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Effective 1,5-, 1,6- and 1,7-remote stereocontrol in reactions of alkoxy- and hydroxy-substituted allylstannanes with aldehydes

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Supplementary Experimental

General Experimental Procedures

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NMR spectra were recorded on Varian Unity 500, Bruker AC-300 or Varian XL spectrometers and IR spectra on a Perkin-Elmer 1710FT spectrometer. For minor diastereoisomers, >10%, present in mixtures, just the distinctive peaks are reported. Low resolution Chemical Ionisation (CI) and Electron Impact (EI)mass spectra were recorded on a Kratos MS25 mass spectrometer coupled to a DS 55 data system or on a VG Trio 2000 mass spectrometer. Fast Atom Bombardment (FAB) mass spectra and all high resolution mass spectra were recorded on a Kratos Concept 1S mass spectrometer coupled to a Mach 3 data system. Compounds containing tin or chlorine showed characteristic clusters of isotope peaks in their mass spectra.

Optical rotations were recorded on an Optical Activity AA-100 polarimeter at 589 nm using chloroform as the solvent at ambient temperature. Analytic high performance liquid chromatography was carried out with a Waters Z module, 10 cm x 8 mm cartridge, C18 5m stationary phase and detection by ultraviolet absorption using a Perkin-Elmer IC-480 detector at 255 nm. Semi-preparative high performance liguid chromatography was carried out using a Gilson 303 pump (with manometric module), Dynamax 83-211-C column 25 cm x 10 mm, 8m silica, detection with a Gilson 131 refractive index detector and Gilson 115 UV detector at 254 nm. Chromatography refers to flash chromatography and was carried out using Merck silica 60H (40-60m, 230-300 mesh) or May and Baker Sorbsil C60 silica gel (40-60m) as the stationary phase.

Petrol refers to light petroleum which distils between 40 ˚C and 60 ˚C. Tin(IV) chloride was dried with phosphorus pentoxide and distilled. Ether refers to diethyl ether. Brine refers to saturated aqueous sodium chloride. All solvents were dried and distilled before use.

Alcohol **3** was prepared as described in the literature.[5] Its e.e. was estimated by ozonolysis with a reductive work to give (*R*)-3-benzyloxy-2-methylpropanol shown to have an e.e. of >85% by Mosher's derivatisation.

General procedure for the reaction of an alkoxyalk-2-enylstannane with an aldehyde in the presence of a Lewis acid

The tin(IV) halide (1.044 M in DCM, 958 µl, 1.00 mmol) was added to the stannane (1.0 mmol) in DCM (10 ml) at -78 ˚C. After 10 min, the aldehyde (3.48 M in DCM, 287 µl, 1.00 mmol) was added and the mixture was maintained at -78 ˚C for 1 h. Saturated aqueous sodium hydrogen carbonate (5 ml) was added and the mixture allowed to warm to room temperature. Ether (50 ml) and water (50 ml) were added and the organic phase was washed with aqueous ammonia (10%, 50 ml) and brine (50 ml), then dried ($MgSO_4$). Concentration under reduced pressure and chromatography of the residue gave the products as colourless oils.

General procedure for the preparation of Mosher's derivatives[34]

The alcohol (0.10 mmol) in carbon tetrachloride (300 µl) was added to the 2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride (0.20 mmol) in pyridine (300 µl) at room temperature and the mixture stirred until no starting material remained, typically 1 - 1.5 h (TLC). 3-Dimethylaminopropylamine (400 µl) was added and the clear solution was stirred for 10 min. Ether (25 ml) and water (25 ml) were added and the organic phase was washed with dilute aqueous hydrogen chloride (1 M, 20 ml), saturated aqueous sodium carbonate (20 ml) and brine (20 ml), then dried ($MgSO_4$). Concentration under reduced pressure gave the Mosher's ester as a colourless oil.

General procedure for the preparation of *O*-acetylmandelates

2-Acetoxy-2-phenylacetic acid (0.30 mmol), DCC (0.30 mmol) and 4-*N*,*N*-dimethylaminopyridine (0.005 mmol) were added to the alcohol (0.10 mmol) in DCM (2 ml) and the mixture stirred at room temperature for 15 h. DCM (15 ml) and water (15 ml) were added and the organic phase washed with dilute aqueous hydrogen chloride (3.5 M, 10 ml), saturated aqueous sodium hydrogen carbonate (10 ml) and brine (10 ml), then dried ($MgSO_4$). Concentration under reduced pressure left a solid which was absorbed onto silica. Chromatography gave the *O*-acetylmandelate as a colourless oil.

4-Benzyloxy-1,1-dibromo-3-methylbut-1-ene 18

Zinc powder (2.19 g, 33.7 mmol), triphenylphosphine (11.18 g, 33.7 mmol) and carbon tetrabromide (8.22 g, 33.7 mmol) were suspended in dichloromethane (50 ml) and the mixture stirred for 24 h. (±)-3-Benzyloxy-2-methylpropanal **17** (1.16 g, 5.52 mmol) in dichloromethane (10 ml) was added and the mixture was stirred at room temperature for 2.5 h. Hexane (250 ml) was added, the mixture filtered and the colourless solution concentrated under reduced pressure. Chromatography of the residue using petrol : ether (50 : 1) as eluent gave the *title compound* **18** (1.62 g, 74%); as a colourless oil (Found: M^+, 333.9390. $C_{12}H_{14}O^{79}Br^{81}Br$ requires *M*, 333.9393); ν_{max}/cm^{-1} 2929, 2856, 1453, 1098 and 785; δ_H (300 MHz; $CDCl_3$) 1.08 (3 H, d, *J* 7.5, 3-CH_3), 2.81 (1 H, m, 3-H), 3.38 (2 H, dd, *J* 5, 1, 4-H_2), 4.55 (2 H, s, PhCH_2), 6.32 (1 H, d, *J* 9, 2-H) and 7.36 (5 H, m, ArH); δ_C (75 MHz; $CDCl_3$) 18.0, 40.9, 75.0, 75.1, 129.5, 129.6, 130.4, 140.2 and 143.1; *m/z* (CI, NH_3) 354 (M^+ + 18, 7%), 352 (M^+ + 18, 14), 350 (M^+ + 18, 7), 175 (51) and 91 (100).

4-Benzyloxy-3-methylbut-1-yne 19

*n*Butyllithium (1.6 M in hexanes; 6.25 ml, 10.05 mmol) was added to the dibromide **18** (1.60 g, 4.79 mmol) in THF (10 ml) at -78 °C and the mixture stirred for 2h, then allowed to warm to room temperature over 1 h. Water (5 ml) was added and the mixture partitioned between ether (50 ml) and water (50 ml). The organic phase was washed with water (50 ml), brine (50 ml) and dried ($MgSO_4$). After concentration under reduced pressure, chromatography of the residue using petrol : ethyl acetate (20 : 1) as eluent, gave the *title compound* **19** (0.55 g, 65%) as a colourless oil (Found: M^+- H, 173.0970. $C_{12}H_{13}O$ requires *M*, 173.0967); ν_{max}/cm^{-1} 3300, 2859, 1454 and 1094; δ_H (300 MHz; $CDCl_3$) 1.28 (3 H, d, *J* 7.5, 3-CH_3), 2.15 (1 H, d, *J* 1, 1-H), 2.82 (1 H, m, 3-H), 3.45 and 3.59 (each 1 H, dd, *J* 8, 7, 4-H), 34.62 (2 H, s, $PhCH_2$) and 7.40 (5 H, m, ArH); δ_C (75 MHz; $CDCl_3$) 17.8, 26.7, 69.2, 73.2, 74.0, 86.6, 127.8, 128.6 and 138.4; *m/z* (CI,NH_3) 192 (M^+ + 18, 100%) and 175 (M^+ + 1, 35).

6-Benzyloxy-1-hydroxy-5-methyl-1-phenylhex-3-yne 20

*n*Butyllithium (1.6 M in hexanes; 2 ml, 3.20 mmol) was added to the alkyne **19** (0.55 g, 3.16 mmol) in THF (7 ml) at -78 °C. After 20 min, boron trifluoride diethyl etherate (0.462 g, 3.25 mmol) was added and, after a further 20 min at -78°C, styrene oxide (0.422 g, 3.70 mmol) was added. The reaction mixture was stirred for 1.5 h, saturated aqueous sodium hydrogen carbonate (5 ml) was added and the mixture allowed to warm to room temperature. The mixture was partitioned between ether (20 ml) and water (20 ml) and the organic phase was washed with water (20 ml), brine (20 ml) and dried ($MgSO_4$). After concentration under reduced pressure, chromatography using petrol : ether (2 : 1) gave the *title compound* **20** (125 mg, 14%) as a colourless oil, assumed to be a 50 : 50 mixture of 1,5-epimers but these could not be distinguished (Found: M^++ NH_4, 312.1981. $C_{20}H_{26}NO_2$ requires *M*, 312.1963); ν_{max}/cm^{-1} 3412, 3030, 2871, 1453 and 1092; δ_H (300 MHz; $CDCl_3$) 1.20 (3 H, d, *J* 7.5, 5-CH_3), 2.62 (2 H, m, 2-H_2), 2.75 (1 H, m, 5-H), 3.38 and 3.48 (each 1 H, dd, *J* 8, 7, 6-H), 4.57 (2 H, s, $PhCH_2$), 4.85 (1 H, t, *J* 5, 1-H) and 7.35 (10 H, m, ArH); δ_C (75 MHz; $CDCl_3$) 18.0, 26.6, 30.2, 72.5, 73.1, 74.2, 77.2, 85.6, 125.8, 127.7, 128.3, 128.4, 138.2 and 142.8; *m/z* (CI, NH_3) 312 (M^+ + 18, 100%), 295 (M^+ + 1, 23) and 294 (M^+, 73).

(1*RS*,5*SR*,3*Z*)- And (1*RS*,5*RS*,3*Z*)-6-benzyloxy-5-methyl-1-phenylhex-3-en-1-ol 7 and 8

A solution of the alkyne **20** (100 mg, 0.34 mmol) and Lindlar's catalyst (palladium on calcium carbonate, poisoned with lead, Pb content 5%, 20 mg) in ethanol (2 ml) was fully degassed and stirred under an atmosphere of hydrogen for 72 h. The mixture was then filtered through celite and the filter-cake was washed with ether (20 ml). After concentration under reduced pressure, chromatography using petrol : ether, (2 : 1) as eluent afforded a mixture of the alcohols **7** and **8** (72 mg, 72%) as a colourless oil, a 50 : 50 mixture of diastereoisomers; ν_{max}/cm^{-1} 3396, 2871, 1453, 1092, 1028, 740 and 700; *m/z* (CI/NH_3) 296 (M^+, 0.9%), 279 (9), 121 (28) and 58 (100). Semi-preparative HPLC gave samples of each diastereoisomer; δ_H (300 MHz; $CDCl_3$) epimer **8** (less polar) 0.95 (3 H, d, *J* 7.5, 4-CH_3), 2.54 (1 H, dt, *J* 14, 5 Hz, 2-H), 2.65 (1 H, m, 2-H'), 2.80 (1 H, m, 4-H and OH), 3.16 (1 H, t, *J* 8, 6-H), 3.32 (1 H, dd, *J* 8, 5, 6-H'), 4.50 (2 H, s, $PhCH_2$), 4.83 (1 H, t, *J* 4, 1-H), 5.25 - 5.40 (2 H, m, 3- and 4-H) and 7.20-7.40 (10 H, m, ArH); δ_H (300 MHz; C_6D_6) 0.90 (3 H, d, *J* 7.5, 4-CH_3), 2.44 - 2.72 (3 H, m, 2-H_2 and OH), 2.85 (1 H, m, 4-H), 3.08 (1 H, t, *J* 8, 6-H), 3.15 (1 H, dd, *J* 8.5, 7, 6-H'), 4.38 (2 H, s, $PhCH_2$), 4.73 (1 H, t, *J* 4, 1-H), 5.35 (1 H, t, *J* 10, 4-H), 5.47 (1 H, dt, *J* 10, 7.5 Hz, 3-H) and 7.15-7.40 (10 H, m, ArH). The more polar epimer **7** had spectroscopic data identical with those determined previously.

(1*S*,5*R*,3*Z*)-6-Benzyloxy-1-(4-methoxyphenyl)-5-methylhex-3-en-1-ol 21

Following the general procedure but with a reaction time of 2 h, stannane **6** (100 mg, 0.209 mmol), tin(IV) chloride (1.044 M in DCM, 200 µl, 0.209 mmol) and 4-methoxybenzaldehyde (60 µl, 0.209 mmol), after chromatography using petrol : ether (7 : 3) as eluent, gave the *title compound* **21** (44 mg, 65%) as a colourless oil, mixture of epimers ratio 96 : 4, $[\alpha]_D$ -68 (*c* = 1.10); (Found: M^+ - OH, 309.1868. $C_{21}H_{25}O_2$ requires *M*, 309.1854); ν_{max}/cm^{-1} 3424, 2957, 1612, 1513, 1248, 1174, 1073, 1036, 832 and 738; δ_H (300 MHz, $CDCl_3$) 0.90 (3 H, d, *J* 7.5, 5-CH_3), 2.38 (1 H, m, 2-H), 2.61 (1 H, dt, *J* 14, 9.5 Hz, 2-H'), 2.89 (1 H, m, 5-H), 3.21 (1 H, t, *J* 8.5, 6-H), 3.35 (1 H, dd, *J* 8.5, 5.5 Hz, 6-H'), 3.79 (3 H, s, OCH_3), 4.55 (2 H, s, $PhCH_2$), 4.64 (1 H, dd, *J* 9, 4, 1-H), 5.37 (1 H, t, *J* 10.5, 4-H), 5.55 (1 H, td, *J* 10, 6, 5-H), 6.88 and 7.29 (each 2 H, d, *J* 8.5, ArH) and 7.36 (5 H, m, ArH); minor 1,5-*syn*-epimer 4.51 (2 H, s, $PhCH_2$); δ_C (75 MHz, $CDCl_3$) 17.3, 32.4, 38.4, 55.3, 73.0, 73.1, 74.8, 113.7, 126.2, 127.0, 127.7, 127.9, 128.4, 136.5, 137.0, 138.1 and 158.8; *m/z* (CI, NH_3) 326 (M^+, 5%), 309 (M^+ - 17, 95), 203 (33) and 137 (100).

Following the general procedure, alcohol **21** (21 mg, 0.064 mmol) and (*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride afforded the corresponding (*R*)-Mosher's ester (32 mg, 92%) as a colourless oil, $[\alpha]_D$ -6.4 (*c* = 1.33) (Found: M^+ + NH_4, 560.2625. $C_{31}H_{37}F_3NO_5$ requires *M*, 560.2623); ν_{max}/cm^{-1} 2957, 1747, 1613, 1515, 1250, 1176, 1120, 992 and 831; δ_H (300 MHz, $CDCl_3$) 0.88 (3 H, d, *J* 6.5, 5-CH_3), 2.57 - 2.84 (3 H, m, 5-H and 2-H_2), 3.24 (2 H, d, *J* 6.5, 6-H_2), 3.53 and 3.80 (each 3 H, s, OCH_3), 4.48 (2 H, s, $PhCH_2$), 5.29 - 5.39 (2 H, m, 3-H and 4-H), 5.89 (1 H, t, *J* 7, 1-H), 6.82 and 7.16 (each 2 H, m, ArH) and 7.26 - 7.70 (10 H, m, ArH); δ_F (470 MHz, $CDCl_3$) -73.0, -73.2, ratio 11 : 89; *m/z* (CI, NH_3) 560 (M^+ + 18, 3%), 326 (54), 309 (82) and 252 (100).

Following the general procedure, alcohol **21** (10 mg, 0.031 mmol) and (*R*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride afforded the corresponding (*S*)-Mosher's ester (13 mg, 77%), $[\alpha]_D$ -71 (*c* = 0.55); ν_{max}/cm^{-1} 2956, 1746, 1516, 1613, 1250, 1175, 1120, 1020 and 831; δ_H (300 MHz, $CDCl_3$) 0.85 (3 H, d, *J* 7, 5-CH_3), 2.53 - 2.79 (3 H, m, 5-H and 2-H_2), 3.17 (2 H, d, *J* 6.5, 6-H_2), 3.43 and 3.81 (each 3 H, s, OCH_3), 4.47 (2 H, s, $PhCH_2$), 5.14 - 5.26 (2 H, m, 3-H and 4-H), 5.93 (1 H, t, *J* 7, 1-H), 6.88 (2 H, m, ArH) and 7.25 - 7.45 (12 H, m, ArH); δ_F (470 MHz, $CDCl_3$) -73.0, -73.2, ratio 90 : 10; *m/z* (CI, NH_3) 326 (41%) and 309 (100).

(1*S*,5*R*,3*Z*)-6-Benzyloxy-1-(4-chlorophenyl)-5-methylhex-3-en-1-ol 22

Following the general procedure, stannane **6** (100 mg, 0.209 mmol), tin(IV) chloride (1.044 M in DCM, 200 µl, 0.209 mmol) and 4-chlorobenzaldehyde (60 µl, 0.209 mmol), after chromatography using petrol : ether (3 : 1) as eluent, gave the *title compound* **22** (46 mg, 67%) as a colourless oil, $[\alpha]_D$ -72 (*c* = 1.85) (Found: M^+ - OH, 313.1360. $C_{20}H_{22}{}^{35}ClO$ requires *M*, 313.1359); ν_{max}/cm^{-1} 3418, 2860, 1492, 1454, 1202, 1091, 1014, 830 and 738; δ_H (300 MHz, $CDCl_3$) 0.89 (3 H, d, *J* 6.5, 5-CH_3), 2.34 (1 H, m, 2-H), 2.56 (1 H, dt, *J* 14, 10, 2-H'), 2.87 (1 H, m, 5-H), 3.18 (1 H, t, *J* 9, 6-H), 3.38 (1 H, dd, *J* 9, 5, 6-H'), 4.55 (2 H, s, $PhCH_2$), 4.65 (1 H, dd, *J* 9.5, 3.5, 1-H), 5.37 (1 H, t, *J* 10.5, 4-H), 5.57 (1 H, td, *J* 10, 6, 3-H) and 7.29-7.38 (9 H, m, ArH); minor *syn*-epimer 4.51 (2 H, s, $PhCH_2$); δ_C (75 MHz, $CDCl_3$) 17.1, 32.4, 38.7, 72.6, 73.2, 74.8, 125.9, 127.1, 127.8, 128.0, 128.4, 128.4, 132.7, 137.1, 137.9 and 143.4; *m/z* (CI, NH_3) 313 (M^+ - 17, 16%) and 106 (100).

(3*S*,7*R*,5*Z*)-8-Benzyloxy-2,7-dimethyloct-5-en-3-ol 23

Following the general procedure, stannane **6** (100 mg, 0.209 mmol), tin(IV) chloride (1.044M in DCM, 200 µl, 0.209 mmol) and 2-methylpropanal (60 µl, 0.209 mmol), after chromatography using petrol : ether (3 : 1), gave the *title compound* **23** (44 mg, 80%) as a colourless oil, $[\alpha]_D$ -3.9 (*c* = 1.34) (Found: M^+ + H, 263.2002. $C_{17}H_{27}O_2$ requires *M*, 263.2011); ν_{max}/cm^{-1} 3459, 2958, 1454, 1366, 1092 and 737; δ_H (300 MHz, $CDCl_3$) 0.92, 0.94 and 0.95 (each 3 H, d, *J* 7, 1-H_3, 2-CH_3 or 7-CH_3), 1.71 (1 H, m, 2-H), 2.15 (1 H, m, 4-H), 2.27 (1 H, dt, *J* 14, 9.5, 4-H'), 2.80 - 2.93 (2 H, m, 7-H and OH), 3.17 (1 H, t, *J* 9, 8-H), 3.30 - 3.39 (2 H, m, 3-H and 8-H'), 4.52 and 4.55 (each 1 H, d, *J* 12.5, PhC*H*H), 5.33 (1 H, t, *J* 10, 6-H), 5.50 (1 H, td, *J* 10, 6, 5-H) and 7.26 - 7.37 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 17.3, 17.8, 18.6, 32.3, 32.4, 33.6, 73.0, 74.8, 75.6, 127.1, 127.6, 127.8, 128.4, 136.1 and 138.1; *m/z* (CI, NH_3) 280 (M^+ + 18, 50%) and 263 (M^+ + 1, 100).

Following the general procedure, alkenol **23** (23 mg, 0.088 mmol) and (*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride afforded the corresponding (*R*)-Mosher's ester (29 mg, 69%) as a colourless oil, $[\alpha]_D$ +9 (*c* = 0.93) (Found: $M^+ + NH_4$, 496.2684. $C_{27}H_{37}F_3NO_4$ requires *M*, 496.2674); ν_{max}/cm^{-1} 2965, 1744, 1453, 1261, 1169, 1121, 1020 and 735; δ_H (300 MHz, $CDCl_3$) 0.81, 0.84 and 0.99 (each 3 H, d, *J* 7, 1-H_3, 2-CH_3 or 7-CH_3), 1.91 (1 H, m, 2-H), 2.37 - 2.52 (2 H, m, 4-CH_2), 2.77 (1 H, m, 7-H), 3.23 - 3.32 (2 H, m, 8-H_2), 3.54 (3 H, s, OCH_3), 4.47 and 4.48 (each 1 H, d, *J* 12, PhC*H*H), 5.00 (1 H, m, 3-H), 5.30 - 5.42 (2 H, m, 5-H and 6-H) and 7.24 - 7.57 (10 H, m, ArH); δ_F (470 MHz, $CDCl_3$) -72.8, -73.0, ratio 90 : 10; *m/z* (CI, NH_3) 496 (M^+ + 18, 86%), 172 (51) and 76 (100).

Following the general procedure, alcohol **23** (17 mg, 0.065 mmol) and (*R*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride afforded the corresponding (*S*)-Mosher's ester (27 mg, 87%) as a colourless oil, $[\alpha]_D$ -71 (*c* = 0.55) (Found: $M^+ + NH_4$, 496.2665. $C_{27}H_{37}F_3NO_4$ requires *M*, 496.2674); ν_{max}/cm^{-1} 2965, 1743, 1453, 1258, 1169, 1120 and 1019; δ_H (300 MHz, $CDCl_3$) 0.91, 0.92 and 0.98 (each 3 H, d, *J* 7, 1-H_3, 2-CH_3 or 7-CH_3), 1.95 (1 H, m, 2-H), 2.30 - 2.41 (2 H, m, 4-H_2), 2.73 (1 H, m, 7-H), 3.21 and 3.24 (each 1 H, dd, *J* 9.5, 7, 8-H), 3.53 (3 H, s, OCH_3), 4.49 (2 H, s, $PhCH_2$), 4.99 (1 H, m, 3-H), 5.20 - 5.28 (2 H, m, 5-H and 6-H) and 7.28 - 7.58 (10 H, m, ArH); δ_F (470 MHz, $CDCl_3$) -72.8, -72.82, -73.0, ratio 7 : 6 : 87, respectively; *m/z* (CI, NH_3) 496 (M^+ + 18, 100%).

Following the general procedure, alkenol **23** (18 mg, 0.069 mmol) and (*R*)-2-acetoxy-2-phenylacetic acid, after chromatography using petrol : ether (4 : 1) as eluent, gave the corresponding (*R*)-*O*-acetylmandelate (15 mg, 50%) as a colourless oil, $[\alpha]_D$ -70 (*c* = 0.55) (Found: $M^+ + NH_4$, 456.2767. $C_{27}H_{38}NO_5$ requires *M*, 456.2750); ν_{max}/cm^{-1} 2964, 1745, 1372, 1233, 1211, 1179, 1057 and 697; δ_H (300 MHz, $CDCl_3$) 0.89, 0.905, 0.915 (each 3 H, d, *J* 7, 1-H_3, 2-CH_3 or 7-CH_3), 1.86 (1 H, m, 2-H), 2.10 - 2.30 (5 H, m, 4-H_2 and O_2CCH_3), 2.64 (1 H, m, 7-H), 3.12 (1 H, dd, *J* 9, 7, 8-H), 3.18 (1 H, dd, *J* 9, 6.5, 8-H'), 4.47 (2 H, s, $PhCH_2$), 4.78 (1 H, dt, *J* 7.5, 5.5, 3-H), 4.96 (1 H, dt, *J* 10.5, 7, 5-H), 5.07 (1 H, dd, *J* 10.5, 9.5, 6-H), 5.88 (1 H, s, 2'-H] and 7.27 - 7.49 (10 H, m, ArH); *m/z* (CI, NH_3) 456 (M^+ + 18, 100%).

Following the general procedure, alkenol **23** (18 mg, 0.069 mmol) and (*S*)-2-acetoxy-2-phenylacetic acid, after chromatography using petrol : ether (4 : 1) as eluent, gave the corresponding (*S*)-*O*-acetylmandelate (14 mg, 46%) as a colourless oil, $[\alpha]_D$ +36 (*c* = 0.50) (Found: $M^+ + NH_4$, 456.2750. $C_{27}H_{38}NO_5$ requires *M*, 456.2750); ν_{max}/cm^{-1} 2964, 1745, 1372, 1233, 1211, 1180, 1058 and 738; δ_H (300 MHz, $CDCl_3$) 0.62, 0.66 and 1.01 (each 3 H, d, *J* 7, 1-H_3, 2-CH_3 or 7-CH_3), 1.73 (1 H, m, 2-H), 2.21 (3 H, s, O_2CCH_3), 2.37 (2 H, t, *J* 6, 4-H_2), 2.80 (1 H, m, 7-H), 3.27 (1 H, dd, *J* 9, 8, 8-H), 3.36 (1 H, dd, *J* 9, 6.5, 8-H'), 4.52 (2 H, s, $PhCH_2$), 4.77 (1 H, q, *J* 6, 3-H), 5.25 - 5.41 (2 H, m, 5-H and 6-H) 5.91 (1 H, s, 2'-H) and 7.25 - 7.48 (10 H, m, ArH); *m/z* (CI, NH_3) 456 (M^+ + 18, 9%), 252 (14), 172 (80) and 44 (100).

(2*R*,6*R*,5*Z*)-8-Benzyloxy-7-methyloct-5-en-3-ol 24

Following the general procedure, stannane **6** (100 mg, 0.209 mmol), tin(IV) chloride (1.044 M in DCM, 200 µl, 0.209 mmol) and propanal (60 µl, 0.209 mmol), after chromatography using petrol : ether (3 : 1) as eluent, gave the *title compound* **24** (36 mg, 69%) as a colourless oil, $[\alpha]_D$ -6.9 (*c* = 1.35) (Found: $M^+ + NH_4$, 266.2129. $C_{16}H_{28}NO_2$ requires *M*, 266.2120); ν_{max}/cm^{-1} 3428, 2960, 1496, 1454, 1359, 1096, 1028, 974, 863 and 736; δ_H (300 MHz, $CDCl_3$) 0.90 (3 H, d, *J* 6.5, 7-CH_3), 0.94 (3 H, t, *J* 7.5, 1-H_3), 1.41 - 1.58 (2 H, m, 2-H_2), 2.10 - 2.21 (1 H, m, 4-H), 2.26 (1 H, dt, *J* 14, 9.5, 4-H'), 2.61 (1 H, br s, OH), 2.86 (1 H, m, 7-H), 3.15 (1 H, t, *J* 9, 8-H), 3.31 (1 H, dd, *J* 9, 5.5, 8-H'), 3.49 (1 H, m, 3-H), 4.49 and 4.53 (each 1 H, d, *J* 12, PhC*H*H), 5.31 (1 H, t, *J* 10.5, 6-H), 5.48 (1 H, td, *J* 10, 6, 5-H) and 7.23 - 7.35 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 10.0, 17.3, 30.1, 32.3, 35.4, 72.3, 73.0, 74.8, 126.5, 127.6, 127.8, 128.4, 136.3 and 138.2; minor *syn*-epimer 10.1, 17.5, 29.8, 34.9, 72.6, 74.9 and 125.4; *m/z* (CI, NH_3) 266 (M^+ + 18, 14%), 249 (M^+ + 1, 4) and 52 (100).

Following the general procedure, alkenol **24** (21 mg, 0.085 mmol) and (*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride afforded the corresponding (*R*)-Mosher's ester (34 mg, 86%) as a colourless oil, $[\alpha]_D$ +15 (*c* = 0.65) (Found: $M^+ + NH_4$,

482.2528. $C_{26}H_{35}F_3NO_4$ requires *M*, 482.2518); ν_{max}/cm^{-1} 2969, 1745, 1454, 1262, 1169, 1121, 1022, 995 and 716; δ_H (300 MHz, $CDCl_3$) 0.80 (3 H, t, *J* 7.5, 1-H_3), 1.00 (3 H, d, *J* 6.5, 7-CH_3), 1.54 - 1.72 (2 H, m, 2-H_2), 2.36 - 2.54 (2 H, m, 4-H_2), 2.78 (1 H, m, 7-H), 3.24 - 3.35 (2 H, m, 8-H_2), 3.56 (3 H, s, OCH_3), 4.50 (2 H, s, $PhCH_2O$), 5.07 (1 H, m, 3-H), 5.31 - 5.42 (2 H, m, 5-H and 6-H) and 7.26 - 7.58 (10 H, m, ArH); δ_F (470 MHz, $CDCl_3$) -72.9, -73.0, ratio 87 : 13; *m/z* (CI, NH_3) 482 (M^+ + 18, 100%), 231 (50) and 106 (63).

Following the general procedure, alkenol **24** (23 mg, 0.093 mmol) and (*R*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride afforded the corresponding (*S*)-Mosher's ester (36 mg, 83%) as a colourless oil, $[\alpha]_D$ -43 (*c* = 0.93) (Found: $M^+ + NH_4$, 482.2515. $C_{26}H_{35}F_3NO_4$ requires *M*, 482.2518); ν_{max}/cm^{-1} 2965, 1744, 1497, 1454, 1269, 1169, 1121, 1022 and 716; δ_H (300 MHz, $CDCl_3$) 0.92 (3 H, t, *J* 7.5, 1-H_3), 0.98 (3 H, d, *J* 6.5, 7-CH_3), 1.58 - 1.74 (2 H, m, 2-H_2), 2.30 - 2.49 (2 H, m, 4-H_2), 2.73 (1 H, m, 7-H), 3.18 - 3.27 (2 H, m, 8-H_2), 3.56 (3 H, s, OCH_3), 4.49 (2 H, s, $PhCH_2O$), 5.05 (1 H, m, 3-H), 5.21 - 5.30 (2 H, m, 5-H and 6-H) and 7.25 - 7.58 (10 H, m, ArH); δ_F (470 MHz, $CDCl_3$) -72.9, -73.0, ratio 12 : 88; *m/z* (CI, NH_3) 482 (M^+ + 18, 100%).

(2*R*,3*S*,7*R*,5*Z*)-2,8-Dibenzyloxy-7-methyloct-5-en-3-ol 25

Following the general procedure, stannane **6** (93 mg, 0.194 mmol), tin(IV) chloride (1.044 M in DCM, 186 µl, 0.194 mmol) and (*R*)-2-benzyloxypropanal (32 mg, 0.194 mmol), after chromatography using petrol : ether (3 : 1) as eluent, gave the *title compound* **25** (48 mg, 70%) as a colourless oil, $[\alpha]_D$ -32 (*c* = 1.70) (Found: M^+ + H, 355.2276. $C_{23}H_{31}O_3$ requires *M*, 355.2273); ν_{max}/cm^{-1} 3449, 2870, 1496, 1454, 1093 and 737; δ_H (300 MHz, $CDCl_3$) 0.93 (3 H, d, *J* 6.5, 7-CH_3), 1.22 (3 H, d, *J* 6, 1-H_3), 2.25 - 2.37 (2 H, m, 4-H_2), 2.47 (1 H, br s, OH), 2.86 (1 H, m, 7-H), 3.19 (1 H, t, *J* 9, 8-H), 3.33 (1 H, dd, *J* 9, 5.5, 8-H'), 3.50 (1 H, m, 2-H), 3.63 (1 H, dt, *J* 8, 5, 3-H), 4.52 (2 H, s, $PhCH_2O$), 4.54 and 4.63 (each 1 H, d, *J* 11.5, PhC*H*H), 5.33 (1 H, t, *J* 10, 6-H), 5.50 (1 H, dt, *J* 10.5, 7.5, 5-H) and 7.27 - 7.38 (10 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 14.9, 17.4, 31.2, 32.4, 71.0, 73.0, 73.5, 74.8, 77.9, 126.5, 127.5, 127.6, 127.7, 127.8, 128.4, 136.0, 138.2 and 138.9; *m/z* (CI, NH_3) 355 (M^+ + 1, 46%), 247 (21) and 91 (100).

Following the general procedure, alkenol **25** (18 mg, 0.051 mmol) and (*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride afforded the corresponding (*R*)-Mosher's ester (25 mg, 88%) as a colourless oil, $[\alpha]_D$ +11 (*c* = 1.13) (Found: $M^+ + NH_4$, 588.2936. $C_{33}H_{41}F_3NO_5$ requires *M*, 588.2936); ν_{max}/cm^{-1} 2854, 1748, 1497, 1454, 1255, 1170, 1020, 736 and 698; δ_H (300 MHz, $CDCl_3$) 1.01 (3 H, d, *J* 6.5, 7-CH_3), 1.13 (3 H, d, *J* 6.5, 1-H_3), 2.40 - 2.63 (2 H, m, 4-H_2), 2.77 (1 H, m, 7-H), 3.19 - 3.37 (2 H, m, 8-H_2), 3.54 (3 H, s, OCH_3), 3.63 (1 H, qd, *J* 6.5, 3.5, 2-H), 4.37 - 4.56 (4 H, m, 2 x $PhCH_2$), 5.32 - 5.46 (3 H, m, 3-H, 5-H and 6-H) and 7.24 - 7.60 (15 H, m, ArH); δ_F (470 MHz, $CDCl_3$) -73.05, -73.1, ratio 86 : 14; *m/z* (CI, NH_3) 588 (M^+ + 18, 93%), 337 (48) and 139 (100).

Following the general procedure, alkenol **25** (20 mg, 0.056 mmol) and (*R*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride, after chromatography using petrol : ether (3 : 1) as eluent, afforded the corresponding (*S*)-Mosher's ester (20 mg, 63%) as a colourless oil, $[\alpha]_D$ -35 (*c* = 0.56) (Found: $M^+ + NH_4$, 588.2940. $C_{33}H_{41}F_3NO_5$ requires *M*, 588.2936); ν_{max}/cm^{-1} 2928, 1748, 1496, 1453, 1272, 1184, 1119, 1020, 723 and 698; δ_H (300 MHz, $CDCl_3$) 1.00 (3 H, d, *J* 6.5, 7-CH_3), 1.24 (3 H, d, *J* 6, 1-H_3), 2.31 - 2.48 (2 H, m, 4-H_2), 2.74 (1 H, m, 7-H), 3.17 - 3.30 (2 H, m, 8-H_2), 3.54 (3 H, s, OCH_3), 3.70 (1 H, qd, *J* 6.5, 2.5, 2-H), 4.49, 4.50, 4.54 and 4.60 (each 1 H, m, PhHC*H*), 5.25 - 5.35 (2 H, m, 5-H and 6-H), 5.46 (1 H, td, *J* 7, 2.5, 3-H) and 7.24 - 7.70 (15 H, m, ArH); δ_F (470 MHz, $CDCl_3$) -72.9, -73.1, ratio 87 : 13; *m/z* (CI, NH_3) 588 (M^+ + 18, 100%), 337 (41), 229 (50), 189 (68) and 139 (74).

Following the general procedure, alkenol **25** (11 mg, 0.031 mmol) and (*R*)-2-acetoxy-2-phenylacetic acid, after chromatography using petrol : ether (3 : 1) as eluent, gave the corresponding (*R*)-O-acetylmandelate (14 mg, 85%) as a colourless oil, $[\alpha]_D$ -52 (*c* = 0.61) (Found: $M^+ + NH_4$, 548.3012. $C_{33}H_{42}NO_6$ requires *M*, 548.3012); ν_{max}/cm^{-1} 2859, 1745, 1454, 1373, 1233, 1178, 1093 and 698; δ_H (300 MHz, $CDCl_3$) 0.92 (3 H, d, *J* 7, 7-CH_3), 1.21 (3 H, d, *J* 6, 1-H_3), 2.20 (3 H, s, O_2CCH_3), 2.26 - 2.44 (2 H, m, 4-H_2), 2.67 (1 H, m, 7-H), 3.07 - 3.22 (2 H, m, 8-H_2), 3.66 (1 H, m, 2-H), 4.44 and 4.46 (each 1 H, d, *J* 11, PhC*H*H), 4.55 (2 H, s, $PhCH_2$), 4.92 - 5.15 (3 H, m, 3-H, 5-H and 6-H), 5.92 (1 H, s, 2'-H) and 7.27 - 7.48 (15 H, m, ArH); *m/z* (CI, NH_3) 548 (M^+ + 18, 58%), 423 (36), 139 (88) and 91 (100).

