Use of 1,3-Dioxin-4-ones and Related Compounds in Synthesis. Part 39.[1] Enantioselective Synthesis of 1,3-Dioxin-4-ones Having 2,3-Dihydroxy- or 2,3,4-Trihydroxyalkyl Groups at the 6-Position: Versatile Building Blocks of Polyhydroxylated 4–7 Carbon Backbones

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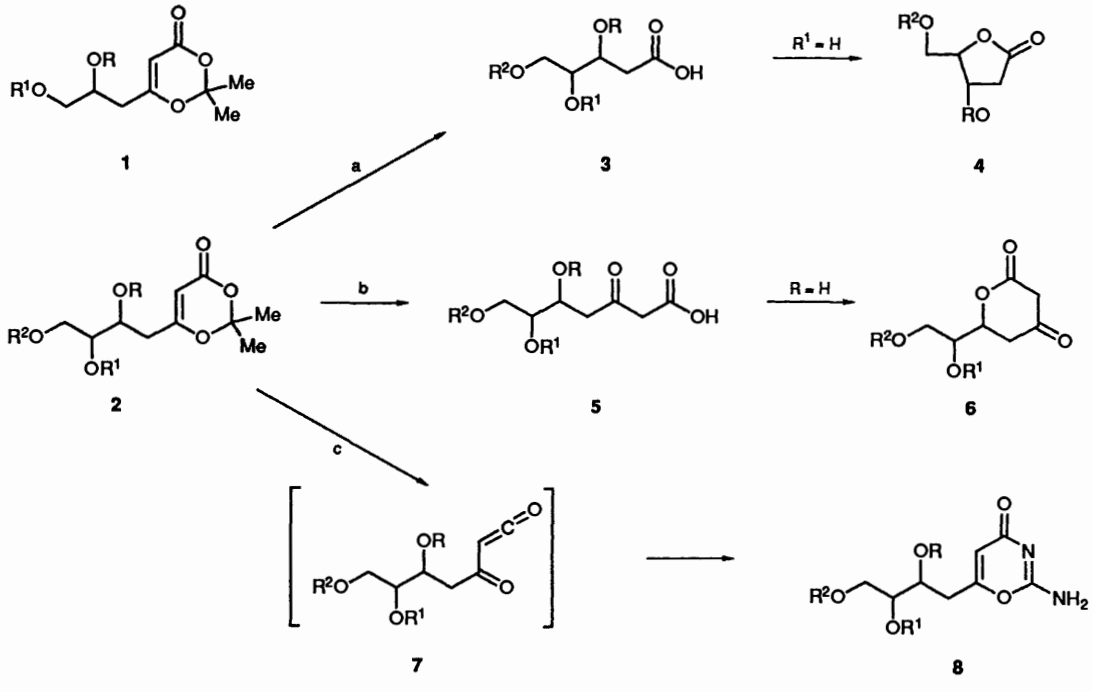
1,3-Dioxin-4-ones having 3-hydroxyprop-1-enyl and 2-hydroxybut-3-enyl groups at the 6-position afford, after the Sharpless asymmetric epoxidation followed by epoxide ring cleavage, the 6-[(2*S*)-2,3-dihydroxypropyl]- and 6-[(2*S*,3*R*)-2,3,4-trihydroxybutyl)dioxinones. The former acts as a four- and six-carbon building block, while the latter as a five- and seven-carbon building block.

1,3-Dioxin-4-ones act as versatile synthons in organic synthesis.[2] We have been interested in synthesizing 6-(2,3-dihydroxypropyl)-2,2-dimethyl-1,3-dioxin-4-one **1** and its higher hydroxymethyl derivative **2** by focusing our attention on the utilization of the dioxinone moiety as the corresponding β-keto acid and acyl ketene equivalents (Scheme 1). Once, dioxinones **1** and **2** are synthesized, the following transformations may be expected. Thus, taking compound **2** as an example, while oxidative cleavage (path a) affords the acids **3** and/or the γ-lactones **4**, hydrolysis at the acetal function (path b)[3] leads to the acids **5** and/or the δ-lactone **6**. Furthermore, by knowing that the 6-electron cycloreversion by heating[4] of the dioxinones to acylketenes **7** takes place readily, their direct manipulation to either heterocycles (*e.g.* **8**) by hetero-Diels–Alder reaction or to ketene trapping compounds by a variety of nucleophiles should also be expected.

In order to economize space, we report our result in two sections: (1) synthesis and reactions of 6-[(2*S*)-2,3-dihydroxypropyl]-2,2-dimethyl-1,3-dioxin-4-ones (*S*)-**1**[5] and (2) those of 2,2-dimethyl-6-[(2*S*,3*R*)-2,3,4-trihydroxybutyl)-1,3-dioxin-4-ones (2*S*,3*R*)-**2**.

Results and Discussion

Synthesis and Reactions of 6-[(2S)-2,3-*Dihydroxypropyl*]-2,2-*dimethyl*-1,3-*dioxin*-4-*ones* (S)-**1**.—Using the readily available 6-methyl derivative **9** as the starting material, the dioxinone (*S*)-**1a** was synthesized as an enantiomerically pure compound (abbreviated as EPC). Although the reaction requires five steps, all reactions except for the first one (*ca.* 70%) proceeded in nearly quantitative yields and are suitable for large-scale preparation. Thus, base-catalysed chloroacetylation to the chloroketone **10** followed by sodium borohydride reduction gave the chloro alcohol **11**. Treatment of this compound **11** with aqueous NaOH–ether at room temperature gave the allylic alcohol **13** as the sole product. Presumably, the epoxide **12** was formed first, which was then cleaved to the alcohol **13**. Epoxidation[6,7] of the alcohol **13** by employing *tert*-butyl

