Base- and Sugar-Modified Cytidine Monophosphate *N*-Acetylneuraminic Acid (CMP-Neu5Ac) Analogues – Synthesis and Studies with α(2–6)-Sialyltransferase from Rat Liver

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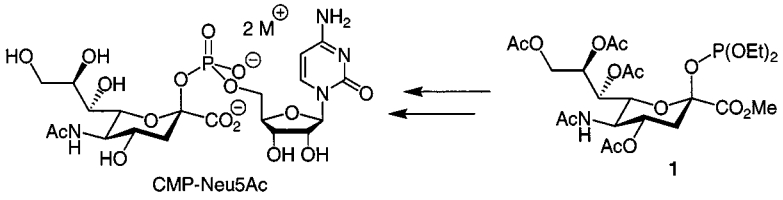
The reaction of sialyl phosphites **1**, **22a–d**, **28**, **39**, and **45** with acyl-protected riboside 5-phosphorous acids **2a**,**b** and **23** directly furnished, without addition of a catalyst, under phosphite/phosphate exchange the corresponding β-configured sialyl riboside monophosphates **3a**,**b**, **24a–d**, **29**, **46**, and **47**. The synthesis of the starting materials, formation of the products, and their treatment with sodium methanolate in methanol and subsequent hydrolysis of the sialic acid ester moiety to provide the unprotected target molecules **4a**,**b**, **25a–d**, **30**, **48**, and **49** is described. Investigations with α(2–6)-sialyltransferase from rat liver showed that base replacement in CMP-Neu5Ac (**4a**,**b**) is not tolerated by the enzyme but that modifications of the 5-, 8-, or 9-position of the neuraminic acid residue (**25a–d**, **30**, **48**, **49**) are tolerated.

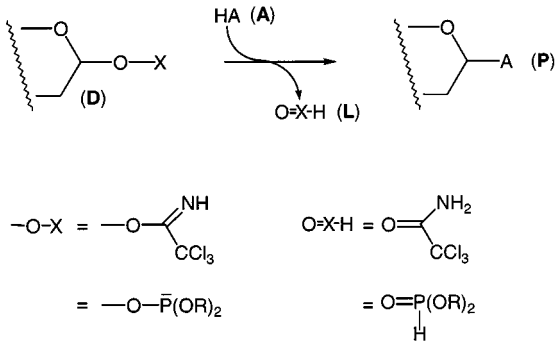
Introduction

Glycoside bond formation in nature is essentially based on glycosyl donors having phosphates, pyrophosphates, or their ribonucleoside and lipid monoester derivatives as leaving groups, and glycosyltransferases as catalysts.[1–3] For instance, for aldoses and 3-deoxy-2-glyculosonates (Kdo, Neu5Ac), nucleoside diphosphate sugars and nucleoside monophosphate derivatives, respectively, are generally encountered as glycosyl donors (Leloir pathway). The different sugars are often linked to different nucleoside moieties as part of the glycosyl donor leaving group. Therefore, glycosyltransferases seem to specifically recognize the sugar and the nucleoside moieties, and generate glycosyl donor properties through activation of the phosphate residue. These factors can be studied with the help of nucleoside phosphate sugars and especially with analogues that are often not accessible by enzymatic means.[3–6]

A particularly interesting target is natural CMP-Neu5Ac (Scheme 1) and base- and sugar-modified analogues thereof, because CMP-Neu5Ac is a glycosyl donor for the enzymatic sialyltransfer to glycoconjugates, i.e. it is required for the biosynthesis of gangliosides and sialylated glycoproteins. Thus, various biological processes are affected by this glycosyl donor, for which successful chemical and enzymatic syntheses have been reported.[4,6–9]



Scheme 1



Scheme 2

A particularly gratifying property of *O*-glycosyl trichloroacetimidates as glycosyl donors **D** [Scheme 2, –OX = $–OC(CCl_3)=NH$] is their direct reaction with Brønsted acids (HA) as glycosyl acceptors **A** under formation of glycosylation products **P** with trichloroacetamide [$O=XH = O=C(CCl_3)NH_2$][10] as the leaving group **L**. This reaction was successfully employed for the synthesis of nucleoside mono- and diphosphate sugars of aldoses.[3,5,11] Similar reaction behaviour can clearly be envisaged for glycosyl phosphites as glycosyl donors **D** [$–OX = OP(OR)_2$]. Such a process would provide, with HA as acceptor **A**, the product **P** upon release of a phosphonate group [$O=XH = O=PH(OR)_2$]. This direct phosphite/phosphate exchange reaction, starting from the diethyl phosphite derivative **1** of Neu5Ac and nucleoside phosphorous acids, gave not only CMP-Neu5Ac but also the corresponding nucleoside analogues UMP-Neu5Ac, AMP-Neu5Ac, and GMP-Neu5Ac in our laborat-

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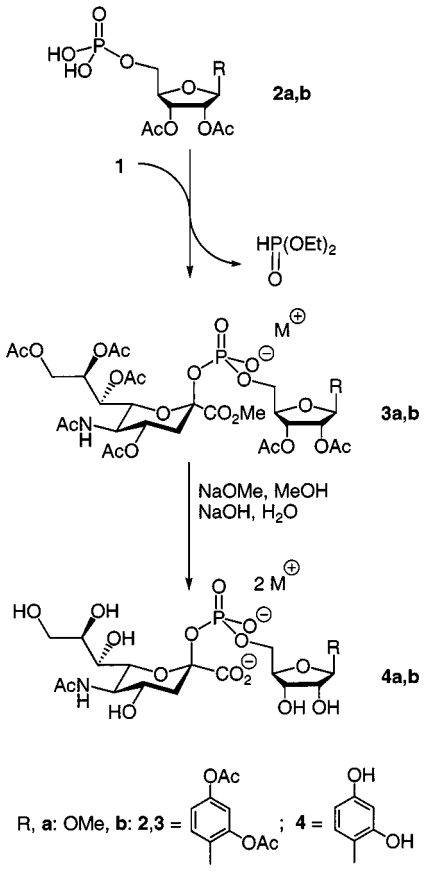
ory.[6,7] Additionally, the *N*-glycolyl derivative CMP-Neu5Gc and new types of glycophospholipids could be prepared using this reaction pathway.[7] We have also employed this methodology in the synthesis of various base- and sugar-modified analogues of CMP-Neu5Ac.[12] These results, along with the glycosyl donor properties of glycosylations with α(2–6)-sialyltransferase from rat liver,[13] are reported in this paper.

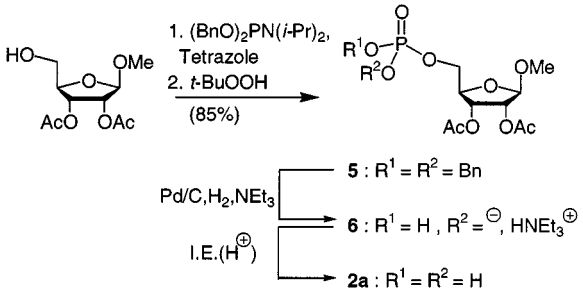
Results and Discussion

Investigations with the recently prepared nucleoside-monophosphate Neu5Ac derivatives in sialyltransferase-catalyzed reactions have shown that some base variations in the glycosyl donor are tolerated.[14] Therefore, more dramatic changes of the base moiety were envisaged in order to ascertain whether the base was required at all or if a structurally related compound could replace the cytosine residue. To this end, it was planned to replace the cytosine residue by a methoxy group and also by the structurally related resorcinol moiety. The 5-phospho-ribofuranosides **2a**,**b** (Scheme 3) were therefore required in which the hydroxy groups of the sugar and the resorcinol moieties were protected by *O*-acetyl groups. On using these compounds the phosphite/phosphate exchange reactions leading to intermediates **3a**,**b** can be performed and, after deprotection, the desired target molecules **4a**,**b** would be readily available.



Scheme 3

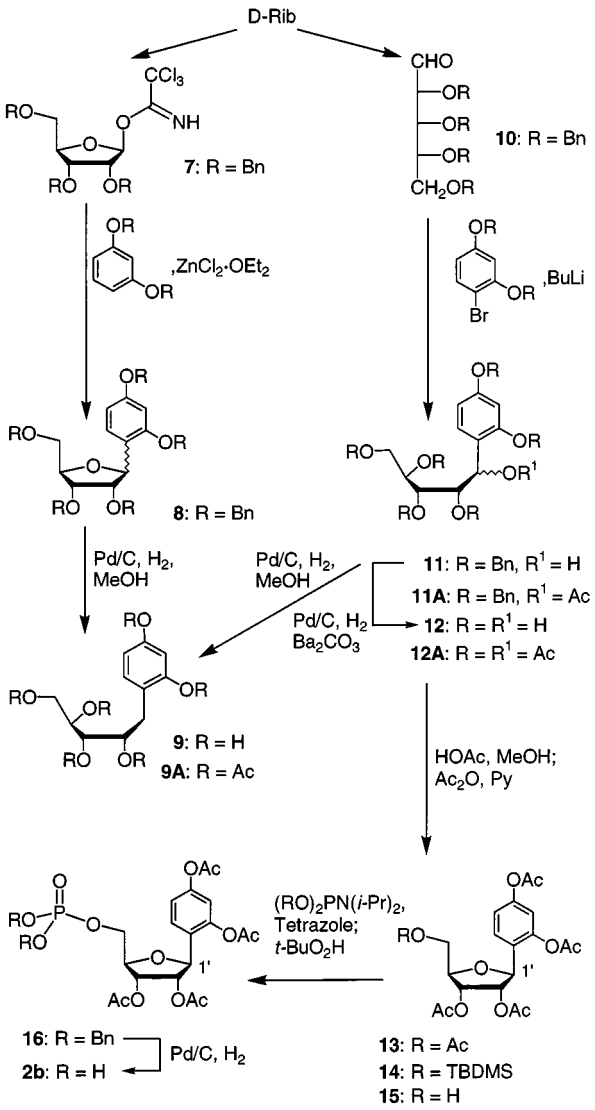
The required methyl 5-phosphoribofuranoside **2a** was prepared from known methyl ribofuranoside[15] (Scheme 4) by phosphitylation of this compound with dibenzyloxydiisopropylaminophosphane, in the presence of tetrazole as a catalyst, and subsequent oxidation with *tert*-butylhydroperoxide to give the phosphorous triester derivative **5**. Hydrogenolytic *O*-debenzylation followed by triethylamine addition furnished triethylammonium salt **6**, which upon ion exchange led to the corresponding phosphorous acid monoester **2a**.



Scheme 4

For the synthesis of **2b**, ribofuranosylation of *O*-benzyl-protected resorcinol with the known compound *O*-(2,3,5-tri-*O*-benzylribofuranosyl)trichloroacetimidate (**7**)[16] as a donor was envisaged (Scheme 5). On using $ZnCl_2$–diethyl ether complex as a catalyst, a 7:1 β/α mixture of *C*-glycoside **8** was obtained. However, hydrogenolytic *O*-debenzylation in MeOH with palladium on carbon as a catalyst led not only to *O*-debenzylation but also to cleavage of the benzylic C–O bond of the tetrahydrofuran ring, thus furnishing 4-tetrahydroxypentylresorcinol derivative **9**, which was structurally assigned as its *O*-acetyl derivative **9A**. In order to circumvent this problem a different strategy was followed. The known tetra-*O*-benzyl-D-ribose **10**[17] was treated with 2,4-dibenzyloxyphenyllithium to afford the addition product **11** as a 9:1 mixture of diastereoisomers; acetylation with acetic anhydride in pyridine gave *O*-acetyl derivative **11A**. However, hydrogenolysis of **11** under the aforementioned conditions gave undesired product **9**. However, when the same reaction was carried out in the presence of barium carbonate, the completely *O*-debenzylated target compound (**12**) was obtained and was transformed into per-*O*-acetyl derivative **12A**. Treatment of **12** with acetic acid in methanol and acetic anhydride/pyridine led to the β-D-ribofuranoside, which was accompanied by some β-D-ribopyranoside. The desired product was isolated as per-*O*-acetyl derivative **13**. Treatment of the *O*-unprotected intermediate with *tert*-butyldimethylsilyl (TBDMS) chloride in the presence of imidazole led to regioselective silylation of the primary hydroxy group of the furanose moiety. Subsequent *O*-acetylation led to clean separation of the 5′-*O*-TBDMS derivative **14** from the pyranosidic material. Treatment of **14** with aqueous acetic acid furnished 5′-*O*-unprotected *C*-ribofuranosylresorcinol **15**. With the help of the procedure described above, **15** was readily transformed into phosphor-

ous triester **16**. Subsequent hydrogenolysis afforded phosphorous acid derivative **2b**.



Scheme 5

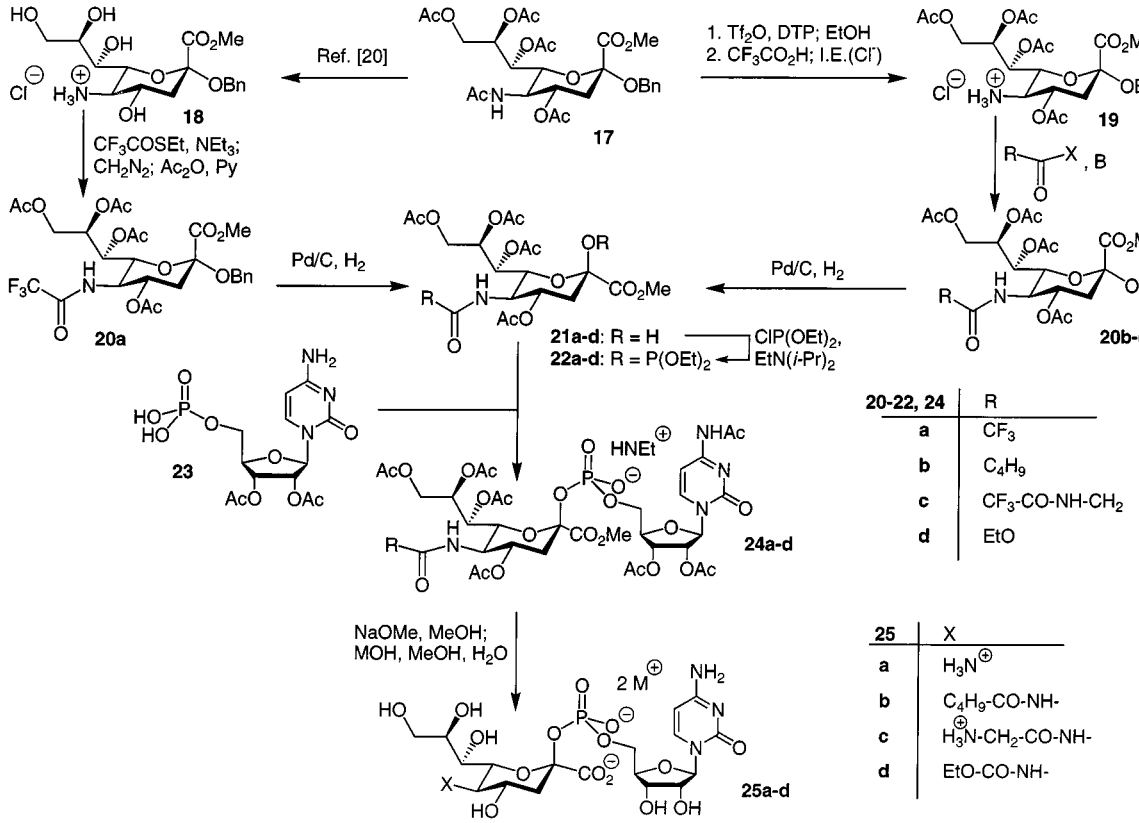
Both compounds **2a** and **2b** reacted directly with sialyl donor **1** in DMF/MeCN (2:1) as solvent to afford the desired β-linked *N*-acetylneuraminyl phosphates **3a** and **3b**, respectively (Scheme 3). De-*O*-acetylation with NaOMe in methanol (Zemplén conditions[18]) followed by methyl ester saponification with NaOH in water afforded target molecules **4a** and **4b**. Their structures could be assigned by NMR (^{1}H, ^{31}P) and mass spectrometry. For the β-sialyl phosphates a $J_{3a,P}$ coupling constant of 5–6 Hz is characteristic,[7] and such values were found for **3a**,**b** and **4a**,**b**. Both final products, **4a** and **4b**, showed no substrate character in assays with α(2–6)-sialyltransferase from rat liver and *p*-nitrophenyl *N*-acetyllactosamine as an acceptor[13] (see Table 1). Therefore, it was concluded that only moderate variations of the base moiety in CMP-Neu5Ac are tolerated by sialyltransferases. Hence, our subsequent studies were directed to variations of the sugar moiety.

Table 1. Investigation of the substrate character of the CMP-Neu5Ac analogues

	K_M [μM]
4a	No substrate
4d	No substrate
25a	Substrate[a]
25b	50 ± 10
25c	Substrate[a]
25d	31 ± 5
30	41 ± 5
48	Substrate[a]
49	Substrate[a]
CMP-Neu5Ac	46 ± 5

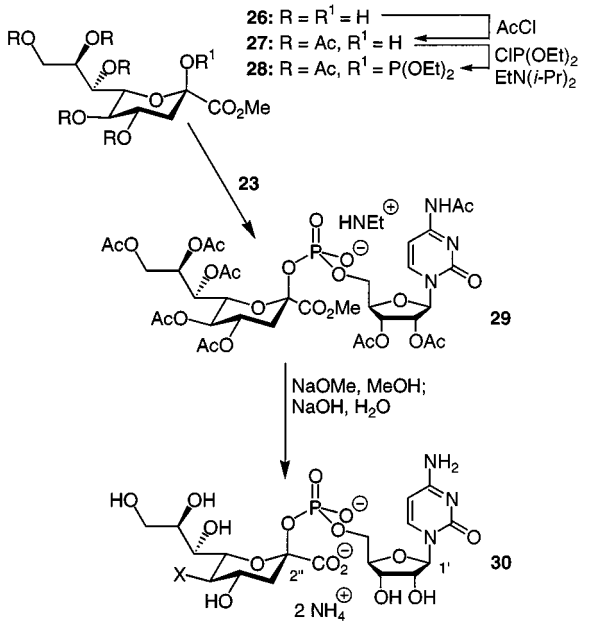
[a] Sialyltransfer was very slow and therefore the reaction was not quantified.

Replacement of the sugar *N*-acetyl group seemed to be a particularly promising approach given that the replacement of the *N*-acetyl group of CMP-Neu5Ac by other *N*-acyl groups is also found in nature.[7,8] To this end, known benzyl sialoside **17**[19] was transformed into *N*,*O*-deacylated derivative **18** (Scheme 6). Attachment of an *N*-trifluoroacetyl group with ethyl trifluorothioacetate in the presence of triethylamine, methyl ester formation with diazomethane, and then *O*-acetylation led to known compound **20a**.[20] Hydrogenolytic *O*-debenzylation afforded 2-*O*-unprotected sialic acid ester **21a**. An alternative procedure for *N*-deacetylation is based on treatment of **17** with trifluoromethanesulfonic acid anhydride (Tf_2O) in the presence of 2,6-di-*tert*-butylpyridine (DTP) followed by addition of ethanol in the presence of DTP to afford an *O*-ethyl acetimidate at the 5-position. This compound gave, upon alcoholysis with trifluoroacetic acid/methanol and ion exchange, 5-ammonium derivative **19**. Reaction of **19** with butyric acid and trifluoroacetylamino acetic acid, along with water-soluble carbodiimide (WSC) as a condensing agent, afforded *N*-acyl derivatives **20b** and **20c**, respectively. Reaction of **19** with ethoxycarbonyl chloride in the presence of pyridine furnished the urethane derivative **20d**. Hydrogenolysis of **20b**–**d** gave **21b**–**d**. *N*-Modified neuraminic acid derivatives **21a**–**d** were then treated with chlorodiethoxyphosphane in the presence of Hünig's base to afford the β-phosphites **22a**–**d**, as evidenced by the ^{1}H-NMR data obtained for 3-H, 4-H, and 7-H.[21,22] Reaction of **22a**–**d** with known *N*,*O*-acetyl-protected CMP derivative **23**[3] furnished, by phosphite/phosphate exchange, the corresponding β-linked CMP-Neu5Ac analogues **24a**–**d**. Removal of all protective groups under the conditions described above gave the 5"-amino-(**25a**), the 5"-*N*-pentanoylamino (**25b**), the 5"-glycylamino (**25c**), and the 5"-ethoxycarbonylamino derivative (**25d**) (^{1}H NMR, $J_{3a,P}$ = 5.8 Hz).[21,22] All compounds were accepted as substrates by α(2–6)-sialyltransferase (Table 1). Compounds **25b** and **25d** exhibited similar affinity to the enzyme as CMP-Neu5Ac. Sialyltransfer with **25a** and amino acid derivative **25c** was very slow and therefore the reaction was not quantified.



