# Heterodiene cycloadditions of $C_2$ symmetric 4,5-disubstituted ketene acetals: the nett asymmetric conjugate addition of recyclable acetic ester enolate equivalents to an activated enone

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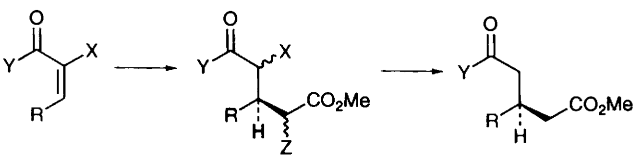
Heterodiene cycloadditions of 3-formylchromone **2** to a series of ketene acetals **1** derived from $C_2$ symmetric 1,2-diarylethane-1,2-diols are diastereoselective. From (*S,S*)-1,2-di(*o*-tolyl)ethane-1,2-diol **6c** the major cycloadduct **3c** was isolated by crystallisation and transformed by acid-catalysed methanolysis into (*S*)-methyl 4-oxo-3,4-dihydro-2*H*-1-benzopyran-2-ylacetate **5**, together with the original 1,2-diol **6c** which could be recycled. The structures of two cyclic carbonates **22a** and **22c** were determined by X-ray diffraction and used as models in seeking a mechanistic rationale for the stereoselective cycloadditions of the analogous ketene acetals **1a** and **1c**.

The nett asymmetric conjugate addition of an acetic ester enolate to an α,β-unsaturated carbonyl function is a useful synthetic manoeuvre, and the typical sequence (Scheme 1)

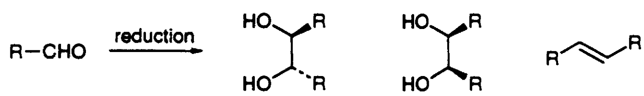


**Scheme 1**

offers various opportunities for activation and/or asymmetric induction. Posner and co-workers have demonstrated that activation by sulfoxide and silicon substituents (at X and Z respectively) can lead to high levels of asymmetric induction,[1] while recent developments include conjugate additions of methyl (phenylsulfanyl)acetate catalysed by homochiral crown ethers,[2] of dialkyl malonates catalysed by (*S*)-proline rubidium salt[3] and 1,1′-bi-2-naphthol–lanthanum complex,[4] and of silylated ester and thiol ester enolates catalysed by homochiral titanium complexes.[5] In the course of our work on heterodiene cycloadditions of chromones[6,7] we carried out a study, herein described in detail,[8] of a variant of this type of conjugate addition process in which the asymmetric induction derives from the diastereoselective heterodiene cycloaddition of a $C_2$ symmetric ketene acetal **1** to a formyl-activated enone, illustrated by the transformation of 3-formylchromone **2** into the ester **5** (Scheme 2). Acid-induced methanolysis of the ortholactone cycloadducts **3** and **4** effects their ring-opening, transesterification and retro-Claisen deformylation, leading to the product **5** and releasing the 1,2-diol **6** for recycling to **1** *via* the corresponding bromoacetaldehyde acetal **7**.

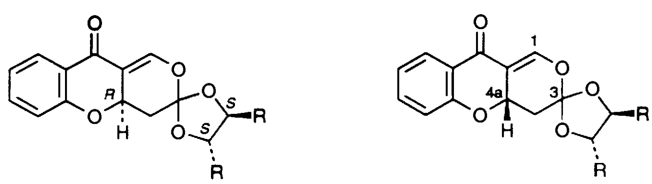
In seeking to develop the above sequence we sought ketene acetals **1** which would (i) provide high diastereoselectivity in the cycloaddition step, (ii) be readily accessible in homochiral form, (iii) involve separable, preferably crystalline, intermediates throughout the sequence and (iv) permit effective recycling. The diols **6a–j** were selected as candidates, and several of these were prepared in racemic form by reductive coupling techniques (Table 1). However, with the notable exception of the

**Table 1** Preparation of racemic diols (±)-**6** *via* reductive coupling of the aldehydes **8**. *Reagents:* i, **8** added to $TiCl_3$–Li; ii, $TiCl_3$–Li added to **8**; iii, $SmI_2$; iv, $FeCl_3$–Li; v, $Ti(cp_2)Cl_2$, $Bu^sLi$



**8** (±)-**6** *meso*-**9** **10**

| Aldehyde | Method | Isolated yields (%) | | |
|---|---|---|---|---|
| **8b** | i | 21 | 7 | 18 |
| **8b** | ii | 48 | 16 | 3 |
| **8b** | iii | 43 | 43 | — |
| **8b** | iv | 75 | 16 | — |
| **8c** | i | 36 | 27 | 2 |
| **8c** | iv | 30 | 10 | — |
| **8d** | v | 30 | 43 | — |
| **8e** | v | 76 | < 1 | — |
| **8f** | i | 15 | 36 | 39 |
| **8f** | v | 43 | 36 | — |



**3** **4**

preparation of (±)-**6e**,[9] the directness of the coupling route was offset by modest yields and/or levels of (±)-selectivity, the formation of *meso*-products **9** in particular giving rise to isolation difficulties. An alternative route to racemic diols, based on the osmium-mediated dihydroxylation of *trans*-alkenes **10**, was generally more effective despite involving more steps. This approach (Table 2) required the preparation of a series of *trans*-alkenes **10**, and in this context Engman's method[10] for the *cis*-to-*trans* isomerisation of stilbenes using tellurium(IV) chloride proved especially valuable.

Preparation of the diols **6** by the osmium-catalysed dihydroxylation[11] of the alkenes **10** was a potentially

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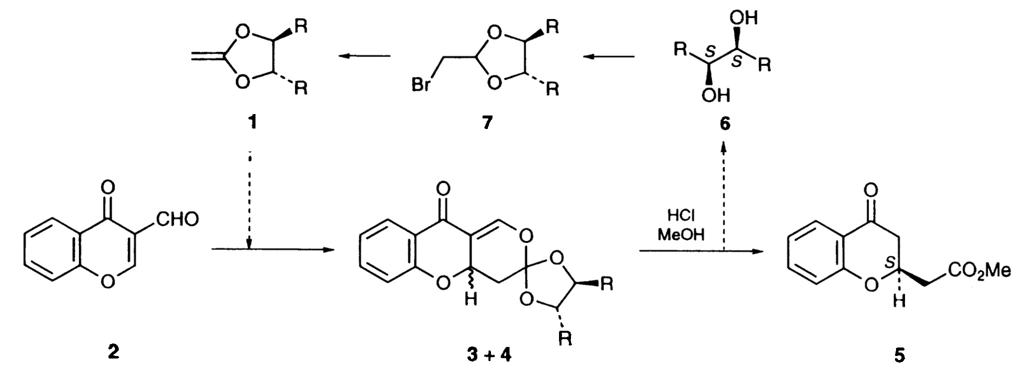
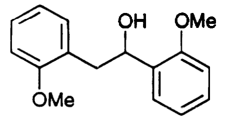
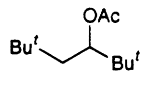



Scheme 2

**Table 2** Preparative routes to the (*E*)-alkenes **10**



**13**



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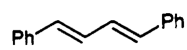
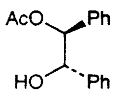


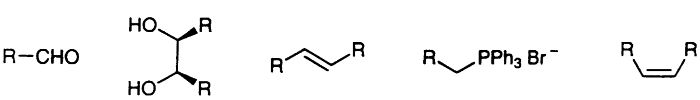
**15**



**16**

| Alkene Precursors | Methods* | Products | Total (%) | Ratio (*E*:*Z*) | Isomerisation Product | Isomerisation Yield (%) |
|---|---|---|---|---|---|---|
| **8b** + **11b** | i | **10b** | 55 | — | — | — |
| **8c** + **11c** | i, ii | **10c** + **12c** | 94 | 1:2 | **10c** | 95 |
| **8d** + **11d** | i, ii | **10d** + **12d** | 81 | 1:7 | **10d** | 93 |
| **13** | iii | **10f** | 95 | — | — | — |
| **14** | iv | **10g** | 90 | — | — | — |
| **15** | v | **10h** | 55 | — | — | — |
| **8i** + **11i** | i, ii | **10i** + **12i** | 93 | 2:1 | **10i** | 83 |

* *Methods:* i, Wittig olefination; ii, $TeCl_4$, $CHCl_3$, reflux; iii, $MeSO_2Cl$, $Et_3N$, $CH_2Cl_2$, 0 °C to room temp., then $K_2CO_3$, MeOH, reflux, 16 h; iv, thermolysis (290 °C); v, three steps.



**8** **9** **10** **11** **12**

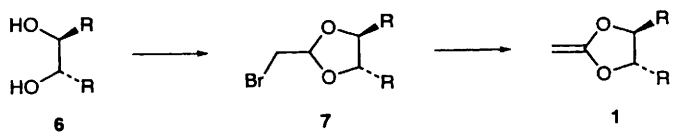
| | R |
|---|---|
| a | Ph |
| b | 2,4,6-$Me_3C_6H_2$ |
| c | 2-$MeC_6H_4$ |
| d | 2-$BrC_6H_4$ |
| e | 1-Naphthyl |
| f | 2-$MeOC_6H_4$ |
| g | $Bu^t$ |
| h | $PhCH_2$ |
| i | 2-$CF_3C_6H_4$ |
| j | *cyclo*-$C_6H_{11}$ |

important component of our strategy for developing the conjugate addition sequence, since the emerging asymmetric dihydroxylation (AD) methodology[12,13] appeared to offer a flexible route to the diols **6** in homochiral form. Indeed, several of the alkenes **10** proved to be effective substrates in both the racemic and asymmetric versions of the dihydroxylation (Table 3). Notable exceptions were the 1,2-dimesityl- and 1,2-bis(2-trifluoromethylphenyl)ethenes **10b** and **10i**, which were quite unreactive. The failure of **10b** to undergo osmylation was unsurprising given the steric requirements of the process but was, nevertheless, disappointing since the corresponding ketene acetal **1b** was to prove one of the most diastereoselective in cycloadditions with the aldehyde **2** (*vide infra*).

Each of the readily available diols **6** was successfully converted into the corresponding bromo acetal **7**, although only the series **a**–**c** provided crystalline products at this stage. The bromo acetals **7a**–**e** could be dehydrobrominated and isolated in solution (80–90% yield) using the method (KOBu$^t$, Aliquat 336®, THF, 0 °C) described by Bailey and Zhou[14] (Table 4). In initial experiments, the ketene acetal **1a** was prepared and used *in situ*, but this proved less satisfactory. The dehydrobromination protocol was ineffective with the bromo acetals **7f**, **7g**, **7h** and **7j**.

Cycloadditions of the ketene acetals **1a**–**e** with the aldehyde **2** proceeded as indicated in Table 5. The cycloadducts **3** and **4** were estimated using 300 MHz $^1H$ NMR spectroscopy, usually

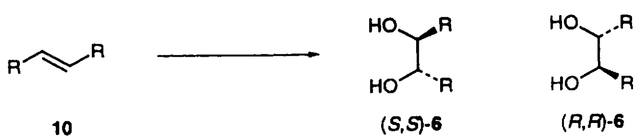
**Table 3** Osmium-catalysed dihydroxylation of (*E*)-alkenes **10**




| Alkene | mmol | Reagents* | Ligand | Product | Yield (%)† | ee (%)† |
|---|---|---|---|---|---|---|
| **10b** | | ‡ | | (±)-**6b** | <2 | — |
| **10c** | 6 | a, b | DABCO | (±)-**6c** | 78 | — |
| **10c** | 50 | a, b, c | DHQ-PCB | (*S*,*S*)-**6c** | 92 | >98 |
| **10c** | 10 | a, c, d | $(DHQ)_2$-PHAL | (*S*,*S*)-**6c** | 88 | >98 |
| **10d** | 4 | a, b | DABCO | (±)-**6d** | 89 | — |
| **10d** | 4 | a, b | DHQ-PCB | (*S*,*S*)-**6d** | 62 | >95 |
| **10f** | 2 | a, b | DABCO | (±)-**6f** | 57 | — |
| **10f** | 5 | a, c, d | $(DHQ)_2$-PHAL | (*S*,*S*)-**6f** | 41§ | >95 |
| **10g** | 5 | a, b | DABCO | (±)-**6g** | 43 | — |
| **10h** | 1 | a, c, d | $(DHQD)_2$-PHAL | (*R*,*R*)-**6h** | 84 | ¶ |
| **10i** | 3 | a, c, d | $(DHQD)_2$-PHAL | (*R*,*R*)-**6i** | 4 | ¶ |

* *Reagents:* a, $K_3Fe(CN)_6$, $K_2CO_3$, $Bu^tOH-H_2O$; b, $OsO_4$; c, $MeSO_2NH_2$; d, $K_2Os_2(OH)_4$; see Experimental for key to ligand abbreviations. † After crystallisation. ‡ Various conditions were attempted, including stoichiometric $OsO_4$. § The starting alkene **10f** (54%) was also recovered. ¶ Not determined.

**Table 4** Preparation of the bromo acetals **7** and the ketene acetals **1**




| Diol | Bromo acetal | Yield (%) | Mp (°C) | Ketene acetal | Efficiently formed |
|---|---|---|---|---|---|
| (±)-**6a** | (±)-**7a** | 90 | 56 | (±)-**1a** | yes |
| (*S*,*S*)-**6a** | (*S*,*S*)-**7a** | 93 | 56 | (*S*,*S*)-**1a** | yes |
| (±)-**6b** | (±)-**7b** | 71 | 124-125 | (±)-**1b** | yes |
| (±)-**6c** | (±)-**7c** | 86 | 42-43 | (±)-**1c** | yes |
| (*S*,*S*)-**6c** | (*S*,*S*)-**7c** | 93 | 59-61 | (*S*,*S*)-**1c** | yes |
| (±)-**6d** | (±)-**7d** | 80 | Oil | (±)-**1d** | yes |
| (*S*,*S*)-**6d** | (*S*,*S*)-**7d** | 80 | Oil | (*S*,*S*)-**1d** | yes |
| (±)-**6e** | (±)-**7e** | 91 | Oil | (±)-**1e** | yes |
| (±)-**6f** | (±)-**7f** | 39 | Oil | (±)-**1f** | no |
| (*S*,*S*)-**6f** | (*S*,*S*)-**7f** | 53 | Oil | (*S*,*S*)-**1f** | no |
| (±)-**6g** | (±)-**7g** | 65 | Oil | (±)-**1g** | no |
| (*R*,*R*)-**6h** | (*R*,*R*)-**7h** | 83 | Oil | (*R*,*R*)-**1h** | no |
| (*R*,*R*)-**6j** | (*R*,*R*)-**7j** | 87 | Oil | (*R*,*R*)-**1j** | no |

by integrating the characteristic signals due to the respective vinylic (1-H) hydrogens. In initial experiments, a THF solution containing the ketene acetal (±)-**1a** in THF was stirred for 3–4 h at −78 °C with the chromone **2** (1 equiv.), and then allowed to reach room temperature overnight. Chromatography of the products over Florisil® yielded small amounts of unchanged **2** (5–10%) and the acetate (±)-**16**, and a mixture of (±)-**3a** and (±)-**4a** (total 61%, ratio 7:3). While limited separation of the two cycloadducts could be achieved by HPLC, there appeared to be extensive decomposition when this technique was used, and the major product (±)-**3a** was more effectively isolated by crystallisation.

The dimesityl ketene acetal (±)-**1b** underwent the cycloaddition with good diastereoselectivity (78% de), but the failure of the corresponding stilbene **10b** in the osmylation precluded the ready availability of **6b** (and hence **1b**) in optically pure form. The most exploitable results were those in the *o*-tolyl (**c**) and *o*-bromophenyl (**d**) series. Cycloaddition of the ketene acetal **1c** to the aldehyde **2** gave **3c**, which could be isolated in pure form by crystallisation. Interestingly, the diastereoselectivity of this cycloaddition appeared to peak (69% de) at −28 °C, suggesting that competing mechanisms may be operating. Overall the *o*-tolyl series was quite effective, since the precursor diol **6c** could be prepared on a large scale in homochiral form by the AD reaction, and could be assayed directly using the $^1H$ NMR shift reagent $Pr(hfc)_3$. The *o*-bromophenyl ketene acetal **1d** proved to be slightly more diastereoselective than the tolyl analogue **1c**, giving the pure crystalline diastereoisomer **3d** in 62% yield after crystallisation. However, the stilbene **10d** was a less convenient substrate for the AD process since the optical purity of the resulting diol **6d** could not be estimated without derivatisation.‡[15,16] The remaining ketene acetal, the di(1-naphthyl) compound **1e**, was only marginally more effective than the original diphenyl system **1a**, and suffered the major drawback that the $^1H$ NMR assay of the cycloadducts **3e** and **4e** was rendered difficult by the complex array of signals from the aromatic hydrogens, which obscured those of the respective vinylic (1-H) protons. Moreover, the major cycloadduct **3e**

‡ We are grateful to Dr Paul Wyatt for providing details of the assay for the diol (*R*,*R*)-**6d**, which is different from that reported in ref. 16.

