An efficient protocol for Sharpless-style racemic dihydroxylation

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Received (in Cambridge) 8th January 1999, Accepted 5th March 1999

Racemic dihydroxylation of alkenes is efficiently accomplished with catalytic osmium (added as $OsCl_3$), stoichiometric $K_3Fe(CN)_6$ and quinuclidine under conditions similar to those of the Sharpless asymmetric hydroxylation.

It is usually easier to carry out a reaction to produce racemic rather than optically active products. There is one notable exception: the Sharpless asymmetric hydroxylation[1] is so straightforward and practical that it is easier to carry out than previous racemic versions. In using this reaction on a variety of olefins we needed to make the racemic compounds to provide reference samples of diols so that we could measure the enantiomeric excess in the asymmetric dihydroxylation. We present a simple and practical racemic version (RD) of the Sharpless dihydroxylation using quinuclidine (which is, of course, achiral) as the ligand and osmium(III) chloride as the catalytic reagent and demonstrate its use on a variety of functionalised olefins.

Our initial experiments were carried out on substituted stilbenes. The optically active diols were used to make dibenzophosphepines[2,3] for use as chiral auxiliaries. We were unable to detect the other enantiomer of these diols in their NMR spectra in the presence of the Pirkle shift reagent.[4] We needed racemic material to check that the enantiomers did indeed give distinct signals in the NMR spectra with Pirkle's reagent. As we were already familiar with the excellence of the Sharpless AD procedure, we felt that a similar racemic procedure might be devised which would be more convenient and efficient than the older Upjohn method.[5] Sharpless mentions in passing doing a racemic dihydroxylation in work on kinetic resolutions[6] and on double diastereoselections.[7] Although he has not described a general racemic protocol, Narasaka's modification has been used to improve diastereoselectivity in the racemic dihydroxylations of trienes.[8]

Although Sharpless reported[9] that quinuclidine retarded dihydroxylation under single phase conditions using *N*-methylmorpholine *N*-oxide (NMO) in aqueous acetone, Minato made the observation[10] that quinuclidine accelerates dihydroxylation under the biphasic conditions of *tert*-butyl alcohol and water. This coupled with a footnote[9,11] by Sharpless that solid $OsCl_3$ gave exactly the same results as osmium tetroxide led us to use a mixture of catalytic $OsCl_3$ with $K_3Fe(CN)_6$ as cooxidant and quinuclidine as ligand in biphasic aqueous *tert*-butyl alcohol. A brief study (Table 1) with 2,2′-dibromostilbene **1** revealed that quinuclidine suppressed the formation of the bright yellow dione **3** while methanesulfonamide was necessary to accelerate the reaction, by increasing catalytic turnover (Scheme 1).

Using this protocol we dihydroxylated a number of stilbenes in good yields (Table 2). The stilbenes were prepared from the corresponding aldehydes (ArCHO) by the very *E*-selective McMurry coupling[12] in excellent yield.[2,3] The yield in the corresponding dihydroxylation using the Sharpless AD-β-mix is given for comparison together with the ee determined by comparison with the racemic material by the Pirkle method.[4]

All the yields are good with the exception of the bis(methylenedioxy) compound **5** which gave only 36%. The yields were rather less than those in the AD reaction (though we give an example later where the reverse is true) as quinuclidine is a less effective ligand than the *Cinchona* alkaloids.

Following the success of the RD with stilbenes—which are among the best substrates for the Sharpless AD reaction

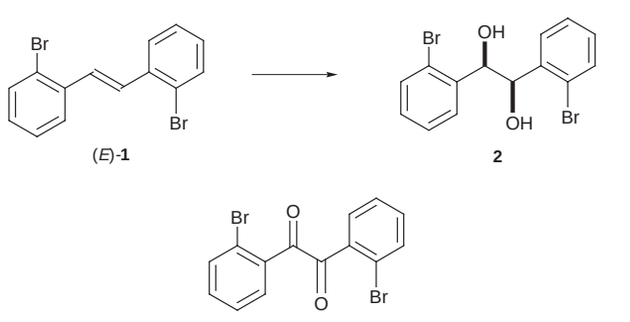
Table 1 Racemic dihydroxylation of 2,2′-dibromostilbene **1**

Additives	Time	Recovered **1** (%)	Dione **3** (%)	Racemic diol **2** (%)
None	42 hours	67	4	18
Quinuclidene	42 hours	68	<0.3	22
Quinuclidine	5 days	20	<0.3	55
Quinuclidene and methanesulfonamide	42 hours	0	<0.5	88

Table 2 Dihydroxylation of stilbenes

Entry	Stilbene	Racemic dihydroxylation yield (%)	AD-β-mix yield, % (ee, %)[a]
1	**1**	90	94 (≥99)
2	**4**	65	—
3	**5**	36	84 (≥99)
4	**6**	82	89 (≥99)
5	**7**	85	96 (≥99)

[a] Determined by comparison of the NMR spectra of racemic and homochiral diols in the presence of Pirkle's reagent.



Scheme 1

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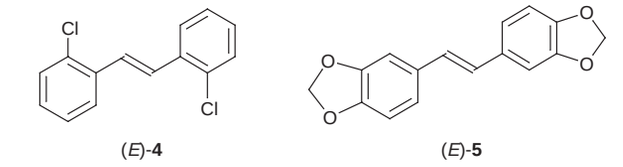
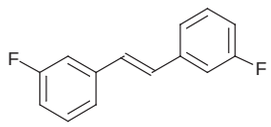
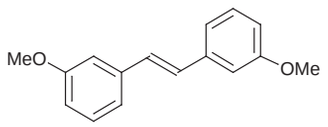


(*E*)-**4**

(*E*)-**5**

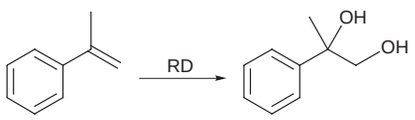


(*E*)-**6**



(*E*)-**7**

anyway—we next checked that our RD procedure also worked well for other simple alkenes. High yields were maintained with simple terminal alkenes: dec-1-ene gave a 78% yield of racemic decane-1,2-diol and the branched terminal alkene **8** gave an impressive 98% yield of the racemic diol **9** (Scheme 2).



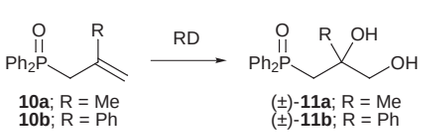
8 (±)-**9**

Scheme 2

This procedure incorporates many of the improvements made in the asymmetric reaction since its first introduction.[13] The co-oxidant $K_3Fe(CN)_6$ is safer and more convenient than NMO, solid $OsCl_3$ is safer than volatile OsO_4 [though Sharpless now prefers solid $K_2OsO_2(OH)_4$], quinuclidine is far better than no ligand at all, and the biphasic system is convenient for work-up. Like many others nowadays, we used the AD reaction before we needed racemic dihydroxylation and we found it convenient to use almost identical conditions. The rest of this paper reports our applications of this protocol to a variety of molecules for different purposes. We also record the very few cases where it failed.

Naturally the Sharpless asymmetric dihydroxylation reaction has been embraced by the organic community so it is surprising that there is considerable inertia when it comes to using the associated reaction conditions for racemic reactions. The Upjohn procedure[5] is still widely used[14–19] and in some cases even by workers who use the AD reaction in the same publication.[20–22]

As part of a study of the application of the AD reaction to allylic and homoallylic phosphine oxides,[23] we also applied the racemic and asymmetric dihydroxylations to two terminal alkenes **10a** and **10b** (Scheme 3).



10a; R = Me
10b; R = Ph

(±)-**11a**; R = Me
(±)-**11b**; R = Ph

Scheme 3

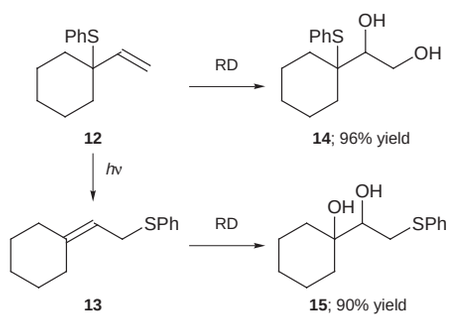
Both compounds gave good yields with the RD reaction (Table 3), better in fact than for the AD reaction, but these alkenes are poor substrates for the AD reaction and give low ees unless there is a phenyl group to form aromatic interactions with the dimeric alkaloid catalyst. Aromatic interactions are not a factor in the RD reaction as there are no alkaloid ligands and quinuclidine does not bind well to benzene rings. Catalysis by quinuclidine is a simple matter of rate acceleration by increased reactivity of the quinuclidine–OsO_4 complex. Unlike the *Cinchona* alkaloids, quinuclidine offers no chiral binding environment for the incoming olefin but simply forms an unencumbered reactive quinuclidine–OsO_4 complex. This might explain why hindered olefins give higher yields in the RD reaction.

Table 3 Dihydroxylation of allylic phosphine oxides

Allylic phosphine oxide	Racemic dihydroxylation yield (%)	Asymmetric dihydroxylation AD-β-mix yield (%)	Asymmetric dihydroxylation ee, %[a] ($[\alpha]_D$)
10a	94	90	55(+7.9)
10b	91	65	86(−28.2)

[a] Determined by comparison of the NMR spectra of racemic and homochiral diols in the presence of Pirkle's reagent.

Simple allylic sulfides **12** and **13**[24] also gave good yields in the RD reaction without any oxidation of the sulfide. The two sulfides **12** and **13** are related by a photochemical [1,3]PhS shift[25] and, though they belong to two different classes of alkenes (**12** is terminal monosubstituted and **13** is trisubstituted), both give excellent yields of diols **14** and **15** (Scheme 4). The AD reaction can also be used on sulfides without oxidation at sulfur.[26]



12 **14**; 96% yield

13 **15**; 90% yield

Scheme 4

When the double bond is disubstituted and further away from the Ph_2PO group than in **10**, both AD (97% yield) and RD (95% yield) continue to perform well but there is a dramatic improvement in the ee from the AD process as *syn*-**17** is formed with >95% ee (Scheme 5). This reaction was carried out with AD-α-mix (previous examples were carried out with AD-β-mix) so the stereochemistry of the optically active diol is indeed as shown.

