Highly Stereoselective Synthesis of 2-Amino-3-*C*-methyl-2,3-dideoxyaldoses by C_3-Chain Elongation via Homoaldol Reaction of Sugar Aldehydes

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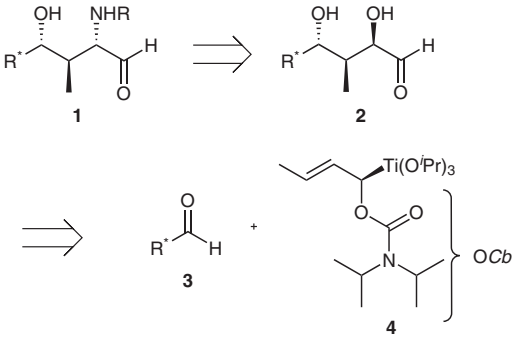
Dedicated to Professor Günter Haufe on the occasion of his 60th birthday

Abstract: A flexible strategy for the stereoselective synthesis of branched amino sugar analogues is described. It is based on a C_3-chain elongation of suitable protected aldoses. By using the sequence homoaldol reaction, epoxidation, and methanolysis α-methyl *allo*-furanosides are obtained. Proximate amination of the corresponding triflates afford the title compounds. All reactions proceed with high yield, high diastereoselectivities, and allow for a broad application.

Key words: homoaldol reaction, stereoselective synthesis, furanosides, aminoaldoses, carbamates

Modified carbohydrates often have interesting biological properties.[2] They play an important role in the synthesis of antibiotics,[3] enzymes,[4] and biological active natural products.[5] In particular, aminodeoxy sugars are valuable targets.[6] 2-Amino-2,3-dideoxy-3-*C*-methylaldoses **1**, to the best of our knowledge, have not been reported yet.[7] Herein we describe a flexible synthesis of compounds **1** (Scheme 1), based on a C_3-chain elongation of suitable protected aldoses **3** by utilization of the homoaldol reaction,[8] which has been developed in our group.[9]



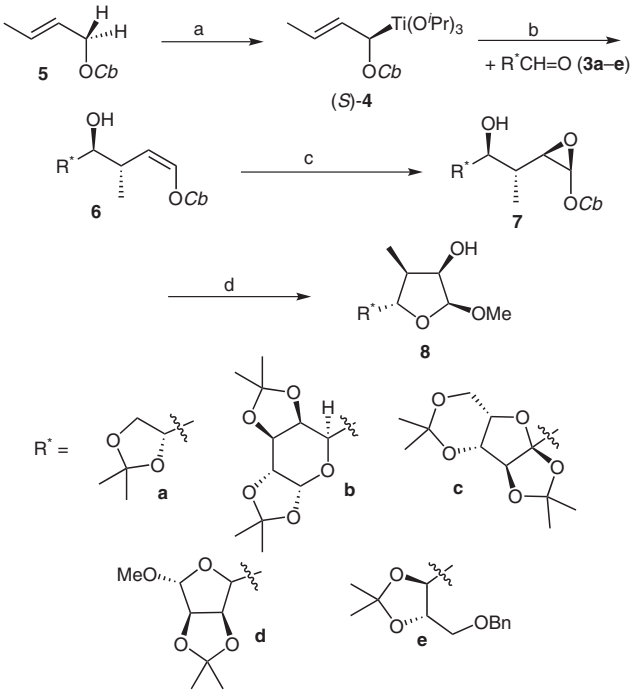
Scheme 1 General synthesis of compounds **1**

Addition of the homoenolate reagent (*S*)-**4**,[10] prepared from (*E*)-but-2-enyl *N*,*N*-diisopropylcarbamate (**5**), to the protected aldoses **3a–e**[11] afforded the 4-hydroxyenol carbamates **6** in diastereomerically pure, highly enantioenriched form (≥98% ee) (Scheme 2, Table 1).[12]

Epoxidation using *tert*-butyl hydroperoxide/VO(acac)$_2$[13] led to diastereomerically pure oxiranes **7**,[12] which upon methanolysis afforded the α-methyl *allo*-furanosides **8** (Scheme 2, Table 1).[12,14,15] The 1,2-*cis*,2,3-*cis*,3,4-*trans* configuration of the furanosides was confirmed by an X-ray crystal structure analysis of **8c** (Figure 1).[16–24]

The stereochemistry of the protected aminofuranosides **11** was proved by NOE experiment of compound **11c** and confirmed the 2,3-*trans*,3,4-*trans* configuration (Figure 2).

The furanosides **8** were quantitatively transformed into triflates **9**[25] by reaction with an excess of triflic anhydride, and the crude triflates were directly treated with excess of sodium azide to yield the azidodeoxyfuranosides **10** with clean inversion at C-2.[26] The yields given for the azides **10** in Table 2 refer to two steps, the triflate and azide formation. The 2,3-*trans* configuration of **10** was concluded from the small coupling constants $^3J_{2,3}$ of 1.5–2.4 Hz in the ^{1}H NMR spectra. Subsequent hydrogenolysis (H_2,



Scheme 2 Synthesis of furanosides **8** by homoaldol reaction, epoxidation, and methanolysis. *Reagents and conditions*: a) *n*-BuLi, (–)-sparteine, *n*-pentane–cyclohexane (6.7:1), –78 °C, 3.5 h, Ti(O*i*-Pr)$_4$, –78 °C, 40 min; b) R*CHO, –78 °C, 4 h; c) *t*-BuOOH, VO(acac)$_2$, CH_2Cl_2, r.t., 15 h; d) $MeSO_3H$, MeOH, CH_2Cl_2, –78 °C, 15 h.

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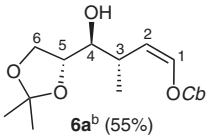
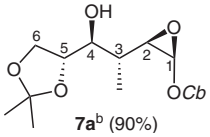
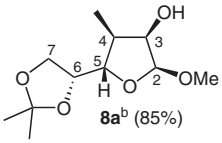
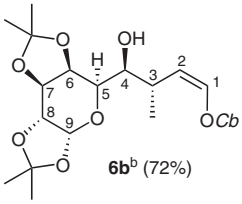
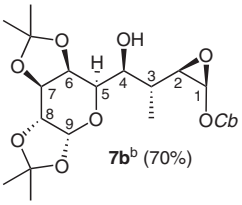
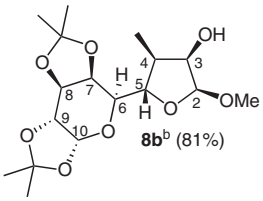
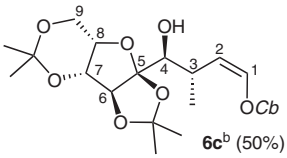
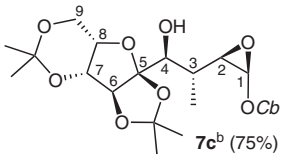
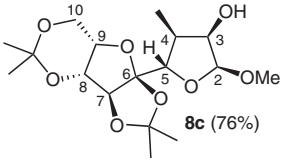
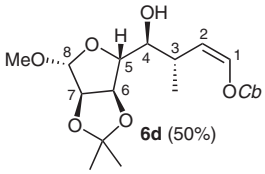
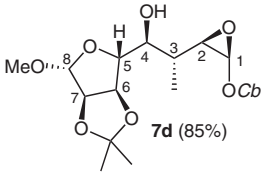
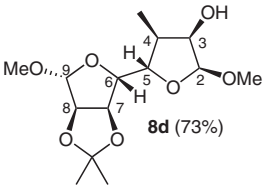
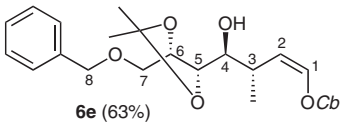
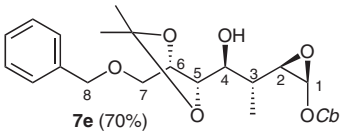
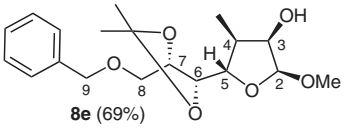
Table 1 Synthesis of Furanosides **8** by Homoaldol Reaction, Subsequent Epoxidation, and Methanolysis

Protected aldose **3**	Carbamate **6**[a] (Yield)	Epoxide **7**[a] (Yield)	Furanoside **8**[a] (Yield)
3a	 **6a**[b] (55%)	 **7a**[b] (90%)	 **8a**[b] (85%)
3b	 **6b**[b] (72%)	 **7b**[b] (70%)	 **8b**[b] (81%)
3c	 **6c**[b] (50%)	 **7c**[b] (75%)	 **8c** (76%)
3d	 **6d** (50%)	 **7d** (85%)	 **8d** (73%)
3e	 **6e** (63%)	 **7e** (70%)	 **8e** (69%)

[a] Numbering of compounds **6a**–**e**, **7a**–**e**, and **8a**–**e** is for the assignment of the ^{1}H and ^{13}C NMR data.
[b] For data and characterization, see ref. 12.

