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Synthesis of a building block for phosphonate analogues of moenomycin A_{12} from D-tartaric acid

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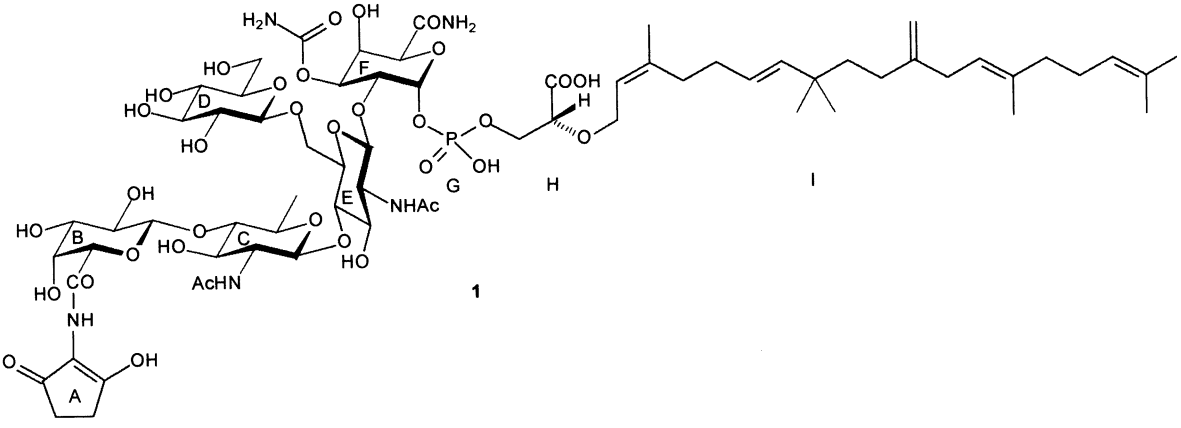
Abstract—An approach for the synthesis of moenomycin A_{12} *C*-glycoside partial structures is reported based on allyltin chemistry.

1. Introduction

Infectious diseases continue to be a leading cause of morbidity and mortality worldwide. Especially the increasing frequency of resistance to existing antibiotics represents a serious public health treat.[1] Thus, there is an urgent need for discovery and development of new agents active against resistant strains. Human cells lack a cell wall but bacteria are surrounded by a cell wall that is crucial for survival. This feature of bacteria is an attractive target for antibiotic action. The biosynthesis of peptidoglycan, the main structural component of the bacterial cell wall, occurs successively in three cell compartments, in the cytoplasm, at the inner face and at the outer face of the cytoplasmic membrane. The immediate precursor of peptidoglycan is lipid II, a disaccharide peptide linked to a C_{55} lipid carrier via a pyrophosphate bridge.[2] The formation of the polymeric peptidoglycan from this precursor at the outer face of the cytoplasmic membrane requires two enzymatic activities, a glycosyl transferase and an acyl serine transferase (transpeptidase).[3] The high molecular weight penicillin binding proteins of *E. coli* combine in a single polypeptide chain the required transglycosylase and transpeptidase activities. The transpeptidation reaction is inhibited by the β-lactam antibiotics. Most of the antibiotics that inhibit the transglycosylation step seem to interfere with the substrate(s) of this reaction.[4,5] The only class of compounds known with certainty to inhibit the enzyme of this reaction, the transglycosylase,[6] are the moenomycins (see, for example, moenomycin A_{12} (**1**),[7] (Scheme 1). A mechanism for their mode of action has been proposed.[8,9] It is assumed that they are anchored to the cytoplasmic membrane via the lipid part



Scheme 1.

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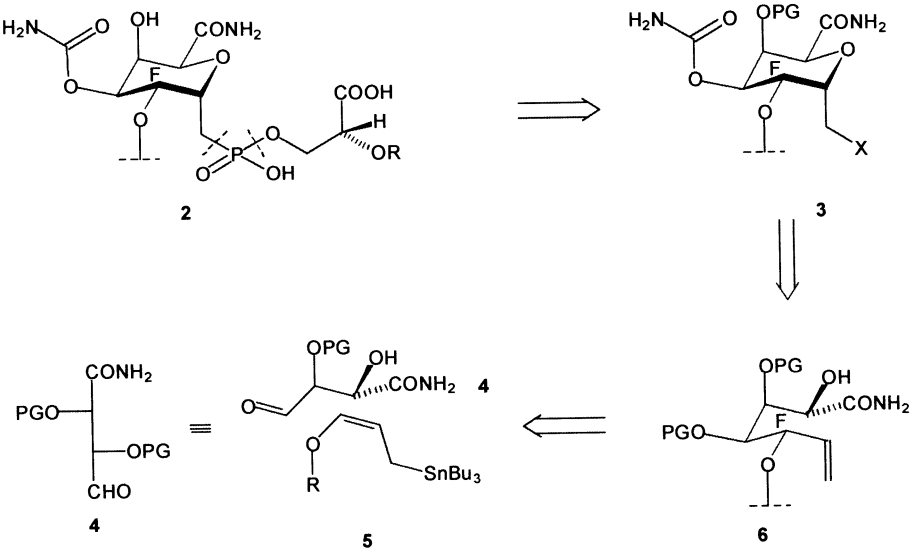


Scheme 2.

and bind then highly selectively to the active site of the enzyme via the C–E–F trisaccharide. Units A, B, and D have been shown to be of minor importance for the antibiotic activity.[10] The moenomycins do not induce resistance readily. However, a weak point in this respect may be the phosphate bond at unit F. Its cleavage by a yet poorly characterized enzyme is the only enzymatic degradation reaction of the moenomycins that is known to-date.[11] Furthermore, some analogues which we expected to be antibiotically active, were devoid of antibiotic activity. It has been speculated, that these compounds are used as substrates by the transglycosylase.[12] With this in mind we embarked on a programme aimed at synthesizing trisaccharide analogues of moenomycin A_{12} in which the phosphate oxygen at C-1 of unit F is replaced by a CH_2 group.[13] It seemed important to retain all other functional groups in ring F as present in moenomycin since they are known to be of major importance as far as antibiotic activity is concerned.[10,14] Some mono- and disaccharide phosphonate models of moenomycin A have already been prepared but obviously their structures were too simple to elicit antibiotic activity.[15]

2. Synthetic planning

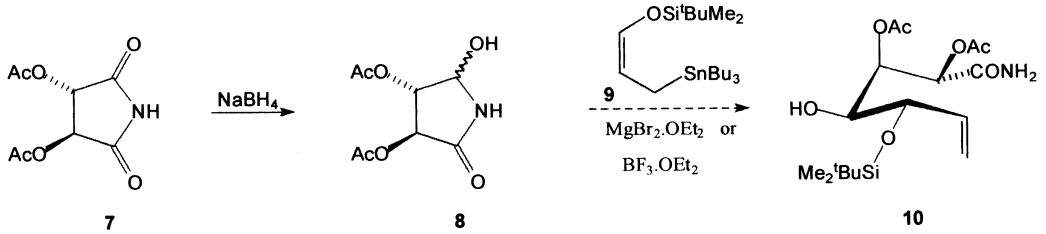
For the synthesis of *C*-glycosides many methods exist. Carbocation, carbanion and radical chemistry can be used to add carbon appendages to C-1 of the starting sugar.[16] We decided to disconnect the target structure as indicated in formula **2** to give a precursor of type **3** (Scheme 2). **2** would be available from **3** by an Arbuzov reaction. Further disconnection of **3** leads to **6**. Electrophilic cyclizations of type **6** compounds is another important route to *C*-glycosides. The most important disconnection is that of **6** which yields the two precursors **4** and **5**. Compound **4** should be easily available from D-tartaric acid. Reagents of type **5** can be made from allyl alcohol by silyl ether formation, deprotonation with butyllithium and trapping the organometallic intermediate with tri-*n*-butyltin chloride.[17]

3. Attempted synthesis of 10 via 8

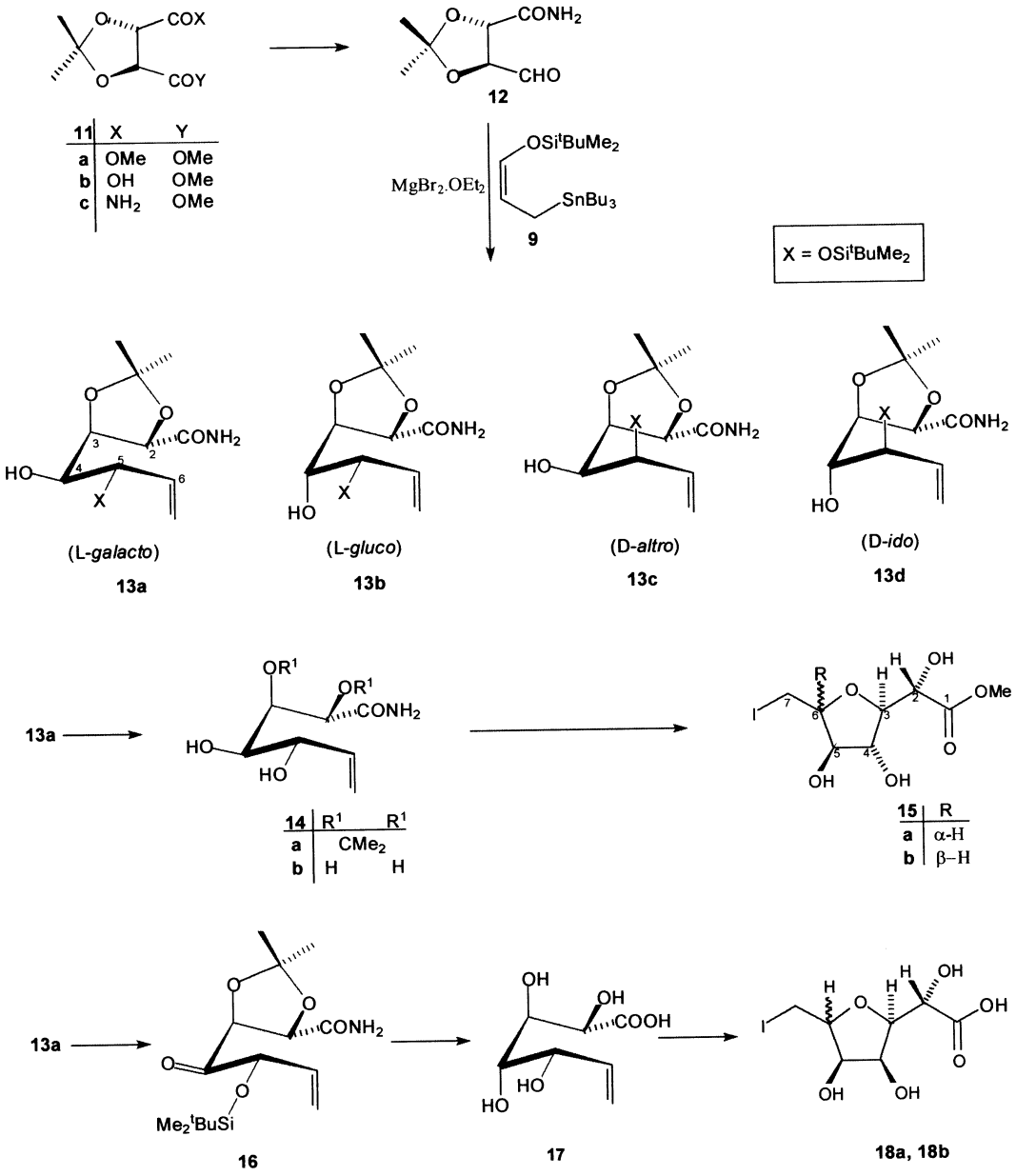
We first tried to prepare **10** by assembling **8** with the known (*Z*)-substituted γ-silyloxyallyl stannane **9** (Scheme 3).[17] Thus, **7** was reduced with sodium borohydride to provide **8** in 41% yield. According to the ^{1}H NMR spectrum which displayed two singlets for the NH protons at 6.54 and 6.58 (no coupling to the adjacent proton, as shown by a homo decoupling experiment), **8** was a 1:1 mixture of two stereoisomers. Under the conditions employed ($MgBr_2{\cdot}OEt_2$ and $BF_3{\cdot}OEt_2$, respectively) **8** turned out to be stable. This means that neither the open-chain aldehyde tautomer of **8** nor a Speckamp *N*-acyl iminium ion[18] could be trapped by **9**.

4. Reaction of 12 with 9

After the failure with **8** we turned to the addition of **9** to aldehyde **12** (Scheme 4). This aldehyde was obtained from



Scheme 3.



Scheme 4.

the known[19] D-tartaric acid derivative **11a** by selective ester hydrolysis (**11a→11b**, KOH (1 equiv.) in methanol,[20] 73%), amide formation using Staab's procedure[21] (91%) and DIBAH reduction in dichloromethane (94%). The missing three carbons could be introduced by coupling **12** with **9**.[17] The yield and the stereoselectivity of this addition was strongly dependent on the activating Lewis acid.[22] Best results were obtained using magnesium dibromide etherate.[23] Under these conditions a heptonic acid amide **A** was obtained in 50% yield as a single stereoisomer. A second isomer **B** was formed when the addition was, for example, catalyzed by zinc bromide (CH_2Cl_2, −30°C). The total yield was lower in this case (23%), however.

The heptonamide **A** obtained from **12** with **9** contains two new stereogenic centers at C-4 and C-5. Thus, it could be either the L-*galacto*, L-*gluco*, D-*altro* or D-*ido* isomer (see **13a**–**13d**, Scheme 4). Note, that the amide carbon in these compounds is C-1. We were unable to deduce the relative configuration at the newly formed stereogenic centers from the ^{1}H NMR spectra. In an attempt to overcome this problem the free OH-group of the heptonamide was oxidized to furnish a ketone **C** that on Luche reduction furnished a stereoisomer **D** of the original addition product of **12** with **9**. But again, attempts to establish the relative configuration proved fruitless. Thus, we decided to determine the configuration after electophilic cyclization. Selective cleavage of the acetonide ring leaving the silyl ether intact was unsuccessful. Acetic acid, ferric chloride, or cupric chloride removed the silyl group whereas the acetonide was stable under these conditions. Thus, all the protecting groups were removed from **A** on refluxing an ethanol–water solution in the presence of Dowex 50-H^+ to afford the completely deprotected product in quantitative yield. Good quality ^{1}H- and ^{13}C NMR spectra were obtained for this compound. They did not show any signals for

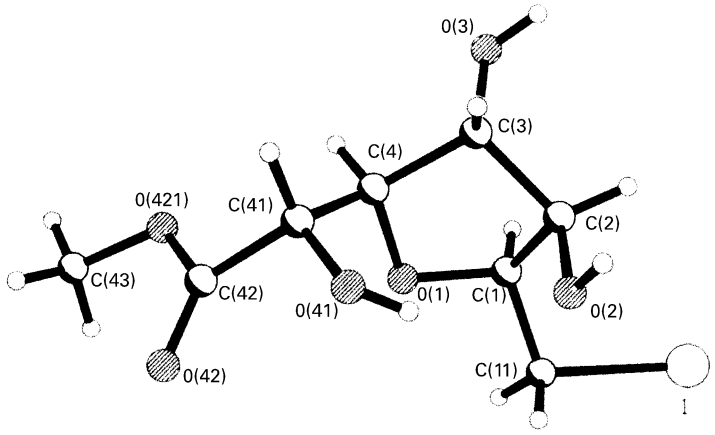
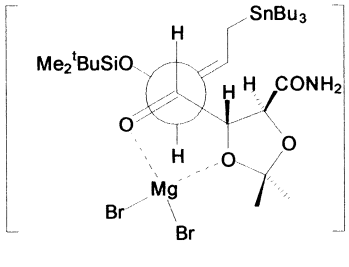


Figure 1.

acetonide or TBDMS groups. The ^{1}H NMR spectra displayed a broad singlet at 7.64 for the $CONH_2$ group. However, it was very complicated to obtain reasonable MS spectra. FAB MS was unsuccessful and the ESI MS spectra of deprotected **A** did not show a signal for the molecular ion. Instead a signal at *m/z* 347.09769 (calculated for $[2M-2NH_3-H]^-$: 347.10565, difference=0.00796) indicated the removal of ammonia. We conclude that under the ESI conditions the amide had been converted to a lactone. Electrophilic mercuric trifluoroacetate-mediated cyclization of deprotected A followed by HgX→I exchange[16] produced two stereoisomeric compounds which according to the NMR spectra were methyl esters. After crystallization of one of them from methanol an X-ray analysis yielded structure **15a** (see Fig. 1) confirming the presence of a methyl ester and demonstrating the lability of the amide group in this system. Not unexpectedly, a furanoid cyclization product had been formed. Most importantly, the X-ray structure proved that the addition of allyl stannane **9** to aldehyde **12** had given the L-*galacto* product **13a** (compound **A**) exactly as desired and as present in unit F of moenomycin A_{12}. The second isomer in the cyclization reaction was then **15b**. The oxidation product of **13a** must be **16** (compound **C**) and the isomer of **13a** obtained by reduction of **16** is the L-*gluco* compound **13b** (**D**). The second isomer (compound **B**) in the zinc bromide-mediated reaction of **12** with **9** was not identical with **13b** and has, thus, either structure **13c** or **13d**.