Scheme 6

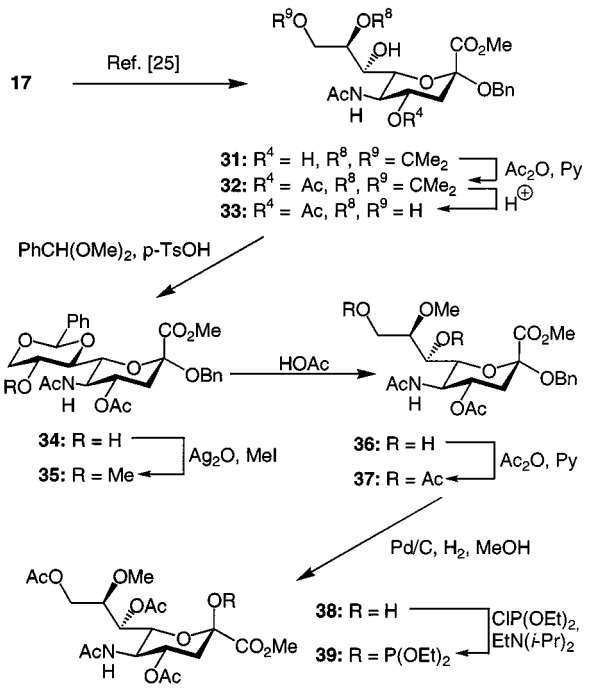
A further interesting example of 5"-modification of CMP-Neu5Ac is the replacement of the Neu5Ac residue by 3-deoxy-2-nonulosonate (Kdn), a residue that lacks the 5"-*N*-acetylamino functionality but has a hydroxy group instead (Scheme 7). Under standard conditions the known Kdn methyl ester **26**[23] was transformed into 2-*O*-unprotected derivative **27**, which reacted with chlorodiethoxyphosphane in the presence of Hünig's base to give phosphite **28**. Reaction of **28** with **23** as described above afforded phosphate **29**, which on deprotection furnished CMP-Kdn **30** (^{1}H NMR: $J_{3a,P}$ = 5.5 Hz). This compound exhibited a similar affinity to α(2–6)-sialyltransferase as the natural substrate. Similar results have been reported only recently.[24] These results demonstrate the tolerance of sialyltransferases to modifications of CMP-Neu5Ac at the 5"-position.



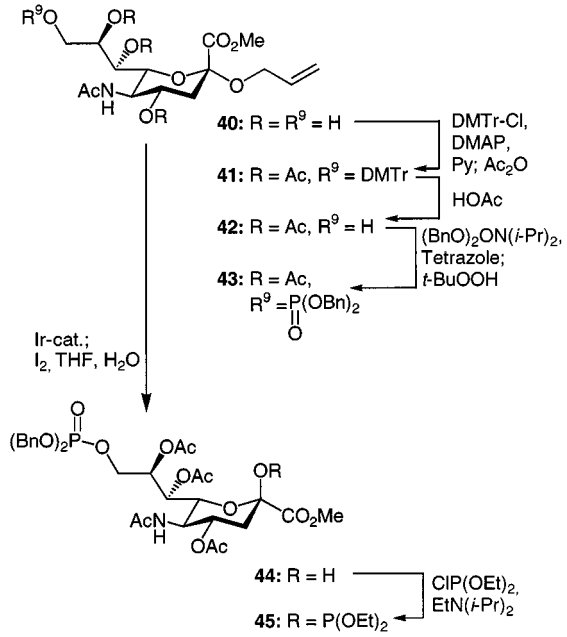
Scheme 7

The tolerance of sialyltransferases to side-chain modifications was studied with two naturally occurring sialic acids, namely the 8-*O*-methyl and the 9-*O*-phosphoryl derivatives of Neu5Ac. To this end, compound **17**[19] was transformed into known 8,9-*O*-isopropylidene derivative **31**[25] (Scheme 8), which on regioselective 4-*O*-acetylation (→ **32**) and then acid-catalyzed de-*O*-isopropylidenation led to 7,8,9-*O*-unprotected derivative **33**. Benzylidenation with benzaldehyde dimethylacetal, in the presence of *p*-toluenesulfonic acid (pTsOH) as a catalyst, afforded mainly 7,9-*O*-benzylidene derivative **34**. 8-*O*-Methylation with methyl iodide/silver oxide gave **35**. Subsequent acid-catalyzed debenzylidenation (→ **36**), *O*-acetylation (→ **37**), and then hydrogenolysis under standard conditions gave 2-*O*-unprotected sialic acid derivative **38**. Reaction with chlorodiethoxyphosphane, as described above, afforded the desired β-phosphite **39**.

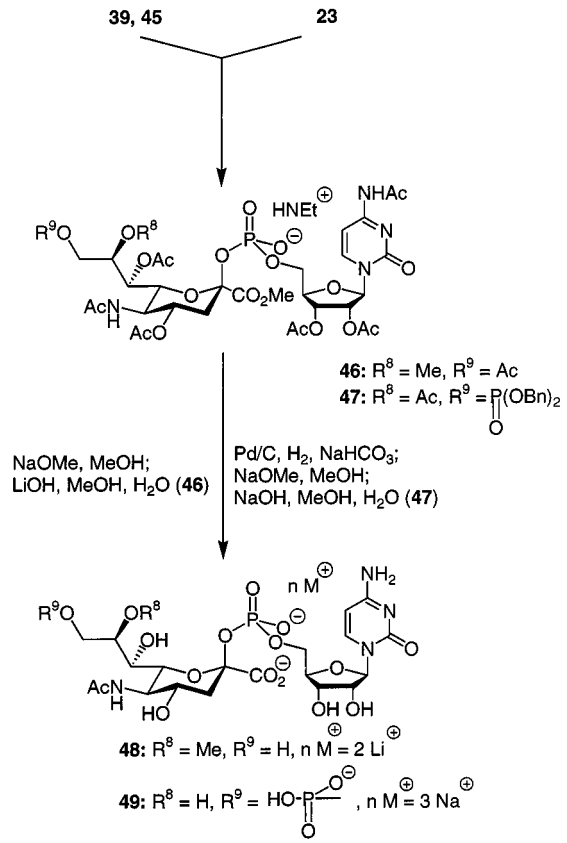
A modified synthetic strategy was required for the synthesis of the 9"-*O*-phosphoryl derivative of CMP-Neu5Ac because two differently linked phosphate residues are pre-



Scheme 8



Scheme 9



Scheme 10

sent in the final product. In order to cope with this situation, known allyl Neu5Ac derivative **40**[26] (Scheme 9) was selected as the starting material. Treatment of **40** with dimethoxytrityl chloride (DMTr-Cl) in pyridine in the presence of 4-dimethylaminopyridine (DMAP, Steglich reagent) afforded the 9-*O*-DMTr derivative, which gave compound **41** upon *O*-acetylation. Acid-catalyzed removal of the DMTr group led to 9-*O*-unprotected **42**; immediate phosphorylation with dibenzyloxydiisopropylaminophosphane in the presence of tetrazole as a catalyst, followed by oxidation with *tert*-butylhydroperoxide afforded dibenzyl phosphate **43**. The 2-*O*-allyl group was then removed with (1,5-cyclooctadiene)bis(methyldiphenylphosphane)iridium(I) hexafluorophosphate[27] as catalyst; subsequent cleavage of the generated enol ether with iodine in THF/water furnished 2-*O*-unprotected compound **44**, which was transformed into diethyl phosphite **45** as described above.

Both compounds **39** and **45** reacted with **23**, thus resulting in the desired phosphite/phosphate exchange reaction to afford β-linked sialyl phosphate derivatives **46** and **47**, respectively (Scheme 10). Deprotection of **46** was carried out as described above with lithium hydroxide in the saponification step, thus leading to CMP-8"-*O*-methyl-Neu5Ac **48** as the dilithio salt. In the case of **47** hydrogenolytic removal of the *O*-benzyl groups of the 9"-*O*-phosphoryl residue had to be performed first. The procedure described above for de-*O*-acylation and methyl ester saponification was then applied to give CMP-9"-*O*-phosphoryl-Neu5Ac **49**. Compounds **48** and **49** were both substrates for α(2–6)-sialyltransferase from rat liver (Table 1), although once again the transfer rate to the acceptor substrate is low.

In conclusion, modified CMP-Neu5Ac derivatives are readily accessible through phosphite/phosphate exchange reactions. Thus, even *N*-deacetylated CMP-neuraminate (**25a**) and CMP-9"-*O*-phosphoryl-Neu5Ac (**49**) could be obtained. In the assay with α(2–6)-sialyltransferase from rat liver, modification of the base residue turned out to be critical. However, modifications at the 5"-amino group of the sialyl residue and modifications of the side chain of the sialyl residue seem to be less critical; even the presence of

charged groups in the sialyl residue of the modified glycosyl donor substrate is tolerated by the enzyme.

Experimental Section

General: Solvents were purified according to standard procedures; boiling range of petroleum ether: 35–60 °C. – Melting points are uncorrected. – Optical rotations: Perkin–Elmer Polarimeter 241 MC; 1-dm cell, temperature 21 °C. – Thin-layer chromatography: silica gel plastic plates 60 F_{254} (Merck); HPTLC glass plates NH_2 (Merck, layer thickness 0.2 mm); plastic plates Cellulose F (Merck, layer thickness 0.2 mm). – Flash chromatography: Silica gel (J. T. Baker, particle size 40 μm). – MPLC was performed at a pressure of 5–10 bar; column: silica gel LiChroprep Si 60 (Merck, 15–25 μm, 28 × 2.5 cm). – Preparative HPLC was performed with an Autochrom system with a Shimadzu LC8A preparative pump and a Rainin Dynamax UV 1 detector at 254 nm; column: LiChrosorb RP-18 (Knauer, 7 μm, 250 × 16 mm); mobile phase: 0.0375 or 0.1 M triethylammonium bicarbonate (TEAB) (pH = 7.2–7.5); flow: 9 mL/min. – Analytical HPLC was performed with a Merck–Hitachi system with an L7200 autosampler and an L4000 UV detector; column: Eurospher 100-C18 (Knauer GmbH, 5 μm, 250 × 4 mm); flow: 0.8 mL/min. – Preparative paper chromatography: cellulose paper (Schleicher Schuell, 2043 Bnyl 500 × 600 nm). – ^{1}H NMR: Bruker AC 250 (250 MHz) Cryospec, Bruker DRX 600 (600 MHz); the resonance of the deuterated solvent was used as internal standard. – ^{31}P NMR: Jeol JNM-GX 400; external standard 85% phosphoric acid. – FAB MS: Varian MAT 112. – MALDI MS: Kratos Kompact Maldi 1. – Elemental analyses: Heraeus CHN-O-Rapid.

(Methyl 2,3-Di-*O*-acetyl-β-D-ribofuranosid-5-yl) Dihydrogen Phosphate (2a): A solution of compound **6** in water/methanol (1:1, 3 mL) was eluted from a column of Dowex 50 (H^+) with water/methanol (1:1, 20 mL). The eluate was lyophilized to yield **2a** (130 mg, 85%) as a colourless solid. – TLC (chloroform/methanol, 3:1): R_f = 0.11, $[\alpha]_D$ = –11.2 (c = 1.0, methanol). – ^{1}H NMR (250 MHz, CD_3OD): δ = 2.07 (s, 3 H, $COCH_3$), 2.13 (s, 3 H, $COCH_3$), 3.43 (s, 3 H, OCH_3), 4.03–4.19 (m, 2 H, 5a-H, 5b-H), 4.29–4.36 (m, 1 H, 4-H), 4.96 (d, $^3J_{1,2}$ < 1.0 Hz, 1 H, 1-H), 5.21 (dd, $^3J_{3,2}$ = 4.9 Hz, $^3J_{1,2}$ < 1.0 Hz, 1 H, 2-H), 5.33 (dd, $^3J_{3,2}$ = 4.9 Hz, $^3J_{3,4}$ = 6.7 Hz, 1 H, 3-H). – ^{31}P NMR (161.7 MHz, CD_3OD): δ_P = 0.43.

[(1,3-Di-*O*-acetylresorcin-4-yl) (2,3-Di-*O*-acetyl-1-deoxy-β-D-ribofuranosid-5-yl)] Dihydrogen Phosphate (2b): To a solution of **16** (300 mg, 0.447 mmol) in methanol/ethyl acetate (1:1, 50 mL) was added palladium on charcoal (10%, 15 mg) and the mixture was stirred at room temp. for 15 min under hydrogen (1 bar). After filtration through Celite, the filtrate was concentrated under reduced pressure. The residue was lyophilized from water to yield **2b** (210 mg, 95%) as a colourless solid. – TLC (*N*-butyl alcohol/acetic acid/water, 3:1:1): R_f = 0.27. – ^{1}H NMR (250 MHz, D_2O): δ = 2.06–2.31 (4 × s, 12 H, 4 × $COCH_3$), 4.21–4.35 (m, 3 H, 4′-H, 5′A-H, 5′B-H), 5.12–5.22 (m, 2 H, 2′-H, 1′-H), 5.40 (dd, $J_{2',3'}$ = $J_{4',3'}$ = 4.8 Hz, 1 H, 3′-H), 6.91 (d, $J_{6,2}$ = 2.3 Hz, 1 H, 2-H), 6.99 (dd, $J_{6,5}$ = 8.5 Hz, $J_{2,6}$ = 2.3 Hz, 1 H, 6-H), 7.85 (d, $J_{6,5}$ = 8.5 Hz, 1 H, 5-H). – ^{31}P NMR (161.7 MHz, D_2O): δ_P = 3.89.

Sodium [(Methyl (5-Acetamido-3,5-dideoxy-D-*glycero*-β-D-*galacto*-2-nonulopyranosyl)onate] (Methyl 2,3-Di-*O*-acetyl-β-D-ribofuranosid-5-yl) Phosphate (3a): A solution of **2a** (100 mg, 0.305 mmol) in *N*,*N*-dimethylformamide/acetonitrile (2:1, 1.0 mL) was cooled to –20 °C. A solution of **1**[21] (240 mg, 0.392 mmol) in dry acetonitrile (800 μL) was added by syringe. The reaction mixture was allowed to warm up to room temperature during 12 h. Triethylamine (500 μL) was added and the solvents were evaporated under reduced pressure. Flash chromatography (chloroform/methanol/triethylamine, 8:1:0.1) of the residue afforded a colourless solid (143 mg, 52%). To a solution of this solid (100 mg, 0.111 mmol) in dry methanol (3 mL) was added sodium methoxide in methanol (0.5 M, 3 drops) and the solution was stirred at room temp. and the reaction monitored by TLC. After completion of the reaction, the mixture was neutralized with Amberlite IRC-50 (H^+), (pH = 8–9), filtered, and concentrated. Flash chromatography through aminophase silica gel (ethanol/water, 4:1) yielded **3a** (51 mg, 81%). – TLC, aminophase (ethanol/water, 3:7): R_f = 0.75. – ^{1}H NMR (250 MHz, D_2O): δ = 1.59 (ddd, $J_{3''a,P}$ = 5.2 Hz, $J_{3''a,4''}$ = 11.0 Hz, $J_{3''e,3''a}$ = 13.2 Hz, 1 H, 3′′a-H), 1.86 (s, 3 H, $NCOCH_3$), 2.33 (dd, $J_{3''e,4''}$ = 4.6 Hz, $J_{3''e,3''a}$ = 13.2 Hz, 1 H, 3′′e-H), 3.24 (s, 1 H, OCH_3), 3.30 (d, J = 9.7 Hz, 1 H, 7′′-H), 3.42 (dd, $J_{8'',9''B}$ = 6.6 Hz, $J_{9''A,9''B}$ = 11.8 Hz, 1 H, 9′′B-H), 3.61–4.03 (m, 12 H, 2′-H, 4′-H, 5′A-H, 5′B-H, 4′′-H, 5′′-H, 6′′-H, 8′′-H, 9′′A-H, $COOCH_3$), 4.09 (dd, $J_{2',3'}$ = 4.7 Hz, $J_{4',3'}$ = 6.5 Hz, 1 H, 3′-H), 4.74 (d, $J_{2',1'}$ < 1 Hz, 1 H, 1′-H). – ^{31}P NMR (161.7 MHz, D_2O): δ_P = –1.28.

Triethylammonium [(1,3-Di-*O*-acetylresorcin-4-yl) (2,3-Di-*O*-acetyl-1-deoxy-β-D-ribofuranosid-5-yl)] {[Methyl (5-Acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-β-D-*galacto*-2-nonulopyranosyl)onate]} Phosphate (3b): A solution of **2b** (100 mg, 0.204 mmol) in *N*,*N*-dimethylformamide/acetonitrile (2:1, 0.5 mL) was cooled to –20 °C. A solution of **1**[21] (200 mg, 0.327 mmol) in dry acetonitrile (400 μL) was added by syringe. The reaction mixture was allowed to warm up to room temp. during 12 h. Triethylamine (300 μL) was added and the solvents were evaporated in vacuo. Flash chromatography (chloroform/methanol/triethylamine, 9:1:0.1) of the residue yielded **3b** (110 mg, 50%) as a colourless solid. – ^{1}H NMR (250 MHz, MeOD): δ =1.21 (t, J = 7.2 Hz, 9 H, 3 × CH_3), 1.87 (s, 3 H, $NCOCH_3$), 1.99–2.35 (8 × s, 25 H, 3′′a-H, 8 × $COCH_3$), 2.78 (dd, $J_{3''e,4''}$ = 4.8 Hz, $J_{3''e,3''a}$ = 13.2 Hz, 1 H, 3′′e-H), 3.13 (q, J = 7.2 Hz, 6 H, 3 × CH_2), 3.84 (s, 3 H, $COOCH_3$), 4.06 (dd, $J_{5'',6''}$ = $J_{4'',5''}$ = 10.5 Hz, 1 H, 5′′-H), 4.15–4.39 (m, 4 H, 4′-H, 5′A-H, 5′B-H, 9′′A-H), 4.50 (dd, $J_{6'',7''}$ = 2.2 Hz, $J_{5'',6''}$ = 10.6 Hz, 1 H, 6′′-H), 4.63 (dd, $J_{8'',9''B}$ = 2.5 Hz, $J_{9''A,9''B}$ = 12.2 Hz, 1 H, 9′′B-H), 5.19–5.41 (m, 4 H, 1′-H, 2′-H, 4′′-H, 8′′-H), 5.42–5.52 (m, 2 H, 3′-H, 7′′-H), 6.98 (d, $J_{5,3}$ = 2.2 Hz, 1 H, 2-H), 7.14 (dd, $J_{6,5}$ = 8.5 Hz, $J_{2,6}$ = 2.2 Hz, 1 H, 6-H), 7.85 (d, $J_{6,5}$ = 8.5 Hz, 1 H, 5-H). – DC (chloroform/methanol, 3:1): R_f = 0.34. – ^{31}P NMR (242.5 MHz, D_2O): δ_P = –3.39. – FAB MS (negative Mode, matrix: methanol/nitrobenzyl alcohol, 1:1): 962 $(M - H^+)^-$.