Following the general procedure, alkenol **25** (13 mg, 0.037 mmol) and (*S*)-2-acetoxy-2-phenylacetic acid, after chromatography using petrol : ether (3 : 1) as eluent, gave the corresponding (*S*)-*O*-acetylmandelate (14 mg, 71%) as a colourless oil, $[\alpha]_D$ +24 (*c* = 0.62) (Found: $M^+ + NH_4$, 548.3010. $C_{33}H_{42}NO_6$ requires *M*, 548.3012); ν_{max}/cm^{-1} 2854, 1745, 1491, 1454, 1372, 1232, 1210, 1179, 1058, 737 and 698; δ_H (300 MHz, $CDCl_3$) 0.96 (3 H, d, *J* 6.5, 7-CH_3), 1.01 (3 H, d, *J* 6.5, 1-H_3), 2.20 (3 H, s, O_2CCH_3), 2.47 (2 H, t, *J* 6, 4-H_2), 2.80 (1 H, m, 7-H), 3.27 (1 H, dd, *J* 8.5, 7.5, 8-H), 3.37 (1 H, dd, *J* 9, 6, 8-H'), 3.46 (1 H, qd, *J* 6.5, 4, 2-H), 4.24, 4.31, 4.51 and 4.54 (each 1 H, d, *J* 12, PhC*H*H), 5.03 (1 H, td, *J* 6.5, 4, 3-H), 5.30 - 5.45 (2 H, m, 5-H and 6-H), 5.93 (1 H, s, 2'-H) and 7.13 - 7.48 (15 H, m, ArH); *m/z* (CI, NH_3) 548 (M^+ + 18, 100%), 139 (77) and 91 (83).

(2*S*,3*S*,7*R*,5*Z*)-2,8-Dibenzyloxy-7-methyloct-5-en-3-ol 26

Following the general procedure, stannane **6** (82 mg, 0.171 mmol), tin(IV) chloride (1.044 M in DCM, 164 µl, 0.171 mmol) and (*S*)-2-benzyloxypropanal (28 mg, 0.171 mmol), after chromatography using petrol : ether (3 : 1) as eluent, gave the *title compound* **26** (44 mg, 73%) as a colourless oil, $[\alpha]_D$ +0.9 (*c* = 1.33) (Found: M^+ + H, 355.2275. $C_{23}H_{31}O_3$ requires *M*, 355.2273); ν_{max}/cm^{-1} 3451, 2870, 1496, 1454, 1093, 1029 and 737; δ_H (300 MHz, $CDCl_3$) 0.96 (3 H, d, *J* 7, 7-CH_3), 1.21 (3 H, d, *J* 6, 1-H_3), 2.23 - 2.38 (2 H, m, 4-H_2), 2.83 (1 H, m, 7-H), 3.20 - 3.35 (2 H, m, 8-H_2), 3.47 - 3.61 (2 H, m, 2-H and 3-H), 4.49 (1 H, d, *J* 11.5, PhC*H*H), 4.52 (2 H, s, $PhCH_2$), 4.66 (1 H, d, *J* 11.5, PhCH*H*), 5.32 (1 H, t, *J* 10, 6-H), 5.53 (1 H, dt, *J* 10.5, 7.5, 5-H) and 7.27 - 7.37 (10 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 15.2, 17.5, 30.8, 32.4, 71.1, 73.0, 74.0, 75.0, 126.2, 127.6, 127.6, 127.7,

128.4, 128.4, 135.4, 138.3 and 138.7; *m/z* (CI, NH_3) 372 (M^+ + 18, 47%), 355 (M^+ + 1, 78) and 91 (100).

Following the general procedure, alcohol **26** (23 mg, 0.065 mmol) and (*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride afforded the corresponding (*R*)-Mosher's ester (32 mg, 88%) as a colourless oil, $[\alpha]_D$ +9.4 (*c* = 1.50) (Found: $M^+ + NH_4$, 588.2932. $C_{33}H_{41}F_3NO_5$ requires *M*, 588.2936); ν_{max}/cm^{-1} 2854, 1747, 1497, 1454, 1271, 1170, 1107, 1021, 736 and 698; δ_H (300 MHz, $CDCl_3$) 1.00 and 1.05 (each 3 H, d, *J* 7, 1-H_3 or 7-CH_3), 2.40 - 2.52 (1 H, m, 4-H), 2.59 (1 H, dt, *J* 15 4.5, 4-H'), 2.79 (1 H, m, 7-H), 3.21 - 3.33 (2 H, m, 8-H_2), 3.51 (3 H, s, OCH_3), 3.68 (1 H, m, 2-H), 4.43 (1 H, d, *J* 12, PhC*H*H), 4.48 (2 H, s, $PhCH_2$), 4.54 (1 H, d, J 12, PhCH*H*), 5.22 (1 H, dt, *J* 7.5, 5, 3-H], 5.27 - 5.47 (2 H, m, 5-H and 6-H) and 7.26 - 7.57 (15 H, m, ArH); δ_F (470 MHz, $CDCl_3$) -72.85, -73.09, 72.87, ratio 5 : 6 89; *m/z* (CI, NH_3) 588 (M^+ + 18, 59%), 189 (62), 139 (81) and 91 (100).

Following the general procedure, alcohol **26** (22 mg, 0.062 mmol) and (*R*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride, after chomatography using petrol : ether (3 : 1) as eluent,gave the corresponding (*S*)-Mosher's ester (17 mg, 48%) as a colourless oil, $[\alpha]_D$ -29 (*c* = 0.74) (Found: $M^+ + NH_4$, 588.2932. $C_{33}H_{41}F_3NO_5$ requires *M*, 588.2936); ν_{max}/cm^{-1} 2927, 1746, 1496, 1453, 1256, 1169, 1107, 1020, 735 and 698; δ_H (300 MHz, $CDCl_3$) 0.97 (3 H, d, *J* 7, 7-CH_3), 1.17 (3 H, d, *J* 6.5, 1-H_3), 2.40 (1 H, m, 4-H), 2.54 (1 H, dt, *J* 14.5, 4.5, 4-H'), 2.73 (1 H, m, 7-H), 3.15 - 3.24 (2 H, m, 8-H_2), 3.52 (3 H, s, OCH_3), 3.72 (1 H, m, 2-H), 4.47 (2 H, s, $PhCH_2$), 4.48 and 4.61 (each 1 H, d, *J* 11.5, PhC*H*H), 5.17 - 5.56 (3 H, m, 3-H, 5-H and 6-H) and 7.24-7.56 (15 H, m, ArH); δ_F (470 MHz, $CDCl_3$) -73.07, -73.08 and -73.2, ratio 6.5 : 6.5 : 87, respectively; *m/z* (CI, NH_3) 588 (M^+ + 18, 100%), 189 (67), 139 (73) and 91 (58).

Following the general procedure, alkenol **26** (11 mg, 0.031 mmol) and (*R*)-2-acetoxy-2-phenylacetic acid, after chromatography using petrol : ether (3 : 1) as eluent, gave the corresponding (*R*)-*O*-acetylmandelate (12 mg, 73%) as a colourless oil, $[\alpha]_D$ -61 (*c* = 0.48) (Found: $M^+ + NH_4$, 548.3013. $C_{33}H_{42}NO_6$ requires *M*, 548.3012); ν_{max}/cm^{-1} 2857, 1743, 1495, 1453, 1231, 1208, 1177, 1051, 736 and 697; δ_H (300 MHz, $CDCl_3$) 0.93 (3 H, d, *J* 7, 7-CH_3), 1.17 (3 H, d, *J* 6.5, 1-H_3), 2.11 - 2.31 (2 H, m, 4-H_2), 2.20 (3 H, s, O_2CCH_3), 2.66 (1 H, m, 7-H), 3.11 - 3.19 (2 H, m, 8-H_2), 3.67 (1 H, m, 2-H), 4.45 (2 H, s, $PhCH_2$), 4.49 and 4.61 (each 1 H, d, *J* 11.5, PhC*H*H), 4.89 - 5.03 (2 H, m, 5-H and 6-H), 5.07 (1 H, m, 3-H), 5.92 (1 H, s, 2'-H) and 7.27 - 7.48 (15 H, m, ArH); *m/z* (CI, NH_3) 548 (M^+ + 18, 31%), 531 (M^+ + 1, 4), 139 (62) and 91 (100).

Following the general procedure, alkenol **26** (14 mg, 0.040 mmol) and (*S*)-2-acetoxy-2-phenylacetic acid, after chromatography using petrol : ether (3 : 1) as eluent, gave the corresponding (*S*)-*O*-acetylmandelate (17 mg, 80%) as a colourless oil, $[\alpha]_D$ +25 (*c* = 0.59) (Found: $M^+ + NH_4$, 548.3015. $C_{33}H_{42}NO_6$ requires *M*, 548.3012); ν_{max}/cm^{-1} 2858, 1745, 1496, 1454, 1233, 1210, 1179, 1057, 737 and 698; δ_H (300 MHz, $CDCl_3$) 0.84 and 0.99 (each 3 H, d, *J* 6.5, 1-H_3 or 7-CH_3), 2.18 (3 H, s, O_2CCH_3), 2.38 (1 H, m, 4-H), 2.52 (1 H, dt, *J* 15, 5.5, 4-H'), 2.81 (1 H, m, 7-H), 3.28 (1 H, dd, *J* 9, 7, 8-H), 3.36 (1 H, dd, *J* 9, 6.5, 8-H'), 3.48 (1 H, m, 2-H), 4.27 and 4.39 (each 1 H, d, *J* 12.5, PhC*H*H), 4.51 (2 H, s, $PhCH_2$), 4.97 (1 H, dt, *J* 7.5, 5, 3-H), 5.27-5.41 (2 H, m, 5-H and 6-H), 5.93 (1 H, s, 2'-H) and 7.17 - 7.49 (15 H, m, ArH); *m/z* (CI, NH_3) 548 (M^+ + 18, 53%), 531 (M^+ + 1, 8), 139 (74) and 91 (100).

(4*R*,2*EZ*)-2,4-Dimethyl-5-hydroxypent-2-en-1-yl(tributyl)-stannane 34

Following the procedure outlined for the synthesis of xanthate **4**, the alcohol **30** (5.08 g, 21 mmol) in benzene (30 ml), sodium hydride (60% dispersion in mineral oil, 0.83 g, 21 mmol) in benzene (25 ml), carbon disulfide (5.0 ml, 84 mmol) and methyl iodide (5.2 ml, 84 mmol) afforded, after chromatography using petrol : ether (2 : 1) as eluent, the xanthate **31** (6.5 g, 94%) as a yellow oil (Found: M^+ + H, 335.1508. $C_{15}H_{31}O_2SiS_2$ requires *M*, 335.1535); ν_{max}/cm^{-1} 2956, 2857, 1471, 1255, 1223, 1200, 1066, 838 and 776; δ_H (300 MHz, $CDCl_3$) 0.07 [6 H, s, $Si(CH_3)_2$], 0.93 [9 H, s, $SiC(CH_3)_3$], 1.00 (3 H, d, *J* 9, 4-CH_3), 1.77 (3 H, d, *J* 1, 2-CH_3), 2.60 (3 H, s, SCH_3), 2.64 (1 H, m, 4-H), 3.47 (2 H, m, 5-H_2), 4.99 (2 H, s, 1-H_2) and 5.38 (1 H, dd, *J* 9.5 1, 3-H); δ_C (75 MHz, $CDC1_3$) -5.3, -5.3, 14.5, 16.9, 18.3, 18.9, 20.1, 35.5, 67.2, 79.7, 129.5, 134.5 and 215.6; *m/z* (Cl, NH_3) 335 (M^+ + 1, 99%), 227 (77) and 30 (100).

Following the procedure outlined for the synthesis of dithiocarbonate **5**, the xanthate **31** (6.3 g, 18 mmol) under reflux in toluene (30 ml) afforded, after chromatography using petrol : ether (20 : 1) the dithiocarbonate **32** (4.52 g, 75%) as a yellow oil, a 60 : 40 mixture of epimers (Found: M^+ + H, 335.1546. $C_{15}H_{31}O_2SiS_2$ requires *M*, 335.1535); ν_{max}/cm^{-1} 2930, 2858, 1647, 1471, 1253, 1092 and 838; δ_H (300 MHz, $CDCl_3$) 0.00 [3.6 H, s, $Si(CH_3)_2$], 0.02 (2.4 H, s, $Si(CH_3)_2$], 0.86 (9 H, s, SiC_4H_9), 0.94 (1.8 H, d, *J* 6.5, 4-CH_3), 0.96 (1.2 H, d, *J* 6.5, 4-CH_3), 1.72 (1.8 H, s, 2-CH_3), 1.76 (1.2 H, s, 2-CH_3), 1.82 (1 H, m, 4-H), 2.37 (1.8 H, s, SCH_3), 2.38 (1.2 H, s, SCH_3), 3.39 (0.6 H, dd, *J* 10, 6.5, 5-H), 3.52 (0.8 H, m, 5-H_2), 3.65 (0.6 H, dd, *J* 10 3.5, 5-H), 4.22 (0.6 H, d, *J* 10, 3-H), 4.32 (0.4 H, d, J 8, 3-H), 4.86 (1 H, m, 1-H) and 4.99 (1 H, br, d, *J* 6.5, 1-H'); δ_C (75 MHz, $CDC1_3$) -5.5, -5.4, 13.0, 13.1, 14.5, 15.6, 18.3, 19.1, 20.1, 25.9, 35.4, 32.0, 37.3, 54.3, 54.5, 64.5, 65.3, 65.5, 114.1, 114.7, 142.9, 143.4, 188.8 and 189.0; *m/z* (Cl, NH_3) 335 (M^+ + 1, 54%) and 97 (100).

Following the procedure outlined for the synthesis of stannane **6**, the dithiocarbonate **32** (1.49 g, 4.4 mmol) in benzene (13 ml), tributyltin hydride (1.82 ml, 6.7 mmol) and AIBN (20 mg) afforded, after chromatography using hexane (with 1% triethylamine) as eluent, the stannane **33** (2.37 g) as a colourless oil with minor organotin residues, a 55 : 45 mixture of (*E*)- and (*Z*)-isomers, $[\alpha]_D$ 13 (*c* = 1.5) (Found: M^+ + H - C_4H_9, 461.2276. $C_{21}H_{46}OSiSn$ requires *M*, 461.2262); ν_{max}/cm^{-1} 2957, 2928, 1654, 1464, 1254, 1081, 961, 837 and 724; δ_H (300 MHz, $CDC1_3$) 0.02 [6 H, s, $Si(CH_3)_2$], 0.87 - 1.82 [44 H, m, $Sn(C_4H_9)_3$, 1-H_2, 2-CH_3, 4-CH_3, and $SiC(CH_3)_3$], 2.33 - 2.58 (1 H, m, 4-H), 3.20 (0.55 H, dd, *J* 9, 7, 5-H), 3.28 (0.45 H m, dd, *J* 9, 7, 5-H), 3.41 (0.55 H, dd, *J* 9, 5.5, 5-H'), 3.45 (0.45 H, dd, *J* 9, 5.5, 5-H'), 4.56 (0.55 H, d, *J* 11, 3-H) and 4.68 (0.45 H, d, *J* 9, 3-H); *m/z* (Cl, NH_3) 308 (40%), 291(40), 171 (45%) and 97 (100).

TBAF (1 M in THF, 13.4 ml, 13.4 mmol) was added to the stannane **33** (2.37 g) in THF (10 ml) at 0 °C. After 5 min, the

mixture was allowed to warm to room temperature, stirred for 19 h, then partitioned between water (50 ml) and ether (75 ml). The organic layer was washed with brine (2 x 25 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using hexane : ether (25 : 1 + 1% triethylamine) as eluent afforded the *title compound* **34** (1.59 g, 88% from dithiocarbonate) as a colourless oil, a 55 : 45 mixture (*E*)- and (*Z*)-isomers, $[\alpha]_D$ -5.5 (*c* = 1.3) (Found: M^+ + H - C_4H_9, 347.1388. $C_{15}H_{32}OSn$ requires *M*, 347.1397); ν_{max}/cm^{-1} 3339, 2926, 1653, 1463, 1379, 1072, 1034, 961 and 725; δ_H (300 MHz, $CDCl_3$) 0.81 - 1.93 [35 H, m, $Sn(C_4H_9)_3$, 1-H_2, 2-CH_3 and 4-CH_3), 2.51 (1 H, m, 4-H), 3.25 and 3.41 (each 1 H, m, 5-H), 4.57 (0.55 H, d, *J* 9.5, 3-H) and 4.68 (0.45 H, d, *J* 9, 3-H); δ_C (75 MHz, $CDCl_3$) 9.5, 9.6, 13.7, 15.7, 17.1, 17.5, 19.0, 22,4, 25.7, 26.3, 27.4, 29.1, 35.6, 35.8, 68.0, 68.1, 122.1, 122.4, 138.4 and 138.5; *m/z* (EI) 347 (59%) and 177 (100).

(4*R*,2*EZ*)-5-methoxymethoxy)-2,4-dimethylpent-2-en-1-yl(tributyl)stannane 35

Methoxymethyl chloride (0.75 ml, 9 mmol) was added to the hydroxystannane **34** (0.99 g, 2.5 mmol) in *N*,*N*-di-*iso*propylethylamine (1.7 ml) at 0 °C. After 30 min, the reaction mixture was allowed to warm to room temperature and stirred for 14 h. Water (5 ml) was added and the mixture was extracted using DCM (3 x 20 ml). The organic extract was washed with brine (2 x 15 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using hexane : ether (10 : 1 + 1% triethylamine) as eluent gave the *title compound* **35** (0.89 g, 79%) as a colourless oil, a 55 : 45 mixture of (*E*)- and (*Z*)-isomers, $[\alpha]_D$ -14 (*c* = 1.4) (Found: M^+ + C_4H_8, 391.1657. $C_{17}H_{36}O_2Sn$ requires *M*, 391.1659); ν_{max}/cm^{-1} 2957, 2872, 1654, 1463, 1151, 1110, 1046 and 923; δ_H (300 MHz, $CDCl_3$) 0.80 - 1.82 [35 H, m, $Sn(C_4H_9)_3$, 1-H_2, 2-CH_3 and 4-CH_3], 2.55 (1 H, m, 4-H), 3.23 (1 H, dd, *J* 9.5, 7, 8-H), 3.34 (3 H, s, OCH_3), 3.37 (1 H, dd, *J* 7, 3.5, 8-H'), 4.60 (2 H, s, OCH_2O), 4.71 (0.55 H, d, *J* 10.5, 3-H) and 4.75 (0.45 H, d, *J* 9.5, 3-H); δ_C (75 MHz, $CDC1_3$) 9.4, 9.6, 13.7, 15.5, 18.0, 18.3, 18.7, 22.2, 26.2, 27.4, 29.1, 29.2, 29.3, 33.2, 33.3, 55.1, 72.9, 73.2, 96.5, 122.5, 122.8, 135.9 and 136.0; *m/z* (CI, NH_3) 391 (4%), 308 (80), 306 (61) and 127 (100).

(*R*)-2,4-Dimethylpent-4-en-1-yl] (*R*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoate 38

Following the general procedure, (*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride (106 mg, 0.41 mmol) and the hydroxystannane **34** (76 mg, 0.19 mmol) but using cooled aqueous hydrogen chloride (0.25 M, 10 ml) in the work-up and chromatography using hexane : ether (25 : 1 + 1% triethylamine) as eluent, gave the (*R*)-Mosher's derivative **36** (40 mg, 38%) as a colourless oil, a mixture of (*E*)- and (*Z*)-isomers, $[\alpha]_D$ +4.2 (*c* = 0.7) (Found: M^+ + H - C_4H_9, 563.1810. $C_{25}H_{39}F_3O_3Sn$ requires *M*, 563.1795); ν_{max}/cm^{-1} 2957, 2926, 1750, 1652, 1464, 1171, 1124, 1080, 1023 and 765; *m/z* (CI, NH_3) 347 (10%), 307 (100) and 305 (80).

Ethanolic hydrogen bromide (3.5%, 0.32 ml, 0.063 mmol) was added to the stannane **36** (30 mg, 0.048 mmol) in ethanol (0.1 ml) at 20 °C. After 30 min, water (1 ml) and saturated aqueous sodium hydrogen carbonate (0.5 ml) were added. The mixture was extracted with ether (4 x 10 ml), and the organic extract was washed with brine (2 x 10 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using hexane : ether (45 : 2) as eluent afforded the *title compound* **38** (14 mg, 87%) as a colourless oil, a 75 : 25 mixture of epimers, $[\alpha]_D$ +27 (*c* = 1.0) (Found: M^+ + NH_4, 348.1800. $C_{17}H_{25}F_3NO_3$ requires *M*, 348.1787); ν_{max}/cm^{-1} 2959, 1750, 1652, 1453, 1273, 1170, 1082, 1024, 894, 766 and 698; δ_H (300 MHz, $CDCl_3$) 0.93 (2 H, d, *J* 7, 2-CH_3), 0.98 (1 H, d, *J* 7, 2-CH_3), 1.70 (0.75 H, s, 4-CH_3), 1.72 (2.25 H, s, 4-CH_3), 1.91 (1 H, m, 2-H), 2.05 - 2.16 (2 H, m, 3-H_2), 3.60 (3 H, s, OCH_3), 4.10 (0.75 H, dd, *J* 11.5, 6.5, 1-H), 4.20 (0.5 H, d, *J* 5, 1-H_2), 4.31 (0.75 H, dd, *J* 11.5, 5, 1-H'), 4.67 (0.25 H, m, 5-H), 4.70 (0.75 H, m, 5-H), 4.80 (1 H, m, 5-H') and 7.44 - 7.58 (5 H, m, ArH); δ_F (470 MHz, $CDC1_3$) -73.10, -73.12, ratio 70 : 30; *m/z* (CI, NH_3) 348 (M^+ + 18, 100%).

(*R*)-2,4-Dimethylpent-4-en-1-yl] (*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoate 39

Following the general procedure, (*R*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride (72 mg, 0.28 mmol) and the hydroxystannane **34** (80 mg, 0.20 mmol) but using cooled aqueous hydrogen chloride (0.25 M, 10 ml) in the work-up and chromatography using hexane : ether (25 : 1 + 1% triethylamine) as eluent, gave the (*S*)-Mosher's derivative **37** (80 mg, 66%) as a colourless oil, a mixture of (*E*)- and (*Z*)-isomers, $[\alpha]_D$ -47 (*c* = 1.2) (Found: M^+ + H - C_4H_9, 563.1817. $C_{25}H_{39}F_3O_3Sn$ requires *M*, 563.1795); ν_{max}/cm^{-1} 2957, 2928, 1750, 1453, 1377, 1273, 1171, 1124, 1081, 1023 and 720; δ_H (300 MHz, $CDCI_3$) 0.78 - 1.83 [35 H, m, m, $Sn(C_4H_9)_3$, 1-H_2, 2-CH_3 and 4-CH_3], 2.70 (1 H, m, 4-H), 3.56 (3 H, s, OCH_3), 3.94 (1 H, m, 5-H), 4.19 (1 H, m, 5-H'), 4.58 and 4.69 (each 0.5 H, m, 3-H) and 7.37 - 7.52 (5 H, m, ArH); *m/z* (Cl, NH_3) 563 (0.4%), 562 (0.1), 348 (100) 308 (58) and 306 (44).

Following the procedure outlined for the synthesis of the alkene **38**, the stannane **37** (50 mg, 0.081 mmol) in ethanol (0.1 ml) and ethanolic hydrogen bromide (3.5%, 0.53 ml, 0.105 mmol), after chromatography using hexane : ether (45 : 2) as eluent, gave the *title compound* **39** (25 mg, 93%) as a colourless oil, a 75 : 25 mixture of epimers, $[\alpha]_D$ -42 (*c* = 1.2) (Found: M^+ + NH_4, 348.1787. $C_{17}H_{25}F_3NO_3$ requires *M*, 348.1787); ν_{max}/cm^{-1} 2967, 1750, 1652, 1453, 1273, 1124, 1170, 1082, 1024, 1001, 895, 766 and 698; δ_H (300 MHz, $CDC1_3$) 0.95 (1 H, d, *J* 7, 2-CH_3), 0.97 (2 H, d, *J* 7, 2-CH_3),1.75 (3 H, s, 4-CH_3), 1.91 (1 H, m, 2-H), 2.05 - 2.19 (2 H, m, 3-H_2), 3.60 (3 H, s, OCH_3), 4.11 (0.25 H, dd, *J* 10.5, 6, 1-H), 4.20 (1.5 H, d, *J* 5, 1-H_2), 4.31 (0.25 H, dd, *J* 10.5, 5 , 1-H'), 4.68 (0.75 H, m, 5-H), 4.71 (0.25 H, m, 5-H), 4.81 (1 H, m, 5-H') and 7.43-7.57 (5 H, m, ArH); δ_F (470 MHz, $CDCl_3$) -73.10, -73.12, ratio 30 : 70; *m/z* (CI, NH_3) 348 (M^+ + 18, 100%).

(1*S*,5*R*,3*Z*)-3,5-Dimethyl-6-(methoxymethoxy)-1-phenylhex-3-en-1-ol 40

Following the general procedure, the stannane **35** (0.20 g, 0.45 mmol) in DCM (4.6 ml), tin(IV) chloride (1.02 M in DCM, 0.53 ml, 0.55 mmol) and benzaldehyde (3.46 M in DCM, 0.16 ml, 0.55 mmol), after chromatography using hexane : ether (3 : 1) as eluent, gave the *title compound* **40** (83 mg, 69%) as a colourless oil, $[\alpha]_D$ -54 (*c* = 0.9) (Found: $M^+ + NH_4$, 282.2087. $C_{16}H_{28}NO_3$ requires *M*, 282.2069); ν_{max}/cm^{-1} 3455, 3062, 3029, 1604, 1453, 1216, 1142, 1108, 1041, 882, 756 and 701; δ_H (300 MHz, $CDCl_3$) 0.87 (3 H, d, *J* 6.5, 5-CH_3), 1.85 (3 H, s, 3-CH_3), 2.15 (1 H, dd, *J* 13.5, 2.5, 2-H), 2.70 (1 H, dd, *J* 13.5, 10.5, 2-H'), 2.82 (1 H, m, 5-H), 3.25 (1 H, t, *J* 9, 6-H), 3.37 (3 H, s, OCH_3), 3.51 (1 H, dd, *J* 9, 4.5, 6-H'), 3.88 (1 H, d, *J* 2.5, OH), 4.60 and 4.65 (each 1 H, d, *J* 6, OHC*H*O), 4.78 (1 H, dt, *J* 10, 2.5, 1-H), 5.14 (1 H, d, *J* 10, 4-H) and 7.25 - 7.40 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 17.3, 23.6, 32.8, 43.4, 55.4, 71.2, 72.5, 96.1, 125.6, 127.1, 128.3, 132.4, 132.8 and 145.3; *m/z* (Cl, NH_3) 282 (M^+ + 18, 3.5%), 264 (M^+, 4%) and 247 (M^+ - 17, 100). A second fraction contained (1*S*,5*R*,3*Z*)-3,5-dimethyl-6-(methoxymethoxy-methoxy)-1-phenyl-hex-3-en-1-ol **41** (8 mg, 6%) as a colourless oil (Found: M^+ - OH, 277.1819. $C_{17}H_{25}O_3$ requires *M*, 277.1804); ν_{max}/cm^{-1} 3464, 3054, 2918, 1266, 1130, 1110, 994 and 740; δ_H (300 MHz, $CDCl_3$) 0.85 (3 H, d, *J* 6.5, 5-CH_3), 1.82 (3 H, s, 3-CH_3), 2.16 (1 H, dd, *J* 13.5, 3, 2-H), 2.67 (1 H, dd, *J* 13.5, 10, 2-H'), 2.81 (1 H, m, 5-H), 3.30 (1 H, t, *J* 9, 6-H), 3.39 (3 H, s, OCH_3), 3.54 (1 H, dd, *J* 9, 4.5, 6-H'), 3.62 (1 H, br, OH), 4.71 (2 H, s, OCH_2), 4.77 (1 H, m, 1-H), 4.77 (2 H, s, OCH_2O), 5.12 (1 H, d, *J* 10, 4-H) and 7.29 - 7.40 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 17.4, 23.7, 32.9, 43.3, 55.9, 71.2, 73.3, 91.8, 93.4, 125.5, 127.0, 128.1, 132.3, 132.4 and 145.0; *m/z* (CI, NH_3) 277 (M^+ - 17, 9%), 247 (83), 215 (52) and 99 (100).

(1*R*,5*R*,3*Z*)-3,5-Dimethyl-6-(methoxymethoxy)-1-phenylhex-3-en-1- ol 45

Triphenylphosphine (0.37 g, 1.3 mmol), 4-nitrobenzoic acid (240 mg, 1.3 mmol) and DEAD (0.16 ml, 1.3 mmol) were added to a stirred solution of the alcohol **40** (90 mg, 0.29 mmol) in toluene (3.5 ml) at 35 °C. After 20 h at room temperature, water (5 ml) was added and the mixture extracted with ether (3 x 15 ml). The organic extracts were washed with brine (2 x 10 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (3 : 1) gave the inverted 4-nitrobenzoate **44** (46 mg, 33%) as a pale yellow oil, $[\alpha]_D$ -18 (*c* = 0.7) (Found: $M^+ + NH_4$, 431.2178. $C_{23}H_{31}NO_6$ requires *M*, 431.2182); ν_{max}/cm^{-1} 2929, 1726, 1608, 1530, 1346, 1273, 1103, 1043 and 874; δ_H (500 MHz, $CDCl_3$) 0.86 (3 H, d, *J* 6.5, 5-CH_3), 1.74 (3 H, s, 3-CH_3), 2.52 (1 H, dd, *J* 13.5, 5.5, 2-H), 2.66 (1 H, m, 5-H), 2.97 (1 H, dd, *J* 13.5, 8.5, 2-H'), 3.10 and 3.17 (each 1 H, dd, *J* 9, 6.5, 6-H), 3.30 (3 H, s, OCH_3), 4.52 (2 H, s, OCH_2O), 5.04 (1 H, d, *J* 9.5, 4-H), 6.15 (1 H, dd, *J* 9, 5.5, 1-H), 7.29 - 7.44 (5 H, m, ArH) and 8.21 and 8.27 (each 2 H, d, *J* 8.5, ArH); δ_C (75 MHz, $CDCl_3$) 18.1, 24.0, 33.1, 39.5, 55.1, 72.5, 76.3, 96.4, 123.4, 126.3, 128.2, 128.5, 130.5, 130.6, 131.7, 135.6, 139.9, 150.4 and 163.6; *m/z* (CI, NH_3) 431 (M^+ + 18, 49%), 391 (42), 279 (91) and 215 (100).

Methanolic sodium hydroxide (1%, 2.4 ml, 0.6 mmol) was added to the 4-nitrobenzoate **44** (35 mg, 0.085 mmol) in methanol (0.5 ml) at room temperature. After 2 h, water (3 ml) was added and the mixture extracted with ether (3 x 25 ml). The organic extracts were washed with brine (2 x 15 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (3 : 1) as eluent gave the *title compound* **45** (16 mg, 72%) as a colourless oil, $[\alpha]_D$ +9.4 (*c* = 0.5) (Found: M^+ - OH, 247.1692. $C_{16}H_{23}O_2$, requires *M*, 247.1698); ν_{max}/cm^{-1} 3452, 2957, 1453, 1152, 1112, 1043, 921, 757 and 701; δ_H (300 MHz, $CDCl_3$) 1.03 (3 H, d, *J* 7, 5-CH_3), 1.69 (3 H, d, *J* 1.5, 3-CH_3), 2.51 (1 H, dd, *J* 13.5, 5, 2-H), 2.51 (1 H, br s, OH), 2.64 (1 H, dd, *J* 13.5, 8, 2-H'), 2.78 (1 H, m, 5-H), 3.23 and 3.33 (each 1 H, dd, *J* 9.5, 6.5, 6-H), 3.39 (3 H, s, OCH_3), 4.63 (2 H, s, OCH_2O), 4.90 (1 H, dd, *J* 7.5, 5, 1-H), 5.19 (1 H, d, *J* 10, 4-H) and 7.32 -7.44 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 18.0, 24.3, 33.0, 42.3, 55.2, 72.0, 72.6, 96.4, 125.7, 127.3, 128.4, 131.8, 132.5 and 144.4; *m/z* (CI, NH_3) 247 (M^+ - OH, 48%), 215 (55) and 99 (100).

(1*S*,5*R*,3*Z*)-1-[(*R*)-2-Acetoxy-2-phenylacetoxy]-3,5-dimethyl-6-(methoxymethoxy)-1-phenylhex-3-ene 42

Following the general procedure, (*R*)-2-acetoxy-2-phenylacetic acid (41 mg, 0.21 mmol) and the alcohol **40** (28 mg, 0.11 mmol), after chromatography using petrol : ether (1 : 1) as eluent afforded the *title compound* **42** (46 mg, 100%) as a colourless oil, $[\alpha]_D$ -67 (*c* = 0.7) (Found: $M^+ + NH_4$, 458.2544. $C_{26}H_{36}NO_6$ requires *M*, 458.2543); ν_{max}/cm^{-1} 2929, 1745, 1232, 1175, 1044, 966 and 739; δ_H (300 MHz, $CDCl_3$) major diastereoisomer 0.64 (3 H, d, *J* 7, 5-CH_3), 1.43 (3 H, s, 3-CH_3), 2.16 (3 H, s, $COCH_3$), 2.35 - 2.55 (3 H, m, 2-H_2 and 5-H), 3.18 (2 H, m, 6-CH_2), 3.32 (3 H, s, OCH_3), 4.57 (2 H, s, OCH_2O), 4.87 (1 H, d, *J* 9.5, 4-H), 5.83 (1 H, t, *J* 7, 1-H), 5.97 (1 H, s, 2'-H) and 7.29 - 7.49 (10 H, m, ArH); *m/z* (CI, NH_3) 458 (M^+ + 18, 100%), 247 (65) and 215 (95).

(1*S*,5*R*,3*Z*)-1-[(*S*)-2-Acetoxy-2-phenylacetoxy]-3,5-dimethyl-6-methoxymethoxy-1-phenylhex-3-ene 43

Following the general procedure, (*S*)-2-acetoxy-2-phenylacetic acid (43 mg, 0.22 mmol) and the alcohol **40** (29 mg, 0.11 mmol), after chromatography using petrol : ether (1 : 1) as eluent afforded the *title compound* **43** (48 mg, 100%) as a colourless oil, $[\alpha]_D$ +21 (*c* = 1.3) (Found: $M^+ + NH_4$, 458.2524. $C_{26}H_{36}NO_6$ requires *M*, 458.2543); ν_{max}/cm^{-1} 2930, 1749, 1208, 1175, 1044, 966 and 923; δ_H (300 MHz, $CDCl_3$) major diastereoisomer 0.66 (3 H, d, *J* 7, 5-CH_3), 1.67 (3 H, s, 3-CH_3), 2.17 (3 H, s, $COCH_3$), 2.40 - 2.69 (3 H, m, 2-H_2 and 5-H), 3.28 (2 H, m, 6-H_2), 3.33 (3 H, s, OCH_3), 4.60 (2 H, s, OCH_2O), 5.01 (1 H, d, *J* 10, 4-H), 5.82 (1 H, t, *J* 7, 1-H), 6.00 (1 H, s, 2'-H) and 7.27 - 7.40 (10 H, m, ArH); *m/z* (CI, NH_3) 458 (M^+ + 18, 58%), 247 (60), 215 (95) and 99 (100).