We also removed the protecting groups from **13b** by hydrolysis in the presence of Dowex 50-H^+. In this case, too, the amide group was hydrolyzed and the free acid **17** was isolated. Cyclization under the conditions detailed above furnished the two furanoid cyclization products **18a** and **18b**. The configuration at C-6 could not be determined by NMR.

The outcome of the addition of the allylstannane **9** to **12** can be explained on the basis of a transition state geometry as indicated in formula **19** in which it is assumed that the $MgBr_2$-promoted addition involves chelation control and that the C=O and C=C bonds are in an antiperiplanar relationship as suggested previously[23] (Scheme 5).



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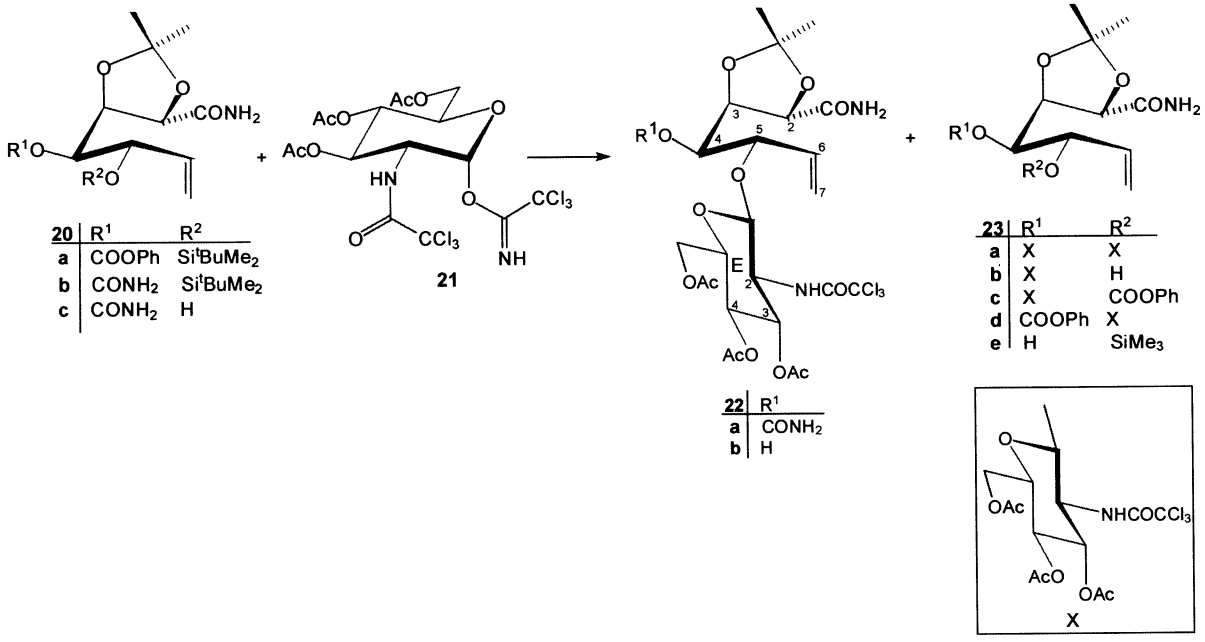
Scheme 5.

5. Attempted synthesis of 26 via 22a

In order to achieve the desired cyclization to a pyranoid ring, functional group manipulations blocking the 3-OH group and liberating the OH group at C-2 became necessary (Scheme 6). The 4-OH group of **13a** was converted into a urethane via the phenyl carbonate (**13a→20a→20b**). The silyl protecting group was removed to give **20c**. Attempts to convert this compound into a trisaccharide on reaction with the oxazoline derived from chitobiose octaacetate failed completely.[22] The reason for the low nucleophilicity of **20c** originates most probably from the electron-withdrawing substituent at C-4. It is known that the Beau–Jacquinet oxazolines (formed from **21**) are much more reactive than the normal oxazolines.[24] And indeed, disaccharide **22a** was formed on reaction of **20c** with **21**. But even in this reaction the yield was low (20%). Unfortunately, all of the known methods that we tried failed to remove the acetonide group from **22a**.

6. Synthesis of 26 via 14a

In order to circumvent these problems, the silyl protecting group was cleaved from **13a** with TBAF in THF. The resulting **14a** was glycosylated via the Beau–Jacquinet procedure. When 0.2 equiv. of TMS–OTf were used we obtained **22b** and **23b** which we were unable to separate. The mixture was converted into the corresponding phenyl carbonates which could be separated to give 1:3 mixture of **23c** and **23d** (76%). Again, we were unable to remove the acetonide group selectively.[22] When the reaction of **14a** and



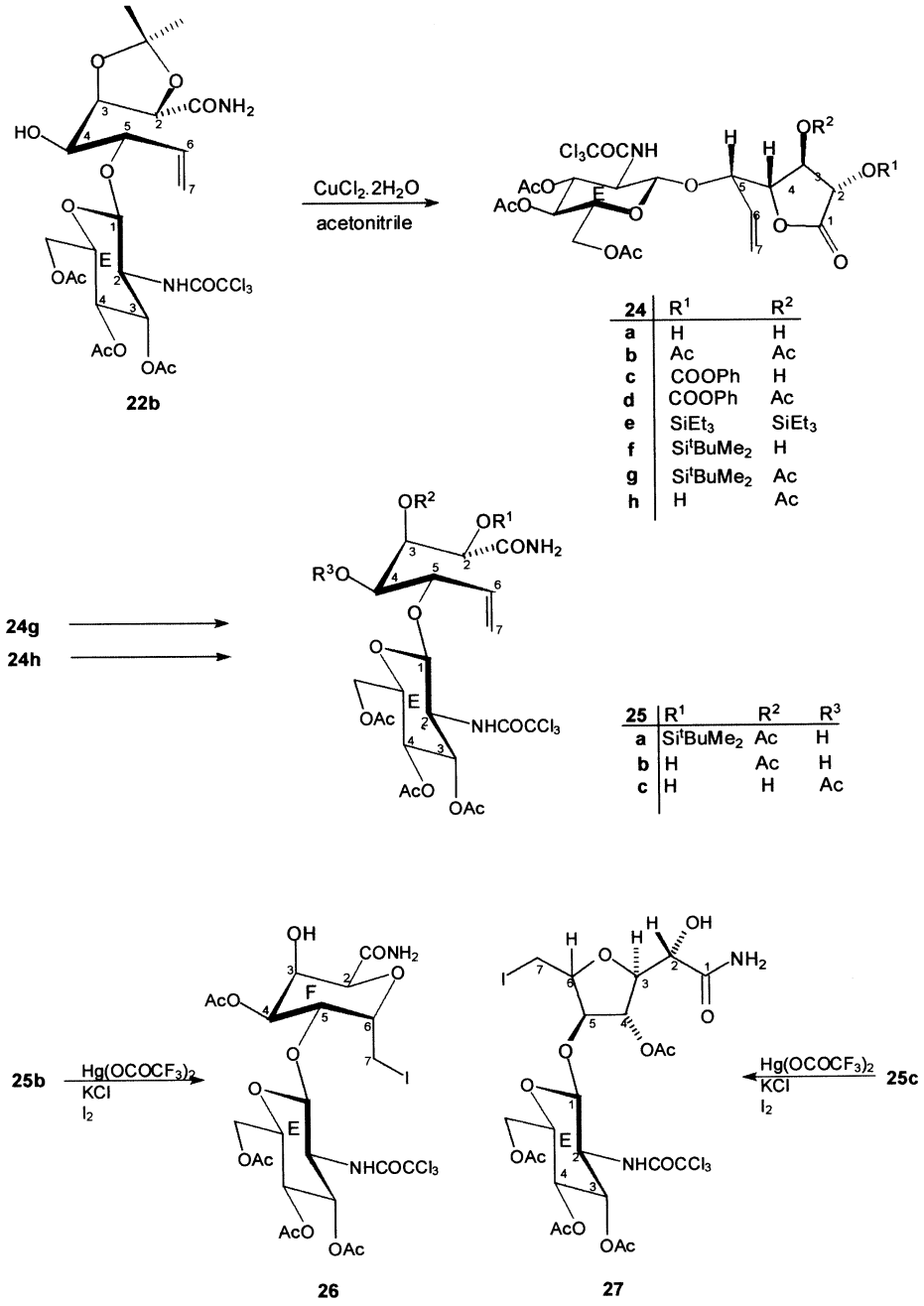
Scheme 6.

21 was performed in the presence of 0.45 equiv. of TMS–OTf disaccharide **22b** was obtained in 32% yield. In addition, the 1→4 disaccharide **23e** (4%) and the trisaccharide **23a** (10%) were isolated. The ^{1}H and ^{13}C signals of compounds **22b** and **23e** were assigned with the help of 2D experiments. The ^{1}H NMR spectrum of **22b** showed $^{3}J_{1E,2E}$=8.1 Hz confirming the β-glycosidic bond, which was also indicated by the ^{13}C chemical shift (δ=100.00) of C-1^{E}. HMBC spectra showed a long-range coupling between 5-H and C-1^{E}, also a long-range coupling between 1^{E}-H and C-5 was identified. The ^{1}H NMR spectrum of **23e** indicated the presence of a trimetyl silyl group (singlet at δ=0.067), which was also seen by the ^{13}C chemical shift (δ=0.39). The ^{1}H NMR coupling constant $^{3}J_{1',2'}$=8.1 Hz and the ^{13}C chemical shift (δ=99.34) of C-1′ confirmed the β-glycosidic bond formation. HMBC spectra showed a long-range coupling between 4-H and C-1′, and a long-range coupling between 1′-H and C-4 was identified. The FAB MS spectrum was in accord with structure **23e**.

On removing the acetonide protecting group from **22b** using cupric chloride dihydrate in acetonitrile[25] lactone **24a** was obtained (94%) demonstrating once again the lability of the amide group (Scheme 7). No signals for acetonide or amide groups were observed in the ^{1}H NMR spectrum. The FAB MS displayed parent ion peaks at *m/z* 606.0 and 628.0 which correspond to $[M+H]^{+}$ and $[M+Na]^{+}$, respectively. The structural assignment of **22b** rests mainly on a careful analysis of the NMR spectra of its diacetyl derivative **24b**. Both ^{1}H- and ^{13}C NMR spectra of **24b** indicated the presence of five acetyl groups (three for the sugar and two for the lactone). In the ^{1}H NMR spectra of **24b** the signals of 2-H and 3-H were shifted to higher frequencies (by 1.3 and 0.8 ppm, respectively) while no significant shift for 4-H was observed compared to that of **24a**. HMBC spectra showed a long-range coupling between 2-H and 3-H and the *C*O of the acetyl groups attached to C-2 and C-3, respectively. This is an indication that the 4-OH in **22b** formed the lactone bond in **24a**. The FAB MS showed parent ion peaks corresponding to $[M+H]^{+}$ and $[M+Na]^{+}$, respectively.

In principle, the lactone is a very nice compound since it contains the 4-OH group in a protected form. Thus, protecting the 3-OH group and opening the lactone ring with ammonia would set the stage for the 6-*exo*-trig cyclization. Attempts to protect the 3-OH group directly failed. Either both OH groups were protected under the reaction conditions (see **24b** and **24e**) or the 2-OH group reacted selectively (see **24c** and **24f**). **24c** was obtained from **24a** with 1 equiv. of phenyl chloroformate in 70% yield. ^{1}H and ^{13}C signals of **24c** were assigned with the help of 2D NMR experiments. HMBC spectra showed a long-range coupling between 2-H and the *C*O of the phenyl carbonate group indicating that the phenyl carbonate group was at C-2. Acetylation of **24c** yielded **24d** in 75% yield. In the ^{1}H NMR spectrum of **24d** the signal of 3-H was shifted to higher frequency (1.0 ppm) while no significant shift for 2-H was observed compared to **24a**. HMBC showed a long-range coupling between 2-H and the *C*O of the phenyl carbonate, also a long-range coupling was identified between 3-H and the acetyl group attached to C-3. Attempts to remove the carbonate group from **24d** proved fruitless.[22]

As a consequence of these observations a two-step protocol was used for the protection of the 3-OH group. Silyl ether **24f** obtained from **24a** in 89% yield was acetylated to give **24g** (94%). HMBC showed a long-range coupling between 3-H and the *C*O of the acetyl group in accord with structure **24g**. Silyl group removal with TBAF gave **24h** (98%). After successful protection of the 3-OH group, opening of the lactone ring with NH_3 in THF furnished two products, 3-acetate **25b** and the 4-isomer **25c** (82% total yield). The presence of the amide group in **25b** was indicated by ^{1}H NMR (broad singlets at 6.00 and 6.79 for the $CONH_2$ group which disappeared after D_2O treatment). 2-H gave a singlet



24	R^1	R^2
a	H	H
b	Ac	Ac
c	COOPh	H
d	COOPh	Ac
e	$SiEt_3$	$SiEt_3$
f	Si^tBuMe_2	H
g	Si^tBuMe_2	Ac
h	H	Ac

25	R^1	R^2	R^3
a	Si^tBuMe_2	Ac	H
b	H	Ac	H
c	H	H	Ac

Scheme 7.

at 4.46 which is unusual in this system. That the acetate was at C-3 was obvious from the long range coupling (HMBC) between 3-H and the acetyl *C*O. In **25c**, the amide was apparent from the ^{1}H NMR spectra (two singlets at 5.91 and 6.87 for the $CONH_2$ group which disappeared after D_2O treatment). The signal of 2-H gave a doublet-type signal with a coupling constant of ^3J=6.3 Hz for the coupling with 2-OH as shown in a COSY experiment and also by D_2O exchange. A second splitting with J=1.4 Hz (for the coupling of 2-H with 3-H) was observed upon recording the spectrum after treatment with D_2O. Similarly, the signal of 3-H could only be fully analyzed after D_2O exchange. The coupling constant $J_{3,4}$ was 9.9 Hz. HMBC spectra showed a long-range coupling between 4-H and the *C*O of the acetate attached to C-4. The formation **25c** can be explained by the migration of the acetyl group (C-3→C-4).

When the lactone opening was performed at the stage of **24g**, amide **25a** was obtained in 94% yield without acetyl group migration.[26] The formation of the amide in **25a** was indicated by ^{1}H NMR (two broad singlets at 5.92, and 6.57 for the $CONH_2$ group). HMBC spectra showed a long-range coupling between 3-H and the *C*O of the 3-acetoxy group. However, when the silyl group was removed from **25a** with TBAF in THF the same mixture of **25b** (46%) and **25c** (38%) resulted as above.

The last step in this synthesis was the ring closure of **25b**. Electrophilic cyclization [(i)$Hg(OCOCF_3)_2$ in THF, (ii) KCl

in water, (iii) I_2] afforded **26** in 28% yield. The acetyl group had again migrated to the equatorial position at C-4. The ^{1}H NMR spectra proved the *C*-glycoside structure. The methylene protons 7^F-H (dd), 7^F-H′(dd), and 6^F-H (ddd) formed an ABX system. The coupling constant $^3J_{5F,6F}$=5.9 Hz confirmed the α position of iodo methyl group at C-6. The coupling constant $^3J_{4F,5F}$=9.8 Hz is in agreement with the *galacto*-configuration of unit F. The primary amide group gave rise to two broad singlets in the ^{1}H NMR spectrum (at 7.79 and 8.60). The ^{13}C NMR spectrum showed the C-7 signal at δ=3.60. The HMBC spectra indicated a long-range coupling between 4-H and the *C*O of the acetate attached to C-4. This is an evidence for the migration of the acetyl group. The cyclization of **25c** furnished **27** in 44% yield. Again, the ^{1}H NMR spectra of **27** showed a *C*-glycoside structure (ABX system for CH_2-7 and 6^F-H. The coupling constant $^3J_{4,5}$=2.6 Hz indicated a furanoid ring formation instead of a pyranoid ring as in **25b**. The configuration at C-6 was not assigned. The amide group was indicated by ^{1}H NMR (two broad singlets at 8.23, and 8.49 for the $CONH_2$ group). The 2-H proton was upfield shifted to 4.85 while that of 4-H was downfield shifted to 6.24. This is evidence that the acetoxy group was linked to C-4 and not to C-2. The ^{13}C NMR spectrum showed the C-7 signal at δ=3.67 ppm. The FAB MS displayed parent ion peaks at *m*/*z* 789.8 and 812.8 which correspond to $[M+H]^+$ and $[M+Na]^+$, respectively.

