Supplementary Material

Asymmetric synthesis of cyclopropanes and dihydrofurans based on phosphine oxide chemistry

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Experimental

For reactions conducted under anhydrous conditions glassware was dried overnight in an oven at 130 °C and was allowed to cool in a dessicator over anhydrous KOH. Anhydrous reactions were carried out under argon. Solvents were BOC standard reagent grade and distilled before use. Reagents/solvents for anhydrous reactions were dried as follows: THF was distilled from sodium wire with benzophenone as indicator. Dichloromethane, hexane, acetonitrile, toluene, pyridine, *N*,*N*-dimethylformamide, triethylamine, dimethylsulfoxide and diisopropylamine were dried and stored over 4 Å molecular sieves. Methanol was dried and stored over 3 Å molecular sieves. *n*-Butyllithium was titrated against diphenylacetic acid before use.[1] Sulfate buffer was prepared by dissolving 1.5 mol of Na_2SO_4 in 0.5 mol H_2SO_4 and adding water to give a final volume of 2000 cm^3. Thin layer chromatography (TLC) was carried out on commercially available pre-coated glass plates (Merck $60F_{254}$). The quoted R_f values are rounded to the nearest 0.05. Dry Column Vacuum Chromatography (DCVC) was performed according to the published procedure.[2] A larger diameter column than that recommended was generally necessary with phosphine oxides due to their tendency to streak on the columns. ^1H, ^{13}C, APT, DEPT, HMQC and COSY NMR spectra were recorded on Bruker Avance 400 (5 mm QNP probe) and Bruker Avance 500 (5 mm dual ^{13}C-^1H cryo probe) Fourier transform spectrometers using an internal deuterium lock. ^{31}P NMR spectra were recorded on a Bruker Avance 400 (5 mm QNP probe) Fourier transform spectrometer using 85% H_3PO_4 as external standard. Solvents were used as internal standard when assigning NMR spectra (δ_H: $CDCl_3$ 7.26 ppm, DMSO-d_6 2.50; δ_C: $CDCl_3$ 77.0 ppm, DMSO-d_6 39.4 ppm). Mestre-C 4.5.6 software,[3] was used for assigning spectra. *J* values are given in Hz and rounded to the nearest 0.5 Hz. LC-MS was run on a Waters Alliance LC/MS system consisting of a Waters 2795 Separations Module, a Waters 2996 Photodiode Array Detector and a Waters Micromass ZQ on a C18 analytical Reverse Phase Supercosil™ ABZ+PLUS column (3.3 cm × 4.6mm, 3μm) using the

following gradient: 0.00-0.70 min 100% solvent A, 0.70-4.20 min 100% solvent A to 100% solvent B, 4.20-7.70 min 100% solvent B, 7.70-8.00 min 100% solvent B to 100% solvent A (solvent A: 10 mM ammonium acetate in water containing 0.1% formic acid; solvent B: 95% acetonitrile in water) with a flow rate of 1 cm^3/min. EI and LSIMS mass spectra were recorded on a Kratos concept 1H double focusing magnetic sector instrument using a MACH 3 data system. +ESI mass spectra were recorded using a Bruker Bio-Apex II FT-ICR instrument or a Micromass Q-Tof 1 machine. Microanalyses were carried out on a CE440 Elemental Analyser from Exeter Analytical, INC. The calculated values were adjusted for residual solvents. Melting points were measured on a microscope hot stage melting point apparatus (C. Reichert Optische Werke AG) and are uncorrected. Infra-red spectra were recorded using a Perkin Elmer Spectrum One (FT-IR) spectrometer with a universal ATR sampling accessory. Optical rotations were recorded on a Perkin Elmer 241 polarimeter using to the sodium D line (589 nm) at 23 ^oC and are given in units of 10^{-1} deg dm^2 g^{-1}. X-ray Crystallographic Data was measured on a Nonius Kappa CCD diffractometer at 180(2) K. Analytical chiral HPLC was carried out on a Daicel Chiralpak AD column (0.46 cm × 25 cm) and guard column with a Spectra-Physics SP8800 pump, a Spectra-Physics SP8450 UV detection system and a ChromJet single channel integrator with a flow rate of 1 cm^3/min.

Method 1: Asymmetric dihydroxylation (AD)

By a method analogous to that reported by Sharpless,[4] the substrate (1 mmol) is heated (if necessary) in *t*-BuOH (10 cm^3) to give a clear solution (Not all substrates were completely soluble). Water (10 cm^3) is added and the mixture cooled to 0 ^oC (Higher temperatures were employed in some cases to increase the solubility of the substrate). A mixture of $K_2OsO_4 \cdot 2\ H_2O$ (1 mol%), $K_3Fe(CN)_6$ (3 eq.), K_2CO_3 (3 eq.), $MeSO_2NH_2$ (1 eq.) and $(DHQD)_2PHAL$ (2 mol%) is added to the cooled solution and it is stirred vigorously until completion of the reaction. Sodium sulfite (10 eq.) was added and the reaction allowed to warm to room temperature with vigorous stirring. The slurry is transferred to a separatory funnel with water (20 cm^3) and extracted with ethyl acetate (3 × 20 cm^3) (Dichloromethane can be used for more polar compounds but tends to give emulsions with Method 1, unless large volumes of dichloromethane are used). The combined organic extracts are washed with aqueous sulfate buffer (20 cm^3), saturated aqueous $NaHCO_3$ (20 cm^3), dried (Na_2SO_4), filtered and evaporated under reduced pressure and the residue purified by column chromatography.

Method 2: Asymmetric dihydroxylation (AD)

As above with an alternative work-up procedure that avoids the formation of emulsions. Sodium sulfite (10 eq.) is added and the reaction allowed to warm to room temperature with vigorous stirring. The slurry is transferred to a separatory funnel and the phases are separated. The organic phase is concentrated *in vacuo* and the residue dissolved in dichloromethane (20 cm^3) and transferred to a separatory funnel with the aqueous phase and water (10 cm^3) and extracted with dichloromethane (2 × 20 cm^3). The combined organic extracts are washed with aqueous sulfate buffer (20 cm^3), saturated aqueous $NaHCO_3$ (20 cm^3), dried (Na_2SO_4), filtered and evaporated under reduced pressure. The residue is purified by column chromatography.

Method 3: Racemic dihydroxylation (RD)

According to the procedure by Warren[5,6] racemic dihydroxylations were performed at room temperature and $(DHQD)_2PHAL$ was replaced with quinuclidine (5 mol%). Worked up was as described in general procedure 1, unless otherwise stated.

Method 4: Synthesis of cyclic carbonates

1,1'-Carbonyldiimidazole (1.5 eq.) is added to a stirred solution of the diol (1 mmol) in dichloromethane (30 cm^3) at room temperature under argon. The reaction mixture is stirred until completion. Water (40 cm^3) is added and the mixture transferred to a separatory funnel with brine (20 cm^3) and extracted with dichloromethane (3 × 20 cm^3). The combined organic phases are dried (Na_2SO_4), filtered and the solvent removed *in vacuo* to give the crude product that is purified by column chromatography.

Method 5: Opening of cyclic carbonates with sodium azide

By the method of Sharpless[7] the cyclic carbonate (1 mmol) is dissolved in anhydrous DMF (10 cm^3). NaN_3 (1.1 eq.) and water (1 eq.) is added and the reaction mixture heated to 110 ^oC with stirring under argon for 48 hours. When the reaction mixture has cooled to room temperature it is transferred to a separatory funnel with water (20 cm^3) and extracted with ethyl acetate (3 × 20 cm^3). The combined organic phases are dried (Na_2SO_4), filtered and concentrated *in vacuo*. Residual DMF is removed on a high vacuum pump and the residue purified by column chromatography.

Method 6: Synthesis of cyclic sulfites

Thionyl chloride (1.5 eq.) is added to a stirred solution of the diol (1 mmol) and pyridine (4 eq.) in dichloromethane (5 cm^3) at room temperature under argon. When the reaction has gone to completion saturated aqueous NH_4Cl (5 cm^3) is added and the mixture transferred to a separatory funnel with water (5 cm^3) and extracted with dichloromethane (3 × 10 cm^3). The combined organic phases are washed with 3 M aqueous HCl (10 cm^3) [Aqueous sulfate buffer (10 cm^3) was used for acid sensitive compounds], dried (Na_2SO_4), filtered and the solvent removed *in vacuo* to give the crude product that is purified by column chromatography.

Method 7: Cyclopropanation

The substrate (1 mmol) is dissolved in anhydrous THF (10 cm^3) and cooled to −78 ^oC with stirring under argon. Freshly prepared LDA (1.05 eq.) cooled to −78 ^oC is added by cannula. After stirring at −78 ^oC for 1-2 hours the reaction mixture is allowed to slowly warm to room temperature overnight. The reaction is quenched with saturated aqueous NH_4Cl (20 cm^3), extracted with ethyl acetate (3 × 20 cm^3), dried (Na_2SO_4), filtered and concentrated *in vacuo* to give the crude product, which is purified by column chromatography.

Method 8: Synthesis of Mosher's amides

Mosher's amide derivatives using racemic Mosher's acid (α-methoxy-α-trifluoromethyl-phenylacetic acid) and (R)-(+)-Mosher's acid were prepared and analysed using ^1H and ^{19}F NMR.

Moshers acid (2.14 mmol) is dissolved in anhydrous dichloromethane (10 cm^3) and cooled to 0 ^oC. Oxalyl chloride (21.4 mmol) is added followed by 1 drop of DMF. After stirring for 1 hour the reaction mixture is concentrated *in vacuo* and the residue suspended in hexane (2 × 25 cm^3) and concentrated *in vacuo* [^{19}F NMR (400 MHz; $CDCl_3$) δ −70.2]. The product was dissolved in anhydrous dichloromethane (10 cm^3) to give a 0.21 M solution of Mosher's acid chloride.

The amine (0.2 mmol) is dissolved in dichloromethane (5 cm^3) and Mosher's acid chloride (0.3 mmol, 1.4 cm^3, 0.21 M in dichloromethane) is added followed by saturated aqueous sodium carbonate (5 cm^3). After stirring overnight the phases are separated and the organic phase dried (Na_2SO_4), filtered and concentrated *in vacuo* to give crude Mosher's amide that is analysed by NMR without further purification.

