Asymmetric synthesis of amino sugars. Part 2.† A novel versatile approach to the chiral non-racemic synthesis of 2-amino-2-deoxy sugars. Preparation of L-glucosamine, L-mannosamine and L-talosamine derivatives

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A novel methodology for asymmetric synthesis of 2-amino-2-deoxy sugars is developed, starting from readily available chiral building block **1** and 2,3-*O*-isopropylideneglyceraldehyde **2**, *via* Julia olefination and subsequent dihydroxylation as key steps. The versatility of this approach is exemplified by the preparation of L-glucosamine, L-mannosamine and L-talosamine derivatives in highly diastereometrically pure forms.

Introduction

2-Amino-2-deoxy sugars are widely distributed in nature and play many important biological roles. They are constituents of nucleoside and aminoglycoside antibiotics,[1] skeletal material (*Crustacea* chitin), connective tissue and body-movement lubricants (glycolipids), serum mucoproteins, and biopolymers responsible for cell recognition, differentiation and protection.[2] Furthermore, the neoconjugates derived from oligosaccharides of natural and synthetic origin containing 2-amino-2-deoxy sugars are of great importance as extremely sensitive selective research and diagnostic tools and synthetic vaccines devoid of side effects. In spite of such omnipresence, only a few 2-amino-2-deoxy sugars are available from natural sources in quantities sufficient to satisfy the growing demands for research, medical and diagnostic uses. Moreover, several 6-deoxyaminohexoses, important carbohydrate units of many antibiotics, also belong to the 2-amino-2-deoxy sugar family normally of the L-form.[3] These 2-amino dideoxyhexoses are rather difficult to obtain by the traditional methods of chemical transformation of monosaccharides.

The well recognised biological importance of 2-amino-2-deoxy sugars has stimulated significant efforts towards the syntheses of this class of compounds. Traditionally they have been synthesized through multistep transformation of other relatively inexpensive and ready available carbohydrates.[4] But recent interest increasingly has focused on non-carbohydrate precursors.[5] Some examples of this non-carbohydrate methodology are direct amination of carbocycles,[6a–c] transformation of isoxazolines[6d–g] and 2-thiazolyl-*N*-alkylhydroxylamines,[6h,i] the use of hetero-Diels–Alder addition,[6j,k] [3 + 2] cycloaddition of nitrones with vinylene carbonate[6l] and the utilization of readily available natural products such as amino acids[6m–q] and lactic acid[6r–t] as chiral pool materials for the construction of amino sugar frameworks. However, some of these approaches still suffer from low stereoselectivity, their need of lengthy reaction sequences, and limited versatility.

In our previous preliminary communication,[7] we have reported a novel methodology for asymmetric synthesis of 2-amino sugars either in D- or L-configuration. The essential feature of our strategy is the transformation of the readily available chiral building blocks **1**[8] and **2**[9,10] into a fully protected derivative of 2-amino polyol **3** followed by cyclization to 2-amino-2-deoxy sugar **4** as shown in Chart 1.

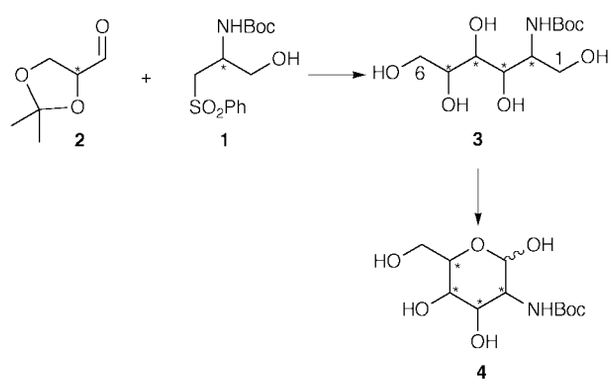

Chart 1

The *E*-selective Julia olefination of (*R*)- or (*S*)-2,3-isopropylideneglyceraldehyde **2** with either (*R*)- or (*S*)-**1** sets two chiral centres within the six-carbon chain of the 2-amino-2-deoxy sugar precursors. The remaining hydroxy functional groups can be introduced by stereoselective dihydroxylation of the double bond. Molecular mechanics calculation of the *E*-olefins reveals significant inherent face differentiation of the double bond (at least for *R*,*R* and *S*,*S* pairs obtained from **2** and **1**) so that the 2-aminohexanepentols with D- and L-*gluco* and D- and L-*manno* configurations can be preferentially obtained by *cis*-dihydroxylation. Other configurations of the 2-aminohexanepentols are potentially available either by regioselective modification of the newly formed hydroxy groups or by *trans*-dihydroxylation of the double bond. After appropriate protection of the two newly created hydroxy groups and transformation of the C-1 functionality of a 2-amino polyol **3** into aldehyde, cleavage of the cyclic acetal, and concomitant intramolecular cyclization would provide the corresponding 2-amino-2-deoxy sugars in their pyranose form.

As part of our continuing efforts in developing a novel efficient methodology for the synthesis of amino sugars, herein we describe the syntheses of fully protected forms of L-mannosamine, L-glucosamine and L-talosamine, which are difficult to obtain by other methods.[11]

† For Part 1 see ref. 7.

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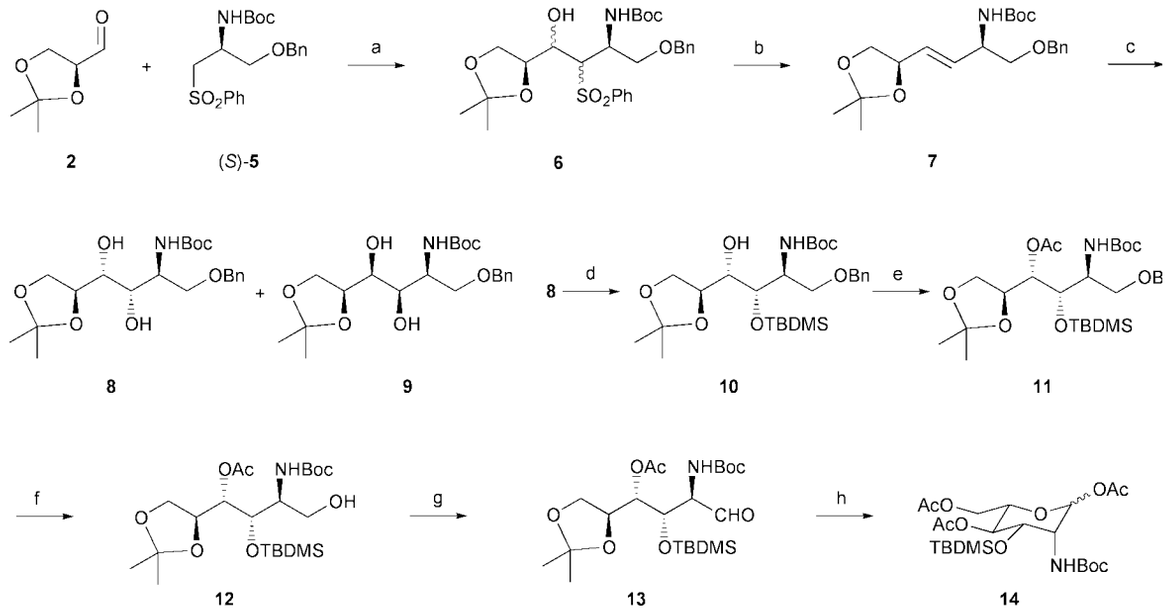


Scheme 1 *Reagents and conditions* (*yields*): (a) *n*-BuLi, THF, −78 °C, 3 h; then RT, 1 h (85%); (b) 6% Na–Hg, Na_2HPO_4, MeOH, 0 °C, 3 h (80%); (c) OsO_4, NMO, THF–H_2O (9 : 1), RT, 3 h (95%); (d) TBDMSCl, imidazole, DMF, RT, 24 h (95%); (e) Ac_2O, Et_3N, DMAP, CH_2Cl_2, RT, 24 h (80%); (f) H_2, 10% Pd/C, EtOAc, RT, 18 h (98%); (g) Py·SO_3, Et_3N, DMSO, 0 °C, 2 h (90%); (h) HCl, MeOH, RT, 8 h; then Ac_2O, Et_3N, DMAP, CH_2Cl_2, RT, 3 h (80%).

Results and discussion

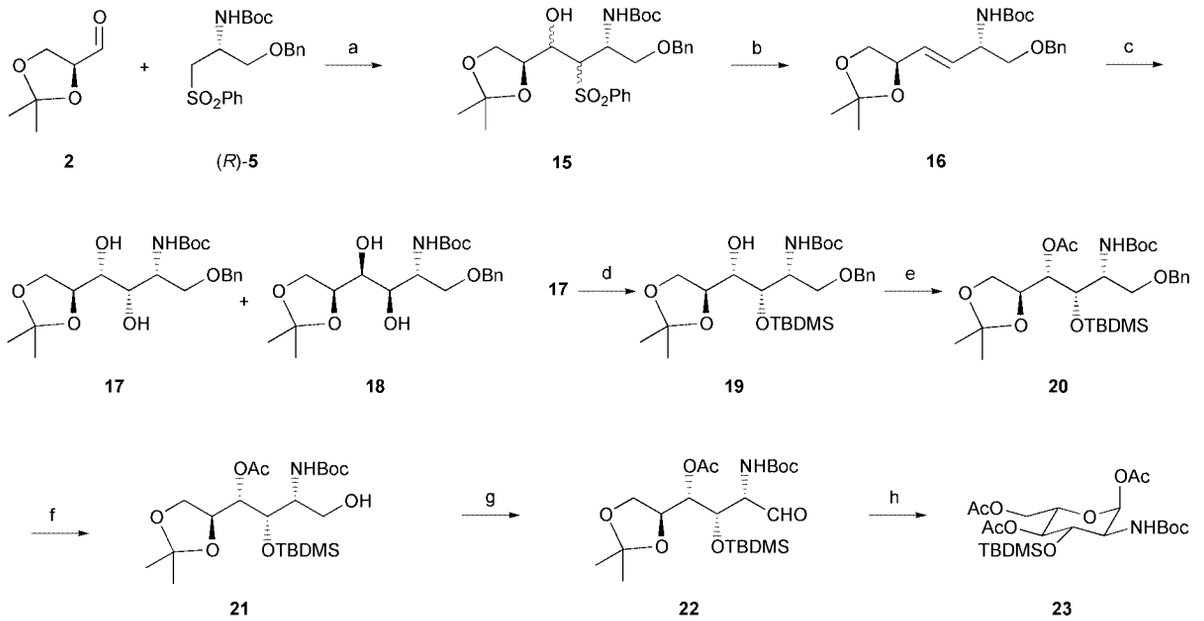
Synthesis of 1,4,6-tri-*O*-acetyl-2-(*tert*-butoxycarbonylamino)-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-L-mannopyranose is shown in Scheme 1.

