Studies on the Synthesis of Trisaccharide Analogues of the Antibiotic Moenomycin A

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A new approach for the synthesis of moenomycin trisaccharide analogues is reported in which three monosaccharide building blocks are used and allows the introduction of different substituents at the 6-position of unit E (*Scheme 2*). Furthermore, a new procedure for the introduction and manipulation of unit F is described (*Scheme 3*).

Introduction. – The moenomycins are a group of compounds that inhibit highly efficiently the transglycosylation step, *i.e.*, the formation of the sugar strands, in the biosynthesis of the bacterial cell wall peptidoglycan component. There is experimental evidence that the transglycosylation proceeds in such a way that the growing polysaccharide chain is the glycosyl donor, whereas the disaccharide derivative lipid II is the glycosyl acceptor (for a review, see [1]). A representation of the transition state is displayed in the *Figure*.

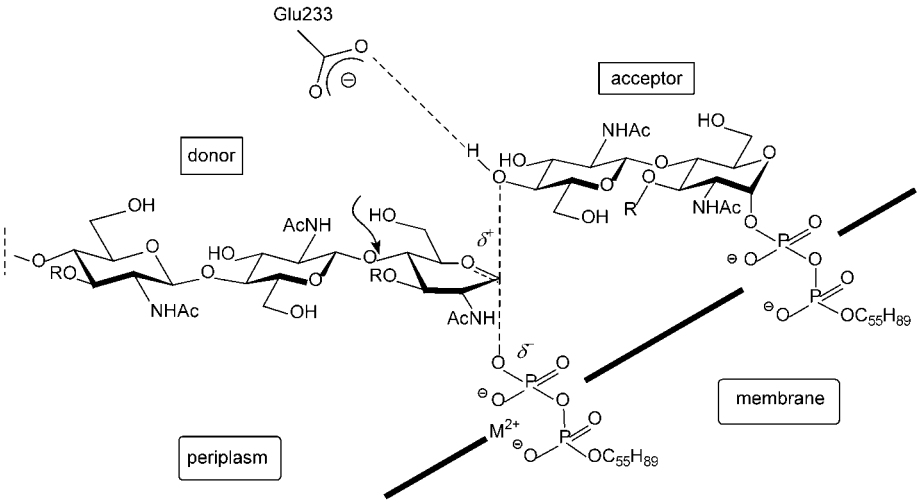

Fig. 1. *Putative mechanism of the transglycosylation reaction*

The transglycosylation is catalyzed by a number of multimodular bifunctional polymerases (that also catalyze the crosslinking transpeptidation reaction) designated

as class-A *high-molecular-mass penicillin-binding proteins* (PBPs). One of them, *viz.* PBP 1b from *E. coli,* has been studied in great detail [2]. Moenomycin A (**1**) binds reversibly to *E. coli* PBP 1b [1]. From structure-activity relationships [3][4], it has been inferred that the moenomycins, after unselective anchoring to the cytoplasmic membrane *via* their lipid moiety (for a discussion, see [5]), bind highly selectively *via* their carbohydrate part to the donor binding subsites of the enzyme. The structural features that are known to be responsible for the antibiotic activity are indicated by full arrows in **2** [3][4]. It is assumed that units C and E of **1** and **2**, respectively, compete with the second and the third sugar unit of the growing peptidoglycan chain for the binding subsites at the enzyme. The different binding of the first two sugar units ($1 \rightarrow 4$ in the growing peptidoglycan strand (see *Figure*) *vs.* $1 \rightarrow 2$ in **1** and **2**, resp.) as indicated by curved arrows has been suggested to be responsible for the inhibition of the enzyme [6]. The conclusions from structure-activity-relationship (SAR) studies are corroborated by NMR results, especially from STD NMR experiments [7][8] from which it has been inferred that the *N*-acetyl groups of units C and E are in contact with the enzyme in the ligand/protein complex [9]. A recent publication by *Kahne* and co-workers [10] requires comment. They found that the inhibition of PBP 1b by moenomycin cannot be overcome by lipid-II and argued that this result disproves the prediction that moenomycin is a competitive inhibitor with respect to lipid II. The position that *Kahne* and co-workers take in their paper ignores completely the SAR results that have accumulated and which have led to the mechanistic picture outlined above [3][4]. Furthermore, an IC_{50} of *ca.* $2 \cdot 10^{-9}$ mol l^{-1} has been determined for moenomycin (using cell-wall-membrane material isolated from *E. coli*) [11]. Most probably, moenomycin is a tight-binding inhibitor [12]. It is, therefore, not at all unreasonable to assume that lipid II, with an affinity for the acceptor site of only *ca.* 2–3 μM, does not overcome binding of moenomycin at the donor site (which is not the lipid II binding site, with the possible exception of the initiating step of the sugar-chain formation). Even the observation that lipid II does not compete with an analogue of moenomycin lacking a large part of the lipid moiety does, in our opinion, not support the conclusions of *Kahne* and co-workers. Indeed, the binding of this compound, which *in vivo* is antibiotically inactive, to PBP 1b is strong enough to permit affinity purification of the enzyme [13][1]).

The moenomycin analogues employed for the SAR and mode-of-action studies have been obtained *i*) by selective degradation of **1** [14], *ii*) by attachment of reporter groups to unit A of **1** [15], and *iii*) by synthesis of moenomycin A trisaccharide analogues [6][16][17]. The latter approach is the most demanding but, of course, also the most promising one, since approaches *i*) and *ii*) allow the preparation of analogues with only limited diversity. Furthermore, reporter groups attached to unit A of **1** are rather far away from that part of the antibiotic which is in contact with the enzyme. Thus, it seems worthwhile to develop synthetic routes towards moenomycin analogues containing at least three sugar units (C–E–F, see formula **1**)[2]). *Sofia* and co-workers reported on the library synthesis of disaccharide analogues, but the substances

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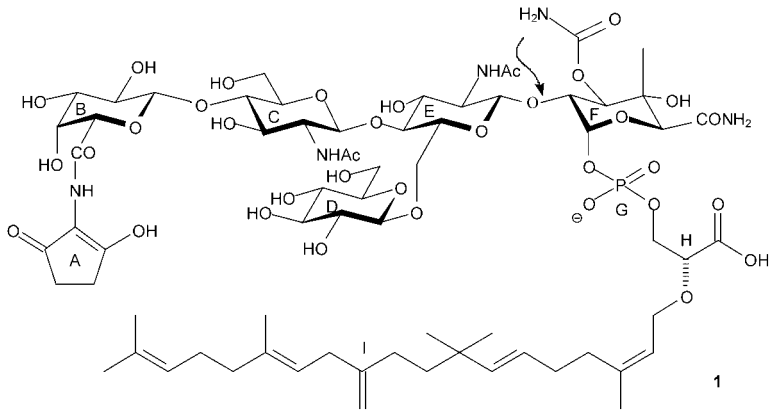
[1]) See also the NMR results [9].

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

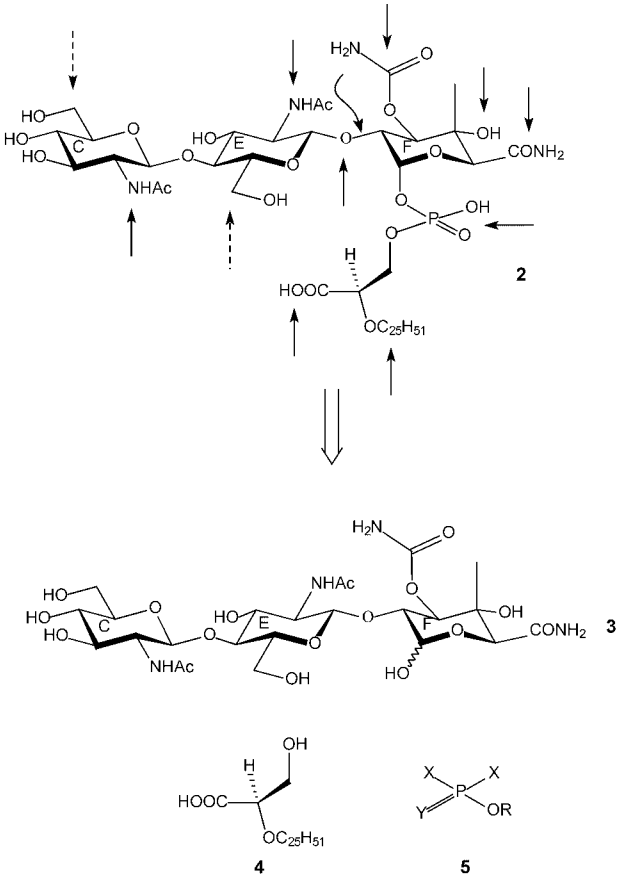


accessible by their route do not meet the structural requirements for a moenomycin-type mode of action [18]. We devised a strategy that is characterized by coupling an oligosaccharide **3** *via* a phosphoric acid diester linker to the 3-OH group of a 2-*O*-alkylated glyceric acid building block **4**, making use of a bis-electrophilic phosphoric acid equivalent **5** (*Scheme 1*; X = leaving group, Y = electron pair). Recently, the problems associated with the synthesis of 2-*O*-substituted glycerates **4** were solved adequately [19]. All previously reported syntheses of moenomycin trisaccharide analogues used a C–E disaccharide building block (chitobiose [16], cellobial [6], lactosamine [17]). Here and in the accompanying publication, we wish to describe a new approach that commences from three monosaccharide building blocks and is flexible in such a way that it allows the introduction of different substituents at C(6) of unit E, the substitution of which is unimportant as far as the antibiotic properties are concerned (see dotted arrows in **2**) [3]. It is anticipated that this position can be used to attach reporter groups much closer to the moenomycin binding site at the enzyme. Furthermore, we describe a new procedure for the introduction and manipulation of unit F [3]).

Synthesis of Trisaccharide 10a with the Phthaloyl (Phth) Protecting Group in Units C and E and a Phenyl Carbonate as a Latent Carbamoyl Group in Unit F. – The *N*-phthaloyl-protected glucosamine derivative **6a** [21] with a free 1-OH group and the corresponding trichloroacetimidate **6b** were synthesized by published methods [22] (*Scheme 2*). Silylation of the anomeric OH group of **6a** with (*tert*-butyl)dimethylsilyl chloride and 1*H*-imidazole in DMF [23] gave silyl derivative **6c** in high yield. Removal of all acetyl groups of **6c** under *Zemplén* conditions (**6c** → **6d**) and subsequent selective silylation of the 6-OH group with (*tert*-butyl)diphenylsilyl chloride and 1*H*-imidazole in DMF afforded compound **6e**, the acetyl derivative **6f**, which was prepared to facilitate ^{1}H-NMR analysis. Me_3SiOTf-Promoted coupling of trichloroacetimidate **6b** with acceptor **6e** that has free OH groups in the 3- and the 4-position in CH_2Cl_2 solution gave

[3]) Unit F was previously prepared from D-glucose, D-glucuronic acid, D-galactose, and D-galacturonic acid. For leading references, see [3][20].

