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# Novel synthesis of 3-acetamido-3-deoxy- and 4-acetamido-4-deoxy-D-altrose from levoglucosenone using regioselective *cis*-oxyamination

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**Abstract**

Two rare amino sugars, 3-acetamido-3-deoxy- and 4-acetamido-4-deoxy-D-altrose, were prepared from levoglucosenone (1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose) respectively by reduction of the carbonyl group, selective *cis*-oxyamination of the carbon–carbon double bond, detosylation of the *p*-toluenesulfonamido group, acetylation, acetolysis of the 1,6-anhydro bond, and finally deacetylation of the *O*-acetyl groups. The regioselectivity in *cis*-oxyamination of the carbon–carbon double bond of allylic alcohol obtained by reduction of levoglucosenone could be controlled by the choice of the protecting groups of the allylic hydroxyl group.

*Keywords:* Amino sugar; 3-Acetamido-3-deoxy-D-altrose; 4-Acetamido-4-deoxy-D-altrose; Levoglucosenone; *cis*-Oxyamination; Sharpless reagent

## 1. Introduction

Various amino sugars exist in Nature [1–3]. For example, D-glucosamine is an important subunit of macromolecules such as peptidoglycans in bacteria, chitin in fungi and insects, or glycoproteins in mammals [1]. Uncommon amino sugars are also found as constituents of secondary metabolites with, for example, antibacterial [4] or antiviral [5,6] pharmacological properties. Replacement of natural amino sugars by artificial ones as component parts of saccharides may endow compounds with new functions or greater biological activity.

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Aminodeoxy hexoses are usually synthesized from appropriate carbohydrates [7–9] and α-amino acids [10]. Although there have been several reports about the syntheses of 4-amino-4-deoxy-D-hexoses [3,11–14] the synthesis of 4-acetamido-4-deoxy-D-altrose (**7**) has not been reported. In this paper, we describe novel ways for the synthesis of two rare amino sugars, 3-acetamido-3-deoxy-D-altrose (**6**) [11] and **7** from levoglucosenone (1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose, **1**) [1], which is readily available by acidic pyrolysis of cellulose [15] and seemed to be an ideal starting material [16,17].

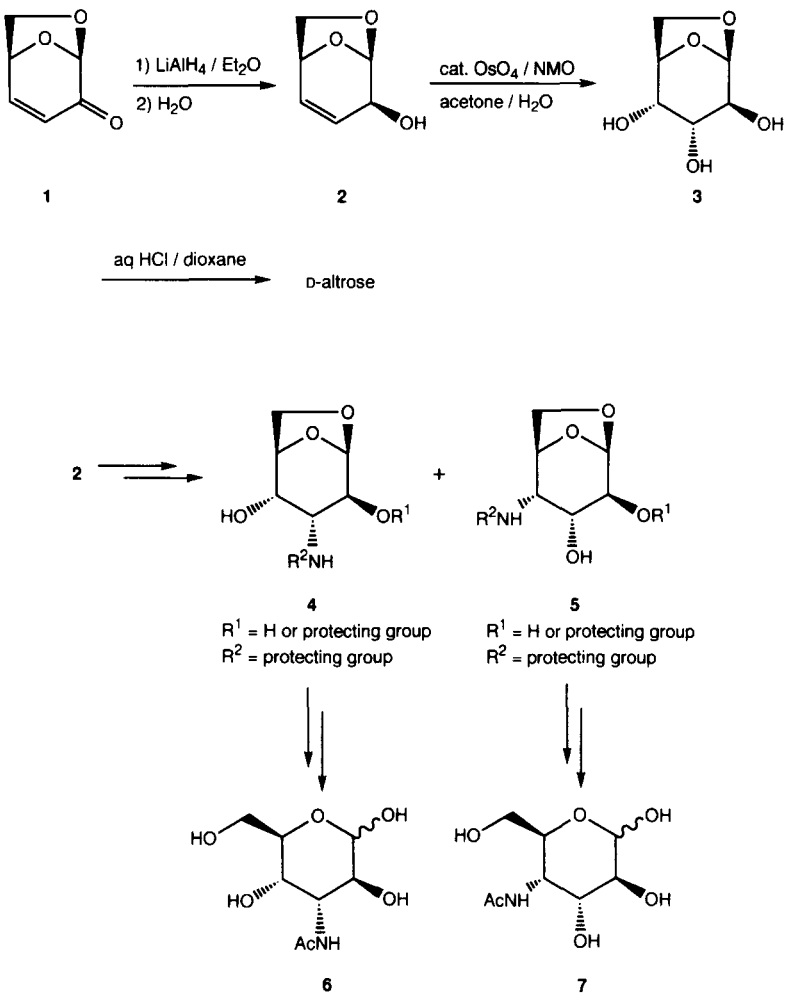
We have previously reported the novel synthesis of D-altrose via D-altrosan (1,6-anhydro-β-D-altropyranose, **3**) [16] by reduction of the carbonyl group of **1**, *cis*-dihydroxylation of the carbon–carbon double bond of 1,6-anhydro-3,4-dideoxy-β-D-*threo*-hex-3-enopyranose (**2**), and cleavage of the 1,6-anhydro bond of **3**. *cis*-Dihydroxylation of **2** with a catalytic amount of osmium tetroxide stereoselectively afforded only one isomer **3**. It was anticipated that *cis*-oxyamination (instead of *cis*-dihydroxylation) of the carbon–carbon double bond of **2** (or 2-*O*-protected derivatives) with the Sharpless reagent [18] would afford two amino-D-altrosan derivatives **4** and **5**, from which **6** and **7** could be derived, respectively (Scheme 1). The regio- and stereo-selectively controlled *cis*-oxyamination allows us to preferentially obtain one of the desired two regioisomers (**6** and **7**). A reduction of the carbonyl group of **1** with lithium aluminium hydride stereoselectively gave **2** in 70.3% yield [15,16]. Shafizadeh and Chin [15] erroneously reported the configurational assignments of two epimers obtained by the reduction of **1** with $LiAlH_4$. The correct assignment was made by Brimacombe and co-workers [19].

## 2. Results and discussion

The introduction of an amino group and hydroxyl group to the carbon–carbon double bond of **2** is achieved by the *cis*-oxyamination reagent (Sharpless reagent) [18] generated in situ from catalytic osmium tetroxide and chloramine-T. Regarding the selectivity of *cis*-oxyamination, we examined the effects of a protecting group on the allylic hydroxyl group on the 2-position of **2** using various 2-*O*-protected compounds (**8–13**) derived from **2**. *cis*-Oxyamination of **2** and **8–13** with catalytic osmium tetroxide and chloramine-T in *tert*-butyl alcohol–water, and further cleavage of the 2-*O*-protecting group of the product afforded a mixture of two regioisomers (**14** and **15**) and a *cis*-dihydroxylated produtct (D-altrosan, **3**) (Scheme 2). The ratio **14**:**15**:**3** was determined by a $^{13}C$ NMR spectral analysis of the mixture [2]. The results are summarized in Table 1. Regarding the regioselectivity between **14** and **15**, the *cis*-oxyamination of 2-*O*-acyl-protected **8–11** gave higher 3-*p*-toluenesulfonamido selectivities than those of **2**, **12**, and **13**, which had no acyl group. The highest 3-*p*-tolenesulfonamido selectivity was obtained by the *cis*-

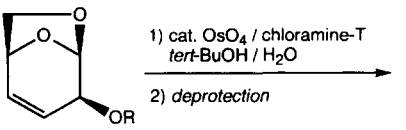
[1] Levoglucosenone (**1**) is available from Yuki Gosei Kogyo Co., Ltd., Hirakawa-cho CH BLDG. 3-24 Hirakawa-cho 2 chome, Chiyoda-ku, Tokyo 102, Japan.

[2] Isolated **14** and **15** were obtained according to the procedures shown in Schemes 3 and 4 (see the related text), respectively, and their $^{13}C$ NMR spectra were recorded. The $^{13}C$ NMR spectral data of **3** was obtained by measurement of our authentic sample [16]. Since **20** and **26**, derived from **14** and **15**, were identified by comparison with authentic data, the structures of **14** and **15** were thus determined.