Coupling of the dilithiate (*S*)-**5**, prepared from chiral synthon (*S*)-**1**,[12] with (2*S*)-2,3-*O*-isopropylideneglyceraldehyde **2** afforded a diastereomeric mixture of hydroxy sulfones **6** in good yield.[13] Treatment of the β-hydroxy sulfone **6** with 6% sodium amalgam furnished the olefin **7** in 80% yield as an easily separable mixture of *E*- and *Z*-isomer (≈4 : 1). The reductive elimination from the corresponding acetate was attempted with anticipation to improve the selectivity,[14] but provided exactly the same ratio of *E*- and *Z*-isomer in only moderate overall yield. We first investigated the dihydroxylation of *E*-olefin **7** using the Sharpless chiral reagent AD-mix-β.[15] The reaction was sluggish and only 40% conversion of the olefin was attained after 48 h to give a mixture of the diols **8** and **9** with 9 : 1 ratio,[16] in good agreement with earlier results on similar substrates.[17] On the other hand, osmium-catalysed dihydroxylation without chiral auxiliary[18] proceeded rapidly and afforded a mixture of these diols in high yield (95%) and with acceptable selectivity (**8** : **9** = 77 : 23). Since the diols were easily separable by preparative column chromatography, we opted for the use of the latter method. With the enantiomerically pure 2-aminohexanepentol **8** in hand, the route to desired 2-amino-2-deoxy-L-mannose derivatives seemed straightforward. However, protection of the hydroxy groups of the diol **8** was found to be more difficult than expected. Attempts to prepare the MEM derivative failed to provide the desired 3,4-bis-protected product and only a mixture of C-3- and C-4-mono-protected diols was obtained in ≈3 : 2 ratio even under forced conditions.

Successful bis-protection was achieved only in the case of acetyl and isopropylidene protecting groups, both of which were of no synthetic use for our goal. The presence of an acetoxy group at the C-3 position of the diol **8** led to undesired α,β-elimination during the oxidation of the C-1 primary alcohol to an aldehyde (step g), whereas 3,4;5,6-di-*O*-isopropylidene protection of the 2-aminohexanepentol **8** caused difficulty in the selective cyclization of the aldehyde **13** to the pyranose form of amino sugar (step h). Although a selective deprotection of the primary isopropylidene group has been reported,[19] significant loss of both isopropylidene groups took place in our case. Eventually, the silylation[20] of diol **8** was found to proceed with very high selectivity, providing C-3-*O*-mono-TBDMS ether **10** in 95% yield with only trace amounts of the undesired regioisomer that is easily separable by column chromatography. Subsequent acetylation of the hydroxy group at the C-4 position in **10** was achieved after 24 h in 80% yield. The fully protected 2-aminohexanepentol **11** was subjected to hydrogenolysis to give α-amino alcohol **12** in excellent yield. The corresponding aldehyde **13** was obtained by oxidation of **12** using either the Dess–Martin periodinane[21] or the complex Py·SO_3 in DMSO.[22] Both methods gave good yields, but we routinely used the latter for reasons of practicality. Swern oxidation and chromium reagents (PCC and PDC) gave poor results. Removal of the acetonide from **13** in MeOH in the presence of a catalytic amount of HCl followed by acetylation afforded, in 80% yield, the fully protected L-mannosamine **14** as a mixture of α- and β-anomers in approximately 2 : 1 ratio. No trace of the corresponding methyl glycosides was found under these mild conditions.

Synthesis of 1,4,6-tri-*O*-acetyl-2-(*tert*-butoxycarbonylamino)-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-L-glucopyranose **23** was then carried out from synthon (*R*)-**5** and (*S*)-2,3-isopropylideneglyceraldehyde **2** in the same synthetic sequence described above for its L-mannopyranose analogue (Scheme 2).

β-Hydroxy sulfone **15** was obtained in the same good yield as **6**, and treatment of **15** with 6% Na–Hg furnished the olefin **16** with the same selectivity (*E* : *Z* ≈ 4 : 1). Dihydroxylation of the olefin **16** afforded a mixture of the diols **17** and **18** in excellent yield but with rather poor selectivity (2 : 1), presumably as a result of change in the steric environment around the double bond (*R*,*S* pair obtained from **1** and **2**). Fortunately, the regioselectivity of silylation of the diol **17** was not changed, and the desired TBDMS ether **19** was obtained in the good yield though sluggishly. On the other hand, acetylation of the hydroxy function in **19** proceeded rapidly (after 1 h, compared with 24 h required for **10**) and afforded totally protected 2-aminohexanepentol **20** in excellent yield. Catalytic hydrogenation of the latter provided the alcohol **21**, which was then oxidized to the α-amino aldehyde **22**. Deprotection of the acetonide in **22** in MeOH in the presence of a catalytic amount of HCl followed



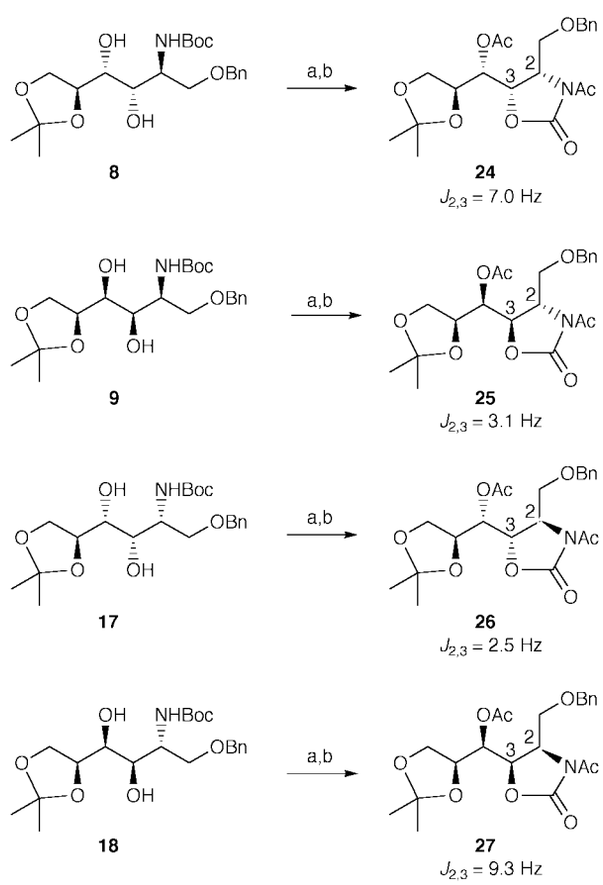
Scheme 2 *Reagents and conditions* (*yields*): (a) *n*-BuLi, THF, −78 °C, 3 h; then RT, 1 h (84%); (b) 6% Na–Hg, Na_2HPO_4, MeOH, 0 °C, 3 h (80%); (c) OsO_4, NMO, THF–H_2O (9 : 1), RT, 3 h (87%); (d) TBDMSCl, imidazole, DMF, RT, 24 h (90%); (e) Ac_2O, Et_3N, DMAP, CH_2Cl_2, RT, 1 h (95%); (f) H_2, 10% Pd/C, EtOAc, RT, 18 h (98%); (g) Py·SO_3, Et_3N, DMSO, 0 °C, 6 h (70%); (h) HCl, MeOH, RT, 48 h; then Ac_2O, Et_3N, DMAP, CH_2Cl_2, RT, 1 h (60%).

by acetylation afforded the fully protected L-glucosamine **23** as almost pure α-anomer.

The stereochemistry of diols **8**, **9**, **17** and **18** was assigned by NMR studies of the corresponding *N*,*O*-diacetyloxazolidinones **24**, **25**, **26** and **27** obtained from **8**, **9**, **17** and **18**, respectively, by treatment with NaH followed by acetylation. The coupling constants $J_{2,3}$ are 7.0 and 9.3 Hz for the 2,3-*threo*-isomers **24** and **27**, and 3.1 and 2.5 Hz for the 2,3-*erythro*-isomers **25** and **26**, respectively. These values are in agreement with corresponding data for related compounds[23] and are also consistent with the dihedral angles from molecular mechanics calculations. Furthermore, an intense nuclear Overhauser effect (NOE) observed between H-2 and H-3, and between H-1 and H-4 in 2D NOESY experiments for oxazolidinone **24** is in accordance with the stereochemistry depicted in Scheme 3.

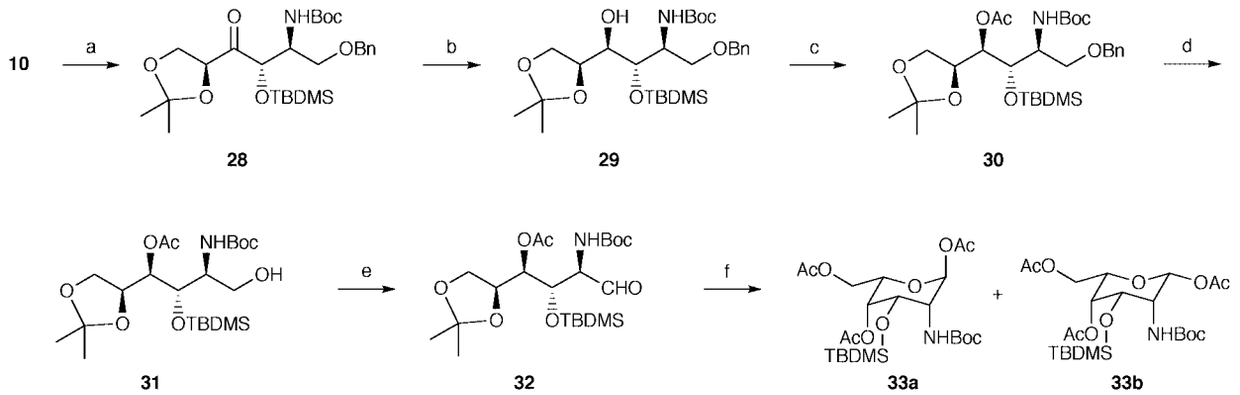
By choosing the appropriate set of starting synthons **1** and **2**, the sequence described above allows the synthesis of suitably protected 2-amino-2-deoxyhexopyranoses of *gluco* and *manno* configurations in both D- and, more interestingly, L-series. Further extension of the scope of our approach is possible by selective modification of the stereochemistry on the intermediates, as was demonstrated (*vide infra*) in the synthesis of a 2-amino-2-deoxy-L-talopyranose derivative. The free hydroxy group at C-4 in the ether **10** provides the possibility for modification of the configuration at this centre. Our first idea was to utilize the chloroacetate modification of the Mitsunobu reaction[24] which was found to be very efficient for the inversion of sterically hindered alcohols. However, upon treatment of **10** with chloroacetic acid in the presence of triphenylphosphine and diethyl azodicarboxylate, merely the starting material was recovered. We therefore directed our attention toward the oxidation of the hydroxy function at C-4 into a keto group, followed by selective reduction to obtain the inverted product (Scheme 4). However, we anticipated that no reasonable model to predict the desired selectivity could be formulated *a piori* for this densely functionalized substrate.

