Supplementary Material

Asymmetric synthesis of orthogonally protected *trans*-cyclopropane γ-amino acids *via* intramolecular ring closure

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Experimental

For reactions conducted under anhydrous conditions glassware was dried overnight in an oven at 130 °C and was allowed to cool in a dessicator over anhydrous KOH. Anhydrous reactions were carried out under argon. Solvents were BOC standard reagent grade and distilled before use. Reagents/solvents for anhydrous reactions were dried as follows: THF was distilled from sodium wire with benzophenone as indicator. Ether was distilled from a mixture of CaH_2 and $LiAlH_4$. Dichloromethane, hexane, acetonitrile, toluene, pyridine, *N*,*N*-dimethylformamide, triethylamine, dimethylsulfoxide and diisopropylamine were dried and stored over 4 Å molecular sieves. Methanol was dried and stored over 3 Å molecular sieves. *n*-Butyllithium was titrated against diphenylacetic acid before use.[1] Sulfate buffer was prepared by dissolving 1.5 mol of Na_2SO_4 in 0.5 mol H_2SO_4 and adding water to give a 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 due to their tendency to streak on the columns. ^1H, ^{13}C, APT, DEPT, HMQC, COSY, and NOE 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. LC-MS was run on a Waters Alliance LC/MS system consisting of a Waters 2795 Separations Module, a Waters 2996 Photodiode Array Detector

and a Waters Micromass ZQ on a C18 analytical Reverse Phase Supercosil^{TM} ABZ+PLUS column (3.3 cm × 4.6mm, 3μm) using the following gradient: 0.00-0.70 min 100% solvent A, 0.70-4.20 min 100% solvent A to 100% solvent B, 4.20-7.70 min 100% solvent B, 7.70-8.00 min 100% solvent B to 100% solvent A (solvent A: 10 mM ammonium acetate in water containing 0.1% formic acid; solvent B: 95% acetonitrile in water) with a flow rate of 1 cm^3/min. EI and LSIMS mass spectra were recorded on a Kratos concept 1H double focusing magnetic sector instrument using a MACH 3 data system. +ESI mass spectra were recorded using a Bruker Bio-Apex II FT-ICR instrument or a Micromass Q-Tof 1 machine. Microanalyses were carried out on a CE440 Elemental Analyser from Exeter Analytical, INC. The calculated values were adjusted for residual solvents. Melting points were measured on a microscope hot stage melting point apparatus (C. Reichert Optische Werke AG) and are uncorrected. Infra-red spectra were recorded using a Perkin Elmer Spectrum One (FT-IR) spectrometer with a universal ATR sampling accessory. Optical rotations were recorded on a Perkin Elmer 241 polarimeter using to the sodium D line (589 nm) at 23 ^oC and are given in units of 10^{-1} deg dm^2 g^{-1}. X-ray Crystallographic Data was measured on a Nonius Kappa CCD diffractometer at 180(2) K. Analytical chiral HPLC was carried out on a Daicel Chiralpak AD column (0.46 cm × 25 cm) and guard column with a Spectra-Physics SP8800 pump, a Spectra-Physics SP8450 UV detection system and a ChromJet single channel integrator with a flow rate of 1 cm^3/min.

Method 1: Asymmetric dihydroxylation (AD)

By a method analogous to that reported by Sharpless,[4] the substrate (1 mmol) is dissolved in *t*-BuOH (10 cm^3). Water (10 cm^3) is added and the mixture cooled to 0 ^oC. A mixture of $K_2OsO_4 \cdot 2H_2O$ (1 mol%), $K_3Fe(CN)_6$ (3 eq.), K_2CO_3 (3 eq.), $MeSO_2NH_2$ (1 eq.) and $(DHQD)_2PHAL$ (2 mol%) is added to the cooled solution and it is stirred vigorously until completion. Sodium sulfite (~10 eq.) is added and the reaction allowed to warm to room temperature with vigorous stirring. The slurry is transferred to a separatory funnel and the phases are separated. The organic phase is concentrated *in vacuo* and the residue dissolved in dichloromethane (20 cm^3) and transferred to a separatory funnel with the aqueous phase and water (10 cm^3). Extracted with dichloromethane (2 × 20 cm^3). The combined organic extracts are washed with aqueous sulfate buffer (20 cm^3), saturated aqueous $NaHCO_3$ (20 cm^3), dried (Na_2SO_4), filtered and evaporated under reduced pressure. The residue is purified by column chromatography.

Method 2: Racemic dihydroxylation

According to the procedure by Warren[5,6] racemic dihydroxylations were performed at room temperature and $(DHQD)_2PHAL$ was replaced with quinuclidine (5 mol%). Sodium sulfite (~10 eq.) is added and the reaction allowed to warm to room temperature with vigorous stirring. The slurry is transferred to a separatory funnel with water (20 cm^3) and extracted with ethyl acetate (3 × 20 cm^3). The combined organic extracts are washed with aqueous sulfate buffer (20 cm^3), saturated aqueous $NaHCO_3$ (20 cm^3), dried (Na_2SO_4), filtered and evaporated under reduced pressure and the residue purified by column chromatography.

Method 3: Diphenylphosphinoylation of alcohols

To a stirred solution of the alcohol (1 mmol) in anhydrous dichloromethane (10 cm^3) under argon is added Et_3N (2 eq.), DMAP (0.2 eq.) and diphenylphosphinoyl chloride (1.1 eq.). When the reaction has gone to completion water (10 cm^3) is added and the mixture transferred to a separatory funnel and extracted with dichloromethane (3 × 20 cm^3). The combined organic phases are washed with saturated aqueous sulfate buffer (25 cm^3), saturated aqueous $NaHCO_3$ (25 cm^3), dried (Na_2SO_4), filtered and the solvent removed *in vacuo* to give the crude product that is purified by column chromatography.

Method 4: Synthesis of cyclic sulfites

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

Method 5: Mesylation of alcohols

To a stirred solution of the alcohol (1 mmol) in anhydrous dichloromethane (5 cm^3) under argon is added anhydrous pyridine (10 eq.) and methanesulfonyl chloride (1.1 eq.). When the reaction has gone to completion sulfate buffer (20 cm^3) is added and the mixture transferred to a separatory funnel with water (10 cm^3) and extracted with dichloromethane (3 × 20 cm^3). The combined organic phases are washed with saturated aqueous $NaHCO_3$ (20 cm^3), dried (Na_2SO_4), filtered and the

solvent removed *in vacuo* to give the crude product that is re-dissolved in toluene and concentrated *in vacuo* to remove pyridine traces. The product is purified by column chromatography.

Method 6: Tosylation of alcohols

To a stirred solution of the alcohol (1 mmol) in anhydrous dichloromethane (10 cm^3) under argon is added triethylamine (2 eq.), DMAP (0.2 eq.) and 4-methylphenylsulfonyl chloride (1.1 eq.). When the reaction has gone to completion sulfate buffer (20 cm^3) is added and the mixture transferred to a separatory funnel with water (10 cm^3) and extracted with dichloromethane (3 × 20 cm^3). The combined organic phases are washed with saturated aqueous $NaHCO_3$ (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.

Method 7 a-c: Cyclopropanation by intramolecular ring closure

7a (LDA): The substrate (1 mmol) is dissolved in anhydrous THF (10 cm^3) and cooled to −78 ^oC with stirring under argon. Freshly prepared LDA cooled to −78 ^oC is added by cannula. After stirring at −78 ^oC for 1-2 hours the reaction mixture is allowed to slowly warm to room temperature overnight. The reaction is quenched with saturated aqueous NH_4Cl (20 cm^3), extracted with ethyl acetate (3 × 20 cm^3), dried (Na_2SO_4), filtered and concentrated *in vacuo* to give the crude product, which is purified by column chromatography.

7b (NaHMDS): Same procedure as method **7a** except that sodium hexamethyldisilazide (2.0 M in THF, 1.05 eq.) is employed instead of LDA, and the temperature is maintained at −78 ^oC for 3-4 hours after the addition of base.

7c (KHMDS): Same procedure as method **7a** except that potassium hexamethyldisilazide (0.5 M in toluene, 1.05 eq.) is employed instead of LDA, and the temperature is maintained at −78 ^oC for 3-4 hours after the addition of base.

Method 8: Opening of cyclic sulfites with sodium azide

The cyclic sulfite (1 mmol) is dissolved in anhydrous DMF (5 cm^3). NaN_3 (2 eq.) is added and the reaction mixture heated to 60 ^oC with stirring under argon for 48 hours. When the reaction mixture has cooled to room temperature it is transferred to a separatory funnel with water (20 cm^3) and extracted with ethyl acetate (3 × 20 cm^3). The combined organic phases are washed with aqueous

sulfate buffer (20 cm^3), dried (Na_2SO_4), filtered and concentrated *in vacuo*. Residual DMF is removed on a high vacuum pump and the residue purified by column chromatography.

