Chemistry of *O*-Silylated Ketene Acetals: Stereocontrolled Synthesis of 3-Benzoylamino-2,3-dideoxypentoses by a 1,3-Addition to Chiral Nitrones

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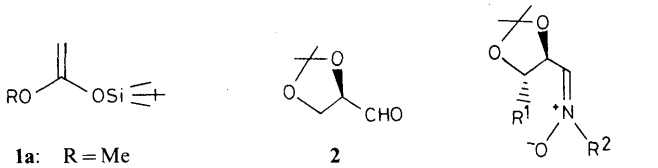
The stereochemistry of 1,3-addition of ketene acetals (1a, b) to the chiral nitrones (4a—d) derived from 2,3-*O*-isopropylidene-D-glyceraldehyde was examined. The reaction of ketene methyl *tert*-butyldimethylsilyl acetal (1a) with the *N*-benzylnitrone (4a) produced a *syn*-1,3-adduct (5a) predominantly, while the reaction of ketene *tert*-butyl *tert*-butyldimethylsilyl acetal (1b) with the *N*-diphenylmethylnitrone (4d) gave an *anti*-1,3-adduct (5h) predominantly. These adducts were readily transformed into the corresponding 3-benzoylamino-2,3-dideoxypentoses (10a, b).

Keywords *O*-silylated ketene acetal; demethyl analogue; *N*-benzoyl-L-daunosamine; *N*-benzoyl-L-acosamine; chiral nitrone; diastereoselective 1,3-addition; silyl group-transfer reaction

For the continuation of our work on the synthesis of anthracyclines and their analogues,[1] we required the hitherto unknown 5-demethyl-L-daunosamine and related 5-demethylaminosugars in optically pure forms. We have previously reported an efficient synthesis of 2-deoxy-D-ribose[2] and L-daunosamine[3] by a silyl group-transfer addition of a ketene silyl acetal (**1**) to a chiral aldehyde (**2**) and chiral nitrone (**3**), respectively. The method might be successfully applied to the synthesis of 5-demethylaminosugars by introducing minor structural changes in either component. In a recent communication,[4] we reported that the bulkiness of the alkyl substituent (R) on the oxygen atom of **1**, the alkyl substituent (R^1) of the dioxolane ring, and the alkyl substituent (R^2) on the nitrogen atom of nitrones (**3** and **4**) is significant in determining the diastereofacial selectivity of the reaction. The stereoselectively obtained *syn*- and *anti*-adducts (*syn*-**5** and *anti*-**5**) were converted to the corresponding 5-demethylaminosugars. We present here a full account of the work, as well as a demonstration of the synthetic utility of the silyl group-transfer addition of **1** to **3** for the preparation of optically pure aminosugars.



1a: R = Me
1b: R = *tert*-Bu

2

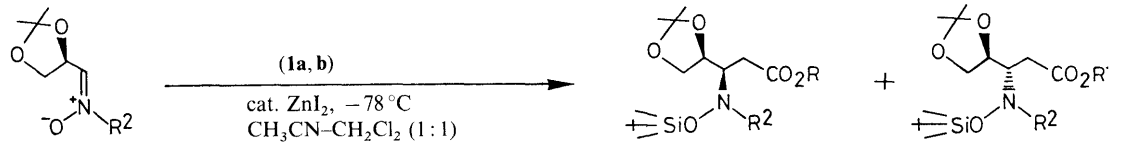
3: R^1 = Me, R^2 = *CH(Me)Ph (*S*)
4: R^1 = H

Fig. 1

Diastereoselective 1,3-Addition of Ketene Silyl Acetals to Chiral Nitrones The starting nitrones (**4a—d**) were prepared[5] by the condensation of 2,3-*O*-isopropylidene-D (or L)-glyceraldehyde with *N*-alkylhydroxylamines and treated with **1a, b**[6] at −78 °C for 1—15 h in the presence of a catalytic amount of zinc iodide in acetonitrile–methylene chloride (1 : 1). The nitrones used, together with details of the products isolated are given in Table I.

It was found that *N*-benzyl-(**4a**) and *N*-(α-phenylethyl)-nitrones (**4b, c**) reacted with **1a** to give predominantly the *syn*-adducts (**5a, c, e**) with stereoselectivities of *ca.* 3.6—9 : 1. In contrast, the *N*-diphenylmethylnitrone (**4d**) gave predominantly the *anti*-adducts (**5g, h**) with selectivities of *ca.* 1 : 2.4—10. The best result for the *syn*-adduct was obtained by the reaction of **1a** and **4a** (entry 1). The reaction of **1a** and **4b** showed higher *syn*-selectivity but the yield was

TABLE I. Diastereoselectivity of the 1,3-Addition of Ketene Silyl Acetals (**1a, b**) to the Chiral Nitrones (**4a—d**)



D-**4a—d** → D-*syn*-**5a—h** + D-*anti*-**5a—h**

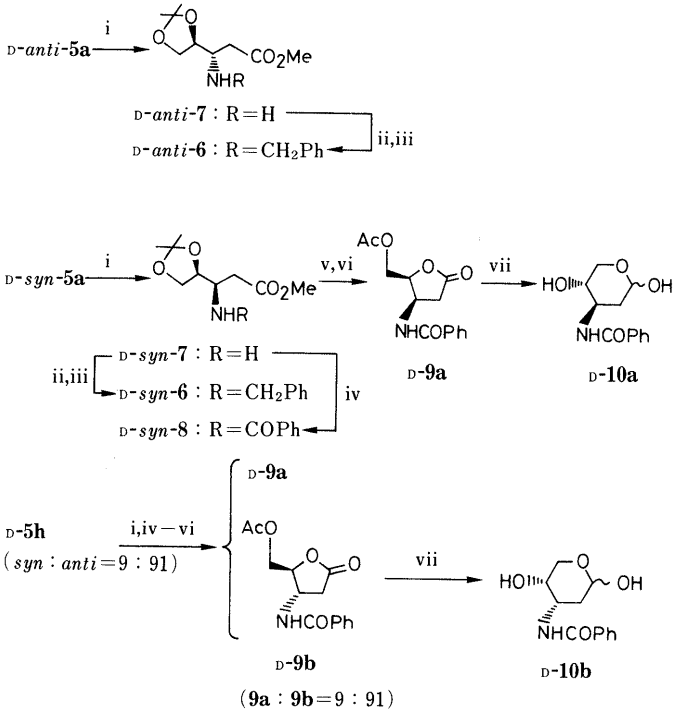
Entry	Nitrone R^2		Ketene silyl acetals R		Products	Yield[a] (%)	Ratio[b] *syn* : *anti*
1	CH_2Ph	(**4a**)	Me	(**1a**)	**5a**	Quant.	89 : 11
2	CH_2Ph	(**4a**)	*tert*-Bu	(**1b**)	**5b**	73	53 : 47
3	*CH(Me)Ph (*R*)	(**4b**)	Me	(**1a**)	**5c**	75	90 : 10
4	*CH(Me)Ph (*R*)	(**4b**)	*tert*-Bu	(**1b**)	**5d**	54	44 : 56
5	*CH(Me)Ph (*S*)	(**4c**)	Me	(**1a**)	**5e**	96	74 : 26
6	*CH(Me)Ph (*S*)	(**4c**)	*tert*-Bu	(**1b**)	**5f**	74	63 : 37
7	$CH(Ph)_2$	(**4d**)	Me	(**1a**)	**5g**	99	29 : 71
8	$CH(Ph)_2$	(**4d**)	*tert*-Bu	(**1b**)	**5h**	86	9 : 91

a) Yields are of chromatographed products. *b*) The ratios were determined by HPLC.

rather low (entry 3). For the *anti*-adduct, the reaction of **1b** and **4d** gave the best result (entry 8).

