Enantiopure D-, L- (and 2-*epi*-) Purpurosamine C-Type Glycosyl Donors from Racemic Acrolein Dimer – Biocatalytic Resolution[☆]

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Both enantiomers of purpurosamine C-type glycosyl donors [(*ent*)-**9**, (*ent*)-**10**, (*ent*)-**11**] and of a 2-azido epimer [(*ent*)-**14**] with a modified pattern of protecting groups have been prepared from racemic 3,4-dihydro-2*H*-pyran-2-carbaldehyde (acrolein dimer, *rac*-**1**, "indirect aziridination", "azidonitration"). In two cases (*rac*-**23β**: methyl 6-*O*-acetyl-2,3,4-trideoxy-2α-trifluoroacetylamino-β-D/L-hexopyranoside, *rac*-**32**: methyl 6-*O*-acetyl-2β-azido-2,3,4-trideoxy-β-D/L-hexopyranoside), efficient resolution has been achieved biocatalytically.

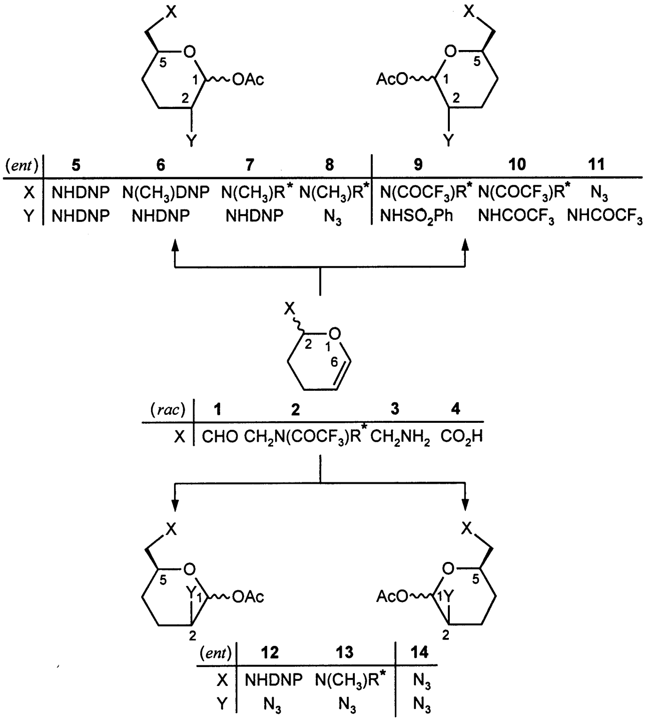
Introduction

The elaboration of synthetic routes to D- and L-purpurosamine C-type glycosyl donors[1] and 2-epimeric analogues[1] is central to our project directed towards the total synthesis of astromicin-type antibiotics[2]. Of the various approaches tested, those starting from acrolein dimer *rac*-**1** (racemic 3,4-dihydro-2*H*-pyran-2-carbaldehyde) and those based on the pioneering work of Brimacombe et al.[3] have led to the 2α-N donors **5**–**8** and the 2β-N donors **12**, **13**, respectively. The protecting measures taken in these donors – at 2-N by DNP or in the form of an azido group and at 6-N by DNP or an alkyl group [R* = 1(*R*)-phenylethyl, S* = 1(*S*)-phenylethyl] – were shown to ultimately pave the way to variously modified sannamycin-type antibiotics (as well as enantiomers and diastereomers)[2]. Nevertheless, certain shortcomings of these synthetic routes – a lack of economy, unsatisfactory overall yields – have stimulated an ongoing search for better alternatives.

In this paper, we report on the glycosyl donors **9**–**11** (*ent*-**9**–**11**) and **14** (*ent*-**14**). The "protection" of the two N functions in these, and the ease of their preparation offer significant advantages.

Donors 9 (*ent*-9) and 10 (*ent*-10)

A weakness of our previous approach was the means (nitrosochlorination[4], azidonitration[5]) by which the 2α-amino functions of **5**–**8** (*ent*-**5**–*ent*-**8**) were introduced into the glycan **2** (*ent*-**2**). Of the standard methods, the conversion of glycals into 1,2-aziridines to be captured in situ by the glycosyl acceptor, e.g. the addition of *N*-acetylnitrenoid species (photolysis of methyl azidoformiate)[6] or of iodonium azide[7] followed by Staudinger reduction and N migration, the latter as "indirect aziridination"[8], proved to be the method of choice for our purposes.



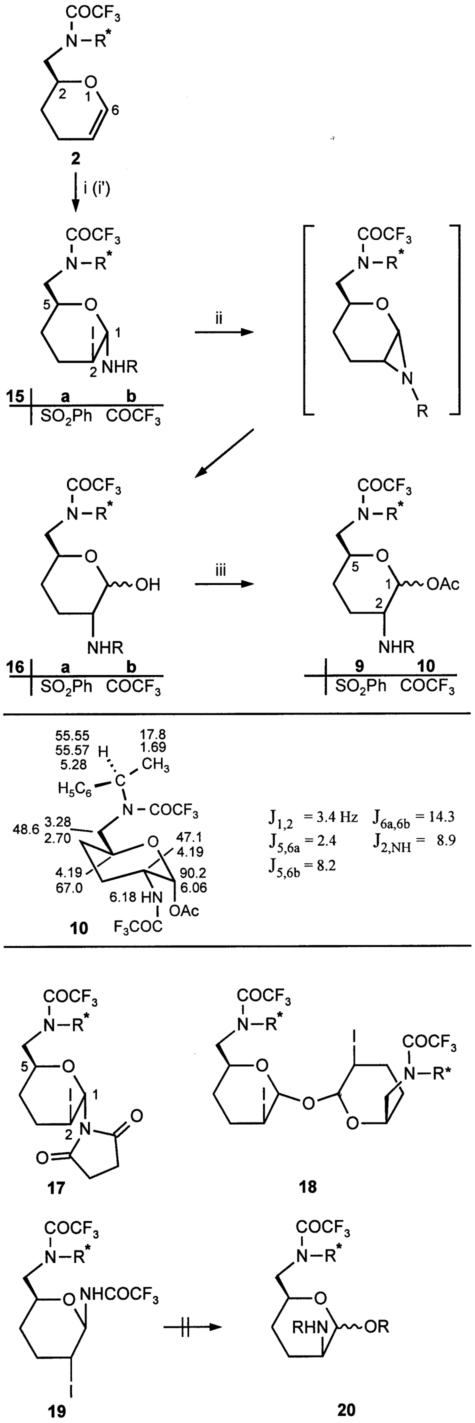
Following the complete reaction (ca. 1.5 h) of the available glycal **2**[1] with *N*-iodosuccinimide as the I^+ source and benzenesulfonamide as the nucleophile in anhydrous CH_3CN at 0°C, a complex mixture of products was obtained (TLC, ^{1}H NMR). From this mixture, the desired 1α-sulfonamido-2β-iodo adduct **15a** was isolated chromatographically as the main component in 76% yield, along with 9% of the 1α-succinimido-2β-iodo adduct **17**[9] as colorless solids. The remaining 15% of material consisted of three complex, non-analyzable fractions; the presence of small amounts of e.g. the 1β,2α-isomer of **15a** could therefore not be ruled out. After treatment of **15a** – in its 1a,2a,5e-$^4C_1$ chair form, which is a prerequisite for the aziridine cyclization, β-HI elimination can in principle compete – with a weak base under mild conditions (triethylamine/THF/

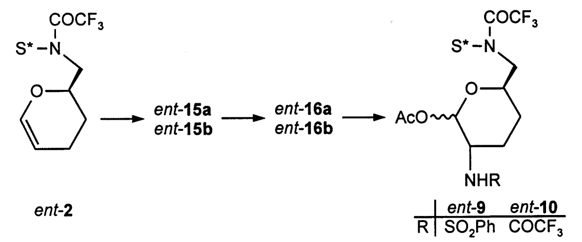
water) only the pyranoses **16a** (α/β anomers ≈ 6:1), and no olefins were present (TLC, ^{1}H NMR) [stronger bases (CH_3ONa/CH_3OH) led to a mixture of β-methyl glycoside, the elimination product and the 6-methylcarbamate derivative (ca. 5:1:1)]. The pyranoses were then directly acetylated (Ac_2O/pyridine), affording cleanly (92%) the donor **9** (1-*O*-acetyl-2α-benzenesulfonamido-2,3,4,6-tetradeoxy-6-{trifluoroacetyl-[(1*R*)-phenylethyl]}amino-α/β-D-hexapyranose). For characterization, the anomers of **9** (α/β ≈ 6:1) were separated by chromatography and isolated as colorless solids. The ^{1}H-NMR coupling constants established the 1a(e),2e,5e-$^4C_1$ conformations; ^{13}C NMR, MS data and EA further corroborated the structural assignment.

When later in the synthetic route[10] the sulfonamido group at C-2 of donor **9** (*ent*-**9**) was found not to be as useful as originally expected, mainly as a result of complications that arose in the deprotection step, the above synthetic sequence was conducted with trifluoroacetamide instead of benzenesulfonamide as the N nucleophile. For two critical steps in particular, en route to the ultimate aminoglycosides (glycosylation, differentiation of N functions), this amino function proved to be stable and could be conveniently deprotected. In a typical run (mmol scale), **2** was reacted with NIS/CF_3CONH_2 under otherwise identical conditions to give a complex mixture of products, from which the following three main components (TLC, ^{1}H NMR) were separated chromatographically: 58% of solid 1α-trifluoroacetylamino-2β-iodo adduct **15b**, a relatively large amount (27%) of succinimide **17** and 6% of the 1β,2α-isomer **19**[11]. Triethylamine (in THF/water) transformed **15b** slowly but almost quantitatively into **16b**, which was directly acetylated to furnish the donor **10** (1-*O*-acetyl-2,3,4,6-tetradeoxy-2α-trifluoroacetylamino-6-{trifluoroacetyl-[(1*R*)-phenylethyl]}amino-α/β-D-hexapyranose) as an approximately 2:1 α/β mixture. For characterization, the prevalent α anomer was chromatographically isolated as colorless solid. It should be noted that **19** could not be transformed analogously into the 2β-amino donor – understandably given the conformational preference – but remained unchanged.

The unacceptably large amount of succinimide **17** (27%) indicates that this is too effective in competing for the intermediate iodonium ion. Hence, [I(*sym*-collidine)$_2$]ClO_4[12] was tested as an alternative I^+ source with a non-nucleophilic anion. However, no improvement resulted when **2** was treated with [I(*sym*-collidine)$_2$]ClO_4 (1.5 equiv.)/CF_3CONH_2 (1.4 equiv.) at 0°C in CH_2Cl_2; the reaction furnished only 40% **15b** and 4% **19**. Occasionally, an additional product was found, which was identified as **18** (4–7%, $J_{1,2}$ < 1.0 Hz); in line with its probable origin, its formation could be suppressed by the total exclusion of moisture. Improved yields could be achieved when the conversion was conducted using CF_3CONH_2 in great excess; with 20 equivalents, the yield of **15b** increased to 69%. Around 6% of **19** was also produced. The remainder of the material (15–20%) turned up in chromatographic fractions too complex to allow any assignments. As detailed in the Experimental Section, the enantiomeric donors *ent*-**9** and *ent*-**10** were prepared analogously in the same overall yield starting from *ent*-**2**.

Scheme 1. **9**: (i) NIS (1.5 equiv.)/$C_6H_5SO_2NH_2$ (1.2 equiv.)/CH_3CN, 0°C, 1.5 h, 76%. – (ii) NEt_3 (4 equiv.)/THF/H_2O, 5:2, r.t., 5 h. – (iii) Ac_2O/pyridine, r.t., 4 h, 92% (two steps), (α/β ≈ 6:1). – **10**: (i) NIS (1.1 equiv.)/CF_3CONH_2/(1.2 equiv.)/CH_3CN, 0°C, 1.5 h, 58%. – (i') [I(*sym*-collidine)$_2$]ClO_4 (1.1 equiv.)/CF_3CONH_2 (20 equiv.)/CH_2Cl_2, r.t., 20 min., 69%. – (ii) NEt_3 (3 equiv.)/THF/H_2O, 5:2, r.t., 14 h. – (iii) Ac_2O/pyridine, r.t., 4 h, 88% (two steps), (α/β = ca. 2:1)





Scheme 2. (i) NIS (1.2 equiv.)/CF_3CONH_2 (1.5 equiv.)/CH_3CN, r.t., 1.5 h, 62%. – (i') [I(*sym*-collidine)$_2$]ClO_4 (1.5 equiv.)/CF_3CONH_2 (1.4 equiv.)/CH_2Cl_2, 70%. – (ii) NEt_3 (4 equiv.)/DMF/MeOH, 2:1, r.t., 40 h, 84%

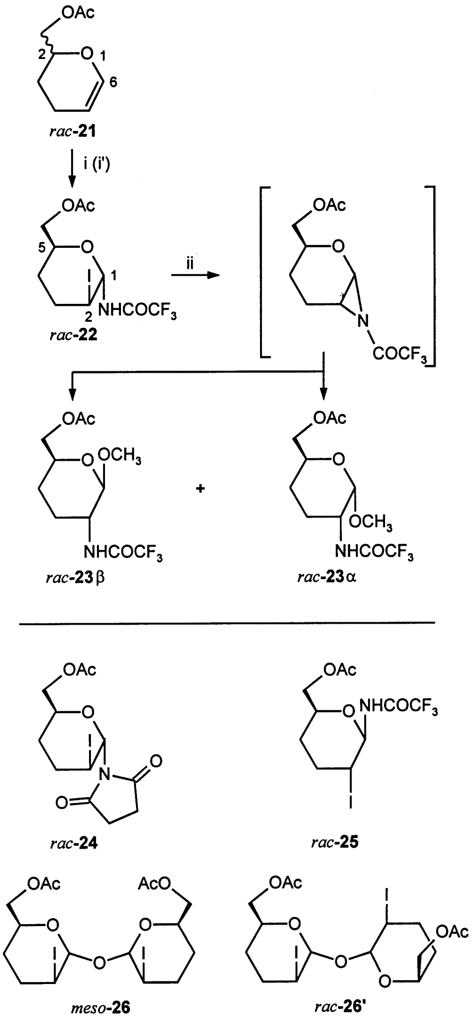


Table 1. Biocatalytic resolution of *rac*-**23β** [*ee* determined by ^1H NMR, Eu(hfc)$_3$]

Lip.	Conv.[%]	(5*S*)-**27a** (D)	(5*R*)-*ent*-**23β** (L)
PPL	38	$[\alpha]_D^{25} = -42.0$, *ee* > 98	
PPL	50	$[\alpha]_D^{25} = -27.2$, *ee* = 59	$[\alpha]_D^{25} = +14.6$, *ee* = 31
PPL	70		$[\alpha]_D^{25} = +43.6$, *ee* > 98
PSL	36	$[\alpha]_D^{25} = -35.7$, *ee* = 79	
PSL	69		$[\alpha]_D^{25} = +44.3$, *ee* > 98

Donor 11 (*ent*-11)

Preparation of the glycal **2** (*ent*-**2**) from *rac*-**1** via condensation with 1*R*(1*S*)-phenylethylamine was highly time consuming and intrinsically 50% of the material (including the chiral auxiliary) was lost. Schemes 2 and 3 depict how, again based on *rac*-**1**, resolution at a later stage of the synthetic route was combined with the "indirect aziridination" method and the introduction of the versatile N_3 function at C-6.

