General Methods. Diethyl ether and THF were distilled from sodium/benzophenone under nitrogen before use. CH_2Cl_2, DMSO and DMF were dried and distilled from CaH_2. Thin layer chromatography (TLC) was performed on Merck 60 F_{254} silica gel backed aluminium plates. Flash chromatography was performed using Merck Silica Gel 230-400 mesh (40-63μm). Melting points were performed on a Büchi melting point apparatus and are uncorrected. NMR spectra were obtained using either a Bruker AC200F spectrometer or a Bruker DX400 spectrometer using $CDCl_3$ as the solvent. Chemical shifts are given in ppm, referenced to the residual solvent peak (δ = 7.24 for $CDCl_3$). Coupling constants (*J*) are given in Hertz (Hz). The terms s, d, t, q, quint, m refer to singlet, doublet, triplet, quartet, quintet, multiplet; br implies the signal is broad. Elemental analyses were performed by the Microanalytical Service, Department of Chemistry, at the University of Queensland. High resolution mass spectra (HRMS) were measured by the Mass Spectroscopy Service, Department of Chemistry, at the University of Queensland. GC/MS analyses were performed on a Shimadzu GC-17A chromatograph fitted with a DB-5 column (J&W Scientific, 30 m, 0.25 mm internal diameter) connected to a Shimadzu QP-5000 mass spectrometer (70 eV). Chiral HPLC performed on a Shimadzu LC-10AT chromatograph fitted with a Chiracel OD column (Daicel Chemical Industries, 25 cm, 0.46 cm diameter) connected to a Shimadzu SPD-M10AVP PDA detector.

Enzymatic Turnover with $P450_{BioI}$. Turnovers with both tetradecanoic and hexadecanoic acids were performed using the following protocol: $P450_{BioI}$ (15 μM), fatty acid (1 μM), *E. coli* flavodoxin reductase (6 μM), cindoxin (30 μM) and catalase (1 μM) were combined in a Wheaton reaction vial. NADPH (1.25 mM) was added to the solution that was left to incubate overnight. Phenylacetic acid (62.5 μM) was then added as an internal standard. The reaction was then acidified with HCl (1 M) extracted with ethyl acetate (3 x 3 mL) and esterified with diazomethane. The turnover mixtures were concentrated before being analysed by GC/MS, as both the free alcohols and derivatised as the trifluoroacetic esters by reaction with TFAI for 10 min at room temperature.

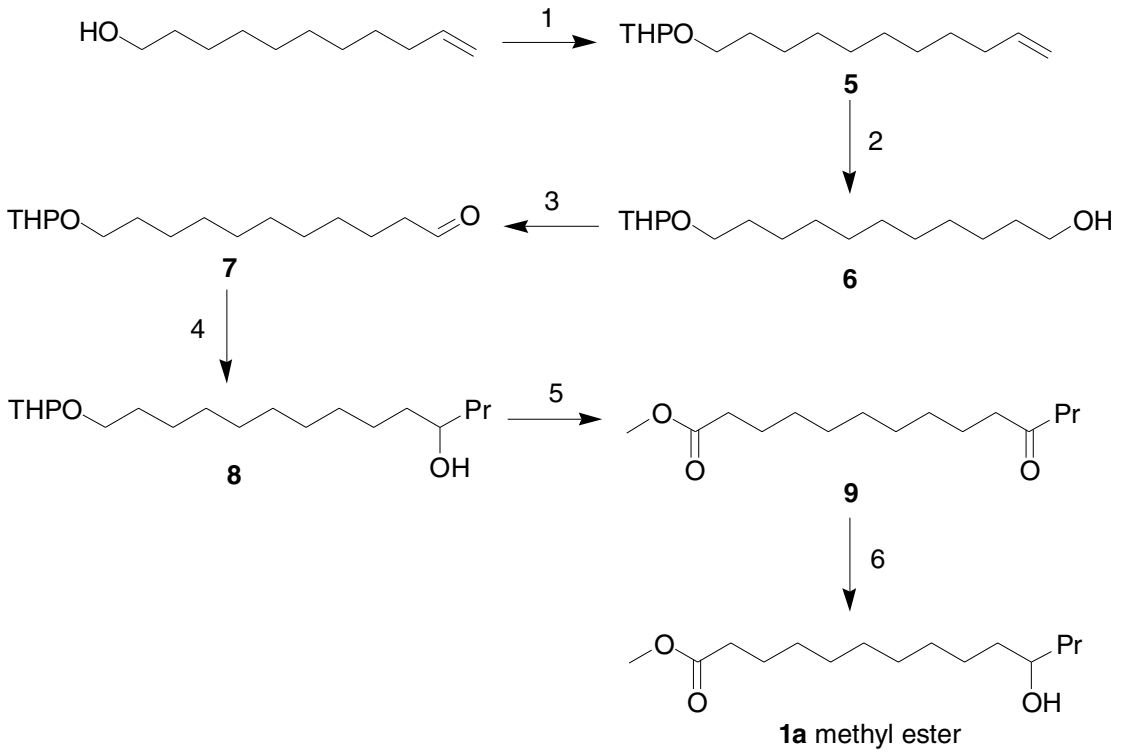
GC Analysis of Turnovers. GC Program for turnover analysis and standard identification: Splitless mode; Column Flow 1.0 mL/min; Split Ratio 100; Total Flow 102.2 mL/min; Injector 250°C; Detector 250°C; Oven 40°C (1.0 min equilibration) hold for 4.0 min, ramp 10°C / min to 250°C and hold for 10.0 min (total program time 40.0

min). Retention times (TFAI derivatised methyl ester standards): **1a** 23.32 min, **1b** 23.59 min, **1c** 23.80 min, **1d** 24.57 min, **2a** 23.82 min, **2b** 23.85 min, **2c** 23.98 min, **2d** 24.22 min, **2e** 24.49 min.

General Procedure for Isolation of hydroxy fatty acids from turnover. Crude extract was purified by preparative TLC (plates conditioned in 10% MeOH in $CHCl_3$) using 10% ethyl acetate in hexanes.

General procedure for benzoylation of hydroxy fatty acid methyl esters (1a-c converted to 4a-c; 2a-e converted to 51a-e). To a solution of hydroxy fatty acid methyl ester (0.001 g) in CH_2Cl_2 (0.2 mL) stirring at room temperature under nitrogen was added sequentially pyridine (0.010 g) and benzoyl chloride (0.010 g). After 3 h the reaction was concentrated *in vacuo* and the crude product purified by preparative TLC (10% ethyl acetate in hexanes) to yield the benzoylated hydroxy fatty acid methyl ester which was then analysed by chiral HPLC.

HPLC Analysis of Turnovers. HPLC Program for tetradecanoic acid turnover analysis and standard identification: Column (Chiracel OD) Flow 1.0 mL/min; 0.25% isopropanol in hexanes; PDA detector (230 nm). Retention times (benzoylated methyl ester standards): ***R*-4a** 12.5 min, ***R*-4b** 13.1 min, ***R*-4c** 14.9 min, ***S*-4a** 16.2 min, ***S*-4b** 18.3 min, ***S*-4c** 20.4 min. HPLC Program for hexadecanoic acid turnover analysis and standard identification: Column Flow 1.0 mL/min; 0.10% isopropanol in hexanes; PDA detector (230 nm). Retention times (benzoylated methyl ester standards): ***R*-51b** 26.1 min, ***R*-51a** 28.0 min, ***R*-51c** & ***R*-51d** 30.2 min, ***R*-51e** 34.7 min, ***S*-51d** & ***S*-51e** 38.1 min, ***S*-51a** 47.2 min, ***S*-51b** & ***S*-51c** 50.9 min.



Reagents and Conditions: (1) Dihydropyran, H^+, CH_2Cl_2; (2) BH_3.DMS, CH_2Cl_2; H_2O_2, Δ; (3) PCC, NaOAc, CH_2Cl_2; (4) PrMgBr, Et_2O, -40°C; (5) (a) H^+, MeOH; (b) CrO_3-H_2SO_4, acetone; (c) CH_2N_2, Et_2O; (6) $NaBH_4$, MeOH, 0°C.

11-(tetrahydropyran-2'-yloxy)undec-1-ene (5). To a solution of undec-10-en-1-ol (0.745 g, 4.1 mmol) in CH_2Cl_2 (30 mL) was added sequentially p-toluenesulfonic acid (0.247 g, 1.42 mmol) and dihydropyran (1.117 g, 13.3 mmol). The solution was stirred for 2 h under a nitrogen atmosphere before being quenched with saturated, aqueous $NaHCO_3$ solution (2 x 30 mL), washed with brine (30 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash chromatography (silica gel, 10% ethyl acetate in hexanes) to afford **5** (0.745 g, 2.8 mmol, 68%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.20-1.66 (20H, m), 1.96 (2H, m), 3.23-3.89 (4H, m), 4.50 (1H, t, J_1 = 2.6 Hz,), 4.80-4.97 (2H, m), 5.73 (1H, d of d of t, J_1 = 16.7 Hz, J_2 = 10.0 Hz, J_3 = 6.7 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.5, 25.4, 26.1, 28.8, 29.0, 29.3 (2C), 29.4, 29.6, 30.6, 33.7, 62.0, 67.5, 98.6, 114.0, 139.0. GC/MS: calcd for $C_{16}H_{30}O_2$, 254; $(M)^+$ found at *m/z* = 254.

11-(tetrahydropyran-2'-yloxy)undecan-1-ol (6). To a solution of **5** (0.745 g, 2.80 mmol) in CH_2Cl_2 (20 mL) under nitrogen atmosphere was added dropwise BH_3.SMe_2 (10

M in THF, 0.326 mL, 3.08 mmol). The temperature was raised to 50°C and the solution heated at reflux for 6 h. After cooling to room temperature the reaction was quenched by sequential addition of 5 M aqueous NaOH solution (20 mL) and 30% H_2O_2 (20 mL). After stirring for 1 h 30% H_2O_2 was added (10 mL) and the solution stirred for 12 h. The solution was extracted with diethyl ether (2 x 30mL), the combined organic layers washed with brine (30 mL), dried over $MgSO_4$ and the solvent removed *in vacuo*. The crude product was purified using flash chromatography (silica gel, 10% ethyl acetate in hexanes) to afford **6** (0.791 g, 2.8 mmol, 100%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.14-1.58 (22H, m), 2.52 (1H, br s), 3.50 (2H, t, J_1 = 6.5 Hz), 3.22-3.46 (2H, m), 3.50 (2H, t, J_1 = 6.6 Hz), 3.54-3.82 (2H, m), 4.49 (1H, t, J_1 = 3.2 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.4, 25.3, 25.6, 26.0, 29.3 (3C), 29.4 (2C), 29.5, 30.5, 32.6, 62.0, 62.5, 67.5, 98.6. GC/MS: calcd for $C_{16}H_{32}O_3$, 272; $(M)^+$ found at *m/z* = 272.

11-(tetrahydropyran-2'-yloxy)undecanal (7). To a solution of **6** (0.326 g, 1.15 mmol) in CH_2Cl_2 (20 mL) was added sequentially sodium acetate (0.300 g, 3.66 mmol) and PCC (0.936 g, 4.34 mmol). The solution was stirred under a nitrogen atmosphere for 1 h before the solution was decanted from the chromium salts and the salts washed with CH_2Cl_2 (2 x 10 mL). The combined organic layers were then filtered through a silica gel plug and the solvent removed *in vacuo*. The crude product was purified using flash chromatography (silica gel, 10% ethyl acetate in hexanes) to afford **7** (0.211 g, 1.8 mmol, 65%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.12-1.65 (22H, m), 2.31 (2H, t, J_1 = 6.7 Hz), 3.21-3.87 (4H, m), 4.50 (1H, m), 9.65 (1H, s). ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.1, 21.6, 25.1, 25.8, 28.7, 28.9 (2C), 29.0, 29.1, 29.3, 30.3, 43.3, 61.4, 66.9, 98.1, 199.4. GC/MS: calcd for $C_{16}H_{30}O_3$, 270; $(M)^+$ found at *m/z* = 270.

