Stereoselective intramolecular acylation of γ′-benzoyloxyphosphine oxides with an internal chlorotrimethylsilane trap: isolation of silylated tetrahedral intermediates

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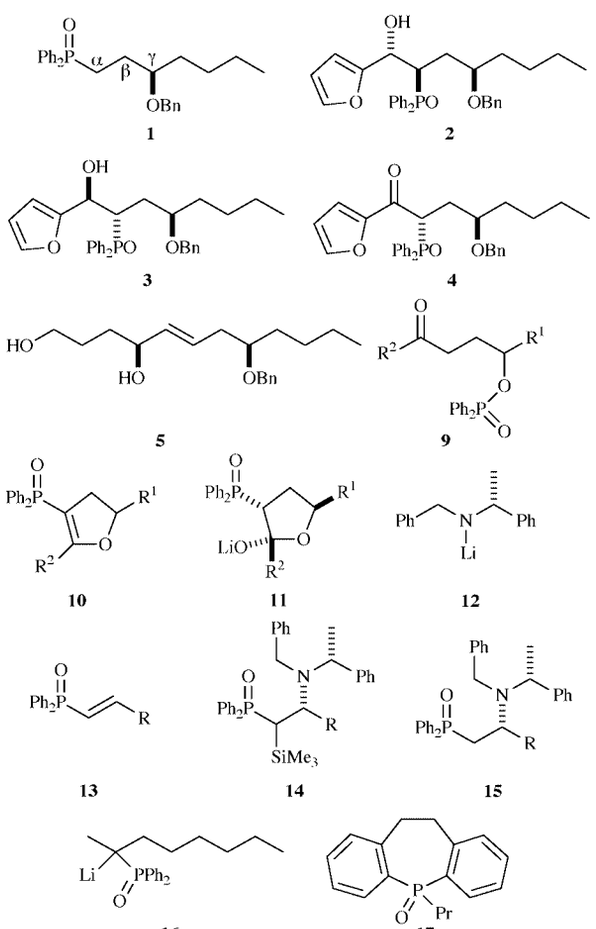
The kinetic products of the intramolecular acylation of γ′-benzoyloxyphosphine oxides were revealed by conducting the reaction in the presence of an internal trapping agent. A high level of stereocontrol over the formation of both the stereogenic centre α to phosphorus and the hemiacetal centre was observed. The stereochemistry of the products was determined by X-ray crystallography and ^{1}H NMR and the stereoselectivity of the reaction is explained in terms of the known structure and configurational instability of lithiated phosphine oxides.

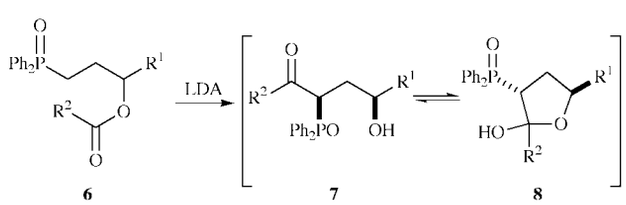
Introduction

As part of our continuing programme of stereocontrol with phosphine oxides,[1] we have investigated the stereoselectivity of reactions[2] of lithiated γ′-benzyloxyphosphine oxides.† Reaction of lithiated **1** with furfuraldehyde in THF was ^{1,3}*syn*-selective and provided mainly the β-hydroxy phosphine oxide **2**.‡ However, the sense of the 1,3-stereocontrol could be reversed by varying either the solvent or the type of electrophile used; reaction of enantiomerically enriched lithiated **1** with furfuraldehyde in toluene provided mainly the diastereomeric phosphine oxide **3** and reaction with ethyl furoate in THF gave mainly the β-keto phosphine oxide **4**. This study led to stereoselective syntheses of all four diastereomers of a β-hydroxy phosphine oxide (including **2** and **3**) and culminated in the formal synthesis of all four stereoisomeric diols (*e.g.* **5**) bearing 1,5-related stereogenic centres across an *E*-alkene.[2a,3]



1 **2** **3** **4** **5** **9** **10** **11** **12** **13** **14** **15** **16** **17**

An alternative approach to 1,3-stereocontrol with phosphine oxides has involved the *intra*molecular acylation[4] of phosphine oxides **6**.[5] Treatment of diphenylphosphinoyl esters **6** with LDA provided hydroxyketones **7** with complete control over the new stereogenic centre α to phosphorus (Scheme 1). Unfortunately,



6 **7** **8**

Scheme 1

the reaction was complicated by the presence of both open chain hydroxyketone **7** and two diastereomeric hemiacetals **8**. Furthermore, the reaction products were rather sensitive, decomposing to phosphinate esters **9** in base, and to dihydrofurans **10** in acid. Unlike the Claisen ester condensation,[6] the reaction is not driven by the formation of a stable enolate anion; instead, by analogy with the Horner–Wittig reaction,[7] the true product of the rearrangement is believed to be the lithium derivative **11** of the hemiacetal **8**.

Internal trapping agents are useful tools for revealing the kinetic products of reactions.[8] Corey has used chlorotrimethylsilane as an internal trapping agent[8] and we have exploited chlorotrimethylsilane and cyclobutanone[9] traps in asymmetric additions[10] of Davies's lithium amide **12** to vinyl phosphine oxides **13** (→**14**→**15**) and in investigations of the configurational stability[11] of lithiated phosphine oxides **16** and the

† The double bond which would be formed by a final Horner–Wittig elimination always joins the α and β carbon atoms; carbon atoms on the other side of the diphenylphosphinoyl group are labelled β′, γ′ *etc.*

‡ We use the stereochemical designator ^{1,3}*syn* to indicate that functional groups on carbons with a 1,3 relationship are both above or both below the plane of the illustration.

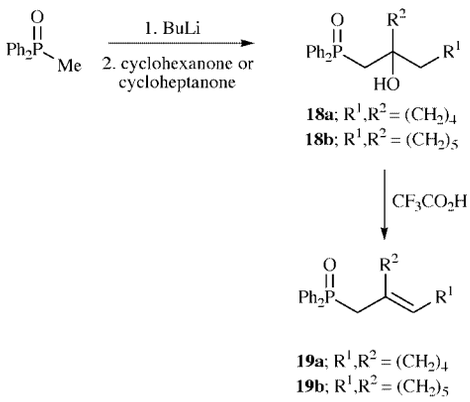
Table 1 Hydroboration–oxidation of the allylic phosphine oxides **19** (Scheme 4)

Starting material	R^1	R^2	Product	Yield (%)
19a	Me	Me	*anti*-**21a**	79
19b	Et	Me	*anti*-**21b**	82
19c	Pr	Me	*anti*-**21c**	84
19d	$-(C_4H_8)-$		*anti*-**21d**	77
19e	$-(C_5H_{10})-$		*anti*-**21e**	86

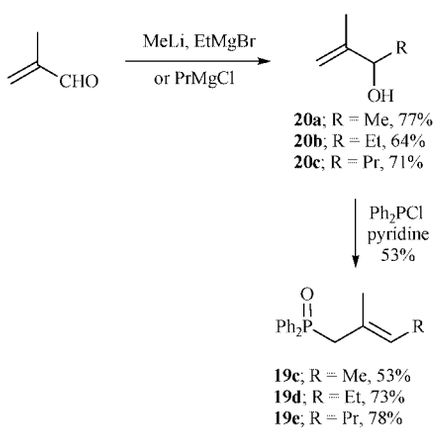
chemical stability[9] of lithium derivatives of phosphine oxides **17**. In this paper, we reveal how a chlorotrimethylsilane internal trap was used to probe the stereoselectivity and mechanism of the intramolecular acylation of γ′-benzoyloxy phosphine oxides (*e.g.* **6**; R^2 = Ph).

Synthesis of γ′-benzoyloxyphosphine oxides

The allylic phosphine oxides **19** were prepared either by acid-catalysed elimination[12] of the β-hydroxy phosphine oxides **18** (Scheme 2) or by [2,3]-sigmatropic Arbusov rearrangement[13,14]



Scheme 2



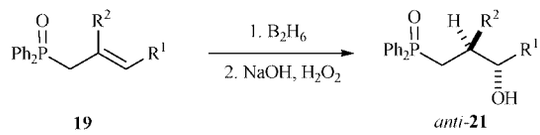
Scheme 3

of the allylic alcohols **20** (Scheme 3). The racemic γ′-hydroxy phosphine oxides *anti*-**21a**–**e** were synthesised by stereospecific hydroboration–oxidation[15] of the allylic phosphine oxides **19** (Scheme 4, Table 1). We also investigated the asymmetric hydroboration of the allylic phosphine oxide **19a**; however, asymmetric hydroboration of **19a** with isopinocampheyl borane ($IpcBH_2$) was extremely sluggish giving the alcohol *anti*-**21d** in just 41% yield after four weeks. The enantiomeric excess of the product was shown to be 65% ee by ^{1}H NMR using Pirkle's chiral shift reagent.[16]

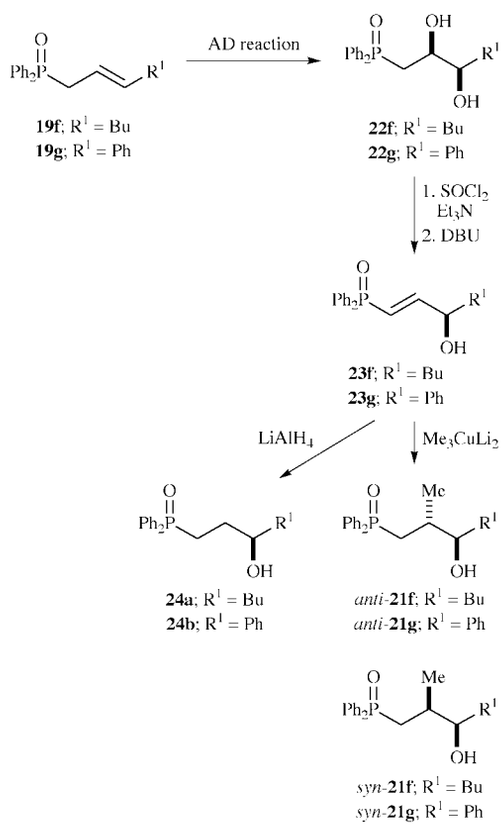
The optically active γ′-hydroxy phosphine oxides **21f**–**g** and **24a**–**b** were synthesised using a Sharpless asymmetric

Table 2 Benzoylation of the γ′-hydroxy phosphine oxides **21** and **24** (Scheme 6)

Starting material	R^1	R^2	Product	Yield (%)
anti-**21a**	Me	Me	*anti*-**25a**	99
anti-**21b**	Et	Me	*anti*-**25b**	89
anti-**21c**	Pr	Me	*anti*-**25c**	81
anti-**21d**	$-(C_4H_8)-$		*anti*-**25d**	90
anti-**21e**	$-(C_5H_{10})-$		*anti*-**25e**	94
anti-**21f**	Bu	Me	*anti*-**25f**	86
syn-**21f**	Bu	Me	*syn*-**25f**	85
anti-**21g**	Ph	Me	*anti*-**25g**	91
syn-**21g**	Ph	Me	*syn*-**25g**	63
24a	H	Bu	**26a**	94
24b	H	Ph	**26b**	94



Scheme 4



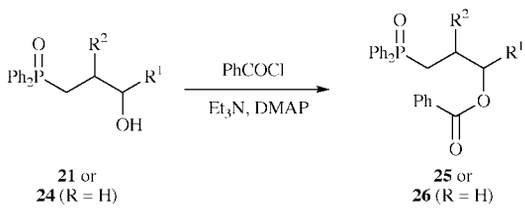
Scheme 5

dihydroxylation reaction[14] to induce asymmetry (Scheme 5). The 1,2-diols **22** were converted into the optically active γ′-hydroxy phosphine oxides **21** and **24** using a two step sequence; the diols **22** were activated and eliminated to give the γ′-hydroxy vinyl phosphine oxides **23** which were reacted with a cuprate reagent or lithium aluminium hydride to give the alcohols **21** and **24** respectively.[10b,17] The reaction sequence **19**→**22**→**23**→**21** provided a useful alternative to asymmetric hydroboration and provided *both* diastereomeric γ′-hydroxy phosphine oxides **21**. The alcohols **21** and **24** were converted into the corresponding benzoates **25** and **26** by treatment with benzoyl chloride, triethylamine and catalytic *N*,*N*-dimethylaminopyridine (Scheme 6; Table 2).

Table 3 Intramolecular acylations of diphenylphosphinoyl benzoates **24** and **26** (Scheme 7)

Entry	Starting material	R^1	R^2	Product	Ee (%)	Ratio[a]	Yield[b] (%)
1	*anti*-**25a**	Me	Me	**27a**	—	>98:2	68
2	*anti*-**25b**	Et	Me	**27b**	—	94:6	64
3	*anti*-**25c**	Pr	Me	**27c**	—	>98:2	65
4	*anti*-**25d**	–(C_4H_8)–		**27d**	—	>98:2	87
5	*anti*-**25e**	–(C_5H_{10})–		**27e**	—	>98:2	83
6	*anti*-**25f**	Bu	Me	**27f**	76	95:5	75
7	*anti*-**25g**	Ph	Me	**27g**	86	91:9	22
8	*syn*-**25f**	Bu	Me	**28f**	76	>98:2	64[c]
9	*syn*-**25g**	Ph	Me	**28g**	86	>96:4	16[d]
10	**26a**	Bu	—	**29a**	76	>98:2	55
11	**26b**	Ph	—	**29b**	86	>98:2	88

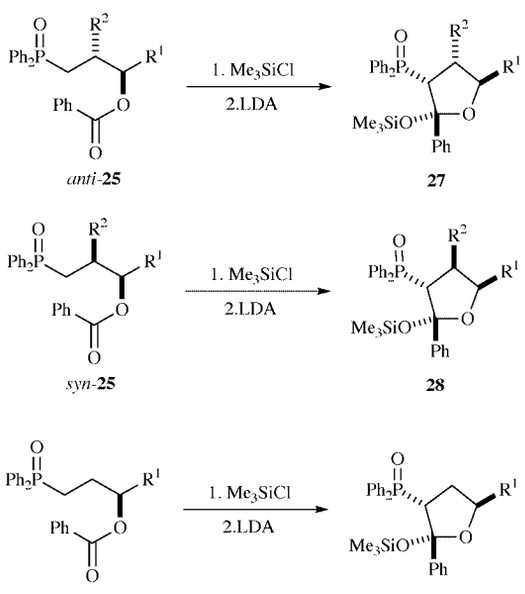
[a] By 400 MHz ^{1}H NMR. [b] Isolated as a mixture of diastereomers. [c] A 20% yield of the hemiacetal **30f** was also obtained. [d] A 52% yield of the hemiacetal. [e] **30g** was also obtained. [e] Decomposed to the dihydrofuran **31** on standing.



