

An Expedient Synthesis of *N*-Acetylneuraminic Acid α -C-Glycosyl Derivatives (“ α -C-Glycosides”) from the Anomeric Acetates

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The reductive metallation of the readily available peracetylated derivatives of methyl *N*-acetylneuramate **3a** and **3b** by samarium diiodide without any additive generates the corresponding anomeric samarium(III) organometallics. These intermediates react efficiently with carbonyl compounds under Barbier conditions, providing a fast synthesis of C-ketosides. The α - and β -acetates are equally effective,

and excellent yields are obtained for coupling with cyclic ketones. The procedure has been conveniently applied to the synthesis of a C-ketoside of *N*-acetylneuraminic acid with an attached linker, ready to use as a building block in the elaboration of multivalent biological probes.

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Introduction

N-Acetylneuraminic acid (Neu5Ac) is the major member of the sialic acid family, a class of about fifty 2-keto-3-deoxy-nonulosonic acids that are important constituents of oligosaccharides, glycoconjugates, and polysaccharides.^[1–3] Neu5Ac is commonly found as the α -ketosidically linked terminal sugar on cell surface glycoconjugates. As a result of this exposed position within glycoconjugates, it is involved in numerous biological phenomena,^[2,3] and this significant role in physiological processes and diseases has stimulated synthetic efforts towards the construction of natural and structurally modified Neu5Ac.^[4,5] Molecular probes containing this important α -linked structural motif, elaborated for biological research, are, however, vulnerable to cleavage. In vivo, the α -glycosidic bond of this terminal residue is cleaved by neuraminidases, while in vitro it is sensitive to very mild acidic conditions. The replacement of the interglycosidic oxygen atom with a carbon atom provides carbon-linked analogues that are stable towards degradation.

In spite of the many available methods for the synthesis of C-glycosides,^[6,7] only a few are applicable to the synthesis of simple C-glycosides of Neu5Ac or related ulosonic acids.^[8] Apart from an interesting de novo approach from D-gluconolactone,^[9] routes to more complex C-glycosides

(e.g., C-disaccharides) rely heavily on reductive samariation of appropriate anomeric substituents of Neu5Ac. This was described by Linhardt and co-workers on the anomeric pyridyl sulfone of Neu5Ac derivative **2** (Figure 1),^[10] as an extension of our work on neutral aldoses^[11] and 2-acetamido-2-deoxy sugars.^[12]

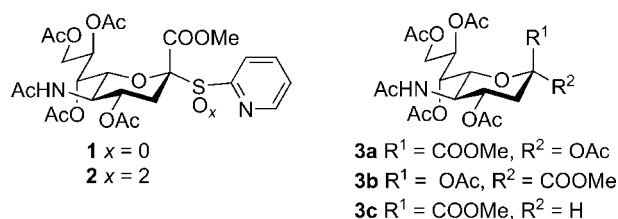


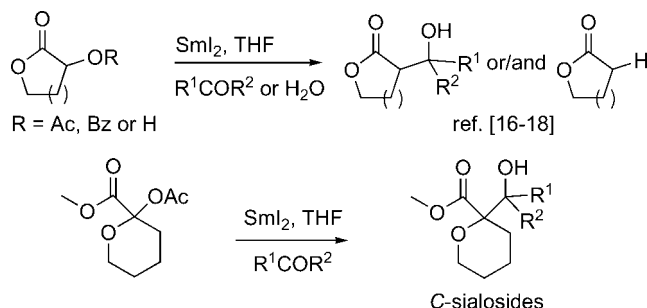
Figure 1. Structure of Neu5Ac derivatives.

It was later reported that the anomeric chloride or the phenyl sulfone could also be used in this procedure without the need for activation by HMPA.^[13] We also showed that the stable and crystalline 2-pyridyl sulfide of *N*-acetylneuraminic acid derivative **1** is an excellent precursor of the anomeric organometallic species in a samarium-Reformatsky procedure.^[14] These results were anticipated, since reduction of an anomeric substituent on this substrate, α to both an ester and an oxygen atom (Reformatsky-type reaction), is much easier than the same procedure on a functional group α to an oxygen atom alone. Here we report an even simpler synthesis based on reductive samariation, in the absence of any additive, of the anomeric acetates **3**.^[15] These compounds, easily prepared from Neu5Ac through high yielding-reactions, are storable intermediates frequently used as starting derivatives in the chemistry of Neu5Ac.

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The possibility of this approach was inferred from Inanaga's reports on the samarium diiodide-induced α -deoxygenation of ester^[16] and acetylated carbohydrate lactones (Scheme 1).^[17] This procedure was further developed by Enholm and co-workers in α -deoxygenation-carbonyl addition reactions of benzoylated lactones.^[18] In work closely related to this, Hanessian and Girard have also achieved efficient and easy anomeric deoxygenation of *O*-acetylated 2-uloseonates (Neu5Ac and KDO) with SmI_2 .^[19] For the success of all these reactions, however, additives that enhance the reducing ability of SmI_2 were needed: HMPA^[16–18] or ethylene glycol.^[19] In the latter reaction, which needed two hours for completion, the presence of the ethylene glycol was crucial, playing the roles both of a proton source and of an extra ligand for coordination to the samarium atom.



Scheme 1.

Results and Discussion

To evaluate the individual behavior of each anomeric acetate – **3a** and **3b** – in the reductive process better, they were first prepared and tested separately. They were easily obtained by previously described procedures (Scheme 2). The α isomer **3a** was selectively prepared via the anomeric chloride **5**. Overnight treatment of Neu5Ac with an acidic methanolic solution provided a quantitative yield of the methyl ester **4**,^[20] which was converted into the chloride **5** by treatment for 24 h in a 1:1 mixture of acetic acid and acetyl chloride, saturated at 0 °C with hydrogen chloride.^[21] Overnight treatment of the crude chloride **5** with 1.5 equiv.

of cesium acetate in acetonitrile at room temperature^[22] gave the desired α derivative **3a** (74% yield from Neu5Ac).

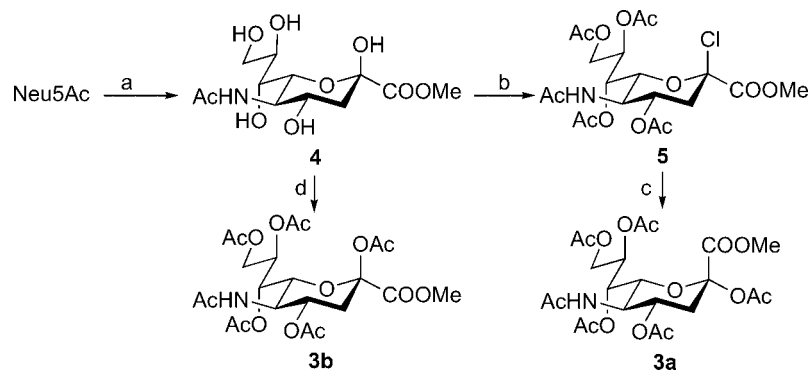
The β -anomer **3b** was purified by flash column chromatography on silica gel (white, crystalline solid in 74% yield) from a 1:4 α/β mixture obtained by standard treatment (acetic anhydride in dry pyridine at room temperature overnight) of the methyl ester **4**.

The anomeric configurations of **3a** and **3b** were readily assigned by their NMR spectroscopic data and comparison with known spectroscopic data.

Separate Reductive Samarium of **3a** and **3b**

The α -acetate **3a** and the β -acetate **3b** were each individually subjected to reductive samarium at room temperature in the presence of several carbonyl compounds – aldehydes or ketones – in the absence of any additive. These reactions were performed under Barbier conditions to provide the desired *C*-sialosides. On addition of a freshly prepared solution of samarium diiodide in THF^[23] (0.1 M) to a THF solution of either **3a** or **3b** (0.33 M) and the carbonyl compound (2 equiv.), decoloration of the blue SmI_2 was noted. This required only 20 min with **3a**, while the time needed for the complete reduction of the axial anomer **3b** was longer, but still less than 2 h. Standard treatment and purification over silica gel furnished the *C*-sialodides in good to moderate yields depending on the carbonyl partner (Table 1). All these experiments were performed at room temperature in the absence of any additive. It was *essential to use a very freshly* prepared SmI_2/THF solution (from samarium metal and diiodoethane),^[23] and the reported results were obtained with solutions never more than 2 days old. Experimentally, we found that the best coupling results were obtained with a SmI_2/THF solution prepared on the same day. The reasons behind this particular behavior are not yet known, though this very precise procedure suggests that an unidentified more active samarium species is present in a fresh solution and disappears with time.

The new products were isolated and fully characterized. The times needed for the reduction of the acetates were much longer than those required for the reductive samaria-



Scheme 2. Preparation of Neu5Ac peracetates **3a** and **3b**. a) MeOH, Dowex H⁺, room temperature, 24 h; b) HCl, AcOH/AcCl (1:1), room temperature; c) CsOAc (1.5 equiv.), MeCN, room temperature; 74% from Neu5Ac; d) Ac₂O, pyridine, room temperature, overnight (**3a/3b** ≈ 1:4 α/β mixture); flash column chromatography on silica gel; 74% of **3b** from Neu5Ac.

Table 1. SmI₂-promoted couplings between acetates **3a** or **3b** and carbonyl compounds.

3a or 3b $\xrightarrow[\text{THF, r.t.}]{\text{SmI}_2 \text{ (3 equiv.)}}$ **6-10**

Entry	Acetate	Carbonyl compound (reaction time)	Product: yield ^[a] (isomer ratio)
1	3a	cyclopentanone (20 min)	6 : 97%
2	3b	cyclopentanone (2 h)	6 : 82%
3	3a	4- <i>tert</i> -butylcyclohexanone (20 min)	7 : 91%
4	3b	4- <i>tert</i> -butylcyclohexanone (2 h)	7 : 83%
5	3a	cyclohexanecarbaldehyde (20 min)	8 : 87% (1.25:1)
6	3b	cyclohexanecarbaldehyde (2 h)	8 : 83% (1.25:1)
7	3a	3-pentanone (20 min)	9 : 44% ^[b]
8	3b	3-pentanone (2 h)	9 : 26% ^[b]
9	3a	<i>n</i> -octanal (20 min)	10 : 39% ^[b] (1:1)
10	3b	<i>n</i> -octanal (2 h)	10 : 33% ^[b] (1:1)

[a] Yields of the purified compounds after silica gel chromatography. [b] The reduction product **3c** (40–44%) was also formed.

tions of the anomeric 2-pyridyl sulfide **1**^[14] or the 2-pyridyl sulfone **2**^[10] (20 min for **3a**, 2 h for **3b**, compared to less than 1 min for **1** or **2**). Despite this longer reaction time, the yields of products were good and no degradation product (e.g., deacylation products) of the starting material was ever observed.

The coupling reaction with cyclopentanone gave the *C*-sialyl derivative **6** in yields of 97% (from **3a**) or 82% (from **3b**) (Table 1, Entries 1 and 2). As expected, and in agreement with previously published results, treatment with a symmetric ketone furnished the *C*-sialoside as a single diastereomer with an equatorial orientation of the newly formed C–C bond (see below). Treatment with 4-*tert*-butylcyclohexanone gave the coupling product **7**, again in a high yield and as a single diastereomer (yields of 91% from **3a** and 83% from **3b**, Table 1, Entries 3 and 4). The bulky *tert*-butyl group induced total discrimination of the two faces of the cyclic ketone. Use of cyclohexanecarbaldehyde as the carbonyl partner provided a mixture of two diastereomers **8** (selectivity of 1.25:1) in 87% and 83% yields (Table 1, Entries 5 and 6). Both diastereomers displayed a standard ⁵C²-chair conformation as determined by ¹H NMR analysis: *J*_{3ax,4}, *J*_{4,5}, and *J*_{5,6} values of 10.2, 11.8, and 10.5 Hz, respectively, for one isomer and *J*_{3ax,4}, *J*_{4,5}, and *J*_{5,6} values of 12, 10.5, and 10.5 Hz, respectively, for the other. The couplings of the anomeric acetates with pentan-3-one and *n*-octanal, providing **9** (44% yield from **3a** and 26% yield from **3b**, Table 1, Entries 7 and 8) and **10** (39% yield from

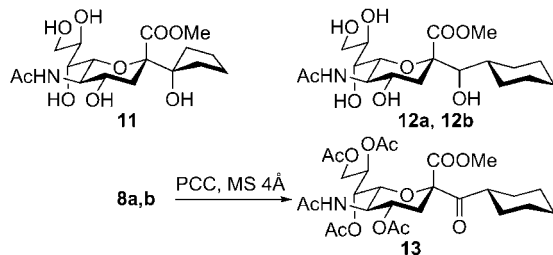
3a and 33% yield from **3b**, Table 1, Entries 9 and 10), were much less efficient, however. The reduction of the carbonyl partners became the main reaction pathway and the formation of the reduction product **3c** from **3a/3b** is believed to result from the protonation of the organometallic intermediate during the workup procedure. This samarium-Reformatsky procedure is necessarily conducted under Barbier conditions for successful coupling reactions. Under these conditions, the reduction of the carbonyl partner may become competitive, consequently affecting the efficiency of the coupling process. In the examples given in Table 1, cyclic ketones and cyclohexanecarbaldehyde gave good results (they were not reduced), but when the carbonyl group of a substrate became more sensitive to reduction by SmI₂ (as with *n*-octanal, Entries 9 and 10), or when the coupling rate was too slow (as with pentan-3-one, less “electrophilic” for steric reasons; Entries 7 and 8), the coupling yields decreased. These lower efficiencies, in relation to the same reactions performed with anomeric 2-pyridyl sulfide **1**,^[14] illustrate the limitations of using acetates **3a** and **3b** as “*C*-sialyl donors”. In relation to this, the axial isomer **3b** was systematically less efficient in the coupling procedure than the equatorial isomer **3a**, probably as a consequence of its slower reduction rate by SmI₂.

