Asymmetric dihydroxylation of allylic phosphine oxides

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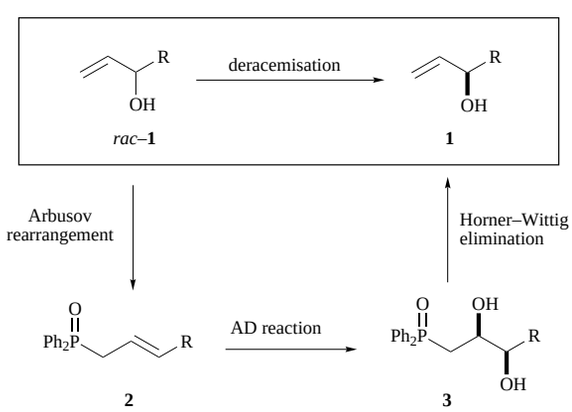
Diphenylphosphinoyl diols have been produced by asymmetric dihydroxylation (AD) of allylic phosphine oxides and have been shown to be useful synthetic intermediates. The results of this study are discussed in terms of the model which has been proposed by Sharpless to explain the enantioselectivity of his AD reaction. The dihydroxylation results are thus of both mechanistic and synthetic value.

Previously,[1] we have described the synthesis of optically active terminal allylic alcohols by Horner–Wittig elimination[2] of diphenylphosphinoyl diols, which were produced using the Sharpless asymmetric epoxidation reaction and a controlled Payne rearrangement. We now report a more direct approach to similar allylic alcohols using another reagent-based approach, the Sharpless asymmetric dihydroxylation.[3] In this paper, we describe some experiments[4] which have allowed the asymmetric dihydroxylation of prochiral allylic phosphine oxides **2** to be optimised. Our results can be explained in terms of the models proposed by Sharpless[5a,b] and Corey[5c] which rationalise the enantioselectivity of the asymmetric dihydroxylation reaction. Recently, diphenylphosphinoyl diols have been established as useful precursors of optically active cyclopropyl ketones[6] and ligands[7] for asymmetric catalysis.

Allylic phosphine oxides **2** are most usually[8] synthesized using the [2,3] sigmatropic Arbusov rearrangement[9] of (racemic) allylic alcohols **1**. Asymmetric dihydroxylation of allylic phosphine oxides **2** and Horner–Wittig elimination should return enantiomerically-enriched samples of the same allylic alcohols **1** (Scheme 1). Deracemisations of carbonyl

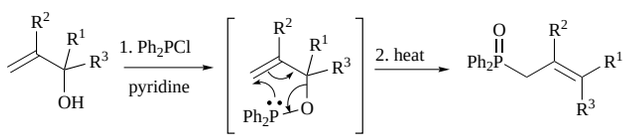


Scheme 1

compounds[10] (by asymmetric protonation of enolates and silyl enol ethers), phosphine oxides[11] and biaryls[12] are also known.

Synthesis of prochiral diphenylphosphinoyl alkenes

Allylic phosphine oxides **2a** and **c–g** were synthesised using the Arbusov rearrangement[9] which allows control over the position and geometry of the new carbon–carbon double bond. Allylic phosphinates **4**, synthesized *in situ* by treating allylic alcohols[13] **1** with chlorodiphenylphosphine and pyridine, rearranged thermally to give allylic phosphine oxides **2a** and **c–g** which could be recrystallised to give the pure *E* isomers in moderate yield (Scheme 2 and Table 1). The stereoselectivity of other [2,3]

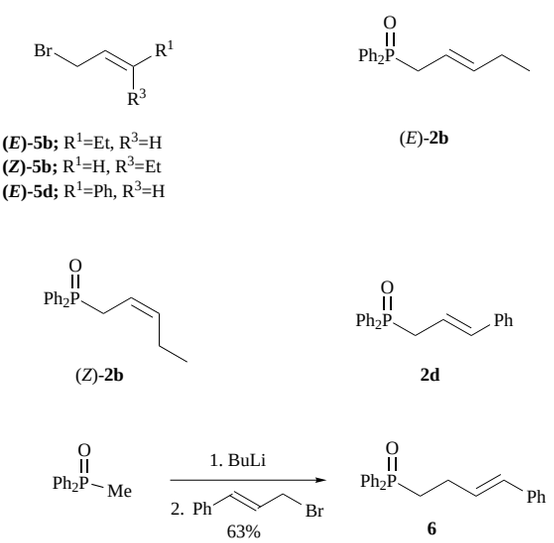


1 **4** **2**

Scheme 2

sigmatropic rearrangements depends similarly on substitution.[14]

Alternatively, treating *ca.* 85:15 mixtures of bromides (*E*)- and (*Z*)-**5b** with Ph_2PLi (prepared according to the method of Ashby[15]), followed by oxidation with aqueous hydrogen peroxide solution,[16] gave mixtures of the allylic phosphine oxides **2b** which could be purified by a single recrystallisation (Table 2, entries 1, 2). In a similar way, we were able to synthesize cinnamyl phosphine oxide **2d** (entry 3): the reaction proceeded in quantitative yield (with no detectable S_N2' side-products) on a 30-g scale, and was a useful alternative to the Arbusov rearrangement which was rather low yielding in this case. We also synthesized homoallylic phosphine oxide **6** by treating lithiated methyldiphenylphosphine oxide with cinnamyl bromide (Scheme 3).



Scheme 3

Asymmetric dihydroxylation of prochiral allylic phosphine oxides using commercially available AD-mixes

As a starting point for our investigations into the asymmetric dihydroxylation of diphenylphosphinoyl alkenes, we dihydroxylated five prochiral allylic phosphine oxides **2** using

Table 1 Synthesis of allylic phosphine oxides **2** by Arbusov rearrangement

Entry	Starting material **1**	Method[a]	R^1	R^2	R^3	Crude ratio[b] *E*:*Z*	Yield[c] **2** (%)
1	**a**	A	Me	H	H	95:5	45
2	**c**	A	Bu	H	H	97:3	43
3	**d**	B	Ph	H	H	94:6	41
4	**e**	B	Ph	H	Me	91:9	19
5	**f**	A	Bu	Me	H	94:6	31
6	**g**	A	c-Hex	Me	H	85:15	35

[a] Methods: A: (i) Ph_2PCl (1.0 equiv.), pyridine (1.0 equiv.), ether; (ii) toluene, heat; B: (i) Ph_2PCl (1.05 equiv.), pyridine; (ii) pyridine, heat. [b] By 400 MHz ^1H NMR. [c] Yield of pure *E* isomer after recrystallisation.

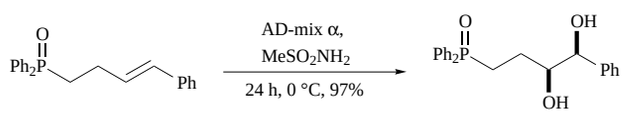
Table 2 Synthesis of allylic phosphine oxides **2** by allylation of lithium diphenylphosphide and oxidation

Entry	Starting material	R^1	R^2	R^3	Product	Yield (%)
1	(*E*)-**5b**[a]	Et	H	H	(*E*)-**2b**	59[b]
2	(*Z*)-**5b**[a]	H	H	Et	(*Z*)-**2b**	45[b]
3	(*E*)-**5d**	Ph	H	H	**2d**	102

[a] Available as a *ca.* 85:15 mixture of isomers. [b] Yield of single isomer after recrystallisation.

the standard procedure and reagents† recommended by Sharpless (Table 3).[17] Most of the reactions proceeded rather sluggishly and took 3–7 days to reach completion.‡ However, we were able to isolate diphenylphosphinoyl diols **3** in moderate to good yields.

In contrast, the dihydroxylation of homoallylic phosphine oxide **6** gave a 97% yield of diol **7** with >95% ee (determined by comparison with a racemic sample prepared using our racemic dihydroxylation conditions[18]) after just 24 h (Scheme 4). Since

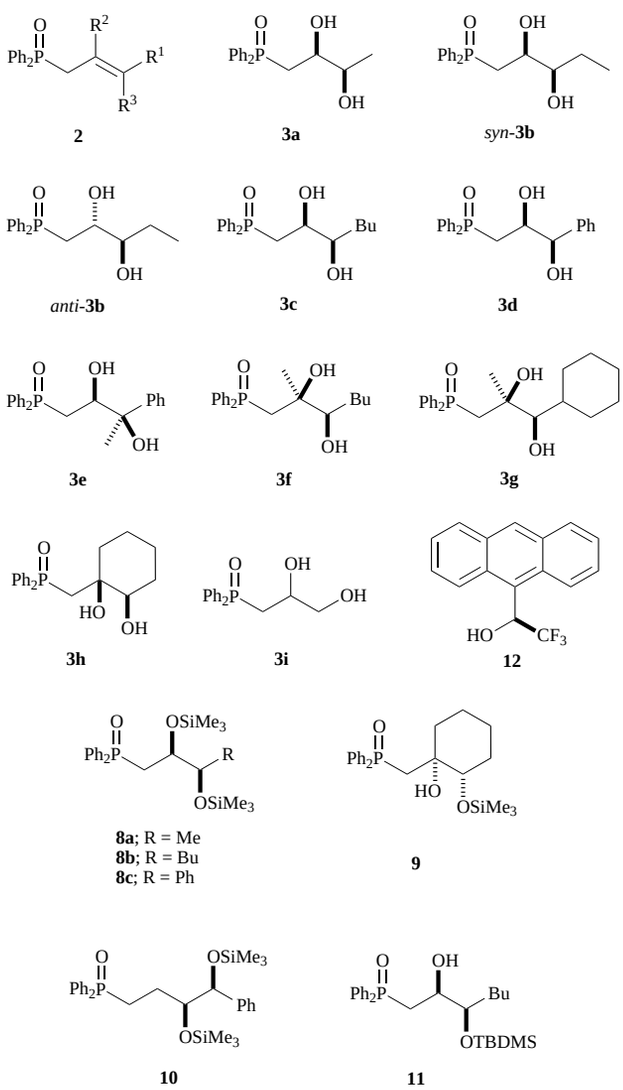


6 **7**

Scheme 4

homoallylic phosphine oxide **6** and allylic phosphine oxides **2a** and **c,d** all contain the potentially coordinating diphenylphosphinoyl group, it is unlikely that the reactions of the allylic phosphine oxides are slowed down by coordination of the phosphinoyl group to the osmium catalyst.[19] Therefore, we suggest that the alkene in allylic phosphine oxides **2** is deactivated by the electron-withdrawing nature or the size of the diphenylphosphinoyl group.

The enantiomeric excesses of diols **3a**, **c,d** and **h** were generally determined by integration of the 400 MHz ^1H NMR spectra of silyl ethers **8** and **9** (see entries 1–5, Table 4 for details) in the presence Pirkle's chiral solvating agent,[20] (*R*)-1-(9-anthryl)-2,2,2-trifluoroethanol **12**. The trimethylsilyl peaks



† The standard reagents are commericially available from Aldrich Chemical Co. as AD-mixes α and β.
‡ Mechanical stirring was necessary on a large scale.

Table 3 Asymmetric dihydroxylation of allylic phosphine oxides using available AD mixes

Entry	Starting material **2**	R^1	R^2	R^3	Method[a]	Time	Product	Yield (%)	Ee (%)
1	**a**	Me	H	H	A	7 d	*ent*-**3a**	84	10[b]
2	**c**	Bu	H	H	A	3 d	*ent*-**3c**	51[c]	49
3	**d**	Ph	H	H	A	5 d	*ent*-**3d**	66	74
4	**h**	$-(CH_2)_4-$		H	A	3 d	*ent*-**3h**	49	18[b]
5	**h**	$-(CH_2)_4-$		H	B	3 d	**3h**	62	14[b]
6	**i**	H	H	H	A[f]	6 d[g]	**3i**	*d*	*e*

[a] Methods: A: AD-mix α (1.4 g $mmol^{-1}$), $MeSO_2NH_2$ (1.0 equiv.), 0 °C; B: AD-mix β (1.4 g $mmol^{-1}$), $MeSO_2NH_2$ (1.0 equiv.), 0 °C. [b] Sense of asymmetric induction uncertain. [c] 61% yield based on recovered starting material. [d] 53% completion by ^1H NMR. [e] Not determined. [f] Methanesulfonamide omitted. [g] 3 days at 0 °C and 3 days at 20 °C.

Table 4 Silylations of diphenylphosphinoyl diols

Entry	Starting material	Method[a]	Product	Yield (%)
1	**3a**	A	**8a** (R = Me)	63
2	**3c**	A	**8b** (R = Bu)	95
3	**3d**	A	**8c** (R = Ph)	73
4	*ent*-**3h**	A	**9**	86
5	**7**	A	**10**	53
6	**3c**	B	**11**	66

[a] Methods: A: Me_3SiCl, Et_3N, CH_2Cl_2; B: TBDMSOTf, 2,6-dimethylpyridine, CH_2Cl_2.

appeared at least 1 ppm upfield of the other signals and provided a useful handle for the determination of enantiomeric excess.

The enantiomeric excesses of diols **3a** and **c,d** were rather disappointing when compared with those reported for other dihydroxylations (entries 1–3, Table 3).[3,17] Within this series of compounds, the enantiomeric excess of diols **3** increases with the ability of the group *trans* to phosphorus to be stabilised by solvophobic and π-interactions: varying this group from methyl to butyl to phenyl caused the enantiomeric excess of diols **3** to increase from 10 to 49 to 74%. We suggest that the group *trans* to phosphorus (and not the diphenylphosphinoylmethyl group §) is bound in the pocket formed by the chiral ligand (Fig. 1).[5] This hypothesis neatly rationalises the variation of the enantiomeric excesses of diols **3a** and **c,d**, and suggests that their absolute stereochemistry can be deduced by placing the substituent *trans* to phosphorus in the attractive 'south-western' quadrant of Sharpless's model.[3] Substrate[22] **2i**, which lacks a substituent *trans* to phosphorus, does not enjoy the benefits of ligand-accelerated catalysis and was dihydroxylated very slowly indeed (entry 6, Table 3).

Allylic phosphine oxide[23] **2h** has substituents *trans* and *gem* to phosphorus which can compete for the cleft of the chiral ligand. In this case, competition for the cleft is reflected by the enantioselectivity of the reaction: the asymmetric induction is low, presumably because the two substituents (which both form part of the same six-membered ring) are able to compete on even terms for the L-shaped cleft of the chiral ligand (entries 4, 5, Table 3).

The diphenylphosphinoylmethyl group, like other large allylic substituents,[3] has a detrimental effect on the enantioselectivity of the AD reaction.[24] We suggest that a bulky allylic substituent *trans* to the stabilised group (which points away from the 'working' alkaloid unit) interferes sterically with the by-stander alkaloid portion of the 'dimeric' ligands (Fig. 1).

