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1,5-Asymmetric induction of chirality using π-allyltricarbonyliron lactone complexes: highly diastereoselective synthesis of α-functionalised carbonyl compounds

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Silyl enol ethers derived from ketone functionalised π-allyltricarbonyliron lactone complexes undergo highly diastereoselective carbon–fluorine and carbon–oxygen bond formation reactions with excellent control at the α-stereogenic centre.

Introduction

The aldol and Mukaiyama aldol reactions[1] are strategically important carbon–carbon bond construction methods and are especially useful in natural product syntheses.[2]

Recently we have found that the templating effects of π-allyltricarbonyliron lactone complexes, that additionally contain alkyl ketone side-chains, cause these complexes to undergo highly diastereoselective Mukaiyama aldol reactions with aldehydes.[3] The products of these reactions formally constitute the introduction of 1,7 asymmetric oxygen-containing stereogenic centres as a result of chiral induction derived from the tricarbonlyiron lactone tethering residue.

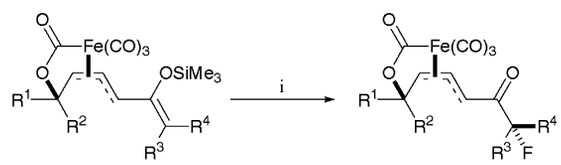
Also the intermediate silyl enol ethers are known to be useful in the formation of carbon–heteroatom bonds in both a regio- and stereo-specific fashion.

Here we show that silyl enol ethers derived from various substituted tricarbonyliron lactone complexes also undergo highly diastereoselective carbon–fluorine and carbon–oxygen bond formation based upon the anticipated conformational preferences of the side-chain enol ethers. Since it is also possible to later remove the templating metal species by a variety of methods, the products from these reactions could find applications in the pharmaceutical and agrochemical industries.[4]

Results and discussion

A number of silyl enol ethers were used in this study (Table 1). The preparation of complexes **1**, **2** and **3** has been previously described in the literature.[3b] New π-allyltricarbonyliron lactone complexes **4** and **5** were readily prepared in four steps starting from known Weinreb amide **6**.[5] Thus treatment of **6** with the Grignard reagents propylmagnesium bromide or phenethylmagnesium chloride afforded ketones **7** and **8** respectively. The regioselective monoepoxidation of these substrates was then investigated using two different methods. Firstly ketone **7** was treated with DMDO,[6] which was found to epoxidise only the more electron rich remote double bond with complete selectivity to afford epoxyenone **9**. Next epoxyenone **10** was prepared using an alternative procedure developed by Heaney *et al.*, in which trifluoroperacetic acid is generated *in situ* from trifluoroacetic acid anhydride (TFAA) and a urea-hydrogen peroxide addition complex.[7] This again proceeded with good selectivity affording epoxy enone **10**. Subsequent tricarbonyliron lactone formation with these epoxy enones proceeded smoothly following our previously reported route. Consequently compound **9** afforded complexes **4** and **11** in a ratio of approximately 3 : 1, while **10** gave **5** and **12** in a ratio of 2 : 1 (Scheme 1).

Table 1 *Reagents and conditions:* (i) Selectfluor®, MeCN, rt



1 R^1=H, R^2=Me, R^3=Me, R^4=H
2 R^1=H R^2=C_5H_{11}, R^3=Me, R^4=H
3 R^1=H, R^2=Ph, R^3=Me, R^4=H
14a R^1=H, R^2=Me, R^3=Et, R^4=H
15a R^1=H, R^2=Me, R^3=CH_2Ph, R^4=H
16a R^1=C_5H_{11}, R^2=H, R^3=Me, R^4=H
17 R^1=H, R^2=Me, R^3=Me, R^4=H
18 R^1=H R^2=C_5H_{11}, R^3=Me, R^4=H
19 R^1=H, R^2=Ph, R^3=Me, R^4=H
20 R^1=H, R^2=Me, R^3=Et, R^4=H
21 R^1=H, R^2=Me, R^3=CH_2Ph, R^4=H
22 R^1=C_5H_{11}, R^2=H, R^3=Me, R^4=H

Entry	Silyl enol ether	Product	Yield (%)	d.e. (%)[a]
1	**1**	**17**	93	> 95
2	**2**	**18**	95	> 95
3	**3**	**19**	92	> 95
4	**14**	**20**	88	94
5	**15**	**21**	96	> 95
6	**16**	**22**	88	> 95

[a] d.e. determined from the crude mixture by 600 or 400 ^{1}H NMR analysis.

The isolation and characterization of ketone complex **13** has also been reported,[3d] and conversion of ketones **4**, **5** and **13** into the corresponding silyl enol ethers **14a**, **15a** and **16a** was readily achieved under standard conditions of treatment with trimethylsilyl triflate (TMSOTf) and Et_3N in DCM at 0 °C (Scheme 2).

We next set out to determine whether the rigid framework of these silyl enol ether complexes, coupled with the preferential conformation adopted by the side chain, would be able to impart diastereocontrol in a subsequent electrophilic fluorination reaction.

Accordingly, the silyl enol ethers were treated at room temperature with Selectfluor® in MeCN following the literature procedure.[8] Prior to reaction, the silyl enol ethers were purified by flash column chromatography on Florisil until the presence of the minor (*Z*)-geometric isomer could not be detected by 600 MHz ^{1}H NMR spectroscopy. The reactions proceeded very smoothly, generating the corresponding α-fluoro ketone in good yield and with excellent levels of diastereoselectivity. The results are summarised in Table 1. After a simple aqueous work-up the products were isolated in an excellent level of purity. Column chromatography was there-

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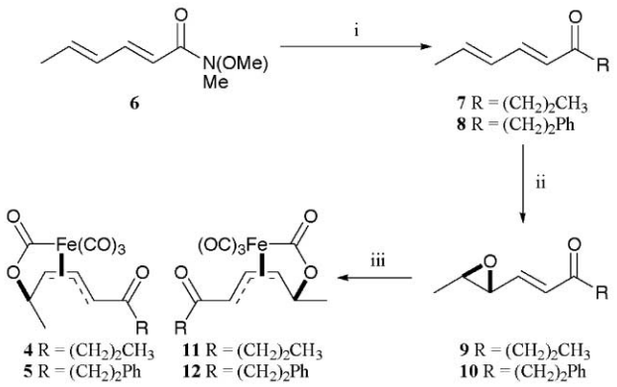
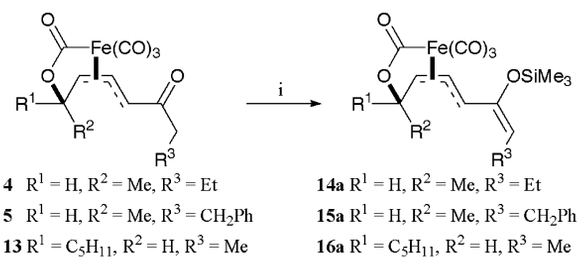


Scheme 1 *Reagents and conditions:* (i) ^{n}PrMgBr, THF, 0 °C, **7** 58%; $Ph(CH_2)_2MgCl$, THF, 0 °C, **8** 72%; (ii) DMDO, CH_2Cl_2, 0 °C, **9** 56%; TFAA, urea–H_2O_2 addition compound, Na_2HPO_4, CH_2Cl_2, 0 °C, **10** 68%; (iii) $Fe_2(CO)_9$, THF, rt, **4** 54%, **11** 15%; **5** 54%, **12** 22%.



Scheme 2 *Reagents and conditions:* (i), Me_3SiOTf (1.5 eq.), Et_3N (1.8 eq.), DCM, 0 °C, **14** 83%, **15** 76%, **16** 78%.

fore usually unnecessary, but when purification was carried out on silica gel, no epimerisation at the α-centre was observed.

It was apparent that, as expected from earlier precedent, a preferential conformation of the silyl enol ether side-chain was being adopted even at room temperature, with the Selectfluor® reagent approaching *anti* to the bulky tricarbonyliron moiety (*vide infra*). Several of the products were found to be crystalline, with compound **17** affording crystals of sufficient quality for X-ray analysis (Fig. 1),[9] thus providing conclusive proof of stereochemistry.

The formation of this diastereoisomer is completely in accord with earlier studies (*vide supra*) and is consistent with the substrate alignment shown below (Fig. 2). The silyl enol ether side-chain adopts the s-*trans* conformation, with the fluorinating reagent approaching *anti* to the tricarbonyliron moiety. Based on the known conformational preference for the silyl enol ether, and the strong stereodirecting ability of the tricarbonyliron moiety, it was assumed that the stereochemical course of the other fluorinations were analogous.

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,[10] (*E*,*E*)-dienes[10] and alkenols.[10,11] For example, fluorinated complex **19** was treated under the standard decomplexation techniques using $Ba(OH)_2$[12] to give a single product **23a**. No scrambling of the α-fluoro stereogenic centre was observed by ^{1}H NMR. Following oxidative demetallation under neutral conditions[13] compound **23b** was obtained from **23a** in good yield (Scheme 3).