Empirical rules were first used to deduce the α configurations of the *C*-sialyl derivatives, with regard to Hasegawa’s observations on the ¹H NMR spectra of α - and β -*O*-glycoside derivatives. We found that the values for δ (4-H), *J*_{7,8},

and $\Delta\delta_{\text{H9a-9b}}$ (numbering is given in formulae **6–10**, Table 1) were in agreement with an equatorial orientation of the new C–C bond. For example, the $\delta(4\text{-H})$ values determined for products **6**, **8a**, and **8b** (after chromatographic separation of the two isomers of **8**) were 4.74, 4.75, and 4.83 ppm, respectively. The $J_{7,8}$ values for the same products were 7.4, 8.1, and 7.8 Hz, respectively, and the $\Delta\delta_{\text{H9a-9b}}$ values were between 0.22 and 0.36 ppm. Experimental evidence for this stereochemical assignment at C2 of the *C*-sialosides was obtained from the values of the $^3J_{\text{C1,H3ax}}$ and $^3J_{\text{C1,H3eq}}$ heteronuclear coupling constants in the corresponding deprotected *C*-ketosides **11**, **12a**, and **12b** (Table 2) obtained by a standard deacetylation procedure (MeONa/MeOH).

Table 2. Values for the heteronuclear ^1H , ^{13}C coupling constants and formulas of the compounds.

Entry	Product	Deacetylated product	$^3J_{\text{C-1,H-3ax}}$ (Hz)	$^3J_{\text{C-1,H-3eq}}$ (Hz)
1	6	11 (90%)	8.4	0
2	8a	12a (92%)	7.7	0
3	8b	12b (92%)	8.0	1.2



These values indicate a *trans*-diaxial orientation of the C-1/C-2 and the C-3/H-3ax bonds and a *gauche* relationship between the C-1/C-2 and the C-3/H-3eq bonds, which clearly demonstrates that reductive samarium in the presence either of a ketone (e.g., **6**) or of an aldehyde (e.g., **8**) selectively furnished the α -*C*-ketosides. In addition, oxidation of the mixture of the two isomers **8a** and **8b**, with PCC in dichloromethane in the presence of molecular sieves, furnished a single ketone **13** in a 50% yield. This shows that the two isomers **8a** and **8b** differ only in the configuration at the exocyclic asymmetric center. These stereochemical conclusions were extended to all the other coupling products.

Reductive Samarium of the Mixture of Anomeric Acetates **3a** and **3b**

Following these preliminary results on separate anomers **3a** and **3b**, we then considered the use of the more practical crude synthetic mixture of **3a** and **3b** obtained by peracetylation of methyl ester **4** with Ac_2O in pyridine (Scheme 2), which contained **3a** and **3b** in a 1 to 4 ratio. Without any other purification (the reaction mixture was co-evaporated

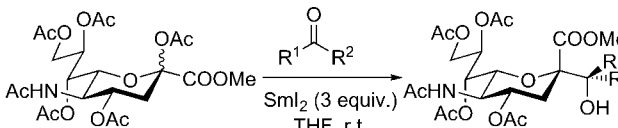
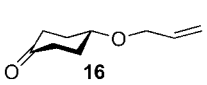
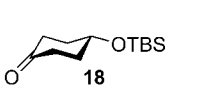
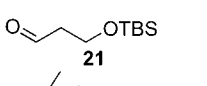
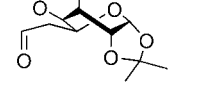
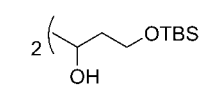
with toluene and filtered through a pad of silica), the **3a/3b** mixture was subjected to the standard reductive samarium conditions in the presence of carbonyl compounds (Table 3). The same carbonyl compounds (4-*tert*-butylcyclohexanone and cyclohexanecarbaldehyde) provided results essentially identical to those obtained above with the separate anomers in a 2 hour reaction, the reduction time needed to complete the reaction with the β anomer **3b** (Table 3, Entries 1 and 2). Cyclohexanone (Entry 3), 4-substituted cyclohexanones **16** and **18** (Entries 5 and 6), and cyclobutanone (Entry 7) were also good substrates, providing the *C*-glycosides **14**, **17**, **19**, and **20**, respectively, in yields of 79–88% (Table 3). Reactions with **16** and **18** were, however, not selective, providing a 1:1 mixture of diastereomers **17** and **19** that were not separated. For each of these products (giving a single spot on TLC), ^1H NMR spectra of the two diastereomers were very similar, and only the values of δ_{COOMe} and δ_{OAc} were significantly different. Reaction in the presence of 1.4 equiv. of cyclohexane-1,4-dione provided the monocondensation product in 30% isolated yield (Entry 4, Table 3). In sharp contrast with cyclohexanecarbaldehyde, and as noted above with the separate anomers and *n*-octanal, low coupling yields were obtained with the 3-(*tert*-butyldimethylsilyloxy)propanal **21** or the galactose-derived aldehyde **23**,^[24] giving **22** and the *C*-disaccharide **24** in 26% and 30% yields, respectively, as 1:1 mixtures of two diastereomers.

Aldehyde **21** was too reactive towards the reduction by SmI_2 and produced the pinacol byproduct **25** in 53% yield together with the reduction product **3c** (17% yield). Similarly, the sugar-derived aldehyde **23** also furnished the pinacol product **26** (30%), the reduction product **3c** (21%), and some starting acetates **3a/3b** (14%).

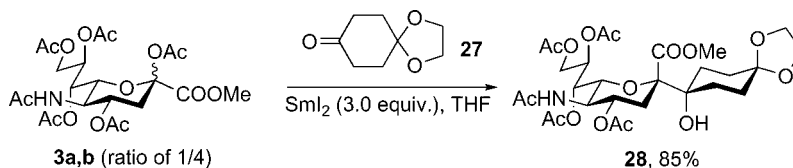
This new coupling process was applied to the rapid construction of a *C*-ketoside that could be used as a stable unit easy to integrate into various dendrimeric or polymeric structures. As discussed above, the use of a symmetric 4-substituted cyclohexanone should provide a high coupling yield without adding a new stereogenic center. The coupling reactions with already functionalized 4-hydroxycyclohexanone were unfortunately not selective (Entries 5 and 6, Table 3). This prompted us to elaborate a functional spacer after the coupling reaction by use of the commercially available 4-dioxolanocyclohexanone (**27**; Scheme 3).

Reductive samarium of the acetates **3a** and **3b** in the presence of 4-dioxolanocyclohexanone (**27**, 2 equiv.) furnished **28** as a single stereomer in an isolated 85% yield. This high-yielding reaction was carried out on a gram scale with respect to the sialyl substrate. Straightforward deprotection of **28** with a HCl/THF solution (5%) at room temperature, followed by acetylation, furnished ketone **15** in an only moderate yield (54%, Scheme 4). Stereoselective reductive opening of the dioxolane ring in **28** was ineffective with either the $\text{Et}_3\text{SiH/TMSOTf}$ or the $\text{NaBH}_3\text{CN/BF}_3\cdot\text{Et}_2\text{O}$ systems, but treatment with TMSOTf (1.2 equiv.) and $\text{BH}_3\cdot\text{Me}_2\text{S}$ (1.2 equiv.) in dichloromethane at 0 °C for 10 min provided alcohol **29** in 83% yield as a 6:1 mixture of diastereomers. This selectivity was improved to 20:1 in

Table 3. SmI₂-promoted coupling of acetates **3a** and **3b** with carbonyl compounds.

		
Entry	Carbonyl compound	Product: yield ^[a] (isomer ratio)
1	4- <i>tert</i> -butylcyclohexanone	7 : 98%
2	cyclohexanecarbaldehyde	8 : 75% (1.25:1)
3	cyclohexanone	14 : 79%
4	1,4-cyclohexanedione ^[b]	15 : 30%
5		17 : 83% (1:1)
6		19 : 85% (1:1)
7	cyclobutanone	20 : 88%
8		22 : 26% ^[c] (1:1)
9		24 : 30% ^[d] (1:1)
		26

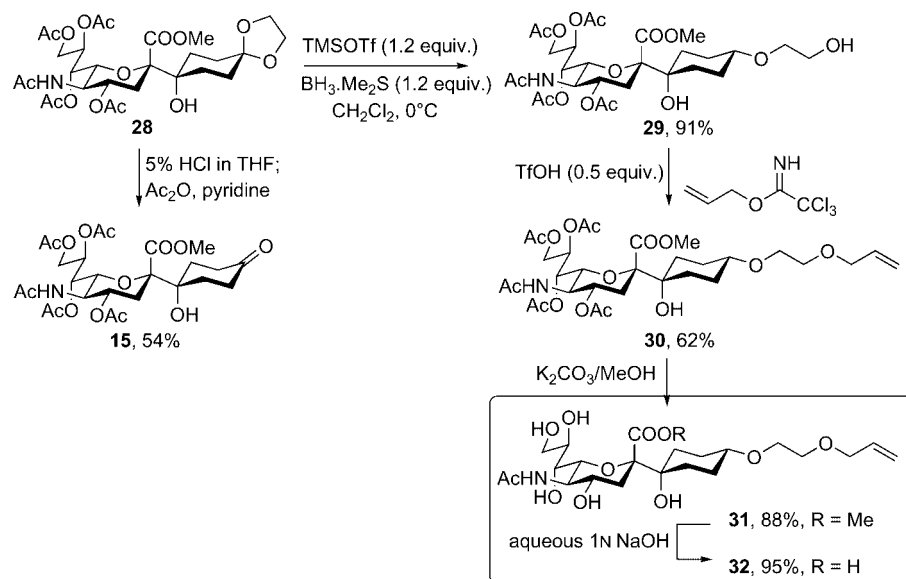
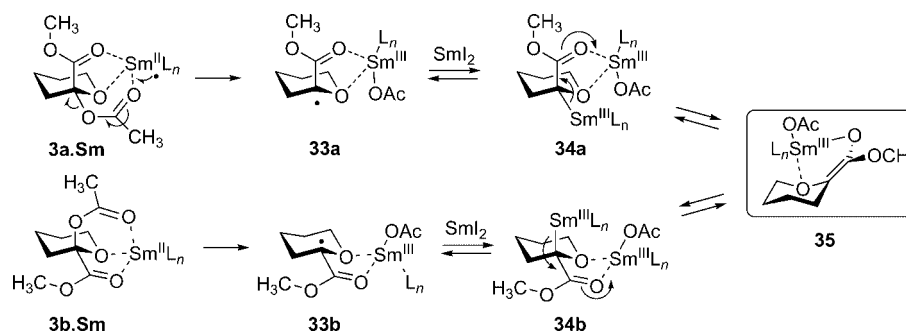
[a] Yields for the purified compounds after silica gel chromatography. [b] With 1.4 equiv. of cyclohexane-1,4-dione. [c] Pinacol **25** (53%) and reduction product **3c** (17%) were also formed. [d] Acetates **3a** and **3b** (14%) were recovered; pinacol **26** (30%) and reduction product **3c** (21%) were also formed.



Scheme 3. Coupling reaction with 4-dioxolanocyclohexanone **27**.

favor of the equatorial isomer by use of the same reagents at -78°C for 4 h, providing a single compound **29** in 91% yield after flash column chromatography.

O-Allylation of the primary alcohol **29** with allyl bromide and silver oxide in toluene failed, but the desired allylated product **30** was obtained in 62% yield by use of

Scheme 4. Selective synthesis of the C-sialoside building block **32**.Scheme 5. Postulated mechanism for the formation of the samarium enolate from **3a** and **3b**.

2 equiv. of the easily prepared allyl trichloroacetimidate in dichloromethane/cyclohexane (1:2) in the presence of trifluoromethanesulfonic acid (0.5 equiv.). The deprotected building block **32** was obtained in a two-step sequence through deacetylation to **31** (88% yield) with potassium carbonate (0.4 equiv.) in methanol followed by saponification of the methyl ester in aqueous NaOH (1 N; 95% yield of **32**).