Scheme 6

Isolation of silylated intermediates of intramolecular acylation reactions

The diphenylphosphinoyl benzoates **25** and **26** were premixed with chlorotrimethylsilane in THF and treated with LDA at −78 °C (Scheme 7 and Table 3). The silyl ethers **27**, **28** and **29**



Scheme 7

were obtained with high diastereoselectivity.[18] Previous studies of intramolecular acylation reactions[5] (in the absence of an internal trapping agent) had suggested that the new stereogenic centre α to phosphorus would be controlled but we were surprised to find that a single epimer at the hemiacetal centre had been trapped. In each case, the kinetic products of the intramolecular acylation reactions were single diastereoisomers of lithium derivatives (*e.g.* **11**) which were trapped as the corresponding silyl ethers.

The products **27**, **28** and **29** are trapped intermediates of

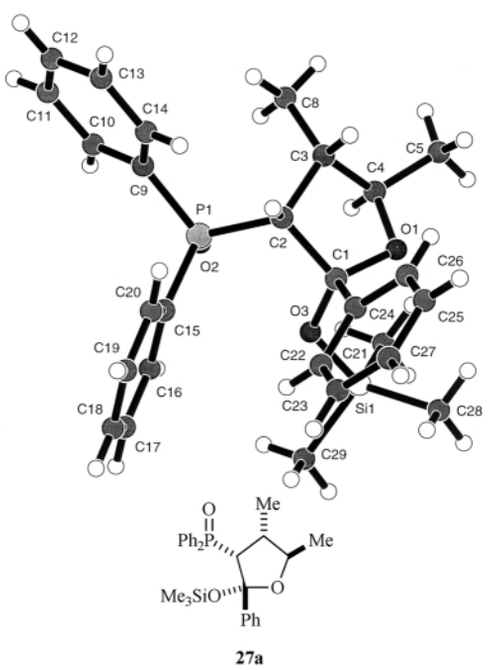
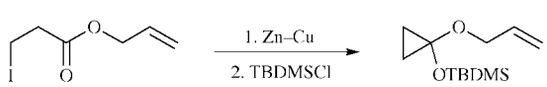


Fig. 1 X-Ray crystal structure of the silyl ether **27a**.

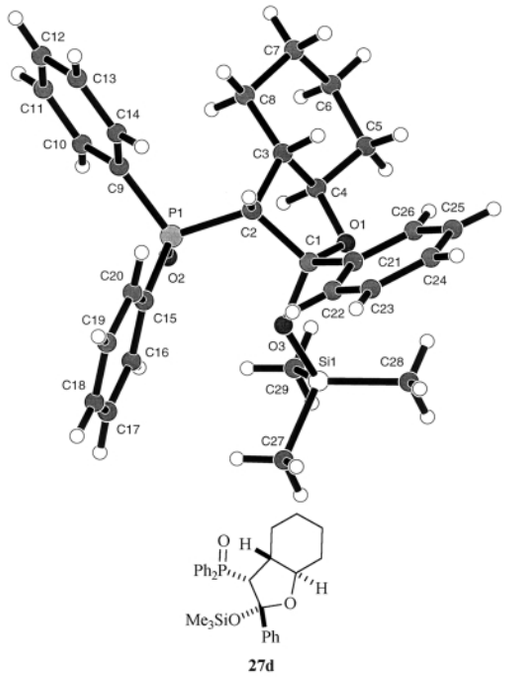
carbonyl substitution reactions in which a benzoyl group has been transferred halfway from oxygen to carbon. It is unusual to trap such an intermediate when a carbon nucleophile displaces a heteroatomic leaving group, though similar tetrahedral intermediates are stable products of additions of organometallic reagents to carboxylic acids[19] and Weinreb[20] amides. Tamura has observed similar products from the intramolecular acylation of iodoesters (Scheme 8).[21] Hemiacetals have been



Scheme 8

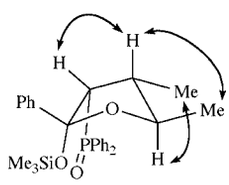
trapped by silylation during the DIBAL-H reduction of esters[22] and with good stereoselectivity during the additions to esters of 2-haloacids.[23]

The relative stereochemistry of the silyl ethers **27**–**29** was determined in three ways. Firstly, we obtained X-ray crystal structures of the silyl ethers **27a** and **27d** (Fig. 1 and 2), which revealed their relative stereochemistry; the diphenylphosphinoyl group and the trimethylsilyloxy groups were both found to adopt pseudo-axial orientations on the tetrahydrofuran ring. Secondly, NOE studies were conducted on the ^{1}H NMR spectra of the silyl ethers **27a**, **28g** and **29a**; the



27d

Fig. 2 X-Ray crystal structure of the silyl ether **27d**.



27a

Fig. 3 Summary of diagnostic NOE interactions in the silyl ethers **27a**.

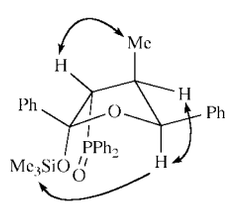


Fig. 4 Summary of diagnostic NOE interactions in the silyl ethers **28g**.

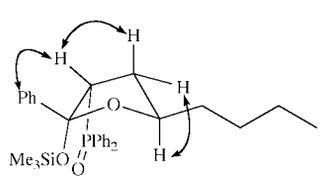


Fig. 5 Summary of diagnostic NOE interactions in the silyl ethers **29a**.

diagnostic NOE interactions are summarised in the Fig. 3–5. Finally, J_{HH} and J_{PH} coupling constants around the tetrahydrofuran ring were found to depend consistently on their relative stereochemistry; the coupling constant correlations observed are summarised in Table 4 and Fig. 6 and were used to assign the stereochemistry of silyl ethers **27f–g**, **28f** and **29b**.

Rationalisation of the stereoselectivity of intramolecular acylation reactions

Previously, we have demonstrated that lithiated phosphine oxides are configurationally unstable, even on the timescale of their reaction with electrophiles such as aldehydes,[24] ketones and chlorotrimethylsilane.[11] We have rationalised the reaction

Table 4 Coupling constant correlations for the silyl ethers **27**, **28** and **29**

Compound	R^1	R^2	J_{ab}	$J_{ab'}$	$J_{bc'}$	$J_{b'c'}$
27a	Me	Me	9.6	—	7.1	—
27b	Et	Me	9.6	—	9.0	—
27c	Pr	Me	9.5	—	[a]	—
27d	–(C_4H_8)–		9.1	—	10.5	—
27e	–(C_5H_{10})–		9.7	—	10.0	—
27f	Bu	Me	9.6	—	9.0	—
27g	Ph	Me	9.0	—	10.3	—
28f	Bu	Me	—	2.8	—	4.6
28g	Ph	Me	—	2.0	—	5.2
29a	Bu	—	10.5	4.2	8.2	5.5
29b	Ph	—	10.9	3.0	9.9	5.5
	maximum value		10.9	4.2	10.5	5.5
	minimum value		9.0	2.0	7.1	4.6

[a] Not determined.

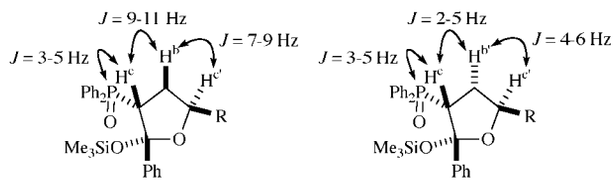
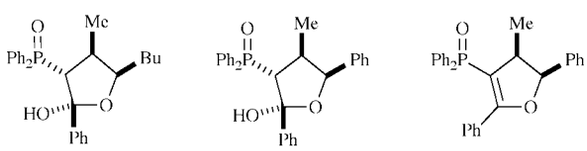


Fig. 6 Coupling constant correlations for silyl ethers **27**–**29**.

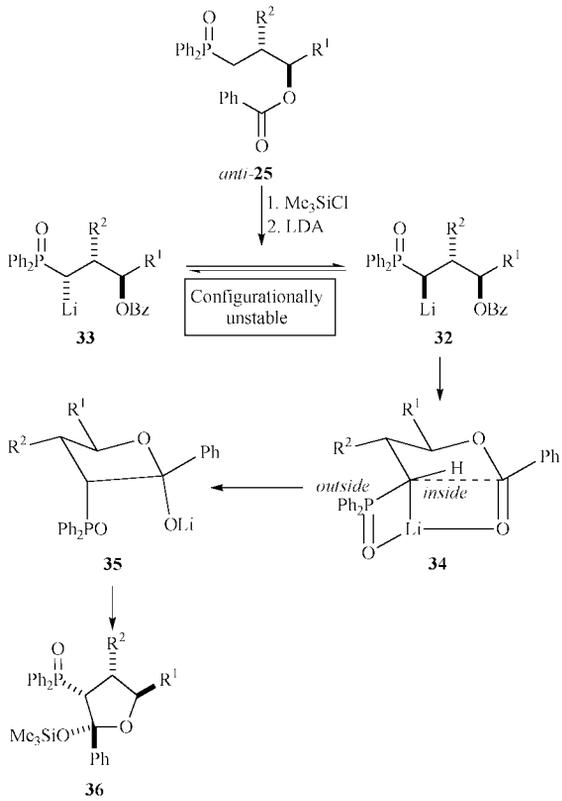


30f **30g** **31**

in terms of the known structure[25,26] and configurational instability[11,24] of lithiated phosphine oxides. Lithiation of phosphine oxides *anti*-**25** (entries 1–7, Table 3) will almost certainly be followed by equilibration to a thermodynamic mixture of lithium derivatives **32** and **33** (Scheme 9). The organolithium **32**, with its P–C–O–Li ring,[25,26] can adopt a conformation (**34**) in which R^1 and R^2 are equatorial, the diphenylphosphinoyl group occupies the "outside" position and the ester sits in its anomerically preferred[27] *Z* conformation. The R^1 and R^2 groups of *anti*-**25** have a profound preference for equatorial orientations in the transition state even when they are not conformationally locked in these positions (as in the benzoates *anti*-**25d**,**e**). The transition state for this acylation reaction resembles this structure in every respect except that the diphenylphosphinoyl group moves into an axial position (→**35**) during carbon–carbon bond formation. The reaction occurs with retention of configuration because there is a 90° angle between the old (C–Li) and new (C–C) bonds. The lithium alkoxide is trapped by chlorotrimethylsilane before epimerisation of the anomeric stereogenic centre or the stereogenic centre α to phosphorus can occur. The organolithium **33** is less reactive because one of the three controlling features would have to be flouted: R^1 and R^2 would need to adopt axial positions (**37**), the diphenylphosphinoyl group would have to occupy the "inside" position (**38**) or the ester would have to sit in its *E* conformation (**39**).

This model illustrates the intimate relationship between configurational stability of organolithiums and the stereoselectivity of S_E2 reactions. In particular, unless the initial lithiation of a chiral reagent like *anti*-**25** is diastereoselective,§ configurational

§ Many diastereoselective lithiation reactions are known (ref. 28).



Scheme 9

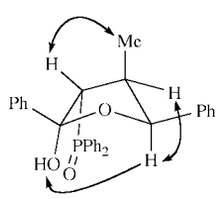
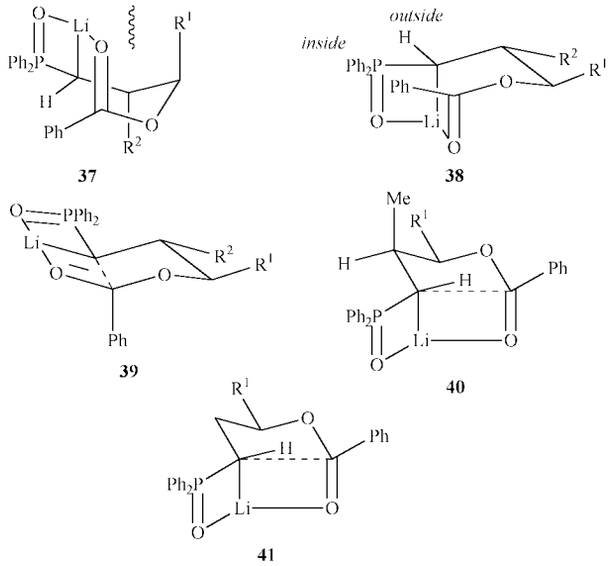


Fig. 7 Summary of diagnostic NOE interactions in the hemiacetal **30g**.

instability is necessary for high-yielding stereoselective reactions, since electrophilic substitution of organolithiums like **32** and **33** would lead to diastereomeric products. The reactions of lithiated phosphine oxides **32** and **33**, and many other organolithiums,[29] are stereoselective because pre-equilibration is fast, allowing the reaction to proceed *via* just one of the diastereomeric organolithiums. These principles have been extended to explain the dynamic kinetic resolution[30] of racemic organolithiums.[31]

A comparison of the intramolecular acylations of the diphenylphosphinoyl benzoates *anti*-**25** and the benzoates *syn*-**25** allowed us to determine the influence of the β′ and γ′ stereogenic centres on the formation of the new chiral centres in the silyl ethers **27** and **28** (compare entries 6, 7 with entries 8, 9, Table 3). The silyl ethers **27** and **28** have the same relative stereochemistry between the stereogenic centres α and γ′ to phosphorus, indicating that the main influence on the diastereoselectivity of the reaction is the γ′ stereogenic centre in the starting material. In fact, the β′ stereogenic centre barely even perturbs the level of the stereoselectivity. In terms of the model of stereoselectivity proposed, it does not matter whether the methyl group occupies an axial position (*anti*-**25**→**34**→**27**) or an equatorial position (*syn*-**25**→**40**→**28**). This is, perhaps, unsurprising because the methyl group of transition state **40** does not suffer unfavourable 1,3 diaxial interactions. Unfortunately, the silyl ethers **28** decomposed on work-up to the corresponding hemiacetals **30**. NOESY analyses of the silyl ether **28g** and the hemiacetal **30g** showed that these compounds had the same relative stereochemistry (Fig. 4 and 7). We suggest that



the high level of substitution on the ring of **30g** may prevent ring-opening and therefore equilibration of the hemiacetal centre.¶

Removal of the β′ substituent altogether confirmed that the γ′ stereogenic centre alone can control the diastereoselectivity of the intramolecular acylation reaction (entries 10–11, Table 3). The benzoates **26** were converted cleanly into the silyl ethers **29** with extremely high diastereoselectivity; the reaction is believed to proceed *via* the transition state **41** in which the R^1 group adopts an equatorial position on the forming tetrahydrofuran ring.