7. Conclusion

The results reported above demonstrate (i) that *d*-tartaric acid can nicely be converted into L-galactoheptonamides (D-galactohepturonamides), i.e. into a structural moiety that is present in moenomycin analogues of type **2**, (ii) that the amide group in this type of compounds is very labile, and (iii) that the acetonide protecting group used for the protection of the OH groups at C-2 and C-3 causes severe problems at later stages of the synthesis. It was found that replacement of acetonide by cyclopentylidene protection did not solve the problems.[22]

8. Experimental

8.1. General

NMR: GEMINI 200 (Varian), GEMINI 2000 (Varian), GEMINI 300 (Varian), DRX 400 (Bruker), DRX 600 (Bruker); chemical shifts are given in δ values. HMBC and HMQC experiments were performed using the DRX 400 and the DRX 600. Mass spectrometry: FAB MS: VG Autospec (Fisons, 3nitrobenzylalcohol matrix), ESI MS: FT-ICR-MS Apex II (Bruker Daltonics, water–methanol, negative ion mode). For other methods, see Ref. 27

8.1.1. (3*S*,4*S*)-3,4-Diacetoxy-5-hydroxy-2-pyrrolidinone (8). Sodium borohydride was added to (3*S*,4*S*)-3,4-diacetoxy-2,5-pyrrolidinedione (**7**)[28] (2.0 g, 9.3 mmol) dissolved in THF (40 mL) and water (2 mL) at −40°C. The reaction progress was followed by TLC ($CHCl_3$–MeOH 90:10). After stirring for 5 h, the reaction mixture was warmed to room temperature during 1 h. The precipitated boron complex was removed from the reaction mixture, and the filtrate was concentrated at room temperature. The crude product was purified by FC eluting with $CHCl_3$–MeOH 90:10, to furnish after solvent evaporation solid **8** (0.82 g, 41%). IR (KBr): 3436 (br), 1748, 1374, 1244, 1059 cm^{-1}. ^{1}H NMR (200 MHz, [D_6]DMSO, homodecoupling): δ=2.01 (s, 6H, CH_3), 5.00 (m, 2H, CH), 5.26 (d, 1H, C*H*OH), 6.54, 6.58 (NH, NH), 8.85 (s, OH). ^{13}C NMR (50 MHz, [D_6]DMSO): δ=20.62, 20.77 ($COCH_3$), 73.84 (CHOH), 79.27, 80.29 (CH), 167.41, 169.75, 169.98 (*C*O). $C_8H_{11}NO_6$ (217.17, 217.06), FAB MS: *m*/*z* 218.0 $[M+H]^+$, 240.0 $[M+Na]^+$.

8.2. Attempted addition of 9 to 8

Hydroxylactam **8** (0.10 g, 0.46 mmol) and magnesium bromide etherate (0.12 g, 0.46 mmol) were dissolved in anhydrous CH_2Cl_2 (15 mL) under an argon atmosphere in an ice-bath. 1-*tert*-Butyl-dimethylsilyloxy-3-tri-*n*-butylstannyl-1-propene (**9**) (0.21 g, 0.46 mmol) in anhydrous CH_2Cl_2 (2 mL) was added. The reaction was monitored by TLC ($CHCl_3$–MeOH 90:10). After 2 h the reaction mixture was removed from the ice-bath and stirred at room temperature for 48 h. No reaction was observed.

In another experiment, $BF_3{\cdot}OEt_2$ (43 μL, 50 mg, 0.34 mmol) was added to a mixture of hydroxylactam **8** (50 mg, 0.23 mmol) and allystannane **9** (0.14 g, 0.30 mmol) in 3 mL of anhydrous CH_2Cl_2 under an argon atmosphere at −10°C. The reaction was monitored by TLC ($CHCl_3$–MeOH 90:10). After 24 h no reaction was observed.

8.2.1. 2,3-*O*-Isopropylidine-D-tartaric acid methyl ester amide (11c). A solution of *N*,*N*-carbonyldiimidazole (2.19 g, 13.3 mmol) in anhydrous THF (25 mL) was added dropwise to a solution of methylhydrogen-2,3-isopropylidene-D-tartrate (**11b**)[20] (2.21 g, 10.8 mmol) in anhydrous THF (50 mL) during 10 min. The reaction mixture was stirred for further 20 min. Gaseous ammonia was bubbled through the reaction mixture at a slow rate for 2 h. The reaction progress was followed by TLC ($CHCl_3$–MeOH 90:10). The solvent was removed, the crude product was purified by FC eluting with $CHCl_3$–MeOH 90:10, to afford after solvent evaporation pure **11c** (2.00 g, 91%) as a colorless oil. R_f: 0.40 ($CHCl_3$–MeOH 90:10). IR (film): 3455 (br), 3376 (br), 3223 (br), 1869, 1750, 1380, 1255, 1213, 1104 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ=1.43, 1.45 (2s, 6H, CH_3), 3.77 (s, 3H, OCH_3), 4.70 (s, 2H, CH), 6.54, 6.90 (2s, 2H, $CONH_2$). ^{13}C NMR (50 MHz, $CDCl_3$, APT): δ=26.54, 26.94 ($C(CH_3)_3$), 53.29 (OCH_3), 77.70, 77.98 (CH), 113.97 ($C(CH_3)_2$), 171.09, 173.32 (CO). $C_8H_{13}NO_5$ (203.19, 203.08), FAB MS: *m*/*z* 204.0 $[M+H]^+$, 226.0 $[M+Na]^+$.

8.2.2. (4*S*,5*S*)-5-Formyl-2,2-dimethyl-[1,3]dioxolane-4-carboxylic acid amide (12). A solution of diisobutylaluminium hydride (10 mL, 1.0 M in CH_2Cl_2) was added dropwise over 1 h at −78° to a solution of **11c** (0.81 g, 3.99 mmol) in anhydrous CH_2Cl_2 (3 mL). The reaction was monitored by TLC ($CHCl_3$–MeOH 90:10). After stirring for additional 8 h, isopropanol (6 mL) was added

dropwise to the reaction mixture. After 20 min citric acid (15% aq., 10 mL) was added to the vigorously stirred mixture. The mixture was warmed gradually to room temperature, the pH was adjusted to 3.5 by the citric acid solution. The reaction mixture was stirred until the two phases had separated, the aqueous phase was extracted with CH_2Cl_2 (5×50 mL), the combined organic extracts were dried over sodium sulfate. The solvent was removed at room temperature yielding **12** (0.64 g, 94%) as an oil which became solid after precipitation from an PE–ethyl acetate mixture. R_f: 0.36 ($CHCl_3$–MeOH 90:10). IR (KBr): 3451 (br), 1678, 1382, 1257, 1218, 1089 cm^{-1}. ^1H NMR (200 MHz, [D_5]pyridine, HH COSY): δ=1.41–1.58 (singlets for CH_3), 4.14–5.85 (many multiplets, CH), 7.21, 8.27, 8.34, 8.83 (unassigned signals), 10.0 (s, CHO). ^{13}C NMR (50 MHz, [D_5]pyridine, HETCOR): 22.25, 24.29 26.32, 26.61, 26.69, 26.76, 26.90, 27.02, 27.35, 27.49 ($C(CH_3)_3$ signals), 69.51, 76.84, 76.93, 79.45, 81.90, 82.94, 83.80 (CH signals), 90.67, 94.13, 95.93, 111.51, 111.58, 111.73 ($C(CH_3)_2$ signals), 113.33, 113.71 (unassigned signals), 172.91, 173.13, 174.75, 175.13, 175.62 ($CONH_2$ signals), 199.54 (*C*HO). $C_7H_{11}NO_4$ (173.17, 173.06), FAB MS: *m/z* 174.2 $[M+H]^+$, 196.0 $[M+Na]^+$.

8.2.3. 5-*O*-(*tert*-Butyldimethylsilyl)-6,7-dideoxy-2,3-*O*-isopropylidene-L-*galacto*-hept-6-enonamide (13a). The aldehyde **12** (0.46 g, 2.7 mmol) and magnesium bromide etherate (0.70 g, 2.7 mmol) were dissolved in anhydrous CH_2Cl_2 (15 mL) under an argon atmosphere in an ice-bath. **9** (1.25 g, 2.7 mmol) in anhydrous CH_2Cl_2 (5 mL) was added. The reaction was monitored by TLC ($CHCl_3$–MeOH 90:10). After 1 h the reaction mixture was removed from the ice-bath and stirred at room temperature for 48 h until all reactants were consumed. The reaction was stopped by the addition of 5 mL of water, then acidified with a few drops of diluted HCl to remove the $MgCl_2$ suspension and stirred until the two phases had separated. The organic phase were removed and the aqueous phase was extracted several times with CH_2Cl_2. The combined organic extracts were dried over Na_2SO_4 and the solvent was removed. The crude product was purified by FC eluting with $CHCl_3$–MeOH 95:5, to yield after solvent evaporation **13a** (0.46 g, 50%). R_f: 0.35 ($CHCl_3$–MeOH 90:10). IR (KBr): 3391 (br), 3271 (br), 1683, 1654, 1378, 1253, 1084 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, homodecoupling): δ=0.05, 0.07 (2s, 6H, $Si(CH_3)_2$), 0.89 (s, 9H, $C(CH_3)_3$), 1.40, 1.46 (2s, 6H, $C(CH_3)_2$), 3.50 (ddd, 1H, 4-H), 3.72 (d, 1H, 4-OH), 4.14 (dd, 1H, 3-H), 4.35 (dd, 1H, 5-H), 4.43 (d, 1H, 2-H), 5.18 (d, 1H, 7-H_a), 5.29 (d, 1H, 7-H_b), 5.97 (ddd, 1H, 6-H), 6.57, 6.62 (2s, 2H, $CONH_2$). $J_{2,3}$=7.0 Hz, $J_{3,4}$=7.3 Hz, $J_{4,5}$=2.6 Hz, $J_{4,OH}$=5.5 Hz, $J_{5,6}$=6.6 Hz, $J_{6,7a}$=10.6 Hz, $J_{6,7b}$=17.2 Hz. ^{13}C NMR (50 MHz, $CDCl_3$, APT, HETCOR): δ=−4.43, −3.63 ($Si(CH_3)_2$), 18.68 ($C(CH_3)_3$), 26.38 ($C(CH_3)_3$), 27.27, 27.51 ($C(CH_3)_2$), 73.75 (C-5), 76.55 (C-4), 78.01 (C-3), 78.41 (C-2), 111.58 ($C(CH_3)_2$), 116.75 (C-7), 138.99 (C-6), 175.10 (*C*O). $C_{16}H_{31}NO_5Si$ (345.51, 345.20), FAB MS: *m/z* 346.1 $[M+H]^+$, 368.1 $[M+Na]^+$.

8.2.4. 6,7-Dideoxy-2,3-*O*-isopropylidene-L-*galacto*-hept-6-enonamide (14a). Acetic acid (10% in water, 1 mL) was added to **13a** (25.0 mg, 0.072 mmol in 2 mL of THF). The reaction was monitored by TLC ($CHCl_3$–MeOH 95:5). After stirring the reaction mixture overnight at room temperature, the solvent was removed under reduced pressure. The product was purified by FC eluting with $CHCl_3$–MeOH 95:5, to yield after solvent evaporation **14a** (13.1 mg, 78%) as colorless solid. IR (KBr): 3436 (br), 1675, 1379, 1255, 1218, 1071 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, HH COSY): δ=1.46, 1.50 (2s, 6H, $C(CH_3)_2$), 3.41 (d, 1H, 5-OH), 3.78 (ddd, 1H, 4-H), 4.12 (dd, 1H, 3-H), 4.30–4.38 (m, 2H, 5-H, 4-OH), 4.46 (d, 1H, 2-H), 5.24 (ddd, 1H, 7-H_a), 5.40 (ddd, 1H, 7-H_b), 6.01 (ddd, 1H, 6-H), 6.13, 6.76 (2s, 2H, $CONH_2$). $J_{2,3}$=8.1 Hz, $J_{3,4}$=6.8 Hz, $J_{5,OH}$=8.4 Hz, $J_{5,6}$=5.1 Hz, $J_{6,7a}$=10.3 Hz, $J_{6,7b}$=17.4 Hz. ^{13}C NMR (100 MHz, $CDCl_3$, HMQC, HMBC): δ=26.23, 27.18 ($C(CH_3)_2$), 71.84 (C-5), 74.61 (C-4), 77.58 (C-2), 79.15 (C-3), 111.46 ($C(CH_3)_2$), 116.29 (C-7), 138.46 (C-6), 175.62 ($CONH_2$). $C_{10}H_{17}NO_5$ (231.24, 231.11), FAB MS: *m/z* 232.1 $[M+H]^+$.

8.2.5. 6,7-Dideoxy-L-*galacto*-hept-6-enonamide (14b). A mixture of **13a** (42 mg, 0.12 mmol), Dowex 50 W X (H^+ form, ~1.0 g) in ethanol–water 2:1 (3 mL) was heated under reflux. The reaction progress was followed by TLC ($CHCl_3$–MeOH 90:10). After 1 h the solution was filtered, the resin was washed with ethanol, and solvents were removed from the combined filtrates. The crude solid product was washed several times with CH_2Cl_2 to afford **14b** (21 mg, 91%) as colorless solid. R_f: 0.44 ($CHCl_3$–MeOH 70:30). ^1H NMR (200, 300 MHz, [D_5]pyridine, HH COSY): δ=4.67 (dd, 1H, 4-H), 4.88 (ddd, 1H, 5-H), 5.11 (d, 1H, 2-H), 5.23–5.32 (m, 2H, 3-H, 7-H_a), 5.65 (ddd, 1H, 7H_b), 6.42 (ddd, 1H, 6-H), 7.64 (bs, 2H, $CONH_2$). $J_{2,3}$=8.8 Hz, $J_{3,4}$=8.1 Hz, $J_{4,5}$=3.1 Hz, $J_{5,6}$=5.5 Hz, $J_{6,7a}$=10.3 Hz, $J_{6,7b}$=16.8 Hz. ^{13}C NMR (50.3 MHz, [D_5]pyridine, HETCOR):=70.87 (C-5), 74.54 (C-3), 75.83 (C-2), 84.21 (C-4), 115.90 (C-7), 139.02 (C-6), 175.96 (*C*O). $C_7H_{13}NO_5$ (191.18, 191.079373). ESI MS: calculated for $[2M-2NH_3-H]^-$: 347.10565, found: 347.09769 (lactone). A mass spectrum in the positive mode or a FAB MS could not be obtained.

8.3. Ring closure of 13a

(a) *Trying NIS*: Trifluoromethanesulfonic acid (17.4 μL, 0.13 mmol) was added to a mixture of **13a** (15.4 mg, 0.44 mmol) and NIS (49 mg, 0.22 mmol) in anhydrous benzene (5 mL) under an argon atmosphere at 5°C. The resulting mixture was stirred for 3 h. The reaction was monitored by TLC ($CHCl_3$–MeOH 80:20). No reaction was observed.

(b) *Trying iodine*: Iodine (24 mg, 0.094 mmol in 0.8 mL of THF) was added to **13a** (11.0 mg, 0.0032 mmol in 0.2 mL of THF) and phthalate buffer (1.0 mL, pH=4). The reaction was monitored by TLC ($CHCl_3$–MeOH 90:10). The reaction mixture was stirred at room temperature for 72 h. After stirring for 120 h the reaction was stopped by the addition of sodium thiosulfate dissolved in a minimum amount of water. After stirring until the solution became colorless, solvents were removed under reduced pressure. The residue was purified by FC eluting with $CHCl_3$–MeOH 90:10, to afford after solvent evaporation compound **14a** (4.8 mg, 65%).

8.4. Ring closure of 14b

Compound **14b** (0.27 g, 1.4 mmol) and mercuric trifluoroacetate (0.65 g, 1.5 mmol) were dissolved in anhydrous THF (5 mL) under an argon atmosphere. The resulting mixture was stirred at room temperature for 60 h, the reaction was monitored by TLC ($CHCl_3$–MeOH 80:20). KCl (0.11 g, 1.4 mmol) dissolved in a minimum amount of water was added. The reaction mixture was stirred for 90 min, until all reactants were consumed as indicated by TLC ($CHCl_3$–MeOH 90:10). Solvents were removed under reduced pressure, and the residue was purified by FC eluting with ethyl acetate–MeOH 90:10, to afford after solvent evaporation 0.35 g of mercury containing compounds. The produced mixture and I_2 (0.36 g, 1.4 mmol) were dissolved in anhydrous THF (5 mL) under an argon atmosphere, the reaction was monitored by TLC ($CHCl_3$–MeOH 95:5). After stirring for 5 h the reaction was stopped by the addition of sodium thiosulfate in a minimum amount of water. After stirring until the solution became colorless, solvents were removed under reduced pressure. The residue was purified by FC eluting with $CHCl_3$–MeOH 95:5, to afford after solvent evaporation compound **15a** (130 mg, 29%) and compound **15b** (12 mg, 3%).