In these coupling reactions, the anomeric configuration of the starting acetate in the Neu5Ac derivatives did not have any influence on the distribution of the reaction products. In addition, we would not originally have expected a facile reduction of acetates **3** without the use of additives to enhance the reducing power of SmI₂. The reaction proceeds through two successive electron transfers and we suggest here that the formation of a chelate structure as in **3a·Sm** and **3b·Sm** (Scheme 5) could be crucial for the initial electron transfer. The carbonyl oxygens of both the anomeric acetate and the methyl ester, together with the endocyclic O-6 oxygen atom, may behave as a tridentate ligand for the samarium atom. This chelation scheme would increase the reducing ability of SmI₂, as do most chelating agents,^[25]

and induce an easy electron transfer from the samarium atom to one of the carbonyls. This first electron transfer produces an anomeric radical (**33a** or **33b**), which is further reduced to an anomeric organosamarium species (**34a** or **34b**), that may rearrange to a samarium enolate **35**. The same reasoning would also apply to the corresponding anomeric 2-pyridyl sulfide **2**.^[14,15]

Conclusions

We have shown that both α - and β -acetates of peracetylated Neu5Ac (**3a** and **3b**) are useful precursors of C-ketosides through reductive samarium at room temperature under Barbier conditions in the presence of carbonyl compounds. The crude mixture of acetates can equally well be used for this selective transformation. This procedure provides rapid access to α -C-ketosides of NeuAc from easily available starting materials, and is remarkably efficient for couplings with cyclic ketones. We have applied this procedure to the preparation of a C-sialyl derivative, which will be used as a stable motif to be integrated into different multivalent structures.

Experimental Section

General: All air-sensitive reactions were carried out under argon. The glassware was oven-dried at 120 °C and cooled in a dessicator. Solvents were purified by distillation just prior to use or dried by standard methods. THF was distilled from sodium and benzophenone. Toluene and acetonitrile were distilled from calcium hydride. Dichloromethane was distilled from phosphorus pentoxide. Methanol and DMF were dried on 3 Å and 4 Å molecular sieves, respectively. Pyridine and triethylamine were dried with KOH. Thin layer chromatography analysis was performed on Merck 60F₂₅₄ sheets with detection by UV and by charring with 5% ethanolic H₂SO₄. Silica gel SDS 60 ACC 35–70 µm was used for flash column chromatography. NMR spectra were recorded at room temperature with Bruker AC 250, AM 250, AM 360, and AM 400 spectrometers. Spin multiplicities are given with the following abbreviations: s (singlet), d (doublet), t (triplet), m (multiplet). Chemical shifts are quoted in ppm (δ scale) and are referenced to residual ¹H in the NMR solvents. The deuterated solvents used were specified for each product: CDCl₃, D₂O, CD₃OD. ¹H NMR spectra of C-glycosyl analogues of N-acetylneuraminic acid were assigned by standard methods with the aid of a combination of single frequency decoupling, TOCSY, and COSY experiments. The ¹³C NMR spectra were assigned by standard methods with the aid of a combination of single frequency decoupling, HSQC, and HMBC experiments. Low- and high-resolution mass spectra [MS(ESI), HRMS] were recorded on a MAT 95S Electrospray Mass Spectrometer. Optical rotations were measured at 28 °C with a Perkin–Elmer 341 polarimeter. Melting points were determined in capillary tubes with a Büchi B-545 apparatus. Elemental analyses were obtained from the “Service de Microanalyses” at the I.C.S.N.-C.N.R.S (Gif-sur-Yvette, France).

Methyl 5-Acetamido-3,5-dideoxy-D-glycero-D-galacto-2-nonulopyranosonate (4): A solution of N-acetylneuraminic acid (2.0 g, 6.46 mmol) in methanol (100 mL) containing Dowex H⁺ resin (500 mg) was stirred overnight at room temperature. The progress of the reaction was monitored by TLC (EtOAc/iPrOH/H₂O, 2:2:1). The solution was filtered and the resin was washed several times with methanol. The filtrate was then evaporated. The methyl ester **4** was obtained as a white solid (1.73 g, 5.36 mmol, 83%). M.p. 183 °C (EtOH) [ref.^[20] m.p. 179–180 °C (MeOH)]. [α]_D²⁸ = –27.5 (*c* = 0.59, MeOH) {ref.^[20] [α]_D = –28 (*c* = 1, H₂O)}. ¹H NMR (D₂O, 250 MHz): δ = 4.10–3.98 (m, 2 H, 6-H, 4-H), 3.90 (dd, *J*_{5,6} = 10.1, *J*_{5,4} = 10.0 Hz, 1 H, 5-H), 3.82 (s, 3 H, CO₂CH₃), 3.82 (dd, *J*_{9a,9b} = 11.6, *J*_{9a,8} = 2.5 Hz, 1 H, 9a-H), 3.71 (ddd, *J*_{8,7} = 8.9, *J*_{8,9b} = 6.1, *J*_{8,9a} = 2.5 Hz, 1 H, 8-H), 3.59 (dd, *J*_{9b,9a} = 11.6, *J*_{9b,8} = 6.1 Hz, 1 H, 9b-H), 3.52 (dd, *J*_{7,8} = 8.9, *J*_{7,6} = 3.0 Hz, 1 H, 7-H), 2.28 (dd, *J*_{3eq,3ax} = 13.0 Hz, *J*_{3eq,4} = 4.7 Hz, 1 H, 3eq-H), 2.03 (s, 3 H, NAc), 1.89 (dd, *J*_{3ax,3eq} = 13.0, *J*_{3ax,4} = 11.4 Hz, 1 H, 3ax-H) ppm. MS (ESI): *m/z* = 346.1 [*M* + Na]⁺.

Methyl 5-Acetamido-2,4,7,8,9-penta-O-acetyl-3,5-dideoxy-D-glycero- β -D-galacto-2-nonulopyranosonate (3b): Acetic anhydride (5 mL) was added to a suspension of methyl 5-acetamido-3,5-dideoxy-D-glycero-D-galacto-2-nonulopyranosate **4** (400 mg, 1.2 mmol) in pyridine (10 mL). The resulting mixture was stirred overnight at room temperature. The end of the reaction was assessed by TLC (toluene/acetone, 2:1). Solvents were concentrated and the resulting traces of pyridine were eliminated by co-evaporation with toluene. The product was obtained as an α/β mixture in a 1:4 ratio. The residue was purified by flash chromatography (toluene/acetone, 5:1) to afford **3b** (488 mg, 0.9 mmol, 74%). M.p. 98 °C (toluene/acetone). [α]_D²⁸ = –32 (*c* = 1.03, CHCl₃) {ref.^[22] [α]_D = –32 (*c* = 1, CHCl₃)}. ¹H NMR (CDCl₃, 250 MHz): δ = 5.46 (d, *J*_{NH,5} = 9.7 Hz, 1 H,

NH), 5.35 (d, *J*_{7,8} = 5.2 Hz, 1 H, 7-H), 5.22 (ddd, *J*_{4,3ax} = 11.5, *J*_{4,5} = 10.6, *J*_{4,3eq} = 5.1 Hz, 1 H, 4-H), 5.08–5.00 (m, 1 H, 8-H), 4.49 (dd, *J*_{9a,9b} = 12.5, *J*_{9a,8} = 2.8 Hz, 1 H, 9a-H), 4.18–4.00 (m, 3 H, 6-H, 5-H, 9b-H), 3.76 (s, 3 H, CO₂CH₃), 2.51 (dd, *J*_{3eq,3ax} = 13.4, *J*_{3eq,4} = 5.1 Hz, 1 H, 3eq-H), 2.12, 2.04, 2.01 (3 $\times$ s, 15 H, 5 $\times$ OAc), 1.86 (s, 3 H, NAc) ppm. MS (ESI): *m/z* = 556.2 [*M* + Na]⁺.

Methyl 5-Acetamido-2-chloro-4,7,8,9-tetra-O-acetyl-3,5-dideoxy-D-glycero- β -D-galacto-2-nonulopyranosonate (5): A solution of methyl 5-acetamido-3,5-dideoxy-D-glycero-D-galacto-2-nonulopyranosate (**4**) (2.0 g, 6.2 mmol) in a mixture of AcCl/AcOH (40 mL, 1:1, v/v) was saturated at 0 °C with anhydrous HCl. The resulting mixture was stirred at room temperature for a day and was then concentrated. Chloride **5** was obtained quantitatively as a foam (3.13 g, 6.2 mmol) and was directly used in the next reaction. ¹H NMR (CDCl₃, 250 MHz): δ = 5.45 (dd, *J*_{7,8} = 7.1, *J*_{7,6} = 2.4 Hz, 1 H, 7-H), 5.42–5.32 (m, 1 H, 4-H), 5.15 (ddd, *J*_{8,7} = 7.1 Hz, *J*_{8,9b} = 5.7, *J*_{8,9a} = 2.7 Hz, 1 H, 8-H), 4.40 (dd, *J*_{9a,9b} = 12.5, *J*_{9a,8} = 2.7 Hz, 1 H, 9a-H), 4.33 (dd, *J*_{6,5} = 10.7, *J*_{6,7} = 2.4 Hz, 1 H, 6-H), 4.18 (dd, *J*_{5,6} = 10.7, *J*_{5,4} = 10.4 Hz, 1 H, 5-H), 4.04 (dd, *J*_{9b,9a} = 12.5, *J*_{9b,8} = 5.7 Hz, 1 H, 9b-H), 3.86 (s, 3 H, CO₂CH₃), 2.76 (dd, *J*_{3eq,3ax} = 13.9, *J*_{3eq,4} = 4.8 Hz, 1 H, 3eq-H), 2.26 (dd, *J*_{3ax,3eq} = 13.9, *J*_{3ax,4} = 11.2 Hz, 1 H, 3ax-H), 2.10, 2.06, 2.04, 2.03 (4 $\times$ s, 12 H, 4 $\times$ OAc), 1.89 (s, 3 H, NAc) ppm.

Methyl 5-Acetamido-2,4,7,8,9-penta-O-acetyl-3,5-dideoxy-D-glycero- α -D-galacto-2-nonulopyranosonate (3a): A solution of **5** (1.0 g, 2.06 mmol) in anhydrous acetonitrile (20 mL) was stirred with anhydrous cesium acetate (600 mg, 2.94 mmol, 1.5 equiv.) overnight at room temperature. The mixture was concentrated and then diluted with dichloromethane (200 mL), and the organic phase was washed with water (40 mL) and concentrated. The residue was eluted from a silica gel column with toluene/acetone, 2:1 to give **3a** (814 mg, 1.52 mmol, 74%). M.p. 106 °C (toluene/acetone). [α]_D²⁸ = +11.5 (*c* = 1.22, CHCl₃) {ref.^[22] [α]_D = +13 (*c* = 1, CHCl₃)}. ¹H NMR (CDCl₃, 250 MHz): δ = 5.40 (d, *J*_{NH,5} = 9.3 Hz, 1 H, NH), 5.35 (dd, *J*_{7,8} = 7.1, *J*_{7,6} = 2.5 Hz, 1 H, 7-H), 5.16 (ddd, *J*_{8,7} = 7.1 Hz, *J*_{8,9b} = 6.0, *J*_{8,9a} = 2.7 Hz, 1 H, 8-H), 4.99 (ddd, *J*_{4,3ax} = 11.8, *J*_{4,5} = 10.3, *J*_{4,3eq} = 4.7 Hz, 1 H, 4-H), 4.67 (dd, *J*_{6,5} = 10.7, *J*_{6,7} = 2.5 Hz, 1 H, 6-H), 4.33 (dd, *J*_{9a,9b} = 12.5, *J*_{9a,8} = 2.7 Hz, 1 H, 9a-H), 4.12 (ddd, *J*_{5,6} = 10.7, *J*_{5,4} = 10.4, *J*_{5,NH} = 9.3 Hz, 1 H, 5-H), 4.03 (dd, *J*_{9b,9a} = 12.5, *J*_{9b,8} = 6.0 Hz, 1 H, 9b-H), 3.73 (s, 3 H, CO₂CH₃), 2.52 (dd, *J*_{3eq,3ax} = 13.1, *J*_{3eq,4} = 4.7 Hz, 1 H, 3eq-H), 2.11, 2.08, 2.01 (3 $\times$ s, 15 H, 5 $\times$ OAc), 1.87 (s, 3 H, NAc) ppm. MS (ESI): *m/z* = 556.2 [*M* + Na]⁺.

Preparation of a Solution of Samarium Diodide in THF (0.1 M): Samarium powder (0.190 g, 1.26 mmol) was placed in a dry flask under argon. 1,2-Diiodoethane (0.280 g, 1.00 mmol) was added and the mixture was stirred for 10 min. THF (10 mL) was slowly added and the contents of the flask were magnetically stirred overnight. For improved results in the coupling reactions with the anomeric acetates, this solution should be used within 2 d.

General Procedure for the SmI₂-Promoted Coupling Reaction with a Carbonyl Compound: The SmI₂-promoted coupling reactions were performed at room temperature under Barbier conditions. A solution of SmI₂ in THF (0.1 M, 3 equiv.) was added to a stirred solution of the sialic acid derivative (1 equiv.) and the carbonyl compound (2 equiv.) in THF at room temperature (blue solution). After the mixture had been stirred until decoloration (yellow-green solution), saturated aqueous NH₄Cl solution and CH₂Cl₂ were added to the reaction mixture. The reaction time depended on the substrate: 20 min from **3a** and 2 h either from **3b** or from a **3a/3b** mixture. The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂. The combined organic phases were washed

with a saturated aqueous NaHCO_3 solution, dried with Na_2SO_4 , and filtered, and the solvents were evaporated. The residue was purified by flash chromatography (toluene/acetone, 2:1) to afford the *C*-sialosides.

