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Synthesis of Both Possible Isomers of the Northwest Quadrant of Altromycin B

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The synthesis of the northwest quadrant of Altromycin B is described. The preparation of the two epimers at the quaternary carbon of the 6-deoxy-*C*-altrose moiety in the northwest quadrant is accomplished starting from D-glucose. A key step of our synthetic sequence is the formation of the *C*-glycoside linkage via the Ramberg−Bäcklund reaction. Two different routes are explored, which differ mainly on the timing of the conversion of glucose to altrose, either before or after the preparation of the *C*-glycoside. The conformation behavior of variously substituted *C*-altropyranoside rings is also discussed.

Introduction

Altromycin B (**1**) is an antitumor antibiotic produced by an actinomycete (strain AB1246E-26) isolated from a South African bushveld soil.[1] Along with Altromycin B eight other minor species (Altromycin A, C, D, E, F, G, H, I) have been isolated from the fermentation broth (Figure 1).[2] Altromycins are members of the family of pluramycin antibiotics. The aglycone chromophore is common for all Altromycins A−I. Altromycins A−D and G differ from one another in the sugar regions of the molecule. Altromycins E and F are 13-deoxy. Altromycins H and I lack the *C*-altrose moiety in the northwest quadrant. Altromycin B showed activity against several kinds of cancer. It has been demonstrated that Altromycin B forms a complex with DNA by covalently binding to the N-7 of guanine via nucleophilic attack of the guanine's nitrogen to the epoxide.[3] A biosynthetic pathway for Altromycin formation has been proposed.[4]

The structures of these molecules have been assigned on the basis of their spectroscopic data, mainly by NMR. No X-ray crystal structure is available. The stereochemistry at carbon 13 as well as of the epoxide moiety has not been assigned. Moreover, it has not been determined whether the carbohydrate moieties are present in the D or L configuration.

Along with a commonly observed aryl-*C*-glycoside linkage in the southeast, Altromycin B incorporates a rare *C*-glycoside in its northwest quadrant. The α-6-deoxy-altrose moiety is linked to the aglycone via a quaternary carbon, and it assumes a flipped chair conformation.

There has been extensive work on the synthesis of *C*-aryl glycosides of the "southeast" type,[5] but in contrast, there is to our knowledge only one report of an "aglycone" synthesis (no carbohydrates) in the pluramycin family[6] and no description of a synthesis of the novel "northwest" *C*-glycoside.

Our goal was to achieve a synthetic route to the northwest quadrant of Altromycin B (Figure 2). An important purpose of our work was to produce materials of known structure and stereochemistry so as to assign, for the first time, the relative configuration at C-13 of the antibiotic by comparison of its spectroscopic data to our synthetic models. The assignment of the absolute configuration at C-13 would not be possible by these means, since our data would be compatible with either a D or L sugar.

Our synthetic plan had two elements: (i) the critical *C*-glycoside bond-forming step would involve the Ramberg−Bäcklund reaction,[7,8,9] and (ii) the carbohydrate stereochemistry would be founded upon the well-known conversion of glucose to altrose.[10] The optimal timing of the conversion, either before or after the *C*-glycoside functionality and stereochemistry were established, was not obvious to us; therefore both sequences outlined in Scheme 1 were undertaken.

Results and Discussion

We first describe our approach from altrose (Scheme 2), which started with the preparation of the partially

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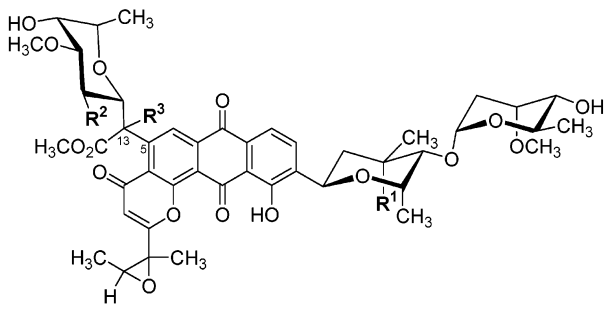

Altromycin	R^1	R^2	R^3
A	$NHCH_3$	OH	OH
B	$N(CH_3)_2$	OH	OH
C	$NHCH_3$	H	OH
D	$N(CH_3)_2$	H	OH
E	$NHCH_3$	OH	H
F	$N(CH_3)_2$	OH	H
G	NH_2	OH	OH
H	$NHCH_3$	5-OH	
I	$N(CH_3)_2$	5-OH	

FIGURE 1. Structures of Altromycins.

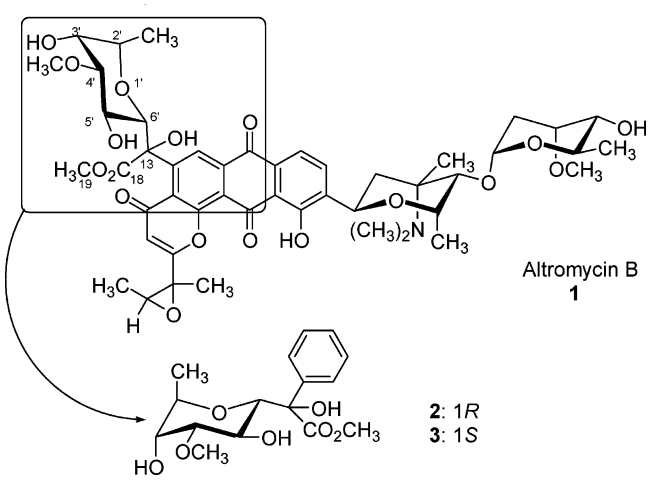

FIGURE 2. The northwest quadrant of Altromycin B.

protected glucose **5** by treatment of α-D-glucose with allyl alcohol at reflux in the presence of an acidic resin as catalyst.[11] We obtained a 3/2 mixture of α- and *β*-allyl glucosides **4**, which were protected as benzylidene derivatives to afford the allyl 4,6-*O*-benzylidene-D-glucopyranoside **5** in 60% yield over two steps.

By treating **5** with *N*-tosylimidazole and 2 equiv of NaH, a mixture of products was obtained.[12] The three main products were isolated by column chromatography. The structure of α-**6** and *β*-**6** was assigned after the basic opening of the epoxide with sodium methoxide and acetylation of the hydroxyl group. The ratio obtained was α-**6**:*β*-**6**:**7** = 2:1:1. The products α-**6** and *β*-**6** could be isolated as a mixture in 48% yield by crystallization from methanol and could be used as a mixture for the next step. Alternatively, the three products could be separated by column chromatography. The presence of the benzylidene protecting group was important in order to ensure a rigid conformation of the pyranose ring and to minimize the possibility of nucleophilic attack of the methoxide at C-2.

The basic opening of the epoxides α- and *β*-**6** by sodium methoxide in DMSO at 95 °C proceeded via nucleophilic axial attack of methoxide, producing the diaxial opening of the epoxide in 80% yield.

The stereochemistry at the anomeric center of α- and *β*-**9** was assigned by measuring the $^{13}C-^{1}H$ coupling constants, whose values were consistent with data reported in the literature for similar models ($^1J_{CH(1)} = \sim 170$ Hz for α-**9** and ∼162 Hz for *β*-**9**).[13] After protection of the hydroxyl group at position 2 with silyl ether (**10**, 90% yield), the allyl ether was cleaved by palladium-catalyzed tributyltin hydride reduction (**11**, 83%).[14]

The trichloroacetimidate **12** was prepared in 60% yield[15] and then employed in the synthesis of the thioaltroside **14**. Treatment of **12** with $BF_3{\cdot}OEt_2$ and benzyl mercaptan produced the thioglycoside **13** in 95% yield with the cleavage of the benzylidene, which could be reinstalled in quantitative yield. The cleavage of the benzylidene could be avoided by running the reaction at low temperature. The two-step procedure (cleavage in the glycosylation step, followed by reinstallation of the benzylidene protecting group) was preferred because it allowed an easier separation of **13** from the excess benzyl mercaptan. In contrast, the similar R_f of benzyl mercaptan and **14** deriving from the temperature-controlled glycosylation made the purification inefficient, and consequently it was difficult to obtain a pure sample of **14** (in addition, the contamination with even small amounts of benzyl mercaptan was very annoying, as a result of the strong stench of this material).

The oxidation of the sulfide **14** to sulfone **15** (95%) set the stage for the key C−C bond-forming step. Thus, the

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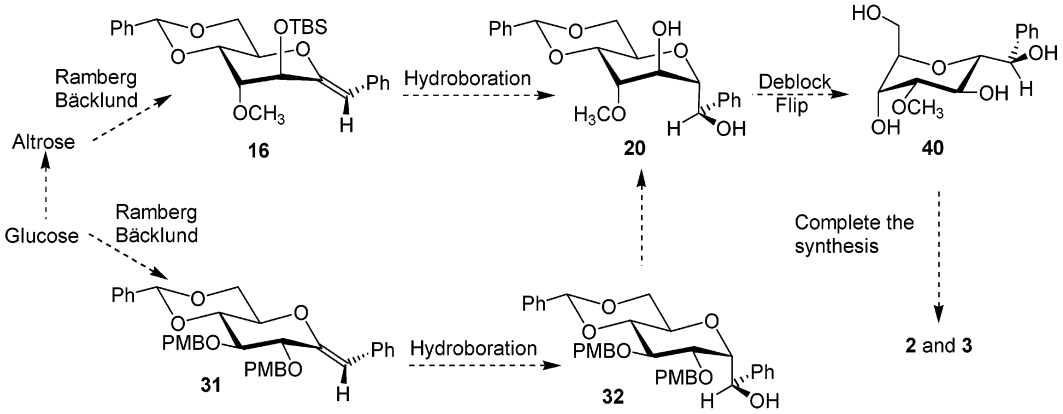
SCHEME 1. Two Routes to the Northwest Quadrant of Altromycin Differing in the Timing of the Glucose-Altrose Transformation



Ramberg−Bäcklund reaction of the sulfone **15** (Scheme 3) using Chan's conditions,[16,9] afforded the *exo*-glycal **16** in 70% yield. We obtained the *Z* isomer only, identified by NOE (6%) between the vinylic proton H-1 and H-3.

The hydroboration/oxidation sequence[17] applied to the *exo*-glycal **16** afforded the *C*-glycosides **17** and **18** in 70% yield and $\alpha/\beta = \sim 1/10$ (Scheme 3). We hoped to achieve higher selectivity toward the α product by delivery of the borane from the axial hydroxyl group on C-3. The silyl ether of **16** was therefore cleaved and the hydroboration reaction on **19** was performed, unfortunately with no improvement in the α/β ratio.[18]

The α configuration of the minor product **20** was confirmed by NOE (3%) between H-1 and H-6. The two anomers **20** and **21** were separated by column chromatography.

We tried to improve the α-selectivity by means of other possible approaches. With the hope that a more flexible ring could yield a more favorable ratio, the hydroboration was conducted on **22**, resulting however in the *β*-isomer **23** as the only product.

The hydride delivery by free hydroxyl groups complexing an aluminum hydride to obtain a stereoselective opening of epoxides has been described.[19] So treatment of *exo*-glycal **19** with dimethyldioxirane[20] afforded the epoxide **24**,[21] which was successively treated with Red-Al with the hope that the axial hydroxyl group could coordinate aluminum hydride and deliver a hydride from the *β*-face of the anomeric carbon. Unfortunately this reduction afforded the acyclic sugar derivative **25**. This can be rationalized by hydride delivery to C-1, the distal epoxide carbon, which cleaves the epoxide to form a hemiketal. Opening of the hemiketal and reduction of the resulting ketone then affords the observed product.

Intramolecular delivery of hydride[22] from a silyl ether (**26**) was not practical because the silane was oxidized by DMDO during the epoxide synthesis step.

Because of the low yield obtained for the required α-*C*-glycoside from the altrose *exo*-glycal (**16** or **19**), we opted for our alternate synthetic approach. Our exploratory hydroborations of *exo*-glucal derivatives afforded reasonable ratio of α/β products, in contrast to those described above with *exo*-altral. Therefore, we decided to postpone the double inversion route to the altrose configuration until we first obtained an α-*C*-glucoside (Scheme 4).

Thus glucose pentaacetate was treated with excess benzyl mercaptan in the presence of 1 equiv of $BF_3 \cdot OEt_2$.[23] Deprotection of the acetates followed by installation of a benzylidene to protect positions 4 and 6 afforded **28** in a 96% overall yield for the three steps.

After protection of the hydroxyls at positions 2 and 3 as *p*-methoxybenzyl ethers (85%), the thioglucoside **29** was then oxidized to sulfone **30** (95% yield) and employed in the Ramberg−Bäcklund reaction to obtain the *exo*-glucal **31** in 70% yield. We obtained the *Z* isomer only, as was determined by a NOESY analysis, which revealed a NOE between the olefinic H-1 centered at 5.60 ppm and the axial H-3 at 3.99 ppm.

The hydroboration of the glucal **31** afforded a 3/1 mixture of the α- and *β*-*C*-glucosides **32** and **33** in 71% combined yield. The two products were separated by flash column chromatography on silica gel. The stereochemistry at the anomeric center of the two products can be easily identified from the coupling constants between the anomeric H-2 and the axial H-3: $J_{2,3} = 4.9$ Hz for **32**, $J_{2,3} = 9.2$ Hz for **33**. We also observed two cross-peaks in the NOESY spectrum of **32** which reveal an effect between H-1 (centered at 5.11 ppm) and both H-4 (at 4.07 ppm) and H-6 (multiplet with H-5 at 3.74−3.70 ppm). At this stage the stereochemistry at C-1 was assigned by assuming a *syn* addition of borane to the double bond and an oxidation with retention of configuration of the organoborane intermediate. This assumption of stereochemistry was confirmed later on in the synthesis.

The large coupling constant (8.5 Hz) between H-1 and the anomeric H-2 of **32** indicates an *anti* relationship with a ca. 180° dihedral angle between the two protons, suggesting the favored conformation around the C-1−C-2

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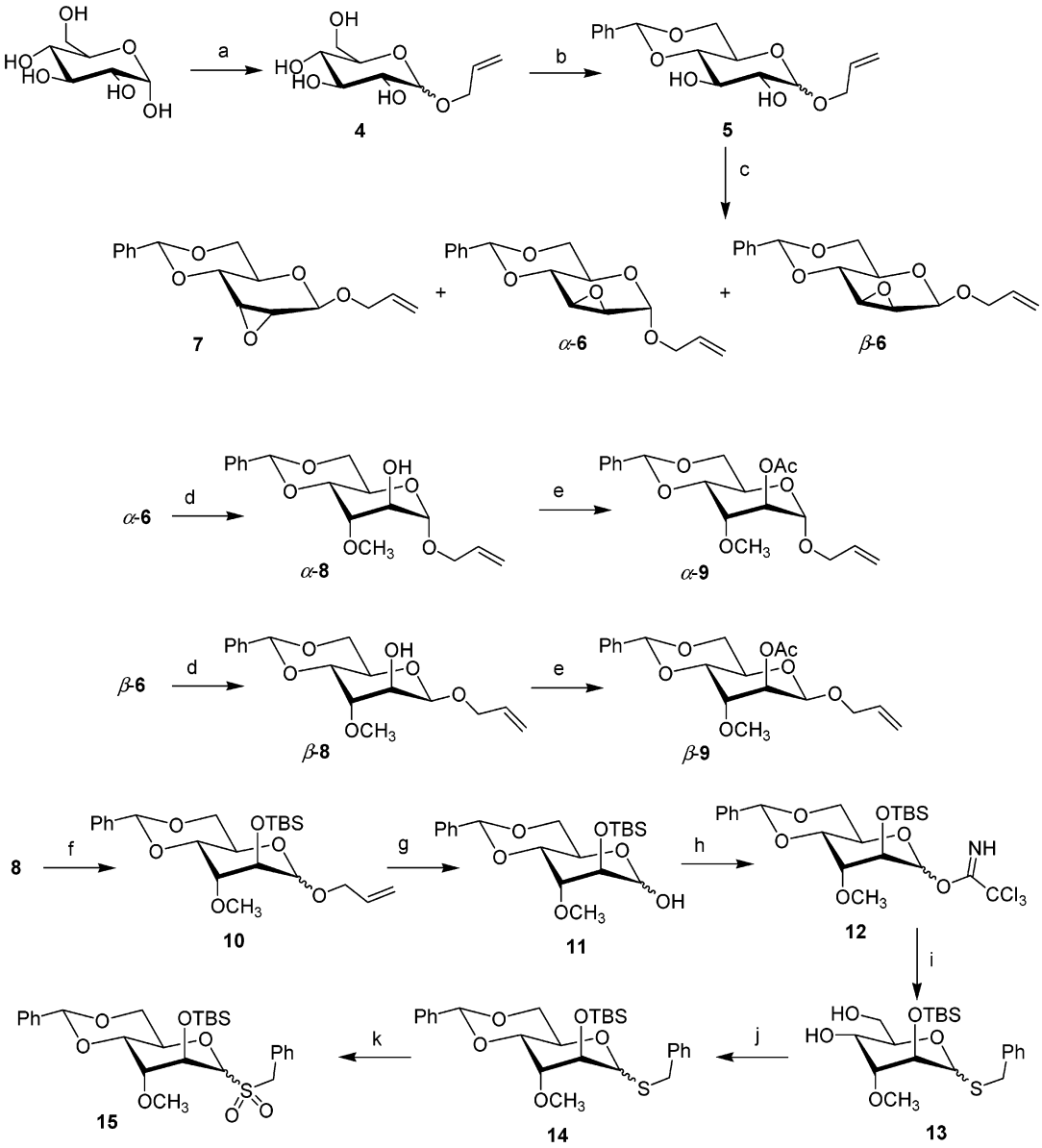
SCHEME 2[a]



[a] Reagents and conditions: (a) allyl alcohol, acidic resin, 70 °C; (b) dimethoxytoluene, TsOH, CH_3CN, 60% for 2 steps; (c) *N*-tosylimidazole, NaH, DMF, **6**: 48%, **7**: 16%; (d) NaOMe, DMSO/MeOH, 95 °C, 80%; (e) Ac_2O, DMAP, EtOAc; (f) TBDMSCl, imidazole, DMF, 90%; (g) $ZnCl_2$, $Pd(PPh_3)_4$, Bu_3SnH, THF, 83%; (h) Cl_3CCN, NaH, CH_2Cl_2, 60%; (i) BnSH, $BF_3{\cdot}OEt_2$, CH_2Cl_2, −78 °C to rt, 95%; (j) dimethoxytoluene, TsOH, CH_3CN; (k) MMPP, THF/EtOH/H_2O, 60 °C, 95%.

bond described in Scheme 4, structure **32**. The alternative *syn* relationship between H-1 and H-2, consistent with the value of the coupling constant, is not favored by steric considerations since it would involve an eclipsed conformation. Also the value observed for the coupling constant $J_{1,2} = 9.2$ Hz in **33** suggests the conformational arrangement depicted in Scheme 4.[24]

The ^{1}H NMR spectrum (25 °C, $CDCl_3$) of **32** shows a well-defined triplet at 4.07 ppm for H-4 in which the coupling constant $J = 7.6$ Hz appears a little too small for a diaxial interaction (normally ∼9 Hz) among H-3, H-4, and H-5, suggesting a distortion of the chair conformation due to steric congestion of the axial anomeric group.

The hydroxyl group of **32** was protected as its SEM ether (**34**, 95%),[25] and the PMB ethers were cleaved with DDQ (**35**, 82%).[26] The coupling constants $J_{2,3} = J_{3,4} = 3.1$ Hz, measured for the triplet corresponding to H-3 in **34** suggest a distortion of the chair to a boat conformation larger than that in **32**, due to the presence of the more sterically demanding SEM ether. The release of steric congestion in **35** after the deprotection of the PMB ethers results in a less distorted chair conformation as confirmed by the coupling constants $J_{3,4} = J_{4,5} = J_{5,6} = 9.2$ Hz, typical of an axial relationship among H-3, H-4, and H-5.

