Diphenylphosphinoyl chloride as a chlorinating agent – the selective double activation of 1,2-diols

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Supplementary Information

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, carbontetrachloride, hexane, acetonitrile, toluene, pyridine, *N*,*N*-dimethylformamide and triethylamine were dried and stored over 4 Å molecular sieves. Methanol was dried and stored over 3 Å molecular sieves. 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 60 F_{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.[1] ^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 standards 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). Spectra were processed using Mestre-C software.[2] *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^{TM} 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 the sodium D line (589 nm) at 22 °C

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.

(4*R*,5*S*)-5-Chloro-4-diphenylphosphinoyloxy-1,5-diphenyl-pentan-1-one 5 and **(4*R*,5*R*)-4,5-bis-diphenylphosphinoyloxy-1,5-diphenyl-pentan-1-one 9**: diol[3] **1** (0.50 g, 1.85 mmol) was dissolved in anhydrous pyridine (10 cm^3) and diphenylphosphinoyl chloride (1.75 g, 7.40 mmol) was added. The reaction mixture was stirred under argon for 14 hours and transferred to a separatory funnel with water (20 cm^3) and extracted with ethyl acetate (50 + 2 × 25 cm^3). The combined organic phases were extracted with aqueous sulfate buffer (50 cm^3), saturated aqueous $NaHCO_3$ (50 cm^3), dried (Na_2SO_4), filtered and concentrated *in vacuo* to give a brown gum. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 0-100% EtOAc in hexanes (v/v) – 10% increments; 2.5-12.5% MeOH in EtOAc (v/v) – 2.5% increments; two fractions of each solvent mixture] to give 0.60 g (66%) of *ketone* **5** as a yellow amorphous solid and 46 mg (3%) of *bis-phosphinate* **9** as a yellow gum; **5**: $[\alpha]_D^{22}$ +19.0 (c. 1.0, $CHCl_3$); R_f 0.65 (EtOAc); *m/z* (+ESI) found: MH^+, 489.1377. ($C_{29}H_{27}ClO_3P$ requires *M*, 489.1386); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1685 (C=O), 1439 (P-Ph) and 1223 (P=O); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.83-7.79 (2H, m, *ortho*-PhP and/or *ortho*-PhC=O), 7.75-7.71 (4H, m, *ortho*-PhP and/or *ortho*-PhC=O), 7.55-7.47 (3H, m, *para*-PhP and *para*-PhC=O), 7.45-7.27 (13H, m, *meta*-PhP, *meta*-PhC=O and *ortho*-, *meta*- and *para*-PhC), 5.20 (1H, d, *J* 4.5, C*H*Ph), 4.87 (1H, ddt, *J* 9.0, 4.5 and 2.5, C*H*CHPh), 3.05 (1H, ddd, *J* 18.0, 9.5 and 5.0, CH_aH$_b$C=O), 2.94 (1H, ddd, *J* 18.0, 9.5 and 6.0, CH$_a$$H_b$C=O), 2.30 (1H, dtd, *J* 14.5, 9.0 and 5.0, CH_aH$_b$CH$_2$C=O) and 2.17-2.10 (1H, m, CH$_a$$H_bCH_2$C=O); ^{31}P NMR (162 MHz; $CDCl_3$) δ 32.7; ^{13}C NMR (126 MHz; $CDCl_3$) δ 198.8 (C1), 137.0, 136.6 (*ipso*-PhC=O and *ipso*-PhCH), 132.9 (*para*-PhC=O), 132.3 (×2) (2 × d, *J* 2.5 and 3.0, *para*-PhP), 131.7 (×2) (d, *J* 138.5, *ipso*-PhP and d, *J* 10.5, *ortho*-PhP), 131.6 (d, *J* 10.5, *ortho*-PhP), 131.3 (d, *J* 134.8, *ipso*-PhP), 128.6 (d, *J* 13.5, *meta*-PhP), 128.6 (d, *J* 13.5, *meta*-PhP), 128.5 (×2), 128.4, 128.0, 127.9 (*ortho*-, *meta*- and *para*-PhCH and *meta*- and *para*-PhC=O), 78.5 (d, *J* 6.5, C4), 65.8 (d, *J* 4.0, C5), 34.4 (C2) and 24.3 (d, *J* 3.5, C3); (Found: C, 68.51; H, 5.31. $C_{29}H_{26}ClO_3P{\cdot}1\ H_2O$ requires C, 68.71; H, 5.57). **9**: $[\alpha]_D^{23}$ +8.1 (c. 1.0, $CHCl_3$); R_f 0.35 (EtOAc); *m/z* (+ESI) found: MH^+, 671.2124. ($C_{41}H_{37}O_5P_2$ requires *M*, 671.2116); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1684 (C=O), 1439 (P-Ph) and 1222 (P=O); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.84-7.76 (4H, m, Ph), 7.73-7.71 (2H, m, Ph), 7.67-7.63 (2H, m, Ph), 7.54-7.44 (6H, m, Ph), 7.41-7.31 (8H, m, Ph), 7.24-7.15 (8H, m, Ph), 5.56 (1H, dd, *J* 9.5 and 6.0, C*H*Ph), 4.95 (1H, ddt, *J* 8.5, 6.5 and 3.5, C*H*CHPh), 2.99 (1H, ddd, *J* 18.0, 9.5 and 6.0, CH_aH$_b$C=O), 2.92 (1H, ddd, *J* 18.0, 9.5 and 5.0, CH$_a$$H_b$C=O), 2.21-2.14 (1H, m, CH_aH$_b$CH$_2$C=O) and 1.80 (1H, dddd, *J* 13.0, 9.0, 8.0 and 5.5, CH$_a$$H_bCH_2$C=O); ^{31}P NMR (162 MHz; $CDCl_3$) δ 32.4 and 32.3; ^{13}C NMR (126 MHz; $CDCl_3$) δ 198.9 (C1), 136.6 (*ipso*-PhC=O), 136.2 (d, *J* 2.5, *ipso*-PhC), 132.8 (*para*-PhC=O), 132.0 (×3) (d, *J* 2.5, *para*-PhP, d, *J* 2.5, *para*-PhP and d, *J* 138.0, *ipso*-PhP), 131.9 (×2), 131.8 (×2), 131.7 (×3), 131.6 (×2), 131.5 (Ph), 131.3 (d, *J* 141.0, *ipso*-PhP), 130.8 (d, *J* 137.0, *ipso*-PhP), 130.9 (d, *J* 133.0, *ipso*-PhP), 128.5, 128.4 (×2), 128.3, 128.2 (×2), 128.1, 128.0, 127.9, 127.7 (Ph), 77.9 (t, *J* 5.5, C5), 77.2 (t, *J* 6.0, C4), 34.2 (C2) and 25.2 (d, *J* 2.0, C3).

