Sannamycin-Type Aminoglycoside Antibiotics – Efficient Syntheses – Biological Activity

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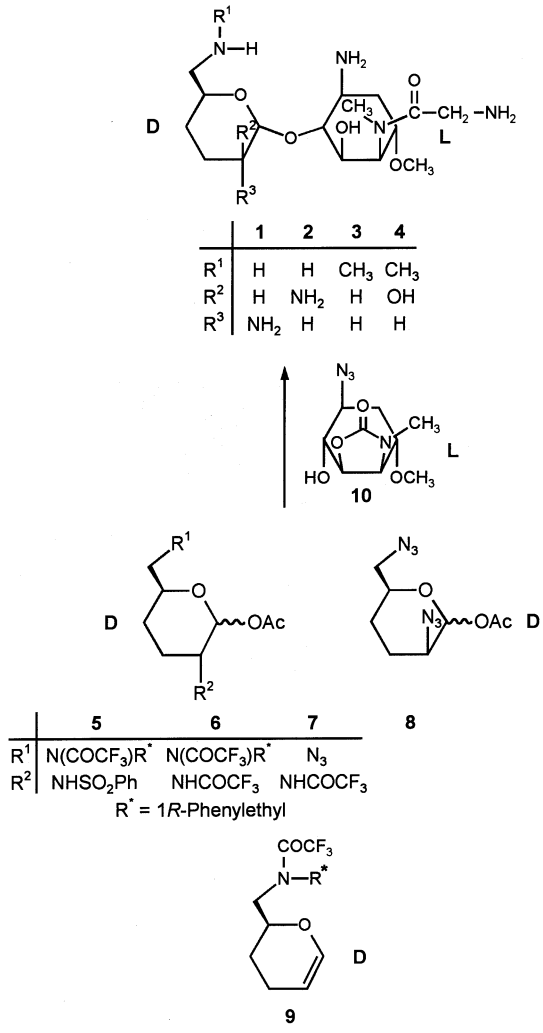
Shorter and more efficient routes to 6′-des(*N*-methyl)sannamycin A (**1**) and its 2′-*epi* analog **2** have been elaborated with the proven sannamine-type acceptor **10** and the glycosyl donors **5**–**8** featuring novel protecting patterns. With glycal **9** as glycosyl donor (and **10**) an expedient access to 2′-desamino- (**3**) and 2′-desamino-2′-*epi*-hydroxysannamycin A (**4**) has been opened. For **4** a modest antibacterial activity was found, while **3** was inactive.

Introduction

In continuation of earlier work directed towards the total synthesis of binuclear aminoglycoside antibiotics[1], efficient routes to (2′-*epi*-)purpurosamine-type glycosyl donors, e.g. the naturally configurated **5**−**8** (D, 5-*R*), have been presented in a preceding paper[2]. The novel *N*-protection patterns {2′-sulfonamido-, 2′-trifluoroacetylamino-, 2′-azido-, 6′-[trifluoroacetyl-(1*R*)-phenylethyl]amino-, 6′-azido-} of these donors were expected to be better suitable for the subsequent synthetic demands (glycosylation, protection/deprotection)[1] and thus to make these routes more economical. In this paper we present the application of the donors **5**−**8**[2] and of the sannamine-type acceptor **10**[3] for the construction of 6′-des(*N*-methyl)sannamycin A (**1**)[1][4] and its 2′-*epi* isomer **2**[1]. Included are routes to the structurally modified sannamycins A **3** and **4** featuring the I^+-mediated addition of **10** to glycal **9** as key step. Structural variations at C-2′ such as desamination (**3**) or hydroxylation (**4**) have been repeatedly reported to induce biological activity[5] at lower toxicity[6].



Glycosylations

The glycosylations in our prior syntheses had generally been effected under Koenigs-Knorr conditions with TMSOTf as promotor, allowing for yields ranging from 51 to 91% and α/β ratios from 1.8:1 to 13:1[1]. In exploratory experiments the novel donors **5** (2′α-benzenesulfonamido) and **6** (2′-trifluoroacetylamino) were found not to be sufficiently tolerant to the above promotor. The desired α-glycosides **11** ($[\alpha]_D^{25} = +36.4$) and **12** ($[\alpha]_D^{25} = +34.5$) were isolated in only moderate yields of 30−45% along with residual acceptor and other α-glycosidic components. Partial dealkylation at 6′-N and epimerization at C-2′ are responsible for some of the side products. There was generally no hint for the formation of β-glycosides (TLC, ^{1}H-NMR, < 3%).

With $BF_3 \cdot OEt_2$ as a milder promotor these complications could be largely avoided. Irrespective of the N-functionalities in the three donors **5**−**7** the treatment with the acceptor **10** under the specified set of conditions (Scheme 1) provided selectively (80−85%, TLC, ^{1}H NMR) the α-glycosides **11**−**13**, which were chromatographically purified

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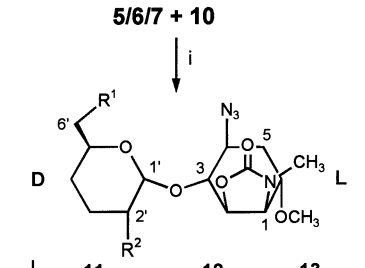
without significant material loss from still minor fractions containing α-glycosidical and glycon components. Even in larger runs (mmolar scale) again no β-glycosides were detected by careful reaction control (TLC, ^{1}H NMR).

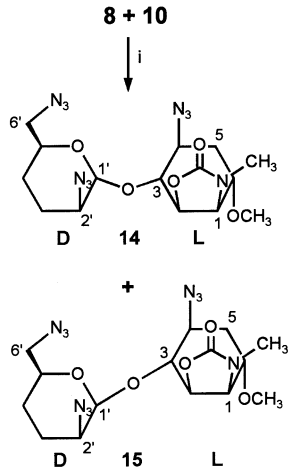
Scheme 1. i) Donor (1.0 equiv.)/acceptor (1.2 equiv.)/$BF_3 \cdot OEt_2$ (1.2 equiv.)/anhydrous CH_2Cl_2, N_2 atm., 1 h, room temp.



	11	12	13
R^1	$N(COCF_3)R^*$	$N(COCF_3)R^*$	N_3
R^2	$NHSO_2Ph$	$NHCOCF_3$	$NHCOCF_3$

The change in stereochemistry at C-2′ in the 2′β-azido donor **8** had no profound consequences for the reaction with donor **10.** Yet, besides ca. 70% of the wanted α-glycoside **14** very small amounts (< 5%) of β-glycoside **15** were identified in the crude reaction mixture and chromatographically isolated.

Scheme 2. i) Donor (1.0 equiv.)/acceptor (1.2 equiv.)/$BF_3 \cdot OEt_2$ (1.2 equiv.)/anhydrous CH_2Cl_2, 1 h, N_2, room temp.



6′-Des(*N*-methyl)sannamycin A (1)

On the way from the differently protected glycosides **11**, **12**, and **13** to the target **1** the general synthetic problem consisted in the sequence and in the selectivity of the deprotection (four N, one O functions) and *N*-glycylation steps.

Glycoside **11** fell out of the competition when the NH−SO_2Ph cleavage posed insurmountable difficulties at whatever stage in the synthetic route. For **12**, in contrast, the first explored sequence[1] via the intermediate trisamine **18a** (**18b**) proved highly economical: The threefold deprotection **12** → **16** → **17a** → **18a** was simply and nearly quantitatively achieved by heating **12** in a 3% aqueous NaOH solution for a longer period of time. The rates of the individual deprotection steps turned out as sufficiently distinct as to allow the selective generation, isolation and identification of the intermediates **16** and **17a**: In 3% methanolic NaOH/water (1:1) at room temperature in **12** the 2′-trifluoroacetylamino group was exclusively removed to give 95% of **16**. Refluxing for 4 h was needed in order to totally and neatly hydrolyze the carbamate ring to give 94% of **17a**. In this medium only after 40 h refluxing the sterically protected 6′-trifluoroacetylamino group had been totally saponified (91% of **18a** isolated). The amines **16**, **17a**, and **18a** − after extractive work-up − were present in such a uniform state that no further purification was necessary; they were transformed into the Z derivatives **18b** and **19b** in a standard way.

In spite of the highly economical access to **18a** (**18b**) the published procedere to **1**[1], implying labor-intensive differentiation of the Z-protected amino functions, was not pursued any further, when it was found that under reductive conditions ($NaBH_4$/EtOH) neat deprotection in **12** at 2′-N and 6′-N to diamine **19a** was possible (87% isolated). In the bis-Z derivative **19b** the carbamate ring was neatly hydrolyzed in refluxing $Ba(OH)_2$/dioxane/water, without any noticeable involvement of the NH−Z groups. In **20** (88%) the stage was set for the relatively slow but nevertheless rather selective *N*-glycylation to yield 81% of **21** ($[\alpha]_D^{25}$ = +86.3). After standard, one-pot catalytic reduction − N_3 → NH_2 hydrogenation, NH−Z and NZR* hydrogenolysis − tetramine **1** was isolated as tetrakis(hydrochloride) (^{1}H NMR, ^{13}C NMR, IR). The average overall yield of 55% for the five operations starting from **12** very favorably compares with the 22% for the much more laborious alternative of Scheme 6 in ref.[1].

Diazidoglycoside **13** had figured as substitute for **12** in case that the latter's kind of protection at 6′-N would pose problems. In fact, the deprotection to give **22** was straightforward under the basic as well as the reductive conditions which had been applied to **12** (93%, quant.). It needs no further comment that **22** in close analogy to the sequence **19** → **1** could serve as precursor of the latter.

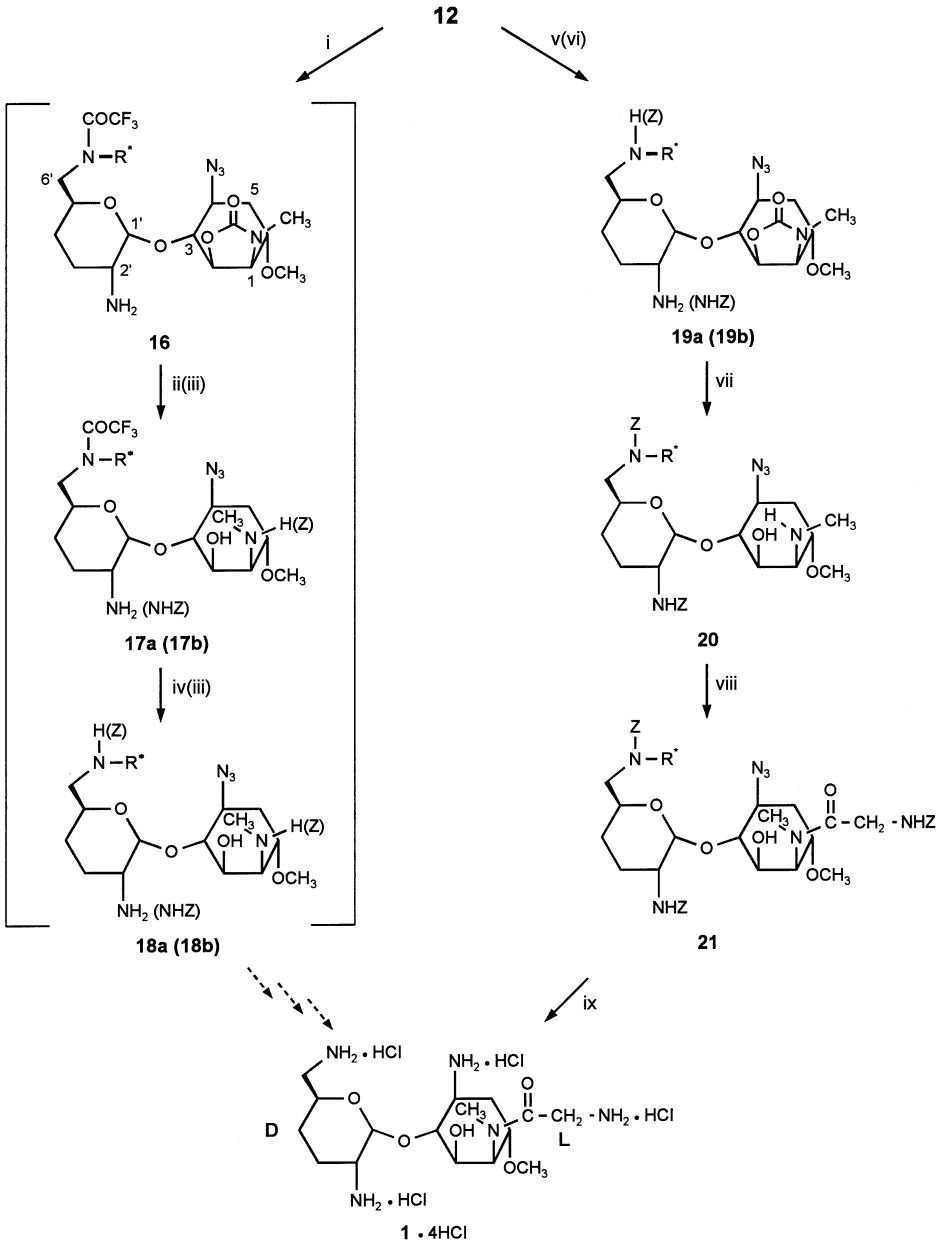
2′-*epi*-6′-Des(*N*-methyl)sannamycin A (2)

With the three 4-, 2′-, 6′-N functions in the 2′-*epi* donor **14** "protected" as azides, the synthesis of the 2′-*epi*-des(*N*-methyl)sannamycin **2** indeed turned out unproblematic (Scheme 4). After only three standard operations − basic carbamate cleavage (→ **23**), *N*-glycylation (→ **24**), and one-pot fourfold deprotection by hydrogenolysis − the salt **2**·4 HCl (^{1}H NMR, ^{13}C NMR, IR, MS) was obtained in an overall yield of 64% based on **14**. For comparison: With the 6′-NHDNP analog of **14** as precursor, the overall yield had been as low as 8% (Scheme 8 in ref.[1].).

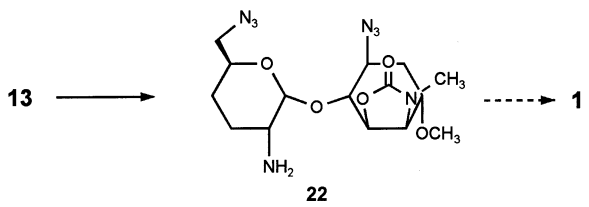
2′-Desaminosannamycin A (3)

The synthetic sequence followed for the 2′-desaminated sannamycin A (**3**, Scheme 5), in principle, implies the I^+-mediated linking of enantiomerically pure glycal **9**[7] with

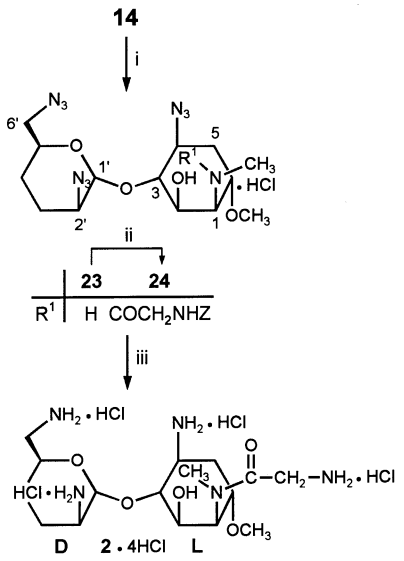
Scheme 3. (i) 3% methanolic NaOH/water (1:1), 1.25 h, room temp., 95%. − (ii) analogous to (i), 4 h, reflux, 94%. − (iii) Z-*O*-suc/DMF, room temp. 20 h. − (iv) analogous to (i), 40 h, reflux, 91%. − (v) $NaBH_4$/ethanol, room temp., 22 h, 87%. − (vi) ZCl (2.4 equiv.)/$NaHCO_3$/acetone/water (1:1), room temp., 94%. − (vii) $Ba(OH)_2$ (5 equiv.)/dioxane/water (2:1), reflux, 8 h, 88%. − (viii) Z-gly-*O*-suc/DMF, 60°C, 26 h, 81%. − (ix) methanol/2 N HCl/H_2 (1 atm)/10% Pd/C, 28 h, 95%



acceptor **10**, 6′-*N*-methylation, the reductive elimination of the introduced iodine, and *N*-glycylation. In line with earlier reports, the reaction of **9** with **10** in the presence of NIS (*N*-iodosuccinimide, **25**[8]) in acetonitrile led stereoselectively (¹H NMR, TLC) to the aspired 2β-iodo-α-glycoside **27** isolated as colorless solid ($[\alpha]_D^{25}$ = +12.3) but only in 42% yield − together with an even larger proportion of the succinimide adduct **33** (51%); no 1′β,2′α isomer **32** was detectable. With [I(*sym*-coll)$_2$]ClO_4 (**26**) as I^+ source − being provided with a less nucleophilic counter ion − in CH_2Cl_2 as solvent **27** was generated in higher yield (> 60%) − now, however, accompanied by significant amounts (25−30%) of isomer **32**. Change to CH_3CN as solvent improved the **27**/**32** ratio to ca. 7:1 but introduced the iodo olefin **34** as additional product: From an exploratory experiment chromatographically 60% of **27**, 8% of **32**, and



Scheme 4. (i) 3% methanolic NaOH/water (1:1), reflux, 2 h, 94%. – (ii) Z-gly-*O*-suc/DMF, 50°C, 16 h, 68%. – (iii) methanol/2 N HCl/H_2 (1 atm)/10% Pd/C, 2 h, quant.



