Reductive decomplexation of π-allyltricarbonyliron lactone complexes: a new route to stereodefined acyclic 1,5-diols and 1,5,7-triols

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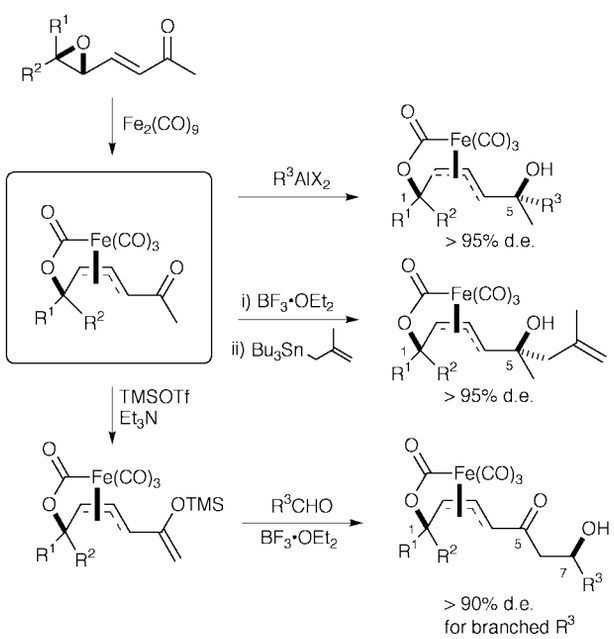
Treatment of π-allyltricarbonyliron lactone complexes with hydride donors causes decomplexation to acyclic alcohols. When sodium borohydride is used, decomplexation is accompanied by some degree of stereochemical scrambling and mixtures of saturated and unsaturated products are obtained. Treatment with sodium triacetoxyborohydride, however, affords only unsaturated products in which the alcohol stereocentres are preserved. Mechanisms for the decomplexation and isomerisation processes are proposed.

The continuing discovery of diverse, biologically interesting natural products provides a constant supply of new challenges for the synthetic chemist. A great deal of attention has been focused on the stereoselective synthesis of polyol structures, which are characteristic components of a number of natural products, including the polyene macrolide antibiotics.[1] While the aldol reaction remains one of the most reliable methods for polyol construction, some extensions to the established aldol methodology and interesting alternative strategies have recently emerged.[2] In many of these approaches, the stereocontrolled construction or functionalisation of the linear carbon chain is facilitated by temporarily restricting the number of degrees of freedom in the molecule. This can be achieved *via* a cyclic intermediate or transition state and often involves metal complexation of the organic substrate. Additional versatility could be introduced by employing a transition metal in this structural role. The ability of the d-block metals to form rigid complexes with high coordination numbers allows the design of systems with built-in stereochemical control features. This has already been demonstrated for a number of organometallic complexes which show high diastereoselectivity in the reactions of appended functional groups.[3] The possibility also arises for the development of new transformations by manipulation of the oxidation state, mode of complexation, coordination number or geometry of the metal centre.

We have recently demonstrated the use of π-allyltricarbonyliron lactone complexes as chiral templates for remote asymmetric induction. Stereochemical information can be transferred from the lactone tether, *via* the bulky tricarbonyliron moiety, allowing the controlled construction of new stereocentres at the periphery of the organic ligand. Excellent diastereoselectivity has been obtained in the manipulation of a ketone group appended to the allyl unit (Scheme 1). Thus a 1,5-stereochemical relationship of oxygen functionalities can be established in a controlled manner by the addition of organoaluminium reagents[4] or allylstannanes[5] into the side-chain ketone. High diastereoselectivity has also been achieved in the Mukaiyama aldol reactions of π-allyltricarbonyliron lactone complexes bearing a silyl enol ether functionality in the side-chain.[6] This reaction constitutes a rare example of an overall 1,7-asymmetric induction (Scheme 1).[7] Regeneration of the ketone functionality at C-5 permits further stereoselective transformations on the products.

The removal of the tricarbonyliron moiety can be accomplished in a variety of ways. Oxidation using ceric ammonium nitrate leads to the stereospecific formation of β-lactones,

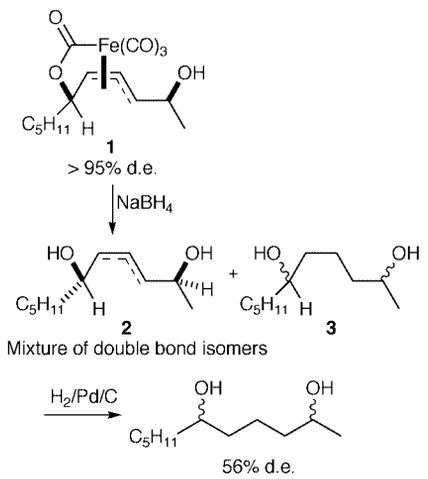


Scheme 1

while δ-lactones can be accessed under exhaustive carbonylation conditions. Treatment with barium hydroxide results in decarboxylation to afford (η^4-diene)tricarbonyliron complexes. These reactions have found use in several natural product syntheses within our group.[8,9] There is no established methodology, however, for the detachment of the organic ligand as an acyclic molecule with the lactone tether stereocentre preserved. The high stereoselectivities obtained in nucleophilic addition and Mukaiyama aldol reactions (Scheme 1) led us to consider the potential of π-allyltricarbonyliron lactone complexes as tools for polyol construction, as the products can be regarded as masked acyclic diols and triols. We therefore required a means of releasing the organic ligand as a linear carbon chain and unmasking the lactone tether stereogenic centre as a free hydroxy group.

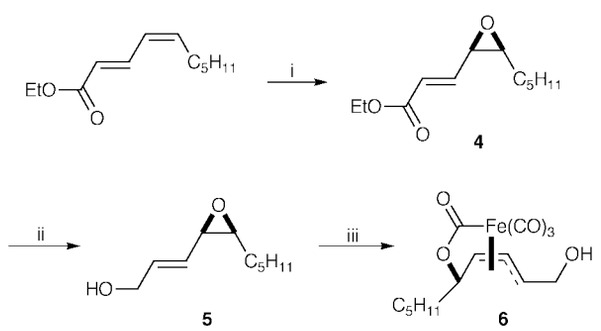
The potential of hydride donors as decomplexing agents rapidly became apparent.[10] Treatment of a methanolic solution of secondary alcohol complex **1** with excess sodium borohydride caused an immediate colour change, the colourless solution turning a deep blood red colour. A mixture of unsaturated and saturated diol decomplexation products **2** and

3 were isolated from the reaction. On hydrogenation of this mixture, however, it was discovered that isomerisation of the methanol stereocentres had occurred, the diastereomeric excess having dropped from greater than 95% to around 56% over the course of the reactions (Scheme 2).



