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Reductive decomplexation of π-allyltricarbonyliron lactone complexes using sodium naphthalenide as a route to stereodefined 1,7-diols and 2,3-diene-1,7-diols

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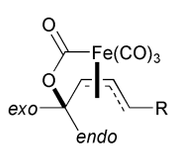
Received 19th June 2003, Accepted 28th July 2003
First published as an Advance Article on the web 13th August 2003

Treatment of π-allyltricarbonyliron lactone complexes, that contain an adjacent leaving group, with lithium naphthalenide causes decomplexation to acyclic dienols in excellent yield and without any stereochemical scrambling of the allylic centre. When an *endo* complex is employed (*E*,*E*)-geometry prevails with good selectivity whereas (*Z*,*E*)-geometry dominates in the case of *exo* complexes. A mechanism consistent with the observed stereo- and regiochemistry is proposed.

Introduction

Organometallic complexes are important templates for organic synthesis programmes.[1] In particular π-allyltricarbonyliron lactone complexes **1** (Fig. 1) are especially useful as they undergo a wide range of chemical transformations. The stability of these compounds compares favourably with the related η[4]-dienetricarbonyliron complexes but their real advantage lies in the greater selectivities achieved in stereocontrolled reactions and the extent of synthetically useful processes available for removal of the metal template.[2]



1

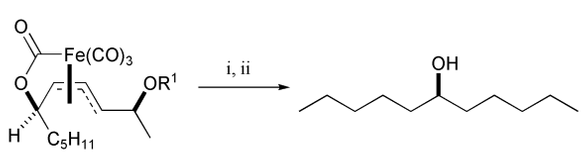
Fig. 1 General structure of π-allyltricarbonyliron lactone complexes.

To date four main methods have been reported for this decomplexation; barium hydroxide mediated decarboxylation followed by oxidative release of the organic ligand affords (*E*,*E*)-dienes;[3] exhaustive carbonylation gives δ-lactones;[3] single electron oxidation gives rise to δ- or β-lactones[4] and borohydride reagents provide enediols.[5] All of these methods have been employed successfully by our group in the synthesis of natural products and bioactive materials.[2,6]

New and selective methods for detaching the iron carbonyl unit leading to functionalised products would also be useful in other synthesis programmes. Furthermore, the mechanistic knowledge derived could aid in the design of new complexes for future applications. In addition the observation that highly selective hydride, alkyl and allyl additions to ketones adjacent to the allyl system in the complexes and that Mukaiyama aldol reactions of appended silyl enol ethers, allow access to polyol fragments in the periphery of the organic ligand, enhances these programmes considerably.[7–10] Here we report in full, a new method of detachment that leads to dienols and eventually stereodefined alcohols.[11]

Results and discussion

The known iron lactone complex **2a**[5] was chosen as the initial starting material for this search for a new decomplexation method. By screening of a number of reagents we found that lithium dimethylcuprate caused the stereo-controlled removal of the iron unit. Thus treatment of the complex with the reagent at −78 °C in THF for 12 hours followed by warming to room temperature afforded a mixture of dienes which had apparently formed *via* elimination of the appended hydroxyl group rather than the anticipated decarboxylation of the lactone tether. Hydrogenation of this mixture produced the symmetrical molecule undecan-6-ol **3**, which also confirms the regio-chemistry of the reductive process (Scheme 1).



2a R^1 = H
2b R^1 = Ac

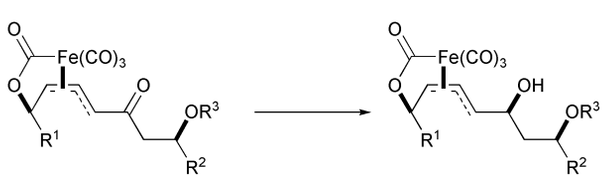
3

Scheme 1 *Reagents and conditions:* For **2a** (i) $LiCuMe_2$, THF −78 °C to rt; (ii) H_2, Pd/C, EtOAc, 78%. For **2b** (i) Lithium naphthalenide, THF −78 °C to rt; (ii) H_2, Pd/C, EtOAc, 92%.

On consideration of a possible mechanism for this cuprate decomplexation reaction it seemed that the cuprate was acting as a single electron reductant and that the iron by-product was most likely to be dilithium tetracarbonylferrate [$Li_2Fe(CO)_4$], the analogous sodium salt being well known in the literature.[12] Four electron equivalents would be required mechanistically if this were the case and indeed, the observation that at least four equivalents were necessary to complete the conversion supported this conclusion. In order to optimise this process further we concentrated on two main ideas. Firstly, a better leaving group than an appended alcohol would be sensible. Secondly, if a copper species was binding to the hydroxyl group and correspondingly aiding its ability to leave, a stronger single electron reductant may be more appropriate. Accordingly we investigated the use of lithium naphthalenide as the reductant. Moreover, as iron complexes bearing acetates are readily prepared from the corresponding alcohols, in high yield, we examined these as suitable precursors as they contain an improved leaving group. Therefore, lactone complex **2b** was prepared and treated with lithium naphthalenide in THF at −78 °C for 12 hours followed by warming to room temperature. Hydrogenation of the product afforded undecan-6-ol **3** as before but in a much improved 92% yield (Scheme 1).

DOI: 10.1039/b306861g

Lithium naphthalenide was therefore established as the method of choice for the reduction process. Next a range of substrates were prepared following methods developed by our group giving access to 1,3-dihydroxy functionality adjacent to the iron moiety.[7–10] It was thought that these complexes would provide interesting substrates to investigate the lithium naphthalenide decomplexation technique as the stereogenic centres would be retained either side of the diene formed. Their preparation involves a Mukaiyama aldol reaction followed by reduction of the carbonyl group to afford the 1,3 diol feature. Whilst this reduction with a protected β-hydroxyl group was known from our previous work using alkyl aluminium hydride transfer reagents,[10] when a free hydroxyl was present, the reaction failed. As this was an important feature, an alternative reduction method was sought. Since borohydride reagents, most notably sodium triacetoxyborohydride, could be employed to decomplex these iron carbonyl complexes at room temperature over 2–3 days[9c] it was thought that there was scope to use these reagents at lower temperature. Thus treatment with sodium borohydride of the iron carbonyl complexes bearing ketone groups in the side chain proceeded in high yield and excellent diastereoselectivity at −78 °C. In these reactions it was necessary to quench well before room temperature to avoid any decomplexation. This method worked well for ketones with an unprotected β-hydroxyl but was low yielding when the hydroxyl was protected. The method therefore proved to be complimentary to the previously reported hydride transfer method (Scheme 2).



Reactant				Product	Yield
4a $R^1 = C_5H_{11}$	$R^2 = C_5H_{11}$	$R^3 = H$	i	**6a**	84%
4b $R^1 = C_5H_{11}$	$R^2 = i$-Pr	$R^3 = H$	i	**6b**	83%
4c $R^1 = C_5H_{11}$	$R^2 = c$-Hex	$R^3 = H$	i	**6c**	81%
4d $R^1 = C_5H_{11}$	$R^2 = Ph$	$R^3 = H$	i	**6d**	87%
5 $R^1 = Ph$	$R^2 = i$-Pr	$R^3 = TBS$	ii	**6e**	62%

Scheme 2 *Reagents and conditions:* (i) $NaBH_4$ (10 eq.), MeOH–CH_2Cl_2 (1 : 1), −78 °C, quenched with precooled (−78 °C) AcOH–THF; (ii) Al(*i*-Bu)$_3$, C_6H_6, 0 °C.

Using these methods, a range of 1,3-dihydroxy iron complexes were prepared in order to investigate the new decomplexation protocol (Table 1).

In all cases it was necessary to protect the outer hydroxyl group prior to formation of the required acetate adjacent to the iron moiety. In the simplest cases **8a**–**9b**, the acetoxy compounds were prepared under standard conditions and in excellent yield. Silicon based protecting groups were used to selectively protect the outer hydroxyl in other examples. The internal hydroxyl group was then converted to a mesylate **10** or an acetate as in **11a** or *via* one-pot procedure to give **11b**. Finally cyclic carbonate compounds were prepared using 1,1-carbonyl diimidazole [CDI] **12a**–**c**, although only one of these, **12a**, was subsequently subjected to the decomplexation conditions. These compounds were prepared for two reasons: firstly, they would provide an alternative substrate where orthogonal protection of the 1,7-dihydroxy decomplexation product was not required and secondly, it was thought that the greater rigidity of the system may increase selectivity for one diene geometry in the product formation.

Once all these substrates were in hand, they were subjected to the reductive decomplexation conditions and the product diene mixtures were futher hydrogenated to afford saturated 1,7-alkanediols (Table 1). Where the leaving group was an acetate **8a**–**9b** the reaction proceeded smoothly and in excellent overall yield to give **16a**–**19b**. It was also possible to use an alternative procedure for the diacetate precursors **8a**,**b**. Namely, using an excess of lithium naphthalenide followed by a methanol work-up led to hydrolysis of the remaining acetate to furnish unprotected diols **16a**,**b** in good yield. When a mesylate was used in place of an acetate group **10** the reaction yielded no isolable product on a 0.15 mmol scale. The cyclic carbonate **12a** underwent the same elimination with the loss of CO_2 to give an unprotected 1,7-alkanediol **16b**.

From a detailed analysis of the ^{1}H 600 MHz NMR spectra of the isolated mixtures of dienes from decomplexations carried out with lithium naphthalenide, three components were identified. Calculation of the coupling constants indicated that these three components were (2*E*,4*E*), (2*Z*,4*E*), (2*E*,4*Z*) in all cases where the allylic alcohol is 1-C (Fig. 2). These mixtures represented almost total mass recovery (92–98% yield) and therefore their NMR spectra could be viewed as reasonably accurate representations of the reaction's selectivity. In total six examples were studied. In the case of *endo* complexes with acetate leaving groups **8b**–**9a**,**11a** the main component was found to be (2*E*,4*E*) **13a**–**d** with approximately equal amounts of (2*Z*,4*E*) **14a**–**d** and (2*E*,4*Z*) **15a**–**d**. For cyclic carbonates it had been hoped that the increased conformational strain would result in greater diastereoselectivity. Indeed this was the case, no (2*E*,4*Z*) **15e** isomer was observed and the yield of the other two components increased **13e**,**14e**. When an *exo* iron lactone complex was employed **9b** the major product switched from (2*E*,4*E*) **13c** to (2*Z*,4*E*) **14c**. Three components were still present with the minor two being the same geometry as previously observed.

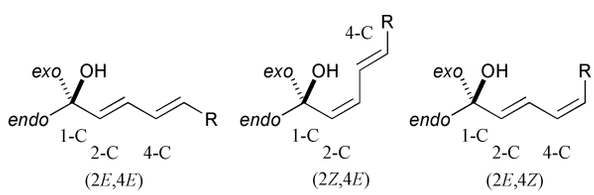
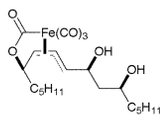
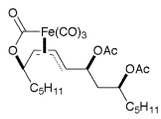
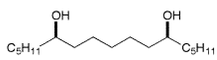
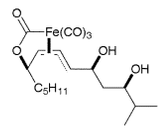
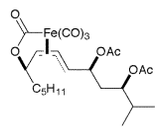
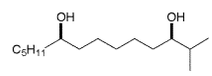
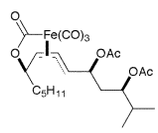
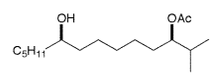


Fig. 2 Diene geometries recorded after demetallation.

Before any mechanism could be proposed it was important to establish that the allylic centre had not been epimerised as had been observed with some reagents that were screened in the development of the $NaBH(OAc)_3$ decomplexation method. It was thought that ^{1}H NMR analysis of 1,7-alkane diols would not reveal if any epimerisation had occurred as the stereogenic centres were distant from one another. Complex **9a** with a more proximal stereogenic centre was prepared and subjected to decomplexation with lithium naphthalenide and alkene hydrogenation. No loss in stereochemical integrity was observed as determined by ^{1}H 600 MHz NMR spectra of **18**. The epimeric *exo* complex **9b** was also submitted to the decomplexation conditions and again no epimerisation was observed.