Owing to our interest in the stereoselective introduction of other 1,2-oxygenation patterns[14] we also investigated the diastereoselective preparation of α-hydroxy ketones *via* oxidation of the silyl enol ether complexes. The epoxidation of silyl enol ether **24**[1d] was first attempted using the classical conditions by treatment with *m*-CPBA at 0 °C in CH_2Cl_2.[15] From high field ^{1}H NMR spectroscopic examination of the crude reaction product it was apparent that a mixture of silylated and non-silylated

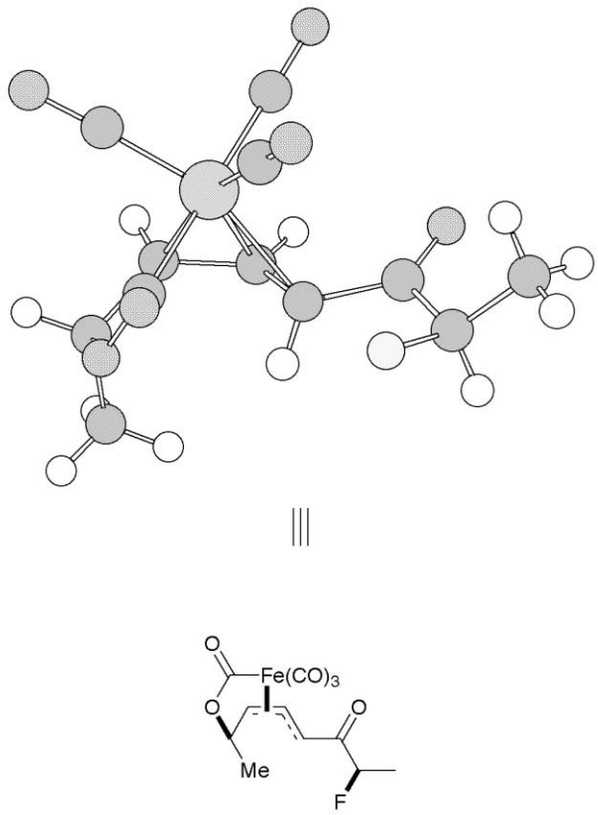


Fig. 1

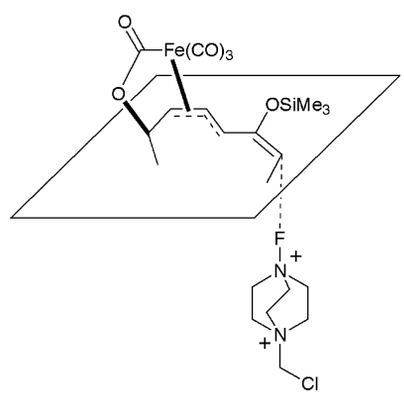
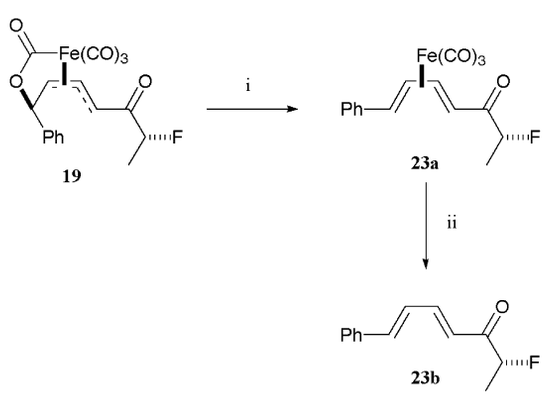


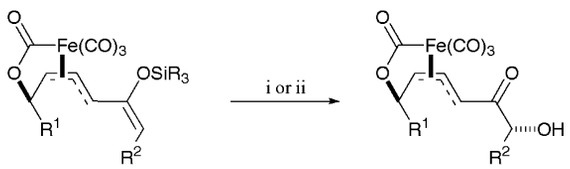
Fig. 2



Scheme 3 *Reagents and conditions:* (i) $Ba(OH)_2$, MeOH, 80%; (ii) CAN, MeCN, 71%.

products had been formed. In order to accurately assess the diastereoselectivity of the transformation, the crude product mixture was treated with HF·pyridine to effect desilylation. Spectroscopic analysis then revealed that the α-hydroxylation

Table 2 *Reagents and conditions*: (i) MTO (cat.), H_2O_2, py, CH_2Cl_2, rt, then HF·py, THF, rt; (ii) *m*-CPBA, CH_2Cl_2, 0 °C, then HF·py, THF, rt



1 R^1 = Me, R^2 = Me, R = Me
2 R^1 = C_5H_{11}, R^2 = Me, R = Me
3 R^1 = Ph, R^2 = Me, R = Me
24 R^1 = Me, R^2 = Me, R = Et

25 R^1 = Me, R^2 = Me
26 R^1 = C_5H_{11}, R^2 = Me
27 R^1 = Ph, R^2 = Me

Entry	Silyl enol ether	Procedure	Product	Yield (%)	d.e. (%)[a]
1	**1**	i	**25**	84	94
2	**24**	ii	**25**	75	84
3	**2**	i	**26**	83	90
4	**3**	i	**27**	83	88
5	**3**	ii	**27**	72	82

[a] d.e. determined from the crude mixture by 600 or 400 MHz ^{1}H NMR analysis.

process had occurred with a pleasing d.e. of 84% and afforded **25** in an isolated yield of 75%. Evidently the iron auxiliary was providing effective stereocontrol in the reaction, and it was also clear that the iron lactone complex was compatible with the harsh reaction conditions employed. Alternatively, treatment of complex **1** with catalytic MTO under the conditions recommended by Sharpless *et al.*[16] also proceeded with good yield and excellent diastereoselectivity to afford the same product **25**. These procedures were then used with a range of silyl enol ethers (Table 2).

Both procedures were found to proceed with good levels of diastereoselectivity. The relative stereochemistry of the major diastereoisomer was assigned on the basis of the precedent for the stereodirecting effect of the tricarbonyliron moiety and the preferential s-*trans* conformation of the silyl enol ether side-chain (*vide supra*).

Conclusions

In summary, this paper has described further novel applications of π-allyltricarbonyliron lactone complexes. Even at room temperature, a preferential conformation is adopted by silyl enol ethers in the side-chain, enabling diastereoselective carbon–heteroatom bond formation at the α-centre. The products contain synthetically attractive functionalisation, and the varied techniques available for decomplexation serve to increase the utility of this new chemistry in asymmetric synthesis. 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, DRX-400 or AC-200 spectrometers and are reported as follows: chemical shift, δ (ppm) [number of protons, multiplicity, coupling constant J (Hz), and assignment]. Residual protic solvent $CHCl_3$ (δ_H = 7.26 ppm) was used as the internal reference. ^{13}C NMR spectra were recorded in $CDCl_3$ at 150 MHz, 100 MHz or 50 MHz on Bruker DRX-600, DRX-400 or AC-200 spectrometers, using the central resonance of $CDCl_3$ (δ_C = 77.0 ppm) as the internal reference. Infra-red spectra were recorded on Perkin-Elmer 983G, FTIR 1620 or Perkin Elmer ATR Spectrum 1 spectrometers. Mass spectra were obtained on Kratos MS890MS, Bruker BIOAPEX 4.7 T FTICR or Micromass Q-TOF spectrometers at the Department of Chemistry, University of Cambridge, and at the EPSRC Mass Spectrometry service at Swansea. The following ionisation techniques were used: electron ionisation (EI), chemical ionisation (CI), fast atom bombardment (FAB), liquid secondary ion mass spectrometry (LSIMS) and electrospray (ES). 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. Aqueous solutions were saturated unless otherwise specified. Petrol refers to petroleum ether bp 40–60 °C. In cases where mixtures of solvents were utilised, the ratios given refer to the volumes used.

All reactions were carried out under an argon atmosphere in oven-dried glassware, which was cooled under a continuous stream of argon immediately prior to use unless otherwise stated. Reactions involving preparation of the iron complexes were carried out using degassed THF. The solvent was degassed by successively evacuating and purging the solvent three times with argon while simultaneously subjecting the solvent to sonication using an 80 W 55 Hz cleaning bath. Et_2O and THF were distilled from sodium benzophenone ketyl, and CH_2Cl_2 from calcium hydride. Other reagents and solvents were used as supplied.

The preparation of compounds **1**, **2**, **3**, **13**, **24**[3d] and **6**[5] is described elsewhere.

(5*E*,7*E*)-Nona-5,7-dien-4-one 7

Ketone **7** was prepared according to the general procedure[5] using propyl magnesium bromide (2 M in Et_2O, 19.4 cm^3, 38.8 mmol), Weinreb amide **6** (4.00 g, 25.8 mmol) and THF (100 cm^3). Purification by flash column chromatography (SiO_2, Et_2O–petrol 1 : 1) afforded *ketone* **7** (2.08 g, 58%) as a yellow oil; ν_{max}(film)/cm^{-1} 3027, 2962, 2934, 2874, 1687, 1667 (C=O), 1640 (C=C), 1597, 1446, 1410, 1377, 1366, 1346, 1329, 1266, 1244, 1228, 1196, 1151, 1128, 1086, 1039, 999, 946, 886, 784, 740, 665; δ_H(200 MHz) 0.75 (3 H, t, J 7.4, 1-H × 3), 1.46 (2 H, sextet, J 7.4, 2-H × 2), 1.68 (3 H, d, J 5.0, 9-H × 3), 2.33 (2 H, t, J 7.4, 3-H × 2), 5.88 (1 H, d, J 15.4, 5-H), 5.96–6.04 (2 H, m, 7-H, 8-H), 6.94 (1 H, dd, J 15.4, 8.2, 6-H); δ_C(50 MHz) 13.6 (1-C), 17.6 (2-C), 18.5 (9-C), 42.2 (3-C), 127.6 (5-C), [130.2, 139.7 (7-C, 8-C)], 142.4 (6-C), 200.4 (4-C); *m*/*z* (EI) 138 (M^+, 25%), 95 (M^+–C_3H_7, 100), 71 (M^+–C_3H_7–CO, 30), 67 ($C_3H_7CO^+$, 45). [Found (M^+) 138.1051. $C_9H_{14}O$ requires M 138.1046].

