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4-O-Benzyl-2,3-O-isopropylidene-L-threose: A Useful Building Block for Stereoselective Synthesis of Monosaccharides

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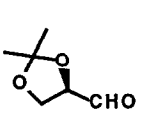
Summary: 4-O-Benzyl-2,3-O-isopropylidene-L-threose, readily available from L-tartaric acid, is a quite useful four-carbon building block for monosaccharide synthesis. The versatility can be reinforced by the coupled use of stereoselective addition reactions, where the suitable choice of organometallics leads to highly anti-selective additions. The building block is particularly useful in the synthesis of rare sugars, the versatility of which is demonstrated by the synthesis of some L-sugars as well as the formal total synthesis of polyoxin J in convergent manner.

Introduction: An impressive advance in the stereoselective organic reactions[1] in the past decade opened a viable approach to a number of stereochemically complex molecules which had been hardly accessible via the conventional methods. Such a circumstance is typically seen in sugar synthesis, where stereoselective C-C bond forming reaction to the chiral building block such as isopropylidene-D-glyceraldehyde (1) provides a flexible route to monosaccharides.[2] This approach would be particularly effective in the synthesis of unnatural sugars or "rare" sugars, which is of considerable concern from biological standpoints. By applying the concept of "Synthetic Control", we have accomplished stereoselective synthesis of some monosaccharides including D-ribose[3a], 2-deoxy-D-ribose[3b], D-ribulose[3c], D-ribonolactone[3d], 2-deoxy-2-amino-D-ribose[3e].

We thought that the exploitation of a new building block would widen the scope of this approach. In 1982, we reported a new four-carbon building block, 4-O-benzyl-2,3-O-isopropylidene-L-threose (2), readily available from naturally abundant L-tartaric acid, which has sizable synthetic utility in monosaccharide synthesis.[4,5] Availability of D-tartaric acid means that the enantiomer of 2 is also available. In this paper, we wish to outline the characteristic features of this new building block in the stereoselective synthesis of monosaccharides.[6]



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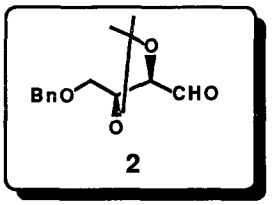

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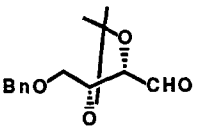

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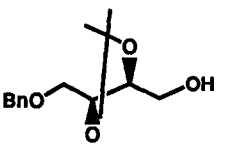
Preparation of **2**: Alcohol **3**, readily available from L-diethyl tartrate by the method of Seebach *et al.*[7], was subjected to the Swern oxidation to give aldehyde **2** as a colorless distillable liquid in 85 % yield. Aldehyde **2** is fairly stable and easy to handle, which is in sharp contrast to aldehyde **1**. The intensity of the aldehyde proton of **2** in ^{1}H NMR reduces to 1/2 after 12 hr presumably due to the trimer or tetramer formation, however, redistillation enables the high-yield regeneration of monomeric **2**.



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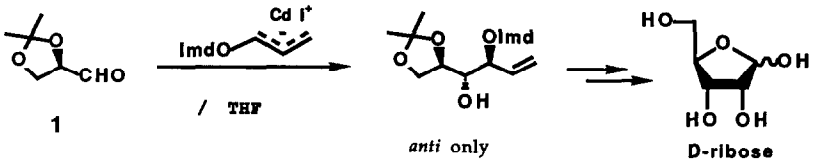
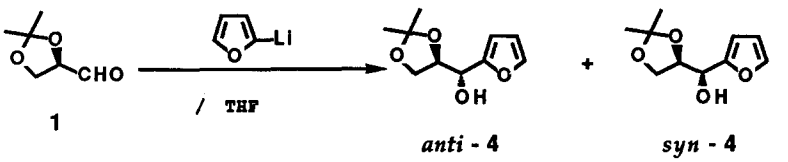
Backgrounds: Our concern in monosaccharide synthesis stemmed from the investigation on the reaction of a new allylic anion species with glyceraldehyde acetonide (**1**), which showed that the suitable choice of metallic species leads to highly *anti*-selective addition to **1**.[3a] Before then, few examples had been known for gaining high stereoselectivity in the addition to **1**. Therefore, this reaction gave us a



hint for monosaccharide synthesis. Actually, stereochemical outcome of the nucleophilic addition to **1** is strongly dictated by the entity of coexisting metal halides as exemplified in Table 1.[3c] The addition of furyllithium to **1** is slightly *syn*-selective (run 1), while it is highly *anti*-selective in the presence of Zn(II) halides. The *anti*-**4** was easily transformed to a naturally occurring ketose, D-ribulose.[3c]

Table 1. Effect of Coexisting Metal Halides in Addition to **1**.

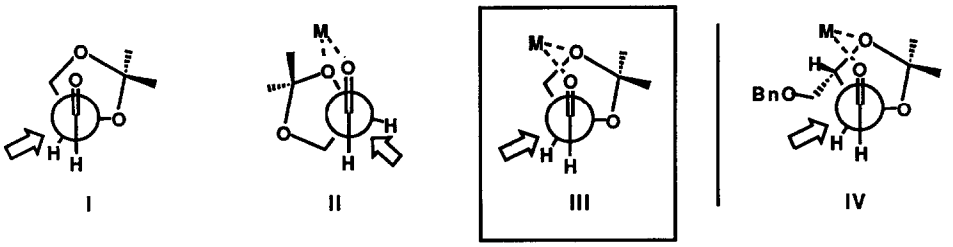


Run	Additive	Temp. (°C)	Yield (%)	*anti* / *syn*
1	None	-78	68	40 / 60
2	$MgBr_2$	0	49	50 / 50
3	$SnCl_4$	0	58	95 / 5 [a]
4	$ZnCl_2$	0	60	90 / 10
5	$ZnBr_2$	0	75	95 / 5
6	ZnI_2	0	57	> 95 / <5

a) Reaction was performed in toluene.

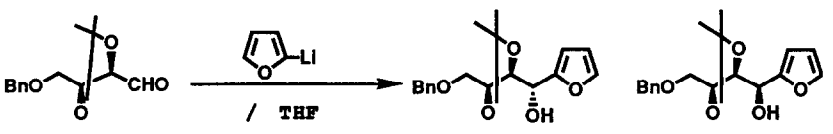
The *anti*-selective addition to **1** is explainable by the Felkin-Anh model[8] as depicted in **I**. The effect of metal chelation may act in two different ways. While α-chelation model **II** leads to opposite facial selection (*syn*), the β-chelation model **III** reinforces the Felkin selectivity stated above. The choice of organometallic species is effective in settling these conflicting factors by **III**.

Anti-Selective additions to **2**: At this stage, we reasoned that the addition of nucleophiles to **2** may be governed by the same principle as above since the $BnOCH_2$-group is disposed *trans* to the reacting formyl group on the dioxolane ring, which would not interfere the reaction course nor the chelation as shown in **IV**.