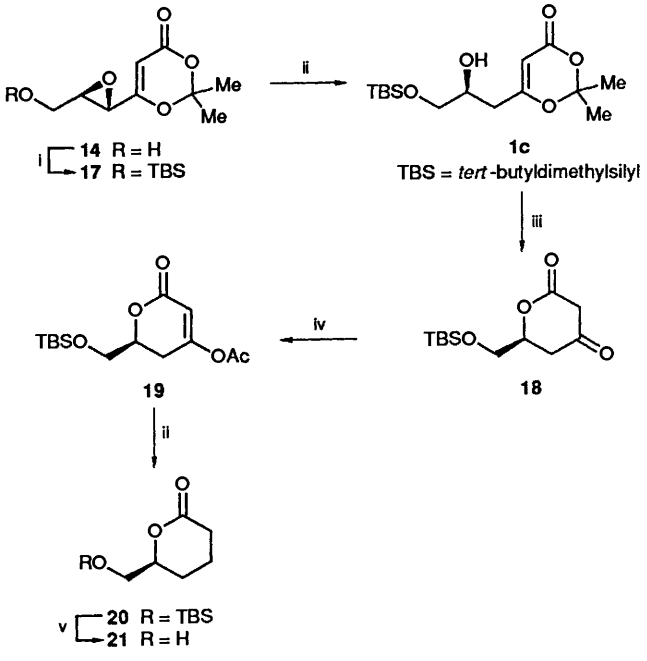


Scheme 1

hydroperoxide (TBHP) as an oxygen donor and titanium tetraisopropoxide–diisopropyl-D-(−)-tartrate (DIPT) as the catalyst, in the presence of 4 Å molecular sieves,* gave the epoxide **14**. ^{1}H NMR analysis of the Mosher ester in $CDCl_3$ indicated ⩾98% enantiomeric excess (ee). Catalytic hydrogenation of the epoxy alcohol **14** in ethyl acetate afforded the diol (*S*)-**1a**.

The absolute structure of the epoxide **14** was determined by its transformation (ozonolysis followed by treatment with trifluoroacetic acid) to (*S*)-3-hydroxybutan-4-olide **15**.† An alternative synthesis of this compound **15** and its use in natural products synthesis as well as transformation to other four-carbon building blocks have been carried out by many researchers.‡ The diol **1a** also afforded, *via* the acetonide **1b**, the protected dihydroxy β-keto ester **16**: the six-carbon building block, which is useful for synthesis of HR 780,[11] a synthetic HMG-CoA reductase inhibitor. Though several synthetic methods for the ester **16** are available, none seems to be satisfactory owing to low availability of the starting materials.[12] When the route shown in Scheme 2 was carried out by using L-(+)-DIPT in the epoxidation step, the enantiomer {6-[(2*R*)-2,3-dihydroxypropyl]-2,2-dimethyl-1,3-dioxin-4-one} was also synthesized with the same efficiency (see Experimental section).

Finally, a new synthetic route for the hydroxylactone **21**[13] which is known as a versatile intermediate for the preparation of leukotriene B according to the present methodology is described. The epoxide **14** was converted into the lactone **21** by the following sequence: (i) protection of the compound **14** by *tert*-butyldimethylsilyl group to give the silylated alcohol **17**, (ii) hydrogenation over 10% Pd–C in ethyl acetate to give the diol **1c**, (iii) base-catalysed ring transposition, (iv) acetylation with acetic anhydride, (v) catalytic hydrogenation, and (vi) deblocking of the silyloxy group with tetrabutylammonium fluoride.

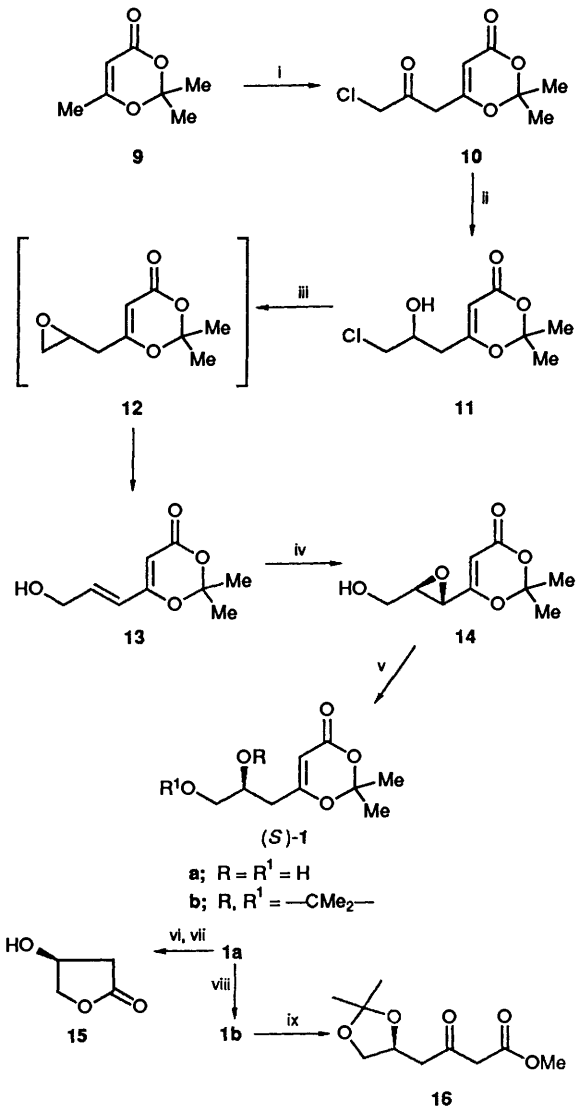


Scheme 3 *Reagents and conditions:* i, TBDMSCl, imidazole, DMF; ii, H_2, Pd–C, AcOEt; iii, K_2CO_3, MeOH; iv, Ac_2O, pyridine; v, Bu_4NF, THF

This synthesis starts from readily available dioxinone **9** and proceeds, as well as with high enantioselectivity (the epoxidation step proceeds in ⩾98% ee), with complete stereo- and regio-selectivities.

Synthesis and Reactions of 2,2-*Dimethyl*-6-[(2S,3R)-2,3,4-*trihydroxybutyl*]-1,3-*dioxin*-4-*ones* **2**.—In order to synthesize title compounds **2**, we have selected 2,2-dimethyl-6-(2-hydroxybut-3-enyl)-1,3-dioxin-4-one **24** as the suitable starting material for the following two reasons: (1) synthesis of this compound **24** seems to be easy from the readily available dioxinone **9**, and (2) kinetic resolution of racemic allylic alcohols by means of Sharpless epoxidation[14] seems to be applicable to this alcohol **24**.