Synthetic transformations of the silyl ethers 27–29

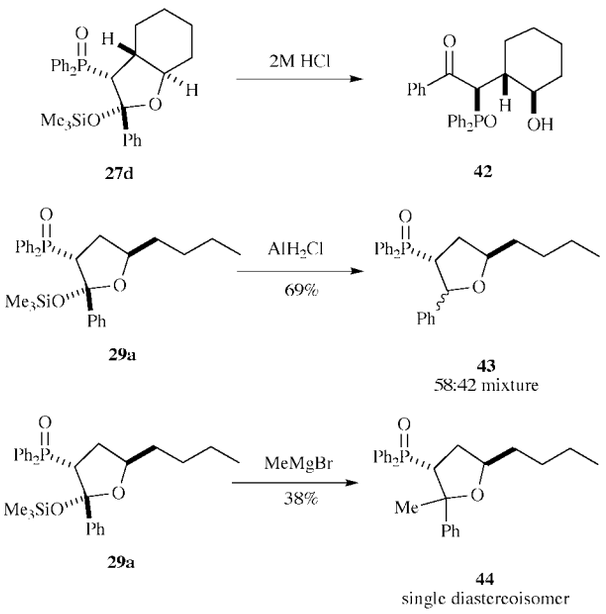
Having trapped the kinetic products of intramolecular acylation reactions, we needed to develop methods to release the masked ketone functionality without losing the 1,3-stereochemical relationship. The trimethylsilyl group of **27d** was removed with aqueous hydrochloric acid to give the β-keto phosphine oxide **42** without epimerisation α to phosphorus (Scheme 10).‖ An alternative strategy involved the reductive cleavage of the silyl ethers **27**–**29** to give β-hydroxy phosphine oxides directly. Treatment of **29a** with dihydroaluminium chloride[33] resulted in *exocyclic* cleavage of the trimethylsilyloxytetrahydrofuran (rather than the *endocyclic* cleavage which we required) to give the tetrahydrofuran **43** as a 58:42 mixture of diastereoisomers. In a similar vein, cleavage[34] of the silyl ether **29a** with methyl magnesium bromide at 80 °C in THF gave the tetrahydrofuran **44** as a single diastereoisomer; again the unwanted *exocyclic* mode of cleavage prevailed. A more remarkable application of the silyl ethers **27**–**29**—the synthesis of optically active cyclopropyl ketones—is described in the following paper.[35]

Summary

Intramolecular acylation of γ′-benzoyloxyphosphine oxides **25**–**26** with LDA in the presence of chlorotrimethylsilane provides the silyl ethers **27**–**29** (*i.e.* hemiacetals trapped as the corresponding trimethylsilyl ethers) as single diastereoisomers. The stereoselectivity of the reaction is largely controlled by the stereogenic centre γ′ to phosphorus and the approach is more stereoselective than the intermolecular[2] acylations of protected

¶ The kinetic barrier to ring-opening of similar diphenylphosphinoyl hemiacetals can render them inert to reduction by sodium borohydride alone (ref. 32).

‖ Deprotection of the silyl ether **27d** resulted in epimerisation of the stereogenic centre α to phosphorus.



Scheme 10

γ′-hydroxy phosphine oxides. We have rationalised the stereoselectivity of the reaction in terms of the structure and configurational instability of lithiated phosphine oxides.

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 indicator for THF. *n*-Butyllithium was titrated against diphenylacetic acid before use. All non-aqueous reactions were carried out under argon using oven-dried glassware.

Flash column chromatography was carried out using Merck Kieselgel 60 (230–400 mesh) according to the method of Still, Kahn and Mitra.[36] Thin layer chromatography was carried out on commercially available pre-coated plates (Merck silica Kieselgel $60F_{254}$). Unless otherwise stated, R_f values were measured with ethyl acetate as eluant. Proton and carbon NMR spectra were recorded on Bruker WM 200, WM 250, WM 400 or AMX 500 Fourier transform spectrometers using an internal deuterium lock. Chemical shifts are quoted in parts per million downfield of tetramethylsilane and values of coupling constants (*J*) are given in Hz. Carbon NMR spectra were recorded with broad band proton decoupling and Attached Proton Test. 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 Buchi 510 melting point apparatus and are uncorrected. Infrared 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. Electron Impact was used unless Fast Atom Bombardment (+FAB) is indicated. 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 $[a]_D^{20}$ are given in units of 10^{-1} deg cm^2 g^{-1}.

3-Methylbut-3-en-2-ol 20a

Methacrolein (3.505 g, 50 mmol, 4.17 cm^3) in dry Et_2O (30 cm^3) at 0 °C was added to methyllithium (45 cm^3, 63 mmol, 1.4 mol dm^{-3}) in dry Et_2O (50 cm^3) cooled to 0 °C. The mixture was allowed to warm to room temperature and then stirred for 1 h. The mixture was then cooled to 0 °C and quenched with saturated aqueous ammonium chloride solution and poured into water (100 cm^3). The mixture was extracted with Et_2O (3 × 50 cm^3) and the combined organics were dried ($MgSO_4$). The solvent was evaporated *in vacuo* with no heating. The residues were distilled using an 8 cm Vigreaux fractionating column to give the allylic alcohol **20a** (3.264 g, 77%) as a colourless liquid, bp 113–116 °C (lit.[37] 115–117 °C); δ_H (200 MHz; $CDCl_3$) 4.98 (1H, m, CH_AH$_B$), 4.92 (1H, m, CH$_A$H$_B$), 4.21 (1H, q, *J* 6.3, C*H*OH), 1.95 (1H, br s, OH), 1.72 (3H, t, *J* 6.5, CCH_3), 1.25 (3H, d, *J* 6.4, CHOHCH_3).

2-Methylpent-1-en-3-ol 20b

By the same general method, ethylmagnesium bromide (18.31 cm^3, 54.93 mmol, 3 mol dm^{-3} and methacrolein gave a residue which was distilled using an 8 cm Vigreaux fractionating column to give the allylic alcohol **20b** (3.2 g, 64%) as a colourless liquid, bp 128–130 °C (lit.[38] 120–122 °C); δ_H (250 MHz; $CDCl_3$) 4.92 (1H, m, CH_AH$_B$), 4.83 (1H, m, CH$_A$H$_B$), 3.98 (1H, t, *J* 6.5, C*H*OH), 1.7 (3H, t, *J* 1.2, CCH_3), 1.57(2H, m, CH_2CH$_3$), 0.88 (3H, t, *J* 7.4, CH$_2$CH_3).

2-Methylhex-1-en-3-ol 20c

By the same general method, propylmagnesium chloride (30.45 cm^3, 60.91 mmol, 2 mol dm^{-3}) and methacrolein (4.22 cm^3, 50.76 mmol) gave a residue which was distilled to give the allylic alcohol **20c** (4.11 g, 71%) as a colourless liquid, bp 70 °C (36 mmHg) [lit.[39] 106 °C (26 mmHg)], δ_H (250 MHz, $CDCl_3$) 4.91 (1H, m, CH_AH$_B$), 4.81 (1H, m, CH_AH$_B$), 4.05 (1H, t, *J* 6.4, C*H*OH), 1.71 (3H, s, CCH_3), 1.61–1.16 (4H, m, CH_2CH_2CH$_3$), 0.92 (3H, t, *J* 7.2, CH_3CH$_2$); δ_C ($CDCl_3$) 147.8$^-$ (*C*CH$_3$), 110.7$^-$ (*C*H$_2$C), 75.8$^+$ (COH), 37.2$^-$ (COH*C*H$_2$), 18.8$^-$ (*C*H$_2$CH$_3$), 17.5$^+$ (C*C*H$_3$), 14.0$^+$ (CH$_2$*C*H$_3$).

(*E*)-4-Diphenylphosphinoyl-3-methylbut-2-ene 19c

Chlorodiphenylphosphine (1 g, 0.814 cm^3, 4.532 mmol) in dry degassed Et_2O (5 cm^3) was added to a solution of pyridine (0.358 g, 367 μdm^3, 4.532 mmol) and 3-methylbut-3-en-2-ol **20a** (0.386 g, 4.532 mmol) in dry, degassed Et_2O (15 cm^3) under an argon atmosphere at −78 °C. The mixture was stirred at −78 °C for 0.5 h then allowed to warm to room temperature. The white precipitate of pyridinium hydrochloride was filtered under argon by cannulation into a filtration chamber. The filtrate was washed with ice cold, dry, degassed Et_2O (2 × 5 cm^3). The ether was evaporated *in vacuo* under an argon atmosphere and dry, degassed toluene (10 cm^3) was added. The mixture was refluxed under argon for 17 h then cooled. The bulk of the toluene was evaporated *in vacuo* and the residues poured into water which were extracted with CH_2Cl_2 (3 × 25 cm^3). The combined organics were washed with 2 mol dm^{-3} HCl then with a saturated solution of sodium bicarbonate and dried ($MgSO_4$). The organics were evaporated *in vacuo* and purified by chromatography on silica gel, eluting with EtOAc:hexane (90:10) to give the allylic phosphine oxide[12] **19c** (0.657 g, 53%, *E*:*Z* 85:15). Recrystallisation from EtOAc gave ***E*-19c**, mp 117–120 °C; R_f 0.3 (Found: M$^+$, 270.1193. $C_{17}H_{19}OP$ requires *M*, 270.1173); δ_H(200 MHz; $CDCl_3$) 7.84–7.38 (10H, m, Ph_2P), 5.23–5.12 (1H, m, C*H*CH$_3$), 3.04 (2H, d, J_{PH} 13.6, PCH$_2$), 1.65 (3H, m, CH$_3$), 1.49 (3H, m, CH$_3$); δ_C($CDCl_3$) 134.2–128.3 (Ph_2P), 126.3 (d, J_{PC} 9.2, PCH$_2$*C*), 124.9 (d, J_{PC} 10.6, *C*CH$_3$), 41.0 (d, J_{PC} 68.2, PC), 17.8 (*C*H$_3$CH), 13.8 (d, J_{PC} 6.8, C*C*H$_3$); *m*/*z* 270 (40%, M$^+$), 202 (100, Ph_2POH), 77 (40, C_6H_5).

(*E*)-1-Diphenylphosphinoyl-2-methylpent-2-ene 19d

By the same general method, chlorodiphenylphosphine (1 g, 0.814 cm^3, 4.532 mmol) and 2-methylpent-1-en-3-ol **20b** (0.518

g, 5.166 mmol) in dry, degassed Et_2O (15 cm^3) gave a crude product which was purified by radial chromatography on silica gel, eluting with EtOAc:hexane (9:1) to give the *allylic phosphine oxide* **19d** (929 mg, 73%, *E*:*Z* 92:8). Recrystallisation from EtOAc gave *E*-**19d**, mp 120–121 °C; R_f 0.34 (Found: M^+ 284.1332, C, 75.7; H, 7.40. $C_{18}H_{21}OP$ requires *M*, 284.1330, C, 76.0; H, 7.40%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1632 (C=C); δ_H(200 MHz; $CDCl_3$) 7.81–7.39 (10H, m, Ph_2P), 5.04 (1H, m, C*H*CH_2), 3.04 (2H, d, J_{PH} 13.5, PCH_2), 1.88 (2H, unresolved dq, C*H*$_2$$CH_3$), 1.69 (3H, d, *J* 1.5, CCH_3), 0.74 (3H, t, *J* 7.5, 3H, CH_2CH_3); $\delta_C(CDCl_3)$ 133.6–131.0 (Ph_2P), 128.4$^+$ (d, J_{PC} 11.6, CH), 125.0$^-$ (d, J_{PC} 10.1, *C*CH), 41.1$^-$ (d, J_{PC} 67.8, PC), 21.4$^-$ (*C*H_2CH_3), 17.9$^+$ (CH_2CH_3), 13.8$^+$ (d, J_{PC} 3.6, C*C*H_3); *m*/*z* 284 (45%, M^+), 202 (100, Ph_2POH), 77 (20, Ph). NOE difference spectra were used to determine the geometry of the major isomer.