Scheme 2

The loss of stereochemical integrity could be explained if the double bond of the unsaturated diol was subject to tricarbonyliron-catalysed positional isomerisation under the reaction conditions.[11] This would lead to formation of an enol, which on tautomerisation to the corresponding ketone would be non-stereospecifically reduced by the excess sodium borohydride. Evidence to support this proposed sequence of events was obtained using deuteration experiments. The racemic primary alcohol complex **6** was prepared as shown in Scheme 3. Treatment with sodium borodeuteride in methanol resulted in a mixture of products, as before, from which the deuteration pattern was determined by analysis of the ^{13}C NMR spectrum. The characteristic 1 : 1 : 1 triplets which signify ^{13}C–^{2}H coupling were observed at 30.4, 36.4, 39.8 and 61.9 ppm. All four signals arose from carbon atoms with one attached proton and our interpretation of the data is as shown in Scheme 4. The pertinent signal is that at 61.9 ppm which represents the -C(H)(D)OH group, showing that the side-chain alcohol position is indeed involved in the reaction sequence. It is not clear whether the lactone tether position is also involved, as deuteration at this position would give rise to a quaternary carbon atom whose triplet signal would probably be masked by noise. In a separate experiment, complex **6** was treated with sodium borohydride in deuterated methanol. In this case there was no observable deuteration in the decomplexation products.



Scheme 3 *Reagents and conditions*: (i) DMDO, CH_2Cl_2, 0 °C, 3.5 h, 77%; (ii) DIBAL-H, THF, −78 °C, 75 min, 76%; (iii) $Fe_2(CO)_9$, THF, 2 h, 58%.

A possible mechanism for the decomplexation is shown in Fig. 1. Hydride delivery to one of the carbonyl ligands would release the lactone tether and produce a formyl ligand, which would rapidly extrude carbon monoxide. The resulting iron hydride species could deliver hydrogen to either terminus of the allyl system to afford a coordinatively unsaturated η^2-complex. If this step was irreversible, detachment of the iron would yield a mixture of unsaturated diols **7a** and **7b**. On the other hand, reversible hydride delivery from the iron would allow positional and geometric isomerisation of the double bond and loss of stereochemical integrity at the methanol centres, resulting in formation of the saturated diol **8** (Table 1).

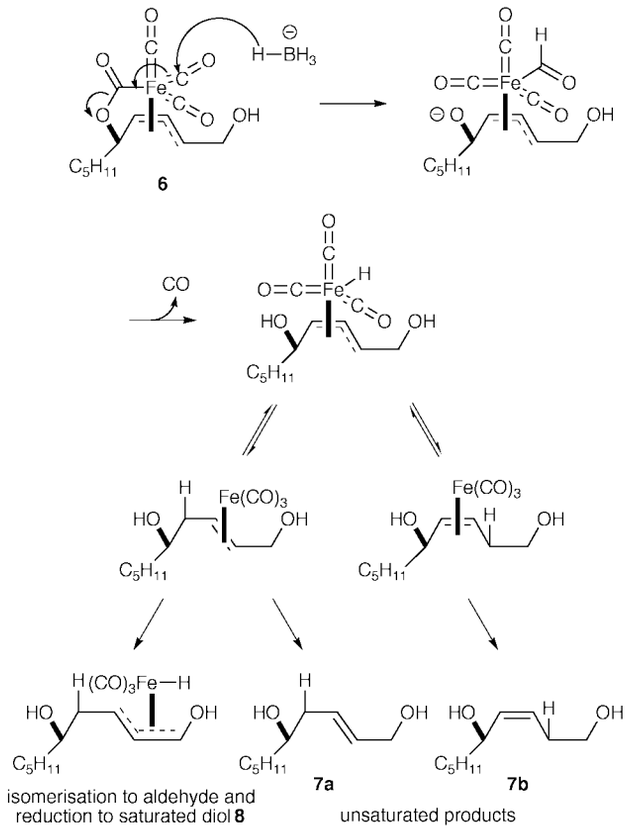
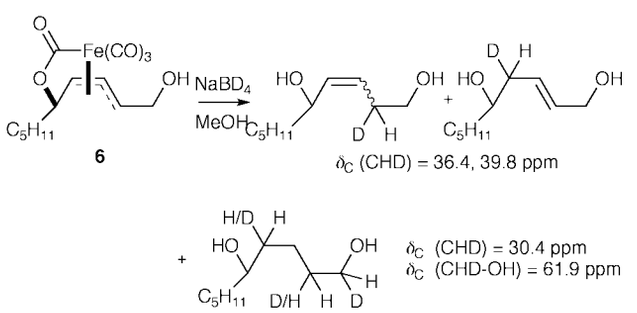


Fig. 1



Scheme 4

Based on the proposed mechanism, the isomerisation of methanol centres in the reaction products should always be accompanied by the conversion of unsaturated diols to saturated ones and this could be used as a convenient measure of the extent of isomerisation. The primary alcohol **6** was found, by this measure, to be more prone to isomerisation under the $NaBH_4$–MeOH conditions than the secondary alcohol **1** (*i.e.* more saturated product was obtained) and **6** was therefore used in an extensive screen of different reducing systems. Selected results are shown in Table 1. In cases where quantitative decomplexation occurred, the ratio of unsaturated to saturated diols was calculated from the proton NMR spectra of the product mixtures, by comparing the sum of the integrals for the olefinic CH protons (δ_H = 5–6 ppm) with that for protons in the C*H*OH region (δ_H = 3–4.5 ppm).

No reaction was observed on treatment of **6** with borane–dimethyl sulfide in THF or sodium cyanoborohydride in methanol–HCl. Treatment with Red-Al, superhydride, K-selectride or $LiAlH_4$ in THF resulted in decomposition to mixtures of diols together with η^4-dienes and other unwanted decomplexation products. Under the Luche reduction conditions[12] (Table 1, entry 2) rapid isomerisation occurred and the saturated alcohol **8** was the major product. When sodium triacetoxyborohydride in THF was used, however, quantitative decomplexation to unsaturated diol products was observed (Table 1, Entry 5).

A variety of different lactone complexes were exposed to the sodium triacetoxyborohydride conditions. Interestingly, in contrast to the decomplexation using sodium borohydride, only complexes containing a free hydroxy group in the side-chain were found to react. Treatment of complexes lacking this hydroxy group, or those in which the alcohol was protected as an acetate, silyl ether or acetonide, only resulted in recovery of the starting material. Sodium triacetoxyborohydride is known to selectively reduce β-hydroxy ketones over ketones without a proximal hydroxy group. It therefore seems likely that the side-chain hydroxy group participates in the decomplexation reaction, for example by directing hydride delivery to a carbon monoxide ligand. This mechanistic difference may be connected with the difference in selectivity observed using the two reducing agents.

A number of lactone complexes bearing side-chain hydroxy groups were decomplexed under the sodium triacetoxyborohydride conditions and the results are shown in Table 2. In each case, the product mixture contained *three* components, rather than two as expected (see Fig. 1). The major component was the *cis* unsaturated diol (*e.g.* **7b**, **19** and **23**), which could in some cases be isolated by careful flash chromatography. In addition, two *trans* unsaturated diols were obtained as an inseparable mixture. The "extra" *trans* product could arise from geometric isomerisation of the π-allyltricarbonyliron hydride intermediate, following the release of the lactone tether (Fig. 2).[8] Such a process would not lead to any stereochemical scrambling at the alcohol centres.