Method 9: Synthesis of Mosher's amides

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

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

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

(*E*)-*tert*-Butyl 5-phenyl-pent-4-enoate 8

tert-Butyl acetate (1.0 g, 8.6 mmol) was dissolved in anhydrous THF (40 cm^3) and cooled to −78 ^oC. Freshly prepared LDA (9.0 mmol) was added by cannula to give a red solution. After ½ hour HMPA (1.5 cm^3, 8.6 mmol) was added. After an additional ½ hour (*E*)-cinnamyl bromide (1.7 g, 8.6 mmol) dissolved in anhydrous THF (10 cm^3) and cooled to −78 ^oC was added by cannula. After 4 hours the reaction was quenched by the addition of saturated aqueous NH_4Cl (20 cm^3) and allowed to warm to room temperature. The reaction mixture was transferred to a separatory funnel with water (10 cm^3) and extracted with ethyl acetate (3 × 50 cm^3). The combined organic phases were washed with water (3 × 50 cm^3), dried (Na_2SO_4), filtered and concentrated *in vacuo* to give a yellow liquid. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 6 × hexanes; 2.5-20% EtOAc in hexanes (v/v) – 2.5% increments; two fractions of each solvent mixture were collected] to give *tert*-butyl ester **8 (**1.92 g, 96%) as a clear colourless liquid. R_f 0.30 (5% EtOAc in hexanes, v/v); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1722 (C=O) and 1149 (C-O); *m/z* (+ESI) found: MNa^+, 255.1367. ($C_{15}H_{20}O_2Na$ requires *M*, 355.1356); ^1H NMR (500 MHz; $CDCl_3$) δ 7.36-7.34 (2H, m, *ortho*-Ph), 7.32-7.29 (2H, m, *meta*-Ph), 7.21 (1H, tt, *J* 7.0 and 1.5. *para*-Ph), 6.44 (1H, d, *J* 16.0, CH=C*H*Ph),

6.22 (1H, dt, *J* 16.0 and 7.0, C*H*=CHPh), 2.53-2.49 (2H, m, CH_2CH=CH), 2.42-2.39 (2H, m, CH_2C=O) and 1.47 [9H, s, C(CH_3)]; ^{13}C NMR (126 MHz; $CDCl_3$) δ 172.3 (C1), 137.4 (*ipso*-Ph), 130.7 (C5), 128.7 (C4), 128.4 (*meta*-Ph), 127.0 (*para*-Ph), 126.0 (*ortho*-Ph), 80.2 [*C*(CH_3)$_3$], 35.2 (C2), 28.5 (C3) and 28.1 [C(*C*H_3)$_3$]; (Found: C, 77.81; H, 8.73. $C_{15}H_{20}O_2$ requires C, 77.55; H, 8.68%). Compound **8** has been reported before with no characterisation.[7]

(4*R*,5*R*)-*tert*-Butyl 4,5-dihydroxy-5-phenyl-pentanoate 9

By method **1** *tert*-butyl ester **8** (3.0 g, 12.9 mmol) after 4 days at 3 ^{o}C gave a viscous yellow liquid that was purified by DCVC [id 6 cm; 50 cm^3 fractions; 3 × hexanes; 10-100% EtOAc in hexanes (v/v) – 10% increments; 3 × EtOAc] to give *diol* **9** (2.95 g, 86%) as white needles. e.e. >95% (determined by chiral HPLC); HPLC [R_T (min), flow rate 1 cm^3/min, 4% EtOH in *iso*-hexane (v/v)]: 18.7; $[\alpha]_D^{23}$ –22 (c. 1.7, $CHCl_3$); mp 55-56 °C (from EtOAc, hexanes); R_f 0.70 (50% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 289.1402. ($C_{15}H_{22}O_4Na$ requires *M*, 289.1416); IR ν_{max}($CHCl_3$)/cm^{-1} 3386 (br., O-H), 1724 (C=O) and 1148 (C-O); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.38-7.28 (5H, m, Ph), 4.43 (1H, d, *J* 7.0, PhC*H*OH), 3.68 (1H, ddd, *J* 9.0, 7.0 and 3.5, CH_2C*H*OH), 3.12 (1H, br s, OH), 3.00 (1H, br s, OH), 2.38 (1H, dt, *J* 16.5 and 7.0, C$H_a$$H_b$C=O), 2.32 (1H, dt, *J* 16.5 and 7.0, $CH_a$$H_b$C=O), 1.70-1.58 (2H, m, CH_2CHOH) and 1.41 [9H, s, C(CH_3)]; ^{13}C NMR (126 MHz; $CDCl_3$) δ 173.7 (C1), 140.8 (*ipso*-Ph), 128.5 (Ph), 128.1 (*para*-Ph), 126.9 (Ph), 80.7 [*C*(CH_3)$_3$], 77.9 (C5), 75.5 (C4), 32.0 (C2), 28.0 [C(*C*H_3)$_3$)] and 27.7 (C3); (Found: C, 67.66; H, 8.44. $C_{15}H_{22}O_4$ requires C, 67.64; H, 8.33%).

(4*RS*,5*RS*)-*tert*-Butyl 4,5-dihydroxy-5-phenyl-pentanoate (±)-9

By method **2** *tert*-butyl ester **8** (0.20 g, 0.90 mmol) after 24 hours gave *diol* **(±)-9** (0.23 g, 95%) as a clear gum that required no further purification. HPLC [R_T (min), flow rate 1 cm^3/min, 4% EtOH in *iso*-hexane (v/v)]: 14.7 and 19.3; All analytical data were identical with that for *tert*-butyl (4*R*,5*R*)-**9** reported above.

(4*R*,5*R*)-*tert*-Butyl 4,5-diphenylphosphinoyloxy-5-phenyl-pentanoate 10

By method **3** diol **9** (0.47 g, 1.76 mmol) after 1 day gave a yellow foam. Purification by DCVC [id 4 cm; 20 cm^3 fractions: 2 × hexanes; 10-100% EtOAc in hexanes (v/v) – 10% increments; 11 × EtOAc] gave *bis-phosphinate* **10** (0.62 g, 52%) as a clear gum. $[\alpha]_D^{23}$ +18 (c. 1, $CHCl_3$); R_f 0.25

(80% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MH^+, 667.2398. ($C_{39}H_{41}O_6P_2$ requires *M*, 667.2378); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1724 (C=O), 1439 (P-Ph) and 1226 (P=O); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.83-7.75 (4H, m, Ph), 7.65-7.61 (2H, m, Ph), 7.53-7.42 (7H, m, Ph), 7.38-7.32 (4H, m, Ph), 7.24-7.14 (8H, m, Ph), 5.50 (1H, dd, *J* 10.0 and 6.0, PhC*H*), 4.84-4.79 (1H, m, PhCHC*H*), 2.25-2.15 (2H, m, CH_2C=O), 2.06-1.99 (1H, m, $CH_aH_bCH_2C$=O), 1.69-1.62 (1H, m, $CH_aH_bCH_2C$=O) and 1.32 [9H, s, $C(CH_3)_3$]; ^{31}P NMR (162 MHz; $CDCl_3$) δ 32.2 (×2); ^{13}C NMR (126 MHz; $CDCl_3$) δ 172.0 (C1), 136.3 (*ipso*-PhC), 132.1 (d, *J* 2.5), 132.0 (d, *J* 3.0) (2 × *para*-PhP), 131.9-131.5 (m, Ph), 131.8 (d, *J* 138.0), 131.4 (d, *J* 140.5) (2 × *ipso*-Ph), 130.5 (×2), 128.5-128.0 (m) (Ph), 127.6 (*para*-PhC), 80.2 [$C(CH_3)_3$], 77.4 (t, *J* 5.5, C5), 76.9 (t, *J* 6.0, C4), 30.6 (C2), 28.0 [$C(CH_3)_3$] and 26.2 (d, *J* 2.5, C3).

(4*RS*,5*RS*)-*tert*-Butyl 4,5-diphenylphosphinoyloxy-5-phenyl-pentanoate (±)-10

By method **3** diol **(±)-9** (0.20 g, 0.75 mmol) after 14 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; 10 × EtOAc] gave *bis-phosphinate* **(±)-10** (0.27 g, 54%) as a clear gum. All analytical data were identical with that for (4*R*,5*R*)-**10** reported above.