(4*E*,6*E*)-1-Phenylocta-4,6-dien-3-one 8

Ketone **8** was prepared according to the general procedure[5] using phenethyl magnesium chloride (1 M in THF, 19.5 cm^3, 19.5 mmol), Weinreb amide **6** (2.00 g, 12.9 mmol) and THF (100 cm^3). Purification by flash column chromatography (SiO_2, Et_2O–petrol 1 : 3) afforded *ketone* **8** (1.86 g, 72%) as a viscous oil; ν_{max}(film)/cm^{-1} 3084, 3061, 3026, 2931, 1947, 1686, 1662 (C=O), 1639 (C=C), 1596 (Ph), 1496, 1453, 1409, 1364, 1328, 1282, 1227, 1186, 1145, 1097, 1075, 1030, 999, 948, 860, 750, 700; δ_H(400 MHz) 1.87 (3 H, d, *J* 4.8, 8-H × 3), 2.88 (2 H, t, *J* 7.3, 2-H × 2), 2.97 (2 H, t, *J* 7.3, 1-H × 2), 6.09 (1 H, d, *J* 15.5, 4-H), 6.16–6.20 (2 H, m, 6-H, 7-H), 7.12–7.31 (6 H, m, Ph–H × 5, 5-H); δ_C(100 MHz) 18.8 (8-C), 30.4 (2-C), 42.5 (1-C), [126.1, 127.6, 128.4, 130.3, 136.9, 140.3, 141.4, 143.0 (Ph–C × 6, 4-C, 5-C, 6-C, 7-C)], 199.5 (3-C); *m*/*z* (ES) 223 (MNa^+, 100%). [Found (MNa^+) 223.1103. $C_{14}H_{16}ONa$ requires *M*Na 223.1099].

Preparation of a stock solution of dimethyldioxirane

Sodium bicarbonate (192 g), water (320 cm^3) and acetone (250 cm^3) were placed in a 5 l, 3-necked round bottomed flask fitted with a short path, non-jacketed distillation head and a 500 cm^3 round bottomed flask as a receiver. The white slurry was stirred for 10 min and Oxone® (400 g) was added in one portion. The apparatus was attached to a water aspirator, sealed, and the receiver was cooled to −78 °C. The effervescence that occurred, and the rate of distillation, were controlled by regulation of the vacuum and the pale yellow distillate, comprising an approximately 0.05 M solution of dimethyldioxirane in acetone (*ca*. 150 cm^3), was collected over a period of 2 h. After this time the vacuum was carefully released, the solution was dried (K_2CO_3) and stored under argon at −60 °C over activated 4 Å molecular sieves.

(5*E*,7*R,8*R**)-7,8-Epoxynon-5-en-4-one 9**

Dimethyldioxirane (DMDO) (150 cm^3 of a *ca.* 0.05 mol dm^{-3} solution in acetone, *ca.* 7.5 mmol) was added *via* cannula to a stirred solution of dienone **7** (0.850 g, 5.74 mmol) in CH_2Cl_2 (30 cm^3) at 0 °C. The reaction mixture was stirred at this temperature for 30 min, then allowed to warm to rt and stirred for a further 4 h. Upon completion of the reaction, $MgSO_4$ was added and the resultant suspension was stirred vigorously for 30 min. Filtration and removal of the solvents *in vacuo* followed by flash column chromatography (SiO_2, Et_2O–petrol 1 : 1) yielded *epoxyenone* **9** (0.520 g, 56%) as a pale yellow liquid; ν_{max}(film)/cm^{-1} 2964, 2932, 1697, 1676 (C=O), 1632 (C=C), 1458, 1424, 1378, 1340, 1308, 1237, 1197, 1130, 1054, 1004, 977, 943, 855, 816, 748, 665; δ_H(200 MHz) 0.93 (3 H, t, *J* 7.4, 1-H × 3), 1.39 (3 H, d, *J* 5.0, 9-H × 3), 1.56–1.73 (2 H, m, 2-H × 2), 2.52 (2 H, t, *J* 7.2, 3-H × 2), 2.98 (1 H, qd, *J* 5.0, 2.0, 8-H), 3.17 (1 H, dd, *J* 6.4, 2.0, 7-H), 6.34–6.57 (2 H, m, 5-H, 6-H); δ_C(50 MHz) 13.3 (1-C), [17.2, 17.3 (2-C, 9-C)], 42.3 (3-C), [57.1, 57.2 (7-C, 8-C)], [131.3, 142.4 (5-C, 6-C)], 199.5 (4-C); *m*/*z* (EI) 155 (MH^+, 5%), 110 (10), 81 (30), 69 (100). [Found (MH^+) 155.1085. $C_9H_{15}O_2$ requires *M*H 155.1072].

(4*E*,6*R,7*R**)-6,7-Epoxy-1-phenyloct-4-en-3-one 10**

Trifluoroacetic anhydride (21.0 cm^3, 150 mmol) was added slowly to a suspension of (4*E*,6*E*)-1-phenylocta-4,6-dien-3-one **8** (3.00 g, 15.0 mmol), urea hydrogen peroxide addition compound (56.5 g, 600 mmol) and disodium hydrogenphosphate (42.1 g, 298 mmol) in CH_2Cl_2 (200 cm^3) at 0 °C. After stirring at rt for 30 min, the mixture was poured cautiously into a vigorously stirred aqueous solution of sodium bicarbonate (500 cm^3). After effervescence ceased, the organic phase was washed sequentially with sodium bicarbonate solution (3 × 100 cm^3) and brine (100 cm^3), dried ($MgSO_4$) and concentrated *in vacuo*. Purification by flash column chromatography (SiO_2, Et_2O–petrol 1 : 1) afforded *epoxy enone* **10** (2.20 g, 68%) as a viscous oil; ν_{max}(film)/cm^{-1} 3061, 3027, 2990, 2928, 1783, 1674 (C=O), 1632 (C=C), 1603, 1496, 1454, 1422, 1378, 1339, 1170, 1095, 1074, 1030, 1004, 976, 941, 864, 826, 749, 700; δ_H(400 MHz) 1.38 (3 H, d, *J* 5.1, 8-H × 3), 2.88–3.00 (5 H, m, 1-H × 2, 2-H × 2, 7-H), 3.16 (1 H, d, *J* 6.7, 6-H), 6.38 (1 H, d, *J* 16.0, 4-H), 6.50 (1 H, dd, *J* 16.0, 6.7, 5-H), 7.17–7.29 (5H, m, Ph–H × 5); δ_C(100 MHz) 17.5 (8-C), [29.9, 42.1 (1-C, 2-C)], [57.4, 57.5 (6-C, 7-C)], [126.1, 128.3, 128.5, 141.0 (Ph–C × 6)], 131.3 (4-C), 142.8 (5-C), 198.4 (3-C); *m*/*z* (ES) 239 (MNa^+, 100%). [Found (MNa^+) 239.1046. $C_{14}H_{16}O_2Na$ requires *M*Na 239.1042].

General procedure for the preparation of π-allyltricarbonyliron lactone complexes

For a 3.2 mmol scale reaction: degassed THF (40 cm^3) was added to diironnonacarbonyl (1.8–2.2 eq.) *via* cannula and the mixture was stirred vigorously in the absence of light for 20 min at rt after which time the epoxy enone (1.0 eq.) was added and the reaction mixture was 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 the triiron dodecacarbonyl)⟶Et_2O–petrol] afforded, in order of elution, the *endo* complex and then the *exo* complex.

[(4*E*,2*R,3*S**)-2-(Carbonyloxy-κC)-6-oxo-(3,4,5-η)-non-4-en-3-yl]tricarbonyliron 4 and [(4*E*,2*R**,3*R**)-2-(carbonyloxy-κC)-6-oxo-(3,4,5-η)-non-4-en-3-yl]tricarbonyliron 11**

Complexes **4** and **11** were prepared according to the general procedure above using epoxy enone **9** (0.400 g, 2.6 mmol) and diironnonacarbonyl (1.70 g, 4.6 mmol) in THF (12 cm^3). After 3 h, work-up as described and purification by flash column chromatography (SiO_2, gradient, petrol⟶Et_2O–petrol 1 : 1) afforded firstly *endo complex* **4** (0.334 g, 54%) as a yellow solid; ν_{max}(film)/cm^{-1} 2967, 2934, 2877, 2088 (CO), 2021 (CO), 1674 (C=O), 1498, 1456, 1406, 1375, 1314, 1236, 1181, 1127, 1087, 1050, 997, 940, 830, 741, 654; δ_H(200 MHz) 0.97 (3 H, t, *J* 7.5, 9-H × 3), 1.36 (3 H, d, *J* 6.5, 1-H × 3), 1.71 (2 H, m, 8-H × 2), 2.68 (2 H, t, *J* 7.6, 7-H × 2), 3.86 (1 H, d, *J* 11.2, 5-H), 4.50 (1 H, dd, *J* 6.5, 4.6, 2-H), 5.04 (1 H, dd, *J* 8.6, 4.6, 3-H), 5.35 (1 H, dd, *J* 11.2, 8.6, 4-H); δ_C(50 MHz) 13.7 (9-C), 17.3 (8-C), 21.8 (1-C0, 45.2 (7-C), 65.9 (5-C), 72.9 (2-C), 85.4 (3-C), 92.0 (4-C0, [199.7, 202.6, 204.0, 205.0, 207.9 (FeCO × 4, 6-C)]; *m*/*z* (ES) 345 (MNa^+, 50%), 247 (100). [Found (MNa^+) 345.0037. $C_{13}H_{14}O_6$FeNa requires *M*Na 345.0032]. *Exo complex* **11** followed (0.093 g, 15%) as a brown oil; ν_{max}(film)/cm^{-1} 2968, 2935, 2878, 2084 (CO), 2012 (CO), 1661 (C=O), 1496, 1456, 1406, 1377, 1305, 1230, 1172, 1126, 1091, 1049, 993, 951, 834, 797, 753; δ_H(200 MHz) 0.97 (3 H, t, *J* 7.4, 9-H × 3), 1.38 (3 H, d, *J* 6.4, 1-H × 3), 1.69–1.73 (2 H, m, 8-H × 2), 2.70 (2 H, t, *J* 7.3, 7-H × 2), 3.89 (1 H, d, *J* 11.2, 5-H), 4.53 (1 H, app. quin, *J* 6.2, 2-H), 5.05 (1 H, dd, *J* 8.7, 4.6, 3-H), 5.54 (1 H, dd, *J* 11.2, 8.7, 4-H); δ_C(50 MHz) 13.7 (9-C), 17.2 (8-C), 24.0 (1-C), 45.2 (7-C), 65.2 (5-C), 70.8 (2-C), 84.4 (4-C), 93.6 (3-C), [199.7, 202.6, 204.0, 205.0, 207.9 (FeCO × 4, 6-C)]; *m*/*z* (ES) 323 (MH^+, 100%), 305 (100), 229 (60). [Found (MH^+) 323.0220. $C_{13}H_{15}O_6$Fe requires *M*H 323.0212].