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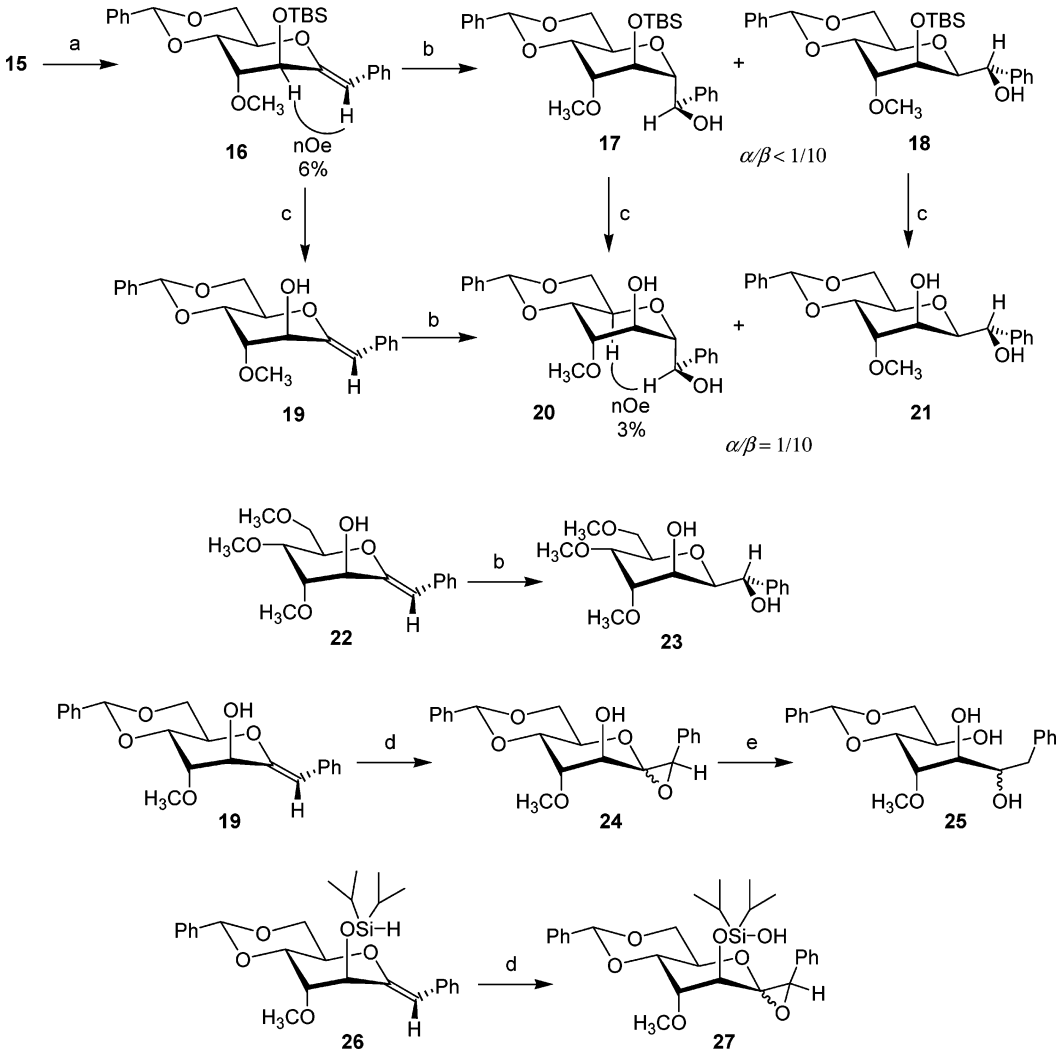
SCHEME 3[a]



[a] Reagents and conditions: (a) CBr_2F_2, KOH on Al_2O_3, CH_2Cl_2/*t*-BuOH, 70%; (b) BH_3, THF, then H_2O_2, KOH, H_2O, 70%; (c) *n*-Bu_4NF, THF; (d) DMDO, CH_2Cl_2; (e) Red-Al, THF.

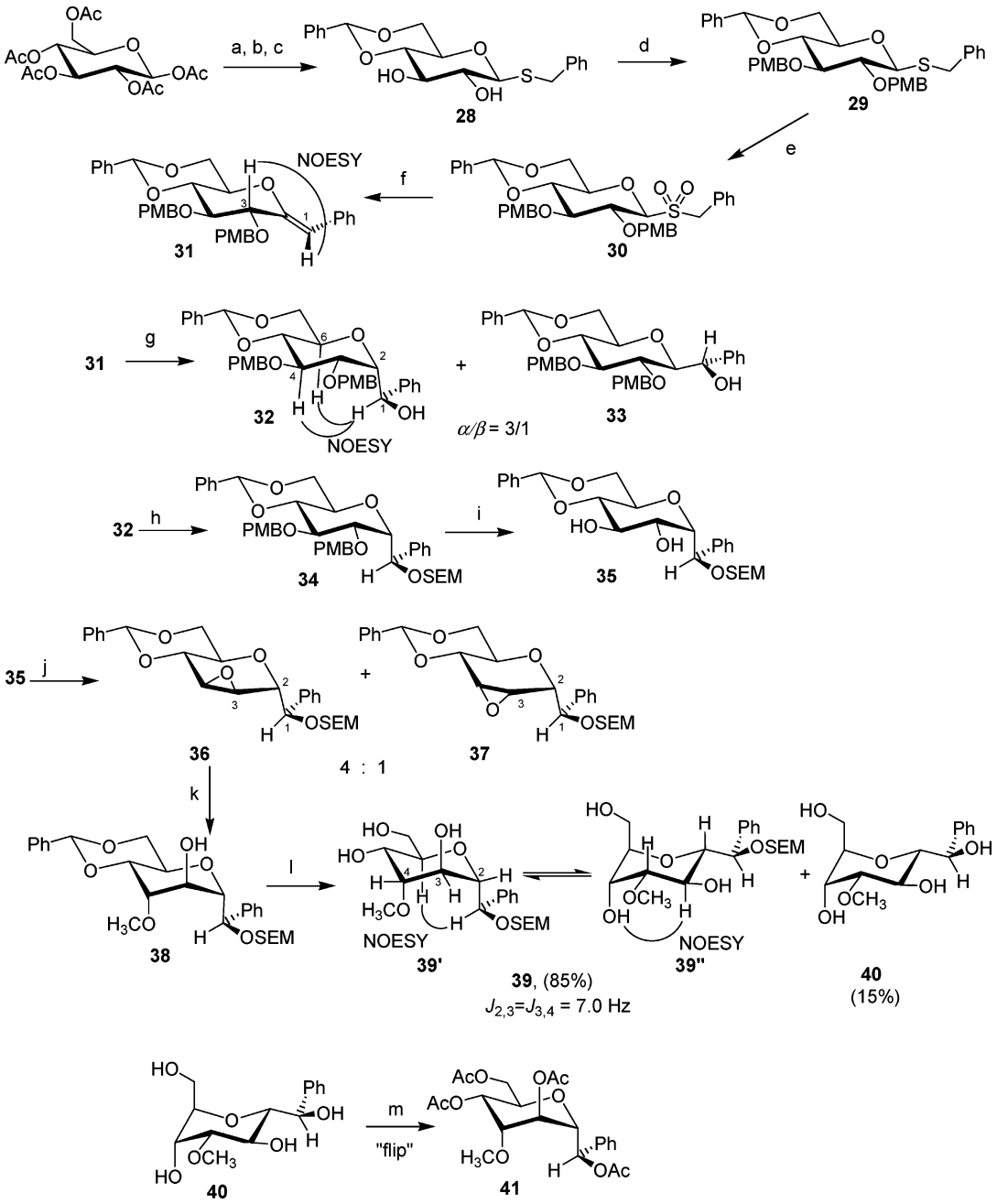
The *C*-glucoside **35** was converted to epoxide in 95% yield.[12] Two products, 2,3-anhydro-*C*-mannoside derivative **36** and 2,3-anhydro-*C*-alloside **37**, were obtained in 4/1 ratio and were separated by column chromatography. The anomeric proton H-2 of the major product **36** is a doublet centered at 4.22 ppm with a coupling constant $J_{2,3} = 0$ Hz, consistent with a dihedral angle close to 90° (see projection a, Figure 3), whereas in the epoxide **37** the anomeric proton H-2 is a doublet of doublets centered at 4.11 ppm with a coupling constant $J_{2,3} = 3.1$ Hz. Such a coupling constant is probably due to a staggered relationship between H-2 and H-3 arising from a pseudo-boat conformation of the sugar ring (projection b, Figure 3). The alternative possibility for **37** is a pseudo-chair conformation, which can be ruled out since a larger coupling constant would be expected from the eclipsed relationship between H-2 and H-3 (projection c, Figure 3).

The configuration of the epoxide **36** was confirmed by basic opening with sodium methoxide (ca. 2 M in methanol) at 120 °C (sealed tube), which gave the altrose derivative **38** in quantitative yield, resulting from the diaxial opening of the epoxide with the installation of the correct functionalities for Altromycin at positions 3 and 4. Lower temperatures resulted in a sluggish reaction.

Deprotection of the SEM ether in **38** with tetrabutylammonium fluoride yielded a product with NMR data identical to that of **20**, confirming the α-stereochemistry assigned previously.

After the cleavage of the benzylidene protecting group (85% yield) the NMR spectrum of **39** showed a coupling constant $J_{2,3} = J_{3,4} = 7.0$ Hz, which is not consistent with either one of the two possible chair conformations. The NOESY spectrum of **39** shows two diagnostic cross-peaks, one revealing an effect (2% NOE) between H-1 and H-6, consistent with the conformation **39′**, and a second one revealing an effect (2% NOE) between H-3 and OH-5, which indicates the presence of the chair conformation **39″**. These NOESY signals would not be compatible with boat or skew conformations, even if the presence of such conformations could not be ruled out from a possible dynamic equilibrium. Furthermore, low-temperature ^1H and ^{13}C NMR spectra show a clear broadening and shifting of signals. These observations indicate the presence of an equilibrium between the two forms **39′** and

SCHEME 4[a]



[a] Reagents and conditions: (a) BnSH, BF_3·OEt_2, CH_2Cl_2; (b) NaOMe, MeOH; (c) dimethoxytoluene, TsOH, CH_3CN, 96% for 3 steps; (d) PMBCl, NaH, THF/DMF, 85%; (e) MMPP, THF/EtOH/H_2O, 60 °C, 95%; (f) CBr_2F_2, KOH on Al_2O_3, CH_2Cl_2/*t*-BuOH, 70%; (g) BH_3, THF, 0 °C to rt, then H_2O_2, H_2O, KOH, 71%; (h) SEMCl, (*i*-Pr)$_2$NEt, CH_2Cl_2, 95%; (i) DDQ, CH_2Cl_2/H_2O, 82%; (j) *N*-tosylimidazole, NaH, DMF, 95%; (k) $NaOCH_3$, CH_3OH, 120 °C, quantitative; (l) TsOH, CH_3OH; (m) Ac_2O, EtOAc, DMAP.

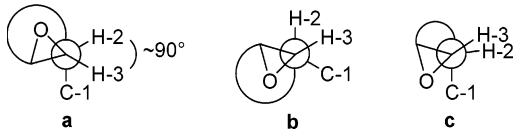
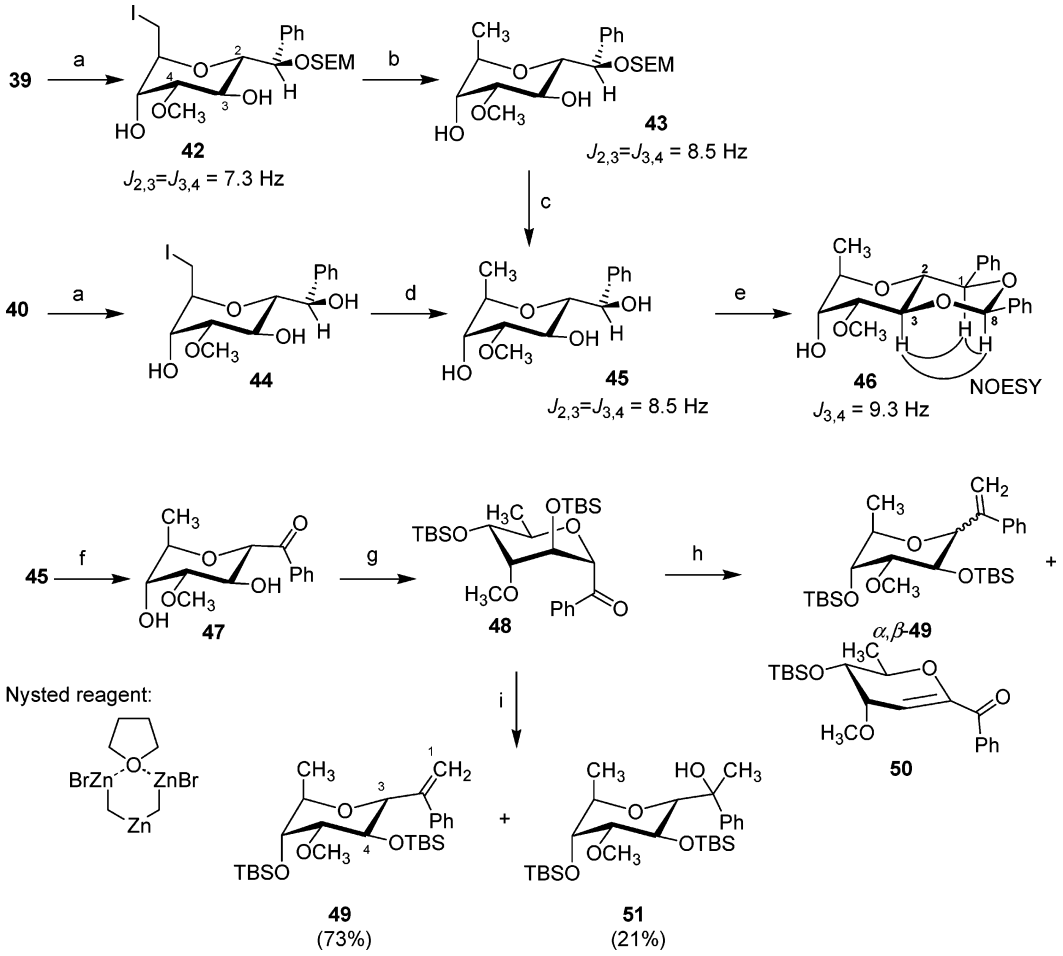


FIGURE 3. Projection along the C-3−C-2 bond of **36** assuming a chair conformation of the sugar ring (a) and **37** in a boat conformation (b) and in a chair conformation (c).

39′′. Unfortunately, the coalescence temperature and a separation of the signals corresponding to each conformer could not be reached and therefore it was not possible to calculate an equilibrium constant from the integration of the signals at low temperature. An approximate equilibrium constant for this equilibrium, $K = 2 \pm 1$, could be extrapolated by comparing the experimental coupling constant with the expected coupling constants of the two chair-conformers (assuming that the populations of other conformers be negligible and the two chairs not distorted).

A side product of the acidic cleavage of the benzylidene of **38** arose from the deprotection of the SEM ether (**40**, 15%). Such side reaction could be limited but not avoided by carefully monitoring the reaction by TLC. In any

SCHEME 5[a]



[a] Reagents and conditions: (a) I_2, PPh_3, imidazole, THF, reflux, 85%; (b) AIBN, Bu_3SnH, PhMe, reflux, 87%; (c) TFA, CH_2Cl_2, quantitative; (d) Bu_3SnH, AIBN, PhMe, reflux, 75%; (e) dimethoxytoluene, cat. TsOH, CH_3CN; (f) DDQ, CH_2Cl_2, 77%; (g) TBDMSCl, imidazole, DMF, 93%; (h) $Ph_3P{=}CH_2$, THF, −10 °C to rt; (i) Nysted reagent, $TiCl_4$, THF/CH_2Cl_2.

event, product **40** could be employed in the successive steps. Longer reaction times afforded only product **40** in quantitative yield.

Interestingly, the acetylation of the *C*-glycoside **40**, which assumes a $^1C_4$-type preferred conformation[27] (as evident from the coupling constants $J_{2,3} = J_{3,4} = 7.6$ Hz and $J_{4,5} = J_{5,6} = 3.2$ Hz), resulted in the flipping of the ring in **41** to a $^4C_1$-type conformation ($J_{2,3}$, $J_{3,4}$, $J_{4,5} = 2.4-3.6$ Hz and $J_{5,6} = 9.2$ Hz). Deprotection of the acetates with catalytic sodium methoxide in **41** afforded **40** without any trace of epimerization at C-1.

The selective iodination of the primary hydroxyl group of **39** (Scheme 5) was achieved in 85% yield.[28] This product probably also consists of an equilibrium between the two chair conformations, as suggested by the coupling constant $J_{2,3} = J_{3,4} = 7.3$ Hz. Furthermore, for **42** broadening and shifting of the ^1H NMR signals were observed at low temperatures.

The radical deiodination of **42** afforded the 6-deoxy derivative **43** (87% yield),[29] whose coupling constants $J_{2,3} = J_{3,4} = 8.5$ Hz suggest a flipped $^1C_4$-type conformation.

The product **45** was obtained by acidic deprotection of the SEM ether in quantitative yield[30] or as an alternative via selective iodination of the primary hydroxyl group in **40** (**44**, 85% yield), followed by radical deiodination (**45**, 75%). Although this last route was shorter by one step (the deprotection of both benzylidene and SEM was achieved in a single step from **38**) and consequently preferred when we scaled up the reaction, the two-step deprotection was preferred in order to obtain an analytically pure sample, since the purification of **44** from the triphenylphosphine oxide byproduct proved to be unsuccessful by conventional column chromatography. Our effort to use polymer-supported triphenylphosphine in the transformation from **40** to **44** was not successful.

At this stage it was possible to confirm the stereochemistry at C-1 obtained in the hydroboration step from **31** to **32** by making the benzylidene derivative **46**. The NOESY spectrum indeed reveals an axial relationship among H-1, H-3 and H-8.

(27) The notation we adopted to describe the conformation of pyranose rings ($^1C_4$ or $^4C_1$) refers to the numbering commonly employed for *O*-glycosides, where the anomeric carbon is C-1.

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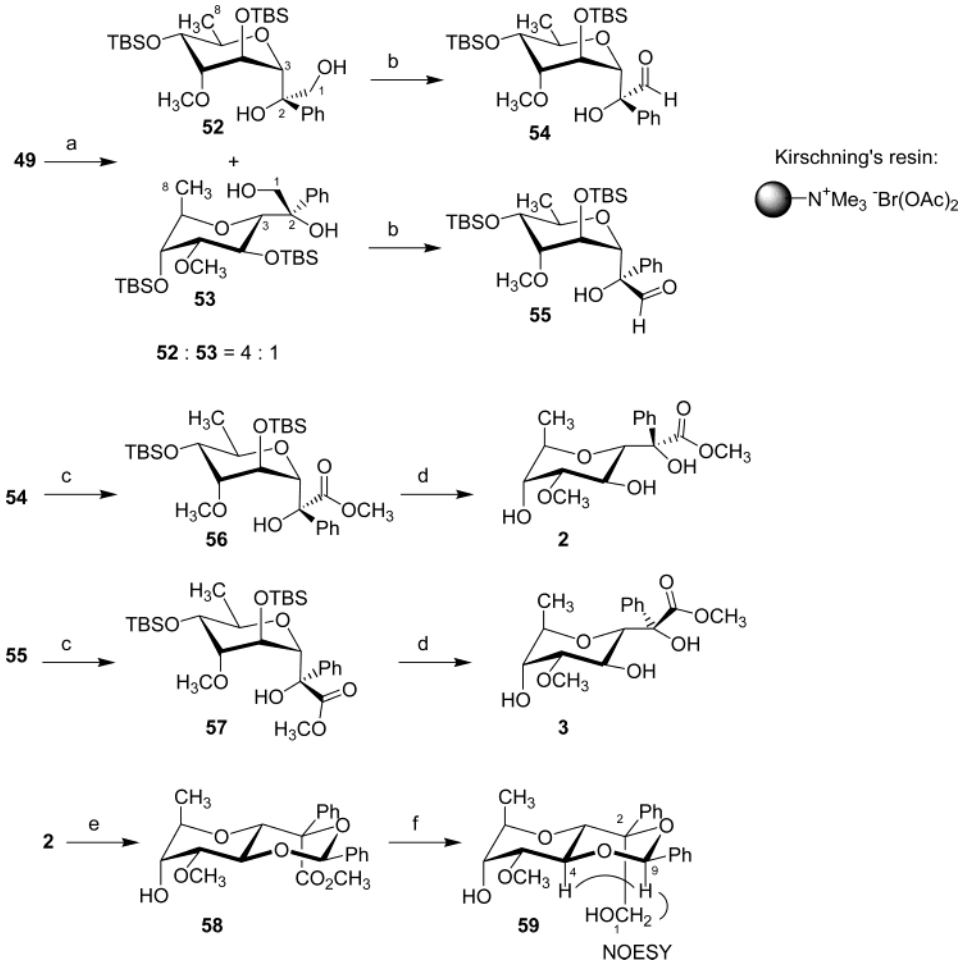
(30) Jansson, G.; Frejd, T.; Kihlberg, J.; Magnusson G. *Tetrahedron Lett.* **1988**, *29*, 361.

