Synthetic Studies of Halichondrin B, an Antitumor Polyether Macrolide Isolated from a Marine Sponge. 6. Synthesis of the C1—C15 Unit *via* Stereoselective Construction of the B and A Rings by Kinetically and Thermodynamically Controlled Michael Reactions with the Aid of Computational Search for Dominant Conformers[1)]

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The C1—C15 unit of halichondrin B was synthesized starting from D-glucose *via* stereoselective construction of the B and A rings, which have 2,6-*trans*- and 2,6-*cis*-disubstituted tetrahydropyran rings, respectively. With the aid of MM2 calculations kinetically and thermodynamically controlled Michael reactions were successfully applied for the construction of the B and A rings, respectively.

Key words Michael reaction; MM2 calculation; conformation; stereoselective synthesis; tetrahydropyran; polyether macrolide

Halichondrin B (1), isolated from a marine sponge, *Halichondria okadai* KADOTA, by Uemura *et al.* in 1985,[2)] is the most active member of the antitumor polyether macrolides in the halichondrin family, and the total synthesis of **1** was achieved by Kishi *et al.* in 1992.[3)] Our continuing interest in the synthesis of polyketide-derived natural products such as typical macrolide and polyether antibiotics[4)] has led to synthetic studies of **1**, and our original synthetic plan consisted of the synthesis and condensation of four units, **2**, **3**, **4** and **5** (Fig. 1). Recently, synthetic studies of these units were published in preliminary form.[1,4b,5)] In this report, we describe the synthesis of the C1—C15 unit (**6**) which is a synthetic equivalent of **2**.[1)] Three precedents for the synthesis of C1—C15 units corresponding to **2** exist.[6—8)] For the synthesis of **6**, stereoselective construction of the three rings A, B and C is, of course, most important, and we planned to synthesize first the C ring starting from D-glucose and then to build up the B and A rings in that order by means of intramolecular Michael reactions. Particular attention was, however, required in order to construct appropriately two different types of rings, the 2,6-*trans*-disubstituted tetrahydro-2*H*-pyran (B) ring and the 2,6-*cis* (A) ring by the same method of cyclization. Therefore we decided to synthesize first the C1—C13 fragment (**7**) in order to establish suitable synthetic conditions for the A and B rings. A retrosynthesis of **7** is shown in Chart 1.

Synthesis of the C1—C13 Fragment (7) As a starting material we chose **13**, which was readily synthesized from D-glucose *via* diacetoneglucose (**12**), in order to use the four consecutive chiral centers of D-glucose at C2—C5 as the C9—C12 chiral centers of **1**, although it is necessary to invert the configuration at the C11 position at a suitable synthetic stage.[9)] Four conventional reaction steps, benzylation, selective hydrolysis, benzoylation and hydrolysis, readily gave **13** from **12**. Conversion of **13** to **14** through opening of the pyranose ring with 1,3-propanedithiol was examined in the presence of various Lewis acids in several solvents, and zinc chloride in acetonitrile at 60 °C gave a reasonable result; the yield of **14** was 63%. Treatment of the triol (**14**) with 4-methoxybenzaldehyde dimethyl acetal in the presence of *dl*-camphorsulfonic acid (CSA) gave only a thermodynamically stable 1,3-dioxane compound, and then the remaining C12 hydroxy group was mesylated to give **15**, which was readily converted to the epoxide (**11**), a precursor for the construction of the C ring, by removal of the benzoyl protecting group, followed by treatment with potassium *tert*-butoxide in tetrahydrofuran (THF).

When **11** was treated with 80% aqueous acetic acid in dichloromethane at room temperature for 4 d, hydrolysis of the 4-methoxybenzylidene (MP) protection and subsequent 5-*exo* cyclization[10)] by the attack of the C9 hydroxy group at the C12 position proceeded slowly to give the expected tetrahydrofuran derivative, which was treated with trityl chloride in the presence of 4-dimethylaminopyridine (DMAP) and triethylamine to protect the resulting primary hydroxy group at C13, and **16** was isolated in good yield. The configuration at C12 was confirmed by the nuclear Overhauser effect (NOE) correlation observed between the C9 and C12 protons. After protection of the C11 secondary hydroxy group with a 4-methoxybenzyl (MPM) group to give **17**, removal of the dithioacetal protection was examined under various conditions, but many usual methods[11)] gave very poor results. Only Vedejs' procedure[12)] provided the expected aldehyde in satisfactory yield. However, after the next Horner–Emmons reaction we observed loss of about one-third of the trityl protecting group, which was therefore replaced by a *tert*-butyldiphenylsilyl (TBDPS) group prior to removal of the dithioacetal protection of **17**.

Treatment of **17** with CSA in methanol at room temperature and protection of the resulting primary hydroxy group with a TBDPS group under usual conditions gave **18** in almost quantitative yield. When **18** was warmed with

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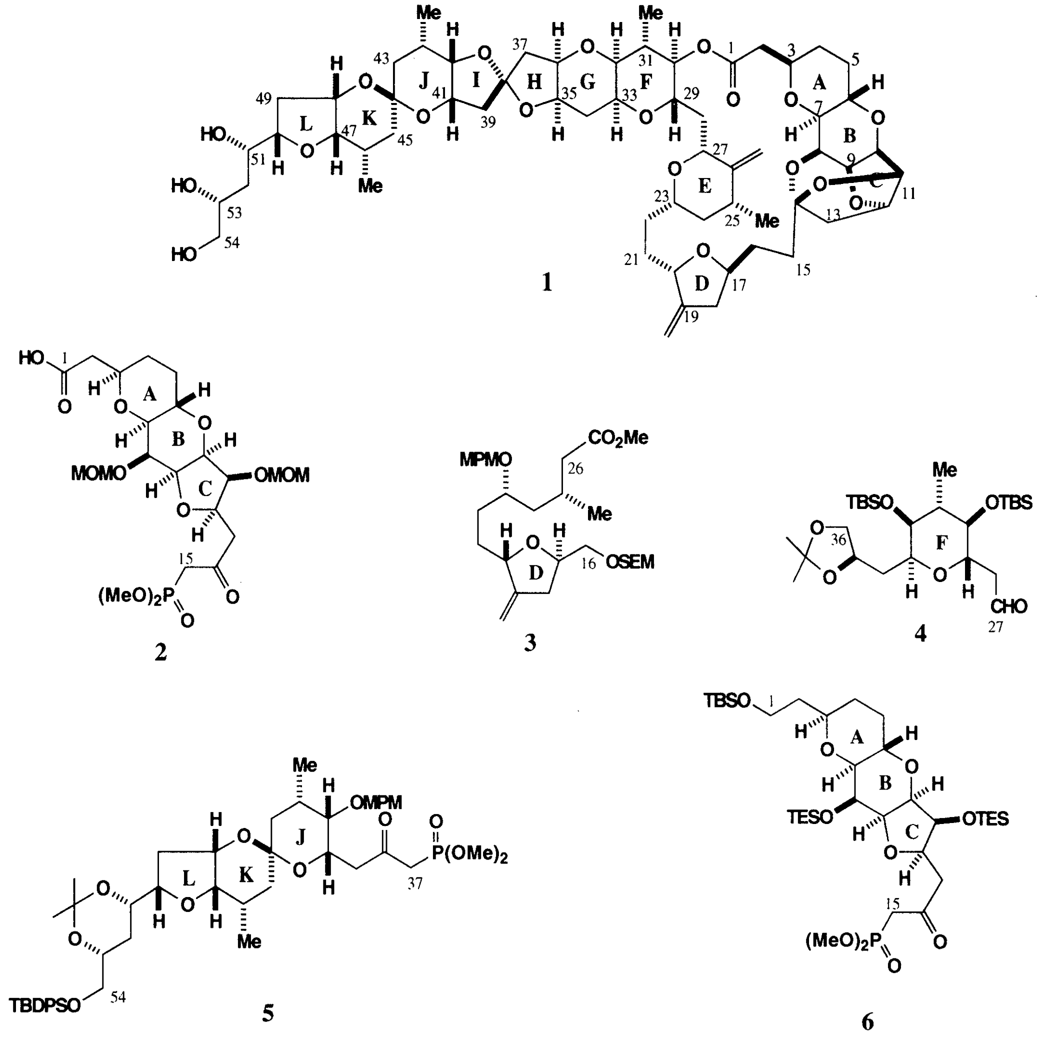


Fig. 1.

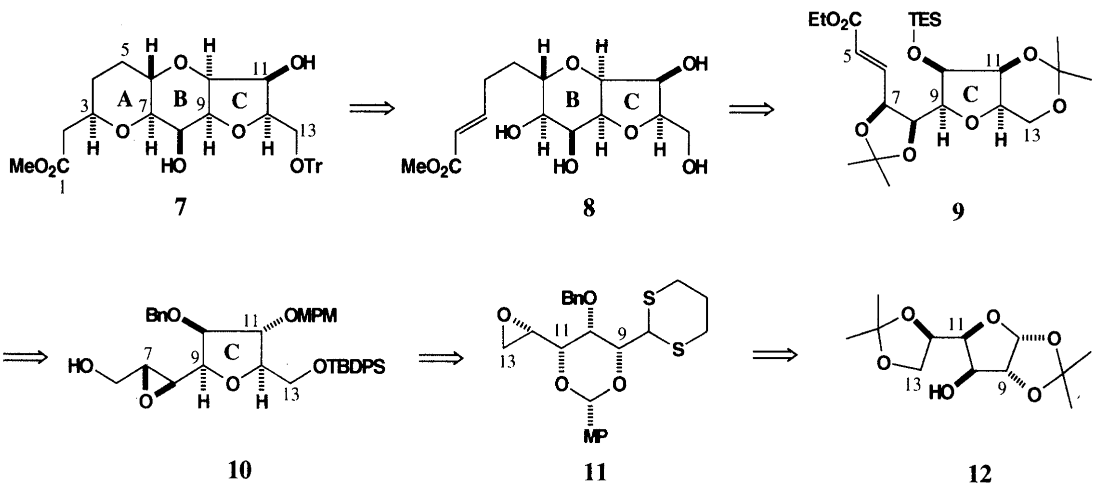
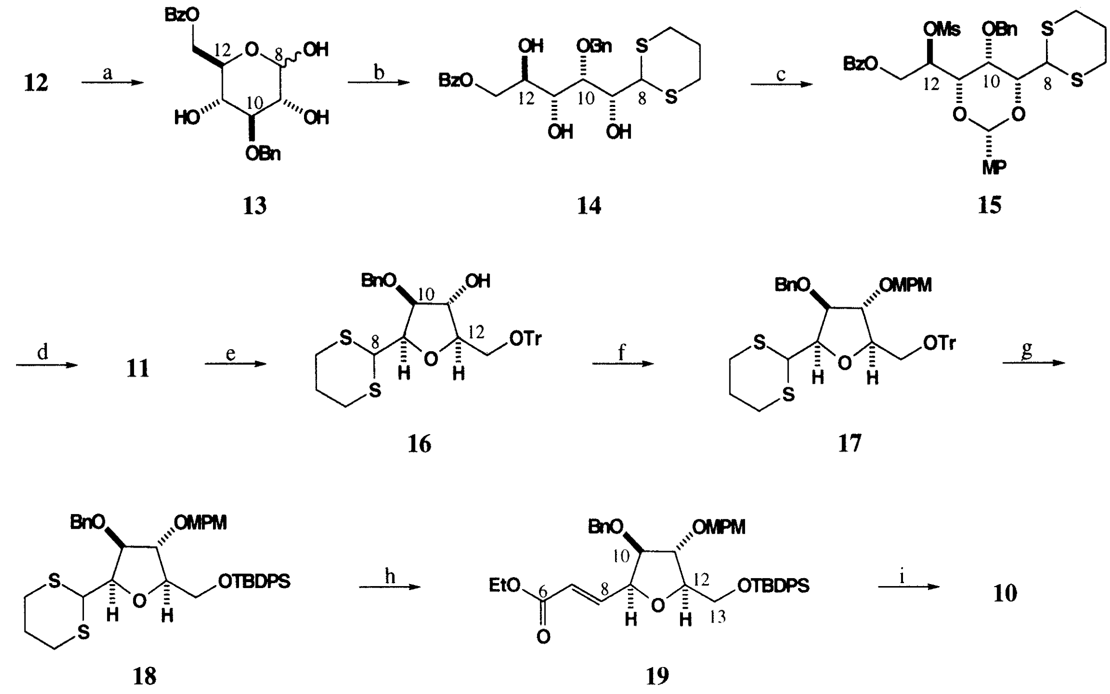


Chart 1

red mercuric oxide and boron trifluoride etherate in THF–water under vigorous stirring, deprotection of the dithioacetal group proceeded quite smoothly to give the aldehyde, which was immediately subjected to the Horner–Emmons reaction with ethyl diisopropoxyphosphonoacetate, and the expected α,β-(*E*)-unsaturated ester (**19**) was selectively obtained in excellent yield. Reduction of the ester group of **19** with diisobutylaluminum hydride (DIBAH) and the subsequent Sharpless asymmetric epoxidation[13] readily gave **10**.

Opening of the epoxide ring of **10** to obtain the triol (**21**) *via* a carbonate proceeded well only by Roush's method.[14] Treatment of **10** with phenyl isocyanate gave the urethane, which we attempted to derive to the carbonate (**20**). When the urethane was treated with 5% perchloric acid in acetonitrile,[15] **20** was isolated in only



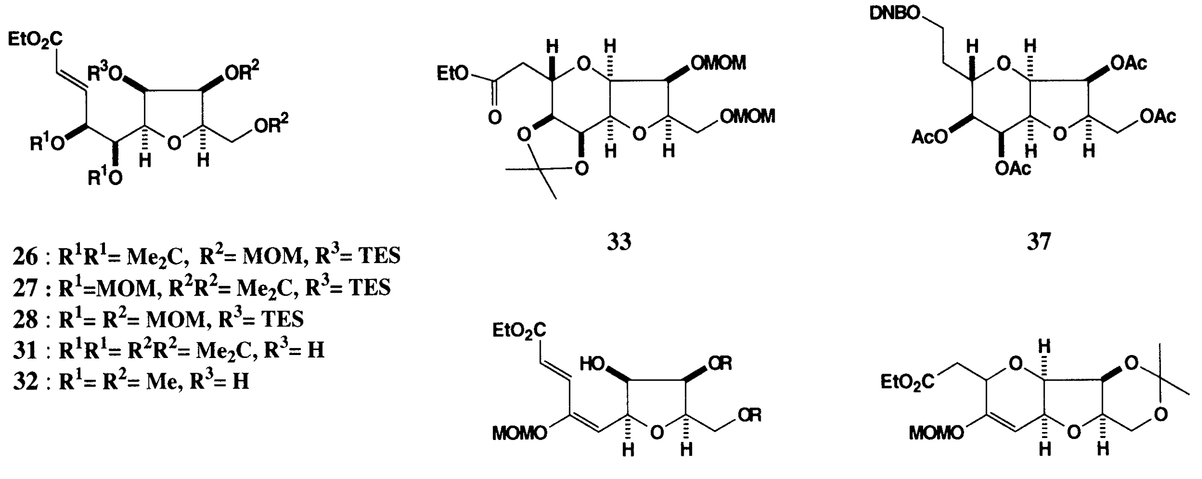
(a) 1) BnCl, NaH, THF-DMSO, rt; 2) 0.8 N-H_2SO_4, MeOH, rt; 3) BzCl, pyridine, CH_2Cl_2, 0 °C; 4) 6N-HCl, THF, reflux (4 steps 66 %). (b) $HS(CH_2)_3SH$, $ZnCl_2$, MeCN, 60 °C (63 %). (c) 1) $MPCH(OMe)_2$, CSA, CH_2Cl_2, rt; 2) MsCl, Et_3N, CH_2Cl_2, 0 °C (2 steps 85 %). (d) 1) K_2CO_3, MeOH-CH_2Cl_2, 0 °C; 2) *t*-BuOK, THF, rt (2 steps 85 %). (e) 1) 80 % AcOH-CH_2Cl_2, rt (84 %); 2) TrCl, DMAP, Et_3N, CH_2Cl_2 (94 %). (f) MPMCl, NaH, THF-DMSO, rt (88 %). (g) 1) CSA, MeOH-CH_2Cl_2, rt; 2) TBDPSCl, imidazole, CH_2Cl_2, rt (2 steps 93 %). (h) 1) HgO, $BF_3 \cdot Et_2O$, THF-H_2O, 60 °C; 2) (*i*-PrO)$_2$P(O)CH_2CO_2Et, *t*-BuOK, THF, -78 °C (2 steps 91 %). (i) 1) DIBAH, CH_2Cl_2, -78 °C (95 %); 2) (-)-DET, (*i*-PrO)$_4$Ti, TBHP, MS, CH_2Cl_2, -20 °C (89 %).

Chart 2

4.6% yield and most of the starting material was decomposed. Boron trifluoride etherate in dichloromethane[14)] gave a similar poor result, but when diethyl ether was used instead of dichloromethane at 0 °C, a smooth reaction occurred to give **20** in good yield. The carbonate (**20**) was then readily hydrolyzed to the triol (**21**).

Conversion of **21** into **9**, which was designed as the most promising substrate for the stereoselective construction of the B ring with the aid of CONFLEX-MM2 calculations (*vide infra*), required 13 conventional steps consisting of inversion of the C11 hydroxy group, exchange of all protecting groups and an extension of two carbon units, and all the steps proceeded without any difficulties. The primary alcohol of **21** was protected with a pivaloyl group and the remaining vicinal diol was converted to an acetonide to give **22**. At this stage the C11 hydroxy group was inverted from the α-configuration to β. The MPM group was removed with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ),[16)] the resulting alcohol was oxidized under Swern's conditions and then carefully reduced with sodium borohydride at −78 °C so as to avoid epimerization at the C10 or C12 position, because all the substituents of the C ring are on one side (β). Hydride reduction from the less-hindered side occurred selectively to give the C11 β-hydroxy compound (**23**), which was confirmed by NOE measurements. Removal of the TBDPS group with tetra-*n*-butylammonium fluoride (TBAF), protection of the resulting diol as an acetonide and then treatment with sodium in liquid ammonia gave **24**, which was easily converted to **25**. Reduction with DIBAH and the subsequent Swern oxidation followed by the Horner–Emmons reaction gave **9**, the expected substrate for the construction of the B-ring. Similarly, **26**, **27** and **28** were synthesized starting from **21**.

The expected product of the intramolecular Michael reaction of **9** to construct the B ring was **29** with a 2,6-*trans*-disubstituted tetrahydropyran ring, which is generally less stable thermodynamically than the corresponding *cis*-isomer (**30**). Molecular mechanics calculations using CONFLEX-MM2[17)] and Macro Model[18)] on an INDIGO computer indicated that **29** was 2.48 and 2.0 kcal/mol, respectively, less stable than **30**, and hence in order to synthesize selectively the *trans*-isomer (**29**) the construction of the B ring had to be conducted under kinetically controlled conditions. For this purpose, we required a substrate which would favor *trans*-cyclization by conformational control of the α,β-unsaturated ester side chain of the substrate; alternatively it might be possible to fix the conformation of the side chain in a favorable form for the *trans*-cyclization. Protection of the C7 and C8 vicinal hydroxy groups as a five-membered acetonide rather than as separate ethers was expected to be suitable for this purpose. This idea was supported by calculation. The most stable conformers of the substrates for the Michael cyclization, **31** and **32** (calculation model for **28**),



26 : R^1R^1= Me_2C, R^2= MOM, R^3= TES
27 : R^1=MOM, R^2R^2= Me_2C, R^3= TES
28 : R^1= R^2= MOM, R^3= TES
31 : R^1R^1= R^2R^2= Me_2C, R^3= H
32 : R^1= R^2= Me, R^3= H

33

37

34 : RR= Me_2C
36 : R= MOM

35

Fig. 2.

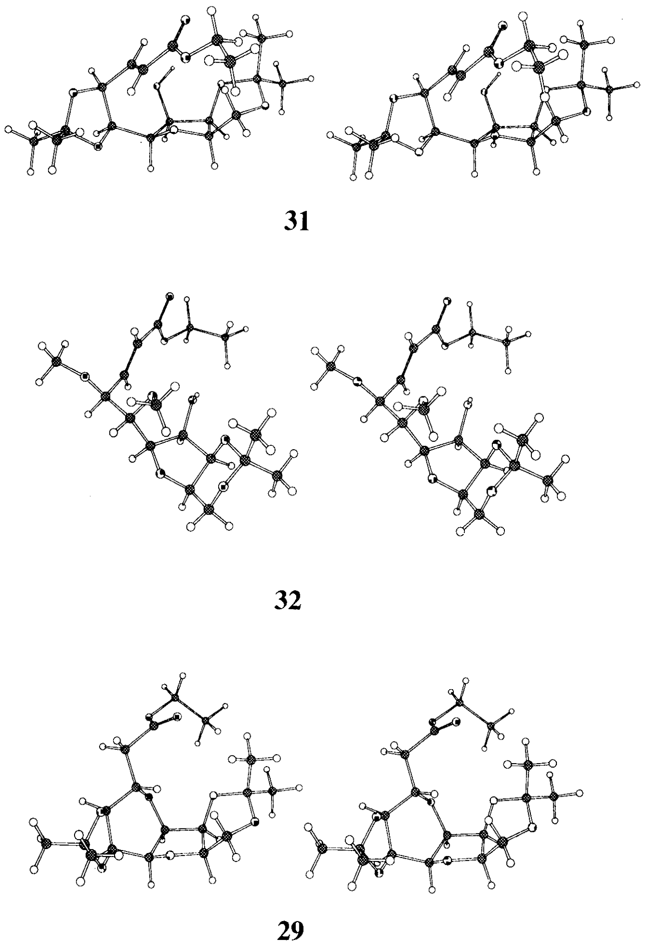


Fig. 3. Stereoviews of the Most Stable Conformers of **31**, **32** and **29**

Table 1. Construction of the B Ring (TBAF, THF, rt)

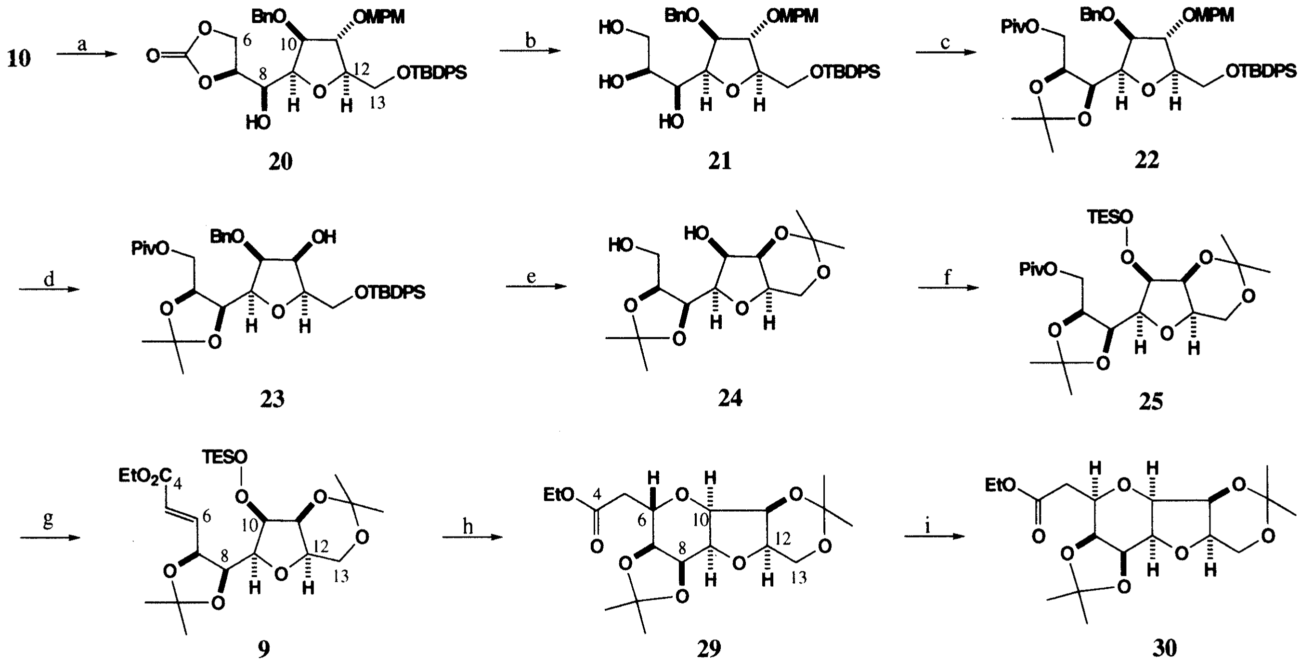
Entry	Substrate	Time (h)	Product	Yield (%)
1	**9**	1.0	**29**	96
2	**26**	1.0	**33**	96
3	**27**	3.0	**34**	44
			35	17
4	**28**	3.0	**36**	71

and the cyclization product (**29**) are shown in Fig. 3. The distance between C6 and C10 oxygen in most of the conformers of **31** (88% population) is less than 3.8 Å, whereas that in **32** (77% population) is more than 4.0 Å and in addition, the C8 ether group appears to hinder the cyclization.

