Supplementary Material

Diphenylphosphinoyl mediated synthesis of ketones

David J. Fox,* Daniel Sejer Pedersen and Stuart Warren

University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, U.K.

EMAIL: djf34@cam.ac.uk

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 Na wire with benzophenone as indicator. *N*,*N*-Dimethylformamide and diisopropylamine was dried and stored over 4 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 total 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 because of 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), Bruker Avance 500 (5 mm dual ^{13}C-^1H cryo probe) and Bruker Avance 700 (5 mm conventional geometry dual ^{13}C-^1H 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. 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.

Method 1: Acylation of diphenylphosphine oxides

According to the method by Warren and co-workers[4] *n*-BuLi (1.05 eq.) is added to a stirred solution of the phosphine oxide (1 mmol) in anhydrous THF (10 cm^3) at 0 ^oC under argon. After 15 minutes the reaction is cooled to −78 ^oC and the acylating agent (1.2 eq.) is added dropwise (solids are dissolved in anhydrous THF cooled to −78 ^oC and added dropwise by cannula). When the reaction has gone to completion saturated aqueous NH_4Cl (10 cm^3) is added and the mixture allowed to warm to room temperature. The mixture is transferred to a separatory funnel with water (10 cm^3) and extracted with ethyl acetate (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 and / or crystallisation.

Method 2a-b: α-Alkylation of β-keto-diphenylphosphine oxides

2a: According to the method by Warren and co-workers[5] sodium methoxide (1.1 eq.) is added to a stirred solution of the phosphine oxide (1 mmol) in anhydrous THF (10 cm^3) at room temperature under argon. After 15 minutes the electrophile (1.2 eq.) is added and stirring is continued until the reaction is completed. Saturated aqueous NH_4Cl (10 cm^3) is added and the mixture transferred to a separatory funnel with water (10 cm^3) and extracted with ethyl acetate (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, which is purified by column chromatography and / or crystallisation.

2b: Sodium hydride (1.1 eq., 60% in mineral oil) is added to a stirred solution of the substrate (1 mmol) in anhydrous DMF (5 cm^3) at room temperature under argon. After 15 minutes the electrophile (1.2 eq.) is added and stirring is continued until the reaction is completed (with heating if necessary). Saturated aqueous NH_4Cl (10 cm^3) is added and the mixture transferred to a separatory funnel with water (10 cm^3) and extracted with ethyl acetate (3 × 20 cm^3). The combined organic phases are washed with 1 M aqueous HCl (20 cm^3),* dried (Na_2SO_4), filtered and the solvent removed *in vacuo* to give the crude product that is purified by column chromatography.

* Aqueous sulfate buffer (20 cm^3) was used for acid sensitive compounds.

Method 3a-c: Dephosphinoylation of β-keto diphenylphosphine oxides

3a: 4 M aqueous NaOH (10 cm^3) is added to a stirred solution of the substrate (1 mmol) in ethanol (10 cm^3) at reflux. When the reaction has gone to completion it is allowed to cool to room temperature and transferred to a separatory funnel with water (10 cm^3) and extracted with ethyl acetate (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.

3b: Identical to method **3a** except that KOH (10 eq.) in methanol is used instead of 4 M aqueous NaOH in ethanol.

3c: Identical to method **3a** except that K_2CO_3 (10 eq.) and water (10 cm^3) is used instead of 4 M aqueous NaOH.

3d: Identical to method **3a** except that NaOMe (10 eq.) and MeOH (10 cm^3) is used instead of 4 M aqueous NaOH and ethanol.

Method 4: γ-Alkylation of β-keto diphenylphosphine oxides

LDA (2.05 eq.) is added to a stirred solution of the phosphine oxide (1 mmol) in anhydrous THF (10 cm^3) at 0 ^oC under argon. After 15 minutes the solution is cooled to −78 ^oC and the electrophile (1.0 eq.) is added. When the reaction has gone to completion saturated aqueous NH_4Cl (10 cm^3) is added and the mixture allowed to warm to room temperature. The mixture is transferred to a separatory funnel with water (10 cm^3) and extracted with ethyl acetate (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, which is purified by column chromatography and / or crystallisation.

1-Diphenylphosphinoyl-propan-2-one 2a

By method **1** diphenylmethylphosphine oxide (25.0 g, 116 mmol) and ethylacetate (11.21 g, 127 mmol, 12.4 cm^3) after 3½ hours gave a yellow solid that was recrystallised from boiling EtOAc to give **2a** (15.74 g, 52%) as white needles. mp 127-129 °C (from EtOAc) (lit.,[6] 129 °C, EtOAc); R_f = 0.30 (EtOAc); *m/z* (+ESI) found: MNa^+, 281.0715. ($C_{15}H_{15}O_2PNa$ requires *M*, 281.0707); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1707 (C=O), 1438 (P-Ph) and 1182 (P=O); ^1H NMR (400 MHz; $CDCl_3$) δ 7.77-7.72 (4H, m, *ortho*-Ph), 7.55-7.51 (2H, m, *para*-Ph), 7.49-7.45 (4H, m, *meta*-Ph), 3.58 (2H, d, *J* 15.0, PCH_2) and 2.31 (3H, s, CH_3C=O); ^{31}P NMR (162 MHz; $CDCl_3$) δ 26.8; ^{13}C NMR (100 MHz; $CDCl_3$) δ 200.8 (d, *J* 5.0, C2), 132.2 (d, *J* 2.5, *para*-Ph), 131.8 (d, *J* 103.0, *ipso*-Ph), 130.8 (d, *J* 10.0, *ortho*-Ph), 128.7 (d, *J* 12.5, *meta*-Ph), 47.9 (d, *J* 56.5, C1) and 32.6 (C3); (Found: C, 69.61; H,

5.80. $C_{15}H_{15}O_2P$ requires C, 69.76; H, 5.85%). The data above are in agreement with that which has been previously reported.[6]

1-Diphenylphosphinoyl-butan-2-one 2b

By method **1** diphenylmethylphosphine oxide (4.0 g, 18.5 mmol) and methyl propionate (1.79 g, 20.4 mmol, 1.96 cm^3) after 2½ hours gave a yellow gum that was purified by DCVC [id 6 cm; 50 cm^3 fractions; 2 × hexanes; 50-100% EtOAc in hexanes (v/v) – 10% increments; 2-16% MeOH in EtOAc (v/v) – 2% increments] to give phosphine oxide **2b** (2.31 g, 46%) as white flakes. mp 104-105 °C (from EtOAc, hexanes, MeOH) (lit.,[4] 104-106 °C, EtOAc); R_f = 0.40 (1% MeOH in EtOAc, v/v); *m/z* (+EI) found: M^+, 272.0967. ($C_{16}H_{17}O_2P$ requires *M*, 272.0966); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1707 (C=O), 1438 (P-Ph) and 1185 (P=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.78-7.72 (4H, m, *ortho*-Ph), 7.56-7.51 (2H, m, *para*-Ph), 7.50-7.45 (4H, m, *meta*-Ph), 3.58 (2H, d, *J* 15.0, PCH_2), 2.66 (2H, q, *J* 7.0, C*H*$_2$Me) and 0.95 (3H, t, *J* 7.0, CH_3); ^{31}P NMR (162 MHz; $CDCl_3$) δ 27.1; ^{13}C NMR (100 MHz; $CDCl_3$) δ 203.4 (d, *J* 5.0, C2), 132.2 (d, *J* 2.0, *para*-Ph), 132.0 (d, *J* 103.0, *ipso*-Ph), 130.9 (d, *J* 10.0, *ortho*-Ph), 128.7 (d, *J* 12.5, *meta*-Ph), 46.8 (d, *J* 57.0, C1), 38.7 (C3) and 7.4 (C4); (Found: C, 70.17; H, 6.47. $C_{16}H_{17}O_2P$ requires C, 70.58; H, 6.29%). The data above are in agreement with that which has been previously reported.[4]

1-Diphenylphosphinoyl-3-methyl-butan-2-one 2c

By method **1** diphenylmethylphosphine oxide (4.0 g, 18.5 mmol) and methyl 2-methylpropionate (2.08 g, 20.4 mmol, 2.34 cm^3) after 3 hours gave a yellow gum that was purified by DCVC [id 6 cm; 50 cm^3 fractions; 2 × hexanes; 50-100% EtOAc in hexanes (v/v) – 10% increments; 2-16% MeOH in EtOAc (v/v) – 2% increments] to give phosphine oxide **2c** (2.61 g, 49%) as white needles. mp 84-85 °C (from EtOAc, hexanes, MeOH); R_f = 0.45 (1% MeOH in EtOAc, v/v); *m/z* (+EI) found: M^+, 286.1137. ($C_{17}H_{19}O_2P$ requires *M*, 286.1123); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1705 (C=O), 1438 (P-Ph) and 1189 (P=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.80-7.74 (4H, m, Ph), 7.56-7.45 (6H, m, Ph), 3.65 (2H, d, *J* 15.0, CH_2), 2.87 (1H, sept., *J* 7.0, CH) and 1.02 (6H, d, *J* 7.0, 2 × CH_3); ^{31}P NMR (162 MHz; $CDCl_3$) δ 27.4; ^{13}C NMR (100 MHz; $CDCl_3$) δ 207.0 (d, *J* 5.0, C2), 132.2 (d, *J* 103.0, *ipso*-Ph), 132.1 (d, *J* 2.0, *para*-Ph), 130.9 (d, *J* 10.0, *ortho*-Ph), 128.7 (d, *J* 12.5, *meta*-Ph), 45.0 (d, *J* 58.0, C1), 42.5 (C3) and 17.8 (2 × CH_3); (Found: C, 71.14; H, 6.87. $C_{17}H_{19}O_2P$ requires C, 71.32; H, 6.69%). The data above are in agreement with that which has been previously reported.[7]

2-Diphenylphosphinoyl-1-phenylethanone 2d

By method **1** diphenylmethylphosphine oxide (22.1 g, 102 mmol) and methyl benzoate (15.3 g, 112 mmol, 14.0 cm^3) after 3 hours gave a yellow amorphous solid that was purified by DCVC [id 6 cm; 50 cm^3 fractions; 50-100% EtOAc in hexanes (v/v) – 10% increments; 2-20% MeOH in EtOAc (v/v) – 2% increments] to give a yellow powder that was recrystallised from EtOAc to give **2d** (15.31 g) as white needles. The mother liquor was concentrated and recrystallised from EtOAc to give an additional 4.94 g of white needles and a combined yield of 20.25 g (62%) of phosphine oxide **2d**. mp 149-151 °C (from EtOAc) (lit.,[4] 138-139 °C, EtOAc); R_f = 0.35 (1% MeOH in EtOAc, v/v); *m/z* (+ESI) found: MNa^+, 343.0880. ($C_{20}H_{17}O_2PNa$ requires *M*, 343.0864); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1677 (C=O), 1438 (P-Ph) and 1182 (P=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.00-7.94 (2H, m, *ortho*-Ph), 7.83-7.67 (4H, m, Ph), 7.55-7.36 (9H, m, Ph) and 4.12 (2H, d, *J* 15.5, CH_2); ^{31}P NMR (162 MHz; $CDCl_3$) δ 27.5; ^{13}C NMR (100 MHz; $CDCl_3$) δ 192.8 (d, *J* 5.5, C1), 137.0 (*ipso*-PhC), 133.6 (*para*-PhC), 132.1 (d, *J* 3.0, *para*-PhP), 132.0 (d, *J* 103.5, *ipso*-PhP), 131.1 (d, *J* 10.0, *ortho*-PhP), 129.2 (PhC), 128.6 (d, *J* 12.5, *meta*-PhP), 128.5 (PhC) and 43.3 (d, *J* 60.0, C2); (Found: C, 74.60; H, 5.46. $C_{20}H_{17}O_2P$ requires C, 74.99; H, 5.35%). The data above is in agreement with that which has been previously reported.[4]

2-Diphenylphosphinoyl-1-furan-2'-yl-ethanone 2e

By method **1** diphenylmethylphosphine oxide (10.0 g, 46.3 mmol) after 3 hours gave a black gum that was purified by DCVC [id 6 cm; 50 cm^3 fractions; 2 × hexanes; 10-100% EtOAc in hexanes (v/v) – 10% increments; 4-20% MeOH in EtOAc (v/v) – 4% increments] to give *phosphine oxide* **2e** (10.93 g, 76%) as yellow needles. mp 106-108 °C (from EtOAc, hexanes, MeOH); R_f 0.35 (5% MeOH in EtOAc, v/v); *m/z* (+EI) found: M^+, 310.0744. ($C_{18}H_{15}O_3P$ requires *M*, 310.0759); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1662 (C=O), 1464 (C-O), 1437 (P-Ph) and 1188 (P=O); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.81-7.76 (4H, m, *ortho*-Ph), 7.53-7.49 (3H, m, *para*-Ph and C5'-CH), 7.46-7.42 (4H, m, *meta*-Ph), 7.27 (1H, br d, *J* 3.5, C3'-CH), 6.46 (1H, dd, *J* 3.5 and 1.5, C4'-CH) and 4.00 (2H, d, *J* 15.5, CH_2); ^{31}P NMR (162 MHz; $CDCl_3$) δ 27.6; ^{13}C NMR (126 MHz; $CDCl_3$) δ 180.5 (d, *J* 5.5, C1), 152.5 (C2'), 147.2 (C5'), 132.1 (d, *J* 3.0, *para*-Ph), 131.8 (d, *J* 104.0, *ipso*-Ph), 131.1 (d, *J* 10.0, *ortho*-Ph), 128.6 (d, *J* 12.5, *meta*-Ph), 119.6 (C3'), 112.7 (C4') and 43.1 (d, *J* 57.5, C2); (Found: C, 69.33; H, 4.97. $C_{18}H_{15}O_3P$ requires C, 69.68; H, 4.87%).

1-Diphenylphosphinoyl-4-phenyl-butan-2-one 2f

By method **1** diphenylmethylphosphine oxide (1.00 g, 3.9 mmol) after 8 hours gave a brown gum. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 10-100% EtOAc in hexanes (v/v) – 10% increments; 2.5-30% MeOH in EtOAc (v/v) – 2.5% increments] gave phosphine oxide **2f** (0.94 g, 69%) as a white powder. mp 90-92 °C (from EtOAc, hexanes, MeOH); R_f 0.20 (50% EtOAc in hexanes, v/v); *m/z* (+EI) found: M^+, 348.1291. ($C_{22}H_{21}O_2P$ requires *M*, 348.1279); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1708 (C=O), 1437 (P-Ph) and 1189 (P=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.76-7.71 (4H, m, *ortho*-PhP), 7.57-7.45 (6H, m, *meta*- and *para*-PhP), 7.25-7.11 (5H, m, Ph), 3.57 (2H, d, *J* 15.0, PCH_2), 2.99 (2H, t, *J* 7.5, CH_2Ph) and 2.81 (2H, t, *J* 7.5, CH_2C=O); ^{31}P NMR (162 MHz; $CDCl_3$) δ 27.0; ^{13}C NMR (125 MHz; $CDCl_3$) δ 202.1 (d, *J* 5.5, C2), 140.6 (*ipso*-PhC), 132.2 (*para*-PhP), 131.8 (d, *J* 103.0, *ipso*-PhP), 130.9 (d, *J* 10.0, *ortho*-PhP), 128.8 (d, *J* 12.5, *meta*-PhP), 128.4, 128.3, 126.0 (3 × Ph), 47.2 (d, *J* 56.5, C1), 46.7 (C3) and 29.3 (C4); (Found: C, 75.61; H, 6.08. $C_{22}H_{21}O_2P$ requires C, 75.85; H, 6.08%). Phosphine oxide **2f** has previously been reported with no characterisation.[8]

1-Diphenylphosphinoyl-4-phenyl-butan-2-one 2f

By method **4** phosphine oxide **2a** (1.0 g, 3.87 mmol) after 4 hours gave a brown syrup that was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 10-100% EtOAc in hexanes (v/v) – 10% increments; 2.5-30% MeOH in EtOAc (v/v) – 2.5% increments] to give phosphine oxide **2f** (0.94 g, 69%) as white needles. All analytical data were identical with that reported above.