(4*R*,5*R*)-4-[2'-(Diphenylphosphinoyl)-ethyl]-5-phenyl-[1,3]-dioxolane-2-one 14

By method **4** diol[8] **13** (0.50 g, 1.4 mmol), after 2½ hours, gave a clear gum. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 70-100% EtOAc in hexanes (v/v) – 10% increments; 2.5-40% MeOH in EtOAc (v/v) – 2.5% increments] to give *cyclic carbonate* **14** (0.48 g, 87%) as a white amorphous solid. e.e. >90% (determined by chiral HPLC); HPLC [R_T (min), flow rate 1 cm^3/min, 15% EtOH in *iso*-hexane (v/v)]: 64.3; $[\alpha]_D^{23}$ +40 (c. 1, $CHCl_3$); R_f 0.50 (5% MeOH in EtOAc, v/v); *m/z* (+EI) found: M^+, 392.1160. ($C_{23}H_{21}O_4P$ requires *M*, 392.1177); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1800 (C=O), 1438 (P-Ph) and 1182 (P=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.78-7.68 (4H, m, Ph), 7.59-7.39 (9H, m, Ph), 7.31-7.27 (2H, m, Ph), 5.15 (1H, d, *J* 7.5, C*H*Ph), 4.54 (1H, ddd, *J* 9.0, 7.5 and 3.0, CH_2CH), 2.62-2.52 (1H, m), 2.37-2.21 (2H, m) and 2.08-1.96 (1H, m) (2 × CH_2); ^{31}P NMR (162 MHz; $CDCl_3$) δ 31.7; ^{13}C NMR (100 MHz; $CDCl_3$) δ 153.8 (C2), 134.9 (*ipso*-Ph), 132.4 (d, *J* 100.5, *ipso*-PhP), 132.2 (d, *J* 3.0, *para*-PhP), 132.1 (d, *J* 3.0, *para*-PhP), 131.6 (d, *J* 100.0, *ipso*-PhP), 130.8 (d, *J* 9.5, *ortho*-PhP), 130.5 (d, *J* 9.5, *ortho*-PhP), 129.8, 129.2 (Ph), 128.9 (d, *J* 11.5, *meta*-PhP), 128.8 (d, *J* 11.5, *meta*-PhP), 126.0 (*para*-Ph), 84.0 (d, *J* 14.0, C4), 83.0 (C5), 25.7 (d, *J* 16.0, C2') and 25.3 (d, *J* 53.0, C1'); (Found: C, 69.47; H, 5.55. $C_{23}H_{21}O_4P \cdot 0.25$ H_2O requires C, 69.60; H, 5.46%).

(4*RS*,5*RS*)-4-[(2'-Diphenylphosphinoyl)-ethyl]-5-phenyl-[1,3]-dioxolane-2-one (±)-14

By method **4** diol **(±)-13** (39 mg, 0.11 mmol), after 1½ hours, gave a yellow gum. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 70-100% EtOAc in hexanes (v/v) – 10% increments; 2.5-30% MeOH in EtOAc (v/v) – 2.5% increments] to give *cyclic carbonate* **(±)-14** (41 mg, 95%) as a white amorphous solid. HPLC [R_T (min), flow rate 1 cm^3/min, 15% EtOH in *iso*-hexane (v/v)]: 62.6 and 70.3; All analytical data were identical with that for (4*R*,5*R*)-**14** reported above.

(1*S*,2*R*)-1-Azido-4-diphenylphosphinoyl-1-phenyl-butan-2-ol 15

By method **5** carbonate **14** (0.20 g, 0.74 mmol) gave a clear gum. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 50-100% EtOAc in hexanes (v/v) – 10% increments; 2.5-35% MeOH in EtOAc (v/v) – 2.5% increments] to give *azide* **15** (0.18 g, 87%) as white needles. $[\alpha]_D^{23}$ +66 (c. 0.9, $CHCl_3$); mp 112-115 °C (from MeOH, EtOAc); R_f 0.30 (EtOAc); *m/z* (+ESI) found: MNa^+, 414.1342. ($C_{22}H_{22}N_3O_2PNa$ requires *M*, 414.1347); IR $\nu_{max}(CH_2Cl_2)/cm^{-1}$

3277 (br., O-H), 2096 (N_3), 1438 (P-Ph) and 1173 (P=O); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.74-7.67 (4H, m, Ph), 7.53-7.43 (6H, m, Ph), 7.36-7.29 (5H, m, Ph), 4.53 (1H, d, *J* 6.0, PhC*H*), 4.44 (1H, d, *J* 4.5, OH), 3.94-3.90 (1H, m, C*H*OH), 2.44-2.39 (2H, m, PCH_2), 1.96 (1H, ddtd, *J* 17.0, 14.5, 7.5 and 3.0, $PCH_2CH_aH_b$), 1.78-1.68 (1H, m, $PCH_2CH_aH_b$); ^{31}P NMR (162 MHz; $CDCl_3$) δ 35.7; ^{13}C NMR (126 MHz; $CDCl_3$) δ 136.7 (*ipso*-PhC), 132.2 (d, *J* 99.5, *ipso*-PhP), 132.0 (d, *J* 99.5, *ipso*-PhP), 131.9 (×2) (Ph), 130.9 (d, *J* 9.5, *ortho*-PhP), 130.7 (d, *J* 9.5, *ortho*-PhP), 128.8 (d, *J* 2.0, *para*-PhP), 128.7 (×2) (d, *J* 11.5, *meta*-PhP and d, *J* 11.5, *meta*-PhP), 128.7 (×2) (d, *J* 2.0, *para*-PhP and Ph), 128.3, 127.6 (Ph), 74.3 (d, *J* 7.5, C2), 69.9 (C1), 26.5 (d, *J* 71.0, C4), 25.0 (d, *J* 4.0, C3); (Found: C, 67.42; H, 5.69. $C_{22}H_{22}N_3O_2P$ requires C, 67.51; H, 5.67%).

(1*S*,2*R*)-1-Azido-2-benzoyloxy-4-diphenylphosphinoyl-1-phenyl-butane 5

Phosphine oxide **15** (0.47 g, 1.2 mmol) was dissolved in anhydrous dichloromethane (20 cm^3) and triethylamine (0.34 cm^3, 2.4 mmol), DMAP (73 mg, 0.6 mmol) and benzoyl chloride (0.28 cm^3, 2.4 mmol) were added. After 19 hours the reaction mixture was transferred to a separatory funnel with aqueous sulfate buffer (50 cm^3) and extracted with dichloromethane (3 × 25 cm^3). The combined organic phases were dried (Na_2SO_4), filtered and concentrated *in vacuo* to give a yellow gum. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 5-100% EtOAc in hexanes (v/v) – 5% increments; two fractions of each solvent mixture were collected] gave *phosphine oxide* **5** (0.44 g, 73%) as white needles. $[\alpha]_D^{23}$ –2.9 (c. 1.1, $CHCl_3$); mp 157-159 °C (from EtOAc, hexanes); R_f 0.40 (80% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 518.1632. ($C_{29}H_{26}N_3O_3PNa$ requires *M*, 518.1610); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 2104 (N_3), 1719 (C=O), 1438 (P-Ph) and 1184 (P=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.96 (2H, br d, *J* 8.0, *ortho*-PhC=O), 7.67-7.60 (4H, m), 7.55-7.35 (9H, m, Ph), 7.31-7.22 (5H, m, Ph), 5.38 (1H, ddd, *J* 8.5, 4.5 and 4.0, C*H*CHPh), 4.86 (1H, d, *J* 5.0, C*H*Ph) and 2.39-2.02 (4H, m, CH_2CH_2); ^{31}P NMR (162 MHz; $CDCl_3$) δ 33.0; ^{13}C NMR (100 MHz; $CDCl_3$) δ 165.6 (C=O), 135.1 (*ipso*-PhCH), 133.3 (*para*-PhC=O), 132.2 (d, *J* 99.5, *ipso*-PhP), 132.1 (d, *J* 99.5, *ipso*-PhP), 131.7 (d, *J* 3.0, *para*-PhP), 131.6 (d, *J* 3.0, *para*-PhP), 130.6 (d, *J* 9.5, *ortho*-PhP), 130.5 (d, *J* 9.5, *ortho*-PhP), 129.6 (Ph), 129.2 (*ipso*-PhC=O), 128.6 (×2), 128.5 (×2), 128.4 (×2) (Ph), 127.1 (*para*-PhCH), 76.5 (d, *J* 15.0, C2), 67.5 (C1), 25.7 (d, *J* 72.0, C4) and 21.8 (d, *J* 2.5, C3); (Found: C, 69.81; H, 5.28; N, 8.11. $C_{29}H_{26}N_3O_3P{\cdot}0.30\ H_2O$ requires C, 69.54; H, 5.35; N, 8.39%).

(2*RS*,4*R*,5*R*)-4,5-Dihydroxy-1,5-diphenyl-2-diphenylphosphinoyl-pentan-1-one (4*R*,5*R*)-17

By method **1** phosphine oxide[8] **16** (0.50 g, 1.15 mmol) after 10 days gave a pink residue that was purified by DCVC [id 4 cm; 20 cm^3 fractions; 50-100% EtOAc in hexanes (v/v) – 5% increments; 1-20% MeOH in EtOAc (v/v) – 1% increments] to give (4*R*,5*R*)-**17** (0.40 g, 74%) as a white amorphous solid. R_f 0.45 (EtOAc); *m/z* (+ESI) found: MNa^+, 493.1560. ($C_{29}H_{27}O_4PNa$ requires *M*, 493.1545); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 3334 (br., O-H), 1674 (C=O), 1438 (P-Ph) and 1184 (P=O); ^1H NMR (500 MHz; $CDCl_3$) Complex; ^{31}P NMR (162 MHz; $CDCl_3$) δ 32.7, 32.4, 32.0, 31.5; ^{13}C NMR (126 MHz; $CDCl_3$) Complex. δ 198.2 (d, *J* 2.0, C=O), 197.9 (d, *J* 2.5, C=O); (Found: C, 73.19; H, 5.83. $C_{29}H_{27}O_4P_1 \cdot 0.25\ H_2O$ requires C, 73.33; H, 5.84%). The data above is in agreement with that which has previously been reported for the diastereoisomers (2*RS*,4*S*,5*S*)-**17**.[9]

(2*RS*,4*R*,5*R*)- and (2*RS*,4*S*,5*S*)-4,5-Dihydroxy-1,5-diphenyl-2-diphenylphosphinoyl-pentan-1-one (±)-17

By method **3** phosphine oxide[8] **16** (0.18 g, 0.42 mmol) after 2 days gave a clear gum that was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 2.5-50% MeOH in EtOAc (v/v) – 2.5% increments] to give diol **(±)-17** (0.16 g, 80%) as a white amorphous solid. All analytical data was identical with that for (4*R*,5*R*)-**17** reported above.