(1'*R*,2'*R*,1''*S*)-*tert*-Butyl 2'-(1''-diphenylphosphinoyloxy-1''-phenyl-methyl)-cyclopropane carboxylate 11

By method **7b** *bis*-phosphinate **10** (0.27 g, 0.41 mmol) gave a yellow gum. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 10-100% EtOAc in hexanes (v/v) – 10% increments; 5 × EtOAc] to give *cyclopropane* **11** (75 mg, 41%) as a white amorphous solid. e.e. >95% (determined by chiral HPLC); HPLC [R_T (min), flow rate 1 cm^3/min, 5% *iso*-propanol in *iso*-hexane (v/v)]: 57.1; $[\alpha]_D^{23}$ –29 (c. 0.7, $CHCl_3$); R_f 0.50 (60% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 471.1684. ($C_{27}H_{29}O_4PNa$ requires *M*, 471.1701); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1717 (C=O), 1439 (PPh), 1220 (P=O) and 1151 (C-O); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.85-7.81 (2H, m, *ortho*-PPh), 7.59-7.54 (2H, m, *ortho*-PPh), 7.53-7.49 (1H, m, *para*-PhP), 7.46-7.42 (2H, m, *meta*-PhP), 7.40-7.37 (1H, m, *para*-PhP), 7.29-7.24 (7H, m, *meta*-PhP and PhC), 5.09 (1H, dd, *J* 9.5 and 7.5, PhC*H*), 1.89 (1H, dddd, *J* 8.5, 7.5, 6.5 and 4.5, PhCHC*H*), 1.62 (1H, ddd, *J* 8.5, 5.0 and 4.5, C*H*C=O), 1.35 [9H, s, $C(CH_3)_3$] and 1.08-1.02 (2H, m, CH_2); ^{31}P NMR (162 MHz; $CDCl_3$) δ 32.3; ^{13}C NMR (126 MHz; $CDCl_3$) δ 172.3 (C1), 139.4 (d, *J* 4.0, *ipso*-PhC), 132.4 (d, *J* 93.0, *ipso*-PhP),

132.1 (d, *J* 2.5, *para*-PhP), 131.9 (d, *J* 3.0, *para*-PhP), 131.6 (d, *J* 10.5, *ortho*-PhP), 131.5 (d, *J* 10.5, *ortho*-PhP), 128.4 (d, *J* 13.0, *meta*-PhP), 128.3 (PhC), 128.2 (PhC), 128.1 (d, *J* 13.5, *meta*-PhP), 126.7 (PhC), 80.4 [*C*$(CH_3)_3$], 78.4 (d, *J* 6.0, C1''), 28.0 [C(*C*$H_3)_3$], 27.2 (C2'), 19.6 (C1') and 13.6 (C3').

(1'*RS*,2'*RS*,1''*SR*)-*tert*-Butyl 2'-(1''-diphenylphosphinoyloxy-1''-phenyl-methyl)-cyclopropane carboxylate (±)-11

By method **7b** *bis*-phosphinate **(±)-10** (0.27 g, 0.44 mmol) gave a yellow residue. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 10-100% EtOAc in hexanes (v/v) – 10% increments; 5 × EtOAc] to give cyclopropane **(±)-11** (25 mg, 14%) as a white amorphous solid. HPLC [R_T (min), flow rate 1 cm^3/min, 5% *iso*-propanol in *iso*-hexane (v/v)]: 39.5 and 58.5; All analytical data were identical with that for (1'*R*,2'*R*,1''*S*)-**11** reported above.

(1'*RS*,4'*R*,5'*R*)-*tert*-Butyl 3-(1'-Oxo-3'-phenyl-[2',5',1']dioxathiolan-4'-yl)-propanoate 15

By method **4** diol **9** (0.60 g, 2.25 mmol), after 4 hours, gave a yellow gum. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 3 × hexanes; 5-50% EtOAc in hexanes (v/v) – 5% increments; 1-5% MeOH in EtOAc (v/v) – 1% increments] to give *cyclic sulfite* **15** (0.60 g, 85%) as a viscous yellow liquid. d.r. = 56:44 (^{1}H NMR, epimers at S); R_f 0.25 (10% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 335.0921. ($C_{15}H_{20}O_5SNa$ requires *M*, 335.0929); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1724 (C=O), 1207 (S=O) and 1150 (C-O); ^{1}H NMR (500 MHz; $CDCl_3$) Two diastereoisomers A: major isomer, B: minor isomer. δ 7.48-7.37 (m, 5H, Ph A,B), 5.51 (d, 1H, *J* 9.5, C*H*Ph A), 4.95 (d, 1H, *J* 9.5, C*H*Ph B), 4.75 (dt, 1H, *J* 9.5 and 3.0, CH_2CH B), 4.38 (dt, 1H, *J* 9.0 and 6.0, CH_2CH A), 2.55-2.31 (m, 4H, 2 × CH_2C=O A,B), 2.16-1.97 (m, 4H, 2 × CH_2CH A,B) and 1.39 [s, 18H, 2 × C$(CH_3)_3$]; ^{13}C NMR (126 MHz; $CDCl_3$) δ 171.4, 171.3 (2 × C1 A,B), 133.8, 133.1 (2 × *ipso*-Ph A,B), 129.8, 129.4, 129.1 (×2), 127.7, 127.2 (6 × Ph A,B), 89.6 (C5 B), 88.3 (C4 A), 84.3 (C5 A), 83.9 (C4 B), 80.9, 83.9 [2 × *C*$(CH_3)_3$ A,B], 31.6, 31.5 (2 × C2 A,B), 28.0 [2 × C(*C*$H_3)_3$ A,B], 27.5 and 25.3 (2 × C3 A,B); (Found: C, 57.96; H, 6.43. $C_{15}H_{20}O_5S$ requires C, 57.67; H, 6.45%).

(4*R*,5*R*)-*tert*-Butyl 4,5-methanesulfonyloxy-5-phenyl-pentanoate 16

By method **5** diol **9** (0.52 g, 1.95 mmol) after 20 hours gave a yellow liquid. Purification by DCVC [id 4 cm; 20 cm^3 fractions: 2 × hexanes; 0-50% EtOAc in hexanes (v/v) – 5% increments; 50-100%

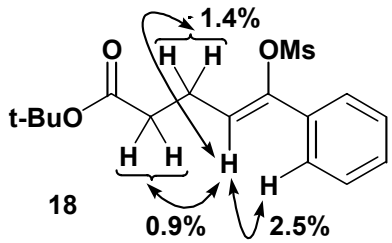
EtOAc in hexanes (v/v) – 10% increments; 5 × EtOAc] gave *mesylate* **16** (0.61 g, 73%) as a white amorphous solid. $[\alpha]_D^{23}$ –35 (c. 0.2, $CHCl_3$); mp 52-54 °C (EtOAc, hexanes); R_f 0.55 (50% EtOAc in hexanes, v/v); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1723 (C=O), 1349 (SO_2) and 1168 (SO_2); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.50-7.41 (5H, m, Ph), 5.52 (1H, d, *J* 8.0, PhC*H*), 5.11 (1H, dt, *J* 8.0 and 6.5, PhCHC*H*), 3.09 (3H, s, CH_3S), 2.62 (3H, s, CH_3S), 2.40 (2H, t, *J* 7.5, CH_2C=O), 1.73-1.67 (2H, m, CH_2CH_2C=O) and 1.40 [9H, s, $C(CH_3)_3$]; ^{13}C NMR (100 MHz; $CDCl_3$) δ 171.4 (C1), 133.7 (*ipso*-Ph), 130.4 (*para*-Ph), 129.5, 127.8 (*ortho*- and *meta*-Ph), 84.3 (C5), 81.6 (C4), 80.9 [$C(CH_3)_3$], 39.5, 39.1 (2 × CH_3S), 30.4 (C2), 28.0 [$C(CH_3)_3$] and 26.4 (C3); (Found: C, 48.79; H, 6.10. $C_{17}H_{26}O_8S_2$ requires C, 48.33; H, 6.20%).

