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.

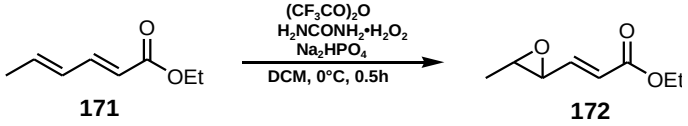
For those cases in which an inseparable mixture of compounds was produced, the data reported was obtained on the mixture. Where

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**)

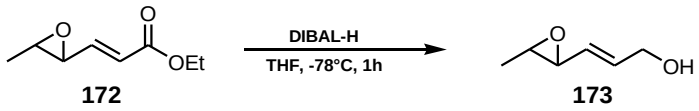


171 **172**

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]

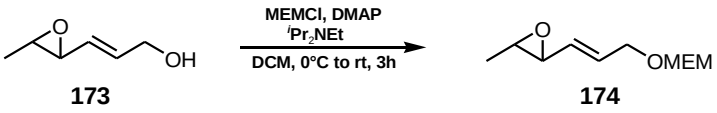
1.3.2 Preparation of (2*E*,4*R**,5*R**)-4,5-epoxy-hex-2-en-1-ol (**173**)



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]

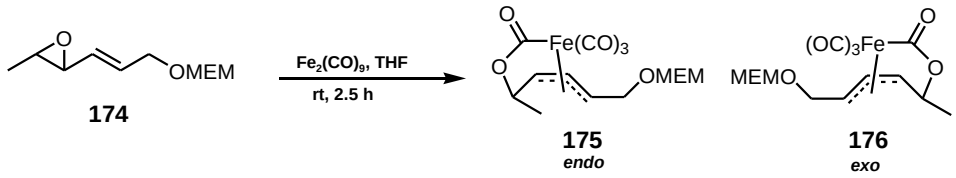
1.3.3 Preparation of (2*E*,4*R**,5*R**)-4,5-epoxy-1-[(2'-methoxy-ethoxymethloxy)]-hex-2-en **(174)**



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.

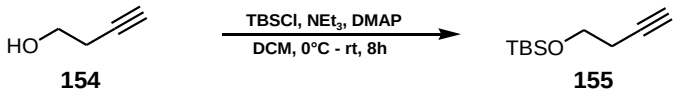
1.3.4 Preparation of [(4*E*,2*SR*,3*SR*)-2-(carbonyloxy-κ*C*)-6-[(2'-methoxyethoxy)-methyloxy]-(3,4,5-η)-hex-4-en-3-yl]tricarbonyliron (**175**) and [(4*E*,2*SR*,3*RS*)-2-(carbonyloxy-κ*C*)-6-[(2'-methoxyethoxy)methyloxy]-(3,4,5-η)-hex-4-en-3-yl]tricarbonyliron (**176**)



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.)

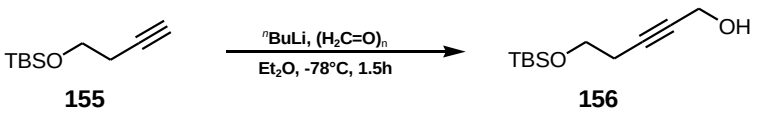
1.3.5 Preparation of 4-(*tert*-butyl-dimethyl-silanyloxy)butyne (**155**)



154 **155**

To a solution of butynyl alcohol **154** (16.5 g, 0.235 mol) in DCM (250 ml) at 0°C was added TBSCl (1.02 eq., 0.24 mol, 36.18 g) and DMAP (MW=122.17, 200 mg, 1.6 mmol). NEt_3 (MW=101.19, d=0.726, bp=89°C, 0.25 mol, 25.29 g = 34.85 ml) was subsequently added *via* syringe and the reaction mixture stirred at 0°C for 2 h, after which it was warmed to rt and stirred for a further 6 h, until completion as judged by tlc. The mixture was poured onto saturated NH_4Cl solution (800 ml) and extracted with Et_2O (3 x 300 ml). The combined organic extracts were washed with brine (500 ml) and dried ($MgSO_4$), filtered, and concentrated *in vacuo*, yielding an oil which was purified by filtration through a pad of SiO_2 (eluent PE:Et_2O 10:1) giving compound **155** (36.10 g, 19.6 mmol, 83%) as colourless oil; ν_{max} **(film)/cm^{-1}**: 3315, 2955, 2929, 2858, 1472, 1463, 1386, 1361, 1255, 1102, 1060, 1006, 938, 915, 820, 775; δ_H **(400 MHz, $CDCl_3$):** 0.06 (6H, s, Si(CH_3) x 2), 0.89 (9H, s, SiC(CH_3)$_3$ x 1), 1.93 (1H, t, *J* 2.6, 1-H), 2.38 (2H, td, *J* 7.3, 2.9, 3-H x 2), 3.72 (2H, t, *J* 7.3, 4-H x 2); δ_C **(100 MHz, $CDCl_3$):** 81.4 (2-C), 69.2 (1-C), 61.7 (4-C), 25.8 (SiC(*C*H_3)$_3$ x 1), 22.8 (3-C), 18.2 (Si*C*(CH_3)$_3$), -5.4 (Si(CH_3) x 2); ***m/z* (+EI):** 207.1 ([MNa^+], 60%). Found: [MNa^+] 207.1182. [$C_{10}H_{20}OsiNa]^+$ requires 207.1181.[148]

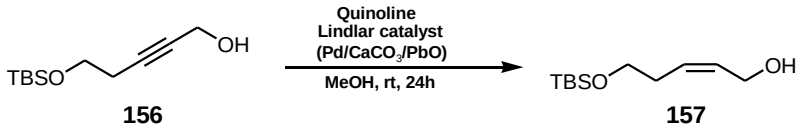
1.3.6 Preparation of 5-(*tert*-butyl-dimethyl-silanyloxy)-pent-2-yn-1-ol (**156**) (Method 1)



155 **156**

^{n}BuLi (1.6M solution in Et_2O, 18.75 ml, 30 mmol) was added to a stirred solution of alkyne **155** (5.0 g, 27 mmol) in Et_2O (20 ml) at -78°C and the mixture stirred for 1 h. Freshly cracked paraformaldehyde (mp=163-165°C) was bubbled through the reaction mixture, which was under a constant argon flow. After 20-30 min, the mixture was diluted with Et_2O (200 ml) and poured onto saturated NaCl solution (150 ml), the phases were separated, and the aqueous layer extracted with Et_2O (2 x 50 ml). The combined organic phases were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification by flash column chromatography (eluent PE:Et_2O 4:1 to 1:1, gradient) yielded alcohol **156** (4.67 g, 21 mmol, 81%) as an oil; ν_{max} **(film)/cm^{-1}:** 3418 (OH), 2929, 2858, 2249, 1471, 1385, 1256, 1101, 1006, 905, 836, 778, 710; δ_H **(400 MHz, $CDCl_3$):** 0.04 (6H, s, Si(CH_3) x 2), 0.86 (9H, s, SiC(CH_3)$_3$ x 1), 2.40 (2H, t, *J* 7.3, 4-H x 2), 2.50 (1H, br s, OH), 3.69 (2H, t, *J* 6.9, 5-H x 2), 4.19 (2H, s, 1-H x 2); δ_C **(100 MHz, $CDCl_3$):** 83.0 (3-C), 79.6 (2-C), 61.8 (5-C), 51.0 (1-C), 25.8 (SiC(*C*H_3)$_3$ x 1), 23.1 (4-C), 18.3 (Si*C*(CH_3)$_3$), -5.1 (Si(CH_3) x 2); ***m/z*** **(+EI):** 237.1287 (([MNa]$^+$, 100%), 238.1320 (12.2%), 238.1282 (5.1%), 239.1255 (3.4%). Found [MNa]$^+$ 237.1288. [$C_{11}H_{22}O_2SiNa$]$^+$ requires 237.1287. Data was consistent with the literature.[149]

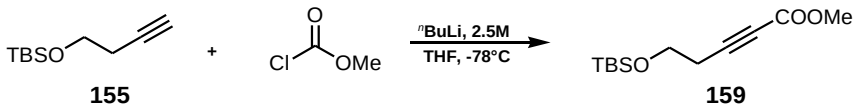
1.3.7 Preparation of 5-(*tert*-butyl-dimethyl-silanyloxy)-pent-2-*Z*-en-1-ol (**157**) (Method 1)



156 **157**

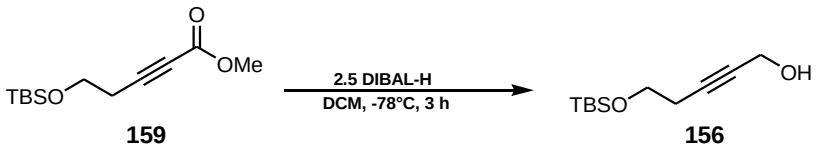
Quinoline (MW=129.16, d=1.093, 200 mg, 1.52 mmol) and Lindlar-catalyst Pd/C/$CaCO_3$/PbO (50 mg) were added to a solution of the alkyne **156** (0.75 g, 3.5 mmol) in MeOH (20 ml). The flask was flushed twice with hydrogen and the reaction mixture then stirred under an atmosphere of hydrogen for 24 h. Et_2O (100 ml) was added, then aqueous HCl (3M) and the mixture was stirred shortly for 2 min, the phases were separated, and the aqueous acidic phase re-extracted with Et_2O (100 ml). The combined organic phases were filtered through a pad of silica, washed with phosphate buffer solution (100 ml), NH_4Cl solution (150 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification by flash column chromatography (eluent PE:Et_2O 5:1) afforded *cis*-alkene **157** (0.35 g, 1.61 mmol, 46%) as a colourless oil; **ν_{max} (film)/cm^{-1}**: 3350 br, 3020; **δ_H (400 MHz, $CDCl_3$):** 0.04 (6H, s, Si(CH_3) x 2), 0.89 (9H, s, SiC(CH_3)$_3$ x 1), 2.23 (1H, br s, OH), 2.32 (2H, app. q, *J* 7.3, 4-H x 2), 3.62 (2H, t, *J* 6.2, 5-H x 2), 4.11 (2H, br s, 1-H x 2), 5.54 (1H, m, 2-H x 1), 5.76 (1H, m, 2-H x 1); **δ_C (100 MHz, $CDCl_3$):** 129.4 (2-C), 128.2 (3-C), 62.3 (5-C), 57.9 (1-C), 30.9 (4-C), 25.9 (SiC(*C*H_3)$_3$ x 1), 18.3 (Si*C*(CH_3)$_3$), -5.4 (Si(CH_3) x 2); ***m/z* (+EI):** 239.1443 ([MNa]$^+$, 100%), 240.1477 (12.2%), 240.1439 (5.1%), 241.1412 (3.4%). Found [MNa]$^+$ 239.1421. [$C_{11}H_{24}O_2SiNa$]$^+$ requires 237.1443. Data was consistent with the literature.[150]

1.3.8 Preparation of 5-(*tert*-butyl-dimethyl-silanyloxy)-pent-2-ynoic acid methyl ester (**159**)



^{n}BuLi (2.5M, 1.1 eq., 71 mmol, 28.6 ml) (titrated according to **Error! Reference source not found.** (page Error! Bookmark not defined.) was added dropwise over 10 min to a solution of the alkyne **155** (1.0 eq., 12.0 g, 65 mmol) at -78°C in THF (100 ml). The mixture was warmed to 0°C, and cooled back down to -78°C before being transferred *via* cannula into a precooled (-78°C) solution of $ClCO_2Me$ (1.1 eq., 6.8 g, 72 mmol) in THF (150 ml). The reaction mixture was then poured onto saturated NH_4Cl solution (200 ml), extracted with Et_2O (3 x 100 ml), the combined organic extracts washed with H_2O (100 ml), brine (100 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification by column chromatography (eluent PE:Et_2O 10:1 to 5:1, gradient) afforded the alkyne ester **159** (12.25 g, 50.6 mmol, 78%) as an oil; **ν_{max} (film) /cm^{-1}:** 2954, 2930, 2885, 2858, 2242, 1709, 1471, 1435, 1254, 1109, 1076, 1056, 908, 837, 710; **δ_H (400 MHz, $CDCl_3$):** 0.03 (6H, s, Si(CH_3) x 2), 0.86 (9H, s, SiC(CH_3)$_3$ x 1), 2.51 (2H, t, *J* 7.0, 4-H x 2), 3.70 (3H, s, OCH_3), 3.74 (2H, t, *J* 7.0, 5-H x 2); **δ_C (100 MHz, $CDCl_3$):** 153.9 (C=O), 86.7 (3-C), 73.6 (2-C), 60.6 (5-C), 52.4 (OCH_3), 25.7 (SiC(CH_3)$_3$ x 1), 23.0 (4-C), 18.2 (Si*C*(CH_3)$_3$), -5.4 (Si(CH_3) x 2); ***m/z* (+EI)**: 265.1236 ([MNa]$^+$, 100%), 266.1269 (13.3%), 266.1232 (5.1%), 267.1204 (3.4%). Found [MNa]$^+$ 265.1233. [$C_{12}H_{22}O_3SiNa$]$^+$ requires 265.1236. Data was consistent with the literature.[151,152]

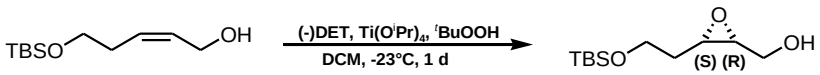
1.3.9 Preparation of 5-(*tert*-butyl-dimethyl-silanyloxy)-pent-2-yn-1-ol (**156**) (Method 2)



159 **156**

Alkynyl alcohol **156** was prepared according to **Error! Reference source not found.** (page Error! Bookmark not defined.) from alkyne ester **159** (8.1 g, 33.5 mmol). Workup as described and flash column chromatography (eluent PE:Et_2O 5:1) afforded alkynyl alcohol **156** (7.0 g, 32.6 mmol, 97%) as an oil; ν_{max} **(film)/cm^{-1}:** 3418 (OH), 2929, 2858, 2249, 1471, 1385, 1256, 1101, 1006, 905, 836, 778, 710; δ_H **(400 MHz, $CDCl_3$):** 0.04 (6H, s, Si(CH_3) x 2), 0.86 (9H, s, SiC(CH_3)$_3$ x 1), 2.40 (2H, t, *J* 7.3, 4-H x 2), 2.50 (1H, br s, OH), 3.69 (2H, t, *J* 6.9, 5-H x 2), 4.19 (2H, s, 1-H x 2); δ_C **(100 MHz, $CDCl_3$):** 83.0 (3-C), 79.6 (2-C), 61.8 (5-C), 51.0 (1-C), 25.8 (SiC(*C*H_3)$_3$ x 1), 23.1 (4-C), 18.3 (Si*C*(CH_3)$_3$), -5.1 (Si(CH_3) x 2); ***m/z* (+EI):** 237.1287 ([MNa]$^+$, 100%), 238.1320 (12.2%), 238.1282 (5.1%), 239.1255 (3.4%). Found [*M*Na]$^+$ 237.1288. [$C_{11}H_{22}O_2SiNa$]$^+$ requires 237.1287. Spectral data was identical to that of the compound synthesised *via* method 1 (*vide supra*).

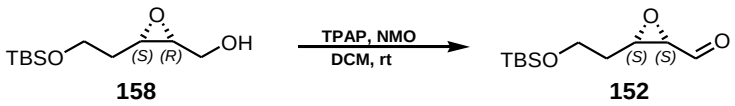
1.3.10 Preparation of 3-[2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-oxiranyl-methanol (**158**)



157 **158**

Epoxy alcohol **158** was prepared according to **Error! Reference source not found.** (page Error! Bookmark not defined.) from allylic alcohol **157** (0.35 g, 1.62 mmol), titanium tetraisopropoxide (MW=284.26, d=0.963, 1.0 eq., 1.62 mmol, 460 mg, 0.477 ml), (-)-D-diethyltartrate (MW=206.19, d=1.205, 1.2 eq., 1.94 mmol, 0.40 ml) and *tert*-butylhydroperoxide [5.0-6.0M solution in decanes] (2.0 eq., 3.24 mmol, 0.59 ml) in DCM (20 ml). Workup was performed as described with $FeSO_4$ (2.5 g) and D/L-tartaric acid (10%, 3.0 g in 30 ml H_2O). Purification by flash column chromatography (eluent PE:Et_2O 9:1 to 1:3, gradient) afforded epoxy alcohol **158** (150 mg, 0.65 mmol, 40% unoptimised) as a colourless oil; ν_{max} **(film)/cm^{-1}:** 3445 (OH), 2955, 2929, 2857, 1471, 1388, 1361, 1254, 1099, 1039, 1005, 925, 820, 811, 774, 661; δ_H **(400 MHz, $CDCl_3$):** 0.05 (6H, s, Si(CH_3) x 2), 0.87 (9H, s, SiC(CH_3)$_3$ x 1), 1.63-1.94 (2H, m, 4-H x 2), 3.04 (1H, s, OH), 3.05 (1H, dt, *J* 4.2, 5.1, 3-H x 1), 3.15 (1H, dt, *J* 4.2, 4.4, 2-H x 1), 3.57-3.75 (2H, m, 1-H x 2), 3.78 (2H, t, *J* 4.8, 5-H x 2); δ_C **(100 MHz, $CDCl_3$):** 60.5 (1-C), 60.4 (5-C), 55.9 (2-C), 54.8 (3-C), 30.7 (4-C), 25.9 (SiC(*C*H_3)$_3$ x 1), 18.4 (Si*C*(CH_3)$_3$), -5.5 (Si(CH_3) x 1), -5.6 (Si(CH_3) x 1); ***m/z*** **(+EI):** 255.1392 ([MNa]$^+$, 100%), 256.1426 (12.2%), 256.1388 (5.1%), 257.1361 (3.4%). Found [*M*Na]$^+$ 255.1393. [$C_{11}H_{24}O_3SiNa$]$^+$ requires 255.1392.