Disodium [(5-Acetamido-3,5-dideoxy-D-*glycero*-β-D-*galacto*-2-nonulopyranosyl)onate] (Methyl-β-D-ribofuranosid-5-yl) Phosphate (4a): To a solution of **3a** (50 mg, 87.5 μmol) in water/methanol (1:1, 1 mL) was added NaOH solution (1 M, 1 mL) and the mixture was stirred for 4 h at room temp. The solution was neutralized with Amberlite IRC-50 (H^+) (pH = 8–9) and filtered. The filtrate was lyophilized, dissolved in water and, after addition of acetone, **4a** (39 mg, 79%) precipitated as a colourless solid. – TLC, aminophase (ethanol/water, 1:1): R_f = 0.37. – ^{1}H NMR (250 MHz, D_2O): δ = 1.43 (ddd, $J_{3''a,P}$ = 6.0 Hz, $J_{3''a,4''}$ = 11.2 Hz, $J_{3''e,3''a}$ = 12.9 Hz, 1 H, 3′′a-H), 1.86 (s, 3 H, $NCOCH_3$), 2.29 (dd, $J_{3''e,4''}$ = 4.7 Hz, $J_{3''e,3''a}$ = 13.0 Hz, 1 H, 3′′e-H), 3.16–3.27 (m, 4 H, OCH_3, 7′′-H), 3.42 (dd, $J_{8'',9''B}$ = 6.8 Hz, $J_{9''A,9''B}$ = 12.2 Hz, 1 H, 9′′B-H), 3.67–3.81 (m, 3 H, 5′′-H, 6′′-H, 9′′A-H), 4.82–3.98 (m, 7 H, 2′-H, 4′-H, 5′A-H, 5′B-H, 4′′-H, 8′′-H, 9′′A-H), 4.11 (dd, $J_{2',3'}$ = 4.9 Hz, $J_{4',3'}$ = 6.1 Hz, 1 H, 3′-H), 4.71 (d, $J_{2',1'}$ < 1 Hz, 1 H, 1′-H). –

^{31}P NMR (161.7 MHz, D_2O): δ_P = –3.83. – FAB MS (negative mode, matrix: glycerine/water, 1:1): 534 $(M - H)^-$.

Bis(triethylammonium) [(5-Acetamido-3,5-dideoxy-D-*glycero*-β-D-*galacto*-2-nonulopyranosyl)onate] [(Resorcin-4-yl) (1-Deoxy-β-D-ribofuranosid-5-yl)] Phosphate (4b): To a solution of **3b** (55 mg, 51.7 μmol) in dry methanol (2 mL) was added sodium methoxide in methanol (0.5 M, 3 drops) and the mixture was stirred for 3 h at room temp. The solution was neutralized with Amberlite IRC-50 (H^+) (pH = 8–9), filtered, concentrated under reduced pressure and lyophilized from water. To a solution of the residue in water/methanol (1:1, 2 mL) was added NaOH solution (1 M, 1 mL) and the mixture was stirred for 4 h at room temp. The solution was neutralized with Amberlite IRC-50 (H^+) (pH = 8–9) and filtered. Lyophilization and HPLC gave **4b** (15 mg, 35%). HPLC: prep. RP-18 column (flow: 9 mL min^{-1}, 0.05 M triethylammonium bicarbonate buffer). – TLC, aminophase (ethanol/water, 3:7): R_f = 0.75. – ^{1}H NMR (250 MHz, D_2O): δ = 1.10 [t, J = 7.1 Hz, 18 H, 2 × $(CH_3)_3$], 1.39–1.53 (m, 1 H, 3′′a-H), 1.84 (s, 3 H, NHCOCH_3), 2.30 (dd, $J_{3''e,4''}$ = 4.2 Hz, $J_{3''e,3''a}$ = 13.0 Hz, 1 H, 3′′e-H), 2.81–2.93 (m, 1 H, 9′′B-H), 2.96–3.09 [m, 12 H, 2 × $(CH_2)_3$], 3.25 (d, J = 9.7 Hz, 1 H, 7′′-H), 5.52–6.03 (m, 2 H, 5′A-H, 9′′A-H), 6.04–6.11 (m, 1 H, 5′B-H), 6.18–6.36 (m, 2 H, 5′′-H, 6′′-H), 3.88 (dd, $J_{3''e,4''}$ = 4.3 Hz, $J_{3''a,4''}$ = 11.5 Hz, 1 H, 4′′-H), 3.91–4.06 (m, 2 H, 4′-H, 8′′-H), 4.18–4.26 (m, $J_{2',3'}$ = 4.9 Hz, 1 H, 2′-H), 4.31–4.41 (m, 1 H, 3′-H), 7.71 (d, $J_{2',1'} < 1$ Hz, 1 H, 1′-H), 8.79 (d, $J_{5,3}$ = 2.2 Hz, 1 H, 2-H), 8.88 (dd, $J_{6,5}$ = 8.5 Hz, $J_{2,6}$ = 2.2 Hz, 1 H, 6-H), 9.61 (d, $J_{6,5}$ = 8.5 Hz, 1 H, 5-H). – ^{31}P NMR (161.7 MHz, D_2O): δ_P = –3.66. – FAB MS (negative mode, matrix: glycerine/water, 1:1): 612 $(M - H^+)^-$.

Dibenzyl (Methyl 2,3-Di-*O*-acetyl-β-D-ribofuranosid-5-yl) Phosphate (5): To a solution of methyl ribofuranoside[15] (2.50 g, 10.1 mmol) and tetrazole (1.41 g. 20.2 mmol) in dry acetonitrile/dichloromethane (3:1, 20 mL) was added dibenzyloxydiisopropylaminophosphane (5.00 g, 14.5 mmol) in dry dichloromethane (10 mL) under nitrogen. After 20 min, a solution of *tert*-butyl hydroperoxide (3 M in dry toluene, 4.0 mL, 0.012 mol) was added and stirring was continued for a further 20 min. The reaction mixture was poured into half-saturated sodium bicarbonate solution and extracted with dichloromethane. The organic layer was separated, dried with magnesium sulfate, and concentrated. Flash chromatography (toluene/acetone, 4:1) yielded **5** (4.32 g, 85%) as a colourless foam. – DC (toluene/acetone, 3:1): R_f = 0.58. – $[\alpha]_D$ = –84.0 (c = 1.0 in chloroform). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.90 (s, 3 H, $COCH_3$), 1.99 (s, 3 H, $COCH_3$), 3.22 (s, 3 H, OCH_3), 3.90–4.11 (m, 2 H, 5A-H, 5B-H), 4.10–4.27 (m, 1 H, 4-H), 4.78 (d, $J_{1,2} < 1.0$ Hz, 1 H, 1-H), 4.93 (2 × d, J = 11.6 Hz, 4 H, 2 × CH_2Ph), 5.11 (dd, $J_{3,2}$ = 4.9 Hz, $J_{1,2} < 1.0$ Hz, 1 H, 2-H), 5.18 (dd, $J_{3,2}$ = 4.9 Hz, $J_{3,4}$ = 6.7 Hz, 1 H, 3-H), 7.23–7.25 (m, 10 H, Ph). – $C_{24}H_{29}O_{10}P$ (505.4): calcd. C 56.69, H 5.72; found C 56.61, H 5.88.

Triethylammonium (Methyl 2,3-Di-*O*-acetyl-β-D-ribofuranosid-5-yl) Hydrogen Phosphate (6): Compound **5** (800 mg, 1.57 mmol) was dissolved in methanol (100 mL) and palladium on charcoal (80 mg, 10% Pd) was added. The mixture was stirred vigorously under hydrogen at normal pressure. After 15 min, the catalyst was filtered off and washed with methanol. Triethylamine (1 mL) was added and the filtrate was concentrated under reduced pressure. Purification by flash chromatography (chloroform/methanol/triethylamine, 3:1:0.1) yielded **5** (546 mg, 81%) as a colourless solid. – TLC (chloroform/methanol/water, 3:1:0.1): R_f = 0.15. – ^{1}H NMR (250 MHz, MeOD): δ = 1.34 (t, J = 7.2 Hz, 9 H, 3 CH_3), 2.06 (s, 3 H, $COCH_3$), 2.12 (s, 3 H, $COCH_3$), 3.43 (q, 6 H, 3 × CH_2), 3.42 (s, 3 H, OCH_3), 3.96–4.01 (m, 2 H, 5A-H, 5B-H), 4.29–4.34 (m, 1 H, 4-H), 4.87 (d, $J_{1,2} < 1.0$ Hz, 1 H, 1-H), 5.23 (dd, $J_{3,2}$ = 4.9 Hz, $J_{1,2} < 1.0$ Hz, 1 H, 2-H), 5.32 (dd, $J_{3,2}$ = 4.9 Hz, $J_{3,4}$ = 6.3 Hz, 1 H, 3-H).

1,3-Di-*O*-benzyl-4-(2,3,5-tri-*O*-benzyl-α/β-D-ribofuranosyl)resorcinol (8): To a solution of 1,3-dibenzylresorcinol (1.00 g, 3.45 mmol) in dry dichloromethane/acetonitrile (3:1, 2.5 mL) was added zinc chloride diethyl ether solution (2.2 M in dry dichloromethane, 80 μL, 0.174 mmol). A solution of **7**[16] (1.00 g, 1.77 mmol) in dry dichloromethane (2.5 mL) was then added dropwise and the mixture stirred for 2 h at room temp. The reaction mixture was poured into half-saturated sodium bicarbonate solution and extracted with dichloromethane. The organic layer was separated, dried with magnesium sulfate, and concentrated. The residue was dissolved in ethanol (70 mL) and, after addition of sodium hydroxide solution (700 mg in 10 mL water), refluxed for 2 h. The mixture was diluted with water and extracted with ethyl acetate. The organic layer was dried with magnesium sulfate and concentrated. Flash chromatography (toluene/acetone, 30:1) yielded **8** (490 mg, 41%) as a yellow oil containing up to 7% of the α isomer. – TLC (toluene/acetone, 30:1): R_f = 0.32. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.52 (dd, $J_{5'A,5'B}$ = 10.8 Hz, $J_{5'A,4'}$ = 2.5 Hz, 1 H, 5′A-H), 3.79 (dd, $J_{5'A,5'B}$ = 10.8 Hz, $J_{5'B,4'}$ = 4.0 Hz, 1 H, 5′B-H), 4.10–4.56 (m, 9 H, 2′-H, 3′-H, 4′-H, 3 × CH_2Ph), 4.89–5.23 (m, 4 H, 2 × CH_2Ph), 5.44 (d, $J_{1',2'}$ = 2.4 Hz, 1 H, 1′-Hβ), 6.57 (d, $J_{2,6}$ = 2.1 Hz, 1 H, 2-H), 6.64 (dd, $J_{2,6}$ = 2.1 Hz, $J_{6,5}$ = 8.4 Hz, 1 H, 6-H), 6.93–7.46 (m, 25 H, 5 × CH_2Ph), 7.58 (d, $J_{6,5}$ = 8.4 Hz, 1 H, 5-H). – $C_{46}H_{44}O_6$ (692.81): calcd. C 79.74, H 6.40; found C 79.32, H 6.42.

4-(1-Deoxy-D-ribit-1-yl)resorcinol (9). – (a) From Compound 8: Compound **8** (2.80 g, 4.04 mmol) was dissolved in methanol (150 mL) and palladium on charcoal (100 mg, 10% Pd) was added. The mixture was stirred under hydrogen at normal pressure. After 5 h, the catalyst was filtered off and washed with methanol. Evaporation of the solvents afforded **9** (740 mg, 75%) as a yellow syrup. – **(b) From Compound 11:** Compound **11** (200 mg, 0.250 mmol) was dissolved in methanol (13 mL) and palladium on charcoal (100 mg, 10% Pd) was added. The mixture was stirred under hydrogen at normal pressure. After 3 h, the catalyst was filtered off and washed with methanol. Evaporation of the solvents afforded **9** (47 mg, 78%) as a yellow syrup. – TLC (chloroform/methanol, 4:1): R_f = 0.19. – $[\alpha]_D$ = –22.6 (c = 1.0 in methanol). – ^{1}H NMR (250 MHz, D_2O): δ = 2.43 (dd, $J_{1'A,1'B}$ = 14.3 Hz, $J_{1'B,2'}$ = 9.4 Hz, 1 H, 1′A-H), 2.47 (dd, $J_{1'A,1'B}$ = 14.3 Hz, $J_{1'B,2'}$ = 2.9 Hz, 1 H, 1′B-H), 3.41–3.55 (m, 2 H, 3′-H, 5′A-H), 3.58–3.69 (m, 2 H, 4′-H, 5′B-H), 3.77–3.84 (m, 1 H, 2′-H), 6.24–6.26 (m, 2 H, 2-H, 6-H), 6.88 (d, $J_{5,6}$ = 8.3 Hz, 1 H, 5-H).

1,3-Di-*O*-acetyl-4-(2,3,4,5-tetra-*O*-acetyl-D-ribit-1-yl)resorcinol (9A): Compound **9** (500 mg, 2.05 mmol) was dissolved in dry pyridine/acetic anhydride (15 mL, 2:1). After stirring for about 12 h, the solution was concentrated in vacuo, coevaporated with toluene and purified by flash chromatography (toluene/acetone, 5:1) to give **9A** (890 mg, 88%) as a colourless solid. – TLC (toluene/acetone, 4:1): R_f = 0.35. – $[\alpha]_D$ = +34 (c = 1.0 in chloroform). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.94–1.32 (6 × s, 18 H, 6 × $COCH_3$), 2.81–2.84 (m, 1 H, 1′A-H, 1′B-H), 4.12 (dd, $J_{5'A,5'B}$ = 12.1 Hz, $J_{5'A,4'}$ = 6.2 Hz, 1 H, 5′A-H), 4.33 (dd, $J_{5'A,5'B}$ = 12.1 Hz, $J_{5'B,4'}$ = 2.6 Hz, 1 H, 5′B-H), 5.21–5.32 (m, 3 H, 2′-H, 3′-H, 4′-H), 6.91–6.97 (m, 2 H, 2-H, 6-H), 7.18 (d, $J_{5,6}$ = 8.3 Hz, 1 H, 5-H). – $C_{24}H_{29}O_{10}P$ (496.5): calcd. C 55.64, H 5.68; found C 55.34, H 5.65.

1,3-Di-*O*-benzyl-4-(2,3,4,5-tetra-*O*-benzyl-D-*allolaltro*-pentit-1-yl)resorcinol (11): A solution of **10**[17] (3.70 g, 0.10 mmol) in dry THF (130 mL) was cooled to –70 °C under nitrogen. *n*-Butylli-

thium in *n*-hexane (1.6 M, 6.0 mL) was added dropwise. After 15 min, a solution of 2,4-dibenzyloxybromobenzene (4.40 g, 8.62 mmol) in dry THF (20 mL) was added dropwise and the reaction mixture was warmed up to 0 °C over 2 h. The mixture was poured into half-saturated ammonium chloride solution and extracted with ethyl acetate. The organic layer was dried with magnesium sulfate and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum ether/ethyl acetate, 7:1) to give **11** (5.38 g, 78%) as a colourless solid that contained the two diastereomers in a ratio of 9:1. – TLC (petroleum ether/ethyl acetate, 5:1): R_f = 0.38. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.62–3.65 (m, 1 H, 5′A-H), 3.68–3.81 (m, 1 H, 5′B-H), 3.92–4.01 (m, 2 H, 3′-H, 4′-H), 4.11–4.19 (m, 2 H, 2′-H, OH), 4.20–5.10 (m, 12 H, 6 × C*H*$_2$Ph), 5.29 (dd, $J_{2',1'}$ = 4.9 Hz, $J_{OH,1'}$ = 6.6 Hz, 1 H, 1′-H), 6.29–6.61 (m, 2 H, 2-H, 6-H), 6.94–7.49 (m, 31 H, 6 × CH$_2$*Ph*, 5-H). – FAB-MS (positive mode, matrix: acetone/nitrobenzyl alcohol, 1:1 and NaI): 823 (M + Na$^+$).

4-(1-*O*-Acetyl-2,3,4,5-tetra-*O*-benzyl-D-*allo*/*altro*-pentit-1-yl)-1,3-di-*O*-benzylresorcinol (11A): Compound **11** (100 mg, 0.125 mmol) was dissolved in dry pyridine/acetic anhydride (3 mL, 2:1). After stirring overnight, the solution was concentrated in vacuo, coevaporated with toluene and purified by flash chromatography (petroleum ether/ethyl acetate, 6:1) to give **11A** (84 mg, 83%) as a colourless oil. The ratio of the two diastereomers was 9:1. – TLC (petroleum ether/ethyl acetate, 7:1): R_f = 0.27. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.98 (s, 3 H, $COCH_3$), 3.63 (dd, $J_{5'A,5'B}$ = 10.5 Hz, $J_{4',5'A}$ = 6 Hz, 1 H, 5′A-H), 3.73 (dd, $J_{5'A,5'B}$ = 10.5 Hz, $J_{4',5'B}$ = 2.6 Hz,1 H, 5′B-H), 3.86 (dd, $J_{2',3'}$ = 4.5 Hz, 1 H, 3′-H), 3.95–4.01 (m, 1 H, 4′-H), 4.16 (dd, $J_{1',2'}$ = $J_{3',2'}$ = 4.5 Hz, 1 H, 2′-H), 4.30–5.11 (m, 12 H, 6 × C*H*$_2$Ph), 6.29–6.61 (m, 2 H, 2-H, 6-H), 6.56 (d, $J_{1',2'}$ = 5.4 Hz, 1 H, 1′-H), 6.94–7.49 (m, 31 H, 6 × CH$_2$*Ph*, 5-H). – $C_{55}H_{54}O_8$ (843.03): calcd. C 78.36, H 6.45; found C 78.29, H 6.53.

4-(D-*allo*/*altro*-Pentit-1-yl)resorcinol (12): Compound **11** (2.50 g, 3.13 mmol) and barium carbonate (620 mg, 3.13 mmol) were dissolved in methanol (100 mL) and palladium on charcoal (80 mg, 10% Pd) was added. The mixture was stirred vigorously under hydrogen at normal pressure. After 2 d, the catalyst was filtered off and washed with methanol. Triethylamine (1 drop) was added and the filtrate was concentrated under reduced pressure to yield **12** (51 mg, 63%, yellow oil) as diastereomeric mixture, 9:1. – TLC (chloroform/methanol, 4:1): R_f = 0.15. – ^{1}H NMR (250 MHz, D_2O): δ = 3.31–3.50 (m, 2 H, 5′A-H, 3′-H), 3.59 (dd, $J_{5'A,5'B}$ = 11.8 Hz, $J_{4',5'B}$ = 3.1 Hz, 1 H, 5′B-H), 3.62–3.72 (m, 1 H, 4′-H), 3.83 (dd, $J_{1',2'}$ = 5.3 Hz, $J_{3',2'}$ = 7.3 Hz, 1 H, 2′-H), 4.86 (d, $J_{1',2'}$ = 5.4 Hz, 1 H, 1′-H), 6.18 (d, J = 2.3 Hz, $J_{2,6}$ = 2.3 Hz, 1 H, 2-H), 6.23 (dd, $J_{2,6}$ = 2.3 Hz, $J_{5,6}$ = 8.3 Hz, 1 H, 6-H), 6.97 (d, $J_{5,6}$ = 8.3 Hz, 1 H, 5-H).

1,3-Di-*O*-acetyl-4-(2,3,4,5-penta-*O*-acetyl-D-*allo*/*altro*-pentit-1-yl)-resorcinol (12A): Compound **12** (500 mg, 1.95 mmol) was dissolved in dry pyridine/acetic anhydride (10 mL, 2:1). After stirring overnight, the solution was concentrated in vacuo, coevaporated with toluene and purified by flash chromatography (petroleum ether/ethyl acetate, 1:1) to give **12A** (910 mg, 85%) as a colourless solid. The ratio of the two diastereomers was 9:1. – TLC (petroleum ether/ethyl acetate, 1:1): R_f = 0.29. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.95–2.23 (7 × s, 21 H, 7 × $COCH_3$), 4.03 (dd, $J_{5'A,5'B}$ = 12.1 Hz, $J_{4',5'A}$ = 6.8 Hz, 1 H, 5′A-H), 4.32 (dd, $J_{5'A,5'B}$ = 12.1 Hz, $J_{4',5'B}$ = 2.9 Hz, 1 H, 5′B-H), 5.26–5.39 (m, 1 H, 4′-H), 5.42–5.51 (m, 2 H, 2′-H, 3′-H), 6.13 (d, $J_{1',2'}$ = 5.5 Hz, 1 H, 1′-H), 6.91–6.95 (m, 2 H, 2-H, 6-H), 7.36 (d, $J_{5,6}$ = 8.1 Hz, 1 H, 5-H). – $C_{25}H_{30}O_{14}.H_2O$ (572.51): calcd. C 52.44, H 5.28; found C 52.48, H 5.44.