SCHEME 6[a]



[a] Reagents and conditions: (a) OsO_4, MMNO, acetone/H_2O/*t*-BuOH, 82%; (b) Kirschning's resin, CH_2Cl_2, cat. TEMPO, quantitative; (c) I_2, NaOH, MeOH, >95%; (d) TBAF, AcOH, THF, >93%; (e) dimethoxytoluene, cat. TsOH, CH_3CN; (f) DIBAL-H, CH_2Cl_2.

Several oxidizing reagents were explored for the oxidation of the benzylic alcohol **45** to ketone (notably, MnO_2,[31] 4-(dimethylamino)pyridinium chlorochromate,[32] $BaMnO_4$/$CuSO_4$/Al_2O_3,[33] NBS), but all proved to be either not reactive or to afford a sluggish reaction. DDQ was the only oxidant that gave satisfactory results (77% yield).

The free hydroxyl groups in positions 3 and 5 of **47** were then protected as silyl ethers in 93% yield. The values of the coupling constants $J_{2,3} = 2.5$ Hz and $J_{5,6} = 7.9$ Hz for the product **48** suggest a preferred $^4C_1$-type conformation. Efforts to install the methylene via Wittig procedures were unsuccessful as a result of epimerization at the anomeric center (α- and *β*-**49**) and competitive elimination to form the glycal **50**.

We consequently opted to employ the Nysted reagent,[34] which gave a satisfactory yield (α-**49**, 73%), with concurrent formation of the byproduct **51** (21%), derived by addition of water to the double bond catalyzed by the acidic conditions employed in the reaction. This side product can be minimized by running the reaction under rigorously anhydrous conditions and by optimizing the reaction time. It is interesting to notice the opposite preferred conformations assumed by the pyranose ring in **48** ($^4C_1$-type, $J_{2,3} = 3.0$ Hz, $J_{5,6} = 7.9$ Hz) and α-**49** ($^1C_4$-type, $J_{3,4} = J_{4,5} = 7.0$ Hz and $J_{5,6} = 3.0$ Hz).

The dihydroxylation of α-**49** with osmium tetroxide[35] gave a separable mixture of the two epimers at C-2 **52** and **53** in 4/1 ratio and 82% combined yield (Scheme 6). Interestingly the difference in a single stereocenter between the two *C*-glycosides **52** and **53** results in completely different conformational behaviors: the $^4C_1$-type is the preferred conformation for major isomer **52** ($J_{3,4} = 0$ Hz, $J_{4,5} = J_{5,6} = 3.2$ Hz and $J_{6,7} = 9.2$ Hz) and $^1C_4$-type is preferred for **53** ($J_{3,4} = J_{4,5} = 9.2$ Hz, $J_{5,6} = J_{6,7} = 2.4$ Hz). The configuration at the quaternary centers was assigned later in the synthesis.

The oxidation of vicinal diols is reported to proceed with low yields, as a result of competitive cleavage of the C−C bond to form a ketone (**48** in our case). This fragmentation of the molecule is particularly accentuated when metal-containing oxidizers are employed. Methods involving IBX,[36] alkali hypochlorites,[37] and more recently

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(34) (a) Watson, A. T.; Park, K.; Wiemer, D. F. *J. Org. Chem.* **1995**, *60*, 5102. (b) Nysted, L. N. U.S. Patent 3,865,848, 1975; *Chem. Abstr.* **1976**, *85*, 94618n. (c) Franck, R. W.; Marzabadi, C. H. *J. Org. Chem.* **1998**, *63*, 2197. (d) Matsubara, S.; Sugihara, M.; Utimoto, K. *Synlett* **1998**, 313.
(35) Schröder, M. *Chem. Rev.* **1980**, *80*, 187.

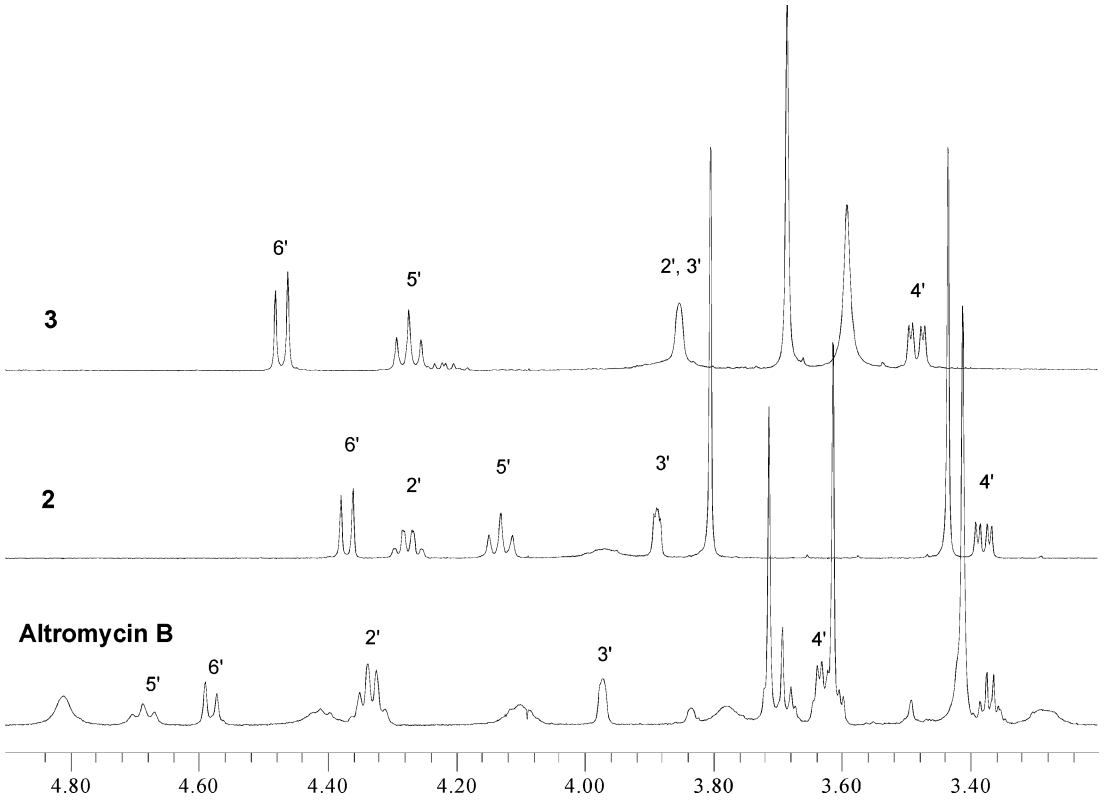

FIGURE 4. Comparison of ^{1}H NMR spectra ($CDCl_3$, 500 MHz) of Altromycin B (**1**) with those of **2** and **3**.

chlorite/hypochlorite catalyzed by TEMPO have been proposed,[38] but when we tested them they did not give very satisfactory results in terms of yields. Therefore we were particularly glad when we observed that the oxidation of **52** and **53** employing the polymer-supported bromite(I) complex recently described by Kirschning[39] gave quantitative yields. The aldehydes **54** and **55** could be isolated without further purification and directly employed in the next step. Both products **54** and **55** assume a $^4C_1$-type conformation.

The oxidation to esters of **54** and **55** was achieved in one step and in ca. 95% yield by alkaline iodine oxidation[40] employing an inverse addition (alkaline solution added to the mixture of iodine and starting material). The TBDMS ethers were then cleaved by action of fluoride in the presence of acetic acid to avoid the hydrolysis of the esters (**2** and **3)**.

The stereochemistry at the quaternary center C-2 (corresponding to C-13 of Altromycin B) was assigned by synthesizing the benzylidene derivative **58** from **2**, followed by reduction of the ester to alcohol with DIBAL-H (**59**). The NOESY spectrum clearly shows two cross-peaks, which evidence an effect between the benzylidene H-9 and, respectively, one proton of the methylene C-1 and H-4.

Comparison of NMR Data of the Synthetic Models with Altromycin B. Both proton and carbon spectral data of the two models **2** and **3** were compared with the data we recorded for the northwest quadrant of Altromycin B in order to assign the stereochemistry at the quaternary C-13.[41] As expected little information about the configuration at that center was obtained from the ^{1}H NMR spectra (Figure 4) since the differences of proton chemical shifts of both synthetic isomers show no trend compared to the corresponding protons in Altromycin B. A way to quantify the discrepancy is to calculate the average of the absolute values of the differences between the chemical shift corresponding to each proton of the two models and Altromycin B. By means of this method we obtain an average difference in chemical shift $\Delta =$ 1.72 for **2** and $\Delta = 1.78$ for **3**.

TABLE 1. Comparison of ^{13}C NMR Shift Values between Altromycin B and the Two Models 2 and 3

	Altromycin B	**2**	**3**
C-13	81.16	79.96	78.56
C-18	170.8	173.68	173.27
C-19	52.85	53.40	53.16
C-2′	74.02	73.48	73.43
C-3′	69.15	69.16	69.85
C-4′	80.43	80.84	81.61
C-5′	68.18	67.39	67.09
C-6′	73.88	77.05	75.59
CH_3-2′	14.29	15.14	14.54
OCH_3-4′	58.14	58.12	58.10

Unfortunately the comparison of ^{13}C chemical shifts was not helpful either. Table 1 lists the values of chemical shifts for relevant carbons of Altromycin B and the two

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(41) In this section the numbering we refer to is the one adopted for Altromycin B (Figure 1).

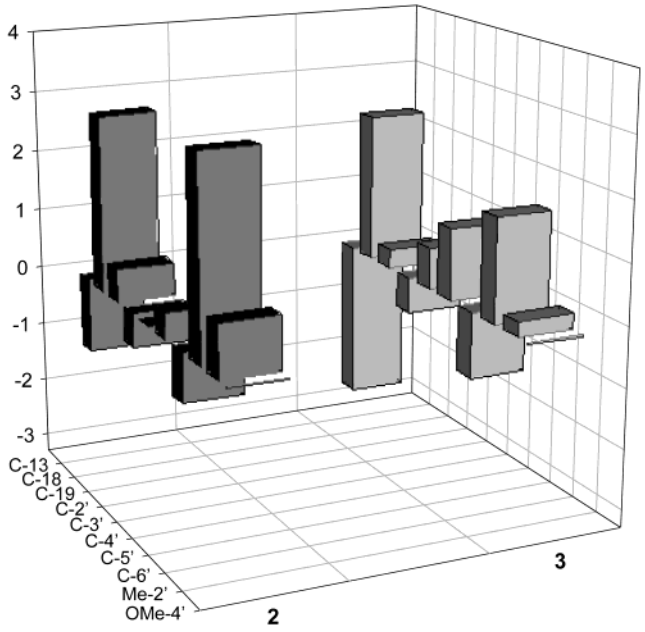


FIGURE 5. Graphical representation of the differences in ^{13}C NMR shift values between Altromycin B and the two models **2** and **3**.

models. Figure 5 exemplifies the trend of the differences in chemical shifts between Altromycin B and each one of the two models.[42] The average of the absolute values of the differences in chemical shifts between Altromycin B and **2** ($\Delta = 0.104$) and **3** ($\Delta = 0.119$) are too close and do not allow us to assign the stereochemistry at C-13.

We also prepared the benzylidene derivatives **60** and **61** of the two model compounds and the analogue **62** of Altromycin B (Scheme 7), with the hope that circular dichroism could give us some information about the stereochemistry at C-13, based on a possible Cotton effect associated with the optically active electronic transitions derived from the asymmetry induced by the presence of two chromophores in an asymmetric environment.[43] Anticipating the bathochromic effect on the UV spectrum, *para*-subsituted bromo benzylidene was chosen, also with the expectation that the presence of a heavy atom could be helpful in the resolution of eventual crystal structure of the Altromycin B derivative.

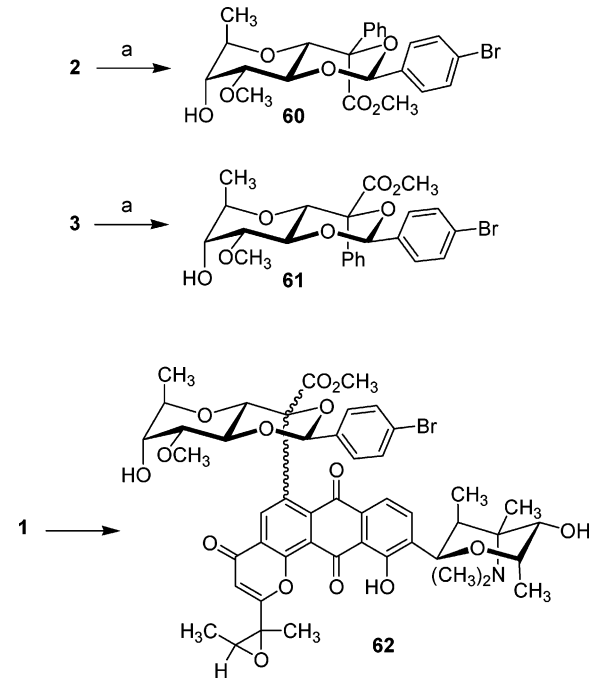
Unfortunately the circular dichroism gave ambiguous results, probably because of the presence of two different chromophores, without allowing us to assign the configuration of the C-13. Furthermore, a complete and unambiguous assignment of the structure of the derivative **62** based on ^{1}H and ^{13}C NMR spectra was not possible because of the complexity of the system, but the mass spectrum was in full agreement with the proposed structure. Under the acidic conditions used for benzylidene formation the 2,6-dideoxy altrose moiety in the southeast quadrant was cleaved.

All of our efforts to crystallize **62** as well as Altromycin B itself were unsuccessful.

(42) (a) Kobayashi, Y.; Lee, J.; Tezuka, K.; Kishi, Y. *Org. Lett.* **1999**, *1*, 2177. (b) Lee, J.; Kobayashi, Y.; Tezuka, K.; Kishi, Y. *Org. Lett.* **1999**, *1*, 2181.

(43) Harada, N.; Nakanishi, K. *Circular Dichroic Spectroscopy—Exciton Coupling in Organic Stereochemistry*; University Science Books: Mill Valley, CA, 1983.

SCHEME 7[a]



[a] Reagents and conditions: (a) 4-bromobenzaldehyde dimethyl acetal, TsOH, CH_3CN.

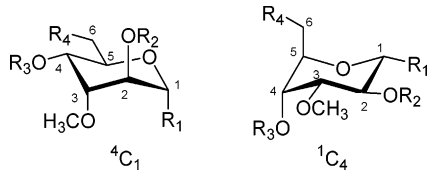


FIGURE 6. Chair conformations of *C*-altrosides.

Ring Conformation of *C*-Altrosides. Throughout the synthesis of the northwest quadrant of Altromycin B we found it interesting to analyze the conformational features of the pyranose rings (Figure 6), which we tried to explain as due mostly to steric effects. We observed that even minimal differences in the structure brought about contrasting conformational behaviors, as is evident from the two different conformations assumed by the two epimers at C-1, **52** and **53**. The conformational properties of each molecule were determined mostly by the values of the coupling constants and in some cases with the support of NOESY spectra. In Table 2 the diagnostic coupling constants of relevant compounds are reported. Each molecule is listed in the preferred conformation assumed on the basis of the values of the coupling constants. In the cases in which equilibrium between the two chair conformations could be assumed the conformation represented is the one that could be supposed to have larger population by analysis of the coupling constants.

Conclusions

The Ramberg−Bäcklund reaction proved to be a valuable synthetic tool for the preparation of *C*-glycosides via *exo*-glycal intermediates, its main advantages being the simple reaction conditions, easy accessibility of the thioglycoside starting materials, and the inexpensive

TABLE 2. Coupling Constant Values and Preferred Conformation in Variably Substituted *C*-Altrosides

compound	preferred conformation	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$
20	$^4C_1$	0	3.1	2.4	9.8
38	$^4C_1$			4.0	9.8
41	$^4C_1$	2.4	4.0	3.4	9.2
39	$^1C_4$	7.0	7.0		
42	$^1C_4$	7.3	7.3	~0	4.3
43	$^1C_4$	8.5	8.5	~3.1	1.8
45	$^1C_4$	8.5	8.5	3.1	1.8
46	$^1C_4$		9.3	3.1	
47	$^1C_4$	6.7	7.3	3.7	
48	$^4C_1$	2.5	4.9	2.4	7.9
49	$^1C_4$	7.0	7.0	3.0	4.3
52	$^4C_1$	0	3.7	3.1	9.2
53	$^1C_4$	9.2	9.2	2.4	2.4
54	$^4C_1$	0	3.4	3	9.6
55	$^4C_1$	3	4	2.7	7
56	$^4C_1$	1.3	3.2	3.2	8.9
57	$^4C_1$	0	3.2	3.2	8.9
2	$^1C_4$	9.2	9.1	3.2	1.6
3	$^1C_4$	9.5	9.5	3.1	

reagents employed. Many other approaches to *C*-glycosides have been described,[44] and it is our opinion that each method presents advantages and disadvantages, making none of them superior to the others. Nevertheless we think that the attractive feature of the Ramberg−Bäcklund route to *C*-glycosides is its generality, because in principle it can be applied to the synthesis of virtually any *C*-glycoside in usually high yield.

The *exo*-glycal product of the Ramberg−Bäcklund reaction can be easily converted to *β*-*C*-glycoside by catalytic or ionic hydrogenation or further functionalized to more complexly substituted *β*-*C*-glycoside by addition reactions to the double bond. *exo*-Glycals have been used successfully by others to prepare a variety of *C*-glycosides.[45] Conversion of *exo*-glycals to α-*C*-glycosides has proven to be more problematic, since in our cases even the most stereoselective hydroboration yielded a mixture of α/*β* products that never exceeded a 3/1 ratio. A specialized approach to α-*C*-galactosides that involves an internal delivery of hydride has been achieved by our group,[9d] but the applicability of this method to sugars other than galactose has not been demonstrated.

The synthesis of the two epimers at C-13 of the northwest quadrant of Altromycin B demonstrates that the Ramberg−Bäcklund reaction can be efficiently employed in the preparation of complex natural products containing *C*-glycosides. Unfortunately the spectroscopic data of our synthetic models did not give definitive information regarding the relative stereochemistry of the quaternary C-13 of Altromycin B. Thus, the complete structure proof of Altromycin awaits either a synthesis that incorporates more structural features of the natural material than our model or a diffractable crystal, which has eluded us to date.

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Experimental Section

The assignment of proton and carbon NMR peaks was supported by routine $^1H-^1H$ COSY and HSQC spectra and for some compounds by DEPT and NOESY spectra.