In terms of a mechanistic rational, addition of two electrons to an iron lactone complex could result in the 18 electron σ-bonded intermediate **20** (Scheme 3). Complexes of this nature have been cited in other mechanisms for the reaction of these complexes.[5b] If the leaving group aligns itself with the π-system of the olefin, which in turn retains its *E*-configuration, then four possible conformations can be proposed for the elimination: s-*cis*, s-*cis* with the leaving group *anti*-periplanar to the Fe–C bond **21a**, s-*cis*, s-*trans* with the leaving group *syn*-periplanar to the Fe–C bond **21b**, s-*trans*, s-*trans* with the leaving group *anti*-periplanar to the Fe–C bond **21c** and finally s-*trans*, s-*cis* with the leaving group *syn*-periplanar to the Fe–C bond **21d**. There appear to be two areas where significant steric clash can occur: firstly between the *endo* substituent on the iron complex and the allylic-acetate when the bond nearest the ferrate species is s-*cis*, **21a** and **21b**, and secondly between the carbonyl ligands and the allylic-acetate when the bond nearest the ferrate

Table 1 *Reagents and conditions:* (a) Ac_2O, DMAP, NEt_3, CH_2Cl_2, 0 °C; (b) (i) TBSOTf, NEt_3, CH_2Cl_2, 0 °C; (ii) MsCl, NEt_3, CH_2Cl_2, 0 °C; (c) (i) TBSOTf, NEt_3, CH_2Cl_2, 0 °C; (ii) Ac_2O, DMAP, NEt_3, CH_2Cl_2, 0 °C; (d) TBSOTf, NEt_3, CH_2Cl_2, 0 °C then Ac_2O, DMAP; (e) CDI, DMAP, CH_2Cl_2; (f) (i) Li naphthalenide (10 eq.), THF, −78 °C to rt, MeOH; (ii) H_2, Pd/C, EtOAc; (g) (i) Li naphthalenide (5 eq.), THF, −78 °C to rt; (ii) H_2, Pd/C, EtOAc

Alcohol	Protection procedure	Protected product	Yield	Decomplexation procedure	Diene geometry [b,c] (*E*,*E*) : (*Z*,*E*) : (*E*,*Z*)	Decomplexed product	Yield [d]
6a 	a	**8a** 	96	f		**16a** 	81
6b 	a	**8b** 	93	f		**16b** 	83
		8b 		g	0.70 : 0.17 : 0.13	**17a** 	93
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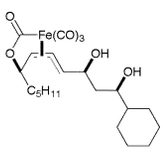
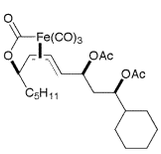
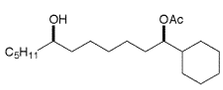
6c 	a	**8c** 	91	g	0.53 : 0.19 : 0.28	**17b** 	91
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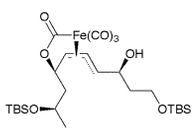
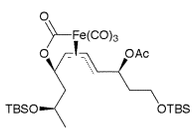
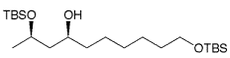
7a 	a	**9a** 	97	g	0.62 : 0.15 : 0.23	**18** 	96
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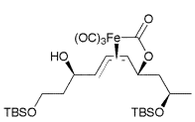
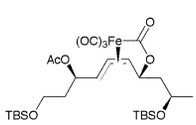
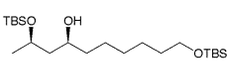
7b 	a	**9b** 	95	g	0.26 : 0.67 : 0.07	**18** 	96
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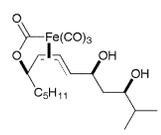
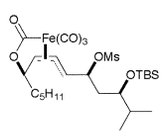
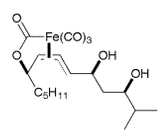
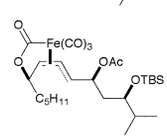
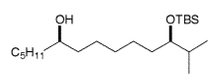
6b 	b	**10** 	66 [a]	g		No isolable product	
6b 	c	**11a** 	75 [a]	g	0.62 : 0.20 : 0.18	**19a** 	95
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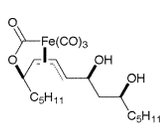
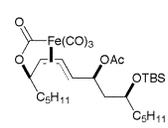
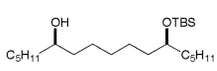
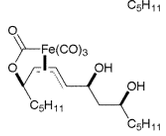
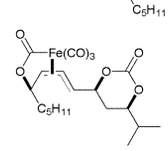
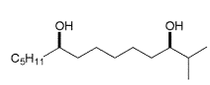
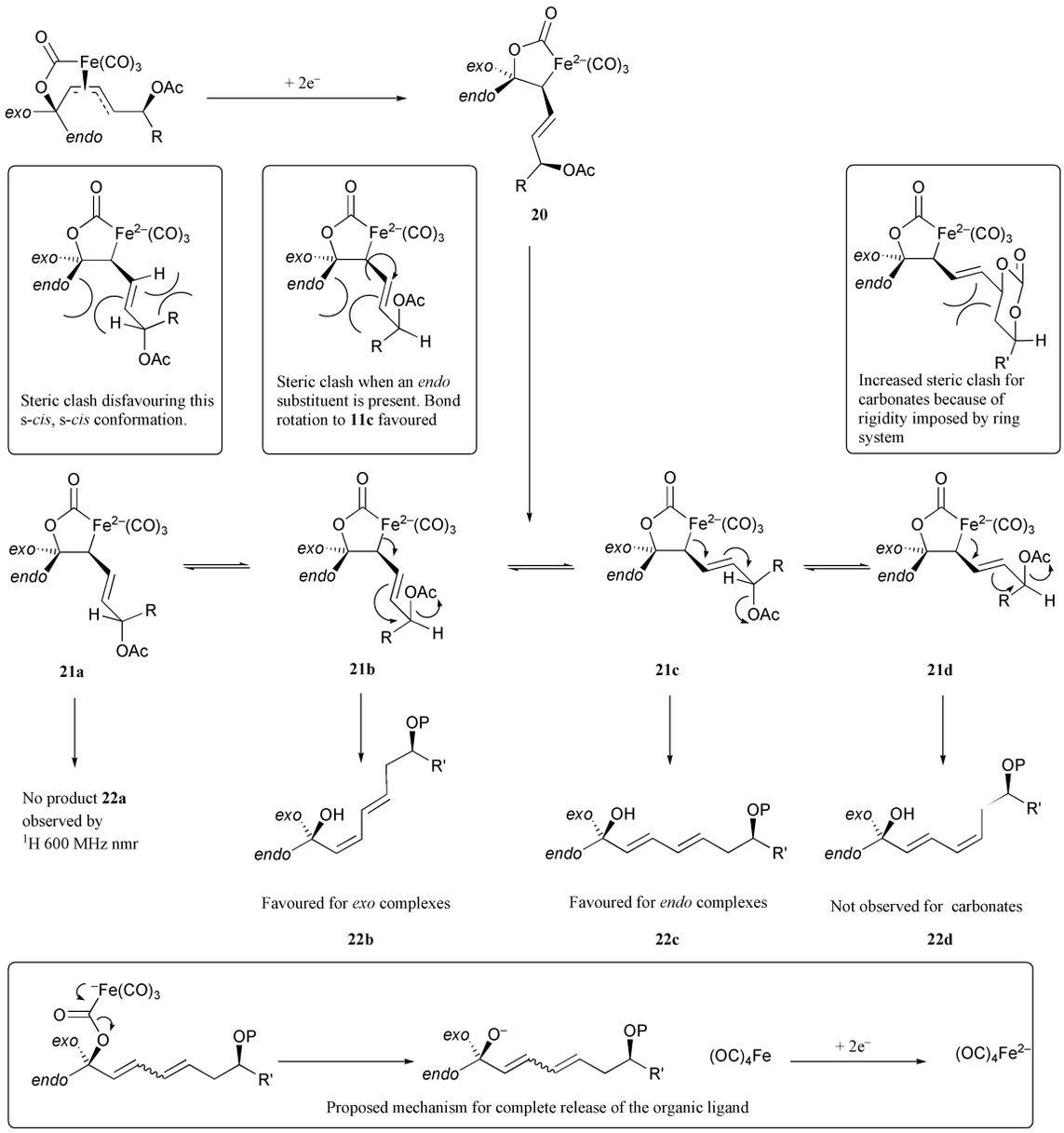
6a 	d	**11b** 	76	g		**19b** 	89
6a 	e	**12a** 	72	g	0.74 : 0.26 : 0.00	**16b** 	96
					13e 14e 15e		

[a] Isolated yield for two steps *via* intermediate **6f**. [b] Where recorded. [c] As determined by the ^{1}H 600 MHz NMR spectra. [d] Isolated yield for two steps.

species is s-*trans*, **21c** and **21d**. For *endo* complexes, the former seems to be the most significant and the major product is an (*E*,*E*)-diene, corresponding to elimination from **21c**. For an *exo* complex the *endo* substituent is a proton and clash with the carbonyl ligands becomes the more significant factor. This results in **21b** being favoured and the major product observed is a (*Z*,*E*)-diene, **22b**. There is no product corresponding to elimination from **21a** and this is probably due to the 1,3-allylic strain of two s-*cis* bonds. (*E*,*Z*)-dienes are observed as a minor component in all examples studied, except in the case of cyclic carbonates. For this substrate, it is presumed that adoption of the s-*cis* bond between the olefin and the leaving group results



Scheme 3 Proposed mechanism for single electron reductive decomplexation.

in larger strain than in the case of the acetate, due to the greater rigidity of the system, and this may account for no product, **22d**, corresponding to this species, **21d**, being observed.

Conclusions

An extremely high yielding reductive decomplexation method for π-allyltricarbonyliron lactone complexes has been developed to afford stereodefined 1,7-alkanediols after hydrogenation. The reaction affords a predictable diene geometry with good selectivity, where *endo* complexes furnish (*E,E*)-dienes and *exo* complexes (*Z,E*)-dienes. A mechanism that is cosistent not only with these recent results but also our previous understanding of these complexes has been proposed. Furthermore, an array of densely functionalised lactone complexes has been synthesised which have potential for natural product synthesis.

Experimental

General experimental

^{1}H NMR spectra were recorded in $CDCl_3$ or C_6D_6 on Bruker DRX-600 or DRX-400 spectrometers and are reported as follows: chemical shift, δ (ppm) [number of protons, multiplicity, coupling constant J (Hz), and assignment]. Residual protic solvent $CHCl_3$ (δ_H = 7.26 ppm) or C_6H_6 (δ_H = 7.20 ppm) was used as the internal reference. ^{13}C NMR spectra were recorded in $CDCl_3$ or C_6D_6 at 150 MHz or 100 MHz on Bruker DRX-600 or DRX-400 or spectrometers, using the central resonance of $CDCl_3$ (δ_C = 77.0 ppm) or C_6D_6 (δ_C = 128.0 ppm) as the internal reference. In distortionless enhancement by polarisation transfer experiments (DEPT135) signals with an odd number of protons attached are designated (−) and those with an even number (+). For those cases where an inseperable mixture of compounds was produced, the data reported was obtained on the mixture. Infra-red spectra were recorded on Perkin-Elmer 983G, FTIR 1620 or Perkin Elmer ATR Spectrum 1 spectrometers. Mass spectra were obtained on Kratos MS890MS, Bruker BIOAPEX 4.7 T FTICR or Micromass Q-TOF spectrometers at the Department of Chemistry, University of Cambridge. The following ionisation techniques were used: electron ionisation (EI), chemical ionisation (CI), fast atom bombardment (FAB) and electrospray (ES). Optical rotation measurements are reported in 10^{-1} deg cm^2 g^{-1}; concentrations (c) are in g 100 dm^{-3}. Flash column chromatography was carried out using Merck Kieselgel (230–400 mesh) unless otherwise indicated. Analytical thin layer chromatography was

performed using precoated glass-backed plates (Merck Kieselgel 60 F254) and visualised by ultraviolet, acidic ammonium molybdate(IV) or acidic potassium permanganate solutions. Aqueous solutions were saturated unless otherwise specified. Petrol refers to petroleum ether boiling point 40–60 °C. In cases where mixtures of solvents were utilised, the ratios given refer to the volumes used. All reactions were carried out under an argon atmosphere in oven-dried glassware, which was cooled under a continuous stream of argon immediately prior to use unless otherwise stated. Et_2O and THF were distilled from sodium benzophenone ketyl. CH_2Cl_2 and PhMe were distilled from calcium hydride.

The preparation of compounds **4a**–**d**,[10] **5**,**6e**[4] and **7a**,**b**[6] is described elsewhere.

General procedures

A NaBH$_4$ reduction. For a 0.50 mmol scale reaction: to a solution of the ketone in CH_2Cl_2 (4 cm^3) at −78 °C was added a pre-cooled (−78 °C) solution of $NaBH_4$ (10 eq.) in MeOH (4 cm^3) *via* cannula and the reaction stirred at this temperature for 2 hours. A pre-cooled (−78 °C) solution of AcOH (2 cm^3) and THF (10 cm^3) was added *via* canula, the mixture was poured onto saturated aqueous $NaHCO_3$ solution (40 cm^3) and extracted with Et_2O (2 × 15 cm^3). The combined organic fractions were washed with brine and dried ($MgSO_4$). Concentration of the filtrate *in vacuo* followed by flash column chromatography afforded the alcohol.

B acetate protection of alcohols. For a 0.5 mmol scale reaction: to a solution of the alcohol (1.0 eq.), NEt_3 (1.3 eq.) and DMAP (0.1 eq.) in CH_2Cl_2 (5 cm^3) at 0 °C was added Ac_2O (1.1 eq.). The reaction was allowed to warm to room temperature, stirred for 2 hours, filtered through a pad of silica and the residue washed with Et_2O (50 cm^3). Concentration of the filtrate *in vacuo* afforded the acetate which was used without further purification.

C Al(*i*-Bu)$_3$ reduction. For a 1.0 mmol scale reaction: to a solution of the ketone (1.0 eq.) in CH_2Cl_2 (6 cm^3) at 0 °C was added Al(*i*-Bu)$_3$ (2.0 eq., 1 mol dm^{-3} in PhMe) dropwise. After 30 min the solution was poured onto pre-cooled (0 °C) 1 mol dm^{-3} aqueous HCl solution (30 cm^3) and stirred vigourously for 20 min. CH_2Cl_2 (20 cm^3) was added and the layers separated. The aqueous layer was extracted with Et_2O (30 cm^3) and the combined organic fractions were washed with brine and dried ($MgSO_4$). Concentration of the filtrate *in vacuo* followed by flash column chromatography afforded the tertiary or secondary alcohol respectively.

D formation of cyclic carbonates. For a 0.30 mmol scale reaction: to a solution of the alcohol and DMAP (0.1 eq.) in CH_2Cl_2 (3 cm^3) at room temperature was added CDI (3.0 eq.) in one portion. After 1 hour the reaction mixture was purified directly by flash column chromatography to afford the carbonate.