(4*R*,5*R*,2'*RS*)-4-[(2'-Diphenylphosphinoyl-3'-oxo-3'-phenyl)-propyl]-5-phenyl-[1,3]-dioxolan-2-one 19

By method **4** phosphine oxide (4*R*,5*R*)-**17** (1.11 g, 2.36 mmol) after 2 hours gave a brown amorphous solid. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 50-100% EtOAc in hexanes (v/v) – 10% increments; 1-22% MeOH in EtOAc (v/v) – 1% increments] to give *cyclic carbonate* **19** (1.15 g, 98%) as an off-white amorphous powder. d.r. 69:31 (^1H NMR, epimers at C2'); e.e. >95% (determined by chiral HPLC); HPLC [R_T (min), flow rate 1 cm^3/min, 0-30 min/0-100% *iso*-propanol in *n*-hexane (v/v)] (4*R*,5*R*,2'*R*)-**19** and (4*R*,5*R*,2'*S*)-**19**: 22.3 (major) and 26.9 (minor); R_f 0.55 (EtOAc); *m/z* (+ESI) found: MH^+, 497.1497. ($C_{30}H_{26}O_5P$ requires *M*, 497.1518); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1795 (OC=O), 1672 (C=O), 1438 (PPh) and 1191 (P=O); ^1H NMR (500 MHz; $CDCl_3$) Two diastereoisomers (4*R*,5*R*,2'*R*)-**19** and (4*R*,5*R*,2'*S*)-**19** A: major, B: minor. δ 7.88-7.82 (m, Ph A,B), 7.68-7.47 (m, Ph A,B), 7.43-7.21 (m, Ph A,B), 5.15 (1H, d, *J* 7.0, C*H*Ph A), 5.09 (1H, d, *J* 7.5, C*H*Ph B), 4.98 (1H, td, *J* 11.5 and 2.0, PCH A), 4.70 (1H, ddd, *J* 17.0, 8.0 and 4.5, PCH B), 4.62 (1H, td, *J* 8.0 and 4.5, $PCHCH_2CH$ B), 4.38 (1H, ddd, *J* 13.0, 7.0 and 2.0,

PCHCH$_2$C*H* A), 3.04-2.98 (1H, m, PCHCH_aH$_b$ A), 2.83-2.75 (1H, m, PCHCH_aH$_b$ B), 2.63-2.54 (1H, m, PCHCH$_a$$H_b$ B), 2.30-2.23 (1H, m, PCHCH$_a$$H_b$ A); ^{31}P NMR (162 MHz; $CDCl_3$) δ 29.3 and 28.9; ^{13}C NMR (100 MHz; $CDCl_3$) Two diastereoisomers (4*R*,5*R*,2'*R*)-**19** and (4*R*,5*R*,2'*S*)-**19**. A: major, B: minor. δ 196.5 (d, *J* 2.5, C3' B), 196.0 (d, *J* 3.5, C3' A), 153.6 (C2 A), 153.4 (C2 B), 137.9-125.7 (m, Ph A,B), 83.2 (C5 A), 83.0 (C5 B), 82.7 (d, *J* 9.5, C4 B), 81.8 (d, *J* 12.5, C4 A), 47.6 (d, *J* 55.0, C2' B), 46.7 (d, *J* 55.5, C2' A), 31.8 (d, *J* 1.5, C1' A), 31.3 (d, *J* 1.5, C1' B); (Found: C, 71.94; H, 5.15. $C_{30}H_{25}O_5P \cdot 0.25\ H_2O$ requires C, 71.92; H, 5.13%).

(4*R*,5*R*,2'*RS*)- and (4*S*,5*S*,2'*RS*)-5-[(2'-Diphenylphosphinoyl-3'-oxo-3'-phenyl)-propyl]-4-phenyl-[1,3]-dioxolan-2-one (±)-19

By method **4** diol **(±)-17** (0.12 g, 0.25 mmol), after 2½ hours, gave a white solid. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 50-100% EtOAc in hexanes (v/v) – 10% increments; 2.5-25% MeOH in EtOAc (v/v) – 2.5% increments] to give *cyclic carbonate* **(±)-19** (0.10 g, 80%) as a white amorphous powder. HPLC [R_T (min), flow rate 1 cm^3/min, 0-30 min/0-100% *iso*-propanol in *n*-hexane (v/v)]: (4*S*,5*S*,2'*R*)-**19** and (4*S*,5*S*,2'*S*)-**19**: 19.8 and 29.9 (64:36 ratio), (4*R*,5*R*,2'*R*)-**19** and (4*R*,5*R*,2'*S*)-**19**: 22.3 and 26.7 (68:32 ratio). All analytical data was identical with that for (4*R*,5*R,*2'*RS*)-**19** reported above.

(2*S*,1'*R*)-2-[(1'-Hydroxy-1'-phenyl)-methyl]-4-diphenylphosphinoyl-5-phenyl-2,3-dihydrofuran 20

By method **5** cyclic carbonate **19** (0.20 g, 0.74 mmol) gave dihydrofuran **20** as a brown gum. The product was purified by DCVC (id 4 cm; 20 cm^3 fractions; 2 × hexanes; 50-100% EtOAc in hexanes (v/v) – 5% increments; 2.5-25% MeOH in EtOAc (v/v) – 2.5% increments) to give the *dihydrofuran* **20** (0.18 g, 89%) as a white amorphous solid. $[\alpha]_D^{23}$ –6.9 (c. 1, $CHCl_3$); mp 212-215 °C (white needles from EtOAc, MeOH, hexanes); R_f 0.55 (EtOAc); *m/z* (+ESI) found: MH$^+$, 453.1619. ($C_{29}H_{26}O_3P$ requires *M*, 453.1620); IR ν_{max}($CHCl_3$)/cm^{-1} 3250 (br., O-H), 1595 and 1492 (C=C), 1438 (P-Ph) and 1170 (P=O); ^{1}H NMR (500 MHz; DMSO-d_6) δ 7.67-7.65 (2H, m, Ph), 7.58-7.28 (15H, m, Ph), 7.24-7.20 (1H, m, Ph), 7.16-7.13 (2H, m, Ph), 5.83 (1H, d, *J* 4.5, OH), 4.95 (1H, td, *J* 9.0 and 4.5, C*H*CH$_2$), 4.79 (1H, t, *J* 4.5, C*H*OH) and 2.65 (2H, dd, *J* 9.0 and 2.5, CH$_2$); ^{31}P NMR (162 MHz; $CDCl_3$) δ 22.3; ^{13}C NMR (126 MHz; $CDCl_3$) δ 166.3 (d, *J* 18.0, C5), 139.3 (*ipso*-PhCH), 133.0 (d, *J* 108.5. *ipso*-PhP), 132.8 (d, *J* 109.0, *ipso*-PhP), 131.4 (×2) (d, *J* 10.0,

ortho-PhP and d, *J* 10.0, *ortho*-PhP), 131.3 (×2) (d, *J* 2.5, *para*-PhP and d, *J* 2.5, *para*-PhP), 129.9 (Ph), 129.4 (*ipso*-PhC=C), 128.9, 128.4 (Ph), 128.2 (×2) (d, *J* 12.0, *meta*-PhP and d, *J* 12.0, *meta*-PhP), 128.0, 127.6, 126.8 (Ph), 98.7 (d, *J* 119.5, C4), 84.6 (d, *J* 10.0, C2), 74.7 (C1') and 35.3 (d, *J* 10.0, C3); (Found: C, 76.04; H, 5.73. $C_{29}H_{25}O_3P \cdot 0.25\ H_2O$ requires C, 76.22; H, 5.62%).

(2*S*,1'*R*)-2-[(1'-Benzoyloxy-1'-phenyl)-methyl]-4-diphenylphosphinoyl-5-phenyl-2,3-dihydro furan 21

Dihydrofuran **20** (50 mg, 0.11 mmol) was dissolved in anhydrous pyridine (2 cm^3) and benzoyl chloride (20 μl, 0.17 mmol) was added. The reaction mixture was stirred at ambient temperature for 2½ hours, quenched with water (10 cm^3) and extracted with dichloromethane (3 × 10 cm^3). The combined organic phases were washed with 2 M aqueous HCl (2 × 10 cm^3) and brine (10 cm^3), dried (Na_2SO_4), filtered and concentrated *in vacuo* to give a yellow solid. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 70-100% EtOAc in hexanes (v/v) – 10% increments; 2-32% MeOH in EtOAc (v/v) – 2% increments] to give a clear gum that was recrystallised to give the *dihydrofuran* **21** (58 mg, 95%) as colourless needles. $[\alpha]_D^{23}$ + 60 (c. 1.5, $CHCl_3$); mp 221-223 °C (from EtOAc, pentane); R_f 0.50 (EtOAc); *m/z* (+EI) found: MH^+, 557.1889. ($C_{36}H_{30}O_4P$ requires *M*, 557.1882); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1722 (C=O), 1597 and 1493 (C=C), 1438 (P-Ph) and 1178 (P=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.15-8.11 (4H, m, Ph), 7.61-7.10 (19H, m, Ph), 7.06-7.02 (2H, m, Ph), 6.20 (1H, d, *J* 3.5, C*H*Ph), 5.29-5.23 (1H, m, CH_2CH), 3.12 (1H, ddd, *J* 15.0, 11.5 and 2.0, CH_aH_b) and 2.83 (1H, ddd, *J* 15.5, 7.0 and 2.5, CH_aH_b); ^{31}P NMR (162 MHz; $CDCl_3$) δ 22.9; ^{13}C NMR (100 MHz; $CDCl_3$) δ 166.7 (d, *J* 18.5, C5), 165.5 (C=O), 135.3 (*ipso*-PhCH), 133.4-127.6 (m, Ph), 97.8 (d, *J* 121.0, C4), 82.3 (d, *J* 10.0, C2), 76.6 (C1') and 35.8 (d, *J* 10.0, C3); (Found: C, 76.60; H, 5.57. $C_{36}H_{29}O_4P \cdot 0.50\ H_2O$ requires C, 76.45; H, 5.35%).

(2*S*,1'*S*)-2-[(1'-Benzoyloxy-1'-phenyl)-methyl]-4-diphenylphosphinoyl-5-phenyl-2,3-dihydro furan 23

Triethylamine (28 mg, 0.27 mmol) and benzoyl chloride (34 mg, 0.25 mmol) were added dropwise to a stirred solution of diol[8] (4*S*,5*S*)-**17** (25 mg, 53 μmol) and DMAP (11 mg, 90 μmol) in dry dichloromethane (4.5 cm^3) at room temperature. The reaction mixture was stirred for 18 hours, quenched with water (4.5 cm^3) and extracted with dichloromethane (3 × 15 cm^3). The combined

organic extracts were dried (Na_2SO_4), filtered and evaporated *in vacuo*. The residue was purified by column chromatography (SiO_2, EtOAc-hexane, 2:1, v/v) to give the *dihydrofuran* **23** (24 mg, 67%) as a colourless oil; $[\alpha]_D^{23}$ +7.7 (c. 0.9, $CHCl_3$); R_f 0.10 (66% EtOAc in hexanes, v/v) 0.12; *m/z* (+EI) found: M^+, 556.1824. ($C_{36}H_{30}O_4P$ requires *M*, 556.1803); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1723 (C=O), 1620 (PhC=C), 1596 (C=C), 1575 (C=C), 1438 (P–Ph) and 1178 (P=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.06 (2H, d, *J* 7.0, *ortho*-PhCO), 7.60-7.19 (23H, m, Ph, Ph_2PO and PhCO), 6.18 (1H, d, *J* 6.0, PhCH), 5.14 (1H, dt, *J* 10.5 and 6.0, CH_2CHO), 2.98 (1H, ddd, *J* 15.5, 11.0 and 2.5, CH_AH_B) and 2.61 (1H, ddd, *J* 15.5, 6.5 and 2.5, CH_aH_b); ^{13}C NMR (100 MHz; $CDCl_3$) δ 166.2 (d, *J* 18.0, C5), 165.5 (C=O), 136-127 (m, Ph_2PO, Ph and PhCO), 98.3 (d, *J* 120.0, C4), 81.9 (d, *J* 10.0, C2), 60.4 (C1') and 36.6 (d, *J* 10.0, C3).

