# Total synthesis of epothilones using functionalised allylstannanes for remote stereocontrol\# 

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## Supplementary Experimental Data

## General experimental procedures

${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra were recorded on Varian Unity 500, Varian Unity Inova 400 and Varian Unity Inova 300 spectrometers with residual non-deuterated solvent as the internal standard. IR spectra were recorded on an ATI Mattson Genesis FTIR as thin films produced by evaporation of a DCM solution on sodium chloride plates unless otherwise stated. Mass spectra were recorded on Fison VG Trio 2000 and Kratos Concept spectrometers. Chemical ionisation (CI) was performed using ammonia. Typical clusters of isoptope peaks were observed for tin containing compounds. Only those corresponding to ${ }^{120} \mathrm{Sn}$ are reported. Chromatography refers to flash column chromatography using Merck silica gel 60H (230-300 mesh).
Tetrahydrofuran (THF) was dried and distilled from sodium metal using benzophenone as an indicator under an atmosphere of nitrogen. Dichloromethane (DCM) was dried and distilled from calcium hydride under an atmosphere of nitrogen. Ether refers to diethyl ether, which was dried and distilled from sodium metal using benzophenone as an indicator under an atmosphere of nitrogen. Light petroleum refers to the fraction of petroleum ether distilled between $40-60^{\circ} \mathrm{C}$. Benzene and hexane were dried over sodium metal. Butyllithium ( 1.6 M in hexanes) was titrated against a solution of propan-2-ol in xylene with $2,2^{\prime}$-bipyridine as an indicator. Triethylamine and diisopropylamine were dried over potassium hydroxide pellets. Brine refers to saturated aqueous sodium chloride. Anhydrous cerium(III) chloride was prepared by heating the heptahydrate overnight at $80^{\circ} \mathrm{C}$ under reduced pressure and was stored under an atmosphere of $\mathrm{N}_{2}$.

## (4R)-2,2-Dimethyl-4-iodomethyl-1,3-dioxolane $15{ }^{8}$

Imidazole ( $20.70 \mathrm{~g}, 0.303 \mathrm{~mol}$ ), triphenylphosphine ( $39.85 \mathrm{~g}, 0.152 \mathrm{~mol}$ ) and iodine ( $38.58 \mathrm{~g}, 0.152 \mathrm{~mol}$ ) were added to the 4 -hydroxymethyl-1,3-dioxolane ( $20.05 \mathrm{~g}, 0.152 \mathrm{~mol}$ ) in THF ( 500 mL ) and the resulting dark purple solution stirred for 16 h . Saturated aqueous sodium bicarbonate ( 500 mL ) and ether ( 500 mL ) were added and the aqueous layer extracted with ether. The organic extracts were washed with water and brine, dried $\left(\mathrm{MgSO}_{4}\right)$ and concentrated under reduced pressure. The residue was triturated with ice-cold ether ( 200 mL ) and the precipitate removed by filtration. The filtrate was concentrated under reduced pressure in a cold-water bath and chromatography of the residue eluting with ethyl acetate-petrol ( $50: 1$ to $35: 1$ ) gave the title compound 15 ( 32.45 g , $88 \%$ ) as a colourless oil (Found: $\mathrm{M}^{+}+\mathrm{H}$, 242.9889. $\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{IO}_{2}$ requires $\mathrm{M}, 242.9884$ ); [ $\left.\alpha\right]_{\mathrm{D}}{ }^{20}+31$ (c 5.3 in EtOH), lit. ${ }^{8}[\alpha]_{\mathrm{D}^{22}}+35.5$ ( $c 13$ in EtOH); $u_{\text {max }} / \mathrm{cm}^{-1} 1372,1225,1150,1059$ and $844 ; \delta_{\mathrm{H}}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 1.33$ and 1.44 (each 3 H , s, $\left.2-\mathrm{CH}_{3}\right), 3.12(1 \mathrm{H}, \mathrm{dd}, J 10.0,8.0,4-\mathrm{CH}), 3.24(1 \mathrm{H}, \mathrm{dd}, J 10.0,4.5,4-\mathrm{CH}), 3.78(1 \mathrm{H}, \mathrm{dd} J 8.5,5.5,5-\mathrm{H}) 4.12(1 \mathrm{H}, \mathrm{dd} J 8.5,6.0,5-\mathrm{H})$ and $4.26(1 \mathrm{H}, \mathrm{m}, 4-\mathrm{H}) ; \delta \mathrm{c}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 6.7,25.5,27.1,69.5,75.5$ and 110.3; $\mathrm{m} / \mathrm{z}(\mathrm{CI}) 243\left(\mathrm{M}^{+}+1,100 \%\right)$ and 227 (16).

## (3RS,5S)-5,6-(Dimethylmethylene)dioxy-2-methylhex-1-en-3-yl phenyl sulfone 17

$n$-Butyllithium in hexane ( $2.5 \mathrm{M}, 50.8 \mathrm{~mL}, 0.127 \mathrm{~mol}$ ) was added dropwise to the sulfone $\mathbf{1 6}(23.79 \mathrm{~g}, 0.121 \mathrm{~mol}) \mathrm{in} \mathrm{THF}(230 \mathrm{~mL})$ at $-78{ }^{\circ} \mathrm{C}$ and the solution stirred for 15 min before DMPU ( $58.40 \mathrm{~mL}, 0.484 \mathrm{~mol}$ ) was added. After 15 min , iodide $\mathbf{1 5}$ ( $29.38 \mathrm{~g}, 0.121$ mol ) was added and the solution stirred for 4 h . Saturated aqueous ammonium chloride was added and the mixture allowed to warm to room temperature. The aqueous phase was extracted with ether and the organic extracts washed with brine, dried $\left(\mathrm{MgSO}_{4}\right)$ and concentrated under reduced pressure. Chromatography of the residue eluting with petrol-ethyl acetate (25:1) gave the title compound $\mathbf{1 7}$ ( $32.26 \mathrm{~g}, 86 \%$ ) as a $75: 25$ mixture of diastereoisomers ( ${ }^{1} \mathrm{H}$ NMR) as a colourless oil (Found: $\mathrm{M}^{+}+\mathrm{NH}_{4}, 328.1589$. $\mathrm{C}_{16} \mathrm{H}_{26} \mathrm{NO}_{4} \mathrm{~S}$ requires $M, 328.1582$ ); $v_{\max } / \mathrm{cm}^{-1} 1447,1375,1307,1148,1081$ and $1062 ; \delta_{\mathrm{H}}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.$ ) major diastereoisomer $1.32(6 \mathrm{H}, \mathrm{s}, 2 \mathrm{x} \mathrm{CH} 3), 1.82\left(3 \mathrm{H}, \mathrm{s}, 2-\mathrm{CH}_{3}\right), 2.05$ and 2.23 (each $\left.1 \mathrm{H}, \mathrm{m}, 4-\mathrm{H}\right), 3.61(1 \mathrm{H}, \mathrm{m}, 6-\mathrm{H}), 3.92(1 \mathrm{H}, \mathrm{dd}, J 12.0,3.0,3-\mathrm{H}), 4.04(2$ $\mathrm{H}, \mathrm{m}, 5-\mathrm{H}, 6-\mathrm{H}), 4.92$ and 5.19 (each $1 \mathrm{H}, \mathrm{s}, 1-\mathrm{H}), 7.58(2 \mathrm{H}, \mathrm{m}, \mathrm{ArH}), 7.68(1 \mathrm{H}, \mathrm{m}, \mathrm{ArH})$ and $7.90(2 \mathrm{H}, \mathrm{m}, \mathrm{ArH})$; minor diastereoisomer 1.35 and 1.42 (each $3 \mathrm{H}, \mathrm{s}, \mathrm{CH}_{3}$ ), $1.82\left(3 \mathrm{H}, \mathrm{s}, 2-\mathrm{CH}_{3}\right)$ and 4.73 and 5.01 (each $1 \mathrm{H}, \mathrm{s}, 1-\mathrm{H}$ ); $\delta \mathrm{c}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.$ ) major diastereomer 21.2, 25.6, 26.9, 31.0, 68.6, 69.1, 72.3, 109.2, 120.5, 128.8, 129.0, 133.5, 136.1 and 137.5; minor diastereoisomer 20.3, 26.8, 31.2, 68.9, 69.3, 73.6, 120.2 and 133.6; $m / z(\mathrm{CI}) 328\left(\mathrm{M}^{+}+18,100 \%\right), 311\left(\mathrm{M}^{+}+1,75\right)$ and 253 (67).

## (2S,4RS)-5-Methyl-4-(phenylsulfonyl)hex-5-ene-1,2-diol 18

Amberlyst-15 ion exchange resin (ca. 1 g ) was added to the sulfone $\mathbf{1 7}$ ( $28.02 \mathrm{~g}, 0.090 \mathrm{~mol}$ ) in methanol ( 200 mL ). The mixture was stirred for 4 h then filtered through a plug of celite and concentrated under reduced pressure. Chromatography of the residue, eluting with light petroleum-ethyl acetate (1:1), gave the title compound $\mathbf{1 8}$ ( $23.43 \mathrm{~g}, 96 \%$ ) as a $75: 25$ mixture of diastereoisomers ( ${ }^{1} \mathrm{H} N M R$ ), a white solid (Found: $\mathrm{M}^{+}+\mathrm{NH}_{4}$, 288.1265. $\mathrm{C}_{13} \mathrm{H}_{22} \mathrm{NO}_{4} \mathrm{~S}$ requires $M, 288.1269$ ); $\mathrm{U}_{\max } / \mathrm{cm}^{-1} 3300-3400,1642,1447,1301$, $1144,1083,914,757,721$ and 690 ; $\delta_{\mathrm{H}}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.$ ) major diastereoisomer 1.78 ( $3 \mathrm{H}, \mathrm{s}, 5-\mathrm{CH} 3$ ), 1.98 and 2.24 (each $1 \mathrm{H}, \mathrm{m}, 3-$ H), $2.79(1 \mathrm{H}$, br. t, $J 5.5, \mathrm{OH}), 3.16(1 \mathrm{H}, \mathrm{br} . \mathrm{d}, J 5.0, \mathrm{OH}), 3.46-3.74(3 \mathrm{H}, \mathrm{m}, 1-\mathrm{H} 2,2-\mathrm{H}), 4.04(1 \mathrm{H}, \mathrm{dd}, J 11.5$ and $3.5,4-\mathrm{H}), 4.84$ and 5.10 (each $1 \mathrm{H}, \mathrm{s}, 6-\mathrm{H}), 7.58(2 \mathrm{H}, \mathrm{m}, \mathrm{ArH}), 7.68(1 \mathrm{H}, \mathrm{m}, \mathrm{ArH})$ and $7.89(2 \mathrm{H}, \mathrm{m}, \mathrm{ArH})$; minor diastereoisomer 4.74 and 4.98 (each $1 \mathrm{H}, \mathrm{s}, 6-$ H); $\delta c\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.$ ) major diastereoisomer 20.6, 29.3, 66.7, 68.8, 69.7, 120.8, 128.8, 129.0, 133.6, 136.4 and 137.1; minor diastereoisomer 20.3, 30.4, 65.8, 68.6, 120.2, 128.7, 129.0, 133.7 and 138.0; $m / z(C I) 288\left(\mathrm{M}^{+}+18,100 \%\right), 271\left(\mathrm{M}^{+}+1,12\right)$ and 148 (15).

Imidazole ( $25.33 \mathrm{~g}, 0.372 \mathrm{~mol}$ ), DMAP ( $1.10 \mathrm{~g}, 9.70 \mathrm{mmol}$ ) and tert-butyldimethylsilyl chloride ( $14.58 \mathrm{~g}, 0.097 \mathrm{~mol}$ ) were added to the diol $18(25.0 \mathrm{~g}, 0.093 \mathrm{~mol})$ in $\operatorname{DCM}(200 \mathrm{~mL})$ at $0^{\circ} \mathrm{C}$. The reaction was allowed to warm to room temperature and stirred for 6 h . Saturated aqueous ammonium chloride was added and the aqueous phase extracted with ether. The organic extracts were washed with brine, dried $\left(\mathrm{MgSO}_{4}\right)$ and concentrated under reduced pressure. Chromatography of the residue, eluting with petrol-ethyl acetate (6:1), gave the title compound $19(32.94 \mathrm{~g}, 90 \%)$ as a $75: 25$ mixture of diastereoisomers, a clear viscous oil that crystallised on standing (Found: $\mathrm{M}^{+}+\mathrm{NH}_{4}, 402.2138 . \mathrm{C}_{19} \mathrm{H}_{36} \mathrm{NO}_{4} \mathrm{SiS}$ requires $M, 402.2134$ ); $\mathrm{U}_{\text {max }} / \mathrm{cm}^{-1} 3538,1471,1447,1305,1256,1146,1084$ and 838; $\delta_{\mathrm{H}}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ major diastereoisomer $0.06\left[6 \mathrm{H}, \mathrm{s}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right], 0.88\left[9 \mathrm{H}, \mathrm{s}, \mathrm{SiC}\left(\mathrm{CH}_{3}\right)_{3}\right], 1.81\left(3 \mathrm{H}, \mathrm{s}, 5-\mathrm{CH}_{3}\right), 1.92(1 \mathrm{H}$, ddd, J14.0, 12.0, 2.0, 3-H), $2.09(1 \mathrm{H}$, ddd, J 14.0, 10.5, 3.0, 3-H), $2.24(1 \mathrm{H}, \mathrm{br} . \mathrm{d}, J 5.0,0 \mathrm{H}$ ), 3.46 ( $3 \mathrm{H}, \mathrm{dd}, J 9.5,6.01-\mathrm{H}$ ), 3.54 ( $1 \mathrm{H}, \mathrm{m}$, $2-\mathrm{H}), 3.62(1 \mathrm{H}, \mathrm{dd}, J 9.5,3.5,1-\mathrm{H}), 3.99(1 \mathrm{H}, \mathrm{dd}, J 12.0,3.0,4-\mathrm{H}$ ), 4.87 and 5.12 (each $1 \mathrm{H}, \mathrm{s}, 6-\mathrm{H}), 7.53(2 \mathrm{H}, \mathrm{m}, \mathrm{ArH}), 7.64(1 \mathrm{H}, \mathrm{m}$, ArH ) and $7.87(2 \mathrm{H}, \mathrm{m}, \mathrm{ArH})$; minor diastereoisomer 4.72 and 4.99 (each $1 \mathrm{H}, \mathrm{s}, 6-\mathrm{H})$; $\delta \mathrm{c}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ major diastereoisomer -5.5 , $18.2,20.9,25.8,29.6,67.0,68.2,68.6,120.6,128.7,129.0,133.5,136.4$ and $137.6 ; m / z(\mathrm{CI}) 402\left(\mathrm{M}^{+}+18,100 \%\right)$ and $385\left(\mathrm{M}^{+}+1\right.$, 23).
(5S,2EZ)-6-tert-Butyldimethylsilyloxy-5-hydroxy-2-methylhex-2-enyl(tributyl)stannane 20
Tributyltin hydride ( $2.36 \mathrm{~mL}, 9.07 \mathrm{mmol}$ ) and AIBN ( 40 mg ) were added to the hydroxy sulfone 19 ( $1.75 \mathrm{~g}, 4.54 \mathrm{mmol}$ ) in benzene $(20 \mathrm{~mL})$ and the solution was degassed then heated under reflux for 1.5 h . After concentration under reduced pressure, chromatography of the residue eluting with ethyl acetate-petrol (75:1) with $1 \%$ TEA, gave the title compound 20 ( $1.50 \mathrm{~g}, 62 \%$ ), a 1:1 mixture of $(E)$ - and ( $Z$ )-isomers, as a clear, colourless oil (Found: $\mathrm{M}^{+}-\mathrm{C}_{4} \mathrm{H} 9,477.2212$. $\mathrm{C}_{21} \mathrm{H}_{45} \mathrm{O}_{2} \mathrm{Si}^{12}{ }^{12} \mathrm{Sn}$ requires $M, 477.2210$ ); $U_{\max } / \mathrm{cm}^{-1} 3477,1654,1463,1254,1112,1074,838$ and 778 ; $\delta \mathrm{H}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 0.00\left[6 \mathrm{H}, \mathrm{s}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right], 0.82\left(15 \mathrm{H}, \mathrm{m}, 3 \times \mathrm{CH}_{3} \mathrm{CH}_{2}\right)$, $0.83\left[9 \mathrm{H}, \mathrm{s}, \mathrm{SiC}\left(\mathrm{CH}_{3}\right)_{3}\right], 1.21$ and 1.39 (each $6 \mathrm{H}, \mathrm{m}, 3 \times \mathrm{CH}$ ), 1.52 and 1.60 (each $1.5 \mathrm{H}, \mathrm{m}, 2-\mathrm{CH}_{3}$ ), 1.64 and 1.68 (each $1 \mathrm{H}, \mathrm{s}, 1-\mathrm{H}$ ), $2.07\left(2 \mathrm{H}, \mathrm{m}, 4-\mathrm{H}_{2}\right), 2.29$ and 2.32 (each $\left.0.5 \mathrm{H}, \mathrm{d}, J 3.6, \mathrm{OH}\right), 3.37(1 \mathrm{H}, \mathrm{m}, 6-\mathrm{H}), 3.56(2 \mathrm{H}, \mathrm{m}, 6-\mathrm{H}, 5-\mathrm{H}), 4.79(0.5 \mathrm{H}, \mathrm{t}, J 7.0,3-\mathrm{H})$ and $4.91(0.5 \mathrm{H}, \mathrm{t}, \mathrm{J} 8.0,3-\mathrm{H}) ; \delta \mathrm{c}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)-5.5,-5.4,9.4,9.6,13.6(2), 15.5,18.2,18.6,22.2,25.8,27.3,29.0,29.1,32.0,32.1,66.5$, 66.7, 71.9, 72.1, 114.4, 114.8, 138.0 and 138.1; $m / z(C I) 535\left(\mathrm{M}^{+}+1,5 \%\right), 477\left(\mathrm{M}^{+}-57,5\right), 308$ (100) and 245 (48).