Optimisation of the conditions for the asymmetric dihydroxylation of allylic phosphine oxides

The enantiomeric excess of the diol **3d** was improved from 74% ee with 1 mol% ligand to 85% ee with more ligand (Table 5). There was also a marked improvement in the yield of the reaction. We suggest that increasing the quantity of chiral ligand causes the reaction of (achiral) uncomplexed osmium tetroxide with allylic phosphine oxide **2d** to become insignificant, so the enantiomeric excess of the diol **3d** increases asymptotically towards 85% ee as more material is drawn through the enantioselective pathway.

We also studied some asymmetric dihydroxylations catalysed by the 'monomeric' ligands DHQD-CLB and DHQD-PHN. In these experiments, we mixed the allylic phosphine oxide with all of the ingredients needed for the dihydroxylation except the osmium source. After vigorous stirring for 30 min at room temperature, osmium trichloride (1 mol%) was added.¶ The reactions were monitored by TLC and, after 1–5 days, we were able to isolate good to excellent yields of diphenylphosphinoyl diols **3a–h**. Enantiomeric excesses were determined by integration of the ^{1}H NMR spectra of silyl ethers **8** and **9** in the presence of Pirkle's chiral solvating agent **12**, or by preparing the Mosher's esters[26] of alcohols[6] **13**. Our results are presented in Table 6.

With *trans*-disubstituted allylic phosphine oxides **2a–d**, the monomeric ligands DHQD-CLB and DHQD-PHN offered substantial advantages over the phthalazine ligands contained in the AD mixes: in each case, we isolated higher yields of diphenylphosphinoyl diols **3a–d** with higher enantiomeric excesses than under the standard AD reaction conditions (compare entries 1–3, Table 3 with entries 1–7, Table 6).

Again, the enantiomeric excesses of the diols **3a–d** improved with the ability of the group *trans* to phosphorus to be stabilised by solvophobic and π-interactions: the enantiomeric excesses (with the ligand DHQD-CLB) increased steadily from 46 to 86% ee as the R^1 group was changed from methyl to ethyl to butyl to phenyl. Fig. 2 rationalises this result in terms of Sharpless's model:[5a,b] in particular, favourable face-to-face interactions between the phenyl ring of the substrate and

§ The sense of the enantioselectivity of the AD reactions of 1,1 *gem*-disubstituted allylic phosphine oxides suggests that the diphenylphosphinoylmethyl group cannot fit snugly into the L-shaped cleft formed by the dihydroxylation catalyst.[21]

Table 5 Asymmetric dihydroxylation of allylic phosphine oxide **2d**

Entry	Reagents[a]	$DHQD_2$-PHAL (mol%)	Yield **3d** (%)	Ee (%)
1	A	1.0[b]	66	74
2	B	2.5	72	84
3	B[c]	5.0	49	85
4	B	7.5	94	85

[a] Reagents: A. AD-mix α, $MeSO_2NH_2$ (1.0 equiv.); B. $OsCl_3$ (1.5 mol%), K_2CO_3 (3.0 equiv.), $K_3Fe(CN)_6$ (3.0 equiv.), $MeSO_2NH_2$ (1.0 equiv.). [b] AD-mix α contains DHQ_2-PHAL. [c] AD mix β was enriched with $OsCl_3$ and $DHQD_2$-PHAL.

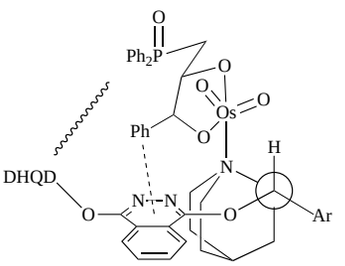
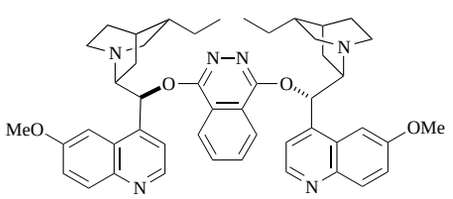
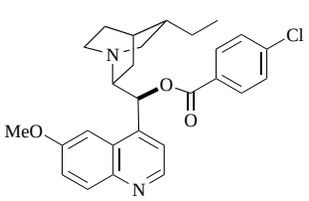


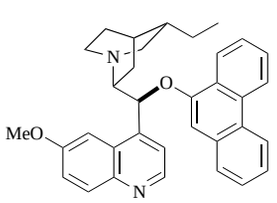
Fig. 1



$DHQD_2$-PHAL
(AD-mix β)



DHQD-CLB



DHQD-PHN

¶ Sharpless has reported that $OsCl_3$ is a suitable osmium source in AD reactions.[25]

Table 6 Asymmetric dihydroxylation of allylic phosphine oxides using 'monomeric' ligands

Entry	Starting material	R^1	R^2	R^3	Chiral ligand	Ligand (mol%)	Yield **3** (%)	Ee (%)
1	**2a**	Me	H	H	DHQD-CLB	15	94	46
2	(*E*)-**2b**	Et	H	H	DHQD-CLB	15	103	76[a]
3	**2c**	Bu	H	H	DHQD-CLB	2	64	58
4	**2c**	Bu	H	H	DHQD-CLB	15	57[b]	76
5	**2c**	Bu	H	H	DHQD-PHN	25	70	75
6	**2d**	Ph	H	H	DHQD-CLB	15	79	86
7	**2d**	Ph	H	H	DHQD-PHN	25	79	88
8	(*Z*)-**2b**	H	H	Et	DHQD-CLB	15	55	22[a]
9	**2e**	Ph	H	Me	DHQD-CLB	15	64	42
10	**2f**	Bu	Me	H	DHQD-CLB	15	103	74
11	**2g**	c-Hex	Me	H	DHQD-CLB	15	96	84
12	**2h**	$-(CH_2)_4-$		H	DHQD-CLB	15	60	62[c]
13	**2h**	$-(CH_2)_4-$		H	DHQD-PHN	25	62	38[c]

[a] Absolute configuration at chiral centre γ to phosphorus shown to be the same by conversion into a common intermediate **13** (R = Et).[30] [b] Isolated in 90% yield on a 6.5 g scale with mechanical stirring. [c] Absolute configuration uncertain.

Table 7 Attempted Horner–Wittig eliminations

Entry	Starting materials	Reagents[a]	Result
1	**11**	A	Ketone **17a** isolated in 26% yield
2	*ent*-**3d**	A	Ketone **17b** isolated in 31% yield
3	**3d**	B	Starting material only by NMR
4	**3d**	C	Ketone **17b** isolated in 39% yield

[a] Reagents: A. KOH, DMSO, 55 °C; B. DBU, DMSO, 50 °C; C. TBAF, THF, heat.

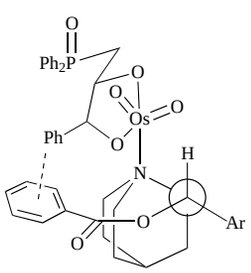


Fig. 2

the ligand are possible without forcing the extremely large diphenylphosphinoylmethyl group into a sterically unfavourable position.

High quantities of chiral ligand (10–25 mol%) were necessary for optimal enantiomeric excesses: reduction of the amount of DHQD-CLB to just 2 mol% compromised the enantiomeric excess of diol **3c** (compare entries 3 and 4, Table 6). Again, we believe that higher levels of ligand channel a greater proportion of the allylic phosphine oxide **2c** through the enantioselective amine-catalysed pathway.

We also studied the asymmetric dihydroxylation of allylic phosphine oxides with other substitution patterns [substrates (*Z*)-**2b** and **2e–h**; Table 6, entries 8–13]. The dihydroxylation of (*Z*)-**2b** was poor, both in terms of yield and enantiomeric excess. The asymmetric dihydroxylation of *cis*-alkenes is often poor,[27] perhaps because one of the substituents must occupy the very hindered position C on the four-membered ring of the proposed[5a,b] osmaoxetane intermediate (Fig. 3).

Dihydroxylation of trisubstituted allylic phosphine oxides **2e–h** was considerably more successful (entries 9–13, Table 6). In particular, phosphine oxide **2f** reacted very much as if the methyl group *gem* to phosphorus was not present at all, giving diol **3f** in a respectable 74% ee (compare entries 4 and 10, Table 6). Although the *gem* substituent of allylic phosphine oxides can be bound in the chiral pocket, it seems reasonable that the substituent *trans* to phosphorus occupies this privileged position, leaving the large diphenylphosphinoylmethyl group held clear of the dihydroxylation catalyst in the open B position (Fig. 3).

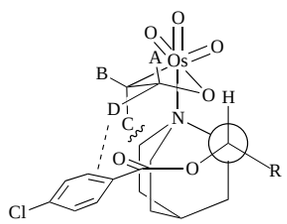


Fig. 3

The new reaction conditions (with monomeric ligands) were particularly successful with the trisubstituted allylic phosphine oxide **2h**: we observed a spectacular improvement from 14% ee with AD-mix β to 62% ee with the monomeric ligand DHQD-CLB. In this case, the DHQD-CLB ligand is considerably better than its cousin DHQD-PHN.

Summary of the dihydroxylation results

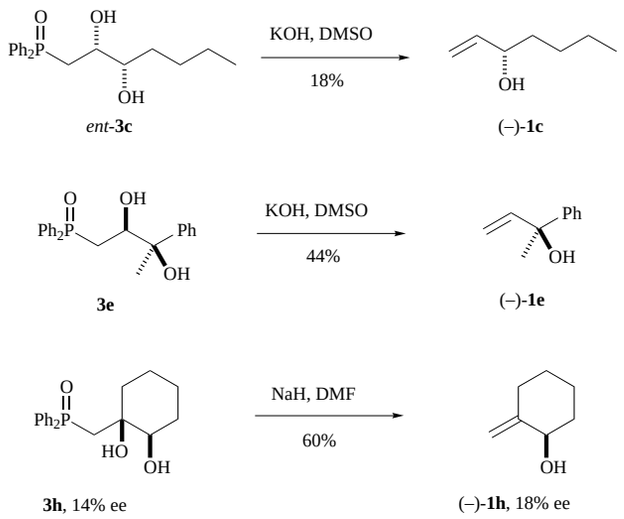
Asymmetric dihydroxylation of allylic phosphine oxides is most enantioselective when the monomeric ligand DHQD-CLB is used and, under these conditions, the enantiomeric excesses obtained are comparable to those reported for related compounds.[28] The enantioselectivity of these asymmetric dihydroxylations depends critically on the substitution of the allylic phosphine oxide **2**, and can be rationalised by proposing that the diphenylphosphinoylmethyl group is never bound in the L-shaped cleft of the dihydroxylation catalyst.

The asymmetric dihydroxylation of allylic silanes[24] and allylic phosphine oxides have several features in common. In particular, the enantioselectivity of the reactions is not improved by replacing the monomeric ligands DHQD-CLB with the generally better dimeric ligands which are found in the AD mixes. We believe that a large allylic substituent may interact badly with the 'by-stander' alkaloid unit of the dimeric ligands (Fig. 1). The removal of this alkaloid unit does remove this poor steric interaction, but it does so at a cost: binding is less favourable because edge-to-face interactions between the bound alkene substituent and the by-stander aromatic ring are lost.[5] Large quantities of the monomeric ligands are needed to ensure that none of the substrate reacts with the uncomplexed osmium tetroxide. It is only worth using the monomeric class of ligands when the alkene substituent *trans* to the group bound by the chiral ligand is particularly large.

Horner–Wittig eliminations

Our attempts to make allylic alcohols **1** from diphenylphosphinoyl diols **3** were only partially successful. Silyl ether **11** (synthesized by treating diol **3c** with 2,6-dimethylpyridine and *tert*-butyldimethylsilyl triflate; entry 6, Table 4) and diols **3** were treated with 3–4 equiv. of base under conditions known to promote the Horner–Wittig elimination (Scheme 5 and Table 7,

entries 1–3).[29] Only the most reliable conditions for the elimination (KOH in DMSO and NaH in DMF) led to the formation of any allylic alcohols, and even these reactions were low yielding (Scheme 5). The Horner–Wittig eliminations of sulfides **14**



ent-**3c** (–)-**1c**

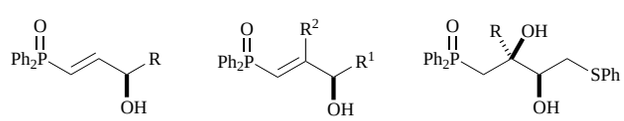
3e (–)-**1e**

3h, 14% ee (–)-**1h**, 18% ee

Scheme 5

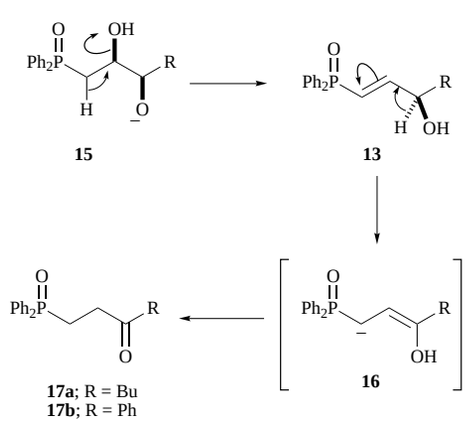
(which are also β,γ-dihydroxy phosphine oxides) were also plagued by side-reactions.[1]

The by-products from our attempted Horner–Wittig eliminations were γ-keto phosphine oxides **17**, suggesting that



13 **21** **14**

elimination of hydroxide from diols **3**, and tautomerisation, was competitive with the required olefination (Scheme 6).‖ Some



15 **13** **16**

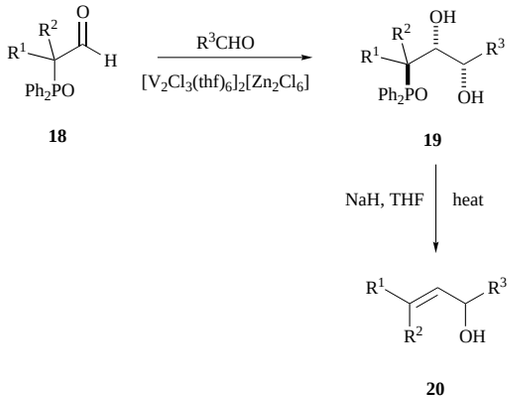
17a; R = Bu
17b; R = Ph

Scheme 6

evidence for this chain of events can be gleaned from the Horner–Wittig eliminations of some diphenylphosphinoyl diols **19** which were synthesized by a pinacol coupling reaction (Scheme 7).[31] With these tertiary phosphine oxides, high yields of allylic alcohols **20** were obtained, perhaps because deprotonation α to phosphorus was not possible.