(2*RS*,2'*RS*,4'*R*,5'*R*)-2-Diphenylphosphinoyl-3-(2'-oxo-5'-phenyl-[1',3',2']dioxathiolan-4'-yl)-1-phenyl-propan-1-one 24

By method **6** phosphine oxide (4*R*,5*R*)-**17** (1.0 g, 2.1 mmol) after 2 hours gave a yellow foam. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 4 × hexanes; 10-100% EtOAc in hexanes (v/v) – 10% increments; 4 × EtOAc; 5-50% MeOH in EtOAc (v/v) – 5% increments) to give *cyclic sulfites* **24** (0.52 g, 47%) as a yellow gum. R_f 0.70 (EtOAc); *m/z* (+ESI) found: MH^+, 517.1239. ($C_{29}H_{26}O_5PS$ requires *M*, 517.1245); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1675 (C=O), 1438 (P-Ph) and 1200 (S=O); ^{1}H NMR (500 MHz; $CDCl_3$) Four diastereoisomers A, B, C and D: δ 7.83-7.20 (m, Ph A,B,C,D), 5.54 (1H, d, *J* 8.0, C*H*Ph A), 5.28 (1H, d, *J* 9.5, C*H*Ph B), 5.09 (1H, ddd, *J* 13.5, 11.5 and 2.5, PCH A), 4.99-4.89 (2H, m, 2 × PCH B,C), 4.98 (1H, d, *J* 9.0, C*H*Ph C), 4.90 (1H, d, *J* 9.5, PhCH D), 4.79 (1H, m, C*H*CH_2 D), 4.68-4.62 (2H, m, PCH D and C*H*CH_2 C), 4.49 (1H, dt, *J* 9.5 and 5.0, C*H*CH_2 B), 4.34-4.30 (1H, m, C*H*CH_2 A), 3.05-2.80 (m), 2.58-2.36 (m) and 2.29-2.22 (m) (4 × PCHCH_2 A,B,C,D); ^{31}P NMR (162 MHz; $CDCl_3$) δ 30.7, 29.8, 29.7 and 29.3; ^{13}C NMR (126 MHz; $CDCl_3$) Four diastereoisomers A, B, C and D: δ 196.8 (d, *J* 2.5), 196.7 (d, *J* 2.5), 196.2 (d, *J* 3.5), 196.1 (d *J* 3.0) (4 × C1 A,B,C,D), 137.9 (×2), 137.4, 137.3 (4 × *ipso*-C=O A,B,C,D), 133.4-126.9 (m, Ph A,B,C,D), 89.9 (C5' C), 89.6 (C5' D), 87.7 (d, *J* 9.5, C4' B), 86.5 (d, *J* 12.0, C4' A), 85.4 (C5' A), 83.6 (d, *J* 11.5, C4' D), 83.2 (C5' B), 82.6 (d, *J* 12.5, C4' C), 48.3 (d, *J* 54.5, C2 D), 47.6 (d, *J* 55.5, C2 B), 47.0 (d, *J* 55.5, 2 × C2 A,C), 30.9, 30.8, 28.6 and 28.2 (4 × C3 A,B,C,D); (Found: C, 67.25; H, 4.92. $C_{29}H_{25}O_5PS$ H_2O requires C, 67.43; H, 4.88%).

(4*R*,5*S*)-5-Azido-1,5-diphenyl-4-diphenylphosphinoyloxy-pentan-1-one 7, **(2*R*,1'*S*)-2-[(1'-azido-1'-phenyl)-methyl]-4-diphenylphosphinoyl-5-phenyl-2,3-dihydrofuran 25** and **(2*S*,1'*R*)-2-[(1'-hydroxy-1'-phenyl)-methyl]-4-diphenylphosphinoyl-5-phenyl-2,3-dihydrofuran 20**

By method **5** phosphine oxide **24** (0.41 g, 0.79 mmol) gave a yellow gum. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 0-100% EtOAc in hexanes (v/v) – 10% increments; 2-8% MeOH in EtOAc (v/v) – 2% increments; two fractions of each solvent mixture were collected] gave ketone **7** (145 mg, 37%) as a clear gum, starting material **24** (53 mg, 13%) as a white solid, azide **25** (68 mg, 18%) as a clear gum and the dihydrofuran **20** (21 mg, 6%) as a clear gum. Analytical data for azide **25**: mp 176-177 °C (from EtOAc, hexanes, MeOH); R_f 0.20 (80% EtOAc in hexanes, v/v); $[\alpha]_D^{23}$ +30.2 (c. 1.3, $CHCl_3$); *m/z* (+EI) found: M^+, 477.1611. ($C_{29}H_{24}N_3O_2P$ requires *M*, 477.1606); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 2100 (N_3), 1438 (P-Ph) and 1181 (P=O); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.77-7.08 (20H, m, Ph), 5.02 (1H, ddd, *J* 11.0, 7.5 and 4.0, PhCHC*H*), 4.86 (1H, d, *J* 4.0, PhC*H*), 2.88 (1H, ddd, *J* 15.0, 11.0, 2.5, CH_aH$_b$) and 2.76 (1H, ddd, *J* 15.5, 7.5 and 2.5, CH$_a$$H_b$); ^{31}P NMR (162 MHz; $CDCl_3$) δ 22.2; ^{13}C NMR (126 MHz; $CDCl_3$) δ 166.0 (d, *J* 18.0, C5), 134.7 (*ipso*-PhCH), 133.0 (d, *J* 109.0. *ipso*-PhP), 132.4 (d, *J* 109.0, *ipso*-PhP), 131.4 (d, *J* 3.0, *para*-PhP), 131.3 (d, *J* 10.0, *ortho*-PhP), 131.3 (d, *J* 3.0, *para*-PhP), 131.2 (d, *J* 10.0, *ortho*-PhP), 130.1 (Ph), 129.1 (*ipso*-*Ph*C=C), 128.8 (×2), 128.6 (Ph), 128.3 (d, *J* 12.0, *meta*-PhP), 128.1 (d, *J* 12.5, *meta*-PhP), 127.6, 127.5, (Ph), 98.6 (d, *J* 119.5, C4), 82.9 (d, *J* 10.0, C2), 67.7 (C1') and 36.1 (d, *J* 10.0, C3); (Found: C, 73.26; H, 5.13; N, 8.81. $C_{29}H_{24}N_3O_2P$ requires C, 72.95; H, 5.07; N, 8.80%). All analytical data for ketone **7** and dihydrofuran **20** were identical to that reported elsewhere in the experimental section.

(4*R*,5*R*)-1,5-Diphenyl-4,5-dihydroxypentan-1-one 27

By method **1** ketone[10] **26** (0.25 g, 1.06 mmol) after 2 days at 5 °C gave a pink residue that was purified by DCVC [id 4 cm; 20 cm^3 fractions; 3 × hexanes; 10-100% EtOAc in hexanes (v/v) – 10% increments] to give *diol* **27** (0.27 g, 94%) as white needles. e.e. >95% (determined by chiral HPLC); HPLC [R_T (min), flow rate 1 cm^3/min, 15% EtOH in *iso*-hexane (v/v)]: 46.3; $[\alpha]_D^{23}$ −13.6 (c. 1.1, MeOH); mp 95-98 °C (from EtOAc, hexanes); R_f 0.25 (50% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 293.1154. ($C_{17}H_{18}O_3Na$ requires *M*, 293.1154); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 3410 (br., O-H) and 1681 (C=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.95-7.92 (2H, m, PhC=O), 7.58-7.53 (1H, m, PhC=O), 7.47-7.42 (2H, m, PhC=O), 7.39-7.28 (5H, m, PhCH), 4.50 (1H, dd, *J* 7.0 and 3.5,

PhC*H*OH), 3.77 (1H, ddt, *J* 9.0, 7.0 and 4.0, $CH_2C\mathit{H}OH$), 3.17 (1H, dt, *J* 18.0 and 7.0, $C\mathit{H}_aH_bC{=}O$), 3.09 (1H, dt, *J* 18.0 and 7.0, $CH_a\mathit{H}_bC{=}O$), 2.98 (1H, d, *J* 4.0, $CH_2CHO\mathit{H}$), 2.79 (1H, d, *J* 3.5, PhCHO*H*) and 1.91-1.76 (2H, m, $C\mathit{H}_2CHOH$); ^{13}C NMR (100 MHz; $CDCl_3$) δ 200.8 (C1), 140.8 (*ipso*-PhCH), 136.7 (*ipso*-PhC=O), 133.2 (*para*-PhC=O), 128.6 (×2), 128.2, 128.1, 126.9 (Ph), 78.1 (C5), 75.5 (C4), 35.0 (C2) and 26.9 (C3); (Found: C, 75.05; H, 6.72. $C_{17}H_{18}O_3$ requires C, 75.53; H, 6.71%).

(4*RS*,5*RS*)-1,5-Diphenyl-4,5-dihydroxypentan-1-one (±)-27

By method **3** ketone[10] **26** (0.10 g, 0.42 mmol) after 2 days gave a clear gum that was purified by DCVC [id 4 cm; 20 cm^3 fractions; 5 × hexanes; 10-90% EtOAc in hexanes (v/v) – 10% increments; 3 × EtOAc] to give *diol* **(±)-27** (104 mg, 90%) as a white amorphous solid. HPLC [R_T (min), flow rate 1 cm^3/min, 15% EtOH in *iso*-hexane (v/v)]: 29.6 and 45.1. All analytical data was identical with that for (4*R*,5*R*)-**27** reported above.