1,3-Di-*O*-acetyl-4-(2,3,5-tri-*O*-acetyl-β-D-ribofuranosyl)resorcinol (13): Compound **12** (1 g, 3.84 mmol) was dissolved in acetic acid/methanol (1:1, 10 mL) and the solution was stirred overnight. The solution was concentrated and coevaporated with toluene. The residue was dissolved in dry pyridine/acetic anhydride (15 mL, 2:1) and kept overnight at room temp. The solution was concentrated and coevaporated with toluene. The crude product was purified by flash chromatography (petroleum ether/ethyl acetate, 1:1) and separated from an isomeric side-product by MPLC (petroleum ether/ethyl acetate, 1:1) to give **13** (1.06 g, 62%). – TLC (petroleum ether/ethyl acetate, 1:1): R_f = 0.24. – $[\alpha]_D$ = –5.7 (*c* = 1.0 in chloroform). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.07–2.29 (5 × s, 15 H, 5 × $COCH_3$), 4.29–4.32 (m, 2 H, 4′-H, 5′A-H), 4.42 (dd, $J_{5'A,5'B}$ = 13.2 Hz, $J_{4',5'B}$ = 4.3 Hz, 1 H, 5′B-H), 5.09–5.16 (m, 2 H, 2′-H, 1′-Hβ), 5.25 (dd, $J_{2',3'}$ = 4.9 Hz, $J_{4',3'}$ = 6.2 Hz, 1 H, 3′-H), 6.96 (d, $J_{6,2}$ = 2.2 Hz, 1 H, 2-H), 7.04 (dd, $J_{6,5}$ = 8.5 Hz, 1 H, 6-H), 7.56 (d, $J_{6,5}$ = 8.5 Hz, 1 H, 5-H). – $C_{21}H_{24}O_{81}$ (452.4): calcd. C 55.75, H 5.35; found C 55.61, H 5.44.

1,3-Di-*O*-acetyl-4-(2,3-di-*O*-acetyl-5-*O*-*tert*-butyldimethylsilyl-β-D-ribofuranosyl)resorcinol (14): Compound **12** (3.00 g, 0.01 mol) was dissolved in acetic acid/methanol (1:1, 10 mL) and the solution stirred for about 12 h at room temp. The solution was concentrated and coevaporated with toluene. The residue was mixed with dry *N*,*N*-dimethylformamide (30 mL) and treated in a ultrasonic bath for 20 min. Imidazole (1.69 g, 0.02 mol) was added and, under vigorous stirring, a solution of *tert*-butylchlorodimethylsilane (2.05 g, 0.01 mol) in dry *N*,*N*-dimethylformamide (10 mL) was added dropwise. Stirring was continued for ca. 12 h. The solvent was evaporated in vacuo and the residue was dissolved in dry pyridine/acetic anhydride (20 mL, 2:1). After stirring for ca. 12 h, the mixture was concentrated and coevaporated with toluene. The crude product was purified by flash chromatography (toluene/acetone, 5:1) to give **14** (2.96 g, 49%) as a colourless solid. – TLC (petroleum ether/ethyl acetate, 1:1): R_f = 0.44. – $[\alpha]_D$ = –11.6 (*c* = 1.0 in chloroform). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.08 [s, 6 H, $Si(CH_3)_2$], 0.89 [s, 9 H, $C(CH_3)_3$], 1.99–2.27 (4 × s, 12 H, 4 × $COCH_3$), 3.82 (dd, $J_{5'A,5'B}$ = 11.2 Hz, $J_{4',5'A}$ = 2.6 Hz, 1 H, 5′A-H), 3.89 (dd, $J_{5'A,5'B}$ = 11.2 Hz, $J_{4',5'B}$ = 2.6 Hz, 1 H, 5′B-H), 4.09–4.15 (m, 1 H, 4′-H), 5.07 (dd, $J_{3',2'}$ = 5.2 Hz, $J_{1',2'}$ = 7.4 Hz, 1 H, 2′-H), 5.16 (d, $J_{1',2'}$ = 7.4 Hz, 1 H, 1′-H), 5.34 (dd, $J_{3',2'}$ = 5.2 Hz, $J_{4',3'}$ = 3.8 Hz, 1 H, 3′-H), 6.91 (d, $J_{6,2}$ = 2.2 Hz, 1 H, 2-H), 6.98 (dd, $J_{6,5}$ = 8.5 Hz, $J_{2,5}$ = 2.2 Hz, 1 H, 6-H), 7.73 (d, $J_{6,5}$ = 8.5 Hz, 1 H, 5-H). – $C_{25}H_{36}O_{10}Si$ (524.6): calcd. C 57.23, H 6.91; found C 56.77, H 6.95.

1,3-Di-*O*-acetyl-4-(2,3-di-*O*-acetyl-β-D-ribofuranosyl)resorcinol: (15): A solution of **14** (3.00 g, 5.72 mmol) in acetic acid/water (8:2, 30 mL) was refluxed for 5 h. The solvents were evaporated in vacuo and the residue was coevaporated with toluene. Flash chromatography (toluene/acetone, 4:1) yielded **15** (1.64 g, 70%) as a colourless solid. – TLC (toluene/acetone, 2:1): R_f = 0.41. – $[\alpha]_D$ = –26.5 (*c* = 1.0 in chloroform). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.04–2.28 (4 × s, 12 H, 4 × $COCH_3$), 3.73 (dd, $J_{5'A,5'B}$ = 12.3 Hz, $J_{4',5'A}$ = 3.7 Hz, 1 H, 5′A-H), 3.88 (dd, $J_{5'A,5'B}$ = 12.3 Hz, $J_{4',5'B}$ = 3.0 Hz, 1 H, 5′B-H), 4.05–4.11 (m, 1 H, 4′-H), 5.08 (d, $J_{1',2'}$ = 5.6 Hz, 1 H, 1′-H), 5.21 (dd, $J_{2',1'}$ = $J_{2',3'}$ = 5.6 Hz, 1 H, 2′-H), 5.28 (dd, $J_{3',2'}$ = $J_{4',3'}$ = 5.6 Hz, 1 H, 3′-H), 6.91 (d, $J_{6,2}$ = 2.3 Hz, 1 H, 2-H), 6.98 (dd, $J_{6,5}$ = 8.5 Hz, $J_{2,6}$ = 2.3 Hz, 1 H, 6-H), 7.73 (d, $J_{6,5}$ = 8.5 Hz, 1 H, 5-H). – $C_{19}H_{22}O_{10}$ (410.38): calcd. C 55.61, H 5.40; found C 55.38, H 5.52.

Dibenzyl [(1,3-Di-*O*-acetylresorcin-4-yl) (2,3-Di-*O*-acetyl-1-deoxy-β-D-ribofuranosid-5-yl)] Phosphate (16): Compound **15** (320 mg, 0.780 mmol) and 1*H*-tetrazole (80 mg, 1.14 mmol) were dissolved in dry acetonitrile/dichloromethane (3:1, 10 mL) under nitrogen. Bis(benzyloxy)(diisopropylamino)phosphane (426 mg, 1.24 mmol) in dry dichloromethane (5 mL) was added by syringe. After 20 min (TLC), a solution of *tert*-butyl hydroperoxide (3 M) in dry toluene (310 μL, 0.935 mmol) was added and stirring was continued for a further 20 min. The reaction mixture was treated with half-saturated sodium bicarbonate solution and extracted with dichloromethane. The organic layer was dried with magnesium sulfate and concentrated in vacuo. Purification by flash chromatography (toluene/acetone, 4:1) yielded **16** (440 mg, 85%) as a colourless solid. – TLC (toluene/acetone, 4:1): R_f = 0.17. – $[\alpha]_D$ = +4.60 (c = 1.0 in chloroform). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.03–2.26 (4 × s, 12 H, 4 × $COCH_3$), 4.16–4.27 (m, 3 H, 4′-H, 5′A-H, 5′B-H), 4.98–5.14 (m, 6 H, 1′-H, 2′-H, 2 × CH_2Ph), 5.72 (dd, $J_{2',3'}$ = $J_{4',3'}$ = 5.0 Hz, 1 H, 3′-H), 6.83 (dd, $J_{5,6}$ = 8.5 Hz, $J_{2,6}$ = 2.2 Hz, 1 H, 6-H), 6.90 (d, $J_{6,2}$ = 2.2 Hz, 1 H, 2-H), 7.32–7.36 (m, 10 H, 2 × Ph), 7.55 (d, $J_{6,5}$ = 8.5 Hz, 1 H, 5-H). – $C_{33}H_{35}O_{13}P$ (670.60): calcd. C 59.10, H 5.26; found C 59.00, H 5.46.

Methyl (Benzyl 4,7,8,9-Tetra-*O*-acetyl-5-amino-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate Hydrochloride (19): To a solution of **17**[19] (1.00 g, 1.72 mmol) and 2,6-di-*tert*-butylpyridine (1.65 g, 8.60 mmol) in dry acetonitrile (6 mL) was added a solution of Tf_2O (1.21 g, 4.30 mmol) in dry acetonitrile (5 mL) dropwise at –25 °C. After stirring for 30 min, a solution of dry ethanol (1.56 g, 0.034 mol) and 2,6-di-*tert*-butylpyridine (1.65 g, 8.6 mmol) in acetonitrile (4 mL) was added. The reaction mixture was treated with half-saturated sodium bicarbonate solution and extracted with dichloromethane. The organic layer was dried with magnesium sulfate and concentrated in vacuo. Purification by flash chromatography (toluene/acetone 15:1) gave the imidate intermediate (520 mg, 50%) as a colourless foam. – TLC (toluene/acetone, 15:1): R_f = 0.58. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.19 (t, J = 7.1 Hz, 3 H, CH_3), 1.73 (s, 3 H, CH_3), 1.83 (dd, $J_{3e,3a}$ = 13.2 Hz, $J_{3a,4}$ = 11.0 Hz, 1 H, 3a-H), 1.95–2.18 (4 × s, 12 H, 4 × $COCH_3$), 2.78 (dd, $J_{3e,3a}$ = 13.2 Hz, $J_{3e,4}$ = 4.9 Hz, 1 H, 3e-H), 3.19 (dd, $J_{5,6}$ = $J_{4,5}$ = 10.2 Hz, 1 H, 5-H), 3.69 (s, 3 H, $COOCH_3$), 3.89–4.22 (m, 4 H, 9A-H, 6-H, CH_2), 4.36 (dd, $J_{9A,9B}$ = 12.5 Hz, $J_{9B,8}$ = 1.9 Hz, 1 H, 9B-H), 4.42 (d, J = 12.0 Hz, 1 H, 0.5 × CH_2Ph), 4.7–4.85 (m, 2 H, 0.5 × CH_2Ph, 4-H), 5.28 (dd, $J_{6,7}$ = 6.8 Hz, 1 H, 7-H), 5.49–5.50 (m, 1 H, 8-H), 7.21–7.38 (m, 5 H, Ph). To a solution of the imidate intermediate (500 mg, 0.82 mmol) in methanol (50 mL) was added trifluoracetic acid (2.5% in methanol, 7.0 mL) dropwise at 0 °C and the mixture was stirred for 2 h. The solution was concentrated and coevaporated with toluene. The residue was dissolved in methanol (20 mL) and stirred for 30 min with Amberlite IRA 420 (Cl^-). The ion-exchange resin was filtered off. The filtrate was concentrated to dryness to yield **19** (450 mg, 95%), which was used without further purification. – TLC (toluene/acetone, 3:1): R_f = 0.18. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.72 (dd, $J_{3a,3e}$ = $J_{4,3a}$ = 11.0 Hz, 1 H, 3a-H), 2.01–2.21 (4 × s, 12 H, 4 × $COCH_3$), 2.82 (dd, $J_{3e,4}$ = 4.3 Hz, $J_{3e,3a}$ = 11.0 Hz, 1 H, 3e-H), 2.91 (dd, J = 10.3 Hz, 1 H, 5-H), 3.52–3.62 (m, 1 H, 9A-H), 3.71 (s, 3 H, CO-OCH_3), 4.22–4.38 (m, 2 H, 6-H, 9B-H), 4.43 (d, J = 11.9 Hz, 1 H, 0.5 CH_2Ph), 4.63 (d, $J_{5,NH}$ = 10.3 Hz, 1 H, NH), 4.78 (d, J = 11.9 Hz, 1 H, 0.5 CH_2Ph), 5.22–5.31 (m, 1 H, 8-H), 5.36 (ddd, $J_{3a,4}$ = 11.0 Hz, $J_{3e,4}$ = 4.3 Hz,1 H, 4-H), 5.52 (dd, $J_{7,8}$ = 8.4 Hz, 1 H, 7-H), 7.23–7.34 (m, 5 H, Ph).

Methyl (Benzyl 4,7,8,9-Tetra-*O*-acetyl-3,5-dideoxy-5-trifluoracetamido-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate (20a): Hydrochloride **18**[20] (3.20 g, 8.96 mmol) and triethylamine (1.40 mL) were dissolved in dry methanol (60 mL) and *S*-ethyl trifluorothioacetate (1.40 mL, 0.011 mol) in dry methanol (13 mL) was added. The solution was stirred for 3 h at room temp. and the reaction monitored by TLC. The solvent was removed and the residue coevaporated with toluene. The residue was dissolved in methanol (40 mL) and stirred for 30 min with Amberlite IR 120 (H^+). The mixture was filtered and to the filtrate was added a solution of diazomethane (0.5 M in ether) until the solution remained yellow. After removal of the solvents, the residue was stirred overnight in dry pyridine/acetic anhydride (2:1, 20 mL). Evaporation of the solvents, codistillation with toluene and flash chromatography (toluene/acetone, 4:1) yielded **20a** (3.6 g, 64%) as a colourless solid. – TLC (toluene/acetone, 4:1): R_f = 0.41. NMR data were identical with published data.[20]

Methyl (Benzyl 4,7,8,9-Tetra-*O*-acetyl-3,5-dideoxy-5-valeroylamino-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate (20b): To a solution of **19** (400 mg, 0.694 mmol) and triethylamine (85 mg, 0.833 mmol) in dry dichloromethane (10 mL) was added a solution of valeric acid (133 mg, 1.30 mmol) in dry dichloromethane (3 mL). WSC (water-soluble carbodiimide, 200 mg) was added in small portions at 0 °C and the mixture was stirred overnight. The mixture was diluted with dichloromethane (10 mL), washed with sodium bicarbonate solution and extracted with dichloromethane. The organic layer was dried with magnesium sulfate and concentrated under reduced pressure. Purification by flash chromatography (toluene/acetone, 6:1) yielded **20b** (300 mg, 71%) as a colourless solid. – TLC (toluene/acetone 3:1): R_f = 0.65. – $[\alpha]_D$ = +2.40 (c = 1.0 in chloroform). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.90 (t, J = 6.6 Hz, 3 H, CH_3), 1.26–1.37 (m, 2 H, C$H_2$$CH_3$), 1.48–1.58 (m, 2 H, C$H_2$$CH_2CH_3$), 1.96–2.17 (m, 15 H, 4 × $COCH_3$, CH_2CO, 3a-H), 2.66 (dd, $J_{3e,4}$ = 4.6 Hz, $J_{3e,3a}$ = 13.1 Hz, 1 H, 3e-H), 3.67 (s, 3 H, $COOCH_3$), 4.08–4.16 (m, 3 H, 5-H, 6-H, 9B-H), 4.34 (dd, $J_{8,9A}$ = 2.6 Hz, $J_{9A,9B}$ = 12.4 Hz, 1 H, 9A-H), 4.42 (d, J = 11.9 Hz, 1 H, 0.5 × CH_2Ph), 4.81 (d, J = 11.9 Hz, 1 H, 0.5 CH_2Ph), 4.85–5.28 (m, 1 H, 4-H), 5.20 (d, $J_{5,NH}$ = 9.4 Hz, 1 H, NH), 5.33 (dd, $J_{7,8}$ = 8.4 Hz, 1 H, 7-H), 5.45 (ddd, $J_{8,9a}$ = 2.6 Hz, $J_{7,8}$ = 8.4 Hz, 1 H, 8-H), 7.23–7.34 (m, 5 H, Ph). – $C_{30}H_{41}NO_{13}$ (623.65): calcd. C 57.78, H 6.63; found C 57.52, H 6.64.

Methyl (Benzyl 4,7,8,9-Tetra-*O*-acetyl-3,5-dideoxy-5-(*N*-trifluoracetylglycylamido)-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate (20c): To a solution of **19** (250 mg, 0.335 mmol) and triethylamine (53 mg, 0.521 mmol) in dry dichloromethane (6 mL) was added a solution of (trifluoroacetylamino)acetic acid (110 mg, 0.652 mmol) in dry dichloromethane (3 mL). WSC (125 mg) was added in small portions at 0 °C and the mixture was stirred overnight. The mixture was diluted with dichloromethane (10 mL), washed with sodium bicarbonate solution and extracted with dichloromethane. The organic layer was dried with magnesium sulfate and concentrated under reduced pressure. Purification by flash chromatography (toluene/acetone, 6:1) yielded **20c** (180 mg, 75%) as a colourless solid. – TLC (toluene/acetone 4:1): R_f = 0.52. – $[\alpha]_D$ = +2.4 (c = 1.0 in chloroform). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.99–2.15 (4 × s, 13 H, 4 × $COCH_3$, 3a-H), 2.67 (dd, $J_{3e,4}$ = 4.6 Hz, $J_{3e,3a}$ = 12.8 Hz, 1 H, 3e-H), 3.65 (s, 3 H, $COOCH_3$), 3.87 (d, $J_{CHa,CHb}$ = $J_{NH,CHa}$ = 5.4 Hz, 1 H, 0.5 × $COCH_2$), 3.99–4.13 (m, 3 H, 5-H, 9A-H, 0.5 × $COCH_2$), 4.18 (dd, $J_{7,6}$ = 2.1 Hz, $J_{8,6}$ = 10.7 Hz, 1 H, 6-H), 4.33 (dd, $J_{8,9B}$ = 2.6 Hz, $J_{9A,9B}$ = 12.5 Hz, 1 H, 9B-H), 4.40 (J = 11.9 Hz, 1 H, 0.5 CH_2Ph), 4.78 (d, J = 11.9 Hz, 1 H, 0.5 CH_2Ph), 4.84–4.91 (m, 1 H, 4-H), 5.29 (d<, $J_{6,7}$ = 2.1 Hz, $J_{7,8}$ = 8.6 Hz, 1 H, 7-H), 5.45 (ddd, $J_{8,9B}$ = 2.6 Hz, $J_{7,8}$ = 8.5 Hz, $J_{9A,8}$ = 5 Hz, 1 H, 8-H), 5.84 (d, $J_{5,NH}$ = 9.8 Hz, 1 H, NH), 7.16–7.38 (m,

6 H, Ph, NH). – $C_{29}H_{35}F_3N_2O_{14}$ (692.59): calcd. C 50.29, H 5.09, N 4.04; found C 49.92, H 5.24, N 3.96.

Methyl (Benzyl 4,7,8,9-Tetra-*O*-acetyl-3,5-dideoxy-5-ethoxycarbonylamino-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate (20d): To a solution of **19** (170 mg, 0.296 mmol) in dry dichloromethane (2.0 mL) was added dry pyridine (120 µL). The solution was cooled to 0 °C and ethoxycarbonyl chloride (140 µL, 1.47 mmol) was added dropwise. The resulting yellow solution was stirred for 30 min at room temp., then poured into sodium bicarbonate solution and extracted with dichloromethane. The organic layer was dried with magnesium sulfate, concentrated and purified by flash chromatography (toluene/acetone, 5:1) to yield **20d** (163 mg, 90%) as a colourless foam. – TLC (toluene/acetone, 3:1): R_f = 0.50. – $[\alpha]_D$ = +8.2 (c = 1.0 in chloroform). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.20 (t, J = 7.1 Hz, 3 H, CH_3), 1.91–2.15 (m, 13 H, 4 × $COCH_3$, 3a-H), 2.66 (dd, $J_{3e,4}$ = 4.6 Hz, $J_{3e,3a}$ = 12.7 Hz, 1 H, 3e-H), 3.65 (s, 3 H, $COOCH_3$), 3.68–3.82 (m, 1 H, 0.5 × OCH_2), 3.99–4.13 (m, 4 H, 5-H, 6-H, 9B-H, 0.5 × OCH_2), 4.32 (dd, $J_{8,9A}$ = 2.4 Hz, $J_{9A,9B}$ = 12.5 Hz, 1 H, 9A-H), 4.39 (d, J = 11.9 Hz, 2 H, 0.5 × CH_2Ph, NH), 4.79–4.92 (m, 2 H, 0.5 × CH_2Ph, 4-H), 5.39–5.50 (m, 2 H, 7-H, 8-H), 7.20–7.36 (m, 5 H, Ph). – MS (MALDI): 636 (M + Na^+ + 1).

