

Supplementary information

Asymmetric synthesis of *trans*-disubstituted cyclopropanes using phosphine oxides and phosphine boranes

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General

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 an atmosphere of argon. Solvents were BOC standard reagent grade and distilled prior to use. Reagents/solvents for anhydrous reactions were dried as follows: THF was dried over Na wire and distilled from a mixture of CaH₂ and LiAlH₄ with triphenylmethane as indicator. Dichloromethane, methanol, *n*-hexane, acetonitrile and toluene were distilled from CaH₂. Triethylamine, was dried and stored over 4 Å molecular sieves. Flash column chromatography was carried out using Merck Kieselgel 60 (230-400 mesh). TLC was run on commercially available pre-coated plates (Merck Kieselgel 60F₂₅₄). ¹H, ¹³C, 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 was 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; δ_{C} : CDCl_3 77.0 ppm; δ_{H} : $\text{DMSO-}d_6$ 2.50 ppm; δ_{C} : $\text{DMSO-}d_6$ 39.4 ppm). J values are given in Hz and were 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 in duplicate using a CE440 Elemental Analyser from Exeter Analytical, INC. and the averages of the two determinations were compared to the theoretical value. 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.

***tert*-Butyl ester 3-(diphenyl-phosphinoyl)-propionate 12**

n-Butyllithium (2.5 mol dm^{-3} solution in hexane, 20.0 cm^3 , 50 mmol) was added dropwise to a stirred solution of methyldiphenylphosphine **11** (10.81 g, 50 mmol) in dry THF (150 cm^3) under argon at 0 °C. The resultant yellow solution was cooled to -78 °C. After 30 min the lithiated phosphine oxide solution was added dropwise *via* cannula to a stirred solution of *tert*-butylbromoacetate (11.1 cm^3 , 75 mmol) in dry THF (100 cm^3) under argon at -78 °C. After 3 h the mixture was allowed to warm to 20 °C and stirred for a further 18 h. The reaction was quenched with saturated aqueous ammonium chloride (5 cm^3) and water (50 cm^3) and the THF removed *in vacuo*. The aqueous layer was extracted with dichloromethane (3 \times 100 cm^3) and the combined organic extracts were washed with water (50 cm^3), brine (50 cm^3), dried (MgSO_4) and

evaporated under reduced pressure. The residue was purified by flash column chromatography (SiO₂, EtOAc-hexane, 2:1, v/v) to give carboxylic ester **12** (6.61 g, 40%) as an amorphous solid. mp 116-118 °C; IR ν_{\max} (CH₂Cl₂)/cm⁻¹ 1727 (C=O), 1438 (P-Ph) and 1282 (P=O); δ_{H} (400 MHz; CDCl₃) 7.74 (4H, ddd, *J* 11.5, 8.5 and 1.5, Ph *ortho*), 7.51-7.46 (6H, m, Ph), 2.58-2.50 (4H, m, CH₂CH₂), 1.36 (9H, s, CCH₃); δ_{C} (125 MHz; CDCl₃) 171.9 (CO₂), 132.7 (*ipso*-Ph, d, *J* 99.0), 132.1 (*para*-Ph, d, *J* 2.5), 131.1 (*ortho*-Ph, d, *J* 9.5), 129.0 (*meta*-Ph, d, *J* 12.0), 81.3 (OCMe₃), 28.2 (CH₃), 27.7 (CH₂CO₂, d, *J* 1) and 25.3 (CH₂P, d, *J* 72.5); δ_{P} (162 MHz; CDCl₃) 31.6 (s); *m/z* (ES) 353 (100%, M+Na) and 297 (53%, M+Na C₄H₇) (Found: MNa⁺, 353.12800. C₁₉H₂₃O₃PNa requires *M*, 353.12825).

tert*-butyl-2-Allyl-3-(diphenyl-phosphinoyl)-propionate **13*

n-Butyllithium (2.35 mol dm⁻³ solution in hexane, 5.91 cm³, 13.9 mmol) was added to a stirred solution of hexamethyldisilazane (3 cm³, 14.1 mmol) in dry THF (70 cm³) under argon at -78 °C. After 20 min. a solution of *tert*-butyl-3-(diphenyl-phosphinoyl)-propionate **12** (4.53 g, 13.7 mmol) in dry THF (55 cm³) under argon at -78 °C, was added *via* cannula. After 1 h allyl bromide (2.38 cm³, 27.4 mmol) was added and the mixture allowed to warm to room temperature over 3 h. After 16 h the THF was removed *in vacuo* and the residue partitioned between dichloromethane (3 × 100 cm³) and water (50 cm³). The organic layer was dried (Na₂SO₄), filtered and evaporated under reduced pressure and the residue purified by flash column chromatography (SiO₂, CH₂Cl₂-MeOH 9:1, v/v) to give phosphine oxide **13** (2.41 g, 48%) as a white solid. mp 93 °C; *R_f* 0.25 (CH₂Cl₂, MeOH 9:1, v/v); IR ν_{\max} (CH₂Cl₂)/cm⁻¹ 1724 (C=O), 1438 (P-Ph) and 1262 (P=O); δ_{H} (400 MHz; CDCl₃) 7.78-7.71 (4H, m, PPh₂), 7.53-7.42 (6H, m, PPh₂), 5.65 (1H, ddt, *J* 17, 10 and 7, CH=CH₂), 5.02 (1H, dd, *J* 10 and 1.5, CH=CH_AH_B *cis*), 4.99 (1H, dd, *J* 17 and 1.5, CH=CH_AH_B *trans*), 2.90 (1H, ddt, *J* 13, 9 and 6, CHCO), 2.80

(1H, ddd, J 15, 9 and 7, CH_AH_BP), 2.39 (2H, dd, J 13 and 6, CH_2), 2.30 (1H, ddd, J 15, 13 and 6, CH_ACH_BP); δ_C (400 MHz; $CDCl_3$) 173.2 (CO_2), 134.1 ($CH=CH_2$), 132.5 (*ipso*- PPh_2 , d, J 100), 131.7 (*para*- PPh_2 , d, J 1.5), 131.1 (*ortho*- PPh_2 , d, J 9.5), 130.7 (*ortho*- PPh_2 , d, J 9), 128.6 (*meta*- PPh_2 , d, J 11.5), 128.6 (*meta*- PPh_2 , d, J 12), 118.0 ($CH=CH_2$), 81.0 ($OCMe_3$), 38.9 (CH), 37.9 ($CH_2-CH=CH_2$), 30.1 (CH_2P , d, J 72), 27.9 (CH_3); m/z (EI) 370.2 (13%, MH^+). 314.2 (92%, $MH^+-C_4H_8$), 269.2 (87%, $MH^+-C_4H_9-OCO$), 215.1 (100%, $Ph_2PO-CH_2^+$) (Found: MH^+ , 370.17172. $C_{22}H_{27}O_3P$ requires M , 370.16978).

2-(*RS*)-2-Benzyl-3-(diphenyl-phosphinoyl)-propionic acid *tert*-butyl ester **14**

n-Butyllithium (2.5 mol dm^{-3} solution in hexane, 0.88 cm^3 , 2.2 mmol) was added to a stirred solution of hexamethyldisilazane (0.51 cm^3 , 2.4 mmol) in dry THF (12 cm^3) under argon at -78 °C. After 20 min a solution of 3-(diphenyl-phosphinoyl)-propionic acid *tert*-butyl ester **12** (0.66 g, 2.0 mmol) in dry THF (8 cm^3), under argon at -78 °C, was added *via* cannula. After 1 h benzyl bromide (0.48 cm^3 , 4.0 mmol) was added and the mixture allowed to warm to room temperature over 3 h. After 16 h the THF was removed *in vacuo* and the residue partitioned between dichloromethane (2×100 cm^3) and water (50 cm^3). The organic layer was dried (Na_2SO_4), filtered and evaporated under reduced pressure and the residue purified by flash column chromatography (SiO_2 , CH_2Cl_2 then CH_2Cl_2 -MeOH 9:1, v/v) to give phosphine oxide **14** (0.54 g, 64%) as an oil; IR ν_{max} (CH_2Cl_2)/ cm^{-1} 1724 (C=O) and 1438 (P-Ph); δ_H (400 MHz; $CDCl_3$) 7.76-7.68 (2H, m, PPh_2), 7.67-7.60 (2H, m, PPh_2), 7.51-7.37 (6H, m, Ph), 7.24-7.13 (3H, m, Ph), 7.12-7.06 (2H, m, Ph), 3.12-3.01 (1H, m, $CHCO$), 2.95 (1H, dd, J 13.5 and 6.5, CH_ACH_BPh), 2.90 (1H, dd, J 13.5 and 8.5, CH_ACH_BPh), 2.79 (1H, ddd, J 15, 10 and 7.5, CH_ACH_BP), 2.32 (1H, ddd, J 15, 12.5 and 5, CH_ACH_BP) and 1.12 [9H, s, $C(CH_3)_3$]; δ_C (125 MHz; $CDCl_3$) 173.2 (CO_2 , d, J 7), 138.1 (*ipso*-Ph) 133.5 and 132.6 (*ipso*- PPh_2 , d, J 98), 131.6 (*para*- PPh_2 , d, J 5), 130.9 (*ortho*- PPh_2 , d, J 9.5), 130.6 (*ortho*- PPh_2 , d, J 9), 129.3 (Ph), 128.6

(*meta*-PPh₂, d, *J* 11.5), 128.5 (*meta*-PPh₂, d, *J* 11.5), 128.2 (Ph), 126.4 (Ph), 80.8 (OCMe₃), 41.3 (CH), 39.9 (CH₂Ph, d, *J* 9), 30.8 (CH₂P, d, *J* 71) and 27.6 (CH₃); δ_p (162 MHz; CDCl₃) 30.7; *m/z* (ES) 443 (81%, M+Na) and 421 (52%, M+H) (Found 443.17520. C₂₆H₂₉O₃PNa requires *M*, 443.17520).

Diphenyl-(3-hydroxypropyl)-phosphine oxide **15**

To a mixture of triphenylphosphine (6.6 g, 25 mmol) and sodium iodide (3.7 g, 25 mmol) in acetonitrile (100 cm³) was added 3-chloropropan-1-ol (2.1 cm³, 25 mmol). The resultant mixture was heated at reflux for 15 h and the solvent removed *in vacuo*. The residue was treated with aqueous potassium hydroxide (30%, 50 cm³) and methanol (20 cm³) and the resulting solution heated at reflux for 24 h. The mixture was treated with saturated aqueous ammonium chloride (30 cm³) and dilute HCl (3N, 5 cm³) and extracted with ethyl acetate (2 × 200 cm³). The combined organic extracts were dried (Na₂SO₄), filtered and the solvents removed *in vacuo* to give an oil. The oil was triturated with diethyl ether to give alcohol **15** (3.9 g, 60%) as prisms. The mother liquors were filtered through a pad of silica (EtOAc) to yield a further batch of alcohol **15** (1.8 g, 27%, 87% overall); mp 95-6 °C (from EtOAc) (lit.,⁷ 99.5-100.5 °C); IR ν_{max} (film)/cm⁻¹ 3338 (br, O-H), 2933 (C-H), 1591 (C=C, Ph) and 1437 (P-Ph); δ_H (500 MHz; CDCl₃) 7.76-7.71 (4H, m, Ph *ortho*), 7.52 (2H, tq, *J* 7.5 and 1.5, Ph *para*), 7.48-7.44 (4H, m, Ph *meta*), 3.70 (2H, t, *J* 5.5, CH₂O), 2.41 (2H, dt, *J* 11.5 and 7, PCH₂) and 1.88 (2H, dtt, *J* 15.5, 7.5 and 5.5, PCH₂CH₂), OH peak not observed; δ_C (125 MHz; CDCl₃) 132.3 (d, *J* 99, *ipso*-Ph), 131.9 (d, *J* 3, *para*-Ph), 130.8 (d, *J* 9.5, *ortho*-Ph), 128.7 (d, *J* 11.5, *meta*-Ph), 62.5 (d, *J* 9, CH₂O), 27.7 (d, *J* 71.5, PCH₂) and 25.5 (d, *J* 4.5, PCH₂CH₂); δ_p (162 MHz; CDCl₃) 35.3; *m/z* (EI) 260 (30%, M⁺), 242 (16, M-H₂O), 215 [100, Ph₂P(O)CH₂], 202 (90, Ph₂POH), 201 (88, Ph₂PO) and 183

(38, M-Ph) (Found: M^+ , 260.09749. $C_{15}H_{17}O_2P$ requires M , 260.09667). The spectroscopic data are consistent with that reported in the literature.¹

2-(*RS*)-Methyl-1-(diphenyl-phosphinoyl)-propan-3-ol 16

Diborane (1.0 mol dm⁻³ solution in THF, 6.0 cm³, 6.0 mmol) was added to a stirred solution of 1-(diphenyl-phosphinoyl)-2-methylprop-2-ene **20** (1.5 g, 5.86 mmol) in dry THF (30 cm³). Stirring was continued for a further 18 h and the mixture quenched with hydrogen peroxide solution (100 vol., 10 cm³) and 10% aqueous sodium hydroxide (10 cm³). The THF was removed *in vacuo* and the aqueous layer extracted with dichloromethane (4 × 50 cm³). The combined organic extracts were washed with water (20 cm³) and brine (20 cm³), dried (Na₂SO₄), filtered and evaporated under reduced pressure. The residue was purified by flash column chromatography (SiO₂, CH₂Cl₂-MeOH 9:1, v/v) to give alcohol **16** (1.09 g, 68%) as a white solid. mp 127 °C; R_f 0.45 (CH₂Cl₂-MeOH, v/v); IR ν_{max} (CH₂Cl₂)/cm⁻¹ 3306 (O-H) and 1438 (P-Ph); δ_H (400 MHz; CDCl₃) 7.8-7.71 (4H, m, Ph), 7.56-7.43 (6H, m, Ph), 4.65 (1H, dd, J 8 and 4, OH), 3.61 (1H, ddd, J 11, 8 and 1.5, CH_AH_BO), 3.46 (1H, ddd, J 11, 7 and 4, CH_AH_BO), 2.33 (2H, dd, J 11 and 7, CH₂P), 2.13-2.03 (1H, m, CHCH₃), 0.99 (3H, d, J 7, CH₃); δ_C (400 MHz; CDCl₃) 133.1 (*ipso*-PPh₂, d, J 101), 131.9 (*para*-PPh₂, d, J 2), 131.0 (*ortho*-PPh₂, d, J 9.5), 130.5 (*ortho*-PPh₂, d, J 9), 128.8 (*meta*-PPh₂, d, J 11), 128.8 (*meta*-PPh₂, d, J 12), 68.4 (CH₂O), 36.2 (CH₂P, d, J 70), 32.3 (CHCH₃, d, J 13.5), 20.1 (CH₃); m/z (EI) 274.1 (25%, MH^+), 244.1 (10%, $MH^+ - CH_2OH$), 215.1 (93%, $Ph_2PO-CH_2^+$), 202.1 (100%, Ph_2PO^+) (Found: MH^+ , 274.11320. $C_{16}H_{19}O_2P$ requires M , 274.11227).