8.4.1. Methyl 3,6-anhydro-7-deoxy-7-iodo-D-*glycero*-L-*galacto*-heptonate (15a). Mp 146–147°C. R_f: 0.17 ($CHCl_3$–MeOH 90:10). ^{1}H NMR (200 MHz, [D_5]pyridine, homodecoupling, HH COSY): δ=3.54 (dd, 1H, 7-H), 3.67 (s, 3H, OCH_3), 3.73 (dd, 1H, 7-H′), 4.63 (broad, 1H, 5-H), 4.81 (ddd, 1H, 6-H), 4.89 (d, 1H, 2-H), 4.93 (dd, 1H, 3-H), 4.97 (broad, 1H, 4-H). $J_{2,3}$=2.9 Hz, $J_{3,4}$=2.6 Hz, $J_{6,7}$=6.2 Hz, $J_{6,7'}$=7.8 Hz, $J_{7,7'}$=9.5 Hz. ^{1}H NMR (200 MHz, [D_5]pyridine+D_2O): δ=3.43 (dd, 1H, 7-H), 3.62 (s, 3H, OCH_3), 3.63 (dd, 1H, 7-H′), 4.62 (dd, 1H, 5-H), 4.63–4.72 (m, 1H, 6-H), 4.83 (d, 1H, 2-H), 4.86 (m, 1H, 3-H), 4.94 (m, 1H, 4-H). $J_{2,3}$=2.8 Hz, $J_{4,5}$=1.9 Hz, $J_{5,6}$=3.4 Hz, $J_{6,7}$=6.3 Hz, $J_{6,7'}$=7.5 Hz, $J_{7,7'}$=8.9 Hz. ^{13}C NMR (75 MHz, [D_5]pyridine, HETCOR): δ=2.53 (C-7), 51.72 (OCH_3), 71.95 (C-2), 77.98 (C-5), 79.37 (C-4), 83.35 (C-6), 88.46 (C-3), 172.88 (C-1). $C_8H_{13}IO_6$ (332.09, 331.98), FAB MS: *m/z* 333.0 $[M+H]^+$, 355.0 $[M+Na]^+$. Crystal data for $C_8H_{13}IO_6$: Siemens P4 diffractometer, Mo Kα radiation, orthorhombic, space group $P2_12_12_1$, a=6.283(2), b=8.481(3), c=20.440(8) Å, U=1089.2(6) Å^3, F(000)=648, Z=4, D_c=2.025 g cm^{-3}, R=0.029[$I>2s(I)$], wR_2=0.072 for 1831 unique reflections ($2\theta_{max}$=60°), Flack absolute structure parameter 0.01(3). Full crystallographic details have been deposited with the Cambridge Crystallographic Data Center (CCDC 150778). Copies may be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit @c.ck.cam.ac.uk).

8.4.2. Methyl 3,6-anhydro-7-deoxy-7-iodo-L-*glycero*-L-*galacto*-heptonate (15b). R_f: 0.20 ($CHCl_3$–MeOH 90:10). ^{1}H NMR (600 MHz, [D_5]pyridine, HH COSY): δ=3.62 (dd, 1H, 7-H), 3.67 (s, 3H, OCH_3), 3.69 (m, 1H, 7-H′), 4.20 (m, 1H, 6-H), 4.68 (dd, 1H, 5-H), 4.92–4.96 (m, 2H, 2-H, 3-H), 5.29 (dd, 1H, 4-H). $J_{3,4}$=6.7 Hz, $J_{4,5}$=6.7 Hz, $J_{5,6}$=6.1 Hz, $J_{6,7}$=4.9 Hz, $J_{6,7'}$=6.4 Hz, $J_{7,7'}$=10.6 Hz. ^{13}C NMR (150 MHz, [D_5]pyridine, HMQC, HMBC): δ=10.90 (C-7), 51.86 (OCH_3), 71.77 (C-2), 77.65 (C-4), 81.68 (C-5), 82.46 (C-6), 85.48 (C-3), 173.82 (C-1). $C_8H_{13}IO_6$ (332.09, 331.97569), ESI MS: *m/z* calculated for $[2M-H]^-$: 662.95138, found 662.94368.

8.4.3. 5-*O*-(*tert*-Butyldimethylsilyl)-6,7-dideoxy-2,3-*O*-isopropylidene-L-*xylo*-hept-6-en-4-ulosonamide (16). Compound **13a** (135 mg, 0.39 mmol) was dissolved in a mixture of anhydrous DMSO (0.75 mL) and acetic anhydride (0.5 mL) under an argon atmosphere. The mixture was stirred at room temperature. Progress of the reaction was followed by TLC ($CHCl_3$–MeOH 94:6). After 5 h the reactants were consumed. The reaction mixture was diluted with CH_2Cl_2 (30 mL) and washed successively with water, saturated sodium bicarbonate and water (5 mL each). The organic phase was dried over sodium sulfate and concentrated under reduced pressure. The crude product was purified by FC eluting with $CHCl_3$–MeOH 94:6, to afford after solvent evaporation **16** (91 mg, 68%). R_f: 0.69 ($CHCl_3$–MeOH 90:10). IR (KBr): 3475, 3344, 2954, 2927, 2858, 1730, 1685, 1381, 1254, 1088 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, HH COSY): δ=0.08, 0.12 (s, 6H, $Si(CH_3)_2$), 0.92 (s, 9H, $C(CH_3)_3$), 1.46, 1.47 (2s, 6H, $C(CH_3)_2$), 4.67 (d, 1H, [2-H or 3-H]), 4.98 (m, 1H, 5-H), 4.99 (m, 1H, [2-H or 3-H]), 5.31 (ddd, 1H, 1H, 7-H_a), 5.47 (ddd, 1H, 7-H_b), 5.93 (ddd, 1H, 6-H), 6.57, 6.62 (2s, 2H, $CONH_2$). $J_{2,3}$=6.2 Hz, $J_{5,6}$=5.9 Hz, $J_{6,7a}$=10.3 Hz, $J_{6,7b}$=16.1 Hz. ^{13}C NMR: (100 MHz, $CDCl_3$, APT, HMQC): δ=−4.55, −4.36 ($Si(CH_3)_2$), 18.81 ($C(CH_3)_3$), 26.21 ($C(CH_3)_3$), 26.90 ($C(CH_3)_2$), 77.07, 78.93, 78.99 (C-2, C-3, C-5), 113.47 ($C(CH_3)_2$), 118.88 (C-7), 134.92 (C-6), 173.10 ($CONH_2$), 205.21 (C-4). $C_{16}H_{29}NO_5Si$ (343.49, 343.18), FAB MS: *m/z* 344.1 $[M+H]^+$, 366.1 $[M+Na]^+$.

8.4.4. 5-*O*-(*tert*-Butyldimethylsilyl)-6,7-dideoxy-2,3-*O*-isopropylidene-L-*gluco*-hept-6-enonamide (13b). Sodium borohydride (2.5 mg, 0.066 mmol) was added in one portion to a solution of **16** (22.4 mg, 0.065 mmol) and $CeCl_3{\cdot}6H_2O$ (26.1 mg, 0.069 mmol) dissolved in methanol (2.5 mL). After stirring at room temperature for 15 min the reactants were consumed as indicated by TLC ($CHCl_3$–MeOH 95:5). Acetone (3 mL) was added to stop the reaction. The solvent was removed under reduced pressure and the remaining oil was dissolved in CH_2Cl_2 (30 mL), and washed with water (2×5 mL). The organic phase was dried over sodium sulfate. The crude product was purified using FC eluting with $CHCl_3$–EtOH 93:7 to furnish after solvent evaporation **13b** (19 mg, 86%). R_f: 0.34 ($CHCl_3$–MeOH 90:10). IR (KBr): 3534 (br), 3411 (br), 3319 (br), 1688, 1658, 1383, 1255, 1083 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, homodecoupling, HH COSY): δ=0.03, 0.06 (s, 6H, $Si(CH_3)_2$), 0.88 (s, 9H, $C(CH_3)_3$), 1.43, 1.48 (2s, 6H, $C(CH_3)_2$), 2.24 (d, 1H, 4-OH), 3.65 (ddd, 1H, 4-H), 4.12 (m, 1H, 5-H), 4.37 (dd, 1H, 3-H), 4.47 (d, 1H, 2-H), 5.21 (m, 1H, 7- H_a), 5.31 (m, 1H, 7-H_b), 5.91 (ddd, 1H, 6-H), 6.18, 6.55 (2s, 2H, $CONH_2$). $J_{2,3}$=8.4 Hz, $J_{3,4}$=1.1 Hz, $J_{4,OH}$=9.5 Hz, $J_{4,5}$=7.7 Hz, $J_{5,6}$=6.6 Hz, $J_{6,7}$=10.3 Hz, $J_{6,7b}$=17.0 Hz. ^{1}H NMR (200 MHz, $CDCl_3$+D_2O): Similar to the previous data but the signal at 2.24 was reduced and the signal at 3.65 became a dd. ^{13}C NMR (50 MHz, $CDCl_3$, APT, HETCOR): δ=−4.56, −3.66 ($Si(CH_3)_2$), 18.58 ($C(CH_3)_3$), 26.23 ($C(CH_3)_3$), 26.58, 27.35 ($C(CH_3)_2$), 72.82 (C-4), 75.35 (C-5), 76.14 (C-2), 78.15 (C-3), 111.09 ($C(CH_3)_2$), 117.57 (C-7), 139.45 (C-6), 174.26 (*C*O). $C_{16}H_{31}NO_5Si$ (345.51, 345.20), FAB MS: *m/z* 346.1 $[M+H]^+$, 368.1 $[M+Na]^+$.

8.4.5. 6,7-Dideoxy-L-*gluco*-hept-6-enoic acid (17). Following the procedure used to deprotect **13a**, **13b** (64 mg, 0.19 mmol) gave **17** (33.5 mg 94%) as a colorless solid. R_f: 0.44 ($CHCl_3$–MeOH 70:30). ^1H NMR (200, 300 MHz, [D_5]pyridine, HH COSY): δ=5.00–5.22 (m, 4H, 2-H, 3-H, 4-H, 5-H), 5.68 (ddd, 1H, 7-H_a), 5.67 (ddd, 1H, 7H_b), 6.42 (ddd, 1H, 6-H). $J_{5,6}$=5.7 Hz, $J_{6,7a}$=10.4 Hz, $J_{6,7b}$=16.7 Hz. ^{13}C NMR (50 MHz, [D_5]pyridine, HMQC): δ=71.27, 74.78, 74.97, 83.99 (C-2, C-3, C-4, C-5), 116.11 (C-7), 139.56 (C-6), 177.06 (*C*O). $C_7H_{12}O_6$ (192.17, 192.063388), ESI MS: *m*/*z* calculated for $[M-H]^-$: 191.06339, found 191.05561.

8.5. Ring closure of 17

Compound **17** (33.5 mg, 0.18 mmol) and mercuric trifluoroacetate (75 mg, 0.18 mmol) were dissolved in 2 mL of anhydrous THF under an argon atmosphere. The resulting mixture was stirred at room temperature for 8 h, the reaction was monitored by TLC ($CHCl_3$–MeOH 90:10). KCl (13.4 mg, 0.18 mmol) dissolved in a minimum amount of water was added to the reaction mixture. The reaction mixture was then stirred for 90 min until all reactants were consumed as indicated by TLC (ethyl acetate–MeOH 90:10). The solvent was removed under reduced pressure, and the residue was purified by FC eluting with ethyl acetate–MeOH 90:10, to afford after solvent evaporation compounds **A** (23.0 mg) and **B** (12.2 mg). Compound **A** and I_2 (2.5 mg, 0.010 mmol) were dissolved in anhydrous THF (1 mL) under an argon atmosphere. The reaction was monitored by TLC ($CHCl_3$–MeOH 95:5). After 4 h the reaction was stopped by the addition of a solution of sodium thiosulfate in a minimum amount of water. After stirring until the solution became colorless, the solvents were removed under reduced pressure. The residue was purified by FC eluting with ethyl acetate, to afford after solvent evaporation compound **18a** (12.7 mg, 22%). The same procedure was used for compound **B**, to afford **18b** (3.0 mg, 5.3%) after purification by FC eluting with $CHCl_3$–MeOH 95:5.

8.5.1. 3,6-Anhydro-7-deoxy-7-iodo-Ξ-*glycero*-L-*gluco*-heptanoic acid (18a). R_f: 0.17 ($CHCl_3$–MeOH 90:10). ^1H NMR (200, 600 MHz, [D_5]pyridine, homodecoupling, HH COSY): δ=3.58 (dd, 1H, 7-H), 3.75 (dd, 1H, 7-H′), 4.42 (ddd, 1H, 6-H), 4.61 (dd, 1H, 5-H), 5.13 (dd, 1H, 3-H), 5.23 (d, 1H, 2-H), 5.28 (dd, 1H, 4-H), 8.34 (s, 1H, OH). $J_{2,3}$=4.8 Hz, $J_{3,4}$=8.1 Hz, $J_{4,5}$=4.2 Hz, $J_{5,6}$=2.8 Hz, $J_{6,7}$=6.5 Hz, $J_{6,7'}$=7.7 Hz, $J_{7,7'}$=9.3 Hz. ^{13}C NMR (50, 150 MHz, [D_5]pyridine, APT, HMQC, HMBC): δ=2.43 (C-7), 69.84 (C-5), 75.01 (C-2), 80.97 (C-4), 84.41 (C-6), 85.74 (C-3), 178.00 (C-1). $C_7H_{11}IO_6$ (318.07, 317.960040), ESI MS: *m*/*z* calculated for $[M-H]^-$: 316.96004, found 316.95206, calculated for $[2M-H]^-$: 634.92008, found: 634.91064.

8.5.2. 3,6-Anhydro-7-deoxy-7-iodo-Ξ-*glycero*-L-*gluco*-heptanoic acid (18b). R_f: 0.95 ($CHCl_3$–MeOH 90:10). ^1H NMR (200, 600 MHz, [D_5]pyridine, HH COSY): δ=3.49 (dd, 1H, 7-H), 3.72 (dd, 1H, 7-H′), 4.30 (ddd, 1H, 6-H), 4.43 (dd, 1H, 5-H), 4.90–5.03 (m, 3H, 2-H, 3-H, 4-H). $J_{4,5}$=4.0 Hz, $J_{5,6}$=3.3 Hz, $J_{6,7}$=6.2 Hz, $J_{6,7'}$=7.9 Hz, $J_{7,7'}$=9.3 Hz. ^{13}C NMR: (75 MHz, [D_5]pyridine, HMQC): δ=3.20 (C-7), 70.21, 73.33, 82.43 (C-2, C-3, C-4), 71.96 (C-5), 82.09 (C-6), 173.04 (C-1). $C_7H_{11}IO_6$ (318.07, 317.960040), ESI MS: *m*/*z* calculated for $[M-H]^-$: 316.96004, found 316.95255, calculated for $[2M-H]^-$: 634.92008, found: 634.91289.

8.5.3. 5-*O*-(*tert*-Butyldimethylsilyl)-6,7-dideoxy-2,3-*O*-isopropylidene-4-*O*-phenoxycarbonyl-L-*galacto*-hept-6-enonamide (20a). Phenyl chloroformate (135 μL, 0.17 g, 1.0 mmol) was injected into a solution of **13a** (0.29 g, 0.84 mmol) and anhydrous pyridine (0.3 mL) in CH_2Cl_2 (3 mL) under an argon atmosphere at 0°C. The reaction progress was followed by TLC ($CHCl_3$–MeOH 95:5). After stirring the reaction mixture for 1 h the reactants were consumed. The reaction was stopped by adding water (5 mL). After extraction with CH_2Cl_2 (3×30 mL), the combined phases were dried with sodium sulfate. The solvent was removed under reduced pressure. The crude product was purified by FC eluting with PE–ethyl acetate 1:1, to furnish after solvent evaporation **20a** (0.24 g, 60%). R_f: 0.6 ($CHCl_3$–MeOH 95:5). ^1H NMR (200 MHz, $CDCl_3$, HH COSY): δ=0.08, 0.13 (s, 6H, $Si(CH_3)_2$), 0.92 (s, 9H, $C(CH_3)_3$), 1.44, 1.50 (2s, 6H, $C(CH_3)_2$), 4.41 (dd, 1H, 3-H), 4.53–4.62 (m, 1H, 2-H, 5-H), 5.01 (dd, 1H, 4-H), 5.27 (m, 1H, 7-H_a), 5.46 (m, 1H, 7-H_b), 5.98 (ddd, 1H, 6-H), 6.20, 6.53 (2s, 2H, $CONH_2$), 7.18–7.45 (m, 5H, Ar–2-H, Ar–2′-H, Ar–4-H, Ar–3-H, Ar–3′-H). $J_{2,3}$=7.0 Hz, $J_{3,4}$=4.0 Hz, $J_{4,5}$=7.0 Hz, $J_{5,6}$=6.2 Hz, $J_{6,7a}$=10.6 Hz, $J_{6,7b}$=17.0 Hz. ^{13}C NMR: (50 MHz, $CDCl_3$, APT, HETCOR): δ=−4.46, −3.90 ($Si(CH_3)_2$), 18.67 ($C(CH_3)_3$), 26.30 ($C(CH_3)_3$), 26.52, 26.33 ($C(CH_3)_2$), 72.16 (C-5), 76.73 (C-2), 77.79 (C-3), 80.70 (C-4), 111.11 ($C(CH_3)_2$), 118.76 (C-7), 121.57 (Ar–C-2, Ar–C-2′), 126.35 (Ar–C-4), 129.85 (Ar–C-3, Ar–C-3′), 137.32 (C-6), 151.83 (O*C*OO), 154.10 (Ar–C-1), 173.72 (*C*ONH_2). $C_{23}H_{35}NO_7Si$ (465.62, 465.22), FAB MS: *m*/*z* 466.4 $[M+H]^+$, 488.3 $[M+Na]^+$.