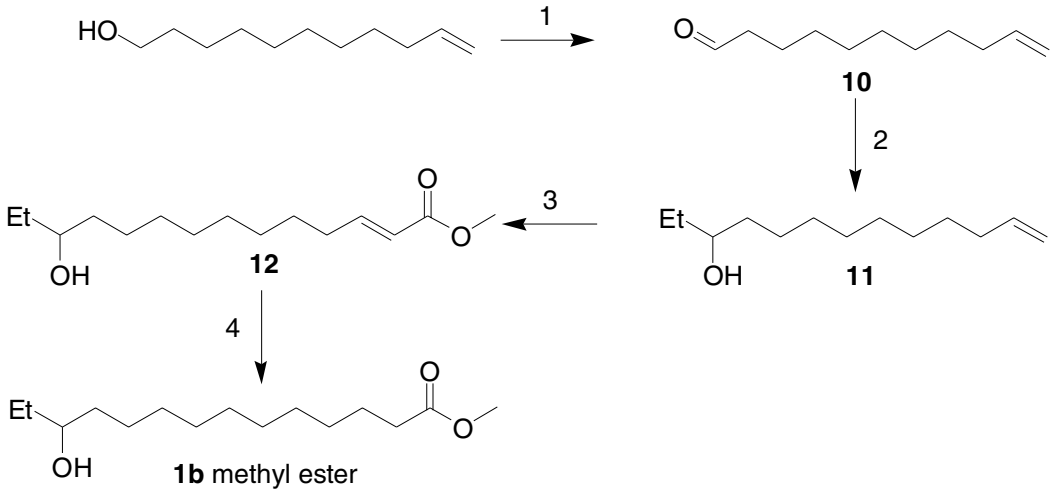
14-(tetrahydropyran-2'-yloxy)tetradecan-4-ol (8). A solution of **7** (0.161 g, 0.57 mmol) in diethyl ether (10 mL) under a nitrogen atmosphere was cooled to –40°C. To this was added a solution of 1-propylmagnesium bromide (0.33 M, 7.0 mL, 1.6 mmol). After 1 h the solution was quenched with saturated, aqueous NH_4Cl (20 mL) and diluted with diethyl ether (20 mL). The aqueous layer was extracted with diethyl ether (3 x 20 mL), the combined organic layers washed with saturated, aqueous $NaHCO_3$ (30 mL), brine (30 mL), dried over $MgSO_4$ and the solvent removed *in vacuo*. The crude product was purified using flash chromatography (silica gel, 10% ethyl acetate in hexanes) to

afford **8** (0.111 g, 0.35 mmol, 62%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.84 (3H, t, J_1 = 7.3 Hz), 1.12-1.40 (28H, m), 1.76 (1H, br s), 3.22-3.85 (5H, m), 4.50 (1H, t, J_1 = 2.9 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 18.7, 19.5, 25.4, 25.6, 26.1, 29.4, 29.5 (3C), 29.6 (2C), 30.6, 37.4, 39.6, 62.1, 67.5, 71.5, 98.6. GC/MS: calcd for $C_{19}H_{38}O_3$, 314; $(M-H)^+$ found at *m/z* = 313.

Methyl 11-oxotetradecanoate (9). To a solution of **8** (0.111 g, 0.35 mmol) in methanol (10 mL) was added p-toluenesulfonic acid (0.050 g, 0.29 mmol) and the solution stirred for 2 h. Solid $NaHCO_3$ was added to quench the reaction and the solvent removed *in vacuo*. Diethyl ether (10 mL) and water (10 mL) were added to the residue and the aqueous layer extracted with diethyl ether (3 x 20 mL), the combined organic layers washed with brine (2 x 30 mL), dried over $MgSO_4$ and the solvent removed *in vacuo*. The crude product was dissolved in acetone (15 mL) and Jones Reagent (8 N) added until the orange colour persisted. The solution was stirred for 30 min, after which water (40 mL) was added quench the reaction. The solution was extracted with hexane (4 x 20 mL), the combined organic layers dried over $MgSO_4$ and the solvent removed *in vacuo*. The residue was dissolved in diethyl ether (20 mL) and extracted with aqueous 1 M NaOH solution (3 x 20 mL). The aqueous layers were combined and acidified to pH 1 using 1 M HCl. The aqueous layer was extracted with diethyl ether (3 x 30 mL), washed with brine (30 mL), dried over $MgSO_4$ and concentrated to a volume of 10 mL. CH_2N_2 solution (0.2 M in diethyl ether) was then added to the solution at 0°C until a slight yellow colour persisted. The solution was blown down with nitrogen to remove the remaining CH_2N_2 and the solution concentrated *in vacuo* to afford **9** (0.063 g, 0.25 mmol, 70%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.85 (3H, t, J_1 = 7.3 Hz), 1.15-1.31 (10H, m), 1.45-1.63 (6H, m), 2.28 (2H, t, J_1 = 7.6 Hz), 2.32 (4H, t, J_1 = 7.7 Hz), 3.61 (3H, s). ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.7, 17.2, 23.7, 24.8, 29.0, 29.1 (2C), 29.2 (2C), 34.0, 42.7, 44.6, 51.4, 174.2, 199.3. GC/MS: calcd for $C_{15}H_{28}O_3$, 256; $(M)^+$ found at *m/z* = 256.

11-Hydroxytetradecanoic acid methyl ester (1a methyl ester). To a solution of **9** (0.057 g, 0.22 mmol) in methanol (20 mL) stirring at 0°C was added $NaBH_4$ (0.017 g, 0.444 mmol). The solution was stirred under a nitrogen atmosphere at 0°C for 30 min after which the reaction was quenched by addition of CH_2Cl_2 (20 mL). The solution was washed with aqueous 5% oxalic acid solution (2 x 20 mL), brine (20 mL), dried over

$MgSO_4$ and the solvent removed *in vacuo*. The crude product was purified using flash chromatography (silica gel, 10% ethyl acetate in hexanes) to afford **1a** (0.041 g, 0.14 mmol, 65%) as a white solid (MP: 39.5-40.5°C; Lit. MP: 41.4-42.0°C)[1]. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.89 (3H, t, J_1 = 7.0 Hz), 1.18-1.45 (18H, m), 1.58 (2H, quint, J_1 = 7.4 Hz), 1.66 (1H, br s), 2.26 (2H, t, J_1 = 7.3 Hz), 3.55 (1H, m), 3.63 (3H, s). ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.1, 18.8, 24.9, 25.6, 29.1, 29.2, 29.3, 29.5, 29.6, 34.1, 37.4, 39.6, 51.4, 71.7, 174.3. GC/MS: calcd for $C_{15}H_{30}O_3$, 258; *m/z* (%) 227 (0.6), 215 (9.0), 186 (15.4), 183 (41.1), 143 (31.1), 74 (48.3), 55 (100), 43 (67.3). Anal. Calcd. For $C_{15}H_{30}O_3$: C, 69.72; H, 11.70. Found C, 69.77; H, 12.02.



Reagents and Conditions: (1) PCC, CH_2Cl_2; (2) EtMgBr, Et_2O, -40°C; (3) (a) O_3, CH_2Cl_2, -78°C; (b) $Ph_3P{=}CHCO_2Me$, CH_2Cl_2, Δ; (4) H_2, Pd/C, MeOH/Hexanes.

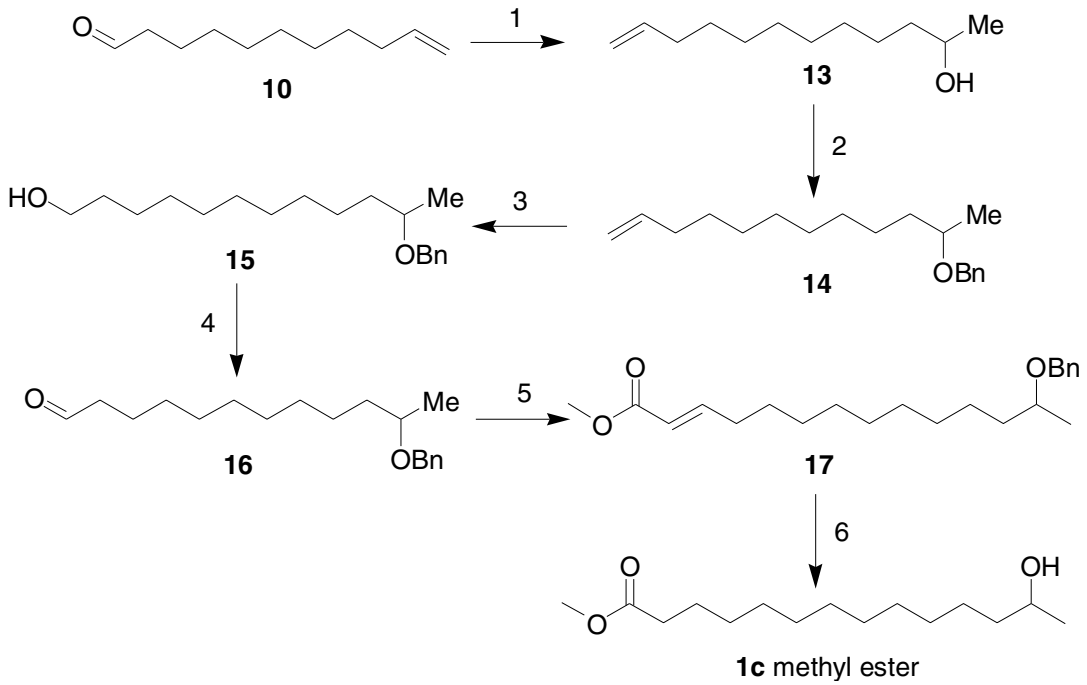
Undec-10-enal (10). Prepared in an analogous method to that used for **7**. The crude product was purified by flash chromatography (silica gel, 3% ethyl acetate in hexanes) to afford **10** (4.763 g, 26.29 mmol, 84%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.20-1.45 (10H, m), 1.58 (2H, quint, J_1 = 7.0 Hz), 1.99 (2H, d of t, J_1 = 6.7 Hz, J_2 = 7.2 Hz), 2.38 (2H, d of t, J_1 = 1.9 Hz, J_2 = 7.2 Hz), 4.85-5.05 (2H, m), 5.73 (1H, d of d of t, J_1 = 13.6 Hz, J_2 = 17.4 Hz, J_3 = 6.7 Hz), 9.72 (1H, t, J_1 = 2.0 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.0, 28.8, 29.0, 29.1, 29.2 (2C), 33.7, 43.8, 114.1, 139.0, 202.9. GC/MS: calcd for $C_{11}H_{20}O$, 168; $(M\text{-}H)^+$ found at *m/z* = 167.

Tridec-12-en-3-ol (11). Prepared in an analogous method to that used for **8**. The crude product was purified using flash chromatography (silica gel, 10% ethyl acetate in hexanes) to afford **11** (0.402 g, 2.01 mmol, 38%) as a clear, colourless oil. ^{1}H NMR (200

MHz, $CDCl_3$) δ 0.89 (3H, t, J_1 = 7.4 Hz), 1.15-1.55 (16H, m), 1.77 (1H, br s), 1.99 (2H, d of t, J_1 = 6.7 Hz, J_2 = 7.2 Hz), 3.46 (1H, m), 4.80-5.00 (2H, m), 5.76 (1H, d of d of t, J_1 = 13.6 Hz, J_2 = 17.4 Hz, J_3 = 6.7 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 9.8, 25.6, 28.8, 29.0, 29.4, 29.5, 29.6, 30.0, 33.7, 36.9, 73.2, 114.0, 139.1. GC/MS: calcd for $C_{13}H_{26}O$, 198; $(M-H_2O)^+$ found at *m/z* = 180.

Methyl 12-hydroxytetradec-2-enoate (12). A solution of **11** (0.402 g, 2.01 mmol) in CH_2Cl_2 (20 mL) was cooled to -78°C and subjected to an ozone atmosphere. After excess ozone had been purged with oxygen dimethyl sulfide (5 mL, excess) was added to quench the reaction. The reaction was then warmed to room temperature and the solvent removed *in vacuo*. To a solution of crude aldehyde in CH_2Cl_2 (20 mL) was added methoxycarbonylmethylene(triphenyl)-phosphorane (1.438 g, 4.02 mmol) and the solution heated at reflux for 12 h. Following removal of the solvent *in vacuo* the crude product was purified by flash chromatography (silica gel, 10% ethyl acetate in hexanes) to afford **12** (0.520 g, 2.01 mmol, 100%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.84 (3H, t, J_1 = 7.4 Hz), 1.15-1.50 (16H, m), 2.04 (1H, br s), 2.10 (2H, d of t, J_1 = 6.0 Hz, J_2 = 7.3 Hz), 3.41 (1H, m), 3.62 (3H, s), 5.73 (1H, d of t, J_1 = 14.2 Hz, J_2 = 1.5 Hz), 6.88 (1H, d of t, J_1 = 14.2 Hz, J_2 = 7.0 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 9.7, 25.5, 27.8, 28.9, 29.1, 29.3, 29.5, 29.9, 32.0, 36.7, 51.2, 72.9, 120.6, 149.7, 167.0. GC/MS: calcd for $C_{15}H_{28}O_3$, 256; $(M-H_2O)^+$ found at *m/z* = 238.

12-Hydroxytetradecanoic acid methyl ester (1b methyl ester). To a solution of **12** (0.520 g, 2.01 mmol) in 30% methanol in hexanes (20 mL) was added 10% Pd/C catalyst (0.020 g). The solution was introduced to a 1 atm hydrogen atmosphere and left to stir for 12 h. The solution was filtered to remove the catalyst before being concentrated *in vacuo*. The crude product was purified by flash chromatography (silica gel, 5% ethyl acetate in hexanes) to afford **1b** (0.522 g, 2.01 mmol, 100%) as a white solid (MP: 41.5-42.5°C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (3H, t, J_1 = 7.4 Hz), 1.20-1.60 (21H, m), 2.28 (2H, t, J_1 = 6.9 Hz), 3.50 (1H, m), 3.64 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.9, 25.0, 25.6, 29.1, 29.2, 29.4 (2C), 29.6, 29.7, 30.2, 34.1, 37.0, 51.4, 73.3, 174.4. GC/MS: calcd for $C_{15}H_{30}O_3$, 258; *m/z* (%) 229 (14.9), 200 (33.2), 197 (60.7), 95 (41.4), 87 (100), 74 (61.7), 59 (88.7), 41 (92.9). Anal. Calcd. For $C_{15}H_{30}O_3$: C, 69.72; H, 11.70. Found C, 70.03; H, 12.05.