16 *syn*-**17**

Scheme 5

The rest of the substrates in this paper are chiral, and more interesting questions of diastereoselectivity arise. The allylic phosphine oxide **18** is a compound we have previously used in an asymmetric synthesis[27] when we dihydroxylated optically active **18** by the Upjohn procedure. Table 4 summarises our

Table 4 Dihydroxylation of the allylic phosphine oxide **18**

	Starting material	
	(+)-**18**	Racemic **18**
Oxidant	0.7 equiv. OsO_4 1.0 equiv. NMO	1% $OsCl_3$ 15% quinuclidine
Diastereoisomeric ratio (*anti*,*syn*:*syn*,*syn*-**19**)	82:18	65:35
Reference	Harmat[27]	This work

Table 5 Racemic dihydroxylation of diphenylphosphinoyl lactones **20**–**22**

Lactone	R	Product	Total yield (%)	Ratio (*syn*:*anti*)	Yield *syn* (%)	Yield *anti* (%)
(*E*)-**20**	Me	**23**	73	62:38	31	18
(*E*)-**21**	Et	**24**	91	66:34	42	26
(*E*)-**22**	$PhCH_2$	**25**	77	54:46	32	31

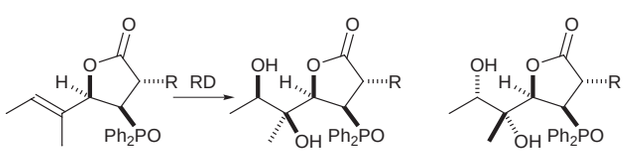
results with phosphine oxide **18**. Although the use of NMO as a cooxidant gives higher diastereoselectivity, it should be noted that this reaction of (+)-**18** uses 70 mol% of osmium—far more than the catalytic 1% used otherwise (Scheme 6).

18 *anti,syn*-**19**

Scheme 6

The next three compounds, the alkenyl lactones (*E*)-**20**–**22**, though stereochemically more complex, were all racemic. They were studied as part of a programme to control remote chiral centres with phosphine oxides.[28] The diastereoselectivity of the dihydroxylation was the only point at issue. In this commonly encountered situation—requiring diastereoselective but not enantioselective control—there is no point in using AD unless one hopes reagent control will override substrate control.

Though all diols **23**–**25** were formed in reasonable yields, the stereoselectivity was disappointing (Table 5, Scheme 7). Nevertheless, we were able to isolate enough of each diastereoisomer *syn*,*syn*-**23**–**25** and *syn*,*anti*-**23**–**25** to continue with the project.[28] The major products are formed by dihydroxylation on the same face of the five-membered ring as the Ph_2PO group. It would seem that the blocking effect of this large group is more than balanced by the delivery of the reagent through interaction with the oxygen atom of the Ph_2PO group.[29,30]



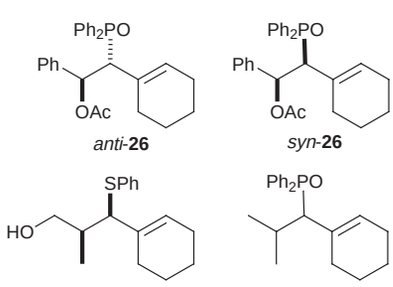
(*E*)-**20**; R = Me
(*E*)-**21**; R = Et
(*E*)-**22**; R = CH_2Ph

syn,*syn*-**23**; R = Me
syn,*syn*-**24**; R = Et
syn,*syn*-**25**; R = CH_2Ph

syn,*anti*-**23**; R = Me
syn,*anti*-**24**; R = Et
syn,*anti*-**25**; R = CH_2Ph

Scheme 7

With compounds **20**–**22** we reach the limit of the reaction. A further series of more crowded alkenes failed to react at all. The acetoxyphosphine oxides **26** did not react, regardless of stereochemistry, while the allylic sulfide *syn*-**27** also failed to react. The AD reaction also failed with the sulfide *syn*-**27** and with the branched phosphine oxide **28**.



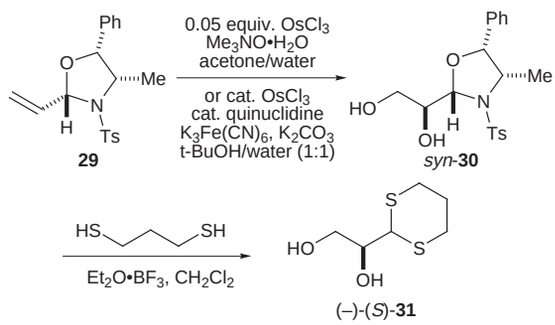
anti-**26** *syn*-**26**

syn-**27** **28**

We conclude with an example which allows a direct comparison between our procedure and a variation of the Upjohn procedure on the interesting enantiomerically enriched norephedrine-derived heterocycle **29** (Scheme 8). Scolastico[31]

Table 6 Direct comparison of the Scolastico procedure and our RD method on **29**

Method	Yield (%)	Ratio (*syn*:*anti*)	Reference
Me_3NO	80	75:25	Scolastico[31]
Our RD	88	72:28	This work



29 *syn*-**30** (–)-(*S*)-**31**

Scheme 8

used 0.05 equivalents of $OsCl_3$ and trimethylamine *N*-oxide (not NMO) as the cooxidant while we used our standard procedure. The two sets of results are very similar in yield and stereoselectivity (Table 6).

The norephedrine chiral auxiliary was removed from the product *syn*-**30** with propane-1,3-dithiol to give the dithiane (−)-(*S*)-**31** in moderate yield. The product from our RD approach had $[\alpha]_D$ −2.6 and an ee of 44%. This shows the poor effciency of substrate control on this alkene with a racemic reagent.

Experimental

Flash chromatography[32] was performed using Merck 9385 Kieselgel 60. Thin layer chromatography (TLC) was performed using commercially available glass plates coated with Merck silica Kieselgel $60F_{254}$. High performance liquid chromatography (HPLC) was performed using a Dynamax pre-packed silica column (25 cm × 21.4 mm internal diameter) using a Gilson model 303 pump and a Cecil Instruments CE212A UV detector at 254 nm. All solvents were distilled before use. Anhydrous solvents were distilled from $LiAlH_4$ in the case of Et_2O and THF, from CaH_2 in the case of CH_2Cl_2, MeOH, hexane and toluene, and from $CaCl_2$ in the case of CCl_4. Triphenylmethane was used as indicator for THF.

Melting points were determined on a Reichert hot stage microscope and are uncorrected. Infra red spectra were recorded on a Perkin Elmer 1600 series FTIR spectrometer. Optical rotations were recorded on a Perkin Elmer 241 polarimeter (using the sodium D line; 589 nm) and $[\alpha]_D$ are given in units of 10^{-1} deg cm^2 g^{-1}.

All NMR instruments used were made by Bruker. Proton, carbon, phosphorus and fluorine NMR spectra were recorded using the AC 250, WM 250 or AM 400 Fourier transform spectrometers, using an internal deuterium lock. Carbon spectra were determined with broad band decoupling and an

attached proton test (APT). Signals from carbon atoms with an odd number of attached protons are designated ($^+$) while those with an even number are designated ($^-$).

All mass spectra were determined by electron impact (EI) unless otherwise stated. Other methods used were chemical ionisation (CI) and fast atom bombardment (FAB). All three methods were performed on a Kratos MS890 spectrometer by technical staff. Microanalyses were performed by technical staff using either Carlo Erba 1106 or Perkin Elmer 240 automatic analysers. ^{1}H NMR peaks marked * exchange with deuterium on shaking with D_2O.

(1*RS*,2*RS*)-1,2-Bis(2-bromophenyl)ethane-1,2-diol 2

2,2′-Dibromostilbene **1** (2.00 g, 5.90 mmol) was reacted in a method similar to that used in the reaction of difluorostilbene **6**. The crude product was purified by flash chromatography, eluting with Et_2O–hexane, to give the racemic diol (1.98 g, 90%) as rectangular prisms, mp 123–124 °C (from hexane–dichloromethane) (lit.,[33] 118.5–119.0 °C); R_f(Et_2O–hexane, 1:1) 0.23; ν_{max}(KBr)/cm^{-1} 3600–2500 (OH), 1592 (Ar) and 1568 (Ar); δ_H(400 MHz; $CDCl_3$) 7.69 (2 H, dd, *J* 1.6 and 7.8, 3-ArH), 7.45 (2 H, dd, *J* 8.1 and 1.1, 6-ArH), 7.35 (2 H, td, *J* 7.6 and 1.1, 4-ArH), 7.14 (2 H, td, *J* 7.9 and 1.7, 5-ArH), 5.31 (2 H, dd, *J* 2.5 and 1.1, ArC*H*) and 2.77 (2 H, dd, *J* 2.6 and 1.3, OH); δ_C(62.9 MHz; $CDCl_3$) 138.7$^-$ (1-ArC), 132.8$^+$ (3-ArC), 129.7$^+$, 129.6$^+$, 127.5$^+$ (5-ArC), 123.0$^-$ (2-ArC) and 75.2$^+$ (Ar*C*OH).

In another experiment performed without methanesulfonamide and without quinuclidine, the yield after 42 h at room temperature was 18% with 67% isolated starting material and 4% of 1,2-bis(2-bromophenyl)ethane-1,2-dione.

In another experiment performed without methanesulfonamide but with 0.28 equiv. of quinuclidine, the yield after 42 h at room temperature was 22% with 68% isolated starting material and less than 0.27% of the dione.

In another experiment performed with 0.28 equiv. of quinuclidine and 1.14 equiv. of methanesulfonamide, the yield after 42 h at room temperature was 88% with less than 0.5% of the dione and no isolated starting material.