Our three-step deracemisation of allylic alcohols **1** (Scheme 1) was lower yielding and less enantioselective than other approaches to similar compounds.[24,32] In particular, our reaction sequence did not compare favourably with the kinetic resolution[33] of allylic alcohols using the Sharpless asymmetric epoxidation.[34]

‖ Attempted protections of vinyl phosphine oxides **13** under basic conditions often promotes tautomerisation to ketones **17**.[30]



18 **19** **20**

Scheme 7

Conclusions

Asymmetric dihydroxylation of allylic phosphine oxides is most enantioselective when the 'monomeric' ligand DHQD-CLB is used in place of the 'dimeric' phthalazine ligands which form part of the commercially available AD-mixes. The magnitude and the sense of the enantioselectivity of these AD reactions can be rationalised by proposing that the diphenylphosphinoylmethyl group is never bound in the chiral pocket[5] of the ligand. The resulting diphenylphosphinoyl diols are useful intermediates in the synthesis of optically active cyclopropyl ketones[6] and allylic alcohols **1**, and are potential intermediates in the synthesis of ligands for asymmetric catalysis.[7]

Experimental

All solvents were distilled before use. THF and Et_2O were freshly distilled from lithium aluminium hydride whilst CH_2Cl_2 and toluene were freshly distilled from calcium hydride. Triphenylmethane was used as an indicator for THF. DMF, DMSO, triethylamine and chlorotrimethylsilane were dried by stirring over and distilling from calcium hydride (at reduced pressure when necessary) and were then stored over activated 4 Å molecular sieves. Butyllithium was titrated against diphenylacetic acid before use. All non-aqueous reactions were carried out under argon using oven-dried glassware.

Flash column chromatography[35] was carried out using Merck Kieselgel 60 (230–400 mesh). Thin layer chromatography was carried out on commercially available pre-coated plates (Merck silica Kieselgel $60F_{254}$).

Proton and carbon NMR spectra were recorded on a Bruker WM 200, WM 250, WM 400 or WM 500 Fourier transform spectrometers using an internal deuterium lock. Values of coupling constants (J) are given in Hz and chemical shifts (δ) in parts per million downfield of tetramethylsilane (ppm). The symbol * after the proton NMR chemical shift indicated that the signal disappears after a D_2O 'shake'. Carbon NMR spectra were recorded with broad band proton decoupling and Attached Proton Test (APT). The symbols $^+$ and $^-$ after the carbon NMR chemical shift indicate odd and even numbers of attached protons respectively.

Melting points were measured on a Reichart hot-stage microscope or a Büchi 510 melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 1600 (FT-IR) spectrophotometer. Mass spectra were recorded on a Kratos double-beam mass spectrometer using a DS503 data system for high-resolution analysis. Microanalyses were carried out by the staff of the University Chemical Laboratory using Carlo Erba 1106 or Perkin-Elmer 240 automatic analysers.

Optical rotations were recorded on a Perkin-Elmer 241 polarimeter (using the sodium D line; 589 nm) and $[\alpha]_D^{20}$ are given in

units of 10^{-1} deg cm^2 g^{-1}. (*R*)-Pirkle's reagent is (*R*)-(–)-2,2,2-trifluoro-1-(9-anthryl)ethanol.

General method for the determination of enantiomeric excess using Pirkle's chiral solvating agent

A 400 MHz ^{1}H NMR spectrum of the optically active phosphine oxide was recorded in the absence of additives. Then, a sample containing 1 mg of optically active phosphine oxide and *ca*. 4–6 mg of Pirkle's chiral solvating agent (3–4 equiv.) was prepared in $CDCl_3$ (1.5 cm^3). The 400 MHz ^{1}H NMR spectrum of this sample was recorded and the peaks corresponding to the individual enantiomers identified. If no splitting was detected, a further Pirkle's reagent (4–6 mg) was added and another 400 MHz ^{1}H NMR spectrum was recorded. The accurate enantiomeric excesses were determined by integration of the ^{1}H NMR spectra in the presence of Pirkle's reagent.

General procedure for the preparation of Mosher's esters

By the method of Mosher,[26a] (*R*)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (8 μl, 36 μmol) was added to a stirred solution of the alcohol (30 μmol) in carbon tetrachloride (3 drops) and pyridine (3 drops). The reaction mixture was stirred for 6 h, diluted with diethyl ether (10 cm^3), washed with hydrochloric acid (5 cm^3), saturated aqueous sodium carbonate (5 cm^3) and water (5 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give a crude product.

General procedure for Arbusov rearrangement of allylic alcohols 1

A solution of chlorodiphenylphosphine (2.22 g, 10.0 mmol) in degassed ether (10 cm^3) was added by cannula to a stirred solution of the allylic alcohol (10.0 mmol) and pyridine (0.78 g, 10.0 mmol) in degassed ether (10 cm^3) at −78 °C under argon. The solution was gradually warmed to 20 °C and stirred for 30 min to give a white suspension. The suspension was filtered under argon using a Schlenk tube, evaporated under reduced pressure and refluxed in toluene (10 cm^3) for 16 h. The reaction was quenched by the addition of saturated aqueous ammonium chloride (20 cm^3). The aqueous fraction was separated and extracted with dichloromethane (3 × 20 cm^3), and the combined organic layer and extract were washed with saturated aqueous sodium hydrogen carbonate (20 cm^3), dried (Na_2SO_4) and evaporated under reduced pressure to give a crude product.

(*E*)-1-Diphenylphosphinoylbut-2-ene 2a

By the general method described above, but-3-en-2-ol **1a** (1.66 g, 23.1 mmol) gave a crude product which was purified by flash chromatography, eluting with EtOAc, to yield a white solid. Integration of the ^{1}H NMR spectrum revealed that the *E*:*Z* ratio was 95:5. Recrystallisation from EtOAc gave the allylic phosphine oxide **2a** (2.66 g, 45%) as needles, mp 104–106 °C (from EtOAc–hexane) (lit.,[9] 90–91 °C); R_f(EtOAc) 0.24 (Found: C, 75.1; H, 6.65; P, 12.4%; M$^+$, 256.1026. $C_{16}H_{17}OP$ requires C, 75.0; H, 6.70; P, 12.1%; *M*, 256.1018); ν_{max}/cm^{-1} ($CHCl_3$) 1436 (P–Ph) and 1182 (P=O); δ_H(250 MHz; $CDCl_3$) 8.0–7.4 (10 H, m, Ph_2PO), 5.7–5.3 (2 H, m, CH=CH), 3.05 (2 H, ddd, *J* 1, 7 and $^2J_{PH}$ 15, PCH_2) and 1.60 (3 H, ddd, *J* 1, 6 and $^5J_{PH}$ 6, Me); δ_C(63 MHz; $CDCl_3$) 134–127 (m, Ph_2PO and $C_AH{=}C_BH$), 119.0$^+$ (d, $^2J_{PC}$ 9, $C_AH{=}C_BH$), 34.6$^-$ (d, $^1J_{PC}$ 70, PCH_2) and 18.1$^+$ (d, $^4J_{PC}$, Me); *m/z* 256.1 (75%, M$^+$), 201.0 (100, Ph_2PO) and 77.0 (80, Ph).

(*E*)-1-Diphenylphosphinoylhept-2-ene 2c

By the general method described above, hept-1-en-3-ol[13a] **1c** (2.00 g, 17.5 mmol) gave a crude product which was purified by flash chromatography, eluting with EtOAc, to yield a white solid. Integration of the ^{1}H NMR spectrum revealed that the *E*:*Z* ratio was 97:3. Recrystallisation from EtOAc gave the *allylic phosphine oxide* **2c** (2.26 g, 43%) as prisms, mp 51–53 °C (from EtOAc–hexane); R_f(EtOAc) 0.34 (Found: M$^+$, 298.1486. $C_{19}H_{23}OP$ requires *M*, 298.1487); ν_{max}/cm^{-1} ($CHCl_3$) 1437 (P–Ph) and 1184 (P=O); δ_H(250 MHz; $CDCl_3$) 7.8–7.3 (10 H, m, Ph_2PO), 5.40 (2 H, m, CH=CH), 3.05 (2 H, dd, *J* 6 and $^2J_{PH}$ 14, PCH_2), 1.9 (2 H, m, C=CCH_2), 1.3–1.0 (4 H, m, 2 × CH_2) and 0.80 (3 H, t, *J* 7, Me); δ_C(63 MHz; $CDCl_3$) 137.5$^+$ (d, $^3J_{PC}$ 12, $C_AH{=}C_BH$), 134–128 (m, Ph_2PO), 118.0$^+$ (d, $^2J_{PC}$ 12, $C_AH{=}C_BH$), 35.0$^-$ (d, $^1J_{PC}$ 69, PCH_2), 32.3$^-$, 31.2$^-$ (d, $^4J_{PC}$ 3, C=CCH_2), 21.9$^-$ and 13.8$^+$ (Me); *m/z* 298.1 (80%, M$^+$) and 201.0 (100, Ph_2PO).

(*E*)-1-Diphenylphosphinoyl-2-methylhept-2-ene 2f

By the general method described above, 2-methylhept-1-en-3-ol[13b] **1f** (2.00 g, 16.5 mmol), pyridine (1.14 cm^3, 14.1 mmol) and chlorodiphenylphosphine (2.53 cm^3, 14.1 mmol) gave a crude product which was purified by flash chromatography, eluting with EtOAc, to yield a white solid (3.09 g, 64%). Integration of the ^{1}H NMR spectrum of this revealed that the *E*:*Z* ratio was 94:6. Recrystallisation from EtOAc–hexane gave the *allylic phosphine oxide* **2f** (1.49 g, 31%) as needles, mp 67–68 °C (from EtOAc–hexane); R_f(EtOAc) 0.39 (Found: C, 76.6; H, 8.00; P, 10.0%; MH$^+$, 313.1733. $C_{20}H_{25}OP$ requires C, 76.9; H, 8.05; P, 9.9%; *M* H, 313.1721); ν_{max}/cm^{-1} ($CHCl_3$) 1632 (C=C), 1438 (P–Ph) and 1172 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.4 (10 H, m, Ph_2PO), 5.05 (1 H, m, CH=C), 3.06 (2 H, d, $^2J_{PH}$ 14, PCH_2), 1.95 (2 H, m, C=CCH_2), 1.70 (3 H, s, Me), 1.2–1.0 (4 H, m, 2 × CH_2) and 0.79 (3 H, t, *J* 7, Me); δ_C(63 MHz; $CDCl_3$) 132.8$^-$ (d, $^1J_{PC}$ 97, *ipso*-PPh), 131–125 (m, Ph_2PO and CH=*C*), 110.0$^+$ (*C*H=C), 40.6$^-$ (d, $^1J_{PC}$ 68, PCH_2), 31.1$^-$ (d, $^4J_{PC}$ 3), 27.4$^-$, 21.6$^-$, 17.7$^+$ (Me) and 13.6$^+$ (Me); *m/z* 313.3 (100%, MH$^+$) and 201.2 (40, Ph_2PO).

(*E*)-1-Cyclohexyl-3-diphenylphosphinoyl-2-methylprop-1-ene 2g

By the general method described above, 1-cyclohexyl-2-methylprop-2-en-1-ol[13c] **1g** (3.35 g, 21.8 mmol), pyridine (1.59 cm^3, 19.7 mmol) and chlorodiphenylphosphine (2.53 cm^3, 14.1 mmol) gave a crude product which was purified by flash chromatography, eluting with EtOAc, to yield a white solid (4.52 g, 62%). Integration of the ^{1}H NMR spectrum revealed that the *E*:*Z* ratio was 85:15. Recrystallisation from EtOAc–hexane gave the *allylic phosphine oxide* **2g** (2.50 g, 34%) as plates, mp 120–123 °C (from EtOAc–hexane); R_f(EtOAc) 0.35 (Found: C, 77.7; H, 9.10; P, 8.1%; M$^+$, 338.1803. $C_{22}H_{27}OP$ requires C, 78.1; H, 9.15; P, 8.0%; *M*, 338.1799); ν_{max}/cm^{-1} ($CHCl_3$) 1648 (C=C), 1438 (P–Ph) and 1178 (P=O); δ_H(250 MHz; $CDCl_3$) 7.8–7.3 (10 H, m, Ph_2PO), 4.75 (1 H, m, CH=C), 2.93 (2 H, d, $^2J_{PH}$ 14, PCH_2) and 1.8–0.6 (13 H); δ_C(63 MHz; $CDCl_3$) 137.1$^+$ (d, $^3J_{PC}$ 11, *C*H=C), 133–128 (m, Ph_2PO and CH=*C*), 112.1$^-$ (*C*Me=C), 40.3$^-$ (d, $^1J_{PC}$ 67, PCH_2) and 40–20 (m); *m/z* 338.2 (70%, M$^+$) and 202.1 (100, Ph_2PO).

General procedure for Arbusov rearrangement of allylic alcohols 2

Chlorodiphenylphosphine (2.27 g, 10.8 mmol) was added dropwise to a stirred solution of the allylic alcohol (10.0 mmol) in pyridine (30 cm^3) at 20 °C under argon. The solution was stirred for 2 h under argon at 20 °C and then refluxed for 16 h. The crude reaction mixture was evaporated under reduced pressure, diluted with dichloromethane (30 cm^3), washed with dilute aqueous hydrochloric acid (1.0 mol dm^{-3}, 3 × 30 cm^3), saturated aqueous sodium hydrogen carbonate (30 cm^3) and water (30 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to yield a crude product.

(*E*)-3-Diphenylphosphinoyl-1-phenylprop-1-ene 2d

By the general method decribed above, 1-phenylprop-2-en-1-ol[13d] **1d** (1.64 g, 12.3 mmol) gave a crude product which was purified by flash chromatography, eluting with EtOAc–hexane (2:1), to yield a white solid. Integration of the ^{1}H NMR spectrum of this revealed that the *E*:*Z* ratio was 94:6. Recrystal-

lisation from hexane–EtOAc gave the allylic phosphine oxide **2d** (1.61 g, 41%) as needles, mp 182–184 °C (from EtOAc) (lit.,[9] 181–182 °C); R_f(EtOAc) 0.32 (Found: C, 79.4; H, 6.05; P, 9.8%; M^+, 318.1171. $C_{21}H_{19}OP$ requires C, 79.2; H, 6.00; P, 9.7%; *M*, 318.1173); ν_{max}/cm^{-1} ($CHCl_3$) 1437 (P–Ph) and 1184 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.1 (15 H, m, Ph_2PO and Ph), 6.41 (1 H, ddd, *J* 1, $^4J_{PH}$ 4 and *J* 16, PhC*H*=CH), 6.16 (1 H, dtd, $^3J_{PH}$ 6, *J* 7 and *J* 16, PhCH=C*H*) and 3.29 (2 H, ddd, *J* 1, 7 and $^2J_{PH}$ 15, PCH_2); δ_C(63 MHz; $CDCl_3$) 135.6$^+$ (d, $^3J_{PC}$ 12, $C_AH{=}C_BH$), 132–126 (m, Ph_2PO), 118.5$^+$ (d, $^2J_{PC}$ 9, $C_AH{=}C_BH$) and 35.6$^-$ (d, $^1J_{PC}$ 69, PCH_2); *m/z* 318.1 (65%, M^+) and 201.1 (100, Ph_2PO).

