Studies on the Sharpless asymmetric epoxidation of unsymmetrical divinylmethanols

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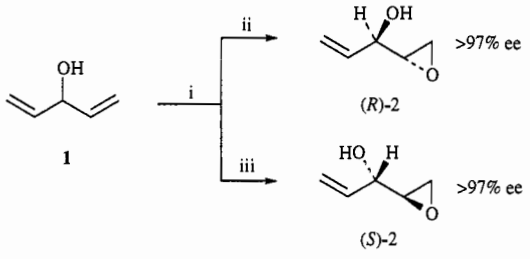
A reaction of racemic unsymmetrical divinylmethanol *rac*-13 under the Sharpless asymmetric epoxidation conditions using stoichiometric amounts of titanium tetraisopropoxide [$Ti(OPr^i)_4$], D-(−)-diisopropyl tartrate (DIPT) and *tert*-butyl hydroperoxide (TBHP) afforded *R*-14 and *R*-15 in 41 and 43% yield, each with > 99% ee, respectively, where the kinetic resolution and subsequent epoxidation had proceeded in an entirely regio- and diastereo-selective manner.

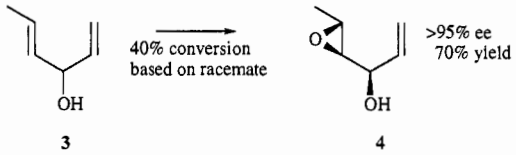
Introduction

In 1980, Sharpless and his co-workers reported the asymmetric epoxidation of a variety of allylic alcohols in high enantiomeric excess (ee) by use of the titanium(IV) alkoxide/optically active tartrate/*tert*-butyl hydroperoxide (TBHP) system.[1] Shortly thereafter, they demonstrated that the same system could be used for the kinetic resolution of secondary allylic alcohols.[2] The Sharpless asymmetric epoxidation has therefore become established as one of the most powerful tools for the introduction of asymmetric centres into a wide variety of prochiral allylic alcohols.[3] This elegant synthetic methodology was extensively applied by several groups to penta-1,4-dien-3-ol **1** (a symmetrical) divinylmethanol, to afford the chiral epoxy alcohol **2**, in good yield, where the kinetic resolution and asymmetric epoxidation process took place with high enantio- and diastereo-selectivity[4] (Scheme 1).



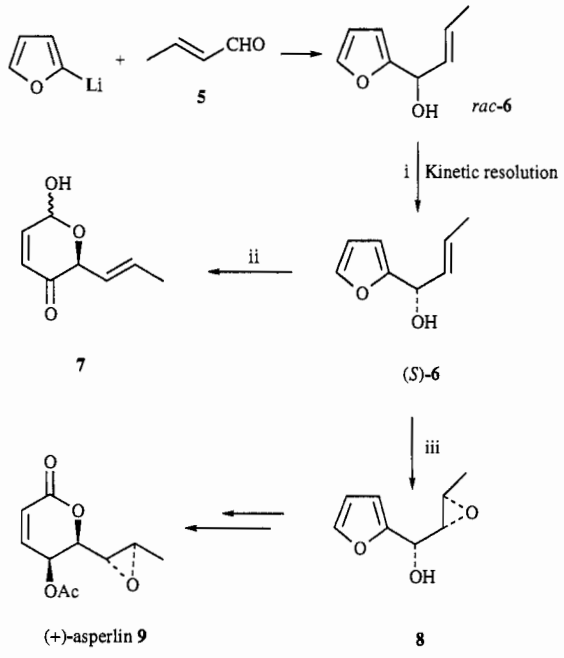
Scheme 1 *Reagents:* i, $Ti(OPr^i)_4$, TBHP, CH_2Cl_2; ii, D-(−)-DIPT; iii, L-(+)-DIPT

Although much effort has been devoted to studying the Sharpless epoxidation of symmetrical divinylmethanols,[5] its application to unsymmetrical divinylmethanols has received relatively little attention.[6] The most striking example reported by Sharpless[7] is the epoxidation of (4*E*)-hexa-1,4-dien-3-ol **3**, which resulted in the selective formation of epoxide **4** among the eight possible monoepoxides, when slightly less than 50 mol% of TBHP was employed (Scheme 2).



Scheme 2 *Reagents:* D-(−)-DIPT, $Ti(OPr^i)_4$, TBHP

In continuation of our work[8a] on the kinetic resolution of racemic secondary 2-furylmethanols *via* the Sharpless asymmetric epoxidation reaction,† we have found that treatment of (±)-(*E*)-1-(2-furyl)but-2-en-1-ol *rac*-**6**, prepared from 2-lithiofuran and crotonaldehyde **5** with diisopropyl D-(−)-tartrate [D-(−)-DIPT], $Ti(OPr^i)_4$ and TBHP (70 mol%) resulted in the recovery of *S*-enantiomer (*S*)-**6** in high optical yield. On the other hand, when the epoxidation of compound (*S*)-**6** was carried out with a stoichiometric amount of TBHP in the presence of L-(+)-DIPT, pyranone **7**, arising from the oxidation of the more reactive furan double bond, was produced predominantly. Oxidation of compound (*S*)-**6** using D-(−)-DIPT, however, provided the epoxy alcohol **8** exclusively. This outcome indicated that, even though two olefins were present with very different electron densities, the reactivity of the double bonds on the furylmethanol (*S*)-**6** varied depending on the chirality of the DIPT employed in the reaction. The procedure developed above was successfully applied to the enantioselective synthesis of (+)-asperlin **9**, an antitumour and antibacterial antibiotic[9] (Scheme 3). This is a peculiar case of a less electron-rich bond



Scheme 3 *Reagents and conditions:* i, D-(−)-DIPT; ii, L-(+)-DIPT, $Ti(OPr^i)_4$, TBHP, CaH_2, MS 3 Å, CH_2Cl_2, −20 °C; iii, D-(−)-DIPT, $Ti(OPr^i)_4$, TBHP, CaH_2, MS 3 Å, CH_2Cl_2, −20 °C

being oxidized selectively under the Sharpless epoxidation conditions.

† Satoh and co-workers reported similar work (ref. 8*b*).

In light of these findings, we undertook a detailed study of the Sharpless asymmetric epoxidation reaction of unsymmetrical divinylmethanols, and in this paper report our results.

Results and discussion

Five racemic divinylmethanols, (4*E*)-4-methylhexa-1,4-dien-3-ol *rac*-**10A**, 5-methylhexa-1,4-dien-3-ol *rac*-**10B**,[10] 1-(cyclohex-1-enyl)prop-2-en-1-ol *rac*-**10C**,[11] (1*E*)-1-phenylpenta-1,4-dien-3-ol *rac*-**10D**[12] and (4*E*)-6,6-dimethylhepta-1,4-dien-3-ol *rac*-**10E**[13] were prepared according to the literature procedures.

Catalytic kinetic resolution of the racemates *rac*-**10** with D-(−)-DIPT as a chiral source under Sharpless' conditions[14] led to the recovery of (*S*)-divinylmethanols (*S*)-**10** with high optical yields, together with the formation of *erythro* (*R*)-epoxy alcohols (*R*)-**11** except for **10B** (entry 2) where the epoxidation of a substrate containing a *Z*-substituent on the reaction site afforded a mixture of *threo* and *erythro* isomers (*R*)-**11B** (Table 1).

Having the chiral divinylmethanols (*S*)-**10** in hand, we investigated further the Sharpless epoxidation of these substrates with a stoichiometric amount of TBHP (Table 2).

Based on a consideration of Sharpless' rules[3] and our previous findings,[9] it was assumed that the more substituted double bonds of unsymmetrical divinylmethanols (*S*)-**10** would be the slow reacting groups in the presence of the catalyst formed by $Ti(OPr^i)_4$ and D-(−)-DIPT, and the less substituted olefins would be expected to be more available for reaction using this catalyst. The use of L-(+)-DIPT in this reaction would be expected to show a converse selectivity (see Fig. 1).

In order to confirm the above assumption concerning regio- and diastereo-selectivities in this reaction, divinylmethanols (*S*)-**10** were epoxidized using the L-(+)-DIPT oxidant (entries 2, 4, 6, 8 and 10 in Table 2). The reactions proceeded cleanly to give epoxides (*S*)-**11** in a regio- and diastereo-selective manner except for entry 4. In entry 4, the poor diastereoselectivity is probably a reflection of the presence of the *Z*-substituent on the double bond. Unexpectedly, the reaction of dienols (*S*)-**10** with D-(−)-DIPT again afforded the same epoxide (*S*)-**11**, without diastereoselectivity,[2] as a mixture of *threo* and *erythro* isomers.

Substrates bearing a bulky substituent R^1 underwent epoxidation on the less substituted double bonds to give the epoxy alcohol (*R*)-**12** as major products when the D-(−)-DIPT oxidant was used (entries 7 and 9 in Table 2). Though there were large steric differences between the two double bonds in substrates (*S*)-**10D** and (*S*)-**10E**, the epoxy alcohols, (*S*)-**11D** and (*S*)-**11E** arising from the oxidation of the sterically less favoured olefins, were produced in 17% and 21% yield, respectively. These findings indicated that steric factors play an important role in determining the regio- and diastereo-selectivities of these reactions. However, complete epoxidation on the less substituted olefins could not be obtained under these reaction conditions. This fact suggested that the relative reactivity of the two double bonds is also an important factor in controlling the regio- and diastereo-selectivities of these reactions.

We thought that introduction of a methyl group at the allylic position of the less substituted olefin would increase the reactivity of this double bond,[7,15] making steric factors the control elements in this reaction. Therefore, we prepared (±)-(1*E*,4*E*)-1-phenylhexa-1,4-diene-3-ol *rac*-**13**.[16] When compound *rac*-**13** was subjected to catalytic Sharpless kinetic resolution, the slow reacting alcohol (*S*)-**13** was recovered in 32% yield with 46% ee, together with the epoxy alcohol (*R*)-**14** in 37% yield (Scheme 4). Isolation of regioisomer (*R*)-**15** (19% yield) and the poor enantiomeric excess of diene (*S*)-**13** in this reaction would suggest that there was no large difference in reactivity between the two double bonds.

This result prompted us to attempt the conversion of the racemate *rac*-**13** directly to the corresponding epoxy alcohols with a stoichiometric amount of TBHP, as shown in Scheme 5.

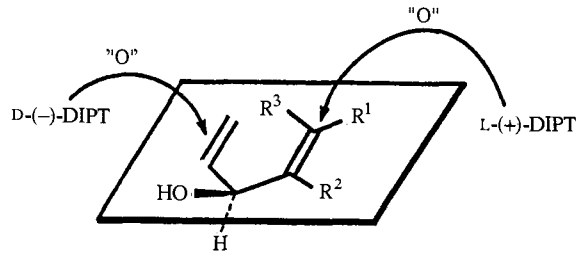
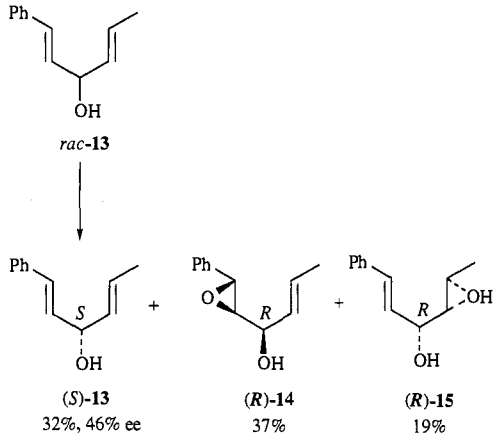
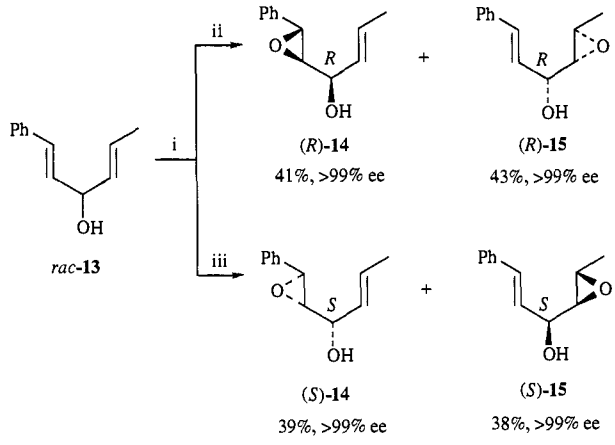


Fig. 1 Regioselective epoxidations of chiral divinylmethanols (*S*)-**10**



Scheme 4 *Reagents and conditions:* D-(−)-DIPT (0.3 mol equiv.), $Ti(OPr^i)_4$ (0.25 mol equiv.), TBHP (0.6 mol equiv.), MS 3 Å, CaH_2, CH_2Cl_2, −20 °C

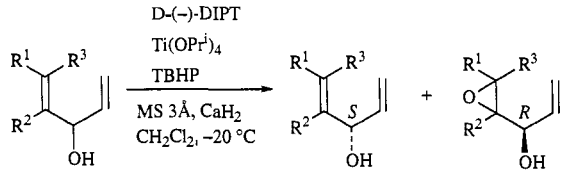


Scheme 5 *Reagents:* i, $Ti(OPr^i)_4$, TBHP, MS 3 Å, CaH_2, CH_2Cl_2; ii, D-(−)-DIPT; iii, L-(+)-DIPT

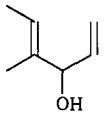
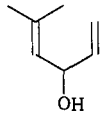
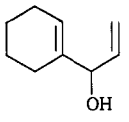
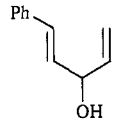
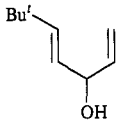
The reaction proceeded smoothly, as expected, to give epoxy alcohols (*R*)-**14** and (*R*)-**15** in 41% (> 99% ee) and 43% (> 99% ee), respectively, with D-(−)-DIPT, and epoxy alcohols (*S*)-**14** and (*S*)-**15** in 39% (> 99% ee) and 38% (> 99% ee), respectively, with L-(+)-DIPT. This outcome demonstrates that (i) introduction of a methyl group onto the olefin increased the reactivity of the double bond, and (ii) under the Sharpless oxidation conditions, kinetic resolution of the racemate *rac*-**13**, and subsequent olefin discrimination and diastereoselective epoxidation, proceeded simultaneously.