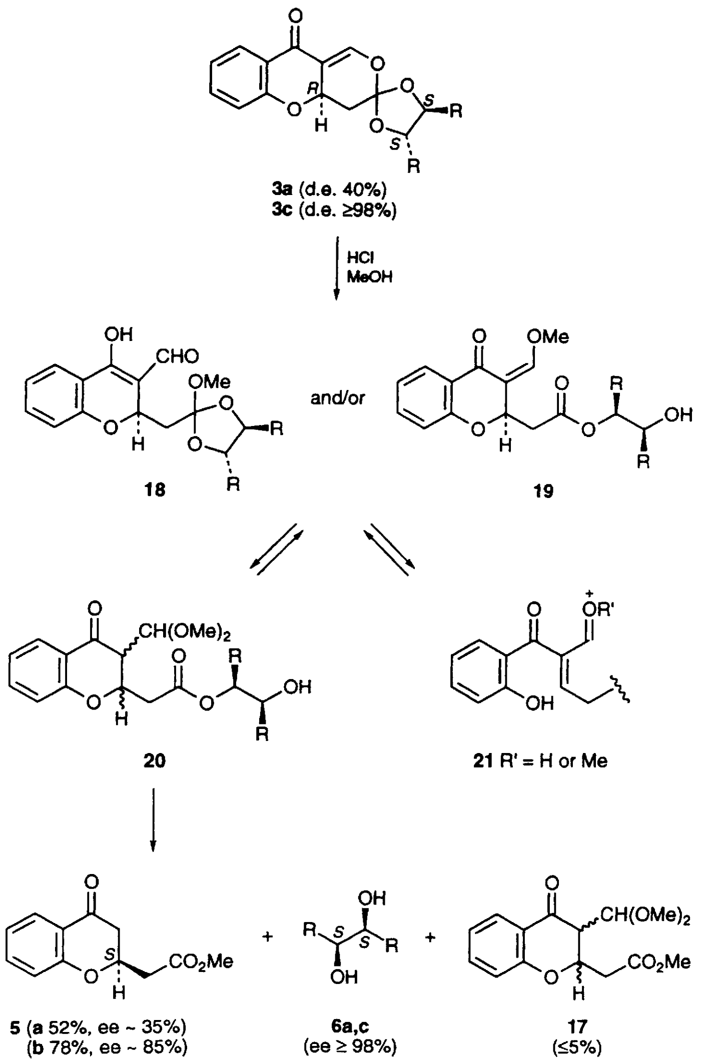
could not be fully characterised owing to its lability, especially during mass spectrometry.

The mixed cycloadducts (±)-**3a** and (±)-**4a** when treated with 3% methanolic HCl (reflux, 16 h) gave the ester (±)-**5**[7] (72%) and the diol (±)-**6a** (81%), along with traces of by-products, two of which were tentatively identified as the *trans*- and *cis*-isomers of **17** on the basis of their $^1$H NMR spectra. The stereochemical assignments for **3a** and **4a** were deduced from a repetition of the sequence starting with (*S*,*S*)-hydrobenzoin (−)-**6a** (Scheme 3). In this case the product (+)-**5** was identified as the (*S*)-enantiomer from its CD spectrum, which was complementary to that of (*S*)-2-methylchroman-4-one.[17] Estimation by $^1$H NMR spectroscopy in the presence of the shift reagent (*R*)-(−)-1-(9-anthryl)-2,2,2-trifluoroethanol (ATFE) of the stereochemical purity of both the ester (+)-**5** (ee 35 ± 5%) and the recovered diol (−)-**6a** (ee ≥98%) suggested that any racemisation during the sequence was minimal. When the methanolysis sequence was repeated with the cycloadduct

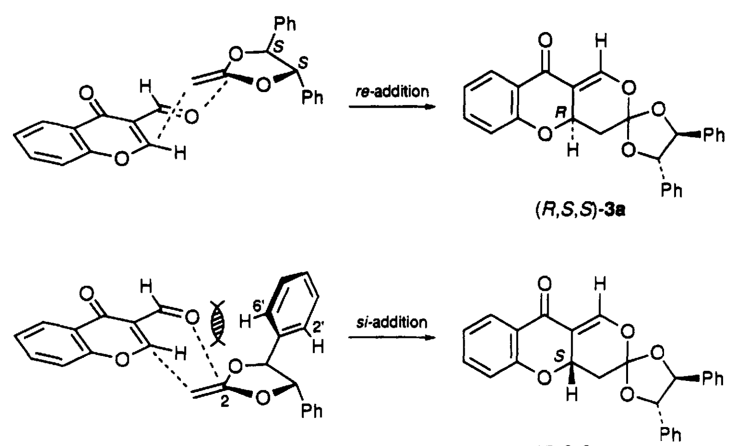
**Table 5** Diastereoselective cycloadditions between the ketene acetals **1** and the aldehyde **2**

| Ketene acetal | Reaction temp. °C | Reaction time (h) | Products | de (%)* | Yield (%)† |
|---|---|---|---|---|---|
| **1a** | −78 to +20 | 18 | **3a** + **4a** | 40 | 61 |
| **1b** | −28 | 40 | **3b** + **4b** | 78 | 54 |
| **1c** | −28 | 40 | **3c** + **4c** | 69 | 70 (46) |
| **1c** | +20 | 40 | **3c** + **4c** | 51 | — |
| **1c** | 0 | 40 | **3c** + **4c** | 57 | — |
| **1c** | −15 | 40 | **3c** + **4c** | 64 | — |
| **1c** | −35 | 40 | **3c** + **4c** | 65 | — |
| **1c** | −40 | 40 | **3c** + **4c** | 62 | — |
| **1d** | −28 | 40 | **3d** + **4d** | 78 | 79 (62) |
| **1e** | 0 | 20 | **3e** + **4e** | 35 | 58 |
| **1e** | −28 | 40 | **3e** + **4e** | 44 | 54 |

* Estimated by 300 MHz $^1$H NMR spectroscopy; the major product is assumed to be **3** in each series. † Isolated yield of **3** + **4**; yields in parentheses refer to crystalline (*R*,*S*,*S*)-**3** obtained after using (*S*,*S*)-**1** as the ketene acetal.




**Scheme 3** (**a**, R = phenyl; **c**, R = 2-methylphenyl)




**Scheme 4** Possible arrangements for concerted cycloaddition of the ketene acetal (*S*,*S*)-**1a** to the aldehyde **2**

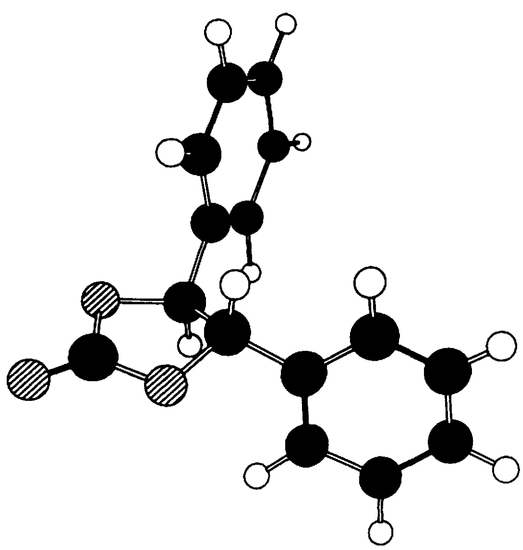


**Fig. 1** X-Ray structure of the diphenyl carbonate **22a**

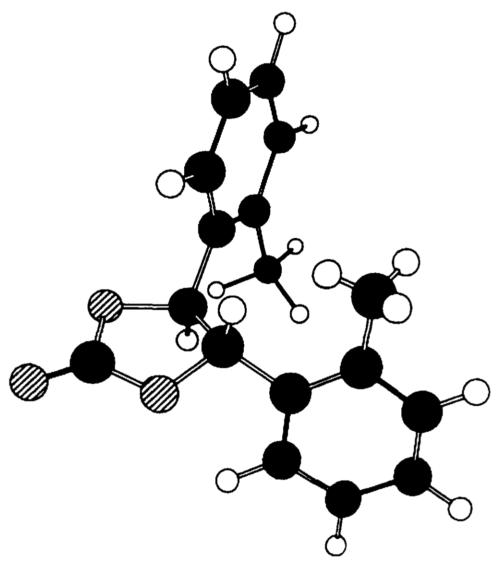


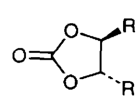
**Fig. 2** X-Ray structure of the di-*o*-tolyl carbonate **22c**

(*R*,*S*,*S*)-**3c**, the product was again (+)-**5**, indicating that the stereochemical assignment for the **3c** was also correct (by analogy and on the basis of the $^1H$ NMR characteristics of their respective cycloadducts, it is assumed that the reactions of the ketene acetals **1b**, **1d** and **1e** with **2** proceed with the same sense of diastereoselection as **1a** and **1c**). However, the product (*S*)-**5** obtained in this case was only *ca.* 85% optically pure. Possible mechanistic sequences leading from **3c** to **5** are shown in Scheme 3. In the course of the reaction the starting material **3c** disappears within minutes at room temperature, presumably due to the breakdown of the labile orthoester function into species such as **18** and/or **19**. Retro-Claisen deformylations and transesterifications leading to **5** will be slower and necessitate prolonged heating, which presumably engenders some racemisation by the acid-catalysed elimination of the phenolic oxygen substituent, leading to the reversible formation of a species such as **21**. Related processes have been described elsewhere.[7,9] Milder methods for functionalising cycloadducts such as **3** with the concomitant release of the chiral auxiliary **6** will clearly be advantageous.

### Mechanistic considerations

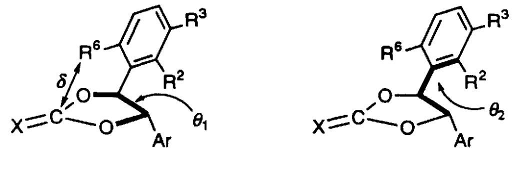
Although non-concerted interactions of the ketene acetal **1a** with the aldehyde **2** can be envisaged, the two possible arrangements in which they might undergo a concerted [4π + 2π] cycloaddition are shown in Scheme 4. The *re*-addition mode leading to **3a** would be expected to predominate, since the alternative *si*-approach appears to involve an unfavourable steric interaction between the diene and the nearby phenyl group.[18] On the basis of this model it was expected that replacing the *ortho*-hydrogen 6′-H with a methyl group would enhance the preference for *re*-addition, and the behaviour of the mesityl system **1b** is consistent with this rationale. However, the results obtained using the ketene acetals **1c–e**, in which the aromatic ring incorporates a single *ortho* substituent, warrant further discussion.

On the basis that they might serve as accurate molecular models of the respective ketene acetals **1a–c**, we prepared the more stable cyclic carbonates **22a–c** for analysis by X-ray



**22a** Ph
**b** 2,4,6-$Me_3C_6H_2$
**c** 2-$MeC_6H_4$

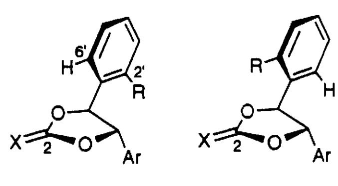
**Table 6** Measured and calculated [20] structural parameters for the carbonates **22** and the ketene acetals **1**



| | X | $R^2$ | $R^3$ | $R^6$ | Dihedral angles (°)* | | | $R^6$–$C^2$ distances (Å)* | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | $\theta_1$ | $\theta_2$ | $\theta_{2'}$ | $\delta$ | $\delta'$ |
| **22a**† | O | H | H | H | 34.2 | 113.5 | 113.5 | 3.69 | 3.69 |
| **22c**† | O | Me | H | H | 28.1 | 116.2 | 110.0 | 3.47 | 3.36 |
| **1a** | $CH_2$ | H | H | H | 27.3 | 94.8 | 94.7 | 3.54 | 3.32 |
| **1b** | $CH_2$ | Me | H | Me | 22.8 | 100.0 | 100.0 | 3.06 | 2.85 |
| **1c** | $CH_2$ | Me | H | H | 26.7 | 102.5 | 102.3 | 3.44 | 3.21 |
| **1d** | $CH_2$ | Br | H | H | 29.0 | 99.5 | 99.5 | 3.43 | 3.25 |
| **1e** | $CH_2$ | –$C_4H_4$– | | H | 30.2 | 89.5 | 89.3 | 3.44 | 3.28 |
| **1f** | $CH_2$ | OMe | H | H | 30.0 | 92.7 | 92.5 | 3.52 | 3.35 |
| **1i** | $CH_2$ | $CF_3$ | H | H | 19.9 | 108.7 | 108.4 | 3.36 | 3.01 |

* Primed data refer to the corresponding measurement from the other Ar group; $\delta$ refers to the internuclear distance indicated (the reference point for **1b** is the closest hydrogen of the 6-methyl group in the energy-minimised structure). † From X-ray diffraction studies.

crystallography. Unfortunately, the mesityl compound **22b** did not crystallise in a form suitable for this purpose, but the crystal structures of the respective diphenyl and ditolyl carbonates **22a** and **22c** were determined (Figs. 1 and 2). Selected parameters for these carbonates are shown in Table 6. In the diphenyl compound **22a** the five-membered ring is twisted with an O–$C_4$–$C_5$–O dihedral angle of 34.2°, whereas in the ditolyl homologue **22c** the ring is slightly flatter, the corresponding angle (28.1°) closely matching that in the unsubstituted parent system, 1,3-dioxolane-2-one (28.3°).[19] However, the most significant feature of the structure of **22c** is the location of the 'extra' methyl group in the 2'- rather than the 6'-position. Molecular mechanics calculations [20] indicate that the conformation **23** observed within the crystal of **22c** is some 8.8 kJ $mol^{-1}$ more stable than the energy minimum which approximates to



**23** X = O **24** X = O
**25** X = $CH_2$ **26** X = $CH_2$

**24**. Similar situations are predicted for all the ketene acetals with a vacant *ortho* position (Table 6) including the tolyl compound **1c**, for which the calculated minimum energy conformation **25** is 8.3 kJ $mol^{-1}$ more stable than that corresponding to **26**. Moreover, energy contour (Ramachandran) plots of $\theta_2$ *versus* $\theta_2'$ for the ketene acetals suggest that the diphenyl system **1a** is relatively flexible, but the barriers to rotation of the aryl groups in **1c–e** are very high and the mesityl system **1b** is essentially rigid. Notwithstanding the limitations of calculated and crystal-derived molecular geometries, the above results imply that for the ketene acetals **1c–e** the group in closest proximity to the $\pi$-bond undergoing cycloaddition is in each case a hydrogen atom whose position is invariant. Given the low selectivity observed with **1e** compared to **1c** and **1d**, we speculate that the observed differences in stereoselectivity arise from structural effects which may include the precise location of this hydrogen atom, but must also reflect other (*e.g.* polar) interactions prior to or during bonding. The calculated molecular parameters for the hitherto unprepared bis(2-trifluoromethylphenyl) compound **1i**, in which the dihedral angle $\theta_1$ is less than 20 °, make it an intriguing candidate for further investigation of these undefined interactions.

From a synthetic point of view, we conclude that higher levels of stereoselectivity in the [4 + 2] cycloadditions of the ketene acetals **1** might yet be realised by variation of the *ortho*-substituent in di(*o*-substituted aryl) substrates, as well as by variations in the diene component. For the present, the ditolyl diols **6c** and **6d** offer several advantages as chiral auxiliaries, being accessible on a large scale, the former being easily assayed by virtue of its methyl substituents, and (in the context of Scheme 2) providing intermediates which can be obtained pure by crystallisation. Developments along these lines are under investigation and will be described in due course.

## Experimental

Mps were determined using an Electrothermal apparatus and are uncorrected. Unless otherwise stated, IR spectra were of thin films on sodium chloride plates, recorded on a Perkin-Elmer 1710FT spectrometer. Unless otherwise indicated, $^1H$ NMR spectra were measured at 300 MHz for solutions in deuteriochloroform with tetramethylsilane as the internal standard, on a Bruker AC300 instrument; *J* values are given in Hz. Mass spectra were measured on a Finnegan 4500 (low resolution) and Kratos Concept S1 (high resolution) instruments using the ammonia chemical ionisation method. Unless indicated, fragment ions with a relative intensity of less than 20% of the base peak are omitted. Optical rotations were measured using an Optical Activity AA10 polarimeter and are recorded in units of $10^{-1}$ deg $cm^2$ $g^{-1}$.

Starting materials and solvents were routinely purified by conventional techniques.[21] Organic solutions were dried using anhydrous magnesium sulfate and concentrated by rotary evaporation. Analytical thin layer chromatography (TLC) was carried out on Camlab Polygram SIL G/$UV_{254}$ plates. Spots were visualised with ethanolic phosphomolybdic acid unless stated. Preparative (column) chromatography was carried out using silica gel (Merck 9385 and the flash technique [22]) or on Florisil® (Aldrich 28,870–5). Compositions of solvent mixtures are quoted as ratios of volume. 'Petroleum' refers to a light petroleum fraction, bp 60–80 °C, unless otherwise stated. 'Ether' refers to diethyl ether. 'DME' refers to 1,2-dimethoxyethane. Unless otherwise indicated, the ratios of products isolated as mixtures were estimated by integration of $^1H$ NMR spectra.