***tert*-Butyl (4*R*,5*S*)-5-chloro-4-diphenylphosphinoyloxy-5-phenyl-pentanoate 6**: diol[4] **2** (0.21 g, 0.79 mmol) was dissolved in anhydrous pyridine (5 cm^3) and diphenylphosphinoyl chloride (0.61 cm^3, 3.2 mmol) was added under argon. After 29 hours aqueous half-saturated $NaHCO_3$ (20 cm^3) was added and the mixture extracted with ethyl acetate (3 × 20 cm^3). The combined organic phases were concentrated *in vacuo* and the residue dissolved in dichloromethane (20 cm^3) and extracted with saturated aqueous $NaHCO_3$ (50 cm^3). The organic phase was 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; 4 × hexanes; 10-100% EtOAc in hexanes (v/v) – 10% increments; 3 × EtOAc] to give 0.32 g (83%) of *phosphinate* **6** as white needles. $[\alpha]_D^{22}$ +18 (c. 1.0, $CHCl_3$); mp 68-69 °C (EtOAc, hexanes); R_f 0.30 (40% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 507.1454. ($C_{27}H_{30}ClO_4PNa$ requires *M*, 507.1468); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1726 (C=O), 1439 (P-Ph) and 1228 (P=O); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.82-7.78 (2H, m, *ortho*-PhP), 7.71-7.67 (2H, m, *ortho*-PhP), 7.55-7.50 (2H, m, *para*-PhP), 7.47-7.40 (4H, m, *meta*-PhP), 7.30-7.27 (5H, m, Ph), 5.14 (1H, d, *J* 5.0, PhC*H*), 4.79-4.74 (1H, m, PhCHC*H*), 2.37-2.27 (1H, m, CH_aH_bC=O), 2.25-2.16 (2H, m, CH_aH_bC=O and CH_aH_bCH_2C=O), 1.97-1.89 (1H, m, CH_aH_bCH_2C=O) and 1.34 [9H, s, C(CH_3)$_3$]; ^{31}P NMR (162 MHz; $CDCl_3$) δ 32.6; ^{13}C NMR (126 MHz; $CDCl_3$) δ 171.9 (C1), 137.1 (*ipso*-Ph), 132.3 (d, *J* 2.5), 132.2 (d, 3.0) (2 × *para*-PhP), 131.7 (d, *J* 10.5), 131.6 (d, *J* 10.0) (2 × *ortho*-PhP), 131.4 (×2) (d, *J* 139.0 and d, *J* 131.5), 128.6-128.4 (m, 2 × *meta*-PhP and 2 × Ph), 127.8 (*para*-Ph), 80.3 [*C*(CH_3)$_3$], 78.2 (d, *J* 6.5, C4), 65.2 (d, *J* 4.0, C5), 30.8 (C2), 28.0 [C(*C*H_3)$_3$] and 25.3 (d, *J* 3.5, C3); (Found: C, 66.86; H, 6.25. $C_{27}H_{30}ClO_4P$ requires C, 66.87; H, 6.24%).

(1*S*,2*R*)-1-Chloro-1-phenyl-2-diphenylphospinoyloxy-propane 7: to a stirred solution of diol[5] **3** (1.23 g, 8.08 mmol) in pyridine (50 cm^3) under argon was added diphenylphosphinoyl chloride (4.38 cm^3, 22.3 mmol) and the solution was stirred for 48 hours before it was quenched with half-saturated aqueous $NaHCO_3$ (50 cm^3) and brine (50 cm^3). The mixture was extracted with EtOAc (80 cm^3 + 50 cm^3 + 20 cm^3) and the combined organic phases were evaporated *in vacuo*. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 0-100% EtOAc in petrol ether (60-80 °C) (v/v) – 10% increments] gave *chloride* **7** (1.79 g, 60%) as a clear colourless oil; $[\alpha]_D^{22}$ +18.4 (c. 0.7, $CHCl_3$); R_f 0.40 [30% petrol ether (60-80 °C) in EtOAc, v/v]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.70 (2H, m, *ortho*-PhP), 7.59-7.53 (2H, m, *ortho*-PhP), 7.48-7.24 (11H, m, Ph), 5.05 (1H, d, *J* 5.5, C*H*Cl), 4.81 (1H, dq, *J* 9.0 and 6.0, C*H*O), 1.42 (d, 3H, *J* 6.0, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.1; ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 132.2 (d, *J* 11.5), 132.1 (d, *J* 11.5), 131.9 (d, *J* 138.5), 131.6 (d, *J* 10.0), 131.6 (d, *J* 10.5), 131.4 (d, *J* 137.0), 128.5 (×2), 128.4 (d, *J* 13.0). 128.4 (d, *J* 13.5), 128.0, 75.6 (d, *J* 6.0), 66.5 (d, *J* 6.5), 18.0 (d, *J* 2.5) (CH_3); *m/z* (+ESI) found: MH^+ 371.0958 ($C_{21}H_{20}O_2ClP^+$ requires 371.0962); (found: C, 66.32%; H, 5.36%; $C_{21}H_{20}O_2ClP{\cdot}0.5\ H_2O$ requires C, 66.41%; H, 5.57%).