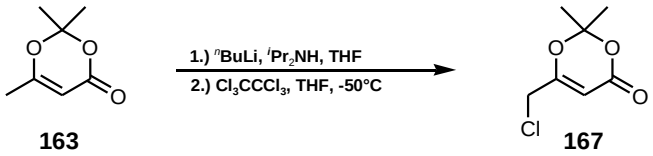
1.3.11 Preparation of 3-[2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-oxirane-2-carbaldehyde (**152**)



158 **152**

TPAP (MW=351.43, 5 mol%, 0.01 mmol, 3.5 mg) was added to epoxy alcohol **158** (50 mg, 0.2 mmol) and NMO (MW=117.15, 1.5 eq., 0.3 mmol, 37.8 mg) in DCM (5 ml) over 4Å molecular sieves (200 mg) at 0°C. The reaction mixture was stirred at this temperature for 3 h, then filtered through a small pad of Florisil, further eluted with Et_2O (200 ml) and washed with brine (50 ml). The phases were separated and the combined organic layers were dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification by flash column chromatography (eluent PE:Et_2O 10:1) afforded aldehyde **152** (22 mg, 0.095 mmol, 48% unoptimised) as an oil; δ_H **(400 MHz, $CDCl_3$):** 0.05 (6H, s, Si(CH_3) x 2), 0.86 (9H, s, SiC(CH_3)$_3$ x 1), 1.84-2.05 (2H, m, 4-H x 2), 3.35-3.44 (2H, m, 2-H x 1, 3-H x 1), 3.81 (2H, t, *J* 4.8, 5-H x 2), 9.45 (1H, d, *J* 5.1, 1-H x 1); δ_C **(100 MHz, $CDCl_3$):** 198.3 (1-C), 59.8 (5-C), 57.6 (2-C), 56.9 (3-C), 31.2 (4-C), 25.9 (SiC(*C*H_3)$_3$ x 1), 18.3 (Si*C*(CH_3)$_3$), -5.5 (Si(CH_3) x 2); which was used immediately in the next coupling step with the phosphonate **153** due to it's instability.

1.3.12 Preparation of 6-chloromethyl-2,2-dimethyl-[1,3]dioxin-4-one (**167**)

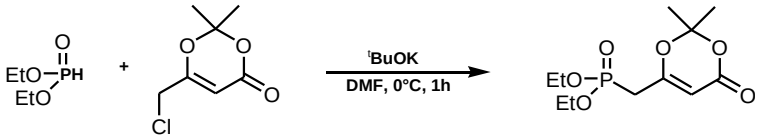


163 **167**

2,2,6-Trimethyl-1,3-dioxin-4-one **163** (24.3 g, 170 mmol, freshly distilled bp=28°C, 0.002 mbar) was added dropwise to a stirring solution of LDA (170 mmol), which was prepared according to **Error! Reference source not found.** (page Error! Bookmark not defined.), at -78°C. A bright yellow suspension formed, which was stirred for 20 min. It was then carefully transferred dropwise, over a period of 30 min, *via* dry Teflon® tubing to a stirred solution of hexachloroethane (MW=236.74, 59.18 g, 250 mmol), in THF (150 ml), which was precooled to -50°C under dry argon. The red solution thus formed was allowed to warm slowly to -10°C over 2 h, after which the reaction mixture was quenched by addition of ice cold dilute aqueous HCl (1.5M, 500 ml). The acidic solution was shaken to dispel the colour and extracted with Et_2O (3 x 300 ml). The combined Et_2O layers were washed with saturated aqueous $NaHCO_3$ solution (2 x 300 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo* to yield a yellow oil containing crystalline hexachloroethane. This was removed by trituration with hexane (2 x 100 ml). Purification by flash column chromatography (eluent PE:Et_2O 3:1 to 2:1, gradient) afforded pure product **167** (9.85 g, 55.8 mmol, 33%) as an oil; ν_{max} **(neat)/cm^{-1}**: 3004, 2254, 1725, 1643, 1392, 1378, 1274, 1251, 1202, 1183, 1016, 904, 701; δ_H **(400 MHz, $CDCl_3$):** 1.68 (6H, s, CH_3 x 2), 4.00 (2H, s, CH_2), 5.51 (1H, s, CH); δ_C **(100 MHz, $CDCl_3$):** 164.5 (CO), 160.3 (C), 107.5 (C), 95.6 (CH), 40.9 (CH_2Cl), 24.7 (CH_3 x 2); ***m/z* (+EI)**: 176.0240 ($[MNa]^+$, 100%), 178.0211 (32%), 177.0274 (7.8%),

179.0244 (2.5%). Found $[M]^+$ 176.0244. $[C_7H_9O_3Cl]^+$ requires 176.0240. Data was consistent with those reported in the literature.[153]

1.3.13 Preparation of 2,2-dimethyl-6-(diethylphosphonomethyl)-1,3-dioxin-4-one (**153**)

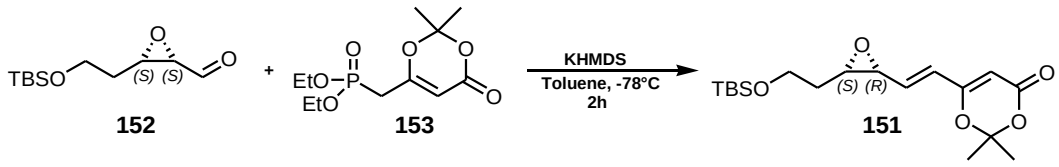


167 **153**

Diethylphosphite (13.81 g, 12.88 ml, 100 mmol, distilled bp=27°C, 0.002 mbar) was added dropwise to a stirring solution of ^{t}BuOK (11.22 g, 100 mmol) in DMF (60 ml), at 0°C. After 30 min, 2,2-dimethyl-6-chloromethyl-1,3-dioxin-4-one **167** (4.00 g, 22.6 mmol) in DMF (20 ml) was added dropwise over 20 min, and the deep purple solution generated was stirred at 0°C for a further 1h. Dropwise addition of concentrated HCl (5 ml) discharged the colour, and the pale brown mixture was filtered through Celite®, eluting with Et_2O (100 ml). The combined organic washings were concentrated *in vacuo*, keeping the bath temperature below 40°C. Excess DMF and diethyl phosphite were removed by vacuum distillation (0.01 mbar, < 45°C) affording the crude product as a thick brown oil, which was diluted with EtOAc (50 ml) and left at 0°C overnight. The solution was decanted from the crystals thus formed, and reduced *in vacuo*. Purification by flash column chromatography (eluent Et_2O:EtOAc 1:1 to 1:4, gradient) yielded compound **153** (3.07 g, 11 mmol, 49%) as a pale yellow oil; ν_{max} **(neat)/cm^{-1}:** 3400 (br), 2984, 2910, 1725, 1633, 1443, 1374, 1252, 1020, 778; δ_H **(400 MHz, $CDCl_3$):** 1.27 (6H, t, *J* 7.0, CH_3 x 2), 1.68 (6H, s, CH_3 x 2), 2.70 (2H, d, *J* 22.4, CH_2), 4.05 (4H, m, CH_2 x 2), 5.31

(1H, d, *J* 3.7, CH); δ_C **(100 MHz, $CDCl_3$):** 163.0 (CO), 159.9 (C), 106.9 (C), 95.9 (d, J_{13CP} 8.84, CH), 62.4 (d, J_{13CP} 6.51, CH_2 x 2), 32.1 (d, J_{13CP} 131.0, CH_2), 24.9 (CH_3 x 2), 16.2 (d, J_{13CP} 6.55, CH_3 x 2); ***m/z* (+EI):** 301.0809 ($[MNa]^+$, 100%), 302.0850 (12.2%), 303.0859 (1.2%). Found $[MNa^+]$ 301.0809. $[C_{11}H_{19}O_6PNa]^+$ requires 301.0817. Data was consistent with those reported in the literature.[153]

1.3.14 Preparation of 6-(2-(3-[2-(*tert*-butyl-dimethyl-silanyloxy)-ethyl]-oxiranyl)-vinyl)-2,2-dimethyl-[1,3]dioxin-4-one (**151**)

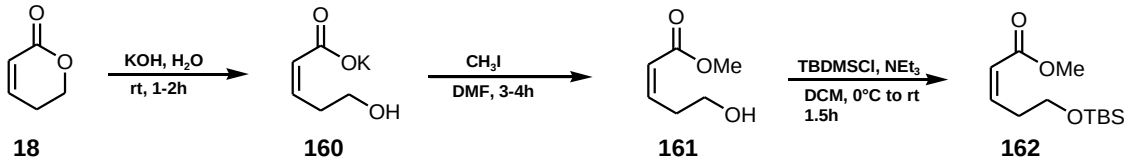


152 **153** **151**

KHMDS [0.5M solution in toluene, MW=199.49, d=0.877] (22 mg, 0.095 mmol, 2.2 eq.) was added to phosphonate ester **153** (53 mg, 0.19 mmol, 2.0 eq.) in toluene (3 ml) at -78°C, and stirring continued for 30 min at that temperature. Epoxy aldehyde **152** (22 mg, 0.095 mmol) was injected *via* cannula over 1 min, and the reaction mixture was stirred at -25°C for 2 h. The reaction mixture was then poured onto EtOAc (40 ml) and washed with saturated NH_4Cl solution (30 ml). The phases were separated and the aqueous layer re-extracted with EtOAc (20 ml). The combined organic phases were washed with brine (40 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification by flash column chromatography (eluent PE:Et_2O 5:1 to 1:2, gradient) afforded epoxy alkene **151** (12 mg, 0.034 mmol, 36%) as an oil; ν_{max} **(film)/cm^{-1}:** 3020, 2979, 2859, 1716, 1654, 1595, 1391, 1276, 1255, 1215, 1108, 1021, 967, 908, 833, 810, 748, 667; δ_H **(400 MHz, $CDCl_3$):** 0.06 (6H,

s, Si(CH_3) x 2), 0.89 (9H, s, SiC(CH_3)$_3$ x 1), 1.56 (2H, m, CH_2), 1.68 (6H, s, CH_3 x 2), 3.33 (1H, app. q, *J* 4.4, CH), 3.55 (1H, app. t, *J* 6.2, CH), 3.77 (2H, t, *J* 5.9, CH_2), 5.34 (1H, s, =CH), 6.21 (1H, d, *J* 15.7, =CH), 6.41 (1H, dd, *J* 15.7, 6.6, =CH); **δ_C (100 MHz, $CDCl_3$):** 161.7, 161.5, 134.7, 126.2, 106.6, 95.2, 60.1, 57.8, 55.7, 31.0, 25.9 (SiC(*C*H_3)$_3$ x 1), 25.1, 24.9, 18.3 (Si*C*(CH_3)$_3$), -5.4 (Si(CH_3) x 1), -5.5 (Si(CH_3) x 1); ***m/z* (+EI):** 377.1759 (85%), 319.1346 (82%), 316.2163 (100%), 287.1513 (30%), 263.0670 (38%), 243.1133 (28%). Found $[MNa]^+$ 377.1759. $[C_{18}H_{30}O_5SiNa]^+$ requires 377.1760.

1.3.15 Preparation of methyl-(*Z*)-5-*tert*-butyldimethylsilyloxy-2-pentenoate (**162)**

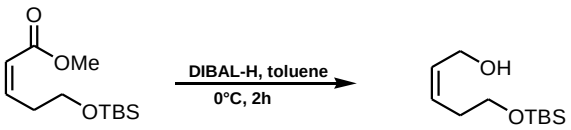


18 **160** **161** **162**

KOH (2.40 g, 42.8 mmol, 1.2 eq.) was added to a solution of commercially available 5,6-dihydro-2-pyrone **18** (MW=98.10, 3.50 g, 35.6 mmol) in H_2O (30 ml). After 2.5 h stirring at rt, the solvent was removed *in vacuo*, and the resulting residue dried for 24 h over P_2O_5 in a dessiccator. The K-salt **160** was then dissolved in little DMF (20 ml) and MeI (MW=141.94, d=2.280, 5.0 eq., 178 mmol, 25.3 g, 11.1 ml) was added under stirring. After 3 h at rt the mixture was poured onto crushed ice (150 ml) and extracted with Et_2O (3 x 100 ml). The combined organic layers were washed with brine (150 ml) and dried ($MgSO_4$) to afford, after removal of the solvent, crude product methyl-(*Z*)-5-hydroxy-2-pentenoate **161**, contaminated with small amounts of DMF. This crude product was dissolved in CH_2Cl_2 (30 ml) and

subsequently NEt_3 (MW=101.19, d=0.726, 1.2 eq., 25.8 mmol, 2.61 g, 3.6 ml), TBSCl (MW=150.73, 1.2 eq., 25.8 mmol, 3.88 g) and DMAP (MW=122.17, 400 mg) were added at 0°C. The reaction mixture was allowed to warm to rt over 1.5 h, before it was diluted with Et_2O (250 ml), washed very quickly (30 sec.) with 1-N HCl (200 ml), then washed with pH 7 buffer solution (100 ml) (prepared according to **Error! Reference source not found.** (page Error! Bookmark not defined.). The phases were separated and the combined organic phases washed with brine (100 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification by column chromatography (eluent PE:Et_2O 9:1) afforded the product **162** (3.9 g, 15.9 mmol, 45% over 3 steps) as an oil; **ν_{max} (film)/cm^{-1}:** 2954, 2929, 2857, 1724, 1645, 1472, 1438, 1407, 1254, 1172, 1098, 1006, 811, 776; **δ_H (400 MHz, $CDCl_3$):** 0.02 (6H, s, $Si(CH_3)$ x 2), 0.86 (9H, s, $SiC(CH_3)_3$ x 1), 2.81-2.86 (2H, m, 4-H x 2), 3.67 (3H, s, OCH_3), 3.70 (2H, t, *J* 6.2, 5-H x 2), 5.82 (1H, d, *J* 11.3, 2-H x 1), 6.28-6.36 (1H, m, 3-H x 1); **δ_C (100 MHz, $CDCl_3$):** 166.6 (C=O), 147.2 (=C), 120.3 (=C), 61.9 (CH_2O), 50.9 (OCH_3), 32.5 (CH_2), 25.9 ($SiC(CH_3)_3$), 18.5 ($SiC(CH_3)_3$), -5.3 ($Si(CH_3)$ x 2); ***m/z* (+EI):** 287.1397 (68%), 269.1458 (5%), 268.1417 (18%), 267.1396 (100%), 243.1183 (21%). Found $[MNa]^+$ 267.1396. $[C_{12}H_{24}O_3SiNa]^+$ requires 267.1392. Spectral data was identical to that of the compound reported in the literature.[150]

1.3.16 Preparation of 5-(*tert*-butyl-dimethyl-silanyloxy)-pent-2-*(Z)*-en-1-ol (**157**) (Method 2)

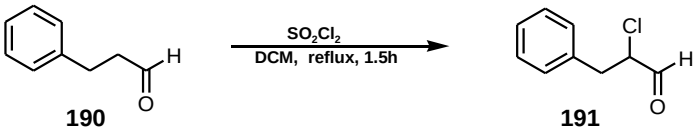


162 **157**

DIBAL-H (1M solution in toluene, MW=142.44, d=0.848, 2.3 eq., 9.4 mmol, 1.34 g, 9.4 ml) was added according to **Error! Reference source not found.** (page Error! Bookmark not defined.) to the ester **162** (1.0 g, 4.1 mmol) in toluene (20 ml). Workup as described and purification by flash column chromatography (eluent PE:Et_2O 5:1) afforded alcohol **157** (0.8 g, 3.7 mmol, 90%). The characterization data were identical to those reported above (on page 10) and to those in the literature.[150]

1.4 Experimental procedures for chapter 4: novel C-2 connected complexes

1.4.1 Preparation of 2-chloro-3-phenylpropanal (**191**)

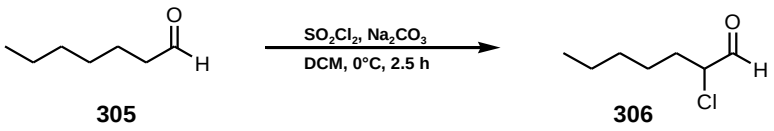


190 **191**

A solution of sulfurylchloride (8.0 ml, 0.1 mol) in DCM (20 ml) was added dropwise to a solution of freshly distilled hydrocinnamaldehyde **190** (13.2 ml, 0.1 mol) in DCM (15 ml) at 0°C and the reaction mixture was then allowed to warm to rt. After 1 h at this temperature, the reaction was heated to reflux for a further 30 min. Distillation under reduced pressure (p=0.5mmHg) afforded the desired mono-chlorinated product. Purification by flash column chromatography (eluent Et_2O:PE 1:3) afforded 2-chloro-3-phenylpropanal **191** (7.6 g, 45%) as a colourless oil.* **δ_H (600 MHz, $CDCl_3$):** 3.10 (1H, dd, *J* 14.5, 8.3, 3´-H x 1), 3.39 (1H, dd, *J* 14.5, 5.7, 3-H x 1), 4.40 (1H, ddd, *J* 2.2, 5.0, 8.0; 2-H x 1), 7.24-7.38 (5H, m, aryl-H x 5), 9.55 (1H, d, *J* 2.0, 1-H x 1); ***m/z* (EI):** Found: $[M]^+$ 168.0339. $[C_9H_9ClO]^+$ requires 168.0342. Data were consistent with those reported in the literature.[154]

* The yellow oil could not be stored for more than a few days, even in the fridge, since polymerisation occurs, forming a yellow solid.