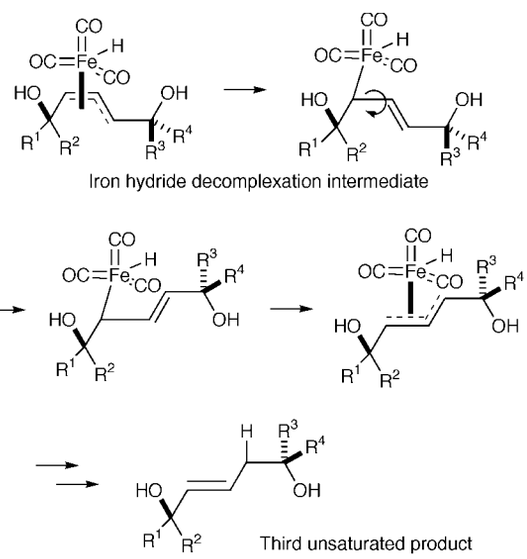
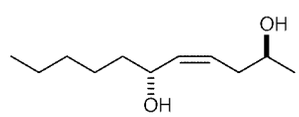


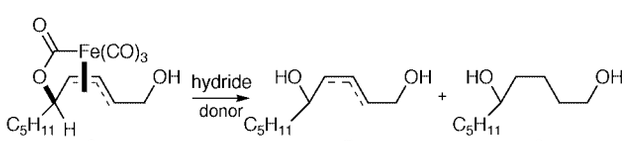
Fig. 2



19

The overall proportion of *cis* to *trans* olefins was typically around 2:1. These products were recombined and hydrogenated in order to facilitate characterisation and determination of the diastereomeric excesses. In the case of the *syn* 5,7-diol complex **13**, prepared by a Mukaiyama aldol reaction of complex **20** followed by stereoselective reduction of the C-5 ketone group,[6] the *cis* unsaturated 1,5,7-triol decomplexation product **23** was isolated in 31% yield (Scheme 5). After recombination with the other ene triol products and hydrogenation according to the standard procedure, the fully saturated, monoprotected 1,5,7-triol **18** was obtained in 57% yield over the two steps, as a single diastereoisomer according to 600 MHz

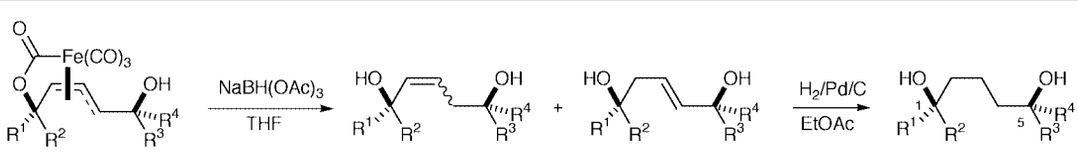
Table 1 Decomplexation of **6** using different reducing agents



Entry	Reagent	Solvent	*T*/°C	*t*/h	Ratio **7**:**8**[a]
1	$NaBH_4$	MeOH	rt	8	21:79
2	$NaBH_4$–$CeCl_3$	MeOH–THF	0	18	43:57
3	$LiBH_4$	THF	0	8	73:27
4	$LiBHEt_3$	THF	−78 to rt	24	>85:<15[b]
5	$NaBH(OAc)_3$	THF	20	24	100:0

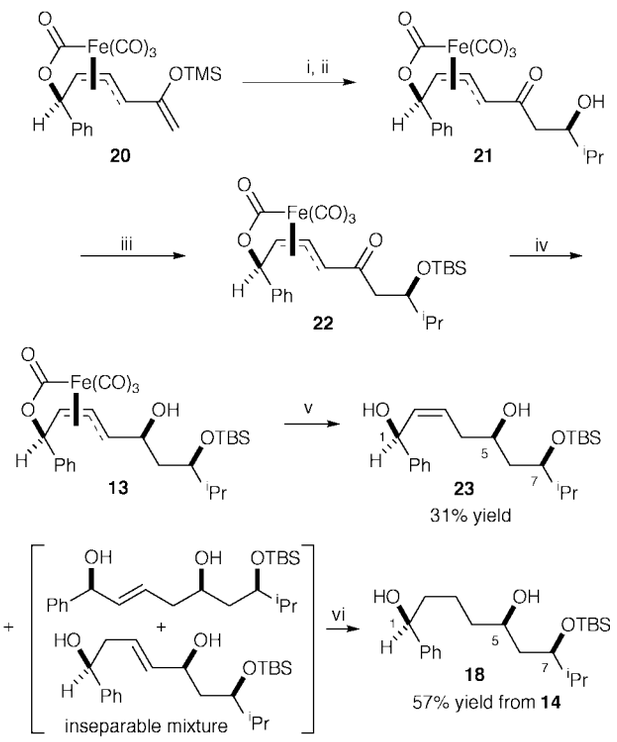
[a] Ratio determined by comparison of integrals in the ^{1}H NMR spectrum of the crude mixture. [b] The crude mixture also contained unwanted by-products.

Table 2 Decomplexation of a range of functionalised π-allyltricarbonyliron complexes using $NaBH(OAc)_3$



Entry	Complex	R^1	R^2	R^3	R^4	Product	Yield (%)[a]	De (%)[b]
1	**6**	C_5H_{11}	H	H	H	**8**	59	—
2	**9**	H	C_5H_{11}	Ph	H	**14**	71	96
3	**10**[c]	Me	H	$(CH_2)_4OR$	H	**15**[d]	63	>96
4	**11**	H	C_5H_{11}	Me	H	**16**	82	>96
5	**12**	H	C_5H_{11}	Me	^{n}Pr	**17**	52	>96
6	**13**	H	Ph	$CH_2CH(OTBS)^iPr$	H	**18**	57	>96

[a] Isolated yield of saturated diol over two steps. [b] Diastereomeric excess determined by comparison of integrals in the 600 MHz ^{1}H NMR spectrum. [c] R = Bn. [d] R = H.



Scheme 5 *Reagents and conditions*: (i) ^{i}PrCHO, BF_3·OEt_2, Et_2O–CH_2Cl_2, −78 °C, 6 h; (ii) HF·pyridine, THF, 30 min, 55% over two steps; (iii) TBSOTf, 2,6-lutidine, CH_2Cl_2, −40 °C, 2 h, 66%; (iv) $^{i}Bu_3Al$, PhH, 0–5 °C, 40 min, 67%; (v) $NaBH(OAc)_3$, THF, 20 °C, 96%; (vi) Pd/C, H_2, EtOAc, 7 h, 57%.

^{1}H NMR analysis. This reaction sequence illustrates the utility of π-allyltricarbonyliron lactone complex chemistry for the construction of remote stereocentres and its potential, in combination with this new decomplexation methodology, for application in the synthesis of linear polyols.