(1*R*,2*S*)-2-Chloro-1,2-diphenyl-1-diphenylphosphinoyloxyethane 8: to a stirred solution of diol[5] **4** (0.429 g, 2.0 mmol) in pyridine (10 cm^3) under argon was added diphenylphosphinoyl chloride (1.53 cm^3, 8.0 mmol) and the solution was stirred for 48 hours before it was quenched with half-saturated aqueous $NaHCO_3$ (40 cm^3). The mixture was extracted with EtOAc (3 × 40 cm^3) and the combined organic phases were evaporated *in vacuo*. The residue was dissolved in dichloromethane (50 cm^3) and

saturated aqueous $NaHCO_3$ (50 cm^3), the organic phase dried with Na_2SO_4, filtered, and evaporated *in vacuo*. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 0-100% EtOAc in petrol ether (60-80 °C) (v/v) – 10% increments; 2 × EtOAc] gave *chloride* **8** (0.617 g, 71%). A sample was recrystallised from $CHCl_3$: petrol ether (60-80 °C) to give a colourless crystalline solid; $[\alpha]_D^{22}$ +22.8 (c. 0.75, $CHCl_3$); mp 172–174 °C; R_f 0.40 [40% petrol ether (60-80 °C) in EtOAc, v/v]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.44 (5H, m, Ph), 7.35-6.93 (15H, m, Ph), 5.73 (1H, dd, *J* 9.0, 6.5, C*H*O), 5.28 (1H, d, *J* 6.5, C*H*Cl); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.5; ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.3, 136.3 (d, *J* 2.0), 132.1 (d, *J* 3.0), 131.9 (d, *J* 3.0), 131.7 (d, *J* 10.5), 131.4 (d, *J* 138.5), 131.4 (d, *J* 10.5), 131.1 (d, *J* 135.5), 128.7, 128.5, 128.3, 128.3 (d, *J* 13.5), 128.1, 128.1 (d, *J* 13.5), 127.8, 80.0 (d, *J* 5.5), 65.5 (d, *J* 6.5); *m/z* (+ESI) found: MH^+ 433.1124 ($C_{26}H_{23}ClO_2P^+$ requires 433.1119); (found: C, 71.80%; H, 5.15%; $C_{26}H_{22}ClO_2P$ 1.5 H_2O requires C, 71.54%; H, 5.17%).

(2*R*,3*S*)-Methyl 3-chloro-2-bis(diphenylphosphinoyloxy)-3-phenylpropanoate 11, (2*R*,3*R*)-methyl 2-chloro-3-bis(diphenylphosphinoyloxy)-3-phenylpropanoate 12 and (2*S*,3*R*)-methyl 2,3-bis(diphenylphosphinoyloxy)-3-phenylpropanoate 13: to a stirred solution of diol[6] **10** (0.098 g, 0.5 mmol) in pyridine (5 cm^3) under argon was added diphenylphosphinoyl chloride (0.38 cm^3, 2.0 mmol) and the solution was stirred for 48 hours before it was quenched with half-saturated aqueous $NaHCO_3$ (10 cm^3). The mixture was extracted with EtOAc (3 × 20 cm^3) and the combined organic phases were evaporated *in vacuo*. The residue was dissolved in dichloromethane (25 cm^3) and saturated aqueous $NaHCO_3$ (40 cm^3), the organic phase dried with Na_2SO_4, filtered, and evaporated *in vacuo*. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 0-100% EtOAc in petrol ether (60-80 °C) (v/v) – 10% increments; then 5-20% MeOH in EtOAc (v/v) – 5% increments] gave *bis-phosphinate* **13** as a light yellow oil (0.073 g, 24%) and a mixture of *chloro-phosphinates* **11** and **12 (11**:**12** 1:2.5 by ^{1}H NMR) (0.115 g, 56%). **11** and **12** ^{1}H NMR (400 MHz, $CDCl_3$) 7.80-7.22 (m, Ph, both isomers), 5.76 (1H, dd, *J* 9.5, 8.0, PhCHOP, minor isomer), 5.25 (1H, d, *J* 8.0, PhCHCl, major isomer), 5.17 (1H, dd, *J* 9.5, 8.0, $POCHCO_2$, major isomer), 4.75 (1H, dd, *J* 8.0, $ClCHCO_2$, minor isomer), 3.69 (3H, s, OCH_3 minor isomer) and 3.60 (3H, s, OCH_3 major isomer); *m/z* (+ESI) found: MH^+ 435.1474 ($C_{23}H_{29}O_4ClP^+$ requires 435.1492). A sample of bis-phosphinate **13** was recrystallised from $CHCl_3$: petrol ether (60-80˚C); $[\alpha]_D^{22}$ −12.0 (c. 0.43, $CHCl_3$); mp 145.5-147.7 °C; R_f 0.05 [40% petrol ether (60-80 °C) in EtOAc, v/v]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.75 (4H, m, Ph), 7.52-7.32 (12H, m, Ph), 7.25-7.09 (9H, m, Ph), 5.81 (1H, dd, *J* 9.5 and 5.5, C*H*Ph), 5.10 (1H, dd, *J* 8.5 and 5.5, C*H*CO), 3.33 (3H, s, C*H*$_3$); ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.2 and 33.3; ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 135.3 (d, *J* 1.5), 132.3, 132.2 (×2), 132.1 (×2), 132.0 (×3), 131.9 (×2), 131.8 (×2), 131.7 (×2), 131.3, 130.5, 130.4 (×2), 129.9, 128.7, 128.4 (×2), 128.3 (×2), 128.2 (×3), 128.0, 127.2, 77.0 (t, *J* 26.0), 76.2 (t, *J* 25.0); *m/z* (+ESI) found: MH^+ 597.1602 ($C_{34}H_{31}O_6P_2^+$ requires 597.1590); (found: C, 67.89%; H, 5.10%; $C_{34}H_{30}O_6P_2$ 0.25 H_2O requires C, 67.94%; H, 5.11%).