(4*R*,5*R*)-4-[(3'-Oxo-3'-phenyl)-propyl]-5-phenyl-[1,3]-dioxolane-2-one 28

By method **4** diol **27** (0.20 g, 0.74 mmol), after 40 minutes, gave a yellow amorphous solid. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 3 × hexanes; 10-100% EtOAc in hexanes (v/v) – 10% increments; 1-5% MeOH in EtOAc (v/v) – 1% increments] to give *cyclic carbonate* **28** (0.20 g, 92%) as white needles. $[\alpha]_D^{23}$ +38.3 (c. 1.2, $CHCl_3$); mp 89-90 °C (from EtOAc, hexanes, MeOH); R_f 0.75 (50% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 319.0934. ($C_{18}H_{16}O_4Na$ requires *M*, 319.0946); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1803 (OC=O) and 1685 (C=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.96-7.93 (2H, m, Ph), 7.59 (1H, tt, *J* 7.5 and 1.5, Ph), 7.50-7.38 (7H, m, Ph), 5.27 (1H, d, *J* 7.5, C*H*Ph), 4.66 (1H, ddd, *J* 9.5, 7.5 and 3.5, $CH_2C\mathit{H}$), 3.29 (1H, ddd, *J* 18.5, 8.0 and 5.5, $C\mathit{H}_aH_bC{=}O$), 3.18 (1H, dt, *J* 18.5 and 7.5, $CH_a\mathit{H}_bC{=}O$), 2.44-2.36 (1H, m, $C\mathit{H}_aH_bCH$) and 2.26-2.17 (1H, m, $CH_a\mathit{H}_bCH$); ^{13}C NMR (100 MHz; $CDCl_3$) δ 198.0 (C3'), 154.1 (C2), 136.3, 135.2 (*ipso*-PhCH and *ipso*- PhC=O), 133.5, 129.8, 129.2, 128.7, 128.0, 126.0 (Ph), 83.5, 83.4 (C4 and C5), 33.6 (C2') and 27.5 (C1'); (Found: C, 72.64; H, 5.43. $C_{18}H_{16}O_4$ requires C, 72.96; H, 5.44%).

(4*R*,5*S*)-5-Azido-4-hydroxy-1,5-diphenyl-pentan-1-one 29

By method **5** cyclic carbonate **28** (0.20 g, 0.74 mmol) after 48 hours gave a yellow gum. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 4 × hexanes; 5-50% EtOAc in hexanes (v/v) – 5% increments] to give *azide* **29** (92 mg, 92%) as yellow needles. $[\alpha]_D^{23}$ +4.3 (c. 1.1, $CHCl_3$); mp 102-104 °C (from EtOAc); R_f 0.70 (50% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 318.1219. ($C_{17}H_{17}N_3O_2Na$ requires *M*, 318.1218); IR $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3448 (br., O-H), 2096 (N_3), 1679 (C=O) and 1250 (C-O); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.96-7.94 (2H, m, *ortho*-PhC=O), 7.56 (1H, tt, *J* 7.5 and 1.5, *para*-PhC=O), 7.47-7.34 (7H, m, Ph), 4.57 (1H, d, *J* 6.0, PhC*H*), 3.89 (1H, ddd, *J* 9.5, 5.5 and 2.5, C*H*OH), 3.19-3.09 (2H, m, CH_2C=O), 2.45 (1H, br s, OH), 2.10-2.04 (1H, m, C$H_a$$H_b$CH) and 1.79 (1H, ddt, *J* 14.5, 10.0 and 6.5, CH_aH_bCH); ^{13}C NMR (126 MHz; $CDCl_3$) δ 200.5 (C1), 136.7, 136.1 (*ipso*-PhCH and *ipso*-PhC=O), 133.2 (*para*-PhC=O), 128.8, 128.5 (×2), 128.0, 127.9 (Ph), 73.8 (C4), 70.6 (C5), 34.9 (C2) and 26.6 (C3).

(4*R*,5*S*)-5-Azido-1,5-diphenyl-4-diphenylphosphinoyloxy-pentan-1-one 7

Azide **29** (0.25 g, 0.85 mmol) was dried by evaporation from anhydrous pyridine (2 × 10 cm^3) and dissolved in anhydrous pyridine (10 cm^3). To the stirred solution, at room temperature, diphenylphosphinoyl chloride (0.5 cm^3, 2.62 mmol) was added dropwise. After 8 hours the reaction was quenched with water (25 cm^3) and extracted with ethyl acetate (3 × 25 cm^3). The combined organic phases were washed with 3 M aqueous HCl (2 × 50 cm^3), saturated aqueous $NaHCO_3$ (50 cm^3), brine (50 cm^3), dried (Na_2SO_4), filtered and evaporated under reduced pressure to give a brown gum. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 0-100% EtOAc in hexanes (v/v) – 5% increments; 2.5-10% MeOH in EtOAc (v/v) – 2.5% increments] to give *phosphinate* **7** (0.35 g, 83%) as white needles. $[\alpha]_D^{23}$ −1.1 (c. 0.4, $CHCl_3$); mp 103-104 °C (from EtOAc); R_f 0.35 (40% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 518.1613. ($C_{29}H_{26}N_3O_3PNa$ requires *M*, 518.1610); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 2103 (N_3), 1685 (C=O) 1439 (P-Ph) and 1226 (P=O); ^{31}P NMR (162 MHz; $CDCl_3$) δ 32.8; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.86-7.74 (6H, m, Ph), 7.57-7.23 (14H, m, Ph), 4.93 (1H, d, *J* 4.0, PhC*H*), 4.77 (1H, tdd, *J* 9.5, 4.0 and 3.0, CHOP), 3.06 (1H, ddd, *J* 18.0, 9.5 and 5.0, C$H_a$$H_b$C=O), 2.91 (1H, ddd, *J* 18.0, 9.5 and 6.0, CH_aH_bC=O), 2.20-2.13 (1H, m, C$H_a$$H_b$$CH_2$C=O) and 2.02-1.94 (1H, m, C$H_a$$H_b$$CH_2$C=O); ^{13}C NMR (100 MHz; $CDCl_3$) δ 198.9 (C1), 136.6, 135.6 (2 × *ipso*-PhC), 132.9 (*para*-PhC), 132.4-130.7 (m, Ph), 128.7 (PhC), 128.7-128.5 (m, PhP), 128.4 (×2), 127.9, 127.2 (PhC), 78.7 (d, *J* 6.0, C4),

69.1 (d, *J* 3.5, C5), 34.5 (C2), 23.7 (d, *J* 3.5, C3); (Found: C, 69.95; H, 5.29; N, 8.19. $C_{29}H_{26}N_3O_3P$ requires C, 70.29; H, 5.29; N, 8.48%).

(1'*R*,2'*R*,1''*R*)-{2'-[(1''-Azido-1''-phenyl)-methyl]-cyclopropyl}-1-phenyl-methanone 8

According to method **7** phosphine oxide **5** (0.36 g, 0.73 mmol) gave a yellow gum. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 0-100% EtOAc in hexanes – 10% increments; 2.5-40% MeOH in EtOAc in hexanes (v/v) – 2.5% increments] to give the *cyclopropane* **8** (0.13 g, 65%) as white needles. e.e. >92% (determined by NMR, Mosher's amide derivative); ^{19}F NMR (400 MHz; $CDCl_3$): Derivative made from R-(+)-Mosher's acid chloride δ –68.97. Derivative made from racemic Mosher's acid chloride δ –68.87 and –68.97; $[\alpha]_D^{23}$ +5.6 (c. 1.1, $CHCl_3$); mp 89-90 °C (from EtOAc); R_f 0.45 (10% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 300.1105. ($C_{18}H_{16}O_4Na$ requires *M*, 300.1113); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 2081 (N_3) and 1659 (C=O); ^{1}H NMR (500 MHz; $CDCl_3$) δ 8.06-8.04 (2H, m, *ortho*-PhC=O), 7.60 (1H, tt, *J* 7.5 and 1.5, *para*-PhC=O), 7.52-7.49 (2H, m, Ph), 7.42-7.34 (5H, m, Ph), 4.25 (1H, d, *J* 8.0, PhC*H*), 2.89 (1H, ddd, *J* 8.5, 4.5 and 4.0, C*H*C=O), 2.13 (1H, dddd, *J* 9.0, 8.0, 6.5 and 4.0, C*H*CHN_3), 1.53 (1H, ddd, *J* 9.0, 5.0 and 4.0, CH_aH_b), 1.15 (1H, ddd, *J* 8.5, 6.5 and 4.0, CH_aH_b); ^{13}C NMR (126 MHz; $CDCl_3$) δ 198.5 (C1), 138.4, 137.5 (2 × *ipso*-Ph), 133.0, 128.9, 128.6 (×2), 128.1, 126.9 (6 × Ph), 67.8 (C1''), 29.7 (C2'), 23.5 (C1'), 15.4 (C3'); (Found: C, 72.30; H, 5.70; N 14.09. $C_{18}H_{16}O_4 \cdot 1/6\ H_2O$ requires C, 72.49; H, 5.67; N, 14.25%).

(1'*R*,2'*R*,1''*R*)-{2'-[(1''-Azido-1''-phenyl)-methyl]-cyclopropyl}-1-phenyl-methanone 8

According to method **7** ketone **7** (0.35 g, 0.71 mmol) gave a yellow gum. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 4 × hexanes; 5-50% EtOAc in hexanes – 5% increments; 60-100% EtOAc in hexanes (v/v) – 10% increments] to give the *cyclopropane* **8** (0.19 g, 95%) as white needles. e.e. >92% (determined by NMR, Mosher's amide derivative). All analytical data was in agreement with that reported above.

(4*R*,5*R*)-1-Furan-2-yl-4,5-dihydroxy-5-phenyl-pentan-1-one 31

By method **2** olefin **30**[11] (46 mg, 0.20 mmol) after 4 days at 3 °C gave a clear gum that was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 50-100% EtOAc in hexanes (v/v) – 10% increments; 5 × EtOAc] to give *diol* **31** (34 mg, 65%) as a clear film. e.e. >93% (determined by

chiral HPLC); HPLC [R_T (min), flow rate 1 cm^3/min, 10% EtOH in *iso*-hexane (v/v)]: 76.6; $[\alpha]_D^{23}$ −24.6 (c. 3.1, $CHCl_3$); R_f 0.25 (80% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 283.0938. ($C_{15}H_{16}O_4Na$ requires *M*, 283.0946); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 3415 (br., O-H), 1663 (C=O), 1467 (furan C-O) and 1023 (C-OH); ^1H NMR (500 MHz; $CDCl_3$) δ 7.55 (1H, dd, *J* 1.5 and 0.5, C5'), 7.34-7.27 (5H, m, Ph), 7.16 (1H, dd, *J* 3.5 and 0.5, C3'), 6.50 (1H, dd, *J* 3.5 and 1.5, C4'), 4.45 (1H, d, *J* 7.0, PhC*H*OH), 3.72 (1H, ddd, *J* 9.0, 7.0 and 3.5, CH_2CHOH), 3.03-2.75 (4H, m, CH_2C=O and 2 × OH) and 1.82-1.70 (2H, m, CH_2CHOH); ^{13}C NMR (126 MHz; $CDCl_3$) δ 189.7 (C1), 152.4 (C2'), 146.5 (C5'), 140.8 (*ipso*-Ph), 128.5 (Ph), 128.1 (*para*-Ph), 126.9 (Ph), 117.4 (C3'), 112.2 (C4'), 77.9 (C5), 75.3 (C4), 34.7 (C2) and 26.8 (C3); (Found: C, 67.53; H, 6.06. $C_{15}H_{16}O_4 \cdot 0.35$ EtOAc requires C, 67.58; H, 6.31%).