Scheme 1

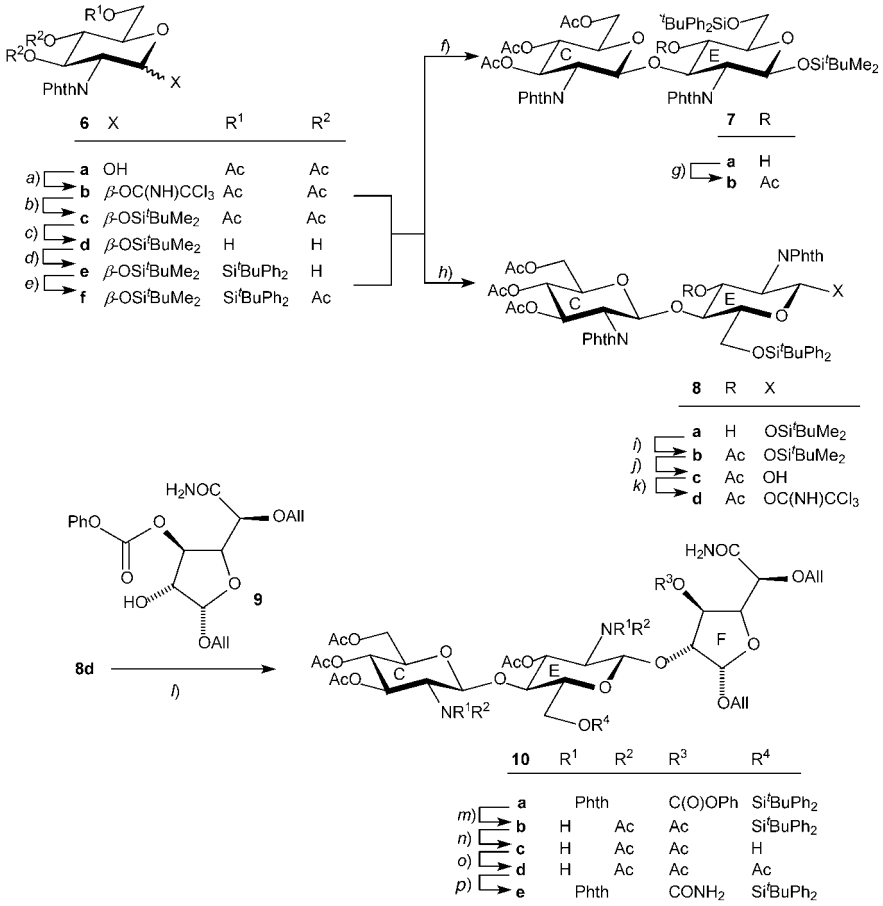


the $1 \rightarrow 3$-linked disaccharide **7a** as the main product (65%), along with 5% of a mixture containing the $1 \rightarrow 4$-linked disaccharide **8a**. Remarkably, in Et_2O solution, the coupling of **6b** with **6e** catalyzed by Me_3SiOTf furnished the $1 \rightarrow 4$-linked disaccharide **8a** as the major product (64%) accompanied by the $1 \rightarrow 3$ isomer **7a** (21%).

The coupling constant $J(1,2^C) = 8.4$ Hz in **7a** confirmed the β-D-glycosidic bond, and the chemical shifts of $C(3^E)$ (δ 82.25) and $C(4^E)$ (δ 70.10) established the $1 \rightarrow 3$ linkage. The structure **7a** was confirmed *via* acetyl derivative **7b**, the ^{1}H-NMR spectrum of which displayed the $H-C(4^E)$ signal at δ 4.85 (at δ *ca.* 3.6 in **7a**). The coupling constant $J(1,2^C) = 7.4$ Hz in **8a** confirmed the β-D-glycosidic bond, and the chemical shifts of $C(3^E)$ (δ 69.80) and $C(4^E)$ (δ 80.54) indicated the formation of a $1 \rightarrow 4$-linked disaccharide. In the acetyl derivative **8b** the coupling constant $J(1,2^C)$ was 8.1 Hz, in agreement with the β-D-glycosidic bond, and the chemical shifts of $H-C(3^E)$ (δ 5.77) and $H-C(4^E)$ (δ 4.38–4.30) established the $1 \rightarrow 4$ linkage.

The next task was to remove the ^{t}BuMe$_2$Si group, leaving the primary ^{t}BuPh$_2$Si ether intact. Selective desilylation at the anomeric position of **8b** with pyridinium *p*-toluenesulfonate [24], I_2/MeOH [25], $BF_3 \cdot Et_2O$ [26], TsOH [27], Me_3SiOTf [28],

Scheme 2



a) [23]. *b*) ^{t}BuMe$_2$SiCl, 1*H*-imidazole, DMF, 20°; 92%. *c*) MeONa, MeOH, 20°; 95%. *d*) ^{t}BuPh$_2$SiCl, 1*H*-imidazole, DMF, 0°; 88%. *e*) Ac_2O, pyridine, 20°; 96%. *f*) Me_3SiOTf, 4-Å molecular sieves, CH_2Cl_2, 0°; 65%. *g*) Conditions *e*; 96%. *h*) Me_3SiOTf, 4-Å molecular sieves, Et_2O, 0°; 64% of **8a**, 21% of **7a**. *i*) Conditions *e*; 96%. *j*) Bu_4NF, THF, −20°; 78%. *k*) Cl_3CN, CH_2Cl_2, K_2CO_3, 20°; 86%. *l*) Conditions *f*; 18%. *m*) $H_2N(CH_2)_2NH_2$, BuOH, 90°, 12 h; then conditions *e*; 48%. *n*) Bu_4NF, THF, 20°; 61%. *o*) Conditions *e*; 77%. *p*) NH_3, pyridine/dioxane, 0°; 42%.

AcOH [26], and KF [29] was not successful. Finally, treatment of **8b** with Bu_4NF under carefully controlled conditions (1 equiv., 1M in THF, −20°) furnished compound **8c**, which, on treatment with Cl_3CCN and K_2CO_3, yielded donor **8d** in a high overall yield (86%) (*Scheme 2*). Coupling of **8d** with the known acceptor **9** [3] catalyzed by Me_3SiOTf in Et_2O/CH_2Cl_2 5:1 furnished trisaccharide **10a** in only 18% yield, probably as a result of unfavorable physical properties of **9**. Compound **9** is rather polar and only slightly soluble in Et_2O due to the carboxamide group. We also tried CH_2Cl_2, $ClCH_2CH_2Cl$, THF, and MeCN as solvents, but the yields were even lower than that in

Et_2O/CH_2Cl_2. Treatment of **10a** with ethane-1,2-diamine [30] in BuOH, followed by acetylation afforded a compound in which the phenoxycarbonyl group was also replaced by an acetyl group. The ^{1}H-NMR spectrum of this compound, which we assume to have structure **10b**, did not show the number of acetyl groups conclusively. To improve the characterization, the silyl ether moiety was cleaved with Bu_4NF in THF to give **10c**. Subsequent acetylation yielded **10d**. The ^{1}H-NMR spectrum of **10c** showed seven acetyl groups. Aromatic proton signals were absent. In agreement with this result, the ^{1}H-NMR spectrum of **10d** displayed eight acetyl signals (ESI-MS: $[M+H]^+$ at m/z 932.35186).

Since the phenyl carbonate group did not survive the phthaloyl-group removal from **10a**, we converted it to a carbamoyl group by treatment with ammonia/dioxane/pyridine [3] to give **10e**. We then tried to remove the phthalimido group of **10e** with hydrazinium acetate [31], 40% $MeNH_2/H_2O$ [32] or ethane-1,2-diamine [30] but neither reagent was successful. In all cases, the carbamoyl group was also removed, and, after acetylation, compound **10b** was obtained.

The results demonstrated that the combination of the Phth protecting group with either a phenyl carbonate or a urethane group at C(3^F) is not compatible in the synthesis of moenomycin-type oligosaccharides.

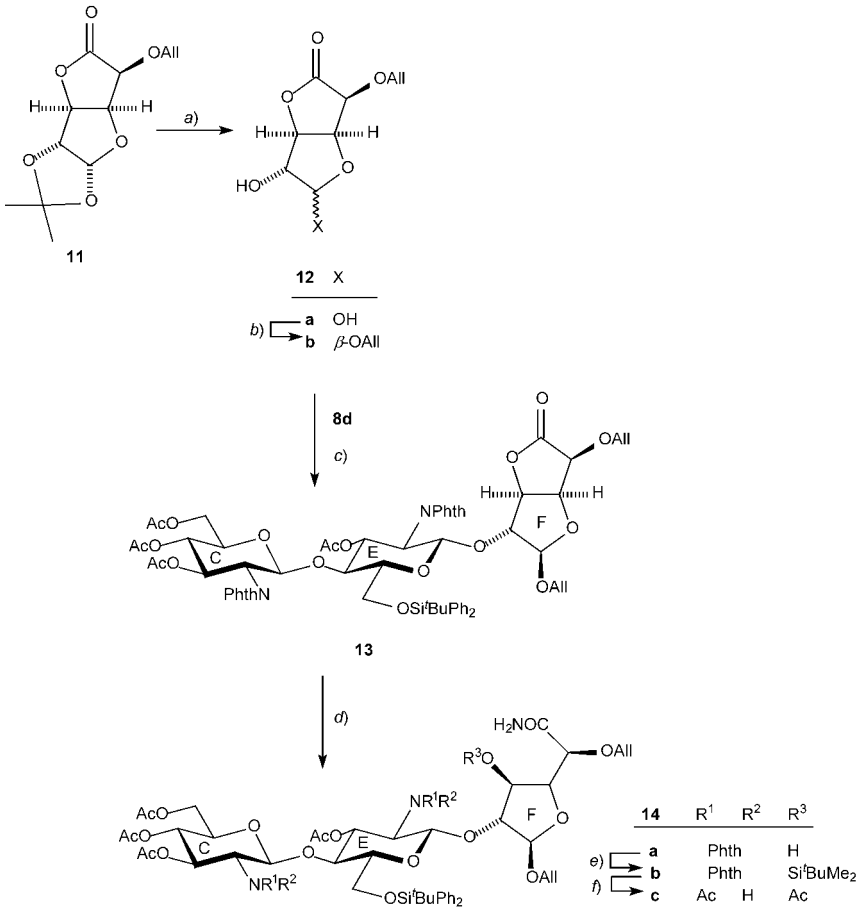
Synthesis of a Moenomycin-Type Trisaccharide *via* a New Unit-F Acceptor. – The low yield (18%) in the coupling of **8d** with **9** demanded to use a more suitable acceptor containing, instead of the amide group, a functional group easily convertible into the uronamide. The modified glucuronolactone **12b** seemed to fulfill these requirements (*Scheme 3*). Compound **12b** was obtained by allylation at the anomeric position of **12a** in the presence of camphorsulfonic acid, **12a** being prepared by removing the isopropylidene acetal moiety in **11** with 90% CF_3COOH/H_2O [33].

