# 1,7-Asymmetric induction of chirality in a Mukaiyama aldol reaction using π-allyltricarbonyliron lactone complexes: highly diastereoselective synthesis of α-substituted β-hydroxy carbonyl compounds

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Silyl enol ethers derived from ethyl ketone functionalised π-allyltricarbonyliron lactone complexes undergo highly diastereoselective Mukaiyama aldol reactions with a variety of achiral aldehydes, with control of both α- and β-stereogenic centres.

## Introduction

The β-hydroxy carbonyl functionality is an extremely common feature in many natural products, usually arising as a result of the polyketide biosynthetic pathway.[1] For the synthetic chemist, the aldol reaction is one of the most important methods for formation of this motif, and remains the subject of intensive research.[2]

Our group has recently described the use of π-allyltricarbonyliron lactone complexes in the highly diastereoselective synthesis of β-hydroxy carbonyl compounds, in a process that formally constitutes a 1,7-asymmetric induction of chirality operating through the π-allyltricarbonyliron tether.[3,4] Here we report the results of an extension of this work, namely Mukaiyama aldol reactions of π-allyltricarbonyliron lactone complexes bearing ethyl ketone functionality. On the basis of previous work it was anticipated that silyl enol ethers derived from such complexes would adopt a preferential conformation relative to the π-allyl system,[4] and that this would enable a diastereoselective aldol reaction to take place.

## Results and discussion

π-Allyltricarbonyliron lactone complexes **1** and **2** were readily prepared in four steps starting from (*E*)-oct-2-en-1-ol (**3**) and (*E*)-cinnamyl alcohol (**4**) respectively (Scheme 1).

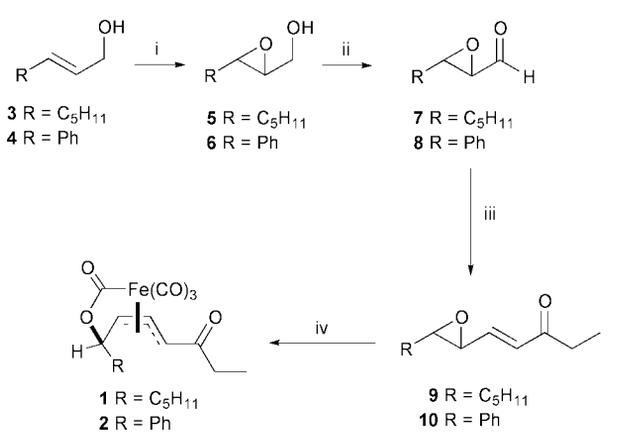
Epoxidation of allylic alcohols **3** and **4** using the standard conditions of $VO(acac)_2$ and TBHP[5] afforded the corresponding epoxides **5** and **6** in good yield. Swern oxidation[6] smoothly afforded aldehydes **7** and **8** which were then homologated under Wadsworth–Horner–Emmons conditions[7] to give epoxyenones **9** and **10** in acceptable yields. The phosphonate reagent required for this step was prepared according to the literature procedure from diethyl methylphosphonate and ethyl propanoate.[8] With the vinyl epoxide precursors in hand reaction with diiron nonacarbonyl under standard conditions[9] readily afforded π-allyltricarbonyliron lactone complexes **1** and **2**.

Complexes **11** and **12** were prepared as a 3:1 mixture, readily separable by column chromatography, in four steps starting from sorbic acid following our previously established protocols.[10]

Treatment of these complexes with trimethylsilyl triflate (TMSOTf) or triethylsilyl triflate (TESOTf) and $Et_3N$ in DCM at 0 °C afforded the respective silyl enol ethers as a mixture of (*E*)- and (*Z*)-geometric isomers in good combined yield (Scheme 2).

**Table 1** Silyl enol ether preparations from ethyl ketone substituted π-allyltricarbonyliron lactone complexes

| Iron complex starting material | Silyl triflate | Silyl enol ether product | (*E*):(*Z*) ratio | Yield (%) |
|---|---|---|---|---|
| **1** | TMSOTf | **13** | 6:1 | 78 |
| **2** | TMSOTf | **14** | 10:1 | 82 |
| **11** | TMSOTf | **15** | 12:1 | 78 |
| **11** | TESOTf | **16** | 9:1 | 73 |
| **12** | TMSOTf | **17** | 8:1 | 75 |




**Scheme 1** *Reagents and conditions*: (i) $VO(acac)_2$, $^tBuOOH$, 4 Å molecular sieves, DCM, 0 °C, 71% (R = Ph), 80% (R = $C_5H_{11}$); (ii) DMSO, $(COCl)_2$, DCM, 1 h, −78 °C then **5** or **6**, 1.5 h, then $Et_3N$, −78 °C to rt, 1.5 h, 89% (R = Ph), 92% (R = $C_5H_{11}$); (iii) $C_2H_5C(O)CH_2P(O)(OEt)_2$, NaH, 0 °C then **7** or **8**, 15 min, 60% (R = Ph), 65% (R = $C_5H_{11}$); (iv) $Fe_2(CO)_9$, THF, rt, 46% (R = Ph), 58% (R = $C_5H_{11}$).

High field NMR spectroscopic analysis indicated a high degree of selectivity in the silyl enol ether formation (Table 1), with the major isomer being assigned as (*E*)- on the basis of NOE experiments.

The Mukaiyama aldol reactions of these enol ethers[3,4,11] with a variety of achiral aldehydes were then investigated (Scheme 3). Prior to reaction, the enol ether mixtures were subjected to column chromatography on Florisil until the ratio of (*E*):(*Z*) isomers improved to at least 20:1.

Addition of a solution of benzaldehyde and $BF_3{\cdot}Et_2O$ in DCM to a solution of (*E*)-silyl enol ether **14** in DCM at −78 °C afforded the corresponding aldol product **18** in good yield and with an excellent de of 95%. These reaction conditions were

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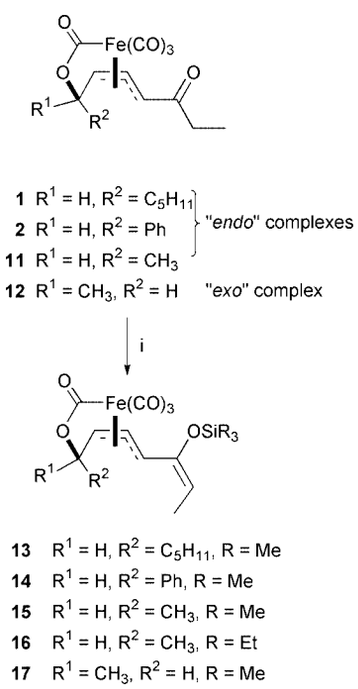
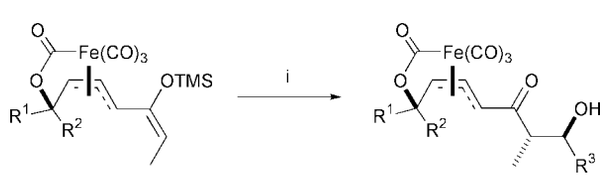
**Table 2** Mukaiyama aldol reaction of achiral aldehydes with π-allyltricarbonyliron lactone complexes

| Entry | Silyl enol ether | Aldehyde | Aldol product | Yield (%)[a] | De (%)[b] |
|---|---|---|---|---|---|
| 1 | **14** | PhCHO | **18** | 65 | 95 |
| 2 | **15** | PhCHO | **19** | 71 | 88 |
| 3 | **17** | PhCHO | **20** | 64 | 62 |
| 4 | **14** | $CH_3(CH_2)_5CHO$ | **21** | 80 | 84 |
| 5 | **13** | $CH_3CH{=}CHCHO$ | **22** | 80 | 80 |
| 6 | **15** | *p*-$NO_2C_6H_4CHO$ | **23** | 82 | >95 |
| 7 | **14** | $CH_3(CH_2)_4C{\equiv}CCHO$ | **24** | 52 | 30 |
| 8 | **15** | $CH_3(CH_2)_4C{\equiv}CCHO$ | **25** | 56 | 17 |

[a] Isolated yield after chromatography. [b] De determined from the crude mixture by 600 or 400 MHz $^1$H NMR analysis after desilylation of aldol products with HF–py work-up.




**Scheme 2** *Reagents and conditions*: (i) $R_3SiOTf$ (1.5 equiv.), $Et_3N$ (1.8 equiv.), DCM, 0 °C.




**Scheme 3** *Reagents and conditions*: (i) $R^3CHO$ (1.5 equiv.), $BF_3{\cdot}Et_2O$ (1.4 equiv.), DCM, −78 °C then $Et_3N$, −78 °C then HF–py, THF, rt.

then repeated with a variety of different aldehydes, and with the (*E*)-silyl enol ethers **14**, **15** and **17**. The results are summarised below (Table 2).