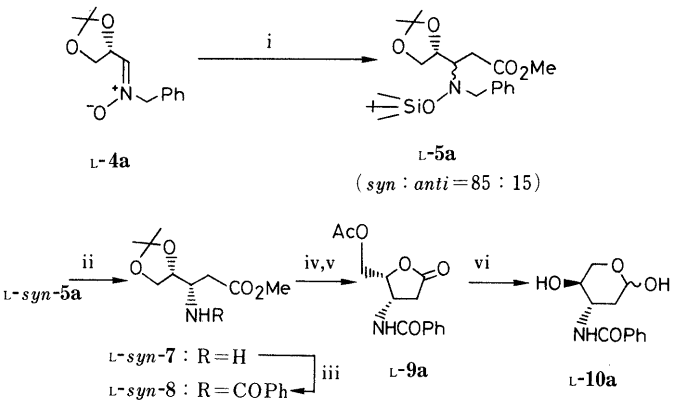
Stereochemical assignment of D-**5a** was made on the basis of spectroscopic data and chemical correlation to the *N*-benzylaminoester (D-**6**). Thus, the major diastereomer separated from D-**5a** (*syn* : *anti* = 89 : 11) by column chromatography on silica gel was subjected to catalytic hydrogenation to give rise to the aminoester (D-**7**), condensation of which with benzaldehyde followed by reduction with sodium borohydride ($NaBH_4$) furnished D-*syn*-**6** in 44% overall yield. Similarly, the minor diastereomer obtained from D-**5a** was converted to D-*anti*-**6**. Stereochemical assignment of D-**5h** was based on conversion to the γ-lactones (D-**9a, b**). Thus, D-*syn*-**7** obtained from D-*syn*-**5a** was converted into D-*syn*-**8** by standard benzoylation, and the γ-lactone (D-**9a**) was obtained by lactonization. On the other hand, a 9 : 91 mixture of diastereomeric esters (D-**5h**) provided a mixture of γ-lactones [D-**9a** : D-**9b** = 9 : 91] by the same procedures as described above. Since D-**9a** was correlated to D-*syn*-**6**, the major diastereomer of D-**5h** has *anti* relative stereochemistry. The structures of other adducts (D-**5b**—**g**) were similarly confirmed by the same method (Chart 1).

Reduction of D-**9a, b** with diisobutyl aluminum hydride (DIBAL) in dry tetrahydrofuran (THF) gave 3-benzoylamino-2,3-dideoxy-D-xylose (D-**10a**) and 3-benzoylamino-2,3-dideoxy-D-ribose (D-**10b**) (demethyl analogue of *N*-benzoyl-L-daunosamine[7]) in 55 and 50% yields, respectively. Similarly, 3-benzoylamino-2,3-dideoxy-L-xylose (L-**10a**) (demethyl analogue of *N*-benzoyl-L-acosamine[7]) was obtained from the chiral nitrone (L-**4a**) prepared from 2,3-*O*-isopropylidene-L-glyceraldehyde.[8] Thus, L-**4a** reacted with **1a** to give an 85 : 15 mixture of diastereomeric 1,3-



i, H_2, 10% Pd/C, AcOH, 3 kg/cm², r.t., 3 d; ii, PhCHO, C_6H_6, reflux, 5 h; iii, $NaBH_4$, MeOH, reflux, 15 min; iv, PhCOCl, Et_3N, cat.DMAP, CH_2Cl_2, r.t., 15 h; v, 80% AcOH, 40 °C, 1 h→reflux, 5 h; vi, Ac_2O, pyridine, r.t., 15 h; vii, DIBAL-H, THF, −78 °C, 1 h

Chart 1



i, **1a**, 0.1 eq ZnI_2, CH_3CN–CH_2Cl_2 (1 : 1), −78 °C, 1 h; ii, H_2, 10% Pd/C, AcOH, 3 kg/cm², r.t., 3 d; iii, PhCOCl, Et_3N, cat.DMAP, CH_2Cl_2, r.t., 15 h; iv, 80% AcOH, 40 °C, 1 h→reflux, 5 h; v, Ac_2O, pyridine, r.t., 15 h; vi, DIBAL-H, THF, −78 °C, 1 h

Chart 2

adducts (L-**5a**) in a quantitative yield. The major diastereomer (L-*syn*-**5a**) was hydrogenated to give L-*syn*-**7**, and benzoylated to give L-*syn*-**8**. Lactonization of L-*syn*-**8** furnished L-**9a**, which was converted into L-**10a** by reaction with DIBAL in 46% overall yield from L-*syn*-**5a** (Chart 2).

Discussion

While the details of diastereofacial selectivity in the 1,3-addition of **1** to **4** remain unknown, a working model is given in Chart 3. The selectivity can be explained by assuming that conformations C and D are the reactive conformations of the addition reaction, since alternative conformations A and B have severe steric interactions and an unfavorable dipole–dipole effect between the dioxolane ring and the bulky siloxy group. The *syn*-product could be produced from conformation C (so-called modified Felkin–Anh model) by the approach of the nucleophile from the face of the iminium cation opposite to the electronegative oxygen, while the *anti* diastereomer was produced from conformer D by the same face approach of the oxygen. As for the effect of the substituent (R) in **1**, the more active conformer C is the preferred form for the smaller nucleophile (**1a**; R = Me), which gives *syn*-adducts predominantly (entries 1, 3, and 5). In the case of the bulky nucleophile (**1b**; R = *tert*-Bu), the nucleophile may be forced to attack the less reactive but less hindered conformer D,[9] resulting in lower stereoselection (entries 2, 4, and 6).

