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Synthetic Studies of Halichondrin B, an Antitumor Polyether Macrolide Isolated from a Marine Sponge. 7. Synthesis of Two C27—C36 Units *via* Construction of the F Ring and Completely Stereoselective *C*-Glycosylation Using Mixed Lewis Acids[1)]

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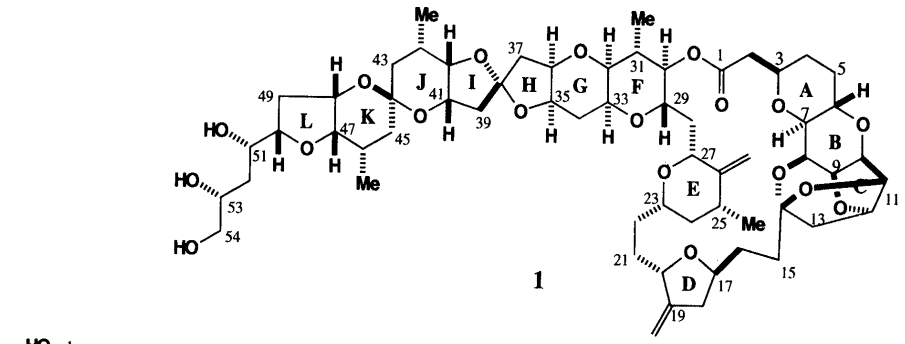
Two C27—C36 units of halichondrin B were synthesized starting from a C31—C34 alcohol, which was easily available from dimethyl L-tartrate, *via* construction of the F ring, methylation at the C31 position and *C*-glycosylation. These crucial reactions proceeded completely stereoselectively, and in particular the stereoselective *C*-glycosylation with allyltrimethylsilane took place only in the presence of both of two Lewis acids, boron trifluoride etherate and trimethylsilyl triflate.

Key words stereoselective synthesis; tetrahydropyran; polyether macrolide; conformation; Lewis acid; *C*-glycosylation

Halichondrin B (**1**) was isolated from a marine sponge, *Halichondria okadai* KADOTA, by Uemura *et al.* in 1985[2)] and is a representative antitumor compound of the halichondrin family. Because of its unusually complex chemical structure and significant biological activity, **1** has received much attention and Kishi *et al.* achieved the first total synthesis of **1** in 1992.[3)] As part of our project to synthesize **1**, recently we reported synthetic studies of the C1—C15 (**2**)[4a,b)] C16—C26 (**3**),[4c)] C27—C36 (**4**)[1)] and C37—C54 (**5**)[4d,e)] units. In the present paper we describe the stereoselective synthesis of **4** and its synthetic equivalent (**6**) starting from L-tartaric acid *via* construction of the F ring, introduction of the C31 methyl group and *C*-glycosylation. Precedents for the synthesis of similar



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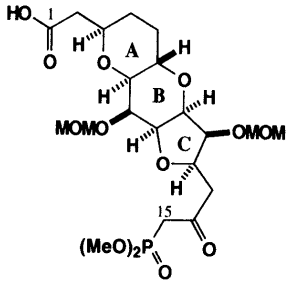

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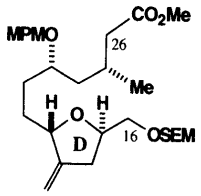

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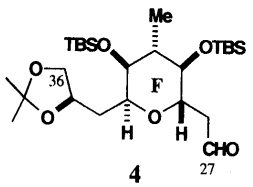

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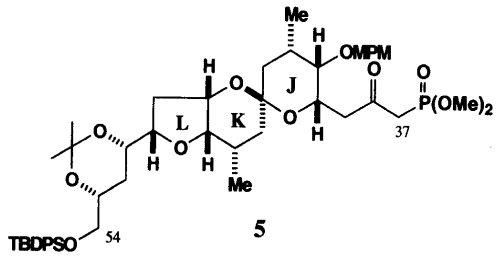

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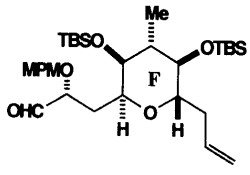

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Fig. 1

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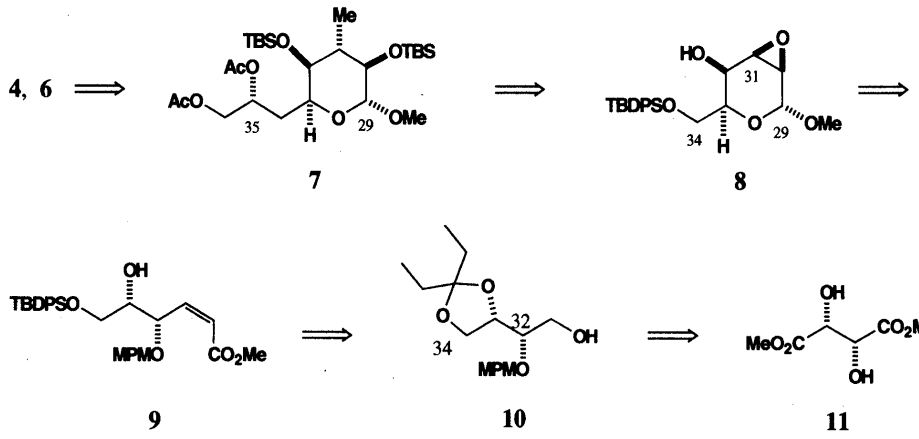
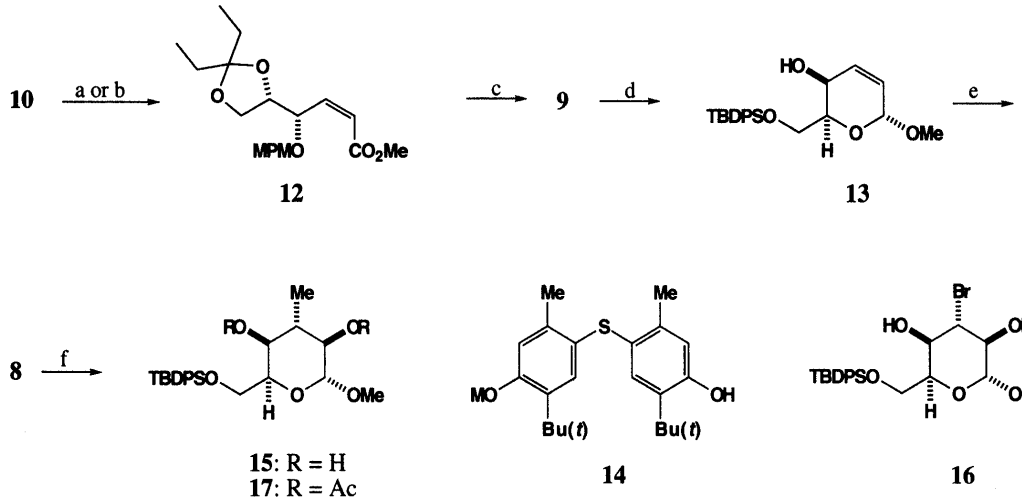


7 8 9 10 11

Chart 1



12 13

15: R = H
17: R = Ac

14 16

(a) 1) Swern oxid., 2) CBr_4, PPh_3, CH_2Cl_2, -78 °C, 3) *n*-BuLi, $ClCO_2Me$, THF, rt, 4) H_2, Pd-$BaSO_4$, EtOAc, rt (4 steps 46 %); (b) 1) Swern oxid., 2) $(CF_3CH_2O)_2P(O)CH_2CO_2Me$, $KN(TMS)_2$, THF, -78 °C (2 steps 90 %); (c) 1) 1N-HCl, MeOH, rt, 2) TBDPSCl, imidazole, CH_2Cl_2, rt (2 steps 94 %); (d) 1) TsOH, benzene, rt, 2) DIBAH, toluene, -78 °C, 3) CSA, MeOH, rt, 4) DDQ, CH_2Cl_2-MeOH, buffer, rt (4 steps 88 %); (e) MCPBA, **14**, CH_2Cl_2, reflux (74 %); (f) MeLi, MeMgCl, THF-Et_2O, rt (97 %).

Chart 2

synthetic units have been reported by Kishi *et al.*,[5] Kim and Salomon[6] and Burke *et al.*[7] Our retrosynthesis of **4** and **6** is shown in Chart 1, and we chose the alcohol (**10**) as the most suitable starting material, since **10** was easily available by a large-scale synthesis from dimethyl L-tartrate (**11**).[8]

Construction of the F Ring The Swern oxidation of **10** followed by treatment with carbon tetrabromide in the presence of triphenylphosphine gave a dibromoolefin, which was converted to an acetylene by treatment with *n*-butyllithium and methyl chloroformate. The Lindlar reduction of the acetylene gave the *Z*-olefin (**12**), which was hydrolyzed with hydrochloric acid followed by treatment with *tert*-butyldiphenylsilyl (TBDPS) chloride to give **9**. These synthetic steps from **10** to **9** were conventional, but the overall yield was only 43%. The acetylene formation step was especially poor, and hence an alternative route *via cis*-selective Horner–Emmons reaction[9] was applied. When the aldehyde derived from **10** was treated with Still's trifluoroethyl phosphonate,[9] the *cis*-selective reaction proceeded with 13 : 1 selectivity to give **12** in 90% yield, and this was readily converted to **13** *via* **9**. Acid treatment of **9** gave a lactone, which was reduced with diisobutylaluminum hydride (DIBAH) and immediately methylated to give a methyl glycoside. Removal of the 4-methoxybenzyl (MPM) protecting group with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ)[10] gave **13**. The F ring was thus constructed, although proper substituents at C29—C31[11] were still lacking.

Introduction of the C31 Methyl Group Since the C31 methyl group and the C30 hydroxy group are *trans* to each other, the epoxide (**8**) was naturally chosen as a suitable intermediate. Treatment of **13** with *m*-chloroperbenzoic acid (MCPBA) in dichloromethane gave **8** only in the presence of a radical scavenger. No reaction of **13** with MCPAB occurred at room temperature, and on heating, **13** decomposed. In the presence of the phenol (**14**)[12] at room temperature, **13** was also recovered, and the expected β-epoxide (**8**)[13] was obtained only under reflux for 40 h, in reasonable yield.

Table 1. Methylation of the Epoxide (**8**)

Entry	Reagent (eq)	Conditions	Yield (%)		
			15	**13**	**16**
1	$Me_2CuCNLi_2$ (5) [2MeLi+CuCN]	Et_2O, 0 °C	55	29	
2	Me_2CuLi (5) [2MeLi+CuBr·SMe_2]	Et_2O, 0 °C	56	39	
3	MeMgBr (10)	Et_2O, r.t.	33		43
4	MeCu (5) [MeMgBr+CuCN]	Et_2O, 0 °C	26		28
5	$Me_2CuMgBr$ (5) [2MeMgBr+CuCN]	Et_2O, 0 °C	32		56
6	Me_3Al (10)	Et_2O, r.t.	0		
7	Me_2Zn (10)	Et_2O, r.t.	0		
8	Me_2Mg (5) [MeMgCl+MeLi] (salt-free)	THF–Et_2O, r.t.	97		

Table 2. Coupling Constants (J, Hz) of Vicinal Protons of *O*-Glycosides and *C*-Glycosides (in $CDCl_3$)

	H29–30	H30–31	H31–32	H32–33
17	0	0	2.0	2.0
20	0	0	1.0	1.0
21	0	0	0	0
24	0	0	2.0	2.0
41	0	0	0	4.5
45	0	1.5	1.5	1.5
7	7.5	10.5	10.5	5.5
33	7.0	10.0	10.0	5.5
31	10.0	10.0	11.0	5.5
32	0	0	0	0
39	9.0	9.5	9.5	5.0
40	9.5	9.5	10.5	6.0

Selective methylation of **8** was unexpectedly difficult (Table 1). Many reagents and reaction conditions were examined.[14] A few gave reasonable results, and the supernatant of a mixture of methylmagnesium chloride and methyllithium in ethyl ether[15] gave an excellent result (entry 8). Copper reagents, which are widely used as nucleophiles for epoxides, were first examined in various solvents, but the yields of the expected product (**15**) were less than 56% (entry 1, 2). A fair amount of **13** was usually obtained, and it was quite difficult to separate **15** from **13**. In the presence of bromide anion, or a mixture of methylmagnesium bromide and cuprous cyanide, the bromohydrin (**16**) was concomitantly formed (entries 3—5). Two salt-free reagents, trimethylaluminum and dimethylzinc, were unreactive (entries 6, 7). When **8** was treated with salt-free dimethylmagnesium, the supernatant of a mixture of methylmagnesium chloride and salt-free methyllithium in ether,[15] at room temperature, the methylation proceeded slowly but cleanly, and **15** was isolated in almost quantitative yield (entry 8).

***C*-Glycosylation Using Mixed Lewis Acids** The α-selective *C*-glycosylation at the C29 position was the most crucial step in the synthesis of **4** and **6**. Although **4** and **6** have a thermodynamically less favorable 2,6-*trans*-disubstituted tetrahydropyran ring, the diacetate of **15** (**17**) was first chosen as a promising substrate for the *C*-glycosylation, because **17** was expected to undergo preferential α-side (axial) attack of nucleophiles on an

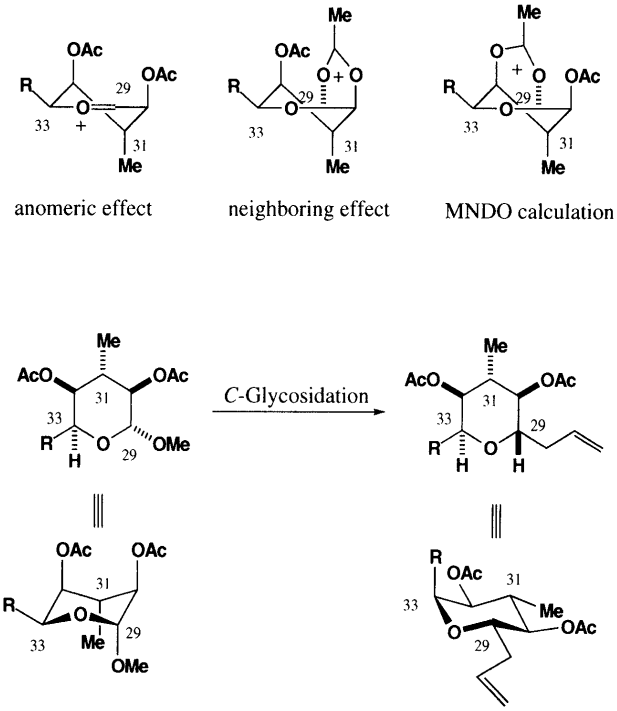
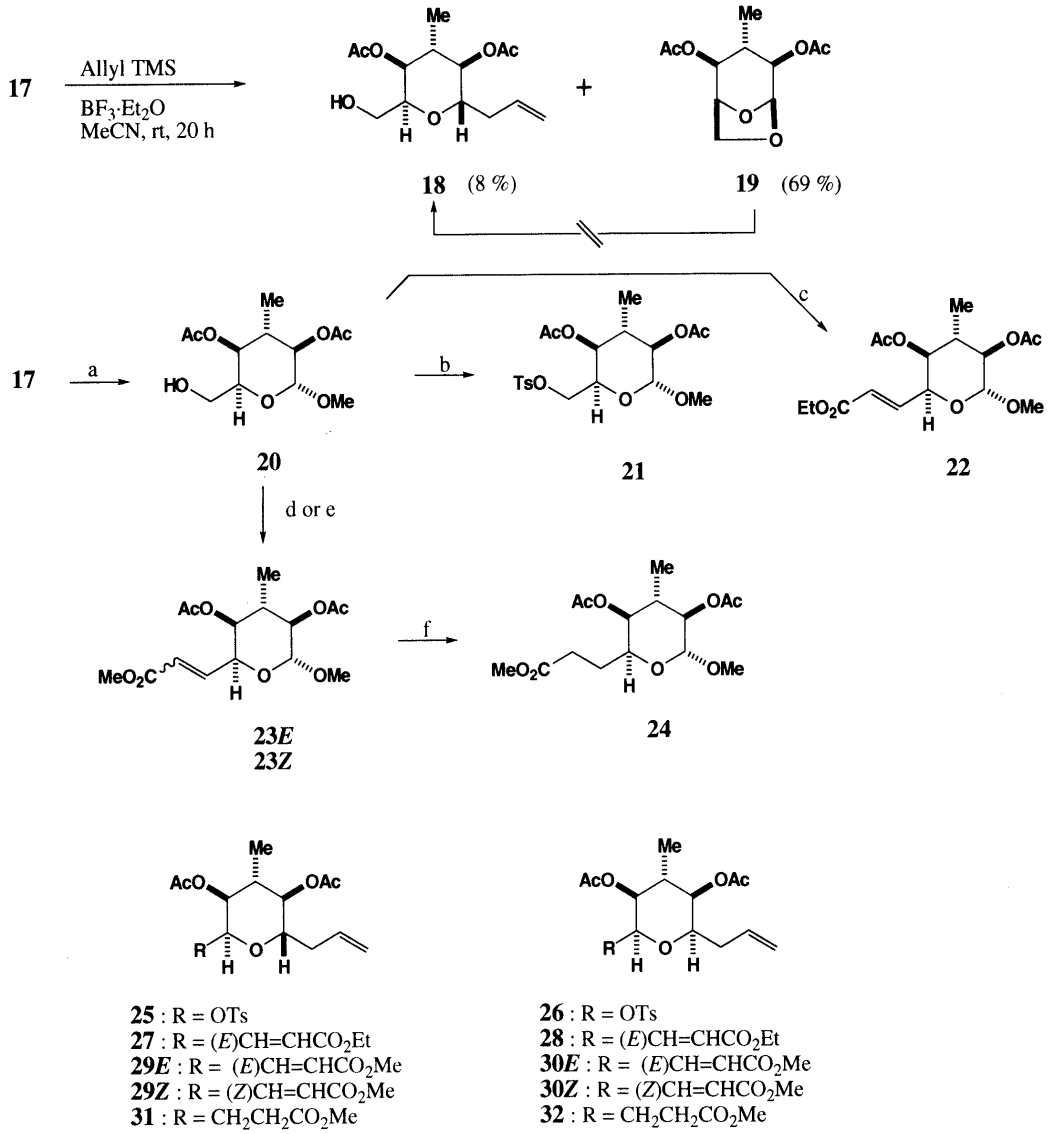


Fig. 2

intermediary pyran oxonium ion due to the anomeric effect[16] and well-known anchimeric assistance of the neighboring acetyl group.[17] A conformational analysis of **17** by NMR (Table 2) seemed to support this assumption, that is, among five substituents on the chair-form tetrahydropyran ring only the TBDPSO-methyl group at the C33 position is equatorial and all the other substituents are axial. Additional support was provided by MNDO calculations[18] for the oxonium ion, a probable intermediary species for which the most stable conformer involved the anchimeric effect of the C32 acetoxy group rather than the neighboring C30 one (Fig. 2).

When **17** was treated with allyltrimethylsilane (AllylTMS) in the presence of boron trifluoride etherate ($BF_3 \cdot Et_2O$) in acetonitrile at room temperature,[16,19] however, the expected product (**18**) with concomitant deprotection of the TBDPS group was obtained in only 8% yield, and the main product was **19** (69%), which we were not able to transform to **18** (Chart 3, Table 3, entry 1). In order to avoid the formation of **19**, **17** was converted to **21**, which has the same conformation as **17** (Table 2) and then subjected to the above allylation. No reaction occurred at room temperature, and on heating under reflux a 1.5:1 mixture of the expected α-allyl compound (**25**) and its β-isomer (**26**) was disappointingly obtained in 65% yield (entry 3). The allylation of **21** in the presence of trimethylsilyl triflate (TMSOTf) instead of $BF_3 \cdot Et_2O$ gave only a poor result (entry 4). When **22**, derived from **17** *via* **20**, was subjected to the reaction in the presence of $BF_3 \cdot Et_2O$, the allylation proceeded rather efficiently (81%), although the stereoselectivity was still poor (entry 5). Similar compounds, **23*E*** and **23*Z***, were treated with AllylTMS in the presence of both Lewis acids, $BF_3 \cdot Et_2O$ and TMSOTf, and similar results were obtained (entries 6, 7). The allylation of **24** was then examined under various conditions, and the best yield was obtained when **24** was



(a) 1) TBAF, AcOH, THF (100 %); (b) TsCl, Et_3N, DMAP, CH_2Cl_2 (98 %); (c) 1) Swern oxid., 2) $(Me_2CHO)_2P(O)CH_2CO_2Et$, *t*-BuOK, THF, rt (61 %); (d) 1) Swern oxid., 2) $(MeO)_2P(O)CH_2CO_2Me$, NaH, THF, rt (64 %; *E*:*Z* = 4:1); (e) 1) Swern oxid., 2) $(CF_3CH_2O)_2P(O)CH_2CO_2Me$, $KN(TMS)_2$, 18-crown-6, THF, -78 °C (37 %; *E*:*Z* = 1:20); (f) H_2, Pd-C, MeOH (94 %)

Chart 3

allylated in the presence of both the Lewis acids in acetonitrile,[20] though the product (99% yield) was a 1.8 : 1 mixture of the expected α-isomer (**31**) and its β-isomer (**32**) (entry 10). Thus, the *C*-glycosylation of all the C30, C32-diacetoxy compounds gave α,β-mixtures of C29-allyl derivatives. These unexpected results were probably caused by the steric hindrance of the idose-type axial methyl group at the C31 position.

