Pergamon

Tetrahedron 55 (1999) 3515–3530

TETRAHEDRON

1,7-Induction of Chirality in Mukaiyama Aldol Reactions using π-Allyltricarbonyliron Lactone and Lactam Complexes as Chiral Templates

Steven V. Ley,* Liam R. Cox, Ben Middleton and Julia M. Worrall.

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK.

Dedicated with respect to our dear friend Derek Barton. We will miss you.

Received 14 July 1998; revised 8 September 1998; accepted 9 September 1998

Abstract: The Mukaiyama aldol reactions of silyl enol ether-substituted π-allyltricarbonyliron lactone and lactam complexes with aldehydes under $BF_3.OEt_2$ activation proceed with moderate to excellent diastereocontrol. The level of diastereocontrol is strongly affected by the nature of the *endo* substituent on the complex, *seven* carbon atoms distant from the reaction site. A detailed investigation of the reaction is presented and a model for the observed stereoselectivity proposed. © 1999 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Natural products with a polyacetate or polypropionate biogenesis continue to attract considerable interest from the scientific community.[1] Their frequently potent biological activity, combined with their limited availability from natural sources, have prompted the development of efficient synthetic routes to the 1,3...(2n+1) oxygenation patterns which are characteristic of these molecules.[2] The aldol reaction in its many forms remains one of the most reliable methods for the assembly of the required 1,3- relationships of oxygen functionality.[3] In the case of the reaction of α-substituted enolates with aldehyde electrophiles, the problem of stereocontrol has been comprehensively addressed[4] allowing facile entry into the polypropionate-derived families of natural products. Preparation of molecules derived from a polyacetate biosynthetic pathway requires the stereoselective reaction between an α-unsubstituted enolate and an aldehyde. In this case only one new stereocentre is created, so relative (*syn/anti*) stereocontrol is no longer an issue. This apparently simplified problem has in fact turned out to be much more challenging. Application of the methods of stereocontrol which perform admirably in the reactions of α-substituted enolates with aldehydes[5,6] to their unsubstituted congeners has consistently provided disappointing results with diminished levels of stereoselectivity.[7,8] Such reduced stereocontrol may be directly attributed to the absence of an α-substituent on the enolate nucleophile as this is often a critical controlling feature in the addition event. Nevertheless in recent years some alternative solutions have emerged, particularly for the reactions of unsubstituted acetate-[9] and thioacetate-derived enolates.[9b,10-14] These have variously involved the use of a metal enolate bearing chiral ligands,[9f-h,14-19] a chiral Lewis acid to activate the electrophilic partner[9a-e,10-13] or a chiral auxiliary appended to the enolate nucleophile.[20-30] The problem of reduced stereoselection has been most pronounced with methyl ketone-derived enolates and controlling the stereochemical outcome of such reactions remains a challenge.[9d,15-19,26-31]

We have recently demonstrated that ketone functionality appended to the allyl terminus of π-allyltricarbonyliron lactone complexes[32] reacts with a variety of nucleophiles affording the corresponding alcohol products in good to excellent yields and with excellent levels of diastereocontrol.[33,34] The outcome of the addition is consistent with nucleophilic attack on the s-*cis* conformation of the ketone *anti* to the bulky $Fe(CO)_3$ unit (Figure 1). Similar results have been obtained with the corresponding η^4-dienone tricarbonyliron complexes.[35] We postulated that an enolate (or

PII: S0040-4020(98)01159-4

enolate equivalent) derived from a methyl ketone group in the side-chain of a lactone complex might also show some degree of stereocontrol in its reactions with aldehydes.

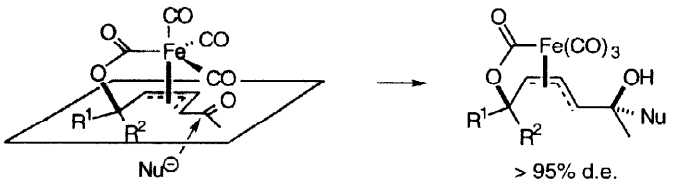
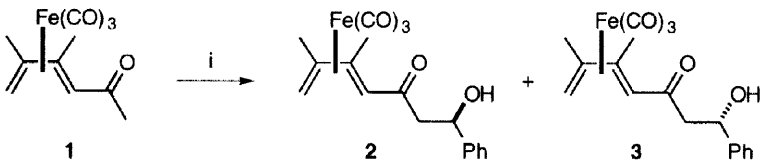


Figure 1

A survey of the literature was somewhat discouraging. In 1992, Franck-Neumann *et al.* disclosed the results of aldol reactions of trimethylsilyl enol ethers derived from methyl ketones appended to the organic ligand of η^4-dienetricarbonyliron complexes.[28] In the best case, reaction of the TMS enol ether formed *in situ* from ketone **1** with benzaldehyde in the presence of $TiCl_4$ afforded two ketol products **2** and **3** in a disappointing 2:1 ratio (Scheme 1). In other cases, starting ketone and elimination products were also isolated and the levels of diastereocontrol were lower still. Some recompense could be gained from the fact that in all cases the ketol products were readily separable allowing access to diastereoisomerically pure β-hydroxy dienone complexes.

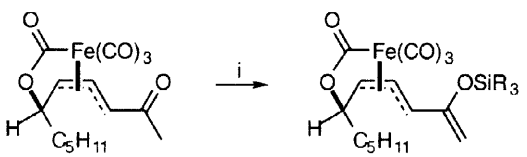


Scheme 1 *Reagents and conditions:* i. TMSOTf, Et_3N, CH_2Cl_2, 0°C, then PhCHO, $TiCl_4$, -78°C, 61% (**2**), 31% (**3**).

The poor diastereocontrol is perhaps not too surprising. In the aldol reaction, the configuration of the new carbinol centre depends only on the ability of the silyl enol ether side-chain to differentiate between the prochiral faces of the aldehyde electrophile. Even if the silyl enol ether adopts a single conformation and is shielded from one face by the tricarbonyliron moiety, *six* open transition states with staggered conformations are potentially accessible (*vide infra*). Undeterred by these results, we set about investigating the analogous reaction using methyl ketone complex **4** as a model substrate.[36]

RESULTS AND DISCUSSION

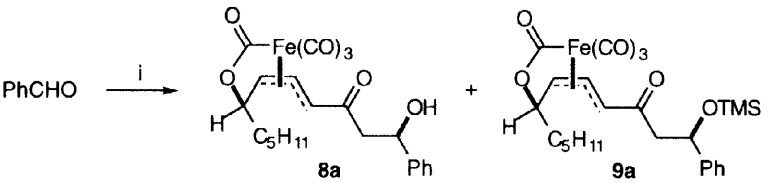
Complex **4** was readily prepared in four steps as previously described.[33] The corresponding silyl enol ether complexes **5** - **7** were obtained in high yield by treatment of ketone **4** with the appropriate trialkylsilyl triflate in the presence of Et_3N in CH_2Cl_2 at 0°C (Scheme 2). The silyl enol ether products proved to be remarkably stable and could be purified by flash column chromatography on Florisil® and stored without significant decomposition at 0°C under argon for several months.



Scheme 2 *Reagents and conditions:* i. R_3SiOTf, Et_3N, CH_2Cl_2, 0°C.

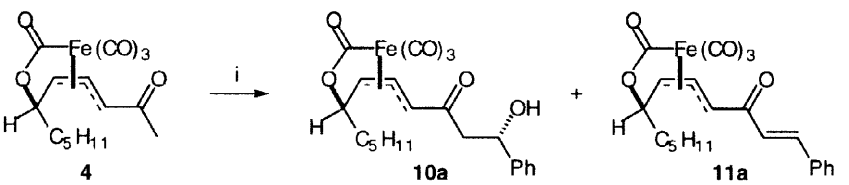
The reaction of TMS enol ether **5** with benzaldehyde was then attempted under standard Mukaiyama aldol conditions using $BF_3.OEt_2$ as the Lewis acid.[38] After aqueous work-up and chromatographic purification, aldol product **8a** was isolated in 47% yield together with a small quantity of the TMS aldol product **9a** (Scheme 3). To our great

delight, the aldol product was obtained as one major diastereoisomer (ratio ≥ 13:1). In addition, a significant quantity (24%) of hydrolysed starting material **4** was isolated. Similar problems were encountered in the work of Franck-Neumann and appreciable time was spent trying to minimise this troublesome side-reaction. A number of alternative Lewis acids ($TiCl_4$, $ZnCl_4$, TMSOTf, $Yb(OTf)_3$, $SnCl_4$) were screened but in all cases the hydrolysis product predominated.



Scheme 3 *Reagents and conditions:* i. $BF_3.OEt_2$, CH_2Cl_2, -78°C, then **5**, 47% (**8a**), 2% (**9a**), > 85% d.e.

Other enolate nucleophiles were also briefly investigated. Treatment of ketone complex **4** with LHMDS at -78°C in THF followed by addition of PhCHO resulted in a complex mixture from which aldol products were isolated in only 20% yield together with 18% of the elimination product **11a** (Scheme 4). Similar results were obtained using the boron enolate, generated under more Lewis acidic conditions from dibutylboron triflate and Hünig's base. Interestingly, in both cases not only was the diastereoselectivity much reduced (~ 30% d.e.) but the major diastereoisomer (**10a**) was the opposite to that obtained in the $BF_3.OEt_2$-mediated Mukaiyama aldol reaction.



Scheme 4 *Reagents and conditions:* i. LHMDS, THF, -78°C, 0.5 h, then PhCHO, 20% (**10a**) *ca.* 30% d.e., 18% (**11a**)

Attention was returned to the most promising lead reaction, the highly diastereoselective Mukaiyama aldol reaction of TMS enol ether **5** under $BF_3.OEt_2$ activation. This was optimised by a series of alterations to the reaction and work-up procedures. Instead of a standard aqueous work-up, Et_3N was used to quench the reaction by removal of the Lewis acid as the insoluble $BF_3.NEt_3$ complex. Filtration through Celite® followed by silica gel chromatography afforded improved yields of aldol products and significantly, remaining TMS enol ether **5**, which according to t.l.c. analysis had been completely consumed. Subsequent reactions were therefore allowed to run for a further 1-2 hours following the apparent consumption of the starting material. Further small optimisations included use of an Et_2O:CH_2Cl_2 mixture (4:1) as solvent and a change in the order of addition such that the aldehyde-BF_3 complex was added to the cooled silyl enol ether solution.

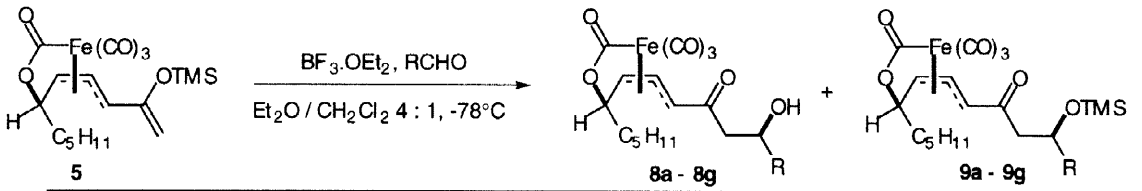
With an optimised procedure in hand, the diastereoselectivity of the $BF_3.OEt_2$-mediated Mukaiyama aldol reaction between TMS enol ether **5** and a variety of aldehydes was investigated. The results are outlined in Table 1. In all cases a mixture of TMS-protected and unprotected aldol products were obtained in good overall yields, together with small quantities of hydrolysed starting material and in some cases, dehydration product. To determine the overall diastereoselectivity of the aldol reaction, after Et_3N work-up and filtration, the crude reaction mixture was treated with HF / pyridine in THF to effect quantitative silyl deprotection of the TMS aldol product. Upon completion, standard aqueous work-up afforded the aldol product, the d.e. of which was determined by comparison of integrals in the ^1H NMR (600 MHz) spectrum.

The highest diastereoselectivities (> 90% d.e.) were observed for the sterically demanding, branched aliphatic aldehydes such as pivalaldehyde, cyclohexanecarboxaldehyde and isobutyraldehyde. Benzaldehyde reacted with a slightly lower (86%) diastereomeric excess. Straight chain aliphatic and α,β-unsaturated aldehydes showed further decreased levels of diastereocontrol. Thus in general it would appear that the more sterically demanding the aldehyde, the more facially selective the reaction.

To determine the relative configuration between the newly created stereogenic centre and that at the lactone tether we employed a similar method to that used by Franck-Neumann,[28,29] taking advantage of the high stereoselectivity in

the reduction of ketones appended to the allyl ligand.[33] The stereochemical outcome of this reaction can be predicted by assuming hydride delivery to the s-*cis* conformation of the ketone *anti* to the sterically bulky tricarbonyliron moiety. Then by establishing whether there is a 1,3-*syn* or 1,3-*anti* relationship between the alcohol functionalities, the relative configuration of the new stereocentre may be elucidated. This is achieved by formation of the corresponding acetonide, which constrains the diol into a conformationally defined six-membered ring.

Table 1 Mukaiyama aldol reactions of aldehydes with π-allyltricarbonyliron lactone complex **5**.

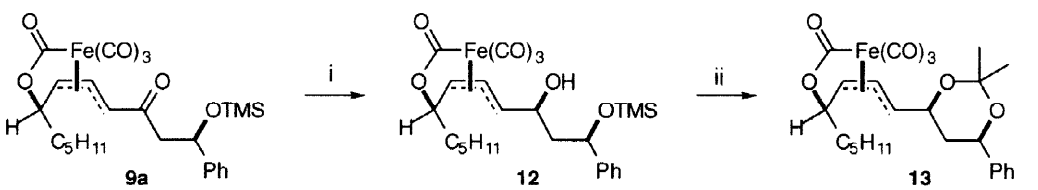


5 8a - 8g 9a - 9g

	Aldehyde	Overall yield (%)[a]	Ratio of **8**:**9**[b]	D.e. (%)[c]
a	PhCHO	81	75:25	86
b	$CH_3(CH_2)_4CHO$	74	23:77	82
c	$CH_3CH(CH_3)CHO$	66	39:61	94
d	$CH_3C(CH_3)_2CHO$	57	26:74	>95[d]
e	cyclohexyl-CHO	75	57:43	91
f	$CH_3(CH_2)_3CH{=}CHCHO$	65[e]	72:28	79
g	$CH_3(CH_2)_4C{\equiv}CCHO$	78	79:21	47

[a] Total isolated yield after chromatography. [b] Determined from isolated yields of TMS and free aldol products. [c] Diastereoisomeric excess determined on the crude reaction mixture by 600 MHz ^1H NMR analysis after silyl deprotection. [d] Only one diastereoisomer was observable in the crude reaction mixture by 600 MHz ^1H NMR analysis. [e] Up to 9% dehydration product **11f** was also isolated.

Treatment of TMS aldol product **9a** with tripropylaluminium afforded the monosilylated diol **12** with excellent diastereoselectivity in full agreement with earlier work.[33] Subsequent removal of the silyl group and acetonide protection afforded complex **13** (Scheme 5). By analysis of the ^{13}C NMR spectrum of acetonide **13**, a *syn* relationship between the alcohol functionalities was established. Chemical shifts for the acetal carbon at 99.7 ppm and the acetal methyl carbons at 19.9 and 29.6 ppm are characteristic of a *syn* diol.[39-41] The acetonide ring assumes a chair conformation with the phenyl group and lactone complex occupying equatorial positions, ensuring that the two acetal methyl groups are in quite different electronic environments (one axial and one equatorial) and have different chemical shifts. An *anti* relationship between the alcohol functionalities would force the corresponding acetonide to adopt a twist boat conformation, placing the acetal methyl carbons in similar electronic environments (normally both would appear at around 25 ppm).

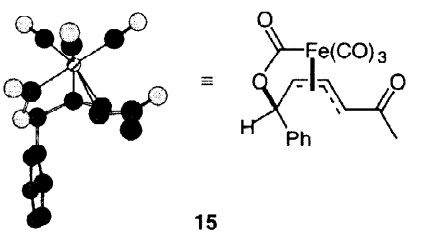


Scheme 5 *Reagents and conditions:* i. $AlPr^n_3$ (2.4 equiv.), CH_2Cl_2, -78 → 0 °C, 1 h, 75%; ii. HF/pyridine (3 equiv., *ca.* 2.25 M in THF), THF, 25 °C, then *p*PTS (0.05 equiv.), 2,2-dimethxoypropane (20 equiv.), DMF, 25 °C, 12 h, 71%.