With *endo* complexes **13**, **14** and **15** the diastereoselectivities are all seen to be good to excellent, with the exception of additions to oct-2-ynal (entries 7 and 8). The decrease in diastereoselectivity in these cases may be attributed to the low steric demand of the linear side chain. Significantly, in all cases only two out of the four possible diastereoisomers were observed. Comparing entries 2 and 3 illustrates the lower diastereoselectivity for Mukaiyama aldol reactions using *exo*-π-allyltricarbonyliron lactone complexes compared with reactions using their *endo* counterparts; this is in agreement with previous work which has demonstrated the strong importance of the *endo* substituent in influencing the orientation of approach of the aldehyde.[4]

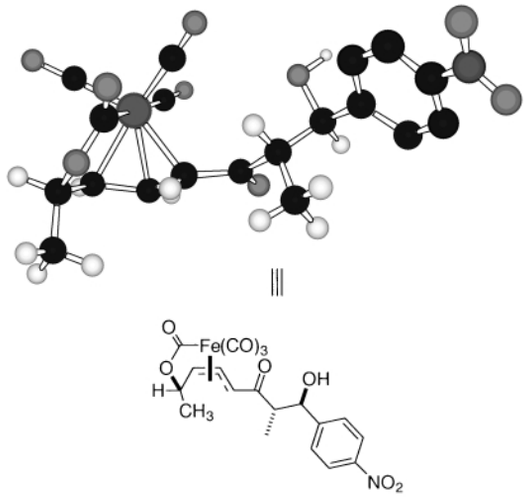



**Fig. 1** X-Ray crystal structure of aldol product **23** (entry 6 of Table 2).

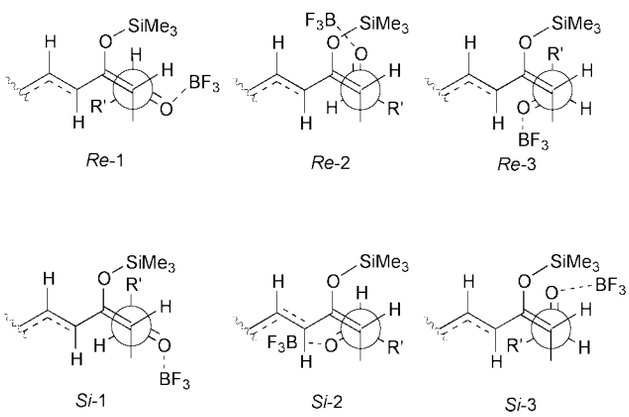



**Fig. 2** Possible transition states for the aldehyde addition event.

The stereochemistry of the major diastereoisomer in these reactions was assigned by analogy with that of aldol product **23**, which was unambiguously assigned *via* single crystal X-ray structure analysis (Fig. 1).[12]

The formation of this diastereoisomer is in complete accordance with previous work.[3,4] An explanation has been proposed for the diastereoselectivity of Mukaiyama aldol reactions of methyl ketone functionalised π-allyltricarbonyliron lactone complexes,[4] and similar arguments may be put forward here. The aldehyde is believed to react with the s-*trans* conformation of the silyl enol ether and approaches from the opposite face to the bulky $Fe(CO)_3$ group. The boron trifluoride Lewis acid is non-chelating, and for steric reasons will coordinate predominantly to the aldehyde oxygen lone pair *anti* to the alkyl or aryl substituent. Six possible transition states may now be drawn (Fig. 2).

The observed product stereochemistry is consistent with a preference for transition states *Re*-1 to *Re*-3 over *Si*-1 to *Si*-3. As previously suggested, our results may be best explained using *Re*-2, with a synclinal arrangement of π-systems and minimised steric interactions. One may also envisage that in *Re*-2 steric interactions between the remote *endo* substituent and R′ are minimised with this particular substrate alignment (Fig. 3).

Using standard methods of decomplexation, there is the opportunity to transform these π-allyltricarbonyliron lactone products into a variety of synthetically useful substrates, including β-, γ- and δ-lactones,[13] (*E*,*E*)-dienes[13] and alkenols.[13,14] For example, silyl protected aldol product **26** was readily prepared in homochiral form, starting from enantiomerically enriched (2*R*,3*R*)-**8**.[15] Complex **26** was then converted in excellent yield to (*E*,*E*)-diene **28** using standard conditions of

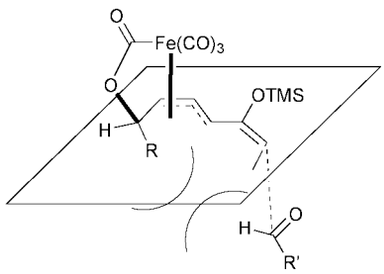
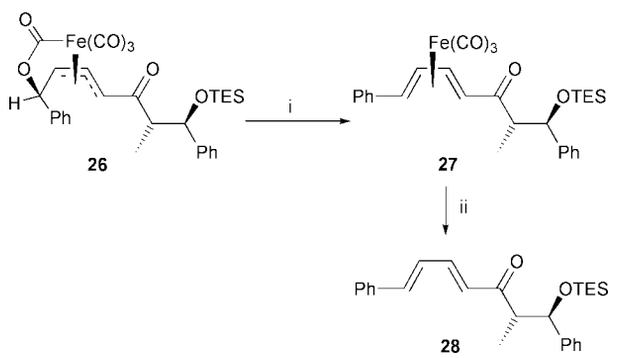



**Fig. 3** Suggested substrate alignment leading to formation of the major diastereoisomer.

treatment with barium hydroxide followed by oxidative removal of the iron group [16] (Scheme 4).




**Scheme 4** *Reagents and conditions*: (i) $Ba(OH)_2$, MeOH, 98%; (ii) $H_2O_2$, NaOH, 94%.

In conclusion, α-substituted enol ethers derived from π-allyltricarbonyliron lactones have been shown to undergo aldol reactions with a variety of achiral aldehydes under boron trifluoride activation. The products are α-methyl β-hydroxy carbonyl compounds, generated in good yields with high selectivity at both α- and β-stereogenic centres *via* remote induction through the π-allyltricarbonyliron tether. Further work is underway to demonstrate the synthetic utility of these new results in natural product synthesis.

## Experimental

$^1$H NMR spectra were recorded in $CDCl_3$ on Bruker DRX-600 or DRX-400 spectrometers and are reported as follows: chemical shift, $\delta$ (ppm) [number of protons, multiplicity, coupling constant $J$ (Hz), and assignment]. Residual protic solvent $CHCl_3$ ($\delta_H = 7.26$ ppm) was used as the internal reference. $^{13}$C NMR spectra were recorded in $CDCl_3$, at 150 or 100 MHz on Bruker DRX-600 or DRX-400 spectrometers, respectively, using the central resonance of $CDCl_3$ ($\delta_C = 77.0$ 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, Bruker BIOAPEX 4.7 T FTICR or Micromass Q-Tof spectrometer at the Department of Chemistry, University of Cambridge, and at the EPSRC Mass Spectrometry service at Swansea. QTOF refers to the data from a quadrupolar time of flight experiment. Melting points were determined on a Reichert hot stage apparatus and are uncorrected. Optical rotation measurements are reported in $10^{-1}$ deg cm$^2$ g$^{-1}$. Flash column chromatography was carried out using Merck Kieselgel (230–400 mesh) unless otherwise indicated. Analytical thin layer chromatography (TLC) was performed using precoated glass-backed plates (Merck Kieselgel 60 F254) and visualised by UV, acidic ammonium molybdate(IV) or acidic potassium permanganate solutions. Reactions were carried out under argon in oven-dried glassware unless otherwise stated. $Et_2O$ and THF were distilled from sodium benzophenone ketyl, and DCM from calcium hydride. Aqueous solutions are saturated unless otherwise specified. Petrol refers to petroleum ether bp 40–60 °C. In the synthesis of the iron lactone complexes, diironnonacarbonyl [$Fe_2(CO)_9$] is used. This is extremely toxic, and ironpentacarbonyl is a highly toxic by-product. All work involving these species was carried out in a well-ventilated hood. Glassware was treated with bleach to destroy iron carbonyl residues before re-use. The preparations of compounds **5**,[10] **6**,[10] **7**,[10] **8**,[10] **11**[10] and **12**[10] have been previously described in the literature.

### (4*E*,6*R**,7*R**)-6,7-Epoxydodec-4-en-3-one 9

Diethyl (2-oxobutyl)phosphonate (1.87 g, 8.99 mmol) was added dropwise to a stirred suspension of NaH (0.330 g of a 60% dispersion in mineral oil, prewashed with hexane (10 cm$^3$, 8.29 mmol) in THF (40 cm$^3$) at room temperature. The resulting solution was stirred at this temperature for a further 15 min before cooling to 0 °C. A solution of (2*S**,3*R**)-2,3-epoxyoctanal **7** (1.060 g, 7.46 mmol) in THF (5 cm$^3$) was added dropwise over 5 min. After 5 min the reaction was quenched by the addition of $NH_4Cl$ solution (15 cm$^3$). The layers were separated and the aqueous layer extracted with $Et_2O$ (3 × 25 cm$^3$). The combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*. Purification by flash column chromatography ($SiO_2$, $Et_2O$–petrol 1:9) afforded *epoxy enone* **9** (0.825 g, 65%) as a colourless oil; $\nu_{max}$ (film)/cm$^{-1}$ 2932, 2859, 2361, 1700, 1677, 1633, 1459, 1362, 1199, 1117, 977, 885 and 844; $\delta_H$ (400 MHz) 0.86 (3 H, t, *J* 6.6, 3 × C(12)H), 1.05 (3 H, t, *J* 7.3, 3 × C(1)H), 1.28–1.30 (4 H, m, 2 × C(10)H and 2 × C(11)H), 1.39–1.45 (2 H, m, 2 × C(9)H), 1.57 (2 H, apparent q, *J* 6.2, 2 × C(8)H), 2.53 (2 H, q, *J* 7.3, 2 × C(2)H), 2.84–2.87 (1 H, m, C(7)H), 3.17 (1 H, d, *J* 5.7, C(6)H), 6.35 (1 H, d, *J* 15.9, C(4)H), 6.49 (1 H, dd, *J* 15.9, 6.9, C(5)H); $\delta_C$ (100 MHz) 7.9 C(1), 13.9 C(12), 22.5 C(10), 25.5 C(9), 31.5 C(11), 31.9 C(8), 33.8 C(2), 56.6 C(6), 61.6 C(7), 131.0 C(4), 142.2 C(5), 199.9 C(3); *m/z* (EI) 196 (M$^+$, 20%), 139 (10), 96 (88), 82 (100) [Found (M$^+$) 196.1471. $C_{12}H_{20}O_2$ requires 196.1463].