1-C-(Methyl 5-Acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero- α -D-galacto-non-2-ulopyranosonate)cyclopentanol (6): *C*-Sialoside **6** was obtained by the general coupling procedure with cyclopentanone as the electrophile in 97% yield from **3a** and 82% yield from **3b** on a 0.04 mmol scale with respect to the acetate derivatives. [a_D] $^{28}_D = -9.5$ ($c = 0.93$, CHCl_3) {ref.^[13b] [a_D] = -10 ($c = 0.9$, CHCl_3)}. ^1H NMR (CDCl_3 , 250 MHz): $\delta = 5.45$ (d, $J_{\text{NH},5} = 9.5$ Hz, 1 H, NH), 5.37 (m, 1 H, 8-H), 5.29 (dd, $J_{7,8} = 7.4$, $J_{7,6} = 1.9$ Hz, 1 H, 7-H), 4.74 (ddd, $J_{4,3\text{ax}} = 11.8$, $J_{4,5} = 9.8$, $J_{4,3\text{eq}} = 4.5$ Hz, 1 H, 4-H), 4.32 (dd, $J_{9a,9b} = 12.4$, $J_{9a,8} = 2.4$ Hz, 1 H, 9a-H), 4.05 (m, 2 H, 6-H, 5-H), 3.96 (dd, $J_{9b,9a} = 12.4$, $J_{9b,8} = 6.6$ Hz, 1 H, 9b-H), 3.76 (s, 3 H, CO_2CH_3), 2.50 (dd, $J_{3\text{eq},3\text{ax}} = 12.8$, $J_{3\text{eq},4} = 4.6$ Hz, 1 H, 3eq-H), 2.14, 2.11, 2.03, 2.00 ($4 \times s$, 12 H, $4 \times \text{OAc}$), 1.85 (s, 3 H, NAc), 1.70–1.60 (m, 8 H, cyclopentyl) ppm. MS (ESI): $m/z = 528.2$ [$\text{M} + \text{Na}$] $^+$. HRMS: calcd. for $\text{C}_{25}\text{H}_{37}\text{O}_{13}\text{NNa}$ 582.21571; found 528.21612.

1-C-(Methyl 5-Acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero- α -D-galacto-non-2-ulopyranosylonate)-4-*tert*-butylcyclohexanol (7): *C*-Sialoside **7** was obtained by the general coupling procedure with 4-*tert*-butylcyclohexanone as the electrophile in 91% yield from **3a** and 83% yield from **3b** on a 0.035 mmol scale with respect to the acetate derivatives. ^1H NMR (CDCl_3 , 250 MHz): $\delta = 5.37$ (m, 1 H, 8-H), 5.30 (dd, $J_{7,8} = 7.4$, $J_{7,6} = 1.9$ Hz, 1 H, 7-H), 5.26 (d, $J_{\text{NH},5} = 8.6$ Hz, 1 H, NH), 4.71 (ddd, $J_{4,3\text{ax}} = 11.8$, $J_{4,5} = 9.8$, $J_{4,3\text{eq}} = 4.5$ Hz, 1 H, 4-H), 4.28 (dd, $J_{9a,9b} = 12.4$, $J_{9a,8} = 2.8$ Hz, 1 H, 9a-H), 4.06–3.94 (m, 3 H, 6-H, 5-H, 9b-H), 3.74 (s, 3 H, CO_2CH_3), 2.42 (dd, $J_{3\text{eq},3\text{ax}} = 12.9$, $J_{3\text{eq},4} = 4.6$ Hz, 1 H, 3eq-H), 2.13, 2.07, 2.01, 1.98 ($4 \times s$, 12 H, $4 \times \text{OAc}$), 1.83 (s, 3 H, NAc), 1.47–1.34 (m, 8 H, cyclohexyl), 0.88 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (CDCl_3 , 90 MHz): $\delta = 170.8$ – 169.1 ($4 \times \text{OCOMe}$, NCOMe, CO_2Me), 98.1 (C-2), 74.7 (COH), 73.4, 70.6, 68.8, 67.9 (C-6, C-8, C-4, C-7), 62.4 (C-9), 52.7 (CH_3O), 47.7 (C-5), 37.3 (C-3), 32.8–29.6 (CH_2 of cyclohexyl), 28.0 [$\text{C}(\text{CH}_3)_3$], 23.1, 22.1, 21.2, 20.8, 20.6 ($4 \times \text{CH}_3\text{OCO}$, CH_3CON) ppm. MS (ESI): $m/z = 652.3$ [$\text{M} + \text{Na}$] $^+$. HRMS: calcd. for $\text{C}_{30}\text{H}_{47}\text{NNaO}_{13}$ 652.29396; found 652.29411.

(RIS)-1-C-(Methyl 5-Acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero- α -D-galacto-non-2-ulopyranosonate)-1-cyclohexylmethanol (8a): *C*-Sialosides **8a** and **8b** were obtained by the general coupling procedure with cyclohexanecarbaldehyde as the electrophile in 87% yield from **3a** and 83% yield from **3b**, on a 0.1 mmol scale with respect to the acetate derivatives. Data for isomer **8a** (isolated after flash chromatography, toluene/acetone, 4:1): ^1H NMR (CDCl_3 , 250 MHz): $\delta = 5.36$ (ddd, $J_{8,7} = 8.7$, $J_{8,9b} = 6.3$, $J_{8,9a} = 2.7$ Hz, 1 H, 8-H), 5.26 (dd, $J_{7,8} = 8.1$, $J_{7,6} = 2.4$ Hz, 1 H, 7-H), 5.16 (d, $J_{\text{NH},5} = 9.5$ Hz, 1 H, NH), 4.75 (ddd, $J_{4,3\text{ax}} = 11.8$, $J_{4,5} = 10.2$, $J_{4,3\text{eq}} = 4.4$ Hz, 1 H, 4-H), 4.27 (dd, $J_{9a,9b} = 12.5$, $J_{9a,8} = 2.5$ Hz, 1 H, 9a-H), 4.16 (dd, $J_{6,5} = 10.5$, $J_{6,7} = 2.5$ Hz, 1 H, 6-H), 4.05 (m, 1 H, 5-H), 3.99 (dd, $J_{9b,9a} = 12.5$, $J_{9b,8} = 6.5$ Hz, 1 H, 9b-H), 3.72 (s, 3 H, CO_2CH_3), 2.34 (dd, $J_{3\text{eq},3\text{ax}} = 12.8$, $J_{3\text{eq},4} = 5.2$ Hz, 1 H, 3eq-H), 2.13, 2.08, 2.02, 2.00 ($4 \times s$, 12 H, $4 \times \text{OAc}$), 1.91 (dd, $J_{3\text{ax},3\text{eq}} = 12.8$, $J_{3\text{ax},4} = 10.2$ Hz, 1 H, 3ax-H), 1.85 (s, 3 H, NAc), 1.46–1.36 (m, 11 H, cyclohexyl) ppm. ^{13}C NMR (CDCl_3 , 90 MHz): $\delta = 171.2$, 171.1, 171.0, 170.6, 170.3, 169.5 ($4 \times \text{OCOMe}$, NCOMe, CO_2Me), 84.1 (C-2), 79.1 (COH), 73.2, 70.1, 68.6, 67.8 (C-6, C-8, C-4, C-7), 62.9 (C-9), 52.6 (CH_3O), 49.5 (C-5), 39.4 (C of cyclohexyl), 34.0 (C-3), 31.8, 26.7, 26.5, 26.2, 26.0 (CH_2 of cyclohexyl), 23.2, 21.3, 20.9, 20.8, 20.6 ($4 \times \text{CH}_3\text{OCO}$, CH_3CON) ppm. MS

(ESI): $m/z = 610.1$ [$\text{M} + \text{Na}$] $^+$. HRMS: $\text{C}_{27}\text{H}_{41}\text{NNaO}_{13}$ calcd. for 610.24756; found 610.24904.

Data for Isomer 8b (isolated after flash chromatography, toluene/acetone, 4:1): ^1H NMR (CDCl_3 , 250 MHz): $\delta = 5.29$ (ddd, $J_{8,7} = 7.8$, $J_{8,9b} = 5.4$, $J_{8,9a} = 2.5$ Hz, 1 H, 8-H), 5.26 (dd, $J_{7,8} = 7.8$, $J_{7,6} = 1.9$ Hz, 1 H, 7-H), 5.21 (d, $J_{\text{NH},5} = 9.8$ Hz, 1 H, NH), 4.83 (ddd, $J_{4,3\text{ax}} = 12.0$, $J_{4,5} = 10.0$, $J_{4,3\text{eq}} = 4.6$ Hz, 1 H, 4-H), 4.32 (dd, $J_{9a,9b} = 12.2$, $J_{9a,8} = 2.5$ Hz, 1 H, 9a-H), 4.05 (dd, $J_{6,5} = 10.0$, $J_{6,7} = 2.0$ Hz, 1 H, 6-H), 4.02 (dd, $J_{9b,9a} = 12.2$, $J_{9b,8} = 5.4$ Hz, 1 H, 9b-H), 3.95 (m, 1 H, 5-H), 3.74 (s, 3 H, CO_2CH_3), 2.43 (dd, $J_{3\text{eq},3\text{ax}} = 12.8$, $J_{3\text{eq},4} = 4.8$ Hz, 1 H, 3eq-H), 2.13, 2.10, 2.02, 2.00 ($4 \times s$, 12 H, $4 \times \text{OAc}$), 2.13 (dd, $J_{3\text{ax},3\text{eq}} = 12.8$, $J_{3\text{ax},4} = 12.0$ Hz, 1 H, 3ax-H), 1.85 (s, 3 H, NAc), 1.56–1.28 (m, 11 H, cyclohexyl) ppm. ^{13}C NMR (CDCl_3 , 90 MHz): $\delta = 171.2$, 170.9, 170.7, 170.3, 170.2, 160.0 (CO, $4 \times \text{OCOMe}$, NCOMe, CO_2Me), 83.4 (C-2), 79.5 (COH), 73.4, 70.0, 69.1, 67.9 (C-6, C-8, C-4, C-7), 62.4 (C-9), 52.3 (CH_3O), 49.6 (C-5), 39.8 (C of cyclohexyl), 34.9 (C-3), 31.8, 26.6, 26.5, 26.4, 26.0 (CH_2 of cyclohexyl), 24.2, 21.3, 20.9, 20.7, 20.6 ($4 \times \text{CH}_3\text{OCO}$, CH_3CON) ppm. MS (ESI): $m/z = 610.1$ [$\text{M} + \text{Na}$] $^+$. HRMS: calcd. for $\text{C}_{27}\text{H}_{41}\text{NNaO}_{13}$ 610.24756; found 610.24850.

3-C-(Methyl 5-Acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero- α -D-galacto-non-2-ulopyranosonate)pentan-3-ol (9): *C*-Sialoside **9** was obtained by the general coupling procedure with pentan-3-one as the electrophile in 44% yield from **3a** and 26% yield from **3b** on a 0.035 mmol scale with respect to the acetate derivatives. ^1H NMR (CDCl_3 , 250 MHz): $\delta = 5.45$ (ddd, $J_{8,7} = 8.2$, $J_{8,9b} = 5.9$, $J_{8,9a} = 2.6$ Hz, 1 H, 8-H), 5.34 (dd, $J_{7,8} = 8.2$, $J_{7,6} = 2.2$ Hz, 1 H, 7-H), 5.21 (d, $J_{\text{NH},5} = 9.8$ Hz, 1 H, NH), 4.85 (ddd, $J_{4,3\text{ax}} = 12.0$, $J_{4,5} = 10.0$, $J_{4,3\text{eq}} = 4.5$ Hz, 1 H, 4-H), 4.30 (dd, $J_{9a,9b} = 12.5$, $J_{9a,8} = 2.6$ Hz, 1 H, 9a-H), 4.11 (dd, $J_{6,5} = 9.8$, $J_{6,7} = 2.2$ Hz, 1 H, 6-H), 4.10 (dd, $J_{9b,9a} = 12.5$, $J_{9b,8} = 5.9$ Hz, 1 H, 9b-H), 3.95 (t, $J_{5,6} = 9.8$ Hz, 1 H, $J_{5,4} = 10.0$ Hz, 5-H), 3.85 (s, 3 H, CO_2CH_3), 2.50 (dd, $J_{3\text{eq},3\text{ax}} = 12.5$, $J_{3\text{eq},4} = 4.5$ Hz, 1 H, 3eq-H), 2.15, 2.11, 2.02, 2.00 ($4 \times s$, 12 H, $4 \times \text{OAc}$), 2.05 (dd, $J_{3\text{ax},3\text{eq}} = 12.5$, $J_{3\text{ax},4} = 12.0$ Hz, 1 H, 3ax-H), 1.92 (s, 3 H, NAc), 1.69–1.47 (m, 4 H, CH_2 of ethyl), 0.91 (t, $J = 7.4$ Hz, 3 H, CH_3 of ethyl), 0.84 (t, $J = 7.4$ Hz, 3 H, CH_3 of ethyl) ppm. MS (ESI): $m/z = 584.2$ [$\text{M} + \text{Na}$] $^+$.