(1*RS*,2*RS*)-1,2-Bis(3,4-methylenedioxyphenyl)ethane-1,2-diol

Potassium ferricyanide (1.98 g, 6.01 mmol, 3 equiv.), potassium carbonate (0.84 g, 6.08 mmol), osmium(III) chloride hydrate (8.5 mg, 0.027 mmol, 0.0135 equiv.), quinuclidine (62.0 mg, 0.558 mmol) and methanesulfonamide (190 mg, 2.00 mmol) were added to water (12 ml) and *tert*-butyl alcohol (12 ml). The mixture was warmed slightly and stirred until all the solids had dissolved and then allowed to cool to room temperature. 3,4:3′,4′-Bis(methylenedioxy)stilbene **5** (553 mg, 2.06 mmol, 1.03 equiv.) was added to the solution, the flask lightly stoppered with a glass stopper, and the mixture stirred vigorously for over 42 h. Anhydrous sodium sulfite (3.0 g, 23.8 mmol) was then added and stirring continued for 1 h before the addition of dichloromethane (20 ml). The layers were separated and the aqueous phase was further extracted with dichloromethane (3 × 10 ml). The combined organic extracts were washed with 2 M KOH (5 ml) and dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by flash chromatography, eluting with Et_2O–hexane (3:7) to give the racemic diol (221 mg, 36%), mp 143–144 °C (from Et_2O–hexane) (lit.,[34] 132 °C, from benzene); R_f(Et_2O–hexane, 2:1) 0.17; ν_{max}(KBr)/cm^{-1} 3469 (OH), 3315 (OH) and 1503 (Ar); δ_H(400 MHz; $CDCl_3$) 6.71 (2 H, d, *J* 1.6, 2-ArH), 6.65 (2 H, d, *J* 8.0, 5-ArH), 6.53 (2 H, dd, *J* 8.0 and 1.6, 6-ArH), 5.93 (2 H, d, *J* 1.4, OC$H_A$$H_B$O), 5.92 (2 H, d, *J* 1.4, OC$H_A$$H_B$O), 4.56 (2 H, s, ArC*H*) and 2.79 (2 H, s, OH); δ_C(100.6 MHz; $CDCl_3$) 147.7$^-$ (3 or 4-ArC), 147.4$^-$ (3 or 4-ArC), 134.0$^-$ (1-ArC), 120.8$^+$ (6-ArC), 108.1$^+$ (5 or 2-ArC), 107.4$^+$ (5 or 2-ArC), 101.2$^-$ (OCO) and 79.1$^+$ (Ar*C*OH); *m*/*z* 303 (57%, MH$^+$), 285 (61, MH − H_2O), 151 (60, ArCHOH) and 133 (100, ArCH-OH − H_2O) (Found: MH$^+$, 303.08810. $C_{16}H_{14}O_6$ requires *M* + 1, 303.08687).

(1*RS*,2*RS*)-1,2-Bis(3-methoxyphenyl)ethane-1,2-diol

3,3′-Dimethoxystilbene **7** (488 mg, 1.78 mmol, 1.02 equiv.) was reacted in a method similar to that used in the reaction of difluorostilbene **6**. The crude product was purified by flash chromatography, eluting with 4:1 Et_2O–hexane, to give the *racemic diol* (468 mg, 85%) as prisms, mp 52–54 °C (from Et_2O–hexane); R_f(Et_2O–hexane, 4:1) 0.23; ν_{max}($CHCl_3$)/cm^{-1} 3564 (OH), 3452 (OH), 1598 (Ar) and 1493 (Ar); δ_H(400 MHz; $CDCl_3$) 7.13 (2 H, t, *J* 8.1, 4-ArH), 6.76 (2 H, dd, *J* 8.1 and 2.5, 3 or 5-ArH), 6.70–6.68 (4 H, m), 4.63 (2 H, s, ArC*H*), 3.69 (6 H, s, OMe) and 3.01 (2 H, s, OH); δ_C(100.6 MHz; $CDCl_3$) 159.6$^-$ (3-ArC), 141.7$^-$ (1-ArC), 129.3$^+$ (5-ArC), 119.4$^+$ (6-ArC), 113.9$^+$ (2-ArC), 112.4$^+$ (4-ArC), 79.0$^+$ (Ar*C*H) and 55.4$^+$ (OMe); *m*/*z* 274 (0.4%, M$^+$), 256 (0.5, M − H_2O) and 138 (100, $ArCH_2OH$) (Found: M$^+$, 274.1200. $C_{16}H_{18}O_4$ requires *M*, 274.1205).

(1*RS*,2*RS*)-1,2-Bis(2-chlorophenyl)ethane-1,2-diol

2,2′-Dichlorostilbene **4** (513 mg, 2.06 mmol, 1.03 equiv.) was reacted in a method similar to that used in the reaction of difluorostilbene **6**. The crude product was purified by flash chromatography, eluting with Et_2O–hexane, to give the racemic diol (367 mg, 64.6%) as needles, mp 107–108 °C (from Et_2O–hexane) (lit.,[35] 105–106 °C from Et_2O–pentane); R_f(Et_2O) 0.62; ν_{max}(Nujol)/cm^{-1} 3426 (OH), 3299 (OH) and 1573 (Ar); δ_H(250 MHz; $CDCl_3$) 7.68 (2 H, dd, *J* 1.4 and 6.8, 2-ArH), 7.36–7.32 (6 H, m), 5.35 (2 H, s, ArC*H*) and 3.14 (2 H, s, OH); δ_C(62.9 MHz; $CDCl_3$) 137.1$^-$ (1-ArC), 132.5$^-$ (2-ArC), 129.4$^+$, 129.0$^+$, 128.99$^+$, 126.7$^+$ and 72.9$^+$ (Ar*C*OH).

(1*RS*,2*RS*)-1,2-Bis(3-fluorophenyl)ethane-1,2-diol

Potassium ferricyanide (18.1 g, 55.1 mmol), potassium carbonate (7.59 g, 55 mmol), osmium(III) chloride hydrate (40.8 mg, 0.130 mmol), quinuclidine (72.0 mg, 0.648 mmol) and methanesulfonamide (1.76 g, 18.5 mmol) were added to water (95 ml) and *tert*-butyl alcohol (95 ml). The mixture was stirred vigorously with a mechanical stirrer until all solids had dissolved. 3,3′-Difluorostilbene **6** (4.02 g, 18.6 mmol) was added and the suspension stirred vigorously for 96 h at room temperature. Anhydrous sodium sulfite (28 g, 0.22 mol) was then added and stirring continued for 1 h before the addition of dichloromethane (175 ml). The layers were separated and the aqueous phase was further extracted with dichloromethane (3 × 100 ml). The combined organic extracts were washed with 2 M KOH (15 ml), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by flash chromatography, eluting with Et_2O–hexane, and then recrystallized (CH_2Cl_2–hexane, 57:43) to give the diol (3.74 g, 81.5%) as needles, mp 128–130.5 °C (from CH_2Cl_2–hexane) (lit.,[36] 118–119 °C, from light petroleum–toluene); R_f(Et_2O–hexane, 2:1) 0.17; ν_{max}(KBr)/cm^{-1} 3471 (OH), 3275 (OH) and 1594 (Ar); δ_H(400 MHz; $CDCl_3$) 7.19 (2 H, td, *J* 7.9 and $^4J_{HF}$ 6.0, 5-ArH), 6.96–6.89 (4 H, m, 4 and 6-ArH), 6.83 (2 H, d, $^3J_{HF}$ 7.7, 2-ArH), 4.67 (2 H, s, ArC*H*) and 2.84 (2 H, s, OH); δ_C(100.6 MHz; $CDCl_3$) 162.6$^-$ ($^1J_{CF}$ 246.2, 3-ArC), 142.1$^-$ ($^3J_{CF}$ 78.4, 1-ArC), 129.7$^+$ ($^3J_{CF}$ 8.1, 5-ArC), 122.6$^+$ ($^4J_{CF}$ 2.3, 6-ArC), 115.0$^+$ ($^2J_{CF}$ 21.1, 4-ArC), 113.8$^+$ ($^2J_{CF}$ 22.0, 2-ArC) and 78.4$^+$ (Ar*C*OH); *m*/*z* 250 (0.1%, M$^+$) and 125 (95, ArCHOH) (Found: M$^+$, 250.0808. $C_{14}H_{12}F_2O_2$ requires *M*, 250.0805).

Decane-1,2-diol

Under the same conditions used for the reaction of difluorostilbene **6**, dec-1-ene (3 g, 4.05 ml, 21.4 mmol), $OsCl_3$·$6H_2O$ (63 mg, 0.21 mmol), $K_3Fe(CN)_6$ (21.1 g, 64.2 mmol), K_2CO_3

(8.85 g, 64.2 mmol) and quinuclidine (23.9 mg, 0.21 mmol) in 1:1 *t*-BuOH–H_2O (210 ml) gave, after column chromatography on silica gel eluting with ether, the diol (2.9 g, 78%) as a solid (for ^1H and ^{13}C NMR see ref. 37).