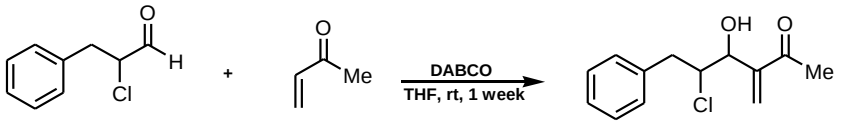
1.4.2 Preparation of 2-chloroheptanal (**306**)



305 **306**

A solution of sulfurylchloride (8.0 ml, 0.1 mmol) in DCM (15 ml) was added dropwise to a solution of freshly distilled heptaldehyde **305** (15.0 ml, 0.1 mmol) in DCM (15 ml) at –10°C and the reaction mixture was allowed to warm to 10-15°C. After 30 min at this temperature the reaction mixture was heated to 50°C and stirred for 2 h. Ice water (100 ml) was then added and the combined phases were extracted with Et_2O (2 x 50 ml) and dried over $MgSO_4$. Filtration and distillation under reduced pressure (p=0.1mmHg, 25°C) afforded a mixture of desired mono-chlorinated product **306** and (2*E*)- and (2*Z*)-hept-2-enal (95:5 – 90:10). Separation by flash column chromatography (eluent Et_2O:PE 1:5) afforded the α-chloro-heptanal **306** (6.1 g, 40%) as a colourless oil. **δ_H (200 MHz, $CDCl_3$):** 0.85 (3H, t, *J* 7.1, 7-H x 3), 1.25-1.70 (6H, m, 4-H x 2, 5-H x 2, 6-H x 2), 1.82 – 1.87 (2H, m, *3*-H x 2), 4.10 (1H, td, *J* 8.5, 3.2, 2-H x 1), 9.61 (1H, d, *J* 2.2, 1-H x 1); ***m/z* (EI):** Found: $[M]^+$ 148.0641. $[C_7H_{13}ClO]^+$ requires 148.0655. Data were consistent with those reported in the literature.[155,154]

1.4.3 Preparation of 5-chloro-4-hydroxy-3-methylene-6-phenyl-hex-2-one (**192**)

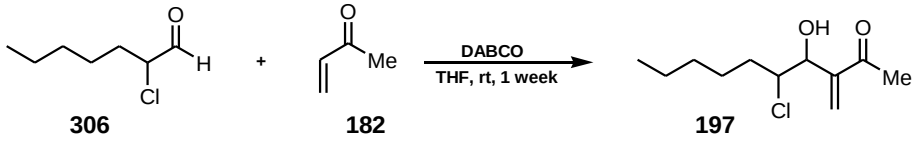


191 **182** **192**

Freshly distilled methylvinylketone **182** (0.31 g, 0.37 ml, 4.4 mmol) was added dropwise to a stirred solution of the α-chlorophenylaldehyde **191** (0.74 g, 4.4 mmol) and DABCO catalyst (0.112 g, 1 mmol) in dry THF (6 ml) at rt. The solution was stirred for one week and then diluted with Et_2O (5 ml). The mixture was then washed with 3N-HCl (2 x 5 ml) and the aqueous layer extracted with Et_2O (2 x 10 ml). The combined organic fractions were washed with Na_2CO_3 solution (10 ml), dried ($MgSO_4$), filtered and then concentrated *in vacuo*. Purification was readily achieved by flash column chromatography on silica gel (eluent Et_2O:PE 1:2) and afforded an inseparable mixture of *cis* and *trans* diastereoisomeric (ratio 2:1) chloro-hydroxy-phenyl-enones **192** (0.30 g, 29%) as a dark yellow oil; ν_{max} **(film)/cm^{-1}:** 3446 br (OH), 3062, 3029, 2922, 1672 (C=O), 1604 (C=C), 1496, 1454, 1366, 1299, 1135, 1078, 974, 670; δ_H **(600 MHz, $CDCl_3$):** 2.35 (3H´, s, 1-H´ x 3), 2.37 (3H, s, 1-H x 3), 2.51 (1H´, d, *J* 9.0, OH´ x 1), 2.57 (1H´, m , 6-H_b´ x 1), 2.90 (1H, dd, *J* 15.0, 9.5, 6-H_b x 1), 3.21 (1H´, m, 6-H_a´ x 1), 3.33 (1H, dd, *J* 15.0, 3.0, 6-H_a x 1), 3.36 (1H, d, *J* 8.0, OH x 1), 4.37 (1H, td, *J* 11.0, 4.1, 5-H x 1), 4.45 (1H´, td, *J* 8.0, 2.0, 5-H´ x 1), 4.48 (1H, app. t, *J* 7.0, 4-H x 1), 4.71 (1H´, app. d, *J* 9.0, 4-H´ x 1), 6.14 (1H´, s, 3-H_a´ x 1), 6.16 (1H, s, 3-H_a x 1), 6.25 (1H, s, 3-H_b x 1), 6.29 (1H´, s, 3-H_b´ x 1), 7.24-7.38 (5H+5H´, m, aryl-H x 5); δ_C **(50 MHz, $CDCl_3$):** 198.6 (C=O), 198.5, 145.0 (C), 142.7 (C), 137.3 (CH_2), 136.7 (CH_2), 129.1, 128.6, 126.7, 124.0 (aryl-C), 62.5 (CH), 59.0 (CH), 55.2 (CH), 54.9 (CH), 38.5 (CH_2),

32.8 (CH_2), 26.1 (CH_3), 26.0 (CH_3); ***m/z* (+EI)** Found: $[MNa]^+$ 261.0633. $[C_{13}H_{15}O_2ClNa]^+$ requires 261.0658.

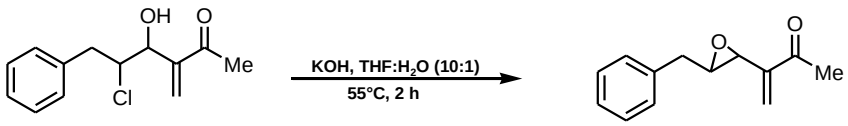
1.4.4 Preparation of 5-chloro-4-hydroxy-deca-2-one (**197**)



Freshly distilled methylvinylketone **182** (1.4 g, 1.66 ml, 20.0 mmol) was added dropwise to a stirred solution of the α-chloroaldehyde **306** (3.0 g, 20.0 mmol) and DABCO (0.56 g, 5.0 mmol) in dry THF (10 ml) at rt. The solution was stirred at this temperature for one week. The reaction was then diluted by adding Et_2O (100 ml) and the reaction mixture was washed with 3N-HCl (2 x 25 ml). The aqueous layer was extracted with Et_2O (2 x 50 ml). The combined organic fractions were washed with Na_2CO_3 solution (50 ml), dried ($MgSO_4$), filtered and then concentrated *in vacuo*. Purification by flash column chromatography (eluent Et_2O:PE 1:2) afforded an inseparable mixture (ratio 3:2) of alkyl-chloro-hydroxy-enones **197** (2.11 g, 48%) as a brown oil; ν_{max} **(film)/cm^{-1}:** 3464 br (OH), 2956, 2929, 2859, 1711, 1672 (C=O), 1637 (C=C), 1461, 1431, 1365, 1259, 1110, 1078, 1022, 975, 887, 799; δ_H **(200 MHz, $CDCl_3$):** 0.85 (3H, app. t, *J* 7.0, 10-H x 3), 1.20-1.88 (8H, m, 9-H x 2, 8-H x 2, 7-H x 2, 6-H x 2), 2.37 (3H, s, 1-H x 3 and 1-H´ x 3), 2.44 (1H, d, *J* 9.0, OH´ x 1), 3.15 (1H, d, *J* 7.0, OH x 1), 4.16 (1H, m, 5-H x 1), 4.19 (1H, m, 5-H´ x 1), 4.43 (1H, t, *J* 7.0, 4-H x 1), 4.68 (1H, m, 4-H´ x 1), 6.11 (1H, s, 3-H_a´ x 1), 6.13 (1H, s, 3-H_a x 1), 6.23 (1H, s, 3-H_b x 1), 6.27 (1H, s, 3-H_b´ x 1); δ_C **(50 MHz, $CDCl_3$):** 200.7 (C=O, 2-C´), 199.4 (C=O, 2-C), 147.6 (C, 3-C´), 145.9 (C, 3-C), 129.1 (=CH_2, 3$_a$-C´),

127.4 (=CH_2, 3_a-C), 75.9 (CH, 4-C´), 71.8 (CH, 4-C), 67.2 (CH, 5-C´), 64.9 (CH, 5-C), 35.4 (CH_2, 6-C and 6-C´), 32.5 (CH_2, 7-C and 7-C´), 31.2 (CH_2, 8-C and 8-C´), 25.9 (CH_3, 1-C), 22.4 (CH_2, 9-C and 9-C´), 13.9 (CH_3, 10-C and 10-C´); ***m/z* (+EI)** Found: $[MNa]^+$ 241.0982. $[C_{11}H_{19}O_2ClNa]^+$ requires 241.0971.

1.4.5 Preparation of (4*R**,5*R**),(4*S**,5*R**)-epoxy-3-methylene-6-phenyl-hex-2-one (**193**) (Method 1)

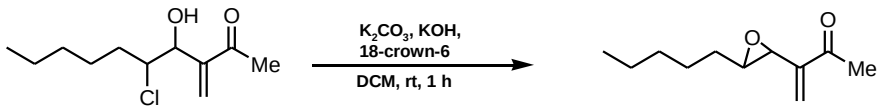


192 **193**

A mixture of *cis*/*trans* (2:1) chloro-hydroxy-phenyl-enones **192** (2.88 g, 12.1 mmol) was slowly injected through a gas-tight syringe into 10 ml THF : H_2O (10:1) solution at 55°C, which contained KOH (0.5 g, 8.9 mmol, MW=56.10). The reaction was stirred at this temperature for approximately 2 h and then worked up by the addition of Et_2O (100 ml). The mixture was washed with brine (2 x 20 ml). The aqueous layer was extracted with Et_2O (2 x 30 ml). The combined organic fractions were washed with saturated Na_2CO_3 solution (50 ml), dried ($MgSO_4$), filtered and then concentrated *in vacuo*. Purification by flash column chromatography on silica gel (eluent Et_2O:PE 1:1 to 100% Et_2O, gradient) afforded an inseparable mixture (ratio 2:1) of *cis* and *trans* epoxy-phenyl-enones **193** (0.75 g, 3.7 mmol, 31%) as a yellow oil; **ν_{max} (film)/cm^{-1}:** 3029, 2919, 1676 (C=O), 1631 (C=C), 1604, 1496, 1454, 1432, 1372, 1287, 980, 665; **δ_H (400 MHz, $CDCl_3$):** 2.35 (3H, s, 1-H x 3), 2.39 (3H´, s, 1-H´ x 3), 2.65 (2H´, m, 6-H´ x 2), 2.84 (1H, td, *J* 6.1, 2.0, 5-H), 2.95 (2H, m, 6-H x 2), 3.48 (1H´, t *J* 7.0, 5-H´), 3.69

(1H, dd, *J* 1.0, 0.9, 4-H), 3.94 (1H´, dd, *J* 3.0, 0.8, 4-H´), 5.92 (1H, s, 3-H_a), 6.03 (1H, s, 3-H_b), 6.05 (1H´, s, 3-H_a´), 6.31 (1H´, s, 3-H_b´), 7.24-7.38 (5H+5H´, m, aryl-H x 5); **δ_C (50 MHz, $CDCl_3$):** 198.6 (C=O, C-2´), 198.5 (C=O, C-2), 145.1 (C, 3-C´), 142.8 (C, 3-C), 137.3, 136.8, 129.1, 128.5 (aryl-C), 126.7 (=CH_2, 3-C_a´), 124.1 (=CH_2, 3-C_a), 62.55 (CH, 5-C), 59.0 (CH, 5-C´), 55.2 (CH, 4-C´), 54.9 (CH, 4-C), 38.5 (CH_2, 6-C), 32.8 (CH_2, 6-C´), 26.1 (CH_3, 1-C); ***m/z* (+EI)** Found: $[MNa]^+$ 225.0887. $[C_{13}H_{14}O_2Na]^+$ requires 225.0891.

1.4.6 Preparation of (4*R**,5*R**),(4*S**,5*R**)-epoxy-3-methylene-deca-2-one (**198**)

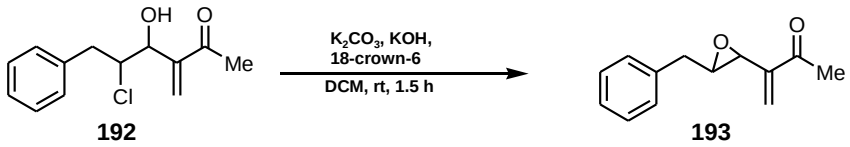


197 **198**

18-Crown-6 (1.21 g, 4.5 mmol), potassium hydroxide (well ground, used as powder, 0.25 g, 4.5 mmol) and K_2CO_3 (0.62 g, 4.5 mmol) were added into a round bottomed flask. The flask was then warmed to 70°C (with a waterbath) and put on a high vacuum line for 30 min – 1 h to evaporate residual water and dry the contents fully. DCM (20 ml) was injected *via* a syringe, under an argon atmosphere. Alkyl-chloro-hydroxy-enone **197** (0.40 g, 1.8 mmol) in DCM (5 ml) was transferred dropwise *via* a cannula needle into the base mixture and stirred at rt for approximately 1 h. The reaction mixture was then worked up by addition of Et_2O (250 ml) and was washed with $NaHCO_3$ solution (2 x 50 ml). The aqueous layer was extracted with Et_2O (2 x 50 ml) and the combined organic fractions washed with Na_2CO_3 solution (50 ml), dried over $MgSO_4$, filtered and then concentrated *in vacuo*. Purification by flash column chromatography (eluent Et_2O:PE 1:4) afforded the epoxy-alkyl-enones **198** (0.34 g, 1.8 mmol, 95%) as an inseparable mixture (1:2) of *cis* and

trans diastereoisomers as a bright yellow oil; ν_{max} **(film)/cm^{-1}:** 2957, 2929, 2858, 1678 (C=O), 1630 (C=C), 1458, 1377, 1288, 1117, 1023, 949, 922; δ_H **(200 MHz, $CDCl_3$):** 0.88 (3H, t, *J* 7.0, 10-H x 3), 1.20–1.88 (8H+8H´, m, 9-H, H´ x 2, 8-H, H´ x 2, 7-H, H´ x 2, 6-H, H´ x 2), 2.36 (3H, s, 1-H), 2.37 (3H´, s, 1-H´), 2.60 (1H, td, *J* 6.0, 2.1, 5-H), 3.18 (1H´, app. q, *J* 4.6, 5-H´), 3.54 (1H, m, 4-H), 3.83 (1H´, m, 4-H´), 5.90 (1H, s, 3-H_a), 5.91 (1H´, s, 3-H_a´), 6.02 (1H, s, 3-H_b), 6.21 (1H´, s, 3-H_b´); δ_C **(50 MHz, $CDCl_3$):** 145.8 (C=O, 2-C) 125.2 (C, 3-C), 123.8 (=CH_2, $3_{a/b}$-C), 62.8 (CH, 4-C), 54.7 (CH, 5-C), 32.0 (CH_2, 6-C), 31.6 (CH_2, 7-C), 31.5 (CH_2, 7-C'), 30.3 (CH_2, 8-C), 25.3 (CH_3, 1-C), 22.5 (CH_2, 9-C), 13.9 (CH_3, 10-C); ***m/z*** **(+EI)** Found: $[MNa]^+$ 205.1201. $[C_{11}H_{18}O_2Na]^+$ requires 205.1204.

1.4.7 Preparation of (4*R**,5*R**),(4*S**,5*R**)-epoxy-3-methylene-6-phenyl-hex-2-one (**193**) (Method 2)

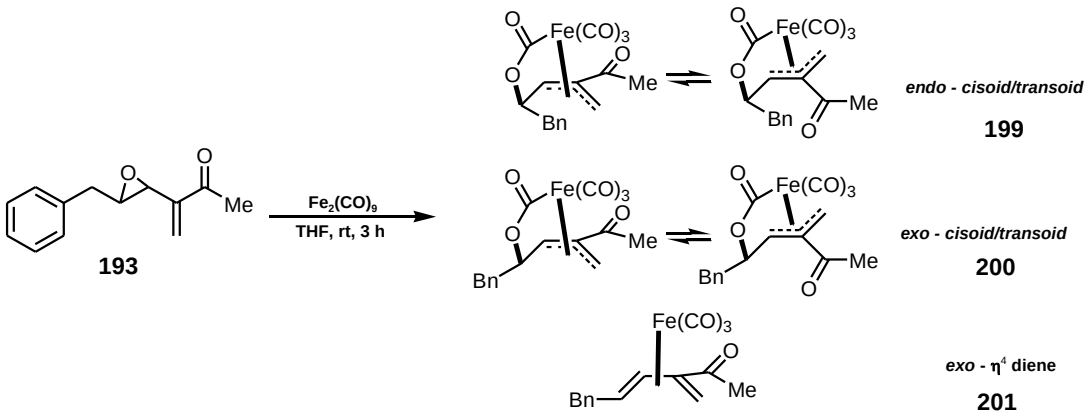


192 **193**

KOH (0.39 g, 7 mmol), K_2CO_3 (0.96 mg , 7 mmol) and 18-crown-6 (3.96 g, 15 mmol) were prepared and dried as previously described (*vide supra*). After the base mixture was dried, DCM (200 ml) was added. The phenyl-chloro-hydroxy-enone **192** (0.80 g, 3.4 mmol) was dissolved in DCM (50 ml) and transferred slowly *via* a cannula needle into the base mixture flask. The reaction was stirred at room temperature until completion, taking approximately 1.5 h. The reaction was then worked up by addition of Et_2O (500 ml) and was washed with NH_4Cl solution (2 x

250 ml). The aqueous layer was extracted with Et_2O (2 x 150 ml) and the combined organic fractions were washed with Na_2CO_3 solution (50 ml), dried over $MgSO_4$, filtered and then concentrated *in vacuo*. Purification by flash column chromatography (eluent Et_2O:PE 1:3) afforded a mixture (ratio 2:1) of inseparable epoxy-phenyl-enones **193** (0.25 g, 1.25 mmol, 37%) as a yellow oil; **ν_{max} (film)/cm^{-1}:** 3029, 2919, 1676 (C=O), 1631 (C=C), 1604, 1496, 1454, 1432, 1372, 1287, 980, 665; **δ_H (400 MHz, $CDCl_3$):** 2.35 (3H, s, 1-H x 3), 2.39 (3H´, s, 1-H´ x 3), 2.65 (2H´, m, 6-H´ x 2), 2.84 (1H, td, *J* 6.1, 2.0, 5-H), 2.95 (2H, m, 6-H x 2), 3.48 (1H´, t, *J* 7.0, 5-H´), 3.69 (1H, dd, *J* 1.0, 0.9, 4-H), 3.94 (1H´, dd, *J* 3.0, 0.8, 4-H´), 5.92 (1H, s, 3-H_a), 6.03 (1H, s, 3-H_b), 6.05 (1H´, s, 3-H_a´), 6.31 (1H´, s, 3-H_b´), 7.24-7.38 (5H+5H´, m, aryl-H x 5); **δ_C (50 MHz, $CDCl_3$):** 198.6 (C=O, C-2´), 198.5 (C=O, C-2), 145.1 (C, 3-C´), 142.8 (C, 3-C), 137.3, 136.8, 129.1, 128.5 (aryl-C), 126.7 (=CH_2, 3-C_a´), 124.1 (=CH_2, 3-C_a), 62.6 (CH, 5-C), 59.0 (CH, 5-C´), 55.2 (CH, 4-C´), 54.9 (CH, 4-C), 38.5 (CH_2, 6-C), 32.8 (CH_2, 6-C´), 26.1 (CH_3, 1-C); ***m/z* (+EI)** Found: $[MNa]^+$ 225.0896. $[C_{13}H_{14}O_2Na]^+$ requires 225.0891.

1.4.8 Preparation of [(3-*EZ*, 5*RS*)-5-(carbonyloxy-κ*C*)-3-methylene-2-oxo-6-phenyl-(1´,3,4-η)-hex-3-en-1´-yl]-tricarbonyliron (**199**), [(3-*EZ*, 5*SR*)-5-(carbonyloxy-κ*C*)-3-methylene-2-oxo-6-phenyl-(1´,3,4-η)-hex-3-en-1´-yl]-tricarbonyliron (**200**) and [(1´,3,4,5-η)-3-methylene-2-oxo-6-phenyl-hex-3-en-(1´,5)-diyl]-tricarbonyliron (**201**)



Compounds **199**, **200** and **201** were prepared according to **Error! Reference source not found.** (page **Error! Bookmark not defined.**) with addition of phenyl epoxide **193** (0.25 g, 1.25 mmol) in THF (5 ml) to a suspension of $Fe_2(CO)_9$ (1.12 g, 3.1 mmol, 2.5 eq.) in THF (20 ml). Purification *via* flash column chromatography (eluent Et_2O:PE 2:98 to 100:0, gradient) afforded the products as a complex equilibrium (*transoid*/*cisoid* species) of a mixture of *endo*/*exo* (3:1) complexes and η^4-diene complex (ratio 3:1:1), overall yield 38%. The data was obtained on the individual complexes after partial separation by flash column chromatography.