First, aldehyde *rac*-**1** was converted into hydroxyacetate *rac*-**21** by standard procedures: [(i) $NaBH_4$/EtOH, (ii) Ac_2O/pyridine, overall yield 84%][13]. The subsequent reaction with the NIS/CF_3CONH_2 reagent as well as that with the [I(*sym*-collidine)$_2$]ClO_4/CF_3CONH_2 combination – performed as **2** → **15a,b** – was not significantly influenced by variation of the substituents at C-6. Under the former set of conditions, 62% of the 1α-trifluoroacetylamino-2β-iodo adduct *rac*-**22**, 1% of the 1β,2α-isomer *rac*-**25** and 31% of the succinimide *rac*-**24** were obtained, while under the latter set of conditions 70% of *rac*-**22** and 5% of *rac*-**25** were isolated. The occasional appearance of up to 7% *meso*-**26**/*rac*-**26'** ($J_{1,2}$ < 1.0 Hz) could again be attributed to traces of moisture.

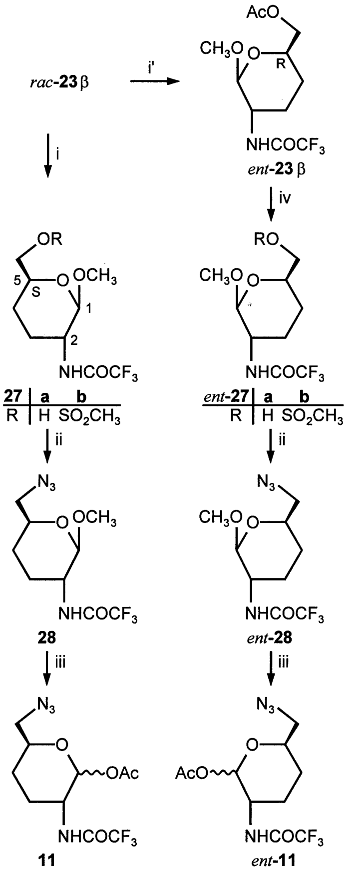
As noted for **15b**, the transformation of *rac*-**22** by triethylamine (DMF/MeOH), in this case into the methyl glycoside *rac*-**23**, proceeded very slowly, requiring 40 h for total conversion (N migration is restricted to the unfavorable 1a,2a,5e-$^4C_1$ conformation). From a standardized experiment, 84% of the β and 9% of the α anomer were isolated chromatographically as colorless solids. Clearly, the minor α anomer could not have been directly derived from an intermediate aziridine; its occurrence proved disadvantageous when only the β anomer could be utilized for the subsequent biocatalytic resolution.

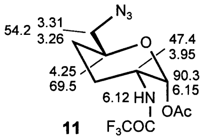
For the resolution of *rac*-**23β** (Scheme 3) a good number of enzymes were tested[14]. Reaction proceeded, albeit extremely slowly, in the presence of PPL and PSL (Table 1) in acetone/pH = 7 buffer. With PPL, the alcohol (5*S*)-**27a** (D) was formed after ca. 40% conversion (96 h), while after ca. 70% conversion (ca. 14 d) the remaining acetate (5*R*)-*ent*-**23β** (L) was isolated. Both products showed very high optical purities (*ee* > 98). With PSL (10 d) under comparable conditions, only for (5*R*)-*ent*-**23β** (L) was a similarly satisfactory result realized.

Standard mesylation of **27a** followed by substitution with azide provided **28** in 92% overall yield ($[\alpha]_D^{25} = -50.6$). For conversion of the latter into the 1-*O*-acetylglycosyl donor **11**, the hitherto used two-step procedure [(i) HOAc/H_2SO_4/CH_3NO_2, 10:10:1, reflux, 5–8 h, (ii) Ac_2O/pyridine][1] was replaced by a more convenient, direct method (CH_2Cl_2/Ac_2O, 100:1/cat. H_2SO_4, 0°C, 1 h). In this way, up to 89% of **11** (1-*O*-acetyl-6-azido-2,3,4,6-tetradeoxy-2α-trifluoroacetylamino-α/β-D-hexopyranose) was isolated as colorless, crystalline, chromatographically separable α/β mixture (≈ 12:1, **11α**: $[\alpha]_D^{25} = +57.6$)[15]. Only in more concentrated solutions did formation of the open-chain hexose derivative **29** become a competing process.

For the conversion of *ent*-**23β** ($[\alpha]_D^{25} = +44.3$) to the enantiomeric donor *ent*-**11** ($[\alpha]_D^{25} = -59.8$), first the ace-

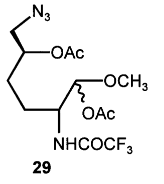
Scheme 3. (i) Acetone/pH = 7 buffer/PPL, 96 h. – (i') Analogous conditions, 14 d. – (ii) 1. CH_3SO_2Cl/pyridine/CH_2Cl_2, 0°C, 2 h, 2. NaN_3/DMF, 80°C, 24 h, 92%. – (iii) Ac_2O/CH_2Cl_2 (1:100)/H_2SO_4, 0°C, 1 h, 89% (α:β 12:1). – (iv) Acetone/pH = 7 buffer/PLE, r.t., 24 h, 93%





11

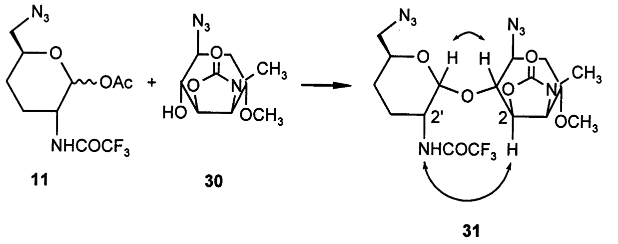
$J_{1,2}$ = 3.2 Hz $J_{3\beta,4\beta}$ = 4.8
$J_{2,3\beta}$ = 4.8 $J_{5,6a}$ = 5.9
$J_{3\alpha,3\beta}$ = 15.0 $J_{6a,6b}$ = 13.1
$J_{3\beta,4\alpha}$ = 4.8 $J_{5,6b}$ = 4.3



29

tate group had to be selectively hydrolyzed. Here, PLE catalysis cleanly gave *ent*-**27a** ($[\alpha]_D^{25}$ = +42.9).

The absolute configuration of **27a** (and thus that of *ent*-**23β** as well) assumed from the 5*S* selectivity of PPL[16] was confirmed by glycosylation of donor **11** with **30**[17] as an optically pure sannamine-type acceptor of known absolute configuration. The reaction was conducted under modified Koenigs-Knorr conditions ($BF_3/OEt_2/CH_2Cl_2$, r.t., 1 h) and provided selectively the α-glycoside **31** (79%). An NOE measured between C2'–NH and 2-H of the product proved the 5*S*-(D)-configuration.



Donor 14 (*ent*-14)

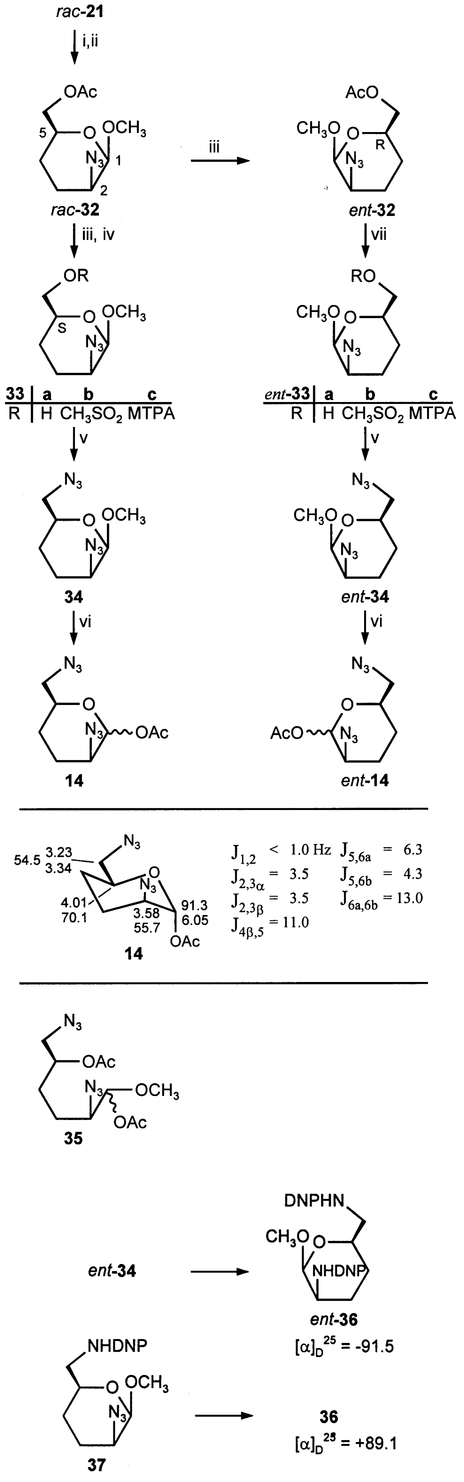
The earlier routes to the donors **12** and **13**, 2-*epi*-purpurosaminides C, implied "azidonitration" of the glycals **2** (*ent*-**2**) and thus suffered from the drawbacks associated with these starting materials as mentioned above. In addition, the introduction of the 2β-N_3 group in **2** (*ent*-**2**) was only moderately stereoselective showing just a ca. 2.6:1 preference for the attack from the β-side[1]. Thus, we set out to obtain **14**, as outlined in Scheme 4, in the hope that the β-selectivity seen in the case of *rac*-**21** – with a sterically less demanding substituent at C-6 equatorially placed in a half-chair conformation – would be enhanced and that an enzymatic resolution similar to that of *rac*-**23β** would become possible. With regard to the latter aspect, we realized that the highly selective formation of one of the 2β-azido anomers (e.g. **32**, **38**) would be desirable.

From the reaction of *rac*-**21** with cerium(IV) ammonium nitrate (CAN) and NaN_3 in CH_3CN at –40°C (anhydrous conditions), after subsequent quenching of the azidonitrates with methanol, a mixture of the four azido methyl glycosides *rac*-**32**, *rac*-**38**–**40** and the bisazide *rac*-**41** was obtained in an NMR spectroscopically determined ratio of ca. 4.8:3.2:1.0:1.0:1.1 in ca. 80% total yield. Clearly, the ratio of β/α azides is as high as 4:1, although 1β-*rac*-**32** is not significantly favored over 1α-*rac*-**38**. Chromatographically, only *rac*-**32** (32%) and *rac*-**41** (7%) could be obtained in pure form. For the resolution of *rac*-**32**, PPL again proved to be the reagent of choice [*n*-hexane, phosphate buffer (pH = 7)]. When the reaction was allowed to proceed to 60–70% conversion, the residual acetate was nearly enantiomerically pure *ent*-**32** (*ee* = 92%). The enantiomerically enriched alcohol (*ee* = 68%) was acetylated once more and again exposed to the same hydrolysis procedure that delivered the alcohol **33a** with *ee* > 90. For the Mosher esters **33c** (*ent*-**33c**), the 1-H signal in the 400 MHz NMR spectra ($CDCl_3$) was base-line separated, allowing a rapid and reliable *ee* determination. The 6-OH → 6-N_3 substitution **33a** → **33b** → diazide **34** was almost quantitatively achieved in a reproducible manner. Subsequent acetolysis, performed analogously to that of **28** in highly dilute $Ac_2O/H_2SO_4/CH_2Cl_2$ solution, consistently yielded (87%) the donor **14** (1-*O*-acetyl-2β,6-diazido-2,3,4,6-tetradeoxy-α,β-D-hexopyranose). It was again only in concentrated solutions that formation of the open-chain sugar **35** became competitive.

The absolute configurations as depicted [**33**: 5*S* (D); *ent*-**33**: 5*R* (L)] were established by transformation of *ent*-**34** into *ent*-**36**.

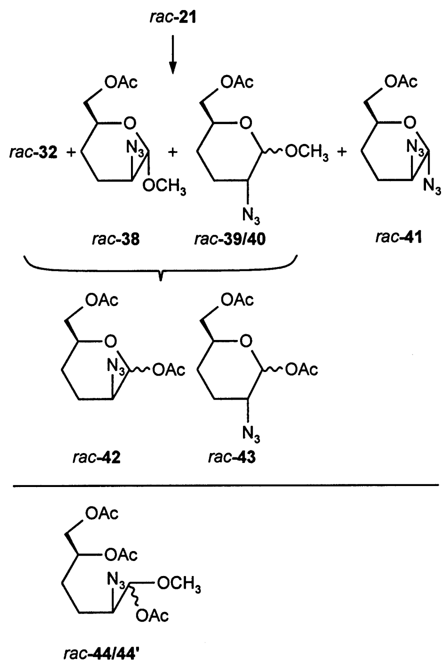
The racemic glycosyl donors *rac*-**42**/*rac*-**43** were conveniently obtained by treatment of the crude mixture of *rac*-

Scheme 4. (i) CAN (2 equiv.)/NaN_3 (1.4 equiv.), −40°C, 2.5 h. − (ii) CH_3OH, 0°C, 2.5 h, 32%. − (iii) *n*-hexane/pH = 7 buffer/PPL, 12 h. − (iv) 1. $Ac_2O/NEt_3/CH_2Cl_2$, r.t., 2. analogous to (iii), but 14 h. − (v) 1. $CH_3SO_2Cl/Et_3N/CH_2Cl_2$, 0°C, 2. NaN_3/DMF, 80°C, 24 h, 97%.− (vi) Ac_2O/CH_2Cl_2 (1:10)/H_2SO_4, 0°C, 1 h, 87% (α/β ≈ 5:1). − (vii) Na_2CO_3/CH_3OH, r.t., 1 h, 94%



32/*rac*-**38**−**41** obtained from azidonitration of *rac*-**21** with Ac_2O/CH_2Cl_2, 10:1/H_2SO_4 cat. (0°C, 4 h). Chromatographically, 55% of *rac*-**42** and 10% of *rac*-**43** (based on *rac*-**21**) were isolated.