(1*S*,5*R*,3*Z*)-3,5-Dimethyl-6-(methoxymethoxy)-1-(4-methoxyphenyl)hex-3-en-1-ol 46

Following the general procedure, stannane **35** (0.156 g, 0.35 mmol), tin(IV) chloride (1.02 M in DCM, 0.41 ml, 0.42 mmol) and 4-methoxybenzaldehyde in DCM (3.56 M, 0.12 ml, 0.42 mmol), after chromatography using hexane : ether (3 : 1) as

eluent, gave the *title compound* **46** (50 mg, 49%) as a colourless oil, $[\alpha]_D$ -40 (*c* = 1.1) (Found: M^+ - OH, 277.1778. $C_{17}H_{25}O_3$ requires *M*, 277.1804); ν_{max}/cm^{-1} 3460, 2957, 1613, 1587, 1513, 1248, 1173, 1142, 1108, 1039 and 924; δ_H (300 MHz, $CDCl_3$) 0.92 (3 H, d, *J* 6.5, 5-CH_3), 1.90 (3 H, s, 3-CH_3), 2.18 (1 H, dd, *J* 13.5, 3, 3-H), 2.75 (1 H, dd, *J* 13.5 10, 3-H'), 2.88 (1 H, m, 5-H), 3.31 (1 H, t, *J* 9, 6-H), 3.41 (3 H, s, OCH_3), 3.56 (1 H, dd, *J* 9, 5, 6-H'), 3.85 (4 H, s, OCH_3 and OH), 4.66 and 4.70 (each 1 H, d, *J* 6.5, OHC*H*O), 4.79 (1 H, dt, *J* 10, 2.5, 1-H), 5.18 (1 H, d, *J* 10, 4-H) and 6.94 and 7.37 (each 2 H, d, *J* 9, ArH); *m/z* (CI, NH_3) 277 (M^+ - 17, 53%) and 137 (100). A less polar fraction contained some (1*S*,5*R*,3*Z*)-3,5-dimethyl-6-(methoxymethoxymethoxy)-1-(4-methoxyphenyl)hex-3-en-1-ol (8 mg, 8%) (Found: M^+ - OH, 307.1933. $C_{18}H_{27}O_4$ requires *M*, 307.1909); ν_{max}/cm^{-1} 3472, 2957, 1726, 1613, 1513, 1249, 1130, 1040, 995 and 745; δ_H (300 MHz, $CDCl_3$) 0.97 (3 H, d, *J* 7, 5-CH_3), 1.63 (3 H, s, 3-CH_3), 2.19 (1 H, dd, *J* 13.5, 3, 2-H), 2.72 (1 H, dd, *J* 13.5, 10, 2-H'), 2.87 (1 H, m, 5-H), 3.29 - 3.38 (2 H, m, 6-H and OH), 3.44 (3 H, s, OCH_3), 3.60 (1 H, m, 6-H'), 3.85 (3 H, s, OCH_3), 4.34 (1 H, m, 1-H), 4.78 and 4.82 (each 2 H, s, OCH_2O), 5.17 (1 H, d, *J* 10, 4-H) and 6.92 and 7.36 (each 2 H, d, *J* 9, ArH); *m/z* (CI, NH_3) 307 (M^+ - 17, 28%), 211 (70) and 137 (100).

(3*S*,7*R*,5*Z*)-8-(Methoxymethoxy)-2,5,7-trimethyloct-5-en-3-ol 47

Following the general procedure, stannane **35** (0.26 g, 0.58 mmol), tin(IV) chloride (1.02 M in DCM, 0.74 ml, 0.75 mmol) and 2-methylpropanal (3.67 M in DCM, 0.20 ml, 0.75 mmol), after chromatography using hexane : ether (3 : 1) as eluent, gave the *title compound* **47** (77 mg, 57%) as a colourless oil, $[\alpha]_D$ -12 (*c* = 0.9) (Found: M^+ + H, 231.1961. $C_{13}H_{27}O_3$ requires *M*, 231.1960); ν_{max}/cm^{-1} 3492, 2958, 1466, 1384, 1146, 1108, 1043, 924 and 876; δ_H (300 MHz, $CDCl_3$) 0.93, 0.98 and 1.00 (each 3 H, d, *J* 6.5, 1-H_3, 2-CH_3 or 7-CH_3), 1.72 (1 H, m, 2-H), 1.81 (3 H, s, 5-CH_3), 1.96 (1 H, dd, *J* 12, 2, 4-H), 2.45 (1 H, dd, *J* 12, 10.5, 4-H'), 2.83 (1 H, m, 7-H), 3.26 (2 H, m, 8-H and OH), 3.36 (3 H, s, OCH_3), 3.50 (2 H, m, 8-H' and 3-H), 4.61 and 4.65 (each 1 H, d, *J* 6.5, OHC*H*O) and 5.13 (1 H, d, *J* 10, 6-H); δ_C (75 MHz, $CDCl_3$) 17.9, 18.5, 18.8, 24.1, 33.2, 34.5, 37.1, 55.7, 73.0, 73.7, 96.5, 132.5 and 133.6; *m/z* (CI, NH_3) 248 (M^+ + 18, 23%), 231 (M^+ + 1, 35), 199 (95) and 45 (100). A less polar fraction contained some (3*S*,7*R*,5*Z*)-8-(methoxymethoxymethoxy)-2,5,7-trimethyloct-5-en-3-ol (2 mg, 1.5%) (Found: M^+ + H, 261.2058, $C_{14}H_{29}O_4$ requires *M*, 261.2066); ν_{max}/cm^{-1} 3493, 2958, 2856, 1464, 1132, 1110, 1075, 996 and 876; δ_H (300 MHz, $CDCl_3$) 0.88, 0.90 and 0.93 (each 3 H, d, *J* 5, 1-H_3, 2-CH_3 or 7-CH_3),1.62 (1 H, m, 2-H), 1.72 (3 H, s, 5-CH_3), 1.90 (1 H, dd, *J* 13, 2, 4-H), 2.35 (1 H, dd, *J* 13, 10.5, 4-H'), 2.77 (1 H, m, 7-H), 2.96 (1 H, d, *J* 2.5, OH), 3.27 (1 H, t, *J* 9, 8-H), 3.35 (3 H, s, OCH_3), 3.42 (1 H, m, 3-H), 3.49 (1 H, dd, *J* 9, 4.5, 8-H'), 4.68 and 4.72 (each 2 H, s, OCH_2O) and 5.06 (1 H, d, *J* 10, 6-H); *m/z* (CI, NH_3) 278 (M^+ + 18, 10%), 261 (M^+ + 1, 37) and 199 (100).

(4*S*,8*R*,2*E*,6*Z*)-6,8-Dimethyl-9-methoxymethoxynona-2,6-dien-4-ol 48

Following the general procedure, stannane **35** (0.197 g, 0.44 mmol), tin(IV) chloride (1.02 M in DCM, 0.52 ml, 0.53 mmol) and (*E*)-but-2-enal (3.62 M in DCM, 0.15 ml, 0.53 mmol), after chromatography using hexane : ether (3 : 1) as eluent, gave the *title compound* **48** (68 mg, 68%) as a colourless oil, $[\alpha]_D$ -2.1 (*c* = 1.7) (Found: M^+ - OH, 211.1692. $C_{13}H_{23}O_2$ requires *M*, 211.1698); ν_{max}/cm^{-1} 3454, 2958, 1451, 1216, 1148, 1109, 1043, 966, 925 and 876; δ_H (300 MHz, $CDCl_3$) 0.94 (3 H, d, *J* 6.5, 8-CH_3), 1.73 (3 H, d, *J* 6, 1-H_3), 1.80 (3 H, s, 6-CH_3), 2.02 (1 H, dd, *J* 13.5, 3, 5-H), 2.52 (1 H, dd, *J* 13.5, 10, 5-H'), 2.83 (1 H, m, 8-H), 3.27 (1 H, t, *J* 9, 9-H), 3.37 (3 H, s, OCH_3), 3.44 (1 H, d, *J* 2.5, OH), 3.51 (1 H, dd, *J* 9, 4.5, 9-H'), 4.19 (1 H, m, 4-H), 4.60 and 4.65 (each 1 H, d, *J* 6.5, OHC*H*O), 5.13 (1 H, d, *J* 10, 7-H), 5.55 (1 H, ddq, *J* 15.5, 7, 2, 3-H) and 5.75 (1 H, dqd, *J* 15.5, 6, 1, 2-H); δ_C (75 MHz, $CDCl_3$) 18.0, 18.4, 24.4, 33.5, 41.5, 56.0, 70.4, 73.2, 96.8, 126.6, 133.0, 133.1 and 134.9; *m/z* (CI, NH_3) 228 (M^+, 21%), 211 (M^+ - 17, 90) and 45 (100). A less polar fraction also contained some (4*S*,8*R*,2*E*,6*Z*)-6,8-dimethyl-9-(methoxymethoxymethoxy)nona-2,6-dien-4-ol (3 mg, 3%); ν_{max}/cm^{-1} 3332, 2956, 2855, 1523, 1464, 1375, 1132, 996 and 665; δ_H (300 MHz, $CDCl_3$) 0.97 (3 H, d, *J* 8, 8-CH_3), 1.74 (3 H, d, *J* 7, 1-H_3), 1.82 (3 H, s, 6-CH_3), 2.03 (1 H, dd, *J* 13.5, 3, 5-H), 2.51 (1 H, dd, *J* 13.5, 10, 5-H'), 2.81 (1 H, m, 8-H), 3.15 (1 H, d, *J* 2.5, OH), 3.35 (1 H, t, *J* 9, 9-H), 3.42 (3 H, s, OCH_3), 3.54 (1 H, dd, *J* 9, 4.5, 9-H'), 4.18 (1 H, m, 4-H), 4.73 and 4.79 (each 2 H, s, OCH_2O), 5.13 (1 H, d, *J* 10, 7-H), 5.54 (1 H, ddq, *J* 15.5, 7, 2, 3-H) and 5.74 (1 H, dqd, *J* 15.5, 6, 1, 2-H).

DMSO (65 µl, 0.92 mmol) in DCM (1 ml) was added to oxalyl chloride (40 µl, 0.46 mmol) in DCM (1 ml) at -78 °C. After 20 min, the alcohol **48** (42 mg, 0.18 mmol) in DCM (1 ml) was added. After 15 min, *N*,*N*-di-*iso*propylethylamine (0.38 ml, 2.21 mmol) was added and the mixture was stirred for 5 min before being allowed to warm to room temperature. After 10 min, the mixture was poured into water and the aqueous phase extracted with DCM. The organic extracts were washed with brine, and dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using hexane : ether (3 : 1) gave the ketone **51** (26 mg, 62%) as a colourless oil, $[\alpha]_D$ -8.7 (*c* = 1.1) (Found: M^+ + H, 227.1647. $C_{13}H_{23}O_3$, requires *M*, 227.1647); ν_{max}/cm^{-1} 2930, 1695, 1629, 1442, 1379, 1151, 1112, 1045, 970 and 923; δ_H (300 MHz, $CDCl_3$) 1.03 (3 H, d, *J* 6.5, 8-CH_3), 1.75 (3 H, d, *J* 1.5, 6-CH_3), 1.93 (3 H, dd, *J* 7, 1.5, 1-H_3), 2.66 (1 H, m, 8-H), 3.31 (2 H, m, 9-H_2), 3.38 (3 H, s, OCH_3), 3.41 (2 H, s, 5-H_2), 4.66 (2 H, s, OCH_2O), 5.25 (1 H, d, *J* 9.5, 7-H), 6.25 (1 H, dq, *J* 15.5, 1.5, 3-H) and 6.95 (1 H, dq, *J* 15.5, 7, 2-H); δ_C (75 MHz, $CDCl_3$) 18.2, 18.7, 24.7, 34.0, 44.9, 55.6, 73.2, 96.9, 129.9, 131.4, 132.2, 143.4 and 198.3; *m/z* (CI, NH_3) 227 (M^+ + 1, 23%) and 195 (100).

Cerium(II1) chloride heptahydrate (56 mg, 0.15 mmol) and sodium borohydride (11 mg, 0.30 mmol) were added to the ketone **51**(31 mg, 0.14 mmol) in methanol (1.5 ml) at 0 °C. After 1 h, saturated aqueous ammonium chloride (3 ml) was added and the mixture was extracted using DCM (4 x 20 ml). The organic extracts were washed with brine (2 x 20 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using hexane : ether (5 : 1) as eluent afforded a mixture of the (4*S*)-alkenol **48** and its (4*R*)-epimer **52** (27 mg, 87%) (Found: M^+ - OH, 211.1694. $C_{13}H_{23}O_2$, requires *M*, 211.1698);

ν_{max}/cm^{-1} 3444, 2931, 1450, 1379, 1215, 1150, 1110, 1043, 966 and 924; δ_H (300 MHz, $CDCl_3$) peaks attributed to the (4*R*)-isomer 1.01 (3 H, d, *J* 7.5, 8-CH_3), 1.62 (3 H, s, 6-CH_3), 1.79 (3 H, d, *J* 7, 1-H$_3$), 2.30 (1 H, dd, *J* 13.5, 5, 5-H), 2.40 (1 H, dd, *J* 13.5, 7, 5-H'), 2.80 (1 H, m, 8-H), 3.39 (5 H, m, OCH_3 and 9-H_2), 4.26 (1 H, m, 4-H), 4.64 (2 H, s, OCH_2O), 5.18 (1 H, d, *J* 9, 7-H), 5.55 (1 H, dqd, *J* 15, 6.5, 1.5, 2-H) and 5.73 (1 H, m, 3-H); *m/z* (CI, NH_3) 211 (M^+ - 17, 100%) and 179 (65).

(1*S*,5*R*,3*Z*)-3,5-Dimethyl-1-phenylhex-3-ene-1,6-diol 49

Following the general procedure, tin(IV) bromide (1.01 M in DCM, 0.42 ml, 0.42 mmol), the stannane **34** (0.142 g, 0.352 mmol) in DCM (3.6 ml) and benzaldehyde (3.46 M in DCM, 0.122 ml, 0.42 mmol), after chromatography using hexane : ether (3 : 1) as eluent, afforded the *title compound* **49** (78 mg, 92%) as a colourless oil, $[\alpha]_D$ -34 (*c* = 1.0) (Found: M^+ - H_2O, 202.1355. $C_{14}H_{18}O$ requires *M*, 202.1357); ν_{max}/cm^{-1} 3330, 3063, 3030, 2926, 1604, 1453, 1059, 1030, 913, 755 and 700; δ_H (300 MHz, $CDCl_3$) 0.87 (3 H, d, *J* 6.5, 5-CH_3), 1.78 (1 H, br, s, OH), 1.90 (3 H, s, 3-CH_3), 2.15 (1 H, dd, *J* 13.5, 3, 2-H), 2.76 (1 H, m, 5-H), 2.80 (1 H, dd, *J* 13.5, 10.5, 2-H'), 3.28 (1 H, t, *J* 10, 6-H), 3.5 (1 H, br s, OH), 3.59 (1 H, dd, *J* 10, 3.5, 6-H'), 4.85 (1 H, dt, *J* 11, 3, 1-H), 5.13 (1 H, d, *J* 10, 4-H) and 7.27 - 7.44 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 17.7, 24.0, 35.4, 43.2, 68.1, 71.7, 126.2, 127.7, 128.8, 133.0, 133.5 and 145.7; *m/z* (CI, NH_3) 202 (M^+ - 18, 100%).

Following the procedure used for the synthesis of the 5-(methoxymethoxy)pent-2-enylstannane **35**, the diol **49** (24 mg, 0.11 mmol) in DCM (0.5 ml), methoxymethyl chloride (0.012 ml, 0.16 mmol) and *N*,*N*-di-*iso*propylethylamine (0.028 ml), after chromatography using hexane : ether (3 : 1) as eluent, gave the methoxymethyl ether **40** (8 mg, 38%) which was identical by IR and NMR to the sample prepared from the reaction of the stannane **35** and benzaldehyde. A second fraction was identified as its regioisomer, (2*R*,6*S*,3*Z*)-2,4-dimethyl-6-(methoxymethoxy)-6-phenylhex-3-en-1-ol **53** (2 mg, 9%), also a colourless oil (Found M^+ + NH_4, 282.2070. $C_{16}H_{24}NO_3$ requires *M*, 282.2069); ν_{max}/cm^{-1} 3449, 2957, 1454, 1152, 1099, 1064, 1036, 756 and 702; δ_H (300 MHz, $CDCl_3$) 0.89 (3 H, d, *J* 6.5, 2-CH_3), 1.92 (3 H, s, 4-CH_3), 2.19 (1 H, dd, *J* 13.5, 3.5, 5-H), 2.71 (1 H, m, 2-H), 2.90 (1 H, dd, *J* 13.5, 10, 5-H'), 3.13 (1 H, dd, *J* 9, 2, OH), 3.31 (1 H, t, *J* 9, 1-H), 3.39 (3 H, s, OCH_3), 3.57 (1 H, m, 1-H'), 4.49 and 4.54 (each 1 H, d, *J* 6.5, OHC*H*O), 4.87 (1 H, dd, *J* 10.5, 4, 6-H), 5.11 (1 H, d, *J* 10, 3-H) and 7.35 - 7.44 (5 H, m, ArH); *m/z* (CI, NH_3) 282 (M^+ - 18, 100%) and 220 (30).

(2*R*,6*S*,3*Z*,7*E*)-2,4-Dimethylnona-3,7-diene-1,6-diol 50

Following the general procedure, stannane **34** (0.121 g, 0.30 mmol) in DCM (3 ml), tin(IV) bromide (1.01 M in DCM, 0.356 ml, 0.36 mmol) and (*E*)-but-2-enal (3.62 M in DCM, 0.99 ml, 0.36 mmol), after chromatography using hexane : ether (3 : 1) as eluent, gave the *title compound* **50** (49 mg, 89%) as a colourless oil, $[\alpha]_D$ +7.8 (*c* = 1.2) (Found: M^+ - OH, 167.1429. $C_{11}H_{19}O$ requires *M*, 167.1435); ν_{max}/cm^{-1} 3331, 2871, 1674, 1449, 1076, 1033, 966 and 882; δ_H (300 MHz, $CDCl_3$) 0.92 (3 H, d, *J* 7, 2-CH_3), 1.74 (3 H, d, *J* 6.5, 9-H$_3$), 1.83 (3 H, s, 4-CH_3), 2.01 (1 H, dd, *J* 13, 3, 5-H), 2.59 (1 H, dd, *J* 13, 10.5, 5-H'), 2.73 (1 H, m, 2-H), 2.85 (2 H, br, s, 2 x OH), 3.28 (1 H, t, *J* 9.5, 1-H), 3.60 (1 H, dd, *J* 9.5, 4, 1-H'), 4.26 (1 H, m, 6-H), 5.10 (1 H, d, *J* 10, 3-H), 5.57 (1 H, ddq, *J* 15, 6.5, 1.5, 7-H) and 5.75 (1 H, dq, *J* 15, 6.5, 2-H); δ_H (75 MHz, $CDCl_3$) 17.7, 18.1, 24.1, 35.5, 40.7, 68.3, 70.4, 126.9, 132.5, 133.6 and 134.7; *m/z* (CI, NH_3) 184 (M^+, 8%) and 167 (100).

Methyl (*R*)-5-Benzyloxyhex-2-enoate 55

Dimethyl sulfoxide (3.99 g, 51.15 mmol) in DCM (15 ml) was added to oxalyl chloride (3.57 g, 28.11 mmol) in DCM (40 ml) at -50 ˚C and, after 5 min, alcohol **54**[13] (4.60 g, 25.56 mmol) in DCM (20 ml) was added. After 15 min, triethylamine (12.83 g, 127 mmol) was added and the suspension was stirred at -50 ˚C for 5 min then allowed to warm to room temperature. After 20 min, water (75 ml) was added and the organic phase was washed with water (3 x 75 ml) and brine (75 ml), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was taken up in DCM (75 ml) and methoxycarbonylmethylene(triphenyl)-phosphorane (9.39 g, 28.11 mmol) in DCM (75 ml) was added. The mixture was stirred at room temperature for 15 h then water (100 ml) was added and the organic phase washed with brine (100 ml), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was absorbed onto silica and chromatography using petrol : ether (6 : 1) as eluent afforded the (*Z*)-isomer of the *title compound* **(Z)-55** (310 mg, 5%) as a colourless oil, $[\alpha]_D$ -14 (*c* = 0.13) (Found: M^+ + H, 235.1330. $C_{14}H_{19}O_3$ requires *M*, 235.1334); ν_{max}/cm^{-1} 2972, 1722, 1645, 1439, 1176, 1133, 1093, 1027 and 736; δ_H (300 MHz, $CDCl_3$) 1.24 (3 H, d, *J* 6, 6-H$_3$), 2.95 (2 H, m, 4-H$_2$), 3.68 (1 H, m, 5-H), 3.72 (3 H, s, OCH_3), 4.52 and 4.58 (each 1 H, d, *J* 12, PhC*H*H), 5.88 (1 H, dt, *J* 11.5, 1.5, 2-H), 6.40 (1 H, dt, *J* 11.5, 7, 3-H) and 7.26 - 7.35 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 19.7, 35.7, 51.2, 70.5, 74.3, 120.8, 127.7, 127.8, 128.5, 139.0, 146.6 and 167.0; *m/z* (CI, NH_3) 235 (M^+ + 1, 100%). The second fraction was the (*E*)-isomer of the *title compound* **(E)-55** (4.19 g, 70%), as a colourless oil, $[\alpha]_D$ -5.2 (*c* = 1.20) (Found: M^+ + NH_4, 252.1593. $C_{14}H_{22}NO_3$ requires *M*, 252.1600); ν_{max}/cm^{-1} 2972, 1724, 1659, 1323, 1272, 1175, 981 and 737; δ_H (300 MHz, $CDCl_3$) 1.24 (3 H, d, *J* 6, 6-H$_3$), 2.34 - 2.55 (2 H, m, 4-H$_2$), 3.67 (1 H, m, 5-H), 3.75 (3 H, s, OCH_3), 4.49 and 4.57 (each 1 H, d, *J* 12, PhC*H*H), 5.89 (1 H, d, *J* 15.5, 2-H), 6.99 (1 H, dt, *J* 15.5, 7.5, 3-H) and 7.26 - 7.35 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 19.8, 39.5, 51.6, 70.7, 73.7, 123.2, 127.7, 127.8, 128.6, 138.7, 145.8 and 167.0; *m/z* (CI, NH_3) 252 (M^+ + 18, 70%), 235 (M^+ + 1, 51) and 91 (100).

(*R*)-5-Benzyloxyhex-2-en-1-ol 56

Di-*iso*butylaluminium hydride in hexanes (1 M, 28 ml, 28.0 mmol) was added to the ester **55** (2.17 g, 9.27 mmol) in DCM (28 ml) at -78 ˚C. After 3 h, water (20 ml) was added and the mixture was allowed to warm to room temperature then filtered through celite and the filtercake was washed with ethyl acetate (100 ml). The organic extracts were washed with water (100 ml), brine (100 ml) and dried ($MgSO_4$). Concentration under reduced pressure afforded the *title compound* **56** (1.86 g, 97%) as a

colourless oil, [a]$_D$ -7.5 (*c* = 0.55) (Found: $M^+ + NH_4$, 224.1649. $C_{13}H_{22}NO_2$ requires *M*, 224.1650); ν_{max}/cm^{-1} 3385, 2865, 1670, 1497, 1454, 1376, 1091, 973 and 738; δ_H (300 MHz, $CDCl_3$) 1.23 (3 H, d, *J* 7.5, 6-H$_3$), 1.51 (1 H, br s, OH), 2.20 - 2.41 (2 H, m, 4-H$_2$), 3.57 (1 H, m, 5-H), 4.09 (2 H, m, 1-H$_2$), 4.50 and 4.57 (each 1 H, d, *J* 12, PhC*H*H), 5.75 (2 H, m, 2-H and 3-H) and 7.25 - 7.35 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 19.4, 39.1, 63.6, 70.2, 74.3, 127.2, 127.4, 128.1, 128.8, 131.2 and 138.6; *m/z* (CI, NH_3) 224 (M^+ + 18, 30%), 207 (M^+ + 1, 4), 189 (M^+ - 17, 19) and 91 (100).

O-[(*R*)-5-Benzyloxyhex-2-en-1-yl] *S*-methyldithiocarbonate 57

Allylic alcohol **56** (2.27 g, 11.02 mmol) in benzene (12.5 ml) was added to a suspension of sodium hydride (485 mg, 60% dispersion in mineral oil, 12.12 mmol) in benzene (12.5 ml) at 5 °C. After 1 h at room temperature, carbon disulfide (3.41 g, 44.87 mmol) was added at 5 °C and the mixture was stirred at room temperature for 3 h. Methyl iodide (6.36 g, 44.79 mmol) was added and the mixture was stirred for 15 h. The mixture was filtered through celite and the filtercake washed with DCM (100 ml). The organic extracts were washed with brine (80 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (15 : 1) afforded the *title compound* **57** (2.87 g, 88%) as a yellow oil, [α]$_D$ -8.3 (*c* = 0.36) (Found: M^+ + H, 297.0979. $C_{15}H_{21}O_2S_2$ requires *M*, 297.0983); ν_{max}/cm^{-1} 2970, 1589, 1453, 1375, 1216, 1057, 971 and 735; δ_H (200 MHz, $CDCl_3$) 1.23 (3 H, d, *J* 6, 6-H$_3$), 2.21 - 2.47 (2 H, m, 4-H$_2$), 2.56 (3 H, s, SCH_3), 3.63 (1 H, m, 5-H), 4.48 and 4.58 (each 1 H, d, *J* 12, PhC*H*H), 5.06 (2 H, d, *J* 7, 1-H$_2$), 5.77 and 5.94 (each 1 H, dt, *J* 15, 6, 2-H or 3-H) and 7.27 - 7.36 (5 H, m, ArH); δ_C (75 MHz, C_6D_6) 19.5, 20.2, 40.3, 71.1, 74.8, 75.0, 126.0, 128.2, 129.2, 129.2, 134.9, 140.3 and 216.7; *m/z* (CI, NH_3) 314 (M^+ + 18, 18%), 297 (M^+ + 1, 50), 108 (68) and 91 (100).

S-[(3*RS*,5*R*)-5-Benzyloxyhex-1-en-3-yl] *S*-methyl dithiocarbonate 58

Xanthate **57** (1.49 g, 5.03 mmol) was heated under reflux in toluene (50 ml) for 15 h. Concentration under reduced pressure gave the *title compound* **58** (1.49 g, 100%) as a yellow oil, a 1 : 1 mixture of diastereoisomers, [α]$_D$ -48 (*c* = 0.34) (Found: M^+ + H, 297.0990. $C_{15}H_{21}O_2S_2$ requires *M*, 297.0983; ν_{max}/cm^{-1} 2929, 1647, 1060, 866 and 736; δ_H (300 MHz, $CDCl_3$) 1.23 and 1.24 (each 1.5 H, d, *J* 6, 6-H$_3$), 1.76 and 2.01 (each 1 H, m, 4-H), 2.41 and 2.42 (each 1.5 H, s, SCH_3), 3.60 and 3.70 (each 0.5 H, m, 5-H), 4.35-4.47 (2 H, m, PhC*H*H and 3-H), 4.57 and 4.59 (each 0.5 H, d, *J* 11.0, PhHC*H*), 5.07 - 5.28 (2 H, m, 1-H$_2$), 5.68-5.91 (1 H, m, 2-H) and 7.25 - 7.38 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 13.2, 13.2, 19.7, 19.8, 41.2, 41.5, 45.7, 70.6, 71.0, 72.3, 72.4, 116.2, 117.3, 127.7, 127.7, 128.0, 128.1, 128.4, 128.5, 137.4, 138.0, 138.8, 138.8, 188.8 and 188.9; *m/z* (CI, NH_3) 314 (M^+ + 18, 46%), 297 (M^+ + 1, 100), 237 (83), 189 (71), 108 (98) and 91 (100).

(*R*)-5-Benzyloxyhex-2-en-1-yl(tributyl)stannane 59

Tributyltin hydride (1.76 g, 6.05 mmol) and α-azo-bis-*iso*-butyronitrile (49 mg, 0.30 mmol) were added to a degassed solution of dithiocarbonate **58** (1.49 g, 5.03 mmol) in benzene (75 ml) and the solution was heated under reflux for 3 h. After concentration under reduced pressure, chromatography of the residue using petrol : ether (50 : 1 + 1% triethylamine) as eluent gave the *title compound* **59** (1.61 g, 67%) as a colourless oil, a 2 : 1 mixture of (*E*)- and (*Z*)-isomers, [α]$_D$ -0.5 (*c* = 1.15) (Found: M^+ - C_4H_7, 423.1724. $C_{21}H_{35}O^{120}Sn$ requires *M*, 423.1709); ν_{max}/cm^{-1} 2925, 1652, 1455, 1375, 1130, 1095, 1028 and 733; δ_H (300 MHz, $CDCl_3$) 0.77 - 1.00 (15 H, m, 3 x Sn$CH_2CH_2CH_2CH_3$), 1.19 (2 H, d, *J* 6.5, 6-H$_3$), 1.24 (1 H, d, *J* 6.5, 6-H$_3$), 1.26 - 1.86 (14 H, m, 3 x $SnCH_2CH_2CH_2CH_3$ and 1-H$_2$), 2.07 - 2.46 (2 H, m, 4-H$_2$), 3.53 (1 H, m, 5-H), 4.50 - 4.62 (2 H, m, $PhCH_2$), 5.14 (0.33 H, dt, *J* 10.5, 7, 2-H), 5.26 (0.67 H, dt, *J* 15, 7.5, 2-H), 5.65 (1 H, m, 3-H) and 7.23 - 7.38 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 9.4, 9.6, 13.9, 14.5, 16.0, 19.6, 19.8, 27.5, 29.5, 34.1, 39.9, 70.5, 70.5, 73.5, 75.7, 120.0, 121.6, 127.5, 127.7, 128.4, 130.3, 132.0 and 139.4; *m/z* (EI) 423 (M^+ - 57, 38%) and 291 (100).

(1*R*,6*R*,3*Z*)-6-Benzyloxy-1-phenylhept-3-en-1-ol 60 and (1*S*, 6*R*,3*Z*)-6-Benzyloxy-1-phenylhept-3-en-1-ol 64

Following the general procedure but at various temperatures from -50 °C to -95 °C with various times for the transmetallation, 2 - 10 min, stannane **59** (100 mg, 0.209 mmol), tin(IV) chloride (200 µl, 0.209 mmol) and benzaldehyde (60 µl, 0.209 mmol), after chromatography using petrol : ether (3 : 1) as eluent gave the (1*R*)-isomer of the *title compound* **60**, [α]$_D$ +52 (*c* = 0.77) (Found: M^+ - OH, 279.1746. $C_{20}H_{23}O$ requires *M*, 279.1749); ν_{max}/cm^{-1} 3407, 2969, 1495, 1453, 1375, 1054, 736 and 699; δ_H (300 MHz, $CDCl_3$) 1.18 (3 H, d, *J* 6, 7-H$_3$), 2.18 (1 H, dt, *J* 14, 6, 2- or 5-H), 2.33 - 2.70 (4 H, m, 2- or 5-H$_2$, 2- or 5-H, OH), 3.52 (1 H, m, 6-H), 4.48 and 4.58 (each 1 H, d, *J* 12, PhC*H*H), 4.71 (1 H, dd, *J* 8, 5, 1-H), 5.48 - 5.66 (2 H, m, 3-H and 4-H) and 7.23 - 7.38 (10 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 19.5, 34.6, 37.7, 70.3, 73.7, 74.2, 125.8, 127.0, 127.4, 127.5, 127.8, 128.3, 129.5, 138.7 and 144.3; *m/z* (CI, NH_3) 314 (M^+ + 18, 2%), 279 (M^+ - 17, 39), 171 (53) and 85 (100). The second fraction was the (1*S*)-isomer of the *title compound* **64**, [α]$_D$ -35.5 (*c* = 1.32); ν_{max} /cm^{-1} 3424, 2969, 1495, 1453, 1134, 1056, 912, 736 and 700; δ_H (300 MHz, $CDCl_3$) 1.21 (3 H, d, *J* 6.5, 7-H$_3$), 2.23 - 2.37 and 2.51 - 2.60 (each 2 H, m, 2- or 5-H$_2$), 2.63 (1 H, br s, OH), 3.58 (1 H, m, 6-H), 4.50 and 4.60 (each 1 H, d, *J* 12, PhC*H*H), 4.76 (1 H, t, *J* 6, 1-H), 5.46 - 5.68 (2 H, m, 3-H and 4-H) and 7.24 - 7.38 (10 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 19.3, 34.4 37.3, 70.4, 73.6, 74.4, 125.9, 126.9, 127.4, 127.6, 127.7, 128.3, 128.4, 129.1, 138.8 and 144.3; *m/z* (CI, NH_3) 279 (M^+ - 17, 9%), 206 (17), 106 (41) and 52 (97). Combined yields were 40 - 75% and product ratios were not reproducible varying from 20 : 80 to 80 : 20.

(1*R*, 6*R*,3*Z*)-1-Acetoxy-6-benzyloxy-1-phenylhept-3-ene 61

Triethylamine (133 mg, 1.317 mmol), 4-*N*,*N*-dimethylamino-pyridine (2 mg, 0.016 mmol) and acetic anhydride (54 mg, 0.53 mmol) were added the alcohol **60** (78 mg, 0.264 mmol) in DCM

(2 ml) and the solution stirred at room temperature for 15 h. DCM (20 ml) and water (20 ml) were added and the organic phase was washed with aqueous hydrogen chloride (3.5 M, 15 ml) and brine (15 ml) then dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (5 : 1) afforded the *title compound* **61** (78 mg, 87%) as a colourless oil, $[\alpha]_D$ +26 (*c* = 0.55) (Found: $M^+ + NH_4$, 356.2238. $C_{22}H_{30}NO_3$ requires *M*, 356.2226); ν_{max}/cm^{-1} 2970, 1740, 1496, 1454, 1373, 1237, 1027, 736 and 699; δ_H (500 MHz, $CDCl_3$) 1.11 (3 H, d, *J* 6, 7-H_3), 2.04 (3 H, s, O_2CCH_3), 2.13, 2.28, 2.53 and 2.66 (each 1 H, dt, *J* 14, 7, 2- or 5-H), 3.43 (1 H, m, 6-H), 4.44 and 4.51 (each 1 H, d, *J* 11.5, PhC*H*H), 5.39 and 5.52 (each 1 H, dt, *J* 11, 7, 3-H or 4-H), 5.74 (1 H, t, *J* 7, 1-H) and 7.24 - 7.32 (10 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 19.5, 21.2, 34.3, 34.6, 70.4, 74.6, 75.5, 125.7, 126.6, 127.4, 127.6, 127.9, 128.3, 128.4, 128.9, 139.0, 140.3 and 170.2; *m/z* (CI, NH_3) 356 ($M^+ + 18$, 24%), 279 (25) and 85 (100).

(1*R*,6*R*,3*Z*)-1-[(*R*)-2-Acetoxy-2-phenylacetoxy]-6-benzyloxy-1-phenylhept-3-ene 62

Folllowing the general procedure, alcohol **60** (13 mg, 0.044 mmol) and (*R*)-2-acetoxy-2-phenylacetic acid, after chromatography using petrol : ether (3 : 1) as eluent, gave the *title compound* **62** (17 mg, 82%) as a colourless oil, $[\alpha]_D$ -23 (*c* = 0.73) (Found: $M^+ + NH_4$, 490.2589. $C_{30}H_{36}NO_5$ requires *M*, 490.2593); ν_{max} /cm^{-1} 2969, 1747, 1496, 1454, 1373, 1232, 1208, 1175, 1058, 738 and 698; δ_H (300 MHz, $CDCl_3$) 1.12 (3 H, d, *J* 6, 7-H_3), 2.04 - 2.33 (2 H, m, 2- or 5-H_2), 2.18 (3 H, s, O_2CCH_3), 2.55 and 2.66 (each 1 H, dt, *J* 14, 7, 2- or 5-H), 3.43 (1 H, m, 6-H), 4.45 and 4.52 (each 1 H, d, *J* 11.5, PhC*H*H), 5.39 and 5.54 (each 1 H, dt, *J* 11, 7, 3-H or 4-H), 5.74 (1 H, t, *J* 6.5, 1-H), 6.00 (1 H, s, 2'-H) and 6.94 - 7.40 (15 H, m, ArH); *m/z* (CI, NH_3) 490 ($M^+ + 18$, 57%), 279 (40) and 171 (100).