The ^{1}H- and ^{13}C-NMR spectra ((D_5)pyridine) showed **12a** to be a 4:1 mixture of the β- and α-D-isomers. The ^{1}H- and ^{13}C-NMR signals of C(1) of the β-D-isomer appeared at δ 6.10 and 105.71, respectively, and those of the α-D-isomer at δ 5.97 and 100.16, respectively. The ^{1}H- and ^{13}C-NMR spectra of the allylation product **12b** (H–C(1) at δ 6.15 (*s*), C(1) at δ 107.44) indicated that only the β-D-glycoside **12b** had been formed [34].

Coupling of donor **8d** with **12b** catalyzed by Me_3SiOTf in Et_2O furnished trisaccharide **13** (42%) (*Scheme 3*). The yield was lower when CH_2Cl_2 or $ClCH_2CH_2Cl$ were used as solvents. Treatment of **13** with NH_3 in THF/MeOH furnished glucofuranosiduronamide **14a**. We also tried NH_3 in THF, pyridine, 1,4-dioxane/pyridine or $(NH_4)_2CO_3$ in DMF, but under all these conditions, yields were lower due to the formation of deacetylation products. Silylation of **14a** at the C(3^F) position with a large excess of ^{t}BuMe$_2$SiCl in pyridine, catalyzed by *N*,*N*-dimethylpyridin-4-amine (DMAP), provided compound **14b** (^{1}H-NMR: ^{t}BuMe$_2$Si at δ 0.92, 0.25, and 0.24). Phthaloyl-group removal with ethane-1,2-diamine in BuOH [23] followed by acetylation converted **14b** into compound **14c**. Unexpectedly, the ^{t}BuMe$_2$Si group of **14b** was replaced by an acetyl group in **14c** (^{1}H-NMR: 7 Ac; no ^{t}BuMe$_2$Si).

We concluded from these results that the new approach was promising but that the phthaloyl group had to be replaced by more-suitable protecting groups prior to introduction of the carbamoyl group or a synthetic equivalent. This will be described in the subsequent communication [35].

Scheme 3



a) CF_3COOH/H_2O 9:1, 20°; 92%. *b*) Allyl alcohol, camphorsulfonic acid, 20°; 49%. *c*) Me_3SiOTf, 4-Å molecular sieves, Et_2O, 20°; 42%. *d*) NH_3, THF/MeOH, 0°; 43%. *e*) ^{t}BuMe$_2$SiCl, pyridine, DMAP, 20°, 74%. *f*) $H_2N(CH_2)_2NH_2$, BuOH, 90°, 12 h; then Ac_2O, pyridine, 20°; 51%.

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Experimental Part

General. See [36].

*(*tert*-Butyl)dimethylsilyl 3,4,6-Tri*-O*-acetyl-2-deoxy-2-phthalimido-β-*D*-glucopyranoside* (**6c**). To a soln. of **6a** (500.0 mg, 1.15 mmol) in dry DMF (5.0 ml), 1*H*-imidazole (156.0 mg, 2.30 mmol) and (*tert*-butyl)dimethylsilyl chloride (230.0 mg, 1.50 mmol) were added at 0°. The mixture was stirred at 20° for 4 h (TLC (petroleum ether/AcOEt 1:1) monitoring). The reaction was stopped by adding MeOH (0.10 ml), the mixture evaporated, the residue dissolved in AcOEt (30 ml), the soln. washed with 5% NaCl soln., the org. phase dried (Na_2SO_4) and evaporated, and the residue purified by FC (petroleum ether/AcOEt 2:1): **6c** (580.2 mg, 92%). M.p. 140.8–141.9° (petroleum ether/AcOEt). R_f (petroleum ether/AcOEt 1:1): 0.62. $[\alpha]_D^{26} = +92$ ($c = 1.0$, CHC_3). ^{1}H-NMR

(^{1}H,^{1}H-COSY; 300 MHz, $CDCl_3$): 7.86–7.73 (*m*, PhthN); 5.84 (*dd*, H–C(3)); 5.56 (*d*, H–C(1)); 5.12 (*dd*, H–C(4)); 4.26 (*dd*, H–C(2)); 4.25 (*dd*, H_a–C(6)); 4.15 (*dd*, H_b–C(6)); 3.92–3.86 (*m*, H–C(5)); 2.09, 2.03, 1.86 (3 *s*, 3 MeCO); 0.68 (*s*, Me_3C); 0.05, −0.06 (2 *s*, 2 Me); $J(1,2) = 8.1$, $J(2,3) = 11.2$, $J(3,4) = 9.0$, $J(4,5) = 10.2$, $J(5,6a) = 5.7$, $J(5,6b) = 2.4$, $J(6a,6b) = 12.0$. ^{13}C-NMR (^{13}C,^{1}H-COSY; 75.5 MHz, $CDCl_3$): 170.65, 170.18, 169.61 (3 Me*C*O); 134.36, 131.40, 123.52 (PhthN); 93.22 (C(1)); 71.87 (C(5)); 70.58 (C(3)); 69.54 (C(4)); 62.45 (C(6)); 56.74 (C(2)); 25.31 (*Me*$_3$C); 20.77, 20.70, 20.55 (3 *Me*CO); 17.57 (Me_3C); −4.31, −5.51 (2 Me). ESI-MS ($C_{26}H_{35}NO_{10}Si$; 549.65, 549.20): 571.8 ([*M* + Na]$^+$).

*(*tert*-Butyl)dimethylsilyl 2-Deoxy-2-phthalimido-β-*D*-glucopyranoside* (**6d**). To a soln. of **6c** (450.0 mg, 0.82 mmol) in MeOH (5.0 ml), 1M NaOMe (0.05 ml) was added. The mixture was stirred at 20° for 4 h (TLC (AcOEt) monitoring). The mixture was neutralized with *Dowex 50 W X2* (H^+ form) and filtered and the resin washed with MeOH. The combined filtrate and washings were evaporated. Purification by FC ($CHCl_3$/MeOH 20 : 1) afforded compound **6d** (330.2 mg, 95%). M.p. 211.0–211.4° (AcOEt). R_f (petroleum ether/AcOEt 1 : 3): 0.08. $[\alpha]_D^{26} = -28$ (*c* = 1.0, MeOH). ^{1}H-NMR (^{1}H,^{1}H-COSY; 300 MHz, (D_5)pyridine): 7.88–7.57 (*m*, PhthN); 5.98 (*d*, H–C(1)); 5.20 (*dd*, H–C(3)); 4.79 (*dd*, H–C(2)); 4.52 (*dd*, H_a–C(6)); 4.40 (*dd*, H_b–C(6)); 4.32 (*t*, H–C(4)); 4.11–4.05 (*m*, H–C(5)); 0.78 (*s*, Me_3C); 0.19. 0.10 (2 *s*, 2 Me); $J(1,2) = 8.4$, $J(2,3) = 10.6$, $J(3,4) = 8.7$, $J(4,5) = 8.7$, $J(5,6a) = 2.2$, $J(5,6b) = 4.8$, $J(6a,6b) = 11.6$. ^{13}C-NMR (^{13}C,^{1}H-COSY; 75.5 MHz, (D_5)pyridine): 134.03, 131.89, 123.05 (PhthN); 94.02 (C(1)); 78.55 (C(5)); 72.31 (C(4)); 71.92 (C(3)); 62.12 (C(6)); 60.40 (C(2)); 25.17 (*Me*$_3$C); 17.42 (Me_3C); −4.30, −5.72 (2 Me). ESI-MS ($C_{20}H_{29}NO_7Si$; 423.54, 423.17): 445.8 ([*M* + Na]$^+$).

*(*tert*-Butyl)dimethylsilyl 6-*O*-[(*tert*-Butyl)diphenylsilyl]-2-deoxy-2-phthalimido-β-*D*-glucopyranoside* (**6e**). To a soln. of **6d** (300.0 mg, 0.71 mmol) and 1*H*-imidazole (100.0 mg, 1.5 mmol) in dry DMF (5.0 ml), (*tert*-butyl)diphenylsilyl chloride (0.22 ml, 0.85 mmol) was added dropwise at 0°. The mixture was stirred at 0° for 2 h (TLC (petroleum ether/AcOEt 1 : 1) monitoring). Workup as described for **6c** afforded **6e** (413.0 mg, 88%). R_f (petroleum ether/AcOEt 1.5 : 1): 0.40. $[\alpha]_D^{26} = -27$ (*c* = 1.0, $CHCl_3$). ^{1}H-NMR (^{1}H,^{1}H-COSY; 300 MHz, $CDCl_3$): 7.81–7.39 (*m*, 2 Ph, PhthN); 5.39 (*d*, H–C(1)); 4.41 (*ddd*, H–C(3)); 4.08 (*dd*, H–C(2)); 3.98–3.88 (*m*, CH_2(6)); 3.70 (*dt*, H–C(4)); 3.63–3.50 (*m*, H–C(5)); 3.39 (*d*, OH–C(4)); 3.13 (*d*, OH–C(3)); 1.07 (*s*, ^{t}*Bu*Ph_2Si); 0.66 (*s*, ^{t}*Bu*Me_2Si); 0.03, −0.09 (2 *s*, 2 Me); $J(1,2) = 8.0$, $J(2,3) = 11.0$, $J(3,4) = 8.0$, $J(4,5) = 8.0$, $J(3,OH) = 4.4$, $J(4,OH) = 2.2$. ^{13}C-NMR (^{13}C,^{1}H-COSY; 75.5 MHz, $CDCl_3$): 135.88–123.57 (PhthN, 2 Ph); 93.64 (C(1)); 75.12 (C(5)); 74.38 (C(4)); 71.73 (C(3)); 65.14 (C(6)); 58.77 (C(2)); 27.07 (*Me*$_3$C (^{t}BuPh$_2$Si)); 25.60 (*Me*$_3$C (^{t}BuMe$_2$Si)); 19.46 (Me_3C (^{t}BuPh$_2$Si)); 17.78 (Me_3C (^{t}BuMe$_2$Si)); −3.87, −5.30 (2 Me). ESI-MS (acetone/H_2O/NH_4CO_3; $C_{36}H_{47}NO_7Si_2$; 661.94, 661.29): 679.32290 ([*M* + NH_4]$^+$; calc. 679.32293).