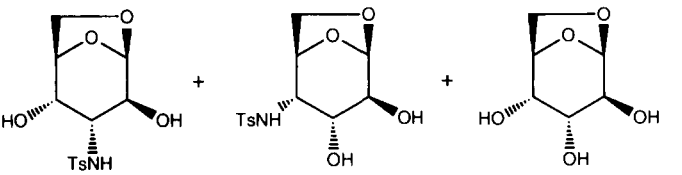



Scheme 1.

oxyamination of the 2-*O*-pivaloyl derivative **9**. On the other hand, **13** was converted exclusively into the 4-*p*-toluenesulfonamide **15**. In previous reports [18,20], the mechanism and regioselectivities in the *cis*-oxyamination by the Sharpless reaction have been discussed on the basis of stereochemistry and electronic theory related to the electron densities or the HOMO–LUMO interaction. It is thought that the combination of the steric and electronic factors may influence the regioselectivities and differ in (the structure of) substrates. So it is difficult to interpret our results precisely on the basis of the results and discussions of previous studies. In any event, the regioselectivity in the *cis*-oxyamination of the carbon–carbon double bond of allylic alcohol **2** could be controlled by the protecting groups of the allylic hydroxyl group of **2**. Our methodology is expected to be applicable to the *cis*-oxyamination of various allylic alcohols.




**2** R = H
**8** R = Ac
**9** R = pivaloyl
**10** R = Bz
**11** R = 3,5-dinitrobenzoyl
**12** R = Bn
**13** R = *tert*-butyldiphenylsilyl




**14** **15** **3**

Scheme 2.

The mixture of **14** and **15** could not be separated by column chromatography. The mixtures obtained by the oxyamination of **9** and **13** were purified by column chromatography to afford pure major oxyaminated components (**16** derived from **9**, and **23** derived from **13**) before the following cleavage of the 2-*O*-protecting groups. Schemes 3 and 4 show the synthesis of **6** and **7** from **9** and **13**, respectively.

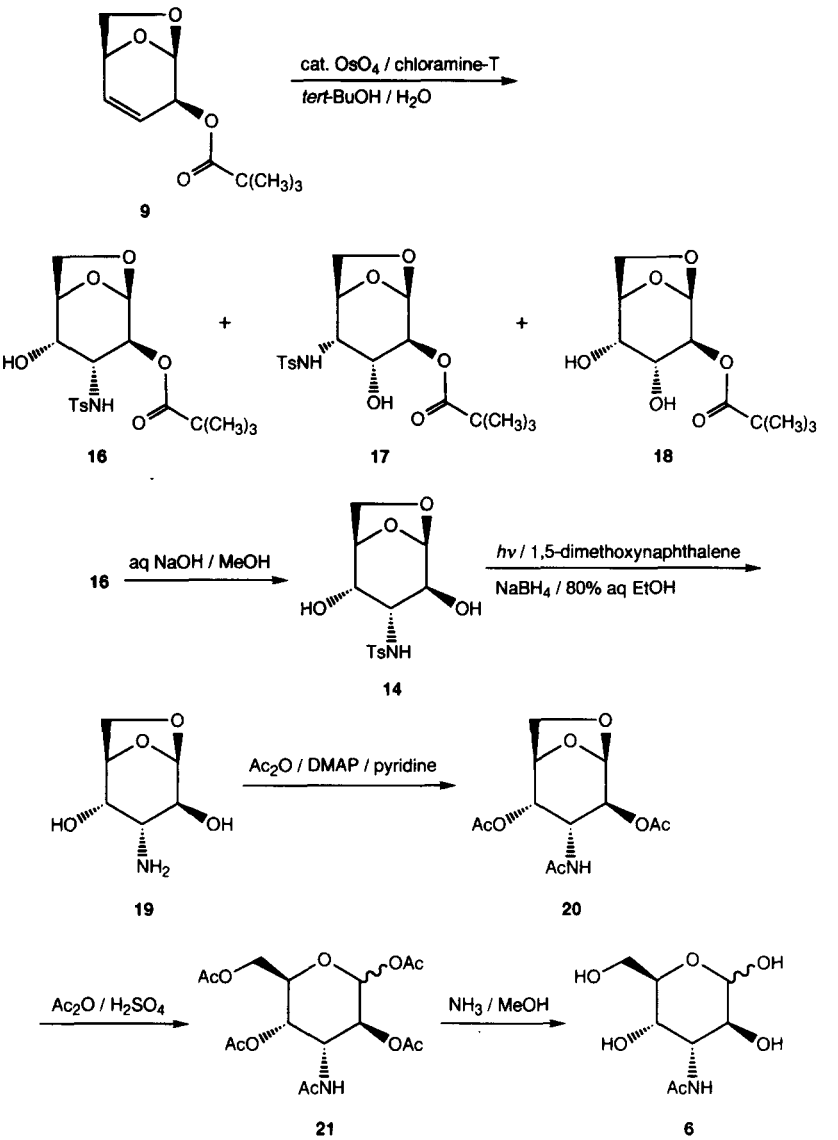
Table 1
*cis*-Oxyamination of allylic alcohol **2** and the 2-*O*-protected derivatives with the Sharpless reagent [a] and further cleavage of the 2-*O*-protecting group

| 2-*O*-Protected allylic alcohol | | Ratio of products obtained [b] | | |
|---|---|---|---|---|
| | | 3-aminated (**14**) | 4-aminated (**15**) | dihydroxylated (**3**) |
| Non-protected | (**2**) | 1 | 1 | 2 |
| Acetyl | (**8**) | 3 | 1 | 4.5 |
| Pivaloyl | (**9**) | 3.5 | 1 | 2 |
| Benzoyl | (**10**) | 3 | 1 | 5 |
| 3,5-Dinitrobenzoyl [c] | (**11**) | 2 | 1 | 22 |
| Benzyl | (**12**) | 1 | 1 | 1 |
| *tert*-Butyldiphenylsilyl | (**13**) | not detected | 2.5 | 1 |

[a] *cis*-Oxyamination was carried out under the following conditions: 1.00 mmol of the substrate, 0.08 mmol of $OsO_4$ (in *tert*-BuOH, 0.10 mol $dm^{-3}$), 1.25 mmol of chloramine-T·$3H_2O$, 9.6 mL of 1:1 *tert*-BuOH–$H_2O$, room temperature, 18 h.

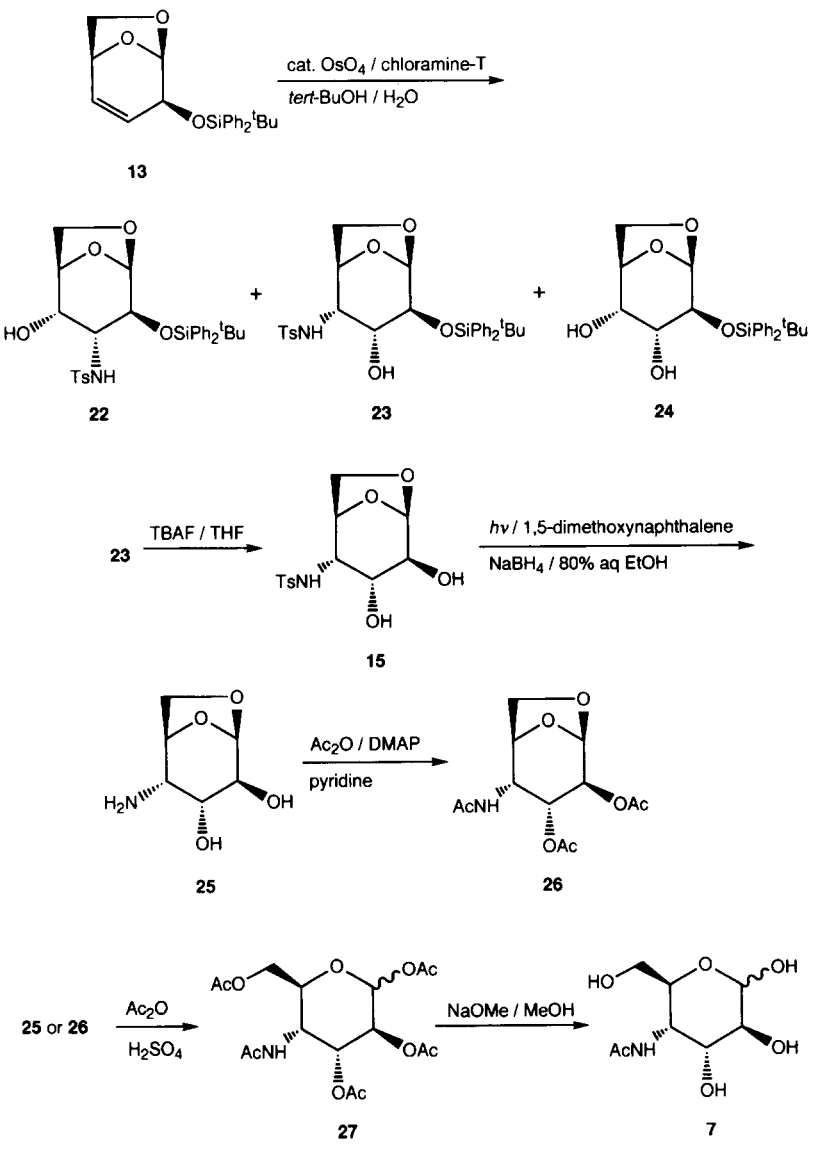
[b] Determination based on the intensities of the peaks (except for those of the *p*-toluenesulfonamido group) in the 75-MHz $^{13}C$ NMR spectra in $CD_3OD$.