E cuprate decomplexation and diene reduction. For a 0.20 mmol scale reaction: to a suspension of CuI (5.0 eq.) in THF (5 cm^3) at −78 °C was added MeLi (10 eq., 1.4 mol dm^{-3} in Et_2O) dropwise. After complete addition the solution was warmed to 0 °C and cooled back to −78 °C and then the alcohol (1.0 eq.) in THF (1 cm^3) was added dropwise. The reaction mixture was stirred at −78 °C overnight, allowed to warm to room temperature, then poured onto NH_4Cl solution and extracted with Et_2O (2 × 10 cm^3). The combined organic fractions were washed with brine and dried ($MgSO_4$). Concentration of the filtrate *in vacuo* followed by flash column chromatography afforded a mixture of dienols. Pd/C (1.0 eq. by weight, 10 wt.% Pd (dry basis) on activated carbon) was suspended in a solution of the dienol mixture in EtOAc (5 cm^3). The mixture was purged 5 times with H_2 and stirred under an atmosphere of H_2. After 2 hours the mixture was filtered and concentrated *in vacuo* to afford the reduced product without any further purification.

Preparation of lithium naphthalenide solution

A suspension of naphthalene (6.5g, 50.7 mmol) and lithium (1.15g, 50.0 mmol, ~30 wt.% dispersion in mineral oil) in THF (50 cm^3) was sonicated for 30 min to yield a dark green solution (~1 mol dm^{-3}).

F lithium naphthalenide decomplexation. For a 0.20 mmol scale reaction: to a solution of the acetate (1.0 eq.) in THF (5 cm^3) at −78 °C was added lithium naphthalenide (5.0 eq.) and the reaction stirred at this temperature overnight. The mixture was allowed to warm to room temperature and filtered through a pad of silica. The residue was washed with Et_2O (50 cm^3) and the filtrate concentrated *in vacuo*. The crude product was purified by flash column chromatography to afford a mixture of dienols.

G lithium naphthalenide decomplexation and reduction. For a 0.20 mmol scale reaction: to a solution of the acetate (1.0 eq.) in THF (5 cm^3) at −78 °C was added lithium naphthalenide (5.0 eq.) and the reaction was stirred at this temperature overnight. The mixture was allowed to warm to room temperature and filtered through a pad of silica. The residue was washed with Et_2O (50 cm^3) and the filtrate concentrated *in vacuo*. The crude product was purified by flash column chromatography to afford a mixture of dienols. Pd/C (1.0 eq. by weight, 10 wt.% Pd (dry basis) on activated carbon) was suspended in a solution of the dienol mixture in EtOAc (5 cm^3). The mixture was purged 5 times with H_2 and stirred under an atmosphere of H_2. After 2 hours the mixture was filtered and concentrated *in vacuo* to afford the reduced product without any further purification.

H decomplexation, acetate cleavage and diene reduction. For a 0.20 mmol scale reaction: to a solution of the acetate (1.0 eq.) in THF (5 cm^3) at −78 °C was added lithium naphthalenide (10 eq.) and the reaction stirred at this temperature overnight. The mixture was allowed to warm to room temperature, MeOH (5 cm^3) was added and the reaction was stirred for a further 2 hours before being filtered through a pad of silica. The residue was washed with Et_2O (50 cm^3) and the filtrate was concentrated *in vacuo*. The crude product was purified by flash column chromatography to afford a mixture of dienols. Pd/C (1.0 eq. by weight, 10 wt.% Pd (dry basis) on activated carbon) was suspended in a solution of the dienol mixture in EtOAc (5 cm^3). The mixture was purged 5 times with H_2 and stirred under an atmosphere of H_2. After 2 hours the mixture was filtered and concentrated *in vacuo* to afford the reduced product without any further purification.

I Pd/C catalysed reduction of dienes. For a 0.5 mmol scale reaction: Pd/C (1.0 eq. by weight, 10 wt.% Pd (dry basis) on activated carbon) was suspended in a solution of the alkene in EtOAc (5 cm^3). The mixture was purged 5 times with H_2 and stirred under an atmosphere of H_2. After 2 hours the mixture was filtered through a pad of Celite and the residue washed with EtOAc (50 cm^3). Concentration of the filtrate *in vacuo* afforded the alkane which required no further purification.

Preparation and characterisation

(3*E*,2*SR*,5*SR*,6*RS*)-6-(Carbonyloxy-κC)-2-hydroxy-(3,4,5-η)-undec-3-en-5-yl]tricarbonyliron 2a. Iron lactone complex **2a** was prepared using general procedure A from [(3*E*,5*SR*,6*RS*)-6-(carbonyloxy-κC)-2-oxo-(3,4,5-η)-undec-3-en-5-yl]tricarbonyliron[8] (220 mg, 0.63 mmol) in CH_2Cl_2 (4 cm^3) and $NaBH_4$

(240 mg, 6.3 mmol) in MeOH (4 cm^3). After 1.5 hours THF–AcOH work-up as described followed by flash column chromatography (eluent – Et_2O–petrol 1 : 1) afforded alcohol **2a** as a yellow gum (190 mg, 86%). Data were consistent with those reported in the literature.[8]

[(3*E*,2*SR*,5*SR*,6*RS*)-2-Acetoxy-6-(carbonyloxy-κC)-(3,4,5-η)-undec-3-en-5-yl]tricarbonyliron 2b. Acetate **2b** was prepared according to general procedure B from iron lactone complex **2a** (130 mg, 0.37 mmol), NEt_3 (49 mg, 0.48 mmol) and DMAP (5 mg, 0.04 mmol) in CH_2Cl_2 (4 cm^3) and Ac_2O (41 mg, 0.41 mmol). Work-up as described above afforded acetate **2b** as a gum (134 mg, 92%); $\nu_{max}(sol^n:CH_2Cl_2)/cm^{-1}$ [2083, 2027 Fe(CO)], 1737 (C=O) and 1664 (C=O); δ_H(400 MHz; $CDCl_3$); 5.38 (1 H, quin, *J* 6.1, 2-H), 4.63 (2 H, m, 4-H and 5-H), 4.26 (1 H, m, 6-H), 3.93 (1 H, dd, *J* 11.7 and 4.9, 3-H), 2.03 (3 H, s, $COCH_3$), 1.56 (3 H, d, *J* 6.5, 1-H × 3), 1.55–1.22 (8 H, m, 7-H × 2, 8-H × 2, 9-H × 2 and 10-H × 2) and 0.88 (3 H, t, *J* 6.8, 11-H × 3); δ_C(100 MHz; $CDCl_3$) 208.7, 206.2, 204.3, 203.3, 170.1, 88.6, 82.6, 77.1, 70.7, 65.8, 36.6, 31.5, 26.6, 22.5, 20.8, 15.2 and 13.9; *m*/*z*(FAB) 395 (100%, MH^+); [Found (MH^+) 395.0816. $C_{17}H_{23}FeO_7$ requires *M*H, 395.0793].

Undecan-6-ol 3. Method 1: alcohol **3** was prepared according to general procedure E from alcohol **2a** (160 mg, 0.45 mmol) in THF (2 cm^3), CuI (433 mg, 2.3 mmol) in THF (8 cm^3) and MeLi (3.2 cm^3, 4.5 mmol; 1.4 M in Et_2O). Work-up as described above followed by flash column chromatography (eluent – Et_2O–petrol 1 : 2⟶1 : 1) and reduction catalysed by Pd/C (160 mg, 10 wt.% Pd (dry basis) on activated carbon) in EtOAc (5 cm^3) afforded the alkanol **3** (61 mg, 78%). The product was identical to sample obtained from Lancaster.

Method 2: alcohol **3** was prepared according to general procedure G from acetate **2b** (110 mg, 0.28 mmol) in THF (5 cm^3) and lithium naphthalenide (1.4 cm^3, 1.4 mmol, 1 mol dm^{-3} solution in THF). Work-up as described followed by flash column chromatography (eluent – Et_2O–petrol 1 : 2⟶1 : 1) and reduction catalysed by Pd/C (110 mg, 10 wt.% Pd (dry basis) on activated carbon) in EtOAc (5 cm^3) afforded the alkanol **3** (44 mg, 92%). The product was identical to sample obtained from Lancaster.

[(8*E*,6*RS*,7*SR*,10*SR*,12*SR*)-6-(Carbonyloxy-κC)-10,12-dihydroxy-(7,8,9-η)-heptadec-8-en-7-yl]tricarbonyliron 6a. Iron lactone complex **6a** was prepared using general procedure A from ketone **4a** (180 mg, 0.40 mmol) in CH_2Cl_2 (3.5 cm^3) and $NaBH_4$ (150 mg, 4.0 mmol) in MeOH (3.5 cm^3). After 2 hours THF–AcOH work-up as described above followed by flash column chromatography (eluent – Et_2O–petrol 1 : 1⟶3 : 1) afforded diol **6a** as a solid (146 mg, 81%); $\nu_{max}(sol^n:CH_2Cl_2)/cm^{-1}$ 3475 (OH), [2081, 2026 Fe(CO)] and 1662 (C=O); δ_H(400 MHz; $CDCl_3$) 4.87 (1 H, dd, *J* 12.1 and 8.3, 8-H), 4.61 (1 H, ddd, *J* 8.3, 4.7 and 0.5, 7-H), 4.51 (1 H, d, *J* 9.8, 10-H), 4.25 (1 H, m, 6-H), 3.97 (2 H, m, 9-H and 12-H), 1.93 (1 H, d, *J* 14.4, 11-H_A), 1.75 (1 H, dt, *J* 14.4 and 10.2, 11-H_B), 1.57–1.02 (18 H, m, 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2, 13-H × 2, 14-H × 2, 15-H × 2, 16-H × 2 and OH × 2) and 0.90 (6 H, m, 1-H × 3 and 17-H × 3); δ_C(100 MHz; $CDCl_3$) 209.7+, 207.0+, 207.0+, 203.3+, 87.9−, 87.2−, 77.3−, 75.9−, 73.6−, 71.5−, 45.0+, 38.4+, 36.7+, 31.7+, 31.6+, 26.6+, 24.8+, 22.5+, 22.5+, 13.9− and 13.9−; *m*/*z*(FAB) 453 (60%, MH^+) and 323 (100); [Found (MH^+) 453.1569. $C_{21}H_{33}FeO_7$ requires *M*H, 453.1576].

[(8*E*,6*RS*,7*SR*,10*SR*,12*RS*)-6-(Carbonyloxy-κC)-10,12-dihydroxy-13-methyl-(7,8,9-η)-tetradec-8-en-7-yl]tricarbonyliron 6b. Iron lactone complex **6b** was prepared using general procedure A from ketone **4b** (260 mg, 0.62 mmol) in CH_2Cl_2 (4 cm^3) and $NaBH_4$ (232 mg, 6.2 mmol) in MeOH (4 cm^3). After 2 hours THF–AcOH work-up as described above followed by flash column chromatography (eluent – Et_2O–petrol 1 : 1⟶3 : 1) afforded diol **6b** as a solid (220 mg, 84%); $\nu_{max}(sol^n:CH_2Cl_2)/cm^{-1}$ 3482 (OH), [2081, 2008 Fe(CO)] and 1662 (C=O); δ_H(400 MHz; $CDCl_3$) 4.89 (1 H, dd, *J* 12.2 and 8.4, 8-H), 4.62 (1 H, dd, *J* 8.4 and 4.6, 7-H), 4.54 (1 H, d, *J* 9.6, 10-H), 4.25 (1 H, q, *J* 7.1, 6-H), 4.18 (1 H, s, OH × 1), 3.98 (2 H, m, 9-H and 12-H), 1.99 (2 H, d, *J* 14.5, 11-H_A and OH × 1), 1.77 (1 H, dt, *J* 14.5 and 10.2, 11-H_B), 1.59–1.26 (9 H, m, 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2 and 13-H), 0.98 (3 H, d, *J* 7.3, 13-CCH_3), 0.97 (3 H, d, *J* 7.3, 14-H × 3) and 0.83 (3 H, t, *J* 6.8, 1-H × 3); δ_C(100 MHz; $CDCl_3$) 209.7, 207.0, 207.0, 203.4, 87.9, 87.2, 77.2, 75.9, 73.3, 71.5, 45.0, 40.6, 36.7, 31.6, 26.6, 22.5, 18.3, 13.9 and 13.9; *m*/*z*(FAB) 425 (100%, MH^+); [Found (MH^+) 425.1262. $C_{19}H_{29}FeO_7$ requires *M*H, 425.1263].

[(4*E*,1*RS*,3*SR*,6*SR*,7*RS*)-7-(Carbonyloxy-κC)-1-cyclohexyl-1,3-dihydroxy-(4,5,6-η)-dodec-4-en-6-yl]tricarbonyliron 6c. Iron lactone complex **6c** was prepared using general procedure A from ketone **4c** (220 mg, 0.48 mmol) in CH_2Cl_2 (4 cm^3) and $NaBH_4$ (180 mg, 4.8 mmol) in MeOH (4 cm^3). After 5 hours THF–AcOH work-up as described above followed by flash column chromatography (eluent – Et_2O–petrol 1 : 1⟶10 : 1) afforded diol **6c** as a solid (183 mg, 83%); $\nu_{max}(sol^n:CH_2Cl_2)/cm^{-1}$ 3476 (OH), [2081, 2009 Fe(CO)] and 1662 (C=O); δ_H(400 MHz; $CDCl_3$) 4.90 (1 H, dd, *J* 12.3 and 8.4, 5-H), 4.62 (1 H, dd, *J* 8.4 and 4.6, 6-H), 4.52 (1 H, d, *J* 9.8, 3-H), 4.26 (2 H, m, 7-H and OH × 1), 4.00 (1 H, dd, *J* 12.3 and 2.7, 4-H), 3.75 (1 H, ddd, *J* 10.4, 5.2 and 1.4, 1-H), 1.99 (1 H, d, *J* 14.4, 2-H_A), 1.93–0.97 (19 H, m, cyclohexyl × 9, 2-H_B, 8-H × 2, 9-H × 2, 10-H × 2, 11-H × 2 and OH) and 0.82 (5 H, m, cyclohexyl × 2 and 12-H × 3); δ_C(100 MHz; $CDCl_3$) 209.7, 207.2, 206.6, 203.4, 88.0, 87.1, 77.1, 76.7, 75.9, 71.5, 44.6, 42.0, 41.3, 36.7, 31.6, 28.6, 27.7, 26.6, 26.0, 22.6, 22.5 and 13.9; *m*/*z*(FAB) 465 (100%, MH^+); [Found (MH^+) 465.1590. $C_{22}H_{33}FeO_7$ requires *M*H, 465.1576].

