1,5-Asymmetric induction of chirality: highly diastereoselective synthesis of homoallylic tertiary alcohols by the Lewis acid-mediated addition of allylstannanes into ketones in the side-chain of π-allyltricarbonyliron lactone complexes

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Allylstannanes add into ketone groups in the side-chain of π-allyltricarbonyliron lactone complexes to afford the corresponding homoallylic tertiary alcohol complexes with very high levels of diastereocontrol. The reaction provides an example of 1,5-asymmetric induction of chirality with the lactone tether acting as the source of induction. The *endo* addition complexes can be converted into (*E*,*E*)-dienes bearing an α tertiary alcohol chiral centre in two steps proceeding *via* the η^4-dienetricarbonyliron complexes. No loss of enantio- or diastereo-purity is observed during decomplexation.

Introduction

In the preceding paper we reported the highly diastereoselective addition of a variety of organoaluminium nucleophiles into ketone groups positioned in the side-chain of π-allyltricarbonyliron lactone complexes, providing a route to diastereoisomerically pure tertiary alcohol complexes. The *endo* lactone addition complexes could be converted into the corresponding (*E*,*E*)-η^4-dienetricarbonyliron complexes upon treatment with aqueous barium hydroxide without loss of any stereochemical integrity in the tertiary alcohol chiral centre. An important addition to the already wide array of functionality which can be transferred using the aluminium methodology would be the use of an allyl moiety since this can be transformed into many other useful groups for organic synthesis.

While much successful work has focused on methods for the stereoselective allylation of aldehydes,[1] the corresponding process using ketones has received relatively little investigation.[2] We reasoned that, just as our ketone complexes had proven to be excellent substrates for the reaction with organoaluminium reagents, so too might they act as sources of diastereoisomerically enriched tertiary homoallylic alcohols upon treatment with an allyl metal species.

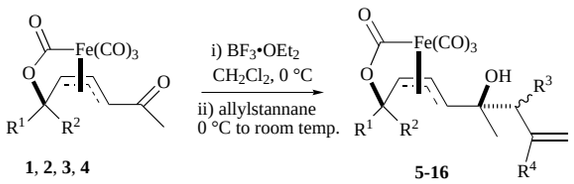
Although a vast number of allylating reagents have been employed in reactions with carbonyl groups,[1] the specific choice in this work was somewhat restricted by a number of factors. First, the instability of π-allyltricarbonyliron lactone complexes towards strongly Lewis basic reagents precluded the use of allyl Grignard reagents and related species. Second, the lower reactivity of ketones compared with their aldehyde congeners combined with the thermal instability of lactone complexes, called for the use of an allyl metal which was Lewis acidic or which reacted under Lewis acidic conditions without the need for elevated reaction temperatures. We therefore reasoned that allyl tin reagents might prove to be attractive nucleophiles for these reactions. Allylstannanes are not Lewis basic; indeed they usually react under Lewis acid activation of the carbonyl group.[3] Using Lewis acids of varying strength enables the reaction to proceed at different temperatures. Allylstannanes are relatively easy to prepare and may be handled without cause for rigorous exclusion of water or molecular oxygen. We recently communicated preliminary results on the addition of allylstannanes into a ketone group in the side-chain of π-allyltricarbonyliron lactone complexes and now report this work here in full.[4]

Results and discussion

Allylstannanes proved to be excellent allylating reagents for our reaction provided that the ketone group was activated by Lewis acid complexation. A number of Lewis acids were screened including titanium tetrachloride ($TiCl_4$), tin tetrachloride ($SnCl_4$) and boron trifluoride–diethyl ether ($BF_3{\cdot}OEt_2$) but the latter proved, by far, to be the most useful in minimising the formation of additional by-products. Thus sequential treatment of a solution of the methyl ketone complex[5] in dichloromethane (DCM) with $BF_3{\cdot}OEt_2$ and the allyl tin species at 0 °C afforded the corresponding S_E2' addition product in good to excellent yield and as one diastereoisomer according to ^{1}H NMR (500 MHz) spectroscopy (Table 1). The use of an excess of Lewis acid and allylstannane was found to increase the rate of reaction especially with more hindered stannanes such as crotyltributylstannane **21** or less reactive ones, for example allenyltributylstannane **19**. In the latter case it was found that warming the reaction mixture to room temperature (25 °C) was necessary to ensure complete consumption of the starting material ketone. Apart from the commercially available allyltributylstannane, all other reagents were synthesised using literature procedures.[6]

A summary of the results from the addition reactions is outlined in Table 1. Allylstannanes containing alkyl substituents at the C-2 position proved to be highly reactive allylating species: methallyltributylstannane **18**[6a] reacted rapidly (1 h) at 0 °C to give the addition product in excellent yield and as a single diastereoisomer. This rapid reaction rate may be explained by the ability of the alkyl group in the C-2 position to efficiently stabilise any accumulation of positive charge on the C-2 carbon in the transition state.[7] Electron withdrawing groups in this position would therefore be expected to decrease the reaction rate. Hence the allyltributylstannane bearing a CH_2OBn group in the C-2 position **20**[6c] reacted more slowly than the methallyl analogue (3 h); incorporation of a methyl ester in this position (**23**[6f]) was so deactivating that reaction was not observed even after 2 days at room temperature, with only starting material being recovered. The highly deactivated γ-silyloxyallyltributylstannane **24**[6g] also failed to react reflecting the inherent lower reactivity of ketones compared with aldehydes. Crotyltributylstannane **21**[6b] reacted at a similar rate to that of allyltributylstannane (3 h). Although the C-3 methyl group does make the stannane more reactive, this electronic activation is balanced by the increased steric hindrance of the methyl substituent at the reacting centre.

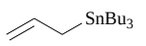
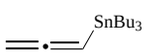
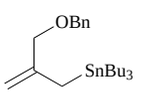
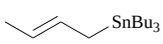
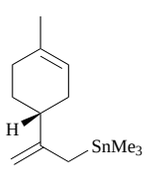
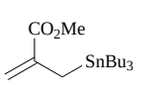
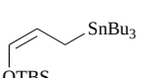
Table 1 Diastereoselective addition of allylstannanes to ketones in the side-chain of π-allyltricarbonyliron lactone complexes



1, **2**, **3**, **4** **5-16**

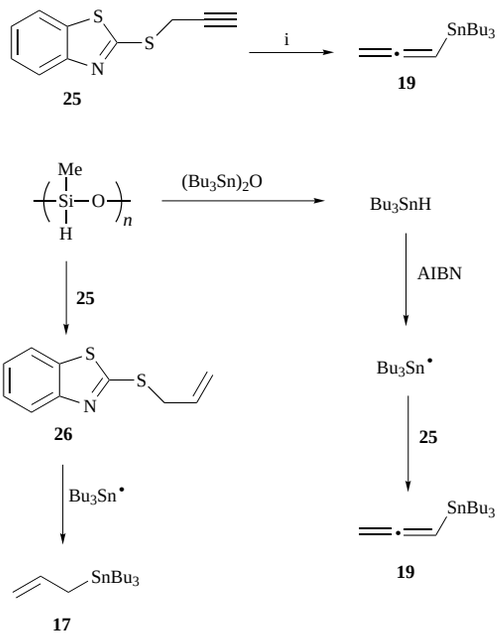
1 R^1 = H, R^2 = Me
2 R^1 = Me, R^2 = H
3 R^1 = H, R^2 = C_5H_{11}
4 R^1 = C_5H_{11}, R^2 = H

5 R^1 = H, R^2 = Me, R^3 = H, R^4 = H
6 R^1 = Me, R^2 = H, R^3 = H, R^4 = H
7 R^1 = H, R^2 = C_5H_{11}, R^3 = H, R^4 = H
8 R^1 = C_5H_{11}, R^2 = H, R^3 = H, R^4 = H
9 R^1 = H, R^2 = Me, R^3 = H, R^4 = Me
10 R^1 = H, R^2 = C_5H_{11}, R^3 = H, R^4 = Me
11 R^1 = H, R^2 = Me, R^3 = H, R^4 = - (triple bond)
12 R^1 = H, R^2 = C_5H_{11}, R^3 = H, R^4 = CH_2OBn
13 R^1 = H, R^2 = C_5H_{11}, R^3 = Me, R^4 = H
14 R^1 = H, R^2 = C_5H_{11}, R^3 = Me, R^4 = H
15 R^1 = H, R^2 = C_5H_{11}, R^3 = H, R^4 = (4'*R*)-1'-methylcyclohex-1'-en-4'-yl
16 R^1 = H, R^2 = C_5H_{11}, R^3 = H, R^4 = (4'*R*)-1'-methylcyclohex-1'-en-4'-yl

Complex	Allylstannane	Product	Yield (%)	de (%)
1		**5**	76	>95
2		**6**	81	>95
3	**17**	**7**	84	>95
4		**8**	80	>95
1		**9**	90	>95
3		**10**	57	>95
	18			
1		**11**	47[a]	95
	19			
3		**12**	65	>95
	20			
3		**13**, **14**	81[b]	95
	21			
3		**15**, **16**	90[c]	>95
	22			
3			no reaction	
	23			
3			no reaction	
	24			

[a] Homoallylic alcohol **5** (4%) and reduction product[8] (35%) were also isolated. [b] Isolated as a 3:2 mixture of diastereoisomers. [c] Isolated as a 1:1 mixture of diastereoisomers.

Allenyltributylstannane **19** was appreciably less reactive than the corresponding allylstannanes although the homopropargylic alcohol complex **11** was produced in moderate yield after 6 h. This reduced reactivity is not surprising when the transition state is considered. Any build-up of positive charge on the C-2 carbon will be better stabilised by an sp^2-hybridised carbon (as in the case of allylstannanes) than an sp-hybridised carbon (as in the case of the allenylstannane). Other addition products were also isolated from this reaction. These were probably due to small amounts of impurities in the allenylstannane which was synthesised from the prop-2-ynylic mercaptobenzothiazole **25** (Scheme 1).[6e] In this reaction polysiloxane acts as the



Scheme 1 *Reagents and conditions*: i, polysiloxane, $(Bu_3Sn)_2O$, AIBN, 90 °C, 5 h, 48%

reducing agent forming tributyltin hydride (Bu_3SnH) *in situ*. Residual Bu_3SnH may account for the formation of the reduction product.[8] It is also conceivable that the polysiloxane partially reduces the triple bond of the prop-2-ynylic mercaptobenzothiazole to the corresponding allyl sulfide **26**. Attack of a tributyltin radical on this species would then generate allyltributylstannane **17**. Although the propargyl alcohol was the major product, the slower rate of reaction of the allenylstannane would allow the impurities to react preferentially.

In all but two cases, where addition product was observed, only one diastereoisomer was present by 500 MHz ^{1}H NMR spectroscopy and hence >95% diastereomeric excess (de) is a conservative estimate for the diastereoselectivity of the reaction. In the cases of the homopropargylic alcohol **11** derived from the addition of allenyltributylstannane and those products derived from crotyltributylstannane addition, **13** and **14**, the presence of a small amount of a product which may be attributable to the other diastereoisomer was observed. However these were present in such small quantities that 95% de would also be a conservative estimate for these reactions.

