1 Experimental section

1.1 General experimental techniques

^{1}H NMR spectra were recorded in $CDCl_3$ or C_6D_6 at 200 MHz, 400 MHz or 600 MHz on Bruker DRX-200, DRX-400 or DRX-600 spectrometers and are reported as follows: chemical shift δ (ppm), (number of protons, multiplicity, coupling constant *J* in Hz, assignment). For spectra recorded in $CDCl_3$, 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 Bruker DRX-200 spectrometers respectively, using the central resonance of $CDCl_3$ (δ_C = 77.0 ppm) as the internal reference. Infra-red spectra were recorded as thin films between sodium chloride plates, deposited from chloroform solution or as a nujol mull in the case of solids, on Perkin Elmer 983G, ATR Spectrum 1 or FTIR 1620 spectrometers. Mass spectra were obtained on a 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), electrospray (ES) and fast atom bombardement (FAB). Liquid Chromatography-Mass Spectrometry (LCMS) spectra were obtained on a Hewlett-Packard Series 1100 instrument. Optical rotation (OR) measurements are reported in 10^{-1} deg cm^2 g^{-1}; the concentration (c) is g/100ml. Melting points were measured on a Reichert hot-stage apparatus and are uncorrected. X-Ray crystal structures were measured, solved and provided by the X-Ray section of the Chemistry department, University of Cambridge.

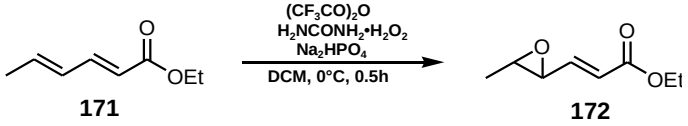
For those cases in which an inseparable mixture of compounds was produced, the data reported was obtained on the mixture. Where

considerable assignment of ^{1}H NMR spectra of individual compounds in mixtures is possible, the interpretation is for each component. Flash column chromatography was carried out using Merck Kieselgel (230-400 mesh) unless otherwise indicated. The solvents for chromatography were distilled. Analytical thin layer chromatography (tlc) was performed using precoated glass-backed plates (Merck Kieselgel 60 F254) and visualised by UV-light (wavelength 254 nm), acidic ammonium molybdate (IV) or acidic potassium permanganate solutions. Petrol (PE) refers to petroleum ether bp = 40-60 °C, which was distilled *prior* to use, and ether refers to diethyl ether (Et_2O). When mixtures of solvents were applied, the ratios stated refer to the volumes used. All reactions were carried out under an argon atmosphere in oven-dried glassware unless otherwise stated. Reactions involving preparation of the iron complexes were carried out using degassed tetrahydrofuran (THF). Solvents were degassed by successively evacuating and purging the solvent three times with argon while simultaneously subjecting the solvent to sonication using a 80W 55KHz cleaning bath. Ether and THF were distilled from sodium benzophenone ketyl; Dichloromethane (DCM) was distilled from calcium hydride. Other reagents and solvents were used as supplied or purified using standard procedures as required.[147] Aqueous solutions are saturated unless otherwise specified. Molecular sieves were powdered and oven-dried. Note that in the synthesis of the π-allyltricarbonyliron lactone complexes, diironnonacarbonyl [$Fe_2(CO)_9$] is used. This is extremely toxic. Furthermore, ironpentacarbonyl [$Fe(CO)_5$] is a highly toxic by-product from the iron reactions. All work involving the handling of these species was carried out in a well ventilated fume hood and all glassware was treated with bleach to destroy any iron carbonyl residues before re-use.