**Preparation of diols by reductive coupling techniques (*cf.* Table 1)**

**1,2-Bis(2,4,6-trimethylphenyl)ethane-1,2-diol (±)-6b.** *Method i.*[23]—Li wire (*ca.* 100 mg, 14 mmol) was added to a suspension of $TiCl_3$ (261 mg, 1.7 mmol) in dry DME (5 $cm^3$) under Ar at room temperature. After being heated under reflux for 1.5 h the mixture was cooled to 0 °C, diluted with DME (3 $cm^3$) and treated with mesitaldehyde **8b** (1.50 g, 10.12 mmol). The mixture was stirred at 0 °C for 1 h and room temperature for a further 1 h, and then hydrolysed at 0 °C by careful addition, with stirring, of saturated aqueous ammonium chloride (5 $cm^3$). After the mixture had been stirred at 0 °C for 3 h, the organic phase was separated and the aqueous phase extracted with ethyl acetate (3 × 20 $cm^3$). The combined organic phases were dried and concentrated, and the residue purified by column chromatography. Elution with petroleum–ethyl acetate (10:1) gave the stilbene **10b** (242 mg, 18%). Further elution with petroleum–ethyl acetate (4:1) gave the diol (±)-**6b** (320 mg, 21%) and the *meso*-diol **9b** (110 mg, 7%). The products had properties identical with those of material prepared by other methods described below.

*Method ii.*—The procedure was similar to method i, but the reducing agent ($TiCl_3$–Li) was added to the solution of mesitaldehyde **8b**. From $TiCl_3$ (1.65 g, 10.7 mmol), lithium wire (0.32 g, 46 mmol) and mesitaldehyde **8b** (9.00 g, 60.7 mmol) was obtained a mixture of the diol (±)-**6b** and the *meso*-diol **9b** (total 5.844 g, 65%; ratio 3:1). The stilbene **10b** (0.241 g, 3%) was also isolated.

*Method iii.*[24]—To a suspension of samarium powder (40 mesh; 1.20 g, 7.98 mmol) in THF (20 $cm^3$) under argon was added 4 drops of a solution of 1,2-diiodoethane (1.125 g, 4.0 mmol) in THF (5 $cm^3$). When the blue colour of $SmI_2$ was apparent, the rest of the solution of 1,2-diiodoethane was added, and the mixture was stirred for a further 15 min, after which 1,2-diiodoethane was no longer detectable in the reaction mixture (TLC, eluting with petroleum–ethyl acetate 20:1). The samarium diiodide solution was transferred under argon to another flask into which mesitaldehyde **8b** (593 mg, 4.0 mmol) was added dropwise at room temperature. The mixture was stirred until the initial blue colour became green (*ca.* 15 min), and then quenched by the addition of 5 drops of saturated aqueous ammonium chloride. After a further 1 h the mixture was evaporated to remove all solvents, the residue was extracted with ethyl acetate and the extract was dried. Evaporation of the extract afforded the crude product as a mixture of diols, which was purified by chromatography (elution with ethyl acetate–petroleum 1:4) to give the diols (±)-**6b** and **9b** (total 512 mg, 86%; ratio 1:1).

*Method iv.*—Into a solution of anhydrous $FeCl_3$ (0.54 g, 3.33 mmol) in refluxing DME (20 $cm^3$) under argon was added lithium wire (95 mg, 13.7 mmol). After being heated under reflux for a further 2 h the mixture was cooled to room temperature and treated with mesitaldehyde **8b** (493 mg, 3.33 mmol). After a further 3 h at reflux temperature the mixture was cooled to room temperature and concentrated. The residue was quenched by stirring it with saturated aqueous ammonium chloride (1 $cm^3$) at 0 °C for 1 h and then at room temperature for 2 h. The mixture was then treated with 1.0 mol $dm^{-3}$ hydrochloric acid (1 $cm^3$) and extracted with ethyl acetate (3 × 20 $cm^3$). The extract was dried and concentrated to give the crude product as a mixture which was purified by chromatography, eluting with ethyl acetate–petroleum (1:4). Early fractions from the column contained the *meso*-diol **9b** (80 mg, 16%), mp 208–209 °C (hexane–chloroform) (lit.,[25] 214–215 °C); δ 2.25 (6 H, s, 4-ArMe), 2.4–2.55 and 2.55–2.7 (12 H, 2 × br s, 2,6-ArMe), 5.59 (2 H, s, ArC*H*OH) and 6.87 (4 H, br s, ArH); *m/z* 316 (M + $NH_4^+$); $R_f$ 0.50 [ethyl acetate–petroleum 1:4; visualised with $Ce(SO_4)_2$]. Later fractions contained the title compound (±)-**6b** (370 mg, 75%), mp 159–160 °C (hexane–chloroform) (lit.,[25] 160–161 °C); δ 1.5–1.7 (12 H, br s, 2,6-ArMe), 1.8–2.2 (2 H, br s, OH), 2.17 (6 H, s, 4-ArMe), 5.39 (2 H, s, ArC*H*OH) and 6.66 (4 H, br s, ArH); *m/z* 316 (M + $NH_4^+$, 22%), 300 (25), 299 (M + $H^+$, 100), 298 (84), 281 (65), 166 (21) and 149 (46); $R_f$ 0.28 [ethyl acetate–petroleum 1:4; visualised with $Ce(SO_4)_2$].

**1,2-Bis(2-methylphenyl)ethane-1,2-diol (±)-6c.** *Method i.*—A procedure analogous to that used for **6b** (method i above) was adopted with $TiCl_3$ (510 mg, 3.3 mmol), lithium wire (200 mg, 28.5 mmol), and 2-methylbenzaldehyde **8c** (1.98 g, 16.5 mmol), to give a mixture which was purified by chromatography. Elution with petroleum–ethyl acetate (10:1; TLC visualised with ceric sulfate) gave the stilbene **10c** (33 mg, 2%), mp 82–83 °C (ethanol) [lit.,[26] 81–82 °C (hexane)], 1,2-bis(2-methylphenyl)ethane (41.7 mg, 2%), and a mixture of the diols (±)-**6c** and **9c** (total 1.272 g, 64%; ratio 1.3:1) which could be further separated by column chromatography (elution with dichloromethane–acetonitrile 4:1) to give the *meso*-diol **9c** (134 mg, 7%), mp 101–103 °C (chloroform–petroleum) [lit.,[27] 104–105 °C (aq. EtOH)] and the diol (±)-**6c** (511 mg, 26%), mp 107–109 °C (chloroform–petroleum) (lit.,[28] 115 °C). A mixed fraction containing **6c** and **9c** (568 mg, 28%) was also recovered; (±)-**6c** has δ 1.64 (6 H, s, 2 × ArMe), 2.85 (2 H, s, 2 × OH), 4.97 (2 H, s, 2 × C*H*OH), 6.90 (2 H, dd, *J ca.* 1, 7.5, 3,3′-ArH), 7.10 (2 H, dt, *J ca.* 1.4, 7.5, 4,4′-ArH), 7.19 (2 H, br t, *J* 7.5, 5,5′-ArH) and 7.61 (2 H, dd, *J ca.* 1.4, 8.5, 6,6′-ArH); *m/z* 260 (M + $NH_4$, 100%), 242 (M, 83) and 231 (40); **9c** has δ 2.16 (6 H, s, 2 × ArMe), 2.1–2.2 (2 H, br s overlapping ArMe signal, 2 × OH), 5.17 (2 H, s, 2 × C*H*OH), 7.05–7.35 (8 H, m, ArH); *m/z* 260 (M + $NH_4$, 100%) and 242 (M, 80).

*Method iv.*—A procedure analogous to that used for (±)-**6b** (method iv above) was adopted with $FeCl_3$ (162 mg, 1.0 mmol), lithium wire (28 mg, 4 mmol), and 2-methylbenzaldehyde **8c** (118 mg, 0.98 mmol), to give a mixture which was purified by chromatography. Elution with petroleum–ethyl acetate (10:1) gave a mixture of the diols (±)-**6c** and **9c** (total 47 mg, 40%; ratio 3:1), 2-methylbenzyl alcohol (58.8 mg, 49%) and recovered aldehyde **8c** (5%).

**1,2-Bis(2-bromophenyl)ethane-1,2-diol (±)-6d.** *Method v.*[9]—To titanocene dichloride (609 mg, 2.44 mmol) in THF (15 $cm^3$) at 0 °C under nitrogen was added $Bu^sMgCl$ in ether (2 mol $dm^{-3}$; 1.22 $cm^3$, 2.44 mmol). The red suspension became a dark green transparent solution, which was added into a solution of 2-bromobenzaldehyde **8d** (366 mg, 2.0 mmol) in THF (5 $cm^3$) at −78 °C dropwise with stirring. The mixture was then allowed to rise to room temperature during 1 h, whereupon the reductive coupling was complete. The mixture was quenched with 1% hydrochloric acid (2.5 $cm^3$), stirred for 10 min, and then treated with 10% aqueous NaOH (5 $cm^3$). After being stirred for 1 h the mixture, no longer red, was vigorously shaken with ether (50 $cm^3$). The layers were separated by centrifugation, and the ethereal layer was concentrated. The residue was extracted with ether (3 × 25 $cm^3$), and the extract dried and evaporated to give a residue which was purified by chromatography. Petroleum–ethyl acetate (2:1) as eluent gave the diols (±)-**6d** and **9d** (269 mg, 73%; ratio 1:1.4); (±)-**6d** has δ 2.84 (2 H, s, OH), 5.28 (2 H, s, C*H*OH), 7.12 (2 H, dt, *J* 1.6, *ca.* 7.7, 4-ArH), 7.32 (2 H, dt, *J* 1.2, *ca.* 7.7, 5-ArH), 7.43 (2 H, dd, *J* 1.1, 7.8, 3-ArH), 7.68 (2 H, dd, *J* 1.6, 7.8, 6-ArH); **9d** has δ 2.65 (2 H, s, OH), 5.53 (2 H, s, C*H*OH), 7.07 (2 H, dt, *J* 1.8, *ca.* 7.5, 4-ArH), 7.18 (2 H, dt, *J* 1.2, *ca.* 7.7, 5-ArH), 7.24 (2 H, dd, *J* 1.8, 7.7, 6-ArH), 7.38 (2 H, dd, *J* 1.2, 7.9, 3-ArH). Other data for (±)-**6d** appear later.

**1,2-Di-1-naphthylethane-1,2-diol (±)-6**[9] *Method v.*—A procedure analogous to that used for (±)-**6d** (method v above) was adopted with titanocene dichloride (1.42 g, 5.7 mmol) in THF (25 $cm^3$), Bu$^s$MgCl in ether (2 mol $dm^{-3}$; 2.85 $cm^3$, 5.7 mmol) and 1-naphthaldehyde **8e** (890 mg, 5.7 mmol) in THF (5 $cm^3$). Chromatography of the product, eluting with petroleum–ethyl acetate (1:1), gave the diols (±)-**6e** and **9e** (689 mg, 77%; ratio *ca.* 100:1). The pure diol (±)-**6e** had mp 174–175 °C (petroleum–ethyl acetate 1:1); δ 2.96 (2 H, s, OH), 5.77 (2 H, s, C*H*OH), 7.25–7.40 (6 H, m, ArH), 7.66–7.73 (6 H, m, ArH) and 7.86 (2 H, d, *J* 8.5, ArH); *m/z* 332 (M + $NH_4$, 40%) and 314 (M, 100). The *meso*-diol **9e** had δ 5.94 (2 H, s, C*H*OH).

**1,2-Bis(2-methoxyphenyl)ethane-1,2-diol (±)-6f.** *Method i.*—A procedure analogous to that used for (±)-**6b** (method i above) was adopted with $TiCl_3$ (1530 mg, 9.9 mmol) in DME (50 $cm^3$), lithium wire (740 mg, 107 mmol) and the addition of 2-methoxybenzaldehyde **8f** (680 mg, 4.99 mmol) in DME (2 $cm^3$). After the mixture had been stirred at room temperature for 16 h and then at 45 °C for 16 h it gave a crude product which was purified by chromatography. Elution with petroleum–ethyl acetate (10:1; TLC visualised with ceric sulfate) gave the stilbene **10f** (232 mg, 39%), mp 134–135 °C (ethanol, −35 °C) [lit.,[29] 140 °C (toluene)]; δ 3.86 (6 H, s, OMe), 6.87 (2 H, br d, *J ca.* 8, 3-ArH), 6.94 (2 H, dt, *J ca.* 1, 7.5, 5-ArH), 7.21 (2 H, dt, *J* 1.6, 7.5, 4-ArH), 7.45 (2 H, s, C=CH) and 7.63 (2 H, dd, *J* 1.6, 7.7, 6-ArH); *m/z* 258 (M + $NH_4$, 100%) and 241 (M + H, 15). Further elution with ethyl acetate gave a mixture of the diols (±)-**6f** and **9f** (total 351 mg, 51%; ratio 0.4:1) which was resolved by further chromatography, eluting with petroleum–ethyl acetate (5:4) to give *meso*-diol **9f**, mp 152–153 °C (chloroform–pentane), and the diol (±)-**6f**, mp 87 °C (MeOH) (lit.,[30] 88–89 °C). The diol **9f** has δ 3.08 (2 H, d, *J* 6.5, OH), 3.68 (6 H, s, OMe), 5.22 (2 H, d, *J* 6.5, C*H*OH), 6.79 (2 H, br d, *J ca.* 8, 3-ArH), 6.87 (2 H, t, *J ca.* 7.5, 5-ArH), 7.16 (2 H, dd, *J* 1.6, 7.90, 4-ArH), 7.20 (2 H, dt, *J* 1.6, 7.5, 6-ArH). The diol **6f** has δ 3.41–3.46 (2 H, m, OH), 3.65 (6 H, s, OMe), 5.00 (2 H, d, *J* 4.4 Hz, C*H*OH), 6.73 (2 H, d, *J* 8.1 Hz, ArH), 6.82 (2 H, t, *J* 7.0, 7.4, ArH), 7.12–7.18 (4 H, m, ArH); *m/z* 274 ($M^+$) and 292 (M + $NH_4$).

*Method v.*—A procedure analogous to that used for (±)-**6d** (method v above) was adopted with titanocene dichloride (233 mg, 0.936 mmol) in THF (8 $cm^3$), Bu$^s$MgCl in ether (2 mol $dm^{-3}$; 0.46 $cm^3$, 0.93 mmol), and the aldehyde **8f** (64 mg, 0.47 mmol) in THF (2 $cm^3$). Chromatography of the product, eluting with petroleum–ethyl acetate (1:1), gave the diols (±)-**6f** and **9f** (total 50.4 mg, 79%; ratio 1.2:1).

**Preparation of (*E*)-1,2-disubstituted ethenes (*cf.* Table 2)**

**(*E*)-1,2-Bis(2,4,6-trimethylphenyl)ethene 10b.** A stirred suspension of the phosphonium salt **11b** (8.13 g, 17.1 mmol) in THF (180 $cm^3$) under $N_2$ at −78 °C was treated dropwise with BuLi in hexane (1.1 mol $dm^{-3}$; 16.4 $cm^3$, 18.0 mmol). After the solution had been allowed to reach room temperature it was stirred for 2 h, and then treated dropwise at the same temperature with a solution of the aldehyde **8b** (2.90 g, 19.6 mmol) in THF (5 $cm^3$). The mixture was then stirred for a further 2 h, after which it was concentrated, and the residue extracted with ether (2 × 50 $cm^3$). The extract was filtered through a column of silica gel, which was then washed with more ether. The residue on evaporation of the eluate was chromatographed (elution with petroleum–ethyl acetate 20:1; visualisation with PMA) to give the pure (*E*)-stilbene **10b** (2.49 g, 55%), mp 128.5–130 °C (lit.,[31] 130–132 °C). Other data for **10b** were identical with those of material prepared as described earlier.