[(4*E*,1*RS*,3*SR*,6*SR*,7*RS*)-7-(Carbonyloxy-κC)-1,3-dihydroxy-1-phenyl-(4,5,6-η)-dodec-4-en-6-yl]tricarbonyliron 6d. Iron lactone complex **6d** was prepared using general procedure A from ketone **4d** (190 mg, 0.42 mmol) in CH_2Cl_2 (3.5 cm^3) and $NaBH_4$ (157 mg, 4.1 mmol) in MeOH (3.5 cm^3). After 5 hours THF–AcOH work-up as described followed by flash column chromatography (eluent – Et_2O–petrol 1 : 1⟶10 : 1) afforded diol **6d** as a solid (166 mg, 87%); $\nu_{max}(sol^n:CH_2Cl_2)/cm^{-1}$ 3500 (OH), [2081, 2007 Fe(CO)] and 1663 (C=O); δ_H(400 MHz; $CDCl_3$) 7.37–7.31 (5 H, m, C_6H_5), 5.02 (1 H, d, *J* 9.6, 1-H), 4.88 (1 H, dd, *J* 12.1 and 8.4, 5-H), 4.62 (2 H, m, 3-H and 6-H), 4.23 (1 H, q, *J* 5.1, 7-H), 4.13 (1 H, s, OH × 1), 3.96 (1 H, dd, *J* 12.1 and 3.0, 4-H), 2.62 (1 H, s, OH × 1), 2.12 (2 H, m, 2-H × 2), 1.62–1.27 (8 H, m, 8-H × 2, 9-H × 2, 10-H × 2 and 11-H × 2) and 0.88 (3 H, t, *J* 6.8, 12-H × 3); δ_C(100 MHz; $CDCl_3$) 209.5+, 207.3+, 206.8+, 203.3+, 143.7+, 128.7−, 128.0+, 125.6−, 87.5−, 87.4−, 77.1−, 76.1−, 75.6−, 71.4−, 47.1+, 36.6+, 31.6+, 26.6+, 22.5+ and 13.9−; *m*/*z*(FAB) 459 (100%, MH^+); [Found (MH^+) 459.1104. $C_{22}H_{27}FeO_7$ requires *M*H, 459.1106].

[(8*E*,6*RS*,7*SR*,10*SR*,12*RS*)-12-(*tert*-Butyl-dimethyl-silanyloxy)-6-(carbonyloxy-κC)-10-hydroxy-13-methyl-(7,8,9-η)-tetradec-8-en-7-yl]tricarbonyliron 6f. To a solution of diol **6b** (380 mg, 0.90 mmol) and NEt_3 (110 mg, 1.1 mmol) in CH_2Cl_2 (5 cm^3) at 0 °C was added TBSOTf (260 mg, 0.98 mmol) dropwise. After 2 hours the mixture was purified directly by flash column chromatography (eluent – Et_2O–petrol 1 : 9⟶1 : 2) to afford TBS protected iron lactone **6f** (396 mg, 82%); $\nu_{max}(sol^n:CH_2Cl_2)/cm^{-1}$ 3474 (OH), [2080, 2006 Fe(CO)] and 1663 (C=O); δ_H(400 MHz; $CDCl_3$) 4.91 (1 H, dd, *J* 12.2 and 8.4, 8-H), 4.61 (1 H, dd, *J* 8.4 and 4.5, 7-H), 4.48 (1 H, d, *J* 9.5, 10-H), 4.25 (1 H, q, *J* 5.2, 6-H), 4.04 (1 H, m, 12-H), 3.98 (1 H, dd, *J* 12.2 and 2.5, 9-H), 3.76 (1 H, s, OH), 2.00 (1 H, dt, *J* 14.3 and 2.5, 11-H_A), 1.73 (1 H, dt, *J* 14.3 and 9.8, 11-H_B), 1.65–1.15 (9 H, m, 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2 and 13-H), 0.91 (18 H, m, 1-H × 3, 13-CCH_3, 14-H × 3 and $SiC(CH_3)_3$), 0.14 (3 H, s, $Si(CH_3)$ × 1)

and 0.13 (3 H, s, $Si(CH_3)$ × 1); δ_C(100 MHz; $CDCl_3$) 209.8, 207.2, 206.5, 203.3, 88.0, 86.8, 77.2, 75.8, 74.0, 70.4, 45.0, 40.4, 36.7, 31.6, 26.6, 25.8, 22.5, 17.9, 17.6, 14.2, 13.9, −3.8 and −4.8; *m*/*z*(ES) 539 (100%, MH^+); [Found (MH^+) 539.2144. $C_{25}H_{43}FeO_7Si$ requires *M*H, 539.2127].

[(6*E*,2*R*,4*R*,5*S*,8*S*)-4-(Carbonyloxy-κC)-2,10-di(*tert*-butyl-dimethyl-silanyloxy)-8-hydroxy-(5,6,7-η)-dec-6-en-5-yl]tricarbonyliron 7a. Iron lactone complex **7a** was prepared using general procedure C from [(6*E*,2*R*,4*R*,5*S*)-4-(carbonyloxy-κC)-2,10-di(*tert*-butyl-dimethyl-silanyloxy)-8-oxo-(5,6,7-η)-dec-6-en-5-yl]tricarbonyliron[6] (280 mg, 0.47 mmol) in CH_2Cl_2 (4 cm^3) and Al(*i*-Bu)$_3$ (1.0 cm^3, 1.0 mmol; 1.0 mol dm^{-3} solution in PhMe). Work-up as described followed by flash column chromatography (eluent – Et_2O–petrol 1 : 3⟶1 : 1) afforded alcohol **7a** as a solid (227 mg, 81%); $[a]_D^{25}$ −99.6 (*c* 0.49 in CH_2Cl_2); ν_{max}(film)/cm^{-1} 3432 (OH), [2082, 2024 (FeCO)] and 1640 (C=O); δ_H(600 MHz; C_6D_6) 4.70 (1 H, dd, *J* 12.1 and 8.5, 6-H), 4.28 (2 H, m, 4-H and 8-H), 4.15 (1 H, d, *J* 12.1, 7-H), 4.07 (1 H, m, 5-H), 4.03 (1 H, m, 2-H), 3.87 (1 H, s, OH × 1), 3.64 (1 H, m, 10-H_A), 3.57 (1 H, m, 10-H_B), 1.97 (1 H, ddd, *J* 13.6, 8.5 and 5.5, 3-H_A), 1.91 (1 H, m, 9-H_A), 1.65 (1 H, ddd, *J* 13.6, 6.8 and 5.1, 3-H_B), 1.54 (1 H, d, *J* 14.1, 9-H_B), 1.16 (3 H, d, *J* 6.0, 1-H × 3), 1.06 (9 H, s, $SiC(CH_3)_3$ × 1), 0.96 (9 H, s, $SiC(CH_3)_3$ × 1), 0.16 (3 H, s, $Si(CH_3)$ × 1), 0.15 (3 H, s, $Si(CH_3)$ × 1), 0.06 (3 H, s, $Si(CH_3)$ × 1) and 0.05 (3 H, s, $Si(CH_3)$ × 1); δ_C(150 MHz; C_6D_6) [210.5, 207.7, 203.9, 202.2 Fe(CO) × 4], 88.1 (7-C), 87.1 (6-C), 76.2 (5-C), 73.9 (4-C), 71.1 (8-C), 66.6 (2-C), 62.6 (10-C), 46.8 (3-C), 40.7 (9-C), 25.8 ($SiC(CH_3)_3$ × 1), 25.6 ($SiC(CH_3)_3$ × 1), 22.9 (1-C), 17.9 ($SiC(CH_3)_3$ × 1), 17.9 ($SiC(CH_3)_3$ × 1), −4.5 ($Si(CH_3)$ × 1), −4.9 ($Si(CH_3)$ × 1), −5.8 ($Si(CH_3)$ × 1) and −5.9 ($Si(CH_3)$ × 1); *m*/*z*(ES) 621 (15%, MNa^+) and 509 (100); [Found (MNa^+) 621.1980. $C_{26}H_{46}FeNaO_8Si_2$ requires *M*Na, 621.1978].

[(6*E*,2*R*,4*R*,5*R*,8*R*)-4-(Carbonyloxy-κC)-2,10-di(*tert*-butyl-dimethyl-silanyloxy)-8-hydroxy-(5,6,7-η)-dec-6-en-5-yl]tricarbonyliron 7b. Iron lactone complex **7b** was prepared using general procedure C from [(6*E*,2*R*,4*R*,5*R*)-4-(carbonyloxy-κC)-2,10-di(*tert*-butyl-dimethyl-silanyloxy)-8-oxo-(5,6,7-η)-dec-6-en-5-yl]tricarbonyliron[6] (320 mg, 0.54 mmol) in CH_2Cl_2 (4.5 cm^3) and Al(*i*-Bu)$_3$ (1.1 cm^3, 1.1 mmol; 1.0 mol dm^{-3} solution in PhMe). Work-up as described followed by flash column chromatography (eluent – Et_2O–petrol 1 : 3⟶1 : 1) afforded alcohol **7b** as a solid (254 mg, 79%); $[a]_D^{25}$ +65.0 (*c* 0.36 in CH_2Cl_2); ν_{max}(film)/cm^{-1} 3448 (OH), [2088, 2004 (FeCO)] and 1642 (C=O); δ_H(600 MHz; C_6D_6) 4.81 (1 H, dd, *J* 11.8 and 8.2, 6-H), 4.26 (1 H, d, *J* 11.8, 7-H), 4.09 (1 H, t, *J* 7.1, 4-H), 4.04 (1 H, sextet, *J* 6.1, 2-H), 3.96 (2 H, m, 5-H and 8-H), 3.90 (1 H, s, OH × 1), 3.66 (1 H, m, 10-H_A), 3.59 (1 H, m, 10-H_B), 1.99 (1 H, ddd, *J* 13.5, 8.6 and 5.6, 3-H_A), 1.91 (1 H, m, 9-H_A), 1.63 (1 H, m, 3-H_B), 1.56 (1 H, d, *J* 14.0, 9-H_B), 1.21 (3 H, d, *J* 6.1, 1-H × 3), 1.07 (9 H, s, $SiC(CH_3)_3$ × 1), 0.96 (9 H, s, $SiC(CH_3)_3$ × 1), 0.20 (3 H, s, $Si(CH_3)$ × 1), 0.16 (3 H, s, $Si(CH_3)$ × 1) and 0.06 (6 H, s, $Si(CH_3)$ × 2); δ_C(150 MHz; C_6D_6) 210.9+, 207.6+, 204.2+, 202.0+, 88.4−, 87.6−, 75.3−, 71.5−, 71.0−, 66.2−, 62.6+, 47.8+, 40.5+, 25.8−, 25.6−, 22.9−, 18.0+, 17.9+, −4.9−, −4.9−, −5.8− and −5.9−; *m*/*z*(ES) 621 (10%, MNa^+) and 509 (100); [Found (MNa^+) 621.1954. $C_{26}H_{46}FeNaO_8Si_2$ requires *M*Na, 621.1978].

[(8*E*,6*RS*,7*SR*,10*SR*,12*SR*)-6-(Carbonyloxy-κC)-10,12-di-acetoxy-(7,8,9-η)-heptadec-8-en-7-yl]tricarbonyliron 8a. Diacetate **8a** was prepared using general procedure B from iron lactone complex **6a** (149 mg, 0.33 mmol), NEt_3 (87 mg, 0.86 mmol) and DMAP (8 mg, 0.07 mmol) in CH_2Cl_2 (3.5 cm^3) and Ac_2O (74 mg, 0.73 mmol). Work-up as described above afforded diacetate **8a** as a gum (170 mg, 96%); ν_{max}(sol^n:CH_2Cl_2)/cm^{-1} [2092, 2030 Fe(CO)], 1742 (C=O) and 1675 (C=O); δ_H(400 MHz; $CDCl_3$) 5.19 (1 H, qd, *J* 6.0 and 1.2, 10-H), 5.04 (1 H, m, 12-H), 4.68 (1 H, m, 8-H), 4.67 (1 H, m, 7-H), 4.26 (1 H, m, 6-H), 3.90 (1 H, m, 9-H), 2.22–1.98 (2 H, m, 11-H × 2), 2.08 (3 H, s, $COCH_3$ × 1), 2.07 (3 H, s, $COCH_3$ × 1), 1.65–1.22 (16 H, m, 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2, 13-H × 2, 14-H × 2, 15-H × 2 and 16-H × 2) and 0.89 (6 H, t, *J* 6.8, 1-H × 3 and 17-H × 3); δ_C(100 MHz; $CDCl_3$) 208.7+, 206.2+, 204.0+, 202.8+, 170.9+, 170.0+, 90.0−, 80.7−, 77.3−, 77.1−, 72.1−, 70.8−, 41.4+, 36.5+, 34.5+, 31.5+, 31.5+, 26.5+, 24.8+, 22.5+, 22.5+, 21.1−, 20.7−, 13.9− and 13.9−; *m*/*z*(FAB) 537 (100%, MH^+); [Found (MH^+) 537.1801. $C_{25}H_{37}FeO_9$ requires *M*H, 537.1787].