1.2 Specific experimental procedures

1.3 Experimental procedures for chapter 3: decarestrictine D

1.3.1 Preparation of (2*E*,4*R**,5*R**)-ethyl-4,5-epoxy-hex-2-enoate (**172**)

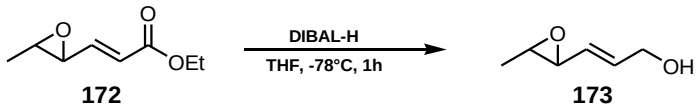


171 **172**

Trifluoroacetic anhydride (14.8 ml, 104 mmol) was added slowly to a suspension of (2*E*,4*E*) ethyl hexa-2,4-dienoate **171** (2.44 g, 17.4 mmol), urea hydrogen peroxide addition compound (37.7 g, 0.39 mol) and disodium hydrogenphosphate (27.6 g, 195 mmol) in DCM (250 ml) at 0°C. After removing from the ice bath, the reaction mixture was stirred at rt for 30 min and then cautiously poured into a vigorously stirred and precooled (0°C) solution of $NaHCO_3$ (800 ml). After effervescence had ceased, the phases were separated and the organic phase washed sequentially with $NaHCO_3$ solution (3 x 300 ml) and NaCl solution (300 ml), dried ($MgSO_4$) and filtered. Concentration *in vacuo* followed by flash column chromatography (eluent PE:Et_2O 7:1) provided the epoxide **172** (1.09 g, 7 mmol, 41%) as a colourless oil; ν_{max} **(film)/cm^{-1}:** 2981, 1716 (C=O), 1655 (C=C), 1446, 1378, 1367, 1340, 1302, 1258, 1185, 1140, 1096, 1031, 1005, 975; δ_H **(400 MHz, $CDCl_3$):** 1.15 (3H, t, *J* 7.1, OCH_2CH_3), 1.24 (3H, d, *J* 5.2, 6-H x 3), 2.84 (1H, qd, *J* 5.2, 2.0, 5-H), 3.05 (1H, dd, *J* 7.0, 2.0, 4-H), 4.07 (2H, q, *J* 7.1, OCH_2CH_3), 5.99 (1H, dd, *J* 15.7, 0.6, 2-H), 6.54 (1H, dd, *J* 15.7, 7.0, 3-H); δ_C **(100 MHz, $CDCl_3$):** 165.5, 144.5, 123.6, 60.4, 57.3, 57.1, 17.4, 14.1; ***m/z*** **(+EI):**

179 ([MNa]$^+$, 100%). Found: [*M*Na]$^+$, 179.060. [$C_8H_{12}O_3Na$]$^+$ requires 179.0684. Data was consistent with those reported in the literature.[16]

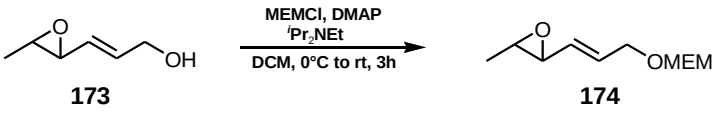
1.3.2 Preparation of (2*E*,4*R**,5*R**)-4,5-epoxy-hex-2-en-1-ol (**173**)



172 **173**

Diisobutylaluminium hydride (17.70 ml of a 1 M solution in THF, 17.70 mmol) was slowly added to the epoxide ester **172** (1.20 g, 7.68 mmol) in THF (10 ml) at -78°C. After stirring at this temperature for 1h, methanol (10 ml) was added slowly and the resultant solution was warmed to rt. Triethanolamine (8 ml) was subsequently added and the mixture was stirred at rt overnight. Filtration through a pad of Celite® followed by washing with Et_2O (150 ml) and concentration *in vacuo* provided the crude product which was purified by flash column chromatography (eluent PE:Et_2O 4:1 to 1:4, gradient) to give alcohol **173** (718 mg, 6.29 mmol, 82%) as a colourless oil; ν_{max} **(film)/cm^{-1}:** 3404 (OH), 2988, 2927, 2862, 1673 (C=C), 1447, 1429, 1379, 1336, 1296, 1245, 1144, 1128, 1092, 1060, 1009; δ_H **(400 MHz, $CDCl_3$):** 1.31 (3H, d, *J* 5.2, 6-H x 3), 1.61 (1H, s, OH), 2.89 (1H, qd, *J* 5.2, 2.1, 5-H), 3.06 (1H, dd, *J* 7.9, 2.1, 4-H), 4.11 (2H, d, *J* 5.2, 1-H x 2), 5.41 (1H, dd, *J* 15.6, 7.8, 3-H), 6.02 (1H, dt, *J* 15.6, 5.2, 2-H); δ_C **(100 MHz, $CDCl_3$):** 134.2 (CH), 128.8 (CH), 62.7 (CH_2), 58.9 (CH), 56.5 (CH), 17.5 (CH_3); ***m/z*** **(+EI)**: Found: $[MNa]^+$, 137.0575. $[C_6H_{10}O_2Na]^+$ requires 137.0578. Data was consistent with those reported in the literature.[16]

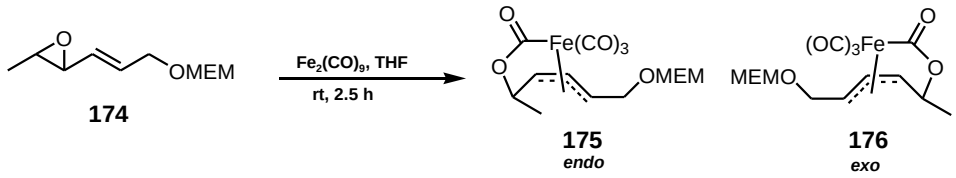
1.3.3 Preparation of (2*E*,4*R**,5*R**)-4,5-epoxy-1-[(2'-methoxy-ethoxymethloxy)]-hex-2-en **(174)**