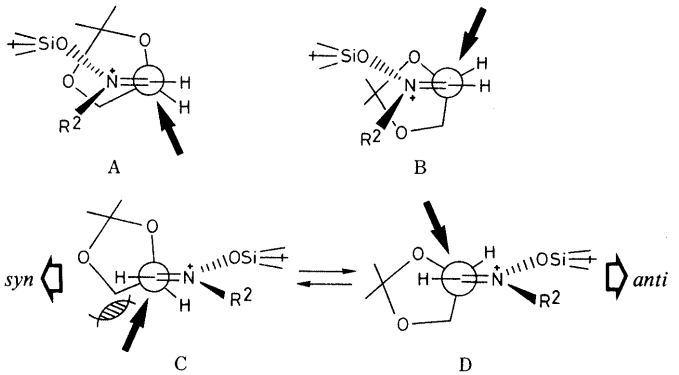


Chart 3

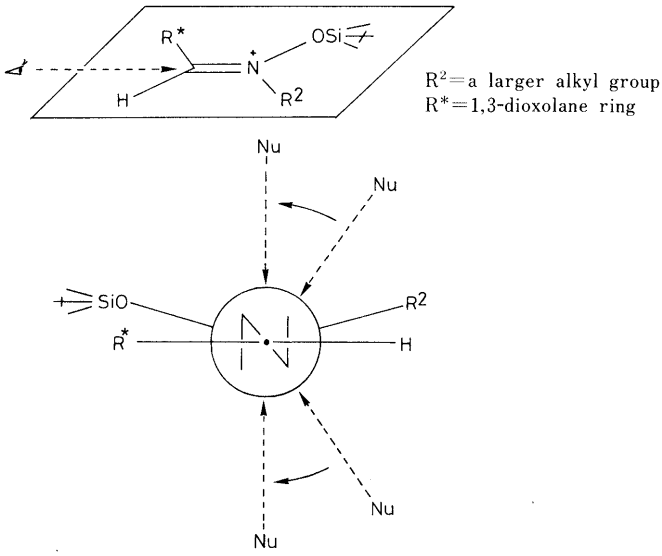


Fig. 2

Although the exact reaction process for the *anti*-selectivity on the addition of **1** to the bulky nitrone (**4d**; $R^2=CHPh_2$) is not clear, it might be explained by the trajectory of the nucleophile in its attack on the iminium cation (Fig. 2) as proposed by Heathcock *et al.*[10] in the Lewis acid-mediated addition of enolsilanes to chiral aldehydes. Thus, in the reaction of nucleophile with the iminium cation, a trajectory is followed that brings the nucleophile far from the bulky substituent on nitrogen ($R^2=CHPh_2$), which emphasizes the steric interaction of conformer C. Therefore, the most matched pair for *anti*-selection *via* conformer D may arise from the reaction of the bulky ketene silyl acetal (**1b**) and the bulky chiral nitrone (**4d**) (entry 8).

Experimental

All melting and boiling points are uncorrected. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on a Hitachi R-22 (90 MHz) or a JEOL JNM-GX 500 (500 MHz) spectrometer (with tetramethylsilane as an internal standard unless otherwise noted). Infrared (IR) absorption spectra were recorded on a JASCO HPIR-102 spectrometer. Low- and high-resolution mass spectra (MS) were obtained with a JEOL JMS D-300 instrument, with a direct inlet system at 70 eV. Optical rotations were measured in a 1-dm cell of 1-ml capacity with a Perkin-Elmer 241 instrument. High-performance liquid chromatography (HPLC) was performed on a JASCO TRIROTAR-II. For column chromatography, E. Merck silica gel (70—230 mesh ASIM) was used.

Ketene Silyl Acetals (1a, b) Ketene silyl acetals (**1a**,[6a,c] **1b**[6d]) were prepared from the corresponding esters by the reported methods.

Hydroxylamines Benzylhydroxylamine,[11] (*R*)- and (*S*)-α-phenylethylhydroxylamine,[12] and benzhydrylhydroxylamine[13] were prepared by the reported methods.

General Procedure for the Preparation of Nitrones (4a—g) Hydroxylamine (2 mmol) and Na_2SO_4 (500 mg) were added to a stirred solution of 2,3-isopropylidene-*O*-isopropylidene-D(or L)-glyceraldehyde (260 mg, 2 mmol) in dry CH_2Cl_2 (2 ml) at room temperature (r.t.). After 15 h, the mixture was partitioned between CH_2Cl_2 (20 ml) and 5% aqueous HCl (30 ml), and the aqueous layer was extracted with CH_2Cl_2 (20 ml × 3). The combined organic layer was washed with saturated aqueous $NaHCO_3$, dried over $MgSO_4$, and evaporated *in vacuo*. The residue was subjected to column chromatography on silica gel with CH_2Cl_2–AcOEt to give the corresponding nitrone.

***N*-[[(4*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl]methylene]benzylamine *N*-Oxide (D-4a)** This (2.2 g, 85%) was prepared from 2,3-*O*-isopropylidene-D-glyceraldehyde (1.5 g, 11 mmol), benzylhydroxylamine (1.4 g, 11 mmol) and Na_2SO_4 (2.5 g) in dry CH_2Cl_2 (11 ml), mp 84 °C (petroleum ether). $[\alpha]_D^{17}$ +108° (*c*=1.03, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2990, 1600. ^{1}H-NMR ($CDCl_3$) δ: 1.33 (3H, s, MeCMe), 1.37 (3H, s, MeCMe), 3.77 (1H, dd, *J*=8, 6 Hz, 3-H), 4.30 (1H, dd, *J*=7, 6 Hz, 3′-H), 4.77 (2H, s, NCH_2Ph), 5.02 (1H, ddd, *J*=8, 7, 5.5 Hz, 2-H), 6.72 (1H, d, *J*=5.5 Hz, 1-H), 7.30 (5H, s, Ph). MS *m/z*: 235 (M^+). *Anal.* Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.13; H, 7.45; N, 5.91.

(1*R*)-*N*-[[(4*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl]methylene]-1-phenylethylamine *N*-Oxide (D-4b) This (277 mg, 58%) was prepared from 2,3-*O*-isopropylidene-D-glyceraldehyde (251 mg, 1.93 mmol), (*R*)-α-phenylethylhydroxylamine (265 mg, 1.93 mmol) and Na_2SO_4 (500 mg) in dry CH_2Cl_2 (2 ml). $[\alpha]_D^{28}$ +12.5° (*c*=3.25, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3000, 1675. ^{1}H-NMR ($CDCl_3$) δ: 1.35 (3H, s, MeCMe), 1.40 (3H, s, MeCMe), 1.78 (3H, d, *J*=7.0 Hz, PhCHMe), 3.75 (1H, dd, *J*=8.2, 5.8 Hz, 3-H), 4.36 (1H, dd, *J*=8.2, 6.8 Hz), 4.97 (1H, q, *J*=7.0 Hz, PhCHMe), 5.12 (1H, ddd, *J*=6.8, 5.8, 4.7 Hz, 2-H), 6.91 (1H, d, *J*=4.7 Hz, 1-H), 7.2—7.5 (5H, m, Ph). MS *m/z*: 249 (M^+). Exact mass Calcd for $C_{14}H_{19}NO_3$: 249.1365. Found: 249.1373.

(1*S*)-*N*-[[(4*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl]methylene]-1-phenylethylamine *N*-Oxide (D-4c) This (271 mg, 58%) was prepared from 2,3-*O*-isopropylidene-D-glyceraldehyde (244 mg, 1.88 mmol), (*S*)-α-phenylethylhydroxylamine (257 mg, 1.88 mmol), and Na_2SO_4 (500 mg) in dry CH_2Cl_2 (2 ml). mp 95—96 °C (*n*-hexane). $[\alpha]_D^{29}$ +69.5° (*c*=2.63, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2990, 1675. ^{1}H-NMR ($CDCl_3$) δ: 1.35 (3H, s, MeCMe), 1.39 (3H, s, MeCMe), 1.78 (3H, d, *J*=7.0 Hz, PhCHMe), 3.86 (1H, dd, *J*=8.4, 5.6 Hz, 3-H), 4.40 (1H, dd, *J*=8.4, 7.2 Hz, 3′-H), 4.96 (1H, q, *J*=7.0 Hz, PhCHMe), 5.07 (1H, ddd, *J*=7.2, 5.7, 5.6 Hz, 2-H), 6.93 (1H, d, *J*=5.7 Hz, 1-H), 7.2—7.5 (5H, m, Ph). Exact mass Calcd for $C_{14}H_{19}NO_3$: 249.1365. Found: 249.1381.