[(4*E*,2*R,3*S**)-2-(Carbonyloxy-κC)-6-oxo-8-phenyl-(3,4,5-η)-oct-4-en-3-yl]tricarbonyliron 5 and [(4*E*,2*R**,3*R**)-2-(carbonyloxy-κC)-6-oxo-8-phenyl-(3,4,5-η)-oct-4-en-3-yl]tricarbonyliron 12**

Epoxy enone **10** (0.380 g, 1.76 mmol) was treated with diironnonacarbonyl (1.32 g, 3.63 mmol) according to the general pro-

cedure described above. Flash column chromatography (SiO_2, Et_2O–petrol, gradient 1 : 20⟶2 : 1) afforded firstly *endo complex* **5** (0.365 g, 54%) as a viscous oil; ν_{max}(film)/cm^{-1} 3028, 2978, 2930, 2361, 2088 (CO), 2020 (CO), 1672 (C=O), 1604, 1498, 1453, 1405, 1363, 1309, 1235, 1181, 1083, 1052, 996, 943, 831, 753, 701, 654, 606; δ_H(400 MHz) 1.35 (3 H, d, *J* 6.3, 1-H × 3), 3.00–3.07 (4 H, m, 7-H × 2, 8-H × 2), 3.83 (1 H, d, *J* 11.2, 5-H), 4.51 (1 H, app. quin, *J* 5.7, 2-H), 5.04 (1 H, dd, *J* 8.7, 4.6, 3-H), 5.53 (1 H, dd, *J* 11.2, 8.7, 4-H), 7.18–7.31 (5 H, m, Ph–H × 5); δ_C(100 MHz) 21.8 (1-C), [29.8, 44.8 (7-C, 8-C)], 65.6 (5-C), 72.9 (2-C), 85.7 (3-C), 91.9 (4-C), [126.3, 128.4, 128.6, 140.4 (Ph–C × 6)], [199.6, 202.3, 203.1, 204.7, 207.8 (FeCO × 4, 6-C)]; *m*/*z* (ES) 407 (MNa^+, 25%), 367 (40), 363 (50), 353 (50), 311 (40). [Found (MNa^+) 407.0202. $C_{18}H_{16}O_6FeNa$ requires *M*Na 407.0188]. *Exo complex* **12** followed (0.148 g, 22%) as a viscous oil; ν_{max}(film)/cm^{-1} 2931, 2088 (CO), 2019 (CO), 1665 (C=O), 1496, 1307, 1051, 700, 650; δ_H(400 MHz) 1.25 (3 H, d, *J* 6.2, 1-H × 3), 3.00–3.06 (4 H, m, 7-H × 2, 8-H × 2), 3.70 (1 H, d, *J* 11.0, 5-H), 4.27 (1 H, app. q, *J* 6.4, 2-H), 4.81 (1 H, d, *J* 8.3, 3-H), 5.73 (1 H, app. t, *J* 10.4, 4-H), 7.17–7.30 (5 H, m, Ph–H × 5); δ_C(100 MHz) 24.0 (1-C), [29.7, 44.8 (7-C, 8-C)], 64.9 (5-C), 70.7 (2-C), 84.6 (3-C), 93.5 (4-C0, [126.3, 128.4, 128.6, 140.4 (Ph–C × 6)], [199.9, 202.2, 203.0, 204.6, 208.1 (FeCO × 4, 6-C)]; *m*/*z* (ES) 407 (MNa^+, 100%), 264 (80), 241 (50). [Found (MNa^+) 407.0196. $C_{18}H_{16}O_6FeNa$ requires *M*Na 407.0188].

General procedure for the preparation of silyl enol ether complexes 14–16

For a 0.30 mmol scale reaction: Et_3N (1.6 eq.) and trialkylsilyl triflate (1.2–1.4 eq.) were added sequentially to a cooled (0 °C) solution of the ketone complex (1.0 eq.) in CH_2Cl_2 (1 cm^3) and the reaction mixture was stirred at 0 °C until the reaction was complete as indicated by TLC (typically 30 min–1 h). The reaction mixture was then poured into Et_2O–H_2O (5 cm^3, 1 : 1), the layers 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, a small sample (*ca*. 5 mg) of the crude material was filtered through a short plug of Florisil washing with Et_2O (10 cm^3) and the filtrate was concentrated *in vacuo*, followed by 600 MHz or 400 MHz ^{1}H NMR spectroscopic analysis, specifically by integration of the silyl group resonances. The silyl enol ether complexes were then further purified by flash column chromatography (Florisil, Et_2O–petrol).

[(4*E*,6*E*,2*R**,3*S**)-2-(Carbonyloxy-κ*C*)-6-trimethylsilyloxy-(3,4,5-η)-nona-4,6-dien-3-yl]tricarbonyliron 14a and [(4*E*,6*Z*,2*R**,3*S**)-2-(carbonyloxy-κ*C*)-6-trimethylsilyloxy-(3,4,5-η)-nona-4,6-dien-3-yl]tricarbonyliron 14b

Silyl enol ethers **14a** and **14b** were prepared according to the general procedure above from TMSOTf (0.123 cm^3, 0.680 mmol), Et_3N (0.120 cm^3, 0.851 mmol), and propyl ketone **4** (0.170 g, 0.570 mmol). After 20 min, work-up as described and purification by flash column chromatography (Florisil, Et_2O–petrol 2 : 3) afforded firstly *(E)-silyl enol ether* **14a** (0.141 g, 61%) as a pale yellow solid; ν_{max}(film)/cm^{-1} 2072 (CO), 2016 (CO), 1995 (CO), 1663, 1627, 1363, 1276, 1252, 1228, 1128, 1085, 1039, 994, 948, 888, 847, 763, 699, 657; δ_H(400 MHz) 0.23 (9 H, s, $Si(CH_3)_3$), 1.06 (3 H, t, *J* 7.5, 9-H × 3), 1.38 (3 H, d, *J* 6.4, 1-H × 3), 2.21 (2 H, m, 8-H × 2), 4.46 (1 H, app. quin, *J* 6.3, 2-H), 4.62 (1 H, dd, *J* 8.1, 4.7, 3-H), 4.76 (1 H, d, *J* 11.9, 5-H), 4.98 (1 H, t, *J* 7.8, 7-H), 5.03 (1 H, dd, *J* 11.9, 8.1, 4-H); δ_C(150 MHz) 0.0 $Si(CH_3)_3$, 14.7 (9-C), 20.1 (8-C), 21.9 (1-C0, 73.4 (2-C0, 75.4 (3-C), 77.0 (5-C), 85.0 (4-C), 114.2 (7-C), 146.3 (6-C), [204.4, 205.4, 205.4, 209.3 (FeCO × 4)]; *m*/*z* (ES) 417 (MNa^+, 100%). [Found (MNa^+) 417.0441. $C_{16}H_{22}O_6FeSiNa$ requires *M*Na 417.0427]. *(Z)-Silyl enol ether* **14b** followed (0.051 g, 22%) as a yellow solid; ν_{max}(film)/cm^{-1} 2965, 2074 (CO), 2001 (CO), 1669, 1455, 1354, 1290, 1255, 1184, 1042, 986, 944, 886, 847, 756, 655; δ_H(400 MHz) 0.27 (9 H, s, $Si(CH_3)_3$), 1.00 (3 H, t, *J* 7.5, 9-H × 3), 1.36 (3 H, d, *J* 6.3, 1-H × 3), 2.08 (2 H, m, 8-H × 2), 4.43 (1 H, app. quin, *J* 5.2, 2-H), 4.56 (1 H, dd, *J* 7.8, 4.7, 3-H), 4.67 (1 H, d, *J* 12.3, 5-H), 4.76 (1 H, dd, *J* 12.3, 2.4, 4-H), 5.18 (1 H, t, *J* 8.2, 7-H); δ_C(100 MHz) 0.7 ($Si(CH_3)_3$), 13.8 (9-C), 20.2 (8-C), 22.0 (1-C), 73.5 (2-C), 75.4 (3-C), 83.2 (4-C), 84.4 (5-C), 119.4 (7-C), 146.3 (6-C), [204.5, 205.4, 206.7, 209.5 (FeCO × 4)]; *m*/*z* (ES) 417 (MNa^+, 15%), 395 (MH^+, 10), 305 (100). [Found (MNa^+) 417.0440. $C_{16}H_{22}O_6FeSiNa$ requires *M*Na 417.0427].