Methyl 4,7,8,9-Tetra-*O*-acetyl-3,5-dideoxy-5-trifluoroacetamido-D-*glycero*-β-D-*galacto*-2-nonulopyranosonate (21a): To a solution of **20a** (1.40 g, 2.21 mmol) in methanol (60 mL) was added palladium on charcoal (140 mg, 10% Pd). The mixture was stirred overnight under hydrogen at normal pressure. The catalyst was filtered off and washed with methanol. Evaporation of the solvents and flash chromatography (toluene/acetone, 4:1) afforded **21a** (980 mg, 81%) as a colourless solid. – TLC (toluene/acetone, 4:1): R_f = 0.28. – $[\alpha]_D$ = +2.4 (c = 1.0 in chloroform). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.95–2.32 (m, 13 H, 4 × $COCH_3$, 3a-H), 3.81 (s, 3 H, $COOCH_3$), 4.01 (dd, $J_{8,9}$ = 6.8 Hz, $J_{9A,9B}$ = 12.3 Hz, 1 H, 9B-H), 4.12 (dd, $J_{5,6}$ = $J_{5,4}$ = 10.2 Hz, 1 H, 5-H), 4.45 (dd, $J_{7,6}$ = 2.3 Hz, $J_{5,6}$ = 10.5 Hz, 1 H, 6-H), 4.68 (dd, $J_{9A,9B}$ = 12.3 Hz, $J_{8,9A}$ = 2.3 Hz, 1 H, 9A-H), 5.13–5.27 (m, 1 H, 4-H), 5.28–5.35 (m, 2 H, 7-H, 8-H), 5.49 (s, 1 H, OH), 7.75 (d, J = 10 Hz, 1 H, NH). – $C_{20}H_{26}F_3NO_{13}$ (545.42): calcd. C 44.04, H 4.80, N 2.07; found C 44.11, H 4.84, N 2.51.

Methyl 4,7,8,9-Tetra-*O*-acetyl-3,5-dideoxy-5-valeroylamino-D-*glycero*-β-D-*galacto*-2-nonulopyranosonate (21b): To a solution of **20b** (250 mg, 0.401 mmol) in methanol (20 mL) was added palladium on charcoal (30 mg, 10% Pd). The mixture was stirred overnight under hydrogen at normal pressure. The catalyst was filtered off and washed with methanol. Evaporation of the solvents and flash chromatography (toluene/acetone, 3:1) afforded **21b** (180 mg, 85%) as a colourless solid. – DC (toluene/acetone, 4:1): R_f = 0.24. – $[\alpha]_D$ = +2.9 (c = 1.0 in chloroform). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.89 (t, J = 7.2 Hz, 3 H, CH_3), 1.23–1.34 (m, 2 H, CH_2CH_3), 1.37–1.59 (m, 2 H, $CH_2CH_2CH_3$), 1.76–2.35 (m, 16 H, 4 × $COCH_3$, 3a-H, 3e-H, $COCH_2$), 3.86 (s, 3 H, $COOCH_3$), 4.00 (dd, J_{9aA9B} = 12.2 Hz, $J_{8,9B}$ = 7.4 Hz, 1 H, 9B-H), 4.13–4.19 (m, 2 H, 5-H, 6-H), 4.42 (dd, $J_{9A,9B}$ = 12.1 Hz, 2 H, 9A-H, OH), 5.19–5.26 (m, 1 H, 4-H, 8-H), 5.30 (dd, $J_{6,7}$ = 6.5 Hz, 1 H, 7-H), 5.5–5.63 (m, 1 H, NH). – $C_{23}H_{35}NO_{13}$ (533.53): calcd. C 51.78, H 6.61, N 2.62; found C 51.58, H 6.49, N 2.78.

Methyl 4,7,8,9-Tetra-*O*-acetyl-3,5-dideoxy-5-(*N*-trifluoracetylglycylamido)-D-*glycero*-β-D-*galacto*-2-nonulopyranosonate (21c): To a solution of **20c** (200 mg, 0.289 mmol) in methanol (10 mL) was added palladium on charcoal (20 mg, 10% Pd). The mixture was stirred overnight under hydrogen at normal pressure. The catalyst was filtered off and washed with methanol. Evaporation of the solvents and flash chromatography (toluene/acetone, 2:1) afforded **21c** (150 mg, 86%) as a colourless solid. – DC (toluene/acetone, 4:1): R_f = 0.28. – $[\alpha]_D$ = +2.0 (c = 1.0 in chloroform). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.90–2.24 (4 × s, 14 H, 4 × $COCH_3$, 3a-H, 3e-H), 3.82 (s, 3 H, $COOCH_3$), 2.32–4.13 (m, 4 H, 5-H, 9A-H, CH_2), 4.30 (d, $J_{7,6}$ = 2.0 Hz, $J_{5,6}$ = 10.5 Hz, 1 H, 6-H), 4.55 (dd, $J_{9A,9B}$ = 12.2 Hz, $J_{8,9B}$ = 2.2 Hz, 1 H, 9B-H), 4.14–5.27 (m, 2 H, 4-H, 8-H), 5.35 (dd, $J_{6,7}$ = 2.1 Hz, $J_{8,7}$ = 4.0 Hz, 1 H, 7-H), 6.82 (d, J = 9.9 Hz, 1 H, NH), 7.44–7.51 (m, 1 H, NH). – $C_{22}H_{29}F_3N_2O_{14}$ (602.47): calcd. C 43.86, H 4.85, N 4.65; found C 43.5, H 4.98, N 4.67.

Methyl 4,7,8,9-Tetra-*O*-acetyl-3,5-dideoxy-5-ethoxycarbonylamino-D-*glycero*-β-D-*galacto*-2-nonulopyranosonate (21d): To a solution of **20d** (250 mg, 0.401 mmol) in methanol (20 mL) was added palladium on charcoal (20 mg, 10% Pd). The mixture was stirred overnight under hydrogen at normal pressure. The catalyst was filtered off and washed with methanol. Evaporation of the solvents and flash chromatography (toluene/acetone, 3:1) afforded **21d** (168 mg, 79%) as a colourless solid. – TLC (toluene/acetone, 2:1): R_f = 0.43. – $[\alpha]_D$ = +0.5 (c = 1.0 in chloroform). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.20 (t, J = 7 Hz, 3 H, CH_3), 1.99–2.25 (m, 14 H, 4 × $COCH_3$, 3a-H, 3e-H), 3.72–3.77 (m, 1 H, 0.5 × OCH_2), 3.82 (s, 3 H, $COOCH_3$), 3.81–4.07 (m, 3 H, 5-H, 9A-H, 0.5 × OCH_2), 4.13 (dd, $J_{7,6}$ = 1.8 Hz, $J_{5,6}$ = 10.5 Hz, 1 H, 6-H), 4.39–4.44 (m, 2 H, OH, 9B-H), 4.78 (d, J = 10.3 Hz, 1 H, NH), 5.12–5.27 (m, 2 H, 4-H, 8-H), 5.37 (dd, $J_{6,7}$ = 1.8 Hz, $J_{8,7}$ = 5.8 Hz, 1 H, 7-H). – MS (MALDI): 545 (M + Na^+ + 1).

Diethyl [Methyl (4,7,8,9-Tetra-*O*-acetyl-3,5-dideoxy-5-trifluoroacetamido-D-*glycero*-β-D-*galacto*-2-nonulopyranosyl)onate] Phosphite (22a): To a solution of **21a** (730 mg, 1.34 mmol) and ethyldiisopropylamine (513 µL) in dry acetonitrile (10 mL) was added diethyl chlorophosphite (380 µL, 2.64 mmol) under nitrogen. After 10 min, the solution was concentrated and coevaporated with toluene. Flash chromatography (toluene/acetone, 6:1) yielded **22a** (783 mg, 88%) as a colourless oil. – TLC (toluene/acetone): R_f = 0.64. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.16–1.26 (m, 6 H, 2 × CH_3), 1.89–2.08 (m, 13 H, 4 × $COCH_3$, 3a-H), 2.50 (dd, $J_{3e,4}$ = 4.8 Hz, $J_{3a,3e}$ = 13.0 Hz, 1 H, 3e-H), 3.76 (s, 3 H, $COOCH_3$), 3.78–3.96 (m, 4 H, 2 × CH_2), 4.05 (dd, $J_{6,5}$ = $J_{4,5}$ = 10.2 Hz, 1 H, 5-H), 4.16 (dd, $J_{8,9B}$ = 7.5 Hz, $J_{9A,9B}$ = 12.5 Hz, 1 H, 9B-H), 4.40 (dd, $J_{7,6}$ = 1.8 Hz, $J_{5,6}$ = 10.5 Hz, 1 H, 6-H), 4.60 (dd, $J_{8,9A}$ = 1.9 Hz, $J_{9B,9A}$ = 12.5 Hz, 1 H, 9A-H), 5.08–5.11 (m, 1 H, 8-H), 5.34–5.42 (m, 2 H, 4-H, 7-H), 7.14 (d, J = 9.9 Hz, 1 H, NH). – ^{31}P NMR (167.7 MHz, $CDCl_3$): δ_P = 137.94. – FAB-MS (positive mode, matrix: acetone/nitrobenzyl alcohol, 1:1 and NaI): 688 (M + Na^+).

Diethyl [Methyl (4,7,8,9-Tetra-*O*-acetyl-3,5-dideoxy-5-valeroylamino-D-*glycero*-α/β-D-*galacto*-2-nonulopyranosyl)onate] Phosphite (22b): To a solution of **21b** (180 mg, 0.338 mmol) and ethyldiisopropylamine (134 µL) in dry acetonitrile (10 mL) was added diethyl chlorophosphite (100 µL, 0.696 mmol) under nitrogen. After 10 min, the solution was concentrated and coevaporated with toluene. Flash chromatography (toluene/acetone, 3:1) yielded **22b** (187 mg, 85%) as an anomeric mixture. – TLC (toluene/acetone, 3:1): R_f = 0.36.

Diethyl [Methyl (4,7,8,9-Tetra-*O*-acetyl-3,5-dideoxy-5-*N*-trifluoroacetylglycylamido-D-*glycero*-β-D-*galacto*-2-nonulopyranosyl)onate] Phosphite (22c): To a solution of **21c** (100 mg, 0.166 mmol) and ethyldiisopropylamine (62 µL) in dry acetonitrile (1.5 mL) was added diethyl chlorophosphite (50 µL, 0.332 mmol) under nitrogen. After 10 min, the solution was concentrated and coevaporated with

toluene. Flash chromatography (toluene/acetone, 4:1) yielded **22c** (100 mg, 83%) as a colourless oil. – TLC (toluene/acetone, 4:1): R_f = 0.30. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.18–1.41 (m, 6 H, 2 CH_3), 1.95–2.19 (m, 13 H, 4 × $COCH_3$, 3a-H), 2.50 (dd, $J_{3e,4}$ = 4.9 Hz, $J_{3a,3e}$ = 13.1 Hz, 1 H, 3e-H), 3.79 (s, 3 H, $COOCH_3$), 3.81–4.19 (m, 8 H, 2 × OCH_2, 5-H, 9A-H, $COCH_2$), 4.30 (dd, $J_{6,7}$ = 2.1 Hz, $J_{5,6}$ = 10.7 Hz, 1 H, 6-H), 4.59 (dd, $J_{8,9B}$ = 2.4 Hz, $J_{9A,9B}$ = 12.3 Hz, 1 H, 9B-H), 5.10 (ddd, $J_{8,9A}$ = 7.3 Hz, 1 H, 8-H), 5.23 (ddd, $J_{3e,4}$ = 4.9 Hz, 1 H, 4-H), 5.38 (dd, $J_{7,8}$ = 2.4 Hz, 1 H, 7-H), 6.05 (m, 1 H, NH), 7.10–7.21 (d, J = 9.8 Hz, 1 H, NH).

Diethyl [Methyl (4,7,8,9-Tetra-*O*-acetyl-3,5-dideoxy-5-ethoxycarbonylamino-D-*glycero*-β-D-*galacto*-2-nonulopyranosyl)onate] Phosphite (22d): To a solution of **21d** (170 mg, 0.336 mmol) and ethyldiisopropylamine (120 μL) in dry acetonitrile (3 mL) was added diethyl chlorophosphite (90 μL, 0.626 mmol) under nitrogen. After 10 min, the solution was concentrated and coevaporated with toluene. Flash chromatography (toluene/acetone, 4:1) yielded **22d** (188 mg, 90%) as a colourless oil. – TLC (toluene/acetone, 4:1): R_f = 0.32. – $[\alpha]_D$ = –19.2 (c = 1.0 in chloroform). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.10–1.29 (m, 9 H, 3 × CH_3), 1.92–2.12 (m, 13 H, 4 × $COCH_3$, 3a-H), 2.48 (dd, $J_{3e,4}$ = 4.9 Hz, $J_{3a,3e}$ = 13.1 Hz, 1 H, 3e-H), 3.77 (s, 3 H, $COOCH_3$), 3.81–4.06 (m, 6 H, 2 × OCH_2, $COOCH_2$), 4.11 (dd, J = 10.4 Hz, 1 H, 5-H), 4.12–4.20 (m, 2 H, 6-H, 9A-H), 4.42 (d, J = 9.9 Hz, 1 H, NH), 4.58 (dd, $J_{8,9B}$ = 2.2 Hz, $J_{9A,9B}$ = 12.3 Hz, 1 H, 9B-H), 5.15 (ddd, $J_{8,9A}$ = 7.9 Hz, $J_{8,9B}$ = 2.2 Hz, $J_{7,8}$ = 2.8 Hz, 1 H, 8-H), 5.22 (ddd, $J_{3e,4}$ = 4.9 Hz, $J_{4,5}$ = 10.4 Hz, $J_{3a,4}$ = 11.1 Hz, 1 H, 4-H), 5.48 (dd, $J_{7,8}$ = 2.8 Hz, 1 H, 7-H). – ^{31}P NMR (161.7 MHz, $CDCl_3$): δ_P = 137.28.

Triethylammonium (*N*-Acetyl-2′,3′-di-*O*-acetylcytidin-5′-yl) [Methyl (4,7,8,9-Tetra-*O*-acetyl-3,5-dideoxy-5-trifluoroacetamido-D-*glycero*-β-D-*galacto*-2-nonulopyranosyl)onate] Phosphate (24a): A solution of **23**[3] (840 mg, 1.88 mmol) in dry *N*,*N*-dimethylformamide/acetonitrile (2:1, 6.0 mL) was cooled to –20 °C. A solution of **22a** (780 mg, 1.17 mmol) in dry acetonitrile (3 mL) was added by syringe. The reaction mixture was allowed to warm up to room temperature during 12 h. Triethylamine (500 μL) was added and the solvents were evaporated in vacuo. Flash chromatography (chloroform/methanol/triethylamine, 8:1:0.1) yielded **24a** (706 mg, 56%) as a colourless solid. – TLC (chloroform/methanol, 6:1): R_f = 0.32. – ^{1}H NMR (250 MHz, D_2O): δ = 1.33 (t, J = 7.2 Hz, 9 H, 3 × CH_3), 1.95–2.22 (m, 22 H, 7 × $COCH_3$, 3a-H), 2.80 (dd, $J_{3''e,4''}$ = 5.0 Hz, $J_{3''e,3''a}$ = 13.2 Hz, 1 H, 3′′e-H), 3.15–3.30 (m, 6 H, 3 × CH_2), 3.85 (s, 3 H, $COOCH_3$), 4.08 (dd, $J_{4'',5''}$ = $J_{6'',5''}$ = 10.5 Hz, 1 H, 5′′-H), 4.19–4.39 (m, 3 H, 5′A-H, 5′B-H, 9′′-B-H), 4.40–4.45 (m, 1 H, 4′-H), 4.56–4.67 (m, 2 H, 6′′-H, 9′′A-H), 5.29–5.34 (m, 1 H, 8′′-H), 5.40–5.49 (m, 2 H, 4′′-H, 8′′-H), 5.51–5.57 (m, 2 H, 2′-H, 3′-H), 6.24 (d, $J_{2',1'}$ = 4.3 Hz, 1 H, 1′-H), 7.58 (d, J = 7.5 Hz, 1 H, 5-H), 8.50 (d, J = 7.5 Hz, 1 H, 6-H). – ^{31}P NMR (161.7 MHz, MeOD): δ_P = –5.50. – FAB MS (negative mode matrix: methanol/nitrobenzyl alcohol, 1:1): 975 $(M - H^+)^-$.

Triethylammonium (*N*-Acetyl-2′,3′-di-*O*-acetylcytidin-5′-yl) [Methyl (4,7,8,9-Tetra-*O*-acetyl-3,5-dideoxy-5-valeroylamino-D-*glycero*-β-D-*galacto*-2-nonulopyranosyl)onate] Phosphate (24b): A solution of **23** (200 mg, 0.445 mmol) in dry *N*,*N*-dimethylformamide/acetonitrile (2:1, 1.5 mL) was cooled to –20 °C. A solution of **22b** (180 mg, 0.276 mmol) in dry acetonitrile (0.5 mL) was added by syringe. The reaction mixture was allowed to warm up to room temperature during 12 h. Triethylamine (500 μL) was added and the solvents were evaporated in vacuo. Flash chromatography (chloroform/methanol/triethylamine, 8:1:0.1) yielded **24b** (143 mg, 49%) as a colourless solid. – TLC (chloroform/methanol, 8:1): R_f = 0.26. – ^{1}H NMR (250 MHz, D_2O): δ = 0.95 (t, J = 7.2 Hz, 3 H, CH_3), 1.28–1.43 (m, 11 H, CH_2CH_3, 3 × CH_3), 1.50–1.60 (m, 2 H, $CH_2CH_2CH_3$), 1.98–2.22 (m, 24 H, 6 × $COCH_3$, $NHCH_3$, $COCH_2$, 3a-H), 2.76 (dd, $J_{3''e,4''}$ = 4.8 Hz, $J_{3''e,3''a}$ = 13.2 Hz, 1 H, 3′′e-H), 3.19–3.34 (m, 6 H, 3 × CH_2), 3.83 (s, 3 H, $COOCH_3$), 4.06–4.12 (m, 1 H, 5′′-H), 4.23–4.35 (m, 3 H, 5′A-H, 5′B-H, 9′′B-H), 4.46–4.52 (m, 2 H, 4′-H, 6′′-H), 4.63 (dd, $J_{9''A9''B}$ = 12.1 Hz, $J_{8'',9''A}$ = 2.6 Hz, 1 H, 9′′A-H), 5.26–5.42 (m, 2 H, 4′′-H, 8′′-H), 5.46 (dd, $J_{6Z',7''}$ = 2.0 Hz, $J_{8'',7''}$ = 4.7 Hz, 1 H, 7′′-H), 5.02–5.11 (m, 2 H, 2′-H, 3′-H), 6.24 (d, $J_{2',1'}$ = 4.4 Hz, 1 H, 1′-H), 7.58 (d, J = 7.5 Hz, 1 H, 5-H), 7.82 (d, J = 9.8 Hz, 1 H, NH), 8.52 (d, J = 7.5 Hz, 1 H, 6-H). – ^{31}P NMR (242.5 MHz, D_2O): δ_P = –2.23. – FAB MS (negative mode, matrix: methanol/nitrobenzyl alcohol): 963 $(M - H)^-$.