(*E*)-1-Diphenylphosphinoyl-3-phenylbut-2-ene 2e

By the general method described above, 2-phenylbut-3-en-2-ol[13e] **1e** (453 mg, 3.03 mmol) gave a white solid. Integration of the ^{1}H NMR spectrum revealed that the *E*:*Z* ratio was 91:9. Recrystallisation from EtOAc gave the *allylic phosphine oxide* **2e** (185 mg, 19%) as needles, mp 143–144 °C (from EtOAc); R_f(EtOAc) 0.36 (Found: M^+, 332.1340. $C_{22}H_{21}OP$ requires *M*, 332.1340); ν_{max}/cm^{-1} ($CHCl_3$) 1630 (C=C), 1437 (P–Ph) and 1180 (P=O); δ_H(250 MHz; $CDCl_3$) 8.0–7.1 (15 H, m, Ph_2PO, Ph and CH=C*H*MePh), 5.77 (1 H, dq, *J* 1 and 7, C*H*=C), 3.28 (2 H, dd, J_{HH} 7 and $^2J_{PH}$ 15, PCH_2) and 1.81 (3 H, dd, *J* 1 and $^5J_{PH}$ 3, Me); δ_C(63 MHz; $CDCl_3$) 145–125 (m, Ph_2PO, $C_AH{=}C_B$ and Ph), 116.1$^+$ (d, $^2J_{PC}$ 9, PCH_2CH=C), 32.0$^-$ (d, $^1J_{PC}$ 69, PCH_2) and 16.3$^+$ (Me); *m/z* 332.1 (45%, M^+), 201.0 (100, Ph_2PO) and 77.0 (55, Ph). The geometry of the double bond was confirmed by a reciprocal NOE between C*H*=C and Me.

General procedure for the synthesis of allylic phosphine oxides by allylation of lithium diphenylphosphide

Butyllithium (1.4 mol dm^{-3} solution in hexanes; 80 cm^3, 112 mmol) was added dropwise to a solution of diphenylphosphine (18.3 g, 99 mmol) in THF (250 cm^3) at −30 °C to give an orange coloured solution. The reaction mixture was then allowed to warm slowly to room temperature over 4 h. The dark-red solution was cooled to −78 °C, and the allyl bromide (114 mmol) in THF (15 cm^3) was added to it by cannula. The reaction mixture was then allowed to warm slowly to room temperature overnight, after which it was treated with hydrogen peroxide (100 vol; 30 cm^3), added dropwise, and stirred for 1 h. Saturated aqueous ammonium chloride was added (200 cm^3) to the mixture after which the layers were separated, and the aqueous layer was extracted with dichloromethane (3 × 100 cm^3). The combined extracts were washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure to give a crude product.

(*E*)-3-Diphenylphosphinoyl-1-phenylprop-1-ene 2d

By the general method described above, butyllithium (1.4 mol dm^{-3} solution in hexanes; 80 cm^3, 112 mmol), diphenylphosphine (18.3 g, 99 mmol) and cinnamyl bromide (22.5 g, 114 mmol) gave the allylic phosphine oxide **2d** (32.5 g, 102%) as needles, mp 182–184 °C (from EtOAc–hexane), identical spectroscopically with that synthesized previously.

(*Z*)-1-Diphenylphosphinoylpent-2-ene 2b

By the general method described above, butyllithium (1.3 mol dm^{-3} solution in hexanes; 5.7 cm^3, 7.4 mmol), diphenylphosphine (1.28 cm^3, 6.8 mmol) and (*Z*)-1-bromopent-2-ene (1.0 g, 6.8 mmol) gave the allylic phosphine oxide (*Z*)-**2b** (1.60 g, 87%) as a white solid. Integration of the 400 MHz ^{1}H NMR of this material indicated an *Z*:*E* ratio of 89:11. Recrystallisation from EtOAc–hexane gave the *allylic phosphine oxide* (*Z*)-**2b** (0.82 g, 45%) as needles, mp 94–95 °C (from EtOAc–hexane); R_f(EtOAc) 0.29 (Found: C, 75.8; H, 6.65; P, 11.8%; M^+, 270.1172. $C_{17}H_{19}OP$ requires C, 75.5; H, 7.05; P, 11.4%; *M*, 272.1171); ν_{max}/cm^{-1} ($CHCl_3$) 1632 (C=C), 1438 (P–Ph) and 1189 (P=O); δ_H(400 MHz; $CDCl_3$) 7.6–7.5 (4 H, m), 7.3–7.15 (6 H, m, Ph_2PO), 5.35 (1 H, m, CH_A=CH_B), 5.23 (1 H, m, CH_A=CH_B), 2.98 (2 H, dd, *J* 8 and $^2J_{PH}$ 15, PCH_2), 1.70 (2 H, m) and 0.60 (3 H, t, *J* 8, Me); δ_C(100 MHz; $CDCl_3$) 136.8$^+$ (d, $^3J_{PC}$ 12, $C_AH{=}C_BH$), 132.5–126 (m, Ph_2PO), 116.5$^+$ (d, $^2J_{PC}$ 9, $C_AH{=}C_BH$), 34.5$^-$ (d, $^1J_{PC}$ 69, PCH_2), 20.6 (d, $^4J_{PC}$ 1) and 13.9$^+$ (Me); *m/z* 318.1 (22%, M^+) and 201.1 (100, Ph_2PO).

(*E*)-1-Diphenylphosphinoylpent-2-ene 2b

By the general method described above, butyllithium (1.3 mol dm^{-3} solution in hexanes; 5.7 cm^3, 7.4 mmol), diphenylphosphine (1.28 cm^3, 6.8 mmol) and (*E*)-1-bromopent-2-ene (1.0 g, 6.8 mmol) gave the allylic phosphine oxide (*E*)-**2b** (1.90 g, 103%) as a white solid. Integration of the 400 MHz ^{1}H NMR of this material indicated an *E*:*Z* ratio of 85:15. Recrystallisation from EtOAc–hexane gave the *allylic phosphine oxide* (*E*)-**2b** (1.08 g, 59%) as plates, mp 76–77 °C (from EtOAc–hexane); R_f(EtOAc) 0.29 (Found: C, 75.5; H, 7.10; P, 11.5%; M^+, 271.1245. $C_{17}H_{19}OP$ requires C, 75.5; H, 7.05; P, 11.4%; *M*, 271.1252); ν_{max}/cm^{-1} ($CHCl_3$) 1633 (C=C), 1438 (P–Ph) and 1164 (P=O); δ_H(400 MHz; $CDCl_3$) 7.7–7.6 (4 H, m), 7.4–7.3 (6 H, m, Ph_2PO), 5.42 (1 H, m, CH_A=CH_B), 5.32 (1 H, m, CH_A=CH_B), 2.98 (2 H, dd, *J* 7 and $^2J_{PH}$ 14, PCH_2), 2.18 (2 H, m) and 0.75 (3 H, t, *J* 7, Me); δ_C(100 MHz; $CDCl_3$) 138.8$^+$ (d, $^3J_{PC}$ 11, $C_AH{=}C_BH$), 133–128 (m, Ph_2PO), 116.9$^+$ (d, $^2J_{PC}$ 9, $C_AH{=}C_BH$) and 34.7$^-$ (d, $^1J_{PC}$ 69, PCH_2), 25.6 and 14.2$^+$ (Me); *m/z* 271.1 (100%, MH^+) and 201.1 (55, Ph_2PO).

1-Phenyl-4-diphenylphosphinoylbut-1-ene 6

Butyllithium (1.35 mol dm^{-3} solution in hexane; 1.7 cm^3, 2.3 mmol) was added to a stirred solution of methyldiphenylphosphine oxide (500 mg, 2.31 mmol) in dry THF (60 cm^3) at 0 °C and the yellow mixture was cooled to −78 °C. Cinnamyl bromide (455 mg, 2.32 mmol) was added dropwise as a solution in THF (5 cm^3) to the mixture which was then stirred for 3 h during which time the colour of the solution changed to black and then to yellow. The temperature of the reaction mixture was raised to 0 °C after which it was stirred for a further 1 h. Saturated aqueous ammonium chloride (30 cm^3) was added to the mixture after which the aqueous phase was separated and extracted with dichloromethane (3 × 20 cm^3). The combined organic extracts were washed with water (30 cm^3) and brine (30 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give a crude product which was purified by flash chromatography, eluting with EtOAc, to give the *homoallylic phosphine oxide* **6** (487 mg, 63%) as needles, mp 120–123 °C (from EtOAc–hexane); R_f(EtOAc) 0.29 (Found: M^+, 332.1326. $C_{22}H_{21}OP$ requires *M*, 332.1330); ν_{max}/cm^{-1} ($CHCl_3$) 1652 (C=C), 1438 (P–Ph) and 1178 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.4 (10 H, m, Ph_2PO), 7.3–7.1 (5 H, m, Ph), 6.36 (1 H, d, *J* 16, PhC*H*=C*H*), 6.17 (1 H, td, *J* 6 and 16, PhCH=C*H*) and 2.62–2.38 (4 H, m, CH=CHCH_2 and PCH_2); δ_C(63 MHz; $CDCl_3$) 133–125 (m, Ph_2PO, Ph and CH=CH), 29.6$^-$ (d, $^1J_{PC}$ 70, PCH_2) and 25.0$^-$ (d, $^2J_{PC}$ 3, PCH_2CH_2); *m/z* 332.1 (45%, M^+) and 202.1 (100, Ph_2POH).

General procedure for asymmetric dihydroxylation using AD-mixes

By the method of Sharpless *et al.*[17] AD-mix (2.80 g) and methanesulfonamide (190 mg, 2.0 mmol, omitted for terminal alkenes) were stirred in 1:1 tertiary butyl alcohol–water (20 cm^3) at 25 °C. The mixture was cooled to 0 °C whereupon some of the dissolved salts were precipitated. The alkene (2.0 mmol) was added immediately to the mixture. The slurry was then stirred vigorously until the reaction was complete. Sodium sulfite (3.00 g, 23.7 mmol) was added to the mixture, the temperature of which was then allowed to warm to 20 °C at which temperature it was stirred for a further 30 min. EtOAc (50 cm^3) was added to the reaction mixture, after which the aqueous fraction was separated and extracted with EtOAc (3 × 25 cm^3). The combined organic layer and extracts were washed with aqueous potassium hydroxide (2 mol dm^{-3}; 2 × 25 cm^3, omitted

for terminal alkenes), water (25 cm^3) and brine (25 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give a crude product.

(1*R*,2*S*)-1-(Diphenylphosphinoylmethyl)cyclohexane-1,2-diol 3h
By the general method described above, methanesulfonamide (219 mg, 2.3 mmol), AD-mix α (3.22 g) and 1-(diphenylphosphinoylmethyl)cyclohexene[23] **2h** (680 mg, 2.3 mmol) gave a crude product which was purified by flash chromatography, eluting with EtOAc, to yield the *vicinal diol* **3h** (330 mg) as needles, mp 159–161 °C (from EtOAc–hexane); R_f(EtOAc) 0.36; $[\alpha]_D^{20}$ +3.3 (*c* 1.0 in $CHCl_3$) (Found: M^+, 330.1369. $C_{19}H_{23}O_3P$ requires *M*, 330.1384); ν_{max}/cm^{-1} ($CHCl_3$) 3384 (OH), 1436 (P–Ph) and 1154 (P=O); δ_H(400 MHz; $CDCl_3$) 7.9–7.4 (10 H, m, Ph_2PO), 4.5 (1 H, s, OH), 3.8 (1 H, s, OH), 3.5 (1 H, dd, *J* 4 and 10, C*H*OH), 2.7 (1 H, dd, $^2J_{PH}$ 14 and $^2J_{HH}$ 16, PCH_AH_B), 2.6 (dd, $^2J_{PH}$ 8 and $^2J_{HH}$ 16, PCH_AH_B) and 2.0–1.0 (8 H, 4 × CH_2); δ_C(100 MHz; $CDCl_3$) 139–129 (m, Ph_2PO), 74.5$^-$ (d, $^2J_{PC}$ 5, COH), 74.0$^+$ (d, $^3J_{PC}$ 6, CHOH), 40.5$^-$ (d, $^1J_{PC}$ 69, PCH_2), 38.5$^-$ (d, $^3J_{PC}$ 7), 29.8$^-$, 23.9$^-$ and 20.8$^-$; *m/z* 330.1 (50%, M^+), 312.1 (40, M–H_2O), 202.1 (100, Ph_2POH) and 77 (20, Ph). Integration of the ^{1}H NMR spectrum of the product in the presence of Pirkle's chiral shift reagent showed an enantiomeric excess of 18%.

(2*R*,3*S*)-1-Diphenylphosphinoylbutane-2,3-diol 3a
By the general method described above, (*E*)-1-diphenylphosphinoylbut-2-ene **2a** (4.55 g, 17.8 mmol), methanesulfonamide (1.69 g, 17.8 mmol) and AD-mix α (24.9 g) gave a crude product after 7 days. Flash chromatography of this, eluting with 5% methanol in EtOAc, gave the *vicinal diol* **3a** (4.31 g, 84%) as a gum, R_f(EtOAc) 0.15; $[\alpha]_D^{20}$ −4.1 (*c* 2.0 in $CHCl_3$, 10% ee) (Found: M^+, 290.1087. $C_{16}H_{19}PO_3$ requires *M*, 290.1072); ν_{max}/cm^{-1} ($CHCl_3$) 3370 (OH), 1438 (P–Ph) and 1176 (P=O); δ_H(400 MHz; $CDCl_3$) 7.7–7.3 (10 H, m, Ph_2PO), 4.7 (1 H, br s, OH), 3.8 (1 H, m, C*H*OH), 3.6 (1 H, m, C*H*OH), 2.6 (1 H, ddd, *J* 10, 15 and 20, PCH_AH_B), 2.45 (1 H, ddd, *J* 3, 10 and 15, PCH_AH_B) and 1.1 (3 H, d, *J* 6, Me); δ_C(63 MHz; $CDCl_3$) 132–128 (m, Ph_2PO), 70.8$^+$ (d, $^3J_{PC}$ 8, *C*HOH), 70.7$^+$ (s, CHOH), 33.1$^-$ ($^1J_{PC}$ 71, PCH_2) and 18.9$^+$ (s, Me); *m/z* 290.1 (5%, M^+), 245 (95, Ph_2POCH_2COH), 201 (100, Ph_2PO) and 77 (60, Ph).