In order to avoid this steric hindrance, the *C*-glycosylation of substrates with an equatorial methyl group at the C31 position was next examined. When the diacetyl protecting groups of **21** were replaced by *tert*-butyldimethylsilyl (TBS) groups, complete inversion of the tetrahydropyran ring occurred to give **33** with the inverted chair form, in which only the C33 substituent is axial and other substituents at C29, C30, C31 and C32 are all equatorial. Allylation of **33** was expected to afford the α-allyl compound since no steric hindrance due to the C31 axial methyl group was present. Treatment of **33** with AllylTMS in the presence of the two Lewis acids interestingly gave the expected C29 α-allyl compound (**34**) alone, although the TBS groups were deprotected and the yield was only 38% (entry 11). The structure of **34** was confirmed by conversion to the acetate (**25**).

The conversion of **33** into **7** was carried out by a series of rather conventional reactions without difficulties. However, the overall yield for fourteen steps was only 6%, and hence **7** was synthesized from **20**. The hydroxy group of **20** was protected with a benzyloxymethyl (BOM) group, then the diacetyl protecting groups were replaced with TBS groups, and the BOM group was removed to give **35** in 75% overall yield for the four steps. The Swern oxidation and the subsequent Wittig reaction gave a vinyl compound, which was subjected to a hydroboration re-

action with disiamylborane to give **36**. The Swern oxidation again followed by the Horner–Emmons reaction gave an α,β-unsaturated ester, which was reduced with DIBAH, and then subjected to the Sharpless epoxidation to give the epoxide (**37**) in 79% overall yield from **35**. The primary alcohol of **37** was tosylated, then converted to an iodide, which was treated with *tert*-butyllithium to open the epoxide ring, and **38** was readily obtained. Acetylation of the alcohol and oxidative cleavage of the double bond gave an aldehyde, which was reduced and finally acetylated to give **7**, a substrate for *C*-glycosylation, in 73% overall yield from **37**.

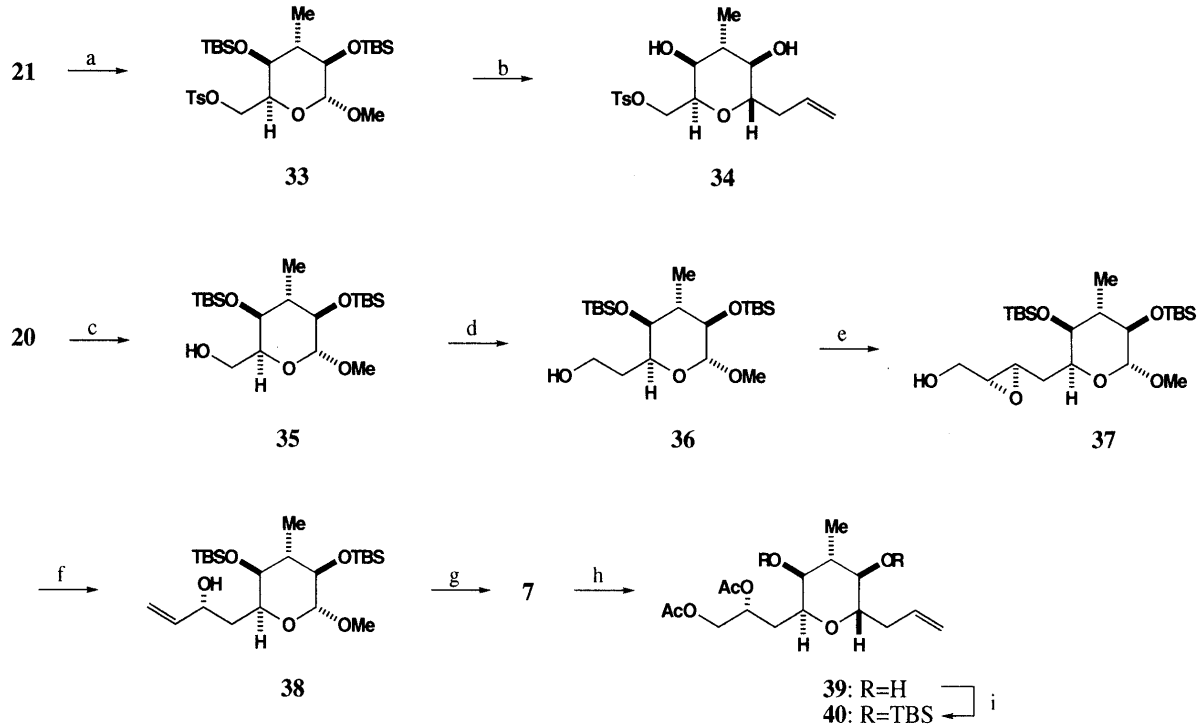
Table 3. *C*-Glycosylation with AllylTMS

Entry	Substrate	Conditions[a]	C29-Allyl product (%)		Other product (%)
			α-Allyl compd.	β-Allyl compd.	
1	**17**	A	**18** (8)		**19** (69)
2	**21**	A	No reaction		
3	**21**	B	**25** (39)	**26** (26)	
4	**21**	C	**25** (19)	**26** (11)	
5	**22**	A	**27** (47)	**28** (34)	
6	**23*E***	D	**29*E*** (39)	**30*E*** (30)	
7	**23*Z***	D	**29Z** (32)	**30*Z*** (25)	
8	**24**	A	**31** (39)	**32** (26)	
9	**24**	C	**31** (55)	**32** (39)	
10	**24**	D	**31** (63)	**32** (36)	
11	**33**	D	**34** (38)		
12	**7**	D	**39** (89)[b]		
13	**7**	A			**41** (85)
14	**7**	C		**42** (25)[c]	**43** (25)[c]
15	**41**	D	**39** (80)		
16	**45**	C	**46** (47)	**42** (42)	

a) A: $BF_3 \cdot Et_2O$, MeCN, r.t.; B: $BF_3 \cdot Et_2O$, MeCN, reflux; C: TMSOTf, MeCN, r.t.; D: $BF_3 \cdot Et_2O$, TMSOTf, MeCN, r.t. *b*) Isolated as **40**. *c*) Isolated after acetylation.

All substituents except the C33 substituent of **7** are equatorial (Table 2) and quite similar to those of **33**. When AllylTMS, $BF_3 \cdot Et_2O$ and TMSOTf were successively added to a stirred acetonitrile solution of **7** at room temperature, the allylation proceeded smoothly, though the TBS groups were again deprotected, to give the expected C29 α-allyl compound (**39**) (entry 12), which was immediately protected with TBS groups and **40** was isolated as the sole product in 89% yield.

In order to clarify the reason why **7** was allylated only to the expected product (**39**) in the presence of both $BF_3 \cdot Et_2O$ and TMSOTf, whereas the C30, C32-*O*-acetyl compounds (**21**—**24**) gave mixtures of α- and β-allyl compounds under the same conditions as well as under other conditions, the following reactions were examined. When **7** was treated with AllylTMS in the presence of $BF_3 \cdot Et_2O$, no allylation occurred and deprotection of the TBS groups proceeded to give only the dihydroxy compound (**41**) in 85% yield (entry 13). In the presence of only TMSOTf, **7** gave the β-allyl product (**42**) and the ring-contracted product (**43**), after acetylation, without



(a) 1) K_2CO_3, MeOH, 2) TBSOTf, Et_3N, CH_2Cl_2 (2 steps 86 %); (b) AllylTMS, $BF_3 \cdot Et_2O$, TMSOTf, MeCN, rt (38 %); (c) 1) BOMCl, $(i\text{-Pr})_2NEt$, CH_2Cl_2, 2) K_2CO_3, MeOH, 3) TBSOTf, 2,6-di-*t*-Bu-Py, CH_2Cl_2 , 4) H_2, 10% Pd $(OH)_2$, AcOEt (4 steps 75 %); (d) 1) Swern oxid., 2) Ph_3PMeBr, *t*-BuOK, THF, 3) $(Sia)_2BH$, THF, 4) 30% H_2O_2, 15% NaOH (4 steps 92 %); (e) 1) Swern oxid., 2) $(i\text{-PrO})_2P(O)CH_2CO_2Et$, *t*-BuOK, THF, 3) DIBAH, CH_2Cl_2, 4) (-)-DET, Ti(*i*-OPr)$_4$, TBHP, MS, CH_2Cl_2 (4 steps 86 %); (f) 1) TsCl, Et_3N, DMAP, CH_2Cl_2, 2) NaI, $NaHCO_3$, MEK, 3) *t*-BuLi, Et_2O (3 steps 89 %); (g) 1) Ac_2O, Et_3N, DMAP, CH_2Cl_2, 2) OsO_4, NMO, MeCOMe-H_2O, 3) $NaIO_4$, THF-H_2O, 4) $NaBH_4$, 5) Ac_2O, Et_3N, DMAP, CH_2Cl_2 (5 steps 81 %); (h) 1) AllylTMS, $BF_3 \cdot Et_2O$, TMSOTf, MeCN, rt; (i) TBSOTf, Et_3N, CH_2Cl_2 (2 steps 89 %)

Chart 4

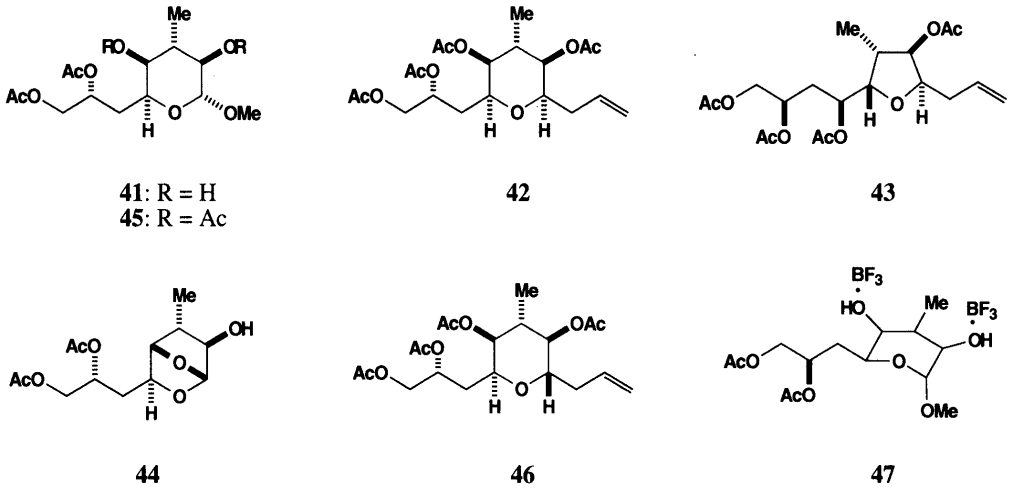
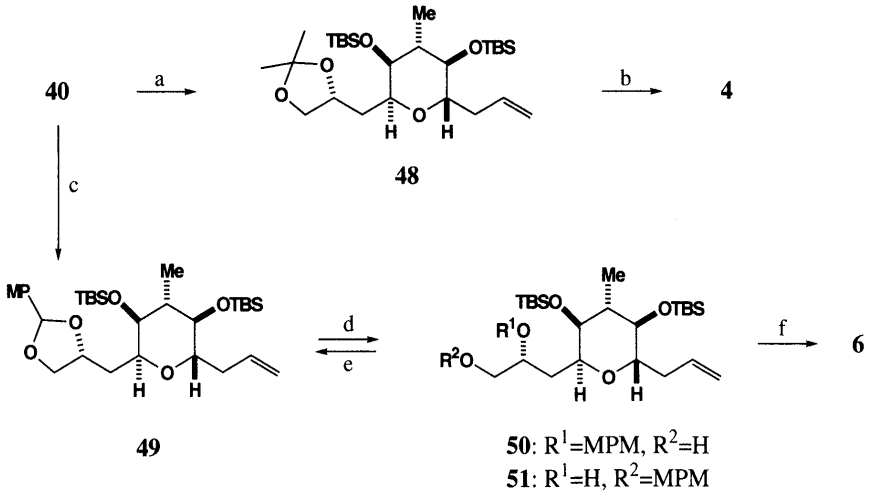


Fig. 3



(a) 1) K_2CO_3, MeOH, 2) $Me_2C(OMe)_2$, CSA, benzene (2 steps 96 %); (b) 1) OsO_4, NMO, acetone-H_2O, 2) $NaIO_4$, THF-MeOH-H_2O (2 steps 98 %); (c) 1) K_2CO_3, MeOH, 2) $MPCH(OMe)_2$, CSA, benzene (2 steps 84 %); (d) DIBAH, CH_2Cl_2, -78 °C, **50** 52 % **51** 20 %; (e) DDQ, CH_2Cl_2; (f) Dess-Martin oxid., CH_2Cl_2 (72 %).

Chart 5

formation of the expected product (**39** or **40**) (entry 14). Compound **43** was probably formed *via* **44**. Interestingly, in a manner reminiscent of **7**, the allylation of **41** in the presence of both the Lewis acids gave **39** in 80% yield (entry 15), although **41** has the same conformation as the diacetyl compounds (**17**, **20**, **21**, **24**) (Table 2). A diacetyl derivative of **41** (**45**) again gave a mixture of α- (**46**) and β-allyl products (**42**) (entry 16). Thus, the allylation of **7** probably took place after conversion to **41** *via* a transition or intermediary structure with a conformation different from the above-mentioned chair conformations. ^{1}H-NMR spectra of **41** in deuteroacetonitrile (CD_3CN) in the presence and absence of $BF_3 \cdot Et_2O$ were then carefully examined. In a CD_3CN solution of **41** the C29 proton and C31-methyl protons were observed at 4.53 ppm (d, $J=2.0$ Hz) and 1.06 ppm (d, $J=7.5$ Hz), respectively. When $BF_3 \cdot Et_2O$ (10 eq) was added, the former signal was remarkably shifted downfield at 6.24 ppm with a change of the coupling constant to $J=6.0$ Hz, while the latter was somewhat shifted to 1.21 ppm with the same coupling constant ($J=7.5$ Hz). These data probably indicate the formation of the complex (**47**) with a boat-like conformation (Fig. 3), which can consistently account for the reactivity of **41**. The allylation must have occurred after conversion of **47** into an oxonium ion, in which the C31-methyl group is still equatorial, with loss of the methoxy group by the attack of a third molecule of a Lewis acid. Since BF_3 was not a sufficiently strong acid, no allylation occurred in the presence of only $BF_3 \cdot Et_2O$. In the presence of both $BF_3 \cdot Et_2O$ and TMSOTf, however a new Lewis acid,[21] which is strong enough to produce the oxonium ion, was formed. The allylation of the oxonium ion must have occurred by the attack of AllylTMS from only the α-side without any steric hindrance due to the C31-methyl group.

Finally, **40** was converted to the title compounds, two C27—C36 units **4** and **6**, which are functionalized at C27 and C36, respectively. The two acetyl protecting groups of **40** were replaced by an isopropylidene group (**48**), and osmylation of the double bond followed by oxidative cleavage of the resulting diol with sodium periodate gave **4** in excellent yield.

After conversion of **40** into the *p*-methoxybenzylidene compound (**49**), reduction with DIBAH gave a mixture of two hydroxy compounds, **50** and **51**. The undesired minor alcohol (**51**) was reverted to **49** by oxidation with DDQ.[22] Dess–Martin oxidation[23] of **50** gave **6**, which was not very stable and so was used immediately for the coupling reaction with the C37—C54 unit (**5**).[4d,24]

Experimental

Methyl (2*Z*,4*S*,5*S*)-4-(4-Methoxybenzyloxy)-5,6-pentylidenedioxy-2-hexenoate (12) a) Dimethyl sulfoxide (DMSO) (0.23 ml, 3.24 mmol) was added to a stirred solution of $(COCl)_2$ (0.21 ml, 2.41 mmol) in CH_2Cl_2 (7 ml) at −78 °C under argon. After 5 min, a solution of **10** (503 mg, 1.62 mmol) in CH_2Cl_2 (10 ml) was slowly added through a cannula during 30 min, and stirring was continued for 20 min. Et_3N (0.9 ml, 6.46 mmol) was slowly added, and the reaction mixture was stirred for 10 min at −78 °C and for another 10 min at −60 °C, then quenched with saturated aqueous NH_4Cl, and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4 and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 1 : 3) to give an aldehyde as a pale yellow oil (448 mg), which was subjected to the next reaction.

A solution of Ph_3P (2.99 g, 11.4 mmol) in CH_2Cl_2 (20 ml) was added dropwise through a cannula to a stirred solution of CBr_4 (1.89 g, 5.7 mmol) in CH_2Cl_2 (20 ml) at 0 °C under argon. After 10 min, the mixture was cooled to −78 °C, and a solution of the aldehyde in CH_2Cl_2 (10 ml) was added dropwise. After 20 min, the reaction mixture was quenched with saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 5 : 1) to give (3*S*,4*S*)-1,1-dibromo-3-(4-methoxybenzyloxy)-4,5-pentylidenedioxy-1-pentene as a colorless oil (643 mg, 82%). $[\alpha]_D^{26}$ +23.7° (*c* = 0.79, $CHCl_3$). IR (neat) cm^{-1}: 2970, 2940, 1615, 1515, 1465, 1305, 1250, 1175, 1035. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (t, 3H, *J* = 7.5 Hz), 0.89 (t, 3H, *J* = 7.5 Hz), 1.55—1.70 (m, 4H), 3.75—3.83 (m, 1H), 3.81 (s, 3H), 3.94—4.01 (m, 1H), 4.12—4.25 (m, 2H), 4.42 (d, 1H, *J* = 12.0 Hz), 4.61 (d, 1H, *J* = 12.0 Hz), 6.41 (d, 1H, *J* = 8.5 Hz), 6.85—6.90 (m, 2H), 7.25—7.30 (m, 2H). ^{13}C-NMR ($CDCl_3$) δ: 8.07, 8.17, 28.86, 29.42, 55.27, 65.67, 70.80, 76.93, 79.00, 93.97, 113.75, 113.95, 129.58, 129.74, 135.69, 159.32. FAB-MS *m/z* (%): 489 ($[^{81}Br_2]M^+ + Na$, 4.5), 487 ($[^{79,81}Br_2]M^+ + Na$, 8.3), 485 ($[^{79}Br_2]M^+ + Na$, 4.7), 466 (2.9), 465 (5.8), 464 (5.9), 463 (9.1), 462 (3.5), 461 (4.7), 437 (20), 435 (34), 433 (22), 327 (32), 297 (10), 241 (12), 213 (10), 154 (14), 121 (100). HR-MS (FAB) Calcd for $C_{18}H_{24}O_4{}^{79}Br_2Na$ ($[^{79}Br_2]M^+ + Na$): 484.9939. Found: 484.9963.

A 1.55 M solution of *n*-BuLi in *n*-hexane (4.2 ml, 6.51 mmol) was added dropwise to a stirred solution of the dibromoolefin (432 mg, 0.93 mmol) in tetrahydrofuran (THF) (10 ml) at −78 °C under argon. After 1 h, freshly distilled $ClCO_2Me$ (0.5 ml, 6.47 mmol) was added dropwise. The reaction mixture was stirred for 30 min, then allowed to warm to room temperature. After 1 h, saturated aqueous $NaHCO_3$ was added, and the reaction mixture was extracted with Et_2O. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 5 : 1) to give methyl (4*S*,5*S*)-4-(4-methoxybenzyloxy)-5,6-pentylidenedioxy-2-hexynoate as a pale yellow oil (210 mg, 62%). $[\alpha]_D^{26}$ +119.5° (*c* = 0.43, $CHCl_3$). IR (neat) cm^{-1}: 2980, 2945, 2220, 1725, 1520, 1255, 1085. ^{1}H-NMR ($CDCl_3$) δ: 0.86 (t, 3H, *J* = 7.5 Hz), 0.87 (t, 3H, *J* = 7.5 Hz), 1.61 (q, 2H, *J* = 7.5 Hz), 1.64 (q, 2H, *J* = 7.5 Hz), 3.80 (s, 3H), 3.81 (s, 3H), 3.84—3.94 (m, 1H), 4.07—4.16 (m, 1H), 4.22—4.31 (m, 2H), 4.52 (d, 1H, *J* = 11.5 Hz), 4.78 (d, 1H, *J* = 11.5 Hz), 6.88 (d, 1H, *J* = 8.5 Hz), 7.29 (d, 2H, *J* = 8.5 Hz). ^{13}C-NMR ($CDCl_3$) δ: 7.99, 8.09, 28.93, 29.44, 52.86, 55.29, 66.69, 69.49, 71.08, 77.20, 78.65, 83.18, 113.90, 114.43, 128.54, 130.01, 153.34, 159.61. FAB-MS *m/z* (%): 385 ($M^+ + Na$, 5.6), 361 ($M^+ - 1$, 8.6), 333 (28), 281 (2.2), 245 (6.4), 225 (5.3), 195 (4.8), 129 (46), 121 (100). HR-MS (FAB) Calcd for $C_{20}H_{26}O_6Na$ ($M^+ + Na$): 385.1637. Found: 385.1640.