**(*E*)-1,2-Bis(2-methylphenyl)ethene 10c.** A vigorously stirred suspension of the phosphonium salt **11c**[32] (80.9 g, 181 mmol) [prepared by heating triphenylphosphine (48 g) and 2-methylbenzyl bromide (33.9 g) in dry toluene (400 $cm^3$) at 80 °C for 2 h, cooling to room temperature, concentration, washing with ether and drying *in vacuo*] in THF (600 $cm^3$) under $N_2$ at 0 °C was treated dropwise with BuLi in hexane (1.4 mol $dm^{-3}$; 130 $cm^3$, 182 mmol). The clear dark-red solution was stirred for 10 min and then treated dropwise at 0 °C (internal temperature) with a solution of 2-methylbenzaldehyde **8c** (21.7 g, 181 mmol) in THF (30 $cm^3$). The red colour faded, and the mixture was allowed to warm to room temperature over 0.5 h, and then stirred for a further 0.5 h. The mixture was then concentrated, treated with ether (500 $cm^3$), and the resulting suspension filtered through a column of silica gel (40 g), the column being washed with more ether (200 $cm^3$). Evaporation of the eluate gave a crude product (7.15 g) which was distilled under reduced pressure (Kugelrohr; oven temperature 120–125 °C/0.02 mmHg). Crystallisation of the distillate (37.06 g, 98%) from ethanol afforded a mixture of the stilbenes **10c** and **12c** (total 35.3 g, 94%) (*E*:*Z* ratio 1:2); **10c** had δ 2.41 (6 H, s, Me), 7.18 (2 H, s, C=CH), 7.15–7.25 (6 H, m, ArH) and 7.58 (2 H, d, *J* 6.6, ArH); **12c** had δ 2.27 (6 H, s, Me), 6.72 (2 H, s, C=CH), 6.85–7.25 (8 H, m, ArH) and 7.58 (2 H, d, *J* 6.6, ArH).

*Isomerisation.*[10]—A solution of the stilbenes **10c** and **12c** (ratio 1:2; total 29.0 g, 139 mmol) in chloroform (ethanol-free; 300 $cm^3$) at room temperature was treated with tellurium(IV) chloride (0.58 g, 2.2 mmol), and stirred until clear. The mixture was then heated under reflux for 24 h, treated with more tellurium(IV) chloride (0.29 g, 1.1 mmol), and then heated under reflux for a further 24 h. After this time the ratio **10c**:**12c** had become >40:1 [monitored by $^1$H NMR spectroscopy; sample preparation by filtering reaction solution (0.5 $cm^3$) through a Pasteur pipette containing silica gel, washing the silica gel with chloroform (0.5 $cm^3$), concentrating the filtrate, and dissolving the residue in $CDCl_3$]. The cooled reaction mixture was washed with saturated aqueous sodium hydrogen carbonate, dried, and evaporated, and the residue distilled under reduced pressure as above. Crystallisation of the distillate (28.32 g, 98%) from ethanol gave the pure *E*-alkene **10c** (27.45 g, 95%), mp 83–84 °C [lit.,[26] 81–82 °C (hexane)].

**(*E*)-1,2-Bis(2-bromophenyl)ethene 10d.** A vigorously stirred suspension of the phosphonium salt **11d** (9.48 g, 18.5 mmol) [prepared by heating triphenylphosphine (5.2 g) and 2-bromobenzyl bromide (4.9 g) in dry toluene (25 $cm^3$) under reflux for 3 h, cooling to room temperature, concentration, diluting with ether (50 $cm^3$) and drying the precipitate *in vacuo*] in THF (150 $cm^3$) under $N_2$ at 0 °C was treated dropwise with BuLi in hexane (1.3 mol $dm^{-3}$; 15.0 $cm^3$, 19.5 mmol). The stirred mixture was then allowed to reach room temperature over 1 h after which it was cooled again to 0 °C, treated dropwise with a solution of 2-bromobenzaldehyde **8d** (4.10 g, 22.2 mmol) in THF (10 $cm^3$), and then stirred at room temperature for 8 d. After the mixture had been concentrated, it was treated with ether (100 $cm^3$), and the resulting suspension filtered through a short column of silica gel, the column being washed with more ether (100 $cm^3$). Evaporation of the eluate gave a crude product (7.15 g) which was chromatographed, eluting with petroleum–ethyl acetate (20:1) to give a mixture of the stilbenes **10d** and **12d** (total 5.04 g, 81%) (*E*:*Z* ratio 1:7); **10d** had δ 7.13 (2 H, dt, *J* 1.2, 7.5, 5,5′-H), 7.32 (2 H, t, *J* 7.5, 4,4′-H), 7.38 (2 H, s, C=CH), 7.57 (2 H, d, *J* 7.5, 3,3′-H) and 7.71 (2 H, dd, *J* 1.2, 7.8, 6,6′-H); **12d** had δ 6.76 (2 H, s, C=CH), 6.94–7.05 (6 H, m, 3,4,5-ArH) and 7.55 (2 H, dd, *J* 1.5, 7.5, 6,6′-H).

*Isomerisation.*—A solution of the stilbenes **10d** and **12d** (ratio 1:7, total 5.00 g, 14.8 mmol) in chloroform (ethanol-free; 125 $cm^3$) at room temperature was treated with tellurium(IV) chloride (1.00 g, 3.7 mmol). The mixture was heated under reflux for 48 h (monitored by $^1$H NMR), after which time the ratio **10d**:**12d** had become 37:1. The tellurium salt was removed by filtration of the reaction solution through a short column of silica gel, eluting with chloroform. Evaporation of the eluate followed by chromatography, eluting with petroleum–ethyl acetate (20:1), and crystallisation from ethanol gave the pure *E*-stilbene **10d** (4.63 g, 93%), mp 119–120 °C (lit.,[33] 108–108.4 °C).

**1,2-Bis(2-methoxyphenyl)ethene 10f.** A solution of 1,2-bis(2-methoxyphenyl)ethanol **13**[34] (10.78 g, 41.7 mmol) in dichloromethane (75 $cm^3$) at 0 °C was treated with triethylamine (6.00 g, 59 mmol). After 10 min the solution was treated dropwise with a solution of methanesulfonyl chloride (5.7 g, 49.8 mmol) in dichloromethane (25 $cm^3$) and then allowed to reach room temperature. After being stirred overnight the mixture was concentrated by removal of the dichloromethane and the residue was dissolved in ether (100 $cm^3$). The solution was washed with 3% aqueous HCl, water, 1% aqueous sodium hydrogen carbonate and brine, dried and evaporated to afford the crude mesylate (14.01 g, 100%). This was dissolved in methanol (150 $cm^3$) and the solution treated with anhydrous potassium carbonate (10.28 g, 74.4 mmol). The mixture was heated under reflux for 16 h after which it was cooled and evaporated. The residue was dissolved in ether (100 $cm^3$) and the solution washed with water (50 $cm^3$), dried and evaporated. The residue was purified by bulb-to-bulb distillation (oven temperature 125–130 °C/0.04 mmHg) to give the stilbene **10f** (9.50 g, 95%). Crystallisation of this from ethanol at −35 °C gave **10f** (8.14 g, 81%), identical with material obtained directly from **8f** as described above (method i).

**(*E*)-1,2-Di-*tert*-butylethene 10g.**[35] The acetate **14** was prepared in 80% yield as described, and heated at 290 °C to generate the (*E*)-alkene **10g** (90%), bp 122–124 °C; δ 0.95 (s, 18 H, 6 × $CH_3$) and 5.29 (s, 2 H, 2 × C=CH).

**(*E*)-1,2-Bis(2-trifluoromethylphenyl)ethene 10i.** A vigorously stirred suspension of the phosphonium salt **11i** (2.31 g, 4.61 mmol) [prepared by heating triphenylphosphine (1.33 g) and 2-trifluoromethylbenzyl bromide (1.20 g) in dry toluene (25 $cm^3$) at 80 °C for 16 h, cooling the mixture to room temperature, concentrating it, diluting it with ether and drying of the precipitate *in vacuo*] in THF (20 $cm^3$) under Ar was cooled to 0 °C and treated dropwise with BuLi in hexane (1.35 mol $dm^{-3}$; 3.5 $cm^3$, 4.73 mmol). The mixture was kept at 0 °C for 10 min and then at 20 °C for 20 min to produce the ylide, which was then treated dropwise with 2-trifluoromethylbenzaldehyde **8i** (802 mg, 4.61 mmol) in THF (2 $cm^3$). The mixture was then stirred at room temperature for 1 h, evaporated, and the residue diluted with ether (20 $cm^3$). The ether solution was filtered through a silica column and the column washed with more ether (10 $cm^3$); evaporation of the eluate and then distillation (Kugelrohr, 120–125 °C, 0.05 mmHg) gave the mixed stilbenes **10i** and **12i** (1.36 g, 93%, *E*/*Z* ratio 2:1). The mixture was heated under reflux in chloroform (8 $cm^3$) with tellurium(IV) chloride (27 mg, 0.1 mmol) for 8 h, after which time more tellurium(IV) chloride (13 mg, 0.05 mmol) was added to it and the heating under reflux continued for a further 8 h, whereupon the isomerisation appeared to be complete by TLC. The reaction mixture was cooled, washed with sat. aq. sodium hydrogen carbonate, dried and evaporated, and the residue was distilled as before to give the *title compound* **10i** (1.21 g, 83%), mp 38–39 °C (methanol) (Found: C, 60.65; H, 3.21. $C_{16}H_{10}F_6$ requires C, 60.77; H, 3.19%); δ 7.64 (2 H, d, *J* 7.7, 3′-H, 3″-H), 7.28–7.14 (4 H, m, 4′-H, 4″-H, 5′-H, 5″-H), 7.02 (2 H, s, 1-H, 2-H) and 6.92 (2 H, d, *J* 7.6, 6′-H, 6″-H).

**Preparation of diols by dihydroxylation methods (*cf.* Table 3)**

**Attempted preparation of 1,2-bis(2,4,6-trimethylphenyl)-ethane-1,2-diol (±)-6b.** The stilbene **10b** was not dihydroxylated under catalytic conditions (5 mol% $OsO_4$, 40–50 °C, 4–7 days) with NMO or $K_3Fe(CN)_6$ as co-oxidant.[11] Further, the stilbene **10b** (1.0 mmol) and $OsO_4$ (1.0 mmol) in *tert*-butyl alcohol–water (5:2) (20–40 °C, 3 d) also failed to give a product. A trace (< 2%) of the diol **6b** was detected using $OsO_4$ (5 mol%) and NMO in acetone–*tert*-butyl alcohol–THF–water (10:10:5:13) at 58 °C over several days, but the major components of the reaction medium were unchanged **10b** (63%) and a mixture of 2,4,6-trimethylbenzoic acid and 1,2-bis(2,4,6-trimethylphenyl)ethane-1,2-dione (total 29%).

**1,2-Bis(2-methylphenyl)ethane-1,2-diol (±)-6c.** To a solution of the *E*-alkene **10c** (1.35 g, 6.48 mmol) in a mixture of *tert*-butyl alcohol (100 $cm^3$) and water (100 $cm^3$) at 60 °C was added potassium ferricyanide (19.74 g, 60 mmol), anhydrous potassium carbonate (7.92 g, 57.3 mmol), osmium tetroxide (2.5% in *tert*-butyl alcohol; 1.0 $cm^3$, 0.08 mmol) and 1,4-diazabicyclo[2.2.2]octane (0.72 g, 6.42 mmol). The mixture was stirred at 60 °C for 88 h, cooled to room temperature and treated with saturated aqueous sodium hydrosulfite (30 $cm^3$). After being stirred for a further 30 min (until the colour changed to light green), the mixture was concentrated, and the residue treated with water (90 $cm^3$) and extracted with chloroform (3 × 120 $cm^3$). The combined extracts were dried and evaporated, and the residue chromatographed (elution with petroleum–ethyl acetate 4:1), which gave the diol (±)-**6c** (1.23 g, 78%), with properties identical with those of material obtained by coupling **8c** (as described above).

**1,2-Bis(2-bromophenyl)ethane-1,2-diol (±)-6d.** A procedure similar to that described above for the conversion of **10c** into (±)-**6c**, was adopted in which the *E*-alkene **10d** (1.502 g, 4.44 mmol) in a mixture of *tert*-butyl alcohol (30 $cm^3$) and water (30 $cm^3$) at 80 °C was treated with potassium ferricyanide (7.31 g, 22.2 mmol), anhydrous potassium carbonate (3.06 g, 22.2 mmol), osmium tetroxide (2.5% in *tert*-butyl alcohol; 0.2 $cm^3$, 0.015 mmol) and 1,4-diazabicyclo[2.2.2]octane (100 mg, 0.9 mmol). The mixture was stirred at 80 °C for 16 h, and worked up as before. Chromatography (elution with petroleum–ethyl acetate 1:1) gave the diol (±)-**6d** (1.47 g, 89%), with properties identical with those of material obtained by coupling **8d** (as described above).

**1,2-Bis(2-methoxyphenyl)ethane-1,2-diol (±)-6f.** A procedure similar to that described above for the conversion of **10c** into (±)-**6c**, was adopted in which the *E*-alkene **10f** (452 mg, 1.88 mmol) in a mixture of *tert*-butyl (30 $cm^3$) and water (30 $cm^3$) at 70 °C was treated with potassium ferricyanide (3.04 g, 9.23 mmol), anhydrous potassium carbonate (1.275 g, 9.23 mmol), osmium tetroxide (2.5% in *tert*-butyl alcohol; 0.5 $cm^3$, 0.04 mmol) and 1,4-diazabicyclo[2.2.2]octane (46 mg, 0.41 mmol). The mixture was stirred at 70 °C for 40 h, and worked up as before, with ethyl acetate (3 × 15 $cm^3$) for extraction. Chromatography (elution with petroleum–ethyl acetate, 5:4) gave the diol (±)-**6f** (296 mg, 57%), with properties identical with those of material obtained by coupling **8f** (as described above).

**1,2-Di-*tert*-butylethane-1,2-diol (±)-6g.** A procedure[36] similar to that described above for the conversion of **10c** into (±)-**6c**, was adopted in which the *E*-alkene **10g** (657 mg, 4.68 mmol) in a mixture of *tert*-butyl alcohol (30 $cm^3$) and water (30 $cm^3$) at 65 °C was treated with potassium ferricyanide (7.73 g, 23.5 mmol), anhydrous potassium carbonate (3.24 g, 23.5 mmol), osmium tetroxide (2.5% in *tert*-butyl alcohol; 1.5 $cm^3$, 0.12 mmol) and 1,4-diazabicyclo[2.2.2]octane (280 mg, 2.5 mmol). The mixture was stirred at 80 °C for 16 h, and worked up as before. Chromatography (elution with petroleum–ethyl acetate 2:1) gave the diol (±)-**6g** (348 mg, 43%), mp 119–120 °C (chloroform–hexane) [lit.,[37] 123–124 °C (hexane–ethyl acetate)]; δ 0.90 (18 H, s, 6 × Me), 2.3 (2 H, br s, 2 × OH) and 3.30 (2 H, s, 2 × CHOH); *m*/*z* 192 (M + $NH_4$, 85%), 175 (M + H, 3%) and 94 (100).

**(*S*,*S*)-1,2-Bis(2-methylphenyl)ethane-1,2-diol (−)-6c.** *With DHQ-PCB.*[12]—To a solution of dihydroquinine *p*-chlorobenzoate (DHQ-PCB) (232 mg, 0.5 mmol) in *tert*-butyl alcohol (75 $cm^3$) and water (75 $cm^3$) at 65 °C was added osmium tetroxide (2.5% in *tert*-butyl alcohol; 0.4 $cm^3$, 0.03 mmol). After 10 min a finely ground mixture of potassium ferricyanide (24.43 g, 74.2 mmol) and anhydrous potassium carbonate (10.24 g, 74.2 mmol) was added to the vigorously stirred solution, followed by the stilbene **10c** (3.09 g, 14.8 mmol). The mixture was stirred at 65 °C for 16 h, cooled to room temperature, and treated with saturated aqueous sodium hydrosulphite (5 $cm^3$). After being stirred for a further 30 min (until the colour changed to green), the mixture was concentrated, and the residue treated with water (100 $cm^3$) and extracted with ethyl acetate (3 × 80 $cm^3$). The combined extracts were dried and evaporated, and the residue was chromatographed (elution with petroleum–ethyl acetate, 2:1) to yield the diol (*S*,*S*)-**6c** (3.42 g, 95%), mp 109–110 °C (petroleum–chloroform), spectroscopically identical with (±)-**6c** obtained as above; $[\alpha]_D^{20}$ −72 ± 2 (*c* 1.07, ethanol), *ee* >98% [estimated from the 300 MHz $^1H$ NMR spectrum of a sample with the shift reagent $Pr(hfc)_3$ (1.2 mol equiv.) in $CDCl_3$, which resolves the signals due to the aryl methyl groups (typically $\delta_{R,R}$ −3.87 (s, ArMe); $\delta_{S,S}$ −3.75 (s, ArMe)]. The used DHQ-PCB could be recovered (>80% yield) from the combined ethyl acetate extracts by extraction into 1 mol $dm^{-3}$ sulfuric acid, followed by adjustment of the pH to 11 with 2 mol $dm^{-3}$ ammonium hydroxide, and extraction with ether. The DHQ-PCB thus obtained could be reused.