1-Diphenylphosphinoyl-2-methylhex-2-ene 19e

By the same general method, chlorodiphenylphosphine (1.0 g, 0.814 cm^3, 4.532 mmol) and 2-methylhex-1-en-3-ol **20c** (0.569 g, 4.985 mmol) gave a crude product which was purified by radial chromatography on silica gel, eluting with EtOAc:hexane (9:1) to give the phosphine oxide **19e** (1.057 g, 78%, *E*:*Z* 96:4). Recrystallisation from EtOAc gave *E*-**19e**, mp 128–130 °C; R_f 0.41 (Found: M^+ 298.1474. $C_{19}H_{23}OP$ requires *M*, 298.1486); δ_H (200 MHz; $CDCl_3$) 7.8–7.42 (10H, m, Ph_2P), 5.04 (1H, br m, CCH), 3.05 (2H, d, J_{PH} 13.7, PCH_2), 1.88 (2H, dt, *J* 7.2 and 11.35, CHC*H*$_2$), 1.70 (3H, m, CCH_3), 1.14 (2H, sex, *J* 7.3, $CH_2CH_2CH_3$), 0.72 (3H, t, *J* 7.3, CH_2CH_3); δ_C (50 MHz; $CDCl_3$) 131.5–131.0 (Ph_2P), 128.4$^+$ (d, J_{PC} 11.5, C*C*H), 125.4$^-$ (*C*CH), 41.1$^-$ (d, J_{PC} 67.9, PC), 30.2$^-$ (CH*C*H_2), 22.5$^+$ (*C*H_2CH_3), 18.1$^+$ (C*C*H_3), 13.6$^+$ (CH_2CH_3); *m*/*z* 298 (50%, M^+), 269 (5, M − C_2H_5), 202 (100, Ph_2POH), 77 (20, Ph).

(1*R**, 2*R**)-2-Diphenylphosphinoylmethylcyclohexanol *anti*-21d

Sodium borohydride (0.12 g, 3.06 mmol) in dry THF (10 cm^3) at 0 °C was added slowly over 1 hour to a solution of the allylic phosphine oxide[12] **19d** (0.50 g, 1.7 mmol) and boron trifluoride–diethyl ether (0.32 cm^3, 2.55 mmol) in dry THF (25 cm^3) at 0 °C. The solution was allowed to warm to room temperature and stirred for 24 hours. Hydrogen peroxide (10 cm^3, 100 vol) and 10% aqueous sodium hydroxide solution (10 cm^3) were added to the reaction mixture which was stirred for a further 30 min. The bulk of the THF was removed *in vacuo* and the residues extracted with EtOAc (3 × 50 cm^3). The combined organics were then washed with water and dried (Na_2SO_4). The solvent was evaporated *in vacuo* to give a mixture of regio-isomers. Column chromatography on silica gel, eluting with EtOAc gave the alcohol[12] *anti*-**21d** (0.286 g, 54%) as white needles, mp 160-162 °C (lit.,[12] 151–152 °C); $\nu_{max}(CHCl_3)/cm^{-1}$ 3330 (OH), 3028, 2988, 2932, 1438; δ_H(250 MHz; $CDCl_3$) 7.8–7.4 (10H, m, Ph_2P), 5.0 (1H, br s, OH), 3.25 (1H, dt, *J* 4.4 and 9.5, C*H*OH), 2.5 (1H, ddd, *J* 7.6, J_{PH} 14.0 and *J* 15.5, PC*H*$_A$H$_B$), 2.2 (1H, ddd, *J* 4.3, J_{PH} 9.4 and *J* 15.5, PCH$_A$*H*$_B$), 1.99–0.77 (9H, m, C_6H_9); δ_C (63 MHz; $CDCl_3$) 133.5–128.6 (Ph_2P), 74.7$^+$ (d, J_{PC} 4.3, COH), 40.8$^+$ (d, J_{PC} 3.32, PC*C*H), 35.5$^-$ (d, J_{PC} 69.7, PCH), 35.1$^-$, 34.5$^-$ (d, J_{PC} 10.2), 25.6$^-$, 22.0$^-$.

Also obtained was 1-diphenylphosphinoylmethylcyclohexanol[12] (0.144 g, 27%).

(1*R**,2*R**)-2-Diphenylphosphinoylmethylcycloheptanol *anti*-21e

Borane–dimethyl sulfide complex (285 µdm^3, 2.903 mmol) was added to a stirred solution of the allylic phosphine oxide[12] **19e** (693 mg, 2.233 mmol) in dry THF at 0 °C. The mixture was allowed to warm to room temperature over 18 h. Excess ethanol was added to quench unreacted borane. An excess 2 mol dm^{-3} sodium hydroxide and 100 volumes hydrogen peroxide was added and the mixture was refluxed for 1 h and poured into brine. The residues were extracted with CH_2Cl_2 (3 × 50 cm^3), the combined organics were dried ($MgSO_4$) and evaporated *in vacuo* to give a crude product which was purified by column chromatography, eluting with EtOAc, to give the alcohol *anti*-**21e** (633 mg, 86%) as a colourless crystalline material, R_f 0.3; δ_H (250 MHz; $CDCl_3$) 7.8–7.4 (10H, m, Ph_2P), 3.58 (1H, dt, *J* 3.5 and 7.7, C*H*OH), 2.59 (1H, ddd, *J* 8.5, J_{PH} 14.1 and *J* 15.3, PC*H*$_A$H$_B$), 2.28 (1H, ddd, *J* 3.6, J_{PH} 9.2 and *J* 15.4, PCH$_A$*H*$_B$), 1.97 (m, 12H, C_7H_{12}). The alcohol *anti*-**21e** was fully characterised as the benzoate *anti*-**25e**.

(2*R**, 3*R**)-4-Diphenylphosphinoyl-3-methylbutan-2-ol *anti*-21a

By the same general method, borane–dimethyl sulfide complex (105 µl, 1.069 mmol and (*E*) 4-diphenylphosphinoyl-3-methylbut-2-ene **19a** (222 mg, 0.822 mmol) gave a crude product which was purified by column chromatography, eluting with EtOAc, to the alcohol *anti*-**21a** (188 mg, 79%) as a colourless oil, R_f 0.18 (Found: M^+ 288.1302. $C_{17}H_{21}O_2P$ requires *M*, 288.1279); $\nu_{max}(CHCl_3)/cm^{-1}$ 3341 (OH), 3028, 2988, 2932, 1438; δ_H (400 MHz; $CDCl_3$) 7.78–7.43 (10H, m, Ph_2P), 4.03 (1H, d, *J* 4.9, OH), 3.56 (1H, sex, *J* 6.2, C*H*OH), 2.53 (1H, ddd, *J* 6.3, J_{PH} 12.8 and *J* 15.4, PC*H*$_A$H$_B$), 2.23 (1H, ddd, *J* 5.6, J_{PH} 10.4 and *J* 15.4, PCH$_A$*H*$_B$), 1.90 (1H, m, PCH$_2$C*H*), 1.15 (d, *J* 6.2, 3H, CHOHC*H*$_3$), 0.95 (d, *J* 6.8, 3H, CHC*H*$_3$); δ_C (100 MHz; $CDCl_3$) 134.1$^-$, 128.4 (Ph_2P), 72.1 (d, J_{PC} 7.5, COH), 36.4 (d, J_{PC} 3.1, PC*C*H), 33.8 (d, J_{PC} 71.2, PCH_2), 21.0 (CHOH*C*H_3), 19.1 (d, J_{PC} 7.4, CHC*H*$_3$); *m*/*z* 289 (40%, MH^+), 288 (10, M^+), 273 (20, M − Me), 244 (60, M − C_2H_4O), 215 (70, M − C_4H_9O), 202 (100, Ph_2PO + 1).

(2*R**, 3*R**)-1-Diphenylphosphinoyl-2-methylpentan-3-ol *anti*-21b

By the same general method, borane–dimethyl sulfide complex (73 µdm^3, 0.727 mmol) and (*E*) 1-diphenylphosphinoyl-2-methylpent-2-ene **19b** (159 mg, 0.559 mmol) gave a crude product which was purified by column chromatography, eluting with EtOAc, to yield the alcohol *anti*-**21b** (139 mg, 82%) as a colourless oil, R_f 0.25 (Found: M^+ 302.1410. $C_{18}H_{23}O_2P$ requires *M*, 302.1436); $\nu_{max}(CHCl_3)/cm^{-1}$ 3353 (OH); δ_H (400 MHz; $CDCl_3$) 7.74–7.37 (10H, m, Ph_2P), 4.13 (1H, d, *J* 5.8, OH), 3.25 (1H, m, C*H*OH), 2.57 (1H, ddd, *J* 5.0, J_{PH} 12.0 and 15.4, PC*H*$_A$H$_B$), 2.15 (1H, ddd, *J* 7.0, J_{PH} 10.8 and 15.4, PCH$_A$*H*$_B$), 1.96 (1H, m, PCH$_2$C*H*), 1.48 (1H, ddq, *J* 7.4, 3.6 and 13.9, C*H*$_A$H$_B$CH$_3$), 1.3 (1H, m, CH$_A$*H*$_B$CH$_3$), 0.93 (3H, d, *J* 6.9, CHCH_3), 0.85 (3H, t, *J* 7.4, CH_2CH_3); δ_C ($CDCl_3$) 133.9–128.6 (Ph_2P), 77.17$^+$ (COH), 34.2$^+$ (d, J_{PH} 3.8, P*C*CH), 33.1$^-$ (d, J_{PH} 71.0, P*C*H$_2$), 27.39$^-$ (*C*H_2CH_3), 19.3$^+$ (d, J_{PH} 6.1, CH*C*H_3), 10.0$^+$ (CH_2CH_3); *m*/*z* 303 (30%, MH^+), 302 (4, M^+), 284 (20, M − 19), 273 (80, M − C_2H_5), 243 (60, M − C_3H_7O), 215 (80, M − $C_5H_{11}O$), 202 (100, Ph_2POH).

(2*R**, 3*R**)-1-Diphenylphosphinoyl-2-methylhexan-3-ol *anti*-21c

By the same general method, borane–dimethyl sulfide complex (84 µl, 0.858 mmol) and (*E*)-1-diphenylphosphinoyl-2-methylhex-2-ene (197 mg, 0.66 mmol) **19c** gave a crude product which was purified by flash column chromatography, eluting with EtOAc, to the alcohol *anti*-**21c** (175 mg, 84%) as a colourless oil, R_f 0.29 (Found: M^+ 316.1589. $C_{19}H_{25}O_2P$ requires *M*, 316.1592); δ_H (400 MHz; $CDCl_3$) 7.95–7.39 (10H, m, Ph_2P), 3.83 (1H, d, *J* 5.5, OH), 3.35 (1H, br s, C*H*OH), 2.55 (1H, ddd, *J* 5.4, J_{PH} 12.2 and *J* 15.4, PC*H*$_A$H$_B$), 2.20 (1H, ddd, *J* 6.5, J_{PH} 10.7 and *J* 15.4, PCH$_A$*H*$_B$), 1.98 (1H, m, PCH$_2$C*H*), 1.42 (2H, m, CHOHC*H*$_2$), 1.28 (2H, m, C*H*$_2$CH$_3$), 0.94 (3H, d, *J* 6.9, CHC*H*$_3$), 0.85 (3H, d, *J* 7, CH_2CH_3); δ_C (100 MHz; $CDCl_3$)

133.8–128.6 (Ph_2P), 75.7$^-$ (d, J_{PC} 7.24, COH), 37.0$^+$ (CHOH-CH_2), 34.8$^-$ (d, J_{PC} 3.7, PCCH), 33.3$^+$ (d, J_{PC} 70.8, PC), 19.4$^-$ (d, J_{PC} 6.8, CHCH_3), 18.9$^+$ (CH_2CH_3), 14.1$^+$ (CH_2CH_3); *m/z* (10%, M + 1), 298 (5, M − H_2O), 273 (40, M − C_3H_7), 243 (20, M − C_4H_9O), 235 (60), 215 (25, $C_6H_{13}O$), 202 (75, Ph_2PO + 1).

(*R*)-1-Diphenylphosphinoylheptan-3-yl benzoate 26a

Triethylamine (614 mg, 6.0 mmol) and benzoyl chloride (750 mg, 5.3 mmol) were added dropwise to (*R*)-1-diphenylphosphinoylheptan-3-ol[10b] **24a** (363 mg, 1.15 mmol) and *N*,*N*-dimethylaminopyridine (34 mg, 0.28 mmol) in dry dichloromethane (10 cm^3) at room temperature. The reaction was stirred for 3 days, quenched with water, extracted with dichloromethane (3 × 20 cm^3), dried ($MgSO_4$) and evaporated to give a crude product. Flash chromatography, eluting with EtOAc, gave the *benzoate* **26a** (452 mg, 94%) as plates, mp 141–144 °C (from EtOAc–hexane); R_f 0.30 (EtOAc); $[\alpha]_D^{20}$ +4.0 (*c* 0.10 in $CHCl_3$; 76% ee) (Found: M$^+$, 420.1846. $C_{26}H_{29}O_3P$ requires *M*, 420.1854); ν_{max}/cm^{-1} ($CHCl_3$) 1712 (C=O), 1437 (P–Ph), 1176 (P=O); δ_H (400 MHz; $CDCl_3$) 8.2–7.95 (2 H, m), 7.7–7.2 (13 H, m, Ph_2PO and remaining Ph), 5.18 (1H, tt, *J* 5.9 and 6.3, CHOBz), 2.35 (2H, m, PCH_2), 2.05 (2H, m), 1.65 (2H, m), 1.25 (4H, m), 0.85 (3H, t, *J* 6.9, Me); δ_C (63 MHz; $CDCl_3$) 168.2$^-$ (C=O), 139–126 (m, Ph_2PO and Ph), 74.8$^+$ (d, $^3J_{PC}$ 15, CHOBz), 33.8$^-$, 29.6$^-$ (d, $^1J_{PC}$ 68, PCH_2), 27.3$^-$, 26.3$^-$ (d, $^2J_{PC}$ 11.9, CH_2), 25.0$^-$, 22.5$^-$, 13.9$^+$ (Me); *m/z* 420.1 (5%, M$^+$), 315.1 (100, M − PhCO).

