Synthesis of β-dimorphecolic acid exploiting highly stereoselective reduction of a side-chain carbonyl group in a π-allyltricarbonyliron lactone complex

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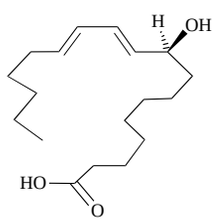
A highly enantioselective synthesis of β-dimorphecolic acid 1 is reported. The synthesis features a diastereoselective reduction of the ketone 4, in which the tricarbonyliron lactone tether induces a 1,5 transfer of chirality, followed by a stereoselective decarboxylation to create all the stereochemical elements of 1. Selective oxidation of the primary alcohol in the diol 17 serves to introduce the acid functionality.

Introduction

β-Dimorphecolic acid, **1**, which was first isolated from the seed oil of *Dimorphotheca aurantiaca*,[1] and its diene congener, α-dimorphecolic acid **2**, belong to a family of linoleic acid



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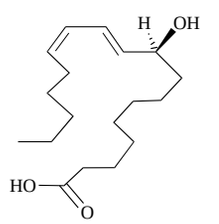

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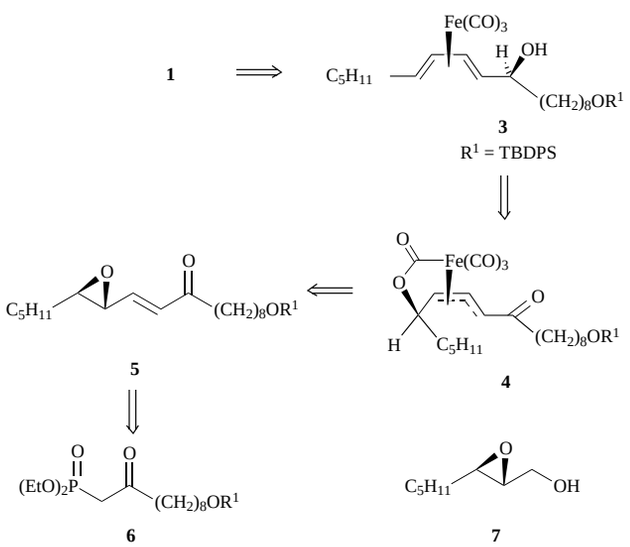
metabolites that exhibit a wealth of biological properties.[2] Owing to their lipid nature, long-chain fatty acids play a vital role in maintaining cellular properties[3] and consequently can elicit a variety of biological responses. This is exemplified by α-dimorphecolic acid, which has been reported to be an inhibitor of acetylcholine esterase (ACE)[4] and aromatase,[5] a calcium specific ionophore,[6] as well as being implicated in the pathogenesis of familial Mediterranean fever.[7] Conversely, little is known of the biological properties associated with β-dimorphecolic acid.[2] This is related to the difficulty in cultivating *Dimorphotheca aurantiaca* seeds and isolating the natural product. We therefore undertook a synthesis of β-dimorphecolic acid which we now report herein in full.[8]

We recently showed that π-allyltricarbonyliron lactone complexes[9] bearing ketone[10] groups in the side-chain undergo diastereoselective addition reactions with a wide range of organoaluminium reagents. In this manner, alkyl, alkenyl, alkynyl and phenyl groups were readily introduced such that the obtained tertiary alcohol adducts were of >95% de. We also observed that the use of organoaluminium reagents possessing β-hydrogen atoms led, in minor amounts, to the formation of by-products in which the side-chain carbonyl group had been reduced. By exploiting this pattern of behaviour, we were able to utilise triisobutylaluminium as an efficient reducing agent for the side-chain carbonyl group.[11] Moreover, the reduction occurred in a highly diastereoselective fashion to provide secondary alcohols with de >95%. The stereochemical outcome of addition reactions to the ketone-containing complexes, determined by X-ray crystallographic analysis and by correlation of derivatives with compounds of known relative configurations, revealed that nucleophilic attack occurs *anti* to the bulky tricarbonyliron unit preferentially on the s-*cis* conformer. The initial adducts obtained from reaction with the organoaluminium reagents can be smoothly decarboxylated to form stereodefined η[4]-dienetricarbonyliron complexes with excellent preservation of stereochemical integrity.[10] Moreover, as these reactions can be performed on enantiomerically enriched material,[10] this route affords masked dienols of high stereochemical purity and complements established methodology.[12] We therefore proposed to use this chemistry to construct the stereochemical elements present in β-dimorphecolic acid.

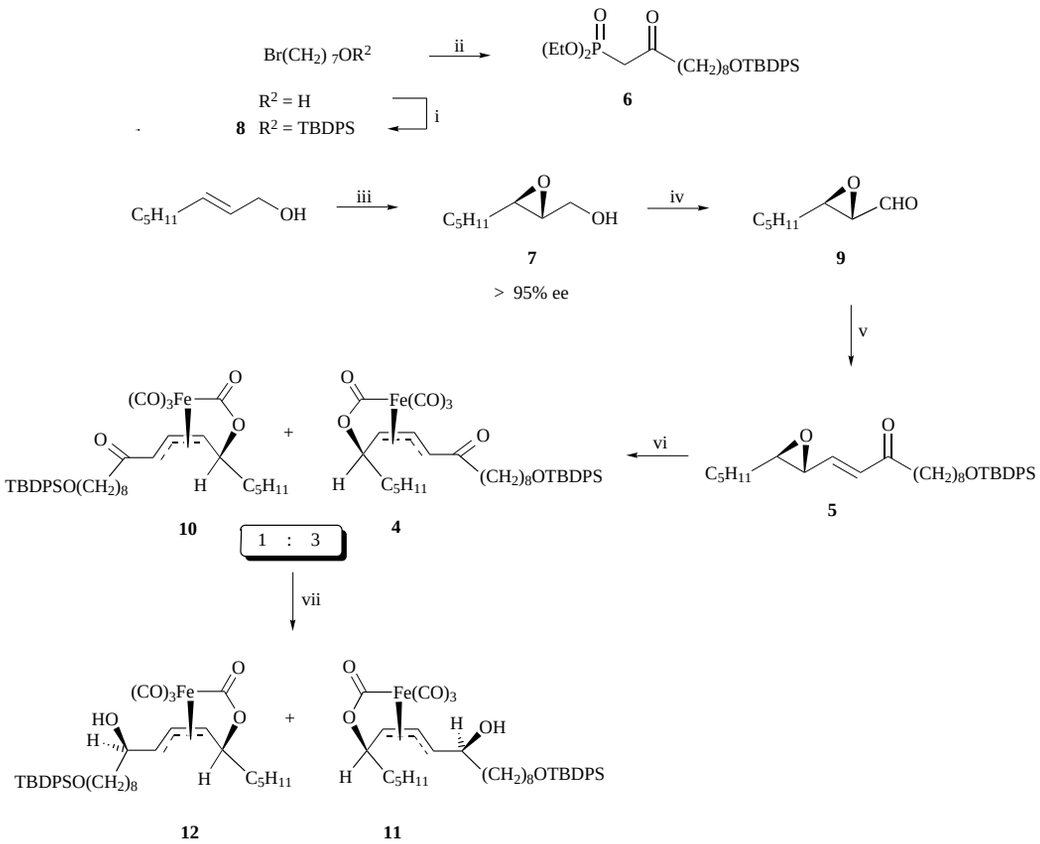


Scheme 1 Retrosynthetic analysis for β-dimorphecolic acid **1**

The retrosynthetic analysis to **1** is outlined in Scheme 1. We envisaged that selective oxidation of the primary alcohol released by decomplexation and deprotection of the η[4]-dienetricarbonyliron complex **3** would provide the acid functionality present in the target molecule. Reduction of the ketone group in the π-allyltricarbonyliron lactone complex **4** followed by decarboxylation would afford this masked dienol **3**. The immediate precursor for the π-allyltricarbonyliron lactone complex **4**, the epoxy enone **5**, was to be derived from the phosphonate **6** and the aldehyde obtained by oxidation of the alcohol function in the epoxy alcohol **7**. Application of the Sharpless asymmetric epoxidation[13] protocol establishes the desired molecular asymmetry.

Results and discussion

Catalytic asymmetric epoxidation of (2*E*)-oct-2-en-1-ol, under conditions described by Sharpless,[14] using D-diethyl tartrate, provided the epoxy alcohol **7** in 70% yield (Scheme 2). Formation of the corresponding Mosher ester,[15] under standard



Scheme 2 *Reagents and conditions:* i, $ClSiPh_2Bu^t$, Et_3N, DMAP (10 mol%), CH_2Cl_2, 0 °C to room temp., 40 min (94%); ii, $(Et_2O)_2P(O)CH_2C(O)CH_3$, NaH, THF, 0 °C to room temp., 45 min, then BuLi, 0 °C, 50 min, then **8**, 0 °C to room temp., 16 h (70%); iii, $Ti(OPr^i)_4$ (15 mol%), D-DET (18 mol%), Bu^tOOH, 4 Å mol. sieves, CH_2Cl_2, −20 °C, 90 min (70%); iv, CrO_3, pyridine, CH_2Cl_2, room temp., 45 min (85%); v, **6**, KHMDS, THF, 0 °C, 40 min, then **9**, −78 °C, 50 min (66%); vi, $Fe_2(CO)_9$, THF, room temp., 3 h (64%, **4**:**10** *ca.* 3:1); vii, Bu^i_3Al, C_6H_6–toluene (4:1), 0 °C, 35 min (53% **11**, 18% **12**)

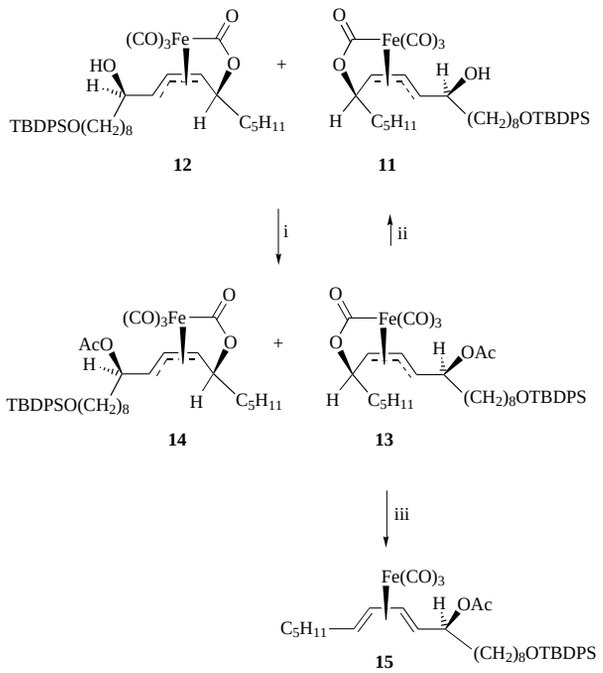
conditions, and comparison with racemic material revealed that **7** had an ee >95%, as determined by 500 MHz ^{1}H NMR analysis. Treatment of **7** with *in situ*-generated Collins' reagent[16] smoothly afforded the aldehyde **9** in 85% yield. The preparation of the phosphonate **6** relied upon the alkylation of the dianion of diethyl (2-oxopropyl)phosphonate with the alkyl bromide **8**, which was obtained from 7-bromoheptanol in 94% yield in the standard manner. Deprotonation of diethyl (2-oxopropyl)-phosphonate sequentially with sodium hydride and butyllithium, according to the method of Grieco and Pognowski,[17] and alkylation with the bromide **8** provided exclusively the α-substituted phosphonate **6** in 70% yield.