In most cases the diastereomeric excesses of the aldol products are comparable with or exceed values reported in the literature.[9d,15-19,26-31] The degree of diastereocontrol is quite remarkable, especially in the light of the results obtained by Franck-Neumann using η^4-dienetricarbonyliron complexes.[28] Since π-allyltricarbonyliron lactone complexes are superficially quite similar to their η^4-diene relatives at least in the immediate vicinity of the reacting

centre, it would appear that the remote lactone portion of the π-allyl complex is having a genuine influence on the selectivity of the reaction.

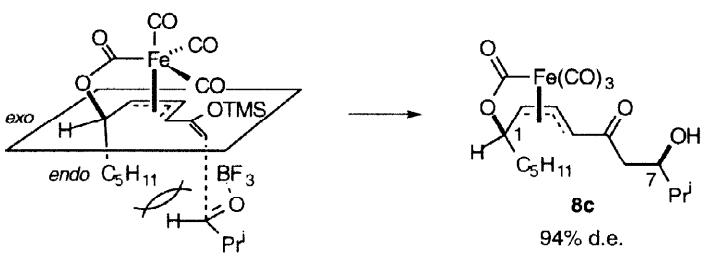
A comparison of the X-ray crystal structures of π-allyltricarbonyliron lactone and η^4-dienetricarbonyliron complexes is quite revealing. The crystal structure of lactone complex **15** (the methyl ketone precursor to silyl enol ether complex **20**) shows that the *endo* phenyl substituent lies beneath and almost perpendicular to the plane of the allyl ligand (Figure 2).[42] In the related η^4-diene complexes, X-ray structures reveal that the diene unit deviates relatively little from planarity and the carbon atoms of the ligand essentially retain their sp^2 characters. X-ray analysis of the tricarbonyliron complex of (2*E*,4*E*)-hexadienoic acid has shown that the *endo* H-substituent actually lies only 0.4 Å below the diene plane while the *exo* methyl substituent lies around 0.2 Å above the plane.[43] As a consequence, neither substituent would be expected to interact strongly with reagents approaching *anti* to the $Fe(CO)_3$ group.



15

Figure 2

The model silyl enol ether complex **5** bears an *endo*-oriented pentyl substituent at the sp^3-hybridised lactone tether position, which projects below the plane of the allyl ligand to create a chiral environment on the lower face of the TMS enol ether side chain. It is possible that this *endo* substituent, *seven* carbon atoms distant from the developing carbinol stereocentre, could interact directly with the incoming aldehyde-Lewis acid complex and thus influence the stereochemical course of the reaction (Figure 3). We set about testing this hypothesis by variation of the nature of the tether and its substitution pattern.



8c

94% d.e.

Figure 3

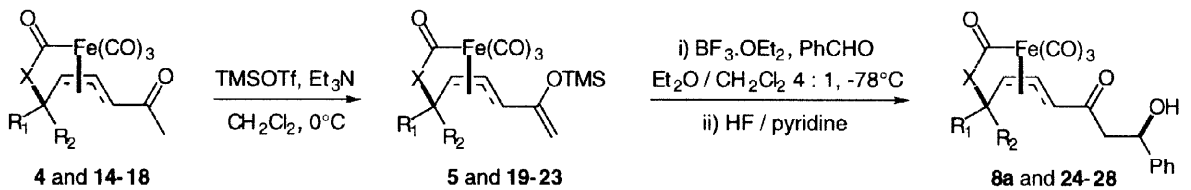
The methyl ketone-substituted π-allyltricarbonyliron lactone and lactam complexes **14** to **18** were prepared using standard protocols[33,44] and converted smoothly into the corresponding TMS enol ether complexes **19** to **23** as before (*vide supra*). Reaction with benzaldehyde under $BF_3.OEt_2$ activation afforded mixtures of TMS protected and unprotected aldol products which were desilylated using HF / pyridine during the work-up. A comparison of the yields and diastereoselectivities obtained is shown in Table 2.[37]

In the case of the *endo* lactone complexes **5**, **19** and **20**, a decrease in the diastereoselectivity of the aldol products was observed on changing R^2 from an alkyl substituent (pentyl or methyl) to a phenyl substituent. This probably reflects the contribution of a favourable interaction between the aromatic rings of *endo* phenyl complex **20** and benzaldehyde. Indeed, the reaction of isobutyraldehyde with complex **20** under the same conditions proceeded with greater than 94% diastereomeric excess. This observation in itself supports our hypothesis that the *endo* substituent is able to interact with the aldehyde-Lewis acid complex in the transition state.

Comparison of the results from *endo*-C_5H_{11} complex **5** with *exo*-C_5H_{11} complex **21** reveals that the disposition of the substituent at the lactone tether has a dramatic effect on the diastereoselectivity. This was further illustrated in the case of the lactam complexes **22** and **23**; with an *endo*-disposed methyl substituent the aldol product **27** was obtained from **22** in an excellent 90% d.e., while an *exo*-oriented methyl substituent gave rise to markedly reduced levels of diastereocontrol (57% d.e.) in the reaction of **23** to afford **28**. These results serve to confirm that the orientation of the

substituent at the tether is indeed a crucial factor in the stereoinduction event. Such remote asymmetric induction is unprecedented in aldol chemistry[45,46] and very rare in the wider field of organic chemistry.[47,48] It is clear that the rigid, conformationally defined iron lactone complex exerts control over the reaction on a number of different levels, illustrating the effectiveness of transition metal complexation as a means of transmitting stereochemical information across distances of several atoms.

Table 2 Reaction of TMS enol ether-substituted lactone and lactam complexes with benzaldehyde.

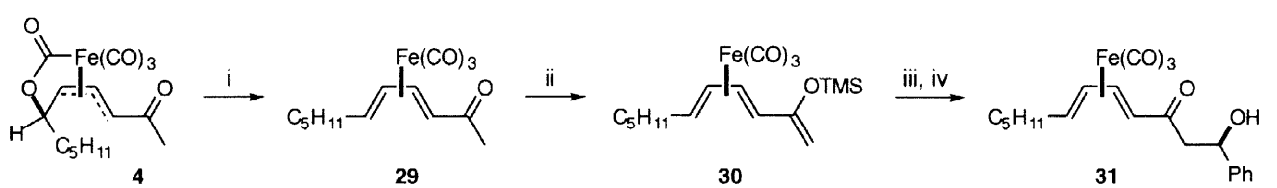


4 and 14-18 5 and 19-23 8a and 24-28

Complex	R^1	R^2	X	Product	Yield (%)	D.e. (%)[a]
5	H	C_5H_{11}	O	**8a**	81	86
19	H	Me	O	**24**	81[b]	87
20	H	Ph	O	**25**	72	67
21	C_5H_{11}	H	O	**26**	53	55
22	H	Me	NBn	**27**	66[b]	90
23	Me	H	NBn	**28**	62[b]	57

[a] Diastereoisomeric excess determined by comparison of integrals in the ^{1}H NMR spectrum of the crude reaction mixture. [b] Reaction carried out in neat CH_2Cl_2 due to low Et_2O solubility of the substrate; this improved the yield and did not affect the d.e.

In order to investigate the influence of sp^3 *vs.* sp^2 hybridisation at the tether position, the stereodirecting ability of TMS enol ether substituted lactone and lactam complexes was directly compared with that of a representative TMS enol ether-substituted η^4-dienetricarbonyliron complex. The (*E,E*)-η^4-dienone complex **29** was prepared in high yield from lactone complex **4** by treatment with barium hydroxide solution.[33] Formation of trimethylsilyl enol ether **30** and reaction with benzaldehyde under the standard conditions resulted in the formation of aldol product **31** with only 25% diastereoisomeric excess (Scheme 6). The selectivity is therefore significantly lower than even that achieved with *exo*-substituted lactone and lactam complexes. The stereochemistry of the major diastereoisomer was determined by acetonide formation as before and shown to be the same as that obtained with the sp^3-tethered complexes.



4 29 30 31

Scheme 6 *Reagents and conditions:* i. $Ba(OH)_2$, MeOH, room temp., 15 min, 92%; ii. Et_3N, TMSOTf, CH_2Cl_2, 0°C, 90 min, 92%; iii. $BF_3.OEt_2$, PhCHO, Et_2O / CH_2Cl_2 4 : 1, -78°C, 1h; iv. HF / py, THF, 30 min, 64% yield over 2 steps, 25% d.e.

The solution conformations of the different types of silyl enol ether complex were studied using nOe experiments. This study revealed another important structural difference between the *exo*-substituted, tethered complexes **21** and **23** and the η^4-diene complex **30** (Figure 4). The orientation of the enol ether side-chains in these complexes was initially assumed to be fixed, as is the case for the parent ketone complexes. The nOe data obtained for lactone complex **21** and lactam complex **23** is entirely consistent with this assumption, showing that the side-chains adopt exclusively the s-*trans* relationship between the olefinic bond and the allyl system. The data obtained for diene complex **30**, however, reveals that both s-*trans* and s-*cis* conformations are significantly populated, the protons at the enol ether terminus showing nOes to both the adjacent internal and external protons of the diene ligand. This increased conformational flexibility in

the η^4-diene system increases the number of potentially accessible transition states for the aldol reaction and is therefore likely to have a detrimental effect on its diastereoselectivity.

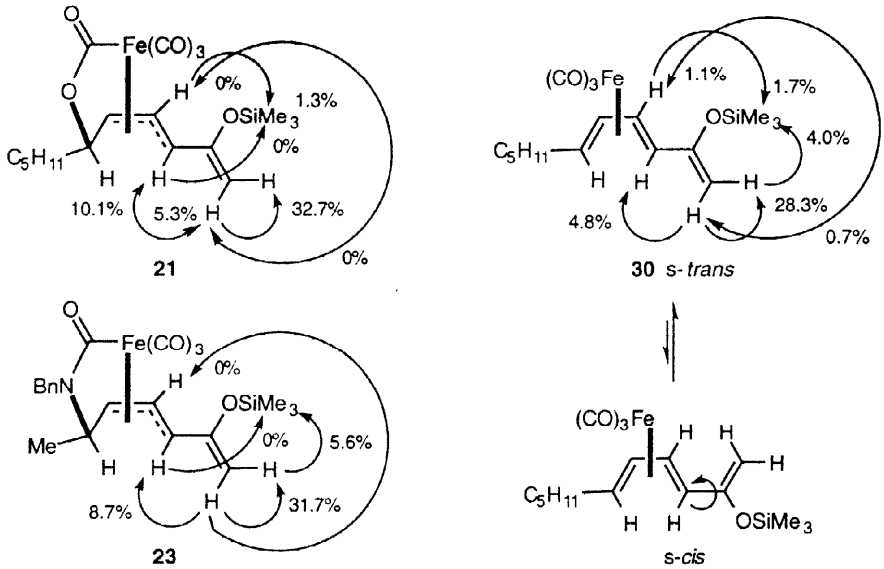
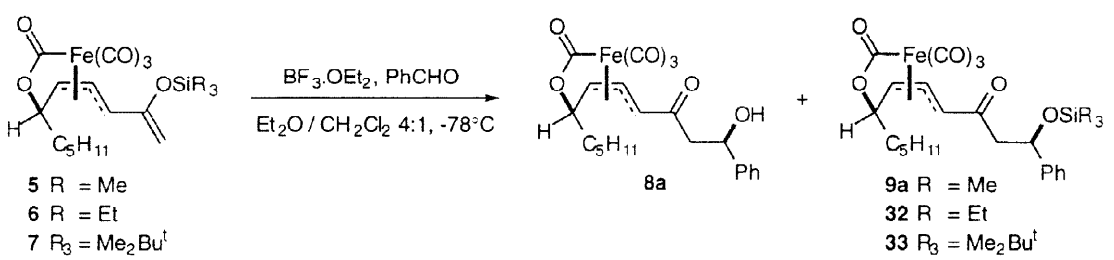


Figure 4

Some additional experiments were carried out to provide further information on the reaction mechanism and help to rationalise the observed stereochemical outcome. The reactions of the TES and TBS enol ethers **6** and **7** with benzaldehyde proceeded more slowly than that of their TMS analogue. More significantly, a decrease in both the d.e. of the (crude, deprotected) aldol product and the isolated yield of silylated aldol product was observed upon proceeding to larger silyl groups (Table 3). While the stereochemical influence of the trialkylsilyl group in the reaction remains unclear, the reduction in selectivity would suggest that unfavourable steric interactions with this group oppose, rather than reinforce, the observed diastereoselection.

Table 3 Variation of the silyl substituent in the Mukaiyama aldol reaction.



Complex	Reaction time (h)	Yield of **8a** (%)[a]	Yield of silyl prod. (%)[a]	D.e. (%)[b]
5	5.5	20	61	86
6	7	12	51	74
7	24	50	4	54

[a] Isolated yields after column chromatography. [b] Diastereomeric excess determined by comparison of integrals in the ^{1}H NMR spectrum of the crude reaction mixture after silyl deprotection.

The information provided by the X-ray and nOe data suggests that the aldehyde reacts with the s-*trans* conformation of the silyl enol ether and approaches from the opposite face to the bulky tricarbonyliron moiety (*vide supra*). The BF_3 Lewis acid is non-chelating and coordinates to the aldehyde oxygen lone pair *anti* to the alkyl or aryl substituent, again for steric reasons.[49] The reaction is assumed to proceed through an open transition state in which the

substituents adopt a staggered conformation.[50] Taking all of these factors into account, six possible transition states may be drawn (Figure 5).

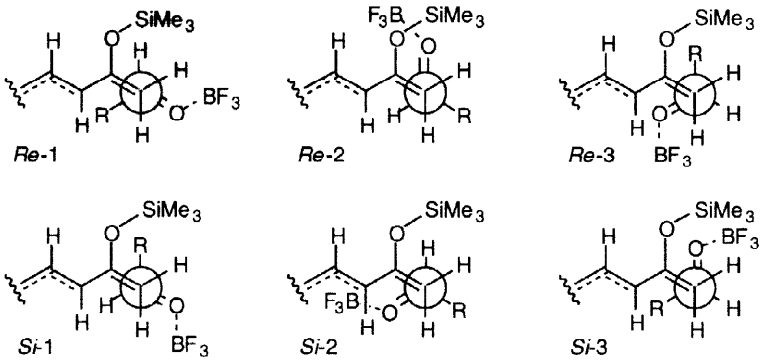


Figure 5

Previous research into the Mukaiyama aldol and similar reactions has shown that there is no particularly favoured arrangement of the π-systems of the nucleophile and electrophile.[51] The observed stereochemical outcome of the reaction is consistent with an overall preference for the transition states *Re*-1 to *Re*-3 over transition states *Si*-1 to *Si*-3. Our results are best explained by transition state *Re*-2, which has a synclinal arrangement of π-systems and in which unfavourable steric interactions are minimised. The approximate position of the *endo* substituent, relative to the reacting groups, can be seen by comparing *Re*-2 in Figure 5 with the "three dimensional" schematic in Figure 3. If *Re*-2 is indeed the favoured transition state, the observed decrease in diastereoselectivity as the size of the silyl group is increased can be attributed to the increasing significance of the (only) *gauche* interaction in this arrangement, allowing other reactive conformations including those favouring *si* attack to be competitive. Furthermore, as the steric bulk of the R group of the aldehyde increases, minimisation of non-bonding interactions with this group will become increasingly important and any predisposition towards transition states *Re*-2 or *Si*-2 would be expected to increase. The most favourable of the transition states leading to *si* attack, in terms of minimisation of steric interactions, would appear to be *Si*-1, which would be expected to become *less* favourable as the size of the R group increases.

CONCLUSIONS

In summary, the Mukaiyama aldol reactions of *endo*-substituted π-allyltricarbonyliron lactone and lactam complexes under boron trifluoride activation proceed with high yields and excellent diastereoselectivities. The silyl enol ether side-chain of the complex adopts exclusively the s-*trans* conformation and is shielded from one face by the bulky tricarbonyliron moiety. The remote *endo* substituent interacts with the incoming aldehyde-Lewis acid complex on the opposite face of the silyl enol ether and acts as a key stereocontrolling element. The Mukaiyama aldol reactions of *exo*-substituted lactone and lactam complexes proceed with moderate diastereoselectivity, while η^4-dienetricarbonyliron complexes react with low selectivity under the same conditions. This may be partly attributed to increased conformational flexibility of the enol ether side-chain in the diene complexes.

The Mukaiyama aldol reaction of π-allyltricarbonyliron lactone and lactam complexes generates a 1,7-relationship of stereogenic centres between the heteroatom tether and the new secondary alcohol. The ketone in the 5-position of the product remains available for further stereoselective transformations. Since the iron lactone and lactam complexes are readily available in homochiral form[33,44] and can be decomplexed to afford stereodefined β- and δ-lactones and lactams,[32] (*E,E*)-dienes[32] and enediols[52] this reaction represents a powerful tool for the rapid construction of a variety of highly functionalised organic molecules.