In summary, a decomplexation reaction has been developed which allows removal of the iron carbonyl moiety from functionalised π-allyltricarbonyliron lactone complexes and conversion into functionalised alcohols without loss of stereochemical integrity. Application of this procedure to the products of nucleophilic addition into ketone complexes constitutes an expedient route to stereodefined 1,5-diols, while application to the products of Mukaiyama aldol reactions allows access to stereodefined 1,5,7-triols.

Experimental

^{1}H NMR spectra were recorded in $CDCl_3$ on Bruker DRX-600, DPX-400 or DPX-200 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) was used as the internal reference. ^{13}C NMR spectra were recorded in $CDCl_3$ at 150, 100 or 50 MHz on Bruker DRX-600, DPX-400 or DPX-200 spectrometers, respectively, using the central resonance of $CDCl_3$ (δ_C = 77.0 ppm) as the internal reference. Infra-red spectra were recorded 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. Melting points were determined on a Reichert hot stage apparatus and are uncorrected. 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 petroleum ether 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. Ether and THF were distilled from sodium benzophenone ketyl; CH_2Cl_2 from calcium hydride. Other reagents and solvents were purified using standard procedures.[13] Aqueous solutions are saturated unless otherwise specified.

The preparation of compounds **1**,[4b] **10**,[14] **11**,[4b] **12**[4b] and **20**[6b] is described elsewhere.

Ethyl (2*E*,4*R**,5*S**)-4,5-epoxydec-2-enoate (4)

To a stirred solution of ethyl (2*E*,4*Z*)-deca-2,4-dienoate[15] (1.47 g, 7.5 mmol) in CH_2Cl_2 (3 ml) at 0 °C was added by cannula a cooled (0 °C) solution of dimethyldioxirane[16] (0.03 M in acetone; 250 ml, 7.5 mmol). The mixture was stirred at 0 °C for 3.5 h. The volatile components were removed under reduced pressure to afford *epoxide* **4** as a pale yellow oil (1.22 g, 77%); ν_{max}(film)/cm^{-1} 2958, 2931, 2860 (CH), 1721 (C=O), 1654 (C=C), 1466, 1379; δ_H(200 MHz) 0.86 (3H, t, *J* 6.7, 10-H × 3), 1.15–1.65 {11H, m, [including 1.29 (3H, t, *J* 7.1, OCH_2CH_3)], 6-H × 2, 7-H × 2, 8-H × 2, 9-H × 2, OCH_2CH_3}, 3.17 (1H, td, *J* 5.6, 4.4, 5-H), 3.49 (1H, ddd, *J* 6.6, 4.4, 1.0, 4-H), 4.20 (2H, q, *J* 7.1, OCH_2CH_3), 6.10 (1H, dd, *J* 15.7, 1.0, 2-H), 6.78 (1H, dd, *J* 15.7, 6.6, 3-H); δ_C(50 MHz) 13.8 (CH_3), 14.1 (CH_3), 22.4 (CH_2), 25.9 (CH_2), 27.4 (CH_2), 31.3 (CH_2), 55.1 (CH), 59.6 (CH), 60.5 (CH_2), 125.1 (CH), 142.0 (CH), 165.5 (C=O).

(2*E*,4*R**,5*S**)-4,5-Epoxydec-2-en-1-ol (5)

Diisobutylaluminium hydride (1.0 M solution in hexanes; 8.9 ml, 8.9 mmol) was added dropwise to a solution of the epoxide **4** (0.86 g, 4.1 mmol) in THF (10 ml) at −78 °C. After stirring at this temperature for 75 minutes, methanol (10 ml) was added and the solution allowed to warm to room temperature. Triethanolamine (4 ml) was added and the solution stirred at room temperature overnight. The mixture was filtered through Celite, eluting with ether. The crude product was concentrated *in vacuo* and purified by flash column chromatography (eluent: ether–petrol, 40 to 60%; gradient) to afford *epoxy alcohol* **5** as a colourless oil (0.52 g, 76%); ν_{max}(film)/cm^{-1} 3418 (OH), 2957, 2928, 2859 (CH), 1459, 1380; δ_H(200 MHz) 0.89 (3H, t, *J* 6.8, 10-H × 3), 1.20–1.60 (8H, m, 6-H × 2, 7-H × 2, 8-H × 2, 9-H × 2), 1.81 (1H, t, *J* 4.7, OH), 3.08 (1H, td, *J* 5.6, 4.4, 5-H), 3.41 (1H, ddd, *J* 7.4, 4.4, 0.8, 4-H), 4.11–4.21 (2H, br m, 1-H × 2), 5.59 (1H, ddt, *J* 15.8, 7.4, 1.2, 3-H), 6.07 (1H, dtd, *J* 15.8, 5.3, 0.8, 2-H); δ_C(50 MHz) 13.9 (CH_3), 22.5 (CH_2), 25.9 (CH_2), 27.7 (CH_2), 31.5 (CH_2), 56.4 (CH), 58.9 (CH), 62.7 (CH_2), 125.4 (CH), 135.6 (CH).

General procedure for the preparation of π-allyltricarbonyliron lactone complexes

THF (degassed; 32 ml) was added to diiron nonacarbonyl (1.9 g, 5.3 mmol) and the mixture stirred vigorously in the dark at room temperature for 10 minutes. The α,β-unsaturated epoxide (2.9 mmol) was added and vigorous stirring continued for 2 h. Toluene (2.5 ml) was then added and the mixture filtered through Celite, eluting with ether. The ethereal solvents were removed *in vacuo* and the toluene solution subjected to flash column chromatography (eluent: ether–petrol, 20 to 70%; gradient) to afford the *endo* π-allyltricarbonyliron lactone complex followed by the *exo* complex.

[(2*E*,4*S,5*S**)-5-(Carbonyloxy-κ*C*)-1-hydroxy-(2,3,4-η)-dec-2-en-4-yl]tricarbonyliron (6).** Prepared according to the general procedure, from epoxy alcohol **5** (0.49 g, 2.9 mmol). Flash chromatography afforded, in order of elution, an inseparable mixture of *endo* primary alcohol complex and a secondary alcohol complex[17] (0.27 g, 27%; not fully characterised) followed by *exo primary alcohol complex* **6** as white crystals (0.57 g, 58%); mp 82–84 °C (Found: C, 49.74; H, 5.28. $C_{14}H_{18}FeO_6$

requires C, 49.73; H, 5.37%); ν_{max}(film)/cm^{-1} 3357 (OH), 2927 (CH), 2081, 2004 (CO), 1650 (C=O); δ_H(600 MHz) 0.89 (3H, t, *J* 6.8, 10-H × 3), 1.23–1.66 (8H, m, 6-H × 2, 7-H × 2, 8-H × 2, 9-H × 2), 2.42 (1H, t, *J* 4.3, OH), 3.95 (1H, dt, *J* 11.8, 3.4, 2-H), 4.03 (1H, t, *J* 6.6, 5-H), 4.09 (1H, dt, *J* 13.9, 4.3, 1-H × 1), 4.35 (1H, dt, *J* 13.9, 3.4, 1-H × 1), 4.48 (1H, d, *J* 7.9, 4-H), 5.04 (1H, dd, *J* 11.8, 7.9, 3-H); δ_C(50 MHz) 13.9 (CH_3), 22.4 (CH_2), 25.1 (CH_2), 31.4 (CH_2), 37.9 (CH_2), 61.9 (CH_2), 75.0 (CH), 75.9 (CH), 80.0 (CH), 88.9 (CH), 203.8 (CO), 206.1 (CO), 209.3 (CO); *m*/*z* (FAB) 361 [(M + Na)$^+$, 28%], 339 (MH, 77), 311 (MH − CO, 23), 255 (MH − 3CO, 100), 227 (MH − 4CO, 72) [Found (MH$^+$) 339.0514. $C_{14}H_{19}FeO_6$ requires *M*H, 339.0531].