A solution of the acetylene (383 mg, 1.06 mmol) in EtOAc (4 ml) was hydrogenated over 5% Pd–$BaSO_4$ (161 mg) and quinoline (21 μl) with vigorous stirring for 15 min. The catalyst was removed by filtration, and washed with CH_2Cl_2. The filtrate was washed with 0.5 N HCl and saturated aqueous $NaHCO_3$, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 5 : 1) to give **12** as a colorless oil (345 mg, 90%). $[\alpha]_D^{27}$ −9.50° (*c* = 1.39, $CHCl_3$). IR (neat) cm^{-1}: 2975, 2940, 2880, 1730, 1650, 1620, 1520, 1465, 1440, 1405, 1305, 1255, 1205, 1085, 1040. ^{1}H-NMR ($CDCl_3$) δ: 0.87 (t, 3H, *J* = 7.5 Hz), 0.90 (t, 3H, *J* = 7.5 Hz), 1.62 (q, 2H, *J* = 7.5 Hz), 1.67 (q, 2H, *J* = 7.5 Hz), 3.70 (s, 3H), 3.80 (s, 3H), 3.82 (dd, 1H, *J* = 8.0, 8.0 Hz), 3.93 (dd, 1H, *J* = 6.5, 8.0 Hz), 4.20 (ddd, 1H, *J* = 5.5, 6.5, 8.0 Hz), 4.44 (d, 1H, *J* = 11.5 Hz), 4.54 (d, 1H, *J* = 11.5 Hz), 5.13 (dd, 1H, *J* = 5.5, 9.0 Hz), 6.48 (d, 1H, *J* = 11.5 Hz), 6.17 (dd, 1H, *J* = 9.0, 11.5 Hz), 6.80—6.93 (m, 2H), 7.18—7.32 (m, 2H). ^{13}C-NMR ($CDCl_3$) δ: 8.06, 8.12, 29.14, 29.56, 51.46, 55.24, 65.78, 71.17, 74.30, 78.04, 113.62, 113.68, 122.79, 129.39, 130.30, 146.22, 166.11. MS *m/z* (%): 364 (M^+, 0.2), 335 (8.8), 142 (12), 129 (44), 121 (100). HR-MS Calcd for $C_{20}H_{28}O_6$ (M^+): 364.1886. Found: 364.1886.

b) A 0.6 M solution of potassium bis(trimethylsilyl)amide [$KN(TMS)_2$] in THF (11.8 ml, 7.08 mmol) was added dropwise to a stirred suspension of di-2,2,2-trifluoroethyl methoxycarbonylmethanephosphonate (2.26 g, 7.10 mmol) and 18-crown-6 ether (7.81 g, 29.55 mmol) in THF (100 ml) at −78 °C under argon. After 30 min, a THF solution (20 ml) of the aldehyde, prepared from **10** (1.84 g, 5.92 mmol) by Swern oxidation as described above, was added through a cannula during 30 min. After 1 h, the reaction mixture was quenched with saturated aqueous NH_4Cl, and extracted with Et_2O. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column as described above to give **12** (1.95 g, 90%).

Methyl (2*Z*,4*S*,5*S*)-5-Hydroxy-4-(4-methoxybenzyloxy)-6-*tert*-butyldiphenylsilyloxy-2-hexenoate (9) A 1 N HCl solution (4 ml) was added to a stirred solution of **12** (215 mg, 0.59 mmol) in MeOH (8 ml) at room temperature. After 2 h, the reaction mixture was diluted with CH_2Cl_2, washed with brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (CH_2Cl_2–MeOH 10 : 1) to give methyl (2*Z*,4*S*,5*S*)-4-(4-methoxybenzyloxy)-5,6-dihydroxy-2-hexenoate as a colorless oil (171 mg, 98%). $[\alpha]_D^{27}$ −5.95° (*c* = 1.08, $CHCl_3$). IR (neat) cm^{-1}: 3400, 2950, 1720, 1650, 1615, 1520, 1440, 1400, 1305, 1250, 1205, 1180, 1120, 1070, 1040. ^{1}H-NMR ($CDCl_3$) δ: 2.60 (dd, 1H, *J* = 6.0, 6.0 Hz), 2.93 (d, 1H, *J* = 5.0 Hz), 3.63—3.78 (m, 3H), 3.75 (s, 3H), 3.81 (s, 3H), 4.38 (d, 1H, *J* = 11.0 Hz), 4.53 (d, 1H, *J* = 11.0 Hz), 5.08 (ddd, 1H, *J* = 1.0, 5.0, 8.5 Hz), 6.06 (dd, 1H, *J* = 1.0, 11.5 Hz), 6.25 (dd, 1H, *J* = 8.5, 11.5 Hz), 6.83—6.97 (m, 2H), 7.20—7.25 (m, 2H). ^{13}C-NMR ($CDCl_3$) δ: 51.63, 55.27, 63.23, 71.56, 73.48, 75.85, 113.90, 123.08, 129.54, 129.72, 147.58, 159.50, 166.84. FAB-MS *m/z* (%): 319 ($M^+ + Na$, 21), 295 ($M^+ - 1$, 12), 279 (2.0), 241 (6.6), 189 (6.1), 159 (12), 137 (44), 121 (100). HR-MS (FAB) Calcd for $C_{15}H_{20}O_6Na$ ($M^+ + Na$): 319.1158. Found: 319.1133.

Imidazole (0.49 g, 7.2 mmol) and then TBDPSCl (1.88 ml, 7.23 mmol) were added to a stirred solution of the diol (1.42 g, 4.81 mmol) in CH_2Cl_2 (14 ml) at 0 °C under argon. After 1 h at room temperature, the reaction mixture was cooled again to 0 °C, diluted with CH_2Cl_2, and quenched with H_2O. The organic layer was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 4 : 1) to give **9** as a colorless oil (2.47 g, 96%). $[\alpha]_D^{26}$ −7.37° (*c* = 1.14, $CHCl_3$). IR (neat) cm^{-1}: 3460, 3070, 3000, 2930, 2850, 1725, 1620, 1520, 1470, 1430, 1400, 1250, 1180, 1115, 1040. ^{1}H-NMR ($CDCl_3$) δ: 1.05 (s, 9H), 2.55 (d, 1H, *J* = 5.5 Hz), 3.65—3.84 (m, 3H), 3.68 (s, 3H), 3.79 (s, 3H), 4.35 (d, 1H, *J* = 11.0 Hz), 4.50 (d, 1H, *J* = 11.0 Hz), 5.20 (ddd, 1H, *J* = 1.0, 3.5, 9.0 Hz), 5.98 (dd, 1H, *J* = 1.0, 12.0 Hz), 6.29 (dd, 1H, *J* = 9.0, 12.0 Hz), 6.79—6.83 (m, 2H), 7.14—7.18 (m, 2H), 7.34—7.43 (m, 6H), 7.64—7.68 (m, 4H). ^{13}C-NMR ($CDCl_3$) δ: 19.23, 26.81, 51.42, 55.24, 64.52, 71.21, 74.03, 74.45, 113.71, 122.29, 127.67, 129.52, 129.66, 130.10, 133.35, 135.60, 147.30, 159.23, 166.17. FAB-MS *m/z* (%): 557 ($M^+ + Na$, 17), 533 ($M^+ - 1$, 1.1), 379 (1.1), 319 (2.1), 287 (2.0), 241 (2.1), 197 (9.5), 181 (4.0), 121 (100). HR-MS (FAB) Calcd for $C_{31}H_{38}O_6SiNa$ ($M^+ + Na$): 557.2336. Found: 557.2319.

(2*R*,5*S*,6*S*)-6-*tert*-Butyldiphenylsilyloxymethyl-5,6-dihydro-5-hydroxy-2-methoxy-2*H*-pyran (13) A solution of **9** (11.8 mg, 22 μmol) and $TsOH \cdot H_2O$ (4.2 mg, 22 mmol) in benzene (1 ml) was stirred for 17 h at room temperature. After addition of excess Et_3N, the reaction mixture was evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 3 : 1) to give (5*S*,6*S*)-6-*tert*-butyldiphenylsilyloxymethyl-5,6-dihydro-5-(4-methoxybenzyloxy)-2*H*-pyran-2-one as a colorless oil (10.6 mg, 95%). $[\alpha]_D^{27}$ +119.6° (*c* = 1.22, $CHCl_3$). IR (neat) cm^{-1}: 3050, 2920, 2850, 1720, 1610, 1515, 1425, 1240, 1100. ^{1}H-NMR ($CDCl_3$) δ: 1.07 (s, 9H), 3.81 (s, 3H), 3.93 (dd, 1H, *J* = 5.5, 10.0 Hz), 4.12 (dd, 1H, *J* = 8.0, 10.0 Hz), 4.18 (dd, 1H, *J* = 3.0, 5.5 Hz), 4.45 (ddd, 1H, *J* = 3.0, 5.5, 8.0 Hz), 4.56 (s, 2H), 6.29—6.47 (m, 1H), 6.11 (d, 1H, *J* = 10.0 Hz), 6.82—6.87 (m, 2H), 6.87 (dd, 1H, *J* = 5.5, 10.0 Hz), 7.17—7.20 (m, 2H), 7.32—7.47 (m, 6H), 7.62—7.68 (m, 4H). ^{13}C-NMR

($CDCl_3$) δ: 19.20, 28.84, 55.29, 61.09, 65.51, 71.67, 79.76, 113.93, 123.70, 127.83, 129.45, 129.63, 129.89, 129.94, 132.77, 132.92, 135.50, 143.00, 159.51, 162.65. FAB-MS *m/z* (%): 503 ($M^+ + 1$, 1.2), 395 (1.1), 341 (0.8), 307 (3.7), 197 (5.8), 154 (14), 137 (12), 121(100). HR-MS (FAB) Calcd for $C_{30}H_{35}O_5Si$ ($M^+ + 1$): 503.2254. Found: 503.2207.

A 0.95 M solution of DIBAH in *n*-hexane (2.2 ml, 2.1 mmol) was added dropwise to a stirred solution of the lactone (531 mg, 1.06 mmol) in toluene (5 ml) at −78 °C under argon. After 1 h, the reaction mixture was quenched with MeOH and then 0.5 N HCl, and extracted with Et_2O. The extract was washed with brine, dried over Na_2SO_4, and evaporated *in vacuo* to leave an oil, which was dissolved in MeOH (10 ml). The solution was stirred with *dl*-camphorsulfonic acid (CSA) (24.5 mg, 0.11 mmol) at room temperature for 30 min, then quenched with Et_3N, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 4 : 1) to give (2*R*,5*S*,6*S*)-6-*tert*-butyldiphenylsilyloxymethyl-5,6-dihydro-2-methoxy-5-(4-methoxybenzyloxy)-2*H*-pyran as a colorless oil (527 mg, 95%), which solidified on standing in a refrigerator, mp 35.5—36.5 °C. $[\alpha]_D^{23}$ +73.5° (*c* = 1.08, $CHCl_3$). IR (neat) cm^{-1}: 2920, 2850, 1610, 1510, 1425, 1245, 1110, 1040. ^{1}H-NMR ($CDCl_3$) δ: 1.06 (s, 9H), 3.38 (s, 3H), 3.72 (dd, 1H, *J* = 2.5, 5.0 Hz), 3.78 (s, 3H), 3.87 (dd, 1H, *J* = 6.0, 10 Hz), 3.97 (dd, 1H, *J* = 6.0, 10 Hz), 4.11 (ddd, 1H, *J* = 2.5, 6.0, 6.0 Hz), 4.50 (d, 1H, *J* = 11.5 Hz), 4.57 (d, 1H, *J* = 11.5 Hz), 4.92 (d, 1H, *J* = 3.0 Hz), 5.96 (dd, 1H, *J* = 3.0, 11.0 Hz), 6.09 (dd, 1H, *J* = 5.0, 11.0 Hz), 6.76—6.82 (m, 2H), 7.13—7.18 (m, 2H), 7.32—7.46 (m, 6H), 7.67—7.72 (m, 4H). ^{13}C-NMR ($CDCl_3$) δ: 19.19, 26.81, 63.15, 66.73, 70.86, 71.13, 95.03, 113.69, 127.45, 127.67, 129.22, 129.36, 129.63, 130.60, 133.45, 133.56, 135.56, 135.61, 159.14. MS *m/z* (%): 517 ($M^+ - 1$, 0.1), 487 (0.5), 429 (0.7), 350 (0.7), 309 (5.4), 293 (35), 241 (45), 163 (50), 121 (100). *Anal.* Calcd for $C_{31}H_{38}O_5Si$: C, 71.78; H, 7.38. Found: C, 71.83; H, 7.43.

MeOH (3 ml), pH 6.86 phosphate buffer (3 ml), and DDQ (1.55 g, 6.8 mmol) were added to a vigorously stirred solution of the ether (1.77 g, 3.4 mmol) in CH_2Cl_2 (60 ml) at room temperature. After 1 h, the reaction mixture was quenched with 10% $NaHCO_3$ (100 ml), and extracted with CH_2Cl_2. The extract was washed with brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 4 : 1) to give **13** as a colorless oil (1.31 g, 97%), which solidified on standing in a refrigerator, mp 58.5—59.5 °C. $[\alpha]_D^{24}$ +52.2° (*c* = 1.03, $CHCl_3$). IR (neat) cm^{-1}: 3450, 3000, 1430, 1115, 1040. ^{1}H-NMR ($CDCl_3$) δ: 1.07 (s, 9H), 1.89 (d, 1H, *J* = 8.5 Hz), 3.41 (s, 3H), 3.86—3.98 (m, 3H), 4.10 (ddd, 1H, *J* = 2.0, 6.0, 6.0 Hz), 4.90 (d, 1H, *J* = 3.0 Hz), 5.90 (dd, 1H, *J* = 3.0, 10.0 Hz), 6.17 (dd, 1H, *J* = 5.0, 10.0 Hz), 7.36—7.47 (m, 6H), 7.69—7.74 (m, 4H). ^{13}C-NMR ($CDCl_3$) δ: 19.17, 26.78, 55.42, 61.81, 63.51, 70.67, 95.22, 127.73, 128.40, 129.71, 129.74, 129.77, 133.18, 133.28, 135.57, 135.63. MS *m/z* (%): 397 ($M^+ - 1$, 0.1), 386 (0.1), 367 (0.2), 349 (0.8), 323 (1.9), 309 (20), 241 (100), 199 (64), 163 (79). *Anal.* Calcd for $C_{23}H_{30}O_4Si$: C, 69.31; H, 7.59. Found: C, 69.30; H 7.65.

(2*R*,3*R*,4*R*,5*S*,6*S*)-6-*tert*-Butyldiphenylsilyloxymethyl-3,4-epoxy-3,4,5,6-tetrahydro-5-hydroxy-2-methoxy-2*H*-pyran (8) A solution of **13** (205 mg, 0.515 mmol), 4,4′-thiobis(6-*tert*-butyl-*m*-cresol) (**14**) (5 mg, 14 μmol), and MCPBA (80%; 278 mg, 1.29 mmol) in CH_2Cl_2 (2.5 ml) was heated under reflux for 40 h under argon. The reaction mixture was cooled to room temperature, quenched with saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 3 : 1) to give **8** as a colorless oil (159 mg, 74%). $[\alpha]_D^{24}$ +4.73° (*c* = 1.24, $CHCl_3$). IR (neat) cm^{-1}: 3475, 2950, 1735, 1590, 1475, 1430, 1390, 1245, 1100. ^{1}H-NMR ($CDCl_3$) δ: 1.05 (s, 9H), 2.27 (d, 1H, *J* = 11.0 Hz), 3.18 (d, 1H, *J* = 3.5 Hz), 3.43 (s, 3H), 3.56 (dd, 1H, *J* = 3.5, 6.0 Hz), 3.66—3.87 (m , 3H), 3.95 (ddd, 1H, *J* = 2.0, 6.0, 11.0 Hz), 4.87 (s, 1H), 7.33—7.46 (m, 6H), 7.64—7.71 (m, 4H). ^{13}C-NMR ($CDCl_3$) δ: 19.14, 26.77, 51.66, 52.56, 55.57, 61.45, 62.43, 69.68, 95.78, 127.68, 129.66, 129.71, 133.27, 133.36, 135.56, 135.59. MS *m/z* (%): 415 ($M^+ + 1$, 0.1), 397 (0.1), 383 (0.1), 339 (1.0), 325 (9.5), 295 (17), 279 (16), 249 (23), 223 (31), 199 (87), 181 (67), 163 (100), 105 (39). HR-MS Calcd for $C_{22}H_{27}O_4Si$ (M^+ −MeO): 383.1678. Found: 383.1694.

(2*R*,3*R*,4*S*,5*S*,6*S*)-6-*tert*-Butyldiphenylsilyloxymethyl-3,5-dihydroxy-2-methoxy-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran (15) a) With MeMgCl–MeLi (Me_2Mg): A 1.4 M salt-free solution of MeLi in Et_2O (21 ml, 28.9 mmol) was added dropwise to a stirred suspension of MeMgCl (3 M THF solution; 9.6 ml, 28.9 mmol) at 0 °C under argon. After 1 h, stirring was stopped, and the supernatant solution was added dropwise through a cannula with glass filter to a stirred solution of **8** (3.0 g, 7.23 mmol) in Et_2O (90 ml) at −78 °C under argon. The reaction mixture was allowed to warm to room temperature, stirred for 3 d, then quenched with MeOH at 0 °C and saturated aqueous NH_4Cl, and extracted with EtOAc. The extract was washed with brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 3 : 1) to give **15** as a colorless oil (3.0 g, 97%). $[\alpha]_D^{26}$ −42.8° (*c* = 1.20, $CHCl_3$). IR (neat) cm^{-1}: 3420, 2950, 1480, 1430, 1115, 1045. ^{1}H-NMR ($CDCl_3$) δ: 1.08 (s, 9H), 1.09 (d, 3H, *J* = 6.5 Hz), 2.23 (m, 1H), 3.30 (s, 3H), 3.44 (br d, 1H, *J* = 9.5 Hz), 3.78 (br dd, 3H, *J* = 3.5, 3.5 Hz), 3.84 (br s, 1H), 3.97 (dd, 1H, *J* = 3.5, 11.0 Hz), 4.03 (dd, 1H, *J* = 3.5, 11.0 Hz), 4.14 (br d, 1H, *J* = 9.5 Hz), 4.45 (br s, 1H), 4.78 (br s, 1H), 7.37—7.49 (m, 6H), 7.67—7.78 (m, 4H). ^{13}C-NMR ($CDCl_3$) δ: 14.53, 19.11, 26.72, 38.21, 55.07, 64.57, 66.90, 70.15, 72.85, 103.62, 127.78, 127.87, 129.98, 132.13, 132.63, 135.55, 135.84. MS *m/z* (%): 431 ($M^+ + 1$, 0.1), 399 (0.1), 394 (0.1), 365 (0.1), 355 (0.5), 341 (5.3), 323 (12), 263 (24), 221 (13), 199 (100), 91 (61). HR-MS Calcd for $C_{24}H_{35}O_5Si$ ($M^+ + 1$): 431.2254. Found: 431.2259.

