788.32411 ([*M* – H]$^-$; calc. 788.32170).

*2-*O*-[2-(Acetylamino)-2-deoxy-β-*D*-glucopyranosyl]-3-*O*-(aminocarbonyl)-α-*D*-glucopyranuronamide 1-[(2*R*)-2-Carboxy-2-(dodecyloxy)ethyl Hydrogen Phosphate]* (**16b**): R_f (CHCl$_3$/MeOH/H$_2$O 18:13:2.7): 0.3. ^{1}H-NMR (300 MHz, D$_2$O; signals that could be assigned): 5.72 (*m,* H–C(1^{F})); 4.86 (*t,* H–C(3^{F})); 4.54 (*d,* H–C(1^{E})); 4.20 (*d,* H–C(5^{F})); 1.89 (*s,* NHAc); 1.48 (*m,* H–C(2^{I})); 1,13 (*m,* CH$_2$(3^{I}) to CH$_2$(11^{I})); 0.71 (*t,* Me(12^{I})), *J*(2F,3F) = 9.6, *J*(3F,4F) = 9.6, *J*(4F,5F) = 10.2, *J*(1E,2E) = 8.0. ^{31}P-NMR (81.0 MHz, D$_2$O): 14.50. ESI-MS (C$_{30}$H$_{54}$N$_3$O$_{18}$P (775.74, 775.31)): 774.31001 ([*M* – H]$^-$; calc. 774.30620), 796.29251 ([*M* + Na – 2 H]$^-$; calc. 796.28812).

*2-*O*-[2-(Acetylamino)-2-deoxy-β-*D*-glucopyranosyl]-3-*O*-(aminocarbonyl)-α-*D*-glucopyranuronic Acid 1-[(2*R*)-2-Carboxy-2-(dodecyloxy)ethyl Hydrogen Phosphate]* (**16c**): R_f (CHCl$_3$/MeOH/H$_2$O 18:13:2.7): 0.29. ^{1}H-NMR: uninformative. ^{31}P-NMR (81.0 MHz, D$_2$O): 14.51. ESI-MS (C$_{30}$H$_{53}$N$_2$O$_{19}$P (776.72, 776.30)): 797.25975 ([*M* + Na – 2 H]$^-$; calc. 797.27190).