(1*R*,6*R*,3*Z*)-1-[(*S*)-2-Acetoxy-2-phenylacetoxy]-6-benzyloxy-1-phenylhept-3-ene 63

Following the general procedure, alcohol **60** (13 mg, 0.044 mmol) and (*S*)-2-acetoxy-2-phenylacetic acid, after chromatography using petrol : ether (3 : 1) as eluent, gave the *title compound* **63** (16 mg, 77%) as a colourless oil, $[\alpha]_D$ +56 (*c* = 0.77) (Found: $M^+ + NH_4$, 490.2589. $C_{30}H_{36}NO_5$ requires *M*, 490.2593); ν_{max} /cm^{-1} 2970, 1747, 1496, 1454, 1373, 1231, 1208, 1175, 1057, 737 and 698; δ_H (300 MHz, $CDCl_3$) 1.08 (3 H, d, *J* 6, 7-H_3), 1.96 - 2.17 (2 H, m, 2- or 5-H_2), 2.18 (3 H, s, O_2CCH_3), 2.39 - 2.61 (2 H, m, 2- or 5-H_2), 3.37 (1 H, m, 6-H), 4.42 and 4.48 (each 1 H, d, *J* 12, PhC*H*H), 5.13 and 5.37 (each 1 H, dt, *J* 10.5 7.5, 3-H or 4-H), 5.76 (1 H, t, *J* 7, 1-H), 5.99 (1 H, s, 2'-H) and 7.25 - 7.48 (15 H, m, ArH); *m/z* (CI, NH_3) 490 ($M^+ + 18$, 34%), 279 (31), 171 (77) and 85 (100).

(1*S*,6*R*,3*Z*)-1-Acetoxy-6-benzyloxy-1-phenylhept-3-ene 65

Triethylamine (24 mg, 0.238 mmol), 4-*N*,*N*-dimethylamino-pyridine (0.5 mg, 0.004 mmol) and acetic anhydride (10 mg, 0.098 mmol) were added to the alcohol **64** (14 mg, 0.047 mmol) in DCM (1 ml) and the solution stirred at room temperature for 15 h. DCM (10 ml) and water (10 ml) were added and the organic phase washed with aqueous hydrogen chloride (3.5 M, 7 ml) and brine (7 ml) then dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (4 : 1) as eluent gave the *title compound* **65** (14 mg, 88%) as a colourless oil, $[\alpha]_D$ -12 (*c* = 0.53) (Found: $M^+ + NH_4$, 356.2231. $C_{22}H_{30}NO_3$ requires *M*, 356.2226); ν_{max}/cm^{-1} 2970, 1740, 1496, 1454, 1373, 1237, 1027, 736 and 699; δ_H (300 MHz, $CDCl_3$) 1.16 (3 H, d, *J* 6, 7-H_3), 2.08 (3 H, s, O_2CCH_3), 2.18, 2.29, 2.53 and 2.70 (each 1 H, dt, *J* 14, 7, 2-H or 5-H), 3.48 (1 H, m, 6-H), 4.47 and 4.53 (each 1 H, d, *J* 12, PhC*H*H), 5.35 - 5.58 (2 H, m, 3-H and 4-H), 5.77 (1 H, t, *J* 7, 1-H) and 7.26 - 7.34 (10 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 19.5, 21.2, 34.3, 34.5, 70.4, 74.6, 75.5, 125.7, 126.6, 127.4, 127.6, 127.9, 128.3, 128.4, 128.9, 139.0, 140.2 and 170.2; *m/z* (CI, NH_3) 356 ($M^+ + 18$, 64%), 279 (68), 171 (93) and 85 (100).

(1*S*,6*R*,3*Z*)-1-[(*R*)-2-Acetoxy-2-phenylacetoxy]-6-benzyloxy-1-phenylhept-3-ene 66

Following the general procedure, alcohol **64** (18 mg, 0.061 mmol) and (*R*)-2-acetoxyphenylacetic acid, after chromatography using petrol : ether (4 : 1) as eluent, gave the *title compound* **66** (23 mg, 80%) as a colourless oil, $[\alpha]_D$ -44 (*c* = 0.99) (Found: $M^+ + NH_4$, 490.2600. $C_{30}H_{36}NO_5$ requires *M*, 490.2593); ν_{max} /cm^{-1} 2969, 1747, 1496, 1454, 1373, 1232, 1208, 1175, 1058, 738 and 698; δ_H (300 MHz, $CDCl_3$) 1.08 (3 H, d, *J* 6, 7-H_3), 1.97 (1 H, dt, *J* 14, 7, 2- or 5-H), 2.08 - 2.22 (4 H, m, 2- or 5-H and O_2CCH_3), 2.45 and 2.57 (each 1 H, dt, *J* 14, 7, 2- or 5-H), 3.38 (1 H, m, 6-H), 4.42 and 4.48 (each 1 H, d, *J* 12, PhC*H*H), 5.13 and 5.38 (each 1 H, m, 3-H or 4-H), 5.78 (1 H, t, *J* 7, 1-H), 5.99 (1 H, s, 2'-H) and 7.25 - 7.53 (15 H, m, ArH); *m/z* (CI, NH_3) 490 ($M^+ + 18$, 59%), 279 (42), 171 (85) and 85 (100).

(1*S*,6*R*,3*Z*)-1-[(*S*)-2-Acetoxy-2-phenylacetoxy]-6-benzyloxy-1-phenylhept-3-ene 67

Following the general procedure, alcohol **64** (20 mg, 0.068 mmol) and (*S*)-2-acetoxyphenylacetic acid, after chromatography using petrol : ether (4 : 1) as eluent, gave the *title compound* **67** (28 mg, 87%) as a colourless oil, $[\alpha]_D$ +37 (*c* = 1.17) (Found: $M^+ + NH_4$, 490.2589. $C_{30}H_{36}NO_5$ requires *M*, 490.2593); ν_{max} /cm^{-1} 2969, 1747, 1496, 1454, 1373, 1232, 1208, 1175, 1058, 738 and 698; δ_H (300 MHz, $CDCl_3$) 1.14 (3 H, d, *J* 6, 7-H_3), 2.05 - 2.21 (4 H, m, 2- or 5-H and O_2CCH_3), 2.27, 2.54 and 2.68 (each 1 H, dt, *J* 14, 7, 2- or 5-H), 3.46 (1 H, m, 6-H), 4.47 and 4.52 (each 1 H, d, *J* 12, PhC*H*H), 5.41 and 5.55 (each 1 H, dt, *J* 10.5, 7, 3-H or 4-H), 5.74 (1 H, t, *J* 6.5, 1-H), 6.01 (1 H, s, 2'-H) and 7.14 - 7.42 (15 H, m, ArH); *m/z* (CI, NH_3) 490 ($M^+ + 18$, 67%), 279 (48) and 85 (100).

(*R*)-6-Benzyloxy-1-phenylhept-3-en-1-one 68

Dimethylsulfoxide (23 mg, 0.295 mmol) in DCM (500 µl) was added to oxalyl chloride (19 mg, 0.150 mmol) in DCM (500 µl) at -50 °C. After 5 min, a mixture of alcohols **60** and **64** (39 mg, 0.132 mmol) in DCM (500 µl) was added and, after 15 min, di-isopropylethylamine (39 mg, 0.675 mmol) was added. The

suspension was stirred at -50 ˚C for 5 min then allowed to warm to room temperature. After 20 min, DCM (10 ml) and water (10 ml) were added and the organic phase was washed with water (2 x 10 ml) and brine (10 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (8 : 1) as eluent gave the *title compound* **68** (19 mg, 49%) as a colourless oil, $[\alpha]_D$ +12 (*c* = 0.89); ν_{max}/cm^{-1} 2970, 1687, 1598, 1496, 1450, 1375, 1209, 1092, 738 and 695; δ_H (300 MHz, C_6D_6) 1.14 (3 H, d, *J* 6, 7-H_3), 2.22 and 2.39 (each 1 H, dt, *J* 14, 7, 5-H), 3.44 (1 H, m, 6-H), 3.52 (2 H, d, *J* 7, 2-H_2), 4.37 and 4.46 (each 1 H, d, *J* 12, PhC*H*H), 5.70 and 6.00 (each 1 H, m, 3-H or 4-H), 7.09 - 7.42 (8 H, m, ArH) and 7.88 - 7.92 (2 H, m, ArH); δ_C (75 MHz, C_6D_6) 19.6, 35.1, 37.7, 70.5, 74.7, 123.9, 127.4, 127.8, 128.4, 128.5, 128.6, 129.2, 132.7, 137.3, 139.8 and 196.7; *m/z* (CI, NH_3) 312 (M^+ + 18, 1%), 295 (M^+ + 1, 1), 93 (85) and 52 (100).

(3*R*,8*R*,5*Z*)-8-Methoxy-2-methylnon-5-en-3-ol 87

Following the general procedure, stannane **74** (420 mg, 1.042 mmol), tin(IV) bromide (1.044 M in DCM, 1.00 ml, 1.044 mmol) and 2-methylpropanal (300 µl, 1.044 mmol), after chromatography using petrol : ether (2 : 1) as eluent, gave the *title compound* **87** (140 mg, 72%) as a colourless oil, [α] +13.5 (*c* = 0.71) (Found: M^+ + H, 187.1695. $C_{11}H_{23}O_2$ requires *M*, 187.1698); ν_{max}/cm^{-1} 3435, 2968, 1466, 1378, 1194, 1134, 1094, 1052, 1003 and 716; δ_H (300 MHz, $CDCl_3$) 0.97 and 0.99 (each 3 H, d, *J* 6.5, 1-H_3 or 2-CH_3), 1.18 (3 H, d, *J* 6, 9-H_3), 1.73 (1 H, m, 2-H), 2.10 - 2.57 (5 H, m, 4-H_2, 7-H_2 and OH), 3.31 - 3.45 (5 H, m, 3-H, 8-H and OCH_3) and 5.52 - 5.67 (2 H, m, 5-H and 6-H); δ_C (75 MHz, $CDCl_3$), 17.8, 18.7, 18.9, 32.2, 33.5, 34.6, 56.1, 75.9, 76.6, 128.4 and 128.9; *m/z* (CI, NH_3) 187 (M^+ + 1, 100).

(3*S*,8*R*,5*Z*)-8-Methoxy-2-methylnon-5-en-3-ol 88

Sodium hydroxide (38 mg, 0.950 mmol) was added to the ester **93** (45 mg, 0.134 mmol) in methanol (4 ml). After 2.5 h at room temperature water (12 ml) was added and the mixture was extracted with ether (2 x 17 ml). The organic extracts were washed with brine (30 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (2 : 1) gave the *title compound* **88** (23 mg, 92%) as a colourless oil, $[\alpha]_D$ +4.8 (*c* = 0.88) (Found: M^+ + H, 187.1690. $C_{11}H_{23}O_2$ requires *M*, 187.1698); ν_{max}/cm^{-1} 3445, 2967, 1465, 1378, 1194, 1134, 1093, 1047 and 1002; δ_H (300 MHz, $CDCl_3$) 0.96 and 0.98 (each 3 H, d, *J* 6.5, 1-H_3 and 2-CH_3), 1.13 (3 H, d, *J* 7, 9-H_3), 1.72 (1 H, m, 2-H), 2.20 - 2.35 (4 H, m, 4-H_2 and 7-H_2), 3.31-3.47 (5 H, m, 3-H, 8-H, and OCH_3) and 5.51 - 5.68 (2 H, m, 5-H and 6-H); δ_C (75 MHz, $CDCl_3$) major epimer **88** 17.7, 18.6, 18.8, 32.2, 33.3, 33.9, 56.1, 76.0, 76.5, 128.2 and 128.4; minor epimer **87** 18.9 and 33.5; *m/z* (CI, NH_3) 204 (M^+ + 18, 10%) and 187 (M^+ + 1, 100).

(3*R*,8*R*,5*Z*)-3-[(*R*)-2-Acetoxy-2-phenylacetoxy]-8-methoxy-2-methylnon-5-ene 89

Following the general procedure, alcohol **87** (14 mg, 0.075 mmol) and (*R*)-2-acetoxy-2-phenylacetic acid, after chromatography using petrol : ether (2 : 1) as eluent gave the *title compound* **89** (22 mg, 81%) as a colourless oil, $[\alpha]_D$ -68 (*c* = 0.94) (Found: $M^+ + NH_4$, 380.2438. $C_{21}H_{34}NO_5$ requires *M*, 380.2437); ν_{max} /cm^{-1} 2968, 1746, 1373, 1233, 1180, 1086, 1056 and 697; δ_H (300 MHz, $CDCl_3$) 0.67 and 0.70 (each 3 H, d, *J* 7, 1-H_3 or 2-CH_3), 1.17 (3 H, d, *J* 6.5, 9-H_3), 1.75 (1 H, m, 2-H), 2.15 - 2.27 (5 H, m, 7-H_2 and O_2CCH_3), 2.29 - 2.42 (2 H, m, 4-H_2), 3.32 - 3.42 (4 H, m, 8-H and OCH_3), 4.80 (1 H, m, 3-H), 5.40 - 5.58 (2 H, m, 5-H and 6-H), 5.94 (1 H, s, 2'-H) and 7.37 - 7.55 (5 H, m, ArH); *m/z* (CI, NH_3) 380 (M^+ + 18, 28%), 363 (M^+ + 1, 20), 331 (22) and 169 (100).

(3*R*,8*R*,5*Z*)-3-[(*S*)-2-Acetoxy-2-phenylacetoxy]-8-methoxy-2-methylnon-5-ene 90

Following the general procedure, alcohol **87** (10 mg, 0.054 mmol) and (*S*)-2-acetoxy-2-phenylacetic acid, after chromatography using petrol : ether (3 : 1) as eluent, gave the *title compound* **90** (10 mg, 51%) as a colourless oil, $[\alpha]_D$ +43 (*c* = 0.49) (Found: $M^+ + NH_4$, 380.2441. $C_{21}H_{34}NO_5$ requires *M*, 380.2437); ν_{max} /cm^{-1} 2968, 1745, 1373, 1233, 1211, 1180, 1086, 1056 and 697; δ_H (300 MHz, $CDCl_3$) 0.97 (6 H, d, *J* 7, 1-*H*$_3$ and 2-CH_3), 1.09 (3 H, d, *J* 6, 9-H_3), 1.91 (1 H, m, 2-H), 2.00 - 2.08 (2 H, m, 7-H_2), 2.13 - 2.25 (5 H, m, 4-H_2 and O_2CCH_3), 3.25 (1 H, m, 8-H), 3.31 (3 H, s, OCH_3), 4.82 (1 H, q, *J* 6, 3-H), 5.12 and 5.28 (each 1 H, m, 5-H or 6-H), 5.93 (1 H, s, 3-H) and 7.33 - 7.55 (5 H, m, ArH); *m/z* (CI, NH_3) 380 (M^+ + 18, 24%), 363 (M^+ + 1, 19), 331 (28) and 169 (100).

(3*R*,8*R*,5*Z*)-8-Methoxy-3-[(*R*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyloxy]-2-methylnon-5-ene 91

Following the general procedure, alcohol **87** (11 mg, 0.059 mmol) and (*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride afforded the *title compound* **91** (21 mg, 89%) as a colourless oil, $[\alpha]_D$ +21 (*c* = 0.98) (Found: $M^+ + NH_4$, 420.2354. $C_{21}H_{33}F_3NO_4$ requires M, 420.2361); ν_{max}/cm^{-1} 2972, 1745, 1453, 1265, 1169, 1124, 1020, 995 and 717; δ_H (300 MHz, $CDCl_3$) 0.97 and 0.98 (each 3 H, d, *J* 7, 1-H_3 or 2-CH_3), 1.14 (3 H, d, *J* 6.5, 9-H_3), 2.01 (1 H, m, 2-H), 2.10 - 2.52 (4 H, m, 4-H_2 and 7-H_2), 3.29 - 3.40 (4 H, m, 8-H and OCH_3), 3.57 (3 H, s, OCH_3), 5.02 (1 H, dt, *J* 7, 5, 3-H), 5.32 - 5.56 (2 H, m, 5-H and 6-H) and 7.40 - 7.62 (5 H, m, ArH); δ_F (470 MHz, $CDCl_3$) -72.9, -73.0, ratio 11 : 89; *m/z* (CI, NH_3) 420 (M^+ + 18, 41%), 169 (82) and 30 (100).

(3*R*,8*R*,5*Z*)-8-Methoxy-3-[(*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyloxy]-2-methylnon-5-ene 92

Following the general procedure, alcohol **87** (16 mg, 0.086 mmol) and (*R*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride afforded the *title compound* **92** (34 mg, 98%) as a colourless oil, $[\alpha]_D$ -25 (*c* = 1.88) (Found: $M^+ + NH_4$, 420.2350. $C_{21}H_{33}F_3NO_4$ requires *M*, 420.2361); ν_{max}/cm^{-1} 2970, 1744, 1259, 1169, 1124, 1019, 996 and 719; δ_H (300 MHz, $CDCl_3$) 0.89 and 0.90 (each 3 H, d, *J* 7, 1-H_3 or 2-CH_3), 1.17 (3 H, d, *J*

6, 9-H_3), 1.98 (1 H, m, 2-H), 2.14 - 2.58 (4 H, m, 4-H_2 and 7-H_2), 3.30 - 3.43 (4 H, m, 8-H and OCH_3), 3.59 (3 H, s, OCH_3), 5.06 (1 H, dt, *J* 7, 5, 3-H), 5.48 (1 H, m, 5- or 6-H), 5.59 (1 H, dt, *J* 10.5, 6.5, 5- or 6-H) and 7.38 - 7.63 (5 H, m, ArH); δ_F (470 MHz, $CDCl_3$) -72.9, -73.0, ratio 82 : 18; *m/z* (CI, NH_3) 420 (M^+ + 18, 27%) and 169 (100).

(3*S*,8*R*,5*Z*)-8-Methoxy-2-methyl-3-(4-nitrobenzoyloxy)non-5-ene 93

Diethyl azodicarboxylate (112 mg, 0.644 mmol) was added to a stirred suspension of the alcohol **87** (80 mg, 0.430 mmol), triphenylphosphine (169 mg, 0.645 mmol) and 4-nitrobenzoic acid (108 mg, 0.647 mmol) in toluene (3 ml) at -35 °C and the mixture was allowed to warm to room temperature. After 18 h, ether (25 ml) and water (25 ml) were added, and the organic phase was washed with brine (20 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (6 : 1 to 2 : 1) gave the *title compound* **93** (65 mg, 45%) as a colourless oil, $[\alpha]_D$ +8.2 (*c* = 0.95) (Found: M^+ + H, 336.1817. $C_{18}H_{26}NO_5$ requires *M*, 336.1811); ν_{max}/cm^{-1} 2969, 1723, 1608, 1529, 1348, 1275, 1101 and 720; δ_H (300 MHz, $CDCl_3$) 1.03 and 1.05 (each 3 H, d, *J* 6.5, 1-H_3 or 2-CH_3), 1.12 (3 H, d, *J* 6, 9-H_3), 2.00 - 2.61 (5 H, m, 4-H_2, 7-H_2 and 2-H), 3.24 - 3.38 (4 H, m, 8-H and OCH_3), 5.09 (1 H, dt, *J* 7.5, 5.5, 3-H), 5.47 - 5.59 (2 H, m, 5-H and 6-H) and 8.21 - 8.35 (4 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 17.6, 18.8, 18.9, 29.5, 31.3, 34.0, 56.1, 76.5, 80.0, 123.5, 126.2, 128.5, 130.6, 136.1, 150.5 and 164.3; *m/z* (CI, NH_3) 353 (M^+ + 18, 11%), 336 (M^+ + 1, 12), 306 (17) and 187 (100). Recovered alcohol **87** (7 mg, 9%) was also isolated.

(1*R*,6*R*,3*Z*)-6-Methoxy-1-(4-methoxyphenyl)hept-3-en-1-ol 94

Following the general procedure, stannane **74** (84 mg, 0.208 mmol), tin(IV) bromide (200 µl, 0.209 mmol) and 4-methoxybenzaldehyde (60 µl, 0.209 mmol), after chromatography using petrol : ether (3 : 2) as eluent, gave the *title compound* **94** (34 mg, 65%) as a colourless oil, $[\alpha]_D$ +80 (*c* = 1.59) (Found: M^+ + H, 251.1634. $C_{15}H_{23}O_3$ requires *M*, 251.1647); ν_{max}/cm^{-1} 3427, 2970, 1612, 1586, 1513, 1248, 1175, 1135, 1087, 1037 and 833; δ_H (300 MHz, $CDCl_3$) 1.18 (3 H, d, *J* 6, 7-H_3), 2.15 (1 H, dt, *J* 14.5, 5, 2- or 5-H), 2.33 - 2.49 (2 H, m, 2 x 2- or 5-H), 2.60 (1 H, m, 2- or 5-H), 3.10 (1 H, br s, OH), 3.30 - 3.43 (4 H, m, 6-H and OCH_3), 3.84 (3 H, s, OCH_3), 4.68 (1 H, dd, *J* 8.5, 4.5, 1-H), 5.53-5.67 (2 H, m, 3-H and 4-H) and 6.92 and 7.32 (each 2 H, m, ArH); δ_C (75 MHz, $CDCl_3$) major epimer **94** 18.9, 34.5, 37.7, 55.3, 56.1, 73.1, 76.5, 113.7, 127.0, 127.5, 129.1, 136.8 and 158.9; minor *anti*-epimer 18.4, 34.0 and 37.3; *m/z* (CI, NH_3) 250 (M^+, 12%), 249 (M^+ - 1, 18), 233 (89) and 137 (100).

Following the general procedure, alcohol **94** (15 mg, 0.060 mmol) and (*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride afforded the (*R*)-Mosher's derivative (26 mg, 93%) as a colourless oil, $[\alpha]_D$ +59 (*c* = 1.11) (Found: M^+, 466.1981. $C_{25}H_{29}F_3O_5$ requires *M*, 466.1967); ν_{max}/cm^{-1} 2932, 1746, 1613, 1516, 1250, 1177, 1122, 1018 and 992; δ_H (300 MHz, $CDCl_3$) 1.09 (3 H, d, *J* 6, 7-H_3), 2.02 - 2.26 (2 H, m, 5-H_2), 2.59 and 2.76 (each 1 H, dt, *J* 14.5, 7, 2-H), 3.25 (1 H, m, 6-H), 3.32, 3.48 and 3.85 (each 3 H, s, OCH_3), 5.34 (1 H, m, 3- or 4-H), 5.48 (1 H, dt, *J* 10.5 7, 3- or 4-H), 5.98 (1 H, t, *J* 7, 1-H), 6.92 (2 H, m, ArH) and 7.31 - 7.48 (7 H, m, ArH); δ_F (470 MHz, $CDCl_3$) -73.0, -73.2, ratio 88 : 12; *m/z* (FAB, Xe) 466 (M^+, 4%), 353 (42), 233 (80) and 189 (100).

Following the general procedure, alcohol **94** (23 mg, 0.092 mmol) and (*R*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride, after chromatography using petrol : ether (3 : 2) as eluent, afforded the (*S*)-Mosher's ester (21 mg, 49%) as a colourless oil, $[\alpha]_D$ -14.6 (*c* = 1.00) (Found: M^+, 466.1960. $C_{25}H_{29}F_3O_5$ requires *M*, 466.1967); ν_{max}/cm^{-1} 2935, 1747, 1613, 1515, 1250, 1176, 1122, 1018, 992, 831 and 717; δ_H (300 MHz, $CDCl_3$) 1.11 (3 H, d, *J* 6, 7-H_3), 2.13 and 2.26 (each 1 H, dt, *J* 14.5, 7, 5-H), 2.61 and 2.80 (each 1 H, dt, *J* 14.5, 7, 2-H), 3.28 (1 H, m, 6-H), 3.32, 3.57 and 3.84 (each 3 H, s, OCH_3), 5.46 (1 H, m, 3- or 4-H), 5.58 (1 H, dt, *J* 10.5. 7, 3- or 4-H), 5.92 (1 H, t, *J* 7, 1-H), 6.86 (2 H, m, ArH) and 7.18 - 7.49 (7 H, m, ArH); δ_F (470 MHz, $CDCl_3$) -73.0, -73.2, ratio 17 : 83; *m/z* (FAB, Xe) 466 (M^+, 3%), 353 (43), 233 (62), 201 (70) and 189 (100).

(1*R*,6*R*,3*Z*)-1-(4-Chlorophenyl)-6-methoxyhept-3-en-1-ol 95

Following the general procedure, stannane **74** (84 mg, 0.208 mmol), tin(IV) bromide (1.044 M in DCM, 200 µl, 0.209 mmol) and 4-chlorobenzaldehyde (60 µl, 0.209 mmol), after chromatography using petrol : ether (3 : 2) as eluent, gave the *title compound* **95** (32 mg, 61%) as a colourless oil, $[\alpha]_D$ +91.5 (*c* = 1.43) (Found: M^+, 254.1072. $C_{14}H_{19}{}^{35}ClO_2$ requires *M*, 254.1074); ν_{max} /cm^{-1} 3415, 2972, 1597, 1492, 1406, 1377, 1136, 1197, 1090, 1014, 831 and 725; δ_H (300 MHz, $CDCl_3$) 1.19 (3 H, d, *J* 6, 7-H_3), 2.13 (1 H, dt, *J* 14, 5, 5-H), 2.31-2.45 (2 H, m, 2 x 2- or 5-H), 2.56 (1 H, dt, *J* 14, 8, 2- or 5-H), 3.29 - 3.44 (4 H, m, 6-H and OCH_3), 4.70 (1 H, dd, *J* 8.5, 4, 1-H), 5.53 - 5.71 (2 H, m, 3-H and 4-H) and 7.35 (4 H, m, ArH); δ_C (75 MHz, $CDCl_3$) major epimer **95** 18.8, 34.6, 37.8, 56.1, 72.7, 76.5, 127.1, 127.2, 128.4, 129.8, 132.8 and 143.2; minor *anti*-epimer 18.6, 34.5 and 37.5; *m/z* (CI, NH_3) 272 (M^+ + 18, 9%), 254 (M^+, 12) and 237 (M^+ - 17, 100).

Following the general procedure, alcohol **95** (17 mg, 0.067 mmol) and (*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride afforded the (*R*)-Mosher's ester (31 mg, 98%) as a colourless oil, $[\alpha]_D$ +51 (*c* = 1.24) (Found: M^+ +NH_4^+, 488.1826. $C_{24}H_{30}{}^{35}ClF_3NO_4$ requires *M*, 488.1815); ν_{max} /cm^{-1} 2972, 1749, 1600, 1494, 1452, 1248, 1171, 1123, 1092, 1015, 827 and 718; δ_H (300 MHz, $CDCl_3$) 1.08 (3 H, d, *J* 6, 7-H_3), 1.99 - 2.21 (2 H, m, 5-H_2), 2.58 and 2.73 (each 1 H, dt, *J* 14.5, 7, 2-H), 3.23 (1 H, m, 6-H), 3.31 and 3.48 (each 3 H, s, OCH_3), 5.32 and 5.51 (each 1 H, m, 3-H or 4-H), 5.97 (1 H, t, *J* 7, 1-H) and 7.29 - 7.43 (9 H, m, ArH); δ_F (470 MHz, $CDCl_3$) -72.9, -73.0, ratio 85 : 15; *m/z* (CI, NH_3) 488 (M^+ + 18, 6%), 237 (48), 205 (28) and 30 (100).

Following the general procedure, alcohol **95** (16 mg, 0.063 mmol) and (*R*)-2--methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride afforded the (*S*)-Mosher's ester (22 mg, 74%) as a colourless oil, $[\alpha]_D$ -20 (*c* = 0.87) (Found: M^+ +NH_4, 488.1815. $C_{24}H_{30}{}^{35}ClF_3NO_4$ requires *M*, 488.1815); ν_{max}/cm^{-1} 2972, 1749, 1494, 1271, 1170, 1123, 1092, 1015 and 717; δ_H (300

MHz, $CDCl_3$) 1.08 (3 H, d, *J* 6, 7-H_3), 2.03 - 2.28 (2 H, m, 5-H_2), 2.59 and 2.77 (each 1 H, dt, *J* 14.5, 7, 2-H), 3.27 (1 H, m, 6-H), 3.32 and 3.58 (each 3 H, s, OCH_3), 5.45 (1 H, m, 3- or 4-H), 5.59 (1 H, dt, *J* 10.5, 7, 3- or 4-H), 5.91 (1 H, t, *J* 7, 1-H) and 7.16 - 7.48 (9 H, m, ArH); δ_F (470 MHz, $CDCl_3$) -72.9, -73.1, ratio 15 : 85; *m/z* (CI, NH_3) 488 (M^+ + 17, 11%), 254 (12), 237 (100) and 205 (60).

(2*S*,7*R*,4*Z*)-2-Methoxyoct-4-en-7-ol 96

Following the general procedure, stannane **74** (353 mg, 0.876 mmol), tin(IV) bromide (1.044 M in DCM, 840 µl, 0.877 mmol) and ethanal (5 M in DCM, 350 µl, 1.75 mmol), after chromatography using petrol : ether (1 : 1) as eluent gave the *title compound* **96** (96 mg, 69%) as a colourless oil, $[\alpha]_D$ +24 (*c* = 0.81) (Found: M^+ + H, 159.1392. $C_9H_{19}O_2$ requires *M*, 159.1385); ν_{max}/cm^{-1} 3399, 2970, 1459, 1375, 1093 and 943; δ_H (300 MHz, $CDCl_3$) 1.18 and 1.23 (each 3 H, d, *J* 6, 1-H_3 or 8-H_3), 2.10 - 2.57 (5 H, m, 3-H_2, 6-H_2 and OH), 3.25 - 3.46 (4 H, m, 2- or 6-H and OCH_3), 3.82 (1 H, m, 2- or 6-H), 5.53 - 5.66 (2 H, m, 4-H and 5-H); δ_C (75 MHz, $CDCl_3$) major epimer **96** 18.9, 23.1, 34.6, 37.2, 56.1, 67.3, 76.5, 127.8 and 129.1; minor *anti*-epimer 18.6, 22.9, 43.0 and 37.0; *m/z* (CI, NH_3) 176 (M^+ + 18, 5%), 159 (M^+ + 1, 100) and 59 (90).

(3*S*,8*R*,5*Z*)-8-Methoxynon-5-en-3-ol 97

Following the general procedure, stannane **74** (84 mg, 0.208 mmol), tin(IV) bromide (1.044 M in DCM, 200 µl, 0.209 mmol) and propanal (60 µl, 0.209 mmol), after chromatography using petrol : ether (2 : 1) as eluent, gave the *title compound* **97** (24 mg, 67%) as a colourless oil, $[\alpha]_D$ +13 (*c* = 0.66) (Found: M^+ + H, 173.1535. $C_{10}H_{21}O_2$ requires *M*, 173.1542); ν_{max}/cm^{-1} 3417, 2970, 1462, 1377, 1093 and 979; δ_H (300 MHz, $CDCl_3$) 0.99 (3 H, t, *J* 7.5, 1-H_3), 1.19 (3 H, d, *J* 6, 9-H_3), 1.54 (2 H, m, 2-H_2), 2.10 - 2.47 (4 H, m, 4-H_2 and 7-H_2), 2.64 (1 H, br s, OH), 3.34 (3 H, s, OCH_3), 3.38 (1 H, m, 8-H), 3.55 (1 H, m, 3-H) and 5.53 - 5.66 (2 H, m, 5-H and 6-H); δ_C (75 MHz, $CDCl_3$) major epimer **97** 10.6, 18.9, 30.0, 34.6, 34.9, 56.1, 72.5, 76.5, 127.9 and 129.0; minor *anti*-epimer 18.7, 29.7, 33.0, 74.7, 127.7 and 128.6; *m/z* (CI, NH_3) 190 (M^+ + 18, 5%), 173 (M^+ + 1, 100), 155 (18) and 59 (66).

Following the general procedure, alcohol **97** (9 mg, 0.052 mmol) and (*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride afforded the (*R*)-Mosher's ester (20 mg, 99%) as a colourless oil, $[\alpha]_D$ +26 (*c* = 0.82) (Found: $M^+ + NH_4$, 406.2214. $C_{20}H_{31}F_3NO_4$ requires *M*, 406.2205); ν_{max}/cm^{-1} 2969, 1744, 1452, 1260, 1170, 1124, 1019, 804 and 719; δ_H (300 MHz, $CDCl_3$) 0.98 (3 H, t, *J* 7.5, 1-H_3), 1.14 (3 H, d, *J* 6, 9-H_3), 1.66 - 1.78 (2 H, m, 2-H_2), 2.11 - 2.50 (4 H, m, 4-H_2 and 7-H_2), 3.37 (4 H, m, 8-H and OCH_3), 3.59 (3 H, s, OCH_3), 5.09 (1 H, m, 3-H), 5.32 - 5.57 (2 H, m, 5-H and 6-H) and 7.40 - 7.61 (5 H, m, ArH); δ_F (470 MHz, $CDCl_3$) -72.9, -73.0, ratio 14 : 86; *m/z* (CI, NH_3) 406 (M^+ + 18, 27%) and 155 (100).

Following the general procedure, alcohol **97** (11 mg, 0.064 mmol) and (*R*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride afforded the (*S*)-Mosher's ester (24 mg, 97%) as a colourless oil, $[\alpha]_D$ -36.5 (*c* = 0.58) (Found: $M^+ + NH_4$, 406.2195. $C_{20}H_{31}F_3NO_4$ requires *M*, 406.2205); ν_{max}/cm^{-1} 2972, 1744, 1452, 1264, 1169, 1124, 1021, 995 and 717; δ_H (300 MHz, $CDCl_3$) 0.86 (3 H, t, *J* 7.5, 1-H_3), 1.17 (3 H, d, *J* 6, 9-H_3), 1.60 - 1.74 (2 H, m, 2-H_2), 2.16 - 2.58 (4 H, m, 4-H_2 and 7-H_2), 3.31 - 3.41 (4 H, m, 8-H and OCH_3), 3.59 (3 H, s, OCH_3), 5.12 (1 H, m, 3-H), 5.44-5.65 (2 H, m, 5-H and 6-H) and 7.40 - 7.63 (5 H, m, ArH); δ_F (470 MHz, $CDCl_3$) -72.9, -73.0, ratio 84 : 16; *m/z* (CI, NH_3) 406 (M^+ + 18, 23%) and 155 (100).

(2*R*,3*R*,8*R*,5*Z*)-2-Benzyloxy-8-methoxynon-5-en-3-ol 98

Following the general procedure, stannane **74** (84 mg, 0.208 mmol), tin(IV) bromide (1.044 M in DCM, 200 µl, 0.209 mmol) and (*R*)-2-benzyloxypropanal (60 µl, 0.209 mmol), after chromatography using petrol : ether (3 : 2) as eluent a mixture of the *title compound* **98** and its (3*S*)-epimer (51 mg, 88%), as a colourless oil, ratio 75 : 25 (^{13}C NMR). Semi-preparative HPLC afforded a sample of the (3*S*)-epimer of the *title compound*, $[\alpha]_D$ -40 (*c* = 0.43) (Found: M^+ + H, 279.1960. $C_{17}H_{27}O_3$ requires *M*, 279.1960); ν_{max}/cm^{-1} 3444, 2972, 1453, 1376, 1251, 1091, 736 and 699; δ_H (300 MHz, $CDCl_3$) 1.13 and 1.20 (each 3 H, d, *J* 6.5, 1-H_3 or 9-H_3), 1.92 (1 H, br s, OH), 2.21 - 2.34 (4 H, m, 4-H_2 and 7-H_2), 3.29 (3 H, s, OCH_3), 3.36, 3.50 and 3.70 (each 1 H, m, 2-H, 3-H or 8-H), 4.50 and 4.61 (each 1 H, d, *J* 11.5, PhC*H*H), 5.48 - 5.62 (2 H, m, 5-H and 6-H) and 7.30 - 7.42 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 14.4, 18.8, 30.6, 34.0, 56.1, 70.8, 73.2, 76.5, 77.3, 127.3, 128.1, 128.3 and 138.5; *m/z* (CI, NH_3) 296 (M^+ + 18, 22%), 279 (M^+ + 1, 100) and 247 (38). The second fraction was the *title compound* **98**, $[\alpha]_D$ -18 (*c* = 0.95) (Found: M^+ + H, 279.1964. $C_{17}H_{27}O_3$ requires *M*, 279.1960); ν_{max}/cm^{-1} 3450, 2972, 1454, 1375, 1137, 1091, 736, and 699; δ_H (300 MHz, $CDCl_3$) 1.20 and 1.27 (each 3 H, d, *J* 6, 1-H_3 or 9-H_3), 2.19 (1 H, dt, *J* 14.5, 5.5, 4- or 7-H), 2.30 - 2.47 (3 H, m, 4- or 7-H_2 and 4- or 7-H), 2.93 (1 H, br s, OH), 3.37 (3 H, s, OCH_3), 3.40 (1 H, m, 2-, 3- or 8-H), 3.50 - 3.65 (2 H, m, 2 x 2-, 3- or 8-H), 4.53 and 4.71 (each 1 H, d, *J* 11.5, PhC*H*H), 5.55-5.69 (2 H, m, 5-H and 6-H) and 7.31 - 7.41 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 15.4, 19.0, 30.8, 34.4, 56.1, 71.0, 74.2, 76.6, 77.5, 127.4, 127.5, 127.6, 128.0, 128.3 and 138.4; *m/z* (CI, NH_3) 296 (M^+ + 18, 4%) and 279 (M^+ + 1, 100).