Analysis of the 400 MHz ^{1}H NMR spectrum of the crude reaction mixture allowed determination of the ratio of **14a** and **14b**, specifically by integration of the trimethylsilyl protons; δ_H(400 MHz) 0.23 (0.64 H, s), 0.27 (0.36 H, s). Calculated ratio **14a** : **14b** = 1.8 : 1.

[(4*E*,6*E*,2*R**,3*S**)-2-(Carbonyloxy-κ*C*)-6-trimethylsilyloxy-(3,4,5-η)-8-phenylocta-4,6-dien-3-yl]tricarbonyliron 15a and [(4*E*,6*Z*,2*R**,3*S**)-2-(carbonyloxy-κ*C*)-6-trimethylsilyloxy-(3,4,5-η)-8-phenylocta-4,6-dien-3-yl]tricarbonyliron 15b

Silyl enol ethers **15a** and **15b** were prepared according to the general procedure above from TMSOTf (0.111 cm^3, 0.61 mmol), Et_3N (0.092 cm^3, 0.66 mmol), and ketone **5** (0.170 g, 0.44 mmol). After 20 min, work-up as described and purification by flash column chromatography (Florisil, Et_2O–petrol 1 : 3) afforded firstly *(E)-silyl enol ether* **15a** (0.088 g, 44%) as a pale yellow solid; ν_{max}(film)/cm^{-1} 2960, 2075 (CO), 2018 (CO), 1668, 1627, 1494, 1452, 1363, 1254, 1172, 1083, 1045, 992, 943, 888, 849, 751, 698, 656, 603; δ_H(400 MHz) 0.23 (9 H, s, $Si(CH_3)_3$), 1.33 (3 H, d, *J* 6.4, 1-H × 3), 3.49–3.60 (2 H, m, 8-H × 2), 4.46 (1 H, app. quin, *J* 5.3, 2-H), 4.65 (1 H, dd, *J* 8.2, 4.7, 3-H), 4.79 (1 H, d, *J* 11.7, 5-H), 5.08 (1 H, dd, *J* 11.7, 8.2, 4-H), 5.18 (1 H, t, *J* 7.9, 7-H), 7.18–7.39 (5 H, m, Ph–H × 5); δ_C(100 MHz) 0.0 ($Si(CH_3)_3$), 21.8 (1-C), 32.7 (8-C0, 73.4 (2-C), 74.5 (3-C0, 77.4 (5-C), 85.5 (4-C), 110.5 (7-C), [126.1, 128.3, 128.5, 140.4 (Ph–C × 6)], 147.7 (6-C), [204.3, 205.3, 205.5, 209.2 (FeCO × 4)]; *m*/*z* (ES) 479 (MNa^+, 100%), 423 (30), 367 (55). [Found (MNa^+) 479.0594. $C_{21}H_{24}O_6FeSiNa$ requires *M*Na 479.0584]. *(Z)-Silyl enol ether* **15b** followed (0.065 g, 32%) as a yellow solid; ν_{max}(film)/cm^{-1} 2916, 2075 (CO), 2018 (CO), 1670, 1494, 1453, 1354, 1293, 1256, 1165, 1044, 998, 944, 848, 753, 699, 654, 604; δ_H(400 MHz) 0.31 (9 H, s, $Si(CH_3)_3$), 1.37 (3 H, d, *J* 6.3, 1-H × 3), 3.30 (1 H, dd, *J* 16.3, 6.3, 8-H), 3.58 (1 H, dd, *J* 16.3, 8.4, 8-H), 4.43 (1 H, app. quin, *J* 5.3, 2-H), 4.60 (1 H, dd, *J* 8.0, 4.7, 3-H), 4.68 (1 H, d, *J* 12.3, 5-H), 4.81 (1 H, dd, *J* 12.3, 8.0, 4-H), 5.40 (1 H, dd, *J* 8.4, 6.3, 7-H), 7.18–7.30 (5 H, m, Ph–H × 5); δ_C(100 MHz) 0.8 ($Si(CH_3)_3$), 21.9 (1-C), 33.0 (8-C), 73.4 (2-C), 75.9 (3-C), 83.1 (5-C), 83.8 (4-C), 115.4 (7-C), [126.2, 128.3, 128.5, 139.7 (Ph–C × 6)], 147.6 (6-C), [204.3, 205.2, 206.2, 209.3 (FeCO × 4)]; *m*/*z* (ES) 479 (MNa^+, 90%), 439 (100), 367 (80). [Found (MNa^+) 479.0572. $C_{21}H_{24}O_6FeSiNa$ requires *M*Na 479.0584].

Analysis of the 400 MHz ^{1}H NMR spectrum of the crude reaction mixture allowed determination of the ratio of **15a** and **15b**, specifically by integration of the trimethylsilyl protons; δ_H(400 MHz) 0.23 (0.59 H, s), 0.31 (0.41 H, s). Calculated ratio **15a** : **15b** = 1.4 : 1.

[(2*E*,4*E*,6*S**,7*S**)-7-(Carbonyloxy-κC)-3-trimethylsilyloxy-(4,5,6-η)-dodeca-2,4-dien-6-yl]tricarbonyliron 16a and [(2*Z*,4*E*,6*S**,7*S**)-7-(carbonyloxy-κC)-3-trimethylsilyloxy-(4,5,6-η)-dodeca-2,4-dien-6-yl]tricarbonyliron 16b

Silyl enol ethers **16a** and **16b** were prepared according to the general procedure above from TMSOTf (0.039 cm^3, 0.22 mmol), Et_3N (0.033 cm^3, 0.24 mmol), and ethyl ketone 13 (0.043 g, 0.12 mmol). After 20 min, work-up as described and purification by flash column chromatography (Florisil, Et_2O–petrol 1 : 1) afforded firstly *(E)-silyl enol ether* **16a** (0.033 g,

63%) as a pale yellow solid; ν_{max}(film)/cm^{-1} 2957, 2931, 2861, 2072 (CO), 1996 (CO), 1660, 1459, 1354, 1254, 1240, 1106, 1069, 1031, 986, 949, 887, 753, 692; δ_H(400 MHz) 0.22 (9 H, s, Si(CH$_3$)$_3$), 0.89 (3 H, t, *J* 6.6, 12-H × 3), 1.25–1.66 (8 H, m, 8-H × 2, 9-H × 2, 10-H × 2, 11-H × 2), 1.75 (3 H, d, *J* 7.3, 1-H × 3), 4.04 (1 H, t, *J* 6.5, 7-H), 4.44 (1 H, d, *J* 7.9, 6-H), 4.63 (1 H, d, *J* 11.7, 4-H), 5.01 (1 H, q, *J* 7.3, 2-H), 5.19 (1 H, dd, *J* 11.7, 7.9, 5-H); δ_C(100 MHz) 0.01 (Si(CH$_3$)$_3$), 11.9 (1-C), 13.9 (12-C), [22.5, 25.2, 31.4, 38.0 (8-C, 9-C, 10-C, 11-C)], 74.2 (4-C), 75.0 (6-C), 75.2 (7-C), 86.4 (5-C), 106.4 (2-C), 147.3 (3-C), [204.7, 205.3, 205.5, 209.7 (FeCO × 4)]; *m*/*z* (FAB) 437 (MH$^+$, 80%), 325 (90), 253 (95), 133 (100). [Found (MH$^+$) 437.1090. $C_{19}H_{29}O_6FeSi$ requires *M*H 437.1083]. *(Z)-Silyl enol ether* **16b** followed (0.008 g, 15%) as a pale yellow solid; ν_{max}(film)/cm^{-1} 2956, 2075 (CO), 2018 (CO), 1662, 1343, 1297, 1255, 1034, 845, 646, 602; δ_H(400 MHz) 0.27 (9 H, s, Si(CH$_3$)$_3$), 0.89 (3 H, t, *J* 6.6, 12-H × 3), 1.26–1.61 (8 H, m, 8-H × 2, 9-H × 2, 10-H × 2, 11-H × 2), 1.64 (3 H, d, *J* 7.1, 1-H × 3), 4.03 (1 H, t, *J* 6.6, 7-H), 4.38 (1 H, d, *J* 7.7, 6-H), 4.53 (1 H, d, *J* 12.1, 4-H), 4.91 (1 H, dd, *J* 12.1, 7.7, 5-H), 5.25 (1 H, q, *J* 7.1, 2-H); δ_C(100 MHz) 0.78 (Si(CH$_3$)$_3$), 12.5 (1-C), 14.0 (12-C), [22.5, 25.2, 31.5, 37.9 (8-C, 9-C, 10-C, 11-C)], 73.4 (4-C), 75.0 (6-C), 83.5 (7-C), 84.5 (5-C), 111.7 (2-C), 147.9 (3-C), [203.5, 204.7, 205.4, 209.8 (CO × 4)]; *m*/*z* (FAB) 437 (MH$^+$, 90%), 397 (75), 323 (95), 251 (85), 131 (100). [Found (MH$^+$) 437.1086. $C_{19}H_{29}O_6FeSi$ requires *M*H 437.1083].