Racemic alcohol **24** can be readily synthesized by aldol-type



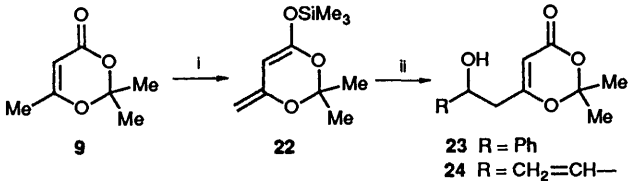
Scheme 2 *Reagents and conditions:* i, LDA (1 equiv.), HMPA, Et_2O, then $ClCH_2COCl$ (0.5 equiv.), −78 °C; ii, $NaBH_4$, MeOH; iii, aqueous NaOH (2 mol dm^{-3}); iv, TBHP, diisopropyl D-(−)tartrate, $Ti(OPr^i)$, molecular sieves 4 Å, CH_2Cl_2, −20 °C; v, H_2, Pd–C, AcOEt; vi, O_3 and then Me_2S, −78 °C; vii, CF_3CO_2H, CH_2Cl_2; viii, $Me_2C(OMe)_2$; $HClO_4$, acetone; ix, MeOH, toluene, reflux

* Use of molecular sieves (3 or 4 Å) in the reactions permitted, without lowering of chemical and optical yields, the use of high concentrations of allyl alcohols even with catalytic amounts (10%) of diethyl tartrate (DET).[8]

† Though **15** was synthesized originally by Mori *et al.*, a more efficient route has been elaborated by Saito *et al.* However, the latter used the costly malic acid as the starting material.[9]

‡ Synthesis of a variety of chiral four-carbon building blocks and their use in synthesis of enantiomerically pure compounds have been reviewed.[10]

reaction between the silyl enol ether **22** with acrolein. Compound **22** was synthesized recently from the dioxinone **9** and used as a four-carbon nucleophile to naphthoquinones.[15] Knowing that it could react with benzaldehyde to give the adduct **23**, the same reaction with acrolein was examined. As expected, the desired adduct **24** was obtained as the sole product.



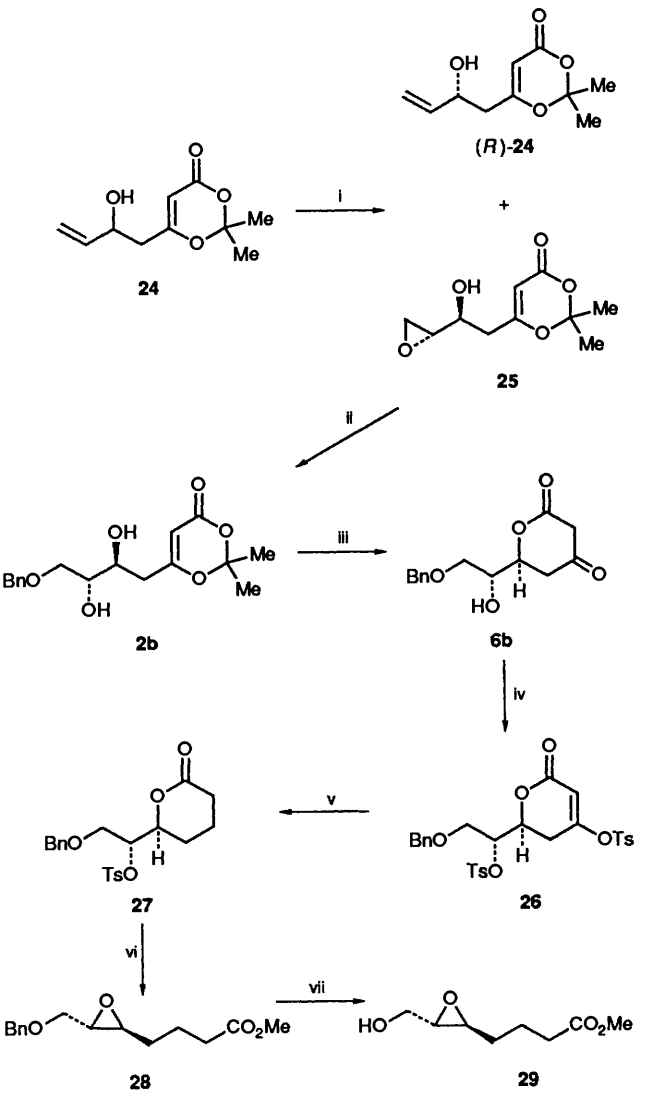
Scheme 4 *Reagents and conditions:* i, LDA, TMSCl, THF, −78 °C; ii, RCHO, $TiCl_4$, CH_2Cl_2, −78 °C

The kinetic resolution of the dioxinone **24** in the presence of L-(+)-diisopropyl tartrate as chiral source afforded the epoxy alcohol **25** with ≥98% ee in 44% yield and the unchanged (*R*)-allylic alcohol (*R*)-**24** with 95% ee in 46% yield. The epoxy alcohol **25** thus obtained was converted into the monobenzylated triol **2b** *via* regiospecific ring opening in the presence of $Ti(OPr^i)_4$.[16] Compound **2b** was subjected to sodium methoxide-mediated one-pot lactonization to give the δ-lactone **6b**, whose tosylation afforded the dihydropyran **26**. Catalytic hydrogenation of compound **26** followed by treatment of the δ-lactone **27** with potassium carbonate in methanol gave the epoxide **28**. This reaction obviously proceeded *via* initial lactone ring cleavage followed by epoxy ring formation. Deblocking of the benzyl group of compound **28** by catalytic hydrogenation gave the epoxy alcohol **29**. Compound **29** was previously synthesized from D-erythrose[17] or from other sources.[18] Identity of the specific rotation data showed again the correctness of the assigned configuration.

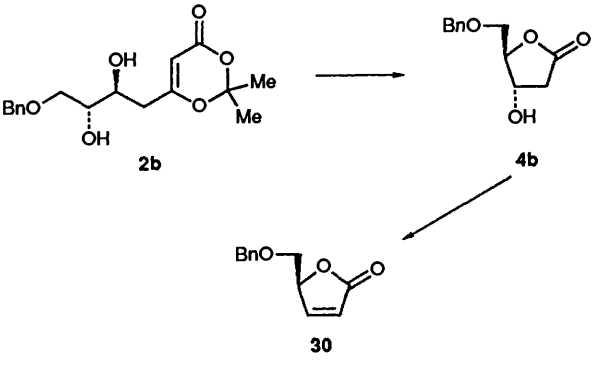
Since the epoxide **29** has already been converted into leukotriene A4,[17,18] the present synthetic scheme implies the formal synthetic route for this compound.

Conclusions.—We have explored a practical and efficient preparation of the dioxinone alcohols **1** and **2** *via* the epoxy alcohols **14** and **25** by the Sharpless oxidation using the naturally occuring L-(+)-tartrate ester and its enantiomer as the chirality-controlling agents. The methodology described above may be extended to the preparation of the reverse enantiomers of the dioxinones **1** and **2**, since epoxidation using the corresponding antipodal tartrates would give rise to the antipodes of the intermediate epoxy alcohols **14** and **25**.