### (4*E*,6*R**,7*R**)-6,7-Epoxy-7-phenylhept-4-en-3-one 10

Diethyl (2-oxobutyl)phosphonate (0.672 g, 3.20 mmol) was added dropwise to a stirred suspension of NaH (0.120 g of a 60% dispersion in mineral oil, prewashed with hexane (5 cm$^3$, 3.00 mmol) in THF (20 cm$^3$) at room temperature. The resulting solution was stirred at this temperature for a further 15 min before cooling to 0 °C. A solution of (2*R**,3*R**)-2,3-epoxycinnamaldehyde (0.400 g, 2.70 mmol) in THF (2 cm$^3$) was added dropwise to the solution over 5 min. After 15 min the reaction was quenched by the addition of $NH_4Cl$ solution (15 cm$^3$). The layers were separated and the aqueous layer extracted with $Et_2O$ (3 × 20 cm$^3$). The combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*. Purification by flash column chromatography ($SiO_2$, $Et_2O$–petrol, gradient 1:9→1:4) afforded *epoxy enone* **10** (0.328 g, 60%) as a white solid (Found: C, 77.0; H, 6.97. $C_{13}H_{14}O_2$ requires C, 77.2; H, 6.98%); $\nu_{max}$ (film)/cm$^{-1}$ 2980, 1696, 1629, 1458, 1119, 976, 840, 756, 698; $\delta_H$ (600 MHz) 1.13 (3 H, t, *J* 7.3, 3 × C(1)H), 2.61 (2 H, q, *J* 7.3, 3 × C(2)H), 3.48 (1 H, dd, *J* 6.7, 1.3, C(6)H), 3.84 (1 H, d, *J* 1.3, C(7)H), 6.46 (1 H, d, *J* 15.9, C(4)H), 6.66 (1 H, dd, *J* 15.9, 6.7, C(5)H), 7.28–7.38 (5 H, m, Ph(H)); $\delta_C$ (150 MHz) 7.9 C(1), 34.0 C(2), 60.9 C(6), 61.1 C(7), 125.5 Ph(C), 128.6 Ph(C), 128.7 Ph(C), 131.3 C(4), 136.0 Ph(C), 141.0 C(5), 199.8 C(3); *m/z* (QTOF) 225 (MNa$^+$, 25%), 96 (55), 81 (100). This compound was also prepared in homochiral form, starting from enantiomerically enriched (2*R*,3*R*)-2,3-epoxycinnamaldehyde [17] $[a]_D^{28}$ −143 (*c* 0.600, DCM).

### General procedure for the preparation of π-allyltricarbonyliron lactone complexes

Degassed THF (40 cm$^3$) was added to diironnonacarbonyl (2.45 g, 6.7 mmol) *via* cannula and the mixture stirred vigorously in the absence of light for 20 min at room temperature after which

time the epoxy enone (3.2 mmol) was added and the reaction mixture stirred vigorously. Upon completion of reaction (typically 2–3 h), the mixture was filtered through a pad of Celite washing with $Et_2O$ (60 $cm^3$). Toluene (2 $cm^3$) was added and the solution was concentrated *in vacuo*. (**CARE**: iron pentacarbonyl is a highly toxic and volatile by-product from the reaction.) The residue was then purified by flash column chromatography on silica gel [$SiO_2$, gradient petrol (to elute off the triirondodecacarbonyl)→$Et_2O$–petrol] afforded, in order of elution, the *endo* complex and then the *exo* complex.

**[(4*E*,6*S**,7*R**)-7-(Carbonyloxy-κ*C*)-3-oxo-(4,5,6-η)-dodec-4-en-6-yl]tricarbonyliron 1.** Epoxy enone **9** (0.670 g, 3.94 mmol) was treated with diironnonacarbonyl (2.20 g, 6.04 mmol) according to the general procedure. Flash column chromatography afforded firstly *endo complex* **1** (0.830 g, 58%) as a brown viscous oil; $\nu_{max}$ (film)/$cm^{-1}$ 2934, 2860, 2088, 2019, 1674, 1499, 1460, 1414, 1361, 1296, 1169, 1117, 1019, 924, 863, 654, 606; $\delta_H$ (600 MHz) 0.89 (3 H, t, *J* 6.5, 3 × C(12)H), 1.20 (3 H, t, *J* 7.3, 3 × C(1)H), 1.29–1.46 (6 H, m, 2 × C(9)H, 2 × C(10)H, 2 × C(11)H), 1.60 (2 H, apparent q, *J* 7.4, 2 × C(8)H), 2.75 (2 H, qd, *J* 7.3, 1.7, 2 × C(2)H), 3.85 (1 H, d, *J* 11.2, C(3)H), 4.35 (1 H, apparent q, *J* 6.3, C(7)H), 5.02 (1 H, dd, *J* 8.6, 4.6, C(6)H), 5.57 (1 H, dd, *J* 1.0, 8.7, C(4)H); $\delta_C$ (150 MHz) 7.9 C(1), 13.9 C(12), 22.4, 26.5, 31.5 C(9), C(10) and C(11), 36.5 C(2), 36.6 C(8), 65.5 C(3), 76.9 C(7), 84.3 C(6), 92.1 C(4), 199.8, 202.6, 204.8, 205.0, 207.9 CO × 5; *m*/*z* (QTOF) 387 ($MNa^+$, 100%), 337 (30), 308 (70), 299 (54) [Found ($MNa^+$) 387.0499. $C_{29}H_{34}O_5FeNaSi$ requires 387.0507]. The *exo* diastereoisomer *[(4E,6S*,7S*)-7-(carbonyloxy-κC)-3-oxo-(4,5,6-η)-dodec-4-en-6-yl]tricarbonyliron* (0.370 g, 26%) followed; $\nu_{max}$ (film)/$cm^{-1}$ 3049, 2933, 2861, 2088, 1686, 1660, 1496, 1461, 1407, 1344, 1301, 1226, 1166, 1113, 1000, 926, 878, 652, 605; $\delta_H$ (600 MHz) 0.90 (3 H, t, *J* 7.2, 3 × C(12)H), 1.18 (3 H, t, *J* 7.5, 3 × C(1)H), 1.26–1.50 (6 H, m, 2 × C(9)H, 2 × C(10)H, 2 × C(11)H), 1.56–1.74 (2 H, m, 2 × C(8)H), 2.71 (2 H, qd, *J* 7.5, 2.6, 2 × C(2)H), 3.75 (1 H, d, *J* 11.4, C(4)H), 4.05 (1 H, apparent t, *J* 7.6, C(7)H), 4.85 (1 H, d, *J* 10.4, C(6)H), 5.74 (1 H, dd, *J* 11.4, 8.5, C(5)H); $\delta_C$ (150 MHz) 7.8 C(1), 13.9 C(12), 22.4, 25.0, 31.3 C(9), C(10) and C(11), 36.5 C(2), 38.0 C(8), 64.7 C(4), 74.5 C(7), 83.1 C(6), 93.8 C(5), 200.1, 202.2, 204.6, 204.9, 208.1 CO × 5; *m*/*z* (QTOF) 387 ($MNa^+$, 95%), 289 (100), 261 (30) [Found ($MNa^+$) 387.0495. $C_{29}H_{34}O_5FeNaSi$ requires 387.0507].