Following the general procedure, the mixture of the alcohol **98** and its (3*S*)-epimer (13 mg, 0.047 mmol) and (*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride afforded the (*R*)-Mosher's ester (22 mg, 95%) as a colourless oil, $[\alpha]_D$ +23 (*c* = 0.84) (Found: $M^+ + NH_4$, 512.2612. $C_{27}H_{37}F_3NO_5$ requires *M*, 512.2625); ν_{max}/cm^{-1} 2974, 1747, 1453, 1257, 1169, 1123, 1020, 720 and 698; δ_H (300 MHz, $CDCl_3$) peaks of the major product only 1.13 and 1.25 (each 3 H, d, *J* 6.5, 1-H_3 or 9-H_3), 2.09 - 2.27 and 2.40 - 2.53 (each 2 H, m, 4-H_2 or 7-H_2), 3.26 - 3.39 (4 H, m, 2- or 8-H, OCH_3), 3.55 (3 H, s, OCH_3), 3.77 (1 H, m, 2- or 8-H), 4.53 and 4.67 (each 1 H, d, *J* 11.5, PhC*H*H), 5.27 (1 H, dt, *J* 7.5, 5.5, 3-H), 5.39 (1 H, m, 5- or 6-H), 5.52 (1 H, dt, *J* 10.5, 7, 5- or 6-H) and 7.29 - 7.62 (10 H, m, ArH); δ_F (470 MHz, $CDCl_3$) -73.0, -73.1, 26 : 74; *m/z* (CI, NH_3) 512 (M^+ + 18, 66%), 261 (59), 139 (98) and 59 (100).

Following the general procedure, the mixture of the alcohol **98** and its (3*S*)-epimer (17 mg, 0.061 mmol) and (*R*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride afforded (*S*)-Mosher's

ester (30 mg, 100%) as a colourless oil, $[\alpha]_D$ -26 (*c* = 1.28) (Found: $M^+ + NH_4$, 512.2630. $C_{27}H_{37}F_3NO_5$ requires *M*, 512.2625); ν_{max}/cm^{-1} 2974, 1746, 1453, 1259, 1169, 1123, 1020, 719 and 698; δ_H (300 MHz, $CDCl_3$) peaks of the major product 1.12 and 1.16 (each 3 H, d, *J* 6.5, 1-H_3 or 9-H_3), 2.15-2.35 and 2.45 - 2.60 (each 2 H, m, 4-H_2 or 7-H_2), 3.30 - 3.39 (4 H, m, 2- or 8-H, OCH_3), 3.56 (3 H, s, OCH_3), 3.73 (1 H, m, 2- or8-H), 4.43 and 4.60 (each 1 H, d, *J* 11.5, PhC*H*H), 5.27 (1 H, dt, *J* 7.5, 5, 3-H), 5.42 - 5.66 (2 H, m, 5-H and 6-H) and 7.27 - 7.65 (10 H, m, ArH); δ_F (470 MHz, $CDCl_3$) -72.9, -73.1, ratio 80 : 20; *m/z* (CI, NH_3) 512 (M^+ + 18, 75%), 261 (51), 139 (79) and 59 (100).

Following the general procedure, the mixture of the alcohol **98** and its (3*S*)-epimer (24 mg, 0.086 mmol) and (*R*)-2-acetoxy-2-phenylacetic acid, after chromatography using petrol : ether (3 : 1), gave the (*R*)-*O*-acetylmandelate (32 mg, 82%) as a colourless oil, $[\alpha]_D$ -35 (*c* = 1.34) (Found: $M^+ + NH_4$, 472.2714. $C_{27}H_{38}NO_6$ requires *M*, 472.2699); ν_{max}/cm^{-1} 2933, 1745, 1454, 1232, 1180, 1090, 1054 and 698; δ_H (300 MHz, $CDCl_3$) peaks of the major product 0.92 and 1.17 (each 3 H, d, *J* 6.5, 1-H_3 or 9-H_3), 2.22 (3 H, s, O_2CCH_3), 2.29 - 2.58 (4 H, m, 4-H_2 and 7-H_2), 3.32 - 3.45 (4 H, m, 8-H and OCH_3), 3.53 (1 H, qd, *J* 6.5, 4.5, 2-H), 4.32 and 4.44 (each 1 H, d, *J* 12, PhC*H*H), 5.01 (1 H, dt, *J* 8, 4.5, 3-H), 5.46 and 5.58 (each 1 H, dt, *J* 10.5, 7, 5-H or 6-H), 5.99 (1 H, s, 2'-H) and 7.22 - 7.55 (10 H, m, ArH); *m/z* (CI, NH_3) 472 (M^+ + 18, 100%).

Following the general procedure, the mixture of the alcohol **98** and its (3*S*)-epimer (24 mg, 0.086 mmol) and (*S*)-2-acetoxy-2-phenylacetic acid, after chromatography using petrol : ether (3 : 1) as eluent, gave the (*S*)-*O*-acetylmandelate (29 mg, 97%); as a colourless oil, $[\alpha]_D$ +32.6 (*c* = 1.26) (Found: $M^+ + NH_4$, 472.2714. $C_{27}H_{38}NO_6$ requires *M*, 472.2699); ν_{max}/cm^{-1} 2933, 1744, 1673, 1373, 1232, 1180, 1091, 1053 and 698; δ_H (300 MHz, $CDCl_3$) peaks of the major product 1.08 and 1.23 (each 3 H, d, *J* 6.5, 1-H_3 or 9-H_3), 2.04 (2 H, t, *J* 6.5, 4- or 7-H_2), 2.18 - 2.25 (5 H, m, 4- or 7-H_2 and O_2CCH_3), 3.24 (1 H, m, 8-H), 3.30 (3 H, s, OCH_3), 3.71 (1 H, qd, *J* 6.5, 4.5, 2-H), 4.53 and 4.67 (each 1 H, d, *J* 12, PhC*H*H), 4.98 - 5.13 (2 H, m, 5- or 6-H and 3-H), 5.28 (1 H, m, 5- or 6-H), 5.96 (1 H, s, 2'-H) and 7.27 - 7.55 (10 H, m, ArH); *m/z* (CI, NH_3) 472 (M^+ + 18, 100%) and 341 (87).

(2*S*,3*R*,8*R*,5*Z*)-2-Benzyloxy-8-methoxynon-5-en-3-ol 99

Following the general procedure, stannane **74** (84 mg, 0.208 mmol), tin(IV) bromide (1.044 M in DCM, 200 µl, 0.209 mmol) and (*S*)-2-benzyloxypropanal (60 µl, 0.209 mmol), after chromatography using petrol : ether (3 : 2) as eluent, gave the *title compound* **99** (42 mg, 73%) as a colourless oil, $[\alpha]_D$ +45 (*c* = 1.58) (Found: M^+ +H, 279.1966. $C_{17}H_{27}O_3$ requires *M*, 279.1960); ν_{max}/cm^{-1} 3453, 2972, 1454, 1376, 1092, 736, and 699; δ_H (300 MHz, $CDCl_3$) 1.20 and 1.27 (each 3 H, d, *J* 6, 1-H_3 or 9-H_3), 2.12 - 2.22 (1 H, m, 2- or 7-H), 2.27 - 2.48 (3 H, m, 2- or 7-H_2 and 2- or 7-H), 2.87 (1 H, br s, OH), 3.35 (3 H, s, OCH_3), 3.40, 3.54 and 3.70 (each 1 H, m, 2-H, 3-H or 8-H), 4.57 and 4.68 (each 1 H, d, *J* 12, PhC*H*H), 5.53-5.66 (2 H, m, 5-H and 6-H) and 7.30 - 7.42 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 14.6, 19.0, 30.7, 34.5, 56.1, 71.0, 73.4, 76.6, 77.7, 127.6, 127.7, 127.8, 128.4, 128.7 and 138.7; *m/z* (CI, NH_3) 279 (M^+ + 1, 83%), 247 (53), 91 (88) and 59 (100).

Following the general procedure, alcohol **99** (12 mg, 0.043 mmol) and (*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride afforded the (*R*)-Mosher's ester (20 mg, 94%) as a colourless oil, $[\alpha]_D$ +13 (*c* = 0.89) (Found: $M^+ + NH_4$, 512.2603. $C_{27}H_{37}F_3NO_5$ requires *M*, 512.2624); ν_{max}/cm^{-1} 2974, 1747, 1453, 1273, 1169, 1123, 1019, 718 and 698; δ_H (300 MHz, $CDCl_3$) 1.15 and 1.28 (each 3 H, d, *J* 6.5, 1-H_3 or 9-H_3), 2.12 - 2.56 (4 H, m, 4-H_2 and 7-H_2), 3.26 - 3.42 (4 H, m, 8-H and OCH_3), 3.59 (3 H, s, OCH_3), 3.74 (1 H, qd, *J* 6.5, 3, 2-H), 4.57 and 4.64 (each 1 H, d, *J* 12, PhC*H*H), 5.35 - 5.59 (3 H, m, 3-H, 5-H and 6-H) and 7.26 - 7.66 (10 H, m, ArH); δ_F (470 MHz, $CDCl_3$) -72.9, -73.1, ratio 90 : 10; *m/z* (CI, NH_3) 512 (M^+ + 18, 73%), 261 (62), 139 (86) and 59 (100).

Following the general procedure, alcohol **99** (14 mg, 0.050 mmol) and (*R*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride afforded the (*S*)-Mosher's ester (25 mg, 100%) as a colourless oil, $[\alpha]_D$ -36 (*c* = 1.07) (Found: $M^+ + NH_4$, 512.2636. $C_{27}H_{37}F_3NO_5$ requires *M*, 512.2624); ν_{max}/cm^{-1} 2974, 1748, 1453, 1378, 1254, 1169, 1122, 1019, 720 and 698; δ_H (300 MHz, $CDCl_3$) 1.15 and 1.17 (each 3 H, d, *J* 7, 1-H_3 or 9-H_3), 2.25 - 2.37 (2 H, m, 4- or 7-H_2), 2.44 (1 H, dt, *J* 16, 5.5, C*H*H), 2.58 (1 H, dt, *J* 15.5, 7.5, CH*H*), 3.34 (3 H, s, OCH_3), 3.37 (1 H, m, 8-H), 3.58 (3 H, s, OCH_3), 3.68 (1 H, qd, *J* 6.5, 3.5, 2-H), 4.45 and 4.52 (each 1 H, d, *J* 11.5, PhC*H*H), 5.40 (1 H, m, 3-H), 5.51 and 5.61 (each 1 H, dt, *J* 10.5, 6.5, 5-H or 6-H) and 7.27 - 7.63 (10 H, m, ArH); δ_F (470 MHz, $CDCl_3$) -73.0, -73.1, ratio 92 : 8; *m/z* (CI, NH_3) 512 (M^+ + 18, 19%), 261 (17), 139 (30) and 30 (100).

Following the general procedure, alcohol **99** (26 mg, 0.094 mmol) and (*R*)-2-acetoxy-2-phenylacetic acid, after chromatography using petrol : ether (3 : 1) gave the (*R*)-*O*-acetylmandelate (38 mg, 89%) as a colourless oil, $[\alpha]_D$ -42 (*c* = 1.75) (Found: $M^+ + NH_4$, 472.2689. $C_{27}H_{38}NO_6$ requires *M*, 472.2699; ν_{max}/cm^{-1} 2932, 1745, 1373, 1232, 1180, 1091, 1056, 738 and 698; δ_H (300 MHz, $CDCl_3$) 1.01 and 1.18 (each 3 H, d, *J* 6.5, 1-H_3 or 9-H_3), 2.14 -2.54 (7 H, m, 4-H_2, 7-H_2 and O_2CCH_3), 3.32 - 3.45 (4 H, m, 8-H and OCH_3), 3.57 (1 H, qd, *J* 5.5, 3.5, 2-H), 4.30 and 4.35 (each 1 H, d, *J* 10, PhC*H*H), 5.08 (1 H, m, 3-H), 5.49 and 5.58 (each 1 H, dt, *J* 10.5, 7, 5-H or 6-H), 5.99 (1 H, s, 2'-H) and 7.19 - 7.55 (10 H, m, ArH); *m/z* (CI, NH_3) 472 (M^+ + 18, 68%) and 59 (100).

Following the general procedure, alcohol **99** (13 mg, 0.047 mmol) and (*S*)-2-acetoxy-2-phenylacetic acid, after chromatography using petrol : ether (2 : 1) as eluent, gave the (*S*)-*O*-acetylmandelate (18 mg, 84%) as a colourless oil, $[\alpha]_D$ +47 (*c* = 0.59) (Found: $M^+ + NH_4$, 472.2690. $C_{27}H_{38}NO_6$ requires *M*, 472.2699; ν_{max}/cm^{-1} 2931, 1744, 1374, 1232, 1179, 1091, 1057, 738 and 698; δ_H (300 MHz, $CDCl_3$) 1.08 and 1.24 (each 3 H, d, *J* 6.5, 1-H_3 or 9-H_3), 2.05 (2 H, t, *J* 6.5, 4- or 7-H_2), 2.23 (3 H, s, O_2CCH_3), 2.37 (2 H, t, *J* 6.5, 4- or 7-H_2), 3.36 (1 H, m, 2- or 8-H), 3.42 (3 H, s, OCH_3), 3.69 (1 H, m, 2- or 8-H), 4.63 (2 H, s, $PhCH_2$), 5.02 (1 H, m, 3-H), 5.13 and 5.30 (each 1 H, m, 5-H or 6-H), 5.94 (1 H, s, 2'-H) and 7.30 - 7.54 (10 H, m, ArH); *m/z* (CI, NH_3) 472 (M^+ + 18, 100%).

(1*R*,6*R*,3*Z*)-1-Phenylhept-3-ene-1,6-diol 100

Following the general procedure, stannane, **73** (81 mg, 0.208 mmol), tin(IV) bromide (1.044 M in DCM, 200 µl, 0.209 mmol) and benzaldehyde (60 µl, 0.209 mmol), after chromatography using petrol : ethyl acetate (1 : 1+1% triethylamine) as eluent, gave the *title compound* **100** (31 mg, 72%) as a colourless oil, containing about 6% of its *anti*-epimer **104**, $[\alpha]_D$ +75 (*c* = 1.26) (Found: $M^+ + NH_4$, 224.1652. $C_{13}H_{22}NO_2$ requires *M*, 224.1650); ν_{max}/cm^{-1} 3357, 2968, 1604, 1453, 1124, 1053, 845, 760 and 701; δ_H (300 MHz, $CDCl_3$) major epimer **100** 1.18 (3 H, d, *J* 6, 7-H_3), 2.10 (1 H, m, 2- or 5-H), 2.22 - 2.42 (2 H, m, 2 x 2- or 5-H), 2.62 (1 H, dt, *J* 14, 8.5, 2- or 5-H), 2.93 (2 H, br s, 2 x OH), 3.79 (1 H, m, 6-H), 4.68 (1 H, dd, *J* 9, 4, 1-H), 5.53 - 5.67 (2 H, m, 3-H and 4-H) and 7.22 - 7.38 (5 H, m, ArH); minor *anti*-epimer **104** 4.77 (1 H, t, *J* 6, 1-H); δ_C (75 MHz, $CDCl_3$) major epimer **100** 23.3, 37.0, 37.5, 67.4, 73.6, 125.8, 127.4, 128.4, 128.5, 129.1 and 144.5; minor anti-epimer **104** 22.9, 36.6 and 66.0; *m/z* (CI, NH_3) 224 ($M^+ + 18$, 9%), 206 (M^+, 64), 189 ($M^+ - 17$, 100) and 171 (36).

(1*R*,6*R*,3*Z*)-1-(4-Nitrophenyl)hept-3-ene-1,6-diol 101

Following the general procedure, stannane **73** (182 mg, 0.468 mmol), tin(IV) bromide (1.044 M in DCM, 447 µl, 0.467 mmol) and 4-nitrobenzaldehyde (71 mg, 0.470 mmol), after chromatography using petrol : ethyl acetate (1 : 1 +1% triethylamine) as the eluent, gave the *title compound* **101** (83 mg, 71%) as a colourless oil, containing 6% of its *anti*-epimer $[\alpha]_D$ +94 (*c* = 0.8) (Found: $M^+ + NH_4$, 269.1506. $C_{13}H_{21}N_2O_4$ requires *M*, 269.1501); ν_{max}/cm^{-1} 3349, 2968, 1603, 1519, 1346, 1109, 1066, 856 and 701; δ_H (300 MHz, $CDCl_3$) major epimer **101** 1.26 (3 H, d, *J* 6.5, 7-H_3), 2.15 (1 H, m, 2- or 5-H), 2.28 - 2.47 (2 H, m, 2 x 2- or 5-H), 2.61 (1 H, dt, *J* 14, 9, 2- or 5-H), 3.20 (2 H, br s, 2 x OH), 3.90 (1 H, m, 6-H), 4.83 (1 H, dd, *J* 9.5, 3.5, 1-H), 5.58 - 5.77 (2 H, m, 3-H and 4-H) and 7.57 and 8.22 (each 2 H, d, *J* 9, ArH); minor *anti*-epimer 4.95 (1 H, dd, *J* 6, 4.5, 1-H); δ_C (75 MHz, $CDCl_3$) 23.6, 36.6, 37.6, 67.4, 72.5, 123.6, 126.5, 127.5, 130.3, 147.2 and 152.1; *m/z* (CI, NH_3) 269 ($M^+ + 18$, 100%), 251 (M^+, 39), 234 (29) and 216 (51).

(2*R*,7*S*,4*Z*)-Oct-4-ene-2,7-diol 102

Following the general procedure, stannane **73** (108 mg, 0.278 mmol), tin(IV) bromide (1.38 M in DCM, 200 µl, 0.276 mmol) and ethanal (25 mg, 0.556 mmol), after chromatography using petrol : ether (1 : 4) as eluent, gave the *title compound* **102** (24 mg, 60%) as a colourless oil, containing 5% of its *anti*-epimer (Found: $M^+ + H$, 145.1233. $C_8H_{17}O_2$ requires *M*, 145.1229); ν_{max}/cm^{-1} 3337, 2968, 1374, 1118, 1077, 942 and 849; δ_H (300 MHz, $CDCl_3$) 1.24 (6 H, d, *J* 6, 1-H_3 and 8-H_3), 2.10 - 2.20 and 2.25 - 2.40 (each 2 H, m, 2 x 3-H or 6-H), 2.82 (2 H, br s, 2 x OH), 3.86 (2 H, m, 2-H and 7-H) and 5.62 (2 H, m, 4-H and 5-H); δ_C (75 MHz, $CDCl_3$) major epimer **102** 23.4, 37.0, 67.4 and 128.6; minor *anti*-epimer 23.1, 36.8 and 128.7; *m/z* (CI, NH_3) 162 ($M^+ + 18$, 70%), 145 ($M^+ + 1$, 100) and 127 (34).

(2*R*,7*R*,4*Z*)-8-Methylnon-4-ene-2,7-diol 103

Following the general procedure, stannane **73** (81 mg, 0.208 mmol), tin(IV) bromide (1.044 M in DCM, 200 µl, 0.209 mmol) and 2-methylpropanal (60 µl, 0.209 mmol), after chromatography using petrol : ethyl acetate (1 : 1 + 1% triethylamine) as eluent, gave the *title compound* **103** (21 mg, 59%) as a colourless oil, containing 7% of its *anti*-epimer, $[\alpha]_D$ -14 (*c* = 0.86) (Found: $M^+ + NH_4$, 190.1807. $C_{10}H_{24}NO_2$ requires *M*, 190.1807); ν_{max}/cm^{-1} 3341, 2962, 1464, 1122, 1048, 871 and 845; δ_H (300 MHz, $CDCl_3$) 0.97 and 0.98 (each 3 H, d, *J* 7, 8-CH_3 or 9-H_3), 1.25 (3 H, d, *J* 6, 1-H_3), 1.72 (1 H, m, 8-H), 2.09 - 2.21 and 2.24 - 2.42 (each 2 H, m, 3-H and 6-H), 2.68 (2 H, br s, 2 x OH), 3.39 (1 H, ddd, *J* 9, 5.5, 3, 7-H), 3.85 (1 H, m, 2-H) and 5.56 - 5.68 (2 H, m, 4-H and 5-H); δ_C (75 MHz, $CDCl_3$) major isomer **103** 17.8, 18.7, 23.5, 31.9, 33.7, 37.0, 67.4, 76.1, 128.8 and 129.5; minor anti-epimer 23.0, 33.2, 36.8, 128.2 and 129.2; *m/z* (CI, NH_3) 190 ($M^+ + 18$, 39%), 173 ($M^+ + 1$, 28), 155 (29) and 137 (14).

(1*R*,6*R*,3*Z*)-1,6-Diacetoxy-1-phenylhept-3-ene 105

Triethylamine (441 mg, 4.37 mmol), 4-*N*,*N*-dimethylaminopyridine (3 mg, 0.025 mmol) and acetic anhydride (178 mg, 1.74 mmol) were added to the diol **100** (90 mg, 0.437 mmol) in DCM (3 ml) and the mixture stirred at room temperature for 15 h. DCM (20 ml) and water (20 ml) were added, and the organic phase was washed with aqueous hydrogen chloride (3.5 M, 15 ml) and brine (15 ml) then dried ($MgSO_4$). Concentration under reduced pressure and chromatography of the residue using petrol : ether (4 : 1) as eluent gave the *title compound* **105** (115 mg, 91%) as a colourless oil, $[\alpha]_D$ +53 (*c* = 0.65) (Found: $M^+ + NH_4$, 308.1857. $C_{17}H_{26}NO_4$ requires *M*, 308.1862); ν_{max}/cm^{-1} 2978, 1736, 1373, 1240, 1023 and 701; δ_H (300 MHz, $CDCl_3$) 1.19 (3 H, d, *J* 6.5, 7-H_3), 2.05 and 2.11 (each 3 H, s, O_2CCH_3), 2.15 - 2.38 and 2.51 - 2.79 (each 2 H, m, 2-H_2 or 5-H_2), 4.88 (1 H, m, 6-H), 5.40 - 5.54 (2 H, m, 3-H and 4-H), 5.79 (1 H, t, *J* 7, 1-H) and 7.30 - 7.40 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 19.5, 21.3, 21.4, 33.6, 34.4, 70.4, 75.4, 126.6, 126.7, 127.5, 128.0, 128.5, 140.1, 170.3 and 170.6; *m/z* (CI, NH_3) 308 ($M^+ + 18$, 81%), 248 (66), 231 (99), 171 (100) and 106 (75).

Ozone was bubbled through the bis-acetate **105** (76 mg, 0.262 mmol) in chloroform (5 ml) at -78 ˚C for 15 min. The solution was purged with oxygen for 10 min, then dimethyl sulfide (169 mg, 2.73 mmol) were added and the mixture allowed to warm to room temperature. After concentration under reduced pressure, the residual oil was dissolved in DCM (2 ml) and methanol (2 ml) and sodium borohydride (65 mg, 1.71 mmol) were added at 0 ˚C. After 15 min at room temperature, aqueous hydrogen chloride (1 M, 2 ml) was added at 0 ˚C. Upon warming to room temperature, DCM (25 ml) and water (25 ml) were added, and the aqueous phase was extracted with DCM (25 ml). The organic extracts were washed with brine (30 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography using petrol : ether (2 : 1 to 1 : 1) as eluent afforded (*R*)-3-acetoxy-1-phenylpropan-1-ol **(*R*)-15** (6 mg, 13%), as a colourless oil, $[\alpha]_D$ +23 (*c* = 0.48) and 3-acetoxy-3-phenylpropan-1-ol **(*R*)-14**[1a] (31 mg, 61%), as a colourless oil, $[\alpha]_D$ +79 (*c* = 0.48); spectroscopic data for these alcohols were identical to those of samples prepared earlier.

(1*R*,6*R*,3*Z*)-6-Methoxy-1-phenylhept-3-en-1-ol 78 and (2*R*, 7*R*,4*Z*)-7-Methoxy-7-phenylhept-4-en-2-ol 106

18-Crown-6 (42 mg, 0.159 mmol) was added to sodium hydride (15 mg, 60% dispersion in mineral oil, 0.375 mmol) in tetrahydrofuran (1 ml). After 15 min at room temperature, the diol **100** (66 mg, 0.320 mmol) in tetrahydrofuran (1 ml) was added. Methyl iodide (455 mg, 3.20 mmol) was added after a further 45 min and the mixture stirred for 15 h. Water (10 ml) and ether (10 ml) were added and the organic phase was washed with brine (10 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography using petrol : ether (2 : 1) as eluent afforded (1*R*,6*R*,3*Z*)-6-methoxy-1-phenylhept-3-en-1-ol **78** (8 mg, 11%), a colourless oil with spectroscopic data identical to those of samples prepared earlier and the *title compound* **106** (32 mg, 45%) as a colourless oil, $[\alpha]_D$ +77 (*c* = 1.40) (Found: $M^+ + NH_4$, 238.1803. $C_{14}H_{24}NO_2$ requires *M*, 238.1807); ν_{max}/cm^{-1} 3422, 2968, 1454, 1098, 846, 760 and 702; δ_H (300 MHz, $CDCl_3$) 1.22 (3 H, d, *J* 6 1-H$_3$), 2.08 - 2.40 (3 H, m, 3- or 6-H$_2$ and 3- or 6-H), 2.53 - 2.76 (2 H, m, 3- or 6-H and OH), 3.23 (3 H, s, OCH_3), 3.78 (1 H, m, 2-H), 4.21 (1 H, dd, *J* 8.5, 4.5, 7-H), 5.51-5.68 (2 H, m, 4-H and 5-H) and 7.28 - 7.44 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 23.2, 36.6, 37.2, 56.7, 67.2, 83.4, 126.6, 127.7, 128.3, 128.4, 128.8 and 141.7; *m/z* (CI, NH_3) 238 (M^+ + 18, 29%), 221 (M^+ + 1, 16), 206 (57), 189 (87), 171 (53) and 121 (100).

(3*R*,8*R*,5*Z*)-8-Methoxy-2-methylnon-5-en-3-ol 87 and (2*R*, 7*R*,4*Z*)-7-Methoxy-8-methylnon-4-en-2-ol 107

18-Crown-6 (46 mg, 0.174 mmol) was added to sodium hydride (17 mg, 60% dispersion in mineral oil, 0.425 mmol) in tetrahydrofuran (1 ml) at room temperature and, after 15 min, diol **103** (60 mg, 0.349 mmol) in tetrahydrofuran (1 ml) was added. Methyl iodide (496 mg, 3.49 mmol) was added after 45 min and the mixture was stirred for 15 h. Water (10 ml) and ether (10 ml) were added and the organic phase was washed with brine (10 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (5 : 1) afforded (3*R*,8*R*,5*Z*)-8-methoxy-2-methylnon-5-en-3-ol **87** (22 mg, 34%), with spectroscopic data identical to those of a sample prepared earlier, and the *title compound* **107** (9 mg, 14%) as a colourless oil, $[\alpha]_D$ -28 (*c* = 0.83) (Found: M^+ + H, 187.1700. $C_{11}H_{23}O_2$ requires *M*, 87.1698); ν_{max}/cm^{-1} 3417, 2964, 1464, 1369, 1096, 941 and 847; δ_H (300 MHz, $CDCl_3$) 0.93 and 0.96 (each 3 H, d, *J* 7, 8-CH$_3$ and 9-H$_3$), 1.25 (3 H, d, *J* 6 1-H$_3$), 1.94 (1 H, m, 8-H), 2.10 - 2.46 (5 H, m, 3-H$_2$, 6-H$_2$ and OH), 3.01 (1 H, m, 2- or 7-H), 3.38 (3 H, s, OCH_3), 3.83 (1 H, m, 2- or 7-H) and 5.52-5.69 (2 H, m, 4-H and 5-H); δ_C (75 MHz, $CDCl_3$) 17.6, 18.4, 23.2, 28.3, 30.3, 37.3, 57.8, 67.4, 86.0, 127.6 and 129.8; *m/z* (CI, NH_3) 204 (M^+ + 18, 8%), 187 (M^+ + 1, 100), 155 (98) and 87 (99).

6-*tert*-Butyl dimethylsilyloxy-4-methylhex-2-en-1-ol 112

A mixture of $NaHCO_3$ (1.41 g, 16.8 mmol), diethyl allylphosphate (3.26 g, 16.8 mmol), THF (28 ml), aldehyde **110** (2.8 g, 14 mmol) and $Pd(OAc)_2$ (10 mol%) were heated under reflux for 72 h. After cooling, DCM (50 ml) and water (50 ml) were added, and the organic phase was dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (9 : 1) as eluent gave the aldehyde **111** (2.64 g, 95%) as a colourless oil; ν_{max}/cm^{-1} 2957, 2930, 2858, 1699, 1256, 988, 836 and 776; δ_H (300 MHz, $CDCl_3$) 0.07 (6 H, s, 2 x SiCH$_3$), 0.92 [9 H, s, SiC(CH$_3$)$_3$], 1.15 (3 H, d, *J* 6.7, 4-CH$_3$), 1.68 (2 H, m, 5-H$_2$), 2.70 (1 H, m, 4-H), 3.67 (2 H, t, *J* 6.4, 6-H$_2$), 6.12 (1 H, ddd, *J* 15.7, 7.9, 1.2, 2-H), 6.84 (1 H, dd, *J* 15.7, 7.5, 3-H) and 9.54 (1 H, d, *J* 7.6, 1-H); δ_C (75 MHz, $CDCl_3$) -5.1, -5.1, 18.5, 19.3, 26.2, 33.9, 38.9, 60.8, 131.5, 164.3 and 194.6; *m/z* (CI, NH_3) 260 (M^+ + 18, 10%), 243 (M^+ + 1, 50%), 185 (20) and 85 (100).

To a the enal **111** (2 g, 8.3 mmol) in THF (40 ml) at -78 ºC was added DIBAL–H (12.45 ml) and the solution stirred at -78 ºC for 30 minutes then allowed to warm to -45 ºC. After 3 h, water (10 cm^3) and ether (20 ml) were added and the mixture allowed to warm to ambient temperature. A solution of Rochelle's salt was added (20 ml) and the mixture was stirred overnight. The aqueous layer was extracted with ether (3 x 20 ml) and the organic extracts washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (1 : 1) as eluent gave the *title compound* **112** (1.7 g, 84%) as a colourless oil; ν_{max}/cm^{-1} 3369, 2956, 2858, 1696 7, 1472, 1388, 1256, 1099, 1006, 836 and 775; δ_H (300 MHz, $CDCl_3$) 0.09 (6 H, s, 2 x SiCH$_3$), 0.93 [9 H, s, SiC(CH$_3$)$_3$], 1.04 (3 H, d, *J* 6.9, 4-CH$_3$), 1.55 (2 H, m, 5-H$_2$), 2.36 (1 H, m, 4-H), 3.64 (2 H, m, 6-H$_2$), 4.13 (2 H, d, *J* 4.7, 1-H$_2$) and 5.64 (2 H, m, 2-H and 3-H); δ_C (75 MHz, $CDCl_3$) -5.0, -5.0, 18.6, 20.6, 26.2, 33.1, 39.9, 61.4, 64.1, 127.7 and 138.9; *m/z* (CI, NH_3) 262 (M^+ +18, 43%), 245 (M^+ +1, 30) and 227 (100).

(*E*)-6-hydroxy-4-methylhex-2-enyl(tributyl)stannane 115

To a solution of the hexenol **112** (200 mg, 0.8 mmol) in dry DCM (4 ml) was added methanesulfonyl chloride (0.06 ml) and the mixture cooled to -7 ºC before the addition of triethylamine (1.13 ml) over 10 min. The solution was stirred for 10 min then partitioned between an aqueous pH 7 buffer and pentane. The organic extract was dried ($MgSO_4$) and concentrated under reduced pressure to leave the mesylate **113** which was used without further purification.

To a solution of the mesylate **113** in THF (4 ml) was added tributyltin lithium [from bistributyl tin (0.41 cm^3) and BuLi (1.6 M in hexanes, 0.48 ml] in THF (4 ml)] via cannula at –78 ºC. After 2 h, the solution was allowed to warm to ambient temperature and stirred overnight. Water was added and the mixture extracted into pentane. The organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : Et_3N (99:1) as eluent gave stannane **114** (275 mg, 53% over the 2 steps) as a colourless oil; ν_{max}/cm^{-1} 2955, 2927, 2856, 1463, 1253, 1099, 836 and 774; δ_H (300 MHz, $CDCl_3$) 0.05 (6 H, s, 2 x SiCH$_3$), 0.85 – 1.00 (27 H, m, 4-CH$_3$, 3 x Sn*C*H$_2$CH$_2$CH$_2$*C*H$_3$, and SiC(CH$_3$)$_3$], 1.10 – 1.64 (14 H, m, 5-H$_2$ and 3 x SnCH$_2$*C*H$_2$*C*H$_2$CH$_3$), 1.59 (2 H, d, *J* 8.5, 1-H$_2$), 2.20 (1 H, m, 4-H), 3.60 (2 H, m, 6-H$_2$), 5.09 (1 H, dd, *J* 16, 7, 3-H) and 5.50

(1 H, dt, *J* 16,7, 2-H); δ_C (75 MHz, $CDCl_3$) -5.0, 9.4, 9.5, 14.0, 14.3, 21.6, 26.2, 27.6, 29.4, 33.6, 40.7, 61.9, 127.7 and 131.8.

To a solution of stannane **114** (170 mg, 0.33 mmol) in THF (0.5 ml was added TBAF in THF (1 M, 0.5 ml, 0.5 mmol) at room temperature. The reaction was stirred overnight, water (10 ml) was added and the mixture extracted into ether (4 x 5 ml). The organic extractss were dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ether : Et_3N (90 : 9 : 1) as eluent gave the *title* c*ompound* **115** (95 mg, 72%) as a colourless oil (Found: M^+, 404.2087. $C_{19}H_{40}OSn$ requires *M*, 404.2096); ν_{max}/cm^{-1} 3342, 2955, 2924, 2870, 2854, 1461, 1072, 1052 and 961; δ_H (300 MHz, $CDCl_3$) 0.95 - 1.05 (18 H, m, 3 x $SnCH_2CH_2CH_2CH_3$ and 4-CH_3), 1.30 (8 H, m, 1-H_2 and 3 x $SnCH_2CH_2CH_2CH_3$), 1.50 (6 H, m, 3 x $SnCH_2CH_2CH_2CH_3$), 1.69 (2 H, m, 5-H_2), 2.21 (1 H, m, 4-H), 3.65 (2 H, m, 6-H_2), 5.10 (1 H, dd, *J* 16, 8, 3-H) and 5.55 (1 H, m, 2-H); *m/z* (EI) 347 (M^+ - 57, 10%), 291 (30), 235 (50) and 41 (100).