When **9** was treated with TBAF in THF to remove the triethylsilyl (TES) protecting group at room temperature for 1 h, the cyclization proceeded quite smoothly to give only the expected product (**29**) in excellent yield (Table 1, Entry 1). The unsaturated ester (**26**) similarly gave **33**, though **27** and **28** produced only side reaction products such as **34**, **35** and **36**. The structure of **29** was confirmed after its transformation to **37**, that is, an NOE correlation was observed between the C5 and C8 protons. As described above, **29** was calculated to be less stable than its C6 isomer (**30**). In fact, treatment of **29** with potassium *tert*-butoxide at −78 °C resulted in a smooth isomerization to **30**.

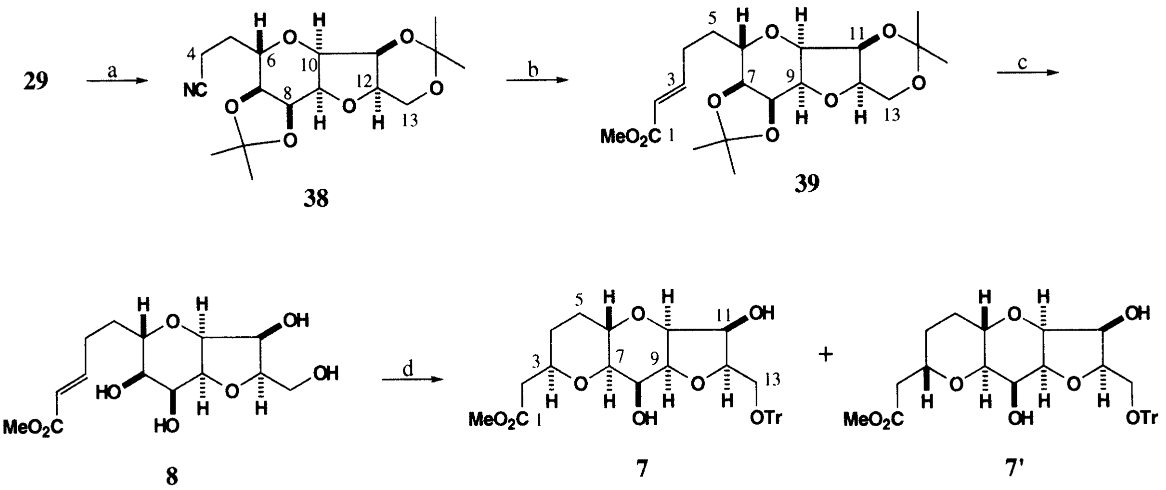
Next, **29** was converted to **8**, which is a substrate for the construction of the A ring with a thermodynamically stable 2,6-*cis*-disubstituted tetrahydropyran. Reduction of **29** with lithium aluminum hydride and conversion of the resulting alcohol to a tosylate followed by treatment with sodium cyanide readily gave the cyanide (**38**), which was reduced with DIBAH, and the resulting aldehyde was subjected to the Wittig reaction to give the α,β-unsaturated ester (**39**) in 91% overall yield for the five steps. Hydrolysis of the acetonide groups with CSA in methanol gave **8**, the substrate for the A ring construction.

Because of its thermodynamic stability, the A ring was expected to be constructed easily. Treatment of **8** with TBAF in THF at room temperature for 10 h, however, unexpectedly gave a 2 : 1 mixture of 2,3-*cis*- and *trans*-disubstituted tetrahydropyran derivatives, whose structures were confirmed after conversion to the trityl derivative (**7**) and its C3 epimer (**7′**). No improvement was obtained by the use of other solvents such as benzene and acetonitrile. Fortunately retreatment of the mixture of **7** and **7′** with TBAF in THF for 15 h resulted in a change of the ratio from 2 : 1 to 19 : 1. The stereoselective



(a) 1) PhNCO, Et_3N, CH_2Cl_2, rt; 2) $BF_3 \cdot Et_2O$, Et_2O, 0 °C (2 steps 85 %). (b) K_2CO_3, MeOH, rt (96 %). (c) 1) PivCl, DMAP, Et_3N, CH_2Cl_2, 0 °C; 2) $CH_2=CH(OMe)Me$, PPTS, CH_2Cl_2, rt (2 steps 64 %). (d) 1) DDQ, CH_2Cl_2-buffer, rt; 2) Swern oxid., -78 °C; 3) $NaBH_4$, THF-MeOH, -78 °C (3 steps 77 %). (e) 1) TBAF, THF, rt; 2) $CH_2=CH(OMe)Me$, TsOH, CH_2Cl_2-benzene, rt; 3) Na, liqNH_3, THF, -78 °C (3 steps 89 %). (f) 1) PivCl, DMAP, CH_2Cl_2-pyridine, rt; 2) TESCl-imidazole, DMAP, DMF, rt (2 steps 81 %). (g) 1) DIBAH, CH_2Cl_2, -78 °C; 2) Swern oxid., -78 °C; 3) $(i\text{-}PrO)_2P(O)CH_2CO_2Et$, *t*-BuOK, THF, -78 °C (3 steps 77 %). (h) TBAF, THF, rt, 1 h (96 %). (i) *t*-BuOK, THF, -78 °C (69 %).

Chart 3

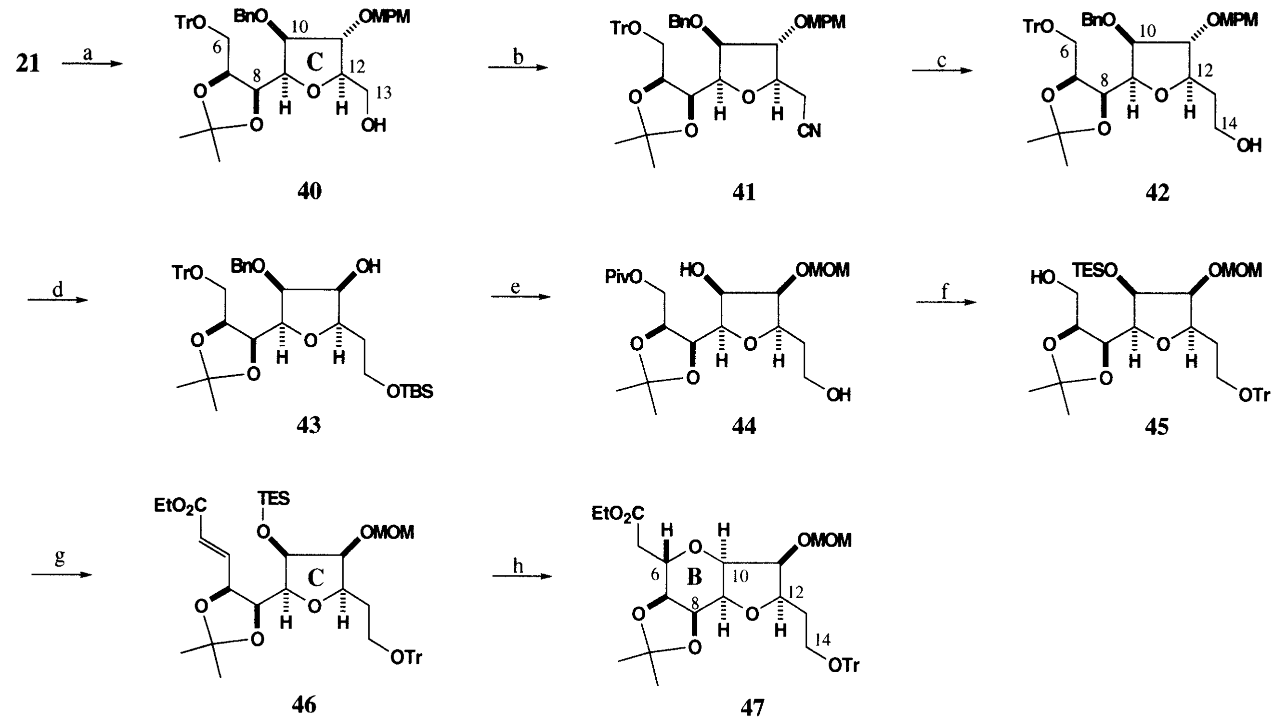


(a) 1) $LiAlH_4$, Et_2O, 0 °C; 2) TsCl, DMAP, Et_3N, CH_2Cl_2, rt; 3) NaCN, DMSO, 60 °C (3 steps 93 %). (b) 1) DIBAH, CH_2Cl_2, -78 °C; 2) $Ph_3P=CHCO_2Me$, CH_2Cl_2, rt (2 steps 98 %). (c) CSA, MeOH, rt (67 %). (d) 1) TBAF, THF, rt; 2) TrCl, DMAP, Et_3N, CH_2Cl_2, rt (2 steps 76 %); 3) TBAF, THF, rt (78 %).

Chart 4

construction of the A and B rings was thus established.

Synthesis of the C1—C15 Unit (6) As a synthetic equivalent to the C1—C15 unit (**2**) we decided to synthesize **6**, which would be obtainable from **7** by two carbon unit elongation. In order to reexamine the A and B ring construction, a series of homologous compounds was synthesized starting from **21**, which was first converted to **40** *via* three conventional steps, *i.e.*, tritylation of the primary alcohol, isopropylidene protection of the remaining diol and removal of the TBDPS protecting group. Tosylation of **40** and the subsequent treatment with sodium cyanide readily gave **41**. The cyano group of **41** was reduced with DIBAH, and the resulting crude aldehyde was immediately treated with sodium boro-



(a) 1) TrCl, DMAP, Et_3N, CH_2Cl_2, rt; 2) CH_2=CH(OMe)Me, PPTS, CH_2Cl_2, rt; 3) TBAF, THF, rt (3 steps 78 %). (b) 1) TsCl, DMAP, Et_3N, CH_2Cl_2, rt; 2) NaCN, DMSO, 80 °C (2 steps 92 %). (c) 1) DIBAH, CH_2Cl_2, -78 °C; 2) $NaBH_4$, THF-MeOH, rt (2 steps 73 %). (d) 1) TBSCl, imidazole, CH_2Cl_2, rt; 2) DDQ, CH_2Cl_2-buffer, rt; 3) Swern oxid.; 4) $NaBH_4$, THF-MeOH, -78 °C (4 steps 91 %). (e) 1) MOMCl, (*i*-Pr)$_2$NEt, DMAP, CH_2Cl_2, 40 °C; 2) Na, liq NH_3, THF, -78 °C; 3) PivCl, DMAP, pyridine, CH_2Cl_2, rt; 4) TBAF, THF, 0 °C (4 steps 87 %). (f) 1) TrCl, Et_3N, DMAP, CH_2Cl_2, rt; 2) TESCl, imidazole, DMAP, DMF, 40 °C; 3) DIBAH, CH_2Cl_2, -78 °C (3 steps 97 %). (g) 1) Swern oxid.; 2) (*i*-PrO)$_2$P(O)CH_2CO_2Et, *t*-BuOK, THF, -78 °C (2 steps 97 %). (h) TBAF, THF, 0 °C, 20 min (98 %).

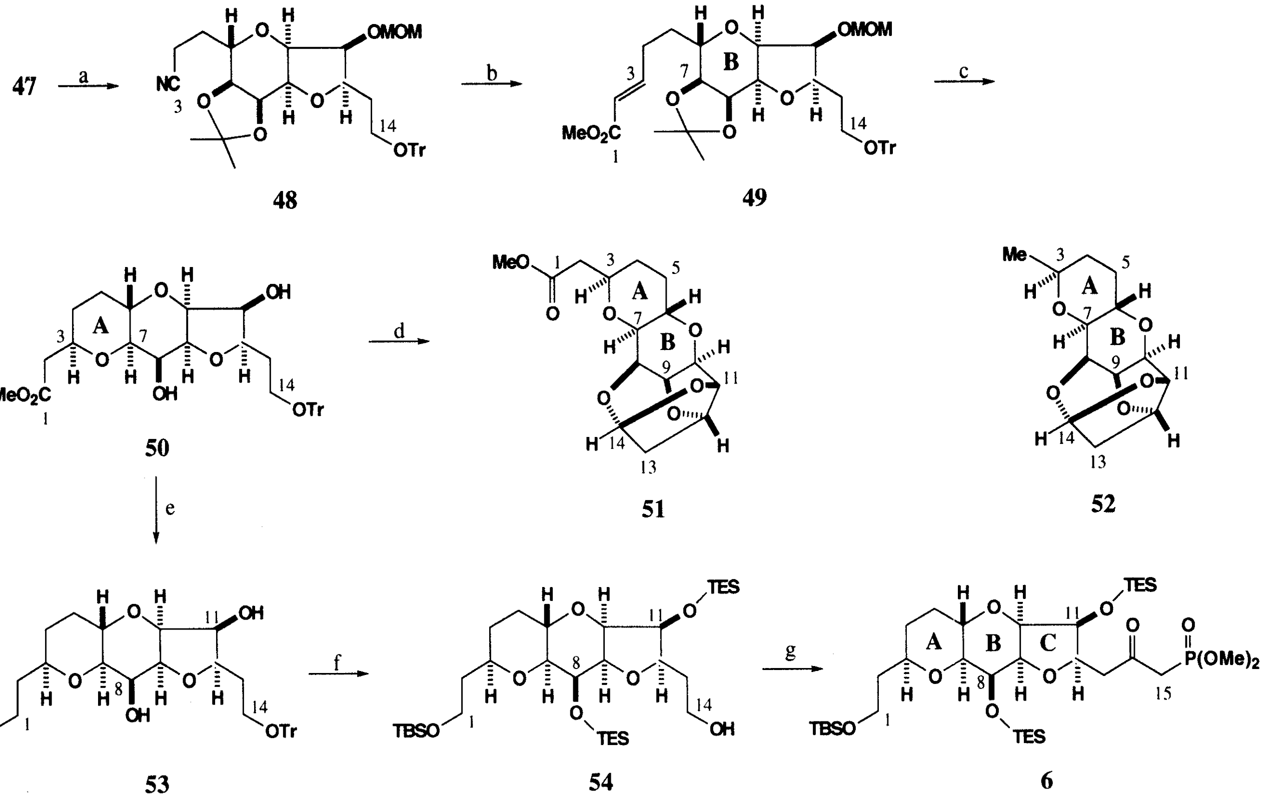
Chart 5

hydride to give **42**, which was treated with *tert*-butyldimethylsilyl (TBS) chloride to protect the primary alcohol and then epimerized at the C11 position to give **43** in excellent yield in a similar manner to the transformation from **22** to **23**. The C11 hydroxy group was protected with a methoxymethyl (MOM) group, and six conventional steps in order to renew protecting groups *via* **44** gave **45**, which was easily converted by usual Swern and Wittig reaction to **46**, a substrate for the B ring construction.

When **46** was treated with TBAF in THF at room temperature for a short while, 20 min, deprotection of the TES group followed by the intramolecular Michael reaction proceeded rather rapidly and **47** with a kinetically formed B ring was selectively obtained in almost quantitative yield.

The next important step was the thermodynamic construction of the A ring, and hence **47** was converted to **49** *via* **48** by a series of six reactions in analogy with the conversion from **29** to **8**. Treatment of **49** with TBAF in THF at room temperature for a long time, 24 h, smoothly gave a cyclization product, which after tritylation was found to be a 1.5 : 1 mixture of the expected compound (**50**) and its C3 epimer. However, when the mixture was treated again with TBAF under the same conditions for 15 h, epimerization at the C3 position occurred to give only **50** and no isomer was detected. Acetylation of two hydroxy groups of **50** and deprotection of the trityl group with CSA in methanol gave a primary alcohol, which was oxidized with Dess–Martin's reagent, and the resulting aldehyde was treated with CSA in dichloromethane to give the acetal (**51**). As shown in Table 2, chemical shifts and coupling constants in the ^{1}H-NMR spectrum of **51** are good agreement with those of **1**,[2b)] Kishi's product[6a)] and Salmon's product.[7a)] The MM calculation clearly showed that **52** (model for **51**) has a fixed conformation with 100% population (Fig. 4), as expected from its molecular model.

Finally **50** was converted to the title compound, the C1—C15 unit (**6**). The ester group of **50** was reduced with lithium aluminum hydride, and the resulting hydroxy group was protected with a TBS group to give **53**. The remaining two secondary hydroxy groups were protected with TES groups, and then the trityl group was reductively removed to give the alcohol (**54**), which was converted to a carboxylic acid by Dess–Martin oxidation followed by sodium chlorite oxidation. The acid was esterified with diazomethane and then reacted with dimethyl methanephosphonate to give **6** in excellent yield. Thus, the synthesis of the C1—C15 unit (**6**) of halichondrin B (**1**) was completed. A synthesis of the C1—C36 part of **1** was recently completed by condensation of **6** with C16—C26 and C27—C36 units and lactonization. The results will be reported soon.



(a) 1) $LiAlH_4$, Et_2O, 0 °C; 2) TsCl, Et_3N, DMAP, CH_2Cl_2, rt, 3) NaCN, DMSO, 60 °C (3 steps 96 %). (b) 1) DIBAH, CH_2Cl_2, -78 °C; 2) $Ph_3P{=}CHCO_2Me$, CH_2Cl_2, rt (2 steps 95 %). (c) 1) CSA, MeOH, rt; 2) TBAF, THF, rt, 1 d; 3) TrCl, DMAP, Et_3N, CH_2Cl_2, rt (3 steps 91 %); 4) TBAF, THF, rt, 15 h (80 %). (d) 1) Ac_2O, DMAP, CH_2Cl_2, rt; 2) CSA, MeOH-H_2O, rt; 3) Dess-Martin oxid., 4) CSA, MeOH, rt (4 steps 49 %). (e) 1) $LiAlH_4$, Et_2O, 0 °C; 2) TBSCl, imidazole, CH_2Cl_2, 0 °C (2 steps 90 %). (f) 1) TESOTf, 2,6-lutidine, CH_2Cl_2, 0 °C; 2) Na, liq NH_3, THF, -78 °C (2 steps 79 %). (g) 1) Dess-Martin oxid.; 2) $NaClO_2$, NaH_2PO_4, $Me_2C{=}CHMe$, *t*-BuOH, rt; 3) CH_2N_2, Et_2O, rt; 4) $MeP(O)(OMe)_2$, *n*-BuLi, THF, -78 °C (4 steps 89 %).

Chart 6

Table 2. Chemical Shifts (δ, ppm) and Coupling Constants (Hz) in the ^1H-NMR Spectra of Halichondrin B (**1**) and **51**

Hydrogen	1	51
2	2.44 (dd, $J=16.5$, 3.0)	2.45 (dd, $J=15.6$, 4.9)
2′	2.57 (dd, $J=16.5$, 9.3)	2.55 (dd, $J=15.6$, 7.8)
3	3.88 (m)	3.83 (m)
4	1.35	1.35—1.45
4′	1.75	1.77 (m)
5	1.41	1.35—1.45
5′	2.04	2.04 (m)
6	4.33 (ddd, $J=9.3$, 9.3, 4.0)	4.25 (ddd, $J=9.3$, 9.3, 4.4)
7	2.98 (dd, $J=9.3$, 2.4)	2.99 (dd, $J=9.3$, 2.0)
8	4.31 (dd, $J=3.6$, 2.4)	4.37 (dd, $J=3.9$, 2.0)
9	4.13 (dd, $J=6.0$, 3.6)	4.10 (dd, $J=6.4$, 3.9)
10	4.18 (dd, $J=6.0$, 4.5)	4.20 (dd, $J=6.4$, 4.4)
11	4.60 (dd, $J=4.5$, 4.5)	4.59 (dd, $J=4.4$, 4.4)
12	4.71 (dd, $J=4.5$, 4.5)	4.69 (ddd, $J=4.4$, 4.4, 2.0)
13	1.98 (dd, $J=12.6$, 4.5)	2.00—2.06
13′	2.09 (d, $J=12.6$)	2.00—2.06

Experimental

6-*O*-Benzoyl-3-*O*-benzyl-D-glucopyranose (13) A solution of **12** (500 mg, 1.92 mmol) in THF (6.0 ml) was added to a stirred suspension of NaH (60% oil dispersion: 84 mg, 2.11 mmol) in dimethyl sulfoxide (DMSO) (2.0 ml) at room temperature under argon. After 15 min, benzyl chloride (253 mg, 2.0 mmol) was added, and stirring was continued for 35 min. The reaction mixture was poured into saturated aqueous NH_4Cl, and extracted with Et_2O. The extract was washed with brine, dried over $MgSO_4$, and evaporated *in vacuo*. The residual oil was treated with 2% H_2SO_4 (1 ml) in MeOH (10 ml) at room temperature for 15 min. The reaction mixture was neutralized with $NaHCO_3$, concentrated *in vacuo*, and extracted with CH_2Cl_2–MeOH (9:1). After removal of insoluble materials by filtration, the filtrate was evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 1:2) to give a diol (562 mg, 94%).

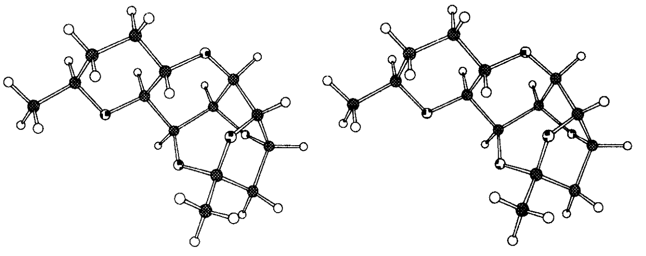


Fig. 4. Stereoview of the Conformer of **52**

Benzoyl chloride (270 mg, 1.92 mmol) was added dropwise to a stirred solution of the diol (562 mg, 1.81 mmol) and pyridine (430 mg, 5.43 mmol) in CH_2Cl_2 (10 ml) at 0 °C. After 1 h, the reaction was quenched with MeOH, then the mixture was diluted with Et_2O, washed with aqueous HCl, H_2O, aqueous $NaHCO_3$ and 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 a benzoate as a colorless oil (700 mg, 93%).

A solution of the benzoate (700 mg, 1.69 mmol) in 6 N HCl (11 ml) and THF (33 ml) was heated under reflux for 5 h. The reaction mixture was quenched with $NaHCO_3$, then concentrated *in vacuo*, and extracted with CH_2Cl_2. After removal of insoluble materials by filtration, the filtrate was evaporated *in vacuo*. The residue was recrystallized from *n*-hexane–EtOAc to give **13** as a colorless fine powder (480 mg, 76%), mp 133—137 °C. IR (nujol) cm^{-1}: 3426, 2955, 2924, 2855, 1696, 1454. ^{1}H-NMR ($CDCl_3$) δ: 2.38 (d, 1H, J=6.5 Hz), 2.93 (d, 1H, J=3.5 Hz), 3.42 (d, 1H, J=3.0 Hz), 3.53—3.69 (m, 3H), 4.09—4.13 (m, 1H), 4.50 (dd, 1H, J=2.0, 12.0 Hz), 4.71 (dd, 1H, J=4.0, 12.0 Hz), 4.85 (d, 1H, J=11.0 Hz), 4.94 (d, 1H, J=11.0 Hz), 5.27 (t, 1H, J=3.0 Hz), 7.28—7.55 (m, 7H), 7.56—7.58 (m, 1H), 8.04 (d, 1H, J=8.5 Hz). ^{13}C-NMR ($CDCl_3$) δ: 63.50, 69.85, 70.25, 72.47, 75.23, 81.68, 92.67, 128.0, 128.1, 128.2, 128.4, 128.6, 129.8, 133.3, 138.4, 167.2. MS m/z (%): 374 (M^+, 0.3), 343 (1.1), 315 (0.2), 250 (0.6), 234 (4.2), 216 (2.0), 165 (4.2), 123 (11), 105 (81), 91 (100), 77 (30). *Anal.* Calcd for $C_{20}H_{22}O_7$: C, 64.16; H, 5.92. Found: C, 64.02; H, 6.02.