Acetolysis of *rac*-**32** in Ac_2O/cat. H_2SO_4 (0°C, 30 min.) in the absence of solvent[5b] furnished 67% *rac*-**42** and 7% of the acyclic *rac*-**44**/**44′**. With Lewis acids such as $ZnCl_2$ or BF_3/OEt_2 instead of H_2SO_4, exclusively the acyclic product *rac*-**44**/**44′** was obtained.



Conclusions

For the total synthesis of astromicin-type antibiotics (and their enantiomers) the situation on the donor side could be significantly improved. The novel donors reported herein are prepared along more efficient and economic routes and feature advantageous "protection" of the N functionalities (stability in glycosylation, ease of differentiation). The nine(ten)-step sequences **2** → **5** (*ent*-**5**) and **2** → **7** (*ent*-**7**)[1], with overall yields of ca. 8%, can now be replaced by the three-step procedures **2** (*ent*-**2**) → **9** (*ent*-**9**) and **2** (*ent*-**2**) → **10** (*ent*-**10**) which proceed in 65−70% and 50−62% yield, respectively, on a gram scale. Of more practical importance, the overall yield of ca. 2% - still respectable in this area[18] - for the routes[1] **1** → **5** (*ent*-**5**) and **1** → **7** (*ent*-**7**) was increased to 10−13% for *rac*-**1** → **11** (*ent*-**11**) and to 7−9% for *rac*-**1** → **14** (*ent*-**14**). Here, a crucial role is played by the efficient enzymatic resolutions of *rac*-**23β** and *rac*-**32**. In the case of *rac*-**32**, the lack of selectivity in the azidonitration step sets the limits. A promising alternative is seen in the recently reported enzymatic resolution of the glycan *rac*-**21**[16a] − after acetolysis of the mixture resulting from the subsequent azidonitration, **42** (*ent*-**42**) is conveniently separable. In this context, the advantage of the acetolysis conditions employed in this project[19] must be stressed once more − even from β-methyl glycosides, which under standard conditions led partially[20] or exclusively[21] to the acyclic products, the 1-*O*-acetylpyranoses were obtained practically quantitatively.

Mechanistically, the occurrence of the β-*gluco* products **19** and *rac*-**25** is remarkable in that β-addition of I^+ to glycals is hardly observed; such additions have only been reported in cases where the usually generated α-manno configuration is hampered by steric congestion[11]. In line with general opinion[8][22], aziridine intermediates are formulated in Schemes 1 and 2 for the 1α → 2α N transfers **15a**, **b** → **16a**, **b** and *rac*-**22** → *rac*-**23β**; the appearance of *rac*-**23α** is evidence for an alternative reaction channel.

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Experimental Section

Melting points were determined with a Monoskop IV (Fa. Bock) and are uncorrected. − Elemental analyses were performed by the Analytische Abteilung des Chemischen Laboratoriums Freiburg i. Br. − IR spectra were measured with a Perkin-Elmer 457 or a Philips PU 9706 spectrometer, ^{1}H-NMR spectra with Bruker AC 250 or AM 400 spectrometers (at 250 or 400 MHz, respectively), and ^{13}C-NMR spectra with a Bruker AM 400 spectrometer (100.6 MHz). Chemical shifts are given relative to TMS (δ = 0), coupling constants in Hz; unless specified otherwise, all spectra were recorded in $CDCl_3$; values marked with an asterisk are interchangeable. − Mass spectra were run with a Finnigan MAT 44S spectrometer (EI, 70 eV, unless specified otherwise), FAB mass spectra with a Finnigan MAT 312 (FAB-Gun Microbeam-7, 6 kV, Xenon, matrix: *m*-nitrobenzyl alcohol), and electron-spray mass spectra with a Finnigan TSQ 7000 (syringe pump: 2µl/min., spray 4−5 kV). − Optical rotations were measured with a PE 241 polarimeter; specific rotation values are given in units of 10^{-1} deg cm^2 g^{-1}. For TLC, silica gel plates 60 F_{254} (Merck, Darmstadt) were employed. − 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 was generally confirmed by TLC.

General Procedures − Mesylation and Azide Substitution (GP 1): To a solution of the alcohol (1.0 mmol) and triethylamine (3.0 mmol) in CH_2Cl_2 (10−20 ml) at 0°C, MsCl (1.5 mmol) was added dropwise. The reaction mixture was stirred at room temp. until total conversion had been achieved (TLC control). After washing with H_2O (20 ml), the aqueous phase was extracted (CH_2Cl_2), the combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. The resulting residue was dissolved in DMF, NaN_3 (3.0 mmol) was added, and the mixture was heated to 80°C for 24 h. After complete reaction (TLC), the mixture was concentrated to dryness and the residue was purified by chromatography on silica gel with the eluent specified.

Hydrolysis of the Acetates (GP 2): A mixture of the acetate (1.0 mmol) and Na_2CO_3 (2.0−4.0 mmol) in MeOH (10 ml) was stirred at room temp. until total conversion had been achieved (TLC control). The reaction mixture was then neutralized with 2 M aq. HCl solution and concentrated in vacuo. After dilution with H_2O and extraction with CH_2Cl_2 or ethyl acetate, the combined organic phases were dried ($MgSO_4$), concentrated in vacuo, and filtered through a short column of silica gel with the eluent specified so as to furnish the alcohol.

Acetolysis of Methyl Glycosides (GP 3): To a solution of the methyl glycoside (1.0 mmol) in Ac_2O (2.2 ml) and CH_2Cl_2 (22 ml), conc. H_2SO_4 (0.5 mmol) was added dropwise at 0°C. After stirring at this temperature until total conversion had been achieved (TLC control), the mixture was neutralized with saturated sodium bicarbonate solution. The aqueous phase was extracted with CH_2Cl_2, the combined extracts were dried ($MgSO_4$) and concentrated in vacuo. The resulting residue was purified by chromatography.

Acetylation of the Alcohols (GP 4): To a solution of the alcohol (1.0 mmol) and triethylamine (2.0−3.0 mmol) in CH_2Cl_2 (15 ml), Ac_2O (1.5 mmol) was added at room temp. After stirring until total conversion had been achieved (TLC control), H_2O (20 ml) was added. The aqueous phase was extracted (CH_2Cl_2), the combined organic phases were dried ($MgSO_4$), concentrated in vacuo, and filtered through a short column of silica gel to furnish the acetate.

1-N-Benzenesulfonamido-1,2,3,4,6-pentadeoxy-2β-iodo-6-{trifluoroacetyl-[(1R)-phenylethyl]}amino-α-D-hexopyranoside (**15a**) *and 1-N-Succinimido-1,2,3,4,6-pentadeoxy-2β-iodo-6-{trifluoroacetyl[(1R)-phenylethyl]}amino-α-D-hexopyranoside* (**17**): *N*-iodosuccinimide (NIS, 1.08 g, 4.80 mmol) was added with stirring to a chilled solution (0°C) of **2** (1.00 g, 3.19 mmol) and benzenesulfonamide (0.60 g, 3.84 mmol) in anhydrous acetonitrile (under N_2). After 0.5 h at this temp., stirring was continued at room temp. for 1 h. The solvent was then removed in vacuo and the remaining syrup was dissolved in CH_2Cl_2. After washing with saturated aqueous sodium thiosulfate solution and water, drying ($MgSO_4$), and concentration, chromatography [silica gel, CH_2Cl_2/acetone, 10:1, R_f (**15a**) = 0.45, R_f (**17**) = 0.55] of the resulting residue yielded **15a** (1.42 g, 76%) and **17** (0.16 g, 9%) as colorless solids. In addition, three fractions were eluted (20 mg, R_f = 0.70; 58 mg, R_f = 0.62; 108 mg, R_f = 0.56), the ^{1}H-NMR spectra of which were too complex to allow any assignment. **15a**: M.p. 68°C. − $[\alpha]_D^{25}$ = +56.9 (*c* = 0.5, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 3279 cm^{-1} (NH), 1685 (NR*CO). − ^{1}H NMR: δ = 7.90/7.58/7.40/7.28 (m, 2 H, 3 H, 3 H, 2 H, aromatic H), 6.52 (d, N−H), 5.28−5.15 (m, 1-, 1′-H), 4.22 (m, 5-H), 4.06 (m, 2-H), 3.20 (dd, 6a-H), 2.70 (dd, 6b-H), 2.10−1.30 (m, 3-, 4-H_2), 1.50 (d, 2′-H); $J_{1,2}$ = 3.0, $J_{1,NH}$ = 8.2, $J_{2,3\alpha}$ = $J_{2,3\beta}$ = 3.1, $J_{5,6a}$ = 3.7, $J_{5,6b}$ = 7.0, $J_{6a,6b}$ = 14.0 Hz. − ^{13}C NMR: δ = 140.5 (C-1″, $PhSO_2NH$), 138.3 (C_s), 132.3−126.9 (10 C, aromatic C), 116.8 (q, CF_3), 83.7 (C-1), 67.5 (C-5), 55.5 (C-1′), 48.8 (C-6), 27.9 (C-4)*, 26.9 (C-3)*, 25.2 (C-2)*, 17.8 (C-2′); $J_{F,CF3}$ = 287.0 Hz. − MS (FAB); *m*/*z* (%): 619 (2) [M + Na]$^+$, 597 (2) [M + H]$^+$, 499 (2) [M − $COCF_3$]$^+$, 491 (2) [M − R*]$^+$, 469 (6) [M − HI]$^+$, 440 (67) [M − $NHSO_2C_6H_5$]$^+$, 365 (17) [M − HI − R* + H]$^+$, 336 (10) [M − $NHSO_2C_6H_5$ − R* + H]$^+$, 312 (17) [M − NH−$SO_2C_6H_5$ − HI]$^+$. **17**: M.p. 157°C. − $[\alpha]_D^{25}$ = +51.9 (*c* = 0.8, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 1716 cm^{-1} (C=O), 1687 (NR*CO). − ^{1}H NMR (400 MHz): δ = 7.50−7.33 (m, 5 H, aromatic H), 5.41 (d, 1-H), 5.29 (q, 1′-H), 5.12 (m, 5-H), 4.32 (m, 2-H), 3.43 (dd, 6a-H), 3.17 (dd, 6b-H), 2.72 (s, 3′-, 4′-H_2), 2.48 (m, 3α-H), 2.09−1.83 (m, 3β-, 4β-H), 1.63 (d, 2′-H), 1.53 (m, 4α-H); $J_{1,2}$ = 10.1 Hz. − ^{13}C NMR: δ = 175.9 (C=O), 138.0 (C_s), 129.1 (C_m), 128.6 (C_o), 127.5 (C_p), 116.8 (q, CF_3), 79.5 (C-1), 74.0 (C-5), 55.5 (C-1′), 54.5 (C-6), 32.4 (C-4)*, 30.1 (C-3)*, 27.9 (C-3′, C-4′), 23.0 (C-2)*, 17.9 (C-2′); $J_{F,CF3}$ = 287.4 Hz. − $C_{20}H_{22}F_3IN_2O_4$ (538.3): calcd. C 44.63, H 4.12, N 5.20; found C 45.13, H 4.14, N 4.85.

2α-Benzenesulfonamido-2,3,4,6-tetradeoxy-6-{trifluoroacetyl-[(1R)-phenylethyl]}-amino-α/β-D-hexopyranose (**16a**) *and 1-O-Acetyl-2α-benzenesulfonamido-2,3,4,6-tetradeoxy-6-{trifluoroacetyl-[(1R)-phenylethyl]}-amino-α/β-D-hexopyranose* (**9α/β**): A solution of **15a** (0.50 g, 0.84 mmol) in THF (50 ml) and water (20 ml) was treated with triethylamine (0.50 ml, 3.59 mmol). The resulting mixture was stirred at room temp. until total conversion was achieved (TLC, 5 h). After addition of water (50 ml) and extraction with CH_2Cl_2 (3 × 60 ml), the combined organic layers were dried ($MgSO_4$) and concentrated to dryness. For characterization, 20 mg of crude **16a** was purified by chromatography [silica gel, CH_2Cl_2/acetone, 10:1, R_f (**16a**) = 0.36]. A solution of the crude **16a** (390 mg) in pyridine (5 ml) and acetic anhydride (5 ml) was stirred at room temp. for 4 h. Concentration in vacuo and chromatography [silica gel, CH_2Cl_2/acetone, 10:1 R_f (**9α**) = 0.58, R_f (**9β**) = 0.52] yielded **9α** (352 mg, 80%) and **9β** (54 mg, 12%) as colorless crystals. **16a**: ^1H NMR: δ = 7.89/7.59/7.32 (m, 2 H, 3 H, 5 H, aromatic H), 5.57 (q, 1′-H, β), 5.29 (q, 1′-H, α), 4.92 (d, 1-H, α), 4.89 (d, NH, α), 4.78 (d, 1-H, β), 4.35 (m, 5-H, β), 4.05 (m, 5-H, α), 3.70 (m, 2-H, β), 3.25 (m, 2-H, α), 3.18 (dd, 6a-H, α,β), 2.80−2.70 (m, 6b-H, α,β), 2.10−1.05 (m, 3-, 4-H_2, a,b), 1.62 (d, 2′-H, β), 1.60 (d, 2′-H, α). − MS (FAB); *m/z* (%): 509 (1) $[M + Na]^+$, 485 (1) $[M]^+$, 469 (5) $[M - OH]^+$, 365 (11) $[M - OH - R^* + H]^+$, 345 (5) $[M - SO_2C_6H_5]^+$, 224 (4) $[M - SO_2C_6H_5 - R^* - OH]^+$, 105 (100) $[R^*]^+$. **9α**: M.p. 66°C. − $[\alpha]_D^{25}$ = +86.2 (*c* = 0.5, $CHCl_3$). − IR (KBr): $\tilde{\nu}$ = 3281 cm^{-1} (NH), 1757 ($OCOCH_3$), 1684 (NR*CO). − ^1H NMR: δ = 7.98/7.58/7.34/7.22 (m, 2 H, 3 H, 3 H, 2 H, aromatic H), 5.78 (d, 1-H), 5.21 (q, 1′-H), 4.68 (d, N-H), 3.98 (m, 5-H), 3.45 (m, 2-H), 3.19 (dd, 6a-H), 2.60 (dd, 6b-H), 2.07 (s, $OCOCH_3$), 1.80−1.52 (m, 3-H_2, 4α-H), 1.60 (d, 2′-H), 1.15 (dddd, 4β-H); $J_{1,2}$ = 3.4, $J_{2,NH}$ = 10.1, $J_{5,6a}$ = 2.1, $J_{5,6b}$ = 8.0, $J_{6a,6b}$ = 14.3, $J_{1',2'}$ = 7.0 Hz. − ^{13}C NMR: δ = 138.3 (C_s), 133.0−126.7 (10 C, aromatic C), 90.8 (C-1), 67.0 (C-5), 55.4 (C-1′), 50.5 (C-2)*, 48.8 (C-6)*, 28.2 (C-4)**, 26.0 (C-3)**, 20.7 (OC-O*C*H$_3$), 17.8 (C-2′). − MS (FAB); *m/z* (%): 469 (16) $[M - OCOCH_3]^+$, 365 (15) $[M - OCOCH_3 - R^* + H]^+$, 289 (11) $[M - SO_2C_6H_5 - COCF_3 + H]^+$, 105 (100) $[R^*]^+$. − $C_{24}H_{26}F_3N_2O_6S$ (527.5): calcd. C 54.64, H 4.97, N 5.31; found C 53.84, H 4.47, N 5.25. **9β**: M.p. 59°C. − $[\alpha]_D^{25}$ = +13.9 (*c* = 0.3, $CHCl_3$). − ^1H NMR: δ = 7.90/7.52/7.33/7.23 (m, 2 H, 3 H, 3 H, 2 H, aromatic H), 5.29 (d, 1-H), 5.26 (q, 1′-H), 5.08 (d, N-H), 3.73 (m, 5-H), 3.30−3.14 (m, 2-, 6a-H), 2.70 (dd, 6b-H), 2.05 (m, 3β-H), 1.84 (s, $OCOCH_3$), 1.70−1.35 (m, 3α-, 4α-H), 1.60 (d, 2′-H), 1.10 (dddd, 4β-H); $J_{1,2}$ = 8.9, $J_{2,NH}$ = 8.2, $J_{5,6b}$ = 7.6, $J_{6a,6b}$ = 14.3, $J_{1',2'}$ = 7.0 Hz. − ^{13}C NMR: δ = 169.4 (O*C*OCH$_3$), 157.6 (q, *C*OCF$_3$), 141.3 (C-1″, $PhSO_2NH$), 138.2 (C_s), 132.7−126.5 (10 C, aromatic C), 116.8 (q, CF_3), 94.4 (C-1), 73.8 (C-5), 55.3 (C-1′), 55.8 (C-2), 48.6 (C-6), 30.3 (C-4)*, 28.3 (C-3)*, 20.5 (OCO*C*H$_3$), 17.7 (C-2′); $J_{F,CF3}$ = 287.4, $J_{F,CO}$ = 35.8 Hz. − MS (FAB); *m/z* (%): 551 (1) $[M + Na]^+$, 529 (1) $[M + H]^+$, 469 (22) $[M - OCOCH_3]^+$, 365 (38) $[M - OCOCH_3 - R^* + H]^+$, 105 (100) $[R^*]^+$. − $C_{24}H_{26}F_3N_2O_6S$ (527.5): calcd. C 54.64, H 4.97, N 5.31; found C 55.05, H 5.35, N 4.97.