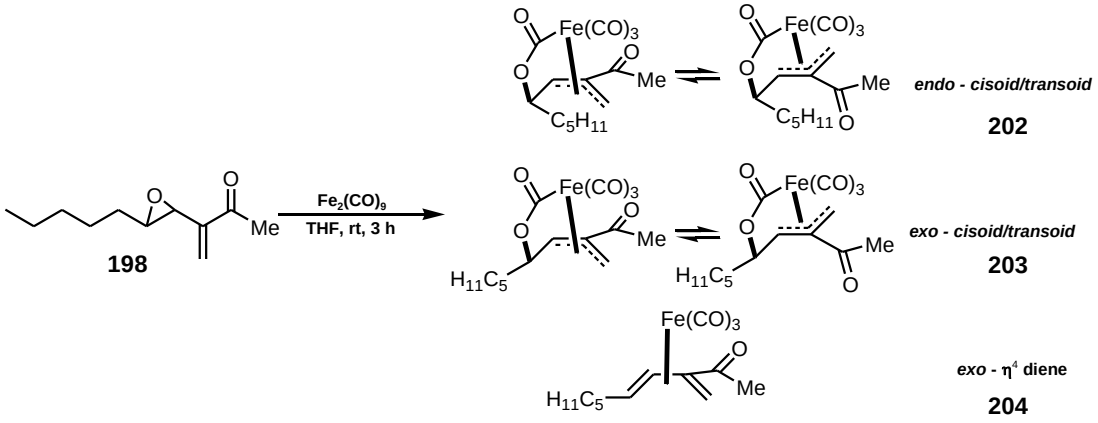
Compound **199**: **ν_{max} (film)/cm^{-1}:** 2933, 2360, 2084, 2012, 1745 (C=O), 1673 (C=C), 1496, 1454, 1379, 1205, 965, 922; **δ_H (600 MHz, $CDCl_3$):** 1.72 (3H, s, 1-H x 3), 1.79 (1H, s, 4-H), 3.05 (1H, m, 6-H_a), 3.18 (1H, m, 6-H_b), 3.60 (1H, s, 1´-H_a), 4.33 (1H, s, 1´-H_b), 5.17 (1H, app. t, 5-H), 7.18-7.37 (5H, m, aryl-H x 5); **δ_C (50 MHz, $CDCl_3$):** 180.3 (CO), 174.8 (CO), 170.4 (CO), 135.9, 129.7, 128.9, 128.8, 128.6, 127.0 (aryl-C), 84.0, 80.0, 65.8, 43.8, 37.8, 24.3, 15.3; ***m/z* (CI):** 371 ($[MH]^+$, 30%), 242 ($[M-(CO^-)_4O]$, 100%). Found: $[MH]^+$ 371.0248 $[C_{17}H_{15}O_6Fe]^+$ requires 371.0218.

Compound **200**: **ν_{max} (film)/cm^{-1}:** 2930, 2350, 2068, 2005, 1997, 1733 (C=O), 1673 (C=C), 1495, 1455, 1372, 1255, 1179, 1096, 1029; **δ_H (600 MHz, $CDCl_3$):** 2.42 (3H, s, 1-H x 3), 2.43 (1H, s, 4-H), 3.02

(1H, dd, *J* 13.0, 6.1, 6-H_a), 3.20 (1H, dd, *J* 13.0, 6.1, 6-H_b), 3.64 (1H, d, *J* 20.2, 1´-H_a), 3.85 (1H, d, *J* 20.2, 1´-H_b), 5.05 (1H, app. t, *J* 5.8, 5-H), 7.27-7.40 (5H, m, aryl-H x 5); **δ_C (50 MHz, $CDCl_3$):** 209.1 (CO), 206.7 (CO), 202.2 (CO), 167.3 (C=O), 139.8, 135.7, 129.2, 128.8, 128.7, 127.2 (aryl-C), 89.5, 80.4, 59.6, 43.6, 32.5, 22.6, 17.4; ***m/z* (CI):** 371 ($[MH]^+$, 100%), 287 ($[M-3CO]^+$, 55%). Found: $[MH]^+$ 371.1045. $[C_{17}H_{15}O_6Fe]^+$ requires 371.0218.

Compound **201**: **ν_{max} (film)/cm^{-1}:** 3029, 2925, 2096, 2050, 1976, 1683 (C=O), 1602 (C=C), 1495, 1454, 1365, 1250, 748, 700; **δ_H (600 MHz, $CDCl_3$):** 0.24 (1H, s, 1´-H_a), 1.48 (1H, s, 5-H), 2.23 (1H, s, 1´-H_b), 2.42 (3H, s, 1-H x 3), 2.97 (1H, dd, *J* 15.0, 6.0, 6-H_a x 1), 3.04 (1H, dd, *J* 15.0, 6.0, 6-H_b x 1), 6.07 (1H, d, *J* 9.3, 4-H), 7.24-7.36 (5H, m, aryl-H x 5); ***m/z* (CI):** 327 ($[MH]^+$, 20%), 242 ($[M-3CO]^+$, 100%). Found: $[MH]^+$ 327.0351. $[C_{16}H_{15}O_4Fe]^+$ requires 327.0320.

1.4.9 Preparation of [(3-*EZ*, 5*RS*)-5-(carbonyloxy-κ*C*)-3-methylene-2-oxo-(1´,3,4-η)-deca-1´-yl]-tricarbonyliron (**202**), [(3-*EZ*, 5*SR*)-5-(carbonyloxy-κ*C*)-3-methylene-2-oxo-(1´,3,4-η)-deca-1´-yl]-tricarbonyliron (**203**) and [(1´,3,4,5-η)-3-methylene-2-oxo-deca-3-en-(1´,5)-diyl]-tricarbonyliron (**204**)



Compounds **202**, **203** and **204** were prepared using **Error! Reference source not found.** (page Error! Bookmark not defined.) with addition of alkyl-epoxide **198** (0.34 g, 1.8 mmol) in THF (5 ml) to a suspension of $Fe_2(CO)_9$ (1.82 g, 5.0 mmol, 2.5 eq.) in THF (25 ml). Purification by flash column chromatography (eluent Et_20:PE 2:98 to 3:2, gradient) afforded the products as a complex equilibrium (*cisoid*/*transoid* species) of a mixture of *endo*/*exo* (2:1) complexes and η^4-diene complex as yellow oils (ratio 2:1:6), in an overall yield of 25%. The data was obtained on the individual complexes after partial separation by flash column chromatography.

Compound **202**: **ν_{max} (film)/cm^{-1}:** 2931, 2859, 2249, 2088, 2018, 1674 (C=O), 1498, 1466, 1418, 1361, 1309, 1234, 1174, 1113, 1018, 915, 864, 732, 654, 612; **δ_H (600 MHz, $CDCl_3$):** 0.92 (3H, s, 10-H x 3), 1.23–1.90 (8H, m, 9-H x 2, 8-H x 2, 7-H x 2, 6-H x 2), 2.37 (3H, s, 1-H x 3), 3.25 (2H, m, 1´-$H_{a/b}$), 5.12 (1H, br s, 5-H x 1), 6.78 (1H, br s, 4-

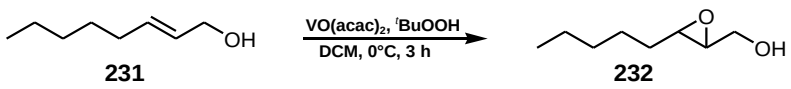
H); δ_H **(600 MHz, C_6D_6):** 0.95 (3H, s, 10-H x 3), 1.24–1.57 (8H, m, 9-H x 2, 8-H x 2, 7-H x 2, 6-H x 2), 1.78 (3H, s, 1-H x 3), 3.05 (1H, d, *J* 19.0, 1´-H_a), 3.20 (1H, d, *J* 19.0, 1´-H_b), 4.35 (1H, br s, 5-H), 5.85 (1H, br s, 4-H); δ_C **(50 MHz, $CDCl_3$):** 210.1, 209.2, 207.1 (3 x CO), 167.6 (C=O), 135.5, 89.7, 79.1, 60.3, 35.1, 31.4, 28.0, 25.1, 24.9, 17.4, 14.0; ***m/z*** **(CI):** 351 ($[MH]^+$, 100%), 266 ($[M\text{-}3CO]^+$, 64%). Found: $[MH]^+$ 351.0512. $[C_{15}H_{19}O_6Fe]^+$ requires 351.0531.

Compound **203**: ν_{max} **(film)/cm^{-1}:** 2930, 2862, 2068, 1988, 1746, 1677 (C=O), 1468, 1380, 1351, 1293, 1253, 1234, 1177, 1125, 1090, 1024, 621; δ_H **(600 MHz, $CDCl_3$):** 0.94 (3H, s, 10-H x 3), 1.23–1.89 (8H, m, 9-H x 2, 8-H x 2, 7-H x 2, 6-H x 2), 2.45 (3H, s, 1-H x 3), 2.46 (1H, s, 4-H), 3.80 (2H, m, 1´-$H_{a/b}$), 4.87 (1H, br. s, 5-H); δ_H **(600 MHz, C_6D_6):** 0.95 (3H, s, 10-H x 3), 1.24–1.80 (8H, m, 9-H x 2, 8-H x 2, 7-H x 2, 6-H x 2), 1.90 (3H, s, 1-H x 3), 2.11 (1H, s, 4-H), 2.82 (1H, d, *J* 18.0, 1´-H_a), 3.40 (1H, d, *J* 18.0, 1´-H_b), 4.19 (1H, br s, 5-H); δ_C **(50 MHz, $CDCl_3$):** 210.2, 209.3, 207.1 (3 x CO), 167.6 (C=O), 138.8, 89.7, 79.5, 60.4, 31.7, 32.3, 31.4, 24.2, 22.4, 17.4, 13.9; ***m/z*** **(CI):** 351 ($[MH]^+$, 100%), 266 ($[M\text{-}3CO]^+$, 47%). Found: $[MH]^+$ 351.0528. $[C_{15}H_{19}O_6Fe]^+$ requires 351.0531.

Compound **204**: δ_H **(600 MHz, $CDCl_3$):** 0.89 (3H, s, 10-H x 3), 1.24–1.75 (8H, m, 9-H x 2, 8-H x 2, 7-H x 2, 6-H x 2), 1.78 (3H, s, 1-H x 3), 2.45 (1H, s, 1´-H_a), 3.61 (1H, s, 1´-H_b), 4.27 (1H, br. s, 4-H), 4.85 (1H, br s, 5-H); δ_C **(50 MHz, $CDCl_3$):** 206.8 (CO), 205.0 (CO), 203.1 (CO), 127.1 (C=O), 83.5 (CH, 5-C), 82.0 (CH, 4-C), 38.4, 38.3, 32.1, 25.9, 25.9, 25.8, 23.1, 14.7; ***m/z*** **(CI):** 307 ($[MH]^+$, 27%), 222 ($[M\text{-}3CO]^+$, 100%). Found: $[MH]^+$ 307.0649. $[C_{14}H_{19}O_4Fe]^+$ requires 307.0633.

1.5 Experimental procedures for chapter 5: chiral enoate ester complexes

1.5.1 Preparation of (2*R**,3*R**)-2,3-epoxy-octan-1-ol (**232**)

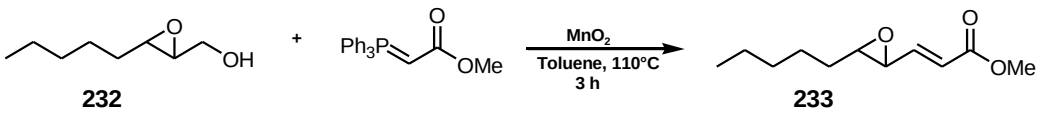


231 **232**

tert-Butyl hydroperoxide (40 ml of a 5M solution in decanes, 200 mmol, 2 eq.) was added *via* cannula to a solution of (2*E*)-oct-2-en-1-ol **231** (MW=128.21, d=0.850, 12.8 g, 15.1 ml, 100 mmol) in DCM (200 ml) at 0°C. Vanadium (III) acetylacetonate (MW=265.16, 2.65 g, 10 mmol) was then added in one portion and the mixture was stirred at 0°C for 1.5 h. Na_2SO_3 solution (200 ml) was added and the reaction mixture stirred for 30 min and gradually warmed to room temperature over 1.5 h. The mixture was filtered through a pad of Celite® washing with DCM (3 x 50 ml) and the filtrate poured into brine (200 ml). The layers were separated and the aqueous phase was extracted with ether (3 x 100 ml). The combined organic extracts were washed with brine (100 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo.* Purification by flash column chromatography (eluent PE:Et_2O 5:1 to 1:1, gradient) afforded epoxy alcohol **232** (8.8 g, 61 mmol, 61%) as a white solid; **ν_{max} (neat)/cm^{-1}:** 3245 (OH), 2954, 2931, 2870, 2850, 1460, 1394, 1375, 1327, 1249, 1139, 1062, 1036, 1005, 988, 937, 849, 833, 713; **δ_H (400 MHz, $CDCl_3$):** 0.88 (3H, t, *J* 6.9, 8-H x 3), 1.25-1.60 (8H, m, 7-H x 2, 6-H x 2, 5-H x 2, 4-H x 2), 1.80-2.05 (1H, br s, OH), 2.87-2.98 (2H, m, 1-H x 2), 3.56-3.64 (1H, dd, *J* 12.4, 4.3, 3-H), 3.87-3.91 (1H, dd, *J* 12.4, 2.5, 2-H); **δ_C (100 MHz, $CDCl_3$):** 61.7, 58.4, 56.0, 31.5, 31.4, 25.5, 22.5,

13.9; ***m/z* (+EI)** Found: $[MNa]^+$ 167.1051. $C_8H_{16}O_2Na$ requires *M*Na, 167.1048. Data were consistent with those reported in the literature.[156]

1.5.2 Preparation of (2*E*,4*R**,5*R**)-methyl-4,5-epoxy-dec-2-enoate (**233**)

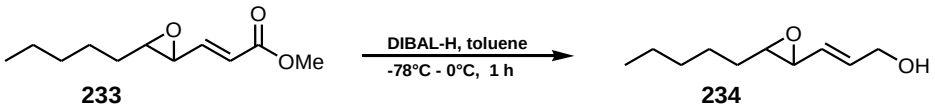


232 **233**

Methyl(triphenylphosphoranylidene)acetate (MW=334.36, 1.2 eq., 11.03 g, 33 mmol) and MnO_2 (MW=86.94, 12 eq., 29.0 g, 330 mmol) was added to a solution of epoxy alcohol **232** (4.0 g, 27.7 mmol) in toluene (200 ml) and the mixture heated under reflux for 3 h. The reaction mixture was filtered through Celite®, washing with DCM (2 x 50 ml), the filtrate concentrated *in vacuo* and the residue purified by flash column chromatography (eluent PE:Et_2O 8:1 to 1:1, gradient) to afford *trans** epoxy enoate **233** (4.11 g, 20.7 mmol, 75%) as a pale yellow oil; **ν_{max} (film)/cm^{-1}:** 2954, 2931, 2859, 1723 (C=O), 1658 (C=C), 1435, 1306, 1272, 1257, 1195, 1178, 1039, 976, 886, 854, 730, 695; **δ_H (400 MHz, $CDCl_3$):** 0.89 (3H, t, *J* 6.9, 10-H x 3), 1.24-1.66 (8H, m, 9-H x 2, 8-H x 2, 7-H x 2, 6-H x 2), 2.84 (1H, td, *J* 5.5, 2.2, 5-H), 3.17 (1H, dd, *J* 7.3, 2.2, 4-H), 3.70 (3H, s, C(O)OCH_3), 6.10 (1H, d, *J* 15.7, 2-H), 6.66 (1H, dd, *J* 15.7, 7.3, 3-H); **δ_C (100 MHz, $CDCl_3$):** 166.0 (1-C), 145.2 (3-C), 122.9 (2-C), 61.4 (4-C), 56.1 (5-C), 51.5 (C(O)O*C*H_3), 31.8 (6-C), 31.4 (7-C), 25.4 (8-C), 22.5 (9-C), 13.9 (10-C); ***m/z* (+EI):** Found $[MNa]^+$ 221.1165. $C_{11}H_{18}O_3Na$ requires 221.1154.

* very minor traces of the *cis* epoxy enoate could be identified in the NMR spectrum.

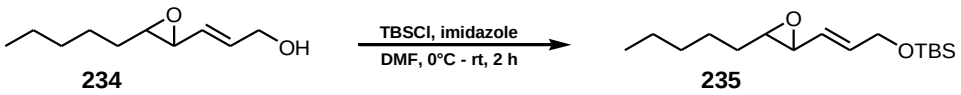
1.5.3 Preparation of (*2E*,4*R**,5*R**)-4,5-epoxy-dec-2-en-1-ol (**234**)



233 **234**

DIBAL-H (31 ml of a 1 M solution in toluene, 2.1 eq., 31 mmol) was gradually added over 10 min to a solution of ester **233** (2.9 g, 14.6 mmol) in toluene (50 ml) at -78°C. The reaction was stirred and allowed to warm up to 0°C over 1 h. H_2O (70 ml) was added and stirring continued for 30 min. Celite® (*ca*. 4 g) and $MgSO_4$ (*ca*. 10 g) were added along with Et_2O (50 ml) and the resulting slurry was stirred for 30 min before being filtered through a pad of Celite®, washing the residue with ether (2 x 50 ml) and EtOAc (3 x 50 ml). The eluate was then concentrated *in vacuo* and the residue purified by flash column chromatography (eluent Et_2O:PE 3:1) to afford epoxy enol **234** (2.1 g, 12.33 mmol, 84%) as a white solid; **ν_{max} (film)/cm^{-1}:** 3374 (OH), 2956, 2928, 2858 (C-H), 1458 (C=C), 1378, 1091 (epoxide), 1007, 965 (*trans* HC=CH), 878 (epoxide); **δ_H (400 MHz, $CDCl_3$):** 0.96 (3H, t, *J* 6.9, 10-H x 3), 1.40-1.62 (9H, 9-H x 2, 8-H x 2, 7-H x 2, 6-H x 2, OH), 2.83 (1H, td, *J* 5.5, 2.1, 5-H), 3.14 (1H, dd, *J* 8.0, 2.2, 4-H), 4.20 (2H, app. t, *J* 5.8, 1-H x 2), 5.47 (1H, dd, *J* 15.3, 7.7, 3-H), 6.05 (1H, dt, *J* 15.7, 5.5, 2-H); **δ_C (100 MHz, $CDCl_3$):** 133.9 (3-C), 128.9 (2-C), 62.7 (1-C), 60.6 (4-C), 57.9 (5-C), 31.9 (6-C), 31.5 (7-C), 25.5 (8-C), 22.5 (9-C), 13.9 (10-C); ***m/z* (+EI):** Found $[MNa]^+$ 193.1197. $C_{10}H_{18}O_2Na$ requires 193.1204.