6-*O*-Benzoyl-3-*O*-benzyl-D-glucose Propylene Dithioacetal (14) $ZnCl_2$ (365 mg, 2.67 mmol) and 1,3-propanedithiol (135 ml, 1.34 mmol) were added to a stirred solution of **13** (207 mg, 0.55 mmol) in CH_3CN (1 ml) at room temperature under argon. The reaction mixture was stirred at 60 °C for 6.5 h, and then cooled to room temperature. Next, 0.1 N HCl was added to dissolve $ZnCl_2$, and the mixture was extracted with CH_2Cl_2. The extract was washed with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 1.5 : 1) to give recovered **13** (24 mg, 12%) and **14** (141 mg, 55%; yield based on the consumed **13**, 63%) as a colorless oil. $[\alpha]_D^{27}$ +23.2° (c=1.49, $CHCl_3$). IR (neat) cm^{-1}: 3400, 1700, 1590, 1490, 1440. ^{1}H-NMR ($CDCl_3$) δ: 1.92— 2.08 (m, 2H), 2.61—2.69 (m, 2H), 2.87—2.97 (m, 2H), 3.03 (d, 1H, J=5.0 Hz), 3.20 (d, 1H, J=4.5 Hz), 3.39 (dd, 1H, J=2.5, 3.0 Hz), 3.79 (ddd, 1H, J=3.0, 5.0, 8.5 Hz), 3.97 (d, 1H, J=8.0 Hz), 4.00—4.07 (m, 1H), 4.13 (ddd, 1H, J=3.0, 4.5, 8.0 Hz), 4.35 (dd, 1H, J=3.0, 3.0 Hz), 4.58 (dd, 1H, J=5.5, 12.0 Hz), 4.67 (dd, 1H, J=3.0, 12.0 Hz), 4.78 (d, 1H, J=11.5 Hz), 4.84 (d, 1H, J=11.5 Hz), 7.27—7.60 (m, 8H), 8.02—8.12 (m, 2H). ^{13}C-NMR ($CDCl_3$) δ: 25.42, 27.14, 27.80, 48.10, 67.10, 71.21, 72.57, 73.06, 75.00, 76.21, 128.11, 128.35, 128.44, 128.58, 129.75, 129.83, 133.30, 137.89, 167.61. EI-MS m/z (%): 466 (M^++2, 0.01), 343 (0.3), 105 (76), 91 (100). HR-MS Calcd for $C_{23}H_{30}O_6S_2$: 466.1485. Found: 466.1496.

6-*O*-Benzoyl-3-*O*-benzyl-5-*O*-mesyl-2,4-*O*-(4-methoxybenzylidene)-D-glucose Propylene Dithioacetal (15) *dl*-CSA (50 mg, 0.2 mmol) was added to a stirred solution of **14** (5.0 g, 10.8 mmol) and 4-methoxybenzaldehyde dimethyl acetal (3.7 ml, 21.6 mmol) in CH_2Cl_2 (50 ml) at 0 °C under argon. The reaction mixture was stirred at room temperature for 1 h, then the reaction was quenched with Et_3N, and the whole was washed with brine, dried over Na_2SO_4, and evaporated *in vacuo* to give an acetal, as a colorless oil (5.4 g, 85%). $[\alpha]_D^{27}$ +0.97° (c=1.12, $CHCl_3$). IR (neat) cm^{-1}: 3450, 1710, 1610, 1510, 1440. ^{1}H-NMR ($CDCl_3$) δ: 1.86—1.99 (m, 1H), 2.05—2.15 (m, 1H), 2.36—2.40 (m, 1H), 2.65—2.74 (m, 1H), 2.75—2.90 (m, 3H), 3.79 (s, 3H), 3.84 (dd, 1H, J=1.0, 9.5 Hz), 3.99 (dd, 1H, J=1.0, 10.5 Hz), 4.13 (dd, 1H, J=1.0, 1.0 Hz), 4.19—4.26 (m, 1H), 4.53 (d, 1H, J=10.5 Hz), 4.56 (dd, 1H, J=5.5, 12.0 Hz), 4.65 (dd, 1H, J=2.0, 12.0 Hz), 4.93 (d, 1H, J=12.0 Hz), 4.97 (d, 1H, J=12.0 Hz), 5.57 (s, 1H), 6.85—6.90 (m, 10H), 7.26—7.62 (m, 10H), 8.04—8.07 (m, 2H). ^{13}C-NMR ($CDCl_3$) δ: 25.92, 28.79, 29.04, 46.86, 55.29, 66.90, 68.31, 69.26, 74.78, 79.55, 80.65, 100.84, 113.52, 127.38, 127.67, 128.02, 128.35, 128.46, 129.72, 130.07, 133.28, 138.83, 159.95, 167.43. EI-MS m/z (%): 582 (M^+, 0.1), 491 (0.7), 463 (2.4), 135 (8.5), 105 (26), 91 (56), 44 (100). HR-MS Calcd for $C_{31}H_{34}O_7S_2$: 582.1746. Found: 582.1752.

Mesyl chloride (MsCl) (23 µl, 0.3 mmol) was added slowly to a stirred solution of the above acetal (57.2 mg, 0.1 mmol) and Et_3N (113 ml, 0.9 mmol) in CH_2Cl_2 (1 ml) at 0 °C under argon. After 30 min, the reaction was quenched by stirring the mixture with MeOH for 30 min, then the whole 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 **15** as a pale yellow oil (66.0 mg, 100%). $[\alpha]_D^{26}$ −1.80° (c=2.60, $CHCl_3$). IR (neat) cm^{-1}: 3400, 1720, 1440, 1340, 1170. ^{1}H-NMR ($CDCl_3$) δ: 1.87—1.98 (m, 1H), 2.06—2.14 (m, 1H), 2.64—2.90 (m, 4H), 3.05 (s, 3H), 3.79 (s, 3H), 4.01 (dd, 1H, J=1.0, 10.5 Hz), 4.10—4.12 (m, 1H), 4.21 (dd, 1H, J=1.5, 6.5 Hz), 4.47 (d, 1H, J=10.5 Hz), 4.64 (dd, 1H, J=6.5, 13.0 Hz), 4.94 (dd, 1H, J=2.5, 13.0 Hz), 4.94 (d, 1H, J=11.5 Hz), 5.05 (d, 1H, J=11.5 Hz), 5.20 (ddd, 1H, J=2.5, 6.5, 6.5 Hz), 5.59 (s, 1H), 6.85—6.89 (m, 2H), 7.24—7.62 (m, 10H), 8.03—8.06 (m, 2H). ^{13}C-NMR ($CDCl_3$) δ: 25.84, 28.88, 29.10, 39.28, 46.71, 55.32, 62.93, 69.84, 75.15, 78.07, 78.91, 80.71, 101.41, 113.64, 127.74, 128.04, 128.42, 128.60, 129.55, 129.59, 129.70, 133.39, 138.26, 160.15, 165.93. EI-MS m/z (%): 660 (M^+, 0.1), 569 (0.8), 541 (1.1), 251 (12), 219 (52), 135 (21), 119 (68), 105 (82), 97 (18), 91 (100). HR-MS Calcd for $C_{32}H_{36}O_9S_3$: 660.1521. Found: 660.1484.

(2*S*,3*R*,4*S*,5*R*)-4-Benzyloxy-5-(1,3-dithian-2-yl)-3,5-(4-methoxybenzylidenedioxy)-1,2-epoxypentane (11) K_2CO_3 (67.8 mg, 0.5 mmol) was added to a stirred solution of **15** (64.8 mg, 0.1 mmol) in MeOH–CH_2Cl_2 (1 : 1, 1 ml) at 0 °C for 1 h. The reaction was quenched with saturated aqueous NH_4Cl, and the mixture was 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 2 : 3) to give an alcohol as a pale yellow oil (53 mg, 97%).

tert-BuOK (207 mg, 1.85 mmol) was added to a stirred solution of the alcohol (343 mg, 0.62 mmol) in THF (5 ml) at 0 °C under argon. The reaction mixture was stirred for 30 min at room temperature, then the reaction was quenched with saturated aqueous NH_4Cl, and the whole was 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 1 : 1) to give **11** as a colorless oil (249 mg, 87%). $[\alpha]_D^{25}$ −39.6° (c= 1.92, $CHCl_3$). IR (neat) cm^{-1}: 3475, 2990, 1610, 1418, 1240, 905. ^{1}H-NMR ($CDCl_3$) δ: 1.89—1.98 (m, 1H), 2.09—2.17 (m, 1H), 2.50—2.55 (m, 2H), 2.73—2.82 (m, 2H), 2.84—2.91 (m, 2H), 3.26 (ddd, 1H, J=3.0, 4.0, 7.0 Hz), 3.38 (dd, 1H, J=1.5, 7.0 Hz), 3.79 (s, 3H), 3.80—3.83 (m, 1H), 3.95 (dd, 1H, J=1.0, 10.5 Hz), 4.82 (d, 1H, J=10.5 Hz), 4.82 (d, 1H, J=11.5 Hz), 4.87 (d, 1H, J=11.5 Hz), 5.55 (s, 1H), 6.87 (d, 1H, J=9.0 Hz), 7.30—7.42 (m, 5H), 7.45 (d, 1H, J=9.0 Hz). ^{13}C-NMR ($CDCl_3$) δ: 25.92, 28.77, 29.10, 43.31, 46.51, 52.25, 55.30, 71.21, 74.73, 80.34, 82.70, 100.97, 113.53, 127.58, 127.94, 128.40, 128.44, 129.44, 137.98, 160.00. EI-MS m/z (%): 460 (M^+, 0.6), 369 (4.2), 341 (15), 251 (14), 135 (11), 119 (28), 91 (100). HR-MS Calcd for $C_{24}H_{28}O_5S_2$: 460.1378. Found: 460.1365. *Anal.* Calcd for $C_{24}H_{28}O_5S_2$: C, 62.58; H, 6.15; S, 13.92. Found: C, 62.26; H, 6.13; S, 13.92.

(2*R*,3*R*,4*S*,5*R*)-4-Benzyloxy-5-(1,3-dithian-2-yl)-3-hydroxy-2-trityloxymethyltetrahydrofuran (16) A solution of **11** (5.8 g, 12.6 mmol) in a 4 : 1 mixture of 80% AcOH and CH_2Cl_2 was stirred at room temperature for 4 d. The reaction mixture was neutralized with saturated aqueous $NaHCO_3$, 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 1 : 1) to give a diol as a pale yellow oil (3.6 g, 84%). $[\alpha]_D^{26}$ 21.4° (c=1.9, $CHCl_3$). IR (neat) cm^{-1}: 3400, 1490, 1450. ^{1}H-NMR ($CDCl_3$) δ: 1.82—1.86 (m, 1H), 1.98—2.12 (m, 2H), 2.30—2.36 (m, 1H), 2.75—2.81 (m, 2H), 2.92—2.99 (m, 2H), 3.72 (ddd, 1H, J=4.0, 7.5, 12.0 Hz), 3.82 (ddd, 1H, J=3.5, 4.0, 12.0 Hz), 3.98—4.00 (m, 1H), 3.99 (dd, 1H, J=1.0, 3.5 Hz), 4.28 (d, 1H, J=10.0 Hz), 4.35—4.37 (m, 1H), 4.38 (dd, 1H, J=3.5, 10.0 Hz), 4.59 (d, 1H, J=11.0 Hz), 4.63 (d, 1H, J=11.0 Hz), 7.23—7.36 (m, 5H). ^{13}C-NMR ($CDCl_3$) δ: 25.60, 27.42, 27.96, 43.42, 62.75, 72.68, 75.48, 80.78, 84.58, 87.09, 127.98, 128.42, 137.45. EI-MS m/z (%): 342 (M^+, 0.5), 251 (33), 119 (100), 91 (65). HR-MS Calcd for $C_{16}H_{22}O_4S_2$: 342.0960. Found: 342.0967.

Trityl chloride (1.91 g, 6.9 mmol) was added to a stirred solution of the diol (1.57 g, 4.6 mmol), Et_3N (1.6 ml, 11.4 mmol) and DMAP (15 mg, 0.14 mmol) in CH_2Cl_2 (15 ml) at room temperature under argon. After 12 h, MeOH (3 ml) was added, and stirring was continued for 30 min. The reaction mixture was 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 20 : 1) to give **16** as a colorless oil (2.52 g, 94%). $[\alpha]_D^{25}$ +2.48° (c=2.84, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.78 (d, 1H, J=3.5 Hz), 1.99—2.17 (m, 2H), 2.67—2.74 (m, 2H), 2.89—2.98 (m, 2H), 3.12 (dd, 1H, J=8.5, 9.0 Hz), 3.51 (dd, 1H, J=5.5, 9.0 Hz), 3.95 (dd, 1H, J=1.0, 3.5 Hz), 4.02 (ddd, 1H, J=2.5, 5.5, 8.5 Hz), 4.15 (d, 1H, J=10.5 Hz), 4.30—4.31 (m, 1H), 4.41 (dd, 1H, J=3.5, 10.5 Hz), 4.46 (d, 1H, J=11.5 Hz), 4.52 (d, 1H, J=11.5 Hz), 7.15—7.31 (m, 15H), 7.39—7.52 (m, 5H). ^{13}C-NMR ($CDCl_3$) δ: 25.66, 27.05, 27.60, 42.81, 64.23, 72.33, 77.03, 80.91, 84.49, 85.61, 86.76, 127.01, 127.80, 128.29, 128.69, 137.86, 143.89. EI-MS m/z (%) 583 (M^+−1, 1.1), 407 (0.7), 241 (30), 251 (17), 243 (100), 119 (87), 91 (64), 77 (3.1). HR-MS Calcd for $C_{35}H_{36}O_4S_2$: 584.2055. Found: 584.2069.

(2*R*,3*R*,4*R*,5*S*)-4-Benzyloxy-5-(1,3-dithian-2-yl)-3-(4-methoxybenzyloxy)-2-trityloxymethyltetrahydrofuran (17) A solution of **16** (160 mg, 0.27 mmol) in THF (0.7 ml) was added slowly to a stirred suspension of 60% oil dispersion of NaH (25 mg, 0.41 mmol) in a 1 : 1 mixture of THF and DMSO (0.8 ml) at 0 °C under argon. The mixture was allowed to warm to room temperature, stirred until evolution of H_2 ceased, and cooled again to 0 °C. MPMCl (41 µl, 0.41 mmol) was slowly added, and the mixture was stirred at room temperature for 3 h. Et_2NH (0.5 ml) was added, and stirring was continued for 2 h. The reaction mixture was washed with saturated aqueous NH_4Cl and 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 **17** as a colorless oil (169 mg, 88%). $[\alpha]_D^{27}$ +11.8° (c=1.40, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.97—2.04 (m, 2H), 2.65—2.73 (m, 2H), 2.88—2.96 (m, 2H), 3.06 (dd, 1H, *J*=9.0, 9.0 Hz), 3.58 (dd, 1H, *J*=5.0, 9.0 Hz), 3.78 (s, 3H), 4.00 (dd, 1H, *J*=0.0, 3.0 Hz), 4.01 (dd, 1H, *J*=0.0, 1.0 Hz), 4.13 (d, 1H, *J*=10.5 Hz), 4.26 (ddd, 1H, *J*=1.0, 5.0, 9.0 Hz), 4.33 (d, 1H, *J*=11.5 Hz), 4.37 (dd, 1H, *J*=3.0, 10.5 Hz), 4.38 (d, 1H, *J*=11.5 Hz), 4.48 (d, 1H, *J*=11.5 Hz), 4.55 (d, 1H, *J*=11.5 Hz), 6.66—6.82 (m, 2H), 7.10—7.28 (m, 16H), 7.38—7.41 (m, 6H). ^{13}C-NMR ($CDCl_3$) δ: 25.70, 26.90, 27.52, 42.65, 55.30, 64.03, 71.09, 72.04, 80.96, 82.41, 82.90, 83.67, 86.69, 113.59, 126.94, 127.56, 127.65, 127.72, 128.24, 128.75, 129.26, 129.88, 127.82, 143.96, 159.36. EI-MS *m/z* (%): 703 ($M^+ - 1$, 0.04), 583 (0.5), 461 (17), 355 (1.7), 251 (7.6), 243 (100), 165 (17), 121 (76), 119 (31), 77 (3.5). HR-MS Calcd for $C_{43}H_{43}O_5S_2$: 703.2552. Found: 703.2554.

(2*R*,3*R*,4*R*,5*S*)-4-Benzyloxy-2-(*tert*-butyldiphenylsilyloxymethyl)-5-(1,3-dithian-2-yl)-3-(4-methoxybenzyloxy)tetrahydrofuran (18) *dl*-CSA (11 mg, 0.45 mmol) was added to a stirred solution of **17** (107 mg, 0.15 mmol) in a 3 : 1 mixture of MeOH and CH_2Cl_2 (125 ml) at room temperature. After 12 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$, 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 1 : 1) to give an alcohol as a colorless oil (77 mg, 100%).

Imidazole (20 mg, 0.3 mmol) and TBDPSCl (78.5 μl, 0.3 mmol) were added to a stirred solution of the alcohol (77 mg, 0.15 mmol) in CH_2Cl_2 (0.75 ml) at room temperature under argon. After 45 min, the reaction mixture 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 **18** as a colorless oil (96 mg, 93%). $[\alpha]_D^{22}$ +12.3° (c=0.644, $CHCl_3$). IR (neat) cm^{-1}: 3400, 1605, 1420. ^{1}H-NMR ($CDCl_3$) δ: 1.03 (s, 9H), 1.90—2.10 (m, 2H), 2.65—2.75 (m, 2H), 2.88—2.98 (m, 2H), 3.65 (dd, 1H, *J*=9.5, 10.0 Hz), 3.80 (s, 3H), 3.85 (dd, 1H, *J*=5.0, 10.0 Hz), 4.05 (dd, 1H, *J*=0.0, 3.0 Hz), 4.14 (d, 1H, *J*=11.0 Hz), 4.16 (dd, 1H, *J*=0.0, 1.5 Hz), 4.19 (ddd, 1H, *J*=1.5, 5.0, 9.0 Hz), 4.38 (dd, 1H, *J*=3.0, 11.0 Hz), 4.45 (d, 1H, *J*=11.5 Hz), 4.47 (d, 1H, *J*=11.0 Hz), 4.50 (d, 1H, *J*=11.0 Hz), 4.54 (d, 1H, *J*=11.5 Hz), 6.84—6.90 (m, 2H), 7.21—7.42 (m, 13H), 7.58—7.63 (m, 4H). ^{13}C-NMR ($CDCl_3$) δ: 19.28, 25.71, 26.92, 26.92, 27.62, 42.83, 55.32, 64.08, 71.16, 72.42, 81.05, 82.55, 82.88, 84.88, 113.95, 127.65, 127.69, 127.85, 128.33, 129.26, 129.65, 129.70, 129.97, 133.38, 133.58, 135.61, 137.86, 159.38. FAB-MS *m/z* (%): 701 ($M^+ + 1$, 25), 197 (38), 119 (31), 91 (100). HR-MS Calcd for $C_{40}H_{49}O_5SiS_2$: 701.2793. Found: 701.2815.

Ethyl (2*E*)-3-[(2*S*,3*R*,4*R*,5*R*)-3-Benzyloxy-5-(*tert*-butyldiphenylsilyloxymethyl)-4-(4-methoxybenzyloxy)tetrahydrofuran-2-yl]prop-2-enate (19) A solution of **18** (116 mg, 0.17 mmol) in THF (2 ml) was slowly added to a stirred suspension of red HgO (108 mg, 0.5 mmol) and $BF_3 \cdot Et_2O$ (61.3 μl, 0.5 mmol) in a 1 : 1 mixture of THF and H_2O (1 ml). The reaction mixture was warmed to 60 °C under vigorous stirring. After 1.5 h, the reaction mixture was filtered with the aid of Celite. The filtrate 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 : 2) to give an aldehyde.

A 1.0 M solution of *tert*-BuOK in THF (0.5 ml, 0.5 mmol) was added to a stirred solution of diisopropyl ethoxycarbonylmethanephosphonate (158 μl, 0.66 mmol) in THF (0.5 ml) at 0 °C under argon. The mixture was stirred at room temperature for 30 min, and then cooled to −78 °C. A solution of the aldehyde in THF (2 ml) was slowly added dropwise. After 30 min, the reaction mixture was quenched with saturated aqueous NH_4Cl, 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 5 : 1) to give **19** as a colorless oil (102 mg, 91%). ^{1}H-NMR ($CDCl_3$) δ: 1.05 (s, 9H), 1.27 (t, 3H, *J*=7.0 Hz), 3.70—3.79 (m, 1H), 3.79 (s, 3H), 3.84 (d, 1H, *J*=4.5, 10.5 Hz), 3.94 (d, 1H, *J*=0.5, 4.0 Hz), 4.07—4.13 (m, 2H), 4.19 (q, 2H, *J*=7.0 Hz), 4.35 (d, 1H, *J*=12.0 Hz), 4.42 (d, 1H, *J*=11.5 Hz), 4.44 (d, 1H, *J*=12.0 Hz), 4.49 (d, 1H, *J*=11.5 Hz), 4.64 (ddd, 1H, *J*=1.5, 4.0, 5.5 Hz), 6.09 (dd, 1H, *J*=1.5, 15.5 Hz), 6.82—6.87 (m, 2H), 6.97 (dd, 1H, *J*=5.5, 15.5 Hz), 7.18—7.73 (m, 13H), 7.63—7.67 (m, 4H). FAB-MS *m/z* (%): 680 (M^+, 18), 679 (33), 181(30), 121 (100), 91 (51). HR-MS Calcd for $C_{41}H_{47}O_7Si$: 679.3091. Found: 679.3091.

(2*S*,3*S*,4*R*,5*R*)-3-Benzyloxy-5-(*tert*-butyldiphenylsilyloxymethyl)-2-[(1*S*,2*S*)-3-hydroxy-1,2-epoxypropyl]-4-(4-methoxybenzyloxy)tetrahydrofuran (10) A solution of **19** (3.75 g, 5.51 mmol) in CH_2Cl_2 (20 ml) was added dropwise to a stirred 0.93 M solution of DIBAH in *n*-hexane (45 ml, 22 mmol) during 30 min at −78 °C under argon. After 45 min, MeOH (4 ml) was added, and stirring was continued for 30 min. The reaction mixture was allowed to warm to room temperature, and then Et_2O and saturated aqueous Rochelle salt were added. After 2 h, the reaction 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 2 : 1) to give an alcohol as a colorless oil (3.34 g, 95%). $[\alpha]_D^{28}$ +23.7° (c=2.40, $CHCl_3$). IR (neat) cm^{-1}: 3400, 1600, 1510. ^{1}H-NMR ($CDCl_3$) δ: 1.06 (s, 9H), 1.20—1.30 (m, 1H), 3.73 (dd, 1H, *J*=8.0, 10.5 Hz), 3.80 (s, 3H), 3.84 (dd, 1H, *J*=5.0, 10.5 Hz), 3.87 (dd, 1H, *J*=1.0, 4.0 Hz), 4.06 (ddd, 1H, *J*=2.5, 5.0, 8.0 Hz), 4.11—4.16 (m, 2H), 4.12 (dd, 1H, *J*=1.0, 2.5 Hz), 4.38 (d, 1H, *J*=12.0 Hz), 4.44 (d, 1H, *J*=11.5 Hz), 4.48 (d, 1H, *J*=12.0 Hz), 4.48 (dd, 1H, *J*=4.0, 7.0 Hz), 4.51 (d, 1H, *J*=11.5 Hz), 5.83—5.91 (m, 1H), 5.91—5.98 (m, 1H), 6.82—6.88 (m, 2H), 7.18—7.43 (m, 13H), 7.63—7.67 (m, 4H). ^{13}C-NMR ($CDCl_3$) δ: 19.31, 26.94, 55.30, 63.15, 64.25, 71.32, 71.71, 81.46, 83.72, 83.94, 84.33, 113.94, 126.83, 127.56, 127.69, 128.38, 129.26, 129.65, 129.70, 130.43, 133.43, 133.61, 135.63, 137.98, 159.34. FAB-MS *m/z* (%): 638 (M^+, 3.1), 637 (6.6), 197 (16), 121 (100), 91 (65). HR-MS Calcd for $C_{39}H_{46}O_6Si$: 638.3063. Found: 638.3060.