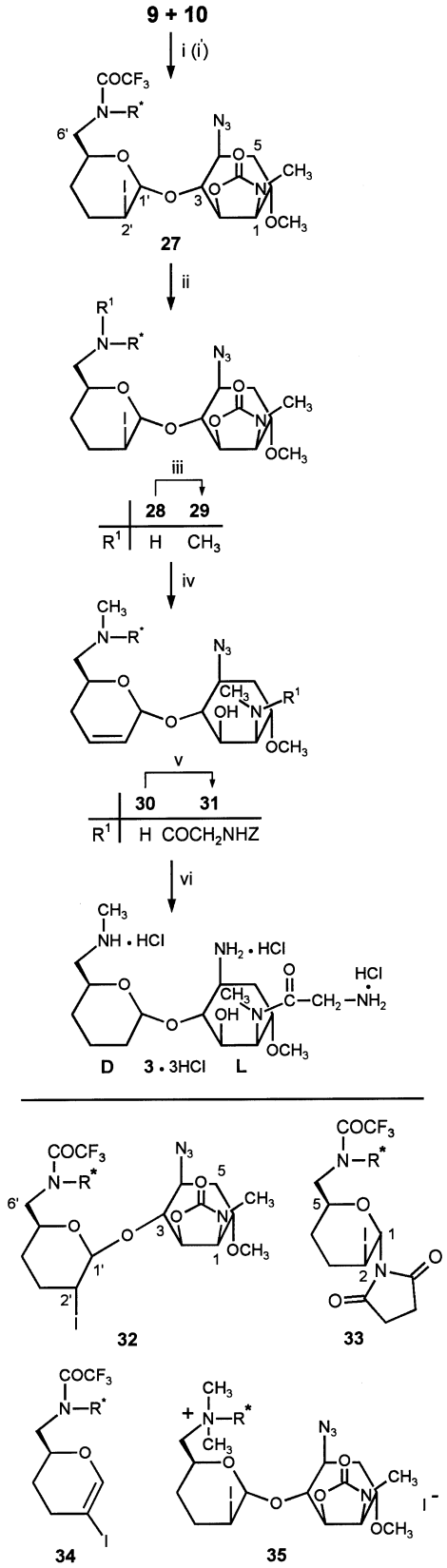
21% of **34** were obtained (together with traces of "dimeric adducts"[2]). It was established that the glycosides **27** and **32** are stable under the given conditions and that the olefin **34** arises solely from donor **9** presumably by deprotonation in the intermediate iodonium ion(s). Ultimately after switching to a 2:1 mixture of CH_2Cl_2/CH_3CN as solvent, from runs taken to total conversion, 70–75% of **27** and 13–17% of **32** and only trace quantities of **34** were isolated.

For the subsequent methylation at 6′-N to give **29** first the trifluoroacetyl group was taken off from **27** with $NaBH_4$ in ethanol to afford 87% of **28**. In the latter, the sterically demanding R* group necessitated rather forcing conditions for the methylation, what favored quaternization to the ammonium ion **35**. As a compromise **28** was taken to partial conversion: With a large excess (20 equivalents) of CH_3I at room temperature and with ca. 20% of **28** left, 70–75% of monomethylamine **29** (no **35**) were secured. Variation of the reaction conditions [even larger excess of CH_3I, higher temperature (60°C), dimethyl sulfate as alkylating agent] had no favorable effects on the relative rates (**28** → **29** → **35**). Carbamate hydrolysis and HI elimination were effected as a one-pot procedure and gave nearly quantitatively olefin **30** ($[\alpha]_D^{25}$ = +8.1). After *N*-glycylation (→ **31**), saturation of the C=C double bond and "deprotection" at 4-N and 6′-N were effected through standard catalytic hydrogenolysis. The overall yield of trishydrochloride **3** amounted to 40–45% for the five operations starting from **27**.

2′-Desamino-2′-*epi*-hydroxysannamycin A (4)

With the 2′β-iodide **27** now available, its utilization for the synthesis of the so far unknown 2′-desamino-2′-*epi*-hydroxysannamycin A became an attractive project. In exploratory experiments it became, however, rapidly and not unexpectedly clear, that iodine → hydroxy substitution in

Scheme 5. (i) **25** (1.5 equiv.)/CH_3CN, room temp. 2 h, 42%. – (i′) **26** (1.5 equiv.)/CH_2Cl_2/CH_3CN (2:1), room temp., 12 h, 72%. – (ii) $NaBH_4$/ethanol, room temp. 6 h, 87%. – (iii) CH_3I (20 equiv.)/K_2CO_3/CH_3CN, room temp. 2 h, 72%. – (iv) 3% methanolic NaOH/water (1:1), reflux, 2 h. – (v) Z-gly-*O*-suc/DMF, 70°C, 20 h, 77%. – (vi) methanol/2 N HCl/H_2 (1 atm)/10% Pd/C, 9 h, 94%



27, competing with β-HI elimination, neither under S_N2- nor S_N1-like conditions could be effected with satisfying selectivity. In order to probe the stereochemical course of radical substitution by oxygen[9], **27** was treated in benzene (50°C, 48 h) with Bu_3SnH, oxygen gas being continuously blown through the solution − with a non-acceptable result. After reduction with $NaBH_4$ (methanol) 37% of 2′β-ol **42**, 8% of 2′α-ol **43,** and 42% of reduced **44** were chromatographically separated from other, small components. For the interception of the intermediate C-2′ radical TEMPO[10] proved to be the reagent of choice: Besides ca. 80% of the 2′β-adduct **36** (m.p. 63°C), only small quantities of the 2′α isomer **45** (m.p. 66−68°C, 4%) and of reduced **46** (6%) were obtained. The gratifyingly high α/β ratio of ca. 20:1 presumably reflects above all steric hindrance towards the bulky TEMPO reagent approaching from the α side.

Under the standard conditions for the N−O cleavage in **36** simultaneously or even faster the 4-azido function was reduced; such a one-pot treatment furnished after chromatography 84% of the 2β-hydroxy-4β-amine **37a**. When the reaction was stopped at an intermediate stage 63% of the 4-amino derivative **47** were found along with 26% of **37a**. After protection in **37a** of the 4-NH_2 function in form of its Z derivative **37b** ($[\alpha]_D^{25} = +29.3$), the ensuing reaction sequence ending with **4**·3 HCl was performed as practiced with **3**. After deprotection at 6′-N (**38**) the subsequent methylation provided 70% of **39,** carbamate hydrolysis 92% of **40**. *N*-glycylation (78% of **41**) and one-pot twofold hydrogenolysis (94%) gave **4**·3 HCl with an overall yield of 25% for the eight operations starting from iodide **27a**.

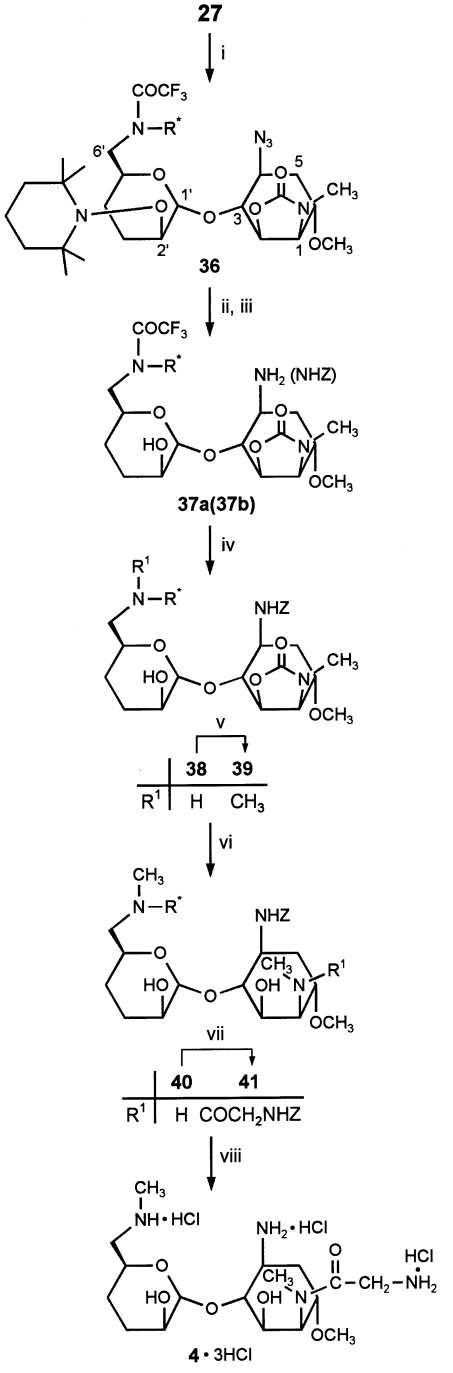
Analytical Data

For all the glycosides pictured in Schemes 1−6 the configurational and conformational details directly follow from the mostly fully assigned ^{1}H-NMR, ^{13}C-NMR (homo/heteronuclear decoupling and NOE experiments), IR, and in part FAB mass spectra. In view of the generally close analogy with the earlier analyses[1][4], no detailed discussion is necessary; some representative NMR assignments are given in Figure 1. The sugar parts irrespective of the kind of substitution at C-2′ − except for **30** − expectedly prefer a $^4C_1$ chair, the protected aglycon parts of **12** and **27** the half-chair conformation with quasi equatorial 3-O and 4-azido, quasi-axial 6-OCH_3 functions. The 1a,2e,3e,4e,6a-chair of **30** and **40** expectedly changes into the 1e,2a,3a,4a,6e-chair of **3**·3 HCl and **4**·3 HCl bringing the voluminous *N*-glycylated amino group into the equatorial position.

Biological Activity

The glycosides **3** and **4** have been subjected as hydrochlorides to the earlier specified agar diffusion tests against a selection of Gram-positive and Gram-negative bacteria (Table 1). For **3** no activity was found. For **4** the minimal inhibitory concentrations (MIC) are again compared with those determined for a commercial mixture of Gentamicin C_1, C_{1a}, C_2 sulfates (Refobacin); there is activity but clearly less than in the case of the amino analog **2**.[1]

Scheme 6. (i) TEMPO (3.0 equiv.)/Bu_3SnH (2 equiv.)/benzene, reflux, 4.5 h, 78%. − (ii) Zn/HOAc, room temp., 40 h, 84%. − (iii) Z-*O*-suc (1.2 equiv.)/DMF, room temp., 14 h, 95%. − (iv) $NaBH_4$/EtOH, room temp., 4 h, 86%. − (v) CH_3I (20 equiv.)/K_2CO_3/CH_3CN, room temp., 2 h, 70%. − (vi) 3% methanolic NaOH/water (1:1), reflux, 2 h, 92%. − (vii) Z-gly-*O*-suc (1.3 equiv.)/DMF, 60°C, 28 h, 78%. − (viii) methanol/2 N HCl/H_2 (1 atm)/10% Pd/C, 8 h, 94%



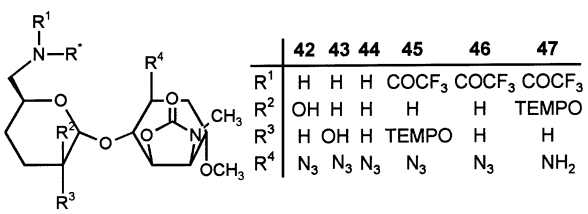


Figure 1. ^{1}H- and ^{13}C-NMR assignments [δ, *J* (Hz), $CDCl_3$ (**12**, **27**, **30**, **40**), D_2O (**3**·3 HCl, **4**·3 HCl)]

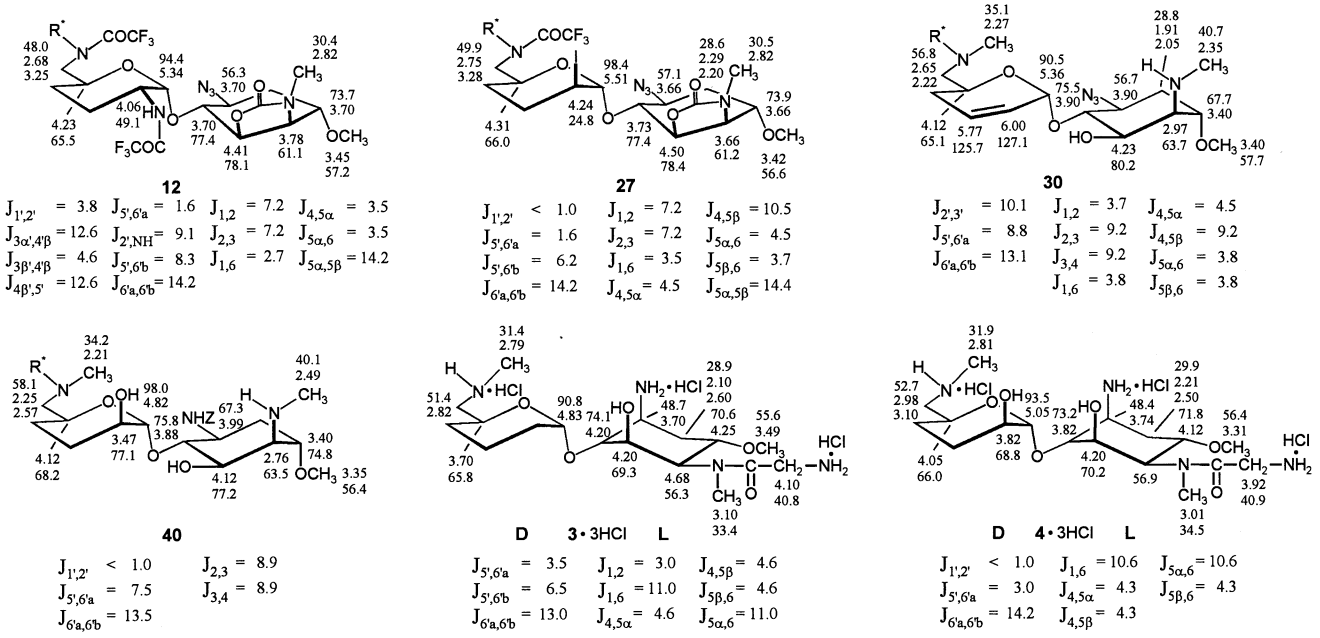


Table 1. Minimal inhibitory concentration (MIC, μg/ml free base)

Organism	**4**	Refobacin
Escherichia coli ATCC 25922	78	0.56
Staphylococcus aureus SG 511	78	0.28
Staphylococcus aureus ATCC 25923	78	0.28
Serratia marcescens E 8382/92[a]	39	0.56
Pseudomonas maltophilia D 141/92[a]	–	1.12
Pseudomonas aeruginosa ATCC 27853	–	1.12
Bacillus subtilis ATCC 6633	9.75	0.017
Acinetobacter baumanii H 5250/92[a]	–	72
Staphylococcus aureus H 5248/92[a]	–	0.07
Enterococcus faecalis D 1160/93[a]	–	9
Enterobacter aerogenes D 1088/93[a]	39	0.28
Salmonella enteritidis[a]	78	0.28
Shigella sonnei ATCC 11060	–	0.56
Citrobacter freundii E 8737/90[a]	78	0.28
Morganella morganii H 1962/93[a]	78	0.28
Klebsiella pneumoniae ATCC 27736	78	0.56
Staphylococcus saprophyticus RV 2/87	9.75	0.36
Corynebacterium diphtheriae	19.5	0.07
Staphylococcus epidermidis E 266/92[a]	19.5	0.017
Streptococcus sanguis D 25/88[a]	–	1.12

[a] Recent clinical isolates from Freiburg.

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Experimental Section

Melting points: Monoskop IV (Fa. Bock), uncorrected. – Elemental analyses: Analytische Abteilung des Chemischen Laboratoriums Freiburg i. Br. – IR spectra: Perkin-Elmer 457 or Philips PU 9706. – ^{1}H NMR: Bruker AC 250, AM 400; ^{13}C NMR: Bruker AM 400. Chemical shifts are given relative to TMS (δ = 0), coupling constants in Hz; if not specified otherwise, the 400-MHz (^{1}H) and 100.6-MHz (^{13}C) spectra recorded in $CDCl_3$ are given; values marked with an asterisk are interchangeable. – Mass spectra: Finnigan MAT 44S (EI 70 eV, if not specified differently), Finnigan MAT 312 (FAB-Gun Microbeam-7, 6 kV, Xenon, matrix: *m*-nitrobenzyl alcohol), or Finnigan TSQ 7000 (syringe pump: 2 μl/min, spray 4–5 kV). – Optical rotations: PE 241 polarimeter; specific rotation values are given in units of 10^{-1} deg cm^2 g^{-1}. – TLC: silica gel plates 60 F_{254} (Merck, Darmstadt). – The silica gel used for column chromatography was Merck (0.040–0.063 mm) or ICN-Silica, ICN, Biomedicals GmbH (0.032–0.063 mm). – The purity of oily compounds has generally been confirmed by careful TLC and NMR control; in many cases elemental analyses turned out to be erratic.

General Procedures. – Glycosylation (GP 1): A solution of glycosyl donor (0.30 mmol) and aglycon (0.36 mmol) in anhydrous CH_2Cl_2 was treated with $BF_3 \cdot OEt_2$ (0.36 mmol) under N_2 at room temp. After stirring for 1 h, the reaction mixture was quenched with saturated $NaHCO_3$ solution and the aqueous layer extracted with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo; the pure glycoside was obtained by chromatography on silica gel with the eluent specified.

N-Glycylation (GP 2): A solution of glycoside (0.05 mmol) and Z-gly-*O*-suc (0.06 mmol) in DMF was stirred at 60°C until total conversion. The solvent was removed in vacuo and the residue chromatographed on silica gel with the eluent specified.

Hydrogenolysis (GP 3): A solution of glycoside (0.02 mmol) in methanol (10 ml) and 2 N HCl (0.1 ml) was treated with H_2 in the presence of 10% Pd/C under atmospheric pressure at room temp.; the catalyst was removed by filtration and the filtrate concentrated in vacuo.