b) With Me_2CuLi: A 1.08 M salt-free solution of MeLi in Et_2O (3.5 ml, 3.78 mmol) was added dropwise to a stirred suspension of CuCN·Me_2S (394 mg, 1.91 mmol) in Et_2O (2 ml) at −78 °C under argon. The mixture was stirred for 10 min each at −78 °C and 0 °C, and cooled again to −78 °C. To this mixture, a solution of **8** (158.7 mg, 0.38 mmol) in Et_2O (2 ml) was added dropwise through a cannula. The whole was allowed to warm to 0 °C, stirred for 2 h, then poured into saturated aqueous NH_4Cl, and extracted with EtOAc. The extract was washed with brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was dissolved in CH_2Cl_2 (2 ml), stirred with Et_3N (0.27 ml, 1.94 mmol), DMAP (20 mg), and Ac_2O (0.18 ml, 1.91 mmol) at room temperature for 1 h, and then evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 3 : 1) to give the acetate of **13**, (2*R*,5*S*,6*S*)-5-acetoxy-6-*tert*-butyldiphenylsilyloxymethyl-5,6-dihydro-2-methoxy-2*H*-pyran, as a colorless oil (67 mg, 39%) and the acetate of **15** (**17**, *vide infra*) as a colorless oil (110 mg, 56%). the acetate of **13**: $[\alpha]_D^{27}$ +111.3° (*c* = 1.13, $CHCl_3$). IR (neat) cm^{-1}: 3075, 3050, 2960, 2930, 2890, 2860, 1740, 1595, 1480, 1435, 1395, 1375, 1240, 1190, 1120, 1050. ^{1}H-NMR ($CDCl_3$) δ: 1.04 (s, 9H), 1.97 (s, 3H), 3.42 (s, 3H), 3.81 (d, 2H, *J* = 6.5 Hz), 4.25 (dt, 1H, *J* = 2.5, 6.5 Hz), 4.93 (d, 1H, *J* = 3.0 Hz), 5.07 (dd, 1H, *J* = 2.5, 5.5 Hz), 6.00 (dd, 1H, *J* = 3.0, 10.0 Hz), 6.19 (dd, 1H, *J* = 5.5, 10.0 Hz), 7.35—7.46 (m, 6H), 7.63—7.70 (m, 4H). ^{13}C-NMR ($CDCl_3$) δ: 19.12, 20.80, 26.68, 55.59, 62.39, 62.91, 69.20, 94.97, 125.81, 127.71, 127.73, 129.71, 129.77, 130.36, 133.25, 135.52, 135.54, 170.31. FAB-MS *m/z* (%): 463 (M^+ + Na, 13), 409 (46), 383 (20), 349 (68), 323 (43), 303 (33), 241 (100), 221 (51), 199 (50), 135 (84). HR-MS (FAB) Calcd for $C_{25}H_{32}O_5SiNa$ (M^+ + Na): 463.1916. Found: 463.1949.

c) With $Me_2CuMgBr$: A 0.82 M solution of MeMgBr in THF (0.3 ml, 0.246 mmol) was added to a stirred suspension of CuCN (11.2 mg, 0.125 mmol) in Et_2O (1 ml) at −78 °C under argon. The mixture was stirred for 10 min each at −78 °C and 0 °C, and cooled again to −78 °C. Then a solution of **8** (10.4 mg, 25 mmol) in Et_2O (1 ml) was added dropwise through a cannula. The reaction mixture was allowed to warm to 0 °C, stirred for 2 h, then quenched with a 1 : 9 mixture of aqueous NH_4OH and saturated aqueous NH_4Cl, and extracted with EtOAc. The extract was washed with brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 3 : 1) to give (2*R*,3*S*,4*S*,5*R*,6*S*)-4-bromo-6-*tert*-butyldiphenylsilyloxy-methyl-3,5-dihydroxy-2-methoxy-3,4,5,6-tetrahydro-2*H*-pyran (**16**) as a colorless oil (6.8 mg, 56%) and **15** (3.6 mg, 32%). **16**: $[\alpha]_D^{24}$ −45.1° (*c* = 0.55, $CHCl_3$). IR (neat) cm^{-1}: 3440, 2930, 2850, 1430, 1115, 1030. ^{1}H-NMR ($CDCl_3$) δ: 1.07(s, 9H), 3.37 (s, 3H), 3.80—3.95 (m, 2H), 3.96—4.09 (m, 2H), 4.18—4.27 (m, 3H), 4.69 (d, 1H, *J* = 2.0 Hz), 4.86 (br s, 1H), 7.38—7.68 (m, 6H), 7.70—7.77 (m, 4H). ^{13}C-NMR ($CDCl_3$) δ: 19.08, 26.72, 45.55, 55.54, 64.46, 66.42, 69.46, 72.27, 102.81, 127.86, 127.95, 130.08, 130.12, 131.91, 132.27, 135.53, 135.77. FAB-MS *m/z* (%): 519 ($^{81}BrM^+$ + Na, 19), 518 ($^{81}BrM^+$ + Na − 1, 64), 517 ($^{79}BrM^+$ + Na, 20), 516 ($^{79}BrM^+$ + Na − 1, 62), 496 ($^{81}BrM^+$, 17), 494 ($^{79}BrM^+$, 16), 437 (5.8), 391 (14), 305 (18), 241 (44), 221 (100). HR-MS (FAB) Calcd for $C_{23}H_{31}{}^{81}BrO_5SiNa$ (M^+ + Na): 519.1001. Found: 519.1025.

(2*R*,3*R*,4*S*,5*S*,6*S*)-6-*tert*-Butyldiphenylsilyloxymethyl-3,5-diacetoxy-2-methoxy-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran (17) Et_3N (1.42 ml, 10.2 mmol), DMAP (40 mg), and Ac_2O (0.96 ml, 10.2 mmol) were added to a stirred solution of **15** (1.47 g, 3.41 mmol) in CH_2Cl_2 (8 ml) at room temperature. After 30 min, the reaction mixture was evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–

EtOAc 3:1) to give **17** as a colorless oil (1.73 g, 99%). $[\alpha]_D^{24}$ −16.4° (c=1.29, $CHCl_3$). IR (neat) cm^{-1}: 2950, 1740, 1430, 1380, 1255, 1240, 1120, 1050. ^{1}H-NMR ($CDCl_3$) δ: 1.05 (s, 9H), 1.21 (d, 3H, J=7.5 Hz), 1.99 (s, 3H), 2.04 (s, 3H), 2.21 (m, 1H), 3.32 (s, 3H), 3.78 (d, 2H, J=7.0 Hz), 4.05 (dt, 1H, J=2.0, 7.0 Hz), 4.58 (br s, 1H), 4.65 (dd, 1H, J=2.0, 2.0 Hz), 4.71 (br s, 1H), 7.33—7.47 (m, 6H), 7.61—7.68 (m, 4H). ^{13}C-NMR ($CDCl_3$) δ: 15.24, 19.09, 21.08, 21.18, 26.75, 34.23, 55.18, 62.40, 65.39, 69.79, 70.81, 99.51, 127.71, 129.74, 129.78, 133.15, 133.27, 135.55, 135.57, 169.90, 170.27. MS m/z (%): 483 (M^+ − MeO, 2.9), 457 (10), 425 (3.6), 397 (6.9), 365 (20), 337 (37), 323 (18), 277 (7.9), 241 (74), 199 (60), 139 (76), 43 (100). HR-MS Calcd for $C_{27}H_{35}O_6Si$ (M^+ − MeO): 483.2203 found: 483.2188.

(2*S*,3*R*,4*S*,5*S*,6*S*)-2-Allyl-3,5-diacetoxy-6-hydroxymethyl-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran (18) and (2*R*,3*R*,4*S*,5*S*,6*S*)-3,5-Diacetoxy-2,6-epoxymethano-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran (19) AllylTMS (62 μl, 0.39 mmol) and $BF_3 \cdot Et_2O$ (80 μl, 0.65 mmol) were added to a stirred solution of **17** (67.3 mg, 0.131 mmol) in MeCN (1 ml) at room temperature under argon. After 20 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 1:1) to give **19** as a colorless oil (22.2 mg, 69%) and **18** as colorless needles (3.1 mg, 8%). **18**: mp 96—98°C. $[\alpha]_D^{27}$ −94.3° (c=0.093, $CHCl_3$). IR ($CHCl_3$) cm^{-1}: 3550, 3020, 1745, 1380, 1220, 1105, 1035. ^{1}H-NMR ($CDCl_3$) δ: 0.95 (d, 3H, J=6.5 Hz), 1.78 (dd, 1H, J=2.0, 9.0 Hz), 1.93—2.30 (m, 3H), 2.08 (s, 3H), 2.09 (s, 3H), 3.53—3.68 (m, 2H), 4.00 (ddd, 1H, J=2.0, 11.0, 11.0 Hz), 4.13 (ddd, 1H, J=4 .0, 5.5, 11.0 Hz), 4.61 (dd, 1H, J=9.5, 9.5 Hz), 4.88 (dd, 1H, J=5.5, 10.5 Hz), 5.06—5.16 (m, 2H), 5.83 (m, 1H). ^{13}C-NMR ($CDCl_3$) δ: 14.21, 20.75, 20.90, 36.12, 36.70, 57.68, 71.17, 72.34, 74.13, 77.20, 117.88, 133.68, 169.98. FAB-MS m/z (%): 287 (M^++1, 61), 255 (7.3), 227 (29), 185 (9.1), 167 (29), 154 (100), 136 (80). HR-MS (FAB) Calcd for $C_{14}H_{23}O_6$ (M^++1): 287.1494. Found: 287.1497. **19**: ^{1}H-NMR ($CDCl_3$) δ: 0.98 (d, 3H, J=6.5 Hz), 1.95—2.10 (m, 1H), 2.07 (s, 3H), 2.10 (s, 3H), 3.75 (dd, 1H, J=5.0, 7.5 Hz), 4.09 (d, 1H, J=7.5 Hz), 4.49—4.55 (m, 2H), 4.74 (dd, 1H, J=3.5, 10.5 Hz), 5.37 (s, 1H).

(2*R*,3*R*,4*S*,5*S*,6*S*)-3,5-Diacetoxy-6-hydroxymethyl-2-methoxy-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran (20) AcOH (2.5 ml, 435 mmol) and a 1 M solution of tetra-*n*-butylammonium fluoride (TBAF) in THF (36.3 ml, 36.3 mmol) were added to a stirred solution of **17** (3.73 g, 7.25 mmol) in THF (40 ml) at 0 °C. After 5 h at room temperature, the reaction mixture was quenched with H_2O, and extracted with Et_2O. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 1:1) to give **20** as a colorless oil (2.0 g, 100%). $[\alpha]_D^{24}$ −70.9° (c=0.73, $CHCl_3$). IR (neat) cm^{-1}: 3450, 2950, 1730, 1440, 1380, 1240, 1120, 1050. ^{1}H-NMR ($CDCl_3$) δ: 1.24 (d, 3H, J=7.5 Hz), 2.09 (s, 3H), 2.12 (s, 3H), 2.13—2.24 (m, 2H), 3.39 (s, 3H), 3.56 (dd, 1H, J=6.0, 11.5 Hz), 3.78 (dd, 1H, J=7.5, 11.5 Hz), 4.11 (ddd, 1H, J=1.0, 6.0, 7.5 Hz), 4.61 (dd, 1H, J=1.0, 1.0 Hz), 4.70 (br s, 1H), 4.72 (br s, 1H). ^{13}C-NMR ($CDCl_3$) δ: 15.39, 21.08, 21.19, 34.62, 55.35, 61.69, 65.52, 70.16, 70.65, 99.70, 169.95, 171.07. MS m/z (%): 245 (M^+ − MeO, 3.4), 185 (6.2), 149 (19), 142 (29), 116 (11), 100 (19), 69 (39), 43 (100). HR-MS Calcd for $C_{11}H_{17}O_6$ (M^+ − MeO): 245.1025. Found: 245.1020.

(2*R*,3*R*,4*S*,5*S*,6*S*)-3,5-Diacetoxy-2-methoxy-4-methyl-3,4,5,6-tetrahydro-6-(4-toluenesulfonyloxy)methyl-2*H*-pyran (21) DMAP (50 mg) and tosyl chloride (TsCl) (194 mg, 1.02 mmol) were added to a stirred solution of **20** (187 mg, 0.677 mmol) in pyridine (1.5 ml) at 0 °C. After 12 h at room temperature, the reaction mixture was quenched with MeOH (0.5 ml) and then 30 min later, with H_2O, and extracted with Et_2O. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 3:1) to give **21** as a colorless oil (287 mg, 98%). $[\alpha]_D^{27}$ −45.4° (c=0.52, $CHCl_3$). IR (neat) cm^{-1}: 2940, 1740, 1605, 1455, 1370, 1245, 1180, 1120, 1050. ^{1}H-NMR ($CDCl_3$) δ: 1.18 (d, 3H, J=7.5 Hz), 1.99 (s, 3H), 2.04 (s, 3H), 2.10—2.23 (m, 1H), 2.46 (s, 3H), 3.34 (s, 3H), 4.08—4.25 (m, 3H), 4.55 (br s, 1H), 4.56 (br s, 1H), 4.64 (br s, 1H), 7.36 (d, 2H, J=8.0 Hz), 7.79 (d, 2H, J=8.0 Hz). ^{13}C-NMR ($CDCl_3$) δ: 15.17, 20.91, 21.11, 21.63, 34.25, 55.47, 63.16, 68.29, 69.51, 70.24, 99.52, 127.97, 129.90, 132.75, 145.05, 169.78, 170.03. FAB-MS m/z (%): 453 (M^++Na, 16), 431 (M^++1, 3.8), 399 (100), 371 (3.8), 307 (4.4), 259 (12), 227 (13), 185 (18), 154 (39), 137 (51). HR-MS (FAB) Calcd for $C_{19}H_{26}O_9SNa$ (M^++Na): 453.1195. Found: 453.1178.

(2*S*,3*R*,4*S*,5*S*,6*S*)-2-Allyl-3,5-diacetoxy-4-methyl-3,4,5,6-tetrahydro-6-(4-toluenesulfonyloxy)methyl-2*H*-pyran (25) and (2*R*,3*R*,4*S*,5*S*,6*S*)-2-Allyl-3,5-diacetoxy-4-methyl-3,4,5,6-tetrahydro-6-(4-toluenesulfonyloxy)-methyl-2*H*-pyran (26) AllylTMS (164 μl, 1.03 mmol) and $BF_3 \cdot Et_2O$ (212 μml, 1.72 mmol) were added to a stirred solution of **21** (149 mg, 0.345 mmol) in MeCN (5 ml) at room temperature under argon. The reaction mixture was heated under reflux for 24 h, then cooled to room temperature, quenched with saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 3:1) to give **25** as a colorless oil (58.5 mg, 39%) and **26** as a colorless oil (38.9 mg, 26%). **25**: $[\alpha]_D^{25}$ −66.2° (c=0.52, $CHCl_3$). IR (neat) cm^{-1}: 2980, 2940, 1740, 1650, 1600, 1435, 1360, 1230, 1180, 1110, 1030. ^{1}H-NMR ($CDCl_3$) δ: 0.91 (d, 3H, J=6.5 Hz), 1.86—2.29 (m, 3H), 2.02 (s, 3H), 2.07 (s, 3H), 2.46 (s, 3H), 3.53 (ddd, 1H, J=4.5, 7.0, 9.5 Hz), 4.14—4.27 (m, 2H), 4.39 (m, 1H), 4.55 (dd, 1H, J=9.5, 9.5 Hz), 4.80 (m, 1H), 4.98—5.09 (m, 2H), 5.72 (m, 1H), 7.36 (d, 2H, J=8.0 Hz), 7.52 (d, 2H, J=8.0 Hz). ^{13}C-NMR ($CDCl_3$) δ: 14.05, 20.64, 20.87, 21.65, 36.29, 36.68, 65.43, 69.98, 71.65, 71.77, 73.80, 117.27, 127.93, 129.89, 132.79, 133.47, 145.08, 169.81, 169.89. FAB-MS m/z (%): 463 (M^++Na, 20), 441 (M^++1, 37), 399 (7.4), 381 (13), 321 (3.9), 269 (14), 209 (8.0), 167 (13), 149 (100), 137 (28). HR-MS (FAB) Calcd for $C_{21}H_{29}O_8S$ (M^++1): 441.1583. Found: 441.1573. **26**: $[\alpha]_D^{20}$ +35.1° (c=0.46, $CHCl_3$). IR (neat) cm^{-1}: 2980, 2960, 1740, 1650, 1605, 1375, 1260, 1170, 1105. ^{1}H-NMR ($CDCl_3$) δ: 1.12 (d, 3H, J=7.5 Hz), 1.96 (s, 3H), 2.05 (s, 3H), 2.05—2.45 (m, 3H), 2.45 (s, 3H), 3.65 (ddd, 1H, J=1.5, 7.0, 9.0 Hz), 3.95 (ddd, 1H, J=1.5, 6.0, 6.5 Hz), 4.08 (dd, 1H, J=6.0, 10.0 Hz), 4.14 (dd, 1H, J=6.5, 10.0 Hz), 4.54 (br s, 3H), 4.56 (brs, 1H), 5.03—5.10 (m, 2H), 5.73 (m, 1H), 7.32—7.36 (m, 2H), 7.76—7.79 (m, 2H). ^{13}C-NMR ($CDCl_3$) δ: 14.67, 20.91, 21.01, 21.64, 35.35, 67.87, 69.28, 70.72, 71.65, 73.98, 117.86, 128.02, 129.89, 132.69, 133.28, 145.02, 169.93, 170.12. FAB-MS m/z (%): 463 (M^++Na, 6.3), 441 (M^++1, 48), 391 (16), 381 (52), 369 (7.5), 291 (25), 269 (100), 209 (21), 167 (21), 154 (61), 149 (85), 137 (61). HR-MS (FAB) Calcd for $C_{21}H_{29}O_8S$ (M^++1): 441.1583. Found: 441.1562.

[2*R*,3*R*,4*S*,5*S*,6*S*,6(1*E*)]-3,5-Diacetoxy-2-methoxy-6-(2-methoxycarbonylethenyl)-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran (23*E*) NaH (60%, 26 mg, 0.65 mmol) was added to a stirred solution of dimethyl methoxycarbonylmethanephosphonate (106 μl, 0.65 mmol) in THF (1 ml) at room temperature under argon. After 20 min, a solution of the aldehyde (18 mg, 66 μmol), prepared by Swern oxidation of **20** (18 mg) as described above, in THF (1 ml) was added through a cannula. The reaction mixture was stirred for 1 h, then quenched with H_2O, and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 3:1) to give a 4:1 *E*, *Z* mixture of **23** as a colorless oil (13.9 mg, 64%). ^{1}H-NMR ($CDCl_3$) δ: 1.23 (d, 2.4H, J=7.5 Hz), 1.33 (d, 0.6H, J=7.5 Hz), 2.06 (s, 2.4H), 2.07 (s, 0.6H), 2.08 (s, 2.4H), 2.09 (s, 0.6H), 2.00—2.34 (m, 1H), 3.37 (s, 0.6H), 3.39 (s, 2.4H), 3.74 (s, 0.6H), 3.78 (s, 2.4H), 4.57—4.97 (m, 3.8H), 5.57—5.71 (m, 0.2H), 5.89 (dd, 0.2H, J=1.5, 11.5 Hz), 6.22 (dd, 0.8H, J=1.5, 16.0 Hz), 6.36 (dd, 0.2H, J=7.0, 11.5 Hz), 6.89 (dd, 0.8H, J=4.0, 16.0 Hz).

[2*R*,3*R*,4*S*,5*S*,6*S*,6(1*Z*)]-3,5-Diacetoxy-2-methoxy-6-(2-methoxycarbonylethenyl)-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran (23*Z*) A 0.6 M solution of $KN(TMS)_2$ in THF (0.42 ml, 0.25 mmol) was added to a stirred solution of di-2,2,2-trifluoroethyl methoxycarbonylmethanephosphonate (101 mg, 0.318 mmol) and 18-crown-6 ether (280 mg, 1.06 mmol) in THF (2 ml) at −78 °C under argon. After 30 min, a solution of the aldehyde (58 mg), prepared by Swern oxidation of **20** (66 mg) as described above, in THF (1 ml) was added dropwise through a cannula during 10 min. After 30 min, the reaction mixture was quenched with saturated aqueous NH_4Cl, and extracted with Et_2O. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 3:1) to give a 20:1 *Z*, *E* mixture of **23** as a colorless oil (25.7 mg, 37%), which was solidified and recrystallized from *n*-hexane to give colorless prisms of **23*Z***; mp 116—118°C. $[\alpha]_D^{27}$ +41.6° (c=0.255, $CHCl_3$). IR ($CHCl_3$) cm^{-1}: 3025, 1730, 1445, 1380, 1240, 1220, 1120. ^{1}H-NMR ($CDCl_3$) δ: 1.33 (d, 3H, J=7.5 Hz), 2.07 (s, 3H), 2.09 (s, 3H), 2.21 (m, 1H), 3.37 (s, 3H), 3.74 (s, 3H), 4.62 (br s, 1H), 4.72 (br s, 1H), 4.89 (br s, 1H), 5.63 (m, 1H), 5.89 (dd, 1H, J=1.5, 11.5 Hz), 6.36 (dd, 1H, J=7.0, 11.5 Hz). ^{13}C-NMR ($CDCl_3$) δ: 15.06, 21.07, 21.22, 34.64, 51.56, 55.51, 62.96, 70.19, 72.42, 99.74, 120.65, 146.23, 165.72, 169.92, 170.27. FAB-MS m/z (%): 353 (M^++Na, 6.7), 331 (M^++1, 10), 299 (100), 289 (6.6), 270 (4.6), 239 (72), 225 (14), 211 (10), 197 (9.1), 179 (67), 154 (34), 137 (37).