D-(−)-Diethyl tartrate (DET) (452 μl, 2.64 mmol) and Ti(O-iso-Pr)$_4$ (589 μl, 1.98 mmol) were added to a stirred suspension of 4 Å molecular sieves (450 mg) in CH_2Cl_2 (2 ml) at −5 °C under argon. After 30 min, the reaction mixture was cooled to −20 °C, then a solution of the alcohol (421 mg, 0.66 mmol) in CH_2Cl_2 (5 ml) was slowly added, and stirring was continued for 30 min. A 3.0 M solution of *tert*-butyl hydroperoxide (TBHP) in 2,2,4-trimethylpentane (660 μl, 1.98 mmol) was slowly added, and the stirring was continued for 3 d. The reaction mixture was filtered with the aid of Celite, and the filtrate was poured into a stirred solution of $FeSO_4 \cdot 7H_2O$ (1.65 g) and tartaric acid (0.5 g) in H_2O at 0 °C. After 15 min, the mixture was extracted with Et_2O. The extract was concentrated and stirred with 30% NaOH in brine (10 ml) at 0 °C for 1 h. The reaction 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 2 : 1) to give **10** as a colorless oil (386 mg, 89%). $[\alpha]_D^{28}$ +25.1° (c=1.38, $CHCl_3$). IR (neat) cm^{-1}: 3450, 2990, 1240, 1110, 820. ^{1}H-NMR ($CDCl_3$) δ: 1.05 (s, 9H), 1.68—1.78 (m, 1H), 3.16 (ddd, 1H, *J*=2.0, 2.5, 4.5 Hz), 3.24 (dd, 1H, *J*=2.0, 6.0 Hz), 3.51—3.60 (m, 1H), 3.72 (dd, 1H, *J*=8.0, 10.5 Hz), 3.78 (s, 3H), 3.80 (dd, 1H, *J*=5.0, 10.5 Hz), 3.85 (dd, 1H, *J*=4.0, 6.0 Hz), 3.84—3.90 (m, 1H), 4.06 (dd, 1H, *J*=1.5, 4.0 Hz), 4.06 (ddd, 1H, *J*=2.5, 5.0, 8.0 Hz), 4.15 (dd, 1H, *J*=1.5, 2.5 Hz), 4.44 (d, 1H, *J*=11.5 Hz), 4.48 (d, 1H, *J*=11.5 Hz), 4.48 (d, 1H, *J*=12.0 Hz), 4.53 (d, 1H, *J*=12.0 Hz), 6.82—6.88 (m, 2H), 7.16—7.43 (m, 13H), 7.61—7.67 (m, 4H). ^{13}C-NMR ($CDCl_3$) δ: 19.30, 26.90, 52.82, 55.30, 57.31, 61.58, 63.84, 71.34, 71.91, 80.72, 82.86, 82.97, 84.42, 113.95, 127.60, 127.69, 127.72, 127.82, 128.47, 129.26, 129.77, 129.81, 133.34, 133.54, 135.61, 137.75, 159.40. FAB-MS *m/z* (%): 653 ($M^+ - 1$, 5.3), 563 (3.8), 533 (2.7), 211 (93), 197 (18), 154 (100). HR-MS Calcd for $C_{39}H_{45}O_7Si$: 653.2934. Found: 653.2899.

(1*S*,2*S*)-1-[(2*S*,3*S*,4*R*,5*R*)-3-Benzyloxy-5-(*tert*-butyldiphenylsilyloxymethyl)-4-(4-methoxybenzyloxy)tetrahydrofuran-2-yl]-2,3-carbonyldioxypropan-1-ol (20) Phenyl isocyanate (76.7 μl, 0.71 mmol) was added to a stirred solution of **10** (385 mg, 0.59 mmol) and Et_3N (296 μl, 2.12 mmol) in CH_2Cl_2 (3.5 ml) at room temperature under argon. After 1.5 h, saturated aqueous $NaHCO_3$ was 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 2 : 1) to give a urethane.

$BF_3 \cdot Et_2O$ (290 μl, 2.36 mmol) was slowly added to a stirred solution of the urethane in Et_2O (5 ml) at 0 °C under argon. After 2 h, THF (4 ml) and 0.1 N HCl (4 ml) were added, stirring was continued for 30 min, and then the reaction 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 4 : 1) to give **20** as a colorless oil (343 mg, 85%). $[\alpha]_D^{26}$ +30.8° (c=0.956, $CHCl_3$). IR (neat) cm^{-1}: 3450, 1780, 1240. ^{1}H-NMR ($CDCl_3$) δ: 1.06 (s, 9H), 2.26 (d, 1H, *J*=5.0 Hz), 3.66 (dd, 1H, *J*=7.0, 10.0 Hz), 3.76 (dd, 1H, *J*=5.5, 10.5 Hz), 3.80 (s, 3H), 3.86 (dd, 1H, *J*=4.0, 7.5 Hz), 4.03

(ddd, 1H, $J=2.5$, 5.0, 7.0 Hz), 4.04 (dd, 1H, $J=1.0$, 4.0 Hz), 4.06 (dd, 1H, $J=1.0$, 2.5 Hz), 4.26 (ddd, 1H, $J=3.0$, 5.0, 7.5 Hz), 4.29 (d, 1H, $J=12.0$ Hz), 4.34 (dd, 1H, $J=8.5$, 8.5 Hz), 4.44 (d, 1H, $J=11.5$ Hz), 4.49 (d, 1H, $J=12.0$ Hz), 4.51 (dd, 1H, $J=6.5$, 8.5 Hz), 4.52 (d, 1H, $J=11.5$ Hz), 4.79 (ddd, 1H, $J=3.0$, 6.5, 8.5 Hz), 6.85—6.90 (m, 2H), 7.17—7.45 (m, 13H), 7.61—7.66 (m, 4H). ^{13}C-NMR (CDCl$_3$) δ: 19.30, 26.88, 55.32, 64.01, 64.56, 68.11, 71.43, 71.69, 77.16, 79.81, 82.02, 82.28, 85.06, 114.03, 127.74, 127.85, 128.29, 128.77, 129.32, 129.54, 129.85, 133.27, 133.38, 135.61, 137.11, 155.32, 159.51. FAB-MS m/z (%): 697 (M$^+$-1, 6.7), 641 (16), 241 (17), 211 (54), 121 (100), 91 (62). HR-MS Calcd for $C_{40}H_{45}O_9Si$: 697.2839. Found: 697.2820.

(2*S*,3*S*,4*R*,5*R*)-3-Benzyloxy-5-(*tert*-butyldiphenylsilyloxymethyl)-4-methoxybenzyloxy-2-[(1*S*,2*S*)-1,2,3-trihydroxypropyl]tetrahydrofuran (21) K_2CO_3 (340 mg, 2.64 mmol) was added to a stirred solution of **20** (343 mg, 0.5 mmol) in MeOH (6 ml) at 0 °C. After 2.5 h at room temperature, the reaction mixture was concentrated *in vacuo*, then the residue was taken up in CH_2Cl_2 and filtered with the aid of Celite. The filtrate was evaporated *in vacuo*, and the residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 1 : 3) to give **21** as a colorless oil (315 mg, 96%). $[\alpha]_D^{25}$ +30.5° ($c=1.90$, CHCl$_3$). IR (neat) cm^{-1}: 3450, 1110. ^{1}H-NMR (CDCl$_3$) δ: 1.05 (s, 9H), 2.40—2.60 (m, 1H), 3.00—3.20 (m, 1H), 3.68 (dd, 1H, $J=7.5$, 11.0 Hz), 3.72—3.82 (m, 4H), 3.80 (s, 3H), 3.93—3.99 (m, 1H), 4.03—4.06 (m, 1H), 4.06—4.14 (m, 1H), 4.37 (d, 1H, $J=11.5$ Hz), 4.42 (d, 1H, $J=11.5$ Hz), 4.47 (d, 1H, $J=11.5$ Hz), 4.53 (d, 1H, $J=11.5$ Hz), 6.83—6.89 (m, 2H), 7.18—7.44 (m, 13H), 7.61—7.67 (m, 4H). ^{13}C-NMR (CDCl$_3$) δ: 19.26, 26.87, 55.30, 63.11, 64.08, 70.28, 71.32, 71.71, 73.06, 81.60, 82.08, 82.74, 85.26, 113.99, 127.76, 127.82, 128.09, 128.66, 129.28, 129.64, 129.77, 129.81, 133.27, 133.43, 135.61, 137.42, 159.45. FAB-MS m/z (%): 673 (M$^+$+1, 7.0), 211 (70), 121 (100), 91 (99). HR-MS Calcd for $C_{39}H_{49}O_8Si$: 673.3197. Found: 673.3218.

(2*S*,3*S*,4*R*,5*R*)-3-Benzyloxy-5-(*tert*-butyldiphenylsilyloxymethyl)-2-[(1*S*,2*S*)-1,2-isopropylidenedioxy-3-trimethylacetyloxypropyl]-4-(4-methoxybenzyloxy)tetrahydrofuran (22) Pivaloyl chloride (0.45 ml, 3.67 mmol) was added dropwise to a stirred solution of **21** (2.01 g, 3.06 mmol), Et$_3$N (1.7 ml, 12.2 mmol), and DMAP (10 mg, 0.08 mmol) in CH_2Cl_2 (10 ml) during 10 min at 0 °C under argon. After 30 min, MeOH (0.2 ml) was added, and stirring was continued for 30 min. The reaction mixture 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 an ester as a colorless oil (1.81 g, 80%). $[\alpha]_D^{26}$ +28.9° ($c=1.45$, CHCl$_3$). IR (neat) cm^{-1}: 3450, 1110. ^{1}H-NMR (CDCl$_3$) δ: 1.05 (s, 1H), 1.18 (s, 1H), 2.93—3.00 (m, 1H), 3.12—3.20 (m, 1H), 3.68 (dd, 1H, $J=7.5$, 10.0 Hz), 3.79 (dd, 1H, $J=5.5$, 10.0 Hz), 3.79 (s, 3H), 3.82—3.90 (m, 2H), 4.05—4.14 (m, 4H), 4.18—4.24 (m, 1H), 4.37 (d, 1H, $J=11.5$ Hz), 4.38—4.45 (m, 1H), 4.45 (d, 1H, $J=11.5$ Hz), 4.49 (d, 1H, $J=11.5$ Hz), 4.53 (d, 1H, $J=11.5$ Hz), 6.83—6.89 (m, 2H), 7.18—7.44 (m, 13H), 7.60—7.66 (m, 4H). ^{13}C-NMR (CDCl$_3$) δ: 19.28, 26.87, 27.21, 38.94, 55.30, 64.01, 65.36, 68.69, 71.27, 71.71, 72.92, 82.08, 82.24, 82.92, 85.15, 113.95, 127.74, 127.98, 128.58, 129.24, 129.72, 129.77, 133.32, 133.47, 135.61, 137.49, 159.40, 179.70. FAB-MS m/z (%): 757 (M$^+$+1, 4.1), 241 (4.7), 211 (46), 121 (100), 91 (77), 57 (32). HR-MS Calcd for $C_{44}H_{57}O_9Si$: 757.3772. Found: 757.3757.

Pyridinium *p*-toluenesulfonate (PPTS) (160 mg, 0.64 mmol) was added to a stirred solution of the ester (1.93 g, 2.6 mmol) and 2-methoxypropene (2 ml, 20.8 mmol) in CH_2Cl_2 (16 ml) at 0 °C under argon. After 50 min at room temperature, the reaction mixture was quenched with saturated aqueous NaHCO$_3$ 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 7 : 1) to give **22** as a colorless oil (1.82 g, 80%). $[\alpha]_D^{17}$ +3.61° ($c=0.432$, CHCl$_3$). IR (neat) cm^{-1}: 1720. ^{1}H-NMR (CDCl$_3$) δ: 1.05 (s, 3H), 1.20 (s, 9H), 1.24 (s, 3H), 1.34 (s, 3H), 3.67 (dd, 1H, $J=8.5$, 10.0 Hz), 3.77 (dd, 1H, $J=5.5$, 10.0 Hz), 3.80 (s, 3H), 3.98—4.06 (m, 3H), 4.07 (ddd, 1H, $J=2.0$, 5.5, 8.5 Hz), 4.21 (dd, 1H, $J=7.0$, 11.5 Hz), 4.31 (dd, 1H, $J=3.5$, 11.5 Hz), 4.34 (ddd, 1H, $J=3.5$, 7.0, 9.0 Hz), 4.40 (d, 1H, $J=11.5$ Hz), 4.41 (dd, 1H, $J=6.0$, 9.0 Hz), 4.46 (d, 1H, $J=11.5$ Hz), 4.48—4.54 (m, 2H), 6.82—6.88 (m, 2H), 7.16—7.44 (m, 13H), 7.60—7.66 (m, 4H). ^{13}C-NMR (CDCl$_3$) δ: 19.31, 25.62, 26.90, 27.23, 27.91, 38.75, 55.32, 63.51, 64.19, 71.07, 71.95, 73.48, 75.66, 78.73, 82.70, 83.10, 85.08, 108.80, 113.91, 127.58, 127.67, 127.71, 128.27, 129.17, 129.65, 129.70, 129.99, 133.49, 133.71, 135.63, 138.22, 159.33. FAB-MS m/z (%): 795 (M$^+$−1, 3.5), 739 (5.0), 241 (6.0), 211 (47), 121 (100), 91 (70), 57 (23). HR-MS Calcd for $C_{47}H_{59}O_9Si$: 795.3928. Found: 795.3979.

(2*S*,3*S*,4*S*,5*R*)-3-Benzyloxy-5-(*tert*-butyldiphenylsilyloxymethyl)-4-hydroxy-2-[(1*S*,2*S*)-1,2-isopropylidenedioxy-3-trimethylacetyloxypropyl]tetrahydrofuran (23) DDQ (1.3 g, 5.75 mmol) was added to a stirred solution of **22** (1.82 g, 2.3 mmol) in a 2 : 1 mixture of CH_2Cl_2 and pH 6.86 phosphate buffer (45 ml) at 0 °C. After 1.5 h at room temperature, the reaction mixture was diluted with H_2O, and extracted with Et$_2$O. 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 an alcohol as a colorless oil (1.39 g, 90%). $[\alpha]_D^{19}$ +2.01° ($c=0.496$, CHCl$_3$). IR (neat) cm^{-1}: 3450, 1720. ^{1}H-NMR (CDCl$_3$) δ: 1.05 (s, 9H), 1.20 (s, 9H), 1.34 (s, 3H), 1.44 (s, 3H), 1.66—1.75 (m, 1H), 3.71 (dd, 1H, $J=8.0$, 10.0 Hz), 3.80 (dd, 1H, $J=5.5$, 10.0 Hz), 3.87 (ddd, 1H, $J=2.5$, 5.5, 8.0), 3.92 (dd, 1H, $J=1.5$, 3.5 Hz), 4.09 (dd, 1H, $J=3.5$, 9.5 Hz), 4.18—4.36 (m, 1H), 4.28—4.36 (m, 3H), 4.40 (dd, 1H, $J=6.0$, 9.5 Hz), 4.56— 4.60 (m, 2H), 7.26—7.46 (m, 11H), 7.61—7.68 (m, 4H). ^{13}C-NMR (CDCl$_3$) δ: 19.31, 25.64, 26.88, 27.23, 27.93, 38.77, 63.48, 64.19, 72.20, 73.54, 75.71, 77.23, 78.46, 85.11, 86.83, 108.82, 127.49, 127.56, 127.74, 128.27, 128.74, 129.77, 133.45, 133.54, 135.57, 138.20, 178.42. FAB-MS m/z (%) 677 (M$^+$+1, 9.7), 619 (67), 575 (56), 91 (100), 85 (77), 57 (61).

DMSO (0.9 ml, 12.6 mmol) was added to a stirred solution of (COCl)$_2$ (0.74 ml, 8.4 mmol) in CH_2Cl_2 (25 ml) at −78 °C under argon. After 15 min, a solution of the alcohol (1.36 g, 2.1 mmol) in CH_2Cl_2 (6 ml) was slowly added dropwise, and stirring was continued for 30 min. A solution of Et$_3$N (2.9 ml, 21 mmol) in CH_2Cl_2 (3 ml) was added dropwise during 10 min. After 45 min, the reaction mixture was poured into saturated aqueous NH$_4$Cl, and extracted with Et$_2$O. 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 2 : 1) to give a ketone.

NaBH$_4$ (635 mg, 16.8 mmol) was added to a stirred solution of the ketone in a 3 : 1 mixture of THF and MeOH (40 ml) at −78 °C. After 40 min, the reaction mixture was poured into saturated aqueous NH$_4$Cl, and extracted with Et$_2$O. 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 **23** (1.2 g, 86%). $[\alpha]_D^{16}$ +0.986° ($c=1.42$, CHCl$_3$). IR (neat) cm^{-1}: 3500, 1720. ^{1}H-NMR (CDCl$_3$) δ: 1.00 (s, 9H), 1.21 (s, 9H), 1.36 (s, 3H), 1.46 (s, 3H), 3.10—3.30 (m, 1H), 3.77— 3.84 (m, 2H), 3.89—3.95 (m, 1H), 4.00 (dd, 1H, $J=5.0$, 11.0 Hz), 4.12 (dd, 1H, $J=4.5$, 5.5 Hz), 4.23 (dd, 1H, $J=7.5$, 11.5 Hz), 4.33 (dd, 1H, $J=3.0$, 11.5 Hz), 4.36—4.44 (m, 2H), 4.47 (dd, 1H, $J=6.0$, 9.5 Hz), 4.69 (d, 1H, $J=11.5$ Hz), 4.80 (d, 1H, $J=11.5$ Hz), 7.26—7.42 (m, 11H), 7.64—7.71 (m, 4H). ^{13}C-NMR (CDCl$_3$) δ: 19.17, 25.68, 26.70, 27.25, 27.95, 38.79, 63.39, 63.42, 72.71, 74.07, 74.73, 75.81, 77.56, 79.79, 80.61, 109.03, 127.63, 127.83, 127.96, 128.40, 129.66, 133.39, 133.47, 135.63, 135.68, 137.91, 178.36. FAB-MS m/z (%) 677 (M$^+$+1, 34), 619 (46), 575 (14), 91 (100), 85 (27), 57 (87). HR-MS Calcd for $C_{39}H_{53}O_8Si$: 677.3510. Found: 677.3488.

(2*S*,3*S*,3a*S*,7a*R*)-3-Hydroxy-2-[(1*S*,2*S*)-3-hydroxy-1,2-isopropylidenedioxypropyl]-5,5-dimethyl-5*H*.7*H*-2,3,3a,7a-tetrahydoro-4,6-dioxabenzo[*b*]furan (24) A 1.0 M solution of TBAF in THF (2.6 ml, 2.66 mmol) was added to a stirred solution of **23** (900 mg, 1.33 mmol) in THF (10 ml) at room temperature. After 30 min, the reaction mixture was diluted with Et$_2$O, 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 a diol (660 mg, 100%).

TsOH (9 mg) was added to a stirred solution of the diol (550 mg, 1.26 mmol) and 2-methoxypropene (1.25 ml, 12.6 mmol) in a 5 : 1 mixture of benzene and CH_2Cl_2 (6 ml) at 0 °C under argon. After 2 h at room temperature, the reaction mixture was quenched with saturated aqueous NaHCO$_3$, and extracted with Et$_2$O. 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 a diacetonide (598 mg, 100%). $[\alpha]_D^{19}$ −37.4° ($c=0.956$, CHCl$_3$). IR (neat) cm^{-1}: 1720. ^{1}H-NMR (CDCl$_3$) δ: 1.23 (s, 9H), 1.37 (s, 9H), 1.41 (s, 3H), 1.43 (s, 3H), 1.48 (s, 3H), 3.68 (ddd, 1H, $J=4.0$, 4.0, 4.0 Hz), 3.83 (dd, 1H, $J=4.0$, 12.5 Hz), 3.95 (dd, 1H, $J=4.0$, 12.5 Hz), 4.10 (dd, 1H, $J=6.5$, 9.0 Hz), 4.16 (dd, 1H, $J=5.0$, 6.5 Hz), 4.32 (dd, 1H, $J=8.0$, 11.5 Hz), 4.33 (dd, 1H, $J=4.0$, 5.0 Hz), 4.38 (dd, 1H, $J=3.0$, 11.5 Hz), 4.44 (ddd, 1H, $J=3.0$, 6.0, 8.0 Hz), 4.63—4.72 (m, 2H), 4.83 (dd, 1H, $J=6.0$, 9.0 Hz), 7.25—7.43 (m, 5H). ^{13}C-NMR (CDCl$_3$) δ: 20.37, 25.90, 27.29, 28.07, 28.16, 38.79, 60.94, 64.08, 70.10, 72.53, 72.92, 74.49, 76.19, 76.90, 79.68, 98.10, 108.92, 127.58, 127.72, 128.22, 138.39, 178.55. FAB-MS m/z (%): 479 (M$^+$+1, 32), 463 (11), 421 (49), 363 (20), 347 (6.2), 307 (11), 289 (8.2), 261 (10), 154 (36), 136 (25), 91 (100), 57 (22).

HR-MS Calcd for $C_{26}H_{39}O_8$: 479.2645. Found: 479.2632.

Na (590 mg, 25.6 mol) was added to stirred liquid NH_3 (*ca.* 20 ml) at −78 °C. After 20 min, a solution of the diacetonide (579 mg, 1.2 mmol) in THF (5 ml) was added dropwise, and stirring was continued for 30 min. The reaction mixture was diluted with Et_2O, treated with NH_4Cl, allowed to warm to room temperature, and then filtered. The filtrate was evaporated *in vacuo*, and the residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 4 : 1) to give **24** (326 mg, 89%). $[\alpha]_D^{18}$ +12.9° (c=0.684, $CHCl_3$). IR (neat) cm^{-1}: 3475, 1440, 1400, 1370. ^1H-NMR ($CDCl_3$) δ: 1.39 (s, 3H), 1.45 (s, 3H), 1.47 (s, 3H), 1.47 (s, 3H), 2.70—2.83 (m, 1H), 3.56 (d, 1H, J=6.0 Hz), 3.72—3.93 (m, 2H), 3.74 (ddd, 1H, J=3.5, 3.5, 4.0 Hz), 3.85 (dd, 1H, J=3.5, 13.0 Hz), 4.00 (dd, 1H, J=6.0, 9.0 Hz), 4.06 (dd, 1H, J=4.0, 13.0 Hz), 4.35—4.42 (m, 1H), 4.36 (dd, 1H, J=3.5, 5.0 Hz), 4.51 (ddd, 1H, J=5.0, 6.0, 6.0 Hz), 4.68 (dd, 1H, J=6.0, 9.0 Hz). ^{13}C-NMR ($CDCl_3$) δ: 20.32, 25.40, 27.93, 28.06, 60.66, 60.85, 69.48, 72.93, 73.76, 75.35, 77.36, 77.87, 98.56, 108.72. FAB-MS *m/z* (%): 305 (M^++1, 24), 247 (43), 189 (11), 154 (100). HR-MS Calcd for $C_{14}H_{25}O_7$: 305.1600. Found: 305.1592.

(2*S*,3*S*,3a*S*,7a*R*)-2-[(1*S*,2*S*)-1,2-Isopropylidenedioxy-3-trimethylacetyloxypropyl]-5,5-dimethyl-3-triethylsilyloxy-5*H*,7*H*-2,3,3a,7a-tetrahydro-4,6-dioxabenzo[*b*]furan (25) Pivaloyl chloride (65 ml, 0.52 mmol) was added to a stirred solution of **24** (18.9 mg, 62 mmol) and DMAP (1.5 mg, 12 mmol) in a 3 : 2 mixture of CH_2Cl_2 and pyridine (0.5 ml) at room temperature. After 1 h, MeOH was added, and stirring was continued for 30 min. 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 (*n*-hexane–EtOAc 2 : 1) to give an ester.

TES chloride (44 μl, 0.26 mmol) was added to a stirred solution of the ester, imidazole (44 mg, 0.65 mmol), and DMAP (1.5 mg, 12 mmol) in dimethyl formamide (DMF) (0.5 ml) at room temperature under argon. After 4 h, MeOH was added, and stirring was continued for 30 min. The reaction mixture 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 2 : 1) to give **25** (25.2 mg, 81%). $[\alpha]_D^{17}$ −11.0° (c=0.484, $CHCl_3$). IR (neat) cm^{-1}: 1720. ^1H-NMR ($CDCl_3$) δ: 0.57—0.68 (m, 6H), 0.97 (t, 9H, J=8.0 Hz), 1.21 (s, 9H), 1.33 (s, 3H), 1.38 (s, 6H), 1.43 (s, 3H), 3.71 (ddd, 1H, J=4.0, 4.5, 5.0 Hz), 3.77 (dd, 1H, J=5.0, 11.5 Hz), 3.86 (dd, 1H, J=5.5, 8.5 Hz), 3.91 (dd, 1H, J=4.0, 11.5 Hz), 4.13 (dd, 1H, J=4.5, 5.0 Hz), 4.27 (dd, 1H, J=8.0, 11.5 Hz), 4.35 (dd, 1H, J=3.0, 11.5 Hz), 4.40 (ddd, 1H, J=3.0, 6.0, 8.0 Hz), 4.49 (dd, 1H, J=5.0, 5.5 Hz), 4.62 (dd, 1H, J=6.0, 8.5 Hz). FAB-MS *m/z* (%): 503 (M^++1, 14), 487 (54), 473 (48), 445 (100), 387 (18), 157 (65), 115 (40), 57 (45). HR-MS Calcd for $C_{25}H_{47}O_8Si$: 503.3040. Found: 503.3068.