The excellent diastereoselectivity observed in the addition of allylstannanes into the ketone group is consistent with the transition state proposed for the addition of organoaluminium reagents into the ketone complexes.[5] The Lewis acid complexes to the lone pair of the ketone oxygen which is *syn* to the methyl group. This activation of the carbonyl group then permits attack of the allylstannane on to the ketone with approach *anti* to the bulky tricarbonyliron moiety. The reaction then proceeds through an open transition state.[3] Adoption of one conformation exclusively by the ketone would ensure the formation of a single diastereoisomer providing the $Fe(CO)_3$ group afforded complete facial control. In the case of crotyltributylstannane two diastereoisomers **13** and **14** are produced. This is also in agreement with the proposed model. The $Fe(CO)_3$ unit exerts absolute control over the formation of the tertiary alcohol centre but no control over the adjacent centre. The difference in effective size of the groups on either side of the carbonyl group

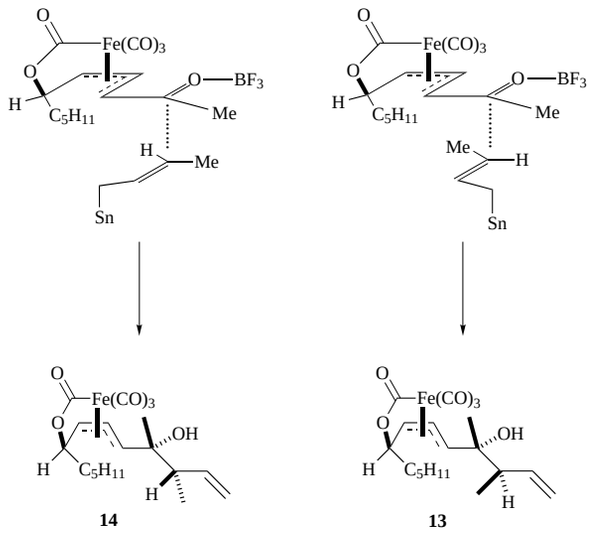
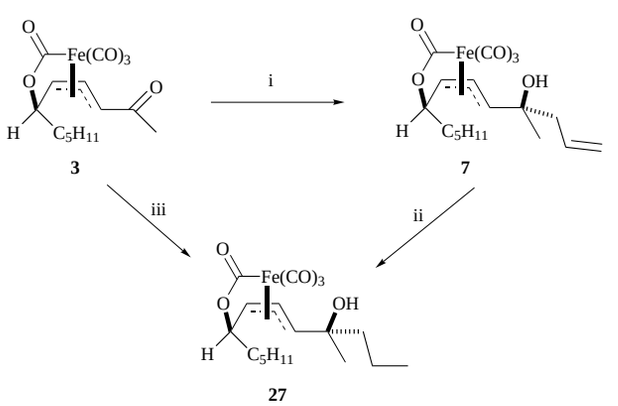


Fig. 1 Reaction of ketone complexes with crotyltributylstannane affords two diastereoisomers

is small, allowing the reaction to proceed equally well through two possible open transition states (Fig. 1).[1]

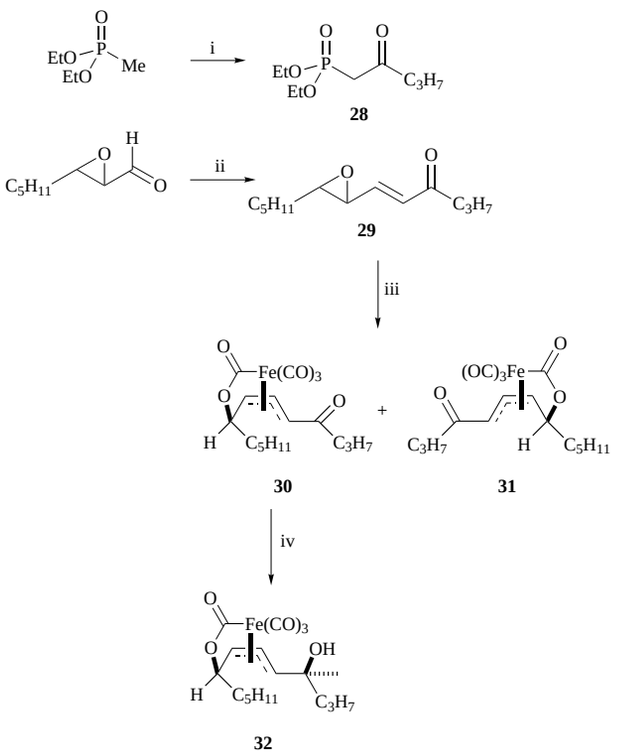
Chemical correlation was used to check the relative configuration between the newly formed chiral centre and that at the lactone tether (Scheme 2). Although unlikely, complexation of



Scheme 2 *Reagents and conditions*: i, allenyltributylstannane, $BF_3{\cdot}OEt_2$, CH_2Cl_2, 0 °C to room temp., 4 h, 84%; ii, Pd/C, H_2, EtOAc, room temp., 2.5 h, 94%; iii, $AlPr^n_3$ (1.0 mol dm^{-3} in toluene), CH_2Cl_2, −78 °C to room temp., 2 h, 6% (reduction product 93%)

a Lewis acid may cause a change in the reactive conformation from the normal s-*cis* to the s-*trans* conformation. This would result in the opposite outcome to that observed in the organoaluminium addition reactions. Thus, hydrogenation of the homoallylic alcohol complex **7** with Pd/C afforded the propyl derivative in 94% yield. Addition of tripropylaluminium ($AlPr^n_3$) into ketone complex **3** afforded 5% of the propyl addition product **27** (the major product resulted from reduction[5] as would be expected from an alkyl group bearing β-hydrogen atoms).[9] Comparison of the 500 MHz ^{1}H NMR spectra showed these two compounds to be identical. Synthesis of the opposite diastereoisomer (that which would result from allyl addition into the s-*trans* conformer of the methyl ketone) was achieved by the addition of trimethylaluminium ($AlMe_3$)[5] into the *endo* propyl ketone complex **30** whose synthesis is outlined in Scheme 3. Comparison of the NMR spectra of **27** and **32** showed that the two diastereoisomers were distinguishable by ^{1}H NMR spectroscopy and confirmed that BF_3-complexed ketones also adopt an s-*cis* reactive conformation and that the reaction proceeds according to our proposed model.

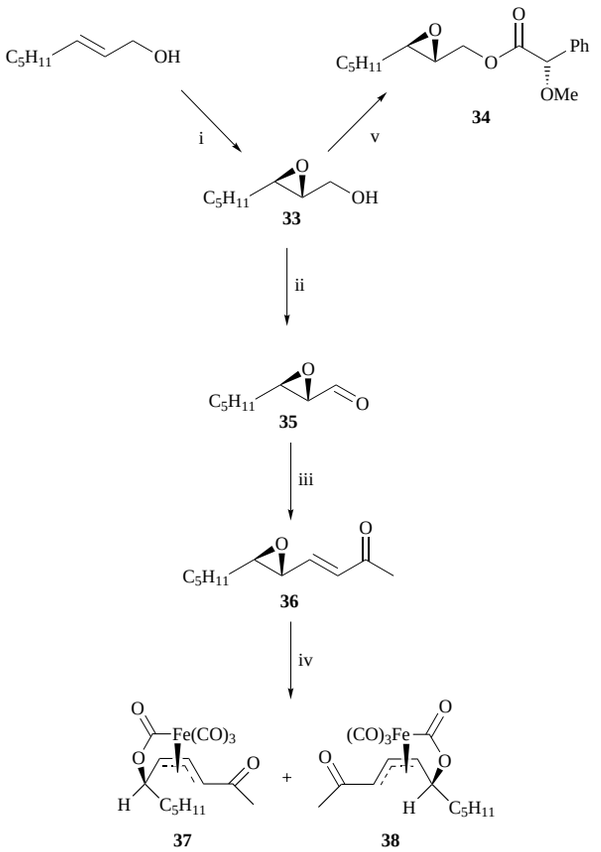
One important advantage over the closely related η^4-dienetricarbonyliron complexes is that π-allyltricarbonyliron lactone complexes can be synthesised in highly enantiomeri-



Scheme 3 *Reagents and conditions*: i, Bu^nLi, THF, −78 °C, then Pr^nCO_2Et, −78 °C, 10 min, then room temp., 2 h, 41%; ii, **28**, NaH, THF, 0 °C, 15 min, then aldehyde, 30 min, 82%; iii, $Fe_2(CO)_9$, THF, room temp., 3 h, 33% (**30**:**31** *ca.* 3:1); iv, $AlMe_3$, CH_2Cl_2, 0 °C to room temp., 4 h, 22%

cally enriched form using Sharpless epoxidation protocols. This avoids the need for a resolution step which is a common route to homochiral η^4-diene complexes.[10] In an attempt to verify that there was no loss of enantiopurity in decomplexing the lactone complexes, methyl ketone complex **37** was synthesised in homochiral form (Scheme 4). Sharpless epoxidation[11] of (*E*)-oct-2-en-1-ol afforded the corresponding epoxide **33** in 52% yield and 96% ee after two recrystallisations as determined by ^{1}H NMR (500 MHz) spectroscopy of the esters **34** derived from (*S*)-(+)-α-methoxyphenylacetyl chloride.[12] Oxidation using standard Swern conditions afforded the epoxy aldehyde **35** which was then subjected to a Horner–Wadsworth–Emmons reaction with diethyl (2-oxopropyl)phosphonate giving the epoxy enone precursor **36** to the lactone complexes. Treatment of **36** with diironnonacarbonyl [$Fe_2(CO)_9$] in tetrahydrofuran (THF) afforded the *endo* and *exo* methyl ketone complexes **37** and **38** respectively. Addition of homochiral stannane **22** derived from (*R*)-limonene[6d] to the *endo* complex **37** generated the addition product **15** in excellent yield and diastereoselectivity (Scheme 5). Carrying out the same reaction with racemic iron complex afforded two diastereoisomers **15** and **16** (Scheme 5), readily distinguishable by ^{1}H NMR spectroscopy. The obtention of only one diastereoisomer from **37** confirmed that the high ee had been maintained in forming the addition product.

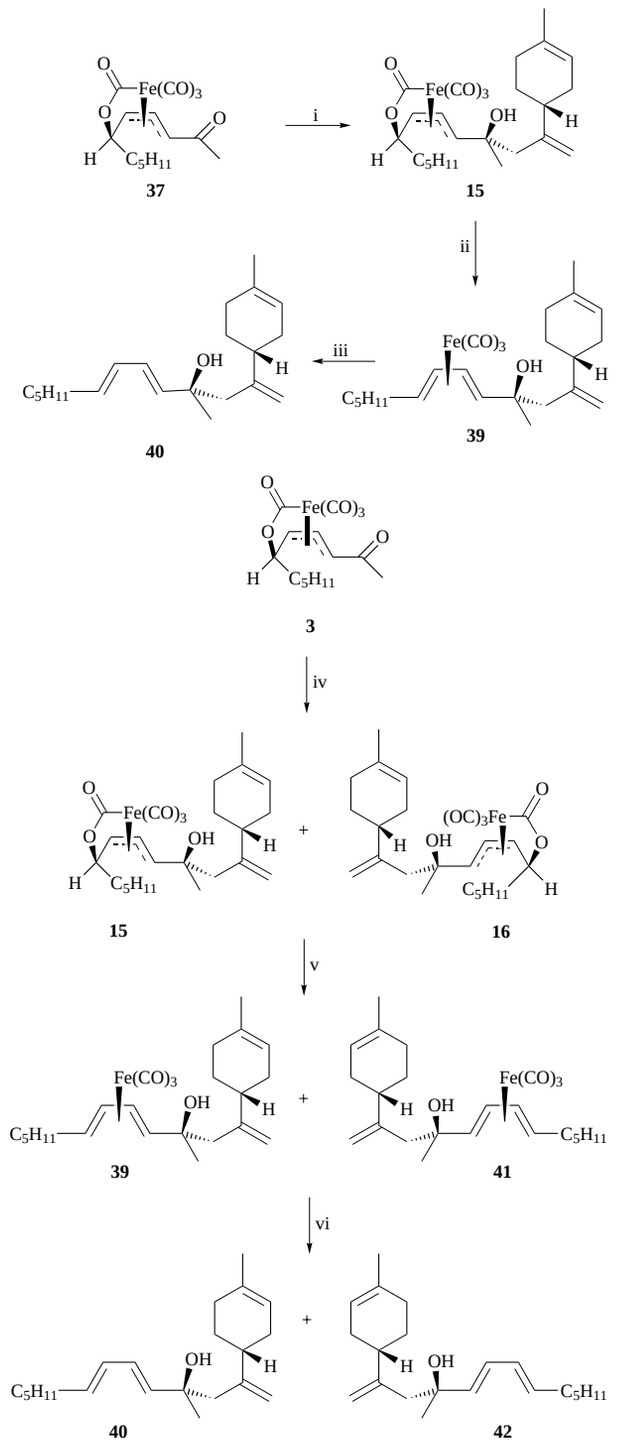
π-Allyltricarbonyliron lactone complexes undergo a number of interesting decomplexation reactions.[13] Of particular interest to us is the partial decomplexation of *endo* complexes to the η^4-dienetricarbonyliron complexes upon treatment with a saturated aqueous solution of barium hydroxide [$Ba(OH)_2$] in methanol (MeOH).[14] The overall result from this reaction is a decarboxylation and an *endo* to *exo* transposition of the alkyl group bonded at the lactone tether. Thus *endo* lactone complexes afford exclusively (*E*,*E*)-diene complexes. Oxidative removal of the $Fe(CO)_3$ unit using alkaline H_2O_2 then releases the free diene ligand.[15] Exposure of **15** to the $Ba(OH)_2$–MeOH conditions resulted in a rapid conversion to the bright yellow η^4-diene complex **39** (Scheme 5). Again the presence of one



Scheme 4 *Reagents and conditions*: i, $Ti(OPr^i)_4$ (5 mol%), D-DET (6 mol%), Bu^tOOH, 4 Å molecular sieves, CH_2Cl_2, −20 °C, 3.5 h, 52%; ii, DMSO, $(COCl)_2$, CH_2Cl_2, 1 h, then **33**, 1.5 h, then Et_3N, −78 °C to room temp., 1.5 h, 76%; iii, $CH_3C(O)CH_2P(O)(OEt)_2$, NaH, 0 °C, then **35**, 30 min, 74%; iv, $Fe_2(CO)_9$, THF, room temp., 2.5 h, 55% (**37**:**38** *ca.* 4:1); v, (*S*)-(+)-PhCH(OMe)COCl, py, CH_2Cl_2, 25 min, quant.

diastereoisomer suggested no loss of stereochemical integrity. Treatment with alkaline hydrogen peroxide (H_2O_2) then afforded the fully decomplexed diene product **40** as one diastereoisomer as evidenced by ^{1}H NMR (500 MHz) spectroscopy. Thus the two-step decomplexation process affords synthetically useful, stereodefined (*E*,*E*)-dienes with an α-hydroxy group without loss of enantiopurity.