2-(*RS*)-Allyl-1-(diphenyl-phosphinoyl)-propan-3-ol 17

Lithium aluminium hydride (0.25 g, 6.51 mmol) was added in portions to a stirred solution of *tert*-butyl-2-allyl-3-(diphenyl-phosphinoyl)-propionate **13** (2.41 g, 6.51 mmol) in dry THF (32.5

cm³) at 0 °C under argon. After 16 h the reaction was quenched with ethyl acetate (25 cm³) and water (2 cm³) and the THF removed *in vacuo*. The residue was partitioned between dichloromethane (3 × 50 cm³) and water (20 cm³). The organic layer was dried (Na₂SO₄), filtered and evaporated under reduced pressure and the residue purified by flash column chromatography (SiO₂, EtOAc-CH₂Cl₂ 2:1, v/v) to give alcohol **17** (1.1 g, 56%) as an oil; *R*_f 0.15 (EtOAc-CH₂Cl₂ 2:1, v/v); IR ν_{max} (CH₂Cl₂)/cm⁻¹ 3362 (O-H), 1438 (P-Ph) and 1275 (P=O); δ_H (400 MHz; CDCl₃) 7.40 (2H, ddd, *J* 11.5, 8.5 and 1.5, Ph *ortho*), 7.57-7.43 (6H, m, Ph), 5.62 (1H, ddt, *J* 17, 10 and 7, CH=CH₂), 5.04 (1H, dd, *J* 10.5 and 1.5, CH=CH_AH_B *cis*), 5.0 (1H, dd, *J* 17 and 1.5, CH=CH_AH_B *trans*), 4.92 (1H, dd, *J* 9 and 4.5, OH), 3.69 (1H, ddd, *J* 12, 9 and 3, CH_AH_BO), 3.53 (1H, ddd, *J* 12, 7 and 4.5, CH_AH_BO), 2.48 (1H, m, CHCH₂P), 2.16 (2H, ddd, *J* 15, 10 and 5.5, CH₂), 1.99 (2H, dd, *J* 13.5 and 8, CH₂P); δ_C (400 MHz; CDCl₃) 135.6 (CH=CH₂), 133.2 (*ipso*-PPh₂, d, *J* 101), 132.0 (*para*-PPh₂), 131.1 (*ortho*-PPh₂, d, *J* 9), 130.5 (*ortho*-PPh₂, d, *J* 9.5), 128.8 (*meta*-PPh₂, d, *J* 11.5), 128.8 (*meta*-PPh₂, d, *J* 12), 117.6 (CH=CH₂), 66.7 (CH₂O), 38.6 (CH₂-CH=CH₂, d, *J* 14), 36.7 (CH, d, *J* 2.5), 33.4 (CH₂P, d, *J* 70); *m/z* (EI) 300.1 (15%, MH⁺), 282.1 (5%, MH⁺-H₂O), 282.1 (44%, MH⁺-CH₂OH), 259.1 (55%, MH⁺-C₃H₅), 215.0 (96%, Ph₂PO-CH₂⁺), 202.0 (100%, Ph₂PO⁺) (Found: MH⁺, 300.12549. C₁₈H₂₁O₂P requires M, 300.12792).

2-(*RS*)-2-Benzyl-1-(diphenyl-phosphinoyl)-propan-3-ol **18**

Lithium aluminium hydride (0.20 g, 5.0 mmol) was added in portions to a stirred solution of 2-benzyl-3-(diphenyl-phosphinoyl)-propionic acid *tert*-butyl ester **14** (2.20 g, 5.0 mmol) in dry THF (25 cm³) at 0 °C under argon. After 16 h the reaction was quenched with ethyl acetate (25 cm³) and water (2 cm³) and the THF removed under reduced pressure. The residue was partitioned between ethyl acetate and water, dried (Na₂SO₄), filtered and partially evaporated. Crystallisation from the crude solution gave alcohol **18** (1.12 g, 64%) as an amorphous solid.

The mother liquors were evaporated, the residue redissolved in THF and treated dropwise with hydrogen peroxide until no further exotherm was observed. The solution was quenched with saturated aqueous sodium bisulfite, filtered and evaporated to yield a second batch of alcohol **18** (0.64 g, 30%, overall 94%) as an amorphous solid; mp 138-140 °C (EtOAc); IR ν_{\max} (CH₂Cl₂)/cm⁻¹ 3288 (O-H) and 1438 (P-Ph); δ_{H} (400 MHz; CDCl₃) 7.60 (2H, ddd, *J* 11.5, 8.5 and 1.5, Ph *ortho*), 7.53-7.34 (7H, m, Ph), 7.28- 7.19 (4H, m, Ph), 7.02 (2H, dd, *J* 7.5 and 1.5, Ph), 5.08 (1H, br s, OH), 3.76 (1H, dd, *J* 11.5 and 1.5, CH_AH_BO), 3.59 (1H, dd, *J* 11.5 and 7, CH_AH_BO), 2.80 (1H, ddd, *J* 13.5, 4.5 and 3.5, CH_AH_BP), 2.42 (1H, dd, *J* 13.5 and 9, CH_AH_BPh), 2.38 (1 H, dd, *J* 13.5 and 8.5, CH_AH_BPh), 2.24-2.11 (2H, m, CH_AH_BP and CHCH₂P); δ_{C} (125 MHz; CDCl₃) 138.9 (*ipso*-Ph), 133.0 and 131.5 (*ipso*-PPh₂, d, *J* 100.5), 131.6 (*para*-PPh₂, d, *J* 4.5), 130.9 (*ortho*-PPh₂, d, *J* 9), 130.4 (*ortho*-PPh₂, d, *J* 9.5), 129.2 (Ph), 128.7 (*meta*-PPh₂, d, *J* 11.5), 128.5 (Ph), 126.3 (Ph), 67.0 (CH₂O), 40.0 (CH₂Ph, d, *J* 13.5), 39.1 (CH, d, *J* 3) and 32.8 (CH₂P, d, *J* 69.5); δ_{P} (162 MHz; CDCl₃) 35.7; *m/z* (ES) 373 (91%, M+Na) and 351 (46%, M+H) (Found MNa⁺ 373.13130. C₂₂H₂₃O₂PNa requires *M*, 373.13333. MH⁺ 351.15200. C₂₂H₂₄O₂P requires *M*, 351.15139).

1-(Diphenyl-phosphinoyl)-2-methylprop-2-ene **20**

Chlorodiphenylphosphine **19** (5.51 g, 25 mmol) was added dropwise to a stirred solution of 2-methyl-2-propen-1-ol (1.8 g, 25 mmol) in pyridine (60 cm³) at 0 °C under argon. After 2 h the reaction was heated to reflux for 16 h. The crude reaction mixture was evaporated under reduced pressure, diluted with dichloromethane (60 cm³), washed with aqueous hydrochloric acid (1.0 M, 3 × 60 cm³), saturated aqueous sodium bicarbonate (60 cm³) and water (60 cm³), dried (Na₂SO₄), filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO₂, EtOAc-CH₂Cl₂ 4:1, v/v) to give phosphine oxide **20** (1.8 g, 28%) as a white solid. mp 132 °C; *R_f* 0.4 (EtOAc-CH₂Cl₂ 4:1, v/v); IR ν_{\max} (CH₂Cl₂)/cm⁻¹ 1438 (P-Ph) and 1265 (P=O); δ_{H} (400

MHz; CDCl₃) 7.76 (4H, ddd, *J* 11.5, 8.5 and 1.5, Ph *ortho*), 7.53-7.43 (6H, m, Ph), 4.85 (1H, ddd, *J* 3, 1.5 and 1, C=CH_AH_B), 4.67 (1H, ddd, *J* 2, 1 and 0.5, C=CH_AH_B), 3.11 (2H, d, *J* 14, CH₂), 1.80 (3H, s, CH₃); δ_C (400 MHz; CDCl₃) 136.2 (C=CH₂, d, *J* 10), 132.9 (*ipso*-PPh₂, d, *J* 100), 131.7 (*para*-PPh₂, d, *J* 2), 131.0 (*ortho*-PPh₂, d, *J* 8.5), 128.5 (*meta*-PPh₂, d, *J* 11.5), 116.2 (C=CH₂, d, *J* 10), 39.5 (CH₂P, d, *J* 68), 24.5 (CH₃); *m/z* (EI) 256.1 (55%, MH⁺), 241.1 (7%, MH⁺-CH₃), 215.1 (10%, Ph₂PO-CH₂⁺), 201.1 (100%, Ph₂PO⁺) (Found: MH⁺, 256.09998. C₁₆H₁₇OP requires *M*, 256.10170).

3-(Benzoyloxy)-propyl-diphenylphosphine oxide **21**

Benzoyl chloride (2.4 cm³, 21 mmol) was added to a stirred solution of 3-(diphenylphosphinoyl)-propanol **15** (4.00 g, 15 mmol), DMAP (1.0 g, 8.2 mmol) and triethylamine (2.9 cm³, 21 mmol) in dichloromethane (50 cm³) at room temperature. After 18 h the mixture was quenched with water (4 cm³) and washed with water (40 cm³). The aqueous layer was extracted with EtOAc (4 × 75 cm³) and the combined organic layers dried (Na₂SO₄), filtered and evaporated under reduced pressure. The residue was recrystallised from EtOAc to give carboxylic ester **21** (4.24 g, 76%) as prisms. mp 110-112 °C (EtOAc); IR ν_{max} (CH₂Cl₂)/cm⁻¹ 1709 (C=O), 1437 (P-Ph) and 1282 (P=O); δ_H (400 MHz; CDCl₃) 7.99 (2H, dd, *J* 8.5 and 1.5, Ph), 7.75 (4H, ddd, *J* 11.5, 8.5 and 1.5, *ortho*-Ph) 7.50-7.43 (9H, m, Ph), 4.36 (2H, t, *J* 6.5, CH₂O), 2.45-2.38 (2H, m, CH₂P), 2.14-2.09 (2H, m, CH₂); δ_C (125 MHz; CDCl₃) 166.3 (PhCO₂), 133.0 (*Ph*CO₂), 132.4 (*ipso*-Ph₂P, d, *J* 98.5), 131.7 (*para*-Ph₂P, d, *J* 2), 130.7 (*ortho*-Ph₂P, d, *J* 9.5), 129.8 (*ipso*-PhCO₂), 129.5 (*Ph*CO₂), 128.7 (*meta*-Ph₂P, d, *J* 11.5), 128.3 (*Ph*CO₂), 64.7 (CH₂OCOPh, d, *J* 15.5), 26.4 (CH₂P, d, *J* 72) and 21.3 (CH₂, *J* 2.5); δ_P (162 MHz; CDCl₃) 33.1; *m/z* (ES) 387 (100%, M+Na) and 365 (27%, M+H) (Found 387.11340. C₂₂H₂₁O₃PNa requires *M*, 387.11260).

2-Methyl-3-(diphenyl-phosphinoyl)-propyl benzoate **22**

Benzoyl chloride (0.7 cm³, 6 mmol) was added to a stirred solution of 2-methyl-1-(diphenyl-phosphinoyl)-propan-3-ol **16** (1.0 g, 3.64 mmol), triethylamine (0.91 cm³, 6.57 mmol) and DMAP (0.573 g, 4.71 mmol) in dry dichloromethane (25 cm³) under argon. After 18 h the mixture was washed with water (25 cm³), aqueous hydrochloric acid (1.0 mol dm⁻³, 25 cm³), dried (Na₂SO₄), filtered and evaporated under reduced pressure. The residue was purified by flash column chromatography (SiO₂, EtOAc-CH₂Cl₂ 4:1, v/v) to give carboxylic ester **22** (1.25 g, 91%) as a white solid; *R*_f 0.5 (EtOAc-CH₂Cl₂ 4:1, v/v); IR ν_{\max} (CH₂Cl₂)/cm⁻¹ 1717 (C=O), 1438 (P-Ph) and 1276 (P=O); δ_{H} (400 MHz; CDCl₃) 7.98 (2H, dd, *J* 8 and 1, PhCO *ortho*), 7.79-7.72 (4H, m, Ph₂P), 7.56 (1H, tt, *J* 7 and 1, PhCO *para*), 7.52-7.39 (8H, m, Ph), 4.19 (2H, dd, *J* 6 and 1, CH₂O), 2.55 (1H, ddd, 15, 10 and 6.5, CH_AH_BP), 2.50-2.44 (1H, m, CHCH₃), 2.21 (1H, ddd, *J* 15, 12 and 6.5, CH_AH_BP), 1.18 (3H, d, *J* 6.5, CH₃); δ_{C} (400 MHz; CDCl₃) 162.3 (CO₂Ph), 133.9 (*ipso*-PPh₂, d, *J* 98), 133.0 (Ph), 131.7 (*para*-PPh₂), 130.8 (*ortho*-PPh₂, *J* 9), 130.6 (*ortho*-PPh₂, *J* 9), 130.0 (*ipso*-Ph), 129.5 (Ph), 128.7 (*meta*-PPh₂, *J* 11.5), 128.4 (Ph), 69.8 (CH₂O, d, *J* 13), 33.2 (CH₂P, d, *J* 71.5), 28.3 (CHCH₃), 18.6 (CH₃, d, *J* 3.5), *m/z* (EI) 378.1 (20%, MH⁺), 273.1 (85%, MH⁺-C₆H₅-CO), 256.1 (62%, MH⁺-C₆H₅-CO₂), 243.1 (30%, MH⁺-C₆H₅-CO₂CH₂), 215.1 (100%, Ph₂PO-CH₂⁺), 202.1 (95%, Ph₂PO⁺) (Found: MH⁺, 378.13759. C₂₃H₂₃O₃P requires M, 378.13848).