## (2S)-1-tert-Butyldimethylsilyloxy-5-methylhex-5-en-2-ol 21

Stannane $\mathbf{2 0}$ ( $300 \mathrm{mg}, 0.562 \mathrm{mmol}$ ) was added to a slurry of silica (ca. 0.5 g of Merck silica gel $60 \mathrm{H}(40-63 \mu, 230-400 \mathrm{mesh}$ ) in DCM $(3.0 \mathrm{~mL})$ and the mixture stirred for 4 h at room temperature. After being filtered, the filtrate was concentrated under reduced pressure. Chromatography of the residue using light petroleum-ethyl acetate (25:1) with $1 \%$ TEA gave the title compound 21 (136 $\mathrm{mg}, 100 \%$ ) as a colourless oil; $[\alpha]_{\mathrm{D}}{ }^{18}-18.4$ (c 1.8, EtOH); (Found: $\mathrm{M}^{+}+\mathrm{H}$, 245.1939. $\mathrm{C}_{13} \mathrm{H}_{29} \mathrm{O}_{2} \mathrm{Si}$ requires $M, 245.1937$ ); $\mathrm{U}_{\max } / \mathrm{cm}^{-1}$ $3332,1465,1255,1120,1083,838$ and 777 ; $\delta \mathrm{H}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 0.08\left[6 \mathrm{H}, \mathrm{s}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right], 0.90\left[9 \mathrm{H}, \mathrm{s}, \mathrm{SiC}\left(\mathrm{CH}_{3}\right)_{3}\right], 1.56\left(2 \mathrm{H}, \mathrm{m}, 3-\mathrm{H}_{2}\right)$, $1.73\left(3 \mathrm{H}, \mathrm{s}, 5-\mathrm{CH}_{3}\right), 2.13\left(2 \mathrm{H}, \mathrm{m}, 4-\mathrm{H}_{2}\right), 2.44(1 \mathrm{H}$, br. d, $J 3.0, \mathrm{OH}), 3.42(1 \mathrm{H}, \mathrm{dd}, J 10.5,8.0,1-\mathrm{H}), 3.63(2 \mathrm{H}, \mathrm{m}, 1-\mathrm{H}, 2-\mathrm{H})$ and 4.71 and 4.72 (each 1 H , br. s, $6-\mathrm{H}$ ); $\delta$ c ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $-5.5,-5.4,18.2,22.4,25.8,30.7,33.6,67.1,71.4,109.9$ and $145.5 ; \mathrm{m} / \mathrm{z}(\mathrm{CI}) 262\left(\mathrm{M}^{+}+\right.$ $18,37 \%), 245\left(\mathrm{M}^{+}+1,100\right)$ and 132 (39).
(1S)-1-tert-Butyldimethylsilyloxymethyl-5-methylhex-5-en-2-yl (R)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate 22 The alcohol 21 ( $37 \mathrm{mg}, 0.152 \mathrm{mmol}$ ) was added to ( $S$ )-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride ( $37 \mu \mathrm{~L}, 0.198 \mathrm{mmol}$ ) and pyridine ( 0.5 mL ) in carbon tetrachloride ( 0.5 mL ) and the solution stirred for 16 h at room temperature. 3(Dimethylamino) propylamine ( 0.4 mL ) was added and the mixture stirred for a further 5 min then diluted with ether and washed with aqueous hydrogen chloride ( 1 M ), saturated aqueous sodium carbonate and brine, then dried $\left(\mathrm{MgSO}_{4}\right)$. Concentration under reduced pressure gave the title compound 22 ( $58 \mathrm{mg}, 83 \%$ ) as a colourless oil (Found: $\mathrm{M}^{+}+\mathrm{H}, 461.2332 . \mathrm{C}_{23} \mathrm{H}_{36} \mathrm{~F}_{3} \mathrm{O}_{4} \mathrm{Si}$ requires $M$, 461.2335); $[\alpha]_{\mathrm{D}^{20}}+14.2$ (c 3.6, EtOH); $\mathrm{U}_{\text {max }} / \mathrm{cm}^{-1} 1748,1650,1451,1257,1170,1124,1019,838$ and $778 ; \delta_{\mathrm{F}}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)-$ 245.16 ( $97 \%$ ) and -244.98 ( $3 \%$ ); $\delta \mathrm{H}\left(300 \mathrm{MHz}^{2} \mathrm{CDCl}_{3}\right) 0.00\left[6 \mathrm{H}, \mathrm{s}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right], 0.86\left[9 \mathrm{H}, \mathrm{s}, \mathrm{SiC}\left(\mathrm{CH}_{3}\right)_{3}\right], 1.72\left(3 \mathrm{H}, \mathrm{s}, 5-\mathrm{CH}_{3}\right), 1.85(2 \mathrm{H}$, $\left.\mathrm{m}, 3-\mathrm{H}_{2}\right), 2.06\left(2 \mathrm{H}, \mathrm{t}, \mathrm{J} 8.0,4-\mathrm{H}_{2}\right), 3.54\left(3 \mathrm{H}, \mathrm{s}, \mathrm{OCH}_{3}\right), 3.68\left(2 \mathrm{H}, \mathrm{m}, 1-\mathrm{H}_{2}\right), 4.68$ and 4.74 (each $\left.1 \mathrm{H}, \mathrm{s}, 6-\mathrm{H}\right), 5.11(1 \mathrm{H}, \mathrm{m}, 2-\mathrm{H}), 7.40(3$ $\mathrm{H}, \mathrm{m}, \mathrm{ArH})$ and $7.59(2 \mathrm{H}, \mathrm{m}, \mathrm{ArH}) ; \delta_{\mathrm{c}}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)-5.8,-5.7,18.1,22.2,25.7,28.3,33.1,55.2,63.4,110.6,121.3,125.2,127.5$, 128.3, 129.4, 132.1, 144.1 and $166.1 ; m / z(C I) 478\left(\mathrm{M}^{+}+18,20 \%\right), 461\left(\mathrm{M}^{+}+1,100\right)$ and 132 (35).
(1S)-1-tert-Butyldimethylsilyloxymethyl-5-methylhex-5-en-2-yl (S)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate 23
Following the procedure used to prepare ester 22, $(R)$-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride gave the title compound 23 ( $55 \mathrm{mg}, 79 \%$ ) as a colourless oil (Found: $\mathrm{M}^{+}+\mathrm{H}, 461.2342$. $\mathrm{C}_{23} \mathrm{H}_{36} \mathrm{~F}_{3} \mathrm{O}_{4} \mathrm{Si}$ requires M , 461.2335); [ $\left.\alpha\right]_{\mathrm{D}}{ }^{20}-32$ (c 4.4 , EtOH); $U_{\max } / \mathrm{cm}^{-1} 1748,1651,1451,1257,1170,1124,1019,838$ and 778 ; $\delta_{\mathrm{F}}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)-245.16$ ( $5 \%$ ) and -244.98 ( $95 \%$ ); $\delta_{\mathrm{H}}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 0.00\left[6 \mathrm{H}, \mathrm{s}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right], 0.82\left[9 \mathrm{H}, \mathrm{s}, \mathrm{SiC}\left(\mathrm{CH}_{3}\right)_{3}\right], 1.60\left(3 \mathrm{H}, \mathrm{s}, 5-\mathrm{CH}_{3}\right), 1.67\left(2 \mathrm{H}, \mathrm{m}, 3-\mathrm{H}_{2}\right), 1.85\left(2 \mathrm{H}, \mathrm{t}, \mathrm{J} 8.0,4-\mathrm{H}_{2}\right)$, $3.55\left(3 \mathrm{H}, \mathrm{s}, \mathrm{OCH}_{3}\right), 3.79\left(2 \mathrm{H}, \mathrm{m}, 1-\mathrm{H}_{2}\right), 4.54$ and 4.64 (each $\left.1 \mathrm{H}, \mathrm{s}, 6-\mathrm{H}\right), 5.08(1 \mathrm{H}, \mathrm{m}, 2-\mathrm{H}), 7.34(3 \mathrm{H}, \mathrm{m}, \mathrm{ArH})$ and $7.55(2 \mathrm{H}, \mathrm{m}, \mathrm{ArH})$; $\delta_{\mathrm{C}}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)-5.6,-5.6,18.1,22.2,25.7,28.2,32.8,55.4,63.8,110.4,121.1,125.0,127.3,128.2,129.4,132.5,144.4$ and 166.1; $\mathrm{m} / \mathrm{z}(\mathrm{CI}) 478\left(\mathrm{M}^{+}+18,23 \%\right), 461\left(\mathrm{M}^{+}+1,100\right)$ and $132(32)$.

## (1R,6S,3Z)-7-tert-Butyldimethylsilyloxy-3-methyl-1-phenylhept-3-ene-1,6-diol 24

Tin(IV) bromide ( $4.49 \mathrm{~mL}, 1 \mathrm{M}$ in DCM, 4.49 mmol ) was added to the stannane $20(2.0 \mathrm{~g}, 3.75 \mathrm{mmol})$ in DCM $(20 \mathrm{~mL})$ at $-78{ }^{\circ} \mathrm{C}$. After 5 min , benzaldehyde ( $0.82 \mathrm{~mL}, 7.49 \mathrm{mmol}$ ) was added and the solution was stirred at $-78{ }^{\circ} \mathrm{C}$ for a further 40 min . Saturated methanolic ammonium chloride was added and the mixture was allowed to warm to room temperature. Ethyl acetate and water were added and the aqueous layer was washed with ethyl acetate. The organic extracts were washed with brine, dried $\left(\mathrm{MgSO}_{4}\right)$ concentrated under reduced pressure. Chromatography of the residue, using light petroleum-ethyl acetate-TEA (87:12:1) as eluent, gave the diol 24 ( 0.968 g, $74 \%$ ), containing ca. $20 \%$ of its $\mathrm{C}(2)$-epimer (HPLC), as a white crystalline solid. Repeated chromatography, eluting with light petroleum-ethyl acetate-TEA (80:20:1) gave a sample of the title compound $\mathbf{2 4}$ (Found: $\mathrm{M}^{+}+\mathrm{NH}_{4}$, 368.2611. $\mathrm{C}_{20} \mathrm{H}_{38} \mathrm{NO}_{3} \mathrm{Si}$ requires $M, 368.2621$ ); $\mathrm{v}_{\max } / \mathrm{cm}^{-1} 3323,1453,1254,1119,1054,838,777$ and 699 ; $\delta \mathrm{H}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ major diastereoisomer $0.00\left[6 \mathrm{H}, \mathrm{s}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right], 0.80\left[9 \mathrm{H}, \mathrm{s}, \mathrm{SiC}\left(\mathrm{CH}_{3}\right)_{3}\right], 1.78\left(3 \mathrm{H}, \mathrm{s}, 3-\mathrm{CH}_{3}\right), 1.95(1 \mathrm{H}, \mathrm{m}, 5-\mathrm{H}), 2.08(1 \mathrm{H}, \mathrm{dd}, J 13.5,3.5$,

2-H), 2.20 ( $1 \mathrm{H}, \mathrm{dt}, J 14.0,10.0,5-\mathrm{H}$ ), $2.66(1 \mathrm{H}, \mathrm{dd}, J 13.5,10.0,2-\mathrm{H}), 2.95(1 \mathrm{H}, \mathrm{br} . \mathrm{s}, \mathrm{OH}$ ), 3.38 ( $1 \mathrm{H}, \mathrm{dd}, J 10.0,8.0,7-\mathrm{H}$ ), 3.52 ( 1 H , dd, $J$ 10.0, $4.0,7-\mathrm{H}), 3.58(1 \mathrm{H}, \mathrm{m}, 6-\mathrm{H}), 4.75(1 \mathrm{H}, \mathrm{dd}, J 10.0,3.5,1-\mathrm{H}), 5.35(1 \mathrm{H}, \mathrm{m}, 4-\mathrm{H})$ and $7.14-7.34(5 \mathrm{H}, \mathrm{m}, \mathrm{ArH})$; minor diastereoisomer $1.68\left(3 \mathrm{H}, \mathrm{s}, 3-\mathrm{CH}_{3}\right)$ and $2.59(1 \mathrm{H}, \mathrm{dd}, J 13.5,9.0,2-\mathrm{H}) ; \delta \mathrm{C}\left(75 \mathrm{MHz}^{2}, \mathrm{CDCl}_{3}\right)-5.4,23.5,25.8,29.7,31.5,42.4,67.1,71.4$, $71.7,124.6,125.5,127.1,128.2,134.5$ and $145.2 ; \mathrm{m} / \mathrm{z}(\mathrm{CI}) 368\left(\mathrm{M}^{+}+18,5 \%\right), 350\left(\mathrm{M}^{+}, 44\right), 333(35)$ and 229 (100)..

