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Enantioselective synthesis of phospholanes using chiral lithium amide desymmetrisation

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Abstract—The enantioselective deprotonation of 1,2,5-triphenylphospholane oxide with a chiral base, followed by electrophilic quenching, gives a range of chiral products in good yield and in ca. 85% ee. The absolute and relative configuration of two of the products was determined by X-ray crystallography. A number of the chiral phospholane oxides were subjected to further transformations, in particular reduction to give enantiomerically pure phospholanes. © 2002 Published by Elsevier Science Ltd.

1. Introduction

As part of our efforts to delineate the applications of chiral lithium amide base reagents, we have described desymmetrisation reactions of diverse types of substrate, including ketones, sulfoxides, chromium arene complexes and various dicarbonyl compounds.[1,2] Extension of this type of process to phosphorus containing compounds was deemed attractive, especially since chiral phosphines are such valuable ligands in asymmetric catalysis. We therefore became interested in an asymmetric approach to such compounds involving reaction of a prochiral cyclic phosphine oxide with a chiral base, exemplified in its simplest form by the conversion of **1** into **2**, Scheme 1.[3]

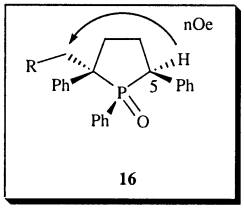
As in similar established chiral lithium amide reactions, it was anticipated that chiral base discrimination between enantiotopic protons located at the two acidic sites (α and α′) would lead to a chiral, non-racemic organolithium intermediate, which upon electrophilic quenching would give potentially useful chiral products. This plan presented a number of challenges, especially since the levels of diastereocontrol required in both the deprotonation and electrophilic quenching steps could not be guaranteed.[4,5]

2. Chiral base reactions of a substituted phospholane

After some preliminary work we decided to investigate in detail the chemistry of the triphenyl substituted phospholane oxide **3**, which is readily available in three steps, via the corresponding phosphole and phosphole oxide, starting from 1,3-diphenylbutadiene.[6] Pleasingly, reaction of this system with chiral lithium amide **4**, followed by quenching with a range of electrophiles, gave the desired products **5**–**15** in good yield and enantiomeric excess, Table 1.

Preliminary reactions showed that the inclusion of LiCl at very low temperature gave better results than reactions at −78°C without this additive.[7] Chiral base **4** also gave better selectivities than a number of alternative bases that were tried.

In each case only one diastereomer was found in respect of the ring stereochemistry, in which electrophilic quenching had occurred to maintain the all-*syn* arrangement of ring phenyl substituents. Evidence for this was obtained from NMR spectroscopy experiments in which nOe enhancements (2–4%) were found between the C-5H proton and protons on the newly introduced substituent, as illustrated for **16**, thereby indicating a *syn* relationship.



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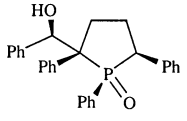

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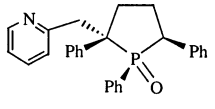

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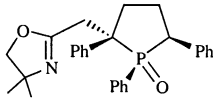

15

The adducts with benzaldehyde and cyclohexylcarboxaldehyde, **11** and **12**, respectively, were formed as mixtures of

Keywords: asymmetric synthesis; chiral lithium amide; phospholane.

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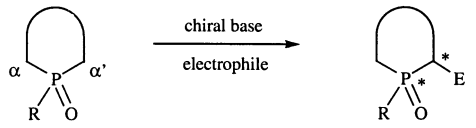


1 2

Scheme 1.

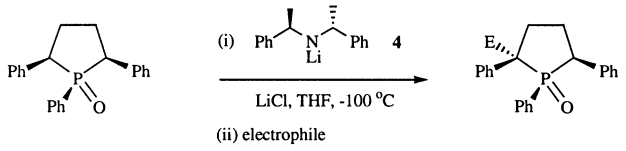
diastereoisomers at the newly formed carbinol centre. In the case of **12**, no selectivity was observed, but in the case of **11** a 7:1 mixture was obtained, the major product having the stereochemistry illustrated (as shown by X-ray crystallography). The quenches involving picolyl chloride, leading to **14**, and 2-chloromethyl-4,4-dimethyloxazoline, leading to **15**, were carried out with the idea of introducing additional functionality with potential for metal chelation.

Lithiated phosphine oxides have been demonstrated to be configurationally unstable under the types of reaction conditions that we are employing.[8] Therefore, the high level of diastereocontrol seen in the above reactions is likely to be the result of very effective steric shielding of one face of the reactive intermediate by the two fixed phenyl substituents, rather than due to configurational stability of the chiral organolithium.

The levels of enantioselectivity are synthetically useful, especially since several of the products are readily enriched to >98% ee by recrystallisation (see Section 6). The small variations in the ee of the products, around an average of about 85%, are probably not significant and do not seem to correlate in any way with the nature of the electrophile employed.

Since all of the products come from a common intermediate organolithium they must all have the same absolute configuration. We sought to assign the absolute configuration

Table 1. Enantioselective substitution of phospholane oxide **3**



3 5-15

Entry	Electrophile	Compound (%)	ee (%)[a]
1	MeI	**5** (87)	84
2	EtI	**6** (89)	90
3	BnBr	**7** (62)	[b]
4	Allyl bromide	**8** (72)	87
5	Prenyl bromide	**9** (93)	88
6	$PhSSO_2Ph$	**10** (60)	82
7	PhCHO	**11** (82)[c]	92
8	Cyclohexyl-CHO	**12** (74)[c]	80
9	Acetone	**13** (85)	86
10	Picolyl chloride	**14** (61)	84
11	Oxazoline[d]	**15** (74)	82

[a] Measured by HPLC.
[b] Not determined.
[c] Mixture of diastereomers.
[d] 2-Chloromethyl-4,4-dimethyloxazoline.

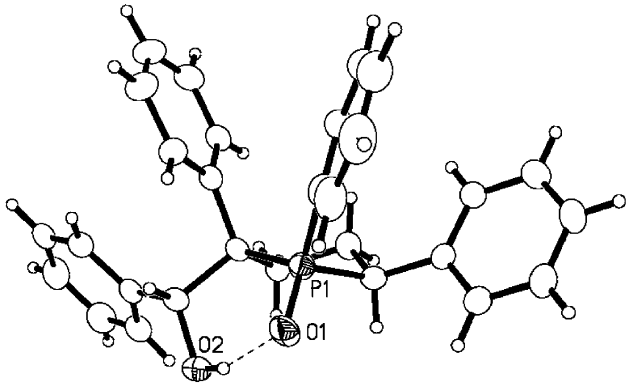


Figure 1. Structure of compound **11**.

by X-ray crystallography using enantiomerically enriched samples. The structures of compounds **11** (major diastereomer) and **13** were determined in this way (Figs. 1 and 2), the collection of low temperature data, including Friedel equivalents, allowing us to determine the Flack parameter and so assign the absolute configurations.

The structure of **11** also shows clearly the full relative stereochemistry, as indicated earlier. Both structures show evidence for intramolecular O–H···O=P hydrogen bonding for **11** [O···O, 2.71 Å; H···O, 1.85 Å; O–$\hat{H}$···O, 157°].

In previous reports we have rationalised the outcome of the chiral base reactions by a simple model, shown in revised form for the phosphine oxide deprotonation in Fig. 3.[9]

The model invokes the free monomer of the lithium amide as the active base in the conformation shown for the solid state (where the base is actually in the form of a homochiral dimer).[10] Approach of the phosphine oxide to the base is via an unhindered quadrant, leading to proton abstraction following co-ordination of the base to the P=O group. Although this primitive representation of the process ignores complications caused by aggregates and mixed aggregates, and possible conformational changes in the base, it seems to have some general predictive power in most cases encountered to date.[11]

During the course of our studies a related paper appeared by

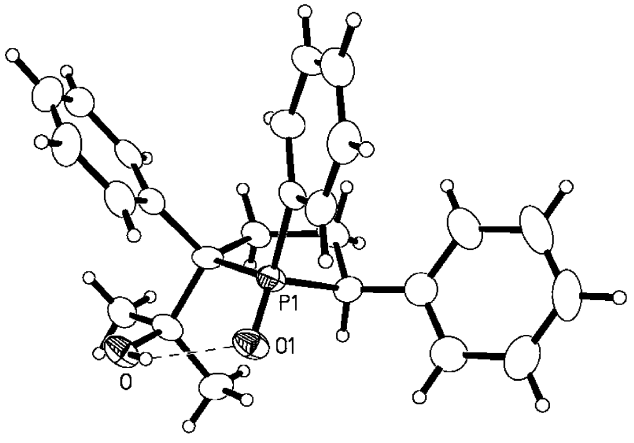


Figure 2. Structure of compound **13**.

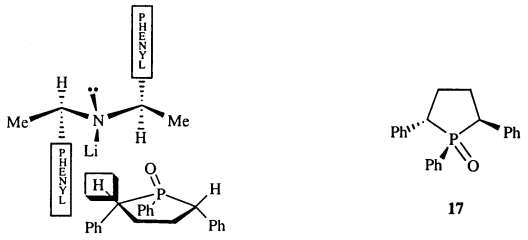


Figure 3.

Fiaud and co-workers.[12] In this work they attempted the enantioselective conversion of **3** into a chiral *trans*-isomer **17** by deprotonation with *sec*-butyllithium-sparteine and reprotonation with various proton sources. This procedure gave either low chemical yields of the desired chiral compound or low enantioselectivities and the results are not easily compared with our own.

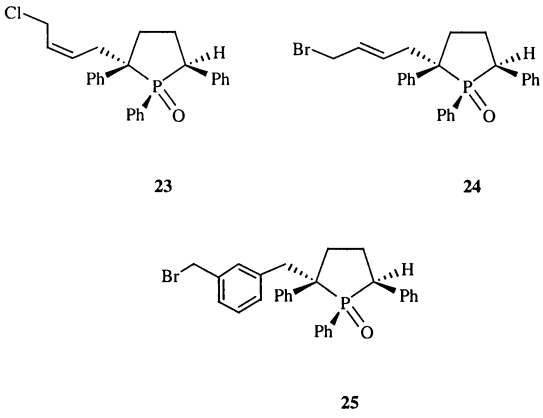
Although we were unable to obtain *trans* compound **17** in non-racemic form from our chiral base reactions, we did observe isomerisation of **3** to give this isomer on prolonged treatment with bases under protic conditions. This result prompted us to isomerise some of the enantiomerically pure phosphine oxides that had been obtained earlier, as shown in Scheme 2.

In each case most of the starting material was converted into the corresponding C-5 diastereoisomer, the transformation being accompanied in each case by a distinctive upfield shift in the C-5H signal in the ^{1}H NMR spectrum.

Along similar lines, we were also able to effect an additional substitution reaction using enantiomerically pure phospholane **5**, Scheme 3.

Deprotonation with *n*-BuLi followed by quenching with either acetic anhydride or benzaldehyde gave **21** and **22**, respectively, again as single C-5 isomers, presumably with the stereochemistry shown.

A further aspect that we were intrigued to explore was the possibility of using the chiral base reaction to link two phospholane rings together. Such an approach might ultimately lead to chiral *bis*-phosphines, which are a very important family of ligands for transition metal catalysis, and the use of linked phospholanes has precedent in the DuPhos ligands.[13] To test this idea we carried out the metallation of **3** with *n*-BuLi and then added various dihalides, including (*Z*)-1,4-dichlorobutene, (*E*)-1,4-dibromobutene and α,α′-dibromo-*m*-xylene. However, in each case we obtained only the mono-alkylated products **23**–**25**.



Even when compounds such as **23** or **24** were re-exposed to an excess of the organolithium derived from **3** none of the desired *bis*-phospholane oxide was observed. This line of investigation was not pursued further.

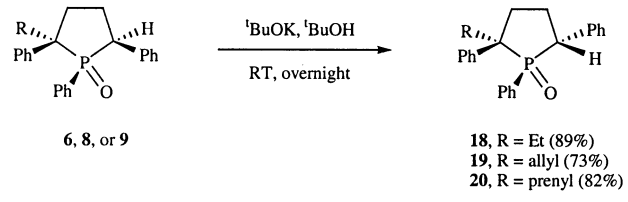
Although we were pleased with the levels of asymmetric induction obtained in the chiral base reactions, phosphine oxide **3** is clearly a rather special case that benefits from additional benzylic stabilisation of the derived organolithium. We briefly screened a range of chiral bases in similar reactions with the simpler system, 1-phenylphospholane oxide, lacking the additional flanking phenyl substituents. However, this gave unsatisfactory results, both in the low yields obtained and in the negligible levels of enantiomeric excess.

3. Further synthetic transformations of chiral phospholane oxides

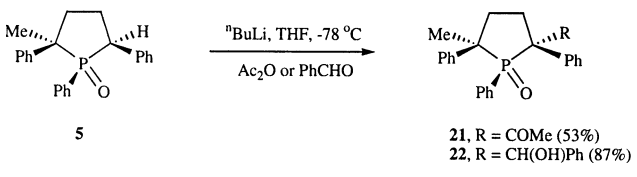
In view of the great interest in phosphines having additional heteroatom functionality, it was of interest to examine the range of transformations possible with some of the phosphine oxides that we had generated in very high enantiomeric purity. Oxidative transformations successfully carried out on enantiomerically pure allyl derivative **8** included hydroboration and oxidative cleavage, leading to new products **26** and **27**, Scheme 4.