[(2*E*,1*R,4*S**,5*R**)-5-(Carbonyloxy-κ*C*)-1-hydroxy-1-phenyl-(2,3,4-η)-dec-2-en-4-yl]tricarbonyliron (9).** The epoxy enone, (2*E*)-4,5-epoxy-1-phenyldec-2-en-1-one (1.1 g, 4.7 mmol; 1:1 mixture of *cis* and *trans* epoxide) was treated with diiron nonacarbonyl (3.1 g, 8.6 mmol), according to the general procedure. Flash chromatography afforded the *endo* and *exo phenyl ketone complexes*, [(2*E*,4*S**,5*S**)- and (2*E*,4*S**,5*R**)-5-(carbonyloxy-κ*C*)-1-hydroxy-1-phenyl-(2,3,4-η)-deca-2-en-4-yl]tricarbonyliron, as an inseparable 1:1 mixture (1.05 g, 57%). Treatment of this mixture with $NaBH_4$ (200 mg, 5.3 mmol) in CH_2Cl_2–MeOH (1:1; 20 ml) followed by flash chromatography afforded several products,[18] including an inseparable mixture of *endo* and *exo secondary alcohol complexes* **9** and *iso*-**9** (448 mg, 42%). The alcohol complexes were separated by treatment with TBSCl (168 mg, 1.1 mmol) and imidazole (97 mg, 1.42 mmol) in DMF (1 ml) at 0 °C for 2 h, which preferentially protected the less hindered, *exo* complex. Flash chromatography and recrystallisation from ether–petrol afforded unreacted *endo* alcohol complex **9** as a single diastereoisomer (141 mg, 31%); mp 105–107 °C (Found: C, 58.15; H, 5.34. $C_{20}H_{22}FeO_6$ requires C, 57.99; H, 5.35%); ν_{max}(film)/cm^{-1} 3385 (OH), 2933 (CH), 2086, 2032, 2014 (CO), 1657 (C=O); δ_H(200 MHz) 0.87 (3H, t, *J* 6.5, 10-H × 3), 1.18–1.67 (8H, m, 6-H × 2, 7-H × 2, 8-H × 2, 9-H × 2), 2.59 (1H, d, *J* 4.1, OH), 4.19–4.31 (2H, m, 2-H, 5-H), 4.60 (1H, ddd, *J* 8.3, 4.6, 0.6, 4-H), 4.82 (1H, dd, *J* 12.1, 8.3, 3-H), 5.20 (1H, t, *J* 4.6, 1-H), 7.28–7.48 (5H, m, Ph); δ_C(50 MHz) 13.9 (CH_3), 22.4 (CH_2), 26.4 (CH_2), 31.5 (CH_2), 36.5 (CH_2), 74.6 (CH), 76.5 (CH), 77.1 (CH), 85.9 (CH), 88.9 (CH), 125.5 (CH), 128.3 (CH), 128.9 (CH), 142.7 (quat. C), 203.2 (CO), 205.3 (CO), 209.1 (CO); *m*/*z* (FAB) 415 (MH$^+$, 31%), 387 (MH − CO, 9), 331 (MH − 3CO, 14), 313 (17), 301 (21), 285 (23), 213 (100), 143 (46), 105 (59) [Found (MH$^+$) 415.0856. $C_{20}H_{23}FeO_6$ requires *M*H, 415.0844].

[(3*E*,1*R,2*S**,7*R**)-1-(Carbonyloxy-κ*C*)-7-hydroxy-8-methyl-5-oxo-1-phenyl-(2,3,4-η)-non-3-en-2-yl]tricarbonyliron (21).** A solution of isobutyraldehyde (16 mg, 0.22 mmol) and $BF_3{\cdot}OEt_2$ (31 mg, 0.22 mmol) in ether (1 ml) was added by syringe to a cooled (−78 °C) solution of the trimethylsilyl enol ether complex **20** (62 mg, 0.15 mmol) in ether (2 ml) and CH_2Cl_2 (0.75 ml). The reaction was stirred at −78 °C for 6 h. Triethylamine (22 mg, 0.22 mmol) was then added and the reaction allowed to warm to room temperature. The mixture was filtered through Celite, eluting with ether–CH_2Cl_2 (4:1). The filtrate was concentrated under reduced pressure and then diluted with THF (0.3 ml) and treated with HF–pyridine (2.25 M in THF; 0.3 ml), with stirring, for 30 minutes. The reaction was diluted with ether (5 ml) and washed with $NaHCO_3$ (5 ml), then brine (5 ml). The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo*. Flash chromatography (eluent: ether–petrol, 35 to 50%; gradient) afforded *aldol complex* **21** of 94% diastereomeric excess (34 mg, 55%); mp 104–105 °C (Found: C, 55.69; H, 4.79. $C_{20}H_{20}FeO_7$ requires C, 56.10; H, 4.71%); ν_{max}(film)/cm^{-1} 3382 (OH), 2924 (CH), 2090, 2023 (CO), 1679 (C=O), 1651; δ_H(200 MHz) 0.95 (3H, d, *J* 6.7, 9-H × 3), 0.97 (3H, d, *J* 6.7, 8-CH_3), 1.66–1.86 (1H, m, 8-H), 2.64 (1H, d, *J* 3.6, OH), 2.80–2.89 (2H, m, 6-H × 2), 3.87–3.99 (1H, m, 7-H), 4.07 (0.97H, d, *J* 11.2, 4-H), 4.20 (0.03H, d, *J* 11.1, 4-H′), 5.25 (1H, dd, *J* 8.7, 4.7, 2-H), 5.44 (1H, d, *J* 4.7, 1-H), 5.59 (1H, dd, *J* 11.2, 8.7, 3-H), 7.25–7.40 (5H, m, Ph); δ_C(50 MHz) 17.6 (CH_3), 18.3 (CH_3), 33.2 (CH), 46.9 (CH_2), 66.3 (CH), 72.2 (CH), 78.2 (CH), 84.7 (CH), 91.9 (CH), 125.8 (CH), 128.6 (CH), 128.8 (CH), 138.1 (quat. C), 199.4 (CO), 201.8 (CO), 204.3 (CO), 204.6 (CO), 207.6 (CO); *m*/*z* (FAB) 451 [(M + Na)$^+$, 21%], 429 (MH, 88), 401 (MH − CO, 11), 345 (MH − 3CO, 36), 317 (MH − 4CO, 57), 299 (56), 227 (88), 107 (100) [Found (MH$^+$) 429.0623. $C_{20}H_{21}FeO_7$ requires *M*H, 429.0637].