The absolute stereochemistry of (*R*)-**15** was unambiguously determined by its conversion into the acid **18** (Scheme 6). The furylmethanol **7**,[9] having known stereochemistry, was treated with diisobutylaluminium hydride (DIBAL)[17] in toluene to give the diol **16**, whose acetonide (compound **17**) formation followed by oxidative cleavage of the furan ring afforded acid **18**. The epoxide (*R*)-**15** was also converted to the acid **18** in a

Table 1 Kinetic resolution of racemic divinylmethanols[a]



rac-**10** (*S*)-**10** (*R*)-**11**

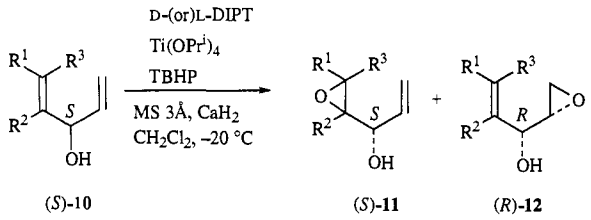
Entry	Substrate *rac*-**10**	Product	Yield (%)[g]	Abs.	ee (%)[h]
1[b]	 *rac*-**10A**	(*S*)-**10A**	32	*S*[j]	99
		erythro-(*R*)-**11A**	45	*R*[j]	
2[c]	 *rac*-**10B**	(*S*)-**10B**	38	*S*	96
		erythro-(*R*)-**11B**[f]	50	*R*	
		threo-(*R*)-**11B**			
3[d]	 *rac*-**10C**	(*S*)-**10C**	40	*S*[j]	99
		erythro-(*R*)-**11C**	40	*R*[j]	
4[b]	 *rac*-**10D**	(*S*)-**10D**	30	*S*	99
		erythro-(*R*)-**11D**	34	*R*	
5[e]	 *rac*-**10E**	(*S*)-**10E**	39	*S*	>95[i]
		erythro-(*R*)-**11E**	47	*R*	

[a] The reaction was carried out with Ti(OPr^i)$_4$, D-(−)-DIPT and TBHP in CH_2Cl_2 in the presence of powdered 3 Å molecular sieves (MS 3 Å) (30 wt% based on the substrate) and CaH_2 (0.2 mol equiv.). [b] Ti(OPr^i)$_4$ (0.25 mol equiv.), D-(−)-DIPT (0.3 mol equiv.) and TBHP (0.65 mol equiv.) were employed. [c] Ti(OPr^i)$_4$ (0.1 mol equiv.), D-(−)-DIPT (0.15 mol equiv.) and TBHP (0.65 mol equiv.) were employed. [d] Ti(OPr^i)$_4$ (0.25 mol equiv.), D-(−)-DIPT (0.3 mol equiv.) and TBHP (0.6 mol equiv.) were employed. [e] Ti(OPr^i)$_4$ (0.5 mol equiv.), D-(−)-DIPT (0.55 mol equiv.) and TBHP (0.6 mol equiv.) were employed. [f] Inseparable mixture of diastereoisomers (*erythro* : *threo* = 1.75 : 1). [g] Isolated yields. [h] Determined by HPLC using CHIRALCEL OB (Daicel Chemical Industries, Ltd.). [i] Determined by 270 MHz ^{1}H NMR analysis of the methoxy(trifluoromethyl)phenylacetate (MTPA) ester of 6,6-dimethylheptan-3-ol after hydrogenolysis of compound (*S*)-**10E**. [j] Absolute stereochemistries were not determined.

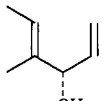
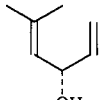
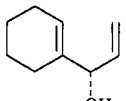
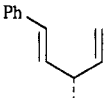
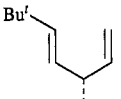
similar manner as described above. The stereochemistry of epoxides (*R*)-**12D** and (*R*)-**12E** were determined by their conversion into the diol **19** or the acid **18**. Protection of the hydroxy group with triethylsilyl chloride (TESCl) and imidazole in CH_2Cl_2, followed by subsequent epoxide opening with lithium dimethylcuprate(I) [18] and deprotection of the silyl group gave the diols **19** and **30**, respectively. The diol **19** was identical with the authentic sample synthesized from epoxide (*R*)-**15**. Compound **30** was further transformed into acid **18** by sequential protection of the diol as the acetonide and oxidation of the double bond with RuO_4, prepared *in situ* from $RuCl_3$ and $NaIO_4$.[19] The absolute stereochemistry of epoxy alcohol *erythro*-(*S*)-**11B** was determined by its conversion into the acid *ent*-**25** in three steps as follows. Reduction of the epoxy alcohol *erythro*-(*S*)-**11B** with DIBAL in Et_2O gave the diol **31**, which, after protection as the acetonide, was oxidatively cleaved to give the acid *ent*-**25**. Acid **25** was also obtained from epoxy alcohol (*R*)-**15** as follows. Protection of the hydroxy group with (TESCl) gave silyl ether **21**, which underwent epoxide ring opening at the C-5 position with lithium dimethylcuprate(I) in Et_2O to afford the alcohol **22** as the major product. Sequential deprotection of the TES group, acetonide formation of the resulting diol **23** and oxidative cleavage of the olefin **24** then gave acid **25**. The spectroscopic data of acid **25** were identical with those of *ent*-**25** except for the specific optical rotation.

In conclusion, we have disclosed some novel aspects of the reactivity of unsymmetrical divinylmethanols under the Sharpless asymmetric epoxidation conditions. This study suggests that the regio- and diastereo-selectivities in this reaction are controlled by the relative reactivity and steric circumstances of both double bonds in the molecule. Based on the above results, it would be assumed that the high regio- and diastereo-selectivities in these reactions would generally be obtained with the use of unsymmetrical divinylmethanols having *different substituents at the* β*-position of both double bonds* as starting materials. This methodology should be

Table 2 Epoxidation of dienol (*S*)-**10** with the Sharpless reagent[a]



(*S*)-**10** (*S*)-**11** (*R*)-**12**

Entry	Substrate (*S*)-**10**	Chirality of DIPT	Products (Yield, %)[g] (*S*)-**11** (*threo*:*erythro*)/(*R*)-**12**
1[b]	 (*S*)-**10A**	D	65[j] (1:2.6)[h,i]/0
2[c]		L	81 (0:1)[h]/0
3[d]	 (*S*)-**10B**	D	60[j] (11:1)[i]/0
4[d]		L	65[j] (1:2.1)[i]/0
5[b]	 (*S*)-**10C**	D	97 (1:10)[h]/0
6[c]		L	89 (0:1)[h]/0
7[e]	 (*S*)-**10D**	D	17 (1:2.5)/39
8[c]		L	91 (0:1)/0
9[f]	 (*S*)-**10E**	D	21 (1.7:1)/48
10[c]		L	79 (0:1)/0

[a] The reaction was carried out with Ti(OPr^i)$_4$, D- or L-DIPT and TBHP in CH_2Cl_2 in the presence of powdered 3 Å molecular sieves (MS 3 Å) (30 wt% based on the substrate) and CaH_2 (0.2 mol equiv.). [b] Ti(OPr^i)$_4$ (0.45 mol equiv.), D-(−)-DIPT (0.5 mol equiv.) and TBHP (1.2 mol equiv.) were employed. [c] Ti(OPr^i)$_4$ (0.25 mol equiv.), D-(−)-DIPT (0.3 mol equiv.) and TBHP (1.2 mol equiv.) were employed. [d] Ti(OPr^i)$_4$ (0.3 mol equiv.), D-(−)-DIPT (0.36 mol equiv.) and TBHP (1.2 mol equiv.) were employed. [e] Ti(OPr^i)$_4$ (1.05 mol equiv.), D-(−)-DIPT (1.05 mol equiv.) and TBHP (1.2 mol equiv.) were employed. [f] Ti(OPr^i)$_4$ (0.5 mol equiv.), D-(−)-DIPT (0.55 mol equiv.) and TBHP (1.2 mol equiv.) were employed. [g] Isolated yields. [h] Absolute stereochemistry was not determined. [i] Based on the ratio of corresponding acetates. [j] Based on the isolated yield of corresponding acetates.

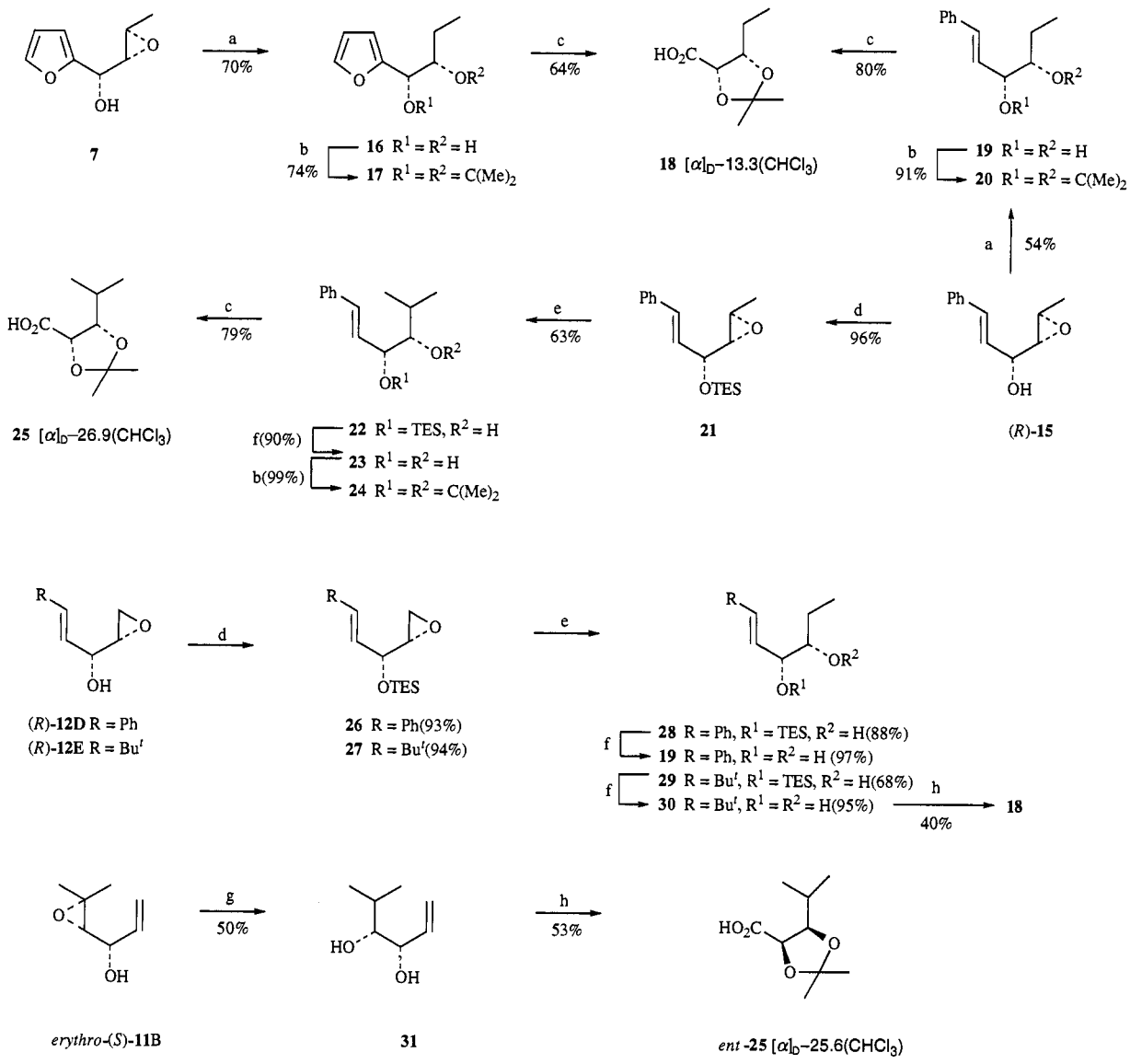
applicable to the efficient synthesis of natural products. Theoretical investigations into these reactions are currently underway in this laboratory.