**[(3*E*,1*R**,2*S**)-1-(Carbonyloxy-κ*C*)-5-oxo-1-phenyl-(2,3,4-η)-hept-3-en-2-yl]tricarbonyliron 2.** Epoxy enone **10** (0.650 g, 3.22 mmol) was treated with diironnonacarbonyl (2.45 g, 6.73 mmol) according to the general procedure. Flash column chromatography ($SiO_2$, $Et_2O$–petrol, gradient 1:20→1:1) afforded pure *endo complex* **2** (0.541 g, 46%) as a yellow solid (Found: C, 55.2; H, 3.81. $C_{17}H_{14}O_6Fe$ requires C, 55.3; H, 3.84%); $\nu_{max}$ (film)/$cm^{-1}$ 2359, 2339, 2089, 2022, 1681, 1497, 1456, 1412, 1357, 1291, 1165, 1116, 1011, 919, 798, 750, 697, 656; $\delta_H$ (600 MHz) 1.18 (3 H, t, *J* 7.3, 3 × C(7)H), 2.75 (2 H, m, 2 × C(6)H), 4.01 (1 H, d, *J* 11.0, C(4)H), 5.25 (1 H, dd, *J* 8.7, 4.6, C(2)H), 5.42 (1 H, d, *J* 4.6, C(1)H), 5.56 (1 H, dd, *J* 11.0, 8.7, C(3)H), 7.29–7.36 (5 H, m, Ph(H)); $\delta_C$ (150 MHz) 7.83 C(7), 36.6 C(6), 66.0 C(4), 78.3 C(1), 84.4 C(2), 92.1 C(3), 125.9 Ph(C), 128.6 Ph(C), 128.8 Ph(C), 138.3 Ph(C), 199.6, 202.0, 204.6, 204.8, 207.8 CO × 5; *m*/*z* (QTOF) 393 ($MNa^+$, 100%), 365 (30), 313 (80), 299 (100), 287 (50), 209 (40), 173 (20) [Found ($MNa^+$) 393.0023. $C_{17}H_{14}O_6FeNa$ requires 393.0032]. This compound was also prepared in homochiral form, starting from enantiomerically enriched epoxy enone (2*R*,3*R*)-**10** $[\alpha]_D^{28}$ +563 (*c* 0.620, DCM).

### General procedure for the preparation of silyl enol ether complexes 13–17

For a 0.30 mmol scale reaction: $Et_3N$ (1.6 equiv.) and trialkylsilyl triflate (1.2–1.4 equiv.) were added sequentially to a cooled (0 °C) solution of the ketone complex (1.0 equiv.) in DCM (1 $cm^3$) and the reaction mixture was stirred at 0 °C. When the reaction was judged to be complete as indicated by TLC (typically 30 min–1 h) the reaction mixture was poured into $Et_2O$–$H_2O$ (5 $cm^3$, 1:1), the layers were separated and the aqueous fraction was further extracted with $Et_2O$ (3 × 5 $cm^3$). The combined organic fractions were washed with brine (5 $cm^3$) and then dried ($MgSO_4$). For the determination of *E*:*Z* isomer ratios, the crude material was filtered through a short plug of Florisil washing with $Et_2O$ (30 $cm^3$) and the filtrate concentrated *in vacuo* followed by 600 MHz $^1H$ NMR spectroscopic analysis. The silyl enol ether complexes were then further purified by rapid flash column chromatography on Florisil.

**[(2*E*,4*E*,6*S**,7*R**)-7-(Carbonyloxy-κ*C*)-3-trimethylsilyloxy-(4,5,6-η)-dodeca-2,4-dien-6-yl]tricarbonyliron 13.** Silyl enol ether **13** was prepared according to the general procedure from TMSOTf (0.107 $cm^3$, 0.59 mmol), $Et_3N$ (0.095 $cm^3$, 0.68 mmol), and ethyl ketone **1** (0.166 g, 0.46 mmol). After 20 min, work-up as described and purification by flash column chromatography (Florisil, $Et_2O$–petrol 1:1) afforded *silyl enol ether* **14** (0.154 g, 78%) as a pale yellow solid; $\nu_{max}$ ($CDCl_3$)/$cm^{-1}$ 2916, 2848, 2078, 2007, 1653, 1469, 1254, 1241, 1104, 1034, 960, 893, 842, 658; $\delta_H$ (600 MHz) 0.22 (9 H, s, $SiMe_3$), 0.88 (3 H, t, *J* 6.6, 3 × C(12)H), 1.21–1.66 (8 H, m, 2 × C(8)H, 2 × C(9)H, 2 × C(10)H, 2 × C(11)H), 1.78 (3 H, d, *J* 7.4, 3 × C(1)H), 4.27 (1 H, apparent q, *J* 7.1, C(7)H), 4.61 (1 H, dd, *J* 8.3, 4.8, C(6)H), 4.74 (1 H, d, *J* 11.9, C(4)H), 5.01 (1 H, q, *J* 7.4, C(2)H), 5.06 (1 H, dd, *J* 11.9, 8.3, C(5)H); $\delta_C$ (150 MHz) −0.02 $SiMe_3$, 11.9 C(1), 13.9 C(12), 22.5, 26.6, 31.6, 36.7 C(8), C(9), C(10), C(11), 74.9 C(4), 76.0 C(6), 77.4 C(7), 85.1 C(5), 106.1 C(2), 147.4 C(3), 204.6, 205.3, 205.9, 209.4 CO × 4; *m*/*z* (QTOF) 459 ($MNa^+$, 50%), 437 (50), 375 (60), 347 (100) [Found ($MNa^+$) 459.0902. $C_{19}H_{28}O_6FeNaSi$ requires 459.0902].

**[(3*E*,5*E*,1*R**,2*S**)-1-(Carbonyloxy-κ*C*)-1-phenyl-5-trimethylsilyloxy-(2,3,4-η)-hepta-3,5-dien-2-yl]tricarbonyliron 14.** Silyl enol ether **14** was prepared according to the general procedure from TMSOTf (0.256 $cm^3$, 1.42 mmol), $Et_3N$ (0.263 $cm^3$, 1.90 mmol), and ethyl ketone **2** (0.350 g, 0.95 mmol). After 20 min, work-up as described and purification by flash column chromatography (Florisil, $Et_2O$–petrol 1:1) afforded silyl enol ether **14** (0.343 g, 82%) as a pale yellow solid; $\nu_{max}$ (film)/$cm^{-1}$ 3035, 2960, 2077, 2019, 1255, 1241, 1170, 1107, 1056, 999, 952, 917, 891, 848, 806, 752, 698, 657, 599; $\delta_H$ (600 MHz) 0.19 (9 H, s, $SiMe_3$), 1.81 (3 H, d, *J* 7.3, 3 × C(7)H), 4.76–4.79 (1 H, m, C(2)H), 4.93 (1 H, d, *J* 11.6, C(4)H), 5.02 (1 H, q, *J* 7.3, C(6)H), 5.07 (1 H, apparent t, *J* 8.1, C(3)H), 5.38 (1 H, d, *J* 4.8, C(1)H), 7.29–7.34 (5 H, m, Ph); $\delta_C$ (150 MHz) −0.08 $SiMe_3$, 11.9 C(7), 75.7 C(4), 76.2 C(2), 76.7 C(1), 85.0 C(3), 106.2 C(6), 125.8 Ph(C), 125.9 Ph(C), 128.0 Ph(C), 128.6 Ph(C), 139.5 Ph(C), 147.2 C(6), 204.3, 205.1, 205.2, 209.2 CO × 4; *m*/*z* (LSIMS) 443 ($MH^+$, 18%), 359 (76), 331 (100), 241 (44), 169 (56), 141 (44) [Found ($MH^+$) 443.0591. $C_{20}H_{23}O_6FeSi$ requires 443.0608]. This compound was also prepared in homochiral form, starting from enantiomerically enriched ethyl ketone (1*R*,2*S*)-**2** $[\alpha]_D^{28}$ +153 (*c* 0.976, DCM).

**[(4*E*,6*E*,2*R*,3*S**)-2-(Carbonyloxy-κ*C*)-6-trimethylsilyloxy-(3,4,5-η)-octa-4,6-dien-3-yl]tricarbonyliron 15.** Silyl enol ether **15** was prepared according to the general procedure from TMSOTf (0.120 $cm^3$, 0.61 mmol), $Et_3N$ (0.105 $cm^3$, 0.75 mmol) and ethyl ketone **11** (0.062 g, 0.20 mmol). After 1 h, work-up as described followed by purification by flash column chromatography (Florisil, $Et_2O$–petrol 2:1) afforded pure *silyl enol ether* **15** (0.063 g, 78%) as a pale yellow solid; $\nu_{max}$ (film)/$cm^{-1}$ 2971, 2360, 2340, 2074, 2015, 1662, 1363, 1374, 1274, 1242, 1107, 1085, 1039, 994, 953, 892, 849, 668, 656; $\delta_H$ (600 MHz) 0.22 (9 H, s, $SiMe_3$), 1.37 (3 H, d, *J* 6.3, 3 × C(1)H), 1.78 (3 H, d, *J* 7.3, 3 × C(8)H), 4.45 (1 H, apparent quintet, *J* 6.3, C(2)H),

4.63 (1 H, dd, *J* 8.1, 4.8, C(3)H), 4.78 (1 H, d, *J* 11.9, C(5)H), 4.99–5.05 (2 H, m, C(4)H, C(7)H); $\delta_C$ (150 MHz) −0.05 $Si(CH_3)_3$, 11.9 C(8), 21.9 C(1), 73.4 C(2), 75.0 C(5), 77.2 C(3), 84.9 C(4), 106.2 C(7), 147.4 C(6), 204.4, 205.2, 205.3, 205.3 (CO × 4); *m/z* (FAB) 381 ($MH^+$, 100%), 297 (70), 269 (78), 195 (30), 145 (91), 130 (36), 107 (66) [Found ($MH^+$) 381.0481. $C_{15}H_{21}O_6FeSi$ requires 381.0457].