Actually, the efficiency of the Zn(II)-mediated stereocontrol is valid for the aldehyde **2**. The addition of furyllithium to **2** is highly *anti*-selective in the presence of $ZnBr_2$, to afford *anti*-**5** in excellent yield. Without $ZnBr_2$, in sharp contrast, the addition was virtually non-stereoselective to give a mixture of *anti*- and *syn*-**5**. *Anti*-**5** was easily transformed to L-tagatose, the unnatural form of a ketose, by which the unambiguous confirmation of the stereostructure of **5** was made.[6a)]

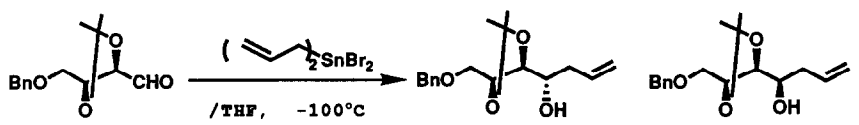
Table 2. Addition of furyllithium to **2**.[6a)]



2 *anti* - **5** *syn* - **5**

Run	Additive	Temp. (°C)	Yield (%)	*anti* / *syn*
1	None	-78	97	63 / 37
2	$ZnBr_2$	0	97	98 / 2

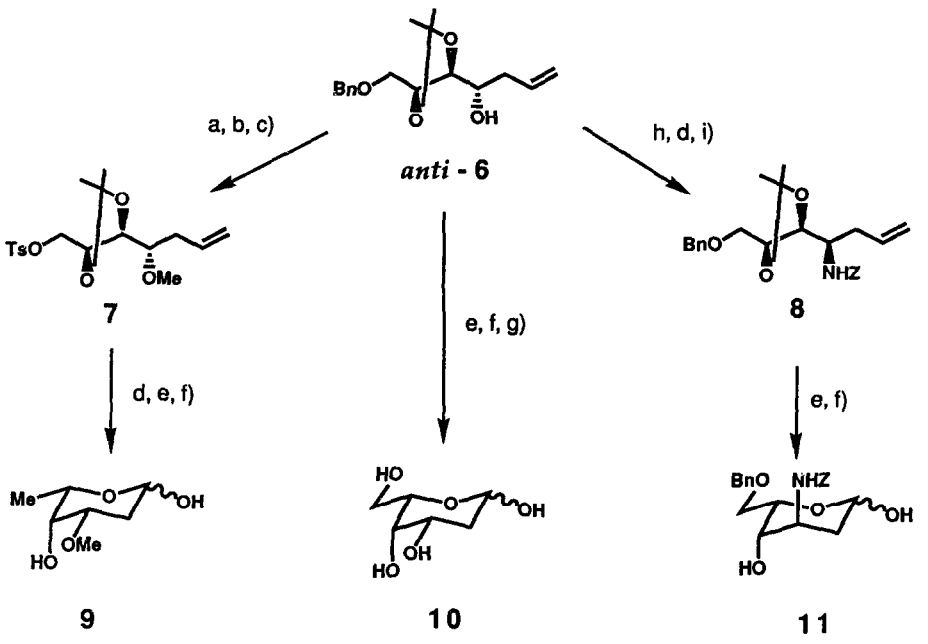
Synthesis of some 2-deoxy-L-sugars of biological interest: [6 b)] Recently, there have been isolated a number of sugar-containing substances of biological significance. The sugars involved are often "rare sugars", which are called so by their unique structural features, such as L-series sugars, deoxy sugars, amino sugars and branched sugars. To explore the possibility of **2** as a building block for such sugars, we undertook synthetic study of some 2-deoxy sugars, an important class of compounds. Relevantly, we examined the addition of various acetaldehyde-enolate equivalents ($^-CH_2CHO$) to **2**.[6b)] A convenient procedure found by this study is indicated below. The allylation by diallyltin(IV) dibromide[9)] proceeds quite smoothly at -100 °C to afford the product in 9/1 selectivity. The diastereomers were easily separable by flash chromatography.



2 *anti* - **6** *syn* - **6**

quantitative; *anti/syn* = 9/1

Scheme 1



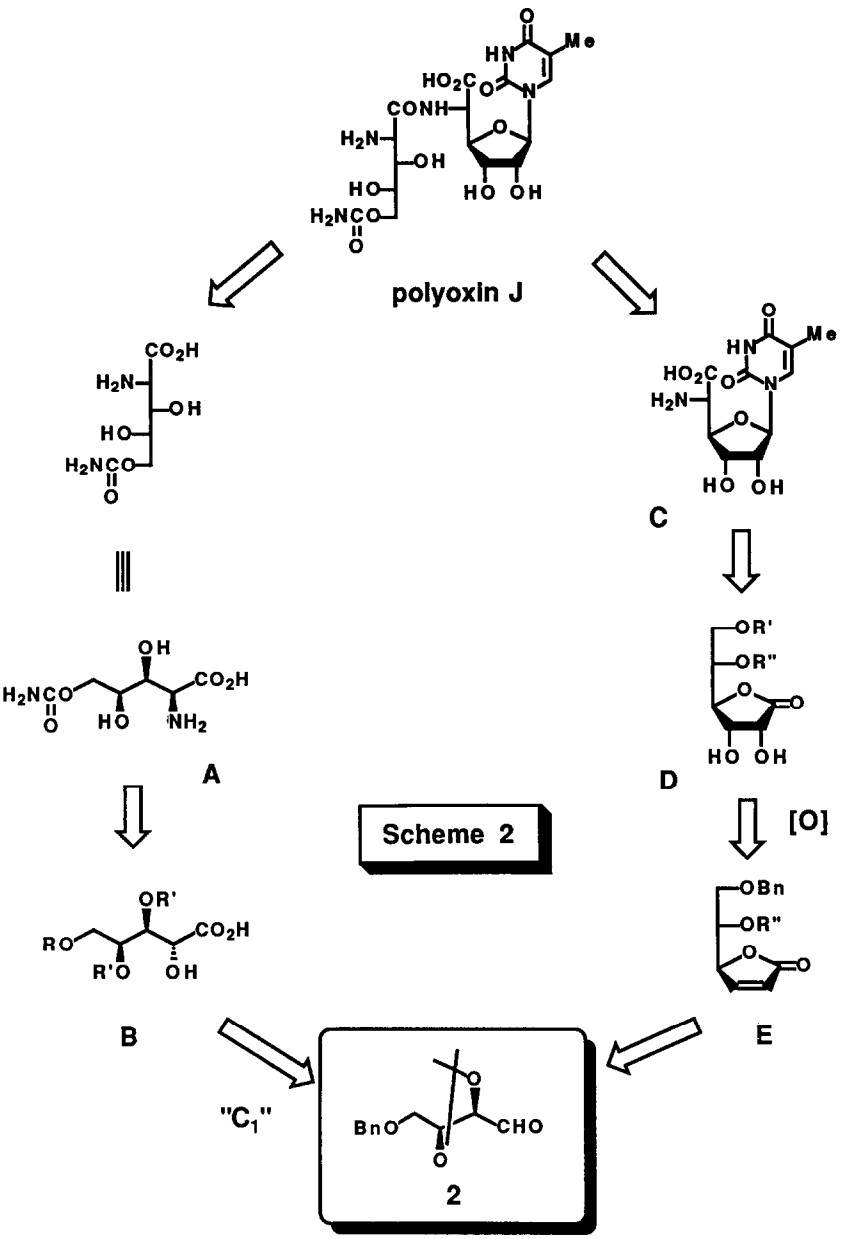
Keys: a) MeI, KOH; b) Na / NH_3; c) TsCl / pyridine; d) $LiAlH_4$; e) OsO_4-$NaIO_4$; f) H_3O^+; g) HCOOH, Pd-C; h) 2-fluoro-1-methylpyridinium tosylate, Et_3N; then LiN_3; i) ZCl, NaOH (Z = $PhCH_2OCO$-).

Anti-**6**, thus obtained, is already an acyclic equivalent of 2-deoxy-L-galactose (**10**). Actually, simple three-step conversion afforded **10** in high yield.