(4*R*,5*R*)-*tert*-Butyl 4,5-bis-(4'-methyl-phenylsulfonyloxy)-5-phenyl-pentanoate 17

Diol **9** (0.25 g, 0.94 mmol) was dissolved in anhydrous pyridine (5 cm^3) and *para*-phenylsulfonyl chloride (1.14 g, 6.0 mmol) was added. After 20 hours the reaction was quenched with saturated aqueous NH_4Cl (15 cm^3) and extracted with ethyl acetate (3 × 25 cm^3). The combined organic phases were dried (Na_2SO_4), filtered and concentrated *in vacuo* to give a clear gum that was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 5-90% EtOAc in hexanes (v/v) – 5% increments] to give *bis-tosylate* **17** (0.39 g, 72%) as a white amorphous solid. $[\alpha]_D^{23}$ +6.38 (c. 1.27, $CHCl_3$); R_f 0.30 (30% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 597.1609. ($C_{29}H_{34}O_8S_2Na$ requires *M*, 597.1593); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1711 (C=O), 1364 (SO_2) and 1171 (SO_2); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.73-7.71 (2H, m, *ortho*-Ts), 7.54-7.52 (2H, m, *ortho*-Ts), 7.31-7.30 (2H, m, *meta*-Ts), 7.21 (1H, tt, *J* 7.5 and 1.5, *para*-Ph), 7.16-7.12 (4H, m, *meta*-Ts and *meta*-Ph), 7.08-7.06 (2H, m, *ortho*-Ph), 5.49 (1H, d, *J* 5.5, C*H*Ph), 4.88 (1H, ddd, *J* 9.1, 9.0 and 5.5, C*H*CHPh), 2.45 (3H, s, CH_3Ar), 2.35 (3H, s, CH_3Ar), 2.23-2.10 (2H, m, CH_2C=O), 1.93-1.86 (1H, m, CH_aH_bCH), 1.61-1.52 (1H, m, CH_aH_bCH) and 1.39 [9H, s, $C(CH_3)_3$]; ^{13}C NMR (126 MHz; $CDCl_3$) δ 171.3 (C1), 144.9, 144.6 (2 × *para*-Ts), 133.3 (×2), 133.1 (2 × *ipso*-Ts and *ipso*-Ph), 129.8, 129.4 (2 × *meta*-Ts), 128.8 (*para*-Ph), 128.3 (*meta*-Ph), 128.0, 127.9 (2 × *ortho*-Ts), 127.3 (*ortho*-Ph), 81.7 (C5), 80.9 (C4), 80.6 [$C(CH_3)_3$], 30.3 (C2), 28.0 [$C(CH_3)_3$], 25.3 (C3), 21.7 and 21.6 (2 × CH_3Ar); (Found: C, 57.30; H, 5.56. $C_{29}H_{34}O_8S_2$·0.15 EtOAc requires C, 57.18; H, 5.69%).

(*Z*)-*tert*-Butyl 5-methanesulfonyloxy-5-phenyl-pent-4-enoate 18

By method **7b** *bis*-mesylate **16** (126 mg, 0.30 mmol) gave a yellow gum. The product was purified by DCVC [id 1 cm; 9 cm^3 fractions; 4 × hexanes; 5-70% EtOAc in hexanes (v/v) – 5% increments; two fractions of each solvent mixture were collected] to give *olefin* **18** (30 mg, 30%) as a clear liquid. R_f 0.35 (30% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 349.1080. ($C_{16}H_{22}O_5SNa$ requires *M*, 349.1086); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1721 (C=O), 1364 (SO_2) and 1174 (SO_2); ^1H NMR (500 MHz; $CDCl_3$) δ 7.49-7.47 (2H, m, *ortho*-Ph), 7.41-7.31 (3H, m, Ph), 5.84 (1H, t, *J* 7.5, PhC=C*H*), 2.98 (3H, s, CH_3S), 2.65 (2H, q, CHCH_2), 2.42 (2H, t, *J* 7.5, CH_2C=O) and 1.45 [9H, s, $C(CH_3)_3$]; ^{13}C NMR (126 MHz; $CDCl_3$) δ 171.9 (C1), 146.4 (C5), 134.5 (*ipso*-Ph), 129.0 (*para*-Ph), 128.7 (*meta*-Ph), 125.7 (*ortho*-Ph), 121.3 (C4), 80.5 [*C*$(CH_3)_3$], 39.4 (CH_3S), 34.5 (C2), 28.1 [C(*C*$H_3)_3$] and 22.6 (C3).



No NOE was observed between the C4 proton and the mesyl group and a strong NOE between the C4 proton and the *ortho*-protons on the aromatic ring was observed indicating that the compound has the (*Z*)-geometry as shown.

(*Z*)-*tert*-Butyl 5-(4-methyl-phenylsulfonyloxy)-5-phenyl-pent-4-enoate 19

According to method **7b** *bis*-tosylate **17** (0.12 g, 0.21 mmol) gave a grey 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; 4 × EtOAc] to give starting material **17** (47 mg, 39%) and olefin **19** (8 mg, 10%) as a clear film. R_f 0.30 (20% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 425.1386. ($C_{22}H_{26}O_5SNa$ requires *M*, 425.1399); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1726 (C=O), 1368 (SO_2), 1177 (SO_2) and 1152 (C-O); ^1H NMR (500 MHz; $CDCl_3$) δ 7.67 (2H, dt, *J* 8.5 and 2.0, *ortho*-Ts), 7.27-7.25 (3H, m, Ar), 7.21-7.17 (4H, m, Ar), 2.43 (2H, q, *J* 7.0, CHCH_2), 2.39 (3H, s, CH_3Ar), 2.29 (2H, t, *J* 7.0, CH_2C=O) and 1.44 [9H, s, $C(CH_3)_3$]; ^{13}C NMR (126 MHz; $CDCl_3$) δ 171.9 (C1), 146.9, 144.9, 134.6, 133.6 (C5, *ipso*-Ph, *ipso*-Ts and *para*-Ts), 129.5, 128.3 (×2), 128.1, 125.7 (Ph and Ts), 120.8 (C4), 80.4 [*C*$(CH_3)_3$], 34.5 (C2), 28.1 [C(*C*$H_3)_3$], 22.3 (C3) and 21.6 (*C*H_3Ar).

(4*R*,5*S*)-*tert*-Butyl 5-azido-4-hydroxy-5-phenyl-pentanoate 26

By method **4** diol **9** (0.74 g, 2.80 mmol) gave a dark brown gum. According to method **8** the crude cyclic sulfite produced a brown gum that was purified by DCVC [id 4 cm, 20 cm^3 fractions; 2 × hexanes; 0-100% EtOAc in hexanes (v/v) – 10% increments; 5 × EtOAc] to give *azide* **26** (0.53 g,

65%) as a yellow gum. $[\alpha]_D^{23}$ +113 (c. 1, $CHCl_3$); R_f 0.50 (30% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 314.1475. ($C_{15}H_{21}N_3O_3Na$ requires *M*, 314.1480); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 3443 (br., O-H), 2101 (N_3), 1724 (C=O) and 1148 (C-O); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.42-7.38 (2H, m, Ph), 7.36-7.33 (3H, m, Ph), 4.52 (1H, d, *J* 6.0, C*H*Ph), 3.84-3.78 (1H, m, C*H*CHPh), 2.54 (1H, br d, *J* 4.0, OH), 2.39 (2H, t, *J* 7.0, CH_2C=O), 1.85 (1H, dtd, *J* 10.0, 7.0 and 2.5, $CH_aH_bCH_2C$=O), 1.64 (1H, tdd, *J* 14.5, 10.0 and 7.0, $CH_aH_bCH_2C$=O) and 1.43 [9H, s, $C(CH_3)_3$]; ^{13}C NMR (126 MHz; $CDCl_3$) δ 173.5 (C1), 136.2 (*ipso*-Ph), 128.8 (Ph), 128.5 (*para*-Ph), 127.8 (Ph), 80.7 [$C(CH_3)_3$], 73.9 (C4), 70.4 (C5), 31.9 (C2), 28.0 [$C(CH_3)_3$] and 27.3 (C3); (Found: C, 61.78; H, 7.25; N, 14.20. $C_{15}H_{21}N_3O_3$ requires C, 61.84; H, 7.27; N, 14.42%).

(4*R*,5*S*)-*tert*-Butyl 5-azido-4-diphenylphosphinoyloxy-5-phenyl-pentanoate 27

By method **3** alcohol **26** (0.38 g, 1.3 mmol) after 42 hours gave a yellow gum. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 0-100% EtOAc in hexanes (v/v) – 10% increments; 4 × EtOAc] gave *phosphinate* **27** (0.43 g, 67%) as a yellow gum. $[\alpha]_D^{23}$ +11.8 (c. 1.0, $CHCl_3$); R_f 0.55 (50% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 514.1878. ($C_{27}H_{30}N_3O_4PNa$ requires *M*, 514.1872); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 2106 (N_3), 1727 (C=O) 1440 (P-Ph), 1231 (P=O) and 1153 (C-O); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.84-7.74 (4H, m, *ortho*-PhP), 7.55-7.50 (2H, m, *para*-PhP), 7.47-7.42 (4H, m, *meta*-PhP), 7.31-7.24 (3H, m, *meta*- and *para*-PhC), 7.19-7.17 (2H, m, *ortho*-PhC), 4.89 (1H, d, *J* 4.0, PhCH), 4.62 (1H, tdd, *J* 9.0, 3.5 and 3.3, PhCHC*H*), 2.91 (1H, ddd, *J* 17.5, 9.5 and 5.0, CH_aH_bC=O), 2.78 (1H, ddd, *J* 17.5, 9.0 and 6.5, CH_aH_bC=O), 2.08-2.0 (1H, m, $CH_aH_bCH_2C$=O), 1.80-1.73 (1H, m, $CH_aH_bCH_2C$=O) and 1.32 [9H, s, $C(CH_3)_3$]; ^{31}P NMR (162 MHz; $CDCl_3$) δ 32.6; ^{13}C NMR (126 MHz; $CDCl_3$) δ 172.0 (C1), 135.6 (*ipso*-PhC), 132.3 (×2) (2 × *para*-PhP), 131.6 (d, *J* 10.5, 2 × *ortho*-PhP), 131.4 (d, *J* 135.0, *ipso*-PhP), 131.2 (d, *J* 138.0, *ipso*-PhP), 128.7 (*ortho*-PhC), 128.5 (d, *J* 13.0, *meta*-PhP), 128.3 (*meta*-PhC), 127.1 (*para*-PhC), 80.3 [$C(CH_3)_3$], 78.4 (d, *J* 6.5, C4), 68.6 (d, *J* 3.0, C5), 31.1 (C2), 27.9 [$C(CH_3)_3$] and 24.6 (d, *J* 4.0, C3); (Found: C, 65.69; H, 6.45. $C_{27}H_{30}N_3O_4P$ requires C, 65.98; H, 6.15%).