3-Diphenylphosphinoyl-butan-2-one 3a

By method **1** diphenylethylphosphine oxide (5.0 g, 21.7 mmol) and ethyl acetate (2.11 g, 23.9 mmol, 2.33 cm^3) after 4 hours gave a white solid that was purified by DCVC [id 6 cm; 50 cm^3 fractions; 2 × hexanes; 50-100% EtOAc in hexanes (v/v) – 10% increments; 4-48% MeOH in EtOAc (v/v) – 4% increments] to give phosphine oxide **3a** (3.70 g, 62%) as a white amorphous solid. mp 117-119 °C (from EtOAc, hexanes, MeOH) (lit.,[4] 117-119 °C, EtOAc); R_f = 0.25 (5% MeOH in EtOAc, v/v); *m/z* (+ESI) found: M^+, 295.0855. ($C_{16}H_{17}O_2P$ requires *M*, 295.0864); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1705 (C=O), 1438 (P-Ph) and 1181 (P=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.83-7.73 (4H, m, Ph), 7.56-7.45 (6H, m, Ph), 3.64 (1H, dq, *J* 12.5 and 7.0, PCH), 2.22 (3H, s, CH_3C=O) and 0.95 (3H, dd, *J* 16.0 and 7.0, PCHCH_3); ^{31}P NMR (162 MHz; $CDCl_3$) δ 30.7; ^{13}C NMR (100 MHz; $CDCl_3$) δ 205.5 (d, *J* 2.5, C2), 132.2 (d, *J* 3.0, *para*-Ph), 132.1 (d, *J* 2.5, *para*-Ph), 131.3 (d, *J*

9.0, *ortho*-Ph), 131.2 (d, *J* 9.0, *ortho*-Ph), 131.1 (d, *J* 99.5, *ipso*-Ph), 130.7 (d, *J* 98.0, *ipso*-Ph), 128.8 (d, *J* 12.0, *meta*-Ph), 128.7 (d, *J* 11.5, *meta*-Ph), 51.0 (d, *J* 57.5, C3), 30.2 (C4) and 11.3 (d, *J* 3.5, C1); (Found: C, 70.60; H, 6.42. $C_{16}H_{17}O_2P$ requires C, 70.58; H, 6.29%). The data above are in agreement with that which has been previously reported.[4]

2-Diphenylphosphinoyl-pentan-3-one 3b

By method **1** diphenylethylphosphine oxide (4.0 g, 17.4 mmol) and methyl propionate (1.68 g, 19.1 mmol, 1.84 cm^3) after 4 hours gave a yellow gum that was purified by DCVC [id 6 cm; 50 cm^3 fractions; 2 × hexanes; 50-100% EtOAc in hexanes (v/v) – 10% increments; 4-48% MeOH in EtOAc (v/v) – 4% increments] to give phosphine oxide **3b** (3.18 g, 63%) as white needles. mp 80-82 °C (from EtOAc, hexanes, MeOH) [lit.,[4] 93-94 °C, EtOAc, light petroleum (b.p. 40-60 °C)]; R_f = 0.45 (5% MeOH in EtOAc, v/v); *m/z* (+ESI) found: M^+, 309.1022. ($C_{17}H_{19}O_2P$ requires *M*, 309.1020); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1706 (C=O), 1438 (P-Ph) and 1180 (P=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.83-7.72 (4H, m, Ph), 7.53-7.43 (6H, m, Ph), 3.58 (1H, dq, *J* 13.5 and 7.0, PCH), 2.54 (2H, q, *J* 7.0, C*H*$_2$CH$_3$), 1.37 (3H, dd, *J* 16.5 and 7.5, PCHC*H*$_3$) and 0.87 (3H, t, *J* 7.0, CH$_2$C*H*$_3$); ^{31}P NMR (162 MHz; $CDCl_3$) δ 31.0; ^{13}C NMR (100 MHz; $CDCl_3$) δ 208.0 (d, *J* 2.5, C3), 132.1 (d, *J* 3.0, *para*-Ph), 132.0 (d, *J* 3.0, *para*-Ph), 131.3 (d, *J* 9.5, *ortho*-Ph), 131.2 (d, *J* 9.0, *ortho*-Ph), 131.1 (d, *J* 99.5, *ipso*-Ph), 130.8 (d, *J* 99.0, *ipso*-Ph), 128.6 (d, *J* 12.0, *meta*-Ph), 128.6 (d, *J* 12.0, *meta*-Ph), 50.3 (d, *J* 57.5, C2), 36.3 (C4), 11.4 (d, *J* 3.5, C1) and 7.4 (C5); (Found: C, 71.22; H, 6.74. $C_{17}H_{19}O_2P$ requires C, 71.32; H, 6.69%). The data above are in agreement with that which has been previously reported.[4]

2-Diphenylphosphinoyl-4-methyl-pentan-3-one 3c

By method **1** diphenylethylphosphine oxide (5.0 g, 18.4 mmol) after 2½ hours gave a white solid that was purified by DCVC [id 6 cm; 50 cm^3 fractions; 2 × hexanes; 50-100% EtOAc in hexanes (v/v) – 10% increments; 2-16% MeOH in EtOAc (v/v) – 2% increments] to give *phosphine oxide* **3c** (3.60 g, 65%) as white flakes. mp 146-147 °C (from EtOAc, hexanes, MeOH); R_f 0.40 (1% MeOH in EtOAc, v/v); *m/z* (+EI) found: M^+, 300.1281. ($C_{18}H_{21}O_2P$ requires *M*, 300.1279); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1704 (C=O), 1438 (P-Ph) and 1185 (P=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.91-7.85 (2H, m, Ph), 7.78-7.72 (2H, m, Ph), 7.57-7.44 (6H, m, Ph), 3.86 (1H, dq, *J* 16.0 and 7.0, PCH), 2.76 [1H, sep, *J* 7.0, C*H*(CH$_3$)$_2$], 1.38 (3H, dd, *J* 16.5 and 7.0, PCHC*H*$_3$), 0.97 [3H, d, *J* 7.0, CH(C*H*$_3$)$_a$(CH$_3$)$_b$] and 0.86 [3H, d, *J* 6.5, CH(CH$_3$)$_a$(C*H*$_3$)$_b$]; ^{31}P NMR (162 MHz; $CDCl_3$) δ 31.1;

^{13}C NMR (100 MHz; $CDCl_3$) δ 211.8 (d, *J* 5.0, C3), 132.2-132.1 (m, 2 × *para*-Ph), 131.6 (d, *J* 10.0, *ortho*-Ph), 131.5 (d, *J* 9.5, *ortho*-Ph), 131.1 (d, *J* 102.5, *ipso*-Ph), 130.9 (d, *J* 99.0, *ipso*-Ph), 128.7 (d, *J* 12.0, *meta*-Ph), 128.6 (d, *J* 12.0, *meta*-Ph), 49.3 (d, *J* 58.0, C2), 41.6 (C4), 18.7 [$CH(CH_3)_a(CH_3)_b$], 17.6 [$CH(CH_3)_a(CH_3)_b$] and 12.2 (d, *J* 3.0, C1); (Found: C, 71.77; H, 7.14. $C_{18}H_{21}O_2P$ requires C, 71.98; H, 7.05%).

2-Diphenylphosphinoyl-4-(2-methyl-[1,3]dioxolan-2-yl)-1-phenyl-butan-1-one 3d

By method **1** 1-diphenylphosphinoyl-4-(2-methyl-[1,3]dioxolan-2-yl)-propane (1.0 g, 3.0 mmol) and methyl benzoate (0.45 g, 3.3. mmol, 0.41 cm^3) after 2 hours gave a white solid that was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 50-100% EtOAc in hexanes (v/v) – 10% increments; 2.5-40% MeOH in EtOAc (v/v) – 2.5% increments] to give phosphine oxide **3d** (0.98 g, 74%) as white flakes. mp 153-154 °C (from EtOAc, hexanes, MeOH) (lit.,[9] 194-197 °C, EtOAc, hexanes); R_f = 0.30 (EtOAc); *m/z* (+EI) found: M^+, 457.1551. ($C_{26}H_{27}O_4P$ requires *M*, 457.1545); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1672 (C=O), 1438 (P-Ph) and 1189 (P=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.91-7.86 (2H, m, Ph), 7.79-7.69 (4H, m, Ph), 7.48-7.27 (9H, m, Ph), 4.74 (1H, ddd, *J* 16.5, 11.0 and 3.0, PCH), 3.86-3.65 (4H, m, OCH_2CH_2O), 2.43-2.31 (1H, m, $PCHCH_aH_b$), 2.11-2.00 (1H, m, $PCHCH_aH_b$), 1.70-1.56 (2H, m, $PCHCH_2CH_2$) and 1.19 (3H, s, CH_3); ^{31}P NMR (162 MHz; $CDCl_3$) δ 30.0; ^{13}C NMR (100 MHz; $CDCl_3$) δ 198.0 (d, *J* 2.5, C1), 138.3 (*ipso*-Ph), 132.9 (*para*-Ph), 132.0 (d, *J* 2.5, *para*-PhP), 131.9 (d, *J* 2.5, *para*-PhP), 131.8 (d, *J* 9.5, *ortho*-PhP), 131.4 (d, *J* 9.0, *ortho*-PhP), 131.2 (d, *J* 99.0, *ipso*-PhP), 130.6 (d, *J* 99.5, *ipso*-PhP), 128.5 (Ph), 128.4 (d, *J* 12.0, *meta*-PhP), 128.3 (d, *J* 12.0, *meta*-PhP), 128.3 (Ph), 109.5 (CCH_3), 64.5 (OCH_{2a}), 64.4 (OCH_{2b}), 51.6 (d, *J* 57.0, C2), 37.1 (d, *J* 11.5, C4), 23.6 (CH_3) and 23.0 (C3); (Found: C, 70.98; H, 6.48. $C_{26}H_{27}O_4P{\cdot}0.25\ H_2O$ requires C, 71.14; H, 6.31%). The data above are in agreement with that which has been previously reported.[9]

(*E*)-1,5-Diphenyl-2-diphenylphosphinoyl-pent-4-en-1-one 3e

By method **2a** phosphine oxide **2d** (0.20 g, 0.62 mmol) after 6 hours gave a white 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; 1-15% MeOH in EtOAc (v/v) – 1% increments] to give phosphine oxide **3e** (0.27g, 99%) as a white powder.

Alternative method:

An alternative method with the *in situ* generation of (*E*)-cinnamyl iodide from (*E*)-cinnamyl chloride can be used. Phosphine oxide **2d** (0.65 g, 2.0 mmol) was dissolved in anhydrous THF (15 cm^3) with stirring. Sodium methoxide (0.11 g, 2.1 mmol) was added and the solution stirred at room temperature for 10 minutes. (*E*)-Cinnamyl chloride (0.29 cm^3, 2.1 mmol) and sodium iodide (0.32 g, 2.1 mmol) was added. The reaction mixture was stirred in the dark for 18 hours and then quenched with saturated aqueous NH_4Cl (25 cm^3), transferred to a separatory funnel with water (25 cm^3) and extracted with ethyl acetate (50 + 2 × 25 cm^3). The combined organic phases were washed with saturated aqueous sodium thiosulfate (500 cm^3), dried (Na_2SO_4), filtered and concentrated *in vacuo* to give a yellow amorphous solid. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 50-100% EtOAc in hexanes (v/v) – 5% increments; 2.5-20% MeOH in EtOAc (v/v) – 2.5% increments] gave 0.84 g (97%) of alkene **3e** as a yellow amorphous powder. mp 154-156 °C (from MeOH, hexanes, EtOAc) (lit.,[10] 153-155 °C, EtOAc, hexanes); R_f = 0.50 (EtOAc); *m/z* (+ESI) found: MNa^+, 459.1489. ($C_{29}H_{25}O_2PNa$ requires *M*, 459.1490); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1673 (C=O), 1438 (P-Ph) and 1173 (P=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.96-7.90 (2H, m, Ph), 7.79-7.72 (4H, m, Ph), 7.52-7.11 (14H, m, Ph), 6.33 (1H, d, *J* 16.0, CH=C*H*Ph), 6.02 (1H, dt, *J* 16.0 and 7.0, C*H*=CHPh), 4.68 (1H, ddd, *J* 16.0, 11.0 and 3.5, PCH), 3.20-3.07 (1H, m, CH_aH$_b$) and 2.90-2.80 (1H, m, CH$_a$$H_b$); ^{31}P NMR (162 MHz; $CDCl_3$) δ 29.5; ^{13}C NMR (100 MHz; $CDCl_3$) δ 197.4 (d, *J* 2.5, C1), 138.1 (d, *J* 1.0, *ipso*-PhC=O), 136.8 (*ipso*-PhCH=CH), 133.0, 132.7 (Ph and C5), 132.2 (d, *J* 3.0, *para*-PhP), 132.1 (d, *J* 3.0, *para*-PhP), 131.9 (d, *J* 9.5, *ortho*-PhP), 131.4 (d, *J* 9.0, *ortho*-PhP), 131.1 (d, *J* 99.5, *ipso*-PhP), 130.4 (d, *J* 99.5, *ipso*-PhP), 128.5 (×3) (d, *J* 12.0, *meta*-PhP, d, *J* 12.0, *meta*-PhP and Ph), 128.4, 127.3, 126.3, 126.1 (×2) (Ph and C4), 52.2 (d, *J* 55.0, C2) and 31.8 (d, *J* 2.0, C3); (Found: C, 79.38; H, 5.81. $C_{29}H_{25}O_2P$ requires C, 79.80; H, 5.77%). The data above are in agreement with that which has been previously reported.[11]

(*Z*)-1,5-Diphenyl-2-diphenylphosphinoylpent-4-en-1-one 3f

By method **2a** phosphine oxide **2d** (1.00 g, 3.1 mmol) after 40 hours gave a white amorphous solid. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 10-100% EtOAc in hexanes (v/v) – 10% increments; 2.5-20% MeOH in EtOAc (v/v) – 2.5% increments] to give a white solid that was recrystallised from EtOAc to give *phosphine oxide* **3f** (0.78 g, 85%) as white needles. mp 171-173 °C (from EtOAc); R_f 0.50 (EtOAc); *m/z* (+ESI) found: MNa^+, 459.1505. ($C_{29}H_{25}O_2PNa$ requires *M*, 459.1490); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1673 (C=O), 1438 (P-Ph) and 1189 (P=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.83-7.66 (6H, m, Ph), 7.46-7.08 (14H, m, Ph), 6.36 (1H, d, *J*

11.5, CH=C*H*Ph), 5.51 (1H, dt, *J* 11.5 and 7.5, C*H*=CHPh), 4.58 (1H, ddd, *J* 15.0, 11.0 and 3.5, PCH), 3.26-3.14 (1H, m, CH_aH$_b$) and 3.04-2.93 (1H, m, CH$_a$$H_b$); ^{31}P NMR (162 MHz; $CDCl_3$) δ 29.5; ^{13}C NMR (100 MHz; $CDCl_3$) δ 197.4 (d, *J* 3.0, C1), 138.0 (d, *J* 0.5, *ipso*-PhC=O), 136.6 (*ipso*-*Ph*CH=CH), 133.0 (C5), 132.0 (×2) (d, *J* 2.5, *para*-PhP and d, *J* 2.5, *para*-PhP), 131.7 (d, *J* 9.5, *ortho*-PhP), 131.4 (×2) (d, *J* 9.0, *ortho*-PhP and Ph), 131.0 (d, *J* 99.0, *ipso*-PhP), 130.6 (d, *J* 100.0, *ipso*-PhP), 128.5-128.2 (m), 126.9 (Ph and C4), 52.2 (d, *J* 56.0, C2) and 27.2 (C3); (Found: C, 78.94; H, 5.82. $C_{29}H_{25}O_2P$·0.25 H_2O requires C, 78.99; H, 5.83%).