*(*tert*-Butyl)dimethylsilyl 3,4-Di-*O*-acetyl-6-*O*-[(*tert*-butyl)diphenylsilyl]-2-deoxy-2-phthalimido-β-*D*-glucopyranoside* (**6f**). Compound **6e** (300.0 mg, 0.45 mmol) was treated with Ac_2O (0.40 ml) and pyridine (0.60 ml) at 20° overnight. The solvents were removed by azeotropic evaporation with toluene. Purification by FC (petroleum ether/AcOEt 4 : 1) afforded **6f** (324.3 mg, 96%). M.p. 142.2–142.8° (petroleum ether/AcOEt). R_f (petroleum ether/AcOEt 1 : 1): 0.78. $[\alpha]_D^{26} = -27$ (*c* = 1.0, $CHCl_3$). ^{1}H-NMR (^{1}H,^{1}H-COSY; 300 MHz, $CDCl_3$): 7.87–7.36 (*m*, 2 Ph, PhthN); 5.86 (*dd*, H–C(3)); 5.60 (*d*, H–C(1)); 5.20 (*t*, H–C(4)); 4.31 (*dd*, H–C(2)); 3.97–3.82 (*m*, H–C(5), CH_2(6)); 1.87 (*s*, 2 MeCO); 1.08 (*s*, ^{t}*Bu*Ph_2Si); 0.72 (*s*, ^{t}*Bu*Me_2Si); 0.14, −0.01 (2 *s*, 2 Me); $J(1,2) = 8.2$, $J(2,3) = 11.0$, $J(3,4) = 9.2$, $J(4,5) = 9{,}2$. ^{13}C-NMR (^{13}C,^{1}H-COSY, 75.5 MHz, $CDCl_3$): 170.64, 169.67 (2 Me*C*O); 135.96–123.75 (2 Ph, PhthN); 93.51 (C(1)); 75.25 (C(5)); 71.24 (C(3)); 69.78 (C(4)); 63.08 (C(6)); 57.20 (C(2)); 26.99 (*Me*$_3$C (^{t}BuPh$_2$Si)); 25.64 (*Me*$_3$C (^{t}BuMe$_2$Si)); 20.90, 20.87 (2 *Me*CO); 19.44 (Me_3C (^{t}BuPh$_2$Si)); 17.83 (Me_3C (^{t}BuMe$_2$Si)); −3.84, −5.23 (2 Me). ESI-MS (acetone/H_2O/NH_4HCO_2; $C_{40}H_{51}NO_9Si_2$; 746.02, 745.31): 763.34397 ([*M* + NH_4]$^+$; calc. 763.34406).

Reaction of **6b** *with* **6e**: **7a** *and* **8a**. a) *In CH_2Cl_2.* To a soln. of **6e** (200.0 mg, 0.30 mmol) and **6b** (200.0 mg, 0.35 mmol) in dry CH_2Cl_2 (5.0 ml), 4-Å molecular sieves (150.0 mg) were added. The mixture was stirred at 20° for 1 h under Ar and then cooled to 0°. Me_3SiOTf in dry CH_2Cl_2 (1M; 45 µl, 45 µmol) was added and the mixture stirred at 0° for 30 min (TLC (petroleum ether/AcOEt 2 : 1) monitoring). The reaction was stopped by adding Et_3N (20 µl), the mixture 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 1.5 : 1) afforded **7a** (212.0 mg, 65%) and a mixture of three compounds (1 → 4-linked disaccharide **8a**, **6e**, and the decomposed donor in a 2.5 : 1 : 1 ratio; 5%).

b) *In Et_2O.* As described in *a*), with **6e** (200.0 mg, 0.30 mmol), **6b** (200.0 mg, 0.35 mmol), dry Et_2O (5.0 ml), 4-Å molecular sieves (150.5 mg), and Me_3SiOTf (8 µl), 45 (µmol). FC (petroleum ether/AcOEt 2 : 1) afforded **8a** (210.6 mg, 64%) and **7a** (70.0 mg, 21%).

*Data of (*tert*-Butyl)dimethylsilyl 6-*O*-[(*tert*-Butyl)diphenylsilyl]-2-deoxy-2-phthalimido-3-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**7a**): R_f (petroleum ether/AcOEt

1.5 :1): 0.31. ^{1}H-NMR (^{1}H,^{1}H-COSY; 300 MHz, $CDCl_3$): 7.72 – 7.36 (m, 2 Ph, 2 Phth); 5.56 (*dd*, H–C(3^C)); 5.41 (*d*, H–C(1^C)); 5.15 (*d*, H–C(1^E)); 5.06 (*t*, H–C(4^C)); 4.60 (*m*, H–C(3^E)); 4.30 (*dd*, H–C(2^C)); 4.21 – 4.18 (*m*, CH_2(6^C)); 4.03 (*dd*, H–C(2^E)); 4.00 – 3.84 (*m*, H–C(5^C), CH_2(6^E), OH–C(4^E)); 3.61 – 3.50 (*m*, H–C(4^E), H–C(5^E)); 2.02, 1.99, 1.72 (3 *s*, 3 MeCO); 1.04 (*s*, ^{t}*Bu*Ph_2Si); 0.53 (*s*, ^{t}*Bu*Me_2Si); 0.01, −0.20 (2 *s*, 2 Me); *J*(1E,2E) = 8.1, *J*(2E,3E) = 10.6, *J*(3E,4E) = 7.4, *J*(4E,OH) = 1.0, *J*(1C,2C) = 8.4, *J*(2C,3C) = 10.6, *J*(3C,4C) = 9.2, *J*(4C,5C) = 9.2. ^{13}C-NMR (^{13}C,^{1}H-COSY; 75.5 MHz, $CDCl_3$): 170.69, 169.98, 169.45 (3 Me*C*O); 135.78, 135.75, 134.15, 133.70, 133.66, 130.94, 129.64, 127.73, 123.20 (2 Ph, 2 PhthN); 98.37 (C(1^C)); 93.41 (C(1^E)); 82.25 (C(3^E)); 76.92 (C(5^E)); 71.98 (C(5^C)); 70.49 (C(3^C)); 70.10 (C(4^E)); 69.02 (C(4^C)); 63.77 (C(6^E)); 62.21 (C(6^C)); 57.55 (C(2^E)); 54.59 (C(2^C)); 26.92 (*Me*$_3$C (^{t}BuPh$_2$Si)); 25.27 (*Me*$_3$C (^{t}BuMe$_2$Si)); 20.67, 20.67, 20.34 (3 *Me*CO); 19.39 (Me$_3$*C* (^{t}BuPh$_2$Si)); 17.39 (Me$_3$*C* (^{t}BuMe$_2$Si)); −4.03, −5.67 (2 Me). ESI-MS ($C_{56}H_{66}N_2O_{16}Si_2$; 1079.31, 1078.40): 1101.38162 ([*M* + Na]$^+$: calc. 1101.38431).

*Data of (*tert*-Butyl)dimethylsilyl 6*-O-*[(*tert*-butyl)diphenylsilyl]-2-deoxy-2-phthalimido-4*-O-*(3,4,6-tri*-O-*acetyl-2-deoxy-2-phthalimido-β*-D-*glucopyranosyl)-β*-D-*glucopyranoside* (**8a**). R_f (petroleum ether/AcOEt 1.5 :1): 0.40. $[\alpha]_D^{26} = +25$ (*c* = 1.0, $CHCl_3$). ^{1}H-NMR (^{1}H,^{1}H-COSY; 300 MHz, $CDCl_3$): 7.84 – 7.35 (*m*, 2 PhthN, 2 Ph); 5.72 (*dd*, H–C(3^C)); 5.60 (*d*, H–C(1^C)); 5.36 (*d*, H–C(1^E)); 5.06 (*t*, H–C(4^C)); 4.47 (*dd*, H–C(3^E)); 4.29 (*dd*, H–C(2^C)); 4.21 – 4.08 (*m*, H–C(2^E)); CH_2(6^C)); 3.94 – 3.83 (*m*, H–C(4^E), H–C(5^E), H–C(5^C)); 3.68 (*dd*, H_a–C(6^E)); 3.53 – 3.48 (*m*, H_b–C(6^E), OH–C(3)); 2.01, 1.90, 1.80 (3 *s*, 3 MeCO); 0.97 (*s*, ^{t}*Bu*Ph_2Si); 0.62 (*s*, ^{t}*Bu*Me_2Si); −0.09, −0.18 (2 *s*, 2 Me); *J*(1E,2E) = 7.4, *J*(2E,3E) = 9.0, *J*(3E,4E) = 9.2, *J*(5E,6aE) = 4.2, *J*(6aE,6bE) = 13.2, *J*(1C,2C) = 7.4, *J*(2C,3C) = 9.0, *J*(3C,4C) = 10.5, *J*(4C,5C) = 10.5. ^{13}C-NMR (^{13}C,^{1}H-COSY; 75.5 MHz, $CDCl_3$): 170.55, 170.06, 169.55 (3 Me*C*O); 135.79, 135.75, 134.33, 134.13, 133.33, 131.93, 130.95, 129.66, 127.78, 127.73, 123.72 (2 Ph, 2 PhthN); 98.06 (C(1^C)); 93.12 (C(1^E)); 80.54 (C(4^E)); 75.10 (C(5^C)); 72.08 (C(5^E)); 70.62 (C(3^C)); 69.80 (C(3^E)); 69.06 (C(4^C)); 62.94 (C(6^E)); 62.21 (C(6^C)); 58.32 (C(2^E)); 54.84 (C(2^C)); 26.95 (*Me*$_3$C (^{t}BuPh$_2$Si)); 25.38 (*Me*$_3$C (^{t}BuMe$_2$Si)); 20.70, 20.47, 20.43 (3 *Me*CO), 19.56 (Me$_3$*C* (^{t}BuPh$_2$Si)); 17.56 (Me$_3$*C* (^{t}BuMe$_2$Si)); −4.17, −5.66 (2 Me). ESI-MS (from acetone/H_2O/NH_4HCO_2; $C_{56}H_{66}N_2O_{16}Si_2$; 1079.31, 1078.40): 1096.42806 ([*M* + NH_4]$^+$, calc. 1096.42891).

*(*tert*-Butyl)dimethylsilyl 4*-O-*Acetyl-6*-O-*[(*tert*-butyl)diphenylsilyl]-2-deoxy-2-phthalimido-3*-O-*(3,4,6-tri*-O-*acetyl-2-deoxy-2-phthalimido-β*-D-*glucopyranosyl)-β*-D-*glucopyranoside* (**7b**). As described for **6f**, with **7a** (18.0 mg, 17 μmol), Ac_2O (0.20 ml), and pyridine (0.30 ml). FC (petroleum ether/AcOEt 1.5 :1) afforded **7b** (18.0 mg, 96%). R_f (petroleum ether/AcOEt 1.5 :1): 0.38. ^{1}H-NMR (^{1}H,^{1}H-COSY; 300 MHz, $CDCl_3$): 7.86 – 7.30 (*m*, 2 Ph, 2 PhthN); 5.47 (*dd*, H–C(3^C)); 5.21 (*d*, H–C(1^C)); 5.14 (*d*, H–C(1^E)); 5.09 (*t*, H–C(4^C)); 4.92 (*t*, H–C(3^E)); 4.85 (*t*, H–C(4^E)); 4.47 (*dd*, H_a–C(6^C)); 4.13 (*dd*, H–C(2^C)); 4.05 (*d*, H_b–C(6^C)); 4.02 (*dd*, H–C(2^E)); 3.79 – 3.59 (*m*, H–C(5^C), H–C(5^E), CH_2(6^E)); 2.11, 1.95, 1.92, 1.74 (4 *s*, 4 MeCO); 1.03 (*s*, ^{t}*Bu*Ph_2Si); 0.55 (*s*, ^{t}*Bu*Me_2Si); 0.00, −0.17 (2 *s*, 2 Me); *J*(1E,2E) = 8.0, *J*(2E,3E) = 8.6, *J*(3E,4E) = 8.6, *J*(4E,5E) = 8.6, *J*(1C,2C) = 8.4, *J*(2C,3C) = 10.6, *J*(3C,4C) = 9.0, *J*(4C,5C) = 9.0, *J*(5C,6aC) = 3.7, *J*(6aC,6bC) = 12.3. ^{13}C-NMR (75.5 MHz, $CDCl_3$): 170.83, 170.26, 169.60, 169.42 (4 Me*C*O); 135.89 – 123.52, 97.59, 93.58 (C(1^C), C(1^E)); 75.56, 74.93, 71.97, 70.86, 69.99, 68.71 (carbohydrate C); 63.55, 61.90 (C(6^C), C(6^E)); 58.34, 54.83 (C(2^C), C(2^E)); 26.95 (*Me*$_3$ (^{t}BuPh$_2$Si)); 25.39 (*Me*$_3$C (^{t}BuMe$_2$Si)); 20.97, 20.79, 20.78, 20.53 (4 *Me*CO); 19.36 (Me$_3$*C* (^{t}BuPh$_2$Si)); 17.52 (Me$_3$*C* (^{t}BuMe$_2$Si)); −3.97, −5.54 (2 Me). ESI-MS ($C_{58}H_{68}N_2O_{17}Si_2$; 1121.35, 1120.41): 1143.39010 ([*M* + Na]$^+$; calc. 1143.39487).