Although we could have further manipulated the acid **27** or ester **28** in order to obtain the corresponding aldehyde, we found that it was more straightforward to obtain this compound by ozonolysis of the prenyl derivative **9**. As shown in Scheme 5, this also allowed easy access to potentially useful alcohol and mesylate derivatives.

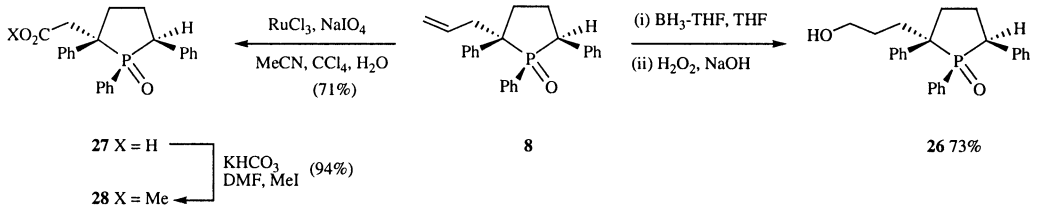
Some further transformations were not successful. For example, attempted McMurry reactions of aldehyde **29** gave only pinacol type diols as mixtures of inseparable



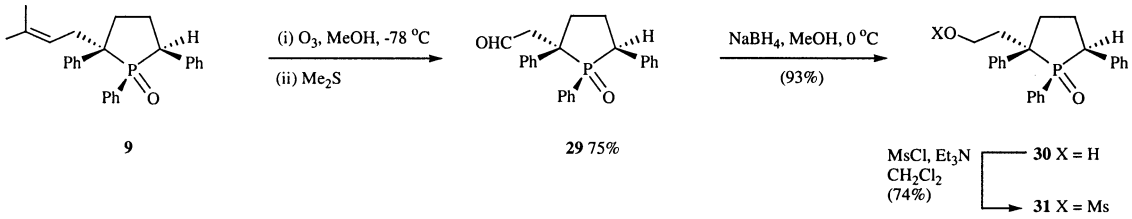
Scheme 2.



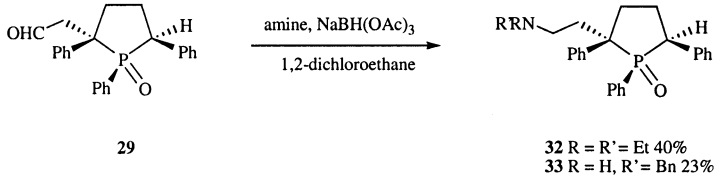
Scheme 3.



Scheme 4.



Scheme 5.



Scheme 6.

diastereomers and further elimination did not prove possible. Similarly, attempted substitution reactions of mesylate **31** with secondary amines, or with Ph_2PLi, did not give the desired products. However, aldehyde **29** did prove amenable to reductive amination, albeit in modest yield, e.g. to give **32** and **33**, Scheme 6.

These preparations were not fully optimised, and indeed we found that higher yields (>50%) could be obtained by an alternative two step procedure involving a separate imine formation step, followed by reduction with $NaBH_4$.

4. Reduction of phosphine oxides to give enantiomerically pure phosphines

With a number of highly enantiomerically enriched samples of phospholane oxides available it was important to establish if they could be reduced to the corresponding phosphines. A wide range of reagents is available for such a transformation, but we chose to focus on the use of the trichlorosilane–pyridine combination in benzene.[14] This reagent has been shown to reduce phosphine oxides with retention of configuration at phosphorus, although we could not be certain that this stereochemical outcome would prevail in our systems. To check this, we first reduced oxide **5** to give a phosphine assigned the structure **34**, Scheme 7.

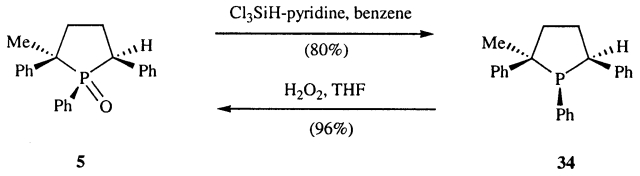
As shown, the phosphine was then re-oxidised using hydrogen peroxide, giving back only compound **5**, with data identical to the initial sample. At no stage were significant amounts of any isomers observed, indicating that both the reduction and oxidation are at least highly stereoselective (possibly even stereospecific).

A number of other phosphine oxides were reduced in this way to give the corresponding enantiomerically pure phosphines, Table 2.

In most cases the reductions were straightforward, the product phosphines being isolated as single isomers in good yield. However, several aspects deserve further comment. It was not possible to reduce the hydroxymethyl types of phospholane oxide **11**–**13** without retro-addition taking place. Therefore, the reduction of compound **11** was carried out on the acetate derivative. The reduction of amine containing systems **32** and **33** was found to be somewhat unreliable, these compounds having a tendency to undergo epimerisation at the C-5 position, as illustrated earlier in Scheme 2. These compounds were best reduced immediately after purification.

5. Summary and conclusion

The chiral lithium amide base reactions of phospholane oxide **3** enable the synthesis of novel chiral phosphine oxides in good yield and enantiomeric excess. This in turn allowed the synthesis of a range of chiral phosphines following reduction. To date we have been unable to carry out substantial screening of these ligands in appropriate metal catalysed processes, but the ease of synthesis and



Scheme 7.

range of functional substituents available makes these compounds interesting for further study.

6. Experimental

6.1. General details

Melting points were determined using a Kofler hot-stage melting point apparatus and are uncorrected. Melting points for all phosphines were determined in sealed tubes after purging with N_2. Infrared (IR) spectra were recorded using a Perkin–Elmer 1600 Series FTIR spectrometer. Mass spectra were recorded on a VG Micromass 70E or VG Autospec spectrometer, using electron impact (EI) or fast atom bombardment (FAB). Micro analyses were performed at the microanalytical laboratory of the University of Nottingham using a Perkin–Elmer 240B elemental analyser. Optical rotations were recorded using a JASCO DIP-370 digital polarimeter, and are recorded in units of 10^{-1} deg cm^2 g^{-1}. All NMR spectra were recorded on either a Bruker AM250, JEOL EX270, Bruker AM400 or Bruker DRX500, with tetramethylsilane as internal standard. Trimethylphosphite was used as an external reference for ^{31}P NMR spectra. *J* values are recorded in Hertz and abbreviations used are s—singlet, d—doublet, t—triplet, q—quartet, m—multiplet, dd—double doublet etc. Multiplicities indicated for ^{13}C NMR were obtained using a DEPT sequence.

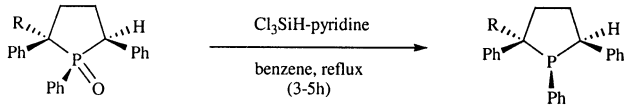
Flash column chromatography was performed using Fluka silica gel 60 (220–440 mesh). Analytical thin layer chromatography (tlc) was performed using CAMLAB silica gel F_{254} precoated plastic plates which were visualised under ultraviolet light and developed with basic potassium permanganate solution. HPLC was performed on Chiralcel OD or OJ columns using a Waters 600E System Controller and a Waters 484 Tuneable Absorbance Detector.

Organic solvents and reagents were dried from the following as required: THF (Na-benzophenone ketyl), acetone ($CaSO_4$), pyridine, triethylamine, dimethyl sulfoxide, dimethylformamide and dichloromethane (calcium hydride). Petrol refers to the fraction boiling between 40 and 60°C and was distilled before use. Unless otherwise stated all other solvents and reagents were used as received from commercial suppliers.

6.2. Typical procedure for chiral base reactions (Table 1)

6.2.1. (1*S*,2*R*,5*S*)-2-Methyl-1,2,5-triphenylphospholane-1-oxide 5. A solution of chiral base **4** containing an equimolar amount of LiCl was prepared by treatment of a suspension of the corresponding secondary amine hydrochloride salt (259 mg, 0.99 mmol) in THF (5 mL), under N_2 at ca. −100°C, with *n*-BuLi (1.4 M in hexanes) (1.39 mL, 1.94 mmol). The suspension was allowed to warm to room temperature over a period of 20 min, during which time all the solid dissolved and the solution turned pale yellow in colour. The reaction mixture was recooled to −100°C (ethanol/N_2) and a solution of 1,2,5-triphenylphospholane oxide **3** (300 mg, 0.90 mmol) in THF (9 mL) was added dropwise over a period of 30 min, maintaining the temperature at −100°C. After stirring the deep orange/red solution at −100°C for a further 30 min, methyl iodide (0.56 mL, 9.04 mmol) was added and stirring of the resultant yellow/orange solution was continued for 2 min before the reaction was quenched with saturated aqueous NH_4Cl (10 mL). In some cases the reaction mixture was stirred for a longer period of time before aqueous quenching, or was allowed to warm up, until TLC indicated complete consumption of starting material.

Table 2. Reduction of phospholane oxides to phospholanes



Entry	R	Phosphine oxide	Phosphine	Yield (%)
1	Me	**5**	**34**	80
2	Et	**6**	**35**	96
3	2-picolyl	**14**	**36**	84
4	Oxazoline	**15**	**37**	76
5	CH(OAc)Ph	**11**[a]	**38**	76
6	$(CH_2)_3OH$	**26**	**39**	81
7	CH_2CO_2Me	**28**	**40**	75
8	$(CH_2)_2NEt_2$	**32**	**41**	44
9	$(CH_2)_2NHBn$	**33**	**42**	79

[a] Reduced in the form of the acetate derivative.

The organic layer was removed and the aqueous layer extracted with CH_2Cl_2 (3×10 mL), the combined organic extracts dried ($MgSO_4$) and the solvent evaporated under reduced pressure to give an off-white solid. Purification by column chromatography (2% EtOH/Et_2O) yielded the title compound **5** as a white solid (272 mg, 87%), mp 197–201°C; $[\alpha]_D^{23}$=+36 (*c* 1.09 in $CHCl_3$); (Found: C, 79.39; H, 6.75. $C_{23}H_{23}OP$ requires C, 79.05; H, 6.69%); ν_{max} ($CHCl_3$) (cm^{-1}) 2968, 1600, 1495, 1454, 1376, 1158, 1108 and 1072; δ_H (400 MHz, $CDCl_3$) 1.87 (3H, d, *J*=13.1 Hz, CH_3), 2.32–2.54 (2H, m, C-3H or C-4H), 2.69 (1H, m, C-3H or C-4H), 2.92 (1H, m, C-3H or C-4H), 4.02 (1H, app. dt, *J*=23.6 and 9.1 Hz, C-5H), 6.87–7.27 (15H, m, ArH); δ_C (68 MHz, $CDCl_3$) 24.0 (d, *J*=12 Hz, CH_2, C-3), 27.2 (CH_3), 34.2 (d, *J*=15 Hz, CH_2, C-4), 45.6 (d, *J*=59 Hz, C and CH, C-2 and C-5), 125.8–131.3 (aromatic CH), 129.1, 136.0 and 142.7 (aromatic C); *m/z* (EI) 346 (M^+, 97%), 220 (48), 205 (24), 143 (31), 118 (84) and 91 (100) (HRMS: Found M^+, 346.1502. $C_{23}H_{23}OP$ requires *M*, 346.1487).

HPLC analysis using a Chiralcel OD column (30% propan-2-ol in hexane as eluent) indicated that the product contained a 92.1:7.9 mixture of enantiomers (84% ee).

Flow rate 1 mL min^{-1}. Detection at 256 nm. Retention times 5.2 min (major) and 11.0 min (minor).

Recrystallisation from EtOH/H_2O afforded material with an enantiomeric excess of 96 and 69% recovery. Alternatively recrystallisation from MeOH/H_2O (×3) afforded material with an enantiomeric excess of ≥99%—$[\alpha]_D^{25}$=+43 (*c* 1.04 in $CHCl_3$), and 30% recovery.

6.2.2. (1*S*,2*R*,5*S*)-2-Ethyl-1,2,5-triphenylphospholane-1-oxide 6. The typical conditions described above were employed, starting with **3** (332 mg, 1.0 mmol). Purification of the crude product by column chromatography (2% EtOH/Et_2O) yielded the title compound **6** as a white solid (322 mg, 89%), mp 196–197°C; $[\alpha]_D^{21}$=+55 (*c* 1.08 in $CHCl_3$); (Found: C, 80.10; H, 6.95. $C_{24}H_{25}OP$ requires C, 79.98; H, 6.99); ν_{max} ($CHCl_3$) (cm^{-1}) 2969, 1600, 1495, 1450, 1157 and 1107; δ_H (400 MHz, $CDCl_3$) 0.74 (3H, t, *J*=7.3 Hz, CH_3), 2.27 (1H, m, C-1′H), 2.36–2.53 (3H, m, C-1′H, C-3H and C-4H), 2.61 (1H, m, C-4H), 2.80 (1H, m, C-3H), 3.98 (1H, app. dt, *J*=23.7 and 8.8 Hz, C-5H) and 6.85–7.19 (15H, m, ArH); δ_C (100 MHz, $CDCl_3$) 7.8 (CH_3), 24.6 (d, *J*=12 Hz, CH_2, C-3), 30.4 (CH_2, C-1′), 30.5 (d, *J*=15 Hz, CH_2, C-4), 46.6 (d, *J*=59 Hz, CH, C-5), 49.9 (d, *J*=62 Hz, C, C-2), 125.8–131.5 (aromatic CH), 129.8 (d, *J*=58 Hz, C, P–C_{Ar}), 136.3 and 140.1 (aromatic C); δ_P(202 MHz, $CDCl_3$) 63.4; *m*/*z* (EI) 360 (M^+, 81%), 345 (78), 332 (100), 256 (31), 216 (23), 117 (45) and 91 (58) (HRMS: Found M^+, 360.1653. $C_{24}H_{25}OP$ requires *M*, 360.1643).