[(8*E*,6*RS*,7*SR*,10*SR*,12*RS*)-(Carbonyloxy-κC)-10,12-di-acetoxy-13-methyl-(7,8,9-η)-tetradec-8-en-7-yl] tricarbonyliron 8b. Diacetate **8b** was prepared using general procedure B from iron lactone complex **6b** (160 mg, 0.38 mmol), NEt_3 (99 mg, 0.98 mmol) and DMAP (9 mg, 0.08 mmol) in CH_2Cl_2 (4 cm^3) and Ac_2O (85 mg, 0.83 mmol). Work-up as described above afforded diacetate **8b** as a gum (178 mg, 93%); ν_{max}(sol^n:CH_2Cl_2)/cm^{-1} [2084, 2017 Fe(CO)], 1736 (C=O) and 1667 (C=O); δ_H(400 MHz; $CDCl_3$) 5.19 (1 H, qd, *J* 6.0 and 1.2, 10-H), 5.06 (1 H, m, 12-H), 4.69 (1 H, m, 8-H), 4.68 (1 H, m, 7-H), 4.26 (1 H, m, 6-H), 3.90 (1 H, m, 9-H), 2.22–1.97 (2 H, m, 11-H × 2), 2.08 (3 H, s, $COCH_3$ × 1), 2.07 (3 H, s, $COCH_3$ × 1), 1.68–1.15 (9 H, m, 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2 and 13-H) and 0.83 (3 H, t, *J* 6.8, 1-H × 3, 13-CCH_3 and 14-H × 3); δ_C(100 MHz; $CDCl_3$) 208.7, 206.2, 204.0, 202.8, 170.8, 170.0, 90.0, 80.7, 77.2, 77.1, 72.0, 70.5, 53.4, 41.5, 36.6, 31.5, 26.5, 22.4, 21.1, 20.7, 18.4, 13.9 and 13.7; *m*/*z*(FAB) 509 (75%, MH^+), 511 (100); [Found (MH^+) 509.1476. $C_{23}H_{33}FeO_9$ requires *M*H, 509.1474].

[(4*E*,1*RS*,3*SR*,6*SR*,7*RS*)-7-(Carbonyloxy-κC)-1,3-di-acetoxy-1-cyclohexyl-(4,5,6-η)-dodec-4-en-6-yl]tricarbonyliron 8c. Diacetate **8c** was prepared using general procedure B from iron lactone complex **6c** (110 mg, 0.24 mmol), NEt_3 (62 mg, 0.62 mmol) and DMAP (3 mg, 0.02 mmol) in CH_2Cl_2 (2.5 cm^3) and Ac_2O (53 mg, 0.52 mmol). Work-up as described above afforded diacetate **8c** as a gum (118 mg, 91%); ν_{max}(film)/cm^{-1} [2079, 2002 Fe(CO)], 1735 (C=O) and 1666 (C=O); δ_H(600 MHz; $CDCl_3$) 5.07 (1 H, m, 3-H), 4.92 (1 H, m, 1-H), 4.77 (1 H, dd, *J* 12.1 and 8.5, 5-H), 4.68 (1 H, dd, *J* 8.2 and 4.7, 6-H), 4.26 (1 H, m, 7-H), 3.87 (1 H, dd, *J* 12.1 and 6.5, 4-H), 2.08 (3 H, s, $COCH_3$ × 1), 2.07 (3 H, s, $COCH_3$ × 1), 2.06 (2 H, m, 2-H × 2), 1.77–1.12 (17 H, m, cyclohexyl × 9, 8-H × 2, 9-H × 2, 10-H × 2 and 11-H × 2), 1.02 (2 H, m, cyclohexyl × 2) and 0.88 (3 H, t, *J* 6.8, 12-H × 3); δ_C(150 MHz; $CDCl_3$) 208.7, 206.3, 204.0, 202.7, 171.1, 169.9, 90.4, 80.6, 77.2, 76.8, 74.2, 72.7, 41.8, 38.9, 36.5, 31.6, 28.8, 28.1, 26.4, 26.2, 26.0, 25.9, 22.4, 21.0, 20.8 and 13.9; *m*/*z*(ES) 571 (50%, MNa^+) and 459 (100); [Found (MNa^+) 571.1620. $C_{26}H_{36}FeNaO_9$ requires *M*Na, 571.1606].

[(6*E*,2*R*,4*R*,5*S*,8*S*)-8-Acetoxy-[2,10-di(*tert*-butyl-dimethyl-silanyloxy)-4-(carbonyloxy-κC)-(5,6,7-η)-dec-6-en-5-yl]tricarbonyliron 9a. Acetate **9a** was prepared using general procedure B from iron lactone complex **7a** (190 mg, 0.32 mmol), NEt_3 (84 mg, 0.84 mmol) and DMAP (4 mg, 0.03 mmol) in CH_2Cl_2 (3 cm^3) and Ac_2O (36 mg, 0.35 mmol). Work-up as described above afforded acetate **9a** as a solid (197 mg, 97%); $[a]_D^{25}$ −126.5 (*c* 0.34 in CH_2Cl_2); ν_{max}(film)/cm^{-1} [2082, 2010 Fe(CO)], 1741 (C=O) and 1668 (C=O); δ_H(600 MHz; C_6D_6) 5.61 (1 H, m, 8-H), 4.30 (1 H, dd, *J* 12.2 and 8.4, 6-H), 4.23 (1 H, quin, *J* 4.4, 4-H), 4.13 (1 H, d, *J* 12.2 and 5.7, 7-H), 4.01 (2 H, m, 2-H and 5-H), 3.67 (1 H, m, 10-H_A), 3.61 (1 H, m, 10-H_B), 2.04 (1 H, m, 9-H_A), 1.88 (1 H, ddd, *J* 13.6, 8.6 and 5.3, 3-H_A), 1.82 (3 H, s, $COCH_3$), 1.81 (1 H, m, 9-H_B), 1.60 (1 H, ddd, *J* 13.6, 6.9 and 4.9, 3-H_B), 1.13 (3 H, d, *J* 6.1, 1-H × 3), 1.05 (18 H, s, $SiC(CH_3)_3$ × 2), 0.15 (3 H, s, $Si(CH_3)$ × 1), 0.14 (3 H, s, $Si(CH_3)$ × 1) and 0.14 (6 H, s, $Si(CH_3)$ × 2); δ_C(150 MHz; C_6D_6) [209.6, 207.1, 203.3, 199.9 Fe(CO) × 4], 169.2 (*C*OCH_3), 89.3 (6-C), 81.6 (7-C), 77.4 (5-C), 73.6 (4-C), 71.6 (8-C), 66.5 (2-C), 58.9 (10-C), 46.7 (3-C), 39.5 (9-C), 25.8 ($SiC(CH_3)_3$ × 1), 25.8

(SiC(CH_3)$_3$ × 1), 22.8 (1-C), 20.0 (COCH_3), 18.1 (SiC(CH$_3$)$_3$ × 1), 18.0 (SiC(CH$_3$)$_3$ × 1), −4.5 (Si(CH$_3$) × 1), −4.9 (Si(CH$_3$) × 1 and −5.7 Si(CH$_3$) × 2); *m*/*z*(ES) 663 (95%, MNa^+) and 551 (100); [Found (MNa^+) 663.2065. $C_{28}H_{48}FeNaO_9Si_2$ requires *M*Na, 663.2084].

[(6*E*,2*R*,4*R*,5*R*,8*R*)-8-Acetoxy-2,10-di(*tert*-butyl-dimethyl-silanyloxy)-4-(carbonyloxy-κC)-(5,6,7-η)-dec-6-en-5-yl]tri-carbonyliron 9b. Acetate **9b** was prepared according to general procedure B from iron lactone complex **7b** (230 mg, 0.38 mmol), NEt_3 (51 mg, 0.50 mmol) and DMAP (4 mg, 0.03 mmol) in CH_2Cl_2 (4 cm^3) and Ac_2O (43 mg, 0.42 mmol). Work-up as described above afforded acetate **9b** as a solid (234 mg, 95%); $[a]_D^{25}$ +93.0 (*c* 0.30 in CH_2Cl_2); ν_{max}(film)/cm^{-1} [2083, 2013 Fe(CO)], 1742 (C=O) and 1666 (C=O); δ_H(600 MHz; C_6D_6) 5.60 (1 H, m, 8-H), 4.43 (1 H, dd, *J* 12.1 and 8.0, 6-H), 4.02 (2 H, m, 2-H and 4-H), 3.96 (1 H, dd, *J* 12.1 and 5.6, 7-H), 3.91 (1 H, d, *J* 8.0, 5-H), 3.62 (1 H, m, 10-H$_A$), 3.58 (1 H, m, 10-H$_B$), 1.97 (2 H, m, 3-H$_A$ and 9-H$_A$), 1.82 (3 H, s, $COCH_3$), 1.80 (1 H, m, 9-H$_B$), 1.56 (1 H, ddd, *J* 13.6, 7.2 and 5.5, 3-H$_B$), 1.20 (3 H, d, *J* 6.1, 1-H × 3), 1.07 (9 H, s, SiC(CH$_3$)$_3$ × 1), 1.05 (9 H, s, SiC(CH$_3$)$_3$ × 1), 0.19 (3 H, s, Si(CH$_3$) × 1), 0.14 (3 H, s, Si(CH$_3$) × 1), 0.14 (3 H, s, Si(CH$_3$) × 1) and 0.14 (3 H, s, Si(CH$_3$) × 1); δ_C(150 MHz; C_6D_6) 210.1+, 207.0+, 203.7+, 199.6+, 169.2+, 90.5−, 81.5−, 76.5−, 71.4−, 71.2−, 65.2−, 58.8+, 47.8+, 39.3+, 25.8−, 25.8−, 22.8−, 20.0−, 18.1+, 18.0+, −4.7−, −5.0−, −5.7− and −5.7−; *m*/*z*(ES) 663 (80%, MNa^+) and 551 (100); [Found (MNa^+) 663.2055. $C_{28}H_{48}FeNaO_9Si_2$ requires *M*Na, 663.2084].

[(8*E*,6*RS*,7*SR*,10*SR*,12*RS*)-12-(*tert*-Butyl-dimethyl-silanyl-oxy)-6-(carbonyloxy-κC)-13-methyl-10-methyl sulfonyloxy-(7,8,9-η)-tetradec-8-en-7-yl]tricarbonyliron 10. To a solution of alcohol **6f** (110 mg, 0.20 mmol) and NEt_3 (25 mg, 0.24 mmol) in CH_2Cl_2 (5 cm^3) at 0 °C was added methanesulfonyl chloride (26 mg, 0.22 mmol) dropwise. After 2 hours the mixture was purified directly by flash column chromatography (eluent – Et_2O–petrol 1 : 9⟶1 : 2) to afford iron lactone **10** (106 mg, 80%); ν_{max}(film)/cm^{-1} [2082, 2003 Fe(CO)] and 1638 (C=O); δ_H(600 MHz; $CDCl_3$) 4.87 (1 H, dd, *J* 11.9 and 8.2, 8-H), 4.65 (1 H, dd, *J* 8.2 and 4.7, 7-H), 4.53 (1 H, d, *J* 9.7, 10-H), 4.25 (1 H, m, 6-H), 3.96 (1 H, dd, *J* 11.9 and 2.9, 9-H), 3.70 (1 H, m, 12-H), 2.14 (1 H, ddd, *J* 14.6, 4.2 and 2.0, 11-H$_A$), 1.98 (1 H, octet, *J* 6.9, 13-H), 1.72 (1 H, ddd, *J* 14.6, 10.4 and 3.3, 11-H$_B$), 1.55 (3 H, m, 4-H$_A$ and 5-H × 2), 1.54 (3 H, s, SO_2CH_3), 1.41–1.26 (5 H, m, 2-H × 2, 3-H × 2 and 4-H$_B$), 0.97 (3 H, d, *J* 6.7, 13-CCH$_3$), 0.91 (12 H, m, 14-H × 3 and SiC(CH$_3$)$_3$), 0.89 (3 H, t, *J* 6.7, 1-H × 3), 0.15 (3 H, s, Si(CH$_3$) × 1) and 0.12 (3 H, s, Si(CH$_3$) × 1); δ_C(150 MHz; $CDCl_3$) 209.5, 206.8, 206.6, 203.6, 86.0, 77.4, 77.2, 76.8, 76.5, 67.8, 41.0, 36.7, 32.2, 31.5, 26.6, 25.9, 25.8, 22.5, 19.9, 18.3, 17.9, 13.9, −4.4 and −4.6; *m*/*z*(ES) 603 (65%, MNa^+) and 491 (100); [Found (MNa^+) 639.1715. $C_{26}H_{44}FeNaO_9SSi$ requires *M*Na, 639.1722].

[(8*E*,6*RS*,7*SR*,10*SR*,12*RS*)-10-Acetoxy-12-(*tert*-butyl-di-methyl-silanyloxy)-6-(carbonyloxy-κC)-13-methyl-(7,8,9-η)-tetradec-8-en-7-yl]tricarbonyliron 11a. Acetate **11a** was prepared according to general procedure B from iron lactone complex **6f** (115 mg, 0.21 mmol), NEt_3 (28 mg, 0.28 mmol) and DMAP (3 mg, 0.02 mmol) in CH_2Cl_2 (2 cm^3) and Ac_2O (24 mg, 0.24 mmol). Work-up as described above afforded acetate **11a** as a gum (113 mg, 91%); ν_{max}(film)/cm^{-1} [2080, 2018 Fe(CO)], 1739 (C=O) and 1664 (C=O); δ_H(600 MHz; $CDCl_3$) 5.55 (1 H, m, 10-H), 4.65 (1 H, dd, *J* 8.3 and 4.6, 7-H), 4.58 (1 H, dd, *J* 12.1 and 8.3, 8-H), 4.25 (1 H, m, 6-H), 3.93 (1 H, dd, *J* 12.1 and 4.3, 9-H), 3.67 (1 H, m, 12-H), 2.06 (3 H, s, $COCH_3$), 1.99 (1 H, quin, *J* 6.9, 11-H$_A$), 1.84 (2 H, m, 11-H$_B$ and 13-H), 1.60–1.27 (8 H, m, 2-H × 2, 3-H × 2, 4-H × 2 and 5-H × 2), 0.88 (18 H, m, 1-H × 3, 13-CCH$_3$, 14-H × 3 and SiC(CH$_3$)$_3$), 0.07 (3 H, s, Si(CH$_3$) × 1) and 0.06 (3 H, s, Si(CH$_3$) × 1); δ_C(150 MHz; $CDCl_3$) 208.8, 206.3, 204.0, 203.3, 170.0, 88.5, 81.7, 77.2, 76.6, 73.2, 71.5, 39.6, 36.7, 33.0, 31.5, 26.6, 25.8, 22.4, 20.7, 18.0, 17.6, 17.2, 13.9, −4.2 and −4.6; *m*/*z*(ES) 603 (65%, MNa^+) and 491 (100); [Found (MNa^+) 603.2040. $C_{27}H_{44}FeNaO_8Si$ requires *M*Na, 603.2053].