Allyl-2,3-anhydro-4,6-*O*-benzylidene-α-D-mannopyranoside (α-6), Allyl-2,3-anhydro-4,6-*O*-benzylidene-*β*-D-mannopyranoside (*β*-6), and Allyl-2,3-anhydro-4,6-*O*-benzylidene-*β*-D-allopyranoside (7).[12] Sodium hydride (60% in mineral oil, 1.1 g, 27 mmol) was washed free of oil with pentane. Dry DMF (30 mL) was added, followed by the addition of allyl 4,6-*O*-benzylidene-D-glucopyranoside (4.16 g, 13.5 mmol) dissolved in dry DMF (30 mL). The mixture was stirred at room temperature for 0.5 h under N_2, then *N*-tosylimidazole (3.2 g, 14.4 mmol) was added, and the mixture was stirred for 4 h. The mixture was poured into iced water (500 mL), and the crystals were under reduced pressure. The product α-**6** containing variable amounts of *β*-**6** was purified by crystallization from methanol (1.82 g, 48%) as a white solid. Alternatively the reaction mixture was extracted with EtOAc/sat. NH_4Cl and purified by flash column chromatography (SiO_2, petroleum ether, 5% EtOAc). The products α-**6**, *β*-**6**, and **7** were isolated in the ratio 2:1:1. α-**6**: R_f 0.44 (PE/EtOAc, 8/2); ^1H NMR (500 MHz, $CDCl_3$) *δ* 7.52−7.48 (2H, m), 7.42−7.36 (3H, m), 5.94 (1H, ddt, *J* = 17.1, 10.4, 5.9 Hz, H-8), 5.57 (1H, s, H-10), 5.34 (1H, dd, *J* = 17.1, 1.4 Hz, H-9a), 5.25 (1H, dd, *J* = 10.4, 1.4 Hz, H-9b), 5.06 (1H, s, H-1), 4.30−4.23 (2H, m, H-7a and H-6eq), 4.10 (1H, dd, *J* = 12.8, 6.4 Hz, H-7b), 3.78 (1H, dt, *J* = 9.9, 4.3 Hz, H-5), 3.72 (1H, t, *J* = 10.1 Hz, H-6ax), 3.68 (1H, d, *J* = 9.2 Hz, H-4), 3.49 (1H, d, *J* = 3.7, H-2 or H-3), 3.21 (1H, d, *J* = 3.7 Hz, H-3 or H-2); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 137.22, 133.77, 129.31, 128.42, 126.28, 117.90 (C-9), 102.55 (C-10), 95.26 (C-1), 75.13 (C-5), 69.57 (C-6), 69.16 (C-7), 62.03 (C-4), 54.04 (C-2 or C-3), 50.87 (C-3 or C-2). *β*-**6**: R_f 0.30 (PE/EtOAc, 8/2); ^1H NMR (500 MHz, $CDCl_3$) *δ* 7.53−7.49 (2H, m), 7.43−7.37 (3H, m), 5.97 (1H, ddt, *J* = 17.1, 10.6, 6.4 Hz, H-8), 5.58 (1H, s, H-10), 5.36 (1H, d, *J* = 17.1 Hz, H-9a), 5.26 (1H, d, *J* = 17.1 Hz, H-9b), 5.09 (1H, s, H-1), 4.45 (1H, dd, *J* = 12.8, 4.9 Hz, H-7a), 4.29 (1H, dd, *J* = 10.5, 4.6 Hz, H-6eq), 4.20 (1H, dd, *J* = 12.8, 6.4 Hz, H-7b), 3.82 (1H, t, *J* = 10.5 Hz, H-6ax), 3.78 (1H, d, *J* = 9.5 Hz, H-4), 3.53 (1H, d, *J* = 3.7 Hz, H-2 or H-3), 3.36 (1H, dt, *J* = 9.8, 4.6 Hz, H-5), 3.29 (1H, d, *J* = 3.7 Hz, H-3 or H-2); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 137.12, 133.71, 129.38, 128.47, 126.26, 118.17 (C-9), 102.63 (C-10), 97.93 (C-1), 74.84 (C-4), 70.51 (C-7), 69.48 (C-6), 68.76 (C-5), 55.29 (C-2 or C-3), 51.16 (C-3 or C-2). **7**: R_f 0.38 (PE/EtOAc, 8/2); ^1H NMR (500 MHz, $CDCl_3$) *δ* 7.52−7.49 (2H, m), 7.40−7.35 (3H, m), 5.94 (1H, ddt, *J* = 16.5, 11.0, 5.5 Hz, H-8), 5.58 (1H, s, H-10), 5.34 (1H, dd, *J* = 17.7, 1.2, Hz, H-9a), 5.25 (1H, d, *J* = 10.4 Hz, H-9b), 5.04 (1H, s, H-1), 4.35 (1H, dd, *J* = 12.4, 5.5 Hz, H-7a), 4.27−4.24 (1H, m, H-6eq), 4.14−4.09 (2H, m, H-5, H-7b), 3.75−3.71 (2H, m, H-4, H-6ax), 3.54 (1H, d, *J* = 4.3 Hz, H-2 or H-3), 3.38 (1H, d, *J* = 4.3 Hz, H-3 or H-2); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 137.26, 133.62, 129.34, 128.45, 126.41, 118.13, 102.91, 96.40, 77.83 (C-5), 70.47 (C-7), 69.28 (C-6), 61.06 (C-4), 55.70, 51.56.

Allyl-3-*O*-methyl-4,6-*O*-benzylidene-α-D-altropyranoside (α-8) and Allyl-3-*O*-methyl-4,6-*O*-benzylidene-*β*-D-altropyranoside (*β*-8). To a 0.2 M solution of α-**6** or *β*-**6** in dry DMSO were added magnesium methoxide (ca. 2 M in methanol, 1.2 equiv) and sodium methoxide (ca. 3 M in methanol, 1.5 equiv). The mixture was stirred at 95 °C under N_2 for 4 h, then it was allowed to cool at room temperature, quenched with saturated aqueous NH_4Cl, and extracted with EtOAc. The product α-**8** (89%) or *β*-**8** (60%) was isolated by flash column chromatography (SiO_2, petroleum ether, 25% EtOAc) as pale yellow oils. α-**8**: ^1H NMR (500 MHz, $CDCl_3$) *δ* 7.52−7.48 (2H, m), 7.39−7.34 (3H, m), 5.92 (1H, ddt, *J* = 17.4, 10.6, 4.9 Hz, H-8), 5.56 (1H, s, H-10), 5.33 (1H, dd, *J* = 17.4, 1.5 Hz, H-9a), 5.22 (1H, d, *J* = 10.6 Hz, H-9b), 4.76 (1H, s, H-1), 4.36 (1H, dt, *J* = 10.1, 5.2 Hz, H-5), 4.30 (1H, dd, *J* = 10.1, 5.2 Hz, H-6eq), 4.24 (1H, dd, *J* = 13.1, 4.9 Hz, H-7a), 4.10−4.04 (2H, m, H-2 and H-7b), 4.02 (1H, dd, *J* = 9.8, 2.8

Hz, H-4), 3.78−3.72 (2H, m, H-3 and H-6ax), 3.57 (3H, s, OCH_3), 1.93 (1H, broad s, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.70, 133.95, 129.14, 128.35, 126.36, 117.78 (C-9), 102.56 (C-10), 99.53 (C-1), 78.15 (C-3), 77.44 (C-4), 69.81 (C-2), 69.52 (C-6), 68.51 (C-7), 60.09 (OCH_3), 59.00 (C-5). β-**8**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.51−7.47 (2H, m), 7.39−7.33 (3H, m), 5.92 (1H, ddt, J = 17.4,10.7, 5.8 Hz, H-8), 5.53 (1H, s, H-10), 5.31 (1H, dd, J = 17.4, 1.2 Hz, H-9a), 5.23 (1H, d, J = 10.4 Hz, H-9b), 4.85 (1H, s, H-1), 4.39 (1H, dd, J = 12.5, 5.2 Hz, H-7a), 4.33 (1H, dd, J = 10.1, 4.9 Hz, H-6eq), 4.14 (1H, dd, J = 12.5, 6.4 Hz, H-7b), 4.03 (1H, dd, J = 9.8, 2.5 Hz, H-4), 3.97 (1H, dt, J = 10.1, 4.9 Hz, H-5), 3.94 (1H, d, J = 2.7 Hz, H-2), 3.84 (1H, t, J = 2.7 Hz, H-3), 3.79 (1H, t, J = 10.1 Hz, H-6), 3.56 (3H, s, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.71, 133.70, 129.07, 128.32, 126.27, 118.04 (C-9), 102.43 (C-8), 97.37 (C-1), 77.86 (C-3 or C-4), 77.66 (C-4 or C-3), 70.61 (C-2), 70.26 (C-7), 69.37 (C-6), 63.58 (C-5), 60.19 (OCH_3).

Allyl-2-*O*-acetyl-3-*O*-methyl-4,6-*O*-benzylidene-α-D-altropyranoside (α-9) and Allyl-2-*O*-acetyl-3-*O*-methyl-4,6-*O*-benzylidene-*β*-D-altropyranoside (*β*-9). Acetic anhydride (2 equiv) was added to a 0.05 M solution of α-**8** or *β*-**8** and DMAP (0.15 equiv) in EtOAc. The mixture was stirred at room temperature under nitrogen until TLC indicated completion of the reaction. Methanol (ca. 150 equiv) was added, and stirring was continued for 10 min. Saturated aqueous NH_4Cl was added, followed by extraction with EtOAc. The organic layer was dried over sodium sulfate, and the solvent was removed under reduced pressure to afford quantitative α-**9** or *β*-**9**. α-**9**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.52−7.48 (2H, m), 7.38−7.34 (3H, m), 5.91 (1H, dddd, J = 17.1, 10.4, 6.1, 4.7 Hz, H-8), 5.58 (1H, s, H-10), 5.33 (1H, dd, J = 17.1, 1.3 Hz, H-9a), 5.22 (1H, d, J = 10.4 Hz, H-9b), 5.14 (1H, d, J = 2.1 Hz, H-2), 4.73 (1H, s, H-1), 4.38 (1H, ddd, J = 10.1, 9.8, 5.5 Hz, H-5), 4.32 (1H, dd, J = 10.1, 5.5 Hz, H-6eq), 4.24 (1H, dd, J = 13.2, 4.7 Hz, H-7a), 4.05 (1H, dd, J = 13.2, 6.1 Hz, H-7b), 3.92 (1H, dd, J = 9.8, 2.9 Hz, H-4), 3.75 (1H, t, J = 10.1 Hz, H-6ax), 3.71 (1H, broad s, H-3), 3.58 (3H, s, OCH_3), 2.14 (3H, s, OAc); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.49 (OAc), 137.62, 133.74, 129.17, 128.37, 126.37, 117.72 (C-9), 102.51 (C-10), 97.06 (C-1), 77.40 (C-4), 75.68 (C-3), 70.19 (C-2), 69.46 (C-6), 68.60 (C-7), 59.77 (OCH_3), 58.66 (C-5), 21.28 (OAc). *β*-**9**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.50−7.47 (2H, m), 7.39−7.34 (3H, m), 5.89 (1H, dddd, J = 17.1, 11.0, 6.1, 5.8 Hz, H-8), 5.53 (1H, s, H-10), 5.29 (1H, dd, J = 17.1, 1.1 Hz, H-9a), 5.22−5.18 (2H, m, H-2 and H9b), 4.95 (1H, s, H-1), 4.38−4.33 (2H, m, H-7a and H-6eq), 4.11(1H, dd, J = 12.8, 6.1 Hz, H-7b), 4.01 (1H, dt, J = 9.8, 5.2 Hz, H-5), 3.89 (1H, dd, J = 9.8, 2.4 Hz, H-4), 3.83 (1H, t, J = 10.1 Hz, H-6ax), 3.76 (1H, broad t, J = 2.8 Hz, H-3), 3.74 (3H, s, OCH_3), 2.18 (3H, s, OAc); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.94 (OAc), 137.54, 133.62, 129.18, 128.38, 126.28, 117.74 (C-9), 102.48 (C-10), 96.58 (C-1), 77.81 (C-4), 76.59 (C-3), 70.58 (C-7), 70.19 (C-2), 69.29 (C-6), 63.83 (C-5), 60.16 (OCH_3), 21.34 (OAc).

Allyl-2-*O*-*tert*-butyldimethylsilyl-3-*O*-methyl-4,6-*O*-benzylidene-α-D-altropyranoside (α-10) and Allyl-2-*O*-*tert*-butyldimethylsilyl-3-*O*-methyl-4,6-*O*-benzylidene-*β*-D-altropyranoside (*β*-10). A mixture of α-**8** (700 mg, 2.17 mmol) or *β*-**8** (1.35 g, 4.20 mmol), imidazole (2.2 equiv), and TBDMSCl (2.2 equiv) in dry DMF (6 mL/mmol of **8**) was stirred at room temperature under nitrogen overnight (16 h). Water (20 mL) was added, and the mixture was extracted with EtOAc (3 × 20 mL). The organic layer was dried over sodium sulfate, and the solvent was removed in vacuo. Column chromatography (SiO_2, petroleum ether, EtOAc 10%) afforded the product α-**10** (850 mg, 90% yield) or *β*-**10** (1.73 g, 94% yield) as pale yellow oils. α-**10**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.53−7.49 (2H, m), 7.39−7.33 (3H, m), 5.91 (1H, dddd, J = 17.1, 10.4, 6.7, 4.9 Hz, H-8), 5.57 (1H, s, H-10), 5.32 (1H, dd, J = 17.1, 1.2 Hz, H-9a), 5.21 (1H, d, J = 10.4 Hz, H-9b), 4.62 (1H, s, H-1), 4.35−4.26 (2H, m, H-5 and H-6eq), 4.22 (1H, dd, J = 13.4 Hz, 4.9 Hz, H-7a), 4.07−3.99 (3H, m, H-2, H-4 and H-7b), 3.75 (1H, t, J = 9.8 Hz, H-6ax), 3.60 (1H, t, J = 2.4 Hz, H-3), 3.57 3H, s, OCH_3), 0.92 (9H, s, TBDMS), 0.11 (3H, s, TBDMS), 0.10 (3H, s, TBDMS); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.92, 134.18, 129.12, 128.37, 126.45, 117.61 (C-9), 102.56 (C-10), 99.80 (C-1), 79.02 (C-3), 77.61, 70.78, 69.67 (C-6), 68.28 (C-7), 60.20 (OCH_3), 58.87 (C-5), 26.09, 18.38, −3.26, −4.67; ESI MS (calcd for $C_{23}H_{36}O_6Si$, 436) *m*/*z* (relative intensity) 437 ($M + H^+$, 55), 438 ($M + H^+$, 18), 454 ($M + NH_4^+$, 100), 455 ($M + NH_4^+$, 29), 890 ($2M + NH_4^+$, 70), 891 ($2M + NH_4^+$, 40). *β*-**10**: ^1H NMR ($CDCl_3$, 500 MHz) δ 7.52−7.46 (2H, m), 7.40−7.33 (3H, m), 5.91 (1H, ddt, J = 17.1, 10.5, 5.4 Hz, H-8), 5.53 (1H, s, H-10), 5.28 (1H, d, J = 17.5 Hz, H-9a), 5.18 (1H, d, J = 10.8 Hz, H-9b), 4.74 (1H, s, H-1), 4.38 (1H, dd, J = 12.7, 5.1 Hz, H-7a), 4.31 (1H, dd, J = 10.2, 5.1 Hz, H-6eq), 4.05 (1H, dd, J = 12.7, 6.0 Hz, H-7b), 4.01 (1H, dd, J = 9.5, 2.2 Hz, H-4), 3.96−3.89 (2H, m, H-2, H-5), 3.83 (1H, t, J = 10.15 Hz, H-6ax), 3.65 (1H, t, J = 2.9 Hz, H-3), 3.55 (3H, s, OCH_3), 0.92 (9H, s), 0.12 (3H, s), 0.11 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.96, 134.24, 129.11, 128.37, 126.41, 117.15 (C-10), 102.57 (C-10), 98.53 (C-1), 80.10 (C-3), 78.11 (C-4), 71.47, 70.53 (C-7), 69.68 (C-6), 64.03, 60.06 (OCH_3), 26.24, 18.69, −4.01, −4.93.

2-*O*-*tert*-Butyldimethylsilyl-3-*O*-methyl-4,6-*O*-benzylidene-α-D-altropyranose (11).[14] Anhydrous $ZnCl_2$ (3.70 g, 27.1 mmol) was added to the solution of α- and *β*-**10** (4.70 g, 10.8 mmol) in dry THF (65 mL), and the mixture was stirred at room temperature for 30 min. Tetrakis(triphenylphosphine)-palladium(0) (3.12 g, 2.70 mmol) was added, and stirring was continued for 30 min. Tributyltin hydride (12.5 g, 42.9 mmol) was added dropwise to the above solution. Upon addition of Bu_3SnH the yellow mixture turned brown. After 1.5 h of stirring, EtOAc (150 mL) was added, and the organic layer was washed with 5% HCl (3 × 30 mL) and then dried over Na_2SO_4. The solvent was removed under reduced pressure, and the product **11** (3.55 g, 83% yield) was purified by column flash chromatography (SiO_2, petroleum ether, EtOAc 20%): ^1H NMR (300 MHz, $CDCl_3$) δ 7.52−7.46 and 7.40−7.33 (m), 5.56 (s), 5.51 (s), 5.04−4.95, 4.85−4.79, 4.36−4.24, 4.10−3.97, 3.91−3.82, 3.80−3.72, 3.71−3.68 (series of m), 3.63 (s), 3.56 (s), 0.96, 0.92, 0.18, 0.17, 0.13, 0.12 (series of s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.71, 129.19, 128.40, 126.36, 126.29, 102.69, 102.58, 96.03, 92.22, 79.84, 79.14, 71.85, 70.22, 69.86, 69.53, 63.28, 60.84, 60.23, 59.27, 26.01, 25.99, 18.34, 13.92, −4.66; ESI MS (calcd for $C_{20}H_{32}O_6Si$, 396) *m*/*z* (relative intensity) 397 ($M + H^+$, 100), 398 ($M + H^+$, 28), 414 ($M + NH_4^+$, 70), 415 ($M + NH_4^+$, 19), 815 ($2M + Na^+$, 38), 816 ($2M + Na^+$, 20).

***O*-(2-*O*-*tert*-Butyldimethylsilyl-3-*O*-methyl-4,6-*O*-benzylidene-α-D-altropyranosyl)trichloroacetimidate (α-12) and *O*-(2-*O*-*tert*-Butyldimethylsilyl-3-*O*-methyl-4,6-*O*-benzylidene-*β*-D-altropyranosyl)trichloroacetimidate (*β*-12).**[15] To a solution of **11** (400 mg, 1.00 mmol) and trichloroacetonitrile (1.0 mL, 10.0 mmol) in dry CH_2Cl_2 (10 mL) was added NaH (192 mg, 7.6 mmol), and the resulting mixture was stirred at room temperature for 6 h. The mixture was slowly poured into cold water (ca. 30 mL), and the product was extracted with CH_2Cl_2 (3 × 30 mL). The organic layer was dried over Na_2SO_4, and then the solvent was removed under reduced pressure. The products α- and *β*-**12** (325 mg, 0.60 mmol, $\alpha/\beta \approx 1/4$, 60% yield) were isolated by column chromatography (SiO_2, petroleum ether, EtOAc 10%, Et_3N 0.5%). α-**12**: ^1H NMR (500 MHz, $CDCl_3$) δ 8.68 (1H, s, NH), 7.52−7.49 (2H, m), 7.39−7.34 (3H, m), 6.06 (1H, s, H-1), 5.53 (1H, s, H-8), 4.37(1H, dd, J = 10.4, 4.9 Hz, H-6eq), 4.15−4.08 (3H, m, H-2, H-4, H-5), 3.85 (1H, t, J = 9.8 Hz, H-6ax), 3.74 (1H, dd, J = 3.1, 2.4 Hz, H-3), 3.59 (3H, s, OCH_3), 0.95 (9H, s), 0.17 (3H, s), 0.15 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.37, 137.69, 129.23, 128.42, 126.41, 102.69 (C-8), 96.00 (C-1), 79.74 (C-3), 77.57, 70.34, 69.39, 64.92, 60.19 (OCH_3), 26.10, 18.40, −4.35, −4.70. *β*-**12**: ^1H NMR (500 MHz, $CDCl_3$) δ 8.51 (1H, s, NH), 7.53−7.50 (2H, m), 7.38−7.33 (3H, m), 5.94 (1H, s, H-1), 5.60 (1H, s, H-7), 4.50 (1H, dt, J = 10.4, 5.5 Hz, H-5), 4.34 (1H, dd, J = 10.4, 5.5 Hz, H-6eq), 4.24 (1H, d, J = 3.1 Hz, H-2), 4.10 (1H, dd, J = 9.8, 3.1 Hz, H-4), 3.77 (1H, t, J = 10.4 Hz, H-6ax), 3.68 (1H, t, J = 3.1 Hz, H-3), 3.52 (3H, s, OCH3), 0.95 (9H, s),

0.17 (3H, s), 0.16 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.20, 137.70, 129.10, 128.33, 126.47, 102.57, 98.36, 78.14, 76.74, 69.48, 67.97, 61.21, 58.86, 26.04, 18.33, −4.52, −4.698.