## (2SR,7SR,4Z)-1-tert-Butyldimethylsilyloxy-5-methyldec-4-ene-2,7-diol 25

Following the procedure outlined for the synthesis of diol 24 , $\operatorname{tin}(\mathrm{IV})$ bromide ( $0.52 \mathrm{~mL}, 1 \mathrm{M}$ in DCM, 0.52 mmol ), the racemic stannane $20(230 \mathrm{mg}, 0.431 \mathrm{mmol})$ in $\mathrm{DCM}(2.5 \mathrm{~mL})$ and butanal ( $0.127 \mu \mathrm{~L}, 0.862 \mathrm{~mL}$ ), after chromatography using light petroleum-ethyl acetate-TEA (87:12:1) as eluant gave the title compound 25 ( $110 \mathrm{mg}, 81 \%$ ) as an (80:20) mixture of diastereoisomers ( ${ }^{1} \mathrm{H}$ NMR) (Found: $\mathrm{M}^{+}+\mathrm{H}, 317.2514 . \mathrm{C}_{17} \mathrm{H}_{3} \mathrm{O}_{3}$ Si requires $M, 317.2512$ ); $\mathrm{umax}^{\text {max }} \mathrm{cm}^{-1} 3368,1463,1255,1091,838$ and 777 ; $\delta_{\mathrm{H}}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 0.05\left[6 \mathrm{H}, \mathrm{s}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right], 0.83\left[9 \mathrm{H}, \mathrm{s}, \mathrm{SiC}\left(\mathrm{CH}_{3}\right)_{3}\right], 0.87\left(3 \mathrm{H}, \mathrm{t}, \mathrm{J} 7.0,10-\mathrm{H}_{3}\right], 1.28-1.50\left(4 \mathrm{H}, \mathrm{m}, 9-\mathrm{H}_{2}, 8-\mathrm{H}_{2}\right)$, $1.73\left(0.6 \mathrm{H}, \mathrm{s}, 5-\mathrm{CH}_{3}\right), 1.77\left(2.4 \mathrm{H}, \mathrm{s}, 5-\mathrm{CH}_{3}\right), 1.93(1 \mathrm{H}, \mathrm{dd}, J 13.5,2.5,6-\mathrm{H}), 2.07(1 \mathrm{H}, \mathrm{m}, 3-\mathrm{H}), 2.27(1 \mathrm{H}, \mathrm{dt}, J 14.0,9.5,3-\mathrm{H}), 2.43(1 \mathrm{H}$, dd, J 13.5, 10.0, 6-H), $2.92(2 \mathrm{H}, \mathrm{br} . \mathrm{s}, 2 \times 0 \mathrm{H}), 3.46(1 \mathrm{H}, \mathrm{dd}, J 10.0,7.5,1-\mathrm{H}), 3.55(1 \mathrm{H}, \mathrm{dd}, J 10.0,4.0,1-\mathrm{H}), 3.67(2 \mathrm{H}, \mathrm{m}, 2-\mathrm{H}, 7-\mathrm{H})$ and $5.37(1 \mathrm{H}, \mathrm{m}, 4-\mathrm{H}) ; \delta_{\mathrm{c}}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ major diastereoisomer -5.5, 14.0, 18.1, 18.9, 23.7, 25.8, 31.5, 39.8, 40.1, 67.0, 68.8, 71.7, 123.9 and 134.9; $\mathrm{m} / \mathrm{z}(\mathrm{CI}) 334\left(\mathrm{M}^{+}+18,21 \%\right)$ and $317\left(\mathrm{M}^{+}+1,100\right)$.

## (1R,6S,3Z)-6,7-(Dimethylmethylene)dioxy-3-methyl-1-phenylhept-3-en-1-ol 27

Tetra- $n$-butylammonium fluoride ( 1.0 M in THF, $4.56 \mathrm{~mL}, 4.56 \mathrm{mmol}$ ) was added to the diol $24(800 \mathrm{mg}, 2.28 \mathrm{mmol})$ in THF ( 4 mL ) at $0^{\circ} \mathrm{C}$. The mixture was allowed to warm to room temperature and stirred for 16 h . After concentration under reduced pressure, chromatography of the residue using $1 \%$ methanol in DCM as the eluant, gave ( $2 S, 7 R, 4 Z$ )-5-methyl-7-phenylhept-4-ene-1,2,7-triol ( $530 \mathrm{mg}, 98 \%$ ) containing ca. $20 \%$ of its $\mathrm{C}(7)$-epimer ( ${ }^{1} \mathrm{H} \mathrm{NMR}$ ) as a colourless oil (Found: $\mathrm{M}^{+}+\mathrm{NH}_{4}, 254.1759 . \mathrm{C}_{14} \mathrm{H}_{24} \mathrm{NO}_{3}$ requires M, 254.1756); $\mathrm{U}_{\max } / \mathrm{cm}^{-1} 3367,1451,1074,1029,754$ and 700 ; $\delta \mathrm{H}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.$ ) major diastereoisomer 1.82 ( $3 \mathrm{H}, \mathrm{s}, 5-\mathrm{CH} 3$ ), 2.00 ( $1 \mathrm{H}, \mathrm{m}, 3-\mathrm{H}$ ), $2.07(1 \mathrm{H}, \mathrm{dd}, J 13.5,3.0,6-\mathrm{H}), 2.35(1 \mathrm{H}, \mathrm{dt}, J 14.1,10.0,3-\mathrm{H}), 2.75(1 \mathrm{H}, \mathrm{dd}, J 13.5,10.5,6-\mathrm{H}), 3.20(1 \mathrm{H}, \mathrm{br} . \mathrm{m}, \mathrm{OH}), 3.42$ ( $1 \mathrm{H}, \mathrm{dd}, J 11.0,7.0,1-\mathrm{H}$ ), $3.55(1 \mathrm{H}, \mathrm{dd}, J 11.0,3.0,1-\mathrm{H}), 3.66(1 \mathrm{H}, \mathrm{m}, 2-\mathrm{H}), 4.10(2 \mathrm{H}, \mathrm{br} . \mathrm{s}, 2 \times 0 \mathrm{H}), 4.74(1 \mathrm{H}, \mathrm{dd}, J 10.5,3.0,7-\mathrm{H})$, $5.40(1 \mathrm{H}, \mathrm{dd}, J 10.0,5.5,4-\mathrm{H})$ and $7.27-7.37\left(5 \mathrm{H}, \mathrm{m}, \mathrm{ArH}\right.$ ); minor diastereoisomer $1.72\left(3 \mathrm{H}, \mathrm{s}, 5-\mathrm{CH}_{3}\right), 2.18(1 \mathrm{H}, \mathrm{dd}, J 14.0,3.5,6-\mathrm{H})$ and $5.28(1 \mathrm{H}, \mathrm{m}, 4-\mathrm{H})$; $\delta \mathrm{c}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ major diastereoisomer 23.5, 31.6, 41.9, 66.7, 71.4, 71.7, 124.5, 125.6, 127.3, 128.3, 134.5 and 144.9; $\mathrm{m} / \mathrm{z}(\mathrm{CI}) 254\left(\mathrm{M}^{+}+1,43 \%\right), 236\left(\mathrm{M}^{+}, 100\right), 219$ (56) and 115 (30).

Toluene $p$-sulphonic acid ( $35 \mathrm{mg}, 0.185 \mathrm{mmol}$ ) was added to the heptenyltriol ( $236 \mathrm{mg}, 1.850 \mathrm{mmol}$ ) in 2,2-dimethoxypropane $(1.5 \mathrm{~mL})$ and the solution stirred at room temperature for 1 h . Triethylamine ( 5 drops ), water and ether were added and the organic layer washed with brine and dried $\left(\mathrm{MgSO}_{4}\right)$. After concentration under reduced pressure chromatography of the residue, eluting with light petroleum-ethyl acetate (20:1), gave the title compound 27 ( $352 \mathrm{mg}, 69 \%$ ) containing ca. $20 \%$ of its C(1)-epimer ( ${ }^{1} \mathrm{H}$ NMNR), as a colourless oil (Found: $\mathrm{M}^{+}+\mathrm{H}, 277.1806 . \mathrm{C}_{17} \mathrm{H}_{25} \mathrm{O}_{3}$ requires $M, 277.1803$ ); $\mathrm{Umax} / \mathrm{cm}^{-1} 3453,1451,1374,1248,1216,1155$, 1062,843 and $701 ; \delta \mathrm{H}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ major diastereoisomer 1.42 and 1.52 (each $\left.3 \mathrm{H}, \mathrm{s}, \mathrm{CH} 3\right), 1.90\left(3 \mathrm{H}, \mathrm{s}, 3-\mathrm{CH}_{3}\right), 2.18(1 \mathrm{H}, \mathrm{m}, 5-$ H), $2.28(1 \mathrm{H}, \mathrm{dd}, J 13.5,4.0,2-\mathrm{H}), 2.40(1 \mathrm{H}, \mathrm{m}, 5-\mathrm{H}), 2.74(1 \mathrm{H}, \mathrm{dd}, J 13.5,10.0,2-\mathrm{H}), 3.10(1 \mathrm{H}, \mathrm{d}, J 3.5,0 \mathrm{H}), 3.54(1 \mathrm{H}, \mathrm{m}, 7-\mathrm{H}), 4.08$ ( $2 \mathrm{H}, \mathrm{m}, 6-\mathrm{H}, 7-\mathrm{H}$ ), $4.88(1 \mathrm{H}, \mathrm{dt}, J 10.0,4.0,1-\mathrm{H}), 5.44(1 \mathrm{H}, \mathrm{t}, J 8.5,4-\mathrm{H})$ and $7.25-7.45(5 \mathrm{H}, \mathrm{m}, \mathrm{ArH})$; minor diastereoisomer 1.38 and 1.44 (each $3 \mathrm{H}, \mathrm{s}, \mathrm{CH}_{3}$ ) and $1.82\left(3 \mathrm{H}, \mathrm{s}, 3-\mathrm{CH}_{3}\right)$; $\delta \mathrm{c}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 23.5,25.6,26.7,32.1,42.6,69.1,71.4,75.7,109.1,124.0,125.5$, 127.1, 128.2, 134.4 and $145.0 ; \mathrm{m} / \mathrm{z}$ (CI) $294\left(\mathrm{M}^{+}+18,7 \%\right), 277\left(\mathrm{M}^{+}+1,14\right), 259$ (55) and 58 (100).

## (1S,6S,3Z)-6,7-(Dimethylmethylene)dioxy-3-methyl-1-phenylhept-3-en-1-yl 4-nitrobenzoate 28

Triphenylphosphine ( $214 \mathrm{mg}, 0.815 \mathrm{mmol}$ ), 4-nitrobenzoic acid ( $136 \mathrm{mg}, 0.815 \mathrm{mmol}$ ) and DEAD ( $142 \mathrm{mg}, 0.815 \mathrm{mmol}$ ) were added to the alcohol $27(150 \mathrm{mg}, 0.544 \mathrm{mmol})$ in benzene $(1.5 \mathrm{~mL})$ and the mixture stirred for 16 h . Water was added and the mixture extracted with ether. The organic extracts were washed with brine and dried $\left(\mathrm{MgSO}_{4}\right)$. After concentration under reduced pressure, chromatography of the residue, eluting with light petroleum-ethyl acetate ( $25: 1$ ), gave the title compound 28 ( $179 \mathrm{mg}, 78 \%$ ) containing ca. $20 \%$ of its $\mathrm{C}(1)$-epimer ( ${ }^{1} \mathrm{H}$ NMR) as a yellow oil (Found: $\mathrm{M}^{+}+\mathrm{NH}_{4}, 443.2173$. $\mathrm{C}_{24} \mathrm{H}_{31} \mathrm{~N}_{2} \mathrm{O}_{6}$ requires $M, 443.2182$ ); $v_{\max } / \mathrm{cm}^{-1} 1725,1528,1345,1271,1102$ and $1064 ; \delta_{\mathrm{H}}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 1.36$ and 1.45 (each $\left.3 \mathrm{H}, \mathrm{s}, \mathrm{CH}_{3}\right), 1.83\left(3 \mathrm{H}, \mathrm{s}, 3-\mathrm{CH}_{3}\right), 2.17$ and 2.35 (each $1 \mathrm{H}, \mathrm{m}, 5-\mathrm{H}), 2.64(1 \mathrm{H}, \mathrm{dd}, J 13.5,6.5,2-\mathrm{H}), 2.96(1 \mathrm{H}, \mathrm{dd}, J 13.5,8.0,2-\mathrm{H}), 3.49(1 \mathrm{H}, \mathrm{m}, 7-\mathrm{H}), 3.88-4.02(2 \mathrm{H}, \mathrm{m}, 6-\mathrm{H}, 7-$ H), $5.28(1 \mathrm{H}, \mathrm{t}, J 7.0,4-\mathrm{H}), 6.19(1 \mathrm{H}, \mathrm{dd}, J 8.0,6.5,1-\mathrm{H}), 7.28-7.50(5 \mathrm{H}, \mathrm{m}, \mathrm{ArH})$ and $8.30(4 \mathrm{H}, \mathrm{m} \mathrm{ArH}) ; \delta_{\mathrm{c}}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 24.0,25.5$, $26.8,32.1,39.3,68.8,75.3,76.0,108.8,123.5,126.3,128.2,128.3,130.6,132.9,135.6,139.7,150.5$ and $163.7 ; \mathrm{m} / \mathrm{z}(\mathrm{CI}) 443\left(\mathrm{M}^{+}+\right.$ $\mathrm{NH}_{4}, 6$ \%), 259 (44), 201 (51) and 58 (100).