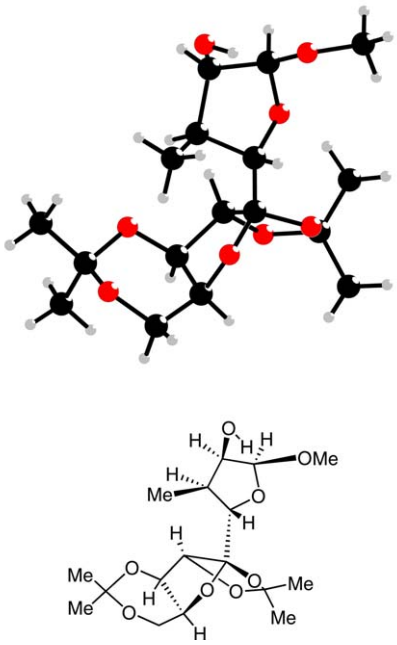


Figure 1 Crystal structure of **8c**

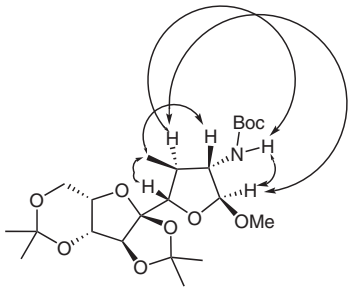
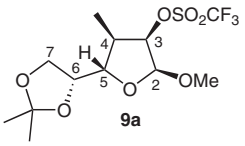
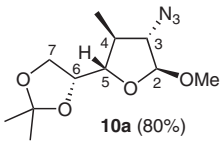
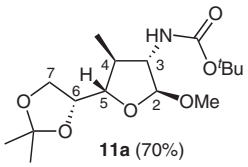
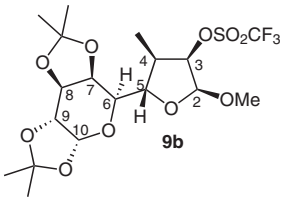
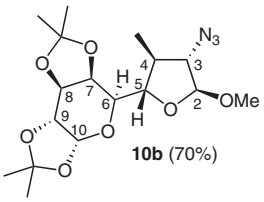
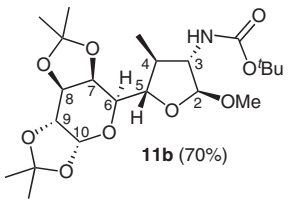
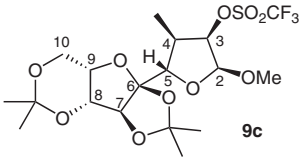
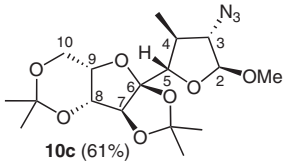
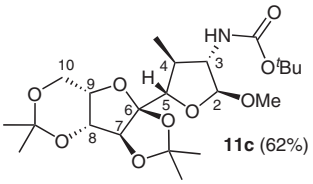
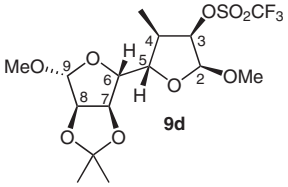
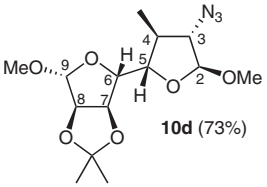
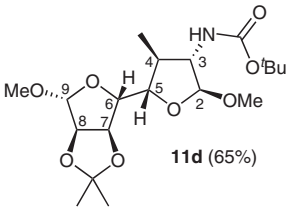
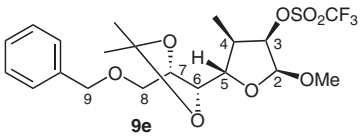
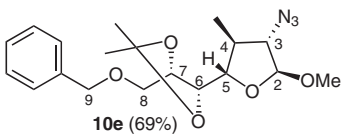


Figure 2 NOE experiment of **11c**

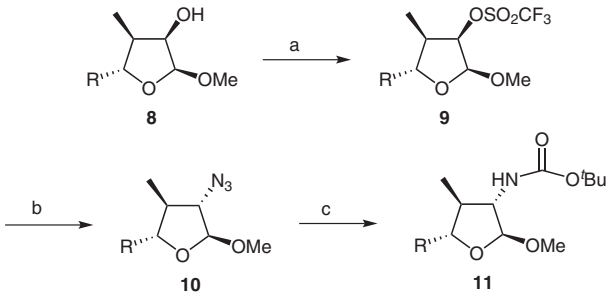
Pd/C) followed by acylation with Boc_2O gave rise to protected aminofuranosides **11** (Scheme 3, Table 2).[27]

The method outlined above gives facile access to chain elongated 2-amino-2,3-dideoxy-3-*C*-methylaldoses **11** via nucleophilic introduction of the terminal C1–C3 to sugar aldehydes, having D-*arabinose* configuration at C2–C4 in compounds **10** and **11**. The absolute configuration at C2– C4 is determined by the *R*- or *S*-configuration of the applied homoenolate reagent;[12] the configuration at C5 to Cω of the applied sugar aldehyde is retained. The prepared furanosides correspond to the following amino

Table 2 Azidolysis, Hydrogenolysis, and Substitution of Furanosides **8**

Furanoside **8**	Triflate **9**[a]	Azide **10** [a] (Yield)	Boc-protected amine **11**[a] (Yield)
8a	 **9a**	 **10a** (80%)	 **11a** (70%)
8b	 **9b**	 **10b** (70%)	 **11b** (70%)
8c	 **9c**	 **10c** (61%)	 **11c** (62%)
8d	 **9d**	 **10d** (73%)	 **11d** (65%)
8e	 **9e**	 **10e** (69%)	

[a] Numbering of compounds **9a–e**, **10a–e**, and **11a–d** is for the assignment of the ^{1}H and ^{13}C NMR data.



Scheme 3 Synthesis of 2-aminofuranosides **11** by amination. *Reagents and conditions*: a) $(CF_3SO_2)_2O$, pyridine, -15 °C → –5 °C, 3 h, b) NaN_3, DMSO, 50 °C, 5–15 h; c) Boc_2O, Pd/C, H_2, THF, r.t., 9 h.

sugars: **11a**: 2-amino-2,3-dideoxy-3-*C*-methyl-D-*altro*-hexose; **11b**: 2-amino-2,3-dideoxy-3-*C*-methyl-L-*lyxo*-L-*galacto*-nonodialdose; **11c**: 2-amino-2,3-dideoxy-3-*C*-methyl-L-*threo*-L-*galacto*-1-aldo-5-ulose; **11d**: 2-amino-2,3-dideoxy-3-*C*-methyl-L-*erythro*-L-*galacto*-octodialdose; **10e**: 3-azido-2,3-dideoxy-3-*C*-methyl-D-*glycero*-D-*altro*-aldoheptose.

The C-3 substituent of the title compounds can be changed by utilization of the appropriate homoenolates, in which the γ-methyl group is exchanged by another residue, and also the C2–C4 L-arabinose series is accessible by using the O'Brien[28] diamine [a good (+)-sparteine mimic] in the deprotonation step of the homoaldol reaction. Taking also in consideration the great versatility in the aldehyde (or ketone) unit a vast variety of amino sugars is accessible.