Reagents and Conditions: (1) MeMgBr, Et_2O, -40°C; (2) NaH, BnBr, *t*-$Bu_4N^+I^-$, THF, 0°C; (3) BH_3.DMS, CH_2Cl_2; H_2O_2, Δ; (4) PCC, CH_2Cl_2; (5) $Ph_3P{=}CHCO_2Me$, $CHCl_3$, Δ; (6) H_2, Pd/C, Hexanes.

Dodec-11-en-2-ol (13). Prepared in an analogous method to that used for **8**. The crude product was purified by flash chromatography (silica gel, 5% ethyl acetate in hexanes) to afford **13** (3.250 g, 17.65 mmol, 100%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.11 (3H, d, J_1 = 6.1 Hz), 1.15-1.50 (14H, m), 1.92 (1H, br s), 2.01 (2H, d of t, J_1 = 5.9 Hz, J_2 = 6.8 Hz), 3.71 (1H, m), 4.90 (2H, m), 5.76 (1H, d of d of t, J_1 = 17.1 Hz, J_2 = 10.2 Hz, J_3 = 6.6 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 23.3, 25.7, 28.8, 29.0, 29.3, 29.5, 29.6, 33.7, 39.2, 98.0, 114.0, 139.1. GC/MS: calcd for $C_{12}H_{24}O$, 184; $(M\text{-}H_2O)^+$ found at *m/z* = 166.

2-benzyloxydodec-11-ene (14). To a solution of sodium hydride (0.516 g, 26.5 mmol) in THF (60 mL) stirring at -10°C under a nitrogen atmosphere was added sequentially a solution of **13** (3.250 g in diethyl ether, 10 mL, 17.65 mmol), benzyl bromide (3.360 g, 19.4 mmol) and tetra-*t*-butylammonium iodide (0.050 g). The solution was allowed to warm to room temperature and stirred for 48 h after which the solution was quenched with saturated aqueous NH_4Cl (50 mL) and diethyl ether (50 mL). The aqueous layer was extracted with diethyl ether (2 x 30 mL), the combined organic layers washed with brine (50 mL), dried over $MgSO_4$ and the solvent removed *in vacuo*. The crude product was purified by flash chromatography (silica gel, hexanes) to afford **14** (4.595 g, 16.68 mmol,

95%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.18 (3H, d, J_1 = 6.1 Hz), 1.20-1.65 (14H, m), 2.05 (2H, d of t, J_1 = 5.9 Hz, J_2 = 6.8 Hz), 3.48 (1H, m), 4.50 (2H, q, J_1 = 12.2 Hz), 4.96 (2H, m), 5.79 (1H, d of d of t, J_1 = 17.1 Hz, J_2 = 10.2 Hz, J_3 = 6.6 Hz), 7.32 (5H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.6, 25.5, 28.9, 29.1, 29.4, 29.5, 29.6, 33.7, 36.6, 70.2, 74.8, 114.1, 127.2, 127.5 (2C), 128.2 (2C), 139.1 (2C). GC/MS: calcd for $C_{19}H_{30}O$, 274; $(M)^+$ found at *m/z* = 274.

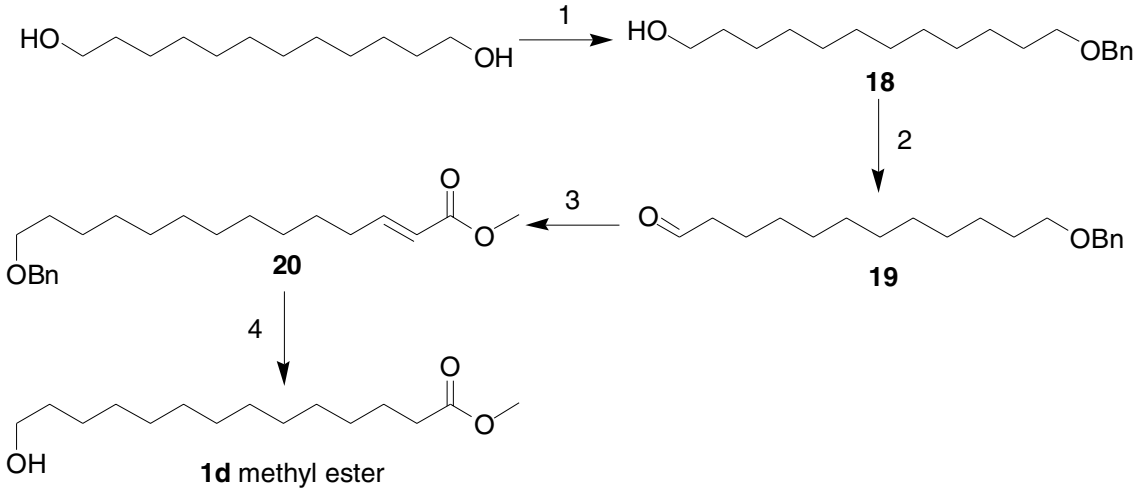
11-benzyloxydodecan-1-ol (15). Prepared in an analogous method to that used for **6**. The crude product was purified by flash chromatography (silica gel, 10% ethyl acetate in hexanes) to afford **15** (3.169 g, 10.85 mmol, 67%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.18 (3H, d, J_1 = 6.1 Hz), 1.20-1.65 (18H, m), 1.84 (1H, br s), 3.48 (1H, m), 3.61 (2H, t, J_1 = 6.6 Hz), 4.50 (2H, q, J_1 = 12.2 Hz), 7.33 (5H, m). ^{13}C NMR (50 MHz, $CDCl_3$) 19.4, 25.4, 25.7, 29.3, 29.4, 29.5 (2C), 29.6, 32.7, 36.5, 62.8, 70.2, 74.8, 127.3, 127.5 (2C), 128.2 (2C), 139.0. GC/MS: calcd for $C_{19}H_{32}O_2$, 292; $(M)^+$ found at *m/z* = 292.

11-benzyloxydodecanal (16). Prepared in an analogous method to that used for **7**. The crude product was purified by flash chromatography (silica gel, neat hexanes) to afford **16** (0.291 g, 1.00 mmol, 93%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.17 (3H, d, J_1 = 5.9 Hz), 1.20-1.65 (16H, m), 2.39 (2H, d of t, J_1 = 1.2 Hz, J_2 = 7.3 Hz), 3.50 (1H, m), 4.50 (2H, q, J_1 = 12.6 Hz), 7.33 (5H, m), 9.73 (1H, t, J_1 = 2.1 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.5, 22.0, 25.4, 29.0, 29.2, 29.4 (2C), 29.6, 36.6, 43.8, 70.2, 74.8, 127.4, 127.5 (2C), 128.2 (2C), 139.0, 202.8. GC/MS: calcd for $C_{19}H_{30}O_2$, 290; $(M)^+$ found at *m/z* = 290.

Methyl 13-benzyloxytetradec-2-enoate (17). To a solution of **16** (0.291 g, 1.00 mmol) in $CHCl_3$ (25 mL) was added methoxycarbonylmethylene(triphenyl)-phosphorane (0.719 g, 1.50 mmol) and the solution heated at reflux for 12 h. Following removal of the solvent *in vacuo* the crude product was purified by flash chromatography (silica gel, 5% ethyl acetate in hexanes) to afford **17** (0.290 g, 0.84 mmol, 84%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.17 (3H, d, J_1 = 6.1 Hz), 1.20-1.65 (16H, m), 2.39 (2H, d of t, J_1 = 1.2 Hz, J_2 = 6.8 Hz), 3.47 (1H, m), 3.70 (3H, s), 4.49 (2H, q, J_1 = 12.0 Hz), 5.80 (1H, d of t, J_1 = 15.6 Hz, J_2 = 1.5 Hz), 6.96 (1H, d of t, J_1 = 15.6 Hz, J_2 = 7.1 Hz), 7.33 (5H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.6, 25.5, 27.9, 29.1, 29.3, 29.4, 29.5, 29.6, 32.2,

36.6, 51.3, 70.2, 74.9, 120.8, 127.3, 127.6 (2C), 128.2 (2C), 139.1, 149.8, 167.2. GC/MS: calcd for $C_{22}H_{34}O_3$, 346; $(M\text{-}PhCHO)^+$ found at *m/z* = 240

13-Hydroxytetradecanoic acid methyl ester (1c methyl ester). Prepared in an analogous method to that used for **1b**. The crude product was purified by flash chromatography (silica gel, 10% ethyl acetate in hexanes) to afford **1c** (0.185 g, 0.72 mmol, 87%) as a white solid (MP: 47.2-47.7°C; Lit. MP: 34.0-35.0°C)[2]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17 (3H, d, J_1 = 6.2 Hz), 1.20-1.45 (20H, m), 1.52 (2H, m), 2.09 (1H, br s), 2.28 (2H, t, J_1 = 7.5 Hz), 3.65 (3H, s), 3.77 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.5, 24.9, 25.8, 29.1, 29.2, 29.4, 29.5, 29.6 (2C), 34.1, 39.3, 51.5, 68.2, 77.2, 174.3. GC/MS: calcd for $C_{15}H_{30}O_3$, 258; *m/z* (%) 214 (6.3), 185 (2.1), 171 (3.8), 143 (11.2), 87 (57.1), 74 (53.4), 55 (57.1), 45 (100). Anal. Calcd. For $C_{15}H_{30}O_3$: C, 69.72; H, 11.70. Found C, 69.68; H, 12.01.



Reagents and Conditions: (1) Ag_2O, BnBr, CH_2Cl_2; (2) PCC, CH_2Cl_2; (3) $Ph_3P{=}CHCO_2Me$, $CHCl_3$, Δ; (4) H_2, Pd/C, Hexanes.

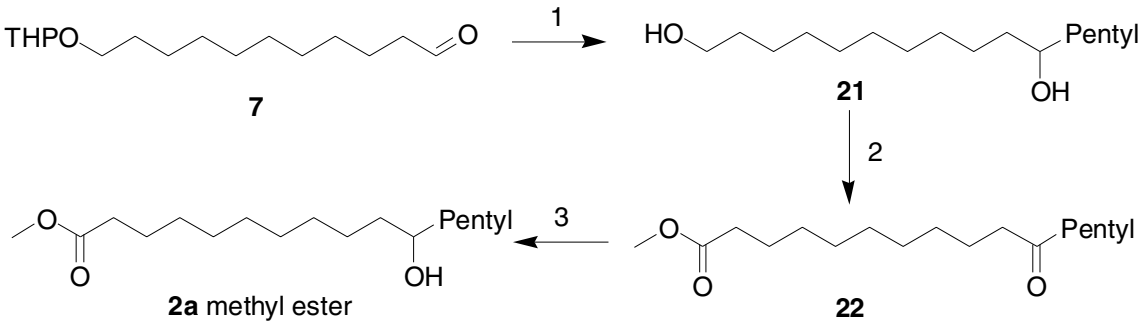
12-benzyloxydodecan-1-ol (18). To a solution of 1,12-dodecanediol (0.300 g, 1.49 mmol) in CH_2Cl_2 (80 mL) was added sequentially silver (I) oxide (0.520 g, 2.23 mmol) and benzyl bromide (0.278 g, 1.63 mmol). The reaction was stirred for seven days and the reaction then filtered through cellite to remove the silver salts and concentrated *in vacuo*. The crude product was purified by flash chromatography (silica gel, 20% ethyl acetate in hexanes) to afford **18** (0.138 g, 0.48 mmol, 32%) as a clear, colourless oil and remaining starting material (0.169 g, 0.84 mmol, 56%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.15-1.35 (16H, m), 1.35-1.65 (6H, m), 2.39 (1H, br s), 3.51 (2H, t, J_1 = 6.3 Hz), 4.43

(2H, s), 7.30 (5H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 25.6, 26.0, 29.3 (4C), 29.4 (2C), 29.6, 36.3, 62.7, 70.4, 72.9, 127.3, 127.5 (2C), 128.2 (2C), 138.4. GC/MS: calcd for $C_{19}H_{32}O_2$, 292; $(M)^+$ found at *m/z* = 292.

12-benzyloxydodecanal (19). Prepared in an analogous method to that used for **7**. The crude product was purified by flash chromatography (silica gel, 50% CH_2Cl_2 in diethyl ether) to afford **19** (0.137 g, 0.47 mmol, 100%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) 1.15-1.45 (12H, m), 1.45-1.70 (6H, m), 2.38 (2H, t, J_1 = 6.6 Hz), 3.44 (2H, t, J_1 = 6.0 Hz), 4.48 (2H, s), 7.31 (5H, m), 9.72 (1H, br s). ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.8, 26.0, 28.9, 29.1, 29.2 (2C), 29.3 (2C), 29.6, 43.7, 70.3, 72.6, 127.2, 127.4 (2C), 128.2 (2C), 139.0, 202.8. GC/MS: calcd for $C_{19}H_{30}O_2$, 290; $(M)^+$ found at *m/z* = 290.