2-Phenylpropane-1,2-diol 9

Under the same conditions used for the reaction of difluorostilbene **6**, 2-phenylpropene **8** (300 mg, 2.54 mmol), $OsCl_3 \cdot 6H_2O$ (7.6 mg, 25 μmol), $K_3Fe(CN)_6$ (2.5 g, 7.62 mmol), K_2CO_3 (1.05 g, 7.62 mmol) and quinuclidine (2.9 mg, 25 μmol) in 1:1 *t*-BuOH–H_2O (25 ml) gave, after column chromatography on silica gel eluting with ether, the diol **9** (377 mg, 97.6%) as a white solid, mp 43 °C (lit.,[38] 43–44 °C); R_f (Et_2O) 0.56; ν_{max}/cm^{-1}(Nujol) 3210 (br, OH), 1600 and 1491 (Ph); δ_H(400 MHz, $CDCl_3$) 7.42–7.26 (5 H, m, Ph), 3.75 (1 H, d, *J* 11.1, C*H*$_2$OH), 3.59 (1 H, d, *J* 7.9, C*H*$_2$OH), 2.85 (1 H, s, OH), 2.24 (1 H, s, OH) and 1.85 (3 H, s, Me); δ_C(400 MHz, $CDCl_3$) 145.0 (*i*-CPh), 128.4, 127.3 and 125.1 (Ph), 74.9 (Ph*C*), 71.1 (CH_2) and 26.0 (Me); Found: $(M - CH_2OH)^+$, 121.0653. C_8H_9O requires *M* − CH_2OH, 121.0653; *m*/*z* 121 (81%, $M^+ - CH_2OH$), 105 (100, PhCO) and 91.1 (51, C_7H_7).

2-Phenylprop-2-en-1-ol

By the method of Gassman and Harrington,[39] ethyl iodide (0.1 ml, 1.3 mmol) was added dropwise to a stirred suspension of magnesium turnings (1.71 g, 70.4 mmol) and a crystal of iodine in THF (50 ml) under argon at room temperature. The mixture was cooled to 0 °C and a solution of α-bromostyrene (8.5 ml, 66.3 mmol) in THF (20 ml) was added dropwise over 1 h to give a dark brown solution. The solution was allowed to warm to room temperature, stirred at room temperature for 30 min and then refluxed for 30 min. After cooling to 0 °C, solid paraformaldehyde (3.05 g, 101.7 mmol) was added in one portion and the mixture was allowed to warm to room temperature. After 7 h at room temperature, saturated aqueous ammonium chloride (10 ml) was added dropwise. Water (20 ml) was added, the layers separated and the aqueous layer extracted with Et_2O (3 × 75 ml). The combined organic extracts were dried (Na_2SO_4) and evaporated under reduced pressure to give the crude product as a yellow oil. Purification by distillation gave 2-phenylprop-2-en-1-ol (4.86 g, 55%) as a colourless liquid, bp 70–72 °C/0.1 mmHg (lit.,[39] 77–79 °C/0.25 mmHg); R_f(1:1 Et_2O–hexane) 0.3; ν_{max}(film)/cm^{-1} 3356 (OH), 1631 (C=C), 1599 (Ph), 1574 (Ph) and 1495 (Ph); δ_H(200 MHz, $CDCl_3$) 7.48–7.30 (5 H, m, Ph), 5.48 (1 H, d, *J* 0.9, C=C*H*$_A$H$_B$), 5.35 (1 H, q, *J* 1.2, C=CH$_A$*H*$_B$), 4.55 (2 H, br d, *J* 6.0, C*H*$_2$OH) and 2.81 (1 H, t, *J* 6.2, CH_2O*H*); δ_C(50 MHz, $CDCl_3$) 147.2$^-$ (*ipso*-Ph), 138.5$^-$ (*C*=CH_2), 128.4$^+$, 127.8$^+$ (*p*-Ph), 126.0$^+$, 112.4$^-$ (C=*C*H$_2$) and 64.8$^-$ (CH_2OH); *m*/*z* 134 (100%, M^+), 103 (100, M − CH_2OH), 92 (80) and 77 (75, Ph) (Found: M^+, 134.0725. $C_9H_{10}O$ requires *M*, 134.0732).

3-Diphenylphosphinoyl-2-methylpropene 10a

Pyridine (4.5 ml, 55.6 mmol) was added dropwise to a stirred solution of 2-methylprop-2-en-1-ol (4.7 ml, 55.9 mmol) in Et_2O (75 ml) under argon at −78 °C. After 15 min at −78 °C, a solution of chlorodiphenylphosphine (10.0 ml, 55.8 mmol) in Et_2O (50 ml) was added dropwise and then the mixture was stirred at −78 °C for 30 min to give a white precipitate. The mixture was allowed to warm to room temperature and filtered under argon using a Schlenk tube. The Et_2O was evaporated under reduced pressure to give a colourless oil which was dissolved in toluene (100 ml) and heated under reflux. After 21 h, the resulting brown solution was cooled and the toluene evaporated under reduced pressure to give the crude product as a yellow-white solid. Recrystallisation from EtOAc gave 3-diphenylphosphinoyl-2-methylpropene **10a** (6.83 g, 48%) and purification of the mother liquors by chromatography on silica with EtOAc as eluant gave more 3-diphenylphosphinoyl-2-methylpropene (797 mg, 6%) as plates, mp 149–151 °C (from EtOAc) (lit.,[40] 144–145 °C); R_f(EtOAc) 0.35.

3-Diphenylphosphinoyl-2-phenylpropene 10b

In the same way, pyridine (1.2 ml, 14.8 mmol), 2-phenylprop-2-en-1-ol (1.98 g, 14.7 mmol) and chlorodiphenylphosphine (2.65 ml, 14.8 mmol) in Et_2O (35 ml) followed by refluxing in toluene (30 ml) gave the crude product as an oil. Purification by chromatography on silica with 4:1 EtOAc–hexane as eluant gave the *phosphine oxide* **10b** (3.59 g, 77%) as needles, mp 89–91 °C (from EtOAc); R_f(EtOAc) 0.4 (Found: M^+, 318.1179. $C_{21}H_{19}OP$ requires *M*, 318.1174); ν_{max}(Nujol)/cm^{-1} 1624 (C=C), 1591 (Ph), 1496 (Ph), 1437 (P=Ph) and 1225 (P=O); δ_H(200 MHz, $CDCl_3$) 7.75–7.64 (4 H, m, *o*-Ph_2PO), 7.49–7.15 (11 H, m, *m*- and *p*-Ph_2PO and Ph), 5.38 (1 H, td, *J* 0.5 and 4.5, C=C*H*$_A$H$_B$), 5.24 (1 H, d, *J* 4.5, C=CH$_A$*H*$_B$) and 3.54 (2 H, dd, *J* 0.6 and 14.2, PCH_2); δ_C(50 MHz, $CDCl_3$) 141.5$^-$ (*ipso*-Ph), 138.6$^-$ (d, J_{PC} 9.5, *C*=CH_2), 131.7–126.4 (Ph_2PO and Ph), 118.1$^-$ (d, J_{PC} 8.8, C=*C*H$_2$) and 36.9$^-$ (d, J_{PC} 67.1, PCH_2); *m*/*z* 318 (70%, M^+), 201 (40, Ph_2PO), 84 (85), 77 (30, Ph) and 49 (100).

(*R*)-3-Diphenylphosphinoyl-2-methylpropane-1,2-diol (*R*)-11a

3-Diphenylphosphinoyl-2-methylpropene **10a** (207 mg, 0.8 mmol) was added in one portion to a stirred solution of AD-mix-β (1.13 g) in 1:1 *tert*-butyl alcohol–water (10 ml) at 0 °C. The resulting orange slurry was stirred vigorously at 0 °C for 72 h. Sodium sulfite (1.4 g) was then added and the mixture allowed to warm to room temperature. After stirring at room temperature for 1 h, CH_2Cl_2 (20 ml) was added and the layers separated. The aqueous layer was extracted with CH_2Cl_2 (5 × 20 ml). The combined organic extracts were dried (Na_2SO_4) and evaporated under reduced pressure to give the crude product as an oil. Purification by chromatography on silica with EtOAc as eluant gave the *diol* (*R*)-**11a** (174 mg, 74%) as fine needles, mp 119–121 °C (from 100:1 EtOAc–MeOH); R_f(EtOAc) 0.15; $[\alpha]_D^{20}$ +7.9 (*c* 1.05 in $CHCl_3$; 56% ee by Pirkle and 55% ee by mono-Mosher's ester derivatisation) (Found: C, 66.4; H, 6.4; P, 10.7%; M^+, 290.1055. $C_{16}H_{19}O_3P$ requires C, 66.2; H, 6.6; P, 10.7%; *M*, 290.1072); ν_{max}(Nujol)/cm^{-1} 3400 (OH), 3262 (OH), 1463 (P–Ph) and 1161 (P=O); δ_H(200 MHz, $CDCl_3$) 7.87–7.66 (4 H, m, *o*-Ph_2PO), 7.59–7.41 (6 H, m, *m*- and *p*-Ph_2PO), 4.24 (1 H, s, COH), 4.01 (1 H, dd, *J* 6.4 and 7.3, CH_2O*H*), 3.57 (1 H, dd, *J* 6.4 and 11.5, C*H*$_A$H$_B$OH), 3.40 (1 H, ddd, *J* 1.2, 7.5 and 11.4, CH$_A$*H*$_B$OH), 2.70 (1 H, dd, *J* 12.4 and 15.3, PC*H*$_A$H$_B$), 2.60 (1 H, dd, *J* 9.0 and 15.2, PCH$_A$*H*$_B$) and 1.19 (3 H, d, *J* 1.4, Me); δ_C(63 MHz, $CDCl_3$) 134.2–128.6 (Ph_2PO), 72.9$^-$ (d, J_{PC} 5.2, COH), 70.3$^-$ (d, J_{PC} 6.4, CH_2OH), 38.65$^-$ (d, J_{PC} 69.4, PCH_2) and 26.8$^+$ (d, J_{PC} 7.6, Me); *m*/*z* 291 (40%, M^+ + H), 290 (10, M^+), 259 (90, M − CH_2OH), 202 (100, Ph_2POH), 201 (80, Ph_2PO) and 77 (20, Ph).