[(3*E*,1*R,2*S**,7*R**)-7-*tert*-Butyldimethylsilyloxy-1-(carbonyloxy-κ*C*)-8-methyl-5-oxo-1-phenyl-(2,3,4-η)-non-3-en-2-yl]tricarbonyliron (22).** To a solution of the aldol complex **21** (30 mg, 0.07 mmol) in CH_2Cl_2 (1 ml) at −40 °C was added 2,6-lutidine (11 mg, 0.10 mmol) followed by TBSOTf (22 mg, 0.08 mmol). After stirring at this temperature for 2 h, the reaction mixture was transferred directly onto a silica flash column. Elution with 20% ether–petrol afforded *TBS protected aldol complex* **22** (25 mg, 66%); ν_{max}(film)/cm^{-1} 2956, 2857 (CH), 2091, 2024 (CO), 1681 (C=O); δ_H(400 MHz) −0.02 (3H, s, SiCH_3), 0.06 (3H, s, SiCH_3), 0.85 (9H, s, SiC(CH_3)$_3$), 0.89 (3H, d, *J* 6.9, 9-H × 3), 0.92 (3H, d, *J* 6.8, 8-CH_3), 1.80 (1H, septet of d, *J* 6.8, 3.9, 8-H), 2.79–2.81 (2H, m, 6-H × 2), 4.03 (1H, d, *J* 11.2, 4-H), 4.14 (1H, dt, *J* 6.5, 4.7, 7-H), 5.24 (1H, dd, *J* 8.7, 4.7, 2-H), 5.44 (1H, d, *J* 4.7, 1-H), 5.55 (1H, dd, *J* 11.2, 8.7, 3-H), 7.28–7.39 (5H, m, Ph); δ_C(100 MHz) −4.5 (Si*C*H$_3$), 17.2 (CH_3), 17.8 (CH_3), 18.0 (Si*C*(CH$_3$)$_3$), 25.8 (SiC(*C*H$_3$)$_3$), 33.7 (CH), 47.0 (CH_2), 66.6 (CH), 72.0 (CH), 78.2 (CH), 84.3 (CH), 92.1 (CH), 125.9 (CH), 128.6 (CH), 128.8 (CH), 138.3 (quat. C), 199.4 (CO), 202.1 (CO); *m*/*z* (FAB) 543 (MH$^+$, 17%), 486 (MH − ^{t}Bu, 13), 453 (18), 431 (MH − 4CO, 100), 373 (55), 301 (25), 187 (90), 131 (67) [Found (MH$^+$) 543.1492. $C_{26}H_{35}FeO_7Si$ requires *M*H, 543.1501].

[(3*E*,1*R,2*S**,5*S**,7*R**)-7-*tert*-Butyldimethylsilyloxy-1-(carbonyloxy-κ*C*)-5-hydroxy-8-methyl-1-phenyl-(2,3,4-η)-non-3-en-2-yl]tricarbonyliron (13).** Triisobutylaluminium (1.0 M solution in toluene; 0.06 ml, 0.06 mmol) was added to a solution of the TBS aldol complex **22** (18 mg, 0.03 mmol) in benzene (0.5 ml) at 5 °C. The mixture was stirred at 0–5 °C for 40 minutes and then quenched with ice-cold NH_4Cl solution (1 ml) and extracted using ether (3 × 2 ml). The combined organic extracts were washed with brine, dried ($MgSO_4$) and the solvents were removed under reduced pressure. Flash chromatography (eluent: 50% CH_2Cl_2–petrol) afforded *monoprotected diol* **13** (11.8 mg, 67%); ν_{max}(film)/cm^{-1} 3410 (OH), 2955 (CH), 2083, 2008 (CO), 1642 (C=O); δ_H(400 MHz) 0.12 (6H, s, Si(CH_3)$_2$), 0.88–0.91 (15H, m, SiC(CH_3)$_3$, 9-H × 3, 8-CH$_3$), 1.70 (1H, ddd, *J* 14.3, 10.5, 9.3, 6-H × 1), 1.83–1.91 (2H, m, 6-H × 1, 8-H), 3.75 (1H, s, OH), 3.92 (1H, dt, *J* 10.5, 3.3, 7-H), 4.17 (1H, dd, *J* 11.9, 1.6, 4-H), 4.40 (1H, d, *J* 9.3, 5-H), 4.87 (1H, dd, *J* 8.5, 4.6, 2-H), 4.93 (1H, dd, *J* 11.9, 8.5, 3-H), 5.36 (1H, d, *J* 4.6, 1-H), 7.25–7.38 (5H, m, Ph); δ_C(100 MHz) −4.8 (Si*C*H$_3$), −3.9 (Si*C*H$_3$), 14.7 (CH_3), 18.0 (Si*C*(CH$_3$)$_3$), 18.8 (CH_3), 25.8 (SiC(*C*H$_3$)$_3$), 33.8 (CH), 38.8 (CH_2), 70.2 (CH), 76.1 (CH), 78.4 (CH), 78.5 (CH), 86.9 (CH), 89.0 (CH), 125.8 (CH), 128.0 (CH), 128.6 (CH), 139.7 (quat. C), 202.8 (CO), 205.6 (CO), 209.6 (CO); *m*/*z* (FAB) 545 (MH$^+$, 12%), 517 (MH − CO, 4), 487 (M − ^{t}Bu, 9), 433 (MH − 4CO, 9), 415 (29), 187 (100) [Found (MH$^+$) 545.1662. $C_{26}H_{37}FeO_7Si$ requires *M*H, 545.1658].

General procedure for the decomplexation reactions using sodium triacetoxyborohydride; synthesis of unsaturated alcohols 19 and 23 and saturated alcohols 8 and 14–18

The π-allyltricarbonyliron lactone complex (0.02 mmol) was dissolved in THF (1 ml) and cooled to 20 °C using a water bath. Sodium triacetoxyborohydride (0.1 mmol) was added and the

solution stirred at 20 °C for 48 h. Acetone (1 ml) was added and the mixture filtered through Celite, eluting with ether. The solvents were evaporated under reduced pressure and the residue subjected to flash chromatography to afford unsaturated alcohols as a mixture of positional and geometric isomers. In some cases, the *cis* double bond isomer was separated from the *trans* isomers during flash chromatography.

The (recombined) mixture of unsaturated alcohols was dissolved in ethyl acetate (0.5 ml) and palladium on carbon (10%; *ca*. 0.1 equiv.) was added. The solution was flushed with hydrogen and stirred at room temperature under a hydrogen atmosphere for 3–7 h. The reaction mixture was then filtered through Celite, eluting with ethyl acetate. The solvent was removed under reduced pressure and the residue purified by flash chromatography to afford the saturated alcohol.