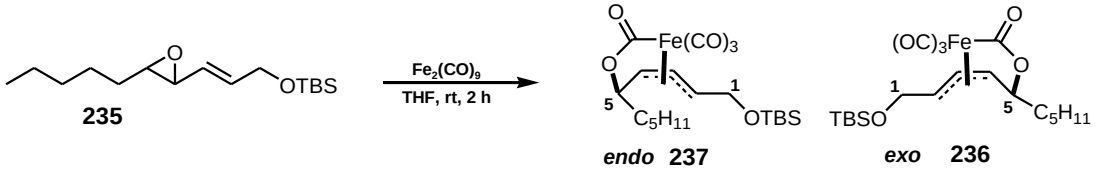
1.5.4 Preparation of (*2E*,4*R**,5*R**)-1-(*tert*-butyl-dimethyl-silanyloxy)-4,5-epoxy-dec-2-en (**235**)



234 **235**

TBS protected epoxy alcohol **235** was prepared according to **Error! Reference source not found.** (page Error! Bookmark not defined.) from TBSCl (MW=150.73, 1.1 eq., 11.7 mmol, 1.76 g), imidazole (MW=68.08, 1.2 eq., 12.6 mmol, 864 mg) and epoxy alcohol **234** (10.6 mmol, 1.80 g) in DMF (180 ml). Due to the acid sensitivity of the product, the reaction mixture was poured onto H_2O (600 ml), the layers separated, and the aqueous extracted with Et_2O (3 x 200 ml). The combined organic phases were washed with brine (150 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo* and the residue purified by flash column chromatography (eluent Et_2O:PE 8:1 to 6:1, gradient) to afford TBS protected epoxy enol **235** (2.12 g, 8.27 mmol, 78%) as an oil; ν_{max} **(film)/cm^{-1}:** 2956, 2929, 2857 (C-H), 1462 (C=C), 1379, 1253, 1124 (epoxide), 1104, 1006, 963 (*trans* HC=CH), 882 (epoxide), 834, 774, 669; δ_H **(400 MHz, $CDCl_3$):** 0.04 (3H, s, Si(CH_3)), 0.06 (3H, s, Si(CH_3)), 0.80-0.96 (12H, m, 10-H x 3, SiC(CH_3)$_3$), 1.35-1.58 (8H, 9-H x 2, 8-H x 2, 7-H x 2, 6-H x 2), 2.78 (1H, td, *J* 5.5, 1.8, 5-H), 3.04 (1H, dd, *J* 7.7, 1.5, 4-H), 4.14 (2H, m, 1-H x 2), 5.41 (1H, dd, *J* 15.3, 8.0, 3-H), 5.92 (1H, dt, *J* 15.4, 4.8, 2-H); δ_C **(100 MHz, $CDCl_3$):** 134.1 (3-C), 127.4 (2-C), 62.8 (1-C); 60.4 (4-C), 57.9 (5-C), 31.9 (6-C), 31.5 (7-C), 25.8 (SiC(*C*H_3)$_3$), 25.5 (8-C), 22.4 (9-C), 18.2 (Si*C*(CH_3)$_3$), 13.9 (10-C), -5.2 (Si(CH_3)), -5.3 (Si(CH_3)); ***m/z*** **(+EI):** Found $[MNa]^+$ 307.2071. $C_{16}H_{32}O_2NaSi$ requires 307.2069.

1.5.5 Preparation of [(2*E*,4*S**,5*R**)-5-(carbonyloxy-κ*C*)-1-(*tert*-butyl-dimethyl-silanyloxy)-(2,3,4-η)-dec-2-en-4-yl]tricarbonyliron (**237**) and [(2*E*,4R*,5R*)-5-(carbonyloxy-κ*C*)-1-(*tert*-butyl-dimethyl-silanyloxy)-(2,3,4-η)-dec-2-en-4-yl]tricarbonyliron (**236**)

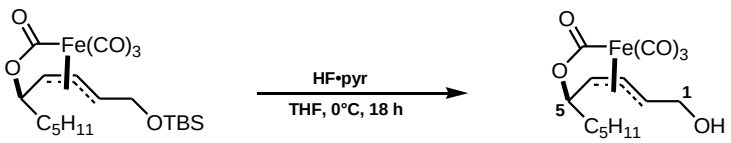


TBS protected epoxy enol **235** (2.1 g, 8.2 mmol) was added according to **Error! Reference source not found.** (page Error! Bookmark not defined.) to a suspension of $Fe_2(CO)_9$ (MW=363.79, 2.5 eq., 7.54 g, 20.4 mmol) in degassed THF (250 ml) which had been vigorously stirred for 20 min in the dark. After stirring for 2 h, toluene (10 ml) was added, and the mixture was filtered through Celite® washing the residue with Et_2O (3 x 100 ml). The volatiles were removed *in vacuo* to yield the crude product as a solution in toluene, which was purified immediately by flash column chromatography (eluent PE:Et_2O 98:2 to 50:50, gradient) to yield, in order of elution*, complexes **237** (1.92 g, 52%) and **236** (0.673 g, 18%) as yellow solids; **237** (major product, *endo* complex); **ν_{max} (neat)/cm^{-1}:** 2930 (CH), 2067 (CO), 2018 (CO), 1998 (CO), 1657 (C=O), 1253, 1127, 1007, 835, 781, 659; **δ_H (400 MHz, $CDCl_3$):** 0.06 (3H, s, $Si(CH_3)$), 0.08 (3H, s, $Si(CH_3)$), 0.80-0.97 (12H, m, 10-H x 3, $SiC(CH_3)_3$), 1.30-1.60 (8H, 9-H x 2, 8-H x 2, 7-H x 2, 6-H x 2), 4.09 (1H, dt, *J* 11.7, 2.9, 2-H), 4.18 (1H, dd, *J* 14.2, 2.9, 1-H), 4.25 (1H, td,

* very little of suspected η^4-diene complex eluted off at first, which was discarded.

J 6.9, 5.1, 5-H), 4.41 (1H, dd, *J* 14.6, 2.2, 1-H), 4.61 (1H, dd, *J* 8.4, 4.7, 4-H), 4.83 (1H, dd, J 12.1, 8.4, 3-H); δ_C **(100 MHz, $CDCl_3$):** 209.3 (CO), 206.5 (CO), 205.6 (CO), 204.0 (CO), 86.0 (3-C), 82.2 (2-C), 76.9 (5-C), 76.2 (4-C), 62.2 (1-C), 36.6 (6-C), 31.4 (7-C), 26.5 (8-C), 25.7 (SiC(CH_3)$_3$) , 22.2 (9-C), 18.3 (SiC(CH_3)$_3$), 13.7 (10-C), -5.7 (Si(CH_3)), -6.0 (Si(CH_3)); ***m/z*** **(+EI):** 475 ([MNa]$^+$, 100%), 447 ([MNa-CO]$^+$, 35%). Found: [MNa]$^+$, 475.1242. [$C_{20}H_{32}O_6FeSiNa$]$^+$ requires 475.1215; **236** (minor product, *exo* complex); ν_{max} **(neat)/cm^{-1}:** 2954 (CH), 2929 (CH), 2857 (CH), 2074 (CO), 2021 (CO), 1998 (CO), 1656 (C=O), 1461, 1324, 1255, 1135, 1038, 976, 832, 774, 655; δ_H **(400 MHz, $CDCl_3$):** 0.07 (3H, s, Si(CH_3)), 0.08 (3H, s, Si(CH_3)), 0.80-0.96 (12H, m, 10-H x 3, SiC(CH_3)$_3$), 1.30-1.60 (8H, 9-H x 2, 8-H x 2, 7-H x 2, 6-H x 2), 4.02 (2H, m, 1-H x 2), 4.15 (1H, dt, *J* 14.6, 2.9, 5-H), 4.39 (1H, dt, *J* 14.6, 1.8, 2-H), 4.45 (1H, d, *J* 8.8, 4-H), 5.05 (1H, dd, *J* 11.3, 7.7, 3-H); δ_C **(100 MHz, $CDCl_3$):** 209.5 (CO), 206.4 (CO), 205.7 (CO), 204.2 (CO), 87.3 (3-C), 81.4 (2-C), 74.9 (5-C), 74.8 (4-C), 62.1 (1-C), 37.9 (6-C), 31.7 (7-C), 25.7 (SiC(CH_3)$_3$), 25.1 (8-C), 22.4 (9-C), 18.4 (SiC(CH_3)$_3$), 13.9 (10-C), -5.6 (Si(CH_3)), -5.7 (Si(CH_3)); ***m/z*** **(+EI):** 475 ([MNa]$^+$, 18%), 447 ([MNa-CO]$^+$, 16%), 307 ([MNa-Fe(CO)$_4$], 100%). Found: [MNa]$^+$ 475.1216. [$C_{20}H_{32}O_6FeSiNa$]$^+$ requires 475.1215.

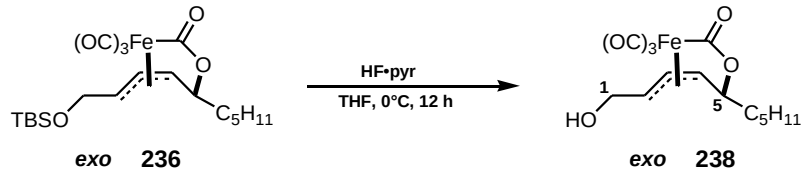
1.5.6 Preparation of [(2*E*,4*S**,5*R**)-5-(carbonyloxy-κ*C*)-1-hydroxy-(2,3,4-η)-dec-2-en-4-yl]tricarbonyliron (**240**)



endo **237** ***endo*** **240**

TBS protected *endo* iron complex **237** (2.0 g, 4.4 mmol) was treated with HF•pyridine solution (2.25 mol/l stock solution prepared according to **Error! Reference source not found.** (page Error! Bookmark not defined.), 25 eq., 110 mmol, 49 ml) in THF (10 ml) at 0°C. The reaction was allowed to warm to rt over 18 h, then poured onto a mixture of $NaHCO_3$ solution : Et_2O (50 ml : 50 ml), the layers were separated, the aqueous extracted with Et_2O (3 x 100 ml) and the combined organic extracts were poured onto saturated $CuSO_4$ solution (100 ml). The phases were again separated and the aqueous layer extracted with Et_2O (2 x 100 ml), the combined organic phases were washed with brine (100 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification by flash column chromatography (eluent Et_2O:PE 2:1 to 3:1, gradient) yielded free alcohol complex **240** (1.26 g, 3.73 mmol, 85%) as a yellow oil; ν_{max} **(neat)/cm^{-1}:** 3352 (OH), 2958 (CH), 2934 (CH), 2860 (CH), 2079 (CO), 2025 (CO), 2001 (CO), 1620 (C=O), 1459, 1330, 1102, 1030, 729, 660; δ_H **(400 MHz, $CDCl_3$):** 0.80-0.91 (3H, t, *J* 6.5, 10-H x 3), 1.25-1.60 (8H, 9-H x 2, 8-H x 2, 7-H x 2, 6-H x 2), 3.10 (1H, br s, OH), 4.05 (1H, dt, *J* 9.1, 2.9, 2-H), 4.09 (1H, d, *J* 4.7, 1-H), 4.22 (1H, td, *J* 6.5, 4.4, 5-H), 4.31 (1H, ddd, *J* 15.0, 10.9, 4.0, 1-H), 4.63 (1H, dd, *J* 8.0, 4.7, 4-H), 4.85 (1H, dd, *J* 11.7, 8.4, 3-H); δ_C **(100 MHz, $CDCl_3$):** 209.1 (CO), 207.8 (CO), 206.2 (CO), 203.6 (CO), 87.6 (3-C), 81.9 (2-C), 77.9 (5-C), 76.5 (4-C), 62.0 (1-C), 36.7 (6-C), 31.5 (7-C), 26.6 (8-C), 22.4 (9-C), 13.9 (10-C); ***m/z* (+EI):** 361 ($[MNa]^+$, 100%), 333 ($[MNa\text{-}CO]^+$, 28%), 277 ($[MNa\text{-}3CO]^+$, 81%). Found: $[MNa]^+$ 361.0367. $[C_{14}H_{18}O_6FeNa]^+$ requires 361.0350.

1.5.7 Preparation of [(2*E*,4R*,5R*)-5-(carbonyloxy-κ*C*)-1-hydroxy-(2,3,4-η)-dec-2-en-4-yl]tricarbonyliron (**238**)



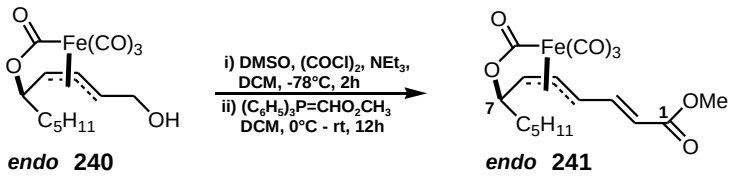
exo **236** ***exo*** **238**

TBS protected *exo* iron complex **236** (1.25 g, 2.7 mmol) was treated* with HF•pyridine solution (2.25 mol/l stock solution prepared according to **Error! Reference source not found.** (page Error! Bookmark not defined.), 15 eq., 110 mmol, 49 ml) in THF (10 ml) at 0°C. The reaction was allowed to warm to rt over 12 h, then poured onto a mixture of $NaHCO_3$ solution : Et_2O (50 ml : 50 ml), the layers were separated, the aqueous phase extracted with EtOAc (3 x 50 ml) and the combined organic extracts were poured onto saturated $CuSO_4$ solution (100 ml). The phases were again separated and the aqueous layer extracted with EtOAc (3 x 50 ml), the combined organic phases were washed with brine (100 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification by flash column chromatography (eluent Et_2O:PE 1:1, 2:1, 3:1, gradient) yielded free alcohol *exo* complex **238** (0.66 g, 1.95 mmol, 72%) as a yellow oil; **ν_{max} (neat)/cm^{-1}:** 3286 (OH), 2954 (CH), 2928 (CH), 2855 (CH), 2071 (CO), 1995 (CO), 1649 (C=O), 1467, 1348, 1120, 1047, 993, 670; **δ_H (400 MHz, $CDCl_3$):** 0.80-0.95 (3H, t, *J* 6.6, 10-H x 3), 1.25-1.60 (8H, 9-H x 2, 8-H x 2, 7-H x 2, 6-H x 2), 2.80 (1H, br s, OH), 3.98 (1H, dt, *J* 11.7, 3.3, 2-H), 4.05 (1H, ddd, *J* 14.6, 6.5, 5.1, 1-H), 4.08 (1H, t, *J* 4.4, 5-H), 4.31 (1H, dt, *J* 13.9, 3.3, 1-H), 4.45 (1H, d, *J*

* when deprotecting the *exo* complex, less equivalents of HF•pyr are required, and also the reaction time is much shorter. This is presumably due to less steric crowding, since the C_5H_{11} alkyl chain points away.

8.0, 4-H), 5.03 (1H, dd, J 11.7, 8.0, 3-H); δ_C **(100 MHz, $CDCl_3$):** 209.1 (CO), 207.9 (CO), 206.2 (CO), 203.8 (CO), 89.1 (3-C), 80.6 (2-C), 75.8 (5-C), 74.9 (4-C), 61.8 (1-C), 37.8 (6-C), 31.4 (7-C), 25.1 (8-C), 22.4 (9-C), 13.9 (10-C); ***m/z* (+EI):** 361 ($[MNa]^+$, 100%), 333 ($[MNa\text{-}CO]^+$, 13%), 277 ($[MNa\text{-}3CO]^+$, 7%). Found: $[MNa]^+$ 361.0367. $[C_{14}H_{18}O_6FeNa]^+$ requires 361.0350.

1.5.8 Preparation of [(2*E*,4*E*,6*S**,7*R**)-7-(carbonyloxy-κC)-2-methoxyoxycarbonyl-(4,5,6-η)-dodeca-2,4-dien-6-yl]tricarbonyliron (**241**)

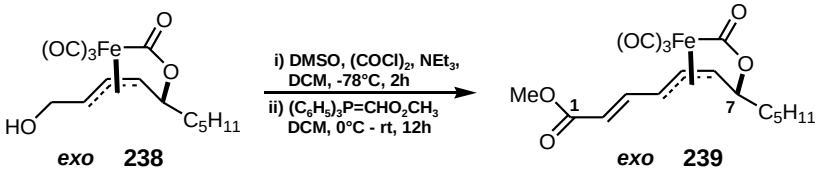


***endo* 240** ***endo* 241**

A solution of DMSO (MW=78.13, d=1.101, 2.5 eq., 440 μl, 6.25 mmol) in DCM (2 ml) was added to a solution of oxalyl chloride (MW=126.93, d=1.455, 1.3 eq., 280 μl, 3.25 mmol) in DCM (10 ml) at –78°C and the mixture stirred at –78°C for 5 min. A solution of alcohol complex **240** (840 mg, 2.5 mmol) in DCM (10 ml) was gradually added over 5 min and stirring continued for 30 min. NEt_3 (MW=101.19, d=0.726, 5.0 eq., 1.74 ml, 12.5 mmol) was added and the mixture allowed to warm to -10°C over 1 h. After 1.5 h, methyl(triphenylphosphoranylidene)acetate (MW=334.36, 5.0 eq., 12.5 mmol, 4.2 g) was added and the mixture allowed to warm to rt overnight. The reaction mixture was poured into brine (50 ml) and extracted with DCM (3 x 50 ml). The combined organic phases were then dried ($MgSO_4$), filtered and concentrated *in vacuo* and the residue was purified by flash column chromatography (eluent

PE:Et_2O 1:1) to afford enoate complex **241** (760 mg, 1.93 mmol, 78%) as a yellow solid; **ν_{max} (neat)/cm^{-1}:** 2951, 2872, 2850, 2073, 2030, 1994, 1704, 1671, 1627, 1431, 1335, 1247, 1169, 1038, 969, 732, 650; **δ_H (400 MHz, $CDCl_3$):** 0.86 (3H, t, *J* 6.5, 12-H x 3), 1.20-1.67 (8H, 11-H x 2, 10-H x 2, 9-H x 2, 8-H x 2), 3.75 (3H, s, C(O)OCH_3), 4.28 (1H, td, *J* 5.8, 5.7, 7-H), 4.51 (1H, app. t, *J* 11.3, 4-H), 4.72 (1H, dd, *J* 8.0, 4.7, 6-H), 4.93 (1H, dd, *J* 11.7, 8.0, 5-H), 6.25 (1H, d, *J* 15.4, 2-H), 6.88 (1H, dd, J 15.4, 10.6, 3-H); **δ_C (100 MHz, $CDCl_3$):** 208.1 (CO), 204.3 (CO), 203.3 (CO), 202.6 (CO), 166.5 (1-C), 145.6 (3-C), 122.0 (2-C), 93.2 (5-C), 79.2 (6-C), 77.2 (7-C), 75.4 (4-C), 51.8 (C(O)O*C*H_3), 36.7 (8-C), 31.4 (9-C), 26.6 (10-C), 22.4 (11-C), 13.9 (12-C); ***m/z* (+EI):** 415 ($[MNa]^+$, 100%), 387 ($[MNa-CO]^+$, 47%), 303 ($[MNa-4CO]^+$, 76%). Found: $[MNa]^+$ 415.0469. $[C_{17}H_{20}O_7FeNa]^+$ requires 415.0456.