*(*tert*-Butyl)dimethylsilyl 3*-O-*Acetyl-6*-O-*[(*tert*-butyl)diphenylsilyl]-2-deoxy-2-phthalimido-4*-O-*(3,4,6-tri*-O-*acetyl-2-deoxy-2-phthalimido-β*-D-*glucopyranosyl)-β*-D-*glucopyranoside* (**8b**). As described for **6f**, with **8a** (180.0 mg, 170 μmol), Ac_2O (0.40 ml), and pyridine (0.60 ml). FC (petroleum ether/AcOEt 2 :1) afforded **8b** (180.1 mg, 96%). R_f (petroleum ether/AcOEt 1.5 :1): 0.40. $[\alpha]_D^{26} = +4$ (*c* = 1.0, $CHCl_3$). ^{1}H-NMR (^{1}H,^{1}H-COSY; 300 MHz, $CDCl_3$): 7.81 – 7.43 (*m*, 2 PhthN, 2 Ph); 5.77 (*dd*, H–C(3^E)); 5.69 (*dd*, H–C(3^C)), 5.56 (*d*, H–C(1^C)); 5.45 (*d*, H–C(1^E)); 5.09 (*t*, H–C(4^C)); 4.38 – 4.30 (*m*, H_a–C(6^C), H–C(4^E)); 4.18 (*dd*, H–C(2^C)); 4.16 (*dd*, H–C(2^E)); 4.06 (*dd*, H_b–C(6^C)); 3.86 (br. *d*, H_a–C(6^E)); 3.76 (*dd*, H_b–C(6^E)); 3.66 – 3.62 (*m*, H–C(5^C)); 3.49 (*dd*, H–C(5^E)); 2.07, 2.00, 1.95, 1.82 (4 *s*, 4 MeCO); 1.11 (*s*, ^{t}*Bu*Ph_2Si); 0.62 (*s*, ^{t}*Bu*Me_2Si); −0.08, −0.20 (2 *s*, 2 Me); *J*(1E,2E) = 7.8, *J*(2E,3E) = 9.0, *J*(3E,4E) = 10.5, *J*(5E,6bE) = 3.0, *J*(6aE,6bE) = 12.0, *J*(1C,2C) = 8.1, *J*(2C,3C) = 9.0, *J*(3C,4C) = 10.5, *J*(4C,5C) = 10.5, *J*(5C,6bC) = 0.8, *J*(6aC,6bC) = 12.0. ^{13}C-NMR (^{13}C,^{1}H-COSY; 75.5 MHz, $CDCl_3$): 170.72, 170.25, 170.21, 169.60 (4 Me*C*O); 136.18, 135.95, 134.38, 133.98, 133.29, 131.47, 129.85, 129.80, 127.85, 127.79, 123.74, 123.74, 123.48 (2 Ph, 2 PhthN); 95.88 (C(1^C)); 92.98 (C(1^E)); 75.46 (C(5^C)); 73.09 (C(4^E)); 71.89 (C(5^E)); 70.89 (C(3^C)); 70.29 (C(3^E)); 68.87 (C(4^C)); 62.84 (C(6^E)); 61.84 (C(6^C)); 57.50 (C(2^E)); 55.08 (C(2^C)); 27.12 (*Me*$_3$C (^{t}BuPh$_2$Si)); 25.39 (*Me*$_3$C (^{t}BuMe$_2$Si)); 20.81, 20.81, 20.77, 20.57 (4 *Me*CO); 19.79 (Me$_3$*C* (^{t}BuPh$_2$Si)); 17.59 (Me$_3$*C* (^{t}BuMe$_2$Si)); −4.21, −5.58 (2 Me). ESI-MS ($C_{58}H_{68}N_2O_{17}Si_2$; 1221.35, 1220.41): 1243.39269 ([*M* + Na]$^+$; calc. 1243.39487).

3-O-*Acetyl-6*-O-*[(*tert-*butyl)diphenylsilyl]-2-deoxy-2-phthalimido-4*-O-*(3,4,6-tri*-O-*acetyl-2-deoxy-2-phthalimido-β*-D-*glucopyranosyl)-β*-D-*glucopyranose* (**8c**). To a soln. of **8b** (150.0 mg, 0.14 mmol) in dry THF (3.0 ml), 1M Bu_4NF in THF (0.14 ml, 0.14 mmol) was added at −20°. The mixture was stirred at −20° for 5 min, then diluted with CH_2Cl_2, and washed with 5% NaCl soln. The org. phase was dried (Na_2SO_4) and evaporated. Purification by FC (petroleum ether/AcOEt 1.5:1) afforded **8c** (105.1 mg, 78%). R_f (petroleum ether/AcOEt 2:1): 0.16. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.88–7.74, 7.52–7.42 (2 *m*, 2 Phth, 2 Ph); 5.80 (*dd*, H−C(3^E)); 5.75 (*dd*, H−C(3^C)); 5.63 (*d*, H−C(1^C)); 5.37–5.33 (*m*, H−C(1^E); OH−C(1^E)); 5.17 (*dd*, H−C(4^C)); 4.47 (*dd*, H_a−C(6^C)); 4.26 (*dd*, H−C(2^C)); 4.25 (*t*, H−C(4^E)); 4.12 (br. *d*, H_b−C(6^C)); 4.05 (*dd*, H−C(2^E)); 3.85–3.79 (*m*, H−C(5^C), H_a−C(6^E)); 3.71 (*dd*, H_b−C(6^E)); 3.48–3.44 (*m*, H−C(5^E)); 2.12, 2.05, 1.99, 1.88 (4 *s*, 4 MeCO); 1.14 (*s*, Me_3C); *J*(1E,2E) = 8.4, *J*(2E,3E) = 9.3, *J*(3E,4E) = 10.2, *J*(4E,5E) = 10.2, *J*(5E,6bE) = 2.4, *J*(6aE,6bE) = 12.0, *J*(1C,2C) = 7.4, *J*(2C,3C) = 9.3, *J*(3C,4C) = 10.2, *J*(4C,5C) = 9.0, *J*(5C,6aC) = 4.5, *J*(6aC,6bC) = 12.0. ^{13}C-NMR (^{13}C,^{1}H-COSY; 75.5 MHz, $CDCl_3$): 170.68, 170.22, 170.10, 169.57 (4 Me*C*O); 136.38, 136.07, 134.45, 134.28, 133.93, 133.45, 131.64, 131.44, 129.81, 127.73, 127.61, 123.76, 123.62 (2 Ph, 2 PhthN); 96.59, 92.08 (C(1^C), C(1^E)); 75.40, 73.45, 71.92, 70.88, 70.45, 68.81 (carbohydrate C); 62.52, 61.83 (C(6^E), C(6^C)); 56.76, 55.11 (C(2^E), C(2^C)); 27.16 (*Me*$_3$C); 20.80, 20.71, 20.71, 20.51 (4 *Me*$_3$CO); 19.59 (Me$_3$*C*). ESI-MS ($C_{52}H_{54}N_2O_{17}Si$; 1007.09, 1006.32): 1029.31075 ([*M* + Na]$^+$; calc. 1029.30845).

3-O-*Acetyl-6*-O-*[(*tert-*butyl)diphenylsilyl]-2-deoxy-2-phthalimido-4*-O-*(3,4,6-tri*-O-*acetyl-2-deoxy-2-phthalimido-β*-D-*glucopyranosyl)-β*-D-*glucopyranosyl Trichloroacetimidate* (**8d**). To a soln. of **8c** (500.0 mg, 0.50 mmol) in dry CH_2Cl_2 (15 ml), trichloroacetonitrile (0.50 ml, 5.0 mmol) and K_2CO_3 (400.0 mg, 2.9 mmol) were added. The mixture was stirred at 20° overnight. The mixture was filtered, and the filter cake was washed with CH_2Cl_2. The combined filtrate and washings were evaporated. Purification by FC (petroleum ether/AcOEt 2:1) afforded **8d** (510.1 mg, 86%). R_f (petroleum ether/AcOEt 1:1): 0.58. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.49 (br. *s*, C=NH); 7.84–7.25 (*m*, 2 Phth, 2 Ph); 6.53 (*d*, H−C(1^E)); 5.81, 5.78 (2 *t*, H−C(3^E), H−C(3^C)); 5.62 (*d*, H−C(1^C)); 5.13 (*t*, H−C(4^C)); 4.49 (*dd*, H−C(2^E)); 4.47–4.41 (*m*, H−C(4^E), H_a−C(6^C)), 4.23 (*dd*, H−C(2^C)); 4.07 (*dd*, H_b−C(6^C)); 3.88 (br. *d*, H_a−C(6^E)); 3.80–3.70 (*m*, H−C(5^C), H_b−C(6^E)); 3.62–3.58 (*m*, H−C(5^E)); 2.10, 2.01, 1.99, 1.843 (4 s, 4 MeCO); 1.10 (*s*, Me_3C); *J*(1E,2E) = 9.0, *J*(2E,3E) = 10.8, *J*(3E,4E) = 10.8, *J*(5E,6aE) = 11.2, *J*(1C,2C) = 8.1, *J*(2C,3C) = 9.8, *J*(3C,4C) = 9.8, *J*(4C,5C) = 9.8, *J*(5C,6bC) = 1.5, *J*(6aC,6bC) = 12.0. ^{13}C-NMR (75.5 MHz, $CDCl_3$): 170.84, 170.34, 170.28, 169.73 (4 Me*C*O); 160.63 (C=NH)); 136.39, 136.14, 134.57, 133.97, 133.15, 131.54, 129.97, 129.91, 127.96, 127.79, 123.92, 123.90 (2 Ph, 2 PhthN); 96.58, 93.47 (C(1^E), C(1^C)); 90.65 (CCl_3); 76.15, 72.69, 72.13, 70.91, 70.60 (carbohydrate C); 62.15, 62.01 (C(6^E), C(6^C)); 55.18, 54.31 (C(2^E), C(2^C)); 27.15 (*Me*$_3$C); 20.93, 20.86, 20.81, 20.66 (4 *Me*CO); 19.88 (Me$_3$*C*). ESI-MS ($C_{54}H_{54}Cl_3N_3O_{17}Si$; 1151.48, 1149.23): 1172.22233 ([*M* + Na]$^+$; calc. 1172.21803).