HPLC analysis using a Chiralcel OD column (30% propan-2-ol in hexane as eluent) indicated that the product contained a 95:5 mixture of enantiomers (90% ee). Flow rate 1 mL min^{-1}. Detection at 256 nm. Retention times 4.6 min (major) and 7.3 min (minor).

Recrystallisation from EtOH/H_2O (×2) afforded material of ≥99% ee with 57% recovery.

6.2.3. (1*S*,2*R*,5*S*)-2-Benzyl-1,2,5-triphenylphospholane-1-oxide 7. The typical conditions described above were employed, starting with **3** (332 mg, 1.0 mmol). Purification of the crude product by column chromatography (20% petrol/Et_2O) yielded the title compound **7** as a white solid (261 mg, 62%), mp 193–195°C; $[\alpha]_D^{22}$=+117 (*c* 0.83 in $CHCl_3$); (Found: C, 82.35; H, 6.55. $C_{29}H_{27}OP$ requires C, 82.33; H, 6.17%); ν_{max} ($CHCl_3$) (cm^{-1}) 2953, 1602, 1496, 1454, 1310, 1154 and 1107; δ_H (400 MHz, $CDCl_3$) 2.34–2.53 (3H, m, C-3H and C-4H), 2.75 (1H, m, C-3H or C-4H), 3.56 (1H, dd, *J*=6.3 and 13.9 Hz, C-1′H), 3.66 (1H, dd, *J*=6.3 and 13.9 Hz, C-1′H), 4.13 (1H, app.dt, *J*=23.7 and 9.6 Hz, C-5H), 6.66–7.26 (20H, m, ArH); δ_C (68 MHz, $CDCl_3$) 24.6 (d, *J*=11 Hz, CH_2, C-4), 30.6 (d, *J*=15 Hz, CH_2, C-3), 43.0 (CH_2, C-1′), 46.7 (d, *J*=59 Hz, CH, C-5), 50.9 (d, *J*=61 Hz, C, C-2), 125.8–131.8 (aromatic CH), 129.5, 136.3, 136.6 and 140.3 (aromatic C); *m*/*z* (EI) 422 (M^+, 50%), 331 (34), 210 (25), 149 (80) and 84 (100) (HRMS: Found M^+, 422.1786. $C_{29}H_{27}OP$ requires *M*, 422.1780).

HPLC analysis using a Chiralcel OD, OJ or Chiralpak AD column failed to separate the enantiomers.

6.2.4. (1*S*,2*R*,5*S*)-2-(Prop-2′-enyl)-1,2,5-triphenylphospholane-1-oxide 8. The typical conditions described above were employed, starting with **3** (332 mg, 1.0 mmol). Purification of the crude product by column chromatography (Et_2O) yielded the title compound **8** as a white solid (269 mg, 72%), mp 183–189°C; $[\alpha]_D^{23}$=+92 (*c* 1.01 in $CHCl_3$); (Found: C, 80.46; H, 6.58. $C_{25}H_{25}OP$ requires C, 80.61; H, 6.77%); ν_{max} ($CHCl_3$) (cm^{-1}) 2975, 1638, 1600, 1495, 1450, 1158 and 1106; δ_H (250 MHz, $CDCl_3$) 2.31–2.74 (4H, m, C-3H and C-4H), 2.86 (1H, ddd, *J*=5.5, 8.8 and 14.2 Hz, C-1′H), 3.10 (1H, m, C-1′H), 3.93 (1H, app. dt, *J*=23.5 and 9.1 Hz, C-5H), 4.97 (1H, d, *J*=10.1 Hz, (*E*)-C-3′H), 5.02, (1H, d, *J*=17.1 Hz, (*Z*)-C-3′H), 5.32 (1H, m, C-2′H) and 6.77–7.19 (15H, m, ArH); δ_C (68 MHz, $CDCl_3$) 24.3 (d, *J*=12 Hz, CH_2, C-3), 30.7 (d, *J*=15 Hz, CH_2, C-4), 42.1 (CH_2, C-1′), 46.5 (d, *J*=59 Hz, CH, C-5), 49.1 (d, *J*=61 Hz, C, C-2), 118.4 (CH_2, C-3′), 125.2–132.7 (aromatic CH), 132.9 (CH, C-2′) and 129.3, 136.2, 140.1 (aromatic C); *m*/*z* (EI) 372 (M^+, 100%), 331 (27), 268 (13), 205 (9), 129 (19) and 91 (38) (HRMS: Found M^+, 372.1639. $C_{25}H_{25}OP$ requires *M*, 372.1643).

HPLC analysis using a Chiralcel OD column (30% propan-2-ol in hexane as eluent) indicated that the product contained a 93.6:6.4 mixture of enantiomers (87% ee). Flow rate 1 mL min^{-1}. Detection at 256 nm. Retention times 4.8 min (major) and 7.0 min (minor).

Material of ≥99% ee was obtained with 59% recovery by a single recrystallisation from EtOAc.

6.2.5. (1*S*,2*R*,5*S*)-2-(3′-Methylbut-2′-enyl)-1,2,5-triphenylphospholane-1-oxide 9. The typical conditions described above were employed, starting with **3** (4.0 g, 12.0 mmol). Purification of the crude product by column chromatography (Et_2O) yielded the title compound **9** as a white solid (4.74 g, 93%), mp 172–175°C; $[\alpha]_D^{27}$=+69 (*c* 1.09 in $CHCl_3$); (Found: C, 81.11; H, 7.45. $C_{27}H_{29}OP$ requires C, 80.96; H, 7.3%); ν_{max} ($CHCl_3$) (cm^{-1}) 2969, 1600, 1495, 1451, 1377, 1155 and 1106; δ_H (400 MHz, $CDCl_3$) 1.58 (3H, s, CH_3), 1.61 (3H, s, CH_3), 2.41–2.51 (2H, m, C-4H, 2.55–2.74 (2H, m, C-3H), 4.03 (1H, app. dt, *J*=23.3 and 9.1 Hz, C-5H), 4.81 (1H, t, *J*=6.5 Hz, C-2′H) and 6.86–7.21 (15H, m, ArH); δ_C (100 MHz, $CDCl_3$) 18.0 (CH_3), 24.5 (d, *J*=11 Hz, CH_2, C-4), 25.8 (CH_3), 30.8 (d, *J*=14 Hz, CH_2, C-3), 36.1 (CH_2, C-1′), 46.4 (d, *J*=58 Hz, CH, C-5), 49.7 (d, *J*=61 Hz, C, C-2), 118.1 (CH, C-2′), 125.9–131.6 (aromatic CH), 129.4, 135.1, 135.1 and 140.6 (aromatic C and C-3′); *m*/*z* (EI) 400 (M^+, 17%), 332 (100), 216 (15), 103 (11), 91 (13) and 47 (6) (HRMS: Found M^+, 400.1954. $C_{27}H_{29}OP$ requires *M*, 400.1956).

HPLC analysis using a Chiralcel OD column (30% propan-2-ol in hexane as eluent) indicated that the product contained a 93.9:6.1 mixture of enantiomers (88% ee). Flow rate 1 mL min^{-1}. Detection at 256 nm. Retention times 7.18 min (major) and 9.90 min (minor).

Recrystallisation from EtOH/H_2O (×3) afforded material of ≥99% ee ($[\alpha]_D^{24}$=+74 (*c* 0.49 in $CHCl_3$)) with 45% recovery.

6.2.6. (1*S*,2*R*,5*S*)-2-Phenylsulfanyl-1,2,5-triphenylphospholane-1-oxide 10. The typical conditions described above were employed, starting with **3** (332 mg, 1.0 mmol). Purification of the crude product by column chromatography (35% light petrol/Et_2O→Et_2O) yielded the title compound **10** as a white solid (264 mg, 60%), mp 219–222°C; $[\alpha]_D^{21}$=+100 (*c* 1.01 in $CHCl_3$); (Found: C, 76.26; H, 5.65; S, 7.30. $C_{28}H_{25}OPS$ requires C, 76.34; H, 5.72; S, 7.28); ν_{max} ($CHCl_3$) (cm^{-1}) 2982, 1600, 1495, 1457, 1374 and 1046; δ_H (400 MHz, $CDCl_3$) 2.35–2.56 (2H, m, C-3H and C-4H), 2.73 (1H, m, C-3H), 2.99 (1H, m, C-4H), 4.51 (1H, ddd, *J*=6.3, 10.6 and 24.7 Hz, C-5H) and 6.91–7.33 (20H, m, ArH); δ_C (68 MHz, $CDCl_3$) 23.2 (d, *J*=9 Hz, CH_2, C-4), 31.6 (d, *J*=16 Hz, CH_2, C-3), 44.4 (d, *J*=64 Hz, CH, C-5), 59.7 (d, *J*=61 Hz, C, C-2), 125.3–136.6 (aromatic CH), 129.0, 136.1 and 139.8 (aromatic C); δ_P(202 MHz, $CDCl_3$) 61.4; *m/z* (EI) 440 (M^+, 62%), 332 (56), 206 (19), 129 (40), 103 (61) and 91 (100) (HRMS: Found M^+, 440.1363. $C_{28}H_{25}OPS$ requires *M*, 440.1364).

HPLC analysis using a Chiralcel OD column (30% propan-2-ol in hexane) indicated that the product contained a 90.6:8.3 mixture of enantiomers (82% ee). Flow rate 1 mL min^{-1}. Detection at 256 nm. Retention times 6.0 min (minor) and 10.2 min (major).

Material of ≥ 99% ee— $[\alpha]_D^{24}$=+124 (*c* 1.03 in $CHCl_3$), was obtained with 40% recovery by a single recrystallisation from EtOH/H_2O.

6.2.7. (1*S*,1′*R*,2*R*,5*S*)-2-(Phenyl-1′-hydroxymethyl)-1,2,5-triphenyl phospholane-1-oxide 11 (accompanied by minor (1′*S*)-isomer). The typical conditions described above were employed, starting with **3** (332 mg, 1.0 mmol). Purification of the crude product by column chromatography (30% petrol/Et_2O→Et_2O) yielded firstly the major diastereomer **11** as a white solid (314 mg, 72%), mp 157–161°C, $[\alpha]_D^{23}$=+97 (*c* 1.04 in $CHCl_3$); (Found: C, 79.60; H, 6.25. $C_{29}H_{27}O_2P$ requires C, 79.43; H, 6.21%); ν_{max} ($CHCl_3$) (cm^{-1}) 3355, 2939, 1808, 1601, 1454, 1326 and 1081; δ_H (400 MHz, $CDCl_3$) 2.25–2.45 (2H, m, C-3H or C-4H), 2.61 (1H, m, C-3H or C-4H), 3.08 (1H, m, C-3H or C-4H), 4.01 (1H, ddd, *J*=7.0, 13.4 and 25.4 Hz, C-5H), 5.72 (1H, dd, *J*=2.5 and 5.1 Hz, C-1′H), 6.12 (1H, d, *J*=2.5 Hz, OH) and 6.80–7.11 (20H, m, ArH); δ_C (68 MHz, $CDCl_3$) 25.3 (d, *J*=10 Hz, CH_2, C-3 or C-4), 25.5 (d, *J*=11 Hz, CH_2, C-3 or C-4), 50.9 (d, *J*=57 Hz, CH, C-5), 58.1 (d, *J*=59 Hz, C, C-2), 78.9 (d, *J*=2 Hz, CH, C-1′), 126.3–131.5 (aromatic CH), 129.3, 135.3, 137.6 and139.0 (aromatic C); δ_P(202 MHz, $CDCl_3$) 67.5; *m/z* (FAB) 439 ($[M+H]^+$, 87%), 421 (100), 332 (75), 154 (36), 69 (56) and 57 (59) (HRMS: Found $[M+H]^+$, 439.1865. $C_{29}H_{27}OP$ requires [M+*H*], 439.1827). Followed by the (1′*S*)-epimer of **11** as a white solid (45 mg, 10%) mp 140–143°C $[\alpha]_D^{21}$=+65 (*c* 1.23 in $CHCl_3$); ν_{max} ($CHCl_3$) (cm^{-1}) 3356, 2927, 1602, 1496, 1454 and 1106; δ_H (400 MHz, $CDCl_3$) 2.41–2.57 (3H, m, C-3H and C-4H), 2.54 (1H, m, C-3H or C-4H), 4.27 (1H, app. dt, *J*=22.9 and 9.1 Hz, C-5H), 5.76 (1H, d, *J*=5 Hz, C-1′H), 5.94 (1H, s, OH) and 6.81–7.23 (20H, m, ArH); δ_C (68 MHz, $CDCl_3$) 24.7 (d, *J*=11 Hz, CH_2, C-4), 31.6 (d, *J*=12 Hz, CH_2, C-3), 47.0 (d, *J*=60 Hz, CH, C-5), 54.9 (d, *J*=60 Hz, C, C-2), 78.5 (d, *J*=3 Hz, CH, C-1′), 125.5–131.7 (aromatic CH), 135.5, 135.7, 137.8 and 137.9 (aromatic C); *m/z* (FAB) 439 ($[M+H]^+$, 34%), 421 (32), 332 (32), 154 (97), 136 (69), 69 (87) and 57 (100) (HRMS: Found $[M+H]^+$, 439.1827. $C_{29}H_{27}OP$ requires [M+*H*], 439.1827).