**[(4*E*,6*E*,2*R**,3*S**)-2-(Carbonyloxy-κ*C*)-6-triethylsilyloxy-(3,4,5-η)-octa-4,6-dien-3-yl]tricarbonyliron 16.** Silyl enol ether **16** was prepared according to the general procedure from TESOTf (0.670 $cm^3$, 0.78 mmol), $Et_3N$ (1.25 $cm^3$, 0.91 mmol) and ethyl ketone **11** (0.075 g, 0.26 mmol). After 1 h, work-up as described followed by purification by flash column chromatography (Florisil, $Et_2O$–petrol, gradient 1:4→2:1) afforded pure *silyl enol ether* **16** (0.080 g, 73%) as a white solid; $\nu_{max}$ (film)/$cm^{-1}$ 2960, 2071, 2013, 1661, 1630, 1456, 1414, 1362, 1275, 1248, 1188, 1106, 1085, 1049, 1004, 951, 888, 796, 772, 750, 720, 656, 634, 601; $\delta_H$ (600 MHz) 0.73 (3 H, q, *J* 8.0, $SiCH_2CH_3$), 0.97 (9 H, t, *J* 8.0, $SiCH_2CH_3$), 1.38 (3 H, d, *J* 6.4, 3 × C(1)H), 1.78 (3 H, d, *J* 7.3, 3 × C(8)H), 4.44–4.47 (1 H, m, C(2)H), 4.63 (1 H, dd, *J* 8.2, 4.7, C(3)H), 4.80 (1 H, d, *J* 12.0, C(5)H), 5.01 (1 H, q, *J* 7.3, C(7)H), 5.10 (1 H, dd, *J* 12.0, 8.3, C(4)H); $\delta_C$ (150 MHz) 4.80 $SiCH_2CH_3$, 6.55 $SiCH_2CH_3$, 11.9 C(8), 21.8 C(1), 73.4 C(2), 75.1 C(5), 76.9 C(3), 84.9 C(4), 105.6 C(7), 147.4 C(6), 204.2, 205.2, 205.9, 209.3 CO × 4; *m/z* (FAB) 423 ($MH^+$, 100%), 395 (10), 339 (58), 311 (85), 159 (45), 131 (35), 115 (58) [Found $MH^+$ 423.0955. $C_{18}H_{27}O_6FeSi$ requires 423.0926].

**[(4*E*,6*E*,2*S**3*S**)-2-(Carbonyloxy-κ*C*)-6-trimethylsilyloxy-(3,4,5-η)-octa-4,6-dien-3-yl]tricarbonyliron 17.** Silyl enol ether **17** was prepared according to the general procedure from TMSOTf (0.041 $cm^3$, 0.22 mmol), $Et_3N$ (0.045 $cm^3$, 0.33 mmol), and ethyl ketone **12** (0.050 g, 0.16 mmol). After 20 min, work-up as described and purification by flash column chromatography (Florisil, $Et_2O$–petrol 2:3) afforded pure *silyl enol ether* **17** (0.048 g, 75%) as a pale yellow solid; $\nu_{max}$ (film)/$cm^{-1}$ 2961, 2081, 2014, 1656, 1450, 1378, 1353, 1308, 1272, 1254, 1241, 1178, 1108, 1092, 1048, 994, 956, 889, 841, 758, 690, 648, 600; $\delta_H$ (600 MHz) 0.21 (9 H, s, $SiMe_3$), 1.37 (3 H, d, *J* 6.4, C(1)H), 1.75 (3 H, d, *J* 7.3, 3 × C(8)H), 4.29 (1 H, q, *J* 6.4, C(2)H), 4.40 (1 H, d, *J* 7.9, C(3)H), 4.64 (1 H, d, *J* 11.7, C(5)H), 5.01 (1 H, q, *J* 7.3, C(7)H), 5.16 (1 H, dd, *J* 11.7, 7.9, C(4)H); $\delta_C$ (150 MHz) −0.04 $SiMe_3$, 11.9 C(8), 23.9 C(1), 71.2 C(2), 73.4 C(5), 74.4 C(3), 86.2 C(4), 106.5 C(7), 147.2 C(6), 204.6, 205.2, 205.6, 209.7 CO × 4; *m/z* (EI) 352 (M-CO, 10%), 296 (12), 196 (100), 165 (50), 73 (35) [Found $(M\text{-}CO)^+$ 352.0416. $C_{14}H_{20}O_5FeSi$ requires 352.0429].

### General procedure for the Mukaiyama aldol reaction

For a 0.20 mmol scale reaction: $BF_3{\cdot}Et_2O$ (redistilled from $CaH_2$, 1.2 equiv.) was added to a solution of the aldehyde (purified according to literature procedures,[17] 2.0 equiv.) in $Et_2O$ (0.82 $cm^3$) at room temperature. After 30 s, the solution was added dropwise over 1–2 min to a cooled (−78 °C) solution of the silyl enol ether (1.0 equiv.) in DCM (1.23 $cm^3$, 2:1). The reaction mixture was maintained at this temperature until the reaction was complete as judged by TLC analysis. Upon completion of the reaction, $Et_3N$ (3.0 equiv.) was added, the reaction mixture stirred vigorously for 1–2 min and then filtered through a pad of Celite washing the residues with DCM (100 $cm^3$). Concentration of the filtrate *in vacuo* afforded a crude mixture of silylated and non-silylated aldol products. In order to provide an accurate de determination, the crude product was dissolved in THF (0.5 $cm^3$) and then treated with HF–pyridine (0.5 $cm^3$ of a *ca*. 2.25 mol $dm^{-3}$ stock solution in THF) at room temperature. After 30 min, the reaction mixture was poured into $NaHCO_3$ solution–$Et_2O$ (5 $cm^3$, 1:1). The layers were separated and the aqueous phase extracted with $Et_2O$ (3 × 5 $cm^3$). The combined organic extracts were poured into $CuSO_4$ solution (5 $cm^3$), the phases separated and the aqueous phase extracted with $Et_2O$ (3 × 5 $cm^3$). The organic fractions were washed with brine (10 $cm^3$), dried ($MgSO_4$) and concentrated *in vacuo*. Analysis of the 600 MHz $^1H$ NMR spectrum of the crude reaction mixture enabled determination of the diastereoselectivity of the aldol reaction.

**[(3*E*,1*R**,2*S**,6*S**,7*R**)-1-(Carbonyloxy-κ*C*)-7-hydroxy-6-methyl-5-oxo-1,7-diphenyl-(2,3,4-η)-hept-3-en-2-yl]tricarbonyliron 18.** Aldol product **18** was prepared according to the general procedure from TMS enol ether **14** (0.087 g, 0.20 mmol), benzaldehyde (0.036 $cm^3$, 0.15 mmol) and $BF_3{\cdot}Et_2O$ (0.028 $cm^3$, 0.09 mmol). After 6 h, treatment with $Et_3N$ (0.085 $cm^3$, 0.60 mmol) and silyl deprotection as described afforded the crude desilylated aldol product. Purification by column chromatography ($SiO_2$, $Et_2O$–petrol, gradient 1:9→2:1) afforded **18** as a white solid (0.053 g, 65%); $\nu_{max}$ (film)/$cm^{-1}$ 3028, 2972, 2927, 2092, 2021, 1677, 1494, 1453, 1415, 1373, 1306, 1236, 1198, 1015, 920, 826, 794, 747, 699, 656, 598, 476; $\delta_H$ (600 MHz) 1.05 (3 H, d, *J* 7.3, C(6)Me), 3.16 (1 H, apparent quintet, *J* 7.3, C(6)H), 4.19 (1 H, d, *J* 11.3, C(4)H), 4.86 (1 H, dd, *J* 8.9, 3.8, C(7)H), 5.25 (1 H, dd, *J* 8.8, 4.8, C(2)H), 5.45 (1 H, d, *J* 2.3, C(1)H), 5.59 (1 H, dd, *J* 11.3, 8.8, C(3)H); $\delta_C$ (150 MHz) 14.6 C(6)Me, 53.9 C(6), 66.3 C(4), 76.2 C(7), 78.2 C(1), 84.6 C(2), 92.5 C(3), 125.8 Ph(C), 126.8 Ph(C), 128.2 Ph(C), 128.6 Ph(C), 128.8 Ph(C), 138.3, 141.6 Ph(C), 199.6, 204.0, 207.2, 208.0 (CO) × 5; *m/z* (FAB) 477 ($MH^+$, 100%), 449 (8), 393 (9), 365 (17), 347 (25), 241 (33) [Found ($MH^+$) 477.0642. $C_{24}H_{21}O_7Fe$ requires 477.0637]. This compound was also prepared in homochiral form, starting from enantiomerically enriched silyl enol ether (1*R*,2*S*)-**14** $[a]_D^{28}$ +295 (*c* 0.826, DCM).