With the epoxy aldehyde **9** and the functionalised phosphonate **6** in hand, we examined their coupling to form the epoxy enone precursor **5** to the π-allyltricarbonyliron lactone complexes. It soon became apparent that the nature of the counterion of the base used to deprotonate the phosphonate **6** played a critical role in determining the course of the subsequent Horner–Wittig homologation. Thus, optimum conditions required the use of potassium bis(trimethylsilyl)amide as base to provide exclusively the epoxy enone **5** in 66% yield; application of the Masamune–Roush procedure,[18] or the use of bases associated with sodium or lithium resulted in reduced isolated yields of **5**.

Treatment of **5** with $Fe_2(CO)_9$ in THF[19] gave two diastereoisomeric π-allyltricarbonyliron lactone complexes, *endo*-**4** and *exo*-**10**, in 64% combined yield and in a ratio of *ca.* 3:1, respectively. Reduction of the side-chain carbonyl groups of the inseparable complexes **4** and **10** with triisobutylaluminium in benzene–toluene (4:1) at 0 °C afforded the corresponding alcohols **11** and **12**, respectively, as an inseparable mixture in 71% combined yield. Analysis of the mixture by HPLC and 500 MHz ^{1}H NMR spectroscopy indicated that both **11** and **12** had a de >95%.

Whilst **11** and **12** could be separated on an analytical scale by HPLC, use of this means of purification on a large scale would be time consuming and tedious. We therefore briefly investigated derivatising the alcohol functionality as the corresponding acetate. Rather than merely providing a means of obtaining diastereoisomerically pure material, orthogonal differentiation of the primary and secondary alcohols present in the required complex **13** may potentially allow the synthesis to proceed through this intermediate. Formation of the acetates **13** and **14**, from **11** and **12** respectively, in the standard manner occurred smoothly in 81% combined yield (Scheme 3). Purification by standard flash column chromatography provided diastereoisomerically pure complexes. To effect decarboxylation, the acetate **13** was treated with barium hydroxide in wet methanol[20] to afford the η^4-dienetricarbonyliron complex **15** in 15% yield, with the low yield being attributed to the formation of material which has so far eluded structural elucidation. Given the poor efficiency of this reaction, the acetate group in **13** was hydrolysed using K_2CO_3 in methanol to afford the alcohol **11** in 53% yield, with no improvement in the yield being observed upon the use of a variety of reagents and conditions. Thus, utilisation of the acetates **13** and **14** was not synthetically appealing, and the diastereoisomeric alcohols **11** and **12** were hence separated by preparative HPLC.

In order to gain insight into the stereochemical outcome of the reduction process, a NOESY experiment was carried out on the mixture of ketones **4** and **10**. This clearly revealed that the s-*cis* conformation was exclusively adopted in the ground state; irradiation of the protons α to the carbonyl group resulted in enhancements of only the terminal protons of the allyl system. On the basis of our previous work,[10] this strongly suggests that the sense of the newly generated stereocentre in **11** would therefore be (*S*) whilst in **12** the (*R*) stereochemistry would be produced. Formation of the Mosher ester of **11**,



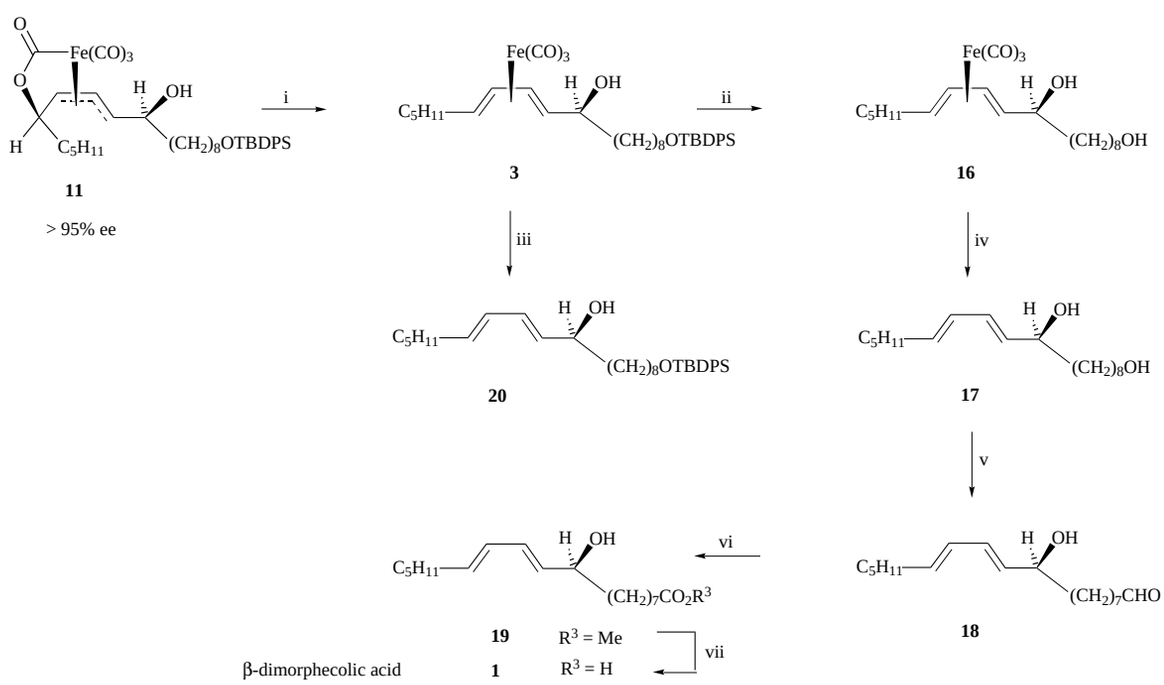
Scheme 3 *Reagents and conditions:* i, Ac_2O, Et_3N, DMAP (10 mol%), CH_2Cl_2, 0 °C, 20 min (65% **13**, 16% **12**); ii, K_2CO_3, MeOH, 0 °C, 1 h then room temp., 2 h (53%); iii, $Ba(OH)_2$, MeOH, room temp., 5 min (15%)

under standard conditions, and comparison with the racemate, indicated that **11** had >95% ee, as determined by 500 MHz ^{1}H NMR analysis. Thus, in proceeding from the epoxy alcohol **7**, there had been no detectable loss of enantiopurity.

Treatment of the required diastereoisomer **11** with barium hydroxide in wet methanol provided the η^4-dienetricarbonyliron complex **3** in 78% yield as a single diastereoisomer and geometric isomer at the diene moiety (Scheme 4). This result is in full accord with the proposed mechanism,[20] in which hydroxide attack occurs on one of the carbonyl groups with concomitant cleavage of the lactone tether. Bond rotation resulting in an *endo*- to *exo*-transposition of the pentyl unit then permits a facile decarboxylation and antiperiplanar elimination of H_2O to occur affording, in the case of *endo* lactone complexes like **11**, the corresponding (*E*,*E*)-η^4-dienetricarbonyliron complex. Unmasking of the diene unit provided some interesting and unexpected results. Cleavage of the silyl ether in **3** using HF–pyridine which occurred in 92% yield to provide **16** was followed by exposure to basic methanolic hydrogen peroxide[21] to rapidly afford the diene **17** in 94% yield. The coupling constants observed between the vinylic protons, 15.1 and 15.2 Hz, are in accord with the assigned *E*,*E* stereochemistry and this stereochemical outcome is consistent with our previous work.[10] When the complex **3** was exposed to the same decomplexation reagent system, however, the reaction was sluggish and the diene **20** was isolated in 46% yield, with the remainder being unreacted starting material.

In order to attain the required level of oxidation for β-dimorphecolic acid we initially subjected the diol **17** to oxidation using PtO_2 and oxygen, conditions reported to selectively oxidise primary alcohols to acids in the presence of secondary allylic alcohols.[22] In our case, however, a mixture of oxidation products was obtained and the selectivity did not alter upon varying the reaction temperature. A stepwise oxidation approach to achieve formation of the acid therefore seemed more beneficial. Treatment of the diol **17** with $RuCl_2(PPh_3)_3$ in benzene[23] provided exclusively the aldehyde **18** in 73% yield (Scheme 4). Oxidation of the aldehyde using buffered sodium hypochlorite, in the presence of 2-methylbut-2-ene as a radical scavenger,[24] afforded the crude acid which was esterified with diazomethane to provide the corresponding methyl ester **19** in 49% overall yield. Following chromatographic purification, hydrolysis of the ester **19** employing LiOH in DME–H_2O occurred in 85% yield to afford β-dimorphecolic acid **1**, which was identical in every respect to that reported in the literature.[25]

The high levels of selectivity observed in this synthesis illustrate the ability of the tricarbonyliron lactone tether of π-allyltricarbonyliron lactone complexes to exert control over distinct elements of stereochemistry. Thus, a 1,5-asymmetric induction creates the stereogenic centre, whilst a highly stereoselective decarboxylation provides the *E*,*E* diene moiety. This short, highly stereoselective synthesis of β-dimorphecolic acid



Scheme 4 *Reagents and conditions:* i, $Ba(OH)_2$, MeOH, room temp., 5 min (78%); ii, HF·pyridine, pyridine, THF, room temp., 18 h (92%); iii, H_2O_2, NaOH, MeOH, 0 °C, 6 h (46%); iv, H_2O_2, NaOH, MeOH, 0 °C, 25 min (94%); v, $Ru(PPh_3)_3Cl_2$, C_6H_6, room temp., 22 h (73%); vi, NaOCl, KH_2PO_4, 2-methylbut-2-ene, Bu^{t}OH–H_2O (1:1), room temp., 1 h, then CH_2N_2, Et_2O, room temp. (49%); vii, LiOH, DME–H_2O (3:1), 0 °C, 30 min then room temp., 3 h (85%)

once again demonstrates the utility of π-allyltricarbonyliron lactone complexes in organic synthesis.