## (1S,6S,3Z)-6,7-(Dimethylmethylene)dioxy-3-methyl-1-phenylhept-3-en-1-ol 29

Sodium hydroxide ( $75 \mathrm{mg}, 1.89 \mathrm{mmol}$ ) was added to the nitrobenzoate $\mathbf{2 8}(160 \mathrm{mg}, 0.377 \mathrm{mmol})$ in anhydrous methanol ( 1.5 mL ) and the solution stirred for 2 h . Saturated aqueous ammonium chloride was added and the mixture extracted with ether. The organic extracts were washed with saturated aqueous sodium bicarbonate and brine, dried $\left(\mathrm{MgSO}_{4}\right)$ and concentrated under reduced pressure to give the title compound 29 ( $89 \mathrm{mg}, 86 \%$ ) containing ca. $20 \%$ of its C(1)-epimer ( ${ }^{1} \mathrm{H}$ NMR) as a colourless oil (Found: $\mathrm{M}^{+}+\mathrm{H}, 277.1803 . \mathrm{C}_{17} \mathrm{H}_{25} \mathrm{O}_{3}$ requires $\mathrm{M}, 277.1803$ ); $\mathrm{U}_{\max } / \mathrm{cm}^{-1} 3449,1451,1374,1248,1216,1155,1062,845,755$ and 701; $\delta_{\mathrm{H}}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ major diastereoisomer 1.38 and 1.44 (each $3 \mathrm{H}, \mathrm{s}, \mathrm{CH}_{3}$ ), $1.82\left(3 \mathrm{H}, \mathrm{s}, 3-\mathrm{CH}_{3}\right), 2.24-2.42(3 \mathrm{H}, \mathrm{m}, 5-\mathrm{H}, 2-\mathrm{H}), 2.63-$ $2.74(2 \mathrm{H}, \mathrm{m}, 2-\mathrm{H}, \mathrm{OH}), 3.60(1 \mathrm{H}, \mathrm{dd}, J 7.5,7.0,7-\mathrm{H}), 3.99-4.13(2 \mathrm{H}, \mathrm{m}, 6-\mathrm{H}, 7-\mathrm{H}), 4.86(1 \mathrm{H}, \mathrm{dd}, J 6.5,4.5,1-\mathrm{H}), 5.44(1 \mathrm{H}, \mathrm{t}, J 7.0,4-\mathrm{H})$ and 7.26-7.44 ( $5 \mathrm{H}, \mathrm{m}, \mathrm{ArH}$ ); minor diastereoisomer 1.42 and 1.52 (each $3 \mathrm{H}, \mathrm{s}, \mathrm{CH}_{3}$ ) and $1.90\left(3 \mathrm{H}, \mathrm{s}, 3-\mathrm{CH}_{3}\right)$; $\delta \mathrm{c}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ $24.0,25.5,26.6,31.5,42.4,68.6,72.0,75.4,108.9,123.0,125.6,127.3,128.2,134.6$ and $144.3 ; m / z(C I) 294\left(M^{+}+18,8 \%\right), 277\left(\mathrm{M}^{+}+\right.$ $1,12), 259$ (47) and 58 (100).
(1S,6S,3Z)-6,7-(Dimethylmethylene)dioxy-3-methyl-1-phenylhept-3-en-1-yl ( $R$ )-2-acetoxy-2-phenylacetate 30
4-Dimethylaminopyridine ( 2 mg ) was added to ( $R$ ) - $O$-acetyl mandelic acid ( $70 \mathrm{mg}, 0.362 \mathrm{mmol}$ ), DCC ( $74 \mathrm{mg}, 0.362 \mathrm{mmol}$ ) and the alcohol 29 ( $50 \mathrm{mg}, 0.181 \mathrm{mmol}$ ) in DCM ( 5 mL ) and the solution stirred for 16 h . Saturated aqueous ammonium chloride was added
and the mixture extracted with ether. The organic extracts were washed with brine, dried $\left(\mathrm{MgSO}_{4}\right)$, and concentrated under reduced pressure. Chromatography of the residue, eluting with light petroleum-ethyl acetate (11:1) gave the title compound $\mathbf{3 0}$ ( $55 \mathrm{mg}, 68 \%$ ) containing ca. $20 \%$ of its $\mathrm{C}(1)$-epimer as a colourless oil (Found: $\mathrm{M}^{+}+\mathrm{NH}_{4}, 470.2543$. $\mathrm{C}_{27} \mathrm{H}_{36} \mathrm{NO}_{6}$ requires $M, 470.2542$ ); $\mathrm{v}_{\text {max }} / \mathrm{cm}^{-1}$ $1748,1372,1230,1176,1058$ and 699 ; $\delta_{\mathrm{H}}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 1.35$ and 1.41 (each $\left.3 \mathrm{H}, \mathrm{s}, \mathrm{CH}_{3}\right), 1.55\left(3 \mathrm{H}, \mathrm{s}, 3-\mathrm{CH}_{3}\right), 1.80$ and 2.06 (each $1 \mathrm{H}, \mathrm{m}, 5-\mathrm{H}), 2.19\left(3 \mathrm{H}, \mathrm{s}, \mathrm{COCH}_{3}\right), 2.35(1 \mathrm{H}, \mathrm{dd}, J 13.5,6.5,2-\mathrm{H}), 2.64(1 \mathrm{H}, \mathrm{dd}, J 13.5,8.0,2-\mathrm{H}), 3.40(1 \mathrm{H}, \mathrm{t}, J 7.5,7-\mathrm{H}), 3.80(1 \mathrm{H}, \mathrm{m}, 6-$ H), $3.90(1 \mathrm{H}, \mathrm{dd}, J 7.5,6.0,7-\mathrm{H}), 5.04(1 \mathrm{H}, \mathrm{t}, J 7.0,4-\mathrm{H}), 5.90(1 \mathrm{H}, \mathrm{m}, 1-\mathrm{H}), 5.98(1 \mathrm{H}, \mathrm{s}, \mathrm{CHPhOAc})$ and $7.30-7.60(10 \mathrm{H}, \mathrm{m}, \mathrm{ArH})$; $\delta \mathrm{c}$ $\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 20.6,23.5,25.6,26.8,31.7,38.8,68.8,74.5,75.4,75.7,108.7,123.3,126.1,127.8,128.0,128.4,128.6,129.2,132.6$, 133.8, 139.5, 168.0 and $170.0 ; m / z(C I) 470\left(\mathrm{M}^{+}+18,100 \%\right), 259$ (46) and 201 (30).
(1S,6S,3Z)-6,7-(Dimethylmethylene)dioxy-3-methyl-1-phenylhept-3-en-1-yl (S)-2-acetoxy-2-phenylacetate 31
Following the procedure outlined for the synthesis of ester 30, DMAP ( 2 mg ), ( $S$ ) -0 -acetyl mandelic acid ( $54 \mathrm{mg}, 0.282 \mathrm{mmol}$ ), DCC ( $58 \mathrm{mg}, 0.282 \mathrm{mmol}$ ) and the alcohol $29(39 \mathrm{mg}, 0.141 \mathrm{mmol})$ in DCM ( 3.5 mL ), after chromatography using light petroleum-ethyl acetate (11:1) as eluant, gave the title compound $\mathbf{3 1}(47 \mathrm{mg}, 72 \%)$ containing ca. $20 \%$ of its C(1)-epimer ( ${ }^{1} \mathrm{H}$ NMR) as a colourless oil (Found: $\mathrm{M}^{+}+\mathrm{NH}_{4}, 470.2544 . \mathrm{C}_{2} \mathrm{H}_{36} \mathrm{NO}_{6}$ requires $\mathrm{M}, 470.2542$ ); $\mathrm{v}_{\max } / \mathrm{cm}^{-1} 1747,1372,1231,1176,1058$ and $698 ; \delta_{\mathrm{H}}(300 \mathrm{MHz}$, $\left.\mathrm{CDCl}_{3}\right) 1.36$ and 1.42 (each $\left.3 \mathrm{H}, \mathrm{s}, \mathrm{CH}_{3}\right), 1.76\left(3 \mathrm{H}, \mathrm{s}, 3-\mathrm{CH}_{3}\right), 2.14\left(2 \mathrm{H}, \mathrm{m}, 5-\mathrm{H}_{2}\right), 2.21\left(3 \mathrm{H}, \mathrm{s}, \mathrm{COCH}_{3}\right), 2.46(1 \mathrm{H}, \mathrm{dd}, J 14.0,6.5,2-\mathrm{H})$, $2.74(1 \mathrm{H}, \mathrm{dd}, J 14.0,8.0,2-\mathrm{H}), 3.48(1 \mathrm{H}, \mathrm{dd}, J 7.5,7.0,7-\mathrm{H}), 3.85-4.00(2 \mathrm{H}, \mathrm{m}, 6-\mathrm{H}, 7-\mathrm{H}), 5.25(1 \mathrm{H}, \mathrm{t}, J 7.0,4-\mathrm{H}), 5.86(1 \mathrm{H}, \mathrm{m}, 1-\mathrm{H})$, $6.05(1 \mathrm{H}, \mathrm{s}, \mathrm{CHPhOAc}), 6.98(2 \mathrm{H}, \mathrm{m}, \mathrm{ArH}), 7.20(3 \mathrm{H}, \mathrm{m}, \mathrm{ArH})$ and $7.30-7.50(5 \mathrm{H}, \mathrm{m}, \mathrm{ArH})$; $\delta \mathrm{c}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 20.6,23.8,25.5,26.8$, $32.0,39.1,68.9,74.4,75.4,75.9,108.7,132.4,125.8,127.7,127.8,128.1,128.6,129.1,132.7,133.5,139.4,167.7$ and $170.1 ; \mathrm{m} / \mathrm{z}$ (CI) $470\left(\mathrm{M}^{+}+18,100 \%\right), 259$ (51) and 201 (30).

## Methyl (2R,3S,10S,4E)-3,7-dimethyl-10,11-(dimethylmethylene)dioxy-7,8-epoxy-2-(4-methoxybenzyl)oxyundeca-4-enoate

 36$m$-Chloroperoxybenzoic acid ( $60 \%$ ) was added portionwise to the diene 35 ( $85 \mathrm{mg}, 0.197 \mathrm{mmol}$ ) in DCM, until TLC indicated complete consumption of the diene. Saturated aqueous sodium thiosulfate, water and DCM were added and the organic layer was washed with brine, dried $\left(\mathrm{MgSO}_{4}\right)$ and concentrated under reduced pressure. Chromatography of the residue, eluting with light petroleum-ethyl acetate ( $6: 1$ ), gave the title compound 36 ( $79 \mathrm{mg}, 88 \%$ ), a $60: 40$ mixture of $\alpha$ - and $\beta$-epoxides, a colourless oil (Found: $\mathrm{M}^{+}+\mathrm{NH}_{4}, 466.2808 . \mathrm{C}_{25} \mathrm{H}_{40} \mathrm{NO}_{7}$ requires $M$, 466.2804); $\mathrm{v}_{\max } / \mathrm{cm}^{-1} 1749,1613,1514,1462,1379,1250,1064$ and 832 ; $\delta_{\mathrm{H}}$ $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 0.98\left(3 \mathrm{H}, \mathrm{d}, J 7.0,3-\mathrm{CH}_{3}\right), 1.16$ and 1.28 (each $3 \mathrm{H}, \mathrm{s}, \mathrm{CH}_{3}$ ), $1.34\left(1.8 \mathrm{H}, \mathrm{s}, 7-\mathrm{CH}_{3}\right), 1.36\left(1.2 \mathrm{H}, \mathrm{s}, 7-\mathrm{CH}_{3}\right), 1.50(0.6 \mathrm{H}$, ddd, $J 14.0,8.5,5.5,9-H), 1.77(0.8 \mathrm{H}, \mathrm{m}, 2 \times 9-\mathrm{H}), 1.93(0.6 \mathrm{H}, \mathrm{ddd}, J 14.0,7.5,3.5,9-\mathrm{H}), 2.05$ and 2.19 (each $1 \mathrm{H}, \mathrm{m}, 6-\mathrm{H}), 2.54(1 \mathrm{H}, \mathrm{m}$, $3-\mathrm{H}), 2.76$ ( $0.4 \mathrm{H}, \mathrm{dd}, J 7.0,5.0,8-\mathrm{H}$ ), 2.81 ( $0.6 \mathrm{H}, \mathrm{dd}, J 8.5,3.5,8-\mathrm{H}$ ), 3.47 ( $0.6 \mathrm{H}, \mathrm{dd}, J 8.0,7.5,11-\mathrm{H}$ ), 3.52-3.79 ( $7.4 \mathrm{H}, \mathrm{m}, 2-\mathrm{H}, 11-\mathrm{H}$, $\left.\mathrm{CO}_{2} \mathrm{CH}_{3}, \mathrm{OCH}_{3}\right), 3.98-4.08(1 \mathrm{H}, \mathrm{m}, 11-\mathrm{H}), 4.14-4.28(2 \mathrm{H}, \mathrm{m}, 10-\mathrm{H}, \mathrm{OHCHAr}), 4.54(1 \mathrm{H}, \mathrm{d}, \mathrm{J} 11.5, \mathrm{OHCHAr}), 5.30-5.46(2 \mathrm{H}, \mathrm{m}, 4-\mathrm{H}, 5-$ H), $6.79(2 \mathrm{H}, \mathrm{d}, J 8.5, \mathrm{ArH})$ and $7.18(2 \mathrm{H}, \mathrm{d}, J 8.5, \mathrm{ArH})$; $\delta \mathrm{c}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 15.9,16.0,21.9,25.5,25.6,26.7,26.8,32.1,33.0,36.5(2)$, $40.3,51.5,55.2,59.7,60.3,60.4,61.1,68.6,69.4,72.1,73.7,73.9,81.8,81.9,108.8,108.9,113.6,125.7,125.8,129.4,129.6,134.3$, 134.4, 159.3 and 172.3; $m / z(C I) 466\left(\mathrm{M}^{+}+18,14 \%\right)$ and 168 (100).

## Methyl (2R,3S,10S)-3,7-dimethyl-10,11-(dimethylmethylene)dioxy-7,8-epoxy-2-(4-methoxybenzyl)oxyundecanoate 37

Platinum(IV) oxide (Adams' catalyst) was added to the unsaturated ester 36 ( $72 \mathrm{mg}, 0.160 \mathrm{mmol}$ ) in anhydrous ethanol ( 5 mL ) and the suspension stirred under an atmosphere of hydrogen for 2 h . The mixture was filtered through celite, the celite being washed with ethanol, and the filtrate and washings were concentrated under reduced pressure to give the title compound $\mathbf{3 7}(70 \mathrm{mg}, 98 \%)$, a 60:40 mixture of $\alpha$ - and $\beta$-epoxides, a colourless oil (Found: $\mathrm{M}^{+}+\mathrm{NH}_{4}, 468.2952 . \mathrm{C}_{25} \mathrm{H}_{42} \mathrm{NO}_{7}$ requires $M, 468.2960$ ); $\mathrm{U}_{\max } / \mathrm{cm}^{-1}$ $1748,1613,1514,1461,1376,1249,1208,1064$ and 830 ; $\delta_{\mathrm{H}}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 0.85\left(3 \mathrm{H}, \mathrm{d}, J 7.0,3-\mathrm{CH}_{3}\right), 1.03-1.58(4 \mathrm{H}, \mathrm{m}), 1.17$ and 1.29 (each $3 \mathrm{H}, \mathrm{s}, \mathrm{CH}_{3}$ ), $1.35\left(1.8 \mathrm{H}, \mathrm{s}, 7-\mathrm{CH}_{3}\right), 1.36\left(1.2 \mathrm{H}, \mathrm{s}, 7-\mathrm{CH}_{3}\right), 1.61-1.95(5 \mathrm{H}, \mathrm{m}), 2.72(0.4 \mathrm{H}, \mathrm{dd}, J 7.5,4.5,8-\mathrm{H}), 2.77(0.6 \mathrm{H}$, dd, J 8.5, 3.5, 8-H), 3.48 ( $0.6 \mathrm{H}, \mathrm{dd}, J 8.0,7.5,11-\mathrm{H}$ ), $3.62(0.4 \mathrm{H}, \mathrm{dd}, J 8.0,7.5,11-\mathrm{H}), 3.65-3.79\left(7 \mathrm{H}, \mathrm{m}, 2-\mathrm{H}^{2} \mathrm{CO}_{2} \mathrm{CH}_{3}, 0 \mathrm{OCH}_{3}\right), 4.03(1 \mathrm{H}$, $\mathrm{m}, 11-\mathrm{H}$ ), 4.13-4.25 ( $2 \mathrm{H}, \mathrm{m}, 10-\mathrm{H}, \mathrm{OHCHAr}$ ), $4.59(1 \mathrm{H}, \mathrm{d}, J 11.5, \mathrm{OHCHAr}), 6.80(2 \mathrm{H}, \mathrm{d}, J 8.5$, ArH) and $7.18(2 \mathrm{H}, \mathrm{d}, \mathrm{J} 8.5$, ArH); סc ( 75 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $14.7,14.8,21.9,22.8,22.9,25.5,25.6,26.7,26.8,32.0,32.8,32.9(2), 33.0,36.3,51.6,55.1,60.1,60.6(2), 61.4,68.6,69.4$, $72.0,73.7,73.9,80.4,80.6,108.8(2), 113.6,129.6(2), 159.3$ and $173.0 ; m / z(C I) 468\left(\mathrm{M}^{+}+18,16 \%\right), 154$ (26) and 121 (100).