**[(4*E*,2*R**,3*S**,7*S**,8*R**)-2-(Carbonyloxy-κ*C*)-8-hydroxy-7-methyl-6-oxo-8-phenyl-(3,4,5-η)-oct-4-en-3-yl]tricarbonyliron 19.** Aldol product **19** was prepared according to the general procedure from TMS enol ether **15** (0.030 g, 0.08 mmol), benzaldehyde (0.016 $cm^3$, 0.15 mmol) and $BF_3{\cdot}Et_2O$ (0.012 $cm^3$, 0.09 mmol). After 6 h, treatment with $Et_3N$ (0.034 $cm^3$, 0.24 mmol) and silyl deprotection as described afforded the crude desilylated aldol product. Purification by column chromatography ($SiO_2$, $Et_2O$–petrol 3:1) afforded **19** as a white solid (0.022 g, 71%); $\nu_{max}$ (film)/$cm^{-1}$ 3454, 2931, 2090, 2021, 1671, 1498, 1453, 1049, 947, 703, 654; $\delta_H$ (600 MHz) 1.07 (3 H, d, *J* 7.2, C(7)Me), 1.40 (3 H, d, *J* 6.4, 3 × C(1)H), 3.15 (1 H, apparent quintet, *J* 7.2, C(7)H), 4.04 (1 H, d, *J* 11.2, C(5)H), 4.55 (1 H, apparent quintet, *J* 6.4, C(2)H), 4.88 (1 H, d, *J* 8.9, C(8)H), 5.07 (1 H, dd, *J* 8.7, 4.6, C(3)H), 5.59 (1 H, dd, *J* 11.2, 8.7, C(4)H); $\delta_C$ (150 MHz) 14.6 C(7)Me, 21.8 C(1), 53.9 C(7), 65.8 C(5), 72.8 C(2), 76.2 C(8), 85.4 C(3), 92.4 C(4), 126.8 Ph(C), 128.2 Ph(C), 128.6 Ph(C), 141.7 Ph(C), 199.7, 202.9, 204.2, 207.3, 208.1 CO × 5; *m/z* (FAB) 415 ($MH^+$, 40%), 303 (30), 285 (31), 197 (24), 154 (100), 107 (41) [Found ($MH^+$) 414.0391. $C_{19}H_{19}O_7Fe$ requires 414.0402].

**[(4*E*,2*S**,3*S**,7*S**,8*R**)-2-(Carbonyloxy-κ*C*)-8-hydroxy-7-methyl-6-oxo-8-phenyl-(3,4,5-η)-oct-4-en-3-yl]tricarbonyliron 20.** Aldol product **20** was prepared according to the general procedure from TMS enol ether **17** (0.031 g, 0.079 mmol), benzaldehyde (0.016 $cm^3$, 0.16 mmol) and $BF_3{\cdot}Et_2O$ (0.020 $cm^3$, 0.16 mmol). After 6 h, treatment with $Et_3N$ (0.033 $cm^3$, 0.24 mmol) and silyl deprotection as described afforded the crude desilylated aldol product. Purification by column chromatography ($SiO_2$, $Et_2O$–petrol 2:1) afforded **20** (0.021 g, 64%) as a white solid; $\nu_{max}$ (film)/$cm^{-1}$ 3476, 2977, 2932, 2091, 2020, 1665, 1495, 1454, 1376, 1309, 1171, 1051, 1008, 952, 838, 768, 736, 703, 653, 604; $\delta_H$ (600 MHz) 1.03 (3 H, d, *J* 7.1, C(7)Me), 1.44 (3 H, d, *J* 6.3, 3 × C(1)H), 2.58 (1 H, br s, OH), 3.11 (1 H, apparent quintet, *J* 7.8, C(7)H), 3.89 (1 H, d, *J* 11.1, C(5)H), 4.32 (1 H, q,

*J* 6.3, C(2)H), 4.83–4.86 (2 H, m, C(3)H and C(8)H), 5.75 (1 H, apparent t, *J* 9.6, C(4)H), 7.30–7.37 (5 H, m, Ph(H)); $\delta_C$ (150 MHz) 14.5 C(7)Me, 24.0 C(1), 53.9 C(7), 65.1 C(5), 70.6 C(2), 76.2 C(8), 84.6 C(3), 94.0 C(4), 126.8 Ph(C), 128.2 Ph(C), 128.6 Ph(C), 141.6 Ph(C), 200.0, 202.7, 204.0, 207.3, 208.3 CO × 5; *m*/*z* (QTOF) 437 ($MNa^+$, 100%), 403 (40), 381 (55), 371 (20) [Found ($MNa^+$) 437.0291. $C_{19}H_{18}O_7FeNa$ requires 437.0300].

**[(3*E*,1*R**,2*S**,6*S**,7*R**)-1-(Carbonyloxy-κ*C*)-7-hydroxy-6-methyl-5-oxo-1-phenyl-(2,3,4-η)-tridec-3-en-2-yl]tricarbonyliron 21.** Aldol product **21** was prepared according to the general procedure from TMS enol ether **14** (0.037 g, 0.081 mmol), heptanal (0.015 $cm^3$, 0.11 mmol) and $BF_3{\cdot}Et_2O$ (0.013 $cm^3$, 0.10 mmol). After 6 h, treatment with $Et_3N$ (0.033 $cm^3$, 0.24 mmol) and work-up as described afforded the crude desilylated aldol product. Purification by column chromatography ($SiO_2$, $Et_2O$–petrol 1 : 1) afforded **21** (0.031 g, 80%) as a colourless oil; $\nu_{max}$ (film)/$cm^{-1}$ 2928, 2091, 2021, 1677, 1496, 1454, 1020, 698, 656, 600; $\delta_H$ (600 MHz) 0.89 (3 H, t, *J* 6.3, 3 × C(13)H), 1.28 (3 H, d, *J* 7.3, C(6)Me), 1.34–1.59 (10 H, m, 2 × C(8)H, 2 × C(9)H, 2 × C(10)H, 2 × C(11)H and 2 × C(12)H), 2.33 (1 H, d, *J* 6.0, OH), 2.86 (1 H, apparent quintet, *J* 7.1, C(6)H), 3.79 (1 H, m, C(7)H), 4.13 (1 H, d, *J* 11.2, C(4)H), 5.24 (1 H, dd, *J* 8.5, 4.7, C(2)H), 5.44 (1 H, d, *J* 4.5, C(1)H), 5.54 (1 H, apparent t, *J* 9.0, C(3)H), 7.29–7.37 (5 H, m, Ph(H); $\delta_C$ (150 MHz) 14.0 C(13), 14.5 C(6)Me, 22.6, 25.4, 29.2, 31.8, 34.6 C(8), C(9), C(10), C(11) and C(12), 52.4 C(6), 66.4 C(4), 73.2 C(7), 78.2 C(1), 84.4 C(2), 92.7 C(3), 125.8 Ph(C), 125.8 Ph(C), 128.6 Ph(C), 128.8 Ph(C), 138.3 Ph(C), 199.6, 202.0, 204.2 CO × 3; *m*/*z* (ES) 485 ($MH^+$, 100%), 373 (34), 242 (55), 241 (57), 107 (80) [Found ($MH^+$) 485.1263. $C_{24}H_{29}O_7Fe$ requires 485.1263].

**[(8*E*,13*E*,6*R**,7*S**,11*S**,12*S**)-6-(Carbonyloxy-κ*C*)-12-hydroxy-11-methyl-10-oxo-(7,8,9-η)-pentadeca-8,13-dien-7-yl]tricarbonyliron 22.** Aldol product **22** was prepared according to the general procedure from TMS enol ether **13** (0.078 g, 0.17 mmol), (*E*)-crotonaldehyde (0.043 $cm^3$, 0.52 mmol) and $BF_3{\cdot}Et_2O$ (0.043 $cm^3$, 0.34 mmol). After 6 h, treatment with $Et_3N$ (0.055 $cm^3$, 0.40 mmol) and silyl deprotection as described afforded the crude desilylated aldol product. Purification by column chromatography ($SiO_2$, $Et_2O$–petrol, gradient 1 : 9→1 : 1) afforded *aldol complex* **22** (0.059 g, 80%) as a white solid; $\nu_{max}$ (film)/$cm^{-1}$ 2916, 2848, 2360, 2092, 2025, 1670, 1462, 1067, 908, 732, 649; $\delta_H$ (600 MHz) 0.89 (3 H, t, *J* 6.7, 3 × C(1)H), 1.22 (3 H, d, *J* 7.2, C(11)Me), 1.28–1.31 (4 H, m, 2 × C(2)H and 2 × C(3)H), 1.37–1.39 (1 H, m, 1 × C(4)H), 1.43–1.48 (1 H, m, 1 × C(4)H), 1.60–1.63 (2 H, m, C(5)H), 1.72 (3 H, dd, *J* 6.4, 1.0, 3 × C(15)H), 2.30 (1 H, d, *J* 4.9, OH), 2.86 (1 H, apparent q, *J* 7.5, C(11)H), 3.93 (1 H, d, *J* 11.2, C(9)H), 4.23 (1 H, apparent q, *J* 5.1, C(12)H), 4.36 (1 H, apparent q, *J* 5.1, C(6)H), 5.01 (1 H, dd, *J* 8.7, 4.6, C(7)H), 5.48 (1 H, dd, *J* 7.5, 1.5, C(13)H), 5.54 (1 H, dd, *J* 11.2, 8.7, C(8)H), 5.77 (1 H, m, C(14)H); $\delta_C$ (150 MHz) 13.9 C(1), 14.4 C(11)Me, 17.7 C(15), 22.5 C(2) or C(3), 26.9 C(4), 31.5 C(2) or C(3), 36.6 C(5), 52.1 C(11), 65.7 C(9), 74.8 C(12), 76.7 C(6), 84.3 C(7), 92.6 C(8), 129.4 C(14), 131.4 C(13), 199.8, 202.7, 204.3, 207.8, 208.1 CO × 5; *m*/*z* (QTOF) 457 ($MNa^+$, 90%), 435 (40), 401 (60), 353 (60), 345 (100), 337 (80), 305 (75) [Found ($MNa^+$) 457.0941. $C_{20}H_{26}O_7$-FeNa requires 457.0926].