Decane-1,5-diol (8). Prepared from primary alcohol complex **6** (24 mg, 0.07 mmol). An inseparable mixture of unsaturated diols was obtained after decomplexation and flash chromatography (eluent: ether). Hydrogenation for 4.5 h and work-up according to the standard procedure (eluent: ether–petrol 60%) afforded the *saturated diol* **8** (7.1 mg, 59%); ν_{max}(film)/cm^{-1} 3373 (OH), 2924, 2870 (CH), 1461; δ_H(600 MHz) 0.89 (3H, t, *J* 6.8, 10-H × 3), 1.25–1.65 (16H, m, 2-H × 2, 3-H × 2, 4-H × 2, 6-H × 2, 7-H × 2, 8-H × 2, 9-H × 2, OH × 2), 3.59–3.64 (1H, m, 5-H), 3.67 (2H, t, *J* 6.4, 1-H × 2); δ_C(150 MHz) 13.9 (CH_3), 21.8 (CH_2), 22.6 (CH_2), 25.3 (CH_2), 31.8 (CH_2), 32.6 (CH_2), 37.0 (CH_2), 37.5 (CH_2), 62.8 (CH_2), 71.8 (CH); *m*/*z* (CI) 193 (MH^+, 15%), 192 (M, 100), 175 (MH − H_2O, 14) [Found (MH^+) 175.1698. $C_{10}H_{23}O_2$ requires *M*H, 175.1698].

(1*R,5*R**)-1-Phenyldecane-1,5-diol (14).** Prepared from secondary alcohol complex **9** (94 mg, 0.22 mmol). An inseparable mixture of unsaturated diols was obtained after decomplexation (reaction time 72 h) and flash chromatography (eluent: ether–petrol 60–80%; gradient). Hydrogenation for 7 h and work-up according to the standard procedure (eluent: ether–petrol 60%) afforded the *saturated diol* **14** (40 mg, 71%); ν_{max}(film)/cm^{-1} 3346 (OH), 2928, 2858, 1453; δ_H(200 MHz) 0.88 (3H, t, *J* 6.5, 10-H × 3), 1.18–1.86 (15H, m, 2-H × 2, 3-H × 2, 4-H × 2, 6-H × 2, 7-H × 2, 8-H × 2, 9-H × 2, OH × 1), 2.15 (1H, br s, OH), 3.46–3.65 (1H, m, 5-H), 4.67 (1H, t, *J* 6.4, 1-H), 7.21–7.37 (5H, m, Ph); δ_C(50 MHz) 14.0 (CH_3), 21.8 (CH_2), 22.6 (CH_2), 25.3 (CH_2), 31.8 (CH_2), 37.1 (CH_2), 37.4 (CH_2), 39.0 (CH_2), 71.8 (CH), 74.5 (CH), 125.8 (CH), 127.4 (CH), 128.4 (CH), 144.8 (quat. C); *m*/*z* (CI) 268 [(M + NH_4)$^+$, 14%], 251 (MH, 18), 250 (M, 100), 231 (38) [Found (M + NH_4)$^+$ 268.2277. $C_{16}H_{30}NO_2$ requires *M* + NH_4, 268.2276].

(5*S*,9*S*)-Decane-1,5,9-triol (15). Prepared from secondary alcohol complex **10** (24.0 mg, 0.054 mmol). An inseparable mixture of unsaturated diols was obtained after decomplexation (reaction time 72 h) and flash chromatography (eluent: ethyl acetate–petrol 65%). Hydrogenation for 6 h and work-up according to the standard procedure (eluent: MeOH–ethyl acetate 5%) afforded the *saturated diol* **15** (6.5 mg, 63%); $[\alpha]_D^{28}$ +6.0 (*c* 0.4 in MeOH); ν_{max}(film)/cm^{-1} 3280 (OH), 2928, 2856, 1453, 1371, 1110, 1054, 1027; δ_H(600 MHz) 1.19 (3H, t, *J* 6.2, 10-H × 3), 1.37–1.65 (12H, m, 2-H × 2, 3-H × 2, 4-H × 2, 6-H × 2, 7-H × 2, 8-H × 2), 1.75 (1H, br s, OH), 1.88 (1H, br s, OH), 2.09 (1H, br s, OH), 3.59–3.68 (3H, m [incl. 3.65, 2H, t, *J* 6.2, 1-H × 2] 1-H × 2, H-5 × 1 or 8-H × 1), 3.77–3.85 (1H, m, H-8 × 1 or 5-H × 1); δ_C(50 MHz) 21.8 (CH_2 × 2), 23.6 (CH_3), 29.7 (CH_2), 32.5 (CH_2), 37.1 (CH_2), 37.2 (CH_2), 39.0 (CH_2), 62.7 (1-C), 67.9 (CH), 71.6 (CH); *m*/*z* (ES) 213 (MNa^+, 100), 197 (4), 180 (8), 149 (6) [Found (MNa)$^+$ 213.1476. $C_{10}H_{22}O_3Na$ requires *M*Na, 213.1467].

(4*Z*,2*S,6*R**)-Undec-4-ene-2,6-diol (19) and (2*S**,6*R**)-undecane-2,6-diol (16).** Prepared from secondary alcohol complex **11** (32 mg, 0.09 mmol). Decomplexation and flash chromatography (eluent: ether–petrol 60%) afforded *cis unsaturated diol* **19** (9.3 mg, 55%). NMR data for **19**: δ_H(600 MHz) 0.89 (3H, t, *J* 6.7, 11-H × 3), 1.22 (3H, d, *J* 6.2, 1-H × 3), 1.23–1.41 (6H, m, 8-H × 2, 9-H × 2, 10-H × 2), 1.43–1.49 (1H, m, 7-H × 1), 1.57–1.62 (1H, m, 7-H × 1), 1.64 (1H, br s, OH), 1.95 (1H, br s, OH), 2.24 (1H, dt, *J* 14.2, 6.4, 3-H × 1), 2.40 (1H, ddd, *J* 14.2, 7.2, 5.0, 3-H × 1), 3.93 (1H, apparent sextet, *J* 6.2, 2-H), 4.39 (1H, apparent q, *J* 6.9, 6-H), 5.55–5.60 (1H, m, 4-H), 5.61 (1H, dd, *J* 11.5, 7.7, 5-H); δ_C(50 MHz) 13.9 (CH_3), 22.6 (CH_3), 25.0 (CH_2), 31.7 (CH_2), 36.6 (CH_2), 37.3 (CH_2), 67.1 (CH), 67.3 (CH), 127.2 (CH), 136.1 (CH).

Further elution afforded a mixture of unsaturated diols (5.5 mg, 32%).