(*S*)-1-Phenyl-3-diphenylphosphinoylpropan-1-yl benzoate 26b

By the same general method, (*S*)-1-phenyl-3-diphenylphosphinoylpropan-1-ol[10b] **24b** (360 mg, 1.07 mmol) gave a crude product after refluxing for 2 h. Flash chromatography, eluting with EtOAc, gave the *benzoate* **26b** (445 mg, 94%) as needles, mp 193–194 °C (from EtOAc–hexane); R_f 0.30 (EtOAc); $[\alpha]_D^{20}$ +23.9 (*c* 0.16 in $CHCl_3$; 86% ee) (Found: C, 76.1; H, 5.65; P, 7.1; M$^+$, 440.1538. $C_{28}H_{25}O_3P$ requires C, 76.3; H, 5.70; P, 7.0%; *M*, 440.1541); ν_{max}/cm^{-1} ($CHCl_3$) 1717 (C=O), 1438 (P–Ph), (P=O); δ_H (400 MHz; $CDCl_3$) 8.07 (2H, dd, *J* 1.6 and 7.1, *ortho*-PhCO), 7.8–7.2 (18H, m, Ph_2PO and remaining Ph), 6.05 (1H, t, *J* 5.1, CHOBz), 2.6–2.3 (4H, m); δ_C (63 MHz; $CDCl_3$) 165.5$^-$ (C=O), 139.3$^-$ (*ipso*-Ph), 134–126 (m, Ph_2PO and Ph × 2), 76.5$^+$ (d, $^3J_{PC}$ 18.3, CHOBz), 28.4$^-$ (CH_2), 25.7$^-$ (d, $^1J_{PC}$ 72, PCH_2); *m/z* 440.1 (50%, M$^+$), 335.1 (100, M − PhCO), 201.1 (60, Ph_2PO), 105 (65, PhCO).

(1*R**,2*R**)-2-Diphenylphosphinoylmethylcyclohexan-1-yl benzoate *anti*-25d

By the same general method, benzoyl chloride (93 µl, 0.8 mmol) and the alcohol *anti*-**21d** gave a crude product which was recrystallised from petrol (bp 40-60 °C) and dichloromethane, with cooling in liquid nitrogen, to give the *benzoate* (0.30 g, 90%) as white plates, mp 132–134 °C; R_f 0.3 (Found: M$^+$, 418.1700. $C_{26}H_{27}O_3P$ requires *M*, 418.1698); ν_{max}($CHCl_3$)/cm^{-1} 1720 (C=O); δ_H (250 MHz; $CDCl_3$) 8.1–7.2 (15H, m, Ph_2P and Ph), 4.78 (1H, ddd, J_{HH} 4.4, 9.6 and 9.7, CHO), 2.66–1.09 (11H, m, C_6H_9 and PCH_2); δ_C($CDCl_3$) 166.1$^-$ (CO), 134.1–128.1 (Ph_2P and Ph), 77.5$^+$ (d, J_{PC} 13.5, CO), 37.2$^+$, 32.6$^-$, 31.8$^-$ (d, J_{PC} 71.8, PCH), 31.8$^-$, 25.0$^-$, 24.4$^-$; *m/z* 418.2 (55%, M$^+$), 313.1 (65), 216.1 (100), 105 (30, PhCO).

(1*R**,2*R**)-2-Diphenylphosphinoylmethylcycloheptan-1-yl benzoate *anti*-25e

By the same general method, benzoyl chloride (1 cm^3, 8.6 mmol) and the alcohol *anti*-**21e** (315 mg, 0.96 mmol) gave a crude product which was purified by column chromatography on silica gel, eluting with EtOAc:hexane (2:1), to give the *benzoate anti*-**25e** (389 mg, 94%) as a colourless oil, R_f 0.46 (Found: M$^+$ 432.1864; C, 74.4; H, 6.7; $C_{27}H_{29}O_3P$ requires *M*, 432.1854; C, 74.3; H, 7.0%); ν_{max}($CHCl_3$)/cm^{-1} 1704 (C=O); δ_H (250 MHz; $CDCl_3$) 8.07–7.35 (15H, m, Ph_2P and Ph), 4.94 (1H, dt, *J* 8.1, 5.2, CHO), 2.46–1.2 (13H, m, C_7H_{11} and PCH_2); δ_C(63 MHz, $CDCl_3$) 166.1$^-$ (COO), 134.9–128.4 (Ph_2P and Ph), 80.9$^+$ (d, J_{PC} 14.0, CHO), 39.1$^+$ (PCCH), 33.4$^-$ (d, J_{PC} 71.7, PC), 32.5$^-$, 30.1$^-$, 28.9$^-$, 25.8$^-$, 22.8$^-$; *m/z* 432 (15%, M$^+$), 327 (30, M − PhCO), 310 (60, M − PhCOOH), 215 (60, Ph_2POCH_2), 202 (Ph_2POH).

(2*R**,3*R**)-4-Diphenylphosphinoyl-3-methylbutan-2-yl benzoate *anti*-25a

By the same general method, benzoyl chloride (151 µl, 1.3 mmol) and the alcohol *anti*-**21a** gave a crude product which was purified on silica gel, eluting with EtOAc:hexane (3:1), to the *benzoate anti*-**25a** as an oil, R_f 0.5 (Found: M$^+$ 392.1568. $C_{24}H_{25}O_3P_1$ requires *M*, 392.1541); ν_{max}($CHCl_3$)/cm^{-1} 1700 (C=O); δ_H (400 MHz, $CDCl_3$) 8.1–7.3 (15H, m, Ph and Ph_2P), 5.01 (1H, quintet, *J* 6.2, CHOCH$_3$), 2.54 (1H, m, PCH_AH$_B$), 2.27 (1H, m, PCH_2CH), 2.14 (1H, m, PCH$_A$$H_B$), 1.26 (3H, d, *J* 6.3, CHOCH_3), 1.14 (3H, d, *J* 6.7, CHCH_3); δ_C ($CDCl_3$) 165.7 (C=O), 134.2–127.9 (Ph_2P and Ph), 75.2 (d, J_{PC} 13.7, CHO), 33.1 (d, J_{PC} 3.3, PCH_2CH), 31.9 (d, J_{PC} 71.8, PC), 17.2 (d, J_{PC} 1.6, CHCH_3), 16.6 (CHOCH_3); *m/z* 393 (13%, MH$^+$), 301 (40), 287 (50, M − COPh), 271 (20, M − CO_2Ph), 243 (25, M − $C_9H_9O_2$), 215 (30, M − $C_{11}H_{13}O_2$), 201 (45, Ph_2PO), 105 (100, PhCO).

(2*R**,3*R**)-1-Diphenylphosphinoyl-2-methylpentan-3-yl benzoate *anti*-25b

By the same general method, benzoyl chloride (238 µdm^3, 2.054 mmol) and the alcohol *anti*-**21b** (207 mg, 0.685 mmol) gave a crude product which was purified on silica gel, eluting with EtOAc:hexane (4:1), to give the *benzoate anti*-**25b** (247 mg, 89%) as a colourless oil, R_f 0.5 (Found: M$^+$ 406.1712. $C_{25}H_{27}O_3P_1$ requires *M*, 406.1698); ν_{max}($CHCl_3$)/cm^{-1} 1712 (C=O); δ_H (400 MHz; $CDCl_3$) 8.07–7.2 (15H, m, Ph_2PO and Ph), 4.97 (1H, app q, *J* 6.0, CHO), 2.53 (1H, ddd, *J* 1.9, J_{PH} 11.1 and *J* 14.8, PCH_AH$_B$), 2.33 (1H, m, CHCH$_3$), 2.18 (1H, ddd, *J* 10.7, J_{PH} 12.2 and *J* 14.9, PCH$_A$$H_B$), 1.63 (2H, quintet, *J* 7.1, CH_2CH_3), 1.11 (3H, d, *J* 6.7, CHCH_3), 0.81 (3H, t, *J* 7.4, CH_2CH_3); δ_C (100 MHz; $CDCl_3$) 166.1$^-$ (CO), 132.8–127.9 (Ph_2P and Ph), 79.7$^+$ (d, J_{PC} 13.4, CO), 32.2$^-$ (d, J_{PC} 72, PC), 31.2$^+$ (d, J_{PC} 3, PCCH), 24.03$^-$ (CH_2CH_3), 17.7$^+$ (CHCH_3), 9.3$^+$ (CH_2CH_3); *m/z* 407 (10%, MH$^+$), 315 (40), 301 (60, M − PhCO), 284 (30, M − PhCO$_2$H), 243 (90, M − $C_{10}H_{11}O_2$), 215 (60, Ph_2POCH_2), 201 (100, Ph_2PO), 105 (100, PhCO).

(1*R**,2*R**)-1-Diphenylphosphinoyl-2-methylhexan-3-yl benzoate *anti*-25c

By the same general method, benzoyl chloride (365 µdm^3, 3.148 mmol) and the alcohol (332 mg, 1.049 mmol) gave a crude product which was purified on silica gel, eluting with EtOAc:hexane (4:1), to give the *benzoate anti*-**25c** (358 mg, 81%) as a colourless oil, R_f 0.5 (Found: M$^+$ 420.1817. $C_{26}H_{29}O_3P$ requires *M*, 420.1854); ν_{max}($CHCl_3$)/cm^{-1} 1716 (C=O); δ_H (400 MHz, $CDCl_3$) 8.0–7.37 (15H, m, Ph_2P and Ph), 5.05 (1H, dt, *J* 4.5, 8.7, CHO), 2.52 (1H, ddd, *J* 1.7, J_{PH} 10.9 and *J* 14.7, PCH_AH$_B$), 2.30 (1H, m, CHCH$_3$), 2.15 (1H, ddd, *J* 10.6, J_{PH} 12.1 and *J* 14.7, PCH$_A$$H_B$), 1.60 (2H, m, CH_2-CH_2CH_3), 1.22 (2H, m, $CH_2CH_2CH_3$), 1.11 (3H, d, *J* 6.7, CHCH_3), 0.84 (t, *J* 7.4, 3H, CH_2CH_3); δ_C (100 MHz; $CDCl_3$) 166.2$^-$ (CO), 134.4–128.1 (Ph_2P and Ph), 78.5$^+$ (d, J_{PC} 13.1, CHO), 33.5$^-$ ($CH_2CH_2CH_3$), 31.9$^+$ (d, J_{PC} 2.9, PCH_2CH), 31.8$^-$ (d, J_{PC} 72.1, PC), 18.6$^-$ (CH_2CH_3), 17.9$^+$ (CHCH_3), 14.0$^+$ (CH_2CH_3); *m/z* 421 (20%, MH$^+$), 329 (40, M − 91), 315 (50, M − PhCO), 298 (60, M − PhCO$_2$H), 243 (95,

M − $C_{11}H_{13}O_2$), 216 (75, Ph_2POCH_3), 202 (75, Ph_2POH), 105 (100, PhCO), 77 (65, Ph).

(1*S*,2*S*)-3-Diphenylphosphinoyl-2-methyl-1-phenylpropan-1-yl benzoate *syn*-25g

By the same general method, (1*S*,2*S*)-3-diphenylphosphinoyl-2-methyl-1-phenylpropan-1-ol[10b] *syn*-**21g** (61 mg, 0.17 mmol) gave a crude product after 2 days. Flash chromatography, eluting with 2:1 EtOAc–hexane, gave the *benzoate syn*-**25g** (50 mg, 63%) as prisms, mp 198–201 °C (from EtOAc–hexane); R_f 0.70 (EtOAc); $[a]_D^{20}$ +32.0 (*c* 0.37 in $CHCl_3$; 86% ee) (Found: C, 76.6; H, 6.90; P, 6.6; M^+, 454.1704. $C_{29}H_{27}O_3P$ requires C, 76.6; H, 6.80; P, 6.8%; *M*, 454.1698); ν_{max}/cm^{-1} ($CHCl_3$) 1718 (C=O), 1423 (P − Ph); δ_H (200 MHz; $CDCl_3$) 8.06 (2H, dd, *J* 0.8 and 7.9, *ortho*-PhCO), 7.7–7.2 (18H, m, Ph_2PO and remaining Ph), 5.86 (1H, d, *J* 6.1, C*H*OBz), 2.63 (1H, m, C*H*Me), 2.46 (1H, ddd, *J* 2.3, 10.0 and $^2J_{HH}$ 14.8, PCH_AH_B), 2.14 (1H, ddd, *J* 10.3, 13.2 and $^2J_{HH}$ 14.8, PCH_AH_B), 1.23 (3H, d, *J* 6.3, Me); δ_C (50 MHz; $CDCl_3$) 165.4^- (C=O), 138.5^- (*ipso*-Ph), 133–126 (m, Ph_2PO and Ph × 2), 80.1^+ (d, $^3J_{PC}$ 15.0, C*H*OBz), 34.1^+ (*C*HMe), 32.6^- (d, $^1J_{PC}$ 71.5, PCH_2), 16.7^+ (Me); *m*/*z* 454.2 (10%, M^+), 349.1 (100, M − PhCO), 105 (95, PhCO).