(4*R*,5*S*)-*tert*-Butyl 5-azido-4-methanesulfonyloxy-5-phenyl-pentanoate 28

According to method **5** alcohol **26** (0.40 g, 1.37 mmol) after 26 hours gave a yellow oil. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 3 × hexanes; 5-100% EtOAc in hexanes (v/v) – 5% increments] gave *mesylate* **28** (0.48 g, 94%) as yellow gum. $[\alpha]_D^{23}$ +105 (c. 1, $CHCl_3$); R_f 0.45 (30%

EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 392.1251. ($C_{16}H_{23}N_3O_5SNa$ requires *M*, 392.1256); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 2108 (N_3), 1726 (C=O) 1366 (SO_2) and 1174 (SO_2); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.43-7.35 (5H, m, Ph), 4.92 (1H, d, *J* 5.0, PhC*H*), 4.89 (1H, ddd, *J* 8.5, 5.0 and 4.0, C*H*CHPh), 2.82 (3H, s, CH_3S), 2.39 (1H, ddd, *J* 17.0, 7.5 and 6.0, CH_aH$_b$C=O), 2.32 (1H, dt, *J* 17.0 and 8.0, CH$_a$$H_b$C=O), 1.98-1.87 (2H, m, CH_2CH$_2$C=O) and 1.40 [9H, s, C(CH_3)$_3$]; ^{13}C NMR (126 MHz; $CDCl_3$) δ 171.6 (C1), 135.0 (*ipso*-Ph), 129.0 (*para*-Ph), 129.0, 127.7 (*ortho*- and *meta*-Ph), 83.1 (C4), 80.8 [*C*(CH_3)$_3$], 68.0 (C5), 38.3 (CH_3S), 30.8 (C2), 28.0 [C(*C*H$_3$)$_3$] and 25.3 (C3); (Found: C, 52.27; H, 6.42; N, 11.62. $C_{16}H_{23}N_3O_5S$ requires C, 52.02; H, 6.28; N, 11.37%).

(4*R*,5*S*)-*tert*-Butyl 5-azido-4-(4'-methyl-phenylsulfonyloxy)-5-phenyl-pentanoate 29

According to method **6** alcohol **26** (0.22 g, 0.76 mmol) after 48 hours gave a brown gum. Purification by DCVC [id 4 cm; 25 cm^3 fractions; 2 × hexanes; 5-40% EtOAc in hexanes (v/v) – 5% increments; two fractions of each solvent mixture were collected) gave *tosylate* **29** (0.25 g, 73%) as a clear gum and starting material **26** (45 mg, 6%). $[\alpha]_D^{23}$ +110 (c. 1, $CHCl_3$); R_f 0.60 (30% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MH^+, 446.1762. ($C_{22}H_{28}N_3O_5S$ requires *M*, 446.1750); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 2107 (N_3), 1727 (C=O) 1367 (SO_2) and 1176 (SO_2); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.79-7.78 (2H, *ortho*-Ts), 7.36-7.29 (5H, m, Ph and *meta*-Ts), 7.25-7.22 (2H, m, Ph), 4.87 (1H, d, *J* 4.0, PhC*H*), 4.84 (1H, ddd, *J* 9.5, 3.5 and 3.0, C*H*CHPh), 2.27 (1H, ddd, *J* 16.5, 8.5 and 5.5, CH_aH$_b$C=O), 2.12 (1H, ddd, *J* 16.5, 8.5 and 7.5, CH$_a$$H_b$C=O), 1.94 (1H, dddd, *J* 15.0, 9.5, 8.5 and 5.5, CH_aH$_b$CH$_2$C=O) and 1.75 (1H, dddd, *J* 15.0, 8.5, 7.5 and 3.0, CH$_a$$H_bCH_2$C=O); ^{13}C NMR (126 MHz; $CDCl_3$) δ 171.6 (C1), 145.1 (*para*-Ts), 134.9, 133.7 (*ipso*-Ph and *ipso*-Ts), 129.9, 128.9 (Ph and *meta*-Ts), 128.6 (*para*-Ph), 127.8 (*ortho*-Ts), 127.2 (Ph), 83.6 (C4), 80.6 [*C*(CH_3)$_3$], 67.7 (C5), 30.7 (C2), 28.0 [C(*C*H$_3$)$_3$], 23.8 (C3) and 21.7 (Ph*C*H$_3$).

(1*R*,2*R*,1'*R*)-*tert*-Butyl 2-(1'-azido-1'-phenyl-methyl)-cyclopropane carboxylate 30

By a modified method **7a**[§] mesylate **28** (1.00 g, 2.73 mmol) gave a yellow gum. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 0-50% EtOAc in hexanes (v/v) – 10% increments – two fractions of each solvent mixture were collected] to give starting material **28** (225 mg, 22%) and cyclopropane **30** (103 mg, 13%) as a clear oil. [§] The temperature was maintained at –78 ^{o}C for 24 hours and then raised to room temperature for an additional 24 hours. $[\alpha]_D^{23}$ +14 (c. 1, $CHCl_3$); R_f 0.25 (5% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 296.1370. ($C_{15}H_{19}N_3O_2Na$

requires *M*, 296.1375); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 2094 (N_3), 1717 (C=O) and 1150 (C-O); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.41-7.33 (5H, m, Ph), 4.05 (1H, d, *J* 8.0, PhC*H*), 1.83 (1H, dddd, *J* 9.0, 8.0, 6.0 and 4.0, PhCHC*H*), 1.76 (1H, dt, *J* 9.0 and 4.0, C*H*C=O), 1.46 [9H, s, $C(CH_3)_3$], 1.17 (1H, dt, *J* 9.0 and 5.0, CH_aH_b) and 0.87 (1H, ddd, *J* 8.5, 6.0 and 4.5, CH_aH_b); ^{13}C NMR (126 MHz; $CDCl_3$) δ 172.2 (C1), 138.5 (*ipso*-Ph), 128.8 (Ph), 128.5 (*para*-Ph), 127.0 (Ph), 80.7 [$C(CH_3)_3$], 67.3 (C1''), 28.1 [$C(CH_3)_3$], 26.1 (C2'), 20.6 (C1') and 12.0 (C3').

(1'*R*,2'*R*,1''*R*)-*tert*-Butyl 2'-(1''-azido-1''-phenyl-methyl)-cyclopropane carboxylate 30

By method **7b** mesylate **28** (126 mg, 0.34 mmol) gave a yellow gum. The product was purified by DCVC [id 1 cm; 9 cm^3 fractions; 6 × hexanes; 1-20% EtOAc in hexanes (v/v) – 1% increments; two fractions of each solvent mixture were collected] to give *cyclopropane* **30** (60 mg, 64%) as a clear oil. All analytical data were identical to that reported above.

(1'*R*,2'*R*,1''*R*)-*tert*-Butyl 2'-(1''-azido-1''-phenyl-methyl)-cyclopropane carboxylate 30

According to method **7b** tosylate **29** (0.13 g, 0.30 mmol) gave a yellow gum. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 6 × hexanes; 2-20% EtOAc in hexanes (v/v) – 2% increments; two fractions of each solvent mixture were collected] to give *cyclopropane* **30** (42 mg, 52%) as a clear gum. All analytical data were identical with that reported above.