HPLC analysis using a Chiralcel OD column (30% propan-2-ol in hexane as eluent) indicated that the major diastereomer contained a 96:4 mixture of enantiomers (92% ee). Flow rate 1 mL min^{-1}. Detection at 256 nm. Retention times 7.0 min (minor) and 8.7 min (major).

Recrystallisation of a sample of **11** from EtOH/H_2O provided material of 100% ee with 70% recovery.

6.2.8. (1*S*,1′*R*/*S*,2*R*,5*S*)-2-(Cyclohexyl-1′-hydroxymethyl)-1,2,5-triphenyl phospholane-1-oxide 12. The typical conditions described above were employed, starting with **3** (332 mg, 1.0 mmol). Purification of the crude product by column chromatography (60% petrol/Et_2O) yielded the title compound **12** as a white solid and inseparable mixture of two diastereomers (329 mg, 74%); δ_H (400 MHz, $CDCl_3$) 0.78–1.79 (22H, m, C-2′H-C-7′H), 2.28–2.68 (5H, m, C-3H or C-4H), 2.85–3.13 (3H, m, C-3H or C-4H), 3.86 (1H, ddd, *J*=7.6, 12.9 and 24.5 Hz, C-5H), 4.05 (1H, app. dt, *J*=23.6 and 9.5 Hz, C-5H), 4.36 (1H, s, C-1′H), 4.50 (1H, d, *J*=10.9 Hz, C-1′H), 5.11 (1H, s, OH) (D_2O exchange), 5.73 (1H, s, OH) (D_2O exchange) and 6.76–7.44 (30H, m, ArH); *m/z* (FAB) 445 ($[M+H]^+$, 38%), 427 (18), 345 (21), 332 (28), 83 (41) and 69 (100) (HRMS: Found $[M+H]^+$, 445.2312. $C_{29}H_{33}O_2P$ requires [M+*H*], 445.2296).

HPLC analysis of the mixture of diastereomers using a Chiralcel OD column (30% propan-2-ol in hexane as eluent) indicated that the major diastereomer contained a 57:7 mixture of enantiomers (80% ee). Flow rate 1 mL min^{-1}. Detection at 256 nm. Retention times 18.3 min (major) and 22.2 min (minor).

6.2.9. (1*S*,2*R*,5*S*)-2-(1′-Hydroxy-1′-methylethyl)-1,2,5-triphenylphospholane-1-oxide 13. The typical conditions described above were employed, starting with **3** (332 mg, 1.0 mmol). Purification of the crude product by column chromatography (15% petrol/Et_2O) yielded the title compound **13** as a white solid (332 mg, 85%), mp 175–177°C; $[\alpha]_D^{23}$=+100 (*c* 1.03 in $CHCl_3$); (Found: C, 77.31; H, 6.97. $C_{25}H_{27}O_2P$ requires C, 76.90; H, 6.97%); ν_{max} ($CHCl_3$) (cm^{-1}) 3392, 2981, 1601, 1496, 1451, 1378, 1129 and 1102; δ_H (400 MHz, $CDCl_3$) 1.20 (3H, s, CH_3), 1.49 (3H, s, CH_3), 2.21 (1H, m, C-4H), 2.55 (1H, m, C-4H), 2.98–3.21 (2H, m, C-3H), 3.98 (1H, ddd *J*=7.2, 13.4 and 25.6 Hz, C-5H), 5.25 (1H, s, OH) (D_2O exchange) and 6.88–7.25 (15H, m, ArH); δ_C (68 MHz, $CDCl_3$) 25.2 (d, *J*=11 Hz, CH_2, C-4), 27.0 (CH_3), 29.0 (CH_3), 29.5 (d, *J*=10 Hz, CH_2, C-3), 51.1 (d, *J*=59 Hz, CH, C-5), 60.4 (d, *J*=59 Hz, C, C-2), 77.3 (C, C-1′), 125.1–132.1 (aromatic C-H), 129.9 (d, *J*=86 Hz, C, P–C_{Ar}), 135.8 and 137.1 (aromatic C); *m/z* (FAB) 391 ($[M+H]^+$, 38%), 373 (56), 332 (35), 154 (45), 69 (81) and 55 (100) (HRMS: Found $[M+H]^+$, 391.1852. $C_{25}H_{28}O_2P$ requires [M+*H*], 390.1827).

HPLC analysis using a Chiralcel OD column (30% propan-2-ol in hexane as eluent) indicated that the product

contained a 93.1:6.9 mixture of enantiomers (86% ee). Flow rate 1 mL min^{-1}. Detection at 256 nm. Retention times 5.6 min (major) and 7.5 min (minor).

Recrystallisation from EtOH/H_2O afforded material of 97% ee with 69% recovery. X-Ray crystals were grown by slow recrystallisation from EtOAc in a coldroom overnight.

6.2.10. (1*S*,2*R*,5*S*)-2-(2′-Pyridylmethyl)-1,2,5-triphenylphospholane-1-oxide 14. The typical conditions described above were employed, starting with **3** (1.0 g, 3.01 mmol). Purification of the crude product by column chromatography (5% EtOH/Et_2O) yielded the title compound **14** as a pale yellow solid (778 mg, 61%), mp 193–194°C; $[\alpha]_D^{24}$=+146 (*c* 1.04 in $CHCl_3$); (Found: C, 79.47; H, 6.14; N, 3.30. $C_{28}H_{26}NOP$ requires C, 79.41; H, 6.19; N, 3.31%); ν_{max} ($CHCl_3$) (cm^{-1}) 2965, 1590, 1569, 1495, 1449 and 1106; δ_H (400 MHz, $CDCl_3$) 2.41–2.56 (2H, m, C-3H or C-4H), 2.79–3.02 (2H, m, C-3H or C-4H), 3.75 (2H, collapsed AB system, C-1′H), 4.15 (1H, ddd, *J*=7.4, 10.3 and 23.1 Hz, C-5H), 6.21 (1H, d, *J*=7.8 Hz, C-3′H), 6.90–7.25 (17H, m, ArH) and 8.51 (1H, d, *J*=5.8 Hz, C-6′H); δ_C (100 MHz, $CDCl_3$) 23.9 (d, *J*=12 Hz, CH_2, C-4), 29.6 (d, *J*=14 Hz, CH_2, C-3), 44.6 (CH_2, C-1′), 45.6 (d, *J*=59 Hz, CH, C-5), 50.3 (d, *J*=61 Hz, C, C-2), 121.1 (CH, C-3′), 124.6 (CH, C-5′), 125.9–131.6 (aromatic CH), 128.6 (d, *J*=87 Hz, C, P–C_{Ar}), 135.0 (CH, C-4′), 136.5 (aromatic C), 140.1 (aromatic C), 148.4 (CH, C-6′) and 157.3 (C-2′); *m*/*z* (EI) 423 (M^+, 100%) 331 (87), 304 (81), 195 (84) and 93 (43) (HRMS: Found M^+, 423.1755. $C_{28}H_{26}NOP$ requires *M*, 423.1752).

HPLC analysis using a Chiralcel OD column (30% propan-2-ol in hexane as eluent) indicated that the product contained a 92:8 mixture of enantiomers (84% ee). Flow rate 1 mL min^{-1}. Detection at 256 nm. Retention times 6.68 min (minor) and 11.02 min (major).

6.2.11. (1*S*,2*R*,5*S*)-2-(4′,4′-Dimethyloxazolinyl-2′-methyl)-1,2,5-triphenyl phospholane-1-oxide 15. The typical conditions described above were employed, starting with **3** (1.50 g, 4.52 mmol) Purification of the crude product by column chromatography (8% EtOH/Et_2O) yielded the title compound **15** as a pale yellow crystalline solid (1.49 g, 74%), mp 188–190°C; $[\alpha]_D^{24}$=+73 (*c* 1.28 in $CHCl_3$); ν_{max} $CHCl_3$) (cm^{-1}) 2959, 1660, 1601, 1495, 1451, 1358, 1107, 988 and 907; δ_H (400 MHz, $CDCl_3$) 0.93 (3H, s, CH_3), 1.10 (3H, s, CH_3), 2.49 (1H, m, C-4H), 2.74 (1H, m, C-4H), 2.83–2.99 (2H, m, C-3H), 3.07 (1H, dd, *J*=3.7 and 14.4 Hz, C-1′H), 3.41 (1H, dd, *J*=8.0 and 14.4 Hz, C-1′H), 3.52 (1H, d, *J*=8.0 Hz, C-4′H), 3.61 (1H, d, *J*=8.0 Hz, C-4′H), 4.0 (1H, app. dt, *J*=24.0 and 9.2 Hz, C-5H), 6.87–7.19 (15H, m, ArH); δ_C (100 MHz, $CDCl_3$) 24.1 (d, *J*=11 Hz, CH_2, C-4), 27.4 (CH_3), 27.7 (CH_3), 31.4 (d, *J*=13 Hz, CH_2, C-3), 35.4 (CH_2, C-1′), 46.2 (d, *J*=59 Hz, CH, C-5), 48.0 (d, *J*=60 Hz, C, C-2), 66.0 (C, C-4′), 77.9 (CH_2, C-5′), 125.6–131.1 (aromatic CH), 128.2, 135.5 and 138.4 (aromatic C) and 161.9 (C=N); *m*/*z* (EI) 443 (M^+, 69%), 324 (58), 215 (100), 91 (27) and 77 (19) (HRMS: Found M^+, 443.2002. $C_{28}H_{30}NO_2P$ requires *M*, 443.2014).

HPLC analysis using a Chiralcel OD column (30% propan-2-ol in hexane as eluent) indicated that the product contained a 91:9 mixture of enantiomers (82% ee). Flow rate 1 mL min^{-1}. Detection at 256 nm. Retention times 15.3 min (major) and 20.9 min (minor).

Recrystallisation from MeOH/H_2O (×3) afforded material of ≥99% ee ($[\alpha]_D^{22}$=+91 (*c* 0.9 in $CHCl_3$)) with 55% recovery.

6.3. Typical procedure for isomerisation of phospholane oxides

6.3.1. (1*S*,2*R*,5*R*)-2-Ethyl-1,2,5-triphenylphospholane-1-oxide 18. To a mixture of potassium *tert*-butoxide (33 mg, 0.29 mmol) and oxide **6** (100 mg, 0.28 mmol, of ≥99% ee material), under N_2 at room temperature, was added *tert*-butanol (4 mL). The solution was allowed to stir at room temperature for 18 h before quenching with NH_4Cl (5 mL). The organic layer was removed and the aqueous layer extracted with CH_2Cl_2 (3×5 mL), the combined organic extracts were washed with saturated $NaHCO_3$ (5 mL), H_2O (5 mL), dried ($MgSO_4$) and the solvent evaporated under reduced pressure to give a white solid. Purification by column chromatography (2.5% EtOH/Et_2O) yielded the title compound **18** as a white solid (89 mg, 89%), mp 181–182°C; $[\alpha]_D^{23}$=+140 (*c* 1.00 in $CHCl_3$); ν_{max} ($CHCl_3$) (cm^{-1}) 3020, 2399, 1601, 1520, 1477, 1424, 1234 and 1190; δ_H (400 MHz, $CDCl_3$) 0.69 (3H, t, *J*=7.4 Hz, CH_3), 2.28–2.70 (6H, m, C-3H, C-4H and C-1′H), 3.48 (1H, app. dt, *J*=11.0 and 8.7 Hz, C-5H) and 6.96–7.40 (15H, m, ArH); δ_C (68 MHz, $CDCl_3$) 9.1 (CH_3), 28.8 (CH_2, C-3), 31.4 (CH_2, C-4 or C-1′), 31.5 (CH_2, C-4 or C-1′), 48.6 (d, *J*=61 Hz, CH, C-5), 53.2 (d, *J*=62 Hz, C, C-2), 127.4–132.7 (aromatic CH), 134.1 (d, *J*=87 Hz, C, P–C_{Ar}), 137.6 and 142.2 (aromatic C); *m*/*z* (EI) 360 (M^+, 43%), 345 (57), 332 (100), 256 (28), 216 (28) and 91 (84) (HRMS: Found M^+, 360.1643. $C_{24}H_{25}OP$ requires *M*, 360.1643).

6.3.2. (1*S*,2*R*,5*R*)-2-(Prop-2′-enyl)-1,2,5-triphenylphospholane-1-oxide 19. The above procedure was employed, starting with **8** (166 mg, 0.45 mmol). Purification of the crude product by column chromatography (3% EtOH/Et_2O) yielded the title compound **19** as a white solid (121 mg, 73%), mp 191–193°C; $[\alpha]_D^{21}$=+139 (*c* 1.34 in $CHCl_3$); ν_{max} ($CHCl_3$) (cm^{-1}) 2977, 1637, 1600, 1494, 1451, 1170 and 1109; δ_H (400 MHz, $CDCl_3$) 2.31–2.68 (4H, m, C-3H and C-4H), 2.98 (1H, ddd, *J*=4.9, 9.0 and 14.3 Hz, C-1′H), 3.07 (1H, m, C-1′H), 3.48 (1H, app. dt, *J*=12.2 and 9.6 Hz, C-5H), 5.01 (1H, d, *J*=10 Hz, (*Z*)-C-3′H), 5.10 (1H, d, *J*=17 Hz, (*E*)-C-3′H), 5.29 (1H, m, C-2′H) and 6.88–7.41 (15H, m, ArH); δ_C (68 MHz, $CDCl_3$) 29.5 (d, *J*=7 Hz, CH_2, C-3 or C-4), 30.5 (d, *J*=11 Hz, CH_2, C-3 or C-4), 39.6 (CH_2, C-1′), 47.4 (d, *J*=61 Hz, CH, C-5), 50.6 (d, *J*=62 Hz, C, C-2), 118.6 (CH_2, C-3′), 126.0–133.0 (aromatic CH and C-2′) and 131.6, 135.9 and 140.6 (aromatic C); *m*/*z* (EI) 372 (M^+, 100%), 331 (67), 268 (43), 205 (26), 143 (21) and 91 (75) (HRMS: Found M^+, 372.1649. $C_{25}H_{25}OP$ requires *M*, 372.1643).