(2*R*,3*S*)-1-Diphenylphosphinoylheptane-2,3-diol 3c
By the general method described above, methanesulfonamide (161 mg, 1.69 mmol), (*E*)-1-diphenylphosphinoylhept-2-ene **2c** (504 mg, 1.69 mmol) and AD-mix α (2.36 g) gave a crude product after being stirred for 3 days. Flash chromatography of this, eluting with EtOAc–hexane (10:1), gave the *vicinal diol* **3c** (289 mg, 51%, 61% based on recovered starting material) as needles, mp 110–113 °C (from EtOAc–hexane); R_f(EtOAc) 0.18; $[\alpha]_D^{20}$ −8.5 (*c* 0.9 in $CHCl_3$) (Found: C, 68.6; H, 7.40; P, 9.4%; MH^+, 333.1592. $C_{19}H_{25}PO_3$ requires C, 68.7; H, 7.60; P, 9.3%; *M* + H, 333.1619); ν_{max}/cm^{-1} ($CHCl_3$) 3418 (OH) and 3306 (OH), 1435 (P–Ph) and 1152 (P=O); δ_H(400 MHz; $CDCl_3$) 7.7–7.4 (10 H, m, Ph_2PO), 4.5 (1 H, br s, OH), 3.9 (1 H, m, C*H*OH), 3.45 (1 H, m, C*H*OH), 3.0 (1 H, br s, OH), 2.65 (1 H, ddd, *J* 10, 12 and 15, PCH_AH_B), 2.45 (1 H, ddd, *J* 3, 9 and 15, PCH_AH_B), 1.6–1.2 (6 H, m, 3 × CH_2) and 0.6 (3 H, t, *J* 7, Me); δ_C(100 MHz; $CDCl_3$) 136–128 (m, Ph_2PO), 74.6$^+$ (d, $^3J_{PC}$ 12, CHOH), 69.5$^+$ (d, $^2J_{PC}$ 5, CHOH), 33.4$^-$ (d, $^1J_{PC}$ 71, PCH_2), 32.9$^-$, 27.9$^-$, 14.0$^-$ and 9.3$^+$ (s, Me); *m/z* 331.2 (2.5%, MH^+), 275 (90, M−BuH), 245 (95, Ph_2POCH_2COH) and 201 (100, Ph_2PO). Integration of the 400 MHz ^{1}H NMR spectrum of the disilyl ether of this material in the presence of Pirkle's shift reagent showed it to have 49% ee.

(1*S*,2*R*)-3-Diphenylphosphinoyl-1-phenylpropane-1,2-diol 3d
By the general method described above, methanesulfonamide (56 mg, 0.59 mmol), (*E*)-3-diphenylphosphinoyl-1-phenylprop-1-ene **2d** (188 mg, 0.59 mmol) and AD-mix α (0.83 g) gave the crude product after being stirred for 5 days. Flash chromatography, eluting with 5% methanol in EtOAc gave the *vicinal diol* **3d** (89 mg, 66%) as needles, mp 112–114 °C (from hexane–EtOAc); R_f(EtOAc) 0.18; $[\alpha]_D^{20}$ −18.8 (*c*. 0.7 in $CHCl_3$) (Found: $M^+ - H_2O$, 334.1128. $C_{21}H_{21}O_3P$ requires $M-H_2O$, 334.1123); ν_{max}/cm^{-1} ($CHCl_3$) 3336 (OH), 1437 (P–Ph) and 1185 (P=O); δ_H(400 MHz; $CDCl_3$) 7.7–7.2 (15 H, m, Ph_2PO and Ph), 4.72 (1 H, br s, OH), 4.58 (1 H, d, *J* 6, PhC*H*OH), 4.13 (1 H, m, PCH_2CHOH), 3.66 (1 H, br s, OH), 2.39 (1 H, ddd, *J* 10, $^2J_{PH}$ 12 and $^2J_{HH}$ 15, PCH_AH_B) and 2.26 (1 H, ddd, *J* 2, $^2J_{PH}$ 8 and $^2J_{HH}$ 15, PCH_AH_B); δ_C(63 MHz; $CDCl_3$) 132–126 (m, Ph_2PO and Ph), 77.8$^+$ (d, $^3J_{PC}$ 14, CHOH), 71.5$^+$ (d, $^2J_{PC}$ 4, CHOH) and 32.5$^-$ (d, $^1J_{PC}$ 71, PCH_2); *m/z* 334.1 (40%, M−H_2O), 245.1 (95, Ph_2POCH_2COH) and 201.1 (100, Ph_2PO). Integration of the 400 MHz ^{1}H NMR spectrum of this material in the presence of Pirkle's shift reagent showed it to have 74% ee.

(1*R*,2*S*)-4-Diphenylphosphinoyl-1-phenylbutane-1,2-diol 7
By the general method described above, methanesulfonamide (572 mg, 6.02 mmol), (*E*)-4-diphenylphosphinoyl-1-phenylbut-1-ene **6** (2.00 g, 6.02 mmol) and AD-mix α (8.43 g) gave the crude product after 24 h. Flash chromatography of the crude product, eluting with 3% methanol in EtOAc, gave the *vicinal diol* **7** (2.13 g, 97%) as needles, mp >220 °C; R_f(EtOAc) 0.15; $[\alpha]_D^{20}$ −4.7 (*c* 1.7 in $CHCl_3$) (Found: $M^+ - H_2O$, 348.1272. $C_{22}H_{23}PO_3$ requires $M - H_2O$, 348.1279); ν_{max}/cm^{-1}($CHCl_3$)3363 (OH), 1437 (P–Ph) and 1169 (P=O); δ_H(400 MHz; $CDCl_3$) 7.8–7.1 (15 H, m, Ph_2PO and Ph), 4.97 (1 H, d, *J* 4, PhC*H*OH), 4.36 (1 H, d, *J* 7, OH), 3.96 (1 H, br s, OH), 3.82 (1 H, m, C*H*OH), 2.35 (2 H, m, PCH_2) and 1.65 (2 H, m, PCH_2CH_2); δ_C(63 MHz; $CDCl_3$) 126–141 (m, Ph_2PO and Ph), 77.5$^+$ (CHOH), 75.7$^+$ (CHOH), 26.4$^-$ (d, $^1J_{PC}$ 72, PCH_2) and 25.6$^-$ (d, $^2J_{PC}$ 6, PCH_2CH_2); *m/z* 348.1 (60%, M − H_2O), 259.1 (100, M–PhCHOH) and 77 (60, Ph). Comparison of ^{1}H NMR of the Mosher's diesters of this compound and its racemate showed that this material had an enantiomeric excess of greater than 95%.

(1*S*,2*R*)-1-(Diphenylphosphinoylmethyl)cyclohexane-1,2-diol 3h
By the general method described above, methanesulfonamide (224 mg, 2.36 mmol), 1-diphenylphosphinoylmethylcyclohexene[23] **2h** (700 mg, 2.36 mmol) and AD-mix β gave the crude product after 3 days. Flash chromatography of the crude product, eluting with 1:1 acetone–light petroleum (bp 60–80 °C), gave the vicinal diol **3h** (487 mg, 62%, 73% based on recovered starting material) as needles, spectroscopically identical with that obtained previously, $[\alpha]_D^{20}$ −3.2 (*c* 0.9 in $CHCl_3$). Integration of the 400 MHz ^{1}H NMR spectrum of the silyl ether of this material in the presence of Pirkle's shift reagent showed it to have 14% ee.

Attempted asymmetric dihydroxylation of 2i
By the general method described above, 3-diphenylphosphinoylprop-1-ene[22] **2i** and AD-mix α (1.15 g) gave a crude product after 3 days at 0 °C and 3 days at 20 °C. The ^{1}H NMR spectrum of the crude reaction product revealed that the reaction was 53% complete; δ_H(400 MHz; $CDCl_3$) 7.9–7.3 (10 H, m, $Ph_2PO^{SM\ +\ diol}$), 5.82 (1 H, m, C*H*=CH_2^{SM}), 5.3–5.1 (2 H, CH=CH_2^{SM}), 4.64 (1 H, br s, OH^{diol}), 4.12 (1 H, m, C*H*OH^{diol}), 3.68 (1 H, dd, *J* 4 and 16, C$H_AH_BOH^{diol}$), 3.60 (1 H, dd, *J* 4 and 16, $CH_ACH_BOH^{diol}$), 3.18 (2 H, tdd, *J* 1, 8 and 16, PCH_2^{SM}), 2.67 (1 H, ddd, *J* 9, 12 and 16, PC$H_AH_B^{diol}$) and 2.43 (1 H, ddd, *J* 4, 9 and 16, PC$H_AH_B^{diol}$).

Modified procedure for the asymmetric dihydroxylation of allylic phosphine oxides
Osmium chloride (3 mg, 0.01 mmol), potassium ferricyanide (987 mg, 3.0 mmol), potassium carbonate (300 mg, 3.00 mmol), ligand (0.02–0.25 mmol, 2–25 mol%) and the allylic phosphine oxide (1.00 mmol) were dissolved in 1:1 tertiary butyl alcohol–water (10 cm^3). The reaction mixture was stirred at 20 °C for 1–7 days after which sodium sulfite (1.5 g, 16.0 mmol) was added

to it and stirring continued for a further 30 min. The aqueous fraction was separated and extracted with dichloromethane (3×15 cm^3), and the combined organic layer and extracts were washed with aqueous potassium hydroxide (2.0 mol dm^{-3}; 2×15 cm^3), water (15 cm^3) and brine (15 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give a crude product.

Asymmetric dihydroxylation of 2d using 2.5 mol% DHQD$_2$-PHAL

By the general method described above, (*E*)-3-diphenylphosphinoyl-1-phenylprop-1-ene **2d** (200 mg, 0.63 mmol), potassium carbonate (131 mg, 0.94 mmol), potassium ferricyanide (628 mg, 1.90 mmol), methanesulfonamide (29 mg, 0.30 mmol), osmium trichloride (3 mg, 0.01 mmol) and DHQD$_2$-PHAL (12.3 mg, 0.015 mmol, 2.5 mol%) gave a crude product after 3 days which was purified by flash chromatography, eluting with 2% methanol in EtOAc, to give the vicinal diol **3d** (159 mg, 72%) as needles, spectroscopically identical with that obtained previously, $[\alpha]_D^{20}$ +14.6 (*c* 0.99 in $CHCl_3$). Integration of the 400 MHz ^{1}H NMR spectrum of the disilyl ether of this material in the presence of Pirkle's shift reagent showed it to have 84% ee.

Asymmetric dihydroxylation of 2d using 5.0 mol% DHQD$_2$-PHAL

By the general method described above, (*E*)-3-diphenylphosphinoyl-1-phenylprop-1-ene **2d** (5.57 g, 17.5 mmol), AD-mix β (24.5 g), methanesulfonamide (1.67 g, 17.5 mmol), osmium trichloride (110 mg, 0.37 mmol) and DHQD$_2$-PHAL (545 mg, 0.70 mmol, 4.0 mol%) gave a crude product after being stirred for 3 days with a mechanical stirrer. Flash chromatography of the crude product, eluting with 5% methanol in EtOAc, gave the vicinal diol **3d** (3.02 g, 49%), $[\alpha]_D^{20}$ +11.4 (*c* 0.89 in $CHCl_3$). Integration of the 400 MHz ^{1}H NMR spectrum of the disilyl ether of this material in the presence of Pirkle's shift reagent showed it to have 85% ee. Recrystallisation from EtOAc–hexane gave the product **3d** (1.55 g, 25%) as needles, spectroscopically identical with that obtained previously, $[\alpha]_D^{20}$ +15.7 (*c* 0.54 in $CHCl_3$). Integration of the 400 MHz ^{1}H NMR spectrum of the disilyl ether of this material in the presence of Pirkle's shift reagent showed it to have 78% ee.

Asymmetric dihydroxylation of 2d using 7.5 mol% DHQD$_2$-PHAL

By the general method described above, (*E*)-3-diphenylphosphinoyl-1-phenylprop-1-ene **3d** (200 mg, 0.63 mmol), potassium carbonate (131 mg, 0.94 mmol), potassium ferricyanide (628 mg, 1.90 mmol), methanesulfonamide (29 mg, 0.30 mmol), osmium trichloride (3 mg, 0.01 mmol) and DHQD$_2$-PHAL (36.8 mg, 0.045 mmol, 7.5 mol%) gave a crude product after 3 days which was purified by flash chromatography, eluting with 2% methanol in EtOAc, to give the vicinal diol **3d** (199 mg, 94%) as needles, $[\alpha]_D^{20}$ +13.5 (*c* 0.99 in $CHCl_3$), spectroscopically identical with that obtained previously. Integration of the 400 MHz ^{1}H NMR spectrum of the disilyl ether of this material in the presence of Pirkle's shift reagent showed it to have 85% ee.

Asymmetric dihydroxylation of 2d using 15.0 mol% DHQD-CLB

By the general method described above, (*E*)-3-diphenylphosphinoyl-1-phenylprop-1-ene **2d** (200 mg, 0.63 mmol), potassium carbonate (261 mg, 1.89 mmol), potassium ferricyanide (624 mg, 1.90 mmol), methanesulfonamide (59 mg, 0.60 mmol), osmium trichloride (3 mg, 0.01 mmol) and DHQD-CLB (38 mg, 0.09 mmol, 15 mol%) gave a crude product after 2 days which was purified by flash chromatography, eluting with 2% methanol in EtOAc, to give the vicinal diol **3d** (174 mg, 79%) as needles, spectroscopically identical with that obtained previously, $[\alpha]_D^{20}$ +12.2 (*c* 0.40 in $CHCl_3$). Integration of the 400 MHz ^{1}H NMR spectrum of the disilyl ether of this material in the presence of Pirkle's shift reagent showed it to have 86% ee.

Asymmetric dihydroxylation of 2d using 25.0 mol% DHQD-PHN

By the general method described above, (*E*)-3-diphenylphosphinoyl-1-phenylprop-1-ene **2d** (200 mg, 0.63 mmol), potassium carbonate (261 mg, 1.89 mmol), potassium ferricyanide (624 mg, 1.90 mmol), methanesulfonamide (59 mg, 0.60 mmol), osmium trichloride (3 mg, 0.01 mmol) and DHQD-PHN (79 mg, 0.16 mmol, 25 mol%) gave a crude product after 2 days which was purified by flash chromatography, eluting with 2% methanol in EtOAc, to give the vicinal diol **3d** (149 mg, 79%) as needles, $[\alpha]_D^{20}$ +10.4 (*c*. 0.50 in $CHCl_3$), spectroscopically identical with that obtained previously. Integration of the 400 MHz ^{1}H NMR spectrum of the disilyl ether of this material in the presence of Pirkle's shift reagent showed it to have 88% ee.