***N*-[[(4*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl]methylene]benzhydrylamine *N*-Oxide (D-4d)** This (485 mg, 41%) was prepared from 2,3-*O*-isopropylidene-D-glyceraldehyde (496 mg, 3.82 mmol), benzhydrylhydroxylamine (760 mg, 3.82 mmol), and Na_2SO_4 (1 g) in dry CH_2Cl_2 (4 ml), mp 116—117 °C (*n*-hexane–AcOEt). $[\alpha]_D^{16}$ +88.3° (*c*=0.945, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2990, 1600, 1580. ^{1}H-NMR ($CDCl_3$) δ: 1.37 (6H, br s, MeCMe), 3.90 (1H, dd, *J*=9, 6 Hz, 3-H), 4.41 (1H, dd, *J*=9, 7 Hz, 3′-H), 5.17 (1H, ddd, *J*=7, 6, 4.5 Hz, 2-H), 6.13 (1H, s, $CHPh_2$), 6.88 (1H, d, *J*=4.5 Hz, 1-H), 7.2—7.5 (10H, m, Ph×2). *Anal.* Calcd for $C_{19}H_{21}NO_3$: C, 73.29; H, 6.80; N, 4.50. Found: C, 73.09; H, 6.76; N, 4.45.

General Procedure for Addition Reaction of Ketene Silyl Acetals (1a, b) to Nitrones (4a—d) A ketene silyl acetal (**1**, 1.2—1.5 mmol) was added to a stirred solution of nitrone (**4**, 1 mmol) and ZnI_2 (16 mg, 0.05 mmol) in dry CH_3CN–CH_2Cl_2 (1:1, 5 ml) at −78 °C under nitrogen. After 1—8 h, saturated aqueous $NaHCO_3$ (1 ml) was added to the mixture under the same conditions. The mixture was allowed to warm to room temperature and poured into water (25 ml). The mixture was extracted with CH_2Cl_2 (20 ml × 3). The extract was dried over $MgSO_4$, and evaporated *in vacuo*. The residue was subjected to column chromatography on silica gel with *n*-hexane–ether to give the adduct (**5**) as a mixture of diastereomers (*anti*-**5** and *syn*-**5**). The ratio of the mixture was determined by HPLC (NUCLEOSIL 50-5, 4.9 mm × 250 mm).

Methyl (4*S*)-3-[*N*-(*tert*-Butyldimethylsiloxy)benzylamino]-4,5-(isopropylidenedioxy)pentanoate (D-5a) i) This mixture of diastereomers (127 mg, quantitative, *syn*:*anti*=89:11) was obtained from D-**4a** (70.5 mg, 0.3 mmol), **1a** (70.5 mg, 0.375 mmol), and ZnI_2 (7.5 mg, 0.024 mmol) in dry CH_3CN–CH_2Cl_2 (1:1, 1 ml). ii) This mixture of diastereomers (80 mg, 90%, *syn*:*anti*=87:13) was obtained from D-**4a** (49.2 mg, 0.209 mmol), **1a** (63.2 mg, 0.336 mmol), and *tert*-butyldimethylsilyl trifluoromethane-sulfonate (4.8 μl, 0.0209 mmol) in dry CH_3CN–CH_2Cl_2 (1:1, 1 ml). HPLC: *n*-hexane:AcOEt=10:1, flow rate: 1.0 ml/min. t_R: D-*anti*-**5a**, 6.64 min; D-*syn*-**5a**, 7.59 min. These mixtures were subjected to column chromatography on silica gel with *n*-hexane–ether (10:1) to give methyl (3*R*,4*S*)-3-[*N*-(*tert*-butyldimethylsiloxy)benzylamino]-4,5-(isopropylidenedioxy)-pentanoate (D-*syn*-**5a**) and methyl (3*S*,4*S*)-3-[*N*-(*tert*-butyldimethylsiloxy)-benzylamino]-4,5-(isopropylidenedioxy)pentanoate (D-*anti*-**5a**). D-*syn*-**5a**: bp 90—100 °C/0.15 mmHg (bath. temp.). $[\alpha]_D^{26}$ +28.8° (*c*=1.25, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1735, 1240, 1050, 825. ^{1}H-NMR ($CDCl_3$) δ: −0.13 (3H, br s, MeSi), 0.04 (3H, br s, MeSi), 0.86 (9H, s, *tert*-BuSi), 1.35 (3H, br s, MeCMe), 1.38 (3H, br s, MeCMe), 2.44 (1H, dd, *J*=15.3, 5.8 Hz, 2-H), 2.80 (1H, dd, *J*=15.3, 7.5 Hz, 2′-H), 3.61 (3H, s, OMe), 3.3—4.6 (6H, m, 3,4,5,5′-H, CH_2Ph), 7.26 (5H, br s, Ph). *Anal.* Calcd for $C_{22}H_{37}NO_5Si$: C, 62.38; H, 8.80; N, 3.31. Found: C, 62.68; H, 8.98; N, 3.33. D-*anti*-**5a**: mp 64—66 °C (MeOH–H_2O). $[\alpha]_D^{26}$ −3.13° (*c*=0.075, CH_2Cl_2). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1730, 1250, 1050, 835. ^{1}H-NMR ($CDCl_3$) δ: −0.19 (3H, br s, MeSi), −0.12 (3H, br s, MeSi), 0.81 (9H, s, *tert*-BuSi), 1.28 (3H, s, MeCMe), 1.29 (3H, s, MeCMe), 2.52 (1H, dd, *J*=15.6, 6.3 Hz, 2-H), 2.91 (1H, dd, *J*=15.6, 6.2 Hz, 2′-H), 3.68 (3H, s, OMe), 3.2—3.9 (6H, m, 3,4,5,5′-H, CH_2Ph), 7.23 (5H, br s, Ph). *Anal.* Calcd for $C_{22}H_{37}NO_5Si$: C,

62.38; H, 8.80; N, 3.31. Found: C, 62.02; H, 8.87; N, 3.25.

***tert*-Butyl (4*S*)-3-[*N*-(*tert*-Butyldimethylsiloxy)benzylamino]-4,5-(isopropylidenedioxy)pentanoate (D-5b)** This mixture of diastereomers (310 mg, 73%, *syn*:*anti* = 53:47) was obtained from D-**4a** (215 mg, 0.915 mmol), **1b** (630 mg, 2.74 mmol), and ZnI_2 (20 mg, 0.06 mmol) in dry CH_3CN–CH_2Cl_2 (1:1, 5 ml). HPLC: *n*-hexane : AcOEt = 25:1, flow rate, 0.5 ml/min. t_R: D-*anti*-**5b**, 16.44 min; D-*syn*-**5b**, 18.76 min. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720. ^{1}H-NMR ($CDCl_3$) δ: −0.22 (53/100 × 3H, s, MeSi), −0.17 (53/100 × 3H, s, MeSi), −0.11 (47/100 × 3H, s, MeSi), 0.07 (47/100 × 3H, s, MeSi), 0.84 (47/100 × 9H, s, *tert*-BuSi), 0.85 (53/100 × 9H, s, *tert*-BuSi), 1.30 (47/100 × 3H, s, MeCMe), 1.33 (53/100 × 3H, s, MeCMe), 1.37 (47/100 × 3H, s, MeCMe), 1.42 (53/100 × 3H, s, MeCMe), 1.46 (53/100 × 9H, s, *tert*-BuO), 1.52 (47/100 × 9H, s, *tert*-BuO), 2.2—3.0 (2H, m, 2,2′-H), 3.4—4.6 (6H, m, 3,4,5,5′-H, CH_2Ph), 7.2—7.5 (5H, m, Ph). Exact mass Calcd for $C_{25}H_{43}NO_5Si$: 465.2911. Found: 465.2913.