[(8*E*,6*RS*,7*SR*,10*SR*,12*SR*)-10-Acetoxy-12-(*tert*-butyl-di-methyl-silanyloxy)-6-(carbonyloxy-κC)-(7,8,9-η)-heptadec-8-en-7-yl]tricarbonyliron 11b. To a solution of diol **6a** (90 mg, 0.20 mmol), NEt_3 (52 mg, 0.52 mmol) and DMAP (3 mg, 0.02 mmol) in CH_2Cl_2 (2 cm^3) at 0 °C was added TBSOTf (58 mg, 0.22 mmol) dropwise and the reaction stirred for 2 hours before Ac_2O (22 mg, 0.22 mmol) was added dropwise. After 1 hour the mixture was purified directly by flash column chromatography (eluent – Et_2O–petrol 1 : 9⟶1 : 2) to afford protected iron lactone **11b** (92 mg, 76%); ν_{max}(sol^n:CH_2Cl_2)/cm^{-1} [2082, 2025 Fe(CO)], 1738 (C=O) and 1667 (C=O); δ_H(400 MHz; $CDCl_3$) 5.53 (1 H, q, *J* 4.8, 10-H), 4.63 (1 H, dd, *J* 8.3 and 4.3, 7-H), 4.58 (1 H, dd, *J* 12.0 and 8.3, 8-H), 4.24 (1 H, m, 6-H), 3.93 (1 H, dd, *J* 12.0 and 4.7, 9-H), 3.83 (1 H, quin, *J* 5.7, 12-H), 2.06 (1 H, m, 11-H$_A$), 2.05 (3 H, s, $COCH_3$), 1.92 (1 H, m, 11-H$_B$), 1.68–1.20 (16 H, m, 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2, 13-H × 2, 14-H × 2, 15-H × 2 and 16-H × 2) and 0.91 (15 H, m, 1-H × 3, 17-H × 3 and SiC(CH$_3$)$_3$), 0.09 (3 H, s, Si(CH$_3$) × 1) and 0.07 (3 H, s, Si(CH$_3$) × 1); δ_C(100 MHz; $CDCl_3$) 208.8, 206.3, 204.1 203.2, 170.0, 88.7, 81.8, 77.2, 71.4, 69.1, 67.4, 44.0, 37.2, 36.5, 31.9, 31.5, 26.6, 25.8, 25.6, 22.6, 22.4, 21.1, 18.0, 13.9, 13.9, −4.0 and −4.5; *m*/*z*(ES) 631 (50%, MNa^+), 609 (60, MH^+) and 734 (100); [Found (MH^+) 609.2588. $C_{29}H_{49}FeO_8Si$ requires *M*H, 609.2546].

[(8*E*,6*RS*,7*SR*,10*SR*,12*RS*)-6-(Carbonyloxy-κC)-10,12-di-*O*-carbonate-13-methyl-(7,8,9-η)-tetradec-8-en-7-yl]tri-carbonyliron 12a. Iron lactone complex **12a** was prepared according to general procedure D from diol **6b** (120 mg, 0.28 mmol) and DMAP (4 mg, 0.03 mmol) in CH_2Cl_2 (2.5 cm^3) and CDI (136 mg, 0.84 mmol). Work-up as described above, flash column chromatography (eluent – Et_2O–petrol 1 : 1⟶Et_2O) afforded cyclic carbonate **12a** as a solid (92 mg, 72%); ν_{max}(film)/cm^{-1} [2084, 2005 (FeCO)], 1750 (C=O) and 1663 (C=O); δ_H(600 MHz; $CDCl_3$) 5.03 (1 H, dt, *J* 11.8 and 2.8, 10-H), 4.93 (1 H, dd, *J* 12.0 and 8.4, 8-H), 4.72 (1 H, dd, *J* 8.4 and 4.7, 7-H), 4.30 (2 H, m, 6-H and 12-H), 3.81 (1 H, dd, *J* 12.0 and 2.8, 9-H), 2.35 (1 H, dd, *J* 14.2 and 3.0, 11-H$_A$), 1.98 (1 H, m, 11-H$_B$), 1.57 (1 H, m, 13-H), 1.49–1.24 (8 H, m, 2-H × 2, 3-H × 2, 4-H × 2 and 5-H × 2), 1.05 (3 H, d, *J* 6.8, 14-H × 3), 1.02 (3 H, d, *J* 6.9, 13-CCH$_3$) and 0.88 (3 H, t, *J* 6.9, 1-H × 3); δ_C(150 MHz; $CDCl_3$) 208.4, 206.1, 204.2, 201.4, 147.7, 87.9, 83.4, 78.1, 77.6, 77.1, 76.2, 53.4, 46.7, 32.3, 31.5, 26.6, 22.4, 17.2, 17.2 and 13.9; *m*/*z*(ES) 473 (40%, MNa^+) and 349 (100); [Found (MNa^+) 473.0890. $C_{20}H_{26}FeNaO_8$ requires *M*Na, 473.0875].

[(4*E*,1*RS*,3*SR*,6*SR*,7*RS*)-7-(Carbonyloxy-κC)-1-cyclohexyl-1,3-di-*O*-carbonate-(4,5,6-η)-dodec-4-en-6-yl]tricarbonyliron 12b. Iron lactone complex **12b** was prepared using general procedure D from diol **6c** (180 mg, 0.39 mmol) and DMAP (5 mg, 0.04 mmol) in CH_2Cl_2 (4 cm^3) and CDI (189 mg, 1.2 mmol). Work-up as described above, flash column chromatography (eluent – Et_2O–petrol 1 : 1⟶Et_2O) afforded cyclic carbonate **12b** as a solid (131 mg, 69%); ν_{max}(sol^n:CH_2Cl_2)/cm^{-1} [2087 and 2017 Fe(CO)], 1754 (C=O) and 1668 (C=O); δ_H(400 MHz; $CDCl_3$) 5.01 (1 H, dt, *J* 12.2 and 3.0, 3-H), 4.92 (1 H, dd, *J* 12.1 and 8.5, 5-H), 4.72 (1 H, dd, *J* 8.5 and 4.6, 6-H), 4.31 (2 H, m, 1-H and 7-H), 3.81 (1 H, dd, *J* 12.1 and 3.0, 4-H), 2.34 (1 H, dt, *J* 14.3 and 3.0, 2-H$_A$), 1.96 (2 H, m, 1-H′ and 2-H$_B$), 1.85–1.04 (16 H, m, cyclohexyl × 8, 8-H × 2, 9-H × 2, 10-H × 2 and 11-H × 2) and 0.89 (5 H, m, cyclohexyl × 2 and 12-H × 3); δ_C(100 MHz; $CDCl_3$) 208.5, 206.1, 204.2, 201.5, 88.0, 83.0, 78.0, 77.5,

77.0, 76.3, 41.9, 36.7, 31.8, 31.5, 27.7, 27.6, 26.6, 26.1, 25.3, 25.2, 22.4 and 13.9; *m*/*z*(FAB) 491 (100%, MH^+); [Found (MH^+) 491.1363. $C_{23}H_{31}FeO_8$ requires *M*H, 491.1368].

[(4*E*,1*RS*,3*SR*,6*SR*,7*RS*)-7-(Carbonyloxy-κC)-1,3-di-*O*-carbonate-1-phenyl-(4,5,6-η)-dodec-4-en-6-yl]tricarbonyliron 12c. Iron lactone complex **12c** was prepared using general procedure D from diol **6d** (153 mg, 0.33 mmol) and DMAP (4 mg, 0.03 mmol) in CH_2Cl_2 (3.5 cm^3) and CDI (162 mg, 1.0 mmol). Work-up as described above, flash column chromatography (eluent – Et_2O–petrol 1 : 1⟶Et_2O) afforded cyclic carbonate **12c** as a solid (119 mg, 74%); ν_{max}(sol^n:CH_2Cl_2)/cm^{-1} [2087 and 2016 Fe(CO)], 1760 (C=O) and 1659 (C=O); δ_H(400 MHz; $CDCl_3$) 7.43–7.35 (5 H, m, C_6H_5), 5.52 (1 H, dd, *J* 11.8 and 2.9, 1-H), 5.18 (1 H, dt, *J* 11.8 and 3.1, 3-H), 4.96 (1 H, dd, *J* 12.1 and 8.4, 5-H), 4.75 (1 H, dd, *J* 8.4 and 4.3, 6-H), 4.29 (1 H, q, *J* 6.5, 7-H), 3.83 (1 H, dd, *J* 12.1 and 3.0, 4-H), 2.63 (1 H, dt, *J* 14.5 and 3.1, 2-H_A), 2.12 (1 H, dt, *J* 14.5 and 11.9, 2-H_B), 1.62–1.27 (8 H, m, 8-H × 2, 9-H × 2, 10-H × 2 and 11-H × 2) and 0.88 (3 H, t, *J* 6.8, 12-H × 3); δ_C(100 MHz; $CDCl_3$) 208.4+, 205.9+, 203.8+, 201.5+, 147.3+, 136.8+, 129.4−, 129.0+, 125.8−, 88.3−, 79.8−, 77.9−, 77.4−, 77.2−, 77.1−, 36.7+, 36.7+, 31.5+, 26.6+, 22.4+ and 13.9−; *m*/*z*(ES) 507 (55%, MNa^+) and 734 (100); [Found (MNa^+) 507.0734. $C_{23}H_{24}FeNaO_8$ requires *M*Na, 507.0718].

(7*E*,9*E*,6*RS*,12*RS*)-12-Acetoxy-6-hydroxy-11-methyl-tetradeca-7,9-diene 13a (7*Z*,9*E*,6*RS*,12*RS*)-12-Acetoxy-6-hydroxy-11-methyl-tetradeca-7,9-diene 14a and (7*E*,9*Z*,6*RS*,12*RS*)-12-Acetoxy-6-hydroxy-11-methyl-tetradeca-7,9-diene 15a. Dienes **13a**, **14a** and **15a** were prepared using general procedure F from iron lactone complex **8b** (140 mg, 0.28 mmol) in THF (6 cm^3) and lithium naphthalenide (1.4 cm^3, 1.4 mmol, 1 mol dm^{-3} solution in THF). Work-up as described above followed by flash column chromatography (eluent – Et_2O–petrol 1 : 3⟶1 : 1) afforded an inseparable mixture of dienes **13a**, **14a** and **15a** (0.70 : 0.17 : 0.13) as an oil (73 mg, 94%); ν_{max}(film)/cm^{-1} 3379 (OH) and 1732 (C=O); δ_H(600 MHz; $CDCl_3$) 6.47 (0.13 H, dd, *J* 14.9 and 11.2, 8-H × 0.13), 6.36 (0.17 H, dd, *J* 14.5 and 11.7, 9-H × 0.17), 6.16 (0.70 H, dd, *J* 15.0 and 10.5, 8-H × 0.70), 6.06 (0.87 H, dd, *J* 15.0 and 10.5, 8-H × 0.17 and 9-H × 0.70), 6.01 (0.13 H, m, 9-H × 0.13), 5.70 (0.13 H, dd, *J* 15.0 and 10.5, 7-H × 0.13), 5.60 (1.57 H, dd, *J* 15.0 and 7.0, 7-H × 0.70 and 10-H × 0.87), 5.40 (0.13 H, m, 10-H × 0.13), 5.31 (0.17 H, m, 7-H × 0.17), 4.75 (1.00 H, m, 12-H × 1.00), 4.55 (0.17 H, m, 6-H × 0.17), 4.17 (0.13 H, d, *J* 5.7, 6-H × 0.13), 4.11 (0.70 H, d, *J* 5.8, 6-H × 0.70), 2.38–2.29 (2.00 H, m, 11-H × 2.00), 2.03 (3.00 H, m, $COCH_3$), 1.83 (1.00 H, m, 13-H × 1.00), 1.58–1.25 (8.00 H, m, 2-H × 2.00, 3-H × 2.00, 4-H × 2.00 and 5-H × 2.00) and 0.89 (9.00 H, m, 1-H × 3.00, 13-CCH_3 and 14-H × 3.00); δ_C(150 MHz; $CDCl_3$) 170.8, 134.7, 132.1, 130.4, 129.8, 77.8, 72.7, 37.3, 34.7, 31.7, 30.9, 25.0, 22.6, 21.1, 18.6, 17.5 and 14.0; *m*/*z*(EI) 264 (5%, $M^+ - H_2O$) and 99 (100); [Found ($M^+ - H_2O$) 264.2081. $C_{17}H_{28}O_2$ requires $M - H_2O$, 264.2089].