1-C-(Methyl 5-Acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero- α -D-galacto-non-2-ulopyranosonate)octanol (10): *C*-Sialoside **10** was obtained by the general coupling procedure with octanal as the electrophile in 39% yield from **3a** and 33% yield from **3b** on a 0.03 mmol scale with respect to the acetate derivatives. ^1H NMR (CDCl_3 , 250 MHz): $\delta = 5.41$ (ddd, $J_{8,7} = 8.2$, $J_{8,9b} = 5.9$, $J_{8,9a} = 2.6$ Hz, 1 H, 8-H), 5.29 (dd, $J_{7,8} = 8.2$, $J_{7,6} = 2.2$ Hz, 1 H, 7-H), 5.20 (d, $J_{\text{NH},5} = 9.8$ Hz, 1 H, NH), 4.75 (ddd, $J_{4,3\text{ax}} = 12.0$, $J_{4,5} = 10.0$, $J_{4,3\text{eq}} = 4.5$ Hz, 1 H, 4-H), 4.36 (dd, $J_{9a,9b} = 12.5$, $J_{9a,8} = 2.6$ Hz, 1 H, 9a-H), 4.21 (dd, $J_{6,5} = 9.8$, $J_{6,7} = 2.2$ Hz, 1 H, 6-H), 4.12 (dd, $J_{9b,9a} = 12.5$, $J_{9b,8} = 5.9$ Hz, 1 H, 9b-H), 4.00–3.95 (m, 1 H, 5-H), 3.71 (s, 3 H, CO_2CH_3), 2.41 (dd, $J_{3\text{eq},3\text{ax}} = 12.5$, $J_{3\text{eq},4} = 4.5$ Hz, 1 H, 3eq-H), 2.13, 2.10, 2.09, 1.95 ($4 \times s$, 12 H, $4 \times \text{OAc}$), 2.05 (dd, $J_{3\text{ax},3\text{eq}} = 12.5$, $J_{3\text{ax},4} = 12.0$ Hz, 1 H, 3ax-H), 1.82 (s, 3 H, NAc), 1.27–1.20 and 0.88–0.81 (m, 15 H, octyl) ppm. MS (ESI): $m/z = 626.2$ [$\text{M} + \text{Na}$] $^+$.

1-C-(Methyl 5-Acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero- α -D-galacto-non-2-ulopyranosonate)-1-cyclohexylmethanol (13): Molecular sieves (4 Å, 82 mg) and PCC (54 mg, 0.24 mmol) were added to a solution of the two diastereomers **8a** and **8b** (29 mg, 0.05 mmol) in dichloromethane (1 mL). The resulting mixture was stirred at room temperature and the progress of the reaction was monitored by TLC (toluene/acetone, 2:1). After 30 min the reaction mixture was diluted with diethyl ether and filtered

through a pad of silica. The filtrate was concentrated and the residue was purified by flash chromatography (toluene/acetone, 2:1) to afford **13** (18 mg, 0.03 mmol, 50%). ¹H NMR (CDCl₃, 250 MHz): δ = 5.48–5.31 (m, 2 H, 7-H, 8-H), 5.20 (d, $J_{\text{NH},5}$ = 9.8 Hz, 1 H, NH), 4.92 (ddd, $J_{4,3\text{ax}}$ = 11.8, $J_{4,5}$ = 9.8, $J_{4,3\text{eq}}$ = 4.7 Hz, 1 H, 4-H), 4.32 (dd, $J_{9\text{a},9\text{b}}$ = 12.3, $J_{9\text{a},8}$ = 2.1 Hz, 1 H, 9a-H), 4.09 (dd, $J_{9\text{a},9\text{b}}$ = 12.3, $J_{9\text{b},8}$ = 5.4 Hz, 1 H, 9b-H), 4.00 (ddd, $J_{5,6}$ = 10.5, $J_{5,\text{NH}}$ = $J_{5,4}$ = 9.8 Hz, 1 H, 5-H), 3.93 (dd, $J_{5,6}$ = 10.5 Hz, $J_{6,7}$ = 2.4 Hz, 1 H, 6-H), 3.74 (s, 3 H, CO₂Me), 2.68 (dd, $J_{3\text{eq},3\text{ax}}$ = 13.4, $J_{3\text{eq},4}$ = 4.7 Hz, 1 H, 3eq-H), 2.14, 2.11, 2.03, 2.01 (4 $\times$ s, 12 H, 4 $\times$ OAc), 1.87 (s, 3 H, NAc) ppm. MS (ESI): m/z = 608.3 [M + Na]⁺. HRMS: calcd. for C₂₇H₃₉NNaO₁₃ 608.2319; found 608.2308.

1-C-(Methyl 5-Acetamido-4,7,8,9-tetra-O-acetyl-3,5-dideoxy-D-glycero- α -D-galacto-non-2-ulopyranosonate)cyclohexanol (14): C-Sialoside **14** was obtained by the general coupling procedure with cyclohexanone as the electrophile in 79% yield from a **3a/3b** mixture on a 0.035 mmol scale with respect to the acetate derivatives. ¹H NMR (CDCl₃, 250 MHz): δ = 5.32 (ddd, $J_{8,7}$ = 8.5, $J_{8,9\text{b}}$ = 5.9, $J_{8,9\text{a}}$ = 2.6 Hz, 1 H, 8-H), 5.30 (dd, $J_{7,8}$ = 8.5, $J_{7,6}$ = 2.1 Hz, 1 H, 7-H), 5.26 (d, $J_{\text{NH},5}$ = 8.6 Hz, 1 H, NH), 4.80 (ddd, $J_{4,3\text{ax}}$ = 11.5, $J_{4,5}$ = 9.8, $J_{4,3\text{eq}}$ = 4.4 Hz, 1 H, 4-H), 4.28 (dd, $J_{9\text{a},9\text{b}}$ = 12.4, $J_{9\text{a},8}$ = 2.8 Hz, 1 H, 9a-H), 4.06–3.94 (m, 3 H, 6-H, 5-H, 9b-H), 3.70 (s, 3 H, CO₂CH₃), 2.39 (dd, $J_{3\text{eq},3\text{ax}}$ = 12.5, $J_{3\text{eq},4}$ = 4.4 Hz, 1 H, 3eq-H), 2.12, 2.10, 2.05, 1.98 (4 $\times$ s, 12 H, 4 $\times$ OAc), 2.04 (dd, $J_{3\text{ax},3\text{eq}}$ = 12.5, $J_{3\text{ax},4}$ = 11.5 Hz, 1 H, 3ax-H), 1.85 (s, 3 H, NAc), 1.47–1.34 (m, 8 H, cyclohexyl) ppm. ¹³C NMR (CDCl₃, 90 MHz): δ = 170.7–169.3 (CO, 4 $\times$ OCOMe, NCOMe, CO₂Me), 97.1 (C-2), 74.6 (COH), 72.4, 70.5, 68.6, 67.7 (C-6, C-8, C-4, C-7), 62.3 (C-9), 52.4 (CH₃O), 47.5 (C-5), 37.8 (C-3), 32.6–29.1 (CH₂ of cyclohexyl), 23.2, 22.1, 21.5, 20.8, 20.1 (4 $\times$ CH₃OCO, CH₃CON) ppm. MS (ESI): m/z = 596.2 [M + Na]⁺.

1-C-(Methyl 5-Acetamido-4,7,8,9-tetra-O-acetyl-3,5-dideoxy-D-glycero- α -D-galacto-non-2-ulopyranosonate)-4-oxo-cyclohexanol (15): C-Sialoside **15** was obtained by the general coupling procedure with cyclohexane-1,4-dione as the electrophile in 30% yield from a **3a/3b** mixture on a 0.035 mmol scale with respect to the acetate derivatives, with 1.4 equiv. of cyclohexane-1,4-dione. ¹H NMR (CDCl₃, 250 MHz): δ = 5.42 (ddd, $J_{8,7}$ = 8.2, $J_{8,9\text{b}}$ = 6.4, $J_{8,9\text{a}}$ = 2.6 Hz, 1 H, 8-H), 5.30 (dd, $J_{7,8}$ = 8.2, $J_{7,6}$ = 1.7 Hz, 1 H, 7-H), 5.24 (d, $J_{\text{NH},5}$ = 10.0 Hz, 1 H, NH), 4.73 (ddd, $J_{4,3\text{ax}}$ = 11.8, $J_{4,5}$ = 9.6, $J_{4,3\text{eq}}$ = 4.3 Hz, 1 H, 4-H), 4.32 (dd, $J_{9\text{a},9\text{b}}$ = 12.3, $J_{9\text{a},8}$ = 2.6 Hz, 1 H, 9a-H), 4.05 (dd, $J_{6,5}$ = 10.2, $J_{6,7}$ = 1.7 Hz, 1 H, 6-H), 3.99–3.97 (m, 2 H, 5-H, 9b-H), 3.80 (s, 3 H, CO₂CH₃), 3.21 (s, 1 H, OH), 2.74 (m, 4 H, CH₂ of cyclohexyl), 2.47 (dd, $J_{3\text{eq},3\text{ax}}$ = 12.6, $J_{3\text{eq},4}$ = 4.3 Hz, 1 H, 3eq-H), 2.17, 2.12, 2.04, 2.01 (4 $\times$ s, 12 H, 4 $\times$ OAc), 2.03 (dd, $J_{3\text{ax},3\text{eq}}$ = 12.6, $J_{3\text{ax},4}$ = 11.8 Hz, 1 H, 3ax-H), 1.86 (s, 3 H, NAc), 1.85–1.80 (m, 4 H, CH₂ of cyclohexyl) ppm. ¹³C NMR (CDCl₃, 90 MHz): δ = 192.0 (CO), 170.8, 170.7, 170.6, 170.4, 169.9, 169.5 (CO, 4 $\times$ OCOMe, NCOMe, CO₂Me), 85.4 (C-2), 73.8 (COH), 73.2, 70.0, 68.4, 67.7 (C-6, C-8, C-4, C-7), 62.6 (C-9), 52.6 (CH₃O), 49.1 (C-5), 32.9 (C-3), 36.6, 36.4, 31.4, 31.3 (CH₂ of cyclohexyl), 23.0, 21.3, 20.8, 20.7, 20.5 (4 $\times$ CH₃OCO, CH₃CON) ppm. MS (ESI): m/z = 610.3 [M + Na]⁺. HRMS: calcd. for C₂₄H₃₅NNaO₁₃ 610.2118; found 610.2145.

4-(Allyloxy)cyclohexanone (16): Sodium hydride (396 mg, 17.2 mmol) and allyl bromide (2.4 mL, 25.8 mmol) were successively added to the commercial *cis/trans* mixture of cyclohexane-1,4-diol (4.0 g, 34.5 mmol) in DMF (30 mL). After a night at room temperature the reaction mixture was hydrolyzed by addition of water (25 mL). The aqueous phase was extracted with CH₂Cl₂, the combined organic phases were dried with Na₂SO₄, and the solvents were evaporated to dryness. After two successive coevaporations

with toluene the crude mixture was treated for 1 h with PCC (9.6 g, 44.8 mmol) in dichloromethane (150 mL) in the presence of molecular sieves (4 Å). After addition of diethyl ether (150 mL), the mixture was filtered through silica and the solvents were evaporated. Flash chromatography on silica gel (cyclohexane/ethyl acetate, 3:1) gave **16** (1.86 g, 12 mmol, 46%) as an oil. ¹H NMR (CDCl₃, 250 MHz): δ = 5.80 (dddd, J = 17.2, 10.4, 5.0, 5.0 Hz, 1 H), 5.18 (dq, J = 17.2, 1.8 Hz, 1 H), 5.13 (dq, J = 10.4, 1.7 Hz, 1 H), 3.92 (m, 2 H), 3.63 (tt, J = 6.6, 3.3 Hz, 1 H), 2.42 (m, 2 H), 2.10 (m, 2 H), 1.93 (m, 2 H), 1.80 (m, 2 H) ppm. ¹³C NMR (CDCl₃, 90 MHz): δ = 210.6, 135.0, 116.3, 72.0, 69.0, 37.0, 30.4 ppm. MS (ES): m/z = 177.1 [M + Na]⁺. HRMS: calcd. for C₉H₁₄O₂Na 177.0891; found 177.0896.