All moisture-sensitive reactions were carried out under an atmosphere of argon in flame-dried glassware sealed by rubber septa. Unless otherwise specified, materials were obtained from commercial sources and used without purification. All solvents (*n*-pentane, Et_2O, CH_2Cl_2) were dried according to standard procedures and purified by distillation prior to use. Addition of chemicals was performed by using disposable plastic syringes. Flash chromatography was performed using Merck silica gel 60 (230–400 mesh) at a pressure of about 1.5 bar and monitored by TLC. Solvents for chromatography (Et_2O, *n*-pentane, cyclohexane, EtOAc) were distilled prior to use. For analytic TLC, Merck aluminum sheets (60 F_{254} silica gel) were used. Visualization was accomplished with permanganate solution and vanillin solution. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX 300 or ARX 400 spectrometer. Chemi-

cal shifts are given in ppm (δ), with TMS (^{1}H) and $CDCl_3$ (^{13}C) as internal standard. The multiplicities are indicated by s (singlet), br s (broad singlet), d (doublet), br d (broad doublet), t (triplet), q (quartet), and m (multiplet). The numbering of the compounds may differ from the IUPAC nomenclature and is defined in Tables 1 and 2. Optical rotations were measured at 20 °C using a Perkin-Elmer 341 spectrometer; the ATR-IR spectra were recorded using a Varian 3100 Excalibur series spectrometer. Elemental analyses were performed at the Department of Organic Chemistry of the University of Münster. ESI-MS (HR-MS) was carried out with a Quattro LCZ (Waters-Micromass, Manchester, UK) with nanospray inlet.

4-Hydroxyalk-1-enyl Carbamates 6a–e; General Procedure

In a three-necked, round-bottomed flask equipped with a cooled dropping funnel and a mechanical stirrer, (*E*)-crotyl carbamate **5** (1.0 equiv) and (–)-sparteine (**12**; 1.1 equiv) were dissolved in a mixture of *n*-pentane–cyclohexane (6.7:1, 1.5 mL/mmol) and cooled to –78 °C. To this solution was added a solution of 1.6 M *n*-BuLi in *n*-hexane (1.1 equiv) dropwise. The mixture was stirred for 3.5 h and a solution of Ti(O*i*-Pr)$_4$ (3.0 equiv) in *n*-pentane (1 mL/mmol), precooled to –78 °C, was added. After a transmetalation time of 40 min, a solution of the aldehyde **3a**, **3b**, **3c, 3d**, or **3e** (1.1 equiv) in *n*-pentane (0.5 mL/mmol) was added at –78 °C, and the stirring was continued for an additional 3 h. The reaction was stopped by the addition of sat. aq NH_4Cl (1 mL/mmol) at –78 °C, warmed to r.t., and washed with sat K/Na tartrate solution (10 mL/mmol). The aqueous layer was separated and extracted with Et_2O (3 × 10 mL/mmol). The combined organic phases were dried (Na_2SO_4), the solvent was evaporated, and the residue was purified by column chromatography on silica gel (Et_2O–*n*-pentane, 1:2 → 2:1).

The experimental data and characterization of 4-hydroxyalk-1-enyl carbamates **6a**–**c** are already published.[12]

[*Z*,3*S*,4*S*,4(2*R*,3*R*,4*R*,5*R*)]-4-Hydroxy-4-(2,3,4-trihydroxy-3,4-*O*-isopropylidene-5-*O*-methyl-2-tetrahydrofuranyl)-3-methylbut-1-enyl *N*,*N*-Diisopropylcarbamate (6d)

According to the General Procedure, the reaction of **5** (2.99 g, 15.0 mmol) with aldehyde **3d** (3.35 g, 16.5 mmol) gave 3.01 g (7.5 mmol, 50%) of **6d** as a colorless solid; mp 94.2 °C; R_f = 0.23 (Et_2O–*n*-pentane, 1:1); $[\alpha]_D^{20}$ –59.5 (*c* 0.75, $CHCl_3$).

IR (ATR): 3467, 2971, 2937, 2877, 1700, 1442, 1439, 1373, 1290, 1193, 1060, 762 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.10 [d, ^3J (3,3-CH_3) = 7.0 Hz, 3 H, 3-CH_3], 1.23 (br s, 12 H, 2′-CH_3), 1.27, 1.43 [s each, 6 H, C(CH_3)$_2$], 2.95 (m, 1 H, 3-H), 3.19 (s, 1 H, 4-OH), 3.38 (s, 3 H, OCH_3), 3.52 (m, 1 H, 4-H), 3.91, 3.99 (br s each, 2 H, 1′-H), 4.28 (br d, $^3J_{4,5}$ = 3.5 Hz, 1 H, 5-H), 4.52 (dd, $^3J_{5,6}$ = 5.5 Hz, $^3J_{6,7}$ = 6.1 Hz, 1 H, 6-H), 4.72 (d, $^3J_{1,2}$ = 6.5 Hz, $^3J_{2,3}$ = 9.8 Hz, 1 H, 2-H), 4.90 (d, $^3J_{6,7}$ = 6.1 Hz, 1 H, 7-H), 4.91 (s, 1 H, 8-H), 7.10 (dd, $^4J_{1,3}$ = 0.9 Hz, 1 H, 1-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.9 (3-CH_3), 20.3 (C-2′), 24.6, 26.3 [C(*C*H_3)$_2$], 32.8 (C-3), 45.8, 46.5 (C-1′), 55.3 (OCH_3), 75.9 (C-4), 80.4 (C-6), 85.7 (C-5), 90.0 (C-7), 109.7 (C-8), 111.9 [*C*(CH_3)$_2$], 112.4 (C-2), 135.6 (C-1), 152.5 (NC=O).

Anal. Calcd for $C_{20}H_{35}NO_7$: C, 59.83; H, 8.79; N, 3.49. Found: C, 59.50; H, 8.71; N, 3.30.

[*Z*,3*S*,4*S*,4(5*R*,6*S*)]-7-*O*-Benzyl-4,5,6,7-tetrahydroxy-5,6-*O*-isopropylidene-3-methylhept-1-enyl *N*,*N*-Diisopropylcarbamate (6e)

According to the General Procedure, the reaction of **5** (1.97 g, 10.0 mmol) with aldehyde **3e** (2.77 g, 11.0 mmol) gave 2.76 g (6.3 mmol, 63%) of **6e** as a colorless oil; R_f = 0.27 (Et_2O–*n*-pentane, 1:1); $[\alpha]_D^{20}$ –76.0 (*c* 0.78, $CHCl_3$).

IR (ATR): 3488, 2971, 2934, 2873, 1684, 1440, 1368, 1289, 1134, 1057, 762 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.12 [d, ^3J (3,3-CH_3) = 7.1 Hz, 3 H, 3-CH_3], 1.23 (br s, 12 H, 2′-CH_3), 1.29, 1.34 [s each, 6 H, C(CH_3)$_2$], 3.08 (d, $^3J_{4,4\text{-OH}}$ = 2.7 Hz, 1 H, 4-OH), 3.02–3.15 (m, 1 H, 3-H), 3.39–3.55 (m, 2 H, 6-H, 7-H_A), 3.63–3.74 (m, 2 H, 5-H, 7-H_B), 3.78, 4.14 (br s each, 2 H, 1′-H), 4.06 (ddd, $^3J_{3,4}$ = 4.7 Hz, $^3J_{4,5}$ = 7.4 Hz, 1 H, 4-H), 4.59 (d, $^2J_{8A,8B}$ = 2.7 Hz, 2 H, 8-CH_2), 4.82 (d, $^3J_{1,2}$ = 6.6 Hz, $^3J_{2,3}$ = 10.3 Hz, 1 H, 2-H), 7.10 (dd, $^4J_{1,3}$ = 0.6 Hz, 1 H, 1-H), 7.26–7.39 (m, 5 H, C_6H_5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.8 (3-CH_3), 20.2 (C-2′), 26.7, 26.9 [C(*C*H_3)$_2$], 32.9 (C-3), 45.4, 46.9 (C-1′), 70.7 (C-7), 73.7 (C-8), 75.9 (C-6), 78.2 (C-4), 80.9 (C-5), 108.9 [*C*(CH_3)$_2$], 110.7 (C-2), 128.5, 128.0, 127.9 (CH_{Ar}), 135.5 (C-1), 137.0 (C_{Ar}), 153.1 (NC=O).