(*R*)-3-Diphenylphosphinoyl-2-phenylpropane-1,2-diol 11b

In the same way, 3-diphenylphosphinoyl-2-phenylpropene **10b** (633 mg, 2.0 mmol) and AD-mix-β (2.92 g) in 1:1 *tert*-butyl alcohol–water (20 ml) gave the crude product as an oil after 72 h at 0 °C. Purification by chromatography on silica with EtOAc as eluant gave the *diol* (*R*)-**11b** (526 mg, 75%) as fine needles, mp 205–207 °C (from EtOAc); R_f(EtOAc) 0.4; $[\alpha]_D^{20}$ −28.2 (*c* 1.4 in $CHCl_3$; 86% ee by Pirkle) (Found: C, 71.6; H, 6.0; P, 8.85%; M^+, 352.1230. $C_{21}H_{21}O_3P$ requires C, 71.6; H, 6.0; P, 8.8%; *M*, 352.1228); ν_{max}(Nujol)/cm^{-1} 3455 (OH), 1438 (P–Ph) and 1231 (P=O); δ_H(200 MHz, $CDCl_3$) 7.75–7.65 (2 H, m, *o*-Ph_2PO), 7.56–7.19 (10 H, m, Ph and Ph_2PO), 7.15 (3 H, m, Ph), 5.67* (1 H, s, COH), 3.78 (1 H, ddd, *J* 1.3, 7.8 and 9.1, C*H*$_A$H$_B$OH), 3.65* (1 H, dd, *J* 5.0 and 7.9, CH_2O*H*), 3.51 (1 H, ddd, *J* 2.8, 4.9 and 7.8, CH$_A$*H*$_B$OH), 3.23 (1 H, dd, *J* 13.4 and 15.1, PC*H*$_A$H$_B$) and 2.60 (1 H, dd, *J* 6.7 and 15.1, PCH$_A$*H*$_B$); δ_C(50 MHz, $CDCl_3$) 143.1$^-$ (*ipso*-Ph), 132.0–125.0 (Ph and

Ph_2PO), 76.5$^-$ (COH), 71.0$^-$ (d, J_{PC} 9.0, CH_2OH) and 37.7$^-$ (d, J_{PC} 70.1, PCH_2); *m*/*z* 353 (30%, $M^+ + H$), 352 (5, M^+), 321 (100, $M - CH_2OH$), 215 (60), 202 (95, Ph_2POH), 201 (100, Ph_2PO) and 77 (70, Ph).

(*RS*)-3-Diphenylphosphinoyl-2-methylpropane-1,2-diol (*RS*)-11a

Osmium(III) chloride (1 mg, 0.003 mmol) was added to a stirred solution of 3-diphenylphosphinoyl-2-methylpropene **10a** (209 mg, 0.73 mmol), potassium ferricyanide (766 mg, 2.3 mmol), potassium carbonate (296 mg, 2.14 mmol) and quinuclidine (4 mg, 0.04 mmol) in 1:1 *tert*-butyl alcohol–water (10 ml) at room temperature. The resulting orange slurry was stirred vigorously at room temperature for 72 h and sodium sulfite (1.5 g) was added. After stirring at room temperature for 1 h, CH_2Cl_2 (20 ml) was added and the layers separated. The aqueous layer was extracted with CH_2Cl_2 (5 × 20 ml) and the combined organic extracts were dried (Na_2SO_4) and evaporated under reduced pressure to give the crude product as an oil. Purification by chromatography on silica with EtOAc as eluant gave the *diol* (*RS*)-**10b** (220 mg, 94%) as cubes, mp 116–118 °C (from EtOAc); R_f(EtOAc) 0.15 (Found: C, 65.7; H, 6.6; P, 10.6. $C_{16}H_{19}O_3P$ requires C, 66.2; H, 6.6; P, 10.7%).

(*RS*)-3-Diphenylphosphinoyl-2-phenylpropane-1,2-diol (*RS*)-11b

In the same way, osmium(III) chloride (1 mg, 0.003 mmol), 3-diphenylphosphinoyl-2-phenylpropene **10b** (252 mg, 0.73 mmol), potassium ferricyanide (805 mg, 2.4 mmol), potassium carbonate (329 mg, 2.4 mmol) and quinuclidine (5 mg, 0.04 mmol) in 1:1 *tert*-butyl alcohol–water (10 ml) gave the *diol* (*RS*)-**11b** (253 mg, 91%) as fine needles, mp 182–184 °C (from EtOAc) after 72 h at room temperature; R_f(EtOAc) 0.4 (Found: C, 71.3; H, 6.0; P, 8.85%. $C_{21}H_{21}O_3P$ requires C, 71.6; H, 6.0; P, 8.8%).

1-[1-(Phenylsulfanyl)cyclohexyl]ethane-1,2-diol 14

Under the same conditions used for the reaction of difluorostilbene **6** the allylic sulfide **12** (25 mg, 0.14 mmol), $K_3Fe(CN)_6$ (0.11 g, 0.42 mmol), K_2CO_3 (40 mg, 0.42 mmol), quinuclidine (0.9 mg, 14 μmol) and $OsCl_3{\cdot}6H_2O$ (84 μg, 14 mmol) in *t*-BuOH–H_2O (1 ml, 1:1) gave, after column chromatography on silica gel eluting with 1:1 light petroleum (bp 40–60 °C)–ether, the *diol* **14** (27 mg, 96%) as an oil; R_f [9:1 light petroleum (bp 40–60 °C)–ether] 0.2; ν_{max}(film, $CDCl_3$)/cm^{-1} 3500–3200 (OH); δ_H(400 MHz, $CDCl_3$) 7.6–7.3 (5 H, m, SPh), 3.8 (1 H, dd, *J* 10.6 and 2.68, CHO), 3.65 (1 H, dd, *J* 10.8 and 7.89, CH_AH_BO), 3.45 (1 H, dt, *J* 7.84 and 3.12, CH_AH_BO), 3.3 (1 H, d, *J* 2.74, CHO*H*), 2.19 (1 H, dd, *J* 8.0 and 3.12, CH_2OH) and 2.04–1.20 (10 H, m, 5 × CH_2); δ_C(100 MHz, $CDCl_3$) 137.2 (*m*-SPh), 130.0$^-$ (*i*-SPh), 129.1 (*p*-SPh), 128.9 (*o*-SPh), 75.2 (CHOH), 62.7$^-$ (CH_2O), 59.3$^-$ (*C*SPh), 30.9$^-$, 30.7$^-$, 26.0$^-$, 21.7$^-$ and 21.6$^-$ (5 × CH_2) (Found: M^+, 252.1181. $C_{14}H_{20}O_2S$ requires M, 252.1183); *m*/*z* 191.1 (60%, $C_6H_{10}SPh$), 109 (30, SPh) and 81.1 (100, C_6H_9).

2-(1-Hydroxycyclohexyl)-1-phenylsulfanylethan-2-ol 15

Under the same conditions used for the reaction of difluorostilbene **6** the allylic sulfide **13** (72 mg, 0.33 mmol), $K_3Fe(CN)_6$ (0.32 g, 0.99 mmol), K_2CO_3 (0.14 g, 0.99 mmol), quinuclidine (0.4 mg, 3.3 μmol), methanesulfonamide (17 mg, 0.16 mmol) and $OsCl_3{\cdot}6H_2O$ (1 μg, 3.3 μmol) in *t*-BuOH–H_2O (3.2 ml, 1:1) gave, after column chromatography on silica gel eluting with 1:1 light petroleum (bp 40–60 °C)–ether, the *diol* **15** (75 mg, 90%) as an oil; R_f [1:1 light petroleum (bp 40–60 °C)–ether] 0.4; ν_{max}(film, $CDCl_3$)/cm^{-1} 3500–3200 (OH); δ_H(400 MHz, $CDCl_3$) 7.39–7.18 (5 H, m, SPh), 3.40 (1 H, dt, *J* 10.51 and 2.18, CHO), 3.28 (1 H, dd, *J* 13.75 and 2.35, CH_AH_BSPh), 2.90 (1 H, dd, *J* 13.82 and 10.50, CH_AH_BSPh), 2.87 (1 H, s, OH), 2.05 (1 H, br s, OH) and 1.75–1.13 (10 H, m, 5 × CH_2); δ_C(100 MHz, $CDCl_3$) 134.00$^-$ (*i*-SPh), 130.11 (*m*-SPh), 129.13 (*p*-SPh), 126.78 (*o*-SPh), 74.11 (HCO), 72.70$^-$ (CO) and 37.02$^-$ (CH_2SPh), 34.64$^-$, 32.48$^-$, 25.75$^-$, 21.55$^-$ and 21.48$^-$ (5 × CH_2) (Found: M^+, 252.1180. $C_{14}H_{20}O_2S$ requires M, 252.1183); *m*/*z* 252.1 (100%, M) and 98 (35, $C_6H_{10}O$).

1-(1-Diphenylphosphinoylbutyl)cyclohexene 18

n-Butyllithium (9.5 ml of a 1.3 M solution in hexanes, 12.3 mmol) was added dropwise to a stirred solution of butyldiphenylphosphine oxide (2.62 g, 10.3 mmol) in THF (60 ml) at −78 °C to give an orange solution. After 15 min, cyclohexanone (1.10 g, 11.3 mmol) was added dropwise. After a further 15 min, the temperature was increased to 0 °C. Saturated ammonium chloride solution (11 ml) was added after 1 h and the majority of the THF removed under reduced pressure. The aqueous suspension was extracted into dichloromethane (3 × 50 ml), and the combined organic extracts washed with saturated brine (2 × 50 ml), dried ($MgSO_4$) and evaporated under reduced pressure to give a crude product which was dissolved in trifluoroacetic acid (25 ml). The solution was refluxed for 45 min and the majority of the trifluoroacetic acid removed under reduced pressure. The reaction mixture was diluted with water (50 ml), extracted with dichloromethane (3 × 30 ml) and the combined organic extracts were washed with saturated sodium bicarbonate solution (30 ml), water (30 ml) and brine (30 ml), dried ($MgSO_4$) and evaporated under reduced pressure. Flash chromatography, eluting with 2:1 EtOAc–hexane, gave the *allylic phosphine oxide* **18** (1.82 g, 53%) as needles, mp 199–201 °C; R_f 0.57 (EtOAc) (Found: C, 77.9; H, 8.05; P, 9.3%; M^+, 338.1799. $C_{22}H_{27}OP$ requires C, 78.1; H, 8.05; P, 9.2%; *M*, 338.1799); ν_{max}/cm^{-1} ($CHCl_3$) 1436 (P–Ph) and 1180 (P=O); δ_H(250 MHz; $CDCl_3$) 8.0–7.3 (10 H, m, Ph_2PO), 5.5 (1 H, m, C=CH), 2.77 (1 H, ddd, *J* 2.5, 7.8 and 12.4, PCH), 2.4–1.2 (12 H, m) and 0.80 (3 H, t, *J* 7, Me); δ_C(63 MHz; $CDCl_3$) 134–127 (m, Ph_2PO), 48.9$^+$ (d, $^1J_{PC}$ 68, PCH), 28.4$^-$ (d, J_{PC} 7), 25.5$^-$, 22.8$^-$, 22.1$^-$, 20.8$^-$ and 13.7$^+$ (Me); *m*/*z* 338.2 (30%, M^+) and 84.0 (100).