## Methyl (2R,3S,10S,7Z)-3,7-dimethyl-10,11-(dimethylmethylene)dioxy-2-(4-methoxybenzyl)oxyundec-7-enoate 38

Potassium selenocyanate ( $2.80 \mathrm{~g}, 19.4 \mathrm{mmol}$ ) was added to a solution of the epoxide 37 ( $350 \mathrm{mg}, 0.78 \mathrm{mmol}$ ) in anhydrous methanol ( 20 mL ) and the solution heated at $65^{\circ} \mathrm{C}$ for 14 h . After filtration with washing of the precipitate with methanol, the filtrate was diluted with water and ether. The organic layer was washed with brine, dried $\left(\mathrm{MgSO}_{4}\right)$ and concentrated under reduced pressure. Chromatography of the residue, eluting with light petroleum-ethyl acetate (9:1), gave the title compound $\mathbf{3 8}$ ( $267 \mathrm{mg}, 79$ $\%$ ) as a colourless oil; $[\alpha]_{\mathrm{D}^{21}}+21$ (c 1.10 in DCM) (Found: $\mathrm{M}^{+}+\mathrm{NH}_{4}, 452.3020 . \mathrm{C}_{25} \mathrm{H}_{42} \mathrm{NO}_{6}$ requires $M, 452.3012$ ); $\mathrm{v}_{\text {max }} / \mathrm{cm}^{-1} 1748$, $1613,1513,1461,1373,1249,1209,1063$ and 833 ; $\delta$ н $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 0.93\left(3 \mathrm{H}, \mathrm{d}, J 7.0,3-\mathrm{CH}_{3}\right), 1.17-1.38\left(4 \mathrm{H}, \mathrm{m}, 4-\mathrm{H}_{2} 5-\mathrm{H}_{2}\right)$, 1.35 and 1.41 (each $3 \mathrm{H}, \mathrm{s}, \mathrm{CH}_{3}$ ), $1.61\left(3 \mathrm{H}, \mathrm{s}, 7-\mathrm{CH}_{3}\right), 1.93(1 \mathrm{H}, \mathrm{m}, 3-\mathrm{H}), 1.97\left(2 \mathrm{H}, \mathrm{m}, 6-\mathrm{H}_{2}\right), 2.19$ and 2.35 (each $\left.1 \mathrm{H}, \mathrm{m}, 9-\mathrm{H}\right), 3.53(1$ $\mathrm{H}, \mathrm{t}, 7.0,11-\mathrm{H}), 3.75\left(3 \mathrm{H}, \mathrm{s}, \mathrm{OCH}_{3}\right), 3.78-3.84\left(4 \mathrm{H}, \mathrm{m}, 2-\mathrm{H}, \mathrm{CO}_{2} \mathrm{CH}_{3}\right), 4.03(2 \mathrm{H}, \mathrm{m}, 10-\mathrm{H}, 11-\mathrm{H}), 4.29$ and 4.67 (each $1 \mathrm{H}, \mathrm{d}, \mathrm{J} 11.5$, OHCHAr), $5.11(1 \mathrm{H}, \mathrm{t}, J 7.0,8-\mathrm{H}), 6.86(2 \mathrm{H}, \mathrm{d}, J 8.5, \mathrm{ArH})$ and $7.27(2 \mathrm{H}, \mathrm{d}, J 8.5, \mathrm{ArH}) ; \delta \mathrm{c}\left(125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 14.8,23.4,25.3,25.6,26.8$, $31.8,32.1,32.8,36.4,51.6,55.2,69.1,72.1,75.9,80.7,108.7,113.6,119.4,129.6(2), 138.2,159.2$ and $173.2 ; m / z(\mathrm{CI}) 452\left(\mathrm{M}^{+}+18\right.$, $100 \%$ ), 359 (20) and 121 (55).

## Methyl (2R,3S,10S,7Z)-3,7-dimethyl-10,11-(dimethylmethylene)dioxy-2-hydroxyundec-7-enoate 39

Dichlorodicyanoquinone ( $123 \mathrm{mg}, 0.540 \mathrm{mmol}$ ) was added to the PMB-ether $38(213 \mathrm{mg}, 0.491 \mathrm{mmol})$ in DCM : water (18:1; 4.0 mL ) and the mixture stirred for 2 h . Saturated aqueous sodium bicarbonate was added and the mixture diluted with DCM. The organic layer was washed five times with saturated aqueous sodium bicarbonate and brine then dried ( $\mathrm{MgSO}_{4}$ ). After concentration under reduced pressure, chromatography of the residue, eluting with light petroleum-ethyl acetate (9:1), gave the title compound 39
( $124 \mathrm{mg}, 80 \%$ ) as a colourless oil; [ $\alpha]_{\mathrm{D}}{ }^{21}-3.2$ (c 4.47 in DCM) (Found: $\mathrm{M}^{+}$, 314.2092. $\mathrm{C}_{17} \mathrm{H}_{30} \mathrm{O}_{5}$ requires $M, 314.2093$ ); $\mathrm{Umax}_{\text {max }} / \mathrm{cm}^{-1}$ $3427,1731,1599,1462,1378,1272,1123$ and $1069 ; \delta_{H}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 0.85\left(3 \mathrm{H}, \mathrm{d}, J 7.0,3-\mathrm{CH}_{3}\right), 1.20-1.61\left(4 \mathrm{H}, \mathrm{m}, 4-\mathrm{H}_{2} 5-\mathrm{H}_{2}\right)$, 1.40 and 1.44 (each $3 \mathrm{H}, \mathrm{s}, \mathrm{CH}_{3}$ ), $1.74\left(3 \mathrm{H}, \mathrm{s}, 7-\mathrm{CH}_{3}\right), 1.94(1 \mathrm{H}, \mathrm{m}, 3-\mathrm{H}), 2.04\left(2 \mathrm{H}, \mathrm{m}, 6-\mathrm{H}_{2}\right), 2.24$ and 2.40 (each $\left.1 \mathrm{H}, \mathrm{m}, 9-\mathrm{H}\right), 2.73(1$ $\mathrm{H}, \mathrm{d}, \mathrm{J} 6.0, \mathrm{OH}), 3.58(1 \mathrm{H}, \mathrm{t}, 7.0,11-\mathrm{H}), 3.83\left(3 \mathrm{H}, \mathrm{s}, \mathrm{CO}_{2} \mathrm{CH}_{3}\right), 3.99-4.17(2 \mathrm{H}, \mathrm{m}, 10-\mathrm{H}, 11-\mathrm{H}), 4.20(1 \mathrm{H}, \mathrm{dd}, J 6.0,3.0,2-\mathrm{H})$ and $5.11(1$ $\mathrm{H}, \mathrm{t}, J 7.0,8-\mathrm{H}) ; \delta_{\mathrm{c}}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 13.4,23.4,25.5,25.6,26.8,31.9,32.1,32.8,36.2,52.4,69.1,73.2,75.9,108.7,119.5,138.2$ and 175.6; m/z (CI) 332 ( $\mathrm{M}^{+}+18,50 \%$ ), $315\left(\mathrm{M}^{+}+1,28\right), 274$ (100) and 101 (70).

## (2R,3S,10S,7Z)-3,7-Dimethyl-10,11-(dimethylmethylene)dioxyundec-7-ene-1,2-diol 40

Lithium aluminium hydride ( 1 M in ether, $331 \mu \mathrm{~L}, 0.31 \mathrm{~mol}$ ) was added dropwise to the ester 39 ( $52 \mathrm{mg}, 0.166 \mathrm{~mol}$ ) in ether ( 1 mL ) at $0{ }^{\circ} \mathrm{C}$ and the mixture stirred at $0{ }^{\circ} \mathrm{C}$ for 2 h . Saturated aqueous sodium sulfate was added carefully, and the mixture acidified with dilute hydrochlogen chloride and extracted with ether. The organic extracts were washed with brine, dried $\left(\mathrm{MgSO}_{4}\right)$ and concentrated under reduced pressure. Chromatography of the residue using light petroleum-ethyl acetate (1:1) as eluent gave the title compound 40 ( $37 \mathrm{mg}, 78 \%$ ) as a colourless oil; $[\alpha]_{\mathrm{D}}{ }^{22}+2.3$ (c 1.58 in DCM) (Found: M ${ }^{+}$, 286.2145. $\mathrm{C}_{16} \mathrm{H}_{30} \mathrm{O}_{4}$ requires $M$, 286.2142); $v_{\max } / \mathrm{cm}^{-1} 3408,1455,1374,1249,1217,1155$ and 1063 ; $\delta_{\mathrm{H}}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 0.84\left(3 \mathrm{H}, \mathrm{d}, \mathrm{J} 6.5,3-\mathrm{CH}_{3}\right), 1.16-1.41(4 \mathrm{H}$, $\left.\mathrm{m}, 4-\mathrm{H}_{2}, 5-\mathrm{H}_{2}\right), 1.38$ and 1.44 (each $\left.3 \mathrm{H}, \mathrm{s}, \mathrm{CH}_{3}\right), 1.58(1 \mathrm{H}, \mathrm{m}, 3-\mathrm{H}), 1.72\left(3 \mathrm{H}, \mathrm{s}, 7-\mathrm{CH}_{3}\right), 2.04\left(2 \mathrm{H}, \mathrm{m}, 6-\mathrm{H}_{2}\right), 2.24$ and 2.40 (each $1 \mathrm{H}, \mathrm{m}$, $9-\mathrm{H}), 2.50(2 \mathrm{H}, \mathrm{m}, 2 \mathrm{x} \mathrm{OH}), 3.51-3.70(4 \mathrm{H}, \mathrm{m}, 1-\mathrm{H} 2,2-\mathrm{H}, 11-\mathrm{H}), 4.00-4.17(2 \mathrm{H}, \mathrm{m}, 10-\mathrm{H}, 11-\mathrm{H})$ and $5.14(1 \mathrm{H}, \mathrm{t}, \mathrm{J} 7.0,8-\mathrm{H})$; $\delta \mathrm{c}(75 \mathrm{MHz}$, $\mathrm{CDCl}_{3}$ ) 14.5, 23.4, 25.3, 25.6, 26.8, 32.0, 32.1, 32.8, 35.6, 65.0, 69.0, 75.5, 75.9, 108.8, 119.4 and $138.2 ; \mathrm{m} / \mathrm{z}(\mathrm{CI}) 304\left(\mathrm{M}^{+}+18,90 \%\right)$, 246 (100), 229 (50) and 211 (62).

## (2S,9S,6Z)-2,6-Dimethyl-9,10-(dimethylmethylene)dioxydec-6-en-1-ol 41

Sodium periodate ( $28 \mathrm{mg}, 0.135 \mathrm{mmol}$ ) was added to the diol $\mathbf{4 0}(35 \mathrm{mg}, 0.122 \mathrm{mmol}$ ) in THF:water ( $3: 1,0.75 \mathrm{~mL}$ ) and the solution stirred for 4 h . Water and ether were added and the aqueous phase was extracted with ether. The organic extracts were washed with brine and dried $\left(\mathrm{MgSO}_{4}\right)$. After concentration under reduced pressure, the residue was immediately taken up in methanol, and sodium borohydride was added. The suspension was stirred for 1 h , then water and ether were added. The aqueous phase was extracted with ether and the organic extracts were washed with brine, dried $\left(\mathrm{MgSO}_{4}\right)$ and concentrated under reduced pressure. Chromatography of the residue, eluting with light petroleum-ethyl acetate (15:1), gave the title compound $\mathbf{4 1}$ ( $23 \mathrm{mg}, 74 \%$ ) as a colourless oil; $[\alpha]_{\mathrm{D}^{21}}+6.0$ ( $c 0.53$ in DCM) (Found: $\mathrm{M}^{+}+\mathrm{NH}_{4}{ }^{+} 274.2375$. $\mathrm{C}_{15} \mathrm{H}_{32} \mathrm{NO}_{3}$ requires $M, 274.2380$ ); $\mathrm{U}_{\text {max }} / \mathrm{cm}^{-1} 3443,1457$, $1374,1257,1218,1154,1062,849,799$ and $758 ; \delta_{\mathrm{H}}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 0.86\left(3 \mathrm{H}, \mathrm{d}, J 7.0,2-\mathrm{CH}_{3}\right), 1.14(1 \mathrm{H}, \mathrm{m}, 3-\mathrm{H}), 1.30-1.59(3 \mathrm{H}$, $\mathrm{m}, 3-\mathrm{H}, 4-\mathrm{H}_{2}$ ), 1.40 and 1.46 (each $3 \mathrm{H}, \mathrm{s}, \mathrm{CH}_{3}$ ), $1.66(1 \mathrm{H}, \mathrm{m}, 2-\mathrm{H}), 1.74\left(3 \mathrm{H}, \mathrm{s}, 6-\mathrm{CH}_{3}\right), 2.06\left(2 \mathrm{H}, \mathrm{m}, 5-\mathrm{H}_{2}\right), 2.26$ and 2.40 (each $1 \mathrm{H}, \mathrm{m}$, $8-\mathrm{H}$ ), 3.48 and 3.53 (each $1 \mathrm{H}, \mathrm{m}, 1-\mathrm{H}$ ), $3.60(1 \mathrm{H}, \mathrm{t}, J 7.0,10-\mathrm{H}), 3.98-4.17(2 \mathrm{H}, \mathrm{m}, 9-\mathrm{H}, 10-\mathrm{H})$ and $5.16(1 \mathrm{H}, \mathrm{t}, \mathrm{J} 7.0,7-\mathrm{H})$; $\delta_{\mathrm{c}}(75 \mathrm{MHz}$, $\mathrm{CDCl}_{3}$ ) $16.5,23.4,25.2,25.6,26.9,32.1(2), 32.9,35.6,68.2,69.0,75.9,108.7,119.3$ and $138.3 ; m / z(\mathrm{CI}) 274\left(\mathrm{M}^{+}+18,100 \%\right), 256$ (12) and 244 (5).

## (3S)-4-(4-Methoxybenzyl)oxy-3-methylbutyronitrile 43

Toluene $p$-sulfonyl chloride ( $26.39 \mathrm{~g}, 0.138 \mathrm{~mol}$ ) was added in several portions to the alcohol $\mathbf{4 2}(28.78 \mathrm{~g}, 13.73 \mathrm{mmol})$ and dry triethylamine ( $27.0 \mathrm{~mL}, 0.206 \mathrm{~mol}$ ) in DCM at $0^{\circ} \mathrm{C}$ and the solution stirred for 16 h at room temperature. Water was added and the organic phase was washed with water, saturated aqueous sodium carbonate and brine, then dried ( $\mathrm{MgSO}_{4}$ ) and concentrated under reduced pressure. Chromatography of the residue using light petroleum-ethyl acetate ( $30: 1$ ) as eluent gave the corresponding toluene $p$-sulfonate ( $41.89 \mathrm{~g}, 84 \%$ ) as a colourless oil (Found: $\mathrm{M}^{+}+\mathrm{NH}_{4}, 382.1686 . \mathrm{C}_{19} \mathrm{H}_{28} \mathrm{NO}_{5} \mathrm{~S}$ requires $M, 382.1688$ ); $[\alpha] \mathrm{D}^{21}-18.4$ (c 3.76 in DCM); $\mathrm{u}_{\max } / \mathrm{cm}^{-1} 1612,1513,1359,1248,1177,1097,1035,974$ and 815 ; $\delta_{\mathrm{H}}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 0.94\left(3 \mathrm{H}, \mathrm{d}, J 7.0,2-\mathrm{CH}_{3}\right)$, $2.14(1 \mathrm{H}, \mathrm{m}, 2-\mathrm{H}), 2.48\left(3 \mathrm{H}, \mathrm{s}, \mathrm{ArCH}_{3}\right), 3.32(1 \mathrm{H}, \mathrm{dd}, J 9.5,7.5,3-\mathrm{H}), 3.37(1 \mathrm{H}, \mathrm{dd}, J 9.5,5.5,3-\mathrm{H}), 3.86(3 \mathrm{H}, \mathrm{s}, 0 \mathrm{OCH} 3), 4.01(1 \mathrm{H}$, dd, J 9.5, 6.0, 1-H), $4.07(1 \mathrm{H}, \mathrm{dd}, J 9.5,5.5,1-\mathrm{H}), 4.38\left(2 \mathrm{H}, \mathrm{s}, \mathrm{OCH}_{2} \mathrm{Ar}\right), 6.90(2 \mathrm{H}, \mathrm{d}, J 8.5, \mathrm{ArH}), 7.20(2 \mathrm{H}, \mathrm{d}, J 8.5, \mathrm{ArH}), 7.36(2 \mathrm{H}, \mathrm{d}, \mathrm{J} 8.0$, ArH ) and 7.83 ( $2 \mathrm{H}, \mathrm{d}, \mathrm{J} .0, \mathrm{ArH}$ ); $\delta_{\mathrm{c}}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.$ ) 13.6, 21.5, 33.6, 55.2, $70.8,72.2,72.7,113.7,127.8,129.0,129.7,130.2,133.0$, 144.5 and 159.1; $\mathrm{m} / \mathrm{z}(\mathrm{CI}) 382\left(\mathrm{M}^{+}+18,70 \%\right)$ and 121 (100).