In summary, the BF_3-activated addition of a variety of allylstannanes into ketone groups in the side-chain of π-allyltricarbonyliron lactone complexes proceeds in a highly diastereoselective fashion providing a new route to stereodefined homoallylic tertiary alcohols which are difficult to synthesise by existing methods. Differentiation of the prochiral faces of the ketone group by the tricarbonyliron lactone unit results in the 1,5-asymmetric induction of chirality in the addition reaction. The model proposed to account for the stereochemistry of the alcohols generated by the addition of organoaluminium reagents into the ketone complexes is entirely consistent with the results obtained by allylstannane addition. The addition complexes can be decomplexed in a facile and high yielding, two-step procedure. In the case of enantiomerically enriched complexes this proceeds without any loss of enantiopurity to generate the corresponding diene possessing an α chiral centre.



Scheme 5 *Reagents and conditions*: i, limonene–allyltrimethylstannane, $BF_3{\cdot}OEt_2$, CH_2Cl_2, 0 °C, 1.5 h, 96%; ii, $Ba(OH)_2$, MeOH, room temp., 10 min, 75%; iii, H_2O_2, NaOH, MeOH, 0 °C, 1 h, 92%; iv, limonene–allyltrimethylstannane, $BF_3{\cdot}OEt_2$, CH_2Cl_2, 0 °C, 2 h, 90% (**15**:**16** 1:1); v, $Ba(OH)_2$, MeOH, room temp., 10 min, 64% (**39**:**41** 1:1); vi, H_2O_2, NaOH, MeOH, 0 °C, 1 h, 95% (**40**:**42** 1:1)

Experimental

^{1}H NMR spectra were recorded in $CDCl_3$ on Bruker AC-200, Bruker AM-250, Bruker AC-250, Bruker DPX-250, 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 $CHCl_3$ (δ_H = 7.26 ppm) was used as the internal reference and coupling constants are quoted in Hz. ^{13}C NMR spectra were recorded in $CDCl_3$, at 100 MHz, 62.5 MHz or 50 MHz on Bruker AM-400, Bruker DPX-250 or Bruker AM-200 spectrometers, respectively, using the central resonance of $CDCl_3$ (δ_C = 77.0 ppm) as the internal reference. Infra-red spectra were recorded as thin films between sodium chloride plates, deposited from chloroform solution or as a Nujol mull in the case of solids on Perkin-Elmer 983G or FTIR 1620 spectrometers. Mass spectra were obtained on a Kratos MS890MS spectrometer or a Bruker BIOAPEX 4.7 T FTICR 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 produced, 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. Analytical thin layer chromatography (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 (Et_2O) refers to diethyl ether.

All reactions were carried out under an argon atmosphere in oven-dried glassware unless otherwise stated. Reactions involving preparation of the iron complexes were carried out using degassed THF. 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. Et_2O and THF were distilled from sodium benzophenone ketyl; DCM from calcium hydride. Other reagents and solvents were purified using standard procedures.[16] Aqueous solutions are saturated unless otherwise specified.

Note that organotin compounds are toxic. All work involving these reagents was carried out in a well ventilated hood. In the synthesis of the iron lactone ketone complexes, diironnonacarbonyl [$Fe_2(CO)_9$] is used. This is also extremely toxic. Further, ironpentacarbonyl is a highly toxic by-product from the reaction. All work involving the handling of these species was carried out in a well ventilated hood. All glassware was treated with bleach to destroy any iron carbonyl residues before re-use.

General procedure for the preparation of homoallylic tertiary alcohol complexes 5–16

$BF_3{\cdot}OEt_2$ (1.5 equiv., 0.15 mmol; distilled from CaH_2 prior to use) and the allylstannane (2.0–3.0 equiv., 0.20–0.30 mmol) were sequentially added to a cooled (0 °C) solution of the π-allyltricarbonyliron lactone methyl ketone complex in DCM (3 cm^3) in the absence of light. The resulting solution was maintained at 0 °C or allowed to warm to room temperature (25 °C) (as necessary—see Results and discussion) until all starting material was consumed as determined by TLC. H_2O (3 cm^3) and KF (excess) were then added and the solution stirred vigorously for 15 min and then filtered through a pad of Celite washing with DCM (2 × 10 cm^3). The two phases were separated and the aqueous phase further extracted with DCM (2 × 5 cm^3). The combined organic phases were dried ($MgSO_4$) and then filtered. Concentration of the filtrate *in vacuo* followed by flash column chromatography (eluent: Et_2O–petrol) afforded the homoallylic tertiary alcohol complex.

[(4*E*,2*R**,3*S**,6*R**)-2-(Carbonyloxy-κ*C*)-6-hydroxy-6-methyl-(3,4,5-η)-nona-4,8-dien-3-yl]tricarbonyliron 5

Complex **5** was prepared according to the general procedure from the methyl ketone complex **1** (0.029 g, 0.10 mmol) using $BF_3{\cdot}OEt_2$ (0.018 cm^3, 0.15 mmol) and allyltributylstannane **17** (0.046 cm^3, 0.15 mmol; obtained from Aldrich Inc. and used without further purification) at 0 °C to room temperature over 3 h. Flash column chromatography (eluent: neat petrol→Et_2O–petrol 1:1; gradient) afforded *alcohol* **5** as an off-white solid (0.025 g, 76%) (Found: C, 50.00; H, 4.81. $C_{14}H_{16}O_6Fe$ requires C, 50.03; H, 4.80%); ν_{max}(Nujol mull)/cm^{-1} 3373 (OH), 2976, 2918, 2084 (CO), 2026 (CO), 2002 (CO), 1617 (C=O), 1456, 1400, 1372, 1360, 1276, 1237, 1178, 1084, 1051, 1014, 946, 927; δ_H(500 MHz) 1.33 (3H, d, *J* 7.1, 1-H × 3), 1.58 (3H, s, 6-Me), 1.70 (1H, s, OH), 2.48 (1H, dd, *J* 14.3, 7.1, 7-H × 1), 2.58 (1H, dd, *J* 14.3, 7.1, 7-H × 1), 4.02 (1H, d, *J* 11.9, 5-H), 4.44 (1H, dd, *J* 7.1, 4.8, 2-H), 4.64 (1H, dd, *J* 8.3, 4.8, 3-H), 4.80 (1H, dd, *J* 11.9, 8.3, 4-H), 5.21 (1H, d, *J* 16.7, 9-H$_{trans}$), 5.26 (1H, d, *J* 9.5, 9-H$_{cis}$), 5.89–5.97 (1H, m, 8-H); δ_C(100 MHz) 21.8 (CH_3, 1-C), 30.3 (CH_3, 6-Me), 50.4 (CH_2, 7-C), 72.3 (quat. C, 6-C), 73.2 (CH), 76.4 (CH), 86.9 (CH), 92.4 (CH), 120.5 (CH_2, 9-C), 132.7 (CH, 8-C), 203.3 (CO), 206.3 (CO), 207.1 (CO), 209.6 (CO); *m*/*z* (FAB) 337 (MH^+, 100%), 309 (14, MH − CO), 297 (35), 280 (10, M − 2CO), 253 (56, MH − 3CO), 235 (9, M − 3CO − OH), 224 (25, M − 4CO), 207 (31, M − 4CO − OH), 190 (16), 183 (15), 148 (17) [Found (MH^+) 337.0382. $C_{14}H_{17}O_6Fe$ requires *M*H, 337.0375].

[(4*E*,2*S**,3*S**,6*R**)-2-(Carbonyloxy-κ*C*)-6-hydroxy-6-methyl-(3,4,5-η)-nona-4,8-dien-3-yl]tricarbonyliron 6

Complex **6** was prepared according to the general procedure from methyl ketone complex **2** (0.071 g, 0.24 mmol) using $BF_3{\cdot}OEt_2$ (0.033 cm^3, 0.26 mmol) and allyltributylstannane **17** (0.113 cm^3, 0.36 mmol) at 0 °C for 1 h and then at room temperature (25 °C) for 2 h. Flash column chromatography (eluent: neat petrol→Et_2O–petrol 1:1; gradient) afforded *alcohol* **6** as a white solid (0.066 g, 81%) (Found: C, 50.16; H, 4.80. $C_{14}H_{16}O_6Fe$ requires C, 50.03; H, 4.80%); ν_{max}(Nujol mull)/cm^{-1} 3397 (OH), 2923, 2853, 2071 (CO), 2019 (CO), 1999 (CO), 1637 (C=O), 1455, 1377, 1334, 1310, 1268, 1220, 1175, 1143, 1117, 1086, 1045, 1016, 955, 933, 915, 847, 662, 614; δ_H(200 MHz) 1.37 (3H, d, *J* 6.1, 1-H × 3), 1.53 (3H, s, 6-Me), 1.86 (1H, br s, OH), 2.42 (1H, dd, *J* 13.3, 8.0, 7-H × 1), 2.57 (1H, dd, *J* 13.3, 8.0, 7-H × 1), 3.89 (1H, d, *J* 12.0, 5-H), 4.21 (1H, q, *J* 6.1, 2-H), 4.41 (1H, d, *J* 8.0, 3-H), 4.98 (1H, dd, *J* 12.0, 8.0, 4-H), 5.19 (1H, d, *J* 17.3, 9-H$_{trans}$), 5.27 (1H, d, *J* 12.8, 9-H$_{cis}$), 5.81–6.02 (1H, m, 8-H); δ_C(62.5 MHz) 23.7 (CH_3, 1-C), 29.8 (CH_3, 6-Me), 50.2 (CH_2, 7-C), 71.2 (CH), 72.0 (quat. C, 6-C), 75.6 (CH), 88.6 (CH), 91.7 (CH), 120.5 (CH_2, 9-C), 132.7 (CH, 8-C), 203.4 (CO), 205.9 (CO), 207.0 (CO), 209.9 (CO); *m*/*z* (FAB) 337 (MH^+), 319 (M − OH), 309 (MH − CO), 297, 280 (M − 2CO), 253 (MH − 3CO), 247, 207 (M − 4CO − OH), 190, 148 [Found (MH^+) 337.0389. $C_{14}H_{17}O_6Fe$ requires *M*H, 337.0375].

[(5*E*,4*R**,7*S**,8*R**)-8-(Carbonyloxy-κ*C*)-4-hydroxy-4-methyl-(5,6,7-η)-trideca-1,5-dien-7-yl]tricarbonyliron 7

Complex **7** was prepared according to the general procedure from methyl ketone complex **3** (1.00 g, 2.86 mmol) using $BF_3{\cdot}OEt_2$ (0.530 cm^3, 4.29 mmol) and allyltributylstannane **17** (2.66 cm^3, 8.57 mmol) at 0 °C to room temperature over 4 h. Flash column chromatography (eluent: Et_2O–petrol 3:17→7:13; gradient) afforded *alcohol* **7** as a cream-coloured solid (0.984 g, 84%) (Found: C, 55.16; H, 6.23. $C_{18}H_{24}O_6Fe$ requires C, 55.09; H, 6.17%); ν_{max}(Nujol mull)/cm^{-1} 3306 (OH), 2922, 2853, 2086 (CO), 2023 (CO), 2005 (CO), 1617 (C=O), 1462, 1376, 1242, 1186, 1163, 1119, 1060, 914, 876, 834, 722, 665, 610; δ_H(200 MHz) 0.88 (3H, t, *J* 6.7, 13-H × 3), 1.16–1.66 (8H, m, 9-H × 2, 10-H × 2, 11-H × 2, 12-H × 2), 1.55 (3H, s, 4-Me), 1.70 (1H, br s, OH), 2.46 (1H, dd, *J* 13.3, 8.0, 3-H × 1), 2.59 (1H, dd, *J* 13.3, 6.7, 3-H × 1), 3.95 (1H, d, *J* 12.0, 5-H), 4.25 (1H, apparent q, *J* 5.3, 8-H), 4.62 (1H, dd, *J* 8.0, 5.3, 7-H), 4.83 (1H, dd, *J* 12.0, 8.0, 6-H), 5.19 (1H, d, *J* 16.5, 1-H$_{trans}$), 5.26 (1H, d, *J* 11.2, 1-H$_{cis}$), 5.82–6.05 (1H, m, 2-H); δ_C(100 MHz) 13.9 (CH_3, 13-C), 22.4 (CH_2), 26.5 (CH_2), 30.1 (CH_3, 4-Me), 31.5 (CH_2), 36.5 (CH_2), 50.3 (CH_2, 3-C), 72.2 (quat. C, 4-C), 75.1 (CH), 77.1 (CH), 87.0 (CH), 92.3 (CH), 120.2 (CH_2, 1-C), 132.8 (CH, 2-C), 203.3 (CO), 206.7 (CO), 207.1 (CO), 209.6 (CO); *m*/*z* (FAB) 415 [(M + Na)$^+$, 24%], 393 (81, MH), 365 (8, MH − CO), 353 (14), 336 (7, M − 2CO), 309 (28, MH − 3CO), 303 (37), 280 (33, M − 4CO), 263 (31, M − 4CO − OH), 246 (16, M − 4CO − O − H_2O), 208 (11,

M − 4CO − Fe − O), 191 (100, M − 4CO − Fe − O − OH), 149 (20), 121 (25) [Found (MH^+) 393.1001. $C_{18}H_{25}O_6Fe$ requires *M*H, 393.1000].