1-N-Benzenesulfonamido-1,2,3,4,6-pentadeoxy-2β-iodo-6-{trifluoroacetyl-[(1S)-phenylethyl]}amino-α-L-hexopyranoside (*ent*-**15a**) *and 1-N-Succinimido-1,2,3,4,6-pentadeoxy-2β-iodo-6-{trifluoroacetyl-[(1S)-phenylethyl]}amino-α-L-hexopyranoside* (*ent*-**17**): Treatment of *ent*-**2** (100 mg, 0.32 mmol) as described above for **2** gave *ent*-**15a** (144 mg, 74%) and *ent*-**17** (17 mg, 10%). ^1H, ^{13}C NMR, IR and MS data were identical to those of **15a**, **17** respectively. *ent*-**15a**: $[\alpha]_D^{25}$ = −58.1 (*c* = 0.5, $CHCl_3$). *ent*-**17**: $[\alpha]_D^{25}$ = −53.0 (*c* = 0.5, $CHCl_3$).

1-O-Acetyl-2α-benzenesulfonamido-2,3,4,6-tetradeoxy-6-{trifluoroacetyl-[(1S)-phenylethyl]}amino-α-D-hexopyranose (*ent*-**9α**): *ent*-**15a** (100 mg, 0.19 mmol) was converted into *ent*-**9α** (72 mg, 73%) as described for **15a**. *ent*-**9α**: $[\alpha]_D^{25}$ = −85.4 (*c* = 0.2, $CHCl_3$).

1-N-Trifluoroacetylamino-1,2,3,4,6-pentadeoxy-2β-iodo-6-{trifluoroacetyl-[(1R)-phenylethyl]}amino-α-D-hexopyranoside (**15b**), *1-N-Trifluoroacetylamino-1,2,3,4,6-pentadeoxy-2α-iodo-6-{trifluoroacetyl-[(1R)-phenylethyl]}amino-β-D-hexopyranoside* (**19**), *and 1,2,3,4,6-Pentadeoxy-2β-iodo-6-{trifluoroacetyl-[(1R)-phenylethyl]}amino-α-D-hexopyranosyl 1,2,3,4,6-Pentadeoxy-2β-iodo-6-{trifluoroacetyl-[(1R)-phenylethyl]}-amino-α-D-hexopyranoside* (**18**): Procedure 1: A solution of **2** (1.0 g, 3.19 mmol) and trifluoroacetic amide (434 mg, 3.84 mmol) in anhydrous acetonitrile was cooled to 0°C (under N_2) and treated with NIS (790 mg, 3.51 mmol). After stirring at 0°C (0.5 h) and at room temp. (1 h), the solvent was removed in vacuo, the remaining syrup was dissolved in CH_2Cl_2, and washed with aqueous sodium thiosulfate solution and water. After drying ($MgSO_4$) and concentration in vacuo, the residue was separated by chromatography [silica gel, ethyl acetate/cyclohexane/$CHCl_3$, 5:5:1, R_f (**15b**) = 0.65, R_f (**17**) = 0.49]; a third fraction (R_f = 0.55−0.60) was chromatographed once again on silica gel [cyclohexane/ethyl acetate, 2:1, R_f (**19**) = 0.46)] to yield **15b** (1.02 g, 58%), **19** (109 mg, 6%) and **17** (0.46 g, 27%). Procedure 2: $[I(\textit{sym}\text{-collidine})_2]ClO_4$ (160 mg, 0.35 mmol) was added to a solution of **2** (100 mg, 0.32 mmol) and trifluoroacetic amide (720 mg, 6.37 mmol) in anhydrous CH_2Cl_2 at room temp. (under N_2). After stirring for 20 min., TLC showed complete conversion, and the solution was washed with saturated aqueous sodium thiosulfate solution, saturated aqueous copper sulfate solution, and water. After drying ($MgSO_4$) and concentration in vacuo, the residue was chromatographed on silica gel [cyclohexane/ethyl acetate, 2:1, R_f (**18**) = 0.80, R_f (**15b**) = 0.60, R_f (**19**) = 0.53] to yield sequentially **15b** (121 mg, 69%), **19** (11 mg, 6%) and **18** (11 mg, 4%). **15b**: ^1H NMR: δ = 7.50−7.30 (m, 5 H, aromatic H), 6.90 (d, NH), 5.65 (dd, 1-H), 5.30 (q, 1′-H), 4.22 (ddd, 2-H), 4.02 (m, 5-H), 3.30 (dd, 6a-H), 2.92 (dd, 6b-H), 2.05 (m, 3-H_2), 1.65 (d, 2′-H), 1.80−1.50 (m, 4-H_2); $J_{1,2}$ = 4.0, $J_{1,NH}$ = 7.8, $J_{2,3\alpha}$ = $J_{2,3\beta}$ = 4.6, $J_{5,6a}$ = 3.1, $J_{5,6b}$ = 7.0, $J_{6a,6b}$ = 14.3, $J_{1',2'}$ = 7.0 Hz. − ^{13}C NMR: δ = 157.7 (q, *C*OCF$_3$), 156.4 (q, *C*OCF$_3$), 138.1 (C_s), 129.1 (C_m), 128.4 (C_o), 127.4 (C_p), 116.7 [q, CF_3 (C-6)], 115.3 [q, CF_3 (C-1)], 80.0 (C-1), 69.9 (C-5), 55.6 (C-1′), 48.1 (C-6), 29.6 (C-4), 26.6 (C-3), 23.7 (C-2), 17.8 (C-2′); $J_{F,CO}$ = 35.9, $J_{F,CO}$ = 37.9, $J_{F,CF3}$ = 287.3, $J_{F,CF3}$ = 288.6 Hz. − MS; *m/z* (%): 552 (11) $[M]^+$, 440 (2) $[M - NHCOCF_3]^+$, 425 (10) $[M - I]^+$, 312 (14) $[M - NHCOCF_3 - HI]^+$, 105 (100) $[R^*]^+$. **19**: IR (KBr): ν = 3299 cm^{-1} (NH), 1736 (NHCO), 1683 (NR*CO), 1561 (NHCO). − ^1H NMR: δ = 7.48−7.35 (m, 5 H, aromatic H), 6.62 (d, NH), 5.31 (q, 1′-H), 5.17 (dd, 1-H), 3.87−3.70 (m, 2-, 5-H), 3.25 (dd, 6a-H), 2.79 (dd, 6b-H), 2.53 (dddd, 3β-H), 2.20 (dddd, 3α-H), 1.68 (d, 2′-H), 1.70 (m, 4α-H), 1.20 (dddd, 4β-H); $J_{1,2}$ = $J_{1,NH}$ = 9.6, $J_{2,3\alpha}$ = $J_{3\alpha,3\beta}$ = $J_{3\alpha,4\beta}$ = 13.2, $J_{3\alpha,4\alpha}$ = 4.3, $J_{3\beta,4\beta}$ = 4.6, $J_{5,6a}$ = 2.4, $J_{5,6b}$ = 7.9, $J_{6a,6b}$ = 14.3, $J_{1',2'}$ = 7.0 Hz. − ^{13}C NMR: δ = 138.3 (C_s), 128.9 (C_m), 128.3 (C_o), 127.3 (C_p), 82.5 (C-1), 75.5 (C-5), 55.3 (C-1′), 48.8 (C-6), 36.7 (C-4)*, 32.0 (C-3)*, 24.8 (C-2)*, 17.6 (C-2′). − MS (FAB); *m/z* (%): 553 (100) $[M + H]^+$, 449 (31) $[M - R^* + H]^+$, 440 (63) $[M - NHCOCF_3]^+$, 425 (22) $[M - I]^+$, 336 (44) $[M - NHCOCF_3 - R^* + H]^+$, 314 (37) $[M - NHCOCF_3 - I + H]^+$. **18**: ^1H NMR: δ = 7.48−7.30 (m, 10 H, aromatic H), 5.32 (q, 1′-H), 5.13 (s, 1-H), 4.20−4.08 (m, 5-, 2-H), 3.25 (dd, 6a-H), 2.76 (dd, 6b-H), 2.20−1.50 (m, 3-, 4-H_2), 1.70 (d, 2′-H); $J_{1,2}$ < 1.0, $J_{5,6a}$ = 2.1, $J_{5,6b}$ = 7.9, $J_{6a,6b}$ = 14.0 Hz. − ^{13}C NMR: δ = 138.4 (C_s), 128.9 (C_m), 128.2 (C_o), 127.2 (C_p), 116.8 (q, CF_3), 96.5 (C-1), 66.3 (C-5), 55.4 (C-1′), 49.6 (C-6), 27.6 (C-4)*, 26.6 (C-3)*, 25.0 (C-2)*, 18.0 (C-2′); $J_{F,CF3}$ = 287.6 Hz. − MS (ESI); *m/z* (%): 835 (38) $[M + K]^+$, 919 (100) $[M + Na]^+$, 440 (21) $[C_{16}H_{18}F_3INO_2]^+$.

1-O-Acetyl-2,3,4,6-tetradeoxy-2α-trifluoroacetylamino-6-{trifluoroacetyl-[(1R)-phenylethyl]}amino-α/β-D-hexopyranose (**10α/β**): A solution of **15b** (400 mg, 0.72 mmol) in THF (15 ml) and water (6 ml) was treated with triethylamine (0.30 ml, 2.17 mmol).

The mixture was stirred at room temp. until total conversion was achieved (TLC, 14 h). After addition of water (30 ml) and extraction with $CHCl_3$ (3 × 60 ml), the organic layer was dried ($MgSO_4$) and concentrated to dryness. The crude product was dissolved in pyridine (5 ml), acetic anhydride (5 ml) was added, and stirring was continued at room temp. for 4 h. Concentration in vacuo and chromatography of the residue [silica gel, cyclohexane/ethyl acetate, 2:1, R_f (**10**) = 0.39] provided **10** (314 mg, 88%, α/β ≈ 2:1) as colorless crystals. The α anomer was found to be separable by chromatography [silica gel, $CHCl_3$/methanol, 50:1, R_f (**10α**) = 0.42, R_f (**10β**) = 0.29]. **10α**: M.p. 62°C. – $[\alpha]_D^{25}$ = +28.4 (*c* = 1.0, $CHCl_3$). – IR (KBr): ṽ = 3322 cm^{-1} (NH), 1780 ($OCOCH_3$), 1725 (NHCO), 1678 (NR*CO), 1560 (NHCO). – ^1H NMR: δ = 7.45–7.25 (m, 5 H, aromatic H), 6.18 (d, NH), 6.06 (d, 1-H), 5.28 (q, 1′-H), 4.23–4.09 (m, 2-, 5-H), 3.28 (dd, 6a-H), 2.70 (dd, 6b-H), 2.12 (s, $OCOCH_3$), 1.69 (d, 2′-H), 2.00–1.60 (m, 4α-H, 3-H_2), 1.30 (dddd, 4β-H); $J_{1,2}$ = 3.4, $J_{2,NH}$ = 8.9, $J_{3\alpha,4\beta}$ = 11.9, $J_{5,6a}$ = 2.4, $J_{5,6b}$ = 8.2, $J_{6a,6b}$ = 14.3 Hz. – ^{13}C NMR: δ = 169.2 (O*C*OCH_3), 157.2 (q, *C*OCF_3), 156.6 (q, *C*OCF_3), 138.3 (C_s), 129.0 (C_m), 128.3 (C_o), 127.3 (C_p), 116.8 [q, CF_3 (C-6)], 115.8 [q, CF_3 (C-2)], 90.2 (C-1), 67.0 (C-5), 55.5 (C-1′), 48.9 (C-6)*, 47.1 (C-2)*, 27.7 (C-4)**, 24.4 (C-3)**, 20.8 (OCO*C*H_3), 17.8 (C-2′); $J_{F,CO}$ = 36.6, $J_{F,CF3}$ = 287.3, $J_{F,CF3}$ = 288.4 Hz. – MS (isobutane, 170 eV); *m/z* (%): 425 (83) $[M - OCOCH_3]^+$, 381 (20) $[M - R^* + 2H]^+$, 321 (100) $[M - OCOCH_3 - R^* + H]^+$, 268 (16) $[M - R^* - NHCOCF_3 + H]^+$, 105 (78) $[R^*]^+$. – MS (NH_3, 170 eV); m/z (%): 502 (100) $[M + NH_4]^+$, 442 (19) $[M - OCOCH_3 + NH_3]^+$, 425 (32) $[M - OCOCH_3]^+$, 398 (25) $[M - R^* + NH_4 + H]^+$. **10β**: ^1H NMR: δ = 7.45–7.25 (m, 5 H, aromatic H), 6.52 (m, NH), 5.44 (d, 1-H), 3.95–3.80 (m, 5-, 2-H), 3.23 (dd, 6a-H), 2.68 (dd, 6b-H), 2.10 (s, $OCOCH_3$), 1.60 (d, 2′-H), 2.00–1.60 (m, 4α-H, 3-H_2), 1.30 (dddd, 4β-H); $J_{1,2}$ = 8.5, $J_{2,NH}$ = 8.9, $J_{5,6a}$ = 2.7, $J_{5,6b}$ = 8.6, $J_{6a,6b}$ = 14.7 Hz. – ^{13}C NMR: δ = 138.1 (C_s), 129.0 (C_m), 128.4 (C_o), 127.3 (C_p), 94.4 (C-1), 73.3 (C-5), 55.5 (C-1′), 49.2 (C-6)*, 48.8 (C-2)*, 28.2 (C-4)**, 27.9 (C-3)**, 20.6 (OCO*C*H_3), 17.7 (C-2′).