8.5.4. 5-*O*-(*tert*-Butyldimethylsilyl)-6,7-dideoxy-2,3-*O*-isopropylidene-4-*O*-carbamoyl-L-*galacto*-hept-6-enonamide (20b). In a pressure reactor (Büchi AG MiniClave) compound **23a** (52.3 mg, 0.11 mmol) was dissolved in CH_2Cl_2 (4 mL). Gaseous ammonia was bubbled for 10 min into the reaction mixture while the apparatus was cooled down using liquid nitrogen. Then the solution was allowed to warm to room temperature. The reaction mixture was stirred at room temperature at ~5 bar for 13 h, by this time all reactants were consumed as indicated by TLC (ethyl acetate). The solvent was removed under reduced pressure. The crude product was purified by FC eluting with ethyl acetate, to afford after solvent evaporation solid **20b** (39.3 mg, 90%). R_f: 0.50 (ethyl acetate). IR (KBr): 3425 (br), 3379 (br), 1722, 1688, 1380, 1254 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$. HH COSY): δ=0.04, 0.07 (s, 6H, $Si(CH_3)_2$), 0.89 (s, 9H, $C(CH_3)_3$), 1.41, 1.45 (2s, 6H, $C(CH_3)_2$), 4.38 (dd, 1H, 3-H), 4.45 (d, 1H, 2-H), 4.46 (dd, 1H, 5-H), 4.90 (dd, 1H, 4-H), 5.16 (bs, 2H, $OCONH_2$), 5.19 (m, 1H, 7-H_a), 5.33 (ddd, 1H, 7-H_b), 5.88 (ddd, 1H, 6-H), 6.22, 6.49 (2d, 2H, $CONH_2$). $J_{2,3}$=6.6 Hz, $J_{3,4}$=5.9 Hz, $J_{5,6}$=6.2 Hz, $J_{6,7a}$=10.4 Hz, $J_{6,7b}$=17.2 Hz, $J_{NH,NH}$=2.8 Hz. ^{13}C NMR (50 MHz, $CDCl_3$, APT, HETCOR): δ=−4.47, −3.86 ($Si(CH_3)_2$), 18.70 ($C(CH_3)_3$), 26.31 ($C(CH_3)_3$), 26.59, 27.51 ($C(CH_3)_2$), 72.83, 77.57, 77.62 (C-2, C-3, C-5), 76.84 (C-4), 111.33 ($C(CH_3)_2$), 117.70 (C-7), 137.74

(C-6), 157.18 (O*C*ONH$_2$), 173.93 (*C*ONH$_2$). $C_{17}H_{32}N_2O_6Si$ (388.53, 388.20), FAB MS: *m/z* 389.2 $[M+H]^+$, 411.2 $[M+Na]^+$.

8.5.5. 6,7-Dideoxy-2,3-*O*-isopropylidene-4-*O*-carbamoyl-L-*galacto*-hept-6-enonamide (20c). Acetic acid (25% in water, 2.5 mL) was added to **20b** (0.10 g, 0.26 mmol). The reaction was followed by TLC (ethyl acetate). After stirring the reaction mixture at 60°C for 2 h, the reactants were consumed. The solvent was removed (codistillation with toluene) under reduced pressure. The resulting solid was washed many times with CH_2Cl_2 to afford **20c** (70 mg, 97%). R_f: 0.30 (ethyl acetate), 0.20 ($CHCl_3$–EtOH 90:10). IR (KBr): 3471 (br), 3438 (br), 1724, 1672, 1613, 1378, 1088 cm^{-1}. ^{1}H NMR (200 MHz, [D$_5$]pyridine, HH COSY): δ=1.46, 1.53 (2s, 6H, C(CH$_3$)$_2$), 4.96 (m, 1H, 5-H), 5.10 (dd, 1H, 3-H), 5.25 (d, 1H, 2-H), 5.25 (m, 1H, 7-H$_a$), 5.76 (m, 1H, 7-H$_b$), 5.81 (dd, 1H, 4-H), 6.40 (ddd, 1H, 6-H), 7.61 (bs, 2H, OCONH$_2$), 8.35, 8.82 (2s, 2H, CONH$_2$). $J_{2,3}$=6.0 Hz, $J_{3,4}$=3.8 Hz, $J_{5,6}$=4.8 Hz, $J_{6,7a}$=10.4 Hz, $J_{6,7b}$=17.1 Hz. ^{13}C NMR (50 MHz, [D$_5$]pyridine, HETCOR): δ=26.37, 27.54 (C(*C*H$_3$)$_2$), 71.82 (C-5), 75.65 (C-4), 76.97 (C-2), 80.47 (C-3), 110.84 (*C*(CH$_3$)$_2$), 115.83 (C-7), 139.56 (C-6), 158.37 (O*C*ONH$_2$), 176.11 (*C*ONH$_2$). $C_{11}H_{18}N_2O_6$ (274.27, 274.12), FAB MS: *m/z* 275.1 $[M+H]^+$, 297.1 $[M+Na]^+$.

8.5.6. 4-*O*-Carbamoyl-5-*O*-[3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroacetamido)-β-D-glucopyranosyl]-6,7-dideoxy-2,3-*O*-isopropylidene-L-*galacto*-hept-6-enonamide (22a). A mixture of **20c** (22 mg, 0.080 mmol) and **21** (57 mg, 0.10 mmol) and activated 3 Å molecular sieves (1.0 g) in anhydrous CH_2Cl_2 (5 mL) was stirred for 1 h at room temperature under an argon atmosphere, then cooled to 0°C. Trimethylsilyl triflate (5 μL, 0.027 mmol) was injected into the reaction flask and the reaction was monitored by TLC (PE–ethyl acetate 1:1). After stirring the mixture for 2 h the reactants were consumed. Triethylamine (0.1 mL) was added to stop the reaction and the mixture was filtered, the molecular sieves were washed with CH_2Cl_2, the solvent was removed under reduced pressure. The crude product was purified by FC eluting with PE–ethyl acetate 1:1, to afford after solvent evaporation **22a** (11.2 mg, 20%). R_f: 0.22 ($CHCl_3$–EtOH 90:10). ^{1}H NMR (400 MHz, $CDCl_3$, HH COSY): δ=1.39 (s, 6H, C(CH$_3$)$_2$), 1.97 (s, 6H, COCH$_3$), 2.06 (s, 3H, COCH$_3$), 3.67 (m, 1H, 5^E-H), 3.86 (m, 1H, 2^E-H), 4.07 (dd, 1H, 6^E-H), 4.19 (dd, 1H, 6^E-H′), 4.38 (m, 2H, 3-H, 5-H), 4.52 (d, 1H, 2-H), 4.78–4.86 (m, 2H, 4-H, 1^E-H), 5.04 (3H, 4^E-H, OCONH$_2$), 5.21 (d, 1H, 7-H$_a$), 5.79 (d, 1H, 7-H$_b$), 5.41 (dd, 1H, 3^E-H), 5.76, 6.50 (2s, 2H, CONH$_2$), 5.86 (m, 1H, 6-H), 7.51 (d, 1H, NH^E). $J_{2,3}$=5.0 Hz, $J_{6,7a}$=11.3 Hz, $J_{6,7b}$=17.0 Hz, $J_{1E,2E}$=8.1 Hz, $J_{2E,3E}$=9.5 Hz, $J_{2E,NH}$=7.1 Hz, $J_{3E,4E}$=9.9 Hz, $J_{4E,5E}$=6.7 Hz, $J_{5E,6E}$<1 Hz, $J_{5E,6'E}$=4.4 Hz, $J_{6E,6'E}$=11.8 Hz. ^{13}C NMR (50 MHz, $CDCl_3$, HMQC): δ=21.12, 21.25 (CO*C*H$_3$ signals), 27.14, 27.64 (C(*C*H$_3$)$_2$), 57.13 (C-2^E), 62.34 (?), 62.68 (C-6^E), 69.14 (C-4^E), 71.80 (C-5^E), 72.36 (C-3^E), 75.33 (C-4), 76.71 (C-2), 77.31, 81.05 (C-3, C-5), 92.88 (CCl_3), 99.59 (C-1^E), 111.87 (*C*(CH$_3$)$_2$), 118.84 (C-7), 134.92 (C-6), 156.91 (O*C*ONH$_2$), 162.72 (*C*OCCl$_3$), 170.02, 171.07, 171.17, 174.04 (*C*OCH$_3$) and (*C*ONH$_2$). $C_{25}H_{34}Cl_3N_3O_{14}$ (706.92, 705.110636), ESI MS: *m/z* calculated for $[M+Na]^+$: 728.10041, found 728.09966, calculated for $[2M+H]^+$: 1411.22123, found 1411.22892, calculated for $[2M+Na]^+$: 1433.21104, found 1433.20709.

8.6. Glycosylation of acceptor 14a

A mixture of **14a** (162 mg, 0.70 mmol), **21** (0.53 g, 0.89 mmol), and activated 3 Å molecular sieves (1.0 g) in anhydrous acetonitrile (2 mL) was stirred for 1 h at room temperature under an argon atmosphere, then cooled to −20°C. Trimethylsilyl triflate (27 μL, 0.15 mmol) was injected into the reaction flask in portions during 1 h. The reaction was monitored by TLC ($CHCl_3$–ethyl acetate 1:1). The reaction mixture was stirred at −20°C for additional 5 h until all reactants were consumed. The reaction was stopped by the addition of triethylamine (0.1 mL), the mixture was filtered, the molecular sieves were washed with CH_2Cl_2. The solvents were removed under reduced pressure. The crude product was purified by FC eluting with $CHCl_3$–EtOH 94:6, to give a mixture of **22b** and **23b** (0.11 g, 22% in a ratio 3:1), and **23a** (0.1739 g, 22%). **22b** and **23b** were not separable at this stage.

The reaction was repeated using the same procedure but the ratio of TMS–OTf was increased (0.21→0.45 equiv.). **14a** (0.40 g, 1.73 mmol), **21** (1.03 g, 1.73 mmol), acetonitrile (2 mL), TMS–OTf (140 μL, 0.45 equiv.) afforded after purification by FC (eluting with $CHCl_3$–EtOH 94:6): **22b** (0.36 g, 32%), **23e** (52 mg, 4.1%), and **23a** (0.18 mg, 9.6%).

8.6.1. 5-*O*-[3,4,6-Tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroacetamido)-β-D-glucopyranosyl]-6,7-dideoxy-2,3-*O*-isopropylidene-L-*galacto*-hept-6-enonamide (22b). R_f: 0.45 ($CHCl_3$–EtOH 90:10). IR (KBr): 3341 (br), 1748, 1677, 1530, 1375, 1238, 1042 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, HH COSY): δ=1.39 (s, 6H, C(CH$_3$)$_2$), 1.956, 1.964, 2.02 (3s, 9H, COCH$_3$), 3.62 (dd, 1H, 4-H), 3.66 (ddd, 1H, 5^E-H), 3.90 (ddd, 1H, 2^E-H), 4.03–4.09 (m, 2H, 3-H, 6^E-H), 4.07 (dd, 1H, 3-H), 4.16 (dd, 1H, 6^E-H′), 4.25 (dd, 1H, 5-H), 4.41 (d, 1H, 2-H), 4.90 (d, 1H, 1^E-H), 5.01 (dd, 1H, 4^E-H), 5.18 (d, 1H, 7-H$_a$), 5.32 (d, 1H, 7-H$_b$), 5.38 (dd, 1H, 3^E-H), 5.97 (ddd, 1H, 6-H), 6.26, 6.62 (2s, 2H, CONH$_2$), 7.52 (d, 1H, NH^E). $J_{2,3}$=7.1 Hz, $J_{3,4}$=6.7 Hz, $J_{4,5}$=4.6 Hz, $J_{5,6}$=7.4 Hz, $J_{6,7a}$=10.6 Hz, $J_{6,7b}$=17.7 Hz, $J_{1E,2E}$=8.1 Hz, $J_{2E,3E}$=10.6 Hz, $J_{2E,NH}$=8.1 Hz, $J_{3E,4E}$=9.5 Hz, $J_{4E,5E}$=9.9 Hz, $J_{5E,6E}$=2.5 Hz, $J_{5E,6'E}$=5.3 Hz, $J_{6E,6'E}$=11.9 Hz. ^{13}C NMR (50 MHz, $CDCl_3$, HMQC, HMBC): δ=20.76, 20.88 (CO*C*H$_3$ signals), 26.53, 27.15 (C(*C*H$_3$)$_2$), 56.73 (C-2^E), 62.37 (C-6^E), 68.93 (C-4^E), 71.93, 71.96 (C-3^E, C-5^E), 75.33 (C-4), 77.50 (C-2, C-3), 82.19 (C-5), 92.61 (CCl_3), 100.00 (C-1^E), 111.55 (*C*(CH$_3$)$_2$), 118.82 (C-7), 135.57 (C-6), 162.39 (*C*OCCl$_3$), 169.61, 170.82, 170.93 (*C*OCH$_3$), 174.50 (CONH$_2$). $C_{24}H_{33}Cl_3N_2O_{13}$ (663.89, 662.10), FAB MS: *m/z* 663.0 $[M+H]^+$, 685.0 $[M+Na]^+$.

8.6.2. 5-*O*-(Trimethylsily)-4-*O*-[3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroacetamido)-β-D-glucopyranosyl]-6,7-dideoxy-2,3-*O*-isopropylidene-L-*galacto*-hept-6-enonamide (23e). R_f: 0.38 ($CHCl_3$–EtOH 90:10). IR (KBr): 3449 (br), 3359 (br), 1750, 1688, 1529, 1374, 1239, 1040 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, HH COSY): δ=0.07 (s, 9H, Si(CH$_3$)$_3$), 1.40, 1.44 (2s, 6H, C(CH$_3$)$_2$), 1.988, 2.008, 2.063 (3s, 9H, COCH$_3$), 3.70 (ddd, 1H, 5′-H), 3.76 (dd, 1H, 4-H),

3.80 (m, 1H, 2′-H), 4.16 (dd, 1H, 6′-H), 4.26 (dd, 1H, 6′-H′), 4.29 (dd, 1H, 3-H), 4.41 (m, 1H, 5-H), 4.62 (d, 1H, 2-H), 5.02 (d, 1H, 1′-H), 5.08 (dd, 1H, 4′-H), 5.20 (d, 1H, 7-H_a), 5.31 (d, 1H, 7-H_b), 5.44 (dd, 1H, 3′-H), 5.88 (m, 1H, 6-H), 5.94, 6.52 (2s, 2H, $CONH_2$), 7.34 (d, 1H, NH′). $J_{2,3}$=6.4 Hz, $J_{3,4}$=7.7 Hz, $J_{4,5}$=2.5 Hz, $J_{5,6}$=5.7 Hz, $J_{6,7a}$=10.2 Hz, $J_{6,7b}$=17.1 Hz, $J_{1',2'}$=8.1 Hz, $J_{2',NH}$=8.1 Hz, $J_{2',3'}$=10.6 Hz, $J_{3',4'}$=9.5 Hz, $J_{4',5'}$=9.9 Hz, $J_{5',6'}$=2.5 Hz, $J_{5',6''}$=4.6, Hz $J_{6',6''}$=12.2 Hz. ^{13}C NMR (74 MHz, $CDCl_3$, APT, HMQC, HMBC): δ=0.39 ($Si(CH_3)_3$), 20.65, 20.70, 20.74 ($COCH_3$), 26.13, 27.26 ($C(CH_3)_2$), 56.75 (C-2′), 61.79 (C-6′), 68.66 (C-4′), 71.07 (C-3′), 71.96 (C-5′), 73.01 (C-5), 76.81 (C-3), 77.74 (C-2), 81.36 (C-4), 92.36 (CCl_3), 99.34 (C-1′), 111.40 ($C(CH_3)_2$), 117.03 (C-7), 138.28 (C-6), 162.11 ($COCCl_3$), 169.54, 170.67, 170.74 ($COCH_3$), 173.68 ($CONH_2$). $C_{27}H_{41}Cl_3N_2O_{13}Si$ (736.07, 734.14), FAB MS: *m/z* 757.0 $[M+Na]^+$.