In connection with our continuing interests to the synthesis and biological evaluation of nucleosides and related compounds,[19,20] the conversion of the dioxinone **2b** to D-didehydrodideoxyribolactone[21] (*e.g.* **30**) is in progress, which provides not only an attractive new route for this compound, but also a practical synthetic method for the 2-deoxyribolactone[22] (*e.g.* **4b**).



Scheme 5 *Reagents and conditions:* i, TBHP, diisopropyl-L-(+)-tartrate, $Ti(OPr^i)_4$, molecular sieves 4 Å, CH_2Cl_2, −20 °C; ii, $Ti(OPr^i)_4$, benzyl alcohol, 50 °C; iii, K_2CO_3, MeOH; iv, toluene-*p*-sulfonyl chloride (*p*-TsCl), Et_3N, DMAP, CH_2Cl_2; v, H_2, Pd–C, pyridine, AcOEt; vi, K_2CO_3, MeOH; vii, H_2, $Pd(OH)_2$, $CHCl_3$, MeOH



Scheme 6

Experimental

M.p.s were determined on a Yanagimoto micromelting point apparatus (MP-S2), and are uncorrected. Optical rotations were measured with a JASCO DIP-340 digital polarimeter, $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. IR spectra were recorded on a JASCO A-102 spectrometer. ^1H NMR spectra were recorded with tetramethylsilane as internal standard on a JEOL JNM PMX-60SI or a JNM-FX500 spectrometer at 60 MHz and 500 MHz, respectively; *J*-values are given in Hz. High-resolution mass spectra were recorded on a JEOL JMS-01SG-2-system. Wakogel (C-200) was employed for silica gel column chromatography. Merck-Kieselgel 60F 254 was employed for TLC. The ratio of solvent mixtures for chromatography is shown as volume/volume. Substrate dioxin-4-one **9** was prepared according to the literature procedure.[23]

6-(3-*Chloro*-2-*oxopropyl*)-2,2-*dimethyl*-1,3-*dioxin*-4-*one* **10**.—Hexamethylphosphoric triamide (HMPA), (21 cm^3, 120 mmol) was added to a solution of LDA [prepared from diisopropylamine (6.67 g, 66 mmol) and BuLi (1.6 mol dm^{-3} solution in hexane, 41.3 cm^3)] in ether (120 cm^3) at −78 °C under an Ar atmosphere, and the mixture was stirred for 30 min. The dioxinone **9** (8.52 g, 60 mmol) was added dropwise, and the mixture was then stirred for 30 min and a solution of chloroacetyl chloride (3.38 g, 30 mmol) in ether (100 cm^3) was added dropwise. The whole procedure was carried out at −78 °C. After the addition of chloroacetyl chloride, the temperature of the reaction mixture was raised gradually to room temperature. After addition of 10% aqueous HCl, the product was taken in ether and the ethereal solution was dried over $MgSO_4$. The residue obtained after evaporation of the solvent was purified by silica gel column chromatography (hexane–AcOEt, 4:1) to give the *title compound* **10** (4.52 g, 69%) as needles; m.p. 64.5–65 °C (from ether–hexane) (Found: C, 49.5; H, 5.1; Cl, 16.4. $C_9H_{11}O_4Cl$ requires C, 49.4; H, 5.1; Cl, 16.2%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1730 and 1645; $\delta_H(CDCl_3)$ 1.73 (6 H, s, Me_2), 3.59 (2 H, s, $=CCH_2$), 4.18 (2 H, s, CH_2Cl) and 5.40 (1 H, s, 5-H).

6-(3-*Chloro*-2-*hydroxypropyl*)-2,2-*dimethyl*-1,3-*dioxin*-4-*one* **11**.—Finely powdered $NaBH_4$ (380 mg, 10 mmol) was added to a solution of the ketone **10** (4.36 g, 20 mmol) in MeOH (50 cm^3) under ice-cooling. After stirring for 5 min, the solvent was evaporated under reduced pressure and the residue was neutralized by the addition of diluted HCl and extracted by AcOEt. After drying over $MgSO_4$, the solvent was evaporated. The residue was purified by silica gel column chromatography (hexane–AcOEt, 3:1) to give the *title compound* **11** (4.3 g, 98%) as a colourless oil (Found: M^+, 220.050. $C_9H_{13}O_4{}^{35}Cl$ requires *M*, 220.050); $\nu_{max}(CHCl_3)/cm^{-1}$ 3160, 1725 and 1640; $\delta_H(CDCl_3)$ 1.87 (6 H, s, Me_2), 2.52 (2 H, d, *J* 6.0, $=CCH_2$), 2.87–3.29 (1 H, br s, OH), 3.62 (2 H, *J* 5.6, CH_2Cl), 3.87–4.43 (1 H, m, C*H*OH) and 5.40 (1 H, s, 5-H).

2,2-*Dimethyl*-6-[(1E)-3-*hydroxyprop*-1-*enyl*]-1,3-*dioxin*-4-*one* **13**.—NaOH (2 mol dm^{-3}; 15 cm^3) was added to a solution of the alcohol **11** (4 g, 18 mmol) in ether (15 cm^3). After stirring for 30 min at room temperature, the whole was extracted with ether. The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (hexane–AcOEt, 2:1) to give the *title compound* **13** (2.32 g, 70%) as a colourless oil (Found: M^+, 184.072. $C_9H_{12}O_4$ requires *M*, 184.0735); $\nu_{max}(CHCl_3)/cm^{-1}$ 3400 and 1730; $\delta_H(CDCl_3)$ 1.73 (6 H, s, Me_2), 2.52 (1 H, br s, OH), 4.36 (2 H, dd, *J* 4.0 and 1.8, CH_2), 5.32 (1 H, s, 5-H), 6.16 (1 H, d, *J* 15.8, $HOCH_2CH{=}CH$) and 6.66 (1 H, dt, *J* 15.8 and 4.0, $HOCH_2CH{=}CH$).