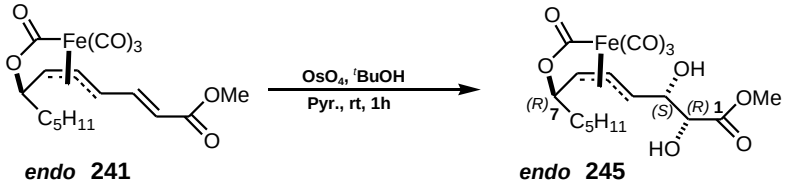
1.5.9 Preparation of [(2*E*,4*E*,6*R**,7*R**)-7-(carbonyloxy-κC)-2-methoxyoxycarbonyl-(4,5,6-η)-dodeca-2,4-dien-6-yl]tricarbonyliron (**239**)



A solution of DMSO (MW=78.13, d=1.101, 2.5 eq., 170 μl, 2.43 mmol) in DCM (1 ml) was added to a solution of oxalyl chloride (MW=126.93, d=1.455, 1.3 eq., 110 μl, 1.26 mmol) in DCM (10 ml) at –78°C and the mixture stirred at –78°C for 5 min. A solution of alcohol complex **238** (330 mg, 0.97 mmol) in DCM (10 ml) was gradually added over 5 min, and stirring continued for 20 min. NEt_3 (MW=101.19, d=0.726, 5.0 eq.,

0.67 ml, 4.85 mmol) was added and the mixture allowed to warm to -10°C over 1 h. After 1.5 h, methyl(triphenylphosphoranylidene)acetate (MW=334.36, 5.0 eq., 4.85 mmol, 1.62 g) was added and the mixture allowed to warm to rt overnight. The reaction mixture was poured into brine (50 ml) and extracted with DCM (3 x 50 ml). The combined organic phases were then dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (eluent PE:Et_2O 1:1) to afford enoate complex **239** (320 mg, 0.82 mmol, 85%) as a yellow solid; **ν_{max} (neat)/cm^{-1}:** 2953, 2930, 2861, 2068, 2020, 1997, 1717, 1706, 1655, 1434, 1348, 1222, 1165, 1012, 718; **δ_H (400 MHz, $CDCl_3$):** 0.85 (3H, t, *J* 6.5, 12-H x 3), 1.22-1.65 (8H, 11-H x 2, 10-H x 2, 9-H x 2, 8-H x 2), 3.75 (3H, s, C(O)OCH_3), 4.07 (1H, t, *J* 6.5, 7-H), 4.41 (1H, app. t, *J* 11.0, 4-H), 4.56 (1H, d, *J* 7.7, 6-H), 5.11 (1H, dd, *J* 11.7, 7.7, 5-H), 6.24 (1H, d, *J* 15.4, 2-H), 6.88 (1H, dd, J 15.4, 11.0, 3-H); **δ_C (100 MHz, $CDCl_3$):** 208.4 (CO), 204.3 (CO), 202.9 (CO), 202.8 (CO), 166.5 (1-C), 145.0 (3-C), 122.2 (2-C), 94.3 (5-C), 78.2 (6-C), 74.8 (7-C), 74.7 (4-C), 51.8 (C(O)O*C*H_3), 37.9 (8-C), 31.3 (9-C), 25.1 (10-C), 22.4 (11-C), 13.9 (12-C); ***m/z* (+EI):** 415 ($[MNa]^+$, 100%), 387 ($[MNa\text{-}CO]^+$, 45%), 303 ($[MNa\text{-}4CO]^+$, 37%). Found: $[MNa]^+$ 415.0461. $[C_{17}H_{20}O_7FeNa]^+$ requires 415.0456.

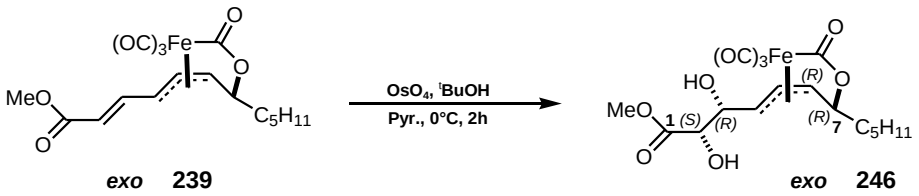
1.5.10 Preparation of [(4*E*,2*R**,3*S**,6*S**,7*R**)-7-(carbonyloxy-κC)-2,3-dihydroxy-2-methoxyoxycarbonyl-(4,5,6-η)-dodeca-4-en-6-yl]tricarbonyliron (**245**)



endo **241** *endo* **245**

OsO_4 (MW=254.20, 1.2 eq., 135 μmol, 1.72 ml of a 2.5 w/w % solution in tert-butanol) was added to a stirred solution of enoate complex **241** (44 mg, 112 μmol) in pyridine (250 μl). After 1 h, excess $Na_2S_2O_5$ (*ca*. 1 g) and H_2O (4 ml) were added and the mixture stirred vigorously for 1 h. The phases were separated and the aqueous phase extracted with DCM (3 x 20 ml). The combined organic fractions were washed with saturated $CuSO_4$ solution (2 x 20 ml) and brine (20 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (eluent Et_2O:PE 3:1) to yield diol complex **245** (27 mg, 56%) as a white solid; **ν_{max} (neat)/cm^{-1}:** 3550 (OH), 2933 (CH), 2870, 2085 (CO), 1993 (CO), 1738 (C=O), 1650, 1441, 1265, 1109, 1000, 666; **δ_H (400 MHz, $CDCl_3$):** 0.85 (3H, t, *J* 6.6, 12-H x 3), 1.19-1.68 (8H, 11-H x 2, 10-H x 2, 9-H x 2, 8-H x 2), 2.63 (1H, s, 3-OH), 3.18 (1H, s, 2-OH), 3.88 (3H, s, C(O)OCH_3), 4.20 (1H, app. q, *J* 7.3, 4-H), 4.26 (1H, td, *J* 6.2, 5.1, 7-H), 4.32 (1H, m, 2-H), 4.50 (1H, m, 3-H), 4.71 (1H, dd, *J* 8.4, 4.7, 6-H), 4.92 (1H, dd, *J* 11.7, 8.0, 5-H); **δ_C (100 MHz, $CDCl_3$):** 209.1 (CO), 206.1 (CO), 205.9 (CO), 203.4 (CO), 172.4 (1-C), 87.2 (5-C), 78.7 (4-C), 76.9 (6-C), 76.6 (7-C), 73.7 (2-C), 71.3 (3-C), 53.3 (C(O)O*C*H_3), 36.5 (8-C), 31.5 (9-C), 26.4 (10-C), 22.4 (11-C), 13.9 (12-C); ***m/z* (+EI):** 449 ($[MNa]^+$, 50%), 365 ($[MNa-3CO]^+$, 100%). Found: $[MNa]^+$ 449.0519. $[C_{17}H_{22}O_9FeNa]^+$ requires 449.0511.

1.5.11 Preparation of [(4*E*,2*S**,3*R**,6*R**,7*R**)-7-(carbonyloxy-κC)-2,3-dihydroxy-2-methoxyoxycarbonyl-(4,5,6-η)-dodeca-4-en-6-yl]tricarbonyliron (**246**)

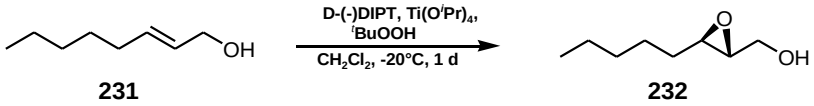


exo **239** *exo* **246**

OsO_4 (MW=254.20, 2.4 ml of a 2.5 w/w % solution in tert-butanol, 1.5 eq., 0.26 mmol) was added to a stirred solution of enoate complex **239** (67 mg, 0.17 mmol) in pyridine (1 ml) at 0°C. After 2 h, excess $Na_2S_2O_5$ (*ca*. 1 g) and H_2O (2 ml) were added and the mixture stirred vigorously for 3 h. The phases were separated and the aqueous phase extracted with DCM (3 x 20 ml). The combined organic fractions were washed with saturated $CuSO_4$ solution (2 x 20 ml) and brine (20 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (eluent Et_2O:PE 5:1) to yield diol complex **246** (37 mg, 51%) as a white solid; **ν_{max} (neat)/cm^{-1}:** 3398 (OH) 2928 (CH), 2860, 2077 (CO), 1997 (CO), 1740 (C=O), 1626, 1438, 1278, 1125, 1093, 995, 655; **δ_H (400 MHz, $CDCl_3$):** 0.88 (3H, t, *J* 6.9, 12-H x 3), 1.23-1.72 (8H, 11-H x 2, 10-H x 2, 9-H x 2, 8-H x 2), 2.97 (1H, d, *J* 6.9, 3-OH), 3.35 (1H, d, J, 4.7, 2-OH), 3.80 (1H, dd, *J* 12.0, 2.9, 4-H), 3.87 (3H, s, C(O)OCH_3), 4.04 (1H, t, *J* 6.9, 7-H), 4.32 (1H, m, 2-H), 4.52 (1H, d, *J* 8.0, 6-H), 4.55 (1H, m, 3-H), 5.09 (1H, dd, *J* 11.7, 7.6, 5-H); **δ_C (100 MHz, $CDCl_3$):** 209.2 (CO), 206.3 (CO), 206.1 (CO), 203.4 (CO), 172.5 (C=O), 88.7 (5-C), 78.4 (4-C), 76.4 (6-C), 75.1 (7-C), 73.4 (2-C), 71.1 (3-C), 53.2 (C(O)O*C*H_3), 37.9 (8-C), 31.4 (9-C), 25.1 (10-C), 22.4 (11-C), 13.9 (12-C); ***m/z* (+EI):** 449 ($[MNa]^+$, 35%), 365 ($[MNa\text{-}3CO]^+$, 30%). Found: $[MNa]^+$ 449.0513. $[C_{17}H_{22}O_9FeNa]^+$ requires 449.0511.

1.6 Experimental procedures for chapter 6: (-)-gloeosporone

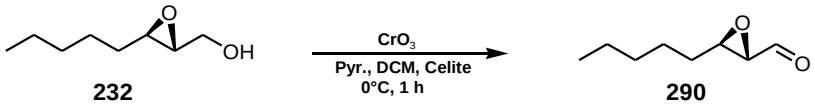
1.6.1 Preparation of (2*R*,3*R*)-2,3-epoxyoctan-1-ol (**232**)



231 **232**

(2*E*)-Octen-1-ol **231** (15.4 g, 0.12 mol) was treated with diisopropyl *D*-tartrate (1.2 eq., 0.144 mol, 33.7 g, 30.5 ml), titanium (IV) isopropoxide (1.0 eq., 0.12 mol, 34.1 g, 35.4 ml), activated, powdered 4Å molecular sieves (*ca*.4 g) and *tert*-butyl hydroperoxide (5-6M in decanes, 2.5 eq., 0.3 mol, 55 ml) in DCM (200 ml) according to **Error! Reference source not found.** (page Error! Bookmark not defined.) to provide epoxy alcohol **232** as a white solid after purification by flash column chromatography (eluent Et_2O:PE 1:2 to 3:2, gradient) (11.4 g, 81%, 83% e.e.). Two recrystallisations from PE at 0°C yielded enantiomerically enriched epoxy alcohol **271** as white needles (8.1 g, 47%, 95% e.e.); mp 37-38°C (from PE) [Lit.[156] 38-39°C (from PE)]; $[\alpha]_D^{25}$ +37.3 (*c* 1.00 $CHCl_3$) [Lit.[156] for enantiomer $[\alpha]_D^{24}$ -42.7 (*c* 4.7 in $CHCl_3$)]; Data was consistent with those reported in the literature.[156] The enantiopurity was determined by formation of the ester from (*S*)-(+)-α-methoxyphenylacetic acid and examination of the ^{1}H NMR (600 MHz) spectrum.

1.6.2 Preparation of (2*S*,3*R*)-2,3-epoxyoctanal (**290**)

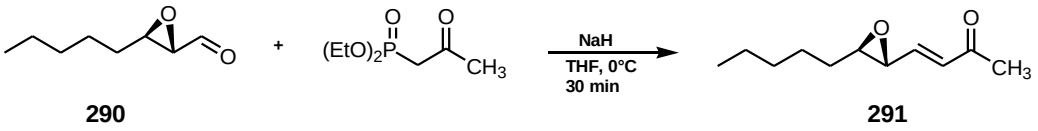


232 **290**

Chromium(VI)oxide (24.9 g, 250 mmol) was added to a solution of pyridine (41 ml, 510 mmol) in DCM (400 ml). After stirring this suspension for 15 min, Celite® (30 g) was added and the resultant slurry was stirred vigorously for a further 5 min before cooling down to 0°C. A solution of epoxy alcohol **232** (3.70 g, 26.4 mmol) was then added *via* cannula. After warming to rt and stirring for 45 min, $NaHSO_4$ (60 g) and Et_2O (400 ml) were added and the mixture was stirred vigorously for 15 min before being filtered through a sandwich of silica/$MgSO_4$/silica, washing with Et_2O (1500 ml). Concentration of the filtrate *in vacuo* followed by flash column chromatography (eluent PE:Et_2O 30:1 to 10:1, gradient) provided* epoxyaldehyde **290** (1.65 g, 11.6 mmol, 44%) as a colourless oil; **ν_{max} (film)/cm^{-1}:** 2957, 2929, 2860, 2733, 1729 (C=O), 1466, 1436, 1379, 1151, 1050, 976; **δ_H (400 MHz, $CDCl_3$):** 0.90 (3H, t, J 7.1, 8-H x 3), 1.30-1.62 (8H, m, 4-H x 2, 5-H x 2, 6-H x 2, 7-H x 2), 3.12 (1H, dd, *J* 6.2, 2.0, 2-H), 3.21 (1H, td, *J* 5.3, 2.0, 3-H), 9.01 (1H, d, *J* 6.1, 1-H); **δ_C (100 MHz, $CDCl_3$):** 198.5 (C=O), 59.2 (CH), 56.8 (CH), 31.4 (CH_2), 31.2 (CH_2), 25.4 (CH_2), 22.5 (CH_2), 13.9 (CH_3); ***m/z* (+EI):** 142 (M^+, 25%), 113 (M-CHO, 52%), 83 (72%), 71 ($Me(CH_2)_4$, 100%), 69 (55%), 55 (90%). Found: $[M]^+$ 142.0988. $C_8H_{14}O_2$ requires 156.0993. $[\alpha]_D^{25}$ -116.3 (*c* 1.00 in $CHCl_3$); Data was consistent with those reported in the literature.[17]

* Two further side products, presumably the esters from overoxidation, eluded before the main product.