Ethyl (2*E*,4*S*,5*S*)-5-[(2*S*,3*S*,3a*S*,7a*R*)-5,5-Dimethyl-3-triethylsilyloxy-5*H*,7*H*-2,3,3a,7a-tetrahydro-4,6-dioxabenzo[*b*]furan-2-yl]-4,5-isopropylidenedioxy-2-heptenate (9) A 1.0 M solution of DIBAH in *n*-hexane (2.9 ml, 2.88 mmol) was added dropwise to a stirred solution of **25** (363 mg, 0.72 mmol) in CH_2Cl_2 (4 ml) at −78 °C under argon. After 1.5 h, MeOH (4 ml) was added, and stirring was continued for 30 min. The reaction mixture was allowed to warm to room temperature, then stirred with Et_2O and saturated aqueous Rochelle salt for 2 h, and 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 1 : 1) to give an alcohol as a colorless oil (296 mg, 98%). ^1H-NMR ($CDCl_3$) δ: 0.58—0.68 (m, 6H), 0.97 (t, 9H, J=8.0 Hz), 1.34 (s, 3H), 1.39 (s, 3H), 1.40 (s, 3H), 1.43 (s, 3H), 2.85—3.00 (m, 1H), 3.66—3.90 (m, 4H), 3.94 (dd, 1H, J=4.0, 12.0 Hz), 3.98 (dd, 1H, J=6.0, 8.0 Hz), 4.18 (dd, 1H, J=5.0, 6.0 Hz), 4.28—4.34 (m, 1H), 4.52 (dd, 1H, J=5.0, 6.0 Hz), 4.61 (dd, 1H, J=6.0, 8.0 Hz).

DMSO (0.7 ml, 9.9 mmol) was added to a stirred solution of $(COCl)_2$ (0.47 ml, 5.4 mmol) in CH_2Cl_2 (2 ml) at −78 °C under argon. After 15 min, a solution of the alcohol (362 mg, 0.87 mmol) in CH_2Cl_2 (3 ml) was slowly added dropwise, and stirring was continued for 30 min. A solution of Et_3N (1.9 ml, 13.5 mmol) was added dropwise during 10 min, and stirring was continued for 1.5 h. The reaction mixture was poured into saturated aqueous NH_4Cl, and 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 2 : 1) to give an aldehyde.

Diisopropyl ethoxycarbonylmethanephosphonate (1.3 ml, 5.4 mmol) was added to a stirred 1.0 M solution of *tert*-BuOK in THF (4.5 ml, 4.5 mmol) at 0 °C under argon. After 30 min at room temperature, the solution was cooled to −78 °C, and a solution of the aldehyde in THF (3 ml) was added dropwise. After 45 min, the reaction was quenched with saturated aqueous NH_4Cl, 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 4 : 1) to give **9** as a colorless oil (347 mg, 83%). $[\alpha]_D^{17}$ −21.3° (c=0.544, $CHCl_3$). IR (neat) cm^{-1}: 1710, 1650, 1160. ^1H-NMR ($CDCl_3$) δ: 0.64 (q, 6H, J=8.0 Hz), 0.97 (t, 9H, J=8.0 Hz), 1.28 (t, 3H, J=7.0 Hz), 1.36 (s, 3H), 1.38 (s, 3H), 1.40 (s, 3H), 1.50 (s, 3H), 3.69 (dd, 1H, J=5.5, 9.0 Hz), 3.73 (ddd, 1H, J=4.0, 4.0, 5.5 Hz), 3.77 (dd, 1H, J=5.5, 11.5 Hz), 3.91 (dd, 1H, J=4.0, 11.5 Hz), 4.13 (dd, 1H, J=4.0, 5.0 Hz), 4.19 (q, 2H, J=7.0 Hz), 4.47 (dd, 1H, J=5.0, 5.5 Hz), 4.73 (dd, 1H, J=6.5, 9.0 Hz), 4.81 (ddd, 1H, J=2.0, 5.0, 6.5 Hz), 6.10 (dd, 1H, J=2.0, 15.5 Hz), 7.15 (dd, 1H, J=5.0, 15.5 Hz). ^{13}C-NMR ($CDCl_3$) δ: 4.85, 6.79, 14.28, 21.18, 25.46, 27.76, 27.80, 60.24, 60.97, 70.10, 73.03, 73.90, 75.46, 77.09, 78.73, 98.24, 109.44, 122.02, 145.90, 166.57. FAB-MS *m/z* (%): 487 (M^++1, 19), 471 (23), 429 (1.6), 371 (75), 355 (26), 287 (59), 199 (84), 115 (93), 87 (100). HR-MS Calcd for $C_{24}H_{43}O_8Si$: 487.2727. Found: 487.2710.

Ethyl [(4a*S*,4b*S*,6*S*,7*S*,8*S*,8a*S*,9a*R*)-7,8-Isopropylidenedioxy-3,3-dimethyl-1,4a,4b,6,7,8,8a,9a-octahydro-3*H*-2,4,5,9-tetrahydrofluoren-6-yl]-acetate (29) A 1.0 M solution of TBAF in THF (2.2 ml, 2.14 mmol) was added to a stirred solution of **9** (374 mg, 0.714 mmol) at room temperature. After 1 h, the reaction mixture was diluted with Et_2O, 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 **29** as a colorless oil (256 mg, 96%). $[\alpha]_D^{17}$ −25.3° (c=2.40, $CHCl_3$). ^1H-NMR ($CDCl_3$) δ: 1.26 (t, 3H, J=7.0 Hz), 1.36 (s, 3H), 1.41 (s, 3H), 1.44 (s, 3H), 1.51 (s, 3H), 2.63—2.68 (m, 2H), 3.70 (ddd, 1H, J=5.0, 5.0, 6.0 Hz), 3.89 (dd, 1H, J=6.0, 12.0 Hz), 4.00 (dd, 1H, J=5.0, 5.0 Hz), 4.04 (dd, 1H, J=6.0, 12.0 Hz), 4.08—4.24 (m, 2H), 4.28 (dd, 1H, J=2.0, 5.0 Hz), 4.29 (dd, 1H, J=2.0, 7.0 Hz), 4.37 (dd, 1H, J=5.0, 7.0 Hz), 4.36—4.42 (m, 1H), 4.47 (dd, 1H, J=5.0, 7.0 Hz). ^{13}C-NMR ($CDCl_3$) δ: 14.19, 21.75, 25.11, 26.17, 26.20, 39.25, 59.80, 60.48, 71.31, 71.75, 72.60, 74.14, 74.42, 74.95, 75.22, 99.25, 110.08, 170.15. FAB-MS *m/z* (%): 373 (M^++1, 17), 315 (100), 289 (5.5). HR-MS Calcd for $C_{18}H_{29}O_8$: 373.1863. Found: 373.1847.

Ethyl [(4a*S*,4b*S*,6*R*,7*S*,8*S*,8a*S*,9a*R*)-7,8-Isopropylidenedioxy-3,3-dimethyl-1,4a,4b,6,7,8,8a,9a-octahydro-3*H*-2,4,5,9-tetraoxafluoren-6-yl]-acetate (30) A solution of **29** (26 mg, 54 mmol) in THF (1.0 ml) was added dropwise to a stirred 1.2 M solution of *tert*-BuOK in THF (179 μl, 215 μmol) at −78 °C under argon. After 30 min, the reaction mixture was poured into saturated aqueous NH_4Cl 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 1 : 1) to give **30** as a colorless oil (18 mg, 69%). $[\alpha]_D^{17}$ −20.0° (c=0.68, $CHCl_3$). ^1H-NMR ($CDCl_3$) δ: 1.01 (t, 3H, J=7.5 Hz), 1.16 (s, 3H), 1.34 (s, 3H), 1.35 (s, 3H), 1.49 (s, 3H), 3.28 (q, 1H, J=4.5 Hz), 3.41 (dd, 1H, J=2.0, 10.0 Hz), 3.43 (dd, 1H, J=3.0, 10.0 Hz), 3.49 (d, 1H, J=7.0 Hz), 3.66 (dd, 1H, J=4.5, 12.0 Hz), 3.78 (dd, 1H, J=4.5, 12.0 Hz), 3.81—3.84 (m, 2H), 4.01 (q, 2H, J=7.5 Hz), 4.37 (dt, 1H, J=7.0, 5.5 Hz), 5.40—5.45 (m, 1H). FAB-MS *m/z* (%): 373 (M^++1, 12), 315 (100), 289 (3.0). HR-MS Calcd for $C_{18}H_{29}O_8$: 373.1863. Found: 373.1839.

[(4a*S*,4b*S*,6*S*,7*S*,8*S*,8a*S*,9a*R*)-7,8-Isopropylidenedioxy-3,3-dimethyl-1,4a,4b,6,7,8,8a,9a-octahydro-3*H*-2,4,5,9-tetraoxafluoren-6-yl]propanenitrile (38) $LiAlH_4$ (82 mg, 2.06 mmol) was added to a stirred solution of **29** (256 mg, 0.687 mmol) in Et_2O (5 ml) at 0 °C under argon. After 45 min, a 1 : 1 mixture of CH_2Cl_2 and MeOH (1 ml) was added and stirring was continued for 30 min. H_2O (80 μl), 30% NaOH (80 μl), and H_2O (240 μl) were added at 10 min intervals, and the mixture was vigorously stirred with Celite and filtered. The filtrate was evaporated *in vacuo*, and the residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 1 : 3) to give an alcohol as a colorless oil (212 mg, 93%).

Tosyl chloride (TsCl) (115 mg, 0.6 mmol) was added to a stirred solution of the alcohol (63.6 mg, 0.193 mmol), Et_3N (170 μl, 1.2 mmol), DMAP (3.7 mg, 0.03 mmol) in CH_2Cl_2 (1 ml) at room temperature under argon. After 10 h, MeOH (60 μl) was added, and stirring was continued for 30 min. The reaction mixture 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 a tosylate as a colorless oil (94.8 mg, 100%). ^1H-NMR ($CDCl_3$) δ: 1.29 (s, 3H), 1.34

(s, 3H), 1.37 (s, 3H), 1.49 (s, 3H), 1.56 (s, 3H), 1.85—2.00 (m, 1H), 2.04—2.20 (m, 1H), 3.65—3.75 (m, 2H), 3.83 (ddd, 1H, $J=3.5$, 9.0, 9.0 Hz), 3.92—4.05 (m, 3H), 4.14 (ddd, 1H, $J=6.0$, 9.5, 9.5 Hz), 4.27—4.36 (m, 3H), 4.39 (dd, 1H, $J=5.0$, 7.0 Hz), 7.31—7.34 (m, 2H), 7.77—7.81 (m, 2H).

NaCN (20 mg, 0.39 mmol) was added to a stirred solution of the tosylate (62 mg, 0.129 mmol) in DMSO (1 ml) at room temperature under argon. After 1.5 h at 60 °C, the reaction mixture was diluted with Et_2O, 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 : 2) to give **38** as a colorless oil (45.6 mg, 100%). $[\alpha]_{\mathrm{D}}^{17}$ $-18.4°$ ($c=0.468$, $CHCl_3$). IR (neat) cm^{-1}: 2220. ^{1}H-NMR ($CDCl_3$) δ: 1.37 (s, 3H), 1.41 (s, 6H), 1.52 (s, 3H), 1.86 (dddd, 1H, $J=6.0$, 9.0, 10.0, 14.0 Hz), 2.14 (dddd, 1H, $J=3.5$, 9.0, 10.0, 14.0 Hz), 2.46 (ddd, 1H, $J=6.0$, 10.0, 17.0 Hz), 2.67 (ddd, 1H, $J=6.0$, 10.0, 17.0 Hz), 3.77 (ddd, 1H, $J=5.0$, 6.0, 7.0 Hz), 3.78 (dd, 1H, $J=7.0$, 12.0 Hz), 3.85 (ddd, 1H, $J=3.5$, 9.0, 9.5 Hz), 3.98 (dd, 1H, $J=7.0$, 9.5 Hz), 3.99 (dd, 1H, $J=4.5$, 5.0 Hz), 4.03 (dd, 1H, $J=6.0$, 12.0 Hz), 4.36 (dd, 1H, $J=5.0$, 7.0 Hz), 4.37 (dd, 1H, $J=4.5$, 7.0 Hz), 4.44 (dd, 1H, $J=5.0$, 7.0 Hz). ^{13}C-NMR ($CDCl_3$) δ: 13.52, 21.97, 24.98, 26.03, 26.08, 30.85, 71.62, 72.57, 73.14, 74.43, 74.73, 74.83, 75.48, 99.54, 110.26, 120.06. FAB-MS *m/z* (%): M^+ 355 (1.0), 295 (5.0), 57 (100), 43 (74).

Methyl [(4a*S*,4b*S*,6*S*,7*S*,8*S*,8a*S*,9a*S*)-7,8-Isopropylidenedioxy-3,3-dimethyl-1,4a,4b,6,7,8,8a,9-octahydro-3*H*-2,4,5,9-tetraoxafluoren-6-yl]-2*E*-pentenoate (39) A solution of **38** (36 mg, 0.106 mmol) in CH_2Cl_2 (1 ml) was added to a stirred 0.93 M solution of DIBAH in *n*-hexane (340 μl, 0.318 mmol) at −78 °C under argon. After 1 h, MeOH (30 μl) was added, and stirring was continued for 20 min. The reaction mixture was allowed warm to room temperature, and stirred with saturated aqueous NH_4Cl (2 ml) for 30 min. After addition of Rochelle salt, the reaction mixture was stirred for 1 h, then 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 (*n*-hexane–EtOAc 1 : 2) to give an aldehyde as a colorless oil (37 mg, 100%).

Methyl triphenylphosphonylideneacetate (183 mg, 0.51 mmol) was added to a stirred solution of the aldehyde (60.5 mg, 0.17 mmol) in CH_2Cl_2 (2 ml) at room temperature. After 9 h, the reaction mixture was evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 1 : 2) to give **39** as a colorless oil (69 mg, 98%). $[\alpha]_{\mathrm{D}}^{18}$ $-13.7°$ ($c=0.888$, $CHCl_3$). IR (neat) cm^{-1}: 1720, 1650, 1210. ^{1}H-NMR ($CDCl_3$) δ: 1.37 (s, 3H), 1.39 (s, 3H), 1.41 (s, 3H), 1.52 (s, 3H), 1.50—1.75 (m, 1H), 1.83—1.95 (m, 1H), 2.27—2.40 (m, 1H), 2.47—2.59 (m, 1H), 3.72 (s, 3H), 3.72 (ddd, 1H, $J=5.0$, 6.0, 6.5 Hz), 3.79 (dd, 1H, $J=6.5$, 11.5 Hz), 3.89 (ddd, 1H, $J=4.0$, 8.0, 8.5 Hz), 3.97 (dd, 1H, $J=4.0$, 5.0 Hz), 3.99 (dd, 1H, $J=7.0$, 8.0 Hz), 4.03 (dd, 1H, $J=6.0$, 11.5 Hz), 4.36 (dd, 1H, $J=5.0$, 8.0 Hz), 4.37 (dd, 1H, $J=5.0$, 7.0 Hz), 4.44 (dd, 1H, $J=5.0$, 7.0 Hz), 5.85 (dd, 1H, $J=1.5$, 16.0 Hz), 7.04 (dd, 1H, $J=6.5$, 16.0 Hz). ^{13}C-NMR ($CDCl_3$) δ: 21.9, 25.04, 26.03, 26.10, 28.40, 33.40, 51.37, 59.84, 71.60, 72.77, 74.18, 74.62, 74.78, 75.29, 75.57, 99.45, 109.97, 120.87, 149.34, 167.15.

Methyl (2*E*)-5-[(2*R*,3*S*,3a*S*,5*S*,6*S*,7*S*,7a*S*)-3,6,7-Trihydroxy-2-(hydroxymethyl)-3,3a,5,6,7,7a-hexahydro-2*H*-furo[3,2-*b*]pyran-5-yl]-2-pentenoate (8) *dl*-CSA (70 mg, 0.315 mmol) was added to a stirred solution of **39** (41.7 mg, 0.105 mmol) in MeOH (1 ml) at room temperature. After 2.5 h, the reaction mixture was neutralized with Amberlyst A26, and filtered. The filtrate was evaporated *in vacuo*. The residue was chromatographed on a silica gel column (CH_2Cl_2–MeOH 10 : 1) to give **8** as a colorless oil (22.2 mg, 67%), which was immediately subjected to the next reaction.

Methyl {(2*R*,3*S*,3a*S*,4a*R*,7*R*,8a*S*,9*S*,9a*S*)-3,9-Dehydroxy-2-(trityloxymethyl)-2,3,3a,4a,5,6,7,8a,9,9a-decahydro-1,4,8-trioxa-1*H*-benz[*f*]-inden-7-yl}acetate (7) A 1 M solution of TBAF in THF (0.1 ml, 0.1 mmol) was added to a stirred solution of **8** (11.2 mg, 35 μmol) in THF (1 ml) at room temperature. After 1.5 h, the reaction mixture was evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 1 : 3, then CH_2Cl_2–MeOH 10 : 1) to give an alcohol as a colorless oil.

Trityl chloride (33 mg, 0.105 mmol) was added to a stirred solution of the alcohol, Et_3N (50 μl, 0.315 mmol), DMAP (3 mg, 24 μmol) in CH_2Cl_2 (0.75 ml) at room temperature. After 15 h, MeOH (10 μl) was added, and stirring was continued for 30 min. The reaction mixture was evaporated *in vacuo*, and the residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 1 : 1) to give a 2 : 1 mixture of **7** and its C3 isomer as a colorless oil (15 mg, 76%).

A 1.0 M solution of TBAF in THF (80 μl, 80 mmol) was added to a stirred solution of the mixture (11.5 mg, 21 μmol) in THF (0.75 ml) at room temperature. After 15 h, the reaction mixture was diluted with Et_2O, 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 **7** as a colorless oil (9.0 mg, 78%). ^{1}H-NMR ($CDCl_3$) δ: 1.36—1.48 (m, 2H), 1.74—1.84 (m, 1H), 2.10—2.20 (m, 1H), 2.24 (dd, 1H, $J=5.5$, 15.5 Hz), 2.59 (dd, 1H, $J=7.5$, 15.5 Hz), 2.82—2.86 (m, 1H), 3.06 (dd, 1H, $J=2.0$, 10.0 Hz), 3.37 (dd, 1H, $J=6.5$, 10.0 Hz), 3.42 (dd, 1H, $J=5.0$, 10.0 Hz), 3.69 (s, 3H), 3.84—3.92 (m, 1H), 3.95—4.04 (m, 5H), 4.05—4.24 (m, 1H), 4.39 (dd, 1H, $J=5.0$, 9.0 Hz), 7.20—7.32 (m, 8H), 7.45—7.50 (m, 7H). ^{13}C-NMR ($CDCl_3$) δ: 29.79, 30.18, 40.40, 51.76, 62.40, 65.87, 66.24, 72.73, 72.95, 74.78, 75.22, 76.70, 80.34, 86.96, 127.03, 127.82, 128.80, 143.87.

(2*S*,3*S*,4*R*,5*R*)-3-Benzyloxy-5-hydroxymethyl-2-[(1*S*,2*S*)-1,2-isopropylidenedioxy-3-trityloxypropyl]-4-(4-methoxybenzyloxy)tetrahydrofuran (40) A solution of trityl chloride (11.5 g, 41.2 mmol) in CH_2Cl_2 (15 ml) was added to a stirred solution of **21** (23.5 g, 35 mmol), Et_3N (17.2 ml, 124 mmol) and DMAP (457 mg, 3.74 mmol) in CH_2Cl_2 (250 ml) was added dropwise at room temperature. After 4 h, the reaction was quenched with MeOH (6.0 ml), and the mixture was concentrated *in vacuo*, diluted with Et_2O (300 ml), 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 a tritylate as a pale yellow oil (28.2 g, 88%). $[\alpha]_{\mathrm{D}}^{18}$ $+10.6°$ ($c=1.68$, $CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.06 (s, 9H), 3.03 (d, 1H, $J=6.0$ Hz), 3.06 (d, 1H, $J=4.5$ Hz), 3.33 (dd, 1H, $J=5.0$, 10.0 Hz), 3.46 (dd, 1H, $J=7.5$, 10.0 Hz), 3.78 (dd, 1H, $J=5.5$, 10.0 Hz), 3.81 (s, 3H), 3.82—3.89 (m, 1H), 3.91 (dd, 1H, $J=3.5$, 8.0 Hz), 4.01 (ddd, 1H, $J=2.0$, 5.5, 7.5 Hz), 4.02—4.05 (m, 1H), 4.06—4.12 (m, 2H), 4.43 (d, 1H, $J=11.5$ Hz), 4.45 (d, 1H, $J=11.5$ Hz), 4.47 (d, 1H, $J=11.5$ Hz), 4.52 (d, 1H, $J=11.5$ Hz), 6.84—6.89 (m, 2H), 7.19—7.48 (m, 26H), 7.63—7.67 (m, 4H). ^{13}C-NMR ($CDCl_3$) δ: 18.3, 26.9, 55.3, 64.1, 65.3, 70.6, 71.2, 71.8, 72.1, 82.0, 82.7, 82.8, 84.8, 87.2, 113.9, 127.1, 127.7, 127.8, 127.9, 128.0, 128.5, 128.6, 129.2, 129.7, 129.8, 129.9, 133.4, 133.5, 135.6, 137.7, 143.7, 159.3.

PPTS (2.5 g, 9.95 mmol) was added to a stirred solution of the tritylate (28.2 g, 33 mmol) and 2-methoxypropene (25.3 ml, 264 mmol) in CH_2Cl_2 (250 ml) at room temperature. After 2 h, the reaction mixture was concentrated *in vacuo*, diluted with Et_2O (500 ml), 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 an acetonide as a colorless oil (31.5 g, 100%). $[\alpha]_{\mathrm{D}}^{18}$ $-0.2°$ ($c=1.7$, $CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.03 (s, 9H), 1.38 (s, 3H), 1.46 (s, 3H), 3.16 (dd, 1H, $J=5.5$, 10.0 Hz), 3.29 (dd, 1H, $J=3.0$, 10.0 Hz), 3.56 (dd, 1H, $J=8.5$, 10.0 Hz), 3.65 (dd, 1H, $J=5.0$, 10.0 Hz), 3.74 (ddd, 1H, $J=2.0$, 5.0, 8.5 Hz), 3.76 (s, 3H), 3.91—3.96 (m, 2H), 3.97 (dd, 1H, $J=0.5$, 2.0 Hz), 4.30—4.37 (m, 3H), 4.39 (d, 1H, $J=11.5$ Hz), 4.50 (br s, 2H), 6.76—6.81 (m, 2H), 7.07—7.50 (m, 28H), 7.59—7.64 (m, 4H). ^{13}C-NMR ($CDCl_3$) δ: 19.3, 25.7, 28.9, 27.7, 55.3, 63.1, 64.1, 71.0, 71.8, 73.5, 77.3, 78.6, 82.6, 83.5, 84.7, 86.5, 108.6, 113.8, 126.8, 127.5, 127.6, 128.7, 128.2, 128.9, 129.1, 129.6, 129.7, 130.1, 133.4, 133.7, 135.6, 138.4, 144.2, 159.2.

A 1.0 M solution of TBAF in THF (66 ml, 66 mmol) was added to a stirred solution of the acetonide (31.5 g, 33 mmol) in THF (200 ml) at room temperature. After 8 h, the reaction mixture was diluted with Et_2O (800 ml), 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 **40** as a colorless oil (21.1 g, 89%). $[\alpha]_{\mathrm{D}}^{18}$ $^{+}17.6°$ ($c=1.53$, $CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.42 (s, 3H), 1.50 (s, 3H), 2.16 (dd, 1H, $J=5.0$, 6.5 Hz), 3.20 (dd, 1H, $J=3.0$, 10.0 Hz), 3.52 (ddd, 1H, $J=4.5$, 6.5, 11.5 Hz), 3.58 (ddd, 1H, $J=3.0$, 5.0, 11.5 Hz), 3.68 (ddd, 1H, $J=3.0$, 3.0, 4.5 Hz), 3.79 (s, 3H), 3.84 (d, 1H, $J=3.0$ Hz), 3.91—3.95 (m, 2H), 4.28 (d, 1H, $J=11.5$ Hz), 4.35 (d, 1H, $J=11.5$ Hz), 4.38—4.45 (m, 2H), 4.56 (d, 1H, $J=11.5$ Hz), 4.60 (d, 1H, $J=11.5$ Hz), 6.80—6.82 (m, 2H), 7.08—7.10 (m, 2H), 7.18—7.48 (m, 14H), 7.49—7.50 (m, 6H). ^{13}C-NMR (400 MHz, $CDCl_3$) δ: 25.7, 27.7, 55.3, 63.0, 63.1, 71.4, 72.0, 73.4, 77.1, 78.8, 82.0, 82.8, 85.3, 86.6, 108.7, 113.9, 126.9, 127.7, 127.9, 128.4, 128.9, 129.2, 129.6, 137.7, 144.1, 159.3.