Methyl 14-benzyloxytetradec-2-enoate (20). Prepared in an analogous method to that used for **17**. The crude product was purified by flash chromatography (silica gel, 10% ethyl acetate in hexanes) to afford **20** (0.123 g, 0.37 mmol, 78%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.20-1.50 (16H, m), 1.61 (2H, quint, J_1 = 6.6 Hz), 2.17 (2H, d of d of t, J_1 = 12.9 Hz, J_2 = 1.5 Hz, J_3 = 7.1 Hz), 3.44 (2H, t, J_1 = 6.6 Hz), 3.70 (3H, s), 4.48 (2H, s), 5.80 (1H, d of t, J_1 = 15.6 Hz, J_2 = 1.5 Hz), 6.94 (1H, d of t, J_1 = 15.6 Hz, J_2 = 7.0 Hz), 7.33 (5H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 26.1, 27.9, 29.0, 29.3 (2C), 29.4 (2C), 29.5, 29.7, 32.1, 51.3, 70.4, 72.8, 120.7, 127.4, 127.5 (2C), 128.3 (2C), 138.6, 149.8, 167.1. GC/MS: calcd for $C_{22}H_{34}O_3$, 346; $(M\text{-methanol})^+$ found at *m/z* = 314.

14-Hydroxytetradecanoic acid methyl ester (1d methyl ester). Prepared in an analogous method to that used for **1b**. The crude product was purified by flash chromatography (silica gel, 10% ethyl acetate in hexanes) to afford **1d** (0.080 g, 0.32 mmol, 87%) as a white solid (MP: 46.0-46.5°C; Lit. MP: 46.0-46.5°C)[3]. ^{1}H NMR (400 MHz, $CDCl_3$) 1.20-1.65 (23H, m), 2.28 (2H, t, J_1 = 7.6 Hz), 3.62 (2H, t, J_1 = 6.7 Hz), 3.64 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.8, 25.6, 29.0, 29.1, 29.3 (2C), 29.4 (2C), 29.5, 30.8, 32.7, 34.0, 51.3, 63.0, 174.3. GC/MS: calcd for $C_{15}H_{30}O_3$, 258; *m/z* (%) 228 (5.3), 185 (2.9), 143 (6.8), 112 (8.2), 74 (100), 55 (95.5), 43 (68.2), 41 (87.8). Anal. Calcd. For $C_{15}H_{30}O_3$: C, 69.72; H, 11.70. Found C, 69.68; H, 12.01.



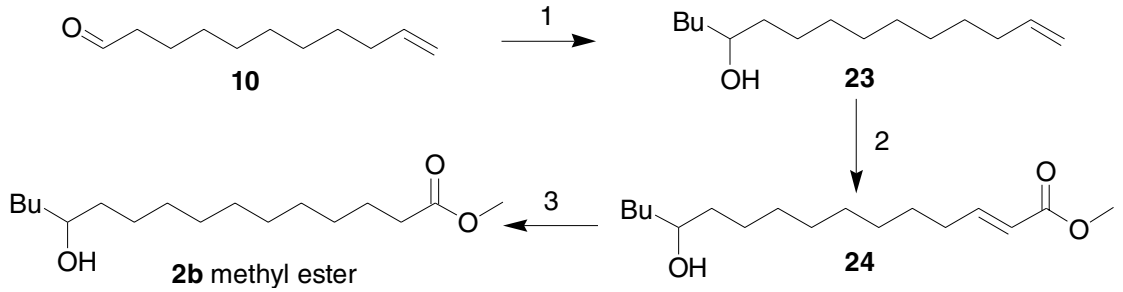
Reagents and Conditions: (1) (a) PentylMgBr, Et_2O, -40°C; (b) H^+, MeOH; (2) (a) CrO_3-H_2SO_4, acetone; (b) CH_2N_2, Et_2O; (3) $NaBH_4$, MeOH, 0°C.

Hexadecan-1,11-diol (21). A solution of **7** (0.700 g, 2.60 mmol) in diethyl ether (5 mL) under a nitrogen atmosphere was cooled to –40°C. To this was added a solution of 1-pentylmagnesium bromide (0.43 M, 15.0 mL, 6.5 mmol). After 5 min the solution was quenched with saturated, aqueous NH_4Cl (20 mL) and diluted with diethyl ether (20 mL). The aqueous layer was extracted with diethyl ether (3 x 20 mL), the combined organic layers washed with saturated, aqueous $NaHCO_3$ (30 mL), brine (30 mL), dried over $MgSO_4$ and the solvent removed *in vacuo*. To the crude product dissolved in methanol (20 mL) was added p-toluenesulfonic acid (0.200 g, 1.1 mmol) and the solution stirred for 3 h. Solid $NaHCO_3$ was added to quench the reaction and the solvent removed *in vacuo*. Ethyl acetate (10 mL) and water (10 mL) were added to the residue and the organic layer washed with brine (30 mL), dried over $MgSO_4$ and the solvent removed *in vacuo*. The crude product was recrystalised (methanol) to afford **21** (0.480 g, 1.85 mmol, 71%) as a white solid (MP: 55-56°C; Lit. MP: 65.8-67.1°C)[4]. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.84 (3H, t, J_1 = 6.5 Hz), 1.12-1.40 (26H, m), 1.70 (2H, br s), 3.54 (1H, m), 3.60 (2H, t, J_1 = 6.5 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 22.6, 25.6 (2C), 25.7 (2C), 26.0, 26.3, 29.3, 29.4, 29.6, 31.8, 32.6, 37.5, 62.9, 71.9. GC/MS: calcd for $C_{16}H_{34}O_2$, 258; $(M\text{-propyl})^+$ found at m/z = 215.

Methyl 11-oxohexadecanoate (22). To a solution of **21** (0.180 g, 0.70 mmol) in acetone (15 mL) was added Jones Reagent (8 N) until the orange colour persisted. The solution was stirred for 30 min, after which water (40 mL) was added quench the reaction. The solution was extracted with hexane (4 x 20 mL), the combined organic layers dried over $MgSO_4$ and the solvent removed *in vacuo*. The residue was dissolved in diethyl ether (20 mL) and extracted with aqueous 1 M NaOH solution (3 x 20 mL). The

aqueous layers were combined and acidified to pH 1 using 1 M HCl. The aqueous layer was extracted with diethyl ether (3 x 30 mL), washed with brine (30 mL), dried over $MgSO_4$ and concentrated to a volume of 10 mL. CH_2N_2 solution (0.2 M in diethyl ether) was then added to the solution at 0°C until a slight yellow colour persisted. The solution was blown down with nitrogen to remove the remaining CH_2N_2 and the solution concentrated *in vacuo* to afford **22** (0.150 g, 0.53 mmol, 75%) as white solid (MP: 39.0-41.0°C; Lit. MP: 38.0-39.0°C)[5]. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.90 (3H, t, J_1 = 6.6 Hz), 1.15-1.40 (14H, m), 1.50-1.70 (6H, m), 2.28 (2H, t, J_1 = 8.0 Hz), 2.35 (4H, t, J_1 = 7.7 Hz), 3.63 (3H, s). ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.7, 22.2, 23.3, 23.6, 24.7, 28.9, 29.0 (3C), 29.1 (2C), 31.2, 33.8, 42.5, 51.2, 174.0, 211.5. GC/MS: calcd for $C_{17}H_{32}O_3$, 284; $(M)^+$ found at *m/z* = 284.

11-Hydroxyhexadecanoic acid methyl ester (2a methyl ester). Prepared in an analogous method to that used for **1a**. The crude product was purified by flash chromatography (silica gel, 20% ethyl acetate in hexanes) to afford **2a** (0.051 g, 0.18 mmol, 64%) as a white solid (MP: 42-43°C; Lit. MP: 44.0-44.5°C)[5]. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.82 (3H, t, J_1 = 6.6 Hz), 1.18-1.48 (21H, m), 1.50-1.65 (4H, m), 2.25 (2H, t, J_1 = 8.0 Hz), 3.51 (1H, m), 3.61 (3H, s). ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 22.6, 24.9, 25.3, 25.6, 29.0, 29.1 (2C), 29.3, 29.5, 29.6, 31.9, 34.0, 37.4, 51.4, 71.9, 174.3. GC/MS: calcd for $C_{17}H_{34}O_3$, 286; *m/z* (%) 215 (8.0), 183 (33.0), 143 (23.0), 87 (68.0), 74 (38.0), 55 (100), 43 (73.0), 41 (88.0).



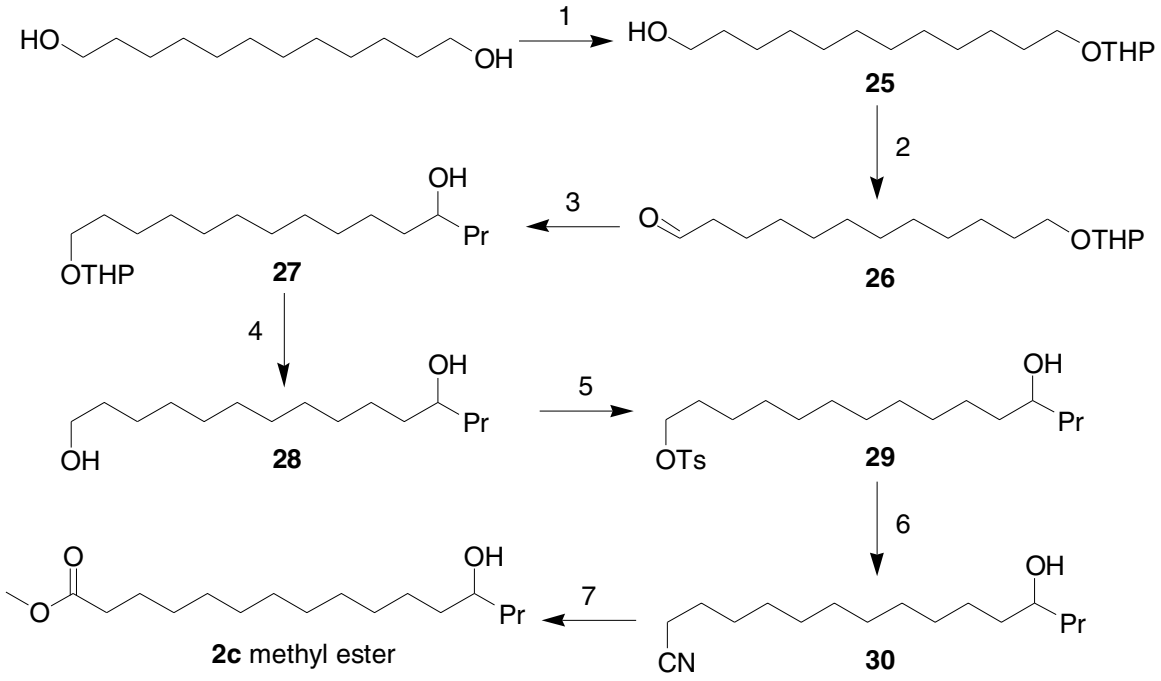
Reagents and Conditions: (1) BuMgBr, Et_2O, -40°C; (2) (a) O_3, CH_2Cl_2, -78°C; (b) $Ph_3P{=}CHCO_2Me$, CH_2Cl_2, Δ; (3) H_2, Pd/C, Hexanes.

Pentadec-14-en-5-ol (23). Prepared in an analogous method to that used for **8**. The crude product was purified using flash chromatography (silica gel, 5% ethyl acetate in hexanes) to afford starting material **10** (0.238 g, 1.42 mmol, 26%) and **23** (0.530 g, 2.35

mmol, 44%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.91 (3H, t, J_1 = 6.3 Hz), 1.15-1.55 (20H, m), 1.59 (1H, br s), 2.04 (2H, d of t, J_1 = 6.5 Hz, J_2 = 6.3 Hz), 3.57 (1H, m), 4.90-5.10 (2H, m), 5.83 (1H, d of d of t, J_1 = 13.6 Hz, J_2 = 17.4 Hz, J_3 = 6.7 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 22.7, 25.6, 27.8, 28.9, 29.0, 29.4, 29.5, 29.7, 33.8, 37.1, 37.4, 71.9, 114.0, 139.1. GC/MS: calcd for $C_{15}H_{30}O$, 226; $(M\text{-}H_2O)^+$ found at *m/z* = 208.