2-Diphenylphosphinoyl-1-phenyl-pent-4-en-1-one 3g

By method **2a** phosphine oxide **2d** (0.30 g, 0.94 mmol) after 48 hours gave a white solid. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 50-100% EtOAc in hexanes (v/v) – 10% increments; 1-10% MeOH in EtOAc (v/v) – 1% increments] gave *phosphine oxide* **3g** (0.25 g, 74%) as a white solid. mp 150-153 °C (from EtOAc, hexanes, MeOH); R_f 0.55 (EtOAc); *m/z* (+ESI) found: MNa$^+$, 383.1176. ($C_{23}H_{21}O_2PNa$ requires *M*, 383.1177); IR ν_{max}(CH_2Cl_2)/cm^{-1} 1675 (C=O), 1438 (P-Ph) and 1191 (P=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.94-7.89 (2H, m, Ph), 7.76-7.69 (4H, m, Ph), 7.49-7.40 (5H, m, Ph), 7.36-7.28 (4H, m, Ph), 5.68 (1H, ddt, *J* 17.0, 10.0 and 7.0, C*H*=CH_2), 4.98 (1H, br dq, *J* 17.0 and 1.5, CH=CH_aH$_b$), 4.91 (1H, br dq, *J* 10.0 and 0.5, CH=CH$_a$$H_b$), 4.62 (1H, ddd, *J* 16.5, 11.5 and 3.0, PC*H*), 3.03-2.93 (1H, m, CH_aH$_b$CH=CH_2) and 2.71-2.63 (1H, m, CH$_a$$H_b$CH=$CH_2$); ^{31}P NMR (162 MHz; $CDCl_3$) δ 29.7; ^{13}C NMR (100 MHz; $CDCl_3$) δ 197.3 (d, *J* 2.5, C2), 138.1 (*ipso*-PhC=O), 134.6, 133.6, 133.0 (PhC=O and C4), 132.1 (d, *J* 3.0, *para*-PhP), 132.0 (d, *J* 2.5, *para*-PhP), 131.9 (d, *J* 9.5, *ortho*-PhP), 131.5 (d, *J* 9.0, *ortho*-PhP), 131.2, 131.1, 129.3, 128.7 (PhC=O and C4), 131.0 (d, *J* 99.5, *ipso*-PhP), 130.4 (d, *J* 99.5, *ipso*-PhP), 128.5 (d, *J* 11.5, *meta*-PhP), 128.4 (×2) (d, *J* 11.0, *meta*-PhP, PhC=O and C4), 117.4 (C5), 51.7 (d, *J* 56.0, C2) and 32.4 (C3).

1,3-Diphenyl-2-diphenylphosphinoyl-propan-1-one 3h

By method **2a** phosphine oxide **2d** (0.20 g, 0.62 mmol) after 28 hours gave a white solid. Purification 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] gave ketone **3h** (0.19 g, 75%) as a white powder. mp 208-210 °C (Transition 203-204 ^{o}C) (from EtOAc, hexanes, MeOH) (lit., [5] 202-204 °C, EtOAc); R_f = 0.50 (EtOAc); *m/z* (+EI) found: M$^+$, 410.1446. ($C_{27}H_{23}O_2P$ requires *M*, 410.1436); IR ν_{max}($CHCl_3$)/cm^{-1} 1672 (C=O), 1438 (P-Ph) and 1186 (P=O); ^{1}H NMR (400 MHz;

$CDCl_3$) δ 7.96-7.91 (2H, m, Ph), 7.79-7.74 (2H, m, Ph), 7.49-7.33 (10H, m, Ph), 7.20-7.06 (6H, m, Ph), 4.81 (1H, ddd, *J* 16.0, 11.5 and 2.5, PCH), 3.55 (1H, ddd, *J* 14.0, 11.5 and 5.0, CH_aH$_b$) and 3.25 (1H, ddd, *J* 14.0, 10.5 and 2.5, CH$_a$$H_b$); ^{31}P NMR (162 MHz; $CDCl_3$) δ 29.5; ^{13}C NMR (100 MHz; $CDCl_3$) δ 197.6 (d, *J* 2.5, C1), 139.1 (d, *J* 13.5, *ipso*-Ph), 138.4 (d, *J* 1.0, *ipso*-Ph), 132.7 (*para*-PhC=O), 132.2 (d, *J* 3.0, *para*-PhP), 132.1 (d, *J* 3.0, *para*-PhP), 131.9 (d, *J* 9.0, *ortho*-PhP), 131.5 (d, *J* 9.0, *ortho*-PhP), 131.0 (d, *J* 99.0, *ipso*-PhP), 130.4 (d, *J* 100.0, *ipso*-PhP), 128.6 (×2) (Ph), 128.5 (×2) (d, *J* 11.5, *meta*-PhP and d, *J* 11.5, *meta*-PhP), 128.2 (×2), 126.6 (Ph), 54.5 (d, *J* 54.5, C2) and 34.1 (d, *J* 1.5, C3); (Found: C, 78.17; H, 5.72. $C_{27}H_{23}O_2P$·0.25 H_2O requires C, 78.15; H, 5.71%). The data above are in agreement with that which has been previously reported.[5]

2-Diphenylphosphinoyl-1,4-diphenyl-butane-1,4-dione 3i

By method **2a** phosphine oxide **2d** (0.30 g, 0.94 mmol) after 27 hours gave a yellow gum. Purification 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] gave ketone **3i** (0.35 g, 86%) as yellow needles. mp 155-156 °C (from EtOAc, hexanes, MeOH); R_f 0.50 (EtOAc); *m/z* (+ESI) found: MNa$^+$, 461.1278. ($C_{28}H_{23}O_3PNa$ requires *M*, 461.1283); IR ν_{max}($CHCl_3$)/cm^{-1} 1676 (C=O), 1438 (P-Ph) and 1195 (P=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.90-7.89 (2H, m, Ph), 7.80-7.75 (6H, m, Ph), 7.48-7.30 (10H, m, Ph), 7.25-7.22 (2H, m, Ph), 5.29 (1H, ddd, *J* 14.5, 11.0 and 2.0, PCH), 4.29 (1H, ddd, *J* 18.5, 11.0 and 4.5, CH_aH$_b$) and 3.55 (1H, ddd, *J* 18.5, 9.0 and 2.0, CH$_a$$H_b$); ^{31}P NMR (162 MHz; $CDCl_3$) δ 29.2; ^{13}C NMR (100 MHz; $CDCl_3$) δ 196.9, 196.8 (C1 and C4), 138.2, 135.8 (*ipso*-PhC=O), 133.6, 132.6 (PhC=O), 132.3 (d, *J* 2.5, *para*-PhP), 132.2 (d, *J* 2.5, *para*-PhP), 131.7 (d, *J* 9.5, *ortho*-PhP), 131.3 (d, *J* 9.0, *ortho*-PhP), 131.1 (PhC=O), 130.7 (d, *J* 100.0, *ipso*-PhP), 130.2 (d, *J* 100.5, *ipso*-PhP), 129.2 (PhC=O), 128.7 (Ph), 128.6-128.5 (m, Ph), 128.4, 128.2, 128.1 (Ph), 46.4 (d, *J* 57.0, C2) and 37.6 (C3); (Found: C, 76.32; H, 5.42. $C_{28}H_{23}O_3P$·0.50 H_2O requires C, 76.16; H, 5.41%). The synthesis of phosphine oxide **3i** has been reported previously with no characterisation.[12]

***tert*-Butyl 3-diphenylphosphinoyl-4-oxo-4-phenyl-butanoate 3j**

By method **2a** phosphine oxide **2d** (0.30 g, 0.94 mmol) after 28 hours gave a white flaky solid. Purification 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] gave *phosphine oxide* **3j** (0.35 g, 84%) as a white powder. mp 167-168 °C (from EtOAc, hexanes, MeOH); R_f 0.60 (EtOAc); *m/z*

(+ESI) found: MNa^+, 457.1540. ($C_{26}H_{27}O_4PNa$ requires *M*, 457.1545); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1726 (ester C=O), 1677 (ketone C=O), 1439 (P-Ph) and 1154 (P=O); ^1H NMR (400 MHz; $CDCl_3$) δ 7.86-7.81 (2H, m, Ph), 7.75-7.72 (2H, m, Ph), 7.71-7.66 (2H, m, Ph), 7.50-7.45 (2H, m, Ph), 7.43-7.37 (4H, m, Ph), 7.33-7.29 (2H, m, Ph), 7.24-7.22 (1H, m, Ph), 5.03 (1H, ddd, *J* 17.5, 11.5 and 3.0, PCH), 3.32 (1H, ddd, *J* 17.5, 11.5 and 5.0, CH_aH_b), 2.82 (1H, ddd, *J* 18.0, 9.5 and 2.5, CH_aH_b) and 1.29 [9H, s, $C(CH_3)_3$]; ^{31}P NMR (162 MHz; $CDCl_3$) δ 28.6; ^{13}C NMR (125 MHz; $CDCl_3$) δ 197.0 (C4), 170.3 (d, *J* 16.5, C1), 138.1 (*ipso*-PhC=O), 132.7 (*para*-PhC=O), 132.2 (d, *J* 2.5, *para*-PhP), 132.2 (d, *J* 2.5, *para*-PhP), 131.8 (d, *J* 9.5, *ortho*-PhP), 131.4 (d, *J* 9.5, *ortho*-PhP), 130.4 (d, *J* 100.0, *ipso*-PhP), 130.0 (d, *J* 100.5, *ipso*-PhP), 128.6 (*ortho*- or *meta*-PhC=O), 128.5 (×2) (d, *J* 12.0, *meta*-PhP and d, *J* 12.0, *meta*-PhP); 128.2 (*ortho*- or *meta*-PhC=O), 81.6 [$C(CH_3)_3$], 47.8 (d, *J* 56.0 (C3), 33.8 (C2) and 27.9 [$C(CH_3)_3$]; (Found: C, 71.43; H, 6.26. $C_{26}H_{27}O_4P{\cdot}0.25\ H_2O$ requires C, 71.14; H, 6.31%).

2-Diphenylphosphinoyl-1-phenyl-tetradecan-1-one 3l

By method **2b** phosphine oxide **2d** (0.30 g, 0.94 mmol) after 48 hours at 80 °C gave a brown viscous liquid. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 3 × hexanes; 40-100% EtOAc in hexanes (v/v) – 10% increments; 1-10% MeOH in EtOAc (v/v) – 1% increments] gave *ketone* **3l** (0.33 g, 71%) as a white waxy solid. mp 41-46 °C (from EtOAc, hexanes, MeOH); R_f 0.75 (EtOAc); *m/z* (+ESI) found: MNa^+, 511.2767. ($C_{32}H_{41}O_2PNa$ requires *M*, 511.2742); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 2923 (CH), 2853 (CH), 1675 (C=O), 1438 (P-Ph) and 1189 (P=O); ^1H NMR (400 MHz; $CDCl_3$) δ 7.93–7.88 (2H, m, *ortho*-PhP), 7.78-7.76 (2H, m, *ortho*-PhC=O), 7.72-7.67 (2H, m, *ortho*-PhP), 7.49-7.37 (6H, m, Ph), 7.34-7.28 (3H, m, Ph), 4.51 (1H, ddd, *J* 16.5, 11.0 and 3.0, PCH), 1.97-1.86 (1H, m, $PCHCH_aH_b$), 1.54 (1H, m, $PCHCH_aH_b$), 1.25-1.11 (20H, m, 10 × CH_2) and 0.87 (3H, t, *J* 7.0, CH_3); ^{31}P NMR (162 MHz; $CDCl_3$) δ 29.9; ^{13}C NMR (100 MHz; $CDCl_3$) δ 198.2 (C1), 138.2 (*ipso*-PhC=O), 133.0 (*para*-PhC=O), 132.0-131.8 (m, Ph), 131.6-131.4 (m, Ph), 130.9 (br. s, Ph), 130.7 (d, *J* 99.5, *ipso*-PhP), 129.1, 129.0 (Ph), 128.5-128.4 (m, Ph), 128.0 (d, *J* 12.0, *meta*-PhP), 52.4 (d, *J* 57.0, C2), 32.8, 31.9, 29.6-28.5 (C4 to C12), 25.7, 25.4 (C3 and C13) and 14.1 (C14).

(*E*)-2-Diphenylphosphinoyl-1-furan-2-yl-5-phenyl-pent-4-en-1-one 3m

By method **2a** phosphine oxide **2e** (100 mg, 0.32 mmol) after 19 hours gave a brown solid. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 4 × hexanes; 50-100% EtOAc in

hexanes (v/v) – 10% increments; 2.5-25% MeOH in EtOAc (v/v) – 2.5% increments] to give *phosphine oxide* **3m** (114 mg, 83%) as a white amorphous solid. mp 193-194 °C (from MeOH, hexanes, EtOAc); R_f 0.30 (20% hexanes in EtOAc, v/v); *m/z* (+EI) found: M^+, 426.1369. ($C_{27}H_{23}O_3P$ requires *M*, 426.1385); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1663 (C=O), 1464 (C-O), 1438 (P-Ph) and 1188 (P=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.96-7.91 (2H, m, *ortho*-PhP), 7.82-7.77 (2H, m, *ortho*-PhP), 7.52-7.38 (6H, m, Ph), 7.37 (1H, dd, *J* 1.5 and 0.5 C5'-CH), 7.24-7.13 (5H, m, Ph), 7.07 (1H, dd, *J* 3.5 and 0.5, C3'-CH), 6.36 (1H, br d, *J* 15.5, CH=C*H*Ph), 6.35 (1H, dd, *J* 3.5 and 1.5, C4'-CH), 6.04 (1H, dt, *J* 15.5 and 7.0, C*H*=CHPh), 4.53 (1H, ddd, *J* 16.0, 11.0 and 3.5, PCH), 3.17-3.07 (1H, m, CH_aH$_b$) and 2.87-2.78 (1H, m, CH$_a$$H_b$); ^{31}P NMR (162 MHz; $CDCl_3$) δ 29.3; ^{13}C NMR (100 MHz; $CDCl_3$) δ 184.8 (d, *J* 2.0, C1), 153.0 (d, *J* 1.5, C2'), 146.7 (C5'), 136.9 (*ipso*-Ph), 132.5 (C5), 132.1 (d, *J* 3.0, *para*-PhP), 132.0 (d, *J* 3.0, *para*-PhP), 131.8 (d, *J* 9.5, *ortho*-PhP), 131.3 (d, *J* 9.0, *ortho*-PhP), 131.2 (d, *J* 99.5, *ipso*-PhP), 130.4 (d, *J* 100.0, *ipso*-PhP), 128.5 (×2) (d, *J* 12.0, *meta*-PhP and d, *J* 12.0, *meta*-PhP), 128.4, 127.3, 126.3, 126.1 (C4 and Ph), 118.4, 112.7 (C3' and C4'), 52.2 (d, *J* 55.0, C2) and 30.8 (C3); (Found: C, 75.14; H, 5.50. $C_{27}H_{23}O_3P{\cdot}0.25\ H_2O$ requires C, 75.25; H, 5.50%).

(*E*)-3-Diphenylphosphinoyl-6-phenyl-hex-5-en-2-one 3n

By method **2a** phosphine oxide **2a** (0.20 g, 0.77 mmol) after 6 hours gave a white solid. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 50-100% EtOAc in hexanes (v/v) – 10% increments; 1-15% MeOH in EtOAc (v/v) – 1% increments] gave *phosphine oxide* **3n** (0.25 g, 87%) as a white powder. mp 184-186 °C (from EtOAc, hexanes, MeOH); R_f 0.45 (EtOAc); *m/z* (+ESI) found: MNa^+, 397.1347. ($C_{24}H_{23}O_2PNa$ requires *M*, 397.1333); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1701 (C=O), 1437 (P-Ph) and 1181 (P=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.88-7.79 (4H, m, *ortho*-PhP), 7.58-7.48 (6H, m, *meta*- and *para*-PhP), 7.28-7.17 (5H, m, Ph), 6.36 (1H, d, *J* 15.5, PhC*H*=CH), 5.99 (1H, dt, *J* 15.5 and 7.0, PhCH=C*H*), 3.75 (1H, ddd, *J* 15.0, 11.5 and 3.5, PCH), 3.07-2.96 (1H, m, CH_aH$_b$), 2.65-2.56 (1H, m, CH$_a$$H_b$) and 2.18 (3H, s, CH_3); ^{31}P NMR (162 MHz; $CDCl_3$) δ 28.8; ^{13}C NMR (100 MHz; $CDCl_3$) δ 204.6 (d, *J* 2.0, C2), 136.6 (*ipso*-Ph), 132.6 (Ph), 132.3 (×2) (d, *J* 3.0, *para*-PhP and d, *J* 3.0, *para*-PhP), 131.3 (d, *J* 9.5, *ortho*-PhP), 131.2 (d, *J* 9.0, *ortho*-PhP), 130.9 (×2) (d, *J* 99.5, *ipso*-PhP and d, *J* 100.0, *ipso*-PhP), 128.9 (d, *J* 12.0, *meta*-PhP), 128.8 (d, *J* 12.0, *meta*-PhP), 128.5, 127.5, 126.2, 125.8, 125.7 (Ph, C5 and C6), 57.2 (d, *J* 54.5, C3), 31.1 (C1) and 30.0 (d, *J* 2.0, C4); (Found: C, 76.41; H, 6.19. $C_{24}H_{23}O_2P{\cdot}0.25\ H_2O$ requires C, 76.07; H, 6.25%).