(7*E*,9*E*,6*RS*,12*RS*)-12-Acetoxy-12-cyclohexyl-6-hydroxy-dodeca-7,9-diene 13b (7*Z*,9*E*,6*RS*,12*RS*)-12-Acetoxy-12-cyclohexyl-6-hydroxy-dodeca-7,9-diene 14b and (7*E*,9*Z*,6*RS*,12*RS*)-12-Acetoxy-12-cyclohexyl-6-hydroxy-dodeca-7,9-diene 15b. Dienes **13b**, **14b** and **15b** were prepared using general procedure F from iron lactone complex **8c** (80 mg, 0.15 mmol) in THF (4 cm^3) and lithium naphthalenide (0.73 cm^3, 0.73 mmol, 1 mol dm^{-3} solution in THF). Work-up as described above followed by flash column chromatography (eluent – Et_2O–petrol 1 : 3⟶1 : 1) afforded an inseparable mixture of dienes **13b**, **14b** and **15b** (0.53 : 0.19 : 0.28) as an oil (43 mg, 92%); ν_{max}(film)/cm^{-1} 3455 (OH) and 1734 (C=O); δ_H(600 MHz; $CDCl_3$) 6.46 (0.28 H, dd, *J* 15.1 and 11.2, 8-H × 0.28), 6.35 (0.19 H, dd, *J* 14.7 and 11.7, 9-H × 0.19), 6.16 (0.53 H, dd, *J* 15.2 and 10.4, 8-H × 0.53), 6.04 (1.00 H, m, 8-H × 0.19 and 9-H × 0.81), 5.70 (0.28 H, dd, *J* 15.1 and 6.7, 7-H × 0.28), 5.64 (0.19 H, quin, *J* 7.5, 10-H × 0.19), 5.60 (1.06 H, dd, *J* 15.2 and 7.1, 7-H × 0.53 and 10-H × 0.53), 5.40 (0.28 H, m, 10-H × 0.28), 5.31 (0.19 H, t, *J* 9.8, 7-H × 0.19), 4.76 (1.00 H, m, 12-H × 1.00), 4.55 (0.19 H, m, 6-H × 0.19), 4.17 (0.28 H, d, *J* 5.3, 6-H × 0.28), 4.11 (0.53 H, d, *J* 5.6, 6-H × 0.53), 2.46–2.29 (3.00 H, m, 11-H × 2.00 and 1-H′ × 1.00), 2.02 (3.00 H, m, $COCH_3$), 1.74–1.12 (16.00 H, m, cyclohexyl × 8, 2-H × 2, 3-H × 2, 4-H × 2 and 5-H × 2), 1.02 (2.00 H, m, cyclohexyl × 2.00) and 0.88 (3 H, m, 1-H × 3.00); δ_C(150 MHz; $CDCl_3$) 170.8, 134.6, 132.1, 130.4, 129.8, 77.1, 72.7, 40.8, 37.3, 34.8, 31.7, 29.0, 28.1, 26.3, 26.0, 25.0, 22.6, 21.1, 21.1 and 14.0; *m*/*z*(EI) 304 (5%, $M^+ - H_2O$) and 69 (100); [Found ($M^+ - H_2O$) 304.2416. $C_{20}H_{32}O_2$ requires $M - H_2O$, 304.2402].

(5*E*,7*E*,2*R*,4*R*)-2,10-Di(*tert*-butyl-dimethyl-silanyloxy)-4-hydroxy-deca-5,7-diene 13c (5*Z*,7*E*,2*R*,4*R*)-2,10-Di(*tert*-butyl-dimethyl-silanyloxy)-4-hydroxy-deca-5,7-diene 14c and (5*E*,7*Z*,2*R*,4*R*)-2,10-Di(*tert*-butyl-dimethyl-silanyloxy)-4-hydroxy-deca-5,7-diene 15c. Method 1: dienes **13c**, **14c** and **15c** were prepared according to general procedure F from iron lactone complex **7a** (140 mg, 0.22 mmol) in THF (5 cm^3) and lithium naphthalenide (1.1 cm^3, 1.1 mmol, 1 mol dm^{-3} solution in THF). Work-up as described above followed by flash column chromatography (eluent – Et_2O–petrol 1 : 3⟶1 : 1) afforded an inseparable mixture of dienes **13c**, **14c** and **15c** (0.62 : 0.15 : 0.23) as an oil (87 mg, 96%); ν_{max}(film)/cm^{-1} 3432 (OH); δ_H(600 MHz; $CDCl_3$) 6.53 (0.23 H, dd, *J* 15.1 and 11.1, 6-H × 0.23), 6.39 (0.15 H, dd, *J* 14.7 and 11.8, 7-H × 0.15), 6.21 (0.62 H, dd, *J* 15.1 and 10.6, 6-H × 0.62), 6.06 (0.85 H, dd, *J* 15.3 and 10.6, 7-H × 0.85), 5.97 (0.15 H, t, *J* 11.0, 6-H × 0.15), 5.71 (0.15 H, m, 8-H × 0.15), 5.67 (0.85 H, m, 5-H × 0.23 and 8-H × 0.62), 5.57 (0.62 H, dd, *J* 15.1 and 6.2, 5-H × 0.62), 5.45 (0.23 H, m, 8-H × 0.23), 5.32 (0.15 H, dd, *J* 10.4 and 9.0, 5-H × 0.15), 4.72 (0.15 H, m, 4-H × 0.15), 4.35 (0.23 H, m, 4-H × 0.23), 4.31 (0.62 H, m, 4-H × 0.62), 4.08 (1.00 H, m, 2-H × 1.00), 3.63 (2.00 H, m, 10-H × 2.00), 2.41 (0.46 H, m, 9-H × 0.46), 2.30 (1.54 H, m, 9-H × 1.54), 1.69–1.58 (2.00 H, m, 3-H × 2.00), 1.19 (3.00 H, m, 1-H × 3.00), 0.90 (18.00 H, m, $SiC(CH_3)_3$), 0.11 (6.00 H, m, $Si(CH_3)$ × 2) and 0.04 (6.00 H, m, $Si(CH_3)$ × 2); δ_C(150 MHz; $CDCl_3$) 133.8, 131.4, 130.9, 129.9, 71.6, 69.2, 62.8, 46.3, 36.2, 25.9, 25.8, 24.5, 18.3, 17.9, −3.9, −4.8, −5.3 and −5.3; *m*/*z*(ES) 437 (100%, MNa^+); [Found (MNa^+) 437.2870. $C_{22}H_{46}NaO_3Si_2$ requires *M*Na, 437.2883].

Method 2: dienes **13c**, **14c** and **15c** were prepared according to general procedure F from iron lactone complex **7b** (160 mg, 0.25 mmol) in THF (5 cm^3) and lithium naphthalenide (1.3 cm^3, 1.3 mmol, 1 mol dm^{-3} solution in THF]). Work-up as described above followed by flash column chromatography (eluent – Et_2O–petrol 1 : 3⟶1 : 1) afforded an inseparable mixture of dienes **13c**, **14c** and **15c** (0.26 : 0.67 : 0.07) as an oil (102 mg, 98%); ν_{max}(film)/cm^{-1} 3431 (OH); δ_H(600 MHz; $CDCl_3$) 6.53 (0.07 H, dd, *J* 15.1 and 11.1, 6-H × 0.07), 6.39 (0.67 H, dd, *J* 14.7 and 11.8, 7-H × 0.67), 6.21 (0.26 H, dd, *J* 15.1 and 10.6, 6-H × 0.26), 6.06 (0.33 H, dd, *J* 15.3 and 10.6, 7-H × 0.33), 5.97 (0.67 H, t, *J* 11.0, 6-H × 0.67), 5.71 (0.67 H, m, 8-H × 0.67), 5.67 (0.33 H, m, 5-H × 0.07 and 8-H × 0.26), 5.57 (0.26 H, dd, *J* 15.1 and 6.2, 5-H × 0.26), 5.45 (0.07 H, m, 8-H × 0.07), 5.32 (0.67 H, dd, *J* 10.4 and 9.0, 5-H × 0.67), 4.72 (0.67 H, m, 4-H × 0.67), 4.35 (0.07 H, m, 4-H × 0.07), 4.31 (0.26 H, m, 4-H × 0.26), 4.08 (1.00 H, m, 2-H × 1.00), 3.63 (2.00 H, m, 10-H × 2.00), 2.41 (0.14 H, m, 9-H × 0.14), 2.30 (1.86 H, m, 9-H × 1.86), 1.69–1.58 (2.00 H, m, 3-H × 2.00), 1.19 (3.00 H, m, 1-H × 3.00), 0.90 (18.00 H, m, $SiC(CH_3)_3$), 0.11 (6.00 H, m, $Si(CH_3)$ × 2) and 0.04 (6.00 H, m, $Si(CH_3)$ × 2); δ_C(150 MHz; $CDCl_3$) 132.8, 131.9, 129.5, 127.1, 69.3, 67.5, 62.7, 46.3, 36.4, 25.9, 25.8, 24.5, 18.3, 17.9, −3.9, −4.8, −5.3 and −5.3; *m*/*z*(ES) 437 (100%, MNa^+); [Found (MNa^+) 437.2869. $C_{22}H_{46}NaO_3Si_2$ requires *M*Na, 437.2883].

(7*E*,9*E*,6*RS*,12*RS*)-12-(*tert*-Butyl-dimethyl-silanyloxy)-6-hydroxy-11-methyl-tetradeca-7,9-diene 13d (7*Z*,9*E*,6*RS*,12*RS*)-12-(*tert*-Butyl-dimethyl-silanyloxy)-6-hydroxy-11-methyl-tetradeca-7,9-diene 14d and (7*E*,9*Z*,6*RS*,12*RS*)-12-(*tert*-Butyl-dimethyl-silanyloxy)-6-hydroxy-11-methyl-tetradeca-7,9-diene 15d. Dienes **13d**, **14d** and **15d** were prepared using general procedure F from iron lactone complex **11a** (85 mg, 0.15 mmol) in THF (4 cm^3) and lithium naphthalenide (0.73 cm^3, 0.73 mmol, 1 mol dm^{-3} solution in THF). Work-up as described above followed by flash column chromatography (eluent – Et_2O–petrol 1 : 3⟶1 : 1) afforded an inseparable mixture of dienes **13d**, **14d** and **15d** (0.62 : 0.20 : 0.18) as an oil (50 mg, 96%); ν_{max}(film)/cm^{-1} 3344 (OH); δ_H(600 MHz; $CDCl_3$) 6.47 (0.18 H, dd, *J* 15.1 and 11.1, 8-H × 0.18), 6.33 (0.20 H, dd, *J* 15.0 and 11.6, 9-H × 0.20), 6.17 (0.62 H, dd, *J* 15.2 and 10.4, 8-H × 0.62), 6.03 (1.00 H, m, 8-H × 0.20 and 9-H × 0.80), 5.70 (1.00 H, m, 7-H × 0.18 and 10-H × 0.82), 5.58 (0.62 H, dd, *J* 15.2 and 6.9, 7-H × 0.62), 5.49 (0.18 H, m, 10-H × 0.18), 5.29 (0.20 H, m, 7-H × 0.20), 4.57 (0.20 H, m, 6-H × 0.20), 4.12 (0.80 H, m, 6-H × 0.80), 3.48 (1.00 H, m, 12-H × 1.00), 2.30–2.20 (2.00 H, m, 11-H × 2.00), 1.61 (1.00 H, m, 13-H × 1.00), 1.57–1.29 (8.00 H, m, 2-H × 2.00, 3-H × 2.00, 4-H × 2.00 and 5-H × 2.00), 0.87 (18.00 H, m, 1-H × 3.00, 13-CCH_3, 14-H × 3.00 and $SiC(CH_3)_3$) and 0.03 (6.00 H, s, $Si(CH_3)$ × 2.00); δ_C(150 MHz; $CDCl_3$) 133.9, 131.9, 131.3, 130.8, 76.7, 72.8, 37.4, 37.3, 32.7, 31.7, 25.9, 25.0, 22.6, 18.5, 18.1, 17.3, 14.0, −4.2 and −4.6; *m*/*z*(EI) 354 (3%, M^+) and 73 (100); [Found (M^+) 354.2937. $C_{21}H_{42}O_2Si$ requires *M*, 354.2954].

(7*E*,9*E*,6*RS*,12*RS*)-6,12-Dihydroxy-12-methyl-tetradeca-7,9-diene and (7*Z*,9*E*,6*RS*,12*RS*)-6,12-Dihydroxy-12-methyl-tetradeca-7,9-diene. Dienes **13e** and **14e** were prepared using general procedure F from iron lactone complex **12a** (80 mg, 0.18 mmol) in THF (5 cm^3) and lithium naphthalenide (0.89 cm^3, 0.89 mmol, 1 mol dm^{-3} solution in THF). Work-up as described above followed by flash column chromatography (eluent – Et_2O–petrol 1 : 1) afforded an inseparable mixture of dienes **13e** and **14e** (0.74 : 0.26) as an oil (41 mg, 96%); ν_{max}(film)/cm^{-1} 3451 (OH); δ_H(600 MHz; $CDCl_3$) 6.44 (0.26 H, dd, *J* 14.6 and 11.6, 9-H × 0.26), 6.20 (0.74 H, dd, *J* 14.9 and 10.4, 8-H × 0.74), 6.13 (0.74 H, dd, *J* 14.9 and 10.4, 9-H × 0.74), 6.05 (0.26 H, t, *J* 11.0, 8-H × 0.26), 5.77 (0.26 H, quin, *J* 7.5, 10-H × 0.26), 5.71 (0.74 H, quin, *J* 7.4, 10-H × 0.74), 5.62 (0.74 H, dd, *J* 14.9 and 6.9, 7-H × 0.74), 5.33 (0.26 H, t, *J* 9.9, 7-H × 0.26), 4.57 (0.26 H, m, 6-H × 0.26), 4.12 (0.74 H, m, 6-H × 0.74), 3.40 (1.00 H, m, 12-H × 1.00), 2.33 (1.00 H, m, 11-H_A × 1.00), 2.17 (1.00 H, m, 11-H_B × 1.00), 1.69 (1.00 H, m, 13-H × 1.00), 1.58–1.28 (8.00 H, m, 2-H × 2.00, 3-H × 2.00, 4-H × 2.00 and 5-H × 2.00) and 0.92 (9.00 H, m, 1-H × 3.00, 13-CCH_3 and 14-H × 3.00); δ_C(150 MHz; $CDCl_3$) 134.8, 132.6, 130.9, 130.3, 75.8, 72.7, 37.6, 37.3, 33.1, 31.7, 25.1, 22.6, 18.7, 17.4 and 14.0; *m*/*z*(EI) 222 (10%, $M^+ - H_2O$) and 69 (100); [Found ($M^+ - H_2O$) 222.1983. $C_{15}H_{26}O$ requires $M - H_2O$, 222.1984].