EXPERIMENTAL

^{1}H NMR spectra were recorded in $CDCl_3$ on Bruker DRX-600, DRX-500 or DPX-200 spectrometers. Coupling constants are quoted in Hz. ^{13}C NMR spectra were recorded in $CDCl_3$, at 150 MHz, 100 MHz or 50 MHz on Bruker DRX-600, AM-400 or DPX-200 spectrometers. IR 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. Reactions were carried out under argon in oven-dried glassware unless otherwise stated. Ether and THF were distilled from sodium benzophenone ketyl; CH_2Cl_2 from calcium hydride. Aqueous solutions are saturated unless otherwise specified. Petrol refers to petroleum ether b.p. 40-60°C. In the synthesis of the iron lactone and lactam complexes, diironnonacarbonyl [$Fe_2(CO)_9$] is used. This is extremely toxic. Iron pentacarbonyl is a highly toxic by-product. All work involving these species was performed in a well ventilated hood. Glassware was treated with bleach to destroy iron carbonyl residues before re-use. Methyl ketone complexes **4**,[33] **14**,[33] **16**,[33] **17**[44] and **18**[44] were prepared as previously described.

[(3E,1R,2S*)-1-(Carbonyloxy-κC)-5-oxo-1-phenyl-(2,3,4-η)-hex-3-en-2-yl]tricarbonyliron (**15**).* THF (degassed; 30 ml) was added to diironnonacarbonyl (1.62 g, 4.44 mmol) and the mixture stirred vigorously in the dark for 10 minutes. (3*E*,5*R**,6*R**)-5,6-Epoxy-6-phenylhex-3-en-2-one (0.437 g, 2.32 mmol) was added. After 3.5 h, toluene (2ml) was added and the mixture filtered through Celite, washing with Et_2O. The ethereal solvents were removed *in vacuo* and the toluene solution subjected to flash column chromatography (eluent: petrol - Et_2O/petrol 40%; gradient) to afford **15** as pale yellow crystals (0.394 g, 48%). (Found C, 54.15; H, 3.48. $C_{16}H_{12}FeO_6$ requires C, 53.96; H, 3.40%); ν_{max}(film)/cm^{-1} 2092 (CO), 2024 (CO), 1683 (C=O), 1498, 1361; δ_H(200 MHz) 2.44 (3H, s, 6-H × 3), 4.03 (1H, d, *J* 11.2, 4-H), 5.26 (1H, dd, *J* 8.7, 4.7, 2-H), 5.43 (1H, d, *J* 4.7, 1-H), 5.57 (1H, dd, *J* 11.2, 8.7, 3-H), 7.25-7.42 (5H, m, Ph); δ_C(50 MHz) 30.2 (CH_3), 66.2 (CH), 78.2 (CH), 84.7 (CH), 91.9 (CH), 125.8 (CH), 128.6 (CH), 128.8 (CH), 138.1 (quat. C), 199.3 (CO), 201.3 (CO), 201.7 (CO), 204.7 (CO), 207.6 (CO); *m/z* (FAB) 357 (MH^+, 52%), 300 (M-2CO, 37), 273 (MH-3CO, 31), 245 (MH-4CO, 100), 228 (77), 171 (50). [Found (MH^+) 357.0076. $C_{16}H_{13}FeO_6$ requires *M*H, 357.0062].

[(4Z,3S,6S*)-2-Oxo-(3,4,5,6-η)-undec-4-en-3,6-diyl]tricarbonyliron (**29**).* $Ba(OH)_{2\,(aq)}$ (1 ml) was added dropwise to a stirred solution of lactone complex **4** (0.287 g, 0.82 mmol) in MeOH (6 ml) at 20°C. After 15 minutes, the reaction mixture was poured into water (20 ml) and extracted with Et_2O (3 × 10 ml). The combined organic fractions were washed with brine (5 ml), dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography (eluent: Et_2O/petrol 5-10%) afforded diene complex **29** as a bright yellow oil (0.230 g, 92%). (Found C, 54.67; H, 5.86. $C_{14}H_{18}FeO_4$ requires C, 54.93; H, 5.93%); ν_{max}(film)/cm^{-1} 2958, 2930, 2857, 2050 (CO), 1975 (CO), 1678 (C=O), 1489, 1455; δ_H(500 MHz) 0.90 (3H, t, *J* 6.8, 11-H × 3), 1.23 (1H, d, *J* 8.2, 3-H), 1.25-1.39 (3H, m, 9-H × 1, 10-H × 2), 1.42-1.53 (3H, m, 6-H, 8-H × 1, 9-H × 1), 1.54-1.66 (2H, m, 7-H × 1, 8-H × 1), 1.68-1.77 (1H, m, 7-H × 1), 2.11 (3H, s, 1-H × 3), 5.23 (1H, dd, *J* 8.2, 5.1, 4-H), 5.79 (1H, dd, *J* 8.0, 5.1, 5-H); δ_C(100 MHz) 13.7, 22.4, 29.5, 31.3, 31.7, 34.1, 53.6, 66.3, 81.2, 87.6, 202.7, 210 (br, CO × 3); *m/z* (FAB) 307 [(MH^+, 9%], 281 (56), 267 (38), 207 (90), 193 (45), 133 (100). [Found (MH^+) 307.0615. $C_{14}H_{19}FeO_4$ requires *M*H, 307.0632].

*General procedure for the synthesis of silyl enol ether complexes **5** - **7**, **19** - **23** and **30**.* For a 0.3 mmol scale reaction; Et_3N (1.4 eq.) and trialkylsilyl triflate (1.2 eq.) were added sequentially to a cooled (0°C) solution of the ketone complex (1.0 eq.) in CH_2Cl_2 (1 ml) and the reaction stirred at 0°C for 1-3 h. On completion the reaction mixture was directly subjected to rapid flash column chromatography (Florisil; Et_2O/petrol) to afford the silyl enol ethers as crystalline solids.

[(3E,5S,6R*)-6-(Carbonyloxy-κC)-2-trimethylsilyloxy-(3,4,5-η)-undeca-1,3-dien-5-yl]tricarbonyliron (**5**).* Prepared using TMSOTf and methyl ketone **4** (0.068 g, 0.19 mmol). After 1 h, flash chromatography (eluent: Et_2O/petrol 10-15%) afforded **5** (0.072 g, 88%). (Found C, 51.38; H, 6.26. $C_{18}H_{26}FeO_6Si$ requires C, 51.17; H 6.21%); ν_{max}(nujol mull)/cm^{-1} 2922, 2853, 2077 (CO), 2011 (CO), 2002 (CO), 1685 (C=O), 1654 (C=C), 1605, 1462; δ_H(200 MHz) 0.25 (9H, s, Si(CH_3)$_3$), 0.89 (3H, t, *J* 6.0, 11-H × 3), 1.12-1.66 (8H, m, 7-H × 2, 8-H × 2, 9-H × 2, 10-H × 2), 4.26 (1H, apparent q, *J* 6.4, 6-H), 4.33-4.43 (2H, m, 1-H × 1, 3-H), 4.57-4.69 (2H, m, 1-H × 1, 5-H), 5.00 (1H, dd, *J* 11.9, 8.5, 4-H); δ_C(50 MHz) -0.3 (Si(CH_3)$_3$), 14.0 (CH_3), 22.5 (CH_2), 26.7 (CH_2), 31.6 (CH_2), 36.8 (CH_2), 76.2 (CH), 77.4 (CH), 79.4 (CH), 85.6 (CH), 94.3 (CH_2), 153.8 (quat. C), 204.3 (CO), 205.5 (CO), 206.2 (CO), 209.2 (CO); *m/z* (FAB) 445 [(M+Na)$^+$, 14%], 423 (MH, 100), 339 (MH-3CO, 53), 311 (MH-4CO, 88), 239 (18), 165 (13), 145 (77). [Found (MH^+) 423.0947. $C_{18}H_{27}FeO_6Si$ requires *M*H, 423.0926].

[(3E,5S,6R*)-6-(Carbonyloxy-κC)-2-triethylsilyloxy-(3,4,5-η)-undeca-1,3-dien-5-yl]tricarbonyliron (**6**).* Prepared using TESOTf and methyl ketone **4** (0.079 g, 0.23 mmol). After 1 h, flash chromatography (eluent: Et_2O/petrol 10-15%) afforded **6** (0.093 g, 89%). (Found C, 54.37; H, 6.92. $C_{21}H_{32}FeO_6Si$ requires C, 54.29; H, 6.95%); ν_{max}(film)/cm^{-1} 2957, 2877, 2079 (CO), 2022 (CO), 1668 (C=O), 1607 (C=C), 1459; δ_H(600 MHz) 0.71-0.75 (6H, m, Si(CH_2CH_3)$_3$), 0.87 (3H, t, *J* 6.8, 11-H × 3), 0.97 (9H, t, *J* 7.9, Si(CH_2CH_3)$_3$), 1.24-1.64 (8H, m, 7-H × 2, 8-H × 2, 9-H × 2, 10-H × 2), 4.26 (1H, apparent q, *J* 5.8, 6-H), 4.38 (1H, d, *J* 12.0, 3-H), 4.40 (1H, br s, 1-H × 1), 4.60 (1H, br s, 1-H × 1), 4.63 (1H, dd, *J* 8.1, 4.7, 5-H), 5.02 (1H, dd, *J* 12.0, 8.1, 4-H); δ_C(62.5 MHz) 4.5 (Si(CH_2CH_3)$_3$), 6.4 (Si(CH_2CH_3)$_3$), 13.9 (CH_3), 22.4 (CH_2), 26.7 (CH_2), 31.5 (CH_2), 36.8 (CH_2), 76.2 (CH), 77.4 (CH), 79.5 (CH), 85.7 (CH), 93.9 (CH_2), 154.0 (quat. C), 204.1 (CO), 205.6 (CO), 206.0 (CO), 209.3 (CO); *m/z* (FAB) 465 (MH^+, 61%), 437 (MH-CO, 14), 425 (24), 381 (MH-3CO, 47), 353 (MH-4CO, 100), 281 (37), 159 (36). [Found (MH^+) 465.1373. $C_{21}H_{33}FeO_6Si$ requires *M*H, 465.1396].

[(3E,5S,6R*)-2-tert-Butyldimethylsilyloxy-6-(carbonyloxy-κC)-(3,4,5-η)-undeca-1,3-dien-5-yl]tricarbonyliron (**7**).* Prepared using TBSOTf and methyl ketone **4** (0.206 g, 0.59 mmol). After 50 min, flash chromatography (eluent: Et_2O/petrol 20%; silica) afforded **7** (0.248 g, 91%). (Found C, 54.29; H, 6.95. $C_{21}H_{32}FeO_6Si$ requires C, 54.29; H, 6.95%); ν_{max}(nujol mull)/cm^{-1} 2954, 2929, 2858, 2077 (CO), 2006 (CO), 1661 (C=O), 1603 (C=C), 1471; δ_H(200 MHz) 0.21 (3H, s, Si(CH_3)), 0.23 (3H, s, Si(CH_3)), 0.76-1.68 (20H, m, [including 0.93 (9H, s, SiC(CH_3)$_3$)], 7-H × 2, 8-H × 2, 9-H × 2, 10-H × 2, 11-H × 3, SiC(CH_3)$_3$), 4.25 (1H, apparent q, *J* 5.5, 6-H), 4.40-4.48 (2H, m, 1-H × 1, 3-H), 4.55-4.66 (2H, m, 1-H × 1, 5-H), 5.00 (1H, dd, *J* 11.9, 8.5, 4-H); δ_C(100 MHz) -4.7 (Si(CH_3)), -4.5 (Si(CH_3)), 13.6 (CH_3), 16.5 (quat. C), 22.3 (CH_2), 25.8 (CH_3), 26.6 (CH_2), 31.4 (CH_2), 36.6 (CH_2), 75.4 (CH), 77.4 (CH), 80.4 (CH), 85.3 (CH), 95.4 (CH_2), 153.9 (quat. C), 204.0 (CO), 205.4 (CO), 205.9 (CO), 209.1 (CO); *m/z* (FAB) 487 [(M+Na)$^+$, 5%], 465 (MH, 80), 381 (MH-3CO, 43), 353 (MH-4CO, 100), 281 (31), 145 (71), 131 (56). [Found (MH^+) 465.1420. $C_{21}H_{33}FeO_6Si$ requires *M*H, 465.1396].

[(4E,2R,3S*)-2-(Carbonyloxy-κC)-6-trimethylsilyloxy-(3,4,5-η)-hepta-4,6-dien-3-yl]tricarbonyliron (**19**).* Prepared using TMSOTf and methyl ketone **14** (0.050 g, 0.17 mmol). After 3h, flash chromatography (eluent: Et_2O/petrol 15-30%) afforded **19** (0.044 g, 71%). ν_{max}(film)/cm^{-1} 2083 (CO), 2029 (CO), 1651 (C=O), 1471, 1382; δ_H(600 MHz) 0.26 (9H, s, Si(CH_3)$_3$), 1.37 (3H, d, *J* 6.4, 1-H × 3), 4.41-4.47 (3H, m, 2-H, 5-H, 7-H × 1), 4.63-4.66 (2H, m, 3-H, 7-H × 1), 4.98 (1H, dd, *J* 11.9, 8.3, 4-H); δ_C(150 MHz) -0.3 (Si(*C*H$_3$)$_3$), 21.9 (CH$_3$), 73.4 (CH), 77.3 (CH), 79.6 (CH), 85.6 (CH), 94.4 (CH$_2$), 153.8 (quat. C), 204.2 (CO), 205.4 (CO), 206.0 (CO), 209.2 (CO); *m/z* (FAB) 367 (MH$^+$, 100%), 339 (MH-CO, 26), 283 (MH-3CO, 75), 255 (MH-4CO, 77), 183 (25), 145 (57). [Found (MH$^+$) 367.0296. $C_{14}H_{19}FeO_6Si$ requires *M*H, 367.0300].

[(3E,1R,2S*)-1-(Carbonyloxy-κC)-1-phenyl-5-trimethylsilyloxy-(2,3,4-η)-hexa-3,5-dien-2-yl]tricarbonyliron (**20**).* Prepared using TMSOTf and methyl ketone **15** (0.079 g, 0.22 mmol). After 3h, flash chromatography (eluent: Et_2O/petrol 25%) afforded **20** (0.084 g, 88%). ν_{max}(film)/cm^{-1} 3053, 2987, 2083 (CO), 2029 (CO), 2025 (CO), 1660, 1422; δ_H(600 MHz) 0.23 (9H, s, Si(CH_3)$_3$), 4.41 (1H, s, 6-H × 1), 4.57 (1H, d, *J* 11.9, 4-H), 4.65 (1H, s, 6-H × 1), 4.86 (1H, dd, *J* 8.4, 4.8, 2-H), 5.01 (1H, dd, *J* 11.9, 8.4, 3-H), 5.36 (1H, d, *J* 4.8, 1-H), 7.26-7.35 (5H, m, Ph); δ_C(150 MHz) -0.34 (Si(*C*H$_3$)$_3$), 76.5 (CH), 78.7 (CH), 80.3 (CH), 85.6 (CH), 94.5 (CH$_2$), 125.8 (CH), 128.1 (CH), 128.6 (CH), 139.4 (quat. C), 153.6 (quat. C), 204.0 (CO), 205.2 (CO), 209.0 (CO); *m/z* (FAB) 429 (MH$^+$, 39%), 389 (41), 373 (MH-2CO, 35), 345 (MH-3CO, 100), 317 (MH-4CO, 49), 129 (35), 115 (33). [Found (MH$^+$) 429.0434. $C_{19}H_{20}FeO_6Si$ requires *M*H, 429.0457].