Moreover, the protection pattern of **6** is selective in a sense that allow the ready manipulation at a specific position. By virtue of this profit, two more sugars of biological significance were prepared in short steps. L-Diginose (**9**) is a 2,6-dideoxy sugar of L-series found in the digitalin-type cardiac steroids, the synthesis of which was achieved in a straightforward manner.

Synthesis of a protected amino sugar **11** represents an approach to the class of amino sugars found in anthracycline antibiotics. Introduction of the azido group was effected with the one-pot procedure based on halopyridinium salt previously reported from our laboratory.[10]

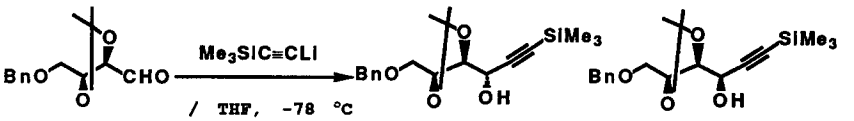
Convergent synthesis of polyoxin J: Polyoxin complex is a group of antifungal antibiotics produced by *Streptomyces cacaoi* var. *asoensis*.[11] Their pronounced biological activity as well as the unique structures have attracted considerable attention of synthetic chemists since the discovery. The gross structure of these compounds is divided into two fragments, the nucloside moiety and the side chain moiety, both of which are unique amino acids and are connected through a peptide bond. Several synthetic approaches have been recorded toward these structures.[12] So far, total synthesis of polyoxin J by Kuzuhara *et al.*[12d] is the only achievement to the full structure of this class of compounds. The synthesis comprises of the carbohydrate-based preparation of two key intermediates, that is, a suitably protected side chain and a nucleoside moiety, followed by their interconnection by peptide coupling. Here, we show another example of the versatility of the building block **2** by the stereoselective synthesis of both of these fragments by utilizing this aldehyde **2** as the common starting material, preliminary report of which appeared in 1984.[6c]



Synthetic plan: Retrosynthetic analysis is shown in Scheme 2. The side chain moiety **A** (5-O-carbamoylpolyoxamic acid) is obtainable by introducing nitrogen functionality to hydroxy acid **B** or its equivalent with inversion, which in turn can be derived from aldehyde **2** by the *anti*-selective addition of a C_1-equivalent. The nucleoside moiety **C** (deoxypolyoxin C) is obtainable also by inverting the C(5) of **D** with a suitable nitrogen nucleophile, which can, in turn, be derived from stereoselective oxidation of γ-butenolide **E**. The aldehyde **2** can serve again as the precursor of butenolide **E** provided that Z-selective Wittig-type homologation is viable. With this plan in mind, we investigated the synthesis of these fragments of polyoxin J.

Synthesis of the side chain moiety: The essential problem for constructing the side chain moiety is the stereoselective introduction of "$^{-}$COOH" equivalent to aldehyde **2** in highly *anti*-selective manner. For this purpose, the addition of $Me_3SiC{\equiv}C^-$ to **2** was investigated and the results are listed in Table 3. Addition of lithium trimethylsilylacetylide to **2** gave excellent yield of adduct **12**, however, without useful level of stereoselectivity. The best selectivity was recorded by employing an equimolar mixture of $TiCl_4$ and $Ti(O\text{-}i\text{-}Pr)_4$ as the additive. By using this reagent combination in THF at -78 °C, highly *anti*-selective alkynyl addition proceeded to afford almost pure *anti*-**12** in 83 % yield.[13] The selectivity holds for the large scale experiments (see Experimental). Use of $ClTi(O\text{-}i\text{-}Pr)_3$[14] also led to an excellent *anti*-selection, although the yield was poor.

Table 3. Stereoselective Addition of $Me_3SiC{\equiv}C^-$ to **2**



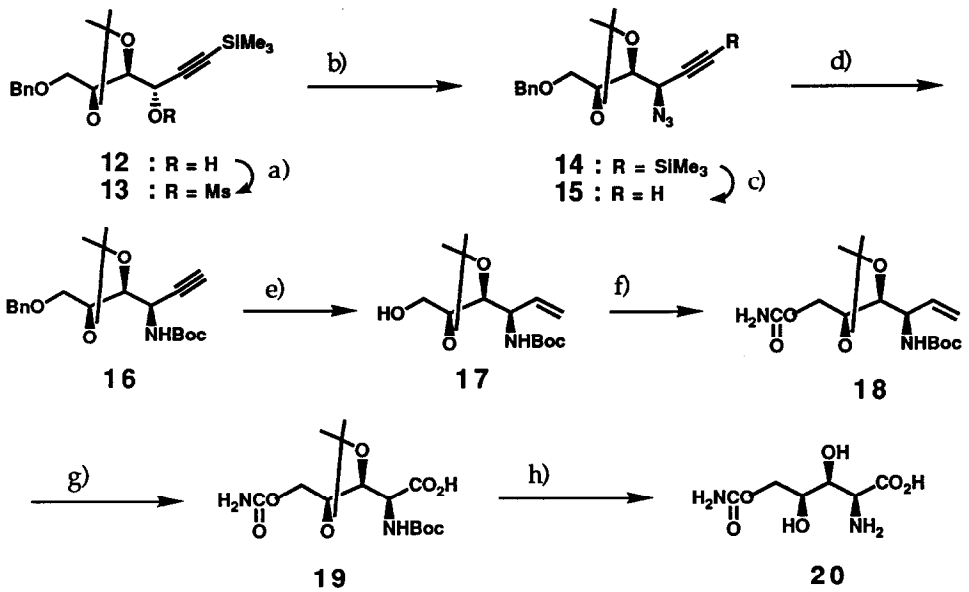
2 *anti* - **12** *syn* - **12**

Run	Additive	Yield (%)	*anti* / *syn*
1	None	97	68 / 32
2	$Ti(O\text{-}iPr)_4$	no reaction	
3	Cp_2TiCl_2	47	83 / 17
4	$ClTi(O\text{-}iPr)_3$	27	98 / 2
5	$TiCl_4$-$Ti(O\text{-}iPr)_4$ (1:1)	83	98 / 2

Further conversion of *anti*-**12** to the side chain moiety is outlined in Scheme 4. Alcohol **12** was mesylated to give **13**, which was treated with LiN_3 in HMPA. By virtue of the propargylic nature of the reaction site, the S_N2 attack proceeded quite facile, which completed at 0 °C within 1 h to give azide **14** in high yield. The terminal TMS-substituent was effective in suppressing the possible side reaction, that is, the S_N2'-type attack to give rise to allenic products. Azide **14** was de-silylated under phase transfer conditions to give **15**, which was treated with $LiAlH_4$ to effect the reduction of azide followed by treatment with $(t\text{-}BuOCO)_2O$ under basic conditions to give urethane **16**. Birch reduction of **16** effected removal of benzyl group with concomitant reduction of the triple bond to give olefinic alcohol **17**. Carbamoylation of **17** was effected by the two-step procedure *via* the mixed active carbonate, the aminolysis of which gave urethane **18**. Oxidative cleavage of the terminal double bond in **18** was effected by $KMnO_4$ to afford carboxylic acid **19**.

In this synthetic scheme, we noticed a problem of reproducibility in the conversion of **16** to **17**, which is sometimes accompanied by the formation of unidentified product(s) presumably arisng from the radical species during the dissolving metal reduction. In our preliminary report in 1984,[6c] physical data of the compounds later than **17** in Scheme 3 was misreported by this problem and the correct data are described in the experimental section. This issue was also pointed out by Saksena *et al.* in their non-stereoselective synthesis of **20** and its C(2)-epimer starting from the aldehyde **2** in 1986.[12e]

Scheme 3



Keys: a) MsCl, Et_3N / CH_2Cl_2 ; b) LiN_3 / HMPA, 0 °C, 1 h (85 % from 12); c) NH_4F, cat. $Bu_4N^+HSO_4^-$ / benzene-H_2O, r. t., 2 h (100 %); d) $LiAlH_4$ / Et_2O, 0 °C, 2 h; $(t\text{-}BuOCO)_2O$, r. t., 12 h, (76 %); e) Na / liq. NH_3, (85 %); f) p-$NO_2C_6H_4OCOCl$; NH_3-MeOH (67 %); g) $KMnO_4$ / acetone (pH 7) (88 %); h) H^+ (ref. 12e).