Methyl (4*S*)-3-[*N*-(*tert*-Butyldimethylsiloxy)-(1*R*)-1-phenylethylamino]-4,5-(isopropylidenedioxy)pentanoate (D-5c) This mixture of diastereomers (117 mg, 75%, *syn*:*anti* = 90:10) was obtained from D-**4b** (88.6 mg, 0.356 mmol), **1a** (77 mg, 0.411 mmol), and ZnI_2 (6 mg, 0.019 mmol) in dry CH_3CN–CH_2Cl_2 (1:1, 2.5 ml). HPLC: *n*-hexane : AcOEt = 20:1, flow rate, 0.5 ml/min. t_R: *anti*-**5c**, 28.14 min; *syn*-**5c**, 31.08 min. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1730. ^{1}H-NMR ($CDCl_3$) δ: 0.21 (6H, s, Me_2Si), 0.95 (9H, s, *tert*-BuSi), 1.08 (3H, s, MeCMe), 1.26 (3H, s, MeCMe), 1.41 (3H, d, J = 7.0 Hz, PhCHMe), 2.30 (1H, dd, J = 15.0, 4.4 Hz, 2-H), 2.62 (1H, dd, J = 15.0, 8.0 Hz, 2′-H), 3.63 (3H, s, OMe), 3.3—4.2 (4H, m, 3,4,5,5′-H), 4.17 (1H, q, J = 7.0 Hz, PhCHMe), 7.15 (5H, m, Ph). Exact mass Calcd for $C_{23}H_{39}NO_5Si$: 437.2597. Found: 437.2597.

***tert*-Butyl (4*S*)-3-[*N*-(*tert*-Butyldimethylsiloxy)-(1*R*)-1-phenylethylamino]-4,5-(isopropylidenedioxy)pentanoate (D-5d)** This mixture of diastereomers (97.3 mg, 54%, *syn*:*anti* = 44:56) was obtained from D-**4b** (94.5 mg, 0.379 mmol), **1b** (261 mg, 1.139 mmol), and ZnI_2 (7 mg, 0.02 mmol) in dry CH_3CN–CH_2Cl_2 (1:1, 2.5 ml). HPLC: *n*-hexane : AcOEt = 30:1; flow rate, 0.5 ml/min. t_R: *anti*-**5d**, 21.11 min; *syn*-**5d**, 26.06 min. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720. ^{1}H-NMR ($CDCl_3$) δ: 0.12 (56/100 × 3H, s, MeSi), 0.16 (56/100 × 3H, s, MeSi), 0.18 (44/100 × 3H, s, MeSi), 0.19 (44/100 × 3H, s, MeSi), 0.93 (56/100 × 9H, s, *tert*-BuSi), 0.95 (44/100 × 9H, s, *tert*-BuSi), 1.05 (44/100 × 3H, s, MeCMe), 1.19 (56/100 × 3H, s, MeCMe), 1.25 (44/100 × 3H, s, MeCMe), 1.26 (56/100 × 3H, s, MeCMe), 1.40 (56/100 × 9H, s, *tert*-BuO), 1.41 (56/100 × 3H, d, J = 7.0 Hz, PhCHMe), 1.46 (44/100 × 9H, s, *tert*-BuO), 1.47 (44/100 × 3H, J = 7.2 Hz, PhCHMe), 2.1—2.6 (2H, m, 2,2′-H), 3.2—4.2 (5H, m, 3,4,5,5′-H, PhCHMe), 7.1—7.5 (5H, m, Ph). Exact mass Calcd for $C_{26}H_{45}NO_5Si$: 479.3065. Found: 479.3055.

Methyl (4*S*)-3-[*N*-(*tert*-Butyldimethylsiloxy)-(1*S*)-1-phenylethylamino]-4,5-(isopylidenedioxy)pentanoate (D-5e) This mixture of diastereomers (171 mg, 96%, *syn*:*anti* = 74:26) was obtained from D-**4c** (101.4 mg, 0.407 mmol), **1a** (82 mg, 0.434 mmol), and ZnI_2 (7 mg, 0.02 mmol) in dry CH_3CN–CH_2Cl_2 (1:1, 5 ml). HPLC: *n*-hexane : AcOEt = 20:1; flow rate, 0.5 ml/min. t_R: *anti*-**5e**, 22.68 min; *syn*-**5e**, 25.76 min. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1725. ^{1}H-NMR ($CDCl_3$) δ: 0.01 (26/100 × 3H, s, MeSi), 0.08 (74/100 × 3H, s, MeSi), 0.13 (26/100 × 3H, s, MeSi), 0.19 (74/100 × 3H, s, MeSi), 0.90 (9H, s, *tert*-BuSi), 1.1—1.7 (9H, m, MeCMe, PhCHMe), 2.05 (74/100H, dd, J = 16, 5.6 Hz, 2-H), 2.43 (26/100H, dd, J = 15, 7 Hz, 2-H), 2.57 (74/100H, dd, J = 16, 6.4 Hz, 2′-H), 2.98 (26/100H, dd, J = 15, 4.2 Hz, 2′-H), 3.50 (74/100 × 3H, s, OMe), 3.64 (26/100 × 3H, s, OMe), 3.3—4.4 (5H, m, 3,4,5,5′-H), 7.2—7.5 (5H, m, Ph). Exact mass Calcd for $C_{23}H_{39}NO_5Si$: 437.2595. Found: 437.2592.

***tert*-Butyl (4*S*)-3-[*N*-(*tert*-Butyldimethylsiloxy)-(1*S*)-1-phenylethylamino]-4,5-(isopropylidenedioxy)pentanoate (D-5f)** This mixture of diastereomers (113 mg, 74%, *syn*:*anti* = 63:37) was obtained from D-**4c** (80 mg, 0.321 mmol), **1b** (111 mg, 0.48 mmol), and ZnI_2 (6 mg, 0.019 mmol) in dry CH_3CN–CH_2Cl_2 (1:1, 5 ml). HPLC: *n*-hexane : AcOEt = 30:1; flow rate, 0.5 ml/min. t_R: *anti*-**5f**, 20.32 min; *syn*-**5f**, 21.68 min. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720. ^{1}H-NMR ($CDCl_3$) δ: 0.04 (63/100 × 3H, s, MeSi), 0.09 (37/100 × 3H, s, MeSi), 0.12 (37/100 × 3H, s, MeSi), 0.19 (63/100 × 3H, s, MeSi), 0.89 (37/100 × 9H, s, *tert*-BuSi), 0.90 (63/100 × 9H, s, *tert*-BuSi), 1.1—1.6 (9H, m, MeCMe, PhCHMe), 1.41 (63/100 × 9H, s, *tert*-BuO), 1.48 (37/100 × 9H, s, *tert*-BuO), 2.0—3.1 (2H, m, 2,2′-H), 3.4—4.3 (5H, m, 3,4,5,5′-H, PhCHMe), 7.2—7.5 (5H, m, Ph). MS *m/z*: 464 (M^+ − Me), 422 (M^+ − *tert*-Bu). Exact mass Calcd for $C_{26}H_{45}NO_5Si$ − Me: 464.2832. Found: 464.2834.