Analysis of the 600 MHz ^{1}H NMR spectrum of the crude reaction mixture allowed determination of the ratio of **16a** and **16b**, specifically by integration of the trimethylsilyl protons; δ_H(600 MHz) 0.22 (0.89 H, s), 0.27 (0.11 H, s). Calculated ratio **16a** : **16b** = 8.1 : 1.

General procedure for the fluorination reaction

For a 0.3 mmol scale reaction: Selectfluor® (1.1 eq.) was added in one portion to a solution of the silyl enol ether (1.0 eq.) in CH_3CN (5 cm^3). The solution was stirred at rt until the reaction was complete as indicated by TLC. The reaction mixture was then poured into a mixture of CH_2Cl_2–H_2O (10 cm^3, 1 : 1). The layers were separated and the aqueous layer further extracted with CH_2Cl_2 (3 × 5 cm^3). The combined organic layers were then washed with brine (15 cm^3), dried ($MgSO_4$) and concentrated *in vacuo*. Analysis of the 600 MHz or 400 MHz ^{1}H NMR spectrum of the crude product enabled determination of the diastereoselectivity of the fluorination reaction, usually by integration of the 4-H proton resonances for the diastereoisomers. In cases where further purification was necessary, the crude product was purified by flash column chromatography (SiO_2, Et_2O–petrol).

[(5*E*,2*R**,3*S**,7*R**)-2-(Carbonyloxy-κC)-7-fluoro-6-oxo-(3,4,5-η)-oct-4-en-3-yl]tricarbonyliron 17

Fluorinated product **17** was prepared according to the general procedure from silyl enol ether **1** (0.017 g, 0.043 mmol) and Selectfluor® (0.013 g, 0.044 mmol). After 15 min, work-up as described afforded *fluorinated complex* **17** (0.013 g, 93%) as a white solid; mp 129 °C (dec.); ν_{max}(film)/cm^{-1} 2930, 2090 (CO), 2023 (CO), 1668 (C=O), 1500, 1447, 1374, 1087, 1051, 997, 948, 832, 653, 604; δ_H(600 MHz) 1.41 (3 H, d, *J* 6.4, 1-H × 3), 1.65 (3 H, dd, *J* 23.8, 6.9, 8-H × 3), 4.23 (1 H, dd, *J* 11.3, 2.1, 5-H), 4.56 (1 H, app. quin, *J* 6.3, 2-H), 5.13 (1 H, dq, *J* 48.7, 6.9, 7-H), 5.13 (1 H, dd, *J* 8.6, 4.7, 3-H), 5.60 (1 H, dd, *J* 11.3, 8.7, 4-H); δ_C(150 MHz) 17.7 (d, *J* 22.3, 8-C), 21.8 (1-C), 59.1 (5-C), 72.8 (2-C), 86.7 (3-C), 92.1 (d, *J* 183, 7-C), 92.8 (4-C), [199.3, 201.0, 204.4, 207.6 (FeCO × 4)], 203.8 (d, *J* 23.6, 6-C); *m*/*z* (ES) 349 (MNa$^+$, 100%), 321 (45), 269 (30), 217 (40), 193 (25). [Found (MNa$^+$) 348.9802. $C_{12}H_{11}O_6FFeNa$ requires *M*Na 348.9787].

Analysis of the 400 MHz ^{1}H NMR spectrum of the crude reaction mixture showed no evidence for any minor diastereoisomers. Calculated d.e. > 95%.

[(4*E*,2*R**,6*S**,7*R**)-7-(Carbonyloxy-κC)-2-fluoro-3-oxo-(4,5,6-η)-dodec-4-en-6-yl]tricarbonyliron 18

Fluorinated product **18** was prepared according to the general procedure from silyl enol ether **2** (0.015 g, 0.033 mmol) and Selectfluor® (0.010 g, 0.034 mmol). After 15 min, work-up as described afforded *fluorinated complex* **18** (0.012 g, 95%) as a white solid; ν_{max}(film)/cm^{-1} 2935, 2092 (CO), 2035 (CO), 1663 (C=O), 1501, 1446, 1372, 1096, 1009, 655, 605; δ_H(600 MHz) 0.88 (3 H, t, *J* 6.7, 12-H × 3), 1.28–1.62 (8 H, m, 8-H × 2, 9-H × 2, 10-H × 2, 11-H × 2), 1.65 (3 H, dd, *J* 23.9, 6.9, 1-H × 3), 4.18 (1 H, dd, *J* 11.3, 2.1, 4-H), 4.38 (1 H, app. q, *J* 6.1, 7-H), 5.10 (1 H, dd, *J* 8.6, 4.6, 6-H), 5.12 (1 H, dq, *J* 48.7, 6.9, 2-H), 5.61 (1 H, dd, *J* 11.3, 8.6, 5-H); δ_C(150 MHz) 13.9 (12-C), 17.7 (d, *J* 22.4, 1-C), [22.4, 26.5, 31.5, 36.6 (8-C, 9-C, 10-C, 11-C)], 59.0 (d, *J* 3.7, 4-C), 76.7 (7-C), 85.7 (6-C), 92.0 (d, *J* 18.3, 2-C), 92.9 (5-C), [199.4, 201.1, 204.0, 204.4, 207.7 (FeCO × 4, 3-C)]; *m*/*z* (ES) 405 (MNa$^+$, 25%), 365 (80), 293 (100), 262 (75). [Found (MNa$^+$) 405.0404. $C_{16}H_{19}O_6FFeNa$ requires *M*Na 405.0407].

Analysis of the 400 MHz ^{1}H NMR spectrum of the crude reaction mixture showed no evidence for any minor diastereoisomers. Calculated d.e. > 95%.

[(3*E*,1*R**,2*S**,6*R**)-1-(Carbonyloxy-κC)-6-fluoro-5-oxo-1-phenyl-(2,3,4-η)-hept-3-en-2-yl]tricarbonyliron 19

Fluorinated product **19** was prepared according to the general procedure from silyl enol ether **3** (0.050 g, 0.11 mmol) and Selectfluor® (0.037 g, 0.12 mmol). After 15 min, work-up as described afforded *fluorinated complex* **19** as a white solid (0.039 g, 92%); ν_{max}(film)/cm^{-1} 2925, 2358, 2094 (CO), 2028 (CO), 1682 (C=O), 1498, 1454, 1416, 1374, 1338, 1240, 1170, 1091, 1010, 918, 795, 735, 698, 655, 601; δ_H(600 MHz) 1.65 (3 H, dd, *J* 23.9, 6.9, 7-H × 3), 4.38 (1 H, d, *J* 11.2, 4-H), 5.13 (1 H, dq, *J* 48.6, 6.9, 6-H), 5.33 (1 H, dd, *J* 8.5, 4.8, 2-H), 5.46 (1 H, d, *J* 4.8, 1-H), 5.59 (1 H, dd, *J* 11.2, 8.5, 3-H), 7.30–7.37 (5 H, m, Ph–H × 5); δ_C(150 MHz) 17.6 (d, *J* 22.2, 7-C), 59.5 (4-C), 78.1 (1-C), 85.8 (2-C), 92.0 (d, *J* 201, 6-C), 92.8 (3-C), [125.8, 128.6, 128.9, 138.2 (Ph–C × 6)], [199.2, 200.5, 203.7, 204.2, 207.5 (FeCO × 4, 5-C)]; *m*/*z* (ES) 389 (MH$^+$, 100%), 361 (100). [Found (MH$^+$) 389.0128. $C_{17}H_{14}O_6FFe$ requires *M*H 389.0118].

Analysis of the 400 MHz ^{1}H NMR spectrum of the crude reaction mixture showed no evidence for any minor diastereoisomers. Calculated d.e. > 95%.

[(4*E*,2*R**,3*S**,7*R**)-2-(Carbonyloxy-κC)-7-fluoro-6-oxo-(3,4,5-η)-non-4-en-3-yl]tricarbonyliron 20

Fluorinated product **20** was prepared according to the general procedure from silyl enol ether **14** (0.008 g, 0.020 mmol) and Selectfluor® (0.008 g, 0.027 mmol). After 15 min, work-up as described afforded *fluorinated complex* **20** (0.006 g, 88%) as a white solid; ν_{max}(film)/cm^{-1}; 2091 (CO), 2024 (CO), 1672 (C=O), 1050, 653; δ_H(400 MHz) 1.12 (3 H, t, *J* 7.4, 9-H × 3), 1.41 (3 H, d, *J* 6.4, 1-H × 3), 1.93–2.11 (2 H, m, 8-H × 2), 4.21 (1 H, dd, *J* 11.3, 2.0, 5-H), 4.56 (1 H, app. quin, *J* 6.2, 2-H), 4.92 (1 H, ddd, *J* 49.3, 8.4, 4.2, 7-H), 5.11 (1 H, dd, *J* 8.6, 4.6, 3-H), 5.58 (1 H, dd, *J* 11.3, 8.6, 4-H); δ_C(150 MHz) 14.0 (9-C), 21.8 (1-C), 25.4 (d, *J* 21.4, 8-C), 59.8 (5-C), 72.8 (2-C), 86.4 (3-C), 93.0 (4-C), 96.5 (d, *J* 185, 7-C), [199.3, 201.2, 204.3, 207.7 (FeCO × 4)], 203.4 (d, *J* 24, 6-C); *m*/*z* (ES) 363 (MNa$^+$, 100 %), 335 (45). [Found (MNa$^+$) 362.9956. $C_{13}H_{13}O_6FFeNa$ requires *M*Na 362.9944].

No minor diastereoisomer was isolated due to low abundance. However, analysis of the 400 MHz ^{1}H NMR spectrum of the crude reaction mixture allowed determination of the d.e. of the fluorinated products, specifically by integration of the 5-H resonance; δ_H(400 MHz) 4.21 (0.97 H, dd), 4.24 (0.03 H, dd). Calculated d.e. = 94%.