Triethylammonium (*N*-Acetyl-2′,3′-di-*O*-acetylcytidin-5′-yl) {Methyl [4,7,8,9-Tetra-*O*-acetyl-3,5-dideoxy-5-(*N*-trifluoroacetylglycylamido)-D-*glycero*-β-D-*galacto*-2-nonulopyranosyl]onate)} Phosphate (24c): A solution of **23** (94 mg, 0.208 mmol) in dry *N*,*N*-dimethylformamide/acetonitrile (2:1, 1.0 mL) was cooled to –20 °C. A solution of **22c** (100 mg, 0.138 mmol) in dry acetonitrile (0.4 mL) was added by syringe. The reaction mixture was allowed to warm up to room temperature during 12 h. Triethylamine (500 μL) was added and the solvents were evaporated in vacuo. Flash chromatography (chloroform/methanol/triethylamine, 7:1:0.1) yielded **24c** (70 mg, 45%) as a colourless solid. – TLC (chloroform/methanol, 3:1): R_f = 0.51. – ^{1}H NMR (250 MHz, D_2O): δ = 1.79–2.03 (m, 22 H, 7 × $COCH_3$, 3a-H), 2.44 (dd, $J_{3''e,4''}$ = 4.9 Hz, $J_{3''e,3''a}$ = 13.3 Hz, 1 H, 3′′e-H), 3.63 (s, 3 H, $COOCH_3$), 3.70–3.71 (m, 2 H, $COCH_2$), 3.79 (dd, $J_{4'',5''}$ = $J_{6'',5''}$ = 10.5 Hz, 1 H, 5′′-H), 3.98–4.07 (m, 2 H, 5′A-H, 5′B-H), 4.15 (dd, $J_{8'',9''B}$ = 6 Hz, $J_{9''A,9''B}$ = 12.3 Hz, 1 H, 9′′B-H), 4.27–4.36 (m, 3 H, 4′-H, 6′′-H, 9′′A-H), 5.01–5.12 (m, 2 H, 4′′-H, 8′′-H), 5.20 (dd, $J_{6'',7''}$ = 1.2 Hz, $J_{8'',7''}$ = 4.8 Hz, 1 H, 7′′-H), 5.28–5.36 (m, 2 H, 2′-H, 3′-H), 6.00 (d, $J_{2',1'}$ = 4.1 Hz, 1 H, 1′-H), 7.22 (d, J = 7.5 Hz, 1 H, 5-H), 8.17 (d, J = 7.5 Hz, 1 H, 6-H). – ^{31}P NMR (242.5 MHz, D_2O): δ_P = –1.91. – FAB MS (negative mode, matrix: glycerol/nitrobenzyl alcohol, 1:1): 1032 $(M - H)^-$.

Triethylammonium (*N*-Acetyl-2′,3′-di-*O*-acetylcytidin-5′-yl) [Methyl (4,7,8,9-Tetra-*O*-acetyl-3,5-dideoxy-5-ethoxycarbonylamino-D-*glycero*-β-D-*galacto*-2-nonulopyranosyl)onate] Phosphate (24d): A solution of **23** (180 mg, 0.400 mmol) in dry *N*,*N*-dimethylformamide/acetonitrile (2:1, 1.5 mL) was cooled to –20 °C. A solution of **22d** (150 mg, 0.234 mmol) in dry acetonitrile (0.5 mL) was added by syringe. The reaction mixture was allowed to warm up to room temperature during 12 h. Triethylamine (500 μL) was added and the solvents were evaporated in vacuo. Flash chromatography (chloroform/methanol/triethylamine, 7:1:0.1) yielded **24d** (150 mg, 61%) as a colourless solid. – TLC (chloroform/methanol, 3:1): R_f = 0.55. – ^{1}H NMR (250 MHz, MeOD): δ = 1.18–1.40 (m, 12 H, 4 × CH_3), 1.98–2.22 (m, 22 H, 7 × $COCH_3$, 3a′′-H), 2.74 (dd, $J_{3''e,4''}$ = 4.8 Hz, $J_{3''e,3''a}$ = 13.2 Hz, 1 H, 3′′e-H), 3.25 (q, J = 7.3 Hz, 6 H, 3 × CH_2), 3.65–3.78 (m, 1 H, 5-H), 3.83 (s, 3 H, $COOCH_3$), 4.00–4.10 (m, 2 H, $COCH_2$), 4.17–4.49 (m, 3 H, 5′A-H, 5′B-H, 9′′B-H), 4.44–4.49 (m, 2 H, 4′-H, 6′′-H), 4.63 (dd, $J_{8'',9''A}$ = 2.8 Hz, $J_{9''A,9''B}$ = 12.2 Hz, 1 H, 9′′A-H), 5.23–5.38 (m, 2 H, 4′′-H, 8′′-H), 5.53–5.59 (m, 3 H, 2′-H, 3′-H, 7′′-H), 6.24 (d, $J_{2',1'}$ = 4.1 Hz, 1 H, 1′-H), 6.70 (d, J = 10.2 Hz, 1 H, NH), 7.59 (d, J = 7.5 Hz, 1 H, 5-H), 8.56 (d, J = 7.5 Hz, 1 H, 6-H). – ^{31}P NMR (161.7 MHz, D_2O): δ_P = –5.44. – FAB MS (negative mode, matrix: methanol, glycerol/nitrobenzyl alcohol, 5:1): 951 $(M - H)^-$.

Lithium [(5-Amino-3,5-dideoxy-D-*glycero*-β-D-*galacto*-2-nonulopyranosyl)onate] (Cytidin-5′-yl) Phosphate (25a): To a solution of **24a** (400 mg, 0.371 mmol) in dry methanol (10 mL) was added sodium

methoxide solution (0.5 M, 5 drops) and the mixture was stirred for 3 h at room temp. The mixture was neutralized with Amberlite IRC-50 (H^+) (pH = 8–9), filtered, and concentrated. The residue was dissolved in water/methanol (1:1, 7 mL) and lithium hydroxide solution (1 M, 2 mL) was added. After stirring for 4 h at room temp., the solution was neutralized with Amberlite IRC-50 (H^+) (pH = 8–9) and filtered. Lyophilization of the filtrate and preparative HPLC (RP-18, 0.05 M $NEt_3H_2CO_3$) yielded **25a** (110 mg, 50%). – TLC, aminophase (ethanol/water, 1:1): R_f = 0.39. – ^{1}H NMR (250 MHz, D_2O): δ = 1.45 (ddd, $J_{3''a,P}$ = 5.8 Hz, $J_{3''a,3''e}$ = 13.2 Hz, $J_{3''a,4''}$ = 11.1 Hz, 1 H, 3″a-H), 2.28 (dd, $J_{3''e,4''}$ = 4.8 Hz, $J_{3''e,3''a}$ = 13.2 Hz, 1 H, 3″e-H), 2.80 (d, J = 10.2 Hz, 1 H, 5″-H), 3.42 (dd, J = 9.5 Hz, 1 H, 7″-H), 3.40–3.51 (m, 1 H, 9″A-H). – ^{31}P NMR (161.7 MHz, D_2O): δ = –4.26. – FAB MS (negative mode matrix: DMSO/glycerol, 1:1): 571 $(M - H^+)^-$.

Disodium (Cytidin-5′-yl) [(3,5-Dideoxy-5-valeroylamino-D-*glycero*-β-D-*galacto*-2-nonulopyranosyl)onate] Phosphate (25b): To a solution of **24b** (100 mg, 0.11 mmol) in dry methanol (3 mL) was added sodium methoxide solution (0.5 M, 3 drops) and the mixture was stirred for 3 h at room temp. The mixture was neutralized with Amberlite IRC-50 (H^+) (pH = 8–9), filtered and concentrated. The residue was dissolved in water/methanol (1:1, 1 mL) and sodium hydroxide solution (1 M, 1 mL) was added. After stirring for 4 h at room temp., the solution was neutralized with Amberlite IRC-50 (H^+) (pH 8–9) and filtered. The filtrate was lyophilized, redissolved in water and precipitated by addition of acetone. Centrifugation and drying under reduced pressure afforded **25b** (39 mg, 61%). – TLC, aminophase (acetonitrile/water, 2:1): R_f = 0.35. – ^{1}H NMR (250 MHz, D_2O): δ = 0.69 (t, J = 7.3 Hz, 3 H, CH_3), 1.11–1.20 (m, 2 H, CH_2CH_3), 1.31–1.50 (m, 3 H, $CH_2CH_2CH_3$, 3″a-H), 2.05–2.11 (m, 2 H, $COCH_2$), 2.26 (dd, $J_{3''e,4''}$ = 4.3 Hz, $J_{3''e,3''a}$ = 13.2 Hz, 1 H, 3″e-H), 3.22 (dd, J = 9.5 Hz, 1 H, 7″-H), 3.38 (dd, $J_{8'',9''B}$ = 9.7 Hz, $J_{9''A,9''B}$ = 12.0 Hz, 1 H, 9″-B-H), 3.61–3.78 (m, 2 H, 9″A-H, 8″-H), 3.78 (d, $J_{5'',6''}$ = 10.0 Hz, 1 H, 5″-H), 3.82 (dd, $J_{3''e,4''}$ = 4.3 Hz, $J_{4'',5''}$ = 10.2 Hz, 1 H, 4″-H), 3.93 (dd, $J_{5'',6''}$ = 10 Hz, 1 H, 6″-H), 3.99–4.18 (m, 5 H, 2′-H, 3′-H, 4′-H, 5′A-H, 5′B-H), 5.79 (d, $J_{2',1'}$ = 4.2 Hz, 1 H, 1′-H), 5.90 (d, J = 7.4 Hz, 1 H, 5-H), 7.76 (d, J = 7.4 Hz, 1 H, 6-H). – ^{31}P NMR (242.5 MHz, D_2O): δ_P = –0.78. – FAB MS (negative mode, matrix: glycerol): 676 $[(M + Na^+)^-]$.

Potassium (Cytidin-5′-yl) [(3,5-Dideoxy-5-glycylamido-D-*glycero*-β-D-*galacto*-2-nonulopyranosyl)onate] Phosphate (25c): Compound **24c** (30 mg, 26.4 μmol) was dissolved in water/methanol (1:9, 0.5 mL) and potassium carbonate (3 mg, 21.7 μmol) was added. After stirring for 20 h at room temp, the solution was neutralized with Amberlite IRC-50 (H^+) (pH = 8–9) and filtered. The filtrate was lyophilized, filtered on a column of P_2-Biogel and concentrated. The residue was dissolved in water and precipitated by addition of acetone. Centrifugation and drying under reduced pressure afforded **25c** (14 mg, 71%). – TLC, aminophase (ethanol/water, 1:1): R_f = 0.23. – ^{1}H NMR (250 MHz, D_2O): δ = 1.45 (ddd, $J_{3''a,3''e}$ = 13.0 Hz, 1 H, 3″a-H), 2.26 (dd, $J_{3''e,4''}$ = 4.8 Hz, $J_{3''e,3''a}$ = 13.0 Hz, 1 H, 3″e-H), 3.22 (dd, J = 9.5 Hz, 1 H, 7″-H), 3.41 (dd, $J_{8'',9''B}$ = 6.3 Hz, $J_{9''A,9''B}$ = 11.8 Hz, 1 H, 9″B-H), 3.58 (d, J = 3.3 Hz, 1 H, 0.5 × $COCH_2$), 3.64 (d, J = 3.3 Hz, 1 H, 0.5 × $COCH_2$), 3.67–3.78 (m, 2 H, 8″-H, 9″B-H), 3.78 (d, $J_{5'',6''}$ = 10.1 Hz, 1 H, 5″-H), 3.82 (dd, $J_{3''e,4''}$ = 4.8 Hz, $J_{4'',5''}$ = 10.1 Hz, 1 H, 4″-H), 3.88–3.99 (d, $J_{5'',6''}$ = 10.1 Hz, 1 H, 6″-H), 4.00–4.19 (m, 5 H, 2′-H, 3′-H, 4′-H, 5′A-H, 5′B-H), 5.78 (d, $J_{2',1'}$ = 4.2 Hz, 1 H, 1′-H), 5.91 (d, J = 7.5 Hz, 1 H, 5-H), 7.76 (d, J = 7.5 Hz, 1 H, 6-H). – ^{31}P NMR (242.5 MHz, D_2O): δ_P = –0.85.

Disodium (Cytidin-5′-yl) [(3,5-Dideoxy-5-ethoxycarbonylamino-D-*glycero*-β-D-*galacto*-2-nonulopyranosyl)onate] Phosphate (25d): To a solution of **24d** (125 mg, 0.119 mmol) in dry methanol (3 mL) was added sodium methanolate solution (0.5 M, 3 drops) and the mixture was stirred for 3 h at room temp. The mixture was neutralized with Amberlite IRC-50 (H^+) (pH = 8–9), filtered and concentrated. The residue was dissolved in water/methanol (1:1, 1 mL) and sodium hydroxide solution (1 M, 1 mL) was added. After stirring for 4 h at room temp., the solution was neutralized with Amberlite IRC-50 (H^+) (pH = 8–9) and filtered. The filtrate was lyophilized, redissolved in acetone and precipitated by addition of water. Centrifugation and drying under reduced pressure afforded **25b** (47 mg, 60%). – TLC, aminophase (acetonitrile/water, 2:1): R_f = 0.19. – ^{1}H NMR (250 MHz, D_2O): δ = 1.04 (t, J = 7.0 Hz, 3 H, CH_3), 1.42 (ddd, $J_{3''a,3''e}$ = 13.2 Hz, 1 H, 3″a-H), 2.24 (dd, $J_{3''e,4''}$ = 4.8 Hz, $J_{3''e,3''a}$ = 13.2 Hz, 1 H, 3″e-H), 3.32 (dd, J = 9.5 Hz, 1 H, 7″-H), 3.37–3.52 (m, 2 H, 5″-H, 9″A-H), 3.65–3.77 (m, 2 H, 6″-H, 9″B-H), 3.82 (dd, $J_{3''e,4''}$ = 4.8 Hz, $J_{4'',5''}$ = 10.7 Hz, 1 H, 4″-H), 3.88–3.99 (m, 3 H, CH_2, 8″-H), 4.00–4.10 (m, 5 H, 2′-H, 3′-H, 4′-H, 5′A-H, 5′B-H), 5.79 (d, $J_{2',1'}$ = 4.2 Hz, 1 H, 1′-H), 5.91 (d, J = 7.5 Hz, 1 H, 5-H), 7.78 (d, J = 7.5 Hz, 1 H, 6-H). – ^{31}P NMR (161.7 MHz, D_2O): δ_P = –4.17. – FAB MS (negative mode, matrix: DMSO/glycerol/acetic acid, 1:1:1): 665 (M + Na)$^-$.

Methyl 4,5,7,8,9-Penta-*O*-acetyl-3-deoxy-D-*glycero*-β-D-*galacto*-2-nonulopyranosonate (27): Compound **26**[23] (500 mg, 1.77 mmol) was dissolved in acetyl chloride (12 mL) and the mixture was stirred for 6 h at room temp. The solution was concentrated and coevaporated with toluene. The residue was redissolved in acetonitrile/water (10 mL, 1:1) and stirred for 3 h at room temp. The reaction mixture was diluted with half-saturated sodium bicarbonate solution and extracted with ethyl acetate. The aqueous layer was concentrated to a half of its original volume and extracted again with ethyl acetate. The combined organic layers were dried with magnesium sulfate and concentrated. Flash chromatography (toluene/acetone, 3:1) afforded **27** (565 mg, 65%) as a colourless solid. – TLC (toluene/acetone 4:1): R_f = 0.40. NMR data were identical with published data.

Diethyl [Methyl (4,5,7,8,9-Penta-*O*-acetyl-3-deoxy-D-*glycero*-β-D-*galacto*-2-nonulopyranosyl)onate] Phosphite (28): To a solution of **27** (360 mg, 0.732 mmol) and ethyldiisopropylamine (270 μL) in dry acetonitrile (8.0 mL) was added diethyl chlorophosphite (216 μL, 1.50 mmol) under nitrogen. After 10 min, the solution was concentrated and coevaporated with toluene. Flash chromatography (toluene/acetone, 6:1) yielded **28** (390 mg, 87%) as a colourless oil. – TLC (toluene/acetone, 6:1): R_f = 0.48. – $[\alpha]_D$ = –8.9 (c = 1.0 in chloroform). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.20–1.29 (m, 6 H, 2 × CH_3), 1.89–2.13 (m, 16 H, 5 × $COCH_3$, 3a-H), 2.53 (dd, $J_{3e,4}$ = 5.1 Hz, $J_{3a,3e}$ = 13.1 Hz, 1 H, 3e-H), 3.76 (s, 3 H, $COCH_3$), 3.76–3.99 (m, 4 H, 2 × CH_2), 4.15 (dd, $J_{8,9B}$ = 6.5 Hz, $J_{9A,9B}$ = 12.4 Hz, 1 H, 9B-H), 4.33 (dd, $J_{7,6}$ = 2.1 Hz, $J_{5,6}$ = 10.2 Hz, 1 H, 6-H), 4.50 (dd, $J_{8,9A}$ = 2.3 Hz, $J_{9B,9A}$ = 12.4 Hz, 1 H, 9A-H), 4.90 (dd, $J_{6,5}$ = $J_{4,5}$ = 9.9 Hz, 1 H, 5-H), 5.14–5.19 (m, 1 H, 4-H), 5.20–5.31 (m, 1 H, 8-H), 5.38 (dd, $J_{6,7}$ = 2.1 Hz, $J_{8,7}$ = 5.1 Hz, 1 H, 7-H). – ^{31}P NMR (161.7 MHz, $CDCl_3$): δ_P = 136.65. – FAB-MS (positive mode, matrix: acetone/nitrobenzyl alcohol, 1:1, and NaI): 613 (M + H^+).

Sodium (*N*-Acetyl-2′,3′-di-*O*-acetylcytidin-5′-yl) [Methyl (4,5,7,8,9-Penta-*O*-acetyl-3-deoxy-D-*glycero*-β-D-*galacto*-2-nonulopyranosyl)-onate] Phosphate (29): A solution of **23** (256 mg, 0.570 mmol) in dry *N*,*N*-dimethylformamide/acetonitrile (2:1, 3 mL) was cooled to –20 °C. A solution of **28** (218 mg, 0.357 mmol) in dry acetoni-

trile (1 mL) was added by syringe. The reaction mixture was allowed to warm up to room temperature during 12 h. Triethylamine (500 μL) was added and the solvents were evaporated in vacuo. Flash chromatography (chloroform/methanol/triethylamine, 7:1:0.1) afforded a colourless solid, which was redissolved in dry methanol (10 mL). Sodium methoxide solution (0.5 M, 5 drops) was added and the mixture was stirred for 1 h at room temp. The mixture was neutralized with Amberlite IRC-50 (H^+) (pH = 8–9), filtered and concentrated. Flash chromatography over aminophase silica gel (ethanol/water, 3:1) yielded **29** (82 mg, 38%). – TLC, aminophase (ethanol/water, 2:1): R_f = 0.37. – ^{1}H NMR (250 MHz, D_2O): δ = 1.50 (ddd, $J_{3''a,P}$ = 5.7 Hz, $J_{3''a,4''}$ = 11.5 Hz, $J_{3''e,3''a}$ = 13.4 Hz, 1 H, 3''a-H), 2.24 (dd, $J_{3''e,4''}$ = 4.8 Hz, $J_{3''e,3''a}$ = 13.4 Hz, 1 H, 3''e-H), 3.42 (dd, $J_{6'',5''}$ = $J_{4'',5''}$ = 9.5 Hz, 1 H, 5''-H), 3.34–3.49 (m, 1 H, 9''B-H), 3.55 (dd, J = 9.6 Hz, 1 H, 7''-H), 3.63 (s, 3 H, $COOCH_3$), 3.69–3.79 (m, 2 H, 8''-H, 9''A-H), 3.81 (ddd, $J_{3''a,4''}$ = 11.5 Hz, $J_{3''e,4''}$ = 4.8 Hz, 1 H, 4''-H), 3.89 (dd, $J_{6'',5''}$ = 9.5 Hz, 1 H, 6''-H), 3.95–4.15 (m, 5 H, 2'-H, 3'-H, 4'-H, 5'A-H, 5'B-H), 5.80 (d, $J_{2',1'}$ = 3.7 Hz, 1 H, 1'-H), 5.89 (d, J = 7.5 Hz, 1 H, 5-H), 7.73 (d, J = 7.5 Hz, 1 H, 6-H). – ^{31}P NMR (161.7 MHz, D_2O): δ_P = –1.13. – FAB MS (negative mode, matrix: glycerol/water, 1:1): 586 [(M – H^+)$^-$].