2-{2-(2*R*,3*R*,4*S*,5*S*)-4-Benzyloxy-5-[(1*S*,2*S*)-1,2-isopropylidenedioxy-3-trityloxypropyl]-3-(4-methoxybenzyloxy)tetrahydrofuranyl}acetonitrile (41) TsCl (9.86 g, 51.8 mmol) was added to a stirred solution of **40** (24.7 g, 34.5 mmol), Et_3N (21.6 ml, 155 mmol), and DMAP (842 mg, 0.69 mmol) in CH_2Cl_2 (290 ml) at 0 °C under argon. After 1.5 h, MeOH was added, and stirring was continued for 30 min. The reaction mixture was diluted with Et_2O, 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 a tosylate as a colorless oil (28.7 g, 96%). $[\alpha]_D^{30}$ +18.9° (*c*=2.14, $CHCl_3$). IR (neat) cm^{-1}: 3050, 3010, 2980, 2925, 1610, 1590, 1485, 1445, 1360, 1170. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.37 (s, 3H), 1.46 (s, 3H), 2.38 (s, 3H), 3.12 (dd, 1H, *J*=5.5, 10.5 Hz), 3.24 (dd, 1H, *J*=3.5, 10.5 Hz), 3.72—3.82 (m, 2H), 3.79 (s, 3H), 3.85—3.91 (m, 3H), 3.94 (dd, 1H, *J*=3.0, 9.5 Hz), 4.15 (dd, 1H, *J*=6.5, 9.5 Hz), 4.23 (ddd, 1H, *J*=3.5, 5.5, 6.5 Hz), 4.30 (s, 2H), 4.46 (s, 2H), 6.59—6.84 (m, 2H), 7.06—7.36 (m, 2H), 7.44—7.50 (m, 16H), 7.44—7.50 (m, 6H), 7.60—7.64 (m, 2H). ^{13}C-NMR ($CDCl_3$) δ: 21.60, 25.64, 27.63, 55.27, 62.84, 69.28, 71.11, 72.00, 73.41, 77.09, 79.06, 81.20, 81.97, 82.44, 86.52, 108.65, 113.88, 126.87, 127.62, 127.67, 128.04, 128.27, 128.84, 129.26, 129.35, 129.66, 132.79, 137.93, 144.02, 144.66, 159.33. FAB-MS *m/z* (%): 870 (M^+, 11), 625 (6.2), 243 (100), 228 (50), 211 (55), 165 (65), 121 (65), 91 (48). HR-MS Calcd for $C_{52}H_{54}O_{10}S$: 870.3438. Found: 870.3493.

NaCN (856 mg, 87.5 mmol) was added to a stirred solution of the tosylate (15.2 g, 17.5 mmol) in DMSO (130 ml) at room temperature under argon, and the mixture was warmed to 80 °C. After having been stirred for 5 h, the reaction mixture was cooled to room temperature, and 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 4 : 1) to give **41** as a colorless oil (12.1 g, 96%). $[\alpha]_D^{26}$ −10.6° (*c*=1.01, $CHCl_3$). IR (neat) cm^{-1}: 3050, 3025, 2975, 2310, 1605, 1510, 1482, 1445, 1375, 1365. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.41 (s, 3H), 1.50 (s, 3H), 2.45 (dd, 1H, *J*=7.0, 16.5 Hz), 2.50 (dd, 1H, *J*=7.5, 16.5 Hz), 3.16 (dd, 1H, *J*=5.0, 10.0 Hz), 3.32 (dd, 1H, *J*=3.5, 10.0 Hz), 3.75 (d, 1H, *J*=1.0 Hz), 3.78 (s, 3H), 3.79 (ddd, 1H, *J*=1.0, 7.0, 7.5 Hz), 3.95 (d, 1H, *J*=3.0 Hz), 4.06 (dd, 1H, *J*=3.0, 9.0 Hz), 4.30—4.39 (m, 3H), 4.39 (dd, 1H, *J*=6.0, 9.0 Hz), 4.39 (dd, 1H, *J*=6.0, 9.0 Hz), 4.54 (d, 1H, *J*=12.0 Hz), 4.61 (d, 1H, *J*=12.0 Hz), 6.78—6.84 (m, 2H), 7.06—7.12 (m, 2H), 7.18—7.38 (m, 14H), 7.46—7.51 (m, 6H). ^{13}C-NMR ($CDCl_3$) δ: 22.35, 25.66, 27.62, 55.29, 62.86, 71.36, 72.59, 73.54, 77.12, 79.63, 79.70, 82.02, 84.93, 86.58, 108.80, 113.92, 117.10, 126.87, 127.71, 127.76, 127.91, 128.44, 128.88, 129.19, 129.35, 137.80, 144.06, 159.42. FAB-MS *m/z* (%): 725 (M^+, 4.8), 724 (8.8), 482 (6.7), 243 (100), 165 (72), 136 (82), 121 (91), 91 (65). HR-MS Calcd for $C_{46}H_{46}O_7N$: 724.3283. Found: 724.3250.

(2*S*,3*S*,4*R*,5*R*)-3-Benzyloxy-5-(2-hydroxyethyl)-2-[(1*S*,2*S*)-1,2-isopropylidenedioxy-3-trityloxypropyl]-4-(4-methoxybenzyl-oxy)tetrahydrofuran (42) A 0.93 M solution of DIBAH in *n*-hexane (35.8 ml, 33.4 mmol) was added dropwise to a vigorously stirred solution of **41** (12.1 g, 16.7 mmol) in CH_2Cl_2 (360 ml) over a period of 1 h at −78 °C under argon. After an additional 1 h, MeOH wad added, and stirring was continued for 20 min. The reaction mixture was allowed to warm to room temperature, then stirred with saturated aqueous NH_4Cl for 30 min, and diluted with Et_2O. After addition of saturated aqueous Rochelle salt, the mixture was vigorously stirred until it became clear, and then 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 2 : 1) to give a crude aldehyde as a colorless oil (10.0 g).

$NaBH_4$ (2.50 g, 66.8 mmol) was added to a stirred solution of the aldehyde (10.0 g) in a 3 : 1 mixture of THF and MeOH (40 ml) at 0 °C under argon. After 4 h at room temperature, the reaction mixture was cooled to 0 °C, treated with saturated aqueous NH_4Cl, and 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 3 : 1—1 : 1) to give **42** as a colorless oil (8.90 g, 73%). $[\alpha]_D^{27}$ +8.37° (*c*=1.86, $CHCl_3$). IR (neat) cm^{-1}: 3475, 3050, 3020, 2975, 2925, 1610, 1510, 1585, 1445, 1375, 1365. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.41 (s, 3H), 1.50 (s, 3H), 1.68—1.82 (m, 2H), 1.98—2.05 (m, 1H), 3.19 (dd, 1H, *J*=6.0, 10.0 Hz), 3.32 (dd, 1H, *J*=3.5, 10.0 Hz), 3.52—3.62 (m, 3H), 3.68 (d, 1H, *J*=3.5 Hz), 3.79 (s, 3H), 3.86 (dd, 1H, *J*=3.5, 9.5 Hz), 3.93 (d, 1H, *J*=3.5 Hz), 4.23 (d, 1H, *J*=11.5 Hz), 4.32 (d, 1H, *J*=11.5 Hz), 4.38 (ddd, 1H, *J*=3.5, 6.0, 6.0 Hz), 4.45 (dd, 1H, *J*=6.0, 9.5 Hz), 4.58 (d, 1H, *J*=12.0 Hz), 4.63 (d, 1H, *J*=12.0 Hz), 6.80—6.84 (m, 2H), 7.06—7.12 (m, 2H), 7.17—7.36 (m, 14H), 7.46—7.51 (m, 6H). ^{13}C-NMR ($CDCl_3$) δ: 25.68, 27.71, 35.70, 55.29, 60.35, 63.11, 71.29, 72.17, 73.39, 77.21, 78.90, 82.55, 83.39, 86.58, 86.85, 108.74, 113.86, 126.85, 127.71, 127.78, 128.35, 128.88, 129.17, 129.66, 138.06, 144.09, 159.33. FAB-MS *m/z* (%): 729 (M^+-1, 2.3), 487 (5.9), 243 (100), 155 (15), 121 (75), 91 (63). HR-MS Calcd for $C_{46}H_{49}O_8$: 729.3428. Found: 729.3382.

(2*S*,3*S*,4*S*,5*R*)-3-Benzyloxy-5-(2-*tert*-butyldimethylsilyloxymethyl)-4-hydroxy-2-[(1*S*,2*S*)-1,2-isopropylidenedioxy-3-trityloxypropyl]tetrahydrofuran (43) TBSCl (673 mg, 4.46 mmol) was added to a stirred solution of **42** (1.63 g, 2.23 mmol) and imidazole (608 mg, 8.92 mmol) in CH_2Cl_2 (20 ml) at 0 °C under argon. After 1.5 h at room temperature, MeOH was added. The reaction mixture was stirred for 20 min, and 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 6 : 1) to give a silylate as a colorless oil (1.88 g, 100%). $[\alpha]_D^{26}$ −3.48° (*c*=0.48, $CHCl_3$). IR (neat) cm^{-1}: 3050, 3010, 2910, 2840, 1605, 1505, 1480, 1440, 1375, 1360. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 0.01 (s, 3H), 0.02 (s, 3H), 0.86 (s, 9H), 1.42 (s, 3H), 1.49 (s, 3H), 1.63—1.79 (m, 2H), 3.20 (dd, 1H, *J*=6.0, 10.0 Hz), 3.36 (dd, 1H, *J*=3.0, 10.0 Hz), 3.46—3.57 (m, 2H), 3.59 (ddd, 1H, *J*=2.5, 6.0, 10.0 Hz), 3.66 (dd, 1H, *J*=0.0, 2.5 Hz), 3.80 (s, 3H), 3.85 (dd, 1H, *J*=3.5, 9.0 Hz), 3.91 (dd, 1H, *J*=0.0, 3.5 Hz), 4.28 (d, 1H, *J*=11.5 Hz), 4.33 (d, 1H, *J*=11.5 Hz), 4.39 (ddd, 1H, *J*=3.0, 6.0, 6.0 Hz), 4.42 (dd, 1H, *J*=6.0, 9.0 Hz), 4.57 (d, 1H, *J*=12.0 Hz), 4.61 (d, 1H, *J*=12.0 Hz), 6.80—6.84 (m, 2H), 7.08—7.36 (m, 16H), 7.48—7.52 (m, 2H). ^{13}C-NMR ($CDCl_3$) δ: −5.25, −5.19, 18.31, 25.79, 25.99, 27.78, 37.44, 55.30, 60.39, 63.28, 71.09, 71.98, 73.70, 77.41, 78.53, 81.80, 82.79, 86.56, 108.63, 113.84, 126.81, 127.60, 127.67, 128.27, 128.95, 129.11, 129.97, 138.42, 144.22, 159.27. FAB-MS *m/z* (%): 843 (M^+-1, 5.4), 333 (84), 243 (100), 228 (43), 165 (56), 121 (75), 91 (64), 73 (60). HR-MS Calcd for $C_{52}H_{63}O_8Si$: 843.4293. Found: 843.4299.

DDQ (108 mg, 0.48 mmol) was added to a stirred solution of the silylate (133 mg, 0.16 mmol) in a 2 : 1 mixture of CH_2Cl_2 and a pH standard solution of phosphate (pH 6.86, 25 °C) (3.0 ml) at 0 °C. After 1 h at room temperature, saturated aqueous $NaHCO_3$ was added, and the mixture was 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 6 : 1) to give an alcohol as a colorless oil (109 mg, 95%). $[\alpha]_D^{28}$ +5.71° (*c*=0.71, $CHCl_3$). IR (neat) cm^{-1}: 3440, 3010, 2940, 2910, 2870, 2840, 1480, 1440, 1375, 1360. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 0.09 (s, 6H), 0.91 (s, 3H), 1.42 (s, 3H), 1.52 (s, 3H), 1.60 (dddd, 1H, *J*=4.5, 9.0, 9.0, 14.0 Hz), 1.74 (dddd, 1H, *J*=4.0, 4.5, 4.5, 14.0 Hz), 3.00—3.05 (m, 1H), 3.23 (ddd, 1H, *J*=4.5, 6.0, 9.0 Hz), 3.24 (dd, 1H, *J*=6.0, 10.0 Hz), 3.35 (dd, 1H, *J*=6.5, 10.0 Hz), 3.62 (ddd, 1H, *J*=4.0, 9.0, 11.0 Hz), 3.76 (dt, 1H, *J*=11.0, 4.5 Hz), 3.80 (dd, 1H, *J*=1.5, 6.0 Hz), 3.92 (dd, 1H, *J*=1.5, 5.0 Hz), 3.95 (dd, 1H, *J*=5.0, 7.5 Hz), 4.41 (ddd, 1H, *J*=3.0, 5.0, 6.0 Hz), 4.45 (dd, 1H, *J*=5.0, 7.5 Hz), 4.59 (d, 1H, *J*=12.0 Hz), 4.64 (d, 1H, *J*=12.0 Hz), 7.18—7.38 (m, 14H), 7.48—7.54 (m, 6H). ^{13}C-NMR ($CDCl_3$) δ: −5.43, −5.38, 18.31, 25.79, 25.90, 27.80, 36.01, 61.01, 63.59, 71.75, 73.61, 77.62, 78.35, 81.90, 84.58, 85.83, 86.47, 108.52, 126.81, 127.41, 127.65, 128.20, 128.95, 138.48, 144.22. FAB-MS *m/z* (%): 724 (M^+, 2.9), 613 (6.6), 333 (38), 307 (48), 243 (100), 165 (43), 154 (70), 136 (95), 91 (50). HR-MS Calcd for $C_{44}H_{56}O_7Si$: 724.3795. Found: 724.3812.

A solution of DMSO (107 µl, 1.51 mmol) in CH_2Cl_2 (0.1 ml) was added dropwise to a stirred solution of $(COCl)_2$ (78.8 µl, 0.91 mmol) in CH_2Cl_2 (0.4 ml) at −78 °C under argon. After 15 min, a solution of the alcohol (109 mg, 0.15 mmol) in CH_2Cl_2 (1.5 ml) was added dropwise, and stirring was continued for 20 min. Et_3N (315 µl, 2.27 mmol) was added dropwise during 30 min. The reaction mixture was allowed to warm to −60 °C, stirred for 1 h, then poured into ice-cold saturated aqueous NH_4Cl, and extracted with Et_2O. The extract was washed with brine, dried over Na_2SO_4, and evaporated *in vacuo* to leave a crude ketone.

$NaBH_4$ (45.5 mg, 0.60 mmol) was added to a stirred solution of the ketone in a 2 : 1 mixture of THF and MeOH (2.25 ml) at −78 °C under argon. After 1.5 h, the reaction mixture was poured into ice-cold saturated aqueous NH_4Cl, and 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 8 : 1) to give **43** as a colorless oil (104 mg, 96%). $[\alpha]_D^{25}$ −12.3° (*c*=0.77, $CHCl_3$). IR (neat) cm^{-1}: 3480, 3050, 2940, 2915, 2870, 2840, 1480, 1440, 1375, 1360. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 0.02 (s, 3H), 0.03 (s, 3H), 0.88 (s, 9H), 1.41 (s, 3H), 1.52 (s, 3H), 1.62 (dddd, 1H, *J*=6.0, 6.5, 6.5, 13.0 Hz), 1.80 (dddd, 1H, *J*=6.0, 6.5, 6.5, 13.0 Hz), 3.09 (d, 1H, *J*=8.0 Hz), 3.23 (dd, 1H, *J*=5.5, 10.0 Hz), 3.37 (dd, 1H, *J*=2.5, 10.0 Hz), 3.45 (dt, 1H, *J*=7.5, 6.0 Hz), 3.53 (dt, 1H, *J*=10.0, 6.5 Hz), 3.60 (dt, 1H, *J*=10.0, 6.5 Hz), 3.65 (dd, 1H, *J*=4.5, 8.5 Hz), 4.02 (dd, 1H, *J*=4.5, 6.0 Hz), 4.10 (ddd, 1H, *J*=6.0, 7.0, 8.0 Hz), 4.38—4.45 (m, 2H), 4.61 (d, 1H, *J*=11.0 Hz), 4.78 (d, 1H, *J*=11.0 Hz), 7.20—7.37 (m, 14H), 7.46—7.53 (m, 6H).

^{13}C-NMR (CDCl$_3$) δ: −5.30, −5.27, 18.29, 25.68, 25.95, 27.60, 32.76, 60.37, 63.22, 71.60, 74.34, 74.51, 77.23, 77.47, 78.68, 80.05, 86.56, 108.08, 126.90, 127.71, 127.82, 127.85, 128.42, 128.88, 137.86, 144.09. FAB-MS *m/z* (%): 724 (M$^+$, 3.8), 465 (10), 378 (12), 333 (32), 165 (43), 136 (51), 91 (60). HR-MS Calcd for $C_{44}H_{56}O_7Si$: 724.3797. Found: 724.3791.

(2*S*,3*S*,4*S*,5*R*)-3-Hydroxy-5-(2-hydroxyethyl)-2-[(1*S*,2*S*)-1,2-isopropylidenedioxy-3-trityloxypropyl]-4-methoxymethyloxytetrahydrofuran (44) MOMCl (1.91 ml, 25.0 mmol) was added to a stirred solution of **43** (3.04 g, 4.19 mmol), diisopropylethylamine (8.80 ml, 14.9 mmol), and DMAP (512 mg, 4.19 mmol) in CH_2Cl_2 (14 ml) at 0 °C under argon. The reaction mixture was warmed to 40 °C, stirred for 33 h, and then diluted with ice-cold MeOH. After 30 min, the reaction 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 6 : 1) to give a MOM compound as a colorless oil (3.14 g, 97%). $[\alpha]_D^{24}$ −21.0° (c=0.57, CHCl$_3$). IR (neat) cm^{-1}: 3050, 3010, 2940, 2910, 2870, 2840, 1480, 1440, 1375, 1360. ^{1}H-NMR (500 MHz, CDCl$_3$) δ: −0.02 (s, 3H), −0.01 (s, 3H), 0.87 (s, 9H), 1.36 (s, 3H), 1.49 (s, 3H), 1.68—1.86 (m, 2H), 3.21 (dd, 1H, J=6.0, 10.0 Hz), 3.34 (s, 3H), 3.39 (dd, 1H, J=2.5, 10.0 Hz), 3.46—3.62 (m, 2H), 3.77 (dd, 1H, J=4.0, 9.0 Hz), 3.81 (ddd, 1H, J=4.0, 7.5, 9.0 Hz), 4.01 (dd, 1H, J=4.0, 4.5 Hz), 4.12 (dd, 1H, J=4.5, 7.0 Hz), 4.36 (ddd, 1H, J=2.5, 6.0, 6.5 Hz), 4.39 (dd, 1H, J=6.5, 9.0 Hz), 4.57 (d, 1H, J=7.0 Hz), 4.62 (d, 1H, J=7.0 Hz), 4.68 (d, 1H, J=11.5 Hz), 4.75 (d, 1H, J=11.5 Hz), 7.18—7.40 (m, 14H), 7.46—7.53 (m, 6H). ^{13}C-NMR (CDCl$_3$) δ: −5.27, −5.19, 18.32, 25.79, 25.99, 27.80, 34.40, 55.76, 60.24, 63.20, 73.70, 74.36, 74.95, 76.76, 77.40, 77.49, 79.08, 86.52, 96.27, 108.76, 126.85, 127.29, 127.40, 127.67, 128.13, 128.93, 138.97, 144.17. FAB-MS *m/z* (%): 767 (M$^+$−1, 0.3), 333 (25), 243 (100), 165 (33), 91 (28), 73 (35), 45 (18). HR-MS Calcd for $C_{46}H_{59}O_8Si$: 767.3979. Found: 767.4011.

Na (586 mg, 25.5 mmol) was added to stirred liquid NH_3 (50 ml) at −78 °C. After 10 min, a solution of the MOM compound (653 mg, 0.85 mmol) in THF (8.0 ml) was added dropwise, and stirring was continued for 30 min. After addition of Et_2O and solid NH_4Cl, the reaction mixture was allowed to warm to room temperature. The insoluble materials were removed by filtration through a cotton plug, and the filtrate was evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 2 : 1) to give a diol as a colorless oil (350 mg, 94%). $[\alpha]_D^{25}$ +43.3° (c=0.42, CHCl$_3$). IR (neat) cm^{-1}: 3480, 2950, 2920, 2880, 2850, 1465, 1460, 1380, 1365. ^{1}H-NMR (500 MHz, CDCl$_3$) δ: 0.04 (s, 3H), 0.05 (s, 3H), 0.88 (s, 9H), 1.38 (s, 3H), 1.43 (s, 3H), 1.77—1.92 (m, 2H), 2.87—3.50 (m, 2H), 3.43 (s, 3H), 3.67 (ddd, 1H, J=5.5, 8.0, 16.0 Hz), 3.71 (ddd, 1H, J=5.0, 10.0, 16.0 Hz), 3.77—3.83 (m, 2H), 3.84 (dd, 1H, J=3.5, 9.5 Hz), 4.20 (ddd, 1H, J=4.5, 7.0, 8.5 Hz), 4.27 (dd, 1H, J=5.0, 7.0 Hz), 4.34—4.38 (m, 1H), 4.38 (q, 1H, J=6.0 Hz), 4.51 (dd, 1H, J=6.0, 9.5 Hz), 4.70 (d, 1H, J=6.5 Hz), 4.77 (d, 1H, J=6.5 Hz). ^{13}C-NMR (CDCl$_3$) δ: −5.38, 18.34, 25.33, 25.95, 27.89, 33.83, 56.22, 59.82, 60.72, 72.09, 75.22, 76.90, 77.34, 77.52, 78.09, 97.15, 108.71. FAB-MS *m/z* (%): 437 (M$^+$+1, 100), 421 (9), 405 (17), 391 (17), 379 (33), 347 (62), 154 (92), 137 (76), 89 (51), 73 (55), 45 (60). HR-MS Calcd for $C_{20}H_{41}O_8Si$: 437.2571. Found: 437.2602.

Pivaloyl chloride (707 μl, 5.84 mmol) was added to stirred solution of the diol (621 mg, 1.46 mmol) and DMAP (52.6 mg, 0.44 mmol) in a 2 : 3 mixture of pyridine and CH_2Cl_2 (10 ml) at room temperature under argon. After 3 h, MeOH wad added, and stirring was continued for 1 h. The reaction mixture was diluted with Et_2O, 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 an alcohol as a colorless oil (727 mg, 97%). $[\alpha]_D^{26}$ −1.05° (c=0.48, CHCl$_3$). IR (neat) cm^{-1}: 3490, 2940, 2920, 2880, 2845, 1720, 1470, 1445, 1370, 1360. ^{1}H-NMR (500 MHz, CDCl$_3$) δ: 0.04 (s, 6H), 0.88 (s, 9H), 1.21 (s, 9H), 1.37 (s, 3H), 1.45 (s, 3H), 1.75—1.87 (m, 2H), 2.87 (d, 1H, J=3.5 Hz), 3.42 (s, 3H), 3.66—3.76 (m, 3H), 4.06 (ddd, 1H, J=4.5, 7.0, 8.5 Hz), 4.17 (dd, 1H, J=7.5, 11.5 Hz), 4.23 (dd, 1H, J=5.0, 7.0 Hz), 4.30—4.34 (m, 1H), 4.39 (ddd, 1H, J=3.0, 6.0, 7.0 Hz), 4.43 (dd, 1H, J=3.0, 11.5 Hz), 4.45 (dd, 1H, J=6.0, 10.5 Hz), 4.61 (d, 1H, J=6.5 Hz), 4.75 (d, 1H, J=6.5 Hz). ^{13}C-NMR (CDCl$_3$) δ: −5.32, 18.36, 25.51, 25.97, 27.21, 27.91, 33.91, 38.75, 56.18, 59.97, 63.02, 72.22, 74.69, 75.71, 76.50, 77.25, 78.26, 97.11, 109.07, 178.29. FAB-MS *m/z* (%): 521 (M$^+$+1, 34), 473 (19), 431 (79), 419 (19), 387 (25), 157 (50), 89 (49), 73 (60), 57 (100), 45 (60). HR-MS Calcd for $C_{25}H_{49}O_9Si$: 521.3146. Found: 521.3174.