HR-MS (FAB) Calcd for $C_{15}H_{22}O_8Na$ ($M^+ + Na$): 353.1212. Found: 353.1218. *Anal.* Calcd for $C_{15}H_{22}O_8$: C, 54.54; H, 6.71. Found: C, 54.34; H, 6.64.

(2*R*,3*R*,4*S*,5*S*,6*S*)-3,5-Diacetoxy-2-methoxy-6-(2-methoxycarbonyl)-ethyl-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran (24) A vigorously stirred solution of **23** (140 mg, 0.423 mmol) in MeOH (6 ml) was hydrogenated over 10% Pd–C (10 mg) for 1 h at room temperature under ordinary pressure. The catalyst was removed by filtration, and washed with CH_2Cl_2. The filtrate was evaporated *in vacuo*, and the residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 3 : 1) to give **24** as a colorless oil (133 mg, 94%). $[\alpha]_D^{25}$ −59.2° (c=0.55, $CHCl_3$). IR (neat) cm^{-1}: 3650, 2950, 1740, 1440, 1380, 1240, 1115, 1050. ^{1}H-NMR ($CDCl_3$) δ: 1.18 (d, 3H, J=7.5 Hz), 1.62—1.76 (m, 1H), 1.86—2.14 (m, 2H), 2.01 (s, 3H), 2.05 (s, 3H), 2.32—2.55 (m, 2H), 3.29 (s, 3H), 3.62 (s, 3H), 3.93 (ddd, 1H, J=2.0, 3.5, 10.5 Hz), 4.57 (br s, 1H), 4.60 (dd, 1H, J=2.0, 2.0 Hz), 4.60 (br s, 1H). ^{13}C-NMR ($CDCl_3$) δ: 15.27, 21.11, 21.19, 25.89, 29.98, 34.69, 51.63, 55.30, 63.96, 70.64, 72.01, 99.81, 169.93, 170.46, 173.51. FAB-MS m/z (%): 355 ($M^+ + Na$, 32), 331 ($M^+ - 1$, 2.4), 301 (100), 273 (2.4), 241 (3.1), 227 (6.1), 213 (7.7), 191 (11), 181 (23). HR-MS (FAB) Calcd for $C_{15}H_{24}O_8Na$ ($M^+ + Na$): 355.1369. Found: 355.1363.

(2*S*,3*R*,4*S*,5*S*,6*S*)-2-Allyl-3,5-diacetoxy-6-(2-methoxycarbonyl)ethyl-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran (31) and (2*R*,3*R*,4*S*,5*S*,-6*S*)-2-Allyl-3,5-diacetoxy-6-(2-methoxycarbonyl)ethyl-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran (32) AllylTMS (36 μl, 227 μmol), $BF_3 \cdot Et_2O$ (46 μl, 0.37 mmol), and TMSOTf (7 μl, 35 μmol) were added successively to a stirred solution of **24** (25.1 mg, 75 μmol) in MeCN (1 ml) at room temperature under argon. After 25 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 3 : 1) to give **31** as colorless needles (16.5 mg, 63%) and **32** as a colorless oil (9.1 mg, 36%). **31**: mp 114—115 °C. $[\alpha]_D^{26}$ −71.9° (c=0.37, $CHCl_3$). IR ($CHCl_3$) cm^{-1}: 3025, 1750, 1445, 1380, 1235, 1100, 1035. ^{1}H-NMR ($CDCl_3$) δ: 0.92 (d, 3H, J=6.5 Hz), 1.72 (m, 1H), 1.94—2.51 (m, 6H), 2.06 (s, 6H), 3.50 (ddd, 1H, J=4.5, 7.0, 10.0 Hz), 3.69 (s, 3H), 4.01 (ddd, 1H, J=3.5, 5.5, 11.0 Hz), 4.56 (dd, 1H, J=10.0, 10.0 Hz), 4.79 (dd, 1H, J=5.5, 11.0 Hz), 5.02—5.10 (m, 2H), 5.80 (m, 1H). ^{13}C-NMR ($CDCl_3$) δ: 13.91, 20.08, 20.85, 20.91, 29.75, 35.75, 36.49, 51.69, 70.18, 71.72, 73.24, 74.62, 117.38, 133.93, 161.58, 170.03, 173.80. FAB-MS m/z (%): 343 ($M^+ + 1$, 76), 311 (28), 283 (42), 255 (12), 223 (91), 181 (55), 169 (45), 115 (100), 95 (55). HR-MS (FAB) Calcd for $C_{17}H_{27}O_7$ ($M^+ + 1$): 343.1757. Found: 343.1727. *Anal.* Calcd for $C_{17}H_{26}O_7$: C, 59.64; H, 7.65. Found: C, 59.56; H, 7.31. **32**: $[\alpha]_D^{27}$ −3.30° (c=0.55, $CHCl_3$). IR (neat) cm^{-1}: 2950, 1745, 1440, 1380, 1255, 1090, 1030. ^{1}H-NMR ($CDCl_3$) δ: 1.16 (d, 3H, J=7.5 Hz), 1.71 (m, 1H), 1.92—2.33 (m, 3H), 2.11 (s, 6H), 2.37—2.60 (m, 3H), 3.62—3.73 (m, 2H), 3.67 (s, 3H), 4.54 (s, 1H), 4.55 (s, 1H), 5.03—5.13 (m, 2H), 5.80 (m, 1H). ^{13}C-NMR ($CDCl_3$) δ: 14.95, 21.11, 21.15, 26.40, 29.83, 35.56, 35.94, 51.58, 71.29, 71.80, 73.00, 74.04, 117.48, 133.79, 170.37, 170.44, 173.68. FAB-MS m/z (%): 343 ($M^+ + 1$, 100), 307 (16), 283 (84), 223 (40), 181 (32), 154 (98), 136 (83). HR-MS (FAB) Calcd for $C_{17}H_{27}O_7$ ($M^+ + 1$): 343.1757. Found: 343.1771.

[2*R*,3*R*,4*S*,5*S*,6*S*,6(1*E*)]-3,5-Diacetoxy-6-(2-ethoxycarbonylethenyl)-2-methoxy-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran (22) DMSO (183 μl, 2.57 mmol) was added dropwise to a stirred solution of $(COCl)_2$ (169 μl, 1.93 mmol) in CH_2Cl_2 (12 ml) at −78°C under argon. After 10 min, a solution of **20** (178 mg, 0.64 mmol) in CH_2Cl_2 (6 ml) was added dropwise during 20 min, and stirring was continued for 20 min. A solution of Et_3N in CH_2Cl_2 (0.72 ml, 5.15 mmol) was added dropwise during 30 min. After 20 min, the reaction mixture was quenched with saturated aqueous NH_4Cl, and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 1 : 2) to give an aldehyde as a colorless oil (165 mg). A 1 N solution of *tert*-BuOK in THF (721 μl, 712 μmol) was added to a stirred solution of diisopropyl ethoxycarbonylmethanephosphonate (218 μl, 916 μmol) in THF (20 ml) at room temperature under argon. After 10 min, the solution was cooled to −78 °C, and a solution of the aldehyde in THF (9 ml) was added dropwise during 30 min. The reaction mixture was allowed to warm to 0 °C, stirred for 10 min, quenched with saturated aqueous NH_4Cl, and extracted with Et_2O. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 1 : 1) to give a 10 : 1 *E*, *Z* mixture of **22** as a colorless oil (134 mg, 61%). ^{1}H-NMR ($CDCl_3$) δ: 1.23 (d, 3H, J=7.5 Hz), 1.29 (t, 3H, J=7.0 Hz), 2.06 (s, 3H), 2.08 (s, 3H), 2.20 (m, 1H), 3.39 (s, 3H), 4.21 (q, 2H, J=7.0 Hz), 4.62 (dd, 1H, J=2.5, 2.5 Hz), 4.69 (ddd, 1H, J=2.0, 2.0, 4.0 Hz), 4.71—4.77 (m, 2H), 6.22 (dd, 1H, J=2.0, 15.5 Hz), 6.87 (dd, 1H, J=4.0, 15.5 Hz).

[2*S*,3*R*,4*S*,5*S*,6*S*,6(1*E*)]-2-Allyl-3,5-diacetoxy-6-(2-ethoxycarbonylethenyl)-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran (27) and [2*R*,3*R*,4*S*,5*S*,-6*S*,6(1*E*)]-2-Allyl-3,5-diacetoxy-6-(2-ethoxycarbonylethenyl)-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran (28) AllylTMS (142 μl, 0.89 mmol) and $BF_3 \cdot Et_2O$ (183 μl, 1.49 mmol) were added to a stirred solution of **22** (103 mg, 0.29 mmol) in MeCN (2 ml) at 0 °C under argon. The reaction mixture was stirred at room temperature for 44 h, then quenched with saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 3 : 1) to give **27** as a colorless oil (49.6 mg, 47%) and **28** (35.9 mg, 34%). **27**: ^{1}H-NMR ($CDCl_3$) δ: 0.92 (d, 3H, J=6.0 Hz), 1.32 (t, 3H, J=7.0 Hz), 1.93 (m, 1H), 2.07 (s, 3H), 2.10 (s, 3H), 2.12—2.31 (m, 2H), 3.65 (m, 1H), 4.24 (q, 2H, J=7.0 Hz), 4.63 (dd, 1H, J=10.0, 10.0 Hz), 4.72 (ddd, 1H, J=2.0, 4.0, 6.0 Hz), 4.84 (dd, 1H, J=6.0, 11.0 Hz), 5.05—5.10 (m, 2H), 5.84 (m, 1H), 6.13 (dd, 1H, J=2.0, 16.0 Hz), 7.02 (dd, 1H, J=4.0, 16.0 Hz). **28**: $[\alpha]_D^{21}$ −15.6° (c=0.40, $CHCl_3$). IR (neat) cm^{-1}: 2980, 1740, 1730, 1660, 1445, 1380, 1300, 1250, 1180, 1035. ^{1}H-NMR ($CDCl_3$) δ: 1.21 (d, 3H, J=7.5 Hz), 1.28 (t, 3H, J=7.0 Hz), 2.04 (s, 3H), 2.10 (s, 3H), 2.13—2.38 (m, 2H), 2.50 (m, 1H), 3.77 (ddd, 1H, J=1.5, 6.0, 7.5 Hz), 4.14—4.26 (m, 2H), 4.39 (ddd, 1H, J=1.5, 2.0, 4.0 Hz), 4.57 (br s, 1H), 4.67 (br s, 1H), 5.05—5.17 (m, 2H), 5.82 (m, 1H), 6.19 (dd, 1H, J=2.0, 15.5 Hz), 6.81 (dd, 1H, J=4.0, 15.5 Hz). ^{13}C-NMR ($CDCl_3$) δ: 14.20, 14.97, 21.02, 21.08, 35.56, 35.70, 60.43, 70.83, 71.28, 73.03, 73.81, 117.78, 122.96, 133.57, 143.21, 165.97, 170.28, 170.36. MS m/z (%): 355 ($M^+ + 1$, 100), 309 (25), 295 (30), 235 (25), 207 (17), 154 (54), 137 (53). HR-MS Calcd for $C_{18}H_{27}O_7$ ($M^+ + 1$): 355.1755. Found: 355.1740.

(2*R*,3*R*,4*S*,5*S*,6*S*)-3,5-Di-(*tert*-butyldimethylsilyloxy)-2-methoxy-4-methyl-3,4,5,6-tetrahydro-6-(4-toluenesulfonyloxy)methyl-2*H*-pyran (33) K_2CO_3 (22 mg, 0.159 mmol) was added to a stirred solution of **21** (34 mg, 79 μmol) in MeOH (1 ml) at room temperature. After 3 h, the reaction mixture was diluted with H_2O, and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, and evaporated *in vacuo* to leave an oil, which was dissolved in CH_2Cl_2 (1 ml). Et_3N (55 μl, 0.395 mmol) and TBSOTf (73 μl, 0.316 mmol) were added to the stirred solution at room temperature under argon. After 1 h, the reaction mixture was diluted with saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 5 : 1) to give **33** as a colorless oil (39 mg, 86%). $[\alpha]_D^{24}$ −30.9° (c=0.22, $CHCl_3$). IR (neat) cm^{-1}: 2950, 2930, 2850, 1600, 1470, 1375, 1260, 1190, 1180, 1080, 1060. ^{1}H-NMR ($CDCl_3$) δ: −0.55 (s, 3H), 0.02 (s, 3H), 0.04 (s, 6H), 0.79 (s, 9H), 0.87 (s, 9H), 0.99 (d, 3H, J=6.5 Hz), 1.49—1.65 (m, 1H), 2.44 (s, 3H), 3.07 (dd, 1H, J=7.0, 10.0 Hz), 3.83 (s, 3H), 3.52 (dd, 1H, J=5.5, 10.0 Hz), 4.04 (ddd, 1H, J=3.0, 5.5, 10.0 Hz), 4.14 (dd, 1H, J=3.0, 11.0 Hz), 4.27 (d, 1H, J=7.0 Hz), 4.41 (dd, 1H, J=10.0, 11.0 Hz), 7.34 (d, 2H, J=8.0 Hz), 7.81 (d, 2H, J=8.0 Hz). ^{13}C-NMR ($CDCl_3$) δ: −4.90, −4.85, −4.60, −4.10, 15.27, 17.84, 18.33, 21.60, 25.65, 25.96, 40.76, 56.31, 66.36, 71.86, 72.93, 74.98, 101.11, 127.97, 129.86, 132.92, 144.85. FAB-MS m/z (%): 597 ($M^+ + Na$, 20), 573 ($M^+ - 1$, 6.3), 543 (20), 517 (27), 485 (7.1), 427 (8.4), 411 (69), 403 (50), 385 (34), 371 (12), 303 (14), 271 (64), 239 (72), 229 (100), 213 (53), 185 (45), 115 (60), 89 (100), 73 (100). HR-MS Calcd for $C_{27}H_{50}O_7SSi_2Na$ ($M^+ + Na$): 597.2713. Found: 597.2725.

(2*R*,3*R*,4*S*,5*S*,6*S*)-2-Allyl-3,5-dihydroxy-4-methyl-3,4,5,6-tetrahydro-6-(4-toluenesulfonyloxy)methyl-2*H*-pyran (34) AllylTMS (108 μl, 0.678 mmol), $BF_3 \cdot Et_2O$ (83 μl, 0.678 mmol) and TMSOTf (66 μl, 0.339 mmol) were added successively to a stirred solution of **33** (39 mg, 68 μmol) in MeCN (1 ml) at room temperature under argon. After 17 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 1 : 1) to give **34** as a colorless oil (9.1 mg, 38%). ^{1}H-NMR ($CDCl_3$) δ: 1.12 (d, 1H, J=6.5 Hz), 1.66 (m, 1H), 1.87 (br m, 1H), 2.01—2.49 (m, 3H), 2.45 (s, 3H), 3.10 (dd, 1H, J=8.0, 8.0 Hz), 3.43 (ddd, 1H, J=4.5, 8.0, 8.0 Hz), 3.58 (dd, 1H, J=5.5, 9.0 Hz), 4.10 (ddd, 1H, J=4.0, 5.5, 8.0 Hz), 4.29 (dd, 1H, J=4.0, 11.0 Hz), 4.39 (dd, 1H, J=8.0, 11.0 Hz), 5.05—5.15 (m, 2H), 5.82 (m, 1H), 7.35 (d, 2H, J=8.0 Hz), 7.81 (d, 2H, J=8.0 Hz).

(2*R*,3*R*,4*S*,5*S*,6*S*)-3,5-Di-(*tert*-butyldimethylsilyloxy)-6-hydroxymethyl-2-methoxy-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran (35) *N*,*N*-Di-

isopropylethylamine (2.7 ml, 15.2 mmol) and BOMCl (2.0 ml, 14.5 mmol) was added to a stirred solution of **20** (2.0 g, 7.24 mmol) in CH_2Cl_2 (3 ml) at 0 °C. After 10 h at room temperature, the reaction mixture was quenched with MeOH, stirred for 30 min, mixed with H_2O, and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 3 : 1) to give (2*R*,3*R*,4*S*,5*S*,6*S*)-6-benzyloxymethloxymethyl-3,5-diacetoxy-2-methoxy-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran as a colorless oil (2.75 g, 96%). $[\alpha]_D^{24}$ −19.9° (*c* = 0.72, $CHCl_3$). IR (neat) cm^{-1}: 2930, 1730, 1460, 1375, 1235, 1170, 1115, 1040. ^{1}H-NMR ($CDCl_3$) δ: 1.22 (d, 3H, *J* = 7.5 Hz), 2.06 (s, 3H), 2.07 (s, 3H), 2.18 (m, 1H), 3.39 (s, 3H), 3.72 (d, 2H, *J* = 6.0 Hz), 4.14 (dt, 1H, *J* = 1.5, 6.0 Hz), 4.60 (br s, 3H), 4.66 (dd, 1H, *J* = 1.5, 2.0 Hz), 4.70 (br s, 1H), 4.76 (d, 1H, *J* = 6.5 Hz), 4.79 (d, 1H, *J* = 6.5 Hz), 7.27—7.396 (m, 5H). MS *m/z* (%): 396 (M^+, 0.03), 395 ($M^+ - 1$, 0.04), 386 (0.2), 364 (0.8), 335 (1.8), 290 (1.4), 258 (4.0), 245 (6.3), 198 (8.0), 171 (7.2), 120 (25), 91 (100), 43 (87). HR-MS Calcd for $C_{20}H_{27}O_8$ ($M^+ - 1$): 395.1706. Found: 395.1725.

K_2CO_3 (1.85 g, 13.4 mmol) was added to a stirred solution of the BOM compound (2.66 g, 6.7 mmol) in MeOH (27 ml) at room temperature. After 40 min, the reaction mixture was diluted with H_2O, and extracted with EtOAc. The extract was washed with brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 1 : 1) to give (2*R*,3*R*,4*S*,5*S*,6*S*)-6-benzyloxymethyloxymethyl-3,5-dihydroxy-2-methoxy-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran as a colorless oil (2.03 g, 97%). $[\alpha]_D^{27}$ −83.9° (*c* = 1.48, $CHCl_3$). IR (neat) cm^{-1}: 3425, 2930, 2900, 1455, 1380, 1115, 1040. ^{1}H-NMR ($CDCl_3$) δ: 1.11 (d, 3H, *J* = 7.5 Hz), 2.24 (m, 1H), 3.38 (s, 3H), 3.45 (m, 1H), 3.73 (br s, 1H), 3.88—3.96 (m, 5H), 4.64 (s, 2H), 4.77 (br s, 1H), 4.82 (d, 1H, *J* = 7.0 Hz), 4.85 (d, 1H, *J* = 7.0 Hz), 7.29—7.37 (m, 5H). FAB-MS *m/z* (%): 313 ($M^+ + 1$, 13), 281 (15), 251 (7.0), 205 (9.3), 173 (27), 137 (11), 91 (100). HR-MS (FAB) Calcd for $C_{16}H_{25}O_6$ ($M^+ + 1$): 313.1651. Found: 313.1636.

2,6-Di-*tert*-butylpyridine (3.6 ml, 16 mmol) and TBSOTf (3.2 ml, 13.9 mmol) were added to a stirred solution of the diol (1.98 g, 6.33 mmol) in CH_2Cl_2 (20 ml) at 0 °C. After 1 h at room temperature, H_2O was added, and the reaction mixture was extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 10 : 1) to give (2*R*,3*R*,4*S*,5*S*,6*S*)-6-benzyloxymethyloxymethyl-3,5-di-(*tert*-butyldimethylsilyl-oxy)-2-methoxy-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran as a colorless oil (3.18 g, 93%). $[\alpha]_D^{25}$ −39.3° (*c* = 1.72, $CHCl_3$). IR (neat) cm^{-1}: 2925, 2875, 2850, 1475, 1380, 1360, 1240, 1075, 1050. ^{1}H-NMR ($CDCl_3$) δ: 0.05 (s, 3H), 0.06 (s, 9H), 0.87 (s, 6H), 0.88 (s, 6H), 0.89 (s, 6H), 1.03 (d, 1H, *J* = 6.0 Hz), 1.71 (m, 1H), 3.11 (dd, 1H, *J* = 7.0, 10.0 Hz), 3.43 (s, 3H), 3.57 (dd, 1H, *J* = 5.0, 10.0 Hz), 3.79 (dd, 1H, *J* = 3.0, 10.0 Hz), 4.00 (dd, 1H, *J* = 10.0, 10.0 Hz), 4.10 (ddd, 1H, *J* = 3.0, 5.0, 10.0 Hz), 4.41 (d, 1H, *J* = 7.0 Hz), 4.46 (s, 2H), 4.83 (s, 2H), 7.28—7.36 (m, 5H). MS *m/z* (%): 509 (M^+ − MeO, 0.1), 483 (0.1), 453 (1.1), 421 (1.0), 375 (0.7), 345 (1.9), 331 (32), 213 (5.6), 199 (10), 172 (8.9), 115 (21), 91 (100). HR-MS Calcd for $C_{27}H_{49}O_5Si_2$ (M^+ − MeO): 509.3118. Found: 509.3145.