(1*S*,2*R*)-3-Diphenylphosphinoyl-2-methyl-1-phenylpropan-1-yl benzoate *anti*-25g

By the same general method, (1*S*,2*R*)-3-diphenylphosphinoyl-2-methyl-1-phenylpropan-1-ol[10b] *anti*-**21g** (135 mg, 0.39 mmol) gave a crude product after 3 days. Flash chromatography, eluting with 2:1 EtOAc–hexane, gave the *benzoate anti*-**25g** (158 mg, 91%) as needles, mp 191–193 °C (from EtOAc–hexane); R_f 0.66 (EtOAc); $[a]_D^{20}$ +2.1 (*c* 0.55 in $CHCl_3$; 86% ee) (Found: M^+, 454.1495. $C_{29}H_{27}O_3P$ requires *M*, 454.1698); ν_{max}/cm^{-1} ($CHCl_3$) 1718 (C=O), 1438 (P–Ph); δ_H (400 MHz; $CDCl_3$) 8.03 (2H, dd, *J* 3.3 and 8.0, *ortho*-PhCO), 7.7–7.2 (18H, m, Ph_2PO and remaining Ph × 2), 5.85 (1H, d, *J* 6.4, C*H*OBz), 2.63 (1H, ddd, *J* 1.1, 10.2 and $^2J_{HH}$ 14.8, PCH_AH_B), 2.57 (1H, m, C*H*Me), 2.19 (1H, ddd, *J* 10.8, 13.2 and $^2J_{HH}$ 14.9, PCH_AH_B), 1.22 (3H, d, *J* 6.8, Me); δ_C (100 MHz; $CDCl_3$) 165.7^- (C=O), 138.7^- (*ipso*-Ph), 134–126 (m, Ph_2PO and Ph × 2), 80.6^+ (d, $^3J_{PC}$ 14.4, C*H*OBz), 34.4^+ (*C*HMe), 31.4^- (d, $^1J_{PC}$ 71.4, PCH_2), 18.3^+ (Me); *m*/*z* 454.2 (5%, M^+), 349.1 (M − PhCO), 105 (90, PhCO).

(2*S*,3*R*)-1-Diphenylphosphinoyl-2-methylheptan-3-yl benzoate *syn*-25f

By the same general method, (2*S*,3*R*)-1-diphenylphosphinoyl-2-methylheptan-3-ol[10b] *syn*-**21f** (332 mg, 0.95 mmol) gave a crude product after 4 days. Flash chromatography, eluting with 2:1 EtOAc–hexane, gave the *benzoate syn*-**25f** (371 mg, 85%) an oil, R_f 0.43 (EtOAc); $[a]_D^{20}$ +1.1 (*c* 1.76 in $CHCl_3$; 76% ee) (Found: M^+, 434.2011. $C_{27}H_{31}O_3P$ requires *M*, 434.2011); ν_{max}/cm^{-1} ($CHCl_3$) 1710 (C=O), 1422 (P–Ph); δ_H (200 MHz; $CDCl_3$) 8.02 (2H, dd, *J* 0.9 and 8.5, *ortho*-PhCO), 7.8–7.3 (13H, m, Ph_2PO and remaining Ph), 5.04 (1H, td, *J* 4.3 and 8.6, C*H*OBz), 2.48 (1H, ddd, *J* 2.3, 9.9 and $^2J_{HH}$ 14.8, PCH_AH_B), 2.35 (1H, m, C*H*Me), 2.14 (1H, ddd, *J* 10.2, 13.1 and $^2J_{HH}$ 14.8, PCH_AH_B), 1.8–1.3 (6H, m), 1.18 (3H, d, *J* 6.9, Me), 0.83 (3H, t, *J* 6.8, Me); δ_C (50 MHz; $CDCl_3$) 165.8^- (C=O), 155.8^- (*ipso*-Ph), 135–128 (m, Ph_2PO and Ph), 78.2^+ (d, $^3J_{PC}$ 12.4, C*H*OBz), 32.7^- (d, $^1J_{PC}$ 71.0, PCH_2), 34.4^+ (*C*HMe), 30.0^-, 27.7^-, 22.2^-, 15.8^+ (Me), 13.7^+ (Me); *m*/*z* 434.2 (1%, M^+), 329.1 (100, M − PhCO), 201.0 (80, Ph_2PO), 105 (100, PhCO).

(2*R*,3*R*)-1-Diphenylphosphinoyl-2-methylheptan-3-yl benzoate *anti*-25f

By the same general method, (2*R*,3*R*)-1-diphenylphosphinoyl-2-methylheptan-3-ol[10b] *anti*-**21f** (623 mg, 1.78 mmol) gave a crude product after 4 days. Flash chromatography, eluting with 2:1 EtOAc–hexane, gave the *benzoate anti*-**25f** (701 mg, 86%) an oil, R_f 0.43 (EtOAc); $[a]_D^{20}$ +0.35 (*c* 0.50 in $CHCl_3$) (Found: MH^+, 435.2104. $C_{27}H_{31}PO_3$ requires *MH*, 435.2086); ν_{max}/cm^{-1} ($CHCl_3$) 1709 (C=O), 1421 (P–Ph); δ_H (400 MHz; $CDCl_3$) 7.98 (2H, dd, *J* 1.4 and 8.5, *ortho*-PhCO), 7.8–7.4 (13H, m, Ph_2PO and remaining Ph), 5.03 (1H, td, *J* 5.0 and 10.1, C*H*OBz), 2.51 (1H, ddd, *J* 1.4, 10.4 and $^2J_{HH}$ 14.7, PCH_AH_B), 2.31 (1H, m, C*H*Me), 2.14 (1H, ddd, *J* 10.8, 12.2 and $^2J_{HH}$ 14.8, PCH_AH_B), 1.8–1.6 (4H, m), 1.3–1.2 (2H, m), 1.13 (3H, d, *J* 6.7, Me), 0.82 (3H, t, *J* 7.1, Me); δ_C (100 MHz; $CDCl_3$) 166.1^- (C=O), 156.0^+ (Ph), 133–128 (m, Ph_2PO and Ph), 78.1^+ (d, $^3J_{PC}$ 16.7, C*H*OBz), 32.8^- (d, $^1J_{PC}$ 70.0, PCH_2), 31.7^+ (d, $^2J_{PC}$ 5.0, *C*HMe), 31.1^-, 27.3^-, 22.5^-, 17.9^+ (Me), 13.8^+ (Me); *m*/*z* 435.2 (100%, MH^+), 215 (100, Ph_2POCH_2), 201.0 (90, Ph_2PO).

(1*R**,6*R**,8*R**,9*R**)-9-Diphenylphosphinoyl-8-phenyl-8-trimethylsilyloxybicyclo[4.3.0]-7-oxanonane 27d

n-Butyl lithium (0.74 cm^3, 1.137 mmol, 1.53 mol dm^{-3} solution in hexanes) was added to a stirred solution of diisopropylamine (0.159 cm^3, 1.137 mmol) in dry THF (5 cm^3) at 0 °C, stirred for 10 min and cooled to −78 °C. Chlorotrimethylsilane (0.385 cm^3, 3.03 mmol) was added to a stirred solution of the benzoate *anti*-**25d** (0.317 g, 0.758 mmol) in dry THF (15 cm^3) at 0 °C. The reaction mixture was cooled to −78 °C and the precooled LDA was added *via* a cannula. The reaction mixture was stirred at −78 °C for 5 min and quenched with water. The residues were poured into water (30 cm^3) and extracted with dichloromethane (3 × 20 cm^3). The combined organic extracts were dried ($MgSO_4$) and evaporated *in vacuo* to give a crude product which was purified by column chromatography on silica gel, eluting with EtOAc:hexane (2:1)→EtOAc, to give the *silyl ether* (324 mg, 87%), mp 164–166 °C; R_f 0.6 (Found: M^+ 490.2105. $C_{29}H_{35}O_3PSi$ requires *M*, 490.2093); ν_{max} (Nujol)/cm^{-1} 3085, 1385 (C=C); δ_H (250 MHz, $CDCl_3$) 7.78–7.09 (15H, m, Ph_2P and Ph), 4.39 (1H, dt, *J* 10.5, 4.1, CHO), 3.32 (1H, dd, J_{PH} 2.3 and *J* 9.1, PCH), 2.24–0.9 (9H, m, C_6H_9), −0.11 (9H, s, $SiMe_3$); δ_C ($CDCl_3$) 146.9^- (*ipso C*), 137.5–125.3 (Ph_2P and remaining Ph), 107.6^- (d, J_{PC} 6.2, COO), 81.6^+ (CO), 54.5^+ (d, J_{PC} 72.44, PCH), 48.7^+ (d, J_{PC} 2.87, PCH*C*H), 31.4^- (CH_2), 27.2^- (d, J_{PC} 4.93, CH_2), 26.1^- (CH_2), 23.4^- (CH_2), 1.1^+ ($SiMe_3$); *m*/*z* 490 (50%, M^+), 475 (25, M − Me), 296 (100, M − $C_{10}H_{14}O_2Si$), 202 (60, Ph_2POH), 198 (50).

Single crystals of **27d** were crystals grown by slow evaporation from EtOAc–hexane as colourless rods.

Crystal structure determination of 27d. Molecular formula $C_{29}H_{35}O_3PSi$ (M_r = 490.63), orthorhombic, *a* = 11.761(2), *b* = 19.813(3), *c* = 23.024(3) Å, *α* = 90, *β* = 90, *γ* = 90, *V* = 5365.1(14) $Å^3$, *T* = 295 K, space group *Pbca* (#61), *Z* = 8, *μ*(Mo-K*α*) = 0.175 mm^{-1}, 4705 reflections collected, 4705 unique (merging with *R* = 0.0000) and 2219 retained in all calculations.[40,41] Refinement converged at R_1 = 0.056 (on *F*). CCDC reference number 207/373.

(1*R**,6*R**,9*R**,10*R**)-10-Diphenylphosphinoyl-9-phenyl-9-trimethylsilyloxybicyclo[5.3.0]-8-oxadecane 27e

By the same general method, the benzoate *anti*-**25e** (0.268 g, 0.62 mmol) gave a crude product which was purified by column chromatography on silica gel, eluting with EtOAc:hexane (3:1), to give the *silyl ether* **27c** (258 mg, 83%); R_f 0.6 (Found: M^+ 504.2250. $C_{30}H_{37}O_3PSi$ requires *M*, 504.2249); ν_{max} ($CHCl_3$)/cm^{-1} 3085, 1385(C=C); δ_H (400 MHz; $CDCl_3$) 7.69–7.04 (10H, m, Ph_2P and Ph), 4.56 (1H, dt, *J* 10.0, 3.2, CHO), 3.44 (1H, dd, J_{PH} 4.0 and *J* 9.7, PCH), 2.43 (1H, m, PCHC*H*), 2.3–1.18 (10H, m, C_7H_{10}), −0.09 (9H, s, $SiMe_3$); δ_C ($CDCl_3$) 146.9^- (*ipso C* on COO*Ph*), 138.4–125.7 (Ph_2P and remaining Ph), 107.7^- (d, J_{PC} 5.2, COO), 83.9^+ (CHO), 56.6^+ (d, J_{PC} 72.0,

PCH), 51.0^{+} (d, J_{PC} 2.4, PCH*C*H), 32.3^{-} (CH_2), 27.5^{-} (d, J_{PC} 6.2, CH_2), 26.6^{-} (CH_2), 26.3^{-} (CH_2), 22.8^{-} (CH_2), 1.4^{-} ($SiMe_3$); *m/z* 504 (20%, M^{+}), 489 (30, M − Me), 310 (100, M − $C_{10}H_{14}O_2Si$), 202 (85, Ph_2PO).

(2*R,3*R**,4*R**,5*R**)-3-Diphenylphosphinoyl-4,5-dimethyl-2-phenyl-2-trimethylsilyloxytetrahydrofuran 27a**

By the same general method, the benzoate *anti*-**25a** (0.188 g, 0.652 mmol) gave a crude product which was purified by column chromatography on silica gel, eluting with EtOAc : hexane (3 : 1), to give the *silyl ether* **27a** (147 mg, 68%); R_f 0.5 (EtOAc : hexane; 1 : 1) (Found: M^{+} 464.1924. $C_{27}H_{33}O_3PSi$ requires *M*, 464.1936); ν_{max} ($CHCl_3$)/cm^{-1} 3016, 3011, 2971; δ_H (200 MHz, $CDCl_3$) 7.74–7.06 (15H, m, Ph_2P and Ph), 4.49 (1H, dq, *J* 6.0, 9.6, CH_3CHO), 3.35 (1H, dd, *J* 9.6 and J_{PH} 3.9, PCH), 2.43 (1H, ddq, *J* 9.9, 7.1, 4.4, PCHC*H*), 1.36 (3H, d, *J* 6.05, CH_3-CHO), 0.92 (d, *J* 7.1, 3H, CH_3CH), −0.7 (9H, s, $SiMe_3$); δ_C (50 MHz; $CDCl_3$) 146.5 (*ipso C* on COO*Ph*), 138.1–125.5 (Ph_2P and remaining Ph), 107.5 (COO), 80.6^{+} (CHO), 55.6^{+} (d, J_{PC} 73.0, PCH), 45.0^{+} ($CHOCH_3$), 18.0^{+} (*C*HCH$_3$), 13.6^{+} (d, J_{PC} 6.04, CH*C*H$_3$), 1.2^{+} ($SiMe_3$); *m/z* 464 (1%, M^{+}), 449 (30, M − Me), 315 (40), 270 (60, M − $C_{10}H_{14}O_2Si$), 255 (30), 226 (20), 202 (100, Ph_2POH).

Single crystals of **27a** were crystals grown by slow evaporation from EtOAc–hexane as colourless rods.

Crystal structure determination of 27d. Molecular formula $C_{27}H_{33}O_3PSi$ (M_r = 464.59), monoclinic, a = 18.753(4), b = 8.349(2), c = 18.019(4) Å, α = 90, β = 111.75(3), γ = 90°, V = 2620.4(10) Å^3, T = 295 K, space group $P2_1/c$ (#61), Z = 4, μ(Mo-Kα) = 0.175 mm^{-1}, 4747 reflections collected, 4599 unique (merging with R = 0.0274) and 2948 retained in all calcluations.[40,41] Refinement converged at R_1 = 0.045 (on *F*). CCDC reference number 207/373.