Potassium cyanide ( $11.31 \mathrm{~g}, 0.174 \mathrm{~mol}$ ) was added to the toluene $p$-sulfonate ( $31.61 \mathrm{~g}, 0.087 \mathrm{~mol}$ ) ) in DMSO ( 125 mL ) and the solution stirred for 20 h at room temperature. Water was added and the aqueous layer was extracted with pentane. The organic extract was washed with water and brine, dried $\left(\mathrm{MgSO}_{4}\right)$ and concentrated under reduced pressure. Chromatography of the residue, eluting with light petroleum-ethyl acetate ( $40: 1$ ), gave the title compound $\mathbf{4 3}$ ( $18.63 \mathrm{~g}, 98 \%$ ) as a colourless oil (Found: $\mathrm{M}^{+}$, 219.1261. $\mathrm{C}_{13} \mathrm{H}_{17} \mathrm{NO}_{2}$ requires $M, 219.1261$ ); [ $\left.\alpha\right]_{\mathrm{D}}{ }^{20}-22.3$ (c 1.3, DCM); $u_{\max } / \mathrm{cm}^{-1} 1611,1513,1461,1301,1247,1175,1095$ and $1033 ; \delta_{\mathrm{H}}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 1.11\left(3 \mathrm{H}, \mathrm{d}, J 7.0,3-\mathrm{CH}_{3}\right), 2.18(1 \mathrm{H}, \mathrm{m}, 3-\mathrm{H}), 2.40(1 \mathrm{H}, \mathrm{dd}, J 16.5,7.0,2-\mathrm{H}), 2.53(1 \mathrm{H}, \mathrm{dd}, J 16.5,5.5,2-\mathrm{H})$ $3.31(1 \mathrm{H}, \mathrm{dd}, J 9.5,8.0,4-\mathrm{H}), 3.47(1 \mathrm{H}, \mathrm{dd}, J 9.5,5.0,4-\mathrm{H}), 3.85\left(3 \mathrm{H}, \mathrm{s}, \mathrm{OCH}_{3}\right), 4.49\left(2 \mathrm{H}, \mathrm{s}, \mathrm{OCH}_{2} \mathrm{Ar}\right), 6.93(2 \mathrm{H}, \mathrm{d}, J 8.5$, ArH$)$ and 7.29 ( $2 \mathrm{H}, \mathrm{d}, J 8.5, \mathrm{ArH}$ ); $\delta \mathrm{c}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 16.2,21.3,31.0,55.2,72.8,72.9,113.8,118.6,129.2,130.0$ and $159.2 ; \mathrm{m} / \mathrm{z}(\mathrm{EI}) 219\left(\mathrm{M}^{+}, 53\right.$ \%), 137 (45) and 121 (100).

## (3S)-4-(4-Methoxybenzyl)oxy-3-methylbutanal 44

Di-isobutylaluminium hydride ( 1 M in heptanes, $8.20 \mathrm{~mL}, 8.20 \mathrm{mmol}$ ) was added dropwise to the nitrile $43(1.50 \mathrm{~g}, 6.85 \mathrm{mmol}$ ) in THF ( 12 mL ) at $0^{\circ} \mathrm{C}$. The mixture was stirred at $0{ }^{\circ} \mathrm{C}$ for 15 min then allowed to warm to room temperature and stirred for a further 5 h . Methanol ( 4 mL ), brine and aqueous hydrogen chloride ( 1 M ) were added. The aqueous layer was washed with ether and the organic extracts were washed with water and brine, and dried $\left(\mathrm{MgSO}_{4}\right)$. After concentration under reduced pressure, chromatography of the residue using light petroleum-ethyl acetate (30:1) as the eluent, gave the title compound 44 ( $1.16 \mathrm{~g}, 76 \%$ ) as a colourless oil (Found: $\mathrm{M}^{+}, 222.1250 . \mathrm{C}_{13} \mathrm{H}_{18} \mathrm{O}_{3}$ requires $M, 222.1255$ ); $[\alpha]_{\mathrm{D}^{20}}-4.4\left(c 0.63, \mathrm{DCM}\right.$ ); $\mathrm{v}_{\mathrm{max}} / \mathrm{cm}^{-1} 1723,1612,1513,1462$, $1301,1248,1175,1092,1034$ and $820 ; \delta_{\mathrm{H}}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 1.00\left(3 \mathrm{H}, \mathrm{d}, J 6.5,3-\mathrm{CH}_{3}\right), 2.29(1 \mathrm{H}, \mathrm{ddd}, J 15.5,6.5,2.0,2-\mathrm{H}), 2.44(1 \mathrm{H}$, $\mathrm{m}, 3-\mathrm{H}), 2.56(1 \mathrm{H}, \mathrm{ddd}, J 15.5,6.0,2.5,2-\mathrm{H}), 3.24(1 \mathrm{H}, \mathrm{dd}, J 9.0,7.5,4-\mathrm{H}), 3.42(1 \mathrm{H}, \mathrm{dd}, J 9.0,5.0,4-\mathrm{H}), 3.83(3 \mathrm{H}, \mathrm{s}, 0 \mathrm{OCH} 3), 4.44(2 \mathrm{H}$, $\left.\mathrm{s}, \mathrm{OCH}_{2} \mathrm{Ar}\right), 6.92(2 \mathrm{H}, \mathrm{d}, J 8.5, \mathrm{ArH}), 7.26(2 \mathrm{H}, \mathrm{d}, J 8.5, \mathrm{ArH})$ and $9.77(1 \mathrm{H}, \mathrm{t}, J 2.0,1-\mathrm{H}) ; \delta \mathrm{c}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 17.0,29.0,48.4,55.2,72.6$, 74.5, 113.7, 129.1, 130.3, 159.1 and 202.3; $m / z$ (EI) 222 ( ${ }^{+}, 47 \%$ ) and 121 (100).

## (2S,7S,9S,4Z)-1-tert-Butyldimethylsilyloxy-10-(4-methoxybenzyl)oxy-5,9-dimethyldec-4-ene-2,7-diol 45

Tin(IV) bromide ( $1.55 \mathrm{~mL}, 1 \mathrm{M}$ in DCM, 1.55 mol ) was added to the stannane $20(750 \mathrm{mg}, 1.40 \mathrm{mmol})$ in DCM $(10 \mathrm{~mL})$ at $-78{ }^{\circ} \mathrm{C}$. After 5 min , the aldehyde $44(468 \mathrm{mg}, 2.11 \mathrm{mmol})$ was added and the solution stirred at $-78{ }^{\circ} \mathrm{C}$ for a further 30 min . Saturated methanolic ammonium chloride was added and the mixture allowed to warm to room temperature. Ethyl acetate and water were added and the aqueous layer was washed with ethyl acetate. The organic extracts were washed with brine, dried $\left(\mathrm{MgSO}_{4}\right)$ and concentrated under reduced pressure. Chromatography of the residue using light petroleum-ethyl acetate-TEA (85:15:1) as eluent gave the title compound $\mathbf{4 5}$ ( $471 \mathrm{mg}, 72 \%$ ) assumed to contain ca. $20 \%$ of its C(7)-epimer, as a colourless oil (Found: $\mathrm{M}^{+}+\mathrm{H}$, 467.3193. $\mathrm{C}_{26} \mathrm{H}_{47} \mathrm{O}_{5} \mathrm{Si}$ requires $M, 467.3192$ ); $\mathrm{v}_{\max } / \mathrm{cm}^{-1} 3412,1612,1513,1464,1249,1088,838$ and $778 ; \delta_{\mathrm{H}}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ major diastereoisomer $0.07\left[6 \mathrm{H}, \mathrm{s}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right], 0.88\left[9 \mathrm{H}, \mathrm{m}, \mathrm{SiC}\left(\mathrm{CH}_{3}\right)_{3}\right], 0.93\left(3 \mathrm{H}, \mathrm{d}, J 6.5,9-\mathrm{CH}_{3}\right), 1.34(1 \mathrm{H}, \mathrm{ddd}, J 14.0,7.0,2.5,8-\mathrm{H})$, $1.52(1 \mathrm{H}, \mathrm{m}, 8-\mathrm{H}), 1.76\left(3 \mathrm{H}, \mathrm{s}, 5-\mathrm{CH}_{3}\right), 1.91(1 \mathrm{H}, \mathrm{dd}, J 13.5,3.0,6-\mathrm{H}), 2.01(1 \mathrm{H}, \mathrm{m}, 9-\mathrm{H}), 2.12$ and 2.22 (each $\left.1 \mathrm{H}, \mathrm{m}, 3-\mathrm{H}\right), 2.45(1 \mathrm{H}$, dd, J 13.5, 9.5, 6-H), 3.18-3.29 ( $2 \mathrm{H}, \mathrm{m}, 10-\mathrm{H}_{2}$ ), 3.43-3.57 ( $2 \mathrm{H}, \mathrm{m}, 1-\mathrm{H}_{2}$ ), $\left.3.62(1 \mathrm{H}, \mathrm{m}, 2-\mathrm{H}), 3.79(3 \mathrm{H}, \mathrm{s}, \mathrm{OCH})_{3}\right), 3.81(1 \mathrm{H}, \mathrm{m}, 7-\mathrm{H}), 4.45$ $\left(2 \mathrm{H}, \mathrm{s}, \mathrm{OCH}_{2} \mathrm{Ar}\right), 5.37(1 \mathrm{H}, \mathrm{t}, J 7.0,4-\mathrm{H}), 6.87(2 \mathrm{H}, \mathrm{d}, J 8.5, \mathrm{ArH})$ and $7.27(2 \mathrm{H}, \mathrm{d}, J 8.5$, ArH$) ; \delta_{\mathrm{c}}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ major diastereoisomer $-5.4,17.7,18.2,23.8,25.8,31.4,31.8,40.4,43.5,55.2,67.1,67.5,71.7,72.6,76.1,113.7,123.8,129.3,130.1,135.0$ and 159.1; $\mathrm{m} / \mathrm{z}$ (CI) 467 (M+ $\mathrm{M}^{+}, 5 \%$ ), 245 (4) and 121 (100).

## (2S,4S,9S,6Z)-2,6-Dimethyl-9,10-(dimethylmethylene)dioxy-1-(4-methoxybenzyl)oxydec-6-en-4-ol 46

Tetra- $n$-butylammonium fluoride ( 1.0 M in THF, $1.54 \mathrm{~mL}, 1.54 \mathrm{mmol}$ ) was added to the diol 45 ( $471 \mathrm{mg}, 1.02 \mathrm{mmol}$ ) in THF ( 5 mL ) at $0{ }^{\circ} \mathrm{C}$ and the mixture allowed to warm to room temperature then stirred for 4 h . After concentration under reduced pressure, chromatography of the residue using $1 \%$ methanol in ethyl acetate as the eluent gave ( $2 S, 7 S, 9 S, 4 Z$ )-10-(4-methoxybenzyloxy)-5,9-dimethyldec-4-ene-1,2,7-triol ( $343 \mathrm{mg}, 95 \%$ ) containing ca. $20 \%$ of its C(7)-epimer, as a colourless oil (Found: $\mathrm{M}^{+}+\mathrm{H}, 353.2325$. $\mathrm{C}_{20} \mathrm{H}_{33} \mathrm{O}_{5}$ requires $M, 353.2328$ ); $v_{\max } / \mathrm{cm}^{-1} 3383,1613,1513,1455,1302,1248,1174,1085,1036,910$ and $734 ; \delta_{\mathrm{H}}(300 \mathrm{MHz}$, $\left.\mathrm{CDCl}_{3}\right) 0.93\left(3 \mathrm{H}, \mathrm{d}, J 6.5,9-\mathrm{CH}_{3}\right), 1.36(1 \mathrm{H}, \mathrm{ddd}, J 14.0,6.5,2.5,8-\mathrm{H}), 1.51(1 \mathrm{H}, \mathrm{m}, 8-\mathrm{H}), 1.75\left(3 \mathrm{H}, \mathrm{s}, 5-\mathrm{CH}_{3}\right), 1.85(1 \mathrm{H}, \mathrm{dd}, J 13.5,2.0$, $6-\mathrm{H}), 1.93-2.07(2 \mathrm{H}, \mathrm{m}, 9-\mathrm{H}, 3-\mathrm{H}), 2.35(1 \mathrm{H}, \mathrm{m}, 3-\mathrm{H}), 2.48(1 \mathrm{H}, \mathrm{dd}, J 13.5,10.0,6-\mathrm{H}), 3.18-3.29\left(2 \mathrm{H}, \mathrm{m}, 10-\mathrm{H}_{2}\right), 3.42(1 \mathrm{H}, \mathrm{dd}, J 11.0$, $6.5,1-\mathrm{H}), 3.50-3.69(3 \mathrm{H}, \mathrm{m}, 1-\mathrm{H}, 2-\mathrm{H}, \mathrm{OH}), 3.79\left(3 \mathrm{H}, \mathrm{s}, \mathrm{OCH}_{3}\right), 3.80(1 \mathrm{H}, \mathrm{m}, 7-\mathrm{H}), 4.21(2 \mathrm{H}, \mathrm{br} . \mathrm{s}, 2 \mathrm{x} \mathrm{OH}), 4.45\left(2 \mathrm{H}, \mathrm{s}, \mathrm{OCH}_{2} \mathrm{Ar}\right), 5.34$ $(1 \mathrm{H}, \mathrm{dd}, J 10.0,5.5,4-\mathrm{H}), 6.88(2 \mathrm{H}, \mathrm{d}, J 8.5, \mathrm{ArH})$ and $7.26(2 \mathrm{H}, \mathrm{d}, J 8.5, \mathrm{ArH}) ; \delta_{\mathrm{c}}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 17.8,23.7,31.5,31.9,40.1,43.8$, $55.2,66.7,67.6,71.6,72.7,76.1,113.7,123.7,129.3,129.9,135.0$ and $159.2 ; m / z(C I) 353\left(\mathrm{M}^{+}+1,9 \%\right)$ and $121(100)$.