*With DHQ-PCB and methanesulfonamide.*—To a mechanically stirred clear solution of DHQ-PCB (465 mg, 1.0 mmol) and osmium tetroxide (2.5% in *tert*-butyl alcohol; 1.5 $cm^3$, 0.12 mmol) in *tert*-butyl alcohol (250 $cm^3$) was added a clear solution of potassium ferricyanide (49.35 g, 150 mmol) and anhydrous potassium carbonate (20.7 g, 150 mmol) in water (250 $cm^3$) at room temperature. When the yellow solution had become clear it was treated with finely powdered methanesulfonamide (4.75 g, 50 mmol), stirred for 15 min and cooled to 0 °C with vigorous mechanical stirring during cooling to give a fine suspension; this was treated with the finely powdered stilbene **10c** (10.40 g, 50 mmol). The vigorous stirring at 0 °C was continued for 40 h, after which time only a faint trace of the stilbene **10c** was detectable by TLC (elution with petroleum–ethyl acetate 2:1; spots visualised using PMA). The stirred mixture was then treated at 0 °C with finely powdered sodium thiosulfate (50 g), and stirred at 0 °C for a further 1 h, after which the solid had become white and the solution almost colourless. The mixture was filtered, the residue was washed with ethyl acetate and the filtrate was concentrated. The residue was treated with water (25 $cm^3$) and extracted with ethyl acetate (2 × 150 $cm^3$). The combined extracts were washed with 2 mol $dm^{-3}$ potassium hydroxide (100 $cm^3$) and 1 mol $dm^{-3}$ sulfuric acid (50 $cm^3$) (the DHQ-PCB could be recovered from the sulfuric acid solution and reused), and dried. Evaporation and crystallisation of the residue from chloroform–petroleum gave the diol (*S*,*S*)-**6c** (two crops, total 11.08 g, 92%, ee <98%).

*With $(DHQ)_2PHAL$.*[13]—A 250 $cm^3$ round-bottomed flask, equipped with a mechanical stirrer, was charged with *tert*-butyl alcohol (50 $cm^3$), water (50 $cm^3$), and very finely ground AD-mix-α [14.0 g; consisting of potassium ferricyanide (9.8 g, 30 mmol), anhydrous potassium carbonate (4.1 g, 30 mmol), $(DHQ)_2$-PHAL (78 mg, 0.1 mmol) and potassium osmate(VI) dihydrate ($K_2OsO_4 \cdot 2H_2O$) (7.4 mg, 0.02 mmol)]. The mixture was stirred at room temperature for *ca.* 15 min to give two clear phases, to which finely powdered methanesulfonamide (0.95 g, 10 mmol) was added. The mixture was cooled to 0 °C (some solid was precipitated) and treated with the finely powdered stilbene **10c** (2.08 g, 10 mmol) in one portion. The heterogeneous slurry was stirred vigorously at 0 °C for 24 h, the reaction being monitored by TLC [elution with petroleum–ethyl acetate (2:1); visualisation with PMA]. The mixture was then stirred at 0 °C, and treated with finely powdered sodium thiosulfate (9.0 g, 47 mmol). After *ca.* 1 h the solid had become white and the solution almost colourless. The suspension was extracted with ethyl acetate (100 $cm^3$) and, after separation of the layers, the aqueous phase was extracted with more ethyl acetate (3 × 30 $cm^3$). The combined extracts were washed with 2 mol $dm^{-3}$ aq. potassium hydroxide (to remove the methanesulfonamide), dried, and concentrated to give the crude diol **6c** (ee >98%) and ligand. The crude product was purified by chromatography over silica gel, eluting with petroleum–ethyl acetate (2:1) (the ligand is not eluted with this solvent system), followed by crystallisation from chloroform–petroleum, which afforded the (*S*,*S*)-diol **6c** (2.13 g, 88%, ee >98%), mp 109–110 °C.

**(*S*,*S*)-1,2-Bis(2-bromophenyl)ethane-1,2-diol (+)-6d.** To a solution of DHQ-PCB (167 mg, 0.36 mmol) in *tert*-butyl alcohol (30 $cm^3$) and water (30 $cm^3$) at 75 °C was added osmium tetroxide (2.5% in *tert*-butyl alcohol; 0.20 $cm^3$, 0.016 mmol). After 10 min a finely ground mixture of potassium ferricyanide (7.42 g, 22.5 mmol) and anhydrous potassium carbonate (3.11 g, 22.5 mmol) was added to the vigorously stirred solution, followed by the stilbene **10d** (1.50 g, 4.44 mmol). The mixture was stirred at 75 °C for 16 h, cooled to room temperature, and the product isolated as described for (−)-**6c** above. Chromatography (elution with petroleum–ethyl acetate 1:1), yielded the diol (*S*,*S*)-**6d** (1.414 g, 86%), mp 105–107 °C (petroleum–chloroform), spectroscopically identical with (±)-**6d** obtained as above. As described in the literature,[15] two recrystallisations from dichloromethane gave (*S*,*S*)-**6d** (1.02 g, 62%) which was assumed to be homochiral, $[\alpha]_D^{22}$ +38.6 ± 0.5 (*c* 1.0, ethanol); $[\alpha]_D^{23}$ +39.9 (*c* 1.0, EtOH) [lit.,[16] (*R*,*R*)-**6d** can be prepared from **10d** in 94% yield with >99% ee using AD-mix-β]. Estimation of the enantiomeric purity of (*S*,*S*)-**6d** using $^1H$ NMR shifts reagents [$Pr(hfc)_3$, $Yb(hfc)_3$, $Eu(hfc)_3$, $Eu(tfc)_3$, (*R*)-(−)-2,2,2-trifluoro-1-(9-anthryl)ethanol] was unsuccessful. The used DHQ-PCB could be recovered (>80% yield) from the combined ethyl acetate extracts by extraction into 1 mol $dm^{-3}$ sulfuric acid, the solution then being adjusted to pH 11 with 2 mol $dm^{-3}$ ammonium hydroxide and extracted with ether. The DHQ-PCB thus obtained could be reused.

**(*S*,*S*)-1,2-Bis(2-methoxyphenyl)ethane-1,2-diol (−)-6f.** A 100 $cm^3$ flask equipped with a magnetic follower was charged with AD-mix-α (7.00 g), *tert*-butyl alcohol (25 $cm^3$), water (25 $cm^3$) and methanesulfonamide (0.475 g, 5.0 mmol), and the mixture then stirred for 15 min at room temperature to give a clear yellow solution. This was then cooled to 0 °C with vigorous stirring to yield a fine suspension into which the finely powdered of stilbene **10f** (1.200 g, 5.0 mmol) was added. The mixture was stirred vigorously at 0 °C for 7 d, the reaction being monitored by TLC (elution with petroleum–ethyl acetate, 2:1). The reaction was quenched by stirring of the mixture with powdered sodium thiosulfate at 0 °C for 2 h, which produced a white suspension. This was filtered, and the two-phase filtrate was concentrated on a rotary evaporator to give a residue which was purified by column chromatography (elution with petroleum–ethyl acetate, 2:1); this afforded the crude diol (0.610 g, 44%), which was purified by crystallisation from chloroform–petroleum to give (*S*,*S*)-**6f** (0.56 g, 41%), ee >95% [estimated from the 300 MHz $^1H$ NMR spectrum of a sample with the shift reagent $Pr(hfc)_3$ (1.1 mol equiv.) in dry $CDCl_3$, which resolves the signals due to the methoxy groups], $[\alpha]_D^{23}$ −10.6 ± 1.8 (*c* 1.13, acetone), mp 69–70 °C {lit.,[25] mp 71–72 °C, $[\alpha]_D^{25}$ −8.2 (MeOH), e.e. 88%}. The chromatography also gave a portion of unchanged stilbene **10f** (0.65 g, 54%).

**(*R*,*R*)-1,4-Diphenylbutane-2,3-diol (+)-6h.** A 25 $cm^3$ round-bottomed flask equipped with a magnetic follower was charged with *tert*-butyl alcohol (5 $cm^3$), water (5 $cm^3$), a finely ground mixture of $K_3Fe(CN)_6$ (0.98 g, 3.0 mmol), $K_2CO_3$ (410 mg, 3.0 mmol) and $(DHQD)_2$-PHAL (7.8 mg, 0.01 mmol) and $OsO_4$ (2.5%, w/w, in *tert*-butyl alcohol; 25.3 mg, 0.0025 mmol). After being stirred for a few minutes at room temperature the mixture was treated with powdered methanesulfonamide (95 mg, 1.0 mmol) and then cooled to 0 °C and treated with the powdered *E*-alkene **10h**[38] (208 mg, 1.00 mmol) in one portion. The slurry was stirred vigorously at 0 °C, and the progress of the reaction monitored by TLC (elution with petroleum–ethyl acetate, 2:1). After 2 days the mixture was treated with powdered $Na_2S_2O_3$ (0.90 g, 5.7 mmol) and stirred at 0 °C for a further 1 h. Ethyl acetate (100 $cm^3$) was added to the mixture after which the phases were separated, and the aqueous layer was extracted with more ethyl acetate (3 × 10 $cm^3$). The combined organic extract was washed with 2 mol $dm^{-3}$ NaOH, dried and concentrated to give the crude product, which was purified by chromatography, eluting with petroleum–ethyl acetate (2:1) to give the *title compound* (*R,R*)-**6h** (203 mg, 84%, ee not determined), $[\alpha]_D^{20}$ +6.0 (*c* 1.33, acetone) (Found: M + $NH_4$, 260.1649. $C_{16}H_{22}NO_2$ requires 260.1650); δ 7.32–7.19 (10 H, m, ArH), 3.8–3.7 (2 H, m, 2 × C*H*OH), 2.95–2.79 (4 H, 2 × overlapping dd, 2 × $CH_2$) and 2.0 (2 H, br s, 2 × OH); *m/z* 260 (M + $NH_4$, 100%).

**(*R,R*)-1,2-Bis(2-trifluoromethylphenyl)ethane-1,2-diol (−)-6i.** A 100 $cm^3$ round-bottomed flask equipped with a magnetic follower was charged with *tert*-butyl alcohol (16 $cm^3$), water (16 $cm^3$), a finely ground mixture of $K_3Fe(CN)_6$ (3.12 g, 9.47 mmol), $K_2CO_3$ (1.31 g, 9.48 mmol) and $(DHQD)_2$-PHAL (24.6 mg, 0.032 mmol), and $OsO_4$ (2.5%, w/w, in *tert*-butyl alcohol, 63.2 mg, 0.0062 mmol). After the mixture had been stirred for *ca.* 15 min at room temperature it was treated with powdered methanesulfonamide (269 mg, 2.83 mmol) cooled to 4 °C and treated with the powdered stilbene **10i** (1.00 g, 3.16 mmol) in one portion. The slurry was stirred vigorously at 24 °C, and the progress of the reaction monitored by TLC (elution with petroleum–ethyl acetate, 2:1). After 4 days the mixture was treated with powdered $Na_2S_2O_3$ (1.9 g, 12 mmol) and stirred at 24 °C for a further 1 h. Ethyl acetate (100 $cm^3$) was added to the mixture after which the phases were separated, and the aqueous layer was extracted with more ethyl acetate (3 × 25 $cm^3$). The combined organic extracts were washed with 2 mol $dm^{-3}$ aq. NaOH, dried and concentrated to give the crude product, which was purified by chromatography, eluting with petroleum–ethyl acetate (2:1) to give the *title compound* (*R,R*)-**6i** (44.2 mg, 4%, ee not determined), $[\alpha]_D^{20}$ −17.4 (*c* 0.65, acetone), mp 132–135 °C (M + $NH_4$, 368.1080. $C_{16}H_{16}F_6NO_2$ requires 368.1085); δ 7.90 (2 H, d, *J* 8.1, 3-H, 3′-H), 7.59–7.54 (4 H, m, 5-H, 6-H, 5′-H, 6′-H), 7.37 (2 H, t, *J ca.* 7.5, 4-H, 4′-H), 5.36 (2 H, s, 2 × C*H*OH) and 2.94 (2 H, s, 2 × OH); *m/z* 368 (M + $NH_4$, 100%).

**Preparation of bromoacetaldehyde acetals (*cf.* Table 4)**

***trans*-2-Bromomethyl-4,5-diphenyl-1,3-dioxolane (±)-7a.** A mixture of hydrobenzoin (±)-**6a** (6.42 g, 30 mmol) and bromoacetaldehyde diethyl acetal (5.94 g, 30.1 mmol) was heated to 130 °C for 3 h, after which TLC indicated that the reaction had gone to completion. Concentration of the mixture gave a pale yellow solid which was purified by filtration through flash silica, eluting with light petroleum (bp 40–60 °C)–ethyl acetate (20:1). Evaporation of the eluate, followed by crystallisation of the residue from ethyl acetate–light petroleum (bp 40–60 °C) gave the *title compound* (±)-**7a** (8.89 g, 93%) as colourless crystals, mp 54 °C (Found: C, 60.5; H, 4.7; Br, 24.8. $C_{16}H_{15}BrO_2$ requires C, 60.21; H, 4.74; Br, 25.03%) (Found: M + $NH_4$, 336.0599. $C_{16}H_{19}BrNO_2$ requires 336.0600); $\nu_{max}$(film)/$cm^{-1}$ 1144, 1011, 761 and 698; δ 3.67 (2 H, d, *J* 3.5, $CH_2Br$), 4.81 (1 H, d, *J* 8.2, 4-H or 5-H), 4.88 (1 H, d, *J* 8.2, 5-H or 4-H), 5.69 (1 H, t, *J* 3.5, 2-H), 7.19–7.23 (2 H, m, ArH) and 7.29–7.35 (8 H, m, ArH); *m/z* 338 [M + $NH_4$ ($^{81}$Br), 100], 336 [M + $NH_4$ ($^{81}$Br), 93], 214 (20), 133 (50) and 106 (20); $R_f$ 0.72.

**(*S,S*)-2-Bromomethyl-4,5-diphenyl-1,3-dioxolane (−)-7a.** The method described above was repeated using (*S,S*)-hydrobenzoin (−)-**6a**[13] (1.07 g, 5.0 mmol) and bromoacetaldehyde diethyl acetal (0.99 g, 5.0 mmol) with the mixture being heated to 135–150 °C for 3 h. Isolation as before afforded the title compound (*S,S*)-**7a** (1.49 g, 93%) as a white solid. Crystallisation from dichloromethane gave colourless crystals (877 mg, 55%), mp 57 °C, $[\alpha]_D^{25}$ −54.1 (*c* 1.11, $CH_2Cl_2$), identical in all other respects with the racemic compound.

***trans*-2-Bromomethyl-4,5-bis(2,4,6-trimethylphenyl)-1,3-dioxolane (±)-7b.** Toluene-*p*-sulfonic acid hydrate (510 mg, 2.7 mmol) was added to a stirred solution of the diol (±)-**6b** (657 mg, 2.2 mmol) in bromoacetaldehyde diethyl acetal (5 $cm^3$) at 85 °C. After 0.5 h the mixture was cooled and treated with an excess of saturated aqueous sodium hydrogen carbonate (**Caution**: $CO_2$ evolution). The organic phase was extracted with ether, and the extract dried and concentrated under reduced pressure. The residue was crystallised from petroleum (bp 40–60 °C) at −20 °C, to give (±)-**7b** (350 mg); flash chromatography of the mother liquors (elution with dichloromethane–petroleum, 3:10) gave a further quantity (277 mg) of the *title compound* (±)-**7b** (total 627 mg, 71%), mp 124–125 °C (hexane) (Found: M + $NH_4$, 420.1543. $C_{22}H_{31}BrNO_2$ requires 420.1539); $\nu_{max}$(Nujol)/$cm^{-1}$ 1615, 1135, 1045, 1025, 1000, 855 and 760; δ 2.09 (12 H, s, 2,6-ArMe), 2.18 (6 H, s, 4-ArMe), 3.60 (2 H, d, *J* 4.7, $BrCH_2$), 5.52 (1 H, d, *J* 9.8, OCHAr), 5.58 (1 H, d, *J* 9.8, OCHAr), 5.70 (1 H, t, *J* 4.7, $BrCH_2CH$) and 6.71 (4 H, s, ArH); *m/z* (peaks > 10%) 422 [M + $NH_4^+$ ($^{81}$Br), 56%], 420 [M + $NH_4^+$ ($^{79}$Br), 47]; $R_f$ 0.50 [dichloromethane–petroleum, 3:10; visualised with $Ce(SO_4)_2$].