2-Allyl-3-(diphenyl-phosphinoyl)-propyl benzoate **23**

Benzoyl chloride (0.73 cm³, 6.23 mmol) was added to a stirred solution of 2-allyl-1-(diphenyl-phosphinoyl)-propan-3-ol **17** (0.80 g, 2.66 mmol), triethylamine (0.93 cm³, 6.7 mmol) and DMAP (0.58 g, 4.8 mmol) in dry dichloromethane (25 cm³) under argon. After 18 h the mixture was washed with water (25 cm³), aqueous hydrochloric acid (1.0 M, 25 cm³), dried (Na₂SO₄), filtered and evaporated under reduced pressure. The residue was purified by flash column

chromatography (SiO₂, CH₂Cl₂-MeOH 9:1, v/v) to give carboxylic ester **23** (0.90 g, 84%) as an oil. *R_f* 0.65 (CH₂Cl₂-MeOH 9:1, v/v); IR ν_{\max} (CH₂Cl₂)/cm⁻¹ 1717 (C=O), 1438 (P-Ph) and 1279 (P=O); δ_{H} (400 MHz; CDCl₃) 7.97 (2H, dd, *J* 8 and 1, PhCO *ortho*), 7.78-7.71 (4H, m, Ph₂P), 7.56 (1H, tt, *J* 7 and 1, PhCO *para*), 7.51-7.36 (8H, m, Ph), 5.71 (1H, ddt, *J* 17, 10 and 7, CH=CH₂), 5.06 (1H, dd, *J* 10 and 1.5 CH=CH_AH_B *cis*), 5.0 (1H, dd, *J* 17 and 1.5, CH=CH_AH_B *trans*), 4.28 (2H, d, *J* 5, CH₂O), 2.51-2.28 (3H, m, CH₂P, CHCH₂O); δ_{C} (400 MHz; CDCl₃) 166.2 (CO₂Ph), 135.0 (CH=CH₂), 133.0 (*ipso*-PPh₂, d, *J* 99), 131.8 (*para*-PPh₂, d, *J* 2), 160.7 (*ortho*-PPh₂, d, *J* 8.5), 130.6 (*ortho*-PPh₂, d, *J* 8), 130.1 (*ipso*-Ph), 128.7 (*meta*-PPh₂, d, *J* 11.5), 128.4 (Ph), 118.1 (CH=CH₂), 69.9 (CH₂O), 37.0 (CH₂-CH=CH₂), 32.5 (CH), 30.2 (CH₂P, d, *J* 71); *m/z* (EI) 404.2 (10%, MH⁺), 363.1 (22%, MH⁺-C₃H₅), 299.1 (35%, MH⁺-C₆H₅-CO), 282.1 (18%, MH⁺-C₆H₅-CO₂), 269.1 (30%, MH⁺-C₆H₅-CO₂CH₂), 215.1 (100%, Ph₂PO-CH₂⁺), 202.1 (92%, Ph₂PO⁺) (Found: MH⁺, 404.15310. C₂₅H₂₅O₃P requires M, 404.15413).

2-Benzyl-3-(diphenyl-phosphinoyl)-propyl benzoate **24**

Benzoyl chloride (0.71 cm³, 6.1 mmol) was added to a stirred solution of 2-benzyl-1-(diphenyl-phosphinoyl)-propan-3-ol **18** (0.93 g, 2.7 mmol), triethylamine (0.93 cm³, 6.7 mmol) and DMAP (0.58 g, 4.8 mmol) in dichloromethane (25 cm³). After 2 days the mixture was washed with water (25 cm³), dried (Na₂SO₄), filtered and evaporated under reduced pressure. The residue was purified by flash column chromatography (SiO₂, CH₂Cl₂-MeOH 9:1, v/v) to give carboxylic ester **24** (0.90 g, 42%) as an oil. IR ν_{\max} (CH₂Cl₂)/cm⁻¹ 1726 (C=O), 1623 (C-H aryl), 1602 (C-H aryl) and 1438 (P-Ph); δ_{H} (400 MHz; CDCl₃) 7.97 (2H, d, *J* 7, *ortho*-PhCO), 7.76-7.71 (2H, m, *ortho*-Ph₂P), 7.65-7.57 (2H, m, *ortho*-Ph₂P), 7.54 (1H, t, *J* 7.5, *para*-PhCO), 7.50-7.33 (8H, m, Ph), 7.23 (2H, t, *J* 7, *meta*-PhCH₂), 7.18 (1H, t, *J* 7, *para*-PhCH₂), 7.11 (2H, d, *J* 7, *ortho*-PhCH₂), 4.27 (2H, d, *J* 5, CH₂O), 2.98 (1H, dd, *J* 13.5 and 6.5, CH_AH_BPh), 2.85 (1H, dd, *J* 13.5

and 8, $\text{CH}_A\text{H}_B\text{Ph}$), 2.66-2.55 (1H, m, CHCH_2P), 2.48 (1H, ddd, J 15, 10.5 and 6.5, $\text{CH}_A\text{H}_B\text{P}$) and 2.37 (1H, ddd, J 15, 12 and 6.5, $\text{CH}_A\text{H}_B\text{P}$); δ_{C} (125 MHz; CDCl_3) 166.1 (CO_2Ph), 138.9 (*ipso*-Ph), 133.3 (*ipso*- PPh_2 , d, J 95), 133.2 (*ipso*- PPh_2 , d, J 98), 133.0 (Ph), 131.7 (*para*- PPh_2 , d, J 4), 130.7 (*ortho*- PPh_2 , d, J 8), 130.6 (*ortho*- PPh_2 , d, J 8), 130.1 (*ipso*-Ph), 129.5 (Ph), 129.3 (Ph), 128.7 (*meta*- PPh_2 , d, J 11.5), 128.5 (Ph), 128.4 (Ph), 126.4 (Ph), 66.5 (CH_2O , d, J 7.5), 39.0 (CH_2Ph , d, J 7.5), 35.0 (CH, d, J 2.5) and 30.5 (CH_2P , d, J 71); δ_{P} (162 MHz; CDCl_3) 31.4; m/z (ES) 477 (100%, $\text{M}+\text{Na}$) and 455 (46%, $\text{M}+\text{H}$) (Found MH^+ 455.17730. $\text{C}_{29}\text{H}_{28}\text{O}_3\text{P}$ requires M , 455.17761).

2-(Diphenyl-phosphinoyl)-4-hydroxy-1-phenyl-butan-1-one **25**

n-Butyllithium (2.2 mol dm^{-3} solution in hexane, 1.8 cm^3 , 4.0 mmol) was added to a stirred solution of diisopropylamine (0.56 cm^3 , 4.0 mmol) in dry THF (10 cm^3) under argon at -78 °C. After 30 min the solution was added *via* cannula to a stirred solution of 3-(benzoyloxy)-propyl-diphenylphosphine oxide **21** (0.73 g, 2.0 mmol) in dry THF (10 cm^3) under argon at -78 °C. Immediately, a white precipitate was observed and the reaction mixture was allowed to stir at -78 °C for 2 h during which time the precipitate dissolved to give a yellow solution. The solution was allowed to warm to 0 °C and stirred for a further 16 h. The reaction was quenched with water (10 cm^3) and the THF removed under reduced pressure. The residue was partitioned between water (50 cm^3) and dichloromethane (3×50 cm^3) and the combined organic layers dried (Na_2SO_4), filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO_2 , dichloromethane then CH_2Cl_2 -MeOH 9:1, v/v) to give phosphine oxide **25** (0.56 g, 77%) as needles. mp 158-160 °C (chloroform, EtOAc); IR ν_{max} (CH_2Cl_2)/ cm^{-1} 3326 (br O-H), 1676 (C=O), 1438 (P-Ph) and 1271 (P=O); In solution the compound exists as 11:1 mixture of the open chain compound and the cyclic ketal. NMR assignments for the open chain

isomer: δ_{H} (400 MHz; CDCl_3) 7.98-7.92 (2H, m, PPh_2 *ortho*), 7.76-7.67 (4H, m, PPh_2 *ortho*, PhCO *ortho*), 7.44-7.25 (9H, m, Ph), 4.88 (1H, ddd, J 16, 8.5 and 5, CHP), 3.74 (1H, dq, J 11 and 6, $\text{CH}_A\text{H}_B\text{O}$), 3.63-3.57 (1H, m, $\text{CH}_A\text{H}_B\text{O}$), 2.48-2.43 (2H, m, CH_ACH_B , OH) and 2.25-2.19 (1H, m, CH_ACH_B); δ_{C} (125 MHz; CDCl_3) 198.0 (COPh), 137.8 (*ipso*-COPh), 133.0 (COPh), 132.1 and 132.0 ($2 \times$ *para*- PPh_2 , d, J 2.5) 132.0 and 131.4 ($2 \times$ *ortho*- PPh_2 , d, J 9.5) 128.5 and 128.4 ($2 \times$ *meta*- PPh_2 , d, J 12), 127.6 (COPh), 126.0 (COPh), 60.6 (CH_2OH , d, J 10), 48.7 (CH PPh_2 , d, J 59) and 31.5 (CH_2 , d, J 3.5); δ_{P} (400 MHz; CDCl_3) 32.8 (cyclic ketal) and 31.5 (open chain); m/z (ES) 387 (100%, $\text{M}+\text{Na}$) and 365 (22%, $\text{M}+\text{H}$) (Found 387.11240. $\text{C}_{22}\text{H}_{21}\text{O}_3\text{PNa}$ requires M , 387.11260).

(±)-Cyclopropyl(phenyl)methanone **26**

By the method of Wallace,¹ a solution of 2-(diphenyl-phosphinoyl)-4-hydroxy-1-phenyl-butan-1-one **25** (0.36 g, 1.0 mmol) and potassium *tert*-butoxide (0.35 g, 3.0 mmol) in *tert*-butanol was stirred at 35 °C for 18 h. The reaction mixture was quenched with water (20 cm^3) and extracted with dichloromethane ($3 \times 30 \text{ cm}^3$). The combined organic layers were dried (Na_2SO_4), filtered and evaporated under reduced pressure. The residue was purified by flash column chromatography (SiO_2 , CH_2Cl_2) to give cyclopropane **26** (0.13 g, 87%) as an oil. IR ν_{max} (CH_2Cl_2)/ cm^{-1} 1667 (C=O), 1597 (aryl-H) and 1579 (aryl-H); δ_{H} (400 MHz; CDCl_3) 7.99 (2H, dd, J 8 and 1.5, Ph *ortho*), 7.52 (1H, tt, J 7.5 and 1.5, Ph *para*), 7.45 (2H, ddt, J 8, 7.5 and 2.5, Ph *meta*), 2.65 (1H, tt, J 8 and 4.5, CH), 1.22 (2H, ddd, J 7, 4.5 and 3.5, CH_AH_B) and 1.02 (2H, ddd, J 8, 7 and 3.5, CH_AH_B); δ_{C} (125 MHz; CDCl_3) 200.5 (CO), 138.0 (*ipso*-Ph), 132.7 (*para*-Ph), 128.3 and 127.9 (*ortho*- and *meta*-Ph), 17.1 (CH) and 11.6 (CH_2); m/z (ES) 146 (52%, M^+) (Found 146.07287. $\text{C}_{10}\text{H}_{10}\text{O}$ requires M , 146.07316). ^1H and ^{13}C NMR Spectra of compound **26** are shown at the end of the experimental section.

(±)-(1'*R*,2'*R*)-(2'-Methylcyclopropyl)phenyl methanone 27

n-Butyllithium (2.35 M solution in hexane, 0.51 cm³, 1.2 mmol) was added to a stirred solution of diisopropylamine (0.17 cm³, 1.2 mmol) in dry THF (5 cm³) under argon at -78 °C. After 30 min the resulting solution was added *via* cannula to a stirred solution of 2-methyl-3-(diphenylphosphinoyl)-propyl benzoate **22** (374 mg, 1.0 mmol) in dry THF (5 cm³) under argon at -78 °C. After 30 min. the solution was allowed to warm to 0 °C and stirred for a further 16 h. The solution was quenched with water (10 cm³) and the THF removed under reduced pressure. The residue was partitioned between water (20 cm³) and dichloromethane (4 × 50 cm³) and the combined organic layers dried (Na₂SO₄), filtered and evaporated under reduced pressure. The residue was purified by flash column chromatography (SiO₂, CH₂Cl₂) to give cyclopropane **27** (87 mg, 54%) as an oil. *R*_f 0.5 (CH₂Cl₂); IR ν_{\max} (CH₂Cl₂)/cm⁻¹ 1664 (C=O); δ_{H} (500 MHz; CDCl₃) 8.00-7.97 (2H, m, Ph *ortho*), 7.55 (1H, tt, *J* 7 and 1.5, Ph *para*) 7.48-7.45 (2H, m, Ph *meta*), 2.39 (1H, dd, *J* 8 and 4, CHCO), 1.64-1.56 (1H, m, CHMe), 1.48 (1H, ddd, *J* 8.5, 4.5 and 3.5, CH_AH_B), 1.21 (3H, d, *J* 6, Me) and 0.88 (1H, ddd, *J* 7.5, 6.5 and 3.5, CH_AH_B); δ_{C} (125 MHz; CDCl₃) 200.1 (CO), 138.1 (Ph *ipso*), 132.6 (Ph *para*), 128.4 and 127.9 (Ph), 26.4 and 21.3 (CH), 20.1 (CH₂) and 18.3 (Me); *m/z* (EI) 160.1 (45%, MH⁺), 145.0 (11%, MH⁺-CH₃), 131.0 (21%, MH⁺-C₂H₅), 119.1 (10%, MH⁺-C₃H₅), 105.0 (100%, PhCO⁺) (Found: MH⁺, 160.08869. C₁₁H₁₂O requires M, 160.08881).