Experimental

Mps were measured with a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were recorded for solutions in $CHCl_3$ on a Hitachi 260-10 spectrophotometer and for thin films on a JASCO FT/IR-200 Fourier transform infrared spectrophotometer. ^1H and ^{13}C NMR spectra were obtained for solutions in $CDCl_3$ on a JEOL GSX-270, and chemical shifts are reported in ppm on the δ-scale from internal Me_4Si. Mass spectra were measured with a JEOL HMS D-300 spectrometer. Elemental analyses were measured with a Yanako MT-5. Optical rotations were taken with a JASCO DIP-360 polarimeter, and are reported in units of 10^{-1} deg cm^2 g^{-1}. Column chromatography was carried out on Silica gel 60 (Merck). Molecular sieves 3 Å (MS 3 Å) were activated by heating at 250 °C *in vacuo* for 3 h.

(4*E*)-4-Methylhexa-1,4-dien-3-ol *rac*-10A

To a stirred solution of (*E*)-2-methylbut-2-enal (7.6 g, 90.3 mmol) in Et_2O (200 ml) was added vinylmagnesium bromide [99.4 ml, 99.4 mmol; 1.0 M solution in tetrahydrofuran (THF)] at 0 °C, and the resulting mixture was stirred at the same temperature for 30 min. After addition of saturated aq. NH_4Cl, the reaction mixture was extracted with Et_2O, and the ethereal layer was washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave a residue, which was purified by column chromatography on silica gel with pentane–Et_2O (8:1, v/v) as eluent to afford *rac*-**10A** (5.4 g, 54%) as an oil; $\nu_{max}(CHCl_3)/cm^{-1}$ 910, 980, 1105, 1375, 2860 and 3430; δ_H 1.61 (6 H, m, 2 × Me), 4.52 (1 H, m, 3-H), 5.15 (1 H, ddd, *J* 1.2, 1.8 and 10.4, 1-H^a), 5.28 (1 H, ddd, *J* 1.2, 1.8 and 17.1, 1-H^b), 5.57 (1 H, m, 5-H) and 5.86 (1 H, ddd, *J* 5.5, 10.4 and 17.1, 2-H);



Scheme 6 *Reagents and conditions:* (a) DIBAL, toluene, 0 °C; (b) *p*-TsOH·H_2O, acetone; (c) $RuCl_3$, $NaIO_4$, CCl_4–CH_3CN–water; (d) TESCl, imidazole, CH_2Cl_2; (e) Me_2CuLi, Et_2O, 0 °C; (f) TBAF, THF; (g) DIBAL, Et_2O, 0 °C; (h) *p*-TsOH·H_2O, acetone; then $RuCl_3$, $NaIO_4$, CCl_4–CH_3CN–water

δ_C 11.5 (q), 13.1 (q), 78.3 (d), 114.7 (t), 121.0 (d), 136.6 (s) and 139.2 (d) [Found: M^+, 112.0898. Calc. for $C_7H_{12}O$: M, 112.0888. Found: (M^+ − 15), 97.0650. Calc. for C_6H_9O: (M − 15), 97.0652].

General procedure for the catalytic kinetic resolution of racemic unsymmetrical divinylmethanols

To a stirred suspension of activated MS 3 Å (30 wt% based on the substrate) and CaH_2 (0.2 mol equiv.) in CH_2Cl_2 (0.4 M in CaH_2) was added $Ti(OPr^i)_4$ at room temperature. The stirred mixture was cooled to −20 °C, and treated with D-(−)-DIPT in CH_2Cl_2 [0.4 M in D-(−)-DIPT]. After stirring of the mixture for 30 min at the same temperature, a solution of the racemic unsymmetrical divinylmethanol *rac*-**10** in CH_2Cl_2 (0.4 M in substrate) was added dropwise to the solution, and the mixture was further stirred for 1 h. TBHP (5.28 M solution in 2,2,4-trimethylpentane) was added over a period of 30 min to this mixture. After stiring of this mixture for 24 h at −20 °C, Me_2S (1.3 mol equiv.) was slowly added and the mixture was stirred for 30 min at the same temperature. To this mixture were added 10% aq. tartaric acid (0.1 mol equiv.), 0.2 M ethereal solution of substrate and NaF (6.25 mol equiv.), and the resulting mixture was vigorously stirred for 3 h at room temperature. The precipitate was filtered off through a pad of Celite. The filtrate was washed successively with saturated aq. $NaHCO_3$ and brine, and dried over Na_2SO_4. Evaporation of the mixture gave a residue, which was purified by column chromatography on silica gel to afford compounds (*S*)-**10** and (*R*)-**11**. The enantiomeric excess (ee) of dienol (*S*)-**10** was determined by HPLC with a CHIRALCEL OB column (Daicel Chemical Industries, Ltd.) except as noted in Table 1.

Catalytic kinetic resolution of *rac*-10A. The reaction was performed on 26.8 mmol scale (3.0 g) of compound *rac*-**10A** with $Ti(OPr^i)_4$ (0.25 mol equiv.), D-(−)-DIPT (0.3 mol equiv.) and TBHP (0.65 mol equiv.) and provided (3*S*,4*E*)-4-methylhepta-1,4-dien-3-ol (*S*)-**10A** and (3*R*,4*S*,5*R*)-4,5-epoxy-4-methylhex-1-en-3-ol *erythro*-(*R*)-**11A**. They were purified by column chromatography on silica gel with pentane–Et_2O (8 : 1, v/v) as eluent. The first fraction gave (*S*)-**10A** (960 mg, 32%) as an oil; $[\alpha]_D^{22}$ −53.3 (*c* 0.7, $CHCl_3$), 99% ee by HPLC using n-hexane–Pr^iOH (99.75 : 0.25, v/v) as eluent. The spectral data of this compound were identical with those of *rac*-**10A**. The second fraction gave *erythro*-(*R*)-**11A** (1.55 g, 45%) as an oil; $[\alpha]_D^{21}$ −23.1 (*c* 1.0, $CHCl_3$); ν_{max}(thin film)/cm^{-1} 739, 858, 928, 993, 1028, 1077, 1130, 1385, 2870, 2932, 3001 and 3438; δ_H 1.29 (3 H, s, 4-Me), 1.32 (3 H, d, *J* 5.5, 6-H_3), 2.27 (1 H, d, *J* 1.8, OH), 3.18 (1 H, q, *J* 5.5, 5-H), 4.09 (1 H, dd, *J* 1.8 and 6.7, 3-H), 5.25 (1 H, dt, *J* 1.8 and 10.4, 1-H^a), 5.39 (1 H, dt, *J* 1.8 and 17.1, 1-H^b) and 5.80 (1 H, ddd, *J* 6.7, 10.4 and 17.1, 2-H); δ_C 13.3 (q), 13.4 (q), 55.3 (d), 62.1 (s), 74.5 (d), 117.2 (t) and 136.1 (d) [Found:

($M^+ - 15$), 113.0598. Calc. for $C_6H_9O_2$: (M − 15), 113.0601. Found: ($M^+ - 17$), 111.0805. Calc. for $C_7H_{11}O$: (M − 17), 111.0808. Found: ($M^+ - 18$), 110.0732. Calc. for $C_7H_{10}O$: (M − 18), 110.0732].

Catalytic kinetic resolution of dienol *rac*-10B. The reaction was performed on 24.7 mmol scale (2.77 g) of compound *rac*-**10B** with $Ti(OPr^i)_4$ (0.1 mol equiv.), D-(−)-DIPT (0.15 mol equiv.) and TBHP (0.65 mol equiv.) and afforded (3*S*)-5-methylhexa-1,4-dien-3-ol (*S*)-**10B** and (3*R*,4*R*)-4,5-epoxy-5-methylhex-1-en-3-ol and (3*R*,4*S*)-4,5-epoxy-5-methylhex-1-en-3-ol *erythro*- and *threo*-(*R*)-**11B**. They were purified by column chromatography on silica gel with pentane–Et_2O (4:1, v/v) as eluent. The first fraction gave compound (*S*)-**10B** (1.04 g, 37.5%) as an oil; $[\alpha]_D^{25}$ −52.0 (*c* 0.97, $CHCl_3$), 96% ee by HPLC using hexane–Pr^iOH (99.92:0.08, v/v) as eluent; ν_{max}(thin film)/cm^{-1} 918, 999, 1008, 1376, 1447, 2915 and 3360; δ_H 1.55 (1 H, br s, OH), 1.72 and 1.75 (each 3 H, each d, *J* 1.2, 2 × Me), 4.86 (1 H, m, 3-H), 5.09 (1 H, dt, *J* 1.2 and 10.4, 1-H^a), 5.19 (1 H, m, 4-H), 5.23 (1 H, dt, *J* 1.2 and 17.3, 1-H^b) and 5.89 (1 H, ddd, *J* 5.5, 10.4 and 17.1, 2-H) (Found: C, 74.5; H, 10.4. Calc. for $C_7H_{12}O$: C, 74.95; H, 10.78%). The spectral data of this compound were identical with those of compound *rac*-**10B**. The second fraction gave *erythro*- and *threo*-(*R*)-**11B** (1.58 g, 50%) as an inseparable mixture. Owing to the difficulty of separation, the mixture was further acetylated as follows. To a stirred solution of this mixture in CH_2Cl_2 (15 cm^3) were added pyridine (2 cm^3, 24.7 mmol), 4-(dimethylamino)pyridine (DMAP) (150 mg, 1.23 mmol) and acetic anhydride (1.75 cm^3, 18.5 mmol), and the resulting mixture was stirred for 1 h at room temperature. After addition of cold water, the mixture was extracted with CH_2Cl_2. The extract was washed successively with saturated aq. $KHSO_4$, saturated aq. $NaHCO_3$ and brine, and dried over Na_2SO_4. Evaporation of the solvent gave a residue, which was purified by column chromatography on silica gel with pentane–Et_2O (9:1, v/v) as eluent. The first fraction gave (3*R*,4*R*)-3-acetoxy-4,5-epoxy-5-methylhex-1-ene (1.21 g, 59%) as an oil; $[\alpha]_D^{25}$ +71.8 (*c* 0.98, $CHCl_3$); ν_{max}(thin film)/cm^{-1} 812, 891, 931, 980, 1024, 1114, 1233, 1272, 1745 and 2968; δ_H 1.34 and 1.36 (each 3 H, each s, 2 × Me), 2.11 (3 H, s, Ac), 2.81 (1 H, d, *J* 8.5, 4-H), 5.04 (1 H, m, 3-H), 5.30 (1 H, dt, *J* 1.2 and 11.0, 1-H^a), 5.37 (1 H, dt, *J* 1.2 and 17.1, 1-H^b) and 5.93 (1 H, ddd, *J* 6.1, 11.0 and 17.1, 2-H); δ_C 18.9 (q), 21.0 (q), 24.4 (q), 59.4 (s), 63.5 (d), 72.2 (d), 118.0 (t), 133.6 (d) and 169.5 (s) (Found: C, 63.45; H, 8.3. Calc. for $C_9H_{14}O_3$: C, 63.51; H, 8.29%). The second fraction gave (3*R*,4*S*)-3-acetoxy-4,5-epoxy-5-methylhex-1-ene (690 mg, 34%) as an oil; $[\alpha]_D^{25}$ −15.8 (*c* 0.88, $CHCl_3$); ν_{max}(thin film)/cm^{-1} 810, 914, 940, 988, 1023, 1081, 1117, 1235, 1372, 1746, 2921 and 2967; δ_H 1.36 and 1.37 (each 3 H, each s, 2 × Me), 2.12 (3 H, s, Ac), 2.90 (1 H, d, *J* 8.5, 4-H), 5.11 (1 H, m, 3-H), 5.29 (1 H, dt, *J* 1.2 and 10.4, 1-H^a), 5.33 (1 H, dt, *J* 1.2 and 17.1, 1-H^b) and 5.83 (1 H, ddd, *J* 5.5, 10.4 and 17.1, 2-H); δ_C 19.2 (q), 21.0 (q), 24.6 (q), 58.3 (s), 63.5 (d), 74.3 (d), 118.1 (t), 132.5 (d) and 169.9 (s) (Found: C, 63.4; H, 8.35%).