6.3.3. (1*S*,2*R*,5*R*)-2-(3′-Methylbut-2′-enyl)-1,2,5-triphenylphospholane-1-oxide 20. The above procedure was employed, starting with **9** (100 mg, 0.25 mmol). Purification of the crude product by column chromatography (2% EtOH/

Et_2O) yielded the title compound **20** as a white solid (82 mg, 82%), mp 178–179°C; $[\alpha]_D^{22}=+110$ (*c* 0.78 in $CHCl_3$); ν_{max} ($CHCl_3$) (cm^{-1}) 2970, 2361, 1602, 1496, 1451, 1377 and 1109; δ_H (400 MHz, $CDCl_3$) 1.60 (6H, s, 2×CH_3), 2.27–2.67 (4H, m, C-3H and C-4H), 2.85 (1H, m, C-1′H), 3.13 (1H, ddd, *J*=5.4, 9.2 and 14.8 Hz, C-1′H), 3.47 (1H, app. dt, *J*=11.8 and 9.0 Hz, C-5H), 4.70 (1H, dd, *J*=5.4 and 6.6 Hz, C-2′H) and 6.93–7.42 (15H, m, ArH); δ_C (68 MHz, $CDCl_3$) 18.3 (CH_3), 25.9 (CH_3), 30.0 (d, *J*=9 Hz, CH_2, C-3 or C-4), 30.7 (d, *J*=11 Hz, CH_2, C-3 or C-4), 33.6 (CH_2, C-1′), 47.8 (d, *J*=61 Hz, CH, C-5), 51.4 (d, *J*=62 Hz, C, C-2), 118.3 (C-2′), 125.9–131.2 (aromatic CH) and 132.8 (d, *J*=87 Hz, C, P–C_{Ar}), 135.1 (aromatic C), 136.1 (C-3′) and 141.1 (aromatic C); *m/z* (EI) 400 (M^+, 48%), 332 (100), 216 (53), 171 (15) and 91 (31) (HRMS: Found M^+, 400.1951. $C_{27}H_{29}OP$ requires *M*, 400.1956).

6.3.4. (1*S*,2*R*,5*R*)-2-Methyl-5-(1′-oxoethyl)-1,2,5-triphenylphospholane-1-oxide 21. To a stirred solution of **5** (100 mg, 0.29 mmol) in THF (5 mL), under N_2 at −78°C, was added *n*-BuLi (1.6 M in hexanes) (0.20 mL, 0.32 mmol). The orange solution was allowed to stir at −78°C for 30 min before the addition of Ac_2O (0.27 mL, 2.9 mmol), and the resultant colourless solution stirred for 2 min before quenching with saturated aqueous NH_4Cl (10 mL). The organic layer was removed and the aqueous layer extracted with CH_2Cl_2 (3×7 mL), the combined organic extracts dried ($MgSO_4$) and concentrated under reduced pressure to give a colourless oil. Purification by column chromatography (10% petrol/Et_2O) yielded the title compound **21** as a white solid (60 mg, 53%), mp 155–157°C; $[\alpha]_D^{23}=-204$ (*c* 0.65 in $CHCl_3$); ν_{max} ($CHCl_3$) (cm^{-1}) 2969, 1698, 1598, 1494, 1456, 1356, 1103 and 888; δ_H (400 MHz, $CDCl_3$) 1.68 (3H, d, *J*=14.0 Hz, CH_3), 2.28–2.46 (2H, m, C-3H or C-4H), 2.46 (3H, s, $COCH_3$), 2.80 (1H, m, C-3H or C-4H), 3.65 (1H, m, C-3H or C-4H) and 7.00–7.28 (15H, m, ArH); δ_C (68 MHz, $CDCl_3$) 26.8 (CH_3), 28.3 (d, *J*=15 Hz, CH_2, C-3), 29.1 ($COCH_3$), 31.8 (d, *J*=13 Hz, CH_2, C-4), 45.7 (d, *J*=65 Hz, C, C-2), 65.1 (d, *J*=53 Hz, C, C-5), 126.0–132.0 (aromatic CH), 130.3, 137.5 and 143.0 (aromatic C) and 203.6 (C=O); δ_P(202 MHz, $CDCl_3$) 62.6; *m/z* (EI) 388 (M^+, 4%), 346 (62), 125 (20), 115 (55), 105 (30) and 103 (100) (HRMS: Found M^+, 388.1587. $C_{25}H_{25}O_2P$ requires *M*, 388.1592).

6.3.5. (1*S*,1′*S*,2*R*,5*R*)-2-Methyl-5-(phenyl-1′-hydroxymethyl)-1,2,5-triphenyl phospholane-1-oxide 22 (accompanied by minor (1′*R*)-isomer). To a stirred solution of **5** (100 mg, 0.29 mmol) in THF (5 mL), under N_2 at −78°C, was added *n*-BuLi (1.6 M in hexanes) (0.20 mL, 0.32 mmol). The orange solution was allowed to stir at −78°C for 30 min before the addition of freshly distilled benzaldehyde (0.27 mL, 2.9 mmol). The colourless solution was stirred for a further 2 min before the reaction was quenched with saturated aqueous NH_4Cl (10 mL). The organic layer was removed and the aqueous layer extracted with CH_2Cl_2 (3×7 mL), the combined organics dried ($MgSO_4$) and concentrated under reduced pressure give a colourless oil. Purification by column chromatography (65% petrol/Et_2O) yielded firstly the major diastereomer of **22** as a white solid (98 mg, 75%), mp 150–152°C; $[\alpha]_D^{24}=+112$ (*c* 0.86 in $CHCl_3$); ν_{max} ($CHCl_3$) (cm^{-1}) 3346, 2930, 1600, 1494, 1456, 1327 and 987; δ_H (400 MHz, $CDCl_3$) 1.97 (3H, d, *J*=13.3 Hz, CH_3), 2.20–2.58 (3H, m, C-3H and C-4H), 3.18 (1H, ddd, *J*=5.0, 14.3 and 14.3 Hz, C-3H or C-4H), 5.72 (1H, d, *J*=4 Hz, C-1′), 6.38 (1H, s, OH) and 6.76–7.11 (20H, m, ArH); δ_C (68 MHz, $CDCl_3$) 23.6 (d, *J*=12 Hz, CH_2, C-3), 25.8 (CH_3), 33.5 (d, *J*=14 Hz, CH_2, C-4), 48.6 (d, *J*=59 Hz, C, C-2), 59.2 (d, *J*=55 Hz, C, C-5), 78.3 (C, C-1′), 125.2–131.9 (aromatic C-H), 131.9, 137.6, 139.3 and 143.7 (aromatic C); δ_P(202 MHz, $CDCl_3$) 73.8; *m/z* (FAB) 453 ($[M+H]^+$, 46%), 435 (33), 346 (40), 307 (26), 154 (100) and 136 (69) (HRMS: Found $[M+H]^+$, 453.1988. $C_{30}H_{29}O_2P$ requires [M+*H*], 453.1983. Followed by the minor diastereomer of **22** as a white solid (15 mg, 12%), mp 135–136°C; $[\alpha]_D^{23}=+72$ (*c* 0.22 in $CHCl_3$); ν_{max} ($CHCl_3$) (cm^{-1}) 3358, 2929, 1600, 1496, 1454, 1146 and 1104; δ_H (400 MHz, $CDCl_3$) 2.02 (3H, d, *J*=13.5 Hz, CH_3), 2.43–2.59 (3H, m, C-3H and C-4H), 2.88 (1H, m, C-3H or C-4H), 5.77 (1H, dd, *J*=2.7 and 5.6 Hz, C-1′H), 5.92 (1H, d, *J*=2.7 Hz, OH) and 6.69–7.17 (20H, m, ArH); δ_C (100 MHz, $CDCl_3$) 29.7 (CH_3), 31.2 (d, *J*=12 Hz, CH_2, C-3), 34.7 (d, *J*=14 Hz, CH_2, C-4), 48.0 (d, *J*=58 Hz, C, C-2), 56.8 (d, *J*=58 Hz, C, C-5), 79.2 (CH, C-1′), 126.0–131.4 (aromatic CH), 135.8, 138.4, 138.5 and 142.9 (aromatic C); *m/z* (FAB) 453 ($[M+H]^+$, 35%), 435 (37), 346 (39), 154 (100), 136 (73) and 69 (58) (HRMS: Found $[M+H]^+$, 453.1987. $C_{30}H_2O_2P$ requires [M+*H*], 453.1983).

6.3.6. (1*S,2*R**,2′*Z*,5*S**)-2-(4′-Chlorobut-(2′)-enyl)-1,2,5-triphenyl phospholane-1-oxide 23.** To a stirred solution of 1,2,5-triphenylphospholane oxide **3** (400 mg, 1.20 mmol) in THF (8 mL), at −78°C under N_2, was added *n*-BuLi (1.6 M in hexanes) (0.83 mL, 1.33 mmol). Stirring of the deep orange/red solution was continued for 30 min before the addition of (*Z*)-1,4-dichlorobut-2-ene (1.27 mL, 12.0 mmol). After stirring the brown solution at −78°C for a further 5 min, the reaction was quenched with saturated aqueous NH_4Cl (10 mL). The organic layer was removed and the aqueous layer extracted with CH_2Cl_2 (3×15 mL), the combined organic extracts dried ($MgSO_4$) and concentrated under reduced pressure to give a yellow oil. Purification by column chromatography (Et_2O) yielded the title compound **23** as a white solid (312 mg, 62%), mp 157–158°C; ν_{max} ($CHCl_3$) (cm^{-1}) 2963, 1601, 1495, 1452, 1154 and 1107; δ_H (400 MHz, $CDCl_3$) 2.41–2.54 (2H, m, C-3H and C-4H), 2.61–2.84 (2H, m, C-3H and C-4H), 3.07 (1H, m, C-1′H), 3.20 (1H, m, C-1′H), 3.90 (1H, dd, *J*=6.9 and 11.6 Hz, C-4′H), 4.04 (1H, app. dt, *J*=23.6 and 8.8 Hz, C-5H), 4.12 (1H, dd, *J*=9.3 and 11.6 Hz, C-4′H), 5.30 (1H, ddd, *J*=2.0, 9.2 and 17.4 Hz, C-2′H), 5.69 (1H, app. q, *J*=9.3 and 17.4 Hz, C-3′H) and 6.86–7.27 (15H, m, ArH); δ_C (100 MHz, $CDCl_3$) 24.6 (d, *J*=12 Hz, CH_2, C-3 or C-4), 31.3 (d, *J*=14 Hz, CH_2, C-3 or C-4), 35.4 (CH_2, C-1′), 39.2 (CH_2, C-4′), 46.8 (d, *J*=58 Hz, CH, C-5), 49.5 (d, *J*=61 Hz, C, C-2), 126.2–131.6 (aromatic CH, olefin CH and 1 aromatic C), 136.1 and 139.8 (aromatic C); *m/z* (FAB) 421 ($[M+H]^+$, 81%), 385 (41), 332 (23), 136 (37), 91 (53), 69 (92) and 55 (100) (HRMS: Found $[M+H]^+$, 421.1486. $C_{26}H_{26}ClOP$ requires [M+*H*], 421.1488).

6.3.7. (1*S,2*R**,2′*E*,5*S**)-2-(4′-Bromobut-(2′)-enyl)-1,2,5-triphenyl phospholane-1-oxide 24.** To a stirred solution of 1,2,5-triphenylphospholane oxide **3** (150 mg, 0.45 mmol) in THF (7 mL), at −78°C under N_2, was added *n*-BuLi

(1.55 M in hexanes) (0.32 mL, 0.50 mmol). Stirring of the deep orange solution was continued for 30 min before the addition of (*E*)-1,4-dibromobut-2-ene (483 mg, 2.26 mmol) in THF (2 mL). After stirring for a further 5 min at −78°C, the reaction was quenched with saturated aqueous NH_4Cl (7 mL). The organic layer was removed and the aqueous layer extracted with CH_2Cl_2 (3×10 mL), the combined organic extracts dried ($MgSO_4$) and the solvent evaporated under reduced pressure to give a white solid. Purification by column chromatography (2% EtOH/Et_2O) yielded the title compound **24** as a white solid (169 mg, 81%), mp 164–165°C; (Found: C, 67.39; H, 5.67. $C_{26}H_{26}OPBr$ requires C, 67.10; H, 5.63%); ν_{max} ($CHCl_3$) (cm^{-1}) 2975, 1601, 1496, 1449, 1157, 1107 and 971; δ_H (400 MHz, $CDCl_3$) 2.42–2.52 (2H, m, C-3H and C-4H), 2.55–2.79 (2H, m, C-3H and C-4H), 2.95 (1H, ddd, *J*=5.8, 9.0 and 14.7 Hz, C-1′H), 3.15 (1H, ddd, *J*=5.8, 6.0 and 13.9 Hz, C-1′H), 3.83 (2H, d, *J*=7.7 Hz, C-4′H), 3.99 (1H, app. dt, *J*=23.6 and 9.1 Hz, C-5H), 5.39 (1H, ddd, *J*=5.1, 9.2 and 15.0 Hz, C-2′H), 5.79 (1H, ddd, *J*=7.5, 7.7 and 15.0 Hz, C-3′H) and 6.86–7.19 (15H, m, ArH); δ_C (68 MHz, $CDCl_3$) 24.6 (d, *J*=11 Hz, CH_2, C-3 or C-4), 31.1 (d, *J*=15 Hz, CH_2, C-3 or C-4), 32.5 (CH_2, C-1′), 40.6 (CH_2, C-4′), 46.8 (d, *J*=59 Hz, CH, C-5), 49.5 (d, *J*=61 Hz, C, C-2), 126.1–131.6 (aromatic CH), 130.2 (CH, C-2′), 130.5 (CH, C-3′), 129.2, 136.2 and 139.9 (aromatic C); *m/z* (FAB) 465 ($[M+H]^+$, 36%), 385 (32), 332 (17), 154 (52), 136 (39), 69 (94) and 57 (100) (HRMS: Found $[M+H]^+$, 465.0963. $C_{26}H_{27}OPBr$ requires [M+*H*], 465.0983).