Synthesis of the nucleoside moiety: The two-carbon homologation of **2** leading to γ-butenolide **25** is the first of our concern here. To gain the requisite (Z)-selectivity, solvent effect in the Wittig reaction of **2** with $Ph_3P{=}CHCO_2Et$ was examined as shown in Table 4.[15] MeOH was found to be the solvent of choice and the Z/E-selectivity reached to the 9/1 level by the reaction at room temperature.

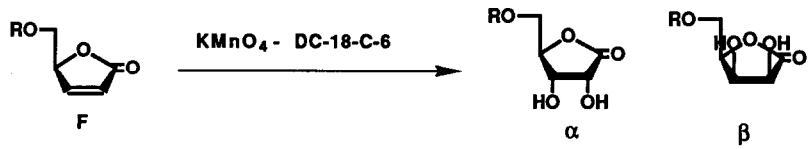
Table 4. Wittig Reaction of **2** with $Ph_3P{=}CHCO_2Et$.

Run	Solvent	Temperature	Yield (%)	Z / E
1	DMF	r. t.	77	27 / 73
2	HMPA	r. t.	75	30 / 70
3	benzene	reflux	85	30 / 70
4	CH_2Cl_2	reflux	88	65 / 35
5	MeOH	reflux	100	80 / 20
6	MeOH	r. t.	88	89 / 11

Acid treatment of **21** afforded unsaturated lactones **22** and **23** in the ratio of 7 : 1. The E-isomer of **21** was simply converted to the corresponding diol. After chromatographic separation, γ-butenolide **22** was isolated in 78 % yield from **2**. More conveniently, single recrystallization of the hydrolysis

products from AcOEt-hexane afforded γ-butenolide **22** as white needles in 47 % yield from **2**. Thus, the stage is set for the stereoselective *vicinal* dihydroxylation of the γ-butenolide.

Relevantly, we examined the oxidation of model compounds **F**, which revealed following characteristic features: (1) Good yields are obtainable by employing $KMnO_4$ as the oxidizing agent in the presence of dicyclohexano-18-crown-6. (2) The stereoselectivity critically depends on the protecting group (R), i.e., the use of bulky silyl group or trityl group led to excellent α-selectivities, while alkyl ether or acyl protection led to considerably decreased selectivity.[16]



F α β

Based on these data, butenolide **22** was silylated to afford silyl ether **24**. Oxidation of **24** with $KMnO_4$-crown ether proceeded in a highly stereoselective manner with the α/β ratio of at least 30 /1. The diol was then protected as the acetonide and the silyl group was removed to give alcohol **26**. Alcohol **26** was methanesulfonylated to give the corresponding mesylate, which was then subjected to S_N2 attack of lithium azide in HMPA to give azide **27**. Half reduction of lactone **27** was achieved in excellent yield by careful addition of DIBAL at -78 °C and subsequent removal of acetonide followed by per-acetylation afforded triacetate **28** in 97 % yield. Nucleoside formation was effected by treatment of **28** with **32** in the presence of TMSOTf to furnish **29** in 98 % yield. Removal of benzyl group without suffering the azide function was effected by the reaction with BBr_3 at -42 °C and the product was acetylated to give **30**. Treatment of **30** with excess NH_3 in MeOH gave 1-(5-azido-5-deoxy-β-D-allofuranosyl)thymine, whose structure was confirmed as the acetonide **31**. Elaboration of **31** to deoxypolyoxin C, the nucleoside moiety of polyoxin J, has been already established,[12d] the synthetic route described here represents a short and efficient approach to the molecule.

In conclusion, aldehyde **2** is a useful building block for monosaccharide synthesis particularly, by coupled with stereoselective C-C-bond forming reactions. This approach would be highly versatile in preparing a number of naturally occurring as well as artificial sugars of biological importance.

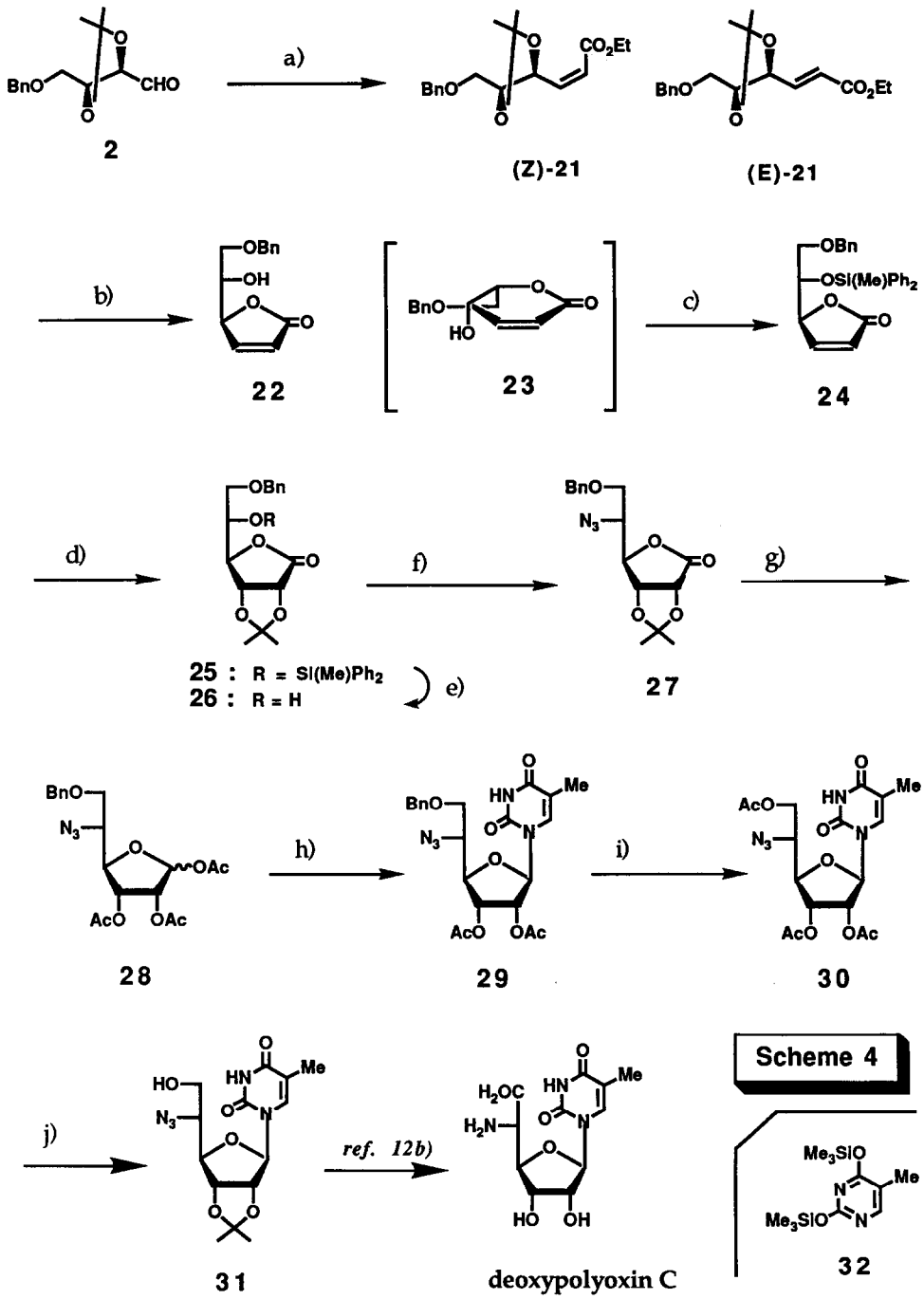
Acknowledgment: The present authors are grateful to Mr. Takamitsu Hosoya and Mr. Takashi Matsumoto, Keio University, for their technical assistance.