Experimental

^{1}H NMR Spectra were recorded in $CDCl_3$, unless otherwise stated, on Bruker AM-200, Bruker AM-400 or Bruker DRX-500 spectrometers and are reported as follows: chemical shift, δ (ppm) (number of protons, multiplicity, coupling constant J and assignment). Residual protic solvent $CHCl_3$ ($\delta_H = 7.26$ ppm) was used as the internal reference and coupling constants are quoted in Hz. ^{13}C NMR Spectra were recorded in $CDCl_3$, unless otherwise stated, at 100 MHz or 50 MHz on Bruker AM-400 or Bruker AM-200 spectrometers, respectively, using the central resonance of $CDCl_3$ ($\delta_C = 77.0$ ppm) as the internal reference. Infra-red spectra were recorded as thin films, as solutions in $CHCl_3$ or as KBr discs on a Perkin-Elmer 983G or FTIR 1620 spectrometer. Mass spectra were obtained on a Kratos MS890MS spectrometer at the Department of Chemistry, University of Cambridge, and at the EPSRC Mass Spectrometry service at Swansea. Microanalyses were determined in the microanalytical laboratories at the University of Cambridge. For those cases in which an inseparable mixture of compounds was formed, the data reported were obtained on the mixture. Where considerable assignment of ^{1}H NMR spectra of individual compounds in mixtures is possible, the interpretation is for each component; in other cases, ^{1}H NMR spectra are interpreted for the mixture. Melting points were determined on a Reichert hot stage apparatus and are uncorrected. Optical rotations were measured with an Optical Activity AA-1000 polarimeter and $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}.

Flash column chromatography was carried out using Merck Kieselgel (230–400 mesh) unless otherwise indicated. Preparative HPLC was performed on a Gilson 303 system using Dynamax Macro silica columns equipped with a UV detector set at 254 nm. Analytical TLC was performed using precoated glass-backed plates (Merck Kieselgel 60 F254) and visualised by UV, acidic ammonium molybdate(IV) or acidic potassium permanganate solutions. Petrol refers to light petroleum bp 40–60 °C, which was distilled prior to use, and ether refers to diethyl ether.

All reactions were carried out under an argon atmosphere in oven-dried glassware unless otherwise stated. Reactions involving iron complexes were carried out using degassed solvents, as was flash column chromatography which was performed under a positive pressure of argon. Solvents were degassed by successively evacuating and purging the solvent three times with argon whilst simultaneously subjecting the solvent to sonication using an 80 W 55 kHz cleaning bath. Diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl; dichloromethane, benzene and toluene from calcium hydride. Other reagents and solvents were purified using standard procedures.[26] Aqueous solutions are saturated unless otherwise specified.

(2*R*,3*R*)-2,3-Epoxyoctan-1-ol 7

(2*E*)-Oct-2-en-1-ol (9.51 g, 74.18 mmol) was treated with D-diethyl tartrate (2.76 g, 13.35 mmol), titanium tetraisopropoxide (3.31 g, 11.13 mmol), 4 Å molecular sieves (2.5 g) and *tert*-butyl hydroperoxide (49.5 cm^3 of a 3 mol dm^{-3} solution in 2,2,4-trimethylpentane, 148.5 mmol) according to the literature procedure[14] to provide the crude epoxy alcohol **7** as a pale yellow oil. Purification by flash column chromatography (eluent petrol–ether 2:3) followed by two recrystallisations from petrol at 0 °C yielded the epoxy alcohol **7** (7.21 g, 70%) which had identical spectroscopic properties to those reported in the literature,[14] $[\alpha]_D^{24}$ +44.9 (*c* 1.12 in $CHCl_3$) {lit.,[14] for enantiomer, $[\alpha]_D^{24}$ −42.7 (*c* 4.7 in $CHCl_3$)}. The enantiopurity was determined by formation of the Mosher ester using (*S*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride: ^{1}H NMR spectroscopy indicated the presence of a single diastereoisomer; δ_H(500 MHz) 0.89 (3 H, t, *J* 6.9, 8-H × 3), 1.26–1.60 (8 H, m, 4-H × 2, 5-H × 2, 6-H × 2, 7-H × 2), 2.84 (1 H, td, *J* 5.6, 2.1, 3-H), 3.01 (1 H, ddd, *J* 5.5, 3.2, 2.1, 2-H), 3.57 (3 H, s, OMe), 4.21 (1 H, dd, *J* 12.1, 5.5, 1-H$_a$), 4.53 (1 H, dd, *J* 12.1, 3.2, 1-H$_b$), 7.37–7.44 (3 H, m, *m*-Ph-*H*, *p*-Ph-*H*), 7.53 (2 H, dd, *J* 7.5, 1.6, *o*-Ph-*H*). For comparison, the ^{1}H NMR for the Mosher ester prepared from (2*R**,3*R**)-**7**: δ_H(200 MHz) 0.89 (3 H, t, *J* 7.0, 8-H × 3), 1.15–1.72 (8 H, m, 4-H × 2, 5-H × 2, 6-H × 2, 7-H × 2), 2.80–2.84 (1 H, m, 3-H), 2.98–3.02 (1 H, m, 2-H), 3.57 (3 H s, OMe), 4.21 (0.5 H, dd, *J* 12.1, 5.7, 1-H$_a$), 4.23 (0.5 H, dd, *J* 12.1, 5.7, 1-H$_{a'}$), 4.53 (0.5 H, dd, *J* 12.1, 3.5, 1-H$_b$), 4.58 (0.5 H, dd, *J* 12.1, 3.5, 1-H$_{b'}$), 7.37–7.44 (3 H, m, *m*-Ph-*H*, *p*-Ph-*H*), 7.49–7.56 (2 H, m, *o*-Ph-*H*).

(2*S*,3*R*)-2,3-Epoxyoctanal 9

Chromium(VI) oxide (10.59 g, 105.9 mmol) was added to a solution of pyridine (17.3 cm^3, 213.9 mmol) in dichloromethane (200 cm^3). After stirring the solution for 15 min, Celite (15 g) was added and the resultant slurry was stirred for a further 5 min before cooling to 0 °C. A solution of the epoxy alcohol **7** (1.78 g, 12.4 mmol) in dichloromethane (20 cm^3) was added *via* a cannula. After warming to room temperature and stirring for a further 45 min, sodium hydrogen sulfate (30 g) and ether (200 cm^3) were added and the slurry was vigorously stirred for 15 min. The mixture was filtered through a sandwich of silica–$MgSO_4$–silica and the residue was washed with ether (1000 cm^3). Concentration *in vacuo* followed by flash column chromatography (eluent petrol–ether 20:1) provided the aldehyde **9** as a colourless oil which froze upon placing in a freezer at −18 °C (1.50 g, 85%); $[\alpha]_D^{24}$ +10.0 (*c* 0.10 in $CHCl_3$); ν_{max}(film)/cm^{-1} 2957, 2930, 2860, 2733, 1729 (C=O), 1467, 1436, 1380, 1150, 1050, 981; δ_H(200 MHz) 0.90 (3 H, t, *J* 7.1, 8-H × 3), 1.30–1.62 (8 H, m, 4-H × 2, 5-H × 2, 6-H × 2, 7-H × 2), 3.12 (1 H, dd, *J* 6.2, 2.0, 2-H), 3.21 (1 H, td, *J* 5.3, 2.0, 3-H), 9.01 (1 H, d, *J* 6.2, 1-H); δ_C(100 MHz) 198.5, 59.2 (CH), 56.8 (CH), 31.4 (CH_2), 31.2 (CH_2), 25.4 (CH_2), 22.5 (CH_2), 13.9 (CH_3); *m/z* (EI) 142 (M^+, 25%), 113 (52, M − CHO), 83 (72), 71 [100, M − Me(CH_2)$_4$], 69 (55), 55 (90) [Found (M^+) 142.0987. $C_8H_{14}O_2$ requires *M*, 142.0993].

7-Bromo-1-*tert*-butyldiphenylsilyloxyheptane 8

tert-Butyldiphenylsilyl chloride (14.13 cm^3, 55.2 mmol) was added in a dropwise manner to a solution of 7-bromoheptan-1-ol (9.81 g, 50.2 mmol) in dichloromethane (80 cm^3) containing triethylamine (8.42 cm^3, 60.2 mmol) and 4-dimethylaminopyridine (605 mg, 5.0 mmol) at 0 °C. The solution was stirred at 0 °C for 20 min and then for a further 20 min whilst warming to room temperature. The reaction mixture was poured into aqueous ammonium chloride (150 cm^3) and the layers were separated. The organic phase was washed with aqueous ammonium chloride (150 cm^3) and the combined aqueous phases were extracted with ether (3 × 150 cm^3). The combined organic phases were washed with brine (100 cm^3) and dried ($MgSO_4$). Concentration *in vacuo* afforded the crude product which was purified by flash column chromatography (eluent petrol–ether 50:1) to provide the *silyl ether* **8** as a colourless oil (20.4 g, 94%) (Found C, 63.68; H, 7.80. $C_{23}H_{33}BrOSi$ requires, 63.87; H, 7.70%); ν_{max}(film)/cm^{-1} 3070, 3049, 3013, 2931, 2857, 1589, 1507, 1486, 1474, 1462, 1428, 1389, 1361, 1264, 1188, 1111, 1029, 1007; δ_H(200 MHz) 1.05 (9 H, s, Bu^t), 1.24–1.59 (8 H, m, 3-H × 2, 4-H × 2, 5-H × 2, 6-H × 2), 1.84 (2 H, quintet, *J* 6.4, 2-H × 2), 3.39 (2 H, t, *J* 6.8, 7-H × 2), 3.66 (2 H, t, *J* 6.4, 1-H × 2), 7.26–7.43 (6 H, m, *m*-Ph-*H*, *p*-Ph-*H*), 7.64–7.71 (4 H, m, *o*-Ph-*H*); δ_C(100 MHz) 135.5 (CH), 134.1 (quat. C), 129.5 (CH), 127.5 (CH), 63.8 (CH_2), 33.8 (CH_2), 32.7 (CH_2), 32.4 (CH_2), 28.4 (CH_2), 28.1 (CH_2), 26.9 (CH_3), 25.5 (CH_2), 19.2 (quat. C); *m/z* (EI) 377 ([M − Bu^t]$^+$, 82%), 375 (82, M − Bu^t), 295 (51, M − HBr), 263 (42), 261 (43), 199 (47), 97

(100, M − Bu^tPh_2OSi − HBr), 55 (78) {Found ([M − Bu^t]$^+$) 375.0786 (^{79}Br). $C_{19}H_{24}BrOSi$ requires *M* − Bu^t, 375.0783}.