(4*RS*,5*RS*)-1-Furan-2-yl-4,5-dihydroxy-5-phenyl-pentan-1-one (±)-31

By method **3** ketone **30**[11] (0.20 mg, 0.88 mmol) after 4 days gave a yellow residue that was purified by DCVC [id 4 cm; 20 cm^3 fractions; 3 × hexanes; 50-100% EtOAc in hexanes (v/v) – 10% increments; 5 × EtOAc] to give *diol* **(±)-31** (0.11 g, 47%) as a yellow gum. HPLC [R_T (min), flow rate 1 cm^3/min, 10% EtOH in *iso*-hexane (v/v)]: 61.4 and 76.3; All analytical data were identical with that for (4*R*,5*R*)-**31** reported above.

(2'*RS*,4'*R*,5'*R*)-1-Furan-2''-yl-3-(2'-oxo-5'-phenyl-[1',3',2']dioxathiolan-4'-yl)-propan-1-one 32

By method **6** diol **31** (0.18 g, 0.69 mmol) after 2 hours gave a black gum. The product was purified by DCVC [id 4 cm; 25 cm^3 fractions; 0-90% EtOAc in hexanes (v/v) – 10% increments; two fractions of each solvent mixture were collected] to give *cyclic sulfite* **32** (0.20 g, 95%) as a yellow gum. d.r. 2:3 (^1H NMR, epimers at S); R_f 0.30 (30% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 329.0464. ($C_{15}H_{14}O_5SNa$ requires *M*, 329.0460); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1676 (C=O), 1469 (furan C-O) and 1206 (S=O); ^1H NMR (500 MHz; $CDCl_3$) Two diastereoisomers A (major) and B (minor): δ 7.58 (1H, dd, *J* 1.5 and 0.5, C5''-CH B), 7.57 (1H, dd, *J* 1.5 and 0.5, C5''-CH A), 7.51-7.48 (m, Ph A,B), 7.45-7.40 (m, Ph A,B), 7.20 (1H, dd, *J* 3.5 and 0.5, C3''-CH B), 7.18 (1H, dd, *J* 3.5 and 0.5, C3''-CH A), 6.53 (1H, d, *J* 3.5, C4''-CH A or B), 6.52 (1H, d, *J* 3.5, C4''-CH A or B), 5.55 (1H, d, *J* 9.0, C*H*Ph B), 5.00 (1H, d, *J* 9.5, C*H*Ph A), 7.18 (1H, td, *J* 9.5 and 3.0, C*H*CHPh A), 4.47 (1H, td, *J* 9.0 and 3.5, C*H*CHPh B), 3.18 (1H, ddd, *J* 18.0, 8.0 and 5.5, CH_aH_bC=O B), 3.14

(1H, ddd, *J* 17.5, 9.5 and 5.5, CH_aH_bC=O A), 3.04 (1H, ddd, *J* 17.5, 8.0 and 7.0, CH_aH_bC=O B), 2.95 (1H, ddd, *J* 17.5, 9.0 and 6.0, CH_aH_bC=O A), 2.33 (1H, dddd, *J* 14.0, 13,0, 6.5 and 3.5, $CH_aH_bCH_2C$=O B), 2.29-2.22 (2H, m, $CH_aH_bCH_2C$=O A and $CH_aH_bCH_2C$=O B) and 2.14 (1H, dtd, *J* 14.5, 9.0 and 5.5, $CH_aH_bCH_2C$=O A); ^{13}C NMR (126 MHz; $CDCl_3$) Two diastereoisomers A (major) and B (minor): δ 187.5 (C1 B), 187.2 (C1 A), 152.2 (×2) (2 × C2'' A,B), 146.6, 146.5 (2 × C5'' A,B), 133.7 (*ipso*-Ph B), 133.0 (*ipso*-Ph A), 129.8, 129.5, 129.1 (×2), 127.7, 127.2 (*ortho*-, *meta*- and *para*-Ph A,B), 117.4 (C3'' B), 117.3 (C3'' A), 112.3 (×2) (C4'' A,B), 89.8 (C5' A), 88.3 (C4' B), 84.4 (C5' B), 84.0 (C4' A), 34.4 (C2 A), 34.0 (C2 B), 25.9 (C3 B) and 23.8 (C3 A); (Found: C, 58.49; H, 4.85. $C_{15}H_{14}O_5S$ requires C, 58.81; H, 4.61%).

(4*R*,5*S*)-1-(Furan-2-yl)-5-azido-4-hydroxy-5-phenyl-pentan-1-one 33

By method **5** cyclic sulfite **32** (0.27 g, 0.88 mmol) after 46 hours gave a yellow gum. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 10-100% EtOAc in hexanes (v/v) – 10% increments; 5 × EtOAc] to give *azide* **33** (0.21 g, 84%) as clear yellow gum. $[\alpha]_D^{23}$ +111 (c. 1, $CHCl_3$); R_f 0.55 (50% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 308.0997. ($C_{15}H_{15}N_3O_3Na$ requires *M*, 308.1011); IR $\nu_{max}(CHCl_3)$/cm^{-1} 3456 (br., O-H), 2102 (N_3), 1668 (C=O) and 1468 (furan C-O); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.57 (1H, dd, *J* 1.5 and 0.5, C5'-H), 7.42-7.34 (5H, m, Ph), 7.19 (1H, dd, *J* 3.5 and 0.5, C3'-H), 6.52 (1H, dd, *J* 3.5 and 1.5, C4'-H), 4.56 (1H, d, *J* 6.0, PhC*H*), 3.88-3.84 (1H, m, C*H*OH), 3.06-2.95 (2H, m, CH_2C=O), 2.41 (1H, br d, *J* 4.5, OH), 2.02 (1H, dtd, *J* 14.5, 7.0 and 2.5, $CH_aH_bCH_2C$=O) and 1.76 (1H, ddt, *J* 14.5, 10.0 and 6.5, $CH_aH_bCH_2C$=O); ^{13}C NMR (126 MHz; $CDCl_3$) δ 189.5 (C1), 152.5 (C2'), 146.5 (C5'), 136.1 (*ipso*-Ph), 128.8 (*ortho*- or *meta*-Ph), 128.6 (*para*-Ph), 127.9 (*ortho*- or *meta*-Ph), 117.3 (C3'), 112.3 (C4'), 73.8 (C4), 70.5 (C5), 34.7 (C2) and 26.4 (C3); (Found: C, 62.99; H, 5.70. $C_{15}H_{15}N_3O_3$ requires C, 63.15; H, 5.30%).

(4*R*,5*S*)-1-(Furan-2'-yl)-5-azido-4-diphenylphosphinoyloxy-5-phenyl-pentan-1-one 34

Alcohol **33** (0.15 g, 0.54 mmol) was dissolved in anhydrous dichloromethane (5 cm^3) and triethylamine (0.11 g, 1,07 mmol), DMAP (13 mg, 0.11 mmol) and diphenylphosphinoyl chloride (0.13 g, 0.56 mmol) were added. After 23 hours the reaction mixture was transferred to a separatory funnel with water (20 cm^3) and extracted with ethyl acetate (3 × 25 cm^3). The combined organic phases were washed with aqueous sulfate buffer (25 cm^3), saturated aqueous $NaHCO_3$ (25 cm^3),

dried (Na_2SO_4), filtered and concentrated *in vacuo* to give a yellow gum. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 10-100% EtOAc in hexanes (v/v) – 10% increments; 5 × EtOAc] to give *phosphinate* **34** (0.23 g, 88%) as a clear gum. $[\alpha]_D^{23}$ –4.5 (c. 1, $CHCl_3$); R_f 0.45 (50% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 508.1402. ($C_{27}H_{24}N_3O_4PNa$ requires *M*, 508.1394); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 2105 (N_3), 1676 (C=O), 1469 (furan C-O), 1439 (P-Ph) and 1226 (P=O); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.84-7.75 (4H, m, *ortho*-Ph), 7.57-7.50 (2H, m, Ph), 7.49 (1H, dd, *J* 1.5 and 1.0, C5'-H), 7.48-7.41 (4H, m, Ph), 7.34-7.27 (3H, m, Ph), 7.23-7.21 (2H, m, Ph), 7.03 (1H, dd, *J* 3.5 and 0.5, C3'-H), 6.45 (1H, dd, *J* 3.5 and 1.5, C4'-H), 4.91 (1H, d, *J* 4.0, PhC*H*), 4.72 (1H, tdd, *J* 9.0, 4.0 and 3.0, PhCHC*H*), 2.91 (1H, ddd, *J* 17.5, 9.5 and 5.0, CH_aH$_b$C=O), 2.78 (1H, ddd, *J* 17.5, 9.0 and 6.5, CH$_a$$H_b$C=O), 2.16 (1H, dtd, *J* 14.5, 9.0 and 5.0, CH_aH$_b$CH$_2$C=O) and 1.97-1.90 (1H, m, CH$_a$$H_bCH_2$C=O); ^{31}P NMR (162 MHz; $CDCl_3$) δ 32.7; ^{13}C NMR (126 MHz; $CDCl_3$) δ 188.1 (C1), 152.3 (C2'), 146.1 (C5'), 135.6 (*ipso*-PhC), 132.4 (d, *J* 3.0, *para*-PhP), 132.3 (d, *J* 2.5, *para*-PhP), 131.7 (d, *J* 10.5, *ortho*-PhP), 131.6 (d, *J* 10.5, *ortho*-PhP), 131.3 (×2) (d, *J* 136.5, *ipso*-PhP and d, *J* 136.5, *ipso*-PhP), 128.7 (*ortho*-PhC), 128.6 (×2) (d, *J* 13.5, *meta*-PhP and d, *J* 13.5, *meta*-PhP), 128.4 (*para*-PhC), 127.2 (*meta*-PhC), 117.1 (C3'), 112.0 (C4'), 78.5 (d, *J* 6.5, C4), 69.0 (d, *J* 3.0, C5), 34.1 (C2) and 23.5 (C3); (Found: C, 64.90; H, 5.07. $C_{27}H_{24}N_3O_4P$·0.05 EtOAc requires C, 65.22; H, 4.90%).