4-Azido-3-O-[2'α-benzenesulfonamido-6'-{trifluoroacetyl[(1R)-phenylethyl]}amino-2',3',4',6'-tetradeoxy-α-D-hexopyranosyl]-1-N,2-O-carbonyl-1,4,5-trideoxy-6-O-methyl-1-methylamino-L-chiro-inositol (**11**): **5** (100 mg, 0.19 mmol) and **10** (56 mg, 0.23 mmol)

were converted according to GP 1 [$BF_3 \cdot OEt_2$ (34 µl, 0.27 mmol)] to yield after chromatography [CH_2Cl_2/acetone, 10:1, R_f (**11**) = 0.49, R_f (**10**) = 0.13] **11** (108 mg, 80%) as colorless oil. $[\alpha]_D^{25}$ = +36.4 (c = 0.1, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 3285 cm^{-1} (NH), 2107 (N_3), 1764 (NCOO), 1665 (6′-NR*$COCF_3$), 1329 ($NHSO_2$), 1164 ($NHSO_2$). − ^{1}H NMR: δ = 7.88 (m, 2 H), 7.55 (m, 3 H), 7.36 (m, 3 H), 7.26 (m, 2 H), 5.27 (q, 1′′-H), 5.18 (d, 1′-H), 4.82 (d, N-H), 4.35 (dd, 2-H), 4.10 (m, 5′-H), 3.71 (dd, 1-H), 3.72−3.55 (m, 3-, 4-, 6-H), 3.41 (s, OCH_3), 3.34 (m, 2′-H), 3.18 (dd, 6′a-H), 2.80 (s, NCH_3), 2.58 (dd, 6′b-H), 2.18 (ddd, 5α-H), 1.68−1.46 (m, 5β-, 4′α-H, 3′-H_2), 1.65 (d, 2′′-H), 1.10 (dddd, 4′β-H); $J_{1',2'}$ = 3.5, $J_{2',NH}$ = 9.9, $J_{5',6'a}$ = 1.6, $J_{5',6'b}$ = 8.3, $J_{6'a,6'b}$ = 14.2, $J_{1'',2''}$ = 6.9, $J_{1,2}$ = $J_{2,3}$ = 7.5, $J_{1,6}$ = 2.1, $J_{4,5\alpha}$ = $J_{5\alpha,6}$ = 4.0, $J_{5\alpha,5\beta}$ = 14.7 Hz. − ^{13}C NMR: δ = 157.9 (C=O), 141.2 (C_s, $PhSO_2NH$), 138.7 (C_s), 132.8−126.8 (10 C), 116.9 (q, $COCF_3$), 94.5 (C-1′), 77.8 (C-2), 77.1 (C-3), 73.8 (C-6), 65.3 (C-5′), 60.9 (C-1), 57.1 (C-4), 56.5 (OCH_3), 55.4 (C-1′′), 51.5 (C-2′), 49.0 (C-6′), 30.4 (NCH_3), 28.4, 28.2, 25.3 (C-5, C-4′, C-3′), 17.9 (C-2′′); $J_{C,F}$ = 287.8 Hz. − MS (FAB); *m/z* (%): 733 (1) $[M + Na]^+$, 711 (5) $[M + H]^+$, 607 (3) [M − R*, + 2 H]$^+$, 569 (2) $[M - SO_2C_6H_5]^+$, 469 (14) $[C_{22}H_{24}N_2O_4SF_3]^+$.

4-Azido-3-O-[2′α-trifluoroacetylamino-6′-{trifluoroacetyl[(1R)-phenylethyl]}amino-2′,3′,4′,6′-tetradeoxy-α-D-hexopyranosyl]-1-N,2-O-carbonyl-1,4,5-trideoxy-6-O-methyl-1-methylamino-L-chiro-inositol (**12**): **6** (500 mg, 1.03 mmol) and **10** (300 mg, 1.24 mmol) were converted according to GP 1 [$BF_3 \cdot EtO_2$ (150 µl, 1.18 mmol)] to yield after chromatography [CH_2Cl_2/acetone, 20:1, R_f (**12**) = 0.33, change of solvent $CHCl_3$/MeOH, 10:1, R_f (**10**) = 0.45] **12** (519 mg, 80%) as colorless oil and residual **10** (42 mg, 14%). [Four further fractions were eluted (CH_2Cl_2/acetone, 20:1): R_f = 0.56 (27 mg) mixture of glycon derivatives; R_f = 0.48 (38 mg), R_f = 0.18 (35 mg) and R_f = 0.10 (46 mg), the latter three contained mixtures of α-glycosides.] $[\alpha]_D^{25}$ = +34.5 (c = 0.2, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 3356 cm^{-1} (NH), 2114 (N_3), 1755 (NCOO), 1689 (2′-$NHCOCF_3$, 6′-NR*$COCF_3$), 1560 (2′-$NHCOCF_3$). − ^{1}H NMR: δ = 7.33 (m, 5 H), 6.40 (d, NH), 5.34 (d, 1′-H), 5.26 (q, 1′′-H), 4.41 (dd, 2-H), 4.23 (m, 5′-H), 4.06 (m, 2′-H), 3.78 (dd, 1-H), 3.80−3.65 (m, 6-, 4-, 3-H), 3.45 (s, OCH_3), 3.25 (dd, 6′a-H), 2.82 (s, NCH_3), 2.68 (dd, 6′b-H), 2.26 (ddd 5α-H), 1.90−1.55 (m, 5β-, 4′α-H, 3′-H_2), 1.21 (dddd, 4′β-H); $J_{1',2'}$ = 3.8, $J_{2',NH}$ = 9.1, $J_{3'\beta,4'\beta}$ = 4.6, $J_{3'\alpha,4'\beta}$ = $J_{4'\alpha,4'\beta}$ = $J_{4'\beta,5'}$ = 12.6, $J_{5',6'a}$ = 1.6, $J_{5',6'b}$ = 8.3, $J_{6'a,6'b}$ = 14.2, $J_{1,2}$ = $J_{2,3}$ = 7.2, $J_{1,6}$ = 2.7, $J_{5\alpha,5\beta}$ = 14.5, $J_{4,5\alpha}$ = $J_{5\alpha,6}$ = 3.5 Hz. − ^{13}C NMR: δ = 157.3 (C=O), 156.7 (C=O), 138.6 (C_s), 128.9 (C_m), 128.2 (C_o), 127.2 (C_p), 116.9 [q, $COCF_3$, (C-6′)], 115.8 [q, $COCF_3$, (C-2′)], 94.4 (C-1′), 78.1 (C-2), 77.4 (C-3), 73.7 (C-6), 65.5 (C-5′), 61.1 (C-1), 57.2 (OCH_3), 56.3 (C-4), 55.5 (C-1′′), 49.1 (C-2′), 48.0 (C-6′), 30.4 (NCH_3), 28.7 (C-5), 27.6 (C-4′), 23.8 (C-3′), 17.9 (C-2′′); $J_{C,F(C\text{-}2')}$ = $J_{C,F(C\text{-}6')}$ = 287.5 Hz. − MS (FAB); *m/z* (%): 689 (8) $[M + Na]^+$, 667 (29) $[M + H]^+$, 563 (54) [M − R*, + 2 H]$^+$, 425 (23) $[C_{18}H_{19}F_6O_3N_2]^+$, 321 (38) $[C_{18}H_{19}F_6O_3N_2 - R^*, + H]^+$, 243 (51) $[C_9H_{13}O_4N_4 + 2 H]^+$, 105 (100) $[R^*]^+$.

4-Azido-3-O-[6′-azido-2′α-trifluoroacetylamino-2′,3′,4′,6′-tetradeoxy-α-D-hexopyranosyl]-1-N,2-O-carbonyl-1,4,5-trideoxy-6-O-methyl-1-methylamino-L-chiro-inositol (**13**),[2] *4-Azido-3-O-[2′β,6′-bisazido-2′,3′,4′,6′-tetradeoxy-α-D-hexopyranosyl]-* (**14**), *and 4-Azido-3-O-[2′α,6′-bisazido-2′,3′,4′,6′-tetradeoxy-β-D-hexopyranosyl]-1-N,2-O-carbonyl-6-O-methyl-1-N-methylamino-1,4,5-trideoxy-L-chiro-inositol* (**15**): **8** (78 mg, 0.37 mmol) and **10** (88 mg, 0.42 mmol) were treated with $BF_3 \cdot OEt_2$ (0.06 ml, 0.49 mmol) according to GP 1 (stirring for 4 h at 0°C); after chromatography [CH_2Cl_2/ethyl acetate, 2:1, R_f (**14**) = 0.59, R_f (**15**) = 0.49, R_f (**10**) = 0.19] **14** (83 mg), **10** (14 mg) and a mixture of **14**/**15** (22 mg) were secured. The latter was separated by preparative TLC (CH_2Cl_2/ethyl acetate, 2:1) to give **14** (12 mg) and **15** (7 mg, total yield: 76%, α/β ≈ 14:1), both as colorless oils. **14**: $[\alpha]_D^{25}$ = −7.4 (c = 0.6, CH_2Cl_2). − IR (KBr): $\tilde{\nu}$ = 2109 cm^{-1} (N_3), 1762 (NCOO). − ^{1}H NMR: δ = 5.20 (s, 1′-H), 4.52 (dd, 2-H), 4.16 (dddd, 5′-H), 3.82 (dd, 3-H), 3.75 (dd, 1-H), 3.69 (ddd, 4-H), 3.67 (ddd, 6-H), 3.57 (dd, 2′-H), 3.42 (s, OCH_3), 3.38 (dd, 6′a-H), 3.18 (dd, 6′b-H), 2.82 (s, NCH_3), 2.19 (dddd, 5α-H), 2.14 (dddd, 3′α-H), 1.89 (dddd, 5β-H), 1.74 (dddd, 3′β-H), 1.70 (dddd, 4′β-H), 1.50 (dddd, 3′α-H); $J_{1,2}$ = $J_{2,3}$ = 7.2, $J_{3,4}$ = 9.9, $J_{4,5\beta}$ = 10.5, $J_{4,5\alpha}$ = 14.5, $J_{5\alpha,6}$ = $J_{5\beta,6}$ = $J_{1,6}$ = 3.0, $J_{2',3'\alpha}$ = $J_{2',3'\beta}$ = $J_{3'\alpha,4'\alpha}$ = $J_{3'\beta,4'\alpha}$ = $J_{3'\beta,4'\beta}$ = $J_{4'\alpha,5'}$ = 3.5, $J_{3'\alpha,3'\beta}$ = $J_{3'\alpha,4'\beta}$ = $J_{4'\alpha,4'\beta}$ = 13.5, $J_{4'\alpha,5'}$ = 3.5, $J_{4'\beta,5'}$ = 11.5, $J_{5',6'a}$ = 6.7, $J_{5',6'b}$ = 4.0, $J_{6'a,6'b}$ = 12.9 Hz. − ^{13}C NMR: δ = 158.0 (C=O), 96.7 (C-1′), 78.3 (C-2), 78.0 (C-3), 74.0 (C-6), 68.7 (C-5′), 61.0 (C-1), 57.1 (OCH_3), 57.0 (C-2′), 56.6 (C-4), 54.8 (C-6′), 30.5 (NCH_3), 28.6 (C-5), 22.7 (C-4′), 22.2 (C-3′). − MS (ESI); *m/z* (%) = 883 (34) $[2 M + K]^+$, 867 (54) $[2 M + Na]^+$, 461 (63) $[M + K]^+$, 445 (100) $[M + Na]^+$, 340 (42). − $C_{15}H_{22}N_{10}O_5$ (422.4). **15**: $[\alpha]_D^{25}$ = −101.8 (c = 0.1, CH_2Cl_2). − IR (KBr): $\tilde{\nu}$ = 2109 cm^{-1} (N_3), 1769 (NCOO). − ^{1}H NMR: δ = 4.87 (d, 1′-H), 4.82 (dd, 2-H), 3.84 (ddd, 4-H), 3.78 (dd, 3-H), 3.78−3.70 (m, 1-, 6-, 5′-H), 3.62 (ddd, 2′-H), 3.44 (dd, 6′a-H), 3.40 (s, OCH_3), 3.23 (dd, 6′b-H), 2.82 (s, NCH_3), 2.11 (dddd, 5α-H), 2.04 (dddd, 3′β-H), 1.77 (dddd, 5β-H), 1.65 (dddd, 3′α-H), 1.59 (dddd, 4′β-H), 1.40 (dddd, 4′α-H); $J_{1,2}$ = 5.9, $J_{2,3}$ = 7.5, $J_{3,4}$ = 9.0, $J_{4,5\alpha}$ = 4.0, $J_{4,5\beta}$ = 11.0, $J_{5\alpha,5\beta}$ = 14.0, $J_{5\alpha,6}$ = 5.0, $J_{5\beta,6}$ = 3.0, $J_{1',2'}$ = 1.6, $J_{2',3'\alpha}$ = 4.5, $J_{2',3'\beta}$ = 2.5, $J_{3'\alpha,3'\beta}$ = 13.5, $J_{3'\alpha,4'\alpha}$ = 3.5, $J_{3'\alpha,4'\beta}$ = 11.3, $J_{3'\beta,4'\alpha}$ = 4.5, $J_{4'\beta,5'}$ = 13.5, $J_{4'\beta,5'}$ = 13.5, $J_{5',6'a}$ = 6.7, $J_{5',6'b}$ = 4.0, $J_{6'a,6'b}$ = 12.9 Hz. − MS (ESI); *m/z* (%) = 883 (36) $[2 M + K]^+$, 867 (58) $[2 M + Na]^+$, 461 (69) $[M + K]^+$, 445 (100) $[M + Na]^+$, 340 (34).

4-Azido-3-O-[2′α-amino-6′-{trifluoroacetyl[(1R)-phenylethyl]}-amino-2′,3′,4′,6′-tetradeoxy-α-D-hexopyranosyl]-1-N,2-O-carbonyl-1,4,5-trideoxy-6-O-methyl-1-methylamino-L-chiro-inositol (**16**): A solution of **12** (15 mg, 0.022 mmol) in 3% methanolic NaOH solution (3 ml) and water (3 ml) was stirred until total conversion [75 min, TLC control, $CHCl_3$/methanol, 10:1, R_f (**12**) = 0.72, R_f (**16**) = 0.15]; the reaction was quenched with pH 7 buffer, the methanol removed in vacuo and the remaining aqueous phase extracted with CH_2Cl_2. After drying ($MgSO_4$) and concentration in vacuo **16** (12 mg, 95%) was obtained as colorless oil. $[\alpha]_D^{25}$ = +25.0 (c = 0.1, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 2107 cm^{-1} (N_3), 1768 (NCOO), 1686 (6′-NR*$COCF_3$). − ^{1}H NMR: δ = 7.30 (m, 5 H), 5.26 (q, 1′′-H), 5.19 (d, 1′-H), 4.54 (dd, 2-H), 4.12 (m, 5′′-H), 3.77−3.61 (m, 1-, 3-, 4-, 6-H), 3.40 (s, OCH_3), 3.26 (dd, 6′a-H), 2.82 (s, NCH_3), 2.82 (m, 2′-H), 2.60 (dd, 6′b-H), 2.18 (ddd, 5α-H), 1.70 (d, 2′′-H), 1.70−1.50, 1.40−1.20 (m, 5β-, 3′-H, 4′-H_2); $J_{1',2'}$ = 3.5, $J_{5',6'a}$ = 8.3, $J_{6'a,6'b}$ = 14.9, $J_{1'',2''}$ = 7.0, $J_{1,2}$ = $J_{2,3}$ = 7.0 Hz. − MS (FAB); *m/z* (%): 593 (2) $[M + Na]^+$, 571 (30) $[M + H]^+$, 329 (96) $[C_{16}H_{20}F_3N_2O_2]^+$, 225 (28) $[C_9H_{13}N_4O_3]^+$, 105 (100) $[R^*]^+$.

4-Azido-3-O-[2′α-benzyloxycarbonylamino-6′-{trifluoroacetyl-[(1R)-phenylethyl]}amino-2′,3′,4′,6′-tetradeoxy-α-D-hexopyranosyl]-1,4,5-trideoxy-6-O-methyl-1-(benzyloxycarbonyl)methylamino-L-chiro-inositol (**17b**): A solution of **12** (50 mg, 0.075 mmol) in 3% methanolic NaOH (10 ml) and water (6 ml) was refluxed for 4 h (TLC). The methanol was removed in vacuo; after extraction with CH_2Cl_2, drying ($MgSO_4$) and concentration in vacuo crude **17a** was left. To a solution of the latter in DMF, Z-*O*-suc (45 mg, 0.18 mmol) was added and the reaction mixture was stirred at room temp. for 20 h. The solvent was removed in vacuo and the remaining residue filtered through silica gel (CH_2Cl_2/acetone, 20:1, R_f = 0.22) to yield **17b** (54 mg, 89%) as colorless oil. $[\alpha]_D^{25}$ = +101.1 (c = 0.1, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 3423 cm^{-1} (OH), 3357 (NH),

2106 (N_3), 1684 (NHCOO), 1512 (NHCOO). − ^{1}H NMR: δ = 7.30 (m, 10 H), 5.55 (br. s, NH), 5.30 (q, 1′′-H), 5.12−4.82 [m, 1′-H, 2CH_2, (Z)], 4.20−3.60 (m, 1-, 2-, 3-, 4-, 6-, 2′-H), 3.36 (s, OCH_3), 3.20 (d, 6′a-H), 2.98 (s, NCH_3), 2.68 (dd, 6′b-H), 2.42 (d, 5α-H), 1.70 (d, 2′′-H), 1.90−1.50/1.10 (m, 4 H/1 H, 5β-H, 3′-, 4′-H_2). − ^{13}C NMR: δ = 157.7 (C=O), 157.3 (C=O), 138.3−127.2 (12 C), 116.8 (q, CO*C*F_3), 99.2 (C-1′), 77.2 (C-2)*, 76.3 (C-3)*, 74.1 (C-1), 69.9 (C-6), 67.3 (C-5′), 66.7, 64.7 [2 CH_2 (Z)], 59.7 (OCH_3)*, 59.5 (C-1′′)*, 56.1 (C-4), 25.5 (C-5), 24.4 (C-4′)*, 24.3 (C-3′)*, 18.0 (C-2′′); $J_{C,F}$ = 287.8 Hz. − MS (FAB); *m/z* (%): 836 (6) [M + Na]$^+$, 814 (24) [M + H]$^+$, 813 (54) [M]$^+$, 463 (15) [$C_{24}H_{26}F_3N_2O_4$]$^+$, 333 (12) [$C_{16}H_{21}N_4O_4$]$^+$, 195 (10) [$C_{16}H_{21}N_4O_4$ − Z, − 3 H]$^+$, 105 (100) [R*]$^+$.