Diethyl (10-*tert*-butyldiphenylsilyloxy-2-oxodecyl)phosphonate 6

Diethyl (2-oxopropyl)phosphonate (10.74 g, 54.89 mmol) was added dropwise to a suspension of sodium hydride [60% dispersion in oil which was previously washed with dry hexane (3 × 20 cm^3), 1.45 g, 59.56 mmol] in tetrahydrofuran (150 cm^3) at 0 °C. A white suspension was initially formed, which dissolved after complete addition of the phosphonate. This solution was stirred for 45 min whilst warming to room temperature. The solution was then recooled to 0 °C and butyllithium (41.1 cm^3 of a 1.6 mol dm^{-3} solution in hexane, 65.76 mmol) was added dropwise over 20 min. After further stirring for 30 min at 0 °C the bromide **8** (6.81 g, 15.72 mmol) in tetrahydrofuran (20 cm^3) was added dropwise. The resultant solution was warmed to room temperature over 30 min and stirred for a further 16 h. The reaction was quenched by the slow addition of aqueous ammonium chloride (30 cm^3), and then poured into aqueous ammonium chloride (200 cm^3). Following separation of the layers, the aqueous phase was extracted with ether (3 × 100 cm^3). The combined organic phases were washed with brine (100 cm^3) and dried ($MgSO_4$) to furnish the crude product after concentration *in vacuo*. Purification by flash column chromatography (eluent ethyl acetate–petrol 1:1) provided the *phosphonate* **6** as a pale yellow oil (5.81 g, 70%) (Found C, 65.84; H, 8.71. $C_{30}H_{47}O_5PSi$ requires C, 65.90; H, 8.67%); ν_{max}(film)/cm^{-1} 3015, 2970, 2845, 1716 (C=O), 1589, 1567, 1472, 1463, 1444, 1428, 1391, 1362, 1256, 1111, 1027; δ_H(200 MHz) 1.04 (9 H, s, Bu^t), 1.20–1.63 [18 H, m, $(OCH_2CH_3)_2$, 4-H × 2, 5-H × 2, 6-H × 2, 7-H × 2, 8-H × 2, 9-H × 2], 2.60 (2 H, t, *J* 7.2, 3-H × 2), 3.06 (2 H, d, *J* 22.8, 1-H × 2), 3.64 (2 H, t, *J* 6.4, 10-H × 2), 4.13 [4 H, apparent quintet, *J* 7.1, $(OCH_2CH_3)_2$], 7.33–7.42 (6 H, m, *m*-Ph-*H*, *p*-Ph-*H*), 7.63–7.68 (4 H, m, *o*-Ph-*H*); δ_C(100 MHz) 202.2 (d, *J* 6.2, C=O), 135.6 (CH), 134.2 (quat. C), 129.5 (CH), 127.6 (CH), 64.0 (CH_2), 62.5 (d, *J* 6.2, CH_2), 44.1 (CH_2), 42.9 (d, *J* 127.1, CH_2), 32.6 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 28.9 (CH_2), 26.9 (CH_3), 25.7 (CH_2), 23.4 (CH_2), 19.2 (quat. C), 16.3 (d, *J* 6.1, CH_3); *m/z* (EI) 489 ([M − Bu^t]$^+$, 100%), 423 (17), 309 (11), 199 (38), 183 (19), 128 (17), 97 (22), 78 (21), 55 (14) {Found ([M − Bu^t]$^+$) 489.2221. $C_{26}H_{38}O_5PSi$ requires *M* − Bu^t, 489.2226}.

(10*E*,12*R*,13*R*)-1-*tert*-Butyldiphenylsilyloxy-12,13-epoxyoctadec-10-en-9-one 5

Potassium bis(trimethylsilyl)amide (3.15 cm^3 of a 0.5 mol dm^{-3} solution in toluene, 1.58 mmol) was added dropwise to the phosphonate **6** (905 mg, 1.65 mmol) in tetrahydrofuran (2 cm^3) at 0 °C. After continued stirring at this temperature for 40 min the solution was cooled to −78 °C and the aldehyde **9** (203 mg, 1.43 mmol) in tetrahydrofuran (2 cm^3) was added dropwise. The reaction was quenched by the slow addition of methanol–water (2 cm^3; 1:5) after further stirring at −78 °C for 50 min. The reaction mixture was poured into saturated ammonium chloride (20 cm^3) and the layers were separated. The organic phase was washed with saturated ammonium chloride (20 cm^3) and the combined aqueous phases were extracted with ether (3 × 20 cm^3). The combined organic phases were washed with brine (30 cm^3), dried ($MgSO_4$) and concentrated *in vacuo*. Purification by flash chromatography (eluent petrol–ether 10:1; column pre-equilibrated with petrol–ether 10:1 containing 2% triethylamine) afforded the *epoxy enone* **5** as a pale yellow oil (505 mg, 66%) (Found C, 76.15; H, 9.31. $C_{34}H_{50}O_3Si$ requires C, 76.35; H, 9.43%); $[\alpha]_D^{24}$ +9.0 (*c* 4.95 in $CHCl_3$); ν_{max}(film)/cm^{-1} 3070, 3049, 2929, 2856, 1698 (C=O), 1632 (C=C), 1463, 1427, 1361, 1189, 1111, 976, 823; δ_H(400 MHz) 0.89 (3 H, t, *J* 7.1, 18-H × 3), 1.03 (9 H, s, Bu^t), 1.21–1.67 (20 H, m, 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2, 6-H × 2, 7-H × 2, 14-H × 2, 15-H × 2, 16-H × 2, 17-H × 2), 2.52 (2 H, t, *J* 7.4, 8-H × 2), 2.89 (1 H, td, *J* 5.6, 1.9, 13-H), 3.20 (1 H, dd, *J* 6.9, 1.9, 12-H), 3.64 (2 H, t, *J* 6.5, 1-H × 2), 6.38 (1 H, d, *J* 15.9, 10-H), 6.51 (1 H, dd, *J* 15.9, 6.9, 11-H), 7.34–7.43 (6 H, m, *m*-Ph-*H*, *p*-Ph-*H*), 7.66 (4 H, dd, *J* 7.7, 1.5, *o*-Ph-*H*); δ_C(100 MHz) 199.7, 142.5 (CH), 135.6 (CH), 134.2 (quat. C), 131.3 (CH), 129.5 (CH), 127.6 (CH), 64.0 (CH_2), 61.6 (CH), 56.7 (CH), 40.7 (CH_2), 32.6 (CH_2), 31.9 (CH_2), 31.5 (CH_2), 29.3 (CH_2), 29.2 (CH_2 × 2), 26.9 (CH_3), 25.7 (CH_2), 25.5 (CH_2), 24.0 (CH_2), 22.5 (CH_2), 19.2 (quat. C), 13.9 (CH_3); *m/z* (EI) 477 ([M − Bu^t]$^+$, 85%), 461 (62), 377 (65), 199 (90), 183 (30), 139 [25, M − $C(O)(CH_2)_8OSiPh_2Bu^t$], 78 (35) {Found ([M − Bu^t]$^+$) 477.2829. $C_{30}H_{41}O_3Si$ requires *M* − Bu^t, 477.2825}.

[(10*E*,12*S*,13*R*)-1-*tert*-Butyldiphenylsilyloxy-13-(carbonyloxy-κ*C*)-9-oxo-(10,11,12-η)-octadec-10-en-12-yl]tricarbonyliron 4 and [(10*E*,12*R*,13*R*)-1-*tert*-butyldiphenylsilyloxy-13-(carbonyloxy-κ*C*)-9-oxo-(10,11,12-η)-octadec-10-en-12-yl]tricarbonyliron 10