[(3E,5S,6S*)-6-(Carbonyloxy-κC)-2-trimethylsilyloxy-(3,4,5-η)-undeca-1,3-dien-5-yl]tricarbonyliron (**21**).* Prepared using TMSOTf and methyl ketone **16** (0.100 g, 0.29 mmol). After 2h, flash chromatography (eluent: Et_2O/petrol 20%) afforded **21** (0.107 g, 88%). ν_{max}(film)/cm^{-1} 2958, 2931, 2860, 2078 (CO), 2020 (CO), 1666 (C=O), 1611 (C=C), 1467, 1316; δ_H(600 MHz) 0.24 (9H, s, Si(CH_3)$_3$), 0.88 (3H, t, *J* 6.4, 11-H × 3), 1.25-1.50 (6H, m, 8-H × 2, 9-H × 2, 10-H × 2), 1.55-1.65 (2H, m, 7-H × 2), 4.02 (1H, t, *J* 6.2, 6-H), 4.26 (1H, d, *J* 11.4, 3-H), 4.38 (1H, s, 1-H × 1), 4.45 (1H, d, *J* 8.1, 5-H), 4.59 (1H, s, 1-H × 1), 5.13 (1H, dd, *J* 11.4, 8.1, 4-H); δ_C(50 MHz) -0.3 (Si(*C*H$_3$)$_3$), 13.9 (CH$_3$), 22.4 (CH$_2$), 25.1 (CH$_2$), 31.4 (CH$_2$), 37.9 (CH$_2$), 74.8 (CH), 75.3 (CH), 78.6 (CH), 87.0 (CH), 94.4 (CH$_2$), 153.7 (quat. C), 204.3 (CO), 205.4 (CO), 209.5 (CO); *m/z* (FAB) 423 (MH$^+$, 46%), 383 (41), 339 (MH-3CO, 32), 311 (MH-4CO, 85), 239 (44), 202 (31), 145 (100). [Found (MH$^+$) 423.0937. $C_{18}H_{26}FeO_6Si$ requires *M*H, 423.0926].

[(4E,2R,3S*)-2-[Carbonyl(benzylamino)-κC]-6-trimethylsilyloxy-(3,4,5-η)-hepta-4,6-dien-3-yl]tricarbonyliron (**22**).* Prepared using TMSOTf and methyl ketone **17** (0.060 g, 0.16 mmol). After 2h, flash chromatography (eluent: Et_2O/petrol 20%) afforded **22** (0.053 g, 75%). ν_{max}(film)/cm^{-1} 2968, 2067 (CO), 2008 (CO), 1640 (C=O), 1592 (C=C), 1494, 1454, 1416; δ_H(600 MHz) 0.25 (9H, s, Si(CH_3)$_3$), 1.18 (3H, d, *J* 6.4, 1-H × 3), 3.43-3.49 (2H, m, 2-H, C*H*HPh), 4.24 (1H, d, *J* 11.9, 5-H), 4.36 (1H, d, *J* 1.6, 7-H × 1), 4.37 (1H, d, *J* 8.2, 3-H), 4.60 (1H, d, *J* 1.6, 7-H × 1), 4.95 (1H, dd, *J* 11.9, 8.2, 4-H), 5.11 (1H, d, *J* 14.9, CH*H*Ph), 7.16 - 7.29 (5H, m, Ph); δ_C(150 MHz) -0.3 (Si(*C*H$_3$)$_3$), 22.0 (1-C), 45.9 (*C*H$_2$Ph), 52.7 (2-C), 71.6 (3-C), 80.0 (5-C), 85.6 (4-C), 93.3 (7-C), 127.0 (CH), 128.0 (CH), 128.4 (CH), 137.2 (quat. C), 154.5 (6-C), 203.8 (CO), 204.1 (CO), 206.8 (CO), 211.2 (CO); *m/z* (FAB) 456 (MH$^+$, 37%), 400 (MH-2CO, 33), 371 (M-3CO, 100), 343 (M-4CO, 16), 149 (37), 136 (39). [Found (MH$^+$) 456.0929. $C_{21}H_{26}FeNO_5Si$ requires *M*H, 456.0930.]

[(4E,2S,3S*)-2-[Carbonyl(benzylamino)-κC]-6-trimethylsilyloxy-(3,4,5-η)-hepta-4,6-dien-3-yl]tricarbonyliron (**23**).* Prepared using TMSOTf and methyl ketone **18** (0.100 g, 0.26 mmol). After 2h, flash chromatography (eluent: Et_2O/petrol 20%) afforded **23** (0.096 g, 81%). ν_{max}(film)/cm^{-1} 2978, 2070 (CO), 2015 (CO), 1688 (C=O), 1610 (C=C), 1506; δ_H (600 MHz) 0.22 (9H, s, Si(CH_3)$_3$), 1.27 (3H, d, *J* 6.4, 1-H × 3), 3.36 (1H, q, *J* 6.3, 2-H), 3.59 (1H, d, *J* 14.5, C*H*HPh), 3.83 (1H, d, *J* 11.9, 5-H), 3.89 (1H, d, *J* 8.2, 3-H), 4.30 (1H, d, *J* 1.5, 7-H × 1), 4.44 (1H, d, *J* 1.5, 7-H × 1), 4.91-4.95 (2H, m, 4-H, CH*H*Ph), 7.16-7.34 (5H, m, Ph); δ_C (150 MHz) -0.3 (Si(*C*H$_3$)$_3$), 21.2 (1-C), 45.1 (*C*H$_2$Ph), 51.7 (2-C), 70.0 (3-C), 80.8 (5-C), 87.1 (4-C), 93.1 (7-C), 127.2 (CH), 128.5 (CH), 128.5 (CH), 138.2 (quat. C), 154.5 (6-C), 201.1 (CO), 204.5 (CO), 206.8 (CO), 211.9 (CO); *m/z* (FAB) 456 (MH$^+$, 52%), 428 (MH-CO, 24), 400 (MH-2CO, 39), 371 (M-3CO, 49), 343 (M-4CO, 39), 278 (28), 183 (32), 145 (100). [Found (MH$^+$) 456.0931. $C_{21}H_{26}FeNO_5Si$ requires *M*H, 456.0930.]

[(4Z,3S,6S*)-2-Trimethylsilyloxy-(3,4,5,6-η)-undeca-1,4-dien-3,6-diyl]tricarbonyliron (**30**).* Prepared using TMSOTf and methyl ketone **29** (0.100 g, 0.33 mmol). After 2h, flash chromatography (eluent: Et_2O/petrol 20%) afforded **30** (0.114 g, 92%). ν_{max}(film)/cm^{-1} 2960, 2873, 2058 (CO), 1996 (CO), 1462, 1383; δ_H(200 MHz) 0.22 (9H, s, Si(CH_3)$_3$), 0.88 (3H, t, *J* 6.4, 11-H × 3), 1.16 (1H, app. q, *J* 7.4, 6-H), 1.22-1.79 (8H, m, 7-H × 2, 8-H × 2, 9-H × 2, 10-H × 2), 1.53 (1H, dd, *J* 8.7, 1.0, 3-H), 4.00 (1H, d, *J* 1.5, 1-H × 1), 4.20 (1H, d, *J* 1.5, 1-H × 1), 5.00 (1H, dd, *J* 8.8, 5.1, 5-H), 5.37 (1H, ddd, *J* 8.8, 5.1, 1.0, 4-H); δ_C(50 MHz) -0.2 (Si(*C*H$_3$)$_3$), 13.9 (CH$_3$), 22.4 (CH$_2$), 31.4 (CH$_2$), 31.8 (CH$_2$), 34.1 (CH$_2$), 60.6 (CH), 63.7 (CH), 79.1 (CH), 83.3 (CH), 89.3 (CH$_2$), 156.7 (quat. C), 212.4 (br, CO × 3). Instability of **30** towards hydrolysis precluded mass spectral analysis.

*General procedure for the Mukaiyama aldol reaction; synthesis of **8a-g**, **9a-g**, **24-28** and **31-33**.* For a 0.20 mmol scale reaction: $BF_3.OEt_2$ (1.5 eq.) was added to a stirred solution of the aldehyde (1.5 eq.) in Et_2O (1 ml) at room temperature. After 1 minute, the solution was added dropwise to a cooled (-78°C) solution of the silyl enol ether (1.0 eq.) in Et_2O/CH_2Cl_2 (2 ml / 0.75 ml) and stirred at -78°C for 3-24 h. On completion, Et_3N (1.5 eq.) was added with vigorous stirring. After 2 minutes the mixture was filtered through Celite washing with Et_2O/CH_2Cl_2 (4:1, 10 ml) and concentrated *in vacuo*. Purification by flash column chromatography (silica; Et_2O/petrol) afforded the silylated and non-silylated aldol products. Alternatively, for the purpose of d.e. determination, the concentrated residue after work-up was diluted with THF (0.4 ml) and treated with HF/pyridine (0.4 ml of a *ca.* 2.25 M soln. in THF) for 30 minutes at room temperature. The mixture was then poured into $NaHCO_{3(aq)}$ (5 ml) and extracted with Et_2O (3 × 5ml), the organic fractions were washed with brine (5ml), dried ($MgSO_4$) and concentrated *in vacuo*. The d.e. was determined by ^{1}H NMR analysis of the crude reaction mixture and subsequent flash chromatography afforded the non-silylated aldol products. Complexes **8a-c**, **8e-g**, **9a**, **b**, **f** and **g**, **24**, **25**, **27**, **28**, **32** and **33** were obtained as inseparable mixtures of diastereoisomers as indicated and data is reported on the mixtures. Assignments for the minor diastereoisomer are primed (').

[(4E,1R,6S*,7R*)-7-(Carbonyloxy-κC)-3-oxo-1-phenyl-1-trimethylsilyloxy-(4,5,6-η)-dodec-4-en-6-yl]tricarbonyliron (**9a**) and [(4E,1R*,6S*,7R*)-7-(carbonyloxy-κC)-1-hydroxy-3-oxo-1-phenyl-(4,5,6-η)-dodec-4-en-6-yl]tricarbonyliron (**8a**).* Prepared

using TMS enol ether **5** (0.099 g, 0.23 mmol), benzaldehyde and $BF_3.OEt_2$. After 5.5 h, Et_3N work-up and flash chromatography (eluent: Et_2O-petrol 15-70%) afforded, in order of elution, *silyl aldol complex* **9a** (0.076 g, 61%; 90% d.e.); ν_{max}(film)/cm^{-1} 3058, 2957, 2933, 2860, 2091 (CO), 2025 (CO), 1674 (C=O), 1497, 1419; δ_H(500 MHz) -0.01 (9H, s, Si(CH_3)$_3$), 0.88 (3H, t, *J* 6.7, 12-H × 3), 1.23-1.58 (8H, m, 8-H × 2, 9-H × 2, 10-H × 2, 11-H × 2), 2.74 (0.05H, dd, *J* 14.4, 3.2, 2-H' × 1), 2.90 (0.95H, dd, *J* 16.3, 3.8, 2-H × 1), 3.17 (0.95H, dd, *J* 16.3, 8.8, 2-H × 1), 3.24 (0.05H, dd, *J* 14.4, 9.4, 2-H' × 1), 3.76 (0.95H, d, *J* 11.2, 4-H),), 3.94 (0.05H, d, *J* 11.6, 4-H'), 4.32 (1H, apparent q, *J* 5.7, 7-H), 5.00 (1H, dd, *J* 8.6, 4.6, 6-H), 5.28 (1H, dd, *J* 8.8, 3.8, 1-H), 5.55 (1H, dd, *J* 11.2, 8.6, 5-H), 7.24-7.81 (5H, m, Ph-*H*); δ_C(50 MHz) -0.1 (Si(CH_3)$_3$), 13.9 (CH_3), 22.4 (CH_2), 26.4 (CH_2), 31.5 (CH_2), 36.6 (CH_2), 53.9 (CH_2), 66.1 (CH), 70.6 (CH), 76.7 (CH), 84.6 (CH), 91.6 (CH), 125.9 (CH), 127.5 (CH), 128.4 (CH), 143.8 (quat. C), 199.9 (CO), 201.1 (CO), 202.4 (CO), 204.3 (CO), 208.0 (CO); *m/z* (FAB) 529 (MH$^+$, 15%), 489 (12), 473 (MH-2CO, 10), 417 (MH-4CO, 51), 401 (20), 179 (100), 145 (98). [Found (MH$^+$) 529.1316. $C_{25}H_{33}FeO_7Si$ requires *M*H, 529.1345]; and then *aldol complex* **8a** (0.022 g, 20%; 80% d.e.); ν_{max}(film)/cm^{-1} 3458 (OH), 3031, 2928, 2858, 2088 (CO), 2016 (CO), 1667 (C=O), 1496, 1454, 1417; δ_H(500 MHz) 0.88 (3H, t, *J* 6.2, 12-H × 3), 1.23-1.62 (8H, m, 8-H × 2, 9-H × 2, 10-H × 2, 11-H × 2), 2.96-3.19 (3H, m, 2-H × 2, OH), 3.79 (0.1H, d, *J* 11.4, 4-H'), 3.83 (0.9H, d, *J* 11.3, 4-H), 4.34 (1H, apparent q, *J* 5.6, 7-H), 5.03 (1H, dd, *J* 8.3, 4.5, 6-H), 5.26-5.28 (1H, m, 1-H), 5.59 (1H, dd, *J* 11.3, 8.3, 5-H), 7.28-7.39 (5H, m, Ph-*H*); δ_C(100 MHz) 13.9 (CH_3), 22.4 (CH_2), 26.5 (CH_2), 31.5 (CH_2), 36.6 (CH_2), 51.7 (CH_2), 65.5 (CH), 70.1 (CH), 77.0 (CH), 84.9 (CH), 92.0 (CH), 125.7 (CH), 127.9 (CH), 128.7 (CH), 142.5 (quat. C), 199.6 (CO), 202.4 (CO), 203.6 (CO), 204.4 (CO), 207.8 (CO); *m/z* (FAB) 457 (MH$^+$, 25%), 399 (20), 345 (MH-4CO, 38), 327 (61), 179 (48), 151 (50), 136 (100). [Found (MH$^+$) 457.0984. $C_{22}H_{25}FeO_7$ requires *M*H, 457.0950].

[(8E,6R,7S*,12S*)-6-(Carbonyloxy-κC)-10-oxo-12-trimethylsilyloxy-(7,8,9-η)-heptadec-8-en-7-yl]tricarbonyliron (**9b**) and [(8E,6R*,7S*,12S*)-6-(carbonyloxy-κC)-12-hydroxy-10-oxo-(7,8,9-η)-heptadec-8-en-7-yl]tricarbonyliron (**8b**).* Prepared using TMS enol ether **5** (0.095 g, 0.23 mmol), hexanal and $BF_3.OEt_2$. After 5 h, Et_3N work-up and flash chromatography (eluent: Et_2O-petrol 15-50%) afforded, in order of elution, *silyl aldol complex* **9b** (0.020 g, 17%; 88% d.e.); ν_{max}(film)/cm^{-1} 2956, 2931, 2860, 2090 (CO), 2029 (CO), 1678 (C=O), 1498, 1467, 1418; δ_H(500 MHz) 0.10 (9H, s, Si(CH_3)$_3$), 0.86-0.90 (6H, m, 1-H × 3, 17-H × 3), 1.23-1.62 (16H, 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), 2.63 (0.06H, br d, *J* 11.4, 11-H' × 1), 2.78 (0.94H, dd, *J* 16.3, 6.7, 11-H × 1), 2.84 (0.94H, dd, *J* 16.3, 4.7, 11-H × 1), 2.92 (0.06H, dd, *J* 14.6, 4.7, 11-H' × 1), 3.90 (1H, d, *J* 11.4, 9-H), 4.18-4.23 (1H, m, 12-H), 4.31-4.36 (1H, m, 6-H), 5.00 (1H, dd, *J* 8.5, 4.6, 7-H), 5.54 (1H, dd, *J* 11.4, 8.5, 8-H); δ_C(150 MHz) 0.3 (Si(CH_3)$_3$), 13.87 (CH_3), 13.94 (CH_3), 22.4 (CH_2), 22.5 (CH_2), 25.1 (CH_2), 26.5 (CH_2), 31.5 (CH_2), 31.8 (CH_2), 36.7 (CH_2), 37.4 (CH_2), 50.7 (CH_2), 66.3 (CH), 68.4 (CH), 76.8 (CH), 84.3 (CH), 91.8 (CH), 199.9 (CO), 202.3 (CO), 202.4 (CO), 204.6 (CO), 208.0 (CO); *m/z* (FAB) 523 (MH$^+$, 13%), 483 (28), 411 (MH-4CO, 100), 395 (26), 173 (42), 145 (57). {Found [(MH-4CO)$^+$] 411.2051. $C_{20}H_{39}FeO_3Si$ requires *M*H-4CO, 411.2018}; and then *aldol complex* **8b** (0.058 g, 57%; 80% d.e.); ν_{max}(film)/cm^{-1} 3472 (OH), 2931, 2859, 2089 (CO), 2020 (CO), 1673 (C=O), 1499, 1467, 1417; δ_H(500 MHz) 0.80-0.94 (6H, m, 1-H × 3, 17-H × 3), 1.18-1.66 (16H, 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), 2.69 (1H, d, *J* 3.9, OH), 2.79 (1H, dd, *J* 17.4, 9.0, 11-H × 1), 2.90 (1H, dd, *J* 17.4, 2.5, 11-H × 1), 3.80 (0.10H, d, *J* 11.4, 9-H'), 3.85 (0.90H, d, *J* 11.1, 9-H), 4.10-4.17 (1H, m, 12-H), 4.35 (1H, apparent q, *J* 5.7, 6-H), 5.04 (1H, dd, *J* 8.6, 4.5, 7-H), 5.58 (1H, dd, *J* 11.1, 8.6, 8-H); δ_C(100 MHz) 14.0 (CH_3), 14.02 (CH_3), 22.4 (CH_2), 22.6 (CH_2), 25.1 (CH_2), 26.5 (CH_2), 31.5 (CH_2), 31.7 (CH_2), 36.6 (CH_2), 36.7 (CH_2), 49.7 (CH_2), 65.6 (CH), 67.7 (CH), 77.0 (CH), 84.8 (CH), 91.9 (CH), 199.6 (CO), 202.5 (CO), 204.5 (CO), 204.7 (CO), 207.7 (CO); *m/z* (FAB) 451 (MH$^+$, 7%), 433 (MH-H_2O, 10), 423 (MH-CO, 14), 339 (MH-4CO, 27), 321 (MH-4CO-H_2O, 100), 249 (30), 165 (34), 149 (41), 123 (56). [Found (MH-CO)$^+$ 423.1446. $C_{20}H_{31}FeO_6$ requires *M*H-CO, 423.1470].