(1*RS*,5*RS*,3*Z*)-5-methyl-1-phenylhept-3-ene-1,7-diol 116

Following the general procedure, tin(IV) bromide (0.11 g, 0.19 mmol) in DCM (1 ml), stannane **115** (100 mg, 0.19 mmol) in DCM (1 ml) and benzaldehyde (70 µl, 0.57 mmol) in DCM (0.5 ml), after the addition of methanolic ammonium chloride and chromatography using petrol : ether : Et_3N (19 : 80 : 1) as eluent, gave the *title* c*ompound* **116** (35 mg, 64%) as a colourless oil (Found: $M^+ + NH_4$, 238.1806. $C_{14}H_{24}O_2N$ requires *M*, 238.1802); ν_{max}/cm^{-1} 3351, 2930, 1454, 1056 and 759; δ_H (300 MHz, $CDCl_3$) 0.96 (3 H, d, *J* 6.9, 5-CH_3), 1.36 and 1.70 (each 1 H, m, 6-H), 2.36 (1 H, m, 2-H), 2.68 (1 H, dt, *J* 10.7, 9.4, 2-H'), 2.75 (1 H, m, 5-H), 3.55 (2 H, m, 7-H_2), 3.7 (2 H, br s, 2 x OH), 4.74 (1 H, dd, *J* 5.7, 3.7, 1-H), 5.31 (1 H, t, *J* 10.7, 4-H), 5.51 (1 H, m, 3-H) and 7.36 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 21.9, 28.6, 38.1, 40.0, 60.9, 74.2, 125.2, 125.9, 127.8, 128.7, 138.7 and 144.9; *m/z* (CI, NH_3) 238 ($M^+ + 18$, 40%), 220 (M^+, 100) and 203 (60).

Following the general procedure, tin(IV) chloride in DCM (1 M, 0.19 ml), stannane **115** (100 mg, 0.19 mmol) in DCM (1 ml) and benzaldehyde (70 µl, 0.57 mmol) in DCM (0.5 ml), after addition of methanolic ammonium chloride and chromatography using petrol : ether : Et_3N (19 : 80 : 1) as eluent, gave the title compound **116** (33 mg, 40%) as a colourless oil.

(1*RS*,5*RS*,3*Z*)-7-*tert*-Butyldimethylsilyloxy-5-methyl-1-phenylhept-3-en-1-ol 117

To a stirred suspension of *tert*-butyldimethylsilyl chloride (24 mg) and imidazole (16 mg) in DCM (1 ml) at 0 ºC was added diol **116** (35 mg) in DCM (1 ml) and the reaction mixture stirred at room temperature. After 0.5 h, brine (10 ml) was added and the mixture extracted with DCM (4 x 10 cm^3). The organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (1 : 1) gave the *title compound* **117** (21 mg, 67%) as a colourless oil (Found: M^+ - C_7H_7, 243.1775. $C_{13}H_{27}O_2Si$ requires *M*, 243.1778); ν_{max}/cm^{-1} 3425, 2902, 2857, 1461, 1258, 1096, 834 and 777; δ_H (300 MHz, $CDCl_3$) 0.06 (6 H, s, 2 x $SiCH_3$), 0.86 (3 H, d, *J* 6.6, 5-CH_3), 0.90 [9 H, s, $SiC(CH_3)_3$], 1.41 and 1.55 (each 1 H, m, 6-H), 2.54 (2 H, m, 2-H_2), 2.60 (1 H, m, 5-H), 3.62 (2 H, t, *J* 6.5, 7-H_2), 4.71 (1 H, dd, *J* 7.8, 5.4, 1-H), 5.36 (2 H, m, 3-H and 4-H), 7.34 (3 H, m, ArH) and 8.02 (2 H, m, ArH); δ_C (75 MHz, $CDCl_3$): -5.0, 1.2, 21.4, 26.2, 28.6, 37.9, 40.4, 61.6, 74.1, 124.0, 126.0, 127.6, 128.5 and 139.4; *m/z* (CI, NH_3) 335 ($M^+ + 1$, 10%), 317 (100), 185 (15), 160 (50) and 132 (30).

(1*SR*,5*RS*,3*Z*)-7-*tert*-Butyldimethylsilyloxy-5-methyl-1-phenylhept-3-en-1-yl 4-nitrobenzoate 118

DIAD (0.18 ml, 0.94 mmol) was added to the alcohol **117** (70 mg, 0.24 mmol), PPh_3 (240 mg, 0.94 mmol) and 4-nitrobenzoic acid (160 mg, 0.94 mmol) in THF at 0 ºC and, after 10 min, the mixture was allowed to warm to room temperature over 30 min then concentrated under reduced pressure. Chromatography of the residue using petrol : ether (30 : 1 to 15 : 1) as eluent gave the *title compound* **118** (69 mg, 63%) as a pale yellow oil; ν_{max}/cm^{-1} 2954, 2928, 2857, 1775, 1727, 1607, 1530, 1343, 1272, 1101, 1014, 836, 776 and 719; δ_H (300 MHz, $CDCl_3$) 0.05 and 0.07 (each 3 H, s, $SiCH_3$), 0.92 [9 H, s, $SiC(CH_3)_3$], 1.30 – 1.60 (2 H, m, 6-H_2), 1.47 (3 H, d, *J* 6.3, 5-CH_3), 2.68 (2 H, m, 2-H and 5-H), 2.99 (1 H, m, 2-H'), 3.54 (2 H, m, 7-H_2), 5.32 (2 H, m, 3-H, 4-H), 6.06 (1 H, dd, *J* 7.6, 6.2, 1-H), 7.42 (5 H, m, ArH) and 8.31 (4 H, m, Ar-H); δ_C (75 MHz, $CDCl_3$) –5.0, 18.5, 21.3, 21.9, 26.2, 28.6, 34.8, 40.4, 61.2, 74.6, 122.7, 123.8, 126.9, 128.6, 128.9, 131.0, 136.1, 139.5, 139.9, 150.8 and 164.1; *m/z* (CI, NH_3) 484 ($M^+ + 1$, 1%), 334 (12) and 317 (100).

(1*RS*,5*SR*,3*Z*)-5-Methyl-1-phenylhept-3-ene-1,7-diol 120

Sodium hydroxide in methanol was added to the ester **118** in methanol and the mixture stirred for 2 h at room temperature. Water was added and the mixture extracted with ether. The organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue gave the secondary alcohol **119** as a colourless oil; ν_{max}/cm^{-1} 3369, 2954, 2928, 2857, 1453, 1255, 1099, 835 and 775; δ_H (300 MHz, $CDCl_3$) 0.07 and 0.09 (each 3 H, s, $SiCH_3$), 0.93 [9 H, s, $SiC(CH_3)_3$], 0.99 (3 H, d, *J* 6.6, 5-CH_3), 1.40 and 1.56 (each 1 H, m, 6-H), 2.26 (1 H, br s, OH), 2.58 (3 H, m, 2-H_2 and 5-H), 3.59 (2 H, m, 7-H_2), 4.77 (1 H, dd, *J* 7.3, 5.3, 1-H), 5.37 (2 H, m, 3-H, 4-H) and 7.38 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) -5.0, -4.9 18.6, 21.6, 26.2, 28.6, 37.7, 40.5, 61.5, 73.9, 123.9, 126.2, 127.7, 128.6, 139.5 and 144.3; *m/z* (CI, NH_3) 335 ($M^+ + 1$, 35%) and 317 (100).

TBAF in THF (1 M, 0.5 ml, 0.5 mmol) was added to the silyl ether **119** (30 mg, 0.09 mmol) in THF (0.5 ml) at room temperature and the solution stirred overnight. Water (5 ml) was added and the mixture extracted into ether (4 x 5 ml). The organic extracts were dried and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (1 : 4) gave the *title compound* **120** (17 mg, 89%) as a colourless oil (Found: $M^+ + NH_4$, 238.1804. $C_{14}H_{24}O_2N$ requires *M*, 238.1802); ν_{max}/cm^{-1} 3351, 2954, 2926, 2873, 1699, 1453 and 1049; δ_H (300 MHz, $CDCl_3$) 0.98 (3 H, d, *J* 6.7, 5-CH_3), 1.34 and 1.61 (each 1 H, m, 6-H), 2.49 (1 H, m, 2-H), 2.68 (2 H, m, 2-H' and 5-H), 3.56 (2 H, m, 7-H_2), 4.83 (1 H, t, *J* 5.9, 1-H), 5.28

(2 H, m, 4-H, 3-H) and 7.36 (5 H, m, ArH); δ_C ($CDCl_3$, 75 MHz) 21.8, 28.7, 30.0, 40.1, 61.1, 73.6, 123.7, 126.1, 127.6, 128.5, 139.0 and 144.1; *m/z* (CI, NH_3) 238 (M^+ + 18, 40%), 220 (100) and 203 (50).

1,7-Bis-*tert*-butyldimethylsilyloxy-5-methyl-1-phenylhept-3-ene 121

tert-Butyldimethylsilyl chloride (450 mg, 3 mmol), imidazole (204 mg, 3 mmol) and DMAP (5 mg) were added to the diol **116** (220 mg, 1 mmol) in DCM (5 ml). After 16 h, the mixture was washed with brine (10 cm^3), and the aqueous layer extracted with DCM (4 x 10 ml). The organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (1 : 1) as eluent gave the *title compound* **121** (380 mg, 82%) as a clear oil (Found: $M^+ + NH_4$, 466.3528. $C_{26}H_{52}NO_2Si_2$ requires *M*, 466.3536.); υ_{max}/cm^{-1} 2954, 2929, 2894, 2857, 1255, 1091, 835 and 775; δ_H ($CDCl_3$, 300 MHz) -0.09 and 0.05 (each 3 H, s, $SiCH_3$), 0.06 (6 H, s, 2 x $SiCH_3$), 0.84 (3 H, d, *J* 6.7, 5-CH_3), 0.91 and 0.92 [each 9 H, s, $SiC(CH_3)_3$], 1.54 (2 H, m, 6-H_2), 2.45 (3 H, m, 2-H_2, 5-H), 3.55 (2 H, m, 7-H_2), 4.67 (1 H, t, *J* 6.2, 1-H), 5.20 (1 H, m, 4-H), 5.35 (1 H, dt, *J* 10.8, 7.5, 3-H) and 7.29 (5 H, m, ArH); δ_C ($CDCl_3$, 75 MHz) -5.0, -5.0, -4.6, -4.4, 18.5, 21.3, 26.1, 26.2, 28.6, 39.3, 40.6, 61.6, 75.5, 124.8, 126.2, 127.1, 128.2, 137.7 and 145.5; *m/z* (CI, NH_3) 466 (M^+ + 18, 10%), 334 (10), 317 (55) and 132 (100).

7-*tert*-Butyldimethylsilyloxy-3-methyl-7-phenylhept-4-en-1-ol 122

HF.pyridine complex (1.2 M in pyridine, 1.68 ml) was added to the bis-*tert*-butyldimethylsilyl ether **121** (300 mg) in THF (2 ml) and pyridine (0.14 ml) at room temperature. After 4 h, more HF.pyridine complex (1.2 M in pyridine, 3.36 ml) was added and the solution was stirred for 16 h. Saturated aqueous sodium bicarbonate was added and the mixture extracted into DCM (3 x 20 cm^3). The organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (60 : 40 to 50 : 50) as eluent gave the *title compound* **122** (160 mg, 72%) as a clear oil (Found: M^+ + H, 335.2403. $C_{20}H_{35}O_2Si$ requires *M*, 334.2328); υ_{max}/cm^{-1} 3397, 2954, 2928, 2857, 1253, 1088, 1068, 835 and 776; δ_H ($CDCl_3$, 300 MHz) -0.05 and 0.06 (each 3 H, s, $SiCH_3$), 0.89 (3 H, d, *J* 6.7, 3-CH_3), 0.92 [9 H, s, $SiC(CH_3)_3$], 1.34 (1 H, m, 2-H), 1.60 (2 H, m, 2-H', OH), 2.46 (1 H, m, 6-H), 2.57 (2 H, m, 3-H and 6-H'), 3.53 (2 H, m, 1-H_2), 4.76 (1 H, dd, *J* 5.3, 7.2, 7-H), 5.23 (1 H, tt, *J* 11.0, 1.6, 4-H), 5.46 (1 H, m, 5-H) and 7.32 (5 H, m, ArH); δ_C ($CDCl_3$, 75 MHz) -4.6, -4.4, 18.6, 21.5, 26.2, 28.9, 39.3, 40.1, 61.3, 75.4, 125.3, 126.2, 127.2, 128.3, 137.4 and 145.5; *m/z* (CI, NH_3) 335 (M^+ + 1, 10%), 220 (100) and 203 (40).

7-*tert*-Butyldimethylsilyloxy-3-methyl-7-phenylhept-4-enoic acid 123

Dess Martin periodinane (400 mg, 0.8 mmol) was added to the alcohol **122** (134 mg, 0.4 mmol) in DCM (4 cm^3) and the suspension stirred vigorously for 1 h at ambient temperature. Aqueous sodium hydroxide (2 M, 4 cm^3) was added and the mixture stirred for 20 min. The aqueous layer was extracted with ether (3 x 20 cm^3), the organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure to leave the corresponding aldehyde (133 mg).

The aldehyde (133 mg) was dissolved in *tert*-butanol and water (50 : 50, 10 ml) and 2-methyl-2-butene (2 M in THF, 2 ml), $NaClO_2$ (180 mg, 2 mmol) and $Na_2H_2PO_4.2H_2O$ (624 mg) were added. After 2 h, brine and ether were added and the aqueous layer was extracted with ether (3 x 10 ml). The organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (1 : 1) as eluent gave the *title compound* **123** (105 mg, 76%) as a clear oil (Found: M^+ + H, 349.2201. $C_{20}H_{33}O_3Si$ requires *M*, 348.2121); υ_{max}/cm^{-1} 2956, 2929, 2857, 1709, 1255, 1087, 1068, 836 and 776; δ_H ($CDCl_3$, 300 MHz) -0.07 and 0.08 (each 3 H, s, $SiCH_3$), 0.93 [9 H, s, $SiC(CH_3)_3$], 0.93 (3 H, d, *J* 6.6, 3-CH_3), 2.23 (2 H, m, 6-H_2), 2.52 (2 H, m, 2-H_2), 2.89 (1 H, m, 3-H), 4.72 (1 H, t, *J* 6.2, 7-H), 5.25 (1 H, dd, *J* 11.0, 9.8, 4-H), 5.40 (1 H, m, 5-H) and 7.32 (5 H, m, ArH); δ_C ($CDCl_3$, 75 MHz) -4.7, -4.4, 18.5, 20.8, 26.1, 29.1, 39.0, 41.6, 75.1, 125.7, 126.2, 127.2, 128.2, 135.5, 145.2 and 178.2; *m/z* (CI, NH_3) 349 (M^+ + 1, 10%), 234 (60) and 217 (100).

7-Hydroxy-3-methyl-7-phenylhept-4-enoic acid 124

The silyl ether **123** (104 mg) was dissolved in MeOH (5 ml) and concentrated aqueous hydrogen chloride (0.13 ml) was added dropwise. After 2 h, aqueous sodium hydroxide (2 M, 0.5 ml) was added and the mixture extracted with DCM (10 cm^3). The aqueous solution was then acidified and re-extracted with DCM (3 x 10 cm^3). These extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using ether as eluent gave the *title compound* **124** (56 mg, 80% yield) as a white solid (Found: $M^+ + NH_4$, 252.1607. $C_{14}H_{22}NO_3$ requires *M*, 252.1600); υ_{max}/cm^{-1} 3424, 2961, 2925 and 1707; δ_H ($CDCl_3$, 300 MHz) 0.97 (3 H, d, *J* 6.7, 3-CH_3), 2.27 (1 H, dd, *J* 16.0, 9.7, 2-H), 2.44 (2 H, m, 2-H' and 6-H), 2.74 (1 H, dt, *J* 14.3, 9, 6-H'), 3.03 (1 H, m, 3-H), 4.74 (1 H, dd, *J* 9.1, 4.4, 7-H), 5.35 (1 H, t, *J* 10.4, 4-H), 5.45 (1 H, m, 5-H) and 7.36 (5 H, m, ArH); δ_C ($CDCl_3$, 75 MHz) 21.2, 28.9, 38.3, 41.4, 74.1, 125.0, 126.7, 127.7, 128.6, 137.4, 144.4 and 177.3; *m/z* (CI, NH_3) 252 (M^+ + 18, 90%), 234 (100), 217 (60) and 115 (60).

3-Methyl-7-phenylhept-5-olide 125

Triethylamine (0.036 cm^3, 0.26 mmol) was added to the hydroxy-acid **124** (39 mg, 0.17 mmol) in THF (4 cm^3). After 10 min, 2,4,6-trichlorobenzoyl chloride (0.031 cm^3, 0.20 mmol) was added and the solution was stirred for 2 h. The reaction mixture was added dropwise over 4 h to toluene (50 cm^3) containing DMAP (291 mg, 2 mmol) heated under reflux. The mixture was heated under reflux for a further 0.5 h then allowed to cool and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (1 : 1) as eluent gave the *title compound* **125** (22 mg, 60%) as a clear oil (Found: $M^+ + NH_4$, 234.1497. $C_{14}H_{20}NO_2$ requires *M*, 234.1494); υ_{max}/cm^{-1} 2959, 2924, 1750, 1269, 1213, 1152, 1077 and 1064; δ_H ($CDCl_3$, 300

MHz) 1.17 (3 H, d, *J* 6.6, 3-CH_3), 2.19 (1 H, dd, *J* 13.3, 11.4, 2-H), 2.34 (1 H, ddd, *J* 13.9, 8.2, 1.61, 6-H), 2.89 (1 H, m, 6-H'), 2.96 (1 H, dd, *J* 13.3, 5.9, 2-H'), 3.45 (1 H, m, 3-H), 5.62 (1 H, ddd, *J* 11.3, 9.4, 1.9, 4-H), 5.72 (1 H, d, *J* 11.4, 7-H), 5.85 (1 H, m, 5-H) and 7.42 (5 H, m, ArH); δ_C ($CDCl_3$, 75 MHz) 20.3, 31.8, 37.4, 46.3, 80.0, 126.3, 126.6, 128.3, 128.8, 140.0, 140.7 and 175.8; *m/z* (CI, NH_3) 234 (M^+ + 18, 100) and 217 (30).

(1*RS*,5*RS*,3*Z*)-1-(4-Methoxyphenyl)-5-methylhept-3-ene-1,7-diol 126

Following the general procedure, tin(IV) bromide (121 mg, 0.28 mmol) in DCM (1 ml), stannane **115** (100 mg, 0.25 mmol) in DCM (1 ml) and 4-methoxybenzaldehyde (70 µl, 0.84 mmol) in DCM (0.5 ml), after addition of methanolic ammonium chloride and chromatography using petrol : ether : Et_3N (19 : 80 : 1) gave the *title compound* **126** (37 mg, 61%) as a colourless oil (Found: $M^+ + NH_4$, 268.1914. $C_{15}H_{26}O_3N$ requires *M*, 268.1907); ν_{max}/cm^{-1} 3351, 2955, 2928, 1613, 1586, 1514, 1456, 1303, 1248, 1175, 1048, 1001 and 832; δ_H (300 MHz, $CDCl_3$) 0.96 (3 H, d, *J* 6.7, 5-CH_3), 1.35 and 1.69 (each 1 H, m, 6-H), 2.28 (1 H, m, 2-H), 2.69 (1 H, dt, *J* 14.2, 9.4, 2-H'), 2.80 (1 H, m, 5-H), 2.98 (2 H, br s, 2 x OH), 3.61 (2 H, m, 7-H_2), 3.83 (3 H, s, OCH_3), 4.65 (1 H, dd, *J* 9.5, 3.8, 1-H), 5.31 (1 H, t, *J* 10.7, 4-H), 5.48 (1 H, m, 3-H) and 6.90 and 7.30 (each 2 H, d, *J* 8.8, ArH); δ_C (75 MHz, $CDCl_3$) 21.9, 28.5, 38.0, 39.9, 55.6, 60.8, 73.8, 114.1, 125.4, 127.4, 137.1, 138.4 and 159.3; *m/z* (CI, NH_3) 250 (M^+, 10%) and 233 (100).

(1*RS*,5*RS*,3*Z*)-1-(4-Chlorophenyl)-5-methylhept-3-ene-1,7-diol 127

Following the general procedure, tin(IV) bromide (121 mg, 0.28 mmol) in DCM (1 ml), stannane **115** (100 mg, 0.28 mmol) in DCM (1 ml) and 4-chlorobenzaldehyde (70 µl, 0.84 mmol) in DCM (0.5 ml), after addition of methanolic ammonium chloride and chromatography using petrol : ether : Et_3N (19 : 80 : 1) gave the *title compound* **127** (42 mg, 67%) as a colourless oil (Found: $M^+ + NH_4$, 272.1408. $C_{14}H_{23}O_2N^{35}Cl$ requires *M*, 272.1412); ν_{max}/cm^{-1} 3340, 2956, 2927, 1492, 1408, 1091, 1050, 1014 and 830; δ_H (300 MHz, $CDCl_3$) 0.97 (3 H, d, *J* 6.7, 5-CH_3), 1.32 and 1.69 (each 1 H, m, 6-H), 2.27 (1 H, m, 2-H), 2.63 (1 H, dt, *J* 14.3, 9.8, 2-H'), 2.76 (1 H, m, 5-H), 3.25 (2 H, br s, 2 x OH), 3.59 (2 H, m, 7-H_2), 4.65 (1 H, dd, *J* 9.5, 3.5, 1-H), 5.33 (1 H, t, *J* 10.6, 4-H), 5.46 (1 H, m, 3-H) and 7.31 (4 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 21.9, 28.5, 38.1, 39.7, 60.8, 73.4, 125.0, 127.3, 127.8, 133.3, 138.8 and 143.5; *m/z* (CI, NH_3) 274 (M^+ + 18, 20%), 272 (M^+ + 18, 60), 256 (M^+, 30), 254 (M^+, 100), 239 (20) and 237 (70).

(1*RS*,5*RS*,3*Z*)-1-(3-Chlorophenyl)-5-methylhept-3-ene-1,7-diol 128

Following the general procedure, tin(IV) bromide (121 mg, 0.28 mmol) in DCM (1 ml), stannane **115** (100 mg, 0.25 mmol) in DCM (1 ml) and 3-chlorobenzaldehyde (70 µl, 0.84 mmol) in DCM (0.5 ml), after addition of methanolic ammonium chloride and chromatography using petrol : ether : Et_3N (19 : 80 : 1) gave the *title compound* **128** (47 mg, 74%) as a colourless oil (Found: $M^+ + NH_4$, 272.1411. $C_{14}H_{23}O_2N^{35}Cl$ requires *M*, 272.1412); ν_{max}/cm^{-1} 3340, 2955, 2926, 1598, 1575, 1432, 1198, 1050 and 785; δ_H (300 MHz, $CDCl_3$) 0.96 (3 H, d, *J* 6.7, 5-CH_3), 1.34 and 1.70 (each 1 H, m, 6-H), 2.29 (1 H, m, 2-H), 2.65 (1 H, dt, *J* 14.4, 9.8, 2-H'), 2.78 (1 H, m, 5-H), 3.30 (2 H, br s, 2 x OH), 3.64 (2 H, m, 7-H_2), 4.64 (1 H, dd, *J* 10.7, 3.4, 1-H), 5.35 (1 H, t, *J* 10.5, 4-H), 5.46 (1 H, m, 3-H) and 7.36 (4 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 21.9, 28.6, 38.1, 39.7, 60.8, 73.4, 124.1, 124.9, 126.1, 127.8, 129.9, 134.5, 138.9 and 147.1; *m/z* (CI, NH_3) 274 (M^+ + 18, 20%), 272 (M^+ + 18, 60), 256 (M^+, 30), 254 (M^+, 100) and 239 (15) and 237 (70).

(1*RS*,5*RS*,3*Z*)-5-Methyl-1-(4-nitrophenyl)hept-3-ene-1,7-diol 129

Following the general procedure, tin(IV) bromide (121 mg, 0.28 mmol) in DCM (1 ml), stannane **115** (100 mg, 0.25 mmol) in DCM (1 ml) and 4-nitrobenzaldehyde (113 mg, 0.75 mmol) in DCM (0.5 ml), after the addition of methanolic ammonium chloride and chromatography using petrol : ether : Et_3N (19 : 80 : 1) gave the *title compound* **129** (41 mg, 62%) (Found: $M^+ + NH_4$, 283.1659. $C_{14}H_{23}O_4N_2$ requires *M*, 283.1652); ν_{max}/cm^{-1} 3368, 2956, 1605, 1520, 1345, 1050 and 855; δ_H (300 MHz, $CDCl_3$) 0.95 (3 H, d, *J* 6.8, 5-CH_3), 1.35 and 1.69 (each 1 H, m, 6-H), 2.34 (1 H, m, 2-H), 2.64 (1 H, dt, *J* 14.4, 9.8, 2-H'), 2.76 (1 H, m, 5-H), 3.64 (2 H, m, 7-H_2), 4.79 (1 H, dd, *J* 9.7, 3.4, 1-H), 5.38 (1 H, t, *J* 10.3, 4-H), 5.48 (1 H, m, 3-H) and 7.54 and 8.21 (each 2 H, d, *J* 8.6, ArH); δ_C (75 MHz, $CDCl_3$) 21.8, 28.5, 38.2, 39.6, 60.8, 73.1, 123.9, 124.5, 126.6, 139.2, 147.4 and 152.6; *m/z* (CI, NH_3) 283 (M^+ + 18, 100%), 265 (M^+, 5) and 218 (30).

(3*RS*,7*RS*,4*Z*)-3,8-Dimethylnon-4-ene-1,7-diol 130

Following the general procedure, tin(IV) bromide (121 mg, 0.28 mmol) in DCM (1 ml), stannane **115** (100 mg, 0.25 mmol) in DCM (1 ml) and 2-methylpropanal (70 µl, 0.84 mmol) in DCM (0.5 ml), after addition of methanolic ammonium chloride and chromatography using petrol : ether : Et_3N (19 : 80 : 1) gave the *title compound* **130** (29 mg, 63%) as a colourless oil (Found: M^+, 186.1618. $C_{11}H_{22}O_2$ requires *M*, 186.1614); ν_{max}/cm^{-1} 3331, 2957, 2928, 2873, 1456, 1369, 1050, 1001 and 740; δ_H (300 MHz, $CDCl_3$) 0.96 (6 H, d, *J* 6.7, 9-H_3 and 8-CH_3), 1.01 (3 H, d, *J* 6.7, 3-CH_3), 1.34 (2 H, m, 2-H_2), 1.70 (1 H, m, 8-H), 2.12 (1 H, m, 6-H), 2.36 (1 H, dt, *J* 14.2, 10.0, 6-H'), 2.78 (3 H, m, 3-H and 2 x OH), 3.44 (1 H, ddd, *J* 10, 7.8, 2.8, 7-H), 3.64 (2 H, m, 1-H_2), 5.31 (1 H, t, *J* 10.1, 4-H) and 5.43 (1 H, m, 5-H); δ_C (75 MHz, $CDCl_3$) 17.7, 18.8, 22.0, 28.4, 32.2, 34.2, 40.0, 60.7, 76.5, 126.3 and 138.1; *m/z* (CI, NH_3) 204 (M^+ + 18, 90%), 187 (M^+ + 1, 70), 186 (M^+, 30) and 169 (100).

(3*RS*,7*SR*,4*Z*)-3-Methyldec-4-ene-1,7-diol 131

Following the general procedure, tin(IV) bromide (121 mg, 0.28 mmol) in DCM (1 ml), stannane **115** (100 mg, 0.25 mmol) in DCM (1 ml) and butanal (70 µl, 0.84 mmol) in DCM (0.5 ml), after addition of methanolic ammonium chloride and chromatography using petrol : ether : Et_3N (19 : 80 : 1) gave the

title compound **131** (30 mg, 65%) as a colourless oil (Found: M^+, 186.1615. $C_{11}H_{22}O_2$ requires *M*, 186.1614); ν_{max}/cm^{-1} 3321, 2956, 2929, 1456, 1124, 1051 and 746; δ_H (300 MHz, $CDCl_3$) 0.97 (3 H, t, *J* 7.6, 10-CH_3), 1.00 (3 H, d, *J* 6.7, 3-CH_3), 1.20 – 1.80 (6 H, m, 2-H_2, 8-H_2 and 9-H_2), 2.12 (1 H, m, 6-H), 2.35 (1 H, dt, *J* 14.2, 9.8, 6-H'), 2.78 (3 H, m, 3-H and 2 x OH), 3.63 (3 H, m, 1-H_2 and 7-H), 5.31 (1 H, t, *J* 10.3, 4-H) and 5.43 (1 H, m, 5-H); δ_C (75 MHz, $CDCl_3$) 14.3, 19.1, 22.0, 28.5, 35.7, 40.0, 40.2, 61.0, 71.5, 125.8 and 138.2; *m/z* (CI, NH_3) 204 (M^+ + 18, 100%), 187 (M^+ + 1, 80) and 169 (70).

(3*RS*,7*RS*,4*Z*,8*E*)-3-Methyldeca-4,8-diene-1,7-diol 132

Following the general procedure, tin(IV) bromide (121 mg, 0.28 mmol) in DCM (1 ml), stannane **115** (100 mg, 0.25 mmol) in DCM (1 ml) and (*E*)-but-2-enal (70 µl, 0.84 mmol) in DCM (0.5 ml), after addition of methanolic ammonium chloride and chromatography using petrol : ether : Et_3N (19 : 80 : 1) gave the *title compound* **132** (35 mg, 76%) as a colourless oil (Found: M^+ + NH_4, 202.1804. $C_{11}H_{24}O_2N$ requires *M*, 202.1802); ν_{max}/cm^{-1} 3321, 2955, 2926, 1452, 1376, 1050, 965, 871 and 745; δ_H (300 MHz, $CDCl_3$) 0.99 (3 H, d, *J* 6.7, 3-CH_3), 1.34 and 1.70 (each 1 H, m, 2-H), 1.73 (3 H, d, *J* 5.7, 10-H_3), 2.15 (1 H, m, 6-H), 2.45 (1 H, dt, *J* 10.0, 14.4, 6-H'), 2.78 (3 H, m, 3-H and 2 x OH), 3.62 (2 H, m, 1-H_2), 4.09 (1 H, m, 7-H), 5.29 (1 H, t, *J* 10.2, 4-H), 5.42 (1 H, m, 5-H), 5.55 (1 H, m, 8-H) and 5.68 (1 H, m, 9-H); δ_C (75 MHz, $CDCl_3$) 17.9, 21.9, 28.5, 35.9, 40.0, 60.7, 72.6, 125.2, 126.8, 134.3 and 138.3; *m/z* (CI, NH_3) 202 (M^+ + 18, 10%), 184 (M^+, 70) and 167 (100).

(1*R*,6*R*,3*Z*)-6-Methyl-1-(4-methoxyphenyl)hept-3-ene-1,7-diol 149

Following the general procedure, tin(IV) bromide (1 M in DCM, 213 µl, 0.213 mmol), stannane **138** (86 mg, 0.213 mmol) and 4-methoxybenzaldehyde (3 M in DCM, 71 µl, 0.213 mmol), after chromatography using ether : petrol (2 : 1 + 1% triethylamine) as eluent, gave the *title compound* **149** (31 mg, 58%) as a colourless oil, a 91 : 9 mixture of epimers $[\alpha]_D$ +66 (*c* = 2) (Found: M^+, 250.1566. $C_{15}H_{22}O_3$ requires *M*, 250.1569); ν_{max}/cm^{-1} 3349, 2960, 1613, 1586, 1514, 1303, 1249, 1175, 1034, 876 and 832; δ_H (300 MHz, $CDCl_3$) major epimer **149** 0.93 (3 H, d, *J* 7, 6-CH_3), 1.70 (1 H, oct, *J* 6.5, 6-H), 1.94 and 2.25 (each 1 H, dt, *J* 14, 7, 5-H), 2.38 (1 H, dt, *J* 14, 5, 2-H), 2.64 (1 H, dt, *J* 14, 8, 2-H'), 2.90 (1 H, br s, OH), 3.43 and 3.53 (each 1 H, dd, *J* 11, 5, 7-H), 3.80 (3 H, s, OCH_3), 4.67 (1 H, dd, *J* 8.5, 4.5, 1-H), 5.52 (2 H, m, 3-H and 4-H) and 6.90 and 7.30 (each 2 H, d, *J* 8.5, ArH); minor 1,6-*syn*-epimer 2.1 (2 H, m 5-H_2); δ_C (75 MHz, $CDCl_3$) 16.9, 31.0, 35.8, 37.3, 55.3, 66.9, 73.4, 113.8, 126.5, 127.0, 131.1, 136.6 and 159.0; *m/z* (CI, NH_3) 250 (M^+, 8%) and 233 (M^+ - 17, 100).

(1*R*,6*R*,3*Z*)-4-Methyl-1-(4-nitrophenyl)hept-3-ene-1,7-diol 150

Following the general procedure, tin(IV) bromide (1 M in DCM, 260 µl, 0.26 mmol), stannane **138** (105 mg, 0.26 mmol) and 4-nitrobenzaldehyde (1.5 M in DCM, 173 µl, 0.26 mmol), after chromatography using ether : petrol (2 : 1 + 1% triethylamine) as eluent, gave the *title compound* **150** (52 mg, 76%) as a colourless oil, a 91 : 9 mixture of epimers $[\alpha]_D$ +51 (*c* = 5) (Found: M^+ + NH_4, 283.1659. $C_{14}H_{23}N_2O_4$ requires *M*, 283.1658); ν_{max}/cm^{-1} 3355, 3080, 1604, 1520, 1347, 1034, 856 and 702; δ_H (500 MHz, $CDCl_3$) major epimer **150** 0.84 (3 H, d, *J* 7, 6-CH_3), 1.65 (1 H, m, 6-H), 1.88 and 2.14 (each 1 H, dt, *J* 11.5, 6, 5-H), 2.35 (1 H, dt, *J* 11.5, 3.5, 2-H), 2.51 (1 H, dt, *J* 11.5, 6.5, 2-H'), 2.80 (1 H, br s, OH), 3.30 - 3.50 (2 H, m, 7-H_2), 3.85 (1 H, br s, OH), 4.74 (1 H, dd, *J* 8.5, 3.5, 1-H), 5.35 - 5.60 (2 H, m, 3-H and 4-H) and 7.46 and 8.12 (each 2 H, d, *J* 8.5, ArH); minor 1,6-*syn*-epimer 2.1 (2 H, m, 5-H_2) and 4.81 (1 H, t, *J* 6, 1-H); δ_C (75 MHz, $CDCl_3$) major epimer **150** 16.8, 30.9, 35.5, 37.4, 66.7, 72.7, 123.6, 125.3, 126.5, 132.0, 147.1 and 152.0; minor 1,6-*syn*-epimer 16.4, 30.5, 35.4, 37.0, 72.6, 125.1 and 131.5; *m/z* (CI, NH_3) 283 (M^+ + 18, 70%), 266 (M^+ + 1, 3), 265 (M^+, 6), 218 (60) and 122 (100).

(2*R*,7*S*,4*Z*)-2-Methylnon-4-ene-1,7-diol 151

Following the general procedure, tin(IV) bromide (1 M in DCM, 0.23 µl, 0.23 mmol), stannane **138** (93 mg, 0.23 mmol) and propanal (1.5 M in DCM, 115 µl, 0.345 mmol), after chromatography using ether : petrol (2 : 1 + 1% triethylamine) as eluent, gave the *title compound* **151** (22 mg, 56%) as a colourless oil, a 93 : 7 mixture of epimers, $[\alpha]_D$ –4.6 (*c* = 2) (Found: M^+ + H, 173.1539. $C_{10}H_{21}O_2$ requires *M*, 173.1542); ν_{max}/cm^{-1} 3338, 2960, 2928, 2876, 1461, 1040 and 983; δ_H (500 MHz, $CDCl_3$) 0.91 (3 H, d, *J* 7, 2-CH_3), 0.94 (3 H, t, *J* 7.5, 9-H_3), 1.48 (2 H, m, 8-H_2), 1.68 (1 H, oct, *J* 7, 2-H), 1.90 (1 H, dt, *J* 14.5, 7.5, 3-H), 2.15 (1 H, dt, *J* 14.5, 5, 3-H'), 2.22 (3 H, m, 6-H_2 and OH), 2.45 (1 H, br s, OH), 3.45 (3 H, m, 1-H_2 and 7-H) and 5.50 (2 H, m, 4-H and 5-H); δ_C (75 MHz, $CDCl_3$) major epimer **151** 10.0, 16.9, 30.0, 31.0, 34.7, 35.9, 66.9, 72.9, 126.8 and 131.0; minor 1,6-*syn*-epimer 15.3, 29.6, 30.6, 34.6, 35.8, 67.1, 72.4, 127.7 and 130.4; *m/z* (CI, NH_3) 190 (M^+ + 18, 95%), 173 (M^+ + 1, 100) and 155 (M^+ - 17, 65).