Prop-2-enyl O-*3,4,6-Tri*-O-*acetyl-2-deoxy-2-phthalimido-β*-D-*glucopyranosyl-(1 → 4)*-O-*3*-O-*acetyl-6*-O-*[(*tert-*butyl)diphenylsilyl]-2-deoxy-2-phthalimido-β*-D-*glucopyranosyl]-(1 → 2)-3*-O-*(phenoxycarbonyl)-5*-O-*prop-2-enyl-α*-D-*glucofuranosiduronamide* (**10a**). As described for **7a** (*a*)), with **8d** (230.0 mg, 0.20 mmol), **9** (100.0 mg, 0.25 mmol), dry CH_2Cl_2/Et_2O 1:5 (6.0 ml) 4-Å molecular sieves (250.4 mg; 1 h), and 1M Me_3SiOTf in CH_2Cl_2 (40 µl, 40 µmmol; 4 h). FC (petroleum ether/AcOEt 1:1) afforded **10a** (50.0 mg, 18%). R_f (petroleum ether/AcOEt 1:2): 0.38. ^{1}H-NMR (^{1}H,^{1}H-COSY; 400 MHz, $CDCl_3$): 7.73–7.29 (*m*, 2 Phth, 3 Ph); 6.36 (br. *s*, 1 H, NH_2); 5.76–5.57 (*m*, 2 CH_2=C*H*CH$_2$); 5.65 (*t*, H−C(3^E)); 5.59 (*t*, H−C(3^C)); 5.52 (*d*, H−C(1^E)); 5.51 (*d*, H−C(1^C)); 5.29 (*t*, H−C(3^F)); 5.23 (br. *s*, 1 H, NH_2); 5.16–4.97 (*m*, 2 C*H*$_2$=CH$_2$), 5.04 (*t*, H−C(4^C)); 4.84 (*d*, H−C(1^F)); 4.50 (*dd*, H−C(4^F)); 4.36 (*dd*, H−C(2^F)); 4.34 (*dd*, H_a−C(6^C)); 4.27 (*t*, H−C(4^E)); 4.15 (*dd*, H−C(2^E)); 4.12 (*dd*, H−C(2^C)); 4.05–3.86 (*m*, 2 CH_2=CHC*H*$_2$, H_b−C(6^C)); 3.90 (*d*, H−C(5^F)); 3.80 (br. *d*, H_a−C(6^E)), 3.70 (*dd*, H_b−C(6^E)), 3.66–3.63 (*m*, H−C(5^C)); 3.45–3.42 (*m*, H−C(5^E)); 2.01, 1.93, 1.86, 1.76 (4 *s*, 4 MeCO); 1.05 (*s*, Me_3C); *J*(1F,2F) = 4.4, *J*(2F,3F) = 7.5, *J*(3F,4F) = 7.5, *J*(4F,5F) = 4.4, *J*(1E,2E) = 8.2, *J*(2E,3E) = 10.2, *J*(3E,4E) = 10.2, *J*(4E,5E) = 10.2, *J*(5E,6bE) = 1.8, *J*(6aE,6bE) = 12.0, *J*(1C,2C) = 8.2, *J*(2C,3C) = 10.2, *J*(3C,4C) = 10.2, *J*(4C,5C) = 10.2, *J*(5C,6aC) = 4.2, *J*(6aC,6bC) = 12.3. ^{13}C-NMR (75.5 MHz, $CDCl_3$): 172.28, 170.86, 170.39, 170.38, 169.73 (4 Me*C*O, $CONH_2$); 152.67, 151.44, 136.28–121.73 (arom. C); 118.74, 117.02 (2 *C*H$_2$=CHCH$_2$); 99.31, 97.40, 96.25 (glycosidic C); 79.69, 79.25, 79.07, 76.03, 75.59, 73.65, 72.97, 72.05, 70.94, 70.90, 68.92, 68.90 (carbohydrate C); 62.60, 1.90 (C(6^C), C(6^E)); 55.23 (C(2^C), C(2^E)); 27.21 (*Me*$_3$C); 20.95, 20.88, 20.85, 20.67 (4 *Me*CO); 19.90 (Me$_3$*C*). ESI-MS ($C_{71}H_{75}N_3O_{24}Si$; 1382.47, 1381.45): 1382.46293 ([*M* + Na]$^+$; calc.1382.45878).

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-*acetyl-5*-O-*prop-2-enyl-α*-D-*glucofuranosiduronamide* (**10b**). To a soln. of **10a** (30.0 mg, 22 µmol) in BuOH (8.0 ml) ethane-1,2-diamine (1.5 ml) was added. The soln. was stirred at 90° for 12 h. After evaporation, the residue was dissolved in pyridine (4.0 ml) and Ac_2O (2.0 ml). The mixture was stirred at 20° overnight. Evaporation and purification by FC

($CHCl_3$/MeOH 9:1) afforded **10b** (12.1 mg, 48%). R_f (CH_2Cl_2/MeOH 9:1): 0.45. ^{1}H-NMR (300 MHz, $CDCl_3$; signals that could be assigned): 7.81–7.74 (*m*, 10 arom H); 5.95–5.81 (*m*, 2 CH_2=C*H*CH_2); 2.10, 2.07, 2.07, 2.06, 2.04, 2.03, 2.02 (7*s*, 7 MeCO); 1.16 (*s*, Me_3C). ESI-MS ($C_{54}H_{73}N_3O_{21}Si$; 1128.27, 1127.45): 1128.45999 ($[M+H]^+$; calc. 1128.45786), 1150.44112 ($[M+Na]^+$; calc. 1150.43980).

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-*acetyl-5*-O-*prop-2-enyl-α*-D-*glucofuranosiduronamide* (**10c**). To a soln. of **10b** (12.0 mg, 11 μmol) in dry THF (1.0 ml), 1M Bu_4NF in THF (11 μl) was added. The mixture was stirred at 20° for 30 min and then evaporated. Purification by FC ($CHCl_3$/MeOH 5:1) afforded **10c** (6.0 mg, 61%). R_f (CH_2Cl_2/MeOH 6:1): 0.36. ^{1}H-NMR (200 MHz, (D_5)pyridine; signals that could be assigned): 9.29, 9.20 (2 *d*, 2 N*H*Ac); 2.17, 2.17, 2.10, 2.10, 2.00, 1.96, 1.96 (7 *s*, 7 MeCO); *J*(2,NH) = 7.6. ESI-MS ($C_{38}H_{55}Cl_3N_3O_{21}$; 889.86, 889.33): 890.34135 ($[M+H]^+$; calc. 890.34008).

Prop-2-enyl O-*3,4,6-Tri*-O-*acetyl-2-(acetylamino)-2-deoxy-β*-D-*glucopyranosyl-(1 → 4)*-O-*3,6-di*-O-*acetyl-2-(acetylamino)-2-deoxy-β*-D-*glucopyranosyl-(1 → 2)-3*-O-*acetyl-5*-O-*prop-2-enyl-α*-D-*glucofuranosiduronamide* (**10d**). As described for **6f**, with **10c** (6.0 mg, 6.7 μmol), Ac_2O (0.40 ml), and pyridine (0.60 ml). FC ($CHCl_3$/MeOH 5:1) afforded **10d** (5.1 mg, 77%). R_f (CH_2Cl_2/MeOH 9:1): 0.38. ^{1}H-NMR (200 MHz, CD_3OD; signals that could be assigned): 5.98–5.75 (*m*, 2 CH_2=C*H*CH_2); 2.03, 1.99, 1.98, 1.92, 1.91, 1.90, 1.84, 1.82 (8 *s*, 8 MeCO). ESI-MS ($C_{40}H_{57}N_3O_{22}$ (931.90, 931.34): 932.35186 ($[M+H]^+$; calc 932.35065).

Prop-2-enyl O-*3,4,6-Tri*-O-*acetyl-2-deoxy-2-phthalimido-β*-D-*glucopyranosyl-(1 → 4)*-O-*6*-O-*[(*tert-*butyl)diphenylsilyl]-2-deoxy-2-phthalimido-β*-D-*glucopyranosyl-(1 → 2)-3*-O-*(aminocarbonyl)-5*-O-*prop-2-enyl-α*-D-*glucofuranosiduronamide* (**10e**). A soln. of **10a** (30.0 mg, 22 μmol) in dry pyridine/dioxane 2:1 (3.0 ml) was cooled to 0°. Gaseous ammonia was bubbled until the starting material disappeared (TLC (petroleum ether/AcOEt 1:2)). Evaporation and purification by FC ($CHCl_3$/MeOH 120:1) afforded **10e** (12.1 mg, 42%). R_f (petroleum ether/AcOEt 1:2): 0.21. ^{1}H-NMR (^{1}H,^{1}H-COSY; 600 MHz, $CDCl_3$): 7.78–7.33 (*m*, 2 Phth, 2 Ph); 6.28 (br. *s*, 1 H, NH_2); 5.70–5.60 (*m*, 2 CH_2=C*H*CH_2); 5.68 (*t*, H–C(3^E)); 5.63 (*t*, H–C(3^C)); 5.50 (*d*, H–C(1^C)); 5.40 (*d*, H–C(1^E)); 5.12–5.06 (*m*, CH_2=CHCH_2, H–C(3^F)); 5.05 (*t*, H–C(4^C)); 5.00–4.93 (*m*, CH_2=CHCH_2); 4.79 (*d*, H–C(1^F)); 4.43 (*dd*, H–C(4^F)); 4.30 (*dd*, H_a–C(6^C)); 4.26 (*dd*, H–C(2^F)); 4.23 (*t*, H–C(4^E)); 4.16 (*dd*, H–C(2^E)); 4.12 (*dd*, H–C(2^C)); 4.04 (br. *d*, H_b–C(6^C)); 3.95–3.79 (*m*, 2 CH_2=CHCH_2, H_a–C(6^E)); 3.76 (*d*, H–C(5^F)); 3.69 (*dd*, H_b–C(6^E)); 3.65–3.63 (*m*, H–C(5^C)); 3.44–3.41 (*m*, H–C(5^E)); 1.99, 1.94, 1.89, 1.76 (4 *s*, 4 MeCO); 1.03 (*s*, Me_3C); *J*(1F,2F) = 4.2, *J*(2F,3F) = 8.4, *J*(3F,4F) = 7.8, *J*(4F,5F) = 3.1, *J*(1E,2E) = 8.4, *J*(2E,3E) = 9.3, *J*(3E,4E) = 9.3, *J*(4E,5E) = 9.3, *J*(5E,6bE) = 3.7, *J*(6aE, 6bE) = 12.0, *J*(1C,2C) = 8.4, *J*(2C,3C) = 9.8, *J*(3C,4C) = 9.8, *J*(4C,5C) = 9.8, *J*(5C,6aC) = 4.8, *J*(6aC,6bC) = 12.5.