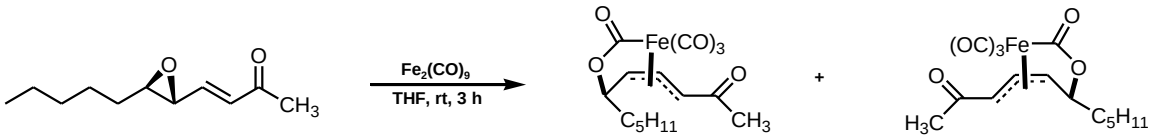
1.6.3 Preparation of (3*E*,5*R*,6*R*)-5,6-epoxy-2-oxoundec-3-ene (**291**)



290 **291**

Diethyl (2-oxopropyl)phosphonate (1.2 eq., 13.9 mmol, 2.7 g, 2.67 ml, d=1.010) was added dropwise to a stirred solution of NaH (MW 24.0, 0.51 g of a 60% dispersion in mineral oil, prewashed with hexane (10 ml), 1.1 eq., 12.7 mmol) in THF (110 ml) at rt over 5 min before cooling to 0°C. A solution of (2*S*,3*R*)-2,3-epoxyoctanal **290** (1.65 g, 11.6 mmol) in THF (10 ml) was subsequently added dropwise over 10 min. After 30 min the reaction mixture was poured into brine (50 ml) and the layers were separated. The aqueous phase was extracted with Et_2O (3 x 100 ml) and the combined organic extracts were washed with brine (50 ml), and then dried ($MgSO_4$). Concentration *in vacuo* followed by flash column chromatography of the residue (eluent Et_2O:PE 1:19 to 1:9, gradient) afforded epoxy enone **291** (1.60 g, 8.8 mmol, 76%) as a colourless oil; ν_{max} **(film)/cm^{-1}:** 2956, 2929, 2858, 1698, 1679 (C=O), 1628 (C=C), 1466, 1432, 1360, 1299, 1257, 1180, 1146, 976, 883, 827, 726; δ_H **(400 MHz, $CDCl_3$):** 0.88 (3H, t, J 7.2, 11-H x 3), 1.21-1.62 (8H, m, 7-H x 2, 8-H x 2, 9-H x 2, 10-H x 2), 2.24 (3H, s, 1-H x 3), 2.89 (1H, td, *J* 5.3, 2.0, 6-H), 3.20 (1H, dd, *J* 6.7, 2.1, 5-H), 6.32 (1H, d, *J* 16.8, 3-H), 6.46 (1H, dd, *J* 16.8, 6.7, 4-H); δ_C **(100 MHz, $CDCl_3$):** 197.3 (C=O), 143.5 (CH), 132.4 (CH), 61.5 (CH), 56.4 (CH), 31.7 (CH_2), 31.4 (CH_2), 27.2 (CH_3), 25.4 (CH_2), 22.5 (CH_2), 13.9 (CH_3); **m/z (+EI):** Found: $[M]^+$ 182.1308. $C_{11}H_{18}O_2$ requires M, 182.1307. $[\alpha]_D^{25}$ +23.8 (c 1.00 in $CHCl_3$) [optical rotation reported in Lit.[23] $[\alpha]_D^{27}$ +27.1 (c 1.0 in $CHCl_3$)]; Data was consistent with those reported in the literature.[23]

1.6.4 Preparation of [(3*E*,5*S*,6*R*)-6-(carbonyloxy-κC)-2-oxo-(3,4,5-η)-undec-3-en-5-yl]tricarbonyliron (**25**) and [(3*E*,5*R*,6*R*)-6-(carbonyloxy-κC)-2-oxo-(3,4,5-η)-undec-3-en-5-yl]tricarbonyliron (**26**)

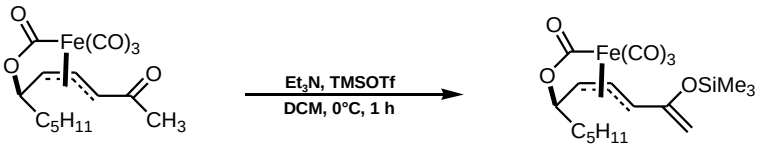


291 ***endo* 25** ***exo* 26**

Treatment of epoxy enone **291** (1.60 g, 8.8 mmol) with $Fe_2(CO)_9$ (MW 363.79, 2.2 eq., 19.4 mmol, 7.04 g) according to **Error! Reference source not found.** (page Error! Bookmark not defined.) afforded after purification with flash column chromatography (eluent PE:Et_2O 1:1) *endo* complex **25** (1.58 g, 4.5 mmol, 51%) as an orange-brown solid; **ν_{max} (film)/cm^{-1}:** 3057, 2957, 2932, 2861, 2086 (CO), 2016 (CO), 1681 (C=O), 1499, 1467, 1362, 1310, 1267, 1234, 1174, 1114, 1019, 738, 703, 655, 613; **δ_H (400 MHz, $CDCl_3$):** 0.88 (3H, t, *J* 6.5, 11-H x 3), 1.20-1.64 (8H, m, 7-H x 2, 8-H x 2, 9-H x 2, 10-H x 2), 2.43 (3H, s, 1-H x 3), 3.85 (1H, d, *J* 10.9, 3-H), 4.34 (1H, td, *J* 6.4, 4.8, 6-H), 5.03 (1H, dd, *J* 8.8, 4.8, 5-H), 5.55 (1H, dd, *J* 10.9, 8.8, 4-H); **δ_C (100 MHz, $CDCl_3$):** 207.8 (CO), 204.9 (CO), 202.4 (CO), 201.6 (CO), 199.7 (CO), 92.0 (CH), 84.6 (CH), 77.3 (CH), 65.8 (CH), 36.7 (CH_2), 31.5 (CH_2), 30.2 (CH_3 ,1-C), 26.5 (CH_2), 22.5 (CH_2), 13.9 (CH_3 ,11-C); ***m/z* (CI):** Found: $[MH]^+$ 351.0556. $C_{15}H_{19}FeO_6$ requires *M*H, 351.0531; $[\alpha]_D^{25}$ -419.3 (*c* 1.00 in $CHCl_3$) [optical rotation reported in Lit.[23] $[\alpha]_D^{26}$ -482.6 (*c* 1.00 in $CHCl_3$)]; Data was consistent with those reported in the literature;[23] and then *exo* complex **26** (0.39 g, 1.1 mmol, 13%) as an orange-brown solid; **ν_{max} (film)/cm^{-1}:** 2957, 2930, 2861, 2089 (CO),

2021 (CO), 1666 (C=O), 1496, 1467, 1420, 1361, 1315, 1227, 1175, 1114, 1069, 1046, 1004, 913, 734, 648; δ_H **(400 MHz, $CDCl_3$):** 0.89 (3H, t, *J* 7.2, 11-H x 3), 1.21-1.69 (8H, m, 7-H x 2, 8-H x 2, 9-H x 2, 10-H x 2), 2.30 (3H, s, 1-H x 3), 3.74 (1H, d, *J* 11.2, 3-H), 4.05 (1H, t, *J* 5.9, 6-H), 4.86 (1H, d, *J* 8.3, 5-H), 5.73 (1H, dd, *J* 11.2, 8.3, 4-H); δ_C **(100 MHz, $CDCl_3$):** 208.0 (CO), 204.9 (CO), 202.2 (CO), 201.3 (CO), 199.7 (CO), 93.6 (CH), 83.5 (CH), 74.4 (CH), 64.8 (CH), 38.0 (CH_2), 31.3 (CH_2), 30.1 (CH_3 , 1-C), 25.1 (CH_2), 22.5 (CH_2), 13.9 (CH_3 , 11-C); ***m/z*** **(CI):** Found: $[MH]^+$ 351.0567. $C_{15}H_{19}FeO_6$ requires *M*H, 351.0531; $[\alpha]_D^{25}$ +411.8 (*c* 1.00 in $CHCl_3$) [optical rotation reported in Lit.[23] $[\alpha]_D^{26}$ +410.4 (*c* 1.00 in $CHCl_3$)]; Data was consistent with those reported in the literature.[23]

1.6.5 Preparation of [(3*E*,5*S*,6*R*)-6-(carbonyloxy-κC)-2-trimethylsilanyloxy-(3,4,5-η)-undec-1,3-dien-5-yl]tricarbonyliron (**279**)

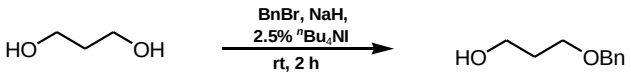


endo **25** **279**

Triethylamine (MW=101.19, d=0.726, 1.2 eq., 5.4 mmol, 0.55 g, 0.75 ml) and trimethylsilyl trifluoromethanesulfonate (MW=222.26, d=1.228, 1.1 eq., 4.95 mmol, 1.10 g, 0.89 ml) were added sequentially to a cooled (0°C) solution of the *endo* ketone complex **25** (MW=350.14, 1.58 g, 4.5 mmol) in DCM (20 ml) and the reaction mixture was stirred at 0°C for 1 h. The reaction mixture was then poured onto H_2O (100 ml) , the layers separated and the aqueous fraction extracted with Et_2O (50 ml).

The organic fractions were washed with brine (100 ml) and dried ($MgSO_4$). Concentration of the filtrate *in vacuo* followed by rapid flash column chromatography (Florisil, eluent PE:Et_2O 5:1 to 1:1, gradient) afforded the silyl enol ether complex **279** (1.62 g, MW=422.33, 3.8 mmol, 84%) as a pale yellow solid; ν_{max} **(film)/cm^{-1}**: 2922, 2853, 2077 (CO), 2011 (CO), 2002 (CO), 1685 (C=O), 1654 (C=C), 1605, 1462; δ_H **(400 MHz, $CDCl_3$):** 0.25 (9H, s, Si(CH_3)$_3$), 0.89 (3H, t, *J* 6.0, 11-H), 1.19-1.68 (8H, m, 7-H x 2, 8-H x 2, 9-H x 2, 10-H x 2), 4.27 (1H, app. q, *J* 6.4, 6-H), 4.33-4.43 (2H, m, 1-H x 1, 3-H), 4.57-4.68 (2H, m, 1-H x 1, 5-H), 5.00 (1H, dd, *J* 11.9, 8.5, 4-H); δ_C **(100 MHz, $CDCl_3$):** 209.2 (CO), 206.2 (CO), 205.5 (CO), 204.3 (CO), 153.8 (quat. C), 94.3 (CH_2), 85.6 (CH), 79.4 (CH), 77.4 (CH), 76.2 (CH), 36.8 (CH_2), 31.6 (CH_2), 26.7 (CH_2), 22.5 (CH_2), 14.0 (CH_3), -0.3 (Si(CH_3)$_3$); ***m/z*** **(CI):** Found: $[MH]^+$ 423.0944. $C_{18}H_{27}FeO_6Si$ requires *M*H, 423.0926; $[\alpha]_D^{25}$ -287.9 (*c* 1.00 in $CHCl_3$); Data was consistent with those for the racemic complex reported in the literature.[23,62]

1.6.6 Preparation of benzyloxy-1-propanol (**295**)

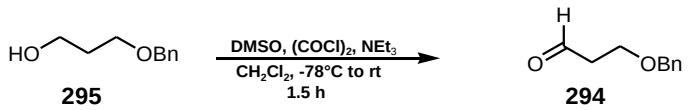


136 **295**

Commercially available propane-1,3-diol **136** (MW=76.1, d=1.053, 25 mmol, 1.9 g) was dissolved in THF (70 ml) and then treated with prewashed (in hexanes) NaH (MW=24.0, 1.0 eq., 25 mmol, 0.6 g, 60% dispersion in oil). The reaction mixture was stirred for 30 min, and then ^{n}Bu_4NI (MW=369.38, 2.5 mol%, 0.625 mmol, 0.23 g) as catalyst was added. Benzylbromide (MW=171.04, d=1.438, 1.0 eq., 25 mmol, 4.27 g,

2.97 ml) was injected *via* syringe and the reaction mixture stirred for 1 h at rt and then refluxed for a further 2 h at 110°C. After cooling to rt, the reaction mixture was poured onto NH_4Cl solution (200 ml) and H_2O (100 ml), the phases separated, the aqueous phase extracted with Et_2O (2 x 50 ml). The combined organic phases were washed with brine (100 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo* to yield a crude mixture of mono- and dibenzylated compounds. Purification by flash column chromatography (eluent PE:Et_2O 10:1 to 1:10, gradient) afforded monobenzylated product **295** (2.8 g, 18.3 mmol, 73%) as an oil; δ_H **(400 MHz, $CDCl_3$):** 1.85 (2H, q, *J* 6.1), 2.30-2.40 (1H, br s, OH), 3.67 (2H, t, *J* 6.1), 3.80 (2H, t, *J* 6.1), 4.53 (2H, s), 7.30 (5H, m); δ_C **(100 MHz, $CDCl_3$):** 138.1, 128.4, 127.7, 127.6, 73.2, 69.2, 61.7, 32.2; Data was consistent with those reported in the literature.[157]

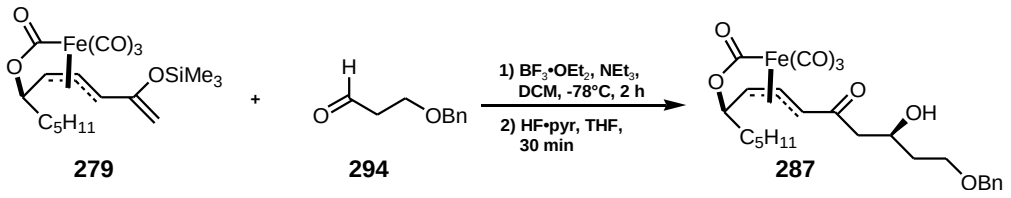
1.6.7 Preparation of 3-benzyloxy-1-propionaldehyde (**294**)



Compound **294** was prepared according to **Error! Reference source not found.** (page Error! Bookmark not defined.) from mono-benzylated propane-1,3-diol **295** (2.8 g, 18.3 mmol), DMSO (MW=78.13, d=1.101, 2.5 eq., 45.9 mmol, 3.6 g, 3.26 ml), oxalylchloride (MW=126.93, d=1.455, 1.2 eq., 21.9 mmol, 2.78 g, 1.91 ml) and NEt_3 (MW=101.19, d=0.726, 5.0 eq., 91.5 mmol, 9.25 g, 12.7 ml). The reaction was quenched by addition of NH_4Cl solution (20 ml), the aqueous phase was extracted with DCM (2 x 50 ml). The combined organic phases were washed with saturated $NaHCO_3$ (2 x 10 ml), brine (10 ml), dried

($MgSO_4$) and concentrated *in vacuo*. Purification by distillation (T=120°C, water pump pressure p=20mmHg) yielded pure, colourless aldehyde **294** (2.1 g, 12.8 mmol, 69%); δ_H **(400 MHz, $CDCl_3$):** 2.60-2.70 (2H, m), 3.80-3.90 (2H, t, *J* 6.1), 4.51 (2H, s), 7.20-7.40 (5H, m), 9.77 (1H, t, *J* 1.8); δ_C **(100 MHz, $CDCl_3$):** 201.0, 137.9, 128.4, 127.7, 127.6, 127.6, 73.2, 63.8, 43.8; Data was consistent with those reported in the literature.[158]

1.6.8 Preparation of [(8*E*,6*R*,7*S*,12*S*)-14-benzyloxy-6-(carbonyloxy-κC)-12-hydroxy-10-oxo-(7,8,9-η)-tetradec-8-en-7-yl]tricarbonyliron (**287**)



Mukaiyama aldol adduct **287** was synthesized according to **Error! Reference source not found.** (page Error! Bookmark not defined.) from TMS enol ether **279** (560 mg, 1.33 mmol), 3-benzyloxy-1-propionaldehyde **294** (3.0 eq., 4.0 mmol, 650 mg), BF_3•OEt_2 (MW=141.93, d=1.120, 1.1 eq., 1.46 mmol, 207 mg, 185 μl). The reaction mixture was worked up after 4 h as described and the crude mixture of silylated and non-silylated products was then deprotected with HF•pyridine (5 ml of 2.25M stock solution). Purification by flash column chromatography (eluent PE:Et_2O 2:1 to 1:2, gradient) afforded the β-hydroxy ketone **287** (425 mg, 0.83 mmol, 63%) as a yellow gum; ν_{max} **(film)/cm^{-1}**: 3492, 2931, 2861, 2248, 2087, 2005, 1735, 1668, 1497, 1454, 1364, 1309, 1242, 1205, 1017, 910, 821, 730, 698, 650; δ_H **(600 MHz, $CDCl_3$):** 0.86 (3H, t, *J* 6.8, 1-H x 3), 1.24-1.60 (8H, m, 2-H x 2, 3-H x 2, 4-H x 2, 5-H x 2), 1.83 (2H, m, 13-H x 2), 2.85 (2H, d, *J* 4.9, 11-H x 2), 3.27 (1H, d, *J* 3.3, OH), 3.70 (2H, m, 14-H x 2), 3.87 (1H, d, *J* 10.9, 9-H), 4.34 (1H, td, *J* 6.4, 4.4, 6-H), 4.38 (1H, m, 12-H), 4.52 (2H, s, C*H*$_2$C$_6$H$_5$), 5.02 (1H, dd, *J* 8.8, 4.4, 7-H), 5.56 (1H, dd, *J* 10.9, 8.2, 8-H), 7.22-7.40 (5H, m, CH_2C_6*H*$_5$); δ_C **(150 MHz, $CDCl_3$):** 207.8 (CO), 204.5 (CO), 203.6 (CO), 202.3 (CO), 199.6 (CO), 137.9 (Ph *ipso*), 128.4 (Ph *meta* x 2), 127.6 (Ph *para*), 127.6 (Ph *ortho* x 2), 92.0 (8-C), 84.6 (7-C), 76.8 (6-C), 73.2 (*C*H$_2$C$_6$H$_5$), 67.9 (14-C), 66.6 (12-C),

65.8 (9-C), 49.9 (11-C), 36.6 (5-C), 36.1 (13-C), 31.4 (4-C), 26.4 (3-C), 22.4 (2-C), 13.8 (1-C); ***m/z* (ES):** Found: $[MNa]^+$ 537.1188. $C_{25}H_{30}FeNaO_8$ requires *M*Na, 537.1188; $[\alpha]_D^{25}$ -297.6 (*c* 1.00 in $CHCl_3$).*

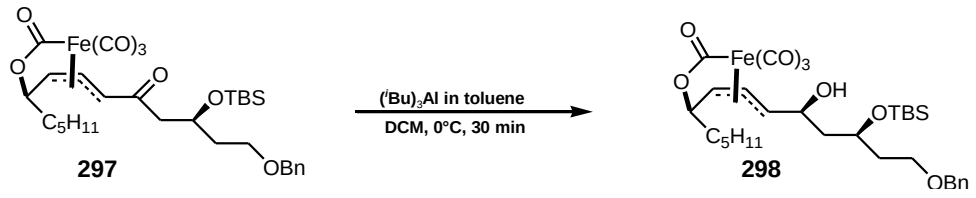
1.6.9 Preparation of [(8*E*,6*R*,7*S*,12*S*)-14-benzyloxy-12-(*tert*-butyl-dimethyl-silanyloxy)-6-(carbonyloxy-κC)-10-oxo-(7,8,9-η)-tetradec-8-en-7-yl]tricarbonyliron (**297**)

TBSOTf (MW=264.34, d=1.151, 1.1 eq., 0.91 mmol, 0.241 g, 0.209 ml) was added dropwise to a solution of the β-hydroxy ketone **287** (425 mg, 0.83 mmol) and NEt_3 (MW=101.19, d=0.726, 1.25 eq., 1.04 mmol, 104 mg, 0.144 ml) in DCM (5 ml) at 0°C. After 6 h the reaction mixture was purified directly by flash column chromatography (eluent PE:Et_2O 5:1 to 1:1) to afford the mono TBS protected iron lactone complex **297** (522 mg, 0.83 mmol, 100%) as a yellow oil; ν_{max} **(neat)/cm^{-1}**: 2929, 2857, 2087, 2010, 1671 (C=O), 1497, 1462, 1361, 1322, 1252, 1017, 910, 835, 776, 731, 697; δ_H **(600 MHz, $CDCl_3$):** 0.05 (3H, s, $Si(CH_3)$), 0.07 (3H, s, $Si(CH_3)$), 0.85 (9H, s, $SiC(CH_3)_3$), 0.89 (3H, t, *J* 7.1, 1-H x 3), 1.26-1.62 (8H, m, 2-H x 2, 3-H x 2, 4-H x 2, 5-H x 2), 1.86 (2H, app. q,

* The minor diastereoisomer was not isolated due to its low abundance. However, analysis of the 400 MHz ^{1}H nmr spectrum of the crude reaction mixture after silyl deprotection allowed an estimation of the d.e. of the aldol products, specifically by integration of the 9-H resonance; δ_H (400 MHz) 3.87 (0.98H, d), 3.83 (0.02H, d). Calculated d.e. = 96%

J 6.5, 13-H x 2), 2.82 (1H, dd, *J* 15.9, 6.0, 11-H), 2.98 (1H, dd, *J* 15.9, 4.9, 11-H'), 3.56 (2H, m, 14-H x 2), 3.86 (1H, d, *J* 10.9, 9-H), 4.32 (1H, td, *J* 7.1, 4.9, 6-H), 4.42 (1H, m, 12-H), 4.49 (2H, m, $CH_2C_6H_5$), 5.01 (1H, dd, *J* 8.8, 4.9, 7-H), 5.52 (1H, dd, *J* 10.9, 8.8, 8-H), 7.20-7.38 (5H, m, $CH_2C_6H_5$); **δ_C (150 MHz, $CDCl_3$):** 207.9 (CO), 204.8 (CO), 202.2 (CO), 202.0 (CO), 199.8 (CO), 138.3 (Ph *ipso*), 128.3 (Ph *meta* x 2), 127.6 (Ph *para*), 127.5 (Ph *ortho* x 2), 91.8 (8-C), 84.4 (7-C), 76.7 (6-C), 72.9 ($CH_2C_6H_5$), 66.3 (14-C), 66.2 (9-C); 65.9 (12-C), 50.6 (11-C), 37.1 (13-C), 36.7 (5-C), 31.4 (4-C), 26.5 (3-C), 25.8 ($SiC(CH_3)_3$), 22.4 (2-C), 17.9 ($SiC(CH_3)_3$), 13.9 (1-C), -4.5 ($Si(CH_3)$), -4.8 ($Si(CH_3)$); ***m/z* (ES):** Found: $[MNa]^+$ 651.2054. $C_{31}H_{44}FeNaO_8Si$ requires *M*Na, 651.2053; $[\alpha]_D^{25}$ -247.2 (*c* 1.00 in $CHCl_3$).