The epoxy enone **5** (740 mg, 1.38 mmol) was added in one portion to a suspension of nonacarbonyldiiron (1.064 g, 2.92 mmol) in degassed tetrahydrofuran (25 cm^3) which had been vigorously stirred for 10 min. After further stirring for 3 h, toluene (6 cm^3) was added, the solution was filtered through a pad of Celite and the residue was washed with ether (100 cm^3). Concentration *in vacuo* afforded the crude products as a solution in toluene which were purified immediately by flash column chromatography (eluent petrol to petrol–ether 3:1 gradient) to afford the *complexes* **4** and **10** as an inseparable mixture of dark yellow oils in the ratio ~3:1, respectively, as determined by ^{1}H NMR spectroscopy (620 mg, 64%); ν_{max}(film)/cm^{-1} 3071, 3015, 2931, 2857, 2091 (CO), 2043 (CO), 1672 (C=O), 1590, 1497, 1463, 1428, 1361, 1306, 1111; δ_H(400 MHz) (for **4**) 0.88 (3 H, t, *J* 6.7, 18-H × 3), 1.04 (9 H, s, Bu^t), 1.20–1.68 (20 H, m, 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2, 6-H × 2, 7-H × 2, 14-H × 2, 15-H × 2, 16-H × 2, 17-H × 2), 2.69 (2 H, t, *J* 7.4, 8-H × 2), 3.64 (2 H, t, *J* 6.4, 1-H × 2), 3.83 (1 H, d, *J* 11.2, 10-H), 4.26–4.38 (1 H, m, 13-H), 5.01 (1 H, dd, *J* 8.6, 4.5, 12-H), 5.54 (1 H, dd, *J* 11.2, 8.6, 11-H), 7.35–7.43 (6 H, m, *m*-Ph-*H*, *p*-Ph-*H*), 7.66 (4 H, dd, *J* 7.2, 1.6, *o*-Ph-*H*); δ_H(400 MHz) (for **10**) 0.88 (3 H, t, *J* 6.7, 18-H × 3), 1.04 (9 H, s, Bu^t), 1.20–1.68 (20 H, m, 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2, 6-H × 2, 7-H × 2, 14-H × 2, 15-H × 2, 16-H × 2, 17-H × 2), 2.66 (2 H, t, *J* 7.4, 8-H × 2), 3.64 (2 H, t, *J* 6.4, 1-H × 2), 3.72 (1 H, d, *J* 11.0, 10-H), 4.04 (1 H, t, *J* 6.5, 13-H), 4.84 (1 H, d, *J* 8.2, 12-H), 5.72 (1 H, dd, *J* 11.0, 8.2, 11-H) 7.35–7.43 (6 H, m, *m*-Ph-*H*, *p*-Ph-*H*), 7.66 (4 H, dd, *J* 7.2, 1.6, *o*-Ph-*H*); δ_C(100 MHz) (for **4**) 208.0, 205.0, 204.3, 202.8, 199.8, 135.6 (CH), 134.2 (quat. C), 129.5 (CH), 127.6 (CH), 92.2 (CH), 84.3 (CH), 76.9 (CH), 65.9 (CH), 63.9 (CH_2), 43.4 (CH_2), 36.7 (CH_2), 32.6 (CH_2), 31.5 (CH_2), 31.4 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 26.9 (CH_3), 26.5 (CH_2), 25.7 (CH_2), 23.8 (CH_2), 22.5 (CH_2), 19.2 (quat. C), 13.9 (CH_3); δ_C(100 MHz) (for **10**) 208.0, 205.0, 204.3, 202.8, 199.9, 135.6 (CH), 134.2 (quat. C), 129.5 (CH), 127.6 (CH), 93.8 (CH), 83.1 (CH), 74.5 (CH), 65.0 (CH), 63.9 (CH_2), 53.4 (CH_2), 38.1 (CH_2), 32.6 (CH_2), 31.4 (CH_2), 31.4 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 26.9 (CH_3), 26.5 (CH_2), 25.1 (CH_2), 23.8 (CH_2), 22.5 (CH_2), 19.2 (quat. C), 13.9 (CH_3); *m/z* (FAB) 703 (MH^+, 18%), 646 (17, MH − Bu^t), 617 (12, M − Bu^t − CO), 591 (100), 574 (37, M − 3CO − CO_2), 533 (65), 519 [16, MH − $Fe(CO)_3$ − CO_2], 395 (10, M − $C_{13}H_{15}FeO_5$), 199 (67) [Found (MH^+) 703.2799. $C_{38}H_{51}FeO_7Si$ requires *M*H, 703.2753].

[(10*E*,9*S*,12*S*,13*R*)-1-*tert*-Butyldiphenylsilyloxy-13-(carbonyloxy-κ*C*)-9-hydroxy-(10,11,12-η)-octadec-10-en-12-yl]tricarbonyliron 11 and [(10*E*,9*R*,12*R*,13*R*)-1-*tert*-butyldiphenylsilyloxy-13-(carbonyloxy-κ*C*)-9-hydroxy-(10,11,12-η)-octadec-10-en-12-yl]tricarbonyliron 12

Triisobutylaluminium (3.14 cm^3 of a 1 mol dm^{-3} solution in toluene, 3.14 mmol) was added dropwise to a stirred solution of the ketones **4** and **10** (957 mg, 1.36 mmol; **4**:**10** ~3:1) in benzene (16.8 cm^3) and toluene (4.2 cm^3) at 0 °C. After stirring at

this temperature for 35 min, aqueous ammonium chloride (3 cm^3) was added dropwise and the resultant solution was stirred for a further 10 min. The crude products were dried by the addition of $MgSO_4$ followed by vigorous stirring of the resultant suspension for a further 10 min whilst warming to room temperature. Filtration through a pad of Celite, washing the residue with ether (100 cm^3) followed by removal of the volatiles *in vacuo* provided the crude products as a solution in toluene. Immediate purification by flash column chromatography (eluent petrol–ether 3:1 to petrol–ether 2:1) provided a mixture of **11** and **12**. Purification by preparative HPLC (Dynamax 41.4 mm column; eluent petrol–ether 3:1; flow rate 60 cm^3 min^{-1}; 150 mg injection in 1 cm^3 dichloromethane) provided, in order of elution, the *alcohol* **11** as a yellow oil (508 mg, 53%), t_r 43.2 min; $[\alpha]_D^{26}$ −76.7 (*c* 1.70 in $CHCl_3$); ν_{max}(film)/cm^{-1} 3424 (OH), 3015, 2931, 2083 (CO), 2029 (CO), 2010 (CO), 1857, 1642 (C=O), 1464, 1428, 1389, 1361, 1216, 1111, 1029; δ_H(500 MHz) 0.88 (3 H, t, *J* 6.5, 18-H × 3), 1.05 (9 H, s, Bu^t), 1.23–1.84 (23 H, m, OH, 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2, 6-H × 2, 7-H × 2, 8-H × 2, 14-H × 2, 15-H × 2, 16-H × 2, 17-H × 2), 3.65 (2 H, t, *J* 6.5, 1-H × 2), 4.01 (1 H, dd, *J* 12.2, 3.6, 10-H), 4.12 (1 H, br s, 9-H), 4.24–4.28 (1 H, m, 13-H), 4.60 (1 H, dd, *J* 8.2, 4.6, 12-H), 4.80 (1 H, dd, *J* 12.2, 8.2, 11-H), 7.36–7.43 (6 H, m, *m*-Ph-*H*, *p*-Ph-*H*), 7.66 (4 H, dd, *J* 7.6, 1.6, *o*-Ph-*H*); δ_C(50 MHz) 209.5, 206.6, 206.4, 203.3, 135.5, 134.0, 129.4, 127.5, 88.0, 77.2, 76.9, 75.8, 72.0, 63.9, 39.9, 36.6, 32.5, 31.5, 29.4, 29.2, 26.8, 26.6, 25.9, 25.7, 22.5, 19.2, 13.9; *m/z* (FAB) 705 (MH^+, 5%), 676 (6, M − CO), 647 (16, M − Bu^t), 575 (54, M − H − 3 CO − CO_2), 558 (26), 517 (27), 199 (100) [Found (MH^+) 705.2887. $C_{38}H_{53}FeO_7Si$ requires *M*H, 705.2909].

Then the *alcohol* **12** as a yellow oil (172 mg, 18%), t_r 57.2 min; $[\alpha]_D^{24}$ +44.6 (*c* 0.70 in $CHCl_3$); ν_{max}(film)/cm^{-1} 3416 (OH), 3071, 3014, 2930, 2083 (CO), 2029 (CO), 2010 (CO), 1642 (C=O), 1464, 1428, 1390, 1216, 1111, 1008; δ_H(400 MHz) 0.89 (3 H, t, *J* 6.7, 18-H × 3), 1.04 (9 H, s, Bu^t), 1.12–1.79 (23 H, m, OH, 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2, 6-H × 2, 7-H × 2, 8-H × 2, 14-H × 2, 15-H × 2, 16-H × 2, 17-H × 2), 3.65 (2 H, t, *J* 6.5, 1-H × 2), 3.90 (1 H, dd, *J* 12.1, 3.8, 10-H), 3.98 (1 H, t, *J* 6.6, 13-H), 4.07–4.13 (1 H, m, 9-H), 4.44 (1 H, d, *J* 8.0, 12-H), 4.96 (1 H, dd, *J* 12.1, 8.0, 11-H), 7.36–7.43 (6 H, m, *m*-Ph-*H*, *p*-Ph-*H*), 7.66 (4 H, dd, *J* 7.7, 1.2, *o*-Ph-*H*); δ_C(100 MHz) 209.8, 206.5, 205.7, 203.8, 135.6 (CH), 134.2 (quat. C), 129.5 (CH), 127.6 (CH), 89.6 (CH), 87.0 (CH), 74.9 (CH), 74.8 (CH), 71.9 (CH), 64.0 (CH_2), 39.8 (CH_2), 37.9 (CH_2), 32.6 (CH_2), 31.5 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 26.9 (CH_3), 25.9 (CH_2), 25.8 (CH_2), 25.3 (CH_2), 22.5 (CH_2), 19.3 (quat. C), 14.0 (CH_3); *m/z* (FAB) 705 (MH^+, 17%), 648 (15, MH − Bu^t), 620 (6, MH − Bu^t − CO), 591 (8, M − Bu^t − 2CO), 575 (100, M − H − 3CO − CO_2), 558 (27), 517 (43), 199 (37) [Found (MH^+) 705.2884. $C_{38}H_{53}FeO_7Si$ requires *M*H, 705.2909].

The enantiopurity of **11** was determined by formation of the Mosher ester using (*S*)-(+)-α-methoxy-α-(trifluoromethyl)-phenylacetyl chloride: ^{1}H NMR spectroscopy indicated the presence of a single diastereoisomer; δ_H(500 MHz) 0.89 (3 H, t, *J* 6.7, 18-H × 3), 1.05 (9 H, s, Bu^t), 1.18–1.68 (22 H, m, 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2, 6-H × 2, 7-H × 2, 8-H × 2, 14-H × 2, 15-H × 2, 16-H × 2, 17-H × 2), 3.57 (3 H, s, OMe), 3.65 (2 H, t, *J* 6.5, 1-H × 2), 3.90 (1 H, dd, *J* 12.4, 3.6, 10-H), 4.14 (1 H, dd, *J* 12.4, 8.3, 11-H), 4.15–4.20 (1 H, m, 13-H), 4.38 (1 H, dd, *J* 8.3, 4.6, 12-H), 5.61 (1 H, ddd, *J* 10.5, 6.7, 3.6, 9-H), 7.35–7.42 (9 H, m, *m*-Ph-*H*, *p*-Ph-*H*, *m*-Ph′-*H*, *p*-Ph′-*H*), 7.54 (2 H, dd, *J* 7.7, 1.2, *o*-Ph′-*H*), 7.66 (4 H, dd, *J* 7.7, 1.3, *o*-Ph-*H*). For comparison, the ^{1}H NMR for the Mosher ester prepared from (10*E*,9*S**,12*S**,13*R**)-**11**: δ_H(500 MHz) 0.89 (3 H, t, *J* 6.7, 18-H × 3), 1.05 (9 H, s, Bu^t), 1.18–1.68 (22 H, m, 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2, 6-H × 2, 7-H × 2, 8-H × 2, 14-H × 2, 15-H × 2, 16-H × 2, 17-H × 2), 3.57 (3 H, s, OMe), 3.65 (2 H, t, *J* 6.5, 1-H × 2), 3.90 (0.5 H, dd, *J* 12.4, 3.6, 10-H), 3.97 (0.5 H, dd, *J* 11.7, 3.6, 10-H′), 4.14 (1 H, dd, *J* 12.4, 8.3, 11-H), 4.15–4.20 (1 H, m, 13-H), 4.27 (0.5 H, dd, *J* 8.3, 4.6, 12-H), 4.38 (0.5 H, dd, *J* 8.3, 4.6, 12-H′), 5.57 (0.5H, ddd, *J* 10.5, 6.7, 3.6, 9-H), 5.61 (0.5 H, ddd, *J* 10.5, 6.7, 3.6, 9-H′), 7.35–7.42 (9 H, m, *m*-Ph-*H*, *p*-Ph-*H*, *m*-Ph′-*H*, *p*-Ph′-*H*), 7.54 (2 H, dd, *J* 7.7, 1.2, *o*-Ph′-*H*), 7.66 (4 H, dd, *J* 7.7, 1.3, *o*-Ph-*H*).