173 **174**

(2-Methoxyethoxy)methyl chloride (MW=124.57, 342 μl, 3.0 mmol) was added slowly to a stirred solution of epoxide **173** (170 mg, 1.49 mmol), $^{i}Pr_2NEt$ (783 μl, 582 mg, 4.5 mmol, d=0.742, MW=129.25) and DMAP (MW=122.7, 18.4 mg, 0.15 mmol) in DCM (10 ml) at 0°C. After allowing to warm to rt and stirring overnight, the reaction mixture was poured into $NaHCO_3$ solution (100 ml), the layers were separated and the aqueous phase extracted with DCM (3 x 30 ml). The combined organic extracts were washed with water (30 ml), brine (30 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (eluent PE:Et_2O 9:1 to 1:2, gradient) to yield product **174** (194 mg, 0.96 mmol, 64%); **ν_{max} (film)/cm^{-1}:** 2928, 2879, 1452 (C=C), 1382, 1338, 1243, 1199, 1175, 1097, 1020, 967, 933, 853, 735; **δ_H (400 MHz, $CDCl_3$):** 1.30 (3H, d, *J* 5.2, 6-H x 3), 2.87 (1H, qd, *J* 5.2, 2.1, 5-H), 3.04 (1H, dd, *J* 7.9, 2.1, 4-H), 3.36 (3H, s, OCH_3), 3.51 (2H, t, *J* 4.7, OCH_2CH_2O), 3.65 (2H, t, *J* 4.7, OCH_2CH_2O), 4.05 (2H, d, *J* 5.2, 1-H x 2), 5.42 (1H, dd, *J* 15.6, 7.8, 3-H), 5.95 (1H, dt, *J* 15.6, 5.2, 2-H); **δ_C (100 MHz, $CDCl_3$):** 130.9 (3-C), 130.3 (2-C), 94.7 (OCH_2O), [71.7, 66.8 (OCH_2CH_2O)], 58.9 (OCH_3), 58.9 (4-C), 56.3 (5-C), 17.4 (6-C); ***m/z* (+EI):** Found: $[MNa]^+$, 225.1109. $[C_{10}H_{18}O_4Na]^+$ requires 225.1103.

1.3.4 Preparation of [(4*E*,2*SR*,3*SR*)-2-(carbonyloxy-κ*C*)-6-[(2'-methoxyethoxy)-methyloxy]-(3,4,5-η)-hex-4-en-3-yl]tricarbonyliron (**175**) and [(4*E*,2*SR*,3*RS*)-2-(carbonyloxy-κ*C*)-6-[(2'-methoxyethoxy)methyloxy]-(3,4,5-η)-hex-4-en-3-yl]tricarbonyliron (**176**)



Iron complexes **175** and **176** were prepared according to Error! Reference source not found. (page **Error! Bookmark not defined.**) from precursor epoxide **174** (145 mg, 0.71 mmol) and $Fe_2(CO)_9$ (2.5 eq., 1.77 mmol, 0.645 g) in THF (20 ml). Crude products were purified by flash chromatography (eluent PE:Et_2O 5:1 to 1:4, gradient) to yield (in order of elution) *endo* iron complex **175** (90 mg, 0.24 mmol, 34%) as a white crystalline solid; **ν_{max} (film)/cm^{-1}:** 3079, 2943, 2888, 2065, 1998, 1650, 1458, 1369, 1171, 1010, 950, 830; **δ_H (400 MHz, $CDCl_3$):** 1.35 (3H, d, *J* 5.2, 1-H x 3), 3.38 (3H, s, OCH_3), 3.52 (2H, t, *J* 4.7, OCH_2CH_2O), 3.65 (2H, t, *J* 4.7, OCH_2CH_2O), 4.05 (1H, dt, *J* 9.1, 2.9, 5-H x 1), 4.08 (1H, dd, *J* 4.7, 3.8, 6-H x 1), 4.22 (1H, dq, J 6.5, 4.3, 2-H), 4.39 (1H, ddd, *J* 15.0, 10.9, 4.0, 6-H x 1), 4.63 (1H, dd, *J* 8.0, 4.7, 3-H x 1), 4.80 (2H, s, OCH_2O), 4.85 (1H, dd, *J* 11.7, 8.4, 4-H x 1); **δ_C (100 MHz, $CDCl_3$):** 209.2 (CO), 207.9 (CO), 206.1 (CO), 203.4 (CO), 95.4 (OCH_2O), 88.3 (4-C), 78.4 (5-C), 77.6 (2-C), 74.3 (3-C), [71.6, 67.2 (OCH_2CH_2O)], 59.0 (OCH_3), 30.3 (6-C), 21.9 (1-C); ***m/z* (+EI):** Found: $[MNa]^+$, 393.0246. $[C_{14}H_{18}O_8FeNa]^+$ requires 393.0249; and *exo* iron complex **176** as oil (21 mg, 0.056 mmol, 8%, not fully characterized) in a combined unoptimised overall yield for both compounds of 0.30 mmol

= 42%. (Single crystal X-ray analysis of compound **175** confirmed the *endo* conformation.)