[c] *cis*-Oxyamination of **11** was carried out using 14.4 mL of 1:1 acetone–$H_2O$ instead of *tert*-BuOH–$H_2O$.




Scheme 3.

*cis*-Oxyamination of **9** gave pure **16** in 53.4% yield. The cleavage of the pivaloyl group of **16** with sodium hydroxide in methanol and water gave **14** in 83.9% yield. The photochemical detosylation [21] of **14** in the presence of 1,5-dimethoxynaphthalene and sodium borohydride in aqueous ethanol afforded 3-amino-1,6-anhydro-3-deoxy-β-D-altropyranose (**19**) in 82.8% yield. The acetamido sugar **6** was prepared from **19** using the procedure of Coxon and Hough [11]. Acetylation of **19** with acetic anhydride in pyridine afforded **20** which, on acetolysis of the 1,6-anhydro bond with sulfuric acid as catalyst and




Scheme 4.

further deacetylation with methanolic ammonia, yielded an $\alpha,\beta$-anomeric mixture **6**. These procedures are shown in Scheme 3.

On the other hand, **7** was derived from **13** (Scheme 4). *cis*-Oxyamination of **13** gave pure **23** in 74.2% yield. Cleavage of the *tert*-butyldiphenylsilyl group of **23** with tetrabutylammonium fluoride in tetrahydrofuran quantitatively afforded **15**. The photochemical detosylation [21] of **15** afforded 4-amino-1,6-anhydro-4-deoxy-$\beta$-D-altropyranose (**25**) in 87.2% yield. Treatment of **25** with acetic anhydride in pyridine gave the triacetylated

product **26** in 70.1% yield. Acetolysis of the 1,6-anhydro bond of **26** with sulfuric acid as catalyst [11] gave **27** in 73.1% yield. Compound **27** was also prepared directly from **25** by an acetolysis similar to the above. Treatment of **27** with sodium methoxide in methanol gave an $\alpha,\beta$-anomeric mixture of **7** in 98.6% yield (33.2% overall yield, seven steps from **1**).

In conclusion, we have developed novel methods for preparing 3-acetamido-3-deoxy- and 4-acetamido-4-deoxy-D-altrose (**6** and **7**) from levoglucosenone (**1**) using regioselectively, controlled *cis*-oxyamination.

## 3. Experimental

*General methods.*—All melting points are uncorrected. Optical rotations were measured with a Jasco DIP-370 polarimeter. IR spectra were measured using a Jasco FTIR-5000 spectrophotometer. $^1$H NMR spectra were recorded at 300 MHz and $^{13}$C NMR spectra at 75 MHz, with $Me_4Si$ as an internal standard on a Bruker AC 300P spectrometer. Column chromatography was performed on Silica Gel 60 (70–230 mesh, E. Merck No. 7734).

*2-O-Acetyl-1,6-anhydro-3,4-dideoxy-β-*D-threo-*hex-3-enopyranose* (**8**).—A solution of **2** (1.28 g, 10.0 mmol) [15,16,19], 1.2 mL of $Ac_2O$, 1.8 mL of $Et_3N$, and a catalytic amount of 4-dimethylaminopyridine in 10 mL of $CH_2Cl_2$ was stirred overnight at room temperature under Ar. The mixture was poured into ice–water and extracted three times with $CH_2Cl_2$. The organic layer was dried (anhyd $MgSO_4$), and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (1:1 hexane–EtOAc), followed by distillation under reduced pressure [bp 100–102°C (2 torr)] to afford 1.42 g (83.3%) of **8**; $n_D^{24}$ 1.4786; $[\alpha]_D^{27}$ −40.7° (*c* 1.3, $CHCl_3$); IR (neat): 2972 (m), 2896 (m), 2364 (w), 1736 (s), 1477 (w), 1437 (w), 1375 (s), 1309 (w), 1241 (s), 1168 (m), 1127 (s), 1077 (m), 1046 (s), 984 (s), 949 (w), 901 (s), 886 (s), 861 (m), 839 (m), 803 (m), 725 (w), 654 (m), 619 (w), 603 (w), 520 (w) and 458 cm$^{-1}$ (m); $^1$H NMR ($CDCl_3$): δ 6.22 (ddd, 1 H, $J_{4,3}$ 10.6, $J_{4,5}$ 4.2, $J_{4,2}$ 1.5 Hz, H-4), 5.66–5.61 (m, 2 H, H-2 and H-3), 5.52 (br, 1 H, H-1), 4.70 (dd, 1 H, $J_{5,6'}$ 4.3, $J_{5,4}$ 4.2 Hz, H-5), 3.99 (d, 1 H, $J_{6,6'}$ 6.6 Hz, H-6), 3.81 (dd, 1 H, $J_{6',6}$ 6.6, $J_{6',5}$ 4.3 Hz, H-6'), 2.14 (s, 3 H, OAc). Anal. Calcd for $C_8H_{10}O_8$: C, 56.47; H, 5.92. Found: C, 56.24; H, 5.83.

*1,6-Anhydro-3,4-dideoxy-2-O-pivaloyl-β-*D-threo-*hex-3-enopyranose* (**9**).—To a stirred, ice-cooled solution of **2** (1.28 g, 10.0 mmol) in 50 mL of pyridine was added 4.82 g (40.0 mmol) of pivaloyl chloride. The mixture was stirred for 3 h at ca. 60–70°C under Ar. After cooling to room temperature, the mixture was slowly poured into ice–water and extracted three times with $Et_2O$. The organic layer was washed with satd aq $CuSO_4$ (four times) and water (twice), and then dried (anhyd $MgSO_4$). The solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (5:1 hexane–EtOAc), followed by distillation under reduced pressure [bp 120–122°C (4 torr)] to afford 2.01 g (94.5%) of **9**; $n_D^{22}$ 1.4616; $[\alpha]_D^{24}$ −27.9° (*c* 0.75, $CHCl_3$); IR (neat): 2976 (s), 2892 (m), 2334 (w), 1729 (s), 1543 (w), 1483 (w), 1462 (m), 1400 (m), 1367 (m), 1311 (m), 1278 (s), 1158 (s), 1125 (s), 1077 (w), 1040 (s), 984 (s), 944 (w), 888 (s), 859 (w), 841 (m), 804 (m), 772 (w) 725 (m), 675 (w), 654 (w), 590 (w), 476 (w), and 456 cm$^{-1}$ (w); $^1$H NMR ($CDCl_3$): δ 6.20 (dddd, 1 H, $J_{4,3}$ 9.8, $J_{4,5}$

4.3, $J_{4,1}$ 1.4, $J_{4,1}$ 0.4 Hz, H-4), 5.65 (dd, 1 H, $J_{2,1}$ 2.2, $J_{2,3}$ 2.2 Hz, H-2), 5.60 (ddd, 1 H, $J_{3,4}$ 9.8, $J_{3,1}$ 2.2, $J_{3,2}$ 2.2 Hz, H-3), 5.47–5.44 (br, 1 H, H-1), 4.69 (dd, 1 H, $J_{5,4}$ 4.3, $J_{5,6'}$ 4.2 Hz, H-5), 3.97 (d, 1 H, $J_{6,6'}$ 6.5 Hz, H-6), 3.79 (ddd, 1 H, $J_{6',6}$ 6.5, $J_{6',5}$ 4.2, $J_{6',1}$ 1.1 Hz, H-6'), 1.24 (s, 9 H, pivaloyl). Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.26; H, 7.49.