The hydroxy group of TBDMS ether **10** was oxidized uneventfully by the tetrapropylammonium perruthenate (TPAP) method[25] and the resultant ketone **28** was reduced with a number of hydride reagents. As can been seen from Table 1, L-Selectride® in THF[26] provided the best result among the reagents examined (sodium borohydride in methanol; DIBAL; zinc borohydride; and sodium borohydride in the presence of $CeCl_3$).



Scheme 3 *Reagents and conditions* (*yields*): (a) NaH, THF, 60 °C, 4 h, (60–80%); (b) Ac_2O, Et_3N, DMAP, 1 h (95%).

The mixture of two alcohols **29** and **10** (85 : 15) was easily separated by column chromatography and the main isomer **29** was acetylated to give the fully protected 2-amino polyol **30** of the desired L-*talo* stereochemistry. The latter was subjected to hydrogenolysis to afford α-amino alcohol **31**. Oxidation of **31**



Scheme 4 *Reagents and conditions* (*yields*): (a) TPAP, NMO, CH_3CN, RT, 2 h (93%); (b) L-Selectride®, THF, −78 °C, 30 min (88%); (c) Ac_2O, Et_3N, DMAP, CH_2Cl_2, RT, 30 min (98%); (d) H_2, 10% Pd/C, EtOAc, RT, 18 h (93%); (e) Py·SO_3, Et_3N, DMSO, 0 °C, 2 h (80%); (f) HCl, MeOH, RT, 48 h; then Ac_2O, Et_3N, DMAP, CH_2Cl_2, RT, 3 h (65%).

Table 1 Reduction of ketone **28**

Entry	Reduction conditions	Yield (%)	Ratio (**29**:**10**)
1	$NaBH_4$–$CeCl_3$–MeOH	85	Only **10**
2	$NaBH_4$–MeOH	90	70:30
3	DIBAL–CH_2Cl_2	95	60:40
4	$Zn(BH_4)_2$–Et_2O	60	50:50
5	L-Selectride®	88	85:15

using the complex Py·SO_3 afforded the expected α-amino aldehyde **32**, which was subjected to acidic methanolysis followed by acetylation. The product obtained in this manner was a mixture of the α- and β-anomers of 1,4,6-tri-*O*-acetyl-2-(*tert*-butoxycarbonylamino)-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-L-talopyranose **33a** and **33b** (2:1) which were separated by column chromatography.

It is noteworthy that the strategy described here can also be highly suitable for the acquisition of chiral, non-racemic furanose forms of 2-amino-2-deoxy sugars as well as polyhydroxylated pyrrolidine and piperidine derivatives.

Conclusions

We have developed a novel, efficient methodology for the stereoselective synthesis of chiral, non-racemic 2-amino-2-deoxy sugars. According to the present approach, the desired stereochemistry of the pyranose ring at the C-2 and C-5-positions is predetermined by appropriate selection of (*R*)- or (*S*)-**1** and (*R*)- or (*S*)-**2** as chiral starting materials. This in turn dictates the stereooutcome at the remaining C-3 and C-4 positions *via* *E*-selective Julia olefination and subsequent dihydroxylation.

Experimental

Reagents, obtained from commercial sources, were used without further purification. THF was distilled from sodium benzophenone ketyl. All other organic solvents were dried and distilled before use. Column chromatography was performed on Merck 60 silica gel (230–400 mesh) at medium pressure (300 mbar).‡ Analytical TLC was carried out on plates precoated with 0.25 mm of silica gel containing 60F-254 indicator. Optical rotations were measured with a Perkin-Elmer 241 polarimeter for samples in $CHCl_3$ solution; $[\alpha]_D$-values are reported in units of 10^{-1} deg cm^2 g^{-1}. IR spectra were obtained on Perkin-Elmer Spectrum BX spectrometer. ^{1}H NMR spectra were recorded at 300, 250, and 200 MHz, and ^{13}C NMR spectra were recorded at 75.5, 62.5, and 50 MHz with chemical shifts reported in ppm (δ) downfield from TMS (internal reference) for ^{1}H and relative to the centre line of the triplet of $CDCl_3$ at δ_C 77.14 for ^{13}C, unless otherwise specified. Chemical ionization mass spectra were recorded on an AEI MS-9 spectrometer (isobutane), and high-resolution mass spectra were obtained on a Kratos MS-80 spectrometer by CI (methane). Elemental analyses were performed by the microanalytical laboratory at the ICSN, CNRS, Gif-sur-Yvette.

‡ 1 bar = 10^5 Pa.

(2*S*,5*S*)-6-Benzyloxy-5-[(*tert*-butoxycarbonyl)amino]-1,2-isopropylidenedioxy-4-(phenylsulfonyl)hexan-3-ol 6

To a solution of (*S*)-**5** (4.05 g, 10 mmol) in THF (100 ml), obtained from (*S*)-**1**,[11] was added *n*-BuLi (1.6 M in hexane; 12.5 mol, 20 mmol) dropwise at −78 °C under dry argon. The mixture was stirred for 20 min and then a solution of (2*S*)-2,3-*O*-isopropylideneglyceraldehyde **2** (1.69 g, 13 mmol) in THF (10 ml) was added. After stirring for 3 h at −78 °C, the reaction mixture was allowed to warm to room temperature while being stirred for 1 h, quenched with saturated aq. NH_4Cl (30 ml) and concentrated. The residue was dissolved in EtOAc (500 ml), the solution washed successively with water (2 × 100 ml) and brine (200 ml), dried over Na_2SO_4, and the solvent was removed under reduced pressure. Flash chromatography of the residue (CH_2Cl_2–EtOAc 25:1) afforded an isomeric mixture of β-hydroxy sulfones **6** (4.55 g, 85%) (Found: C, 60.2; H, 6.9; N, 2.6; S, 6.0. $C_{27}H_{37}NO_8S$ requires C, 60.5; H, 7.0; N, 2.6; S, 6.0%); ν_{max} (neat)/cm^{-1} 3483, 3428, 2984, 2934, 2880, 1714, 1692, 1498, 1454, 1449, 1370, 1308, 1251; δ_H ($CDCl_3$) 7.97–7.92 (2H, m), 7.68–7.50 (3H, m), 7.32–7.15 (5H, m), 5.93–5.98 (1H, m), 4.65–4.52 (1H, m), 4.50–4.31 (2H, m), 4.30–4.20 (1H, m), 4.18–4.08 (1H, m), 4.08–3.95 (2H, m), 3.85–3.75 (1H, m), 3.70–3.45 (3H, m), 1.44, 1.42 (9H, 2s), 1.40, 1.35, 1.31, 1.24 (6H, 4s); δ_C ($CDCl_3$) 155.3, 155.2, 137.5, 137.3, 134.1, 134.0, 129.6, 129.3, 129.2, 128.6, 128.4, 128.0, 127.8, 127.6, 110.0, 109.9, 80.0, 79.6, 75.7, 73.1, 72.2, 71.6, 70.6, 69.3, 68.8, 67.9, 66.1, 65.0, 63.5, 60.5, 49.8, 48.6, 28.4, 26.9, 26.3, 25.2, 25.1, 21.1; *m*/*z* (CI) 536 [M + H]$^+$, 480, 436.

(2*R*,5*R*)-1-Benzyloxy-2-[(*tert*-butoxycarbonyl)amino]-5,6-isopropylidenedioxyhex-3-ene

To a solution of hydroxy sulfone **6** (4.55 g, 8.5 mmol) in HPLC-grade methanol (70 ml) containing Na_2HPO_4 (12.1 g, 85 mmol) was added 6% Na-Hg (25 g, 65 mmol) at 0 °C. The mixture was stirred at this temperature for 3 h. Mercury was removed by decanting the reaction mixture, and methanol was evaporated. The residue was diluted in water (200 ml) and extracted with EtOAc (3 × 100 ml). The organic extracts were washed successively with water (2 × 100 ml) and brine (100 ml), dried over Na_2SO_4 and evaporated. Flash chromatography of the residue, eluting with heptane–EtOAc 3:1, provided two olefins (2.54 g, 80%): 1.95 g (77%) of the *E*-isomer **7** and 0.59 g (23%) of the *Z*-isomer.

***E*-Isomer 7.** $[a]_D^{20}$ −7.3 (*c* 2.0) (Found: C, 66.5; H, 8.7; N, 3.6. $C_{21}H_{31}NO_5$ requires C, 66.8; H, 8.3; N, 3.7%); ν_{max} (neat)/cm^{-1} 3348, 3030, 2982, 2934, 2869, 1715, 1511, 1498, 1455, 1391, 1368, 1247; δ_H ($CDCl_3$) 7.33–7.30 (5H, m), 5.83 (1H, dd, *J* 5.1, 15.6 Hz), 5.64 (1H, ddd, *J* 1.2, 7.1, 15.6 Hz), 4.92 (1H, br s), 4.58–4.44 (3H, m), 4.35 (1H, br), 4.07 (1H, dd, *J* 6.1, 8.0 Hz), 3.56 (1H, t, *J* 8.0 Hz), 3.54–3.45 (2H, m), 1.44 (9H, s), 1.41, 1.38 (6H, 2s); δ_C ($CDCl_3$) 155.4, 137.9, 132.4, 128.9, 128.5, 127.8, 127.7, 109.4, 79.6, 76.6, 73.2, 72.0, 69.5, 51.4, 28.4, 26.7, 26.0; *m*/*z* (CI) 378 $[M + H]^+$, 278, 264.