Methyl 12-hydroxyhexadec-2-enoate (24). Prepared in an analogous method to that used for **12**. The crude product was purified by flash chromatography (silica gel, 3% ethyl acetate in hexanes) to afford **24** (0.382 g, 1.50 mmol, 64%) as a white solid (MP 29.0-30.0°C). ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.83 (3H, t, J_1 = 6.6 Hz), 1.00-1.50 (20H, m), 1.93 (1H, br s), 2.11 (2H, d of t, J_1 = 7.3 Hz, J_2 = 7.1 Hz), 3.49, (1H, m), 3.64 (3H, s), 5.74 (1H, d of t, J_1 = 15.6 Hz, J_2 = 1.5 Hz), 6.89 (1H, d of t, J_1 = 15.6 Hz, J_2 = 7.1 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.9, 22.6, 25.4, 27.7, 27.8, 28.9, 29.2, 29.3, 29.5, 32.0, 37.0, 37.3, 51.2, 71.6, 120.6, 149.6, 167.0. GC/MS: calcd for $C_{17}H_{32}O_3$, 284; $(M\text{-}H_2O)^+$ found at *m/z* = 266.

12-Hydroxyhexadecanoic acid methyl ester (2b methyl ester). Prepared in an analogous method to that used for **1b**. The crude product was purified by flash chromatography (silica gel, 3% ethyl acetate in hexanes) to afford **2b** (0.220 g, 0.86 mmol, 98%) as a white solid (MP: 47.0-48.0°C; Lit. MP: 47.7-48.5°C)[6]. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.84 (3H, t, J_1 = 6.7 Hz), 1.10-1.60 (24H, m), 1.71 (1H, br s), 2.24 (2H, t, J_1 = 7.5 Hz), 3.50 (1H, m), 3.60 (3H, s). ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 22.7, 24.8, 25.6, 27.8, 29.0, 29.1, 29.3, 29.4, 29.5, 29.6, 34.0, 37.1, 37.4, 51.3, 71.7, 174.3. GC/MS: calcd for $C_{17}H_{34}O_3$, 286; *m/z* (%) 229 (17.7), 200 (25.2), 197 (60.9), 157 (21.3), 143 (22.6), 87 (100), 74 (50.0), 69 (67.7). Anal. Calcd. For $C_{17}H_{34}O_3$: C, 71.28; H, 11.96. Found C, 71.45; H, 12.22.



Reagents and Conditions: (1) Dihydropyran, I_2, CH_2Cl_2; (2) PCC, NaOAc, CH_2Cl_2; (3) PrMgBr, Et_2O, -40°C; (4) H^+, MeOH; (5) TsCl, pyridine, 0°C; (6) NaCN, DMF, 70°C; (7) HCl/ MeOH.

12-(tetrahydropyran-2'-yloxy)dodecan-1-ol (25). Prepared in an analogous method to that used for **5**. The crude product was purified by flash chromatography (silica gel, 20% ethyl acetate in hexanes) to afford **25** (1.62 g, 5.62 mmol, 54%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.11-1.74 (26H, m), 2.33 (1H, br s), 3.52 (2H, t, J_1 = 6.8 Hz), 3.22-3.85 (4H, m), 4.49 (1H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.5, 25.4, 25.6, 26.1, 29.3 (3C), 29.4 (2C), 29.6, 30.6, 32.6, 62.1 (2C), 62.6, 67.5, 98.6. GC/MS: calcd for $C_{17}H_{34}O_3$, 286; $(M)^+$ found at *m/z* = 286.

12-(tetrahydropyran-2'-yloxy)dodecanal (26). Prepared in an analogous method to that used for **7**. The crude product was purified by flash chromatography (silica gel, 20% ethyl acetate in hexanes) to afford **26** (1.220 g, 4.30 mmol, 88%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.20-1.90 (24H, m), 2.38 (2H, d of t, J_1 = 1.7 Hz, J_2 = 7.3 Hz), 3.28-3.90 (4H, m), 4.54 (1H, m), 9.65 (1H, s). ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.7, 22.0, 25.5, 26.2, 29.1, 29.3 (2C), 29.4, 29.5 (2C), 29.7, 30.8, 43.9, 62.3, 67.7, 98.8, 202.9. GC/MS: calcd for $C_{17}H_{32}O_3$, 284; $(M)^+$ found at *m/z* = 284.

15-(tetrahydropyran-2'-yloxy)pentadecan-4-ol (27). Prepared in an analogous method to that used for **8**. The crude product was purified using flash chromatography

(silica gel, 20% ethyl acetate in hexanes) to afford **27** (0.580 g, 1.76 mmol, 100%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.89 (3H, t, J_1 = 7.0 Hz), 1.16-1.87 (32H, m), 3.26-3.81 (4H, m), 4.52 (1H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 18.7, 19.6, 25.4, 25.6, 26.1, 29.3 (2C), 29.4 (2C), 29.5 (2C), 29.7, 30.7, 37.4, 39.6, 62.2, 67.5, 71.5, 98.7. GC/MS: calcd for $C_{20}H_{40}O_3$, 328; $(M\text{-}C_5H_{10}O)^+$ found at *m/z* = 243.

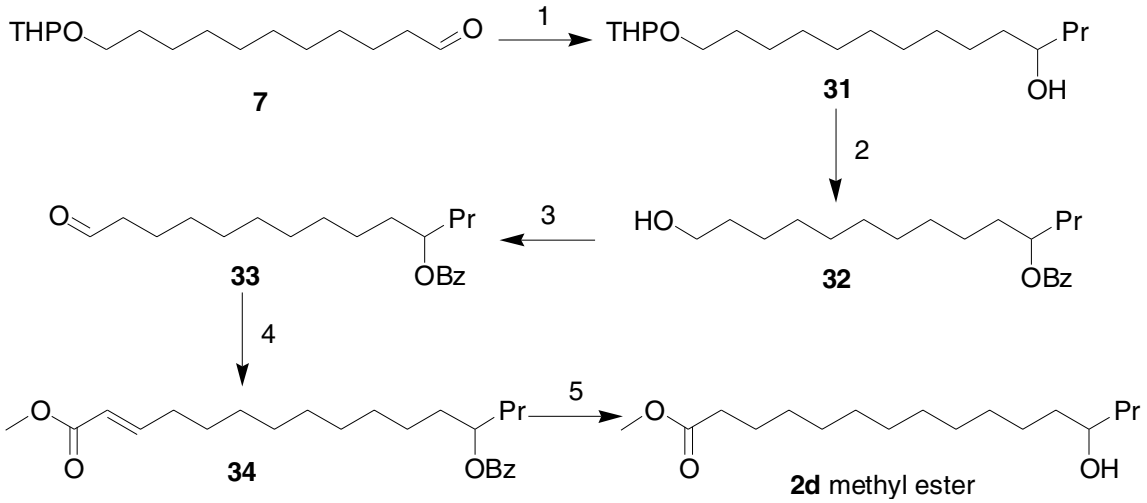
Pentadecan-1,12-diol (28). To a solution of **27** (1.31 g, 4.00 mmol) in methanol (25 mL) was added p-toluenesulfonic acid (0.230 g, 1.3 mmol) and the solution stirred for 1 h before the solvent removed *in vacuo*. The crude product was purified using flash chromatography (silica gel, 20% ethyl acetate in hexanes) to afford **28** (0.920 g, 3.76 mmol, 94%) as a white solid (MP: 56.0-58.0°C). ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (3H, t, J_1 = 6.5 Hz), 1.17-1.60 (24H, m), 1.77 (2H, br s), 3.49-3.62 (1H, m), 3.58 (2H, t, J_1 = 6.6 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.1, 18.8, 20.9, 25.6, 25.7, 29.4, 29.5 (2C), 29.6, 32.7, 37.4, 39.5, 60.4, 62.7, 71.6. GC/MS: calcd for $C_{15}H_{32}O_2$, 244; $(M\text{-propyl})^+$ found at *m/z* = 201.

12-hydroxypentadecyl toluene-4-sulfonate (29). To a solution of **28** (0.550 g, 2.25 mmol) in pyridine (10 mL) was added p-toluenesulfonyl chloride (0.450 g, 2.4 mmol) and the solution stirred at 0°C for 30 min before being quenched with water (30 mL). The aqueous layer was extraced with diethyl ether (3 x 30 mL) and the combined organic layers washed with aqueous HCl (1 M, 30 mL), brine (30 mL), dried over $MgSO_4$ and the solvent removed *in vacuo*. The crude product was purified using flash chromatography (silica gel, 20% ethyl acetate in hexanes) to afford **29** (0.610 g, 1.51 mmol, 67%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87 (3H, t, J_1 = 6.5 Hz), 1.08-1.66 (25H, m), 2.38 (3H, s), 3.52 (1H, m), 3.95 (2H, t, J_1 = 6.3 Hz), 7.27 (2H, d, J_1 = 7.8 Hz), 7.70 (2H, d, J_1 = 7.8 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 18.7, 21.5, 25.2, 25.5, 28.6, 28.8, 29.2, 29.3, 29.4, 29.6, 37.3, 39.5, 70.6, 71.5, 95.3, 127.7 (2C), 129.7 (2C), 133.0, 144.5.

13-hydroxyhexadecanenitrile (30). To a solution of **29** (0.500 g, 1.25 mmol) in DMF (10 mL) was added sodium cyanide (0.400 g, 8.0 mmol) and the solution stirred at 70°C for 2 h before being quenched with water (50 mL). The aqueous layer was extraced with diethyl ether (3 x 30 mL) and the combined organic layers washed with brine (30 mL), dried over $MgSO_4$ and the solvent removed *in vacuo*. The crude product was purified

using flash chromatography (silica gel, 20% ethyl acetate in hexanes) to afford **30** (0.230 g, 0.91 mmol, 73%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.86 (3H, t, J_1 = 6.5 Hz), 1.17-1.70 (25H, m), 2.28 (2H, t, J_1 = 7.1 Hz), 3.52 (1H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 17.0, 18.7, 25.5, 28.5, 28.6, 29.2, 29.3 (2C), 29.5, 29.6, 37.4, 39.6, 71.5, 95.4, 119.8. GC/MS: calcd for $C_{16}H_{31}NO$, 253; $(M)^+$ found at *m/z* = 253.

13-Hydroxyhexadecanoic acid methyl ester (2c methyl ester). To a solution of **30** (0.200 g, 0.79 mmol) in methanol (15 mL) previously saturated with anhydrous HCl gas was stirred for 12 h before being quenched with water (100 mL). The aqueous layer was extraced with diethyl ether (3 x 30 mL) and the combined organic layers washed with brine (30 mL), dried over $MgSO_4$ and the solvent removed *in vacuo*. The crude product was purified using flash chromatography (silica gel, 20% ethyl acetate in hexanes) to afford **2c** (0.170 g, 0.62 mmol, 79%) as a white solid (MP: 51.0-52.0°C; Lit. MP: 42.5-45.5°C)[7]. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (3H, t, J_1 = 6.5 Hz), 1.20-1.72 (25H, m), 2.27 (2H, t, J_1 = 7.5 Hz), 3.61 (1H, m), 3.68 (3H, s). ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.1, 18.8, 24.9, 25.6, 29.1, 29.2, 29.3 (2C), 29.4, 29.5 (2C), 29.6, 37.5, 39.7, 51.4, 71.7, 174.4. GC/MS: calcd for $C_{17}H_{34}O_3$, 286; *m/z* (%) 243 (6.0), 211 (13.0), 171 (7.0), 143 (10.0), 107 (18.0), 87 (54.0), 74 (46.0), 55 (100).



Reagents and Conditions: (1) PrMgBr, Et_2O, -40°C; (2) (a) NaH, BnBr, *t*-$Bu_4N^+I^-$, THF, 0°C; (b) H^+, MeOH; (3) PCC, CH_2Cl_2; (4) $Ph_3P{=}CHCO_2Me$, $CHCl_3$, Δ; (5) H_2, Pd/C, Hexanes.

14-(tetrahydropyran-2'-yloxy)tetradecan-3-ol (31). Prepared in an analogous method to that used for **8**. The crude product was purified using flash chromatography (silica gel, 20% ethyl acetate in hexanes) to afford **31** (0.810 g, 2.58 mmol, 94%) as a clear,

colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.89 (3H, t, J_1 = 7.3 Hz), 1.18-1.88 (30H, m), 3.28-3.93 (4H, m), 4.53 (1H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 9.8, 19.6, 25.6, 26.2, 29.4 (3C), 29.5 (2C), 29.6, 29.7 (2C), 30.1, 30.7, 36.9, 62.2, 67.6, 73.4, 98.7.