Toluene $p$-sulfonic acid ( $7 \mathrm{mg}, 0.04 \mathrm{mmol}$ ) was added to the triol ( $128 \mathrm{mg}, 0.36 \mathrm{mmol}$ ) in 2,2-dimethoxypropane ( 2 mL ) and the solution stirred at room temperature for 1 h . Triethylamine ( 5 drops), water and ether were added and the organic layer was washed with brine and dried $\left(\mathrm{MgSO}_{4}\right)$. After concentration under reduced pressure, chromatography of the residue eluting with light petroleum-ethyl acetate (20:1), gave the title compound 46 ( $117 \mathrm{mg}, 83 \%$ ) as a colourless oil (Found: $\mathrm{M}^{+}+\mathrm{H}, 393.2641$. $\mathrm{C}_{23} \mathrm{H}_{37} \mathrm{O}_{5}$ requires $M, 393.2641$ ); $v_{\text {max }} / \mathrm{cm}^{-1} 3480,1612,1513,1455,1373,1247,1154,1065$ and 843 ; $\delta_{\mathrm{H}}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 0.95(3 \mathrm{H}$, d, J 7.0, 2-CH3), $1.28(1 \mathrm{H}, \mathrm{m}, 3-\mathrm{H}), 1.35$ and 1.42 (each $\left.3 \mathrm{H}, \mathrm{s}, \mathrm{CH}_{3}\right), 1.48(1 \mathrm{H}, \mathrm{m}, 3-\mathrm{H}), 1.75(3 \mathrm{H}, \mathrm{s}, 6-\mathrm{CH} 3), 1.93-2.10(2 \mathrm{H}, \mathrm{m}, 2-\mathrm{H}, 5-$ H), $2.23(1 \mathrm{H}, \mathrm{m}, 8-\mathrm{H}), 2.30-2.45(2 \mathrm{H}, \mathrm{m}, 5-\mathrm{H}, 8-\mathrm{H}), 3.12(1 \mathrm{H}, \mathrm{d}, J 3.5, \mathrm{OH}), 3.24-3.38(2 \mathrm{H}, \mathrm{m}, 1-\mathrm{H} 2), 3.53(1 \mathrm{H}, \mathrm{t}, J 7.5,10-\mathrm{H}), 3.80(3 \mathrm{H}$, $\left.\mathrm{s}, \mathrm{OCH}_{3}\right), 3.83(1 \mathrm{H}, \mathrm{m}, 4-\mathrm{H}), 3.92(1 \mathrm{H}, \mathrm{dd}, J 7.5,6.0,10-\mathrm{H}), 4.11(1 \mathrm{H}, \mathrm{m}, 9-\mathrm{H}), 4.47(2 \mathrm{H}, \mathrm{s}, \mathrm{OCH} 2 \mathrm{Ar}), 5.36(1 \mathrm{H}, \mathrm{t}, \mathrm{J} 7.5,7-\mathrm{H}), 6.88(2 \mathrm{H}$, d, $J 9.0, \mathrm{ArH}$ ) and $7.26(2 \mathrm{H}, \mathrm{d}, J 9.0, \mathrm{ArH})$; $\delta \mathrm{c}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ 17.6. 23.8. 25.6. 26.7.31.1. 32.2. 40.5. 42.9. 55.2. 67.6. 69.1. 72.6. 75.8. 76.1. 108.9. 113.7.122.6. 129.2. 130.3. 135.4 and 159.1; $m / z(C I) 393\left(\mathrm{M}^{+}+1,6 \%\right), 335$ (9) and 121 (100).

## $O$-(2S,4S,9S,6Z)-2,6-Dimethyl-9,10-(dimethylmethylene)dioxy-1-(4-methoxybenzyl)oxydec-6-en-4-yl <br> thiocarbonate 47

$O$-Phenyl thiochloroformate ( $128 \mu \mathrm{~L}, 0.849 \mathrm{mmol}$ ) was added dropwise to the alcohol 46 ( $333 \mathrm{mg}, 0.934 \mathrm{mmol}$ ) and pyridine ( 254 $\mu \mathrm{L}, 3.14 \mathrm{mmol})$ in DCM ( 1.0 mL ) and the solution stirred for 16 h . Water and ether were added and the organic phase was washed with cold aqueous hydrogen chloride ( 1 M ), saturated aqueous sodium bicarbonate and brine, then dried $\left(\mathrm{MgSO}_{4}\right)$ and concentrated under reduced pressure. Chromatography of the residue, eluting with light petroleum-ethyl acetate (50:1), gave the title compound 47 ( $406 \mathrm{mg}, 91 \%$ ) containing ca. $20 \%$ of its $\mathrm{C}(4)$-epimer as a light yellow oil (Found: $\mathrm{M}^{+}+\mathrm{NH}_{4}, 546.2877$. $\mathrm{C}_{30} \mathrm{H}_{44} \mathrm{NO}_{6} \mathrm{~S}$ requires $M$, 546.2889 ); $\delta \mathrm{H}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$, major diastereoisomer $1.05\left(3 \mathrm{H}, \mathrm{d}, \mathrm{J} 6.5,2-\mathrm{CH}_{3}\right), 1.39$ and 1.46 (each $3 \mathrm{H}, \mathrm{s}, \mathrm{CH} 3$ ), $1.49(1 \mathrm{H}, \mathrm{m}, 3-\mathrm{H})$, $1.82(3 \mathrm{H}, \mathrm{s}, 6-\mathrm{CH} 3), 1.92-2.06(2 \mathrm{H}, \mathrm{m}, 2-\mathrm{H}, 3-\mathrm{H}), 2.30-2.50\left(3 \mathrm{H}, \mathrm{m}, 8-\mathrm{H}_{2}, 5-\mathrm{H}\right), 2.70(1 \mathrm{H}, \mathrm{dd}, \mathrm{J} 13.5,7.5,5-\mathrm{H}), 3.30-3.50\left(2 \mathrm{H}, \mathrm{m}, 1-\mathrm{H}_{2}\right)$ $3.60(1 \mathrm{H}, \mathrm{t}, J 7.5,10-\mathrm{H}), 3.84\left(3 \mathrm{H}, \mathrm{s}, \mathrm{OCH}_{3}\right), 4.07(1 \mathrm{H}, \mathrm{dd}, J 8.0,6.0,10-\mathrm{H}), 4.16(1 \mathrm{H}, \mathrm{m}, 9-\mathrm{H}), 4.48(2 \mathrm{H}, \mathrm{s}, \mathrm{OCH} 2 \mathrm{Ar}), 5.36(1 \mathrm{H}, \mathrm{t}, J 7.0$, $7-\mathrm{H}), 5.73(1 \mathrm{H}, \mathrm{m}, 4-\mathrm{H}), 6.92(2 \mathrm{H}, \mathrm{d}, \mathrm{J} 9.0, \mathrm{ArH}), 7.11(2 \mathrm{H}, \mathrm{m}, \mathrm{ArH}), 7.23-7.35(3 \mathrm{H}, \mathrm{m}, \mathrm{ArH}, \mathrm{ArH})$ and $7.44(2 \mathrm{H}, \mathrm{m}, \mathrm{ArH})$; $\delta \mathrm{c}(75 \mathrm{MHz}$, $\mathrm{CDCl}_{3}$ ) major diastereoisomer 17.1, 24.2, 25.6, 26.8, 30.0, 32.3, 36.8, 38.1, 55.2, 69.0, 72.6, 75.4, 75.7, 81.9, 108.8, 113.7, 121.9, 123.4, $126.4,129.2,129.4,130.5,133.2,153.3,159.0$ and $194.7 ; \mathrm{m} / \mathrm{z}(\mathrm{CI}) 546$ ( $\mathrm{M}^{+}+18,2 \%$ ), 392 (4), 317 (6), 197 (10) and 121 (100).

## (2S,9S,6Z)-2,6-Dimethyl-9,10-(dimethylmethylene)dioxy-1-(4-methoxybenzyl)oxydec-6-ene 48

Tributyltin hydride ( $336 \mathrm{mg}, 1.15 \mathrm{mmol}$ ) and AIBN ( $16 \mathrm{mg}, 0.104 \mathrm{mmol}$ ) were added to the thiocarbonate 47 ( $406 \mathrm{mg}, 0.769 \mathrm{mmol}$ ) in benzene ( 10 mL ). The solution was degassed then heated under reflux for 1.5 h . After concentration under reduced pressure, chromatography of the residue, eluting with petrol and $1 \%$ TEA, gave the title compound 48 ( $208 \mathrm{mg}, 72 \%$ ) as a clear, colourless oil; $[\alpha]]^{20}+16$ (c 1.20 in DCM) (Found: $\mathrm{M}^{+}, 376.2620 . \mathrm{C}_{23} \mathrm{H}_{36} \mathrm{O}_{4}$ requires $M, 376.2612$ ); $\mathrm{v}_{\max } / \mathrm{cm}^{-1} 1613,1513,1456,1372,1302$, $1247,1152,1090,1065$ and 845 ; $\delta$ H $\left(300 \mathrm{MHz}^{2}, \mathrm{CDCl}_{3}\right) 0.95\left(3 \mathrm{H}, \mathrm{d}, \mathrm{J} 6.5,2-\mathrm{CH}_{3}\right), 1.14(1 \mathrm{H}, \mathrm{m}, 4-\mathrm{H}), 1.30-1.50\left(2 \mathrm{H}, \mathrm{m}, 4-\mathrm{H}, 3-\mathrm{H}_{2}\right)$, 1.40 and 1.46 (each $3 \mathrm{H}, \mathrm{s}, \mathrm{CH}_{3}$ ), $1.72\left(3 \mathrm{H}, \mathrm{s}, 6-\mathrm{CH}_{3}\right), 1.80(1 \mathrm{H}, \mathrm{m}, 2-\mathrm{H}), 2.04\left(2 \mathrm{H}, \mathrm{m}, 5-\mathrm{H}_{2}\right), 2.25$ and 2.42 (each $\left.1 \mathrm{H}, \mathrm{m}, 8-\mathrm{H}\right), 3.25(1$ $\mathrm{H}, \mathrm{dd}, J 9.0,6.5,1-\mathrm{H}), 3.32(1 \mathrm{H}, \mathrm{dd}, J 9.0,6.0,1-\mathrm{H}), 3.58(1 \mathrm{H}, \mathrm{t}, J 7.0,10-\mathrm{H}), 3.84\left(3 \mathrm{H}, \mathrm{s}, \mathrm{OCH}_{3}\right), 4.03-4.27(2 \mathrm{H}, \mathrm{m}, 9-\mathrm{H}, 10-\mathrm{H}), 4.48$ (2 $\left.\mathrm{H}, \mathrm{s}, \mathrm{OCH}_{2} \mathrm{Ar}\right), 5.14(1 \mathrm{H}, \mathrm{t}, J 7.0,7-\mathrm{H}), 6.92(2 \mathrm{H}, \mathrm{d}, J 9.0, \mathrm{ArH})$ and $7.28(2 \mathrm{H}, \mathrm{m}, \mathrm{ArH}) ; \delta_{\mathrm{C}}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 17.1,23.4,25.2,25.6,26.8$, $32.1(2), 33.3,33.5,55.2,69.1,72.6,75.6,75.9,108.7,113.6,119.2,129.0,130.8,138.5$ and $159.0 ; m / z(C I) 394\left(\mathrm{M}^{+}+18,10 \%\right), 319$ (13) and 121 (100).

DDQ ( $155 \mathrm{mg}, 0.682 \mathrm{mmol}$ ) was added to the PMB-ether 48 ( $233 \mathrm{mg}, 0.620 \mathrm{mmol}$ ) in DCM:water ( $18: 1 ; 4.0 \mathrm{~mL}$ ) and the solution stirred for 2 h . Saturated aqueous sodium bicarbonate and DCM were added and the organic layer was washed five times with
saturated aqueous sodium bicarbonate and brine, then dried $\left(\mathrm{MgSO}_{4}\right)$. After concentration under reduced pressure, chromatography of the residue, eluting with light petroleum-ethyl acetate ( $9: 1$ ) gave the alcohol $\mathbf{4 1}(125 \mathrm{mg}, 79 \%)$ as a colourless oil; $[\alpha] \mathrm{D}^{22}+6.0\left(c 0.96\right.$ in DCM) (Found: $\mathrm{M}^{+}+\mathrm{NH}_{4}, 274.2375$. $\mathrm{C}_{15} \mathrm{H}_{32} \mathrm{NO}_{3}$ requires $M, 274.2380$ ), with spectroscopic data identical with those of the sample prepared earlier.

## (3S)-3-tert-Butyldimethylsilyloxy-2,2-dimethylpent-4-en-1-ol 62

Tebbe reagent ( $2.0 \mathrm{~mL}, 0.5 \mathrm{M}$ in toluene, 1.00 mmol ) was added dropwise to the lactol $\mathbf{6 1}(246 \mathrm{mg}, 1.00 \mathrm{mmol})$ at $0^{\circ} \mathrm{C}$. The mixture was allowed to warm to room temperature and was stirred for a further 0.5 h . Sodium hydroxide was carefully added ( 0.1 M ) until no further gas evolved and the reaction mixture was dried $\left(\mathrm{NaSO}_{4}\right)$ and filtered through Celite. After concentration under reduced pressure, chromatography of the residue using light petroleum-ethyl acetate ( $25: 1$ ) gave the title compound $\mathbf{6 2}$ ( $193 \mathrm{mg}, 79 \%$ ) as a light orange oil, b.p. $180^{\circ} \mathrm{C} / 20-25 \mathrm{mmHg}$, (Found: $\mathrm{M}^{+}+\mathrm{H}$, 245.1932. $\mathrm{C}_{13} \mathrm{H}_{29} \mathrm{O}_{2} \mathrm{Si}$ requires $M$, 245.1937) [ $\alpha \mathrm{D}_{\mathrm{D}} 21-6.2$ ( $c 5.5$ in DCM); $U_{\max } / \mathrm{cm}^{-1} 3451,1642,1472,1254,1075,1047,837$ and $776 ; \delta_{\mathrm{H}}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 0.03$ and 0.09 (each $\left.3 \mathrm{H}, \mathrm{s}, \mathrm{SiCH}_{3}\right), 0.78(3 \mathrm{H}, \mathrm{s}, 2-$ $\left.\mathrm{CH}_{3}\right), 0.90\left[9 \mathrm{H}, \mathrm{s}, \mathrm{SiC}\left(\mathrm{CH}_{3}\right)_{3}\right], 1.00(3 \mathrm{H}, \mathrm{s}, 2-\mathrm{CH}), 2.90(1 \mathrm{H}, \mathrm{dd}, J 7.5,4.0, \mathrm{OH}), 3.28(1 \mathrm{H}, \mathrm{dd}, J 11.0,7.5,1-\mathrm{H}), 3.62(1 \mathrm{H}, \mathrm{dd}, J 11.0,4.0$, $1-\mathrm{H}), 3.92(1 \mathrm{H}, \mathrm{d}, J 7.53-\mathrm{H}), 5.16$ and 5.20 (each $1 \mathrm{H}, \mathrm{m}, 5-\mathrm{H})$ and $5.88(1 \mathrm{H}, \mathrm{ddd}, J 17.0,11.0,7.5,4-\mathrm{H})$; $\delta \mathrm{c}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)-5.2,-4.1$, $18.0,20.9,22.6,25.8,38.9,70.3,82.4,116.8$ and $137.9 ; m / z(C I) 245\left(\mathrm{M}^{+}+1,100 \%\right)$ and $83(90)$.

## ( $3 R, 5 S$ )- and ( $3 S, 5 S$ )-5-tert-Butyldimethylsilyloxy-4,4-dimethylhept-6-en-3-ol 63

Dess-Martin periodinane ( $2.60 \mathrm{~g}, 6.15 \mathrm{mmol}$ ) was added to the alcohol $62(1.00 \mathrm{~g}, 4.09 \mathrm{mmol})$ in DCM ( 10 mL ) and the suspension stirred for 0.5 h then diluted with ether ( 100 mL ) and poured into a vigorously stirred solution of sodium thiosulphate ( 15 g ) in saturated aqueous sodium bicarbonate ( 100 mL ). After 5 min , the organic layer was washed with saturated aqueous sodium bicarbonate and water then dried $\left(\mathrm{MgSO}_{4}\right)$. Concentration under reduced pressure gave (3S)-tert-butyldimethylsilyloxy-2,2-dimethylpent-4-enal ( $997 \mathrm{mg}, 100 \%$ ) as a colourless oil used immediately (Found: $\mathrm{M}^{+}+\mathrm{H}, 243.1782 . \mathrm{C}_{13} \mathrm{H}_{27} \mathrm{O}_{2} \mathrm{Si}^{2}$ requires M , 243.1780); [ $\alpha]_{\mathrm{D}^{21}}-12.1$ (c 1.75 in DCM); $\mathrm{v}_{\max } / \mathrm{cm}^{-1} 1730,1471,1255,1083$ and 837 ; $\delta_{\mathrm{H}}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)-0.03$ and 0.01 (each 3 H , s , $\left.\mathrm{SiCH}_{3}\right), 0.83\left[9 \mathrm{H}, \mathrm{m}, \mathrm{SiC}\left(\mathrm{CH}_{3}\right)_{3}\right], 0.94$ and 1.00 (each $\left.3 \mathrm{H}, \mathrm{s}, 2-\mathrm{CH}_{3}\right), 4.14(1 \mathrm{H}, \mathrm{d}, J 7.5,3-\mathrm{H}), 5.20\left(2 \mathrm{H}, \mathrm{m}, 5-\mathrm{H}_{2}\right), 5.78(1 \mathrm{H}, \mathrm{m}, 4-\mathrm{H})$ and $9.56(1 \mathrm{H}, \mathrm{s}, 1 \mathrm{H}) ; \delta \mathrm{C}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)-5.2,-4.0,16.6,18.0,19.0,25.6,50.6,78.4,117.4,136.7$ and $206.2 ; \mathrm{m} / \mathrm{z}(\mathrm{CI}) 260\left(\mathrm{M}^{+}+18,3 \%\right)$, 243 ( $\mathrm{M}^{+}+1,38$ ), 171 (85) and 132 (100).