[(10*E*,9*S*,12*S*,13*R*)-9-Acetoxy-1-*tert*-butyldiphenylsilyloxy-13-(carbonyloxy-κ*C*)-(10,11,12-η)-octadec-10-en-12-yl]tricarbonyliron 13 and [(10*E*,9*R*,12*R*,13*R*)-9-acetoxy-1-*tert*-butyldiphenylsilyloxy-13-(carbonyloxy-κ*C*)-(10,11,12-η)-octadec-10-en-12-yl]tricarbonyliron 14

Acetic anhydride (100 μl, 1.00 mmol) was slowly added to a mixture of the alcohols **11** and **12** (542 mg, 0.77 mmol, **11**:**12** ~4:1), triethylamine (142 μl, 1.08 mmol) and 4-dimethylaminopyridine (10 mg, 0.08 mmol) in dichloromethane (20 cm^3) at 0 °C. After stirring at 0 °C for 30 min, ether (30 cm^3) was added and the solution was poured into aqueous sodium hydrogen carbonate (40 cm^3). After separating the layers, the organic phase was washed sequentially with aqueous sodium hydrogen carbonate solution (1 × 40 cm^3), aqueous ammonium chloride (2 × 50 cm^3) and then water (30 cm^3). The aqueous phase was extracted with ether (2 × 50 cm^3) and the combined organic extracts were washed with brine (50 cm^3) and dried ($MgSO_4$). Concentration *in vacuo* followed by flash column chromatography (eluent petrol–ether 4:1) of the residue provided, in order of elution, the *acetate* **13** as a yellow oil (375 mg, 65%); $[\alpha]_D^{24}$ −99.8 (*c* 0.50 in $CHCl_3$); ν_{max}($CHCl_3$)/cm^{-1} 3015, 2931, 2857, 2083 (CO), 2026 (CO), 1737 (C=O), 1667 (C=O), 1589, 1464, 1428, 1371, 1232, 1217, 1111, 1023, 823; δ_H(200 MHz) 0.88 (3 H, t, *J* 6.5, 18-H × 3), 1.04 (9 H, s, Bu^t), 1.28–1.91 (22 H, m, 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2, 6-H × 2, 7-H × 2, 8-H × 2, 14-H × 2, 15-H × 2, 16-H × 2, 17-H × 2), 2.08 [3 H, s, OC(O)Me], 3.65 (2 H, t, *J* 6.3, 1-H × 2), 3.93 (1 H, dd, *J* 11.5, 5.7, 10-H), 4.25 (1 H, td, *J* 5.8, 4.4, 13-H), 4.57 (1 H, dd, *J* 11.5, 8.3, 11-H), 4.66 (1 H, dd, *J* 8.3, 4.4, 12-H), 5.22 (1 H, td, *J* 7.1, 5.7, 9-H), 7.32–7.46 (6 H, m, *m*-Ph-*H*, *p*-Ph-*H*), 7.64–7.70 (4 H, m, *o*-Ph-*H*); *m/z* (FAB) 747 (MH^+, 56%), 663 (12, MH − 3CO), 647 (11, MH − Bu^t − MeCO), 634 (9, MH − Bu^t − 2CO), 617 (43), 575 (40, MH − Bu^t − MeCO − CO − CO_2), 563 [12, MH − $Fe(CO)_3$ − CO_2], 517 (28), 441 (14), 313 (22), 199 (100), 183 (29), 121 (46) [Found (MH^+) 747.3016. $C_{40}H_{55}FeO_8Si$ requires *M*H, 747.3015].

Then the *acetate* **14** as a yellow oil (92 mg, 16%) (Found C, 64.20; H, 7.46. $C_{40}H_{54}FeO_8Si$ requires C, 64.33; H, 7.29%); $[\alpha]_D^{24}$ +84.1 (*c* 2.23 in $CHCl_3$); ν_{max}($CHCl_3$)/cm^{-1} 3071, 3014, 2930, 2857, 2082 (CO), 2013 (CO), 1738 (C=O), 1661 (C=O), 1589, 1513, 1464, 1428, 1372, 1343, 1327, 1303, 1230, 1111, 998; δ_H(500 MHz) 0.89 (3 H, t, *J* 6.6, 18-H × 3), 1.04 (9 H, s, Bu^t), 1.14–1.87 (22 H, m, 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2, 6-H × 2, 7-H × 2, 8-H × 2, 14-H × 2, 15-H × 2, 16-H × 2, 17-H × 2), 2.08 [3 H, s, OC(O)Me], 3.65 (2 H, t, *J* 6.3, 1-H × 2), 3.84 (1 H, dd, *J* 12.1, 5.6, 10-H), 3.99 (1 H, t, *J* 6.2, 13-H), 4.48 (1 H, d, *J* 7.3, 12-H), 4.75 (1 H, dd, *J* 12.1, 7.3, 11-H), 5.22 (1 H, td, 6.9, 5.6, 9-H), 7.36–7.46 (6 H, m, *m*-Ph-*H*, *p*-Ph-*H*), 7.66 (4 H, dd, *J* 7.3, 1.6, *o*-Ph-*H*); δ_C(100 MHz) 209.1, 206.3, 204.0, 203.3, 170.4, 135.6 (CH), 134.2 (quat. C), 129.5 (CH), 127.6 (CH), 90.8 (CH), 80.7 (CH), 76.0 (CH), 74.8 (CH), 74.4 (CH), 64.0 (CH_2), 37.9 (CH_2), 36.9 (CH_2), 32.6 (CH_2), 31.4 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 26.9 (CH_3), 25.8 (CH_2), 25.5 (CH_2), 25.2 (CH_2), 22.5 (CH_2), 20.8 (CH_3), 19.6 (quat. C), 19.3 (CH_2), 14.0 (CH_3); *m/z* (FAB) 747 (MH^+, 21%), 635 (10), 617 (46), 575 (32, M − MeCO − 3CO − CO_2), 559 [14, M − OC(O)Me − 3CO − CO_2], 503 [12, M − OC(O)Me − $Fe(CO)_3$ − CO_2], 121 (55), 105 (72).

[(11*Z*,9*S*,10*R*,13*S*)-9-Acetoxy-1-*tert*-butyldiphenylsilyloxy-(10,11,12,13-η)-octadeca-10,12-diene]tricarbonyliron 15

Saturated aqueous barium hydroxide (~ 1 cm^3) was added to the acetate **13** (53 mg, 0.08 mmol) in methanol (1 cm^3). After stir-

ring for 5 min, the solution was partitioned between water (20 cm^3) and ether (20 cm^3), and the aqueous phase was extracted with ether (4 × 20 cm^3). The combined organic fractions were washed with brine (20 cm^3) and dried ($MgSO_4$). Concentration *in vacuo* followed by flash column chromatography (eluent petrol to petrol–ether 1:6 gradient) provided the *diene complex* **15** as a yellow oil (7 mg, 15%); $[\alpha]_D^{24}$ −74.3 (*c* 1.02 in $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 3018, 2930, 2857, 2045 (CO), 1976 (CO), 1731 (C=O), 1464, 1428, 1375, 1245, 1216; δ_H(500 MHz) 0.89 (3 H, t, *J* 7.0, 18-H × 3), 1.04 (9 H, s, Bu^t), 1.17–1.69 (24 H, m, 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2, 6-H × 2, 7-H × 2, 8-H × 2, 10-H, 13-H, 14-H × 2, 15-H × 2, 16-H × 2, 17-H × 2), 2.08 [3 H, s, OC(O)Me], 3.64 (2 H, t, *J* 6.5, 1-H × 2), 4.75 (1 H, apparent q, *J* 6.7, 9-H), 5.01 (1 H, dd, *J* 8.3, 5.2, 11-H or 12-H), 5.04 (1 H, dd, *J* 8.3, 5.2, 11-H or 12-H), 7.36–7.43 (6 H, m, *m*-Ph-*H*, *p*-Ph-*H*), 7.66 (4 H, dd, *J* 7.6, 1.1, *o*-Ph-*H*); δ_C(100 MHz) 200.1 (br), 170.1, 135.6 (CH), 134.2 (quat. C), 129.5 (CH), 127.6 (CH), 84.0 (CH), 80.6 (CH), 75.5 (CH), 64.7 (CH), 64.0 (CH_2), 63.0 (CH), 37.5 (CH_2), 34.1 (CH_2), 32.6 (CH_2), 31.8 (CH_2), 31.4 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 27.5 (CH_2), 26.9 (CH_3), 25.7 (CH_2), 25.4 (CH_2), 22.5 (CH_2), 21.0 (CH_3), 19.2 (quat. C), 14.0 (CH_3); *m/z* (FAB) 618 ([M − 3CO]$^+$, 100%), 575 (8, M − 3CO − MeCO), 517 (9, M − Bu^t − 3CO − CO_2), 503 (12) {Found ([M − 3CO]$^+$) 618.3192. $C_{36}H_{54}FeO_3Si$ requires *M* − 3CO, 618.3191}.

[(10*E*,9*S*,12*S*,13*R*)-1-*tert*-Butyldiphenylsilyloxy-13-(carbonyl-oxy-κ*C*)-9-hydroxy-(10,11,12-η)-octadec-10-en-12-yl]-tricarbonyliron 11

Potassium carbonate (6 mg, 0.045 mmol) was added to a solution of the acetate **13** (8 mg, 0.013 mmol) in methanol (2.5 cm^3) at 0 °C. After stirring at this temperature for 1 h, the solution was warmed to room temperature and stirring was continued for 2 h. The solution was poured into aqueous ammonium chloride (20 cm^3), dichloromethane (10 cm^3) was added and the layers were separated. The aqueous phase was extracted with dichloromethane (2 × 10 cm^3), the combined organic phases were washed with brine (20 cm^3) and dried ($MgSO_4$). Concentration *in vacuo* followed by flash column chromatography (eluent petrol–ether 4:1 to 2:1) provided the alcohol **11** (4 mg, 53%), which was identical in every respect to that prepared earlier.