1-N-Trifluoroacetylamino-1,2,3,4,6-pentadeoxy-2β-iodo-6-{trifluoroacetyl-[(1S)-phenylethyl]}amino-α-L-hexopyranoside (*ent*-**15b**) *and 1-O-Acetyl-2,3,4,6-tetradeoxy-2α-trifluoroacetylamino-6-{trifluoroacetyl-[(1S)-phenylethyl]}-amino-α-L-hexopyranose* (*ent*-**10α**): Conversion of *ent*-**2** (100 mg, 0.32 mmol) as described for **2** by using NIS provided *ent*-**15b** (98 mg, 55%) and *ent*-**17** (41 mg, 24%). The former was transformed into *ent*-**10** (α/β ≈ 2:1, 74 mg, 86%) as described for **15b**. *ent*-**10α**: $[\alpha]_D^{25}$ = −26.6 (*c* = 0.3, $CHCl_3$).

1-N-Trifluoroacetylamino-6-O-acetyl-1,2,3,4-tetradeoxy-2β-iodo-α-D/L-hexopyranoside (*rac*-**22**), *1-N-Trifluoroacetylamino-6-O-acetyl-1,2,3,4-tetradeoxy-2α-iodo-β-D/L-hexopyranoside* (*rac*-**25**), *1-N-Succinimido-6-O-acetyl-1,2,3,4-tetradeoxy-2β-iodo-α-D/L-hexopyranoside* (*rac*-**24**), *and 6-O-Acetyl-1,2,3,4-tetradeoxy-2β-iodo-α-D/L-hexopyranosyl 6-O-Acetyl-1,2,3,4-tetradeoxy-2β-iodo-α-D/L-hexopyranoside* (*meso*-**26**/*rac*-**26′**): Procedure 1: To a solution of *rac*-**21** (1.0 g, 6.41 mmol) and trifluoroacetic amide (1.09 g, 9.65 mmol) in anhydrous acetonitrile, NIS (1.73 g, 7.69 mmol) was added at 0°C (under N_2). After stirring for 1.5 h at room temp., the solvent was removed in vacuo, the residue was dissolved in CH_2Cl_2, and the resulting solution was washed with saturated aqueous sodium thiosulfate solution and water. The organic layer was dried ($MgSO_4$), concentrated to dryness, and chromatographed [silica gel, ethyl acetate/cyclohexane/$CHCl_3$, 5:5:1, R_f (*rac*-**25**) = 0.53, R_f (*rac*-**22**) = 0.44, R_f (*rac*-**24**) = 0.23] to provide sequentially *rac*-**22** (1.57 g, 62%), *rac*-**25** (37 mg, 1.4%) and *rac*-**24** (0.76 g, 31%). Procedure 2: $[I(sym\text{-collidine})_2]ClO_4$ (450 mg, 0.96 mmol) was added to a solution of *rac*-**21** (100 mg, 0.64 mmol) and trifluoroacetic amide (101 mg, 0.89 mmol) in anhydrous CH_2Cl_2 at 0°C (under N_2). After stirring for 1 h at 0°C and for 2 h at room temp., the reaction was complete (TLC control). The organic layer was washed with saturated aqueous sodium thiosulfate solution, saturated aqueous copper sulfate solution, and water, dried ($MgSO_4$), and concentrated to dryness. The residue was chromatographed (silica gel, ethyl acetate/cyclohexane/$CHCl_3$, 5:5:1) to yield *rac*-**22** (179 mg, 70.3%), *rac*-**25** (14 mg, 5.5%) and *meso*-**26**/*rac*-**26′** (7 mg, 2%, R_f = 0.7). *rac*-**22**: IR (KBr): ṽ = 3330 cm^{-1} (NH), 1736 ($OCOCH_3$), 1713 (NHCO), 1524 (NHCO). – ^1H NMR: δ = 6.79 (d, NH), 5.62 (dd, 1-H), 4.35 (dd, 6a-H), 4.42–4.08 (m, 6b-, 2-, 5-H), 2.30 (m, 3-H_2), 2.11 (s, $OCOCH_3$), 1.82 (m, 4-H_2); $J_{1,2}$ = 8.0, $J_{1,NH}$ = 6.4, $J_{5,6a}$ = 8.6, $J_{6a,6b}$ = 12.8 Hz. – ^{13}C NMR: δ = 79.3 (C-1), 70.8 (C-5), 63.9 (C-6), 30.4 (C-2), 25.8 (C-4), 24.4 (C-3), 20.8 (OCO*C*H_3). – MS (FAB); *m/z* (%): 396 (14) $[M + H]^+$, 283 (13) $[M - NHCOCF_3]^+$. *rac*-**25**: IR (KBr): ṽ = 3275 cm^{-1} (NH), 1716 (C=O), 1560 (NHCO). – ^1H NMR: δ = 6.81 (d, NH), 5.33 (dd, 1-H), 4.09 (d, 6-H_2), 4.02–3.90 (m, 2-, 5-H), 2.67 (dddd, 3β-H), 2.32 (dddd, 3α-H), 2.12 (s, $OCOCH_3$), 1.62 (m, 4-H_2); $J_{1,2}$ = $J_{1,NH}$ = 10.1, $J_{2,3\alpha}$ = $J_{3\alpha,3\beta}$ = $J_{3\alpha,4\beta}$ = 13.7, $J_{2,3\beta}$ = $J_{3\beta,4\alpha}$ = $J_{3\alpha,4\alpha}$ = 4.3 Hz. – ^{13}C NMR: δ = 170.9 (C=O), 82.4 (C-1), 76.1 (C-5), 65.9 (C-6), 36.6 (C-2), 30.3 (C-4), 25.6 (C-3), 20.9 (OCO*C*H_3). – MS (FAB); *m/z* (%): 396 (54) $[M + H]^+$, 283 (100) $[M - NHCOCF_3]^+$, 268 (39) $[M - I]^+$, 208 (8) $[M - HI - OCOCH_3]^+$. *rac*-**24**: ^1H NMR: δ = 5.58 (d, 1-H), 5.21 (ddd, 5-H), 4.43 (m, 6-H_2), 4.42 (m, 2-H), 2.70 (s, 3′-, 4′-H_2), 2.52 (dddd, 3α-H), 2.30 (dddd, 3β-H), 2.11 (s, $OCOCH_3$), 2.10 (m, 4β-H), 1.60 (dddd, 4α-H); $J_{1,2}$ = 10.7, $J_{2,3\beta}$ = $J_{3\alpha,3\beta}$ = $J_{3\beta,4\alpha}$ = 12.9, $J_{2,3\alpha}$ = $J_{3\beta,4\beta}$ = $J_{3\alpha,4\alpha}$ = $J_{3\alpha,4\beta}$ = $J_{5,6a}$ = 4.6, $J_{5,6b}$ = 12.2 Hz. – ^{13}C NMR: δ = 175.9 (CON), 170.8 (O*C*OCH_3), 78.8 (C-1), 72.2 (C-5), 62.2 (C-6), 32.7 (C-2), 27.9 (C-3′, C-4′), 27.8 (C-4)*, 22.7 (C-3)*, 20.8 (OCO*C*H_3). – MS (isobutane, 170 eV); *m/z* (%): 382 (29) $[M + H]^+$, 283 (19) $[M - succ]^+$, 256 (41) $[M - HI + 2H]^+$, 254 (8) $[M - HI]^+$, 158 (100) $[M - succ - HI + 2H]^+$. *meso*-**26**/*rac*-**26′**: ^1H NMR: δ = 5.30 (s, 1-H), 5.27 (s, 1-H), 4.28 (m, 5-H), 4.22–4.02 (m, 2-H, 6-H_2), 2.30–1.40 (m, 4-, 3-H_2), 2.14/2.09 (s, $OCOCH_3$); $J_{1,2}$ > 1.0 Hz. – ^{13}C NMR: δ = 99.3/96.5 (C-1), 68.4/67.9 (C-5), 66.3/66.2, (C-6), 27.4/27.2 (C-4)*, 27.1/26.9 (C-3)*, 23.4/23.3 (C-2), 20.9/20.8 (O*C*OCH_3). – MS (FAB); *m/z* (%): 605 (14) $[M + Na]^+$, 583 (8) $[M + H]^+$, 282 (100) $[C_8H_{12}IO_3]^+$.

Methyl 6-O-Acetyl-2,3,4-trideoxy-2α-trifluoroacetylamino-α/β-D/L-hexopyranoside (*rac*-**23α/β**): A solution of *rac*-**22** (0.50 g, 1.27 mmol) in DMF (20 ml) and methanol (10 ml) was treated with triethylamine (0.71 ml, 5.1 mmol) and stirring was continued at room temp. until the conversion was complete (TLC, 40 h). Concentration in vacuo and chromatography [silica gel, $CHCl_3$/methanol, 50:1, R_f (*rac*-**23α**) = 0.30, R_f (*rac*-**23β**) = 0.11] yielded *rac*-**23β** (299 mg, 84%) and *rac*-**23α** (32 mg, 9%) as colorless crystals. *rac*-**23β**: M.p. 152°C. – IR (KBr): ṽ = 3277 cm^{-1} (NH), 1734 ($OCOCH_3$), 1694 (NHCO), 1567 (NHCO). – ^1H NMR: δ = 6.23 (br. s, NH), 4.36 (d, 1-H), 4.12 (m, 6-H), 3.80 (m, 5-H), 3.64 (m, 2-H), 3.51 (s, OCH_3), 2.39 (m, 3β-H), 2.10 (s, $OCOCH_3$), 1.78–1.50 (m, 3α-H, 4-H_2); $J_{1,2}$ = 7.9 Hz. – ^{13}C NMR: δ = 102.8 (C-1), 73.7 (C-5), 63.9 (C-6), 56.2 (OCH_3), 51.4 (C-2), 27.2 (C-4), 26.3 (C-3), 20.8 (OCO*C*H_3). – MS (FAB); *m/z* (%): 322 (5) $[M + Na]^+$, 307 (18) $[M - OCH_3 + Na]^+$, 300 (17) $[M + H]^+$, 268 (100) $[M - OCH_3]^+$. – $C_{11}H_{16}F_3NO_5$ (299.3): calcd. C 44.15, H 5.38, N 4.68; found C 43.62, H 5.32, N 4.43. *rac*-**23α**: M.p. 77°C. – IR (KBr): ṽ = 3319 cm^{-1} (NH), 1737 ($OCOCH_3$), 1700 (NHCO), 1551 (NHCO). – ^1H NMR: δ = 6.47 (d, NH), 4.70 (d, 1-H), 4.20–4.02 (m, 5-H, 6-H_2), 3.93 (m, 2-H), 3.47 (s, OCH_3), 2.10 (s, $OCOCH_3$), 1.97 (m, 3β-H), 1.86–1.55 (m, 3α-H, 4-H_2); $J_{1,2}$ = 3.7, $J_{2,NH}$ = 8.6 Hz. – ^{13}C NMR: δ = 97.1 (C-1), 66.4 (C-5)*, 66.1 (C-6)*, 54.9

(OCH$_3$), 48.2 (C-2), 26.1 (C-4), 24.1 (C-3), 20.8 (OCO*C*H$_3$). − MS (FAB); *m/z* (%): 322 (2) $[M + Na]^+$, 307 (9) $[M - CH_3 + Na]^+$, 300 (12) $[M + H]^+$, 268 (100) $[M - OCH_3]^+$.

*Methyl 2,3,4-Trideoxy-2α-trifluoroacetylamino-β-*D*/*L*-hexopyranoside* (*rac*-**27a**): A mixture of *rac*-**23β** (15 mg, 0.05 mmol) and PLE in phosphate buffer (pH = 7, 0.1 N, 6 ml) and acetone (0.2 ml) was shaken at room temp. for 24 h. After filtration and extraction with CH$_2$Cl$_2$, the organic layer was dried (MgSO$_4$), concentrated in vacuo, and the remaining residue was chromatographed [silica gel, CHCl$_3$/methanol, 10:1, R_f (*rac*-**27a**) = 0.23] to furnish *rac*-**27a** (12 mg, 94%) as colorless crystals, m.p. 114°C. − IR (KBr): $\tilde{\nu}$ = 3282 cm^{-1} (OH), 1699 (NHCO), 1568 (NHCO). − ^{1}H NMR: δ = 6.20 (br. s, NH), 4.39 (d, 1-H), 3.78−3.60 (m, 2-, 5-H, 6-H$_2$), 3.52 (s, OCH$_3$), 2.38 (m, 3β-H), 1.95 (dd, OH), 1.72−1.53 (m, 3α-H, 4-H$_2$); $J_{1,2}$ = 8.2 Hz. − ^{13}C NMR: δ = 103.0 (C-1), 77.2 (C-5), 65.2 (C-6), 56.3 (OCH$_3$), 51.6 (C-2), 27.5 (C-4), 25.7 (C-3). − MS (FAB); *m/z* (%): 280 (2) $[M + Na]^+$, 258 (17) $[M + H]^+$, 226 (88) $[M - OCH_3]^+$, 208 (7) $[M - OCH_3 - H_2O]^+$. − $C_9H_{14}F_3NO_4$ (257.2): calcd. C 42.03, H 5.48, N 5.45; found C 42.30, H 5.38, N 5.03.