Benzyl-2-*O*-*tert*-butyldimethylsilyl-3-*O*-methyl-1-thio-α,β-D-altropyranoside (13). To a solution of **12** (280 mg, 0.52 mmol) and benzyl mercaptan (106 mg, 0.85 mmol) in dry CH_2Cl_2 (106 mg, 0.85 mmol) cooled at −78 °C was added dropwise $BF_3{\cdot}OEt_2$ (6 mg, 0.04 mmol). The mixture was stirred at −78 °C for 40 min and then at room temperature for 20 min. A saturated solution of $NaHCO_3$ (15 mL) was added, and the product was extracted with EtOAc (3 × 25 mL). The product **13** was isolated as a 2/1 ratio of anomers in 95% yield by column chromatography (SiO_2, petroleum ether, EtOAc 50%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.34−7.30 (5H, m), 4.80 (1H, s), 4.04−4.02, 3.93−3.91, 3.89−3.83, 3.80−3.75, 3.74−3.68, 3.45−3.37 (series of m), 3.47 (3H, s), 3.41 (3H, s), 0.92 (9H, s), 0.81 (9H, s), 0.16 (3H, s), 0.11 (3H, s), −0.04 (3H, s), −0.10 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 138.46, 138.33, 129.20, 129.05, 128.63, 127.18, 127.14, 83.99, 81.73, 81.54, 80.48, 77.31, 70.52, 69.77, 65.41, 65.33, 63.57, 63.28, 58.94. 58.61, 36.46, 35.94, 26.09, 25.92, 18.42, 18.25, −4.27, −4.41, −4.79, −4.88.

Benzyl-2-*O*-*tert*-butyldimethylsilyl-3-*O*-methyl-4,6-*O*-benzylidene-1-thio-α,β-D-altropyranoside (14). A solution of **13** (1.35 g, 3.26 mmol), benzaldehyde dimethyl acetal (1.48 g, 9.72 mmol), and *p*-toluenesulfonic acid (60 mg, 0.32 mmol) dissolved in acetonitrile (40 mL) was stirred at room temperature for 9 h. Acidic resin was added, and the mixture was filtered. The solvent was removed under reduced pressure to obtain the product **14** in 98% yield. The product consisted of a mixture of α- and β-anomers, but it was not possible to assign the NMR peaks corresponding to each anomer: ^{1}H NMR ($CDCl_3$, 500 MHz, major anomer) δ 7.51−7.48(2H, m), 7.38−7.33, 7.33−7.29, 7.27−7.23 (8H, series of m), 5.52 (1H, s), 4.78 (1H, s, H-1), 4.27 (1H, dd, J = 10.4, 4.9 Hz, H-6eq), 4.00 (1H, dd, J = 9.8, 2.4 Hz, H-4), 3.92−3.86 (3H, m, H-2, H-5, H-7), 3.81 (1H, t, J = 10.4 Hz, H-6ax), 3.56 (1H, t, J = 2.4 Hz, H-3), 3.48 (3H, s), 0.94 (9H, s), 0.16 (3H, s), 0.12 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz, major anomer) δ 138.19, 137.82, 129.14, 128.67, 128.41, 127.20, 126.40, 102.58, 82.35, 79.38, 77.71, 73.13, 69.52, 66.79, 59.89, 35.70, 26.23, 26.15, 18.49, −4.32, −4.42.

***O*-*tert*-Butyldimethylsilyl-3-*O*-methyl-4,6-*O*-benzylidene-1-sulfonyl-α,β-D-altropyranoside (15).** The thioglucoside **14** (150 mg, 0.30 mmol) was dissolved in THF (8 mL), ethanol (8 mL), and water (7 mL). Magnesium monoperoxyphthalate hexahydrate (MMPP, 80%, 500 mg, 0.81 mmol) was added, and the mixture was stirred for 3 h at ∼65 °C. The solvent was partially evaporated. Water was added, and the product was extracted with dichloromethane. The organic layer was washed with a saturated solution of $NaHCO_3$ and then dried over sodium sulfate. The solvent was removed under reduced pressure to obtain the sulfone **15** (145 mg, 90% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52−7.48 and 7.42−7.34 (m), 5.552 (1H, s), 5.546 (1H, s), 4.63 (d, J = 1.1 Hz), 4.58 (1H, J = 3.3 Hz), 4.50−4.47, 4.46−4.43, 4.41−4.34, 4.23−4.20, 4.17−4.15, 4.14−4.08, 4.04−3.97, 3.69−3.65 (series of m), 3.54 (3H, s), 3.51 (3H, s), 0.97 (9H, s), 0.77 (9H, s), 0.20 (3H, s), 0.07 (3H, s), −0.05 (3H, s), −0.23 (3H, s); ESI MS (calcd for $C_{27}H_{38}O_7SSi$, 534) m/z (relative intensity) 535 (M + H^+, 51), 552 (M + NH_4^+, 100), 553 (M + NH_4^+, 37).

(*Z*)-2,6-Anhydro-1-deoxy-1-phenyl-3-*O*-*tert*-butyldimethylsilyl-4-*O*-methyl-5,7-*O*-benzylidene-D-altro-hept-1-enitol (16).[9] The sulfone **15** (1.10 g, 2.06 mmol) was dissolved in dichloromethane (10 mL) and *tert*-butyl alcohol (10 mL). The mixture was cooled in an ice bath and 30% KOH on alumina (3.0 g) was added, followed by dibromodifluoromethane (ca. 5 mL, 55 mmol). The mixture was stirred at 0 °C for 1 h and at room temperature for 3 h. The mixture was filtered through Celite, the filtrate was collected and the solvent was removed under reduced pressure. The crude was purified by flash column chromatography (SiO_2, petroleum ether, EtOAc 10%, Et_3N 0.3%) to obtain **16** (1.00 g, 70% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (2H, d, J = 7.3 Hz), 7.53−7.49 (2H, m), 7.40−7.35 (3H, m), 7.30 (2H, t, J = 7.3 Hz), 7.20 (1H, t, J = 7.3 Hz), 5.78 (1H, s, H-1), 5.60 (1H, s, H-8), 4.48 (1H, dd, J = 10.1, 5.2 Hz, H-7eq), 4.33−4.30 (2H, m, H-3 and H-5), 4.24 (1H, dt, J = 10.1, 5.2 Hz, H-6), 3.93 (1H, t, J = 10.1 Hz, H-7ax), 3.73 (1H, t, J = 2.7 Hz, H-4), 3.58 (3H, s, OCH_3), 0.91 (9H, s, TBDMS), 0.15 (3H, s, TBDMS), 0.09 (3H, s, TBDMS); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.00 (C-2), 137.66, 135.08, 129.22, 128.95, 128.42, 128.30, 126.90, 126.42, 114.43 (C-1), 102.76 (C-8), 79.49 (C-4), 77.71 (C-3 or C-5), 73.37 (C-5 or C-3), 69.63 (C-7), 67.13 (C-6), 59.65 (OCH_3), 26.08, 18.42, −4.11, −4.54; ESI MS (calcd for $C_{27}H_{36}O_5Si$, 468) m/z (relative intensity) 469 (M + H^+, 100), 470 (M + H^+, 47), 954 (2M + NH_4^+, 49), 955 (2M + NH_4^+, 29).

(*Z*)-2,6-Anhydro-1-deoxy-1-phenyl-4-*O*-methyl-5,7-*O*-benzylidene-D-altro-hept-1-enitol (19). To a solution of *exo*-glycal **16** (120 mg, 0.26 mmol) dissolved in THF (6 mL) was added tetrabutylammonium fluoride (1 M in THF, 0.27 mL), and the mixture was stirred at room temperature for ca. 2 h. The solvent was removed under reduced pressure, and the product (70 mg, 76% yield) was purified by column chromatography (SiO_2, petroleum ether, EtOAc 30%) as a white solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (2H, d, J = 7.3 Hz), 7.52−7.48 (2H, m), 7.40−7.35 (3H, m), 7.30 (2H, t, J = 7.3 Hz), 7.21 (1H, d, J = 7.3 Hz), 5.76 (1H, s), 5.61 (1H, s), 4.50 (1H, dd, J = 10.4, 4.9 Hz, H-7eq), 4.37 (1H, d, J = 3.7 Hz, H-3), 4.34 (1H, dd, J = 9.8, 2.4 Hz, H-5), 4.28 (1H, dt, J = 10.0, 4.9 Hz, H-6), 3.94 (1H, t, J = 10.4 Hz, H-7ax), 3.86 (1H, t, J = 3.1 Hz, H-4), 3.58 (3H, s, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.23 (C-2), 137.81, 134.88, 129.19, 129.11, 128.39, 127.23, 126.46, 114.68 (C-1), 102.83 (C-8), 78.19 (C-4), 77.45 (C-5), 73.13 (C-3), 69.54 (C-7), 67.24 (C-6), 59.79 (OCH_3); ESI MS (calcd for $C_{21}H_{22}O_5$, 354) m/z (relative intensity) 355 (M + H^+, 100), 356 (M + H^+, 31), 377 (M + Na^+, 59), 378 (M + Na^+, 20), 731 (2M + Na^+, 19), 732 (2M + Na^+, 9).

(1*R*)-2,6-Anhydro-1-phenyl-4-*O*-methyl-5,7-*O*-benzylidene-α-D-altro-heptitol (20) and (1*S*)-2,6-Anhydro-1-phenyl-4-*O*-methyl-5,7-*O*-benzylidene-β-D-altro-heptitol (21).[17] To a solution of the *exo*-glycal **19** (400 mg, 1.13 mmol) in dry THF (12 mL) was added borane (1 M in THF, 1.3 mL) at 0 °C (ice bath) under nitrogen. The mixture was stirred at low temperature for 1 h and then at room temperature for an additional 2 h. The reaction was monitored by taking a small aliquot (ca. 0.05 mL) of the reaction mixture and checking the TLC after basic oxidative workup. The reaction mixture was cooled at 0 °C, and KOH (5% in water, 2 mL) and H_2O_2 (30%, 2 mL) were added dropwise. The mixture was stirred for 30 min at room temperature, water (12 mL) was added, and then an extraction with EtOAc (3 × 20 mL) was performed. The organic layer was dried over sodium sulfate, and the two products **20** (30 mg, 0.08 mmol, 7%) and **21** (270 mg, 0.72 mmol, 64%) were separated by column chromatography (SiO_2, petroleum ether, EtOAc 30%). Alternatively, the hydroboration was conducted on the *exo*-glycal **16** (100 mg, 0.21 mmol), which was treated with borane (1 M in THF, 0.4 mL) in THF (5 mL) under the same conditions described above. After basic oxidative workup and column chromatography (petroleum ether, EtOAc 10%) an inseparable mixture of the **17** and **18** (80 mg) was obtained. An aliquot (32 mg) of this product was treated with TBAF (1 M in THF, 0.07 mL) in THF (3 mL) for 1 h at room temperature. By comparison of the ^{1}H NMR spectrum of the reaction crude with the spectra of **20** and **21**, it was possible to calculate the ratio α/β = 1/10. **20**: R_f 0.24 (PE/EtOAc, 4/6); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51−7.48 (2H, m), 7.40−7.35 and 7.30−7.29 (8H, m), 5.54 (1H, s, H-8), 5.37 (1H, d, J = 8.5 Hz, H-1), 4.46 (1H, d, J = 3.1 Hz, H-3), 4.32 (1H, dt, J = 9.8, 5.5 Hz, H-6), 4.12 (1H, dd, J = 9.8, 5.5 Hz, H-7eq), 4.08 (1H, dd, J = 9.8, 2.4 Hz, H −5), 3.88 (1H, d, J = 8.5 Hz, H-2), 3.85 (1H, t, J = 3.1 Hz, H-4), 3.68 (3H, s, OCH_3), 3.59 (1H, t, J = 9.8 Hz, H-7ax); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.46, 137.94, 129.08, 128.64, 128.33, 128.02, 126.50, 126.36, 102.61

(C-8), 83.12 (C-2 or C-4), 78.53 (C-4 or C-2), 77.80 (C-5), 72.43 (C-1), 69.87 (C-7), 68.12 (C-3), 62.38 (C-6), 60.36 (OCH_3). **21**: R_f 0.39 (PE/EtOAc, 4/6); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50−7.47 (2H, m), 7.45−7.32 (8H, m), 5.56 (1H, s, H-8), 5.20 (1H, t, J = 3.1 Hz, H-1), 4.33 (1H, dd, J = 10.4, 4.9 Hz, H-7eq), 4.15 (1H, dd, J = 9.8, 2.4 Hz, H-5), 4.05 (1H, dt, J = 9.8, 4.9 Hz, H-6), 4.00 (1H, broad s, OH), 3.88 (1H, d, J = 3.1 Hz, H-2), 3.84 (1H, broad d, J = 3.1 Hz, H-3), 3.81 (1H, t, J = 10.4 Hz, H-7ax), 3.62 (1H, t, J = 3.1 Hz, H-4), 3.42 (3H, s, OCH_3), 2.86 (1H, d, J = 3.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.15, 138.10, 129.05, 128.82, 128.34, 128.19, 126.41, 125.92, 102.64 (C-8), 78.44 (C-5), 77.62 (C-4), 77.38 (C-2), 76.15 (C-1), 69.69 (C-7), 69.27 (C-2), 67.36 (C-6), 59.83 (OCH_3); ESI MS (calcd for $C_{21}H_{24}O_6$, 372) m/z (relative intensity) 395 (M + Na^+, 100), 396 (M + Na^+, 23), 767 (2M + Na^+, 42), 768 (2M + Na^+, 22).

Benzyl-2,3-bis-*O*-(4-methoxybenzyl)-4,6-*O*-benzylidene-1-thio-*β*-D-glucopyranoside (29). The thioglucoside **28** (14.80 g, 39.5 mmol) dissolved in DMF (75 mL) and THF (40 mL) was added dropwise at 0 °C (ice bath) to a suspension of NaH (0.107 mol, 60% dispersion in mineral oil, washed free of oil with pentane) in DMF (25 mL) and THF (15 mL), followed by addition of PMBCl (0.10 mol) and tetrabutylammonium iodide (7.9 mmol). The mixture was stirred at low temperature for 30 min and then at room temperature overnight (10 h). Methanol (8 mL) was added dropwise. The mixture was stirred for 1 h, and then the solvent was partially removed under reduced pressure. Saturated aqueous NH_4Cl (100 mL) was added, and the product was extracted with EtOAc (3 × 100 mL). The organic layer was dried over sodium sulfate, and the solvent was removed. The crude was dissolved in EtOAc (ca. 70 mL), and such solution was poured in an Erlenmeyer flask containing petroleum ether (ca. 700 mL). The flask was stored in a freezer for 1 h, and then the white crystals formed were filtered and washed with cold petroleum ether (ca. 100 mL) to obtain 20.88 g (86% yield) of **29**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50−7.44 (2H, m), 7.38−7.21 (12H, m), 6.86−6.78 (4H, m), 5.54 (1H, s), 4.83 (1H, d, J = 11.0 Hz), 4.75−4.65 (3H, m), 4.38 (1H, d, J = 9.9 Hz), 4.30 (1H, dd, J = 10.6, 4.9 Hz), 3.95 (1H, d, J = 13.2 Hz), 3.86 (1H, d, J = 13.2 Hz), 3.76 (3H, s), 3.74 (3H, s), 3.77−3.61 (3H, m), 3.44 (1H, t, J = 9.1 Hz), 3.33 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.39, 159.27, 137.55, 137.40, 130.71, 130.27, 129.92, 129.69, 129.04, 128.95, 128.61, 128.24, 127.27, 126.06, 113.83, 101.21, 84.76, 82.57, 81.74, 81.00, 75.51, 74.93, 70.31, 68.81, 55.41, 55.38, 35.00; ESI MS (calcd for $C_{36}H_{38}O_7S$, 614) m/z (relative intensity) 632 (M + NH_4^+, 100), 633 (M + NH_4^+, 36).

Benzyl-2,3-bis-*O*-(4-methoxybenzyl)-4,6-*O*-benzylidene-1-sulfonyl-*β*-D-glucopyranoside (30). The sulfone **30** (11.0 g, 95% yield) was prepared from **29** (11.0 g, 17.9 mmol) by following the same procedure described for **15**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48−7.44 (2H, m), 7.40−7.34 (8H, m), 7.30−7.23 (4H, m), 6.85−6.81 (4H, m), 5.58 (1H, s, H-7), 4.85 (1H, d, J = 11.0 Hz, PMB), 4.81 (1H, d, J = 9.8 Hz, PMB), 4.77 (1H, d, J = 9.8 Hz, PMB), 4.72 (1H, d, J = 11.0 Hz, PMB), 4.44−4.39 (2H, m, H-6eq and H-1′a), 4.27−4.21 (2H, m, H-1 and H-1′b), 4.11 (1H, t, J = 9.2 Hz, H-2), 3.87 (1H, t, J = 9.8 Hz, H-6ax), 3.82−3.71 (8H, m, H-3, H-4 and PMB), 3.39 (1H, dt, J = 9.8, 4.9 Hz, H-5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.45, 159.36, 136.99, 131.00, 130.31, 129.71, 129.13, 129.06, 128.96, 128.29, 127.19, 126.04, 113.91, 113.86, 101.40, 88.00 (C-1), 82.14, 80.80, 76.41 (C-2), 75.51, 75.00, 70.80 (C-5), 68.34 (C-6), 57.99 (C-7), 55.39; ESI MS (calcd for $C_{36}H_{38}O_9S$, 646) m/z (relative intensity) 664 (M + NH_4^+, 100), 665 (M + NH_4^+, 42).

(*Z*)-2,6-Anhydro-1-deoxy-1-phenyl-3,4-bis-*O*-(4-methoxybenzyl)-5,7-*O*-benzylidene-D-gluco-hept-1-enitol (31).[9] The sulfone **30** (2.70 g, 4.17 mmol) was converted to the *exo*-glucal **31** in 70% yield by using the same reaction conditions as described for the preparation of **16**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (2H, d, J = 7.3 Hz), 7.49 (2H, dd, J = 7.3, 1.2 Hz), 7.41−7.35 (m, 3H), 7.32 (2H, t, J = 7.3 Hz), 7.28−7.23 (4H, m), 7.20 (1H, t, J = 7.3 Hz), 6.89 (2H, d, J = 8.5 Hz), 6.85 (2H, d, J = 8.5 Hz), 5.60 (1H, s, H-1), 5.56 (1H, s, H-8), 4.66 (1H, d, J = 11.6 Hz, PMB), 4.65 (1H, d, J = 11.6 Hz, PMB), 4.60 (1H, d, J = 11.6 Hz, PMB), 4.57 (1H, dd, J = 10.4, 5.5 Hz, H-7eq), 4.45 (1H, d, J = 11.6 Hz, PMB), 4.34 (1H, dt, J = 9.8, 5.5 Hz, H-6), 3.99 (1H, d, J = 2.4 Hz, H-3), 3.94 (1H, dd, J = 7.3, 2.4 Hz, H-4), 3.90−3.84 (2H, m, H-5 and H-7a), 3.82 (3H, s, PMB), 3.79 (3H, s, PMB); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.44, 159.37, 147.89, 137.40, 135.12, 130.28, 129.97, 129.56, 129.52, 129.09, 128.74, 128.34, 128.29, 126.58, 126.30, 114.04, 113.94, 110.16 (C-1), 101.54 (C-8), 82.14 (C-5), 81.18 (C-4), 80.17 (C-3), 72.41, 70.29, 69.56 (C-7), 66.32 (C-6), 55.45; ESI MS (calcd for $C_{36}H_{36}O_7$, 580) m/z (relative intensity) 598 (M + NH_4^+, 100), 599 (M + NH_4^+, 37).