(1'*R*,2'*R*,1''*R*)-*tert*-Butyl 2'-(1''-amino-1''-phenyl-methyl)-cyclopropane carboxylate 34

Azide **30** (169 mg, 0.62 mmol) was dissolved in methanol (10 cm^3) and the flask was flushed with argon. $Pd(OH)_2$ on carbon (32 mg; 20wt% dry basis) was added and the flask was flushed with hydrogen, fitted with a hydrogen balloon and stirred vigorously. After stirring overnight (23 hours) the reaction mixture was filtered through a plug of celite and washed with boiling methanol (2 × 25 cm^3). The combined organic phases were concentrated *in vacuo* to give a yellow solid that was triturated with dichloromethane and dried under reduced pressure to give amine **34** (140 mg, 91%) as a white amorphous powder. e.e. >92% determined by NMR of Mosher's amide derivatives. ^{19}F NMR (400 MHz; $CDCl_3$): Derivative made from R-(+)-Mosher's acid chloride δ –68.90. Derivative made from racemic Mosher's acid chloride δ –68.78 and –68.90; $[\alpha]_D^{23}$ –50 (c. 0.3, MeOH); *m/z* (+ESI) found: MH^+, 248.1645. ($C_{15}H_{22}NO_2$ requires *M*, 248.1651); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 2900 (v br NH_2 and CH), 1706 (C=O) and 1155 (C-O); ^{1}H NMR (500 MHz; $CDCl_3$) δ 8.69 (2H, br s, NH_2),

7.54-7.52 (2H, m, *ortho*-Ph), 7.44 (2H, br tt, *J* 7.5 and 1.5, *meta*-Ph), 7.39 (1H, tt, *J* 7.5 and 1.5, *para*-Ph), 3.80 (1H, d, *J* 9.5, PhC*H*), 1.88-1.80 (2H, m, PhCHC*H* and C*H*C=O), 1.42 [9H, s, $C(CH_3)_3$], 0.96 (1H, ddd, *J* 8.5, 6.0 and 4.5, CH_aH_b) and 0.90 (1H, dt, *J* 9.0 and 4.5, CH_aH_b); ^{13}C NMR (126 MHz; $CDCl_3$) δ 171.4 (C1), 134.5 (*ipso*-Ph), 128.7 (*meta*-Ph), 128.5 (*para*-Ph), 127.1 (*ortho*-Ph), 80.1 [$C(CH_3)_3$], 56.2 (C1''), 27.7 [$C(CH_3)_3$], 24.6 (C2'), 20.9 (C1') and 12.8 (C3').

(*E*)-*tert*-Butyl hept-4-enoate 35

tert-Butyl acetate (1.0 g, 8.6 mmol) was dissolved in anhydrous THF (40 cm^3) and cooled to −78 ^oC. Freshly prepared LDA (2.76 M, 9.0 mmol) was added by cannula to give a red solution. After ½ hour HMPA (1.5 cm^3, 8.6 mmol) was added. After an additional ½ hour (*E*)-cinnamyl bromide (1.7 g, 8.6 mmol) dissolved in anhydrous THF (10 cm^3) and cooled to −78 ^oC was added by cannula. After 6 hours the reaction was quenched by the addition of saturated aqueous NH_4Cl (20 cm^3) and allowed to warm to room temperature. The reaction mixture was transferred to a separatory funnel with water (10 cm^3) and extracted with ethyl acetate (3 × 50 cm^3). The combined organic phases were washed with water (3 × 50 cm^3), dried (Na_2SO_4), filtered and concentrated *in vacuo* to give *tert-butyl ester* **35** (1.45 g, 91%) as a light brown liquid that required no further purification. R_f 0.35 (5% EtOAc in hexanes, v/v); *m/z* (+ESI) found: M^+, 184.1457. ($C_{11}H_{20}O_2$ requires *M*, 184.1463); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1731 (C=O) and 1148 (C-O); ^1H NMR (500 MHz; $CDCl_3$) δ 5.48 (1H, dt, *J* 15.5 and 6.0, EtC*H*=CH), 5.39-5.34 (1H, m, EtCH=C*H*), 2.25 (2H, br s), 2.24 (2H, br s) (CH_2CH_2C=O), 1.97 (2H, quintet, *J* 7.5, CH_3CH_2), 1.42 [9H, s, $C(CH_3)_3$] and 0.93 (3H, t, *J* 7.5, CH_3); ^{13}C NMR (126 MHz; $CDCl_3$) δ 172.6 (C1), 133.0 (C5), 127.1 (C4), 80.0 [$C(CH_3)_3$], 35.5 (C2), 28.1 [C3 and $C(CH_3)_3$], 25.5 (C6) and 13.8 (C7); (Found: C, 72.02; H, 11.07. $C_{11}H_{20}O_2$ requires C, 71.70; H, 10.94%).

(4*R*,5*R*)-*tert*-Butyl 4,5-dihydroxy-heptanoate 36

By method **1** olefin **35** (0.97 g, 5.3 mmol) after 8 hours at 0 ^oC gave *diol* **36** (0.94 g, 81%) as a clear gum that required no further purification. $[\alpha]_D^{23}$ +10.3 (c. 2.8, $CHCl_3$); *m/z* (+ESI) found: MNa^+, 241.1416. ($C_{11}H_{22}O_4Na$ requires *M*, 241.1411); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 3435 (br., O-H), 1729 (C=O) and 1153 (C-O); ^1H NMR (500 MHz; $CDCl_3$) δ 3.43 (1H, ddd, *J* 13.0, 5.0 and 4.0, EtCHC*H*), 3.31 (1H, br dt, *J* 8.5 and 4.5, EtC*H*), 2.44-2.34 (2H, m, CH_2C=O), 1.83-1.68 (2H, m, CH_2CHOH), 1.62-1.53 (1H, m, CH_aH_bMe), 1.50-1.40 (1H, m, CH_aH_bMe), 1.44 [9H, s, $C(CH_3)_3$] and 0.97 (3H, t, *J*

7.5, CH_3); ^{13}C NMR (126 MHz; $CDCl_3$) δ 173.9 (C1), 80.7 [$C(CH_3)_3$], 75.7 (C5), 73.5 (C4), 32.0 (C2), 28.6 (C3), 28.0 [$C(CH_3)_3$)], 26.3 (C6) and 10.0 (C7).

(4*RS*,5*RS*)-*tert*-Butyl 4,5-dihydroxy-heptanoate (±)-36

By method **2** olefin **35** (0.11 g, 0.60 mmol) after 1 day gave *diol* **(±)-36** (0.11 g, 87%) as a clear gum that required no further purification. All analytical data for **(±)-36** were identical with that for (4*R*,5*R*)-**36** reported above.

(4*R*,5*R*)-*tert*-Butyl 4,5-diphenylphosphinoyloxy-heptanoate 37

By method **3** diol **36** (0.57 g, 2.6 mmol) after 16 hours gave a yellow gum. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 0-100% EtOAc in hexanes (v/v) – 10% increments] gave *bis-phosphinate* **37** (1.20 g, 74%) as a clear gum. e.e. >85% (determined by chiral HPLC); HPLC [R_T (min), flow rate 1 cm^3/min, 20% *iso*-propanol in *iso*-hexane, v/v]: 24.8; $[\alpha]_D^{23}$ +18.5 (c. 1, $CHCl_3$); R_f 0.55 (EtOAc); *m/z* (+ESI) found: MH^+, 619.2285. ($C_{35}H_{41}O_6P_2$ requires *M*, 619.2378); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1723 (C=O), 1439 (P-Ph) and 1225 (P=O); ^1H NMR (500 MHz; $CDCl_3$) δ 7.67-7.59 (8H, m, *ortho*-Ph), 7.42-7.36 (4H, m, *para*-Ph), 7.34-7.26 (8H, m, *meta*-Ph), 4.55 (1H, tt, *J* 8.0 and 4.0, EtCHC*H*), 4.38 (1H, m, Et*CH*CH), 2.25 (1H, ddd, *J* 15.5, 9.5 and 5.5, $CH_aH_bC{=}O$), 2.14-2.03 (2H, m, $CH_aH_bC{=}O$ and $CH_aH_bCH_2C{=}O$), 1.96 (1H, m, $CH_aH_bCH_2C{=}O$), 1.84-1.76 (1H, m, CH_aH_bMe), 1.73-1.64 (1H, m, CH_aH_bMe), 1.36 [9H, s, $C(CH_3)_3$] and 0.76 (3H, t, *J* 7.5, CH_3); ^{31}P NMR (162 MHz; $CDCl_3$) δ 31.5 and 31.4; ^{13}C NMR (126 MHz; $CDCl_3$) δ 172.1 (C1), 132.3, 132.2-132.1 (m), 131.7, 131.6, 131.5, 131.2, 131.1, 131.0, 128.5-128.3 (m) (16 × Ph), 80.2 [$C(CH_3)_3$], 77.6 (dd, *J* 6.5 and 3.5, C5), 75.3 (dd, *J* 6.5 and 4.0, C4), 31.3 (C2), 28.0 [$C(CH_3)_3$], 25.9 (d, *J* 3.5, C6), 23.5 (d, *J* 3.5, C3) and 9.9 (C7); (Found: C, 66.43; H, 6.61. $C_{35}H_{40}O_6P_2$·0.05 EtOAc requires C, 66.68; H, 6.42%).