Anal. Calcd for $C_{25}H_{39}NO_6$: C, 66.79; H, 8.74; N, 3.12. Found: C, 66.66; H, 9.00; N, 2.98.

1,2-Epoxy-4-hydroxyalkyl Carbamates 7a–e; General Procedure

Homoaldol adduct **6** (1.0 equiv) was dissolved in CH_2Cl_2 (3 mL/mmol) under argon. VO(acac)$_2$ (2 mol%, 0.05 mmol) and *t*-BuOOH (3.0 equiv) were added at r.t. and the reaction mixture was allowed to stir for 15 h. The reaction was stopped by the addition of Me_2S (3.0 equiv) and the mixture was stirred for an additional 30 min. The mixture was extracted with sat. aq $NaHCO_3$ (7 mL/mmol) and the combined organic extracts were dried ($MgSO_4$). The solvent was evaporated and the crude product was purified by flash column chromatography on silica gel (Et_2O–*n*-pentane, 1:1 → 2:1).

The experimental data and characterization of epoxides **7a**–**c** are already published.[12]

[3*R*,4*S*,4(2*R*,3*R*,4*R*,5*R*)]-1,2-Epoxy-4-(2,3,4-trihydroxy-3,4-*O*-isopropylidene-5-*O*-methyl-2-tetrahydrofuranyl)-4-hydroxy-3-methylbutyl *N*,*N*-Diisopropylcarbamate (7d)

According to the General Procedure, **6d** (0.79 g, 1.9 mmol) was converted with VO(acac)$_2$ (11.0 mg, 0.04 mmol) and *t*-BuOOH (0.36 mL, 2.9 mmol) into the product **7d** (0.70 g, 1.67 mmol, 85%) as a colorless oil; R_f = 0.28 (Et_2O–*n*-pentane, 3:1); $[\alpha]_D^{20}$ –36.8 (*c* 1.36, $CHCl_3$).

IR (ATR): 3471, 2972, 2936, 1702, 1529, 1435, 1371, 1210, 1046, 897, 762 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.12 [d, ^3J (3,3-CH_3) = 7.2 Hz, 3 H, 3-CH_3], 1.22 (d, $^3J_{1',2'}$ = 6.9 Hz, 12 H, 2′-CH_3), 1.32, 1.48 [s each, 6 H, C(CH_3)$_2$], 1.64 (s, 1 H, 4-OH), 1.98 (m, 1 H, 3-H), 3.08 (dd, $^3J_{1,2}$ = 2.8 Hz, $^3J_{2,3}$ = 9.1 Hz, 1 H, 2-H), 3.44 (s, 3 H, OCH_3), 3.74 (m, 1 H, 4-H), 3.79, 4.00 (br s each, 2 H, 1′-H) 3.82 (d, $^3J_{6,7}$ = 2.4 Hz, 1 H, 6-H), 4.48 (d, $^3J_{7,8}$ = 2.4 Hz, 1 H, 7-H), 4.59 (d, $^3J_{4,5}$ = 6.1 Hz 1 H, 5-H), 4.97 (s, 1 H, 8-H), 5.69 (d, $^3J_{1,2}$ = 2.8 Hz, 1 H, 1-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6 (3-CH_3), 21.2, 21.4 (C-2′), 24.7, 26.3 [C(*C*H_3)$_2$], 35.9 (C-3), 45.8, 46.6 (C-1′), 55.5 (OCH_3) 56.6 (C-2), 75.1 (C-1), 76.2 (C-4), 80.4 (C-6), 85.8 (C-5), 90.4 (C-7), 110.0 (C-8), 111.9 [*C*(CH_3)$_2$], 153.8 (NC=O).

Anal. Calcd for $C_{20}H_{35}NO_8$: C, 57.54; H, 8.45; N, 3.35. Found: C, 57.18; H, 8.24; N 2.96.

[3*R*,4*S*,4(5*R*,6*S*)]-7-*O*-Benzyl-1,2-epoxy-4,5,6,7-tetrahydroxy-5,6-*O*-isopropylidene-3-methylheptyl *N*,*N*-Diisopropylcarbamate (7e)

According to the General Procedure, **6e** (0.45 g, 1.0 mmol) was converted with VO(acac)$_2$ (6.4 mg, 0.03 mmol) and *t*-BuOOH (0.5 mL, 3.1 mmol) into the product **7e** (0.32 g, 0.7 mmol, 70%) as

a colorless oil; R_f = 0.37 (Et_2O–*n*-pentane, 1:1); $[\alpha]_D^{20}$ +4.9 (*c* 1.05, $CHCl_3$).

IR (ATR): 3453, 2972, 2934, 2876, 1701, 1500, 1434, 1370, 1212, 1047, 896, 699 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.11 [d, ^3J (3,3-CH_3) = 7.4 Hz, 3 H, 3-CH_3], 1.22 (d, $^3J_{1',2'}$ = 6.8 Hz, 12 H, 2′-CH_3), 1.34, 1.35 [s each, 6 H, $C(CH_3)_2$], 2.10 (ddq, $^3J_{2,3}$ = 9.5 Hz, $^3J_{3,4}$ = 2.6 Hz, 1 H, 3-H), 3.16 (dd, $^3J_{1,2}$ = 2.8 Hz, 1 H, 2-H), 3.51–3.59, 3.68–3.81, 3.97–4.05 (m each, 6 H, OH, 4-H, 5-H, 6-H, 7-H_A, 7-H_B), 3.71, 4.11 (br s each, 2 H, 1′-H), 4.59, 4.61 (s each, 2 H, 8-H_A, 8-H_B), 5.66 (d, $^3J_{1,2}$ = 2.8 Hz, 1 H, 1-H), 7.29–7.38 (m, 5 H, C_6H_5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.3 (3-CH_3), 20.8 (C-2′), 26.7, 26.8 [$C(CH_3)_2$], 35.2 (C-3), 46.8 (C-1′), 56.6 (C-2), 70.6 (C-7), 73.9 (C-4), 74.9 (C-8), 75.7 (C-6), 78.7 (C-1), 81.1 (C-5), 108.9 [$C(CH_3)_2$], 128.6, 128.0 (CH_{Ar}), 136.8 (C_{Ar}), 154.4 (NC=O).

Anal. Calcd for $C_{25}H_{39}NO_7$: C, 64.49; H, 8.44; N, 3.01. Found: C, 64.42; H, 8.79; N 2.94.

γ-Lactol Methyl Ethers 8a–e; General Procedure

1,2-Epoxy-4-hydroxyalkyl carbamate **7** (1.0 equiv) and MeOH (74 equiv) were dissolved in CH_2Cl_2 (2 mL/mmol) under argon. The reaction mixture was cooled to –78 °C and was treated with $MeSO_3H$ (0.9 equiv). The mixture was stirred for 15 h at –78 °C, the reaction stopped by the addition of NaH_2PO_4/Na_2HPO_4 buffer (20 mL/mmol), and diluted with Et_2O (10 mL/mmol). The organic layer was washed with brine (20 mL/mmol) and dried ($MgSO_4$). The solvent was evaporated and the crude product was purified by flash column chromatography on silica gel (Et_2O–*n*-pentane, 1:2 → 2:1).

The experimental data and characterization for tetrahydrofurans **8a** and **8b** are already published.[12]

[2*S*,3*R*,4*S*,5*S*,5(2*S*,3*S*,4*R*,5*S*)]-5-(2,3,4-Trihydroxy-5-hydroxymethyl-2,3;4,5′-di-*O*-isopropylidene-2-tetrahydrofuranyl)-2-methoxy-4-methyltetrahydrofuran-3-ol (8c)

According to the General Procedure, **7c** (0.64 g, 1.3 mmol) was converted with MeOH (4.05 mL, 100.0 mmol) and $MeSO_3H$ (0.08 mL, 1.2 mmol) into the product **8c** (0.37 g, 1.03 mmol, 76%) as a colorless solid; mp 110.5 °C; R_f = 0.28 (Et_2O–*n*-pentane, 1:1); $[\alpha]_D^{20}$ –66.9 (*c* 0.52, $CHCl_3$).