[(11*Z*,9*S*,10*R*,13*S*)-1-*tert*-Butyldiphenylsilyloxy-9-hydroxy-(10,11,12,13-η)-octadec-10,12-diene]tricarbonyliron 3

Saturated aqueous barium hydroxide (~1 cm^3) was added to a stirred solution of the alcohol **11** (457 mg, 0.81 mmol) in methanol (6 cm^3) until precipitation ceased to occur. After stirring for a further 5 min, ether (20 cm^3) and water (20 cm^3) were added. Following separation of the layers, the aqueous phase was extracted with ether (3 × 20 cm^3) and the combined organic extracts were then washed with brine (30 cm^3) and dried ($MgSO_4$). Concentration *in vacuo* followed by filtration through a pad of Florisil provided the crude product, which was purified by flash column chromatography (eluent petrol–ether 9:1) to afford the *diene complex* **3** as a bright yellow oil (335 mg, 78%); $[\alpha]_D^{24}$ +1.2 (*c* 0.60 in $CHCl_3$); ν_{max}(film)/cm^{-1} 3418 (OH), 3019, 2930, 2857, 2042 (CO), 1973 (CO), 1589, 1521, 1466, 1428, 1216, 1111, 1008, 929; δ_H(500 MHz) 0.89 (3 H, t, *J* 6.9, 18-H × 3), 1.04 (9 H, s, Bu^t), 1.07–1.71 (25 H, m, OH, 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2, 6-H × 2, 7-H × 2, 8-H × 2, 10-H, 13-H, 14-H × 2, 15-H × 2, 16-H × 2, 17-H × 2), 3.41–3.48 (1 H, m, 9-H), 3.65 (2 H, t, *J* 6.5, 1-H × 2), 5.04 (1 H, dd, *J* 8.8, 5.0, 11-H or 12-H), 5.14 (1 H, dd, *J* 8.8, 5.0, 11-H or 12-H), 7.35–7.46 (6 H, m, *m*-Ph-*H*, *p*-Ph-*H*), 7.66 (4 H, dd, *J* 7.7, 1.3, *o*-Ph-*H*); δ_C(100 MHz) 210.1 (br, CO), 135.6 (CH), 134.2 (quat. C), 129.5 (CH), 127.6 (CH), 84.3 (CH), 81.0 (CH), 74.1 (CH), 68.9 (CH), 65.2 (CH), 64.0 (CH_2), 39.9 (CH_2), 34.1 (CH_2), 32.6 (CH_2), 31.8 (CH_2), 31.4 (CH_2), 29.5 (CH_2 × 2), 29.3 (CH_2), 26.9 (CH_3) 25.9 (CH_2), 25.8 (CH_2) 22.5 (CH_2), 19.2 (quat. C), 14.0 (CH_3); *m/z* (FAB) 643 ([M − OH]$^+$, 7%), 618 (52), 559 (100 M − 3CO − OH), 313 (48), 193 (77), 183 (44), 121 (41) {Found ([M − 3CO − OH]$^+$) 559.3091. $C_{34}H_{51}FeOSi$ requires *M* − 3CO − OH, 559.3056}.

Stock solution of HF·pyridine in pyridine–tetrahydrofuran

Pyridine hydrofluoride (*ex* fluka; 11.4 cm^3) was added to a stirred solution of pyridine (42 cm^3) in tetrahydrofuran (120 cm^3) in a 250 cm^3 poly(vinyl chloride) bottle under argon. The resulting colourless solution was stored under argon at −20 °C and was used as the stock solution in all the following deprotections.

[(11*Z*,9*S*,10*R*,13*S*)-1,9-Dihydroxy-(10,11,12,13-η)-octadeca-10,12-diene]tricarbonyliron 16

HF·pyridine stock solution (122 cm^3) was added dropwise to a stirred solution of the diene complex **3** (473 mg, 0.72 mmol) in tetrahydrofuran (28 cm^3). Stirring was continued for 18 h, after which hexane (200 cm^3) was added and stirring was continued for a further 10 min. The solution was slowly poured into aqueous sodium hydrogen carbonate (400 cm^3) at 0 °C and the biphasic mixture was vigorously stirred for 20 min. The layers were separated and the organic phase was washed with aqueous sodium hydrogen carbonate until effervescence ceased. The aqueous phase was then extracted with ether (3 × 100 cm^3) and the combined organic extracts were washed with brine (200 cm^3) and dried (Na_2SO_4). Concentration *in vacuo* was followed by azeotropic removal of pyridine using toluene (2 × 100 cm^3). Flash column chromatography of the residue (eluent petrol–ether 5:1 to petrol–ether 1:3) afforded the *diol* **16** as a green oil (279 mg, 92%) (Found C, 59.67; H, 7.93. $C_{21}H_{34}FeO_5$ requires C, 59.69; H, 8.12%); $[\alpha]_D^{22}$ −14.7 (*c* 0.70, $CHCl_3$); ν_{max}(film)/cm^{-1} 3385 (OH), 3010, 2929, 2850, 2039 (CO), 1966 (CO), 1664, 1466, 1379, 1216, 1127, 1054, 880; δ_H(500 MHz) 0.89 (3 H, t, *J* 7.0, 18-H × 3), 1.03 (1 H, apparent t, *J* 8.8, 10-H), 1.06–1.12 (1 H, m, 13-H), 1.23–1.57 (24 H, m, OH × 2, 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2, 6-H × 2, 7-H × 2, 8-H × 2, 14-H × 2, 15-H × 2, 16-H × 2, 17-H × 2), 3.41–3.47 (1 H, m, 9-H), 3.63 (2 H, br t, *J* 6.7, 1-H × 2), 5.05 (1 H, dd, *J* 8.8, 5.0, 11-H or 12-H), 5.14 (1 H, dd, *J* 8.8, 5.0, 11-H or 12-H); δ_C(50 MHz) 212.1 (br), 84.2, 80.9, 73.9, 66.8, 65.1, 62.9, 39.8, 34.1, 32.7, 31.7, 31.4, 29.4 (2 signals), 29.3, 25.8, 25.6, 22.4, 13.9; *m/z* (CI) 405 ([M − OH]$^+$, 5%), 338 (17, M − 3CO), 284 (100), 282 [42, M − $Fe(CO)_3$], 265 [73, M − $Fe(CO)_3$ − OH], 249 [12, MH − $Fe(CO)_3$ − 2OH] {Found ([M − OH]$^+$) 405.1728. $C_{21}H_{33}FeO_4$ requires *M* − OH, 405.1728}.

Preparation of sodium hydroxide–hydrogen peroxide solution

Hydrogen peroxide (9 cm^3 of a 30% aqueous solution) was added to a stirred solution of sodium hydroxide (450 mg, 11 mmol) in methanol (15 cm^3) at 0 °C. The solution was used immediately.

(10*E*,12*E*,9*S*)-1,9-Dihydroxyoctadeca-10,12-diene 17

A solution of the diol **16** (279 mg, 0.65 mmol) in methanol (9 cm^3) at 0 °C was treated with sodium hydroxide–hydrogen peroxide solution (*vide infra*) (11.1 cm^3). After stirring at 0 °C for 25 min, water (30 cm^3) and ether (30 cm^3) were added and the layers were separated. The aqueous phase was extracted with ether (3 × 30 cm^3) and the combined organic extracts were washed sequentially with aqueous ammonium chloride (30 cm^3) and brine (50 cm^3) and then dried (Na_2SO_4). Concentration *in vacuo* followed by flash column chromatography (eluent petrol–ether 2:3) afforded the *diene* **17** as a colourless solid (173 mg, 94%), mp 43–45 °C (Found C, 76.31; H, 12.00. $C_{18}H_{34}O_2$ requires C, 76.53; H, 12.14%); $[\alpha]_D^{24}$ +4.4 (*c* 0.55 in $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 3400 (OH), 3016, 2929, 2856, 1659, 1457, 1379, 1216, 1053, 990; δ_H(500 MHz) 0.89 (3 H, t, *J* 6.8, 18-H × 3), 1.26–1.57 (22 H, m, OH × 2, 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2, 6-H × 2, 7-H × 2, 8-H × 2, 15-H × 2, 16-H × 2, 17-

H × 2), 2.07 (2 H, apparent q, *J* 7.2, 14-H × 2), 3.63 (2 H, t, *J* 6.6, 1-H × 2), 4.10 (1 H, apparent q, *J* 6.8, 9-H), 5.56 (1 H, dd, *J* 15.2, 6.8, 10-H), 5.70 (1 H, dt, *J* 15.1, 7.2, 13-H), 6.01 (1 H, dd, *J* 15.1, 10.5, 12-H), 6.16 (1 H, dd, *J* 15.2, 10.5, 11-H); δ_C(100 MHz) 135.7 (CH), 133.6 (CH), 131.0 (CH), 129.4 (CH), 72.9 (CH), 63.1 (CH_2), 37.3 (CH_2), 32.8 (CH_2), 32.6 (CH_2), 31.4 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 28.9 (CH_2), 25.7 (CH_2), 25.4 (CH_2), 22.5 (CH_2), 14.0 (CH_3); *m/z* (CI) 300 ($[M + NH_4]^+$, 5%), 282 (17, M), 265 (100, M − OH) {Found ($[M + NH_4]^+$) 300.2903. $C_{18}H_{38}NO_2$ requires *M* + NH_4, 300.2902}.