***trans*-2-Bromomethyl-4,5-bis(2-methylphenyl)-1,3-dioxolane (±)-7c.** A procedure similar to that described above for the preparation of (±)-**7b** was adopted with the diol (±)-**2b** (160 mg, 0.66 mmol), bromoacetaldehyde diethyl acetal (2 $cm^3$), and toluene-*p*-sulfonic acid hydrate (100 mg, 0.5 mmol) heated at 80 °C for 0.5 h. Work-up as described, followed by flash chromatography, eluting with petroleum–ethyl acetate (10:1) gave the *title compound* (±)-**7c** (197 mg, 86%), mp 42–43 °C (hexane, −38 °C) (Found: C, 62.4; H, 5.4. $C_{18}H_{19}BrO_2$ requires C, 62.26; H, 5.52%) (Found: M + $NH_4$, 364.0918. $C_{18}H_{23}BrNO_2$ requires 364.0913); $\nu_{max}$(Nujol)/$cm^{-1}$ 1145, 1010, 855 and 765 $cm^{-1}$; δ 1.66 (6 H, s, 2 × ArMe), 3.70 (2 H, d, *J* 3.5, $BrCH_2$), 5.09 (1 H, d, *J* 8.4, OCHAr), 5.12 (1 H, d, *J* 8.4, OCHAr), 5.74 (1 H, t, *J* 3.5, $BrCH_2CH$), 6.99 (2 H, br d, *J ca.* 7.5 Hz, 3,3′-ArH), 7.13–7.30 (4 H, m, 4,4′,5,5′-ArH), 7.56 (1 H, d, *J* 7.5, 6-ArH) and 7.75 (1 H, d, *J* 7.5, 6′-ArH); *m/z* 366 [M + $NH_4^+$ ($^{81}$Br), 100%], 364 [M + $NH_4^+$ ($^{79}$Br), 96] and 147 (81).

**(*S,S*)-2-Bromomethyl-4,5-bis(2-methylphenyl)-1,3-dioxolane (−)-7c.** A 250 $cm^3$ flask equipped with a magnetic follower was charged with the diol (*S,S*)-**6c** (10.40 g, 43 mmol), bromoacetaldehyde diethyl acetal (60 $cm^3$, 78.6 g), and toluene-*p*-sulfonic acid hydrate (10 g, 53 mmol), and the mixture heated at 80–90 °C (sand-bath temperature) for 2 h with vigorous stirring. The flask was then allowed to cool after which it was treated with ice (50 g) and ether (50 $cm^3$), followed cautiously by 2 mol $dm^{-3}$ aqueous sodium carbonate (to pH 11). The two phases were separated, and the aqueous layer was extracted with ether (3 × 50 $cm^3$). The combined ethereal phases were dried and subjected to rotary evaporation followed by distillation *in vacuo* (0.03–0.08 mmHg) to recover some of the excess of bromoacetaldehyde diethyl acetal (52.5 g). The residue was dissolved in a mixture of petroleum–ethyl acetate (10:1 v/v;

total 50 $cm^3$) and filtered through a glass column containing silica gel (10 g), the column being washed with more petroleum–ethyl acetate (10:1 v/v; 100 $cm^3$). After removal of the solvents from the combined filtrates the residue was crystallised from hexane (20 $cm^3$) at −35 °C to give the pure crystalline bromo acetal (−)-**7c** (10.87 g, 73%). The mother liquid was concentrated to recover an additional portion of bromoacetaldehyde diethyl acetal (5.2 g; total 57.7 g, 82% of the theoretical excess) and the residue was recrystallised as before to give a second crop (3.05 g) of crystalline bromo acetal (−)-**7c** (total 13.92 g, 93%), mp 59–61 °C (hexane, −35 °C); $[\alpha]_D^{23}$ −34.5 ± 0.5 (*c* 1.42, ethanol).

***trans*-4,5-Bis(2-bromophenyl)-2-bromomethyl-1,3-dioxolane (±)-7d.** A procedure similar to that described above for the preparation of (±)-**7b** was adopted with the diol (±)-**6d** (536 mg, 1.44 mmol), bromoacetaldehyde diethyl acetal (10 $cm^3$), and toluene-*p*-sulfonic acid hydrate (365 mg, 1.9 mmol) heated at 100 °C for 3.5 h. Work-up as described, followed by flash chromatography, eluting with petroleum–dichloromethane (1:1) [TLC detection by $Ce(SO_4)_2$], gave the *title compound* (±)-**7d** (551 mg, 80%) as an oil (Found: M + $NH_4$, 491.8816. $C_{16}H_{17}Br_3NO_2$ requires 491.8811); $\nu_{max}$(neat)/$cm^{-1}$ 1145, 1015 and 760; δ 3.69 (2 H, d, *J* 3.4, $BrCH_2$), 5.33 (1 H, d, *J* 8.0, OCHAr), 5.38 (1 H, d, *J* 8.0, OCHAr), 5.74 (1 H, t, *J* 3.4, $BrCH_2CH$), 7.1–7.2 (2 H, m, 4,4′-ArH), 7.3–7.45 (4 H, m, 3,3′,5,5′-ArH), 7.60 (1 H, dd, *J* 1.6, 7.8, 6-ArH) and 7.84 (1 H, dd, *J* 1.6, 7.8, 6′-ArH); *m/z* 498 (30%), 496 [M + $NH_4^+$ ($^{81}Br_2$ + $^{79}Br$), 95], 494 [M + $NH_4^+$ ($^{81}Br$ + $^{79}Br_2$), 100], 492 (30), 319 (22) and 317 (21).

**(*S,S*)-4,5-Bis(2-bromophenyl)-2-bromomethyl-1,3-dioxolane (−)-7d.** A procedure similar to that described above for the preparation of (±)-**7d** was adopted with the diol (*S,S*)-**6d** (205 mg, 0.55 mmol), bromoacetaldehyde diethyl acetal (3 $cm^3$), and toluene-*p*-sulfonic acid hydrate (222 mg, 1.2 mmol) heated at 100 °C for 4 h. Isolation as before gave the title compound (*S,S*)-**7d** (211 mg, 80%) as an oil; $[\alpha]_D^{20}$ −11.3 (*c* 6.7, acetone).

***trans*-2-Bromomethyl-4,5-bis(1-naphthyl)-1,3-dioxolane (±)-7e.** A procedure similar to that described above for the preparation of (±)-**7b** was adopted with the diol (±)-**6e** (224.5 mg, 0.71 mmol), bromoacetaldehyde diethyl acetal (3 $cm^3$) and toluene-*p*-sulfonic acid hydrate (150 mg, 0.8 mmol) heated at 70 °C for 3 h. Work-up as described, followed by flash chromatography, eluting with petroleum–ethyl acetate (2:1) [TLC detection by $Ce(SO_4)_2$], gave the *title compound* (±)-**7e** (272 mg, 91%) as an oil (Found: M + $NH_4$, 436.0911. $C_{24}H_{23}BrNO_2$ requires 436.0913); $\nu_{max}$(neat)/$cm^{-1}$ 1145, 1020, 805, 780 and 740; δ 3.81 (2 H, d, *J* 3.6, $BrCH_2$), 5.79 (1 H, d, *J* 7.5, OCHAr), 5.89 (1 H, t, *J* 3.6, $BrCH_2CH$), 5.97 (1 H, d, *J* 7.5, OCHAr), 6.94 (1 H, apparent t, *J ca.* 8, 3-ArH), 7.04 (1 H, apparent t, *J ca.* 8, 3′-ArH), 7.17 (1 H, d, *J* 8.5, 2-ArH), 7.25–7.32 (2 H, m, 2′,4-ArH), 7.42–7.50 (3 H, m, ArH) and 7.73–7.84 (6 H, m, ArH); *m/z* 438 [M + $NH_4^+$ ($^{81}Br$), 30%], 436 [M + $NH_4^+$ ($^{79}Br$), 25] and 183 (100).

***trans*-2-Bromomethyl-4,5-bis(2-methoxyphenyl)-1,3-dioxolane (±)-7f.** A procedure similar to that described above for the preparation of (±)-**7b** was adopted with the diol (±)-**6f** (293 mg, 1.07 mmol), bromoacetaldehyde diethyl acetal (3 $cm^3$) and toluene-*p*-sulfonic acid hydrate (230 mg, 1.2 mmol) heated at 80 °C for 0.5 h. Work-up as described, followed by triple flash chromatography, eluting with (i) dichloromethane–pentane–ethyl acetate (10:10:1), (ii) toluene, and (iii) pentane–ether (5:4) [TLC detection by $Ce(SO_4)_2$], gave the *title compound* (±)-**7f** (158 mg, 39%) as an oil (Found: M + $NH_4$, 396.0809. $C_{18}H_{23}BrNO_4$ requires 396.0811); δ 3.46 (3 H, s, ArMe), 3.52 (3 H, s, ArMe), 3.62 (2 H, d, *J* 3.9, $BrCH_2$), 5.28 (1 H, d, *J* 7.5, OCHAr), 5.44 (1 H, d, *J* 7.5, OCHAr), 5.63 (1 H, t, *J* 3.9, $BrCH_2CH$), 6.78 (2 H, apparent t, *J* 8, 3,3′-ArH), 6.9–7.0 (2 H, m, 5,5′-H), 7.21–7.27 (2 H, m, 4,4′-ArH), 7.42 (1 H, dd, *J* 1.6, 7.6, 6-ArH) and 7.63 (1 H, dd, *J* 1.6, 7.6, 6′-ArH); *m/z* 398 [M + $NH_4^+$ ($^{81}Br$), 100%], 396 [M + $NH_4^+$ ($^{79}Br$), 82], 274 (100), 257 (30) and 163 (25).

**(*S,S*)-2-Bromomethyl-4,5-bis(2-methoxyphenyl)-1,3-dioxolane (+)-7f.** A procedure similar to that described above for the preparation of (±)-**7f** was adopted with a stirred solution of the diol (*S,S*)-**6f** (710 mg, 2.59 mmol) in bromoacetaldehyde diethyl acetal (15 $cm^3$) heated with toluene-*p*-sulfonic acid hydrate (0.54 g) at 95 °C. After 2 h the mixture was treated with ice, followed by ether (20 $cm^3$) and sodium hydrogen carbonate (*ca.* 0.5 g) (**CAUTION**: $CO_2$ evolution). The organic phase was then separated, dried, and concentrated under reduced pressure (eventually at 0.1–0.01 mmHg). The residue was purified by chromatography twice, eluting firstly with petroleum–dichloromethane–ethyl acetate (10:1:1) and secondly with toluene, to give the title compound (*S,S*)-**7f** (525 mg, 53%) as an oil which was dried at 220 °C/0.01 mmHg for 10 min; $[\alpha]_D^{22}$ + 16 ± 1 (*c* 2.03, acetone).

***trans*-2-Bromomethyl-4,5-di-*tert*-butyl-1,3-dioxolane (±)-7g.** A procedure similar to that described above for the preparation of (±)-**7b** was adopted with the diol (±)-**6g** (340 mg, 1.95 mmol), bromoacetaldehyde diethyl acetal (3 $cm^3$), and toluene-*p*-sulfonic acid hydrate (250 mg, 1.3 mmol) heated at 100 °C for 0.5 h. Work-up as described, followed by flash chromatography, eluting with petroleum–ethyl acetate (10:3), gave the *title compound* (±)-**7g** (355 mg, 65%) as an oil [Found: M + $NH_4$, 296.1234. $C_{12}H_{27}BrNO_2$ requires 296.1226]; $\nu_{max}$(neat)/$cm^{-1}$ 1145, 1045, 1025, 990 and 680; δ 0.89 (9 H, s, $CMe_3$), 0.93 (9 H, s, $CMe_3$), 3.29 (2 H, d, *J* 4.8, $BrCH_2$), 3.69 (1 H, d, *J* 3.5, $OCHBu^t$), 3.78 (1 H, d, *J* 3.5, $OCHBu^t$) and 5.33 (1 H, t, *J* 4.8, $BrCH_2CH$); *m/z* (peaks > 30%) 298 [M + $NH_4^+$ ($^{81}Br$), 34%], 296 [M + $NH_4^+$ ($^{79}Br$), 34], 185 (100), 113 (50) and 99 (85).

***trans*-2-Bromomethyl-4,5-bis(phenylmethyl)-1,3-dioxolane (*R,R*)-7h.** A procedure similar to that described above for the preparation of (±)-**7b** was adopted with the diol (*R,R*)-**6h** (26.7 mg, 0.11 mmol), bromoacetaldehyde diethyl acetal (1 $cm^3$), and toluene-*p*-sulfonic acid hydrate (25 mg, 0.13 mmol) heated at 120 °C (bath temperature) for 2 h. After neutralisation, extraction and evaporation as described, the excess of bromoacetaldehyde diethyl acetal was removed under reduced pressure (0.1 mmHg) and the residue purified by flash chromatography, eluting with petroleum–ethyl acetate (5:1), then petroleum–dichloromethane (5:1) and finally by petroleum–ether (5:1), to give the *title compound* (*R,R*)-**7h** (31.7 mg, 83%) as an unstable oil [Found: M + $NH_4$, 364.0914. $C_{18}H_{23}BrNO_2$ requires 364.0913]; δ 2.58–2.68 (2 H, m, 2 × CHAr), 2.81–2.89 (2 H, m, 2 × CHAr), 3.34 (2 H, d, *J* 3.9, $BrCH_2$), 3.95–4.1 (2 H, m, OCHAr), 5.20 (1 H, t, *J* 3.9 Hz, $BrCH_2CH$) and 7.1–7.35 (10 H, m, ArH); *m/z* (peaks > 10%) 366 [M + $NH_4^+$ ($^{81}Br$), 100%] and 364 [M + $NH_4^+$ ($^{79}Br$), 82].

***trans*-2-Bromomethyl-4,5-dicyclohexyl-1,3-dioxolane (*R,R*)-7j.** A procedure similar to that described above for the preparation of (±)-**7b** was adopted with the diol (−)-**6j**[39] (174 mg, 0.77 mmol), bromoacetaldehyde diethyl acetal (4 $cm^3$), and toluene-*p*-sulfonic acid hydrate (200 mg, 1.1 mmol) heated at 80 °C for 0.5 h. Work-up as described, followed by flash chromatography, eluting with petroleum–ethyl acetate (10:1), gave the *title compound* (*R,R*)-**7j** (221 mg, 87%) as an oil (Found: M + $NH_4$, 348.1537. $C_{16}H_{31}BrNO_2$ requires 348.1539); δ 0.89 (9 H, s, $CMe_3$), 0.9–1.9 (22 H, s, 2 × c-$C_6H_{11}$), 3.34 (2 H, d, *J* 4.0, $BrCH_2$), 3.66 (1 H, d, *J* 3.5, OC*H*R), 3.68 (1 H, d, *J* 3.5, OC*H*R) and 5.11 (1 H, t, *J* 4.0, $BrCH_2CH$); *m/z* 350 [M + $NH_4^+$ ($^{81}Br$), 98%], 348 [M + $NH_4^+$ ($^{79}Br$), 100], 286 (21) and 263 (28).

**Dehydrobrominations (*cf.* Table 4)**[14]

***trans*-2-Methylene-4,5-diphenyl-1,3-dioxolane (±)-1a.** To *trans*-2-bromomethyl-4,5-diphenyl-1,3-dioxolane (±)-**7a** (319 mg, 1.0 mmol) in THF (10 $cm^3$) under argon was added a solution of potassium *tert*-butoxide (337 mg, 3.0 mmol) in THF (5 $cm^3$). Aliquat 336® (404 mg, 1.0 mmol) in THF (25 $cm^3$) was added to the mixture, which was then stirred in ice for 10 min and finally placed in a freezer (−25 °C) overnight. A yellow solution was produced which was cannulated under argon into another flask, and evaporated to remove the THF. The residue was diluted with ether and the solution was passed through an alumina column using more ether (100 $cm^3$). Evaporation of the eluate gave the title compound as a colourless oil (215 mg, 90%); δ 3.45 (2 H, s, $CH_2$), 5.08 (2 H, s, 4-H and 5-H) and 7.05–7.3 (10 H, m, ArH). Later analysis by NMR indicated that the ketene acetal (±)-**1a** and the decomposition product **16** were present in a ratio of 2:1. The ketene acetal appeared to be stable for 4–5 h in the freezer, but decomposition then became significant and was greatly accelerated by moisture. NMR signals attributed to the decomposition product: δ 2.11 (3 H, s, COMe), 2.54 (1 H, d, *J* 3.5, OH), 4.90 (2 H, dd, *J* 3.5, 7.4, C*H*OH), 5.83 (1 H, d, *J* 7.4, C*H*OAc) and 7.05–7.25 (10 H, m, ArH). Authentic (±)-**16**[40] had mp 86 °C; δ 2.11 (3 H, s, COMe), 2.59 (1 H, br s, OH), 4.90 (2 H, d, *J* 7.4, C*H*OH), 5.83 (1 H, d, *J* 7.4, C*H*OAc) and 7.05–7.25 (10 H, m, ArH); *m/z* 274 (M + $NH_4$, 56%) and 214 (100) (Found: M + $NH_4$, 274.1439. $C_{16}H_{20}NO_3$ requires 274.1443).