*1,6-Anhydro-2-*O*-benzoyl-3,4-dideoxy-β-*D*-*threo*-hex-3-enopyranose* (**10**).—To a stirred solution of **2** (0.64 g, 5.00 mmol) and 1.7 mL of $Et_3N$ in 10 mL of $CH_2Cl_2$ was slowly added 0.7 mL of benzoyl chloride at 0°C. The mixture was stirred for 1.5 h at room temperature under Ar. Then it was slowly poured into ice–water and extracted three times with $CHCl_3$. The organic layer was dried (anhyd $MgSO_4$), and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (6:1 → 5:1 hexane–EtOAc) to give 1.09 g (94.0%) of **10** that was recrystallized from hexane–$CH_2Cl_2$; mp 119–120°C; $[\alpha]_D^{29}$ +27.3° (*c* 0.55, $CHCl_3$); IR (KBr): 2990 (w), 2952 (w), 2922 (w), 2890 (w), 1715 (s), 1603 (w), 1584 (w), 1495 (w), 1475 (w), 1458 (m), 1394 (w), 1365 (m), 1336 (m), 1276 (s), 1187 (m), 1176 (m), 1118 (s), 1073 (m), 1052 (m), 1027 (s), 994 (m), 973 (m), 936 (w), 890 (m), 870 (s), 822 (w), 801 (m), 716 (s), 661 (m), 543 (w), 482 (m), 458 (m) and 439 $cm^{-1}$ (w); $^1H$ NMR ($CDCl_3$): δ 8.09 (dd, 2 H, *J* 7.2, *J* 0.7 Hz, *o*-H of Ph), 7.57 (ddd, 1 H, *J* 7.8, *J* 7.2, *J* 0.7 Hz, *p*-H of Ph), 7.44 (dd, 2 H, *J* 7.8, *J* 0.7 Hz, *m*-H of Ph), 6.26 (ddd, 1 H, $J_{4,3}$ 9.6, $J_{4,5}$ 4.2, $J_{4,2}$ 0.7 Hz, H-4), 5.79–5.74 (m, 3 H, H-1, H-2, and H-3), 4.74 (dd, 1 H, $J_{5,6'}$ 4.2, $J_{5,4}$ 4.2 Hz, H-5), 4.03 (d, 1 H, $J_{6,6'}$ 6.6 Hz, H-6), 3.84 (dd, 1 H, $J_{6',6}$ 6.6, $J_{6',5}$ 4.2 Hz, H-6'). Anal. Calcd for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21. Found: C, 67.20; H, 5.25.

*1,6-Anhydro-2-*O*-(3,5-dinitrobenzoyl)-3,4-dideoxy-β-*D*-*threo*-hex-3-enopyranose* (**11**). —To a stirred solution of **2** (1.28 g, 10.0 mmol) and 1.7 mL of $Et_3N$ in 20 mL of $CH_2Cl_2$ was added 2.84 g (12.0 mmol) of 3,5-dinitrobenzoyl chloride at 0°C. The mixture was stirred for 3 h at room temperature under Ar. Then it was slowly poured into ice–water and extracted three times with $CHCl_3$. The organic layer was dried (anhyd $MgSO_4$), and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (2:1 hexane–EtOAc) to afford 2.96 g (92.0%) of **11** that was recrystallized from hexane–$CHCl_3$; mp 160–162°C; $[\alpha]_D^{26}$ +17.5° (*c* 0.47, $CHCl_3$); IR (KBr): 3102 (m), 2990 (w), 2944 (w), 2896 (m), 2364 (m), 2344 (m), 1727 (s), 1630 (m), 1539 (s), 1460 (m), 1394 (w), 1346 (s), 1315 (s), 1292 (m), 1276 (s), 1168 (m), 1127 (m), 1079 (m), 1056 (w), 1025 (m), 980 (m), 924 (m), 915 (m), 888 (m), 864 (m), 849 (w), 816 (m), 804 (m), 770 (m), 731 (m), 719 (m), 679 (m), 520 (w), 482 (w), 456 (w), and 435 $cm^{-1}$ (w); $^1H$ NMR ($CDCl_3$): δ 9.25 (dd, 1 H, *J* 2.1, *J* 2.1 Hz, *p*-H of Ph), 9.20 (d, 2 H, *J* 2.1 Hz, *o*-H of Ph), 6.37 (ddd, 1 H, $J_{4,3}$ 9.8, $J_{4,5}$ 4.3, $J_{4,2}$ 0.7 Hz, H-4), 5.83–5.81 (m, 2 H, H-1 and H-2), 5.77 (ddd, 1 H, $J_{3,4}$ 9.8, $J_{3,2}$ 2.2, $J_{3,1}$ 2.2 Hz, H-3), 4.79 (dd, 1 H, $J_{5,6'}$ 4.3, $J_{5,4}$ 4.3 Hz, H-5), 4.05 (d, 1 H, $J_{6,6'}$ 6.7 Hz, H-6), 3.86 (dd, 1 H, $J_{6',6}$ 6.7, $J_{6',5}$ 4.3 Hz, H-6'). Anal. Calcd for $C_{13}H_{10}N_2O_8$: C, 48.46; H, 3.13; N, 8.69. Found: C, 48.46; H, 3.13; N, 8.69.

*1,6-Anhydro-2-*O*-benzyl-3,4-dideoxy-β-*D*-*threo*-hex-3-enopyranose* (**12**).—To a stirred, ice-cooled solution of 8 mL of $Me_2SO$ was slowly added 0.72 g (15.0 mmol) of NaH in oil (ca. 50%). To this mixture, **2** (1.28 g, 10.0 mmol) in 8 mL of $Me_2SO$ was added dropwise with stirring, followed by ice-cooling under Ar, and stirring for 1 h at room temperature. To this mixture, 3.42 g (20.0 mmol) of benzyl chloride was added

dropwise and stirred for 2 h at room temperature. The mixture was poured into ice–water and extracted with $Et_2O$. The organic layer was dried (anhyd $MgSO_4$), and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (4:1 hexane–EtOAc) to quantitatively afford 2.20 g of **12**; $[\alpha]_D^{24}$ −13.2° (*c* 1.69, $CHCl_3$); IR (neat): 3034 (w), 2954 (m), 2888 (m), 1497 (m), 1456 (m), 1386 (m), 1359 (m), 1307 (m), 1286 (m), 1251 (w), 1168 (m), 1127 (s), 1098 (s), 1056 (s), 1029 (m), 982 (s), 930 (m), 884 (s), 862 (m), 824 (m), 801 (m), 741 (m), 725 (m), 700 (m), 600 (w), and 455 $cm^{-1}$ (m); $^1H$ NMR ($CDCl_3$): δ 7.40–7.27 (m, 5 H, Ph), 6.10 (ddd, 1 H, $J_{4,3}$ 10.0, $J_{4,5}$ 4.1, $J_{4,2}$ 1.5 Hz, H-4), 5.71 (ddd, 1 H, $J_{3,4}$ 10.0, $J_{3,2}$ 2.2, $J_{3,1}$ 2.2 Hz, H-3), 5.56 (dd, 1 H, $J_{1,2}$ 2.2, $J_{1,3}$ 2.2 Hz, H-1), 4.68 (d, 2 H, *J* 1.4 Hz, $OCH_2$ of Bn), 4.64 (dd, 1 H, $J_{5,6'}$ 4.1, $J_{5,4}$ 4.1 Hz, H-5), 4.28 (br, 1 H, H-2), 3.98 (d, 1 H, $J_{6,6'}$ 6.5 Hz, H-6), 3.79 (ddd, 1 H, $J_{6',6}$ 6.5, $J_{6',5}$ 4.1, $J_{6',2}$ 1.2 Hz, H-6′). Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.48; H, 6.50.