5-O-*Prop-2-enyl*-D-*glucofuranosidurono-6,3-lactone* (*α*/*β*-D-anomers 1:4; **12a**). A mixture of **11** (800.0 mg, 3.13 mmol) and 90% CF_3COOH/H_2O (5.0 ml) was stirred at 20° for 40 min. After evaporation, the residue was purified by FC ($CHCl_3$/MeOH 5:1): **12a** (620.4 mg, 92%). R_f (AcOEt): 0.10. M.p. 120.8–121.3° (CH_2Cl_2/MeOH). $[\alpha]_D^{26} = +33$ (*c* = 1.0, MeOH). ^{1}H-NMR (^{1}H,^{1}H-COSY; 300 MHz, (D_5)pyridine; *β*-D-anomer): 6.07 (*s*, H–C(1)); 6.13–5.94 (*m*, C*H*=CH_2CH_2); 5.44–5.14 (*m*, CH=CH_2CH_2, H–C(3), H–C(4)); 4.90 (*s*, H–C(2)); 4.76–4.40 (*m*, H–C(5), CH=CH_2CH_2). ^{13}C-NMR (^{13}C,^{1}H-COSY; 50 MHz, (D_5)pyridine); *β*-D-anomer: 173.83 (CO); 135.01 (*C*H=CH_2CH_2); 117.87 (CH=*C*H_2CH_2); 105.63 (C(1)); 85.37 (C(3)); 79.08 (C(2)); 77.29 (C(4)); 76.45 (C(5)); 71.91 (CH=CH_2*C*H_2); *α*-D-anomer: 173.83 (CO); 134.76 (*C*H=CH_2CH_2); 117.87 (CH=*C*H_2CH_2); 100.03 (C(1)); 85.91 (C(3)); 76.60 (C(2)); 75.61 (C(4)); 75.47 (C(5)); 71.91 (CH=CH_2*C*H_2). ESI-MS ($C_9H_{12}O_6$; 216.19, 216.06),: 238.8 ($[M+Na]^+$).

Prop-2-enyl 5-O-*Prop-2-enyl-β*-D-*glucofuranosidurono-6,3-lactone* (**12b**). To a soln. of **12a** (1.00 g, 4.63 mmol) in prop-2-en-1-ol (20 ml), camphorsulfonic acid (1.00 g, 4.30 mmol) was added. The mixture was stirred at 20° for 2.5 h (TLC (petroleum ether/AcOEt 1:2) monitoring). The reaction was stopped by adding pyridine (10 ml). The solvents were removed by azeotropic evaporation with toluene. The residue was diluted with $CHCl_3$, the soln. washed with aq. $NaHCO_3$ soln. and then with H_2O, dried (Na_2SO_4), and evaporated, and the residue purified by FC (petroleum ether/AcOEt 1:1): **12b** (580.1 mg, 49%). R_f (petroleum ether/AcOEt 1:1.5): 0.33. M.p. 64.7–65.3° (petroleum ether/AcOEt). $[\alpha]_D^{26} = -9$ (*c* = 1.0, $CHCl_3$). ^{1}H-NMR (^{1}H,^{1}H-COSY; 300 MHz, $CDCl_3$): 6.08–5.81 (*m*, 2 C*H*=CH_2CH_2); 5.45–5.18 (*m*, 2 CH=CH_2CH_2); 5.15 (*s*, H–C(1)); 5.05 (*dd*, H–C(4)); 4.90 (*d*, H–C(3)); 4.45 (*s*, H–C(2)); 4.38–4.29, 3.99–3.92 (2 *m*, 2 CH=CH_2*C*H_2); 4.23 (*d*, H–C(5)); *J*(3,4) = 5.1, *J*(4,5) = 6.6. ^{13}C-NMR (^{13}C,^{1}H-COSY; 75.5 MHz, $CDCl_3$): 173.58 (CO); 133.72, 133.63 (2 *C*H=CH_2CH_2); 119.33, 118.33 (2 CH=*C*H_2CH_2); 107.44 (C(1)); 83.78 (C(3)); 77.75 (C(2)); 76.25 (C(4)); 74.30 (C(5)); 71.95, 68.78 (2 CH=CH_2*C*H_2). ESI-MS ($C_{12}H_{16}O_6$; 256.26, 256.09): 278.9 ($[M+Na]^+$).

Prop-2-enyl O-*3,4,6-Tri*-O-*acetyl-2-deoxy-2-phthalimido-β*-D-*glucopyranosyl-(1 → 4)*-O-*3*-O-*acetyl-6*-O-*[(*tert-*butyl)diphenylsilyl]-2-deoxy-2-phthalimido-β*-D-*glucopyranosyl]-(1 → 2)-5*-O-*prop-2-enyl-β*-D-*glucofuranosidurono-6,3-lactone* (**13**). As described for **8a** (*b*)), with **8d** (200.0 mg, 0.17 mmol), **12b** (80.0 mg, 0.31 mmol),

dry Et_2O (5.0 ml), 4-Å molecular sieves (200.4 mg; 1 h), and Me_3SiOTf (6.0 µl; 3 h). **13** (96.2 mg, 42%). R_f (petroleum ether/AcOEt 1:2): 0.30. ^{1}H-NMR (^{1}H,^{1}H-COSY; 400 MHz, $CDCl_3$): 7.87–7.32 (*m*, 2 Phth, 2 Ph); 6.00–5.81, 5.83–5.71 (2 *m*, 2 CH_2=C*H*CH_2); 5.80 (*dd*, H–C(3^C)); 5.64 (*d*, H–C(1^C)); 5.61 (*dd*, H–C(3^E)); 5.52 (*d*, H–C(1^E)); 5.34–5.09 (*m*, 2 CH_2=CHCH_2); 5.16 (*t*, H–C(4^C)); 5.09 (*s*, H–C(1^F)); 4.62 (*d*, H–C(3^F)); 4.56 (*dd*, H–C(4^F)); 4.46 (*dd*, H_a–C(6^C)); 4.45 (*t*, H–C(4^E)); 4.31 (*s*, H–C(2^F)); 4.27–4.18 (*m*, 2 CH_2=CHCH_2, H–C(2^E), H–C(2^C)); 4.12 (*dd*, H_b–C(6^C)); 3.99 (*d*, H–C(5^F)); 3.87 (br. *d*, H_a–C(6^E)); 3.80–3.72 (*m*, H–C(5^C); H_b–C(6^E)); 3.48–3.45 (*m*, H–C(5^E)); 2.12, 2.05, 2.00, 1.88 (4 *s*, 4 MeCO); 1.17 (*s*, Me_3C); *J*(3F,4F) = 4.9, *J*(4F,5F) = 6.6, *J*(1E,2E) = 8.3, *J*(2E,3E) = 9.6, *J*(3E,4E) = 9.6, *J*(4E,5E) = 9.6, *J*(6aE,6bE) = 11.6, *J*(1C,2C) = 8.4, *J*(2C,3C) = 10.7, *J*(3C,4C) = 9.1, *J*(4C,5C) = 9.1, *J*(5C,6aC) = 5.0, *J*(5C,6bC) = 1.5, *J*(6aC,6bC) = 12.6. ^{13}C-NMR (75.5 MHz, $CDCl_3$): 172.24, 170.74, 170.40, 170.29, 169.71 (4 Me*C*O, CO); 136.22–123.91 (arom. C); 118.88, 117.86 (2 *C*H_2=CHCH_2); 105.97 (C(1^F)); 96.50, 96.45 (C(1^C), C(1^E)),; 82.99, 80.70, 76.19, 75.90, 74.01, 72.58, 72.06, 71.75, 70.94, 70.84, 68.91, 68.63 (carbohydrate C); 62.24, 61.90 (C(6^C), C(6^E)); 55.17 (C(2^C), C(2^E)); 27.21 (*Me*$_3$C); 20.89, 20.84, 20.75, 20.63 (4 *Me*CO); 19.79 (Me_3*C*). ESI-MS ($C_{64}H_{68}N_2O_{22}Si$; 1245.33, 1244.40): 1245.41563 ([*M* + H]$^+$; calc. 1245.41057), 1262.44215 ([*M* + NH_4]$^+$; calc. 1262.43712), 1267.39607, ([*M* + Na]$^+$; calc. 1267.39252).

Prop-2-enyl O-*3,4,6-Tri*-O-*acetyl*-*2-deoxy*-*2*-*phthalimido*-*β*-D-*glucopyranosyl*-(*1* → *4*)-O-*3*-O-*acetyl*-*6*-O-*[(*tert-*butyl)diphenylsilyl]*-*2-deoxy*-*2*-*phthalimido*-*β*-D-*glucopyranosyl*-(*1* → *2*)-*5*-O-*prop*-*2*-*enyl*-*β*-D-*glucofuranosiduronamide* (**14a**). At 0° **13** (100.0 mg, 0.079 mmol) was added to a sat. ammonia soln. in THF/MeOH 10:1 (10 ml). The mixture was stirred at 0° for 1.5 h. The ammonia was removed with a stream of N_2 at 0°. Evaporation and purification by FC ($CHCl_3$/MeOH 20:1) furnished **14a** (45.0 mg, 43%). R_f (petroleum ether/AcOEt 1:2): 0.23. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.89–7.43 (*m*, 2 Phth, 2 Ph); 6.55 (br. *s*, 1 H, NH_2); 5.89–5.71 (*m*, 2 CH_2=C*H*CH_2); 5.80 (*t*, H–C(3^C)); 5.66 (*t*, H–C(3^E)); 5.65 (*d*, H–C(1^C)); 5.48 (*d*, H–C(1^E)); 5.40 (br. *s*, 1 H, NH_2); 5.25–5.10 (*m*, 2 CH_2=CHCH_2, H–C(4^C)); 4.98 (*s*, H–C(1^F)); 4.50–4.40 (*m*, H–C(4^E), H_a–C(6^C)); 4.28–3.78 (*m*, 2 CH_2=CHCH_2, H–C(2^E), H–C(2^C), H–C(2^F), H–C(3^F), H–C(4^F), H–C(5^C), H–C(5^F), CH_2(6^E), H_b–C(6^C)); 3.47–3.42 (*m*, H–C(5^E)); 2.12, 2.05, 2.00, 1.88 (4 *s*, 4 MeCO); 1.17 (*s*, Me_3C); *J*(1E,2E) = 8.3, *J*(2E,3E) = 9.6, *J*(3E,4E) = 9.6, *J*(1C,2C) = 8.4, *J*(2C,3C) = 9.1, *J*(3C,4C) = 9.1. ESI-MS ($C_{64}H_{71}N_3O_{22}Si$; 1262.36, 1261.43); 1262.43483 ([*M* + H]$^+$; calc. 1262.43775).