6.3.8. (1*S,2*R**,5*S**)-2-(3′-Bromomethylbenzyl)-1,2,5-triphenylphospholane-1-oxide 25.** To a stirred solution of 1,2,5-triphenylphospholane oxide **3** (150 mg, 0.45 mmol) in THF (7 mL), at −78°C under N_2, was added *n*-BuLi (1.55 M in hexanes) (0.32 mL, 0.50 mmol). Stirring of the deep orange/red solution was continued for 30 min before the addition of αα′-dibromo-*m*-xylene (239 mg, 0.90 mmol) in THF (2 mL). After stirring at −78°C for a further 5 min, the reaction was quenched with saturated aqueous NH_4Cl (7 mL). The organic layer was removed and the aqueous layer extracted with CH_2Cl_2 (3×10 mL), the combined organic extracts dried ($MgSO_4$) and concentrated under reduced pressure to give a pale yellow oil. Purification by column chromatography (Et_2O) yielded the title compound **25** as a white foam (177 mg, 76%); ν_{max} ($CHCl_3$) (cm^{-1}) 2973, 1601, 1495, 1449 and 1106; δ_H (400 MHz, $CDCl_3$) 2.31–2.55 (3H, m, C-3H and C-4H), 2.74 (1H, m, C-3H or C-4H), 3.54 (1H, dd, *J*=6.1 and 13.8 Hz, C-1′H), 3.63 (1H, dd, *J*=5.4 and 13.8 Hz, C-1′H), 4.12 (1H, app. dt, *J*=23.4 and 8.8 Hz, C-5H), 4.27 (2H, s, C-4′H) and 6.60–7.26 (19H, m, ArH); δ_C (68 MHz, $CDCl_3$) 25.0 (d, *J*=11 Hz, CH_2, C-4), 31.1 (d, *J*=15 Hz, CH_2, C-3), 33.9 (CH_2, C-1′), 43.4 (CH_2, C-2′), 47.2 (d, *J*=59 Hz, CH, C-5), 51.2 (d, *J*=61 Hz, C, C-2), 125.9–132.3 (aromatic CH), 136.9, 137.0, 137.3, 137.5 and 140.6 (aromatic C); *m/z* (FAB) 515 ($[M+H]^+$, 5%), 176 (7), 154 (37), 136 (30), 83 (47), 69 (100) and 55 (93) (HRMS: Found $[M+H]^+$, 515.1138. $C_{30}H_{28}OPBr$ requires [M+*H*], 515.1139).

6.3.9. (1*S*,2*R*,5*S*)-2-(3′-Hydroxypropyl)-1,2,5-triphenylphospholane-1-oxide 26. To a stirred solution of enantiomerically pure (≥99% ee) **8** (600 mg, 1.61 mmol) in THF (20 mL), cooled to 0°C under N_2, was added a solution of BH_3·THF (1.0 M in THF) (4.84 mL, 4.84 mmol). Stirring was continued for 60 min before the addition of MeOH (6 mL). After 5 min 2 M aqueous NaOH (12 mL) and 30% aqueous H_2O_2 (2.7 mL) were added to the reaction mixture and stirring continued for a further 60 min. The reaction mixture was then diluted with H_2O (10 mL), extracted with CH_2Cl_2 (3×10 mL), the combined organic extracts dried ($MgSO_4$) and concentrated under reduced pressure to give a pale yellow oil. Purification by column chromatography (6% EtOH/Et_2O) yielded the title compound **26** as a white foam (459 mg, 73%), $[\alpha]_D^{24}$=+16 (*c* 1.24 in $CHCl_3$); ν_{max} ($CHCl_3$) (cm^{-1}) 3340, 2955, 1601, 1496, 1454, 1155, 1106 and 1048; δ_H (400 MHz, $CDCl_3$) 1.20 (1H, m, C-1′H), 1.51 (1H, m, C-1′H), 2.30–2.52 (4H, m, 2×C-2′H, C-3H and C-4H), 2.64 (1H, m, C-3H or C-4H), 2.85 (1H, m, C-3H or C-4H), 2.93 (1H, bs, OH), 3.61 (2H, t, *J*=6.4 Hz, C-3′H), 4.00 (1H, app. dt, *J*=23.7 and 9.5 Hz, C-5H) and 6.86–7.26 (15H, m, ArH); δ_C (68 MHz, $CDCl_3$) 26.0 (d, *J*=12 Hz, CH_2, C-3 or C-4), 28.3 (d, *J*=10 Hz, CH_2, C-1′), 32.6 (d, *J*=13 Hz, CH_2, C-3 or C-4), 35.4 (CH_2, C-2′), 47.9 (d, *J*=59 Hz, CH, C-5), 50.7 (d, *J*=61 Hz, C, C-2), 63.6 (CH_2, C-3′), 127.3–132.8 (aromatic CH), 130.5, 137.3 and 141.4 (aromatic C); *m/z* (EI) 390 (M^+, 45%), 332 (100), 205 (3), 151 (3), 118 (16) and 91 (49) (HRMS: Found M^+, 390.1763. $C_{25}H_{27}O_2P$ requires 390.1749).

6.3.10. (1*S*,2*R*,5*S*)-2-Carboxymethyl-1,2,5-triphenylphospholane-1-oxide 27. To a stirred suspension of enantiomerically pure (≥99% ee) **8** (141 mg, 0.38 mmol) in H_2O (2.5 mL)/CH_3CN (1.7 mL)/CCl_4 (1.7 mL), at room temperature, was added $NaIO_4$ (340 mg, 1.59 mmol), followed by $RuCl_3$·$3H_2O$ (4 mg, 0.015 mmol). After stirring for 15 min the reaction mixture was extracted with CH_2Cl_2 (3×10 mL), the combined organic extracts were dried ($MgSO_4$) and the solvent removed under reduced pressure to give a black solid. Purification by column chromatography (5% EtOH/Et_2O) yielded the title compound **27** as a colourless solid (105 mg, 71%), mp 180–182°C; $[\alpha]_D^{24}$=+154 (*c* 2.1 in $CHCl_3$); ν_{max} ($CHCl_3$) (cm^{-1}) 2953, 2603, 1723, 1601, 1496, 1451, 1105 and 908; δ_H (400 MHz, $CDCl_3$) 2.50 (1H, m, C-3H or C-4H), 2.69 (1H, m, C-3H or C-4H), 2.84 (1H, m, C-3H or C-4H), 3.19 (1H, m, C-3H or C-4H), 3.32 (1H, dd, *J*=8.2 and 15.6 Hz, C-1′H), 3.43 (1H, dd, *J*=11.4 and 15.6 Hz, C-1′H), 4.06 (1H, ddd, *J*=8.6, 10.5 and 24.6 Hz, C-5H) and 6.85–7.35 (15H, m, ArH); δ_C (68 MHz, $CDCl_3$) 25.7 (d, *J*=11 Hz, CH_2, C-4), 32.8 (d, *J*=12 Hz, CH_2, C-3), 44.1 (CH_2, C-1′), 47.6 (d, *J*=59 Hz, CH, C-5), 48.7 (d, *J*=60 Hz, C, C-2), 125.5–133.0 (aromatic CH+aromatic C), 135.1, 138.9 (aromatic C) and 172.2 (CO_2H); *m/z* (EI) 390 (M^+, 31%), 346 (69), 250 (100), 220 (32), 146 (65) and 91 (74) (HRMS: Found M^+, 390.1370. $C_{24}H_{23}O_3P$ requires *M*, 390.1385).

6.3.11. (1*S*,2*R*,5*S*)-2-Methylcarboxymethyl-1,2,5-triphenylphospholane-1-oxide 28. To a stirred solution of **27** (106 mg, 0.27 mmol) in DMF (2 mL), under N_2 at room temperature, was added $KHCO_3$ (41 mg, 0.41 mmol). After stirring for 30 min MeI (0.03 mL, 0.54 mmol) was added and stirring continued for a further 30 min. The solution was then poured into H_2O (5 mL), extracted with EtOAc (3×10 mL), the combined organic extracts dried

($MgSO_4$) and concentrated under reduced pressure to give a pale yellow oil. Purification by column chromatography (3% EtOH/Et_2O) yielded the title compound **28** as a white solid (103 mg, 94%), mp 170–171°C; $[\alpha]_D^{21}=+53$ (*c* 1.14 in $CHCl_3$); (Found: C, 74.10; H, 6.23. $C_{25}H_{25}O_3P$ requires C, 74.24; H, 6.23%); ν_{max} ($CHCl_3$) (cm^{-1}) 2953, 1730, 1601, 1495, 1451, 1348, 1155 and 1107; δ_H (250 MHz, $CDCl_3$) 2.46–2.88 (4H, m, C-3H and C-4H), 3.05–3.17 (2H, m, C-1′H), 3.42 (3H, s, CH_3), 3.98 (1H, app. dt, *J*=24.4 and 9.3 Hz, C-5H) and 6.87–7.18 (15H, m, ArH); δ_C (68 MHz, $CDCl_3$) 25.3 (d, *J*=11 Hz, CH_2, C-4), 32.3 (d, *J*=12 Hz, CH_2, C-3), 42.1 (CH_2, C-1′), 47.4 (d, *J*=59 Hz, CH, C-5), 48.2 (d, *J*=60 Hz, C, C-2), 51.3 (CH_3, CO_2CH_3), 126.2–131.6 (aromatic CH), 128.4, 135.8 and 139.0 (aromatic C) and 170.9 (C, CO_2); *m/z* (EI) 404 (M^+, 32%), 345 (23), 285 (100), 160 (56), 104 (26) and 91 (63) (HRMS: Found M^+, 404.1560. $C_{25}H_{25}O_3P$ requires *M*, 404.1541).

6.3.12. (1*S*,2*R*,5*S*)-2-(2′-Oxoethyl)-1,2,5-triphenylphospholane-1-oxide 29. Ozone was bubbled through a solution of enantiomerically pure **9** (850 mg, 2.13 mmol) in CH_2Cl_2 (20 mL) at −78°C for 45 min, after which time the solution developed a permanent blue colouration. Nitrogen was then bubbled through the solution to remove excess ozone, before the addition of dimethylsulfide (2 mL). The mixture was allowed to warm to room temperature and stirred for a further 2 h before washing with H_2O (10 mL). The organic layer was separated, dried ($MgSO_4$) and the solvent evaporated under reduced pressure to give a white foam. Purification by column chromatography (4% EtOH/Et_2O) yielded the title compound **29** as a white foam (601 mg, 75%); $[\alpha]_D^{23}=+89$ (*c* 0.36 in $CHCl_3$); ν_{max} ($CHCl_3$) (cm^{-1}) 2970, 1719, 1600, 1495, 1450 and 1107; δ_H (400 MHz, $CDCl_3$) 2.48–2.62 (2H, m, C-4H), 2.67 (1H, m, C-3H), 3.09–3.19 (1H, overlapping m, C-3H), 3.16 (1H, ddd, *J*=3.0, 5.7 and 16.2 Hz, C-1′H), 3.57 (1H, ddd, *J*=1.2 Hz, 7.5 and 16.2, C-1′H), 3.97 (1H, app. dt, *J*=24.5 and 9.5 Hz, C-5H), 6.86–7.30 (15H, m, ArH) and 9.52 (1H, dd, *J*=1.4 and 3.0 Hz, CHO); δ_C (68 MHz, $CDCl_3$) 25.3 (d, *J*=11 Hz, CH_2, C-4), 32.5 (d, *J*=12 Hz, CH_2, C-3), 47.2 (d, *J*=60 Hz, CH, C-5), 47.7 (d, *J*=60 Hz, C, C-2), 51.0 (CH_2, C-1′), 124.9–131.7 (aromatic C and CH), 135.6, 139.0 (aromatic C) and 201.1 (CHO); *m/z* (FAB) 375 ($[M+H]^+$, 82%), 307 (30), 289 (14), 154 (100), 136 (68) and 91 (26) (HRMS: Found $[M+H]^+$, 375.1529. $C_{24}H_{23}PO_2$ requires [M+*H*], 375.1514).