***trans*-2-Methylene-4,5-bis(2,4,6-trimethylphenyl)-1,3-dioxolane (±)-1b.** A stirred solution of the bromo acetal (±)-**7b** (14.5 mg, 0.036 mmol) in dry THF (1.0 $cm^3$) at 0 °C under argon was treated first with solid potassium *tert*-butoxide (12.5 mg, 0.112 mmol) and then, after 3 min, with a solution of Aliquat 336® (16 mg, 0.04 mmol) in THF (1 $cm^3$). After 3 h at 0 °C the reaction was complete, and the mixture was diluted with ether (4 $cm^3$) and filtered through a small column containing basic alumina (*ca.* 0.7 g) to remove the catalyst and the excess of base. The filtrate was evaporated and the residue, containing (±)-**1b** (*ca.* 80%), used directly in the next step. The dioxolane **1b** (contaminated with methyldioctylamine) had δ 2.0–2.2 (12 H, br, 4 × ArMe), 2.22 (6 H, s, 2 × ArMe), 3.36 (2 H, s, C=$CH_2$), 5.75 (2 H, s, C*H*Ar) and 6.76 (4 H, s, ArH); *m/z* (peaks > 10%) 323 (M + $H^+$).

***trans*-4,5-Bis(2-methylphenyl)-2-methylene-1,3-dioxolane (±)-1c.** A stirred solution of the bromo acetal (±)-**7c** (20.0 mg, 0.058 mmol) in dry THF (2 $cm^3$) at −15 °C under argon was treated first with solid potassium *tert*-butoxide (24 mg, 0.214 mmol) and then, after 3 min, with a solution of Aliquat 336® (16 mg, 0.04 mmol) in THF (1 $cm^3$). After 15 h at −15 °C the reaction was complete, and the mixture was diluted with THF (4 $cm^3$) and filtered through a small column containing basic alumina (*ca.* 0.7 g) to remove the catalyst and the excess of base. The filtrate was evaporated and the residue, containing (±)-**1c** (*ca.* 90%), used directly in the next step. The dioxolane **1c** had δ 1.82 (6 H, s, 2 × ArMe), 3.44 (2 H, s, C=$CH_2$), 5.35 (2 H, s, C*H*Ar), 7.06 (2 H, dd, *J ca.* 1, 7.5, 3,3′-ArH), 7.18–7.30 (4 H, m, 4,4′,5,5′-ArH), 7.54 (2 H, dd, *J ca.* 1.5, 8, 6,6′-ArH); *m/z* (peaks > 10%) 267 (M + H).

***trans*-4,5-Bis(2-bromophenyl)-2-methylene-1,3-dioxolane (±)-1d.** A stirred solution of the bromo acetal (±)-**7d** (129 mg, 0.27 mmol) in dry THF (6 $cm^3$) at 0 °C under argon was treated first with solid potassium *tert*-butoxide (137 mg, 1.22 mmol) and then, after 3 min, with a solution of Aliquat 336® (96 mg, 0.24 mmol) in THF (6 $cm^3$). After 1 h at 0 °C the reaction was complete, and the mixture was diluted with THF (8 $cm^3$) and filtered through a small column containing basic alumina (*ca.* 1.5 g) to remove the catalyst and the excess of base. The filtrate was evaporated and the residue, containing (±)-**1d** (*ca.* 90%), used directly in the next step. The dioxolane **1d** had δ 3.49 (2 H, s, C=$CH_2$), 5.66 (2 H, s, C*H*Ar) and 7.1–7.7 (8 H, m, ArH).

***trans*-2-Methylene-4,5-di-1-naphthyl-1,3-dioxolane (±)-1e.** A stirred solution of the bromo acetal (±)-**7e** (37.6 mg, 0.090 mmol) in dry THF (2 $cm^3$) at −15 °C under argon was treated first with solid potassium *tert*-butoxide (30 mg, 0.27 mmol) and, after 3 min, with a solution of Aliquat 336® (32 mg, 0.079 mmol) in THF (2 $cm^3$). After 16 h at −28 °C the reaction was complete, and the mixture was diluted with THF (8 $cm^3$) and filtered through a small column containing basic alumina (*ca.* 0.7 g) to remove the catalyst and the excess of base. The filtrate was evaporated and the residue, containing (±)-**1e** (*ca.* 90%), used directly in the next step. The dioxolane **1e** had δ 3.60 (2 H, s, C=$CH_2$), 6.12 (2 H, s, C*H*Ar) and 7.16–8.10 (14 H, m, ArH).

**Heterodiene cycloadditions (*cf.* Table 5)**

**4,4a-Dihydro-4′,5′-diphenylspiro[3*H*,10*H*-pyrano[4,3-*b*][1]-benzopyran-3,2′-[1,3]dioxolan]-10-ones 3a and 4a.** To a solution of (±)-**7a** (319 mg, 1.0 mmol) in THF (3 $cm^3$) under Ar was added a solution of potassium *tert*-butoxide in THF (1.0 mol $dm^{-3}$; 1.0 $cm^3$, 1.0 mmol), and the mixture was stirred at room temperature for 1 h. After this the mixture was cooled to −78 °C, treated with a solution of the chromone **2** (139 mg, 0.8 mmol) in THF (3 $cm^3$) and stirred at −78 °C for 3 h; it was then allowed to reach room temperature overnight. After evaporation of the reaction mixture the residue was diluted with dichloromethane, filtered, and the filtrate evaporated. Analysis by NMR spectroscopy indicated the presence of the cycloadducts **3a** and **4a** (ratio *ca.* 7:3; de 40%). The crude product was purified by flash chromatography over Florisil®, eluting with petroleum (bp 40–60 °C)–ethyl acetate (10:1), to afford the mixed cycloadducts (total 201 mg, 61%) as a pale yellow solid. The major product **3a** crystallised in pure form from fractions of the column eluate. HPLC separation of the two cycloadducts was attempted using a Zorbax silica column (21 × 250 mm), with hexane–ethyl acetate (19:1) as the eluent. A sample (50 mg) was pre-dissolved in hexane–ethyl acetate (1:1), and passed through the column to give **3a** (4 mg) and **4a** (5 mg). The samples were freeze-dried from dioxane. The *title compound* (±)-**3a** had mp 168 °C (petroleum–ethyl acetate) (Found: M + H, 413.1385. $C_{26}H_{21}O_5$ requires 413.1389); $\nu_{max}/cm^{-1}$ 1674 and 1610; δ 2.71 (1 H, dd, *J* 10.8, 12.5, 4β-H), 2.85 (1 H, dd, *J* 6.7, 12.5, 4α-H), 5.02 (1 H, d, *J* 8.8, C*H*Ph), 5.35 (1 H, d, *J* 8.8, C*H*Ph), 5.38 (1 H, partially obscured ddd, *J* 1.5, 6.7, 10.8, 4a-H), 6.97 (1 H, dd, *J ca.* 1, 8.3, 6-H), 7.06 (1 H, ddd, *J ca.* 1, 7.8, 8.1, 8-H), 7.2–7.5 (11 H, m, 7-H and 2 × Ph), 7.69 (1 H, d, *J* 1.7, 1-H) and 7.96 (1 H, dd, *J* 1.7, 7.8, 9-H); *m/z* (peaks ⩾10%) 413 (M + H, 10%), 239 (100), 192 (30) and 175 (23). The *title compound* (±)-**4a** had mp 148 °C (Found: M + H, 413.1382. $C_{26}H_{21}O_5$ requires 413.1389); $\nu_{max}/cm^{-1}$ 1674 and 1610; δ(200 MHz) 2.72 (1 H, dd, *J* 10.9, 12.7, 4β-H), 2.88 (1 H, dd, *J* 6.7, 12.7, 4α-H), 5.03 (1 H, d, *J* 8.9, C*H*Ph), 5.19 (1 H, d, *J* 8.9, C*H*Ph), 5.42 (1 H, ddd, *J* 1.6, 6.7, 10.9, 4a-H), 6.98 (1 H, d, *J* 8.3, 6-H), 7.06 (1 H, overlapping ddd, *J ca.* 1, 7, 8, 8-H), 7.2–7.5 (11 H, m, 7-H and 2 × Ph), 7.64 (1 H, d, *J* 1.6, 1-H) and 7.96 (1 H, dd, *J* 1.7, 7.8, 9-H); *m/z* (peaks ⩾10%) 413 (M + H, 11%), 239 (100), 192 (58) and 175 (60). The chromatography also gave the chromone **2** (5–10%) and the acetate **16**.

*Repeat of the reaction.* To a solution of (*S,S*)-**7a** (120 mg, 0.38 mmol) in THF (2 $cm^3$) under nitrogen was added a solution of potassium *tert*-butoxide in THF (1.0 mol $dm^{-3}$; 0.4 $cm^3$, 0.4 mmol), and the mixture was stirred at room temperature for 1 h. It was then cooled to −78 °C and treated with a solution of the chromone **2** (65 mg, 0.37 mmol) in THF (2 $cm^3$). The reaction mixture was stirred at −78 °C for 4 h, allowed to reach room temperature overnight and then evaporated. The residue was then diluted with dichloromethane, filtered, and the filtrate evaporated. Analysis of the residue by NMR spectroscopy indicated the presence of the cycloadducts **3a** and **4a** (ratio *ca.* 7:3; de 40%). The crude product was purified by flash chromatography over silica gel, eluting with petroleum (bp 40–60 °C)–ethyl acetate (10:1), to afford the mixed cycloadducts (total 70 mg, 45%) as a colourless solid. The stereochemistry of these products was assigned as (4a*R*,4′*S*,5′*S*)-**3a** and (4a*S*,4′*S*,5′*S*)-**4a** on the basis of experiments carried out on the 7:3 mixture (*vide infra*).

**4′,5′-Bis(2,4,6-trimethylphenyl)-4,4a-dihydrospiro[3*H*,10*H*-pyrano[4,3-*b*][1]benzopyran-3,2′-[1,3]dioxolan]-10-ones (±)-3b and (±)-4b.** Into a solution of (±)-**1b** [prepared as described above from the bromo acetal (±)-**7b** (14.0 mg, 0.035 mmol)] in THF (2 $cm^3$) at −28 °C under Ar was slowly added the powdered chromone **2** (4.0 mg, 0.023 mmol), and the mixture was stirred at −28 °C for 40 h. After evaporation of the mixture the solid residue was chromatographed, eluting with petroleum–ethyl acetate (4:1) containing 2% v/v triethylamine, to give the mixed ortholactones (±)-**3b** and (±)-**4b** (total 6.2 mg, 54%, ratio 8.2:1, de 78%). The major isomer (±)-**3b** had mp 178–180 °C (decomp.) (chloroform–petroleum) [Found: M + H (FAB), 497.2336. $C_{32}H_{33}O_5$ requires 497.2328]; $\nu_{max}$(Nujol)/$cm^{-1}$ 1675 and 1610; $\delta$ 7.95 (1 H, dd, *J* 1.7, 7.8, 9-H), 7.64 (1 H, d, *J* 1.6, 1-H), 7.50–7.40 (1 H, m, 7-H), 7.04 (1 H, ddd, *J* 1, 7.8, 8.1, 8-H), 6.94 (1 H, dd, *J ca.* 1, 8.3, 6-H), 6.74 (2 H, s, ArH), 6.71 (2 H, s, ArH), 6.03 (1 H, d, *J* 10.5, 4′-H or 5′-H), 5.78 (1 H, d, *J* 10.5, 5′-H or 4′-H), 5.37 (1 H, ddd, *J* 1.6, 6.5, 10.7, 4a-H), 2.87 (1 H, dd, *J* 6.5, 12.5, 4-$H_{eq}$), 2.67 (1 H, dd, *J* 10.7, 12.5, 4-$H_{ax}$) and 2.2–2.1 (total 18 H, 3 × s, 6 × ArMe); *m/z* (FAB; peaks > 10%) 497 (M + H, 18%), 322 (11), 281 (30), 264 (32), 263 (32), 251 (31), 234 (14), 217 (19), 175 (**2** + H, 100), 147 (91) and 133 (43).

The minor isomer **4b** was distinguished by signals at $\delta$ 7.61 (1 H, d, *J* 1.5, 1-H) and 5.90 (1 H, d, *J* 10.6, 4′-H or 5′-H).

**4′,5′-Bis(2-methylphenyl)-4,4a-dihydrospiro[3*H*,10*H*-pyrano-[4,3-*b*][1]benzopyran-3,2′-[1,3]dioxolan]-10-ones 3c and 4c.** *Racemic.*—To a solution of (±)-**1c** [prepared as described above from the bromo acetal (±)-**7c** (20.0 mg, 0.058 mmol)] in THF (1 $cm^3$) at −78 °C was added the powdered chromone **2** (6.0 mg, 0.035 mmol), and the mixture was stirred at −28 °C for 40 h. After evaporation of the mixture the residue was analysed by NMR spectroscopy (ratio *ca.* 5.4:1; de 69%), and then purified by chromatography, eluting with petroleum–ethyl acetate (4:1), to give the mixed title compounds (±)-**3c** and (±)-**4c** (total 10.7 mg, 70%). The product ratio was estimated on the basis of integration of the following NMR signals: $\delta_H$(**3c**) 7.74 (1 H, d, *J* 1.6, 1-H); $\delta_H$(**4c**) 7.66 (1 H, d, *J* 1.5, 1-H). The product ratios for repetitions of this cycloaddition at other temperatures are indicated in Table 5.

*Homochiral.*—Into a solution of (*S*,*S*)-**1c** [prepared as described above from the bromo acetal (*S*,*S*)-**7c** (113 mg, 0.325 mmol)] in THF (12 $cm^3$) at −28 °C was added the powdered chromone **2** (48 mg, 0.28 mmol), and the mixture was stirred for 40 h. After evaporation of the mixture the residue was purified by chromatography, eluting with petroleum–ethyl acetate (1:1) containing 2% (v/v) triethylamine, to give the mixed ortholactones (4a*R*,4′*S*,5′*S*)-**3c** and (4a*S*,4′*S*,5′*S*)-**4c** (total 85.3 mg, 70%). Crystallisation from ether (−30 °C) gave the *title compound* (*R*,*S*,*S*)-**3c** (55.3 mg, 46%, de > 98%), mp 139–141 °C (Found: C, 76.2; H, 5.3. $C_{28}H_{24}O_5$ requires C, 76.35; H, 5.49%); $[\alpha]_D^{20}$ +252 (*c* 1.0, acetone); $\nu_{max}$(Nujol)/$cm^{-1}$ 1670 and 1610; $\delta$ 7.96 (1 H, dd, *J* 1.7, 7.8, 9-H), 7.74 (1 H, d, *J* 1.6, 1-H), 7.54–7.59 (2 H, m, 6″-H and 6‴-H), 7.45 (1 H, ddd, *J* 1.7, 7.4, 8.5, 7-H), 7.31–7.16 (4″-H, 4‴-H, 5″-H, 5‴-H), 7.07–6.95 (4 H, m, 6-H, 8-H, 3″-H, 3‴-H), 5.59 (1 H, d, *J* 9.2, 4′-H or 5′-H), 5.37 (1 H, ddd, *J* 1.6, 6.5, 10.8, 4a-H), 5.32 (1 H, d, *J* 9.2, 5′-H or 4′-H), 2.88 (1 H, dd, *J* 6.5, 12.6, 4-$H_{eq}$), 2.72 (1 H, dd, *J* 10.8, 12.6, 4-$H_{ax}$), 1.79 (3 H, s, ArMe) and 1.66 (3 H, s, ArMe); *m/z* (FAB; main peaks) 441 (M + H, 15%), 267 (**1c** + H, 35), 215 (12), 208 (25), 195 (52) and 175 (**2** + H, 100); (CI; main peaks) 441 (M + H, trace), 267 (**1c** + H, 74), 192 (**2** + $NH_4$, 100) and 175 (**2** + H, 50).

**4′,5′-Bis(2-bromophenyl)-4,4a-dihydrospiro[3*H*,10*H*-pyrano-[4,3-*b*][1]benzopyran-3,2′-[1,3]dioxolan]-10-ones 3d and 4d.** *Racemic.*—Into a solution of (±)-**1d** [prepared as described above from the bromo acetal (±)-**7d** (25.0 mg, 0.052 mmol)] in THF (2 $cm^3$) at −28 °C was added the powdered chromone **2** (6.0 mg, 0.035 mmol), and the mixture was stirred for 40 h. After removal of the solvent the residue was purified by column chromatography, eluting initially with petroleum–ethyl acetate (1:1) containing 1% (v/v) of triethylamine, and then with petroleum–dichloromethane–ethyl acetate (20:20:1) containing 1% (v/v) of triethylamine, to give the crude ortholactones (±)-**3d** and (±)-**4d** (total 15.5 mg, 79%, ratio by NMR spectroscopy *ca.* 8:1; de 78%). Crystallisation of the mixture from petroleum gave a sample of pure (±)-**3d** (10.5 mg, 53%), mp 181–182 °C. The product ratio was estimated on the basis of integration of the following NMR signals: $\delta_H$(**3d**) 7.71 (1 H, d, *J* 1.6, 1-H); (**4d**) 7.56 (1 H, d, *J* 1.7, 1-H).