(1′S,2′R)-2,2-*Dimethyl*-6-(1′,2′-*epoxy*-3′-*hydroxypropyl*)-1,3-*dioxin*-4-*one* **14**.—D-(−)-Diisopropyl tartrate (4.5 g, 19.2 mmol) was added to a mixture of $Ti(OPr^i)_4$ (5.5 g, 19.2 mmol), activated powdered molecular sieves 4 Å (980 mg) and CH_2Cl_2 (150 cm^3) at −20 °C. After stirring for 10 min, the allylic alcohol **13** (2.94 g, 16 mmol) was added to the mixture. The mixture was stirred for 40 min at the same temperature, and *tert*-butyl hydroperoxide (TBHP) (3.0 mol dm^{-3} solution in 2,2,4-trimethylpentane, 12.8 cm^3, 38.4 mmol) was added. The mixture was stirred for 24 h at −20 °C. The mixture was warmed to 0 °C, and saturated aqueous sodium sulfate (18 cm^3) was added followed by ether (80 cm^3). The mixture was allowed to come to room temperature, stirred for 5 h, and filtered through a pad of Celite. The filtrate was dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (hexane–AcOEt, 3:1) to give the *title compound* **14** (3.0 g, 94%) as a colourless oil (Found: M^+, 200.068. $C_9H_{12}O_5$ requires *M*, 200.068); $[\alpha]_D^{22}$ +36.8 (*c* 1.0, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 3400 and 1730; $\delta_H(CDCl_3)$ 1.71 (6 H, s, Me_2), 3.10 (1 H, br s, OH), 3.25–3.60 (2 H, m, CH × 2), 3.70–4.00 (2 H, m, CH_2) and 5.56 (1 H, s, 5-H).

When the above reaction was carried out by using L-(+)-diisopropyl tartrate, the enantiomer of compound **14** [(1′*R*,2′*S*)-derivative: $[\alpha]_D^{25}$ −34.7 (*c* 1.75, $CHCl_3$)] was obtained in 95% yield.

(S)-6-(2,3-*Dihydroxypropyl*)-2,2-*dimethyl*-1,3-*dioxin*-4-*one* (S)-**1a**.—A mixture of the epoxide **14** (1.0 g, 5 mmol), 10% Pd–C (120 mg) and AcOEt (10 cm^3) was shaken in hydrogen under atmospheric pressure for 30 min at room temperature. After filtration to remove the catalyst, the filtrate was concentrated. The residue was purified by silica gel column chromatography (hexane–AcOEt, 1:1) to give the *title compound* (*S*)-**1a** (970 mg, 96%) as a colourless oil [Found: *m/z* 203.094. $C_9H_{15}O_5$ (M + 1) requires *m/z* 203.092]; $[\alpha]_D^{20}$ −22.8 (*c* 2.16, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 3450 and 1720; $\delta_H(CDCl_3)$ 1.74 (6 H, s, Me_2), 2.40 (2 H, d, *J* 6.0, CH_2), 2.50–3.30 (2 H, br s, OH × 2), 3.62 (2 H, m, $HOCH_2$), 3.98 (1 H, m, OCH) and 5.34 (1 H, s, 5-H).

When the above reaction was carried out by using the enantiomer of compound **14** [(1′*R*,2′*S*)-derivative], compound (*R*)-**1a** was obtained in 96% yield; $[\alpha]_D^{20}$ +22.1 (*c* 1.63, $CHCl_3$).

(S)-2,2-*Dimethyl*-6-(2,3-*isopropylidenedioxypropyl*)-1,3-*dioxin*-4-*one* **1b**.—A solution of the diol (*S*)-**1a** (303 mg, 1.5 mmol), 2,2-dimethoxypropane (1.2 cm^3) and a catalytic amount of 70% perchloric acid in acetone (10 cm^3) was stirred for 2 h at room temperature. The mixture was neutralized with conc. aqueous ammonium hydroxide, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane–AcOEt, 8:1) to give the *title compound* **1b** (312 mg, 86%) as a colourless oil [Found: *m/z* 243.118. $C_{12}H_{19}O_5$ (M + 1) requires *m/z* 243.123]; $[\alpha]_D^{27}$ −23.0 (*c* 2.34, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 1725; $\delta_H(CDCl_3)$ 1.36 (3 H, s, Me), 1.43 (3 H, s, Me), 1.70 (6 H, s, Me_2), 2.40–2.60 (2 H m, CH_2), 3.50–4.60 (3 H, OCH and OCH_2) and 5.34 (1 H, s, 5-H).

(S)-*Dihydro*-4-*hydroxyfuran*-2(3H)-*one* **15**.—A solution of the diol (*S*)-**1a** (188 mg, 0.93 mmol) in MeOH (15 cm^3) was cooled to −78 °C, and O_3 was passed into the solution with stirring for 3 h. Me_2S (0.5 cm^3) was added to this solution at −78 °C. After stirring for 1 h at the same temperature and then for 1 h at room temperature, the solvent was evaporated under reduced pressure. The residue was dissolved in CH_2Cl_2 (10 cm^3) and CF_3CO_2H (23 mg, 0.2 mmol) was added to this solution. The whole was stirred for 20 h at room temperature. After evaporation of the solvent, the residue was purified by silica gel column chromatography (hexane–AcOEt, 2:1) to give the *title compound* **15** (73.1 mg, 77%) as a colourless oil (Found: M^+, 102.035. $C_4H_6O_3$ requires *M*, 102.032); $[\alpha]_D^{31}$ −83.2 (*c* 0.41, EtOH) [lit.,[9] $[\alpha]_D^{9}$ −85.9 (*c* 2.2, EtOH)].

Methyl (S)-5,6-*Isopropylidenedioxy*-3-*oxohexanoate* **16**.—A solution of the dioxinone **1b** (244 mg, 1.0 mmol) and abs. MeOH (160 mg, 5.0 mmol) in toluene (20 cm^3) was refluxed for 1.5 h. After the solvent was evaporated under reduced pressure, the residue was purified by silica gel column chromatography (hexane–AcOEt, 10:1) to give the *title compound* **16** (212 mg, 98%) as a colourless oil (Found: M^+, 216.097. $C_{10}H_{16}O_5$ requires *M*, 216.100); $[\alpha]_D^{28}$ +4.0 (*c* 2.08, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 1750 and 1720; $\delta_H(CDCl_3$, keto:enol form = *ca.* 8:1) 1.35 (3 H, s, Me), 1.41 (3 H, s, Me), 2.87 (2 H, t, *J* 5.8, CH_2), 3.50 (2 H × 8/9, s, $COCH_2CO$), 3.75 (3 H, s, OMe), 4.05–

4.70 (3 H, m, OCH_2 and CH), 5.09 (1 H × 1/9, s, =CH) and 12.07 (1 H × 1/9, br s, OH).