(2*R*,3*R*)-Ethyl 2-chloro-3-(diphenylphosphinoyloxy)-4-methylpentanoate 15: to a stirred solution of diol[7] **14** (0.600 g, 3.4 mmol) in pyridine (15 cm^3) under argon was added diphenylphosphinoyl chloride

(2.6 cm^3, 14 mmol) and the solution was stirred for 48 hours before it was quenched with half-saturated aqueous $NaHCO_3$ (30 cm^3). The mixture was extracted with EtOAc (3 × 40 cm^3) and the combined organic phases were evaporated *in vacuo*. The residue was dissolved in CH_2Cl_2 (40 cm^3) and saturated aqueous $NaHCO_3$ (60 cm^3), the organic phase dried with Na_2SO_4, filtered, and evaporated *in vacuo*. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 0-100% EtOAc in petrol ether (60-80 °C) (v/v) – 10% increments; then 5-20% MeOH in EtOAc (v/v) – 5% increments] gave *chloride* **15** as colourless crystals (0.610 g, 45%); $[\alpha]_D^{22}$ −6.6 (c. 0.80, $CHCl_3$); mp 66-68 °C; R_f 0.40 [40% petrol ether (60-80 °C) in EtOAc, v/v]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.74 (4H, m, Ph), 7.51-7.37 (6H, m, Ph), 4.90-4.82 (1H, m, C*H*OP), 4.58 (1H, d, *J* 6.5, C*H*Cl), 3.96-3.78 2H, (m, CH_2), 2.27 (1H, dq, *J* 13.5 and 6.5, C*H*CH_3), 1.19-1.11 (3H, m, CH_3CH_2), 0.94 (3H, d, *J* 7.0, CH_3CH), 0.83 (3H, d, *J* 7.0, CH_3CH); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.0; ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 132.2 (d, *J* 137.0 Hz), 132.1 (d, *J* 137.0), 132.1 (d, *J* 2.5), 131.5 (d, *J* 10.5), 128.4 (d, *J* 13.5), 80.4 (d, *J* 7.0), 62.2, 58.5 (d, *J* 3.5), 29.8 (d, *J* 3.5), 19.0, 17.0, 13.7; *m/z* (+ESI) found MH^+ 395.1163 ($C_{20}H_{25}ClO_4P^+$ requires 395.1174); (found: C, 60.71%; H, 6.08%; $C_{20}H_{24}ClO_4P$ requires C, 60.84%; H, 6.13%).

(1*R*,2*R*)-1-Diphenylphosphinoyloxy-2-hydroxy-1,2-diphenylethane 16: to a stirred solution of diol **4** (0.214 g, 1.0 mmol) in pyridine (5 cm^3) under argon was added diphenylphosphinoyl chloride (0.19 cm^3, 1.0 mmol) and the solution was stirred for 48 hours before it was quenched with half-saturated aqueous $NaHCO_3$ (20 cm^3). The mixture was extracted with EtOAc (2 × 30 + 20 cm^3) and the combined organic phases were evaporated *in vacuo*. The residue was dissolved in dichloromethane (25 cm^3) and saturated aqueous $NaHCO_3$ (40 cm^3), the organic phase dried with Na_2SO_4, filtered, and evaporated *in vacuo*. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 0-100% EtOAc in petrol ether (60-80 °C) (v/v) – 10% increments] gave *phosphinate* **16** as a clear colourless oil (0.100 g, 24%). A sample of **16** was recrystallised from $CHCl_3$: petrol ether (60-80 °C); $[\alpha]_D^{22}$ +75.1 (c. 0.80, $CHCl_3$); mp 154.9-157.5 °C; R_f 0.25 [60% petrol ether (60-80 °C) in EtOAc v/v]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.81 (2H, m, Ph), 7.68-7.63 (2H, m, Ph), 7.56-7.48 (4H, m, Ph), 7.36-7.31 (2H, m, Ph), 7.20-7.03 (6H, m, Ph), 6.99-6.97 (2H, m, Ph), 6.92-6.90 (2H, m, Ph), 5.22 (1H, br s, O*H*), 5.11 (1H, t, *J* 8.5, C*H*OP), 4.99 (1H, d, *J* 8.0, C*H*OH); ^{31}P NMR (162 MHz, $CDCl_3$) δ 37.2; ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 136.9 (d, *J* 6.0), 132.6 (d, *J* 3.0), 132.4 (d, *J* 3.0), 132.3 (d, *J* 10.5), 131.4 (d, *J* 10.5), 131.1 (d, *J* 165.0), 129.7 (d, *J* 151.0), 128.6 (d, *J* 13.5), 186.6 (d, *J* 13.0), 128.2, 128.0, 127.8, 127.6, 127.5, 127.2, 85.6 (d, *J* 7.0), 78.4 (d, *J* 2.0); *m/z* (ESI+): found: MH^+ 415.1457 ($C_{26}H_{24}O_3P^+$ requires 415.1458); (found: C, 75.19%; H, 5.61%; $C_{26}H_{23}O_3P$ 0.25 H_2O requires C, 75.35%; H, 5.59%).