(4*RS*,5*RS*)-*tert*-Butyl 4,5-diphenylphosphinoyloxy-heptanoate (±)-37

By method **3** diol **(±)-36** (82 mg, 0.38 mmol) after 24 hours gave a white gum. Purification by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 10-100% EtOAc in hexanes (v/v) – 10% increments; 6 × EtOAc] gave *bis-phosphinate* **(±)-37** (0.11 g, 48%) as a clear gum. HPLC [R_T (min), flow rate 1 cm^3/min, 20% *iso*-propanol in *iso*-hexane (v/v)]: 24.8 and 33.2; All analytical data were identical with that for (4*R*,5*R*)-**37** reported above.

(4*R*,5*R*)-*tert*-Butyl 4,5-methanesulfonyloxy-heptanoate 38

By method **5** diol **36** (0.52 g, 2.38 mmol) after 20 hours gave a yellow liquid. Purification by DCVC [id 4 cm; 20 cm^3 fractions: 2 × hexanes; 0-100% EtOAc in hexanes (v/v) – 10% increments; 4 × EtOAc] gave *bis-mesylate* **38** (0.60 g, 67%) as a clear gum. $[\alpha]_D^{23}$ +15 (c. 1, $CHCl_3$); R_f 0.50 (50% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 397.0961. ($C_{13}H_{26}O_8S_2Na$ requires *M*, 397.0968); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1722 (C=O), 1333 (SO_2) and 1172 (SO_2); ^{1}H NMR (400 MHz; $CDCl_3$) δ 4.88 (1H, ddd, *J* 9.0, 5.0 and 4.0, CH_2CH_2CH), 4.71 (1H, dt, *J* 7.5 and 5.0, CH_3CH_2CH), 3.10 (3H, s, CH_3S), 3.09 (3H, s, CH_3S), 2.49-2.36 (2H, m, CH_2C=O), 2.09 (1H, dtd, *J* 15.5, 7.5 and 4.0, $CH_aH_bCH_2C$=O), 1.96-1.85 (2H, m, $CH_aH_bCH_2C$=O and $CH_aH_bCH_3$), 1.76 (1H, dp, *J* 14.5 and 7.5, $CH_aH_bCH_3$), 1.44 [9H, s, $C(CH_3)_3$] and 1.06 (3H, t, *J* 7.5, CH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 171.5 (C1), 82.0 (C5), 81.1 [$C(CH_3)_3$], 79.3 (C4), 38.8, 38.6 (2 × CH_3S), 30.3 (C2), 28.0 [$C(CH_3)_3$], 25.7 (C3), 23.5 (C6) and 9.1 (C7); (Found: C, 36.20; H, 6.17. $C_{13}H_{26}O_8S_2$·0.3 EtOAc requires C, 35.82; H, 6.08%).

(4*R*,5*R*)-*tert*-Butyl 4,5-*bis*-(4'-methyl-phenylsulfonyloxy)-heptanoate 39

By method **6** diol **36** (0.46 g, 2.11 mmol) after 4 days gave a brown gum. Purification by DCVC [id 4 cm; 20 cm^3 fractions: 2 × hexanes; 5-50% EtOAc in hexanes (v/v) – 5% increments; two fractions of each solvent mixture were collected] gave *bis-tosylate* **39** (0.72 g, 64%) as a clear gum. $[\alpha]_D^{23}$ +41 (c. 1, $CHCl_3$); R_f 0.45 (30% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 549.1606. ($C_{25}H_{34}O_8S_2Na$ requires *M*, 549.1593); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1726 (C=O), 1366 (S=O) and 1175 (C-O); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.81 (2H, d, *J* 8.5, *ortho*-Ar), 7.79 (2H, d, *J* 8.5, *ortho*-Ar), 7.37 (2H, d, *J* 8.5, *meta*-Ar), 7.35 (2H, d, *J* 8.5, *meta*-Ar), 4.69 (1H, dt, *J* 9.5 and 3.5, CH_2CH_2CH), 4.47 (1H, dt, *J* 9.0 and 4.0, CH_3CH_2CH), 2.47 (3H, s, CH_3Ar), 2.46 (3H, s, CH_3Ar), 2.12 (1H, ddd, CH_aH_bC=O), 1.99-1.90 (2H, m, CH_aH_bC=O and $CH_aH_bCH_2C$=O), 1.78-1.63 (2H, m, $CH_aH_bCH_2C$=O and $CH_aH_bCH_3$), 1.57-1.48 (1H, m, $CH_aH_bCH_3$), 1.42 [9H, s, $C(CH_3)_3$] and 0.64 (3H, t, *J* 7.5, CH_3); ^{13}C NMR (126 MHz; $CDCl_3$) δ 171.3 (C1), 145.2, 145.1 (2 × *para*-Ar), 133.1, 133.0 (2 × *ipso*-Ar), 129.9, 129.8 (2 × *meta*-Ar), 128.2, 128.1 (2 × *ortho*-Ar), 82.1 (C5), 80.7 [$C(CH_3)_3$], 79.8 (C4), 30.8, (C2), 28.0 [$C(CH_3)_3$], 24.1 (C3), 21.7 (br. C6 and 2 × CH_3Ar) and 9.6 (C7); (Found: C, 56.91; H, 6.62. $C_{25}H_{34}O_8S_2$ requires C, 57.01; H, 6.51%).

(1'*R*,2'*R*,1''*R*)-*tert*-Butyl 2'-(1''-Diphenylphosphinoyloxy-propyl)-cyclopropane carboxylate 40

By method **7a** *bis*-phosphinate **37** (0.80 g, 1.29 mmol) gave a yellow gum. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 10-100% EtOAc in hexanes (v/v) – 10% increments; 5 × EtOAc;] to give *cyclopropane* **40** (0.39 g, 75%) as a white amorphous solid. e.e. >96% (determined by chiral HPLC); HPLC [R_T (min), flow rate 1 cm^3/min, 5% *iso*-propanol in *iso*-hexane (v/v)]: 24.4; $[\alpha]_D^{23}$ −25 (c. 1, $CHCl_3$); mp 91-92 °C (EtOAc, hexanes); R_f 0.60 (80% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 423.1721. ($C_{23}H_{29}O_4PNa$ requires *M*, 423.1701); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1718 (C=O), 1439 (P-Ph), 1217 (P=O) and 1151 (C-O); ^{1}H NMR (500 MHz; $CDCl_3$) δ 7.84-7.75 (4H, m, *ortho*-Ph), 7.53-7.48 (2H, m, *para*-Ph), 7.46-7.41 (4H, m, *meta*-Ph), 3.91 (1H, tt, *J* 8.5 and 6.0, EtC*H*), 1.84-1.78 (2H, m, CH_2CH$_3$), 1.55 (1H, ddt, *J* 8.5, 6.5 and 4.0, C*H*CHEt), 1.44-1.41 [10H, m, CHC=O and C(CH$_3$)$_3$], 0.97 (3H, t, *J* 7.5, CH$_3$), 0.87 (1H, dt, *J* 8.5 and 5.0, ring-CH_aH_b) and 0.75 (1H, ddd, *J* 8.5, 6.5 and 4.5, ring-CH_aH_b); ^{31}P NMR (162 MHz; $CDCl_3$) δ 31.0; ^{13}C NMR (126 MHz; $CDCl_3$) δ 172.5 (C1), 132.6 (×2) (d, *J* 138.5, *ipso*-Ph and d, *J* 136.0, *ipso*-Ph), 132.0 (d, *J* 3.0, *para*-Ph), 131.9 (d, *J* 2.5, *para*-Ph), 131.7 (d, *J* 10.0, *ortho*-Ph), 131.4 (d, *J* 10.5, *ortho*-Ph), 128.4 (×2) (d, *J* 13.5, *para*-Ph d, *J* 13.0, *para*-Ph), 80.5 [*C*(CH$_3$)$_3$], 80.1 (d, *J* 6.4, C1''), 29.4 (d, *J* 4.0, C2''), 28.1 [C(*C*H$_3$)$_3$], 25.6 (d, *J* 3.5, C2'], 20.1 (C1'), 13.6 (C3') and 9.5 (C3''); (Found: C, 68.79; H, 7.34. $C_{23}H_{29}O_4P$ requires C, 68.98; H, 7.30%).