A 1.0 M solution of TBAF in THF (2.74 ml, 2.74 mmol) was added to a stirred solution of the alcohol (712 mg, 1.37 mmol) in THF (14 ml) at 0 °C. After 3 h, the reaction mixture was diluted with Et_2O, 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 : 2) to give **44** as a colorless oil (543 mg, 98%). $[\alpha]_D^{25}$ −4.58° (c=0.41, CHCl$_3$). IR (neat) cm^{-1}: 3490, 2950, 2920, 2880, 1720, 1470, 1450, 1375, 1360. ^{1}H-NMR (500 MHz, CDCl$_3$) δ: 1.26 (s, 9H), 1.46 (s, 3H), 1.61 (s, 3H), 1.85 (dddd, 1H, J=4.0, 5.0, 7.0, 14.0 Hz), 1.93 (dddd, 1H, J=5.0, 6.0, 7.0, 14.5 Hz), 2.06—2.13 (m, 1H), 2.93 (d, 1H, J=3.5 Hz), 3.43 (s, 3H), 3.73 (dd, 1H, J=3.5, 9.5 Hz), 3.75—3.83 (m, 2H), 4.14 (ddd, 1H, J=4.0, 7.0, 9.0 Hz), 4.20 (dd, 1H, J=8.0, 12.5 Hz), 4.27 (dd, 1H, J=5.0, 7.0 Hz), 4.31—4.36 (m, 1H), 4.38—4.43 (m, 1H), 4.40 (dd, 1H, J=3.0, 12.5 Hz), 4.48 (dd, 1H, J=6.0, 9.5 Hz), 4.70 (d, 1H, J=6.5 Hz), 4.76 (d, 1H, J=6.5 Hz). ^{13}C-NMR (CDCl$_3$) δ: 25.46, 27.20, 27.89, 32.99, 38.79, 56.24, 60.52, 62.89, 71.93, 74.51, 75.55, 77.65, 78.35, 78.44, 97.13, 109.13, 178.49. FAB-MS *m/z* (%): 407 (M$^+$+1, 61), 391 (32), 349 (38), 317 (100), 242 (14), 215 (29), 185 (20), 167 (30), 154 (81), 137 (63), 57 (80), 45 (33). HR-MS Calcd for $C_{19}H_{35}O_9$: 407.2281. Found: 407.2267.

(2*S*,3*S*,4*S*,5*R*)-2-[(1*S*,2*S*)-3-Hydroxy-1,2-isopropylidenedioxypropyl]-4-methoxymethyloxy-3-triethylsilyloxy-5-(2-trityloxyethyl)tetrahydrofuran (45) Trityl chloride (3.0 g, 10.6 mmol) was added to a stirred solution of **44** (1.51 g, 3.53 mmol), Et_3N (4.8 ml, 31.8 mmol), and DMAP (173 mg, 1.41 mmol) in CH_2Cl_2 (27 ml) at 0 °C under argon. After 15 h at room temperature, ice-cold MeOH was added, and stirring was continued for 30 min. The reaction mixture was diluted with Et_2O, 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 a tritylate as a colorless oil (2.24 g, 98%). $[\alpha]_D^{24}$ −4.96° (c=0.51, CHCl$_3$). IR (neat) cm^{-1}: 3490, 3040, 2980, 2910, 1720, 1480, 1470, 1440, 1375, 1360. ^{1}H-NMR (500 MHz, CDCl$_3$) δ: 1.21 (s, 9H), 1.36 (s, 3H), 1.44 (s, 3H), 1.86—1.98 (m, 2H), 2.81 (d, 1H, J=3.5 Hz), 3.13 (dt, 1H, J=9.0, 6.0 Hz), 3.20 (dt, 1H, J=9.0, 7.0 Hz), 3.37 (s, 3H), 3.37 (dd, 1H, J=7.5, 12.0 Hz), 4.14 (dd, 1H, J=7.5, 12.0 Hz), 4.14—4.21 (m, 2H), 4.26 (dd, 1H, J=3.0, 12.0 Hz), 4.14—4.33 (m, 2H), 4.38 (dd, 1H, J=6.0, 9.5 Hz), 4.61 (d, 1H, J=6.5 Hz), 4.69 (d, 1H, J=6.5 Hz), 7.19—7.33 (m, 9H), 7.37—7.48 (m, 6H). ^{13}C-NMR (CDCl$_3$) δ: 25.51, 27.23, 27.89, 31.53, 38.80, 56.20, 60.28, 62.91, 72.20, 74.63, 75.60, 76.72, 77.21, 78.29, 86.49, 97.15, 109.05, 126.87, 127.72, 128.69, 144.33, 178.24. FAB-MS *m/z* (%): 647 (M$^+$−1, 4.7), 605 (5.3), 604 (3.8), 561 (5.3), 559 (21), 331 (28), 243 (100), 85 (47). HR-MS Calcd for $C_{38}H_{47}O_9$: 647.3220. Found: 647.3180.

TESCl (517 μl, 3.08 mmol) was added to a stirred solution of the tritylate (807 mg, 1.24 mmol), imidazole (847 mg, 12.4 mmol), and DMAP (76 mg, 0.62 mmol) in DMF (10 ml) at 0 °C under argon. The reaction mixture was warmed to 40 °C, stirred for 15 h, and then cooled to 0 °C. MeOH was added, and stirring was continued for 30 min. The reaction mixture was diluted with Et_2O, washed with brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 6 : 1) to give a silylate as a colorless oil (947 mg, 100%). $[\alpha]_D^{25}$ −3.45° (c=0.47, CHCl$_3$). IR (neat) cm^{-1}: 3040, 2940, 2860, 1720, 1480, 1475, 1440, 1375, 1360. ^{1}H-NMR (500 MHz, CDCl$_3$) δ: 0.63 (q, 6H, J=8.0 Hz), 0.97 (t, 6H, J=8.0 Hz), 1.23 (s, 9H), 1.31 (s, 3H), 1.40 (s, 3H), 1.89 (dddd, 1H, J=3.5, 6.5, 9.0, 14.5 Hz), 1.97 (tq, 1H, J=5.0, 9.5 Hz), 3.09 (ddd, 1H, J=5.0, 6.0, 9.0 Hz), 3.20 (dt, 1H, J=5.5, 9.0 Hz), 3.36 (s, 3H), 3.80 (dd, 1H, J=4.0, 9.5 Hz), 4.13 (dd, 1H, J=4.0, 7.0 Hz), 4.19—4.34 (m, 6H), 4.61 (d, 1H, J=6.5 Hz), 4.69 (d, 1H, J=6.5 Hz), 7.19—7.33 (m, 9H), 7.47—7.49 (m, 6H). ^{13}C-NMR (CDCl$_3$) δ: 4.94, 6.90, 25.70, 27.27, 27.91, 32.06, 38.77, 55.83, 60.21, 63.68, 73.17, 74.20, 75.22, 75.70, 77.26, 77.34, 86.32, 96.09, 108.85, 126.77, 127.65, 128.73, 144.49, 178.38. FAB-MS *m/z* (%): 761 (M$^+$−1, 0.5), 675 (6), 243 (100), 187 (21), 165 (38), 115 (12), 87 (10), 57 (15). HR-MS Calcd for $C_{44}H_{61}O_9Si$: 761.4085. Found: 761.4147.

A solution of the silylate (2.63 g, 3.45 mmol) in CH_2Cl_2 (4.0 ml) was added dropwise to a stirred 1.0 M solution of DIBAH in *n*-hexane (29.7 ml, 27.6 mmol) diluted with CH_2Cl_2 (10 ml) at −78 °C under argon. After 1.5 h, MeOH was added, and stirring was continued for 20 min. The reaction mixture was diluted with Et_2O, allowed to warm to 0 °C, then vigorously stirred with saturated Rochelle salt until it became clear, and 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 4 : 1) to give **45** as a colorless oil (2.32 g, 99%). $[\alpha]_D^{27}$ +21.6° (c=0.46, CHCl$_3$). IR (neat) cm^{-1}: 3475, 3040, 2940, 2860, 1480, 1440, 1375, 1360. ^{1}H-NMR (500 MHz, CDCl$_3$) δ: 0.64 (q, 6H, J=8.0 Hz), 0.98 (t, 9H, J=8.0 Hz), 1.32 (s, 3H), 1.38 (s, 3H), 1.09—2.04 (m, 2H), 2.92 (dd, 1H, J=5.0, 9.0 Hz), 3.10—3.20 (m, 2H), 3.36 (s, 3H), 3.63 (ddd, 1H, J=5.0, 9.0, 12.0 Hz), 3.73 (ddd, 1H,

J=5.0, 7.5, 12.0 Hz), 3.87 (dd, 1H, J=3.5, 9.5 Hz), 4.18 (dd, 1H, J=4.0, 7.5 Hz), 4.21 (dt, 1H, J=7.5, 5.0 Hz), 4.30—4.38 (m, 3H), 4.60 (d, 1H, J=6.5 Hz), 4.67 (d, 1H, J=6.5 Hz), 7.21—7.31 (m, 9H), 7.37—7.40 (m, 6H). ^{13}C-NMR ($CDCl_3$) δ: 4.94, 6.88, 25.29, 27.93, 32.15, 55.85, 60.39, 61.12, 72.88, 74.60, 75.82, 76.90, 77.67, 77.85, 86.43, 96.03, 108.17, 126.85, 127.72, 128.66, 144.42. FAB-MS m/z (%): 564 {$M^+ - 116(-Et_3Si)$, 0.7}, 484 (1.5), 243 (100), 165 (52), 115 (48), 87 (37), 59 (36), 45 (30).

Ethyl (2*E*)-5-[2-(2*S*,3*S*,4*S*,5*R*)-4-Methoxymethyloxy-3-triethylsilyloxy-5-(2-trityloxyethyl)tetrahydrofuranyl]-4,5-isopropylidenedioxy-2-pentenate (46) A solution of DMSO (217 μl, 3.07 mmol) in CH_2Cl_2 (0.5 ml) was added dropwise to a stirred solution of $(COCl)_2$ (178 μl, 2.04 mmol) in CH_2Cl_2 (1.5 ml) at −78 °C under argon. After 15 min, a solution of **45** (347 mg, 0.51 mmol) in CH_2Cl_2 (3 ml) was added dropwise, and stirring was continued for 20 min. Et_3N (712 μl, 5.11 mmol) was added dropwise during 30 min. The reaction mixture was allowed to warm to −40 °C, stirred for 20 min, then poured into ice-cold saturated aqueous NH_4Cl, and 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 1 : 3) to give an aldehyde.

A 1.0 M solution of *tert*-BuOK in THF (2.0 ml, 2.0 mmol) was added dropwise to a stirred solution of ethyl diisopropylphosphonoacetate (608 μl, 2.56 mmol) in THF (1.0 ml) at 0 °C under argon. After 20 min, the solution was cooled to −78 °C, then a solution of the aldehyde in THF (2.0 ml) was added, and stirring was continued for 40 min. The reaction mixture was poured into ice-cold saturated aqueous NH_4Cl, and 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 6 : 1) to give **46** as a colorless oil (371 mg, 97%). $[\alpha]_D^{25}$ −14.8° (c=0.32, $CHCl_3$). IR (neat) cm^{-1}: 3050, 2950, 2860, 1715, 1650, 1485, 1440, 1375, 1360. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 0.62 (q, 6H, J=8.0 Hz), 0.96 (t, 9H, J=8.0 Hz), 1.24 (t, 3H, J=7.0 Hz), 1.35 (s, 3H), 1.48 (s, 3H), 1.89 (dddd, 1H, J=3.5, 6.5, 8.5, 14.5 Hz), 2.00 (ddt, 1H, J=10.0, 14.5, 5.0 Hz), 3.13 (ddd, 1H, J=5.0, 6.5, 8.5 Hz), 3.19 (dt, 1H, J=5.5, 8.5 Hz), 3.35 (s, 3H), 3.63 (dd, 1H, J=4.0, 6.5 Hz), 4.12 (dd, 1H, J=4.0, 7.0 Hz), 4.16 (q, 1H, J=7.0 Hz), 4.18 (q, 1H, J=7.0 Hz), 4.27 (ddd, 1H, J=3.5, 7.0, 10.0 Hz), 4.29 (t, 1H, J=4.0 Hz), 4.38 (dd, 1H, J=7.0, 9.5 Hz), 4.60 (d, 1H, J=6.5 Hz), 4.61 (ddd, 1H, J=1.5, 4.5, 7.0 Hz), 4.67 (d, 1H, J=6.5 Hz), 6.05 (dd, 1H, J=1.5, 15.5 Hz), 7.04 (dd, 1H, J=4.5, 15.5 Hz), 7.20—7.31 (m, 9H), 7.39—7.46 (m, 6H). ^{13}C-NMR ($CDCl_3$) δ: 4.94, 6.90, 14.28, 25.56, 27.71, 32.06, 55.83, 60.28, 60.37, 72.99, 75.15, 75.73, 77.03, 77.27, 77.89, 86.34, 96.10, 109.62, 122.13, 126.81, 127.69, 128.73, 144.51, 145.57, 166.40. FAB-MS m/z (%): 746 (M^+, 0.8), 485 (4), 378 (4), 287 (12), 259 (20), 243 (100), 165 (53), 115 (35), 87 (33), 45 (31). HR-MS Calcd for $C_{43}H_{55}O_9Si$: 746.3850. Found: 746.3808.

Ethyl {(2*R*,3*S*,3a*S*,5*S*,6*S*,7*S*,7a*R*)-6,7-Isopropylidenedioxy-3-methoxymethoxy-2-(2-trityloxyethyl)-3,3a,5,6,7,7a-hexahydro-2*H*-furo[3,2-*b*]pyran-5-yl}acetate (47) A 1.0 M solution of TBAF in THF (233 μl, 0.23 mmol) was added to a stirred solution of **46** (58.0 mg, 0.08 mmol) in THF (1.0 ml) at 0 °C. After 20 min, the reaction mixture was diluted with Et_2O, 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 : 2) to give **47** as a colorless oil (48.0 mg, 98%). $[\alpha]_D^{24}$ −50.4° (c=0.85, $CHCl_3$). IR (neat) cm^{-1}: 3040, 2960, 2910, 2875, 1725, 1480, 1440, 1370, 1360. ^{1}H-NMR (500 Hz, $CDCl_3$) δ: 1.02 (t, 3H, J=7.0 Hz), 1.33 (s, 3H), 1.51 (s, 3H), 2.11 (m, 1H), 2.35 (m, 1H), 2.55 (dd, 1H, J=8.0, 14.0 Hz), 2.74 (dd, 1H, J=4.0, 14.0 Hz), 3.75 (s, 3H), 3.40—3.47 (m, 2H), 3.53 (m, 1H), 3.70—3.77 (m, 2H), 3.96 (t, 1H, J=6.5 Hz), 3.98—4.06 (m, 3H), 4.10 (dd, 1H, J=7.5, 9.0 Hz), 4.46 (ddd, 1H, J=4.0, 8.0, 9.0 Hz), 4.56 (d, 1H, J=6.5 Hz), 4.74 (d, 1H, J=6.5 Hz), 7.07—7.11 (m, 3H), 7.18—7.22 (m, 6H), 7.62—7.64 (m, 6H). ^{13}C-NMR ($CDCl_3$) δ: 14.69, 26.49, 27.40, 30.30, 41.00, 56.16, 60.66, 62.07, 72.61, 74.31, 75.30, 75.38, 75.63, 77.13, 77.84, 87.53, 97.00, 110.92, 127.55, 128.42, 128.59, 129.09, 145.55, 170.45. FAB-MS m/z (%): 633 (M^++1, 5.1), 391 (25), 341 (17), 243 (100), 45 (99). HR-MS Calcd for $C_{37}H_{45}O_9$: 633.3051. Found: 633.3057.

5-[(2*R*,3*S*,3a*S*,5*S*,6*S*,7*S*,7a*S*)-6,7-Isopropylidenedioxy-3-methoxymethoxy-2-(2-trityloxyethyl)-3,3a,5,6,7,7a-hexahydro-2*H*-furo[3,2-*b*]pyran-5-yl]propanenitrile (48) $LiAlH_4$ (326 mg, 8.58 mmol) was added to a stirred solution of **47** (1.81 g, 2.86 mmol) in Et_2O (37 ml) at 0 °C under argon. After 1 h, MeOH was added, and stirring was continued for 30 min. H_2O (330 μl), 30% NaOH (330 μl) and H_2O (1.0 ml) were added at 10 min intervals, and then the mixture was vigorously stirred with Celite. After removal of insoluble materials by filtration, the filtrate was evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 1 : 1) to give an alcohol as a colorless oil (1.71 g, 100%). $[\alpha]_D^{22}$ −47.0° (c=0.40, $CHCl_3$). IR (neat) cm^{-1}: 3490, 2960, 2910, 2875, 1725, 1480, 1440, 1370, 1360. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.31 (s, 3H), 1.34 (s, 3H), 1.64—1.72 (m, 1H), 1.92—2.03 (m, 2H), 2.03—2.14 (m, 2H), 2.97 (t, 1H, J=7.0 Hz), 3.19—3.31 (m, 2H), 3.29 (s, 3H), 3.67—3.82 (m, 2H), 3.86 (dt, 1H, J=4.0, 9.5 Hz), 3.92 (t, 1H, J=4.0 Hz), 3.93 (ddd, 1H, J=5.0, 6.0, 8.5 Hz), 4.04 (dd, 1H, J=8.0, 9.0 Hz), 4.27—4.35 (m, 3H), 4.58 (d, 1H, J=6.5 Hz), 4.65 (d, 1H, J=6.5 Hz), 7.18—7.32 (m, 9H), 7.40—7.45 (m, 6H). ^{13}C-NMR ($CDCl_3$) δ: 25.48, 26.26, 29.37, 37.03, 56.15, 59.62, 61.12, 72.55, 73.32, 74.36, 74.69, 75.64, 77.03, 77.25, 86.58, 96.54, 100.28, 126.85, 127.78, 128.68, 144.31. FAB-MS m/z (%): 591 (M^++1, 1.2), 575 (1.3), 460 (11), 391 (4.3), 307 (41), 289 (25), 243 (66), 165 (23), 154 (67), 136 (100). HR-MS Calcd for $C_{35}H_{43}O_8$: 591.2958. Found: 591.2946.

TsCl (1.64 g, 2.86 mmol) was added to a stirred solution of the alcohol (1.69 g, 2.86 mmol), Et_3N (3.60 ml, 25.7 mmol) and DMAP (350 mg, 2.86 mmol) in CH_2Cl_2 (27.5 ml) at 0 °C under argon. After 1.5 h, MeOH was added, and stirring was continued for 30 min. The reaction mixture was diluted with Et_2O, 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 a tosylate as a colorless oil (2.05 g, 96%). $[\alpha]_D^{24}$ −43.3° (c=0.41, $CHCl_3$). IR (neat) cm^{-1}: 3040, 2910, 2860, 1585, 1480, 1440, 1355, 1160. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.28 (s, 3H), 1.31 (s, 3H), 1.78—1.88 (m, 1H), 1.88—1.98 (m, 1H), 1.98—2.12 (m, 2H), 2.40 (s, 3H), 3.14—3.20 (m, 2H), 3.21 (s, 3H), 3.67 (dt, 1H, J=3.5, 9.0 Hz), 3.82—3.89 (m, 2H), 3.91 (dd, 1H, J=8.0, 9.0 Hz), 4.08—4.22 (m, 2H), 4.20—4.24 (m, 2H), 4.25 (dd, 1H, J=4.0, 8.0 Hz), 4.41 (d, 1H, J=6.5 Hz), 4.54 (d, 1H, J=6.5 Hz), 7.18—7.34 (m, 11H), 7.40—7.45 (m, 6H), 7.76—7.81 (m, 2H). ^{13}C-NMR ($CDCl_3$) δ: 21.60, 25.48, 26.21, 29.13, 34.35, 55.93, 61.12, 67.25, 70.94, 73.26, 74.36, 74.67, 75.37, 76.06, 77.47, 86.56, 96.09, 110.31, 126.83, 127.76, 127.89, 128.68, 129.79, 144.33, 144.62. FAB-MS m/z (%): 745 (M^++1, 3.1), 460 (7.5), 341 (10), 307 (26), 289 (24), 243 (65), 219 (19), 165 (30), 136 (100), 107 (41), 89 (48), 77 (40). HR-MS Calcd for $C_{42}H_{49}O_{10}S$: 745.3047. Found: 745.3085.

NaCN (216 mg, 4.42 mmol) was added to a stirred solution of the tosylate (657 mg, 0.88 mmol) in DMSO (10 ml) at room temperature under argon. The reaction mixture was stirred for 3.3 h at 60 °C, then cooled to 0 °C, diluted with Et_2O, 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 **48** as a colorless oil (550 mg, 100%). $[\alpha]_D^{24}$ −51.8° (c=0.40, $CHCl_3$). IR (neat) cm^{-1}: 3050, 2925, 2975, 2240, 1480, 1440, 1380, 1365. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.31 (s, 3H), 1.33 (s, 3H), 1.80 (tq, 1H, J=9.0, 6.0 Hz), 1.93—2.15 (m, 3H), 2.41 (ddd, 1H, J=7.0, 9.0, 17.0 Hz), 2.50 (ddd, 1H, J=6.0, 9.0, 17.0 Hz), 3.16—3.32 (m, 2H), 3.27 (s, 3H), 3.68 (dt, 1H, J=3.5, 9.0 Hz), 3.86—3.92 (m, 2H), 3.94 (dd, 1H, J=8.0, 9.0 Hz), 4.23—4.28 (m, 2H), 4.30 (dd, 1H, J=4.0, 8.0 Hz), 4.53 (d, 1H, J=6.5 Hz), 4.64 (d, 1H, J=6.5 Hz), 7.18—7.32 (m, 9H), 7.40—7.45 (m, 6H). ^{13}C-NMR ($CDCl_3$) δ: 13.46, 25.49, 26.21, 29.13, 30.87, 56.07, 61.05, 72.81, 73.30, 74.38, 74.71, 75.22, 76.35, 77.49, 86.54, 96.38, 110.52, 119.81, 126.83, 127.76, 128.68, 144.33. FAB-MS m/z (%): 584 (M^+−15, 1.0), 460 (2.8), 341 (9.1), 307 (25), 289 (25), 243 (50), 219 (21), 154 (50), 136 (100), 120 (22), 107 (27), 89 (33), 77 (24).

Methyl (2*E*)-5-[(2*R*,3*S*,3a*S*,5*S*,6*S*,7*S*,7a*S*)-6,7-Isopropylidenedioxy-2-(2-trityloxyethyl)-3,3a,5,6,7,7a-hexahydro-2*H*-furo[3,2-*b*]pyran-5-yl]-2-pentanoate (49) A 0.93 M solution of DIBAH in *n*-hexane (2.8 ml, 2.6 mmol) was added dropwise to a vigorously stirred solution of **48** (540 mg, 0.87 mmol) in CH_2Cl_2 (12 ml) during 10 min at −78 °C under argon. After 1 h, MeOH was added, and stirring was continued for 20 min. The reaction mixture was allowed to warm to room temperature, stirred with saturated aqueous NH_4Cl for 30 min, then diluted with Et_2O, vigorously stirred with saturated aqueous Rochelle salt until it became clear, and 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 1 : 1) to give an aldehyde as a colorless oil (497 mg, 95%). $[\alpha]_D^{24}$ −57.7° (c=0.38, $CHCl_3$). IR (neat) cm^{-1}: 3040, 2910, 2870, 1715, 1480, 1440, 1375, 1360. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.31 (s, 3H), 1.33 (s, 3H), 1.79 (dddd, 1H, J=6.0, 8.0, 8.0, 14.0 Hz), 1.92—2.01 (m, 1H), 2.01—2.12 (m, 2H), 2.49—2.59 (m, 2H), 3.18—3.30 (m, 2H), 3.26 (s, 3H), 3.69 (ddd, 1H, J=4.0, 8.0, 9.0 Hz), 3.84—3.90 (m, 2H), 3.97 (dd, 1H, J=8.0, 9.0 Hz), 4.23—4.28

(m, 2H), 4.28 (dd, 1H, J=4.0, 8.0 Hz), 4.55 (d, 1H, J=6.5 Hz), 4.65 (d, 1H, J=6.5 Hz), 7.19—7.29 (m, 9H), 7.41—7.43 (m, 6H), 9.77 (s, 1H). ^{13}C-NMR ($CDCl_3$) δ: 25.52, 25.30, 27.40, 29.21, 31.87, 55.99, 61.20, 73.39, 73.44, 74.40, 74.80, 75.68, 76.31, 77.49, 86.30, 96.33, 110.25, 126.83, 127.76, 128.70, 144.38, 202.10. FAB-MS m/z (%): 557 {$M^+ - 45$ ($-CH_2OCH_3$), 0.5}, 460 (7.1), 371 (5.6), 341 (9.8), 307 (43), 289 (40), 243 (63), 219 (38), 165 (42), 136 (100), 120 (46), 107 (47), 89 (52), 77 (42).