IR (ATR): 3515, 2995, 2932, 2832, 1451, 1386, 1369, 1283, 1249, 1200, 1144, 1088, 1076, 1003, 833 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.16 [d, ^3J (3,3-CH_3) = 7.1 Hz, 3 H, 4-CH_3], 1.35, 1.41, 1.42, 1.48 [s each, 12 H, $C(CH_3)_2$], 2.49 (d, $^3J_{4,OH}$ = 7.5 Hz, 1 H, OH), 2.54 (ddq, $^3J_{3,4}$ = 7.6 Hz, $^3J_{4,5}$ = 6.6 Hz, 1 H, 4-H), 3.48 (s, 3 H, OCH_3), 3.99–4.10 (m, 4 H, 5-H, 9-H, 10-H_A, 10-H_B), 4.21 (ddd, $^3J_{2,3}$ = 2.5 Hz, 1 H, 3-H), 4.22 (d, $^3J_{8,9}$ = 2.5 Hz, 1 H, 8-H), 4.40 (br s, 1 H, 7-H), 4.97 (d, $^3J_{2,3}$ = 2.5 Hz, 1 H, 2-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.8 (4-CH_3), 18.8, 26.8, 27.8, 28.6 [$C(CH_3)_2$], 36.4 (C-4), 55.8 (OCH_3), 60.2 (C-10), 72.0 (C-8), 73.3 (C-3), 73.7 (C-9), 84.5 (C-5), 85.2 (C-7), 103.6 (C-2), 97.2, 111.9 [$C(CH_3)_2$], 116.1 (C-6).

Anal. Calcd for $C_{17}H_{28}O_8$: C, 56.65; H, 7.83. Found: C, 56.54; H, 7.75.

[2*S*,3*R*,4*S*,5*S*,5(2*R*,3*R*,4*R*,5*R*)]-5-(2,3,4-Trihydroxy-3,4-*O*-isopropylidene-5-*O*-methyl--2-tetrahydrofuranyl)-2-methoxy-4-methyltetrahydrofuran-3-ol (8d)

According to the General Procedure, **7d** (0.35 g, 0.8 mmol) was converted with MeOH (2.50 mL, 61.4 mmol) and $MeSO_3H$ (0.05 mL, 0.8 mmol) into the product **8d** (0.18 g, 0.61 mmol, 73%) as a colorless oil; R_f = 0.32 (Et_2O–*n*-pentane, 3:1); $[\alpha]_D^{20}$ –73.7 (*c* 0.65, $CHCl_3$).

IR (ATR): 3496, 2982, 2937, 2836, 1701, 1456, 1414, 1373, 1210, 1193, 1088, 1035, 948 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.11 [d, ^3J (4,4-CH_3) = 7.2 Hz, 3 H, 4-CH_3], 1.31, 1.47 [s each, 6 H, $C(CH_3)_2$], 2.22 (m, 1 H, 4-H), 2.49 (d, $^3J_{3,3\text{-}OH}$ = 8.6 Hz, 1 H, 3-OH), 3.34, 3.43 (s each, 3 H each, OCH_3) 3.67 (dd, $^3J_{4,5}$ = 5.3 Hz, $^3J_{5,6}$ = 9.5 Hz, 1 H, 5-H), 3.93 (dd, $^3J_{6,7}$ = 1.3 Hz, 1 H, 6-H), 4.20 (m, 1 H, 3-H), 4.55 (dd, $^3J_{7,8}$ = 6.1 Hz, $^3J_{8,9}$ = 10.5 Hz, 1 H, 8-H), 4.83 (dd, $^3J_{6,7}$ = 1.3 Hz, 1 H, 7-H), 4.89 (d, $^3J_{2,3}$ = 4.5 Hz, 1 H, 2-H), 4.95 (s, 1 H, 9-H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.9 (4-CH_3), 25.0, 26.5 [$C(CH_3)_2$], 38.9 (C-4), 55.4, 55.5 (OCH_3), 73.0 (C-3), 81.9 (C-6), 83.7 (C-8), 85.1 (C-5), 89.5 (C-7), 103.1 (C-2), 109.6 [$C(CH_3)_2$], 112.4 (C-9).

Anal. Calcd for $C_{14}H_{24}O_7$: C, 55.25; H, 7.95. Found: C, 55.60; H, 8.02.

[2*S*,3*R*,4*S*,5*S*,5(2*R*,3*S*)]-5-(3-*O*-Benzyl-1,2,3-trihydroxy-1,2-*O*-isopropylidene)-2-methoxy-4-methyltetrahydrofuran-3-ol (8e)

According to the General Procedure, **7e** (0.32 g, 0.7 mmol) was converted with MeOH (0.04 mL, 51.8 mmol) and methanesulfonic acid (0.05 mL, 0.6 mmol) into the product **8e** (0.17 g, 0.48 mmol, 69%) as a colorless oil; R_f = 0.45 (Et_2O–*n*-pentane, 2:1); $[\alpha]_D^{20}$ +56.4 (*c* 0.53, $CHCl_3$).

IR (ATR): 3528, 2985, 2933, 2878, 1715, 1454, 1411, 1370, 1249, 1214, 1094, 1067, 1010 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.09 [d, ^3J (4,4-CH_3) = 7.2 Hz, 3 H, 4-CH_3], 1.41, 1.42 [s each, 6 H, $C(CH_3)_2$], 2.21 (m, 1 H, 4-H), 2.44 (d, $^3J_{3,OH}$ = 8.2 Hz, 1 H, OH), 3.41 (s, 3 H, OCH_3), 3.58 (dd, $^3J_{7,8A}$ = 6.0 Hz, $^2J_{8A,8B}$ = 10.3 Hz, 1 H, 8-H_A), 3.67 (dd, $^3J_{7,8B}$ = 3.6 Hz, 1 H, 8-H_B), 3.76–3.85 (m, 2 H, 5-H, 6-H), 4.05 – 4.11 (m, 1 H, 7-H), 4.16 (ddd, $^3J_{2,3}$ = 4.4 Hz, $^3J_{3,4}$ = 3.7 Hz, 1 H, 3-H), 4.61 (s, 2 H, 9-CH_2), 4.84 (d, $^3J_{2,3}$ = 4.4 Hz, 1 H, 2-H), 7.27–7.36 (m, 5 H, C_6H_5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.8 (4-CH_3), 27.0, 27.1 [$C(CH_3)_2$], 37.8 (C-4), 55.5 (OCH_3), 70.8 (C-6), 73.1 (C-8), 73.4 (C-9), 78.6 (C-3) 79.6 (C-7), 84.7 (C-5), 103.3 (C-2), 109.8 [$C(CH_3)_2$], 128.3, 127.6 (CH_{Ar}), 138.2 (C_{Ar}).

Anal. Calcd for $C_{19}H_{28}O_6$: C, 64.75; H, 8.01. Found: C, 65.15; H, 8.27.

Azido Deoxyfuranosides 10a–e; General Procedure

*Preparation of Triflates **9***: A solution of furanoside **8** (1.0 equiv) in pyridine (5 mL/mmol) at –15 °C was treated with Tf_2O (2.0 equiv). The mixture was allowed to stir for 3 h at -5 °C. The reaction was stopped by the addition of aq NH_4Cl (10 mL/mmol), and warmed to r.t. The organic layer was separated and the aqueous layer was extracted with Et_2O (10 mL/mmol) and the combined organic extracts were washed with aq NH_4Cl (10 mL/mmol), aq $NaHCO_3$ (10 mL/mmol), and brine (10 mL/mmol), and dried (Na_2SO_4). The solvent was evaporated and the crude product **9** was used without further purification.

*Conversion of Triflates **9** into Azides **10***: Triflates **9** and NaN_3 (5 equiv) were dissolved in DMSO (5 mL/mmol) and the mixture was warmed to 50 °C (5–15 h). The mixture was cooled to r.t. and the reaction was stopped by the addition of H_2O (3 mL/mmol). The organic layer was separated and the aqueous layer was extracted with Et_2O (10 mL/mmol). The combined organic layers were washed with brine (10 mL/mmol) and dried (Na_2SO_4). The solvent was evaporated and the residue was purified by column chromatography on silica gel (Et_2O–*n*-pentane, 1:3 → 2:1).