Diammonium (Cytidin-5'-yl) [(3-Deoxy-D-*glycero*-β-D-*galacto*-2-nonulopyranosyl)onate] Phosphate (30): To a solution of **29** (40 mg, 65.5 μmol) in water/methanol (1:1, 2 mL) was added sodium hydroxide solution (1 M, 1 mL) and the mixture was stirred for 3 h at room temp. The solution was neutralized with Amberlite IRC-50 (H^+) (pH = 8–9) and filtered. The filtrate was lyophilized and purified by preparative paper chromatography (isopropyl alcohol/water/ammonia, 55:35:10) to give **30** (30 mg, 79%). – TLC, aminophase (ethanol/water, 1:1): R_f = 0.31. – ^{1}H NMR (250 MHz, D_2O): δ = 1.42 (ddd, $J_{3''a,P}$ = 5.5 Hz, $J_{3''a,4''}$ = 11.6 Hz, $J_{3''e,3''a}$ = 12.8 Hz, 1 H, 3''a-H), 2.24 (dd, $J_{3''e,4''}$ = 4.8 Hz, $J_{3''e,3''a}$ = 12.8 Hz, 1 H, 3''e-H), 3.39 (d, $J_{5'',6''}$ = 9.8 Hz, 1 H, 5''-H), 3.49 (dd, $J_{8'',9''B}$ = 5.4 Hz, $J_{9''A,9''B}$ = 12.3 Hz, 1 H, 9''-B-H), 3.59 (dd, J = 7.5 Hz, 1 H, 7''-H), 3.70–3.86 (m, 3 H, 4''-H, 9''A-H, 8''-H), 3.91 (dd, $J_{5'',6''}$ = 9.8 Hz, 1 H, 6''-H), 3.99–4.18 (m, 5 H, 2'-H, 3'-H, 4'-H, 5'A-H, 5'B-H), 5.79 (d, $J_{2',1'}$ = 4.2 Hz, 1 H, 1'-H), 5.92 (d, J = 7.4 Hz, 1 H, 5-H), 7.79 (d, J = 7.4 Hz, 1 H, 6-H). – ^{31}P NMR (161.7 MHz, D_2O): δ_P = –4.07. – FAB MS (negative mode, matrix: water/glycerol): 572 [(M – H)$^-$].

Methyl (Benzyl 5-Acetamido-4-*O*-acetyl-3,5-dideoxy-8,9-*O*-isopropylidene-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate (32): To a solution of **31**[23] (1.10 g, 2.43 mmol) in dry dichloromethane (12.0 mL) was added dry pyridine (600 μL) and acetic anhydride (570 μL). After stirring overnight the solution was concentrated and coevaporated with toluene. Flash chromatography (toluene/acetone, 3:1) afforded **32** (1.26 g, 88%) as a colourless solid. – TLC (toluene/acetone): R_f = 0.51. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.39 (s, 3 H, CH_3), 1.36 (s, 3 H, CH_3), 1.93 (s, 3 H, NHCOCH_3), 1.94–2.07 (m, 4 H, 3a-H, $COCH_3$), 2.65 (dd, $J_{3e,4}$ = 4.9 Hz, $J_{3e,3a}$ = 12.8 Hz, 1 H, 3e-H), 3.42–3.54 (m, 2 H, 6-H, 7-H), 3.70 (s, 3 H, $COOCH_3$), 3.92 (dd, $J_{6,5}$ = 10.3 Hz, $J_{NH,5}$ = 7.9 Hz, 1 H, 5-H), 3.98–4.13 (m, 2 H, 8-H, 9A-H), 4.29 (dd, $J_{8,9B}$ = 6.3 Hz, $J_{9A,9B}$ = 12.5 Hz, 1 H, 9B-H), 4.35 (d, J = 4.5 Hz, 1 H, OH), 4.55 (d, J = 11.6 Hz, 1 H, 0.5 × CH_2Ph), 4.80 (d, J = 11.6 Hz, 1 H, 0.5 × CH_2Ph), 4.90 (ddd, $J_{4,5}$ = 10.5 Hz, $J_{3e,4}$ = 4.9 Hz, 1 H, 4-H), 5.95 (d, $J_{5,NH}$ = 7.8 Hz, 1 H, NH), 7.19–7.28 (m, 5 H, Ph). – $C_{24}H_{33}NO_{10}$·0.5 H_2O (511.97): calcd. C 57.14, H 6.79, N 2.77; found C 57.35, H 6.84, N 2.99.

Methyl (Benzyl 5-Acetamido-4-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate (33): Compound **32** (1.0 g, 1.69 mmol) was dissolved in acetic acid/water (4:1, 15 mL) and the mixture was heated to 80 °C. After 2 h, the solution was concentrated and purified by flash chromatography (toluene/acetone, 1:1), to yield **33** (654 mg, 85%) as a colourless solid. – TLC (toluene/acetone, 1:1): R_f = 0.17. – $[\alpha]_D$ = –12.4 (c = 1.0 in chloroform). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.97 (s, 3 H, NHCOCH_3), 2.04–2.15 (m, 4 H, 3a-H, $COCH_3$), 2.48 (br. s, 1 H, OH), 2.65 (dd, $J_{3e,4}$ = 4.9 Hz, $J_{3e,3a}$ = 12.9 Hz, 1 H, 3e-H), 3.46 (dd, $J_{6,7}$ = 1.6 Hz, $J_{5,6}$ = 10.4 Hz, 1 H, 6-H), 3.51–3.57 (m, 1 H, 7-H), 3.74 (s, 3 H, $COOCH_3$), 3.75–3.79 (m, 2 H, 9A-H, OH), 3.85–4.04 (m, 3 H, 5-H, 8-H, 9B-H), 4.46 (d, J = 11.6 Hz, 1 H, 0.5 × CH_2Ph), 4.84 (d, J = 11.6 Hz, 1 H, 0.5 × CH_2Ph), 4.77 (m, 1 H, OH), 4.90 (ddd, $J_{4,5}$ = 10.5 Hz, $J_{3e,4}$ = 4.9 Hz, 1 H, 4-H), 5.95 (d, $J_{5,NH}$ = 7.6 Hz, 1 H, NH), 7.19–7.30 (m, 5H, Ph). – $C_{21}H_{29N}O_{10}$ · 0.5 H_2O (464.47): calcd. C 54.30, H 6.51, N 3.00; found C 54.20, H 6.59, N 3.00.

Methyl (Benzyl 5-Acetamido-4-*O*-acetyl-7,9-*O*-benzylidene-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate (34): To a solution of **33** (590 mg, 1.30 mmol) in dry acetonitrile (8.0 mL) was added *p*-toluenesulfonic acid monohydrate (8.0 mg) and benzaldehyde dimethylacetal (590 μL, 3.93 mmol). After stirring for 15 h, the reaction mixture was poured into half-saturated sodium bicarbonate solution and extracted with ethyl acetate. The organic layer was dried with magnesium sulfate and concentrated. Flash chromatography (toluene/acetone, 1:1) yielded **34** (590 mg, 84%) as a colourless foam. – TLC (toluene/acetone, 1:1): R_f = 0.36 – $[\alpha]_D$ = –54.2 (c = 1.0 in chloroform). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.93 (s, 3 H, NHCOCH_3), 1.95–2.05 (m, 4 H, 3a-H, $COCH_3$), 2.65 (dd, $J_{3e,4}$ = 5.0 Hz, $J_{3e,3a}$ = 12.6 Hz, 1 H, 3e-H), 3.95 (d, J = 4.8 Hz, 1 H, OH), 3.59–3.71 (m, 2 H, 7-H, 9A-H), 3.76 (s, 3 H, $COOCH_3$), 3.99 (dd, $J_{6,7}$ = 1.1 Hz, $J_{5,6}$ = 10.4 Hz, 1 H, 6-H), 4.15–4.40 (m, 3 H, 5-H, 8-H, 9B-H), 4.41 (d, J = 11.6 Hz, 1 H, 0.5 × CH_2Ph), 4.80 (d, J = 11.6 Hz, 1 H, 0.5 × CH_2Ph), 4.99 (ddd, $J_{4,5}$ = 10.5 Hz, $J_{3e,4}$ = 5.0 Hz, 1 H, 4-H), 5.28 (d, $J_{5,NH}$ = 7.6 Hz, 1 H, NH), 5.45 (s, 1 H, CHPh), 7.19–7.61 (m, 10 H, 2 × Ph). – $C_{28}H_{33}NO_{10}$ (543.57): calcd. C 61.87, H 6.12, N 2.58; found C 61.85, H 6.14, N 2.64.

Methyl (Benzyl 5-Acetamido-4-*O*-acetyl-7,9-*O*-benzylidene-3,5-dideoxy-8-*O*-methyl-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate (35): Alcohol **34** (370 mg, 0.681 mmol) was dissolved in methyl iodide (3 mL). Drierite (330 mg, 2.43 mmol) and freshly prepared silver oxide (260 mg, 1.13 mmol) were added and the mixture was stirred overnight at room temp. The reaction mixture was filtered through Celite. The filtrate was treated with half-saturated sodium bicarbonate solution and extracted with ethyl acetate. The organic layer was dried with magnesium sulfate and concentrated in vacuo. Flash chromatography (toluene/acetone, 3:1) yielded **35** (338 mg, 89%) as a colourless foam. – TLC (toluene/acetone, 2:1): R_f = 0.33. – $[\alpha]_D$ = –59.8 (c = 1.0 in chloroform). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.93 (s, 3 H, NHCOCH_3), 1.95–2.05 (m, 4 H, 3a-H, $COCH_3$), 2.59 (dd, $J_{3e,4}$ = 4.7 Hz, $J_{3e,3a}$ = 12.8 Hz, 1 H, 3e-H), 3.50–3.59 (m, 2 H, 7-H, 9A-H), 3.52 (s, 3 H, OCH_3), 3.69 (dd, $J_{8,9B}$ = 6.5 Hz, $J_{9A,9B}$ = 11.8 Hz, 1 H, 9B-H), 3.77 (s, 3 H, $COOCH_3$), 3.99 (dd, $J_{6,7}$ = 1.1 Hz, $J_{5,6}$ = 10.5 Hz, 1 H, 6-H), 4.35 (dd, $J_{5,6}$ = 10.5 Hz, 1 H, 5-H), 4.35–4.5 (m, 1 H, 8-H), 4.51 (d, J = 11.6 Hz, 1 H, 0.5 × CH_2Ph), 4.86 (d, J = 11.6 Hz, 1 H, 0.5 × CH_2Ph), 4.99 (ddd, $J_{4,5}$ = 10.5 Hz, $J_{3e,4}$ = 4.7 Hz, 1 H, 4-H), 5.28 (d, $J_{5,NH}$ = 7.6 Hz, 1 H, NH), 5.42 (s, 1 H, CHPh), 7.19–7.62 (m, 10 H, 2 × Ph). – $C_{29}H_{35}NO_{10}$ (557.61): calcd. C 62.47, H 6.33, N 2.51; found C 62.22, H 6.45, N 2.36.

Methyl (Benzyl 5-Acetamido-4-*O*-acetyl-3,5-dideoxy-8-*O*-methyl-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate (36): A solution of **35** (200 mg, 0.359 mmol) in acetic acid/water (4:1, 6 mL) was heated

to 80 °C. After 3 h, the solvents were evaporated in vacuo. Flash chromatography (toluene/acetone, 1:2) yielded **36** (146 mg, 87%) as a colourless solid. – TLC (toluene/acetone, 1:2): R_f = 0.24. – $[\alpha]_D$ = –32.2 (c = 1.0 in chloroform). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.90 (s, 3 H, NHCOCH_3), 1.93–2.07 (m, 4 H, $COCH_3$, 3a-H), 2.65 (dd, $J_{3e,4}$ = 4.8 Hz, $J_{3e,3a}$ = 12.8 Hz, 2 H, 3e-H, OH), 3.42 (s, 3 H, OCH_3), 3.42–3.51 (m, 2 H, 7-H, 9A-H), 3.62 (dd, $J_{5,6}$ = 10.6 Hz, 1 H, 6-H), 3.67 (s, 3 H, $COOCH_3$), 3.70–3.78 (m, 2 H, 8-H, 9B-H), 4.10 (dd, $J_{NH,5}$ = 8.1 Hz, $J_{5,6}$ = 10.6 Hz, 1 H, 5-H), 4.52 (d, J = 11.7 Hz, 1 H, 0.5 × CH_2Ph), 4.68 (d, J = 3.1 Hz, 1 H, OH), 4.99 (ddd, $J_{4,5}$ = 10.6 Hz, $J_{3e,4}$ = 4.8 Hz, 1 H, 4-H), 4.80 (d, J = 11.7 Hz, 1 H, 0.5 × CH_2Ph), 5.98 (d, $J_{5,NH}$ = 8.1 Hz, 1 H, NH), 7.20–7.27 (m, 5 H, Ph). – MALDI: 492 [(M + Na)$^+$].

Methyl (Benzyl 5-Acetamido-4,7,8-tri-*O*-acetyl-3,5-dideoxy-8-*O*-methyl-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate (37): A solution of **36** (180 mg, 0.384 mmol) in dry pyridine/acetic anhydride (2:1, 10 mL) was stirred overnight at room temp. The solution was concentrated and coevaporated with toluene. Flash chromatography (toluene/acetone, 2:1) afforded **37** (187 mg, 88%) as a colourless solid. – TLC (toluene/acetone, 2:1): R_f = 0.38. – $[\alpha]_D$ = –12.7 (c = 1.0 in chloroform). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.85 (s, 3 H, NHCOCH_3), 1.94–2.08 (m, 10 H, 3 × $COCH_3$, 3a-H), 2.67 (dd, $J_{3e,4}$ = 4.8 Hz, $J_{3e,3a}$ = 12.8 Hz, 1 H, 3e-H), 3.50 (s, 3 H, OCH_3), 3.67–3.73 (m, 1 H, 8-H), 3.75 (s, 3 H, $COOCH_3$), 3.75–4.08 (m, 2 H, 5-H, 9B-H), 4.13 (dd, $J_{6,7}$ = 1.8 Hz, $J_{5,6}$ = 10.7 Hz, 1 H, 6-H), 4.23 (dd, $J_{8,9B}$ = 3.0 Hz, $J_{9A,9B}$ = 12.3 Hz, 1 H, 9A-H), 4.54 (d, J = 11.7 Hz, 1 H, 0.5 × CH_2Ph), 4.84 (d, J = 11.7 Hz, 1 H, 0.5 × CH_2Ph), 4.99 (ddd, $J_{4,5}$ = 10.6 Hz, $J_{3e,4}$ = 4.8 Hz, 1 H, 4-H), 5.12 (dd, $J_{6,7}$ = 1.8 Hz, $J_{8,7}$ = 9.0 Hz, 1 H, 7-H), 5.18 (d, $J_{5,NH}$ = 9.9 Hz, 1 H, NH), 7.20–7.27 (m, 5 H, Ph). – $C_{26}H_{35}NO_{12}$ (553.56): calcd. C 56.41, H 6.37, N 2.53; found C 56.53, H 6.47, N 2.43.

Methyl 5-Acetamido-4,7,9-tri-*O*-acetyl-3,5-dideoxy-8-*O*-methyl-D-*glycero*-β-D-*galacto*-2-nonulopyranosonate (38): To a solution of **37** (140 mg, 0.253 mmol) in methanol (10 mL) was added palladium on charcoal (10%, 10 mg) and the mixture was stirred overnight under hydrogen at normal pressure. After filtration through Celite, the filtrate was concentrated under reduced pressure. Flash chromatography (toluene/acetone, 1:1) afforded **38** (115 mg, 84%) as a colourless solid. – TLC (toluene/acetone 2:1): R_f = 0.17. – $[\alpha]_D$ = –31.8 (c = 1.0 in chloroform). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.84 (s, 3 H, NHCOCH_3), 2.00–2.06 (3s, 9 H, 3 × $COCH_3$), 2.15 (dd, $J_{3e,4}$ = 5.2 Hz, $J_{3e,3a}$ = 12.8 Hz, 1 H, 3e-H), 2.28 (dd, $J_{3e,3a}$ = 12.8 Hz, 1 H, 3a-H), 3.41 (s, 3 H, OCH_3), 3.52 (ddd, $J_{9B,8}$ = 4.9 Hz, $J_{8,7}$ = 9.1 Hz, 1 H, 8-H), 3.85 (s, 3 H, $COOCH_3$), 3.95 (dd, $J_{9B,8}$ = 4.9 Hz, $J_{9A,9B}$ = 12.3 Hz, 1 H, 9B-H), 4.09–4.22 (m, 3 H, 5-H, 9A-H, OH), 4.35 (dd, $J_{7,6}$ = 2.2 Hz, $J_{5,6}$ = 10.8 Hz, 1 H, 6-H), 5.17 (dd, $J_{6,7}$ = 2.2 Hz, $J_{8,7}$ = 9.1 Hz, 1 H, 7-H), 5.26 (ddd, $J_{3e,4}$ = 5.2 Hz, $J_{4,5}$ = 10.5 Hz, 1 H, 4-H), 5.36 (d, J = 12.2 Hz, NH). – $C_{19}H_{29}NO_{12}$ (463.44): calcd. C 49.24, H 6.31, N 3.02; found C 49.28, H 6.42, N 3.27.

Diethyl [Methyl (5-Acetamido-4,7,9-tri-*O*-acetyl-3,5-dideoxy-8-*O*-methyl-D-*glycero*-β-D-*galacto*-2-nonulopyranosyl)onate] Phosphite (39): To a solution of **38** (100 mg, 0.216 mmol) and ethyldiisopropylamine (81 μL) in dry acetonitrile (3.0 mL) was added diethyl chlorophosphite (62 μL, 0.431 mmol) under nitrogen. After 10 min, the solution was concentrated and coevaporated with toluene. Flash chromatography (toluene/acetone, 4:1) yielded **39** (100 mg, 93%) as a colourless oil. – TLC (toluene/acetone, 6:1): R_f = 0.39. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.12–1.35 (m, 6 H, 2 × CH_3), 1.85 (s, 3 H, NHCOCH_3) 1.95–2.12 (m, 10 H, 3 × $COCH_3$, 3a-H), 2.48 (dd, $J_{3e,4}$ = 4.8 Hz, $J_{3a,3e}$ = 13.1 Hz, 1 H, 3e-H), 3.42 (s, 3 H, OCH_3), 3.66 (ddd, $J_{7,8}$ = 8.5 Hz, $J_{8,9B}$ = 7.9 Hz, 1 H, 8-H), 3.79 (s, 3 H, $COOCH_3$), 3.80–4.18 (m, 6 H, 2 × OCH_2, 5-H, 9B-H), 4.24 (dd, $J_{8,9A}$ = 2.8 Hz, $J_{9A,9B}$ = 11.2 Hz, 1 H, 9A-H), 4.30 (dd, $J_{6,5}$ = 10.6 Hz, $J_{7,6}$ = 2.1 Hz, 1 H, 6-H), 5.18–5.20 (m, 2 H, 7-H, NH), 5.30 (dd, 5.31, $J_{3e,4}$ = 4.8 Hz, $J_{5,4}$ = 10.5 Hz, 1 H, 4-H). – FAB MS (positive mode, matrix: dichloromethane/nitrobenzyl alcohol and NaI): 664 [(M + Na$^+$)].

Methyl (Allyl 5-Acetamido-4,7,8-tri-*O*-acetyl-3,5-dideoxy-9-*O*-dimethoxytrityl-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate (41): To a solution of **40**[26] (1.4 g, 3.86 mmol) in dry pyridine (14 mL) was added 4-dimethylaminopyridine (94 mg, 0.771 mmol) and dimethoxytrityl chloride (1.56 g, 4.63 mmol) and the mixture was stirred overnight. Acetic anhydride (6 mL) was added and the mixture was stirred for a further 12 h. The mixture was concentrated and coevaporated with toluene. Flash chromatography (toluene/acetone, 3:1) afforded **41** (2.07 g, 69%) as a colourless solid. – TLC (toluene/acetone, 3:1): R_f = 0.33. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.81–2.22 (m, 13 H, 3 × $COCH_3$, NHCOCH_3, 3a-H), 2.58 (dd, $J_{3e,4}$ = 4.5 Hz, $J_{3e,3a}$ = 12.7 Hz, 1 H, 3e-H), 3.04 (dd, $J_{9A,9B}$ = 12.3 Hz, $J_{8,9B}$ = 4.1 Hz, 1 H, 9B-H), 3.19 (dd, $J_{9A,9B}$ = 12.3 Hz, 1 H, 9A-H), 3.78 (s, 9 H, 2 × OCH_3, $COOCH_3$), 3.81–3.92 (m, 2 H, 5-H, 0.5 × CH_2O), 4.19 (d, $J_{5,6}$ = 10.3 Hz, 1 H, 6-H), 4.20–4.29 (m, 1 H, 0.5 × CH_2O), 4.95 (ddd, $J_{4,3a}$ = 12.4 Hz, $J_{3e,4}$ = 4.5 Hz, $J_{5,4}$ = 10.3 Hz, 1 H, 4-H), 5.13 (dd, J = 1.2 Hz, 1 H, –CH=CH_2), 5.20–5.30 (m, 2 H, NH, –CH=CH_2), 5.40–5.49 (m, 2 H, 7-H, 8-H), 5.77–5.91 (m, 1 H, CH=CH_2), 6.78–7.43 (m, 13 H, Ph, 2 × OMe*Ph*).