*1,6-Anhydro-2-*O*-(*tert*-butyldiphenylsilyl)-3,4-dideoxy-β-*D*-*threo*-hex-3-enopyranose* (**13**).—To a stirred solution of **2** (1.28 g, 10.0 mmol) and 0.82 g (12.0 mmol) of imidazole in 20 mL of DMF was added 3.30 g (12.0 mmol) of *tert*-butylchorodiphenylsilane at room temperature. The mixture was stirred for 18 h at room temperature under Ar, at the end of which time it was slowly poured into ice–water and extracted three times with $Et_2O$. The organic layer was dried (anhyd $MgSO_4$), and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (4:1 hexane–EtOAc) to quantitatively afford 3.67 g of **13** as a colorless solid; mp 74.0–75.5°C; $[\alpha]_D^{26}$ −7.1° (*c* 1.3, EtOH); IR (KBr): 3074 (m), 3060 (w), 3040 (w), 3020 (w), 3004 (w), 2946 (s), 2886 (s), 2862 (s), 1984 (w), 1901 (w), 1847 (w), 1682 (w), 1636 (w), 1618 (w), 1591 (m), 1568 (w), 1489 (m), 1473 (s), 1431 (s), 1388 (s), 1365 (m), 1315 (s), 1288 (m), 1251 (m), 1183 (m), 1166 (m), 1110 (s), 1069 (w), 1048 (m), 1009 (w), 984 (s), 975 (w), 932 (m), 884 (s), 853 (s), 830 (s), 797 (m), 745 (m), 719 (s), 708 (s), 694 (s), 673 (m), 629 (m), 605 (m), 509 (s), 480 (s), and 447 $cm^{-1}$ (s); $^1H$ NMR ($CDCl_3$): δ 7.73–7.67 (m, 4 H, Ph), 7.43–7.35 (m, 6 H, Ph), 5.95 (ddd, 1 H, $J_{4,3}$ 9.9, $J_{4,5}$ 4.1, $J_{4,2}$ 1.4 Hz, H-4), 5.53 (ddd, 1 H, $J_{3,4}$ 9.9, $J_{3,1}$ 2.2, $J_{3,2}$ 2.1 Hz, H-3), 5.26 (dd, 1 H, $J_{1,2}$ 2.2, $J_{1,3}$ 2.2 Hz, H-1), 4.54 (dd, 1 H, $J_{5,6'}$ 4.1, $J_{5,4}$ 4.1 Hz, H-5), 4.52 (br, 1 H, H-2), 3.97 (d, 1 H, $J_{6,6'}$ 6.5 Hz, H-6), 3.76 (ddd, 1 H, $J_{6',6}$ 6.5, $J_{6',5}$ 4.1, $J_{6',2}$ 1.1 Hz, H-6′), 1.09 (s, 9 H, *tert*-butyl). Anal. Calcd for $C_{22}H_{26}O_3Si$: C, 72.09; H, 7.15. Found: C, 71.87; H, 7.10.

cis-*Oxyamination [18] of allylic alcohol* **2** *and the* 2-O-*protected derivatives* (**8–13**). —*General procedure.* To a stirred solution of 1.00 mmol of **2** or the 2-*O*-protected derivative in 4.8 mL of *tert*-BuOH was added a solution of 0.35 g (1.25 mmol) of chloramine-T · $3H_2O$ in 4.8 mL of $H_2O$ at room temperature. To this solution, 0.8 mL of a solution (0.1 mol $dm^{-3}$) of $OsO_4$ in *tert*-BuOH was added. The mixture was stirred for 18 h at room temperature, at the end of which time the solvent was evaporated under reduced pressure. The 2-*O*-protecting groups of the products of the residue were removed by appropriate procedures to give a mixture of **14**, **15**, and **3**. The ratio of these products was determined based on the intensities of the peaks (except those of the *p*-toluenesulfonamido group) in the 75-MHz $^{13}C$ NMR spectrum ($CD_3OD$) [20].

*1,6-Anhydro-3-deoxy-2-*O*-pivaloyl-3-*p*-toluenesulfonamido-β-*D*-altropyranose* (**16**). —To a stirred solution of **9** (15.7 g, 73.7 mmol) in 360 mL of *tert*-BuOH was added a

solution of 25.0 g (88.8 mmol) of chloramine-T · $3H_2O$ in 360 mL of $H_2O$ at room temperature. To this solution, 56.0 mL of a solution (0.1 mol $dm^{-3}$) of $OsO_4$ in *tert*-BuOH was added. The mixture was stirred for 18 h at room temperature. Then 3.50 g of $Na_2S_2O_5$ was added to the mixture with ice-cooling, and the mixture was vigorously stirred for 10 min at room temperature. The mixture was evaporated under reduced pressure. Two isomers (**16** and **17**) and the *cis*-hydroxylation product **18** from the residue were separated by column chromatography on silica gel (4:1 → 3:1 hexane–EtOAc). The first fraction gave crude **17**, the second, 15.7 g (53.4%) of pure **16**, and the third, crude **18**.

Physicochemical data for **16**: mp 66.0–69.0°C; $[\alpha]_D^{22}$ −99.2° (*c* 0.48, $CHCl_3$); IR (KBr): 3484 (m), 3292 (m), 2976 (m), 1734 (s), 1601 (w), 1483 (m), 1460 (m), 1402 (m), 1338 (m), 1288 (m), 1164 (s), 1139 (m), 1094 (s), 1046 (m), 1023 (m), 1000 (m), 969 (w), 915 (m), 893 (m), 874 (m), 816 (m), 787 (w), 770 (w), 710 (m), 671 (s), 584 (m), 549 (m), and 503 $cm^{-1}$ (m); $^1H$ NMR ($CDCl_3$): δ 7.76 (d, 2 H, *J* 8.1 Hz, aromatic CH of Ts), 7.31 (d, 2 H, *J* 8.1 Hz, aromatic CH of Ts), 5.43 (d, 1 H, $J_{NH,3}$ 8.3 Hz, NH), 5.34 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1), 4.70 (dd, 1 H, $J_{2,3}$ 9.4, $J_{2,1}$ 1.6 Hz, H-2), 4.55 (ddd, 1 H, $J_{5,6}$ 5.3, $J_{5,4}$ 1.7, $J_{5,6'}$ 1.3 Hz, H-5), 3.81 (dd, 1 H, $J_{6,6'}$ 8.2, $J_{6,5}$ 5.3 Hz, H-6), 3.76 (dd, 1 H, $J_{6',6}$ 8.2, $J_{6',5}$ 1.3 Hz, H-6′), 3.64–3.54 (m, 2 H, H-3 and H-4), 2.68 (d, 1 H, $J_{OH,4}$ 7.6 Hz, OH), 2.42 (s, 3 H, $CH_3$ of Ts), 1.11 (s, 9 H, pivaloyl). Anal. Calcd for $C_{18}H_{25}NO_7S$: C, 54.12; H, 6.31; N, 3.51; S, 8.03. Found: C, 54.11; H, 6.35; N, 3.60; S, 7.91.