*Methyl 2,3,4-Trideoxy-2α-trifluoroacetylamino-β-*D*-hexopyranoside* (**27a**) *and Methyl 6-O-Acetyl-2,3,4-trideoxy-2α-trifluoroacetylamino-β-*L*-hexopyranoside* (*ent*-**23β**): Procedure 1: A mixture of *rac*-**23β** (500 mg, 1.67 mmol) and PPL (50 mg, 2 U/mg, Fluka) in phosphate buffer (pH = 7, 0.1 N, 150 ml) and acetone (15 ml) was shaken at room temp. for 96 h. After filtration and extraction with CH$_2$Cl$_2$ (3 × 40 ml), the organic layer was dried (MgSO$_4$), filtered, and concentrated in vacuo. The residue was chromatographed [silica gel, CHCl$_3$/methanol, 10:1, R_f (*ent*-**23β**) = 0.45, R_f (**27a**) = 0.23] to yield **27a** (160 mg, 37%, *ee* > 98) and **23β**/*ent*-**23β** (300 mg). A mixture of the resulting **23β**/*ent*-**23β** (300 mg, 1.0 mmol) and PPL (50 mg) in phosphate buffer (pH = 7, 0.1 N, 90 ml) and acetone (9 ml) was then shaken at room temp. for 9 d. Work-up as described above afforded *ent*-**23β** (145 mg, 29%, *ee* > 98) and **27a**/*ent*-**27a** (109 mg, 42%). Procedure 2: A solution of *rac*-**23β** (500 mg, 1.67 mmol) in phosphate buffer (pH = 7, 0.1 N, 150 ml) and acetone (15 ml) was shaken with PPL (75 mg) for 14 d at room temp. After 3 d, a further aliquot of PPL (50 mg) was added. Analogous work-up as that described above yielded *ent*-**23β** (138 mg, 28%, *ee* > 98) and **27a**/*ent*-**27a** (284 mg, 62%). The *ee* was determined from the ^{1}H-NMR spectra (400 MHz) of **23β**.*ent*-**23β** in the presence of 0.8−1 equiv. of Eu(hfc)$_3$. In comparison with *rac*-**23β**, **23β** showed a singlet for 1-OCH$_3$ at δ = 3.56, whereas the signal for *ent*-**23β** appeared at δ = 3.57. **27**: $[\alpha]_D^{25}$ = −42.0 (*c* = 0.5, CHCl$_3$). ent-**23b**: $[\alpha]_D^{25}$ = +44.3 (*c* = 0.5, CHCl$_3$).

*Methyl 2,3,4-Trideoxy-2α-trifluoroacetylamino-β-*L*-hexopyranoside* (*ent*-**27a**): A solution of *ent*-**23β** (45 mg, 0.15 mmol) in phosphate buffer (pH = 7, 0.1 N, 18 ml) and acetone (0.6 ml) was shaken with PLE at room temp. for 24 h. Analogous work-up yielded *ent*-**27a** (36 mg, 93%). − $[\alpha]_D^{25}$ = +42.9 (*c* = 0.5, CHCl$_3$).

*Methyl 2,3,4-Trideoxy-6-O-methylsulfonyl-2α-trifluoroacetylamino-β-*D*-hexopyranoside* (**27b**) *and Methyl 6-Azido-2,3,4,6-tetradeoxy-2α-trifluoracetylamino-β-*D*-hexopyranoside* (**28**): Treatment of **27a** (50 mg, 0.19 mmol) according to GP 1 yielded after chromatography (silica gel, cyclohexane/ethyl acetate, 2:1, R_f = 0.32) **28** (49 mg, 92%) as colorless crystals. **27b** could be isolated after mesylation (filtration through silica gel, cyclohexane/ethyl acetate, 2:1, R_f = 0.28). **27b**: ^{1}H NMR (400 MHz): δ = 6.28 (br. s, NH), 4.38 (d, 1-H), 4.27 (d, 6-H$_2$), 3.85 (m, 5-H), 3.65 (m, 2-H), 3.49 (s, OCH$_3$), 3.05 (s, OSO$_2$CH$_3$), 2.37 (dddd, 3β-H), 1.76 (dddd, 4α-H), 1.66 (dddd, 3α-H), 1.57 (m, 4β-H); $J_{1,2}$ = 8.0, $J_{2,3\beta}$ = $J_{3\beta,4\alpha}$ = $J_{3\beta,4\beta}$ = 3.8, $J_{2,3\alpha}$ = $J_{3\alpha,4\beta}$ = $J_{3\alpha,3\beta}$ = $J_{4\beta,5}$ = 12.6, $J_{3\alpha,4\alpha}$ = 4.0, $J_{4\alpha,4\beta}$ = 13.1 Hz. **28**: M.p. 78°C. − $[\alpha]_D^{25}$ = −50.6 (*c* = 0.4, CHCl$_3$). − ^{1}H NMR (400 MHz): δ = 6.20 (br. s, NH), 4.48 (d, 1-H), 3.74 (m, 5-H), 3.63 (m, 2-H), 3.51 (s, OCH$_3$), 3.44 (dd, 6a-H), 3.14 (dd, 6b-H), 2.38 (dddd, 3β-H), 1.69 (dddd, 4α-H), 1.61 (dddd, 3α-H), 1.52 (m, 4β-H); $J_{1,2}$ = 8.0, $J_{2,3\alpha}$ = $J_{3\alpha,4\beta}$ = 11.2, $J_{2,3\beta}$ = $J_{3\beta,4\alpha}$ = $J_{3\beta,4\beta}$ = 4.8, $J_{3\alpha,3\beta}$ = 12.3, $J_{3\alpha,4\alpha}$ = 3.2, $J_{4\alpha,4\beta}$ = $J_{4\beta,5}$ = 12.6 , $J_{5,6a}$ = 7.8, $J_{5,6b}$ = 3.5, $J_{6a,6b}$ = 13.4 Hz. − ^{13}C NMR: δ = 102.8 (C-1), 75.8 (C-5), 56.4 (OCH$_3$), 54.3 (C-6), 51.5 (C-2), 27.4 (C-4)*, 27.3 (C-3)*. − MS (FAB); *m/z* (%): 305 (9) $[M + Na]^+$, 283 (49) $[M + H]^+$, 251 (100) $[M - OCH_3]^+$, 240 (12) $[M - N_3]^+$, 139 (60) $[M - OCH_3 - NHCOCF_3]^+$.

*Methyl 6-Azido-2,3,4,6-tetradeoxy-2α-trifluoroacetylamino-β-*L*-hexopyranoside* (*ent*-**28**): Treatment of *ent*-**27a** (20 mg, 0.08 mmol) as described for **27a** gave *ent*-**28** (21 mg, 95%). − ^{1}H, ^{13}C NMR, MS data were identical to those of **28**. *ent*-**28**: $[\alpha]_D^{25}$ = +49.4 (*c* = 0.4, CHCl$_3$).

*1-O-Acetyl-6-azido-2,3,4,6-tetradeoxy-2α-trifluoroacetylamino-α-*D*-hexopyranose* (**11**): Treatment of **28** (40 mg, 0.14 mmol) according to GP 3 (0.3 ml Ac$_2$O/30 ml CH$_2$Cl$_2$/one drop of conc. H$_2$SO$_4$, 0°C, 1 h) yielded after chromatography (silica gel, cyclohexane/ethyl acetate, 1:2, R_f = 0.20) **11** (39 mg, 89% , α/β ≈ 12:1) as colorless crystals. **11α** was found to be separable by chromatography [silica gel, CHCl$_3$/methanol, 10:1, R_f (**11α**) = 0.58], m.p. 63°C. − $[\alpha]_D^{25}$ = +57.6 (*c* = 0.2, CHCl$_3$). − IR (KBr): $\tilde{\nu}$ = 3328 cm^{-1} (NH), 2104 (N$_3$), 1749 (OCOCH$_3$), 1719 (NHCO), 1561 (NHCO). − ^{1}H NMR (400 MHz): δ = 6.15 (d, 1-H), 6.12 (br. s, NH), 4.25 (m, 5-H), 3.95 (m, 2-H), 3.31 (dd, 6a-H), 3.26 (dd, 6b-H), 2.18 (s, OCOCH$_3$), 2.04 (dddd, 3β-H), 1.90−1.60 (m, 3α-H, 4-H$_2$); $J_{1,2}$ = 3.2, $J_{2,3\beta}$ = $J_{3\beta,4\alpha}$ = $J_{3\beta,4\beta}$ = 4.8, $J_{3\alpha,3\beta}$ = 15.0, $J_{5,6a}$ = 5.9, $J_{5,6b}$ = 4.3, $J_{6a,6b}$ = 13.1 Hz. − ^{13}C NMR: δ = 90.3 (C-1), 69.5 (C-5), 54.2 (C-6), 47.4 (C-2), 26.9 (C-4), 23.8 (C-3), 20.9 (OCO*C*H$_3$). − MS (FAB); *m/z* (%): 333 (14) $[M + Na]^+$, 291 (13) $[M + Na - N_3]^+$, 274 (9) $[M + Na - OCOCH_3]^+$, 251 (24) $[M - OCOCH_3]^+$, 162 (6) $[M + Na - OCOCH_3 - NHCOCF_3]^+$, 139 (51) $[M - OCOCH_3 - NHCOCF_3]^+$.

*1-O-Acetyl-6-azido-2,3,4,6-tetradeoxy-2α-trifluoroacetylamino-β-*L*-hexopyranose* (*ent*-**11**): Treatment of *ent*-**28** (20 mg, 0.07 mmol) as described for **11** gave *ent*-**11** (20 mg, 91%). − ^{1}H, ^{13}C NMR, IR, MS data were identical to those of **11**. *ent*-**11**: $[\alpha]_D^{25}$ = −59.8 (*c* = 0.2, CHCl$_3$).

*4-Azido-3-O-[6′-azido-2′,3′,4′,6′-tetradeoxy-2′α-trifluoroacetylamino-α-*D*-hexopyranosyl]-1-N,2-O-carbonyl-1,4,5-trideoxy-6-O-methyl-1-(methylamino)-*L*-chiro-inositol* (**31**): To a solution of **11** (30 mg, 0.097 mmol) and **30** (26 mg, 0.11 mmol) in anhydrous CH$_2$Cl$_2$, BF$_3$·OEt$_2$ (13 µl, 0.11 mmol) was added (under N$_2$). After stirring for 1 h at room temp., the reaction mixture was quenched with saturated sodium bicarbonate solution. Extraction with CH$_2$Cl$_2$, drying (MgSO$_4$), concentration in vacuo, and chromatography on silica gel [CHCl$_3$/MeOH, 10:1, R_f (**31**) = 0.59, R_f (**30**) = 0.4] gave **31** (38 mg, 79%) as a colorless oil. − ^{1}H NMR (400 MHz): δ = 6.48 (d, NH), 5.26 (d, 1′-H), 4.48 (dd, 2-H), 4.20−4.07 (m, 2′-, 5′-H), 3.78 (dd, 1-H), 3.81−3.64 (m, 3-, 4-, 6-H), 3.42 (s, OCH$_3$), 3.33 (dd, 6′a-H), 3.25 (dd, 6′b-H), 2.81 (s, NCH$_3$), 2.28 (ddd, 5α-H), 1.98 (ddd,5β-H), 1.75−1.60 (m, 4′-, 3′-H$_2$); $J_{1',2'}$ = 3.8, $J_{2',NH}$ = 10.2, $J_{5',6'a}$ = 6.5, $J_{5',6'b}$ = 4.0, $J_{6'a,6'b}$ = 12.9, $J_{1,2}$ = $J_{2,3}$ = 7.2, $J_{4,5\alpha}$ = $J_{5\alpha,6}$ = 4.3, $J_{5\alpha,5\beta}$ = 13.7, $J_{1,6}$ = 2.7 Hz. − ^{13}C NMR: δ = 94.9 (C-1′), 78.0 (C-2)*, 77.2 (C-3)*, 69.8 (C-5′), 65.5 (C-6), 61.0 (C-1), 57.1 (OCH$_3$), 56.8 (C-4), 53.3 (C-6′), 48.8 (C-2′), 30.6 (NCH$_3$), 28.4 (C-5′), 28.1 (C-4′), 23.3 (C-3′). − MS (FAB); *m/z* (%): 515 (16) $[M + Na]^+$, 493 (16) $[M + H]^+$, 251 (3) $[C_8H_{10}N_4O_2F_3]^+$, 241 (42) $[C_9H_{13}N_4O_4]^+$, 139 (68) $[C_6H_9N_3O - C_8H_{10}N_4O_2F_3 - NHCOCF_3]^+$.