Catalytic kinetic resolution of compound *rac*-10C. The reaction was performed on 6.56 mmol scale (0.91 g) of substrate *rac*-**10C** with $Ti(OPr^i)_4$ (0.25 mol equiv.), D-(−)-DIPT (0.3 mol equiv.) and TBHP (0.6 mol equiv.) and afforded (1*S*)-1-(cyclohex-1-enyl)prop-2-en-1-ol (*S*)-**10C** and (1*R*,1′*S*,2′*S*)-(1,2-epoxycyclohexyl)prop-2-en-1-ol *erythro*-(*R*)-**11C**. They were purified by column chromatography on silica gel with pentane–Et_2O (9:1, v/v) as eluent. The first fraction gave compound (*S*)-**10C** (359 mg, 40%) as an oil; $[\alpha]_D^{23}$ −19.3 (*c* 0.91, $CHCl_3$), 99% ee by HPLC using hexane–Pr^iOH (99.95:0.05, v/v) as eluent; ν_{max}(thin film)/cm^{-1} 920, 989, 1138, 1437, 2837, 2858, 2929 and 3390; δ_H 1.54–1.76 (5 H, m, 4′- and 5′-H_2, and OH), 1.95–2.09 (4 H, m, 3′- and 6′-H_2), 4.47 (1 H, d, *J* 6.1, 1-H), 5.14 (1 H, ddd, *J* 1.2, 1.8 and 10.4, 3-H^a), 5.27 (1 H, ddd, *J* 1.2, 1.8 and 17.1, 3-H^b), 5.74 (1 H, m, 2′-H) and 5.87 (1 H, ddd, *J* 6.1, 10.4 and 17.1, 2-H) (Found: M^+, 138.1040; C, 78.0; H, 10.4. Calc. for $C_9H_{14}O$: M, 138.1043; C, 78.21; H, 10.21%). The spectral data of this compound were identical with those of *rac*-**10C**. The second fraction gave compound *erythro*-(*R*)-**11C** (611 mg, 51%) as an oil; $[\alpha]_D^{26}$ −15.1 (*c* 1.0, $CHCl_3$); ν_{max}(thin film)/cm^{-1} 744, 871, 924, 996, 1048, 1132, 1435, 2831, 2939 and 3440; δ_H 1.16–1.55 (4 H, m, 4′- and 5′-H_2), 1.68–2.05 (4 H, m, 3′- and 6′-H_2), 2.34 (1 H, br s, OH), 3.25 (1 H, d, *J* 3.1, 2′-H), 4.04 (1 H, d, *J* 6.1, 1-H), 5.26 (1 H, ddd, *J* 1.2, 1.8 and 10.4, 3-H^a), 5.39 (1 H, ddd, *J* 1.2, 1.8 and 17.1, 3-H^b) and 5.81 (1 H, ddd, *J* 6.1, 10.4 and 17.1, 2-H); δ_C 19.6 (t), 20.3 (t), 24.5 (t), 24.8 (t), 55.3 (d), 61.7 (s), 73.6 (d), 118.2 (t) and 136.1 (d) [Found: ($M^+ - 17$), 137.0965. Calc. for $C_9H_{13}O$: (M − 17), 137.0965. Found: ($M^+ - 18$), 136.0895. Calc. for $C_9H_{12}O$: (M − 18), 136.0888].

Catalytic kinetic resolution of compound *rac*-10D. The reaction was performed on 10.3 mmol scale (1.65 g) of compound *rac*-**10D** with $Ti(OPr^i)_4$ (0.25 mol equiv.), D-(−)-DIPT (0.3 mol equiv.) and TBHP (0.65 mol equiv.) and afforded (1*E*,3*S*)-1-phenylpenta-1,4-dien-3-ol (*S*)-**10D** and (3*R*,4*R*,5*R*)-4,5-epoxy-5-phenylpent-1-en-3-ol *erythro*-(*R*)-**11D**. They were purified by column chromatography on silica gel with hexane–EtOAc (7:1, v/v) as eluent. The first fraction gave dienol (*S*)-**10D** (491 mg, 30%) as an oil; $[\alpha]_D^{24}$ +40.8 (*c* 0.35, $CHCl_3$), 99% ee by HPLC using hexane–Pr^iOH (99.5:0.5, v/v) as eluent; ν_{max}(thin film)/cm^{-1} 701, 756, 1450, 1495, 1612, 1743, 2929, 3028 and 3430; δ_H 1.78 (1 H, br s, OH), 4.81 (1 H, m, 3-H), 5.20 (1 H, dt, *J* 1.2 and 10.4, 5-H^a), 5.34 (1 H, dt, *J* 1.2 and 17.1, 5-H^b), 5.98 (1 H, ddd, *J* 6.1, 10.4 and 17.1, 4-H), 6.23 (1 H, dd, *J* 6.7 and 15.9, 2-H), 6.62 (1 H, d, *J* 15.9, 1-H) and 7.21–7.41 (5 H, m, Ph) (Found: M^+, 160.0880; C, 82.2; H, 7.6. Calc. for $C_{11}H_{12}O$: M, 160.0886; C, 82.46; H, 7.55%). The spectral data of this compound were identical with those of *rac*-**10D**. The second fraction gave compound *erythro*-(*R*)-**11D** (606 mg, 34%) as an oil; $[\alpha]_D^{24}$ +9.47 (*c* 1.0, $CHCl_3$); ν_{max}(thin film)/cm^{-1} 698, 753, 881, 932, 994, 1463, 1497, 2985 and 3430; δ_H 2.10 (1 H, d, *J* 2.4, OH), 3.18 (1 H, dd, *J* 1.8 and 3.7, 4-H), 3.96 (1 H, d, *J* 1.8, 5-H), 4.46 (1 H, m, 3-H), 5.29 (1 H, dt, *J* 1.2 and 10.4, 1-H^a), 5.44 (1 H, dt, *J* 1.2 and 17.1, 1-H^b), 5.92 (1 H, ddd, *J* 6.7, 10.4 and 17.1, 2-H) and 7.26–7.34 (5 H, m, Ph); δ_C 55.1 (d), 64.0 (d), 70.4 (d), 117.4 (t), 125.6 (d), 128.1 (d), 128.3 (d), 135.6 (d) and 136.5 (s) (Found: M^+, 176.0833; C, 82.2; H, 7.6%. Calc. for $C_{11}H_{12}O_2$: M, 176.0836; C, 82.46; H, 7.55%).

Catalytic kinetic resolution of compound *rac*-10E. The reaction was performed on 5.93 mmol scale (830 mg) of compound *rac*-**10E** with $Ti(OPr^i)_4$ (0.5 mol equiv.), D-(−)-DIPT (0.55 mol equiv.) and TBHP (0.6 mol equiv.) and afforded (3*S*,4*E*)-6,6-dimethylhepta-1,4-dien-3-ol (*S*)-**10E**, (3*R*,4*R*,5*R*)-4,5-epoxy-6,6-dimethylhept-1-en-3-ol *erythro*-(*R*)-**11E** and (1*S*,2*R*,3*R*,4*E*)-1,2-epoxy-6,6-dimethylhept-4-en-3-ol (*R*)-**12E**. They were purified by column chromatography on silica gel with pentane–Et_2O (15:1, v/v) as eluent. The first fraction gave compound (*S*)-**10E** (320 mg, 39%) as an oil; $[\alpha]_D^{23}$ −20.5 (*c* 1.0, $CHCl_3$); ν_{max}(thin film)/cm^{-1} 921, 972, 989, 1117, 1263, 1363, 1463, 1477, 1639, 2867, 2905, 2960 and 3350; δ_H 1.02 (9 H, s, Bu^t), 1.55 (1 H, d, *J* 1.8, OH), 4.58 (1 H, m, 3-H), 5.12 (1 H, dt, *J* 1.2 and 10.4, 1-H^a), 5.25 (1 H, dt, *J* 1.2 and 17.1, 1-H^b), 5.41 (1 H, dd, *J* 6.7 and 15.9, 4-H), 5.72 (1 H, dd, *J* 1.2 and 15.9, 5-H) and 5.91 (1 H, ddd, *J* 6.1, 10.4 and 17.1, 2-H) [Found: M^+, 140.1191. Calc. for $C_9H_{16}O$: M, 140.1199. Found: ($M^+ - 18$), 122.1093. Calc. for C_9H_{14}: (M − 18), 122.1094]. The spectral data of this compound were identical with those of *rac*-**10E**. The ee of (*S*)-**10E** was determined to be > 95% by ^1H NMR analysis of the Mosher's ester of (3*S*)-6,6-dimethylheptane obtained by hydrogenation of compound (*S*)-**10E**. The second fraction gave *erythro*-(*R*)-**11E** (440 mg, 47%) as an oil; $[\alpha]_D^{22}$ −34.2 (*c* 0.63, $CHCl_3$); ν_{max}(thin film)/cm^{-1} 922, 993, 1365, 1482, 2870 and 3440; δ_H 0.93 (9 H, s, Bu^t), 2.10 (1 H, br s, OH), 2.81 (1 H, d, *J* 2.4, 5-H), 2.95 (1 H, dd, *J* 2.4 and 3.7, 4-H), 4.30 (1 H, m, 3-H), 5.25 (1 H, ddd, *J* 1.2, 1.8 and 10.4, 1-H^a), 5.38 (1 H, ddd, *J* 1.2, 1.4 and 17.1, 1-H^b) and 5.83 (1 H, ddd, *J* 6.7, 10.4 and 17.1, 2-

H); δ_C 25.6 (q), 30.1 (s), 57.1 (d), 62.9 (d), 70.3 (d), 116.8 (t) and 136.1 (d) [Found: (M^+ − 17), 139.1125. Calc. for $C_9H_{15}O$: (M − 17), 139.1123]. The third fraction gave compound (*R*)-**12E** (70 mg, 8%) as an oil; $[\alpha]_D^{20}$ −68.8 (*c* 0.31, $CHCl_3$); ν_{max}(thin film)/cm^{-1} 837, 862, 906, 914, 974, 1015, 1026, 1086, 1260, 1363, 1463, 1477, 2866, 2905, 2960 and 3430; δ_H 1.03 (9 H, s, Bu^t), 2.14 (1 H, br s, OH), 2.77 (2 H, m, 1-H_2), 3.06 (1 H, dd, *J* 3.1 and 4.3, 2-H), 4.27 (1 H, dd, *J* 3.1 and 6.7, 3-H), 5.34 (1 H, dd, *J* 6.7 and 15.9, 4-H) and 5.84 (1 H, d, *J* 15.9, 5-H); δ_C 29.4 (q), 33.1 (s), 43.5 (t), 54.3 (d), 70.3 (d), 122.0 (d) and 146.2 (d) [Found: (M^+ − 18), 138.1055. Calc. for $C_9H_{14}O$: (M − 18), 138.1045. Found: (M^+ − 33), 123.0812. Calc. for $C_8H_{11}O$: (M − 33), 123.0811].

General procedure for the epoxidation of compounds (*S*)-10 with Sharpless' reagent

To a suspension of activated MS 3 Å (30 wt% based on the substrate) and CaH_2 (0.2 mol equiv.) in CH_2Cl_2 (0.4 M in CaH_2) was added Ti(OPr^i)$_4$ at room temperature. The stirred mixture was cooled to −20 °C, and treated with D-(−)- or L-(+)-DIPT in CH_2Cl_2 (0.4 M in DIPT). After the mixture had been stirred for 30 min at the same temperature, a solution of a dienol (*S*)-**10** in CH_2Cl_2 (0.4 M in substrate) was added dropwise to the solution, and the mixture was further stirred for 1 h. TBHP (5.28 M solution in 2,2,4-trimethylpentane) was added over a period of 30 min to this mixture. After stirring of the mixture for 24 h at −20 °C, Me_2S (1.3 mol equiv.) was slowly added and the mixture was stirred for 30 min at the same temperature. To this mixture were added 10% aq. tartaric acid (0.1 mol equiv.), 0.2 M ethereal solution of substrate and NaF (6.25 mol equiv.), and the resulting mixture was vigorously stirred for 3 h at room temperature. The precipitate was filtered off through a pad of Celite. The filtrate was washed successively with saturated aq. $NaHCO_3$ and brine, and dried over Na_2SO_4. Evaporation of the mixture gave a residue, which was purified by column chromatography on silica gel to afford products (*S*)-**11** and/or (*R*)-**12**.