[(8E,6R,7S*,12R*)-6-(Carbonyloxy-κC)-13-methyl-10-oxo-12-trimethylsilyloxy-(7,8,9-η)-tetradec-8-en-7-yl]tricarbonyliron (**9c**) and [(8E,6R*,7S*,12R*)-6-(carbonyloxy-κC)-12-hydroxy-13-methyl-10-oxo-(7,8,9-η)-tetradec-8-en-7-yl]tricarbonyliron (**8c**).* Prepared using TMS enol ether **5** (0.101 g, 0.24 mmol), isobutyraldehyde and $BF_3.OEt_2$. After 5 h, Et_3N work-up and flash chromatography (eluent: Et_2O-petrol 10-50%) afforded, in order of elution, *silyl aldol complex* **9c** (0.031 g, 26%); ν_{max}(film)/cm^{-1} 3056, 2959, 2087 (CO), 2034 (CO), 1673 (C=O), 1498, 1467, 1419, 1386; δ_H(200 MHz) 0.10 (9H, s, Si(CH_3)$_3$), 0.85-0.93 (9H, m, 1-H × 3, 14-H × 3, 13-CH_3), 1.21-1.83 (9H, m, 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2, 13-H), 2.77-2.89 (2H, m, 11-H × 2), 3.91 (1H, d, *J* 11.2, 9-H), 4.07 (1H, apparent q, *J* 5.4, 12-H), 4.34 (1H, apparent q, *J* 5.7, 6-H), 5.00 (1H, dd, *J* 8.7, 4.7, 7-H), 5.55 (1H, dd, *J* 11.2, 8.7, 8-H); δ_C(50 MHz) 0.2 (Si(CH_3)$_3$), 13.9 (CH_3), 17.8 (CH_3), 18.1 (CH_3), 22.4 (CH_2), 26.4 (CH_2), 31.4 (CH_2), 33.7 (CH), 36.7 (CH_2), 47.4 (CH_2), 66.3 (CH), 72.7 (CH), 76.7 (CH), 84.1 (CH), 91.8 (CH), 200.0 (CO), 202.4 (2 × CO), 204.5 (CO), 208.0 (CO); *m/z* (FAB) 495 (MH$^+$, 17%), 455 (20), 383 (MH-4CO, 75), 367 (38), 145 (100). [Found (MH$^+$) 495.1496. $C_{22}H_{35}FeO_7Si$ requires *M*H, 495.1501]; and then *aldol complex* **8c** (0.040 g, 40%; 92% d.e.); ν_{max}(film)/cm^{-1} 3503 (OH), 3056, 2959, 2932, 2873, 2090 (CO), 2016 (CO), 1670 (C=O), 1499, 1467, 1418, 1368; δ_H(600 MHz) 0.88 (3H, t, *J* 6.6, 1-H × 3), 0.94 (3H, d, *J* 3.9, 14-H × 3), 0.97 (3H, d, *J* 3.8, 13-CH_3), 1.20-1.82 (9H, m, 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2, 13-H), 2.64-2.92 (3H, m, 11-H × 2, OH), 3.83 (0.04H, d, *J* 11.2, 9-H'), 3.84-3.96 {1.96H, m, [including 3.87 (0.96H, d, *J* 11.2, 9-H)], 9-H, 12-H}, 4.35 (1H, apparent q, *J* 5.6, 6-H), 5.03 (1H, dd, *J* 8.6, 4.5, 7-H), 5.58 (1H, dd, *J* 11.2, 8.6, 8-H); δ_C(50 MHz) 13.8 (CH_3), 17.6 (CH_3), 18.3 (CH_3), 22.4 (CH_2), 26.4 (CH_2), 31.4 (CH_2), 33.2 (CH), 36.6 (CH_2), 46.8 (CH_2), 65.8 (CH), 72.2 (CH), 76.7 (CH), 84.7 (CH), 91.9 (CH), 199.6 (CO), 202.4 (CO), 204.5 (CO), 204.7 (CO), 207.8 (CO); *m/z* (FAB) 423 (MH$^+$, 14%), 339 (MH-3CO, 6), 311 (MH-4CO, 34), 293 (MH-4CO-H_2O, 39), 239 (19), 221 (23), 133 (100). [Found (MH$^+$) 423.1225. $C_{19}H_{27}FeO_7$ requires *M*H, 423.1259].

[(8E,6R,7S*,12R*)-6-(Carbonyloxy-κC)-13,13-dimethyl-10-oxo-12-trimethylsilyloxy-(7,8,9-η)-tetradec-8-en-7-yl] tricarbonyliron (**9d**) and [(8E,6R*,7S*,12R*)-6-(carbonyloxy-κC)-13,13-dimethyl-12-hydroxy-10-oxo-(7,8,9-η)-tetradec-8-en-7-yl] tricarbonyliron (**8d**).* Prepared using TMS enol ether **5** (0.062 g, 0.15 mmol), pivalaldehyde and $BF_3.OEt_2$. After 23 h, Et_3N work-up and flash chromatography (eluent: Et_2O-petrol 10-40%) afforded, in order of elution, *silyl aldol complex* **9d** (0.011 g, 15%); ν_{max}(film)/cm^{-1} 2958, 2870, 2089 (CO), 2022 (CO), 1674 (C=O), 1498, 1478, 1379; δ_H(600 MHz) 0.09 (9H, s, Si(CH_3)$_3$), 0.82-0.93 {12H, m, [including 0.88 (9H, s, 13-Me × 2, 14-H × 3)], 1-H × 3, 14-H × 3, 13-Me × 2}, 1.20-1.63 (8H, m, 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2), 2.74 (1H, dd, *J* 17.7, 8.4, 11-H × 1), 2.91 (1H, br d, *J* 17.7, 11-H × 1), 3.85 (1H, d, *J* 11.0, 9-H), 3.94 (1H, br d, *J* 8.4,

12-H), 4.33-4.38 (1H, m, 6-H), 5.01 (1H, dd, *J* 8.7, 4.9, 7-H), 5.54-5.57 (1H, dd, *J* 11.0, 8.7, 8-H); δ_C(150 MHz) 0.5 (Si(CH_3)$_3$), 13.9 (CH_3), 22.4 (CH_2), 26.0 (CH_3), 26.5 (CH_2), 31.5 (CH_2), 35.3 (quat. C), 36.7 (CH_2), 47.5 (CH_2), 66.0 (CH), 75.3 (CH), 76.8 (CH), 83.9 (CH), 92.0 (CH), 200.0 (CO), 202.5 (CO), 202.8 (CO), 204.7 (CO), 207.9 (CO); *m/z* (electrospray) 1039 [(2M+Na)$^+$, 32%], 531 (M+Na, 100), 509 (MH, 7). {Found [(M+Na)$^+$] 531.1469. $C_{23}H_{36}FeNaO_7Si$ requires *M*+Na, 531.1477}; and then *aldol complex* **8d** (0.027 g, 42%); ν_{max}(film)/cm^{-1} 3508 (OH), 3055, 2956, 2090 (CO), 2019 (CO), 1672 (C=O), 1499, 1468, 1417; δ_H(200 MHz) 0.88 (3H, t, *J* 6.6, 1-H × 3), 0.95 (9H, s, 13-Me × 2, 14-H × 3), 1.22-1.63 (8H, m, 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2), 2.60-2.92 (3H, m, 11-H × 2, OH), 3.81-3.92 {2H, m, [including 3.90 (1H, d, *J* 11.1, 9-H)], 9-H, 12-H}, 4.35 (1H, apparent q, *J* 5.7, 6-H), 5.04 (1H, dd, *J* 8.7, 4.6, 7-H), 5.59 (1H, dd, *J* 11.1, 8.7, 8-H); δ_C(50 MHz) 13.9 (CH_3), 22.4 (CH_2), 25.5 (CH_3), 26.4 (CH_2), 31.4 (CH_2), 34.3 (quat. C), 36.6 (CH_2), 44.9 (CH_2), 65.9 (CH), 74.8 (CH), 76.7 (CH), 84.7 (CH), 91.9 (CH), 199.6 (CO), 202.5 (CO), 204.4 (CO), 204.9 (CO), 207.8 (CO); *m/z* (FAB) 459 [(M+Na)$^+$, 12%], 437 (MH, 26), 353 (MH-3CO, 16), 325 (MH-4CO, 92), 221 (59), 165 (52), 151 (54), 121 (66), 111 (99), 107 (100). [Found (MH$^+$) 437.1233. $C_{20}H_{29}FeO_7$ requires *M*H, 437.1263].

[(4E,1R,6S*,7R*)-7-(Carbonyloxy-κC)-1-cyclohexyl-3-oxo-1-trimethylsilyloxy-(4,5,6-η)-dodec-4-en-6-yl]tricarbonyliron (**9e**) and [(4E,1R*,6S*,7R*)-7-(carbonyloxy-κC)-1-cyclohexyl-1-hydroxy-3-oxo-(4,5,6-η)-dodec-4-en-6-yl]tricarbonyliron (**8e**).* Prepared using TMS enol ether **5** (0.086 g, 0.20 mmol), cyclohexanecarboxaldehyde and BF_3.OEt_2. After 3.5 h, Et_3N work-up and flash chromatography (eluent: Et_2O/petrol 20-60%) afforded, in order of elution, *silyl aldol complex* **9e** (0.047 g, 43%); (Found C, 56.21; H, 7.13. $C_{25}H_{38}FeO_7Si$ requires C, 56.18; H 7.17%); ν_{max}(film)/cm^{-1} 3055, 2929, 2855, 2089 (CO), 2020 (CO), 1674 (C=O), 1498, 1451, 1419; δ_H(200 MHz) 0.09 (9H, s, Si(CH_3)$_3$), 0.85-1.77 {22H, m, [including 0.88 (3H, t, *J* 6.4, 12-H × 3)], C_6H_{11}, 8-H × 2, 9-H × 2, 10-H × 2, 11-H × 2, 12-H × 3}, 2.80 - 2.83 (2H, m, 2-H × 2), 3.92 (1H, d, *J* 11.6, 4-H), 4.02 (1H, apparent q, *J* 5.4, 1-H), 4.34 (1H, apparent q, *J* 5.9, 7-H), 5.00 (1H, dd, *J* 8.6, 4.1, 6-H), 5.44 (1H, dd, *J* 11.6, 8.6, 5-H); δ_C(50 MHz) 0.3 (Si(CH_3)$_3$), 13.9 (CH_3), 22.4 (CH_2), 26.2 (CH_2 × 2), 26.4 (CH_2), 26.5 (CH_2), 28.6 (CH_2), 28.7 (CH_2), 31.4 (CH_2), 36.6 (CH_2), 43.8 (CH), 47.9 (CH_2), 66.4 (CH), 72.4 (CH), 76.7 (CH), 84.1 (CH), 91.8 (CH), 200.0 (CO), 202.3 (CO), 202.5 (CO), 204.6 (CO), 208.0 (CO); *m/z* (FAB) 535 (MH$^+$, 0.8%), 507 (MH-CO, 0.5), 495 (3), 478 (M-2CO, 0.7), 461 (M-Si(CH_3)$_3$, 0.3), 451 (MH-3CO, 0.6), 423 (MH-4CO, 11), 133 (100). {Found [(MH-4CO)$^+$] 423.2013. $C_{21}H_{39}FeO_3Si$ requires *M*H-4CO, 423.2018}; and then *aldol complex* **8e** (0.030 g, 32%; 92% d.e.); ν_{max}(film)/cm^{-1} 3488 (OH), 2926, 2855, 2089 (CO), 2019 (CO), 1673 (C=O), 1499, 1417; δ_H(600 MHz) 0.89 (3H, t, *J* 6.8, 12-H × 3), 1.00-1.82 (19H, m, C_6H_{11}, 8-H × 2, 9-H × 2, 10-H × 2, 11-H × 2), 2.60 (1H, d, *J* 4.0, OH), 2.80 (1H, dd, *J* 17.2, 9.6, 2-H × 1), 2.88 (1H, dd, *J* 17.2, 2.4, 2-H × 1), 3.82 (0.04H, d, *J* 11.4, 4-H'), 3.87 (0.96H, d, *J* 11.2, 4-H), 3.90-3.95 (1H, m, 1-H), 4.35 (1H, apparent q, *J* 5.8, 7-H), 5.03 (1H, dd, *J* 8.7, 4.6, 6-H), 5.58 (1H, dd, *J* 11.2, 8.7, 5-H); δ_C(150 MHz) 13.9 (CH_3), 22.4 (CH_2), 26.0 (CH_2), 26.1 (CH_2), 26.4 (CH_2), 26.5 (CH_2), 28.3 (CH_2), 28.8 (CH_2), 31.5 (CH_2), 36.7 (CH_2), 43.2 (CH), 47.1 (CH_2), 65.9 (CH), 71.7 (CH), 77.0 (CH), 84.7 (CH), 92.0 (CH), 199.7 (CO), 202.4 (CO), 204.5 (CO), 204.9 (CO), 207.8 (CO); *m/z* (FAB) 463 (MH$^+$, 50%), 351 (100, MH-4CO), 333 (56), 221 (38), 165 (48), 136 (73). [Found (MH$^+$) 463.1458. $C_{22}H_{31}FeO_7$ requires *M*H, 463.1419].