1-C-(Methyl 5-Acetamido-4,7,8,9-tetra-O-acetyl-3,5-dideoxy-D-glycero- α -D-galacto-non-2-ulopyranosonate)-4-allyloxycyclohexanol (17): C-Sialosides **17** were obtained as a 1:1 mixture by the general coupling procedure with 4-(allyloxy)cyclohexanone (**16**) as the electrophile in 83% yield from **3a/3b** on a 0.04 mmol scale with respect to the acetate derivatives. ¹H NMR (CDCl₃, 250 MHz): δ = 5.92 [dddd, J = 16.0, 10.5, 5.1, 5.0 Hz, 1 H, CH (allyl)], 5.42 (m, 2 H, 7-H, 8-H), 5.30 (d, $J_{\text{NH},5}$ = 7.9 Hz, 1 H, NH), 5.27 [ddt, J = 16.0, 2.0, 1.3 Hz, 1 H, CH (allyl)], 5.15 [ddt, J = 10.5, 2.0, 2.0 Hz, 1 H, CH (allyl)], 4.74 (ddd, $J_{4,3\text{ax}}$ = 11.3, $J_{4,5}$ = 10.2, $J_{4,3\text{eq}}$ = 4.6 Hz, 1 H, 4-H), 4.37 (dd, $J_{9\text{a},9\text{b}}$ = 12.4, $J_{9\text{a},8}$ = 2.5 Hz, 0.5 H, 9a-H), 4.35 (dd, $J_{9\text{a},9\text{b}}$ = 12.4, $J_{9\text{a},8}$ = 2.5 Hz, 0.5 H, 9a-H), 4.12–3.92 [m, 5 H, 5-H, 6-H, 9b-H, CH₂ (allyl)], 3.80 (s, 1.5 H, CO₂CH₃), 3.78 (s, 1.5 H, CO₂CH₃), 3.22 (m, 1 H), 2.75 (s, 0.5 H, OH), 2.68 (s, 0.5 H, OH), 2.49 (dd, $J_{3\text{eq},3\text{ax}}$ = 12.8, $J_{3\text{eq},4}$ = 4.5 Hz, 0.5 H, 3eq-H), 2.48 (dd, $J_{3\text{eq},3\text{ax}}$ = 12.8, $J_{3\text{eq},4}$ = 4.5 Hz, 0.5 H, 3eq-H), 2.18 (s, 1.5 H, OCOCH₃), 2.17 (s, 1.5 H, OCOCH₃), 2.13, 2.06, and 2.03 (3 $\times$ s, 9 H, 3 $\times$ OCOCH₃), 1.88 (s, 3 H, NCOCH₃) ppm. ¹³C NMR (CDCl₃, 90 MHz): δ = 171.0, 170.8, 170.2, 170.0, 135.6, 135.5, 116.5, 115.8, 86.1, 85.7, 75.0, 74.2, 73.2, 71.6, 70.47, 70.3, 68.9, 68.7, 68.5, 67.8, 52.5, 52.3, 49.4, 32.9, 30.0, 29.9, 27.2, 27.0, 25.8, 25.4, 25.0, 23.1, 21.3, 20.8 ppm. MS (ES): m/z = 652.2 [M + Na]⁺. HRMS: calcd. for C₂₉H₄₃NNaO₁₄ 652.2581; found 652.2589.

4-(tert-Butyldimethylsilyloxy)cyclohexanone (18): *tert*-Butyldimethylsilyl chloride (6.45 g, 43 mmol) and imidazole (5.85 g, 86 mmol) were successively added to the commercial *cis/trans* mixture of cyclohexane-1,4-diol (5.0 g, 43 mmol) in DMF (40 mL). After a night at room temperature the reaction mixture was hydrolyzed by addition of water (40 mL). The aqueous phase was extracted with CH₂Cl₂, the combined organic phases were dried with Na₂SO₄, and the solvents were evaporated to dryness. After two successive coevaporations with toluene the crude mixture was treated for 1.5 h with PCC (12 g, 56 mmol) in dichloromethane (200 mL) the presence of molecular sieves (4 Å). After addition of diethyl ether (200 mL) the mixture was filtered through silica and the solvents were evaporated. Flash chromatography on silica gel (cyclohexane/ethyl acetate, 4:1) gave **18** (2.73 g, 12 mmol, 28%) as a colorless oil. ¹H NMR (CDCl₃, 250 MHz): δ = 4.07 (m, 1 H), 2.59 (m, 2 H), 2.15 (m, 2 H), 1.85 (m, 2 H), 0.85 (s, 9 H, *t*Bu), 0.03 (s, 6 H, Me₂Si) ppm. ¹³C NMR (CDCl₃, 90 MHz): δ = 211.2, 65.8, 36.7, 34.1, 25.7, 17.9, –4.9 ppm. MS (ES): m/z = 251.1 [M + Na]⁺. HRMS: calcd. for C₁₂H₂₄NaO₂Si 251.1443; found 251.1448.

1-C-(Methyl 5-Acetamido-4,7,8,9-tetra-O-acetyl-3,5-dideoxy-D-glycero- α -D-galacto-non-2-ulopyranosonate)-4-(tert-butyldimethylsilyloxy)cyclohexanol (19): C-Sialosides **19** were obtained as a 1:1 mixture by the general coupling procedure with 4-(*tert*-butyldimethylsilyloxy)cyclohexanone (**18**) in 85% yield from **3a/3b** on a 0.04 mmol scale with respect to the acetate derivatives. ¹H NMR (CDCl₃, 300 MHz): δ = 5.41 (ddd, $J_{8,7}$ = 8.0, $J_{8,9\text{b}}$ = 6.6, $J_{8,9\text{a}}$ =

2.5 Hz, 1 H, 8-H), 5.31 (dd, $J_{7,8} = 8.0$, $J_{7,6} = 1.1$ Hz, 1 H, 7-H), 5.24 (d, $J_{\text{NH},5} = 9.4$ Hz, 1 H, NH), 4.76 (ddd, $J_{4,3\text{ax}} = 11.2$, $J_{4,5} = 10.4$, $J_{4,3\text{eq}} = 4.5$ Hz, 1 H, 4-H), 4.35 (dd, $J_{9\text{a},9\text{b}} = 12.4$, $J_{9\text{a},8} = 2.5$ Hz, 0.5 H, 9a-H), 4.33 (dd, $J_{9\text{a},9\text{b}} = 12.4$, $J_{9\text{a},8} = 2.5$ Hz, 0.5 H, 9a-H), 4.20–4.05 (m, 2 H, 5-H, 6-H), 4.00 (dd, $J_{9\text{b},9\text{a}} = 12.4$, $J_{9\text{b},8} = 6.6$ Hz, 1 H, 9b-H), 3.80 (s, 1.5 H, CO_2CH_3), 3.78 (s, 1.5 H, CO_2CH_3), 2.62 (s, 1 H, OH), 2.49 (dd, $J_{3\text{eq},3\text{ax}} = 12.8$, $J_{3\text{eq},4} = 4.5$ Hz, 0.5 H, 3eq-H), 2.47 (dd, $J_{3\text{eq},3\text{ax}} = 12.8$, $J_{3\text{eq},4} = 4.5$ Hz, 0.5 H, 3eq-H), 2.17, 2.13, 2.05, and 2.03 (4 $\times$ s, 12 H, 4 $\times$ OCOCH_3), 1.88 (s, 3 H, NCOCH_3), 1.87 (s, 3 H, NCOCH_3), 0.89 (s, 9 H, *t*Bu), 0.88 (s, 9 H, *t*Bu), 0.05 (6 H, Me_2Si), 0.04 (3 H, MeSi), 0.3 (3 H, MeSi) ppm. ^{13}C NMR (CDCl_3 , 90 MHz): $\delta = 171.1$, 171.0, 170.6, 170.3, 170.2, 170.0, 86.0, 85.8, 75.5, 74.1, 73.3, 73.1, 71.1, 70.5, 70.2, 68.8, 68.6, 67.8, 67.7, 65.5, 62.6, 52.4, 52.2, 49.6, 33.0, 32.7, 30.8, 30.7, 30.2, 30.0, 29.7, 28.9, 28.7, 25.8, 25.5, 25.0, 23.1, 21.2, 20.9, 20.8, 18.1, 18.0, -4.5, -4.9 ppm. MS (ES): $m/z = 726.2$ [$\text{M} + \text{Na}$] $^+$. HRMS: calcd. for $\text{C}_{32}\text{H}_{53}\text{NNaO}_{14}\text{Si}$ 726.3133; found 726.3165.

1-C-(Methyl 5-Acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero- α -D-galacto-non-2-ulopyranosonate)cyclobutanol (20): C-Sialoside **20** was obtained by the general coupling procedure with cyclobutanone as the electrophile in 88% yield from a **3a/3b** mixture on a 0.04 mmol scale with respect to the acetate derivatives. ^1H NMR (CDCl_3 , 250 MHz): $\delta = 5.40$ (ddd, $J_{8,7} = 7.9$, $J_{8,9\text{b}} = 6.5$, $J_{8,9\text{a}} = 2.4$ Hz, 1 H, 8-H), 5.30 (dd, $J_{7,8} = 7.9$, $J_{7,6} = 2.6$ Hz, 1 H, 7-H), 5.18 (d, $J_{\text{NH},5} = 10.1$ Hz, 1 H, NH), 4.78 (ddd, $J_{4,3\text{ax}} = 12.5$ Hz, $J_{4,5} = 9.9$, $J_{4,3\text{eq}} = 4.8$ Hz, 1 H, 4-H), 4.30 (dd, $J_{9\text{a},9\text{b}} = 12.3$, $J_{9\text{a},8} = 2.4$ Hz, 1 H, 9a-H), 4.15 (dd, $J_{6,5} = 10.6$, $J_{6,7} = 2.6$ Hz, 1 H, 6-H), 4.11–3.97 (m, 2 H, 5-H, 9b-H), 3.75 (s, 3 H, CO_2CH_3), 2.53 (dd, $J_{3\text{eq},3\text{ax}} = 12.9$, $J_{3\text{eq},4} = 4.8$ Hz, 1 H, 3eq-H), 2.38 (m, 6 H, cyclobutyl), 2.14, 2.11, 2.03, 2.02 (4 $\times$ s, 12 H, 4 $\times$ OAc), 2.04 (dd, $J_{3\text{ax},3\text{eq}} = 12.9$, $J_{3\text{ax},4} = 12.5$ Hz, 1 H, 3ax-H), 1.86 (s, 3 H, NAc) ppm. ^{13}C NMR (CDCl_3 , 90 MHz): $\delta = 171.0$, 170.7, 170.6, 170.3, 170.1, 169.5 (4 $\times$ OCOMe , NCOMe , CO_2Me), 79.1 (C-2), 73.1, 70.2, 68.6, 67.8 (C-6, C-8, C-4, C-7), 62.8 (C-9), 52.4 (CH_3O), 49.5 (C-5), 33.3 (C-3), 31.0, 30.3 (CH_2 of cyclobutyl), 23.2, 21.3, 20.9, 20.7, 20.6 (4 $\times$ CH_3OCO , CH_3CON), 13.0 (CH_2 of cyclobutyl) ppm. MS (ESI): $m/z = 568.2$ [$\text{M} + \text{Na}$] $^+$. HRMS: calcd. for $\text{C}_{24}\text{H}_{35}\text{NNaO}_{13}$ 568.2001; found 568.2010.

3-(tert-Butyldimethylsilyloxy)propanal (21): PCC (10 g, 0.046 mol) was added in one portion to a solution of 3-(tert-butyldimethylsilyloxy)propanol (6.0 g, 0.031 mol) in dichloromethane (100 mL). The mixture was then stirred for 3 h at room temperature. The solution was separated from the black insoluble material, which was extracted with diethyl ether (4 $\times$ 50 mL). The combined organic phase was filtered through silica (10 g) and evaporated to afford aldehyde **21** (4.4 g, 0.023 mol, 76%). ^1H NMR (CDCl_3 , 360 MHz): $\delta = 9.76$ (d, $J = 1.6$ Hz, 1 H, CHO), 3.96 (t, $J = 6.0$ Hz, 2 H, CH_2O), 2.57 (t, $J = 6.0$ Hz, 2 H, CH_2CHO), 0.86 (s, 9 H, *t*Bu), 0.03 (s, 6 H, Me_2Si) ppm. ^{13}C NMR (CDCl_3 , 90 MHz): $\delta = 202.0$, 58.8, 46.6, 26.0, 18.3, and -5.5 ppm. MS (ESI): $m/z = 211.1$ [$\text{M} + \text{Na}$] $^+$.

1-C-(Methyl 5-Acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero- α -D-galacto-non-2-ulopyranosonate)-3-(tert-butyldimethylsilyloxy)propanol (22): C-Sialosides **22** were obtained by the general coupling procedure with 3-(tert-butyldimethylsilyloxy)propanal as the electrophile in 26% yield from a **3a/3b** mixture on a 0.03 mmol scale with respect to the acetate derivatives. M.p. 78 $^\circ\text{C}$ (toluene/acetone). Data for the (1:1) mixture of isomers: ^1H NMR (CDCl_3 , 360 MHz): $\delta = 5.40$ –5.27 (m, 2 H, 8-H, 7-H), 4.75 (ddd, $J_{4,3\text{ax}} = 11.9$, $J_{4,5} = 9.7$, $J_{4,3\text{eq}} = 4.6$ Hz, 1 H, 4-H), 4.32 and 4.31 (2 $\times$ dd, $J_{9\text{a},9\text{b}} = 12.2$, $J_{9\text{a},8} = 2.4$ Hz, 2 H, 9a-H), 4.11–3.93 (m, 3 H, 6-H, 5-H, 9b-H), 3.88–3.73 (m, 3 H, CH_2OTBDMS , CHOH), 3.72 and

3.71 (2 $\times$ s, 6 H, CO_2CH_3), 3.09 (s, 1 H, OH), 2.42 (2 $\times$ dd, $J_{3\text{eq},3\text{ax}} = 12.8$, $J_{3\text{eq},4} = 4.6$ Hz, 2 H, 3eq-H), 2.10, 2.09, 2.07, 1.99 (4 $\times$ s, 12 H, 4 $\times$ OAc), 2.00 (m, 1 H, 3ax-H), 1.91 (s, 3 H, NAc), 1.60–1.50 (m, 2 H, CH_2), 0.84 (s, 9 H, *t*Bu), 0.01 (s, 6 H, Me_2Si) ppm. ^{13}C NMR (CDCl_3 , 90 MHz): $\delta = 171.0$, 170.9, 170.7, 170.6, 170.3, and 170.1 (4 $\times$ OCOCH_3 , NCOCH_3 , CO_2CH_3), 83.4 (C-2), 73.3, 70.2, 69.1, 68.8 (C-4, C-6, C-7, C-8), 70.1 (COH), 62.7 (C-9), 60.4 (CH_2O), 52.5 (CH_3O), 49.4 (C-5), 33.9 (CH_2), 32.9 (C-3), 25.8 [(CH_3) $_3$], 23.1, 21.2, 20.8, 20.7, and 20.5 (8 $\times$ CH_3OCO , 2 $\times$ CH_3CON), 18.2 [$\text{C}(\text{CH}_3)_3$], -5.4 [(CH_3) $_2\text{Si}$] ppm. MS (ESI): $m/z = 686.3$ [$\text{M} + \text{Na}$] $^+$.