Recombination of the products and hydrogenation for 3 h followed by work-up according to the standard procedure (eluent: ether–petrol 70–100%; gradient) afforded the *saturated diol* **16** (14 mg, 82%); mp 54–56 °C; ν_{max}(film)/cm^{-1} 3430 (OH), 2967, 2930, 2860 (CH), 1461; δ_H(600 MHz) 0.89 (3H, t, *J* 6.9, 11-H × 3), 1.20 (3H, d, *J* 6.2, 1-H × 3), 1.24–1.61 (15H, m, 3-H × 2, 4-H × 2, 5-H × 2, 7-H × 2, 8-H × 2, 9-H × 2, 10-H × 2, OH × 1), 1.68 (1H, br s, OH × 1), 3.58–3.63 (1H, m, 2-H), 3.82 (1H, apparent sextet, *J* 5.9, 6-H); δ_C(50 MHz) 13.9 (CH_3), 21.6 (CH_2), 22.6 (CH_2), 23.4 (CH_3), 25.3 (CH_2), 31.8 (CH_2), 37.2 (CH_2), 37.4 (CH_2), 39.1 (CH_2), 68.0 (CH), 71.8 (CH); *m*/*z* (CI) 206 [(M + NH_4)$^+$, 100%], 189 (MH, 30), 188 (M, 12), 171 (MH − H_2O, 16) [Found (MH^+) 189.1854. $C_{11}H_{25}O_2$ requires *M*H, 189.1854].

(4*R,8*R**)-4-Methyltridecane-4,8-diol (17).** Prepared from tertiary alcohol complex **12** (40 mg, 0.10 mmol). An inseparable mixture of unsaturated diols was obtained after decomplexation (reaction time 72 h) and flash chromatography (eluent: ether–petrol 50–100%; gradient). Hydrogenation for 3 h and work-up according to the standard procedure (eluent: ether–petrol 50%) afforded the *saturated diol* **17** (12 mg, 52%); mp 36–41 °C (Found: C, 72.93; H, 13.04. $C_{14}H_{30}O_2$ requires C, 72.99; H, 13.12%); ν_{max}(film)/cm^{-1} 3376 (OH), 2962, 2932, 2872 (CH), 1466; δ_H(600 MHz) 0.89 (3H, t, *J* 6.9, 13-H × 3), 0.92 (3H, t, *J* 7.2, 1-H × 3), 1.16 (3H, s, 4-CH_3), 1.25–1.51 (19H, m, 2-H × 2, 3-H × 2, 5-H × 2, 6-H × 2, 7-H × 2, 9-H × 2, 10-H × 2, 11-H × 2, 12-H × 2, OH × 1), 1.66 (1H, br s, OH × 1), 3.58–3.63 (1H, m, 8-H); δ_C(50 MHz) 13.9 (CH_3), 14.6 (CH_3), 17.1 (CH_2), 19.9 (CH_2), 22.6 (CH_2), 25.3 (CH_2), 26.8 (CH_3), 31.8 (CH_2), 37.5 (CH_2), 37.8 (CH_2), 41.7 (CH_2), 44.4 (CH_2), 71.8 (CH), 72.7 (quat. C); *m*/*z* (CI) 248 [(M + NH_4)$^+$, 13%], 231 (MH, 6), 230 (M, 29), 214 (14), 213 (MH − H_2O, 100), 211 (10) [Found (M + NH_4)$^+$ 248.2590. $C_{14}H_{34}NO_2$ requires *M* + NH_4, 248.2590].

(2*Z*,1*S,5*R**,7*R**)-7-*tert*-Butyldimethylsilyloxy-8-methyl-1-phenylnon-2-ene-1,5-diol (23) and (1*S**,5*R**,7*R**)-7-*tert*-butyldimethylsilyloxy-8-methyl-1-phenylnonane-1,5-diol (18).** Prepared from monoprotected diol complex **13** (12 mg, 0.02 mmol). Decomplexation and flash chromatography (eluent: ether–petrol 50%) afforded *cis unsaturated, monoprotected triol* **23** (2.5 mg, 31%). NMR data for **23**: δ_H(400 MHz) 0.10 (3H, s, SiCH_3), 0.12 (3H, s, SiCH_3), 0.83 (3H, d, *J* 7.0, 9-H × 3), 0.88 (3H, d, *J* 6.8, 8-CH_3), 0.91 (9H, s, SiC(CH_3)$_3$), 1.50–1.59 (2H, m, 6-H × 2), 1.84 (1H, septet of d, *J* 6.9, 3.9, 8-H), 2.32 (1H, ddd, *J* 13.6, 7.2, 5.7, 4-H × 1), 2.61 (1H, dddd, *J* 13.6, 8.9, 4.9, 1.0, 4-H × 1), 3.19 (1H, br s, OH), 3.83 (1H, dt, *J* 9.2, 3.9, 7-H), 3.90–3.95 (1H, m, 5-H), 5.51 (1H, d, *J* 8.4, 1-H), 5.67 (1H, dt, *J* 10.7, 8.1, 3-H), 5.86 (1H, dd, *J* 10.7, 8.4, 2-H), 7.31–7.43 (5H, m, Ph); δ_C(100 MHz) −4.7 (SiCH_3), −4.0 (SiCH_3), 15.3 (CH_3), 18.0 (SiC(CH_3)$_3$), 18.6 (CH_3), 25.8 (SiC(CH_3)$_3$), 33.7 (CH), 35.0 (CH_2), 35.2 (CH_2), 69.0 (CH), 70.5 (CH), 77.0 (CH), 78.1 (CH), 126.0 (CH), 127.3 (CH), 128.4 (CH), 135.8 (CH), 143.6 (quat. C).

Further elution afforded a mixture of unsaturated, monoprotected triols (5.4 mg, 65%).

Recombination of the products and hydrogenation for 7 h followed by work-up according to the standard procedure (eluent: ether–petrol 50%) afforded the *saturated, monoprotected triol* **18** (4.7 mg, 57%); ν_{max}(film)/cm^{-1} 3342 (OH), 2954, 2850 (CH), 1470; δ_H(400 MHz) 0.08 (3H, s, $SiCH_3$), 0.10 (3H, s, $SiCH_3$), 0.81 (3H, d, *J* 6.9, 9-H × 3), 0.86–0.91 [12H, m, 8-CH_3 and $SiC(CH_3)_3$], 1.31–1.62 (7H, m, 3-H × 2, 4-H × 2, 6-H × 2, OH × 1), 1.70–1.89 (3H, m, 2-H × 2, 8-H), 1.95 (1H, br s, OH), 3.68–3.75 (1H, m, 5-H), 3.76–3.81 (1H, m, 7-H), 4.70 (1H, t, *J* 6.2, 1-H), 7.24–7.37 (5H, m, Ph); δ_C(100 MHz) −4.7 ($SiCH_3$), −4.1 ($SiCH_3$), 15.6 (CH_3), 18.0 [$SiC(CH_3)_3$], 18.4 (CH_3), 21.6 (CH_3), 25.9 [$SiC(CH_3)_3$], 33.6 (CH), 36.6 (CH_2), 37.4 (CH_2), 39.1 (CH_2), 71.2 (CH), 74.5 (CH), 77.8 (CH), 125.9 (CH), 127.5 (CH), 128.4 (CH), 144.8 (quat. C); *m/z* (EI) 380 (M^+, 9%), 347 (13), 305 (49), 187 (20), 161 (68), 147 (88), 107 (88), 75 (100) [Found (M^+) 380.2747. $C_{22}H_{40}SiO_3$ requires *M*, 380.2747].

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