3-Diphenylphosphinoyl-4-phenyl-butane-2-one 3o

By method **2a** phosphine oxide **2a** (0.30 g, 1.16 mmol) after 27 hours gave a yellow solid. Purification 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] gave ketone **3o** (0.29 g, 72%) as a white powder. mp 189-192 °C (from EtOAc, hexanes, MeOH) (lit.,[13] 167 ± 1 °C, Et_2O); R_f = 0.50 (EtOAc); *m/z* (+ESI) found: MNa^+, 371.1161. ($C_{22}H_{21}O_2PNa$ requires *M*, 371.1177); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1707 (C=O), 1438 (P-Ph) and 1188 (P=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.92-7.82 (4H, m, Ph), 7.59-7.48 (6H, m, Ph), 7.24-7.14 (3H, m, Ph), 7.07-7.04 (2H, m, Ph), 3.98 (1H, td, *J* 12.0 and 3.0, MeCOC*H*), 3.40 (1H, ddd, *J* 14.5, 11.5 and 5.5, CH_aH$_b$), 3.02 (1H, br ddd, *J* 14.0, 10.5 and 3.5, CH$_a$$H_b$) and 2.02 (3H, s, CH_3); ^{31}P NMR (162 MHz; $CDCl_3$) δ 29.0; ^{13}C NMR (125 MHz; $CDCl_3$) δ 204.5 (d, *J* 2.5, C2), 138.4 (d, *J* 13.5, *ipso*-Ph), 132.4 (d, *J* 2.5, *para*-PhP), 132.3 (d, *J* 3.0, *para*-PhP), 131.4 (d, *J* 9.5, *ortho*-PhP), 131.3 (d, *J* 9.5, *ortho*-PhP), 130.9 (d, *J* 100.0, *ipso*-PhP), 130.8 (d, *J* 99.0, *ipso*-PhP), 128.9 (d, *J* 12.0, *meta*-PhP), 128.8 (d, *J* 12.0, *meta*-PhP), 128.7, 128.3, 126.8 (Ph), 58.8 (d, *J* 54.0, C3), 32.4 (d, *J* 2.0, C4) and 31.7 (C1); (Found: C, 75.70; H, 6.13. $C_{22}H_{21}O_2P$ requires C, 75.85; H, 6.08%). The data above are in agreement with that which has been previously reported.[13]

(*E*)-4-Diphenylphosphinoyl-1,7-diphenyl-hept-6-en-3-one 3r

By method **2a** phosphine oxide **2f** (0.57 g, 1.6 mmol) after 5 hours gave a white solid. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 50-100% EtOAc in hexanes (v/v) – 10% increments; 5-35% MeOH in EtOAc (v/v) – 5% increments] gave *phosphine oxide* **3r** (0.71 g, 95%) as a white amorphous solid. mp 173-174 °C (from EtOAc, hexanes, MeOH); R_f 0.30 (50% EtOAc in hexanes, v/v); *m/z* (+EI) found: M^+, 464.1917. ($C_{31}H_{29}O_2P$ requires *M*, 464.1905); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1706 (C=O), 1438 (P-Ph) and 1189 (P=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.88-7.71 (m, 5H, Ph), 7.58-7.45 (m, 6H, Ph), 7.28-7.09 (m, 7H, Ph), 7.02-7.00 (m, 2H, Ph), 3.77 (ddd, *J* 13.0, 11.5 and 3.5, 1H, PCH), 3.03-2.93 (m, 1H, CH_2) and 2.87-2.55 (m, 5H, CH_2); ^{31}P NMR (162 MHz; $CDCl_3$) δ 28.8; ^{13}C NMR (100 MHz; $CDCl_3$) δ 205.6 (d, *J* 2.5, C3), 140.6 (*ipso*-PhCH$_2$), 136.6 (*ipso*-*Ph*CH=CH), 132.3 (d, *J* 2.5, *para*-PhP), 132.2 (d, *J* 2.5, *para*-PhP), 132.6 (Ph), 131.4 (d, *J* 9.0, *ortho*-PhP), 131.3 (d, *J* 9.0, *ortho*-PhP), 130.9 (d, *J* 99.0, *ipso*-PhP), 130.8 (d, *J* 101.0, *ipso*-PhP), 128.8 (×2) (d, *J* 12.0, *meta*-PhP and d, *J* 12.0, *meta*-PhP), 128.5, 128.3 (×2), 127.5, 126.2, 126.0, 125.9, 125.8, 125.7 (Ph, C6 and C7), 56.8 (d, *J* 54.5, C4), 45.8 (C2), 30.2 (d, *J* 1.0)

and 29.1 (C1 and C5); (Found: C, 78.63; H, 6.25. $C_{31}H_{29}O_2P \cdot 0.50\ H_2O$ requires C, 78.63; H, 6.39%).

(*E*)-4-Diphenylphosphinoyl-1,7-diphenyl-hept-6-en-3-one 3r

By method **4** phosphine oxide **3n** (0.20 g, 0.5 mmol) after 4 hours gave a white solid. Purification 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] gave *phosphine oxide* **3r** (0.13 g, 52%) as a white amorphous solid. All analytical data were identical with that reported above.

(4*RS*,6*RS*)-(*E*)-6-Diphenylphosphinoyl-4-methyl-1-phenyl-nona-1,8-dien-5-one 3s

By method **1a** phosphine oxide **7c** (0.30 g, 0.77 mmol) after 3 days gave a yellow solid. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 0-100% EtOAc in hexanes (v/v) – 10% increments; 5 × EtOAc] gave *phosphine oxide* **3s** (0.22 g, 82%) as white needles, d.r. 54:46. R_f 0.40 (70% EtOAc in hexanes, v/v); *m/z* (+EI) found: MNa^+, 451.1178. ($C_{28}H_{29}O_2PNa$ requires *M*, 451.1803); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1706 (C=O), 1438 (P-Ph) and 1191 (P=O); ^{1}H NMR (500 MHz; $CDCl_3$) Two diastereoisomers A: major isomer, B: minor isomer. δ 7.88-7.82 (m, Ph A,B), 7.74-7.68 (m, Ph A,B), 7.55-7.43 (m, Ph A,B), 7.40-7.36 (m, Ph A,B), 7.28-7.25 (m, Ph A,B), 7.19-7.15 (m, Ph A,B), 6.31 (1H, d, *J* 16.0, CH=C*H*Ph B), 6.23 (1H, d, *J* 16.0, CH=C*H*Ph A), 5.99 (1H, dt, *J* 15.5 and 7.5, C*H*=CHPh B), 5.87 (1H, dt, *J* 16.0 and 7.5, C*H*=CHPh A), 5.64-5.56 (2 × 1H, m, C*H*=CH_2 A,B), 5.00-4.90 (2 × 2H, m, CH=CH_2 A,B), 3.97-3.90 (2 × 1H, m, PCH A,B), 2.82-2.69 (m A,B), 2.64-2.58 (m A,B), 2.41-2.32 (m A,B), 2.27-2.22 (m A,B), 2.06-2.00 (m A,B), 0.98 (3H, d, *J* 7.0, CH_3 A) and 0.81 (3H, d, *J* 6.5, CH_3 B); ^{31}P NMR (162 MHz; $CDCl_3$) δ 30.1 and 29.9; ^{13}C NMR (126 MHz; $CDCl_3$) Two diastereoisomers A: major isomer, B: minor isomer. δ 209.0 (d, *J* 2.5), 208.7 (d, *J* 2.5) (C5 A,B), 137.3, 137.0 (*ipso*-Ph A,B), 134.8 (d, *J* 11.5), 134.7 (d, *J* 12.0) (C8 A,B), 132.4-131.4 (m, Ph A,B), 130.9 (d, *J* 99.5), 130.8 (d, *J* 99.5), 130.5 (d, *J* 99.0), 130.3 (d, *J* 99.0) (*ipso*-PhP A,B), 128.7-125.9 (m, Ph A,B), 117.6, 117.5 (C9 A,B), 55.8 (d, *J* 54.5), 55.0 (d, *J* 54.0) (C6 A,B), 47.5 (×2) (C4 A,B), 35.8 (×2) (C3 A,B), 31.6, 31.4 (C7 A,B), 15.8 (CH_3 A) and 14.5 (CH_3 B); (Found: C, 76.48; H, 6.68. $C_{28}H_{29}O_2P \cdot 0.50\ H_2O$ requires C, 76.87; H, 6.91%).

(*E*)-3-Diphenylphosphinoyl-3-methyl-6-phenyl-hex-5-en-2-one 4b

By method **2a** phosphine oxide **3a** (0.10 g, 0.37 mmol) after 3½ hours gave a yellow solid. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 10-100% EtOAc in hexanes (v/v) –

10% increments; 2.5-15% MeOH in EtOAc (v/v) – 2.5% increments] gave *phosphine oxide* **4b** (0.14 g, 97%) as white needles. mp 124-125 °C (from EtOAc, hexanes, MeOH); R_f 0.30 (50% EtOAc in hexanes, v/v); *m/z* (+EI) found: M^+, 388.1597. ($C_{25}H_{25}O_2P$ requires *M*, 388.1592); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1698 (C=O), 1437 (P-Ph) and 1187 (P=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.95-7.90 (2H, m, *ortho*-PhP), 7.87-7.82 (2H, m, *ortho*-PhP), 7.59-7.46 (6H, m, *meta*- and *para*-PhP), 7.28-7.17 (5H, m, Ph), 6.39 (1H, d, *J* 15.5, PhC*H*=CH), 5.90 (1H, dt, *J* 15.5 and 6.0, PhCH=C*H*), 3.39 (1H, dt, *J* 14.0 and 7.0, CH_aH_b), 2.56-2.49 (1H, m, CH_aH_b), 2.22 (3H, s, CH_3C=O) and 1.46 (3H, d, *J* 15.5, CH_3CP); ^{31}P NMR (162 MHz; $CDCl_3$) δ 32.9; ^{13}C NMR (125 MHz; $CDCl_3$) δ 208.3 (C2), 136.7 (*ipso*-Ph), 134.5 (Ph), 132.3 (d, *J* 8.5, *ortho*-PhP), 132.2 (×2) (br. s, *para*-PhP and d, *J* 8.5, *ortho*-PhP), 130.3 (×2) (d, *J* 96.0, *ipso*-PhP and d, *J* 95.5, *ipso*-PhP), 128.6 (d, *J* 11.5, *meta*-PhP), 128.5 (×2) (d, *J* 11.5, *meta*-PhP), 127.5 (×2), 126.2, 123.2, 123.1 (Ph, C5 and C6), 57.3 (d, *J* 56.0, C3), 37.4 (C4), 29.7 (C1) and 29.7 (PC*C*H_3); (Found: C, 76.62; H, 6.50. $C_{25}H_{25}O_2P \cdot 0.25\ H_2O$ requires C, 76.42; H, 6.54%).

(*E*)-4-Diphenylphosphinoyl-4-methyl-7-phenyl-hept-6-en-3-one 4c

By method **2a** phosphine oxide **3b** (0.30 g, 1.05 mmol) after 24 hours gave a yellow gum. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 10-100% EtOAc in hexanes (v/v) – 10% increments; 5-50% MeOH in EtOAc (v/v) – 5% increments] gave *phosphine oxide* **4c** (0.34 g, 81%) as a yellow gum. R_f 0.55 (EtOAc); *m/z* (+ESI) found: MNa^+, 425.1650. ($C_{26}H_{27}O_2PNa$ requires *M*, 425.1646); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1698 (C=O), 1438 (P-Ph) and 1183 (P=O); ^{1}H NMR (400 MHz;$CDCl_3$) δ 7.96-7.91 (2H, m, *ortho*-PhP), 7.84-7.78 (2H, m, *ortho*-PhP), 7.55-7.44 (6H, m, *meta*- and *para*-PhP), 7.26-7.15 (5H, m, Ph), 6.36 (1H, d, *J* 15.5, PhC*H*=CH), 5.87 (1H, dt, *J* 15.5 and 7.5, PhCH=C*H*), 3.35 (1H, dt, *J* 14.5 and 7.0, CH_aH_bC=O), 2.66-2.40 (3H, m, CH_aH_bC=O and CH_2CH=CH), 1.46 (3H, d, *J* 15.5, CH_3CP) and 0.81 (3H, t, *J* 7.0, CH_2CH_3); ^{31}P NMR (162 MHz; $CDCl_3$) δ 33.0; ^{13}C NMR (100 MHz; $CDCl_3$) δ 210.8 (C3), 136.8 (*ipso*-Ph), 134.4 (Ph), 132.2 (d, *J* 8.5, *ortho*-PhP), 132.1 (×2) (d, *J* 8.5, *ortho*-PhP and d *J* 3.0, *para*-PhP), 132.0 (d, *J* 3.0, *para*-PhP), 130.6 (d, *J* 95.5, *ipso*-PhP), 130.4 (d, *J* 95.5, *ipso*-PhP), 128.5 (d, *J* 11.5, *meta*-PhP), 128.4 (×2) (Ph and d, *J* 11.5, *meta*-PhP), 127.4, 126.1, 123.5, 123.3 (Ph, C6 and C7), 56.9 (d, *J* 56.0, C4), 37.6, 34.9 (C2 and C5), 17.7 and 7.7 (C1 and C4-CH_3).

(*E*)-4-Diphenylphosphinoyl-2,4-dimethyl-7-phenyl-hept-6-en-3-one 4d

By method **2a** phosphine oxide **3c** (0.30 g, 1.0 mmol) after 24 hours gave a brown gum. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 10-100% EtOAc in hexanes (v/v) – 10% increments; 2.5-20% MeOH in EtOAc (v/v) – 2.5% increments] gave *phosphine oxide* **4d** (0.34 g, 80%) as white needles. mp 133-135 °C (from EtOAc, hexanes, MeOH); R_f 0.55 (EtOAc); *m/z* (+ESI) found: MNa^+, 439.1805. ($C_{27}H_{29}O_2PNa$ requires *M*, 439.1803); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1694 (C=O), 1437 (P-Ph) and 1185 (P=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.02-7.97 (2H, m, *ortho*-PhP), 7.85-7.79 (2H, m, *ortho*-PhP), 7.58-7.43 (6H, m, *meta*- and *para*-PhP), 7.27-7.16 (5H, m, Ph), 6.33 (1H, d, *J* 15.5, PhC*H*=CH), 5.88 (1H, dt, *J* 15.5, 8.0 and 6.5, PhCH=C*H*), 3.32 (1H, dt, *J* 14.0 and 7.0, C$H_a$$H_b$CH=CH), 3.24 [1H, sept., *J* 6.5, C*H*$(CH_3)_2$], 2.51 (1H, dtd, *J* 14.0, 8.5 and 1.0, CH$_a$*H*$_b$CH=CH), 1.57 (3H, d, *J* 15.5, C4-CH_3), 0.88 (3H, d, *J* 6.5, C2-CH_{3a}) and 0.80 (3H, d, *J* 6.5, C2-CH_{3b}); ^{31}P NMR (162 MHz; $CDCl_3$) δ 33.9; ^{13}C NMR (100 MHz; $CDCl_3$) δ 215.3 (C3), 136.9 (*ipso*-Ph), 134.3 (Ph), 132.5 (d, *J* 8.5, *ortho*-PhP), 132.3 (d, *J* 9.0, *ortho*-PhP), 132.1 (d *J* 3.0, *para*-PhP), 132.0 (d, *J* 3.0, *para*-PhP), 131.0 (d, *J* 95.5, *ipso*-PhP), 130.7 (d, *J* 95.0, *ipso*-PhP), 128.5 (×2) (d, *J* 11.0, *meta*-PhP and Ph), 128.4 (d, *J* 11.5, *meta*-PhP), 127.4, 126.1, 123.9, 123.8 (Ph, C6 and C7), 57.6 (d, *J* 56.5, C4), 38.0 (C5), 37.7 (C2), 19.9, 19.6 [CH(*C*$H_3)_2$] and 17.5 (C4-CH_3). (Found: C, 77.43; H, 7.07. $C_{27}H_{29}O_2P$·0.10 EtOAc requires C, 77.38; H, 7.06%).