(6*RS*,12*RS*)-6,12-Dihydroxy-heptadecane 16a. Alcohol **16a** was prepared according to general procedure H from acetate **8a** (105 mg, 0.20 mmol) in THF (5 cm^3), lithium naphthalenide (2.0 cm^3, 2.0 mmol, 1 mol dm^{-3} solution in THF) and MeOH (5 cm^3). Work-up as described above followed by flash column chromatography (eluent – Et_2O–petrol 1 : 1) and reduction catalysed by Pd/C (100 mg, 10 wt.% Pd (dry basis) on activated carbon) in EtOAc (5 cm^3) afforded alkanol **16a** (43 mg, 81%); ν_{max}(sol^n:CH_2Cl_2)/cm^{-1} 3350 (OH); δ_H(400 MHz; $CDCl_3$) 3.59 (2 H, m, 6-H and 12-H), 1.62–1.05 (28 H, m, 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2, 7-H × 2, 8-H × 2, 9-H × 2, 10-H × 2, 11-H × 2, 13-H × 2, 14-H × 2, 15-H × 2, 16-H × 2 and OH × 2) and 0.90 (6 H, t, *J* 6.9, 1-H × 3 and 17-H × 3); δ_C(100 MHz; $CDCl_3$) 72.0, 37.5, 37.4, 31.9, 29.7, 25.6, 25.3, 22.6 and 14.0; *m*/*z*(FAB) 273 (10%, MH^+), 149 (100); [Found (MH^+) 273.2787. $C_{17}H_{37}O_2$ requires *M*H, 273.2794].

(3*RS*,9*RS*)-3,9-Dihydroxy-2-methyl-tetradecane 16b. Method 1: alcohol **16b** was prepared according to general procedure H from acetate **8b** (90 mg, 0.18 mmol) in THF (5 cm^3), lithium naphthalenide (1.8 cm^3, 1.8 mmol, 1 mol dm^{-3} solution in THF) and MeOH (5 cm^3). Work-up as described above followed by flash column chromatography (eluent – Et_2O–petrol 1 : 1) and reduction catalysed by Pd/C (100 mg, 10 wt.% Pd (dry basis) on activated carbon) in EtOAc (5 cm^3) afforded alkanol **16b** (36 mg, 83%); ν_{max}(sol^n:CH_2Cl_2)/cm^{-1} 3602 (OH); δ_H(400 MHz; $CDCl_3$) 3.60 (2 H, m, 3-H and 9-H), 1.56–1.28 (21 H, m, 2-H, 4-H × 2, 5-H × 2, 6-H × 2, 7-H × 2, 8-H × 2, 10-H × 2, 11-H × 2, 12-H × 2, 13-H × 2 and OH × 2) and 0.91 (9 H, m, 1-H × 3, 2-CCH_3 and 17-H × 3); δ_C(100 MHz; $CDCl_3$) 72.0, 71.7, 39.7, 37.5, 37.4, 37.4, 31.9, 30.2, 29.7, 25.6, 25.3, 22.6, 18.8, 14.1 and 14.0; *m*/*z*(FAB) 245 (10%, MH^+), 137 (100); [Found (MH^+) 245.2478. $C_{15}H_{33}O_2$ requires *M*H, 245.2480].

Method 2: alcohol **16b** was prepared according to general procedure I from diene mixture **13e** and **14e** (0.74 : 0.26) (32 mg, 0.13 mmol) with Pd/C (30 mg, 10 wt.% Pd (dry basis) on activated carbon) in EtOAc (1 cm^3). After 2 hours work-up as described afforded alkanol **16b** as an oil (33 mg, 100%). Data were consistent with those reported (*vide supra*).

(3*RS*,9*RS*)-3-Acetoxy-9-hydroxy-2-methyl-tetradecane 17a. Alcohol **17a** was prepared according to general procedure I from diene mixture **13a**, **14a** and **15a** (0.70 : 0.17 : 0.13) (25 mg, 0.09 mmol) with Pd/C (25 mg, 10 wt.% Pd (dry basis) on activated carbon) in EtOAc (1 cm^3). After 2 hours work-up as described above afforded alkanol **17a** as an oil (25 mg, 99%); ν_{max}(film)/cm^{-1} 3468 (OH) and 1733 (C=O); δ_H(600 MHz; $CDCl_3$) 4.73 (1 H, m, 3-H), 3.58 (1 H, m, 9-H), 2.04 (3 H, s, $COCH_3$), 1.80 (1 H, m, 2-H), 1.56–1.22 (19 H, m, 4-H × 2, 5-H × 2, 6-H × 2, 7-H × 2, 8-H × 2, 10-H × 2, 11-H × 2, 12-H × 2, 13-H × 2 and OH) and 0.89 (9 H, m, 1-H × 3, 2-CCH_3 and 14-H × 3); δ_C(150 MHz; $CDCl_3$) 171.0, 78.4, 71.9, 37.5, 37.4, 31.9, 31.4, 31.0, 29.6, 29.5, 25.5, 25.3, 22.6, 21.1, 18.5, 17.5 and 14.0; *m*/*z* (EI) 268 (5%, $M^+ - H_2O$) and 69 (100); [Found ($M^+ - H_2O$) 268.2386. $C_{17}H_{32}O_2$ requires $M - H_2O$, 268.2402].

(1*RS*,7*RS*)-1-Acetoxy-1-cyclohexyl-7-hydroxy-dodecane 17b. Alcohol **17b** was prepared according to general procedure I from diene mixture **13b**, **14b** and **15b** (0.53 : 0.19 : 0.28) (38 mg, 0.12 mmol) with Pd/C (38 mg, 10 wt.% Pd (dry basis) on activated carbon) in EtOAc (1 cm^3). After 2 hours work-up as described afforded alkanol **17b** as an oil (38 mg, 99%); ν_{max}(film)/cm^{-1} 3430 (OH) and 1736 (C=O); δ_H(600 MHz; $CDCl_3$) 4.73 (1 H, m, 1-H), 3.58 (1 H, m, 7-H), 2.04 (3 H, s, $COCH_3$), 1.74–1.22 (28 H, m, cyclohexyl × 9, 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2, 6-H × 2, 8-H × 2, 9-H × 2, 10-H × 2, 11-H × 2 and OH), 1.00 (2 H, m, cyclohexyl × 2) and 0.89 (3 H, t, *J* 6.9, 12-H × 3); δ_C(150 MHz; $CDCl_3$) 171.0, 78.0, 71.9, 41.2, 37.5, 37.4, 31.9, 31.0, 29.5, 29.0, 28.0, 26.4, 26.1, 26.0, 25.5, 25.4, 25.3, 22.6, 21.1 and 14.1; *m*/*z* (ES) 349 (40%, MNa^+) and 347 (100); [Found (MNa^+) 349.2708. $C_{20}H_{38}NaO_3$ requires *M*Na, 349.2719].

(2*RS*,4*SR*)-2,10-Di(*tert*-butyl-dimethyl-silanyloxy)-4-hydroxy-decane 18. Method 1: alcohol **18** was prepared according to general procedure I from diene mixture **13c**, **14c** and **15c** (0.26 : 0.67 : 0.07) (90 mg, 0.22 mmol) with Pd/C (90 mg,10 wt.% Pd (dry basis) on activated carbon) in EtOAc (2 cm^3). After 2 hours work-up as described above afforded alkanol **18** as an oil (91 mg, 100%); $[\alpha]_D^{25}$ −13.6 (*c* 0.25 in CH_2Cl_2); ν_{max}(film)/cm^{-1} 3425 (OH); δ_H(600 MHz; $CDCl_3$) 4.08 (1 H, m, 2-H), 3.74 (1 H, m, 4-H), 3.59 (2 H, t, *J* 6.6, 10-H × 2), 1.55–1.28 (12 H, m, 3-H × 2, 5-H × 2, 6-H × 2, 7-H × 2, 8-H × 2, 9-H × 2 and OH), 1.18 (3 H, d, *J* 6.2, 1-H × 3), 0.91 (9 H, m, $SiC(CH_3)_3$ × 1), 0.89 (9 H, m, $SiC(CH_3)_3$ × 1), 0.12 (3 H, m, $Si(CH_3)$ × 1), 0.11 (3 H, m, $Si(CH_3)$ × 1) and 0.04 (6 H, m, $Si(CH_3)$ × 2); δ_C(150 MHz; $CDCl_3$) 71.5, 70.2, 63.3, 45.8, 37.6,

32.8, 29.5, 25.9, 25.8, 25.8, 25.4, 24.6, 18.3, 17.9, −3.9, −4.8, −5.3 and −5.3; *m*/*z* (ES) 441 (100%, MNa^+); [Found (MNa^+) 441.3178. $C_{22}H_{50}NaO_3Si_2$ requires *M*Na, 441.3196].

Method 2: alcohol **18** was prepared according to general procedure I from diene mixture **13c**, **14c** and **15c** (0.62 : 0.15 : 0.23) (71 mg, 0.17 mmol) with Pd/C (71 mg, 10 wt.% Pd (dry basis) on activated carbon) in EtOAc (2 cm^3). After 2 hours work-up as described afforded alkanol **18** as an oil (70 mg, 98%). Data were consistent with those reported (*vide supra*).

(3*RS*,9*RS*)-3-(*tert*-Butyl-dimethyl-silanyloxy)-9-hydroxy-2-methyl-tetradecane 19a. Alcohol **19a** was prepared according to general procedure I from diene mixture **13d**, **14d** and **15d** (0.62 : 0.20 : 0.18) (30 mg, 0.08 mmol) with Pd/C (30 mg, 10 wt.% Pd (dry basis) on activated carbon) in EtOAc (1 cm^3). After 2 hours work-up as described above afforded alkanol **19a** as an oil (30 mg, 99%); ν_{max}(film)/cm^{-1} 3421 (OH); δ_H(600 MHz; $CDCl_3$) 3.60 (1 H, m, 9-H), 3.41 (1 H, m, 3-H), 1.68 (1 H, m, 2-H), 1.56–1.28 (19 H, m, 4-H × 2, 5-H × 2, 6-H × 2, 7-H × 2, 8-H × 2, 10-H × 2, 11-H × 2, 12-H × 2, 13-H × 2 and OH), 0.89 (12 H, m, 14-H × 3 and $SiC(CH_3)_3$), 0.85 (3 H, d, *J* 6.8, 2-CCH_3), 0.83 (3 H, d, *J* 6.8, 1-H × 3) and 0.02 (6 H, s, $Si(CH_3)$ × 2); δ_C(150 MHz; $CDCl_3$) 76.8, 72.0, 37.4, 33.1, 32.7, 31.9, 30.0, 25.9, 25.6, 25.5, 25.3, 22.6, 18.2, 18.1, 17.6, 14.1, 14.0, −4.3 and −4.5; *m*/*z* (EI) 341 (40%, M^+ − OH) and 69 (100); [Found (M^+ − OH) 341.3250. $C_{21}H_{45}OSi$ requires *M* − OH, 341.3240].

(6*RS*,12*RS*)-6-(*tert*-Butyl-dimethyl-silanyloxy)-12-hydroxy-heptadecane 19b. Alcohol **19b** was prepared according to general procedure G from acetate **11b** (70 mg, 0.12 mmol) in THF (3 cm^3) and lithium naphthalenide (0.58 cm^3, 0.58 mmol, 1 mol dm^{-3} solution in THF). Work-up as described above followed by flash column chromatography (eluent – Et_2O–petrol 1 : 3⟶1 : 1) and reduction catalysed by Pd/C (70 mg, 10 wt.% Pd (dry basis) on activated carbon) in EtOAc (3 cm^3) afforded alkanol **19b** (40 mg, 89%); ν_{max}(sol^n:CH_2Cl_2)/cm^{-1} 3423 (OH); δ_H(400 MHz; $CDCl_3$) 3.60 (2 H, m, 6-H and 12-H), 1.58–1.15 (27 H, m, 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2, 7-H × 2, 8-H × 2, 9-H × 2, 10-H × 2, 11-H × 2, 13-H × 2, 14-H × 2, 15-H × 2, 16-H × 2 and OH), 0.90 (15 H, m, 1-H × 3, 17-H × 3 and $SiC(CH_3)_3$) and 0.04 (6 H, s, $Si(CH_3)$ × 2); δ_C(100 MHz; $CDCl_3$) 72.4, 72.0, 37.8, 37.8, 37.5, 37.4, 32.1, 31.9, 29.6, 25.9, 25.9, 25.6, 25.3, 25.0, 22.6, 22.6, 18.1, 14.0, 14.0, −4.4 and −4.4; *m*/*z* (FAB) 386 (20%, M^+), 215 (100); [Found (M^+) 386.3584. $C_{23}H_{50}O_2Si$ requires *M*, 386.3580].

Acknowledgements

We thank the EPSRC (C. J. H.), the Isaac Newton Trust Bursary Scheme (C. J. H.), the B. P. Endowment (S. V. L.) and the Novartis Research Fellowship (S. V. L.) for support of this work, and E. A. Wright for helpful discussions.

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