(1*R*)-2,6-Anhydro-1-phenyl-3,4-bis-*O*-(4-methoxybenzyl)-5,7-*O*-benzylidene-α-D-gluco-heptitol (32) and (1*S*)-2,6-Anhydro-1-phenyl-3,4-bis-*O*-(4-methoxybenzyl)-5,7-*O*-benzylidene-*β*-D-gluco-heptitol (33).[17] By following the same procedure described for the preparation of **17** and **18**, hydroboration of **31** (1.0 g, 1.7 mmol) afforded the two products **32** (533 mg, 0.89 mmol, 53%) and **33** (180 mg, 0.30 mmol, 18%), which were separated by column chromatography (SiO_2, petroleum ether, EtOAc 10%). **32**: R_f 0.30 (petroleum ether, EtOAc 30%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51−7.47 (2H, m), 7.41−7.25 (12H, m), 6.91−9.85 (4H, m), 5.51 (1H, s, H-8), 5.11 (1H, dd, J = 8.5, 2.4 Hz, H-1), 4.86 (1H, d, J = 11.0 Hz), 4.79 (1H, d, J = 11.0 Hz), 4.74 (1H, d, J = 11.0 Hz), 4.57 (1H, d, J = 11.0 Hz), 4.07 (1H, t, J = 7.6 Hz, H-4), 4.02 (1H, dd, J = 8.5, 4.9 Hz, H-2), 3.99−3.92 (2H, m, H-3 and H-7eq), 3.90 (1H, d, J = 2.4 Hz, OH), 3.811 (3H, s, OCH_3), 3.806 (3H, s, OCH_3), 3.74−3.70 (2H, m, H-5 and H-6), 3.48−3.44 (1H, m, H-7ax); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.86, 159.49, 140.82, 137.52, 130.57, 130.08, 129.74, 129.31, 129.04, 128.46, 128.34, 128.02, 126.98, 126.14, 114.27, 114.02, 101.31 (C-8), 82.73 (C-5 or C-6), 79.65 (C-3), 78.79 (C-4), 76.75 (C-2), 74.21, 74.02, 73.38 (C-1), 69.56 (C-7), 65.28 (C-6 or C-5), 55.52; ESI MS (calcd for $C_{36}H_{38}O_8$, 598) m/z (relative intensity) 616 (M + NH_4^+, 100), 617 (M + NH_4^+, 38). **33**: R_f 0.18 (petroleum ether, EtOAc 30%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50−7.47 (2H, m), 7.39−7.27 (8H, m), 7.22 (2H, d, J = 8.5 Hz), 7.15 (2H, d, J = 8.5 Hz), 6.87 (2H, d, J = 8.5 Hz), 6.82 (2H, d, J = 8.5 Hz), 5.54 (1H, s, H-8), 4.92−4.86 (3H, m, H-1 and PMB), 4.67 (1H, d, J = 11.0 Hz, PMB), 4.43 (1H, d, J = 10.4 Hz, PMB), 4.34 (1H, dd, J = 10.4, 4.9 Hz, H-7eq), 3.88 (1H, t, J = 9.2 Hz, H-4), 3.83−3.78 (4H, m, H-2 and OCH_3 at 3.80 ppm), 3.77 (3H, s, OCH_3), 3.69 (1H, t, J = 9.8 Hz, H-7ax), 3.54 (1H, t, J = 9.2 Hz, H-5), 3.45 (1H, td, J = 9.8, 4.9 Hz, H-6), 3.35 (1H, t, J = 9.2 Hz, H-3), 3.12 (1H, d, J = 5.5 Hz, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.40, 159.38, 140.01, 137.50, 130.61, 130.34, 129.84, 129.39, 128.99, 128.29, 128.15, 127.94, 127.90, 126.08, 114.03, 113.98, 101.29 (C-8), 83.45 (C-4), 82.53 (C-5), 81.89 (C-2), 78.97 (C-3), 74.71, 74.54 (C-1), 74.22, 70.35 (C-6), 68.97 (C-7), 55.47, 55.42; ESI MS (calcd for $C_{36}H_{38}O_8$, 598) m/z (relative intensity) 616 (M + NH_4^+, 100), 617 (M + NH_4^+, 37).

(1*R*)-2,6-Anhydro-1-phenyl-1-*O*-[2-(trimethylsilyl)-ethoxymethyl]-3,4-bis-*O*-(4-methoxybenzyl)-5,7-*O*-benzylidene-α-D-gluco-heptitol (34).[25] The *C*-glucoside **32** (1.07 g, 1.79 mmol) was dissolved in dry methylene chloride (4 mL), in the presence of diisopropylethylamine (1.05 g, 8.1 mmol). To this solution SEMCl (0.9 g, 8.1 mmol) was added and the mixture was stirred at room temperature under nitrogen atmosphere for ca. 10 h. Methylene chloride (15 mL) was added and the organic layer was washed with saturated aqueous NH_4Cl (2 × 10 mL). The organic layer was dried over sodium sulfate and the solvent removed under reduced pressure. Column chromatography (SiO_2, EtOAc 10%, petroleum ether) afforded 1.29 g (98% yield) of the product **34**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (2H, m), 7.39−7.26 (12H, m), 6.89−6.86 (4H, m), 5.45 (1H, s, H-8), 4.78 (1H, d, J = 8.5 Hz, H-1), 4.74 (1H, d, J = 11.6 Hz, 1/2 AB system, SEM), 4.72 (1H, d, J = 11.6 Hz, 1/2 AB system, SEM), 4.61−4.57 and 4.54−4.49 (4H, m, PMB), 4.19 (1H, dd, J = 8.5, 3.1 Hz, H-2), 4.05 (1H, t, J = 3.1 Hz, H-3), 3.97−9.92 (2H, m, H-4 and H-7), 3.83−3.79 (7H,

m, H-5 and 2 OCH_3 at 3.81 ppm), 3.74 (1H, td, J = 10.3, 4.9 Hz, H-6), 3.47 (1H, ddd, J = 11.6, 9.8, 5.5 Hz, SEM), 3.39 (1H, t, J = 10.3 Hz, H-7), 3.30 (1H, ddd, J = 11.6, 9.8, 5.5 Hz, SEM), 0.73 (1H, ddd, J = 13.4, 11.6, 5.5 Hz, SEM), 0.57 (1H, ddd, J = 13.4, 11.6, 5.5 Hz, SEM), −0.11 (9H, s, SEM); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.30, 139.74, 137.65, 130.50, 130.22, 129.50, 129.43, 128.79, 128.25, 128.12, 127.97, 127.61, 126.09, 113.85, 100.97, 93.72, 82.19 (C-5), 78.46 (C-3), 77.81 (C-1), 77.68 (C-4), 75.82 (C-2), 72.58, 71.99, 69.84 (C-7), 65.79, 64.11 (C-6), 55.34, 18.05, −1.25; ESI MS (calcd for $C_{42}H_{56}O_9Si$, 728) m/z (relative intensity) 746 (M + NH_4^+, 100), 747 (M + NH_4^+, 51), 751 (M + Na^+, 35), 752 (M + Na^+, 19).

(1*R*)-2,6-Anhydro-1-phenyl-1-*O*-[2-(trimethylsilyl)-ethoxymethyl]-5,7-*O*-benzylidene-α-D-gluco-heptitol (35).[26] To the *C*-glucoside **34** (1.13 g, 1.55 mmol) dissolved in methylene chloride (15 mL) and water (7 mL) was added 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ, 1.0 g, 4.4 mmol). The mixture was stirred vigorously for ca. 1.5 h at room temperature. A saturated solution of sodium bicarbonate in water (15 mL) was added dropwise, and the product was extracted with methylene chloride (4 × 15 mL). The organic layer was dried over sodium sulfate, and the solvent was removed in vacuo. Column chromatography (SiO_2, EtOAc 15%, petroleum ether) yielded the product **35** (644 mg, 1.32 mmol, 85%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52−7.48 (2H, m), 7.40−7.33 (8H, m), 5.50 (1H, s, H-8), 5.25 (1H, d, J = 8.5 Hz, H-1), 4.64 (1H, d, J = 6.7 Hz, SEM), 4.50 (1H, d, J = 6.7 Hz, SEM), 4.29 (1H, d, J = 6.1 Hz, OH), 4.26 (1H, dd, J = 8.5, 4.9 Hz, H-2), 4.11 (1H, t, J = 9.2 Hz, H-4), 3.98 (1H, ddd, J = 8.5, 6.1, 4.9 Hz, H-3), 3.94 (1H, dd, J = 10.4, 4.9 Hz, H-7), 3.78−3.71 (2H, m, H-6 and SEM), 3.58 (1H, t, J = 9.2 Hz, H-5), 3.54−3.45 (2H, m, H-7 and SEM), 2.73 (1H, bs, OH), 0.94−0.83 (2H, m, SEM), 0.01 (9H, s, SEM); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.64, 137.26, 129.22, 128.79, 128.37, 127.75, 126.40, 101.95 (C-8), 92.76, 82.08 (C-5), 77.54 (C-1), 76.25 (C-2), 74.18 (C-3), 72.99 (C-4), 69.41 (C-7), 66.78, 65.72 (C-6), 18.38, −1.11; ESI MS (calcd for $C_{26}H_{40}O_7Si$, 488) m/z (relative intensity) 506 (M + NH_4^+, 100), 507 (M + NH_4^+, 33), 994 (2M + NH_4^+, 28), 995 (2M + NH_4^+, 22).

(1*R*)-2,6-Anhydro-1-phenyl-1-*O*-[2-(trimethylsilyl)-ethoxymethyl]-3,4-anhydro-5,7-*O*-benzylidene-α-D-manno-heptitol (36) and (1*R*)-2,6-Anhydro-1-phenyl-1-*O*-[2-(trimethylsilyl)ethoxymethyl]-3,4-anhydro-5,7-*O*-benzylidene-α-D-allo-heptitol (37).[12] Sodium hydride (60% in mineral oil, 175 mg, 4.4 mmol) was washed free of oil with pentane. The *C*-glucoside **35** (990 mg, 2.03 mmol), dissolved in dry DMF (30 mL), was added dropwise at 0 °C (ice bath), under nitrogen. The mixture was stirred at 0 °C for 15 min under N_2, then a solution of *N*-tosylimidazole (511 mg, 2.30 mmol) in DMF (10 mL) was added dropwise, and the mixture was stirred for 15 min at 0 °C and then at room temperature for 1 h. Saturated aqueous NH_4Cl (40 mL) was added, and the product was extracted with EtOAc (4 × 40 mL). The organic layer was dried over sodium sulfate, the solvent was removed in vacuo, and the products **36** (740 mg, 1.57 mmol, 77%) and **37** (190 mg, 0.40 mmol, 20%) were isolated by column chromatography (SiO_2, EtOAc 5 to 10%, petroleum ether). **36**: R_f 0.4 (PE/EtOAc, 8/2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53−7.49 (2H, m), 7.42−7.31 (8H, m), 5.55 (1H, s, H-8), 5.03 (1H, d, J = 7.3 Hz, H-1), 4.69 (1H, d, J = 6.7 Hz, SEM), 4.61 (1H, d, J = 6.7 Hz, SEM), 4.22 (1H, d, J = 7.3 Hz, H-2), 4.07−4.01 (1H, m, H-7), 3.74 (1H, td, J = 9.8, 6.7 Hz, SEM), 3.63−3.49 (6H, m), 0.93−0.82 (1H, m), 0.01 (9H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.18, 137.31, 129.25, 128.73, 128.41, 127.46, 126.25, 102.35 (C-8), 93.06, 77.92 (C-1), 76.06, 75.97, 69.79 (C-7), 66.25, 65.47, 54.68, 50.37, 18.36, −1.08; ESI MS (calcd for $C_{26}H_{38}O_6Si$, 470) m/z (relative intensity) 488 (M + NH_4^+, 100), 489 (M + NH_4^+, 34), 963 (2M + Na^+, 8). **37**: R_f 0.3 (PE/EtOAc, 8/2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52−7.49 (2H, m), 7.40−7.33 and 7.32−7.28 (8H, m), 5.53 (1H, s, H-8), 4.99 (1H, d, J = 9.2 Hz, H-1), 4.72 (1H, d, J = 6.7 Hz, SEM), 4.61 (1H, d, J = 6.7 Hz, SEM), 4.11 (1H, dd, J = 9.2, 3.1 Hz, H-2), 4.01−3.93 (3H, m, H-5, H-6 and H-7eq), 3.76 (1H, ddd, J = 11.6, 9.2, 5.5 Hz, SEM), 3.74 (1H, m, H-3, partially overlapped with ddd at 3.76 ppm), 3.62 (1H, d, J = 4.9 Hz, H-4), 3.52−3.43 (2H, m, H-7ax and SEM), 0.92 (1H, ddd, J = 13.4, 11.6, 5.5 Hz), 0.78 (1H, ddd, J = 13.4, 11.6, 5.5 Hz), −0.03 (9H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.38, 137.40, 129.25, 128.42, 128.38, 128.16, 127.73, 126.41, 102.76, 93.06, 78.35, 75.79 (C-1), 74.08 (C-2), 69.21 (C-7), 65.67, 62.40, 54.15 (C-3), 51.90 (C-4), 18.13, −1.14; ESI MS (calcd for $C_{26}H_{38}O_6Si$, 470) m/z (relative intensity) 488 (M + NH_4^+, 100), 489 (M + NH_4^+, 36), 958 (2M + NH_4^+, 13), 963 (2M + Na^+, 9).

(1*R*)-2,6-Anhydro-1-phenyl-1-*O*-[2-(trimethylsilyl)-ethoxymethyl]-4-*O*-methyl-5,7-*O*-benzylidene-α-D-altro-heptitol (38). The epoxide **36** (1.0 g, 2.1 mmol) was dissolved in a solution of sodium methoxide in methanol (ca. 2 M, 16 mL) in a pressure tube. The tube was sealed, and the mixture was stirred at ca. 120 °C (oil bath) for 20 h. The solution was allowed to cool to room temperature, and then acidic resin was added until neutral pH was obtained (monitored by pH paper). The resin was filtered off, and the solvent was removed under reduced pressure to obtain a quantitative yield (1.0 g) of the *C*-altroside **38**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50−7.46 (2H, m), 7.41−7.28 (8H, m), 5.51 (1H, s, H-8), 5.33 (1H, d, J = 10.4 Hz, H-1), 4.65 (1H, d, J = 6.1 Hz, SEM), 4.56 (1H, d, J = 6.1 Hz, SEM), 4.47 (1H, t, J = 4.0 Hz, H-3), 4.08 (1H, dt, J = 9.8, 5.5 Hz, H-6), 4.03 (1H, dd, J = 9.8, 4.0 Hz, H-7eq), 3.87−3.84 (2H, m, H-2 and H-4), 3.65 (3H, s, OCH_3), 3.56 (1H, ddd, J = 11.6, 9.2, 6.0 Hz, SEM), 3.49 (1H, t, J = 10.4 Hz, H-7ax), 3.38 (1H, ddd, J = 11.6, 9.2, 6.0 Hz, SEM), 1.92 (1H, d, J = 5.5 Hz, OH), 0.80 (1H, ddd, J = 13.4, 11.6, 5.5 Hz, SEM), 0.66 (1H, ddd, J = 13.4, 11.6, 5.5 Hz, SEM), −0.04 (9H, s, SEM); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.98, 137.88, 129.11, 128.47, 128.38, 128.10, 127.71, 126.31, 102.47 (SEM, OCH_2O), 93.59, 81.92, 78.84, 77.88 (C-5), 75.84 (C-1), 69.61 (C-7), 68.89 (C-3), 65.81, 61.85 (C-6), 60.57, 18.16, −1.11; ESI MS (calcd for $C_{27}H_{42}O_7Si$, 502) m/z (relative intensity) 520 (M + NH_4^+, 100), 521 (M + NH_4^+, 35).

(1*R*)-2,6-Anhydro-1-phenyl-1-*O*-[2-(trimethylsilyl)-ethoxymethyl]-4-*O*-methyl-α-D-altro-heptitol (39) and (1*R*)-2,6-Anhydro-1-phenyl-4-*O*-methyl-α-D-altro-heptitol (40). To the benzylidene-protected *C*-glycoside **38** (1.0 g, 2.0 mmol) dissolved in methanol (50 mL) was added *p*-toluensulfonic acid monohydrate (200 mg, 1.05 mmol), and the mixture was stirred at room temperature. When the consumption of all of the starting material was detected by TLC, the reaction was quenched by addition of triethylamine (3 mL). The solvent was removed under reduced pressure, and the two products **39** (white solid, 705 mg, 1.7 mmol, 85%) and **40** (oil, 85 mg, 0.3 mmol, 15%) were separated by column chromatography (SiO_2, methanol 3%, EtOAc). Longer reaction time afforded **40** in quantitative yield. **39**: $[\alpha]^{25}_D$ = −57.0 (c = 2.85, CH_2Cl_2); mp 64−67 °C. Anal. Calcd for $C_{20}H_{34}O_7Si$: C, 57.94; H, 8.27. Found: C, 57.93; H, 8.25; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40−7.29 (5H, m), 4.91 (1H, d, J = 8.5 Hz, H-1), 4.64 (1H, d, J = 6.7 Hz, SEM), 4.55 (1H, d, J = 6.7 Hz, SEM), 4.10 (1H, dt, J = 7.0, 2.4 Hz, H-3), 3.89−3.84 (2H, m, H-5 and H-6), 3.72−3.65 (2H, m, H-2 and SEM), 3.63−3.57 (1H, m, H-7a), 3.56 (3H, s, OCH_3), 3.50−3.41 (3H, m, H-4, H-7b, SEM), 3.35 (1H, d, J = 2.4 Hz, OH-3), 2.54 (1H, d, J = 4.3 Hz, OH-5), 1.32 (1H, OH-7), 0.89−0.75 (2H, m, SEM), −0.01 (9H, s, SEM); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.81, 128.54, 128.02, 93.08 (SEM, OCH_2O), 81.62 (C-4), 79.42 (C-1), 76.93 (C-2), 75.95 (C-5 or C-6), 69.34 (C-3), 66.27 (SEM, $OCH_2CH_2SiMe_3$), 65.67 (C-5 or C-6), 60.64 (C-7), 58.61 (OCH_3), 18.32 (SEM, $OCH_2CH_2SiMe_3$), −1.09 (SEM, $Si(CH_3)_3$); ESI MS (calcd for $C_{20}H_{38}O_7Si$, 414) m/z (relative intensity) 432 (M + NH_4^+, 100), 433 (M + NH_4^+, 33), 851 (2M + Na^+, 16). **40**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (2H, d, J = 7.6 Hz), 7.37 (2H, t, J = 7.6 Hz), 7.32 (1H, t, J = 7.6 Hz), 4.96 (1H, d, J = 7.6 Hz, H-1), 4.14 (1H, t, J = 7.6 Hz), 3.98 (1H, ddd, J = 8.9, 4.4, 3.2 Hz, H-6), 3.94 (1H, t, J = 3.2 Hz, H-5), 3.69 (1H, dd, J = 11.4, 8.9 Hz, H-7a), 3.64 (1H, t, J = 7.6 Hz, H-2), 3.54 (3H, s, OCH_3), 3.51 (1H, dd, J = 11.4, 4.4

Hz, H-7b), 3.40 (1H, dd, J = 7.6, 3.2 Hz, H-4); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.30, 128.77, 128.61, 127.02, 81.67 (C-4), 76.81 (C-6), 76.34 (C-2), 75.99 (C-1), 69.55 (C-3), 65.39 (C-5), 59.99 (C-7), 58.10 (OCH_3); ESI MS (calcd for $C_{14}H_{20}O_6$, 284) m/z (relative intensity) 307 (M + Na^+, 100), 308 (M + Na^+, 14), 591 (2M + Na^+, 6).

(1*R*)-2,6-Anhydro-1-phenyl-1,3,5,7-tetrakis-*O*-acetyl-4-*O*-methyl-α-D-altro-heptitol (41). The *C*-glycoside **40** (40 mg, 0.14 mmol) was acetylated following the same reaction conditions described for the preparation of **9** (EtOAc, 5 mL, DMAP, 5 mg and Ac_2O, 0.2 mL). The product **41** was isolated in quantitative yield: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40−7.28 (5H, m), 6.36 (1H, d, J = 9.8 Hz, H-1), 5.35 (1H, dd, J = 4.3, 2.4 Hz, H-3), 5.04 (1H, dd, J = 9.2, 3.1 Hz, H-5), 4.21 (1H, dt, J = 9.2, 2.4 Hz, H-6), 4.17−4.12 (2H, m, H-2 and H-7a), 3.89 (1H, dd, J = 11.6, 2.4 Hz, H-7b), 3.75 (1H, t, J = 3.7 Hz, H-4), 3.49 (3H, s, OCH_3), 2.11 (3H, s, OAc), 2.10 (3H, s, OAc), 2.09 (3H, s, OAc), 1.91 (3H, s, OAc); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.49, 169.88, 169.85, 169.31, 137.57, 128.46, 128.39, 127.71, 76.66 (C-2), 76.46 (C-4), 72.76 (C-1), 68.06 (C-6), 67.67 (C-3), 67.38 (C-5), 62.97 (C-7), 59.31 (OCH_3), 21.25, 21.06, 20.82; ESI MS (calcd for $C_{22}H_{28}O_{10}$, 452) m/z (relative intensity) 470 (M + NH_4^+, 100), 471 (M + NH_4^+, 26).