[2*S*,3*S*,4*S*,5*S*,5(1*R*)]-3-Azido-5-(1,2-dihydroxy-1,2-*O*-isopropylideneethyl)-2-methoxy-4-methyltetrahydrofuran (10a)

According to the General Procedure, the reaction of furanoside **8a** (0.07 g, 0.3 mmol) with Tf_2O (0.15 g, 0.5 mmol) in pyridine followed by the treatment of triflate **9a** with NaN_3 (48.8 mg, 0.8 mmol) gave 61.7 mg (0.24 mmol, 80%) of **10a** as a colorless oil; R_f = 0.57 (Et_2O–*n*-pentane, 1:1); $[\alpha]_D^{20}$ +60.0 (*c* 1.08, $CHCl_3$).

IR (ATR): 2988, 2935, 2835, 2098, 1457, 1371, 1253, 1215, 1105, 1065, 1025 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.25 [d, ^3J (4,4-CH_3) = 7.1 Hz, 3 H, 4-CH_3], 1.35, 1.43 [s each, 6 H, C(CH_3)$_2$], 2.13 (ddq, $^3J_{3,4}$ = 6.1 Hz, $^3J_{4,5}$ = 4.8 Hz, 1 H, 4-H), 3.35 (s, 3 H, OCH_3), 3.52 (dd, $^3J_{5,6}$ = 1.6 Hz, 1 H, 5-H), 3.57–3.68 (m, 1 H, 6-H), 3.86–4.17 (m, 2 H, 7-H_A, 7-H_B), 4.09 (dd, $^3J_{2,3}$ = 1.6 Hz, 1 H, 3-H), 4.82 (d, $^3J_{2,3}$ = 1.6 Hz, 1 H, 2-H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.4 (4-CH_3), 25.2, 26.7 [C(*C*H_3)$_2$], 43.0 (C-4), 55.1 (OCH_3), 67.3 (C-7), 73.0 (C-3), 77.7 (C-6), 84.8 (C-5), 107.5 (C-2), 109.5 [*C*(CH_3)$_2$].

Anal. Calcd for $C_{11}H_9N_3O_4$: C, 51.35; H, 7.44; N, 16.33. Found: C, 51.61; H, 7.56; N, 16.04.

[2*S*,3*S*,4*S*,5*S*,5(2*R*,3*S*,4*S*,5*R*,6*R*)]-3-Azido-5-(3,4,5,6-tetrahydroxy-3,4;5,6-di-*O*-isopropylidene-2-tetrahydropyranyl)-2-methoxy-4-methyltetrahydrofuran (10b)

According to the General Procedure, the reaction of furanoside **8b** (0.16 g, 0.4 mmol) with Tf_2O (0.23 g, 0.8 mmol) in pyridine followed by the treatment of triflate **9b** with NaN_3 (61.0 mg, 0.1 mmol) gave 0.12 g (0.31 mmol, 70%) of **10b** as a colorless oil; R_f = 0.60 (Et_2O–*n*-pentane, 1:1); $[\alpha]_D^{20}$ –10.3 (*c* 0.85, $CHCl_3$).

IR (ATR): 2999, 2927, 2855, 2103, 1458, 1381, 1255, 1211, 1103, 1067, 1001 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.13 [d, ^3J (4,4-CH_3) = 7.3 Hz, 3 H, 4-CH_3], 1.32, 1.36, 1.45, 1.56 [s each, 12 H, C(CH_3)$_2$], 2.70 (m, 1 H, 4-H), 3.40 (s, 3 H, OCH_3), 3.82 (dd, $^3J_{5,6}$ = 9.6 Hz, $^3J_{6,7}$ = 1.9 Hz 1 H, 6-H), 3.96 (dd, $^3J_{2,3}$ = 2.4 Hz, $^3J_{3,4}$ = 6.0 Hz, 1 H, 3-H), 4.25 (dd, $^3J_{4,5}$ = 6.2 Hz, 1 H, 5-H), 4.29 (dd, $^3J_{8,9}$ = 2.4 Hz, $^3J_{9,10}$ = 5.2 Hz 1 H, 9-H), 4.38 (dd, $^3J_{7,8}$ = 8.1 Hz 1 H, 7-H), 4.60 (dd, $^3J_{7,8}$ = 8.1 Hz, 1 H, 8-H), 4.84 (d, $^3J_{2,3}$ = 2.4 Hz, 1 H, 2-H), 5.50 (d, $^3J_{9,10}$ = 5.2 Hz, 1 H, 10-H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.8 (4-CH_3), 24.4, 24.9, 25.6, 26.0 [C(*C*H_3)$_2$], 37.8 (C-4), 55.5 (OCH_3), 66.3 (C-9), 69.7 (C-8), 70.6 (C-7), 70.8 (C-3), 76.9 (C-6), 83.3 (C-5), 96.5 (C-10), 106.6 (C-2), 108.6, 109.0 [*C*(CH_3)$_2$].

HRMS-ESI (EM): *m*/*z* calcd for [$C_{17}H_{27}N_3O_7$ + Na]$^+$: 408.1741; found: 408.1744.

[2*S*,3*S*,4*S*,5*S*,5(2*S*,3*S*,4*R*,5*S*)]-3-Azido-5-(2,3,4-trihydroxy-5-hydroxymethyl-2,3;4,5′-di-*O*-isopropylidene-2-tetrahydrofuranyl)-2-methoxy-4-methyltetrahydrofuran (10c)

According to the General Procedure, the reaction of furanoside **8c** (0.26 g, 0.7 mmol) with Tf_2O (0.36 g, 1.3 mmol) in pyridine followed by the treatment of triflate **9c** with NaN_3 (0.12 g, 1.9 mmol) gave 0.17 g (0.44 mmol, 61%) of **10c** as a colorless solid; mp 91.4 °C; R_f = 0.52 (EtOAc–cyclohexane, 1:1); $[\alpha]_D^{20}$ –39.6 (*c* 1.07, $CHCl_3$).

IR (ATR): 2970, 2934, 2902, 2825, 2103, 1454, 1379, 1275, 1245, 1081, 1177, 1127, 1021, 970, 833 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.29 [d, ^3J (4,4-CH_3) = 6.9 Hz, 3 H, 4-CH_3], 1.37, 1.43, 1.44, 1.49 [s each, 12 H, C(CH_3)$_2$], 2.59 (m, 1 H, 4-H), 3.38 (s, 3 H, OCH_3), 3.56 (dd, $^3J_{2,3}$ = 2.3 Hz, $^3J_{3,4}$ = 5.8 Hz, 1 H, 3-H), 3.99–4.13 (m, 4 H, 5-H, 9-H, 10-H_A, 10-H_B), 4.25 (d, $^3J_{7,8}$ = 2.1 Hz 1 H, 8-H), 4.55 (s, 1 H, 7-H), 4.84 (d, $^3J_{2,3}$ = 2.3 Hz, 1 H, 2-H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.5 (4-CH_3), 18.7, 26.8, 27.9, 28.6 [C(*C*H_3)$_2$], 40.1 (C-4), 55.2 (OCH_3), 60.1 (C-10), 71.9 (C-8), 72.8 (C-3), 73.7 (C-9), 83.3 (C-5), 86.4 (C-7), 107.1 (C-2), 97.4, 112.0 [*C*(CH_3)$_2$], 116.0 (C-6).

Anal. Calcd for $C_{17}H_{27}N_3O_7$: C, 52.98; H, 7.06; N,10.90. Found: C, 53.04; H, 7.15; N, 10.65.

[2*S*,3*S*,4*S*,5*S*,5(2*R*,3*R*,4*R*,5*R*)]-3-Azido-5-(2,3,4-trihydroxy-3,4-*O*-isopropylidene-5-*O*-methyl-2-tetrahydrofuranyl)-2-methoxy-4-methyltetrahydrofuran (10d)

According to the General Procedure, the reaction of furanoside **8d** (0.18 g, 0.6 mmol) with Tf_2O (0.30 g, 1.1 mmol) in pyridine followed by the treatment of triflate **9d** with NaN_3 (0.12 g, 2.8 mmol) gave 0.14 g (0.44 mmol, 73%) of **10d** as a colorless resin; R_f = 0.68 (Et_2O–*n*-pentane, 1:1); $[\alpha]_D^{20}$ –58.2 (*c* 0.53, $CHCl_3$).