8.6.3. 4,5-Di-*O*-[3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroacetamido)-β-D-glucopyranosyl]-6,7-dideoxy-2,3-*O*-isopropylidene-L-*galacto*-hept-6-enonamide (23a). R_f: 0.45 ($CHCl_3$–EtOH 90:10). IR (KBr): 3448 (br), 3366 (br), 1750, 1527, 1374, 1235, 1042 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$, HH COSY): δ=1.41, 1.43 (2s, 6H, $C(CH_3)_2$), 1.993 (s, 6H, $COCH_3$), 1.998, 2.004, 2.070, 2.075 (4s, 12H, $COCH_3$), 3.64 (m, 1H, 5^E-H), 3.75 (m, 2H, 2^E-H, 5′-H), 3.85 (dd, 1H, 4-H), 3.89 (m, 1H, 2′-H), 4.02 (d, 1H, 6^E-H), 4.16 (m, 2H, 6^E-H′, 6′-H), 4.26 (d, 1H, 6′-H′), 4.30 (dd, 1H, 5-H), 4.44 (dd, 1H, 3-H), 4.73 (d, 1H, 2-H), 4.91 (d, 1H, 1^E-H), 4.96 (dd, 1H, 4^E-H), 5.04 (m, 2H, 1′-H, 4′-H), 5.20 (d, 1H, 7-H_a), 5.28 (d, 1H, 7-H_b), 5.52 (dd, 1H, 3′-H), 5.61 (dd, 1H, 3^E-H), 6.03 (m, 1H, 6-H), 6.55 (bs, 2H, $CONH_2$), 7.73 (d, 1H, NH^E), 7.94 (bs, 1H, NH′). $J_{2,3}$=5.2 Hz, $J_{3,4}$=6.5 Hz, $J_{4,5}$=2.6 Hz, $J_{5,6}$=8.4 Hz, $J_{6,7a}$=10.5 Hz, $J_{6,7b}$=17.2 Hz, $J_{1E,2E}$=8.4 Hz, $J_{2E,3E}$=9.9 Hz, $J_{2E,NH}$=8.4 Hz, $J_{3E,4E}$=9.4 Hz, $J_{4E,5E}$=9.4 Hz, $J_{5E,6E}$=2.1 Hz, $J_{6E,6'E}$=12.0 Hz, $J_{2',3'}$=9.9 Hz, $J_{3',4'}$=9.9 Hz, $J_{5',6''}$=5.5 Hz, $J_{6',6''}$=12.0 Hz. ^{13}C NMR (50 MHz, $CDCl_3$, HMQC, HMBC): δ=20.91, 21.02, 21.15 ($COCH_3$ signals), 27.40, 28.27 ($C(CH_3)_2$), 57.03, 57.10 (C-2^E, C-2′), 62.46, 62.65 (C-6^E, C-6′), 69.15, 69.42 (C-4^E, C-4′), 70.89, 71.14 (C-5^E, C-5′), 71.95, 72.36 (C-3^E, C-3′), 77.31 (C-2), 78.14 (C-3), 81.61 (C-4), 82.67 (C-5), 92.55, 92.77 (CCl_3), 99.86 (C-1^E, C-1′), 112.15 ($C(CH_3)_2$), 118.64 (C-7), 136.94 (C-6), 162.07, 163.28 ($COCCl_3$), 164.48 (?), 169.93, 170.31, 170.89, 171.09, 171.15, 171.21 ($COCH_3$), 174.77 ($CONH_2$). $C_{38}H_{49}Cl_6N_3O_{21}$ (1096.53, 1093.10), FAB MS: *m/z* 1116.2 $[M+Na]^+$.

8.7. Phenyl carbonate protection of the mixture 22b and 23b

Phenyl chloroformate (18 μL, 22 mg, 0.14 mmol) was added to the mixture of **22b** and **23b** (57 mg, 0.086 mmol) in anhydrous CH_2Cl_2 (3 mL) and anhydrous pyridine (0.1 mL) at 0°C under an argon atmosphere. The reaction was followed by TLC (PE–ethyl acetate–triethylamine 30:70:0.1). After stirring for 1 h, the reactants were consumed. The reaction was stopped by addition of water (5 mL). After extraction with CH_2Cl_2 (3×30 mL), the combined organic phases were dried over sodium sulfate. Solvents were removed under reduced pressure. The crude product was purified by FC eluting with PE–ethyl acetate–triethylamine 30:70:0.1, to furnish after solvent evaporation **23c** (14.6 mg, 21%) and **23d** (36 mg, 53%).

8.7.1. 4-*O*-[3,4,6-Tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroacetamido)-β-D-glucopyranosyl]-6,7-dideoxy-2,3-*O*-isopropylidene-5-*O*-phenoxycarbonyl-L-*galacto*-hept-6-enonamide (23c). R_f: 0.21 (PE–ethyl acetate–TEA 30:70:1). IR (KBr): 3450 (br), 3257 (br), 1752, 1689, 1374, 1243, 1080, 1043 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, HH COSY): δ=1.42, 1.46 (2s, 6H, $C(CH_3)_2$), 2.01, 2.02, 2.07 (3s, 9H, $COCH_3$), 3.75 (ddd, 1H, 5′-H), 3.94 (ddd, 1H, 2′-H), 4.11 (m, 1H, 4-H), 4.19 (dd, 1H, 6′-H), 4.29 (dd, 1H, 6′-H′), 4.42 (dd, 1H, 3-H), 4.63 (d, 1H, 2-H), 5.06 (d, 1H, 1′-H), 5.14 (dd, 1H, 4′-H), 5.25–5.46 (m, 3H, 3′-H, 5-H, 7-H_a), 5.51 (narrow m, 1H, 7-H_b), 5.76 (d, 1H, CONH), 5.91 (ddd, 2H, 6-H), 6.55 (d, 1H, CONH′), 7.15–7.42 (m, 6H, Ar–H's, NH′). $J_{2,3}$=6.2 Hz, $J_{3,4}$=5.5 Hz, $J_{5,6}$=6.91 Hz, $J_{6,7a}$=10.3 Hz, $J_{6,7b}$=17.2 Hz, $J_{NH,NN}$=2.5 Hz, $J_{1',2'}$=8.2 Hz, $J_{3',4'}$=9.5 Hz, $J_{4',5'}$=9.9 Hz, $J_{5',6'}$=2.7 Hz, $J_{5',6''}$=4.3 Hz, $J_{6',6''}$=12.4 Hz. ^{13}C NMR (50 MHz, $CDCl_3$, HMQC, HMBC): δ=20.94, 20.99, 21.06 ($COCH_3$), 26.61, 27.47 ($C(CH_3)_2$), 56.91 (C-2′), 62.09 (C-6′), 68.79 (C-4′), 71.62 (C-3′), 72.44 (C-5′), 77.07 (C-2), 77.69 (C-3), 79.02 (C-5), 79.20 (C-4), 92.59 (CCl_3), 100.08 (C-1′), 112.13 ($C(CH_3)_2$), 121.35 (C-7), 121.43 (Ar–C-2, Ar–C-2′), 126.61 (Ar–C-4), 130.03 (Ar–C-3, Ar–C-3′), 132.36 (C-6), 151.56 (Ar–C-1), 152.89 (OCOO), 162.69 ($COCCl_3$), 169.95, 171.16, 171.29 ($COCH_3$), 173.88 ($CONH_2$). $C_{31}H_{37}Cl_3N_2O_{15}$ (784.00, 782.13), FAB MS: *m/z* 804.9 $[M+Na]^+$.

8.7.2. 5-*O*-[3,4,6-Tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroacetamido)-β-D-glucopyranosyl]-6,7-dideoxy-2,3-*O*-isopropylidene-4-*O*-phenoxycarbonyl-L-*galacto*-hept-6-enonamide (23d). R_f: 0.29 (PE–ethyl acetate–TEA 30:70:1). IR (KBr): 3441, 1751, 1688, 1374, 1245, 1078, 1045 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$, HH COSY): δ=1.44, 1.46 (2s, 6H, $C(CH_3)_2$), 2.01, 2.02, 2.08 (3s, 9H, $COCH_3$), 3.72 (ddd, 1H, 5^E-H), 3.83 (m, 1H, 2^E-H), 4.10 (dd, 1H, 6^E-H), 4.24 (dd, 1H, 6^E-H′), 4.46 (dd, 1H, 3-H), 4.56 (dd, 1H, 5-H), 4.68 (d, 1H, 2-H), 4.99 (d, 1H, 1^E-H), 5.03–5.12 (m, 2H, 4^E-H, 4-H), 5.32 (d, 1H, 7-H_a), 5.46 (d, 1H, 7-H_b), 5.54 (dd, 1H, 3^E-H), 5.95 (m, 2H, 6-H, CONH), 6.56 (d, H, CONH′), 7.16–7.41 (m, 5H, Ar–H's), 7.52 (d, 1H, NH^E). $J_{2,3}$=6.6 Hz, $J_{3,4}$=4.9 Hz, $J_{5,6}$=6.8 Hz, $J_{6,7a}$=10.3 Hz, $J_{6,7b}$=17.3 Hz, $J_{NH,NH}$=2.9 Hz, $J_{1E,2E}$=8.4 Hz, $J_{2E,NH}$=8.1 Hz, $J_{3E,4E}$=9.5 Hz, $J_{4E,5E}$=9.9 Hz, $J_{5E,6E}$=2.3 Hz, $J_{5E,6'E}$=4.9 Hz, $J_{6E,6'E}$=12.3 Hz. ^{13}C NMR (75 MHz, $CDCl_3$, HMQC, HMBC): δ=22.60, 22.65, 22.74 ($COCH_3$), 28.42, 28.93 ($C(CH_3)_2$), 58.79 (C-2^E), 64.11 (C-6^E), 70.74 (C-4^E), 73.11 (C-3^E), 73.90 (C-5^E), 78.61 (C-2), 79.28 (C-3), 80.56 (C-4), 81.67 (C-5), 94.4 (CCl_3), 100.85 (C-1^E), 113.05 ($C(CH_3)_2$), 121.79 (C-7), 123.09 (Ar–C-2, Ar–C-2′), 128.03 (Ar–C-4), 131.40 (Ar–C-3, Ar–C-3′), 136.06 (C-6), 153.20 (Ar–C-1), 155.55 (OCOO), 163.99 ($COCCl_3$), 171.52, 172.43, 172.62 ($COCH_3$), 175.11 ($CONH_2$). $C_{31}H_{37}Cl_3N_2O_{15}$ (784.00, 782.13), FAB MS: *m/z* 805 $[M+Na]^+$.

8.7.3. 6,7-Dideoxy-5-*O*-[3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroacetamido)-β-D-glucopyranosyl]-L-*galacto*-hept-6-enono-1,4-lactone (24a). $CuCl_2 \cdot 2H_2O$ (0.40 g, 2.4 mmol) was added to **22b** (0.23 g, 0.35 mmol) in

acetonitrile (5 mL). A heavy dark red precipitate was observed immediately. The reaction progress was followed by TLC ($CHCl_3$–EtOH 93:7). After heating the reaction mixture under reflux for 5 h the reactants were consumed. The solvent was removed under reduced pressure, the residue was taken up into ethyl acetate (60 mL) and extracted several times with a solution of half-saturated $NaHCO_3$ until the aqueous phase became colorless. The organic phase was dried over sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by FC eluting with $CHCl_3$–EtOH 93:7, to afford after solvent evaporation **24a** (197 mg, 94%). R_f: 0.21 ($CHCl_3$–EtOH 90:10). IR (KBr): 3463 (br), 3374 (br), 1748, 1531, 1372, 1237, 1042 cm^{-1}. ^1H NMR (600 MHz, [D_5]pyridine, HH COSY): δ=1.99, 2.00, 2.09 (3s, 9H, $COCH_3$), 3.90 (m, 1H, 5^E-H), 4.32 (d, 1H, 6^E-H), 4.50–4.56 (m, 2H, 2^E-H, 6^E-H′), 4.68 (dd, 1H, 4-H), 4.77 (dd, 1H, 5-H), 4.91 (dd, 1H, 3-H), 5.02 (d, 1H, 2-H), 5.30 (d, 1H, 7-H_a), 5.46 (dd, 1H, 4^E-H), 5.56 (m, 2H, 7-H_b, 1^E-H), 6.09 (dd, 1H, 3^E-H), 6.35 (ddd, 1H, 6-H), 10.75 (d, 1H, NH^E). $J_{2,3}$=8.5 Hz, $J_{3,4}$=7.7 Hz, $J_{4,5}$=6.2 Hz, $J_{5,6}$=7.4 Hz, $J_{6,7a}$=10.2 Hz, $J_{6,7b}$=17.4 Hz, $J_{NH,2E}$=8.2 Hz, $J_{3E,4E}$=9.7 Hz, $J_{5E,6E}$=2.3 Hz, $J_{5E,6'E}$=5.2 Hz, $J_{6E,6'E}$=11.8 Hz. ^{13}C NMR (50 MHz, [D_5]pyridine, HMQC, HMBC): δ=18.94, 19.01, 19.04 ($COCH_3$), 55.60 (C-2^E), 60.85 (C-6^E), 68.19 (C-4^E), 70.58 (C-5^E), 70.85 (C-3^E), 73.11 (C-3), 73.90 (C-2), 80.34 (C-5), 81.75 (C-4), 92.38 (CCl_3), 99.19 (C-1^E), 117.21 (C-7), 133.53 (C-6), 161.83 ($COCCl_3$), 168.30 ($COCH_3$ at C-4^E), 168.89, 168.94 ($COCH_3$ at C-3^E and C-6^E), 173.98 (C-1). $C_{21}H_{26}Cl_3NO_{13}$ (606.79, 605.05), FAB MS: *m/z* 606.0 $[M+H]^+$, 628.0 $[M+Na]^+$.

8.7.4. 2,3-Di-*O*-acetyl-6,7-dideoxy-5-*O*-[3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroacetamido)-β-D-glucopyranosyl]-L-*galacto*-hept-6-enono-1,4-lactone (24b). Acetic anhydride (0.5 mL) was added to **24a** (19 mg, 0.031 mmol) dissolved in a minimum amount of anhydrous pyridine. After stirring the reaction mixture overnight, the solvent was removed under reduced pressure and the residue was purified by FC eluting with ethyl acetate–PE 1:1, to afford after solvent evaporation pure **24b** (15.2 mg, 70%). IR (KBr): 3455 (br), 1799 (s), 1751, 1372, 1236, 1044 cm^{-1}. ^1H NMR (400 MHz, [D_5]pyridine, HH COSY): δ=1.99, 2.01, 2.06, 2.09, 2.10 (5s, 15H, $COCH_3$), 3.92 (ddd, 1H, 5^E-H), 4.31 (dd, 1H, 6^E-H), 4.50 (dd, 1H, 6^E-H′), 4.61 (m, 1H, 2^E-H), 4.85 (dd, 1H, 5-H), 4.91 (dd, 1H, 4-H), 5.29 (d, 1H, 7-H_a), 5.43–5.52 (m, 3H, 1^E-H, 4^E-H, 7-H_b), 6.01–6.06 (m, 2H, 3-H, 3^E-H), 6.10 (ddd, 1H, 6-H), 6.30 (d, 1H, 2-H), 10.66 (d, 1H, NH^E). $J_{2,3}$=7.1 Hz, $J_{3,4}$=6.7 Hz, $J_{4,5}$=6.4 Hz, $J_{5,6}$=7.4 Hz, $J_{6,7a}$=10.6 Hz, $J_{6,7b}$=17.0 Hz, $J_{NH,2E}$=8.7 Hz, $J_{5E,6E}$=2.5 Hz, $J_{5E,6'E}$=5.3 Hz, $J_{6E,6'E}$=12.4 Hz. ^{13}C NMR: (50 MHz, [D_5]pyridine, HMQC, HMBC): δ=20.38, 20.59, 20.62, 20.68, 20.71 ($COCH_3$), 57.03 (C-2^E), 62.61 (C-6^E), 69.81 (C-4^E), 72.44 (C-5^E), 72.74, 73.50 (C-3, C-3^E), 73.80 (C-2), 81.29 (C-5), 82.42 (C-4), 94.13 (CCl_3), 100.10 (C-1^E), 120.31 (C-7), 134.14 (C-6), 163.61 ($COCCl_3$), 169.84, 170.14, 170.38, 170.41, 170.70, 170.85 (*C*O). $C_{25}H_{30}Cl_3NO_{15}$ (690.87, 689.07), FAB MS: *m/z* 690.0 $[M+H]^+$, 712.0 $[M+Na]^-$.