(1'S,2'R)-6-[1',2'-*Epoxy*-3'-(tert-*butyldimethylsilyloxy*)*propyl*]-2,2-*dimethyl*-1,3-*dioxin*-4-*one* **17**.—*tert*-Butyldimethylchlorosilane (1.13 g, 7.5 mmol) and imidazole (510 mg, 7.5 mmol) were added to a solution of the epoxide **14** (1.0 g, 5.0 mmol) in DMF (15 cm^3) under ice-cooling. After stirring for 3 h at room temperature, ice–water was added to the mixture and the whole was extracted with ether. The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (hexane–AcOEt, 20:1) to give *title compound* **17** (1.32 g, 84%) as a colourless oil [Found: *m/z* 257.120. $C_{12}H_{21}O_4Si$ (M + 1 − Me_2CO) requires *m/z* 257.121]; $[\alpha]_D^{25}$ +31.2 (*c* 2.38, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 1730; $\delta_H(CDCl_3)$ 0.08 (6 H, s, $SiMe_2$), 0.93 (9 H, s, Me × 3), 1.73 (6 H, s, Me_2), 3.15–3.45 (2 H, m, CH × 2), 3.72–3.95 (2 H, m, CH_2) and 5.55 (1 H, s, 5-H).

(S)-6-[3-(tert-*Butyldimethylsilyloxy*)-2-*hydroxypropyl*]-2,2-*dimethyl*-1,3-*dioxin*-4-*one* **1c**.—A mixture of compound **17** (1.26 g, 4 mmol), 10% Pd–C (200 mg), and AcOEt (10 cm^3) was shaken in hydrogen under atmospheric pressure for 20 min at room temperature. After filtration to remove the catalyst, the filtrate was concentrated. The residue was purified by silica gel column chromatography (hexane–AcOEt, 8:1) to give the *title compound* **1c** (1.26 g, 99%) as needles; m.p. 51 °C (from ether–hexane) (Found: C, 57.0; H, 8.85. $C_{15}H_{28}O_5Si$ requires C, 56.9; H, 8.9%); $[\alpha]_D^{18}$ −15.6 (*c* 1.22, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 3400 and 1730; $\delta_H(CDCl_3)$ 0.07 (6 H, s, $SiMe_2$), 0.92 (9 H, s, Me × 3), 1.69 (6 H, s, Me_2), 2.38 (2 H, d, *J* 6.0, CH_2), 2.50 (1 H, br s, OH), 3.45–3.70 (2 H, m, OCH_2), 3.70–4.10 (1 H, m, CH) and 5.35 (1 H, s, 5-H).

(S)-6-[(tert-*Butyldimethylsilyloxy*)*methyl*]-5,6-*dihydropyran*-2(3H),4-*dione* **18**.—A solution of compound **1c** (1.1 g, 3.5 mmol) and potassium carbonate (731 mg, 5.3 mmol) in MeOH (15 cm^3) was stirred at room temperature overnight. The solvent was evaporated under reduced pressure and the residue was neutralized by the addition of diluted HCl and extracted by AcOEt. After drying over $MgSO_4$, the extract was purified by silica gel column chromatography (hexane–AcOEt, 2:1) to give the *title compound* **18** (840 mg, 93%) as needles; m.p. 142–143 °C (from AcOEt–hexane) (Found: C, 55.9; H, 8.6. $C_{12}H_{22}O_4Si$ requires C, 55.8; H, 8.6%); $[\alpha]_D^{21}$ −7.6 (*c* 1.0, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 1760 and 1730; $\delta_H(CDCl_3)$ 0.09 (6 H, s, $SiMe_2$), 0.91 (9 H, s, Me × 3), 2.73 (2 H, d, *J* 6.0, CH_2), 3.46 (2 H, s, CH_2), 3.75–4.00 (2 H, m, OCH_2) and 4.55–4.90 (1 H, m, CH).

(S)-4-*Acetoxy*-6-[(tert-*butyldimethylsilyloxy*)*methyl*]-5,6-*dihydropyran*-2-*one* **19**.—A mixture of compound **18** (748 mg, 2.9 mmol), Ac_2O (0.5 cm^3) and pyridine (10 cm^3) was stirred for 30 min at room temperature. The solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography (hexane–AcOEt, 10:1) to give the *title compound* **19** (700 mg, 77%) as a colourless oil [Found: *m/z* 301.147. $C_{14}H_{25}O_5Si$ (M + 1) requires *m/z* 301.147]; $[\alpha]_D^{20}$ −74.5 (*c* 1.23, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 1780, 1720 and 1150; $\delta_H(CDCl_3)$ 0.08 (6 H, s, $SiMe_2$), 0.88 (9 H, s, Me × 3), 2.23 (3 H, s, COMe), 2.50–2.90 (2 H, m, CH_2), 3.82 (2 H, d, *J* 5.0, OCH_2), 4.48 (1 H, quintet, *J* 5.0, OCH) and 5.92 (1 H, d, *J* 2.0, =CH).

(S)-6-[(tert-*Butyldimethylsilyloxy*)*methyl*]*tetrahydropyran*-2-*one* **20**.—A mixture of compound **19** (540 mg, 1.8 mmol), 10% Pd–C (160 mg), and AcOEt (5 cm^3) was shaken in hydrogen under atmospheric pressure for 3 h at room temperature. After filtration to remove the catalyst, the filtrate was concentrated. The residue was purified by silica gel column chromatography (hexane–AcOEt 5:1) to give the *title compound* **20** (417 mg, 95%) as a colourless oil [Found: *m/z* 245.158. $C_{12}H_{25}O_3Si$ (M + 1) requires *m/z* 245.157]; $[\alpha]_D^{22}$ −1.63 (*c* 1.22, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 1730; $\delta_H(CDCl_3)$ 0.07 (6 H, s, $SiMe_2$), 0.90 (9 H, s, Me × 3), 1.60–2.20 (4 H, m, CH_2 × 2), 2.32–2.70 (2 H, m, CH_2), 3.77 (2 H, d, *J* 5.0, OCH_2) and 4.37 (1 H, m, CH).

(S)-6-*Hydroxymethyltetrahydropyran*-2-*one* **21**.—Bu_4NF (1.0 mol dm^{-3} THF solution, 2.1 cm^3, 2.1 mmol) was added to a solution of compound **20** (342 mg, 1.4 mmol) in THF (20 cm^3) under ice-cooling. The reaction mixture was stirred for 30 min at room temperature. After evaporation of the solvent, the residue was diluted with water and extracted with AcOEt. The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (hexane–AcOEt, 1:1) to give the *title compound* **21** (149 mg, 82%) as a colourless oil; $[\alpha]_D^{19}$ +33.5 (*c* 1.72, $CHCl_3$) [lit.,[13] +34.7 (*c* 1.3, $CHCl_3$)].