A solution of the TBS compound (87.6 mg, 0.16 mmol) in EtOAc (3 ml) was hydrogenated over 10% $Pd(OH)_2$–C (20 mg) for 7 h at room temperature and under ordinary pressure. The catalyst was removed by filtration and washed with CH_2Cl_2. The filtrate was evaporated *in vacuo*, and the residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 7 : 1) to give **35** as a colorless fine crystalline powder (59.3 mg, 87%). mp 82.5—83.5 °C. $[\alpha]_D^{21}$ −45.4° (*c* = 0.54, $CHCl_3$). IR (neat) cm^{-1}: 3475, 3020, 2930, 2855, 1475, 1465, 1365, 1260, 1220, 1080, 1060, 1005. ^{1}H-NMR ($CDCl_3$) δ: 0.06 (s, 6H), 0.07 (s, 3H), 0.08 (s, 3H), 0.88 (s, 9H), 0.89 (s, 9H), 1.03 (d, 3H, *J* = 6.5 Hz), 1.76 (m, 1H), 1.97 (br s, 1H), 3.12 (dd, 1H, *J* = 6.5, 10.0 Hz), 3.43 (s, 3H), 3.61 (dd, 1H, *J* = 5.0, 10.0 Hz), 3.75—3.99 (m, 3H), 4.36 (d, 1H, *J* = 6.5 Hz). MS (FAB) *m/z* (%): 421 ($M^+ + 1$, 10), 389 (14), 331 (40), 257 (100), 199 (19), 171 (16), 115 (21), 73 (91). HR-MS (FAB) Calcd for $C_{20}H_{45}O_5Si_2$ ($M^+ + 1$): 421.2808. Found: 421.2816. *Anal.* Calcd for $C_{20}H_{44}O_5Si_2$: C, 57.09; H, 10.54. Found: C, 56.99, H, 10.80.

(2*R*,3*R*,4*S*,5*S*,6*S*)-3,5-Di-(*tert*-butyldimethylsilyloxy)-6-(2-hydroxyethyl)-2-methoxy-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran (36) DMSO (0.21 ml, 2.92 mmol) was added dropwise to a stirred solution of $(COCl)_2$ (0.19 ml, 2.19 mmol) in CH_2Cl_2 (14 ml) at −78 °C under argon. After 10 min, a solution of **35** (307 mg, 0.729 mmol) in CH_2Cl_2 (9 ml) was added dropwise through a cannula during 20 min, and stirring was continued for 20 min. A solution of Et_3N (0.81 ml, 5.83 mmol) in CH_2Cl_2 (1 ml) was added dropwise through a cannula during 30 min. The reaction mixture was allowed to warm to −40 °C, stirred for 40 min, then quenched with saturated aqueous NH_4Cl, and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 5 : 1) to give an aldehyde, which was immediately subjected to the next reaction. IR (neat) cm^{-1}: 2930, 2860, 1735, 1470, 1255, 1120, 1080. ^{1}H-NMR ($CDCl_3$) δ: 0.05 (s, 6H), 0.12 (s, 6H), 0.87 (s, 9H), 0.91 (s, 9H), 1.05 (d, 3H, *J* = 6.5 Hz), 1.57 (m, 1H), 3.07 (dd, 1H, *J* = 7.0, 9.5 Hz), 3.52 (s, 3H), 3.78 (dd, 1H, *J* = 6.0, 10.5 Hz), 4.33 (d, 1H, *J* = 6.0 Hz), 4.60 (d, 1H, *J* = 7.0 Hz), 9.94 (s, 1H).

A 1 M solution of *tert*-BuOK in THF (1.1 ml, 1.1 mmol) was added to a stirred solution of methyltriphenylphosphonium bromide (390 mg, 1.09 mmol) in THF (15 ml) at −20 °C under argon. After 30 min, a solution of the aldehyde in THF (10 ml) was added dropwise at −78 °C under argon. The reaction mixture was allowed to warm to room temperature, stirred for 40 h, then quenched with saturated aqueous NH_4Cl, and extracted with Et_2O. The extract was dried over Na_2SO_4, and evaporated *in vacuo*, and the residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 10 : 1) to give (2*R*,3*R*,4*S*,5*S*,6*S*)-3,5-di-(*tert*-butyldimethylsilyloxy)-2-methoxy-4-methyl-3,4,5,6-tetrahydro-6-vinyl-2*H*-pyran as a colorless oil (293 mg, 96%). $[\alpha]_D^{20}$ −96.9° (*c* = 1.10, $CHCl_3$). IR (neat) cm^{-1}: 2940, 2870, 1475, 1465, 1365, 1255, 1125, 1085. ^{1}H-NMR ($CDCl_3$) δ: 0.03 (s, 3H), 0.05 (s, 3H), 0.06 (s, 6H), 0.88 (s, 18H), 1.03 (d, 3H, *J* = 6.5 Hz), 1.67 (m, 1H), 3.08 (dd, 1H, *J* = 7.5, 10.0 Hz), 3.45 (s, 3H), 3.54 (dd, 1H, *J* = 6.0, 10.0 Hz), 4.36—4.42 (m, 1H), 4.38 (d, 1H, *J* = 7.5 Hz), 5.38 (ddd, 1H, *J* = 2.0, 2.0, 11.0 Hz), 6.11 (ddd, 1H, *J* = 4.5, 11.0, 17.5 Hz). ^{13}C-NMR ($CDCl_3$) δ: −4.84, −4.36, −3.97, 14.79, 18.00, 18.38, 25.76, 26.01, 40.32, 56.26, 72.84, 75.64, 75.85, 100.38, 118.56, 132.95. FAB-MS *m/z* (%): 417 ($M^+ + 1$, 1.0), 401 (3.8), 385 (14), 359 (18), 327 (17), 253 (13), 211 (16), 185 (23), 147 (21), 115 (16), 89 (34), 73 (100). HR-MS (FAB) Calcd for $C_{21}H_{43}O_4Si_2$ ($M^+ - 1$): 415.2700. Found: 415.2720.

$BH_3 \cdot Me_2S$ (90%, 1.1 ml, 13.0 mmol) was added to vigorously stirred 2-methyl-2-butene (2.76 ml, 26 mmol) at 0 °C under argon. After 2 h, the resulting disiamylborane was dissolved in THF (10 ml), and this solution was added dropwise to a stirred solution of the olefin (1.57 g, 3.76 mmol) in THF (15 ml) through a cannula at 0 °C. After 7 h, 15% NaOH (5 ml) and then 30% H_2O_2 were carefully added, and stirring was continued for 10 h at room temperature. The reaction mixture was diluted with H_2O, and extracted with Et_2O. The extract was washed with 0.5 N HCl and brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 10 : 1) to give **36** as a colorless oil (1.59 g, 97%). $[\alpha]_D^{20}$ −49.0° (*c* = 0.72, $CHCl_3$). IR (neat) cm^{-1}: 3425, 2950, 2860, 1475, 1465, 1390, 1360, 1250, 1080. ^{1}H-NMR ($CDCl_3$) δ: 0.05 (s, 3H), 0.06 (s, 6H), 0.07 (s, 3H), 0.88 (s, 9H), 0.89 (s, 9H), 1.04 (d, 3H, *J* = 6.5 Hz), 1.66—2.11 (m, 4H), 3.10 (dd, 1H, *J* = 7.0, 10.0 Hz), 3.42 (s, 3H), 3.52 (dd, 1H, *J* = 5.5, 10.0 Hz), 3.78—3.88 (m, 2H), 4.02 (ddd, 1H, *J* = 4.0, 5.5, 11.0 Hz), 4.35 (d, 1H, *J* = 7.0 Hz). ^{13}C-NMR ($CDCl_3$) δ: −4.83, −4.73, −4.23, −4.03, 15.26, 18.05, 18.36, 25.84, 25.99, 28.27, 39.85, 56.25, 60.90, 73.02, 74.30, 75.54, 101.31. FAB-MS *m/z* (%): 435 ($M^+ + 1$, 6.0), 403 (8.6), 343 (23), 271 (78), 253 (19), 213 (22), 185 (16), 159 (15), 145 (15), 139 (24), 89 (39), 73 (100). HR-MS (FAB) Calcd for $C_{21}H_{47}O_5Si_2$ ($M^+ + 1$): 435.2962. Found: 435.2942.

[2*R*,3*R*,4*S*,5*S*,6*S*,6(2*S*,3*R*)]3,5-Di-(*tert*-butyldimethylsilyloxy-2-methoxy-4-methyl-6-(2,3-epoxy-4-butanol)-3,4,5,6-tetrahydro-2*H*-pyran (37) DMSO (25.5 μl, 0.36 mmol) was added dropwise to a stirred solution of $(COCl)_2$ (23.5 μl, 0.27 mmol) in CH_2Cl_2 (3 ml) at −78 °C under argon. After 10 min, a solution of **36** (40.4 mg, 93 μmol) in CH_2Cl_2 (2 ml) was added dropwise through a cannula during 20 min, and stirring was continued for 20 min. A solution of Et_3N (100 μl, 0.72 mmol) in CH_2Cl_2 (3 ml) was added dropwise during 30 min. The reaction mixture was stirred for each 30 min at −78 °C and at −40 °C, then quenched with saturated aqueous NH_4Cl, and extracted with CH_2Cl_2. The extract was chromatographed on a silica gel column (*n*-hexane–EtOAc 5 : 1) to give an aldehyde, which was subjected to the next reaction.

A 1 M solution of *tert*-BuOK in THF (108 μl, 108 μmol) was added to a stirred solution of diisopropyl ethoxycarbonylmethanephosphonate (32 μl, 135 μmol) in THF (1.5 ml) at 0 °C under argon. After 30 min, a solution of the aldehyde in THF (1 ml) was added dropwise through a cannula at −78 °C during 20 min. The reaction mixture was allowed to warm to 0 °C, stirred for 20 min, then quenched with saturated aqueous NH_4Cl, and extracted with Et_2O. The extract was dried over Na_2SO_4,

and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 5 : 1) to give [2*R*,3*R*,4*S*,5*S*,6*S*,6(2*E*)]-3,5-di-(*tert*-butyldimethylsilyloxy)-6-(3-ethoxycarbonyl-2-propenyl)-2-methoxy-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran as a colorless oil (46 mg, 98%). $[\alpha]_D^{19}$ −68.2° (*c* = 0.96, $CHCl_3$). IR (neat) cm^{-1}: 2920, 2850, 1720, 1650, 1470, 1360, 1310, 1250, 1080, 1045. ^{1}H-NMR ($CDCl_3$) δ: 0.04 (s, 3H), 0.05 (s, 3H), 0.06 (s, 3H), 0.07 (s, 3H), 0.88 (s, 18H), 1.04 (d, 3H, *J* = 6.0 Hz), 1.28 (t, 3H, *J* = 7.0 Hz), 1.72 (m, 1H), 2.47 (dddd, 1H, *J* = 2.0, 3.0, 6.5, 16.0 Hz), 2.67 (dddd, 1H, *J* = 1.0, 8.0, 11.5, 16.0 Hz), 3.08 (dd, 1H, *J* = 7.5, 10.5 Hz), 3.36 (s, 3H), 3.55 (dd, 1H, *J* = 5.5, 10.5 Hz), 3.98 (ddd, 1H, *J* = 3.0, 5.5, 11.5 Hz), 4.19 (q, 2H, *J* = 7.0 Hz), 4.23 (d, 1H, *J* = 7.5 Hz), 5.97 (ddd, 1H, *J* = 1.0, 2.0, 11.5 Hz), 7.04 (ddd, 1H, *J* = 6.5, 8.0, 15.5 Hz). ^{13}C-NMR ($CDCl_3$) δ: −4.79, −4.35, −3.98, 14.26, 15.17, 18.00, 18.40, 25.79, 26.02, 28.58, 39.87, 56.35, 60.23, 72.82, 74.77, 75.45, 101.46, 123.27, 145.90, 166.31. FAB-MS *m/z* (%): 502 (M^+, 0.1), 487 (0.5), 471 (0.6), 445 (7.7), 413 (26), 339 (16), 313 (17), 281 (20), 229 (19), 207 (36), 172 (18), 159 (54), 115 (39), 89 (55), 73 (100). HR-MS (FAB) Calcd for $C_{25}H_{50}O_6Si_2$ (M^+): 502.3146. Found: 502.3113.

A 1 M solution of DIBAH in THF (0.36 ml, 0.36 mmol) was added dropwise to a stirred solution of the α,β-unsaturated ester (46 mg, 91 μmol) in CH_2Cl_2 (2 ml) at −78 °C under argon. After 4.5 h, the reaction mixture was quenched with 0.5 N HCl, and extracted with CH_2Cl_2. The extract was washed with brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 3 : 1) to give [2*R*,3*R*,4*S*,5*S*,6*S*,6(2*E*)]-3,5-di-(*tert*-butyldimethylsilyloxy)-6-(4-hydroxybutenyl)-2-methoxy-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran as a colorless oil (40.4 mg, 97%), which solidified on standing in a refrigerator, mp 65.5—66.6 °C. $[\alpha]_D^{20}$ −55.7° (*c* = 0.90, $CHCl_3$). IR (neat) cm^{-1}: 3400, 2920, 2850, 1470, 1460, 1360, 1250, 1085, 1050. ^{1}H-NMR ($CDCl_3$) δ: 0.03 (s, 3H), 0.04 (s, 3H), 0.06 (s, 6H), 0.89 (s, 18H), 1.03 (d, 3H, *J* = 6.0 Hz), 1.27 (dd, 1H, *J* = 5.5, 5.5 Hz), 1.73 (m, 1H), 2.28—2.39 (m, 1H), 2.46—2.60 (m, 1H), 3.07 (dd, 1H, *J* = 7.5, 10.5 Hz), 3.38 (s, 3H), 3.53 (dd, 1H, *J* = 5.5, 10.5 Hz), 3.88 (ddd, 1H, *J* = 3.5, 5.5, 12.0 Hz), 4.10—4.16 (m, 2H), 4.26 (d, 1H, *J* = 7.5 Hz), 5.76—5.81 (m, 2H). ^{13}C-NMR ($CDCl_3$) δ: −4.81, −4.29, −3.96, 15.22, 18.01, 18.40, 25.80, 26.03, 28.19, 39.85, 56.32, 63.70, 73.00, 75.61, 100.32, 129.49, 131.19. MS *m/z* (%): 460 (M^+, 0.03), 429 (M^+ − MeO, 0.4), 403 (1.5), 389 (3.7), 371 (17), 297 (14), 239 (18), 215 (13), 171 (17), 165 (20), 159 (50), 147 (18), 131 (21), 115 (37), 89 (65), 73 (100). HR-MS Calcd for $C_{22}H_{45}O_4Si_2$ (M^+ − MeO): 429.2856. Found: 429.2835.

A mixture of powdered molecular sieves 4 Å (500 mg), a solution D-(−)-diethyl tartrate (DET) (404 mg, 1.96 mmol) in CH_2Cl_2 (1.5 ml), and (iso-PrO)$_4$Ti (0.58 ml, 1.96 mmol) was stirred at −20 °C for 30 min under argon. A solution of the allyl alcohol (180 mg, 391 μmol) in CH_2Cl_2 (1.5 ml), and then a 3 M solution of *tert*-butylhydroperoxide (TBHP) in 2,2,4-trimethylpentane (0.65 ml, 1.96 mmol) were added dropwise through a cannula. After 24 h, a solution of $Fe_2(SO_4)_3 \cdot 7H_2O$ (6.6 g) and tartaric acid (2.2 g) in H_2O (22 ml) was added, and insoluble materials were removed by filtration with the aid of Celite and washed with CH_2Cl_2 several times. The filtrate was extracted with CH_2Cl_2, and the extract was vigorously stirred with 30% NaOH (50 ml) for 1 h. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 5 : 1) to give **37** as a colorless oil (169.8 mg, 91%). $[\alpha]_D^{21}$ −36.5° (*c* = 0.73, $CHCl_3$). IR (neat) cm^{-1}: 3420, 2930, 2850, 1470. 1460, 1385, 1360, 1250, 1080. ^{1}H-NMR ($CDCl_3$) δ: 0.03 (s, 3H), 0.06 (s, 9H), 0.88 (s, 18H), 1.02 (d, 3H, *J* = 6.5 Hz), 1.66 (m, 1H), 1.86—2.87 (m, 2H), 2.97 (ddd, 1H, *J* = 2.5, 2.5, 7.5 Hz), 3.07 (dd, 1H, *J* = 7.5, 10.0 Hz), 3.14 (ddd, 1H, *J* = 2.5, 5.0, 6.5 Hz), 3.46 (s, 3H), 3.54 (dd, 1H, *J* = 5.5, 10.0 Hz), 3.66 (ddd, 1H, *J* = 5.0, 7.5, 12.0 Hz), 3.95 (ddd, 1H, *J* = 2.5, 5.0, 12.0 Hz), 4.00 (ddd, 1H, *J* = 4.5, 5.5, 12.0 Hz), 4.36 (d, 1H, *J* = 7.5 Hz). ^{13}C-NMR ($CDCl_3$) δ: −4.82, −4.24, −3.97, 15.13, 17.97, 18.37, 25.79, 26.01, 27.52, 39.76, 54.03, 56.34, 57.06, 61.60, 72.77, 74.34, 75.63, 100.59. MS *m/z* (%): 476 (M^+, 0.03), 445 (0.1), 429 (0.2), 387 (5.4), 331 (4.4), 313 (3.9), 287 (34), 255 (18), 199 (10), 181 (17), 172 (19), 159 (36), 147 (31), 115 (43), 73 (100). HR-MS Calcd for $C_{23}H_{48}O_6Si_2$ (M^+): 476.2990. Found: 476.2969.

[2*R*,3*R*,4*S*,5*S*,6*S*,6(2*S*)]-3,5-Di-(*tert*-butyldimethylsilyloxy)-6-(2-hydroxy-3-butenyl)-2-methoxy-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran (38) Et_3N (0.18 ml, 1.3 mmol), DMAP (40 mg) and TsCl (185 mg, 0.971 mmol) were added successively to a stirred solution of **37** (154 mg, 0.324 mmol) in CH_2Cl_2 (2 ml) at 0 °C. After 1 h, at room temperature, the reaction mixture was quenched with MeOH (0.5 ml), stirred for 30 min, then diluted with saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 3 : 1) to give [2*R*,3*R*,4*S*,5*S*,6*S*,6(2*S*,3*R*)]-3,5-di-(*tert*-butyldimethylsilyloxy)-2-methoxy-4-methyl-6-[2,3-epoxy-4-(4-toluenesulfonyl)oxybutyl]-3,4,5,6-tetrahydro-2*H*-pyran as a colorless oil (201 mg, 98%). $[\alpha]_D^{21}$ −24.6° (*c* = 0.72, $CHCl_3$). IR (neat) cm^{-1}: 2930, 2860, 1600, 1460, 1365, 1250, 1180, 1080. ^{1}H-NMR ($CDCl_3$) δ: 0.02 (s, 3H), 0.05 (s, 9H), 0.87 (s, 9H), 0.88 (s, 9H), 1.01 (d, 3H, *J* = 6.5 Hz), 1.63 (m, 1H), 1.86—1.96 (m, 2H), 2.45 (s, 3H) , 2.94—3.04 (m, 2H), 3.05 (dd, 1H, *J* = 7.5, 10.0 Hz), 3.41 (s, 3H), 3.51 (dd, 1H, *J* = 5.5, 10.0 Hz), 3.95 (m, 1H), 3.99 (dd, 1H, *J* = 5.5, 11.5 Hz), 4.23 (dd, 1H, *J* = 3.5, 11.5 Hz), 4.29 (d, 1H, *J* = 7.5 Hz), 7.34 (d, 2H, *J* = 7.5 Hz), 7.80 (d, 2H, *J* = 8.5 Hz). ^{13}C-NMR ($CDCl_3$) δ: −4.87, −4.28, −4.01, 15.07, 17.92, 18.33, 21.61, 25.75, 25.97, 27.28, 39.68, 53.36, 54.78, 56.30, 70.04, 72.61, 73.87, 75.50, 100.50, 127.93, 129.84, 132.71, 144.99. MS *m/z* (%): 629 (M^+ − 1, 0.02), 599 (M^+ − MeO, 0.5), 573 (4.6), 541 (6.9), 467 (5.2), 441 (18), 409 (9.3), 369 (6.3), 295 (14), 229 (93), 159 (44), 129 (40), 115 (44), 95 (44), 89 (61), 73 (100). HR-MS Calcd for $C_{29}H_{51}O_7SSi_2$ (M^+ − MeO): 599.2895. Found: 599.2909.