Asymmetric dihydroxylation of 2a using 15.0 mol% DHQD-CLB

By the general method described above, (*E*)-1-diphenylphosphinoylbut-2-ene **2a** (1.59 g, 5.9 mmol), potassium carbonate (2.4 g, 17.3 mmol), potassium ferricyanide (5.7 g, 17.3 mmol), methanesulfonamide (550 mg, 5.8 mmol), osmium trichloride (30 mg, 0.10 mmol) and DHQD-CLB (352 mg, 0.88 mmol, 15.0 mol%) gave a crude product after 2 days which was purified by flash chromatography, eluting with 8% methanol in EtOAc, to give the vicinal diol **3a** (1.60 mg, 94%) as an oil, $[\alpha]_D^{20}$ −3.1 (*c* 1.62 in $CHCl_3$), spectroscopically identical with that obtained previously. Integration of the 500 MHz ^{1}H NMR spectrum of the Mosher's ester of a derivative **13** (R = Me) of this material showed it to have 46% ee.

(2*R*,3*S*)-1-Diphenylphosphinoylpentane-2,3-diol *syn*-3b

By the general method described above, 1-diphenylphosphinoylpent-2-ene **2b** (700 mg, 2.59 mmol, 92:8 *E*:*Z* mixture), potassium carbonate (1.06 g, 7.7 mmol), potassium ferricyanide (2.5 g, 7.6 mmol), methanesulfonamide (245 mg, 2.6 mmol), osmium trichloride (11 mg, 36 μmol) and DHQD-CLB (154 mg, 0.38 mmol, 15.0 mol%) gave a crude product after being stirred for 1 day. Flash chromatography of the crude product, eluting with 8% methanol in EtOAc, gave the *vicinal diol syn*-**3b** (816 mg, 103%, 92:8 *syn*:*anti*) as an oil, R_f(8% methanol in EtOAc) 0.23; $[\alpha]_D^{20}$ −0.3 (*c* 0.78 in $CHCl_3$) (Found: M^+, 304.1233. $C_{17}H_{21}PO_3$ requires *M*, 304.1228); ν_{max}/cm^{-1} ($CHCl_3$) 3359 (OH) 1438 (P–Ph) and 1172 (P=O); δ_H(400 MHz; $CDCl_3$) 7.8–7.4 (10 H, m, Ph_2PO), 4.51 (1 H, br s, OH), 3.98 (1 H, m, C*H*OH), 3.40 (1 H, m, C*H*OH), 2.99 (1 H, br s, OH), 2.70 (1 H, ddd, *J* 8, 10 and 12, PCH_AH_B), 2.42 (1 H, ddd, *J* 3, 9 and 15, PCH_AH_B), 1.52 (2 H, m) and 0.95 (3 H, t, *J* 7, Me); δ_C(100 MHz; $CDCl_3$) 134–128 (m, Ph_2PO), 76.1$^+$ (d, $^3J_{PC}$ 12, CHOH), 69.1$^+$ (d, $^2J_{PC}$ 5, CHOH), 33.5$^-$ (d, $^1J_{PC}$ 71, PCH_2), 26.2$^-$ and 10.1$^+$ (Me); *m/z* 304.1 (1%, M^+), 245.1 (80, M^+ − CHOHEt), 202.1 (Ph_2POH) and 201.0 (100, Ph_2PO). Integration of the 500 MHz ^{1}H NMR spectrum of the Mosher's ester of a derivative[6] **13** (R = Et) of this material showed it to have 76% ee.

Asymmetric dihydroxylation of 2c using 2.0 mol% DHQD-CLB

By the general method described above, (*E*)-1-diphenylphosphinoylhept-2-ene **2c** (200 mg, 0.67 mmol), potassium carbonate (139 mg, 1.00 mmol), potassium ferricyanide (668 mg, 2.03 mmol), methanesulfonamide (31 mg, 0.32 mmol), osmium trichloride (3 mg, 0.01 mmol) and DHQD-CLB (6.4 mg, 13 μmol, 2.0 mol%) gave a crude product after 3 days which was purified by flash chromatography, eluting with EtOAc, to give the vicinal diol **3c** (142 mg, 64%) as needles, $[\alpha]_D^{20}$ +3.1 (*c* 0.50 in $CHCl_3$), spectroscopically identical with that obtained previously. Integration of the 400 MHz ^{1}H NMR spectrum of the

disilyl ether of this material in the presence of Pirkle's shift reagent showed it to have 58% ee.

Asymmetric dihydroxylation of 2c using 15.0 mol% DHQD-CLB

By the general method described above, (*E*)-1-diphenylphosphinoylhept-2-ene **2c** (200 mg, 0.67 mmol), potassium carbonate (139 mg, 1.00 mmol), potassium ferricyanide (668 mg, 2.03 mmol), methanesulfonamide (31 mg, 0.32 mmol), osmium trichloride (3 mg, 0.01 mmol) and DHQD-CLB (48 mg, 100 μmol, 15 mol%) gave a crude product after 3 days which was purified by flash chromatography, eluting with 3% methanol in EtOAc, to give the vicinal diol **3c** (127 mg, 57%) as needles, $[\alpha]_D^{20}$ +7.0 (*c* 0.40 in $CHCl_3$, 76% ee), spectroscopically identical with that obtained previously. Integration of the 400 MHz ^{1}H NMR spectrum of the disilyl ether of this material in the presence of Pirkle's shift reagent showed it to have 76% ee. This reaction was also performed on a 6.5 g scale in 90% yield.

Asymmetric dihydroxylation of 2c using 25.0 mol% DHQD-PHN

By the general method described above, (*E*)-1-diphenylphosphinoylhept-2-ene **2c** (200 mg, 0.67 mmol), potassium carbonate (277 mg, 2.00 mmol), potassium ferricyanide (668 mg, 2.03 mmol), methanesulfonamide (64 mg, 0.67 mmol), osmium trichloride (3 mg, 0.01 mmol) and DHQD-PHN (85 mg, 0.17 mmol, 25 mol%) gave a crude product after 1 day which was purified by flash chromatography, eluting with 3% methanol in EtOAc, to give the vicinal diol **3c** (155 mg, 70%) as needles, $[\alpha]_D^{20}$ +8.0 (*c*. 0.40 in $CHCl_3$), spectroscopically identical with that obtained previously. Integration of the 400 MHz ^{1}H NMR spectrum of the disilyl ether of this material in the presence of Pirkle's shift reagent showed it to have 75% ee.

Asymmetric dihydroxylation of 2h using 13.0 mol% DHQD-CLB

By the general method described above, 1-(diphenylphosphinoylmethyl)cyclohexene[23] **2h** (200 mg, 0.68 mmol), potassium carbonate (281 mg, 2.00 mmol), potassium ferricyanide (671 mg, 2.03 mmol), methanesulfonamide (63 mg, 0.67 mmol), osmium trichloride (3 mg, 0.01 mmol) and DHQD-CLB (41 mg, 88 μmol, 13 mol%) gave a crude product after 1 day which was purified by flash chromatography, eluting with EtOAc, to give the vicinal diol **3h** (138 mg, 62%) as needles, $[\alpha]_D^{20}$ −2.0 (*c* 1.40 in $CHCl_3$), spectroscopically identical with that obtained previously. Integration of the 400 MHz ^{1}H NMR spectrum of the disilyl ether of this material in the presence of Pirkle's shift reagent showed it to have 60% ee.

Asymmetric dihydroxylation of 2h using 25.0 mol% DHQD-PHN

By the general method described above, 1-(diphenylphosphinoylmethyl)cyclohexene[23] **2h** (200 mg, 0.68 mmol), potassium carbonate (281 mg, 2.00 mmol), potassium ferricyanide (671 mg, 2.03 mmol), methanesulfonamide (63 mg, 0.67 mmol), osmium trichloride (3 mg, 0.01 mmol) and DHQD-PHN (85 mg, 170 μmol, 25 mol%) gave a crude product after 1 day which was purified by flash chromatography, eluting with 1% methanol in EtOAc, to give the vicinal diol **3h** (138 mg, 62%) as needles, $[\alpha]_D^{20}$ −1.5 (*c* 1.40 in $CHCl_3$), spectroscopically identical with that obtained previously. Integration of the 400 MHz ^{1}H NMR spectrum of the disilyl ether of this material in the presence of Pirkle's shift reagent showed it to have 38% ee.

(2*S*,3*R*)-1-Diphenylphosphinoyl-3-phenylbutane-2,3-diol 3e

By the general method described above, (*E*)-1-diphenylphosphinoyl-3-phenylbut-2-ene **2e** (80 mg, 0.24 mmol), potassium carbonate (130 mg, 0.94 mmol), potassium ferricyanide (245 mg, 0.74 mmol), methanesulfonamide (23 mg, 0.24 mmol), osmium trichloride (3 mg, 0.01 mmol) and DHQD-CLB (11.5 mg, 25 μmol, 10 mol%) gave a crude product after 1 day which was purified by flash chromatography, eluting with 2% methanol in EtOAc, to give the *vicinal diol* **3e** (56 mg, 64%) as an oil, R_f(EtOAc) 0.15; $[\alpha]_D^{20}$ +5.7 (*c*. 0.21 in $CHCl_3$) (Found: $M^+ - H_2O$, 348.1278. $C_{22}H_{23}PO_3$ requires $M - H_2O$, 348.1279); ν_{max}/cm^{-1} ($CHCl_3$) 3344 (OH), 1438 (P–Ph) and 1160 (P=O); δ_H(400 MHz; $CDCl_3$) 7.8–7.2 (15 H, m, Ph_2PO and Ph), 4.66 (1 H, d, *J* 2, CHO*H*), 4.23 (1 H, m, C*H*OH), 3.43 (1 H, s, OH), 2.39 (2 H, m, PCH_2) and 1.55 (3 H, s, Me); δ_C(63 MHz; $CDCl_3$) 144.5$^-$ (*ipso*-Ph), 134–126 (m, Ph_2PO and Ph), 76.2$^-$ (d, $^3J_{PC}$ 13, *C*MeOH), 73.7$^+$ (d, $^2J_{PC}$ 5, CHOH), 31.9$^-$ (d, $^1J_{PC}$ 72, PCH_2) and 21.0$^+$ (s, Me); *m/z* 348.1 (60%, M − H_2O), 245.1 [100, $Ph_2P(O)CH_2CHO$], 201.0 (95, Ph_2PO) and 77 (55, Ph). Integration of the 400 MHz ^{1}H NMR spectrum of this material in the presence of Pirkle's shift reagent showed it to have 42% ee.

(2*S*,3*R*)-1-Diphenylphosphinoyl-2-methylheptane-2,3-diol 3f

By method F2, (*E*)-1-diphenylphosphinoyl-2-methylhept-2-ene **2f** (1.0 g, 3.2 mmol), potassium ferricyanide (3.1 g, 9.4 mmol), potassium carbonate (1.3 g, 9.4 mmol), DHQD-CLB (188 mg, 0.48 mmol), methanesulfonamide (301 mg, 3.2 mmol) and osmium trichloride (15 mg, 51 μmol) gave a crude product, which was purified by flash chromatography, eluting with 2% methanol in EtOAc, to give the *vicinal diol* **3f** (1.18 g, 106%) as an oil, R_f(EtOAc) 0.30; $[\alpha]_D^{20}$ −6.3 (*c* 0.63 in $CHCl_3$) (Found: MH^+, 347.1776. $C_{20}H_{27}PO_3$ requires MH^+, 347.1776); ν_{max}/cm^{-1} ($CHCl_3$) 3359 (OH), 1438 (P–Ph) and 1174 (P=O); δ_H(400 MHz; $CDCl_3$) 7.8–7.4 (10 H, m, Ph_2PO), 4.83 (1 H, br s, OH), 3.52 (1 H, br s, OH), 3.50 (1 H, t, *J* 7, C*H*OH), 2.63 (2 H, d, $^2J_{PH}$ 11, PCH_2), 1.5–1.15 (6 H, m), 1.15 (3 H, s, Me) and 0.82 (3 H, t, *J* 7, Me); δ_C(100 MHz; $CDCl_3$) 134–128 (m, Ph_2PO), 77.2$^+$ (CHOH), 75.5$^-$ (d, $^2J_{PC}$ 5, *C*MeOH), 38.1$^-$ (d, $^1J_{PC}$ 69, PCH_2), 30.6$^-$, 29.1$^-$, 24.4$^+$ (d, $^3J_{PC}$ 7, Me), 22.2$^-$ and 14.0$^+$ (Me); *m/z* 347.2 (4%, MH^+), 259.1 (100, M−CHOHBu) and 201.0 (95, Ph_2PO). Integration of the 500 MHz ^{1}H NMR spectrum of the Mosher's ester of a derivative **21** (R^1 = Bu, R^2 = Me) of this material showed it to have 74% ee.

(1*R*,2*S*)-1-Cyclohexyl-3-diphenylphosphinoyl-2-methylpropane-1,2-diol 3g

By method F2, (*E*)-1-cyclohexyl-3-diphenylphosphinoyl-2-methylprop-1-ene **2g** (2.01 g, 5.9 mmol), potassium ferricyanide (5.8 g, 17.6 mmol), potassium carbonate (2.4 g, 17.4 mmol), DHQD-CLB (350 mg, 0.89 mmol), methanesulfonamide (560 mg, 5.8 mmol) and osmium trichloride (35 mg, 105 mmol) gave a crude product, which was purified by flash chromatography, eluting with 3% methanol in EtOAc, to give the *vicinal diol* **3g** (2.12 g, 96%) as an oil, R_f(5% methanol in EtOAc) 0.58; $[\alpha]_D^{20}$ +1.1 (*c* 1.41 in $CHCl_3$) (Found: MH^+, 373.1932. $C_{22}H_{29}PO_3$ requires *M*H, 373.1932); ν_{max}/cm^{-1} ($CHCl_3$) 3348 (OH), 1438 (P–Ph) and 1174 (P=O); δ_H(400 MHz; $CDCl_3$) 7.8–7.4 (10 H, m, Ph_2PO), 4.4–4.2 (3 H, m, OH and CHOH), 2.71 (1 H, dd, $^2J_{PH}$ 1 and *J* 1, PCH_AH_B), 2.61 (1 H, dd, $^2J_{PH}$ 9 and *J* 15, PCH_AH_B), 1.9–1.0 (10 H, m) and 1.29 (3 H, s, Me); δ_C(100 MHz; $CDCl_3$) 134–128 (m, Ph_2PO), 79.8$^+$ (d, $^3J_{PC}$ 5), 75.6$^-$ (d, $^2J_{PC}$ 5, *C*MeOH), 41.0$^-$ (d, $^1J_{PC}$ 69, PCH_2), 37.3$^+$, 31.6$^-$, 26.9$^-$, 26.5$^+$ and 26.4$^+$ (Me) (some peaks coincident); *m/z* 373.2 (10%, MH^+), 289.1 (80, M^+ − c-Hex), 259.1 (100, M^+ − c-Hex-CHOH) and 202.1 (80, Ph_2POH). Integration of the 500 MHz ^{1}H NMR spectrum of the Mosher's ester of a derivative **21** (R^1 = c-Hex, R^2 = Me) of this material showed it to have 84% ee.