[(5*E*,4*R,7*S**,8*S**)-8-(Carbonyloxy-κ*C*)-4-hydroxy-4-methyl-(5,6,7-η)-trideca-1,5-dien-7-yl]tricarbonyliron 8**

Complex **8** was prepared according to the general procedure from methyl ketone complex **4** (0.440 g, 1.26 mmol) using $BF_3{\cdot}OEt_2$ (0.238 cm^3, 1.94 mmol) and allyltributylstannane **17** (1.170 cm^3, 3.77 mmol) at 0 °C for 2.75 h. Flash column chromatography (eluent: Et_2O–petrol 1 : 4→1 : 1; gradient) afforded *alcohol* **8** as a golden yellow oil (0.392 g, 80%) (Found: C, 55.34; H, 6.20. $C_{18}H_{24}O_6Fe$ requires C, 55.09; H, 6.17%); ν_{max}(film)/cm^{-1} 3413 (OH), 3078, 2932, 2861, 2081 (CO), 2006 (CO), 1634 (C=O), 1461, 1379, 1344, 1305, 1280, 1238, 1166, 1131, 913, 734, 660, 609; δ_H(200 MHz) 0.90 (3H, t, *J* 5.3, 13-H × 3), 1.19–1.72 {11H, m, [including 1.52 (3H, s, 4-Me)], 4-Me, 9-H × 2, 10-H × 2, 11-H × 2, 12-H × 2}, 1.86 (1H, s, OH), 2.43 (1H, dd, *J* 13.3, 7.5, 3-H × 1), 2.57 (1H, dd, *J* 13.3, 7.5, 3-H × 1), 3.88 (1H, d, *J* 12.0, 5-H), 3.95 (1H, t, *J* 6.7, 8-H), 4.44 (1H, d, *J* 8.0, 7-H), 5.00 (1H, dd, *J* 12.0, 8.0, 6-H), 5.19 (1H, d, *J* 18.1, 1-H_{trans}), 5.27 (1H, d, *J* 9.9, 1-H_{cis}), 5.80–6.03 (1H, m, 2-H); δ_C(100 MHz) 13.9 (CH_3, 13-C), 22.4 (CH_2), 25.2 (CH_2), 29.6 (CH_3, 4-Me), 31.4 (CH_2), 37.7 (CH_2), 50.1 (CH_2, 3-C), 71.8 (quat. C, 4-C), 74.1 (CH), 75.1 (CH), 88.6 (CH), 91.6 (CH), 120.3 (CH_2, 1-C), 132.8 (CH, 2-C), 203.4 (CO), 206.4 (CO), 207.0 (CO), 210.0 (CO); *m*/*z* (FAB) 415 [$(M + Na)^+$, 28%], 393 (100, MH), 353 (13), 336 (M − 2CO), 309 (40, MH − 3CO), 280 (23, M − 4CO), 264 (16, M − 4CO − O), 246 (27, M − 4CO − O − H_2O), 209 (17, MH − 4CO − O − Fe), 191 (54, MH − 4CO − O − H_2O) [Found (MH^+) 393.0998. $C_{18}H_{25}O_6Fe$ requires *M*H, 393.1000].

[(4*E*,2*R,3*S**,6*R**)-2-(Carbonyloxy-κ*C*)-6-hydroxy-6,8-dimethyl-(3,4,5-η)-nona-4,8-dien-3-yl]tricarbonyliron 9**

Complex **9** was prepared according to the general procedure from methyl ketone complex **1** (0.0319 g, 0.11 mmol) using $BF_3{\cdot}OEt_2$ (0.019 cm^3, 0.15 mmol) and methallyltributylstannane **18** (0.150 cm^3, *ca.* 0.45 mmol) at 0 °C for 2 h. Flash column chromatography (eluent: Et_2O–petrol 3 : 7→1 : 1; gradient) afforded *alcohol* **9** as a white solid (0.0344 g, 90%) (Found: C, 51.49; H, 5.29. $C_{15}H_{18}O_6Fe$ requires C, 51.45; H, 5.18%); ν_{max}(Nujol mull)/cm^{-1} 3400 (OH), 2923, 2853, 2078 (CO), 2030 (CO), 2007 (CO), 1967 (CO), 1632 (C=O), 1455, 1376, 1354, 1321, 1160, 1114, 1063, 1017, 950, 892; δ_H(200 MHz) 1.34 (3H, d, *J* 6.6, 1-H × 3), 1.56 (3H, s, 6-Me), 1.89 (3H, s, 8-Me), 1.93 (1H, s, OH), 2.45 (1H, d, *J* 14.0, 7-H × 1), 2.53 (1H, d, *J* 14.0, 7-H × 1), 4.05 (1H, d, *J* 12.0, 5-H), 4.38–4.50 (1H, m, 2-H), 4.61 (1H, dd, *J* 8.0, 4.5, 3-H), 4.78–4.82 (2H, m, 4-H, 9-H × 1), 5.01–5.05 (1H, m, 9-H × 1); δ_C(100 MHz) 21.6 (CH_3, 1-C), 25.0 (CH_3, 8-Me), 31.1 (CH_3, 6-Me), 53.3 (CH_2, 7-C), 72.7 (quat. C, 6-C), 73.4 (CH), 76.2 (CH), 87.0 (CH), 93.2 (CH), 116.6 (CH_2, 9-C), 141.8 (quat. C, 8-C), 203.3 (CO), 206.5 (CO), 207.2 (CO), 209.7 (CO); *m*/*z* (FAB) 373 [$(M + Na)^+$, 31%], 351 (88, MH), 333 (7, M − OH), 323 (13, MH − CO), 311 (36), 295 (12, MH − 2CO), 267 (48, MH − 3CO), 249 (14, MH − 3CO − H_2O), 238 (42, M − 4CO), 221 (50, MH − 4CO − H_2O), 204 (14, M − 4CO − H_2O − O), 183 (25), 162 (20), 149 (100, MH − 4CO − H_2O − O − Fe), 121 (28) [Found (MH^+) 351.0512. $C_{15}H_{19}O_6Fe$ requires *M*H, 351.0531].

[(5*E*,4*R,7*S**,8*R**)-8-(Carbonyloxy-κ*C*)-4-hydroxy-2,4-dimethyl-(5,6,7-η)-trideca-1,5-dien-7-yl]tricarbonyliron 10**

Complex **10** was prepared according to the general procedure from methyl ketone complex **3** (0.074 g, 0.21 mmol) using $BF_3{\cdot}OEt_2$ (0.039 cm^3, 0.32 mmol) and methallyltributylstannane **18** (0.400 cm^3, *ca.* 1.27 mmol) at 0 °C for 1 h. Flash column chromatography (eluent: Et_2O–petrol 1 : 9→1 : 3; gradient) afforded *alcohol* **10** (0.049 g, 57%) (Found: C, 56.22; H, 6.58. $C_{19}H_{26}O_6Fe$ requires C, 56.14; H, 6.45%); ν_{max}(Nujol mull)/cm^{-1} 3366 (OH), 2924, 2854, 2024 (CO), 2007 (CO), 1976 (CO), 1623 (C=O), 1461, 1376, 1222, 1144, 1118, 1048, 1014, 963, 892, 865; δ_H(200 MHz) 0.89 (3H, t, *J* 6.7, 13-H × 3), 1.17–1.70 (8H, m, 9-H × 2, 10-H × 2, 11-H × 2, 12-H × 2), 1.56 (3H, s, 4-Me), 1.86 (1H, s, OH), 1.90 (3H, s, 2-Me), 2.45 (1H, d, *J* 13.6, 3-H × 1), 2.54 (1H, d, *J* 13.6, 3-H × 1), 4.00 (1H, d, *J* 12.8, 5-H), 4.20–4.29 (1H, m, 8-H), 4.59 (1H, dd, *J* 9.6, 4.8, 7-H), 4.83 (1H, dd, *J* 12.8, 9.6, 6-H), 4.82 (1H, br s, 1-H × 1), 5.03 (1H, br s, 1-H × 1); δ_C(100 MHz) 13.9 (CH_3, 13-C), 22.4 (CH_2), 24.9 (CH_3, 2-Me), 26.6 (CH_2), 30.9 (CH_3, 4-Me), 31.5 (CH_2), 36.4 (CH_2), 53.2 (CH_2, 3-C), 72.6 (quat. C, 4-C), 74.9 (CH), 77.3 (CH), 87.1 (CH), 93.1 (CH), 116.4 (CH_2, 1-C), 141.7 (quat. C, 2-C), 203.3 (CO), 206.7 (CO), 207.2 (CO), 209.6 (CO); *m*/*z* (FAB) 429 [$(M + Na)^+$, 19%], 407 (66, MH), 389 (8, M − OH), 379 (11, MH − CO), 367 (50), 349 (21), 323 (31, MH − 3CO), 317 (43), 294 (36, M − 4CO), 277 (63), 260 (26), 239 (25), 223 (16, MH − 4CO − Fe − O), 205 (100, MH − 4CO − Fe − O − H_2O), 179 (23), 162 (31), 149 (26), 121 (32) [Found (MH^+) 407.1157. $C_{19}H_{27}O_6Fe$ requires *M*H, 407.1164].

[(4*E*,2*R,3*S**,6*R**)-2-(Carbonyloxy-κ*C*)-6-hydroxy-6-methyl-(3,4,5-η)-non-4-en-8-yn-3-yl]tricarbonyliron 11**

Complex **11** was prepared according to the general procedure from methyl ketone complex **1** (0.045 g, 0.15 mmol) using $BF_3{\cdot}OEt_2$ (0.040 cm^3, 0.31 mmol) and allenyltributylstannane **19** (0.120 cm^3) at 0 °C for 0.5 h and then at room temperature (25 °C) for 6 h. Flash column chromatography (eluent: petrol→Et_2O–petrol 3 : 2; gradient) afforded in order of elution, homoallylic alcohol complex **5** (*vide supra*) (0.002 g, 4%); and then homopropargylic *alcohol* **11** as an off-white solid (0.024 g, 47%); ν_{max}(Nujol mull)/cm^{-1} 3347 (OH), 3277 (acetylenic C–H), 2923, 2853, 2092 (CO), 2032 (CO), 2005 (CO), 1617 (C=O), 948, 838, 668; δ_H(500 MHz) 1.36 (3H, d, *J* 6.2, 1-H × 3), 1.67 (3H, s, 6-Me), 2.10 (1H, apparent t, *J* 2.5, 9-H), 2.67 (1H, dd, *J* 16.5, 2.5, 7-H × 1), 2.73 (1H, dd, *J* 16.5, 2.5, 7-H × 1), 4.03 (1H, d, *J* 12.2, 5-H), 4.45 (1H, apparent q, *J* 6.2, 2-H), 4.68 (1H, dd, *J* 8.4, 4.7, 3-H), 4.94 (1H, dd, *J* 12.2, 8.4, 4-H); δ_C(100 MHz) 21.9 (CH_3, 1-C), 29.8 (CH_3, 6-Me), 36.4 (CH_2, 7-C), 71.6 (quat. C), 72.6 (quat. C), 73.3 (CH), 76.9 (CH), 79.5 (CH), 87.2 (CH), 89.8 (CH), 203.0 (CO), 206.1 (CO), 206.9 (CO), 209.4 (CO); *m*/*z* (FAB) 357 [$(M + Na)^+$, 15%], 335 (100, MH), 318 (5, MH − OH), 279 (22, MH − 2CO), 251 (19, MH − 3CO), 222 (34, M − 4CO), 205 (36, M − 4CO − OH), 189 (15, M − 4CO − OH − O), 165 (43, M − 4CO − Fe − H), 150 (17, M − 4CO − Fe − O), 128 (35), 115 (68) [Found (MH^+) 335.0219. $C_{14}H_{15}O_6Fe$ requires *M*H, 335.0218]; and then the reduction product as a white solid (0.015 g, 35%).[5]