[(8E,13E,6R,7S*,12R*)-6-(Carbonyloxy-κC)-10-oxo-12-trimethylsilyloxy-(7,8,9-η)-octadeca-8,13-dien-7-yl]tricarbonyliron (**9f**), [(8E,11E,13E,6R*,7S*)-6-(carbonyloxy-κC)-10-oxo-(7,8,9-η)-octadeca-8,11,13-trien-7-yl]tricarbonyliron (**11f**) and [(8E,13E,6R*,7S*,12R*)-6-(carbonyloxy-κC)-12-hydroxy-10-oxo-(7,8,9-η)-octadeca-8,13-dien-7-yl]tricarbonyliron (**8f**).* Prepared using TMS enol ether **5** (0.095 g, 0.23 mmol), (*E*)-hept-2-enal and BF_3.OEt_2. After 5.75 h, Et_3N work-up and flash chromatography (eluent: Et_2O/petrol 15-70%) afforded, in order of elution, *silyl aldol complex* **9f** (0.056 g, 47%; 75% d.e.); ν_{max}(film)/cm^{-1} 3054, 2957, 2929, 2860, 2088 (CO), 2017 (CO), 1681 (C=O), 1499, 1466, 1419; δ_H(600 MHz) 0.07 (9H, s, Si(CH_3)$_3$), 0.86-0.90 (6H, m, 1-H × 3, 18-H × 3), 1.22-1.63 (12H, m, 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2, 16-H × 2, 17-H × 2), 1.99-2.01 (2H, m, 15-H × 2), 2.61 (0.13H, dd, *J* 14.3, 4.3, 11-H' × 1), 2.78 (0.87H, dd, *J* 15.8, 4.3, 11-H × 1), 2.87 (0.87H, dd, *J* 15.8, 7.8, 11-H × 1), 3.00 (0.13H, dd, *J* 14.3, 8.8, 11-H' × 1), 3.89 (0.87H, d, *J* 11.2, 9-H), 3.92 (0.13H, d, *J* 10.8, 9-H'), 4.32 (1H, apparent q, *J* 5.8, 6-H), 4.67 (1H, apparent q, *J* 6.2, 12-H), 5.00 (1H, dd, *J* 8.5, 4.5, 7-H), 5.45 (1H, dd, *J* 15.3, 6.8, 13-H), 5.53 (1H, dd, *J* 11.2, 8.5, 8-H), 5.64 (1H, dt, *J* 15.3, 6.7, 14-H); δ_C(50 MHz) 0.2 (Si(CH_3)$_3$), 13.80 (CH_3), 13.84 (CH_3), 22.1 (CH_2), 22.4 (CH_2), 26.5 (CH_2), 31.2 (CH_2), 31.4 (CH_2), 31.6 (CH_2), 36.7 (CH_2), 51.6 (CH_2), 66.3 (CH), 69.4 (CH), 76.7 (CH), 84.4 (CH), 91.7 (CH), 131.6 (CH), 131.8 (CH), 199.9 (CO), 201.5 (CO), 202.3 (CO), 204.4 (CO), 208.0 (CO); *m/z* (FAB) 557 [(M+Na)$^+$, 6%], 535 (MH, 39), 423 (MH-4CO, 78), 405 (MH-4CO-H_2O, 41), 333 (55), 185 (84), 145 (100), 129 (74). [Found (MH$^+$) 535.1803. $C_{25}H_{39}FeO_7Si$ requires *M*H, 535.1814]; and then *dienone* **11f** (*ca.* 0.01g, 9%); ν_{max}(film)/cm^{-1} 2957, 2929, 2859, 2088 (CO), 2020 (CO), 1667 (C=O), 1632 (C=C), 1592 (C=C), 1499, 1456; δ_H(600 MHz) 0.88 (3H, t, *J* 6.8, 1-H × 3 or 18-H × 3), 0.91 (3H, t, *J* 7.3, 18-H × 3 or 1-H × 3), [1.25-1.48 (9H, m), 1.57-1.63 (3H, m), 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2, 16-H × 2, 17-H × 2], 2.22 (2H, apparent q, *J* 7.2, 15-H × 2), 4.12 (1H, d, *J* 11.1, 9-H), 4.37 (1H, apparent q, *J* 5.7, 6-H), 5.02 (1H, dd, *J* 9.0, 4.6, 7-H), 5.69 (1H, dd, *J* 11.1, 9.0, 8-H), 6.24-6.35 (3H, m, 11-H, 13-H, 14-H), 7.37 (1H, dd, *J* 15.4, 10.6, 12-H); δ_C(50 MHz) 13.8 (CH_3), 13.9 (CH_3), 22.2 (CH_2), 22.4 (CH_2), 26.5 (CH_2), 30.6 (CH_2), 31.5 (CH_2), 32.9 (CH_2), 36.6 (CH_2), 65.2 (CH), 77.1 (CH), 84.0 (CH), 92.0 (CH), 126.8 (CH), 128.8 (CH), 145.6 (CH), 148.3 (CH), 192.8 (quat. C), 200.0, 203.4, 204.6, 208.1 (CO); *m/z* (electrospray) 467 [(M+Na)$^+$, 53%], 445 (MH, 17), 271 (63), 251 (58), 223 (100). {Found [(M+Na)$^+$] 467.1148. $C_{22}H_{28}FeNaO_6$ requires *M*+Na, 467.1133}; and then *aldol complex* **8f** (0.019 g, 18%; 60% d.e.); ν_{max}(film)/cm^{-1} 3462 (OH), 2957, 2929, 2860, 2091 (CO), 2024 (CO), 1666 (C=O), 1498, 1466, 1418; δ_H(200 MHz) 0.86-0.93 (6H, m, 1-H × 3, 18-H × 3), 1.19-1.65 (12H, m, 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2, 16-H × 2, 17-H × 2), 2.04 (2H, br q, *J* 6.8, 15-H × 2), 2.64 (1H, d, *J* 4.2, OH), 2.89-2.94 (2H, m, 11-H × 2), 3.82 (0.2H, d, *J* 11.0, 9-H'), 3.86 (0.8H, d, *J* 11.6, 9-H), 4.35 (1H, apparent q, *J* 5.6, 6-H), 4.55-4.68 (1H, m, 12-H), 5.04 (1H, dd, *J* 8.6, 4.6, 7-H), 5.47-5.63 (2H, m, 8-H, 13-H), 5.75 (1H, dt, *J* 15.5, 6.4, 14-H); δ_C(50 MHz) 13.80 (CH_3), 13.84 (CH_3), 22.1 (CH_2), 22.4 (CH_2), 26.4 (CH_2), 31.1 (CH_2), 31.4 (CH_2), 31.7 (CH_2), 36.6 (CH_2), 49.8 (CH_2), 65.7 (CH), 68.7 (CH), 76.7 (CH), 84.7 (CH), 92.0 (CH), 130.5 (CH), 132.8 (CH), 199.6 (CO), 202.3 (CO), 203.7 (CO), 204.5 (CO), 207.8 (CO); *m/z* (electrospray) 485 [(M+Na)$^+$, 100%], 463 (MH, 15), 373 (46), 251 (9), 223 (11). [Found (MH$^+$) 463.1425. $C_{22}H_{31}FeO_7$ requires *M*H, 463.1419].

[(8E,6R,7S*,12R*)-6-(Carbonyloxy-κC)-10-oxo-12-trimethylsilyloxy-(7,8,9-η)-nonadec-8-en-13-yn-7-yl]tricarbonyliron (**9g**) and [(8E,6R*,7S*,12R*)-6-(carbonyloxy-κC)-12-hydroxy-10-oxo-(7,8,9-η)-nonadec-8-en-13-yn-7-yl]tricarbonyliron (**8g**).* Prepared using TMS enol ether **5** (0.059 g, 0.14 mmol), oct-2-ynal and $BF_3.OEt_2$. After 2.5 h, Et_3N work-up and flash column chromatography (eluent: Et_2O/petrol 20-50%) afforded, in order of elution, *silyl aldol complex* **9g** (0.047 g, 62%; 26% d.e.); ν_{max}(film)/cm^{-1} 2957, 2933, 2861, 2248 (C≡C), 2088 (CO), 2016 (CO), 1681 (C=O), 1499, 1467, 1418, 1367; δ_H(200 MHz) 0.14 (3.33H, s, Si(C*H*$_3$)$_3$'), 0.17 (5.67H, s, Si(C*H*$_3$)$_3$), 0.82-0.94 (6H, m, 1-H × 3, 19-H × 3), 1.20-1.64 (14H, m, 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2, 16-H × 2, 17-H × 2, 18-H × 2), 2.18 (2H, br t, *J* 6.2, 15-H × 2), 2.88 (0.63H, dd, *J* 15.2, 5.0, 11-H × 1), 2.93 (0.37H, dd, *J* 15.9, 4.5, 11-H' × 1), 3.11 (0.37H, dd, *J* 15.9, 8.1, 11-H' × 1), 3.18 (0.63H, dd, *J* 15.2, 8.1, 11-H × 1), 3.91 (0.37H, d, *J* 11.1, 9-H'), 3.94 (0.63H, d, *J* 11.2, 9-H), 4.33 (1H, apparent q, *J* 5.8, 6-H), 4.82-5.06 (2H, m, 7-H, 12-H), 5.54 (0.63H, dd, *J* 11.2, 8.7, 8-H), 5.56 (0.37H, dd, *J* 11.1, 8.7, 8-H'); δ_C(50 MHz) -0.1 (Si(*C*H$_3$)$_3$'), 0.0 (Si(*C*H$_3$)$_3$), 13.8 (CH_3, 1-C, 19-C), 18.5 (CH_2), 22.1 (CH_2), 22.3 (CH_2), 26.5 (CH_2), 28.0 (CH_2), 28.1 (CH_2'), 31.0 (CH_2), 31.4 (CH_2), 36.7 (CH_2), 51.7 (CH_2), 51.8 (CH_2'), 58.3 (CH), 59.4 (CH'), 65.7 (CH'), 66.4 (CH), 76.6 (CH'), 76.7 (CH), 80.1 (quat. C), 80.2 (quat. C'), 84.71 (CH'), 84.74 (CH), 85.8 (quat. C'), 86.1 (quat. C), 91.6 (CH'), 91.7 (CH), 199.7 (CO), 199.8 (CO'), 200.4 (CO'), 201.4 (CO), 201.9 (CO), 202.1 (CO'), 204.1 (CO'), 204.7 (CO), 207.9 (CO), 208.0 (CO'); *m/z* (FAB) 547 (MH^+, 29%), 519 (MH-CO, 8), 507 (12), 457 (M-OSi(CH$_3$)$_3$, 12), 435 (MH-4CO, 100), 419 (20), 197 (57), 145 (89). [Found (MH^+) 547.1842. $C_{26}H_{39}FeO_7Si$ requires *M*H, 547.1814]; and then *aldol complex* **8g** (0.011 g, 16%; 53% d.e.); ν_{max}(film)/cm^{-1} 3446 (OH), 2957, 2932, 2860, 2249 (C≡C), 2092 (CO), 2028 (CO), 1672 (C=O), 1499, 1467, 1418, 1366; δ_H(600 MHz) 0.85-0.91 (6H, m, 1-H × 3, 19-H × 3), 1.20-1.63 (14H, m, 2-H × 2, 3-H × 2, 4-H × 2, 5-H × 2, 16-H × 2, 17-H × 2, 18-H × 2), 2.19 (2H, br t, *J* 8.5, 15-H × 2), 2.81 (0.77H, d, *J* 5.1, OH), 2.92 (0.23H, d, *J* 6.2, OH'), 3.03-3.09 (1H, m, 11-H × 1), 3.12-3.20 (1H, m, 11-H × 1), 3.82 (0.77H, d, *J* 11.1, 9-H), 3.83 (0.23H, d, *J* 11.0, 9-H'), 4.36 (1H, apparent q, *J* 5.7, 6-H), 4.82-4.87 (0.23H, m, 12-H'), 4.87-4.92 (0.77H, m, 12-H), 5.06 (1H, dd, *J* 8.4, 4.5, 7-H), 5.57-5.61 (1H, m, 8-H); δ_C(50 MHz) 13.9 (CH_3 × 2), 18.6 (CH_2), 22.1 (CH_2), 22.4 (CH_2), 26.4 (CH_2), 28.1 (CH_2), 31.0 (CH_2), 31.4 (CH_2), 36.6 (CH_2), 50.1 (CH_2'), 50.3 (CH_2), 58.60 (CH'), 58.63 (CH), 65.2 (CH), 76.8 (CH), 79.2 (quat. C), 79.3 (quat. C'), 85.0 (CH), 86.3 (quat. C'), 86.5 (quat. C), 91.8 (CH'), 92.0 (CH), 199.5 (CO), 201.9 (CO), 202.8 (CO), 204.6 (CO), 207.6 (CO); *m/z* (FAB) 475 (MH^+, 10%), 385 (14), 363 (MH-4CO, 28), 345 (51), 221 (41), 207 (41), 147 (100), 107 (70). [Found (MH^+) 475.1441. $C_{23}H_{31}FeO_7$ requires *M*H, 475.1419].

[(4E,2R,3S*,8R*)-2-(Carbonyloxy-κC)-8-hydroxy-6-oxo-8-phenyl(3,4,5-η)-oct-4-en-3-yl]tricarbonyliron (**24**).* Prepared using TMS enol ether **19** (0.045 g, 0.12 mmol), benzaldehyde and $BF_3.OEt_2$. Neat CH_2Cl_2 was used as solvent. After 6.5 h, Et_3N work-up and desilylation using HF/pyridine afforded the crude aldol product (d.c. 87% by ^1H NMR analysis). Flash chromatography (eluent: Et_2O/petrol 60-70%) afforded *aldol complex* **24** (0.038 g, 78%); ν_{max}(film)/cm^{-1} 3414 (OH), 2095, 2047, 2030 (CO), 1668 (C=O), 1499, 1055; δ_H(600 MHz) 1.35 (3H, d, *J* 5.8, 1-H × 3), 3.01 (1H, br s, OH), 3.07 (1H, d, *J* 16.9, 7-H × 1), 3.16 (1H, dd, *J* 16.9, 9.1, 7-H × 1), 3.87 (1H, d, *J* 11.1, 5-H), 4.49-4.55 (1H, m, 2-H), 5.06 (1H, dd, *J* 8.6, 4.4, 3-H), 5.25-5.30 (1H, m, 8-H), 5.58 (1H, apparent t, *J* 9.7, 4-H), 7.26-7.42 (5H, m, Ph); δ_C(150 MHz) 21.8 (CH_3), 51.7 (CH_2), 65.6 (CH), 70.0 (CH), 72.8 (CH), 86.0 (CH), 91.9 (CH), 125.7 (CH), 127.9 (CH), 128.7 (CH), 142.6 (quat. C), 199.5 (CO), 202.2 (CO), 203.4 (CO), 204.3 (CO), 207.7 (CO); *m/z* (FAB) 401 (MH^+, 100%), 316 (M-3CO, 22), 271 (70), 120 (29), 107 (53). [Found (MH^+) 401.0322. $C_{18}H_{17}FeO_7$ requires *M*H, 401.0324].

[(3E,1R,2S*,7R*)-1-(Carbonyloxy-κC)-7-hydroxy-5-oxo-1,7-diphenyl-(2,3,4-η)-hept-3-en-2-yl]tricarbonyliron (**25**).* Prepared using TMS enol ether **20** (0.027 g, 0.06 mmol), benzaldehyde and $BF_3.OEt_2$. After 5 h, Et_3N work-up and desilylation using HF/pyridine afforded the crude aldol product (d.e. 67% by ^1H NMR analysis). Flash chromatography (eluent: Et_2O/petrol 35-60%) afforded *aldol complex* **25** (0.021 g, 72%); ν_{max}(film)/cm^{-1} 3450 (OH), 3059, 2093 (CO), 2027 (CO), 1681 (C=O), 1496; δ_H(600 MHz) 2.92 (1H, d, *J* 3.4, OH), 3.09 (1H, ddd, *J* 17.4, 6.0, 3.2, 6-H × 1), 3.20 (1H, dd, *J* 17.4, 9.3, 6-H × 1), 4.01 (0.17H, d, *J* 11.9, 4-H'), 4.03 (0.83H, d, *J* 11.3, 4-H), 5.25-5.29 (2H, m, 2-H and 7-H), 5.44 (1H, d, *J* 4.7, 1-H), 5.61 (1H, dd, *J* 11.1, 8.8, 3-H), 7.26-7.44 (10H, m, Ph × 2); δ_C(150 MHz) 51.8 (CH_2), 66.0 (CH), 70.0 (CH), 78.2 (CH), 85.0 (CH), 91.9 (CH), 125.6 (CH), 125.7 (CH), 125.8 (CH), 127.9 (CH), 128.6 (CH), 128.7 (CH), 128.8 (CH), 138.1 (quat. C), 142.5 (quat. C), 199.3 (CO), 201.4 (CO), 203.3 (CO), 204.1 (CO), 207.6 (CO); *m/z* (FAB) 463 (MH^+, 11%), 351 (MH-4CO, 14), 227 (23), 157 (40), 133 (100), 128 (24), 105 (23). [Found (MH^+) 463.0465. $C_{23}H_{19}FeO_7$ requires *M*H, 463.0480].