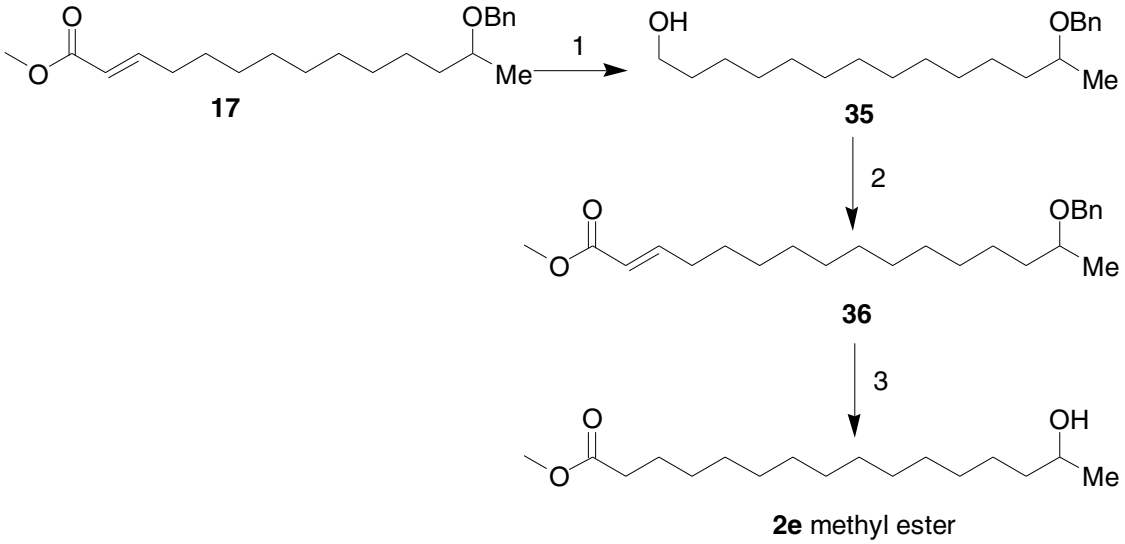
12-benzyloxytetradecan-1-ol (32). To a solution of sodium hydride (0.200 g, 50%, 5.0 mmol) in THF (12 mL) stirring at 0°C under a nitrogen atmosphere was added sequentially a solution of **31** (0.700 g in diethyl ether, 10 mL, 2.2 mmol), benzyl bromide (0.420 g, 2.5 mmol) and tetra-*t*-butylammonium iodide (0.055 g). The solution was allowed to warm to reflux and stirred for 6 h after which the solution was quenched with water (50 mL) and diethyl ether (50 mL). The aqueous layer was extracted with diethyl ether (2 x 30mL), the combined organic layers washed with brine (50 mL), dried over $MgSO_4$ and the solvent removed *in vacuo*. To the crude product dissolved in methanol (20 mL) was added p-toluenesulfonic acid (0.046 g, 0.24 mmol) and the solution stirred for 1 h. Solid $NaHCO_3$ was added to quench the reaction and the solvent removed *in vacuo*. Diethyl ether (10 mL) and water (10 mL) were added to the residue and the organic layer washed with brine (30 mL), dried over $MgSO_4$ and the solvent removed *in vacuo*.The crude product was purified by flash chromatography (silica gel, 20% ethyl acetate in hexanes) to afford **32** (0.350 g, 2.45 mmol, 49%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (3H, t, J_1 = 7.6 Hz), 1.23-1.70 (22H, m), 2.40 (1H, br s), 3.28 (1H, d of t, J_1 = 5.8 Hz, J_2 = 5.8 Hz), 3.52 (2H, t, J_1 = 6.3 Hz), 4.45 (2H, s), 7.35 (5H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 9.4, 25.2, 25.6 (2C), 26.1 (2C), 29.3, 29.5 (2C), 29.7, 32.6, 33.2, 62.5, 70.5, 80.0, 127.2, 127.6 (2C), 128.1 (2C), 138.9.

12-benzyloxytetradecanal (33). Prepared in an analogous method to that used for **7**. The crude product was purified by flash chromatography (silica gel, 10% ethyl acetate in hexanes) to afford **33** (0.260 g, 0.82 mmol, 87%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.79 (3H, t, J_1 = 7.1 Hz), 1.08-1.56 (20H, m), 2.27 (2H, d of t, J_1 = 1.7 Hz, J_2 = 7.3 Hz), 3.18 (1H, d of t, J_1 = 5.9 Hz, J_2 = 5.9 Hz), 4.36 (2H, s), 7.23 (5H, m), 9.20 (1H, t, J_1 = 1.7 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 9.4, 22.0, 25.3, 26.2, 29.0, 29.2, 29.3, 29.4 (2C), 29.7, 33.3, 43.8, 70.6, 80.1, 127.2, 127.6 (2C), 128.2 (2C), 139.1, 198.3.

Methyl 14-benzyloxyhexadec-2-enoate (34). Prepared in an analogous method to that used for **17**. The crude product was purified by flash chromatography (silica gel, 10% ethyl acetate in hexanes) to afford **34** (0.170 g, 0.45 mmol, 81%) as a clear, colourless oil.

^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (3H, t, J_1 = 7.6 Hz),1.16-1.60 (19H, m), 2.16 (2H, m), 3.27 (2H, d of t, J_1 = 5.6 Hz, J_2 = 5.6 Hz), 3.67 (3H, s), 4.45 (2H, s), 5.77 (1H, d of t, J_1 = 15.6 Hz, J_2 = 1.7 Hz), 6.93 (1H, d of t, J_1 = 15.6 Hz, J_2 = 6.8 Hz), 7.30 (5H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 9.5, 25.0, 25.3, 26.2, 29.0, 29.4 (2C), 29.5 (2C), 29.7, 32.1, 33.3, 51.2, 70.6, 72.8, 120.7, 127.2, 127.6 (2C), 128.2 (2C), 139.1, 149.7, 167.1. GC/MS: calcd for $C_{24}H_{38}O_3$, 374; $(M\text{-benzaldehyde})^+$ found at *m/z* = 268.

14-Hydroxyhexadecanoic acid methyl ester (2d methyl ester). Prepared in an analogous method to that used for **1b**. The crude product was purified by flash chromatography (silica gel, 20% ethyl acetate in hexanes) to afford **2d** (0.120 g, 0.32 mmol, 70%) as a white solid (MP: 53.0-54.0°C; Lit. MP: 47.0-48.0°C)[8]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (3H, t, J_1 = 7.3 Hz), 1.15-1.69 (25H, m), 2.25 (2H, t, J_1 = 7.8 Hz), 3.47 (1H, m), 3.61 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.8, 24.9, 25.6, 29.1, 29.2, 29.4 (2C), 29.5 (3C), 29.7, 30.1, 34.0, 36.9, 51.4, 73.2, 174.3. GC/MS: calcd for $C_{17}H_{34}O_3$, 286; *m/z* (%) 257 (5.9), 228 (12.7), 225 (13.8), 143 (13.7), 97 (20.5), 87 (52.6), 74 (52.9), 41 (100).



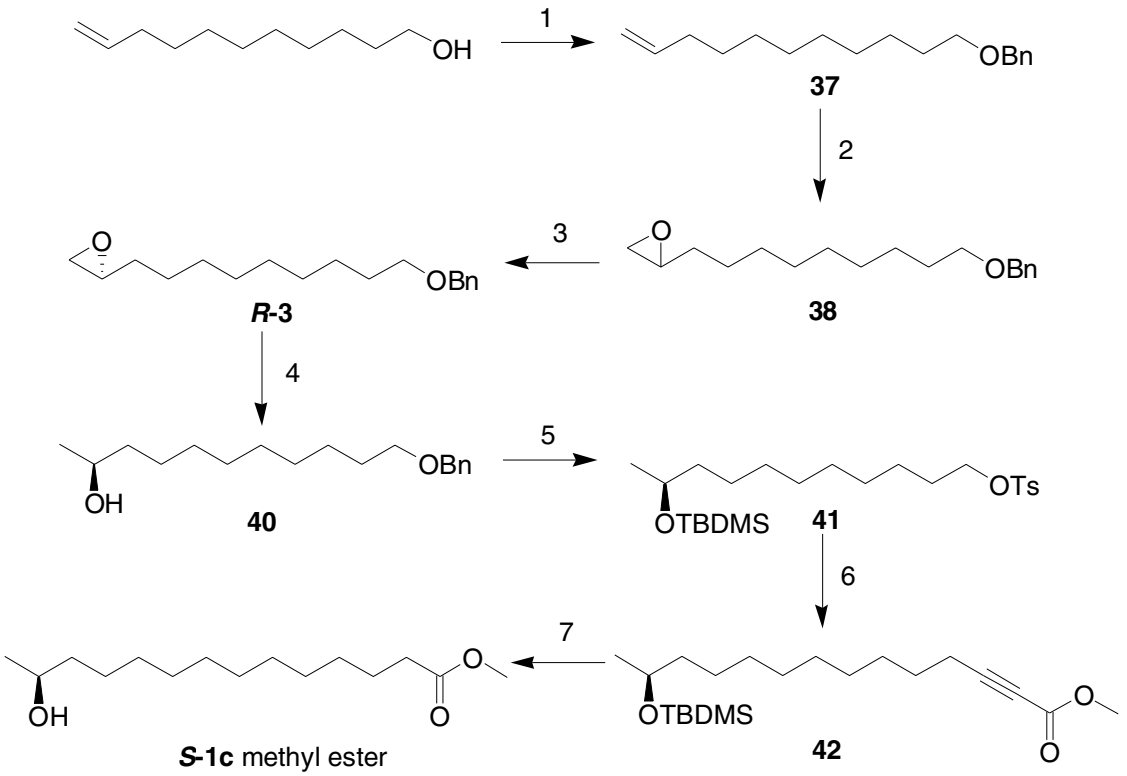
Reagents and Conditions: (1) LAH, THF, 0°C; (2) (a) PCC, CH_2Cl_2; (b) $Ph_3P{=}CHCO_2Me$, $CHCl_3$, Δ; (3) H_2, Pd/C, Hexanes.

13-benzyloxytetradecan-1-ol (35). To a solution of lithium aluminium hydride (0.500 g, 3.61 mmol) in THF (20 mL) stirring at 0°C under a nitrogen atmosphere was added **17** (0.600 g in 10 mL THF, 1.80 mmol). After 12 h the reaction was quenched by addition of sodium sulphate decahydrate (6.000 g, excess) and stirred for a further 4 h. The solution

was then filtered to remove the insoluble salts and the salts washed with ethyl acetate (4 x 25 mL). The combined organic layers were concentrated *in vacuo* to afford **35** (0.500 g, 1.62 mmol, 90%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.15 (3H, d, J_1 = 6.1 Hz), 1.15-1.65 (23H, m), 3.45 (1H, m), 3.59 (2H, t, J_1 = 6.6 Hz), 4.48 (2H, q, J_1 = 11.6 Hz), 7.30 (5H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.6, 25.5, 25.7, 29.4 (2C), 29.6 (2C), 29.7 (3C), 32.7, 36.6, 63.0, 70.2, 74.9, 127.3, 127.5 (2C), 128.2 (2C), 139.1. GC/MS: calcd for $C_{21}H_{36}O_2$, 320; $(M\text{-}C_6H_6)^+$ found at *m/z* = 242.

Methyl 15-benzyloxyhexadec-2-enoate (36). To a solution of **35** (0.500 g, 1.62 mmol) in CH_2Cl_2 (15 mL) stirring under a nitrogen atmosphere was added PCC (2.040 g, 4.06 mmol). After 6 h the reaction mixture was reduced in volume and purified by flash chromatography (silica gel, 10% ethyl acetate in hexanes) to afford crude aldehyde (0.420 g, 1.54 mmol) as a clear, colourless oil. To a solution of the aldehyde in $CHCl_3$ (50 mL) was added methoxycarbonylmethylene(triphenyl)-phosphorane (0.770 g, 2.60 mmol) and the solution heated at reflux for 12 h. Following removal of the solvent *in vacuo* the crude product was purified by flash chromatography (silica gel, 3% ethyl acetate in hexanes) to afford **36** (0.330 g, 1.03 mmol, 67%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.14 (3H, d, J_1 = 6.1 Hz), 1.15-1.65 (20H, m), 2.14 (2H, m), 3.45 (1H, m), 3.67 (3H, s), 4.46 (2H, q, J_1 = 12.0 Hz), 5.78 (1H, d of t, J_1 = 15.6 Hz, J_2 = 1.5 Hz), 6.93 (1H, d of t, J_1 = 15.6 Hz, J_2 = 7.1 Hz), 7.30 (5H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.5, 25.4, 27.8, 29.0, 29.2, 29.4 (3C), 29.5 (2C), 32.0, 36.5, 51.1, 70.1, 74.7, 120.6, 127.1, 127.4 (2C), 128.1 (2C), 139.0, 149.5, 166.9. GC/MS: calcd for $C_{24}H_{38}O_3$, 374; $(M\text{-benzaldehyde})^+$ found at *m/z* = 268.

15-Hydroxyhexadecanoic acid methyl ester (2e methyl ester). Prepared in an analogous method to that used for **1b**. The crude product was purified by flash chromatography (silica gel, 10% ethyl acetate in hexanes) to afford **2e** (0.210 g, 0.87mmol, 84%) as a white solid (MP: 55.0-56.0°C; Lit. MP: 57.0-59.0°C)[3]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (3H, d, J_1 = 6.2 Hz), 1.20-1.65 (25H, m), 2.28 (2H, t, J_1 = 7.5 Hz), 3.64 (3H, s), 3.77 (1H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ 23.3, 24.8, 25.7, 29.0, 29.1, 29.3, 29.4, 29.5 (4C), 29.6, 33.9, 39.2, 51.3, 67.8, 174.2. GC/MS: calcd for $C_{17}H_{34}O_3$, 286; *m/z* (%) 271 (0.7), 242 (28.9), 236 (8.1), 199 (15.1), 143 (26.0), 87 (79.1), 74 (100), 55 (93.4). Anal. Calcd. For $C_{17}H_{34}O_3$: C, 71.28; H, 11.96. Found C, 71.39; H, 11.69.