(1*R*,2*R*)-1,2-Bis(diphenylphosphinoyloxy)-1,2-diphenylethane 17: to a stirred solution of diol **4** (0.214 g, 1.0 mmol) in CH_2Cl_2 (10 cm^3) under argon were added triethylamine (0.28 cm^3, 2.1 mmol), DMAP (0.024 g, 0.2 mmol), and diphenylphosphinoyl chloride (0.19 cm^3, 1.0 mmol) and the solution was stirred for 46 hours before water (20 cm^3) and dichloromethane (25 cm^3) were added, the aqueous phase was extracted with dichloromethane (2 × 25 cm^3) and the combined organic phases were

extracted with sulfate buffer (20 cm^3) and saturated aqueous $NaHCO_3$ (20 cm^3). The organic phase was dried with Na_2SO_4, filtered, and evaporated *in vacuo*. Purification by
DCVC [id 4 cm; 20 cm^3 fractions; 0-100% EtOAc in petrol ether (60-80 °C) (v/v) – 10% increments; then 5-20% MeOH in EtOAc (v/v) – 10% increments] gave *bis-phosphinate* **17** as clear colourless oil (0.220 g, 36%); $[\alpha]_D^{22}$ +53.2 (c. 0.95, $CHCl_3$); R_f 0.35 (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.76 (4H, m, Ph), 7.55-7.49 (4H, m, Ph), 7.40-7.35 (2H, m, Ph), 7.28-7.23 (6H, m, Ph), 7.14-7.10 (4H, m, Ph), 7.02-6.88 (10H, m, Ph), 5.75-5.67 (2H, m, C*H*OP); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.5; ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.9 (d, *J* 1.5), 132.2, 132.0, 131.9 (×2), 131.8, 131.7 (×3), 131.6, 131.5 (d, *J* 140.0), 131.3 (d, *J* 133.5), 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 79.4 (t, *J* 6.0); *m/z* (ESI+) found: MH^+ 615.1848 ($C_{38}H_{33}O_4P_2^+$ requires 615.1849); (found: C, 73.46%; H, 5.27%; $C_{38}H_{32}O_4P_2$ 0.33 H_2O requires C, 73.54%; H, 5.31%).

(1*R*,2*S*)-2-Chloro-1,2-diphenyl-1-diphenylphosphinoyloxyethane 8: to a stirred solution of hydroxy-phosphinate **16** (60 mg, 0.145 mmol) in pyridine (5 cm^3) under argon was added diphenylphosphinoyl chloride (0.58 mmol) and the solution was stirred for 48 hours before it was quenched with half-saturated aqueous $NaHCO_3$ (20 cm^3). The mixture was extracted with EtOAc (3 × 20 cm^3) and the combined organic phases were evaporated *in vacuo*. The residue was dissolved in dichloromethane (50 cm^3) and saturated aqueous $NaHCO_3$ (50 cm^3), the organic phase dried with Na_2SO_4, filtered, and evaporated *in vacuo* to give crude chloro-phosphinate **8** (>95% conversion by ^{1}H NMR).

Reaction of diol 4 with Ph_2PCl_3 in pyridine: to a solution of Ph_2PCl (0.72 cm^3, 4.0 mmol) in CCl_4 (20 cm^3) under argon at −15 ºC was added SO_2Cl_2 (0.32 cm^3, 4.0 mmol) (dropwise), and the mixture was stirred for 2 hours at −15 to −10 ºC.[8] The solvent was removed *in vacuo* to give Ph_2PCl_3 as a white crystalline solid. The solid was dissolved in pyridine under argon and diol **4** (0.86 g, 4.0 mmol) was added. The reaction was stirred at ambient temperature for 48 hours. Evaporation of the pyridine gave a crude product containing diol **4**, chloro-phosphinate **8** and hydroxy-phosphinate **16** in a 43:31:26 ratio (by ^{1}H NMR).

(4*R*,5*R*)-5-Azido-1,5-diphenyl-4-diphenylphosphinoyloxy-pentan-1-one 21: chloride **5** (0.25 g, 0.51 mmol) was dissolved in anhydrous DMF (5 cm^3). To the stirred solution, at room temperature under argon, sodium azide (40 mg, 0.62 mmol) was added and the reaction mixture heated to 120 °C. After 28 hours the reaction was transferred to a separatory funnel with water (25 cm^3) and brine (10 cm^3) and extracted with ethyl acetate (50 + 2 × 25 cm^3). The combined organic phases were extracted 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 0.17 g (67%) of *azide* **21** as yellow needles. $[\alpha]_D^{22}$ −62 (c. 1.2, $CHCl_3$); mp 91-92 °C (EtOAc, hexanes); R_f 0.35 (50% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 518.1619. ($C_{29}H_{26}N_3O_3PNa$ requires *M*, 518.1609); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 2103 (N_3), 1684 (C=O) 1439 (P-Ph) and 1224 (P=O); ^{1}H NMR (500

MHz; $CDCl_3$) δ 7.87-7.83 (2H, m, *ortho*-PhC=O or *ortho*-PPh), 7.77-7.71 (4H, m, *ortho*-PhC=O or *ortho*-PPh), 7.53-7.47 (3H, m, Ph), 7.45-7.31 (11H, m, Ph), 4.97 (1H, d, *J* 7.0, PhC*H*), 4.73 (1H, tdd, *J* 9.0, 7.0 and 3.0, PhCHC*H*), 3.07-2.89 (2H, m, CH_2C=O), 2.08-2.02 (1H, m, CH_aH$_b$CH$_2$C=O) and 1.88-1.81 (1H, m, CH$_a$$H_bCH_2$C=O); ^{31}P NMR (162 MHz; $CDCl_3$) δ 32.8; ^{13}C NMR (126 MHz; $CDCl_3$) δ 198.8 (C1), 136.5, 135.5 (2 × *ipso*-PhC), 133.0 (*para*-PhC=O), 132.2 (×3) (d, *J* 91.5, *ipso*-PPh, d, *J* 2.5, *para*-PhP and d, *J* 3.0, *para*-PhP), 131.7 (d, *J* 10.5, *ortho*-PhP), 131.6 (d, *J* 10.0, *ortho*-PhP), 131.1 (d, *J* 89.0, *ipso*-PhP), 128.8 (PhC), 128.6 (d, *J* 13.0, *meta*-PhP), 128.4 (d, *J* 13.5, *meta*-PhP), 128.4, 128.0, 127.9 (PhC), 77.6 (d, *J* 7.0, C4), 69.4 (d, *J* 4.1, C5), 34.4 (C2), 26.3 (d, *J* 3.0, C3); (Found: C, 70.29; H, 5.31. $C_{29}H_{26}N_3O_3P$ requires C, 70.29; H, 5.29%).