(±)-(1'*R*,2'*R*)-Phenyl[2-(prop-2'-enyl)cyclopropyl] methanone **28**

n-Butyllithium (2.35 M solution in hexane, 0.85 cm³, 2.0 mmol) was added to a stirred solution of diisopropylamine (0.28 cm³, 2.0 mmol) in dry THF (10 cm³) under argon at -78 °C. After 30 min the resulting solution was added *via* cannula to a stirred solution of 2-allyl-3-(diphenylphosphinoyl)-propyl benzoate **28** (0.68 g, 1.67 mmol) in dry THF (8.5 cm³) under argon at -78 °C. After 30 min the solution was allowed to warm to 0 °C and stirred for a further 16 h. The solution was quenched with water (10 cm³) and the THF removed under reduced pressure. The residue was partitioned between water (20 cm³) and dichloromethane (4 × 50 cm³) and the combined organic layers dried (Na₂SO₄), filtered and evaporated under reduced pressure. The residue was purified by flash column chromatography (SiO₂, CH₂Cl₂) to give cyclopropane **28** (0.24 mg, 76%) as an oil. *R*_f 0.55 (CH₂Cl₂); IR ν_{max} (CH₂Cl₂)/cm⁻¹ 1656 (C=O); δ_{H} (500 MHz; CDCl₃) 8.00-7.98 (2H, m, Ph *ortho*), 7.55 (1H, tt, *J* 7.5 and 1.5, Ph *para*), 7.48-7.44 (2H, m, Ph *meta*), 5.85 (1H, ddt, *J* 17, 10.5 and 6.5, CH=CH₂), 5.10 (1H, dq, *J* 17 and 1.5, CH=CH_{cis}H_{trans}), 5.02 (1H, dq, *J* 10 and 1.5, CH=CH_{cis}H_{trans}), 2.47 (1H, dt, *J* 8 and 4.5, CHCO), 2.27 (1H, dtt, *J* 15.5, 6.5 and 1.5, CH_AH_BCH=CH₂), 2.14 (1H, dtt, *J* 15.5, 7 and 1, CH_AH_BCH=CH₂), 1.65-1.71 (1H, m, CHCH₂CH=CH₂), 1.51 (1H, ddd, *J* 8.5, 4.5 and 4, COCHCH_AH_B) and 0.96 (1H, ddd, *J* 8, 6.5 and 3.5, COCHCH_AH_B); δ_{C} (125 MHz; CDCl₃) 199.9 (CO), 138.0 (Ph *ipso*), 136.2 (CH=CH₂), 132.7 (Ph *para*), 128.5 and 128.0 (Ph), 115.7 (CH=CH₂), 36.9 (CH₂CH=CH₂), 25.5 and 24.6 (CH) and 18.1 (COCHCH₂); *m/z* (EI) 186.1 (12%, MH⁺), 157.1 (17%, MH⁺-C₂H₅), 144.1 (100%, MH⁺-C₃H₆) (Found: MH⁺, 186.10681. C₁₃H₁₄O requires M, 186.10447).

(±)-(1'R,2'S)-Phenyl[2'-(phenylmethyl)cyclopropyl] methanone 29

n-Butyllithium (2.5 M solution in hexane, 0.80 cm³, 2.0 mmol) was added to a stirred solution of diisopropylamine (0.28 cm³, 2.0 mmol) in dry THF (5 cm³) under argon at -78 °C. After 30 min the resulting solution was added *via* cannula to a stirred solution of 2-benzyl-3-(diphenylphosphinoyl)-propyl benzoate **24** (0.45 g, 1.0 mmol) in dry THF (5 cm³) under argon at -78 °C. After 30 min the solution was allowed to warm to 0 °C and stirred for a further 16 h. The reaction was quenched with water (10 cm³) and the THF removed under reduced pressure. The residue was partitioned between water (20 cm³) and dichloromethane (3 × 50 cm³) and the combined organic layers dried (Na₂SO₄), filtered and evaporated under reduced pressure. The residue was purified by flash column chromatography (SiO₂, CH₂Cl₂) to give cyclopropane **29** (0.27 g, 99 %) as an oil; *R*_f 0.55 (CH₂Cl₂); IR ν_{\max} (CH₂Cl₂)/cm⁻¹ 1665.4 (C=O), 1598 (C-H aryl) and 1580 (C-H aryl); δ_{H} (500 MHz; CDCl₃) 7.92-7.90 (2H, m, PhCO *ortho*), 7.54 (1H, tt, *J* 7.5 and 1.5, Ph *para*), 7.45-7.42 (2H, m, Ph), 7.31-7.28 (2H, m, Ph), 7.25-7.20 (3H, m, Ph), 2.83 (1H, dd, *J* 15 and 7, CH_AH_BPh), 2.77 (1H, dd, *J* 15 and 7, CH_AH_BPh), 2.54 (1H, dt, *J* 8 and 4.5, CHCO), 1.92 (1H, dtdd, *J* 8.5, 7, 6.5 and 4, CHCH₂Ph), 1.57 (1H, ddd, *J* 8.5, 4.5 and 4, CH_AH_BCHCO) and 1.05 (1H, ddd, *J* 8, 6.5 and 3.5, CH_AH_BCHCO); δ_{C} (125 MHz; CDCl₃) 199.8 (CO), 140.1 and 138.0 (Ph *ipso*), 132.6 (Ph *para*), 128.5 (×2), 128.4 and 128.0 (Ph), 126.3 (Ph *para*), 38.8 (PhCH₂), 26.9 and 24.9 (CH) and 18.5 (COCHCH₂); *m/z* (ES) 236 (70%, M⁺) (Found 236.11930. C₁₇H₁₆O requires *M*, 236.12012).

(S)-4-Benzyl-3-[3-(diphenyl-phosphinoyl)-propionyl]-2-oxazolidinone 36

By the method of Evans,² pivaloyl chloride (0.34 cm³, 2.7 mmol) was added to a stirred solution of 3-(diphenyl-phosphinoyl)-propionic acid **40** (0.83 g, 3.0 mmol) and triethylamine (0.55 cm³, 3.9 mmol) in dry THF (18 cm³) under argon at -78 °C. The mixture was allowed to warm to 0 °C

for 60 min and then cooled to $-78\text{ }^{\circ}\text{C}$ again. A solution of (*S*)-(-)-4-benzyl-2-oxazolidinone **38** (0.54 g, 3.0 mmol) in dry THF (12 cm^3), under argon at $-78\text{ }^{\circ}\text{C}$, was treated dropwise with *n*-butyllithium (2.5 M solution in hexane, 4.0 cm^3 , 10 mmol) and the resulting solution added rapidly to the above suspension by cannula. After 1 h at $-78\text{ }^{\circ}\text{C}$ the mixture was allowed to warm to room temperature, poured into water (50 cm^3) and extracted with EtOAc (75 cm^3). The organic layer was washed with saturated aqueous NaHCO_3 (50 cm^3) and brine (50 cm^3), dried (Na_2SO_4), filtered and evaporated under reduced pressure. The residue was purified by flash column chromatography (SiO_2 , CH_2Cl_2 -MeOH, 95:5, v/v) to give oxazolidinone **36** (0.72 g, 62%) as an amorphous solid. mp $49\text{-}50\text{ }^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{25}$ ($c=1.0$, CHCl_3) $+33.3$; IR ν_{max} (CH_2Cl_2)/ cm^{-1} 1784 (C=O), 1698 (C=O), 1437 (P-Ph) and 1282 (P=O); δ_{H} (400 MHz; CDCl_3) 7.78-7.75 (4H, m, Ph_2P), 7.51-7.47 (6H, m, Ph_2P), 7.31-7.25 (3H, m, Ph), 7.17-7.15 (2H, m, Ph), 4.60 (1H, m, CHN), 4.17-4.08 (2H, m, CH_2O), 3.27-3.22 (3H, m, CH_2), 2.74-2.67 (3H, m, CH_2); δ_{C} (125 MHz; CDCl_3) 171.6 (OCNCO₂, d, J 15), 153.1 (OCNCO₂), 134.9 (*ipso*- CH_2Ph), 132.4 and 132.3 ($2 \times$ *ipso*- Ph_2P , d, J 99), 131.9 (CH_2Ph), 130.9 ($\times 2$) ($2 \times$ *ortho*- Ph_2P , d, J 9), 129.3 and 128.9 (*para*- Ph_2P and CH_2Ph) 128.7 (*meta*- Ph_2P , d, J 11.5), 127.3 (CH_2Ph), 66.3 (CH_2O), 55.2 (CHN), 37.8 (CH_2Ph), 28.3 (CH_2CON) and 24.3 (CH_2PPh_2 , d, J 72.5); δ_{P} (162 MHz; CDCl_3) 32.2; m/z (ES) 456 (93%, $\text{M}+\text{Na}^+$) and 434 (46%, $\text{M}+\text{H}^+$) (Found 456.13360. $\text{C}_{25}\text{H}_{24}\text{PNNaO}_4$ requires M , 456.13406).

(*S*)-3,4-Dibenzyl-2-oxazolidinone **38**

(*S*)-(-)-4-Benzyl-2-oxazolidinone **37** (1.77 g, 10 mmol) in dry DMF (15 cm^3) was added to a stirred suspension of hexane washed sodium hydride (0.48 g, 12 mmol) in dry DMF (15 cm^3) under argon at $0\text{ }^{\circ}\text{C}$. After 1 h at $0\text{ }^{\circ}\text{C}$, benzyl bromide (2.4 cm^3 , 20 mmol) was added and the reaction mixture stirred at ambient temperature for 16 h. The reaction mixture was quenched

with saturated ammonium chloride (10 cm³) and the DMF removed *in vacuo*. The residue was taken up in EtOAc (50 cm³) washed with 0.1 M aqueous HCl (2 × 40 cm³), dried (MgSO₄), filtered and evaporated. The residue was purified by flash column chromatography (SiO₂, CH₂Cl₂) to give oxazolidinone **38** (2.16 g, 81%) as an oil; [α]_D²⁰ (c=1.0, CHCl₃) -10.9; R_f 0.30 (CH₂Cl₂); IR ν_{max} (CH₂Cl₂)/cm⁻¹ 1757 (C=O) and 1697 (C-H Ph); δ_H (400 MHz; CDCl₃) 7.36-7.25 (8H, m, Ph), 7.04 (2H, d, *J* 7.5, Ph), 4.85 (1H, d, *J* 15, PhCH_AH_BN), 4.13 (1H, d, *J* 15, PhCH_AH_BN), 4.13 (1H, t, *J* 8.5, CH_AH_BO), 3.99 (1H, dd, *J* 8.5 and 6, CH_AH_BO), 3.80 (1H, dddd, *J* 9, 8.5, 6 and 4.5, CH), 3.09 (1H, dd, *J* 13.5 and 4.5, PhCH_AH_BCH) and 2.63 (1H, dd, *J* 13.5 and 9, PhCH_AH_BCH); δ_C (125 MHz; CDCl₃) 158.1 (NCO₂), 135.9 and 135.5 (2 × *ipso*-Ph), 129.0, 128.9, 128.8 and 128.2 (2 × *ortho*- and 2 × *meta*-Ph), 128.0, 127.1 (*para*-Ph), 66.7 (CH₂O), 55.1 (CHN), 46.1 (PhCH₂N) and 38.2 (PhCH₂); *m/z* (ES) 290 (100%, M+Na⁺) (Found 290.11570. C₁₇H₁₇NNaO₂ requires *M*, 290.11570).

3-(Diphenyl-phosphinoyl)-propionic acid **39**

Trifluoroacetic acid (3.0 cm³, 39 mmol) was added to a stirred solution of *tert*-butyl 3-(diphenyl-phosphinoyl)-propionate (1.00 g, 3.0 mmol) in dichloromethane (10 cm³) at room temperature. After 18 h the reaction mixture was evaporated and the residue partitioned between dichloromethane (50 cm³) and water (20 cm³). The organic layer was dried (Na₂SO₄), filtered and evaporated *in vacuo*. The residue was partitioned between dichloromethane (50 cm³) and saturated aqueous sodium sulfate (20 cm³). The organic layer was dried (Na₂SO₄), filtered and evaporated under reduced pressure to give carboxylic acid **39** (0.83 g, 99%) as an oil. IR ν_{max} (CH₂Cl₂)/cm⁻¹ 1720 (C=O) and 1434 (P-Ph); δ_H (400 MHz; CDCl₃) 10.70 (1H, br s, OH), 7.71 (4H, ddd, *J* 12, 7.5 and 1.5, *ortho*-Ph) 7.52-7.25 (6H, m, Ph), 2.70-2.60 (4H, m, CH₂CH₂); δ_C (125 MHz; CDCl₃) 174.1 (CO₂H, d, *J* 13), 132.6 (*para*-Ph, d, *J* 2), 131.3 (*ipso*-Ph, d, *J* 101),

131.1 (*ortho*-Ph, d, *J* 9.5), 129.2 (*meta*-Ph, d, *J* 12), 27.0 (CH₂CO₂H) and 24.9 (CH₂P, d, *J* 72.5);
 δ_{P} (162 MHz; CDCl₃) 35.7; *m/z* (ES) 297 (100%, M+Na) (Found: MNa⁺, 297.06480.
C₁₅H₁₅PNaO₃ requires *M*, 297.06565).