Anhydrous cerium(III) chloride ( $2.82 \mathrm{~g}, 11.45 \mathrm{mmol}$ ) was added to the pentenal ( $997 \mathrm{mg}, 4.09 \mathrm{mmol}$ ) in THF ( 100 mL ) and the suspension cooled to $0{ }^{\circ} \mathrm{C}$ and stirred for 0.5 h before ethyl magnesium bromide ( $5.73 \mathrm{~mL}, 1 \mathrm{M}$ in ether, 5.73 mmol ) was added dropwise. The mixture was stirred at $0^{\circ} \mathrm{C}$ for 1 h and saturated aqueous ammonium chloride was added. The mixture was allowed to warm to room temperature and diluted with ether. The mixture was filtered through celite and the aqueous layer extracted twice with ether. The organic extracts were washed with brine, dried $\left(\mathrm{MgSO}_{4}\right)$ and concentrated under reduced pressure. Chromatography of the residue, eluting with light petroleum-ethyl acetate (15:1), gave the alcohol $\mathbf{6 2}$ ( $80 \mathrm{mg}, 8 \%$ ) as a colourless oil and the C(3)-epimers of the title compound 63 ( $845 \mathrm{mg}, 76 \%$ ), ratio ca. $50: 50$; less polar epimer (Found: $\mathrm{M}^{+}+\mathrm{H}, 273.2256$. $\mathrm{C}_{15} \mathrm{H}_{33} \mathrm{O}_{2} \mathrm{Si}$ requires $M, 273.2250$ ); $[\alpha]_{\mathrm{D}}{ }^{20}-32.7$ ( $c 1.43 \mathrm{in} \mathrm{DCM);} u_{\max } / \mathrm{cm}^{-1} 3506,1468,1254,1048,838$ and 777 ; $\delta \mathrm{H}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ 0.00 and 0.06 (each $3 \mathrm{H}, \mathrm{s}, \mathrm{SiCH}_{3}$ ), $0.70\left(3 \mathrm{H}, \mathrm{s}, 4-\mathrm{CH}_{3}\right), 0.85\left[9 \mathrm{H}, \mathrm{m}, \mathrm{SiC}\left(\mathrm{CH}_{3}\right)_{3}\right], 0.94\left(3 \mathrm{H}, \mathrm{s}, 4-\mathrm{CH}_{3}\right), 0.96\left(3 \mathrm{H}, \mathrm{m}, 1-\mathrm{H}_{3}\right), 1.20-1.42(2$ $\left.\mathrm{H}, \mathrm{m}, 2-\mathrm{H}_{2}\right), 3.48(1 \mathrm{H}, \mathrm{m}, 3-\mathrm{H}), 3.86(1 \mathrm{H}, \mathrm{d}, J 7.5,5-\mathrm{H}), 4.24(1 \mathrm{H}, \mathrm{br} . \mathrm{s}, \mathrm{OH}), 5.10-5.20\left(2 \mathrm{H}, \mathrm{m}, 7-\mathrm{H}_{2}\right)$ and $5.90(1 \mathrm{H}$, ddd, $J 17.0,10.5$, $7.5,4-\mathrm{H}) ; \delta_{\mathrm{c}}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)-5.0,-3.6,11.3,17.0,18.0,20.4,24.3,25.8,41.9,79.1,82.1,116.7$ and $138.7 ; \mathrm{m} / \mathrm{z}(\mathrm{CI}) 273\left(\mathrm{M}^{+}+1,100\right.$ \%); more polar isomer, $[\alpha]_{\mathrm{D}^{20}}-6.2\left(c 0.93\right.$ in DCM); $\delta_{\mathrm{H}}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 0.00$ and 0.04 (each $3 \mathrm{H}, \mathrm{s}, \mathrm{SiCH}_{3}$ ), 0.72 and 0.86 (each 3 H , s, $\left.4-\mathrm{CH}_{3}\right), 0.88\left[9 \mathrm{H}, \mathrm{m}, \mathrm{SiC}\left(\mathrm{CH}_{3}\right)_{3}\right], 0.96\left(3 \mathrm{H}, \mathrm{t}, J, 7.5,1-\mathrm{H}_{3}\right), 1.26$ and 1.54 (each $\left.1 \mathrm{H}, \mathrm{m}, 2-\mathrm{H}\right), 2.54(1 \mathrm{H}, \mathrm{d}, J 4.0,0 \mathrm{O}), 3.36(1 \mathrm{H}, \mathrm{ddd}, J$ $10.5,4.0,2.0,3-\mathrm{H}), 3.96(1 \mathrm{H}, \mathrm{d}, J 8.0,5-\mathrm{H}), 5.10-5.20\left(2 \mathrm{H}, \mathrm{m}, 7-\mathrm{H}_{2}\right)$ and $5.82(1 \mathrm{H}, \mathrm{ddd}, J 16.5,11.0,8.0,4-\mathrm{H}) ; \delta \mathrm{C}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)-5.2$, $-4.2,11.1,17.9,19.6,22.6,24.3,25.8,40.7,77.5,84.8,117.1$ and 137.2.
( $3 R, 5 S$ )- and ( $3 S, 5 S$ )-7-[Di-(4-methoxyphenyl)(phenyl)methoxy]-5-tert-butyldimethylsilyloxy-4,4-dimethylheptan-3-ol 65 Borane.THF ( 2 M in THF, $6.49 \mathrm{~mL}, 12.98 \mathrm{mmol}$ ) was added dropwise to the alkenol $63(1.77 \mathrm{~g}, 6.49 \mathrm{mmol})$ in THF ( 50 mL ) at $0{ }^{\circ} \mathrm{C}$. The solution was allowed to warm to room temperature and was stirred for 6 h . Aqueous sodium hydroxide ( $5 \%, 10 \mathrm{~mL}$ ) and $30 \%$ hydrogen peroxide ( 5 mL ) were added and the mixture stirred for 0.5 h . Water and ethyl acetate were added and the aqueous layer was extracted three times with ethyl acetate. The organic extracts were washed with saturated aqueous ammonium chloride and brine, then dried $\left(\mathrm{MgSO}_{4}\right)$. After concentration under reduced pressure, chromatography of the residue eluting with light petroleumethyl acetate ( $10: 1$ to $3: 1$ ) gave the diol $\mathbf{6 4}$ as a colourless oil together with minor amounts of the less polar (5S)-5-tert-butyldimethylsilyloxy-4,4-dimethylheptan-3,6-diols as a complex mixture of diastereoisomers.

Di-(4-methoxyphenyl)(phenyl)methyl chloride ( $1.52 \mathrm{~g}, 4.70 \mathrm{mmol}$ ) and DMAP ( $55 \mathrm{mg}, 0.45 \mathrm{mmol}$ ) were added to the diol 64 $(1.30 \mathrm{~g}, 4.48 \mathrm{mmol})$ and $N, N$-di-isopropylethylamine ( $1.56 \mathrm{~mL}, 8.96 \mathrm{mmol}$ ) in DCM ( 20 mL ) and the mixture stirred at room temperature for 16 h . Saturated aqueous ammonium chloride was added and the organic layer washed with brine then dried ( $\mathrm{MgSO}_{4}$ ). After concentration under reduced pressure, chromatography of the residue, eluting with light petroleum-ethyl acetate (18:1), gave the C(3)-epimers of the title compound $65(1.99 \mathrm{~g}, 52 \%$ from alkenols 63$)$, ratio ca. $50: 50$, as colourless oils; less polar epimer, $[\alpha]_{\mathrm{D}^{20}}-6.1$ (c 0.98 in DCM); $\mathrm{u}_{\text {max }} / \mathrm{cm}^{-1} 3484,1608,1509,1466,1301,1252,1176,1071,1038$ and $833 ; \delta_{\mathrm{H}}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)-$ 0.25 and 0.00 (each $3 \mathrm{H}, \mathrm{s}, \mathrm{SiCH}_{3}$ ), $0.76\left[9 \mathrm{H}, \mathrm{m}, \mathrm{SiC}\left(\mathrm{CH}_{3}\right)_{3}\right], 0.77$ and 0.96 (each $\left.3 \mathrm{H}, \mathrm{s}, 4-\mathrm{CH}_{3}\right), 1.03\left(3 \mathrm{H}, \mathrm{t}, \mathrm{J} 7.5,1-\mathrm{H}_{3}\right), 1.15-1.55(2 \mathrm{H}$, $\mathrm{m}, 2-\mathrm{H}_{2}$ ), 1.87 and 2.11 (each $\left.1 \mathrm{H}, \mathrm{m}, 6-\mathrm{H}\right), 3.01(1 \mathrm{H}, \mathrm{ddd}, J 8.5,7.5,7.5,7-\mathrm{H}), 3.31(1 \mathrm{H}, \mathrm{dt}, J 8.5,5.0,7-\mathrm{H}), 3.53$ ( $1 \mathrm{H}, \mathrm{dd}, J 7.5,2.0,5-$ H), 3.66 ( $1 \mathrm{H}, \mathrm{dd}, J 9.5,2.0,3-\mathrm{H}$ ), $3.80\left(6 \mathrm{H}, \mathrm{s}, \mathrm{ArOCH}_{3}\right)$, 4.25 ( $1 \mathrm{H}, \mathrm{br} . \mathrm{s}, \mathrm{OH}$ ), $6.83(4 \mathrm{H}, \mathrm{d}, J 9.0, \mathrm{ArH}$ ), $7.15-7.35$ ( $7 \mathrm{H}, \mathrm{m}, \mathrm{ArH}$ ) and 7.43 ( $2 \mathrm{H}, \mathrm{m}, \mathrm{ArH}$ ); $m / z(\mathrm{ES}) 610\left(\mathrm{M}^{+}+18,6 \%\right), 451(6), 303(98)$ and $102(100)$; more polar epimer, $[\alpha]_{\mathrm{D}}{ }^{20}-1.0(c 0.78$ in DCM); $\delta \mathrm{H}(300$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right)-0.25$ and -0.09 (each $\left.3 \mathrm{H}, \mathrm{s}, \mathrm{SiCH}_{3}\right), 0.75\left(3 \mathrm{H}, \mathrm{s}, 4-\mathrm{CH}_{3}\right), 0.80\left[9 \mathrm{H}, \mathrm{m}, \mathrm{SiC}\left(\mathrm{CH}_{3}\right)_{3}\right], 0.84\left(3 \mathrm{H}, \mathrm{s}, 4-\mathrm{CH}_{3}\right), 1.00(3 \mathrm{H}, \mathrm{t}, \mathrm{J} 7.0,1-$ $\mathrm{H}_{3}$ ), $1.27(1 \mathrm{H}, \mathrm{m}, 2-\mathrm{H}), 1.47-1.69(2 \mathrm{H}, \mathrm{m}, 2-\mathrm{H}, 6-\mathrm{H}), 2.09(1 \mathrm{H}, \mathrm{m}, 6-\mathrm{H}), 2.29(1 \mathrm{H}, \mathrm{br} . \mathrm{s}, \mathrm{OH}), 3.04(1 \mathrm{H}, \mathrm{t}, J \mathrm{~J} .0,7-\mathrm{H}), 3.27-3.41(2 \mathrm{H}, \mathrm{m}$, 3-H, 7-H), $3.61(1 \mathrm{H}, \mathrm{dd}, J 6.0,3.0,5-\mathrm{H}), 3.79\left(6 \mathrm{H}, \mathrm{s}, \mathrm{ArOCH}_{3}\right), 6.83(4 \mathrm{H}, \mathrm{d}, J 9.0, \mathrm{ArH}), 7.15-7.35(7 \mathrm{H}, \mathrm{m}, \mathrm{ArH})$ and $7.43(2 \mathrm{H}, \mathrm{m}, \mathrm{ArH})$.

Dess-Martin periodinane ( $92 \mathrm{mg}, 0.218 \mathrm{mmol}$ ) was added to the alcohol $65(66 \mathrm{mg}, 0.145 \mathrm{mmol})$ in DCM ( 1 mL ) and the suspension stirred for 0.5 h . Ether ( 15 mL ) was added and the mixture poured into a vigorously stirred solution of sodium thiosulphate ( 2 g ) in saturated aqueous sodium bicarbonate ( 10 mL ). After 5 min , the organic layer was washed with saturated aqueous sodium bicarbonate and water, and then dried $\left(\mathrm{MgSO}_{4}\right)$. Concentration under reduced pressure gave the title compound $66(66 \mathrm{mg}, 99 \%)$ as a colourless gum, $[\alpha]^{21}-46.6$ (c 1.3 in $D C M$ ); $v_{\max } / \mathrm{cm}^{-1} 1704,1583,1509,1465,1251,1177,1039$ and 832 ; $\delta_{\mathrm{H}}\left(400 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)$ 0.20 and -0.10 (each $\left.3 \mathrm{H}, \mathrm{s}, \mathrm{SiCH}_{3}\right), 0.80\left[9 \mathrm{H}, \mathrm{m}, \mathrm{SiC}\left(\mathrm{CH}_{3}\right)_{3}\right], 0.92\left(3 \mathrm{H}, \mathrm{s}, 4-\mathrm{CH}_{3}\right), 0.96\left(3 \mathrm{H}, \mathrm{t}, J 7.0,1-\mathrm{H}_{3}\right), 1.01\left(3 \mathrm{H}, \mathrm{s}, 4-\mathrm{CH}_{3}\right), 1.72$ and 1.90 (each $1 \mathrm{H}, \mathrm{m}, 6-\mathrm{H}$ ), 2.14 and 2.20 (each $1 \mathrm{H}, \mathrm{dq}, J 19.0,7.0,2-\mathrm{H}), 3.16(1 \mathrm{H}, \mathrm{m}, 7-\mathrm{H}), 3.20\left(6 \mathrm{H}, \mathrm{s}, \mathrm{ArOCH}_{3}\right), 3.34(1 \mathrm{H}, \mathrm{m}, 7-\mathrm{H}), 4.10$ $(1 \mathrm{H}, \mathrm{dd}, J 7.5,2.5,5-\mathrm{H}), 6.72(4 \mathrm{H}, \mathrm{d}, J 9.0, \mathrm{ArH}), 7.02(1 \mathrm{H}, \mathrm{m}, \mathrm{ArH}), 7.14(2 \mathrm{H}, \mathrm{m}, \mathrm{ArH}), 7.42(4 \mathrm{H}, \mathrm{d}, J 9.0, \mathrm{ArH})$ and $7.58(2 \mathrm{H}, \mathrm{m}, \mathrm{ArH})$; $\delta_{c}\left(75 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right)-4.5,-4.4,7.6,18.0,20.2,21.1,25.8,31.3,34.6,52.5,54.3,61.7,74.4,86.2,113.1,128.1,128.3,130.1,136.5,136.6$, 145.6, 158.7 and 213.3; $m / z\left(\mathrm{ES}^{+}\right) 608\left(\mathrm{M}^{+}+18,7 \%\right), 496(10), 303$ (100) and 271 (52).