[(5*E*,4*R,7*S**,8*R**)-2-Benzyloxymethyl-8-(carbonyloxy-κ*C*)-4-hydroxy-4-methyl-(5,6,7-η)-trideca-1,5-dien-7-yl]tricarbonyliron 12**

Complex **12** was prepared according to the general procedure from methyl ketone complex **3** (0.074 g, 0.21 mmol) using $BF_3{\cdot}OEt_2$ (0.039 cm^3, 0.32 mmol) and allyl tributylstannane **20** (1.106 g, 2.31 mmol) at 0 °C for 3 h. Flash column chromatography (eluent: petrol→Et_2O–petrol 3 : 7; gradient) afforded *alcohol* **12** as a yellow–brown oil (0.070 g, 65%); ν_{max}(film)/cm^{-1} 3389 (OH), 3066, 3032, 2932, 2860, 2080 (CO), 2005 (CO), 1664 (C=O), 1496, 1455, 1374, 1303, 1259, 1208, 1028, 911, 733, 699, 661, 612; δ_H(200 MHz) 0.90 (3H, t, *J* 6.4, 13-H × 3), 1.14–1.64 {11H, m, [including 1.51 (3H, s, 4-Me)], 4-Me, 9-H × 2, 10-H × 2, 11-H × 2, 12-H × 2}, 2.53 (1H, d, *J* 12.9, 3-H × 1), 2.68 (1H, d, *J* 12.9, 3-H × 1), 3.94 (1H, d, *J* 11.4, 5-H), 4.04 (2H, br s, PhCH_2 × 2), 4.16–4.29 (1H, m, 8-H), 4.48–4.64 (3H, m, 7-H, CH_2OBn × 2), 4.64–4.73 (1H, m, 6-H), 5.05 (1H, br s, 1-H × 1), 5.31 (1H, br s, 1-H × 1), 7.26–7.40 (5H, m, Ar-*H*); δ_C(100 MHz) 14.0 (CH_3, 13-C), 22.5 (CH_2), 26.7 (CH_2), 31.0 (CH_3, 4-Me), 31.6 (CH_2), 36.5 (CH_2), 50.8 (CH_2, 3-C), 72.0 (quat. C, 4-C), 73.1 (CH_2), 74.6 (CH), 74.9 (CH_2), 77.1 (CH), 87.5 (CH), 93.4 (CH), 121.5 (CH_2, 1-C), 128.1 (CH), 128.2 (CH), 128.6 (CH), 136.5 (quat. C), 140.5 (quat. C), 203.3 (CO), 206.8 (CO), 207.3

(CO), 209.9 (CO); *m/z* (FAB) 535 [(M + Na)$^+$, 12], 513 (26, MH), 473 (9), 455 (9, M − H − 2CO), 423 (26), 400 (26, M − 4CO), 383 (100, M − 4CO − OH), 293 (6), 276 (11), 239 (11), 217 (29), 149 (16) [Found (MH$^+$) 513.1557. $C_{26}H_{33}O_7Fe$ requires *M*H, 513.1575].

[(5*E*,3*R,4*S**,7*S**,8*R**)-8-(Carbonyloxy-κ*C*)-4-hydroxy-3,4-dimethyl-(5,6,7-η)-trideca-1,5-dien-7-yl]tricarbonyliron 13 and [(5*E*,3*S**,4*S**,7*S**,8*R**)-8-(carbonyloxy-κ*C*)-4-hydroxy-3,4-dimethyl-(5,6,7-η)-trideca-1,5-dien-7-yl]tricarbonyliron 14**

Complexes **13** and **14** were prepared according to the general procedure from methyl ketone complex **3** (0.193 g, 0.55 mmol) using $BF_3{\cdot}OEt_2$ (0.102 cm^3, 0.83 mmol) and (*E*)-crotyltributylstannane **21** (0.530 cm^3, *ca.* 1.65 mmol) at 0 °C for 1.75 h and then at room temperature for a further 2 h. Flash column chromatography (eluent: Et_2O–petrol 3:7→1:1; gradient) afforded a 3:2 mixture of *alcohols* **13** and **14** as a whitish solid (major diastereoisomer unknown) (0.181 g, 81%) (Found: C, 56.09; H, 6.42. $C_{19}H_{26}O_6Fe$ requires C, 56.17; H, 6.45%); ν_{max}(film)/cm^{-1} 3382 (OH), 3057, 2960, 2932, 2861, 2080 (CO), 2003 (CO), 1634 (C=O), 1460, 1421, 1374, 1266, 1154, 1116, 1035, 920, 870, 826, 741, 704, 662, 612; δ_H(500 MHz) 0.87 (3H, t, *J* 6.6, 13-H × 3), 1.14–1.61 {14H, m, [including 1.46 (1.8H, s, 4-Me)], and [including 1.53 (1.2H, s, 4-Me)], 3-Me, 4-Me, 9-H × 2, 10-H × 2, 11-H × 2, 12-H × 2}, 1.92 (0.4H, s, OH), 1.96 (0.6H, s, OH), 2.38–2.48 (1H, m, 3-H), 3.98–4.03 (1H, m, 5-H), 4.21–4.26 (1H, m, 8-H), 4.58–4.62 (1H, m, 7-H), 4.77 (0.4H, dd, *J* 12.4, 8.3, 6-H), 4.85 (0.6H, dd, *J* 12.4, 8.3, 6-H), 5.14–5.19 (2H, m, 1-H × 2), 5.78–5.88 (1H, m, 2-H); δ_C(50 MHz) 13.9 (CH_3, 13-C), 15.5 (CH_3, 3-Me or 4-Me), 22.4 (CH_2), 26.5 (CH_2), [26.6, 26.8, 28.3 (CH_3, 4-Me and 3-Me)], 31.6 (CH_2), 36.6 (CH_2), [51.5, 52.6 (CH, 3-C)], [73.6, 74.1 (quat. C, 4-C)], [74.4, 74.7 (CH)], 77.1 (CH), 87.4 (CH), [92.2, 92.6 (CH)], [117.4, 118.0 (CH_2, 1-C)], [139.0, 139.6 (CH, 2-C)], 203.3 (CO), 206.2 (CO), 206.5 (CO), 207.1 (CO), 209.7 (CO); *m/z* (FAB) 407 (MH$^+$, 45%), 367 (58), 349 (16, M − 2CO − H), 323 (23, MH − 3CO), 293 (22, M − H − 4CO), 277 (44, M − 4CO − O − H), 260 (21, M − 4CO − O − H − OH), 205 (100, M − 4CO − O − OH − Fe), 148 (21), 136 (30) [Found (MH$^+$) 407.1172. $C_{19}H_{27}O_6Fe$ requires *M*H, 407.1157].

[(5*E*,4*R*,7*S*,8*R*,4′*R*)-8-(Carbonyloxy-κ*C*)-4-hydroxy-4-methyl-2-(1′-methylcyclohex-1′-en-4′-yl)-(5,6,7-η)-trideca-1,5-dien-7-yl]tricarbonyliron 15 and [(5*E*,4*S*,7*R*,8*S*,4′*R*)-8-(carbonyloxy-κ*C*)-4-hydroxy-4-methyl-2-(1′-methylcyclohex-1′-en-4′-yl)-(5,6,7-η)-trideca-1,5-dien-7-yl]tricarbonyliron 16

Complexes **15** and **16** were prepared according to the general procedure from methyl ketone complex **3** (0.103 g, 0.29 mmol) using $BF_3{\cdot}OEt_2$ (0.055 cm^3, 0.44 mmol) and allyltrimethylstannane **22** (0.300 cm^3, *ca.* 1.54 mmol) at 0 °C for 2 h. Flash column chromatography (eluent: neat petrol→Et_2O–petrol 1:3; gradient) afforded a 1:1 mixture of *alcohols* **15** and **16** as a yellow–brown oil (0.129 g, 90%) (Found: C, 61.77; H, 7.10. $C_{25}H_{34}O_6Fe$ requires C, 61.71; H, 7.05%); ν_{max}(film)/cm^{-1} 3424 (OH), 2926, 2079 (CO), 2003 (CO), 1642 (C=O), 1454, 1377, 1308, 1199, 1117, 1036, 912, 796, 733, 662; δ_H(500 MHz) 0.88 (3H, t, *J* 6.5, 13-H × 3), 1.16–1.66 {16H, m, [including 1.54 (1.5H, s, 4-Me)], and [including 1.55 (1.5H, s, 4-Me)], and [including 1.65 (3H, s, 1′-Me)], 4-Me, 1′-Me, 9-H × 2, 10-H × 2, 11-H × 2, 12-H × 2, 5′-H × 2}, 1.82–2.26 (5H, m, 3′-H × 2, 6′-H × 2, 4′-H), 2.50 (1H, d, *J* 13.5, 3-H × 1), 2.60 (1H, dd, *J* 13.5, 2.6, 3-H × 1), 4.02 (1H, d, *J* 12.2, 5-H), 4.21–4.25 (1H, m, 8-H), 4.56–4.59 (1H, m, 7-H), 4.76 (0.5H, dd, *J* 12.2, 8.4, 6-H), 4.80 (0.5H, dd, *J* 12.2, 8.4, 6-H), 4.92 (1H, s, 1-H × 1), 5.04–5.05 (1H, m, 1-H × 1), 5.40 (1H, br s, 2′-H); δ_C(100 MHz) 13.9 (CH_3, 13-C), 22.5 (CH_2), 23.4 (CH_3, 1′-Me), 26.9 (CH_2), 27.0 (CH_2), [28.6, 28.9 (CH_2)], [30.6, 30.7 (CH_2)], 30.9 (CH_3, 4-C), 31.0 (CH_2), 31.2 (CH_3, 4-C), [31.5, 31.7 (CH_2)], [40.2, 40.4 (CH, 4′-C)], [50.7, 50.9 (CH_2, 3-C)], [72.4, 72.6 (quat. C, 4-C)], 75.0 (CH), 77.4 (CH), [87.0, 87.1 (CH)], [93.3, 93.4 (CH)], [113.0, 113.3 (CH_2, 1-C)], [120.3, 120.4 (CH, 2′-C)], [133.7, 133.8 (quat. C)], [150.6, 150.8 (quat. C)], 203.4 (CO), 206.7 (CO), 207.2 (CO), 209 (CO); *m/z* (FAB) 509 [(M + Na$^+$), 12%], 487 (100, MH), 459 (9, MH − CO), 447 (12), 429 (11, M − 2CO − H), 402 (9, M − 3CO), 397 (17), 374 (43, M − 4CO), 357 (70, M − 4CO − OH), 285 (55, M − 4CO − O − OH − Fe), 251 (28), 239 (38), 208 (26), 191 (29), 179 (27), 165 (30), 148 (38), 119 (58) [Found (MH$^+$) 487.1779. $C_{25}H_{35}O_6Fe$ requires *M*H, 487.1783].

[(5*E*,4*R,7*S**,8*R**)-8-(Carbonyloxy-κ*C*)-4-hydroxy-4-methyl-(5,6,7-η)-trideca-5-en-7-yl]tricarbonyliron 27**

Method A. Pd (10% on charcoal, 0.038 g) was added to EtOAc (degassed, 8 cm^3) and the reaction vessel then flushed with argon. A solution of alcohol **7** (0.145 g, 0.37 mmol) in EtOAc (2 cm^3) was then added *via* cannula and the reaction mixture stirred at room temperature (25 °C). The reaction vessel was evacuated and fitted with a balloon containing H_2 gas. After 2.5 h, the reaction mixture was filtered through a pad of Celite washing with EtOAc (10 cm^3). Concentration of the filtrate *in vacuo* and purification of the residue by flash column chromatography (eluent: Et_2O–petrol 1:1) afforded *alcohol* **27** as a pale yellow solid (0.137 g, 94%); ν_{max}(film)/cm^{-1} 3450 (OH), 2957, 2927, 2851, 2081, 2006 (CO), 1639 (C=O), 1465, 1378, 1265, 1169, 1120, 1021, 896, 738, 665; δ_H(500 MHz) 0.89 (3H, t, *J* 6.8, 13-H × 3), 1.00 (3H, t, *J* 7.1, 1-H × 3), 1.17–1.80 {15H, m, [including 1.54 (3H, s, 4-Me)], 4-Me, 2-H × 2, 3-H × 2, 9-H × 2, 10-H × 2, 11-H × 2, 12-H × 2}, 2.17 (1H, s, OH), 4.04 (1H, d, *J* 12.4, 5-H), 4.27 (1H, apparent q, *J* 5.8, 8-H), 4.61 (1H, dd, *J* 8.4, 4.6, 7-H), 4.85 (1H, dd, *J* 12.4, 8.4, 6-H); δ_C(50 MHz) 13.8, 14.4, 17.8, 22.4, 26.3, 30.1, 31.5, 36.4, 48.4, 72.6, 74.7, 77.2, 86.9, 93.9, 203.3, 207.0, 207.1, 209.7; *m/z* (FAB) 395 (MH$^+$, 28%), 381 (23), 372 (12), 351 (12), 337 (16, M − H − 2CO), 325 (12), 311 (19, MH − 3CO), 293 (28, MH − 3CO − H_2O), 265 (31, MH − 4CO − H_2O), 249 (26, MH − 4CO − O − H_2O), 231 (20), 219 (24), 207 (26), 193 (100, MH − 4CO − O − Fe − H_2O), 175 (68), 161 (28), 147 (50), 131 (51), 121 (48) [Found (MH$^+$) 395.1154. $C_{18}H_{27}O_6Fe$ requires *M*H, 395.1157].