Methyl 3-(boronatodiphenylphosphinyl)propionate 42

By a modification of the method of Imamoto,³ a solution of chlorodiphenylphosphine **19** (4.5 cm³, 25 mmol) in dry THF (10 cm³), stirred at 0 °C under argon, was treated with BH₃.THF (1.0 M solution in THF, 35 cm³, 35 mmol) dropwise over 45 min. The reaction mixture was stirred for a further 15 min and lithium aluminium hydride (1.1 g, 30 mmol) was added in portions. The resulting grey mixture was stirred for a further 4 h at 0 °C and then carefully poured into a mixture of ice (100 cm³) and concentrated HCl (10 cm³). The mixture was extracted with ethyl acetate and the combined organic layers dried (Na₂SO₄), filtered and evaporated under reduced pressure to give the crude phosphine borane as an oil. The oil was treated with dry methanol (75 cm³) and methyl acrylate (2.3 cm³, 25 mmol) was added. The solution was cooled to 0 °C under argon and a suspension of sodium methoxide (0.68 g, 12.5 mmol) in dry methanol (12.5 cm³) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for a further 16 h before quenching with saturated aqueous ammonium chloride (75 cm³). The methanol was removed *in vacuo* and the residue partitioned between water (25 cm³) and dichloromethane (2 × 100 cm³). The combined organic extracts were dried (Na₂SO₄), filtered and the solvents removed *in vacuo* to give phosphine borane **42** (6.9 g, 96%) as an oil. A portion of the oil was crystallised from ethyl acetate to give prisms. mp 45-6 °C (EtOAc); IR ν_{max} (film)/cm⁻¹ 2952 (C-H), 2380 (B-H), 1736 (C=O) and 1437 (P-Ph); δ_{H} (400 MHz; CDCl₃) 7.70-7.65 (4H, m, Ph *ortho*), 7.52-7.42 (6H, m, Ph), 3.63 (3H, Me), 2.58-2.49 (4H, m, CH₂CH₂) and 1.36-0.53 (3H, m, BH₃); δ_{C} (125 MHz; CDCl₃) 172.7 (d, *J* 17, CO₂), 132.1 (d, *J* 9.5, Ph *ortho*), 131.5 (d, *J*

2.5, Ph *para*), 128.9 (d, *J* 10, Ph *meta*), 128.5 (d, *J* 55.5, Ph *ipso*), 52.0 (OMe), 27.8 (d, *J* 3, PCH₂CH₂) and 20.9 (d, *J* 39, PCH₂); δ_P (162 MHz; CDCl₃) 16.9-16.5 (m); *m/z* (EI) 286 (24%, M⁺), 272 (93, M⁺-BH₃) and 257 (100, Ph₂PCH₂CH₂CO₂) (Found: M⁺, 286.12856. C₁₆H₂₀BO₂P requires *M*, 286.12940).

3-(Boronatodiphenylphosphinyl)propionic acid **43**

To a solution of methyl 3-(boronatodiphenylphosphinyl)propionate **42** (14 g, 50 mmol) in methanol (250 cm³) was added aqueous potassium hydroxide (2.8 g, 50 mmol, 250 cm³) and the resulting mixture stirred at room temperature for 18 h. The methanol was removed *in vacuo* and the residue washed with dichloromethane (2 × 250 cm³). The pH of the aqueous layer was adjusted to 1 by the addition of dilute aqueous hydrochloric acid and washed with dichloromethane (3 × 250 cm³). The combined organic layers were dried (Na₂SO₄), filtered and the solvent removed *in vacuo* to give the carboxylic acid **43** (11 g, 78%) as an amorphous solid. mp 116-7 °C; *R_f* 0.6 (Et₂O-hexane 1:1, v/v); IR ν_{\max} (film)/cm⁻¹ 3056 (br, CO₂H), 2379 (B-H), 1711 (C=O) and 1437 (P-Ph); δ_H (500 MHz; CDCl₃) 7.69-7.65 (4H, m, Ph *ortho*), 7.52-7.43 (6H, m, Ph), 6.0-5.0 (1H, br s, OH), 2.60-2.49 (4H, m, CH₂CH₂) and 1.26-0.62 (3H, br m, BH₃); δ_C (125 MHz; CDCl₃) 176.7 (d, *J* 17, CO₂), 132.1 (d, *J* 9.5, Ph *ortho*), 131.5 (d, *J* 2.5, Ph *para*), 129.0 (d, *J* 10, Ph *meta*), 128.3 (d, *J* 55.5, Ph *ipso*), 27.6 (d, *J* 3, PCH₂CH₂) and 20.7 (d, *J* 39.5, PCH₂); δ_P (162 MHz; CDCl₃) 16.9-16.4 (m); *m/z* (ES) 272 (82%, M+H) (Found MH⁺ 273.12284. C₁₅H₁₉O₂PB requires *M*, 273.12157). The spectroscopic data are consistent with that reported in the literature.⁴

(S)-3-[3'-(Boronatodiphenylphosphinyl)propionyl]-4-(phenylmethyl)oxazolidin-2-one 44

To a mechanically stirred solution of 3-(boronatodiphenylphosphinyl)propionic acid **43** (15 g, 56 mmol) and triethylamine (10 cm³, 72 mmol), in dry THF (300 cm³) at -78 °C under argon, was added pivaloyl chloride (6.5 cm³, 53 mmol). The mixture was stirred at 0 °C for 1 h and then cooled to -78 °C. A solution of (S)-(-)-4-(phenylmethyl)oxazolidin-2-one **37** (9.9 g, 56 mmol) in dry THF (200 cm³), stirred at -78 °C under argon, was treated with *n*-butyllithium (1.6 M solution in hexanes, 35 cm³, 56 mmol) and the resulting solution was added to the above suspension *via* cannula. The mixture was stirred for 1 h, allowed to warm to room temperature and the solvents removed *in vacuo*. The residue was partitioned between ethyl acetate (2 × 250 cm³) and water (20 cm³). The combined organic extracts were dried (Na₂SO₄), filtered and the solvents removed *in vacuo*. The residue was purified by flash column chromatography (SiO₂, EtOAc-hexane 1:4, v/v) to give oxazolidinone **44** (17 g, 71%) as an amorphous solid. mp 85-7 °C; $[\alpha]_D^{22}$ (c=0.5, CHCl₃) +31.1; IR ν_{\max} (film)/cm⁻¹ 2924 (C-H), 2381 (B-H), 1778 and 1698 (C=O) and 1437 (P-Ph); δ_H (500 MHz; CDCl₃) 7.73-7.68 (4H, m, PPh₂), 7.52-7.43 (6H, m, PPh₂), 7.33-7.24 (3H, m, Ph), 7.18-7.16 (2H, m, Ph), 4.60 (1H, ddt, *J* 10, 7 and 3.5, CHN), 4.18-4.12 (2H, m, CH₂O), 3.26 (1H, dd, *J* 13.5 and 3.5, PhCH_AH_B), 3.20-3.14 (2H, m, CH₂CH₂), 2.70 (1H, dd, *J* 13.5 and 10, PhCH_AH_B), 2.68-2.56 (2H, m, CH₂CH₂) and 1.30-0.67 (3H, br m, BH₃); δ_C (125 MHz; CDCl₃) 171.6 (d, *J* 15, OCNCO₂), 153.1 (OCNCO₂), 135.1 (Ph *ipso*), 132.3 (d, *J* 9, PPh₂ *ortho*), 132.2 (d, *J* 9.5, PPh₂ *ortho*), 131.4 (d, *J* 3, PPh₂ *para*), 131.4 (d, *J* 3, PPh₂ *para*), 129.3 (Ph), 129.0 (Ph), 128.9 (d, *J* 11, PPh₂ *meta*), 128.9 (d, *J* 11.5, PPh₂ *meta*), 128.7 (d, *J* 55, PPh₂ *ipso*), 128.6 (d, *J* 55, PPh₂ *ipso*), 127.3 (Ph *para*), 66.4 (CH₂O), 55.3 (CHN), 37.8 (CH₂Ph), 29.8 (d, *J* 4, PCH₂CH₂) and 20.2 (d, *J* 39, PCH₂); δ_P (162 MHz; CDCl₃) 17.6-17.3 (m); *m/z* (ESI) 454 (100%, MNa⁺) and 440 (47, M-¹¹BH₃) (Found 454.17110. C₂₅H₂₇O₃BNNaP requires *M*, 454.17193).

(4*S*,2'*R*)-3-[3'-(Boronatodiphenylphosphinyl)-2'-methylpropionyl]-4-(phenylmethyl)oxazolidin-2-one 45

To a solution of hexamethyldisilazane (0.23 cm³, 1.1 mmol) in dry THF (6 cm³), stirred at -78 °C under argon, was added *n*-butyllithium (1.5 M solution in hexanes, 0.68 cm³, 1.05 mmol). After 20 min a solution of (*S*)-3-[3'-(boronatodiphenylphosphinyl)propionyl]-4-(phenylmethyl)oxazolidin-2-one **44** (0.43 g, 1.0 mmol) in dry THF (6 cm³), at -78 °C under argon, was added *via* cannula. After 1 h methyl iodide (0.12 cm³, 2.0 mmol) was added and the reaction mixture allowed to warm to room temperature. After 42 h the solvent was removed *in vacuo* and the residue partitioned between dichloromethane (50 cm³) and water (25 cm³). The organic layer was dried (Na₂SO₄), filtered and the solvent removed *in vacuo*. The residue was purified by flash column chromatography (SiO₂, EtOAc-hexane 1:3, v/v) to give oxazolidinone **45** (0.34 g, 76%) as an oil; $[\alpha]_{\text{D}}^{23}$ (c=0.5, CHCl₃) +58.3; IR ν_{max} (film)/cm⁻¹ 2926 (C-H), 2380 (B-H), 1776 and 1694 (C=O), 1605 (C=C, Ph) and 1437 (P-Ph); δ_{H} (500 MHz; CDCl₃) 7.74-7.70 (2H, m, PPh₂ *ortho*), 7.67-7.63 (2H, m, PPh₂ *ortho*), 7.51-7.38 (6H, m, PPh₂), 7.31-7.28 (2H, m, Ph), 7.26-7.23 (1H, m, Ph *para*), 7.15-7.13 (2H, m, Ph), 4.37 (1H, ddt, *J* 9.5, 7 and 3.5, CHN), 4.15-4.03 (3H, m, CH₂O and CHMe), 3.17-3.10 (2H, m, CH_AH_BPh and PCH_AH_B), 2.74 (1H, dd, *J* 13.5 and 9.5, PhCH_AH_B), 2.26 (1H, ddd, *J* 14.5, 12 and 2.5, PCH_AH_B), 1.30 (3H, dd, *J* 7 and 1, Me) and 1.12-0.64 (3H, m, BH₃); δ_{C} (125 MHz; CDCl₃) 175.2 (d, *J* 2.5, CONCO₂), 152.7 (CONCO₂), 135.1 (Ph *ipso*), 132.5 (d, *J* 9, PPh₂ *ortho*), 132.5 (d, *J* 9.5, PPh₂ *ortho*), 131.4 (d, *J* 2.5, PPh₂ *para*), 131.1 (d, *J* 2.5, PPh₂ *para*), 129.4 (Ph), 129.3 (d, *J* 55.0, PPh₂ *ipso*), 128.9 (d, *J* 10, PPh₂ *meta*), 128.9 (Ph), 128.9 (d, *J* 55, PPh₂ *ipso*), 128.6 (d, *J* 10, PPh₂ *meta*), 127.3 (Ph *para*), 66.2 (CH₂O), 55.3 (CHN), 37.8 (PhCH₂), 33.3 (d, *J* 2, CHMe), 29.0 (d, *J* 36, PCH₂) and 20.9 (d, *J* 11.5, Me); δ_{P} (162 MHz; CDCl₃) 15.6-15.3 (m); *m/z* (ESI) 468 (65%, MNa⁺), 454 (51,

MNa–BH₃), 446 (33, MH) and 369 (100, MH–Ph) (Found: MNa⁺, 468.19000. C₂₆H₂₉NO₃PBNa requires *M*, 468.18758).

(4*S*,2'*R*)-3-{2'-[(Boronatodiphenylphosphinyl)methyl]pent-4-enoyl}-4-(phenylmethyl)oxazolidin-2-one 46

To a solution of (*S*)-3-[3'-(boronatodiphenylphosphinyl)propionyl]-4-(phenylmethyl)oxazolidin-2-one **44** (0.50 g, 1.2 mmol) in dry THF (8.5 cm³), stirred at -78 °C under argon, was added LHMDS (0.4 M solution in THF, 2.9 cm³, 1.2 mmol) prepared as described for the synthesis of compound **45**. After 1 h allyl bromide (0.20 cm³, 2.3 mmol) was added and the reaction mixture allowed to warm to room temperature over 18 h. The solvent was removed *in vacuo* and the residue partitioned between dichloromethane (50 cm³) and water (25 cm³). The organic layer was dried (Na₂SO₄), filtered and the solvent removed *in vacuo*. The residue was purified by flash column chromatography (SiO₂, EtOAc-hexane 1:3, v/v) to give oxazolidinone **46** (0.26 g, 46%) as an amorphous solid. mp 68-70 °C; [α]_D^{22.5} (c=0.5, CHCl₃) +45.7; IR ν_{\max} (film)/cm⁻¹ 2918 (C-H), 2377 (B-H), 1775 and 1694 (C=O), 1640 (C=C), 1605 (C=C, Ph) and 1437 (P-Ph); δ_{H} (500 MHz; CDCl₃) 7.72-7.68 (2H, m, PPh₂ *ortho*), 7.66-7.61 (2H, m, PPh₂ *ortho*), 7.50 (1H, tq, *J* 7.0 and 1.5, PPh₂ *para*), 7.47-7.43 (3H, m, Ph and PPh₂ *para*), 7.42-7.38 (2H, m, PPh₂ *meta*), 7.32-7.29 (2H, m, PPh₂ *meta*), 7.25 (1H, tt, *J* 7.5 and 1.5, Ph *para*), 7.17-7.15 (2H, m, Ph), 5.69 (1H, dddd, *J* 17, 10, 7.5 and 6.5, CH=CH₂), 5.11-5.09 (1H, m, CH=CH_{trans}H_{cis}), 5.08 (1H, dq, *J* 17 and 1.5, CH=CH_{trans}H_{cis}), 4.37 (1H, ddt, *J* 10, 6.5 and 3.5, CHN), 4.15-4.04 (3H, m, CHCON and CH₂O), 3.16 (1H, dd, *J* 13.5 and 3.5, CH_AH_BPh), 3.01 (1H, ddd, *J* 14.5, 11 and 8.5, PCH_AH_B), 2.64 (1H, dd, *J* 13.5 and 10, CH_AH_BPh), 2.52-2.47 (1H, m, CH_AH_BCH=CH₂), 2.38 (1H, ddd, *J* 14.5, 12.5 and 1.5, PCH_AH_B), 2.26 (1H, dt, *J* 13.5 and 8, CH_AH_BCH=CH₂) and 1.08-0.62 (3H, m, BH₃); δ_{C} (125 MHz; CDCl₃) 173.9 (d, *J* 1, OCNCO₂), 152.8 (OCNCO₂), 135.3 (Ph

ipso), 133.9 (CH=CH₂), 132.6 (d, *J* 9, PPh₂ *ortho*), 132.4 (d, *J* 9.5, PPh₂ *ortho*), 131.5 (d, *J* 2.5, PPh₂ *para*), 131.1 (d, *J* 2.5, PPh₂ *para*), 129.4 (d, *J* 55, PPh₂ *ipso*), 129.4 and 128.9 (Ph), 128.8 (d, *J* 10, PPh₂ *meta*), 128.7 (d, *J* 55, PPh₂ *ipso*), 128.6 (d, *J* 10, PPh₂ *meta*), 127.3 (Ph *para*), 118.8 (CH=CH₂), 66.1 (CH₂O), 55.5 (CHN), 39.0 (d, *J* 11.5, CH₂CH=CH₂), 38.0 (CH₂Ph), 37.2 (d, *J* 2.5, CHCO) and 26.0 (d, *J* 36.5, PCH₂); δ_P (162 MHz; CDCl₃) 15.6-15.8 (m); *m/z* (ESI) 494 (34%, MNa⁺) and 480 (100, MNa-BH₃) (Found: MNa⁺, 494.20520. C₂₈H₃₁NO₃PBNa requires *M*, 494.20323).