**[(4*E*,2*R**,3*S**,7*S**,8*R**)-2-(Carbonyloxy-κ*C*)-8-hydroxy-7-methyl-8-(4′-nitrophenyl)-6-oxo-(3,4,5-η)-oct-4-en-3-yl]tricarbonyliron 23.** Aldol product **23** was prepared according to the general procedure from TMS enol ether **15** (0.080 g, 0.20 mmol), 4-nitrobenzaldehyde (0.045 g, 0.30 mmol) and $BF_3{\cdot}Et_2O$ (0.040 $cm^3$, 0.32 mmol). After 6 h, treatment with $Et_3N$ (0.083 $cm^3$, 0.60 mmol) and silyl deprotection as described afforded the crude desilylated aldol product. Purification by column chromatography ($SiO_2$, $Et_2O$–petrol 3 : 1) afforded *aldol complex* **23** (0.077 g, 82%) as a white solid; mp 123–127 °C; $\nu_{max}$ (film)/$cm^{-1}$ 3454 (br), 2979, 2092, 2023, 1668, 1606, 1520, 1456, 1419, 1376, 1347, 1314, 1180, 1051, 1003, 948, 912, 851, 834, 732, 703, 655, 601; $\delta_H$ (600 MHz) 1.13 (3 H, d, *J* 7.2, C(7)Me), 1.39 (3 H, d, *J* 6.2, 3 × C(1)H), 3.07 (1 H, d, *J* 4.4, OH), 3.12 (1 H, apparent t, *J* 7.5, C(7)H), 3.96 (1 H, d, *J* 11.2, C(5)H), 4.55 (1 H, apparent t, *J* 5.4, C(2)H), 4.99 (1 H, dd, *J* 7.8, 4.6, C(8)H), 5.09 (1 H, dd, *J* 8.4, 4.4, C(3)H), 5.58 (1 H, apparent t, *J* 9.4, C(4)H), 7.55 (2 H, d, *J* 8.3, 2 × C(10)H), 8.22 (2 H, d, *J* 8.3, 2 × C(11)H); $\delta_C$ (150 MHz) 14.7 C(7)Me, 21.8 C(1), 53.4 C(7), 65.1 C(5), 72.8 C(2), 75.2 C(8), 86.2 C(3), 92.3 C(4), 123.8 C(9), 127.7 C(10), 147.7 C(11), 149.0 C(12), 199.4 C(6), 202.5, 204.2, 206.8, 207.7 CO × 5; *m*/*z* (ES) 482 ($MNa^+$, 50%), 281 (48), 265 (100) [Found ($MNa^+$) 482.0157. $C_{19}H_{17}NO_9FeNa$ requires 482.0150].

Crystal data for **23**. Empirical formula $C_{19.50}H_{18}ClFeO_9$, $M = 501.65$, monoclinic, $a = 11.432$ (8), $b = 24.740$ (12), $c = 7.678$ (4) Å, $U = 2169.6$ (22) $Å^3$, $T = 220$ K, space group $P2_1/c$, $Z = 4$, $\mu = 0.869$ $mm^{-1}$, 7141 reflections measured, 3827 unique ($R_{int} = 0.0492$) which were used in all calculations. $R1 = 0.0808$, $wR2 = 0.1356$ (all data).†

**[(3*E*,1*R**,2*S**,6*S**,7*R**)-1-(Carbonyloxy-κ*C*)-7-hydroxy-6-methyl-5-oxo-1-phenyl-(2,3,4-η)-tetradec-3-en-8-yn-2-yl]tricarbonyliron 24.** Aldol product **24** was prepared according to the general procedure from TMS enol ether **14** (0.026 g, 0.057 mmol), oct-2-ynal (0.011 $cm^3$, 0.074 mmol) and $BF_3{\cdot}Et_2O$ (0.009 $cm^3$, 0.07 mmol). After 6 h, treatment with $Et_3N$ (0.100 $cm^3$, 0.72 mmol) and silyl deprotection as described afforded the crude desilylated aldol product. Purification by column chromatography ($SiO_2$, $Et_2O$–petrol 1 : 1) afforded *aldol complex* **24** (0.015 g, 52%) as a white solid; $\nu_{max}$ (film)/$cm^{-1}$ 2933, 2093, 2023, 1677, 1497, 1455, 1013, 698, 656, 600; $\delta_H$ (600 MHz) 0.83–0.91 (6 H, m, 3 × C(14)H and C(6)Me), 1.29–1.37 (4 H, m, 2 × C(12)H and 2 × C(13)H), 1.51 (2 H, apparent quintet, *J* 6.6, 2 × C(11)H), 2.20 (2 H, t, *J* 7.1, 2 × C(10)H), 2.51 (1 H, d, *J* 6.2, OH), 3.08 (1 H, apparent quintet, *J* 7.3, C(6)H), 4.11 (1 H, d, *J* 11.0, C(4)H), 4.59 (1 H, apparent t, *J* 6.8, C(7)H), 5.25 (1 H, dd, *J* 8.6, 4.8, C(2)H), 5.45 (1 H, d, *J* 4.8, C(1)H), 5.56 (1 H, dd, *J* 11.0, 8.6, C(3)H), 7.29–7.38 (5 H, m, Ph(H)); $\delta_C$ (150 MHz) 11.8 C(12) or C(13), 14.3 C(14), 18.6 C(10), 22.1 C(6)Me, 28.1 C(11), 31.0 C(12) or C(13), 53.0 C(6), 64.1 C(7), 65.7 C(4), 78.2 C(1), 79.0 C(8) or C(9), 84.5 C(2), 87.4 C(8) or C(9), 92.6 C(3), 125.8, 128.6, 128.7, 128.8, 138.2 Ph(C) × 5, 199.4, 201.9, 203.9, 206.2, 206.8, CO × 5; *m*/*z* (QTOF) 517 ($MNa^+$, 30%), 419 (20), 405 (20) [Found ($MNa^+$) 517.0196. $C_{25}H_{26}O_7FeNa$ requires 517.0926].

**[(4*E*,2*R**,3*S**,7*S**,8*R**)-2-(Carbonyloxy-κ*C*)-8-hydroxy-7-methyl-6-oxo-(3,4,5-η)-pentadec-4-en-9-yn-3-yl]tricarbonyliron 25.** Complex **25** was prepared according to the general procedure from TMS enol ether **15** (0.016 g, 0.04 mmol), oct-2-ynal (0.009 $cm^3$, 0.07 mmol) and $BF_3{\cdot}Et_2O$ (0.007 $cm^3$, 0.06 mmol). After 6 h, treatment with $Et_3N$ (0.050 $cm^3$, 0.36 mmol) and work-up as described afforded the crude desilylated aldol products. Purification by column chromatography ($SiO_2$, $Et_2O$–petrol, gradient 1 : 9→1 : 1) afforded *aldol complex* **25** (0.010 g, 56%) as a white solid; $\nu_{max}$ (film)/$cm^{-1}$ 2928, 2090, 2019, 1671, 1498, 1456, 1049, 654; $\delta_H$ (600 MHz) 0.90 (3 H, t, *J* 7.1, 3 × C(15)H), 1.19–1.53 (12 H, m, including 1.36 [3 H, d, *J* 7.3, C(7)Me] and 1.39 [3 H, d, *J* 6.4, 3 × C(1)H] 2 × C(12)H, 2 × C(13)H and 2 × C(14)H), 2.20 (2 H, td, *J* 7.2, 1.9, 2 × C(11)H), 2.53 (1 H, d, *J* 6.4, OH), 3.06 (1 H, apparent quintet, *J* 7.3, C(7)H), 3.96 (1 H, d, *J* 11.2, C(5)H), 4.53–4.56 (1 H, m, C(2)H), 4.59 (1 H, apparent t, *J* 6.4, C(8)H), 5.06 (1 H, dd, *J* 8.8, 4.7, C(3)H), 5.55 (1 H, dd, *J* 11.2, 8.8, C(4)H); $\delta_C$ (150 MHz) 13.9 C(15), 14.4 C(7)Me, 18.6 C(11), 21.8 C(1), 22.1,

† CCDC reference number 207/421. See http://www.rsc.org/suppdata/p1/b0/b002056g/ for crystallographic files in .cif format.