Epoxidation of dienol (*S*)-10A with D-(−)-DIPT. The reaction was performed on 1.88 mmol scale (210 mg) of compound (*S*)-**10A** with Ti(OPr^i)$_4$ (0.45 mol equiv.), D-(−)-DIPT (0.5 mol equiv.) and TBHP (1.2 mol equiv.) and afforded (3*S*,4*R*,5*S*)-4,5-epoxy-4-methylhex-1-en-3-ol *erythro*-(*S*)-**11A** and (3*S*,4*S*,5*R*)-4,5-epoxy-4-methylhex-1-en-3-ol *threo*-(*S*)-**11A** as an inseparable mixture. Owing to the difficulty of separation, the alcohols were further transformed into the corresponding acetates as follows. To a stirred solution of the alcohols (*S*)-**11A** in CH_2Cl_2 (3 cm^3) were added pyridine (0.32 cm^3, 3.98 mmol) and acetic anhydride (0.25 cm^3, 2.66 mmol), and the resulting mixture was stirred at 0 °C under argon for 3 h. After addition of cold water, the mixture was extracted with Et_2O. The extract was washed successively with 0.5 M HCl, saturated aq. $NaHCO_3$ and brine, and dried over Na_2SO_4. Evaporation of the solvent gave a residue, which was purified by column chromatography on silica gel with pentane–Et_2O (18:1, v/v) as eluent. The first fraction gave (3*S*,4*R*,5*S*)-3-acetoxy-4,5-epoxy-4-methylhex-1-ene (106 mg, 47%) as an oil; ν_{max}(thin film)/cm^{-1} 874, 1024, 1233, 1372, 1746, 2361, 2933 and 3003; δ_H 1.25 (3 H, s, 4-Me), 1.29 (3 H, d, *J* 5.5, 6-H_3), 2.09 (3 H, s, Ac), 3.06 (1 H, q, *J* 5.5, 5-H), 5.05 (1 H, d, *J* 6.7, 3-H), 5.27 and 5.37 (each 1 H, each ddd, *J* 1.2, 10.4 and 17.1, 1-H_2) and 5.83 (1 H, ddd, *J* 6.7, 10.4 and 17.1, 2-H); δ_C 12.8 (q), 13.7 (q), 21.0 (q), 57.4 (d), 59.8 (s), 77.2 (d), 118.9 (t), 132.4 (d) and 169.7 (s) [Found: (M^+ − 43), 127.0758. Calc. for $C_7H_{11}O_2$: (M − 43), 127.0758]. The second fraction gave (3*S*,4*S*,5*R*)-3-acetoxy-4,5-epoxy-4-methylhex-1-ene (40 mg, 18%) as an oil; ν_{max}(thin film)/cm^{-1} 1024, 1236, 1371, 1747 and 2932; δ_H 1.29 (3 H, s, 4-Me), 1.30 (3 H, d, *J* 5.5, 6-H_3), 2.12 (3 H, s, Ac), 3.03 (1 H, q, *J* 5.5, 5-H), 5.02 (1 H, d, *J* 6.1, 3-H), 5.25 and 5.31 (each 1 H, each dt, *J* 1.2, 10.4 and 17.1, 1-H_2) and 5.79 (1 H, ddd, *J* 6.1, 10.4 and 17.1, 2-H); δ_C 12.8 (q), 13.5 (q), 21.1 (q), 56.3 (d), 60.9 (s), 78.5 (d), 118.4 (t), 132.7 (d) and 169.9 (s) [Found: (M^+ − 43), 127.0759. Found: (M^+ − 59), 111.0808. Calc. for $C_7H_{11}O$: (M − 59), 111.0808].

Epoxidation of dienol (*S*)-10A with L-(+)-DIPT. The reaction was performed on 2.23 mmol scale (250 mg) of dienol (*S*)-**10A** with Ti(OPr^i)$_4$ (0.25 mol equiv.), L-(+)-DIPT (0.3 mol equiv.) and TBHP (1.2 mol equiv.). After purification by column chromatography on silica gel with pentane–Et_2O (8:1, v/v) as eluent, (3*S*,4*R*,5*S*)-4,5-epoxy-4-methylhex-1-en-3-ol *erythro*-(*S*)-**11A** (231 mg, 81%) was obtained as an oil; $[\alpha]_D^{27}$ +32.2 (*c* 0.37, $CHCl_3$). The spectral data of this compound were identical with those of *erythro*-(*R*)-**11A**.

Epoxidation of dienol (*S*)-10B with D-(−)-DIPT. The reaction was performed on 2.68 mmol scale (300 mg) of compound (*S*)-**10B** with Ti(OPr^i)$_4$ (0.3 mol equiv.), D-(−)-DIPT (0.36 mol equiv.) and TBHP (1.2 mol equiv.). After purification by column chromatography on silica gel with pentane–Et_2O (9:1, v/v) as eluent, (3*S*,4*S*)-4,5-epoxy-5-methylhex-1-en-3-ol *erythro*-(*S*)-**11B** and (3*R*,4*S*)-4,5-epoxy-5-methylhex-1-en-3-ol *threo*-(*S*)-**11B** were obtained as an inseparable mixture. Owing to the difficulty in separation, the mixture was further acetylated as follows. To a stirred solution of this mixture in CH_2Cl_2 (5 cm^3) were added pyridine (0.79 cm^3), DMAP (95 mg) and acetic anhydride (0.74 cm^3), and the resulting mixture was stirred for 1 h at room temperature. After addition of cold water, the mixture was extracted with CH_2Cl_2. The extract was washed successively with saturated aq. $KHSO_4$, saturated aq. $NaHCO_3$ and brine, and dried over Na_2SO_4. Evaporation of the mixture gave a residue, which was purified by column chromatography on silica gel with pentane–Et_2O (9:1, v/v) as eluent. The first fraction gave (3*S*,4*S*)-3-acetoxy-4,5-epoxy-5-methylhex-1-ene (23.3 mg, 51%) as an oil; $[\alpha]_D^{24}$ −68.3 (*c* 0.32, $CHCl_3$). The spectral data of this compound were identical with those of (3*R*,4*R*)-3-acetoxy-4,5-epoxy-5-methylhex-1-ene produced by the kinetic resolution of dienol *rac*-**10B**. The second fraction gave (3*S*,4*R*)-3-acetoxy-4,5-epoxy-5-methylhex-1-ene (250 mg, 55%) as an oil; $[\alpha]_D^{26}$ +15.4 (*c* 1.12, $CHCl_3$). The spectral data of this compound were identical with those of (3*R*,4*S*)-3-acetoxy-4,5-epoxy-5-methylhex-1-ene produced by the kinetic resolution of dienol *rac*-**10B**.

Epoxidation of dienol (*S*)-10B with L-(+)-DIPT. The reaction was performed on 2.68 mmol scale (300 mg) of compound (*S*)-**10B** with Ti(OPr^i)$_4$ (0.3 mol equiv.), L-(+)-DIPT (0.36 mol equiv.) and TBHP (1.2 mol equiv.) providing (3*S*,4*S*)-4,5-epoxy-5-methylhex-1-en-3-ol *erythro*-(*S*)-**11B** and (3*S*,4*R*)-4,5-epoxy-5-methylhex-1-en-3-ol *threo*-(*S*)-**11B** as an inseparable mixture. Owing to the difficulty in separation, the mixture was further acetylated as follows. To a stirred solution of this mixture in CH_2Cl_2 (6 cm^3) were added pyridine (0.68 cm^3), DMAP (57 mg) and acetic anhydride (0.67 cm^3), and the resulting mixture was stirred for 1 h at room temperature. After addition of cold water, the mixture was extracted with CH_2Cl_2. The extract was washed successively with saturated aq. $KHSO_4$, saturated aq. $NaHCO_3$ and brine, and dried over Na_2SO_4. Evaporation of the solvent gave a residue, which was purified by column chromatography on silica gel with pentane–Et_2O (9:1, v/v) as eluent. The first fraction gave (3*S*,4*S*)-3-acetoxy-4,5-epoxy-5-methylhex-1-ene (198 mg, 43.5%) as an oil; $[\alpha]_D^{24}$ −72.0 (*c* 1.13, $CHCl_3$). The spectral data of this compound were identical with those of (3*S*,4*S*)-3-acetoxy-4,5-epoxy-5-methylhex-1-ene described above. The second fraction gave (3*S*,4*R*)-3-acetoxy-4,5-epoxy-5-methylhex-1-ene (95 mg, 21%) as an oil; $[\alpha]_D^{24}$ +15.2 (*c* 0.83, $CHCl_3$). The spectral data of this compound were identical with those of (3*S*,4*R*)-3-acetoxy-4,5-epoxy-5-methylhex-1-ene described above.

Epoxidation of dienol (*S*)-10C with D-(−)-DIPT. The reaction was performed on 1.09 mmol scale (150 mg) of compound (*S*)-**10C** with Ti(OPr^i)$_4$ (0.45 mol equiv.), D-(−)-DIPT (0.5 mol equiv.) and TBHP (1.2 mol equiv.). After purification by column chromatography on silica gel with

pentane–Et_2O (8:1, v/v) as eluent, (1*S*,1′*R*,2′*R*)-(1,2-epoxycyclohexyl)prop-2-en-1-ol *erythro*-(*S*)-**11C** and (1*S*,1′*S*,2′*S*)-(1,2-epoxycyclohexyl)prop-2-en-1-ol *threo*-(*S*)-**11C** (162 mg, 96%) were obtained as an inseparable oily mixture. The ratio of products *erythro*-(*S*)-**11C** and *threo*-(*S*)-**11C** (10:1) was determined by ^1H NMR analysis.

Epoxidation of dienol (*S*)-10C with L-(+)-DIPT. The reaction was performed on 0.6 mmol scale (83 mg) of dienol (*S*)-**10C** with $Ti(OPr^i)_4$ (0.25 mol equiv.), D-(−)-DIPT (0.3 mol equiv.) and TBHP (1.2 mol equiv.). After purification by column chromatography on silica gel with pentane–Et_2O (8:1, v/v) as eluent, *erythro*-(*S*)-**11C** (82 mg, 89%) was obtained as an oil; $[\alpha]_D^{23}$ +22.9 (*c* 0.82, $CHCl_3$). The spectral data of this compound were identical with those of *erythro*-(*R*)-**11C** produced by kinetic resolution of dienol *rac*-**10C**.

Epoxidation of dienol (*S*)-10D with D-(−)-DIPT. The reaction was performed on 1.88 mmol scale (300 mg) of compound (*S*)-**10D** with $Ti(OPr^i)_4$ (1.05 mol equiv.), D-(−)-DIPT (1.1 mol equiv.) and TBHP (1.2 mol equiv.) and gave (3*S*,4*S*,5*S*)-4,5-epoxy-5-phenylpent-1-en-3-ol *erythro*-(*S*)-**11D**, (3*S*,4*R*,5*R*)-4,5-epoxy-5-phenylpent-1-en-3-ol *threo*-(*S*)-**11D**, (1*E*,3*R*,4*S*)-4,5-epoxy-1-phenylpent-1-en-3-ol (*R*)-**12D** and recovered starting material (*S*)-**10D**. These compounds were purified by column chromatography on silica gel with hexane–EtOAc (7:1, v/v) as eluent. The first fraction gave the recovered starting material (*S*)-**10D** (56 mg, 19%) as an oil. The second fraction gave epoxides *erythro*-(*S*)-**11D** and *threo*-(*S*)-**11D** (54 mg, 17%) as an inseparable oily mixture. The ratio of *erythro*-(*S*)-**11D** to *threo*-(*S*)-**11D** (2.5:1) was determined by ^1H NMR analysis. The third fraction gave epoxide (*R*)-**12D** (127 mg, 39%) as an oil; $[\alpha]_D^{27}$ −68.8 (*c* 0.84, $CHCl_3$); ν_{max}(thin film)/cm^{-1} 695, 749, 846, 969, 1028, 1071, 1105, 1255, 1450, 1495, 2998, 3026, 3059 and 4320; δ_H 2.35 (1 H, d, *J* 1.8, OH), 2.78 (1 H, dd, *J* 3.7 and 4.9, 5-H^a), 2.85 (1 H, dd, *J* 3.1 and 4.9, 5-H^b), 3.17 (1 H, ddd, *J* 3.1, 3.7 and 6.7, 4-H), 4.50 (1 H, m, 3-H), 6.18 (1 H, dd, *J* 6.7 and 15.9, 2-H), 6.70 (1 H, d, *J* 15.9, 1-H) and 7.22–7.41 (5 H, m, Ph); δ_C 43.6 (t), 54.1 (d), 70.1 (d), 126.4 (d), 126.6 (d), 128.1 (d), 128.7 (d), 132.9 (d) and 136.2 (s) (Found: M^+, 176.0836. Calc. for $C_{11}H_{12}O_2$: M, 176.0836).