(4*S*,2'*R*)-4-Benzyl-3-[3-(boronatodiphenyl-phosphinyl)-2-benzyl-propionyl]-2-

oxazolidinone 47

n-Butyllithium (2.5 M solution in hexane, 0.44 cm³, 1.1 mmol) was added to a stirred solution of hexamethyldisilazane (0.25 cm³, 1.2 mmol) in dry THF (6 cm³) under argon at -78 °C. After 20 min a solution of (*S*)-4-benzyl-3-[3-(boronatodiphenyl-phosphinyl)-propionyl]-2-oxazolidinone **44** (0.40 g, 1.0 mmol) in dry THF (4 cm³) under argon at -78 °C was added *via* cannula. After 1 h benzyl bromide (0.24 cm³, 2.0 mmol) was added and the reaction mixture allowed to warm to room temperature over 3 h, stirring for a further 16 h. The reaction mixture was evaporated under reduced pressure and the residue partitioned between dichloromethane (50 cm³) and water (25 cm³), the organic layer dried (Na₂SO₄), filtered and evaporated under reduced pressure. The residue was purified by flash column chromatography (SiO₂, CH₂Cl₂-hexane 1:1, v/v) to give oxazolidinone **47** (0.20 g, 37%) as an amorphous solid, mp 56-58 °C; $[\alpha]_D^{25}$ (c=1.0, CHCl₃) +55.8; *R*_f 0.60 (CH₂Cl₂-hexane 1:1, v/v); ν_{\max} (CHCl₃)/cm⁻¹ 1778 (C=O), 1697 (C=O) and 1437 (P-Ph); δ_H (400 MHz; CDCl₃) 7.47-7.38 (4H, m, Ph₂P), 7.37-7.19 (14H, m, Ph), 7.17 (2H, dd, *J* 6.5 and 1.5, Ph), 4.57-4.48 (1H, m, CHN), 4.23-4.12 (1H, m, CHCO), 4.18 (1H, t, *J* 8.5, CH_AH_BO), 4.09 (1H, dd, *J* 9 and 2.5, CH_AH_BO), 3.21 (1H, dt, *J* 13 and 3.5, CH_AH_BPh), 3.17 (1H, dd, *J* 13 and

3.5, CH_AH_BPh aux), 2.94 (1H, ddd, J 14.5, 11 and 6.5, CH_AH_BP), 2.69 (1H, dd, J 13.5 and 9.5, CH_AH_BPh aux), 2.55 (1H, dd, J 13 and 10.5, CH_AH_BPh) and 2.35 (1H, t, J 14, CH_AH_BP); δ_C (125 MHz; $CDCl_3$) 174.0 (OCNCO₂), 153.1 (OCNCO₂), 137.5 (Ph *ipso*), 135.2 (Ph *ipso*), 132.5 (Ph *ortho*, d, J 9), 131.9 (Ph *ortho*, d, J 9), 131.2 (Ph *para*, d, J 2), 131.0 (Ph *para*, d, J 2), 129.7 (Ph), 129.4 (Ph), 128.9-128.6 (Ph, m), 127.3 (Ph), 126.9 (Ph), 66.3 (CH₂O), 55.6 (CHN), 40.1 (COCHBn), 40.1 and 38.0 (CH₂Bn) and 24.5 (CH₂P, d, J 36.5); δ_P (162 MHz; $CDCl_3$) 15.7; m/z (ES) 521 (15%, M⁺) (Found 521.23074. C₃₂H₃₃O₃BNP requires M , 521.22911).

In a second reaction:

To a solution of (*S*)-3-[3'-(boronatodiphenylphosphinyl)propionyl]-4-(phenylmethyl)oxazolidin-2-one **44** (0.43 g, 1.0 mmol) in dry THF (7.5 cm³), stirred at -78 °C under argon, was added LHMDS (0.4 mol dm⁻³ solution in THF, 2.5 cm³, 1.0 mmol) prepared as described for the synthesis of compound **45**. After 1 h, benzyl bromide (0.24 cm³, 2.0 mmol) was added and the reaction mixture allowed to warm to room temperature over 18 h. The solvent was removed *in vacuo* and the residue partitioned between dichloromethane (50 cm³) and water (25 cm³). The organic layer was dried (Na₂SO₄), filtered and the solvent removed *in vacuo*. The residue was purified by flash column chromatography (SiO₂, EtOAc-hexane 1:3, v/v) to give oxazolidinone **47** (0.30 g, 57%) as an oil. δ_H (400 MHz; $CDCl_3$) 7.48-7.39 (4H, m, Ph₂P), 7.36-7.21 (14H, m, Ph), 7.18-7.16 (2H, m, Ph), 4.52 (1H, dddd, J 10.5, 6.5, 3 and 2, CHN), 4.24-4.11 (1H, m, CHCON), 4.18 (1H, t, J 8.5, CH_AH_BO), 4.09 (1H, dd, J 9 and 2.5, CH_AH_BO), 3.22 (1H, dt, J 13 and 4, CH_AH_BPh), 3.17 (1H, dd, J 13.5 and 3.5, CH_AH_BPh Aux), 2.96 (1H, ddd, J 14.5, 11 and 6.5, PCH_AH_B), 2.70 (1H, dd, J 13.5 and 9.5, CH_AH_BPh Aux), 2.56 (1H, dd, J 13 and 11, CH_AH_BPh), 2.36 (1H, t, J 14, PCH_AH_B) and 1.16-0.51 (3H, m, BH₃); m/z (EI) 521 (15%, M⁺), 416 (100, M-Bn), 303 (63, M-AuxCO), 199 (89, Ph₂PCH₂) and 185 (80, Ph₂P) (Found 521.23074. C₃₂H₃₃O₃BNP requires M , 521.22911).

(R)-Diphenyl-(3-hydroxy-2-methylpropyl)phosphine borane 48

By the method of Roques,⁵ to a suspension of sodium borohydride (27 mg, 0.72 mmol) and lithium chloride (31 mg, 0.72 mmol) in ethanol:THF (2.9 cm³:2.9 cm³), stirred at 0 °C under nitrogen, was added a solution of (4*S*,2'*R*)-3-[3'-(boronatodiphenylphosphinyl)-2-methylpropionyl]-4-(phenylmethyl)oxazolidin-2-one **45** (80 mg, 0.18 mmol) in ethanol:THF (0.72 cm³:0.72 cm³). The resulting mixture was stirred for 18 h, allowing to warm to room temperature slowly. The mixture was treated with acetone (1 cm³) and the solvents removed *in vacuo*. The residue was partitioned between EtOAc (2 × 25 cm³) and water (15 cm³) and the combined organic layers dried (Na₂SO₄), filtered and the solvents removed *in vacuo* to give an oil. The oil was purified by flash column chromatography (SiO₂, EtOAc-hexane 1:1, v/v) to give alcohol **48** (50 mg, 99%) as an oil; *R*_f 0.3 (EtOAc-hexane, 1:1, v/v); [α]_D²³ (c=0.5, CHCl₃) -4.7; IR ν_{max} (film)/cm⁻¹ 3372 (br, O-H), 2925 (C-H), 2381 (B-H), 1589 (C=C, Ph) and 1436 (P-Ph); δ_H (500 MHz; CDCl₃) 7.73-7.68 (4H, m, Ph), 7.49-7.40 (6H, m, Ph), 3.51 (1H, ddd, *J* 11, 5 and 1.5, CH_AH_BO), 3.40 (1H, dd, *J* 11 and 6, CH_AH_BO), 2.58-2.50 (1H, m, PCH₄H_B) 2.09-2.02 (2H, m, CH and PCH₄H_B), 1.53 (1H, br s, OH), 1.32-0.70 (3H, m, BH₃) and 0.93 (3H, d, *J* 6.5, Me); δ_C (125 MHz; CDCl₃) 132.2 (d, *J* 9, PPh₂ *ortho*), 132.0 (d, *J* 9, PPh₂ *ortho*), 131.2 (d, *J* 2.5, PPh₂ *para*), 131.1 (d, *J* 2.5, P PPh₂ *para*), 130.1 (d, *J* 55.5, PPh₂ *ipso*), 130.0 (d, *J* 54.5, PPh₂ *ipso*), 128.8 (d, *J* 10, PPh₂ *meta*), 67.8 (d, *J* 9.0, CH₂O), 31.8 (CH), 28.8 (d, *J* 36, PCH₂) and 18.6 (d, *J* 5.5, Me); δ_P (162 MHz; CDCl₃) 14.9-14.4 (m); *m/z* (ESI) 295 (58%, MNa⁺) and 281 (100, MNa-BH₃) (Found: MNa⁺, 295.14000. C₁₆H₂₂OPBNa requires *M*, 295.13990).

(R)-Diphenyl[3-(hydroxymethyl)pent-4-enyl]phosphine borane 49

By the method of Roques,⁵ to a suspension of sodium borohydride (84 mg, 2.2 mmol) and lithium chloride (94 mg, 2.2 mmol) in ethanol:THF (8.8 cm³:8.8 cm³), stirred at 0 °C under

nitrogen, was added a solution of (4*S*,2'*R*)-3-{2'-[(boronatodiphenylphosphinyl)methyl]pent-4-enoyl}-4-(phenylmethyl)oxazolidin-2-one **46** (0.26 g, 0.55 mmol) in ethanol:THF (2.2 cm³:2.2 cm³). The resulting mixture was stirred for 18 h, allowing to warm to room temperature slowly. The mixture was treated with acetone (2 cm³) and the solvents removed *in vacuo*. The residue was partitioned between EtOAc (2 × 50 cm³) and water (25 cm³) and the combined organic layers dried (Na₂SO₄), filtered and the solvents removed *in vacuo* to give an oil. The oil was purified by flash column chromatography (SiO₂, EtOAc-hexane 1:3, v/v) to give alcohol **49** (93 mg, 57%) as an oil. IR ν_{\max} (film)/cm⁻¹ 3399 (O-H), 2912 (C-H), 2377 (B-H), 1640 (C=C) and 1436 (P-Ph); δ_{H} (500 MHz; CDCl₃) 7.72-7.67 (4H, m, Ph *ortho*), 7.49-7.38 (6H, m, Ph), 5.67-5.59 (1H, m, CH=CH₂), 5.02-5.01 (1H, m, CH=CH_AH_B), 5.00-4.98 (1H, m, CH=CH_AH_B), 3.57 (1H, dd, *J* 11 and 5, CH_AH_BOH), 3.52 (1H, dd, *J* 11 and 4.5, CH_AH_BOH), 2.42 (1H, ddd, *J* 14.5, 11 and 7.5, PCH_AH_B), 2.20 (1H, ddd, *J* 14.5, 12.5 and 5.5, PCH_AH_B), 2.16 (2H, t, *J* 7, CH₂CH=CH₂), 2.02-1.95 (1H, m, CHCH₂OH) and 1.35-0.70 (3H, m, BH₃); δ_{C} (125 MHz; CDCl₃) 135.8 (CH=CH₂), 132.3 (d, *J* 9, PPh₂ *ortho*), 132.0 (d, *J* 9, PPh₂ *ortho*), 131.2 (d, *J* 2.5, PPh₂ *para*), 131.1 (d, *J* 2.5, PPh₂ *para*), 130.1 (d, *J* 55.5, PPh₂ *ipso*), 129.6 (d, *J* 55, PPh₂ *ipso*), 128.8 (d, *J* 10, PPh₂ *meta*), 117.4 (CH=CH₂), 64.6 (d, *J* 6, CH₂OH) 37.3 (d, *J* 8, CH₂CH=CH₂), 36.0 (CHCH₂OH) and 26.1 (d, *J* 35.5, PCH₂); δ_{P} (162 MHz; CDCl₃) 14.9-14.5 (m); *m/z* (ESI) 321 (46%, MNa⁺) and 307 (100, MNa-BH₃) (Found: MNa⁺, 321.15380. C₁₈H₂₄OPBNa requires *M*, 321.15555).