IR (ATR): 2981, 2930, 2837, 2099, 1455, 1372, 1254, 1210, 1091, 1074, 1023 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.26 [d, ^3J (4,4-CH_3) = 6.9 Hz, 3 H, 4-CH_3], 1.33, 1.49 [s each, 6 H, C(CH_3)$_2$], 2.15 (m, 1 H, 4-H), 3.35, 3.36 (s each, 3 H each, OCH_3), 3.59 (dd, $^3J_{2,3}$ = 1.5 Hz, $^3J_{3,4}$ = 4.4 Hz, 1 H, 3-H), 3.67 (dd, $^3J_{4,5}$ = 6.4 Hz, $^3J_{5,6}$ = 9.2 Hz, 1 H, 5-H), 4.10 (dd, $^3J_{6,7}$ = 1.3 Hz 1 H, 6-H), 4.57 (dd, $^3J_{7,8}$ = 6.1 Hz, $^3J_{8,9}$ = 10.1 Hz, 1 H, 8-H), 4.84–4.89 (m, 2 H, 2-H, 7-H), 4.97 (s, 1 H, 9-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.4 (4-CH_3), 25.0, 26.6 [C(*C*H_3)$_2$], 43.2 (C-4), 55.2, 55.4 (OCH_3), 73.0 (C-3), 82.0 (C-6), 84.3 (C-8), 85.1 (C-5), 89.3 (C-7), 107.8 (C-2), 110.0 [*C*(CH_3)$_2$], 112.5 (C-9).

HRMS-ESI (EM): *m*/*z* calcd for [$C_{14}H_{23}N_3O_6$ + Na]$^+$: 352.1479; found: 352.1477.

[2*S*,3*S*,4*S*,5*S*,5(2*R*,3*S*)]-3-Azido-5-(3-*O*-benzyl-1,2,3-trihydroxy-1,2-*O*-isopropylidene)-2-methoxy-4-methyltetrahydrofuran (10e)

According to the General Procedure the reaction of furanoside **8e** (0.35 g, 0.1 mmol) with Tf_2O (58.0 mg, 0.2 mmol) in pyridine followed by the treatment of triflate **9e** with NaN_3 (33.0 mg, 0.8 mmol) gave 26.0 mg (0.07 mmol, 69%) of **10e** as a colorless oil; R_f = 0.68 (Et_2O–*n*-pentane, 1:1); $[\alpha]_D^{20}$ +41.0 (*c* 1.00, $CHCl_3$).

IR (ATR): 2987, 2932, 2879, 2099, 1455, 1370, 1251, 1214, 1169, 1104, 1065, 1026, 967, 856 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.23 [d, ^3J (4,4-CH_3) = 7.0 Hz, 3 H, 4-CH_3], 1.41, 1.43 [s each, 6 H, C(CH_3)$_2$], 2.16 (m, 1 H, 4-H), 3.30 (s, 3 H, OCH_3), 3.50 (dd, $^3J_{2,3}$ = 1.9 Hz, $^3J_{3,4}$ = 5.0 Hz, 1-H, 3-H), 3.59 (dd, $^3J_{7,8A}$ = 6.3 Hz, $^2J_{8A,8B}$ = 10.4 Hz, 1 H, 8-H_A), 3.68 – 3.74 (m, 2 H, 5-H, 8-H_B), 3.83 (dd, $^3J_{5,6}$ = 7.0 Hz, $^3J_{6,7}$ = 7.6 Hz, 1 H, 6-H), 4.15 (ddd, $^3J_{7,8B}$ = 3.3 Hz, 1 H, 7-H), 4.62 (d, $^2J_{9A,9B}$ = 2.3 Hz,, 2 H, 9-CH_2), 4.79 (d, $^3J_{2,3}$ = 1.9 Hz, 1 H, 2-H), 7.27–7.36 (m, 5 H, C_6H_5).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.2 (4-CH_3), 27.0, 27.2 [C(*C*H_3)$_2$], 42.9 (C-4), 55.1 (OCH_3), 70.7 (C-6), 72.8 (C-8), 73.4 (C-9), 79.1 (C-3) 79.3 (C-7), 84.9 (C-5), 107.7, 110.0 [*C*(CH_3)$_2$], 127.6, 127.7, 128.3 (CH_{Ar}), 138.1 (C_{Ar}).

HRMS-ESI (EM): *m*/*z* calcd for [$C_{19}H_{27}N_3O_5$ + Na]$^+$: 400.1843; found 400.1452.

Aminofuranosides 11a–d; General Procedure

Azide **10** (1.0 equiv), Pd/C (10 mol%), and Boc_2O (1.2 equiv) were suspended in THF (1 mL/mmol). The mixture was stirred at r.t. for 9 h under H_2 atmosphere. The reaction was stopped by filtration through a pad of kieselguhr with Et_2O (10 mL/mmol) and the filtrate was concentrated. The residue was purified by flash column chromatography on silica gel (Et_2O–*n*-pentane, 1:3 → 2:1).

[2*S*,3*S*,4*S*,5*S*,5(1*R*)]-3-[*N*-(*tert*-Butoxycarbonyl)amino]-5-(1,2-dihydroxy-1,2-*O*-isopropylideneethyl)-2-methoxy-4-methyltetrahydrofuran (11a)

According to the General Procedure, **10a** (0.18 g, 0.7 mmol) was converted with Pd/C (35.0 mg, 10 mol%) and Boc_2O (0.18 g, 0.8 mmol) under H_2 atmosphere to **11a** (0.16 g, 0.48 mmol, 70%); colorless oil; R_f = 0.38 (Et_2O–*n*-pentane, 1:1); $[\alpha]_D^{20}$ +8.7 (*c* 0.71, $CHCl_3$).

IR (ATR): 3353, 2983, 2913, 2831, 1695, 1518, 1457, 1366, 1244, 1221, 1173, 1105, 1063, 1022 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.28 [d, ^3J (4,4-CH_3) = 7.4 Hz, 3 H, 4-CH_3], 1.38, 1.48 [s each, 6 H, $C(CH_3)_2$], 1.42 [s, 9 H, $C(CH_3)_3$], 1.96 (m, 1 H, 4-H), 3.33 (s, 3 H, OCH_3), 4.31–4.39 (m, 1 H, 5-H), 3.61–3.69 (m, 1 H, 6-H), 3.73–3.82 (m, 2 H, 7-H_A, 7-H_B), 4.10 (dd, $^3J_{2,3}$ = 1.2 Hz, $^3J_{3,4}$ = 8.5 Hz, 1 H, 3-H), 4.78 (s, 1 H, NH), 5.31 (br d, $^3J_{2,3}$ = 1.2 Hz, 1 H, 2-H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.6 (4-CH_3), 24.6, 26.0 [$C(CH_3)_2$], 28.3 [$C(CH_3)_3$], 40.2 (C-4), 54.6 (OCH_3), 62.2 (C-7), 66.1 (C-3), 76.4 (C-6), 79.2 [$C(CH_3)_3$], 85.6 (C-5), 109.3 (C-2), 109.8 [$C(CH_3)_2$], 155.0 (C=O).

Anal. Calcd for $C_{16}H_{29}NO_6$: C, 57.99; H, 8.82; N, 4.23. Found: C, 57.96; H, 8.88; N, 4.28.

[2*S*,3*S*,4*S*,5*S*,5(2*R*,3*S*,4*S*,5*R*,6*R*)]-3-[*N*-(*tert*-Butoxycarbonyl)amino]-5-(3,4,5,6-tetrahydroxy-3,4;5,6-di-*O*-isopropylidene-2-tetrahydropyranyl)-2-methoxy-4-methyltetrahydrofuran (11b)

According to the General Procedure, **10b** (67.0 mg, 0.2 mmol) was converted with Pd/C (10.0 mg, 10 mol%) and Boc_2O (53.0 mg, 0.2 mmol) under H_2 atmosphere to **11b** (55.1 mg, 0.12 mmol, 70%); colorless solid; mp 145.4 °C; R_f = 0.24 (Et_2O–*n*-pentane, 1:1); $[\alpha]_D^{20}$ –84.3 (*c* 0.73, $CHCl_3$).