(*E*)-4-Acetyl-4-diphenylphosphinoyl-1-phenylhepta-1,6-diene 4e

By method **2a** phosphine oxide **3n** (0.50 g, 1.34 mmol) after 3 days gave a yellow solid. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 0-100% EtOAc in hexanes (v/v) – 10% increments] gave *phosphine oxide* **4e** (0.30 g, 54%) as a yellow gum. R_f 0.40 (EtOAc); *m/z* (+EI) found: M^+, 414.1739. ($C_{27}H_{27}O_2P$ requires *M*, calcd 414.1749); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1698 (C=O), 1438 (P-Ph) and 1185 (P=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.94-7.90 (4H, m, *ortho*-PhP), 7.55-7.45 (6H, m, *meta*- and *para*-PhP), 7.27-7.14 (5H, m, Ph), 6.31 (1H, d, *J* 16.0, CH=C*H*Ph), 5.95 (1H, dt, *J* 15.5 and 7.5, C*H*=CHPh), 5.68 (1H, ddt, *J* 17.0, 10.0 and 7.0, C*H*=CH_2), 5.09-5.03 (2H, m, CH=CH_2), 3.11-2.98 (3H, m), 2.90-2.81 (1H, m) (2 × CH_2CP) and 2.07 (3H, s, CH_3); ^{31}P NMR (162 MHz; $CDCl_3$) δ 30.4; ^{13}C NMR (100 MHz; $CDCl_3$) δ 207.9 (C=O), 137.0 (*ipso*-Ph), 133.9 (Ph), 132.8 (d, *J* 9.5, *ortho*-PhP), 132.3 (d, *J* 8.5, *ortho*-PhP), 132.1 (×2) (d, *J* 2.5, *para*-PhP and d, *J* 3.0, *para*-PhP), 131.0 (d, *J* 95.0, *ipso*-PhP), 130.9 (d, *J* 94.5, *ipso*-PhP), 128.6 (d, *J* 12.0, *meta*-PhP), 128.5 (d, *J* 11.5, *meta*-PhP), 128.4, 127.3, 126.1, 124.6 (×2) (C1, C2, C6 and Ph), 119.3 (C7), 61.2 (d, *J* 54.0, C4), 35.6, 34.7 (C3 and C5) and 29.8 (CH_3).

(*E*)-4-Diphenylphosphinoyl-7-methyl-1-phenyl-4-(3'-phenyl-prop-2'-en-yl)-oct-6-en-3-one 4f

By method **2a** phosphine oxide **3r** (0.30 g, 0.65 mmol) after 3 days gave a yellow solid. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 5-50% EtOAc in hexanes (v/v) – 5% increments] gave *phosphine oxide* **4f** (0.28 g, 87%) as a yellow gum. R_f 0.50 (50% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MH^+, 533.2621. ($C_{36}H_{38}O_2P$ requires *M*, 533.2609); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1701 (C=O), 1438 (P-Ph) and 1163 (P=O); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.94-7.89 (4H, m, Ph), 7.55-7.45 (6H, m, Ph), 7.25-7.12 (8H, m, Ph), 7.02-7.00 (2H, m, Ph), 6.23 (1H, d, *J* 16.0, CH=C*H*Ph), 5.91 (1H, dt, *J* 15.5 and 7.0, C*H*=CHPh), 4.90 [1H, t, *J* 6.5, C*H*=C$(CH_3)_2$], 3.08-2.91 (3H, m), 2.86-2.74 (3H, m), 2.64-2.50 (2H, m) (4 × CH_2), 1.56 (3H, s, CH_3) and 1.49 (3H, s, CH_3); ^{31}P NMR (162 MHz; $CDCl_3$) δ 31.1; ^{13}C NMR (126 MHz; $CDCl_3$) δ 209.3 (C3), 140.9 (*ipso*-PhCH$_2$), 137.2 (*ipso*-*Ph*CH=CH), 135.2 (C7), 133.4 (CH=*C*HPh), 132.3 (×2) (d, *J* 8.5, *ortho*-PhP and d, *J* 8.5, *ortho*-PhP), 132.0 (d, *J* 2.5, *para*-PhP), 131.9 (d, *J* 2.5, *para*-PhP), 131.2 (×2) (d, *J* 94.5, *ipso*-PhP and d, *J* 94.5, *ipso*-PhP), 128.5-128.3 (m), 127.1, 126.0, 125.9 (Ph and C3'), 124.9 (d, *J* 7.5, C2'), 118.3 (C6), 61.2 (d, *J* 54.5, C4), 43.3 (C2), 34.9, 29.8, 29.7 (C1, C5 and C1'), 26.0 (CH_3) and 18.1 (CH_3).

(1-Diphenylphosphinoyl-cyclopentyl)-phenyl-methanone 4g

By method **2b** phosphine oxide **2d** (0.32 g, 1.0 mmol), sodium hydride (90 mg, 2.2 mmol, 60% in mineral oil) and 1,4-diiodobutane (0.37 g, 1.2 mmol) after 17 hours gave a brown 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; 6 × EtOAc] to give *phosphine oxide* **4g** (0.17 g, 46%) as white needles. mp 133-134 °C (from EtOAc, hexanes); R_f 0.40 (70% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 397.1328. ($C_{24}H_{23}O_2PNa$ requires *M*, 397.1333); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1662 (C=O), 1437 (P-Ph) and 1228 (P=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.04-8.02 (2H, m, *ortho*-PhC), 7.90-7.85 (4H, m, *ortho*-PhP), 7.50-7.45 (2H, m), 7.44-7.37 (5H, m), 7.32-7.27 (2H, m) (*meta*- and *para*-PhC, *meta*- and *para*-PhP), 2.79-2.70 (2H, m), 2.48-2.37 (2H, m) (2 × CH_2CC=O) and 1.46-1.33 (4H, m, CH_2CH_2); ^{31}P NMR (162 MHz; $CDCl_3$) δ 35.3; ^{13}C NMR (100 MHz; $CDCl_3$) δ 202.2 (d, *J* 2.0, C=O), 137.0 (*ipso*-PhC), 132.3 (d, *J* 8.5, *ortho*-PhP), 131.8 (×2) (*para*-PhC and d, *J* 2.9, *para*-PhP), 131.4 (d, *J* 97.5, *ipso*-PhP), 129.9 (*ortho*- or *meta*-PhC), 128.3 (d, *J* 11.5, *meta*-PhP), 127.7 (*ortho*- or *meta*-PhC), 64.2 (d, *J* 57.5, *C*C=O), 34.8 (2 × *C*H$_2$CC=O) and 25.9 (CH_2CH_2); (Found: C, 76.83; H, 6.25. $C_{24}H_{23}O_2P$ requires C, 76.99; H, 6.19%).

(*E*)-1,5-Diphenyl-pent-4-en-1-one 5a

By method **3a** phosphine oxide **3e** (0.21 g, 0.48 mmol) after 4 hr gave yellow needles. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 4 × hexanes; 2-38% EtOAc in hexanes (v/v) – 2% increments] to give ketone **5a** (0.11 g, 99%) as white needles. mp 57-59 °C (from EtOAc, hexanes) (lit.,[14] 59-60 °C); R_f = 0.45 (10% hexanes in EtOAc, v/v); *m/z* (+ESI) found: M^+, 236.1204. ($C_{17}H_{16}O$ requires *M*, 236.1201); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1684 (C=O); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.99 (2H, dt, *J* 7.5 and 1.5, *ortho*-PhC=O), 7.57 (1H, tt, *J* 7.5 and 1.5, *para*-PhC=O), 7.48 (2H, t, *J* 7.5, *meta*-PhC=O), 7.35 (2H, d, *J* 7.0, *ortho*-PhCH), 7.29 (2H, t, *J* 7.5, *meta*-PhCH), 7.20 (1H, tt, *J* 7.5 and 1.5, *para*-PhCH), 6.48 (1H, d, *J* 16.0, CH=C*H*Ph), 6.30 (1H, dt, *J* 16.0 and 7.0, C*H*=CHPh), 3.17 (2H, t, *J* 7.5, CH_2C=O) and 2.69 (2H, qd, *J* 7.0 and 1.0, CH_2CH_2C=O); ^{13}C NMR (126 MHz; $CDCl_3$) δ 199.3 (C1), 137.5, 137.0 (*ipso*-PhCH and PhC=O), 133.1, 130.8, 129.2, 128.6, 128.5, 128.1, 127.1, 126.1 (Ph, C4 and C5), 38.3 (C2) and 27.5 (C3); (Found: C, 86.09; H, 6.89. $C_{17}H_{16}O$ requires C, 86.41; H, 6.82%). The data above are in agreement with that which has been previously reported.[14]

(*E*)-6-Phenyl-hex-5-en-2-one 5b

By method **3a** phosphine oxide **3n** (0.14 g, 0.38 mmol) after 4½ hours gave a clear yellow oil. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 4 × hexanes; 2-38% EtOAc in hexanes (v/v) – 2% increments] to give ketone **5b** (61 mg, 92%) as a yellow oil. R_f = 0.25 (10% EtOAc in hexanes, v/v); *m/z* (+EI) found: M^+, 174.1047. ($C_{12}H_{14}O$ requires *M*, 174.1045); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1711 (C=O); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.33-7.18 (5H, m, Ph), 6.40 (1H, d, *J* 16.0, PhC*H*=CH), 6.19 (1H, dt, *J* 16.0 and 7.0, PhCH=C*H*), 2.6 (2H, t, *J* 7.5, CH_2C=O), 2.48 (2H, q, *J* 7.0, CH_2CH=CH) and 2.16 (3H, s, CH_3); ^{13}C NMR (126 MHz; $CDCl_3$) δ 208.0 (C2), 137.4 (*ipso*-Ph), 130.7, 128.8, 128.5, 127.1, 126.0 (Ph, C5 and C6), 43.2 (C3), 30.0 (C1) and 27.1 (C4); (Found: C, 82.82; H, 8.09. $C_{12}H_{14}O$ requires C, 82.72; H, 8.10%). The data above are in agreement with that which has been previously reported.[14,15]

4-Phenyl-butan-2-one 5c

By method **3a** phosphine oxide **3o** (0.25 g, 0.72 mmol) after 1½ hours gave a yellow liquid. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 4 × hexanes; 2-20% EtOAc in hexanes (v/v) – 2% increments; 22.5-50% EtOAc in hexanes (v/v) – 2.5% increments] to give ketone **5c** (86 mg, 86%) as a clear liquid. *m/z* (+EI) found: M^+, 148.0892. ($C_{10}H_{12}O$ requires *M*, 148.0888); IR

$\nu_{max}(CHCl_3)/cm^{-1}$ 1714 (C=O); ^1H NMR (400 MHz; $CDCl_3$) δ 7.29-7.25 (2H, m, *ortho*-Ph), 7.19-7.16 (3H, m, *meta*- and *para*-Ph), 2.89 (2H, t, *J* 7.5, CH_2), 2.75 (2H, t, *J* 7.5, CH_2) and 2.13 (3H, s, CH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 207.8 (C2), 140.9 (*ipso*-Ph), 128.4, 128.2 (*ortho*- and *meta*-Ph), 126.1 (*para*-Ph), 45.1 (C3), 30.0 (C4) and 29.7 (C1); (Found: C, 79.81; H, 8.15. $C_{10}H_{12}O \cdot 1/11$ EtOAc requires C, 79.68; H, 8.21%). The data above are in agreement with that which has been previously reported.[16]

1,3-Diphenylpropan-1-one 5d

By method **3a** phosphine oxide **3h** (0.16 g, 0.39 mmol) after 1 hour gave a grey solid. 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 ketone **5d** (79 mg, 96%) as white needles. mp 71-72 ^oC (from EtOAc, hexanes) [lit.,[17] 70-72 ^oC (ethanol)]; R_f = 0.60 (20% EtOAc in hexanes, v/v); *m/z* (+EI) found: MNa^+, 233.0940. ($C_{15}H_{14}ONa$ requires *M*, 233.0942); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1683 (C=O); ^1H NMR (400 MHz; $CDCl_3$) δ 7.98-7.95 (2H, m, *ortho*-PhC=O), 7.55 (1H, tt, *J* 7.5 and 1.5, *para*-PhC=O), 7.47-7.43 (2H, m, *meta*-PhC=O), 7.32-7.25 (4H, m, *ortho*- and *meta*-$PhCH_2$), 7.21 (1H, tt, *J* 7.0 and 1.5, *para*-$PhCH_2$), 3.31 (2H, t, *J* 8.0, CH_2C=O) and 3.07 (2H, t, *J* 7.5, C*H*$_2$Ph); ^{13}C NMR (100 MHz; $CDCl_3$) δ 199.2 (C1), 141.3 (*ipso*-PhCH), 136.9 (*ipso*-PhC=O), 133.0 (*para*-PhC=O), 128.6, 128.5, 128.4, 128.0 (Ph), 126.1 (*para*-PhCH), 40.4 (C2) and 30.1 (C3); (Found: C, 85.42; H, 6.68. $C_{15}H_{14}O$ requires C, 85.68; H, 6.71%). The data above are in agreement with that which has been previously reported.[17]

1-Phenyl-pent-4-en-1-one 5e

By method **3a** phosphine oxide **3g** (0.20 g, 0.56 mmol) after 1½ hours gave a yellow liquid. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 4 × hexanes; 2.5-40% EtOAc in hexanes (v/v) – 2.5% increments] to give ketone **5e** (80 mg, 78%) as a clear liquid. R_f = 0.65 (20% EtOAc in hexanes, v/v); *m/z* (+EI) found: M^+, 160.0887. ($C_{11}H_{12}O$ requires *M*, 160.0888); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1684 (C=O); ^1H NMR (700 MHz; $CDCl_3$) δ; 7.97-7.96 (2H, m, *ortho*-Ph), 7.57 (1H, tt, *J* 7.5 and 1.0, *para*-Ph), 7.47 (2H, br. t, *J* 8.0, *meta*-Ph), 5.91 (1H, ddt, *J* 17.0, 10.5 and 6.5, C*H*=CH_2), 5.09 (1H, br. dq, *J* 17.0 and 1.5, CH=CH_aH$_b$), 5.02 (1H, br. dq, *J* 10.0 and 1.5, CH=CH_a*H$_b$*), 3.08 (2H, t, *J* 7.5, CH_2C=O) and 2.52-2.49 (2H, m, C*H*$_2$CH=CH_2); ^{13}C NMR (175 MHz; $CDCl_3$) δ 199.4 (C1), 137.3 (C4), 136.9 (*ipso*-Ph), 133.0 (*para*-Ph), 128.6, 128.0 (*ortho*- and

meta-Ph), 115.3 (C5), 37.8 (C2) and 28.2 (C3). The data above are in agreement with that which has been previously reported.[18]

1-Phenyl-tetradecan-1-one 5f

By method **3a** phosphine oxide **3l** (0.28 g, 0.58 mmol) after 3½ hours gave a yellow solid. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 4 × hexanes; 2.5-40% EtOAc in hexanes (v/v) – 2.5% increments] to give ketone **5f** (0.12 g, 68%) as a white powder. mp 54-55 °C (from EtOAc, hexanes) (lit.,[19] 52.5 °C); R_f = 0.65 (1% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 311.2351. ($C_{20}H_{32}ONa$ requires *M*, 311.2351); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 2911 (CH), 2849 (CH) and 1685 (C=O); ^{1}H NMR (700 MHz; $CDCl_3$) δ 7.96 (2H, d, *J* 7.5, *ortho*-Ph), 7.55 (1H, t, *J* 7.5, *para*-Ph), 7.46 (2H, t, *J* 7.5, *meta*-Ph), 2.96 (2H, t, *J* 7.5, CH_2C=O), 1.73 (2H, q, *J* 7.5, CH_2CH_2C=O), 1.39-1.26 (20H, m, 10 × CH_2) and 0.88 (3H, t, *J* 7.0, CH_3); ^{13}C NMR (175 MHz; $CDCl_3$) δ 200.6 (C1), 137.1 (*ipso*-Ph), 132.9 (*para*-Ph), 128.5, 128.1 (*ortho*- and *meta*-Ph), 38.7 (C2), 31.9 (C12), 29.7 (×3), 29.6, 29.5 (×2), 29.4 (×2) (C4-C11), 24.4 (C3), 22.7 (C13) and 14.1 (C14); (Found: C, 83.38; H, 11.23. $C_{20}H_{32}O$ requires C, 83.27; H, 11.18%). The data above are in agreement with that which has been previously reported.[19]