Methyl 6-O-Acetyl-2α-azido-2,3,4-trideoxy-α/β-D/L-hexopyranoside (*rac*-**39**/*rac*-**40**), *Methyl 6-O-Acetyl-2β-azido-2,3,4-trideoxy-α/β-D/L-hexopyranoside* (*rac*-**38**/*rac*-**32**) *and 6-O-Acetyl-1,2β-diazido-1,2,3,4-tetradeoxy-αα-D/L-hexopyranose* (*rac*-**41**): Anhydrous acetonitrile was added at −40°C (N_2) to a mixture of *rac*-**21** (3.0 g, 19.2 mmol), cerium(IV) ammonium nitrate (21.0 g, 38.3 mmol) and NaN_3 (1.8 g, 27.7 mmol). After stirring at −40°C for 2.5 h, MeOH (5 ml) was added, the reaction mixture was stirred for a further 2.5 h at 0°C, and then concentrated in vacuo. After the addition of H_2O (200 ml) and extraction with CH_2Cl_2 (3 × 50 ml), the combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. The crude residue (*rac*-**39/40**:*rac*-**38**:*rac*-**32**:*rac*-**41** ≈ 2.0:3.2:4.8:1.1) was separated by chromatography [silica gel, cyclohexane/ethyl acetate, 4:1, R_f (*rac*-**41**) = 0.38, R_f (*rac*-**39**/*rac*-**40**/*rac*-**38**) = 0.28, R_f (*rac*-**32**) = 0.18] to give *rac*-**32** (1.40 g, 32%), *rac*-**41** (0.31 g, 7%) and a mixture of *rac*-**39, rac-40** and *rac*-**38** (1.75 g, 40%) as colorless oils. *rac*-**32**: IR (film): $\tilde{\nu}$ = 2094 (N_3), 1733 (OCOCH$_3$). − ^{1}H NMR: δ = 4.48 (d, 1-H), 4.20 (dd, 6a-H), 4.13 (dd, 6b-H), 3.74 (dddd, 5-H), 3.60 (ddd, 2-H), 3.53 (s, OCH$_3$), 2.09 (s, OCOCH$_3$), 2.05 (dddd, 3β-H), 1.74 (dddd, 3α-H), 1.62 (dddd, 4β-H), 1.47 (dddd, 4α-H); $J_{1,2} = 1.5$, $J_{2,3\alpha} = J_{2,3\beta} = J_{3\beta,4\alpha} = 3.5$, $J_{3\alpha,3\beta} = J_{3\alpha,4\beta} = J_{4\alpha,4\beta} = 13.5$, $J_{3\alpha,4\alpha} = 4.5$, $J_{3\beta,4\beta} = 4.0$, $J_{4\alpha,5} = 3.0$, $J_{4\beta,5} = 10.5$, $J_{5,6a} = 6.2$, $J_{5,6b} = 4.3$, $J_{6a,6b} = 11.5$ Hz. − ^{13}C NMR: δ = 170.9 (O*C*OCH$_3$), 102.3 (C-1), 73.4 (C-5), 66.1 (C-6), 57.6 (C-2), 56.5 (OCH$_3$), 26.4 (C-4)*, 22.2 (C-3)*, 20.8 (OCO*C*H$_3$). − MS (isobutane, 170 eV); *m*/*z* (%): 230 (10) [M + H]$^+$, 202 (8), 198 (90) [M − CH$_3$O]$^+$, 170 (21), 142 (76). *rac*-**39**/*rac*-**40** (as a mixture from incomplete acetolysis, described in the following procedure): IR (KBr): $\tilde{\nu}$ = 2090 cm^{-1} (N_3), 1720 (OCOCH$_3$). − ^{1}H NMR: δ = 4.75 (d, 1-H, α), 4.20−4.05 (m, 1-H, β, 6-H$_2$, α,β), 3.97 (m, 5-H, α), 3.58 (m, 5-H, β), 3.57 (s, OCH$_3$, β), 3.49 (s, OCH$_3$, α), 3.35−3.16 (m, 2-H α,β), 2.12 (s, OCOCH$_3$, α,β), 2.25−1.60 (m, 3-, 4-H$_2$, α,β); $J_{1,2}(\alpha) = 3.1$ Hz. − ^{13}C NMR: δ = 170.8 (C=O), 105.5 (C-1, β), 98.8 (C-1, α), 75.0 (C-5, β), 73.4 (C-5, α), 66.2 (C-6, α), 66.0 (C-6, β), 60.3 (C-2, β), 57.7 (C-2, α), 56.6 (OCH$_3$, β), 55.0 (OCH$_3$, α), 28.0 (C-4, β)*, 27.8 (C-4, α)**, 26.6 (C-3, α)**, 26.2 (C-3, β)*, 22.2 (OCO*C*H$_3$, α), 22.1 (OCO*C*H$_3$, β). − MS (NH$_3$, 170 eV); *m*/*z* (%): 230 (7) [M + H]$^+$, 198 [M − CH$_3$O]$^+$, 170 (22), 142 (39). − $C_9H_{15}N_3O_4$ (229.2). *rac*-**41**: IR (film): $\tilde{\nu}$ = 2100 (N_3), 1734 (OCOCH$_3$). − ^{1}H NMR: δ = 5.33 (s, 1-H), 4.24−4.07 (m, 5-, 6-H$_2$), 3.42 (dd, 2-H), 2.10 (s, OCOCH$_3$), 2.05 (dddd, 3α-H), 1.90 (dddd, 3β-H), 1.70 (dddd, 4β-H), 1.61 (m, 4α-H); $J_{2,3\alpha} = J_{3\beta,4\alpha} = 3.0$, $J_{2,3\beta} = 1.3$, $J_{3\alpha,4\beta} = J_{3\beta,4\beta} = 4.3$, $J_{3\alpha,3\beta} = J_{3\alpha,4\beta} = J_{4\alpha,4\beta} = 14.0$, $J_{4\beta,5} = 11.5$ Hz. − ^{13}C NMR: δ = 170.8 (C=O), 87.7 (C-1), 69.0 (C-5), 66.0 (C-6), 56.4 (C-2), 22.1 (C-4)*, 21.5 (C-3)*, 20.8 (OCO*C*H$_3$). − MS (NH$_3$, 170 eV); *m*/*z* (%): 258 (100) [M + NH$_4$]$^+$, 241 (2) [M + H]$^+$, 198 (2) [M − N$_3$]$^+$. − $C_8H_{12}N_6O_3$ (240.2).

1,6-Di-O-acetyl-2β-azido-2,3,4-trideoxy-α/β-D/L-hexopyranose (*rac*-**42**), *1,6-Di-O-acetyl-2α-azido-2,3,4-trideoxy-α/β-D/L-hexopyranose* (*rac*-**43**): Procedure 1: A solution of *rac*-**39**, *rac*-**40** and *rac*-**38** (1:1:3, 1.57 g, 6.9 mmol) was treated according to GP 3 [Ac_2O (15 ml)/CH_2Cl_2 (150 ml)/H_2SO_4 (0.2 ml, 3.7 mmol), 0°C, 4 h]. The aqueous phase was then extracted with CH_2Cl_2 (2 × 50 ml), the combined organic phases were dried ($MgSO_4$), and concentrated in vacuo. Chromatography of the resulting residue [silica gel, cyclohexane/ethyl acetate, 3:1, R_f (*rac*-**42**) = 0.11, R_f (*rac*-**43**) = 0.18, R_f (*rac*-**39**/*rac*-**40**) = 0.26] furnished *rac*-**43** (0.13 g, 7%, α/β ≈ 4:1), *rac*-**42** (0.90 g, 51%, α/β ≈ 2:1), a mixture of *rac*-**43** and *rac*-**42** (0.17 g, 10%) and *rac*-**39**/*rac*-**40** (0.36 g, 23%, α:β 2:1) (total yield 68%; based on conversion 91%) as colorless oils. Procedure 2: Treatment of the crude product mixture (*rac*-**32**, *rac*-**39**/*rac*-**40**, *rac*-**38** and *rac*-**41**; 276 mg) obtained from the azidonitration of *rac*-**21** (205 mg, 1.3 mmol) according to GP 3 (0°C, 8 h) gave *rac*-**43** (35 mg, 10% based on *rac*-**21**, α/β ≈ 4:1) and *rac*-**42** (184 mg, 55% based on *rac*-**21,** α/β ≈ 2:1) (total yield: 65% based on *rac*-**21**) as colorless oils, after twofold chromatography (silica gel, cyclohexane/ethyl acetate, 3:1). *rac*-**43**: IR (film): $\tilde{\nu}$ = 2113 cm^{-1} (N_3), 1757 (OCOCH$_3$). − ^{1}H NMR: δ = 6.21 (d, 1-H, α), 5.52 (d, 1-H, β), 4.17−4.05 (m, 6-H$_2$), 4.04 (m, 5-H, α), 3.83 (m, 5-H, β), 3.40 (m, 2-H, β), 3.36 (m, 2-H, α), 2.17/2.09 (s, OCOCH$_3$), 2.26−1.44 (m, 3-, 4-H$_2$, α, β); $J_{1,2}(\alpha) = 3.5$ Hz. − ^{13}C NMR: δ = 170.8/169.0 (O*C*OCH$_3$), 95.2 (C-1, β), 90.8 (C-1, α), 74.5 (C-5, β), 68.2 (C-5, α), 65.8 (C-6, α), 65.3 (C-6, β), 59.3 (C-2, β), 56.8 (C-2, α), 27.7 (C-4, β)*, 27.4 (C-4, α)**, 26.1 (C-3, β)*, 22.3 (C-3, α)**, 21.1/20.8 (OCO*C*H$_3$). − MS; *m*/*z* (%): 198 (1) [M − OCOCH$_3$]$^+$, 140 (6). *rac*-**42**: IR (film): $\tilde{\nu}$ = 2105 cm^{-1} (N_3), 1749 (OCOCH$_3$). − ^{1}H NMR: δ = 6.06 (s, 1-H, α), 5.82 (d, 1-H, β), 4.20−4.00 (m, 5-, α, 6-H$_2$ α, β), 3.90 (m, 5-H, β), 3.70 (m, 2-H, β), 3.58 (m, 2-H, α), 2.20/2.14/2.10 (s, OCOCH$_3$), 2.20−1.45 (m, 3-, 4-H$_2$, α, β); $J_{1,2}(\beta) = 1.6$ Hz. − ^{13}C NMR: δ = 170.9/170.8/168.9/168.8 (O*C*OCH$_3$), 93.7 (C-1, β), 91.5 (C-1, α), 74.5 (C-5, β), 68.9 (C-5, α), 66.2 (C-6, α), 65.8 (C-6, β), 56.8 (C-2, β), 55.7 (C-2, α), 26.1 (C-4, β)*, 22.4 (C-4, α)**, 21.6 (C-3, β)*, 21.4 (C-3, α)**, 21.0/20.9/20.8 (OCO*C*H$_3$). − MS (NH$_3$, 170 eV); *m*/*z* (%): 275 (100) [M + NH$_4$]$^+$, 247 (6), 170 (21), 142 (13).

1-(R/S)-5,6-Tri-O-acetyl-2S-azido-2,3,4-trideoxy-D/L-hexose Methyl Hemiacetal (*rac*-**44**/*rac*-**44′**): To a solution of *rac*-**32** (81 mg, 0.35 mmol) in Ac_2O (4 ml), conc. H_2SO_4 (3 drops) was added at 0°C. After stirring for 30 min. at this temp., the solution was poured into H_2O (50 ml), neutralized with solid Na_2CO_3, and the resulting aqueous mixture was extracted with CH_2Cl_2 (3 × 30 ml). The combined organic phases were dried ($MgSO_4$), concentrated in vacuo and the residue was separated by chromatography on silica gel [CH_2Cl_2/acetone, 80:1, R_f (*rac*-**42α**) = 0.32, R_f (*rac*-**42β**) = 0.25, R_f (*rac*-**44**/*rac*-**44′**) = 0.19] to give *rac*-**42** (61 mg, 67%) and *rac*-**44**/*rac*-**44′** (diastereomeric mixture, 8 mg, 7%) as colorless oils. − ^{1}H NMR: δ = 5.72 (s, 1-H), 5.70 (d, 1-H), 5.09 (m, 5-H), 4.23 (dd, 6a-H), 4.05 (dd, 6b-H), 3.50/3.47 (s, OCH$_3$), 2.17/2.15/2.08 (s, OCOCH$_3$), 1.86−1.42 (m, 3-, 4-H$_2$); $J_{1,2} = 1.2$, $J_{5,6a} = 3.8$, $J_{5,6b} = 6.1$, $J_{6a,6b} = 12.0$ Hz. − ^{13}C NMR: δ = 170.7/170.5 (O*C*OCH$_3$), 98.9/98.8 (C-1), 70.7 (C-5), 64.8 (C-6), 63.0 (OCH$_3$), 57.7/57.5 (C-2), 27.2 (C-4)*, 24.5 (C-3)*, 21.0/20.7 (OCO*C*H$_3$).

Methyl 2β-Azido-2,3,4-trideoxy-β-D/L-hexopyranoside (*rac*-**33a**): Treatment of *rac*-**32** (140 mg, 0.6 mmol) according to GP 2 (room temp., 1 h) provided − after filtration through a short column (ca. 5 cm) of silica gel (cyclohexane/ethyl acetate, 1:1, R_f = 0.16) − *rac*-**33a** (110 mg, 96%) as a colorless oil. − IR (film): $\tilde{\nu}$ = 3444 cm^{-1} (OH), 2094 (N_3), 1733 (OCOCH$_3$). − ^{1}H NMR: δ = 4.51 (d, 1-H), 3.70−3.50 (m, 2-, 5-H, 6-H$_2$), 3.58 (s, OCH$_3$), 2.12 (br. t, OH), 2.04 (dddd, 3β-H), 1.78 (dddd, 3α-H), 1.64 (m, 4β-H), 1.37 (dddd, 4α-H); $J_{1,2} = 1.5$, $J_{2,3\alpha} = 3.5$, $J_{2,3\beta} = J_{3\beta,4\alpha} = J_{3\beta,4\beta} = 3.0$, $J_{3\alpha,3\beta} = J_{3\alpha,4\beta} = J_{4\alpha,4\beta} = 12.6$, $J_{3\alpha,4\alpha} = J_{4\alpha,5} = 4.3$ Hz. − ^{13}C NMR: δ = 102.5 (C-1), 76.6 (C-5), 65.5 (C-6), 57.8 (C-2), 56.6 (OCH$_3$), 26.8 (C-4)*, 21.4 (C-3)*. − MS (NH$_3$, 170 eV), *m*/*z* (%): 205 (100) [M + NH$_4$]$^+$, 160 (3) [M − OH]$^+$, 142 (5).

Methyl 2β-Azido-2,3,4-trideoxy-6-O-[(R)-(−)-α-methoxy-α-trifluoromethylphenylacetyl]-β-D/L-hexopyranoside (**33c**/*dia*-**33c**): To a solution of *rac*-**33a** (8 mg, 0.043 mmol) and DMAP (15 mg, 0.12 mmol) in CH_2Cl_2 (5 ml), (*R*)-(−)-Mosher′s acid chloride (0.065 mmol in CH_2Cl_2) was added. The solution was stirred for 1 h at room temp. and then concentrated in vacuo. The resulting residue was filtered through a short column (4 cm) of silica gel (cyclohexane/ethyl acetate, 1:1, R_f = 0.55) to give **33c**/*dia*-**33c** (18 mg, 100%). − ^{1}H NMR (400 MHz): δ = 7.54−7.40 (m, 5 H, aromatic H), 4.46 [d, 1-H (D/*R*)], 4.43 [d, 1-H (L/*R*)], 4.40−4.35 (m, 6-H$_2$), 3.89−3.76

(m, 5-H), 3.65−3.60 (m, 2-H), 3.56 (s, OCH$_3$), 3.45 [s, OCH$_3$ (MTPA) (D/*R*)], 3.43 [s, OCH$_3$ (MTPA) (L/*R*)], 2.05−2.00 (m, 3β-H), 1.78−1.70 (m, 3α-H), 1.65−1.40 (m, 4-H$_2$).