[(4E,1R,6S*,7S*)-7-(Carbonyloxy-κC)-1-hydroxy-3-oxo-1-phenyl-(4,5,6-η)-dodec-4-en-6-yl]tricarbonyliron (**26**) and [(4E,1S*,6S*,7S*)-7-(carbonyloxy-κC)-1-hydroxy-3-oxo-1-phenyl-(4,5,6-η)-dodec-4-en-6-yl]tricarbonyliron (**26'**).* Prepared using TMS enol ether **21** (0.075 g, 0.19 mmol), benzaldehyde and $BF_3.OEt_2$. After 8 h, Et_3N work-up and desilylation using HF/pyridine afforded the crude aldol product (d.e. 55% by ^1H NMR analysis). Flash chromatography (eluent: Et_2O/petrol 30-60%) afforded, in order of elution, *aldol complex* **26** (0.033 g, 41%); ν_{max}(film)/cm^{-1} 3418 (OH), 2930 (CH), 2088, 2016 (CO), 1651 (C=O), 1495; δ_H(600 MHz) 0.89 (3H, t, *J* 6.7, 12-H × 3), 1.25-1.72 (8H, m, 8-H × 2, 9-H × 2, 10-H × 2, 11-H × 2), 2.93 (1H, br s, OH), 3.04 (1H, dd, *J* 17.0, 1.1, 2-H × 1), 3.13 (1H, dd, *J* 17.0, 8.7, 2-H × 1), 3.74 (1H, d, *J* 10.4, 4-H), 4.03 (1H, t, *J* 6.6, 7-H), 4.88 (1H, d, *J* 6.7, 6-H), 5.22-5.29 (1H, m, 1-H), 5.78 (1H, apparent t, *J* 8.4, 5-H), 7.28-7.41 (5H, m, Ph); δ_C(50 MHz) 13.9 (CH_3), 22.4 (CH_2), 25.0 (CH_2), 31.3 (CH_2), 38.0 (CH_2), 51.9 (CH_2), 64.6 (CH), 70.0 (CH), 74.3 (CH), 83.6 (CH), 93.6 (CH), 125.6 (CH), 127.9 (CH), 128.6 (CH), 142.5 (quat. C), 199.8 (CO), 201.7 (CO), 203.4 (CO), 204.2 (CO); *m/z* (FAB) 457 (MH^+, 87%), 373 (MH-3CO, 29), 345 (MH-4CO, 80), 327 (73), 239 (59), 221 (50), 179 (43), 167 (51), 165 (50), 151 (52), 127 (47), 107 (100). [Found (MH^+) 457.0947. $C_{22}H_{25}FeO_7$ requires *M*H, 457.0950]; and then the *minor diastereoisomer* **26'** (0.010 g, 12%); ν_{max}(film)/cm^{-1} 3410 (OH), 2975 (CH), 2089, 2020 (CO), 1682 (C=O), 1383; δ_H(600 MHz) 0.90 (3H, t, *J* 6.6, 12-H × 3), 1.26-1.72 (8H, m, 8-H × 2, 9-H × 2, 10-H × 2, 11-H × 2), 3.02 (1H, dd, *J* 17.2, 2.6, 2-H), 3.08 (1H, br s, OH), 3.15 (1H, dd, *J* 17.2, 9.4, 2-H), 3.72 (1H, d, *J* 11.0, 4-H), 4.05 (1H, t, *J* 6.5, 7-H), 4.89 (1H, d, *J* 8.2, 6-H), 5.25 (1H, br d, *J* 9.3, 1-H), 5.78 (1H, dd, *J* 11.0, 8.2, 5-H), 7.26-7.40 (5H, m, Ph); δ_C(50 MHz) 13.9 (CH_3), 22.4 (CH_2), 25.0 (CH_2), 31.3 (CH_2), 38.0 (CH_2), 51.6 (CH_2), 64.8 (CH), 70.3 (CH), 74.4 (CH), 83.7 (CH), 93.7 (CH), 125.5 (CH), 127.9 (CH), 128.6 (CH), 142.4 (quat. C), 199.9 (CO), 201.6 (CO), 204.1 (CO), 204.8 (CO), 207.9 (CO); *m/z*

(FAB) 457 (MH^+, 66%), 373 (MH-3CO, 19), 345 (MH-4CO, 34), 328 (39), 239 (24), 167 (33), 152 (39), 120 (54), 107 (100). [Found (MH^+) 457.0938. $C_{22}H_{25}FeO_7$ requires *M*H, 457.0950].

[(4E,2R,3S*,8R*)-2-[Carbonyl(benzylamino)-κC]-6-oxo-8-hydroxy-8-phenyl-(3,4,5-η)-octa-4-en-3-yl]tricarbonyliron (27).* Prepared using TMS enol ether **22** (0.050 g, 0.110 mmol), benzaldehyde and $BF_3.OEt_2$. Neat CH_2Cl_2 was used as solvent. After 16h, Et_3N work-up and desilylation using HF/pyridine afforded the crude aldol product (d.e. 90% by ^1H NMR analysis). Flash chromatography (eluent: Et_2O/petrol 50%) afforded *aldol complex* **27** (0.036 g, 66%); ν_{max}(film)/cm^{-1} 2931, 2079 (CO), 2008 (CO), 1678 (C=O), 1589, 1494, 1454; δ_H(600 MHz) 1.18 (3H, d, *J* 6.4, 1-H × 3), 3.08 (1H, dd, *J* 17.3, 3.2, 7-H × 1), 3.15-3.20 (2H, m, 7-H × 1, OH), 3.47 (1H, d, *J* 14.9, PhC*H*H), 3.54 (1H, apparent quintet, *J* 6.3, 2-H), 3.72 (1H, d, *J* 11.0, 5-H), 4.75 (1H, dd, *J* 8.5, 6.7, 3-H), 5.06 (1H, d, *J* 14.9, PhCH*H*), 5.24-5.27 (1H, m, 8-H), 5.56 (1H, dd, *J* 11.0, 8.5, 4-H), 7.15-7.42 (10H, m, Ph × 2); δ_C(150 MHz) 22.0 (1-C), 46.3 (*C*H_2Ph), 51.5 (7-C), 52.2 (2-C), 67.1 (5-C), 70.1 (8-C), 79.2 (3-C), 91.3 (4-C), 125.8, 127.3, 127.8, 127.9, 128.6, 128.6 (Ar*C*H), 136.6 (quat. C), 142.7 (quat. C), 199.9 (CO), 200.2 (CO), 204.1 (CO), 205.7 (CO), 209.6 (CO); *m/z* (FAB) 490 (MH^+, 14%), 462 (MH-CO, 7), 406 (MH-3CO, 25), 378 (MH-4CO, 8), 298 (15), 272 (17), 256 (24), 133 (100). [Found (MH^+) 490.0978. $C_{25}H_{24}FeNO_6$ requires *M*H, 490.0953.]

[(4E,2S,3S*,8R*)-2[Carbonyl(benzylamino)-κC]-6-oxo-8-hydroxy-8-phenyl-(3,4,5-η)-octa-4-en-3-yl]tricarbonyliron (28).* Prepared using TMS enol ether **23** (0.197 g, 0.432 mmol), benzaldehyde and $BF_3.OEt_2$. Neat CH_2Cl_2 was used as solvent. After 16h, Et_3N work-up and desilylation using HF/pyridine afforded the crude aldol product (d.e. 57% by ^1H NMR analysis). Flash chromatography (eluent: Et_2O/petrol 50%) afforded *aldol complex* **28** (0.109 g, 52%; 57% d.e.); ν_{max}(film)/cm^{-1} 3416, 2975, 2932, 2079 (CO), 2000 (CO), 1682 (C=O), 1592, 1495, 1454; δ_H(600 MHz) 1.35 (0.66H, d, *J* 6.4, 1-H' × 3), 1.36 (2.34H, d, *J* 6.4, 1-H × 3), 2.92 (1H, dd, *J* 17.3, 2.9, 7-H × 1), 3.05-3.10 (2H, m, 7-H × 1, OH), 3.31 (0.22H, d, *J* 11.6, 5-H'), 3.33 (0.78H, d, *J* 11.2, 5-H), 3.40-3.49 (1H, m, 2-H), 3.58 (0.78H, d, *J* 14.5, PhC*H*H), 3.60 (0.22H, d, *J* 14.3, PhC*H*H'), 4.27 (0.22H, d, *J* 8.7, 3-H'), 4.29 (0.78H, d, *J* 8.8, 3-H), 4.90 (0.78H, d, *J* 14.5, PhCH*H*), 4.92 (0.22H, d, *J* 14.3, PhCH*H*'), 5.19 (1H, br. d, *J* 9.5, 8-H), 5.52 (0.22H, dd, *J* 11.6, 8.7, 4-H'), 5.58 (0.78H, dd, *J* 11.2, 8.8, 4-H), 7.14-7.41 (10H, m, Ph × 2); δ_C(150 MHz) 21.4 (1-C), 45.5 (Ph*C*H_2), 51.3 (2-C), 51.5 (7-C'), 51.6 (7-C), 67.4 (5-C'), 67.5 (5-C), 70.0 (8-C), 70.2 (8-C'), 77.9 (3-C), 78.2 (3-C'), 93.2 (4-C'), 93.2 (4-C), 125.6, 125.7, 127.5, 127.8, 128.5, 128.7 (Ar*C*H), 137.6, 142.7, 142.8 (quat. C), 197.3 (CO), 197.6 (CO), 200.0 (CO), 203.9 (CO), 205.5 (CO), 210.3 (CO), 210.4 (CO); *m/z* (FAB) 490 (MH^+, 100%), 462 (MH-CO, 15), 405 (M-3CO, 75), 378 (MH-4CO, 29), 299 (29), 272 (27), 256 (29), 165 (26), 152 (29), 120 (41), 107 (78). [Found (MH^+) 490.0964. $C_{25}H_{24}FeNO_6$ requires *M*H, 490.0953.]

[(5Z,1R,4S*,7S*)-1-Hydroxy-1-phenyl-3-oxo-(4,5,6,7-η)-dodec-5-en-4,7-diyl]tricarbonyliron (31) and [(5Z,1S*,4S*,7S*)-1-hydroxy-1-phenyl-3-oxo-(4,5,6,7-η)-dodec-5-en-4,7-diyl]tricarbonyliron (31').* Prepared using TMS enol ether **30** (0.080 g, 0.21 mmol), benzaldehyde and $BF_3.OEt_2$. After 5h, Et_3N work-up and desilylation using HF/pyridine afforded the crude aldol product (d.e. 25% by ^1H NMR analysis). Flash chromatography (eluent: Et_2O/petrol 30%) afforded, in order of elution, the *aldol complex* **31** (0.037 g, 43%); ν_{max}(film)/cm^{-1} 3444 (OH), 2929, 2857 (CH), 2054, 1978 (CO), 1661 (C=O), 1493, 1454; δ_H(600 MHz) 0.90 (3H, t, *J* 6.5, 12-H × 3), 1.16 (1H, d, *J* 8.1, 4-H), 1.25-1.38 (4H, m, 10-H × 2, 11-H × 2), 1.40-1.48 (2H, m, 9-H × 2), 1.50 (1H, apparent q, *J* 7.7, 7-H), 1.58-1.65 (1H, m, 8-H × 1), 1.69-1.76 (1H, m, 8-H × 1), 2.76-2.84 (2H, m, 2-H × 2), 3.52 (1H, d, *J* 2.9, OH), 5.11-5.15 (1H, m, 1-H), 5.25 (1H, dd, *J* 8.6, 5.1, 6-H), 5.83 (1H, dd, *J* 7.6, 5.3, 5-H), 7.28 (1H, t, *J* 6.7, Ph), 7.34-7.38 (4H, m, Ph); δ_C(150 MHz) 13.9 (CH_3), 22.4 (CH_2), 31.3 (CH_2), 31.7 (CH_2), 34.1 (CH_2), 50.5 (CH_2), 53.5 (CH), 66.4 (CH), 70.0 (CH), 80.8 (CH), 87.9 (CH), 125.5 (CH), 127.4 (CH), 128.4 (CH), 142.9 (quat. C), 205.4 (br, CO × 3); *m/z* (FAB) 435 [(M+Na)$^+$, 67%], 413 (MH, 53), 356 (M-2CO, 39), 328 (M-3CO, 100), 291 (74), 238 (25). [Found (MH^+) 413.1052. $C_{21}H_{24}FeO_5$ requires *M*H, 413.1051]; and then the *minor diastereoisomer* **31'** as a mixture with unidentified by-products. Selected NMR data; δ_H(200 MHz) 2.77 (2H, d, *J* 6.2, 2-H), 5.83 (1H, dd, *J* 8.9, 5.1, 5-H).

[(4E,1R,6S*,7R*)-7-(Carbonyloxy-κC)-3-oxo-1-phenyl-1-triethylsilyloxy-(4,5,6-η)-dodec-4-en-6-yl]tricarbonyliron (32).* Prepared using TES enol ether **6** (0.050 g, 0.11 mmol), benzaldehyde and $BF_3.OEt_2$. After 7 h, Et_3N work-up and flash column chromatography (eluent: Et_2O/petrol 10-50%) afforded, in order of elution, *silyl aldol complex* **32** (0.031 g, 51%; 82% d.e.); ν_{max}(film)/cm^{-1} 2954, 2934, 2875, 2088 (CO), 2019 (CO), 1667 (C=O), 1494, 1454, 1417, 1371, 1317, 1265; δ_H(250 MHz) 0.44-0.51 (6H, m, Si(CH_2CH$_3$)$_3$), 0.81-0.90 {12H, m, [including 0.84 (9H, t, *J* 7.8, Si(CH$_2$CH_3)$_3$)], 12-H × 3, Si(CH$_2$CH_3)$_3$}, 1.21-1.62 (8H, m, 8-H × 2, 9-H × 2, 10-H × 2, 11-H × 2), 2.72 (0.09H, dd, *J* 14.2, 3.8, 2-H' × 1), 2.97 (0.91H, dd, *J* 15.8, 4.9, 2-H × 1), 3.15 (0.91H, dd, *J* 15.8, 7.8, 2-H × 1), 3.24 (0.09H, dd, *J* 14.2, 9.0, 2-H' × 1), 3.69 (0.91H, d, *J* 11.2, 4-H), 3.92 (0.09H, d, *J* 11.2, 4-H'), 4.29 (1H, apparent q, *J* 5.6, 7-H), 4.97 (0.91H, dd, *J* 8.7, 4.6, 6-H), 5.04 (0.09H, dd, *J* 8.7, 4.6, 6-H'), 5.24 (1H, dd, *J* 7.8, 4.9, 1-H), 5.48 (0.91H, dd, *J* 11.2, 8.7, 5-H), 5.56 (0.09H, dd, *J* 11.2, 8.7, 5-H'), 7.21-7.38 (5H, m, Ph); δ_C(62.5 MHz) 4.7 (Si(*C*H$_2$CH$_3$)$_3$), 6.7 (Si(CH$_2$*C*H$_3$)$_3$), 13.9 (CH_3), 22.4 (CH_2), 26.5 (CH_2), 31.5 (CH_2), 36.7 (CH_2), 54.2 (CH_2), 66.0 (CH), 70.8 (CH), 76.7 (CH), 84.5 (CH), 91.7 (CH), 126.0 (CH), 127.6 (CH), 128.4 (CH), 144.0 (quat. C), 199.9 (CO), 201.2 (CO), 202.4 (CO), 204.6 (CO), 208.0 (CO); *m/z* (electrospray) 609 [(M+K)$^+$, 19%], 593 (M+Na, 100), 571 (MH, 4). {Found [(M+Na)$^+$] 593.1651. $C_{28}H_{38}FeNaO_7Si$ requires *M*+Na, 593.1634}; and then *aldol complex* **8a** (0.006 g, 12%; 67% d.e.) which was spectroscopically identical to material prepared earlier (*vide supra*).

[(4E,1R,6S*,7R*)-1-(tert-Butyldimethylsilyloxy)-7-(carbonyloxy-κC)-3-oxo-1-phenyl-(4,5,6-η)-dodec-4-en-6-yl]tricarbonyliron (33).* Prepared using TBS enol ether **7** (0.098 g, 0.21 mmol), benzaldehyde and $BF_3.OEt_2$. After 24 h, Et_3N work-up and flash column chromatography (eluent: Et_2O/petrol 15-80%) afforded, in order of elution, *silyl aldol complex* **33** (0.004 g, 4%; 60% d.e.); ν_{max}(film)/cm^{-1} 2956, 2930, 2857, 2091 (CO), 2021 (CO), 1673 (C=O), 1497, 1471; δ_H(600 MHz) - 0.16 (3H, s, Si*C*H_3), 0.02 (3H, s, Si*C*H_3), 0.85 (9H, s, SiC(CH_3)$_3$), 0.87 (3H, t, *J* 6.9, 12-H × 3), 1.23-1.54 (8H, m, 8-H × 2, 9-H × 2, 10-H × 2, 11-H × 2), 2.72 (0.17H, dd, *J* 14.2, 3.8, 2-H' × 1), 2.97 (0.83H, dd, *J* 16.2, 4.5, 2-H × 1), 3.15 (0.83H, dd, *J* 16.2, 8.2, 2-H × 1), 3.24 (0.17H, dd, *J* 14.2, 9.0, 2-H' × 1), 3.69 (0.83H, d, *J* 11.2, 4-H), 3.92 (0.17H, d, *J* 11.2, 4-H'), 4.29-4.32 (1H, m, 7-H), 4.99 (0.83H, dd, *J* 8.6, 4.6, 6-H), 5.04 (0.17H, dd, *J* 8.7, 4.6, 6-H'), 5.23 (1H, dd, *J* 8.2, 4.5, 1-H), 5.50 (0.83H, dd, *J* 11.2, 8.6, 5-H), 5.56 (0.17H, dd, *J* 11.2, 8.7, 5-H'), 7.23-7.25 (1H, m, Ph), 7.30-7.35 (4H, m, Ph); δ_C(150 MHz) -5.0 (Si*C*H_3), -4.8 (Si*C*H_3), 13.7 (CH_3), 18.1

(Si*C*(CH_3)$_3$), 22.4 (CH_2), 25.7 (SiC(*C*H_3)$_3$), 26.5 (CH_2), 31.5 (CH_2), 36.7 (CH_2), 54.2 (CH_2), 65.7 (CH), 70.9 (CH), 76.8 (CH), 84.5 (CH), 91.7 (CH), 126.0 (CH), 127.6 (CH), 128.4 (CH), 143.9 (quat. C), 199.8 (CO), 201.1 (CO), 204.7 (CO), 207.7 (CO), 207.9 (CO); *m/z* (FAB) 571 (MH^+, 5%), 514 (M-2CO, 8), 459 (MH-4CO, 44), 443 (13), 401 (M-4CO-Bu^t, 42), 221 (100), 145 (55), 131 (64). {Found (electrospray), [(M+Na)$^+$] 593.1623. $C_{28}H_{38}FeNaO_7Si$ requires *M*+Na, 593.1634}; and then *aldol complex* **8a** (0.048 g, 50%; 33% d.e.) which was spectroscopically identical to material prepared earlier (*vide supra*).