Method B. $AlPr^n_3$ (0.570 cm^3 of a 1.0 mol dm^{-3} solution in toluene, 0.34 mmol) was added dropwise to a stirred, cooled (−78 °C) solution of methyl ketone complex **3** (0.050 g, 0.14 mmol) in DCM (5 cm^3) and the solution allowed to warm to room temperature over 2 h. Aqueous NH_4Cl (15 drops) was then added to the cooled (0 °C) reaction and the solution stirred vigorously for 10 min. $MgSO_4$ (excess) was added with further vigorous stirring for 10 min. The reaction mixture was then filtered through a pad of Celite washing with DCM (10 cm^3) and toluene (1 cm^3). Concentration of the filtrate *in vacuo* afforded the crude product which was subjected to purification by flash column chromatography (eluent: neat petrol→Et_2O–petrol 7:13; gradient) afforded in order of elution, *alcohol* **27** (0.004 g, 6 %) whose spectroscopic properties were identical to the product obtained by Method A (*vide supra*) and then the reduction product (0.047 g, 93%).[5]

Diethyl (2-oxo-pentyl)phosphonate 28[17]

Bu^nLi (4.14 ml of a 1.6 mol dm^{-3} solution in hexanes, 6.90 mmol) was added dropwise to a stirred solution of diethyl methylphosphonate (1.00 g, 6.57 mmol) in THF (16.0 cm^3) at −78 °C. After 15 min a solution of ethyl butyrate (0.87 cm^3, 6.57 mmol) in THF (1.8 cm^3) was added over 10 min and the reaction mixture left at −78 °C for a further 30 min before removal of the cooling bath and warming to room temperature (25 °C). After 2 h at ambient temperature the reaction mixture was concentrated *in vacuo* and the residue dissolved in H_2O (9 cm^3). The solution was neutralised by dropwise addition of concentrated hydrochloric acid and then extracted with $CHCl_3$ (3 × 3 cm^3). The combined organic extracts were washed with H_2O (2 × 1 cm^3) and dried ($MgSO_4$). Concentration *in vacuo*

afforded a yellow oil from which the remaining solvent and starting material diethyl methylphosphonate were distilled off (30–60 °C, 0.4 mmHg) to afford pure *phosphonate* **28** as a pale yellow oil (0.60 g, 41%); ν_{max}(film)/cm^{-1} 2966, 1715 (C=O), 1445, 1394, 1254, 1164, 1024, 967, 793; δ_H(200 MHz) 0.84 (3H, t, *J* 7.3, 5-H), 1.26 (6H, t, *J* 7.1, 2′-H), 1.54 (2H, apparent sextet, *J* 6.7, 4-H), 2.53 (2H, t, *J* 6.7, 3-H), 3.00 (2H, d, J_{H-P} 23.0, 1-H), 4.00–4.13 (4H, m, 1′-H); δ_C(100 MHz) 13.5 (CH_3, 5-C), 16.3 (CH_3, d, J_{C-P} 6.1, 2′-C), 16.8 (CH_2, 4-C), 42.3 (CH_2, d, J_{C-P} 12.6, 1-C), 45.9 (CH_2, 3-C), 62.5 (CH_2, d, J_{C-P} 6.2, 1′-C), 202.1 (quat. C, d, J_{C-P} 5.9, 2-C); *m*/*z* (FAB) 223 (MH^+, 100%), 195 (15), 179 (8), 167 (53), 149 (12) [Found (MH^+) 223.1083. $C_9H_{20}O_4P$ requires *M*H, 223.1099].

(5*E*,7*R,8*R**)-7,8-Epoxytridec-5-en-4-one 29**

Phosphonate **28** (0.385 g, 1.69 mmol) was added dropwise to a stirred suspension of NaH [0.064 g of 60% dispersion in mineral oil, prewashed with hexane (5 cm^3)] in THF (10 cm^3) at room temperature (25 °C) over 5 min. The resulting colourless solution was stirred at this temperature for a further 15 min before cooling to 0 °C. A solution of (2*S**,3*R**)-2,3-epoxyoctanal[5] (0.200 g, 1.41 mmol) in THF (1 cm^3) was then added in a dropwise fashion over 10 min. After 30 min the reaction mixture was poured into brine (20 cm^3) and the layers separated. The aqueous phase was extracted with Et_2O (3 × 10 cm^3) and the combined organic extracts washed with brine (10 cm^3), and then dried ($MgSO_4$). Concentration *in vacuo* followed by flash column chromatography of the residue (eluent: Et_2O–petrol 1:19→1:9; gradient) afforded *epoxy enone* **29** as a colourless oil (0.243 g, 82%) (Found: C, 74.05; H, 10.66. $C_{13}H_{22}O_2$ requires C, 74.24; H, 10.54%); ν_{max}(film)/cm^{-1} 2959, 2931, 2872, 1698, 1677 (C=O), 1632 (C=C), 1465, 1409, 1376, 1308, 1271, 1237, 1195, 1128, 1040, 977, 916, 875, 735; δ_H(250 MHz) 0.82–0.91 (6H, m, 1-H × 3, 13-H × 3), 1.22–1.66 (10H, m, 2-H × 2, 9-H × 2, 10-H × 2, 11-H × 2, 12-H × 2), 2.47 (2H, t, *J* 7.3, 3-H × 2), 2.84 (1H, td, *J* 5.5, 2.0, 8-H), 3.16 (1H, dd, *J* 6.7, 2.0, 7-H), 6.33 (1H, d, *J* 15.9, 5-H), 6.48 (1H, dd, *J* 15.9, 6.7, 6-H); δ_C(62.5 MHz) 13.7 (CH_3), 13.9 (CH_3), 17.4 (CH_2), 22.5 (CH_2), 25.4 (CH_2), 31.5 (CH_2), 31.8 (CH_2), 42.4 (CH_2), 56.5 (CH), 61.5 (CH), 131.3 (CH), 142.4 (CH), 199.4 (C=O); *m*/*z* (CI) 228 [$(M + NH_4)^+$, 12%], 211 (68, MH), 195 (7, MH − O), 139 [9, $C_5H_{11}CH(O)CHCH{=}CH$], 110 (89), 81 (100), 71 [32, $CH_3(CH_2)_2CO$], 43 (4, $CH_3CH_2CH_2$) [Found (MH^+) 211.1703. $C_{13}H_{23}O_2$ requires *M*H, 211.1698].

[(5*E*,7*S,8*R**)-8-(Carbonyloxy-κ*C*)-4-oxo-(5,6,7-η)-tridec-5-en-7-yl]tricarbonyliron 30 and [(5*E*,7*S**,8*S**)-8-(carbonyloxy-κ*C*)-4-oxo-(5,6,7-η)-tridec-5-en-7-yl]tricarbonyliron 31**

THF (12 cm^3, degassed) was added to $Fe_2(CO)_9$ (0.780 g, 2.14 mmol) and the mixture stirred vigorously at room temperature (25 °C) in the absence of light for 20 min after which time epoxy enone **29** (0.243 g, 1.16 mmol) was added. The resulting solution was vigorously stirred for 3 h and then filtered through a pad of Celite washing with Et_2O (40 cm^3, degassed). Toluene (0.8 cm^3) was added and the solution concentrated *in vacuo* [**CARE:** $Fe(CO)_5$ is a toxic by-product from the reaction—carry out all experimental work in a well ventilated hood]. Purification of the residue by flash column chromatography (eluent: neat petrol→Et_2O–petrol 3:2; gradient) afforded in order of elution, *ketone* **30** as a yellow–brown, viscous oil (0.108 g, 25%); ν_{max}(film)/cm^{-1} 3053, 2959, 2933, 2874, 2088 (CO), 2019 (CO), 1675 (C=O), 1498, 1465, 1405, 1367, 1317, 1268, 1233, 1169, 1127, 1020, 913, 733; δ_H(200 MHz) 0.85–1.02 (6H, m, 1-H × 3, 13-H × 3), 1.29–1.79 (10H, m, 2-H × 2, 9-H × 2, 10-H × 2, 11-H × 2, 12-H × 2), 2.70 (2H, t, *J* 7.2, 3-H × 2), 3.84 (1H, d, *J* 11.2, 5-H), 4.35 (1H, apparent q, *J* 5.8, 8-H), 5.02 (1H, dd, *J* 8.6, 4.4, 7-H), 5.56 (1H, dd, *J* 11.2, 8.6, 6-H); δ_C(50 MHz) 13.6 (CH_3), 13.8 (CH_3), 17.2 (CH_2), 22.3 (CH_2), 26.4 (CH_2), 31.4 (CH_2), 36.5 (CH_2), 45.1 (CH_2), 65.7 (CH), 76.8 (CH), 84.3 (CH), 92.1 (CH), 199.7 (CO), 202.7 (CO), 204.0 (CO), 205.0 (CO), 207.9 (CO); *m*/*z* (FAB) 379 (MH^+, 57%), 351 (6, MH − CO), 295 (13, MH − 3CO), 267 (100, MH − 4CO), 250 (10, M − 4CO − O), 239 (6), 207 (7), 195 (26, MH − 4CO − O − Fe) [Found (MH^+) 379.0881. $C_{17}H_{23}O_6Fe$ requires *M*H, 379.0844]; and then *ketone* **31** as a yellow–brown solid (0.034 g, 8%); ν_{max}(film)/cm^{-1} 3055, 2953, 2933, 2874, 2090 (CO), 2024 (CO), 1666 (C=O), 1495, 1466, 1422, 1378, 1344, 1324, 1304, 1265, 1127, 1043, 1005, 896, 742; δ_H(200 MHz) 0.84–0.99 (6H, m, 1-H × 3, 13-H × 3), 1.29–1.75 (10H, m, 2-H × 2, 9-H × 2, 10-H × 2, 11-H × 2, 12-H × 2), 2.65 (2H, t, *J* 7.3, 3-H × 2), 3.72 (1H, d, *J* 11.0, 5-H), 4.84 (1H, d, *J* 8.3, 7-H), 4.04 (1H, t, *J* 6.6, 8-H), 5.72 (1H, dd, *J* 11.0, 8.3, 6-H); δ_C(50 MHz) 13.7 (CH_3), 13.9 (CH_3), 17.2 (CH_2), 22.4 (CH_2), 25.0 (CH_2), 31.3 (CH_2), 38.0 (CH_2), 45.1 (CH_2), 64.9 (CH), 74.5 (CH), 83.1 (CH), 93.7 (CH), 200.0 (CO), 204.0 (CO × 2), 204.8 (CO), 208.1 (CO); *m*/*z* (FAB) 379 (MH^+, 56%), 351 (8, MH − CO), 295 (37, MH − 3CO), 267 (100, MH − 4CO), 250 (12, M − 4CO − O), 207 (8), 195 (16, MH − 4CO − O − Fe) [Found (MH^+) 379.0880. $C_{17}H_{23}O_6Fe$ requires *M*H, 379.0844].