*1,6-Anhydro-3-deoxy-3-*p*-toluenesulfonamido-β-*D*-altropyranose* (**14**).—To a stirred solution of **16** (756 mg, 1.89 mmol) in 4 mL of MeOH was added 4 mL of aq 10% NaOH. The mixture was stirred for 14 h at room temperature, and then passed over Amberlite IR-120B ($H^+$) resin. The eluting solution was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel (EtOAc) to afford 501 mg (83.9%) of **14** that was recrystallized from $Et_2O$–MeOH; mp 212.5–213.4°C; $[\alpha]_D^{24}$ −134° (*c* 0.61, MeOH); IR (KBr): 3530 (m), 3418 (s), 3320 (s), 3288 (m), 3070 (w), 2974 (w), 2910 (w), 2364 (w), 1601 (w), 1493 (w), 1448 (w), 1425 (w), 1404 (w), 1319 (s), 1292 (m), 1251 (w), 1201 (w), 1187 (w), 1156 (s), 1112 (s), 1091 (s), 998 (m), 982 (m), 963 (s), 924 (m), 909 (m), 870 (m), 849 (m), 816 (s), 793 (w), 702 (w), 671 (s), 584 (m), 565 (m), 545 (m), 513 (m), and 501 $cm^{-1}$ (m); $^1H$ NMR ($CDCl_3$): δ 7.81 (d, 2 H, *J* 8.2 Hz, aromatic CH of Ts), 7.30 (d, 2 H, *J* 8.2 Hz, aromatic CH of Ts), 5.86 (d, 1 H, $J_{NH,3}$ 8.3 Hz, NH), 5.34 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 4.50 (dd, 1 H, $J_{5,6}$ 5.3, $J_{5,4}$ 2.3 Hz, H-5), 4.18 (br, 1 H, OH), 3.76 (dd, 1 H, $J_{6,6'}$ 8.0, $J_{6,5}$ 5.3 Hz, H-6), 3.64 (dd, 1 H, $J_{6',6}$ 8.0 Hz, H-6′), 3.60–3.52 (m, 2 H, H-2 and H-4), 3.41 (d, 1 H, *J* 6.3 Hz, OH), 3.24 (ddd, 1H, $J_{3,2}$ 8.7, $J_{3,OH}$ 8.3, $J_{3,4}$ 4.3 Hz, H-3), 2.43 (s, 3 H, $CH_3$ of Ts); $^{13}C$ NMR ($CD_3OD$) δ 145.2 (1 C, aromatic C of Ts), 141.1 (1 C, aromatic C of Ts), 131.3 (2 C, aromatic CH of Ts), 128.9 (2 C, aromatic CH of Ts), 104.2 (1 C, C-1), 79.2 (1 C, C-5), 72.8 (1 C, C-2), 71.3 (1 C, C-4), 67.4 (1 C, C-6), 57.4 (1 C, C-3), 22.3 (1 C, $CH_3$ of Ts). Anal. Calcd for $C_{13}H_{17}NO_6S$: C, 49.52; H, 5.43; N, 4.44; S, 10.17. Found: C, 49.30; H, 5.54; N, 4.52; S, 10.19.

*3-Amino-1,6-anhydro-3-deoxy-β-*D*-altropyranose* (**19**) *[22]*.—A solution of **14** (501 mg, 1.59 mmol), 157 mg (0.83 mmol) of 1,5-dimethoxynaphthalene, and 327 mg (8.64 mmol) of $NaBH_4$ in 200 mL of an aq 80% EtOH solution was irradiated under Ar with

a 100-W high-pressure mercury lamp for 7 h. After the addition of acetone to decompose excess $NaBH_4$, the solvent was evaporated under reduced pressure. The residue was dissolved in water, and the insoluble material was extracted with $Et_2O$. Then the aqueous layer was passed over Amberlite IRA-410 ($OH^-$) resin. The eluting solution was evaporated under reduced pressure, and the residue was purified by column chromatography on Iatrobeads (10:5:1 $CHCl_3$–MeOH–aq 25% $NH_4OH$) to afford 212 mg (82.8%) of **19** as a syrup; $[\alpha]_D^{23}$ −159° (*c* 0.85, $H_2O$); IR (neat): 3300 (br), 1628 (m), 1520 (m), 1404 (w), 1342 (m), 1245 (w), 1139 (s), 1073 (s), 980 (s), 955 (s), 909 (s), 864 (s), 832 (m), 785 (m), 698 (w), 652 (w), and 429 $cm^{-1}$ (m); $^1H$ NMR ($D_2O$): $\delta$ 5.36 (d, 1 H, $J_{1,2}$ 1.4 Hz, H-1), 4.66 (ddd, 1 H, $J_{5,6'}$ 5.5, $J_{5,4}$ 2.5, $J_{5,6}$ 0.9 Hz, H-5), 3.93 (dd, 1 H, $J_{4,3}$ 4.3, $J_{4,5}$ 2.5 Hz, H-4), 3.86 (dd, 1 H, $J_{6,6'}$ 8.4, $J_{6,5}$ 0.9 Hz, H-6), 3.78 (dd, 1 H, $J_{6',6}$ 8.4, $J_{6',5}$ 5.5 Hz, H-6'), 3.55 (dd, 1 H, $J_{2,3}$ 9.6, $J_{2,1}$ 1.4 Hz, H-2), 2.96 (dd, 1 H, $J_{3,2}$ 9.6, $J_{3,4}$ 4.3 Hz, H-3).

*Preparation of 3-acetamido-2,4-di-*O*-acetyl-1,6-anhydro-3-deoxy-β-*D*-altropyranose* (**20**) *[11,22,23].*—To a stirred solution of **19** (212 mg, 1.32 mmol) in 30 mL of pyridine was added 10 mL of $Ac_2O$ and a catalytic amount of 4-dimethylaminopyridine at room temperature. The mixture was stirred for 2 h at ca. 60–70°C under Ar. After cooling to room temperature, the mixture was poured into the ice–water containing $NaHCO_3$ and the solution was extracted three times with $CHCl_3$. The organic layer was washed with satd aq $CuSO_4$ (four times) and water (twice). Then it was dried (anhyd $MgSO_4$). The solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (1:2 → 1:5 hexane–EtOAc) to afford 285 mg (75.4%) of **20** that was recrystallized from hexane–$CHCl_3$; mp 181.4–182.2°C (lit. [11] mp 176–177°C (EtOH); lit. [22] mp 175–176°C (EtOH)); $[\alpha]_D^{26}$ −168° (*c* 0.47, $H_2O$) (lit. [11] $[\alpha]_D$ −147° (*c* 0.44, $H_2O$); lit. [22] $[\alpha]_D^{20}$ −157.2° (*c* 1, $H_2O$); lit. [23] $[\alpha]_D$ −156° (*c* 0.96, $H_2O$)); IR (KBr): 3274 (m), 3068 (w), 3018 (w), 2974 (w), 2912 (w), 2842 (w), 1748 (s), 1653 (s), 1555 (s), 1489 (w), 1437 (w), 1373 (s), 1234 (s), 1199 (w), 1154 (m), 1123 (m), 1096 (m), 1050 (s), 1011 (m), 984 (m), 942 (m), 901 (m), 878 (m), 847 (w), 812 (w), 789 (m), 700 (m), 679 (m), 654 (m), 615 (m), 601 (m), 516 (w), 480 (m), 460 (m), and 429 $cm^{-1}$ (w); $^1H$ NMR ($CDCl_3$): $\delta$ 5.67 (d, 1 H, $J_{NH,3}$ 8.8 Hz, NH), 5.41 (d, 1 H, $J_{1,2}$ 1.3 Hz, H-1), 4.96 (dd, 1 H, $J_{4,3}$ 4.6, $J_{4,5}$ 2.2 Hz, H-4), 4.91 (dd, 1 H, $J_{2,3}$ 9.8, $J_{2,1}$ 1.3 Hz, H-2), 4.74 (dd, 1 H, $J_{5,6'}$ 5.5, $J_{5,4}$ 2.2 Hz, H-5), 4.55 (ddd, 1 H, $J_{3,2}$ 9.8, $J_{3,NH}$ 8.8, $J_{3,4}$ 4.6 Hz, H-3), 4.03 (d, 1 H, $J_{6,6'}$ 8.3 Hz, H-6), 3.85 (dd, 1 H, $J_{6',6}$ 8.3, $J_{6',5}$ 5.5 Hz, H-6'), 2.18 (s, 3 H, Ac), 2.11 (s, 3 H, Ac), 1.95 (s, 3 H, Ac). Anal. Calcd for $C_{12}H_{17}NO_7$: C, 50.17; H, 5.96; N, 4.88. Found: C, 49.98; H, 5.85; N, 4.91.