(10*E*,12*E*,9*S*)-1-*tert*-Butyldiphenylsilyloxy-9-hydroxyoctadeca-10,12-diene 20

Portions (1.5 cm^3) of sodium hydroxide–hydrogen peroxide solution (*vide infra* for preparation) were added each hour for 4 h to a stirred solution of **3** (50 mg, 0.075 mmol) in methanol (0.7 cm^3) at 0 °C. After stirring for 6 h at this temperature, ether (10 cm^3) was added and the mixture was poured into aqueous ammonium chloride (20 cm^3). After separating the layers, the aqueous phase was extracted with ether (3 × 10 cm^3) and the combined organic extracts were then washed with brine (20 cm^3) and dried ($MgSO_4$). Concentration *in vacuo* followed by flash column chromatography (eluent petrol–ether 8:1 to petrol–ether 5:1) afforded the *diene* **20** as a colourless oil (18 mg, 46%); $[\alpha]_D^{23}$ +5.2 (*c* 1.20 in $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 3400 (OH), 2929, 2856, 1659, 1589, 1464, 1427, 1389, 1216, 1111, 986; δ_H(500 MHz) 0.89 (3 H, t, *J* 6.7, 18-H × 3), 1.04 (9 H, s, Bu^t), 1.17–1.67 (20 H, m, 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2, 6-H × 2, 7-H × 2, 8-H × 2, 15-H × 2, 16-H × 2, 17-H × 2), 2.07 (2 H, apparent q, *J* 7.1, 14-H × 2), 3.65 (2 H, t, *J* 6.5, 1-H × 2), 4.10 (1 H, apparent q, *J* 6.5, 9-H), 5.57 (1 H, dd, *J* 15.2, 6.5, 10-H), 5.70 (1 H, dt, *J* 15.1, 7.1, 13-H), 6.02 (1 H, dd, *J* 15.1, 10.4, 12-H), 6.16 (1 H, dd, *J* 15.2, 10.4, 11-H), 7.36–7.43 (6 H, m, *m*-Ph-*H*, *p*-Ph-*H*), 7.66 (4 H, dd, *J* 6.6, 1.8, *o*-Ph-*H*); δ_C(100 MHz) 135.6 (CH × 2), 134.2 (quat. C), 133.6 (CH), 131.0 (CH), 129.5 (CH), 129.4 (CH), 127.6 (CH), 72.9 (CH), 64.0 (CH_2), 37.4 (CH_2), 32.7 (CH_2), 32.6 (CH_2), 31.4 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 28.9 (CH_2), 26.9 (CH_3), 25.8 (CH_2), 25.5 (CH_2), 22.5 (CH_2), 19.2 (quat. C), 14.1 (CH_3); *m/z* (CI) 538 ($[M + NH_4]^+$, 5%), 520 (27, M), 503 (100, M − OH), 463 (10, M − Bu^t), 385 (10), 256 (12), 247 (22) {Found ($[M + NH_4]^+$) 538.4080. $C_{34}H_{56}NO_2Si$ requires *M* + NH_4, 538.4080}.

(10*E*,12*E*,9*S*)-9-Hydroxyoctadeca-10,12-dienal 18

A solution of the diol **17** (58 mg, 0.21 mmol) in benzene (2 cm^3) was added *via* a cannula to a stirred solution of tris(triphenylphosphine)ruthenium dichloride (199 mg, 0.20 mmol) in benzene (2 cm^3). After stirring at room temperature for 22 h, the mixture was filtered through a pad of Florisil and the residue was washed with ether (200 cm^3). Concentration *in vacuo* afforded the crude product which was purified by flash column chromatography (eluent petrol–ether 5:2, column pre-equilibrated with petrol–ether 5:2 containing 1% triethylamine) to yield the *aldehyde* **18** as a colourless oil (42 mg, 73%); $[\alpha]_D^{24}$ −2.6 (*c* 1.05 in $CHCl_3$); $\nu_{max}(CHCl_3)/cm^{-1}$ 3420 (OH), 3016, 2929, 2856, 1721 (C=O), 1658, 1591, 1466, 1435, 1390, 1216, 1096; δ_H(500 MHz) 0.89 (3 H, t, *J* 6.7, 18-H × 3), 1.23–1.66 (19 H, m, OH, 3-H × 2, 4-H × 2, 5-H × 2, 6-H × 2, 7-H × 2, 8-H × 2, 15-H × 2, 16-H × 2, 17-H × 2), 2.07 (2 H, apparent q, *J* 7.0, 14-H × 2), 2.41 (2 H, td, *J* 6.9, 1.6, 2-H × 2), 4.10 (1 H, apparent q, *J* 7.0, 9-H), 5.57 (1 H, dd, *J* 15.2, 7.0, 10-H), 5.70 (1 H, dt, *J* 15.2, 7.0, 13-H), 6.02 (1 H, dd, *J* 15.2, 10.5, 12-H), 6.17 (1 H, dd, *J* 15.2, 10.5, 11-H), 9.76 (1 H, t, *J* 1.6, 1-H); δ_C(50 MHz) 202.8, 135.5, 133.4, 130.8, 129.2, 72.6, 43.7, 37.1, 32.4, 31.2, 29.2, 29.1, 28.9, 28.7, 25.2, 22.3, 21.8, 13.9; *m/z* (EI) 280 (M^+, 12%), 279 (10, M − H), 263 (100, M − OH) [Found (M^+) 280.2402. $C_{18}H_{32}O_2$ requires *M*, 280.2402].

(10*E*,12*E*,9*S*)-Methyl 9-hydroxyoctadeca-10,12-dienoate 19

Potassium dihydrogen phosphate (144 mg, 1.08 mmol) and sodium hypochlorite (36 mg, 0.40 mmol) were sequentially added to a stirred solution of the aldehyde **18** (13 mg, 0.046 mmol) in *tert*-butyl alcohol (0.6 cm^3) and water (0.6 cm^3) containing 2-methylbut-2-ene (172 μl, 2.08 mmol). After further stirring for 1 h, the solution was cooled to 0 °C, aqueous sodium sulfite (~3 cm^3) was added dropwise and stirring was continued at 0 °C for 30 min. The solution was then poured into aqueous ammonium chloride (20 cm^3) and extracted with ether (3 × 15 cm^3) and brine (20 cm^3) and then dried (Na_2SO_4). The solution was concentrated *in vacuo* to a small volume (~3 cm^3) and diazomethane, prepared according to the literature procedure,[27] was added with stirring until decolourisation ceased to occur. Argon was bubbled through the solution for 10 min after which concentration *in vacuo* afforded the crude product. Flash column chromatography (eluent petrol–ether 4:1) provided the ester **19** as a pale yellow oil (7 mg, 49%); $[\alpha]_D^{24}$ +6.0 (*c* 0.40 in $CHCl_3$), {lit.,[25] $[\alpha]_D$ +5.2 (*c* 5.00 in $CHCl_3$}; $\nu_{max}(CHCl_3)/cm^{-1}$ 3435 (OH), 3018, 2928, 2856, 1731 (C=O), 1464, 1437, 1377, 1216, 1175, 1112, 990; δ_H(500 MHz) 0.89 (3 H, t, *J* 6.7, 18-H × 3), 1.23–1.64 (19 H, m, OH, 3-H × 2, 4-H × 2, 5-H × 2, 6-H × 2, 7-H × 2, 8-H × 2, 15-H × 2, 16-H × 2, 17-H × 2), 2.07 (2 H, apparent q, *J* 6.9, 14-H × 2), 2.30 (2 H, t, *J* 7.5, 2-H × 2), 3.66 (3 H, s, CO_2Me), 4.10 (1 H, apparent q, *J* 7.0, 9-H), 5.57 (1 H, dd, *J* 15.2, 7.0, 10-H), 5.70 (1 H, dt, *J* 15.2, 6.9, 13-H), 6.01 (1 H, dd, *J* 15.2, 10.4, 12-H), 6.16 (1 H, dd, *J* 15.2, 10.4, 11-H); δ_C(50 MHz) 174.3, 135.6, 133.5, 131.0, 129.4, 72.8, 51.4, 37.2, 34.1, 32.6, 31.4, 29.7, 29.3, 29.1, 28.9, 25.3, 24.9, 22.5, 14.0; *m/z* (CI) 328 ($[M + NH_4]^+$, 4%), 310 (25, M), 293 (100, M − OH) {Found ($[M + NH_4]^+$) 328.2852. $C_{19}H_{38}NO_3$ requires *M* + NH_4, 328.2852}.

(10*E*,12*E*,9*S*)-9-Hydroxyoctadeca-10,12-dienoic acid (β-dimorphecolic acid) 1

Lithium hydroxide (12 mg, 0.29 mmol) was added in one portion to a stirred solution of the ester **19** (16 mg, 0.052 mmol) in dimethoxyethane (2.4 cm^3) and water (0.8 cm^3) at 0 °C. After stirring at this temperature for 30 min, the solution was warmed to room temperature and stirred for a further 3 h, after which the mixture was poured into aqueous sodium hydroxide (5 cm^3 of a 0.3 mol dm^{-3} solution). The aqueous phase was washed with ether (3 × 15 cm^3) and was then acidified to pH 1 with 0.3 mol dm^{-3} HCl. The aqueous phase was extracted with ether (3 × 15 cm^3) and the combined organic extracts were washed with brine (30 cm^3) and dried (Na_2SO_4). Concentration *in vacuo* provided the crude product as a cream-coloured solid which was then triturated with acetone to provide the acid **1** (13 mg, 85%), mp 38–40 °C (lit.,[25] 39–40 °C); $[\alpha]_D^{24}$ +15.4 (*c* 1.0 in MeOH) [lit.,[25] $[\alpha]_D^{24}$ +15.2 (*c* 5.0 in MeOH]; ν_{max}(KBr)/cm^{-1} 3422 (OH), 2925, 2870, 1712–1458 (C=O, C=C), 1321, 1211, 986; δ_H(500 MHz, CD_3OD) 0.89 (3 H, t, *J* 6.8, 18-H × 3), 1.23–1.61 (18 H, m, 3-H × 2, 4-H × 2, 5-H × 2, 6-H × 2, 7-H × 2, 8-H × 2, 15-H × 2, 16-H × 2, 17-H × 2), 2.06 (2 H, apparent q, *J* 7.1, 14-H × 2), 2.21 (2 H, t, *J* 7.5, 1-H × 2), 4.00 (1 H, apparent q, *J* 6.6, 9-H), 5.51 (1 H, dd, *J* 15.1, 6.6, 10-H), 5.66 (1 H, dt, *J* 15.1, 7.1, 13-H), 6.02 (1 H, dd, *J* 15.1, 10.5, 12-H), 6.14 (1 H, dd, *J* 15.1, 10.5, 11-H); *m/z* (FAB) 279 ($[M - OH]^+$, 100%), 319 (80), 160 (26), 109 (38) {Found ($[M - OH]^+$) 279.2319. $C_{18}H_{31}O_2$ requires *M* − OH, 279.2324}.

Acknowledgements

We are grateful to the EPSRC (Research Studentship to G. M.), Pfizer Central Research and the BP 1702 endowment (to S. V. L.) for generously funding this work.

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Paper 6/07376J
Received 29*th October* 1996
Accepted 9*th December* 1996