4-Azido-3-O-{2′α-amino-6′-[(1R)-phenylethyl]amino-2′,3′,4′,6′-tetradeoxy-α-D-hexopyranosyl}-1,4,5-trideoxy-6-O-methyl-1-methylamino-L-chiro-inositol (**18a**): A solution of **12** (15 mg, 0.022 mmol) in 6 ml 3% methanolic NaOH (6 ml) and water (3 ml) was refluxed for 40 h (TLC). Methanol was removed in vacuo, the residue diluted with water and extracted with CH_2Cl_2. The organic phase was dried ($MgSO_4$) and concentrated in vacuo, **18a** (9 mg, 91%) was isolated as colorless oil. $[\alpha]_D^{25}$ = +29.3 (*c* = 0.1, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 3338 cm^{-1} (NH, OH), 2103 (N_3). − ^{1}H NMR: δ = 7.30 (m, 5 H), 5.10 (d, 1′-H), 4.08 (m, 5′-H), 3.89 (dd, 2-H), 3.78 (q, 1′′-H), 3.67 (dd, 3-H), 3.55 (ddd, 6-H), 3.44 (ddd, 4-H), 3.39 (s, OCH_3), 2.97 (dd, 1-H), 2.82 (m, 2′-H), 2.58 (dd, 6′a-H), 2.46 (dd, 6′b-H), 2.38 (s, NCH_3), 2.10 (ddd, 5α-H), 1.98 (ddd, 5β-H), 1.75−1.20 (m, 3′-, 4′-H_2), 1.35 (d, 2′′-H); $J_{1',2'}$ = 3.5, $J_{1,2}$ = 4.0, $J_{2,3}$ = $J_{3,4}$ = 9.6, $J_{1,6}$ = $J_{5\alpha,6}$ = $J_{5\beta,6}$ = 3.2 Hz. − ^{13}C NMR: δ = 128.4 (C_m), 126.8 (C_o), 126.7 (C_p), 101.7 (C-1′), 83.2 (C-2)*, 77.3 (C-3)*, 75.6 (C-6), 67.7 (C-5′), 62.6 (C-1), 59.1 (OCH_3)*, 58.2 (C-4)*, 56.9 (C-1′′)*, 52.0 (C-6′), 50.0 (C-2′), 35.2 (NCH_3), 29.1 (C-5′), 28.7 (C-4′)*, 28.4 (C-3)*, 24.5 (C-2′′). − MS (FAB); *m/z* (%): 461 (5) [M + Na]$^+$, 449 (30) [M + H]$^+$, 233 (18) [$C_{18}H_{21}N_2O$]$^+$, 215 (8) [$C_8H_{15}N_4O_4$]$^+$, 105 (67) [R*]$^+$.

4-Azido-3-O-[2′α-benzyloxycarbonylamino-6′-{benzyloxycarbonyl[(1R)-phenylethyl]}amino-2′,3′,4′,6′-tetradeoxy-α-D-hexopyranosyl]-1,4,5-trideoxy-6-O-methyl-1-(benzyloxycarbonyl)methylamino-L-chiro-inositol (**18b**): To a solution of **18a** (15 mg, 0.03 mmol) in anhydrous DMF, Z-*O*-suc (27 mg, 0.11 mmol) was added and the reaction mixture was stirred at room temp. for 24 h. The solvent was removed in vacuo and the remaining residue chromatographed on silica gel (CH_2Cl_2/acetone, 20:1, R_f = 0.16) to yield **18b** (26 mg, 92%) as colorless oil. $[\alpha]_D^{25}$ = +71.2 (*c* = 0.2, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 3422 cm^{-1} (OH, NH), 2104 (N_3), 1710 (NCOO), 1686 (NHCOO), 1561 (NHCOO). − ^{1}H NMR: (= 7.30 (m, 15 H), 5.45 (br. s, NH), 5.25 (m, 1′′-H), 5.28−4.80 [m, 1′-H, 2 CH_2 (Z)], 4.10−3.65 (m, 1-, 2-, 3-, 4-, 6-, 2′-, 5′-H), 3.34 (s, OCH_3), 3.12 (m, 6′a-H), 2.98 (s, NCH_3), 2.80 (dd, 6′b-H), 2.30 (m, 5α-H), 1.56 (d, 2′′-H), 1.80−1.40/1.15 (m, 4 H/1 H, 5β-H, 3′-, 4′-H_2). − MS (FAB); *m/z* (%): 873 (3) [M + Na]$^+$, 851 (30)[M + H]$^+$, 717 (11) [M − Z, + 2 H]$^+$, 501 (76) [$C_{30}H_{33}N_2O_5$]$^+$, 397 (46) [$C_{30}H_{33}N_2O_5$ − R*, + H]$^+$, 366 (8) [$C_{30}H_{33}N_2O_5$ − Z]$^+$, 353 (37) [$C_{30}H_{33}N_2O_5$ − NHZ, + 2 H]$^+$, 350 (18) [$C_{16}H_{21}N_4O_5$ + H]$^+$, 333 (66) [$C_{16}H_{21}N_4O_4$]$^+$, 315 (14) [$C_{16}H_{21}N_4O_4$ − H_2O]$^+$, 302 (8) [$C_{16}H_{21}N_4O_4$ − OCH_3]$^+$, 263 (12) [$C_{30}H_{33}N_2O_5$ − Z, − R*, + 2 H]$^+$, 198 (10) [$C_{16}H_{21}N_4O_4$ − Z]$^+$, 105 (100) [R*]$^+$. − $C_{46}H_{54}O_{10}N_6$ (851.0).

4-Azido-3-O-{2′α-amino-6′-[(1R)-phenylethyl]amino-2′,3′,4′,6′-tetradeoxy-α-D-hexopyranosyl}-1-N,2-O-carbonyl-1,4,5-trideoxy-6-O-methyl-1-methylamino-L-chiro-inositol (**19a**): To a solution of **12** (58 mg, 0.087 mmol) in ethanol $NaBH_4$ (30 mg, 0.79 mmol) was added. After stirring for 22 h at room temp. [TLC, $CHCl_3$/methanol, 10:1, R_f (**12**) = 0.72, R_f (**19a**) = 0.05], the solvent was removed in vacuo, the residue dissolved in water, extracted with CH_2Cl_2, dried ($MgSO_4$), and concentrated in vacuo, **19a** (36 mg, 87%) was isolated as colorless oil. $[\alpha]_D^{25}$ = +28.4 (*c* = 0.1, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 3359 cm^{-1} (NH), 2105 (N_3), 1763 (NCOO). − ^{1}H NMR: δ = 7.30 (m, 5 H), 5.12 (d, 1′-H), 4.56 (dd, 2-H), 3.92 (m, 5′-H), 3.87 (dd, 3-H), 3.81 (dd, 1-H), 3.77 (ddd, 4-H), 3.76 (m, 1′′-H), 3.68 (m, 6-H), 3.40 (s, OCH_3), 2.84 (s, NCH_3), 2.79 (m, 2′-H), 2.54 (dd, 6′a-H), 2.48 (dd, 6′b-H), 2.14 (ddd, 5α-H), 1.74−1.43 (m, 5β-H, 3′-, 4′-H_2), 1.32 (d, 2′′-H); $J_{1',2'}$ = 3.2, $J_{5',6'a}$ = 3.8, $J_{5',6'b}$ = 7.0, $J_{6'a,6'b}$ = 12.3, $J_{1,2}$ = $J_{2,3}$ = 6.7, $J_{3,4}$ = 9.4, $J_{4,5\alpha}$ = $J_{5\alpha,6}$ = 4.8, $J_{5\alpha,5\beta}$ = 14.2 Hz. − ^{13}C NMR: δ = 158.1 (C=O), 128.4 (C_m), 126.7 (C_o), 126.7 (C_p), 99.0 (C-1′), 77.9 (C-2)*, 77.2 (C-3)*, 74.3 (C-6), 67.8 (C-5′), 61.0 (C-1), 57.8 (OCH_3)*, 57.0 (C-4)*. 57.0 (C-1′′)*, 51.8 (C-6′), 50.4 (C-2′), 30.4 (NCH_3), 28.5 (C-5′), 28.4 (C-4′), 27.8 (C-3′), 24.6 (C-2′′). − MS (FAB); *m/z* (%): 475 (100) [M + H]$^+$, 307 (10) [M − NHR*, − NH_2, − OCH_3]$^+$, 249 (4) [$C_{14}H_{21}N_2O_2$]$^+$, 233 (26) [$C_{14}H_{21}N_2O$]$^+$, 129 (7) [$C_{14}H_{21}N_2O$ − R*, + H]$^+$, 105 (19) [R*]$^+$.

4-Azido-3-O-[2′α-benzyloxycarbonylamino-6′-{benzyloxycarbonyl[(1R)-phenylethyl]}amino-2′,3′,4′,6′-tetradeoxy-α-D-hexopyranosyl]-1-N,2-O-carbonyl-1,4,5-trideoxy-6-O-methyl-1-methylamino-L-chiro-inositol (**19b**): To a mixture of **19a** (36 mg, 0.076 mmol) in acetone (5 ml) and water (5 ml) sodium hydrogen carbonate (50 mg, 0.6 mmol) and Z chloride (26 µl, 0.184 mmol) were added. After stirring for 2 h at room temp. acetone was removed in vacuo, the aqueous phase diluted and extracted with CH_2Cl_2; drying ($MgSO_4$), concentration in vacuo, and chromatography on silica gel (ethyl acetate/cyclohexane, 2:1, R_f = 0.26) gave **19b** (53 mg, 94%) as colorless oil. $[\alpha]_D^{25}$ = +34.6 (*c* = 0.2, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 3334 cm^{-1} (NH), 2105 (N_3), 1768 (NCOO), 1698 (NHCOO), 1520 (NHCOO). − ^{1}H NMR: δ = 7.30 (m, 10 H), 5.51 (br. s, NH), 5.28 (br. s, 1′′-H), 5.11 [br. s, 2 CH_2 (Z)], 4.84 (d, 1′-H), 4.41 (dd, 2-H), 4.09 (m, 5′-H), 3.81−3.58 (m, 2′-, 1-, 3-, 4-, 6-H), 3.39 (s, OCH_3), 3.20 (m, 6′a-H), 2.82 (m, 6′b-H), 2.80 (s, NCH_3), 2.10 (m, 5α-H), 1.78 (m, 5β-H), 1.60 (d, 2′′-H), 1.70−1.48/1.22 (m, 3 H/1 H, 3′-, 4′-H_2). − ^{13}C NMR: (= 157.9, 155.6 (C=O), 136.8−127.2 (12 C), 95.1 (C-1′), 77.2 (C-2)*, 76.9 (C-3)*, 73.9 (C-6), 67.3 (C-5′), 67.2, 66.9 [CH_2 (Z)], 60.9 (C-1), 57.1 (OCH_3)*, 56.7 (C-1′′)*, 54.8 (C-4)*, 54.7 (C-2′)*, 49.4, 49.3 (C-6′)*, 30.5 (NCH_3), 28.0 (C-5), 27.8 (C-4′), 24.6 (C-3′), 17.8 (C-2′′). − MS (FAB); *m/z* (%): 766 (5) [M + Na]$^+$, 744 (27) [M + H]$^+$, 640 (19) [M − R*, + 2 H]$^+$, 607 (9) [M − Z, − H]$^+$, 502 (58), 502 (18) [M − R*, − Z, − H; or $C_{30}H_{33}N_2O_5$ + H]$^+$, 397 (43) [$C_{30}H_{33}N_2O_5$ − R*, + H]$^+$, 263 (9) [$C_{30}H_{33}N_2O_5$ − R*, − Z, + 2 H]$^+$, 105 (100) [R*]$^+$.

4-Azido-3-O-[2′α-benzyloxycarbonylamino-6′-{benzyloxycarbonyl[(1R)-phenylethyl]}amino-2′,3′,4′,6′-tetradeoxy-α-D-erythro-hexopyranosyl]-1,4,5-trideoxy-6-O-methyl-1-methylamino-L-chiro-inositol (**20**): A mixture of **19b** (48 mg, 0.065 mmol) and $Ba(OH)_2 \cdot 8\ H_2O$ (102 mg, 0.323 mmol) in dioxane/water (30 ml/15 ml) was refluxed for 8 h. The solvent was removed in vacuo and the residue digested with CH_2Cl_2 (5 × 10 ml); the combined organic phases were dried ($MgSO_4$), concentrated in vacuo, and chromatographed on silica gel [$CHCl_3$/methanol, 10:1, 1% NEt_3, R_f (**19b**) = 0.76, R_f (**20**) = 0.29], **20** (41 mg, 88%) was isolated as colorless oil. $[\alpha]_D^{25}$ = +86.3 (*c* = 0.1, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 3336 cm^{-1} (OH, NH), 2104 (N_3), 1697 (NHCOO), 1526 (NHCOO). − ^{1}H NMR: δ = 7.30 (m, 10 H), 5.25−5.05 [m, 1′-H, 1′′-H, 2 CH_2 (Z)], 4.15 (m, 5′-H), 3.90−3.50 (m, 2′-, 2-, 3-, 4-, 6-H), 3.48 (s, OCH_3), 3.18 (m, 6′a-H), 2.91 (m, 6′b-H), 2.76 (m, 1-H), 2.32 (s, NCH_3), 2.00 (m, 5α-H), 1.77 (m, 5β-H), 1.70−1.40 (m, 3′-, 4′-H_2), 1.60 (d, 2′′-H). − ^{13}C NMR: δ = 156.7, 155.9 (C=O), 128.5−127.2 (10 C), 96.9,

96.7 (C-1′), 77.2 (C-2)*, 76.8 (C-3)*, 74.6 (C-6)*, 67.3 (C-5′), 66.7, 65.1 [2 CH_2, (Z)], 62.8 (C-1), 56.8 (OCH_3)*, 55.0 (C-4, C-1′′)*, 49.9, 49.3 (C-6′)*, 48.6, 48.5 (C-2′)*, 29.7 (NCH_3), 28.7 (C-5)*, 28.0 (C-4′)*, 24.6 (C-3′), 17.9 (C-2′′). − MS (FAB); *m/z* (%): 729 (5) $[M + Na]^+$, 717 (100) $[M + H]^+$, 674 (2) $[M - N_3]^+$, 609 (3) $[M - R^*, + 2H]^+$, 501 (9) $[C_{30}H_{33}N_2O_5]^+$, 460 (3) $[M - NRZ^*, - 2\ H]^+$, 353 (10) $[C_{30}H_{33}N_2O_5 - NHZ, + 2\ H]^+$, 397 (6) $[C_{30}H_{33}N_2O_5 - R^*, + H]^+$, 245 (4) $[C_{30}H_{33}N_2O_5 - NRZ^*, - 2\ H]^+$, 199 (4) $[C_{18}H_{15}N_2O_2]^+$, 105 (24) $[R^*]^+$.

4-Azido-3-O-[2′α-benzyloxycarbonylamino-6′-{benzyloxycarbonyl[(1R)-phenylethyl]}amino-2′,3′,4′,6′-tetradeoxy-α-D-hexopyranosyl]-1,4,5-trideoxy-6-O-methyl-1-(benzyloxycarbonylglycyl)methylamino-L-chiro-inositol (**21**): **20** (30 mg, 0.042 mmol) was treated according to GP 2 [Z-gly-*O*-suc (15 mg, 0.05 mmol), 26 h, 60°C] to provide after twofold chromatography (CH_2Cl_2/ethyl acetate, 1:1, R_f = 0.37) **21** (31 mg, 81%) as colorless oil. − IR (KBr): $\tilde{\nu}$ = 3411 cm^{-1} (OH), 2103 (N_3), 1701 (NHCOO), 1638 (NHCO), 1509 (NHCO). − ^{1}H NMR: δ = 7.30 (m, 15 H), 5.70 (br. s NH), 5.30−4.80 [m, 1′-H, 1′′-H, 3 CH_2 (Z)], 4.52 (d, NH), 4.10−3.50 [m, 1-, 2-, 3-, 4-, 6-, 2′-, 5′-H, CH_2 (Gly)], 3.32 (s, OCH_3), 3.14 (dd, 6′a-H), 2.97 (s, NCH_3), 2.81 (dd, 6′b-H), 2.35 (m, 5β-H), 1.95−1.45 (m, 5α-H, 3′-H_2, 4′α-H), 1.52 (d, 2′′-H), 1.15 (dddd, 4′β-H). − ^{13}C NMR: δ = 169.0 (C=O, gly), 156.5, 156.3 (C=O, carbamate), 128.6−127.5 (15 C), 94.7 (C-1′), 80.7 (C-2)*, 76.6 (C-3)*, 74.1 (C-6), 69.3 (C-5′), 67.3 (CH_2, Z), 66.8 (CH_2, Z), 60.2 (C-1), 55.8 (OCH_3)*, 54.9 (C-4)*, 54.5 (C-1′′)*, 50.1 (C-6′), 49.4 (C-2′), 43.1 (CH_2), 28.3 (NCH_3), 25.4 (C-5), 22.8 (C-3′), 15.1 (C-2′′). − MS (FAB); *m/z* (%): 909 (38) $[M + H]^+$, 804 (2) $[M - R^*, + H]^+$, 774 (3) $[M - R^*, - N(CH_3)COCH_2NHZ, - H]^+$, 502 (3) $[M - 3\ Z, + H]$, 501 (9) $[C_{30}H_{33}N_2O_5]^+$, 460 (4) $[M - 3\ Z, - N_3, - H]^+$, 397 (5) $[C_{30}H_{33}N_2O_5 - R^*, + H]^+$, 390 (36) $[C_{18}H_{24}N_5O_6]^+$, 365 (3) $[C_{30}H_{33}N_2O_5 - NHZ, + 2\ H]^+$, 105 (22) $[R^*]^+$.

4-Amino-3-O-(2′α-amino-6′-amino-2′,3′,4′,6′-tetradeoxy-α-D-hexopyranosyl)-1,4,5-trideoxy-6-O-methyl-1-(glycyl)methylamino-L-chiro-inositol (**1**): **21** (20 mg, 0.022 mmol) was treated according to GP 3 (28 h) to give **1** (11 mg, 95%) as solid tetrahydrochloride salt.[1]

4-Azido-3-O-(2′α-amino-6′-azido-2′,3′,4′,6′-tetradeoxy-α-D-hexopyranosyl)-1-N,2-O-carbonyl-1,4,5-trideoxy-6-O-methyl-1-methylamino-L-chiro-inositol (**22**). − *Alternative 1:* A solution of **13** (15 mg, 0.030 mmol), 3% methanolic NaOH solution (3 ml), and water (3 ml) was stirred at room temp. for 45 min [total conversion, TLC, $CHCl_3$/methanol, 10:1, R_f (**13**) = 0.59, R_f (**22**) = 0.24]. The reaction mixture was quenched with pH 7 buffer, the methanol removed in vacuo, and the aqueous residue extracted with CH_2Cl_2. After drying ($MgSO_4$) and concentration in vacuo, **22** (11 mg, 93%) was isolated as colorless oil. − *Alternative 2:* A solution of **13** (15 mg, 0.030 mmol) in ethanol was treated with $NaBH_4$ (5 mg, 0.13 mmol); after 3 h stirring at room temp., the reaction was complete (TLC). The solution was concentrated in vacuo, the residue dissolved in water and extracted with CH_2Cl_2. After drying of the organic phase ($MgSO_4$) and concentration in vacuo, **22** (12 mg, quant.) was isolated as colorless oil. − IR (KBr): $\tilde{\nu}$ = 2106 cm^{-1} (N_3), 1755 (NCOO). − ^{1}H NMR: δ = 5.18 (d, 1′-H), 4.56 (dd, 2-H), 4.05 (m, 5′-H), 3.82 (dd, 3-H), 3.78−3.64 (m, 1-, 4-, 6-, 2′-H), 3.42 (s, OCH_3), 3.30 (dd, 6′a-H), 3.21 (dd, 6′b-H), 2.81 (s, NCH_3), 2.32 (ddd, 5α-H), 1.90−1.50 (m, 5β-H, 3′-, 4′-H_2); $J_{1',2'}$ = 3.5, $J_{1,2} = J_{2,3}$ = 7.5, $J_{3,4}$ = 9.4, $J_{5',6'a}$ = 6.4, $J_{5',6'b}$ = 4.6, $J_{6'a,6'b}$ = 12.6 Hz. − MS (CI, isobutane, 200 eV); *m/z* (%): 397 (13) $[M + H]^+$, 379 (15) $[M - NH_2, - H]^+$, 243 (100) $[C_9H_{13}N_4O_4 + 2\ H]^+$, 225 (21) $[C_9H_{13}N_4O_3]^+$, 155 (32) $[C_6H_{11}N_4O]^+$. − $C_{15}H_{24}N_8O_5$ (396.4).