(2*R,3*R**,4*R**,5*R**)-3-Diphenylphosphinoyl-5-ethyl-4-methyl-2-phenyl-2-trimethylsilyloxytetrahydrofuran 27b**

By the same general method, the benzoate *anti*-**25b** (56 mg, 0.138 mmol) gave a crude mixture which was purified by column chromatography on silica gel, eluting with EtOAc : hexane (1 : 1), to give the *silyl ether* **27b** (42 mg, 64%; 94 : 6 ratio of diastereoisomers) as a colourless oil, R_f 0.45 (EtOAc : hexane, 1 : 1) (Found: M^{+} 478.2089. $C_{28}H_{35}O_3PSi$ requires *M*, 478.2093); δ_H (200 MHz, $CDCl_3$) 7.8–6.95 (15H, m, Ph_2P and Ph), 4.33 (1H, dt, *J* 3.05, 9.0, CHO), 3.34 (1H, dd, J_{PH} 4.2 and *J* 9.6, PCH), 2.42 (1H, m, C*H*CH$_3$), 1.80 (1H, ddq, *J* 3.1, 7.4, 21.2, CH_AH$_B$CH$_3$), 1.55 (1H, dq, *J* 7.2, 21.2, CH$_A$*H*$_B$CH$_3$), 1.1 (3H, t, *J* 7.4, CH_2CH_3), 0.94 (3H, d, *J* 7.1, CHCH_3), −0.06 (s, 9H, $SiMe_3$); *m/z* 478 (0.5%, M^{+}), 463 (5, M − Me), 315 (8), 284 (12, M − $C_{10}H_{14}O_2Si$), 202 (40, Ph_2POH), 121 (100, PhCOO).

(2*R,3*R**,4*R**,5*R**)-3-Diphenylphosphinoyl-4-methyl-2-phenyl-5-propyl-2-trimethylsilyloxytetrahydrofuran 27c**

By the same general method, the benzoate *anti*-**25c** (140 mg, 0.333 mmol) gave a crude product which was purified by column chromatography on silica gel, eluting with EtOAc : hexane (1 : 1) to give the *silyl ether* **27c** (106 mg, 65%) as a colourless oil, R_f 0.4 (EtOAc : hexane, 1 : 1) (Found: M^{+} 492.2280. $C_{29}H_{37}O_3PSi$ requires *M*, 492.2250); ν_{max} ($CHCl_3$)/cm^{-1} 3060, 2964, 1486, 1459; δ_H (200 MHz, $CDCl_3$) 7.73–6.73 (m, 15H, Ph_2P and Ph), 4.37 (1H, m, CHO), 3.34 (1H, dd, J_{PH} 4.2 and *J* 9.5, PCH), 2.43 (1H, m, PCHC*H*), 1.64 (4H, m, $CH_2CH_2CH_3$), 1.01 (3H, d, *J* 2.6, CHCH_3), 0.96 (3H, t, *J* 6.9, CH_2CH_3), −0.07 (s, 9H, $SiMe_3$); δ_C ($CDCl_3$) 146.7 (*ipso C* on COO*Ph*), 138.2–125.5 (Ph_2P and remaining C on Ph), 107.6 (d, J_{PC} 4.6, COO), 84.5 (CO), 55.4 (d, J_{PC} 72.8, PCH), 43.1 (PCH*C*H), 35.6 (CH*C*H$_2$), 19.7 (*C*H$_2$CH$_3$), 14.4 (CH$_2$*C*H$_3$), 14.1 (d, J_{PC} 6.2, CH*C*H$_3$), 1.3 ($SiMe_3$); *m/z* 493 (1%, MH^{+}), 492 (1, M^{+}), 477 (22, M − Me), 449 (5, M − C_3H_7), 415 (10, M − Ph), 359 (35), 298 (38, M − $C_{10}H_{14}O_2Si$), 201 (100, Ph_2PO).

(2*R*,3*R*,5*R*)-5-Butyl-3–diphenylphosphinoyl-2-phenyl-2-trimethylsilyloxytetrahydrofuran 29a

A stock solution of LDA was prepared by the dropwise addition of *n*-butyllithium (1.5 cm^3 of a 1.7 mol dm^{-3} solution in hexanes) to a stirred solution of diisopropylamine (252 mg, 2.5 mmol) in dry THF (10.7 cm^3) at 0 °C. LDA (*ca.* 0.2 M solution in THF, generally 1.85 mmol) was added dropwise to a solution of (*R*)-1-diphenylphosphinoylheptan-3-yl benzoate **26a** (550 mg, 1.25 mmol) and chlorotrimethylsilane (540 mg, 5.0 mmol) in dry THF (8 cm^3) at −78 °C until the starting material was completely consumed. The reaction was quenched with water (10 cm^3), the aqueous suspension extracted with dichloromethane (4 × 10 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give a crude product which was purified by flash chromatography, eluting with 3 : 2 EtOAc–hexane, to give the *silylated hemiacetal* **29a** (352 mg, 55%) as an oil, R_f 0.66 (EtOAc); $[\alpha]_D^{20}$ +9.3 (*c* 0.48 in $CHCl_3$; 76% ee) (Found: M^{+}, 492.2215. $C_{29}H_{38}O_3PSi$ requires *M*, 492.2249); ν_{max}/cm^{-1} ($CHCl_3$) 1438 (P–Ph), 1176 (P=O); δ_H (400 MHz; $CDCl_3$) 7.8–7.1 (15H, m, Ph_2PO and Ph), 4.62 (1H, tt, *J* 5.5 and 8.2, BuC*H*), 3.38 (1H, td, *J* 4.2 and 10.5, PCH), 2.53 (1H, dddd, *J* 4.4, 5.5, 12.6 and 16.0, PCHCH_AH$_B$), 1.95 (1H, m, PCHCH$_A$*H*$_B$), 1.7–1.3 (6H, m), 0.94 (3H, t, *J* 6.5, Me), −0.08 (9H, s, $SiMe_3$); δ_C (100 MHz; $CDCl_3$) 145.9^{-} (*ipso*-Ph), 136–126 (m, Ph_2PO and remaining Ph), 107.9^{-} (COSi), 79.3^{+} (d, $^3J_{PC}$ 3.6, *C*HBu), 56.3^{+} (d, $^1J_{PC}$ 73, PCH), 34.9^{-}, 34.1^{-}, 28.4^{-}, 22.8^{-}, 14.0^{+} (Me), 1.2^{+} ($SiMe_3$); *m/z* 492.2 (40%, M^{+}), 202.1 (100, Ph_2POH), 201.1 (95, Ph_2PO). The relative stereochemistry was confirmed by a 500 MHz NOESY experiment.

In a separate experiment, (*R*)-1-diphenylphosphinoylheptan-3-yl benzoate **26a** (38 mg, 90 μmol), chlorotrimethylsilane (39 mg, 0.36 mmol) and LDA (0.12 mmol) gave the *silylated hemiacetal* **29a** (10 mg, 25%) and recovered starting material (19 mg, 50%).

(2*R*,3*R*,5*S*)-2,5-Diphenyl-3-diphenylphosphinoyl-2-trimethylsilyloxytetrahydrofuran 29b

By the same general method, (*S*)-3-diphenylphosphinoyl-1-phenylpropan-1-yl benzoate **26b** (50 mg, 0.11 mmol) gave a crude product which was purified by flash chromatography to yield the *silylated hemiacetal* **29b** (51 mg, 88%) as an oil, R_f 0.71 (EtOAc); $[\alpha]_D^{20}$ +23.1 (*c* 0.20 in $CHCl_3$; 86% ee) (Found: M^{+}, 512.1952. $C_{31}H_{33}O_3PSi$ requires *M,* 512.1936); ν_{max}/cm^{-1} ($CHCl_3$) 1438 (P–Ph), 1176 (P=O); δ_H (400 MHz; $CDCl_3$) 7.9–7.1 (20H, m, Ph_2PO and 2 × Ph), 5.72 (1H, dd, *J* 5.5 and 9.9, PhC*H*), 3.42 (1H, td, *J* 3.4 and 10.9, PCH), 2.86 (1H, dddd, *J* 3.1, 5.5, 12.7 and 16.3, PCHCH_AH$_B$), 2.33 (1H, ddt, *J* 10.4, 12.6 and 20.6, PCHCH$_A$*H*$_B$) and −0.05 (9H, s, $SiMe_3$); δ_C (100 MHz; $CDCl_3$) 145.7^{-}, 140.7^{-} (*ipso*-Ph × 2), 136–125 (m, Ph_2PO and remaining Ph × 2), 108.1^{-} (COSi), 80.1^{+} (*C*HPh), 52.9^{+} (d, $^1J_{PC}$ 72, PCH), 36.6^{-}, 1.2^{+} ($SiMe_3$); *m/z* 512.2 (10%, M^{+}), 201.1 (100, Ph_2PO).

(2*R*,3*R*,4*R*,5*R*)-5-Butyl-3-diphenylphosphinoyl-4-methyl-2-phenyl-2-trimethylsilyloxytetrahydrofuran 27f

By the same general method, *anti*-**25f** (505 mg, 1.16 mmol) gave a crude product which was purified by flash chromatography, eluting with 3 : 2 hexane–EtOAc, to give the *silylated hemiacetal* **27f** (441 mg, 75%; 95 : 5 ratio of diastereomers) as an oil, R_f 0.73 (EtOAc); $[\alpha]_D^{20}$ +19.3 (*c* 1.08 in $CHCl_3$; 76% ee) (Found: M^{+} − Me, 491.2162. $C_{30}H_{39}O_3PSi$ requires *M* − *Me*, 491.2172); ν_{max}/cm^{-1} ($CHCl_3$) 1423 (P–Ph), 1219 (P=O); δ_H (400 MHz; $CDCl_3$) 7.8–6.9 (15H, m, Ph_2PO and Ph), 4.35 (1H, dt, *J* 2.6 and 9.0, C*H*Bu), 3.36 (1H, dd, *J* 4.2 and 9.6, PCH), 2.41 (1H, m, C*H*Me), 1.9–1.3 (6H, m), 0.95 (6H, m, Me × 2), −0.08 (9H,

s, $SiMe_3$); δ_C (100 MHz; $CDCl_3$) 146.6$^-$ (*ipso*-Ph), 137–125 (m, Ph_2PO and remaining Ph), 107.6$^-$ (d, $^2J_{PC}$ 4.6, COSi), 84.7$^+$ (*C*HBu), 55.4$^+$ (d, $^1J_{PC}$ 72.1, PCH), 47.0 (d, $^2J_{PC}$ 8.4, *C*HMe), 33.1$^-$, 28.5$^-$, 23.0$^-$, 14.1$^+$ (d, $^3J_{PC}$ 6.7, Me), 14.0$^+$ (Me), 1.3$^+$ ($SiMe_3$); *m*/*z* 491.2 (10%, M$^+$ − Me) 359 (100), 201.1 (100, Ph_2PO).

(2*R*,3*R*,4*S*,5*R*)-5-Butyl-3-diphenylphosphinoyl-4-methyl-2-phenyl-2-trimethylsilyloxytetrahydrofuran 28f

By the same general method, *syn*-**25f** (288 mg, 0.66 mmol) gave a crude product which was purified by flash chromatography, eluting with 1:1 hexane–EtOAc, to give the *silylated hemiacetal* **28f** (216 mg, 64%; <98:2 ratio of diastereomers) as an oil, R_f 0.72 (EtOAc); $[\alpha]_D^{20}$ +14.2 (*c* 1.06 in $CHCl_3$; 76% ee) (Found: M$^+$, 506.2380. $C_{30}H_{40}O_3PSi$ requires *M*, 506.2406); ν_{max}/cm^{-1} ($CHCl_3$) 1552 (Ph), 1423 (P–Ph), 1225 (P=O); δ_H (400 MHz; $CDCl_3$) 7.8–7.0 (15H, m, Ph_2PO and Ph), 4.64 (1H, td, *J* 4.6 and 9.1, C*H*Bu), 2.92 (1H, dd, *J* 2.8 and 4.2, PCH), 2.85 (1H, m, C*H*Me), 1.8–1.3 (6H, m), 0.92 (3H, d, *J* 7.0, Me), 0.90 (3H, t, *J* 7.2, Me), −0.12 (9H, s, $SiMe_3$); δ_C (100 MHz; $CDCl_3$) 146.1$^-$ (*ipso*-Ph), 137–125 (m, Ph_2PO and remaining Ph), 107.1$^-$ (d, $^2J_{PC}$ 4.6, COSi), 81.2$^+$ (*C*HBu), 61.0$^+$ (d, $^1J_{PC}$ 71.4, PCH), 39.1$^+$ (*C*HMe), 29.9$^-$, 28.9$^-$, 23.0$^-$, 16.1$^+$ (d, $^3J_{PC}$ 9.3, Me), 14.0$^+$ (Me), 1.2$^+$ ($SiMe_3$); *m*/*z* 506.2 (10%, M$^+$), 201.1 (100, Ph_2PO).

TLC analysis showed that another compound appeared on work-up: also obtained were the *hemiacetals* **30f** (63 mg, 20%, 87:13 ratio of diastereomers) as an oil. On standing, the hemiacetals decomposed slowly to the *vinyl phosphine oxide* **31f**, R_f 0.25 (1:1 hexane–EtOAc); δ_H (400 MHz; $CDCl_3$) 7.8–7.0 (m, Ph_2PO and Ph), 4.63 (1H, dt, *J* 5.2 and 8.2, BuC*H*^{vin}), 4.46 (1H, td, *J* 5.3 and 7.7, BuC*H*$^{major\ hemiacetal}$), 3.63 (1H, td, *J* 3.4 and 8.9, BuC*H*$^{minor\ hemiacetal}$), 2.9–0.8 (m); δ_C (100 MHz; $CDCl_3$) 166.9$^-$ (d, $^2J_{PC}$ 18.7, PC=*C*^{vin}), 143.0$^-$ (*ipso*-Ph^{hemiacetal}), 135–125 (m, Ph_2PO and remaining Ph), 106.5$^-$ (d, $^1J_{PC}$ 118, PC^{vin}), 104.6$^-$ (d, $^2J_{PC}$ 1.4, COH^{hemiacetal}), 86.4$^+$ (d, $^3J_{PC}$ 9.9, *C*HBu$^{vin/hemiacetal}$), 79.6$^+$ (d, $^3J_{PC}$ 4.0, *C*HBu$^{hemiacetal/vin}$), 57.7$^+$ (d, $^1J_{PC}$ 67.9, PCH^{hemiacetal}), 44.0$^+$ (*C*HMe), 37.9$^+$ (*C*HMe), 34–22$^-$ (m, CH_2), 17–14$^+$ (m, Me).