$NaHCO_3$ (53 mg, 0.627 mmol) and NaI (71 mg, 0.47 mmol) were added to a stirred solution of the tosylate (198 mg, 0.313 mmol) in MeCOEt (2 ml). The reaction mixture was heated at 60 °C for 12 h, then cooled to room temperature, diluted with saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 10 : 1) to give [2*R*,3*R*,4*S*,5*S*,6*S*,6(2*S*,3*R*)]-3,5-di-(*tert*-butyldimethylsilyloxy)-6-(4-iodo-2,3-epoxybutyl)-2-methoxy-4-methyl-3,4,5,6-tetra-hydro-2*H*-pyran as a colorless oil (178 mg, 97%). $[\alpha]_D^{21}$ −43.4° (*c* = 0.89, $CHCl_3$). IR (neat) cm^{-1}: 2940, 2870, 1475, 1465, 1390, 1360, 1255, 1085. ^{1}H-NMR ($CDCl_3$) δ: 0.05 (s, 3H), 0.06 (s, 9H), 0.88 (s, 18H), 1.02 (d, 3H, *J* = 6.5 Hz), 1.66 (m, 1H), 1.86 (ddd, 1H, *J* = 3.5, 5.0, 15.0 Hz), 2.06 (ddd, 1H, *J* = 5.5, 11.5, 15.0 Hz), 2.96—3.11 (m, 4H), 3.28 (m, 1H), 3.48 (s, 3H), 3.53 (dd, 1H, *J* = 5.5, 10.5 Hz), 4.02 (ddd, 1H, *J* = 3.5, 5.5, 11.5 Hz), 4.34 (d, 1H, *J* = 7.5 Hz). ^{13}C-NMR ($CDCl_3$) δ: −4.82, −4.19, −3.97, 14.75, 15.10, 17.99, 18.38, 25.80, 26.01, 27.35, 39.71, 56.55, 57.41, 60.47, 72.62, 73.95, 75.61, 100.57. MS *m/z* (%): 585 (M^+ − 1, 0.02), 555 (0.3), 529 (2.8), 497 (5.5), 423 (4.2), 397 (12), 365 (19), 313 (13), 241 (11), 199 (13), 172 (20), 159 (39), 115 (45), 89 (64), 73 (100). HR-MS Calcd for $C_{23}H_{46}O_5Si_2I$ (M^+ − 1): 585.1929. Found: 585.1879.

A 1.7 M solution of *tert*-BuLi in toluene (0.7 ml, 1.19 mmol) was added dropwise to a stirred solution of the iodide (173 mg, 0.296 mmol) in Et_2O (3 ml) at −78 °C under argon. After 1 h, the reaction mixture was quenched with saturated aqueous NH_4Cl, and extracted with Et_2O. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 5 : 1) to give **38** as a colorless oil (128 mg, 94%), which solidified on standing in a refrigerator, mp 59.0—61.0 °C. $[\alpha]_D^{23}$ −45.9° (*c* = 0.50, $CHCl_3$). IR (neat) cm^{-1}: 3425, 2930, 2860, 1470, 1460, 1390, 1360, 1250, 1080. ^{1}H-NMR ($CDCl_3$) δ: 0.02 (s, 3H), 0.06 (s, 9H), 0.88 (s, 18H), 1.03 (d, 3H, *J* = 6.5 Hz), 1.64—1.81 (m, 2H), 2.04 (ddd, 1H, *J* = 7.5, 11.5, 14.5 Hz), 2.59 (d, 1H, *J* = 2.5 Hz), 3.09 (dd, 1H, *J* = 7.0, 10.0 Hz), 3.45 (s, 3H), 3.48 (dd, 1H, *J* = 5.0, 10.0 Hz), 4.01 (ddd, 1H, *J* = 2.5, 5.0, 11.5 Hz), 4.34 (m, 1H), 4.42 (d, 1H, *J* = 7.0 Hz), 5.14 (ddd, 1H, *J* = 1.5, 1.5, 10.5 Hz), 5.28 (ddd, 1H, *J* = 1.5, 1.5, 17.0 Hz), 5.88 (ddd, 1H, *J* = 6.5, 10.5, 17.0 Hz). ^{13}C-NMR ($CDCl_3$) δ: −4.85, −4.75, −4.27, −4.03, 15.20, 18.01, 18.34, 25.80, 25.99, 32.26, 39.83, 56.36, 72.63, 72.85, 75.09, 75.54, 101.30, 115.19, 140.25. MS *m/z* (%): 429 (M^+ − MeO, 0.1), 411 (0.2), 385 (0.4), 371 (10), 317 (8.0), 271 (9.8), 239 (14), 215 (15), 171 (44), 159 (23), 131 (26), 115 (32), 89 (49), 73 (100). *Anal.* Calcd for $C_{23}H_{48}O_5Si_2$: C, 59.95; H, 10.50. Found: C, 59.89; H, 10.66.

[2*R*,3*R*,4*S*,5*S*,6*S*,6(2*S*)]-6-(2,3-Diacetoxypropyl)-3,5-di-(*tert*-butyldimethylsilyloxy)-2-methoxy-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran (7) Et_3N (58 μml, 0.417 mmol), DMAP (20 mg), and Ac_2O (39 μl, 0.417 mmol) were added successively to a stirred solution of **38** (128 mg, 0.277 mmol) in CH_2Cl_2 (2 ml) at room temperature. After 1 h, the reaction mixture was evaporated *in vacuo*, and the residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 7 : 1) to give [2*R*,3*R*,4*S*,5*S*,6*S*,-6(2*S*)]-6-(2-acetoxy-3-butenyl)-3,5-di-(*tert*-butyldimethylsilyloxy)-2-methoxy-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran as a colorless oil (127.4 mg, 91%). $[\alpha]_D^{23}$ −55.7° (*c* = 1.07, $CHCl_3$). IR (neat) cm^{-1}: 2950, 2930, 2860, 1735, 1470, 1460, 1370, 1240, 1110, 1080. ^{1}H-NMR ($CDCl_3$) δ: 0.01 (s, 3H), 0.05 (s, 3H), 0.06 (s, 6H), 0.89 (s, 18H), 1.02 (d, 3H,

J=6.0 Hz), 1.62—1.84 (m, 2H), 2.07 (s, 3H), 2.17 (ddd, 1H, J=4.0, 12.0, 13.5 Hz), 3.04 (dd, 1H, J=7.5, 10.5 Hz), 3.50 (s, 3H), 3.50 (dd, 1H, J=6.0, 10.5 Hz), 3.90 (ddd, 1H, J=3.0, 6.0, 12.0 Hz), 4.40 (d, 1H, J=7.5 Hz), 5.26 (br d, 1H, J=10.5 Hz), 5.35 (br d, 1H, J=17.0 Hz), 5.44 (m, 1H), 5.80 (ddd, 1H, J=7.5, 10.5, 17.0 Hz). MS m/z (%): 471 (M^+ −MeO, 0.3), 455 (0.1), 445 (1.4), 395 (1.9), 385 (11), 353 (20), 331 (23), 279 (12), 253 (27), 171 (30), 159 (28), 117 (40), 89 (56), 73 (100). HR-MS Calcd for $C_{24}H_{47}O_5Si_2$ (M^+ −MeO): 471.2962. Found: 471.2977.

N-Methylmorpholine *N*-oxide (NMO) hydrate (16 mg, 0.115 mmol) and a 4% solution of OsO_4 in *tert*-BuOH (0.8 ml) were added to a stirred solution of the acetate (30 mg, 59 μmol) in acetone–H_2O (5 : 1, 2 ml) at room temperature. After 4 h, excess $Na_2S_2O_3$ and Celite were added, and then insoluble materials were removed by filtration and washed with CH_2Cl_2. The filtrate was washed with 0.5 N HCl and brine, dried over Na_2SO_4, and evaporated *in vacuo* to leave a diol as an oil, which was subjected to the next reaction without purification.

A solution of $NaIO_4$ (55 mg, 0.256 mmol) in H_2O (2.5 ml) was added to a vigorously stirred solution of the diol in THF (2 ml) at room temperature. After 12 h, $NaBH_4$ (44 mg, 1.16 mmol) was added portionwise at 0 °C, and stirring was continued for 1 h at room temperature. The reaction mixture was diluted with saturated aqueous NH_4Cl, and extracted with Et_2O. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was dissolved in CH_2Cl_2 (1 ml), and then Et_3N (12 μl, 87 μmol), DMAP (10 mg) and Ac_2O (8 μl, 87 μmol) were added at room temperature. The reaction mixture was evaporated *in vacuo*, and the residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 3 : 1) to give **7** as a colorless oil (26.6 mg, 84%). $[\alpha]_D^{24}$ −54.4° (c=0.83, $CHCl_3$). IR (neat) cm^{-1}: 2970, 2950, 2870, 1745, 1465, 1370, 1250, 1225, 1085. ^{1}H-NMR ($CDCl_3$) δ: 0.03 (s, 3H), 0.06 (s, 9H), 0.89 (s, 9H), 1.01 (s, 9H), 1.02 (d, 3H, J=6.5 Hz), 1.69 (m, 1H), 1.92—2.13 (m, 2H), 2.07 (s, 3H), 2.08 (s, 3H), 3.05 (dd, 1H, J=7.5, 10.0 Hz), 3.47 (s, 3H), 3.52 (dd, 1H, J=6.0, 10.5 Hz), 3.95 (ddd, 1H, J=3.5, 6.0, 12.0 Hz), 4.18 (dd, 1H, J=5.5, 12.0 Hz), 4.36 (dd, 1H, J=3.0, 12.0 Hz), 4.37 (d, 1H, J=7.5 Hz), 5.28 (m, 1H). HR-MS m/z (%) 517 (M^+ −MeO, 0.5), 491 (1.7) 459 (5.8), 399 (6.0), 371 (12), 359 (9.3), 299 (35), 256 (12), 239 (20), 193 (23), 159 (49), 117 (92), 89 (58), 73 (100), 43 (70). HR-MS Calcd for $C_{25}H_{49}O_7Si_2$ (M^+ −MeO): 517.3017. Found: 517.3041.

[2*S*,3*R*,4*S*,5*S*,6*S*,6(2*S*)]-2-Allyl-6-(2,3,-diacetoxypropyl)-3,5-di-(*tert*-butyldimethylsilyloxy)-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran (40) AllylTMS (39 μl, 0.242 μmol), $BF_3 \cdot Et_2O$ (30 μl, 0.241 mmol), and TMSOTf (23 μl, 0.12 mmol) were added successively to a stirred solution of **7** (13.5 mg, 25 μmol) in MeCN (1 ml) at room temperature under argon. After 20 h, the reaction mixture was diluted with saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue (crude **39**) was dissolved in CH_2Cl_2, (1 ml), and Et_3N (16 μl, 0.115 mmol) and TBSOTf (22 μl, 95 μmol) were added at room temperature under argon. After 30 min, Et_3N was added, and the reaction mixture was evaporated *in vacuo*. The residue was chromatographed on a silica column (*n*-hexane–EtOAc 7 : 1) to give **40** as a colorless oil (12.2 mg, 89%). $[\alpha]_D^{27}$ −53.3° (c=0.30, $CHCl_3$). IR (neat) cm^{-1}: 2950, 2930, 2850, 1760, 1740, 1650, 1480, 1370, 1260, 1230, 1110, 1070. ^{1}H-NMR ($CDCl_3$) δ: 0.03 (s, 3H), 0.06 (s, 3H), 0.08 (s, 3H), 0.09 (s, 3H), 0.89 (s, 9H), 0.90 (s, 9H), 1.00 (d, 3H, J=6.5 Hz), 1.64 (m, 1H), 1.86—2.19 (m, 3H), 2.06 (s, 6H), 2.58 (m, 1H), 2.97 (dd, 1H, J=9.5, 9.5 Hz), 3.41 (ddd, 1H, J=2.0, 9.5, 9.5 Hz), 3.46 (dd, 1H, J=6.0, 10.5 Hz), 3.89 (ddd, 1H, J=3.5, 6.0, 12.0 Hz), 4.14 (dd, 1H, J=5.0, 12.0 Hz), 4.32 (dd, 1H, J=3.0, 12.0 Hz), 5.02—5.12 (m, 2H), 5.16 (m, 1H), 5.87 (dddd, 1H, J=7.0, 7.5, 10.0, 12.0 Hz). ^{13}C-NMR ($CDCl_3$) δ: −4.92, −4.20, −3.10, 15.32, 17.95, 18.34, 20.86, 21.24, 24.59, 25.79, 26.10, 37.18, 40.76, 64.04, 69.69, 72.76, 72.90, 116.84, 135.29, 170.28, 170.67. FAB-MS m/z (%): 559 (M^+ + 1, 16), 501 (33), 441 (13), 427 (13), 367 (39), 307 (21), 267 (22), 213 (67), 175 (51), 117 (100).

[2*R*,3*R*,4*S*,5*S*,6*S*,6(2*S*)]-6-(2,3-Diacetoxypropyl)-3,5-dihydroxy-2-methoxy-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran (41) AllylTMS (29 μl, 0.182 mmol) and $BF_3 \cdot Et_2O$ (22.5 μl, 0.182 mmol) were added to a stirred solution of **7** (10 mg, 18 μmol) in MeCN (0.5 ml) at room temperature under argon. After 15 min, the reaction mixture was quenched with saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 3 : 1) to give **41** as a colorless oil (5.0 mg, 85%). $[\alpha]_D^{24}$ −61.0° (c=0.48, $CHCl_3$). IR (neat) cm^{-1}: 3460, 2940, 1745, 1580, 1440, 1380, 1240, 1120, 1045. ^{1}H-NMR ($CDCl_3$) δ: 1.10 (d, 3H, J=7.5 Hz), 1.92 (ddd, 1H, J=6.0, 12.0, 14.5 Hz), 2.04—2.10 (m, 1H), 2.06 (s, 3H), 2.07 (s, 3H), 2.18 (m, 1H), 3.02 (br, 1H), 3.13 (br, 1H), 3.39 (s, 1H), 3.40 (s, 3H), 3.44 (d, 1H, J=4.5 Hz), 3.94 (dd, 1H, J=6.0, 6.0 Hz), 4.18 (dd, 1H, J=7.0, 12.0 Hz), 4.30 (dd, 1H, J=3.0, 12.0 Hz), 4.64 (s, 1H), 5.28 (m, 1H). FAB-MS m/z (%): 321 (M^+ + 1, 19), 307 (18), 289 (61), 229 (54), 154 (100), 136 (78). HR-MS (FAB) Calcd for $C_{14}H_{25}O_8$ (M^+ + 1): 321.1549. Found: 321.1563.

[2*R*,3*R*,4*S*,5*S*,6*S*,6(2*S*)]-2-Allyl-6-(2,3-diacetoxypropyl)-3,5-di-(*tert*-butyldimethylsilyloxy)-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran (42) and [2*R*,3*R*,4*R*,5*S*,5(1*S*,3*S*)]-3-Acetoxy-2-allyl-4-methyl-5-(1,3,4-triacetoxybutyl)tetrahydrofuran (43) AllylTMS (39 μl, 0.249 mmol) and TMSOTf (23.7 μl, 0.123 mmol) were successively added to a stirred solution of **7** (13.5 mg, 25 μmol) in MeCN (0.5 ml) at 0 °C under argon. After 30 min, the reaction mixture was quenched with saturated aqueous $NaHCO_3$, and extracted with Et_2O. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was dissolved in CH_2Cl_2 (1 ml) and stirred with Et_3N (17 μl, 0.123 mmol) and Ac_2O (11 μl, 0.12 mmol) for 1 h. The reaction mixture was diluted with H_2O, and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was subjected to silica gel TLC (*n*-hexane–EtOAc 1 : 1) to give **42** (2.5 mg, 25%) and **43** (2.5 mg, 25%) as colorless oils. **42**: $[\alpha]_D^{20}$ −7.15° (c=0.49, $CHCl_3$). IR (neat) cm^{-1}: 2950, 1740, 1650, 1440, 1380, 1250, 1090, 1040. ^{1}H-NMR ($CDCl_3$) δ: 1.16 (d, 3H, J=7.5 Hz), 1.71 (ddd, 1H, J=4.0, 6.0, 14.5 Hz), 2.01 (ddd, 1H, J=6.5, 9.0, 14.5 Hz), 2.06 (s, 3H), 2.07 (s, 3H), 2.10 (s, 6H), 2.18—2.29 (m, 2H), 2.42 (m, 1H), 3.67 (dd, 1H, J=6.5, 6.5 Hz), 3.79 (dd, 1H, J=2.5, 9.0 Hz), 4.13 (dd, 1H, J=6.5, 12.0 Hz), 4,23 (dd, 1H, J=3.0, 12.0 Hz), 4.53 (s, 1H), 4.55 (s, 1H), 5.06—5.10 (m, 2H), 5.25 (m, 1H), 5.77 (m, 1H). ^{13}C-NMR ($CDCl_3$) δ: 14.95, 20.80, 21.15, 32.74, 35.65, 35.83, 64.80, 69.19, 70.84, 70.93, 71.80, 74.11, 117.93, 133.58, 170.27, 170.35, 170.42, 170.70. FAB-MS m/z (%): 415 (M^+ + 1, 22), 391 (9), 373 (17), 355 (97), 295 (61), 253 (26), 233 (15), 193 (39), 175 (60), 154 (62), 43 (100). HR-MS (FAB) Calcd for $C_{20}H_{31}O_9$ (M^+ + 1): 415.1968. Found: 415.1981. **43**: $[\alpha]_D^{21}$ +0.80° (c=0.38, $CHCl_3$). IR (neat) cm^{-1}: 3000, 2950, 1745, 1650, 1440, 1380, 1250, 1055. ^{1}H-NMR ($CDCl_3$) δ: 1.10 (d, 3H, J=7.0 Hz), 1.88 (ddd, 1H, J=7.0, 7.0, 14.0 Hz), 1.94 (m, 1H), 2.05 (s, 3H), 2.06 (s, 3H), 2.08 (s, 3H), 2.09 (s, 3H), 2.23 (ddd, 1H, J=7.0, 7.0, 14.0 Hz), 2.26—2.41 (m, 1H), 4.07 (dd, 1H, J=6.5, 12.0 Hz), 4.12 (dd, 1H, J=6.0, 6.0 Hz), 4.24 (ddd, 1H, J=4.5, 9.0, 9.0 Hz), 4.32 (dd, 1H, J=3.0, 12.0 Hz), 5.01—5.07 (m, 3H), 5.09—5.14 (m, 2H), 5.74 (m, 1H). FAB-MS m/z (%): 415 (M^+ + 1, 59), 391 (8), 373 (17), 355 (36), 307 (14), 295 (37), 235 (24), 175 (53), 154 (100). HR-MS (FAB) Calcd for $C_{20}H_{31}O_9$ (M^+ + 1): 415.1968. Found: 415.1986.

[2*S*,3*R*,4*S*,5*S*,6*S*,6(2*S*)]-2-Allyl-6-(2,3-diacetoxypropyl)-3,5-dihydroxy-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran (39) AllylTMS (16.9 μl, 0.106 mmol), $BF_3 \cdot Et_2O$ (13 μl, 0.106 mmol) and TMSOTf (10 μl, 53 μmol) were successively added to a stirred solution of **41** (3.4 mg, 10.6 μmol) in MeCN (0.5 ml) at 0 °C under argon. After 3 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 10 : 1) to give **39** as a colorless oil (3.5 mg, 80%). $[\alpha]_D^{26}$ −53.8° (c=0.32, $CHCl_3$). IR (neat) cm^{-1}: 3460, 3020, 1740, 1375, 1220, 1015. ^{1}H-NMR ($CDCl_3$) δ: 1.16 (d, 3H, J=6.5 Hz), 1.61—1.80 (m, 2H), 1.89—2.13 (m, 3H), 2.08 (s, 6H), 2.27 (m, 1H), 2.52 (m, 1H), 3.04 (m, 1H), 3.45—3.63 (m, 2H), 3.96 (ddd, 1H, J=5.5, 5.5, 9.5 Hz), 4.22 (dd, 1H, J=5.0, 11.5 Hz), 4.26 (dd, 1H, J=3.5, 11.5 Hz), 5.06—5.19 (m, 2H), 5.24 (m, 1H), 5.91 (m, 1H). FAB-MS m/z (%): 331 (M^+ + 1, 21), 307 (22), 289 (23), 271 (17), 253 (14), 219 (14), 155 (100), 136 (77). HR-MS (FAB) Calcd for $C_{16}H_{27}O_7$ (M^+ + 1): 331.1757. Found: 331.1757.