4-Azido-3-O-(2′β,6′-bisazido-2′,3′,4′,6′-tetradeoxy-α-D-hexopyranosyl)-6-O-methyl-1-N-methylamino-1,4,5-trideoxy-L-chiro-inositol Hydrochloride (**23**): A solution of **14** (34 mg, 0.077 mmol) and NaOH (188 mg, 3.3 mmol) in methanol/water 1:1 (8 ml) was refluxed for 2 h. The methanol was removed in vacuo, the residue diluted with water and extracted with CH_2Cl_2. The organic phase was concentrated to 5 ml and extracted with 0.01 N HCl (5 ml). The aqueous phase was evaporated in vacuo to yield pure **23** (30 mg, 94%) as colorless solid. $[\alpha]_D^{25}$ = +100.7 (*c* = 0.20, H_2O). − IR (KBr): $\tilde{\nu}$ = 3406 cm^{-1} (OH), 2109 (N_3). − ^{1}H NMR (D_2O/CH_3CN): δ = 4.89 (s, 1′-H), 4.28 (dd, 2-H), 4.15 (dd, 3-H), 3.99 (ddd, 4-H), 3.96 (m, 5′-H), 3.67 (dd, 6-H), 3.62 (dd, 2′-H), 3.31 (s, OCH_3), 3.27 (d, 6′a-H), 3.26 (d, 6′b-H), 3.18 (dd, 1-H), 2.62 (s, NCH_3), 2.32 (dt, 5α-H), 1.95 (dddd, 3′α-H), 1.81−1.67 (m, 3′β-, 5β-H), 1.60 (dddd, 4′β-H), 1.36 (m, 4′α-H); $J_{1,2} = J_{2,3} = J_{3,4} = J_{4,5\alpha} = J_{4,5\alpha}$ = 3.5, $J_{1,6} = J_{5\alpha,6} = J_{5\alpha,5\beta}$ = 10.5, $J_{5\alpha,5\beta}$ = 13.5, $J_{5\beta,6}$ = 4.0, $J_{1',2'} < 1.0$, $J_{2',3'\alpha} = J_{3'\alpha,4'\alpha} = J_{3'\beta,4'\beta}$ = 4.0, $J_{2',3'\beta}$ = 2.0, $J_{3'\alpha,3'\beta} = J_{3'\alpha,4'\beta} = J_{4'\alpha,4'\beta} = J_{4'\beta,5'}$ = 13.5, $J_{5',6'a}$ = 4.5, $J_{5',6'b}$ = 6.0, $J_{6'a,6'b}$ = 5.0 Hz. − ^{13}C NMR (D_2O/CH_3CN): δ = 98.5 (C-1′), 75.1 (C-2)*, 72.1 (C-3)*, 70.2 (C-6)*, 65.6 (C-5′), 61.3 (C-1), 58.4 (OCH_3), 57.4 (C-2′), 57.0 (C-4), 54.6 (C-6′), 30.7 (NCH_3), 28.8 (C-5), 22.4 (C-4′), 21.7 (C-3′). − MS (ESI); *m/z* (%) = 419 (2) $[M + Na]^+$, 397 (100) $[M + H]^+$.

4-Azido-3-O-(2′β,6′-bisazido-2′,3′,4′,6′-tetradeoxy-α-D-hexopyranosyl)-1-N-(N-benzyloxycarbonylglycyl)-6-O-methyl-1-N-methylamino-1,4,5-trideoxy-L-chiro-inositol (**24**): Treatment of **23** (30 mg, 0.73 mmol) according to GP 2 (Z-gly-*O*-suc, 16 h, 50°C) gave after twofold chromatography (CH_2Cl_2/ethyl acetate, 2:1, R_f = 0.12) **24** (30 mg, 68%) as colorless oil. $[\alpha]_D^{25}$ = +51.8 (*c* = 0.10, CH_2Cl_2). − IR (KBr): $\tilde{\nu}$ = 3410 cm^{-1} (OH), 2109 (N_3), 1725 (NHCOO). − ^{1}H NMR: δ = 7.40−7.25 (m, 5 H), 5.79 (br. s, NH), 5.12 (s, CH_2, Gly), 4.89 (s, 1′-H), 4.45 (dd, 1-H), 4.14−4.05 (m, 2-, 3-, 6-H), 4.00−3.88 (m, 5′-H, CH_2, Z), 3.66 (dd, 2′-H), 3.36 (dd, 6′a-H), 3.36 (s, OCH_3), 3.16 (dd, 6′b-H), 3.16 (m, 4-H), 3.05 (s, NCH_3), 2.44 (ddd, 5α-H), 2.05 (dddd, 3′α-H), 1.93−1.82 (m, 5β-, 3′β-H), 1.69 (dddd, 4′β-H), 1.43 (dddd, 4′α-H); $J_{1,2}$ = 2.5, $J_{1,6}$ = 11.0, $J_{4,5\alpha} = J_{5\alpha,6}$ = 4.0, $J_{5\alpha,5\beta}$ = 13.5, $J_{1',2'} < 1.0$, $J_{2',3'\beta} = J_{3'\beta,4'\alpha}$ = 2.5, $J_{2',3'\alpha} = J_{3'\alpha,4'\alpha}$ = 4.0, $J_{3'\alpha,3'\beta} = J_{3'\alpha,4'\beta} = J_{4'\alpha,4'\beta} = J_{4'\beta,5'}$ = 13.0, $J_{4'\alpha,5'}$ = 5.5, $J_{5',6'a}$ = 8.0, $J_{5',6'b}$ = 3.0, $J_{6'a,6'b}$ = 13.0 Hz. − ^{13}C NMR: δ = 169.3 (C=O, gly), 156.3 (C=O, carbamate), 136.5 (C_s), 128.5−128.0 (5 C), 97.7 (C-1′), 75.6 (C-2)*, 73.0 (C-3)*, 69.8 (C-6)*, 69.5 (C-5′)*, 66.9 [CH_2 (Z)], 59.9 (C-1), 57.8 (C-2′), 56.7 (OCH_3), 56.0 (C-4), 54.8 (C-6′), 43.3 (CH_2, gly), 32.3 (NCH_3), 30.3 (C-5), 22.6 (C-4′), 22.3 (C-3′). − MS (ESI); *m/z* (%) = 626 (43) $[M + K]^+$, 610 (100) $[M + Na]^+$, 588 (9) $[M + H]^+$. − $C_{24}H_{33}N_{11}O_7$ (587.6).

4-Amino-3-O-(2′β,6′-diamino-2′,3′,4′,6′-tetradeoxy-α-D-hexopyranosyl)-1-N-glycyl-6-O-methyl-1-N-methylamino-1,4,5-trideoxy-L-chiro-inositol (**2**): **24** (19 mg, 0.03 mmol) was treated according to GP 3 (2 h) to provide **2** (16 mg, quant.) as solid tetrahydrochloride.[1]

4-Azido-3-O-[2′β-iodo-6′-{trifluoroacetyl[(1R)-phenylethyl]}-amino-2′,3′,4′,6′-tetradeoxy-α-D-hexopyranosyl]- (**27**) *and 4-Azido-3-O-[2′α-iodo-6′-{trifluoroacetyl[(1R)-phenylethyl]}amino-2′,3′,4′,6′-tetradeoxy-β-D-hexopyranosyl]-1-N,2-O-carbonyl-1,4,5-trideoxy-6-O-methyl-1-methylamino-L-chiro-inositol* (**32**), *2′-Iodo-2′,3′,4′,6′-tetradeoxy-6′-{trifluoroacetyl[(1R)-phenylethyl]}amino-D-hex-1′-enopyranose* (**34**): To a mixture of **9** (134 mg, 0.43 mmol), **10** (104 mg, 0.43 mmol) and molecular sieve (3 Å, 500 mg) in anhydrous CH_2Cl_2/CH_3CN (2:1) **26** (300 mg, 0.66 mmol) was added. After stirring for 16 h at room temp., the reaction was complete [TLC, cyclohexane/ethyl acetate, 1:1, R_f (**27**) = 0.25, R_f (**32**) =

0.30]. The sieve was filtered off and the solution washed with saturated Na_2SO_3, then with saturated $CuSO_4$ solution. The organic phase was dried ($MgSO_4$), concentrated in vacuo, and the residue chromatographed on silica gel [CH_2Cl_2/ethyl acetate, 15:1, R_f (**27**) = 0.31, R_f (**32**) = 0.17] to yield **27** (210 mg, 72%) and **32** (47 mg, 16%) as colorless crystals. Conversion in CH_2Cl_2 led (1 h, room temp.) to **27** (182 mg, 62%) and **32** (77 mg, 26%), in CH_3CN [24 h, after 12 h second addition of **26** (150 mg, 0.33 mmol), room temp.] to **27** (175 mg, 60%), **32** (23 mg, 8%) and **34** (39 mg, 21%) as by-product.

27: M.p. 63°C. − $[\alpha]_D^{25}$ = +12.3 (*c* = 0.1, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 2100 cm^{-1} (N_3), 1762 (NCOO), 1675 (NR*$COCF_3$). − ^1H NMR: δ = 7.31 (m, 5 H), 5.51 (s, 1′-H), 5.27 (q, 1′′-H), 4.50 (dd, 2-H), 4.31 (m, 5′-H), 4.24 (m, 2′-H), 3.73 (m, 3-H), 3.70−3.60 (m, 1-, 4-, 6-H), 3.42 (s, OCH_3), 3.28 (dd, 6′a-H), 2.82 (s, NCH_3), 2.75 (dd, 6′b-H), 2.29 (m, 5α-H), 2.20 (m, 5β-H), 1.87 (m, 4′-H), 1.71 (d, 2′′-H), 1.68−1.35 (m, 4′-H, 3′-H_2); $J_{1',2'} < 1$, $J_{5',6'a}$ = 1.6, $J_{5',6'b}$ = 6.2, $J_{6'a,6'b}$ = 14.2, $J_{1,2} = J_{2,3}$ = 7.2, $J_{1,6}$ = 3.5, $J_{4,5\alpha}$ = 4.5, $J_{4,5\beta}$ = 10.5, $J_{5\alpha,6}$ = 4.5, $J_{5\beta,6}$ = 3.7, $J_{5\alpha,5\beta}$ = 14.4 Hz. − ^{13}C NMR: δ = 158.1 (C=O), 138.9 (C_s), 129.0 (C_m), 128.1 (C_o), 127.3 (C_p), 117.0 (q, CO*C*F_3), 98.4 (C-1′), 78.4 (C-2), 77.4 (C-3), 73.9 (C-6), 66.0 (C-5′), 61.2 (C-1), 57.1 (C-4), 56.6 (OCH_3), 55.5 (C-1′′), 49.7 (C-6′), 30.5 (NCH_3), 28.6 (C-5), 27.5 (C-4′), 27.4 (C-3′), 24.8 (C-2′), 18.0 (C-2′′); $J_{C,F}$ = 287.7 Hz. − MS (CI, NH_3, 170 eV); *m/z* (%): 699 (14) [M + NH_3, + H]$^+$, 595 (6) [M + NH_3, + 2 H, − R*]$^+$, 578 (12) [M + NH_3, − R*, − CH_3]$^+$, 440 (38) [$C_{16}H_{18}F_3INO_2$]$^+$, 336 (12) [$C_{16}H_{18}F_3INO_2$ − R*, + H]$^+$, 314 (84) [$C_{16}H_{18}F_3INO_2$ − I, + H]$^+$, 260 (100) [$C_9H_{13}N_4O_4$ + NH_3, + 2 H]$^+$, 243 (24) [$C_9H_{13}N_4O_4$ + 2 H]$^+$. − $C_{25}H_{31}F_3IN_5O_6$ (681.5): calcd. C 44.07, H 4.59, N 10.28; found C 44.24, H 4.56, N 10.11.

32: ^1H NMR: δ = 7.45−7.29 (m, 5 H), 5.31 (q, 1′′-H), 4.65 (d, 1′-H), 4.63 (dd, 2-H), 3.87 (ddd, 4-H), 3.79 (dd, 3-H), 3.74 (ddd, 2′-H), 3.66 (dd, 1-H), 3.62 (ddd, 6-H), 3.52 (m, 5′-H), 3.40 (s, OCH_3), 3.12 (d, 6′a-, 6′b-H), 2.88 (s, NCH_3), 2.39 (dddd, 3′β-H), 2.06 (m, 5α-H), 2.00 (dddd, 3′α-H), 1.77 (ddd, 5β-H), 1.70 (d, 2′′-H), 1.30 (m, 4′α-H), 1.17 (dddd, 4′β-H); $J_{1,2}$ = 7.5, $J_{2,3}$ = 5.5, $J_{3,4} = J_{4,5\alpha} = J_{4,5\beta} = J_{5\alpha,6} = J_{5\beta,6}$ = 3.5, $J_{1,6}$ = 7.0, $J_{1',2'}$ = 8.5, $J_{2',3'\alpha} = J_{3'\alpha,3'\beta} = J_{3'\alpha,4'\beta} = J_{4'\beta,5}$ = 13.5, $J_{2',3'\beta} = J_{5',6'a} = J_{5',6'b}$ = 5.0, $J_{3'\alpha,4'\alpha}$ = 4.5, $J_{3'\beta,4'\alpha} = J_{3'\beta,4'\beta}$ = 3.5 Hz. − ^{13}C NMR: δ = 158.0 (C=O), 157.6 (C=O), 138.1 (C_s), 128.9 (C_m), 128.4 (C_o), 127.6 (C_p), 104.0 (C-1′), 116.8 (q, CO*C*F_3), 79.2 (C-2), 76.7 (C-3), 76.4 (C-6), 74.7 (C-5′), 60.3 (C-1), 56.9 (OCH_3), 56.8 (C-4), 55.4 (C-1′′), 48.3 (C-6′), 36.2 (C-5′)*, 30.5 (NCH_3), 32.1 (C-2′)*, 27.6 (C-4)*, 27.5 (C-3)*, 17.9 (C-2′′); $J_{C,F}$ = 287.9 Hz. − MS (ESI); *m/z* (%): 720 (56) [M + K]$^+$, 704 (25) [M + Na]$^+$, 682 (100) [M + H]$^+$, 578 (7), 444 (18).

34: ^1H NMR: δ = 7.38 (m, 5 H), 6.62 (d, 1′-H), 5.30 (q, 1′′-H), 4.18 (m, 5′-H), 3.30 (dd, 6′a-H), 2.80 (dd, 6′b-H), 2.47 (m, 3′α-H), 2.25 (m, 3′β-H), 1.81 (dddd, 4′α-H), 1.69 (d, 2′′-H), 1.59 (dddd, 4′β-H); $J_{3'\alpha,4'\alpha} = J_{4'\alpha,3'\beta} = J_{4'\alpha,5}$ = 3.75, $J_{3'\alpha,4'\beta,} = J_{4'\beta,5}$ = 14.0, $J_{4'\alpha,4'\beta}$ = 14.0, $J_{5',6'a}$ = 3.0, $J_{5',6'b}$ = 9.0, $J_{6'a,6'b}$ = 14.0 Hz. − ^{13}C NMR: δ = 146.6 (C-1′), 138.3 (C_s), 129.0 (C_m), 128.3 (C_o), 127.2 (C_p), 76.6 (C-5′), 55.4 (C-1′′), 49.4 (C-6′), 32.1 (C-3′)*, 28.3(C-4′), 18.0 (C-2′′). − MS (CI, isobutane, 70 eV); *m/z* (%): 440 (91) [M + H]$^+$, 336 (18) [M − R*, + 2 H]$^+$, 314 (100) [M − I, + 2 H]$^+$, 210 (99) [M − R*, − I, + 3 H]$^+$, 105 (32) [R*]$^+$.