*1,6-Anhydro-2-*O*-(*tert*-butyldiphenylsilyl)-4-deoxy-4-*p*-toluenesulfonamido-β-*D*-altropyranose* (**23**).—To a stirred mixed solution of **13** (4.12 g, 11.3 mmol) in 54 mL of *tert*-BuOH was added a solution of 3.96 g (14.1 mmol) of chloramine-T · $3H_2O$ in 54 mL of $H_2O$ at room temperature. To this solution, 9.0 mL of a solution (0.1 mol $dm^{-3}$) of $OsO_4$ in *tert*-BuOH was added. The mixture was stirred for 18 h at room temperature. Then 4.00 g of $Na_2S_2O_5$ was added with ice-cooling, and the mixture was vigorously stirred for 10 min at room temperature. The mixture was evaporated under reduced pressure. Two isomers (**22** and **23**) and the *cis*-hydroxylation product **24** from the residue were separated by column chromatography on silica gel (4:1 hexane–EtOAc). The first fraction gave 4.11 g (74.2%) of pure **23**, and the second, 0.22 g (3.9%) of pure **22**.

Physicochemical data for **23**: mp 156.5–160.0°C; $[\alpha]_D^{28}$ −52.0° (*c* 0.96, $CHCl_3$); IR (KBr): 3572 (m), 3542 (m), 3250 (m), 3074 (m), 3048 (m), 2956 (s), 2896 (m), 2862 (w), 1968 (w), 1901 (w), 1754 (w), 1601 (w), 1591 (w), 1489 (m), 1470 (m), 1446 (m), 1429 (m), 1400 (m), 1348 (m), 1332 (s), 1307 (m), 1274 (w), 1234 (w), 1174 (s), 1122 (s), 1093 (s), 1004 (s), 977 (m), 938 (s), 861 (s), 818 (s), 783 (s), 743 (s), 702 (s), 681 (s), 658 (w), 630 (m), 613 (m), 578 (w), 555 (m), 545 (m), and 503 $cm^{-1}$ (s); $^1H$ NMR ($CDCl_3$): δ 7.73–7.67 (m, 6 H, aromatic CH), 7.48–7.37 (m, 6 H, aromatic CH), 7.30 (d, 2 H, *J* 8.4 Hz, aromatic CH), 4.98 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 4.89 (d, 1 H, $J_{NH,4}$ 7.4 Hz, NH), 4.25 (ddd, 1 H, $J_{5,6}$ 4.8, $J_{5,4}$ 2.6, $J_{5,6'}$ 2.2 Hz, H-5), 3.90 (ddd, 1 H, $J_{3,2}$ 8.4, $J_{3,OH}$ 7.5, $J_{3,4}$ 5.7 Hz, H-3), 3.72–3.65 (m, 2 H, H-6 and H-6′), 3.49 (ddd, 1 H, $J_{4,NH}$ 7.4, $J_{4,3}$ 5.7, $J_{4,5}$ 2.2 Hz, H-4), 3.39 (dd, 1 H, $J_{2,3}$ 8.4, $J_{2,1}$ 1.5 Hz, H-2), 2.43 (s, 3 H, $CH_3$ of Ts), 1.94 (d, 1H, $J_{OH,3}$ 7.5 Hz, OH), 1.07 (s, 9 H, *tert*-butyl); $^{13}C$ NMR ($CDCl_3$) δ 144.0, 136.8, 135.8, 133.5, 133.0, 130.0, 127.9, 127.2, 101.6, 75.5, 75.4, 68.6, 66.2, 56.3, 26.9, 21.6, 19.3. Anal. Calcd for $C_{29}H_{35}NO_6SSi$: C, 62.91; H, 6.37; N, 2.53; S, 5.79. Found: C, 62.71; H, 6.44; N, 2.50; S, 5.67.

Physicochemical data for **22**: mp 180.8–182.2°C; $[\alpha]_D^{26}$ −43.0° (*c* 1.00, $CHCl_3$); IR (KBr): 3472 (m), 3382 (m), 2978 (m), 2960 (m), 2930 (m), 2898 (s), 2858 (m), 1591 (w), 1475 (w), 1431 (m), 1392 (m), 1363 (m), 1348 (m), 1307 (w), 1265 (w), 1238 (w), 1106 (s), 1096 (s), 996 (m), 984 (m), 911 (m), 882 (m), 853 (m), 818 (m), 777 (m), 743 (m), 706 (s), 690 (w), 667 (m), 638 (w), 611 (w), 584 (w), 547 (m), 518 (m), 493 (m), and 443 $cm^{-1}$ (w); $^1H$ NMR ($CDCl_3$): δ 7.76–7.72 (d, 2 H, *J* 8.4 Hz, aromatic CH), 7.69–7.63 (m, 4 H, aromatic CH), 7.49–7.34 (m, 6 H, aromatic CH), 7.29–7.26 (d, 2 H, *J* 7.7 Hz, aromatic CH), 4.96 (br, 1 H, H-1), 4.69 (br, 1 H, NH), 4.38 (ddd, 1 H, $J_{5,6}$ 4.7, $J_{5,6'}$ 2.4, $J_{5,4}$ 2.4 Hz, H-5), 3.73–3.70 (m, 2 H, H-6 and H-6′), 3.51–3.47 (m, 3 H, H-2, H-3, and H-4), 2.42 (s, 3 H, $CH_3$ of Ts), 2.19 (d, 1H, $J_{OH,4}$ 7.3 Hz, OH), 1.02 (s, 9 H, *tert*-butyl). Anal. Calcd for $C_{29}H_{35}NO_6SSi$: C, 62.91; H, 6.37; N, 2.53; S, 5.79. Found: C, 62.53; H, 6.39; N, 2.52; S, 5.82.

*1,6-Anhydro-4-deoxy-4-*p*-toluenesulfonamido-β-*D*-altropyranose* (**15**).—To a stirred solution of **23** (351 mg, 0.63 mmol) in 7 mL of THF was added 1.4 mL of a solution (1.00 mol $dm^{-3}$) of tetrabutylammonium fluoride in THF. The mixture was stirred for 4 h at room temperature. In order to trap tetrabutylammonium ions, Amberlite IR-120B ($H^+$) resin was added to this solution and then filtered off. Aqueous $NaHCO_3$ was added to the filtrate, and the mixture was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (1:5 hexane–EtOAc) to quantitatively afford 202 mg of **15**; mp 84.5–86.2°C; $[\alpha]_D^{24}$ −115° (*c* 0.47, MeOH); IR (KBr): 3434 (br), 2974 (m), 2908 (m), 1926 (w), 1731 (w), 1601 (m), 1495 (m), 1450 (m), 1309 (m), 1251 (m), 1164 (s), 1139 (s), 1087 (s), 1021 (m), 996 (m), 942 (m), 866 (m), 849 (m), 816 (m), 708 (m), 690 (m), 658 (m), and 547 $cm^{-1}$ (m); $^1H$ NMR ($CD_3OD$): δ 7.81 (d, 2 H, *J* 8.1 Hz, aromatic CH), 7.35 (d, 2 H, *J* 8.1 Hz, aromatic CH), 5.20 (br, 1 H, H-1), 4.29–4.27 (m, 1 H, H-5), 3.72–3.67 (m, 2 H, H-3 and H-6), 3.60 (dd, 1 H, $J_{6',6}$ 7.8, $J_{6',5}$ 5.7 Hz, H-6′), 3.54–3.52 (m, 1 H, H-4), 3.42 (d, 1 H, $J_{2,3}$ 9.0 Hz, H-2), 2.42 (s, 3 H, $CH_3$ of Ts); $^{13}C$ NMR ($CD_3OD$) δ 145.4 (1 C, aromatic C of Ts), 140.5 (1 C, aromatic C of Ts), 131.4 (2 C, aromatic C of Ts), 129.0 (2 C, aromatic C of Ts), 104.1 (1 C, C-1), 78.3 (1 C, C-5), 74.9 (1 C, C-2), 69.7 (1 C, C-3), 67.8 (1 C, C-6), 58.6 (1 C, C-4), 22.3 (1 C, $CH_3$ of Ts); HRMS: *m*/*z* 315.0789 (+1.3 mmu, $C_{13}H_{17}NO_6S$, $M^+$).