Experimental

General. Infrared (IR) spectra were recorded on Hitachi 260-30 spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded on Varian EM-390 (90 MHz), Jeol FX-90Q (90 MHz) or Jeol GX-400 (400 MHz) spectrometer. Optical rotations were recorded on JASCO DIP-181. Mass spectra were obtained by Jeol JMS-D300 spectrometer.

Preparation of **2**: To a cooled (-78 °C) solution of $(COCl)_2$ (0.98 g, 7.7 mmol) in CH_2Cl_2 (15 mL) was added DMSO (1.15 g, 14.7 mmol) in CH_2Cl_2 (3 mL) and the mixture was stirred for 5 min, to which was added **3** (1.67 g, 6.6 mmol) in CH_2Cl_2 (6 mL). After stirring for 2 h at -78 °C, Et_3N (3.37 g, 33 mmol) in CH_2Cl_2 (6 mL) was added and the temperature was gradually raised to 0 °C during 1 h. The mixture was poured into a cold phosphate buffer (pH 7; 200 mL) and the products were extracted with Et_2O. The organic layer was washed with water and concentrated. The residue was diluted with Et_2O and washed with water (x3) to ensure the removal of Et_3N•HCl and dried. Distillation at reduced pressure gave **2** (1.41 g, 85 %) as a colorless oil. Bp: 121 °C / 0.4 mmHg; $[\alpha]_D^{21}$ +16.8° (c 1.10, $CHCl_3$); NMR ($CDCl_3$): δ = 1.4 (3H, s), 1.5 (3H, s), 3.4-3.6 (2H, m), 4.0-4.2 (2H, m), 4.5 (2H, s), 7.1 (5H, s), 9.5 (1H, s); IR (neat): 1725, 740, 700 cm^{-1}; Found: C, 66.86; H, 7.30 %; Calcd for $C_{14}H_{18}O_4$, C, 67.18; H, 7.25 %; HRMS: *m/e*, 250.1219; Calcd for $C_{14}H_{18}O_4$, 250.1204, M^+.

Preparation of **5**: To a solution of n-BuLi (0.64 M in hexane; 1.0 mmol) at -78 °C was added furan (102 mg, 1.5 mmol) in THF (3 mL), which was stirred at r. t. for 2 h. The mixture was cooled to 0°C, to which was added well-dried $ZnBr_2$ (237 mg, 1.0 mmol) , and the solution was stirred for 10 min. Aldehyde **2** (200 mg, 0.8 mmol) in THF (2 mL) was added to the mixture and stirring was continued for 2 h at 0 °C. The reaction was stopped by adding 4% $NaHCO_3$ and the products were extracted with Et_2O and dried. Purification by TLC (petroleum ether-AcOEt) gave **5** as a colorless oil (261 mg, 98



Keys: a) $Ph_3P{=}CHCO_2Et$ / MeOH, r. t. (Z / E = 89 / 11); b) HCl / THF, (47 % from 2); c) $Ph_2MeSiCl$, 2,6-lutidine / CH_2Cl_2 (91%); d) $KMnO_4$ - dicyclohexano-18-C-6 / CH_2Cl_2; $Me_2C(OMe)_2$, cat. TsOH / CH_2Cl_2 (79 %); e) NH_4F, cat. $Bu_4N^+HSO_4^-$ / AcOEt-H_2O, (96%); f) MsCl, Et_3N / CH_2Cl_2; NaN_3 / HMPA, 80 ° C (95 %); g) DIBAL / toluene, -78°C; 70 % AcOH, 90 °C, 2 h; Ac_2O, cat. DMAP / pyridine (97 %), h) 32, TMSOTf / $CHCl_3$, reflux, 1.5 h (98 %); i) BBr_3 / CH_2Cl_2, -42 °C, then MeOH; Ac_2O, cat. DMAP / pyridine (83 %); j) NH_3 / MeOH; $Me_2C(OMe)_2$, cat. TsOH / acetone (97 %).

%). The isomeric purity was determined to be *anti*/*syn* = 98/2 by HPLC [LiChrosorb SI-60 (Merck); hexane-AcOEt = 4/1]. *Anti*-**5**: NMR ($CDCl_3$): δ = 1.3 (6H, s), 3.1-4.5 (5H, m), 4.35 (2H, s), 4.7 (1H, d, J=3Hz), 6.2 (2H, s), 7.1-7.3 (6H, m); IR (neat): 3430, 860, 740, 700 cm^{-1}. *Cf. Syn*-**5**: NMR ($CDCl_3$): δ = 1.35 (3H, s), 1.40 (3H, s), 3.0 (br, 1H), 3.1-3.6 (2H, m), 4.0-4.3 (2H, m), 4.5 (2H, s), 4.5-4.9 (1H, m), 6.3 (2H, s), 7.1-7.4 (6H, m); IR (neat): 3430, 1080, 865, 740, 700 cm^{-1}.

Preparation of **6**: To a cooled (-100 °C) solution of **2** (0.87 g, 3.5 mmol) in THF (10 mL) was added diallyltin(IV) dibromide (1.46 g, 4.0 mmol) in THF (10 mL). After stirring for 5 h, the reaction was stopped by adding a small amount of pH 7 phosphate buffer. The precipitates were removed by filtration (Celite) and the filtrate was concentrated. Purification on column chromatography (petroleum ether-Et_2O) gave alcohol **6** (1.0 g, quantitative), which was composed of *anti* and *syn* isomers (*anti*/*syn* = 9:1; HPLC: Merck LiChrosorb SI60; hexane-AcOEt). The isomers were separated by flash column chromatography (hexane-AcOEt). *Anti*-**6**: Bp: 150 °C / 0.15 mmHg (bath temp.); $[\alpha]_D^{20}$ +3.5° (c 1.2, benzene); NMR ($CDCl_3$) δ = 1.4 (6H, s), 2.0-2.5 (2H, m), 2.7 (1H, br), 3.4-3.8 (4H, m), 4.0-4.3 (1H, m), 4.6 (2H, s), 4.9-5.3 (2H, m), 5.6-6.1 (1H, m), 7.3 (5H, s); IR (neat): 1635, 910, 730, 695 cm^{-1}; Anal.: Found: C, 69.72; H, 8.25 %; Calcd for $C_{17}H_{24}O_4$, C, 69.83; H, 8.27 %. *Syn*-**6**: NMR ($CDCl_3$): δ = 1.4 (6H, s), 2.0-2.4 (3H, m), 3.3-3.9 (4H, m), 4.0-4.3 (1H, m), 4.6 (2H, s), 4.9-5.3 (2H, m), 5.6-6.1 (1H, m), 7.3 (5H, s); IR (neat): 3450, 1380, 1090, 740, 705 cm^{-1}.