***Z*-Isomer.** $[a]_D^{20}$ +3.7 (*c* 2.0) (Found: MH^+, 378.2282. $C_{21}H_{32}NO_5$ requires *m*/*z*, 378.2280); ν_{max} (neat)/cm^{-1} 3347, 3030, 2982, 2933, 2969, 1715, 1511, 1498, 1455, 1391, 1368, 1247; δ_H ($CDCl_3$) 7.35–7.30 (5H, m), 5.68 (1H, dd, *J* 10.4, 11.0 Hz), 5.33 (1H, dd, *J* 8.7, 11.0 Hz), 5.10–4.90 (2H, m), 4.65–4.55 (1H, m), 4.57, 4.49 (2H, 2d, *J* 11.9 Hz), 4.18 (1H, dd, *J* 6.2, 8.1 Hz), 3.61–3.45 (2H, m), 1.44 (9H, s), 1.41, 1.36 (6H, 2s); δ_C ($CDCl_3$) 155.1, 137.9, 131.9, 130.3, 129.8, 128.5, 127.9, 127.8, 109.4, 79.6, 73.4, 72.3, 72.2, 69.8, 48.0, 28.5, 26.9, 25.9; *m*/*z* (CI) 378 $[M + H]^+$, 278, 264.

1-*O*-Benzyl-2-[(*tert*-butoxycarbonyl)amino]-2-deoxy-5,6-*O*-isopropylidene-L-mannitol 8 and 1-*O*-benzyl-2-[(*tert*-butoxycarbonyl)amino]-2-deoxy-5,6-*O*-isopropylidene-L-iditol 9

To a solution of *E*-isomer **7** (1.885 g, 5 mmol) in 15 ml of THF–H_2O (9:1) were successively added a solution of osmium tetraoxide (0.2 M in ^{t}BuOH; 2.5 ml, 0.5 mmol) and *N*-methylmorpholine *N*-oxide (NMO) (60% weight in H_2O; 2.58 ml, 15 mmol). The mixture was stirred at room temperature for 3 h, quenched by addition of saturated aq. Na_2SO_3 (50 ml), and stirred for an additional 30 min. THF was evaporated, and the residue was diluted with water (50 ml) and extracted with EtOAc (3 × 100 ml). The combined organic extracts were washed successively with water (100 ml) and brine (100 ml), dried over Na_2SO_4 and evaporated. Flash chromatography of the residue, eluting with heptane–EtOAc 1:1, provided the two diols (2.055 g, 95%): 1.58 g and 0.47 g (77:23).

Major isomer 8. $[a]_D^{20}$ +5.6 (*c* 1.2) (Found: C, 61.3; H, 8.8; N, 3.3. $C_{21}H_{33}NO_7$ requires C, 61.3; H, 8.9; N, 3.4%); ν_{max} (neat)/cm^{-1} 3439br, 2981, 2933, 1709, 1504, 1454, 1367, 1248; δ_H ($CDCl_3$) 7.35–7.25 (5H, m), 5.29 (1H, d, *J* 7.9 Hz), 4.57, 4.50 (2H, 2d, *J* 11.8 Hz), 4.22–4.08 (3H, m), 3.97–3.87 (2H, m), 3.80–3.72 (1H, m), 3.68–3.58 (2H, m), 3.49 (1H, dd, *J* 3.4, 7.2 Hz), 2.73 (1H, d, *J* 8.9 Hz), 1.44 (9H, s), 1.38, 1.34 (6H, 2s); δ_C ($CDCl_3$) 157.3, 137.8, 128.5, 127.8, 109.2, 80.5, 74.8, 73.5, 71.4, 69.9, 68.9, 67.8, 52.1, 28.3, 26.9, 25.3; *m*/*z* (CI) 468 $[M + 57]^+$, 412 $[M + H]^+$, 356, 312.

Minor isomer 9. $[a]_D^{20}$ +7.7 (*c* 1.5) (Found: MH^+, 412.2327. $C_{21}H_{34}NO_7$ requires *m*/*z*, 412.2325); ν_{max} (neat)/cm^{-1} 3440br, 3031, 2980, 2933, 1709br, 1504, 1455, 1367, 1248; δ_H ($CDCl_3$) 7.22–7.15 (5H, m), 5.21 (1H, d, *J* 9.1 Hz), 4.55, 4.48 (2H, 2d, *J* 11.8 Hz), 4.35–4.25 (1H, m), 4.18–3.92 (3H, m), 3.90–3.68 (2H, m), 3.65–3.63 (2H, m), 3.50–3.15 (2H, m), 1.43 (s), 1.36 (s) (15H); δ_C ($CDCl_3$) 156.2, 137.7, 128.5, 127.9, 127.8, 109.6, 79.7, 76.1, 73.3, 71.7, 71.1, 70.2, 66.0, 51.3, 28.3, 26.4, 25.3 ; *m*/*z* (CI) 468 $[M + 57]^+$, 412 $[M + H]^+$, 356, 312.

1-*O*-Benzyl-2-[(*tert*-butoxycarbonyl)amino]-3-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-5,6-*O*-isopropylidene-L-mannitol 10

A solution of diol **8** (1.223 g, 3 mmol), imidazole (1.02 g, 15 mmol), and *tert*-butyldimethylsilyl chloride (TBDMSCl) (1.13 g, 7.5 mmol) in DMF (10 ml) was stirred at room temperature for 24 h. The mixture was dissolved in EtOAc (300 ml), and the solution was washed successively with water (50 ml), 1 M HCl (50 ml), saturated aq. $NaHCO_3$ (50 ml) and brine (50 ml) and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography, eluting with heptane–EtOAc 5:1, to afford **10** (1.48 g, 95%) as colourless oil; $[a]_D^{20}$ +11.0 (*c* 1.5) (Found: C, 61.2; H, 8.9; N, 2.8. $C_{27}H_{47}NO_7Si$ requires C, 61.7; H, 9.03; N, 2.7%); ν_{max} (neat)/cm^{-1} 3428br, 2980, 2954, 2931, 2886, 2858, 1715, 1693, 1501, 1473, 1455, 1367, 1253; δ_H ($CDCl_3$) 7.18–7.05 (5H, m), 5.30 (1H, d, *J* 7.1 Hz), 4.57, 4.45 (2H, 2d, *J* 11.9 Hz), 4.10–4.03 (2H, m), 4.02–3.78 (3H, m), 3.75–3.40 (3H, m), 2.85 (1H, d, *J* 7.1 Hz), 1.42 (9H, s), 1.36, 1.32 (6H, 2s), 0.91 (9H, s), 0.15, 0.14 (6H, 2s); δ_C ($CDCl_3$) 156.0, 138.0, 128.5, 127.7, 109.4, 79.4, 75.0, 73.3, 72.4, 69.5, 69.4, 68.1, 53.6, 28.5, 27.0, 26.1, 25.4, 18.3, −4.4, −4.5; *m*/*z* (CI) 582 $[M + 57]^+$, 526 $[M + H]^+$, 470, 436.

4-*O*-Acetyl-1-*O*-benzyl-2-[(*tert*-butoxycarbonyl)amino]-3-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-5,6-*O*-isopropylidene-L-mannitol 11

A solution of **10** (1.05 g, 2 mmol), triethylamine (0.93 ml, 6.6 mmol), Ac_2O (0.58 ml, 6 mmol) and DMAP (100 mg) in 5 ml of CH_2Cl_2 was stirred at room temperature for 24 h. Methanol (3 ml) was added, and stirring was continued for 30 min. The solvent was diluted with EtOAc (150 ml), and the mixture was washed successively with water (50 ml), 1 M HCl (50 ml), saturated aq. $NaHCO_3$ (50 ml) and brine (50 ml), dried over Na_2SO_4 and evaporated. After removal of the solvent, the residue was purified by column chromatography, eluting with heptane–EtOAc 5:1, to afford **11** (910 mg, 80%); $[a]_D^{20}$ −7.3 (*c* 0.6) (Found: MH^+, 568.3309. $C_{29}H_{50}NO_8Si$ requires *m*/*z*, 568.3306); ν_{max} (neat)/cm^{-1} 3455, 3362, 2980, 2957, 2931, 2887, 2858, 1751, 1716, 1496, 1474, 1455, 1368, 1228; δ_H ($CDCl_3$) 7.35–7.39 (5H, m), 5.16 (1H, dd, *J* 2.5, 6.8 Hz), 4.84 (1H, d, *J* 6.6 Hz), 4.50 (2H, s), 4.23–4.12 (2H, m), 4.02 (1H, t, *J* 4.8 Hz), 3.92–3.80 (2H, m), 3.70–3.62 (1H, m), 3.50 (1H, dd, *J* 3.5, 9.4 Hz), 2.06 (3H, s), 1.43 (9H, s), 1.36, 1.34 (6H, 2s), 0.88 (9H, s), 0.10, 0.09 (6H, 2s); δ_C ($CDCl_3$) 170.3, 155.6, 138.1, 128.5, 127.8, 109.4, 79.4, 74.0, 73.5, 73.2, 70.8, 68.5, 66.4, 52.7, 28.5, 26.6, 26.0, 25.7, 21.3, 18.4, −4.4, −4.5; *m*/*z* (CI) 568 $[M + H]^+$, 512, 468.

4-*O*-Acetyl-2-[(*tert*-butoxycarbonyl)amino]-3-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-5,6-*O*-isopropylidene-L-mannitol 12

A stirred solution of **11** (850 mg, 1.5 mmol) in EtOAc (5 ml) was treated with hydrogen in the presence of 10% Pd/C (80 mg) at atmospheric pressure for 18 h. After removal of the catalyst by filtration through Celite, the solvent was evaporated. Purification of the residue by column chromatography, eluting with heptane–EtOAc 1:1, afforded **12** (680 mg, 98%); $[a]_D^{20}$ −26.7 (*c* 1.5) (Found: C, 55.2; H, 9.1; N, 2.8. $C_{22}H_{43}NO_8Si$ requires C, 55.3; H, 9.1; N, 2.9%); ν_{max} (neat)/cm^{-1} 3455br, 2958, 2932, 2890, 2859, 1749, 1712, 1500, 1474, 1370, 1252; δ_H ($CDCl_3$) 5.28 (1H, br d, *J* 6.2 Hz), 5.12 (1H, dd, *J* 6.2, 8.0 Hz), 4.22–4.05 (3H, m), 3.92–3.80 (3H, m), 3.60–3.70 (1H, m), 2.10 (3H, s), 1.44 (9H, s), 1.38, 1.35 (6H, 2s), 0.90 (9H, s), 0.13, 0.12 (6H, 2s); δ_C ($CDCl_3$) 170.1, 156.1, 109.6, 79.7, 73.9, 73.4, 72.0, 66.2, 62.4, 54.5, 28.4, 26.5, 25.9, 25.5, 21.2, 18.2, −4.6, −4.7; *m*/*z* (CI) 534 $[M + 57]^+$, 478 $[M + H]^+$, 434, 426, 378, 360.