4-Azido-3-O-{2′β-iodo-6′-[(1R)-phenylethyl]amino-2′,3′,4′,6′-tetradeoxy-α-D-hexopyranosyl}-1-N,2-O-carbonyl-1,4,5-trideoxy-6-O-methyl-1-methylamino-L-chiro-inositol (**28**): A solution of **27** (100 mg, 0.15 mmol) in anhydrous ethanol (30 ml) was treated with $NaBH_4$ (17 mg, 0.45 mmol) at room temp.; after stirring for 6 h, the reaction was complete [TLC control, $CHCl_3$/methanol, 10:1, R_f (**27**) = 0.74, R_f (**28**) = 0.5]. Excess of $NaBH_4$ was destroyed with acetic acid (pH = 7), the solvent removed in vacuo and the residue dissolved in water. Extraction with CH_2Cl_2, drying ($MgSO_4$), concentration in vacuo, and filtration through silica gel ($CHCl_3$/methanol, 10:1) provided **28** (77 mg, 87%) as colorless oil. $[\alpha]_D^{25}$ = +8.0 (*c* = 0.1 $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 2106 cm^{-1} (N_3), 1765 (NCOO). − ^1H NMR: δ = 7.32 (m, 5 H), 5.44 (s, 1′-H), 4.50 (dd, 2-H), 4.29 (m, 2′-H), 4.09 (m, 5′-H), 3.85−3.60 (m, 1-, 3-, 4-, 6-, 1′′-H, NH), 3.40 (s, OCH_3), 2.81 (s, NCH_3), 2.54 (m, 6′a-, 6′b-H), 2.18 (m, 5-H_2), 1.90/1.65 (m, 3 H/1 H, 4′-, 3′-H_2), 1.32 (d, 2′′-H); $J_{1',2'} < 1$, $J_{1,2}$ = 7.3, $J_{2,3}$ = 6.4 Hz. − ^{13}C NMR: δ = 158.1 (C=O), 128.8 (C_m), 126.8 (C_o), 126.7 (C_p), 99.2 (C-1′), 77.8 (C-2)*, 77.4 (C-3)*, 74.0 (C-6), 68.9 (C-5′), 60.9 (C-1), 57.7 (OCH_3)*, 57.1 (C-1′′)*, 56.8 (C-4)*, 51.7 (C-6′), 30.4 (NCH_3), 28.5 (C-5′), 28.0 (C-4′)*, 27.4 (C-3′)*, 24.7 (C-2′), 24.5 (C-2′′). − MS (FAB); *m/z* (%): 586 (86) [M + H]$^+$, 482 (6) [M + 2 H, − R*]$^+$, 458 (6) [M − I]$^+$, 307 (22) [M − R*, − OCH_3, − CH_3, − I]$^+$, 330 (8) [$C_{14}H_{19}INO$ + H, − CH_3]$^+$, 240 (29) [$C_9H_{13}N_4O_4$ − H, $C_{14}H_{19}INO$ − R*, + H]$^+$, 105 (100) [R*]$^+$.

4-Azido-3-O-{2′β-iodo-6′-[methyl,(1R)-phenylethyl]amino-2′,3′,4′,6′-tetradeoxy-α-D-hexopyranosyl}-1-N,2-O-carbonyl-1,4,5-trideoxy-6-O-methyl-1-methylamino-L-chiro-inositol (**29**), *4-Azido-3-O-{2′β-iodo-6′-[dimethyl,(1R)-phenylethyl]amino-2′,3′,4′,6′-tetradeoxy-α-D-hexopyranosyl}-1-N,2-O-carbonyl-1,4,5-trideoxy-6-O-methyl-1-methylamino-L-chiro-inositol Iodide* (**35**): A solution of **28** (50 mg, 0.085 mmol) in anhydrous acetonitrile was treated with K_2CO_3 (70 mg, 0.5 mmol) and CH_3I (106 µl, 1.70 mmol). After stirring for 2 h at room temp., excess of CH_3I was destroyed with 2 N NaOH. The acetonitrile was removed in vacuo, the remaining solution diluted and extracted with CH_2Cl_2. After drying ($MgSO_4$) and concentration in vacuo, chromatography on silica gel [ethyl acetate, R_f (**29**) = 0.45, R_f (**28**) = 0.25] gave **29** (37 mg, 72%) and **28** (11 mg, 22%) as colorless oils. After 24 h reaction time, **29** (24 mg, 47%) and **35** (29 mg, 46%) were isolated chromatographically [$CHCl_3$/methanol, 5:1, R_f (**29**) = 0.40, R_f (**35**) = 0.21], the latter as yellowish solid.

29: $[\alpha]_D^{25}$ = +13.9 (*c* = 0.1, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 2105 cm^{-1} (N_3), 1774 (NCOO). − ^1H NMR: δ = 7.30 (m, 5 H), 5.41 (s, 1′-H), 4.50 (dd, 2-H), 4.27 (m, 2′-H), 4.09 (m, 5′-H), 3.80 (dd, 3-H), 3.76−3.60 (m, 1-, 4-, 6-, 1′′-H), 3.39 (s, OCH_3), 2.80 (s, NCH_3), 2.60 (dd, 6′a-H), 2.48 (dd, 6′b-H), 2.22 (s, NCH_3), 2.10 (dddd, 5α-H), 1.90 (dddd, 5β-H), 1.71 (m, 4′-H_2), 1.60 (m, 3′-H_2), 1.47 (d, 2′′-H); $J_{1',2'} < 1$, $J_{5',6'a}$ = 6.2, $J_{5',6'b}$ = 5.9, $J_{6'a,6'b}$ = 13.4, $J_{1,2}$ = 7.8, $J_{2,3}$ = 6.4, $J_{3,4}$ = 9.6, $J_{4,5\alpha}$ = 4.5, $J_{5\alpha,6}$ = 4.5, $J_{4,5\beta}$ = 7.0, $J_{5\alpha,5\beta}$ = 14.2 Hz. − ^{13}C NMR: δ = 128.1 (C_m), 127.9 (C_o), 126.7 (C_p), 99.3 (C-1′), 78.0 (C-2)*, 77.4 (C-3)*, 74.2 (C-6)*, 68.9 (C-5′), 63.0 (C-1′′), 61.0 (C-1), 58.4 (OCH_3)*, 57.1 (C-6′)*, 56.9 (C-4)*, 39.5 (NCH_3), 30.5 (NCH_3), 28.5 (C-5′), 28.4 (C-4′)*, 28.4 (C-3*), 25.7 (C-2′′). − MS (FAB); *m/z* (%): 600 (42) [M]$^+$, 496 (6) [M − R*, + H]$^+$, 307 (44) [M − R*N(CH_3), − OCH_3, − HI]$^+$, 246 (10) [$C_{15}H_{21}INO_2$ − HI]$^+$, 243 (12) [$C_9H_{13}N_4O_4$ + 2 H]$^+$, 232 (12) [$C_{15}H_{21}INO$ − HI, + 2 H]$^+$, 184 (10) [$C_9H_{13}N_4O_3$ − N_3, + H]$^+$, 179 (12) [$C_9H_{13}N_4O_3$ − CH_3, − OCH_3]$^+$, 136 (100) [RN(CH_3)H_2]$^+$, 105 (100) [R*]$^+$.

35: M.p. 169°C. − IR (KBr): $\tilde{\nu}$ = 2103 cm^{-1} (N_3), 1760 (NCOO). − ^1H NMR: δ = 7.65 (m, 2 H), 7.49 (m, 3 H), 5.42 (s, 1′-H), 4.72 (q, 1′′-H), 4.58 (dd, 2-H), 4.39 (m, 2′-H), 3.85 (dd, 1-H), 3.79−3.70 (m, 3-, 4-, 6-H), 3.55 [s, NCH_3(q)], 3.43 (s, OCH_3), 3.38 (dd, 6′a-H), 3.11 [s, NCH_3 (q)], 2.95 (dd, 6′b-H), 2.81 (s, NCH_3), 2.25 (m, 5α-H), 3′α-H), 2.07 (dddd, 3′β-H), 1.90 (dddd, 1 H, 4′α-H), 1.83 (d, 2′′-H), 1.71 (dddd, 4′β-H), 1.60 (ddd, 5β-H); $J_{1',2'} < 1$, $J_{2',3'\alpha} = J_{2',3'\beta} = J_{3'\alpha,4'\alpha} = J_{3'\beta,4'\beta} = J_{3'\beta,4'\alpha} = J_{4'\alpha,5}$ =

3.8, $J_{3'\alpha,3'\beta} = J_{4'\alpha,4'\beta} = 13.0$, $J_{3'\alpha,4'\beta} = J_{4'\alpha,5'} = 12.3$, $J_{1,2} = J_{2,3} = 7.2$, $J_{4,5\alpha} = J_{5\alpha,6} = 3.8$, $J_{4,5\beta} = 10.2$, $J_{5\alpha,5\beta} = 13.0$ Hz. − ^{13}C NMR: δ = 158.3 (C=O), 144.8 (C_s), 132.6 (C_m), 139.9 (C_o), 129.5 (C_p), 102 6 (C-1′), 83.0 (C-2), 76.6 (C-3), 74.7 (C-5′)*, 73.4 (C-6)*, 66.7 (C-6′)*, 65.4 (C-1′′)*, 60.5 (C-1), 58.0 (C-4)*, 57.5 (OCH_3)*, 48.1 (NCH_3), 47.5 (NCH_3), 30.4 (NCH_3), 28.5 (C-5), 26.8 (C-4′), 26.3 (C-3′), 24.7 (C-2′), 15.5 (C-8′). − MS (CI, isobutane, 200 eV); *m/z* (%): 614 (4) $[M]^+$, 599 (2) $[M - CH_3, + H]^+$, 552 (7) $[M - 2 \times CH_3, - OCH_3, - H]^+$, 510 (100) $[M - R^*, + H]^+$, 382 (41) $[M - R^*, - I]^+$, 268 (14) $[C_{16}H_{24}INO - R^*]^+$, 243 (3) $[C_9H_{13}N_4O_4 + 2 H]^+$, 105 (71) $[R^*]^+$, 140 (7) $[C_{16}H_{24}INO, - R^*, - HI]^+$.

4-Azido-3-O-{6′-[methyl,(1R)-phenylethyl]amino-2′,3′,4′,6′-tetradeoxy-α-D-hex-2′-eno-pyranosyl}-1,4,5-trideoxy-6-O-methyl-1-methylamino-L-chiro-inositol (**30**): A solution of **29** (30 mg, 0.05 mmol) in 3% methanolic NaOH (5 ml) and water (5 ml) was refluxed for 2 h (TLC, $CHCl_3$/methanol, 10:1, R_f = 0.24). The solution was concentrated to half its volume and diluted with water. After extraction with CH_2Cl_2 and drying ($MgSO_4$), concentration in vacuo gave **30** (21 mg, 94%) as colorless oil. $[\alpha]_D^{25} = +8.1$ (*c* = 0.1, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 3433 cm^{-1} (OH), 2107 (N_3). − ^{1}H NMR: δ = 7.30 (m, 5 H), 6.00 (m, 2′-H), 5.77 (m, 3′-H), 5.36 (br. s, 1′-H), 4.23 (dd, 2-H), 4.12 (m, 5′-H), 3.90 (dd, 3-H), 3.90 (ddd, 4-H), 3.62 (q, 1′′-H), 3.54 (ddd, 6-H), 3.40 (s, OCH_3), 2.97 (dd, 1-H), 2.65 (dd, 6′a-H), 2.35 (s, NCH_3), 2.27 (s, NCH_3), 2.22 (dd, 6′b-H), 2.05 (m, 5α-H), 1.91 (m, 5β-H), 1.85−1.70 (m, 4′-H_2), 1.40 (d, 2′′-H); $J_{2',3'} = 10.1$, $J_{5',6'a} = 8.8$, $J_{6'a,6'b} = 13.1$, $J_{1,2} = 3.7$, $J_{2,3} = J_{3,4} = 9.2$, $J_{4,5\alpha} = 4.5$, $J_{4,5\beta} = 9.2$, $J_{5\alpha,6} = J_{5\beta,6} = J_{1,6} = 3.8$ Hz. − ^{13}C NMR: δ = 142.2 (C_s), 128.8 (C_m), 128.1 (C_o, C_p), 127.1 (C-2′), 125.7 (C-3′), 90.5 (C-1′), 80.2 (C-2)*, 75.5 (C-3)*, 67.7 (C-6), 65.1 (C-5′), 64.2 (C-1′′), 63.7 (C-1), 57.7 (OCH_3)*, 56.8 (C-6′)*, 56.7 (C-4)*, 40.7 (NCH_3), 35.1 (NCH_3), 28.8 (C-5), 28.3 (C-4′), 18.7 (C-2′′). − MS (FAB); *m/z* (%): 446 (46) $[M]^+$, 307 (8) $[M - R^*, - H_2O, - CH_3, - H]^+$, 230 (10) $[C_{15}H_{20}NO]^+$, 165 (18) $[C_8H_{15}N_4O_2 - H_2O, - CH_3, - H]^+$, 155 (20) $[C_8H_{15}N_4O_2 - N_3, - 2 H]^+$, 136 (100) $[R^*(NCH_3)H_3]^+$, 105 (98) $[R^*]^+$.

4-Azido-3-O-{6′-[methyl,(1R)-phenylethyl]amino-2′,3′,4′,6′-tetradeoxy-α-D-hex-2′-eno-pyranosyl}-1,4,5-trideoxy-6-O-methyl-1-(benzyloxycarbonylglycyl)methylamino-L-chiro-inositol (**31**): **30** (20 mg, 0.045mmol) was treated according to GP 2 [Z-gly-*O*-suc (21 mg, 0.07 mmol), DMF, 20 h, 70°C] to yield after twofold chromatography ($CHCl_3$/methanol, 10:1, R_f = 0.36) **31** (22 mg, 77%) as colorless oil. − IR (KBr): $\tilde{\nu}$ = 2103 cm^{-1} (N_3), 1719 (NHCOO), 1655 (NHCO), 1560 (NHCO). − ^{1}H NMR: δ = 7.30 (m, 10 H), 6.00 (m, 2′-H), 5.80 (m, 3′-H), 5.72 (m, 1′-H), 5.60 [s, CH_2, (Z)], 4.45 (dd, 1-H), 4.20−3.85 [m, 5′-, 2-, 3-, 6-H, CH_2, (Gly)], 3.69−3.62 (m, 4-, 1′′-H), 3.34 (s, OCH_3), 2.98 (s, NCH_3), 2.60 (dd, 6′α-H), 2.32 (s, NCH_3), 1.95 (m, 5β-H), 1.85 (m, 5α-H), 1.48 (d, 2′′-H), 1.32−1.20 (m, 4′-H_2). − ^{13}C NMR: δ = 129.2−127.8 (10 C), 127.0 (C-2′), 125.3 (C-3′), 95.3 (C-1′), 77.2 (C-2)*, 76.9 (C-3)*, 75.5 (C-6)*, 69.9 (C-5′), 66.8 [CH_2, (Z)], 63.9 (C-1′′), 60.1 (C-1), 58.1 (OCH_3)*, 58.0 (C-6′)*, 55.8 (C-4)*, 43.4 [CH_2, (Gly)], 40.5 (NCH_3), 30.2 (NCH_3), 29.7 (C-5), 28.6 (C-4′), 18.0 (C-2′′). − MS (FAB); *m/z* (%): 637 (14) $[M]^+$, 400 (18) $[M - R^*, - Z, - 2 H]^+$, 390 (8) $[C_{18}H_{24}N_5O_5]^+$, 358 (20) $[C_{18}H_{24}N_5O_5 - OCH_3, - H]^+$, 343 (6) $[C_{18}H_{24}N_5O_5 - OCH_3, - H_2O]^+$, 326 (5) $[C_{18}H_{24}N_5O_5 - OCH_3, - CH_3, - H_2O]^+$, 289 (18) $[M - R^*N(CH_3), - Z\text{-}Gly\text{-}N(CH_3), + 2 H]^+$, 230 (16) $[C_{15}H_{20}NO]^+$, 105 (96) $[R^*]^+$.

4-Amino-3-O-(6′-methylamino-2′,3′,4′,6′-tetradeoxy-α-D-hexopyranosyl)-1,4,5-trideoxy-6-O-methyl-1-(glycyl)methylamino-L-chiro-inositol (**3**): **31** (20 mg, 0.031 mmol) was treated according to GP 3 (9 h) to give **3** (13 mg, 89%, TLC: 2-propanol/water/25% NH_3, 4:1:1, R_f = 0.40) as solid trishydrochloride. − IR (KBr): $\tilde{\nu}$ = 1735 cm^{-1} (NHCO), 1655 (sec. NH_2^+), 1459 (prim. NH_3^+), 1038 (m, OH). − ^{1}H NMR (D_2O, CH_3CN): δ = 4.83 (br. s, 1′-H), 4.68 (dd, 1-H), 4.25 (ddd, 6-H), 4.20 (m, 2-, 3-H), 4.10 (m, CH_2), 3.70 (m, 4-, 5′-H), 3.49 (s, OCH_3), 3.10 (s, NCH_3), 2.82 (m, 6′-H), 2.79 (s, NCH_3), 2.60 (ddd, 5β-H), 2.10 (m, 5α-H), 1.80−1.50 (m, 2′-, 3′-, 4′-H_2); $J_{5',6'a} = 3.5$, $J_{5',6'b} = 6.5$, $J_{6'a,6'b} = 13.0$, $J_{1,2} = 3.0$, $J_{1,6} = 11.0$, $J_{4,5\alpha} = 4.6$, $J_{4,5\beta} = J_{5\beta,6} = 4.6$, $J_{5\alpha,5\beta} = 13.7$, $J_{5\alpha,6} =$ 11 Hz. − ^{13}C NMR (D_2O, CH_3CN): δ = 90.8 (C-1′), 74.1 (C-3), 70.4 (C-6), 69.3 (C-2), 65.8 (C-5′), 56.3 (C-1), 55.6 (OCH_3), 51.4 (C-6′), 48.7 (C-4), 40.8 (CH_2), 33.4 (NCH_3), 31.4 (NCH_3), 28.9 (C-5), 27.3 (C-2′), 26.8 (C-4′), 21.9 (C-3′). − MS (FAB); *m/z* (%): 369 (24) $[M - 4 H]^+$, 335 (22) $[M - 4 H, - NH_2, - H_2O]^+$, 277 (100) $[M - 4 H, - NH_2, - H_2O, - COCH_2NH_2]^+$, 243 (75) $[C_{10}H_{20}N_3O_4 - 3 H]^+$, 185 (100) $[C_{10}H_{20}N_3O_4 - 3 H, - COCH_2NH_2]^+$, 128 (63) $[C_7H_{14}NO]^+$.

4-Azido-3-O-{2′β,6′-[(1R)-phenylethyl]amino-3′,4′,6′-trideoxy-α-D-hexopyranosyl}- (**42**), *4-Azido-3-O-{2′α,6′-[(1R)-phenylethyl]-amino-3′,4′,6′-trideoxy-α-D-hexopyranosyl}-* (**43**), *and 4-Azido-3-O-{6′-[(1R)-phenylethyl]amino-2′,3′,4′,6′-tetradeoxy-α-D-hexopyranosyl}-1-N,2-O-carbonyl-1,4,5-trideoxy-6-O-methyl-1-methylamino-L-chiro-inositol* (**44**): Through a solution of **27** (50 mg, 0.073 mmol) in benzene (30 ml) in the presence of Bu_3SnH (58 µl, 0.22 mmol) a continuous stream of oxygen was run (48 h at 50°C). The reaction mixture was concentrated in vacuo to 5 ml and diluted with methanol (30 ml). After addition of $NaBH_4$ (30 mg), the mixture was stirred for 4 h at room temp.; methanol was removed in vacuo, the residue dissolved in water and extracted with CH_2Cl_2. After drying ($MgSO_4$), concentration in vacuo, and chromatograpy on silica gel [$CHCl_3$/methanol, 10:1, R_f (**44**) = 0.43, R_f (**43**) = 0.2, R_f (**42**) = 0.15], the three components **44** (14 mg, 42%), **43** (3 mg, 8%), and **42** (13 mg, 37%) were isolated as colorless oils.