(1'*R*,2'*R*,1''*R*)-{2'-[(1''-Azido-1''-phenyl)-methyl]-cyclopropyl}-1-(furan-2'''-yl)-methanone 35

By method **7** ketone **34** (0.20 g, 0.41 mmol) after 21 hours gave a yellow gum. The product was purified by DCVC [id 4 cm; 25 cm^3 fractions; 2 × hexanes; 10-70% EtOAc in hexanes – 10% increments; two fractions of each solvent mixture] to give the *cyclopropane* **35** (33 mg, 30%) as white needles. e.e. >96% (determined by NMR, Mosher's amide derivative); ^{19}F NMR (400 MHz; $CDCl_3$): Derivative made from R-(+)-Mosher's acid chloride δ –68.97. Derivative made from racemic Mosher's acid chloride δ –69.08 and –68.97; $[\alpha]_D^{23}$ +108 (c. 0.4, $CHCl_3$); mp 72-74 °C (from EtOAc, hexanes); R_f 0.45 (10% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 290.0916. $C_{15}H_{13}N_3O_2Na$ requires *M*, 290.0905); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 2086 (N_3), 1652 (C=O) and 1468 (furan C-O); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.64 (1H, dd, *J* 1.5 and 0.5, C5'''-H), 7.41-7.33 (5H, m, Ph), 7.28 (1H, dd, *J* 3.5 and 0.5, C3'''-H), 6.58 (1H, dd, *J* 3.5 and 1.5, C4'''-H), 4.22 (1H, d, *J* 7.5, PhC*H*), 2.83 (1H, br dt, *J* 8.5 and 4.5, CHC=O), 2.10 (1H, dddd, *J* 9.0, 7.5, 6.5 and 4.0,

C*H*CHN$_3$), 1.50 (1H, ddd, *J* 9.0, 5.0 and 4.5, C*H*$_a$H$_b$), 1.12 (1H, ddd, *J* 8.5, 6.5 and 4.5, CH$_a$*H*$_b$); ^{13}C NMR (126 MHz; $CDCl_3$) δ 187.0 (C1), 152.9 (C2'''), 146.6 (C5'''), 138.3 (*ipso*-Ph), 128.9 (*ortho*-Ph), 128.6 (*para*-Ph), 126.9 (*meta*-Ph), 117.1 (C3'''), 112.4 (C4'''), 67.4 (C1''), 29.3 (C2'), 23.4 (C1') and 14.8 (C3'); (Found: C, 67.42; H, 5.12. $C_{15}H_{13}N_3O_2$ requires C, 67.40; H, 4.90%).

(2*S*,1'*R*)-2-[(1'-Hydroxy-1'-phenyl)-methyl]-4-diphenylphosphinoyl-5-phenyl-2,3-dihydrofuran 20

To a solution of cyclic carbonate **19** (0.88 g, 1.77 mmol) in anhydrous dichloromethane was added DBU (0.32 g, 2.12 mmol, 0.32 cm^3). The reaction mixture was stirred under argon at room temperature overnight, transferred to a separatory funnel with 3 M aqueous HCl (20 cm^3) and extracted with dichloromethane (20 cm^3). The combined organic phases were dried (Na_2SO_4), filtered and concentrated *in vacuo* to give a yellow gum. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 50-90% EtOAc in hexanes (v/v) – 10% increments; 4 × EtOAc; 2-12% MeOH in EtOAc (v/v) – 2% increments – two fractions of each solvent mixture were collected] to give the *dihydrofuran* **20** (0.53 g, 66%) as white needles. All analytical data were identical with that reported above.

(2*S*,1'*R*)-2-[(1'-Hydroxy-1'-phenyl)-methyl]-4-diphenylphosphinoyl-5-phenyl-2,3-dihydrofuran 20

According to method **4** diol (4*R*,5*R*)-**17** (0.30 g, 0.64 mmol) after 2 hours gave cyclic carbonate **19** according to TLC. DBU (0.22 g, 1.4 mmol, 0.22 cm3) was added and the reaction mixture stirred overnight (19 hours). The reaction mixture was transferred to a separatory funnel with 3 M aqueous HCl (20 cm^3) and extracted with dichloromethane (2 × 25 cm^3). The combined organic phase were washed with saturated aqueous $NaHCO_3$ (20 cm^3), dried (Na_2SO_4), filtered and concentrated *in vacuo* to give a yellow gum. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 50-90% EtOAc in hexanes (v/v) – 10% increments; 5 × EtOAc; 2-10% MeOH in EtOAc (v/v) – 2% increments – two fractions of each solvent mixture were collected) to give the *dihydrofuran* **20** (0.18 g, 63%) as white needles. All analytical data were identical with that reported above.

(2*R*,1'*R*)-2-[(1'-Hydroxy-1'-phenyl)-methyl]-4-diphenylphosphinoyl-5-phenyl-2,3-dihydrofuran 36

To a solution of diol (4*R*,5*R*)-**17** (0.20 g, 0.43 mmol) in methanol (10 cm^3) a drop of thionyl chloride was added. After stirring for 3 hours at room temperature the reaction mixture was transferred to a separatory funnel with saturated aqueous $NaHCO_3$ (20 cm^3), brine (20 cm^3) and water (20 cm^3) and extracted with dichloromethane (2 × 25 cm^3). The combined organic phases were dried (Na_2SO_4), filtered and concentrated *in vacuo* to give a yellow gum that was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 50-90% EtOAc in hexanes (v/v) – 10% increments; 5 × EtOAc; 2-12% MeOH in EtOAc (v/v) – 2% increments – two fractions of each solvent mixture were collected] to give the *dihydrofuran* **36** (0.12 g, 63%) as a white amorphous solid. $[\alpha]_D^{23}$ −16 (c. 1.1, $CHCl_3$); mp 82-84 °C (from EtOAc, MeOH, hexanes); R_f 0.25 (EtOAc); *m/z* (+ESI) found: MNa^+, 475.1456. ($C_{29}H_{25}O_3PNa$ requires *M*, 475.1439); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 3280 (br., O-H), 1595 and 1493 (C=C), 1438 (P-Ph) and 1173 (P=O); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.59-7.54 (3H, m, Ph), 7.47-7.43 (2H, m, Ph), 7.39-7.28 (9H, m, Ph), 7.25-7.22 (3H, m, Ph), 7.16 (1H, tt, *J* 7.5 and 1.5, Ph), 7.09-7.06 (2H, m, Ph), 4.95 (1H, dt, *J* 10.5 and 7.0, C*H*CH_2), 4.84 (1H, d, *J* 6.5, C*H*OH),2.74 (1H, ddd, *J* 15.5, 10.5 and 2.5, CH_aH_b) and 2.62 (1H, ddd, *J* 15.5, 7.0 and 2.5, CH_aH_b); ^{31}P NMR (162 MHz; $CDCl_3$) δ 21.9; ^{13}C NMR (126 MHz; $CDCl_3$) δ 165.8 (d, *J* 18.5, C5), 139.0 (*ipso*-PhCH), 132.8 (d, *J* 109.0, *ipso*-PhP), 132.7 (d, *J* 109.0, *ipso*-PhP), 131.4-131.3 (m, Ph), 130.0 (Ph), 129.4 (*ipso*-PhC=C), 128.9, 128.5 (Ph), 128.3 (d, *J* 12.0, *meta*-PhP), 128.2 (d, *J* 12.0, *meta*-PhP), 127.6, 127.3 (Ph), 98.9 (d, *J* 119.5, C4), 84.5 (d, *J* 10.0, C2), 75.5 (C1') and 36.2 (d, *J* 10.0, C3); (Found: C, 69.88; H, 5.45. $C_{29}H_{25}O_3P$·0.2 EtOAc requires C, 69.66; H, 5.17%).

(2*R*,1'*S*)-2-[(1'-Phenyl-1'-phenylsulfanyl)-methyl]-4-diphenylphosphinoyl-5-phenyl-2,3-dihydrofuran 37

Dihydrofuran **36** (0.20 g, 0.44 mmol) was dissolved in anhydrous dichloromethane (5 cm^3) and triethylamine (0.12 cm^3, 0.88 mmol) and methanesulfonyl chloride (0.10 g, 0.88 mmol) was added. After stirring overnight (24 hours) the reaction mixture was transferred to a separatory funnel with 3 M aqueous HCl (20 cm^3) and extracted with dichloromethane (2 × 25 cm^3). The combined organic phases were washed with saturated aqueous $NaHCO_3$ (20 cm^3), dried (Na_2SO_4), filtered and concentrated *in vacuo* to give a yellow gum that was dried by evaporation from anhydrous toluene.

To a solution of benzenethiol (53 mg, 0.48 mmol) in anhydrous THF (5 cm^3) was added NaH (20 mg, 0.48 mmol, 60% in mineral oil) followed by the crude mesylate product dissolved in anhydrous

THF (5 cm^3). The reaction mixture was stirred overnight (22 hours) and transferred to a separatory funnel with half saturated aqueous Na_2CO_3 (50 cm^3) and extracted with ethyl acetate (2 × 25 cm^3). The combined organic phases were dried (Na_2SO_4), filtered and concentrated *in vacuo* to give a yellow solid that was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 50-90% EtOAc in hexanes (v/v) – 10% increments; 2-8% MeOH in EtOAc (v/v) – 2% increments – two fractions of each solvent mixture were collected] to give the *dihydrofuran* **37** (110 mg, 45%, 2 steps) as white needles. $[\alpha]_D^{23}$ +57 (c. 0.6, $CHCl_3$); mp 184-185 °C (from EtOAc, MeOH, hexanes); R_f 0.50 (EtOAc); *m/z* (+ESI) found: MNa^+, 567.1526. ($C_{35}H_{29}O_2PSNa$ requires *M*, 567.1524); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1596 and 1493 (furan C=C), 1438 (P-Ph) and 1182 (P=O); ^1H NMR (500 MHz; $CDCl_3$) δ 7.57-7.56 (2H, m, Ph), 7.50-7.46 (2H, m, Ph), 7.48-7.26 (13H, m, Ph), 7.21-7.13 (6H, m, Ph), 7.08-7.05 (2H, m, Ph), 5.18 (1H, ddd, *J* 11.0, 7.0 and 5.0, C*H*CH_2), 4.28 (1H, d, *J* 5.0, C*H*SPh), 3.04 (1H, ddd, *J* 15.0, 11.0 and 2.5, CH_aH_b) and 2.66 (1H, ddd, *J* 15.5, 7.0 and 2.5, CH_aH_b); ^{31}P NMR (162 MHz; $CDCl_3$) δ 21.7; ^{13}C NMR (126 MHz; $CDCl_3$) δ 166.2 (d, *J* 18.0, C5), 137.5, 133.9 (2 × *ipso*-Ph), 133.1 (d, *J* 109.0. *ipso*-PhP), 132.5 (d, *J* 109.0, *ipso*-PhP), 132.5 (Ph), 131.3 (d, *J* 10.0, *ortho*-PhP), 131.2 (d, *J* 2.5, *para*-PhP), 131.1 (×2) (d, *J* 9.5, *ortho*-PhP and d, *J* 2.5, *para*-PhP), 129.9, 129.3 (Ph), 129.2 (*ipso*-Ph), 128.9, 128.7, 128.4 (3 × Ph), 128.2 (d, *J* 12.0, *meta*-PhP), 127.9 (d, *J* 12.5, *meta*-PhP), 127.8, 127.5 (×2) (3 × Ph), 98.0 (d, *J* 119.5, C4), 82.3 (d, *J* 10.0, C2), 58.0 (C1') and 38.6 (d, *J* 10.0, C3); (Found: C, 76.27; H, 5.37. $C_{35}H_{29}O_2PS \cdot 0.35$ EtOAc requires C, 76.30; H, 5.43%).