(1*R*,2*R*)-1-Azido-2-diphenylphosphinoyloxy-1-phenylpropane 22: to a stirred solution of chlorophosphinate **7** (0.370 g, 1.0 mmol) in DMF (20 cm^3) under argon was added sodium azide (0.260 g, 4.0 mmol) and the mixture was stirred at 120 °C. After 48 hours heating was stopped, water (20 cm^3) and brine (20 cm^3) were added and the aqueous phase was extracted with EtOAc (3 × 25 cm^3), the combined organic phases were extracted with sulfate buffer (25 cm^3) followed by saturated aqueous $NaHCO_3$ (25 cm^3), dried with Na_2SO_4, filtered, and evaporated *in vacuo*. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 0-100% EtOAc in petrol ether (60-80 °C) (v/v) – 10% increments] gave *azido-phosphinate* **22** as a clear light yellow oil (0.280 g, 74%); $[\alpha]_D^{22}$ –94.5 (c. 1.7, $CHCl_3$); R_f 0.30 [40% petrol ether (60-80 °C) in EtOAc, v/v]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.72 (4H, m, Ph), 7.45-7.31 (6H, m, Ph), 7.30-7.19 (5H, m, Ph), 4.71-4.59 (2H, m, C*H*), 1.18 (3H, d, *J* 6.0, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.1; ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.7, 132.2 (d, *J* 139.5), 132.2 (d, *J* 3.0), 132.1 (d, *J* 3.0), 131.7 (d, *J* 10.5), 131.5 (d, *J* 10.0), 131.4 (d, *J* 136.0), 128.7 (×2), 128.5 (d, *J* 13.0), 128.4 (d, *J* 13.5), 127.8, 74.9 (d, *J* 6.5), 70.5 (d, *J* 6.5), 19.0 (d, *J* 1.5); *m/z* (ESI+) found: MH$^+$ 378.1374 ($C_{21}H_{21}N_3O_2P^+$ requires 378.1366); (found: C, 65.43%; H, 5.36%; N, 10.79%; $C_{21}H_{20}N_3O_2P$ 0.5 H_2O requires C, 65.28%; H, 5.48%; N, 10.88%).

(1*R*,2*R*)-2-Azido-1,2-diphenyl-1-(diphenylphosphinoyloxy)ethane 23: to a stirred solution of chlorophosphinate **8** (0.110 g, 0.25 mmol) in DMF (10 cm^3) under argon was added sodium azide (0.066 g, 1.0 mmol) and the mixture was stirred at 120 °C. After 48 hours heating was stopped, water (10 cm^3) and brine (10 cm^3) were added and the aqueous phase was extracted with EtOAc (2 × 30 + 10 cm^3), the combined organic phases were extracted with sulfate buffer (30 cm^3), saturated aqueous $NaHCO_3$ (30 cm^3), dried with Na_2SO_4, filtered, and evaporated *in vacuo*. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 0-100% EtOAc in petrol ether (60-80 °C) (v/v) – 10% increments] gave *azido-phosphinate* **23** as a clear light yellow oil (0.060 g, 55%); $[\alpha]_D^{22}$ –44.4 (c. 0.23, $CHCl_3$); R_f 0.35 [40% petrol ether (60-80 °C) in EtOAc, v/v]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.80 (2H, m, Ph), 7.61-7.41 (5H, m, Ph), 7.39-7.31 (1H, m, Ph), 7.26-6.93 (12H, m, Ph), 5.48 (1H, dd, *J* 9.5 and 7.5, C*H*OP), 4.97 (1H, d, *J* 7.5, C*H*N$_3$); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.4; ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.3 (d, *J* 2.5), 135.0, 132.2 (d, *J* 3.0), 131.9 (d, *J* 3.0), 131.8 (d, *J* 10.5 Hz), 131.6 (d, *J* 139.5), 131.6 (d, *J* 10.5), 131.1 (d, *J* 134.5), 128.5, 128.4 (×2), 128.2 (×3), 128.0, 127.9, 127.5, 79.8 (d, *J* 6.0), 70.7 (d, *J* 5.5); *m/z*

(ESI+) found: MH^+ 440.1541 ($C_{26}H_{23}N_3O_2P^+$ requires 440.1522); (found: C, 69.72%; H, 5.07%; N, 8.87; $C_{26}H_{22}N_3O_2P \cdot 2/3H_2O$ requires C, 69.17%; H, 5.21%; N, 9.31%).