(±)-2,2-*Dimethyl*-6-(2-*hydroxybut*-3-*enyl*)-1,3-*dioxin*-4-*one* **24**.—$TiCl_4$ (1.0 mol dm^{-3} solution in CH_2Cl_2, 55 mmol) was added to a solution of acrolein (2.8 g, 50 mmol) and CH_2Cl_2 (200 cm^3) at −78 °C under Ar atmosphere. The complex was stirred for 20 min and the enol silane **22**[15] (10.7 g, 50 mmol) was added by syringe over a 1 h period. After 3 h, reaction was quenched by rapidly injecting saturated aqueous $NaHCO_3$ (125 cm^3). The mixture was warmed to room temperature. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated. The residue was purified by silica gel column chromatography (hexane–AcOEt, 4:1) to give the *title compound* **24** (7.2 g, 73%) as a colourless oil [Found: *m/z* 199.078. $C_{10}H_{15}O_4$ (M + 1) requires *m/z* 199.097]; $\nu_{max}(CHCl_3)/cm^{-1}$ 3450, 1735 and 1642; $\delta_H(CDCl_3)$ 1.70 (6 H, s, Me_2), 2.12 (1 H, br s, OH), 2.47 (2 H, d, *J* 6.5, CH_2), 4.44 (1 H, q, *J* 6.5, C*H*OH), 5.05–5.50 (2 H, m, CH_2=CH), 5.34 (1 H, s, 5-H) and 5.80–6.00 (1 H, m, CH_2=C*H*].

(±)-2,2-*Dimethyl*-6-(2-*hydroxy*-2-*phenylethyl*)-1,3-*dioxin*-4-*one* **23**.—When the above reaction was carried out by using benzaldehyde, the *title compound* **23** was obtained in 52% yield; m.p. 80–81 °C (from ether–hexane) (Found: C, 67.4; H, 6.55. $C_{14}H_{16}O_4$ requires C, 67.7; H, 6.5%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3450, 1730 and 1640; $\delta_H(CDCl_3)$ 1.65 (6 H, s, Me_2), 2.02–2.55 (1 H, br s, OH), 2.68 (2 H, d, *J* 7.0, CH_2), 4.98 (1 H, t, *J* 7.0, C*H*OH), 5.27 (1 H, s, 5-H) and 7.32 (5 H, s, Ph).

(2'S,3'R)-6-(3',4'-*Epoxy*-2'-*hydroxybutyl*)-2,2-*dimethyl*-1,3-*dioxin*-4-*one* **25**.—L-(+)-DIPT (8.43 g, 36 mmol) was added to a solution of $Ti(OPr^i)_4$ (9.38 g, 33 mmol) and activated powdered 4 Å molecular sieves (1 g) in CH_2Cl_2 (100 cm^3) at −20 °C. After 30 min, TBHP (3.0 mol dm^{-3} solution, 15 cm^3, 45 mmol) was added. The mixture was stirred for 1 h at −20 °C and to this solution the allylic alcohol **24** (5.94 g, 30 mmol) in CH_2Cl_2 (30 cm^3) was added. After 20 h, the mixture was warmed to 0 °C, and saturated aqueous sodium sulfate (40 cm^3) was added followed by ether (100 cm^3). The mixture was stirred at room temperature then for 5 h, and then filtered through a pad of Celite. The filtrate was dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (hexane–AcOEt, 4:1) to give a colourless oil (*R*)-**24** (2.7 g, 46%). Further elution with hexane–AcOEt (2:1) gave a colourless oil **25** (2.82 g, 44%); m.p. 54 °C (from ether–hexane) (Found: C, 56.3; H, 6.3. $C_{10}H_{14}O_5$ requires C, 56.1; H, 6.6%); $[\alpha]_D^{26}$ −11.6 (*c* 1.0, $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 3450 and 1730; $\delta_H(CDCl_3)$ 1.71 (6 H, s, Me_2), 2.05 (1 H, br s, OH),

2.43 (1 H, dd, *J* 15.0 and 9.0, CH_2), 2.54 (1 H, dd, *J* 15.0 and 4.0, CH_2), 2.80 (1 H, dd, *J* 5.0 and 3.2, epoxy-H), 2.84 (1 H, dd, *J* 5.0 and 3.0, epoxy-H), 3.07 (1 H, q, *J* 3.0, epoxy-H), 4.10 (1 H, m, C*H*OH) and 5.39 (1 H, s, 5-H).

(*R*)-**24**: $[\alpha]_D^{24}$ +15.2 (*c* 1.37, $CHCl_3$).

(2'S,3'R)-6-(4'-*Benzyloxy*-2',3'-*dihydroxybutyl*)-2,2-*dimethyl*-1,3-*dioxin*-4-*one* **2b**.—A mixture of the epoxide **25** (2.0 g, 9.3 mmol) and $Ti(OPr^i)_4$ (3.18 g, 11.2 mmol) in $PhCH_2OH$ (200 cm^3) was stirred for 36 h at 50 °C under Ar atmosphere. The solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography (hexane–AcOEt, 3:1) to give the *title compound* **2b** (2.55 g, 85%) as a colourless oil [Found: *m/z* 264.098. $C_{14}H_{16}O_5$ (M − Me_2CO) requires *m/z* 264.100]; $[\alpha]_D^{22}$ −20.3 (*c* 1.28, $CHCl_3$); ν_{max}($CHCl_3$)/cm^{-1} 3500 and 1720; δ_H($CDCl_3$) 1.70 (6 H, s, Me_2), 2.35 (1 H, dd, *J* 14.5 and 10.0, 1'-H), 2.54 (1 H, dd, *J* 14.5 and 3.0, 1'-H), 2.43 (1 H, br s, OH), 2.63 (1 H, br s, OH), 3.61–3.68 (2 H, m, OCH_2), 3.72 (1 H, m, CH), 3.98 (1 H, m, CH), 4.55 (1 H, d, *J* 12.0, PhC*H*), 4.59 (1 H, d, *J* 12.0, PhC*H*), 5.34 (1 H, s, 5-H) and 7.25–7.40 (5 H, m, Ph).