anti,*syn*- and *syn*,*syn*-1-(1-diphenylphosphinoylbutyl)cyclohexane-1,2-diol 19

In a method similar to that used in the reaction of difluorostilbene **6**, 1-(1-diphenylphosphinoylbutyl)cyclohexene **18** (100 mg, 0.30 mmol), osmium trichloride (3 mg, 10 μmol), potassium carbonate (122 mg, 0.88 mmol), potassium ferricyanide (295 mg, 0.90 mmol), quinuclidine (5 mg, 50 μmol) and methanesulfonamide (55 mg, 58 mmol) gave a crude product. ^{1}H NMR showed that no starting material remained and that the ratio of diols[27] *anti*,*syn*-**19**:*syn*,*syn*-**19** was 65:35.

Dihydroxylation of β-diphenylphosphinoyl-γ-lactones

Dihydroxylation of lactone (*E*)-20. Osmium(III) chloride hydrate (3.6 mg, 12 μmol, 0.024 equiv.) was added to a stirred mixture of potassium ferricyanide (494 mg, 1.50 mmol, 3.0 equiv.), potassium carbonate (208 mg, 1.50 mmol, 3.0 equiv.), quinuclidine (1.7 mg, 15 μmol, 0.03 equiv.), methanesulfonamide (47 mg, 0.49 mmol, 1.0 equiv.), water (5 ml) and *t*-butyl alcohol (5 ml). After a few minutes stirring (to ensure the mixture was homogeneous), lactone (*E*)-**20** (181 mg, 0.510 mmol) was added as a solid and the reaction was stirred vigorously. After 41 h, anhydrous sodium sulfite (0.76 g, 6.0 mmol) was added and stirring was continued for a further hour. The reaction mixture was diluted with water (15 ml) and dichloromethane (15 ml). The layers were separated and the aqueous phase extracted with dichloromethane (3 × 15 ml). The combined organic extracts were washed with aqueous potassium hydroxide (2 M, 25 ml), water (25 ml) and brine (25 ml), then dried (Na_2SO_4). Evaporation under reduced pressure gave the crude product as a solid (142 mg, 73%). ^{1}H NMR showed

this to be a 62:38 mixture of *syn*:*anti* diastereoisomers. Flash column chromatography (followed by chromatotron purification of the mixed fractions), eluting with 3:2 ethyl acetate–hexane, gave firstly *(3RS,4SR,5SR)-4-diphenylphosphinoyl-5-[(1RS,2SR)-1,2-dihydroxy-1-methylpropyl]-3-methyltetrahydrofuran-2-one syn*,*syn*-**23** (62 mg, 31%) as rectangular prisms, mp 234–236 °C (from EtOAc–MeOH); R_f(EtOAc) 0.43; ν_{max}($CDCl_3$)/cm^{-1} 3570 (OH), 3435–3130 (H-bonded OH), 1775 (lactone C=O), 1590 (Ph), 1440 (PPh), 1180 and 1170 (P=O and C–O); δ_H(400 MHz; $CDCl_3$) 7.89–7.45 (10 H, m, Ph_2PO), 5.42 (1 H, s, MeCO*H*), 4.72 (1 H, dd, J_{HB} 7.6 and J_{PH} 1.5, PCH_BC*H*O), 3.96 (1 H, dq, J_{HOH} 2.1 and *J* 6.4, MeC*H*OH), 3.37 (1 H, tq, J_{PA} and J_{AB} 11.8, *J* 7.0, CH_AMe), 3.27 (1 H, ddd, J_{AB} 11.8, J_{HB} 7.6 and J_{PB} 6.2, PCH_BCH_AMe), 2.68 (1 H, d, J_{HOH} 2.1, MeCHO*H*), 1.05 (3 H, d, *J* 6.4, *Me*CHOH), 0.97 (3 H, s, *Me*COH) and 0.50 (3 H, d, *J* 7.0, CH_AMe); δ_C(100 MHz; $CDCl_3$) 177.5$^-$ ($^3J_{PC}$ 16.3, C=O), 132.8–128.9 (Ph_2PO), 83.9$^+$ (PCH*C*HO), 78.0$^-$ (Me*C*OH), 69.7$^+$ (Me*C*HOH), 46.0$^+$ ($^1J_{PC}$ 72.0, P*C*HCHMe), 35.4$^+$ (PCH*C*HMe), 18.5$^+$ (Me), 17.0$^+$ (Me) and 16.0$^+$ (Me); *m*/*z* 388 (<1%, M^+), 373 (2, M − Me), 343 (54, M − MeCHOH), 202 (100, Ph_2POH), 201 (48, Ph_2PO) and 77 (20, Ph) (Found: M^+, 388.1438. $C_{21}H_{25}O_5P$ requires *M*, 388.1440). The second compound to be eluted from the column was *(3RS,4SR,5SR)-4-diphenylphosphinoyl-5-[(1SR,2RS)-1,2-dihydroxy-1-methylpropyl]-3-methyltetrahydrofuran-2-one anti*,*syn*-**23** (36 mg, 18%) as rectangular prisms, mp 211–213 °C (from EtOAc–MeOH); R_f(EtOAc) 0.35; ν_{max}($CDCl_3$)/cm^{-1} 3565 (OH), 3455–3140 (H-bonded OH), 1770 (lactone C=O), 1600 (Ph), 1440 (PPh) and 1170 (P=O and C–O); δ_H(400 MHz; $CDCl_3$) 7.84–7.46 (10 H, m, Ph_2PO), 5.34 (1 H, s, MeCO*H*), 5.21 (1 H, dd, J_{HB} 8.0 and J_{PH} 2.0, PCH_BC*H*O), 3.73 (1 H, dq, J_{HOH} 9.2 and *J* 6.4, MeC*H*OH), 3.26 (1 H, dt, J_{AB} 12.0, J_{HB} and J_{PB} 7.8, PCH_BCH_AMe), 3.27 (1 H, tq, J_{PA} and J_{AB} 12.2, *J* 6.9, CH_AMe), 2.08 (1 H, d, J_{HOH} 9.2, MeCHO*H*), 1.29 (3 H, s, *Me*COH), 1.07 (3 H, d, *J* 6.4, *Me*CHOH) and 0.54 (3 H, d, *J* 6.9, CH_AMe); δ_C(100 MHz; $CDCl_3$) 177.8$^-$ ($^3J_{PC}$ 16.5, C=O), 132.9–129.1 (Ph_2PO), 80.7$^+$ (PCH*C*HO), 75.8$^-$ (Me*C*OH), 70.5$^+$ (Me*C*HOH), 45.8$^+$ ($^1J_{PC}$ 73.0, P*C*HCHMe), 35.9$^+$ (PCH*C*HMe), 18.6$^+$ (Me), 17.0$^+$ (Me) and 16.8$^+$ (Me); *m*/*z* 388 (<1%, M^+), 373 (1, M − Me), 343 (60, M − MeCHOH), 202 (100, Ph_2POH), 201 (58, Ph_2PO) and 77 (37, Ph) (Found: M^+, 388.1463. $C_{21}H_{25}O_5P$ requires *M*, 388.1440) (Found: C, 64.8; H, 6.4; P, 8.0. $C_{21}H_{25}O_5P$ requires C, 64.9; H, 6.5; P, 8.0%). The stereochemistry of the new chiral centre was assigned—and the stereochemistry of the other chiral centres was confirmed—by X-ray crystallography.