[2*S*,3*R*,4*S*,5*S*,6*S*,6(2*S*)]-3,5-Diacetoxy-6-(2,3-diacetoxypropyl)-2-methoxy-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran (45) Et_3N (10 μl, 71 μmol) and Ac_2O (6.7 μl, 71 μmol) were added to a stirred solution of **41** (8.7 mg, 27 μmol) in CH_2Cl_2 (0.5 ml) at room temperature. After 30 min, the reaction mixture was quenched with H_2O, and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 1 : 1) to give **45** as a colorless oil (10.4 mg, 94%). $[\alpha]_D^{19}$ −42.3° (c=0.37, $CHCl_3$). IR (neat) cm^{-1}: 2930, 1725, 1430, 1370, 1240, 1110, 1040. ^{1}H-NMR ($CDCl_3$) δ: 1.20 (d, 3H, J=7.5 Hz), 1.80 (ddd, 1H, J=4.5, 7.0, 14.5 Hz), 2.00 (ddd, 1H, J=5.5, 9.0, 14.5 Hz), 2.06 (s, 3H), 2.07 (s, 3H), 2.08 (s, 3H), 2.12 (s, 3H), 2.15 (m, 1H), 3.42 (s, 3H), 4.10 (ddd, 1H, J=1.5, 4.5, 9.0 Hz), 4.30 (dd, 1H, J=6.5, 12.0 Hz), 4.58 (dd, 1H, J=1.5, 1.5 Hz), 4.59 (dd, 1H, J=3.5, 12.0 Hz), 4.59 (d, 1H, J=1.5 Hz), 4.66 (s, 1H), 5.26

(m, 1H). ^{13}C-NMR ($CDCl_3$) δ: 15.21, 20.75, 21.03, 21.08, 21.19, 31.93, 34.60, 55.94, 62.02, 64.64, 68.93, 70.52, 71.89, 100.02, 169.93, 170.17, 170.37, 170.40, 170.66. FAB-MS *m/z* (%): 403 (M^+-1, 3.2), 373 (100), 313 (12), 271 (11), 211 (17), 193 (25), 154 (25), 136 (32). HR-MS (FAB) Calcd for $C_{18}H_{27}O_{10}$ (M^+-1): 403.1604. Found: 403.1636.

[2*S*,3*R*,4*S*,5*S*,6*S*,6(2*S*)]-2-Allyl-6-(2,3-diacetoxypropyl)-3,5-di-(*tert*-butyldimethylsilyloxy)-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran (46) AllylTMS (15.7 μml, 99 μmol) and TMSOTf (9.6 μl, 50 μmol) were added successively to a stirred solution of **45** (4.4 mg, 10.9 μmol) in MeCN (0.5 ml) at 0 °C under argon. After 1.5 h at room temperature, the reaction mixture was quenched with saturated aqueous $NaHCO_3$, and extracted with Et_2O. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 1 : 1) to give **42** (1.9 mg, 42%) and **46** (2.1 mg, 47%) as colorless oils. **46**: $[\alpha]_D^{28}$ −83.5° (*c* = 0.23, $CHCl_3$). IR ($CHCl_3$) cm^{-1}: 3030, 2950, 2930, 1740, 1380, 1240, 1030. ^{1}H-NMR ($CDCl_3$) δ: 0.91 (d, 3H, *J* = 6.5 Hz), 1.75 (m, 1H), 1.90—2.33 (m, 4H), 2.07 (s, 9H), 2.08 (s, 3H), 3.66 (m, 1H), 4.10—4.30 (m, 3H), 4.56 (dd, 1H, *J* = 10.0, 10.0 Hz), 4.75 (dd, 1H, *J* = 6.0, 11.0 Hz), 5.00—5.19 (m, 3H), 5.83 (m, 1H). ^{13}C-NMR ($CDCl_3$) δ: 13.77, 20.72, 20.90, 21.11, 25.86, 35.68, 36.53, 64.05, 68.67, 69.25, 70.42, 73.07, 74.40, 117.40, 133.73, 169.83, 166.99, 170.37, 170.57. FAB-MS *m/z* (%): 437 (M^+ + Na, 28), 415 (M^+ + 1, 72), 391 (18), 355 (100), 307 (22), 295 (49), 235 (25), 175 (40), 154 (100). HR-MS (FAB) Calcd for $C_{20}H_{31}O_9$ (M^+ + 1): 415.1968. Found: 415.1963.

[2*S*,3*S*,4*R*,5*S*,6*S*,6(2*S*)]-2-Allyl-3,5-bis-*tert*-butyldimethylsilyloxy-6-(2,3-isopropylidenedioxypropyl)-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran (48) K_2CO_3 (138.5 mg, 1.0 mmol) was added to a stirred solution of **40** (280 mg, 0.5 mmol) in MeOH (3 ml) at room temperature. After 30 min, the reaction mixture was diluted with H_2O, and extracted with CH_2Cl_2. The extract was washed with brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residual diol was subjected to the next reaction without purification.

2,2-Dimethoxypropane (104 mg, 3.92 mmol) and CSA (20 mg) were added to a stirred solution of the above diol in benzene (5 ml) at room temperature. After 10 min, saturated aqueous $NaHCO_3$ was added, and the mixture was extracted with Et_2O. The extract was washed with brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 5 : 1) to give **48** as a colorless oil (253 mg, 98%). $[\alpha]_D^{21}$ −68.8° (*c* = 0.16, $CHCl_3$). IR (neat) cm^{-1}: 2970, 2950, 2920, 2870. ^{1}H-NMR ($CDCl_3$) δ: 0.03 (s, 3H), 0.05 (s, 3H), 0.08 (s, 3H), 0.09 (s, 3H), 0.89 (s, 9H), 0.90 (s, 9H), 1.00 (d, 3H, *J* = 6.5 Hz), 1.35 (s, 3H), 1.40 (s, 3H), 1.60—1.69 (m, 1H), 1.73 (ddd, 1H, *J* = 3.0, 9.0, 14.5 Hz), 1.91—2.00 (m, 1H), 2.28 (ddd, 1H, *J* = 4.5, 11.5, 14.5 Hz), 2.52—2.60 (m, 1H), 2.97 (t, 1H, *J* = 9.5 Hz), 3.40 (dt, 1H, *J* = 2.5, 9.5 Hz), 3.44 (d, 1H, *J* = 6.0, 11.0 Hz), 3.45 (d, 1H, *J* = 10.5 Hz), 3.55 (t, 1H, *J* = 7.5 Hz), 3.74 (ddd, 1H, *J* = 3.0, 6.0, 11.5 Hz), 4.06 (dd, 1H, *J* = 5.5, 8.0 Hz), 4.18—4.26 (m, 1H), 5.01—5.10 (m, 2H), 5.78—5.9 (m, 1H). ^{13}C-NMR ($CDCl_3$) δ: −4.84, −4.09, −3.25, −3.02, 15.34, 18.02, 18.34, 25.82, 26.10, 26.93, 27.65, 37.13, 40.78, 69.13, 73.04, 73.10, 73.50, 73.78, 76.61, 108.52, 116.50, 135.55. FAB-MS *m/z* (%): 513 (M^+-1, 5.4), 512 (7.6), 457 (10), 399 (9.9), 315 (36), 225 (53), 147 (100). HR-MS (FAB) Calcd for $C_{27}H_{53}O_5Si_2$ (M^+ + H − 2): 513.3434. Found: 513.3403.

[2*S*,3*S*,4*R*,5*S*,6*S*,6(2*S*)]-3,5-Bis-*tert*-butyldimethylsilyloxy-2-formylmethyl-6-(2,3-isopropylidenedioxypropyl)-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran (4) NMO (426 mg, 3.15 mmol) and a solution of OsO_4 (80 mg, 0.315 mmol) in *tert*-BuOH (2 ml) were added to a stirred solution of **48** (541 mg, 1.05 mmol) in a 10 : 1 mixture of H_2O and acetone (6 ml) at room temperature. After 2 h, Celite (2 g) and aqueous $Na_2S_2O_4$ (10 ml) were added, and stirring was continued for 30 min. The mixture was filtered, and the filtrate was extracted with Et_2O. The extract was washed with brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residual oil (545 mg, 94%) was dissolved in THF (5.5 ml) and stirred. To this solution, a solution of $NaClO_2$ (1.06 g, 4.95 mmol) in H_2O (3.5 ml) and MeOH (5 ml) were added at room temperature. After 2 h, H_2O was added, and the mixture was extracted with Et_2O. The extract was washed with brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 5 : 1) to give **4** as colorless crystals (502 mg, 98%), mp 68—69.6 °C. $[\alpha]_D^{29}$ −41.2° (*c* = 0.068, $CHCl_3$). IR (neat) cm^{-1}: 2975, 2950, 2800, 2875, 1735. ^{1}H-NMR ($CDCl_3$) δ: 0.03 (s, 3H), 0.07 (s, 6H), 0.09 (s, 3H), 0.88 (s, 9H), 0.89 (s, 9H), 1.02 (d, 3H, *J* = 7.0 Hz), 1.35 (s, 3H), 1.39 (s, 3H), 1.71 (ddd, 1H, *J* = 7.0, 9.5, 10.5 Hz), 1.80 (ddd, 1H, *J* = 3.0, 7.0, 15.0 Hz), 2.25 (ddd, 1H, *J* = 6.0, 11.5, 15.0 Hz), 2.30 (ddd, 1H, *J* = 4.0, 10.0, 15.0 Hz), 2.74 (ddd, 1H, *J* = 1.0, 1.5, 15.0 Hz), 3.03 (t, 1H, *J* = 9.5 Hz), 3.46 (dd, 1H, *J* = 6.0, 10.5 Hz), 3.51 (t, 1H, *J* = 8.0 Hz), 3.96 (dt, 1H, *J* = 2.5, 9.5 Hz), 3.76 (ddd, 1H, *J* = 3.0, 6.0, 11.5 Hz), 4.04 (dd, 1H, *J* = 5.5, 8.0 Hz), 4.21 (ddd, 1H, *J* = 6.0, 7.5, 12.5 Hz), 9.74 (dd, 1H, *J* = 1.5, 3.0 Hz). ^{13}C-NMR ($CDCl_3$) δ: −4.70, −3.90, −3.05, 15.27, 15.73, 15.84, 25.76, 25.83, 27.05, 27.80, 41.00, 46.95, 69.10, 69.25, 72.55, 73.63, 74.56, 75.80, 118.50, 201.50. FAB-MS *m/z* (%): 501 (M^+-14, 3.5), 401 (6.4), 327 (4.2), 269 (22), 225 (17), 171 (22), 101 (49), 73 (100). HR-MS (FAB) Calcd for $C_{25}H_{49}O_6Si_2$ (M^+-15): 501.3070. Found: 501.3103. *Anal.* Calcd for $C_{26}H_{52}O_6Si_2$: C, 60.42; H, 10.14. Found: C, 60.37; H, 10.06.

[2*S*,3*R*,4*S*,5*S*,6*S*,6(2*S*)]-2-Allyl-3,5-di-(*tert*-butyldimethylsilyloxy)-6-[2,3-(4-methoxybenzylidenedioxy)propyl]-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran (49) K_2CO_3 (13.3 mg, 96 μmol) was added to a stirred solution of **40** (27 mg, 48 μmol) in MeOH (0.5 ml) at room temperature. After 30 min, the reaction mixture was diluted with H_2O, and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, and evaporated *in vacuo* to leave a crude diol as a colorless oil (21.5 mg). ^{1}H-NMR ($CDCl_3$) δ: 0.02 (s, 3H), 0.06 (s, 3H), 0.08 (s, 3H), 0.09 (s, 3H), 0.87 (s, 9H), 0.90 (s, 9H), 1.00 (d, 3H, *J* = 6.5 Hz), 1.59—1.71 (m, 2H), 1.90 —2.02 (m, 2H), 2.21 (dd, 1H, *J* = 6.0, 6.0 Hz), 2.62 (m, 1H), 2.99 (dd, 1H, *J* = 9.5, 9.5 Hz), 3.23 (d, 1H, *J* = 1.5 Hz), 3.43 (dd, 1H *J* = 6.0, 10.5 Hz), 3.46—3.54 (m, 2H), 3.62 (m, 1H), 3.90 (m, 1H), 4.01 (m, 1H), 5.09—5.15 (m, 2H), 5.79 (m, 1H).

p-Anisaldehyde dimethylacetal (12.4 mg, 68 μmol) and CSA (2 mg) were added to a stirred solution of the diol (21.5 mg) in benzene (0.5 ml) at room temperature. After 2 h, Et_3N (0.1 ml) was added, and the mixture was stirred for 10 min, then quenched with saturated aqueous $NaHCO_3$, and extracted with Et_2O. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 10 : 1) to give **49** as a colorless oil (24 mg, 84%). IR (neat) cm^{-1}: 2970, 2950, 2870, 1620, 1520, 1480, 1470, 1395, 1365, 1310, 1260, 1180, 1100. ^{1}H-NMR ($CDCl_3$) δ: 0.03 (s, 3H), 0.07 (s, 3H), 0.09 (s, 3H), 0.10 (s, 3H), 0.91 (s, 18H), 1.02 (d, 3H, *J* = 6.5 Hz), 1.69 (m, 1H), 1.85 (ddd, 1H, *J* = 3.0, 9.0, 14.5 Hz), 1.96 (ddd, 1H, *J* = 7.0, 7.0, 14.5), 2.37 (ddd, 1H, *J* = 4.5, 12.0, 14.5 Hz), 2.57 (dd, 1H, *J* = 6.0, 14.0 Hz), 2.99 (dd, 1H, *J* = 9.5, 9.5 Hz), 3.41 (ddd, 1H, *J* = 2.0, 9.5, 9.5 Hz), 3.48 (dd, 1H, *J* = 6.0, 10.5 Hz), 3.66 (dd, 1H, *J* = 7.5, 7.5 Hz), 3.79—3.85 (m, 1H), 3.81 (s, 3H), 4.30 (dd, 1H, *J* = 6.0, 7.5 Hz), 4.36 (m, 1H), 4.97—5.09 (m, 2H), 5.81 (m, 1H), 5.90 (s, 1H), 6.88—6.91 (m, 2H), 7.39—7.42 (m, 2H).

[2*S*,3*R*,4*S*,5*S*,6*S*,6(2*S*)]-2-Allyl-6-[3-Hydroxy-2-(4-methoxybenzyloxy)-propyl]-3,5-di-(*tert*-butyldimethylsilyloxy)-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran (50) and [2*S*,3*R*,4*S*,5*S*,6*S*,6(2*S*)]-2-Allyl-6-[2-hydroxy-3-(4-methoxybenzyloxy)propyl]-3,5-di-(*tert*-butyldimethylsilyl-oxy)-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran (51) A 0.93 M solution of DIBAH in *n*-hexane (1.28 ml, 1.19 mmol) was added portionwise to a stirred solution of **49** (202 mg, 0.341 mmol) in CH_2Cl_2 (5.5 ml) at −78 °C under argon. After 1 h, MeOH was added dropwise to decompose excess DIBAH, then saturated aqueous Rochelle salt and Et_2O were added. The mixture was stirred for 30 min at room temperature, and extracted with Et_2O. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 5 : 1) to give **50** (105 mg, 52%) and **51** (40 mg, 20%) as colorless oils. **50**: $[\alpha]_D^{22}$ −53.9° (*c* = 0.31, $CHCl_3$). IR (neat) cm^{-1}: 3440, 2970, 2950, 2875, 1620, 1520, 1480, 1470, 1370, 1260, 1110, 1080. ^{1}H-NMR ($CDCl_3$) δ: 0.03 (s, 3H), 0.05 (s, 3H), 0.09 (s, 3H), 0.10 (s, 3H), 0.88 (s, 9H), 0.92 (s, 9H), 1.01 (d, 3H, *J* = 6.5 Hz), 1.67 (m, 1H), 1.81 (ddd, 1H, *J* = 2.5, 9.5, 14.5 Hz), 1.96 (m, 1H), 2.08—2.17 (m, 2H), 2.53 (m, 1H), 2.98 (dd, 1H, *J* = 9.5, 9.5 Hz), 3.30 (ddd, 1H, *J* = 2.5, 9.5, 9.5 Hz), 3.46 (dd, 1H, *J* = 6.0, 10.5 Hz), 3.55 (dd, 1H, *J* = 5.0, 10.0 Hz), 3.63 (ddd, 1H, *J* = 2.5, 5.0, 10.0 Hz), 3.73—3.79 (m, 1H), 3.80 (s, 3H), 3.87 (ddd, 1H, *J* = 2.5, 6.0, 12.0 Hz), 4.46 (d, 1H, *J* = 11.0 Hz), 4.57 (d, 1H, *J* = 11.0 Hz), 4.99—5.08 (m, 2H), 5.73 (m, 1H), 6.86—6.90 (m, 2H), 7.26—7.29 (m, 2H). ^{13}C-NMR ($CDCl_3$) δ: −4.94, −4.15, −3.25, −3.02, 15.40, 17.96, 18.34, 24.51, 25.82, 26.12, 37.11, 40.73, 53.40, 55.27, 63.28, 70.81, 72.81, 72.92, 73.19, 76.24, 76.56, 113.90, 116.84, 129.30, 130.52, 135.41, 159.29. **51**: $[\alpha]_D^{22}$ −30.7° (*c* = 0.068, $CHCl_3$). IR (neat) cm^{-1}: 3530, 2950, 2870, 1620, 1520, 1480, 1470, 1365, 1260, 1080. ^{1}H-NMR ($CDCl_3$) δ: 0.01 (s, 3H), 0.05 (s, 3H), 0.08 (s, 3H), 0.09 (s, 3H), 0.86 (s, 9H), 0.90 (s, 9H), 1.10 (d, 3H, *J* = 6.5 Hz), 1.65 (m, 1H), 1.81 (ddd, 1H, *J* = 2.5, 4.5, 14.5 Hz), 1.89—2.22 (m, 2H), 2.60 (m, 1H), 2.94 (d, 1H, *J* = 2.5 Hz), 2.98 (dd, 1H, *J* = 9.5, 9.5 Hz), 3.40—3.52 (m, 4H), 3.80 (s, 3H), 3.92—4.02 (m, 2H), 4.49 (s, 2H), 5.06—5.13 (m, 2H), 5.80 (m, 1H), 6.84—6.88 (m, 2H), 7.23—7.27 (m, 2H). ^{13}C-NMR ($CDCl_3$) δ: −4.88, −4.21, −3.29, −3.04, 15.36, 17.98, 18.31, 25.81,

26.08, 27.01, 37.38, 40.80, 55.29, 70.89, 72.86, 72.95, 73.03, 73.72, 76.56, 76.72, 113.75, 117.68, 129.30, 130.38, 135.15, 159.18.

[2*S*,3*R*,4*S*,5*S*,6*S*,6(2*S*)]-2-Allyl-3,5-di-(*tert*-butyldimethylsilyloxy)-6-[2-(4-methoxybenzyloxy)-3-propanal]-4-methyl-3,4,5,6-tetrahydro-2*H*-pyran (6) The Dess–Martin reagent (31 mg, 73 μmol) was added to a stirred solution of **50** (17.3 mg, 29 μmol) in CH_2Cl_2 (1 ml) at room temperature under argon. After 20 min, saturated aqueous $Na_2S_2O_3$ was added, and stirring was continued for 10 min. The reaction mixture was diluted with saturated aqueous $NaHCO_3$, and extracted with Et_2O. The extract was dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 5 : 1) to give **6** as a colorless oil (12.4 mg, 72%), which was immediately subjected to the next reaction. ^{1}H-NMR ($CDCl_3$) δ: 0.02 (s, 3H), 0.05 (s, 3H), 0.08 (s, 3H), 0.09 (s, 3H), 0.88 (s, 9H), 0.90 (s, 9H), 0.99 (d, 3H, J=6.5 Hz), 1.59 (m, 1H), 1.97—2.10 (m, 2H), 2.20 (ddd, 1H, J=3.0, 12.0, 15.0 Hz), 2.46 (m, 1H), 2.99 (dd, 1H, J=9.5, 9.5 Hz), 3.19 (ddd, 1H, J=2.5, 9.5, 9.5 Hz), 3.44 (dd, 1H, J=6.0, 10.5 Hz), 3.80 (s, 3H), 3.87 (ddd, 1H, J=2.0, 2.0, 7.5 Hz), 4.10 (ddd, 1H, J=2.0, 6.0, 13.5 Hz), 4.52 (d, 1H, J=11.5 Hz), 4.58 (d, 1H, J=11.5 Hz), 5.00—5.06 (m, 2H), 5.75 (m, 1H), 6.86—6.89 (m, 2H), 7.25—7.31 (m, 2H), 9.69 (d, 1H, J=2.0 Hz).

References and Notes

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