Reagents and Conditions: (1) NaH, BnBr, *t*-$Bu_4N^+I^-$, THF, 0°C; (2) MCPBA, CH_2Cl_2, 0°C; (3) *R,R*-Salen Complex, H_2O, 0°C; (4) LAH, THF, 0°C; (5) (a) TBDMSCl, C_4NH_4, MeCN; (b) H_2, Pd-C, Hexanes; (c) TsCl, DABCO, THF; (6) n-BuLi, HMPA, Propiolic Acid ,THF, 0°C; (7) (a) H_2, Pd-C, Hexanes; (b) TBAF, THF.

1-Benzyloxyundec-10-ene (37). Prepared in an analogous method to that used for **14**. The crude product was purified by flash chromatography (silica gel, 5% ethyl acetate in hexanes) to afford **37** (2.30 g, 8.84 mmol, 94%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.16-1.35 (m, 12H), 1.44-1.60 (m, 2H), 1.89-2.02 (m, 2H), 3.37 (t, 2H), 4.42 (s, 2H), 4.82 (d of d of t, 1H), 4.91 (d of d of t, 1H), 5.72 (d of d of t, 1H), 7.12-7.30 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 26.2, 28.9, 29.1, 29.4 (2C), 29.5, 29.7, 33.8, 70.5, 72.8, 114.1, 127.6 (3C), 128.3, 128.4, 138.7, 139.2. GC/MS: calcd for $C_{18}H_{28}O$, 260; $(M)^+$ found at *m/z* = 260.

2-(9-Benzyloxynonyl)-oxirane (38). To a solution of **37** (2.20 g, 8.46 mmol) in CH_2Cl_2 (90 mL) stirring at 0ºC under a nitrogen atmosphere was added *m*-chloroperbenzoic acid (50%, 2.92 g, 8.5 mmol). After addition was complete the reaction was stirred at room temperature for 12 h before being quenched with 5% aqueous sodium sulfite (50 mL). Following separation of the layers the organic layer was washed with saturated, aqueous

$NaHCO_3$ (50 mL), dried over $MgSO_4$ and concentrated *in vacuo* to afford **38** (2.22 g, 8.04 mmol, 95%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.20-1.70 (m, 16H), 2.44 (d of d, 1H), 2.72 (d of d, 1H), 2.84-2.92 (m, 1H), 3.45 (t, 2H), 4.48 (s, 2H), 7.20-7.38 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 25.9, 26.1, 29.1, 29.4 (2C), 29.5, 29.7, 32.4, 47.1, 52.3, 70.4, 72.8, 127.4, 127.6 (2C), 128.3 (2C), 138.6. GC/MS: calcd for $C_{18}H_{28}O_2$, 276; $(M\text{-}OH)^+$ found at *m/z* = 259.

***S*-2-(9-Benzyloxynonyl)-oxirane (*S*-3)** To a solution of acetic acid (0.003 g, 0.05 mmol) in toluene (0.5 mL) was added *S*,*S*-(Salen)CoIII(OAc) complex (0.0089 g, 0.015 mmol) and stirred at 25ºC while open to the air for 3 h. The solution was concentrated *in vacuo* and the brown residue dried under high vacuum. **38** (1.00 g, 90.36 mmol) was added and the mixture cooled to 0ºC before water (0.0358 g, 0.198 mmol) was added. The reaction was allowed to return to room tempurature over a period of 5 h and stirred for 30 h before being purified by flash chromatography (silica gel, 10% ethyl acetate in hexanes) to afford ***S*-3** (0.490 g, 44.28 mmol, 49%) in 91% ee (Chiracel OD, 0.5% isopropyl alcohol in hexanes, 1 mL/min flow rate, UV detector 220 nm: retention time for *R*-epoxide 16.4 min; *S*-epoxide 18.1 min) as a clear, colourless oil that was spectroscopically identical to **38**. The diol was eluted with 50% ethyl acetate in hexanes to afford **39** (0.500 g, 42.47 mmol, 47%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.31-1.50 (m, 14H), 1.49-1.68 (m, 2H), 2.02 (br s, 2H), 3.34-3.48 (m, 2H), 3.44 (t, 2H), 3.55-3.72 (m, 1H), 4.48 (s, 2H), 7.20-7.35 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 25.5, 26.1, 28.4, 29.4 (2C), 29.6, 29.7, 33.1, 66.7, 70.5, 72.2, 72.8, 127.5, 127.6 (2C), 128.3 (2C), 138.6. Under identical conditions utilising the *R*,*R*-(Salen)CoIII(OAc) complex the ***R*-3** was obtained in 88% ee.

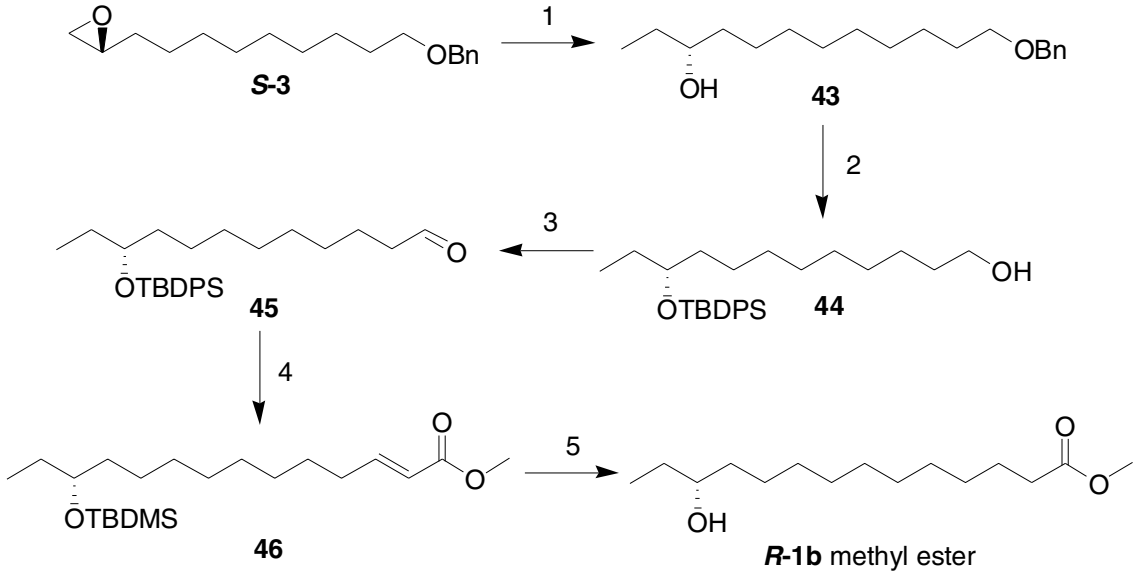
***S*-11-Benzyloxyundecan-2-ol (40)** Prepared in an analogous method to that used for **35** utilizing ***R*-3**. The crude product was purified by flash chromatography (silica gel, 10% ethyl acetate in hexanes) to afford **40** (0.870 g, 3.13 mmol, 90%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.08 (d, 3H), 1.10-1.42 (m, 13H), 1.43-1.62 (m, 2H), 1.53-1.96 (m, 2H), 3.37 (t, 2H), 3.66 (sextet, 1H), 4.41 (s, 2H), 7.10-7.29 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 23.3, 25.7, 26.1, 29.4 (2C), 29.5 (2C), 29.7, 39.2, 68.0, 70.4, 72.7, 127.4, 127.5 (2C), 128.2 (2C), 138.6.

***S*-10-(t-Butyl-dimethyl-silanyloxy)-undecyl toluene-4-sulfonate (41)** To a solution of **40** (0.700 g, 2.50 mmol) in acetonitrile (15 mL) stirring at room temperature under a nitrogen atmosphere was added sequentially TBDMSCl (0.339 g, 2.6 mmol) and imidazole (0.204 g, 3.0 mmol). After 6 h the mixture was diluted with diethyl ether (50 mL), filtered and washed dilute, aqueous HCl (3 x 30 mL). After drying over $MgSO_4$ and concentration *in vacuo* the residue was dissolved in hexanes (20 ml) and 10% Pd/C catalyst (0.020 g) was added. The atmosphere above the mixture was displaced with hydrogen and the reaction stirred for 30 min before being filtered and concentrated *in vacuo*. The residue was dissolved in THF (15 mL) and *p*-tosyl chloride (0.960 g, 3.0 mmol) and DABCO (0.340 g, 3.0 mmol) added sequentially under an nitrogen atmosphere. After 1 h the mixture was diluted with diethyl ether (40 mL), washed with dilute, aqueous HCl (30 mL), dried over $MgSO_4$ and concetrated *in vacuo*. The crude product was purified by flash chromatography (silica gel, 10% ethyl acetate in hexanes) to afford **41** (0.640 g, 1.88 mmol, 60%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.01 (s, 6H), 0.86 (s, 9H), 1.07 (d, 3H), 1.12-1.42 (m, 14H), 1.51-1.68 (m, 2H), 2.42 (s, 3H), 3.65-3.80 (m, 1H), 3.99 (t, 2H), 7.31 (d, 2H), 7.75 (d, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ -4.8 (2C), 18.1, 20.0, 23.8 (3C), 25.3, 25.9, 28.8, 28.9, 29.3, 29.4 (2C), 29.6, 39.7, 68.6, 70.6, 127.8 (2C), 129.8 (2C), 133.1, 144.6.

Methyl *S*-13-(t-butyl-dimethyl-silanyloxy)-tetradec-2-ynoate (42) To a solution of propiolic acid (0.140 g, 2.0 mmol) in THF (10 mL) stiring at 0°C under an nitrogen atmosphere was added dropwise n-BuLi (2.66 mL, 1.5M in hexanes, 4.0 mmol). The solution was warmed to room temperature and stirred for 1 h. A solution of **41** (0.420 g. 0.99 mmol) in HMPA (1.5 mL) was then added and the reaction stirred for 24 h at room temperature before being quenched with saturated, aqueous LiCl (30 mL). The aqueous layer was extracted with diethyl ether (30 mL) and the organic layers washed with saturated, aqueous LiCl (3 x 30 mL). The solution was dried over $MgSO_4$ and treated with CH_2N_2 (0.03 M in diethyl ether) until a faint yellow colour persisted. Following concentration *in vacuo* the crude product was purified by flash chromatography (silica gel, 10% ethyl acetate in hexanes) to afford **42** (0.260 g, 0.70 mmol, 71%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.07 (s, 6H), 0.89 (s, 9H), 1.13 (d, 3H), 1.22-1.62 (m, 16H), 2.33 (t, 2H), 3.72-3.82 (m, 1H), 3.76 (s, 3H). ^{13}C NMR (50 MHz,

$CDCl_3$) δ -4.8 (2C), 18.1, 18.5, 23.7 (3C), 25.6, 25.8, 27.4, 28.7, 28.9, 29.2, 29.4, 29.5, 39.6, 52.4, 68.5, 72.7, 89.9, 154.2.

***S*-13-Hydroxytetradecanoic acid methyl ester (*S*-1c methyl ester).** To a solution of **42** (0.220 g, 0.59 mmol) in ethanol (5 mL) was added 10% Pd/C catalyst (0.010 g). The solution was introduced to a 1 atm hydrogen atmosphere and left to stir for 12 h. The solution was filtered to remove the catalyst before being concentrated *in vacuo*. The residue was dissolved in THF (1 mL), tetrabutylammonium fluoride (0.16 mL, 1 M, 0.16 mmol) added and the solution stirred for 30 h. Following concnetration *in vacuo* the crude product was purified by flash chromatography (silica gel, 10% ethyl acetate in hexanes) to afford ***S*-1c** (0.113 g, 0.44 mmol, 74%) as a white solid (MP: 47.2-47.7°C; Lit. MP: 34.0-35.0°C)[1,9] that was spectroscopically identical to **1c**. GC/MS: calcd for $C_{15}H_{30}O_3$, 258; *m/z* (%) 214 (6.3), 185 (2.1), 171 (3.8), 143 (11.2), 87 (57.1), 74 (53.4), 55 (57.1), 45 (100).



Reagents and Conditions: (1) MeMgBr, $CuLi_2Cl_4$, Et_2O, -10°C; (2) (a) TBDPSCl, C_4NH_4, MeCN; (b) H_2, Pd-C, Hexanes; (3) CO_2Cl_2, DMSO, CH_2Cl_2, TEA, -72°C; (4) $Ph_3P{=}CHCO_2Me$, $CHCl_3$, Δ; (5) (a) H_2, Pd-C, Hexanes; (b) TBAF, THF.