(4*R*,5*R*)-5-Azido-4-hydroxy-1,5-diphenylpentan-1-one 24: to a stirred solution of azido-phosphinate **21** (0.049 g, 0.10 mmol) in methanol (5 cm^3) under argon was added potassium carbonate (0.055 g, 0.40 mmol). After stirring overnight the reaction mixture was evaporated to dryness and the residue purified by DCVC [id 4 cm; 20 cm^3 fractions; 0-100% EtOAc in petrol ether (60-80 °C) (v/v) – 10% increments] to give *azido-alcohol* **24** as a clear colourless oil (22 mg, 75%); $[\alpha]_D^{22}$ –90.0 (c. 1.2, $CHCl_3$); R_f 0.50 [50% petrol ether (60-80 °C) in EtOAc, v/v]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92-7.88 (2H, m, Ph), 7.54-7.49 (1H, m, Ph), 7.44-7.29 (7H, m, Ph), 4.40 (1H, d, *J* 7.5, C*H*N_3), 3.85-3.78 (1H, m, C*H*OH), 3.18-3.01 (2H, m, CH_2CHOH), 2.68 (1H, br s, O*H*), 1.78-1.68 (2H, m, CH_2C=O); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.0, 136.7, 136.3, 133.1, 129.0, 128.8, 128.5, 128.4, 128.0, 127.8, 73.9, 72.1, 60.4, 34.6, 27.3; m/z (ESI+) found: MNa^+ 318.1201 ($C_{17}H_{17}N_3O_2Na^+$ requires 318.1213).

(1*R*,2*R*)-1-Azido-1-phenylpropan-2-ol 25: to a stirred solution of azido-phosphinate **22** (0.034 g, 0.10 mmol) in methanol (2 cm^3) under argon was added potassium carbonate (0.028 g, 0.20 mmol). After stirring overnight the reaction mixture was evaporated to dryness and the residue purified by DCVC [id 4 cm; 20 cm^3 fractions; 0-100% EtOAc in petrol ether (60-80 °C) (v/v) – 10% increments] to give azido-alcohol **25** as a clear light yellow oil (15 mg, 86%); $[\alpha]_D^{22}$ –167.8 (c. 1.0, $CHCl_3$); R_f 0.40 [40% petrol ether (60-80 °C) in EtOAc, v/v]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.27 (5H, m, Ph), 4.30 (1H, d, *J* 8.0, C*H*N_3), 3.92-3.84 (1H, m, C*H*OH), 2.43 (1H, br s, O*H*), 1.03 (3H, d, *J* 6.5, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.6, 128.9, 128.7, 73.3, 70.8, 19.1; *m/z* (ESI+) found: MNa^+ 200.0792 ($C_9H_{11}N_3ONa^+$ requires 200.7943).

(1*R*,2*R*)-2-Azido-1,2-diphenylethanol 26: to a stirred solution of azido-phosphinate **23** (0.060 g, 0.14 mmol) in methanol (3 cm^3) under argon was added potassium carbonate (0.038 g, 0.27 mmol). After stirring overnight the reaction mixture was evaporated to dryness and the residue purified by DCVC [id 4 cm; 20 cm^3 fractions; 0-100% EtOAc in petrol ether (60-80 °C) (v/v) – 10% increments] to give azido-alcohol **26** as a clear light yellow oil (19 mg, 57%); $[\alpha]_D^{22}$ –85.4 (c. 0.85, $CHCl_3$); R_f 0.65 [40% petrol ether (60-80 °C) in EtOAc, v/v]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26-7.17 (6H, m, Ph), 7.11-7.05 (4H, m, Ph), 4.74 (1H, d, *J* 8.0, C*H*), 4.68 (1H, d, *J* 7.5, C*H*), 2.79 (1H, br s, O*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.2, 136.0, 128.5, 128.2, 128.1 (×2), 127.8, 126.8, 78.0, 72.9; *m/z* (ESI+) found: MNa^+ 262.0943 ($C_{14}H_{13}N_3ONa^+$ requires 262.0951). Data consistent with that previously reported.[9]

(2*R*,3*R*)-2,3-Diphenyloxirane 27: to a stirred solution of chloro-phosphinate **8** (0.200 g, 0.46 mmol) in methanol (10 cm^3) under argon was added potassium carbonate (0.256 g, 1.85 mmol). After stirring overnight the reaction mixture was evaporated to dryness and the residue purified by DCVC [id 4 cm; 20 cm^3 fractions; 0-100% EtOAc in petrol ether (60-80 °C) (v/v) – 10% increments] to give epoxide **27** as white crystals (0.078 g, 86%); $[\alpha]_D^{22}$ +250.8 (c. 0.85, $CHCl_3$), (lit. $[\alpha]_D^{22}$ +239.2).[10] NMR data

consistent with that previously reported.[11] The ^{1}H NMR spectrum of the crude product showed no trace of *cis*-epoxide product.

(1*R*,2*S*)-2-Azido-1,2-diphenylethanol 28: to a stirred solution of epoxide **27** (0.020 g, 0.10 mmol) in wet DMF (5 cm^3) under argon was added sodium azide (0.054 g, 0.83 mmol) and the mixture was stirred at 100 °C. After 48 hours heating was stopped and half-saturated aqueous $NaHCO_3$ (20 cm^3) was added. The mixture was extracted with EtOAc (3 × 20 cm^3), the combined organic phases washed with sulfate buffer (20 cm^3), saturated aqueous $NaHCO_3$ (20 cm^3), dried with Na_2SO_4, filtered, and evaporated *in vacuo*. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 0-100% EtOAc in petrol ether (60-80 °C) (v/v) – 10% increments] gave azido-alcohol **28** as a clear light yellow oil 0.018 g (75%); $[\alpha]_D^{22}$ +67.8 (c. 0.90, $CHCl_3$) (lit. $[\alpha]_D^{22}$ +44)[9]; R_f 0.30 [40% petrol ether (60-80 °C) in EtOAc, v/v]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.22 (10H, m, Ph), 4.71-4.59 (1H, br d, *J* 6.5, C*H*OH), 4.68 (1H, d, *J* 7.0, C*H*N_3), 2.09 (1H, br d, *J* 2.5, O*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.6, 135.9, 128.7, 128.6, 128.4, 128.3, 128.0, 127.0, 77.0, 71.2; *m/z* (ESI+) found: MNa^+ 262.0939 ($C_{14}H_{13}N_3ONa^+$ requires 262.0951). NMR data consistent with that previously reported.[9]