O-*3,4,6-Tri-*O*-acetyl-2-(acetylamino)-2-deoxy-β-*D*-glucopyranosyl-(1 → 4)-*O*-3-*O*-acetyl-2-(acetylamino)-6-*O*-[(*tert*-butyl)diphenylsilyl]-2-deoxy-β-*D*-glucopyranosyl-(1 → 2)-4-*O*-acetyl-3-*O*-(aminocarbonyl)-α-*D*-glucopyranuronamide 1-[(2*R*)-2-([1,1′-Biphenyl]-3-ylmethoxy)-3-methoxy-3-oxopropyl 2,2,2-Trichloro-1,1-dimethylethyl Phosphate]* (**17a**). To a soln. of 1*H*-1,2,4-triazole (18.2 mg, 0.26 mmol) in CH$_2$Cl$_2$/pyridine 4:1 (0.6 ml), 2,2,2-trichloro-1,1-dimethylethyl phosphorodichloridite (14 µl, 0.069 mmol) was added at 0° under Ar. The mixture was stirred at 0° for 30 min. A soln. of **10c** (60.0 mg, 0.055 mmol), in CH$_2$Cl$_2$/pyridine 7:1 (2.0 ml) was added and the mixture was stirred at 0° for 2 h. After addition of methyl 2-*O*-([1,1′-biphenyl]-3-ylmethyl)glycerate (50.0 mg, 0.18 mmol) in CH$_2$Cl$_2$/pyridine 7:1 (0.6 ml) in three portions within 2 h at 0°, bis(trimethylsilyl) peroxide (22 µl, 0.10 mmol) was injected, and the mixture was stirred at 0° for 1 h, then at 20° for 17 h. The solvents were removed by azeotropic evaporation with toluene. The residue was purified by FC (CHCl$_3$/MeOH 20:1): pure P-diastereoisomer **17a** (20.0 mg, 27%) and mixture of the P-diastereoisomers (30.1 mg, 41%). R_f (CH$_2$Cl$_2$/MeOH 8:1): 0.58, 0.56. $[\alpha]_D^{26} = -2$ (*c* = 1.0, CHCl$_3$). ^{1}H-NMR (^{1}H,^{1}H-COSY; 600 MHz, (D$_5$)pyridine): 8.78–7.35 (*m,* 4 Ph, 2 N*H*Ac, 2 NH$_2$); 6.51 (*dd*, H–C(1^{F})); 6.05 (*t,* H–C(3^{F})); 6.00 (*t,* H–C(3^{C})); 5.99 (*t,* H–C(4^{F})); 5.68 (*t,* H–C(3^{E})); 5.49 (*d,* H–C(1^{C})); 5.41 (*t,* H–C(4^{C})); 5.15 (*d,* H–C(1^{E})); 5.14 (*d,* H–C(5^{F})); 5.05, 4.85 (*AB*, PhC$_6$H$_4$C*H*$_2$); 4.88–4.84, 4.81–4.77 (2 *m,* CH$_2$(3^{H})); 4.72 (*dd*, H$_a$–C(6^{C})); 4.69–4.68 (*m,* H–C(2^{H})); 4.49–4.45 (*m,* H–C(2^{E})); 4.48 (*t,* H–C(4^{E})); 4.31 (*dd*, H–C(2^{F})); 4.28 (*dd*, H$_b$–C(6^{C})); 4.23–4.18 (*m,* CH$_2$(6^{E})); 4.08–4.03 (*m,* H–C(2^{C})); 3.97–3.95 (*m,* H–C(5^{C})); 3.73 (*s,* MeO); 3.66–3.64 (*m,* H–C(5^{E})); 2.22, 2.20, 2.18, 2.16, 2.07, 2.02, 2.01, 2.00, 1.99 (9*s,* 7 MeCO, 2 Me); 1.20 (*s,* Me$_3$C); *J*(1F,2F) = 3.7, *J*(1F,P) = 5.2, *J*(2F,3F) = 9.4, *J*(3F,4F) = 9.4, *J*(4F,5F) = 9.4, *J*(1E,2E) = 8.4, *J*(2E,3E) = 9.4,

J(3E,4E) = 9.4, J(4E,5E) = 9.4, J(1C,2C) = 7.9, J(2C,3C) = 9.4, J(3C,4C) = 9.4, J(4C,5C) = 9.4, J(5C,6aC) = 4.2, J(5C,6bC) = 1.5, J(6aC,6bC) = 11.5, $^2J_{AB}$ = 12.0. ^{31}P-NMR (121.5 MHz, (D_5)pyridine): −5.40. ESI-MS ($C_{70}H_{88}Cl_3N_4O_{28}PSi$ (1598.90, 1596.42)): 1597.42460 ([M + H]$^+$; calc. 1597.42303).