(1'*RS*,2'*RS*,1''*RS*)-*tert*-Butyl 2-(1-Diphenylphosphinoyloxy-propyl)-cyclopropane carboxylate (±)-40

By method **7a** *bis*-phosphinate **(±)-37** (97 mg, 0.16 mmol) gave a white 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; 6 × EtOAc] to give cyclopropane **(±)-40** (10 mg, 16%) as a clear gum. HPLC [R_T (min), flow rate 1 cm^3/min, 5% *iso*-propanol in *iso*-hexane (v/v)]: 20.3 and 24.1; All analytical data were identical with that for (1'*R*,2'*R*,1''*R*)-**40** reported above.

(1'*R*,2'*R*,1''*R*)-Methyl 2'-(1''-hydroxy-propyl)-cyclopropane carboxylate 44

Cyclopropane **40** (0.12 g, 0.30 mmol) was dissolved in anhydrous methanol (5 cm^3) and sodium methoxide (81 mg, 1.50 mmol) was added. The reaction mixture was heated to reflux for 4 hours, allowed to cool to room temperature and transferred to a separatory funnel with aqueous sulfate

buffer (25 cm^3) and extracted with ethyl acetate (3 × 20 cm^3). The combined organic phases were dried (Na_2SO_4), filtered and carefully concentrated *in vacuo* to give a white gum. The product was purified by DCVC [id 4 cm; 20 cm^3 fractions; 2 × hexanes; 10-90% EtOAc in hexanes (v/v) – 10% increments; 5 × EtOAc;] to give *cyclopropane* **44** (34 mg, 72%) as a clear liquid. $[\alpha]_D^{23}$ −78 (c. 0.5, $CHCl_3$); R_f 0.40 (50% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 181.0835. ($C_8H_{14}O_3Na$ requires *M*, 181.0841); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 3450 (br., O-H), 1730 (C=O) and 1174 (C-O); ^1H NMR (500 MHz; $CDCl_3$) δ 3.67 (3H, s, OCH_3), 3.17 (1H, td, *J* 7.0 and 5.5, C*H*OH), 1.68-1.52 (5H, m, OH, C*H*C*H*C=O and C$H_2$$CH_3$), 1.16 (1H, dt, *J* 9.0 and 4.5, ring-CH_aH_b), 0.97 (3H, t, *J* 7.5, CH_2CH_3) and 0.95 (1H, ddd, *J* 8.5, 6.5 and 4.5, ring-CH_aH_b); ^{13}C NMR (126 MHz; $CDCl_3$) δ 174.3 (C1), 74.2 (C1''), 51.8 (OCH_3), 30.1 (C2''), 27.7 (C2'), 17.7 (C1'), 11.9 (C3') and 9.9 (C3'').

(7*R*,1'*R*)-7-(1'-Methanesulfonyloxy-propyl)-2,2,4-trioxo-[1,2]oxathiepane 45

By method **7b** *bis*-mesylate **41** (112 mg, 0.30 mmol) and NaHMDS (0.17 cm^3, 0.33 mmol) gave a yellow gum. The product was purified by DCVC [id 1 cm; 9 cm^3 fractions; 4 × hexanes; 10-100% EtOAc in hexanes (v/v) – 10% increments – two fractions of each solvent mixture were collected] to give *oxathiepane* **45** (10 mg, 11%) as a yellow oil. $[\alpha]_D^{23}$ −53.8 (c. 0.5, $CHCl_3$); R_f 0.55 (80% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 323.0230. ($C_9H_{16}O_7S_2Na$ requires *M*, 323.0235; IR $\nu_{max}(CHCl_3)/cm^{-1}$ 1717 (C=O), 1359 (SO_2) and 1166 (SO_2); ^1H NMR (400 MHz; $CDCl_3$) δ 4.98 (1H, ddd, *J* 11.0, 4.5 and 2.0, C7-CH), 4.70 (1H, ddd, *J* 7.5, 6.0 and 4.5, C2'-CH), 4.35 (1H, d, *J* 16.0, SCH_aH_b), 4.27 (1H, d, *J* 16.0, SCH_aH_b), 3.16 (1H, ddd, *J* 15.0, 12.5 and 3.0, $CH_2CH_aH_bC$=O), 3.11 (3H, s, Ms), 2.81 (1H, ddd, *J* 15.0, 7.0 and 2.0, $CH_2CH_aH_bC$=O), 2.30 (1H, dddd, *J* 15.0, 13.0, 11.0 and 2.0, C$H_aH_bCH_2C$=O), 2.15 (1H, ddt, *J* 15.5, 7.0 and 2.5, $CH_aH_bCH_2C$=O), 1.96-1.78 (2H, m, CH_2Me) and 1.07 (3H, t, *J* 7.5, CH_3); ^{13}C NMR (126 MHz; $CDCl_3$) δ 196.4 (C4), 84.2, 82.4 (C7 and C1'), 63.6 (C3), 40.5 (C5), 39.0 (CH_3S), 28.4, 24.3 (C6 and C2') and 9.3 (C3').

(1'*R*,2'*R*,1''*S*)-*tert*-Butyl 2'-(1''-azido-propyl)-cyclopropanoate 43

According to method **7b** *bis*-tosylate **42** (0.27 g, 0.51 mmol) gave a white gum. The crude product was dissolved in anhydrous DMF (5 cm^3), sodium azide (40 mg, 0.62 mmol) was added and the reaction mixture heated to 50 ^oC overnight (19 hours). The reaction mixture was transferred to a separatory funnel with water (20 cm^3) and extracted with ethyl acetate (3 × 20 cm^3). The combined organic phases were washed with 3 M aqueous HCl (2 × 20 cm^3), saturated aqueous $NaHCO_3$ (20

cm^3), dried (Na_2SO_4), filtered and concentrated *in vacuo* to give a clear gum. The product was purified by DCVC [id 1 cm; 7 cm^3 fractions; 4 × hexanes; 2-6% EtOAc in hexanes (v/v) – 2% increments; seven fractions of each solvent mixture were collected] to give *cyclopropane* **43** (75 mg, 62%) as a clear gum. e.e. >94% determined by NMR of Mosher's amide derivatives. ^{19}F NMR (400 MHz; $CDCl_3$): Derivative made from R-(+)-Mosher's acid chloride δ −69.33. Derivative made from racemic Mosher's acid chloride δ −69.17 and −69.32; $[\alpha]_D^{23}$ −51 (c. 1.3, $CHCl_3$); R_f 0.45 (10% EtOAc in hexanes, v/v); *m/z* (+ESI) found: MNa^+, 248.1370. $C_{11}H_{19}N_3O_2Na$ requires *M*, 248.1370); IR $\nu_{max}(CHCl_3)/cm^{-1}$ 2095 (N_3), 1721 (C=O) and 1154 (C-O); ^1H NMR (500 MHz; $CDCl_3$) δ 2.76 (1H, ddd, *J* 8.5, 7.5 and 6.0, C*H*N_3), 1.66-1.58 (3H, m, C$H_2$$CH_3$ and CHC=O), 1.49 (1H, tdd, *J* 8.5, 6.0 and 4.0, C*H*CHC=O), 1.43 [9H, s, $C(CH_3)_3$], 1.16 (1H, dt, *J* 9.0 and 4.5, ring-C$H_a$$H_b$), 0.98 (3H, t, *J* 7.5, C$H_3$$CH_2$) and 0.76 (1H, ddd, *J* 8.5, 6.0 and 4.5, ring-$CH_a$$H_b$); ^{13}C NMR (126 MHz; $CDCl_3$) δ 172.4 (C1), 80.6 [*C*$(CH_3)_3$], 66.1 (C1''), 28.0 [C(*C*$H_3)_3$], 27.8 (C2''), 24.9 (C2'), 19.6 (C1'), 12.0 (C3') and 10.3 (C3''); (Found: C, 58.45; H, 8.55. $C_{11}H_{19}N_3O_2$ requires C, 58.64; H, 8.50%).

Crystal data for cyclopropane **40**: $C_{23}H_{29}O_4P$, *M* = 400.43, Triclinic, *P*1, *a* = 5.8939(2), *b* = 8.5144(3), *c* = 11.3355(4) Å, α = 82.108(2), β = 87.448(2), γ = 82.337(2)°, *U* = 558.23(3) $Å^3$, *Z* = 1, μ(Mo-Kα) = 0.147 mm^{-1}, 5699 reflections collected at 180(2) K using an Oxford Cryosystems Cryostream cooling apparatus, 3689 unique (R_{int} = 0.025); *R*1 = 0.035, *wR*2 = 0.096 [$I > 2\sigma(I)$], Absolute structure parameter -0.08(8).
The structures were solved with SHELXS-97,[8] and refined with SHELXL-97.[8]
CCDC reference number 600428. See http://www.rsc.org/suppdata/ for crystallographic data in .cif or other electronic format.

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