IR (ATR): 3350, 2979, 2935, 2897, 1701, 1522, 1457, 1368, 1253, 1211, 1167, 1101, 1065, 1001 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.20 [d, ^3J (4,4-CH_3) = 6.9 Hz, 3 H, 4-CH_3], 1.32, 1.35, 1.44, 1.53 [s each, 12 H, $C(CH_3)_2$], 1.43 [s, 9 H, $C(CH_3)_3$], 2.24 (m, 1 H, 4-H), 3.34 (s, 3 H, OCH_3), 3.80 (br d, $^3J_{5,6}$ = 9.5 Hz, 1 H, 6-H), 4.27–4.31 (m, 2 H, 3-H, 5-H), 4.32 (dd, $^3J_{8,9}$ = 2.3 Hz, $^3J_{9,10}$ = 5.1 Hz, 1 H, 9-H), 4.42 (dd, $^3J_{7,6}$ = 1.9 Hz, $^3J_{7,8}$ = 8.0 Hz, 1 H, 7-H), 4.59 (dd, $^3J_{8,9}$ = 2.3 Hz, 1 H, 8-H), 4.79 (s, 1 H, NH), 5.49 (d, $^3J_{2,3}$ = 2.6 Hz, 1 H, 2-H), 5.51 (d, $^3J_{9,10}$ = 5.1 Hz, 1 H, 10-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.4 (4-CH_3), 24.8, 24.9, 25.8, 26.0 [$C(CH_3)_2$9, 28.3 [$C(CH_3)_3$], 36.6 (C-4), 55.5 (OCH_3), 66.4 (C-3), 70.5 (C-9), 70.8 (C-8), 70.9 (C-7), 76.6 (C-6), 77.3 [$C(CH_3)_3$], 78.5 (C-5), 96.4 (C-10), 109.3 (C-2), 108.7, 109.1 [$C(CH_3)_2$], 155.1 (C=O).

Anal. Calcd for $C_{22}H_{37}NO_9$: C, 57.50; H, 8.12; N, 3.05. Found: C, 57.29; H, 8.19; N, 3.10.

[2*S*,3*S*,4*S*,5*S*,5(2*S*,3*S*,4*R*,5*S*)]-3-[*N*-(*tert*-Butoxycarbonyl)amino]-5-(2,3,4-trihydroxy-5-hydroxymethyl-2,3;4,5′-di-*O*-isopropylidene-2-tetrahydrofuranyl)-2-methoxy-4-methyltetrahydrofuran (11c)

According to the General Procedure, **10c** (0.17 g, 0.4 mmol) was converted with Pd/C (22.0 mg, 10 mol%) and Boc_2O (0.11 g, 0.5 mmol) under H_2 atmosphere to **11c** (0.12 g, 0.26 mmol, 62%); colorless solid; mp 101.5 °C; R_f = 0.59 (EtOAc–cyclohexane, 1:1); $[\alpha]_D^{20}$ +7.5 (*c* 0.57, $CHCl_3$).

IR (ATR): 3349, 2981, 2944, 2896, 2830, 1705, 1523, 1460, 1371, 1254, 1200, 1172, 1098, 1069, 1024 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.30 [d, ^3J (4,4-CH_3) = 7.3 Hz, 3 H, 4-CH_3], 1.36, 1.41, 1.43, 1.49 [s each, 12 H, $C(CH_3)_2$], 1.42 [s, 9 H, $C(CH_3)_3$], 2.34 (m, 1 H, 4-H), 3.35 (s, 3 H, OCH_3), 3.73 (br d, $^3J_{3,4}$ = 6.6 Hz, 1 H, 3-H), 3.99–4.12 (m, 4 H, 5-H, 9-H, 10-H_A, 10-H_B), 4.27 (d, $^3J_{7,8}$ = 2.3 Hz, 1 H, 8-H), 4.54 (br s, 1 H, 7-H), 4.82 (s, 1 H, NH), 5.48 (d, $^3J_{2,3}$ = 1.5 Hz, 1 H, 2-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.9 (4-CH_3), 19.7, 26.6, 28.4, 28.5 [$C(CH_3)_2$], 28.4 [$C(CH_3)_3$], 40.0 (C-4), 54.7 (OCH_3), 60.1 (C-10), 62.2 (C-8), 72.3 (C-3), 73.6 (C-9), 78.9 [$C(CH_3)_3$], 85.2 (C-5), 86.8 (C-7), 109.8 (C-2), 97.5, 111.7 [$C(CH_3)_2$], 115.3 (C-6), 155.4 (C=O).

Anal. Calcd for $C_{22}H_{37}NO_9$: C, 57.50; H, 8.12; N, 3.05. Found: C, 57.40; H, 8.15; N, 3.15.

[2*S*,3*S*,4*S*,5*S*,5(2*R*,3*R*,4*R*,5*R*)]-3-[*N*-(*tert*-Butoxycarbonyl)amino]-5-(2,3,4-trihydroxy-3,4-*O*-isopropylidene-5-*O*-methyl-2-tetrahydrofuranyl)-2-methoxy-4-methyltetrahydrofuran (11d)

According to the General Procedure, **10d** (0.11 g, 0.3 mmol) was converted with Pd/C (16.5 mg, 10 mol%) and Boc_2O (0.08 g, 0.4 mmol) under H_2 atmosphere to **11d** (84.6 mg, 0.21 mmol, 65%); light yellow oil; R_f = 0.44 (Et_2O–*n*-pentane, 1:1); $[\alpha]_D^{20}$ –25.3 (*c* 0.75, $CHCl_3$).

IR (ATR): 3360, 2978, 2932, 2835, 2830, 1704, 1518, 1457, 1368, 1242, 1211, 1163, 1103, 1072, 1023 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.26 [d, ^3J (4,4-CH_3) = 7.2 Hz, 3 H, 4-CH_3], 1.33, 1.50 [s each, 6 H, $C(CH_3)_2$], 1.43 [br s, 9 H, $C(CH_3)_3$], 1.91 (m, 1 H, 4-H), 3.34, 3.38 (s each, 3 H each, OCH_3), 3.64–3.77 (m, 2 H, 3-H, 5-H), 4.06 (dd, $^3J_{5,6}$ = 8.5 Hz, $^3J_{6,7}$ = 1.8 Hz, 1 H, 6-H), 4.57 (d, $^3J_{7,8}$ = 6.1 Hz, 1 H, 8-H), 4.78–4.81 (m, 2 H, 2-H, 7-H), 4.88 (s, 1 H, NH), 4.97 (s, 1 H, 9-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.5 (4-CH_3), 25.3, 26.7 [$C(CH_3)_2$], 28.4 [$C(CH_3)_3$], 43.9 (C-4), 54.8, 55.9 (OCH_3), 63.8 (C-3), 79.6 [$C(CH_3)_3$], 81.7 (C-6), 84.3 (C-8), 85.1 (C-5), 89.5 (C-7), 108.8 (C-2), 109.9 [$C(CH_3)_2$], 112.7 (C-9), 155.1 (C=O).

HRMS-ESI (EM): *m*/*z* calcd for $[C_{19}H_{33}NO_8 + Na]^+$: 426.2098; found: 426.2099.

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(16) X-ray crystal structure analysis of **7c**: Formula $C_{17}H_{28}O_8$, M = 360.39, colorless crystal 0.30 × 0.20 × 0.10 mm, a = 10.0328(3), b = 9.4646(3), c = 10.1594(3) Å, β = 106.772(2)°, V = 923.66(5) Å^3, ρ_{calc} = 1.296 g cm^{-3}, μ = 0.861 mm^{-1}, empirical absorption correction (0.782 ≤ T ≤ 0.919), Z = 2, monoclinic, space group $P2_1$ (No. 4), λ = 1.54178 Å, T = 223 K, ω and φ scans, 5102 reflections collected ± h, ± k, ± l), [(sin θ)/λ] = 0.60 Å^{-1}, 2615 independent (R_{int} = 0.030) and 2563 observed reflections [I ≥ 2 σ (I)], 233 refined parameters, R = 0.034, wR^2 = 0.089, Flack parameter –0.10 (19), max. residual electron density 0.14 (–0.18) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.
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(24) CCDC 747428 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(1223)336033, E-mail: deposit@ccdc.cam.ac.uk].
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