D-erythro-L-glucio- α -D-galacto-Pentadecopyranose, 11-(Acetyl amino)-8,12-anhydro-6,9,11-trideoxy-8-C-(methoxycarbonyl)-1,2,3,4-bis-*O*-(1-methylthylidene)-10,13,14,15-tetraacetate (24): C-Sialoside **24** was obtained by the general coupling procedure with the galactose-derived aldehyde **23**^[24] in 30% yield from a **3a/3b** mixture on a 0.04 mmol scale with respect to the acetate derivatives. Data for the (*R/S*) mixture: ^1H NMR (CDCl_3 , 360 MHz): $\delta = 5.49$ (d, $J_{1',2'} = 4.9$ Hz, 1 H, 1'-H), 5.43 (ddd, $J_{8,7} = 7.2$, $J_{8,9\text{b}} = 6.4$, $J_{8,9\text{a}} = 2.5$ Hz, 2 H, 8-H), 5.33–5.23 (m, 2 H, 7-H), 4.78 (ddd, $J_{4,3\text{ax}} = 11.9$, $J_{4,5} = 10.1$, $J_{4,3\text{eq}} = 4.4$ Hz, 2 H, 4-H), 4.60 (dd, $J = 7.8$, $J = 2.5$ Hz, 1 H, 2'-H), 4.37–3.85 (m, 20 H, 3'-H, 4'-H, 5'-H, 2 6'-H, 5-H, 6-H, 9a-H, 9b-H, 7''-H), 3.76 (s, 3 H, CO_2Me), 3.74 (s, 3 H, CO_2Me), 2.46 (dd, $J_{3\text{eq},3\text{ax}} = 12.8$, $J_{3\text{eq},4} = 4.4$ Hz, 1 H, 3eq-H), 2.35 (dd, $J_{3\text{eq},3\text{ax}} = 13.4$, $J_{3\text{eq},4} = 4.58$ Hz, 1 H, 3eq-H), 2.16, 2.15, 2.14, 2.13 (4 $\times$ s, 12 H, OAc), 2.03, 2.02, 2.01, 2.00 (4 $\times$ s, 12 H, OAc), 1.88 (t, $J_{3\text{ax},3\text{eq}} = 13.4$, $J_{3\text{ax},4} = 11.9$ Hz, 1 H, 3ax-H), 1.85 (s, 6 H, NAc), 1.54, 1.52, 1.49, 1.45, 1.38, 1.36, 1.31, 1.30 (8 $\times$ s, 24 H, CH_3) ppm. MS (ESI): $m/z = 770.3$ [$\text{M} + \text{Na}$] $^+$. HRMS: calcd. for $\text{C}_{33}\text{H}_{49}\text{NNaO}_{18}$ 770.2853; found 770.2845.

General Procedure for Deacetylation: A suspension of the acetylated sialic acid derivative (0.02 mmol) in methanol (2 mL) was treated with a catalytic amount of sodium. The resulting mixture was stirred overnight at room temperature. The progress of the reaction was monitored by TLC ($\text{EtOAc}/i\text{PrOH}/\text{H}_2\text{O}$, 2:2:1). The mixture was neutralized with Amberlite IR-120 (H^+) resin and filtered. The resin was washed several times with methanol. The filtrate was evaporated and the residue was purified by flash chromatography ($\text{CH}_2\text{Cl}_2/\text{MeOH}$, 95:5) to afford the corresponding product.

1-C-(Methyl 5-Acetamido-3,5-dideoxy-D-glycero- α -D-galacto-non-2-ulopyranosonate)cyclopentanol (11): Compound **11** was obtained by the general deacetylation procedure in 90% yield from **6** on a 0.02 mmol scale. ^1H NMR (CD_3OD , 250 MHz): $\delta = 3.86$ –3.40 (m, 3 H, 8-H, 9a-H), 3.79 (s, 3 H, CO_2CH_3), 3.68 (t, $J_{5,6} = J_{5,\text{NH}} = J_{5,4} = 10.5$ Hz, 1 H, 5-H), 3.64 (dd, $J_{9\text{b},9\text{a}} = 10.9$, $J_{9\text{b},8} = 5.2$ Hz, 1 H, 9b-H), 3.48 (dd, $J_{7,8} = 9.0$, $J_{7,6} = 1.7$ Hz, 1 H, 7-H), 3.45–3.40 (m, 2 H, 4-H, 6-H), 2.62 (dd, $J_{3\text{eq},3\text{ax}} = 12.5$, $J_{3\text{eq},4} = 4.4$ Hz, 1 H, 3eq-H), 2.01 (s, 3 H, NAc), 2.00 (dd, $J_{3\text{ax},3\text{eq}} = 12.5$, $J_{3\text{ax},4} = 8.4$ Hz, 1 H, 3ax-H), 1.92–1.31 (m, 8 H, cyclopentyl) ppm. ^{13}C NMR (CD_3OD , 90 MHz): $\delta = 175.4$, 174.7 (NCOMe , CO_2Me), 86.5 (C-2), 82.0 (COH), 75.9, 72.9, 70.3, 69.4 (C-6, C-8, C-4, C-7), 64.8 (C-9), 54.1 (C-5), 53.2 (CH_3O), 37.8 (C-3), 36.6, 35.6, 25.8, 24.9 (CH_2 of cyclopentyl), 22.7 (CH_3CON) ppm. MS (ESI): $m/z = 414.1$ [$\text{M} + \text{Na}$] $^+$. HRMS: calcd. for $\text{C}_{17}\text{H}_{29}\text{NNaO}_9$ 414.4025; found 414.4075.

(*R/S*)-1-C-(Methyl 5-Acetamido-3,5-dideoxy-D-glycero- α -D-galacto-non-2-ulopyranosonate)-1-cyclohexylmethanol (12a and 12b): Compounds **12a** and **12b** were obtained by the general deacetylation procedure in 92% yield both from **8a** and from **8b** on a 0.02 mmol scale.

Data for Isomer 12a: ^1H NMR (CD_3OD , 250 MHz): $\delta = 3.86$ –3.79 (m, 2 H, 8-H, 9a-H), 3.79–3.71 (m, 1 H, 4-H), 3.79 (s, 3 H,

CO₂CH₃), 3.68 (t, $J_{5,6} = J_{5,NH} = J_{5,4} = 10.5$ Hz, 1 H, 5-H), 3.64 (dd, $J_{9b,9a} = 10.9$, $J_{9b,8} = 5.2$ Hz, 1 H, 9b-H), 3.54 (d, $J = 4.3$ Hz, 1 H, 1'-H), 3.48 (dd, $J_{7,8} = 9.0$, $J_{7,6} = 1.7$ Hz, 1 H, 7-H), 3.44 (dd, $J_{6,5} = 10.5$, $J_{6,7} = 1.7$ Hz, 1 H, 6-H), 2.55 (dd, $J_{3eq,3ax} = 12.9$, $J_{3eq,4} = 4.2$ Hz, 1 H, 3eq-H), 2.02 (s, 3 H, NAc), 1.85 (dd, $J_{3ax,3eq} = 12.9$, $J_{3ax,4} = 8.4$ Hz, 1 H, 3ax-H), 1.80–1.10 (m, 11 H, cyclohexyl) ppm. ¹³C NMR (CD₃OD, 90 MHz): $\delta = 175.4$, 174.7 (CO, NCOMe, CO₂Me), 85.6 (C-2), 80.9 (COH), 75.7, 72.5, 70.2, 69.2 (C-6, C-8, C-4, C-7), 64.8 (C-9), 54.2 (C-5), 53.1 (CH₃O), 40.6 (C of cyclohexyl), 36.8 (C-3), 33.0, 28.5, 27.8, 27.5, 27.4 (CH₂ of cyclohexyl), 22.7 (CH₃CON) ppm. MS (ESI): $m/z = 442.1$ [M + Na]⁺. HRMS: calcd. for C₁₉H₃₃NNaO₉ 442.20530; found 442.20567.

Data for Isomer 12b: ¹H NMR (CD₃OD, 250 MHz): $\delta = 3.83$ (dd, $J_{9a,9b} = 11.4$, $J_{9a,8} = 2.4$ Hz, 1 H, 9a-H), 3.82–3.72 (m, 1 H, 8-H), 3.81 (s, 3 H, CO₂CH₃), 3.76 (dd, $J_{6,5} = 10.0$, $J_{6,7} = 1.9$ Hz, 1 H, 6-H), 3.69 (t, $J_{5,6} = J_{5,NH} = J_{5,4} = 10.0$ Hz, 1 H, 5-H), 3.66 (dd, $J_{9b,9a} = 11.4$, $J_{9b,8} = 5.7$ Hz, 1 H, 9b-H), 3.63–3.58 (m, 1 H, 4-H), 3.51 (dd, $J_{7,8} = 9.1$, $J_{7,6} = 1.9$ Hz, 1 H, 7-H), 2.44 (dd, $J_{3eq,3ax} = 12.9$, $J_{3eq,4} = 4.6$ Hz, 1 H, 3eq-H), 2.17 (dd, $J_{3ax,3eq} = 12.9$, $J_{3ax,4} = 11.1$ Hz, 1 H, 3ax-H), 2.01 (s, 3 H, NAc), 1.94–1.10 (m, 11 H, cyclohexyl) ppm. ¹³C NMR (CD₃OD, 90 MHz): $\delta = 175.2$, 175.0 (CO, NCOMe, CO₂Me), 85.5 (C-2), 80.0 (COH), 75.9, 72.9, 70.3, 69.1 (C-6, C-8, C-4, C-7), 64.6 (C-9), 54.1 (C-5), 53.2 (CH₃O), 42.3 (C of cyclohexyl), 39.1 (C-3), 32.9, 28.3, 27.8, 27.4, 27.3 (CH₂ of cyclohexyl), 22.8 (CH₃CON) ppm. MS (ESI): $m/z = 442.1$ [M + Na]⁺. HRMS: calcd. for C₁₉H₃₃NNaO₉ 442.20530; found 442.20549.

1-C-(Methyl 5-Acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero- α -D-galacto-non-2-ulopyranosonate)-4-dioxolanylcyclohexanol (28): A freshly prepared solution of SmI₂ in THF (0.1 M, 100 mL, 10 mmol of SmI₂) was added at 20 °C under Ar to a stirred THF (10 mL) solution of acetates **3a** and **3b** (1.77 g, 3.32 mmol) and 4-dioxolanocyclohexanone (1.00 g, 6.64 mmol). After the mixture had been stirred for 2 h, saturated aqueous NH₄Cl was added and the reaction mixture was extracted three times with CH₂Cl₂. The combined organic phases were washed twice with water and dried with Na₂SO₄, and the solvents were evaporated to dryness. Flash chromatography on silica gel (toluene/acetone, 1:1) gave **28** (1.78 g, 85%). [α_D]₂₈⁸⁹ = –36.4 ($c = 0.14$, CH₂Cl₂). ¹H NMR (CDCl₃, 360 MHz): $\delta = 5.62$ (d, $J_{NH,5} = 9.5$ Hz, 1 H, NH), 5.52 (ddd, $J_{8,7} = 8.1$, $J_{8,9b} = 6.6$, $J_{8,9a} = 2.5$ Hz, 1 H, 8-H), 5.39 (dd, $J_{7,8} = 8.1$, $J_{7,6} = 1.1$ Hz, 1 H, 7-H), 4.84 (ddd, $J_{4,3ax} = 11.2$, $J_{4,5} = 10.4$, $J_{4,3eq} = 4.5$ Hz, 1 H, 4-H), 4.43 (dd, $J_{9a,9b} = 12.4$, $J_{9a,8} = 2.5$ Hz, 1 H, 9a-H), 4.22–3.97 (m, 2 H, 5,6-H), 4.21 (dd, $J_{9b,9a} = 12.4$, $J_{9b,8} = 6.6$ Hz, 1 H, 9b-H), 4.05 [m, 4 H, O(CH₂)₂-O], 3.89 (s, 3 H, CO₂CH₃), 2.95 (s, 1 H, OH), 2.58 (dd, $J_{3eq,3ax} = 12.8$, $J_{3eq,4} = 4.5$ Hz, 1 H, 3eq-H), 2.27, 2.22, 2.15, and 2.12 (4 $\times$ s, 12 H, 4 $\times$ OCOCH₃), 1.96 (s, 3 H, NCOCH₃), 1.94 (dd, $J_{3ax,3eq} = 12.8$, $J_{3ax,4} = 11.2$ Hz, 1 H, 3ax-H), 1.93–1.60 (m, 8 H, CH₂ of cyclohexyl) ppm. ¹³C NMR (CDCl₃, 90 MHz): $\delta = 170.8$, 170.7, 170.5, 170.1, 169.9, and 169.8 (4 $\times$ OCOCH₃, NCOCH₃, CO₂CH₃), 108.1, 85.7 (C-2), 74.1 (COH), 73.1, 70.3, 68.7, 67.7 (C-4, C-6, C-7, C-8), 64.9, 63.9 (OCH₂CH₂O), 62.9 (C-9), 52.2 (CH₃O), 49.0 (C-5), 32.9 (C-3), 29.9, 29.7, 29.2, and 28.9 (4 $\times$ CH₂ of cyclohexyl), 22.9, 21.1, 20.7, 20.6, and 20.5 (4 $\times$ CH₃OCO, CH₃CON) ppm. M.p. 208 °C (toluene/acetone). MS (ES): $m/z = 654$ [M + Na]⁺. HRMS: calcd. for C₂₈H₄₁NNaO₁₅ 654.2368; found 654.2383. C₂₈H₄₁NO₁₅ (631.63): calcd. C 53.24, H 6.54, N 2.22; found C 53.33, H 6.44, N 1.94.