Dihydroxylation of lactone (*E*)-21

Using the same method as that used for (*E*)-**20** osmium(III) chloride hydrate (4.0 mg, 13 μmol, 0.027 equiv.), potassium ferricyanide (492 mg, 1.49 mmol, 3.0 equiv.), potassium carbonate (208 mg, 1.51 mmol, 3.0 equiv.), quinuclidine (2.6 mg, 23 μmol, 0.05 equiv.), methanesulfonamide (48 mg, 0.50 mmol, 1.0 equiv.), water (5 ml), *tert*-butyl alcohol (5 ml) and lactone (*E*)-**21** (185 mg, 0.501 mmol) gave, after 47 h, the crude product as a solid (184 mg, 91%). ^{1}H NMR showed this to be a mixture of 66:34 *syn*:*anti* diastereoisomers. Flash column chromatography (followed by chromatotron purification of the mixed fractions), eluting with 1:1 ethyl acetate–hexane, gave firstly *(3RS,4SR,5SR)-4-diphenylphosphinoyl-5-[(1RS,2SR)-1,2-dihydroxy-1-methylpropyl]-3-ethyltetrahydrofuran-2-one syn*,*syn*-**24** (85 mg, 42%) as rectangular prisms, mp 222–223 °C (from EtOAc–MeOH); R_f (EtOAc) 0.44; ν_{max}($CDCl_3$)/cm^{-1} 3570 (OH), 3415–3130 (H-bonded OH), 1775 (lactone C=O), 1590 (Ph), 1440 (PPh), 1180 and 1170 (P=O and C–O); δ_H(400 MHz; $CDCl_3$) 7.89–7.44 (10 H, m, Ph_2PO), 5.48 (1 H, s, MeCO*H*), 4.71 (1 H, dd, *J* 7.6 and J_{PH} 3.2, PCHC*H*O), 3.97 (1 H, dq, J_{HOH} 2.3 and *J* 6.4, MeC*H*OH), 3.42 (1 H, ddd, J_{HC} 11.3, *J* 7.6 and J_{PH} 6.2, $PCHCH_CEt$), 3.36 (1 H, tdd, J_{HC} and J_{PC} 11.3, J_{AC} 5.8 and J_{BC} 3.2, $CHCH_AH_BMe$), 2.72 (1 H, d, J_{HOH} 2.3, MeCHO*H*), 1.30 (1 H, dqd, J_{AB} 13.5, *J* 7.3 and J_{BC} 3.2, CH_AH_BMe), 1.05 (3 H, d, *J* 6.4, *Me*CHOH), 0.99 (3 H, s, *Me*COH), 0.58 (3 H, t, *J* 7.3, CH_AH_BMe) and 0.42 (1 H, dquintet, J_{AB} 13.5, *J* and J_{BC} 6.9, CH_AH_BMe); δ_C(100 MHz; $CDCl_3$) 176.5$^-$ ($^3J_{PC}$ 15.2, C=O), 132.9–129.0 (Ph_2PO), 83.7$^+$ (PCH*C*HO), 77.9$^-$ (Me*C*OH), 69.8$^+$ (Me*C*HOH), 41.0$^+$ (PCH*C*HEt), 40.4$^+$ ($^1J_{PC}$ 72.2, P*C*HCHEt), 22.0$^-$ (*C*H_2Me), 18.5$^+$ (Me), 16.0$^+$ (Me) and 9.0$^+$ (CH_2Me); *m*/*z* 387 (1%, [M − Me]$^+$), 357 (40, M − MeCHOH), 202 (100, Ph_2POH), 201 (51, Ph_2PO) and 77 (41, Ph) (Found: [M − Me]$^+$, 387.1361. $C_{22}H_{27}O_5P$ requires *M* − Me, 387.1361). The stereochemistry of the new chiral centre was assigned by ^{1}H NMR correlation with lactone *syn*,*syn*-**23**. The second compound to be eluted from the column was *(3RS,4SR,5SR)-4-diphenylphosphinoyl-5-[(1SR,2RS)-1,2-dihydroxy-1-methylpropyl]-3-ethyltetrahydrofuran-2-one anti*,*syn*-**24** (52 mg, 26%) as rectangular prisms, mp 203–205 °C (from EtOAc–MeOH); R_f(EtOAc) 0.32; ν_{max}($CDCl_3$)/cm^{-1} 3565 (OH), 3445–3150 (H-bonded OH), 1775 (lactone C=O), 1590 (Ph), 1440 (PPh) and 1170 (P=O and C–O); δ_H(400 MHz; $CDCl_3$) 7.83–7.45 (10 H, m, Ph_2PO), 5.37 (1 H, s, MeCO*H*), 5.17 (1 H, dd, *J* 8.0 and J_{PH} 5.3, PCHC*H*O), 3.72 (1 H, dq, J_{HOH} 9.3 and *J* 6.4, MeC*H*OH), 3.43 (1 H, dt, J_{HC} 10.8, *J* and J_{PH} 8.4, $PCHCH_CEt$), 3.08 (1 H, dddd, J_{PC} 13.7, J_{HC} 10.7, J_{AC} 5.4 and J_{BC} 4.2, $CHCH_AH_BMe$), 2.30 (1 H, d, J_{HOH} 9.3, MeCHO*H*), 1.35 (1 H, dqd, J_{AB} 12.3, *J* 7.1 and J_{BC} 4.2, CH_AH_BMe), 1.29 (3 H, s, *Me*COH), 1.08 (3 H, d, *J* 6.4, *Me*CHOH), 0.59 (3 H, t, *J* 7.0, CH_AH_BMe) and 0.53 (1 H, dquintet, J_{AB} 12.3, J_{AC} and *J* 6.5, CH_AH_BMe); δ_C(100 MHz; $CDCl_3$) 176.9$^-$ ($^3J_{PC}$ 14.2, C=O), 132.8–129.0 (Ph_2PO), 81.1$^+$ (PCH*C*HO), 75.8$^-$ ($^3J_{PC}$ 1.6, Me*C*OH), 70.8$^+$ (Me*C*HOH), 41.7$^+$ (PCH*C*HEt), 40.5$^+$ ($^1J_{PC}$ 72.5, P*C*HCHEt), 22.1$^-$ (*C*H_2Me), 19.0$^+$ (Me), 16.8$^+$ (Me) and 9.1$^+$ (CH_2Me); *m*/*z* 402 (<1%, M^+), 384 (2, M − H_2O), 357 (41, M − MeCHOH), 219 (25, $Ph_2PO_2H_2$), 202 (100, Ph_2POH), 201 (59, Ph_2PO) and 77 (23, Ph) (Found: M^+, 402.1586. $C_{22}H_{27}O_5P$ requires *M*, 402.1596) (Found: C, 65.7; H, 6.8; P, 7.7. $C_{22}H_{27}O_5P$ requires C, 65.7; H, 6.8; P, 7.7%). The stereochemistry of the new chiral centre was assigned by ^{1}H NMR correlation with lactone *anti*,*syn*-**23**.

Dihydroxylation of lactone (*E*)-22

Using the same method as that used for (*E*)-**20** osmium(III) chloride hydrate (4.5 mg, 15 μmol, 0.03 equiv.), potassium ferricyanide (495 mg, 1.50 mmol, 3.0 equiv.), potassium carbonate (206 mg, 1.49 mmol, 3.0 equiv.), quinuclidine (1.7 mg, 15 μmol, 0.03 equiv.), methanesulfonamide (48 mg, 0.50 mmol, 1.0 equiv.), water (5 ml), *tert*-butyl alcohol (5 ml) and lactone (*E*)-**22** (215 mg, 0.501 mmol) gave, after 66.5 h, the crude product. Flash column chromatography, eluting with ethyl acetate, efficiently removed baseline impurities to give the *lactone* **25** as a solid (179 mg, 77%). ^{1}H NMR showed this to be a mixture of 54:46 *syn*:*anti* diastereoisomers. Chromatotron separation of the diastereoisomers, eluting with 1:1 ethyl acetate–hexane, gave firstly *(3RS,4SR,5SR)-3-benzyl-4-diphenylphosphinoyl-5-[(1RS,2SR)-1,2-dihydroxy-1-methylpropyl]-tetrahydrofuran-2-one syn*,*syn*-**25** (75 mg, 32%) as rectangular prisms, mp 216–217 °C (from EtOAc–MeOH); R_f(EtOAc) 0.45; ν_{max}($CDCl_3$)/cm^{-1} 3570 (OH), 3400–3130 (H-bonded OH), 1775 (lactone C=O), 1590 (Ph), 1440 (PPh) and 1170 (P=O and C–O); δ_H(400 MHz; $CDCl_3$) 7.71–6.79 (15 H, m, Ph_2PO and Ph), 5.66 (1 H, s, MeCO*H*), 4.40 (1 H, dd, *J* 7.6 and J_{PH} 6.9, PCHC*H*O), 3.95 (1 H, dq, J_{HOH} 3.3 and *J* 6.4, MeC*H*OH), 3.56 (1 H, dddd, J_{PC} 14.5, J_{HC} 9.3, J_{AC} 5.9 and J_{BC} 3.8, $CHCH_AH_BPh$), 3.31 (1 H, dt, J_{HC} 9.3, *J* and J_{PH} 7.7, $PCHCH_CBn$), 2.97 (1 H, dd, J_{AB} 14.4 and J_{BC} 3.8, CH_AH_BPh), 2.94 (1 H, d, J_{HOH} 3.3, MeCHO*H*), 1.76 (1 H, dd, J_{AB} 14.4 and J_{AC} 5.9, CH_AH_BPh), 0.99 (3 H, d, *J* 6.4, *Me*CHOH) and 0.99 (3 H, s, *Me*COH); δ_C(100 MHz; $CDCl_3$) 176.2$^-$ ($^3J_{PC}$ 12.3, C=O), 135.5–127.3 (Ph_2PO and Ph), 84.1$^+$ (PCH*C*HO), 77.2$^-$