(2*R*,3*R*)-1-Diphenylphosphinoylpentane-2,3-diol *anti*-3b

By the general method described above, (*Z*)-1-diphenylphosphinoylpent-2-ene **2b** (86:14 *Z*:*E* mixture; 200 mg, 0.74 mmol), potassium carbonate (304 mg, 2.2 mmol), potassium ferricyanide (727 mg, 2.2 mmol), methanesulfonamide (70 mg, 0.66 mmol), osmium trichloride (3 mg, 10 μmol) and DHQD-CLB (44 mg, 0.11 mmol, 15.0 mol%) gave a crude product after

being stirred for 1 day. Flash chromatography of the crude product, eluting with 8% methanol in EtOAc, gave the *vicinal diol anti*-**3b** (86:14 *anti*:*syn*; 816 mg, 103%) as an oil, R_f(8% methanol in EtOAc) 0.23; $[\alpha]_D^{20}$ −3.1 (*c* 2.54 in $CHCl_3$) (Found: M^+, 304.1211. $C_{17}H_{21}PO_3$ requires *M*, 304.1228); ν_{max}/cm^{-1} ($CHCl_3$) 3376 (OH), 1438 (P−Ph) and 1175 (P=O); δ_H(400 MHz; $CDCl_3$) 7.8–7.4 (10 H, m, Ph_2PO), 4.85 (1 H, br s, OH), 3.96 (1 H, m, C*H*OH), 3.61 (1 H, m, C*H*OH), 2.73 (1 H, br s, OH), 2.59 (1 H, ddd, *J* 7, 9 and 12, PCH_AH_B), 2.41 (1 H, ddd, *J* 2, 8 and 15, PCH_AH_B), 1.42 (2 H, m) and 0.91 (3 H, t, *J* 7, Me); δ_C(100 MHz; $CDCl_3$) 133–128 (m, Ph_2PO), 75.6$^+$ (d, $^3J_{PC}$ 12, CHOH), 69.7$^+$ (d, $^2J_{PC}$ 5, CHOH), 29.9$^-$ (d, $^1J_{PC}$ 72, PCH_2), 25.1$^-$ and 10.2$^+$ (Me); *m/z* 304.1 (1%, M^+), 245.1 (100, M^+ − CHOHEt) and 77.0 (25, Ph). Integration of the 500 MHz ^{1}H NMR spectrum of the Mosher's ester of a derivative **13** (R = Et) of this material showed it to have 22% ee.

Large scale synthesis of diol 3d

Potassium ferricyanide (94.6 g, 287 mmol), potassium carbonate (19.3 mg, 137 mmol), methanesulfonamide (9.0 g, 94 mmol), DHQD-CLB (3.25 g, 7.5 mol%) and allylic phosphine oxide **2d** (30.5 g, 96 mmol) were dissolved in 1:1 tertiary butyl alcohol–water (120 cm^3) and the mixture stirred at 25 °C for 10 min. Osmium trichloride (444 mg, 1.5 mmol) was then added to the reaction mixture after which it was stirred for 5 days. Sodium sulfite (63 g, 500 mmol) was then added to the reaction mixture and the slurry stirred for 30 min. The layers were separated and the aqueous fraction was extracted with dichloromethane (3 × 200 cm^3). The combined organic layer and extracts were washed with aqueous potassium hydroxide (2.0 mol dm^{-3}; 2 × 100 cm^3), water (200 cm^3) and brine (200 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give a crude product. Recystallisation of this from EtOAc–hexane and flash chromatography of the mother liquors, eluting with 4% methanol in EtOAc, gave the vicinal diol **3d** (30.4 g, 90%) as needles, spectroscopically identical with that obtained previously.

(1*RS*,2*SR*)-4-Diphenylphosphinoyl-1-phenylbutane-1,2-diol 7

By the general method described above, osmium(III) chloride (3 mg, 0.01 mmol), methanesulfonamide (40 mg, 0.35 mmol), potassium ferricyanide (337 mg, 1.04 mmol), potassium carbonate (142 mg, 1.04 mmol), quinuclidine (3 mg, 25 μmol, 7.5 mol%) and homoallylic phosphine oxide **6** (117 mg, 0.35 mmol) gave a crude product which was purified by flash chromatography, eluting with 5% methanol in EtOAc to give the diol **7**, mp >220 °C (from EtOAc–hexane), spectroscopically identical with that obtained previously.

General procedure for the silylation of diols with chlorotrimethylsilane and triethylamine

Triethylamine (0.25 cm^3, 1.82 mmol) and chlorotrimethylsilane (0.15 cm^3, 1.32 mmol) were added dropwise to a stirred solution of the diol (0.44 mmol) in dry THF (5 cm^3) at 20 °C. The reaction mixture was stirred for 1 h under argon after which saturated aqueous ammonium chloride (10 cm^3) was added to it. The aqueous layer was separated and extracted with dichloromethane (3 × 10 cm^3) and the combined organic layer and extracts were washed with brine (10 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give a crude product.

(2*R*,3*S*)-1-Diphenylphosphinoyl-2,3-bis(trimethylsilyloxy)butane 8a

By the general method described above, (2*R*,3*S*)-1-diphenylphosphinoylbutane-2,3-diol **3a** (156 mg, 0.53 mmol) gave a crude product. Flash chromatography of this, eluting with 2:1 EtOAc–hexane, gave the *disilyl ether* **8a** (147 mg, 63%) as needles, mp 85–87 °C (from hexane–EtOAc); R_f(EtOAc) 0.61; $[\alpha]_D^{20}$ −3.7 (*c*. 1.0 in $CHCl_3$) (Found: M^+, 434.1861. $C_{22}H_{35}PO_3Si_2$ requires *M*, 434.1870); ν_{max}/cm^{-1} ($CHCl_3$) 1437 (P−Ph) and 1179 (P=O); δ_H(400 MHz; $CDCl_3$) 7.7–7.3 (10 H, m, Ph_2PO), 4.2 (1 H, dddd, *J* 3, 5, 8 and $^3J_{PH}$ 12, PCH_2CH), 3.8 (1 H, ddq, $^4J_{PH}$ 2, *J* 5 and *J* 6, MeC*H*OSiMe$_3$), 2.65 (1 H, ddd, *J* 3, $^2J_{PH}$ 13 and $^2J_{HH}$ 15, PCH_AH_B), 2.4 (1 H, ddd, *J* 8, $^2J_{PH}$ 9 and $^2J_{HH}$ 15, PCH_AH_B), 1.1 (3 H, d, *J* 6, Me), 0.1 (9 H, s, $SiMe_3$) and −0.1 (9 H, s, $SiMe_3$); δ_C(63 MHz; $CDCl_3$) 135–128 (m, Ph_2PO), 70.3–70.1 (m, 2 × COSiMe$_3$), 30.3$^-$ (d, $^1J_{PC}$ 73, PCH_2), 16.5$^+$ (Me), 0.2$^+$ ($SiMe_3$) and 0.1$^+$ ($SiMe_3$); *m/z* 434 (15%, M^+), 317.1 (100, M−MeCHOSiMe$_3$) and 73.0 (95, $OSiMe_3$). Integration of the 400 MHz ^{1}H NMR spectrum of this material in the presence of Pirkle's shift reagent showed it to have 18% ee.

(2*R*,3*S*)-1-Diphenylphosphinoyl-2,3-bis(trimethylsilyloxy)-heptane 8b

By the general method described above, (2*R*,3*S*)-1-diphenylphosphinoylheptane-2,3-diol **3c** (133 mg, 0.40 mmol) gave a crude product. Flash chromatography of this, eluting with EtOAc, gave the *disilyl ether* **8b** (178 mg, 95%) as plates, mp 89–92 °C (from EtOAc–hexane); R_f(EtOAc) 0.62; $[\alpha]_D^{20}$ −10.9 (*c* 1.2 in $CHCl_3$) (Found: C, 65.4; H, 7.25; P, 6.3%; MH^+, 477.2444. $C_{25}H_{41}O_3PSi_2$ requires C, 65.3; H, 7.50; P, 6.2%; *M* H, 477.2410); ν_{max}/cm^{-1} ($CHCl_3$) 1441 (P−Ph) and 1193 (P=O); δ_H(400 MHz; $CDCl_3$) 8.0–7.4 (10 H, m, Ph_2PO), 4.20 (1 H, dddd, *J* 2, 4, 10 and $^3J_{PH}$ 10, PCH_2CH), 3.61 (1 H, ddd, *J* 2, 4 and 10, BuC*H*OSi), 2.62 (1 H, ddd, *J* 2, $^2J_{PH}$ 15 and $^2J_{HH}$ 16, PCH_AH_B), 2.44 (1 H, ddd, *J* 8, $^2J_{PH}$ 10 and $^2J_{HH}$ 16, PCH_AH_B), 1.5–1.1 (6 H, m, 3 × CH_2), 0.95 (3 H, t, *J* 7, Me), 0.09 (9 H, s, $SiMe_3$) and −0.10 (9 H, s, $SiMe_3$); δ_C(63 MHz; $CDCl_3$) 130–127 (m, Ph_2PO), 74.7$^+$ (d, $^3J_{PC}$ 11, PCH_2CH), 69.8$^+$ (d, $^3J_{PC}$ 5, BuCHOSiMe$_3$), 30.9$^-$, 29.0$^-$ (d, $^1J_{PC}$ 68, PCH_2), 30.1$^-$, 22.8$^-$, 14.1$^+$, 0.4$^+$ ($SiMe_3$) and 0.3$^+$ ($SiMe_3$); *m/z* 477.2 (15%, MH^+), 318.1 (100, MH − BuCHOSiMe$_3$), 274.1 (80, $Ph_2POSiMe_3$) and 202 (85, Ph_2POH). Analysis of the 400 MHz ^{1}H NMR spectrum of this material in the presence of Pirkle's chiral shift reagent indicated that it had 49% ee.

(1*S*,2*R*)-1-Phenyl-3-diphenylphosphinoyl-1,2-bis(trimethylsilyloxy)propane 8c

By the general method described above, (1*S*,2*R*)-1-phenyl-3-diphenylphosphinoylpropane-1,2-diol **3d** (74 mg, 0.21 mmol) gave a crude product. Flash chromatography of this, eluting with 2:1 EtOAc–light petroleum (bp 40–60 °C), gave the *disilyl ether* **8c** (76 mg, 73%) as needles, mp 97–99 °C (from EtOAc–hexane); R_f(EtOAc) 0.67; $[\alpha]_D^{20}$ −4.8 (*c* 1.0 in $CHCl_3$) (Found: M^+−Me, 481.1759. $C_{27}H_{37}O_3PSi_2$ requires *M* − Me, 481.1783); ν_{max}/cm^{-1} ($CHCl_3$) 1460 (P−Ph) and 1184 (P=O); δ_H(400 MHz; $CDCl_3$) 7.6–7.3 (15 H, m, Ph_2PO and Ph), 4.83 (1 H, d, *J* 4, PhC*H*OSi), 4.30 (1 H, m, PCH_2CHOSi), 2.63 (1 H, ddd, *J* 4, $^2J_{PH}$ 13 and $^2J_{HH}$ 15, PCH_AH_B), 2.12 (1 H, dd, $^2J_{PH}$ 8 and $^2J_{HH}$ 15, PCH_AH_B), 0.02 (9 H, s, $SiMe_3$) and –0.17 (9 H, s, $SiMe_3$); δ_C(63 MHz; $CDCl_3$) 131–126 (m, Ph_2PO and Ph), 72–70 (m, 2 × CHOSi), 32.0$^-$ (d, $^1J_{PC}$ 73, PCH_2), 0.1$^+$ ($SiMe_3$) and 0.0$^+$ ($SiMe_3$); *m/z* 481.2 (40%, M^+ − Me), 317 (100, M^+ − PhCHOSiMe$_3$) and 201 (50, Ph_2PO). Analysis of the 400 MHz ^{1}H NMR spectrum of this material in the presence of Pirkle's chiral shift reagent indicated that it had 74% ee.

(1*S*,2*S*)-1-Phenyl-4-diphenylphosphinoyl-1,2-bis(trimethylsilyloxy)butane 10

By the general method described above, (1*S*,2*S*)-1-phenyl-4-diphenylphosphinoylbutane-1,2-diol **7** (31 mg, 0.085 mmol) gave a crude product. Flash chromatography of this (EtOAc) gave the *disilyl ether* **10** (23 mg, 53%) as an oil, R_f(EtOAc) 0.54; $[\alpha]_D^{20}$ +1.7 (*c* 0.9 in $CHCl_3$) (Found: M^+ − Me, 495.1942. $C_{28}H_{39}O_3PSi_2$ requires *M* − Me, 495.1941); ν_{max}/cm^{-1} ($CHCl_3$) 1437 (P−Ph) and 1169 (P=O); δ_H(400 MHz; $CDCl_3$) 7.7–7.1 (15 H, m, Ph_2PO and Ph), 4.45 (1 H, d, *J* 5, C*H*Ph), 3.77 (1 H, td, *J* 5 and 7, CHOSi), 2.26 (1 H, m, PCH_AH_B), 2.17 (1 H, m, PCH_AH_B), 1.7–1.4 (2 H, m, PCH_2CH_2), 0.01 (9 H, s, $SiMe_3$) and −0.07 (9 H, s, $SiMe_3$); δ_C(63 MHz; $CDCl_3$) 141–127 (m, Ph_2PO

and Ph), 78.0$^+$ (*C*HOSiMe$_3$), 77.0$^+$ (*C*HOSiMe$_3$), 28.0$^-$ (d, $^1J_{PC}$ 72, PCH$_2$), 0.5$^+$ (SiMe$_3$) and 0.1$^+$ (SiMe$_3$); *m/z* 495.2 (40%, M − Me), 331.1 (100, M−PhCHOSiMe$_3$) and 73 (95, SiMe$_3$). Comparison of the 400 MHz ^{1}H NMR spectra of the Mosher's esters of this material and racemic material indicated that this sample had greater than 95% ee.