1-C-(Methyl 5-Acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero- α -D-galacto-non-2-ulopyranosonate)-4-(2'-hydroxyethoxy)cyclohexanol (29): Trimethylsilyl trifluoromethanesulfonate (0.48 mL,

2.66 mmol) and borane–dimethyl sulfide complex (0.25 mL, 2.66 mmol) were successively added to a magnetically stirred solution of acetal **28** (1.40 g, 2.22 mmol) in dry dichloromethane (7 mL) cooled to –78 °C. After the mixture had been stirred at –78 °C for 4 h, saturated aqueous sodium hydrogen carbonate was added and the reaction mixture was extracted three times with CH₂Cl₂. The combined organic phases were dried with Na₂SO₄ and the solvents were evaporated. Flash chromatography on silica gel (toluene/acetone, 1:1) gave **29** (1.28 g, 2.02 mmol, 91%). M.p.: 95 °C (toluene/acetone). [α_D]₂₈⁸⁹ = 50.4 ($c = 0.11$, CH₂Cl₂). ¹H NMR (CDCl₃, 360 MHz): $\delta = 5.40$ (ddd, $J_{8,7} = 8.3$, $J_{8,9b} = 6.2$, $J_{8,9a} = 2.6$ Hz, 1 H, 8-H), 5.28 (dd, $J_{7,8} = 8.3$, $J_{7,6} = 1.4$ Hz, 1 H, 7-H), 4.73 (ddd, $J_{4,3ax} = 11.1$, $J_{4,5} = 10.4$, $J_{4,3eq} = 4.4$ Hz, 1 H, 4-H), 4.31 (dd, $J_{9a,9b} = 12.4$, $J_{9a,8} = 2.6$ Hz, 1 H, 9a-H), 4.08–3.94 (m, 2 H, 5-H, 6-H), 3.98 (dd, $J_{9b,9a} = 12.4$, $J_{9b,8} = 6.2$ Hz, 1 H, 9b-H), 3.77 (s, 3 H, CO₂CH₃), 3.71 (t, $J = 4.9$ Hz, 2 H, OCH₂), 3.56 (t, $J = 4.9$ Hz, 2 H, CH₂OH), 3.19 (m, 1 H, CH of cyclohexyl), 2.67 (s, 1 H, OH), 2.45 (dd, $J_{3eq,3ax} = 12.7$, $J_{3eq,4} = 4.4$ Hz, 1 H, 3eq-H), 2.15, 2.10, 2.03, and 2.00 (4 $\times$ s, 12 H, OAc), 1.90 (dd, $J_{3ax,3eq} = 12.7$, $J_{3ax,4} = 11.1$ Hz, 1 H, 3ax-H), 1.85 (s, 3 H, NCOCH₃), 1.80–1.60 (m, 8 H, CH₂ of cyclohexyl) ppm. ¹³C NMR (CDCl₃, 90 MHz): $\delta = 170.8$, 170.6, 170.5, 170.1, 169.9, and 169.8 (4 $\times$ OCOCH₃, NCOCH₃, CO₂CH₃), 85.7 (C-2), 77.9 (CH of cyclohexyl), 74.1 (COH), 73.2, 70.3, 68.7, 67.8 (C-4, C-6, C-7, C-8), 68.9 (OCH₂), 62.6 (C-9), 62.0 (CH₂OH), 52.5 (CH₃O), 49.3 (C-5), 32.9 (C-3), 30.0, 29.9, 27.2, and 27.0 (4 $\times$ CH₂ of cyclohexyl), 23.1, 21.4, 21.2, 20.8, and 20.7 (4 $\times$ CH₃OCO, CH₃CON) ppm. MS (ES): $m/z = 656.2$ [M + Na]⁺. HRMS: calcd. for C₂₈H₄₃NNaO₁₅ 656.2525; found 656.2539. C₂₈H₄₃NO₁₅ (633.65): calcd. C 53.07, H 6.84, N 2.21; found C 53.29, H 7.23, N 1.86.

1-C-(Methyl 5-Acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero- α -D-galacto-non-2-ulopyranosonate)-4-(2'-allyloxyethoxy)cyclohexanol (30): Allyl trichloroacetimidate (678 mg, 3.34 mmol) and trifluoromethanesulfonic acid (74 μ L, 0.84 mmol) were successively added to a stirred solution of alcohol **30** (1.06 g, 1.67 mmol) in a dry dichloromethane/cyclohexane mixture (6/12 mL). After having been stirred for 4 h at room temperature, the mixture was diluted with CH₂Cl₂ and the organic phase was washed with saturated aqueous sodium hydrogen carbonate. The aqueous phase was extracted with CH₂Cl₂, the combined organic phases were dried with Na₂SO₄, and the solvents were evaporated. Flash chromatography on silica gel (toluene/acetone, 1:1) gave **30** (697 mg, 1.03 mmol, 62%). M.p. 56 °C (toluene/acetone). [α_D]₂₈⁸⁹ = –22.4 ($c = 0.12$, MeOH). ¹H NMR (CDCl₃, 360 MHz): $\delta = 5.83$ (ddt, $J = 16.1$, $J = 10.7$, $J = 5.5$ Hz, 1 H, OCH₂CHCH₂), 5.46 (d, $J_{NH,5} = 9.6$ Hz, 1 H, NH), 5.32 (ddd, $J_{8,7} = 8.0$, $J_{8,9b} = 6.7$, $J_{8,9a} = 2.3$ Hz, 1 H, 8-H), 5.22 (dd, $J_{7,8} = 8.0$, $J_{7,6} = 1.4$ Hz, 1 H, 7-H), 5.19 (dd, $J = 16.1$, $J = 1.2$ Hz, 1 H, OCH₂CHCH₂), 5.09 (dd, $J = 10.7$, $J = 1.2$ Hz, 1 H, OCH₂CHCH₂), 4.66 (ddd, $J_{4,3ax} = 11.6$, $J_{4,5} = 11.1$, $J_{4,3eq} = 4.4$ Hz, 1 H, 4-H), 4.26 (dd, $J_{9a,9b} = 12.4$, $J_{9a,8} = 2.3$ Hz, 1 H, 9a-H), 4.03–3.89 (m, 3 H, 5-H, 6-H, 9b-H), 3.94 (m, 2 H, OCH₂CHCH₂), 3.71 (s, 3 H, CO₂CH₃), 3.55 (t, $J = 5.0$ Hz, 2 H, OCH₂), 3.50 (t, $J = 5.0$ Hz, 2 H, CH₂Oallyl), 3.18 (m, 1 H, CH of cyclohexyl), 2.51 (s, 1 H, OH), 2.39 (dd, $J_{3eq,3ax} = 12.8$, $J_{3eq,4} = 4.4$ Hz, 1 H, 3eq-H), 2.08, 2.04, 1.97, and 1.94 (4 $\times$ s, 12 H, 4 $\times$ OCOCH₃), 1.84 (dd, $J_{3ax,3eq} = 12.8$, $J_{3ax,4} = 11.6$ Hz, 1 H, 3ax-H), 1.79 (s, 3 H, NCOCH₃), 1.80–1.60 (m, 8 H, CH₂ of cyclohexyl) ppm. ¹³C NMR (CDCl₃, 90 MHz): $\delta = 171.8$, 171.5, 171.4, 170.2, 170.1, and 169.9 (4 $\times$ OCOCH₃, NCOCH₃, CO₂CH₃), 134.6 (OCH₂CHCH₂), 116.8 (OCH₂CHCH₂), 85.5 (C-2), 77.9 (CH of cyclohexyl), 74.1 (COH), 73.9, 70.2, 68.6, 67.6 (C-4, C-6, C-7, C-8), 72.0 (OCH₂CHCH₂), 69.6 (CH₂Oallyl), 67.1 (OCH₂), 62.5 (C-9), 52.3 (CH₃O), 49.1 (C-5), 32.8 (C-3), 29.9, 29.7, 27.0, and 26.8

(4 × CH₂ of cyclohexyl), 23.0, 21.1, 20.7, 20.6, and 20.5 (4 × CH₃OCO, CH₃CON) ppm. MS (ES): *m/z* = 696.4 [M + Na]⁺. HRMS: calcd. for C₃₁H₄₇NNaO₁₅ 696.2838 found 696.2850. C₃₁H₄₇O₁₅N: calcd. C 55.27; H 7.03; N 2.08.

1-C-(Methyl 5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosonate)-4-(2'-allyloxyethoxy)cyclohexanol (31): Compound **30** (400 mg, 0.59 mmol) was de-*O*-acetylated in dry methanol (20 mL) containing K₂CO₃ (33 mg, 0.24 mmol). The mixture was stirred overnight at room temperature. Neutralization with an ion-exchange resin and filtration through silica gel (dichloromethane/methanol, 85:15) afforded product **31** (264 mg, 0.52 mmol, 88%). M.p. 72 °C (toluene/acetone). [*a*_D]₂₈⁸⁹ = −21.8 (*c* = 0.11, MeOH). ¹H NMR (CD₃OD, 360 MHz): δ = 5.90 (ddt, *J* = 16.5, *J* = 10.5, *J* = 5.3 Hz, 1 H, OCH₂CHCH₂), 5.28 (dd, *J* = 16.5, *J* = 1.7 Hz, 1 H, OCH₂CHCH₂), 5.16 (dd, *J* = 10.5, *J* = 1.7 Hz, 1 H, OCH₂CHCH₂), 4.02 (m, 2 H, OCH₂CHCH₂), 3.87–3.77 (m, 2 H, 8-H, 9a-H), 3.68–3.54 (m, 5 H, 9b-H, 7-H, 6-H, 5-H, 4-H), 3.51 (m, 4 H, OCH₂CH₂Oallyl), 3.30 (s, 3 H, CO₂Me), 3.23 (m, 1 H, CH of cyclohexyl), 2.55 (dd, *J*_{3eq,3ax} = 12.5, *J*_{3eq,4} = 3.9 Hz, 1 H, 3eq-H), 2.01 (s, 3 H, NCOCH₃), 1.85 (dd, *J*_{3ax,3eq} = 12.5, *J*_{3ax,4} = 8.4 Hz, 1 H, 3ax-H), 1.80–1.40 (m, 8 H, CH₂ of cyclohexyl) ppm. MS (ES): *m/z* = 528.3 [M + Na]⁺. HRMS: calcd. for C₂₃H₃₉NNaO₁₁ 528.2415; found 528.2430.

(5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosidic)acid-4-(2'-allyloxy ethoxy)cyclohexanol (32): The methyl ester was cleaved under these conditions: compound **31** (6.0 mg, 0.020 mmol) in water (2 mL) containing an aqueous NaOH solution (1 N, pH = 14) was stirred overnight at room temperature. Neutralization with ion-exchange resin and filtration through silica gel (dichloromethane/methanol, 85:15) afforded product **32** (9.3 mg, 0.019 mmol, 95%). ¹H NMR (CD₃OD, 360 MHz): δ = 5.90 (ddt, *J* = 16.5, *J* = 10.5, *J* = 5.3 Hz, 1 H, OCH₂CHCH₂), 5.28 (dd, *J* = 16.5, *J* = 1.7 Hz, 1 H, OCH₂CHCH₂), 5.14 (dd, *J* = 10.5, *J* = 1.7 Hz, 1 H, OCH₂CHCH₂), 4.02 (m, 2 H, OCH₂CHCH₂), 3.87–3.77 (m, 2 H, 8-H, 9a-H), 3.68–3.54 (m, 5 H, 9b-H, 7-H, 6-H, 5-H, 4-H), 3.51 (m, 4 H, OCH₂CH₂Oallyl), 3.20 (m, 1 H, CH of cyclohexyl), 2.53 (dd, *J*_{3eq,3ax} = 12.5, *J*_{3eq,4} = 3.9 Hz, 1 H, 3eq-H), 2.01 (s, 3 H, NCOCH₃), 1.85 (dd, *J*_{3ax,3eq} = 12.5, *J*_{3ax,4} = 8.4 Hz, 1 H, 3ax-H), 1.80–1.40 (m, 8 H, CH₂ of cyclohexyl) ppm. MS (ES): *m/z* = 514.3 [M + Na]⁺.

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