1,4-Diphenyl-butane-1,4-dione 5g

By method **3a** phosphine oxide **3i** (0.28 g, 0.64 mmol) after 1 hour gave a yellow solid. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 4 × hexanes; 2.5-40% EtOAc in hexanes (v/v) – 2.5% increments] to give ketone **5g** (103 mg, 67%) as yellow needles. mp 149-151 °C (from EtOAc, hexanes) (lit.,[20] 151 °C); R_f = 0.60 (10% EtOAc in hexanes, v/v); *m/z* (+EI) found: M^+, 238.1003. ($C_{16}H_{14}O_2$ requires *M*, 238.0994); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1676 (C=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.05-8.03 (4H, m, *ortho*-Ph), 7.57 (2H, tt, *J* 7.5 and 1.5, *para*-Ph), 7.50-7.45 (4H, m, *meta*-Ph) and 3.46 (4H, s, 2 × CH_2); ^{13}C NMR (100 MHz; $CDCl_3$) δ 198.6 (C=O), 136.7 (*ipso*-Ph), 133.1 (*para*-Ph). 128.5, 128.0 (*ortho*- and *meta*-Ph) and 32.5 (2 × CH_2); (Found: C, 79.69; H, 6.14. $C_{16}H_{14}O_2 \cdot 1/6\ H_2O$ requires C, 79.65; H, 5.99%). The data above are in agreement with that which has been previously reported.[20]

4-Oxo-4-phenyl-butanoic acid 5h

By method **3a** phosphine oxide **3j** (0.30 g, 0.69 mmol) after 1 hour gave a yellow gum (The reaction mixture was acidified with 3 M aqueous HCl (50 cm^3) before extraction with

dichloromethane). The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 0-100% EtOAc in hexanes (v/v) – 10% increments; 2.5-25% MeOH in EtOAc (v/v) – 2.5% increments] to give ketone **5h** (95 mg, 77%) as white needles. mp 120-121 °C (from EtOAc, MeOH) (lit.,[21] 114-116 °C); R_f = 0.15 (EtOAc); *m/z* (+ESI) found: MNa^+, 201.0536. ($C_{10}H_{10}O_3Na$ requires *M*, 201.0528); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 2973 (br., O-H), 1713 (C=O) and 1682 (C=O); ^1H NMR (400 MHz; $CDCl_3$) δ 10.16 (1H, br s, OH), 7.96-7.94 (2H, m, *ortho*-Ph), 7.56 (1H, tt, *J* 7.5 and 1.5, *para*-Ph), 7.47-7.43 (2H, m, *meta*-Ph), 3.27 (2H, t, *J* 6.5, C3-H) and 2.76 (2H, t, *J* 6.5, C2-H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 198.0 (C4), 178.9 (C1), 136.4 (*ipso*-Ph), 133.3 (*para*-Ph), 128.6, 128.1 (*ortho*- and *meta*-Ph), 33.2 (C3) and 28.2 (C2); (Found: C, 66.31; H, 5.59. $C_{10}H_{10}O_3 \cdot 1/7\ H_2O$ requires C, 66.29; H, 5.75%). The data above are in agreement with that which has been previously reported.[21]

4-(2-Methyl-[1,3]dioxolan-2-yl)-1-phenyl-butan-1-one 5i

By method **3b** phosphine oxide **3d** (0.94 g, 2.15 mmol) gave a yellow gum. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 2.5-40% EtOAc in hexanes (v/v) – 2.5% increments] to give ketone **5i** (0.41 g, 82%) as a clear liquid. R_f 0.10 (10% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 257.1148. ($C_{14}H_{18}O_3Na$ requires *M*, 257.1154); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1683 (C=O) and 1164 (C-O); ^1H NMR (500 MHz; $CDCl_3$) δ 7.94-7.92 (2H, m, *ortho*-Ph), 7.52 (1H, tt, *J* 7.5 and 1.5, *para*-Ph), 7.44-7.41 (2H, m, *meta*-Ph), 3.94-3.88 (4H, m, OCH_2CH_2O), 2.98 (2H, t, *J* 7.5, $CH_2C{=}O$), 1.66-1.60 (2H, m, CH_2), 1.73-1.70 (2H, m, CH_2) and 1.32 (3H, s, CH_3); ^{13}C NMR (126 MHz; $CDCl_3$) δ 199.9 (C1), 136.7 (*ipso*-Ph), 132.8 (*para*-Ph), 128.4, 127.9 (*meta*- and *ortho*-Ph), 109.8 (C2'), 64.5 (C4' and C5'), 38.3, 23.7 (C2 and C4) and 18.7 (C3); (Found: C, 71.72; H, 7.79. $C_{14}H_{18}O_3$ requires C, 71.77; H, 7.74%). Ketone **5i** has been reported previously with no characterisation.[22,23]

(*E*)-1,7-Diphenyl-hept-6-en-3-one 5j

By method **3b** phosphine oxide **3r** (0.64 g, 1.4 mmol) after 4 hours gave a yellow gum. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 2.5-40% EtOAc in hexanes (v/v) – 2.5% increments] to give ketone **5j** (0.30 g, 81%) as a clear liquid. R_f = 0.35 (10% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 287.1404. ($C_{19}H_{20}ONa$ requires *M*, 287.1412); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1711 (C=O); ^1H NMR (500 MHz; $CDCl_3$) δ 7.33-7.25 (6H, m, Ph), 7.22-7.18 (4H, m, Ph), 6.39 (1H, d, *J* 16.0, CH=C*H*Ph), 6.17 (1H, dt, *J* 16.0 and 7.0, C*H*=CHPh), 2.92 (2H, t,

J 7.5, CH_2Ph), 2.76 (2H, t, *J* 7.5, CH_2CH_2Ph), 2.57 (2H, t, *J* 7.0, $CH_2CH_2CH{=}CH$) and 2.48 (2H, q, *J* 7.0, $CH_2CH_2CH{=}CH$); ^{13}C NMR (125 MHz; $CDCl_3$) δ 209.1 (C3), 141.0 (*ipso*-$PhCH_2$), 137.3 (*ipso*-PhC=O), 130.7 (C7), 128.8 (C6), 128.4, 128.3, 127.0, 126.1, 126.0 (Ph), 44.4 (C2), 42.4 (C4), 29.7 (C1) and 27.0 (C5); (Found: C, 86.47; H, 7.68. $C_{19}H_{20}O$ requires C, 86.32; H, 7.63%). The data above are in agreement with that which has been previously reported.[24]

(*Z*)-1,5-Diphenylpent-4-en-1-one 5k

By method **3a** phosphine oxide **3f** (0.54 g, 1.23 mmol) after 4 hours gave a yellow solid. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 2.5-40% EtOAc in hexanes (v/v) – 2.5% increments] to give ketone **5k** (0.27 g, 93%) as white needles. mp 45-46 °C (from EtOAc, hexanes); R_f 0.40 (10% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 259.1090. ($C_{17}H_{16}ONa$ requires *M*, 259.1099); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1683 (C=O); ^1H NMR (400 MHz; $CDCl_3$) δ 7.97-7.94 (2H, m, *ortho*-PhC=O), 7.55 (1H, tt, *J* 7.5 and 1.5, *para*-PhC=O), 7.47-7.43 (2H, m, *meta*-PhC=O), 7.36-7.29 (4H, m, *ortho*- and *meta*-PhCH), 7.25-7.21 (1H, m, *para*-PhCH), 6.49 (1H, dt, *J* 11.5 and 1.5, CH=C*H*Ph), 5.72 (1H, dt, *J* 11.5 and 7.5, C*H*=CHPh), 3.11 (2H, t, *J* 7.5, $CH_2C{=}O$) and 2.69 (2H, qd, *J* 7.5 and 2.0, $CH_2CH_2C{=}O$); ^{13}C NMR (100 MHz; $CDCl_3$) δ 199.2 (C1), 137.2, 136.8 (*ipso*-PhCH and PhC=O), 133.0, 130.9, 129.9, 128.7, 128.5, 128.2, 128.0, 126.7 (Ph, C4 and C5), 38.6 (C2) and 23.2 (C3); (Found: C, 86.40; H, 6.90. $C_{17}H_{16}O$ requires C, 86.40; H, 6.82%). Ketone **5k** has been reported previously with no characterisation.[25]

(*E*)-4-Methyl-1-phenyl-nona-1,8-dien-5-one 5l

By method **3a** phosphine oxide **3s** (120 mg, 0.28 mmol) after 3½ 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 *ketone* **5l** (50 mg, 78%) as clear viscous liquid. R_f 0.35 (10% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 251.1410. ($C_{16}H_{20}ONa$ requires *M*, 251.1412); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1707 (C=O); ^1H NMR (500 MHz; $CDCl_3$) δ 7.34-7.28 (4H, m, *ortho*- and *meta*-Ph), 7.21 (1H, tt, *J* 7.0 and 1.5, *para*-Ph), 6.41 (1H, d, *J* 16.0, CH=C*H*Ph), 6.12 (1H, dt, *J* 16.0 and 7.5, C*H*=CHPh), 5.80 (1H, ddt, *J* 17.0, 10.5 and 6.5, $CH{=}CH_2$), 5.03 [1H, dq, *J* 17.0 and 1.5, $CH{=}CH_aH_b$], 4.97 [1H, dq, *J* 10.0 and 1.5, $CH{=}CH_aH_b$], 2.69 (1H, sext., *J* 7.0, $CHCH_3$), 2.62-2.51 (3H, m, $CH_2C{=}O$ and $CH_aH_bCH{=}CHPh$), 2.35-2.31 (2H, m, $CH_2CH{=}CH_2$), 2.25 (1H, dtd, *J* 14.0, 7.5 and 1.0, $CH_aH_bCH{=}CHPh$) and 1.14 (3H, d, *J* 7.0, CH_3); ^{13}C NMR (126 MHz; $CDCl_3$) δ 212.9

(C5), 137.2 (×2) (*ipso*-$PhCH_2$ and C8), 130.0 (C1), 128.4 (*meta*-Ph), 127.3 (C2), 127.1 (*para*-Ph), 126.0 (*ortho*-Ph), 115.1 (C9), 46.3 (C4), 40.5 (C6), 36.2 (C3), 27.6 (C7) and 16.2 (CH_3).

(*E*)-1-Furan-2-yl-5-phenyl-pent-4-en-1-one 5m

By method **3b** phosphine oxide **3m** (0.33 g, 0.77 mmol) after 5 hours gave a brown gum. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 4 × hexanes; 5-50% EtOAc in hexanes (v/v) – 5% increments] gave *ketone* **5m** (0.13 g, 72%) as a yellow liquid. R_f 0.20 (10% EtOAc in hexanes, v/v); *m/z* (+EI) found: M^+, 226.1003. ($C_{15}H_{14}O_2$ requires *M*, 226.0994); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1671 (C=O) and 1467 (furan C-O); ^1H NMR (500 MHz; $CDCl_3$) δ 7.58 (1H, dd, *J* 1.5 and 0.5, C5'-CH), 7.35-7.33 (2H, m, *ortho*-Ph), 7.30-7.27 (2H, m, *meta*-Ph), 7.22-7.18 (2H, m, C3'-CH and *para*-Ph), 6.53 (1H, dd, *J* 3.5 and 1.5, C4'-CH), 6.46 (1H, d, *J* 16.0, CH=C*H*Ph), 6.27 (1H, dt, *J* 16.0 and 7.0, C*H*=CHPh), 3.04 (2H, t, *J* 7.5, CH_2C=O) and 2.64 (2H, qd, *J* 7.0 and 1.5, CH_2CH_2C=O); ^{13}C NMR (126 MHz; $CDCl_3$) δ 188.5 (C1), 152.6 (C2'), 146.2 (C5'), 137.3 (*ipso*-Ph), 130.8 (C5), 128.7 (C4), 128.4 (*meta*-Ph), 127.0 (*para*-Ph), 125.9 (*ortho*-Ph), 116.9 (C3'), 112.1 (C4'), 38.0 (C2) and 27.3 (C3); (Found: C, 79.78; H, 6.26. $C_{15}H_{14}O_2$ requires C, 79.62; H, 6.24%).

(*E*)-1,3-[$^2H_5$]-6-Phenyl-hex-5-en-2-one 5n

By method **3a** phosphine oxide **3n** (0.14 g, 0.38 mmol), EtOD (5 cm^3) and 4 M NaOD in D_2O (5 cm^3) gave a clear yellow oil. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 4 × hexanes; 2.5-22.5% EtOAc in hexanes (v/v) – 2.5% increments – two fractions of each solvent mixture were collected] to give *ketone* **5n** (0.14 g, 77%) as a yellow oil. R_f 0.35 (20% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 202.1251. ($C_{12}H_9D_5ONa$ requires *M*, 202.1251); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1707 (C=O); ^1H NMR (500 MHz; $CDCl_3$) δ 7.34-7.28 (4H, m, *ortho*- and *meta*-Ph), 7.20 (1H, tt, *J* 7.0 and 1.5, *para* -Ph), 6.41 (1H, d, *J* 16.0, PhC*H*=CH), 6.20 (1H, dt, *J* 16.0 and 7.0, PhCH=C*H*) and 2.47 (2H, d, *J* 7.0, CH_2CH=CH); ^{13}C NMR (126 MHz; $CDCl_3$) δ 208.2 (C2), 137.3 (*ipso*-Ph), 130.7 (C6), 128.7 (C5), 128.4 (*meta*-Ph), 127.0 (*para*-Ph), 126.0 (*ortho*-Ph), 42.4 (quintet, *J* 19.5, C3), 29.2 (septet, *J* 19.5, C1) and 26.9 (C4); (Found: C, 80.60; H, 8.09. $C_{12}H_9D_5O$ requires C, 80.40; H, 8.10%).

(*E*)-2,4-[$^2H_4$]-1,7-Diphenyl-hept-6-en-3-one 5o

By method **3a** phosphine oxide **3r** (0.28 g, 0.60 mmol), EtOD (5 cm^3) and 4 M NaOD in D_2O (5 cm^3) gave a clear yellow oil. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 4 ×

hexanes; 2.5-16% EtOAc in hexanes (v/v) – 2.5% increments – two fractions of each solvent mixture were collected] to give *ketone* **5o** (0.13 g, 81%) as a yellow liquid. R_f 0.25 (10% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 291.1657. ($C_{19}H_{16}D_4ONa$ requires *M*, 291.1659); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1706 (C=O); ^1H NMR (500 MHz; $CDCl_3$) δ 7.35-7.28 (6H, m, Ph), 7.24-7.19 (4H, m, Ph), 6.41 (1H, d, *J* 16.0, CH=C*H*Ph), 6.19 (1H, dt, *J* 16.0 and 7.0, C*H*=CHPh), 2.92 (2H, s, CH_2Ph) and 2.48 (2H, d, *J* 7.0, CD_2CH_2CH=CH); ^{13}C NMR (125 MHz; $CDCl_3$) δ 209.3 (C3), 140.9 (*ipso*-$PhCH_2$), 137.3 (*ipso*-PhC=O), 130.7 (C7), 128.7 (C6), 128.4, 128.2 (*ortho*- and *meta*-Ph), 127.0 (*para*-PhCH=), 126.0 (*para*-$PhCH_2$), 125.9 (*ortho*- or *meta*-Ph), 43.6 (quintet, *J* 19.5, C2), 41.7 (quintet, *J* 19.0, C4), 29.5 (C1) and 26.9 (C5); (Found: C, 85.09; H, 7.69. $C_{19}H_{16}D_4O$ requires C, 85.03; H, 7.51%).