(1*S*,2*R*)-1-(Diphenylphosphinoylmethyl)-2-trimethylsilyloxycyclohexanol 9

By the general method described above, (1*S*,2*S*)-1-(diphenylphosphinoylmethyl)cyclohexane-1,2-diol **3h** (21 mg, 0.063 mmol) gave a crude product. Flash chromatography of this, eluting with EtOAc, gave the *silyl ether* **9** (23 mg, 88%) as needles, mp 150–151 °C (from EtOAc–hexane); R_f(EtOAc) 0.52; $[\alpha]_D^{20}$ −4.8 (*c* 0.8 in CHCl$_3$) (Found: M$^+$, 402.1782. $C_{22}H_{31}PO_3Si$ requires *M*, 402.1780); ν_{max}/cm^{-1} (CHCl$_3$) 3350 (OH), 1432 (P−Ph) and 1187 (P=O); δ_H(400 MHz; CDCl$_3$) 7.9–7.4 (10 H, m, Ph$_2$PO and Ph), 3.65 (1 H, dd, *J* 6 and 9, CHOSi), 3.17 (1 H, s, OH), 2.95 (1 H, dd, $^2J_{PH}$ 9 and *J* 12, PC*H*$_A$H$_B$), 2.36 (1 H, dd, $^2J_{HH}$ 12 and $^2J_{PH}$ 15, PCH$_A$*H*$_B$), 2.12 (1 H, m), 1.7–1.1 (7 H, m) and 0.12 (9 H, s, SiMe$_3$); δ_C(63 MHz; CDCl$_3$) 135–127 (m, Ph$_2$PO and Ph), 75.9$^-$ (d, $^3J_{PC}$ 8, CHOSi), 74.0$^+$ (d, $^2J_{PC}$ 4, CHOH), 37.8$^-$ (d, $^1J_{PC}$ 71, PCH$_2$), 36.7$^-$, 30.6$^-$, 23.9$^-$, 20.8$^-$ and 0.1$^+$ (SiMe$_3$); *m/z* 402.2 (20%, M$^+$). Analysis of the 400 MHz ^{1}H NMR spectrum of this material in the presence of Pirkle's chiral shift reagent indicated that it had 60% ee.

(2*S*,3*R*)-1-Diphenylphosphinoyl-3-*tert*-butyldimethylsilyloxyheptan-2-ol 11

By the general method described above, 2,6-dimethylpyridine (239 mg, 1.24 mmol) and *tert*-butyldimethylsilyl trifluoromethylsulfonate (180 mg, 0.68 mmol) were added dropwise to a solution of (2*S*,3*R*)-1-diphenylphosphinoylheptane-2,3-diol **3c** (103 mg, 0.31 mmol) in dry dichloromethane (3 cm^3) at 0 °C. After 16 h, the reaction mixture was diluted with water and extracted with dichloromethane (3 × 10 cm^3). The combined organic extracts were washed with aqueous hydrochloric acid (1.0 mol dm^{-3}; 10 cm^3), dried (MgSO$_4$) and evaporated to give a crude product which was purified by flash chromatography, eluting with EtOAc–hexane (1:1), to yield the *silyl ether* **11** (91 mg, 66%) as an oil, R_f(EtOAc) 0.83; $[\alpha]_D^{20}$ +30.9 (*c* 1.8 in CHCl$_3$, 76% ee) (Found: M$^+$, 446.2405. $C_{25}H_{39}O_3PSi$ requires *M*, 446.2411); ν_{max}/cm^{-1} (CHCl$_3$) 3409 (OH), 1437 (P−Ph) and 1157 (P=O); δ_H(400 MHz; CDCl$_3$) 7.8–7.4 (10 H, m, Ph$_2$PO), 4.34 (1 H, br s, OH), 3.98 (1 H, m), 3.69 (1 H, m), 2.52 (1 H, ddd, *J* 2, 7 and $^2J_{HH}$ 15, PC*H*$_A$H$_B$), 2.37 (1 H, ddd, *J* 11, 12 and $^2J_{HH}$ 15, PCH$_A$*H*$_B$), 1.7–1.3 (6 H, m), 0.87 (3 H, d, *J* 7, Me), 0.79 (9 H, s, Bu^t), −0.01 (3 H, s, SiMe) and −0.25 (3 H, s, SiMe); δ_C(100 MHz; CDCl$_3$) 134–129 (m, Ph$_2$PO), 74.1$^+$, 69.5$^+$ (CHOH and CHOSi), 30.6$^-$ (d, $^1J_{PC}$ 71, PCH$_2$), 30.6$^-$, 28.3$^-$, 25.7$^+$ (Bu^t), 22.9$^-$, 17.9$^-$ (Bu^t), 14.1$^+$ (Me), −4.6$^+$ (s, SiMe) and −4.7$^+$ (s, SiMe); *m/z* 446.2 (10%, M$^+$), 431.2 (70, M − Me), 389.2 (65, M − Bu), 245.1 (100, M − Ph$_2$PO) and 201.0 (60, Ph$_2$PO).

General procedure for Horner–Wittig eliminations

Potassium hydroxide (126 mg, 2.23 mmol) and the β-hydroxyphosphine oxide (1.0 mmol) were stirred in DMSO (8 cm^3) at 55 °C for 2 h. The reaction mixture was quenched with water (10 cm^3) and extracted with ether (3 × 10 cm^3) and the combined extracts were dried (MgSO$_4$) and evaporated under reduced pressure to give a crude product.

(*S*)-Hept-1-en-3-ol 1c

By the general method described above, (2*R*,3*S*)-1-diphenylphosphinoylheptane-2,3-diol **3c** (987 mg, 2.97 mmol) and potassium hydroxide (366 mg, 6.54 mmol) gave a crude product, flash chromatography of which, eluting with light petroleum (bp 30–40 °C)–ether (2:1) gave the *allylic alcohol* **1c** (55 mg, 18%) as an oil, bp 152–154 °C (lit.,[13a] 153–155 °C); R_f(EtOAc) 0.67; $[\alpha]_D^{20}$ −1.6 (*c* 0.54 in CHCl$_3$) {lit.,[36] −21.6 for *R* isomer (*c* 1.02 in EtOH)} (Found: M$^+$, 114.1044. $C_7H_{14}O$ requires *M*, 114.1044); ν_{max}/cm^{-1} (neat) 3341 (OH) and 1644 (C=C); δ_H(250 MHz; CDCl$_3$) 5.85 (1 H, ddd, *J* 6, 10 and 16, CH$_2$=C*H*), 5.20 (1 H, dd, *J* 1 and 16, C*H*$_A$H$_B$=CH), 5.10 (1 H, dd, *J* 1 and 10, CH$_A$*H*$_B$=CH), 4.05 (1 H, m, C*H*OH), 2.15 (1 H, br s, OH) and 1.6–0.9 (9 H, m, 3 × CH$_2$ and Me); δ_C(63 MHz; CDCl$_3$) 141.3$^+$ (CH=CH$_2$), 114.5$^-$ (CH=CH$_2$), 73.3$^+$ (CHOH), 36.7$^-$, 27.5$^-$, 22.6$^-$ and 14.0$^+$ (Me); *m/z* 114.1 (5%, M$^+$) and 57.1 (100, CH$_2$=CHCHOH).

Attempted Horner–Wittig elimination of phosphine oxide 11

By the general method described above, (2*R*,3*S*)-1-diphenylphosphinoyl-3-(*tert*-butyldimethylsilyloxy)heptan-2-ol **11** (138 mg, 0.31 mmol) and potassium hydroxide (17 mg, 0.31 mmol) gave a crude product after 1 h. Flash chromatography of this, eluting with light petroleum (bp 30–40 °C)–ether (2:1) gave the *ketone* **17** (R = Bu) (36 mg, 26%) as an oil, R_f(EtOAc) 0.30 (Found: M$^+$, 314.1432. $C_{19}H_{23}O_2P$ requires *M*, 314.1435); ν_{max}/cm^{-1} (CHCl$_3$) 1714 (C=O), 1437 (P−Ph) and 1173 (P=O); δ_H(400 MHz; CDCl$_3$) 7.8–7.4 (10 H, m, Ph$_2$PO), 2.71 (2 H, AA′BB′ m), 2.53 (2 H, AA′BB′ m), 2.34 [2 H, t, *J* 7, (CO)CH$_2$], 1.46 (2 H, quin, *J* 7, CH$_2$CH$_2$Me), 1.24 (2 H, sextet, *J* 7, CH$_2$Me) and 0.86 (3 H, t, *J* 7, Me); δ_C(63 MHz; CDCl$_3$) 208.8$^-$ (C=O), 134–128 (m, Ph$_2$PO), 42.5$^-$ (*C*H$_2$CO), 34.2$^-$ (d, $^2J_{PC}$ 2, PCH$_2$*C*H$_2$), 25.9$^-$, 23.3$^-$ (d, $^1J_{PC}$ 73, PCH$_2$), 22.3$^-$ and 13.8$^+$ (Me); *m/z* 314.1 (20%, M$^+$), 285.1 (100, M − Et), 272.1 (75, M − CO) and 202.1 (100, Ph$_2$POH).

Attempted Horner–Wittig elimination of diol 3d

By the general method described above, (1*S*,2*R*)-1-phenyl-3-diphenylphosphinoylpropane-1,2-diol **3d** (1.0 g, 2.9 mmol) and potassium hydroxide (354 mg, 6.31 mmol) gave a crude product. Flash chromatography of this, eluting with 2:1 light petroleum (bp 30–40 °C)–ether gave *phenyl ketone* **17** (R = Ph) (305 mg, 31%) as an oil, R_f(EtOAc) 0.21 (Found: M$^+$, 334.1123. $C_{21}H_{19}O_2P$ requires *M*, 334.1123); ν_{max}/cm^{-1} (CHCl$_3$) 1685 (C=O), 1435 (P−Ph) and 1176 (P=O); δ_H(400 MHz; CDCl$_3$) 8.0–7.4 (15 H, m, Ph$_2$PO and Ph), 3.28 (2 H, *AA*′BB′ m) and 2.78 (2 H, AA′*BB*′ m); δ_C(63 MHz; CDCl$_3$) 197.8$^-$ (C=O), 135–127 (m, Ph$_2$PO and Ph), 30.7$^-$ (CH$_2$CO) and 23.7$^-$ (d, $^1J_{PC}$ 74, PCH$_2$); *m/z* 334.1 (80%, M$^+$), 306.1 (90), 201.1 (90, Ph$_2$PO), 105 (100, PhCO) and 77 (90, Ph).

(*S*)-2-Phenylbut-3-en-2-ol 1e

By the general method described above, (2*S*,3*R*)-3-phenyl-1-diphenylphosphinoylbutane-2,3-diol **3e** (29 mg, 79 μmol) and potassium hydroxide gave a crude product which was purified by flash chromatography, eluting with ether, to give the *allylic alcohol* **1e** (5.3 mg, 44%) as an oil, R_f(3:1 hexane–EtOAc) 0.28; $[\alpha]_D^{20}$ −2.1 (*c* 0.38 in CHCl$_3$) (Found: M$^+$, 148.0888. $C_{10}H_{12}O$ requires *M*, 148.0888); ν_{max}/cm^{-1} (neat) 3420 (OH) and 1638 (C=C); δ_H(250 MHz; CDCl$_3$) 7.5–7.2 (5 H, m, Ph), 6.16 (1 H, dd, *J* 11 and 18, C*H*=CH$_2$), 5.27 (1 H, dd, *J* 1 and 18, CH=C*H*$_A$H$_B$), 5.14 (1 H, dd, *J* 1 and 11, CH=CH$_A$*H*$_B$), 1.91 (1 H, br s, OH) and 1.66 (3 H, s, Me); δ_C(63 MHz; CDCl$_3$) 146.4$^-$, 144.9$^+$ (H$_2$C=CH), 128.2$^+$, 127.0$^+$, 125.1$^+$, 112.3$^-$, 74.7$^-$ (COH) and 29.3$^+$ (Me); *m/z* 148.1 (10%, M$^+$) and 77.0 (100, Ph).

(*R*)-2-Methylenecyclohexanol 1h

Sodium hydride (60% dispersion in oil; 49 mg, 1.22 mmol) was added to a stirred solution of diol **3h** (200 mg, 0.61 mmol) in dry DMF (7 cm^3) at 20 °C. The reaction was stirred at 60 °C for 1 h and then cooled to 20 °C, diluted with brine (10 cm^3) and extracted into ether (3 × 10 cm^3). The combined organic extracts were washed with water (10 cm^3) and saturated brine (10 cm^3), dried (MgSO$_4$) and evaporated under reduced pressure to give a crude product which was purified by flash chromatography, eluting with hexane–EtOAc (1:1), to give the allylic alcohol **1h** (40 mg, 60%) as a liquid, R_f(1:1 hexane–

EtOAc) 0.55; $[a]_D^{20}$ −1.2 (*c* 1.4 in $CHCl_3$) {lit.,[37] +10.6 for *S* isomer (*c* 1.76 in $CHCl_3$)}; ν_{max}/cm^{-1} ($CHCl_3$) 3358 (OH) and 1653 (C=C); δ_H(250 MHz; $CDCl_3$) 4.87 (1 H, br s, C=CH_AH$_B$), 4.74 (1 H, br s, C=CH$_A$$H_B$), 4.08 (1 H, m, C*H*OH) and 2.45–1.0 (9 H, m, 4 × CH_2 and OH); δ_C(63 MHz; $CDCl_3$) 151.5$^-$ (CH_2=C), 105.0$^-$ (CH_2=C), 72.5$^+$ (CHOH), 36.5$^-$, 33.4$^-$, 29.6$^-$ and 27.7$^-$. Integration of the 235 MHz ^{19}F NMR spectrum of the Mosher's esters of this material showed that it had 12% ee.

Attempted Horner–Wittig elimination of diol 3d using DBU in DMSO

A solution of diol **3d** (95 mg, 0.27 mmol) and DBU (82 mg, 0.54 mmol) in DMSO (2 cm^3) was stirred at 50 °C for 2 days. The reaction mixture was quenched with water (5 cm^3) and extracted into ether (3 × 5 cm^3), dried ($MgSO_4$) and evaporated to give a crude product, analysis of the crude product by 400 MHz ^{1}H NMR spectroscopy showed that only starting material and residual DMSO were present.

Attempted elimination of disilyl ether 8c using TBAF in THF

A solution of disilyl ether **8c** (155 mg, 0.30 mmol) and TBAF (1.1 mol dm^{-3} solution in THF; 0.85 cm^3) in dry THF (5 cm^3) was refluxed for 16 h. The reaction mixture was quenched with water (10 cm^3) and extracted into ether (3 × 10 cm^3) and the combined extracts were dried ($MgSO_4$) and evaporated to give a crude product. Flash chromatography of this, eluting with EtOAc, gave the phenyl ketone **17** (R = Ph) (59 mg, 39%) as an oil, spectroscopically identical with that obtained previously.

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