($^3J_{PC}$ 2.7, Me*C*OH), 69.9$^+$ (Me*C*HOH), 42.3$^+$ (PCH*C*HBn), 40.0$^+$ ($^1J_{PC}$ 70.4, P*C*HCHBn), 34.9$^-$ (*C*H_2Ph), 18.9$^+$ (Me) and 16.1$^+$ (Me); *m*/*z* 464 (1%, M$^+$), 446 (3, M − H_2O), 419 (25, M − MeCHOH), 202 (81, Ph_2POH), 201 (58, Ph_2PO), 105 (100, C_8H_9), 91 (37, C_7H_7) and 77 (46, Ph) (Found: M$^+$, 464.1726. $C_{27}H_{29}O_5P$ requires *M*, 464.1753) (Found: C, 69.2; H, 6.4; P, 6.7. $C_{27}H_{29}O_5P$ requires C, 69.8; H, 6.3; P, 6.7%). The stereochemistry of the new chiral centre was assigned by ^{1}H NMR correlation with lactone *syn*,*syn*-**23**. The second compound to be eluted from the column was *(3RS,4SR,5SR)-3-benzyl-4-diphenylphosphinoyl-5-[(1SR,2RS)-1,2-dihydroxy-1-methylpropyl]tetrahydrofuran-2-one anti*,*syn*-**25** (72 mg, 31%) as needles, mp 200–201 °C (from EtOAc–MeOH); R_f(EtOAc) 0.36; $\nu_{max}(CDCl_3)/cm^{-1}$ 3565 (OH), 3435–3150 (H-bonded OH), 1775 (lactone C=O), 1590 (Ph), 1495 (Ph), 1440 (PPh) and 1170 (P=O and C–O); δ_H(400 MHz; $CDCl_3$) 7.73–6.79 (15 H, m, Ph_2PO and Ph), 5.59 (1 H, s, MeCO*H*), 4.87 (1 H, t, *J* and J_{PH} 8.3, PCHC*H*O), 3.67 (1 H, dq, J_{HOH} 9.3 and *J* 6.4, MeC*H*OH), 3.41 (1 H, q, J_{HC}, *J* and J_{PH} 8.4, PC*H*CH_CBn), 3.33 (1 H, ddt, J_{PC} 13.9, J_{HC} 8.8, J_{AC} and J_{BC} 5.1, C$H_C$$CH_AH_B$Ph), 2.41 (1 H, d, J_{HOH} 9.3, MeCHO*H*), 2.93 (1 H, dd, J_{AB} 14.3 and J_{BC} 4.5, CH_AH_BPh), 1.96 (1 H, dd, J_{AB} 14.3 and J_{AC} 5.6, C$H_A$$H_B$Ph), 1.28 (3 H, s, *Me*COH) and 1.08 (3 H, d, *J* 6.4, *Me*CHOH); δ_C(100 MHz; $CDCl_3$) 176.5$^-$ ($^3J_{PC}$ 11.2, C=O), 135.4–127.4 (Ph_2PO and Ph), 82.2$^+$ (PCH*C*HO), 75.6$^-$ ($^3J_{PC}$ 2.4, Me*C*OH), 71.2$^+$ (Me*C*HOH), 43.0$^+$ (PCH*C*HBn), 40.6$^+$ ($^1J_{PC}$ 70.4, P*C*HCHBn), 35.1$^-$ ($^3J_{PC}$ 2.5, *C*H_2Ph), 19.5$^+$ (Me) and 16.9$^+$ (Me); *m*/*z* 446 (2%, M − H_2O), 419 (5, M − MeCHOH), 202 (29, Ph_2POH), 201 (24, Ph_2PO), 105 (100, C_8H_9), 91 (24, C_7H_7) and 77 (58, Ph) (Found: [M − H_2O]$^+$, 446.1646. $C_{22}H_{27}O_5P$ requires *M* − H_2O, 446.1647) (Found: C, 69.1; H, 6.4; P, 6.5. $C_{27}H_{29}O_5P$ requires C, 69.8; H, 6.3; P, 6.7%). The stereochemistry of the new chiral centre was assigned by ^{1}H NMR correlation with lactone *anti*,*syn*-**23**.

Attempted racemic dihydroxylation of acetate *anti*-26

Under the same conditions used for the reaction of difluorostilbene **6**, osmium(III) chloride (2 mg, 0.007 mmol), acetate *anti*-**26** (110 mg, 0.25 mmol), potassium ferricyanide (251 mg, 0.8 mmol), potassium carbonate (103 mg, 0.75 mmol), quinuclidine (1 mg, 0.01 mmol) and methanesulfonamide (30 mg, 0.3 mmol) in 1:1 *tert*-butyl alcohol–water (5 ml) gave the crude product as an oil after 48 h at room temperature which contained only acetate *anti*-**26** (by TLC and ^{1}H NMR).

Attempted racemic dihydroxylation of acetate *syn*-26

Under the same conditions used for the reaction of difluorostilbene **6**, osmium(III) chloride (2 mg, 0.007 mmol), acetate *syn*-**26** (95 mg, 0.2 mmol), potassium ferricyanide (219 mg, 0.7 mmol), potassium carbonate (92 mg, 0.7 mmol), quinuclidine (1 mg, 0.01 mmol) and methanesulfonamide (31 mg, 0.3 mmol) in 1:1 *tert*-butyl alcohol–water (5 ml) gave the crude product as an oil after 48 h at room temperature which contained only acetate *syn*-**26** (by TLC and ^{1}H NMR).

(2*S*,4*S*,5*R*)-2-[(1′*S*)-1′,2′-dihydroxyethyl]-4-methyl-5-phenyl-3-*p*-tolylsulfonyloxazolidine *syn*-30 and (2*S*,4*S*,5*R*)-2-[(1′*R*)-1′,2′-dihydroxyethyl]-4-methyl-5-phenyl-3-*p*-tolylsulfonyloxazolidine *anti*-30

Under the same conditions used for the reaction of difluorostilbene **6**, osmium(III) chloride (20 mg, 0.07 mmol), alkenyl oxazolidine *cis*-**29** (8.0 g, 23.3 mmol), potassium ferricyanide (24.5 g, 74.4 mmol), potassium carbonate (9.6 g, 69.6 mmol) and quinuclidine (185 mg, 1.7 mmol) in *tert*-butyl alcohol–water (1:1; 200 ml) gave the crude product as an oil after 20 h at room temperature. Purification by chromatography on silica with EtOAc–hexane (1:1) as eluant gave a 72:28 ratio (by ^{1}H NMR) of 1,2-diols *syn*-**30** and *anti*-**30** (7.75 g, 88%) as a non-crystallisable foam, R_f(1:1 EtOAc–hexane) 0.2; $[a]_D^{20}$ +18.6 (*c* 0.9 in $CHCl_3$) (Found: C, 60.1; H, 6.3; N, 3.5%; M$^+$ + H, 378.1378. $C_{19}H_{23}NO_5S$ requires C, 60.5; H, 6.1; N, 3.7%; *M* + H, 378.1375); $\nu_{max}(CHCl_3)/cm^{-1}$ 3692 (OH), 3668 (OH), 1598 (C_6H_4), 1495 (C_6H_4), 1347 (SO_2N) and 1164 (SO_2N); δ_H(400 MHz, $CDCl_3$) 7.84 (2 H, d, *J* 8.3, *o*-$C_6H_4SO_2^{syn}$), 7.83 (2 H, d, *J* 8.5, *o*-$C_6H_4SO_2^{anti}$), 7.42 (4 H, d, *J* 8.0, 2 × *m*-$C_6H_4SO_2$), 7.37–7.07 (10 H, m, 2 × Ph), 5.13 (1 H, d, *J* 3.5, $OCHN^{anti}$), 5.06 (1 H, d, *J* 6.3, $OCHN^{syn}$), 4.24 (1 H, d, *J* 5.6, $PhCHO^{anti}$), 4.18 (1 H, d, *J* 5.4, $PhCHO^{syn}$), 4.14–3.83 (8 H, m, 2 × C*H*N, 2 × C*H*OH and 2 × CH_2OH), 3.70* (1 H, br s, OH^{anti}), 2.92* (1 H, br s, OH^{syn}), 2.47 (6 H, s, 2 × C_6H_4Me), 0.87 (3 H, d, *J* 6.9, CHMe^{syn}) and 0.84 (3 H, d, *J* 6.8, CHMe^{anti}); δ_C(50 MHz, $CDCl_3$) 144.9$^-$ (*ipso*-$C_6H_4SO_2^{syn}$), 144.8$^-$ (*ipso*-$C_6H_4SO_2^{anti}$), 134.7$^-$(^{anti}), 134.6$^-$(^{syn}), 133.8$^-$(^{anti}), 133.6$^-$(^{syn}), 130.2–125.7$^+$ (C_6H_4Me and Ph), 90.7$^+$ ($OCHN^{anti}$), 90.6$^+$ ($OCHN^{syn}$), 81.1$^+$ ($PhCHO^{anti}$), 80.9$^+$ ($PhCHO^{syn}$), 74.3$^+$ ($CHOH^{syn}$), 73.35$^+$ ($CHOH^{anti}$), 62.9$^-$ (CH_2OH^{anti}), 62.5$^-$ (CH_2OH^{syn}), 59.0$^+$ (CHN^{syn}), 58.5$^+$ (CHN^{anti}), 21.5$^+$ (2 × C_6H_4Me), 17.1$^+$ (CHMe^{syn}) and 17.0$^+$ (CHMe^{anti}); *m*/*z* 378 (60%, M$^+$ + H), 316 (90, M − $CHOHCH_2OH$), 288 (70) and 91 (100, C_6H_4Me).

Formation of dithianes

Boron trifluoride–diethyl ether (1.5 mmol) was added dropwise to a stirred solution of the acetal (1.0 mmol) and propane-1,3-dithiol (5 mmol) in CH_2Cl_2 (5 ml) under argon at room temperature. After the required length of time (16–72 h) at room temperature, water (5 ml) was added and the layers separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 10 ml). The combined organic extracts were washed with 10% sodium hydroxide (3 × 10 ml), dried (Na_2SO_4) and evaporated under reduced pressure to give the crude product.

Conversion of 1,2-diols *syn*-30 and *anti*-30 into the dithiane (*S*)-31. By the above method, a solution of a 72:28 ratio of 1,2-diols *syn*-**30** and *anti*-**30** (169 mg, 0.45 mmol), boron trifluoride–diethyl ether (60 μl, 0.5 mmol) and propane-1,3-dithiol (250 μl, 2.5 mmol) in CH_2Cl_2 (7.5 ml) gave the crude product as an oil after 48 h at room temperature. Purification by chromatography on silica with EtOAc as eluant gave the dithiane (*S*)-**31** (27 mg, 34%) as a colourless oil R_f(EtOAc) 0.4; $[a]_D^{20}$ −2.6 (*c* 1.2 in MeOH; 44% ee) [lit.,[41] $[a]_D^{20}$ +6.0 (*c* 1.08 in MeOH) for dithiane (*R*)-**31**].

Acknowledgements

We thank the EPSRC for grants (to J. E., H. J. M., A. N., P. O'B. and P. W.), Zeneca Fine Chemicals for grants (to J. E. and P. W.), and Rhône-Poulenc-Rorer for a grant (to H. J. M.). We dedicate this paper with gratitude, affection and respect to Ralph Raphael. All the authors worked in the Lensfield Road laboratories when Ralph was a familiar figure there.

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