(2*S*,1'*S*)-2-[(1'-Phenyl-1'-phenylsulfanyl)-methyl]-4-diphenylphosphinoyl-5-phenyl-2,3-dihydrofuran 38

Dihydrofuran **20** (0.20 g, 0.44 mmol) was dissolved in anhydrous dichloromethane (5 cm^3) and triethylamine (0.12 cm^3, 0.88 mmol) and methanesulfonyl chloride (0.10 g, 0.88 mmol) was added. After stirring overnight (24 hours) the reaction mixture was transferred to a separatory funnel with 3 M aqueous HCl (20 cm^3) and extracted with dichloromethane (2 × 25 cm^3). The combined organic phases were washed with saturated aqueous $NaHCO_3$ (20 cm^3), dried (Na_2SO_4), filtered and concentrated *in vacuo* to give a yellow gum that was dried by evaporation from anhydrous toluene.

To a solution of benzenethiol (53 mg, 0.48 mmol) in anhydrous THF (5 cm^3) was added NaH (20 mg, 0.48 mmol, 60% in mineral oil) followed by the crude mesylate product dissolved in anhydrous THF (5 cm^3). The reaction mixture was stirred overnight (19 hours) and transferred to a separatory

funnel with half saturated aqueous Na_2CO_3 (50 cm^3) and extracted with ethyl acetate (2 × 25 cm^3). The combined organic phases were dried (Na_2SO_4), filtered and concentrated *in vacuo* to give a yellow gum that was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 50-90% EtOAc in hexanes (v/v) – 10% increments; 2-8% MeOH in EtOAc (v/v) – 2% increments – two fractions of each solvent mixture were collected] to give the *dihydrofuran* **38** (95 mg, 40%, 2 steps) as yellow needles. $[\alpha]_D^{23}$ +93.2 (c. 0.6, $CHCl_3$); mp 162-163 °C (from EtOAc, MeOH, hexanes); R_f 0.45 (EtOAc); *m/z* (+ESI) found: MNa^+, 567.1524. ($C_{35}H_{29}O_2PSNa$ requires *M*, 567.1524); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1596 and 1492 (C=C), 1438 (P-Ph) and 1186 (P=O); ^1H NMR (500 MHz; $CDCl_3$) δ 7.63-7.59 (2H, m, Ph), 7.55-7.53 (2H, m, Ph), 7.47-7.43 (1H, m, Ph), 7.40-7.25 (12H, m, Ph), 7.23-7.20 (3H, m, Ph), 7.18-7.12 (3H, m, Ph), 7.08-7.05 (2H, m, Ph), 5.15 (1H, ddd, *J* 11.0, 7.0 and 5.0, C*H*CH_2), 4.47 (1H, d, *J* 5.0, C*H*SPh), 3.05 (1H, ddd, *J* 15.5, 11.0 and 2.5, CH_aH_b) and 2.76 (1H, ddd, *J* 15.5, 7.0 and 2.5, CH_aH_b); ^{31}P NMR (162 MHz; $CDCl_3$) δ 21.9; ^{13}C NMR (126 MHz; $CDCl_3$) δ 166.2 (d, *J* 18.5, C5), 137.9, 134.0 (2 × *ipso*-Ph), 133.2 (d, *J* 109.0. *ipso*-PhP), 132.2 (d, *J* 109.0, *ipso*-PhP), 132.4 (Ph), 131.5 (d, *J* 10.0, *ortho*-PhP), 131.4 (d, *J* 2.5, *para*-PhP), 131.3 (d, *J* 10.0, *ortho*-PhP), 131.2 (d, *J* 2.5, *para*-PhP), 129.9 (Ph), 129.4 (*ipso*-Ph), 129.0, 128.9, 128.8, 128.5 (Ph), 128.3 (d, *J* 12.0, *meta*-PhP), 128.0 (d, *J* 12.5, *meta*-PhP), 127.8, 127.5 (×2) (Ph), 98.3 (d, *J* 120.0, C4), 83.0 (d, *J* 10.5, C2), 57.7 (C1') and 37.9 (d, *J* 10.0, C3); (Found: C, 74.64; H, 5.50. $C_{35}H_{29}O_2PS{\cdot}1.0\ H_2O$ requires C, 74.71; H, 5.55%).

(2*R*,1'*S*)-2-[(1'-Azido-1'-phenyl)-methyl]-4-diphenylphosphinoyl-5-phenyl-2,3-dihydrofuran 25

Dihydrofuran **36** (0.20 g, 0.44 mmol) was dissolved in anhydrous dichloromethane (5 cm^3) and triethylamine (0.12 cm^3, 0.88 mmol) and methanesulfonyl chloride (0.10 g, 0.88 mmol) was added. After stirring overnight (23 hours) the reaction mixture was transferred to a separatory funnel with 3 M aqueous HCl (20 cm^3) and extracted with dichloromethane (2 × 20 cm^3). The combined organic phases were washed with saturated aqueous $NaHCO_3$ (50 cm^3), dried (Na_2SO_4), filtered and concentrated *in vacuo* to give a yellow gum that was dried by evaporation from anhydrous toluene. The crude product was dissolved in anhydrous DMF (5 cm^3) and sodium azide (43 mg, 0.66 mmol) was added. The reaction mixture was stirred overnight (22 hours) at 60 ^oC under argon and transferred to a separatory funnel with half saturated aqueous $NaHCO_3$ (50 cm^3) and extracted with ethyl acetate (2 × 25 cm^3). The combined organic phases were dried (Na_2SO_4), filtered and

concentrated *in vacuo* to give a brown gum. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 50-90% EtOAc in hexanes (v/v) – 10% increments; 2-8% MeOH in EtOAc (v/v) – 2% increments – two fractions of each solvent mixture were collected] gave the *dihydrofuran* **25** (0.13 g, 62%, 2 steps) as white needles. All analytical data was identical to that reported above.

(2*S*,4*S*,5*S*,1'*R*)-4-Diphenylphosphinoyl-2-[(1'-hydroxy-1'-phenyl)-methyl]-5-phenyl-tetrahydrofuran 39

Dihydrofuran **20** (100 mg, 0.22 mmol) was dissolved in methanol (5 cm^3) and glacial acetic acid (1.5 cm^3) was added. The reaction flask was flushed with argon and $Pd(OH)_2$ on charcoal (20 wt%, 10 mg) was added. The reaction flask was flushed with hydrogen, fitted with a hydrogen balloon and stirred vigorously for 12 hours, Celite was added to the reaction mixture and stirring was continued for 15 minutes. The slurry was filtered through a plug of celite and the catalyst washed with boiling methanol (3 × 20 cm^3). The combined organic phases were concentrated *in vacuo* to give a white gum that was re-evaporated from toluene (50 cm^3) to give a white powder. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 3 × hexanes; 10-100% EtOAc in hexanes (v/v) – 10% increments; 2.5-20% MeOH in EtOAc (v/v) – 2.5% increments] to give the *tetrahydrofuran* **39** (58 mg, 58%) as white needles. $[\alpha]_D^{23}$ −50 (c. 0.1, $CHCl_3$); mp >230 °C (from CH_2Cl_2); R_f 0.65 (EtOAc); *m/z* (+ESI) found: MNa^+, 477.1605. ($C_{36}H_{29}O_4PNa$ requires *M*, 477.1596); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 3339 (br., O-H) and 1439 (P-Ph); ^1H NMR (500 MHz; DMSO-d_6) δ 7.79-7.75 (2H, m, Ph), 7.48-7.18 (13H, m, Ph), 7.00-6.87 (5H, m, Ph), 5.69 (1H, d, *J* 4.0, OH), 5.10 (1H, dd, *J* 14.5 and 8.0, PCHC*H*Ph), 4.85-4.83 (1H, m, C*H*OH), 4.07 (1H, dt, *J* 8.5 and 6.0, C*H*CHOH), 4.02-3.96 (1H, m, PC*H*), 2.40-2.30 (1H, m, CH_aH_b) and 1.99-1.92 (1H, m, CH_aH_b); ^{31}P NMR (162 MHz; $CDCl_3$) δ 27.9; ^{13}C NMR (126 MHz; DMSO-d_6) 143.3 (*ipso*-PhCHOH), 138.2 (d, *J* 5.5, *ipso*-PhCHCHP), 135.3 (d, *J* 97.0, *ipso*-PhP), 133.4 (d, *J* 101.0, *ipso*-PhP), 131.2, 130.7 (2 × Ph), 130.2 (d, *J* 8.5, *ortho*-PhP), 130.1 (d, *J* 9.0, *ortho*-PhP), 129.2-126.5 (m, Ph), 82.8 (d, *J* 8.0, C5), 81.4 (C2), 73.8 (C1'), 41.6 (d, *J* 75.0, C3) and 28.6 (C4); (Found: C, 76.16; H, 6.01. $C_{36}H_{29}O_4P \cdot 0.25$ H_2O requires C, 75.89; H, 6.04%).

Crystal data for **20**: $C_{29}H_{25}O_3P$, *M* = 452.46, Hexagonal, *P6₁*, *a* = 11.1634(1), *b* = 11.1634(1), *c* = 33.8352(5) Å, α = 90°, β = 90°, γ = 120°, *U* = 3651.68(7) $Å^3$, *Z* = 6, μ(Mo-Kα) = 0.141 mm^{-1}, 16946 reflections collected at 200(2) K using an Oxford Cryosystems Cryostream cooling

apparatus, 3114 unique (R_{int} = 0.046); $R1$ = 0.058, $wR2$ = 0.142 [$I > 2\sigma(I)$], Absolute structure parameter -0.02(17).

Crystal data for **25**: $C_{29}H_{24}N_3O_2P$, M = 477.48, Triclinic, $P1$, a = 8.4713(3), b = 8.5479(3), c = 17.4621(6) Å, α = 83.267(2)°, β = 83.693(2)°, γ = 74.518(2)°, U = 1206.09(7) Å^3, Z = 2, μ(Mo-Kα) = 0.146 mm^{-1}, 12870 reflections collected at 180(2) K using an Oxford Cryosystems Cryostream cooling apparatus, 8246 unique (R_{int} = 0.068); $R1$ = 0.070, $wR2$ = 0.165 [$I > 2\sigma(I)$], Absolute structure parameter 0.01(13).

Crystal data for **39**: $C_{29}H_{27}O_3P$, M = 454.48, Orthorhombic, $P2_12_12_1$, a = 5.9419(1), b = 14.3610(3), c = 26.6529(7) Å, U = 2274.34(9) Å^3, Z = 4, μ(Mo-Kα) = 0.151 mm^{-1}, 14297 reflections collected at 180(2) K using an Oxford Cryosystems Cryostream cooling apparatus, 2966 unique (R_{int} = 0.095); $R1$ = 0.046, $wR2$ = 0.103 [$I > 2\sigma(I)$], Absolute structure parameter -0.02(13).

The structures were solved with SHELXS-97,[12] and refined with SHELXL-97.[12]

CCDC reference numbers 297304, 297305 and 297306. See http://www.rsc.org/suppdata/ for crystallographic data in .cif or other electronic format.

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