*4-Amino-1,6-anhydro-4-deoxy-β-D-altropyranose* (**25**) *[24].*—A solution of **15** (400 mg, 1.27 mmol), 125 mg (0.66 mmol) of 1,5-dimethoxynaphthalene, and 245 mg (6.48 mmol) of $NaBH_4$ in 200 mL of an aq 80% EtOH solution was irradiated under Ar with a 100-W high-pressure mercury lamp for 10 h. After the addition of acetone to decompose excess $NaBH_4$, the solvent was evaporated under reduced pressure. The residue was dissolved in water and the insoluble material was extracted with $Et_2O$. Then the aqueous layer was passed over Amberlite IRA-410 ($OH^-$) resin. The eluting solution was evaporated under reduced pressure, and the residue was purified by column chromatography on Iatrobeads (10:5:1 $CHCl_3$–MeOH–aq 25% $NH_4OH$) to afford 180 mg (87.2%) of **25** as syrup; $^1H$ NMR ($CD_3OD$): $\delta$ 5.25 (br, 1 H, H-1), 4.56 (br, 1 H, H-5), 3.84–3.17 (m, 5 H, H-2, H-3, H-4, H-6 and H-6′).

*4-Acetamido-2,3-di-O-acetyl-1,6-anhydro-4-deoxy-β-D-altropyranose* (**26**) *[24].*—To a stirred solution of **25** (131 mg, 0.81 mmol) in 10 mL of pyridine was added 4 mL of $Ac_2O$ and a catalytic amount of 4-dimethylaminopyridine at room temperature. The mixture was stirred for 10 h at room temperature under Ar. After cooling to room temperature, the mixture was poured into ice–water containing $NaHCO_3$ and extracted three times with $CHCl_3$. The organic layer was washed with satd aq $CuSO_4$ (four times) and water (twice). Then it was dried (anhyd $MgSO_4$). The solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (1:2 hexane–EtOAc) to afford 164 mg (70.1%) of **26**; $[\alpha]_D^{28}$ −112° (*c* 0.53, $CHCl_3$) (lit. [24] $[\alpha]_D$ −114° (*c* 0.53, $CHCl_3$)); IR (KBr): 3386 (w), 2984 (w), 2912 (w), 2342 (w), 1748 (s), 1663 (m), 1543 (m), 1437 (w), 1377 (m), 1234 (s), 1133 (m), 1058 (s), 1015 (w), 980 (w), 911 (m), 874 (w), 855 (w), 812 (w), 793 (w), 754 (m), 679 (m), 598 (m), 561 (w), 514 (w), 482 (w), 464 (m), and 429 $cm^{-1}$ (w); $^1H$ NMR ($CDCl_3$): $\delta$ 5.98 (d, 1 H, $J_{NH,4}$ 8.7 Hz, NH), 5.48 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 5.22 (dd, 1 H, $J_{3,2}$ 9.6, $J_{3,4}$ 5.4 Hz, H-3), 4.88 (dd, 1 H, $J_{2,3}$ 9.6, $J_{2,1}$ 1.5 Hz, H-2), 4.62 (ddd, 1 H, $J_{4,NH}$ 8.7, $J_{4,3}$ 5.4, $J_{4,5}$ 1.9 Hz, H-4), 4.56 (dd, 1 H, $J_{5,6'}$ 5.4, $J_{5,4}$ 1.9 Hz, H-5), 4.03 (d, 1 H, J_{6,6′} 8.2 Hz, H-6), 3.87 (dd, 1 H, $J_{6',6}$ 8.2, $J_{6',5}$ 5.4 Hz, H-6′), 2.11 (s, 3 H, Ac), 2.06 (s, 3 H, Ac), 2.00 (s, 3 H, Ac); HRMS: *m/z* 288.1071 (+1.2 mmu, $C_{12}H_{18}NO_7$, $MH^+$).

*4-Acetamido-1,2,3,6-tetra-O-acetyl-4-deoxy-α,β-D-altropyranoses* (**27**).—*(a) By acetolysis of* **26**. To a stirred and ice-cooled solution of **26** (104 mg, 0.36 mmol) in 5.0 mL of $Ac_2O$ was slowly added dropwise a solution of 0.1 mL of $H_2SO_4$ in 5.0 mL of $Ac_2O$. The mixture was stirred for 21 h at room temperature under Ar. Then it was slowly poured into ice–water containing 40.0 g of $NaHCO_3$. After stirring for 2 h at room temperature, the mixture was extracted five times with $CHCl_3$, and then dried (anhyd $MgSO_4$). The solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (9:1 $CHCl_3$–MeOH) to afford 103 mg (73.1%) of an amorphous solid of **27** that was an $\alpha,\beta$-anomeric mixture (determined by $^{13}C$ NMR spectral analysis to be a 3:1 mixture; however, it was not possible to assign the major anomer as $\alpha$ or $\beta$) that could not be separated; $[\alpha]_D^{28}$ +62.4° (*c* 1.13, $CHCl_3$); IR (KBr): 3382 (br), 2994 (w), 1750 (s), 1663 (m), 1543 (m), 1437 (w), 1375 (m), 1222 (s), 1162 (m), 1050 (m), 1015 (w), 969 (m), 901 (w), 756 (w), 667 (w), 640 (w), 603 (w), 513 (w), and 435 $cm^{-1}$ (w); $^1H$ NMR ($CDCl_3$) of the main anomer: $\delta$ 6.01 (br, 1 H, H-1), 5.60 (d, 1 H, $J_{NH,4}$ 9.8 Hz, NH), 5.02 (d, 1 H, $J_{2,3}$ 3.1 Hz, H-2), 4.95 (dd, 1 H, $J_{3,2}$ 3.1, $J_{3,4}$ 3.1 Hz, H-3), 4.60 (ddd, 1 H, $J_{4,5}$ 9.9, $J_{4,NH}$ 9.8, $J_{4,3}$ 3.1 Hz, H-4), 4.23–4.12 (m, 3

H, H-5, H-6, and H-6′), 2.18 (s, 3 H, Ac), 2.17 (s, 3 H, Ac), 2.10 (s, 3 H, Ac), 2.01 (s, 3 H); HRMS: $m/z$ 390.1365 (+3.5 mmu, $C_{16}H_{24}NO_{10}$, $MH^+$).

*(b) By acetolysis of* **25**. To a stirred, ice-cooled solution of **25** (180 mg, 1.12 mmol) in 10.0 mL of $Ac_2O$ was slowly added dropwise a solution of 0.2 mL of $H_2SO_4$ in 10.0 mL of $Ac_2O$. The mixture was stirred for 39 h at room temperature under Ar. Then it was slowly poured into ice–water containing 40.0 g of $NaHCO_3$. After stirring for 2 h at room temperature, the mixture was extracted five times with $CHCl_3$, and then dried (anhyd $MgSO_4$). The solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (9:1 $CHCl_3$–MeOH) to afford 322 mg (74.0%) of **27** that was an $\alpha,\beta$-anomeric mixture. The analytical and spectral data of **27** thus obtained were in agreement with those of **27** obtained from **26**.

*4-Acetamido-4-deoxy-*D*-altropyranose* (**7**).—A solution of **27** (261 mg, 0.67 mmol) and 17 mg (0.32 mmol) of NaOMe in 1.7 mL of MeOH was stirred for 1 h at 0°C under Ar and kept overnight in a refrigerator. The mixture was then evaporated under reduced pressure below room temperature and thoroughly dried in vacuo. The residue was dissolved in water, and the solution was passed over Dowex 50W-X2 ($H^+$) resin. The evaporation of the mixture under reduced pressure afforded 146 mg (98.6%) of **7** as a colorless oil of an $\alpha,\beta$-anomeric mixture (determined by $^{13}C$ NMR spectral analysis as 2:1; however, it was not possible to assign the major anomer as $\alpha$ or $\beta$); $[\alpha]_D^{23}$ +54.1° (*c* 1.28, $H_2O$); $^1H$ NMR ($D_2O$): $\delta$ 4.88 (s, H-1 of the major anomer), 4.85 (s, H-1 of the minor anomer), 4.09–3.27 (m, H-2, H-3, H-4, H-5, H-6, and H-6′ of the two anomers), 1.81 (s, Ac of the minor anomer), 1.80 (s, Ac of the major anomer); $^{13}C$ NMR ($D_2O$), major anomer: $\delta$ 175.1, 92.7, 74.1, 71.2, 70.5, 62.6, 46.2, 23.0, minor anomer: $\delta$ 175.1, 94.8, 69.9 (2 C), 68.8, 62.2, 46.5, 23.0; HRMS: $m/z$ 222.0869 (+0.2 mmu, $C_8H_{16}NO_6$, $MH^+$).

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