(R)-Diphenyl[3-hydroxy-2-(phenylmethyl)propyl]phosphine borane 50

By the method of Roques,⁵ to a suspension of sodium borohydride (87 mg, 2.3 mmol) and lithium chloride (98 mg, 2.3 mmol) in ethanol:THF (8.8 cm³:8.8 cm³), stirred at 0 °C under nitrogen, was added a solution of (4*S*,2'*R*)-3-[3'-(boronatodiphenylphosphinyl)-2-

(phenylmethyl)propionyl]-4-(phenylmethyl)oxazolidin-2-one **47** (0.30 g, 0.57 mmol) in ethanol:THF (2.2 cm³:2.2 cm³). The resulting mixture was stirred for 18 h, allowing to warm to room temperature slowly. The mixture was treated with acetone (2 cm³) and the solvents removed *in vacuo*. The residue was partitioned between EtOAc (2 × 50 cm³) and water (25 cm³) and the combined organic layers dried (Na₂SO₄), filtered and the solvents removed *in vacuo* to give an oil. The oil was purified by flash column chromatography (SiO₂, EtOAc-hexane 1:1, v/v) to give alcohol **50** (0.19 g, 95%) as an oil. $[\alpha]_{\text{D}}^{25}$ (c=0.5, CHCl₃) +3.9; ν_{max} (film)/cm⁻¹ 3404 (br, O-H), 2924 (C-H), 2377 (B-H), 1603 (C=C, Ph) and 1436 (P-Ph); δ_{H} (500 MHz; CDCl₃) 7.67-7.63 (2H, m, PPh₂ *ortho*), 7.59-7.55 (2H, m, PPh₂ *ortho*), 7.47-7.36 (6H, m, PPh₂), 7.26-7.22 (2H, m, Ph), 7.18 (1H, tt, *J* 7 and 1.5, Ph *para*), 7.10-7.08 (2H, m, Ph), 3.60-3.58 (1H, m, CH_AH_BO), 3.52-3.50 (1H, m, CH_AH_BO), 2.72 (1H, dd, *J* 13.5 and 7, CH_AH_BPh), 2.68 (1H, dd, *J* 14 and 7.5, CH_AH_BPh), 2.47 (1H, ddd, *J* 14.5, 10 and 7.5, PCH_AH_B), 2.24 (1H, ddd, *J* 14.5, 13 and 5, PCH_AH_B), 2.19-2.11 (1H, m, CHCH₂OH), 1.45 (1H, br s, OH), 1.41-0.78 (3H, m, BH₃); δ_{C} (125 MHz; CDCl₃) 139.5 (Ph *ipso*), 132.2 (d, *J* 9, PPh₂ *ortho*), 131.9 (d, *J* 9, PPh₂ *ortho*), 131.2 (d, *J* 2.5, PPh₂ *para*), 131.1 (d, *J* 2.5, PPh₂ *para*), 130.4 (d, *J* 55.5, PPh₂ *ipso*), 129.3 (Ph), 129.2 (d, *J* 55, PPh₂ *ipso*), 128.8 (d, *J* 10, PPh₂ *meta*), 128.8 (d, *J* 10, PPh₂ *meta*), 128.4 (Ph), 126.2 (Ph *para*), 64.2 (d, *J* 5.5, CH₂OH), 39.1 (d, *J* 8, CH₂Ph), 38.4 (CHBn) and 26.1 (d, *J* 35.5, PCH₂); δ_{P} (162 MHz; CDCl₃) 14.8-14.3 (m); *m/z* (ESI) 371 (82%, MNa⁺) and 357 (100, MNa-BH₃) (Found: MNa⁺, 371.17150. C₂₂H₂₆OPBNa requires *M*, 371.17120).

(R)-[3-(Benzoyloxy)-2-methylpropyl]diphenylphosphine oxide 51

By the method of Pellon,⁶ a solution of (*R*)-diphenyl(3-hydroxy-2-methylpropyl)phosphine borane **48** (0.14 g, 0.50 mmol) in toluene (1.5 cm³) was treated with DABCO (56 mg, 0.50 mmol) and the resulting mixture heated at 40 °C for 18 h. The mixture was treated with excess

hydrogen peroxide solution and the residue quenched with sodium metabisulfite. The mixture was partitioned between dichloromethane (15 cm³) and water (15 cm³), the organic layer dried (Na₂SO₄), filtered and the solvent removed *in vacuo* to give crude (*R*)-diphenyl-(3-hydroxy-2-methylpropyl)phosphine oxide. δ_{H} (400 MHz; CDCl₃) 7.79-7.69 (4H, m, Ph *ortho*), 7.56-7.42 (6H, m, Ph), 3.61 (1H, dd, *J* 11 and 4, CH_AH_BO), 3.45 (1H, dd, *J* 11.5 and 7.5, CH_AH_BO), 2.36 (1H, dd, *J* 14 and 8.5, PCH_AH_B), 2.32 (1H, dd, *J* 8.5 and 4, PCH_AH_B), 2.14-2.04 (1H, m, PCH₂CH) and 0.98 (3H, dd, *J* 7 and 1.5, Me); δ_{C} (125 MHz; CDCl₃) 133.1 (d, *J* 99.5, Ph *ipso*), 131.9 (d, *J* 2.5, Ph *para*), 131.8 (d, *J* 98, Ph *ipso*), 130.9 (d, *J* 9, Ph *ortho*), 130.6 (d, *J* 9.5, Ph *ortho*), 128.8 (d, *J* 11.5, Ph *meta*), 128.7 (d, *J* 11.5, Ph *meta*), 68.3 (d, *J* 4.5, CH₂O), 35.7 (d, *J* 69.5, PCH₂), 32.1 (d, *J* 4, PCH₂CH) and 19.9 (d, *J* 13, Me); δ_{P} (162 MHz; CDCl₃) 35.4; *m/z* (ESI) 275 (55%, MH⁺) (Found: MH⁺, 275.1190. C₁₆H₂₀O₂P requires *M*, 275.1201). The spectroscopic data are consistent with that reported previously.⁷ The crude product was dissolved in dichloromethane (4.5 cm³) and triethylamine (0.10 cm³, 0.70 mmol), DMAP (30 mg, 0.25 mmol) and benzoyl chloride (0.08 cm³, 0.70 mmol) was added. The resulting solution was stirred at room temperature under argon for 32 h. The mixture was washed with water (25 cm³) and the aqueous layer extracted with ethyl acetate (4 × 20 cm³). The combined organic extracts were dried (Na₂SO₄), filtered and the solvents removed *in vacuo*. The residue purified by flash column chromatography (SiO₂, CH₂Cl₂-MeOH 19:1, v/v) to give phosphine oxide **51** (0.18 g, 96%) as an oil; $[\alpha]_{\text{D}}^{23.5}$ (c=0.5, CHCl₃) +8.5; δ_{H} (500 MHz; CDCl₃) 7.98-7.96 (2H, m, PhCO₂ *ortho*), 7.78-7.73 (4H, m, PPh₂ *ortho*), 7.55 (1H, t, *J* 7.5, Ph *para*), 7.51-7.39 (8H, m, Ph), 4.21-4.15 (2H, m, CH₂O), 2.56 (1H, ddd, *J* 15, 10.5 and 4.5, PCH_AH_B), 2.53-2.45 (1H, m, PCH₂CH), 2.22 (1H, ddd, *J* 15, 12.5 and 8.5, PCH_AH_B) and 1.17 (3H, d, *J* 7, Me); δ_{C} (125 MHz; CDCl₃) 166.3 (CO₂), 133.8 (d, *J* 98, PPh₂ *ipso*), 133.0 (PhCO₂ *para*), 132.8 (d, *J* 98, PPh₂ *ipso*), 131.8 (d, *J* 3, PPh₂ *para*), 131.7 (d, *J* 3, PPh₂ *para*), 130.8 (d, *J* 9, PPh₂ *ortho*), 130.6 (d, *J* 9.5, PPh₂ *ortho*), 130.1

(*PhCO*₂ *ipso*), 129.5 (*PhCO*₂), 128.7 (d, *J* 11, *PPh*₂ *meta*), 128.7 (d, *J* 12, *PPh*₂ *meta*), 128.2 (*PhCO*₂), 69.7 (d, *J* 12, *CH*₂*O*), 33.2 (d, *J* 71.5, *PCH*₂), 28.3 (d, *J* 3.5, *PCH*₂*CH*) and 18.6 (d, *J* 4.5, *Me*); δ_{P} (162 MHz; *CDCl*₃) 31.6; *m/z* (ESI) 379 (100%, *MH*⁺) (Found: *MH*⁺, 379.1472. *C*₂₃*H*₂₄*O*₃*P* requires *M*, 379.1463).

(*R*)-{2-[(Benzoyloxy)methyl]pent-4-enyl}diphenylphosphine oxide 52

By the method of Pellon,⁶ to DABCO (35 mg, 0.31 mmol) was added a solution of (*R*)-diphenyl[3-(hydroxymethyl)pent-4-enyl]phosphine borane **49** (93 mg, 0.31 mmol) in toluene (1 cm³) and the resulting mixture heated at 40 °C for 18 h. The mixture was treated with excess hydrogen peroxide solution and quenched with sodium metabisulfite. The mixture was partitioned between dichloromethane (10 cm³) and water (10 cm³), the organic layer dried (*Na*₂*SO*₄), filtered and the solvent removed *in vacuo* to give crude (*R*)-diphenyl-[3-(hydroxymethyl)pent-4-enyl]phosphine oxide. δ_{H} (400 MHz; *CDCl*₃) 7.79-7.67 (4H, m, *Ph ortho*), 7.56-7.42 (6H, m, *Ph*), 5.60 (1H, dddd, *J* 17, 10, 7.5 and 6.5, *CH=CH*₂), 5.04 (1H, br d, *J* 10, *CH=CH*_{*cis*}*H*_{*trans*}), 4.99 (1H, dq, *J* 17 and 1.5, *CH=CH*_{*cis*}*H*_{*trans*}), 3.69 (1H, br d, *J* 11, *CH*_{*A*}*H*_{*B*}*O*), 3.53 (1H, dd, *J* 11.5 and 7, *CH*_{*A*}*H*_{*B*}*O*), 2.47 (1H, ddd, *J* 15.5, 8 and 2.5, *PCH*_{*A*}*H*_{*B*}), 2.22 (1H, dd, *J* 15 and 9.5, *PCH*_{*A*}*H*_{*B*}), 2.19-2.12 (1H, m, *PCH*₂*CH* or *CH*_{*A*}*H*_{*B*}*CH=CH*₂) and 2.03-1.94 (2H, m, *PCH*₂*CH* or *CH*_{*A*}*H*_{*B*}*CH=CH*₂ and *CH*_{*A*}*H*_{*B*}*CH=CH*₂); δ_{P} (162 MHz; *CDCl*₃) 35.4. The mixture was dissolved in dichloromethane (3 cm³) and triethylamine (0.06 cm³, 0.44 mmol), DMAP (19 mg, 0.16 mmol) and benzoyl chloride (0.05 cm³, 0.44 mmol) was added. The resulting solution was stirred at room temperature under argon for 18 h. The mixture was washed with water (25 cm³) and the aqueous layer extracted with ethyl acetate (4 × 20 cm³). The combined organic extracts were dried (*Na*₂*SO*₄), filtered and the solvents removed *in vacuo*. The residue was purified by flash column chromatography (*SiO*₂, *CH*₂*Cl*₂-*MeOH* 39:1, v/v). The residue was dissolved in dichloromethane (5 cm³) and ethylenediamine (0.5 cm³), washed with

water (5 cm³) and sulfate buffer (0.75 M Na₂SO₄ and 0.25 M H₂SO₄ aqueous solution) (5 cm³) and the organic layer dried (Na₂SO₄), filtered and the solvent removed *in vacuo* to give phosphine oxide **52** (88 mg, 70%) as an oil; $[\alpha]_D^{22.5}$ (c=0.5, CHCl₃) +13.2; δ_H (500 MHz; CDCl₃) 7.97-7.95 (2H, m, PhCO₂ *ortho*), 7.78-7.74 (4H, m, PPh₂ *ortho*), 7.56-7.38 (9H, m, Ph), 5.70 (1H, ddt, *J* 17, 10 and 7, CH=CH₂), 5.05-5.03 (1H, m, CH=CH_{cis}H_{trans}), 5.02 (1H, dd, *J* 17 and 1.5, CH=CH_{cis}H_{trans}), 4.27 (2H, d, *J* 4.5, CH₂O), 2.51-2.36 (4H, m, PCH₂CH and CH_AH_BCH=CH₂) and 2.31 (1H, dt, *J* 14 and 7, CH_AH_BCH=CH₂); δ_C (125 MHz; CDCl₃) 166.2 (CO₂), 134.9 (CH=CH₂), 133.2 (d, *J* 98.5, PPh₂ *ipso*), 133.0 (PhCO₂ *para*), 132.6 (d, *J* 95.5, PPh₂ *ipso*), 131.9 (d, *J* 2, PPh₂ *para*), 130.8 (d, *J* 9, PPh₂ *ortho*), 130.7 (d, *J* 9, PPh₂ *ortho*), 130.1 (PhCO₂ *ipso*), 129.5 (PhCO₂ *ortho*), 128.7 (d, *J* 11.5, PPh₂ *meta*), 128.4 (PhCO₂ *meta*), 118.1 (CH=CH₂), 66.8 (d, *J* 8, CH₂O), 37.1 (d, *J* 7.5, CH₂CH=CH₂), 32.5 (d, *J* 3, PCH₂CH) and 30.5 (d, *J* 71, PCH₂); δ_P (162 MHz; CDCl₃) 32.5; *m/z* (ESI) 405 (100%, MH⁺) (Found: MH⁺, 405.1610. C₂₅H₂₆O₃P requires *M*, 405.1620).