Methoxycarbonylmethylenetriphenylphosphorane (850 mg, 2.43 mmol) was added to a stirred solution of the aldehyde (488 mg, 0.81 mmol) in CH_2Cl_2 (12 ml) at room temperature. After 15 h, the solvent was removed *in vacuo*. The residue was chromatographed on a silica gel column (n-hexane–EtOAc 1 : 2) to give **49** as a colorless oil (536 mg, 100%). $[\alpha]_D^{24}$ $-48.3°$ (c=0.41, $CHCl_3$). IR (neat) cm^{-1}: 3040, 2930, 2875, 1715, 1650, 1480, 1440, 1375, 1360. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.32 (s, 3H), 1.33 (s, 3H), 1.62 (dddd, 1H, J=5.5, 8.0, 10.0, 14.0 Hz), 1.81 (dddd, 1H, J=4.0, 5.5, 10.0, 14.0 Hz), 1.93—2.03 (m, 1H), 2.03—2.14 (m, 1H), 2.22—2.33 (m, 1H), 2.33—2.44 (m, 1H), 3.18—3.30 (m, 2H), 3.25 (s, 3H), 3.69 (s, 3H), 3.70 (ddd, 1H, J=4.0, 8.5, 9.0 Hz), 3.84—3.92 (m, 2H), 3.96 (dd, 1H, J=8.0, 9.0 Hz), 4.25—4.31 (m, 3H), 4.52 (d, 1H, J=6.5 Hz), 4.66 (d, 1H, J=6.5 Hz), 5.85 (dt, 1H, J=15.5, 2.0 Hz), 7.01 (dt, 1H, J=15.5, 7.0 Hz), 7.18—7.31 (m, 9H), 7.40—7.46 (m, 6H). ^{13}C-NMR ($CDCl_3$) δ: 25.53, 26.26, 28.00, 29.21, 33.61, 51.41, 55.96, 61.19, 73.41, 73.52, 74.38, 74.78, 75.82, 76.21, 77.47, 86.52, 96.21, 110.17, 120.99, 126.81, 127.74, 128.68, 144.37, 149.16, 167.14. FAB-MS m/z (%): 659 ($M^+ + 1$, 1.6), 460 (6.5), 397 (5.4), 371 (4.9), 341 (8.0), 307 (43), 289 (39), 243 (61), 219 (21), 165 (46), 136 (100), 107 (47), 89 (51), 77 (46). HR-MS Calcd for $C_{39}H_{47}O_9$: 659.3220. Found: 659.3230.

Methyl {(2*R*,3*S*,3a*S*,4a*S*,7*R*,8a*S*,9*R*,9a*R*)-3,9-Dihydroxy-2-(2-trityloxymethyl)-1,4,8-trioxaperhydrobenz[*f*]inden-7-yl}acetate (50) *dl*-CSA (114 mg, 0.49 mmol) was added to a stirred solution of **49** (162 mg, 0.25 mmol) in MeOH (2.5 ml) at room temperature. After 60 h, the reaction mixture was neutralized with Et_3N, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (CH_2Cl_2–MeOH 10 : 1) to give a tetraol (250 mg), which was dissolved in THF (8.0 ml). This solution was stirred with a 1.0 M solution of TBAF in THF (1.97 ml, 1.97 mmol) for 24 h. The reaction mixture was passed through a silica gel pad with CH_2Cl_2–MeOH (10 : 1), and the filtrate was evaporated *in vacuo*. The residue was chromatographed on a silica gel column (CH_2Cl_2–MeOH 10 : 1) to give a crude ester (338 mg). Trityl chloride (275 mg, 0.25 mmol) was added to a stirred solution of the crude ester, Et_3N (412 μl, 2.95 mmol) and DMAP (30.1 mg, 0.25 mmol) in CH_2Cl_2 (6.0 ml) at room temperature. After 14 h, MeOH was added, and stirring was continued for 30 min. The reaction mixture was evaporated *in vacuo*, and the residue was chromatographed on a silica gel column (n-hexane–EtOAc 1 : 1) to give a diasteroisomeric mixture (1.7 : 1) of **50** and its isomer as a colorless oil (129 mg, 91%).

A solution of the mixture (129 mg, 0.224 mmol) in THF (7.0 ml) was stirred with a 1.0 M solution of TBAF in THF (1.12 ml, 1.12 mmol) at room temperature. After 15 h, the reaction mixture was diluted with Et_2O, 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 **50** as a colorless oil (103 mg, 80%). $[\alpha]_D^{25}$ $-49.1°$ (c=0.42, $CHCl_3$). IR (neat) cm^{-1}: 3310, 3040, 2930, 2860, 1725, 1480, 1440, 1430. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.32 (s, 3H), 1.33 (s, 3H), 1.62 (dddd, 1H, J=5.5, 8.0, 10.0, 14.0 Hz), 1.81 (dddd, 1H, J=4.0, 5.5, 10.0, 14.0 Hz), 1.93—2.03 (m, 1H), 2.03—2.14 (m, 1H), 2.22—2.33 (m, 1H), 2.33—2.44 (m, 1H), 3.18—3.30 (m, 2H), 3.25 (s, 3H), 3.69 (s, 3H), 3.70 (ddd, 1H, J=4.0, 8.5, 9.0 Hz), 3.84—3.92 (m, 2H), 3.96 (dd, 1H, J=8.0, 9.0 Hz), 4.25—4.31 (m, 3H), 4.52 (d, 1H, J=6.5 Hz), 4.66 (d, 1H, J=6.5 Hz), 5.85 (dt, 1H, J=15.5, 2.0 Hz), 7.01 (dt, 1H, J=15.5, 7.0 Hz), 7.18—7.31 (m, 9H), 7.40—7.46 (m, 6H). ^{13}C-NMR ($CDCl_3$) δ: 25.53, 26.26, 28.00, 29.21, 33.61, 51.41, 55.96, 61.19, 73.41, 73.52, 74.38, 74.78, 75.82, 76.21, 77.47, 86.52, 96.21, 110.17, 120.99, 126.81, 127.74, 128.68, 144.37, 149.16, 167.14. FAB-MS m/z (%): 501 ($M^+ - 59$, 1.0), 460 (6.3), 371 (4.2), 341 (6.1), 307 (32), 154 (61), 136 (100), 107 (20), 89 (18), 77 (12).

Methyl (3*R*,6*S*,7*S*,8*S*,9*R*,10*S*,11*S*,12*S*,14*S*)-3,7-6,10-8,14-9,12-11,14-Pentaepoxytetradecanoate (51) Acetic anhydride (20 μl, 297 μmol) and DMAP (7.2 mg, 59 μmol) were added to a stirred solution of **50** (17 mg, 29 μmol) in CH_2Cl_2 (1.0 ml) at room temperature. After 1.5 h, the reaction was quenched with MeOH (0.1 ml) and the mixture was evaporated *in vacuo*. The residue was passed through a short silica gel column (n-hexane–EtOAc 1 : 1) to give a diacetate as a colorless oil (14.4 mg, 74%).

CSA (2.8 mg, 12 μmol) was added to a stirred solution of the diacetate (14.4 mg, 22 μmol) in a mixture of MeOH (0.5 ml) and H_2O (0.25 ml) at room temperature. After 12 h, the reaction mixture was diluted with CH_2Cl_2, washed with aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was passed through a short silica gel column (n-hexane–EtOAc 1 : 4) to give an alcohol as a colorless oil (7.3 mg, 80%).

A solution of the alcohol (7.3 mg, 17.5 μmol), Dess-Martin's reagent (22.3 mg, 53 μmol) and pyridine (8.5 μl, 105 μmol) in CH_2Cl_2 (1 ml) was stirred for 90 min at room temperature. The reaction mixture was diluted with Et_2O, washed with aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, and evaporated *in vacuo* to leave a crude aldehyde (6.3 mg).

The aldehyde (6.3 mg, 15 μmol) was treated with CSA (35 mg, 152 μmol) in MeOH (0.5 ml) at room temperature. After 2 d, the reaction was quenched with Et_3N, and the mixture was evaporated *in vacuo*. The residue was chromatographed on a silica gel column (n-hexane–EtOAc 1 : 8) to give **51** as a colorless oil (3.9 mg, 82%). ^{1}H-NMR ($CDCl_3$) δ: 1.35—1.45 (m, 2H), 1.77 (m, 1H), 2.00—2.06 (m, 2H), 2.04 (m, 1H), 2.45 (dd, 1H, J=4.9, 15.6 Hz), 2.55 (dd, 1H, J=7.8, 15.6 Hz), 2.99 (dd, 1H, J=2.0, 9.3 Hz), 3.83 (m, 1H), 4.10 (dd, 1H, J=3.9, 6.4 Hz), 4.20 (dd, 1H, J=4.4, 6.4 Hz), 4.25 (ddd, 1H, J=4.4, 9.3, 9.3 Hz), 4.59 (dd, 1H, J=4.4, 4.4 Hz), 4.69 (ddd, 1H, J=2.0, 4.4, 4.4 Hz).

(2*R*,3*S*,3a*S*,4a*S*,7*R*,8a*S*,9*R*,9a*R*)-7-(2-*tert*-Butyldimethylsilyloxyethyl-3,9-dihydroxy-2-(2-trityloxyethyl)-1,4,8-trioxaperhydrobenz[*f*]-indene (53) $LiAlH_4$ (130 mg, 3.45 mmol) was added to a stirred solution of **50** (495 mg, 0.86 mmol) in Et_2O (17 ml) at 0 °C under argon. After 1 h, MeOH was added, and stirring was continued for 30 min. H_2O (130 μl), 30% NaOH (130 μl) and H_2O (390 μl) were added at 10 min intervals, and the mixture was vigorously stirred with Celite. After removal of insoluble materials by filtration, the filtrate was evaporated *in vacuo*. The residue was chromatographed on a silica gel column (n-hexane–EtOAc 1 : 1) to give a triol as a colorless oil (475 mg, 100%). $[\alpha]_D^{20}$ $-41.1°$ (c=0.46, $CHCl_3$). IR (neat) cm^{-1}: 3220, 3050, 2930, 2870, 1590, 1485, 1440, 1240, 1235. ^{1}H-NMR (400 MHz, C_6D_6) δ: 1.00—1.12 (m, 2H), 1.22 (m, 1H), 1.37 (m, 1H), 1.54 (m, 1H), 2.04 (m, 1H), 2.13 (dt, 1H, J=13.0, 6.5 Hz), 2.50 (m, 1H), 2.58 (dd, 1H, J=2.0, 9.5 Hz), 3.19 (ddd, 1H, J=4.0, 8.5, 12.5 Hz), 3.41 (t, 2H, J=6.5 Hz), 3.54—3.68 (m, 2H), 3.76 (dd, 1H, J=4.5, 9.0 Hz), 3.78—3.90 (m, 4H), 4.13 (dd, 1H, J=4.5, 9.0 Hz), 4.23 (ddd, 1H, J=4.5, 9.5, 10.5 Hz), 4.90 (br d, 1H, J=12.0 Hz), 7.04—7.10 (m, 3H), 7.13—7.20 (m, 6H), 7.59—7.63 (m, 6H). ^{13}C-NMR (C_6D_6) δ: 30.32, 30.42, 30.53, 37.73, 60.61, 66.04, 66.37, 72.99, 73.43, 76.06, 77.29, 77.75, 78.97, 88.18, 127.16, 127.89, 129.53, 129.15, 144.92. FAB-MS m/z (%): 543 ($M^+ - 3$, 0.9), 481 (2.8), 371 (3.3), 307 (24), 289 (14), 243 (12), 219 (10), 154 (61), 136 (100), 107 (14), 89 (16), 77 (14).

TBS chloride (673 mg, 4.46 mmol) was added to a stirred solution of the triol (1.63 g, 2.23 mmol) and imidazole (608 mg, 8.92 mmol) in CH_2Cl_2 (20 ml) at 0 °C under argon. After 1.5 h at room temperature, MeOH was added, and stirring was continued for 20 min. The reaction mixture was diluted with Et_2O, washed with brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (n-hexane–EtOAc 6 : 1) to give **53** as a colorless oil (1.88 g, 100%). $[\alpha]_D^{17}$ $-48.5°$ (c=0.42, $CHCl_3$). IR (neat) cm^{-1}: 3350, 3050, 2950, 1445, 1260, 1215, 1170. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.04 (s, 3H), 0.04 (s, 3H), 0.89 (s, 9H), 1.34—1.46 (m, 2H), 1.60—1.78 (m, 3H), 1.89—2.06 (m, 2H), 2.15 (m, 1H), 2.98 (dd, 1H, J=2.0, 9.5 Hz), 3.06 (d, 1H, J=1.5 Hz), 3.17—3.28 (m, 2H), 3.57 (m, 1H), 3.67 (dt, 1H, J=10.0, 5.0 Hz), 3.74 (ddd, 1H, J=5.5, 8.5, 10.0 Hz), 3.84 (ddd, 1H, J=3.0, 5.0, 11.0 Hz), 3.97—4.08 (m, 2H), 4.09—4.19 (m, 2H), 4.32 (d, 1H, J=11.5 Hz), 4.37 (ddd, 1H, J=2.5, 5.0, 11.5 Hz), 7.20—7.30 (m, 9H), 7.40—7.45 (m, 6H). ^{13}C-NMR ($CDCl_3$) δ: -5.10, -5.03, 18.38, 25.97, 29.76, 30.14, 30.73, 38.52, 60.48, 66.30, 66.33, 72.42, 73.03, 75.11, 75.60, 76.72, 78.79, 88.85, 126.99, 127.82, 128.66, 144.15.

(2*R*,3*S*,3a*S*,4a*S*,7*S*,8a*S*,9*R*,9a*R*)-7-(2-*tert*-Butyldimethylsilyloxyethyl)-2-(2-hydroxyethyl)-3,9-bis(triethylsilyloxy)-1,4,8-trioxaperhydrobenz[*f*]-indene (54) TES triflate (1.5 ml, 6.54 mmol) was added to a stirred solution of **53** (432 mg, 0.65 mmol) and 2,6-lutidine (2.3 ml, 19.6 mmol) in CH_2Cl_2 (26 ml) at 0 °C under argon. After 1.5 h, MeOH was added, and stirring was continued for 20 min. The reaction mixture was diluted with Et_2O, washed with brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (n-hexane–EtOAc 15 : 1) to give a TES compound as a colorless oil.

Na (600 mg, 26.2 mmol) was added to stirred liquid NH_3 (50 ml) at -78 °C under argon. After 10 min, a solution of the TES compound in THF (10 ml) was added dropwise, and stirring was continued for 30 min. After addition of Et_2O and solid NH_4Cl, the reaction mixture was allowed to warm to room temperature. The insoluble materials were removed by filtration through a cotton plug, and the filtrate was evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 3 : 1) to give **54** as a colorless oil (350 mg, 79%). $[\alpha]_D^{19}$ $-62.8°$ ($c=0.40$, $CHCl_3$). IR (neat) cm^{-1}: 3420, 2940, 2860, 1445, 1405, 1380, 1240, 1190. ^1H-NMR (400 MHz, C_6D_6) δ: 0.16 (s, 3H), 0.16 (s, 3H), 0.74 (q, 6H, $J=8.0$ Hz), 0.91 (q, 6H, $J=8.0$ Hz), 1.05 (s, 9H), 1.12 (t, 9H, $J=8.0$ Hz), 1.22 (t, 9H, $J=8.0$ Hz), 1.31 (ddd, 1H, $J=4.0$, 10.5, 14.0 Hz), 1.40—1.49 (m, 2H), 1.55 (dddd, 1H, $J=3.0$, 5.0, 7.0, 14.0 Hz), 1.67 (dddd, 1H, $J=4.0$, 6.5, 8.5, 14.0 Hz), 1.69 (br s, 1H), 1.79 (dddd, 1H, $J=5.0$, 5.0, 9.0, 14.0 Hz), 2.17 (m, 1H), 2.23 (dddd, 1H, $J=4.5$, 7.0, 10.0, 14.0 Hz), 2.83 (dd, 1H, $J=2.0$, 9.5 Hz), 3.51 (dddd, 1H, $J=2.0$, 4.0, 9.0, 10.5 Hz), 3.69—3.93 (m, 7H), 4.05 (dd, 1H, $J=5.0$, 9.5 Hz), 4.17 (dd, 1H, $J=2.0$, 5.0 Hz), 4.20 (ddd, 1H, $J=5.0$, 9.5, 10.5 Hz). ^{13}C-NMR (C_6D_6) δ: -5.23, -5.14, 5.38, 5.60, 7.34, 7.54, 18.55, 25.15, 30.74, 31.04, 32.59, 39.23, 60.01, 61.01, 65.44, 74.43, 74.47, 74.82, 75.64, 77.82, 79.74. FAB-MS *m/z* (%): 647 (M^++1, 49), 645 (3.2), 617 (20), 243 (24), 213 (11), 201 (15), 57 (100). HR-MS Calcd for $C_{32}H_{67}O_7Si_3$: 647.4195. Found: 647.4209.

Dimethyl {3-{2-(2*R*,3*S*,3a*S*,4a*S*,7*S*,8a*S*,9*R*,9a*R*)-7-(2-*tert*-Butyldimethylsilyloxyethyl)-3,9-bis(triethylsilyloxy)-1,4,8-trioxaperhydrobenz[*f*]indenyl}oxopropyl}phosphonate (6) A solution of **54** (32.1 mg, 50 mmol) in CH_2Cl_2 (3.0 ml) was added to a stirred solution of the Dess–Martin reagent (105 mg, 0.25 mmol) and pyridine (0.1 ml, 1.24 mmol) in CH_2Cl_2 (2.0 ml) at room temperature under argon. After 30 min, the reaction mixture was diluted with Et_2O, then saturated aqueous $NaHCO_3$ and saturated aqueous $Na_2S_2O_3$ were added. After 30 min, the reaction mixture was extracted with Et_2O. The extract was washed with brine, dried over Na_2SO_4, and evaporated *in vacuo* to give a crude aldehyde. A solution of $NaClO_2$ (67 mg, 0.75 mmol) and NaH_2PO_4 (89 mg, 0.75 mmol) in H_2O (1.0 ml) was added to a stirred solution of the aldehyde and 2-methyl-2-butene (0.5 ml, 37.6 mmol) in *tert*-BuOH (2.0 ml) at room temperature. After 20 min, the reaction mixture was diluted with Et_2O, and washed with brine, then a solution of CH_2N_2 in Et_2O was added until the yellow color of CH_2N_2 persisted. After 30 min, excess CH_2N_2 was quenched with AcOH. The reaction mixture was washed with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, and evaporated *in vacuo*. The residue was chromatographed on a silica gel column (*n*-hexane–EtOAc 2 : 1) to give an ester as a colorless oil (30.9 mg, 92%). $[\alpha]_D^{18}$ $-64.0°$ ($c=0.40$, $CHCl_3$). IR (neat) cm^{-1}: 2940, 2860, 1735, 1455, 1430, 1400, 1300, 1280, 1240. ^1H-NMR (400 MHz, $CDCl_3$) δ: 0.04 (s, 3H), 0.05 (s, 3H), 0.63 (q, 6H, $J=8.0$ Hz), 0.64 (q, 6H, $J=8.0$ Hz), 0.89 (s, 9H), 0.95 (t, 9H, $J=8.0$ Hz), 0.96 (t, 9H, $J=8.0$ Hz), 1.22—1.42 (m, 2H), 1.58—1.72 (m, 3H), 2.05 (m, 1H), 2.63 (dd, 1H, $J=5.5$, 16.5 Hz), 2.78 (dd, 1H, $J=7.5$, 16.5 Hz), 2.86 (dd, 1H, $J=2.0$, 9.5 Hz), 3.46 (m, 1H), 3.69 (s, 3H), 3.72 (dddd, 1H, $J=6.0$, 8.0, 10.0, 18.0 Hz), 4.05 (m, 1H), 4.25 (dd, 1H, $J=5.5$, 9.5 Hz), 4.10 (dd, 1H, $J=2.0$, 9.5 Hz), 4.13 (dd, 1H, $J=4.0$, 5.5 Hz), 4.31 (ddd, 1H, $J=4.0$, 5.5, 7.5 Hz). ^{13}C-NMR ($CDCl_3$) δ: -5.39, -5.30, 4.88, 5.03, 7.02, 7.10, 18.40, 25.99, 30.10, 30.82, 34.73, 38.74, 51.52, 59.82, 65.45, 67.12, 73.42, 74.23, 74.58, 76.70, 77.25, 77.34, 172.35. FAB-MS *m/z* (%): 675 (M^++1, 33), 481 (8.0), 409 (11), 271 (19), 157 (23), 57 (100). HR-MS Calcd for $C_{33}H_{67}O_8Si_3$: 675.4144. Found: 675.4114.

A 1.60 M solution of *n*-BuLi in *n*-hexane (1.49 ml, 2.47 mmol) was added dropwise to a stirred solution of dimethyl methanephosphonate (669 μl, 6.16 mmol) in THF (11 ml) at -78 °C under argon. After 30 min, a solution of the ester (277 mg, 0.41 mmol) in THF (8.0 ml) was added, and stirring was continued for 30 min. The reaction mixture was poured into ice-cold saturated aqueous NH_4Cl, and 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 (Et_2O–EtOAc 1 : 3) to give **6** as a colorless oil (305 mg, 97%). $[\alpha]_D^{17}$ $-59.6°$ ($c=1.22$, $CHCl_3$). IR (neat) cm^{-1}: 2940, 2855, 1710, 1455, 1400, 1380, 1250, 1190, 1175. ^1H-NMR (400 MHz, C_6D_6) δ: 0.15 (s, 3H), 0.15 (s, 3H), 0.74 (q, 6H, $J=8.0$ Hz), 0.75 (q, 6H, $J=8.0$ Hz), 1.05 (s, 9H), 1.11 (t, 9H, $J=8.0$ Hz), 1.21 (t, 9H, $J=8.0$ Hz), 1.29 (ddd, 1H, $J=5.1$, 11.0, 14.0 Hz), 1.34—1.50 (m, 2H), 1.65 (dddd, 1H, $J=4.0$, 6.5, 8.5, 14.0 Hz), 1.77 (dddd, 1H, $J=5.0$, 5.0, 9.0, 14.0 Hz), 2.14 (m, 1H), 2.79 (dd, 1H, $J=2.0$, 9.5 Hz), 3.06 (dd, 1H, $J=13.5$, 22.5 Hz), 3.06 (dd, 1H, $J=5.5$, 17.5 Hz), 3.16 (dd, 1H, $J=13.5$, 22.5 Hz), 3.28 (dd, 1H, $J=7.0$, 17.5 Hz), 3.43 (d, 3H, $J=11.0$ Hz), 3.44 (d, 3H, 11.0 Hz), 3.48 (m, 1H), 3.75 (ddd, 1H, $J=4.5$, 6.5, 10.0 Hz), 3.78 (dd, 1H, $J=5.5$, 8.5 Hz), 3.87 (ddd, 1H, $J=5.5$, 8.5, 10.0 Hz), 4.00 (dd, 1H, $J=3.5$, 5.5 Hz), 4.03 (dd, 1H, $J=5.5$, 8.5 Hz), 4.14 (dd, 1H, $J=2.0$, 5.5 Hz), 4.18 (m, 1H), 4.31 (ddd, 1H, $J=3.5$, 5.5, 7.5 Hz). ^{13}C-NMR (C_6D_6) δ: -5.25, -5.14, 5.29, 5.64, 7.34, 7.54, 18.53, 26.15, 30.67, 31.07, 39.25, 41.57, 42.83, 44.72, 52.21, 52.29, 52.38, 59.99, 65.57, 67.61, 74.07, 74.45, 75.51, 76.87, 77.75, 199.78, 199.85. FAB-MS *m/z* (%): 767 (M^++1, 49), 766 (4.0), 737 (66), 709 (17), 503 (9.8), 347 (23), 251 (20), 57 (100). HR-MS Calcd for $C_{35}H_{72}O_{10}Si_3P$: 767.4171. Found: 767.4131.

References and Notes

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