***R*-12-Benzyloxydodecan-3-ol (43)** To a $CuLi_2Cl_4$ solution (0.01 M in diethyl ether, 10 mL) stirring at -10°C under a nitrogen atmosphere was added a solution of methylmagnesium bromide (0.53 mL, 3 M in diethyl ether, 1.6 mmol). After 15 min ***S*-3** (0.220 g, 0.80 mmol) in diethyl ether (5 mL) was added dropwise. After stirring for 30 min the reaction was quenched with saturated, aqueous NH_4Cl (15 mL). The aqueous

phase was extracted with diethyl ether (2 x 20 mL) and the organic layer washed with brine (30 mL) dried over $MgSO_4$ and concnetrated *in vacuo*. The crude product was purified by flash chromatography (silica gel, 10% ethyl acetate in hexanes) to afford **43** (0.195 g, 0.64 mmol, 84%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.92 (t, 3H), 1.21-1.72 (m, 19H), 3.44 (t, 2H), 3.40-3.55 (m, 1H), 4.48 (s, 2H), 7.22-7.37 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 9.8, 25.6, 26.1, 29.4(2C), 29.5 (2C), 29.6, 29.7, 36.9, 70.4, 72.8, 73.2, 127.4, 127.6 (2C), 128.3 (2C), 138.6. GC/MS: calcd for $C_{18}H_{30}O_2$, 278; $(M-H_2O, C_6H_5)^+$ found at *m/z* = 183.

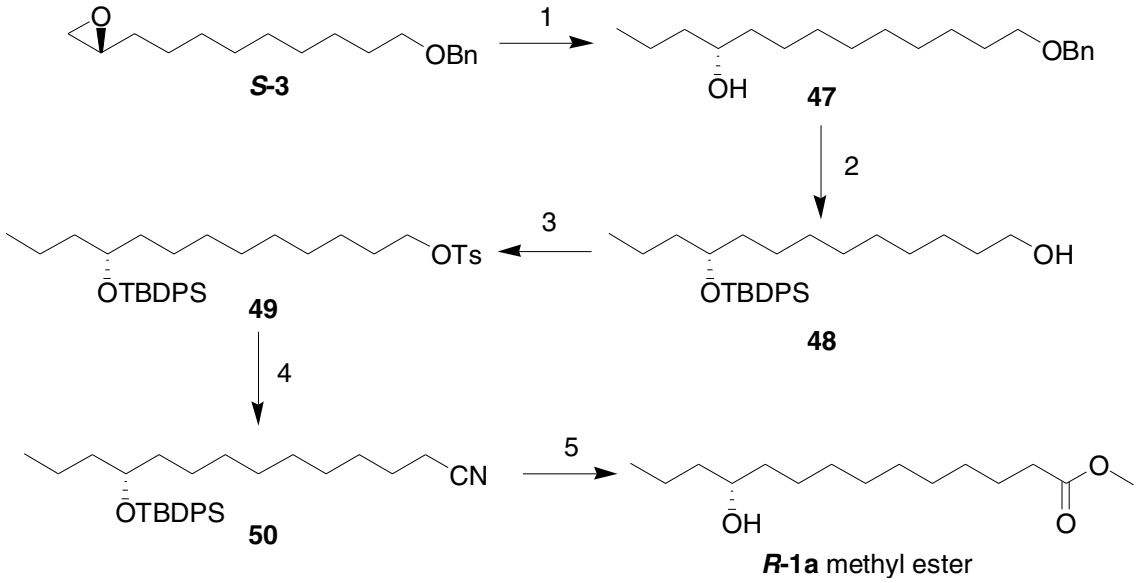
***R*-10-(t-Butyl-diphenyl-silanyloxy)-dodecan-1-ol (44)** To a solution of **43** (0.190 g, 0.65 mmol) in acetonitrile (5 mL) stirring at room temperature under a nitrogen atmosphere was added sequentially TBDPSCl (0.190 g, 0.70 mmol) and imidazole (0.110 g, 1.74 mmol). After 12 h the mixture was diluted with diethyl ether (50 mL), filtered and washed dilute, aqueous HCl (3 x 30 mL). After drying over $MgSO_4$ and concentration *in vacuo* the residue was dissolved in hexanes (20 ml) and 10% Pd/C catalyst (0.020 g) was added. The atmosphere above the mixture was displaced with hydrogen and the reaction stirred for 30 min before being filtered and concentrated *in vacuo*. The crude product was purified by flash chromatography (silica gel, 20% ethyl acetate in hexanes) to afford **44** (0.190 g, 0.61 mmol, 94%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.63 (t, 3H), 0.87-1.49 (m, 29H), 3.49 (t, 2H), 3.52 (quintet, 1H), 7.22-7.58 (m, 10H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 9.2, 19.4 (3C), 24.8, 25.7, 27.0, 28.9, 29.4 (2C), 29.5, 29.6, 32.8, 35.6, 63.0, 74.3, 127.3 (2C), 129.3 (4C), 134.8 (4C), 135.9 (2C).

***R*-10-(t-Butyl-diphenyl-silanyloxy)-dodecanal (45)** To a solution of oxalyl chloride (0.064 g, 0.51 mmol) in CH_2Cl_2 (3 mL) stirring at -78°C under a nitrogen atmosphere was added a solution of DMSO (0.08 5g, 1.1 mmol) in CH_2Cl_2 (0.5 mL). After 2 min was added a solution of **44** (0.200 g, 0.46 mmol) in CH_2Cl_2 (0.5 mL). After 20 min triethylamine (0.2 mL, 1.4 mmol) was added and the reaction mixture stirred for 5 min before being warmed to room temperature. The reaction was quenched with CH_2Cl_2 (20 mL) and then concentrated *in vacuo*. The crude product was purified by flash chromatography (silica gel, 20% ethyl acetate in hexanes) to afford **45** (0.151 g, 0.46 mmol, 75%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.76 (t, 3H), 1.00-1.65 (m, 25H), 2.39 (d of t, 2H), 3.61 (quintet, 1H), 7.28-7.72 (m, 10H), 9.70 (t, 1H). ^{13}C

NMR (50 MHz, $CDCl_3$) δ 9.2, 19.4 (3C), 22.0, 24.8, 27.1, 28.9, 29.1, 29.2, 29.3, 29.5, 35.6, 43.9, 74.3, 127.3 (2C), 129.3 (4C), 134.8 (4C), 135.9 (2C), 203.0. GC/MS: calcd for $C_{28}H_{42}O_2Si$, 438; $(M\text{-}t\text{-butyl})^+$ found at *m/z* = 381.

Methyl *R*-12-(t-butyl-diphenyl-silanyloxy)-tetradec-2-enoate (46) Prepared in an analogous method to that used for **17**. The crude product was purified by flash chromatography (silica gel, 10% ethyl acetate in hexanes) to afford **46** (0.102 g, 0.21 mmol, 94%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.77 (t, 3H), 1.02-1.48 (m, 25H), 2.09-2.30 (m, 2H), 3.61 (quintet, 1H), 3.72 (s, 3H), 5.82 (d of t, 1H), 6.96, d of t, 1H), 7.30-7.71 (m, 10H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 9.2, 19.4 (3C), 24.8, 27.1, 28.0, 28.9, 29.1, 29.3, 29.4 (2C), 29.6, 32.2, 35.6, 74.3, 120.7, 127.3 (2C), 129.3 (4C), 134.8 (4C), 135.9 (2C), 149.9, 167.2.

***R*-12-Hydroxytetradecanoic acid methyl ester (*R*-1b methyl ester)** Prepared in an analogous method to that used for **3c**. The crude product was purified by flash chromatography (silica gel, 20% ethyl acetate in hexanes) to afford ***R*-1b** (0.033 g, 0.13 mmol, 63%) as a white solid (MP: 41.5-42.5°C) that was spectroscopically identical to **1b**. GC/MS: calcd for $C_{15}H_{30}O_3$, 258; *m/z* (%) 229 (14.9), 200 (33.2), 197 (60.7), 95 (41.4), 87 (100), 74 (61.7), 59 (88.7), 41 (92.9).



Reagents and Conditions: (1) EtMgBr, $CuLi_2Cl_4$, Et_2O, -10°C; (2) (a) TBDPSCl, C_4NH_4, MeCN; (b) H_2, Pd-C, Hexanes; (3) TsCl, DABCO, THF; (4) NaCN, DMF, 70°C; (5) (a) H_2, Pd-C, Hexanes; (b) TBAF, THF.

***R*-13-Benzyloxy-tridecan-4-ol (47)** Prepared in an analogous method to that used for **43** utilizing ***S*-3**. The crude product was purified by flash chromatography (silica gel, 10% ethyl acetate in hexanes) to afford **47** (0.410 g, 1.34 mmol, 74%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.81-0.92 (m, 3H), 1.21-1.71 (m, 21H), 3.44 (t, 2H), 3.52-3.66 (m, 1H), 4.48 (s, 2H), 7.22-7.37 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.1, 18.8, 25.6, 26.2, 29.4 (2C), 29.5 (2C), 29.7, 37.5, 39.6, 70.5, 71.7, 72.8, 127.4, 127.6 (2C), 128.3 (2C), 138.7.

***R*-10-(t-butyl-diphenyl-silanyloxy)-tridecan-1-ol (48)** Prepared in an analogous method to that used for **44**. The crude product was purified by flash chromatography (silica gel, 20% ethyl acetate in hexanes) to afford **48** (0.170 g, 0.48 mmol, 66%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.75 (t, 3H), 1.05-1.65 (m, 30H), 3.63 (t, 2H), 3.72 (quintet, 1H), 7.32-7.82 (m, 10H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.1, 18.1, 19.4 (3C), 24.8, 25.7, 27.0, 29.4 (2C), 29.5, 29.6, 32.7, 36.3, 38.6, 63.0, 73.0, 127.3 (2C), 129.3 (4C), 134.8 (4C), 135.9 (2C).

***R*-Methanesulfonic acid 10-(t-butyl-diphenyl-silanyloxy)-tridecyl ester (49)** Prepared in an analogous method to that used for **29**. The crude product was purified by flash chromatography (silica gel, 20% ethyl acetate in hexanes) to afford **49** (0.122 g, 0.23 mmol, 92%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.74 (t, 3H) 1.1-1.46 (m, 31H), 1.67-1.82 (m, 2H), 2.98 (s, 3H) 3.7 (quintet, 1H), 4.11 (t, 2H), 7.27-7.72 (m, 10H) ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.1, 18.1, 19.4 (3C), 24.8, 25.4, 27.1, 29.0, 29.1, 29.3, 29.4, 29.6, 36.2, 37.3, 38.6, 70.2, 73.0, 127.3 (4C), 129.3 (6C), 134.8 (4C), 135.9 (3C), 144.6.

***R*-11-(t-Butyl-diphenyl-silanyloxy)-tetradecanenitrile (50)** Prepared in an analogous method to that used for **30**. The crude product was purified by flash chromatography (silica gel, 20% ethyl acetate in hexanes) to afford **50** (0.086 g, 0.18 mmol, 80%) as a clear, colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.76 (t, 3H), 1.03-1.52 (m, 27H), 1.64 (quintet, 2H), 2.31 (t, 2H), 3.71 (quintet, 1H), 7.31-7.72 (m, 10H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.2, 17.1, 18.1, 19.4 (3C), 24.8, 25.3, 27.1, 28.6, 28.7, 29.2, 29.3, 29.5, 36.3, 38.6, 73.0, 119.8, 127.3 (2C), 129.3 (4C), 134.8 (4C), 135.9 (2C).

***R*-11-Hydroxytetradecanoic acid methyl ester (*R*-1a methyl ester)** Prepared in an analagous method to that used for **2c**. The crude product was purified by flash chromatography (silica gel, 20% ethyl acetate in hexanes) to afford ***R*-1a** (0.029 g, 0.11 mmol, 59%) as a white solid (MP: 39.5-40.5°C; Lit. MP: 41.4-42.0°C)[2] that was spectroscopically identical to **1a**. GC/MS: calcd for $C_{15}H_{30}O_3$, 258; *m/z* (%) 227 (0.6), 215 (9.0), 186 (15.4), 183 (41.1), 143 (31.1), 74 (48.3), 55 (100), 43 (67.3).

(1) Kobayashi, S.; Furukawa, J.-i.; Sakai, T.; Sakairi, N. *Carbohydrate Research* **2002**, *337*, 1047-1053.
(2) Voss, G.; Gerlach, H. *Helvetica Chimica Acta* **1983**, *66*, 2294-307.
(3) Tulloch, A. P.; Spencer, J. F. T. *Canadian Journal of Chemistry* **1968**, *46*, 1523-8.
(4) Baser, I. A. *Fette, Seifen, Anstrichmittel* **1972**, *74*, 524-6.
(5) Ono, M.; Yamada, F.; Noda, N.; Kawasaki, T.; Miyahara, K. *Chemical & Pharmaceutical Bulletin* **1993**, *41*, 1023-6.
(6) Lefort, D.; Vorob'ev, V. D.; Somov, G. V.; Nikishin, G. I. *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya* **1967**, 648-53.
(7) Cross, B. E.; Hendley, P. *Journal of the Chemical Society, Perkin Transactions 1: Organic and Bio-Organic Chemistry (1972-1999)* **1975**, 2523-5.
(8) Tulloch, A. P. *Chemistry and Physics of Lipids* **1971**, *6*, 235-65.
(9) Furukawa, J.-I.; Kobayashi, S.; Nomizu, M.; Nishi, N.; Sakairi, N. *Tetrahedron Letters* **2000**, *41*, 3453-3457.