(1*R*)-2,6-Anhydro-1-phenyl-1-*O*-[2-(trimethylsilyl)-ethoxymethyl]-4-*O*-methyl-7-deoxy-7-iodo-α-D-altro-heptitol (42).[28] A mixture of the *C*-glycoside **39** (860 mg, 2.07 mmol), imidazole (456 mg, 6.7 mmol), triphenylphosphine (840 mg, 3.2 mmol), and iodine (863 mg, 3.4 mmol) in dry THF (35 mL) was stirred under reflux for 2 h. The solvent was removed under reduced pressure, and the product was purified by column chromatography (SiO_2, EtOAc 10−40%, petroleum ether), to isolate the colorless oil **42** (887 mg, 1.69 mmol, 82%): $[\alpha]^{25}_D$ = −52.2 (c = 1.7, $CHCl_3$). Anal. Calcd for $C_{20}H_{33}IO_6Si$: C, 45.80; H, 6.34. Found: C, 45.97; H, 6.21. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (2H, d, J = 7.3 Hz), 7.34 (2H, d, J = 7.3 Hz), 7.30 (1H, d, J = 7.3 Hz), 4.87 (1H, d, J = 7.9 Hz, H-1), 4.63 (1H, J = 6.7 Hz, SEM), 4.54 (1H, J = 6.7 Hz, SEM), 4.12 (1H, dd, J = 7.9, 4.3 Hz, H-5), 4.06 (1H, dt, J = 7.3, 2.4 Hz, H-3), 3.88 (1H, dt, J = 7.3, 4.3 Hz, H-6), 3.73−3.66 (2H, m, H-2 and SEM), 3.57 (3H, s, OCH_3), 3.48−3.41 (2H, m, H-4 and SEM), 3.39 (1H, d, J = 2.4 Hz, OH-3), 3.20 (1H, dd, J = 10.4, 6.7 Hz, H-7a), 3.07 (1H, dd, J = 10.4, 7.3 Hz, H-7b), 2.46 (1H, d, J = 4.3 Hz, OH-5), 0.90−0.77 (2H, m, SEM), −0.01 (9H, s, SEM); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.50, 128.41, 128.38, 128.34, 92.94 (SEM, OCH_2O), 80.69 (C-4), 79.86 (C-1), 76.60 (C-2), 75.68 (C-6), 69.55 (C-3), 67.09 (C-5), 66.22 (SEM, $OCH_2CH_2SiMe_3$), 58.55 (OCH_3), 18.30 (SEM, $OCH_2CH_2SiMe_3$), 2.92 (C-7), −1.09 (SEM, $Si(CH_3)_3$).

(1*R*)-2,6-Anhydro-1-phenyl-1-*O*-[2-(trimethylsilyl)-ethoxymethyl]-4-*O*-methyl-7-deoxy-α-D-altro-heptitol (43).[29] A mixture of **42** (100 mg, 0.19 mmol), tributyltin hydride (120 mg, 0.41 mmol) and AIBN (5 mg), in toluene (8 mL) was refluxed for 2 h. The solvent was removed under reduced pressure, and the product **43** (60 mg, 79% yield) was isolated by column chromatography (SiO_2, petroleum ether, EtOAc 10 to 40%) as a colorless oil: $[\alpha]^{25}_D$ = −86.0 (c = 1.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (2H, d, J = 7.3 Hz), 7.32 (2H, t, J = 7.3 Hz), 7.28 (1H, t, J = 7.3 Hz), 4.84 (1H, d, J = 7.3 Hz, H-1), 4.63 (1H, d, J = 6.7 Hz, SEM), 4.51 (1H, d, J = 6.7 Hz, SEM), 4.08 (1H, dq, J = 7.3, 1.8 Hz, H-6), 3.88 (1H, t, J = 8.5 Hz, H-3), 3.82 (1H, bq, J = ∼3.1 Hz, H-5), 3.76−3.69 (2H, m, H-2 and SEM), 3.53 (3H, s, OCH_3), 3.48−3.42 (2H, m, H-4 and SEM), 2.43 (1H, d, J = 3.1 Hz, OH-5), 1.10 (3H, d, J = 7.3 Hz, H-7), 0.95−0.77 (2H, m, SEM), −0.01 (9H, s, SEM); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.92, 128.34, 128.25, 128.13, 93.01 (SEM, OCH_2O), 81.13 (C-4), 80.43 (C-1), 75.23 (C-2), 72.69 (C-6), 70.47 (C-3), 69.49 (C-5), 66.20 (SEM, $OCH_2CH_2SiMe_3$), 58.14 (OCH_3), 18.42(SEM, $OCH_2CH_2SiMe_3$), 15.48 (C-7), −1.075 (SEM, $Si(CH_3)_3$); ESI MS (calcd for $C_{20}H_{38}O_6Si$, 398) m/z (relative intensity) 416 (M + NH_4^+, 100), 417 (M + NH_4^+, 31), 819 (2M + Na^+, 15).

(1*R*)-2,6-Anhydro-1-phenyl-4-*O*-methyl-7-deoxy-7-iodo-α-D-altro-heptitol (44).[28] Iodination of **40** (670 mg, 2.36 mmol) was achieved by following the same procedure described in the preparation of **42**. The product **44** (ca. 780 mg, 85% yield) was purified by column chromatography (SiO_2, EtOAc 20 to 60%, petroleum ether), but the product remained contaminated with triphenylphosphine oxide. Attempts at further purification were unsuccessful: ^{1}H NMR (500 MHz, $CDCl_3$) δ aromatic region contaminated by TPPO, 4.89 (1H, dd, J = 7.0, 3.7 Hz, H-1), 4.14 (1H, dt, J = 7.0, 3.3 Hz, H-5), 4.09−3.95 (3H, m, H-3, H-6, OH-1), 3.61 (1H, t, J = 7.7 Hz, H-2), 3.56 (1H, broad s, OH-3), 3.51 (3H, s, OCH_3), 3.38 (1H, dd, J = 7.7, 3.7 Hz, H-4), 3.23 (1H, dd, J = 10.6, 6.6 Hz, H-7a), 3.12 (1H, dd, J = 10.6, 8.1 Hz, H-7b), 2.67 (1H, d, J = 3.3 Hz, OH-5); ^{13}C NMR (75 MHz, $CDCl_3$) δ Aromatic region contaminated by TPPO, 80.83 (C-4), 76.46 (C-6), 76.41 (C-2), 75.85 (C-1), 69.38 (C-3), 66.79 (C-5), 58.19 (OCH_3), 2.68 (C-7); ESI MS (calcd for $C_{14}H_{19}IO_5$, 394) m/z (relative intensity) 412 (M + NH_4^+, 100), 413 (M + NH_4^+, 17), 811 (2M + Na^+, 81), 812 (2M + Na^+, 25).

(1*R*)-2,6-Anhydro-1-phenyl-4-*O*-methyl-7-deoxy-α-D-altro-heptitol (45).[29] The *C*-glycoside **45** was obtained via radical deiodination of **44** in 75% yield following the same procedure described for the preparation of **43**. Alternatively, **45** was prepared via deprotection of the SEM ether by treating **43** with a 2/1 solution of methylene chloride/trifluoroacetic acid (1.5 mL per 50 mg of starting material). After complete deprotection of SEM ether was detected by TLC, toluene (2 mL per mL of reaction solution) was added, and the solvent was removed under reduced pressure. A second cycle of addition/evaporation of toluene afforded a pure sample of the product **45** in quantitative yield as a white solid, without necessity of further purification: $[\alpha]^{25}_D$ = −10.8 (c = 0.65, $CHCl_3$); mp 94−96 °C. Anal. Calcd for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51. Found: C, 62.71; H, 7.34. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (2H, d, J = 7.3 Hz), 7.35 (2H, t, J = 7.3 Hz), 7.29 (1H, t, J = 7.3 Hz), 4.88 (1H, d, J = 6.7 Hz, H-1), 4.15 (1H, dt, J = 7.3, 1.8 Hz, H-6), 3.94 (1H, t, J = 8.5 Hz, H-3), 3.86 (1H, dd, J = 3.1, 1.8 Hz, H-5), 3.70 (1H, dd, J = 8.5, 6.7 Hz, H-2), 3.49 (3H, s, OCH_3), 3.43 (1H, dd, J = 8.5, 3.1 Hz, H-4), 1.16 (3H, d, J = 7.3 Hz, H-7); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.30, 128.29, 127.86, 127.07, 81.04 (C-4), 76.26 (C-1), 74.74 (C-2), 73.02 (C-6), 70.05 (C-3), 68.94 (C-5), 57.67 (OCH_3), 15.29 (C-7).

(1*R*)-2,6-Anhydro-1-phenyl-1,3-*O*-benzylidene-4-*O*-methyl-7-deoxy-α-D-altro-heptitol (46). A solution of *C*-glycoside **45** (14 mg, 0.05 mmol), benzaldehyde dimethyl acetal (0.08 mL, 0.05 mmol), and *p*-toluenesulfonic acid (1 crystal), dissolved in acetonitrile (2.5 mL), was stirred at room temperature for 2 h. Triethylamine (0.2 mL) was added, and the solvent was removed under reduced pressure. The product **46** was purified by column chromatography (SiO_2, petroleum ether, EtOAc 30%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (2H, d, J = 7.3 Hz), 7.48 (2H, d, J = 7.3 Hz), 7.39−7.28 (6H, m), 5.85 (1H, s, H-8), 4.79 (1H, d, J = 8.5 Hz, H-1), 4.26−4.21 (2H, m, H-3 and H-6), 3.96 (1H, bd, J = 3.1 Hz, H-5), 3.68 (1H, dd, J = 9.3, 3.1 Hz, H-4), 3.63−3.58 (4H, m, H-2 and OCH_3), 2.75 (1H, s, OH), 1.15 (2H, d, J = 7.3 Hz, H-7); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.36, 137.81, 128.99, 128.30, 127.42, 126.43, 101.62 (C-8), 81.34 (C-1), 79.38 (C-3 or C-6), 77.75 (C-4), 74.14 (C-3 or C-6), 71.36 (C-5), 70.08 (C-2), 59.04 (OCH_3), 15.41 (C-7); ESI MS (calcd for $C_{22}H_{28}O_5$, 356) m/z (relative intensity) 379 (M + Na^+, 100), 380 (M + Na^+, 21), 735 (2M + Na^+, 62), 726 (2M + Na^+, 29).

2,6-Anhydro-1-phenyl-1-keto-4-*O*-methyl-7-deoxy-α-D-altro-heptitol (47). DDQ was added (250 mg, 1.1 mmol) to the *C*-glycoside **45** (250 mg, 0.93 mmol) dissolved in methylene chloride (16 mL), and the mixture was stirred for 8 h under gentle reflux. Additional DDQ (200 mg 0.88 mmol) was added, and the mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure, and the product was purified by column chromatography (alumina, activated basic, Brockmann I; solvent, methanol 0−10%, EtOAc). The ketone **47** (190 mg, 0.71 mmol) was isolated in

77% yield as an oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (2H, d, J = 7.3 Hz), 7.57 (2H, t, J = 7.3 Hz), 7.46 (1H, t, J = 7.3 Hz), 4.71 (1H, d, J = 6.7 Hz, H-2), 4.56 (1H, bq, J = 5−7 Hz, H-3), 4.15 (1H, q, J = 6.7 Hz, H-6), 3.81 (1H, bq, J = 5.0−3.6 Hz, H-5), 3.56 (1H, dd, J = 7.3, 3.7 Hz, H-4), 3.45(3H, s, OCH_3), 2.72 (1H, d, J = 4.9 Hz, OH-3), 2.44 (1H, d, J = 5.5 Hz, OH-5), 1.40 (3H, d, J = 6.7 Hz, H-7); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.90 (C-1), 136.04, 133.36, 129.13, 128.55, 79.96 (C-4), 77.17 (C-2), 72.68 (C-6), 69.34 (C-5), 68.03 (C-3), 58.32, 16.15 (C-7).

2,6-Anhydro-1-phenyl-1-keto-3,5-bis-*O*-*tert*-butyldimethylsilyl-4-*O*-methyl-7-deoxy-α-D-altro-heptitol (48). A mixture of the *C*-glycoside **47** (54 mg, 0.21 mmol), imidazole (48 mg, 0.7 mmol), and TBDMSCl (105 mg, 0.7 mmol) in dry DMF (2.5 mL) was stirred at room temperature under nitrogen overnight (12 h). Water (8 mL) was added, and the mixture was extracted with EtOAc (3 × 8 mL). The organic layer was dried over sodium sulfate, and the solvent was removed under reduced pressure. Column chromatography (SiO_2, petroleum ether, EtOAc 5%) afforded the product **48** (oil, 97 mg, 93% yield): $[\alpha]^{25}_D$ = +48.9 (c = 0.9, $CHCl_3$). Anal. Calcd for $C_{26}H_{48}O_5Si_2$: C, 63.11; H, 9.37. Found: C, 63.11; H, 9.39. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (2H, d, J = 7.3 Hz), 7.51 (1H, t, J = 7.3 Hz), 7.42 (2H, t, J = 7.3 Hz), 4.74 (1H, dd, J = 4.9, 3.0 Hz, H-3), 4.61 (1H, d, J = 2.4 Hz, H-2), 3.91 (1H, quintet, J = 6.1 Hz, H-6), 3.82 (1H, dd, J = 7.9, 2.4 Hz, H-5), 3.28 (4H, s, OCH_3 and H-4), 1.17 (3H, d, J = 6.1 Hz, H-7), 0.92 (9H, s), 0.82 (9H, s), 0.11 (3H, s), 0.10 (3H, s), 0.09 (3H, s), 0.07 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.33, 137.21, 132.42, 128.67, 128.24, 82.02 (C-2), 81.88 (C-4), 71.10 (C-5), 70.10 (C-6), 69.59 (C-3), 58.29(OCH_3), 26.10, 25.96, 18.43, 18.34, 17.87, −3.22, −3.99, −4.34, −4.39, −4.50; ESI MS (calcd for $C_{26}H_{46}O_5Si_2$, 494) m/z (relative intensity) 495 (M + H^+, 20), 512 (M + NH_4^+, 100), 513 (M + NH_4^+, 40).

3,7-Anhydro-1,2,8-trideoxy-2-phenyl-4,6-bis-*O*-*tert*-butyldimethylsilyl-5-*O*-methyl-α-D-altro-oct-1-enitol (α-49).[34] To a slurry of Nysted reagent (20 wt % suspension in THF, 320 mg, 0.7 mmol) and ketone **48** (74 mg, 0.15 mmol) in dry THF (2 mL) at −78 °C under N_2 was added dropwise a solution of $TiCl_4$ (1 M in CH_2Cl_2, 0.6 mL). The mixture turned yellow and was warmed to room temperature and stirred overnight (14 h). The resulting dark slurry was then cooled in an ice bath, and triethylamine (0.5 mL) was added, followed by silica gel. The mixture was warmed to room temperature and was filtered through a plug of silica gel using ethyl acetate as a wash. The filtrate was concentrated and the product α-**49** (oil, 54 mg, 0.11 mmol, 73%) was isolated by column chromatography (SiO_2, EtOAc 5%, petroleum ether): $[\alpha]^{25}_D$ = +3.6 (c = 0.83, $CHCl_3$). Anal. Calcd for $C_{27}H_{48}O_4Si_2$: C, 65.80; H, 9.82. Found: C, 65.52; H, 9.79. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (2H, d, J = 7.3 Hz), 7.29 (2H, t, J = 7.3 Hz), 7.24 (1H, t, J = 7.3 Hz), 5.48 (1H, s, H-1a), 5.37 (1H, s, H-1b), 4.40 (1H, d, J = 7.0 Hz, H-3), 4.17 (1H, dq, J = 6.7, 4.3 Hz, H-7), 4.10 (1H, t, J = 7.0 Hz, H-4), 3.92 (1H, dd, J = 4.3, 3.0 Hz, H-6), 3.25 (3H, s, OCH_3), 3.19 (1H, dd, J = 7.0, 3.0 Hz, H-5), 1.30 (3H, d, J = 6.7 Hz, H-8), 0.94 (9H, s), 0.81 (9H, s), 0.10 (3H, s), 0.09 (3H, s), −0.08 (3H, s), −0.24 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.11, 139.63, 128.16, 127.61, 127.51, 116.80 (C-1), 82.68 (C-5), 79.29 (C-3), 72.40 (C-7), 70.83 (C-6), 69.84 (C-4), 57.62-(OCH_3), 26.17, 26.01, 18.40, 18.36, 16.17, −4.18, −4.31, −4.63, −4.86; ESI MS (calcd for $C_{27}H_{48}O_4Si_2$, 492) m/z (relative intensity) 493 (M + H^+, 55), 494 (M + H^+, 23), 510 (M + NH_4^+, 100), 511 (M + NH_4^+, 44).

2,6-Anhydro-1-phenyl-1-keto-3,7-dideoxy-4-*O*-methyl-5-*O*-*tert*-butyldimethylsilyl-D-altro-hept-2-enitol (50). To a solution of methyltriphenylphosphonium bromide (50 mg, 0.14 mmol) in dry THF (2.5 mL) was added *n*-BuLi (1.6 M in hexanes, 0.08 mL) at −10 °C under nitrogen. The yellow mixture was stirred at −10 °C for ca. 1 h, and then the *C*-glucoside **48** (20 mg, 0.41 mmol, in 2.5 mL dry THF) was added dropwise. The mixture was stirred at −10 °C for 1 h and at room temperature for 2 h. A saturated solution of NH_4Cl (8 mL) was added, and an extraction with EtOAc (3 × 8 mL) was performed. The organic layer was dried, and the solvent was removed under reduced pressure. The product consisted of a mixture of starting material **48**, the glycal **50**, and the two inseparable anomers α- and β-**49** in a ratio 1/1/1/1. The glycal **50** was isolated by column chromatography (SiO_2, petroleum ether, EtOAc 5%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (2H, d, J = 7.3 Hz), 7.55 (1H, t, J = 7.3 Hz), 7.44 (2H, t, J = 7.3 Hz), 5.84 (1H, d, J = 5.5 Hz, H-3), 4.29 (1H, dq, J = 9.2, 6.7 Hz, H-6), 3.77 (1H, dd, J = 5.5, 3.7 Hz, H-4), 3.73 (1H, dd, J = 9.2, 4.3 Hz, H-5), 3.48 (3H, s, OCH_3), 1.41 (3H, d, J = 6.7 Hz, H-7), 0.95 (9H, s), 0.142 (3H, s), 0.138 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.47, 152.11, 136.68, 132.79, 129.89, 128.25, 107.79, 72.98, 72.49, 57.70, 26.14, 18.53, 18.03, −3.79, −4.37, −3.79, −4.37.