6.3.13. (1*S*,2*R*,5*S*)-2-(2′-Hydroxyethyl)-1,2,5-triphenylphospholane-1-oxide 30. To a stirred solution of **29** (650 mg, 1.74 mmol) in MeOH (10 mL) at 0°C was added $NaBH_4$ (131 mg, 3.48 mmol), portionwise. The solution was stirred at 0°C for 20 min before concentrating under reduced pressure to give a colourless oil. Purification by column chromatography (10% EtOH/Et_2O) yielded the title compound **30** as a white foam (610 mg, 93%), mp 116–117°C (recrystallisation from EtOAc/petrol); $[\alpha]_D^{22}=+62$ (*c* 0.71 in $CHCl_3$); ν_{max} ($CHCl_3$) (cm^{-1}) 3315, 2953, 1600, 1582, 1495, 1452, 1106, 1062 and 908; δ_H (400 MHz, $CDCl_3$); 2.39–2.49 (2H, m, C-1′H), 2.58–2.93 (4H, m, C-3H and C-4H), 3.51–3.61 (2H, m, C-2′H), 4.05 (1H, app. dt, *J*=23.8 and 9.0 Hz, C-5H), 4.43 (1H, bs, OH) and 6.88–7.23 (15H, m, ArH); δ_C (68 MHz, $CDCl_3$) 24.4 (d, *J*=11 Hz, CH_2, C-4), 33.1 (d, *J*=13 Hz, CH_2, C-3), 42.8 (CH_2, C-1′), 46.0 (d, *J*=60 Hz, CH, C-5), 49.3 (d, *J*=61 Hz, C, C-2), 58.7 (CH_2, C-2′), 126.3–131.8 (aromatic CH), 128.8, 135.7 and 140.1 (aromatic C); *m/z* (EI) 376 (M^+, 29%), 332 (53), 232 (10), 117 (26), 88 (100) and 49 (39) (HRMS: Found M^+, 376.1598. $C_{24}H_{25}O_2P$ requires *M*, 76.1592).

6.3.14. (1*S*,2*R*,5*S*)-2-(1,2,5-Triphenylphospholane-1-oxido)ethyl methane sulfonate 31. To a stirred solution of **30** (600 mg, 1.60 mmol) in CH_2Cl_2 (7 mL) at 0°C was added Et_3N (0.27 mL, 1.91 mmol) and the solution stirred for 30 min before the addition of CH_3SO_2Cl (0.15 mL, 1.91 mmol). The reaction mixture was allowed to warm to room temperature and stirred overnight before the solvent was removed under reduced pressure to give an off-white solid. Purification by column chromatography (6% EtOH/Et_2O) yielded the title compound **31** as a white solid (540 mg, 74%), mp 167–169°C; $[\alpha]_D^{23}=+20$ (*c* 1.16 in $CHCl_3$); ν_{max} ($CHCl_3$) (cm^{-1}) 2954, 1601, 1495, 1453, 1360, 1107, 972 and 903; δ_C (68 MHz, $CDCl_3$) 25.2 (d, *J*=11 Hz, CH_2, C-3 or C-4), 32.4 (d, *J*=12 Hz, CH_2, C-3 or C-4), 36.8 (CH_2, C-1′), 37.1 (CH_3), 47.1 (d, *J*=60 Hz, CH, C-5), 48.3 (d, *J*=60 Hz, C, C-2), 66.8 (d, *J*=12 Hz, CH_2, C-2′), 126.3–131.5 (aromatic CH and aromatic C) and 135.4, 138.4 (aromatic C); *m/z* (FAB) 455 ($[M+H]^+$, 40%), 377 (48), 359 (20), 154 (34), 95 (58), 81 (60) and 55 (100) (HRMS: Found $[M+H]^+$, 455.1439. $C_{25}H_{27}OPS$ requires [M+*H*], 455.1446).

6.3.15. (1*S*,2*R*,5*S*)-2-(Diethylaminoethyl)-1,2,5-triphenylphospholane-1-oxide 32. To a stirred solution of enantiopure aldehyde **29** (100 mg, 0.27 mmol) in MeOH (2 mL), under N_2, was added Et_2NH (0.14 mL, 1.34 mmol) and the solution stirred at room temperature for 17 h. $NaBH(OAc)_3$ (170 mg, 0.80 mmol) was then added to the reaction mixture and stirring continued for a further 2 h before quenching with 2 M aqueous NaOH (5 mL). The organic layer was removed and the aqueous layer extracted with CH_2Cl_2 (3×10 mL), the combined organic extracts dried ($MgSO_4$) and concentrated under reduced pressure to give a yellow glass. Purification by column chromatography (8% MeOH/CH_2Cl_2) yielded the title compound **32** as a colourless glass (47 mg, 40%); $[\alpha]_D^{24}=+39$ (*c* 2.15 in $CHCl_3$); ν_{max} ($CHCl_3$) (cm^{-1}) 2963, 2350, 1601, 1495, 1454, 1107 and 908; δ_H (400 MHz, $CDCl_3$) 1.14 (6H, t, *J*=7.2 Hz, 2×CH_3), 2.44–2.59 (4H, m, C-3H, C-4H and 2×C-4′H), 2.65–2.96 (8H, m, C-3H, C-4H, 2×C-1′H, 2×C-2′H and 2×C-4′H), 4.03 (1H, app. dt, *J*=24.2 and 8.8 Hz, C-5H) and 6.88–7.36 (15H, m, ArH); δ_C (100 MHz, $CDCl_3$) 9.6 (2×CH_3), 24.8 (d, *J*=11 Hz, CH_2, C-3 or C-4), 31.2 (CH_2, C-1′), 31.7 (d, *J*=13 Hz, CH_2, C-3 or C-4), 46.4 (2×CH_2, C-4′), 46.57 (CH_2, C-2′), 46.58 (d, *J*=59 Hz, CH, C-5), 48.2 (d, *J*=61 Hz, C, C-2), 126.3–131.6 (aromatic CH and aromatic C), 135.6 and 138.7 (aromatic C); *m/z* (FAB) 432 ($[M+H]^+$, 30%), 307 (29), 259 (14), 154 (100), 136 (73) and 57 (28) (HRMS: Found $[M+H]^+$, 432.2448. $C_{28}H_{34}NOP$ requires [M+*H*], 432.2456).

6.3.16. (1*S*,2*R*,5*S*)-2-(Benzylaminoethyl)-1,2,5-triphenylphospholane-1-oxide 33. To a stirred solution of enantiopure aldehyde **29** (150 mg, 0.40 mmol) in MeOH (2 mL), under N_2, was added $BnNH_2$ (0.046 mL, 0.43 mmol) and the solution stirred at room temperature for 13 h. $NaBH(OAc)_3$

(136 mg, 0.64 mmol) was then added to the reaction mixture and stirring continued for a further 22 h before quenching with 2 M aqueous NaOH (7 mL). The reaction mixture was extracted with CH_2Cl_2 (3×15 mL), the combined organic extracts dried ($MgSO_4$) and concentrated under reduced pressure to give a yellow gum. Purification by column chromatography (6% MeOH/CH_2Cl_2) yielded the title compound **33** as a colourless glass (42 mg, 23%), $[\alpha]_D^{23}=+22$ (*c* 2.0 in $CHCl_3$); ν_{max} ($CHCl_3$) (cm^{-1}) 3366, 2956, 1600, 1495, 1454, 1106 and 908; δ_H (400 MHz, $CDCl_3$) 2.31–2.91 (9H, m, C-3H, C-4H, C-1′H, C-2′H and NH), 3.68 (2H, d, *J*=6.1 Hz, C-4′H), 3.98 (1H, app. dt, *J*=23.4 and 8.9 Hz, C-5H) and 6.86–7.31 (20H, m, ArH); δ_C (68 MHz, $CDCl_3$) 24.8 (d, *J*=11 Hz, CH_2, C-4), 31.9 (d, *J*=13 Hz, CH_2, C-3), 37.5 (CH_2, C-1′), 44.5 (d, *J*=10 Hz, CH_2, C-2′), 46.5 (d, *J*=59 Hz, CH, C-5), 49.0 (d, *J*=61 Hz, C, C-2), 53.3 (CH_2, C-4′), 125.5–131.7 (aromatic CH), 128.9, 135.7, 139.0 and 139.6 (aromatic C); *m/z* (FAB) 466 ($[M+H]^+$, 11%), 307 (32), 289 (14), 154 (100) and 136 (65) (HRMS: Found $[M+H]^+$, 466.2303. $C_{31}H_{32}NOP$ requires [M+*H*], 466.2300).

6.4. Typical procedure for reduction of phospholane oxides to corresponding phosphines (Table 2)

6.4.1. (1*S*,2*R*,5*S*)-2-Methyl-1,2,5-triphenylphospholane 34. To a stirred solution of Cl_3SiH (0.70 mL, 6.94 mmol) in benzene (2 mL) was added pyridine (1.68 mL, 20.8 mmol), under N_2. A solution of enantiomerically pure phospholane oxide **5** (480 mg, 1.39 mmol) in benzene (10 mL) was added to the resulting white suspension and the mixture heated to reflux until starting material was consumed (3–5 h). After cooling the reaction mixture to 0°C, ice-cold 2 M aqueous NaOH (65 mL) was added, the reaction mixture extracted with benzene (2×20 mL), the combined organic extracts dried ($MgSO_4$) and the solvent removed under reduced pressure to give a white solid. Purification by column chromatography (Et_2O) yielded the title compound **34** as a white solid (335 mg, 73%), mp 146–147°C; $[\alpha]_D^{28}=+88$ (*c* 0.74 in $CHCl_3$); (Found: C, 83.20; H, 6.96. $C_{23}H_{23}P$ requires C, 83.60; H, 7.02%); ν_{max} ($CHCl_3$) (cm^{-1}) 2954, 2867, 1598, 1494, 1452 and 1074; δ_H (400 MHz, $CDCl_3$) 1.70 (3H, d, *J*=17.9 Hz, CH_3), 2.23 (1H, m, C-3H or C-4H), 2.50–2.59 (2H, m, C-3H or C-4H), 2.92 (1H, m, C-3H or C-4H), 4.12 (1H, app. dt, *J*=9.3 and 11.0 Hz, C-5H), 6.67–7.35 (15H, m, ArH); δ_C (100 MHz, $CDCl_3$) 30.8 (d, *J*=4 Hz, CH_2, C-3), 33.0 (d, *J*=30 Hz, CH_3), 38.3 (d, *J*=5 Hz, CH_2, C-4), 45.4 (d, *J*=17 Hz, CH, C-5), 51.0 (d, *J*=14 Hz, C, C-2), 125.4–134.6 (aromatic CH), 134.1, 140.1 and 147.2 (aromatic C); *m/z* (FAB) 330 (M^+, 100%), 259 (20), 154 (94), 136 (64), 91 (54) and 57 (64) (HRMS: Found M^+, 330.1538. $C_{23}H_{23}P$ requires *M*, 330.1537).

6.4.2. (1*S*,2*R*,5*S*)-2-Ethyl-1,2,5-triphenylphospholane 35. The typical procedure described above was followed, starting with enantiomerically pure **6** (800 mg), and the crude material purified by column chromatography (50% EtOAc/petrol) to give the title compound **35** as a white solid (724 mg, 96%), mp 120–123°C; $[\alpha]_D^{21}=+10$ (*c* 1.9 in $CHCl_3$); ν_{max} ($CHCl_3$) (cm^{-1}) 2965, 2873, 1598, 1494, 1450 and 1077; δ_H (400 MHz, $CDCl_3$) 0.78 (3H, t, *J*=7.3 Hz, CH_3), 1.96 (1H, ddd, *J*=6.1, 7.3 and 15.7 Hz, C-1′H), 2.13–2.53 (4H, m, C-3H, C-4H and C-1′H), 2.79 (1H, m, C-4H), 4.05 (1H, app. dt, *J*=12.4 and 8.9 Hz, C-5H) and 6.67–7.36 (15H, m, ArH); δ_C (68 MHz, $CDCl_3$) 9.0 (d, *J*=17 Hz, CH_3), 31.0 (d, *J*=5 Hz, CH_2, C-3 or C-4), 34.7 (d, *J*=4 Hz, CH_2, C-3 or C-4), 36.1 (d, *J*=31 Hz, CH_2, C-1′), 45.5 (d, *J*=17 Hz, CH, C-5), 55.4 (d, *J*=15 Hz, C, C-2), 125.3–135.0 (aromatic CH), 133.7, 140.3 and 144.4 (aromatic C); *m/z* (EI) 344 (M^+, 50%), 316 (36), 234 (12), 205 (14), 115 (16), 91 (40) and 53 (100) (HRMS: Found M^+, 344.1697. $C_{24}H_{25}P$ requires *M*, 344.1694).