O-*3,4,6-Tri*-O-*acetyl-2-(acetylamino)-2-deoxy-β*-D-*glucopyranosyl-(1 → 4)*-O-*3*-O-*acetyl-6*-O-*[(*tert-*butyl)-diphenylsilyl]-2-deoxy-β*-D-*glucopyranosyl-(1 → 2)-4*-O-*acetyl-3*-O-*(aminocarbonyl)-α*-D-*glucopyranuronamide 1-[(2*R*)-2-([1,1′-Biphenyl]-3-ylmethoxy)-3-methoxy-3-oxopropyl Hydrogen Phosphate]* (**18a**). To a soln. of **17a** (40.0 mg, 0.025 mmol) in dry pyridine (2.0 ml), Zn−Cu couple (freshly prepared; 120.0 mg, 1.82 mmol) and pentane-2,4-dione (0.16 ml, 1.36 mmol) were added. The mixture was stirred under Ar overnight. Excess Zn−Cu was removed by filtration, and the residue was washed with MeOH. After evaporation, the residue was dried at 10 Pa for 1 h, then taken up in H_2O/EtOH 8:1 (9.0 ml). *Dowex 50 W X2* (H^+ form, 2.0 g) was added, and the mixture was stirred for 1 h. After filtration, the resin was washed with MeOH. The org. solvents were evaporated and the remaining aq. soln. was lyophilized. The crude product was purified by FC ($CHCl_3$/MeOH 5:1): 7 mg of **18a** (R_f (CH_2Cl_2/MeOH 4:1): 0.48) and a fraction containing **18a** and a second compound (R_f 0.46). Total yield: 29.0 mg, *ca.* 87%). **18a**: $[\alpha]_D^{26} = -2$ (c = 1.0, $CHCl_3$). ^{1}H-NMR (^{1}H,^{1}H-COSY; 600 MHz, $CDCl_3$/CD_3OD 1:1): 7.69–7.30 (*m,* 4 Ph, 2 N*H*Ac, 2 NH_2); 5.71 (br. *s*, H−C(1^F)); 5.17 (*t,* H−C(3^F)); 5.09 (*t,* H−C(4^F)); 5.06 (*t,* H−C(3^C)); 4.98 (*t,* H−C(3^E)); 4.93 (*t,* H−C(4^C)); 4.74, 4.58 (*AB*, $PhC_6H_4CH_2$); 4.55 (*d,* H−C(1^C)); 4.52 (*d,* H−C(1^E)); 4.40 (*d,* H−C(5^F)); 4.28 (*dd*, H_a−C(6^C)); 4.26–4.21 (*m,* CH_2(3^H)); 4.15–4.12 (*m,* H−C(2^H)); 3.98–3.94 (*m,* H−C(2^E)); 3.91 (*t,* H−C(4^E)); 3.89 (*dd*, H_b−C(6^C)); 3.76–3.70 (*m,* H−C(2^F), H−C(2^C), CH_2(6^E)); 3.60–3.57 (*m,* H−C(5^E)); 3.45–3.42 (*m,* H−C(5^C)); 3.31 (*s,* MeO); 2.00, 1.99, 1.98, 1.97, 1.96, 1.91, 1.68 (7*s,* 7 MeCO); 1.07 (*s,* Me_3C); J(2F,3F) = 9.9, J(3F,4F) = 9.9, J(4F,5F) = 9.9, J(1E,2E) = 7.9, J(2E,3E) = 9.4, J(3E,4E) = 9.4, J(4E,5E) = 9.4, J(1C,2C) = 7.9, J(2C,3C) = 9.9, J(3C,4C) = 9.9, J(4C,5C) = 9.9, J(5C,6aC) = 4.2, J(5C,6bC) = 1.6, J(6aC,6bC) = 12.0, $^2J_{AB}$ = 12.0. ^{31}P-NMR (121.5 MHz, (D_5)pyridine): −2.63. ESI-MS ($C_{66}H_{83}N_4O_{28}PSi$ (1439.45, 1438.47)): 1437.46137 ([M − H]$^-$; calc. 1437.46279).