42: IR (KBr): $\tilde{\nu}$ = 3449 cm^{-1} (OH), 2106 (N_3), 1763 (NCOO). − ^{1}H NMR: δ = 7.31 (m, 5 H), 5.16 (s, 1′-H), 4.52 (dd, 2-H), 4.02 (m, 5′-H), 3.87−3.60 (m, 2′-, 1′′-, 1-, 3-, 4-, 6-H), 3.42 (s, OCH_3), 2.82 (s, NCH_3), 2.50 (m, 6′a-, 6′b-H), 2.16 (dddd, 5α-H), 2.00 (m, 5β-H), 1.78−1.40 (m, 3′-, 4′-H_2), 1.32 (d, 2′′-H); $J_{1',2'} < 1$, $J_{1,2} = J_{2,3} = 7.2$, $J_{4,5\alpha} = J_{5\alpha,6} = 4.7$, $J_{5\alpha,5\beta} = 15$ Hz. − ^{13}C NMR: δ = 128.4 (C_m), 126.7 (C_p), 98.4 (C-1′), 77.9 (C-2)*, 77.2 (C-2′)*, 77.1 (C-3)*, 74.2 (C-6), 65.9 (C-5′), 61.0 (C-1), 57.8 (C-1′′)*, 57.1 (C-4)*, 56.8 (OCH_3)*, 51.8 (C-6′), 30.4 (NCH_3), 29.7 (C-5), 28.5 (C-4′)*, 24.7 (C-3′)*, 22.4 (C-2′′). − MS (FAB); *m/z* (%): 476 (40) $[M]^+$, 460 (7) $[M - CH_3, - H]^+$, 433 (8) $[M - N_3, + H]^+$, 372 (6) $[M - R^*, + H]^+$, 307 (12) $[M - R^*, - OCH_3, - CH_3, - H_2O]^+$, 234 (12) $[C_{14}H_{20}NO_2]^+$, 217 (8) $[C_{14}H_{20}NO_2 - OH]^+$, 179 (26) $[C_9H_{13}N_4O_3 - OCH_3 - CH_3]^+$, 105 (100) $[R^*]^+$.

43: IR (KBr): $\tilde{\nu}$ = 3448 cm^{-1} (OH), 2106 (N_3), 1758 (NCOO). − ^{1}H NMR: δ = 7.32 (m, 5 H), 5.30 (d, 1′-H), 4.60 (dd, 2-H), 3.97 (m, 5′-H), 3.88 (dd, 3-H), 3.82−3.60 (m, 2′-, 1-, 4-, 6-, 1′′-H), 3.43 (s, OCH_3), 2.87 (s, NCH_3), 2.55 (dd, 6′a-H), 2.48 (dd, 6′b-H), 2.20 (ddd, 5α-H), 1.85−1.40 (m, 5β-H, 3′-, 4′-H_2), 1.35 (d, 2′′-H); $J_{1',2'} = 3.5$, $J_{5',6'a} = 3.5$, $J_{5',6'b} = 7.2$, $J_{6'a,6'b} = 12.3$, $J_{1,2} = J_{2,3} = 7.2$, $J_{2,3} = 9.4$, $J_{4,5\alpha} = J_{5\alpha,6} = 4.6$, $J_{5\alpha,5\beta} = 14.2$ Hz. − MS (FAB); *m/z* (%): 476 (77) $[M]^+$, 460 (82) $[M - CH_3, - H]^+$, 372 (4) $[M - R^* + H]^+$, 329 (4) $[M - R^*, - N_3]^+$, 307 (24) $[M - R^*, - OCH_3, - CH_3, - H_2O]^+$, 242 (8) $[C_9H_{13}N_4O_4 + H]^+$, 234 (18) $[C_{14}H_{20}NO_2]^+$, 183 (16) $[C_9H_{13}N_4O_3 - N_3]^+$, 179 (46) $[C_9H_{13}O_3N_4 - OCH_3, - CH_3]^+$, 105 (100) $[R^*]^+$.

44: IR (KBr): $\tilde{\nu}$ = 2105 cm^{-1} (N_3), 1769 (NCOO). − ^{1}H NMR: δ = 7.31 (m, 5 H), 5.30 (br. s, 1′-H), 4.50 (dd, 2-H), 3.97 (m, 5′-H), 3.85−3.60 (m, 1-, 3-, 4-, 6-, 1′′-H), 3.40 (s, OCH_3), 2.81 (s, NCH_3), 2.46 (m, 6′a-, 6′b-H), 2.10 (dddd, 5α-H), 1.82 (m, 5β-H), 1.75−1.35 (m, 2′-, 3′-, 4′-H_2), 1.30 (d, 2′′-H); $J_{1,2} = J_{2,3} = 6.7$,

$J_{4,5\alpha} = J_{5\alpha,6} = 4.3$, $J_{5\alpha,5\beta} = 14.0$ Hz. − MS (FAB); *m/z* (%): 460 (100) $[M]^+$, 307 (12) $[M - R^*, - OCH_3, - CH_3, - 2\ H]^+$, 234 (14) $[C_{14}H_{20}NO_2]^+$, 218 (16) $[C_{14}H_{20}NO]^+$, 183 (10) $[C_9H_{13}N_4O_3 - N_3]^+$, 179 (44) $[C_9H_{13}N_4O_3 - OCH_3, - CH_3]^+$, 105 (100) $[R^*]^+$.

4-Azido-3-O-[6′-{trifluoroacetyl[(1R)-phenylethyl]}amino-2′β-O-(2,2,6,6-tetramethylpiperidinyl)-3′,4′,6′-trideoxy-α-D-hexopyranosyl]- (**36**), *4-Azido-3-O-[6′-{trifluoroacetyl[(1R)-phenylethyl]}amino-2′α-O-(2°,2°,6°,6°-tetramethylpiperidinyl)-3′,4′,6′-trideoxy-α-D-hexopyranosyl]-* (**45**), *and 4-Azido-3-O-[6′-{trifluoroacetyl[(1R)-phenylethyl]}amino-2′,3′,4′,6′-tetra-deoxy-α-D-hexopyranosyl]-1-N,2-O-carbonyl-1,4,5-trideoxy-6-O-methyl-1-methylamino-L-chiro-inositol* (**46**): A solution of **27** (114 mg, 0.167 mmol), TEMPO (78 mg, 0.5 mmol), and Bu_3SnH (89 µl, 0.335 mmol) in anhydrous benzene (50 ml) was refluxed for 4.5 h (total conversion, TLC). The solvent was removed in vacuo and the residue chromatographed on silica gel [CH_2Cl_2/acetone, 10:1, R_f (**27**) = 0.62, R_f (**45**) = 0.72, R_f (**46**) = 0.65, R_f (**36**) = 0.49] to give **45** (5 mg, 4%), **46** (6 mg, 6%) and **36** (93 mg, 78%), **36** and **45** as colorless solids, **46** as colorless oil.

36: M.p. 63°C. − IR (KBr): $\tilde{\nu}$ = 2102 cm^{-1} (N_3), 1764 (NCOO), 1676 (NR*$COCF_3$). − ^{1}H NMR: δ = 7.32 (m, 5 H), 5.53 (s, 1′-H), 5.25 (q, 1′′-H), 4.52 (dd, 2-H), 4.20 (m, 5′-H), 3.80−3.60 (m, 1-, 3-, 4-, 6-, 2′-H), 3.41 (s, OCH_3), 3.28 (dd, 6′a-H), 2.85 (s, NCH_3), 2.66 (dd, 6′b-H), 2.10 (ddd, 5α-H), 1.90 (m, 5β-H), 1.73 (d, 2′′-H), 1.52 (s, 4CH_3), 1.65−1.15 (m, 3′-, 4′-, 3°-, 4°-, 5°-H_2); $J_{1',2'} < 1$, $J_{5',6'a} = 2.1$, $J_{5',6'b} = 8.9$, $J_{6'a,6'b} = 14.0$, $J_{1,2} = 7.3$, $J_{2,3} = 6.1$, $J_{4,5\alpha} = J_{5\alpha,6} = 4.3$, $J_{5\alpha,5\beta} = 14.7$ Hz. − ^{13}C NMR: δ = 158.1 (C=O), 139.1 (C_s), 128.8 (C_m), 127.9 (C_o), 127.2 (C_p), 117.0 (q, CO*C*F_3), 95.3 (C-1′), 78.1 (C-2)*, 77.4 (C-2′)*, 75.7 (C-3)*, 74.3 (C-6)*, 65.2 (C-5′), 61.1 (C-1), 59.0 (C-2°, C-6°), 56.9 (OCH_3)*, 56.7 (C-4)*, 55.5 (C-1′′), 49.9 (C-6′), 40.4 (C-3°, C-4°, C-5°), 30.5 (NCH_3), 28.1 (C-5), 23.5 (C-4′)*, 23.1 (C-3′)*, 18.0 (CH_3)*, 17.2 (C-2′′)*; $J_{C,F}$ = 287.4 Hz. − MS (FAB); *m/z* (%): 733 (20) [M + Na]$^+$, 711 (100) $[M]^+$, 485 (14) $[C_{25}H_{36}F_3N_2O_4]^+$, 469 (20) $[C_{25}H_{36}F_3N_2O_3]^+$, 450 (12) $[M - R^*, - C_9H_{18}NO]^+$, 422 (15) $[M - R^*N(COCF_3), - N_3, - OCH_3]^+$, 341 (50) $[M - R^*N(COCF_3), - C_9H_{18}NO, + 2\ H]^+$, 329 (6) $[C_{25}H_{36}F_3N_2O_3 - C_9H_{18}NO]^+$, 307 (40) $[M - R^*\text{-}N(COCF_3), - OCH_3, - C_9H_{18}NO, + H]^+$, 243 (17), $[C_9H_{13}N_4O_4 - 2\ H]^+$, 200 (22) $[C_9H_{13}N_4O_4 - N_3, + H]^+$, 196 (48) $[C_9H_{13}N_4O_4 - OCH_3, - CH_3, + H]^+$, 105 (100) $[R^*]^+$. − $C_{34}H_{49}F_3N_6O_7$ (710.8): calcd. C 57.45, H 6.95, N 11.82; found C 57.39, H 7.18, N 10.82.

45: M.p. 66−68°C. − $[\alpha]_D^{25}$ = +13.6 (*c* = 0.1, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 2107 cm^{-1} (N_3), 1771 (NCOO), 1686 (NR*$COCF_3$). − ^{1}H NMR: δ = 7.32 (m, 5 H), 5.40 (d, 1′-H), 5.24 (m, 1′′-H), 4.60 (dd, 2-H), 4.17 (m, 5′-H), 3.70−3.50 (m, 1-, 3-, 4-, 6-, 2′-H), 3.42 (s, OCH_3), 3.22 (dd, 6a′-H), 2.88 (s, NCH_3); 2.59, (dd, 6′b-H), 2.08 (m, 5-H), 1.85 (dddd, 3′β-H), 1.70 (d, 2′′-H), 1.50−1.00 (m, 3′-, 4′-, 3°-, 4°-, 5°-H_2, 4 CH_3); $J_{1',2'} = 3.5$, $J_{2',3'\beta} = J_{3'\beta,4'\beta} = 7.8$, $J_{3'\alpha,3'\beta} = 16.3$, $J_{3'\beta,4'\alpha} = 4.0$, $J_{5',6'a} = 1.3$, $J_{5',6'b} = 8.3$, $J_{6'a,6'b} = 14.0$, $J_{1,2} = J_{2,3} = 7.3$ Hz. − ^{13}C NMR: δ = 138.9 (C_s), 128.8 (C_m), 128.0 (C_o), 127.2 (C_p), 95.8 (C-1′), 79.6 (C-2)*, 78.0 (C-2′)*, 75.9 (C-3)*, 74.6 (C-6)*, 65.6 (C-5′), 61.1 (C-1), 57.0 (OCH_3)*, 56.9 (C-4)*, 55.4 (C-1′′), 49.3 (C-6′), 40.3 (C-3°, C-4°, C-5°), 30.5 (NCH_3), 28.8 (C-5), 28.1 (C-4′), 23.9 (C-3′), 18.0 (CH_3)*, 17.2 (C-2′′)*. − MS (FAB); *m/z* (%): 711 (39) $[M]^+$, 554 (15) $[M - C_9H_{18}NO, - H]^+$, 469 (6) $[C_{25}H_{36}F_3N_2O_3]^+$, 450 (8) $[M - R^*, - C_9H_{18}NO]^+$, 422 (20) $[M - R^*N(COCF_3), - OCH_3, - N_3]^+$, 243 (8) $[C_9H_{13}N_4O_4 + 2\ H]^+$, 199 (8) $[C_9H_{13}N_4O_4 - N_3]^+$, 196 (21) $[C_9H_{13}N_4O_4 - OCH_3, - CH_3, + H]^+$, 105 (100) $[R^*]^+$. − $C_{34}H_{49}F_3N_6O_7$ (710.8): calcd. C 57.45, H 6.95, N 11.82; found C 57.15, H 6.89, N 11.50.

46: IR (KBr): $\tilde{\nu}$ = 2100 cm^{-1} (N_3), 1761 (NCOO), 1674 (NR*$COCF_3$). − ^{1}H NMR: δ = 7.32 (m, 5 H), 5.40 (br. s, 1′-H), 5.23 (q, 1′′-H), 4.52 (dd, 2-H), 4.20 (m, 5′-H), 3.70 (m, 1-, 3-, 4-, 6-H), 3.42 (s, OCH_3), 3.23 (dd, 6′a-H), 2.82 (s, NCH_3), 2.59 (dd, 6′b-H), 2.18 (ddd, 5α-H), 1.72 (d, 2′′-H), 1.90−1.50 (m, 5β-H, 2′-, 3′-, 4′-H_2); $J_{5',6'a} = 2.4$, $J_{5',6'b} = 8.9$, $J_{6'a,6'b} = 14.9$, $J_{1,2} = J_{2,3} = 7.3$, $J_{4,5\beta} = J_{5\beta,6} = 3.7$, $J_{4,5\alpha} = J_{5\alpha,6} = 4.5$, $J_{5\alpha,5\beta} = 14.4$ Hz. − ^{13}C NMR: δ = 158.2 (C=O), 139.0 (C_s), 128.8 (C_m), 128.0 (C_o), 127.3 (C_p), 117.1 (q, CO*C*F_3), 95.1 (C-1′), 78.7 (C-2)*, 76.1 (C-3)*, 74.2 (C-6)*, 65.7 (C-5′), 61.3 (C-1), 56.9 (OCH_3), 56.8 (C-4), 55.4 (C-1′′), 50.1 (C-6′), 30.4 (NCH_3), 29.2 (C-5), 28.6 (C-2′), 17.9 (C-3′, C-4′)*, 17.4 (C-2′′)*. − MS (EI), *m/z* (%): 555 (6) $[M]^+$, 450 (2) $[M - R^*]^+$, 313 (62) $[C_{16}H_{19}F_3NO_2 + H]^+$, 243 (96) $[C_9H_{13}N_4O_4 + 2H]^+$, 216 (21) $[C_{16}H_{19}F_3NO_2 - COCF_3 - H]^+$, 210 (28) $[C_{16}H_{19}F_3NO_2 - R^*, + H]^+$, 105 (100) $[R^*]^+$. − MS (NH_3, 170 eV); *m/z* (%): 573 (44) $[M + NH_4]^+$, 528 (6) $[M + NH_3, - CH_3, - OCH_3]^+$, 331 (10) $[C_{16}H_{19}F_3NO_2 + NH_3]^+$, 314 (100) $[C_{16}H_{19}F_3NO_2]^+$, 260 (44) $[C_9H_{13}N_4O_4 + NH_3, + 2\ H]^+$, 243 (7) $[C_9H_{13}N_4O_4 + 2\ H]^+$.

4-Amino-3-O-[2′β,6′-{trifluoroacetyl[(1R)-phenylethyl]}amino-3′,4′,6′-trideoxy-α-D-hexopyranosyl]- (**37a**) *and 4-Amino-3-O-[6′-{trifluoroacetyl[(1R)-phenylethyl]}amino-2′β-O-(2°,2°,6°,6°-tetramethylpiperidinyl)-3′,4′,6′-trideoxy-α-D-hexopyranosyl]-1-N,2-O-carbonyl-1,4,5-trideoxy-6-O-methyl-1-methylamino-L-chiro-inositol* (**47**): To a solution of **36** (85 mg, 0.12 mmol) in acetic acid (10 ml) was added zinc powder (150 mg). After stirring for 40 h at room temp., the zinc was removed by filtration, the filtrate was neutralized with saturated sodium hydrogen carbonate solution, and extracted with CH_2Cl_2. After drying ($MgSO_4$), concentration in vacuo, and chromatography on silica gel ($CHCl_3$/methanol, 10:1, R_f = 0.22), **37a** (55 mg, 84%) was obtained as colorless oil. If the reaction was quenched after 6 h, besides **37a** (26%) the precursor **47** (63%) was isolated.