[(4*E*,3*R,4*S**,7*R**)-2-(Carbonyloxy-κC)-7-fluoro-6-oxo-8-phenyl-(3,4,5-η)-oct-4-en-3-yl]tricarbonyliron 21**

Fluorinated product **21** was prepared according to the general procedure from silyl enol ether **15** (0.026 g, 0.057 mmol) and Selectfluor® (0.024 g, 0.081 mmol). After 15 min, work-up as described afforded *fluorinated complex* **21** (0.022 g, 96%) as a white solid; ν_{max}(film)/cm^{-1} 2924, 2091 (CO), 2023 (CO), 1672 (C=O), 1498, 1454, 1359, 1313, 1086, 1051, 999, 943, 832, 700, 653; δ_H(400 MHz) 1.37 (3 H, d, *J* 6.4, 1-H × 3), 3.18–3.36 (2 H, m, 8-H × 2), 4.14 (1 H, dd, *J* 11.3, 1.9, 5-H), 4.55 (1 H, app. quin, *J* 6.1, 2-H), [5.10–5.16, 5.25–5.30 (2 H, m, 3-H, 7-H)], 5.58 (1 H, dd, *J* 11.3, 8.8, 4-H), 7.29–7.39 (5 H, m, Ph–H × 5); δ_C(100 MHz) 21.8 (1-C), 38.2 (d, *J* 20.6, 8-C), 59.7 (d, *J* 3.7, 5-C), 72.7 (2-C), 86.9 (3-C), 92.6 (4-C), 95.6 (d, *J* 188, 7-C), [127.2, 128.7, 129.5, 135.3 (Ph–C × 6)], [199.2, 201.0, 202.3, 204.1, 207.6 (FeCO × 4, 6-C)]; *m*/*z* (ES) 425 (MNa$^+$, 90%), 397 (45), 313 (100). [Found (MNa$^+$) 425.0095. $C_{18}H_{15}O_6FFeNa$ requires *M*Na 425.0094].

Analysis of the 400 MHz ^{1}H NMR spectrum of the crude reaction mixture showed no evidence for any minor diastereoisomers. Calculated d.e. > 95%.

[(4*E*,2*R,6*S**,7*S**)-7-(Carbonyloxy-κC)-2-fluoro-3-oxo-(4,5,6-η)-dodec-4-en-6-yl]tricarbonyliron 22**

Fluorinated product **22** was prepared according to the general procedure from silyl enol ether **16** (0.018 g, 0.040 mmol) and Selectfluor® (0.012 g, 0.040 mmol). After 15 min, work-up as described afforded *fluorinated complex* **22** (0.013 g, 88%) as a white solid; ν_{max}(film)/cm^{-1} 2931, 2090 (CO), 2024 (CO), 1665 (C=O), 1495, 1334, 1000, 651, 604; δ_H(400 MHz) 0.90 (3 H, t, *J* 6.8, 12-H × 3), 1.26–1.71 (8 H, m, 8-H × 2, 9-H × 2, 10-H × 2, 11-H × 2), 1.63 (3 H, dd, *J* 23.9, 7.0, 1-H × 3), 4.08 (2 H, m, 4-H, 7-H), 4.93 (1 H, d, *J* 7.1, 6-H), 5.10 (1 H, dq, *J* 48.7, 7.0, 2-H), 5.80 (1 H, dd, *J* 10.9, 7.1, 5-H); δ_C(100 MHz) 13.9 (12-C), 17.6 (d, *J* 22.4, 1-C), [22.4, 25.1, 31.3, 38.1 (8-C, 9-C, 10-C, 11-C)], 58.2 (4-C), 74.3 (7-C), 84.4 (6-C), 92.0 (d, *J* 183, 2-C), 94.7 (5-C), [199.6, 200.7, 203.8, 204.3, 207.8 (FeCO × 4, 3-C)]; *m*/*z* (FAB) 383 (82%), 271 (85), 133 (100). [Found (MH$^+$) 383.0589. $C_{16}H_{20}O_6FFe$ requires *M*H 383.0593].

Analysis of the 400 MHz ^{1}H NMR spectrum of the crude reaction mixture showed no evidence for any minor diastereoisomers. Calculated d.e. > 95%.

[(2*Z*,1*R,4*S**,6*R**)-6-Fluoro-5-oxo-1-phenyl-(1,2,3,4-η)-hept-2-en-1,4-diyl]tricarbonyliron 23a**

$Ba(OH)_2$ solution (0.50 cm^3) was added dropwise to a solution of fluorinated complex **19** (0.060 g, 0.16 mmol) in MeOH (2 cm^3) at rt. After 1 min 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 *η^4-diene complex* **23a** (0.044 g, 80%) as a bright yellow oil; ν_{max}(film)/cm^{-1} 2359, 2056 (CO), 1987 (CO), 1723, 1710, 1672, 1641, 1599, 1548, 1530, 1512, 1489, 1463, 1443, 1353, 1321, 1183, 1102, 760, 695; δ_H(400 MHz) 1.58 (3 H, dd, *J* 24.2, 6.9, 7-H × 3), 1.99 (1 H, dd, *J* 7.7, 3.3, 2-H), 2.67 (1 H, d, *J* 8.8, 4-H), 4.89 (1 H, dq, *J* 50.0, 6.9, 6-H), 6.04–6.08 (2 H, m, 1-H, 3-H), 7.21–7.36 (5 H, m, Ph–H × 5); δ_C(100 MHz) 19.1 (d, *J* 22.2, 7-C), 45.8 (d, *J* 3.9, 4-C), 63.3 (2-C), [81.1, 83.9 (1-C, 3-C)], 92.6 (d, *J* 183, 6-C), [126.4, 127.3, 128.9, 138.4 (Ph–C × 6)], 205.2 (d, *J* 22.9, 5-C), no visible signals for CO ligands; *m*/*z* (ES) 367 (MNa$^+$, 100%). [Found (MNa$^+$) 367.0030. $C_{16}H_{13}O_4FFeNa$ requires *M*Na 367.0039].

(4*E*,6*E*,2*R)-2-Fluoro-3-oxo-7-phenylhepta-4,6-diene 23b**

A solution of diene complex **23a** (0.037 g, 0.11 mmol) in MeCN (3 cm^3) at −30 °C was treated with a solution of ceric(IV) ammonium nitrate (CAN) (177 mg, 0.32 mmol) in dry MeCN (3 cm^3). After 1 h at −30 °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* **23b** (0.016 g, 71%) as an oil; ν_{max}(film)/cm^{-1} 2923, 2853, 2361, 2057, 1994, 1686 (CO), 1584 (C=C), 1449, 1352, 1284, 1001, 752, 690; δ_H(400 MHz) 1.54 (3 H, dd, *J* 24.1, 6.9, 1-H × 3), 5.05 (1 H, dq, *J* 49.5, 6.8, 2-H), 6.69 (1 H, dd, *J* 15.2, 3.2, 4-H), 6.90–7.06 (2 H, m, 6-H, 7-H), 7.29–7.50 (5 H, m, Ph–H × 5), 7.56 (1 H, dd, *J* 15.2, 10.7, 5-H); δ_C(100 MHz) 18.0 (d, *J* 22.4, 1-C), 92.1 (d, *J* 181, 2-C), [122.7, 126.7, 127.4, 128.9, 129.5, 135.9, 143.2, 145.2 (Ph–C × 6, 4-C, 6-C, 7-C)], 197.9 (d, *J* 22.4, 3-C); *m*/*z* (ES) 227 (MNa$^+$, 100%). [Found (MNa$^+$) 227.0849. $C_{13}H_{13}OFNa$ requires *M*Na 227.0843].

Preparation of a stock solution of HF·pyridine in pyridine–THF

Pyridine hydrofluoride (11.4 cm^3) was added dropwise to a stirred, cooled (0 °C) solution of pyridine (52 cm^3) in THF (120 cm^3) in a 250 cm^3 polyvinylchloride bottle under argon. The resulting pale yellow solution was stored under argon at −20 °C and was used as the stock solution where mentioned in the following reactions.

General procedure for the preparation of α-hydroxy ketones 25, 26 and 27

For a 0.3 mmol scale reaction: methyltrioxorhenium (1 crystal) was added to a solution of the silyl enol ether (1.0 eq.), pyridine (0.12 eq.) and H_2O_2 solution (1.5 eq.) in CH_2Cl_2 (5 cm^3). The solution was stirred at rt until the reaction was complete as indicated by TLC. The reaction mixture was then poured into a mixture of CH_2Cl_2–H_2O (10 cm^3, 1 : 1). The layers were separated and the aqueous layer further extracted with CH_2Cl_2 (3 × 5 cm^3). The combined organic layers were then washed with brine (15 cm^3) and dried ($MgSO_4$). Concentration of the filtrate *in vacuo* afforded a crude mixture of silylated and non silylated products. In order to provide an accurate d.e. 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 rt. 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 or 400 MHz ^{1}H NMR spectrum of the crude product enabled determination of the diastereoselectivity of the α-hydroxylation reaction by integration of the 4-H proton resonances for the diastereoisomers.

In cases where further purification was necessary, the crude product was purified by flash column chromatography (SiO_2, Et_2O–petrol).