Preparation of **12**: To a solution of $Me_3SiC{\equiv}CH$ (7.1 g, 72.4 mmol) in THF (300 mL) at -78 °C was added n-BuLi (hexane solution; 51 mL, 66 mmol), and the mixture was stirred for 15 min. A mixture of $Ti(O\text{-}iPr)_4$ (13.5 g, 48 mmol) and $TiCl_4$ (9.1 g, 48 mmol) in petroleum ether (240 mL), prepared beforehand in another flask, was added slowly to the acetylide solution, which was stirred for 1 h. To this mixture was added **2** (14.8 g, 60 mmol) in THF (300 mL), and stirring was continued for 2 h. The reaction was stopped by adding pH 7 phosphate buffer. After filtration (Celite), the products were extracted with AcOEt and dried. Purification by column chromatography (AcOEt-hexane) gave **12** as a colorless oil (17.1 g, 83 %). Bp: 103 °C / 0.4 mmHg; $[\alpha]_D^{20}$ -2.7° (c 0.47, CCl_4); NMR ($CDCl_3$; 400 MHz): δ = 0.16 (s, 9H), 1.44 (s, 3H), 1.46 (s, 3H), 2.54 (d, 1H, J=4.9Hz), 3.68 (dd, 1H, J_1=5.4Hz, J_2=10.3Hz), 3.73 (dd, 1H, J_1=10.3Hz, J_2=3.9Hz), 4.02 (dd, 1H, J_1=3.9Hz, J_2=8.3Hz), 4.29 (ddd, J_1=8.3Hz, J_2=5.4Hz, J_3=3.9Hz), 4.55 (dd, 1H, J_1=3.9Hz, J_2=4.9Hz), 4.60 (s, 2H), 7.2-7.35 (m, 5H); IR (neat): 3430, 2900, 2170, 1500, 1460, 1370, 1250, 1080, 840 cm^{-1}; Anal.: Found: C, 65.23; H, 8.35 %; Calcd for $C_{19}H_{28}O_4Si$; C, 65.48; H, 8.10 %; HRMS: *m*/*e*, 333.1522; Calcd for $C_{18}H_{25}O_4Si$, 333.1522, $(M\text{-}CH_3)^+$.

Preparation of **14**: To a solution of **12** (170 mg, 0.49 mmol) and Et_3N (100 mg, 0.98 mmol) in CH_2Cl_2 (3 mL) at 0°C was added MsCl (172 mg, 1.5 mmol) and the mixture was stirred for 5 min. After adding pH 7 phosphate buffer, products were extracted with Et_2O. Combined organic layer was washed successively with water (x2) and brine and dried. After evaporation, crude **13** was used in the next step. The ^1H NMR spectrum ($CDCl_3$; 400 MHz) of a purified sample of **13**, prepared by another run, follows: δ: 0.19 (s, 3H), 1.45 (s, 3H), 1.47 (s, 3H), 3.13 (s, 3H), 3.69 (d, 2H, J=4.9 Hz), 4.17 (dd, 1H, J_1=2.9Hz, J_2=8.3Hz), 4.25 (dt, 1H, J_1=8.3Hz, J_2=4.9Hz), 4.60 (s, 2H), 5.35 (d, 1H, 2.9 Hz), 7.26-7.36 (m, 5H).

To the solution of mesylate **13** in HMPA (1.5 mL) was added LiN_3 (49 mg, 1.0 mmol) at 0°C and the mixture was stirred for 1 h. After diluted with Et_2O, the organic layer was washed several times with water and dried. Purification by TLC (AcOEt-hexane) gave **14** as an oil (155 mg, 85 %). $[\alpha]_D^{23}$ -60.7° (c 1.02, CCl_4); NMR ($CDCl_3$; 400 MHz): δ = 0.19 (s, 9H), 1.45 (s, 3H), 1.46 (s, 3H), 3.63 (dd, 1H, J_1=10.3Hz, J_2=5.9Hz), 3.72 (dd, 1H, J_1=10.3Hz, J_2=3.4Hz), 3.94 (dd, 1H, J_1=5.9Hz, J_2=7.8Hz), 4.2-4.23 (m, 1H), 4.23 (d, 1H, J=5.9Hz), 4.60 (s, 2H), 7.25-7.35 (m, 5H); IR (neat): 2100, 1500, 1450, 1370, 1250 cm^{-1}; Anal.: Found: C, 60.87; H, 7.59; N, 11.02 %; Calcd for $C_{19}H_{27}O_3N_3Si$; C, 61.10, H, 7.29; N, 11.25 %.

Preparation of **15**: In the presence of n-$Bu_4N^+HSO_4^-$ (224 mg), two-phase mixture of **14** (10.0 g, 26.9 mmol) in benzene (90 mL) and satd. NH_4F solution (90 mL) was vigorously stirred for 2 h. Extraction (Et_2O) and purification by column chromatography (AcOEt-hexane) gave **15** as a colorless oil (8.08 g, quantitative). $[\alpha]_D^{19}$ -76.5° (c 1.52, CCl_4); NMR ($CDCl_3$; 400 MHz): δ = 1.45 (s, 3H), 1.48 (s, 3H), 2.58 (d, 1H, J=2.4Hz), 3.63 (dd, 1H, J_1=12.7Hz, J_2=4.9Hz), 3.66 (dd, 1H, J_1=12.7Hz, J_2=4.9Hz), 4.00 (dd, 1H, J_1=4.9Hz, J_2=7.8Hz), 4.16 (dd, 1H, J_1=4.9Hz, J_2=2.4Hz), 4.22 (dt, 1H, J_1=7.8Hz, J_2=4.9Hz), 4.59 (s, 2H), 7.26-7.38 (m, 5H); IR (neat): 2100, 1500, 1450, 1380, 1230 cm^{-1}; Anal.: Found: C, 63.57; H, 6.11; N, 13.69 %; Calcd for $C_{16}H_{19}O_3N_3$; C, 63.77, H, 6.36; N, 13.95 %.

Preparation of **16**: To a suspension of $LiAlH_4$ (30 mg, 0.80 mmol) in Et_2O (1.5 mL) at 0°C was added **15** (97 mg, 0.32 mmol) in Et_2O (1 mL) and the mixture was stirred for 2 h. The reaction was stopped by carefully adding $Na_2SO_4 \cdot 10H_2O$ and filtered. After evaporation, the residue was dissolved in 1,4-dioxane (1.5 mL) and 1N NaOH (0.5 mL), to which was added $(t\text{-}BuOCO)_2O$ (262 mg, 1.2 mmol). After stirring overnight, the products were extracted with AcOEt and the organic layer was washed with brine. Purification by column chromatography (AcOEt-hexane) gave **16** as a colorless oil (70 mg, 76 %), which was crystallized on standing. Mp. 60-61 °C; $[\alpha]_D^{28}$ -26.7° (c 1.47, CCl_4); NMR ($CDCl_3$; 400 MHz): δ = 1.41 (s, 3H), 1.44 (s, 6H), 1.45 (s, 3H), 1.56 (s, 3H), 2.31 (d, 1H, J=2.4Hz), 3.58 (dd, 1H, J_1=5.4Hz, J_2=10.3Hz), 3.67 (dd, 1H, J_1=5.4Hz, J_2=10.3Hz), 3.98 (dd, 1H, J_1=7.8Hz, J_2=2.9Hz), 4.13 (dt, 1H, J_1=7.8Hz, J_2=5.4Hz), 4.59 (d, 1H, J=12Hz), 4.6-4.7 (m, 1H), 4.63 (d, 1H, J=12Hz), 5.3-5.35 (br, 1H), 7.25-7.40 (m, 5H); IR (neat): 3300, 3000, 1720, 1500, 1380, 1250 cm^{-1}; HRMS: *m*/*e*, 360.1829; Calcd for $C_{20}H_{26}NO_5$, 360.1812, $(M\text{-}CH_3)^+$.