Methyl 6-O-Acetyl-2β-azido-2,3,4-trideoxy-β-L-hexopyranoside (*ent*-**32**) *and Methyl 2β-Azido-2,3,4-trideoxy-β-D-hexopyranoside* (**33a**): A mixture of *rac*-**32** (560 mg, 2.45 mmol) and PPL (15 mg, 2 U/mg, Fluka) in phosphate buffer (50 ml, 0.01 M, pH = 7) and *n*-hexane (25 ml) was stirred for 12 h at room temp. [TLC, cyclohexane/ethyl acetate, 1:1, R_f (**32**) = 0.37, R_f (**33a**) = 0.16]. The aqueous phase was then extracted with CH$_2$Cl$_2$ (5 × 40 ml), the combined extracts were dried (MgSO$_4$), and concentrated in vacuo. The residue was separated on silica gel (cyclohexane/ethyl acetate, 1:1) to furnish *ent*-**32** (227 mg, 41%, *ee* = 92) and **33a** (257 mg, 56%, *ee* = 68) as colorless oils. The latter (247 mg, 1.32 mmol, *ee* = 68) was acetylated according to GP 4 to yield **32** (290 mg, 96%), which was hydrolyzed for 14 h at room temp. in the presence of PPL (6 mg) in phosphate buffer (30 ml, 0.01 M, pH 7) and *n*-hexane (15 ml) to afford **33a** (121 mg, 51%, *ee* = 91) and **32** (135 mg, 47%) as colorless oils after chromatography. *ent*-**32**: $[\alpha]_D^{25} = +108.8$ (*c* = 0.46, CH$_2$Cl$_2$). **33a**: $[\alpha]_D^{25} = -117.8$ (*c* = 0.49, CH$_2$Cl$_2$). − ^{1}H, ^{13}C NMR, IR, MS data were identical to those of *rac*-**32** and *rac*-**33a**.

Methyl 2β-Azido-2,3,4-trideoxy-β-L-hexopyranoside (*ent*-**33a**): *ent*-**32** (300 mg, 1.31 mmol) was treated according to GP 2 (room temp., 1 h) to give *ent*-**33a** (230 mg, 94%) as a colorless oil. − $[\alpha]_D^{25} = +123.8$ (*c* = 0.40, CH$_2$Cl$_2$). − ^{1}H, ^{13}C NMR, IR, MS data were identical to those of *rac*-**33a**.

Methyl 2β-Azido-2,3,4-trideoxy-6-O-methylsulfonyl-β-D-hexopyranoside (**33b**) *and Methyl 2β,6-Diazido-2,3,4,6-tetradeoxy-β-D-hexopyranoside* (**34**): **33a** (100 mg, 0.53 mmol) was treated according to GP 1. The crude product was chromatographed (silica gel, cyclohexane/ethyl acetate, 1:1, R_f = 0.68) to give **34** (110 mg, 97%) as a colorless oil. **33b** could be purified by chromatography (silica gel, cyclohexane/ethyl acetate, 1:1, R_f = 0.27, colorless oil, 142 mg, almost quantitative). **33b**: $[\alpha]_D^{25} = -92.2$ (*c* = 0.52, CH$_2$Cl$_2$). − IR (film): $\tilde{\nu}$ = 2092 cm^{-1} (N$_3$). − ^{1}H NMR: δ = 4.51 (d, 1-H), 4.30 (dd, 6a-H), 4.28 (dd, 6b-H), 3.83 (dddd, 5-H), 3.64 (ddd, 2-H), 3.57 (s, OCH$_3$), 3.11 (s, OSO$_2$CH$_3$), 2.05 (dddd, 3β-H), 1.78 (dddd, 3α-H), 1.67 (dddd, 4β-H), 1.50 (dddd, 4α-H); $J_{1,2} = 1.8$, $J_{2,3\alpha} = J_{2,3\beta} = J_{3\beta,4\beta} = J_{3\beta,4\alpha} = 4.0$, $J_{3\alpha,3\beta} = J_{3\alpha,4\beta} = J_{4\alpha,4\beta} = 13.5$, $J_{3\alpha,4\alpha} = 3.2$, $J_{4\alpha,5} = 3.0$, $J_{4\beta,5} = 10.5$, $J_{5,6a} = 4.3$, $J_{5,6b} = 5.5$, $J_{6a,6b} = 11.5$ Hz. − ^{13}C NMR: δ = 102.3 (C-1), 73.3 (C-6), 71.2 (C-5), 57.4 (C-2), 56.7 (OCH$_3$), 37.6 (OSO$_2$CH$_3$), 26.1 (C-4)*, 21.6 (C-3)*. − C$_8$H$_{15}$N$_3$O$_5$S (265.3). **34**: $[\alpha]_D^{25} = -139.0$ (*c* = 0.70, CH$_2$Cl$_2$). − IR (film): $\tilde{\nu}$ = 2086 cm^{-1} (N$_3$). − ^{1}H NMR: δ = 4.51 (d, 1-H), 3.73 (dddd, 5-H), 3.68 (ddd, 2-H), 3.57 (s, OCH$_3$), 3.52 (dd, 6a-H), 3.08 (dd, 6b-H), 2.04 (dddd, 3β-H), 1.86 (dddd, 3α-H), 1.62 (dddd, 4β-H), 1.42 (dddd, 4α-H); $J_{1,2} = 1.5$, $J_{2,3\alpha} = J_{2,3\beta} = J_{3\beta,4\alpha} = J_{3\beta,4\beta} = J_{5,6b} = 3.5$, $J_{3\alpha,3\beta} = J_{3\alpha,4\beta} = J_{4\alpha,4\beta} = 13.0$, $J_{3\alpha,4\alpha} = 4.6$, $J_{4\alpha,5} = 3.0$, $J_{4\beta,5} = 10.5$, $J_{5,6a} = 8.0$, $J_{6a,6b} = 12.1$ Hz. − ^{13}C NMR: δ = 102.4 (C-1), 75.8 (C-5), 57.6 (C-2), 56.7 (OCH$_3$), 54.4 (C-6), 26.8 (C-4)*, 23.0 (C-3)*. − MS (NH$_3$, 170 eV); *m*/*z* (%): 230 (100) [M + NH$_4$]$^+$, 185 (7).

Methyl 2β-Azido-2,3,4-trideoxy-6-O-methylsulfonyl-β-D-hexopyranoside (*ent*-**33b**) *and Methyl 2β,6-Diazido-2,3,4,6-tetradeoxy-β-L-hexopyranoside* (*ent*-**34**): *ent*-**33a** (70 mg, 0.37 mmol) was treated according to GP 1 to give *ent*-**34** (76 mg, 96%) as a colorless oil. − $[\alpha]_D^{25} = +141.9$ (*c* = 0.75, CH$_2$Cl$_2$). − ^{1}H, ^{13}C NMR, IR, MS data were identical to those of **34**. *ent*-**33b** could be isolated as described for **33b**. *ent*-**33a** (198 mg, 1.06 mmol) gave *ent*-**33b** (281 mg, quant.) as a colorless oil. − $[\alpha]_D^{25} = +88.4$ (*c* = 0.37, CH$_2$Cl$_2$).

1-O-Acetyl-2β,6-diazido-2,3,4,6-tetradeoxy-α/β-D-hexopyranose (**14**): **34** (79 mg, 0.37 mmol) was treated according to GP 3. Filtration through a short column of silica gel (cyclohexane/ethyl acetate, 1:1, R_f = 0.49) gave **14** (78 mg, 87%, α/β ≈ 5:1) as a colorless oil. − IR (film): $\tilde{\nu}$ = 2086 cm^{-1} (N$_3$), 1749 (OCOCH$_3$). − ^{1}H NMR: δ = 6.05 (s, 1-H, α), 5.80 (d, 1-H, β), 4.01 (dddd, 5-H, α), 3.82 (dddd, 5-H, β), 3.72 (ddd, 2-H, β), 3.58 (dd, 2-H, α), 3.47 (dd, 6a-H, β), 3.44 (dd, 6b-H, β), 3.34 (dd, 6a-H, α), 3.23 (dd, 6b-H, α), 2.17/2.14 (s, OCOCH$_3$), 2.15−1.45 (m, 3-, 4-H$_2$, α, β); α: $J_{1,2} < 1.0$, $J_{2,3\alpha} = J_{2,3\beta} = 3.5$, $J_{4\alpha,5} = 3.0$, $J_{4\beta,5} = 11.0$, $J_{5,6a} = 6.3$, $J_{5,6b} = 4.3$, $J_{6a,6b} = 13.0$, β: $J_{1,2} = 1.8$, $J_{2,3\alpha} = J_{2,3\beta} = 3.5$, $J_{4\alpha,5} = 3.0$, $J_{4\beta,5} = 11.0$, $J_{5,6a} = 7.0$, $J_{5,6b} = 4.3$, $J_{6a,6b} = 13.0$ Hz. − ^{13}C NMR: δ = 168.8 (C=O), 93.7 (C-1, β), 91.3 (C-1, α), 76.0 (C-5, β), 70.1 (C-5, α), 56.8 (C-2, β), 55.7 (C-2, α), 54.5 (C-6, α), 54.2 (C-6, β), 26.5 (C-4, β)*, 22.4 (C-3, β)*, 22.3 (C-3, C-4, α), 21.8 (OCO*C*H$_3$). − Racemic Acrolein Dimer MS (NH$_3$, 170 eV); *m*/*z* (%): 258 (100) [M + NH$_4$]$^+$, 175 (6), 170 (21), 166 (17), 140 (10), 110 (5).

1-O-Acetyl-2β,6-diazido-2,3,4,6-tetradeoxy-α/β-L-hexopyranose (*ent*-**14**): *ent*-**34** (112 mg, 0.53 mmol) was treated according to GP 3. Filtration through a short column of silica gel (cyclohexane/ethyl acetate, 1:1, R_f = 0.49) gave *ent*-**14** (114 mg, 90%, α/β ≈ 5:1) as a colorless oil. − ^{1}H, ^{13}C NMR, IR, MS data were identical to those of **14**.

Methyl 2,3,4,6-tetradeoxy-2β,6-di-(2′,4′-dinitrophenylamino)-β-L-hexopyranoside (*ent*-**36**): A solution of *ent*-**34** (16 mg, 0.075 mmol) in MeOH (5 ml) was hydrogenated in the presence of 10% Pd/C (10 mg, 1 atm H$_2$, 3 h, room temp.). The catalyst was then removed by filtration (Celite) and the filtrate was concentrated in vacuo to give the crude diamine. A suspension of the diamine, dinitrofluorobenzene (0.02 ml, 0.02 mmol), and NaHCO$_3$ (0.10 g, 1.20 mmol) in acetone/H$_2$O (10 ml, 1:1) was refluxed for 1 h. The mixture was then concentrated in vacuo, and the residue was extracted with ethyl acetate (4 × 20 ml). The combined extracts were dried (MgSO$_4$) and concentrated in vacuo, and the residue was purified on silica gel (cyclohexane/ethyl acetate, 1:3, R_f = 0.20) to furnish *ent*-**36** (34 mg, 92%) as a yellow solid, m.p. 94−99°C. − $[\alpha]_D^{25} = -91.5$ (*c* = 0.20, CH$_2$Cl$_2$). − IR (KBr): $\tilde{\nu}$ = 3336 cm^{-1} (NH), 1515 (m, N=O). − ^{1}H NMR: δ = 9.15/9.12 (d, 3″-H, DNP), 9.03 (br. d, NH), 8.95 (dd, NH), 8.31/8.25 (dd, 5″-H, DNP), 7.02/6.94 (d, 6″-H, DNP), 4.73 (d, 1-H), 4.10−3.95 (m, 2-, 5-H), 3.57 (s, OCH$_3$), 3.72−3.50 (m, 6-H$_2$), 2.24 (dddd, 3β-H), 2.00 (dddd, 3α-H), 1.80−1.60 (m, 4-H$_2$); $J_{1,2} = 1.8$, $J_{2,NH} = 7.5$, $J_{2,3\alpha} = J_{3\alpha,4\alpha} = 3.0$, $J_{2,3\beta} = J_{3\beta,4\alpha} = J_{3\beta,4\beta} = 3.5$, $J_{3\alpha,3\beta} = J_{3\alpha,4\beta} = 14.0$, $J_{6a,NH} = 4.5$, $J_{6b,NH} = 6.5$, $J_{3,5(DNP)} = 2.5$, $J_{5,6(DNP)} = 9.5$ Hz. − ^{13}C NMR: δ = 149.7/149.0 (C-1″, DNP), 136.6 (C-2″, DNP), 130.9/130.6 (C-5″, DNP), 124.6/124.4 (C-3″, DNP), 116.3/116.1 (C-6″, DNP), 102.6 (C-1), 75.5 (C-5), 56.5 (OCH$_3$), 51.4 (C-2), 48.1 (C-6), 26.4 (C-4)*, 23.8 (C-3)*. − MS (FAB); *m*/*z* (%): 493 (20) [M + H]$^+$.

Methyl 2,3,4,6-Tetradeoxy-2β,6-di-(2′,4′-dinitrophenylamino)-β-D-hexopyranoside (**36**): To a solution of **37** (79 mg, 0.22 mmol) in acetone (40 ml) and H$_2$O (10 ml), Amberlite IRA 400 (OH$^-$) (10 ml) was added. After stirring for 14 h at room temp., the resin was removed by filtration and the acetone was evaporated in vacuo. After washing with CH$_2$Cl$_2$ and concentration in vacuo, the resulting crude amine was dissolved in MeOH (10 ml) and hydrogenated in the presence of 10% Pd/C (25 mg, 1.5 h, 1 atm H$_2$, room temp.). The catalyst was then removed by filtration (Celite) and the filtrate was concentrated in vacuo to afford the crude diamine. A suspension of the latter, dinitrofluorobenzene (0.08 ml, 0.06 mmol), and NaHCO$_3$ (0.20 g, 2.40 mmol) in acetone/H$_2$O (10 ml, 1:1) was refluxed for 1 h, concentrated in vacuo, and extracted with ethyl acetate (4 × 10 ml). After drying (MgSO$_4$) and concentration in vacuo, the residue was purified by chromatography (silica gel, cyclohexane/ethyl acetate, 1:3, R_f = 0.20) to furnish **36** (50 mg, 45%) as a yellow solid, m.p. 93−97°C. − $[\alpha]_D^{25}$ = +89.1 (c = 0.11, CH_2Cl_2). − ^1H, ^{13}C NMR, IR, MS data were identical to those of *ent*-**36**.

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