*Homochiral.*—Into a solution of (*S*,*S*)-**1d** [prepared as described above from the bromo acetal (*S*,*S*)-**7d** (129.4 mg, 0.271 mmol)] in THF (6 $cm^3$) at −28 °C was added the powdered chromone **2** (44.3 mg, 0.25 mmol), and the mixture was stirred for 40 h. After evaporation of the mixture the residue was purified by column chromatography as above, to give the mixed ortholactones (4a*R*,4′*S*,5′*S*)-**3d** and (4a*S*,4′*S*,5′*S*)-**4d** (total 108.2 mg, 7.5%). Crystallisation from hexane gave the *title compound* (*R*,*S*,*S*)-**3d** (89.7 mg, 62%), mp 168–170 °C (hexane) (Found: C, 54.7; H, 3.1. $C_{26}H_{18}Br_2O_5$ requires C, 54.76; H, 3.18%); $[\alpha]_D^{20}$ +38.6 (*c* 0.73, acetone); $\nu_{max}$(Nujol)/$cm^{-1}$ 1675 and 1610; $\delta$ 7.96 (1 H, dd, *J* 1.7, 7.8, 9-H), 7.71 (1 H, d, *J* 1.6, 1-H), 7.64 (2 H, apparent d, *J* 7.8, 6″-H and 6‴-H), 7.51–7.38 (5 H, m, 7-H, 3‴-H, 3″-H, 5″-H, 5‴-H), 7.22–7.14 (2 H, m, 4″-H, 4‴-H), 7.06 (1 H, apparent t, *J ca.* 7, 8-H), 6.97 (1 H, d, *J* 8.3, 6-H), 5.78 (1 H, d, *J* 8.7, 4′-H or 5′-H), 5.59 (1 H, d, *J* 8.7, 5′-H or 4′-H), 5.36 (1 H, ddd, *J* 1.5, 6.6, 10.8, 4a-H), 2.90 (1 H, dd, *J* 6.6, 12.5, 4-$H_{eq}$) and 2.73 (1 H, dd, *J* 10.8, 12.5, 4-$H_{ax}$); *m/z* (FAB) 571 (M + H, $^{81}Br$ + $^{79}Br$, 15%), 397 (**1d** + H, 30) and 175 (**2** + H, 100).

**4′,5′-Di-1-naphthyl-4,4a-dihydrospiro[3*H*,10*H*-pyrano[4,3-*b*]-[1]benzopyran-3,2′-[1,3]dioxolan]-10-ones 3e and 4e.** To a solution of (±)-**1e** [prepared as described above from the bromo acetal (±)-**7e** (40.0 mg, 0.095 mmol)] in THF (2 $cm^3$) at −3 °C was slowly added the powdered chromone **2** (13.9 mg, 0.080 mmol), and the mixture was stirred at 0 °C for 40 h. After evaporation of the mixture the residue was chromatographed, eluting with petroleum–ethyl acetate (2:1) containing 1% (v/v) triethylamine, to give the mixed ortholactones (±)-**3e** and (±)-**4e** (total 23.8 mg, 58%, ratio *ca.* 2.1:1, de 35%) which were only partially characterised; $\nu_{max}$(Nujol)/$cm^{-1}$ 1680; $\delta$ (signals due to both products unless indicated) 8.1–6.8 (18 H, m, ArH), 7.79 (0.7 H, d, *J* 1.5, 1-H of **3e**), 6.22 and 6.15 (total 1.7 H, 2 × d, *J* 8.8, 2 × C*H*Ar of **3e**, obscuring 1 × C*H*Ar of **4e**), 5.98 (1 H, d, *J* 8.9, 1 × C*H*Ar of **4e**), 5.55–5.45 (1 H, m, 4a-H), 3.07 (1 H, dd, *J* 6.5, 12.5, 4-$H_{eq}$) and 2.91–2.83 (1 H, m, 4-$H_{ax}$); *m/z* 513 (M + H, trace), 339 (**1e** + H, 33%), 192 (**2** + $NH_4$, 100), 175 (**2** + H, 55). The susceptibility of the adducts to mass spectral fragmentation (CI and FAB) prevented accurate mass measurement.

*Repeat of the cycloaddition.* A repeat of the reaction at −28 °C for 40 h gave the mixed products (±)-**3e** and (±)-**4e** (total 22.5 mg, 55%, ratio *ca.* 2.6:1, de 44%).

**Methanolysis of the ortholactone (±)-3a.** A solution of the cycloadduct (±)-**3a** (130 mg, 0.315 mmol) in 3% methanolic HCl (12.5 $cm^3$)[41] was heated under reflux for 16 h after which it was cooled and quenched with saturated aqueous sodium hydrogen carbonate (5 $cm^3$). The aqueous phase was extracted with ethyl acetate (30 $cm^3$), and the extract was dried and evaporated. Flash chromatography of the residue, eluting with petroleum (bp 40–60 °C)–ethyl acetate (5:1), afforded the ester (±)-**5** (50 mg, 72%) as a pale yellow waxy solid, identical with an authentic sample;[7] δ 2.72 (1 H, dd, *J* 5.5, 15.9, 2-H), 2.768 (1 H, d, *J* 8.7, 3'-H), 2.771 (1 H, d, *J* 7.1, 3'-H), 2.86 (1 H, dd, *J* 7.3, 15.9, 2-H), 3.73 (3 H, s, OMe), 4.90 (1 H, m, 2'-H), 6.95 (1 H, dd, *J* 1.0, 8.5, 8'-H), 7.01 (1 H, ddd, *J* 1.0, 7.2, 7.9, 6'-H), 7.46 (1 H, ddd, *J* 1.7, 7.2, 8.5, 7'-H) and 7.86 (1 H, dd, *J* 1.7, 7.9, 5'-H). Also recovered from the column was hydrobenzoin (±)-**6a** (55 mg, 81%). Varying amounts of two by-products were observed. The structure *trans*-**17** was assigned to the major of these on the basis of the following data; $\nu_{max}$(film)/$cm^{-1}$ 1743, 1690 and 1608; δ 2.84 (1 H, dd, *J* 8.2, 16.5, 2-H), 2.98 (1 H, dd, *J* 4.3, 16.5, 2-H), 3.01 (1 H, dd, *J* 4.0, 8.1, 3'-H), 3.37 (3 H, s, OMe), 3.42 (3 H, s, OMe), 3.70 (3 H, s, OMe), 5.01 [1 H, d, *J* 4.0, C*H*(OMe)$_2$], 5.10 (1 H, apparent dt, *J* 4.3, 8.1, 8.2, 2'-H), 6.92 (1 H, d, *J* 8.4, 8'-H), 6.99 (1 H, apparent t, *J ca.* 8, 6'-H), 7.45 (1 H, apparent dt, *J* 1.7, *ca.* 8, 7'-H) and 7.84 (1 H, dd, *J* 1.7, 7.9, 5'-H); *m/z* (peaks ≥5%) 312 (M + $NH_4$, 5%), 295 (M + H, 5), 280 (10), 263 (45), 258 (5), 249 (11), 248 (100), 230 (13) and 75 (40). The minor by-product was presumed to be *cis*-**17**, which had δ 3.10 (1 H, dd, *J* 3.2, 6.8, 3'-H), 3.31 (3 H, s, OMe), 3.35 (3 H, s, OMe), 3.71 (3 H, s, OMe) and 4.78 [1 H, d, *J* 6.8, C*H*(OMe)$_2$].

**Methanolysis of the mixed ortholactones (*R*,*S*,*S*)-3a and (*S*,*S*,*S*)-4a.** A solution of the mixed cycloadducts **3** and **4** (ratio 7:3, total 41 mg, 0.10 mmol), derived from the ketene acetal (*S*,*S*)-**1a**, in 3% methanolic HCl (10 $cm^3$) was heated under reflux for 16 h. Isolation as before gave (*S*)-methyl-4-oxo-3,4-dihydro-2*H*-1-benzopyran-2-ylacetate (+)-**5** (11.5 mg, 52%) as a pale yellow solid; $\lambda_{max}$(MeOH)/nm 252 and 316; CD spectrum (MeOH) negative Cotton effect at 310 nm, positive Cotton effect at 340 nm. Adding *ca.* 4 equiv. of (*R*)-(−)-1-(9-anthryl)-2,2,2-trifluoroethanol [(*R*)-TFAE] to a *ca.* 0.1 mol $dm^{-3}$ solution of the ester **5** in $CDCl_3$ caused the signal at δ 2.86 to split into two double doublets (separation 6 Hz, 0.02 ppm). The higher field signal was due to complexation of shift reagent to the major product **3a** (68% of the combined integral; ee 36%). The chromatography also gave (*S*,*S*)-hydrobenzoin (−)-**6a** (12 mg, 56%). Adding *ca.* 4 equiv. of (*R*)-TFAE to a *ca.* 0.1 mol $dm^{-3}$ deuteriochloroform solution of the recovered diol **6a** produced only one peak (due to C*H*Ph) at δ 4.53 (ee >98%). When the spectrum of (±)-**6a** was recorded under the same conditions, the signal at δ 4.69 (2 H, s, C*H*Ph) was cleanly resolved into two singlets at δ 4.53 and 4.50 (separation 7 Hz).

**Methanolysis of the ortholactone (*R*,*S*,*S*)-3c.** A solution of (*R*,*S*,*S*)-**3c** (de ≥98%, 69.4 mg, 0.16 mmol) in 3% methanolic HCl (15 $cm^3$) was heated under reflux for 16 h, with a gentle stream of air bubbling through the reaction system. After cooling and concentration of the solution, the residue was purified by chromatography [elution with petroleum–ethyl acetate (4:1), then dichloromethane–ethyl acetate (9:1)] to give the ester (*S*)-**5** (27.2 mg, 78%), ee *ca.* 85% by NMR in the presence of 4.0 equiv. (*R*)-TFAE, followed by the diol (*S*,*S*)-**6c** (21 mg, 55%), ee 97 ± 1% by NMR in the presence of Pr(hfc)$_3$ (1.2 equiv.) [$R_f$ values (ethyl acetate–dichloromethane 1:19): **5**, 0.54; **6c**, 0.25]. Small amounts of *trans*-**17** and *cis*-**17** were apparent in the $^1$H NMR spectrum of the crude reaction product. A sample of (*S*)-**5** prepared from (*R*,*S*,*S*)-**3c** of de 69% had $[\alpha]_D^{20}$ +38 (*c* 1.23, acetone).

**4,5-Bis(2,4,6-trimethylphenyl)-1,3-dioxolan-2-one (±)-22b.** To a stirred solution of the diol (±)-**6b** (0.64 g, 2.14 mmol) and dry pyridine (0.35 $cm^3$, 0.34 g, 4.3 mmol) in ethanol-free chloroform (20 $cm^3$) at 0 °C was added a solution of phosgene in toluene (20% w/v; 1 $cm^3$). After 1 h further portions of pyridine (0.5 $cm^3$, 0.49 g, 6.18 mmol) and phosgene in toluene (20% w/v; 1 $cm^3$) were added to the reaction mixture. After a further 20 min TLC indicated that the diol had been consumed, and the solution was therefore allowed to warm to room temperature and then diluted with water. The organic phase was separated, washed first with saturated aqueous copper(II) sulfate to remove the pyridine, and then once with water, dried ($CaSO_4$), filtered and evaporated to dryness. The residue was chromatographed over silica gel (50 g), eluting with petroleum (bp 40–60 °C)–ethyl acetate (4:1), to give the *title compound* (±)-**22b** (0.467 g, 67%) as a white solid, mp 168.5–170 °C (Found: C, 77.9; H, 7.5. $C_{21}H_{24}O_3$ requires C, 77.75; H, 7.46%); $\nu_{max}$(Nujol)/$cm^{-1}$ 1821; δ (300 MHz) 6.81 (4 H, s, ArH), 5.97 (2 H, s, 4-H and 5-H), 2.24 (6 H, s, 4',4''-Me) and 2.11 (12 H, br s, 2',6',2'',6''-Me); *m/z* (CI) 342 (M + $NH_4$, 100%).

**4,5-Bis(2-Methylphenyl)-1,3-dioxolan-2-one (±)-22c.** A solution of the diol (±)-**6c** (1.111 g, 4.6 mmol) and dry pyridine (0.75 $cm^3$, 0.733 g, 9.3 mmol) in ethanol-free chloroform (70 $cm^3$) at 0 °C was stirred for 1.5 h, and then treated with a solution of phosgene in toluene (20% w/v; 2 $cm^3$). Further portions of pyridine (0.2 $cm^3$, 0.2 g, 2.5 mmol) and phosgene in toluene (20% w/v; 2 $cm^3$) were added to the reaction mixture at 30 min intervals until TLC indicated that the diol had been consumed (three such additions were necessary). The solution was allowed to warm to room temperature when it was diluted with water. The organic phase was separated and first washed with saturated aqueous copper(II) sulfate to remove the pyridine, and then once with water. The aqueous washings were back-extracted with chloroform, and the combined organic phases were dried, filtered and evaporated to dryness. The residue was chromatographed over silica gel (50 g), eluting with petroleum (bp 40–60 °C)–ethyl acetate (4:1) to give the *title compound* (±)-**22c** (1.19 g, 97%) as a white solid, mp 122.5–124.5 °C [petroleum (bp 80–100 °C)–ethanol] (Found: C, 76.4; H, 6.1. $C_{17}H_{16}O_3$ requires C, 76.10; H, 6.01%); $\nu_{max}$(Nujol)/$cm^{-1}$ 1802; δ (300 MHz) 7.55–7.50 (2 H, m, 6'-H, 6''-H), 7.35–7.25 (4 H, m, 4',5'-H, 4'',5''-H), 7.15–7.10 (2 H, m, 3'-H, 3''-H), 5.68 (2 H, s, 4,5-H) and 1.92 (6 H, s, 2 × Me); *m/z* (CI) 286 (M + $NH_4$, 100%).

**Crystal data.** *For* **22a**.[42]—Colourless crystals from ethanol–water: $C_{15}H_{12}O_3$, $M = 240.2$, Orthorhombic, *Pbcn*, $a = 14.006(3)$, $b = 11.267(3)$, $c = 7.657(1)$ Å, $U = 1208.3(4)$ Å$^3$, $Z = 4$, $D_c = 1.321$ g $cm^{-3}$, λ(Mo-Kα) = 0.710 73 Å, $\mu = 0.86$ $cm^{-1}$, $F(000) = 504$, $T = 233$ K. Intensity data in the range $3° < 2\theta < 50°$ were collected using a θ–2θ scan technique on a Siemens R3m/V diffractometer. The intensities of three reflections measured periodically showed a decrease of less than 2% over the data collection. A total of 2426 reflections were collected of which 1067 were independent, and 806 for which $I > 2.0\sigma(I)$ were used in the refinement. The structure was solved by direct methods and refined using full-matrix least squares routines. The molecule has crystallographic $C_2$ symmetry. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The hydrogen atoms were obtained from difference maps and were refined isotropically using a riding model. At convergence $R = 4.04$ and $wR = 4.60\%$ ($R = 5.67\%$ and $wR = 4.92\%$ for all data), $w = [\sigma^2(F) + 0.0004F^2]^{-1}$, $S = 1.48$, $\Delta/\sigma < 0.001$ with a data-to-parameter ratio of 9.7:1. The final difference map showed no feature greater than +0.15 e Å$^{-3}$ or less than −0.2 e Å$^{-3}$.

*For* **22c**.—Colourless crystals from petroleum (bp 80–100 °C)–ethanol: $C_{17}H_{16}O_3$, $M = 268.3$, monoclinic, $P2_1/c$, $a = 7.245(2)$, $b = 16.409(5)$, $c = 12.351(3)$ Å, $\beta = 96.03(2)°$, $U = 1460.2(7)$ Å$^3$, $Z = 4$, $D_c = 1.220$ g $cm^{-3}$, λ(Mo-Kα) = 0.710 73 Å, $\mu = 0.77$ $cm^{-1}$, $F(000) = 568$, $T = 233$ K. Intensity data in the range $3° < 2\theta < 50°$ were collected using a θ–2θ scan technique on a Siemens R3m/V diffractometer. The intensities of three reflections measured periodically showed no significant decrease over the data collection. A total of 2935 reflections were collected of which 2605 were independent, and

1806 for which $I > 2.0\sigma(I)$ were used in the refinement. The structure was solved by direct methods and refined using full-matrix least squares routines. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The hydrogen atoms were obtained from difference maps with the exception of those on C-27, which were placed in calculated positions. All hydrogen atoms were refined isotropically using a riding model. At convergence $R = 5.56$ and $wR = 7.07\%$ ($R = 8.95\%$ and $wR = 7.77\%$ for all data), $w = [\sigma^2(F) + 0.0008F^2]^{-1}$, $S = 1.78$, $\Delta/\sigma < 0.001$ with a data-to-parameter ratio of 10.0:1. The final difference map showed no feature greater than +0.22 e Å$^{-3}$ or less than −0.31 e Å$^{-3}$.

Calculations were performed using the SHELXTL-PLUS program package on a MICROVAX II. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. *See Instructions for Authors (1995), J. Chem. Soc., Perkin Trans. 1*, 1995, Issue No. 1.

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