Preparation of **17**: To a solution of **16** (75 mg, 0.20 mmol) in liq. NH_3 (3 mL) was added Na (ca. 20 mg, 0.8 mmol) and the mixture was stirred for 20 min. Solid NH_4Cl was added to the mixture and NH_3 was allowed to evaporate at r. t. Extraction followed by purification by column chromatography (AcOEt-hexane) gave **17** as a colorless oil (43 mg, 75 %). $[\alpha]_D^{26}$ +24.8° (c 0.86, acetone); NMR ($CDCl_3$; 400 MHz): δ = 1.41 (s, 3H), 1.43 (s, 3H), 1.44 (s, 3H), 1.45 (s, 6H), 2.3-2.6 (br, 1H), 3.7-3.9 (m, 3H), 4.03-4.06 (m, 1H), 4.2-4.4 (br, 1H), 4.95-4.97 (br, 1H), 5.22 (d, 1H, J=10.3Hz), 5.28 (d, 1H, J=17Hz, 5.86 (ddd, 1H, J_1=17Hz, J_2=10.3Hz, J_3=5.4Hz); IR (neat): 3450, 3000, 1700, 1500, 1250 cm^{-1}; HRMS (In-beam): *m/e*, 288.1815; Calcd for $C_{14}H_{26}NO_5$, 288.1810, $(M+1)^+$.

Preparation of **18**: To a solution of 17 (71 mg, 0.24 mmol) in pyridine (1 mL) at 0°C was added p-nitrophenylchloroformate (75 mg, 0.37 mmol) and the mixture was stirred for 3 h. After diluted with AcOEt, the organic layer was washed successively with cold water, satd. $CuSO_4$ solution, brine and dried. After evaporation, the residue was dissolved in MeOH (30 mL), to which was added 8 % NH_3-MeOH at 0°C and the mixture was stirred for 10 min and evaporated. Purification by column chromatography (AcOEt-hexane) gave **18** as white crystals (55 mg, 67 %). $[\alpha]_D^{28}$ +11.2° (c 0.37, MeOH); NMR ($CDCl_3$; 400 MHz): δ = 1.40 (s, 3H), 1.44, (s, 3H), 1.45 (s, 9H), 3.9-4.1 (m, 2H), 4.1-4.5 (m, 3H), 4.6-5.0 (br, 3H), 5.23 (dd, 1H, J_1=10.3Hz, J_2=1.5Hz), 5.28 (dd, 1H, J_1=17.1Hz, J_2=1.5Hz), 5.86 (ddd, 1H, J_1=5.4Hz, J_2=10.3Hz, J_3=17.1Hz); IR (KBr): 3370, 1690, 1680, 1660, 1640, 1515, 1420, 1250 cm-1; HRMS: *m/e*, 259.0908; Calcd for $C_{10}H_{15}N_2O_6$, 259.0910, $(M-CH_3-C_4H_9)^+$.

Preparation of **19**: To a solution of **18** (67.5 mg, 0.21 mmol) in acetone (3 mL) and pH 7 phosphate buffer (0.5 mL) at 0°C was added $KMnO_4$ (169 mg, 1.05 mmol) in small portions and the mixture was stirred for 3 h. After diluted with CH_2Cl_2, Na_2SO_3 was added and the pH was adjusted to 3 by carefully adding 1 N HCl. After drying, evaporation gave **19** as a colorless oil (63 mg, 87 %). For analytical purpose, a small sample was treated with CH_2N_2 and purified by TLC (Et_2O-petroleum ether). NMR ($CDCl_3$; 400 MHz): δ = 1.39 (s, 3H), 1.42 (s, 3H), 1.46 (s, 9H), 3.80 (s, 3H), 4.00-4.05 (m, 1H), 4.23-4.30 (m, 3H), 4.51 (broad d, 1H), 4.65-4.90 (br, 2H), 5.28 (broad d, 1H); HRMS (In-beam): *m/e*, 363.1746; Calcd for $C_{15}H_{27}N_2O_8$, 363.1764, $(M+1)^+$.

Preparation of **22**: To an ice-cooled solution of **2** (2.38 g, 9.5 mmol) in MeOH (10 mL) was added ethoxycarbonyltriphenylphosphorane (3.65 g, 10.5 mmol) in small portions and the mixture was stirred at r. t. overnight. After the solvent was evaporated in vacuo, the residue was passed through a silica-gel short column (petroleum ether-Et_2O) to remove Ph_3P=O to give a mixture of olefin **21** (Z/E = 9/1). Without separation, the isomeric mixture was dissolved in THF (10 mL), to which was added 3 N HCl (10 mL) and stirring was continued overnight. After the mixture was saturated with salt, products were extracted with Et_2O and dried and evaporated. Recrystallization from AcOEt-hexane gave **22** as white crystals (1.04 g, 47 %). Mp: 79-81 °C (AcOEt-hexane); $[\alpha]_D^{21}$ -73° (c 1.0, $CHCl_3$); NMR ($CDCl_3$): δ = 2.8 (1H, br), 3.4-3.8 (2H, m), 3.9 (1H, ddd, J_1=5Hz, J_2=4.8 Hz, J_3=6.5Hz), 4.5 (2H, s), 5.1 (1H, ddd, J_1=5Hz, J_2=1.9 Hz, J_3=1.6 Hz), 6.1 (1H, dd, J_1=5.7Hz, J_2=1.9 Hz), 7.3 (5H, s), 7.4 (1H, dd, J_1=5.7Hz, J_2=1.6 Hz); IR (CH_2Cl_2): 3590, 3050, 2880, 1760, 1610, 1500, 1460, 1365, 1165, 1100, 830 cm^{-1}; Anal.: Found: C, 66.62; H, 6.13 %; Calcd for $C_{13}H_{14}O_4$, C, 66.65; H, 6.02 %.

Preparation of **24**: At 0°C, to a mixture of **22** (4.8 g, 20.5 mmol) and 2,6-lutidine (5.06 g, 24.6 mmol) in CH_2Cl_2 (60 mL) was added $Ph_2MeSiCl$ (5.73 g, 24.6 mmol) in CH_2Cl_2 (15 mL) which was stirred for 30 min at 0 °C and at r. t. for 2 h. After diluted with CH_2Cl_2, the mixture was washed with water, satd. $CuSO_4$ solution, satd. Na_2SO_4 solution. After drying and evaporation, purification by column chromatography (AcOEt-hexane) gave **24** (8.88 g, 91 %) as a colorless oil. $[\alpha]_D^{21}$ -55° (c 1.0, $CHCl_3$); NMR (CCl_4): δ = 0.6 (3H, s), 3.2-3.6 (2H, m), 3.7-4.2 (1H, m), 4.3 (2H, s), 4.8-5.0 (1H, m), 5.8 (1H, dd, J_1=5.7Hz, J_2=1.6 Hz), 6.9-7.6 (16H, m); IR (neat): 3050, 2900, 2850, 1780, 1750, 1600, 1580 cm^{-1}.