(2*S*)-3,7-Anhydro-2-phenyl-4,6-bis-*O*-*tert*-butyldimethylsilyl-5-*O*-methyl-8-deoxy-α-D-altro-octitol (52) and (2*R*)-3,7-Anhydro-2-phenyl-4,6-bis-*O*-*tert*-butyldimethylsilyl-5-*O*-methyl-8-deoxy-α-D-altro-octitol (53).[35] To a solution of **49** (105 mg, 0.21 mmol) in acetone (8 mL) at 0 °C (ice bath) were added 4-methylmorpholine-*N*-oxide (50 wt % in H_2O, 0.15 mL, 0.72 mmol) and osmium tetroxide (2.5 wt % in *t*-BuOH, 0.2 mL, 0.016 mmol). The mixture was stirred at 0 °C for 6 h and then at room temperature overnight (14 h). Sodium sulfite (ca. 10 mg) was added, and the mixture was stirred for 1 h. Ethyl acetate was added (20 mL), and the mixture was dried over sodium sulfate. The mixture was filtered, and the filtrate was concentrated under reduced pressure. The two diastereomers **52** (white solid, 72 mg, 0.14 mmol, 66%) and **53** (colorless oil, 18 mg, 0.034 mmol, 16%) were isolated by column chromatography (SiO_2, EtOAc 10%, petroleum ether). **52**: R_f 0.24 (PE/EtOAc, 8/2); $[\alpha]^{25}_D$ = +27.0 (c = 0.8, $CHCl_3$); mp 69−71 °C. Anal. Calcd for $C_{27}H_{50}O_6Si_2$: C, 61.55; H, 9.57. Found: C, 61.30; H, 9.52. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (2H, d, J = 7.3 Hz), 7.37 (2H, t, J = 7.3 Hz), 7.26 (1H, t, J = 7.3 Hz), 5.76 (1H, s, OH-2), 4.42 (1H, dq, J = 9.2, 6.1 Hz, H-7), 4.09 (1H, dd, partially covered by s at 4.08 ppm, J = 4.3 Hz, H-1a), 4.08 (1H, s, H-3), 3.87 (1H, dd, J = 11.0, 8.5 Hz, H-1b), 3.75 (1H, dd, J = 9.2, 3.1 Hz, H-6), 3.67 (1H, d, J = 3.7 Hz, H-4), 3.56 (3H, s, OCH_3), 3.26 (1H, t, J = 3.1 Hz, H-5), 2.39 (1H, dd, J = 8.5, 4.9 Hz, OH-1), 1.23 (3H, d, J = 6.1 Hz, H-8), 0.91 (9H, s), 0.80 (9H, s), 0.10 (3H, s), 0.08 (3H, s), −0.25 (3H, s), −0.28 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.67, 128.73, 127.38, 125.79, 83.69 (C-3), 81.93 (C-5), 79.02 (C-2), 71.53 (C-6), 70.13 (C-1), 68.96 (C-7), 68.54 (C-4), 60.20 (OCH_3), 25.99, 25.81, 19.10, 18.19, 17.91, −3.84, −4.57, −4.91, −5.10; ESI MS (calcd for $C_{27}H_{50}O_6Si_2$, 526) m/z (relative intensity) 527 (M + H^+, 100), 528 (M + H^+, 42). **53**: R_f 0.3 (PE/EtOAc, 8/2); $[\alpha]^{25}_D$ = −37.9 (c = 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (2H, d, J = 7.3 Hz), 7.28 (2H, t, J = 7.3 Hz), 7.23 (1H, t, J = 7.3 Hz), 4.68 (1H, s, OH-2), 4.17 (1H, t, J = 9.2 Hz, H-4), 4.13 (1H, dq, J = 7.3, 2.4 Hz, H-7), 3.97 (1H, d, J = 9.2 Hz, H-3), 3.94 (1H, t, J = 2.4 Hz, H-6), 3.85 (1H, broad t, J = 11 Hz, H-1a), 3.48 (1H, dd, J = 11.0, 3.7 Hz, H-1b), 3.26 (1H, dd, partially covered by s at 3.25 ppm, J = 2.4 Hz, H-5), 3.25 (3H, s, OCH_3), 2.30 (1H, dd, J = 9.8, 3.7 Hz, OH-1), 1.29 (3H, d, J = 7.3 Hz, H-8), 0.90 (9H, s), 0.82 (9H, s), 0.09 (3H, s), 0.04 (3H, s), −0.02 (3H, s), −0.21 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.99, 127.83, 127.33, 127.28, 81.83 (C-5), 78.76 (C-2), 75.16 (C-3), 74.69 (C-7), 70.96 (C-4), 69.78 (C-6), 69.47 (C-1), 56.00 (OCH_3), 26.54, 25.86, 18.70, 18.25, 15.05, −3.38, −4.46, −4.57, −4.64; ESI MS (calcd for $C_{27}H_{50}O_6Si_2$, 526) m/z (relative intensity) 527 (M + H^+, 100), 528 (M + H^+, 42).

(2*R*)-3,7-Anhydro-2-phenyl-4,6-bis-*O*-*tert*-butyldimethylsilyl-5-*O*-methyl-8-deoxy-α-D-altro-octital (54) and (2*S*)-3,7-Anhydro-2-phenyl-4,6-bis-*O*-*tert*-butyldimethylsilyl-5-*O*-methyl-8-deoxy-α-D-altro-octital (55).[39] A mixture of the alcohol **52** or **53** (1 equiv), freshly prepared polymer-bound bromite(I) (6 equiv), and a catalytic amount of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy, free radical) in dry methylene chloride (60 mL/mmol of alcohol) was stirred at room temperature until completion of the reaction (monitored by TLC, normally less than 2 h). The mixture was filtered, the resin

was washed with methylene chloride, and the combined filtrate and organic washings were concentrated under reduced pressure to yield the diastereomeric aldehydes (quantitative yield) as oils. Further purification was unnecessary, and the products were directly subjected to the next step. **54**: $[\alpha]^{25}_D = +14.6$ (*c* = 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.69 (1H, s, H-1), 7.54 (2H, t, *J* = 7.5 Hz), 7.38 (2H, t, *J* = 7.5 Hz), 7.29 (1H, t, *J* = 7.5 Hz), 6.03 (1H, s, OH), 4.50 (1H, s, H-3), 4.37 (1H, dq, *J* = 9.6, 6.2 Hz, H-7), 3.74 (1H, dd, *J* = 9.6, 2.7 Hz, H-6), 3.66 (1H, d, *J* = 3.4 Hz, H-4), 3.57 (3H, s, OCH_3), 3.27 (1H, t, *J* = 3.4 Hz, H-5), 1.19 (3H, d, *J* = 6.2 Hz, H-8), 0.91 (9H, s), 0.81 (9H, s), 0.09 (3H, s), 0.08 (3H, s), −0.22 (3H, s), −0.26 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.29 (C-1), 138.29, 128.87, 128.10, 126.04, 84.59 (C-2), 82.62 (C-3), 81.84 (C-5), 71.52 (C-6), 69.49 (C-7), 67.93 (C-4), 60.23 (OCH_3), 25.97, 25.79, 19.00, 18.17, 17.90, −3.87, −4.61, −4.93, −5.04; ESI MS (calcd for $C_{27}H_{48}O_6Si_2$, 524) *m*/*z* (relative intensity) 525 ($M + H^+$, 92), 526 ($M + H^+$, 36), 542 ($2M + NH_4^+$, 100), 543 ($2M + NH_4^+$, 34). **55**: $[\alpha]^{25}_D = +37.6$ (*c* = 0.85, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.53 (1H, s, H-1), 7.57 (2H, d, *J* = 7.5 Hz), 7.37 (2H, t, *J* = 7.5 Hz), 7.29 (1H, t, *J* = 7.5 Hz), 4.34 (1H, d, *J* = 2.7 Hz, H-3), 4.14 (1H, quintet, *J* = 6.8 Hz, H-7), 4.08 (1H, t, *J* = 3.8 Hz, H-4), 3.79 (1H, dd, *J* = 7.5, 2.7 Hz, H-6), 3.56 (3H, s, OCH_3), 3.38 (1H, dd, *J* = 4.8, 2.7 Hz, H-5), 1.00 (3H, d, *J* = 6.8 Hz, H-8), 0.91 (9H, s), 0.90 (9H, s), 0.13 (3H, s), 0.10 (3H, s), 0.09 (3H, s), 0.07 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.05 (C-1), 137.07, 128.57, 127.91, 126.58, 83.92 (C-2), 82.22 (C-5), 80.99 (C-3), 71.42 (C-6), 70.31 (C-7), 70.17 (C-4), 59.50 (OCH_3), 26.09, 25.99, 18.23, 18.21, 17.69, −4.00, −4.30, −4.54, −4.60.

(2*R*)-Methyl-3,7-anhydro-2-phenyl-4,6-bis-*O*-*tert*-butyldimethylsilyl-5-*O*-methyl-8-deoxy-α-D-altro-octitolate (56) and (2*S*)-Methyl-3,7-anhydro-2-phenyl-4,6-bis-*O*-*tert*-butyldimethylsilyl-5-*O*-methyl-8-deoxy-α-D-altro-octitolate (57).[40] The aldehyde **54** or **55** was dissolved in MeOH (35 mL/mmol of aldehyde) and cooled at 0 °C (ice bath). Iodine (3 equiv) was added, followed by dropwise addition of a KOH solution in methanol (1.2 M, 8 equiv). The mixture was stirred at low temperature for 15 min and then from 0 °C to room temperature for 30 min. The reaction was quenched by addition of solid ammonium chloride, and the solvent was removed under reduced pressure. An extraction with EtOAc/saturated NH_4Cl yielded the product **56** or **57**, which can be directly employed in the next step. Otherwise, analytically pure sample could be obtained via column chromatography (SiO_2, EtOAc 5%, petroleum ether). **56**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (2H, d, *J* = 7.6 Hz), 7.36 (2H, t, *J* = 7.6 Hz), 7.29 (1H, t, *J* = 7.6 Hz), 5.80 (1H, s, OH), 4.60 (1H, broad s, H-3), 4.37 (1H, dq, *J* = 8.9, 6.3 Hz, H-7), 3.77 (3H, s, CO_2CH_3), 3.76 (1H, dd, partially covered by s at 3.77 ppm, *J* = 2.6 Hz, H-6), 3.69 (1H, dd, *J* = 3.2, 1.3 Hz, H-4), 3.55 (3H, s, OCH_3), 3.26 (1H, t, *J* = 3.2 Hz, H-5), 1.21 (3H, d, *J* = 6.3 Hz, H-8), 0.90 (9H, s), 0.80 (9H, s), 0.09 (3H, s), 0.07 (3H, s), −0.22 (3H, s), −0.34 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.09 (C-1), 139.83, 128.62, 128.12, 126.26, 83.21 (C-3), 82.55 (C-2), 82.09 (C-5), 71.85 (C-6), 69.82 (C-7), 67.93 (C-4), 60.20 (OCH_3), 53.02 (CO_2CH_3), 25.97, 25.86, 18.84, 18.16, 17.91, −3.81, −4.64, −4.89, −5.07; ESI MS (calcd for $C_{28}H_{50}O_7Si_2$, 554) *m*/*z* (relative intensity) 555 ($M + H^+$, 100), 556 ($M + H^+$, 43). **57**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (2H, d, *J* = 7.6 Hz), 7.34 (2H, t, *J* = 7.6 Hz), 7.26 (1H, covered by $CHCl_3$ at 7.26 ppm), 6.05 (1H, broad s, OH), 4.49 (1H, s, H-3), 4.32 (1H, dq, *J* = 8.9, 6.3 Hz, H-7), 4.07 (1H, d, *J* = 3.2 Hz, H-4), 3.76 (1H, dd, *J* = 8.9, 3.2 Hz, H-6), 3.73 (3H, s, CO_2CH_3), 3.62 (3H, s, OCH_3), 3.41 (1H, t, *J* = 3.2 Hz, H-5), 0.99, (3H, d, *J* = 6.3 Hz, H-8), 0.92 (9H, s), 0.91 (9H, s), 0.16 (3H, s), 0.12 (3H, s), 0.09 (3H, s), 0.07 (3H, s).

(2*R*)-Methyl-3,7-anhydro-2-phenyl-5-*O*-methyl-8-deoxy-α-D-altro-octitolate (2) and (2*S*)-Methyl-3,7-anhydro-2-phenyl-5-*O*-methyl-8-deoxy-α-D-altro-octitolate (3). To a solution of *C*-glycoside **56** or **57** dissolved in THF (1 mL per 0.01 mmol of starting material) in the presence of AcOH (0.5 equiv) was added tetrabutylammonium fluoride (1 M in THF, ca. 3 equiv), and the mixture was stirred at room temperature until TLC indicated completion of the reaction. The solvent was removed under reduced pressure, and the product **2** or **3** was purified by column chromatography (SiO_2, petroleum ether, EtOAc 50%). The yield was typically >93%. **2**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (2H, d, *J* = 7.0 Hz), 7.39 (2H, t, *J* = 7.0 Hz), 7.32 (1H, t, *J* = 7.0 Hz), 4.37 (1H, d, *J* = 9.2 Hz, H-3), 4.27 (1H, dq, *J* = 7.0, 1.3 Hz, H-7), 4.13 (1H, t, *J* = 9.1 Hz, H-4), 3.89 (1H, dd, *J* = 3.2, 1.9 Hz, H-6), 3.80 (3H, s, CO_2CH_3), 3.44 (3H, OCH_3), 3.38 (1H, dd, *J* = 8.9, 3.2 Hz, H-5), 1.32 (3H, d, *J* = 7.0 Hz, H-8); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.68 (C-1), 137.51, 128.71, 128.62, 126.11, 80.84 (C-5), 79.96 (C-2), 77.05 (C-3), 73.48 (C-7), 69.16 (C-6), 67.39 (C-4), 58.12 (OCH_3), 53.40 (CO_2CH_3), 15.14 (C-8); ESI MS (calcd for $C_{16}H_{22}O_7$, 326) *m*/*z* (relative intensity) 349 ($M + Na^+$, 100), 350 ($M + Na^+$, 19), 675 ($2M + Na^+$, 38), 676 ($2M + Na^+$, 15). **3**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (2H, d, *J* = 7.6 Hz), 7.31 (2H, t, *J* = 7.6 Hz), 7.24 (1H, t, *J* = 7.6 Hz), 4.47 (1H, d, *J* = 9.5 Hz, H-3), 4.27 (1H, t, *J* = 9.5 Hz, H-4), 3.85 (2H, broad s, H-6 and H-7), 3.69 (3H, s, CO_2CH_3), 3.59 (3H, s, OCH_3), 3.48 (1H, dd, *J* = 9.5, 3.1 Hz, H-5), 1.12 (3H, d, *J* = 5.7 Hz, H-8); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.27 (C-1), 140.68, 128.04, 127.61, 126.35, 81.61 (C-5), 78.56 (C-2), 75.59 (C-3), 73.43 (C-7), 69.85 (C-6), 67.09 (C-4), 58.10 (OCH_3), 53.16 (CO_2CH_3), 14.54 (C-8); ESI MS (calcd for $C_{16}H_{22}O_7$, 326) *m*/*z* (relative intensity) 349 ($M + Na^+$, 100), 350 ($M + Na^+$, 19), 675 ($2M + Na^+$, 38), 676 ($2M + Na^+$, 14).

(2*R*)-Methyl-3,7-anhydro-2-phenyl-2,4-*O*-benzylidene-5-*O*-methyl-8-deoxy-α-D-altro-octitolate (58). A solution of *C*-glycoside **2** (5 mg, 0.015 mmol), benzaldehyde dimethyl acetal (0.07 mL), and *p*-toluenesulfonic acid (1 crystal), dissolved in acetonitrile (1.5 mL), was stirred at room temperature for 3 h. Acidic resin was added, and the mixture was filtered. The solvent was removed under reduced pressure: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (2H, d, *J* = 8.3 Hz), 7.60 (2H, d, *J* = 8.3 Hz), 7.43−7.29 (6H, m), 6.13 (1H, s, H-9), 4.57 (1H, t, *J* = 9.5 Hz, H-4), 4.39 (1H, q, *J* = 8.3 Hz, H-7), 3.94 (1H, broad s, H-6), 3.78−3.75 (4H, m, H-3 and CO_2CH_3), 3.58−3.55 (4H, m, H-5 and OCH_3), 1.17 (3H, d, *J* = 7 Hz, H-8).

(2*S*)-Methyl-3,7-anhydro-2-phenyl-2,4-*O*-benzylidene-5-*O*-methyl-8-deoxy-α-D-altro-octitol (59). To a solution of **58** (5 mg, 0.012 mmol), in CH_2Cl_2 (1.5 mL) was added DIBAL-H (1 M in hexanes, 28 μL) at −78 °C under nitrogen. The mixture was stirred at −78 °C for 1.5 h and then at room temperature for 1.5 h. EtOAc (0.2 mL) was added, and the mixture was stirred for 30 min. The solvent was removed under reduced pressure, and the product was purified by column chromatography (SiO_2, petroleum ether, EtOAc 50%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (2H, d, *J* = 7.6 Hz), 7.62 (2H, d, *J* = 7 Hz), 7.44−7.34 (5H, m), 7.29 (1H, t, *J* = 7 Hz), 6.22 (1H, s, H-9), 4.56 (1H, dd, *J* = 12.7, 5.7 Hz, H-1a), 4.48 (1H, t, *J* = 10 Hz, H-4), 4.35 (1H, t, *J* = 7.6 Hz, H-7), 4.31 (1H, dd, *J* = 12.7, 7.0 Hz, H-1b), 3.93 (1H, d, *J* = 3.2 Hz, H-6), 3.76 (1H, d, *J* = 10 Hz, H-3), 3.56 (1H, s, OCH_3), 3.52 (1H, dd, *J* = 9.5, 3.2 Hz, H-5), 1.69 (1H, t, *J* = 7 Hz, OH-1), 1.16 (3H, d, *J* = 7.6 Hz, H-8).

(2*R*)-Methyl-3,7-anhydro-2-phenyl-2,4-*O*-(4-bromobenzylidene)-5-*O*-methyl-8-deoxy-α-D-altro-octitolate (60) and (2*S*)-Methyl-3,7-anhydro-2-phenyl-2,4-*O*-(4-bromobenzylidene)-5-*O*-methyl-8-deoxy-α-D-altro-octitolate (61). A solution of *C*-glycoside **2** or **3** (5 mg, 0.015 mmol), *p*-bromobenzaldehyde dimethyl acetal (8 μL, 0.039 mmol), and *p*-toluenesulfonic acid (1 crystal), dissolved in acetonitrile (1.5 mL), was stirred at room temperature for 2 h. Triethylamine (0.2 mL) was added, and the solvent was removed under reduced pressure. The product **60** or **61** (quantitative yield) was purified by column chromatography (SiO_2, petroleum ether, EtOAc 40%). **60**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (2H, dd, *J* = 8.3, 1.9 Hz), 7.53 (2H, d, *J* = 8.3 Hz), 7.47 (2H, d, *J* = 8.3 Hz), 7.37−7.31 (3H, m), 6.12 (1H, s, H-9), 4.53 (1H, t, *J* = 9.5 Hz, H-4), 4.40 (1H, q, *J* = 7.0 Hz, H-7), 3.94 (1H, broad s, H-6),

3.78 (3H, s, CO_2CH_3), 3.77 (1H, d, H-3, partially overlapped with s at 3.78 ppm), 3.56 (3H, s, OCH_3), 3.55 (1H, dd, J = 3.2 Hz, H-5, partially overlapped with s at 3.56 ppm), 2.62 (1H, d, J = 2.5 Hz, OH), 1.19 (3H, d, J = 7.0 Hz, H-8); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.28 (C-1), 139.19, 136.72, 131.63, 128.46, 128.34, 128.22, 125.95, 97.86 (C-9), 81.38 (C-2), 78.12 (C-5), 75.55 (C-4), 74.43 (C-7), 72.17 (C-3), 70.76 (C-6), 58.79 (OCH_3), 52.84 (CO_2CH_3), 14.74 (C-8). **61**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (2H, d, J = 8.9 Hz), 7.49 (2H, d, J = 8.3 Hz), 7.43−7.33 (5H, m), 5.57 (1H, s, H-9), 4.47 (1H, q, J = 7.0 Hz, H-7), 4.44−4.38 (2H, m, H-3 and H-4), 3.99 (1H, d, J = 1.9 Hz, H-6), 3.72 (3H, s, CO_2CH_3), 3.62 (1H, dd, J = 8.3, 3.2 Hz, H-5), 3.53 (3H, s, OCH_3), 2.60 (1H, s, OH), 1.38 (3H, d, J = 7.0 Hz, H-8); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.53 (C-1), 136.41, 135.67, 131.62, 129.11, 128.87, 128.78, 128.27, 123.35, 95.86 (C-9), 81.89 (C-2), 78.21 (C-5), 74.26 (C-3 or C-7), 74.06 (C-3 or C-7), 71.36 (C-4), 70.72 (C-6), 58.90 (OCH_3), 53.26 (CO_2CH_3), 14.56 (C-8).

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Supporting Information Available: Table outlining reaction conditions employed in the hydroboration of *exo*-glycal, variable temperature ^{13}C NMR spectra of the compound **39**, NOESY spectrum of **59**, ^{1}H and ^{13}C NMR spectra, and CD spectra of **60**, **61**, and **62**. This material is available free of charge via the Internet at http://pubs.acs.org.

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