(2*R*,3*R*,4*R*,5*S*)-2,5-Diphenyl-3-diphenylphosphinoyl-4-methyl-2-trimethylsilyloxytetrahydrofuran 27g

By the same general method, *anti*-**25g** (36 mg, 79 μmol) gave a crude product which was purified by flash chromatography, eluting with 2:1 hexane–EtOAc, to give the *silylated hemiacetal* **27g** (9 mg, 22%; 91:9 ratio of diastereomers) as an oil, R_f 0.63 (2:1 EtOAc–EtOAc); δ_H (400 MHz; $CDCl_3$) 7.8–7.1 (20H, m, Ph_2PO and 2 × Ph), 5.31 (1H, d, *J* 10.3, PhC*H*), 3.53 (1H, dd, *J* 3.6 and 9.2, PCH), 2.73 (1H, qddd, *J* 7.1, 9.2, 9.9 and 24.3, C*H*Me), 0.88 (3H, d, *J* 7.2, Me), −0.06 (9H, s, $SiMe_3$).

In a separate experiment, the *silylated hemiacetal* **27g** decomposed on workup: a 32:68 mixture of the silyl ether **27g** and the *vinyl phosphine oxide* **31g**, R_f 0.62 (EtOAc); $[\alpha]_D^{20}$ +25.3 (*c* 0.60 in $CHCl_3$; 76% ee) (Found: M$^+$, 408.1754. $C_{26}H_{27}O_2P$ requires *M*, 408.1748); ν_{max}/cm^{-1} ($CHCl_3$) 1617 (C=C), 1438 (P–Ph), 1169 (P=O); δ_H (400 MHz; $CDCl_3$) 7.7–7.0 (15H, m, Ph_2PO and Ph), 4.73 (quin, *J* 7.4, BuC*H*), 2.88 (1H, ddd, *J* 2.5, $^2J_{HH}$ 9.9 and $^3J_{PH}$ 14.7, PCCH_AH_B), 2.50 (1H, ddd, *J* 2.3, $^2J_{HH}$ 9.9 and $^3J_{PH}$ 14.7, PCCH_AH_B), 1.8–1.1 (6H, m) and 0.90 (3H, t, *J* 7.0, Me); δ_C (100 MHz; $CDCl_3$) 166.5$^-$ (d, $^2J_{PC}$ 18, PC=*C*), 134–127 (m, Ph_2PO and Ph), 97.8$^-$ (d, $^1J_{PC}$ 120, PC), 82.2$^+$ (d, $^3J_{PC}$ 10.0, BuC*H*), 40.3$^-$ (d, $^2J_{PC}$ 9.2, $PCCH_2$), 35.6$^-$, 27.7$^-$, 22.5$^-$, 14.0$^+$ (Me); *m*/*z* 408.1 (100%, M$^+$), 345.1 (65, M − Bu), 201.1 (60, Ph_2PO) were isolated.

(2*R*,3*R*,4*S*,5*S*)-2,5-Diphenyl-3-diphenylphosphinoyl-4-methyl-2-trimethylsilyloxytetrahydrofuran 28g

By the same general method, *syn*-**25g** (42 mg, 93 μmol) gave a crude product which was purified by flash chromatography, eluting with 1:1 hexane–EtOAc, to give the *silylated hemiacetal* **28g** (7.4 mg, 16%; >96:4 ratio of diastereomers) as an oil, R_f 0.70 (EtOAc); $[\alpha]_D^{20}$ +19.3 (*c* 1.08 in $CHCl_3$; 86% ee) (Found: M$^+$ − Me, 511.1846. $C_{32}H_{35}O_3PSi$ requires *M* − *Me*, 511.1859); ν_{max}/cm^{-1} ($CHCl_3$) 1422 (P–Ph), 1233 (P=O); δ_H (400 MHz; $CDCl_3$) 7.9–7.0 (20H, m, Ph_2PO and Ph), 5.83 (1H, d, *J* 5.2, PhC*H*), 3.07 (1H, dd, *J* 1.9 and 3.9, PCH), 3.05 (1H, m, MeC*H*), 0.63 (3H, d, *J* 7.2, Me), −0.09 (9H, s, $SiMe_3$); δ_C (100 MHz; $CDCl_3$) 146.0$^-$, 138.3$^-$ (*ipso*-Ph × 2), 134–125 (m, Ph_2PO and remaining Ph), 107.1$^-$ (COSi), 82.2$^+$ (*C*HPh), 60.9$^+$ (d, $^1J_{PC}$ 70.8, PCH), 41.1$^+$ (*C*HMe), 17.4$^+$ (d, $^3J_{PC}$ 9.5, Me), 1.2$^+$ ($SiMe_3$); *m*/*z* 511.2 (15%, M$^+$ − Me), 201.1 (80, Ph_2PO). The relative stereochemistry was determined by a 500 MHz NOESY experiment.

Also obtained was the *hemiacetal* **30g** (22 mg, 52%) as an oil which decomposed on standing to the *vinyl phosphine oxide* **31g** (Found: M$^{+(vin)}$, 436.1494. $C_{29}H_{25}O_2P$ requires *M*, 436.1493); R_f 0.33 (EtOAc); $[\alpha]_D^{20}$ +16.7 (*c* 0.46 in $CHCl_3$); ν_{max}/cm^{-1} ($CHCl_3$) 3491 (OH), 1416 (P–Ph), 1198 (P=O); δ_H (400 MHz; $CDCl_3$) 7.8–7.1 (20H, m, Ph_2PO and Ph × 2), 6.90 (1H, s, OH), 5.83 (1H, d, *J* 6.3, PhC*H*), 3.06 (1H, ddqd, *J* 4.3, 6.3, 7.1 and $^3J_{PH}$ 16.4, C*H*Me), 2.90 (1H, t, *J* 4.3, PCH), 0.46 (3H, d, *J* 7.1, Me); δ_C (100 MHz; $CDCl_3$) 142.8$^-$, 138.1$^-$ (*ipso*-Ph × 2), 132–126 (m, Ph_2PO and remaining Ph), 104.9$^-$ (COH), 80.9$^+$ (*C*HPh), 57.3$^+$ (d, $^1J_{PC}$ 67.6, PCH), 39.5$^+$ (*C*HMe), 18.4$^+$ (d, $^3J_{PC}$ 5.5, Me); *m*/*z* 436.2 (10%, M$^{+(vin)}$), 201.1 (90, Ph_2PO), 105.0 (100, PhCO), 77 (90, Ph). The relative stereochemistry was determined by a 500 MHz NOESY experiment.

Treatment of silylated hemiacetal 29a with dihydroaluminium chloride

Lithium aluminium hydride (9.4 mg, 0.24 mmol) and aluminium trichloride (9.4 mg, 70 μmol) were stirred in ether (2 cm^3) at 0 °C for 5 min. The reaction mixture was warmed to room temperature and a solution of the silylated hemiacetal **29a** (32 mg, 64 μmol) in ether (2 cm^3) was added dropwise. The reaction was stirred for 2 h, quenched with water (3 cm^3), extracted with dichloromethane (3 × 3 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give a crude product. Flash chromatography, eluting with 2:1 EtOAc-–hexane, gave the *tetrahydrofurans* **43** (22 mg, 69%; 58:42 mixture) as an oil, R_f 0.62 (EtOAc); $[\alpha]_D^{20}$ +10.8 (*c* 2.10 in $CHCl_3$; 76% ee) (Found: M$^+$, 404.1915. $C_{26}H_{29}O_2P$ requires *M*, 404.1905); ν_{max}/cm^{-1} ($CHCl_3$) 1438 (P–Ph), 1177 (P=O); δ_H (400 MHz; $CDCl_3$) 7.8–6.8 (15H, m, Ph_2PO and Ph), 5.32 (1H, dd, *J* 6.8 and 11.9, PhC*H*^{major}), 5.08 (1H, dd, *J* 7.7 and 12.7, PhC*H*^{minor}), 4.61 (1H, m, BuC*H*^{major}), 4.13 (1H, m, BuC*H*^{minor}), 3.51 (1H, dq, *J* 4.0 and 8.1, PCH^{major}), 3.02 (1H, tt, *J* 5.1 and 6.8, PCH^{minor}), 2.70 (1H, m, major), 2.52 (1H, m, minor), 2.1–1.3 (7H, m), 0.85 (3H, m, Me$^{major\ +\ minor}$); δ_C (100 MHz; $CDCl_3$) 141.3$^-$ (*ipso*-Ph^{minor}), 137.8$^-$ (d, *J* 4.4, *ipso*-Ph^{major}), 135–126 (m, Ph_2PO and remaining Ph), 81.8$^+$ (PhCH^{major}), 80.3$^+$ (PhCH^{minor}), 79.9$^+$ (d, $^3J_{PC}$ 4.0, BuC*H*^{minor}), 79.3$^+$ (d, $^3J_{PC}$ 7.5, BuC*H*^{major}), 45.1$^+$ (d, $^1J_{PC}$ 72.7, PCH^{minor}), 43.2$^+$ (d, $^1J_{PC}$ 74.5, PCH^{major}), 35.9$^-$ (major), 34.9$^-$ (minor), 34.1$^-$ (minor), 32.6$^-$ (major), 28.2$^-$ (major + minor), 22.8$^-$ (minor), 22.7$^-$ (major), 14.1$^+$ (Me^{major}), 14.0$^+$ (Me^{minor}); *m*/*z* 404.2 (2.7%, M$^+$), 201.1 (100, Ph_2POH).

Treatment of silylated hemiacetal with methylmagnesium bromide

Methylmagnesium bromide (0.11 cm^3 of a 3.0 mol dm^{-3} solution, 0.36 mmol) was added dropwise to a stirred solution of silylated hemiacetal **29a** (33 mg, 67 μmol) in dry toluene (5 cm^3). The reaction was heated at 80 °C for 2 days, quenched with water, extracted with dichloromethane (3 × 5 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give a crude product. Flash chromatography, eluting with 2:1 EtOAc–hexane, gave the tetrahydrofuran **44** (12 mg, 38%, >95:5 ratio

of diastereomers) as an oil, R_f 0.50 (EtOAc); $[a]_D^{20}$ +26.5 (*c* 1.10 in $CHCl_3$; 76% ee) (Found: M^+, 402.1747. $C_{27}H_{31}O_2P$ requires *M*, 402.1748); ν_{max}/cm^{-1} ($CHCl_3$) 1438 (P–Ph), 1182 (P=O); δ_H (400 MHz; $CDCl_3$) 7.7–7.0 (15H, m, Ph_2PO and Ph), 4.54 (1H, quin, *J* 6.9, BuC*H*), 3.22 (1H, q, *J* 7.5, PCH), 2.48 (1H, m, $PCHCH_AH_B$), 1.93 (1H, m, $PCHCH_AH_B$), 1.74 (3H, s, Me), 1.7–1.2 (6H, m), 0.90 (3H, t, *J* 7.2, Me); δ_C (100 MHz; $CDCl_3$) 143.1$^-$ (*ipso*-Ph), 134–127 (m, Ph_2PO and remaining Ph), 86.1$^-$ (MePhC), 78.8$^+$ (d, $^3J_{PC}$ 9.5, BuC*H*), 49.0$^+$ (d, $^1J_{PC}$ 73.8, PCH), 37.1$^-$, 33.9$^-$, 31.6$^+$ (Me), 28.1$^-$, 22.8$^-$, 14.1$^+$ (Me); *m*/*z* 402.1 (100%, M^+), 201.1 (90, Ph_2PO).

Deprotection of (1*R**,6*R**,8*R**,9*R**)-9-Diphenylphosphinoyl-8-phenyl-8-trimethylsilyloxybicyclo[4.3.0]-7-oxanonane 27d

The silyl ether **27d** (25.8 mg, 0.053 mmol) was dissolved in dry methanol (5 cm^3) to which $HCl_{(aq)}$ (4 cm^3, 2 mol dm^{-3}) was added. The mixture was stirred for 1 h, quenched with sodium bicarbonate and extracted with CH_2Cl_2 (3 × 10 cm^3). The combined organics were dried ($MgSO_4$) and evaporated *in vacuo*. The residues were purified by column chromatography on silica gel eluting with EtOAc : hexane (6 : 1) to give the hydroxy ketone **42** (20 mg, 78%) as a colourless oil, R_f 0.2 (Found: M^+ 418.1699. $C_{26}H_{27}O_3P$ requires *M*, 418.1698); ν_{max} ($CHCl_3$)/cm^{-1} 3504 (OH), 1665 (C=O); δ_H (250 MHz, $CDCl_3$) 8.05–7.26 (15H, m, Ph_2P and Ph), 5.13 (1H, dd, *J* 4.7 and J_{PH} 14.9, PCH), 3.36 (1H, broad dt, C*H*OH), 2.33–0.84 (9H, m, C_6H_9); *m*/*z* 418 (2%, M^+), 400 (20, M − H_2O), 371 (15), 320 (15, M − $C_6H_{10}O$), 313 (10, M − PhCO), 296 (10, M − $PhCO_2H$), 219 (55), 200 (60, $C_{14}H_{10}O$), 157 (60), 105 (100, PhCO).

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