(2*R*,7*R*,4*Z*)-2,8-Dimethylnon-4-ene-1,7-diol 152

Following the general procedure, tin(IV) bromide (1 M in DCM, 0.597 µl, 0.597 mmol), stannane **138** (241 mg, 0.597 mmol) and 2-methylpropanal (3 M in DCM, 199 µl, 0.597 mmol), after chromatography using ether : petrol (2 : 1 + 1% triethylamine) as eluent, gave the *title compound* **152** (89 mg, 80%) as a colourless oil, $[\alpha]_D$ –4.6 (*c* = 1.3) (Found: M^+ + H, 187.1695. $C_{11}H_{23}O_2$ requires *M*, 187.1698); ν_{max}/cm^{-1} 3346, 2959, 1465, 1040 and 870; δ_H (300 MHz, $CDCl_3$) major epimer **152** 0.895, 0.905 and 0.91 (each 3 H, d, *J* 7, 2-CH_3, 8-CH_3 and 9-H_3), 1.66 (2 H, m, 2-H and 8-H), 1.88 (1 H, dt, *J* 14, 6.5, 3-H), 2.10 (1 H, m, 3-H'), 2.23 (3 H, m, 6-H_2 and OH), 2.50 (1 H, br s, OH), 3.35 (1 H, m, 7-H), 3.40 and 3.52 (each 1 H, dd, *J* 10.5, 5, 1-H) and 5.50 (2 H, m, 4-H and 5-H); minor 1,6-*syn*-epimer 1.97 (2 H, m, 3-H_2); δ_C (75 MHz, $CDCl_3$) major epimer **152** 17.0, 17.6, 18.7, 31.0, 32.0, 33.5, 35.8, 66.8, 76.3, 127.3 and 131.0; minor 1,6-*syn*-epimer 16.3, 30.5, 33.3, 35.7, 67.0, 127.5 and 130.1; *m/z* (CI, NH_3) 204 (M^+ + 18, 100%), 187 (M^+ + 1, 75) and 169 (M^+ - 17, 86).

(3*R*,8*R*,5*Z*)-9-*tert*-Butyldimethylsilyloxy-2,8-dimethylnon-5-

en-3-ol 153

Following the procedure uses to prepare silyl ether **143**, alcohol **152** (89 mg, 0.478 mmol), after chromatography using petrol : ether (6 : 1) as eluent, gave the *title compound* **153** (112 mg, 78%) as a colourless oil, $[\alpha]_D$ +8.3 (*c* = 2.1) (Found: M^+ + H, 301.2565. $C_{17}H_{37}O_2Si$ requires *M*, 301.2563); υ_{max}/cm^{-1} 3379, 2957, 1471, 1255, 1095, 838 and 776; δ_H (300 MHz, $CDCl_3$) 0.05 (6 H, s, 2 x CH_3Si), 0.91 (3 H, d, *J* 7, 8-CH_3), 0.93 [9 H, s, $SiC(CH_3)_3$], 0.97 and 0.99 (each 3 H, d, *J* 3.5, 2-CH_3 or 1-H_3), 1.60 (1 H, d, *J* 4, OH), 1.72 (2 H, m, 2-H and 8-H), 1.94 (1 H, dt, *J* 14, 7, 4-H), 2.25 (3 H, m, 4-H' and 7-H_2), 3.45 (3 H, m, 3-H and 9-H_2) and 5.55 (2 H, m, 5-H and 6-H); δ_C (75 MHz, $CDCl_3$) -5.3, -5.3, 16.5, 17.6, 18.4, 18.8, 26.0, 31.0, 32.3, 33.1, 36.3, 67.9, 75.6, 126.7 and 131.5; *m/z* (CI, NH_3) 301 (M^+ + 1, 100%).

(3*R*,8*R*,5*Z*)-3-[(*R*)-2-Acetoxy-2-phenylacetoxy]-9-*tert*-butyldimethylsilyloxy-2,8-dimethylnon-5-ene 154

Following the general procedure, alcohol **153** (44 mg, 0.147 mmol) and (*R*)-2-acetoxy-2-phenylacetic acid, after chromatography using petrol : ether (5 : 1) as eluent, gave the *title compound* **154** (42 mg, 60%) as a colourless oil, $[\alpha]_D$ -50 (*c* = 4.2) (Found: M^+ + H, 477.3027. $C_{27}H_{45}O_5Si$ requires M, 477.3036); ν_{max}/cm^{-1} 2958, 1749, 1372, 1233, 1211, 1180, 1086, 1059, 838 and 777; δ_H (300 MHz, $CDCl_3$) 0.05 (6 H, s, 2 x $SiCH_3$), 0.67 and 0.70 (each 3 H, d, *J* 7, 1-H_3 and 2-CH_3), 0.95 [12 H, m, 8-CH_3, $SiC(CH_3)_3$], 1.70 (2 H, m, 2-H and 8-H), 1.90 (1 H, dt, *J* 14, 7, 7-H), 2.20 (4 H, m, 7-H' CH_3CO_2), 2.37 (2 H, m, 4-H_2), 3.47 (2 H, m, 9-H_2), 4.80 (1 H, q, *J* 5, 3-H), 5.47 (2 H, m, 5-H and 6-H), 5.95 (1 H, s, 2'-H) and 7.35 - 7.55 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) -5.3, 16.4, 16.8, 18.4, 18.5, 20.8, 26.0, 29.3, 30.9, 36.3, 67.9, 74.7, 79.7, 125.2, 127.7, 128.7, 129.1, 130.8, 134.3, 168.6 and 170.2; *m/z* (CI, NH_3) 494 (M^+ + 18, 20%) and 477 (M^+ + 1, 100).

(3*R*,8*R*,5*Z*)-3-[(*S*)-2-Acetoxy-2-phenylacetoxy]-9-*tert*-butyldimethylsilyloxy-2,8-dimethylnon-5-ene 155

Following the general procedure, alcohol **153** (44 mg, 0.147 mmol) and (*S*)-2-acetoxy-2-phenylacetic acid, after chromatography using petrol : ether (5 : 1) as eluent, gave the *title compound* **155** (67 mg, 96%) as a colourless oil, $[\alpha]_D$ +32 (*c* = 6.7) (Found: M^+ + H, 477.3019. $C_{27}H_{45}O_5Si$ requires *M*, 477.3036); ν_{max}/cm^{-1} 2958, 1749, 1471, 1372, 1233, 1179, 1086, 1058, 838 and 777; δ_H (300 MHz, $CDCl_3$) 0.05 (6 H, s, 2 x $SiCH_3$), 0.83 (3 H, d, *J* 6.5, 8-CH_3), 0.95 [15 H, m, 1-H_3, 2-CH_3 and $SiC(CH_3)_3$], 1.56 (1 H, oct, *J* 6.5, 8-H), 1.73 (2 H, m, 7-H_2), 1.90 (3 H, m, 2-H, 4-H_2), 2.20 (3 H, s, CH_3CO_2), 3.38 (2 H, m, 9-H_2), 4.81 (1 H, q, *J* 7, 3-H), 5.05 and 5.25 (each 1 H, m, 5-H or 6-H), 5.94 (1 H, s, 2'-H), 7.40 - 7.55 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) -5.3, 16.4, 17.5, 18.3, 18.7, 20.7, 26.0, 29.0, 30.7, 31.2, 36.2, 67.8, 74.8, 79.9, 124.9, 127.7, 128.6, 129.1, 130.5, 134.0, 168.7 and 170.3; *m/z* (CI, NH_3) 494 (M^+ + 18, 15%), 477 (M^+ + 1, 70) and 283 (100).

(5*R*)-6-Methoxy-5-methylhex-2-enyl(tributyl)stannane 156

The 6-hydroxyhex-2-enyl(tributyl)stannane **138** (259 mg, 0.641 mmol) in THF (1 ml) was added to sodium hydride (31 mg, 0.769 mmol) in THF (2 ml) and the mixture stirred for 1 h. Methyl iodide (200 µl, 3.21 mmol) was added and the stirring was continued for 18 h. Ether was added and the mixture washed with water and brine, then dried ($MgSO_4$). Following concentration under reduced pressure, chromatography of the residue using petrol : ether (50 : 1 + 1% triethylamine) as eluent, gave the *title compound* **156** (206 mg, 77%) as a colourless oil, a 4 : 1 mixture of (*E*)- and (*Z*)-isomers, $[\alpha]_D$ -2.0 (*c* = 3.5) (Found: M^+- C_4H_9, 361.1553. $C_{16}H_{33}O^{120}Sn$ requires *M*, 361.1553); ν_{max}/cm^{-1} 2957, 2925, 1462, 1114 and 961; δ_H (300 MHz, $CDCl_3$) 0.87 - 0.98 (18 H, m, 5-CH_3 and 3 x $SnCH_2CH_2CH_2CH_3$), 1.30 - 1.60 (13 H, m, 5-H and 3 x $SnCH_2CH_2CH_2CH_3$), 1.72 (2 H, d, *J* 7, 1-H_2), 1.85 and 2.10 (each 1 H, m, 4-H), 3.18 (1 H, m, 6-H), 3.27 (1 H, dd, *J* 9, 6, 6-H'), 3.37 (3 H, s, CH_3O), 5.12 (0.2 H, m, 2- or 3-H), 5.23 and 5.55 (each 0.8 H, dt, *J* 15, 7, 2- or 3-H) and 5.95 (0.2 H, m, 2- or 3-H); *m/z* (EI) 418 (M^+, 3%), 416 (M^+, 2), 361 (M^+ - 57, 50), 361 (M^+ - 57, 40), 235 (90), 233 (80), 179 (95), 177 (100) and 175 (60).

(5*R*)-6-Methoxymethoxy-5-methylhex-2-enyl(tributyl) stannane 157

Chloromethyl methyl ether (83 µl, 1.1 mmol) was added to a solution of di-*iso*propylethylamine (387 µl, 2.2 mmol) and the 6-hydroxyhex-2-enyl(tributyl)stannane **138** (222 mg, 0.55 mmol) in DCM (2 ml) and the mixture stirred for 18 h. DCM was added and the mixture washed with water and brine then dried ($MgSO_4$). After concentration under reduced pressure, chromatography of the residue using petrol : ether (50 : 1 + 1% triethylamine) as eluent gave the *title compound* **157** (170 mg, 69%) as a colourless oil, a 4 : 1 mixture of (*E*)- and (*Z*)-isomers, $[\alpha]_D$ +2.4 (*c* = 3.8) (Found: M^+ - C_4H_9, 391.1651. $C_{17}H_{35}O^{120}Sn$ requires *M*, 391.1659); ν_{max}/cm^{-1} 2956, 2925, 1463, 1152, 1113, 1048 and 961; δ_H (300 MHz, $CDCl_3$) 0.85 - 0.95 (15 H, m, 3 x $SnCH_2CH_2CH_2CH_3$), 0.99 (3 H, d, *J* 7, 5-CH_3), 1.25 - 1.60 (13 H, m, 5-H and 3 x $SnCH_2CH_2CH_2CH_3$), 1.73 (2 H, d, *J* 7.5, 1-H_2), 1.85 and 2.13 (each 1 H, m, 4-H), 3.30 - 3.45 (5 H, m, CH_3O and 6-H_2), 4.62 (2 H, s, OCH_2O), 5.12 (0.2 H, m, 2- or 3-H), 5.25 (0.8 H, dt, *J* 15, 7, 2- or 3-H) and 5.60 (1 H, m, 2- or 3-`H); δ_C (75 MHz, $CDCl_3$) 9.1, 9.4, 13.7, 14.2, 16.8, 17.1, 27.4, 29.2, 30.9, 34.2, 34.3, 36.8, 55.1, 72.9, 76.9, 98.6, 121.9, 123.3, 129.7 and 130.9; *m/z* (EI) 448 (M^+, 2%), 446 (M^+, 1.5), 391 (M^+ - 57, 13), 389 (M^+ - 57, 1), 291 (100) and 289 (80).

(5*R*)-6-Benzyloxy-5-methylhex-2-enyl(tributyl)stannane 158

The 6-hydroxyhex-2-enyl(tributyl)stannane **138** (208 mg, 0.52 mmol) in *N*,*N*-dimethylformamide (2 ml) was added to sodium hydride (25 mg, 60% dispersion in mineral oil, 0.62 mmol) in *N*,*N*-dimethylformamide (1 ml) and the mixture stirred for 1 h. Tetrabutylammonium iodide (8 mg, 0.02 mmol) and benzyl bromide (67 µl, 0.57 mmol) were added and the stirring continued for 50 h. Ether was added and the mixture washed with water and brine, then dried ($MgSO_4$). After concentration under

reduced pressure, chromatography of the residue using petrol : ether (50 : 1 +1% triethylamine) as eluent, gave the *title compound* **158** (58 mg, 23%) as a colourless oil, $[\alpha]_D$ -2.9 (*c* = 3.5) (Found: M^+ - C_4H_9, 437.1857. $C_{22}H_{37}O^{120}Sn$ requires *M*, 437.1866); ν_{max}/cm^{-1} 2956, 2925, 1455, 1376, 1099, 961, 734 and 697; δ_H (300 MHz, $CDCl_3$) 0.88 - 1.00 (18 H, m, 5-CH_3 and 3 x Sn$CH_2CH_2CH_2CH_3$), 1.30 - 1.60 (13 H, m, 5-H and 3 x $SnCH_2CH_2CH_2CH_3$), 1.73 (2 H, d, *J* 8, 1-H_2), 1.87 and 2.16 (each 1 H, m, 4-H), 3.35 (2 H, m, 6-H_2), 4.55 (2 H, s, $PhCH_2$), 5.13 (0.2 H, m, 2- or 3-H), 5.24 and 5.57 (each 0.8 H, dt, *J* 15, 7.5, 2- or 3-H), 5.68 (0.2 H, m, 2- or 3-H) and 7.20 - 7.35 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 9.2, 9.4, 13.7, 14.2, 16.9, 17.2, 27.4, 29.2, 30.9, 34.2, 34.3, 36.9, 73.0, 75.7, 122.1, 123.4, 127.4, 127.5, 128.3, 129.4, 130.8 and 138.9; *m/z* (EI) 437 (M^+ - 57, 3%), 435 (M^+ - 57, 2) and 91 (100). Recovered starting material **138** (110 mg, 52%) was also isolated.

(3*S*,9*R*,5*Z*)-2-Methyldec-5-ene-3,9-diol 174

Following the general procedure, stannane **163** (100 mg, 0.248 mmol), tin(IV) bromide (1.024 M in DCM, 238 µl, 0.248 mmol) and 2-methylpropanal (72 µl, 0.251 mmol), after chromatography using petrol : ether (1 : 1 + 1% triethylamine) as eluent gave the *title compound* **174** (29 mg, 63%) as a colourless oil, a 90 : 10 mixture of epimers, $[\alpha]_D$ -19 (*c* = 1.3) (Found: $M^+ + NH_4$, 204.1961. $C_{11}H_{26}NO_2$ requires *M*, 204.1964; ν_{max}/cm^{-1} 3358, 2963, 2930, 1464, 1372, 1129, 1047, 999, 871 and 730; δ_H (300 MHz, $CDCl_3$) 0.95 and 0.98 (each 3 H, d, *J* 7, 1-H_3 or 2-CH_3), 1.22 (3 H, d, *J* 6, 10-H_3), 1.53 (2 H, q, *J* 7, 8-H_2), 1.73 (1 H, m, 2-H), 2.09 (2 H, s, 2 x OH), 2.16 - 2.30 (4 H, m, 4-H_2 and 7-H_2), 3.40 (1 H, q, *J* 6, 3-H), 3.84 (1 H, m, 9-H) and 5.48 and 5.60 (each 1 H, dt, *J* 10.5, 7.5, 5-H or 6-H); δ_C (75 MHz, $CDCl_3$) major epimer **174** 17.7, 18.9, 23.6, 23.9, 32.0, 33.1, 38.8, 67.7, 76.3, 126.2 and 132.6; minor 1,7-*anti*-epimer **175** 17.5, 18.7, 23.5, 33.5, 66.5, 126.9 and 132.1; *m/z* (CI, NH_3) 204 (M^+ + 18, 98%), 187 (M^+ + 1, 100) and 169 (M^+ - 17, 86).

(3*R*,9*R*,5*Z*)-2-Methyldec-5-ene-3,9-diol 175

Sodium hydroxide (94 mg, 2.35 mmol) was added to the ester **179** (151 mg, 0.336 mmol) in methanol (9 ml). Water (15 ml) was added after 3 h at room temperature. The mixture was extracted with ether (2 x 20 ml) and the organic extracts were washed with brine (30 ml), dried ($MgSO_4$) and concentrated under reduced pressure to leave the monosilyated diol **180** which was used without purification.

TBAF in THF (1 M, 1.00 ml, 1.00 mmol) was added to the monosilylated diol **180** in THF (0.5 ml) and the mixture stirred at room temperature for 50 h. Water (2 ml) was added and the mixture stirred for 1 h then extracted with ether (4 x 5 ml). The organic extracts were washed with brine (10 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ethyl acetate (1 : 1) as eluent, gave the *title compound* **175** (41 mg, 66% from ester **179**) as a colourless oil, $[\alpha]_D$ -15 (*c* = 1.89) (Found: $M^+ + NH_4$, 204.1959. $C_{11}H_{26}NO_2$ requires *M*, 204.1963); ν_{max}/cm^{-1} 3347, 2963, 2929, 1465, 1371, 1131, 1048, 1000 and 872; δ_H (500 MHz, $CDCl_3$) 0.90 and 0.91 (each 3 H, d, *J* 6.5, 1-H_3 and 2-CH_3), 1.15 (3 H, d, *J* 6, 10-H_3), 1.44 - 1.50 (2 H, m, 8-H_2), 1.66 (1 H, m, 2-H), 2.00 - 2.34 (4 H, m, 4-H_2 and 7-H_2), 2.45 (2 H, s, 2 x OH), 3.35 (1 H, ddd, *J* 9, 5.5, 3, 3-H), 3.76 (1 H, m, 9-H) and 5.38 - 5.51 (2 H, m, 5-H and 6-H); δ_C (75 MHz, $CDCl_3$) 17.6, 18.8, 23.5, 23.6, 32.0, 33.6, 38.4, 66.4, 76.1, 126.8 and 131.9; *m/z* (CI, NH_3) 204 (M^+ + 18, 100%), 187 (M^+ + 1, 26) and 169 (M^+ - 17, 14).

(3*S*,9*R*,5*Z*)-9-*tert*-Butyldimethylsilyloxy-2-methyldec-5-en-3-ol 176, (3*S*,9*R*,5*Z*)-3-*tert*-butyldimethylsilyloxy-2-methyldec-5-en-9-ol 177 and (3*S*,9*R*,5*Z*)-3,9-Bis-*tert*-butyldimethylsilyloxy-2-methyldec-5-ene 178

Imidazole (91 mg, 1.338 mmol) and *tert*-butyldimethylsilyl chloride (202 mg, 1.387 mmol) were added to the diol **174** (258 mg, 1.344 mmol) in *N*,*N*-dimethylformamide (1 ml) and the solution stirred at room temperature for 15 h. Water (2 ml) was added and the mixture was extracted with ether (4 x 10 ml). The organic extracts were washed with brine (30 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (8 : 1 to 1 : 2) as eluent gave the *title compound* **178** (49 mg, 9 %) as a colourless oil, $[\alpha]_D$ -0.8 (*c* = 1.67) (Found: M^+ + H, 415.3443. $C_{23}H_{51}O_2Si_2$ requires *M*, 415.3428); ν_{max}/cm^{-1} 2958, 2930, 1472, 1364, 1136, 1006, 1254, 1054, 836 and 774; δ_H (300 MHz, $CDCl_3$) 0.05 and 0.06 (each 3 H, s, $SiCH_3$), 0.08 (6 H, s, 2 x $SiCH_3$), 0.88 and 0.91 (each 3 H, d, *J* 6, 1-H_3 or 2-CH_3], 0.93 [18 H, s, 2 x $SiC(CH_3)_3$], 1.17 (3 H, d, *J* 6, 10-H_3), 1.39 - 1.58 (2 H, m, 8-H_2), 1.73 (1 H, m, 2-H), 1.96 - 2.24 (4 H, m, 4-H_2 and 7-H_2), 3.51 (1 H, m, 3-H), 3.83 (1 H, m, 9-H) and 5.43 (2 H, m, 5-H and 6-H); δ_C (75 MHz, $CDCl_3$) -4.7, -4.6, -4.4, -4.1, 17.1, 18.2, 18.8, 23.7, 23.9, 25.9, 31.9, 32.5, 39.7, 68.4, 76.8, 126.5 and 130.7; *m/z* (CI, NH_3) 433 (12%), 416 (18) and 283 (100). The second fraction was the *title compound* **176** (261 mg, 65%) as a colourless oil, $[\alpha]_D$ -16 (*c* = 1.26) (Found: M^+ + H, 301.2571. $C_{17}H_{37}O_2Si$ requires *M*, 301.2563); ν_{max}/cm^{-1} 3372, 2959, 2930, 1471, 1375, 1255, 1136, 1091, 1004, 836 and 775; δ_H (300 MHz, $CDCl_3$) 0.08 (6 H, s, 2 x $SiCH_3$), 0.93 [9 H, s, $SiC(CH_3)_3$], 0.97 and 0.98 (each 3 H, d, *J* 7, 1-H_3 or 2-CH_3), 1.18 (3 H, d, *J* 10-H_3), 1.40 - 1.60 (3 H, m, 8-H_2 and OH), 1.74 (1 H, m, 2-H), 2.00 - 2.30 (4 H, m, 4-H_2 and 7-H_2), 3.42 (1 H, m, 3-H), 3.84 (1 H, m, 9-H) and 5.45 and 5.61 (each 1 H, dt, *J* 10, 6.5, 5-H or 6-H); δ_C (75 MHz, $CDCl_3$) -4.7, -4.3, 17.5, 18.1, 18.8, 23.7, 23.8, 25.9, 32.2, 33.1, 39.6, 68.2, 76.2, 125.8 and 133.0; *m/z* (CI, NH_3) 318 (M^+ + 18, 10%), 301 (M^+ + 1, 100) and 240 (26). The third fraction was the *title compound* **177** (4 mg, 1%) as a colourless oil (Found: M^+ + H, 301.2570. $C_{17}H_{37}O_2Si$ requires *M*, 301.2563); ν_{max}/cm^{-1} 3344, 2959, 2930, 1471, 1253, 1053, 939, 836 and 774; δ_H (300 MHz, $CDCl_3$) 0.07 and 0.08 (each 3 H, s, $SiCH_3$), 0.90 and 0.92 (each 3 H, d, *J* 7, 1-H_3 or 2-CH_3], 0.93 [9 H, s, $SiC(CH_3)_3$], 1.24 (3 H, d, *J* 6, 10-H_3), 1.49 - 1.61 (3 H, m, 8-H_2 and OH), 1.73 (1 H, m, 2-H), 2.12 - 2.26 (4 H, m, 4-H_2 and 7-H_2), 3.52 (1 H, m, 3-H), 3.52 (1 H, m, 9-H) and 5.48 (2 H, m, 5-H and 6-H); *m/z* (CI, NH_3) 318 (M^+ + 18, 3%), 301 (M^+ + 1, 54) and 169 (100). A fourth fraction contained recovered starting material **174** (12 mg, 5%).

(3*R*,9*R*,5*Z*)-9-*tert*-Butyldimethylsilyloxy-2-methyldec-5-en-3-yl 4-nitrobenzoate 179

Diethyl azodicarboxylate (216 mg, 1.241 mmol) was added to a suspension of the alcohol **176** (187 mg, 0.622 mmol), triphenylphosphine (326 mg, 1.244 mmol) and 4-nitrobenzoic acid (208 mg, 1.246 mmol) in toluene (4.5 ml) at -35 ˚C and the mixture was allowed to warm to room temperature. After 5 h, ether (30 ml) and water (30 ml) were added and the organic phase was washed with brine (30 ml) and dried ($MgSO_4$). Concentration under reduced pressure gave a solid that was absorbed onto silica. Chromatography using petrol : ether (10 : 1) as eluent afforded the *title compound* **179** (170 mg, 61%) as a colourless oil, $[\alpha]_D$ -15 (*c* = 1.01) (Found: M^+ + H, 450.2699. $C_{24}H_{40}NO_5Si$ requires *M*, 450.2676); ν_{max}/cm^{-1} 2961, 1725, 1608, 1531, 1348, 1274, 1101, 1001, 837, 775 and 720; δ_H (300 MHz, $CDCl_3$) 0.07 and 0.08 (each 3 H, s, $SiCH_3$), 0.92 [9 H, s, $SiC(CH_3)_3$], 1.03 and 1.05 (each 3 H, d, *J* 6.5, 1-H_3 and 2-CH_3), 1.13 (3 H, d, *J* 6, 10-H_3), 1.32 - 1.56 (2 H, m, 8-H_2), 1.90 - 2.12 (2 H, m, 4- or 7-H_2), 2.20 (1 H, m, 2-H), 2.38 - 2.60 (2 H, m, 2- or 7-H_2), 3.81 (1 H, m, 9-H), 5.09 (1 H, dt, *J* 7.5, 5, 3-H), 5.40 and 5.50 (each 1 H, dt, *J* 10.5, 7.5, 5-H or 6-H) and 8.21 - 8.35 (4 H, m, ArH); δ_C (75 MHz, $CDCl_3$), -4.7, -4.3, 17.6, 18.1, 18.8, 23.8, 23.8, 25.9, 29.3, 31.3, 39.5, 68.2, 80.0, 123.5, 124.2, 130.7, 132.6, 136.1, 150.5 and 163.3; *m/z* (CI, NH_3) 467 (M^+ + 18, 35%) and 450 (M^+ + 1, 100).

(3*S*,9*R*,5*Z*)-3-[(*R*)-2-Acetoxy-2-phenylacetoxy]-9-*tert*-butyldimethylsilyloxy-2-methyldec-5-ene 181

Following the general procedure, alcohol **176** (22 mg, 0.073 mmol) and (*R*)-2-acetoxyphenylacetic acid, after chromatography using petrol : ether (5 : 1) as eluent gave the *title compound* **181** (33 mg, 95%) as a colourless oil, $[\alpha]_D$ -36 (*c* = 1.48) (Found: M^+ + H, 477.3032. $C_{27}H_{45}O_5Si$ requires *M*, 477.3036); ν_{max}/cm^{-1} 2961, 2930, 1748, 1373, 1233, 1210, 1136, 1179, 1085, 1053, 836 and 775; δ_H (300 MHz, $CDCl_3$) 0.06 and 0.08 (each 3 H, s, $SiCH_3$), 0.93 [9 H, s, $SiC(CH_3)_3$], 0.95 and 0.96 (each 3 H, d, *J* 6.5, 1-H_3 and 2-CH_3), 1.12 (3 H, d, *J* 6, 10-H_3), 1.28 - 1.44 (2 H, m, 8-H_2), 1.81 - 1.98 (3 H, m, 4- or 7-H_2 and 2-H), 2.20 (2 H, m, 2- or 7-H_2), 2.22 (3 H, s, CH_3CO_2), 3.77 (1 H, m, 9-H), 4.82 (1 H, q, *J* 6, 3-H), 4.99 and 5.24 (each 1 H, m, 5-H or 6-H), 5.93 (1 H, s, 2'-H) and 7.38 - 7.54 (5 H, m, ArH); *m/z* (CI, NH_3) 494 (M^+ + 18, 43%), 477 (M^+ + 1, 100) and 151 (78).

(3*S*,9*R*,5*Z*)-3-[(*S*)-2-Acetoxy-2-phenylacetoxy]-9-*tert*-butyldimethylsilyloxy-2-methyldec-5-ene 182

Following the general procedure, alcohol **176** (23 mg, 0.077 mmol) and (*S*)-2-acetoxy-2-phenylacetic acid, after chromatography using petrol : ether (5 : 1) as eluent gave the *title compound* **182** (27 mg, 74%) as a colourless oil, $[\alpha]_D$ -47 (*c* = 1.15) (Found: $M^+ + NH_4$, 494.3303. $C_{27}H_{48}NO_5Si$ requires *M*, 494.3301); ν_{max} /cm^{-1} 2961, 2931, 1749, 1373, 1233, 1180, 1135, 1057, 1002, 836 and 775; δ_H (300 MHz, $CDCl_3$) 0.09 and 0.10 (each 3 H, s, $SiCH_3$), 0.68 and 0.70 (each 3 H, d, *J* 6.5, 1-H_3 or 2-CH_3], 0.93 [9 H, s, $SiC(CH_3)_3$], 1.18 (3 H, d, *J* 6, 10-H_3), 1.43 - 1.60 (2 H, m, 8-H_2), 1.75 (1 H, m, 2-H), 1.96 - 2.21 (2 H, m, 4- or 7-H_2), 2.23 (3 H, s, CH_3CO_2), 2.30 - 2.40 (2 H, m, 4- or 7-H_2), 3.84 (1 H, m, 9-H), 4.80 (1 H, m, 3-H), 5.35 (1 H, dt, *J* 7, 5.5, 5- or 6-H), 5.50 (1 H, m, 5- or 6-H), 5.96 (1 H, s, 2'-H) and 7.38 - 7.53 (5 H, m, ArH); *m/z* (CI, NH_3) 494 (M^+ + 18, 100%), 477 (M^+ + 1, 9) and 380 (68).

(1*S*,7*R*,3*Z*)-1-(4-Methoxyphenyl)oct-3-ene-1,7-diol 183

Following the general procedure, stannane **163** (100 mg, 0.248 mmol), tin(IV) bromide (1.024 M in DCM, 238 µl, 0.248 mmol) and 4-methoxybenzaldehyde (72 µl, 0.251 mmol), after chromatography using petrol : ether (1 : 3 + 1% triethylamine) as eluent gave the *title compound* **183** (29 mg, 47%) as a colourless oil, a 89 : 11 mixture of epimers, $[\alpha]_D$ -49 (*c* = 1.35) (Found: M^+ - OH, 233.1532. $C_{15}H_{21}O_2$ requires *M*, 233.1542); ν_{max}/cm^{-1} 3377, 2927, 1612, 1513, 1247, 1175, 1036 and 833; δ_H (300 MHz, $CDCl_3$) major epimer **183** 1.19 (3 H, d, *J* 6.5, 8-H_3), 1.42 - 1.56 (2 H, m, 6-H_2), 2.04 - 2.33 (4 H, m, 2- or 5-H_2 and 2 x OH), 2.55 (2 H, m, 2- or 5-H_2), 3.82 (1 H, m, 7-H), 3.84 (3 H, s, OCH_3), 4.71 (1 H, t, *J* 6.5, 1-H), 5.40 (1 H, m, 3- or 4-H), 5.54 (1 H, dt, *J* 10.5, 7, 3- or 4-H) and 6.91 and 7.31 (each 2 H, d, *J* 8.5, ArH); minor 1,7-*anti*-epimer 4.65 (1 H, t, *J* 6.5, 1-H); δ_C (75 MHz, $CDCl_3$) major epimer **183** 23.6, 23.9, 37.0, 38.7, 55.3, 67.5, 73.4, 113.7, 125.3, 127.1, 132.7, 136.3 and 159.0; minor 1,7-*anti*-epimer 55.1 and 67.8; *m/z* (CI, NH_3) 268 (M^+ + 18, 2%), 250 (M^+, 23), 233 (M^+ - 17, 100) and 163 (42).

(1*S*,7*R*,3*Z*)-1-(4-Chlorophenyl)oct-3-ene-1,7-diol 184

Following the general procedure, stannane **163** (100 mg, 0.248 mmol), tin(IV) bromide (1.024 M in DCM, 238 µl, 0.248 mmol) and 4-chlorobenzaldehyde (72 µl, 0.251 mmol), after chromatography using petrol : ether (1 : 2 + 1% triethylamine) as eluent gave the *title compound* **184** (45 mg, 71%) as a colourless oil, a 92 : 8 mixture of epimers $[\alpha]_D$ -65 (*c* = 2.35) (Found: $M^+ + NH_4$, 272.1414. $C_{14}H_{23}{}^{35}ClNO_2$ requires *M*, 272.1417); ν_{max}/cm^{-1} 3353, 2965, 1597, 1491, 1407, 1090, 1014 and 830; δ_H (500 MHz, $CDCl_3$) major epimer **184** 1.09 (3 H, d, *J* 7, 8-H_3), 1.39 (2 H, m, 6-H_2), 2.08 and 2.45 (each 2 H, m, 2-H_2 or 5-H_2), 2.75 (2 H, br s, 2 x OH), 3.73 (1 H, m, 7-H), 4.66 (1 H, t, *J* 6, 1-H), 5.27 and 5.48 (each 1 H, dt, *J* 10.5, 7, 3-H or 4-H) and 7.24 - 7.32 (4 H, m, ArH); minor 1,7-*anti*-epimer 4.61 (1 H, dd, *J* 9, 4.5, 1-H); δ_C (75 MHz, $CDCl_3$) major epimer **184** 23.6, 23.9, 37.0, 38.5, 67.5, 72.9, 124.6, 127.3, 128.4, 133.0, 133.3 and 142.6; minor 1,7-*anti*-epimer 37.4, 38.2 and 73.1; *m/z* (CI, NH_3) 274 (M^+ + 18, 20%), 272 (M^+ + 18, 55), 256 (M^+, 30), 254 (M^+, 100), 239 (M^+ - 17, 15) and 237 (M^+ - 17, 38).

(1*S*,7*R*,3*Z*)-1-(2-Naphthyl)oct-3-ene-1,7-diol 185

Following the general procedure, stannane **163** (250 mg, 0.62 mmol), tin(IV) bromide (1.24 M in DCM, 0.5 ml, 0.62 mmol) and 2-naphthaldehyde (97 mg 0.622 mmol), after chromatography using petrol : ether (1 : 1 + 1% triethylamine) as eluent gave the *title compound* **185** (109 mg, 65%) as a colourless oil, a 93 : 7 mixture of epimers, $[\alpha]_D$ -84 (*c* = 0.55) (Found: $M^+ + NH_4$, 288.1968. $C_{18}H_{26}NO_2$ requires *M*, 288.1964); ν_{max} /cm^{-1} 3356, 2964, 2924, 1373, 1125, 1053, 858, 820 and 749; δ_H (300 MHz, $CDCl_3$) major epimer **185** 1.16 (3 H, d, *J* 6, 8-H_3), 1.36 - 1.57 (2 H, m, 6-H_2), 2.09 (2 H, s, 2 x OH), 2.18 (2 H, q, *J*

7, 5-H_2), 2.67 (2 H, t, *J* 7, 2-H_2), 3.78 (1 H, m, 7-H), 4.96 (1 H, t, *J* 6.5, 1-H), 5.46 and 5.58 (each 1 H, dt, *J* 10.5, 7.5, 3-H or 4-H), 7.52 (3 H, m, ArH) and 7.86 (4 H, m, ArH); minor 1,7-*anti*-epimer 4.90 (1 H, m, 1-H); δ_C (75 MHz, $CDCl_3$) 23.6, 23.9, 37.0, 38.6, 67.5, 73.8, 124.1, 124.5, 125.0, 125.8, 126.2, 127.7, 128.0, 128.1, 132.9, 133.1, 133.3 and 141.5; *m/z* (CI, NH_3) 288 (M^+ + 18, 33%), 270 (100) and 253 (36).