(R)-[3-(Benzoyloxy)-2-(phenylmethyl)propyl]diphenylphosphine oxide 53

By the method of Pellon,⁶ to DABCO (31 mg, 0.27 mmol) was added a solution of (*R*)-diphenyl[3-hydroxy-2-(phenylmethyl)propyl] phosphine borane **50** (95 mg, 0.27 mmol) in toluene (1 cm³) and the resulting mixture heated at 40 °C for 18 h. The mixture was treated with excess hydrogen peroxide solution and quenched with sodium metabisulfite. The mixture was partitioned between dichloromethane (10 cm³) and water (10 cm³), the organic layer dried (Na₂SO₄), filtered and the solvent removed *in vacuo* to give crude (*R*)-diphenyl[3-hydroxy-2-(phenylmethyl)propyl]phosphine oxide. δ_H (400 MHz; CDCl₃) 7.63-7.57 (2H, m, PPh₂ *ortho*), 7.53-7.34 (7H, m, Ph), 7.27-7.19 (4H, m, Ph), 7.03-7.00 (2H, m, Ph), 3.77 (1H, dd, *J* 11.5 and 3, CH_AH_BO), 3.59 (1H, dd, *J* 11.5 and 6.5, CH_AH_BO), 2.80 (1H, ddd, *J* 13.5, 5 and 3.5, PCH_AH_B),

2.42 (1H, dd, J 13.5 and 9.5, PhCH_AH_B), 2.37 (1H, dd, J 13.5 and 8.5, PhCH_AH_B) and 2.28-2.13 (2H, m, PCH_AH_B and PCH₂CH). The mixture was dissolved in dichloromethane (3 cm³) and triethylamine (0.05 cm³, 0.38 mmol), DMAP (17 mg, 0.14 mmol) and benzoyl chloride (0.04 cm³, 0.38 mmol) added. The resulting solution was stirred at room temperature under argon for 18 h. The mixture was washed with water (25 cm³) and the aqueous layer extracted with ethyl acetate (4 × 20 cm³). The combined organic extracts were dried (Na₂SO₄), filtered and the solvents removed *in vacuo*. The residue was purified by flash column chromatography (SiO₂, CH₂Cl₂-MeOH 19:1, v/v) to give phosphine oxide **53** (57 mg, 46%) as an oil; $[\alpha]_D^{22}$ (c=0.5, CHCl₃) +5.4; δ_H (500 MHz; CDCl₃) 7.98-7.96 (2H, m, PhCO₂ *ortho*), 7.74-7.70 (2H, m, PPh₂ *ortho*), 7.63-7.59 (2H, m, PPh₂ *ortho*), 7.56 (1H, tt, J 7.5 and 1, PhCO₂ *para*), 7.50-7.37 (8H, m, PPh₂ *meta* and *para* and PhCO₂ *meta*), 7.25-7.22 (2H, m, PhCH₂ *meta*), 7.18 (1H, tt, J 7 and 1.5, PhCH₂ *para*), 7.11-7.10 (2H, m, PhCH₂ *ortho*), 4.27 (2H, dd, J 5 and 1, CH₂O), 2.97 (1H, dd, J 13.5 and 6.5, PhCH_AH_B), 2.86 (1H, dd, J 13.5 and 8, PhCH_AH_B), 2.65-2.55 (1H, m, PCH₂CH), 2.47 (1H, ddd, J 15.5, 10.5 and 6.5, PCH_AH_B) and 2.37 (1H, ddd, J 15.5, 12 and 6, PCH_AH_B); δ_C (125 MHz; CDCl₃) 166.1 (CO₂), 138.9 (Ph *ipso*), 133.3 (d, J 98, PPh₂ *ipso*), 133.1 (d, J 98, PPh₂ *ipso*), 133.0 (Ph *para*), 131.8 (d, J 2.5, PPh₂ *para*), 131.7 (d, J 2.5, PPh₂ *para*), 130.7 (d, J 9, PPh₂ *ortho*), 130.6 (d, J 9, PPh₂ *ortho*), 130.1 (Ph *ipso*), 129.5 and 129.4 (Ph), 128.7 (d, J 11.5, PPh₂ *meta*), 128.5 and 128.4 (Ph), 126.4 (Ph *para*), 66.7 (d, J 7.5, CH₂O), 39.0 (d, J 7.5, CH₂Ph), 35.0 (d, J 3, PCH₂CH) and 30.4 (d, J 71, PCH₂); δ_P (162 MHz; CDCl₃) 31.5; m/z (EI) 454 (13%, M⁺) and 91 (100, CH₂Ph) (Found: M⁺, 454.17166. C₂₉H₂₇O₃P requires M , 454.16978).

(1'R,2'R)-(2'-Methylcyclopropyl)phenyl methanone 54

LDA was prepared by the addition of *n*-butyllithium (1.6 M solution in hexanes, 1.25 cm³, 2.0 mmol) to a solution of diisopropylamine (0.28 cm³, 2.0 mmol) in dry THF (8.5 cm³), stirred at -78 °C under nitrogen. After 1 h a solution of (*R*)-[3-(benzyloxy)-2-methylpropyl]diphenylphosphine oxide **51** (38 mg, 0.1 mmol) in dry THF (0.4 cm³), stirred at -78 °C under nitrogen, was treated with the LDA solution (0.2 mol dm⁻³ solution in THF, 0.6 cm³, 0.12 mmol). After 1 h, the mixture was allowed to warm to 0 °C and stirred for 48 h at this temperature. The reaction was quenched with water (1 cm³) and the solvent removed *in vacuo*. The residue was partitioned between water (2 cm³) and ethyl acetate (3 × 5 cm³), the combined organic extracts dried (Na₂SO₄), filtered and the solvents removed *in vacuo*. The residue was purified by flash column chromatography (SiO₂, CH₂Cl₂) to give cyclopropane **54** (10 mg, 60%) as an oil; $[\alpha]_D^{22}$ (c=0.42, CHCl₃) -77.1; *m/z* (EI) 160 (36%, M⁺) and 105 (100, PhCO) (Found: M⁺, 160.08832. C₁₁H₁₂O requires *M*, 160.08882). The IR, ¹H- and ¹³C-NMR spectroscopic data are consistent with that reported above for (±)-(1'R,2'R)-(2'-methylcyclopropyl)phenyl methanone **27**. ¹H and ¹³C NMR Spectra of compound **55** are shown at the end of the experimental section.

(1'R,2'R)-Phenyl[2-(prop-2'-enyl)cyclopropyl] methanone 55

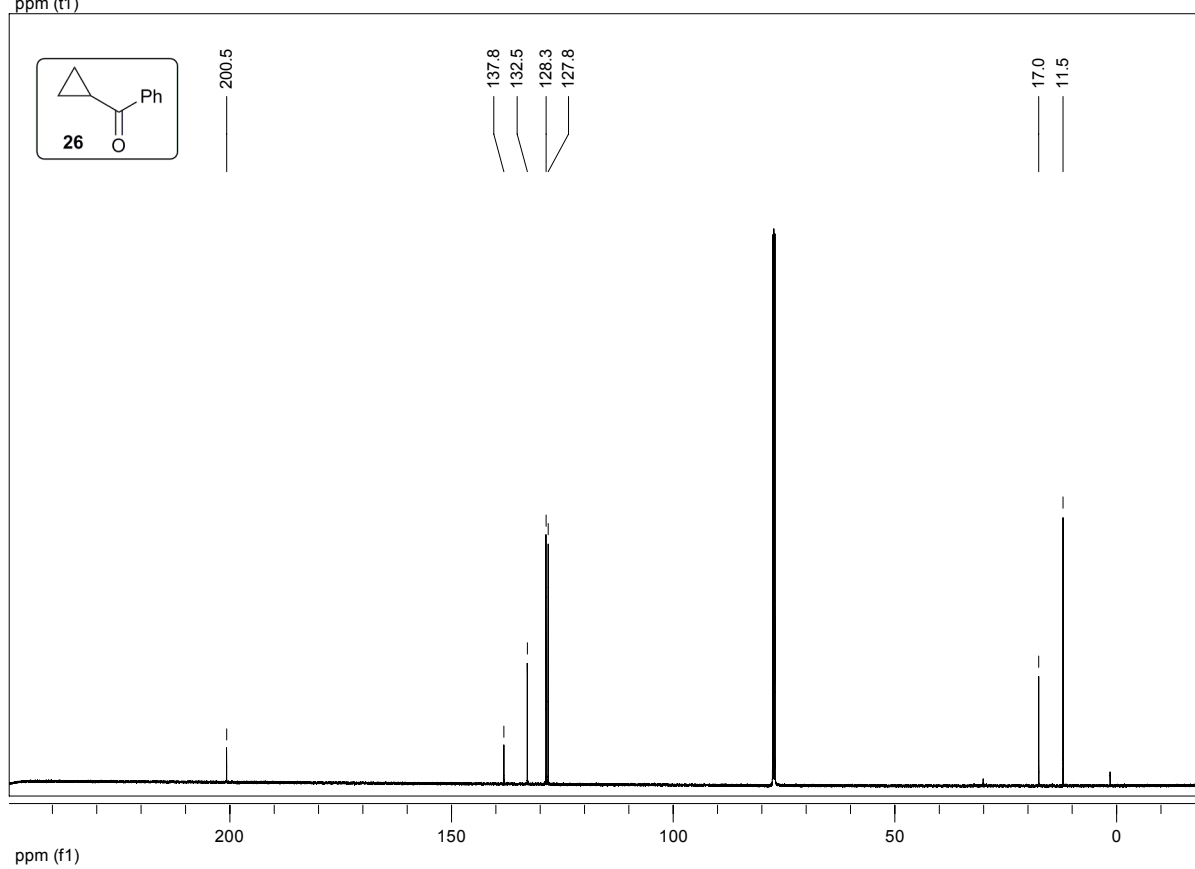
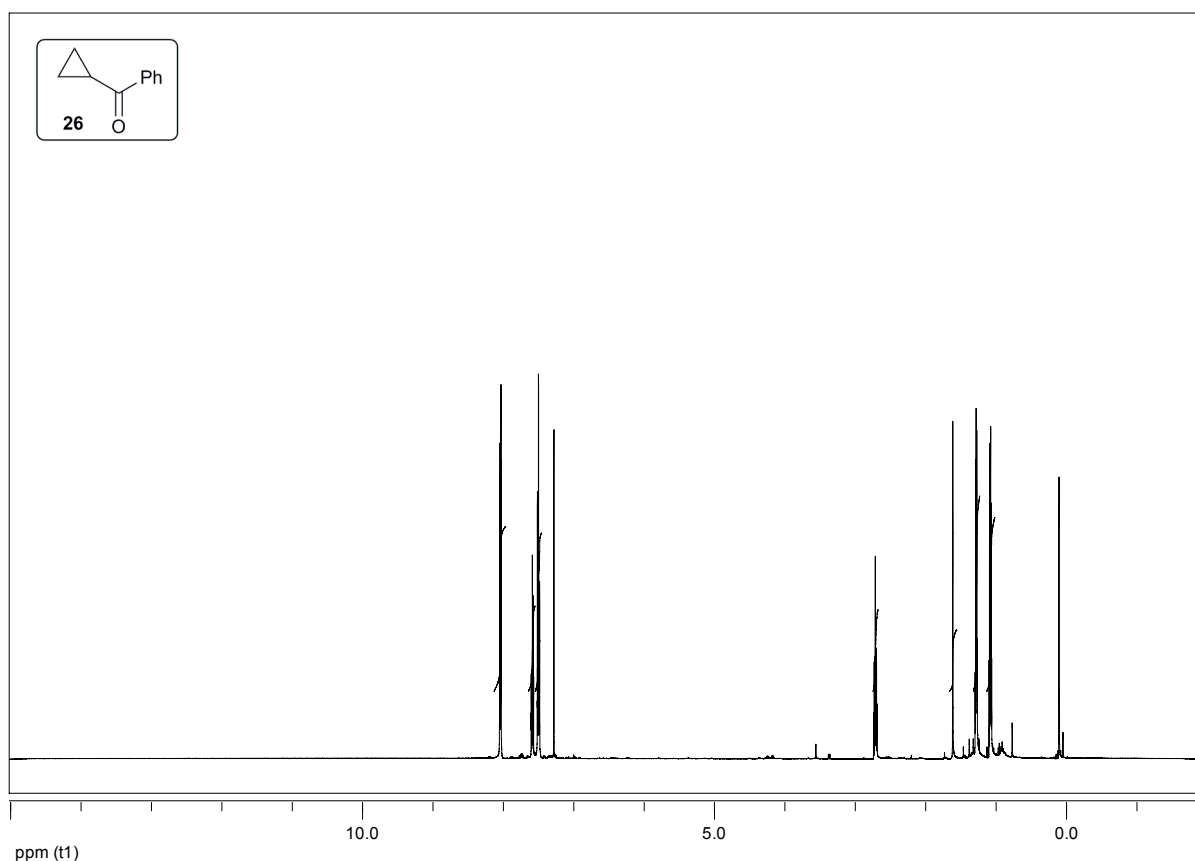
By the same method described for the synthesis of cyclopropane **54**, (*R*)-{2-[(benzyloxy)methyl]pent-4-enyl}diphenylphosphine oxide **52** (40 mg, 0.1 mmol) gave cyclopropane **55** (14 mg, 77%) as an oil. $[\alpha]_D^{21}$ (c=0.65, CHCl₃) -46.4; *m/z* (EI) 186 (32%, M) (Found: M⁺, 186.10430. C₁₃H₁₄O requires *M*, 186.10447). The IR, ¹H- and ¹³C-NMR spectroscopic data are consistent with that reported above for (±)-(1'R,2'R)-phenyl[2-(prop-2'-

enyl)cyclopropyl] methanone **28**. ^1H and ^{13}C NMR Spectra of compound **55** are shown at the end of the experimental section.

(1'R,2'S)-Phenyl[2'-(phenylmethyl)cyclopropyl] methanone 56

By the same method described for the synthesis of cyclopropane **54**, (*R*)-[3-(benzoyloxy)-2-(phenylmethyl)propyl]diphenylphosphine oxide **53** (46 mg, 0.1 mmol) gave cyclopropane **57** (17 mg, 72%) as an oil; $[\alpha]_{\text{D}}^{21.5}$ ($c=0.84$, CHCl_3) -25.5 ; m/z (EI) 236 (27%, M) (Found: M^+ , 236.11887. $\text{C}_{17}\text{H}_{16}\text{O}$ requires M , 236.12012). The IR, ^1H - and ^{13}C -NMR spectroscopic data are consistent with that reported above for (\pm)-(1'*R*,2'*S*)-Phenyl[2'-(phenylmethyl)cyclopropyl] methanone **29**. ^1H and ^{13}C NMR Spectra of compound **56** are shown at the end of the experimental section.

(±)-Cyclopropyl(phenyl)methanone **26**



(1'*R*,2'*R*)-(2'-Methylcyclopropyl)phenyl methanone 54