(1'R,6S)-6-(2'-*Benzyloxy*-1'-*hydroxyethyl*)-5,6-*dihydropyran*-2(3H),4-*dione* **6b**. A solution of compound **2b** (966 mg, 3.0 mmol) and potassium carbonate (1.38 g, 10 mmol) in MeOH (12 cm^3) was stirred at room temperature overnight. The solvent was evaporated under reduced pressure and the residue was neutralized by the addition of diluted HCl and extracted with AcOEt. After drying over $MgSO_4$, the extract was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (hexane–AcOEt, 2:1) to give the *title compound* **6b** (681 mg, 86%) as a colourless oil (Found: M^+, 264.098. $C_{14}H_{16}O_5$ requires *M*, 264.098); $[\alpha]_D^{24}$ −44.3 (*c* 1.63, $CHCl_3$); ν_{max}($CHCl_3$)/cm^{-1} 3450, 1770 and 1730; δ_H($CDCl_3$) 2.70 (2 H, d, *J* 6.5, CH_2), 2.90 (1 H, br s, OH), 3.47 (2 H, s, $COCH_2CO$), 3.50–4.00 (3 H, m, OCH_2 and CH), 4.53 (2 H, s, PhCH_2), 4.50–4.90 (1 H, m, CH) and 7.33 (5 H, s, Ph).

(1'R,6S)-6-(2'-*Benzyloxy*-1'-*tosyloxyethyl*)-4-*tosyloxy*-5,6-*dihydropyran*-2-*one* **26**.—Toluene-*p*-sulfonyl chloride (1.14 g, 6.0 mmol) was added to a solution of compound **6b** (528 mg, 2.0 mmol), Et_3N (808 mg, 8.0 mmol) and DMAP (49 mg, 0.04 mmol) in CH_2Cl_2 (20 cm^3) under ice-cooling. After stirring for 5 h at room temperature, the whole was washed by water. The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (hexane–AcOEt, 5:1) to give the *title compound* **26** (961 mg, 84%) as a colourless oil [Found: *m/z* 417.1045. $C_{21}H_{21}O_7S$ (M − Ts) requires *m/z* 417.101]; $[\alpha]_D^{20}$ −35.7 (*c* 1.26, $CHCl_3$); ν_{max}($CHCl_3$)/cm^{-1} 1730, 1370 and 1175; δ_H($CDCl_3$) 2.43 (3 H, s, Me), 2.49 (3 H, s, Me), 2.40–2.54 (2 H, m, CH_2), 3.57 (1 H, dd, *J* 11.0 and 4.5, BnOC*H*), 3.70 (1 H, dd, *J* 11.0 and 4.0, BnOC*H*), 4.39 (1 H, d, *J* 12.0, PhC*H*), 4.43 (1 H, d, *J* 12.0, PhC*H*), 4.63–4.74 (2 H, m, CH × 2), 5.77 (1 H, d, *J* 2.2, =CH) and 7.18–7.84 (13 H, m, Ar).

(1'R,6S)-6-(2'-*Benzyloxy*-1'-*tosyloxyethyl*)*tetrahydropyran*-2-*one* **27**.—A mixture of the ditosylate **26** (572 mg, 1.0 mmol), 10% Pd–C (400 mg), pyridine (316 mg, 4.0 mmol), and AcOEt (10 cm^3) was shaken in hydrogen under atmospheric pressure for 30 min at room temperature. After filtration to remove the catalyst, the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane–AcOEt, 3:1) to give the *title compound* **27** (347 mg, 86%) as needles; m.p. 87–88 °C (from AcOEt–hexane) (Found: C, 62.4; H, 6.1; S, 7.95. $C_{21}H_{24}O_6S$ requires C, 62.4; H, 6.0; S, 7.9%); $[\alpha]_D^{20}$ +2.6 (*c* 1.62, $CHCl_3$); ν_{max}($CHCl_3$)/cm^{-1} 1740, 1365 and 1175; δ_H($CDCl_3$) 1.60–2.05 (4 H, m, CH_2 × 2), 2.32–2.59 (2 H, m, CH_2), 2.42 (3 H, s, Me), 3.61 (1 H, dd, *J* 11.0 and 5.0, BnOC*H*), 3.73 (1 H, dd, *J* 11.0 and 5.0, BnOC*H*), 4.40 (1 H, d, *J* 12.0, PhC*H*), 4.45 (1 H, d, *J* 12.0, PhC*H*), 4.58 (1 H, m, CH), 4.71 (1 H, q, *J* 5.0, CH), 7.20–7.35 (7 H, m, Ar) and 7.77 (2 H, d, *J* 8.8, Ar).

Methyl (S,S-trans)-4-(3-*Benzyloxymethyloxiran*-2-*yl*)*butanoate* **28**.—A mixture of compound **27** (162 mg, 0.4 mmol) and potassium carbonate (121 mg, 0.88 mmol) in abs. MeOH (6 cm^3) was stirred for 10 min at room temperature. The solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography (ether) to give the *title compound* **28** (64 mg, 61%) as a colourless oil (Found: M^+, 264.138. $C_{15}H_{20}O_4$ requires *M*, 264.136); $[\alpha]_D^{20}$ −17.9 (*c* 1.70, $CHCl_3$); ν_{max}($CHCl_3$)/cm^{-1} 1735; δ_H($CDCl_3$) 1.50–1.84 (4 H, m, CH_2 × 2), 2.38 (2 H, td, *J* 7.8 and 2.0, CH_2), 2.84 (1 H, m, epoxy-H), 2.95 (1 H, m, epoxy-H), 3.48 (1 H, dd, *J* 12.0 and 6.0, BnOC*H*), 3.67 (3 H, s, Me), 3.71 (1 H, dd, *J* 12.0 and 4.0, BnOC*H*), 4.55 (1 H, d, *J* 13.0, PhCH), 4.60 (1 H, d, *J* 13.0, PhC*H*) and 7.34 (5 H, s, Ph).

Methyl (S,S-trans)-4-(3-(*Hydroxymethyloxiran*-2-*yl*)*butanoate* **29**.—A mixture of compound **28** (52.8 mg, 0.2 mmol), 20% Pd $(OH)_2$ (15 mg), $CHCl_3$ (2 drops), and MeOH (3 cm^3) was shaken in hydrogen under atmospheric pressure for 20 min at room temperature. After filtration to remove the catalyst, the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane–AcOEt 1:1) to give title compound **29** (35 mg, 99%) as a colourless oil; $[\alpha]_D^{19}$ −31.6 (*c* 0.88, $CHCl_3$) [lit.,[17] −32.9 (*c* 0.33, $CHCl_3$)].

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