37a: $[\alpha]_D^{25}$ = +17.2. − (*c* = 0.1, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 1765 cm^{-1} (NCOO), 1678 (NR*$COCF_3$). − ^{1}H NMR: δ = 7.48 (m, 5 H), 5.26 (q, 1′′-H), 5.18 (s, 1′-H), 4.43 (dd, 2-H), 4.32 (m, 5′-H), 3.72 (ddd, 1-H), 3.63 (m, 2′-, 6-H), 3.49 (dd, 3-H), 3.48 (s, OCH_3), 3.16 (dd, 6′a-H), 2.95 (ddd, 4-H), 2.83 (s, NCH_3), 2.70 (dd, 6′b-H), 2.12 (dddd, 5α-H), 1.92 (m, 5β-H), 1.62 (d, 2′′-H), 1.70−1.20 (m, 3′-, 4′-H_2); $J_{1',2'} < 1$, $J_{5',6'a} = 2.4$, $J_{5',6'b} = 9$, $J_{6'a,6'b} = 14$, $J_{1,2} = J_{2,3} = 7.3$, $J_{3,4} = 10$, $J_{4,5\alpha} = 4.3$, $J_{4,5\beta} = 10.0$, $J_{5\alpha,5\beta} = 14.6$, $J_{1,6} = 4.0$ Hz. − ^{13}C NMR: δ = 138.6 (C_s), 128.9 (C_m), 128.2 (C_o), 127.2 (C_p), 117.0 (q, CO*C*F_3), 97.9 (C-1′), 80.4 (C-2)*, 78.6 (C-2′)*, 74.5 (C-3)*, 65.6 (C-6), 64.1 (C-5′), 62.0 (C-1), 56.6 (C-1′′)*, 55.7 (OCH_3)*, 49.6 (C-6′), 45.8 (C-4), 31.0 (NCH_3), 30.3 (C-5), 25.1 (C-4′), 22.6 (C-3′), 17.8 (C-2′′). − MS (FAB); *m/z* (%): 568 (9) $[M + Na + H]^+$, 546 (51) $[M]^+$, 424 (9) $[M - R^*, - OH]^+$, 350 (8) $[M - R^*, - CO_2, - OCH_3, - NH_2]^+$, 330 (25) $[C_{16}H_{19}F_3NO_3]^+$, 226 (18) $[C_{16}H_{19}F_3NO_3 - R^*, + H]^+$, 217 (63) $[C_9H_{15}N_2O_4 + 2\ H]^+$, 199 (19) $[C_9H_{15}N_2O_3]^+$, 155 (25) $[C_9H_{15}N_2O_3 - CO_2]^+$, 105 (100) $[R^*]^+$.

47: $[\alpha]_D^{25}$ = +40.8 (*c* = 0.1, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 1768 cm^{-1} (NCOO), 1684 (NR*$COCF_3$). − ^{1}H NMR: δ = 7.30 (m, 5 H), 5.54 (s, 1′-H), 5.27 (q, 1′′-H), 4.45 (dd, 2-H), 4.31 (m, 5′-H), 3.72−3.58 (m, 2′-, 1-, 6-H), 3.40 (dd, 3-H), 3.38 (s, OCH_3), 3.20 (dd, 6′a-H), 2.95 (ddd, 4-H), 2.82 (s, NCH_3), 2.10 (m, 5α-H), 1.90 (m, 5β-H), 1.70 (d, 2′′-H), 1.80−1.20 (m, 3′-, 4′-H_2, 4 CH_3, 3′′-, 4′′-, 5′′-H_2); $J_{1',2'} < 1$, $J_{5',6'a} = 2.7$, $J_{5',6'b} = 9.9$, $J_{6'a,6'b} = 14.2$, $J_{1,2} = J_{2,3} = 7.2$ Hz. − MS (FAB); *m/z* (%): 685 (36) $[M]^+$, 469 (4) $[C_{25}H_{36}F_3N_2O_3]^+$, 424 (6) $[M - R^*, - C_9H_{18}NO]^+$, 330 (10) $[C_{25}H_{36}F_3N_2O_3 - C_9H_{18}N, + H]^+$, 217 (8) $[C_9H_{15}N_2O_4 + 2\ H]^+$, 200 (28) $[C_9H_{15}N_2O_3 + H, C_9H_{15}N_2O_4 - NH_2, + H]^+$, 105 (100) $[R^*]^+$.

3-O-[2′β,6′-{Trifluoroacetyl[(1R)-phenylethyl]}amino-3′,4′,6′-trideoxy-α-D-hexopyranosyl]-1-N,2-O-carbonyl-1,4,5-trideoxy-6-O-methyl-4-(benzyloxycarbonylamino)-1-methylamino-L-chiro-inositol (**37b**): A solution of **37a** (50 mg, 0.09 mmol) and Z-*O*-suc (27 mg, 0.11 mmol) in DMF (20 ml) was stirred 14 h at room temp.; the solvent was removed in vacuo and the residue chromatographed on silica gel ($CHCl_3$/methanol, 10:1, R_f = 0.43) to provide **37b** (59 mg, 95%) as colorless oil. $[\alpha]_D^{25}$ = +29.3 (*c* = 0.1, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 3365 cm^{-1} (OH), 1765 (NCOO), 1677 (NR*$COCF_3$). − ^{1}H NMR: δ = 7.32 (m, 10 H), 6.00 (d, NH), 5.22 (m, 1′-, 1′′-H, CH_2), 5.01 [d, CH_2, (Z)], 4.52 (dd, 2-H), 4.32 (m, 5′-H), 4.04 (dddd, 4-H), 3.73 (dd, 1-H), 3.68 (ddd, 6-H), 3.57 (m, 2′-H), 3.46 (dd, 3-H), 3.39 (s, OCH_3), 3.07 (dd, 6′a-H), 2.82 (s, NCH_3), 2.66 (dd, 6′b-H), 2.70 (ddd, 5α-H), 1.68 (d, 2′′-H), 1.65−1.10 (m, 5β-H, 4′-, 3′-H_2); $J_{1',2'}$ < 1, $J_{5',6'a}$ = 2.9, $J_{5',6'b}$ = 10.2, $J_{6'a,6'b}$ = 13.7, $J_{1,2}$ = $J_{2,3}$ = 7.2, $J_{3,4}$ = $J_{4,5\beta}$ = 11, $J_{4,5\alpha}$ = 3.5, $J_{5\alpha,5\beta}$ = 13.4, $J_{5\alpha,6}$ = $J_{5\beta,6}$ = 3.5, $J_{1,6}$ = 3.2 Hz. − ^{13}C NMR: δ = 158.3 (C=O), 156.5 (C=O), 138.3 (C_s), 129.3−127.2 (10 C), 117.3 (q, $COCF_3$), 96.5 (C-1′), 79.1 (C-2)*, 74.8 (C-2′)*, 73.9 (C-3)*, 72.8 (C-6)*, 66.4 (CH_2), 65.3 (C-5′), 62.5 (C-4), 61.6 (C-1), 56.7 (OCH_3), 56.1 (C-1′′), 49.5 (C-6′), 30.1 (NCH_3), 29.5 (C-5), 25.5 (C-4′)*, 24.7 (C-3′)*, 17.5 (C-2′′); $J_{C,F}$ = 287.9 Hz. − MS (FAB); *m/z* (%): 680 (16) $[M + H]^+$, 589 (8) $[M - C_7H_7]^+$, 529 (10) $[M - NHZ, - H]^+$, 513 (18) $[M - NHZ, - OH]^+$, 407 (18) $[M - NHZ, - R^*, - H_2O]^+$, 351 (100) $[C_{17}H_{21}N_2O_6 + 2 H]^+$, 330 (100) $[C_{16}H_{19}F_3NO_3]^+$, 260 (73) $[C_{17}H_{21}N_2O_6 + 2 H, - C_7H_7]^+$, 226 (100) $[C_{16}H_{19}F_3NO_3 - R^* + H]^+$, 200 (100) $[C_{17}H_{21}N_2O_6 - NHZ, + H]^+$, 105 (100) $[R^*]^+$.

3-O-{2′β,6′-[(1R)-Phenylethyl]amino-3′,4′,6′-trideoxy-α-D-threo-hexopyranosyl}-1-N,2-O-carbonyl-1,4,5-trideoxy-6-O-methyl-4-(benzyloxycarbonylamino)-1-(methylamino)-L-chiro-inositol (**38**): A solution of **37b** (60 mg, 0.088 mmol) in anhydrous ethanol (8 ml) was treated with $NaBH_4$ (10 mg, 0.26 mmol) at room temp.; after 4 h stirring at romm temp., conversion was complete [TLC, $CHCl_3$/methanol, 10:1, R_f (**37b**) = 0.52, R_f (**38**) = 0.12]. The solvent was removed in vacuo, the residue dissolved in water and extracted with CH_2Cl_2. After drying ($MgSO_4$) and concentration in vacuo the crude product was filtered through silica gel ($CHCl_3$/methanol, 10:1) to yield **38** (44 mg, 86%) as colorless oil. $[\alpha]_D^{25}$ = +12.1 (*c* = 0.2, $CHCl_3$). − ^{1}H NMR: δ = 7.28 (m, 10 H), 5.21 [d, CH_2, (Z)], 5.01 (br. s, 1′-H), 4.56 (dd, 2-H), 4.10 (m, 5′-H), 3.96 (m, 4-H), 3.80−3.70 (m, 1-, 6-H), 3.68−3.64 (m, 1′′-, 2′-H*), 3.52 (m, 3-H*), 3.40 (s, OCH_3), 2.80 (s, NCH_3), 2.38−2.12 (m, 6′a-, 6′b-, 5α-H), 1.80−1.30 (m, 5β-H, 3′-, 4′-H_2), 1.30 (d, 2′′-H). − ^{13}C NMR: δ = 158.6 (C=O), 156.7 [C=O, (Z)], 136.9 (C_s), 128.6−126.5 (10 C), 99.5 (C-1′), 79.3 (C-2)*, 77.3 (C-2′)*, 73.8 (C-3)*, 66.6 (C-6), 65.8 (C-5′), 61.7 (C-1), 58.6 (C-1′′)*, 56.4 (OCH_3)*, 50.8 (C-6′), 30.3 (NCH_3), 29.8 (C-5), 25.5 (C-3′), 23.3 (C-4′)*, 22.5 (C-2′′). − MS (FAB); *m/z* (%): 584 (100) $[M]^+$, 306 (9) $[C_{17}H_{21}N_2O_6 - CO_2, + H]^+$, 250 (8) $[C_{14}H_{20}NO_3]^+$, 234 (29) $[C_{14}H_{20}NO_2]^+$.

3-O-{2′β,6′-[(1R)-Phenylethyl]methylamino-3′,4′,6′-trideoxy-α-D-hexopyranosyl}-1-N,2-O-carbonyl-1,4,5-trideoxy-6-O-methyl-4-(benzyloxycarbonylamino)-1-(methylamino)-L-chiro-inositol (**39**): A solution of **38** (25 mg, 0.043 mmol) in acetonitrile (10 ml) was treated with K_2CO_3 (300 mg, 2.17 mmol) and CH_3I (53 µl, 0.857 mmol). After stirring for 2 h at room temp., the excess of CH_3I was destroyed with 2 N NaOH (5 ml). The reaction mixture was concentrated to its half, diluted with water and extracted with CH_2Cl_2. After drying ($MgSO_4$), concentration in vacuo and chromatography on silica gel [$CHCl_3$/methanol, 10:1, R_f (**38**) = 0.12, R_f (**39**) = 0.24], **39** (18 mg, 70%) and **38** (6 mg, 24%) were obtained as colorless oils. $[\alpha]_D^{25}$ = +10.2 (*c* = 0.2, $CHCl_3$). − ^{1}H NMR: δ = 7.30 (m, 10 H), 5.88 (m, NH), 5.08 [m, CH_2, (Z)], 4.86 (br. s, 1′-H), 4.52 (dd, 2-H), 3.96 (m, 5′-H), 3.84 (m, 4-H), 3.72−3.58 (m, 6-, 1-, 1′′-, 2′-, 3-H), 3.40 (s, OCH_3), 2.82 (s, NCH_3), 2.45 (dd, 6′a-H), 2.34−2.22 (m, 6′b-, 5α-H), 2.17 (s, NCH_3), 1.80 (m, 5β-H), 1.65−1.45 (m, 3′-, 4′-H_2), 1.28 (d, 2′′-H); $J_{1',2'}$ = 1.9, $J_{1,2}$ = $J_{2,3}$ = 7.1 Hz. − MS (FAB); *m/z*: 598 (100) $[M]^+$, 306 (15) $[C_{17}H_{21}N_2O_6 - CO_2, + H]^+$, 289 (10) $[C_{17}H_{21}N_2O_5 - CO_2]^+$, 248 (9) $[C_{15}H_{22}NO_2]^+$.

3-O-{2′β,6′-[(1R)-Phenylethyl]methylamino-3′,4′,6′-trideoxy-α-D-hexopyranosyl}-1,4,5-trideoxy-6-O-methyl-4-(benzyloxycarbonylamino)-1-(methylamino)-L-chiro-inositol (**40**): A solution of **39** (15 mg, 0.025 mmol) in 3% methanolic NaOH (3 ml) and water (3 ml) was refluxed for 2 h. After total conversion [TLC, $CHCl_3$/methanol, 10:1, R_f (**39**) = 0.24, R_f (**40**) = 0.07], the solution was concentrated in vacuo, diluted with water, and extracted with CH_2Cl_2. Drying ($MgSO_4$) and concentration in vacuo gave **40** (13 mg, 92%) as colorless oil. $[\alpha]_D^{25}$ = +39.5 (*c* = 0.2, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 3398 cm^{-1} (OH), 1719 (NHCOO), 1509 (NHCOO). − ^{1}H NMR: δ = 7.30 (m, 10 H), 5.70 (m, NH), 5.08 [m, CH_2, (Z)], 4.82 (br. s, 1′-H), 4.17−4.07 (m, 5′-H, 2-H), 3.99 (m, 4-H), 3.88 (dd, 3-H), 3.65 (q, 1′′-H), 3.47 (m, 2′-H), 3.40 (m, 6-H), 3.35 (s, OCH_3), 2.76 (m, 1-H), 2.57 (dd, 6′a-H), 2.49 (s, NCH_3), 2.28−2.18 (m, 6′b-, 5α-H), 2.21 (s, NCH_3), 2.05−1.65 (m, 5β-, 4′α-H, 3′-H_2), 1.45 (dddd, 4′β-H), 1.35 (d, 2′′-H); $J_{1',2'}$ < 1, $J_{5',6'a}$ = 7.5, $J_{6'a,6'b}$ = 13.5, $J_{2,3}$ = $J_{3,4}$ = 8.9 Hz. − ^{13}C NMR: δ = 157.0 [C=O, (Z)], 136.7 (C_s), 128.5−126.7 (10 C), 98.0 (C-1′), 77.2 (C-2)*, 77.1 (C-2′)*, 75.8 (C-3)*, 74.8 (C-6)*, 68.2 (C-5′)*, 67.3 (C-4), 66.6 (CH_2, Z), 63.7 (C-1′′)*, 63.5 (C-1), 58.1 (C-6′), 56.4 (OCH_3), 40.1 (NCH_3), 34.2 (NCH_3), 29.7 (C-5), 25.4 (C-3′), 23.3 (C-4′), 17.7 (C-2′′). − MS (FAB); *m/z* (%): 572 (13) $[M + H]^+$, 307 (9) $[C_{16}H_{23}N_2O_4]^+$, 289 (8) $[C_{16}H_{23}N_2O_4 - H_2O]^+$, 105 (82) $[R^*]^+$.

3-O-{2′β,6′-[(1R)-Phenylethyl]methylamino-3′,4′,6′-trideoxy-α-D-hexopyranosyl}-1,4,5-trideoxy-6-O-methyl-4-(benzyloxycarbonylamino)-1-(benzyloxycarbonylglycyl)methylamino-L-chiro-inositol (**41**): Treatment of **40** (13 mg, 0.023 mmol) according to GP 2 [Z-gly-*O*-suc (9 mg, 0.029 mmol), DMF, 28 h, 60°C] led after chromatography ($CHCl_3$/methanol, 25:1, R_f = 0.18) to **41** (14 mg, 78%) as colorless oil. − ^{1}H NMR (250 MHz): δ = 7.30 (m, 15 H), 5.30−5.00 [m, 1′-H, 2 CH_2, (Z)], 4.60 (m, 2-H), 4.10 (m, 5′-H), 3.95 (m, 2′-H), 3.80−3.60 (m, 1′′-, 4-, 6-, 3-, 1-H, CH_2, Gly), 3.40 (s, OCH_3), 2.80 (s, NCH_3), 2.20 (s, NCH_3), 2.50−1.20 (m, 6′a-, 6′b-, 5-H, 4′-, 3′-H_2), 1.47 (d, 2′′-H). − MS (FAB); *m/z* (%): 786 (4) $[M + Na]^+$, 764 (17) $[M + H]^+$, 499 (23) $[C_{26}H_{32}N_3O_7]^+$, 248 (17) $[C_{15}H_{22}NO_2]^+$.

4-Amino-3-O-(2′β,6′-methylamino-3′,4′,6′-trideoxy-α-D-hexopyranosyl)-1,4,5-trideoxy-6-O-methyl-1-(glycyl)methylamino-L-chiro-inositol (**4**): **41** (13 mg, 0.017 mmol) was treated according to GP 3 (8 h) to give **4** (8 mg, 94%) as solid tetrakis(hydrochloride). − ^{1}H NMR (D_2O, CH_3CN): δ = 5.05 (br. s, 1′-H), 4.20 (m, 2-H), 4.12 (ddd, 6-H), 4.05 (m, 5′-H), 3.95 (m, CH_2), 3.89−3.81 (m, 3-H, 2′-H), 3.74 (m, 4-H), 3.31 (s, OCH_3), 3.10 (dd, 6′a-H), 3.01 (s, NCH_3), 2.98 (dd, 6′b-H), 2.81 (s, NCH_3), 2.50 (dd, 5β-H), 2.21 (m, 5α-H), 1.88/1.65 (m, 2 H/1 H, 3′-, 4′α-H), 1.50 (dddd, 4′β-H); $J_{1',2'}$ < 1, $J_{5',6'a}$ = 3.0, $J_{6'a,6'b}$ = 14.2, $J_{1,6}$ = $J_{5\alpha,6}$ = 10.6, $J_{4,5\alpha}$ = $J_{4,5\beta}$ = $J_{5\beta,6}$ = 4.3, $J_{5\alpha,5\beta}$ = 14.8 Hz. − ^{13}C NMR (D_2O, CH_3CN): δ = 93.5 (C-1′), 73.2 (C-3), 71.8 (C-6), 70.2 (C-2), 68.8 (C-2′), 66.0 (C-5′), 56.9 (C-1), 56.4 (OCH_3), 52.7 (C-6′), 48.4 (C-4), 40.9 (CH_2), 34.5 (NCH_3), 31.9 (NCH_3), 29.9 (C-5), 27.3 (C-4′), 22.7 (C-3′). − MS (FAB); *m/z* (%): 413 (5) $[M + Na]^+$, 391 (27) $[M + H]^+$, 247 (7) $[C_{10}H_{20}N_3O_4]^+$, 144 (6) $[C_7H_{14}NO_2]^+$.

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