8.7.5. 6,7-Dideoxy-2-*O*-phenoxycarbonyl-5-*O*-[3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroacetamido)-β-D-glucopyranosyl]-L-*galacto*-hept-6-enono-1,4-lactone (24c). Phenyl chloroformate (13.2 μL, 16.4 mg, 0.11 mmol) was added to **24a** (60.4 mg, 0.10 mmol) and anhydrous pyridine (0.1 mL) in anhydrous CH_2Cl_2 (4 mL) at −20°C under an argon atmosphere. The reaction progress was followed by TLC ($CHCl_3$–MeOH 90:10). After stirring the reaction mixture for 2 h, the reactants were consumed. The reaction was stopped by adding water (5 mL). After extraction with CH_2Cl_2 (3×30 mL), the combined organic phases were dried over sodium sulfate, and the solvent was removed under reduced pressure. The crude product was purified by FC eluting with $CHCl_3$–MeOH 90:10, to furnish **24c** (50.1 mg, 70%). R_f: 0.29 ($CHCl_3$–EtOH 90:10). IR (KBr): 3425 (br), 1796 (s), 1751, 1372, 1239, 1043 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, HH COSY): δ=1.95, 1.96, 2.01 (3s, 9H, $COCH_3$), 3.63 (ddd, 1H, 5^E-H), 3.99 (m, 1H, 2^E-H), 4.04 (dd, 1H, 6^E-H), 4.18 (dd, 1H, 6^E-H′), 4.23 (dd, 1H, 4-H), 4.30 (dd, 1H, 5-H), 4.60 (dd, 1H, 3-H), 4.80 (d, 1H, 1^E-H), 5.02 (dd, 1H, 4^E-H), 5.22–5.40 (m, 4H, 2-H, 7-H_a, 7-H_b, 3^E-H), 5.91 (ddd, 1H, 6-H), 7.13–7.35 (m, 6H, Ar–H's, NH^E). $J_{2,3}$=8.1 Hz, $J_{3,4}$=7.8 Hz, $J_{4,5}$=5.0 Hz, $J_{5,6}$=7.4 Hz, $J_{6,7a}$=10.6 Hz, $J_{6,7b}$=17.7 Hz, $J_{1E,2E}$=8.1 Hz, $J_{3E,4E}$=9.5 Hz, $J_{5E,6E}$=2.5 Hz, $J_{5E,6'E}$=5.0 Hz, $J_{6E,6'E}$=12.4 Hz. ^{13}C NMR: (75 MHz, $CDCl_3$, HMQC, HMBC): δ=20.46, 20.47, 20.63 ($COCH_3$), 55.81 (C-2^E), 61.80 (C-6^E), 68.18 (C-4^E), 71.45 (C-3), 71.62 (C-3^E), 72.02 (C-5^E), 78.39 (C-2), 79.48 (C-5), 82.07 (C-4), 92.13 (CCl_3), 99.89 (C-1^E), 120.58 (C-7), 120.69 (Ar–C-2, Ar–C-2′), 126.54 (Ar–C-4), 129.52 (?), 129.57 (Ar–C-3, Ar–C-3′), 132.33 (C-6), 150.67 (Ar–C-1), 153.13 (OCOO), 162.28 ($COCCl_3$), 168.11 (C-1), 169.26 ($COCH_3$ at C-4^E), 170.76 ($COCH_3$ at C-6^E), 170.97 ($COCH_3$ at C-3^E). $C_{28}H_{30}Cl_3NO_{15}$ (726.90, 725.07), FAB MS: *m/z* 748.0 $[M+Na]^+$.

8.7.6. 3-*O*-Acetyl-6,7-dideoxy-2-*O*-phenoxycarbonyl-5-*O*-[3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroacetamido)-β-D-glucopyranosyl]-L-*galacto*-hept-6-enono-1,4-lactone (24d). Acetic anhydride (0.5 mL) was added to **24c** (60.4 mg, 0.083 mmol) dissolved in a minimum amount of anhydrous pyridine. After stirring the reaction mixture overnight, the solvent was removed under reduced pressure and the residue was purified by FC eluting with ethyl acetate–PE 1:1, to afford after solvent evaporation pure **24d** (47.5 mg, 75%). IR (KBr): 3420 (br), 1752, 1372, 1235, 1044 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, HH COSY): δ=1.97 (s, 6H, $COCH_3$), 2.01, 2.05 (2s, 6H, $COCH_3$), 3.65 (ddd, 1H, 5^E-H), 4.01 (m, 1H, 2^E-H), 4.06 (dd, 1H, 6^E-H), 4.17 (dd, 1H, 6^E-H′), 4.24 (dd, 1H, 5-H), 4.34 (dd, 1H, 4-H), 4.84 (d, 1H, 1^E-H), 5.04 (dd, 1H, 4^E-H), 5.25–5.40 (m, 3H, 7-H_a, 7-H_b, 3^E-H), 5.39 (d, 1H, 2-H), 5.61 (dd, 1H, 3-H), 5.81 (ddd, 1H, 6-H), 7.10–7.38 (m, 6H, Ar–Hs, NH^E). $J_{2,3}$=7.2 Hz, $J_{3,4}$=6.7 Hz, $J_{4,5}$=5.7 Hz, $J_{5,6}$=7.5 Hz, $J_{6,7a}$=10.2 Hz, $J_{6,7b}$=17.3 Hz, $J_{1E,2E}$=8.1 Hz, $J_{4E,5E}$=9.9 Hz, $J_{5E,6E}$=2.5 Hz, $J_{5E,6'E}$=5.2 Hz, $J_{6E,6'E}$=11.9 Hz. ^{13}C NMR: (50 MHz, $CDCl_3$, HMQC, HMBC): δ=20.68, 20.72, 20.84 ($COCH_3$ signals), 56.20 (C-2^E), 62.14 (C-6^E), 68.58 (C-4^E), 71.92 (C-3^E), 72.22 (C-3, C-5^E), 76.13 (C-2), 81.14 (C-4), 81.54 (C-5), 92.46 (CCl_3), 100.51 (C-1^E), 120.72 (C-7), 120.98 (Ar–C-2, C-2′), 126.79 (Ar–C-4), 129.83 (Ar–C-3, Ar–C-3′), 129.93 (?), 132.27 (C-6), 150.00 (Ar–C-1), 152.83 (OCOO), 162.21 ($COCCl_3$), 167.38 (C-1), 169.46 ($COCH_3$ at C-4^E), 169.88 ($COCH_3$ at C-3), 170.72 ($COCH_3$ at C-6^E), 170.98 ($COCH_3$ at C-3^E). $C_{30}H_{32}Cl_3NO_{16}$ (768.94, 767.08), FAB MS: *m/z* 790.0 $[M+Na]^+$.

8.8. Attempted phenyl carbonate cleavage from 24d

A mixture of **24d** (27.8 mg, 0.036 mmol), imidazole (60 mg, 0.88 mmol) and water (40 μL) in dioxane (4 mL) was stirred at room temperature for 24 h. Monitoring by TLC ($CHCl_3$–EtOH 90:10) revealed that no reaction took place.

8.8.1. 2-*O*-(*tert*-Butyldimethylsilyl)-6,7-dideoxy-5-*O*-[3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroacetamido)-β-D-glucopyranosyl]-L-*galacto*-hept-6-enono-1,4-lactone (24f). TBDMS–OTf (34 μL, 1.15 mmol) was injected into a reaction flask containing **24a** (48.4 mg, 0.079 mmol) and anhydrous pyridine (30 μL) in anhydrous CH_2Cl_2 (2 mL) under an argon atmosphere at −50°C. The reaction was followed by TLC (toluene–acetone 1:1). After stirring at −50°C for 5 h, the reaction was stopped by the addition of saturated aq. Na_2CO_3 (2 mL). After extraction with with CH_2Cl_2 (3×15 mL), the combined phases were dried over sodium sulfate, and the solvent was removed under reduced pressure. The crude product was purified by FC eluting with ethyl acetate–PE 60:40, to afford after solvent evaporation **24f** (50.4 mg, 89%). R_f: 0.23 (PE–ethyl acetate 1:1). IR (KBr): 3505 (br), 3421 (br), 1789 (s), 1752, 1726 (s), 1236, 1154, 1042 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$, HH COSY): δ=0.15, 0.18 (2s, 6H, $Si(CH_3)_2$), 0.92 (s, 9H, $C(CH_3)_3$), 2.03 (s, 6H, $COCH_3$), 2.08 (1s, 3H, $COCH_3$), 3.69 (ddd, 1H, 5^E-H), 3.90–4.40 (m, 7H, 2-H, 3-H, 4-H, 5-H, 2^E-H, CH_2-6^E), 4.87 (d, 1H, 1^E-H), 5.09 (dd, 1H, 4^E-H), 5.26–5.48 (m, 3H, 7-H_a, 7-H_b, 3^E-H), 5.97 (ddd, 1H, 6-H), 7.19 (d, 1H, NH^E). $J_{5,6}$=7.3 Hz, $J_{6,7a}$=10.3 Hz, $J_{6,7b}$=17.4 Hz, $J_{1E,2E}$=8.1 Hz, $J_{2E,NH}$=9.2 Hz, $J_{3E,4E}$=9.5 Hz, $J_{4E,5E}$=9.9 Hz, $J_{5E,6E}$=2.2, 4.8 Hz. ^{13}C NMR (50 MHz, $CDCl_3$, HETCOR): δ=−4.91, −4.58 ($Si(CH_3)_2$), 18.39 ($C(CH_3)_3$), 20.66, 20.85 ($COCH_3$ signals), 22.81 (?), 25.76 ($C(CH_3)_3$), 56.07 (C-2^E), 62.03 (C-6^E), 68.36 (C-4^E), 71.98, 72.32 (C-3^E, C-5^E), 74.65, 75.15, 80.35, 81.46 (C-2, C-3, C-4, C-5), 92.37 (CCl_3), 100.37 (C-1^E), 120.64 (C-7), 132.89 (C-6), 162.43 ($COCCl_3$), 169.40, 170.78, 171.10, 172.55 (CO). $C_{27}H_{40}Cl_3NO_{13}Si$ (721.06, 719.13), FAB MS: *m/z* 742.0 $[M+Na]^+$.

8.8.2. 3-*O*-Acetyl-2-*O*-(*tert*-butyldimethylsilyl)-6,7-dideoxy-5-*O*-[3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroacetamido)-β-D-glucopyranosyl]-L-*galacto*-hept-6-enono-1,4-lactone (24g). Acetic anhydride (0.5 mL) was added to **24f** (122.8 mg, 0.17 mmol) in anhydrous pyridine (0.4 mL). The reaction mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure and the residue was purified by FC eluting with PE–ethyl acetate1:1 to afford after solvent evaporation **24g** (121 mg, 94%) R_f: 0.47 ($CHCl_3$–EtOH 90:10). IR (KBr): 3499 (br), 1802 (s), 1750, 1529, 1371, 1235, 1043 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, HH COSY): δ=0.08, 0.11 (2s, 6H, $Si(CH_3)_2$), 0.85 (s, 9H, $C(CH_3)_3$), 1.96, 1.97, 2.02, 2.05 (4s, 12H, $COCH_3$), 3.62 (ddd, 1H, 5^E-H), 4.02–4.09 (m, 2H, 2^E-H, 6^E-H), 4.13–4.20 (m, 3H, 4-H, 5-H, 6^E-H′), 4.35 (d, 1H, 2-H), 4.76 (d, 1H, 1^E-H), 5.03 (dd, 1H, 4^E-H), 5.21–5.34 (m, 4H, 3-H, 7-H_a, 7-H_b, 3^E-H), 5.28 (ddd, 1H, 6-H), 7.04 (d, 1H, NH^E). $J_{2,3}$=6.7 Hz, $J_{5,6}$=7.2 Hz, $J_{6,7a}$=10.5 Hz, $J_{6,7b}$=17.5 Hz, $J_{1E,2E}$=8.1 Hz, $J_{2E,NH}$=9.2 Hz, $J_{5E,6E}$=2.5 Hz, $J_{5E,6'E}$=5.2 Hz, $J_{6E,6'E}$=12.2 Hz. ^{13}C NMR (50 MHz, $CDCl_3$, HMQC, HMBC): δ=−5.35, −4.75 ($Si(CH_3)_2$), 18.21 ($C(CH_3)_3$), 20.66, 20.71, 20.84 ($COCH_3$ signals), 25.53 ($C(CH_3)_3$), 55.89 (C-2^E), 62.04 (C-6^E), 68.40 (C-4^E), 72.13, 72.18 (C-3^E, C-5^E), 72.90 (C-2), 74.52 (C-3), 80.95, 81.20 (C-4, C-5), 92.44 (CCl_3), 100.97 (C-1^E), 120.18 (C-7), 132.67 (C-6), 162.06 ($COCCl_3$), 169.31 ($COCH_3$ at C-4^E), 169.68 ($COCH_3$ at C-3), 170.57 ($COCH_3$ at C-6^E), 170.71 ($COCH_3$ at C-3^E), 171.28 (C-1). $C_{29}H_{42}Cl_3NO_{14}Si$ (763.09, 761.14), FAB MS: *m/z* 784.2 $[M+Na]^+$.

8.8.3. 5-*O*-[3,4,6-Tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroacetamido)-β-D-glucopyranosyl]-6,7-dideoxy-2-*O*-(*tert*-butyldimethylsilyl)-3-*O*-acetyl-L-*galacto*-hept-6-enonamide (25a). Ammonia was bubbled through a solution of **24g** (20 mg, 0.026 mmol) in THF (2 mL) at 0°C. The reaction was monitored by TLC using ethyl acetate. After 8 h the reactants were consumed, the solvent was removed under reduced pressure, and the crude product was purified by FC eluting with ethyl acetate to furnish after solvent evaporation **25a** (19.2 mg, 94%). R_f: 0.52 (ethyl acetate). IR (KBr): 3469, 1747, 1533, 1238, 1043 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, HH COSY): δ=0.08, 0.12 (2s, 6H, $Si(CH_3)_2$), 0.85 (s, 9H, $C(CH_3)_3$), 1.966, 1.973, 2.03, 2.05 (4s, 12H, $COCH_3$), 3.62 (ddd, 1H, 5^E-H), 4.02–4.09 (m, 2H, 2^E-H, 6^E-H), 4.12–4.20 (m, 3H, 4-H, 5-H, 6^E-H′), 4.35 (d, 1H, 2-H), 4.76 (d, 1H, 1^E-H), 5.04 (dd, 1H, 4^E-H), 5.12–5.35 (m, 4H, 3-H, 7-H_a, 7-H_b, 3^E-H), 5.82 (ddd, 1H, 6-H), 5.92, 6.57 (2s, 2H, $CONH_2$), 7.08 (d, 1H, NH). $J_{2,3}$=6.7 Hz, $J_{5,6}$=6.9 Hz, $J_{6,7a}$=10.2 Hz, $J_{6,7b}$=17.2 Hz, $J_{1E,2E}$=8.5 Hz, $J_{2E,NH}$=9.2 Hz, $J_{4E,5E}$=9.9 Hz, $J_{5E,6E}$=2.5 Hz, $J_{5E,6'E}$=5.0 Hz. ^{13}C NMR (50 MHz, $CDCl_3$, HMQC, HMBC): δ=−5.09, −4.89 ($Si(CH_3)_2$), 18.28 ($C(CH_3)_3$), 20.75, 20.81, 20.88, 21.30 ($COCH_3$), 25.96 ($C(CH_3)_3$), 55.77 (C-2^E), 62.28 (C-6^E), 68.74 (C-4^E), 70.17, 72.04 (C-3^E, C-5^E), 72.44 (C-2), 72.85, 73.82 (C-3, C-4), 84.38 (C-5), 92.60 (CCl_3), 101.48 (C-1^E), 118.14 (C-7), 135.66 (C-6), 162.94 ($COCCl_3$), 169.43, 170.16, 170.74, 171.21 ($COCH_3$), 175.55 ($CONH_2$). $C_{29}H_{45}Cl_3N_2O_{14}Si$ (780.13, 778.17), FAB MS: *m/z* 779.1 $[M+H]^+$, 801.1 $[M+Na]^+$.

8.9. TBDMS cleavage of 25a

A solution of tetrabutylammonium fluoride in THF (1 M, 150 μL, 0.15 mmol) was added to **25a** (104 mg, 0.13 mmol) in anhydrous THF (2 mL) at −13°C. The reaction progress was followed by TLC ($CHCl_3$–EtOH 90:10). After stirring for 1 h the reactants were consumed. The reaction was worked up by the addition of half-saturated ammonium chloride solution (2 mL) and extraction with ethyl acetate (3×20 mL). The combined organic phases were dried over sodium sulfate, and the solvent was removed under reduced pressure. The crude products were purified by FC eluting with ethyl acetate to afford after solvent evaporation **25b** (41.2 mg, 46%) and **25c** (33.4 mg, 38%).