28.2, 31.0 C(12), C(13), C(14), 53.0 C(7), 64.2 C(8), 65.2 C(5), 72.8 C(2), 79.0 C(9) or C(10), 85.6 C(3), 87.4 C(9) or C(10), 92.4 C(4), 199.5, 202.5, 204.1, 206.3, 207.9 CO × 5; *m/z* (QTOF) 455 ($MNa^+$, 20%), 413 (52), 343 (55), 287 (32) [Found ($MNa^+$) 455.0756. $C_{20}H_{24}O_7FeNa$ requires 455.0764].

**[(3*E*,1*R*,2*S*,6*S*,7*R*)-1-(Carbonyloxy-κ*C*)-6-methyl-5-oxo-1,7-diphenyl-7-triethylsilyl-(2,3,4-η)-hept-2-en-2-yl]tricarbonyliron 26.** $Et_3N$ (0.018 $cm^3$, 0.13 mmol) and TESCl (0.021 $cm^3$, 0.12 mmol) were added sequentially to a solution of homochiral aldol complex (1*R*,2*S*,6*S*,7*R*)-**18** (0.038 g, 0.080 mmol) and imidazole (1 crystal) in DCM (1 $cm^3$) at room temperature. After 1 hour, the mixture was diluted with $Et_2O$ (5 $cm^3$), successively washed with water (5 $cm^3$) and brine (5 $cm^3$), dried ($MgSO_4$) and concentrated *in vacuo*. Purification by flash column chromatography ($SiO_2$, $Et_2O$–petrol 1 : 4) afforded *silyl ether* **26** as a colourless oil (0.050 g, 98%) $[\alpha]_D^{28}$ 204 (*c* 0.100, DCM); $\nu_{max}$ (film)/$cm^{-1}$ 3030, 2954, 2911, 2876, 2091, 2023, 1682, 1455, 1084, 1070, 1009, 820, 741, 699, 656; $\delta_H$ (600 MHz) 0.60 (6 H, q, *J* 7.8, $SiCH_2CH_3$), 0.93 (9 H, t, *J* 7.8, $SiCH_2CH_3$), 0.98 (3 H, d, *J* 8.0, C(6)Me), 3.07 (1 H, apparent quintet, *J* 7.3, C(6)H), 4.12 (1 H, d, *J* 11.4, C(4)H), 4.89 (1 H, d, *J* 8.8, C(7)H), 5.24 (1 H, dd, *J* 8.7, 4.7, C(2)H), 5.46 (1 H, d, *J* 4.7, C(1)H), 5.57 (1 H, dd, *J* 11.4, 8.7, C(3)H), 7.27–7.30 (10 H, m, Ph(H)); $\delta_C$ (150 MHz) 4.7 $SiCH_2CH_3$, 6.4 $SiCH_2CH_3$, 14.3 C(6)Me, 55.3 C(6), 69.3 C(4), 76.2 C(7), 78.2 C(2), 84.1 C(1), 92.5 C(3), 125.7 Ph(C), 126.7 Ph(C), 127.1 Ph(C), 127.9 Ph(C), 128.2 Ph(C), 128.5 Ph(C), 128.8 Ph(C), 138.4 Ph(C), 142.2 Ph(C), 146.9 Ph(C), 200.0, 202.3, 204.3, 205.1, 208.0, CO × 5; *m/z* (ES) 591 ($MH^+$, 37%), 479 (75), 341 (35), 221 (100), 157 (75) [Found ($MH^+$) 591.1502. $C_{30}H_{35}O_7FeSi$ requires 591.1501].

**[(2*Z*,1*R*,4*S*,6*S*,7*R*)-6-Methyl-5-oxo-1,7-diphenyl-7-triethylsilyloxy-(1,2,3,4-η)-hept-2,4-ene-1,4-diyl]tricarbonyliron 27.** $Ba(OH)_2$ solution (0.50 $cm^3$) was added dropwise to a solution of silyl protected aldol complex **26** (0.020 g, 0.034 mmol) in MeOH (1 $cm^3$) at room temperature. After 2 minutes the reaction mixture was poured into $Et_2O$–$H_2O$ (10 $cm^3$, 1 : 1). The layers were separated and the aqueous phase extracted with $Et_2O$ (3 × 5 $cm^3$). The combined organic fractions were washed with brine (5 $cm^3$), dried ($MgSO_4$) and concentrated *in vacuo*. Purification by flash column chromatography ($SiO_2$, $Et_2O$–petrol 1 : 9) afforded *η⁴-diene complex* **27** (0.018 g, 98%) as a bright yellow oil $[\alpha]_D^{28}$ −39.1 (*c* 0.092, DCM); $\nu_{max}$ (film)/$cm^{-1}$ 3028, 2955, 2876, 2056, 1988, 1674, 1600, 1488, 1462, 1372, 1316, 1239, 1168, 1084, 1067, 1006, 819, 744, 700, 618, 602; $\delta_H$ (600 MHz) 0.52 (6 H, q, *J* 8.0, $SiCH_2CH_3$), 0.83 (9 H, t, *J* 8.0, $SiCH_2CH_3$), 0.93 (3 H, d, *J* 7.9, C(6)Me), 1.61 (1 H, d, *J* 7.5, C(4)H), 2.45 (1 H, d, *J* 8.6, C(2)H), 2.84 (1 H, apparent quintet, *J* 7.7, C(6)H), 4.83 (1 H, d, *J* 8.5, C(7)H), 5.96–6.00 (2 H, m, C(1)H and C(3)H), 7.21–7.32 (10 H, m, Ph(H)); $\delta_C$ (150 MHz) 4.8 $SiCH_2CH_3$, 6.4 $SiCH_2CH_3$, 14.8 C(6)Me, 52.6 C(4), 55.6 C(6), 62.1 C(2), 77.0 C(7), 82.5, 83.1 C(1) and C(3), 126.3 Ph(C), 127.0 Ph(C), 127.0 Ph(C), 128.1 Ph(C), 128.8 Ph(C), 138.9 Ph(C), 142.8 Ph(C) × 10, 207.5 CO; *m/z* (QTOF) 569 ($MNa^+$, 100%), 558 (30) [Found ($MNa^+$) 569.1423. $C_{29}H_{34}O_5FeNaSi$ requires 569.1445].

### Preparation of a NaOH–$H_2O_2$ solution

$H_2O_2$ (10 $cm^3$ of a 30% aqueous solution) was added to a stirred solution of NaOH (0.61 g, 1.53 mmol) in MeOH (15 $cm^3$) at 0 °C. The solution was then used immediately.

**(4*E*,6*E*,1*R*,2*S*)-2-Methyl-3-oxo-1,7-diphenyl-1-triethylsilyloxyhepta-4,6-diene 28.** A solution of diene complex **27** (0.016 g, 0.029 mmol) in MeOH (1 $cm^3$) at 0 °C was treated with freshly prepared NaOH–$H_2O_2$ solution (*vide supra*) (0.5 $cm^3$). After 5 minutes at 0 °C the reaction mixture was poured into $Et_2O$–$H_2O$ (10 $cm^3$, 1 : 1) and the layers separated. The aqueous layer was extracted with $Et_2O$ (3 × 5 $cm^3$) and the combined organic extracts washed with brine (5 $cm^3$), dried ($MgSO_4$) and then concentrated *in vacuo*. Purification by flash column chromatography ($SiO_2$, $Et_2O$–petrol 1 : 9) afforded *diene* **28** (0.011 g, 94%) as a yellow oil $[\alpha]_D^{28}$ −62.9 (*c* 0.17, DCM); $\nu_{max}$ (film)/$cm^{-1}$ 2954, 2359, 1658, 1586, 1453, 1068, 823, 747, 701, 652; $\delta_H$ (600 MHz) 0.39 (6 H, apparent quintet, *J* 7.6, $SiCH_2CH_3$), 0.76 (9 H, t, *J* 7.9, $SiCH_2CH_3$), 0.78 (3 H, d, *J* 7.0, C(2)Me), 3.18 (1 H, dd, *J* 9.1, 7.0, C(2)H), 4.76 (1 H, d, *J* 9.1, C(1)H), 6.43 (1 H, d, *J* 15.3, C(4)H), 6.93 (1 H, dd, *J* 15.6, 10.5, C(6)H), 7.00 (1 H, d, *J* 15.6, C(7)H), 7.27–7.38 and 7.48–7.50 (10 H, m, Ph(H)), 7.41 (1 H, dd, *J*, 15.3, 10.5, C(5)H); $\delta_C$ (150 MHz) 4.6 $SiCH_2CH_3$, 6.6 $SiCH_2CH_3$, 14.1 C(2)Me, 52.4 C(2), 77.9 C(1), 127.0 Ph(C), 127.0 Ph(C), 127.2 Ph(C), 127.6 Ph(C), 128.1 Ph(C), 129.0 Ph(C), C(5) and C(6), 130.6 C(4), 136.2 Ph(C), 141.0 C(7), 142.2 Ph(C), 143.2 Ph(C), 203.4 CO; *m/z* (ES) 407 ($MH^+$, 10%), 377 (15), 221 (100), 157 (45), 115 (27) [Found (MH) 407.2407. $C_{26}H_{35}O_2Si$ requires 407.2406].

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