[(5*E*,4*S,7*S**,8*R**)-8-(Carbonyloxy-κ*C*)-4-hydroxy-4-methyl-(5,6,7-η)-tridec-5-en-7-yl]tricarbonyliron 32**

$AlMe_3$ (0.280 cm^3 of a 2.0 mol dm^{-3} solution in hexanes, 0.56 mmol) was added dropwise to a stirred solution of the ketone **30** (0.108 g, 0.29 mmol) in DCM (2.3 cm^3) at 0 °C. After stirring for 4 h, aqueous NH_4Cl (0.1 cm^3) was added dropwise and the resultant solution stirred for a further 10 min warming to room temperature (25 °C). $MgSO_4$ (excess) was then added followed by further vigorous stirring of the resulting slurry for 15 min. Filtration through a pad of Celite washing the residue with Et_2O (20 cm^3) followed by removal of the volatiles *in vacuo* and flash column chromatography (eluent: Et_2O–petrol 3:10→1:1; gradient) afforded tertiary *alcohol* **32** as a yellow–brown oil (0.025 g, 22%); ν_{max}(film)/cm^{-1} 3415 (OH), 2959, 2931, 2872, 2081 (CO), 2003 (CO), 1640 (C=O), 1468, 1378, 1297, 1266, 1149, 1033, 737, 662, 610; δ_H(500 MHz) 0.88 (3H, t, *J* 6.4, 13-H × 3), 0.99 (3H, t, *J* 6.9, 1-H × 3), 1.16–1.78 {15H, m, [including 1.49 (3H, s, 4-Me)], 2-H × 2, 3-H × 2, 9-H × 2, 10-H × 2, 11-H × 2, 12-H × 2, 4-Me}, 4.10 (1H, d, *J* 12.3, 5-H), 4.26 (1H, apparent q, *J* 5.5, 8-H), 4.60 (1H, dd, *J* 8.2, 4.6, 7-H), 4.89 (1H, dd, *J* 12.3, 8.2, 6-H); δ_C(50 MHz) 13.9, 14.3, 17.6, 22.5, 26.5, 30.0, 31.5, 36.5, 47.7, 73.2, 75.2, 77.3, 86.7, 93.5, 203.7, 206.3, 206.9, 209.6; *m*/*z* (FAB) 395 (MH^+, 46%), 367 (7, MH − CO), 355 (6), 338 (9, M − 2CO), 311 (15, MH − 3CO), 293 (7, MH − 3CO − H_2O), 283 (11, MH − 4CO), 265 (28, MH − 4CO − H_2O), 249 (5, MH − 4CO − H_2O − O), 239 (15), 193 (100, MH − 4CO − O − H_2O − Fe), 123 (19) [Found (MH^+) 395.1188. $C_{18}H_{27}O_6Fe$ requires *M*H, 395.1157].

(2*R*,3*R*)-2,3-Epoxyoctan-1-ol 33

(2*E*)-Oct-2-en-1-ol (12.82 g, 0.100 mol) was treated with D-diethyl tartrate (1.24 g, 6.0 mmol), titanium isopropoxide (1.42 g, 5.0 mmol), 4 Å molecular sieves (3 g) and *tert*-butyl hydroperoxide (67 cm^3 of a 3 mol dm^{-3} solution in 2,2,4-trimethylpentane, 0.200 mol) according to the literature procedure[11] to provide the crude epoxy alcohol **33** as a white solid after purification by flash column chromatography (eluent: Et_2O–petrol 1:2→3:2; gradient) (12.10 g, 84%, 84% ee). Two recrystallisations from petrol at 0 °C yielded enantiomerically enriched epoxy alcohol **33** as a white crystalline solid (7.45 g, 52%, 96% ee); mp 37–38 °C (from petrol) [lit.,[11] 38–39 °C (from petrol)]; $[\alpha]_D^{27}$ +38.6 (*c* 1.00 in $CHCl_3$) {lit.,[11] for enantiomer $[\alpha]_D^{24}$ −42.7 (*c* 4.7 in $CHCl_3$)} (Found: C, 66.56; H, 11.18. $C_8H_{16}O_2$ requires C, 66.63; H, 11.18%); which had identical spectroscopic properties to those reported in the literature.[11] The enantiopurity was determined by formation of the ester from (*S*)-(+)-α-methoxyphenylacetic acid and examination of the ^{1}H NMR spectra.

(2′*R,3′*R**,α*S*)-2,3-Epoxyoctyl α-methoxyphenylacetate**

(*S*)-(+)-α-Methoxyphenylacetyl chloride (prepared from (*S*)-(+)-α-methoxyphenylacetic acid and oxalyl chloride)[18] (0.060 cm^3, *ca*. 0.31 mmol) was added to a solution of the racemic epoxy alcohol **33** (0.040 g, 0.28 mmol) and pyridine (0.035 cm^3, 0.42 mmol) in DCM (1.5 cm^3) at room temperature (25 °C). After 25 min the reaction mixture was poured into aqueous $NaHCO_3$ (20 cm^3) and Et_2O (20 cm^3). The layers were separated. The organic layer was washed with aqueous NH_4Cl (2 × 20 cm^3). The combined organic extracts were washed with brine (10 cm^3) and then dried ($MgSO_4$). After concentration of the filtrate *in vacuo*, the residue was redissolved in DCM (3 cm^3) and filtered through a small plug of Florisil. Removal of the volatiles *in vacuo* afforded the *ester* as a pale yellow oil (0.081 g, quant.; 1:1 mixture of diastereoisomers); ν_{max}(film)/cm^{-1} 2931, 2859, 1754 (C=O), 1494, 1455, 1250, 1174, 1114, 1006, 890, 697; δ_H(500 MHz) 0.88 (3H, t, *J* 6.7, 8-H × 3), 1.21–1.52 (8H, m, 4-H × 2, 5-H × 2, 6-H × 2, 7-H × 2), 2.67 (0.5H, td, *J* 5.6, 1.9, 3-H), 2.73 (0.5H, td, *J* 5.6, 1.9, 3-H), 2.84–2.86 (0.5H, m, 2-H), 2.90–2.92 (0.5H, m, 2-H), 3.41 (3H, s, OMe), 4.02 (1H, dd, *J* 12.1, 5.9, 1-H × 1), 4.34 (0.5H, dd, *J* 12.1, 5.9, 1-H × 1), 4.37 (0.5H, dd, *J* 12.1, 3.4, 1-H × 1), 4.80 [0.5H, s, C*H*(OMe)Ph], 4.80 [0.5H, s, C*H*(OMe)Ph], 7.32–7.45 (5H, m, aryl-H); δ_C(100 MHz) 14.0 (CH_3, 8-C), 22.5 (CH_2), 25.4 (CH_2), 31.4 (CH_2), 31.5 (CH_2), [54.9, 55.1 (CH)], [56.4, 56.5 (CH)], [57.4, 57.4 (CH_3, OMe)], [65.0, 65.3 (CH_2, 1-C)], {82.4, 82.4 [CH, *C*H(OMe)Ph]}, 127.2 (CH), [128.7, 128.8 (CH)], 128.9 (CH), 136.0 (quat. C), 170.5 (C=O); *m*/*z* (EI) 292.5 (M^+, 0.2%), 258 (0.6), 165 (0.2), 143 (0.8), 121 (100, PhCHOMe), 91 (8, C_7H_7), 77 (12, Ph) (Found: M^+, 292.1679. $C_{17}H_{24}O_4$ requires *M*, 292.1674). For comparison the ^{1}H NMR spectrum for the ester **34** prepared from enantiomerically enriched epoxy alcohol (after two recrystallisations), (2′*R*,3′*R*,α*S*)-2,3-epoxyoctyl α-methoxyphenylacetate; δ_H(500 MHz) 0.88 (3H, t, *J* 6.7, 8-H × 3), 1.23–1.43 (6H, m, 5-H × 2, 6-H × 2, 7-H × 2), 1.46–1.50 (2H, m, 4-H × 2), 2.67 (1H, td, *J* 5.6, 1.9, 3-H), 2.90–2.92 (1H, m, 2-H), 3.41 (3H, s, OMe), 4.02 (1H, dd, *J* 12.1, 5.9, 1-H × 1), 4.37 (1H, dd, *J* 12.1, 3.4, 1-H × 1), 4.80 [1H, s, C*H*(OMe)Ph], 7.32–7.45 (5H, m, aryl-H). From the ^{1}H NMR spectra of the crude product the ee of the starting alcohol was determined to be 96%.

(2*S*,3*R*)-2,3-Epoxyoctanal 35

Dimethyl sulfoxide (3.84 cm^3, 0.055 mol) in DCM (27 cm^3) was added dropwise to a cooled (−78 °C) solution of oxalyl chloride (2.37 cm^3, 0.027 mol) in DCM (27 cm^3) over a period of 30 min. After 1 h, a solution of the epoxy acohol **33** (3.00 g, 0.021 mol) in DCM (22 cm^3) was added dropwise over 30 min and stirring at −78 °C continued for a further 1.5 h. Et_3N (10.17 cm^3, 0.074 mol) was then added dropwise over 10 min and the solution left at −78 °C for 30 min before the reaction mixture was allowed to warm to room temperature. After 1 h at 25 °C, the reaction mixture was poured into H_2O (100 cm^3) and the layers separated. The aqueous layer was then extracted with DCM (2 × 50 cm^3) and the combined organic fractions dried ($MgSO_4$). Filtration and evaporation of the solvent *in vacuo* afforded the crude aldehyde which was subjected to purification by flash column chromatography [eluent: Et_2O–petrol (30–40 °C boiling point fraction] 1:19→3:17; gradient) to afford aldehyde **35** as a colourless liquid (2.25 g, 76%) which had identical spectroscopic properties to those reported in the literature.[9] $[\alpha]_D^{27}$ −9.4 (*c* 1.00 in $CHCl_3$).

(3*E*,5*R*,6*R*)-5,6-Epoxyundec-3-en-2-one 36

Epoxy enone **36** was prepared according to the procedure described for the preparation of enone **29** (*vide supra*) using NaH (0.480 g of a 60% dispersion in mineral oil, 12.0 mmol), diethyl (2-oxopropyl)phosphonate (2.52 cm^3, 13.1 mmol) and epoxy aldehyde **35** (1.55 g, 10.9 mmol). Purification of the crude product by flash column chromatography (eluent: Et_2O–petrol 1:19→1:9; gradient) afforded epoxy enone **36** as a colourless liquid (1.48 g, 74%) which had identical spectroscopic properties to those reported in the literature.[5] $[\alpha]_D^{27}$ +27.1 (*c* 1.00 in $CHCl_3$).

[(3*E*,5*S*,6*R*)-6-(Carbonyloxy-κ*C*)-2-oxo-(3,4,5-η)-undec-3-en-5-yl]tricarbonyliron 37 and [(3*E*,5*R*,6*R*)-6-(carbonyloxy-κ*C*)-2-oxo-(3,4,5-η)-undec-3-en-5-yl]tricarbonyliron 38

Treatment of epoxy enone **36** (1.20 g, 6.60 mmol) with $Fe_2(CO)_9$ (5.00 g, 17.6 mmol) in THF (70 cm^3) according to the procedure described for the preparation of complexes **30** and **31** (*vide supra*) afforded *endo* complex **37** as an orange–brown solid (0.97 g, 42%) which had identical spectroscopic properties to those reported in the literature.[5] $[\alpha]_D^{26}$ +410.4 (*c* 1.00 in $CHCl_3$); and then *exo* complex **38** as an orange–brown solid (0.30 g, 13%) which had identical spectroscopic properties to those reported in the literature.[5] $[\alpha]_D^{26}$ +410.4 (*c* 1.00 in $CHCl_3$).

[(5*E*,4*R*,4′*R*,7*S*,8*R*)-8-(Carbonyloxy-κ*C*)-4-hydroxy-4-methyl-2-(1′-methylcyclohex-1′-en-4′-yl)-(5,6,7-η)-trideca-1,5-dien-7-yl]tricarbonyliron 15

Complex **15** was prepared according to the general procedure from enantiomerically enriched methyl ketone complex **37** (0.068 g, 0.19 mmol) using $BF_3{\cdot}OEt_2$ (0.037 cm^3, 0.30 mmol) and allyltrimethylstannane **22** (0.200 cm^3, *ca*. 1.03 mmol) at 0 °C for 1.5 h. Flash column chromatography (eluent: Et_2O–petrol 1:9→1:3; gradient) afforded alcohol complex **15** as a pale yellow solid (0.091 g, 96%) which was matched with one of the diastereoisomers produced from the reaction of stannane **22** with racemic methyl ketone **3** (*vide supra*); $[\alpha]_D^{27}$ −102.7 (*c* 1.00 in $CHCl_3$); δ_H(200 MHz) 0.88 (3H, t, *J* 6.5, 13-H × 3), 1.16–1.66 {16H, m, [including 1.55 (3H, s, 4-Me)], and [including 1.65 (3H, s, 1′-Me)], 9-H × 2, 10-H × 2, 11-H × 2, 12-H × 2, 5′-H × 2, 1′-Me, 4-Me}, 1.82–2.26 (5H, m, 3′-H × 2, 6′-H × 2, 4′-H), 2.50 (1H, d, *J* 13.5, 3-H × 1), 2.60 (1H, dd, *J* 13.5, 2.6, 3-H × 1), 4.02 (1H, d, *J* 12.2, 5-H), 4.22 (1H, apparent q, *J* 5.7, 8-H), 4.57 (1H, dd, *J* 8.4, 4.5, 7-H), 4.76 (1H, dd, *J* 12.2, 8.4, 6-H), 4.91 (1H, s, 1-H × 1), 5.05 (1H, s, 1-H × 1), 5.40 (1H, br s, 2′-H).