Methyl (4*S*)-3-[*N*-(*tert*-Butyldimethylsiloxy)benzhydrylamino]-4,5-(isopropylidenedioxy)pentanoate (D-5g) This mixture of diastereomers (78.5 mg, 99%, *syn*:*anti* = 29:71) was obtained from D-**4d** (49.3 mg, 0.159 mmol), **1a** (45 mg, 0.238 mmol), and ZnI_2 (5 mg, 0.016 mmol) in dry CH_3CN–CH_2Cl_2 (1:1, 1.5 ml). HPLC: *n*-hexane : CH_2Cl_2 = 2:1; flow rate, 0.5 ml/min. t_R: *syn*-**5g**, 11.41 min; *anti*-**5g**, 12.32 min. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1730. ^{1}H-NMR ($CDCl_3$) δ: −0.50 (71/100 × 3H, s, MeSi), −0.19 (29/100 × 3H, s, MeSi), −0.16 (29/100 × 3H, s, MeSi), −0.07 (71/100 × 3H, s, MeSi), 0.76 (71/100 × 9H, s, *tert*-BuSi), 0.77 (29/100 × 9H, s, *tert*-BuSi), 1.19 (71/100 × 3H, s, MeCMe), 1.24 (71/100 × 3H, s, MeCMe), 1.33 (29/100 × 3H, s, MeCMe), 1.37 (29/100 × 3H, s, MeCMe), 2.42 (71/100H, dd, J = 16.2, 7.2 Hz, 2-H), 2.88 (71/100H, dd, J = 16.2, 4.5 Hz, 2′-H), 1.9—2.9 (29/100 × 2H, m, 2,2′-H), 3.58 (71/100 × 3H, s, OMe), 3.59 (29/100 × 3H, s, OMe), 3.4—4.3 (4H, m, 3,4,5,5′-H), 5.00 (71/100H, s, CHPh$_2$), 5.18 (29/100H, s, CHPh$_2$), 7.1—7.5 (10H, m, ArH). Exact mass Calcd for $C_{25}H_{42}NO_5Si$: 499.2751. Found: 499.2748.

***tert*-Butyl (4*S*)-3-[*N*-*tert*-Butyldimethylsiloxy)benzhydrylamino]-4,5-(isopropylidenedioxy)pentanoate (D-5h)** This mixture of diastereomers (64 mg, 86%, *syn*:*anti* = 91:9) was obtained from D-**4d** (42.6 mg, 0.137 mmol), **1b** (95 mg, 0.41 mmol), and ZnI_2 (5 mg, 0.016 mmol) in dry CH_3CN–CH_2Cl_2 (1:1, 1.5 ml). HPLC: *n*-hexane : CH_2Cl_2 = 15:4; flow rate, 0.5 ml/min. t_R: *syn*-**5h**, 13.86 min; *anti*-**5h**, 15.35 min. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720. ^{1}H-NMR ($CDCl_3$) δ: −0.43 (3H, s, MeSi), −0.06 (3H, s, MeSi), 0.76 (9H, s, *tert*-BuSi), 1.23 (3H, s, MeCMe), 1.24 (3H, s, MeCMe), 1.40 (9H, s, *tert*-BuO), 2.30 (1H, dd, J = 16.3, 7.3 Hz, 2-H), 2.63 (1H, dd, J = 16.3, 4.0 Hz, 2′-H), 3.45—4.27 (4H, m, 3,4,5,5′-H), 5.03 (1H, s, NCHPh$_2$), 7.1—7.5 (10H, m, ArH). Exact mass Calcd for $C_{31}H_{47}NO_5Si$: 541.3224. Found: 541.3230.

Methyl (3*R*,4*S*)-3-Amino-4,5-(isopropylidenedioxy)pentanoate (D-*syn*-7) A mixture of D-*syn*-**5a** (500 mg, 1.18 mmol) and 10% Pd/C (350 mg) in AcOH (10 ml) was shaken at room temperature for 3 d under hydrogen (3 kg/cm^2). The mixture was filtered, and then the filtrate was concentrated *in vacuo*. The residue was partitioned between CH_2Cl_2 (50 ml) and saturated aqueous $NaHCO_3$ (20 ml). The aqueous layer was extracted with CH_2Cl_2 (20 ml × 3). The combined organic layer was dried over $MgSO_4$ and evaporated *in vacuo*. The residue was subjected to column chromatography on silica gel with CH_2Cl_2–MeOH (25:1) to give **7** (212 mg, 89%) as a syrup. $[\alpha]_D^{16}$ +12.6° (*c* = 0.76, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3300, 1725, 1440, 1370, 1260. ^{1}H-NMR ($CDCl_3$) δ: 1.31 (3H, s, MeCMe), 1.39 (3H, s, MeCMe), 2.4—2.55 (2H, m, 2,2′-H), 2.8—3.2 (3H, m, NH_2, 3-H), 3.68 (3H, s, OMe), 3.6—4.25 (3H, m, 4,5,5′-H). MS *m/z*: 204 (M^+ + 1), 188 (M^+ − Me). Exact mass Calcd for $C_9H_{17}NO_4$ + H: 204.1234. Found: 204.1233.

Methyl (3*R*,4*S*)-3-Benzylamino-4,5-(isopropylidenedioxy)pentanoate (D-*syn*-6) A mixture of D-*syn*-**7** (14 mg, 0.061 mmol) and benzaldehyde (7.3 mg, 0.07 mmol) in dry benzene (3 ml) was refluxed with stirring for 1 h. The mixture was evaporated *in vacuo*, and the residue was dissolved in MeOH (2 ml). $NaBH_4$ (12 mg, 0.345 mmol) was added to the stirred solution, and the mixture was refluxed for 0.5 h, then concentrated *in vacuo*, and the residue was partitioned between $CHCl_3$ (15 ml) and H_2O (10 ml). The aqueous layer was extracted with $CHCl_3$ (10 ml × 3), and then the combined organic layer was dried over $MgSO_4$ and evaporated *in vacuo*. The residue was subjected to column chromatography on silica gel with *n*-hexane–AcOEt (4:1) to give D-*syn*-**6** (9 mg, 44%) as a syrup. $[\alpha]_D^{14}$ −8.04° (*c* = 1.29, EtOH) [lit.[14] $[\alpha]_D$ −8.0° (*c* = 1.3, EtOH)]. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1725, 1250. ^{1}H-NMR ($CDCl_3$) δ: 1.33 (3H, s, MeCMe), 1.38 (3H, s, MeCMe), 1.77 (1H, br s, NH), 2.50 (2H, br d, J = 6 Hz, 2,2′-H), 3.14 (1H, br q, J = 6 Hz, 3-H), 3.67 (3H, s, OMe), 3.7—4.4 (5H, 4,5,5′-H, NCH_2Ph), 7.25 (5H, br s, Ph).

Methyl (3*S*,4*S*)-3-Amino-4,5-(isopropylidenedioxy)pentanoate (D-*anti*-7) This (21 mg, 81%, syrup) was prepared from D-*anti*-**5a** (53.6 mg, 0.127 mmol) and 10%-Pd/C (66 mg) in AcOH (3 ml) by a method similar to that used for the preparation of D-*syn*-**7**. $[\alpha]_D^{18}$ −5.57° (*c* = 0.862, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3300, 1725, 1440, 1370, 1260. ^{1}H-NMR ($CDCl_3$) δ: 1.33 (3H, s, MeCMe), 1.39 (3H, s, MeCMe), 2.35—3.2 (5H, m, 2,2′,3-H, NH_2), 3.69 (3H, s, OMe), 3.6—4.2 (3H, m, 4,5,5′-H).