Epoxidation of dienol (*S*)-10D with L-(+)-DIPT. The reaction was performed on 1.25 mmol scale (200 mg) with $Ti(OPr^i)_4$ (0.25 mol equiv.), D-(−)-DIPT (0.3 mol equiv.) and TBHP (1.2 mol equiv.). After purification by column chromatography on silica gel with hexane–EtOAc (5:1, v/v) as eluent, (3*S*,4*S*,5*S*)-4,5-epoxy-5-phenylpent-1-en-3-ol *erythro*-(*S*)-**11D** (201 mg, 91%) was obtained as an oil; $[\alpha]_D^{24}$ −10.2 (*c* 0.4, $CHCl_3$). The spectral data of this compound were identical with those of *erythro*-(*R*)-**11D**.

Epoxidation of dienol (*S*)-10E with D-(−)-DIPT. The reaction was performed on 2.86 mmol scale (400 mg) with $Ti(OPr^i)_4$ (0.5 mol equiv.), D-(−)-DIPT (0.55 mol equiv.) and TBHP (1.2 mol equiv.) and provided (3*S*,4*S*,5*S*)-4,5-epoxy-6,6-dimethylhept-1-en-3-ol *erythro*-(*S*)-**11E**, (3*S*,4*R*,5*R*)-4,5-epoxy-6,6-dimethylhept-1-en-3-ol *threo*-(*S*)-**11E** and (2*S*,3*R*,4*E*)-1,2-epoxy-6,6-dimethylhept-4-en-3-ol (*R*)-**12E**. These compounds were purified by column chromatography on silica gel with pentane–Et_2O (15:1, v/v) as eluent. The first fraction gave diastereoisomers *erythro*-(*S*)-**11E** and *threo*-(*S*)-**11E** (95 mg, 21%) as an inseparable oily mixture. The ratio of *erythro*-(*S*)-**11E** to *threo*-(*S*)-**11E** (1:1.7) was determined by ^1H NMR analysis. The second fraction gave compound (*R*)-**12E** (211 mg, 48%) as an oil; $[\alpha]_D^{20}$ −69.8 (*c* 0.52, $CHCl_3$). The spectral data of this compound were identical with those of the authentic specimen produced by kinetic resolution of dienol *rac*-**10E**.

Epoxidation of dienol (*S*)-10E with L-(+)-DIPT. The reaction was performed on 0.71 mmol scale (100 mg) with $Ti(OPr^i)_4$ (0.25 mol equiv.), L-(+)-DIPT (0.3 mol equiv.) and TBHP (1.2 mol equiv.). After purification by column chromatography on silica gel with pentane–Et_2O (15:1, v/v) as eluent, (3*S*,4*S*,5*S*)-4,5-epoxy-6,6-dimethylhept-1-en-3-ol *erythro*-(*S*)-**11E** (88 mg, 79%) was obtained as an oil; $[\alpha]_D^{22}$ +34.5 (*c* 0.33, $CHCl_3$). The spectral data of this compound were identical with those of *erythro*-(*R*)-**11E** produced by kinetic resolution of dienol *rac*-**10E**.

Catalytic kinetic resolution of dienol *rac*-13. The reaction was performed on 1.77 mmol scale (1.7 g) of *rac*-**13** with $Ti(OPr^i)_4$ (0.25 mol equiv.), D-(−)-DIPT (0.3 mol equiv.) and TBHP (0.6 mol equiv.) and provided (1*E*,3*S*,4*E*)-1-phenylhexa-1,4-dien-3-ol (*S*)-**13**, (1*R*,2*R*,3*R*,4*E*)-1,2-epoxy-1-phenylhex-4-en-3-ol (*R*)-**14** and (1*E*,3*R*,4*R*,5*R*)-4,5-epoxy-1-phenylhex-1-en-3-ol (*R*)-**15**. They were purified by column chromatography on silica gel with hexane–EtOAc (10:1, v/v) as eluent. The first fraction gave dienol (*S*)-**13** (539 mg, 32%) as an oil; the ee was 46%, determined by HPLC with CHIRALCEL AD (Daicel Chemical Industries, Ltd.) and hexane–Pr^iOH (98:2, v/v) as eluent; $\nu_{max}(CHCl_3)/cm^{-1}$ 965, 1030, 1180, 1370, 1435, 1490, 1600, 1675, 2860 and 3430; δ_H 1.66 (1 H, d, *J* 3.7, OH), 1.74 (3 H, d, *J* 6.7, Me), 4.76 (1 H, m, 3-H), 5.63 (1 H, dddd, *J* 1.2, 3.1, 6.7 and 15.3, 4-H), 5.78 (1 H, dq, *J* 6.7 and 15.3, 5-H), 6.24 (1 H, dd, *J* 6.1 and 15.9, 2-H), 6.59 (1 H, d, *J* 15.9, 1-H) and 7.20–7.41 (5 H, m, Ph) (Found: M^+, 174.1046. Calc. for $C_{12}H_{14}O$: M, 174.1045). The spectral data of this compound were identical with those of *rac*-**13**. The second fraction gave compound (*R*)-**14** (684 mg, 37%) as an oil; ν_{max}(thin film)/cm^{-1} 698, 749, 884, 966, 1086, 1439, 1448, 1462, 1498, 1605, 1676, 2856, 2880, 2916, 2939, 2978, 3030, 3064 and 3430; δ_H 1.73 (3 H, d, *J* 6.7, Me), 2.08 (1 H, d, *J* 1.8, OH), 3.15 (1 H, dd, *J* 2.4 and 3.1, 2-H), 3.96 (1 H, d, *J* 2.4, 1-H), 4.40 (1 H, m, 3-H), 5.53 (1 H, dddd, *J* 1.8, 3.1, 7.3 and 15.3, 4-H), 5.87 (1 H, dq, *J* 6.7 and 15.3, 5-H) and 7.26–7.39 (5 H, m, Ph); δ_C 17.7 (q), 55.0 (d), 64.3 (d), 70.1 (d), 125.7 (d), 128.1 (d), 128.3 (d), 128.5 (d), 129.7 (d) and 136.7 (s) (Found: M^+, 190.0989. Calc. for $C_{12}H_{14}O_2$: M, 190.0992). The third fraction gave compound (*R*)-**15** (347 mg, 19%) as prisms, mp 52.5–53 °C (from hexane–Et_2O); ν_{max}(thin film)/cm^{-1} 695, 755, 872, 970, 1020, 1071, 1102, 1379, 1449, 1495, 1577, 1599, 2927, 2976, 3026, 3059, 3083 and 3415; δ_H 1.36 (3 H, d, *J* 5.5, Me), 2.07 (1 H, d, *J* 2.4, OH), 2.91 (1 H, dd, *J* 2.4 and 3.7, 4-H), 3.14 (1 H, dq, *J* 2.4 and 5.5, 5-H), 4.48 (1 H, m, 3-H), 6.19 (1 H, dd, *J* 6.7 and 15.9, 2-H), 6.71 (1 H, d, *J* 15.9, 1-H) and 7.22–7.42 (5 H, m, Ph); δ_C 17.2 (q), 51.4 (d), 61.3 (d), 70.2 (d), 126.6 (d), 126.8 (d), 128.0 (d), 128.6 (d), 132.6 (d) and 136.3 (s) (Found: M^+, 190.0988).

Epoxidation of dienol *rac*-13 with D-(−)-DIPT. The reaction was performed on 2.53 mmol scale (440 mg) of dienol *rac*-**13** with $Ti(OPr^i)_4$ (1.05 mol equiv.), D-(−)-DIPT (1.1 mol equiv.) and TBHP (1.1 mol equiv.) to afford (1*R*,2*R*,3*R*,4*E*)-1,2-epoxy-1-phenylhex-4-en-3-ol (*R*)-**14** and (1*E*,3*R*,4*R*,5*R*)-4,5-epoxy-1-phenylhex-1-en-3-ol (*R*)-**15**. They were purified by column chromatography on silica gel with hexane–EtOAc (10:1, v/v) as eluent. The first fraction gave compound (*R*)-**14** (197 mg, 41%) as an oil; $[\alpha]_D^{22}$ −21.9 (*c* 0.5, $CHCl_3$); the ee was >99%, determined by HPLC with CHIRALPAK AD (Daicel Chemical Industries, Ltd.) and hexane–Pr^iOH (9:1, v/v) as eluent. The spectral data of this compound were identical with those of compound (*R*)-**14** produced by kinetic resolution of dienol *rac*-**13**. The second fraction gave isomer (*R*)-**15** (208 mg, 43%) as prisms, mp 52.5–53 °C (from hexane–Et_2O); $[\alpha]_D^{23}$ −35.3 (*c* 0.27, $CHCl_3$); the ee was >99%, determined by HPLC with CHIRALPAK AD (Daicel Chemical Industries, Ltd.) and hexane–Pr^iOH (9:1, v/v) as eluent. The spectral data of this compound were identical with those of compound (*R*)-**15** produced by kinetic resolution of dienol *rac*-**13**.

Epoxidation of dienol *rac*-13 with L-(+)-DIPT. The reaction was performed on 2.87 mmol scale (500 mg) with $Ti(OPr^i)_4$ (1.05 mol equiv.), L-(+)-DIPT (1.1 mol equiv.) and TBHP (1.1 mol equiv.) and afforded (1*S*,2*S*,3*S*,4*E*)-1,2-epoxy-1-phenylhex-4-en-3-ol (*S*)-**14** and (1*E*,3*S*,4*S*,5*S*)-4,5-epoxy-1-phenylhex-1-en-3-ol (*S*)-**15**. They were purified by column chromatography on silica gel with hexane–EtOAc (10:1, v/v) as

eluent. The first fraction gave compound (*S*)-**14** (213 mg, 39%) as an oil; $[\alpha]_D^{23}$ +22.3 (*c* 0.72, $CHCl_3$); the ee was >99%, determined by HPLC with CHIRALPAK AD (Daicel Chemical Industries, Ltd.) and hexane–Pr^{i}OH (9:1, v/v) as eluent. The spectral data of this compound were identical with those of enantiomer (*R*)-**14**. The second fraction gave isomer (*S*)-**15** (208 mg, 38%) as prisms, mp 52.5–53 °C (from hexane–Et_2O); $[\alpha]_D^{23}$ +34.7 (*c* 0.54, $CHCl_3$); the ee was >99%, determined by HPLC with CHIRALPAK AD (Daicel Chemical Industries, Ltd.) and hexane–Pr^{i}OH (9:1, v/v) as eluent. The spectral data of this compound were identical with those of enantiomer (*R*)-**15**.

(1*S*,2*S*)-1-(2-Furyl)butane-1,2-diol 16

To a stirred solution of the furylmethanol **7** (720 mg, 4.68 mmol) in toluene (7.2 cm^3) was added dropwise a 0.98 M hexane solution of DIBAL (11.9 cm^3, 1.17 mmol), and the mixture was stirred for 2 h at 0 °C under argon. After addition of water at 0 °C, the precipitate was filtered off. The filtrate was washed successively with saturated aq. NH_4Cl and brine, and dried over Na_2SO_4. Evaporation of the mixture gave a residue, which was purified by column chromatography on silica gel with hexane–EtOAc (3:1, v/v) as eluent to afford the diol **16** (510 mg, 70%) as needles; $[\alpha]_D^{26}$ −14.6 (*c* 0.05, $CHCl_3$); mp 56.8–57.4 °C (from pentane–Et_2O); ν_{max}(thin film)/cm^{-1} 738, 920, 978, 1028, 1067, 1119, 1238, 1441, 1464, 1506, 2933, 2965 and 3330; δ_H 0.99 (3 H, t, *J* 7.3, Me), 1.28–1.56 (2 H, m, 3-H_2), 1.88 (1 H, d, *J* 6.1, 2-OH), 2.49 (1 H, d, *J* 6.1, 1-OH), 3.85 (1 H, m, 2-H), 4.67 (1 H, dd, *J* 4.3 and 6.1, 1-H), 6.35 (1 H, d, *J* 3.7, 3'-H), 6.37 (1 H, dd, *J* 1.8 and 3.7, 4'-H) and 7.41 (1 H, d, *J* 1.8, 5'-H) (Found: C, 61.6; H, 7.55. Calc. for $C_8H_{12}O_3$: C, 61.52; H, 7.74%).