(1'*R*,2'*R*,1''*S*)-{2'-[(1''-Hydroxy-1''-phenyl)-methyl]-cyclopropyl}-1-phenyl-methanone 30: to a stirred solution of chloro-phosphinate **5** (0.049 g, 0.10 mmol) in methanol (2 cm^3) under argon was added potassium carbonate (0.038 g, 0.27 mmol) and after stirring for 48 hours the reaction mixture was evaporated *in vacuo*. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 0-100% EtOAc in petrol ether (60-80 °C) (v/v) – 10% increments] gave cyclopropane **30** as a white amorphous solid (0.020 g, 79%). Data consistent with that previously reported.[12]

(1'*R*,2'*R*,1''*S*)-{2'-[(1''-Azido-1''-phenyl)-methyl]-cyclopropyl}-1-phenyl-methanone 31 and **(1'*S*,2'*R*,1''*S*)-{2'-[(1''-azido-1''-phenyl)-methyl]-cyclopropyl}-1-phenyl-methanone 32:** ketone **21** (0.13 g, 0.26 mmol) was dissolved in anhydrous THF (5 cm^3) under argon and cooled to -78 °C. Freshly prepared LDA (0.27 mmol) in anhydrous THF (3 cm^3) cooled to -78 °C was added by cannula and the reaction mixture stirred at -78 °C for 2 hours and then warmed to 0 °C. The reaction was maintained at 0 °C for 4 hours and then allowed to warm to room temperature overnight (16 hours). Saturated aqueous NH_4Cl (10 cm^3) was added and the mixture transferred to a separatory funnel with water (10 cm^3) and extracted with CH_2Cl_2 (3 × 25 cm^3). The combined organic phases were dried with Na_2SO_4, filtered and concentrated *in vacuo* to give a yellow gum. The product was purified by DCVC [id 4 cm; 25 cm^3 fractions; 0-50% EtOAc in hexanes – 5% increments; two fractions of each solvent mixture were collected] to give 34 mg (47%) of *cyclopropanes* **31** and **32** in a 9:1 ratio. An analytically pure sample of cyclopropane **31** was obtained. Analytical data for cyclopropane **31**: $[\alpha]_D^{22}$ −100 (c. 0.6, $CHCl_3$); R_f 0.35 (15% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 300.1106. $C_{17}H_{15}N_3ONa$ requires *M*, 300.1107); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 2097 (N_3) and 1669 (C=O); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.87-7.85 (2H, m, *ortho*-PhC=O), 7.55 (1H, tt, *J* 7.5 and 1.0, *para*-PhC=O), 7.44-7.33 (5H, m, Ph), 4.40 (1H, d, *J* 6.5, PhC*H*), 2.68 (1H, dt, *J* 8.5 and 4.5, C*H*C=O), 2.11 (1H, dtd, *J* 8.5, 6.5 and 4.0,

C*H*CHN$_3$), 1.63 (1H, ddd, *J* 9.0, 5.0 and 4.0, C*H*$_a$H$_b$), 1.32 (1H, ddd, *J* 8.5, 6.5 and 4.0, CH$_a$*H*$_b$); ^{13}C NMR (126 MHz; $CDCl_3$) δ 198.6 (C1), 138.3, 137.5 (2 × *ipso*-Ph), 133.0, 128.9, 128.7, 128.5, 128.0, 127.1 (6 × Ph), 66.8 (C1''), 29.0 (C2'), 21.9 (C1') and 16.0 (C3'). NMR data for cyclopropane **32** (extracted from NMR spectra of a mixture of **31** and **32**. Peaks were overlapping in the aromatic region): ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.70-7.68 (2H, m, *ortho*-PhC=O), 7.44-7.33 (6H, m, Ph), 4.54 (1H, d, *J* 10.0, PhC*H*), 2.78 (1H, ddd, *J* 9.0, 7.5 and 5.5, C*H*C=O), 2.04 (1H, dtd, *J* 9.0, 8.5 and 7.0, C*H*CHN$_3$), 1.84 (1H, ddd, *J* 7.0, 5.5 and 4.5, C*H*$_a$H$_b$), 1.44 (1H, td, *J* 8.0 and 4.5, CH$_a$*H*$_b$); ^{13}C NMR (126 MHz; $CDCl_3$) δ 198.8 (C1), 139.2, 138.6 (2 × *ipso*-Ph), 132.7, 128.3, 127.8, 126.7, (4 × Ph, two phenyl peaks were overlapping with compound **31** peaks and could not be identified), 63.3 (C1''), 30.2 (C2'), 22.1 (C1') and 14.5 (C3').

Crystal data for chloro phosphinate **6**: $C_{27}H_{30}ClO_4P$, M = 484.93, Orthorhombic, $P2_12_12_1$, a = 5.8203(10), b = 11.4038(2), c = 37.8022(9) Å, α = 90°, β = 90°, γ = 90°, U = 2509.1(4) Å^3, Z = 4, μ(Mo-Kα) = 0.247 mm^{-1}, 10165 reflections collected at 180(2) K using an Oxford Cryosystems Cryostream cooling apparatus, 4316 unique (R_{int} = 0.056); $R1$ = 0.053, $wR2$ = 0.127 [$I > 2\sigma(I)$].)], Absolute structure parameter 0.02(10).

The structure was solved with SHELXS-97,[13] and refined with SHELXL-97.[13] CCDC reference number 600429. See http://www.rsc.org/suppdata for crystallographic data in .cif or other electronic format.

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