4-*O*-Acetyl-2-[(*tert*-butoxycarbonyl)amino]-3-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-5,6-*O*-isopropylidene-L-mannose 13

To a solution of **12** (600 mg, 1.25 mmol) in DMSO (3 ml) were added successively triethylamine (1.2 ml, 8.25 mmol) and Py·SO_3 (954 mg, 6 mmol) at 0 °C. After 2 h, the mixture was dissolved in EtOAc (100 ml) and washed successively with water (3 × 20 ml), 1 M HCl (30 ml), saturated aq. $NaHCO_3$ (30 ml) and brine (30 ml), dried over Na_2SO_4 and evaporated. After removal of the solvent, the residue was purified by column chromatography, eluting with heptane–EtOAc 3:1, to afford **13** (477 mg, 90%); $[a]_D^{20}$ −26.7 (*c* 1.5) (Found: C, 55.6; H, 8.6; N, 2.8. $C_{22}H_{41}NO_8Si$ requires C, 55.6; H, 8.7; N, 3.0%); ν_{max} (neat)/cm^{-1} 3437br, 2958, 2932, 2896, 2859, 1752br, 1713br, 1490,

1474, 1370, 1253; δ_H ($CDCl_3$) 9.67 (1H, s), 5.55 (1H, d, *J* 6.0 Hz), 5.25 (1H, t, *J* 7.0 Hz), 4.50 (1H, dd, *J* 3.0, 7.0 Hz), 4.34 (1H, dd, *J* 2.6, 8.5 Hz), 4.23 (1H, 2d, *J* 7.0, 14.0 Hz), 4.05 (1H, dd, *J* 6.0, 8.3 Hz), 3.79 (1H, t, *J* 8.0 Hz), 2.11 (3H, s), 1.45 (9H, s), 1.42, 1.35 (6H, 2s), 0.85 (9H, s), 0.08, 0.07 (6H, 2s); δ_C ($CDCl_3$) 198.2, 169.9, 155.4, 110.2, 80.1, 74.5, 73.7, 73.2, 66.8, 63.0, 28.3, 26.5, 26.0, 25.7, 21.1, 18.1, −4.7 ; *m*/*z* (CI) 476 $[M + H]^+$, 418, 362, 318.

1,4,6-Tri-*O*-acetyl-2-[(*tert*-butoxycarbonyl)amino]-3-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-L-mannopyranose 14

A solution of **13** (143 mg, 0.3 mmol) in methanol (3 ml) was treated with conc. HCl (2.5 µl) and the mixture was stirred for 8 h at room temperature. After addition of triethylamine (0.1 ml), the solvent was evaporated. To a solution of the residue in CH_2Cl_2 (2 ml) were added triethylamine (0.93 ml, 6.6 mmol), Ac_2O (0.58 ml, 6 mmol) and DMAP (100 mg) successively. The mixture was stirred at room temperature for 3 h. Methanol (3 ml) was added, and stirring was continued for 30 min. The solvent was evaporated, and the residue was dissolved in EtOAc (30 ml), washed successively with water (15 ml), 1 M HCl (15 ml), saturated aq. $NaHCO_3$ (15 ml) and brine (15 ml), dried over Na_2SO_4 and evaporated. After removal of the solvent, the residue was purified by column chromatography, eluting with heptane–EtOAc 3:1, to afford **14** as a mixture of the α- and β-anomer in the ratio 2:1 (118 mg, 80%); $[\alpha]_D^{20}$ +2.8 (*c* 1) (Found: C, 51.7; H, 7.6; N, 2.4. $C_{23}H_{41}NO_{10}Si\cdot H_2O$ requires C, 51.40; H, 8.0; N, 2.6%); ν_{max} (neat)/cm^{-1} 3449, 3031, 2959, 1748, 1714, 1504, 1392, 1369, 1233; δ_H ($CDCl_3$) 6.15 (br s, α-anomer H-1) and 5.85 (d, $J_{1,2}$ 2.4 Hz, β-anomer H-1) (1H), 5.05–4.80 (m, α-H-4 and β-H-4, α-NH and β-NH) (2H), 4.45–4.30 (m), 4.28 (m), 4.04 (dd, *J* 2.5 and 12.3 Hz), 3.95–3.85 (m), 3.82–3.75 (m) (5H), 2.14 (s), 2.10 (s), 2.09 (s), 2.08 (s) (9H), 1.44 (s, 9H), 0.89 (s), 0.86 (s) (9H), 0.12 (s), 0.10 (s), 0.09 (s) (6H); δ_C ($CDCl_3$) 170.8, 170.6, 169.8, 169.6, 169.2, 168.4 (CH_3CO), 155.7 (Me_3COCO), 92.3 (C-1, α-anomer), 91.6 (C-1, β-anomer), 80.2 (Me_3COCO, α), 80.0 (Me_3COCO β), 72.9 (C-3-β or C-5-β interchangeable attribution), 70.1 (C-3-α or C-5-α), 69.3 (C-5-β or C-3-β), 68.8 (C-5-α or C-3-α), 68.4 (C-4-β), 68.1 (C-4-α), 62.9 (C-6-β), 62.3 (C-6-α), 53.9 (C-2-β), 51.1 (C-2-α), 28.3 (Me_3CO-CO), 25.0 (Me_3CSiMe_2), 21.0 and 20.8 (CH_3CO), 17.9 (Me_3-$CSiMe_2$), −4.8 (Me_3CSiMe_2 β), −5.0 (Me_3CSiMe_2 α); *m*/*z* (CI) 537 $[M + NH_4]^+$, 436.

(2*S*,5*R*)-6-Benzyloxy-5-[(*tert*-butoxycarbonyl)amino]-1,2-isopropylidenedioxy-4-(phenylsulfonyl)hexan-3-ol 15

Starting with (*R*)-**5** (4.05 g, 10 mmol), obtained from (*R*)-**1**,[11] exactly the same procedure as described for the preparation of compound **6** furnished **15** (4.5 g, 84%) (Found: MH^+, 536.2285. $C_{27}H_{38}NO_8S$ requires *m*/*z*, 536.2379); ν_{max} ($CHCl_3$)/cm^{-1} 3543, 3439, 3031, 3012, 2985, 2932, 1709, 1498, 1448, 1393, 1368, 1308, 1250; δ_H ($CDCl_3$) 8.05–7.90 (2H, m), 7.70–7.40 (3H, m), 7.30–7.15 (5H, m), 6.15 (d, *J* 8.5 Hz), 5.98 (d, *J* 8.8 Hz), 5.15 (d, *J* 8.5 Hz) (1H), 4.60–4.30 (3H, m), 4.10–4.00 (2H, m), 4.00–3.80 (2H, m), 3.80–3.60 (2H, m), 3.60–3.36 (2H, m), 1.45 (9H, s), 1.42, 1.40 (6H, 2s); δ_C ($CDCl_3$) 155.2, 139.6, 139.2, 138.1, 137.6, 137.3, 134.1, 134.0, 129.6, 129.4, 129.1, 128.5, 128.3, 127.9, 127.8, 127.7, 127.5, 110.1, 109.9, 109.7, 79.7, 79.5, 69.7, 67.8, 67.3, 66.9, 66.3, 65.9, 60.3, 56.6, 48.6, 47.9, 46.7, 28.3, 28.2, 26.7, 26.3, 26.0, 25.5, 20.9; *m*/*z* (ESI) 558 $[M + Na]^+$, 536 $[M + H]^+$, 406, 349.

(2*S*,5*R*)-1-Benzyloxy-2-[(*tert*-butoxycarbonyl)amino]-5,6-isopropylidenedioxyhex-3-ene

Starting from **15** (4.15 g, 7.8 mmol), exactly the same procedure as described for the preparation of compound **7** provided a mixture of two olefins (2.34 g, 80%): *E*-isomer **16** 1.80 g (77%) and *Z*-isomer 0.54 g (23%).

***E*-Isomer 16.** $[\alpha]_D^{20}$ −11.3 (*c* 1.5) (Found: MH^+, 378.2308. $C_{21}H_{32}NO_5$ requires *m*/*z*, 378.2280); ν_{max} (neat)/cm^{-1} 3348br, 3064, 3030, 2982, 2934, 2869, 1715, 1511, 1498, 1455, 1391, 1368, 1247; δ_H ($CDCl_3$) 7.20–7.10 (5H, m), 5.82 (1H, dd, *J* 5.8, 15.6 Hz), 5.66 (1H, ddd, *J* 0.9, 6.8, 15.6 Hz), 4.87 (1H, br s), 4.58–4.45 (3H, m), 4.33 (1H, br s), 4.08 (1H, dd, *J* 6.3, 8.3 Hz), 3.62–3.47 (3H, m), 1.44 (9H, s), 1.42, 1.39 (6H, 2s); δ_C ($CDCl_3$) 155.3, 138.0, 132.4, 129.3, 128.5, 127.9, 127.8, 109.4, 79.7, 76.7, 73.3, 72.1, 69.5, 51.7, 28.5, 26.8, 26.0; *m*/*z* (CI) 378 $[M + H]^+$, 266, 210.

***Z*-Isomer.** $[\alpha]_D^{20}$ −8.7 (*c* 1.0) (Found: MH^+, 378.2272); ν_{max} (neat)/cm^{-1} 3348br, 2982, 2934, 2869, 1715, 1511, 1498, 1455, 1368, 1247; δ_H ($CDCl_3$) 7.30–7.20 (5H, m), 5.60–5.50 (2H, m), 5.00–4.75 (2H, m), 4.60–4.45 (3H, m), 3.94 (1H, dd, *J* 6.3, 8.1 Hz), 3.50–3.42 (3H, m), 1.44 (9H, s), 1.41, 1.36 (6H, 2s); δ_C ($CDCl_3$) 155.2, 137.9, 131.7, 129.3, 128.6, 128.0, 127.8, 109.5, 73.4, 72.7, 72.4, 69.6, 48.6, 28.5, 26.8, 26.0; *m*/*z* (CI) 378 $[M + H]^+$, 322, 278.