1-Phenyl-heptan-1-one 5p

Diphenylhexylphosphine oxide (2.0 g, 7.0 mmol) was dissolved in anhydrous THF (20 cm^3) and cooled to 0 ^oC. *n*-Butyl lithium (2.52 M, 2.91 cm^3, 7.3 mmol) was added dropwise. After 15 minutes the solution was cooled to –78 ^oC and methyl benzoate (0.96 cm^3, 7.7 mmol) was added. After 4 hours the reaction mixture was concentrated *in vacuo* and the residue dissolved in ethanol (40 cm^3) with heating. 4 M aqueous NaOH (80 cm^3) was added and the mixture was heated to reflux for 3½ hours. The reaction mixture was cooled to room temperature, transferred to a separatory funnel with water (100 cm^3) and extracted with ethyl acetate (3 × 100 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; 4 × hexanes; 5-50% EtOAc in hexanes (v/v) – 5% increments] to give ketone **5p** (0.82 g, 66%) as a clear liquid. R_f = 0.40 (10% EtOAc in hexanes, v/v); *m/z* (+EI) found: MNa^+, 190.1363. ($C_{13}H_{18}ONa$ requires *M*, 190.1358); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 2928 (C-H) and 1684 (C=O); ^1H NMR (500 MHz; $CDCl_3$) δ 7.95-7.93 (2H, m, *ortho*-Ph), 7.51 (1H, tt, *J* 7.5 and 1.5, *para*-Ph), 7.43-7.70 (2H, m, *meta*-Ph), 2.93 (2H, t, *J* 7.5, CH_2C=O), 1.71 (2H, quintet, *J* 7.5, CH_2CH_2C=O), 1.40-1.28 (6H, m, 3 × CH_2) and 0.88 (3H, t, *J* 7.0, CH_3); ^{13}C NMR (125 MHz; $CDCl_3$) δ 200.3 (C1), 136.9 (*ipso*-Ph), 132.7 (*para*-Ph), 128.4, 127.9 (*ortho*- and *meta*-Ph), 38.4 (C2), 31.6, 28.9 (C4 and C5), 24.2, 22.4 (C3 and C6) and 13.9 (C7); (Found: C, 82.28; H, 9.63. $C_{13}H_{18}O$ requires C, 82.06; H, 9.53%). The data above are in agreement with that which has been previously reported.[26]

5-Methyl-1-phenyl-hex-4-en-1-one 5q

Phosphine oxide **2d** (0.80 g, 2.50 mmol) was dissolved in anhydrous THF (20 cm^3) and NaOMe (0.15 g, 2.75 mmol) was added. After 45 minutes prenyl bromide (0.45 g, 0.35 cm^3, 3.0 mmol) was added and the reaction mixture stirred at room temperature for 18 hours. The reaction mixture was concentrated *in vacuo* and the residue dissolved in ethanol (25 cm^3) with heating. 4 M aqueous NaOH (50 cm^3) was added at the mixture was heated to reflux for 6 hours. The reaction mixture was allowed to cool to room temperature and transferred to a separatory funnel with water (50 cm^3) and extracted with ethyl acetate (3 × 50 cm^3). The combined organic phases were dried (Na_2SO_4), filtered and concentrated *in vacuo* to give a yellow residue. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 3 × hexanes; 5-25% EtOAc in hexanes (v/v) – 5% increments; two fractions of each solvent mixture were collected] to give ketone **5q** (0.42 g, 89%) as white needles. mp 30-31 °C (from EtOAc, hexanes) (lit.,[27] 29-32 °C); R_f = 0.60 (20% EtOAc in hexanes, v/v); *m/z* (+EI) found: M^+, 188.1201. ($C_{13}H_{16}O$ requires *M*, 188.1198); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1684 (C=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.96-7.94 (2H, m, *ortho*-Ph), 7.53 (1H, tt, *J* 7.5 and 1.5, *para*-Ph), 7.46-7.42 (2H, m, *meta*-Ph), 5.19-5.15 [1H, m, C*H*=C$(CH_3)_2$], 2.98 (2H, t, *J* 7.5, CH_2C=O), 2.42 (2H, q, *J* 7.5, CH_2CH_2C=O), 1.68 (3H, s, CH_3) and 1.63 (3H, s, CH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 199.9 (C1), 136.9 (*ipso*-Ph), 132.8 (*para*-Ph), 132.6 (C5), 128.4, 127.9 (*ortho*- and *meta*-Ph), 122.9 (C4), 38.6 (C2), 25.6 (CH_3), 22.8 (C3) and 17.6 (CH_3); (Found: C, 82.86; H, 8.61. $C_{13}H_{16}O$ requires C, 82.94; H, 8.57%). The data above are in agreement with that which has been previously reported.[27]

(*E*)-3-Methyl-6-phenyl-hex-5-en-2-one 6a

By method **3a** phosphine oxide **4b** (0.45 g, 1.2 mmol) after 5 hours gave an orange gum. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 0-50% EtOAc in hexanes (v/v) – 5% increments] to give ketone **6a** (0.21 g, 96%) as a clear yellow liquid. R_f = 0.25 (10% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 211.1089. ($C_{13}H_{16}ONa$ requires *M*, 211.1099); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1709 (C=O); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.34-7.28 (4H, m, *ortho*- and *meta*-Ph), 7.21 (1H, tt, *J* 7.0 and 1.5, *para*-Ph), 6.42 (1H, d, *J* 16.0, CH=C*H*Ph), 6.13 (1H, dt, *J* 16.0 and 7.5, C*H*=CHPh), 2.67 (1H, sext., *J* 7.0, C*H*CH_3), 2.56 (1H, dtd, *J* 14.0, 7.0 and 1.5, CH_aH_b), 2.27 (1H, dtd, *J* 14.0, 7.5 and 1.0, CH_aH_b), 2.17 (3H, s, CH_3C=O) and 1.15 (3H, d, *J* 7.0, CHCH_3); ^{13}C NMR (126 MHz; $CDCl_3$) δ 211.9 (C2), 137.3 (*ipso*-Ph), 132.1, 128.5, 127.3, 127.2, 126.1, (Ph, C5 and C6), 47.1 (C3), 36.2 (C4), 28.5 (C1) and 16.1 (C3-CH_3). The data above are in agreement with that which has been previously reported.[15]

(*E*)-4-Methyl-7-phenyl-hept-6-en-3-one 6b

By method **3a** phosphine oxide **4c** (156 mg, 0.39 mmol) after 7 hours gave a yellow gum. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 2.5-40% EtOAc in hexanes (v/v) – 2.5% increments] to give *ketone* **6b** (72 mg, 91%) as clear viscous liquid. R_f = 0.40 (10% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 225.1256. ($C_{14}H_{18}ONa$ requires *M*, 225.1255); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1709 (C=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.34-7.27 (4H, m, *ortho*- and *meta*-Ph), 7.20 (1H, tt, *J* 7.0 and 1.5, *para*-Ph), 6.40 (1H, d, *J* 16.0, CH=C*H*Ph), 6.17 (1H, dt, *J* 16.0 and 7.5, C*H*=CHPh), 2.69 (1H, sext., *J* 7.0, C*H*CH_3), 2.55 (1H, dtd, *J* 14.0, 7.0 and 1.5, CH_aH_bCH=CH), 2.52-2.42 (2H, m, CH_2CH_3), 2.25 (1H, dtd, *J* 14.0, 7.0 and 1.0, CH_aH_bCH=CH), 1.14 (3H, d, *J* 6.5, CHCH_3) and 1.05 (3H, t, *J* 7.5, CH_3CH_2); ^{13}C NMR (100 MHz; $CDCl_3$) δ 214.4 (C3), 137.4 (*ipso*-Ph), 132.0, 128.5, 127.5, 127.1, 126.0 (Ph, C6 and C7), 46.1 (C4), 36.4, 34.6 (C2 and C5), 16.4 (C4-CH_3) and 7.7 (C1). The data above are in agreement with that which has been previously reported.[28]

(*E*)-2,4-Dimethyl-7-phenyl-hept-6-en-3-one 6c

By method **3a** phosphine oxide **4d** (0.26 g, 0.62 mmol) gave a yellow gum. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 2.5-40% EtOAc in hexanes (v/v) – 2.5% increments] to give *ketone* **6c** (0.13 g, 97%) as a clear liquid. R_f 0.55 (10% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 239.1403. ($C_{15}H_{20}ONa$ requires *M*, 239.1406); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1683 (C=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.31-7.23 (4H, m, Ph), 7.17 (1H, tt, *J* 7.0 and 1.5, *para*-Ph), 6.37 (1H, d, *J* 16.0, CH=C*H*Ph), 6.09 (1H, dt, *J* 15.5 and 7.5, C*H*=CHPh), 2.82 (1H, sext., *J* 7.0, C*H*CH_2), 2.72 [1H, sept., *J* 7.0, C*H*$(CH_3)_2$], 2.51 (1H, dtd, *J* 14.0, 7.0 and 1.5, CH_aH_bCH=CH), 2.23-2.16 (1H, m, CH_aH_bCH=CH), 1.19 (3H, d, *J* 7.0, CH_3), 1.07 (3H, d, *J* 7.0, CH_3) and 1.04 (3H, d, *J* 7.0, CH_3); **^{13}C NMR** (100 MHz; $CDCl_3$) δ 217.6 (C3), 137.4 (*ipso*-Ph), 131.9, 128.5, 127.6, 127.1, 126.0, (C6, C7 and Ph), 44.5, 39.9 (C2 and C4), 36.6 (C5), 18.2 (×2) and 16.7 (3 × CH_3); (Found: C, 83.64; H, 9.43. $C_{15}H_{20}O$ requires C, 83.28; H, 9.32%).

(*E*)-4-Acetyl-1-phenylhepta-1,6-diene 6d

By method **3b** phosphine oxide **4e** (136 mg, 0.33 mmol) after 7 hours gave a yellow gum. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 4 × hexanes; 5-50% EtOAc in hexanes (v/v) – 5% increments] gave *ketone* **6d** (50 mg, 71%) as a yellow liquid. R_f 0.30 (10% EtOAc in hexanes, v/v); *m/z* (+EI) found: M^+, 214.1368. ($C_{15}H_{18}O$ requires *M*, 214.1358); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1709

(C=O); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.34-7.28 (m, 4H, *ortho*- and *meta*-PhP), 7.21 (tt, 1H, *J* 7.0 and 1.5, *meta*-PhP), 6.41 (d, 1H, *J* 16.0, CH=C*H*Ph), 6.11 (dt, 1H, *J* 16.0 and 7.5, C*H*=CHPh), 5.74 (ddt, 1H, *J* 17.0, 10.0 and 7.0, C*H*=CH_2), 5.08 (dq, 1H, *J* 17.0 and 1.5, CH=CH_aH_b), 5.06 (m, 1H, CH=CH_aH_b), 2.76-2.70 (m, 1H, CHC=O), 2.51 (dtd, 1H, *J* 14.5, 7.5 and 1.5), 2.43-2.34 (m, 2H), 2.30-2.24 (m, 1H) (2 × CH_2) and 2.16 (s, 3H, CH_3); ^{13}C NMR (126 MHz; $CDCl_3$) δ 211.0 (C=O), 137.1 (*ipso*-Ph), 135.2, 132.2, 128.5, 127.2, 126.9, 126.0 (C1, C2, C6 and Ph), 117.1 (C7), 52.3 (C4), 35.3, 34.3 (C3 and C5) and 29.7 (CH_3); (Found: C, 83.90; H, 8.49. $C_{15}H_{18}O$ requires C, 84.07; H, 8.47%).

(*E*)-7-Methyl-1-phenyl-4-(3'-phenyl-prop-2'-en-yl)-oct-6-en-3-one 6e

By method **3a** phosphine oxide **4f** (65 mg, 0.12 mmol) after 8 hours gave a white solid. 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 *ketone* **6e** (33 mg, 80%) as clear viscous liquid. R_f 0.50 (20% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 355.2024. ($C_{24}H_{28}ONa$ requires *M*, 355.2038); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1709 (C=O); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.30-7.13 (10H, m, Ph), 6.36 (1H, dt, *J* 16.0 and 1.0, CH=C*H*Ph), 6.05 (1H, dt, *J* 15.5 and 7.5, C*H*=CHPh), 5.00 [1H, m, C*H*=$C(CH_3)_2$], 2.86 (2H, t, *J* 7.5, CH_2Ph), 2.79-2.68 (2H, m, C*H*$_2$$CH_2$Ph), 2.66-2.61 (1H, m, C*H*C=O), 2.49-2.43 (1H, m, CH_aH_bCH=CH), 2.33-2.25 [2H, m, CH_aH_bCH=CH and CH_aH_bCH=$C(CH_3)_2$], 2.18-2.12 [1H, m, CH_aH_bCH=$C(CH_3)_2$], 1.67 [3H, br. d, *J* 1.0, CH=$C(CH_3)_2$] and 1.57 [3H, br. s, CH=$C(CH_3)_2$]; ^{13}C NMR (126 MHz; $CDCl_3$) δ 212.7 (C3), 141.3 (*ipso*-PhCH_2), 137.3, 134.0 (C7 and *ipso*-*Ph*CH=CH), 132.0 (C3'), 128.5, 128.4 (×2) (Ph), 127.3, 127.1 (C2' and Ph), 126.0 (×2) (Ph), 121.0 (C6), 52.5 (C4), 44.8 (C2), 34.6 (C1'), 30.1 (C5), 29.4 (C1), 25.8 (CH_3) and 17.8 (CH_3).

(*E*)-1-Diphenylphosphinoyl-6-phenyl-hex-5-en-2-one 7a

By method **4** phosphine oxide **2a** (2.73 g, 10.6 mmol) after 6 hours gave a brown solid that was purified by DCVC [id 6 cm; 20 cm^3 fractions; 4 × hexanes; 10-100% EtOAc in hexanes (v/v) – 10% increments – two fractions of each solvent mixture were collected; Fraction size increased to 50 cm^3 - 2-20% MeOH in EtOAc (v/v) – 2% increments] to give *phosphine oxide* **7a** (2.58 g, 65%) as a yellow amorphous solid. mp 135-137 °C (from EtOAc, hexanes, MeOH); R_f 0.15 (50% EtOAc in hexanes, v/v); *m/z* (+EI) found: M^+, 374.1440. ($C_{24}H_{23}O_2P$ requires *M*, 374.1436); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1709 (C=O), 1438 (P-Ph) and 1195 (P=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.77-7.71 (4H, m, *ortho*-PhP), 7.54-7.42 (6H, m, *meta*- and *para*-PhP), 7.26-7.15 (5H, m, Ph), 6.33 (1H,

dt, *J* 15.5 and 1.5, PhC*H*=CH), 6.07 (1H, dt, *J* 16.0 and 6.0, PhCH=C*H*), 3.59 (2H, d, *J* 15.0, PCH_2), 2.84 (2H, t, *J* 7.0, CH_2CH_2C=O) and 2.39 (2H, qd, *J* 7.0 and 1.5, CH_2CH_2C=O); ^{31}P NMR (162 MHz; $CDCl_3$) δ 27.1; ^{13}C NMR (100 MHz; $CDCl_3$) δ 202.1 (d, *J* 5.5, C2), 137.4 (*ipso*-Ph), 132.3 (d, *J* 3.0, *para*-PhP), 131.8 (d, *J* 103.5, *ipso*-PhP), 130.9 (d, *J* 9.9, *ortho*-Ph), 130.8 (Ph), 128.7 (d, *J* 12.5, *meta*-Ph), 128.5, 128.4, 127.0, 126.0 (Ph, C5 and C6), 47.2 (C1), 44.7 (C4) and 26.6 (C3); (Found: C, 75.47; H, 6.17. $C_{24}H_{23}O_2P{\cdot}0.5\ H_2O$ requires C, 75.18; H, 6.31%).

(*E*)-2-Diphenylphosphinoyl-7-phenyl-hept-6-en-3-one 7b

By method **4** phosphine oxide **3a** (0.55 g, 2.0 mmol) after 6 hours gave a yellow gum that was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 10-100% EtOAc in hexanes (v/v) – 10% increments; 3 × EtOAc; 2.5-20% MeOH in EtOAc (v/v) – 2.5% increments] to give *phosphine oxide* **7b** (0.43 g, 55%) as a clear gum. R_f 0.55 (EtOAc); *m/z* (+ESI) found: MNa^+, 411.1496. ($C_{25}H_{25}O_2PNa$ requires *M*, 411.1490); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1706 (C=O), 1438 (P-Ph) and 1187 (P=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.84-7.74 (4H, m, *ortho*-PhP), 7.54-7.42 (6H, m, *meta*- and *para*-PhP), 7.27-7.17 (5H, m, Ph), 6.31 (1H, d, *J* 16.0, PhC*H*=CH), 6.04 (1H, dt, *J* 16.0 and 7.0, PhCH=C*H*), 3.70 (1H, dq, *J* 14.5 and 7.0, PCH), 2.76 (2H, t, *J* 7.0, CH_2C=O), 2.34 (2H, qd, *J* 7.0 and 1.0, CH_2CH_2C=O) and 1.40 (3H, dd, *J* 16.0 and 7.0, CH_3); ^{31}P NMR (162 MHz; $CDCl_3$) δ 31.0; ^{13}C NMR (100 MHz; $CDCl_3$) δ 206.5 (d, *J* 2.5, C3), 137.4 (*ipso*-Ph), 132.1 (×2) (d, *J* 3.0, *para*-PhP and d, *J* 3.0, *para*-PhP), 131.2 (×2) (d, *J* 9.5, *ortho*-PhP and d, *J* 9.0, *ortho*-PhP), 130.9 (d, *J* 99.5, *ipso*-Ph), 130.6 (×2) (C7 and d, *J* 99.0, *ipso*-Ph), 128.6 (×3) (d, *J* 12.0, *meta*-Ph and C6 or *para*-Ph and d, *J* 12.0, *meta*-Ph), 128.3 (*ortho*- or *meta*-Ph), 126.9 (C6 or *para*-Ph), 125.9 (*ortho*- or *meta*-Ph), 50.4 (C2), 42.4 (C4), 26.6 (C5) and 11.3 (d, *J* 3.5, C1).