6.4.3. (1*S*,2*R*,5*S*)-2-(2′-Pyridylmethyl)-1,2,5-triphenylphospholane 36. The typical procedure described above was followed, starting with **14** (350 mg of 84% ee material), and the crude material purified by column chromatography (Et_2O) to give the title compound **36** as a pale yellow solid (283 mg, 84%), mp 123–125°C; $[\alpha]_D^{23}=+124$ (*c* 1.17 in $CHCl_3$); ν_{max} ($CHCl_3$) (cm^{-1}) 2953, 1592, 1569, 1494, 1449, 1081 and 996; δ_H (400 MHz, $CDCl_3$) 2.51–2.64 (3H, m, C-3H and C-4H), 2.79 (1H, m, C-3H or C-4H), 3.43 (1H, dd, *J*=7.9 and 12.6 Hz, C-1′H), 3.57 (1H, dd, *J*=9.2 and 12.6 Hz, C-1′H), 4.0 (1H, app. dt, *J*=13.1 and 9.0 Hz, C-5H), 6.23 (1H, d, *J*=7.8 Hz, C-3′H), 6.71–7.29 (17H, m, aromatic CH, C-4′H and C-5′H) and 8.50 (1H, d, *J*=4.6 Hz, C-6′H); δ_C (68 MHz, $CDCl_3$) 31.2 (d, *J*=5 Hz, CH_2, C-4), 33.6 (d, *J*=5 Hz, CH_2, C-3), 45.3 (d, *J*=17 Hz, CH, C-5), 50.7 (d, *J*=33 Hz, CH_2, C-1′), 56.1 (d, *J*=15 Hz, C, C-2), 121.3 (CH, C-3′), 124.8–135.2 (aromatic CH), 133.4 (d, *J*=28 Hz, C, P–C_{Ar}), 140.2 (aromatic C), 144.1 (aromatic C), 148.4 (CH, C-6′) and 157.9 (d, *J*=20 Hz, C, C-2′); *m/z* (FAB) 408 ($[M+H]^+$, 36%), 307 (33), 288 (30), 154 (100) and 137 (64) (HRMS: Found $[M+H]^+$, 408.1884. $C_{28}H_{26}NP$ requires [M+*H*], 408.1881).

6.4.4. (1*S*,2*R*,5*S*)-2-(4′, 4′-Dimethyloxazolinyl-2′-methyl)-1,2,5-triphenyl phospholane 37. The typical procedure described above was followed, starting with enantiomerically pure **15** (182 mg), and the crude material purified by column chromatography (40% EtOAc/petrol) to give the title compound **37** as a white solid (133 mg, 76%), mp 121–123°C; $[\alpha]_D^{23}=+70$ (*c* 0.55 in $CHCl_3$); ν_{max} ($CHCl_3$) (cm^{-1}) 2964, 1660, 1598, 1494, 1462, 1366 and 990; δ_H (400 MHz, $CDCl_3$) 1.00 (3H, s, CH_3), 1.16 (3H, s, CH_3), 2.57–2.85 (4H, m, C-3H and C-4H), 2.89 (1H, dd, *J*=5.7 and 13.7 Hz, C-1′H), 3.12 (1H, dd, *J*=11.0 and 13.7 Hz, C-1′H), 3.62 (1H, d, *J*=8.0 Hz, C-3′H), 3.67 (1H, d, *J*=8.0 Hz, C-3′H), 4.11 (1H, app. dt, *J*=12.6 and 9.0 Hz, C-5H) and 6.69–7.31 (15H, m, ArH); δ_C (100 MHz, $CDCl_3$) 28.1 (CH_3), 28.4 (CH_3), 31.0 (d, *J*=4 Hz, CH_2, C-4), 35.0 (d, *J*=4 Hz, CH_2, C-3), 45.4 (d, *J*=18 Hz, CH, C-5), 54.1 (d, *J*=15 Hz, C, C-2), 66.5 (C, C-4), 78.9 (CH_2, C-3′), 125.4–134.9 (aromatic CH), 133.2, 139.9 and 143.0 (aromatic C); *m/z* (FAB) 428 ($[M+H]^+$, 75%), 372 (11), 308 (44), 154 (100) and 136 (72) (HRMS: Found $[M+H]^+$, 428.2107. $C_{28}H_{30}NOP$ requires [M+*H*], 428.2143).

6.4.5. (1*S*,1′*R*,2*R*,5*S*)-2-(1′-Acetoxyphenylmethyl)-1,2,5-triphenylphospholane 38. The typical procedure described above was followed, starting with the *O*-acetate derivative of enantiomerically pure **11** (449 mg, prepared by reacting **11** with Ac_2O and DMAP in pyridine), and the crude material purified by column chromatography (Etc_2O) to

give the title compound **38** as a white solid (330 mg, 76%), mp 96–97°C; $[\alpha]_D^{28}=+131$ (c 1.39 in $CHCl_3$); ν_{max} ($CHCl_3$) (cm^{-1}) 2957, 1738, 1598, 1494, 1452, 1372 and 1026; δ_H (400 MHz, $CDCl_3$) 2.30 (3H, s, CH_3), 2.48–2.63 (4H, m, C-3H and C-4H), 3.95 (1H, app. dt, J=13.4 and 8.9 Hz, C-5H), 6.46 (1H, d, J=5.4 Hz, C-1′H), 6.68–7.25 (20H, m, ArH); δ_C (68 MHz, $CDCl_3$) 21.5 (CH_3), 31.6 (CH_2, C-3 or C-4), 32.2 (CH_2, C-3 or C-4), 47.8 (d, J=16 Hz, CH, C-5), 61.3 (d, J=20 Hz, C, C-2), 82.8 (d, J=26 Hz, CH, C-1′), 125.5–136.2 (aromatic CH), 133.8 (d, J=28 Hz, C, P–C_{Ar}), 137.5, 139.5, 141.5 (aromatic C) and 169.7 (C=O); m/z (FAB) 465 ($[M+H]^+$, 7%) 421 (13), 391 (10), 307 (44), 289 (20), 154 (100) and 136 (65) (HRMS: Found $[M+H]^+$, 465.1964. $C_{31}H_{29}O_2P$ requires [M+H], 465.1983).

6.4.6. (1*S*,2*R*,5*S*)-2-(3′-Hydroxypropyl)-1,2,5-triphenylphospholane 39. The typical procedure described above was followed, starting with enantiomerically pure **26** (400 mg), and the crude product purified by column chromatography (40% EtOAc/petrol) to give the title compound **39** as a white foam (312 mg, 81%), $[\alpha]_D^{22}=+38$ (c 1.9 in $CHCl_3$); ν_{max} ($CHCl_3$) (cm^{-1}) 3625, 2946, 2873, 1673, 1494, 1451, 1266 and 1047; δ_H (400 MHz, $CDCl_3$) 1.23 (1H, m, C-1′H), 1.52 (1H, m, C-1′H), 2.37–2.50 (4H, 2×C-2′H, C-3H and C-4H), 2.70 (1H, m, C-3H or C-4H), 2.83, (1H, m, C-3H or C-4H), 2.94 (1H, bs, OH), 3.62 (2H, t, J=6.5 Hz, C-3′H), 4.09 (1H, app. q, J=9.3 and 11.1 Hz, C-5H) and 6.69–7.32 (15H, m, ArH); δ_C (68 MHz, $CDCl_3$) 28.0 (CH_2, C-3 or C-4), 31.0 (CH_2, C-1′), 35.3 (CH_2, C-2′), 39.6 (CH_2, C-3 or C-4), 45.2 (d, J=17 Hz, CH, C-5), 54.6 (d, J=13 Hz, C, C-2), 62.9 (CH_2, C-3′) and 125.3–144.3 (aromatic C and CH); m/z (FAB) 375 ($[M+H]^+$, 4%), 316 (3), 154 (20), 95 (37), 81 (46), 69 (74) and 55 (100) (HRMS: Found $[M+H]^+$, 375.1844. $C_{25}H_{27}OP$ requires [M+H], 375.1878).

6.4.7. (1*S*,2*R*,5*S*)-2-(Methylcarboxymethyl)-1,2,5-triphenylphospholane 40. The typical procedure described above was followed, starting with enantiomerically pure **28** (100 mg), and the crude product purified by column chromatography (Et_2O) to give the title compound **40** as a white solid (70 mg, 75%), mp 135–136°C; $[\alpha]_D=+49$ (c 1.65 in $CHCl_3$); ν_{max} ($CHCl_3$) (cm^{-1}) 2952, 2927, 1728, 1599, 1494, 1451 and 1317; δ_H (400 MHz, $CDCl_3$) 2.52–2.68 (3H, m, C-3H and C-4H), 2.80 (1H, m, C-3H or C-4H), 2.88 (1H, dd, J=6.2 and 14.3 Hz, C-1′H), 3.15 (1H, dd, J=10.2 and 14.3 Hz, C-1′H), 3.37 (3H, s, CH_3), 4.04 (1H, app. dt, J=12.9 and 7.1 Hz, C-5H) and 6.60–7.22 (15H, ArH); δ_C (68 MHz, $CDCl_3$) 31.1 (CH_2, C-4), 34.9 (CH_2, C-3), 45.3 (d, J=17 Hz, CH, C-5), 46.6 (CH_2, C-1′), 51.3 (CH_3), 53.5 (d, J=15 Hz, C, C-2), 125.4–135.0 (aromatic CH and 1 aromatic C), 139.7 and 142.8 (aromatic C) and 170.1 (C=O); m/z (FAB) 388 ($[M+H]^+$, 1%), 373 (4), 281 (7), 147 (30), 91 (11) and 73 (100) (HRMS: Found $[M+H]^+$, 389.1677. $C_{25}H_{25}O_2P$ requires [M+H], 389.1670).

6.4.8. (1*S*,2*R*,5*S*)-2-(Diethylaminoethyl)-1,2,5-triphenylphospholane 41. The typical procedure described above was followed, starting with enantiomerically pure **32** (45 mg), and the crude product purified by column chromatography (6% MeOH/CH_2Cl_2) to give the title compound **41** as a white solid (18 mg, 44%), $[\alpha]_D^{21}=+13$ (c 0.7 in $CHCl_3$); ν_{max} ($CHCl_3$) (cm^{-1}) 2950, 2351, 1600, 1494, 1455, 1071 and 907; δ_H (400 MHz, $CDCl_3$) 1.17 (6H, t, J=6.9 Hz, 2×CH_3), 2.20–2.62 (4H, m, C-3H, C-4H and 2×C-4′H), 2.65–2.90 (8H, m, C-3H, C-4H, 2×C-1′H, 2×C-2′H and 2×C-4′H), 3.84 (1H, app. dt, J=11.0 and 7.0 Hz, C-5H) and 6.95–7.34 (15H, m, ArH); δ_C (100 MHz, $CDCl_3$) 11.0 (2×CH_3), 29.7 (CH_2, C-3 or C-4), 30.9 (CH_2, C-1′), 35.6 (CH_2, C-3), 45.4 (d, J=17 Hz, CH_2, C-2′), 46.8 (CH_2, 2×C-4′), 53.8 (d, J=15 Hz, C, C-2), 48.0 (d, J=18 Hz, CH, C-5), 125.4–135.0 (aromatic CH and one aromatic C), 139.8 and 143.7 (aromatic C); m/z (FAB) 416 ($[M+H]^+$, 8%), 343 (4), 109 (21), 95 (37), 69 (70) and 55 (100) (HRMS: Found $[M+H]^+$, 416.2511. $C_{28}H_{34}NP$ requires [M+H], 416.2507).

6.4.9. (1*S*,2*R*,5*S*)-2-(Benzylaminoethyl)-1,2,5-triphenylphospholane 42. The typical procedure described above was followed, starting with enantiomerically pure **33** (50 mg), and the crude product purified by column chromatography (5% MeOH/CH_2Cl_2) to give the title compound **42** as a white solid (38 mg, 79%); $[\alpha]_D^{25}=+16$ (c 0.51 in $CHCl_3$); ν_{max} ($CHCl_3$) (cm^{-1}) 2953, 2757, 1682, 1599, 1495, 1456 and 1106; δ_H (400 MHz, $CDCl_3$) 2.31–2.97 (8H, m, C-3H, C-4H, C-1′H and C-2′H), 3.48 (1H, d, J=6.8 Hz, C-4′H), 4.20 (1H, app. q, J=9.6 and 13.3 Hz, C-5) and 6.66–7.53 (20H, m, ArH); δ_C (100 MHz, $CDCl_3$) 30.9 (CH_2, C-3 or C-4), 36.2 (CH_2, C-3 or C-4), 45.1 (CH_2, C-1′), 48.3 (CH_2, C-2′), 51.5 (CH, d, J=18 Hz, C-5), 53.8 (CH_2, C-4′), 53.7 (CH_2, d, J=16 Hz, C-2) and 125.4–139.7 (aromatic C and CH); m/z (FAB) 450 ($[M+H]^+$, 6%), 207 (12), 147 (30), 133 (61), 91 (56) and 73 (100) (HRMS: Found $[M+H]^+$, 450.2326. $C_{31}H_{32}NP$ requires [M+H], 450.2351).

6.5. X-Ray crystallography

6.5.1. Benzaldehyde adduct 11. Crystal data: $C_{29}H_{27}O_2P$, M=438.48, monoclinic, a=12.219(6), b=7.524(6), c=13.258(5) Å, β=108.44(3)°, U=1156.3(12) Å^3, T=220(2) K, space group $P2_1$ (No. 4), Z=2, D_c=1.259 cm^{-3}, μ(Mo Kα)=0.143 mm^{-1}, 4019 unique reflections measured, corrected for absorption (R_{int} 0.037) and crystal decay (29%), and used in all calculations. Final R_1 [3241 $F>4\sigma(F)$]=0.0687 and wR(all F^2) was 0.189. The Flack absolute structure parameter refined to 0.0(2). CCDC number 172595.

6.5.2. Acetone adduct 13. Crystal data: $C_{25}H_{27}O_2P$, M=390.44, monoclinic, a=11.740(3), b=6.5473(9), c=13.506(3) Å, β=100.65(2)°, U=1020.3(4) Å^3, T=150(2) K, space group $P2_1$ (No. 4), Z=2, D_c=1.271 cm^{-3}, μ(Mo Kα)=0.153 mm^{-1}, 3568 unique reflections measured, corrected for absorption (R_{int} 0.042), and used in all calculations. Final R_1 [3016 $F>4\sigma(F)$]=0.0777 and wR(all F^2) was 0.215. The Flack absolute structure parameter refined to −0.3(2). CCDC number 172594.

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