8.9.1. 3-*O*-Acetyl-5-*O*-[3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroacetamido)-β-D-glucopyranosyl]-6,7-dideoxy-L-*galacto*-hept-6-enonamide (25b). R_f: 0.42 ($CHCl_3$–EtOH 90:10). IR (KBr): 3436, 1793 (s), 1749, 1530, 1373, 1235, 1043 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, HH COSY): δ=1.96 (s, 6H, $COCl_3$), 2.01, 2.02 (2s, 6H, $COCH_3$), 3.64 (m, 1H, 5^E-H), 3.86 (dd, 1H, 4-H), 3.98 (dd, 1H, 5-H), 4.01–4.08 (m, 2H, 2^E-H, 6^E-H), 4.17 (dd, 1H, 6^E-H′), 4.46 (bs, 1H, 2-H), 4.75 (d, 1H, 1^E-H), 5.02 (dd, 1H, 4^E-H), 5.17–5.35 (m, 4H, 3-H, 7-H_a, 7-H_b, 3^E-H), 5.90 (ddd, 1H, 6-H), 6.00, 6.79

(2s, 2H, $CONH_2$), 7.61 (d, 1H, NH). $J_{4,5}$=5.0 Hz, $J_{5,6}$=7.6 Hz, $J_{6,7a}$=10.2 Hz, $J_{6,7b}$=17.5 Hz, $J_{1E,2E}$=8.4 Hz, $J_{2E,NH}$=7.8 Hz, $J_{3E,4E}$=9.4 Hz, $J_{4E,5E}$=9.9 Hz, $J_{5E,6E}$= 2.6 Hz, $J_{5E,6'E}$=5.2 Hz, $J_{6E,6'E}$=12.0 Hz. ^{1}H NMR (400 MHz, $CDCl_3$+D_2O): Similar to the previous data, but there was no signal at δ=6.00, 6.79 and 7.61. ^{13}C NMR (50 MHz, $CDCl_3$, HMQC, HMBC): δ=20.77, 20.91, 21.12 (CO*C*H$_3$ signals), 56.50 (C-2^E), 62.18 (C-6^E), 68.53 (C-4^E), 71.33 (C-2), 72.06, 72.12 (C-3^E, C-5^E), 72.42, 73.20 (C-3, C-4), 82.66 (C-5), 92.37 (CCl_3), 100.18 (C-1^E), 119.97 (C-7), 134.85 (C-6), 163.29 (*C*OCCl$_3$), 169.53, 170.38, 170.84, 171.16 (*C*OCH$_3$), 174.13 ($CONH_2$). $C_{23}H_{31}Cl_3N_2O_{14}$ (665.86, 664.08), FAB MS: *m/z* 665.1 $[M+H]^+$, 687.1 $[M+Na]^+$.

8.9.2. 4-*O*-Acetyl-5-*O*-[3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroacetamido)-β-D-glucopyranosyl]-6,7-dideoxy-L-*galacto*-hept-6-enonamide (25c). R_f: 0.37 ($CHCl_3$–EtOH 90:10). IR (KBr): 3450, 1745, 1675, 1374, 1239, 1043 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$, HH COSY): δ=1.94, 1.95, 2.00, 2.01 (4s, 12H, $COCH_3$), 3.64 (m, 1H, 5^E-H), 3.81 (doublet-type signal, 1H, 2-H), 4.04 (dd, 1H, 6^E-H), 4.12–4.15 (m, 3H, 2^E-H, 6^E-H′, 2-OH), 4.25 (m, 1H, 3-H), 4.53 (d, 1H, 5-H), 4.81 (d, 1H, 3-OH), 4.86 (d, 1H, 1^E-H), 4.96–4.98 (m, 2H, 4-H, 4^E-H), 5.08 (d, 1H, 7-H$_a$), 5.12 (dd, 1H, 3^E-H), 5.24 (d, 1H, 7-H$_b$), 5.72 (ddd, 1H, 6-H), 5.91, 6.87 (2s, 2H, $CONH_2$), 8.28 (d, 1H, NH). $J_{2,2\text{-OH}}$=6.3 Hz, $J_{3,3\text{-OH}}$=7.8 Hz, $J_{5,6}$=5.5 Hz, $J_{6,7a}$=10.5 Hz, $J_{6,7b}$=16.7 Hz, $J_{1E,2E}$=8.4 Hz, $J_{2E,NH}$=9.4 Hz, $J_{3E,4E}$= 9.4 Hz, $J_{5E,6'E}$<1 Hz, $J_{5E,6'E}$=4.7 Hz, $J_{6E,6'E}$=11.5 Hz. ^{1}H NMR (300 MHz, $CDCl_3$+D_2O, HH COSY): δ=2.00, 2.01, 2.06, 2.09 (4s, 12H, $COCH_3$), 3.72 (ddd, 1H, 5^E-H), 3.89 (d, 1H, 2-H), 4.11 (dd, 1H, 6^E-H), 4.16–4.23 (m, 2H, 2^E-H, 6^E-H′), 4.31 (dd, 1H, 3-H), 4.61 (dd, 1H, 5-H), 4.90–4.96 (m, 2H, 1^E-H, 3^E-H), 5.01 (dd, 1H, 4^E-H), 5.17 (dm, 1H, 7-H$_a$), 5.25 (dd, 1H, 4-H), 5.33 (d, 1H, 7-H$_b$), 5.79 (ddd, 1H, 6-H). $J_{2,3}$=1.4 Hz, $J_{3,4}$=9.9 Hz, $J_{4,5}$=1.4 Hz, $J_{5,6}$= 5.3 Hz, $J_{6,7a}$=10.8 Hz, $J_{6,7b}$=16.6 Hz, $J_{1E,2E}$=8.5 Hz, $J_{2E,NH}$=8.8 Hz, $J_{4E,5E}$=9.9 Hz, $J_{5E,6E}$=2.7, 5.5 Hz, $J_{6E,6'E}$= 12.2 Hz. ^{13}C NMR (50 MHz, $CDCl_3$, HMQC, HMBC): δ=20.75, 20.81, 21.85, 21.05 (CO*C*H$_3$), 55.50 (C-2^E), 62.47 (C-6^E), 68.68 (C-3), 69.34 (C-4^E), 71.77 (C-2), 72.05 (C-5^E), 72.72 (C-3^E), 74.17 (C-4), 78.68 (C-5), 92.68 (CCl_3), 101.19 (C-1^E), 117.07 (C-7), 135.56 (C-6), 162.77 (*C*OCCl$_3$), 169.52, 170.77, 170.84, 172.15 (*C*OCH$_3$), 174.92 ($CONH_2$). $C_{23}H_{31}Cl_3N_2O_{14}$ (665.86, 664.08), FAB MS: *m/z* 665.0 $[M+H]^+$, 687.0 $[M+Na]^+$.

8.9.3. 3-*O*-Acetyl-6,7-dideoxy-5-*O*-[3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroacetamido)-β-D-glucopyranosyl]-L-*galacto*-hept-6-enono-1,4-lactone (24h). Tetrabutylammonium fluoride trihydrate (95 mg, 0.12 mmol) in THF (2 mL) was added to **24g** (95 mg, 0.12 mmol) in THF (2 mL) at −13°C. The reaction progress was followed by TLC (ethyl acetate). After stirring for 20 min, the reactants were consumed. The reaction was stopped by the addition of half-saturated NH_4Cl solution (2 mL), then extracted several times with ethyl acetate. The combined organic phases were dried over sodium sulfate, the solvent was removed under reduced pressure, the residue was purified by FC eluting with ethyl acetate to afford after solvent evaporation **24h** (76.4 mg, 98%). R_f: 0.40 ($CHCl_3$–EtOH 90:10). IR (KBr): 3436 (br), 1764, 1373, 1238, 1042 cm^{-1}. ^{1}H NMR (200, 400 MHz, $CDCl_3$, HH COSY): δ=1.95, 1.96, 2.03, 2.06 (4s, 12H, $COCH_3$), 3.66 (ddd, 1H, 5^E-H), 3.97–4.12 (m, 3H, 2^E-H, CH_2-6^E), 4.18–4.26 (m, 2H, 4-H, 5-H), 4.47 (d, 1H, 2-H), 4.82 (d, 1H, 1^E-H), 5.02 (dd, 1H, 4^E-H), 5.22–5.36 (m, 4H, 7-H$_a$, 7-H$_b$, 3^E-H, 3-H), 5.85 (ddd, 1H, 6-H), 7.26 (d, 1H, NH). $J_{5,6}$=7.4, Hz $J_{6,7a}$= 10.6 Hz, $J_{6,7b}$=17.7 Hz, $J_{1E,2E}$=8.1 Hz, $J_{2E,NH}$=9.2 Hz, $J_{4E,5E}$=9.9 Hz, $J_{5E,6E}$=2.5, 4.6 Hz. ^{13}C NMR (50 MHz, $CDCl_3$, HMQC, HMBC): δ=20.74, 20.89, 21.10, 21.19 (CO*C*H$_3$), 56.13 (C-2^E), 62.15 (C-6^E), 68.59 (C-4^E), 72.06, 72.17 (C-3^E, C-5^E), 72.80 (C-2), 75.73 (C-3), 81.42, 81.55 (C-4, C-5), 92.45 (CCl_3), 100.57 (C-1^E), 120.49 (C-7), 132.93 (C-6), 162.47 (*C*OCCl$_3$), 169.53, 170.87, 170.91, 171.21, 172.50 (C-1). $C_{23}H_{28}Cl_3NO_{14}$ (648.83, 647.06), FAB MS: *m/z* 648.1 $[M+H]^+$, 670.1 $[M+Na]^+$.

8.10. Ammonia opening of 24h

Ammonia was bubbled through a solution of **24h** (71 mg, 0.11 mmol) in THF (2 mL) at 0°C. The reaction was monitored by TLC using ethyl acetate. After 5 h the reactants were consumed, the solvent was removed under reduced pressure, and the crude product was purified by FC eluting with ethyl acetate to furnish after solvent evaporation **25b** and **25c** (59 mg, 82%).

8.10.1. 4-*O*-Acetyl-2,6-anhydro-7-deoxy-7-iodo-5-*O*-[3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroacetamido)-β-D-glucopyranosyl]-D-*glycero*-L-*galacto*-heptonamide (26). Compound **25b** (22.7 mg, 0.034 mmol) and mercuric trifluoroacetate (29.19 mg, 0.068 mmol) were dissolved in 4 mL of anhydrous THF under an argon atmosphere. After stirring the reaction mixture at room temperature for 48 h the reactants were consumed as indicated by TLC ($CHCl_3$–MeOH 80:20). KCl (15 mg, 0.20 mmol) dissolved in a minimum amount of water was added. The mixture was then stirred for 90 min until all reactants were consumed as indicated by TLC ($CHCl_3$–MeOH 90:10). Solvents were removed under reduced pressure. The residue and I_2 (16.8 mg, 0.066 mmol) were dissolved in anhydrous THF (2 mL) under an argon atmosphere, the reaction was monitored by TLC ($CHCl_3$–EtOH 95:5). After stirring for 4 h the reaction was stopped by the addition of sodium thiosulfate dissolved in a minimum amount of water. After stirring until the solution became colorless, the reaction mixture was diluted with ethyl acetate, dried over sodium sulfate, and the solvents were removed under reduced pressure. The crude product was purified by FC eluting with $CHCl_3$–EtOH 95:5, to afford after solvent evaporation **26** (7.5 mg, 28%). R_f: 0.53 ($CHCl_3$–EtOH 90:10). ^{1}H NMR (300 MHz, $CDCl_3$, HH COSY): δ=2.01, 2.05, 2.12, 2.16 (4s, 12H, $COCH_3$), 3.92 (dd, 1H, 7^F-H), 4.00 (ddd, 1H, 5^E-H), 4.14 (dd, 1H, 7^F-H′), 4.29 (m, 1H, 2^E-H), 4.36 (dd, 1H, 6^E-H), 4.50 (dd, 1H, 6^E-H′), 4.78 (d, 1H, 2^F-H), 4.91 (m, 1H, 6^F-H), 5.06 (dd, 1H, 5^F-H), 5.37 (m, 1H, 3^F-H), 5.53 (dd, 1H, 4^E-H), 5.68–5.72 (m, 2H, 4^F-H, 1^E-H), 6.18 (dd, 1H, 3^E-H), 7.79, 8.60 (2s, 2H, $CONH_2$), 10.66 (d, 1H, NH). $J_{2F,3F}$=1.7 Hz, $J_{4F,5F}$=9.8 Hz, $J_{5F,6F}$=5.9 Hz, $J_{6F,7F}$=3.3 Hz, $J_{6F,7'F}$<1 Hz, $J_{7F,7F'}$=11.3 Hz, $J_{NHF,NHF}$=2.2 Hz, $J_{1E,2E}$=10.2 Hz, $J_{2E,NH}$= 8.0 Hz, $J_{2E,3E}$=10.6 Hz, $J_{3E,4E}$=9.2 Hz, $J_{4E,5E}$=9.9 Hz, $J_{5E,6E}$=2.5 Hz, $J_{5E,6'E}$=4.7 Hz, $J_{6E,6'E}$=12.1 Hz. ^{13}C NMR: (75 MHz, $CDCl_3$, HMQC, HMBC): δ=3.60 (C-7^F), 20.10, 20.19, 20.42, 21.07 (CO*C*H$_3$), 56.98 (C-2^E), 61.92 (C-6^E),

67.47 (C-3^F), 69.24 (C-4^E), 71.22 (C-3^E), 71.84 (C-5^E), 72.66, 72.71 (C-2^F, C-4^F), 74.68 (C-5^F), 76.43 (C-6^F), 93.33 (CCl_3), 100.40 (C-1^E), 162.70 (*C*$OCCl_3$), 169.48, 170.01, 170.10, 170.13 (*C*OCH_3), 171.45 ($CONH_2$). $C_{23}H_{30}Cl_3IN_2O_{14}$ (791.76, 789.98), FAB MS: *m/z* 789.9 $[M+H]^+$, 812.9 $[M+Na]^+$.

8.10.2. 4-*O*-Acetyl-3,6-anhydro-7-deoxy-7-iodo-5-*O*-[3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroacetamido)-β-D-glucopyranosyl]-Ξ-*glycero*-L-*galacto*-heptonamide (27). Following the procedure used to prepare **26**, compound **25c** (33.1 mg, 0.050 mmol), mercuric trifluoroacetate (30 mg, 0.070 mmol), anhydrous THF (4 mL) and I_2 (17.0 mg, 0.067 mmol) afforded **27** (17.2 mg, 44%). R_f: 0.44 ($CHCl_3$–EtOH 90:10). ^{1}H NMR (400 MHz, $CDCl_3$, HH COSY): δ=1.98, 2.01, 2.04, 2.10 (4s, 12H, $COCH_3$), 3.56 (dd, 1H, 7-H), 3.68 (dd, 1H, 7-H′), 3.97 (ddd, 1H, 5^E-H), 4.39 (dd, 1H, 6^E-H), 4.44 (dd, 1H, 6^E-H′), 4.52 (m, 1H, 6-H), 4.65 (m, 1H, 2^E-H), 4.72 (dd, 1H, 3-H), 4.78 (dd, 1H, 5-H), 4.85 (d, 1H, 2-H), 5.50 (dd, 1H, 4^E-H), 5.61 (d, 1H, 1^E-H), 6.00 (dd, 1H, 3^E-H), 6.24 (dd, 1H, 4-H), 8.23, 8.49 (2s, 2H, $CONH_2$), 10.62 (d, 1H, NH). $J_{2,3}$=5.8 Hz, $J_{3,4}$=4.5 Hz, $J_{4,5}$=2.6 Hz, $J_{5,6}$=4.7 Hz, $J_{6,7}$=8.9 Hz, $J_{6,7'}$=4.7 Hz, $J_{7,7'}$=9.9 Hz, $J_{1E,2E}$=8.4 Hz, $J_{2E,NH}$=8.9 Hz, $J_{2E,3E}$=10.2 Hz, $J_{3E,4E}$=9.4 Hz, $J_{4E,5E}$=9.9 Hz, $J_{5E,6E}$=2.1 Hz, $J_{5E,6'E}$=4.7 Hz, $J_{6E,6'E}$=12.0 Hz. ^{13}C NMR: (75 MHz, $CDCl_3$, HMQC, HMBC): δ=3.67 (C-7), 20.79, 20.88, 21.03, 21.11 (CO*C*H_3), 56.84 (C-2^E), 62.61 (C-6^E), 69.92 (C-4^E), 72.63 (C-5^E), 73.08, 73.19 (C-2, C-3^E), 78.92 (C-4), 82.19, 82.33 (C-5, C-6), 84.74 (C-3), 94.11 (CCl_3), 99.60 (C-1^E), 163.72 (*C*$OCCl_3$), 170.14, 170.74, 170.80, 170.86 (*C*OCH_3), 175.60 ($CONH_2$). $C_{23}H_{30}Cl_3IN_2O_{14}$ (791.76, 789.98), FAB MS: *m/z* 789.8 $[M+H]^+$, 812.8 $[M+Na]^+$.

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