[(4*E*,7*R,3*S**,2*R**)-2-(Carbonyloxy-κC)-7-hydroxy-6-oxo-(3,4,5-η)-oct-4-en-3-yl]tricarbonyliron 25**

Method A: complex **25** was prepared according to the general procedure using silyl enol ether **1** (0.035 g, 0.089 mmol), methyltrioxorhenium (1 crystal), pyridine (1 M in CH_2Cl_2, 0.011 cm^3, 0.011 mmmol) and H_2O_2 solution (30% aqueous solution, 0.015 cm^3, 0.13 mmol). Work-up as described followed by column chromatography (SiO_2, Et_2O–petrol 1 : 2) afforded *α-hydroxy ketone* **25** (0.024 g, 84%) as a viscous oil; ν_{max}(film)/cm^{-1} 3444 (br, OH), 2981, 2091 (CO), 2024 (CO), 1673 (C=O), 1498, 1452, 1360, 1313, 1181, 1087, 1051, 1001, 949, 833, 735, 655, 604; δ_H(400 MHz) 1.40 (3 H, d, *J* 6.4, 1-H × 3), 1.53 (3 H, d, *J* 7.0, 8-H × 3), 3.29 (1 H, d, *J* 5.1, OH), 3.95 (1 H, d, *J* 11.1, 5-H),

4.53–4.58 (2 H, m, 2-H, 7-H), 5.12 (1 H, dd, *J* 8.6, 4.6, 3-H), 5.65 (1 H, dd, *J* 11.1, 8.6, 4-H); δ_C(100 MHz) 20.4 (8-C), 21.8 (1-C), 60.5 (5-C), [72.6, 72.9 (2-C, 7-C)], 86.3 (3-C), 92.6 (4-C), [199.2, 201.8, 204.2, 206.5, 207.5 (FeCO × 4, 7-C)]; *m*/*z* (ES) 347 (MNa^+, 40%), 297 (40), 235 (100), 213 (80). [Found (MNa^+) 346.9812. $C_{12}H_{12}O_7FeNa$ requires *M*Na 346.9825].

No minor diastereoisomer was isolated due to low abundance. However, analysis of the 400 MHz ^{1}H NMR spectrum of the crude reaction mixture allowed estimation of the d.e. of the α-hydroxylated products, specifically by integration of the 5-H resonance; δ_H(400 MHz) 3.88 (0.03 H, d), 3.95 (0.97 H, d). Calculated d.e. = 94%.

Method B: *m*-CPBA (0.015 g, 0.087 mmol) was added in one portion to a solution of silyl enol ether **24** (0.020 g, 0.047 mmol) in CH_2Cl_2 (3 cm^3) and cooled to 0 °C. The reaction mixture was stirred at 0 °C for 10 min, then poured into CH_2Cl_2–$NaHCO_3$ solution (10 cm^3, 1 : 1). The layers were separated and the aqueous phase extracted with CH_2Cl_2 (3 × 5 cm^3). The combined organic extracts were washed with brine (10 cm^3), dried ($MgSO_4$) and concentrated *in vacuo*. 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 rt. 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*. Purification by column chromatography (SiO_2, Et_2O–petrol 1 : 2) afforded *α-hydroxy ketone* **25** (0.011 g, 75%) as a viscous oil. Data were consistent with material prepared by Method A (*vide supra*).

No minor diastereoisomer was isolated due to low abundance. However, analysis of the 400 MHz ^{1}H NMR spectrum of the crude reaction mixture allowed estimation of the d.e. of the α-hydroxylated products, specifically by integration of the 5-H resonance; δ_H(400 MHz) 3.88 (0.08 H, d), 3.95 (0.92 H, d). Calculated d.e. = 84%.

[(4*E*,2*R**,6*S**,7*R**)-7-(Carbonyloxy-κC)-2-hydroxy-3-oxo-(4,5,6-η)-dodec-4-en-6-yl]tricarbonyliron 26

Complex **26** was prepared according to the general procedure using silyl enol ether **2** (0.023 g, 0.051 mmol), methyltrioxorhenium (1 crystal), pyridine (1 M in CH_2Cl_2, 0.006 cm^3, 0.006 mmol) and H_2O_2 solution (30% aqueous solution, 0.009 cm^3, 0.077 mmol). Work-up as described followed by column chromatography (SiO_2, Et_2O–petrol 1 : 2) afforded *α-hydroxy ketone* **26** (0.016 g, 83%) as a viscous oil; ν_{max}(film)/cm^{-1} 3550–3100 (br, OH), 2917, 2091 (CO), 2022 (CO), 1673 (C=O), 1042; δ_H(400 MHz) 0.89 (3 H, t, *J* 6.7, 12-H × 3), 1.26–1.63 (8 H, m, 8-H × 2, 9-H × 2, 10-H × 2, 11-H × 2), 1.53 (3 H, d, *J* 6.5, 1-H × 3), 3.27 (1 H, d, *J* 5.4, OH), 3.89 (1 H, d, *J* 11.1, 4-H), 4.39 (1 H, m, 7-H), 4.56 (1 H, m, 2-H), 5.09 (1 H, dd, *J* 8.7, 4.6, 6-H), 5.67 (1 H, dd, *J* 11.1, 8.7, 5-H); δ_C(100 MHz) 13.9 (12-C), 20.4 (1-C), [22.4, 31.5 (10-C, 11-C)], 26.4 (9-C), 36.5 (8-C), 60.4 (4-C), [72.5, 77.2 (2-C, 7-C)], 85.3 (6-C), 92.8 (5-C), [199.3, 201.8, 204.3, 206.6, 207.5 (FeCO × 4, 3-C)]; *m*/*z* (ES) 381 (MH^+, 30%), 291 (100). [Found (MH^+) 381.0624. $C_{16}H_{21}O_7Fe$ requires *M*H 381.0631].

No minor diastereoisomer was isolated due to low abundance. However, analysis of the 400 MHz ^{1}H NMR spectrum of the crude reaction mixture allowed estimation of the d.e. of the products, specifically by integration of the 4-H resonance; δ_H(400 MHz) 3.86 (0.05 H, d), 3.89 (0.95 H, d). Calculated d.e. = 90%.

[(3*E*,1*R**,2*S**,6*R**)-1-(Carbonyloxy-κC)-6-hydroxy-5-oxo-1-phenyl-(2,3,4-η)-hept-3-en-2-yl]tricarbonyliron 27

Method A: complex **27** was prepared according to the general procedure using silyl enol ether **3** (0.067 g, 0.15 mmol), methyltrioxorhenium (1 crystal), pyridine (1 M in CH_2Cl_2, 0.018 cm^3, 0.018 mmmol) and H_2O_2 solution (30% aqueous solution, 0.025 cm^3, 0.22 mmol). Work-up as described followed by column chromatography (SiO_2, Et_2O–petrol 1 : 2) afforded *α-hydroxy ketone* **27** (0.048 g, 83%) as a viscous oil; ν_{max}(film)/cm^{-1} 3500–3400 (br, OH), 3062, 2981, 2093 (CO), 2026 (CO), 1681 (C=O), 1496, 1454, 1417, 1304, 1115, 1014, 943, 860, 825, 797, 737, 699, 656, 601; δ_H(400 MHz) 1.50 (3 H, d, *J* 7.0, 7-H × 3), 4.12 (1 H, d, *J* 11.2, 4-H), 4.56 (1 H, q, *J* 7.0, 6-H), 5.31 (1 H, dd, *J* 8.6, 4.6, 2-H), 5.46 (1 H, d, *J* 4.6, 1-H), 5.64 (1 H, dd, *J* 11.2, 8.6, 3-H), 7.27–7.37 (5 H, m, Ph–H × 5); δ_C(100 MHz) 20.2 (7-C), 61.2 (4-C), 72.6 (6-C), 78.2 (1-C), 85.2 (2-C), 92.8 (3-C), [125.7, 128.7, 128.9, 138.2 (Ph–C × 6)], [199.1, 201.2, 204.1, 206.6, 207.4 (FeCO × 4, 5-C)]; *m*/*z* (ES) 409 (MNa^+, 10%), 387 (20), 365 (50), 354 (50), 297 (100). [Found (MNa^+) 408.9973. $C_{17}H_{14}O_7FeNa$ requires *M*Na 408.9981].

No minor diastereoisomer was isolated due to low abundance. However, analysis of the 400 MHz ^{1}H NMR spectrum of the crude reaction mixture allowed estimation of the d.e. of the products, specifically by integration of the 4-H resonance; δ_H(400 MHz) 4.01 (0.06 H, d), 4.12 (0.94 H, d). Calculated d.e. = 88%.

Method B: *m*-CPBA (0.013 g, 0.074 mmol) was added in one portion to a solution of silyl enol ether **3** (0.028 g, 0.062 mmol) in CH_2Cl_2 at 0 °C. The reaction mixture was stirred at 0 °C for 10 min, then poured into CH_2Cl_2–$NaHCO_3$ solution (10 cm^3, 1 : 1). The layers were separated and the aqueous phase extracted with CH_2Cl_2 (3 × 5 cm^3). The combined organic extracts were washed with brine (10 cm^3), dried ($MgSO_4$) and concentrated *in vacuo*. 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 rt. 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*. Purification by column chromatography (SiO_2, Et_2O–petrol 1 : 3) afforded *α-hydroxy ketone* **27** (0.017 g, 72%) as a viscous oil. Data were consistent with material prepared by Method A (*vide supra*).

No minor diastereoisomer was isolated due to low abundance. However, analysis of the 400 MHz ^{1}H NMR spectrum of the crude reaction mixture allowed estimation of the d.e. of the products, specifically by integration of the 4-H resonance; δ_H(400 MHz) 4.01 (0.09 H, d), 4.12 (0.91 H, d). Calculated d.e. = 82%.

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