(*E*)-1-Diphenylphosphinoyl-3-methyl-6-phenyl-hex-5-en-2-one 7c

By method **4** phosphine oxide **2b** (0.55 g, 2.0 mmol) after 3 hours gave a yellow gum that was purified by DCVC [id 4 cm; 20 cm^3 fractions; 0-100% EtOAc in hexanes (v/v) – 10% increments; 2.5-15% MeOH in EtOAc (v/v) – 2.5% increments] to give *phosphine oxide* **7c** (0.35 g, 45%) as white needles. mp 84-85 °C (from EtOAc, hexanes, MeOH); R_f 0.75 (EtOAc); *m/z* (+ESI) found: MNa^+, 411.1502. ($C_{24}H_{23}O_2PNa$ requires *M*, 411.1502); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1705 (C=O), 1438 (P-Ph) and 1192 (P=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.77-7.70 (4H, m, *ortho*-PhP), 7.55-7.37 (6H, m, *meta*- and *para*-PhP), 7.27-7.16 (5H, m, Ph), 6.33 (1H, dt, *J* 16.0 and 1.0, PhC*H*=CH), 6.03 (1H, dt, *J* 16.0 and 7.5, PhCH=C*H*), 3.67 (1H, dd, *J* 18.0 and 13.5, PCH_aH_b), 3.63 (1H, dd, *J* 17.5 and

13.5, PCH_aH_b), 3.03 (1H, sext., *J* 7.0, C*H*Me), 2.51-2.43 (1H, m, $CHCH_aH_b$), 2.24-2.16 (1H, m, $CHCH_aH_b$) and 1.05 (3H, d, *J* 7.0, CH_3); ^{31}P NMR (162 MHz; $CDCl_3$) δ 27.3; ^{13}C NMR (100 MHz; $CDCl_3$) δ 206.3 (d, *J* 5.5, C2), 137.2 (*ipso*-Ph), 132.2-132.1 (m, 2 × *para*-PhP and Ph), 132.1 (d, *J* 103.0, *ipso*-PhP), 131.9 (d, *J* 103.0, *ipso*-PhP), 130.9 (br. d, *J* 9.5, 2 × *ortho*-Ph), 128.7 (d, *J* 12.5, *meta*-Ph), 128.7 (d, *J* 12.0, *meta*-PhP), 128.4, 127.1, 127.0, 126.1 (Ph, C5 and C6), 47.7 (C3), 46.0 (d, *J* 57.5, C1), 35.9 (C4) and 15.8 (CH_3); (Found: C, 76.54; H, 6.56. $C_{24}H_{23}O_2P \cdot 0.25\ H_2O$ requires C, 76.42; H, 6.54%).

(*E*)-2-Diphenylphosphinoyl-4-methyl-7-phenyl-hept-6-en-3-one 7d

By method **4** phosphine oxide **3b** (0.57 g, 2.0 mmol) after 5 hours gave a yellow gum that was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 10-100% EtOAc in hexanes (v/v) – 10% increments; 3 × EtOAc; 2.5-20% MeOH in EtOAc (v/v) – 2.5% increments] to give *phosphine oxide* **7d** (0.18 g, 22%) as a clear gum, d.r. 54:46. R_f 0.55 (EtOAc); *m/z* (+ESI) found: MNa^+, 425.1632. ($C_{26}H_{27}O_2PNa$ requires *M*, 425.1646); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1707 (C=O), 1438 (P-Ph) and 1178 (P=O); ^{1}H NMR (400 MHz; $CDCl_3$) Two diastereoisomers A: major isomer, B: minor isomer. δ 7.89-7.71 (m, Ph A,B), 7.56-7.40 (m, Ph A,B), 7.33-7.18 (m, Ph A,B), 6.34 (1H, d, *J* 16.0, CH=C*H*Ph B), 6.29 (1H, d, *J* 16.0, CH=C*H*Ph A), 6.07 (1H, dt, *J* 15.5 and 7.5, C*H*=CHPh B), 5.94 (1H, dt, *J* 16.0 and 7.5, C*H*=CHPh A), 3.96-3.86 (2 × 1H, m, PCH A,B), 2.98-2.86 (m A,B), 2.40-2.32 (m A,B), 2.22-2.04 (m A,B), 1.41-1.30 (m, C*H*$_3$CHP A,B), 1.05 (3H, d, *J* 7.0, CH_3 A) and 0.90 (3H, d, *J* 6.5, CH_3 B); ^{31}P NMR (162 MHz; $CDCl_3$) δ 31.6 and 31.4; ^{13}C NMR (100 MHz; $CDCl_3$) Two diastereoisomers A: major isomer, B: minor isomer. δ 210.7 (d, *J* 3.0), 210.4 (d, *J* 3.0) (C3 A,B), 137.3, 137.0 (*ipso*-Ph A,B), 132.3-125.4 (m, Ph, C6 and C7 A,B), 50.2 (d, *J* 57.5), 49.1 (d, *J* 57.5) (C2 A,B), 47.2, 46.7 (C4 A,B), 37.0, 35.5 (C5 A,B), 16.6, 15.3 (C4-CH_3 A,B), 12.0 (d, *J* 3.0, C1 A,B) and 11.8 (d, *J* 3.0, C1 A,B).

1-Diphenylphosphinoyl-4-hydroxy-4-phenyl-butan-2-one 7g

By method **4** phosphine oxide **2a** (1.0 g, 3.87 mmol) after 1½ hours gave a yellow gum that 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 *phosphine oxide* **7g** (1.28 g, 90%) as a white amorphous solid. mp 100-101 °C (from EtOAc, hexanes, MeOH); R_f 0.45 (EtOAc); *m/z* (+ESI) found: MNa^+, 387.1131. ($C_{22}H_{21}O_3PNa$ requires *M*, 387.1126); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1706 (C=O), 1437 (P-Ph) and 1178 (P=O); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.76-

7.71 (4H, m, *ortho*-PhP), 7.58-7.46 (6H, m, *meta*- and *para*-PhP), 7.34-7.20 (5H, m, Ph), 5.12 (1H, dt, *J* 9.5 and 3.5, C*H*OH), 3.99 (1H, d, *J* 4.0, CHO*H*), 3.66 (2H, d, *J* 14.5, PCH_2), 3.11 (1H, dd, *J* 16.5 and 9.5, CH_aH_bC=O) and 2.97 (1H, dd, *J* 16.5 and 3.0, CH_aH_bC=O); ^{31}P NMR (162 MHz; $CDCl_3$) δ 28.4; ^{13}C NMR (100 MHz; $CDCl_3$) δ 202.9 (d, *J* 5.5, C2), 142.9 (*ipso*-Ph), 132.4 (d, *J* 2.5, 2 × *para*-PhP), 131.5 (×2) (d, *J* 104.0, *ipso*-PhP and d, *J* 103.5, *ipso*-PhP), 130.9 (d, *J* 10.0, *ortho*-Ph), 130.8 (d, *J* 10.0, *ortho*-Ph), 128.8 (d, *J* 12.5, 2 × *meta*-Ph), 128.4, 127.4, 125.6 (Ph), 69.9 (C4), 54.3 (C3) and 47.5 (d, *J* 56.0, C1); (Found: C, 72.22; H, 5.82. $C_{22}H_{21}O_3P$ requires C, 72.52; H, 5.81%).

(*E*)-6-Phenyl-hex-5-en-2-one 8a

By method **3b** phosphine oxide **7a** (0.40 g, 1. 1 mmol) after 7 hours gave a yellow solid. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 2.5-40% EtOAc in hexanes (v/v) – 2.5% increments] gave ketone **8a** (0.16 g, 86%) as a yellow liquid. All analytical data were identical with that reported for **5b** above.

(*E*)-7-Phenyl-hept-6-en-3-one 8b

By method **3a** phosphine oxide **7b** (80 mg, 0.21 mmol) after 7 hours gave a white solid. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 4 × hexanes; 5-50% EtOAc in hexanes (v/v) – 5% increments] gave ketone **8b** (33 mg, 85%) as a yellow liquid. R_f = 0.35 (10% EtOAc in hexanes, v/v); *m/z* (+EI) found: M^+, 188.1206. ($C_{13}H_{16}O$ requires *M*, 188.1201); IR $\nu_{max}(CHCl_3)$/cm^{-1} 1712 (C=O); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.34-7.27 (4H, m, *ortho*- and *meta*-Ph), 7.20 (1H, tt, *J* 7.0 and 1.5, *para*-Ph), 6.41 (1H, d, *J* 16.0, CH=C*H*Ph), 6.12 (1H, dt, *J* 16.0 and 7.0, C*H*=CHPh), 2.59 (2H, t, *J* 7.5, CH_2C=O), 2.51-2.47 (2H, m, CH_2CH=CH), 2.45 (2H, q, *J* 7.5, CH_2CH_3) and 1.07 (3H, t, *J* 7.5, CH_2CH_3); ^{13}C NMR (126 MHz; $CDCl_3$) δ 210.7 (C3), 137.4 (*ipso*-Ph), 130.6 (C7), 129.0 (C6), 128.5 (*ortho*-Ph), 127.0 (*para*-Ph), 126.0 (*meta*-Ph), 41.8 (C4), 36.0 (C2), 27.2 (C5) and 7.8 (C1). The data above are in agreement with that which has been previously reported.[29]

(*E*)-3-Methyl-6-phenyl-hex-5-en-2-one 8c

By method **3b** phosphine oxide **7c** (0.26 g, 0.67 mmol) after 6½ hours gave a yellow gum. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 2.5-40% EtOAc in hexanes (v/v) – 2.5% increments] to give ketone **8c** (0.12 g, 93%) as a clear gum. All analytical data were identical with that reported for **6a** above.

(*E*)-4-Methyl-7-phenyl-hept-6-en-3-one 8d

By method **3a** phosphine oxide **7d** (80 mg, 0.20 mmol) after 7 hours gave a yellow gum. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 4 × hexanes; 5-50% EtOAc in hexanes (v/v) – 5% increments] gave ketone **8d** (28 mg, 70%) as a yellow liquid. R_f = 0.35 (10% EtOAc in hexanes, v/v); *m/z* (+EI) found: M^+, 202.1359. ($C_{14}H_{18}O$ requires *M*, 202.1358); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1712 (C=O); ^1H NMR (500 MHz; $CDCl_3$) δ 7.34-7.27 (4H, m, *ortho*- and *meta*-PhP), 7.20 (1H, tt, *J* 7.0 and 1.5, *para*-PhP), 6.40 (1H, d, *J* 16.0, CH=C*H*Ph), 6.12 (1H, dt, *J* 15.5 and 7.5, C*H*=CHPh), 2.69 (1H, sext., *J* 7.0, C*H*C=O), 2.58-2.42 (3H, m, CH_2CH=CH and $CH_aH_bCH_3$), 2.25 (1H, dtd, *J* 14.0, 7.5 and 1.0, $CH_aH_bCH_3$), 1.13 (3H, d, *J* 7.0, CHCH_3) and 1.05 (3H, t, *J* 7.5, CH_2CH_3); ^{13}C NMR (126 MHz; $CDCl_3$) δ 214.5 (C3), 137.3 (*ipso*-Ph), 132.0 (C7), 128.5 (*ortho*- or *meta*-Ph), 127.5 (C6), 127.1 (*para*-Ph), 126.0 (*ortho*- or *meta*-Ph), 46.1 (C4), 36.4 (C5), 34.6 (C2), 16.4 (C4-CH_3) and 7.7 (C1). The data above are in agreement with that which has been previously reported.[28]

References

1. W. G. Kofron and L. M. Baclawski, *J.Org.Chem.*, 1976, **41**, 1879.
2. D. Sejer Pedersen and C. Rosenbohm, *Synthesis*, 2001, 2431.
3. Mestre-C software, ver. 4.5.6, www.mestrec.com.
4. R. S. Torr and S. Warren, *J.Chem.Soc.Pak.*, 1979, **1**, 15.
5. R. S. Torr and S. Warren, *J.Chem.Soc., Perkin Trans.1*, 1983, 1173.
6. B. Corbel, L. Medinger, J. P. Haelters, and G. Sturtz, *Synthesis*, 1985, 1048.
7. T. Mochizuki, S. Hayakawa, and K. Narasaka, *Bull.Chem.Soc.Japan*, 1996, **69**, 2317.
8. C. R. Holmquist and E. J. Roskamp, *Tetrahedron Lett.*, 1992, **33**, 1131.
9. C. A. Cornish and S. Warren, *J.Chem.Soc., Perkin Trans.1*, 1985, 2585.
10. C. R. Tyzack, PhD dissertation: *Stereocontrolled Synthesis Using Phosphine Oxides*, Cambridge University, University Chemical Laboratory, 2001.
11. T. Boesen, D. J. Fox, W. Galloway, D. S. Pedersen, C. R. Tyzack, and S. Warren, *Org.Biomol.Chem.*, 2005, **3**, 630.
12. Ronals G. Harvey and Elwood V. Jensen, *Tetrahedron Lett.*, 1963, **26**, 1801.
13. G. Bartoli, M. Bosco, R. Dalpozzo, E. Marcantoni, and L. Sambri, *Chemistry-A European Journal*, 1997, **3**, 1941.
14. M. Tasuda, K. Hayashi, Y. Katoh, I. Shibata, and A. Baba, *J.Am.Chem.Soc.*, 1998, **120**, 715.
15. Shuichi Oi, M. Moro, H. Ito, Y. Honma, S. Miyano, and Y. Inoue, *Tetrahedron*, 2002, **58**, 91.
16. J. F. Hayes, M. Shipman, and H. Twin, *J.Org.Chem.*, 2002, **67**, 935.
17. F. Alonso and M. Yus, *Tetrahedron*, 1998, **54**, 1921.
18. C. E. Elliott, D. O. Miller, and D. J. Burnell, *J.Chem.Soc., Perkin Trans.1*, 2002, 217.
19. F. C. Whitmore, R. W. Schiessler, C. S. Rowland, and J. N. Cosby, *J.Am.Chem.Soc.*, 1947, **69**, 235.
20. M. Yasuda, T. Oh-hata, I. Shibata, A. Baba, and H. Matsuda, *J.Chem.Soc., Perkin Trans.1*, 1993, 859.
21. A. T. Au, *Synthetic Commun.*, 1984, **14**, 749.
22. A. Mansri, P.-F. Casals, B. T. Fan, and G. Lapluye, *Bull.Soc.Chim.Fr.*, 1994, **131**, 247.

23. D. J. Ramón and M. Yus, *J.Org.Chem.*, 1991, **56**, 3825.
24. P Claeson, U. Pongprayoon, T. Sematong, P. Tuchinda, V. Reutrakul, P. Soontornsaratune, and W. C. Taylor, *Planta Medica*, 1996, **62**, 236.
25. K. Nishiyama, K. Ishikawa, Ila Sarkar, D. C. Lankin, and G. M. Griffin, *Heterocycles*, 1977, **6**, 1337.
26. K. Oguma, M. Miura, T. Satoh, and M. Nomura, *J.Organometallic Chem.*, 2002, **648**, 297.
27. J. P. Michael and M. M. Nkwelo, *Tetrahedron*, 1990, **46**, 2549.
28. A. R. Katritzky, Z. Z. Huang, and Y. F. Fang, *J.Org.Chem.*, 1999, **64**, 7625.
29. S. Y. Lee, C.-W. Lee, and D. Y. Oh, *J.Org.Chem.*, 1999, **64**, 7017.