1-*O*-Benzyl-2-[(*tert*-butoxycarbonyl)amino]-2-deoxy-5,6-*O*-isopropylidene-L-glucitol 17 and 1-*O*-benzyl-2-[(*tert*-butoxycarbonyl)amino]-2-deoxy-5,6-*O*-isopropylidene-L-gulitol 18

Starting from **16** (1.4 g, 3.7 mmol), exactly the same procedure as described for the preparation of compounds **8** and **9** furnished a mixture of two isomers (1.323 g, 87%). The diols **17** (major, 882 mg) and **18** (minor, 441 mg) were separated by column chromatography, eluting with CH_2Cl_2–acetone 5:1.

Isomer 17. $[\alpha]_D^{20}$ −10.3 (*c* 1.5) (Found: C, 61.1; H, 7.9; N, 3.2. $C_{21}H_{33}NO_7$ requires C, 61.3; H, 8.1, N, 3.4%); ν_{max} (neat)/cm^{-1} 3442br, 3333br, 2982, 2933, 1710, 1505, 1455, 1369, 1249; δ_H ($CDCl_3$) 7.30–7.22 (5H, m), 5.26 (1H, d, *J* 8.1 Hz), 4.52 (2H, s), 4.17–4.00 (2H, m), 4.00–3.85 (3H, m), 3.70 (1H, d, *J* 10 Hz), 3.65–3.56 (2H, m), 3.50 (1H, br s), 3.34 (1H, br s), 1.43 (9H, s), 1.38, 1.34 (6H, 2s); δ_C ($CDCl_3$) 156.6, 137.4, 129.7, 128.5, 127.9, 127.8, 109.2, 80.0, 76.6, 75.7, 73.5, 72.2, 70.2, 66.9, 52.7, 28.4, 26.8, 25.3; *m*/*z* (ESI) 434 $[M + Na]^+$, 412 $[M + H]^+$, 356, 312.

Isomer 18. $[\alpha]_D^{20}$ −10.6 (*c* 2.4) (Found: C, 61.4; H, 7.6; N, 3.1%). ν_{max} (neat)/cm^{-1} 3443br, 2981, 2933, 1710, 1499, 1454, 1368, 1249; δ_H ($CDCl_3$) 7.35–7.30 (5H, m), 5.24 (1H, d, *J* 8.5 Hz), 4.57, 4.50 (2H, 2d, *J* 11.7 Hz), 4.30 (1H, m), 4.05 (1H, dd, *J* 6.4, 8.2 Hz), 4.38–4.00 (2H, m), 3.80–3.66 (1H, m), 3.62–3.52 (3H, m), 3.00 (1H, d, *J* 8.3 Hz), 1.43 (s), 1.39 (s) (15H); δ_C ($CDCl_3$) 156.9, 137.8, 128.6, 128.0, 127.8, 109.9, 80.5, 77.8, 73.6, 71.7, 69.8, 68.7, 66.1, 52.2, 28.4, 26.6, 25.7; *m*/*z* (ESI) 434 $[M + Na]^+$, 412 $[M + H]^+$, 356, 312.

1-*O*-Benzyl-2-[(*tert*-butoxycarbonyl)amino]-3-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-5,6-*O*-isopropylidene-L-glucitol 19

Starting from **17** (700 mg, 1.7 mmol), exactly the same procedure as described for the preparation of compound **10** gave **19** (805 mg, 90%); $[\alpha]_D^{20}$ −3.0 (*c* 1.2) (Found: C, 61.2; H, 8.8; N, 2.6. $C_{27}H_{47}NO_7Si$ requires C, 61.7; H, 9.0; N, 2.7%); ν_{max} (neat)/cm^{-1} 3450br, 2981, 2954, 2931, 2885, 2858, 1715, 1497, 1473, 1455, 1381, 1368, 1254; δ_H ($CDCl_3$) 7.35–7.30 (5H, m), 4.92 (1H, d, *J* 8.3 Hz), 4.53 (2H, s), 4.18–4.05 (2H, m), 4.00–3.85 (2H, m), 3.82–3.65 (1H, m), 3.57–3.43 (2H, m), 3.02 (1H, d, *J* 6.3 Hz), 1.43 (9H, s), 1.36, 1.32 (6H, 2s), 0.89 (9H, s), 0.15 (6H, s); δ_C ($CDCl_3$) 155.4, 137.5, 129.8, 128.6, 128.5, 127.9, 109.2, 79.5, 75.2, 73.4, 71.3, 69.9, 68.0, 67.7, 53.0, 28.5, 27.0, 26.0, 25.4, 18.2, −4.3, −4.6; *m*/*z* (CI) 526 $[M + H]^+$, 426, 368.

4-*O*-Acetyl-1-*O*-benzyl-2-[(*tert*-butoxycarbonyl)amino]-3-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-5,6-*O*-isopropylidene-L-glucitol 20

Starting from **19** (650 mg, 1.24 mmol), exactly the same

procedure as described for the preparation of compound **11** furnished **20** (667 mg, 95%) after 1 h of stirring; $[\alpha]_D^{20}$ −40.7 (*c* 1.2) (Found: C, 61.3; H, 8.9; N, 2.5. $C_{29}H_{49}NO_8Si$ requires C, 61.3; H, 8.7; N, 2.5%); ν_{max} (neat)/cm^{-1} 3450, 3354, 2995, 2958, 2932, 1745, 1717, 1498, 1455, 1368, 1230; δ_H ($CDCl_3$) 7.37–7.22 (5H, m), 5.12 (1H, t, *J* 5.3 Hz), 4.94 (1H, d, *J* 8.6 Hz), 4.52, 4.48 (2H, 2d, *J* 11.5 Hz), 4.28 (1H, dt, *J* 5.7, 6.3 Hz), 4.12 (1H, dd, *J* 2.0, 5.2 Hz), 3.98–3.82 (2H, m), 3.79 (1H, dd, *J* 6.7, 8.2 Hz), 3.50–3.38 (2H, m), 2.07 (3H, s), 1.45 (9H, s), 1.36, 1.33 (6H, 2s), 0.90 (9H, s), 0.14, 0.10 (6H, 2s); δ_C ($CDCl_3$) 170.3, 155.4, 138.2, 128.5, 127.7, 127.6, 109.3, 79.7, 73.9, 73.8, 72.9, 68.9, 68.6, 65.8, 51.0, 28.5, 26.5, 26.0, 25.3, 21.3, 18.3, −4.3, −4.7; *m*/*z* (CI) 568 $[M + H]^+$, 468.

4-*O*-Acetyl-2-[(*tert*-butoxycarbonyl)amino]-3-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-5,6-*O*-isopropylidene-L-glucitol 21

Starting from **20** (650 mg, 1.15 mmol), exactly the same procedure as described for the preparation of compound **12**, afforded **21** (535 mg, 98%): $[\alpha]_D^{20}$ −11.4 (*c* 2.2) (Found: C, 55.6; H, 8.7; N, 2.8. $C_{22}H_{43}NO_8Si$ requires C, 55.3; H, 9.1; N, 2.9%); ν_{max} (neat)/cm^{-1} 3446br, 2982, 2956, 2932, 2887, 2859, 1747, 1716, 1497, 1474, 1370, 1232; δ_H ($CDCl_3$) 5.13–5.03 (2H, m), 4.28–4.20 (1H, m), 4.18–4.05 (2H, m), 3.99 (1H, t, *J* 7.5 Hz), 3.78 (1H, t, *J* 7.5 Hz), 3.70–3.60 (1H, m), 3.60–3.50 (1H, m), 2.50 (1H, br s), 2.10 (3H, s), 1.45 (9H, s), 1.38, 1.35 (6H, 2s), 0.92 (9H, s), 0.16, 0.15 (6H, 2s); δ_C 170.4, 156.3, 109.5, 80.1, 73.9, 69.3, 66.2, 63.2, 53.9, 28.5, 26.6, 26.0, 25.3, 21.3, 18.3, −4.3, −4.6; *m*/*z* (CI) 478 $[M + H]^+$.

4-*O*-Acetyl-2-[(*tert*-butoxycarbonyl)amino]-3-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-5,6-*O*-isopropylidene-L-glucose 22

Starting from **21** (160 mg, 0.34 mmol), exactly the same procedure as described for the preparation of compound **13** gave **22** (111 mg, 70%); $[\alpha]_D^{20}$ +89.7 (*c* 2.0) (Found: C, 55,6; H, 8.6; N, 2.8. $C_{22}H_{41}NO_8Si$ requires C, 55.6; H, 8.7; N, 3.0%); ν_{max} (neat)/cm^{-1} 3434, 2981, 2957, 2933, 2889, 2859, 1747, 1715, 1497, 1473, 1370, 1227; δ_H ($CDCl_3$) 9.85 (1H, s), 5.35 (1H, d, *J* 6.5 Hz), 5.04 (1H, dd, *J* 1.5, 7.8 Hz), 4.59 (1H, dd, *J* 1.7, 5.9 Hz), 4.36 (1H, t, *J* 6.3 Hz), 4.21–4.12 (1H, m), 3.83–3.78 (1H, m), 1.98 (3H, s), 1.44 (9H, s), 1.37, 1.33 (6H, 2s), 0.96 (9H, s), 0.28, 0.21 (6H, s); δ_C ($CDCl_3$) 199.1, 170.4, 155.3, 109.6, 80.3, 73.5, 71.8, 71.1, 66.7, 61.9, 28.3, 26.7, 25.9, 20.8, 18.2, −4.4, −4.9; *m*/*z* (ESI) 498 $[M + Na]^+$, 398.

1,4,6-Tri-*O*-acetyl-2-[(*tert*-butoxycarbonyl)amino]-3-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-L-glucopyranose 23

Starting from **22** (90 mg, 0.19 mmol), exactly the same procedure as described for the preparation of compound **14** afforded **23** (65 mg, 60%) as the α-anomer; $[\alpha]_D^{20}$ −57.5 (*c* 1.6) (Found: C, 53.5; H, 8.3; N, 2.6. $C_{23}H_{41}NO_{10}Si$ requires C, 53.2; H, 8.0; N, 2.7%); ν_{max} (neat)/cm^{-1} 3447, 3029, 2958, 1747, 1715, 1503, 1390, 1368, 1228; δ_H ($CDCl_3$) 6.10 (1H, d, *J* 3.4 Hz, H-1), 5.04 (1H, dd, *J* 8.9, 10.0 Hz, H-4), 4.33 (1H, d, *J* 9.6 Hz, NH), 4.25–4.10 (1H, m), 4.10–3.95 (2H, m), 3.90–3.70 (2H, m), 2.18 (s), 2.10 (s) (9H), 1.44 (9H, s), 0.85 (9H, s), 0.10, 0.05 (6H, 2s); δ_C ($CDCl_3$) 170.9, 169.4, 169.1 (CH_3CO), 154.7 (Me_3COCO), 91.9 (C-1), 80.1 (Me_3COCO), 71.2 (C-3 or C-5 interchangeable attribution), 70.9 (C-5 or C-3), 70.2 (C-4), 62.2 (C-6), 54.1 (C-2), 28.3 (Me_3COCO), 25.0 (Me_3CSiMe_2), 21.3, 21.2 and 20.8 (CH_3CO), 18.0 (Me_3CSiMe_2), −4.8 (Me_3CSiMe_2); *m*/*z* (CI) 537 $[M + NH_4]^+$, 436.