Methyl (Allyl 5-Acetamido-4,7,8-tri-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate (42): A solution of **41** (1.3 g, 1.67 mmol) in acetic acid/water (4:1, 15 mL) was stirred for 1 h at room temp. Evaporation of the solvents in vacuo and purification by flash chromatography (toluene/acetone, 1:1) yielded **42** (645 mg, 79%) as a colourless solid. – TLC (toluene/acetone, 1:1): R_f = 0.20. – $[\alpha]_D$ = –27.5 (c = 1.0 in chloroform). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.62 (s, 3 H, NHCOCH_3), 1.86–2.21 (m, 10 H, 3 × $COCH_3$, 3a-H), 2.58 (dd, $J_{3e,4}$ = 4.5 Hz, $J_{3e,3a}$ = 12.7 Hz, 1 H, 3e-H), 2.97 (dd, $J_{9A,OH}$ = 10.2 Hz, $J_{9B,OH}$ = 4.8 Hz, 1 H, OH), 3.49 (dd, $J_{9A,9B}$ = 12.3 Hz, $J_{8,9B}$ = 4.1 Hz, 1 H, 9B-H), 3.75 (s, 3 H, $COOCH_3$), 3.77–3 86 (m, 2 H, 9A-H, 0.5 × CH_2O), 4.02 (d, $J_{5,6}$ = 10.3 Hz, 1 H, 6-H), 4.15 (dd, $J_{6,5}$ = 10.3 Hz, 1 H, 5-H), 4.21–4.28 (m, 1 H, 0.5 × CH_2O), 4.80 (ddd, $J_{4,3a}$ = 12.4 Hz, $J_{3e,4}$ = 4.5 Hz, $J_{5,4}$ = 10.3 Hz, 1 H, 4-H), 5.11–5.19 (m, 3 H, NH, 7-H, 8-H), 5.21–5.23 (m, 1 H, –CH=CH_2), 5.28–5.30 (m, 1 H, –CH=CH_2), 5.77–5.28 (m, 1 H, CH=CH_2). – MALDI: 512 (M + Na). – $C_{21}H_{31}NO_{12}$ ·0.5 H_2O (498.17): calcd. C 50.63, H 6.47, N 2.81; found C 50.55, H 6.67, N 2.71.

Methyl (Allyl 5-Acetamido-4,7,8-tri-*O*-acetyl-9-*O*-dibenzylphosphoryl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate (43): Alcohol **42** (300 mg, 0.613 mmol) and 1*H*-tetrazole (84 mg, 1.20 mmol) were dissolved in dry acetonitrile/dichloromethane (3:1, 3 mL) under nitrogen. Bis(benzyloxy)(diisopropylamino)phosphane (340 mg, 0.988 mmol) in dry dichloromethane (2 mL) was added by syringe. After 20 min (TLC), a solution of *tert*-butyl hydroperoxide in dry toluene (3 M, 300 μL, 0.920 mmol) was added and the mixture was stirred for a further 20 min. The reaction mixture was treated with half-saturated sodium bicarbonate solution and extracted with dichloromethane. The organic layer was dried with magnesium sulfate and concentrated in vacuo. Purification by flash chromatography (toluene/acetone, 2:1) yielded **43** (460 mg, 82%) as a colourless foam. – TLC (toluene/acetone, 1:1): R_f = 0.41. – $[\alpha]_D$ = –17.5 (c = 1.0 in chloroform). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.75–2.10 (m, 13 H, 4 × $COCH_3$, NHCOCH_3, 3a-

H), 2.59 (dd, $J_{3e,4}$ = 4.6 Hz, $J_{3e,3a}$ = 12.8 Hz, 1 H, 3e-H), 3.73 (s, 3 H, $COOCH_3$), 3.78–3.88 (m, 1 H, 0.5 × CH_2O), 3.93–4.12 (m, 3 H, 9A-H, 5-H, 6-H), 4.19–4.32 (m, 2 H, 9B-H, 0.5 × CH_2O), 4.83 (ddd, $J_{4,3a}$ = 12.4 Hz, $J_{3e,4}$ = 4.6 Hz, $J_{5,4}$ = 10.3 Hz, 1 H, 4-H), 4.98 (d, J = 11.6 Hz, 2 H, CH_2Ph), 4.49 (d, J = 11.6 Hz, 2 H, CH_2Ph), 5.05–5.38 (m, 5 H, NH, 7-H, 8-H, –CH=CH_2), 5.71–5.88 (m, 1 H, CH=CH_2), 7.25–7.39 (m, 10 H, 2 × Ph). – ^{31}P NMR (161.7 MHz, $CDCl_3$): δ_P = –0.60.

Methyl 5-Acetamido-4,7,8-tri-*O*-acetyl-9-*O*-dibenzylphosphoryl-3,5-dideoxy-D-*glycero*-β-D-*galacto*-2-nonulopyranosonate (44): To a solution of **43** (270 mg, 0.360 mmol) in dry THF (5 mL) under nitrogen was added (1,5-cyclooctadiene)bis(methyldiphenylphosphane)iridium(I) hexafluorophosphate (1 mg). The red mixture was degassed and set under nitrogen – this procedure was repeated three times. The mixture was stirred under hydrogen for 5 min, until the red colour vanished. The solution was degassed again and stirred overnight under nitrogen. The solvents were evaporated in vacuo and the residue was dissolved in THF/water (4:1, 10 mL). Iodine (183 mg, 0.721 mmol) was added and the mixture was stirred for 1 h, then diluted with water and extracted with chloroform. The organic layer was washed several times with sodium thiosulfate solution, dried with magnesium sulfate, and concentrated. The residue was first purified by flash chromatography (toluene/acetone, 2:1) and finally by MPLC (toluene/acetone, 3:2) to yield **44** (166 mg, 65%) as a colourless foam. – TLC (toluene/acetone, 2:1): R_f = 0.41. – $[\alpha]_D$ = –3.6 (c = 1.0 in chloroform). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.81–2.17 (m, 13 H, 4 × $COCH_3$, $NHCOCH_3$, 3a-H), 2.21 (dd, $J_{3e,4}$ = 4.6 Hz, $J_{3e,3a}$ = 12.8 Hz, 1 H, 3e-H), 3.68 (s, 3 H, $COOCH_3$), 3.92–4.17 (m, 2 H, 5-H, 9B-H), 4.33 (dd, $J_{8,9}$ = 2.2 Hz, $J_{9A,9B}$ = 12.2 Hz, 1 H, 9A-H), 4.68–4.76 (ddd, $J_{6,7}$ = 2.2 Hz, $J_{5,6}$ = 10.1 Hz, 1 H, 6-H), 4.93–5.02 (m, 4 H, 2 × CH_2Ph), 4.18 (ddd, $J_{3e,4}$ = 4.6 Hz, $J_{4,3a}$ = 12.4 Hz, $J_{5,4}$ = 10.3 Hz, 1 H, 4-H), 5.31 (dd, $J_{8,7}$ = 8.7 Hz, $J_{6,7}$ = 2.1 Hz, 1 H, 7-H), 5.43–5.48 (m, 1 H, 8-H), 6.33 (br. s, 1 H, OH), 6.42 (d, J = 10.2 Hz, 1 H, NH), 7.24–7.36 (m, 10 H, 2 × Ph). MALDI: 730 [M + Na].

[Methyl (5-Acetamido-4,7,8-tri-*O*-acetyl-9-*O*-dibenzylphosphoryl-3,5-dideoxy-D-*glycero*-β-D-*galacto*-2-nonulopyranosyl)onate] Diethyl Phosphite (45): To a solution of **44** (140 mg, 0.197 mmol) and ethyldiisopropylamine (74 μL) in dry acetonitrile (2.5 mL) was added diethyl chlorophosphite (60 μL, 0.696 mmol) under nitrogen. After 10 min, the solution was concentrated and coevaporated with toluene. Flash chromatography (toluene/acetone, 3:1) yielded **45** (138 mg, 88%) as a colourless oil. – TLC (toluene/acetone, 3:1): R_f = 0.37. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.11–1.40 (m, 6 H, 2 × CH_3), 1.72–2.12 (m, 13 H, 4 × $COCH_3$, 3a-H), 2.44 (dd, $J_{3e,4}$ = 4.8 Hz, $J_{3a,3e}$ = 13.1 Hz, 1 H, 3e-H), 3.71 (s, 3 H, $COOCH_3$), 3.27–4.29 (m, 7 H, 5-H, 9A-H, 9B-H, 2 × CH_2), 4.62–4.73 (m, 1 H, 6-H), 4.93–5.07 (m, 4 H, 2 × CH_2Ph), 5.08–5.18 (m, 1 H, NH), 5.23 (ddd, $J_{3e,4}$ = 4.8 Hz, $J_{4,5}$ = 10.5 Hz, 1 H, 4-H), 5.32 (d, J = 9.9 Hz, 1 H, 7-H), 5.88–5.93 (m, 1 H, 8-H), 7.25–7.39 (m, 10 H, 2 × Ph).

Triethylammonium (*N*-Acetyl-2′,3′-di-*O*-acetylcytidin-5′-yl) [Methyl (5-Acetamido-4,7,9-tri-*O*-acetyl-3,5-dideoxy-8-*O*-methyl-D-*glycero*-β-D-*galacto*-2-nonulopyranosyl)onate] Phosphate (46): A solution of **23** (95 mg, 0.211 mmol) in dry *N*,*N*-dimethylformamide/acetonitrile (2:1, 1.0 mL) was cooled to –20 °C. A solution of **39** (70 mg, 0.120 mmol) in dry acetonitrile (0.2 mL) was added by syringe. The reaction mixture was allowed to warm up to room temperature during 12 h. Triethylamine (200 μL) was added and the solvents were evaporated in vacuo. Flash chromatography (chloroform/methanol/triethylamine, 10:1:0.1) yielded **46** (64 mg, 54%) as a colourless solid. – TLC (chloroform/methanol, 10:1): R_f = 0.26. – ^{1}H NMR (250 MHz, MeOD): δ = 1.34 (t, J = 7.3 Hz, 9 H, 3 × CH_3), 1.90–2.22 (m, 22 H, 7 × $COCH_3$, 3a′′-H), 2.80 (dd, $J_{3''e,4''}$ = 4.8 Hz, $J_{3''e,3''a}$ = 13.2 Hz, 1 H, 3′′e-H), 3.22 (q, J = 7.3 Hz, 6 H, 3 × CH_2), 3.51 (s, 3 H, OCH_3), 3.85 (s, 3 H, $COOCH_3$), 3.79–3.89 (m, 1 H, 9′B-H), 3.99–4.02 (m, 2 H, 5′′-H, 8′′-H), 4.21 (dd, $J_{5'A,5'B}$ = 11.6 Hz, $J_{4',5'B}$ = 2.8 Hz, 1 H, 5′B-H), 4.25 (dd, $J_{4'.5'A}$ = 4.3 Hz, $J_{5'A,5'B}$ = 11.6 Hz, 1 H, 5′A-H), 4.32 (dd, $J_{8'',9''A}$ = 2.6 Hz, $J_{9''A,9''B}$ = 11.8 Hz, 1 H, 9′′A-H), 4.42–4.48 (m, 1 H, 4′-H), 4.52 (dd, $J_{5'',6''}$ = 10.2 Hz, $J_{7'',6''}$ = 2.0 Hz, 1 H, 6′′-H), 5.29 (dd, $J_{6'',7''}$ = 2.0 Hz, $J_{8'',7''}$ = 8.7 Hz, 1 H, 7′′-H), 5.38 (ddd, $J_{3''e,4''}$ = 4.8 Hz, $J_{3''a,4''}$ = 11.0 Hz, 1 H, 4′′-H), 5.51–5.58 (m, 2 H, 2′-H, 3′-H), 6.27 (d, $J_{2',1'}$ = 4.1 Hz, 1 H, 1′-H), 7.60 (d, J = 7.5 Hz, 1 H, 5-H), 8.52 (d, J = 7.5 Hz, 1 H, 6-H). – ^{31}P NMR (161.7 MHz, D_2O): δ_P = –5.96. – FAB MS (negative mode, matrix: methanol/nitrobenzyl alcohol, 1:1): 893 [(M – H^+)$^-$].

Triethylammonium (*N*-Acetyl-2′,3′-di-*O*-acetylcytidin-5′-yl) [Methyl (5-Acetamido-4,7,8-tri-*O*-acetyl-9-*O*-dibenzylphosphorono-3,5-dideoxy-D-*glycero*-β-D-*galacto*-2-nonulopyranosyl)onate] Phosphate (47): A solution of **23** (120 mg, 0.267 mmol) in dry *N*,*N*-dimethylformamide/acetonitrile (2:1, 1.0 mL) was cooled to –20 °C. A solution of **45** (110 mg, 1.38 × 10^{-4} mol) in dry acetonitrile (0.5 mL) was added by syringe. The reaction mixture was allowed to warm up to room temperature during 12 h. Triethylamine (500 μL) was added and the solvents were evaporated in vacuo. Flash chromatography (chloroform/methanol/triethylamine, 9:1:0.1) yielded **47** (85 mg, 50%) as a colourless solid. – TLC (chloroform/methanol, 6:1): R_f = 0.54. – ^{1}H NMR (250 MHz, MeOD): δ = 1.33 (t, J = 7.3 Hz, 9 H, 3 × CH_3), 1.87–2.25 (m, 22 H, 7 × $COCH_3$, 3a′′-H), 2.78 (dd, $J_{3''e,4''}$ = 4.8 Hz, $J_{3''e,3''a}$ = 13.0 Hz, 1 H, 3′′e-H), 3.22 (q, J = 7.3 Hz, 6 H, 3 × CH_2), 3.80 (s, 3 H, $COOCH_3$), 4.06 (d, J = 10.5 Hz, 1 H, 5′′-H), 4.18–4.39 (m, 3 H, 9′′B-H, 5′A-H, 5′B-H), 4.41–4.45 (m, 1 H, 4′-H), 4.52 (dd, $J_{8'',9''A}$ = 2.2 Hz, $J_{9''A,9''B}$ = 10.7 Hz, 1 H, 9′′A-H), 4.71–4.79 (m, 1 H, 6′′-H), 5.08–5.13 (m, 4 H, 2 × CH_2Ph), 5.29–5.40 (m, 2 H, 7′′-H, 8′′-H), 5.50–5.59 (m, 2 H, 2′-H, 3′-H), 6.23 (d, $J_{2',1'}$ = 4.1 Hz, 1 H, 1′-H), 7.35–7.48 (m, 10 H, 2 × Ph), 7.56 (d, J = 7.5 Hz, 1 H, 5-H), 7.98 (d, J = 7.5 Hz, 1 H, NH), 8.52 (d, J = 7.5 Hz, 1 H, 6-H). – ^{31}P NMR (161.7 MHz, MeOD): δ_P = –0.82, –5.04. – FAB MS (negative mode, matrix: nitrobenzyl alcohol): 1139 [(M – H^+)$^-$].

Dilithium [(5-Acetamido-3,5-dideoxy-8-*O*-methyl-D-*glycero*-β-D-*galacto*-2-nonulopyranosyl)onate] (Cytidin-5′-yl) Phosphate (48): To a solution of **46** (45 mg, 45.3 μmol) in dry methanol (2 mL) was added sodium methoxide solution (0.5 M, 3 drops) and the mixture was stirred for 3 h at room temp. The mixture was neutralized with Amberlite IRC-50 (H^+) (pH = 8–9), filtered and concentrated. The residue was dissolved in water/methanol (1:1, 1 mL) and lithium hydroxide solution (1 M, 0.5 mL) was added. After stirring for 4 h at room temp., the solution was neutralized with Amberlite IRC-50 (H^+), pH = 8–9, and filtered. Lyophilization of the filtrate and preparative HPLC (RP-18, 0.05 M $NEt_3H_2CO_3$) yielded **48** (16 mg, 58%). – TLC, aminophase (ethanol/water, 1:1): R_f = 0.40. – ^{1}H NMR (250 MHz, D_2O): δ = 1.51 (ddd, $J_{3''a,3''e}$ = 13.2 Hz, 1 H, 3′′a-H), 1.86 (s, 3 H, $NHCOCH_3$), 2.39 (dd, $J_{3''e,4''}$ = 4.8 Hz, $J_{3''e,3''a}$ = 13.2 Hz, 1 H, 3′′e-H), 3.27 (s, 3 H, OCH_3), 3.33–3.58 (m, 3 H, 7′′-H, 5′′-H, 9′′A-H), 3.68–3.99 (m, 4 H, 4′′-H, 6′′-H, 8′′-H, 9′′B-H), 4.00–4.21 (m, 5 H, 2′-H, 3′-H, 4′-H, 5′A-H, 5′B-H), 5.88 (d, $J_{2',1'}$ = 3.1 Hz, 1 H, 1′-H), 5.91 (d, J = 7.5 Hz, 1 H, 5-H), 7.80 (d, J = 7.5 Hz, 1 H, 6-H). – ^{31}P NMR (161.7 MHz, D_2O): δ_P = –5.47. – FAB MS (negative mode, matrix: glycerol/DMSO, 1:1): 633 [(M + Li^+ – 2 H^+)$^-$].

Trisodium [(5-Acetamido-4,7,8-tri-*O*-acetyl-3,5-dideoxy-9-*O*-phosphorono-D-*glycero*-β-D-*galacto*-2-nonulopyranosyl)onate] (Cytidin-5′-yl) Phosphate (49): To a solution of **47** (30 mg, 26.3 μmol) in dioxane (4 mL) was added sodium bicarbonate (10 mg) and palladium on charcoal (10%, 3 mg) and the mixture was stirred for 12 min under hydrogen. Triethylamine (1 drop) was added and the catalyst was filtered off and washed with methanol. Sodium methanolate in methanol (0.5 M, pH ≈ 13) was added to the filtrate and the mixture was stirred for 3 h at room temp. The solution was neutralized with Amberlite IRC-50 (H^+) (pH = 8–9) and filtered. The filtrate was diluted with water (10 mL) and after lyophilization it was redissolved in water (2 mL) and treated with sodium hydroxide solution (1M, 0.5 mL, pH ≈ 13) for 3 h. The solution was neutralized with Amberlite IRC-50 (H^+) (pH = 8), filtered and lyophilized. Purification by preparative HPLC (RP-18, 0.05 M $NEt_3H_2CO_3$) and ion exchange (Na^+), yielded **49** (11 mg, 64%). – TLC, cellulose (2-propanol/water/ammonia, 55:35:5): R_f = 0.05. – ^{1}H NMR (250 MHz, D_2O): δ = 1.48 (ddd, $J_{3''a,3''e}$ = 13.2 Hz, 1 H, 3′′a-H), 1.87 (s, 3 H, NHCOCH_3), 2.32 (dd, $J_{3''e,4''}$ = 4.8 Hz, $J_{3''e,3''a}$ = 13.2 Hz, 1 H, 3′′e-H), 3.45 (d, $J_{8'',7''}$ = 8.7 Hz, 1 H, 7′′-H), 3.71–3.92 (m, 5 H, 4′′-H, 5′′-H, 8′′-H, 9′′A-H, 9′′B-H), 3.99 (d, $J_{5'',6''}$ = 10.2 Hz, 1 H, 6′′-H), 4.01–4.19 (m, 5 H, 2′-H, 3′-H, 4′-H, 5′A-H, 5′B-H), 5.81 (d, $J_{2',1'}$ = 3.1 Hz, 1 H, 1′-H), 5.97 (d, J = 7.5 Hz, 1 H, 5-H), 7.79 (d, J = 7.5 Hz, 1 H, 6-H). – ^{31}P NMR (161.7 MHz, D_2O): δ_P = –4.17, +5.29. – FAB MS (negative mode, matrix: DMSO/nitrobenzyl alcohol/glycerol, 1:1:1): 705 [(M + 2 Na – 2 H^+)$^-$].

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