[(6*Z*,4*R*,4′*R*,5*S*,8*S*)-4-Hydroxy-4-methyl-2-(1′-methylcyclohex-1′-en-4′-yl)-(5,6,7,8-η)-trideca-1,6-dien-5,8-diyl]tricarbonyliron 39

Saturated aqueous $Ba(OH)_2$ (0.50 cm^3) was added to a stirred solution of alcohol **15** (0.090 g, 0.19 mmol) in MeOH (1.5 cm^3). After 10 min, Et_2O (5 cm^3) and H_2O (5 cm^3) were added. The layers were separated and the aqueous phase extracted with Et_2O (3 × 10 cm^3). The combined organic phases were washed with brine (10 cm^3) and then dried ($MgSO_4$). Concentration *in vacuo* followed by purification by flash column chromatography (eluent: Et_2O–petrol 3:97) afforded *diene complex* **39** as a bright, yellow oil (0.062 g, 75%); $[\alpha]_D^{27}$ +28.4 (*c* 1.00 in $CHCl_3$) (Found: C, 65.25; H, 7.73. $C_{24}H_{34}O_4Fe$ requires C, 65.16; H, 7.75%); ν_{max}(film)/cm^{-1} 3551 (OH), 3079, 2960, 2925, 2855, 2039 (CO), 1962 (CO), 1636 (C=C), 1453, 1375, 1222, 1195, 1156, 1048, 1019, 962, 899, 814, 797; δ_H(500 MHz) 0.89 (3H, t, *J* 6.9, 13-H × 3), 0.93 (1H, apparent q, *J* 7.7, 8-H), 1.04 (1H, d, *J* 8.9, 5-H), 1.20–1.47 (11H, m, [including 1.32 (3H, s, 4-Me)], 5′-H × 2, 10-H × 2, 11-H × 2, 12-H × 2, 4-Me), 1.51–1.58 (1H, m, 9-H × 1), 1.64–1.72 {5H, m, [including 1.64 (3H, s, 1′-Me)], and [including 1.66 (1H, s, OH)], 9-H × 1, 1′-Me, OH}, 1.79–1.83 (2H, m, 3′-H × 1, 6′-H × 1), 1.93–1.97 (1H, m, 6′-H × 1), 2.08–2.18 (2H, m, 3′-H × 1, 4′-H), 2.32 (2H, s, 3-H × 2), 4.83 (1H, s, 1-H × 1), 4.96 (1H, s, 1-H × 1), 5.00 (1H, dd, *J* 8.7, 5.1, 7-H), 5.26 (1H, dd, *J* 8.9, 5.1, 6-H), 5.39 (1H, br s, 2′-H); δ_C(62.5 MHz) 14.0 (CH_3, 13-C), 22.5 (CH_2), 23.4 (CH_3, 1′-Me), 28.4 (CH_2), 30.7 (CH_2), 31.4 (CH_2), 31.8 (CH_3, 4-Me), 31.8 (CH_2 × 2), 34.1 (CH_2), 40.6 (CH, 4′-C), 50.6 (CH_2, 3-C), 63.8 (CH), 72.3 (quat. C, 4-C), 74.5 (CH), 79.7 (CH), 82.4 (CH), 112.1 (CH_2, 1-C), 120.5 (CH, 2′-C), 133.7 (quat. C),

151.4 (quat. C), no visible signals for CO ligands; *m/z* (FAB) 425 [(M − OH^+), 20%], 414 (7, M − CO), 386 (15, M − 2CO), 358 (100, M − 3CO), 341 (56, M − 3CO − OH), 285 (14, M − 3CO − OH − Fe), 251 (7), 241 (8), 221 (13), 207 (10), 189 (12), 173 (13), 147 (33) {Found [(M − 3CO)$^+$] 358.1946. $C_{21}H_{34}OFe$ requires *M* − 3CO, 358.1959}.

[(6*Z*,4*R*,4′*R*,5*S*,8*S*)-4-Hydroxy-4-methyl-2-(1′-methylcyclohex-1′-en-4′-yl)-(5,6,7,8-η)-trideca-1,6-dien-5,8-diyl]tricarbonyliron 39 and [(6*Z*,4*S*,4′*R*,5*R*,8*R*)-4-hydroxy-4-methyl-2-(1′-methylcyclohex-1′-en-4′-yl)-(5,6,7,8-η)-trideca-1,6-dien-5,8-diyl]tricarbonyliron 41

Saturated aqueous $Ba(OH)_2$ (0.45 cm^3) was added to a stirred solution of alcohol complexes **39** and **41** (0.070 g, 0.18 mmol) in MeOH (1.5 cm^3). After 10 min, Et_2O (5 cm^3) and H_2O (5 cm^3) were added. The layers were separated and the aqueous phase extracted with Et_2O (3 × 10 cm^3). The combined organic phases were washed with brine (10 cm^3) and then dried ($MgSO_4$). Concentration *in vacuo* followed by purification by flash column chromatography (eluent: Et_2O–petrol 3:97) afforded a 1:1 mixture of diastereoisomeric diene complexes **39** and **41** as a bright yellow oil (0.040 g, 64%); (*vide supra* for a comparison of spectroscopic data) δ_H(500 MHz) 0.89 (3H, t, *J* 6.9, 13-H × 3), 0.93 (1H, apparent q, *J* 7.7, 8-H), 1.04 (0.5H, d; 0.5H, d overlapping creating apparent t, *J* 7.8, 5-H), 1.20–1.44 {11H, m, [including 1.32 (3H, s, 4-Me)], 5′-H × 2, 10-H × 2, 11-H × 2, 12-H × 2, 4-Me}, 1.47–1.59 (1H, m, 9-H × 1), 1.64–1.70 {4H, m, [including 1.64 (3H, s, 1′-Me)], 9-H × 1, 1′-Me}, 1.82–2.15 (5H, m, 3′-H × 2, 4′-H × 1, 6′-H × 2), 2.32 (2H, s, 3-H × 2), 4.83 (1H, s, 1-H × 1), 4.97 (1H, s, 1-H × 1), 4.99 (0.5H, m, 7-H), 5.01 (0.5H, m, 7-H), 5.23 (0.5H, dd, *J* 8.9, 5.1, 6-H), 5.26 (0.5H, dd, *J* 9.0, 5.1, 6-H), 5.39 (1H, br s, 2′-H); δ_C(62.5 MHz) 14.0 (CH_3, 13-C), 22.5 (CH_2), 23.4 (CH_3, 1′-Me), [28.4, 28.5 (CH_2)], [30.7, 30.8 (CH_2)], 31.4 (CH_2), 31.8 (CH_3, 4-Me), [31.8, 31.8 (CH_2)], 31.8 (CH_2), 34.1 (CH_2), [40.6, 40.8 (CH, 4′-C)], [50.6, 50.6 (CH_2, 3-C)], 63.8 (CH), [72.1, 72.3 (quat. C, 4-C)], [74.5, 74.6 (CH)], [79.6, 79.7 (CH)], [82.3, 82.4 (CH)], [112.0, 112.1 (CH_2, 1-C)], [120.5, 120.6 (CH, 2′-C)], [133.7, 133.7 (quat. C)], [151.4, 151.5 (quat. C)], no visible signals for CO ligands.

Preparation of an NaOH–H_2O_2 solution

H_2O_2 (9 cm^3 of a 30% aqueous solution) was added to a stirred solution of NaOH (0.45 g, 11 mmol) in MeOH (15 cm^3) at 0 °C. The solution was used immediately.

(5*E*,7*E*,4*R*,4′*R*)-4-Hydroxy-4-methyl-2-(1′-methylcyclohex-1′-en-4′-yl)-trideca-1,5,7-triene 40

A solution of diene complex **39** (0.044 g, 0.10 mmol) in MeOH (0.5 cm^3) at 0 °C was treated with NaOH–H_2O_2 solution (*vide supra*) (8 cm^3). After 1 h at 0 °C, H_2O (10 cm^3) and Et_2O (10 cm^3) were added and the layers were separated. The aqueous phase was extracted with Et_2O (3 × 10 cm^3) and the combined organic extracts washed sequentially with NH_4Cl solution (10 cm^3) and brine (10 cm^3) and then dried ($MgSO_4$). Concentration *in vacuo* followed by purification by flash column chromatography (eluent: Et_2O–petrol 1:19) afforded *tetraene* **40** as a colourless oil (0.030 g, 92%). $[\alpha]_D^{27}$ + 44.6 (*c* 1.00 in $CHCl_3$); ν_{max}(film)/cm^{-1} 3422 (OH), 3078, 3016, 2959, 2923, 2855, 1721, 1637 (C=C), 1453, 1376, 1309, 1226, 1156, 1112, 1080, 1019, 990, 938, 894, 797, 759, 732; δ_H(500 MHz) 0.89 (3H, t, *J* 6.9, 13-H × 3), 1.26–1.42 {11H, m, [including 1.30 (3H, s, 4-Me)], 10-H × 2, 11-H × 2, 12-H × 2, 5′-H × 2, 4-Me}, 1.63 (3H, s, 1′-Me), 1.81–2.10 (7H, m, 6′-H × 2, 3′-H × 2, 4′-H, 9-H × 2), 2.30 (1H, d, *J* 13.5, 3-H × 1), 2.38 (1H, d, *J* 13.5, 3-H × 1), 4.88 (1H, s, 1-H × 1), 4.93 (1H, s, 1-H × 1), 5.37 (1H, br s, 2′-H), 5.63–5.69 {2H, m, [including 5.65 (d, *J* 15.2, 5-H)], 5-H, 8-H}, 6.00 (1H, dd, *J* 15.1, 10.7, 7-H), 6.17 (1H, dd, *J* 15.2, 10.7, 6-H); δ_C(62.5 MHz) 14.1 (CH_3, 13-C), 22.5 (CH_2), 23.4 (CH_3, 1′-Me), 28.4 (CH_3, 4-Me), 28.8 (CH_2), 29.0 (CH_2), 30.7 (CH_2), 31.1 (CH_2), 31.4 (CH_2), 32.6 (CH_2), 40.3 (CH, 4′-C), 48.5 (CH_2, 3-C), 72.0 (quat. C, 4-C), 111.9 (CH_2, 1-C), 120.7 (CH), 127.4 (CH), 129.5 (CH), 133.5 (quat. C), 134.8 (CH), 137.7 (CH), 151.1 (quat. C); *m/z* (electrospray) 325 [(M + Na^+), 100%], 285 (32, MH − H_2O) [Found (M + Na^+) 325.2493. $C_{21}H_{34}NaO$ requires *M* + Na, 325.2507].

(5*E*,7*E*,4*R*,4′*R*)-4-Hydroxy-4-methyl-2-(1′-methylcyclohex-1′-en-4′-yl)-trideca-1,5,7-triene 40 and (5*E*,7*E*,4*S*,4′*R*)-4-hydroxy-4-methyl-2-(1′-methylcyclohex-1′-en-4′-yl)-trideca-1,5,7-triene 42

Treatment of complexes **39** and **41** (1:1, 0.040 g, 0.09 mmol) with H_2O_2–NaOH (6.0 cm^3) in MeOH (0.5 cm^3) at 0 °C afforded diastereoisomeric dienyl tertiary alcohols **40** and **42** (1:1, 0.027 g, 95%) as a colourless oil which had similar spectroscopic data as for the diastereoisomerically pure alcohol **40** (*vide supra*) apart from the following differences; δ_H(500 MHz) as for **40** except 1.56 (1H, s, OH), 1.74–2.10 {8H, m, [including 1.88 (1H, s, OH)], 6′-H × 2, 3′-H × 1.5, 4′-H × 1, 9-H × 2, OH}, 2.16 (0.5H, br d, *J* 16.5, 3′-H × 0.5), 2.29 (1H, dd, *J* 13.5, 4.4, 3-H × 1), 4.87 (1H, d, *J* 3.8, 1-H × 1); δ_C(62.5 MHz) 14.0 (CH_3, 13-C), 22.5 (CH_2), [23.4, 23.4 (CH_3, 1′-Me)], 28.2 (CH_2), [28.4, 28.5 (CH_3, 4-Me)], [28.8, 29.0 (CH_2)], [30.7, 30.8 (CH_2)], [31.2, 31.4 (CH_2)], 32.3 (CH_2), 32.6 (CH_2), [40.3, 40.4 (CH, 4′-C)], [48.5, 48.8 (CH_2, 3-C)], [71.8, 72.0 (quat. C, 4-C)], 111.9 (CH_2, 1-C), [120.6, 120.7 (CH)], [127.3, 127.4 (CH)], [129.5, 129.5 (CH)], [133.5, 133.9 (quat. C)], [134.7, 134.8 (CH)], 137.7 (CH), [151.1, 151.7 (quat. C)].

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