2-Acetamido-4-*O*-acetyl-1-*O*-benzyl-2-*N*,3-*O*-carbonyl-2-deoxy-5,6-*O*-isopropylidene-L-mannitol 24

A solution of diol **8** (300 mg, 0.73 mmol) in THF (3 ml) containing 60% NaH (59 mg, 1.46 mmol) was stirred at 60 °C for 4 h. The reaction mixture was quenched with water (20 ml) and concentrated. The residue was dissolved in EtOAc (300 ml), washed successively with water (2 × 50 ml) and brine (50 ml), dried over Na_2SO_4, and the solvent was evaporated. To a solution of the residue in CH_2Cl_2 (2 ml) were added triethylamine (0.46 ml, 3.3 mmol), Ac_2O (0.29 ml, 3 mmol) and DMAP (50 mg) successively. The mixture was stirred at room temperature for 1 h. Methanol (1 ml) was added, and stirring was continued for 30 min. The solvent was evaporated, and the residue was dissolved in EtOAc (150 ml). The organic extracts were washed successively with water (30 ml), 1 M HCl (30 ml), saturated aq. $NaHCO_3$ (50 ml) and brine (50 ml), dried over Na_2SO_4 and evaporated. After removal of the solvent, the residue was purified by column chromatography, eluting with heptane–EtOAc 1:2, to afford **24** (110 mg, 73%); $[\alpha]_D^{20}$ +57.0 (*c* 2.3) (Found: C, 59.4; H, 6.5; N, 3.1. $C_{21}H_{27}NO_8$ requires C, 59.8; H, 6.5; N, 3.3%); ν_{max} (neat)/cm^{-1} 2982, 2937, 2884, 1790, 1749, 1705, 1496, 1480, 1455, 1374, 1294; δ_H ($CDCl_3$) 7.35–7.25 (5H, m), 5.50 (1H, t, *J* 7.0 Hz), 4.69 (1H, t, *J* 7.0 Hz), 4.59 (1H, ddd, *J* 2.0, 4.8, 7.0 Hz), 4.55, 4.40 (2H, 2d, *J* 12.0 Hz), 4.10–3.98 (2H, m), 3.85 (1H, dd, *J* 2.0, 10.4 Hz), 3.75–3.65 (2H, m), 2.47 (3H, s), 2.07 (3H, s), 1.28, 1.20 (6H, 2s); δ_C ($CDCl_3$) 170.0, 169.4, 152.9, 137.2, 128.5, 128.1, 128.0, 110.1, 76.0, 74.9, 73.6, 69.7, 67.3, 65.3, 56.1, 26.0, 25.3, 23.6, 20.8 *m*/*z* (CI) 422 $[M + H]^+$.

2-Acetamido-4-*O*-acetyl-1-*O*-benzyl-2-*N*,3-*O*-carbonyl-2-deoxy-5,6-*O*-isopropylidene-L-iditol 25

Starting from **9** (80 mg, 0.24 mmol), exactly the same procedure as described for the preparation of compound **24** gave **25** (80 mg, 80%); $[\alpha]_D^{20}$ +17.3 (*c* 2.3) (Found: C, 59.7; H, 6.7; N, 3.1%); ν_{max} (neat)/cm^{-1} 2988, 2937, 2866, 1790, 1749, 1706, 1497, 1455, 1375, 1292, 1217; δ_H ($CDCl_3$) 7.35–7.20 (5H, m), 5.06 (1H, t, *J* 4.7 Hz), 4.66 (1H, dd, *J* 3.1, 4.7 Hz), 4.52 (2H, s), 4.55–4.45 (1H, m), 4.35 (1H, ddd, *J* 1.5, 6.2, 10.9 Hz), 4.05 (1H, dd, *J* 8.7, 9.6 Hz), 3.79 (1H, dd, *J* 5.9, 8.7 Hz), 3.69 (1H, dd, *J* 5.0, 9.8 Hz), 3.57 (1H, dd, *J* 2.9, 9.8 Hz), 2.47 (3H, s), 2.04 (3H, s), 1.39, 1.29 (6H, 2s); δ_C 170.1, 169.8, 153.1, 137.4, 128.6, 128.1, 127.8, 110.3, 74.3, 73.4, 73.1, 67.7, 65.4, 55.4, 26.1, 25.3, 23.6, 20.6; *m*/*z* (CI) 422 $[M + H]^+$.

2-Acetamido-4-*O*-acetyl-1-*O*-benzyl-2-*N*,3-*O*-carbonyl-2-deoxy-5,6-*O*-isopropylidene-L-glucitol 26

Starting from **17** (300 mg, 0.73 mmol), exactly the same procedure as described for the preparation of compound **24** gave **26**. After removal of the solvent, the residue was purified by column chromatography, eluting with CH_2Cl_2–acetone 4:1, to afford **26** (180 mg, 60%); $[\alpha]_D^{20}$ −6.1 (*c* 2.0) (Found: MH^+, 422.1773. $C_{21}H_{28}NO_8$ requires *m*/*z*, 422.1815); ν_{max} (neat)/cm^{-1} 3065, 2988, 2938, 2884, 1789, 1750, 1705, 1497, 1480, 1455, 1372, 1294, 1225; δ_H ($CDCl_3$) 7.30–7.20 (5H, m), 5.03 (1H, dd, *J* 2.5, 7.9 Hz), 4.80 (1H, t, *J* 2.5 Hz), 4.55, 4.50 (2H, 2d, *J* 12.0 Hz), 4.38–4.22 (2H, m), 4.04 (1H, dd, *J* 6.1, 8.7 Hz), 3.79 (1H, dd, *J* 5.5, 8.7 Hz), 3.70 (1H, dd, *J* 4.9, 9.8 Hz), 3.62 (1H, dd, *J* 3.0, 9.8 Hz), 2.48 (3H, s), 2.03 (3H, s), 1.39, 1.35 (6H, 2s); δ_C ($CDCl_3$) 170.1, 169.9, 153.3, 137.4, 128.6, 128.1, 127.7, 110.1, 75.1, 73.4, 73.3, 73.2, 67.6, 66.7, 55.5, 26.6, 25.3, 23.6, 20.5; *m*/*z* (ESI) 444 $[M + Na]^+$, 422 $[M + H]^+$.

2-Acetamido-4-*O*-acetyl-1-*O*-benzyl-2-*N*,3-*O*-carbonyl-2-deoxy-5,6-*O*-isopropylidene-L-gulitol 27

Starting from diol **18** (80 mg, 0.20 mmol), exactly the same procedure as described for the preparation of compound **26** gave **27** (49 mg, 60%); $[\alpha]_D^{20}$ −63.6 (*c* 3.2) (Found: MH^+, 422.1780); ν_{max} (neat)/cm^{-1} 3056, 2988, 2937, 2884, 1790, 1749, 1705, 1497, 1480, 1455, 1373, 1294, 1226; δ_H ($CDCl_3$) 7.40–7.30 (5H, m), 5.57 (1H, dd, *J* 2.2, 9.3 Hz), 4.79 (1H, dd, *J* 6.7, 9.3 Hz), 4.70–4.62 (1H, m), 4.52, 4.47 (2H, 2d, *J* 8.1 Hz), 4.21 (1H, m), 3.80–3.60 (4H, m), 2.47 (3H, s), 2.14 (3H, s), 1.41, 1.26 (6H, 2s); δ_C ($CDCl_3$) 170.3, 169.9, 152.8, 136.9, 128.7, 128.3, 110.3, 75.7, 73.7, 73.5, 68.9, 65.4, 65.1, 55.5, 26.0, 25.2, 23.7, 21.0; *m*/*z* (ESI) 444 $[M + Na]^+$, 422 $[M + H]^+$.

1-*O*-Benzyl-2-[(*tert*-butoxycarbonyl)amino]-3-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-5,6-*O*-isopropylidene-L-*lyxo*-hex-4-ulose 28

To a solution of **10** (900 mg, 1.71 mmol) in CH_3CN (15 ml) were added successively NMO (382 mg, 2.57 mmol), TPAP (50 mg, 10% mol) and molecular sieves (1.5 g). After 2 h, the solvent was evaporated, 100 ml of heptane–EtOAc 1:1 was added, and the mixture was filtered through silica gel. After evaporation of solvents, the residue was purified by column chromatography, eluting with heptane–EtOAc 5:1, to afford **28** (835 mg, 93%); $[\alpha]_D^{20}$ +10.9 (*c* 2.3) (Found: C, 62.2; H, 9.2; N, 2.5. $C_{27}H_{45}NO_7Si$ requires C, 61.9; H, 8.7; N, 2.7%); ν_{max} (neat)/cm^{-1} 3454, 2980, 2954, 2932, 2897, 2832, 1716, 1498, 1368, 1254; δ_H ($CDCl_3$) 7.38–7.32 (5H, m), 4.87 (1H, d, *J* 9.3 Hz), 4.83 (1H, t, *J* 7.0 Hz), 4.49–4.44 (1H, m), 4.42 (2H, s), 4.19–4.11 (2H, m), 4.05–3.99 (1H, m), 3.60–3.50 (1H, m), 1.44 (9H, s), 1.41, 1.37 (6H, 2s), 0.93 (9H, s), 0.10, 0.07 (6H, 2s); δ_C 206.8, 155.2, 137.4, 128.5, 127.9, 110.8, 79.8, 76.8, 76.5, 73.2, 67.9, 66.2, 52.6, 28.4, 25.9, 25.6, 18.3, −4.7, −5.1; *m*/*z* (CI) 524 $[M + H]^+$, 468, 438, 424.