(1*S*,2*S*)-1-(2-Furyl)-1,2-isopropylidenedioxybutane 17

To a stirred solution of the diol **16** (500 mg, 3.21 mmol) in dry acetone (5 cm^3) was added portionwise a catalytic amount of toluene-*p*-sulfonic acid monohydrate (*p*-TsOH), and the resulting mixture was stirred for 1 h at room temperature. After addition of saturated aq. $NaHCO_3$, the organic solvent was evaporated off to leave an oily product, which was extracted with EtOAc. The extract was washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave a residue, which was purified by column chromatography on silica gel with hexane–EtOAc (20:1, v/v) as eluent to afford the acetonide **17** (463 mg, 74%) as an oil; $[\alpha]_D^{26}$ −6.6 (*c* 1.03, $CHCl_3$); ν_{max}(thin film)/cm^{-1} 738, 874, 1011, 1043, 1062, 1149, 1166, 1218, 1244, 1369, 1381, 2879, 2939 and 2983; δ_H 0.89 (3 H, t, *J* 7.3, Me), 1.18–1.46 (2 H, m, 3-H_2), 1.43 and 1.60 (each 3 H, each s, CMe_2), 4.23 (1 H, dt, *J* 6.1 and 8.6, 2-H), 5.10 (1 H, d, *J* 6.1, 1-H), 6.28 (1 H, d, *J* 3.1, 3'-H), 6.33 (1 H, dd, *J* 1.8 and 3.1, 4'-H) and 7.39 (1 H, d, *J* 1.8, 5'-H) (Found: M^+, 196.1106. Calc. for $C_{11}H_{16}O_3$: M, 196.1099).

(2*S*,3*S*)-2,3-Isopropylidenedioxypentanoic acid 18 from the furan 17

To a stirred solution of the acetonide **17** (100 mg, 0.51 mmol) in CCl_4–CH_3CN–water (1:1:1) (8 cm^3) were added $NaIO_4$ (1.09 g, 5.1 mmol) and $RuCl_3$ (4 mg, 0.02 mmol), and the resulting mixture was stirred for 30 min at room temperature. After addition of saturated aq. $NaHCO_3$, the mixture was washed with EtOAc. The aqueous layer was acidified (pH 3) with 1 M HCl, and extracted with Et_2O. The extract was washed with brine and dried over Na_2SO_4. Evaporation of the mixture gave a residue, which was purified by column chromatography on silica gel with $CHCl_3$–MeOH (10:1, v/v) as eluent to afford the acid **18** (56.4 mg, 64%) as an oil; $[\alpha]_D^{26}$ −13.3 (*c* 1.03, $CHCl_3$); ν_{max}(thin film)/cm^{-1} 783, 873, 995, 1013, 1093, 1110, 1167, 1220, 1242, 1371, 1382, 1458, 1733, 2882, 2940, 2984 and 3160; δ_H 1.06 (3 H, t, *J* 7.3, Me), 1.36–1.78 (8 H, m, 4-H_2 and CMe_2), 4.30 (1 H, ddd, *J* 4.3, 6.7 and 9.2, 3-H), 4.58 (1 H, d, *J* 6.7, 2-H) and 7.80–9.60 (1 H, br s, CO_2H); δ_C 10.8 (q), 23.6 (t), 25.4 (q), 27.0 (q), 76.8 (d), 79.2 (d), 110.7 (s) and 174.9 (s) [Found: (M^+ − 15), 159.0660. Calc. for $C_7H_{11}O_4$: (M − 15), 159.0658].

(1*E*,3*R*,4*S*)-1-Phenylhex-1-ene-3,4-diol 19 from oxirane (*R*)-15

Reduction of the epoxide (*R*)-**15** (300 mg, 1.58 mmol) with DIBAL was carried out by the same procedure as for the preparation of diol **16** from epoxide **7** to give the diol **19** (165 mg, 54%) as needles; $[\alpha]_D^{26}$ −9.6 (*c* 0.38, $CHCl_3$); mp 93.4–94.2 °C (from pentane–Et_2O); ν_{max}(thin film)/cm^{-1} 689, 750, 875, 967, 987, 1014, 1056, 1134, 1456, 2341, 2360, 2893, 2932, 2960 and 3260; δ_H 1.01 (3 H, t, *J* 7.3, Me), 1.40–1.62 (2 H, m, 5-H_2), 2.03 (1 H, d, *J* 4.3, 4-OH), 2.07 (1 H, m, 3-OH), 3.71 (1 H, m, 4-H), 4.29 (1 H, m, 3-H), 6.30 (1 H, dd, *J* 6.7 and 15.9, 2-H), 6.66 (1 H, d, *J* 15.9, 1-H) and 7.22–7.65 (5 H, m, Ph) (Found: C, 74.9; H, 8.4. Calc. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39%).

(1*E*,3*R*,4*S*)-3,4-Isopropylidenedioxy-1-phenylhex-1-ene 20

The oily acetonide **20** (175 mg, 91%) was synthesized by the same procedure as for the preparation of the acetonide **17** from diol **16**; $[\alpha]_D^{25}$ +8.8 (*c* 1.75, $CHCl_3$); ν_{max}($CHCl_3$)/cm^{-1} 865, 965, 1010, 1155, 1365, 1445 and 2870; δ_H 0.97 (3 H, t, *J* 7.3, Me), 1.43–1.66 (8 H, m, 5-H_2 and CMe_2), 4.12 (1 H, dt, *J* 6.1 and 8.5, 4-H), 4.68 (1 H, dd, *J* 6.1 and 7.9, 3-H), 6.17 (1 H, dd, *J* 7.9 and 15.9, 2-H), 6.61 (1 H, d, *J* 15.9, 1-H) and 7.21–7.41 (5 H, m, Ph) (Found: M^+, 232.1462. Calc. for $C_{15}H_{20}O_2$: M, 232.1462).

(2*S*,3*S*)-2,3-Isopropylidenedioxypentanoic acid 18 from the styrene 20

The oily acid **18** (90 mg, 80%) was synthesized by the same procedure as for the preparation of the acid **18** from the furan **17**; $[\alpha]_D^{25}$ −13.5 (*c* 0.99, $CHCl_3$) [Found: (M^+ − 15), 159.0656. Calc. for $C_7H_{11}O_4$: (M − 15), 159.0656]. The spectral data of this compound were identical with those of the acid **18** derived from the furan **17**.

(1*E*,3*R*,4*S*,5*R*)-4,5-Epoxy-1-phenyl-3-(triethylsiloxy)hex-1-ene 21

To a stirred solution of the epoxy alcohol (*R*)-**15** (182 mg, 0.96 mmol) in CH_2Cl_2 (3 cm^3) was added imidazole (130 mg, 1.92 mmol) and TESCl (0.24 cm^3, 1.44 mmol), and the resulting mixture was stirred for 10 min at room temperature under argon. After addition of saturated aq. NH_4Cl, the mixture was extracted with Et_2O. The extract was washed with brine and dried over Na_2SO_4. Evaporation of the mixture gave a residue, which was purified by column chromatography on silica gel with hexane–EtOAc (26:1, v/v) as eluent to afford the silyl ether **21** (278 mg, 96%) as an oil; $[\alpha]_D^{28}$ −17.6 (*c* 1.0 $CHCl_3$); ν_{max}($CHCl_3$)/cm^{-1} 870, 925, 965, 1000, 1115, 1415, 1450 and 2880; δ_H 0.63 (6 H, q, *J* 7.9, 3 × $SiCH_2CH_3$), 0.97 (9 H, t, *J* 7.9, 3 × $SiCH_2CH_3$), 1.33 (3 H, d, *J* 5.5, Me), 2.76 (1 H, dd, *J* 2.4 and 4.9, 4-H), 3.01 (1 H, dq, *J* 2.4 and 5.5, 5-H), 4.16 (1 H, dd, *J* 4.9 and 6.1, 3-H), 6.25 (1 H, dd, *J* 6.1 and 15.9, 2-H), 6.62 (1 H, d, *J* 15.9, 1-H) and 7.21–7.41 (5 H, m, Ph) [Found: (M^+ − 29), 275.1465. Calc. for $C_{16}H_{23}O_2Si$: (M − 29), 275.1465].

(3*S*,4*R*,5*E*)-2-Methyl-6-phenyl-4-(triethylsiloxy)hex-5-en-3-ol 22

To a stirred suspension of CuI (370 mg, 1.94 mmol) in Et_2O (5 cm^3) was added a 1.06 M Et_2O solution of methyllithium (3.66 cm^3, 3.88 mmol) at 0 °C under argon. After stirring of the mixture for 10 min at the same temperature, a solution of the silyl ether **21** (295 mg, 0.97 mmol) in Et_2O (5 cm^3) was added. The resulting mixture was further stirred for 30 min at 0 °C. After addition of saturated aq. NH_4Cl, the mixture was extracted with Et_2O. The extract was washed with brine and dried over Na_2SO_4. Evaporation of the mixture gave a residue, which was purified by column chromatography on silica gel with hexane–EtOAc (30:1, v/v) as eluent. The first fraction gave silyl ether **22** (197 mg, 63%) as an oil; $[\alpha]_D^{26}$ −59.3 (*c* 1.0,

$CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 880, 900, 970, 1005, 1150, 1305, 1375, 1415, 1455, 2900 and 3560; δ_H 0.59 (6 H, q, *J* 8.5, 3 × $SiCH_2CH_3$), 0.90–1.03 (15 H, m, 2 × Me and 3 × $SiCH_2CH_3$), 1.62–1.75 (1 H, m, 2-H), 2.56 (1 H, d, *J* 1.8, OH), 3.32 (1 H, ddd, *J* 1.8, 3.1 and 7.9, 3-H), 4.32 (1 H, dd, *J* 3.1 and 7.9, 4-H), 6.27 (1 H, dd, *J* 7.9 and 15.9, 6-H), 6.56 (1 H, d, *J* 15.9, 5-H) and 7.21–7.41 (5 H, m, Ph) [Found: (M^+ − 73), 247.1513. Calc. for $C_{15}H_{23}OSi$: (M − 73), 247.1518]. The second fraction gave (2*R*,3*R*,4*S*)-3-methyl-6-phenyl-4-(triethylsiloxy)hex-5-en-2-ol as an oil; $\nu_{max}(CHCl_3)/cm^{-1}$ 965, 1000, 1115, 1300, 1360, 1380, 1405, 1450, 2900 and 3440; δ_H 0.64 (6 H, q, 7.9, 3 × $SiCH_2CH_3$), 0.82 (3 H, d, *J* 7.3, 3-Me), 0.97 (9 H, t, *J* 7.9, 3 × $SiCH_2CH_3$), 1.15 (3 H, d, *J* 6.1, 1-H_3), 1.80 (2 H, m, 3-H and OH), 3.81 (1 H, dq, *J* 3.1 and 6.1, 2-H), 4.45 (1 H, dd, *J* 3.7 and 6.7, 4-H), 6.30 (1 H, dd, *J* 6.7 and 15.9, 5-H), 6.54 (1 H, d, *J* 15.9, 6-H) and 7.22–7.41 (5 H, m, Ph) (Found: M^+, 320.2172. Calc. for $C_{19}H_{32}O_2Si$: M, 320.2172).

(1*E*,3*R*,4*S*)-5-Methyl-1-phenylhex-1-ene-3,4-diol 23

To a stirred solution of the silyl ether **22** (190 mg, 0.63 mmol) in THF (3 cm^3) was added dropwise a 1 M THF solution of tetrabutylammonium fluoride (TBAF) (0.27 cm^3, 0.94 mmol) at 0 °C, and the resulting mixture was stirred for 1 h at the same temperature under argon. After addition of water, the organic solvent was evaporated to leave an oily product, which was extracted with EtOAc. The extract was washed with brine and dried over Na_2SO_4. Evaporation of the solvent gave a residue, which was purified by column chromatography on silica gel with hexane–EtOAc (4:1, v/v) as eluent to afford the diol **23** (116 mg, 90%) as needles; $[\alpha]_D^{28}$ +0.176 (*c* 0.84, $CHCl_3$); mp 85.1–85.8 °C (from pentane–Et_2O); $\nu_{max}(CHCl_3)/cm^{-1}$ 965, 990, 1185, 1385, 1455, 2900 and 3430; δ_H 0.94 and 1.04 (each 3 H, each d, *J* 6.7, 2 × Me), 1.72 (1 H, dq, *J* 6.7 and 7.9, 5-H), 2.02 (1 H, d, *J* 4.9, 3-OH), 2.05 (1 H, d, *J* 4.3, 4-OH), 3.46 (1 H, ddd, *J* 3.7, 4.3 and 7.9, 4-H), 4.38 (1 H, ddd, *J* 3.7, 4.9 and 7.9, 3-H), 6.36 (1 H, dd, *J* 7.9 and 15.9, 2-H), 6.69 (1 H, d, *J* 15.9, 1-H) and 7.23–7.65 (5 H, m, Ph) (Found: C, 75.5; H, 8.7. Calc. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80%).