O-*3,4,6-Tri*-O-*acetyl-2-(acetylamino)-2-deoxy-β*-D-*glucopyranosyl-(1 → 4)-3*-O-*acetyl-2-(acetylamino)-6*-O-*[(*tert-*butyl)diphenylsilyl]-2-deoxy-β*-D-*glucopyranosyl-(1 → 2)-4*-O-*acetyl-3*-O-*(aminocarbonyl)-α*-D-*glucopyranuronamide 1-[(2*R*)-2-(Hexadecyloxy)-3-methoxy-3-oxopropyl 2,2,2-Trichloro-1,1-dimethylethyl Phosphate]* (**17b**). As described for **17a**, with 1*H*-1,2,4-triazole (15.2 mg, 0.22 mmol), CH_2Cl_2/pyridine 4:1 (0.6 ml), 2,2,2-trichloro-1,1-dimethylethyl phosphorodichloridite (12 µl, 0.058 mmol), **10c** (50.0 mg, 0.046 mmol), CH_2Cl_2/pyridine 7:1 (2.0 ml), methyl 2-*O*-hexadecylglycerate [31] (36.0 mg, 0.10 mmol), CH_2Cl_2/pyridine 7:1 (0.6 ml), bis(trimethylsilyl) peroxide (18 µl, 0.87 mmol): P-diastereoisomer mixture **17b** (2.5:1; 13.1 mg, 17%). R_f (CH_2Cl_2/MeOH 8:1): 0.50, 0.49. ^{1}H-NMR (^{1}H,^{1}H-COSY; 600 MHz, (D_5)pyridine; major isomer in the mixture): 8.90 (*d*, N*H*Ac); 8.78, 7.83 (2 br. *s*, NH_2); 8.40–7.00 (*m,* N*H*Ac, NH_2); 6.50 (br. *s*, H−C(1^F)); 6.06–6.00 (*m,* H−C(3^F), H−C(3^C), H−C(4^F)); 5.70–5.67 (overlapped by solvent, H−C(3^E)); 5.51 (*d,* H−C(1^C)); 5.41 (*t,* H−C(4^C)); 5.14 (*d,* H−C(1^E)); 5.07–5.04 (*m,* H−C(5^F)); 4.94–4.53 (*m,* H−C(2^H), CH_2(3^H), CH_2(1^1), H_a−C(6^C)); 4.49–4.44 (*m,* H−C(2^E), H−C(4^E)); 4.31–4.26 (*m,* H−C(2^F), H_b−C(6^C)); 4.23–4.16 (*m,* CH_2(6^E)); 4.06–4.03 (*m,* H−C(2^C)); 3.99–3.96 (*m,* H−C(5^C)); 3.73 (*s,* MeO); 3.65–3.61 (*m,* H−C(5^E)); 2.25, 2.22, 2.18, 2.16, 2.11, 2.02, 2.01, 2.00, 1.99 (9*s,* 7 MeCO, 2 Me); 1.28–1.24 (*m,* $(CH_2)_{14}$); 1.20 (*s,* Me_3C); 0.86 (*t,* Me of unit I); J(1E,2E) = 8.3, J(1C,2C) = 7.8, J(3C,4C) = 9.9, J(4C,5C) = 9.9, 2J(H,NH) = 7.9. ^{31}P-NMR (121.5 MHz, (D_5)pyridine): −8.96 (major isomer), −8.41 (minor isomer).