1-*O*-Benzyl-2-[(*tert*-butoxycarbonyl)amino]-3-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-5,6-*O*-isopropylidene-L-talitol 29

L-Selectride® (1.9 ml, 1.9 mmol) was added dropwise to a solution of **28** (490 mg, 0.94 mmol) in THF at −78 °C. After 30 min, the reaction mixture was allowed to warm to 0 °C, then water (2 ml), H_2O_2 (30%; 5.7 mmol), and $NaHCO_3$ (5.7 mmol) were added successively and stirring was continued for 30 min at 50 °C. The mixture was dissolved in water (100 ml) and extracted with EtOAc (3 × 70 ml). The organic extracts were washed successively with water (2 × 50 ml) and brine (50 ml), dried over Na_2SO_4 and evaporated. After removal of the solvent, the residue was purified by column chromatography, eluting with heptane–EtOAc 3:1, to afford two alcohols **29** (365 mg) and **10** (65 mg) in 88% total yield, in the ratio 85:15. Compound **29**: $[\alpha]_D^{20}$ +6.5 (*c* 2.8) (Found: C, 61.2; H, 8.8; N, 2.6. $C_{27}H_{47}NO_7Si$ requires C, 61.7; H, 9.0; N, 2.7%); ν_{max} (neat)/cm^{-1} 3450br, 2981, 2954, 2931, 2858, 1716, 1473, 1497, 1455, 1369, 1254; δ_H ($CDCl_3$) 7.38–7.22 (5H, m), 4.86 (1H, d, *J* 7.3 Hz), 4.51 (2H, s), 4.30 (1H, dt, *J* 2, 7.6 Hz), 4.20–4.10 (1H, m), 4.03 (1H, t, *J* 7.0 Hz), 3.93 (1H, dd, *J* 3.7, 7.2 Hz), 3.85 (1H, t, *J* 7.8 Hz), 3.70–3.55 (2H, m), 3.48–3.38 (1H, m), 2.67 (1H, br d, *J* 8.6 Hz), 1.44 (9H, s), 1.42, 1.37 (6H, 2s), 0.9 (9H, s), 0.1 (6H, s); δ_C ($CDCl_3$) 155.7, 138.0, 128.5, 127.9, 109.0, 79.5, 74.4, 73.8, 73.0, 71.2, 68.5, 66.4, 52.1, 28.5, 26.5, 26.1, 25.5, 18.3, −4.3, −4.5; *m*/*z* (ESI) 548 $[M + Na]^+$, 526 $[M + H]^+$, 426.

4-*O*-Acetyl-1-*O*-benzyl-2-[(*tert*-butoxycarbonyl)amino]-3-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-5,6-*O*-isopropylidene-L-talitol 30

Starting from **29** (430 mg, 0.82 mmol), exactly the same procedure as described for the preparation of compound **11** furnished **30** (455 mg, 98%) after 30 min of stirring; $[\alpha]_D^{20}$ −1.3 (*c* 2.1) (Found: C, 61.1; H, 8.6; N, 2.4. $C_{29}H_{49}NO_8Si$ requires C, 61.3; H, 8.7; N, 2.5%); ν_{max} (neat)/cm^{-1} 3451, 3354, 2932, 2895, 2859, 1747, 1718, 1499, 1368, 1230; δ_H ($CDCl_3$) 7.39–7.22 (5H, m), 4.98 (1H, t, *J* 5.0 Hz), 4.89 (1H, d, *J* 10.3 Hz), 4.47 (2H, s), 4.34 (1H, dt, *J* 5.1, 8.4 Hz), 4.10–4.00 (2H, m), 3.97–3.84 (1H, m), 3.78 (1H, t, *J* 9.9 Hz), 3.60 (2H, d, *J* 5.8 Hz), 2.10 (3H, s), 1.45 (9H, s), 1.38, 1.34 (6H, 2s), 0.87 (9H, s), 0.12, 0.07 (6H, 2s); δ_C ($CDCl_3$) 170.6, 155.6, 138.1, 128.5, 127.9, 127.8, 109.4, 79.5, 74.1, 73.0, 72.6, 68.0, 66.0, 52.0, 28.5, 26.2, 26.0, 25.8, 21.2, 18.3, −4.4, −4.8; *m*/*z* (CI) 568 $[M + H]^+$, 468.

4-*O*-Acetyl-2-[(*tert*-butoxycarbonyl)amino]-3-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-5,6-*O*-isopropylidene-L-talitol 31

Starting from **30** (444 mg, 0.78 mmol), exactly the same procedure as described for the preparation of compound **12** furnished **31** (348 mg, 93%); $[\alpha]_D^{20}$ −13.8 (*c* 2.5) (Found: C, 55.2; H, 8.9; N, 2.8. $C_{22}H_{43}NO_8Si$ requires C, 55.3; H, 9.1; N, 2.9%); ν_{max} (neat)/cm^{-1} 3452br, 2957, 2933, 2889, 2859, 1744, 1713, 1504, 1473, 1369, 1252; δ_H ($CDCl_3$) 5.17 (1H, d, *J* 7.5 Hz), 5.10–5.07 (1H, m), 4.35–4.31 (1H, m), 4.16–4.05 (4H, m), 3.77–3.64 (3H, m), 2.14 (3H, s), 1.46 (9H, s), 1.40, 1.33 (6H, 2s), 0.90 (9H, s), 1.14 (6H, s); δ_C ($CDCl_3$) 170.6, 155.2, 109.8, 79.7, 74.3, 73.9, 73.5, 66.0, 63.2, 52.4, 28.5, 26.1, 25.9, 25.6, 21.1, 18.1, −4.8; *m*/*z* (ESI) 500 $[M + Na]^+$, 478 $[M + H]^+$, 378.

4-*O*-Acetyl-2-[(*tert*-butoxycarbonyl)amino]-3-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-5,6-*O*-isopropylidene-L-talose 32

Starting from **31** (200 mg, 0.42 mmol), exactly the same procedure as described for the preparation of compound **13** gave **32** (160 mg, 80%); $[\alpha]_D^{20}$ −74.3 (*c* 2.8) (Found: C, 55.6; H, 8.6; N, 2.8. $C_{22}H_{41}NO_8Si$ requires C, 55.6; H, 8.7; N, 3.0%); ν_{max} (neat)/cm^{-1} 3434, 2981, 2954, 2932, 2889, 2859, 1746, 1715, 1498, 1474, 1370, 1227; δ_H ($CDCl_3$) 9.74 (1H, s), 5.46 (1H, br d, *J* 8.8 Hz), 5.12 (1H, dd, *J* 3.1, 9.4 Hz), 4.72 (1H, dd, *J* 3.1, 8.6 Hz), 4.46–4.37 (2H, m), 4.10 (1H, dd, *J* 8.7, 10.4 Hz), 3.71 (1H, dd, *J* 7.5, 10.4 Hz), 2.09 (3H, s), 1.45 (9H, s), 1.43, 1.35 (6H, 2s), 0.85 (9H, s), 0.11, 0.10 (6H, 2s); δ_C ($CDCl_3$) 197.9, 170.6, 110.0, 79.9, 73.6, 72.6, 72.3, 66.1, 63.1, 28.4, 26.1, 25.7, 25.4, 21.0, −4.9; *m*/*z* (CI) 476 $[M + H]^+$, 376, 318.

1,4,6-Tri-*O*-acetyl-2-[(*tert*-butoxycarbonyl)amino]-3-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-L-talopyranose 33

A solution of **32** (95 mg, 0.2 mmol) in methanol (3 ml) was treated with conc. HCl (2.5 μl) and the mixture was stirred for 48 h at room temperature. After addition of triethylamine (0.1 ml), the solvent was evaporated. To a solution of the residue in CH_2Cl_2 (2 ml) were added successively triethylamine (0.93 ml, 6.6 mmol), Ac_2O (0.58 ml, 6 mmol) and DMAP (100 mg). The mixture was stirred at room temperature for 3 h. Methanol (3 ml) was added, and stirring was continued for 30 min. The solvent was evaporated, and the residue was dissolved in EtOAc (50 ml), and the solution was washed successively with water (15 ml), 1 M HCl (15 ml), saturated aq. $NaHCO_3$ (20 ml) and brine (20 ml), dried over Na_2SO_4 and evaporated. After removal of the solvent, the residue was purified by column chromatography, eluting with heptane–EtOAc 3:1, to afford **33** (70 mg, 65%): 47 mg of α-anomer **33a** and 23 mg of β-anomer **33b**.

α-Anomer 33a. $[\alpha]_D^{20}$ −29.1 (*c* 1.6) (Found: C, 53.5; H, 8.1; N, 2.8. $C_{23}H_{41}NO_{10}Si$ requires C, 53.2; H, 8.0; N, 2.7%); ν_{max} (neat)/cm^{-1} 3447, 3032, 2957, 1749, 1715, 1503, 1392, 1368, 1233; δ_H ($CDCl_3$) 6.10 (1H, br s), 5.40 (1H, br d, *J* 9.1 Hz), 5.27 (1H, d, *J* 3.1 Hz), 4.25–4.40 (4H, m), 3.90–3.80 (1H, m), 2.15, 2.12, 2.05 (9H, 3s), 1.43 (9H, s), 0.86 (9H, s), 0.10 (6H, s); δ_C ($CDCl_3$) 170.7, 169.0, 168.4, 155.6, 93.7, 79.7, 69.5, 68.6, 63.9, 62.1, 51.8, 28.5, 25.6, 21.0, 20.8, 18.0, −5.0, −5.1; *m*/*z* (CI) 537 $[M + NH_4]^+$, 436.

β-Anomer 33b. $[\alpha]_D^{20}$ +8.2 (*c* 0.9) (Found: C, 53.4, H, 8.2, N, 2.9%); ν_{max} (neat)/cm^{-1} 3448, 3031, 2958, 1747, 1715, 1504, 1396, 1369, 1231; δ_H ($CDCl_3$) 5.69 (1H, d, *J* 1.8 Hz), 5.33 (1H, br d, *J* 9.9 Hz), 5.22–5.18 (1H, m), 4.22–4.08 (3H, m), 4.00–3.90 (2H, m), 2.14, 2.11, 2.06 (9H, 3s), 1.44 (9H, s), 0.86 (9H, s), 0.10, 0.09 (6H, 2s); δ_C ($CDCl_3$) 170.7, 169.2, 169.0, 156.1, 92.7, 79.4, 72.5, 68.9, 67.3, 65.8, 62.2, 52.3, 28.4, 25.6, 21.0, 20.8, 20.7, 18.0, −4.9, −5.0; *m*/*z* (CI) 537 $[M + NH_4]^+$, 436.

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