Methyl (3*S*,4*S*)-3-Benzylamino-4,5-(isopropylidenedioxy)pentanoate (D-*anti*-6) This (7 mg, 16%, syrup) was prepared from D-*anti*-**7** (30 mg, 0.148 mmol) in a manner similar to that used for the preparation of D-*syn*-**7**. $[\alpha]_D^{18}$ +14.4° (*c* = 0.222, EtOH) [lit.[14] $[\alpha]_D$ +14.6° (*c* = 1.0, EtOH)]. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1725, 1250. ^{1}H-NMR ($CDCl_3$) δ: 1.32 (3H, s, MeCMe), 1.39 (3H, s, MeCMe), 1.80 (1H, br s, NH), 2.5—2.67 (2H, m, 2,2′-H), 2.9—3.3 (1H, m, 3-H), 3.68 (3H, s, OMe), 3.7—4.2 (5H, m, 4,5,5′-H, NCH_2Ph), 7.25 (5H, br s, Ph).

Methyl (3*R*,4*S*)-3-Benzoylamino-4,5-(isopropylidenedioxy)pentanoate (D-*syn*-8) Benzoyl chloride (0.05 ml) was added to a stirred solution of D-*syn*-**7** (35.1 mg, 0.173 mmol), NEt_3 (0.1 ml), and 4-dimethylaminopyridine (DMAP, 5 mg, 0.041 mmol) in dry CH_2Cl_2 (1 ml) at room temperature under nitrogen. After 15 h, the mixture was diluted with CH_2Cl_2 (10 ml),

washed with 10% HCl and a saturated aqueous solution of $NaHCO_3$ and then dried over $MgSO_4$. After evaporation, the residue was subjected to column chromatography on silica gel with CH_2Cl_2–AcOH (5 : 1) to give D-*syn*-**8** (41 mg, 79%) as colorless crystals, mp 80.5—81 °C (*n*-hexane). $[\alpha]_D^{16}$ +36.9° (*c* = 0.45, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450, 1730, 1670. ^{1}H-NMR ($CDCl_3$) δ: 1.36 (3H, s, MeCMe), 1.47 (3H, s, MeCMe), 2.70 (2H, d, *J* = 6.6 Hz, 2,2′-H), 3.67 (3H, s, OMe), 3.7—4.8 (4H, m, 3,4,5,5′-H), 6.75 (1H, br d, *J* = 8 Hz, NH), 7.2—7.55 (3H, m, ArH), 7.6—7.9 (2H, m, ArH). *Anal.* Calcd for $C_{16}H_{21}NO_5$: C, 62.53; H, 6.89. Found: C, 62.36; H, 6.97.

(3*R*,4*S*)-5-Acetoxy-3-benzoylamino-4-pentanolide (D-9a) A solution of D-*syn*-**8** (16.5 mg, 0.054 mmol) in 80% AcOH (3 ml) was stirred at 40—50 °C for 1 h, and then refluxed with stirring for 5 h. After evaporation, the residue was dissolved in pyridine (3 ml), and acetic anhydride (2.1 g) was added at room temperature. After being stirred for 15 h, the mixture was evaporated *in vacuo*. The residue was subjected to column chromatography on silica gel with CH_2Cl_2–MeOH (10 : 1) to give D-**9a** (15 mg, quant.) as colorless crystals, mp 148—149 °C (*n*-hexane–AcOEt). $[\alpha]_D^{15}$ +90.1° (*c* = 0.38, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1780, 1740, 1660. ^{1}H-NMR ($CDCl_3$) δ: 2.04 (3H, s, OAc), 2.63 (1H, dd, *J* = 18, 4.3 Hz, 2-H), 3.02 (1H, dd, *J* = 18, 8.7 Hz, 2′-H), 4.33 (1H, dd, *J* = 12.7, 6.2 Hz, 5-H), 4.45 (1H, dd, *J* = 12.7, 6.2 Hz, 5′-H), 4.92 (1H, td, *J* = 6.2, 3.8 Hz, 4-H), 5.25 (1H, m, 3-H), 7.32—7.53 (4H, m, NH, ArH), 7.79—8.28 (2H, m, ArH). *Anal.* Calcd for $C_{14}H_{15}NO_5$: C, 60.64; H, 5.45; N, 5.05. Found: C, 60.23; H, 5.37; N, 4.92.

(3*S*,4*S*)-5-Acetoxy-3-benzoylamino-4-pentanolide (D-9b) A mixture of D-**5h** (46 mg, 0.086 mmol, *syn* : *anti* = 9 : 91) and 10% Pd/C (50 mg) in AcOH (5 ml) was shaken at room temperature for 3 d under hydrogen (3 kg/cm^2). After evaporation, benzoylation of crude *tert*-butyl (4*S*)-3-amino-4,5-(isopropylidenedioxy)pentanoate (21.1 mg) with NEt_3 (13 mg), DMAP (0.1 mg), and benzoyl chloride (18 mg, 0.13 mmol) in CH_2Cl_2 (1 ml) gave *tert*-butyl (4*S*)-3-benzoylamino-4,5-(isopropylidenedioxy)-pentanoate (26 mg). A solution of this benzoylaminoester (20.7 mg) in 80% AcOH was stirred at 40 °C for 1 h, then refluxed for 5 h, and evaporated. Pyridine (1.22 g) and acetic anhydride (1.5 g) were added to the residue, then the mixture was stirred for 15 h, and evaporated *in vacuo*. The residue was subjected to preparative thin layer chromatography (P-TLC) on silica gel with CH_2Cl_2–MeOH to give D-**9b** (13.8 mg, 73%, from D-**5h**) and D-**9a** (1.5 mg, 8% from D-**5h**). D-**9b**: mp 124—126 °C (*n*-hexane–AcOEt). $[\alpha]_D^{21}$ −2.94° (*c* = 0.425, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1780, 1745, 1600. ^{1}H-NMR ($CDCl_3$) δ: 2.11 (3H, s, OAc), 2.65 (1H, dd, *J* = 18.3, 4.3 Hz, 2-H), 3.11 (1H, dd, *J* = 18.3, 8.5 Hz, 2′-H), 4.34 (1H, dd, *J* = 12.2, 4.3 Hz, 5-H), 4.45 (1H, dd, *J* = 12.2, 3.1 Hz, 5′-H), 4.67—4.82 (2H, m, 3,4-H), 6.88 (1H, br d, *J* = 6.1 Hz, NH), 7.43—7.56 (3H, m, ArH), 7.79—8.28 (2H, m, ArH). Exact mass Calcd for $C_{14}H_{15}NO_5$: 277.0950. Found: 277.0961.