Prop-2-enyl O-*3,4,6-Tri*-O-*acetyl*-*2-deoxy*-*2*-*phthalimido*-*β*-D-*glucopyranosyl*-(*1* → *4*)-O-*3*-O-*acetyl*-*6*-O-*[(*tert-*butyl)diphenylsilyl]*-*2-deoxy*-*2*-*phthalimido*-*β*-D-*glucopyranosyl*-(*1* → *2*)-*5*-O-*prop*-*2*-*enyl*-*3*-O-*[(*tert-*butyl)dimethylsilyl]*-*β*-D-*glucofuranosiduronamide* (**14b**). To a soln. of **14a** (100.0 mg, 0.078 mmol) in dry pyridine (1.0 ml), ^{t}BuMe$_2$SiCl (80.1 mg, 0.53 mmol) and DMAP (5.0 mg) were added. The mixture was stirred at 20° overnight. Evaporation and purification by FC (petroleum ether/AcOEt 1:1) afforded **14b** (80.1 mg, 74%). R_f (petroleum ether/AcOEt 1:1.5): 0.25. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.88–7.43 (*m*, 2 Phth, 2 Ph); 6.29 (br. *s*, NH); 5.83–5.71 (*m*, 2 CH_2=C*H*CH_2); 5.80 (*dd*, H–C(3^C)); 5.65 (*t*, H–C(3^E)); 5.64 (*d*, H–C(1^C)); 5.48 (*d*, H–C(1^E)); 5.25–5.07 (*m*, 2 CH_2=CHCH_2, H–C(4^C)); 4.95 (*s*, H–C(1^F)); 4.48 (*dd*, H_a–C(6^C)); 4.44 (*t*, H–C(4^E)); 4.28–3.73 (*m*, 2 CH_2=CHCH_2, H–C(2^C), H–C(2^E), H–C(2^F), H–C(3^F), H–C(4^F), H–C(5^C), H–C(5^F), CH_2(6^E), H_b–C(6^C)); 3.43–3-41 (*m*, H–C(5^E)); 2.12, 2.05, 2.00, 1.87 (4 *s*, 4 MeCO); 1.16 (*s*, Me_3C (^{t}BuPh$_2$Si), 0.92 (*s*, Me_3C (^{t}BuMe$_2$Si); 0.25, 0.24 (2 *s*, 2 Me); *J*(1E,2E) = 8.4, *J*(2E,3E) = 9.3, *J*(3E,4E) = 9.3, *J*(4E,5E) = 9.3, *J*(1C,2C) = 8.4, *J*(2C,3C) = 10.5, *J*(3C,4C) = 9.3, *J*(5C,6aC) = 1.9, *J*(6aC,6bC) = 11.9. ESI-MS ($C_{70}H_{85}N_3O_{22}Si_2$; 1376.62, 1375.52): 1376.52107 ([*M* + H]$^+$; calc. 1376.52423).

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-*acetyl*-*5*-O-*prop*-*2*-*enyl*-*β*-D-*glucofuranosiduronamide* (**14c**). As described for **10b**, with **14b** (80.0 mg, 0.058 mmol), BuOH (2.0 ml), ethane-1,2-diamine (0.50 ml), pyridine (0.50 ml), and Ac_2O (0.30 ml). FC (AcOEt) afforded **14c** (36.1 mg, 51%). R_f (CH_2Cl_2/MeOH 10:1): 0.68. ^{1}H-NMR (300 MHz, $CDCl_3$; signals that could be assigned): 7.82–7.47 (*m*, 2 Ph); 2.11, 2.07, 2.04 (3 *s*, 7 MeCO); 1.15 (*s*, Me_3C (^{t}BuPh$_2$Si)). ESI-MS ($C_{54}H_{73}N_3O_{21}Si$; 1128.27, 1127.45), 1128.46179 ([*M* + H]$^+$; calc. 1128.45786), 1150.44419 ([*M* + Na]$^+$; calc. 1150.43980).

REFERENCES

[1] J. van Heijenoort, *Glycobiology* **2001**, *11*, 25R.

[2] M. Terrak, T. K. Ghosh, J. van Heijenoort, J. van Beemen, M. Lampilas, J. Aszodi, J. A. Ayala, J.-M. Ghuysen, M. Nguyen-Destèche, *Mol. Microbiol.* **1999**, *34*, 350, and ref. cit. therein; A. M. Di Guilmi, A. Dessen, O. Diedeberg, T. Vernet, *J. Bacteriol.* **2003**, *185*, 1650; B. Schwartz, J. A. Markwalder, S. P. Seitz, Y. Wang, R. L. Stein, *Biochemistry*, **2002**, *41*, 12552.

[3] N. El-Abadla, M. Lampilas, L. Hennig, M. Findeisen, P. Welzel, D. Müller, A. Markus, J. van Heijenoort, *Tetrahedron* **1999**, *55*, 699, and ref. cit. therein.
[4] K. Stembera, S. Vogel, A. Buchynskyy, J. A. Ayala, P. Welzel, *ChemBioChem* **2002**, *3*, 559.
[5] A. Anikin, A. Buchynskyy, U. Kempin, K. Stembera, P. Welzel, G. Lantzsch, *Angew. Chem.* **1999**, *111*, 3931; *Angew. Chem., Int. Ed.* **1999**, *38*, 3703.
[6] O. Ritzeler, L. Hennig, M. Findeisen, P. Welzel, D. Müller, A. Markus, G. Lemoine, M. Lampilas, J. van Heijenoort, *Tetrahedron* **1997**, *53*, 1675.
[7] M. Mayer, B. Meyer, *J. Am. Chem. Soc.* **2001**, *123*, 6108, and ref. cit. therein.
[8] M. Vogtherr, T. Peters, *J. Am. Chem. Soc.* **2000**, *122*, 6093.
[9] T. Rühl, M. Daghish, A. Buchynskyy, K. Barche, D. Volke, K. Stembera, U. Kempin, D. Knoll, L. Hennig, M. Findeisen, R. Oehme, S. Giesa, J. Ayala, P. Welzel, *Bioorg. Med. Chem.* **2003**, *11*, 2965.
[10] L. Chen, D. Walker, B. Sun, S. Walker, D. Kahne, *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 5658.
[11] A. A. Branstrom, S. Midha, R. C. Goldman, *FEMS Microbiol. Lett*. **2000**, *191*, 187.
[12] R. A. Copeland, 'Enzymes', VCH Publishers, Inc., New York, 1996, p. 225
[13] K. Stembera, A. Buchynskyy, S. Vogel, D. Knoll, A. A. Osman, J. A. Ayala, P. Welzel, *ChemBioChem* **2002**, *3*, 332.
[14] S. Vogel, A. Buchynskyy, K. Stembera, K. Richter, L. Hennig, D. Müller, P. Welzel, F. Maquin, C. Bonhomme, M. Lampilas, *Bioorg. Med. Chem. Lett.* **2000**, *10*, 1963, and ref. cit. therein
[15] A. Buchynskyy, K. Stembera, D. Knoll, S. Vogel, U. Kempin, A. Biallass (née Donnerstag), L. Hennig, M. Findeisen, D. Müller, P. Welzel, *Tetrahedron* **2002**, *58*, 7741, and ref. cit. therein.
[16] J. Lüning, U. Möller, D. Müller, P. Welzel, A. Markus, Y. van Heijenoort, J. van Heijenoort, *Tetrahedron* **1993**, *49*, 10587.
[17] G. Range, R. Krähmer, P. Welzel, D. Müller, G. F. Herrmann, U. Kragl, A. Markus, C. Wandrey, Y. van Heijenoort, J. van Heijenoort, *Tetrahedron* **1997**, *53*, 1695.
[18] E. R. Baizman, A. A. Branstrom, C. B. Longley, N. Allanson, M. J. Sofia, D. Gange, R. C. Goldman, *Microbiology* **2000**, *146*, 3129.
[19] U. Eichelberger, M. Mansourova, L. Hennig, M. Findeisen, S. Giesa, D. Müller, P. Welzel, *Tetrahedron* **2001**, *57*, 9737; U. Eichelberger, I. Neundorf, L. Hennig, M. Findeisen, S. Giesa, D. Müller, P. Welzel, *Tetrahedron* **2002**, *58*, 545; M. Mansourova, K. Rohr, L. Hennig, M. Findeisen, R. Oehme, S. Giesa, P. Welzel, *Eur. J. Org. Chem*. **2003**, 2656.
[20] F.-T. Ferse, K. Floeder, L. Hennig, M. Findeisen, P. Welzel, D. Müller, J. van Heijenoort, *Tetrahedron* **1999**, *55*, 3749.
[21] A. Medgyes, E. Farkas, A. Liptak, V. Pozsgay, *Tetrahedron* **1997**, *53*, 4159.
[22] G. Grundler, R. R. Schmidt, *Carbohydr. Res.* **1985**, *135*, 203.
[23] W. Kinzy, R. R. Schmidt, *Liebigs Ann. Chem.* **1985**, *8*, 1537.
[24] C. Prakash, S. Saleh, I. A. Blair, *Tetrahedron Lett*. **1989**, *30*, 19.
[25] B. H. Lipshutz, J. Keith, *Tetrahedron Lett*. **1998**, *39*, 2495.
[26] T. D. Nelson, R. D. Crouch, *Synthesis* **1996**, 1031.
[27] R. K. Boeckman, A. B. Charette, T. Asberom, B. H. Johnston, *J. Am. Chem. Soc*. **1991**, *113*, 5337.
[28] V. Bou, J. Vilarrasa, *Tetrahedron Lett*. **1990**, *31*, 567.
[29] A. G. Myers, D. Y. Gin, D. H. Rogers, *J. Am. Chem. Soc*. **1994**, *116*, 4697.
[30] O. Kanie, S. C. Crawley, M. M. Palcic, O. Hindsgaul, *Carbohydr. Res.* **1993**, *243*, 139; C. Unverzagt, *Carbohydr. Res.* **1997**, *305*, 423.
[31] H.-H. Lee, D. A. Schwartz, J. F. Harris, J. P. Carver, J. J. Krepinsky, *Can. J. Chem.* **1986**, 1912.
[32] G. Skorna, R. Stemmer, I. Ugi, *Chem. Ber.* **1978**, *111*, 806.
[33] M. Pietraszkiewicz, P. Sinay, *Tetrahedron Lett*. **1979**, *20*, 4741.
[34] J. Madaj, A. Trynda, A. Konitz, A. Nowacki, A. Wiśniewski, *Carbohydr. Res.* **1998**, *308*, 431.
[35] G. Yang, M. Mansourova, L. Hennig, M. Findeisen, R. Oehme, S. Giesa, P. Welzel, *Helv. Chim. Acta* **2004**, *87*, 1807.
[36] D. Volke, M. Daghish, L. Hennig, M. Findeisen, S. Giesa, R. Oehme, P. Welzel, *Helv. Chim. Acta* **2003**, *86*, 4214.

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