Preparation of **26**: To a vigorously stirred solution of **24** (475 mg, 1.0 mmol) and dicyclohexano-18-crown-6 (48 mg) in CH_2Cl_2 (7.5 mL) at -42 °C was added $KMnO_4$ (190 mg, 1.19 mmol) in small portions and stirred for 4 hr. The reaction was stopped by adding Na_2SO_3 (300 mg) followed by careful neutralization with 1N H_2SO_4 and the products were extracted with CH_2Cl_2. After drying and evaporation, the crude diols was dissolved in CH_2Cl_2 (5 mL), to which was added $MeC_2(OMe)_2$ (110 mg, 1.05 mmol) and cat. p-TsOH and stirred for 2 h. The mixture was diluted with CH_2Cl_2 and washed successively with water, satd. $NaHCO_3$ solution, satd. NaCl solution and dried. Chromatography on TLC (petroleum ether-Et_2O) gave **25** (377 g, 79 %) as a colorless oil. NMR (CCl_4) δ = 0.6 (3H, s), 1.1 (3H, s) 1.3 (3H, s), 3.2-3.5 (2H, m), 3.9-4.1 (1H, m), 4.15 (2H, s), 4.25 (2H, s), 4.5 (1H, d, J=1.6 Hz), 6.9-7.6 (15H, m).

The silyl ether **25**, thus obtained, was desilylated: In the presence of n-$Bu_4N^+HSO_4^-$ (20 mg), two-phase mixture of **25** (150 mg, 0.27 mmol) in AcOEt (2 mL) and 50 % NH_4F solution (1 mL) was vigorously stirred overnight. Extraction and chromatography on TLC (AcOEt-hexane) gave **26** as white crystals (80 mg, 96 %). Mp: 80-83 °C (AcOEt-Et_2O); $[\alpha]_D^{27}$ -10° (c 1.0, $CHCl_3$); NMR (CCl_4): δ = 1.3 (3H, s), 1.4 (3H, s), 2.7-3.1 (1H, br), 3.45-3.65 (2H, m), 3.7-4.1 (1H, m), 4.5 (3H, s), 4.7 (2H, s), 7.3 (5H, s); IR (KBr): 3420, 2950, 2900, 1780, 1635 cm^{-1}.

Preparation of **27**: To a solution of **26** (720 mg, 2.33 mmol) and Et_3N (285 mg, 2.82 mmol) in CH_2Cl_2 (8 mL) at 0 °C was added CH_3SO_2Cl (295 mg, 2.58 mmol) in CH_2Cl_2 (2 mL) and the mixture was stirred for 3 h at r. t. After diluted with CH_2Cl_2, the mixture was washed successively with water and brine. After drying and evaporation, the residue was

dissolved in HMPA (10 mL), to which was added NaN_3 (175 mg, 2.69 mmol) and heated 3 h at 80 °C for. The mixture was diluted with AcOEt, which was washed successively with water, brine and dried. Purification by column chromatography (AcOEt-hexane) gave **27** (738 mg, 95 %) as a colorless oil. $[\alpha]_D^{25}$ -61° (c 1.0, $CHCl_3$); NMR ($CDCl_3$): δ = 1.3 (3H, s), 1.4 (3H, s), 3.5-4.0 (3H, m), 4.4-4.7 (5H, m), 7.2 (5H, s); IR (neat): 3000, 2950, 2870, 2100, 1780 cm^{-1}.

Preparation of **28**: To a solution of azide **27** (240 mg, 0.60 mmol) in toluene (8 mL) at -78 °C was added DIBAL (1M / toluene; 0.72 mL). The reaction was immediately stopped by adding satd. NH_4Cl solution and pH 7 phosphate buffer. The products were extracted with AcOEt, and the organic layer was dried and evaporated. The residue was dissolved in 70 % AcOH and heated at 90 °C for 2 h. Solvents were evaporated at reduced pressure and co-evaporated with benzene for two times. The products were acetylated in standard manner (Ac_2O-pyridine), and purification by TLC (AcOEt-hexane) gave **28** (293 mg, 97 %) as an α/β mixture. NMR ($CDCl_3$): α-isomer: δ = 2.1 (9H, s), 3.5-4.0 (3H, m), 4.3 (1H, t, J=3Hz), 4.5 (2H, s), 5.1-5.5 (2H, m), 6.4 (1H, d, J=4Hz), 7.3 (5H, s); β-isomer: δ = 2.1 (9H, s), 3.4-4.0 (3H, m), 4.3 (1H, t, J=6Hz), 4.5 (2H, s), 5.3-5.7 (2H, m), 6.1 (1H, s), 7.3 (5H, s); IR (neat; α/β-mixture): 3020, 2920, 2850, 2100, 1750 cm^{-1}.

Preparation of **29**: A solution of **28** (755 mg, 1.79 mmol), **32** (1200 mg, 4.44 mmol), and TMSOTf (600 mg, 2.7 mmol) in $CHCl_3$ (10 mL) was heated under reflux for 1.5 h. The mixture was diluted with $CHCl_3$, which was washed successively with satd. $NaHCO_3$ solution and brine and dried. Purification by column chromatography (AcOEt-hexane) gave **30** (855 mg, 98 %) as a colorless oil. $[\alpha]_D^{25}$ -5.9° (c 2.5, $CHCl_3$); NMR ($CDCl_3$): δ = 1.9 (3H, s), 2.1 (6H, s), 3.5-4.2 (4H, m), 4.5 (2H, s), 5.3 (1H, d, J=5Hz), 5.35 (1H, s), 6.0 (1H, d, J=5Hz), 7.1-7.3 (6H, m), 10.0 (1H, br); IR (neat): 3200, 3060, 2940, 2860, 2100, 1760, 1750, 1730, 1720, 1700, 1680 cm^{-1}.

Preparation of **30**: To a solution of **29** (814 mg, 1.64 mmol) in CH_2Cl_2 (8 mL) was added BBr_3 (830 mg, 3.31 mmol) in CH_2Cl_2 (8 mL) at -42 °C and the mixture was stirred for 3 h. Abs. MeOH (40 mL) was added to the mixture which was stirred for 1 h at -20 °C. Solid $NaHCO_3$ was added at 0 °C and the mixture was stirred for 0.5 h. After filtration and evaporation, usual acetylation (Ac_2O-pyridine) and purification by column chromatography (AcOEt-hexane) gave **30** (608 mg, 83 %) as an oil. $[\alpha]_D^{25}$ +8.9° (c 0.93, $CHCl_3$); NMR ($CDCl_3$): δ= 1.9 (3H, s), 2.1 (9H, s), 3.9-4.5 (4H, m), 5.35 (1H, d, J=5Hz), 5.4 (1H, s), 5.9 (1H, d, J=5Hz), 7.1 (1H, s), 9.8 (1H, br); IR (neat): 3190, 3050, 2100, 1750, 1730, 1700, 1680 cm^{-1}.

Preparation of **31**: A solution of **30** (608 mg, 1.38 mmol) in 8 % NH_3-MeOH (10 mL) was at 0 °C for 1 h and stirring was continued at r. t. overnight. After volatile compounds were removed under reduced pressure, the residue was dissolved in dry acetone (10 mL), to which was added 2,2-dimethoxypropane (233 mg, 2.14 mmol) and cat. p-TsOH and the mixture was stirred at r. t. overnight. After evaporation, purification by TLC (AcOEt-hexane) gave **31** (472 mg, 97 %) as white crystals. Mp: 157-158 °C (*lit.* [12b] 158-159 °C); $[\alpha]_D^{28}$ -13° (c 1.0, pyridine) [*lit.*[12b]] $[\alpha]_D^{25}$ -13.2° (c 0.24, pyridine)]; NMR ($CDCl_3$-CD_3OD): δ = 1.3 (3H, s), 1.5 (3H, s), 1.8 (3H, s), 3.6-4.1 (4H, m), 4.7-5.1 (2H, m), 5.7 (1H, d, J=1.8Hz), 7.3 (1H, s); IR (KBr): 3540, 3310, 2140, 2100, 1720, 1710, 1690, 1680, 1670 cm^{-1}.

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