3-Benzoylamino-2,3-dideoxy-D-xylose (D-10a) A 1.76 M solution of DIBAL in hexane (0.12 ml, 0.21 mmol) was added to a stirred solution of D-**9a** (9.8 mg, 0.0353 mmol) in dry THF (2 ml) at −78 °C under nitrogen. The mixture was stirred for 3 h, then MeOH–H_2O (4 : 1, 0.5 ml) was added under the same conditions. The mixture was allowed to warm to room temperature, and saturated aqueous $NaHCO_3$ (0.2 ml) was added. The resulting precipitate was filtered off and the filtrate was evaporated *in vacuo*. The residue was subjected to P-TLC on silica gel with CH_2Cl_2–MeOH (10 : 1) to give D-**10a** (4.6 mg, 55%) as colorless crystals, mp 153.5—155 °C (*n*-hexane–acetone). $[\alpha]_D^{11}$ −10.0° (*c* = 0.210, EtOH). IR ν_{max}^{KBr} cm^{-1}: 3250, 1630. ^{1}H-NMR (DMSO-d_6) δ: signals due to α-anomer of pyranose form; 1.59 (1H, td, *J* = 12.5, 3.0 Hz, 2-H), 1.82 (1H, ddd, *J* = 12.5, 4.0, 2.1 Hz, 2′-H), 3.25—3.65 (3H, m, 4,5,5′-H), 4.15—4.25 (1H, m, 3-H), 4.88 (1H, d, *J* = 5 Hz, 4-OH), 5.10 (1H, br s, 1-H), 6.13 (1H, d, *J* = 4.2 Hz, 1-OH), 7.42—7.55 (3H, m, ArH), 7.81—7.89 (2H, m, ArH), 8.12 (1H, d, *J* = 8.5 Hz, NH); signals due to β-anomer of pyranose form; 1.46 (1H, td, *J* = 12.5, 9.0 Hz, 2-H), 1.94 (1H, ddd, *J* = 12.5, 3.9, 2 Hz, 2′-H), 3.15 (1H, dd, *J* = 11.5, 9.5 Hz, 5-H), 3.79 (1H, dd, *J* = 11.5, 5.0 Hz, 5′-H), 3.86—3.96 (1H, m, 3-H), 4.71 (1H, ddd, *J* = 9.0, 6.2, 2.0 Hz, 1-H), 4.92 (1H, d, *J* = 5.0 Hz, 4-OH), 6.57 (1H, d, *J* = 6.2 Hz, 1-OH), 7.42—7.5 (3H, m, ArH), 7.81—7.89 (2H, m, ArH), 8.25 (1H, d, *J* = 7.9 Hz, NH). These assignments are in good accord with those of related amino sugars.[15] MS *m/z*: 201 ($M^+ - 2H_2O$). Exact mass Calcd for $C_{12}H_{11}NO_2 - 2H_2O$: 201.0791. Found: 201.0796.

3-Benzoylamino-2,3-dideoxy-D-*ribo*-pentapyranose (D-10b) This (5.5 mg, 50%) was prepared from D-**9b** (13 mg, 0.047 mmol) and a 1.75 M solution of DIBAL in hexane (0.15 ml, 0.264 mmol) in dry THF (1 ml) in a manner similar to that used for the preparation of D-**10a**, mp 207—209 °C (acetone). $[\alpha]_D^{25}$ −37.5° (*c* = 0.0826, pyridine). IR ν_{max}^{KBr} cm^{-1}: 3310, 1635. ^{1}H-NMR (DMSO-d_6) δ: signals due to α-anomer of pyranose form; 1.65 (1H, ddd, *J* = 12, 4, 2.6 Hz, 2-H), 1.82 (1H, td, *J* = 12, 9 Hz, 2′-H), 3.64 (1H, m, 4-H), 3.748 (1H, dd, *J* = 12.1, 2.9 Hz, 5-H), 4.11 (1H, m, 3-H), 4.65 (1H, ddd, *J* = 9, 6.4, 2.6 Hz, 1-H), 4.87 (1H, d, *J* = 4.8 Hz, 4-OH), 6.58 (1H, d, *J* = 6.4 Hz, 1-OH), 7.43—7.56 (4H, m, ArH), 7.82—7.91 (1H, m, ArH), 7.96 (1H, d, *J* = 8 Hz, NH); signals due to β-anomer of pyranose form; 1.49 (1H, dd, *J* = 12, 3.5 Hz, 2-H), 2.06 (1H, td, *J* = 12, 4 Hz, 2′-H), 3.70 (1H, m, 4-H), 3.95 (1H, br d, *J* = 11.9 Hz, 5-H), 4.38 (1H, m, 3-H), 4.90 (1H, d, *J* = 4.6 Hz, 4-OH), 5.16 (1H, m, 1-H), 6.11 (1H, d, *J* = 3.6 Hz, 1-OH), 7.43—7.56 (3H, m, ArH), 7.82—7.91 (3H, m, ArH, NH). These assignments are in good accord with those of related amino sugars.[15] Exact mass Calcd for $C_{12}H_{15}NO_4$: 237.0998. Found: 237.0996.

***N*-[[(4*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl]methylene]benzylamine *N*-Oxide (L-4a)** This (231 mg, 55%) was prepared from 2,3-*O*-isopropylidene-L-glyceraldehyde (232 mg, 2.38 mmol) and benzylhydroxylamine (293 mg, 2.38 mmol) in a manner similar to that used for the preparation of D-**4a**, mp 84—85 °C (Et_2O). $[\alpha]_D^{19}$ −110° (*c* = 0.738, $CHCl_3$). All spectral data were identical with those of D-**4a**.

Methyl (4*R*)-3-[*N*-(*tert*-Butyldimethylsiloxy)benzylamino]-4,5-(isopropylidenedioxy)pentanoate (L-5a) This (322 mg, quant.) was prepared from L-**4a** (179 mg, 0.763 mmol), **1a** (179 mg, 0.954 mmol), and ZnI_2 (22 mg, 0.069 mmol) in a manner similar to that used for the preparation of D-**4a**. Further purification by column chromatography on silica gel with *n*-hexane–ether (10 : 1) gave pure L-*syn*-**5a**, $[\alpha]_D^{18}$ −27.16° (*c* = 0.69, $CHCl_3$). All spectral data were identical with those of D-*syn*-**5a**.

Methyl (3*S*,4*R*)-3-Amino-4,5-(isopropylidenedioxy)pentanoate (L-*syn*-7) This (66.2 mg, 92%) was prepared from L-*syn*-**5a** (150 mg, 0.355 mmol) and 10%-Pd/C (300 mg) in AcOH (15 ml) under hydrogen (3 kg/cm^2). $[\alpha]_D^{19}$ −13.8° (*c* = 0.434, $CHCl_3$). All spectral data were identical with those of D-*syn*-**7**.

Methyl (3*S*,4*R*)-3-Benzoylamino-4,5-(isopropylidenedioxy)pentanoate (L-*syn*-8) This (44.2 mg, 75%) was prepared from L-*syn*-**7** (39 mg, 0.19 mmol), benzoyl chloride (56.2 mg, 0.4 mmol), NEt_3 (0.1 ml), and DMAP (1 mg) in a manner similar to that used for the preparation of D-*syn*-**8**. mp 80—81 °C (*n*-hexane). $[\alpha]_D^{16}$ −36.0° (*c* = 1.07, $CHCl_3$). All spectral data were identical with those of D-*syn*-**8**.

(3*S*,4*R*)-5-Acetoxy-3-benzoylamino-4-pentanolide (L-9a) This (11 mg, 76%) was obtained by lactonization of L-*syn*-**8** (16 mg, 0.052 mmol) with 80% AcOH (1.5 ml) followed by acetylation with pyridine (3 g) and acetic anhydride (2 g). mp 149—149.5 °C (*n*-hexane–AcOEt). $[\alpha]_D^{16}$ −96.44° (*c* = 0.21, $CHCl_3$). All spectral data were identical with those of D-**9a**.

3-Benzoylamino-2,3-dideoxy-L-xylose (L-10a) This (5.8 mg, 67%) was prepared from L-**9a** (10 mg, 0.0361 mmol) and 1.75 M solution of DIBAL in hexane (0.13 ml) in a manner similar to that used for the preparation of D-**10a**. mp 154—156 °C (*n*-hexane–acetone). $[\alpha]_D^{11}$ +9.2° (*c* = 0.283, EtOH). All spectral data were identical with those of D-**10a**.

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