O-*2-(Acetylamino)-2-deoxy-β*-D-*glucopyranosyl-(1 → 4)*-O-*2-(acetylamino)-2-deoxy-β*-D-*glucopyranosyl-(1 → 2)-3*-O-*(aminocarbonyl)-α*-D-*glucopyranuronamide 1-[(2*R*)-2-Carboxy-2-(hexadecyloxy)ethyl Hydrogen Phosphate]* (**20b**). As described for **18a**, with **17b** (13.0 mg, 8.0 µmol), pyridine (2.0 ml), Zn−Cu (40.0 mg, 0.60 mmol), pentane-2,4-dione (55 µl, 47 mmol), and *Dowex 50 W X2* (H^+ form, 2.00 g). The crude **18b** was dissolved in dry THF (0.50 ml), 1M Bu_4NF in THF (80 µl) was added, and the mixture stirred at 20° for 40 min (TLC (CH_2Cl_2/MeOH 4:1) monitoring). The mixture was evaporated, the residue dried and then dissolved in degassed (Ar stream, sonication) MeOH (*p.a*)/H_2O (bidist.) 2:1 (0.50 ml), and the soln. cooled to 0°. Then 0.3M LiOH (degassed; 0.22 ml, 8 equiv.) was added, and the mixture was stirred at 0° for 30 min, then at 20° for 6 h. Excess base was neutralized by addition of *Dowex 50 W X2* (H^+ form). Stirring at 20° was continued for 5 min. After filtration, the resin was washed with MeOH/H_2O 1:1. The combined filtrate and washings were evaporated, and the remaining aq. soln. was lyophilized. The crude product was purified by FC ($CHCl_3$/MeOH/H_2O 18:11:2.7) to yield three compounds which were shown by ESI-MS to be incompletely deprotected products. The 1st compound (ESI-MS: 1047.46264 ([M − H]$^-$)) contained the COOMe group, the 2nd (ESI-MS: 1089.46987 ([M − H]$^-$)) 1 Ac and the COOMe group, and the 3rd (ESI-MS: 1131.47812 ([M − H]$^-$)) 2 Ac and the COOMe group. The mixture was submitted to the deprotection conditions as described above (0.3M LiOH (0.11 ml, 4 equiv., 3 h). FC ($CHCl_3$/MeOH/H_2O 18:11:2.7), and filtration through *Sephadex LH 20* with MeOH/H_2O 1:1 yielded **20b** (4.0 mg, 49%). R_f ($CHCl_3$/MeOH/H_2O 18:11:2.7): 0.20. ^{1}H-NMR (^{1}H,^{1}H-COSY;

600 MHz, CD_3OD): 5.92 (br. *s*, H–C(1^F)); 5.07 (*t*, H–C(3^F)); 4.64 (*d*, H–C(1^E)); 4.45 (*d*, H–C(1^C)); 4.32 (*d*, H–C(5^F)); 4.31–4.10 (*m*, CH_2(3^H), H–C(2^H); 3.90 (br. *d*, H_a–C(6^E)); 3.79 (br. *d*, H_a–C(6^C)); 3.73 (*dd*, H–C(2^C)); 3.71 (*t*, H–C(4^F)); 3.66–3.56 (*m*, H–C(2^E), H–C(2^F), H_b–C(6^E), H_b–C(6^C), OCH_2^I); 3.51 (*t*, H–C(4^E)); 3.42 (*t*, H–C(3^C)); 3.36–3.29 (*m*, H–C(3^E), H–C(4^C), H–C(5^E), H–C(5^C)); 2.01, 1.99 (2*s*, 2 MeCO); 1.59–1.66, 1.28–1.39 (2*m*, $(CH_2)_{14}^I$); 0.90 (*t*, Me^I); *J*(2F,3F) = 9.4, *J*(3F,4F) = 9.4, *J*(4F,5F) = 9.4, *J*(1E,2E) = 8.0, *J*(3E,4E) = 9.0, *J*(4E,5E) = 9.0, *J*(6aE,6bE) = 11.4, *J*(1C,2C) = 8.4, *J*(2C,3C) = 9.9, *J*(3C,4C) = 9.9, *J*(6aC,6bC) = 12.4. ^{13}C-NMR (^{1}H,^{13}C-COSY; 100 MHz, CD_3OD): 102.74, 102.44, 95.56 (C(1^F)); 80.62, 78.91, 77.14, 75.31, 75.00, 73.69, 72.62, 71.32, 71.22, 70.92, 70.70, 70.43, 66.22, 61.55, 60.36, 57.17, 56.17, 32.06, 29.81-29.40, 26.12, 22.72, 20.04, 13.42. ESI-MS ($C_{42}H_{75}N_4O_{23}P$ (1035.04, 1034.46)): 1033.44931 ($[M-H]^-$; calc. 1033.44869).

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