[(4E,1R,3S*,6S*,7R*)-7-(Carbonyloxy-κC)-3-hydroxy-1-phenyl-1-trimethylsilyloxy-(4,5,6-η)-dodec-4-en-6-yl]tricarbonyliron (12)*. AlPr^n (1.0 M in toluene; 0.24 ml, 0.24 mmol) was added dropwise to a cooled (-78°C) solution of ketone **9a** (0.049 g, 0.10 mmol) in CH_2Cl_2 (3.5 ml). The reaction was stirred at -78°C for 40 minutes, then allowed to warm to 0°C over 10 minutes. $NH_4Cl_{(aq)}$ (0.1 ml) was then added dropwise, stirring vigorously at 0°C for 10 minutes. $MgSO_4$ (excess) was added and the mixture stirred for a further 10 minutes, then filtered through Celite washing with CH_2Cl_2 (20 ml). Concentration *in vacuo* followed by flash chromatography afforded *monoprotected diol* **12** as an oil (0.037 g, 75%); ν_{max}(film)/cm^{-1} 3442 (OH), 2940 (CH), 2086 (CO), 2009 (CO), 1674, 1638; δ_H(500 MHz) 0.02 (9H, s, Si(CH_3)$_3$), 0.88 (3H, t, *J* 6.6, 12-H × 3), 1.22-1.63 (8H, m, 8-H × 2, 9-H × 2, 10-H × 2, 11-H × 2), 2.06-2.14 (2H, m, 2-H × 2), 3.96 (1H, d, *J* 11.9, 4-H), 3.99 (1H, s, OH), 4.22-4.25 (1H, m, 7-H), 4.58-4.62 (2H, m, 3-H, 6-H), 4.89 (1H, dd, *J* 11.9, 8.5, 5-H), 4.95 (1H, dd, *J* 8.7, 4.4, 1-H), 7.26-7.35 (5H, m, Ph); δ_C(50 MHz) 0.0 (Si(CH$_3$)$_3$), 13.9 (CH$_3$), 22.4 (CH$_2$), 26.6 (CH$_2$), 31.5 (CH$_2$), 36.7 (CH$_2$), 48.7 (CH$_2$), 70.9 (CH), 75.9 (CH), 76.7 (CH), 77.2 (CH), 86.9 (CH), 87.4 (CH), 125.8 (CH), 127.9 (CH), 128.5 (CH), 143.3 (quat. C), 203.4 (CO), 206.1 (CO), 206.8 (CO), 209.7 (CO); *m/z* (FAB) 531 (MH^+, 17%), 419 (MH-4CO, 14), 401 (35), 385 (13), 337 (13), 239 (14), 179 (100), 109 (77). [Found (MH^+) 531.1490. $C_{25}H_{35}FeSiO_7$ requires *M*H, 531.1501].

[(4E,1R,3S*,6S*,7R*)-7-(Carbonyloxy-κC)-1,3-di-O-isopropylidene-1-phenyl-(4,5,6-η)-dodec-4-en-6-yl]tricarbonyliron (13)*. A solution of **12** (0.037 g, 0.07 mmol) in THF (0.3 ml) was treated with HF/pyridine (0.090 ml of a *ca*. 2.25 M solution in THF, 0.20 mmol) for 25 min at room temperature. The reaction mixture was then diluted with Et_2O (5 ml) and washed sequentially with $NaHCO_3$ (5 ml) and $CuSO_4$ (5 ml) solutions and brine (10 ml), dried ($MgSO_4$) and concentrated *in vacuo* to furnish a white solid. This was dissolved in DMF (1 ml). 2,2-Dimethoxypropane (0.171 ml, 0.14 mmol) and *p*PTS (cat.) were added. The solution was stirred for 3 h and then partitioned between H_2O and CH_2Cl_2 (5 ml, 1:1). The layers were separated and the aqueous phase was further extracted with CH_2Cl_2 (3 × 5 ml). The combined organic fractions were dried ($MgSO_4$), concentrated *in vacuo* and purified by flash chromatography (eluent: Et_2O-petrol 1:3; Florisil) to yield *acetonide* **13** (0.024 g, 71% from **12**); ν_{max}(film)/cm^{-1} 3055, 2993, 2956, 2932, 2860, 2081 (CO), 2008 (CO), 1664 (C=O), 1496, 1454; δ_H(500 MHz) 0.88 (3H, t, *J* 6.8, 12-H × 3), 1.26-1.58 {14H, m, [including 1.46 (3H, s, acet. CH_3) and 1.58 (3H, s, acet. CH_3)], 8-H × 2, 9-H × 2, 10-H × 2, 11-H × 2, acet. CH_3 × 2}, 1.89 (1H, apparent q, *J* 12.1, 2-H$_{ax}$), 2.01 (1H, d, *J* 12.1, 2-H$_{eq}$), 3.93 (1H, dd, *J* 12.1, 3.2, 4-H), 4.23 (1H, apparent q, *J* 5.7, 7-H), 4.51 (1H, d, *J* 11.6, 3-H), 4.62 (1H, dd, *J* 8.2, 4.6, 6-H), 4.81 (1H, dd, *J* 12.1, 8.2, 5-H), 4.96 (1H, dd, *J* 11.4, 2.2, 1-H), 7.27-7.40 (5H, m, Ph); δ_C(100 MHz) 13.9 (CH$_3$), 19.9 (acet. *C*H$_{3ax}$), 22.5 (CH$_2$), 26.7 (CH$_2$), 29.6 (acet. *C*H$_{3eq}$) 31.5 (CH$_2$), 36.7 (CH$_2$), 40.0 (CH$_2$, 2-C), 68.5 (CH), 71.4 (CH), 76.2 (CH), 77.1 (CH), 84.3 (CH), 88.0 (CH), 99.7 (quat. C, acetonide), 126.0 (CH), 127.9 (CH), 128.6 (CH), 141.3 (quat. C), 203.5 (CO), 205.7 (CO), 206.5 (CO), 209.4 (CO); *m/z* (FAB) 499 (MH^+, 34%), 471 (MH-CO, 9), 414 (M-3CO, 20), 370 (20), 329 (35), 313 (19), 237 (50), 209 (22), 179 (100), 163 (36), 136 (58). [Found (MH^+) 499.1423. $C_{25}H_{31}FeO_7$ requires *M*H, 499.1419].

ACKNOWLEDGEMENTS

We gratefully acknowledge financial support from the EPSRC (to L.R.C., B.M. and J.M.W.), the Isaac Newton Trust (to L.R.C. and B.M.), Zeneca Pharmaceuticals (to L.R.C. and B.M.), the BP Endowment and the Novartis Research Fellowship (to S.V.L.). We are also grateful to the EPSRC mass spectrometry service at Swansea.

REFERENCES

1. (a) Omura, S.; Ed. *Macrolide Antibiotics*; Academic Press: New York, 1984. (b) O'Hagan, D.; Ed. *The Polyketide Metabolite*; Ellis Horwood: Chichester, 1991.
2. Schneider, C. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1375.
3. For reviews on stereoselectivity in the aldol reaction see: (a) Evans, D. A.; Nelson, J. V.; Taber, T. R. In *Topics in Stereochemistry*; Eliel, E. L., Allinger, N. L., Wilen, S. H., Eds.; Wiley Interscience: New York, 1982; Vol. 13, p 1. (b) Heathcock, C. H. In *Asymmetric Synthesis*, Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, p 111. (c) Heathcock, C. H.; Moon Kim, B.; Williams, S. F.; Masamune, S.; Raithke, M. W.; Weipert, P.; Paterson, I.; Gennari, C. in *Comprehensive Organic Synthesis: Additions to C-X π-Bonds Part 2*; Trost, B. M.; Fleming, I.; Heathcock, C. H., Eds.; Pergamon Press: Oxford, 1991; Vol. 2, pp 133-319 and 629-660. (d) Heathcock, C. H. in *Modern Synthetic Methods*; Scheffold, R., Ed.; VCH: New York, 1992; p 1. (e) Franklin, A. S.; Paterson, I. *Contemp. Org. Synth.* **1994**, *1*, 317.
4. Abiko, A.; Liu, J-F.; Masamune, S. *J. Am. Chem. Soc.* **1997**, *119*, 2586 and references therein.
5. Mioskowski, C.; Solladié, G. *J. Chem. Soc., Chem. Commun*. **1977**, 162.
6. Evans, D. A.; Bartroli, J.; Shih, T. L. *J. Am. Chem. Soc*. **1981**, *103*, 2127.
7. Braun, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 24.
8. Braun, M. In *Advances in Carbanion Chemistry*, Snieckus, V., Ed.; Jai: London, 1992, Vol. 1, p 177.

9. For some leading references see: (a) Singer, R. A.; Carreira, E. M. *J. Am. Chem. Soc.* **1995**, *117*, 12360. (b) Evans, D. A.; Murry, J. A.; Kozlowski, M. C. *J. Am. Chem. Soc.* **1996**, *118*, 5814. (c) Mukaiyama, T.; Takashima, T.; Kusaka, H.; Shimpuku, T. *Chem. Lett.* **1990**, 1777. (d) Ishihara, K.; Maruyama, T.; Mouri, M.; Gao, Q.; Furuta, K.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3483. (e) Kiyooka, S.; Kaneko, Y.; Komura, M.; Matsuo, H.; Nakano, M. *J. Org. Chem.* **1991**, *56*, 2276. (f) Krüger, J.; Carreira, E. M. *J. Am. Chem. Soc.* **1998**, *120*, 837. (g) Duthaler, R. O.; Herold, P.; Lottenbach, W.; Oertle, K.; Riediker, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 495. (h) Denmark, S. E.; Winter, S. B. D.; Su, X.; Wong, K-T. *J. Am. Chem. Soc.* **1996**, *118*, 7404.
10. Mukaiyama, T.; Inubushi, A.; Suda, S.; Hara, R.; Kobayashi, S. *Chem. Lett.* **1990**, 1015.
11. Mikami, K.; Matsukawa, S. *J. Am. Chem. Soc.* **1994**, *116*, 4077.
12. Keck, G. E.; Krishnamurthy, D. *J. Am. Chem. Soc.* **1995**, *117*, 2363.
13. Kobayashi, S.; Uchiro, H.; Fujishita, Y.; Shiina, I.; Mukaiyama, T. *J. Am. Chem. Soc.* **1991**, *113*, 4247.
14. Gennari, C.; Moresca, D.; Vieth, S.; Vulpetti, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1618.
15. Sodeoka, M.; Ohrai, K.; Shibasaki, M. *J. Org. Chem.* **1995**, *60*, 2648.
16. Muraoka, M.; Kawasaki, H.; Koga, K. *Tetrahedron Lett.* **1988**, *29*, 337.
17. Paterson, I.; Goodman, J. M. *Tetrahedron Lett.* **1989**, *30*, 997 and references therein.
18. Ando, A.; Miura, T.; Tatematsu, T.; Shioiri, T. *Tetrahedron Lett.* **1993**, *34*, 1507.
19. Denmark, S. E.; Stavenger, R. A.; Wong, K-T. *J. Org. Chem.* **1998**, *63*, 918.
20. Katsuki, T.; Yamaguchi, M. *Tetrahedron Lett.* **1985**, *26*, 5807.
21. Kishikawa, K.; Yamamoto, M.; Kohmoto, S.; Yamada, K. *Chem. Lett.* **1989**, 787.
22. Oppolzer, W.; Starkemann, C. *Tetrahedron Lett.* **1992**, *33*, 2439 and references therein.
23. Yan, T-H.; Hung, A-W.; Lee, H-C.; Chang, C-S. *J. Org. Chem.* **1994**, *59*, 8187 and references therein.
24. Otsuka, K.; Ishizuka, T.; Kimura, K.; Kunieda, T. *Chem. Pharm. Bull.* **1994**, *42*, 748.
25. Powers, T. S.; Shi, Y.; Wilson, K. J.; Wulff, W. D.; Rheingold, A. L. *J. Org. Chem.* **1994**, *59*, 6882.
26. Narasaka, K.; Miwa, T.; Hiyashi, H.; Ohta, M. *Chem. Lett.* **1984**, 1399.
27. Lagu, B. R.; Crane, H. M.; Liotta, D. C. *J. Org. Chem.* **1993**, *58*, 4191 and references therein.
28. Franck-Neumann, M.; Colson, P-J.; Geoffroy, P.; Taba, K. M. *Tetrahedron Lett.* **1992**, *33*, 1903.
29. (a) Franck-Neumann, M.; Bissinger, P.; Geoffroy, P. *Tetrahedron Lett.* **1997**, *38*, 4469. (b) *ibid.* **1997**, *38*, 4473. (c) *ibid.* **1997**, *38*, 4477.
30. Palomo, C.; González, A.; Garciá, J. M.; Landa, C.; Oiarbide, M.; Rodríguez, S.; Linden, A. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 180.
31. Corey, E. J.; Cywin, C. L.; Roper, T. D. *Tetrahedron Lett.* **1992**, *33*, 6907.
32. Ley, S. V.; Cox, L. R.; Meek, G. *Chem. Rev.* **1996**, *96*, 423 and references therein.
33. Ley, S. V.; Cox, L. R.; Meek, G.; Metten, K-H.; Piqué, C.; Worrall, J. M. *J. Chem. Soc., Perkin Trans. 1* **1997**, 3299.
34. Ley, S. V.; Cox, L. R. *J. Chem. Soc., Perkin Trans. 1* **1997**, 3315.
35. Franck-Neumann, M.; Chemla, P.; Martina, D. *Synlett* **1990**, 641.
36. Ley, S. V.; Cox, L. R. *Chem. Commun.* **1998**, 227.
37. Ley, S. V.; Cox, L. R.; Middleton, B.; Worrall, J. M. *Chem. Commun.* **1998**, 1339.
38. Mukaiyama, T. *Org. React.* **1982**, *28*, 203.
39. Evans, D. A.; Reiger, D. L.; Cage, J. R. *Tetrahedron Lett.* **1990**, *31*, 7099.
40. Rychnovsky, S. D.; Skalitzky, D. J. *Tetrahedron Lett.* **1990**, *31*, 945.
41. Rychnovsky, S. D.; Rogers, B.; Yang, G. *J. Org. Chem.* **1993**, *58*, 3511.
42. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this paper.
43. Eiss, R. *Inorg. Chem.* **1970**, 9, 1650.
44. Ley, S. V.; Middleton, B. *Chem. Commun.*, in press.
45. Paterson, I.; Gibson, K. R.; Oballa, R. M. *Tetrahedron Lett.* **1996**, *37*, 8585 and references therein.
46. Evans, D. A.; Coleman, P. J.; Côté, B. *J. Org. Chem.* **1997**, *62*, 788 and references therein.
47. Molander, G. A.; Bobbitt, K. L. *J. Am. Chem. Soc.* **1993**, *115*, 7517.
48. Carey, J. S.; Thomas, E. J. *J. Chem. Soc., Chem. Commun.* **1994**, 283.
49. Reetz, M. T.; Hüllmann, M.; Massa, W.; Berger, S.; Rademacher, P.; Heymanns, P. *J. Am. Chem. Soc.* **1986**, *108*, 2405.
50. Heathcock, C. H.; Davidsen, S. K.; Hug, K. T.; Flippin, L. A. *J. Org. Chem.* **1986**, *51*, 3027.
51. Fleming, I.; Barbero, A.; Walter, D. *Chem. Rev.* **1997**, *97*, 2063 and references therein.
52. Ley, S. V.; Burckhardt, S.; Cox, L. R.; Worrall, J. M. *Chem. Commun.* **1998**, 229.