(2*R*,8*R*,4*Z*)-Non-4-ene-2,8-diol 186

Following the general procedure, stannane **163** (100 mg, 0.25 mmol), tin(IV) bromide (1.24 M in DCM, 238 µl, 0.248 mmol) and ethanal (72 µl, 0.251 mmol), after chromatography using petrol : ethyl acetate (1 : 2 + 1% triethylamine) as eluent, gave the *title compound* **186** (14 mg, 36%) as a colourless oil, a 90 : 10 mixture of epimers, $[\alpha]_D$ -20 (*c* = 0.50) (Found: $M^+ + NH_4$, 176.1652. $C_9H_{22}NO_2$ requires *M*, 176.1650); ν_{max}/cm^{-1} 3341, 2967, 1374, 1124, 1079, 939 and 845; δ_H (300 MHz, $CDCl_3$) 1.22 and 1.24 (each 3 H, d, *J* 6, 1-H_3 or 9-H_3), 1.54 (2 H, q, *J* 7, 7-H_2), 2.05 (2 H, br s, 2 x OH), 2.17 - 2.32 (4 H, m, 3-H_2 and 6-H_2), 3.79 - 3.94 (2 H, m, 2-H and 8-H) and 5.42 - 5.66 (2 H, m, 4-H and 5-H); δ_C (75 MHz, $CDCl_3$) major epimer **186** 22.8, 23.6, 23.9, 36.8, 38.8, 67.6, 67.6, 125.6 and 132.7; minor 1,7-*anti*-epimer 23.2, 23.5, 36.9, 38.6, 66.8, 67.0, 126.1 and 132.4; *m/z* (CI, NH_3) 176 (M^+ + 18, 100%).

(2*R*,8*R*,5*Z*)-Dec-5-ene-2,8-diol 187

Following the general procedure, stannane **163** (100 mg, 0.248 mmol), tin(IV) bromide (1.024 M in DCM, 238 µl, 0.248 mmol) and propanal (72 µl, 0.251 mmol), after chromatography using petrol : ethyl acetate (1 : 1 + 1% triethylamine), gave the *title compound* **187** (26 mg, 61%) as a colourless oil, a 91 : 9 mixture of epimers, $[\alpha]_D$ -17 (*c* = 0.99) (Found: $M^+ + NH_4$, 190.1807. $C_{10}H_{24}NO_2$ requires *M*, 190.1807); ν_{max}/cm^{-1} 3343, 2965, 1460, 1375, 1118, 1087, 1023 and 974; δ_H (500 MHz, $CDCl_3$) 0.93 (3 H, t, *J* 6.5, 10-H_3), 1.16 (3 H, d, *J* 6.5, 1-H_3), 1.42 - 1.56 (4 H, m, 3-H_2 and 9-H_2), 2.12 - 2.48 (6 H, m, 4-H_2, 7-H_2 and 2 x OH), 3.55 (1 H, tt, *J* 7, 5, 8-H), 3.78 (1 H, m, 2-H) and 5.42 and 5.54 (each 1 H, dt, *J* 11, 8, 5-H or 6-H); δ_C (75 MHz, $CDCl_3$) major epimer **187** 10.2, 23.7, 24.0, 29.6, 34.6, 38.8, 67.5, 72.7, 125.5 and 132.5; minor 1,7-*anti*-epimer 10.1, 23.8, 23.9, 30.0, 34.8, 38.5, 66.7, 126.2 and 132.1; *m/z* (CI, NH_3) 190 (M^+ + 18, 100%) and 173 (M^+ + 1, 4).

(2*R*,8*R*,5*Z*)-10-Methylundec-5-ene-2,8-diol 188

Following the general procedure, stannane **163** (100 mg, 0.25 mmol), tin(IV) bromide (1.23 M in DCM, 24 µl, 0.25 mmol) and 3-methylbutanal (72 µl, 0.25 mmol), after chromatography using petrol : ethyl acetate (1 : 1 + 1% triethylamine) as eluent, gave the *title compound* **188** (29 mg, 58%) as a colourless oil, an 85 : 15 mixture of epimers, $[\alpha]_D$ -7.7 (*c* = 1.15) (Found: $M^+ + NH_4$, 218.2120. $C_{12}H_{28}NO_2$ requires *M*, 218.2120); ν_{max}/cm^{-1} 3345, 2957, 1467, 1369, 1132, 1079 and 842; δ_H (500 MHz, $CDCl_3$) 0.87 and 0.89 (each 3 H, d, *J* 6.5, 11-H_3 and 10-CH_3), 1.15 (3 H, d, *J* 6, 1-H_3), 1.21 (1 H, ddd, *J* 13.5, 8.5, 4, 9-H), 1.39 (1 H, ddd, *J* 14, 8.5, 5.5, 9-H'), 1.47 (2 H, q, *J* 7, 3-H_2), 1.74 (1 H, m, 10-H), 2.06 - 2.28 (6 H, m, 4-H_2, 7-H_2 and 2 x OH), 3.65 - 3.72 (1 H, m, 8-H), 3.77 (1 H, m, 2-H) and 5.41 and 5.52 (each 1 H, m, 5-H or 6-H); δ_C (75 MHz, $CDCl_3$) major epimer **188** 22.2, 23.5, 23.7, 24.0, 24.7, 35.6, 38.8, 46.0, 67.5, 69.3, 125.5 and 132.6; minor 1.7-anti-epimer 35.8, 38.6, 46.5, 66.8, 69.4, 126.1 and 132.2; *m/z* (CI, NH_3) 218 (M^+ + 18, 100%), 201 (M^+ + 1, 18) and 183 (M^+ - 17, 17).

(3*S*,9*R*,5*Z*)-2,2-Dimethyldec-5-ene-3,9-diol 189

Following the general procedure, stannane **163** (100 mg, 0.25 mmol), tin(IV) bromide (1.024M in DCM, 24 µl, 0.25 mmol) and 2,2-dimethylpropanal (72 µl, 0.251 mmol), after chromatography using petrol : ethyl acetate (1 : 1 + 1% triethylamine) as eluent, gave the *title compound* **189** (19 mg, 38%) as a colourless oil, $[\alpha]_D$ -18 (*c* = 0.88) (Found: $M^+ + NH_4$, 218.2120. $C_{12}H_{28}NO_2$ requires *M*, 218.2120); ν_{max}/cm^{-1} 3374, 2962, 1365, 1180, 1130, 1074 and 1008; δ_H (300 MHz, $CDCl_3$) 0.91 [9 H, s, $C(CH_3)_3$], 1.17 (3 H, d, *J* 6, 10-H_3), 1.45 - 1.55 (2 H, m, 8-H_2), 1.80 (2 H, br s, 2 x OH), 2.04 - 2.26 (4 H, m, 4-H_2 and 7-H_2), 3.21 (1 H, m, 3-H), 3.79 (1 H, m, 9-H) and 5.38 - 5.64 (2 H, m, 5-H and 6-H); δ_C (75 MHz, $CDCl_3$) 23.7, 24.1, 25.8, 29.8, 34.8, 38.9, 68.0, 79.1, 127.2 and 132.5; *m/z* (CI, NH_3) 218 (M^+ + 18, 36%), 217 (36), 201 (M^+ + 1, 59), 200 (59), 183 (M^+ - 17, 62), 182 (85) and 100 (100).

(*R*)-6-Methoxyhept-2-enyl(tributyl)stannane 190

The hydroxyheptenylstannane **163** (805 mg, 2.0 mmol) in THF (8 ml) was added to a suspension of sodium hydride (100 mg of a 60% dispersion in mineral oil, 2.50 mmol) in THF (1 ml) at room temperature. After 1 h at 40 °C, methyl iodide (1.42 g, 10.0 mmol) was added at room temperature and the mixture was stirred for 15 h. Water (10 ml) was added and the mixture was extracted with ether (4 x 15 ml). The organic extracts were washed with brine (50 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography using petrol : ether (25 : 1 + 1% triethylamine) afforded the *title compound* **190** (693 mg, 83%) as a colourless oil, a 2 : 1 mixture of (*E*)- and (*Z*)-isomers, $[\alpha]_D$ +1.9 (*c* = 1.13) (Found: M^+ - C_4H_9, 361.1559. $C_{16}H_{33}O^{120}Sn$ requires *M*, 361.1553); ν_{max}/cm^{-1} 2957, 2926, 1464, 1375, 1132, 1089 and 960; δ_H (300 MHz, $CDCl_3$) 0.83 - 0.98 (15 H, m, 3 x Sn$CH_2CH_2CH_2CH_3$), 1.16 (2 H, d, *J* 6, 7-H_3), 1.18 (1 H, d, *J* 6.5, 7-H_3), 1.27 - 1.83 (16 H, m, 1-H_2, 5-H_2 and 3 x $SnCH_2CH_2CH_2CH_3$), 2.05 (2 H, m, 4-H_2), 3.29 - 3.37 (4 H, m, OCH_3 and 6-H), 5.08 (0.33 H, dt, *J* 10.5, 7, 2- or 3-H), 5.22 (0.67 H, dt, *J* 15, 7.5, 2- or 3-H), 5.57 (1 H, m, 2- or 3-H); δ_C (75 MHz, $CDCl_3$) 9.1, 9.3, 13.7, 14.1, 19.0, 19.1, 22.9, 27.4, 28.7, 29.2, 36.3, 36.8, 55.9, 76.3, 76.4, 123.8, 125.2, 128.6 and 129.4; *m/z* (EI) 361 (M^+ - 57, 28%), 359 (26), 291 (95), 289 (60), 235 (91), 233 (65), 179 (100) and 177 (95). A second fraction contained unchanged starting material **161** (93 mg, 12%).

(*R*)-6-Methoxymethoxyhept-2-enyl(tributyl)stannane 191

Di-*iso*propylethylamine (430 mg, 3.333 mmol) and chloromethyl methyl ether (137 mg, 1.702 mmol) were added to the hydroxyalkenylstannane **163** (348 mg, 0.863 mmol) in DCM (2

ml) and the mixture stirred for 15 h. Water (10 ml) and DCM (10 ml) were added, and the organic phase was washed with brine (10 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (40 : 1) as eluent afforded the *title compound* **191** (129 mg, 33%) as a colourless oil, $[\alpha]_D$ -5.0 (*c* = 1.15) (Found: $M^+ - C_4H_9$, 391.1658. $C_{17}H_{35}O_2{}^{120}Sn$ requires *M*, 391.1659); ν_{max}/cm^{-1} 2956, 2926, 1464, 1376, 1147, 1102, 1040, 960 and 920; δ_H (300 MHz, $CDCl_3$) 0.85 - 0.97 (15 H, m, 3 x $SnCH_2CH_2CH_2CH_3$), 1.20 (3 H, d, *J* 6, 7-H_3), 1.26 - 1.83 (16 H, m, 1-H_2, 5-H_2 and 3 x $SnCH_2CH_2CH_2CH_3$), 2.06 (2 H, m, 4-H_2), 3.40 (3 H, s, OCH_3), 3.72 (1 H, m, 6-H), 4.67 and 4.73 (each 1 H, d, *J* 7, OHCHO), 5.24 (1 H, dt, *J* 15, 7.5, 2- or 3-H) and 5.57 (1 H, dt, *J* 15, 8, 2- or 3-H); δ_C (75 MHz, $CDCl_3$) 9.1, 13.7, 14.2, 20.3, 27.4, 28.8, 29.2, 37.6, 55.3, 72.9, 95.0, 125.0 and 129.5; *m/z* (EI) 448 (M^+, 4%), 446 (M^+, 4), 391 (M^+ - 57, 39), 389 (M^+ - 57, 20), 291 (100), 289 (80), 235 (86), 179 (88) and 177 (80).

(*R*)-6-Benzyloxyhept-2-enyl(tributyl)stannane 192

The hydroxyalkenylstannnane **163** (170 mg, 0.422 mmol) in *N*,*N*-dimethylformamide (2 ml) was added to sodium hydride (20 mg of a 60% dispersion in mineral oil, 0.50 mmol) and the mixture stirred at room temperature for 1 h. Tetrabutylammonium iodide (7 mg, 0.02 mmol) and benzyl bromide (80 mg, 0.47 mmol) were added and the mixture was stirred for 50 h. Water (10 ml) was added and the mixture was extracted with ether (4 x 15 ml). The organic extracts were washed with brine (50 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (40 : 1+1% triethylamine) as eluent afforded the *title compound* **192** (101 mg, 49%) as a colourless oil, $[\alpha]_D$ -12 (*c* = 0.79); ν_{max}/cm^{-1} 2957, 2925, 1455, 1375, 1068, 961, 733 and 697; δ_H (300 MHz, $CDCl_3$) 0.86 - 1.00 (15 H, m, 3 x $SnCH_2CH_2CH_2CH_3$), 1.23 (3 H, d, *J* 6.5, 7-H_3), 1.29 - 1.84 (16 H, m, 1-H_2, 5-H_2 and 3 x $SnCH_2CH_2CH_2CH_3$), 2.11 (2 H, m, 4-H_2), 3.57 (1 H, m, 6-H), 4.49 and 4.60 (each 1 H, d, *J* 12, PhHCH), 5.24 and 5.58 (each 1 H, dt, *J* 15.5, 7.5, 2-H or 3-H) and 7.30 - 7.43 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 9.2, 13.8, 14.2, 19.6, 27.4, 28.8, 29.2, 37.2, 70.4, 74.6, 125.3, 127.4, 127.7, 128.3, 129.4 and 139.2. The second fraction included unchanged starting material **163** (66 mg, 39%).

(2*S*,3*S*,9*R*,5*Z*)-2-Benzyloxydec-5-ene-3,9-diol 193

Following the general procedure, stannane **163** (250 mg, 0.62 mmol), tin(IV) bromide (272 mg, 0.62 mmol) in DCM (0.5 ml) and (*S*)-2-benzyloxypropanal (112 mg, 0.68 mmol) in DCM (0.5 ml), after chromatography using petrol : ethyl acetate (1 : 1 + 1% triethylamine) as eluent gave the *title compound* **193** (96 mg, 56%) as a colourless oil, an 85 : 15 mixture of epimers, $[\alpha]_D$ +24 (*c* = 1.24) (Found: $M^+ + NH_4$, 296.2218. $C_{17}H_{30}NO_3$ requires *M*, 296.2225); ν_{max}/cm^{-1} 3399, 2968, 1454, 1374, 1073, 736 and 699; δ_H (500 MHz, $CDCl_3$) major epimer **193** 1.14 and 1.29 (each 3 H, d, *J* 6.5, 1-H_3 or 10-H_3), 1.48 (2 H, q, *J* 7, 8-H_2), 2.06 - 2.38 (6 H, m, 4-H_2, 7-H_2 and 2 x OH), 3.38 - 3.53 (2 H, m, 2- or 3-H and 9-H), 3.76 (1 H, m, 2- or 3-H), 4.42 and 4.64 (each 1 H, d, *J* 11, PhHCH), 5.44 (1 H, dt, *J* 10.5, 8, 5- or 6-H), 5.50 (1 H, dt, *J* 10.5, 5- or 6-H) and 7.24 - 7.35 (5 H, m, ArH); minor epimer **194** 1.175 and 1.188 (each 3 H, d, *J* 6.5, 1-H_3 or 10-H_3); δ_C (75 MHz, $CDCl_3$) major epimer **193** 15.6, 23.6, 23.9, 30.6, 38.7, 67.3, 71.0, 74.7, 77.7, 125.1, 127.6, 128.3, 131.6 and 138.1 minor epimer **194** 23.5, 29.2, 36.2, 67.6, 74.5, 126.2, 127.5 and 132,8; *m/z* (CI, NH_3) 296 (M^+ + 18, 100%) and 279 (M^+ + 1, 22).

(2*S*,3*S*,9*R*,5*Z*)-2-Benzyloxy-9-*tert*-butyldimethylsilyloxydec-5-en-3-ol 195 and (2*S*,3*S*,9*R*,5*Z*)-2-Benzyloxy-3,9-bis-*tert*-butyldimethylsilyloxydec-5-ene 196

Imidazole (30 mg, 0.441 mmol) and *tert*-butyldimethylsilyl chloride (60 mg, 0.395 mmol) were added to the diol **193** (112 mg, 0.403 mmol) in *N*,*N*-dimethylformamide (0.5 ml) and and the mixture stirred at room temperature for 15 h. Water (2 ml) was added and the mixture was extracted with ether (4 x 10 ml). The organic extracts were washed with brine (30 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ether (4 : 1) afforded the *title compound* **196** (9 mg, 5%) as a colourless oil (Found: $M^+ + NH_4$, 524.3956. $C_{29}H_{58}NO_3Si_2$ requires *M*, 524.3955); ν_{max}/cm^{-1} 2930, 1462, 1375, 1255, 1086, 835 and 775; δ_H (300 MHz, $CDCl_3$) -0.03 and 0.00 (each 3 H, s, $SiCH_3$), 0.06 (6 H, s, 2 x $SiCH_3$), 0.84 and 0.87 [each 9 H, s, $SiC(CH_3)_3$], 1.09 and 1.12 (each 3 H, d, *J* 6.5, 1-H_3 and 10-H_3), 1.32 - 1.51 (2 H, m, 8-H_2), 1.91 - 2.37 (4 H, m, 4-H_2 and 7-H_2), 3.46 (1 H, m), 3.62-3.83 (2 H, m), 4.49 and 4.57 (each 1 H, d, *J* 12, PhHCH), 5.40 (2 H, m, 5-H and 6-H) and 7.25 - 7.34 (5 H, m, ArH); *m/z* (CI, NH_3) 524 (M^+ + 17, 100%), 507 (M^+ + 1, 72) and 285 (38). The second fraction was the *title compound* **195** (97 mg, 61%) as a colourless oil, $[\alpha]_D$ +16 (*c* = 1.10) (Found: $M^+ + NH_4$, 410.3090. $C_{23}H_{44}NO_3Si$ requires *M*, 410.3090); ν_{max}/cm^{-1} 3460, 2930, 1461, 1375, 1254, 1137, 1091, 1004, 836 and 775; δ_H (300 MHz, $CDCl_3$) 0.03 (6 H, s, 2 x $SiCH_3$), 0.88 [9 H, s, $SiC(CH_3)_3$], 1.11 and 1.20 (each 3 H, d, *J* 6, 1-H_3 and 10-H_3), 1.35 - 1.56 (2 H, m, 8-H_2), 1.93 - 2.34 (4 H, m, 4-H_2 and 7-H_2), 2.50 (1 H, br s, OH), 3.38 - 3.54 (2 H, m), 3.78 (1 H, m), 4.43 and 4.65 (1 H, d, *J* 11, PhHCH), 5.37 - 5.54 (2 H, m, 5-H and 6-H) and 7.25 - 7.35 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$), -4.7, -4.3, 15.7, 18.2, 23.8, 23.9, 26.0, 30.9, 39.6, 68.2, 71.0, 74.7, 77.7, 125.1, 127.6, 128.3, 131.8 and 138.2; *m/z* (CI, NH_3) 410 (M^+ + 18, 100%) and 393 (M^+ + 1, 43). The third fraction contained unchanged starting material **193** (17 mg, 15%).

(2*S*,3*S*,9*R*,5*Z*)-3-[(*R*)-2-Acetoxy-2-phenylacetoxy]-2-benzyloxy-9-*tert*-butyldimethylsilyloxydec-5-ene 197

Following the general procedure, alcohol **195** (27 mg, 0.069 mmol) and (*R*)-2-acetoxy-2-phenylacetic acid, after chromatography using petrol : ether (4 : 1) as eluent, gave the *title compound* **197** (28 mg, 71%) as a colourless oil, $[\alpha]_D$ -36 (*c* = 1.18) (Found: $M^+ + NH_4$, 586.3565. $C_{33}H_{52}NO_6Si$ requires *M*, 586.3563); ν_{max}/cm^{-1} 2930, 1748, 1373, 1233, 1210, 1197, 1087, 1057, 1004, 836, 775, 737 and 697; δ_H (300 MHz, $CDCl_3$) 0.00 and 0.01 (each 3 H, s, $SiCH_3$), 0.85 [9 H, s, $SiC(CH_3)_3$], 1.05 and 1.17 (each 3 H, d, *J* 6.5, 1-H_3 and 10-H_3), 1.21 - 1.38 (2 H, m, 8-H_2), 1.83 (2 H, q, *J* 8, 4- or 7-H_2), 2.15 (3 H, s, CH_3CO_2), 2.17 - 2.29 (2 H, m, 4- or 7-H_2), 3.59 - 3.73 (2 H, m, 2-H and 9-H), 4.48 and 4.59 (each 1 H, d, *J* 12, PhHCH), 4.84 - 5.01 [2 H, m, 5- or 6-H and 3-H), 5.18 (1 H, m, 5- or 6-H), 5.90

(1 H, s, 2'-H) and 7.23 - 7.47 (10 H, m, ArH); *m/z* (CI, NH_3) 586 (M^+ + 18, 100%), 217 (47) and 77 (51).

(2*S*,3*S*,9*R*,5*Z*)-3-[(*S*)-2-Acetoxy-2-phenylacetoxy]-2-benzyloxy-9-*tert*-butyldimethylsilyloxydec-5-ene 198

Following the general procedure, alcohol **195** (25 mg, 0.064 mmol) and (*S*)-2-acetoxy-2-phenylacetic acid, after chromatography using petrol : ether (4 : 1) as eluent, gave the *title compound* **198** (32 mg, 88%) as a colourless oil, $[\alpha]_D$ +32 (*c* = 1.25) (Found: $M^+ + NH_4$, 586.3572. $C_{33}H_{52}NO_6Si$ requires *M*, 586.3563); ν_{max}/cm^{-1} 2930, 1749, 1374, 1232, 1179, 1086, 1057, 1004, 836, 775, 737 and 697; δ_H (300 MHz, $CDCl_3$) 0.04 (6 H, s, 2 x $SiCH_3$), 0.86 [12 H, m, $SiC(CH_3)_3$ and 1-H_3], 1.10 (3 H, d, *J* 6, 10-H_3), 1.33 - 1.55 (2 H, m, 8-H_2), 1.91 - 2.13 (2 H, m, 4- or 7-H_2), 2.17 (3 H, s, CH_3CO_2), 2.23 - 2.48 (2 H, m, 4- or 7-H_2), 3.47 (1 H, m, 2-H), 3.75 (1 H, m, 9-H), 4.25 and 4.38 (1 H, d, *J* 12, PhHC*H*), 4.96 (1 H, dt, *J* 7.5, 5, 3-H), 5.29 (1 H, m, 5- or 6-H), 5.47 (1 H, dt, *J* 10.5, 7, 5-or 6-H), 5.93 (1 H, s, 2'-H) and 7.16 - 7.49 (10 H, m, ArH); *m/z* (CI, NH_3) 586 (M^+ + 18, 100%).

(2*R*,3*S*,9*R*,5*E*)-2-Benzyloxydec-5-ene-3,9-diol 199 and (2*R*,3*R*,9*R*,5*Z*)-2-Benzyloxydec-5-ene-3,9-diol 200

Following the general procedure, stannane **163** (578 mg, 1.43 mmol), tin(IV) bromide in (1.24 M in DCM, 1.15 ml, 1.43 mmol) and (*R*)-2-benzyloxypropanal (235 mg, 1.43 mmol) in DCM (1 ml) gave the title compounds (267 mg, 67%) as a colourless oil, ratio **199** : **200** = 65 : 35 Partial separation was achieved by chromatography using petrol : ethyl acetate (3 : 1) as eluent to give the *title compound* **199**, as a colourless oil, $[\alpha]_D$ -37 (*c* = 1.11) (Found: $M^+ + NH_4$, 296.2252. $C_{17}H_{30}NO_3$ requires *M*, 296.2226; ν_{max}/cm^{-1} 3389, 2929, 1496, 1454, 1374, 1090, 1029, 974, 738 and 699; δ_H (300 MHz, $CDCl_3$) 1.22 and 1.23 (each 3 H, d, *J* 6, 1-H_3 and 10-H_3), 1.50 - 1.60 (2 H, m, 8-H_2), 2.01 (2 H, br s, 2 x OH), 2.09 - 2.26 (4 H, m, 4-H_2 and 7-H_2), 3.54 (1 H, qd, *J* 6, 4, 2-H), 3.77 (1 H, ddd, *J* 7.5, 5.5, 4, 3-H), 3.83 (1 H, m, 9-H), 4.54 and 4.65 (each 1 H, d, *J* 11.5, PhHC*H*), 5.49 (1 H, dt, *J* 15, 7, 5- or 6-H), 5.60 (1 H, dt, *J* 15, 6, 5- or 6-H) and 7.30 - 7.41 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 14.4, 24.0, 29.6, 36.2, 39.1, 68.1, 71.2, 73.3, 77.6, 127.0, 128.2, 128.9, 133.8 and 139.0; *m/z* (CI, NH_3) 296 (M^+ + 18, 100%), 279 (M^+ + 1, 83) and 171 (31). The second fraction was the *title compound* **200**, as a colourless oil, $[\alpha]_D$ -55 (*c* = 1.36) (Found: $M^+ + NH_4$, 296.2229. $C_{17}H_{30}NO_3$ requires *M*, 296.2226); ν_{max}/cm^{-1} 3391, 2968, 1454, 1374, 1073, 1029, 736 and 699; δ_H (300 MHz, $CDCl_3$) 1.20 and 1.25 (each 3 H, d, *J* 6, 1-H_3 or 10-H_3), 1.53 (2 H, m, 8-H_2), 2.04 - 2.43 (4 H, m, 4-H_2 and 7-H_2), 2.63 (2 H, br s, 2 x OH), 3.42 - 3.58 (2 H, m), 3.83 (1 H, m), 4.48 and 4.70 (each 1 H, d, *J* 11.5, PhHC*H*), 5.52 (2 H, m, 5-H and 6-H) and 7.28 - 7.42 (5 H, m, ArH); δ_C (75 MHz, $CDCl_3$) 15.5, 23.5, 30.7, 38.4, 66.3, 71.1, 74.8, 78.2, 126.1, 127.8, 128.4, 131.7 and 138.3; *m/z* (CI, NH_3) 296 (M^+ + 18, 100%).

Imidazole (27 mg, 0.397 mmol) and *tert*-butyldimethylsilyl chloride (55 mg, 0.365 mmol) were added to the diol **199** (101 mg, 0.36 mmol) in *N*,*N*-dimethylformamide (600 µl) and the mixture stirred at room temperature for 15 h. Water (2 ml) was added and the mixture was extracted with ether (4 x 10 ml). The organic extracts were washed with brine (30 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using petrol : ethyl acetate (4 : 1 to 2 : 1) gave the silyl ether **201** (78 mg, 55%) as a colourless oil; δ_H (300 MHz, $CDCl_3$) 0.08 (6 H, s, 2 x $SiCH_3$), 0.93 [9 H, s, $SiC(CH_3)_3$], 1.16 and 1.23 (each 3 H, d, *J* 6, 1-H_3 or 10-H_3), 1.40 - 1.62 (2 H, m, 8-H_2), 1.87 (1 H, br s, OH), 1.97 - 2.32 (4 H, m, 2 x 4-H_2 and 7-H_2), 3.54 (1 H, m), 3.73 - 3.87 (2 H, m), 4.55 and 4.65 (each 1 H, d, *J* 12, PhHC*H*), 5.40 - 5.64 (2 H, m, 5-H and 6-H) and 7.30 - 7.42 (5 H, m, ArH). The second fraction was the unchanged starting material **199** (35 mg, 35%).

(2*R*,3S,9*R*,5*E*)-3-[(*R*)-2-Acetoxy-2-phenylacetoxy]-2-benzyloxy-9-*tert*-butyldimethylsilyloxydec-5-ene 202

Following the general procedure, alcohol **201** (30 mg, 0.077 mmol) and (*R*)-2-acetoxy-2-phenylacetic acid, after chromatography using petrol : ether (4 : 1) as eluent gave the *title compound* **202** (34 mg, 78%) as a colourless oil, $[\alpha]_D$ -40 (*c* = 1.39) (Found: $M^+ + NH_4$, 586.3578. $C_{33}H_{52}NO_6Si$ requires *M*, 586.3564); ν_{max}/cm^{-1} 2930, 1748, 1374, 1233, 1179, 1086, 1057, 1005, 836, 775, 737 and 697; δ_H (300 MHz, $CDCl_3$) 0.09 and 0.10 (each 3 H, s, $SiCH_3$), 0.94 [9 H, s, $SiC(CH_3)_3$], 1.13 and 1.24 (each 3 H, d, *J* 6, 1-H_3 and 10-H_3), 1.28 - 1.45 (2 H, m, 8-H_2), 1.74 - 1.95 (2 H, m, 4- or 7-H_2), 2.20 - 2.30 (5 H, m, 4- or 7-H_2 and CH_3CO_2), 3.64-3.83 (2 H, m, 9-H and 2-H, 4.62 (2 H, s, $PhCH_2$), 4.94 - 5.06 [2 H, m, 5- or 6-H and 3-H), 5.23 (1 H, dt, *J* 15, 6, 5- or 6-H), 5.96 (1 H, s, 2'-H) and 7.30 - 7.56 (10 H, m, ArH); *m/z* (CI, NH_3) 586 (M^+ + 18, 100%).

(2*R*,3S,9*R*,5*E*)-3-[(*S*)-2-Acetoxy-2-phenylacetoxy]-2-benzyloxy-9-*tert*-butyldimethylsilyloxydec-5-ene 203

Following the general procedure, alcohol **201** (30 mg, 0.077 mmol) and (*S*)-2-acetoxy-2-phenylacetic acid, after chromatography using petrol : ether (4 : 1) as eluent gave the *title compound* **203** (33 mg, 75%) as a colourless oil, $[\alpha]_D$ +27 (*c* = 1.46) (Found: $M^+ + NH_4$, 586.3580. $C_{33}H_{52}NO_6Si$ requires *M*, 586.3564); ν_{max}/cm^{-1} 2930, 1749, 1374, 1232, 1210, 1179, 1085, 1057, 1005, 836, 775 and 736; δ_H (300 MHz, $CDCl_3$) 0.10 (6 H, s, 2 x $SiCH_3$), 0.93 [9 H, s, $SiC(CH_3)_3$], 1.00 (3 H, d, *J* 6.5, 1-H_3), 1.16 (3 H, d, *J* 6, 10-H_3), 1.41 - 1.58 (2 H, m, 8-H_2), 1.93-2.11 (2 H, m, 4- or 7-H_2), 2.21 (3 H, s, CH_3CO_2), 2.36 - 2.45 (2 H, m, 4- or 7-H_2), 3.51 (1 H, m, 2-H), 3.82 (1 H, m, 9-H), 4.33 and 4.38 (each 1 H, d, *J* 11.5, PhHC*H*), 5.03 (1 H, m, 3-H), 5.37 and 5.56 (each 1 H, dt, *J* 15.5, 7, 5-H or 6-H), 5.99 (1 H, s, 2'-H) and 7.20 - 7.56 (10 H, m, ArH); *m/z* (CI, NH_3) 586 (M^+ + 18, 93%), 528 (8) and 69 (100).

(2*R*,3*R*,9*R*,5*Z*)-2-Benzyloxy-9-*tert*-butyldimethylsilyloxydec-5-en-3-ol 204

Imidazole (14 mg, 0.21 mmol) and *tert*-butyldimethylsilyl chloride (28 mg, 0.19 mmol) were added to the diol **200** (52 mg, 0.187 mmol) in *N*,*N*-dimethylformamide (0.3 □l) and the mixture stirred at room temperature for 15 h. Water (2 ml) was added and the mixture extracted with ether (4 x 10 ml). The organic extracts were washed with brine (30 ml), dried ($MgSO_4$) and concentrated

under reduced pressure. Chromatography of the residue using petrol : ether (4 : 1) as eluent afforded the *title compound* **204** (24 mg, 33%) as a colourless oil, $[\alpha]_D$ -40 (*c* = 0.41) (Found: M^+ + H, 393.2824. $C_{23}H_{41}O_3Si$ requires *M*, 393.2825); ν_{max}/cm^{-1} 3421, 2957, 2929, 1375, 1254, 1208, 1090, 1073, 1030, 1004, 836, 775, 735 and 698; δ_H (300 MHz, $CDCl_3$) 0.05 and 0.06 (each 3 H, s, $SiCH_3$), 0.93 [9 H, s, $SiC(CH_3)_3$], 1.17 and 1.25 (each 3 H, d, *J* 6, 1-H_3 and 10-H_3), 1.40-1.59 (2 H, m, 8-H_2), 1.96-2.40 (5 H, m, 4-H_2, 7-H_2 and OH), 3.44-3.57 (2 H, m), 3.83 (1 H, m), 4.49 and 4.70 (each 1 H, d, *J* 11.5, PhHC*H*), 5.46 - 5.60 (2 H, m, 5-H and 6-H) and 7.35 - 7.42 (5 H, m, ArH); *m/z* (CI, NH_3) 410 (M^+ + 18, 58%), 393 (M^+ + 1, 100) and 296 (77). A second fraction contained unchanged starting material **200** (21 mg, 40%).

(2*R*,3*R*,9*R*,5*Z*)-3-[(*R*)-2-Acetoxy-2-phenylacetoxy]-2-benzyloxy-9-*tert*-butyldimethylsilyloxydec-5-ene 205

Following the general procedure, alcohol **204** (14 mg, 0.036 mmol) and (*R*)-2-acetoxy-2-phenylacetic acid, after chromatography using petrol : ether (4 : 1) as eluent, gave the *title compound* **205** (18 mg, 89%) as a colourless oil, $[\alpha]_D$ -49 (*c* = 0.6) (Found: $M^+ + NH_4$, 586.3584. $C_{33}H_{52}NO_6Si$ requires *M*, 586.3564); ν_{max}/cm^{-1} 2930, 1748, 1373, 1232, 1210, 1179, 1057, 1006, 836, 775, 736 and 697; δ_H (300 MHz, $CDCl_3$) 0.08 (6 H, s, 2 x $SiCH_3$), 0.92 [12 H, m, 1-H_3 and $SiC(CH_3)_3$], 1.16 (3 H, d, *J* 6, 10-H_3), 1.49 (2 H, m, 8-H_2), 2.00 - 2.25 (2 H, m, 4- or 7-H_2), 2.21 (3 H, s, CH_3CO_2), 2.40 - 2.50 (2 H, m, 4- or 7-H_2), 3.52 (1 H, m, 2-H), 3.83 (1 H, m, 9-H), 4.31 and 4.43 (each 1 H, d, *J* 12, PhHC*H*), 5.01 (1 H, dt, *J* 6.5, 4, 3-H), 5.36 and 5.53 (each 1 H, m, 5-H or 6-H), 5.98 (1 H, s, 2'-H) and 7.22 - 7.55 (10 H, m, ArH); *m/z* (CI, NH_3) 586 (M^+ + 18, 100%).

(2*R*,3*R*,9*R*,5*Z*)-3-[(*S*)-2-Acetoxy-2-phenylacetoxy]-2-benzyloxy-9-*tert*-butyldimethylsilyloxydec-5-ene 206

Following the general procedure, alcohol **204** (10 mg, 0.036 mmol) and (*S*)-2-acetoxy-2-phenylacetic acid, after chromatography using petrol : ether (4 : 1) as eluent, gave the *title compound* **206** (13 mg, 88%) as a colourless oil, $[\alpha]_D$ +18 (*c* = 0.46) (Found: $M^+ + NH_4$, 586.3568. $C_{33}H_{52}NO_6Si$ requires *M*, 586.3564); ν_{max}/cm^{-1} 2929, 1747, 1373, 1233, 1210, 1179, 1057, 1004, 836, 775, 737 and 697; δ_H (300 MHz, $CDCl_3$) 0.06 and 0.08 (each 3 H, s, $SiCH_3$), 0.91 [9 H, s, $SiC(CH_3)_3$], 1.11 and 1.22 (each 3 H, d, *J* 6, 1-H_3 or 10-H_3), 1.28 - 1.42 (2 H, m, 8-H_2), 1.76 and 2.00 (each 1 H, m, 4- or 7-H), 2.21 (3 H, s, CH_3CO_2), 2.25 - 2.33 (2 H, m, 4- or 7-H_2), 3.66 - 3.76 (2 H, m, 2-H and 9-H), 4.53 and 4.65 (each 1 H, d, *J* 12, PhHC*H*), 4.91 - 5.08 (2 H, m, 3-H and 5- or 6-H), 5.24 (1 H, m, 5- or 6-H), 5.95 (1 H, s, 2'-H) and 7.29 - 7.52 (10 H, m, ArH); *m/z* (CI, NH_3) 586 (M^+ + 18, 100%).

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