(3*R*,4*S*)-3,4-Isopropylidenedioxy-5-methyl-1-phenylhex-1-ene 24

The acetonide **24** (98 mg, 99%, needles) was synthesized by the same procedure as for the preparation of the acetonide **17** from diol **16**; $[\alpha]_D^{26}$ +63.9 (*c* 0.75, $CHCl_3$); mp 56.1–56.9 °C (from pentane–Et_2O); $\nu_{max}(CHCl_3)/cm^{-1}$ 875, 970, 1005, 1130, 1160, 1370, 1450 and 2900; δ_H 0.85 and 1.05 (each 3 H, each d, *J* 6.1, 2 × Me), 1.39 and 1.54 (each 3 H, each s, CMe_2), 1.80 (1 H, m, 5-H), 3.79 (1 H, dd, *J* 5.5 and 9.8, 4-H), 4.60 (1 H, dd, *J* 5.5 and 8.6, 3-H), 6.22 (1 H, dd, *J* 8.6 and 15.9, 2-H), 6.58 (1 H, d, *J* 15.9, 1-H) and 7.21–7.41 (5 H, m, Ph) (Found: M^+, 246.1620. Calc. for $C_{16}H_{22}O_2$: M, 246.1620).

(2*S*,3*S*)-2,3-Isopropylidenedioxy-4-methylpentanoic acid 25

The oily acid **25** (63.5 mg, 79%) was synthesized by the same procedure as for the preparation of the acid **18** from the furan **17**; $[\alpha]_D^{28}$ +26.9 (*c* 0.59, $CHCl_3$); ν_{max}(thin film)/cm^{-1} 875, 1087, 1165, 1222, 1245, 1370, 1383, 1728, 2343, 2360, 2376, 2940, 2964, 2986 and 3020; δ_H 1.02 and 1.04 (each 3 H, each d, *J* 6.1, 2 × Me), 1.39 and 1.61 (each 3 H, each s, CMe_2), 1.84 (1 H, m, 4-H), 3.96 (1 H, dd, *J* 6.7 and 9.2, 3-H), 4.58 (1 H, d, *J* 6.7, 2-H) and 8.56–9.88 (1 H, br s, CO_2H); δ_C 19.5 (q), 19.9 (q), 25.5 (q), 26.7 (q), 28.7 (d), 76.7 (d), 83.9 (d), 110.5 (s) and 176.4 (s) [Found: (M^+ − 15), 173.0814. Calc. for $C_8H_{13}O_4$: (M − 15), 173.0814].

(1*E*,3*R*,4*S*)-4,5-Epoxy-1-phenyl-3-(triethylsiloxy)pent-1-ene 26

The oily silyl ether **26** (123 mg, 93%) was synthesized by the same procedure as for the preparation of the silyl ether **21** from epoxide (*R*)-**15**; $[\alpha]_D^{24}$ −47.4 (*c* 1.06, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 975, 1005, 1130, 1430, 1465, 1615 and 2900; δ_H 0.63 (6 H, q, *J* 8.6, 3 × $SiCH_2CH_3$), 0.97 (9 H, t, *J* 8.6, 3 × $SiCH_2CH_3$), 2.75 (2 H, m, 5-H_2), 3.02 (1 H, m, 4-H), 4.24 (1 H, m, 3-H), 6.24 (1 H, dd, *J* 6.7 and 15.9, 2-H), 6.63 (1 H, d, *J* 15.9, 1-H) and 7.20–7.41 (5 H, m, Ph) (Found: M^+, 290.1708. Calc. for $C_{17}H_{26}O_2Si$: M, 290.1702).

(3*S*,4*R*,5*E*)-6-Phenyl-4-(triethylsiloxy)hex-5-en-3-ol 28

The oily alcohol **28** (98 mg, 88%) was synthesized by the same procedure as for the preparation of the silyl ether **22** from epoxide **21**; $[\alpha]_D^{22}$ −67.6 (*c* 1.02, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 895, 955, 980, 1305, 1380, 1460, 1605, 2890 and 3500; δ_H 0.63 (6 H, q, *J* 7.9, 3 × $SiCH_2CH_3$), 0.92–1.02 (12 H, m, Me and 3 × $SiCH_2CH_3$), 1.38–1.54 (2 H, m, 2-H_2), 2.36 (1 H, d, *J* 3.1, OH), 3.57 (1 H, m, 3-H), 4.20 (1 H, dd, *J* 4.9 and 7.9, 4-H), 6.23 (1 H, dd, *J* 7.9 and 15.9, 5-H), 6.53 (1 H, d, *J* 15.9, 6-H) and 7.21–7.40 (5 H, m, Ph) [Found: (M^+ − 18), 288.1912. Calc. for $C_{18}H_{28}OSi$: (M − 18), 288.1910].

(1*E*,3*R*,4*S*)-1-Phenylhexene-3,4-diol 19 from silyl ether 28

The diol **19** (67 mg, 97%, needles) was synthesized by the same procedure as for the preparation of the diol **23** from silyl ether **22**; $[\alpha]_D^{23}$ −8.95 (*c* 0.43, $CHCl_3$); mp 93.8–94.5 °C (from pentane–Et_2O) [Found: (M^+ − 18), 174.1045. Calc. for $C_{12}H_{14}O$: (M − 18), 174.1045]. The spectral data of this compound were identical with those of the diol **19** derived from epoxide (*R*)-**15**.

(3*E*,5*R*,6*S*)-6,7-Epoxy-2,2-dimethyl-5-(triethylsiloxy)hept-3-ene 27

The oily silyl ether **27** (178 mg, 94%) was synthesized by the same procedure as for the preparation of the silyl ether **21** from epoxide (*R*)-**15**; $[\alpha]_D^{26}$ −20.7 (*c* 0.66, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 980, 1005, 1120, 1360, 1455 and 2880; δ_H 0.58 (6 H, q, *J* 7.9, 3 × $SiCH_2CH_3$), 0.94 (9 H, t, *J* 7.9, 3 × $SiCH_2CH_3$), 1.02 (9 H, s, Bu^t), 2.66 and 2.72 (each 1 H, each ddd, *J* 2.4, 3.7 and 5.5, 7-H_2), 2.94 (1 H, ddd, *J* 2.4, 3.7 and 4.3, 6-H), 4.03 (1 H, dd, *J* 4.3 and 6.1, 5-H), 5.37 (1 H, dd, *J* 6.1 and 15.9, 4-H) and 5.70 (1 H, d, *J* 15.9, 3-H) [Found: (M^+ − 29), 241.1630. Calc. for $C_{13}H_{25}O_2Si$: (M − 29), 241.1625].

(3*S*,4*R*,5*E*)-7,7-Dimethyl-4-(triethylsiloxy)oct-5-en-3-ol 29

The oily alcohol **29** (128 mg, 68%) was synthesized by the same procedure as for the preparation of the diol **22** from epoxide **21**; $[\alpha]_D^{25}$ −18.8 (*c* 0.85, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 980, 1005, 1370, 1420, 1465, 2895 and 3580; δ_H 0.58 (6 H, q, *J* 7.3, 3 × $SiCH_2CH_3$), 0.94 (3 H, t, *J* 7.9, Me), 0.95 (9 H, t, *J* 7.3, 3 × $SiCH_2CH_3$), 1.02 (9 H, s, Bu^t), 1.38 (2 H, m, 2-H_2), 2.29 (1 H, d, *J* 3.1, OH), 3.47 (1 H, m, 3-H), 3.95 (1 H, dd, *J* 4.3 and 7.9, 4-H), 5.37 (1 H, dd, *J* 7.9 and 15.9, 5-H) and 5.63 (1 H, d, *J* 15.9, 6-H) [Found: (M^+ − 29), 257.1938. Calc. for $C_{14}H_{29}O_2Si$: (M − 29), 257.1937].

(3*S*,4*R*,5*E*)-7,7-Dimethyloct-5-ene-3,4-diol 30

The diol **30** (73.1 mg, 95%, needles) was synthesized by the same procedure as for the preparation of diol **23** from silyl ether **22**; $[\alpha]_D^{27}$ −11.7 (*c* 0.43, $CHCl_3$); mp 44.0–44.1 °C (from pentane–Et_2O); $\nu_{max}(CHCl_3)/cm^{-1}$ 930, 995, 1005, 1090, 1375, 1475, 2900 and 3470; δ_H 0.97 (3 H, t, *J* 7.3, Me), 1.03 (9 H, s, Bu^t), 1.42 (2 H, m, 2-H_2), 2.07–2.20 (2 H, br s, 2 × OH), 3.59 (1 H, m, 3-H), 4.03 (1 H, dd, *J* 3.7 and 7.3, 4-H), 5.44 (1 H, dd, *J* 7.3 and 15.9, 5-H) and 5.76 (1 H, d, *J* 15.9, 6-H) [Found: (M^+ − 18), 154.1359. Calc. for $C_{10}H_{18}O$: (M − 18), 154.1358].

(2*S*,3*S*)-2,3-Isopropylidenedioxypentanoic acid 18 from diol 30

To a stirred solution of the diol **30** (110 mg, 0.64 mmol) in dry acetone (1 cm^3) was added portionwise a catalytic amount of *p*-TsOH. After stirring of the mixture for 1 h at room temperature, a mixed solvent [CCl_4–CH_3CN–water (1:1:1), 6 cm^3], $RuCl_3$ (5.3 mg, 0.03 mmol) and $NaIO_4$ (1.37 g, 6.4 mmol)

were added to the solution. After stirring of the mixture for 30 min at room temperature, the precipitate was filtered off. Evaporation of the mixture left an oily product, which was extracted with Et_2O. The extract was washed with saturated aq. $NaHCO_3$. The aqueous layer was acidified (pH 3) with 1 M HCl and extracted with Et_2O. The extract was dried over Na_2SO_4. Evaporation of the mixture gave a residue, which was purified by column chromatography on silica gel with hexane–EtOAc (1:2, v/v) as eluent to afford the acid **18** (46 mg, 40%) as an oil; $[\alpha]_D^{30}$ −13.9 (*c* 0.25, $CHCl_3$) [Found: (M^+ − 15), 159.0657. Calc. for $C_7H_{11}O_4$: (M − 15), 159.0657]. The spectral data of this compound were identical with those of the acid **18** derived from the furan **17**.

(3*S*,4*R*)-5-Methylhex-1-ene-3,4-diol 31

Reduction of the epoxide *erythro*-(*S*)-**11B** (1.1 g, 8.59 mmol) with DIBAL was carried out in Et_2O (11 cm^3) by a similar procedure to that for the preparation of diol **16** from epoxide **7** to give the diol **31** (560 mg, 50%) as needles; $[\alpha]_D^{26}$ −24.9 (*c* 0.41, $CHCl_3$); mp 61.5–62.4 °C (from pentane–Et_2O); ν_{max}($CHCl_3$)/cm^{-1} 920, 995, 1095, 1190, 1380, 2900 and 3440; δ_H 0.92 and 1.02 (each 3 H, each d, *J* 6.7, 2 × Me), 1.55–1.78 (1 H, m, 5-H), 1.92 and 2.02 (each 1 H, each d, *J* 4.9 and 5.5, 2 × OH), 3.37 (1 H, m, 4-H), 4.22 (1 H, m, 3-H), 5.30 (1 H, ddd, *J* 1.2, 1.8 and 10.4, 1-H^a), 5.37 (1 H, ddd, *J* 1.2, 1.8 and 17.1, 1-H^b) and 5.99 (1 H, ddd, *J* 6.7, 10.4 and 17.1, 2-H) [Found: (M^+ − 34), 96.0944. Calc. for C_7H_{12}: (M − 34), 96.0939. Found: (M^+ − 35), 95.0854. Calc. for C_7H_{11}: (M − 35), 95.0859].

(2*R*,3*R*)-2,3-Isopropylidenedioxy-4-methylpentanoic acid *ent*-25

The oily acid *ent*-**25** (76.5 mg, 53%) was synthesized by the same procedure as for the preparation of the acid **18** from diol **30**; $[\alpha]_D^{27}$ −25.6 (*c* 0.77, $CHCl_3$) [Found: (M^+ − 15), 173.0819. Calc. for $C_8H_{13}O_4$: (M − 15), 173.0814]. The spectral data of this compound were identical with those of the acid **25**.

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