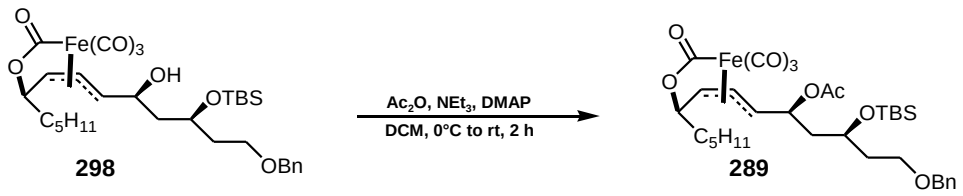
1.6.10 Preparation of [(8*E*,6*R*,7*S*,10*S*,12*S*)-14-benzyloxy-12-(*tert*-butyl-dimethyl-silanyloxy)-6-(carbonyloxy-κC)-10-hydroxy-(7,8,9-η)-tetradec-8-en-7-yl]tricarbonyliron (**298**)



$^{i}Bu_3Al$ (1M solution in toluene, d=0.848, 2.0 eq., 1.34 mmol, 1.34 ml) was added according to **Error! Reference source not found.** (page Error! Bookmark not defined.) to a solution of the TBS protected Mukaiyama aldol adduct **297** (423 mg, 0.67 mmol) in DCM (5 ml) at 0°C. Workup as described followed by flash column chromatography (eluent PE:Et_2O 5:1 to 3:1, gradient) afforded the secondary alcohol iron

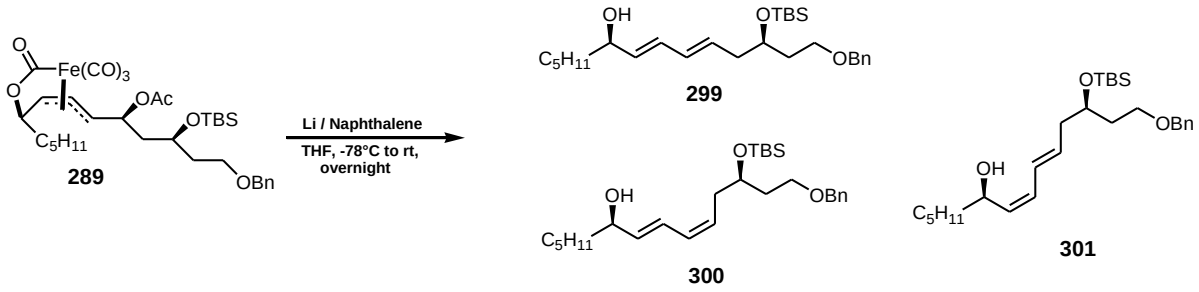
lactone complex **298** (353 mg, 0.56 mmol, 83%) as a yellow oil; **ν_{max} (neat)/cm^{-1}**: 3419 (br, OH), 2929, 2857, 2077, 2000, 1667, 1636, 1462, 1360, 1252, 1004, 835, 775, 657; **δ_H (400 MHz, $CDCl_3$):** 0.05 (3H, s, Si(CH_3)), 0.08 (3H, s, Si(CH_3)), 0.85 (9H, s, SiC(CH_3)$_3$), 0.89 (3H, t, *J* 7.1, 1-H x 3), 1.30-1.64 (8H, m, 2-H x 2, 3-H x 2, 4-H x 2, 5-H x 2), 1.80 (2H, m, 11-H x 2), 1.86 (2H, m, 13-H x 2), 3.52 (2H, t, *J* 5.8, 14-H x 2), 3.70 (1H, s, OH), 3.94 (1H, d, *J* 9.5, 9-H), 4.16 (1H, m, 12-H), 4.25 (1H, td, *J* 6.9, 5.1, 6-H), 4.45 (1H, m, 10-H), 4.49 (2H, d, *J* 3.3, $CH_2C_6H_5$), 4.60 (1H, dd, *J* 8.4, 4.4, 7-H), 4.85 (1H, dd, *J* 12.1, 8.4, 8-H), 7.22-7.35 (5H, m, $CH_2C_6H_5$); **δ_C (100 MHz, $CDCl_3$):** 209.7 (CO), 207.1 (CO), 206.2 (CO), 203.3 (CO), 138.0 (Ph *ipso*), 128.4 (Ph *meta* x 2), 127.7 (Ph *para*), 127.6 (Ph *ortho* x 2), 88.2 (8-C), 87.0 (7-C), 77.3 (6-C), 75.9 (10-C), 73.1 ($CH_2C_6H_5$), 71.1 (14-C), 69.6 (9-C), 66.2 (12-C), 45.3 (11-C), 37.8 (13-C), 36.7 (5-C), 31.5 (4-C), 26.6 (3-C), 25.7 (SiC(CH_3)$_3$), 22.4 (2-C), 17.8 (SiC(CH_3)$_3$), 13.9 (1-C), -4.0 (Si(CH_3)), -4.7 (Si(CH_3)); ***m/z* (CI)** Found: $[MH]^+$ 631.2380. $C_{31}H_{47}FeO_8Si$ requires *M*H, 631.2390; $[\alpha]_D^{25}$ -62.4 (*c* 1.00 in $CHCl_3$).

1.6.11 Preparation of [(8*E*,6*R*,7*S*,10*S*,12*S*)-10-acetoxy-14-benzyloxy-12-(*tert*-butyl-dimethyl-silanyloxy)-6-(carbonyloxy-κC)-(7,8,9-η)-tetradec-8-en-7-yl]tricarbonyliron (**289**)



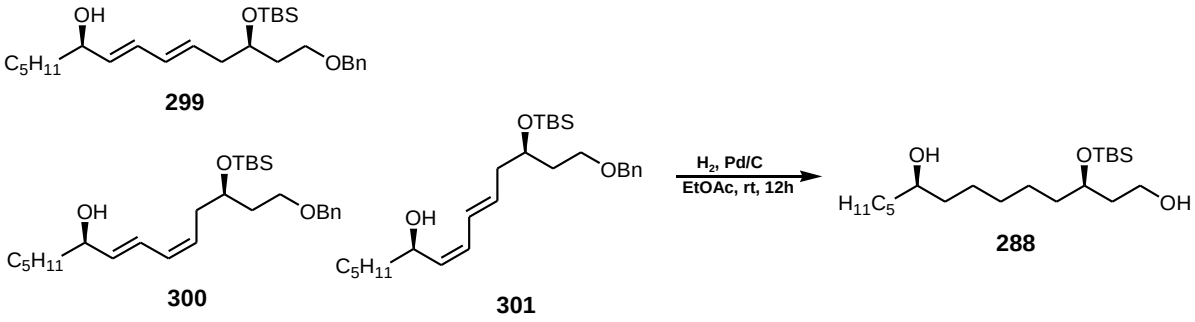
Acetic anhydride (MW=102.09, d=1.082, 1.1 eq., 0.57 mmol, 58.3 mg, 53.8 μl) was added according to **Error! Reference source not found.** (page Error! Bookmark not defined.) to a solution of the alcohol **298** (330 mg, 0.52 mmol), NEt_3 (MW=101.19, d=0.726, 1.3 eq., 0.68 mmol, 68.8 mg, 94.8 μl) and DMAP (MW=122.17, 0.1 eq., 0.052 mmol, 6.3 mg) in DCM (5 ml) at 0°C. Workup as described without further purification yielded the acetate complex **289** (340 mg, 0.51 mmol, 98%) as a colourless oil; **ν_{max} (neat)/cm^{-1}**: 2929, 2857, 2077, 2000, 1740 (C=O), 1667 (C=O), 1463, 1370, 1224, 1098, 1005, 835, 774, 734, 697, 655; **δ_H (400 MHz, $CDCl_3$):** 0.05 (3H, s, $Si(CH_3)$), 0.08 (3H, s, $Si(CH_3)$), 0.86 (9H, s, $SiC(CH_3)_3$), 0.89 (3H, t, *J* 7.1, 1-H x 3), 1.20-1.66 (8H, m, 2-H x 2, 3-H x 2, 4-H x 2, 5-H x 2), 1.80 (2H, app. q, *J* 5.8, 11-H x 2), 2.03 (3H, s, $COCH_3$), 2.10 (2H, m, 13-H x 2), 3.58 (2H, m, 14-H x 2), 3.90 (1H, dd, *J* 6.5, 5.1, 9-H), 3.96 (1H, m, 12-H), 4.20 (1H, td, *J* 6.9, 5.1, 6-H), 4.47 (1H, m, 10-H), 4.49 (2H, d, *J* 3.3, $CH_2C_6H_5$), 4.60 (1H, dd, *J* 8.4, 4.4, 7-H), 5.45 (1H, dd, *J* 12.1, 8.4, 8-H), 7.23-7.37 (5H, m, $CH_2C_6H_5$); **δ_C (100 MHz, $CDCl_3$):** 208.8, 206.4, 204.1, 202.9, 170.0, 138.4, 128.3, 127.7, 127.6, 127.5, 89.0, 81.7, 73.0, 71.7, 66.6, 66.3, 44.7, 36.5, 36.3, 31.5, 26.5, 25.8 ($SiC(CH_3)_3$), 22.4, 20.6, 17.9 ($SiC(CH_3)_3$), 13.9, -4.5 ($Si(CH_3)$), -4.6 ($Si(CH_3)$); ***m/z* (ES):** Found: $[MH]^+$ 673.2477. $C_{33}H_{49}FeO_9Si$ requires *M*H, 673.2495; $[\alpha]_D^{25}$ -139.7 (*c* 1.00 in $CHCl_3$).

1.6.12 Preparation of (7*E*,9*E*,6*R*,12*R*)-14-benzyloxy-12-(*tert*-butyl-dimethyl-silanyloxy)-6-hydroxy-tetradeca-7,9-diene (**299**), (7*E*,9*Z*,6*R*,12*R*)-14-benzyloxy-12-(*tert*-butyl-dimethyl-silanyloxy)-6-hydroxy-tetradeca-7,9-diene (**300**) and (7*Z*,9*E*,6*R*,12*R*)-14-benzyloxy-12-(*tert*-butyl-dimethyl-silanyloxy)-6-hydroxy-tetradeca-7,9-diene (**301**)



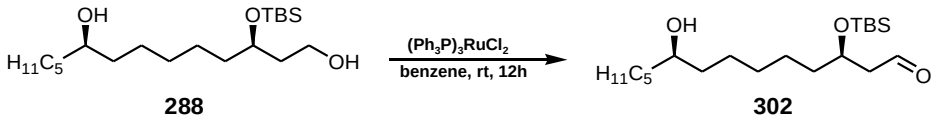
Dienes **299**, **300** and **301** were prepared according to **Error! Reference source not found.** (page Error! Bookmark not defined.) from iron lactone complex **289** (55 mg, 0.08 mmol, MW=672.66) in THF (1 ml) and lithium naphthalenide (5 eq., 0.41 mmol, 0.41 ml, 1M solution in THF, prepared according to **Error! Reference source not found.** (page **Error! Bookmark not defined.**)). Workup as described followed by flash column chromatography (eluent PE:Et_2O 5:1 to 1:1, gradient) afforded an inseparable mixture of dienes **299**, **300** and **301** (0.5: 0.2:0.3) as an oil (36 mg, 0.08 mmol, 98%); ν_{max} **(neat)/cm^{-1}**: 3358 (OH), 2927, 2855, 2079, 1973, 1455, 1361, 1252, 1092, 1043, 989, 835, 774, 734, 697; δ_H **(400 MHz, $CDCl_3$):** 0.05 (3H, s, Si(CH_3)), 0.08 (3H, s, Si(CH_3)), 0.84 (9H, s, SiC(CH_3)$_3$), 0.89 (3H, t, *J* 7.1, 1-H x 3), 1.21-1.63 (8H, m, 2-H x 2, 3-H x 2, 4-H x 2, 5-H x 2), 1.75 (2H, m, 11-H x 2), 2.26 (2H, m, 13-H x 2), 3.54 (1H, s, OH), 3.58 (1H, m, 12-H), 3.91 (0.5H, m, 6-H x 0.5), 4.12 (0.5H, m, 6-H x 0.5), 4.49 (2H, app. q, *J* 11.7, $CH_2C_6H_5$), 5.29 (0.3H, m, 7-H x 0.3), 5.49 (0.2H, m, 10-H x 0.2), 5.58 (0.5H, dd, *J* 15.0, 6.9, 7-H x 0.5), 5.69 (1H, m, 7-H x 0.2, 10-H x 0.8), 6.04 (1H, m, 8-H x 0.3, 9-H x 0.7), 6.17 (0.5H, dd, *J* 15.3 10.2, 8-H x 0.5), 6.32 (0.3H, dd, *J* 15.0 10.9, 9-H x 0.3), 6.44 (0.2H, dd, *J* 15.0 10.9, 8-H x 0.2), 7.24-7.38 (5H, m, $CH_2C_6H_5$); δ_C **(100 MHz, $CDCl_3$):** 138.5, 134.3, 131.9, 130.6, 128,3, 127.7, 127.4, 125.8, 72.9, 72.7, 69.2, 67.0, 41.2, 41.0, 37.4, 37.3, 36.9, 31.8, 25.8 (SiC(CH_3)$_3$), 25.1, 24.9, 22.6, 18.1 (SiC(CH_3)$_3$), 14.0, -4.3 (Si(CH_3)), -4.7 (Si(CH_3)); ***m/z*** **(ES)** Found: $[MH]^+$ 447.3267. $C_{27}H_{47}O_3Si$ requires *M*H, 447.3294.

1.6.13 Preparation of (3*R*,9*R*)-3-(*tert*-butyl-dimethyl-silanyloxy)-tetradecane-1,9-diol (**288**)



Alkene **288** was prepared according to **Error! Reference source not found.** (page Error! Bookmark not defined.) from diene mixture **299**, **300** and **301** (120 mg, 0.27 mmol, MW=446.74), Pd/C (1 eq., 10 wt.%, 0.27 mmol, 283 mg) under H_2 atmosphere in EtOAc (5 ml). After 12 h, workup as described followed by flash column chromatography (eluent PE:Et_2O 2:1 to 1:1, gradient) afforded alkene **288** as an oil (81 mg, 0.22 mmol, 83%); ν_{max} **(neat)/cm^{-1}**: 3394 (OH), 2928, 2856, 2370, 2358, 2299, 1462, 1254, 1059, 835, 773, 734, 661; δ_H **(400 MHz, $CDCl_3$):** 0.07 (3H, s, Si(CH_3)), 0.09 (3H, s, Si(CH_3)), 0.89 (9H, s, SiC(CH_3)$_3$), 0.89 (3H, t, *J* 7.1, 14-H x 3), 1.25-1.52 (18H, m, 4-H x 2, 5-H x 2, 6-H x 2, 7-H x 2, 8-H x 2, 10-H x 2, 11-H x 2, 12-H x 2, 13-H x 2), 1.65 (1H, m, 2-H), 1.81 (1H, m, 2-H'), 2.40 (2H, s, 1-OH, 9-OH), 3.58 (1H, m, 9-H), 3.70 (1H, m, 1-H), 3.83 (1H, m, 1-H'), 3.91 (1H, m, 3-H); δ_C **(100 MHz, $CDCl_3$):** 71.9, 71.8, 60.3, 37.7, 37.4, 37.3, 36.7, 31.9, 29.8, 25.8 (SiC(CH_3)$_3$), 25.5, 25.3, 25.3, 25.2, 22.6, 17.9 (SiC(CH_3)$_3$), 14.0, -4.4 (Si(CH_3)), -4.7 (Si(CH_3)); ***m/z*** **(+ES)** Found: $[MNa]^+$ 383.2966. $C_{20}H_{44}O_3SiNa$ requires *M*Na, 383.2957.

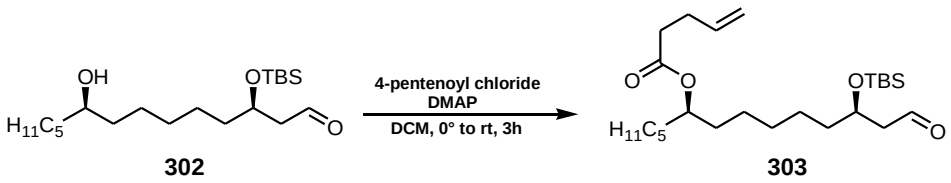
1.6.14 Preparation of (3*R*,9*R*)-3-(*tert*-butyl-dimethyl-silanyloxy)-9-hydroxy-tetradecanal (**302**)



288 **302**

A solution of diol **288** (70 mg, 0.19 mmol, MW=360.65) in benzene (3 ml) was added *via* cannula to a stirred solution of tris(triphenylphosphine)ruthenium dichloride (1 eq., 0.19 mmol, 186 mg, MW=958.85) in benzene (5 ml). The reaction mixture was stirred at rt for 12 h, then filtered through a pad of Florisil®. The residue was washed with Et_2O (3 x 50 ml). Concentration of the filtrate *in vacuo* followed by flash column chromatography (PE:Et_2O 1:1) afforded aldehyde **302** (53 mg, 0.15 mmol, 78%) as an oil; ν_{max} **(neat)/cm^{-1}**: 3432 (OH), 2928, 2857, 1725 (C=O), 1463, 1434, 1361, 1255, 1094, 1005, 938, 806, 744, 693; δ_H **(400 MHz, $CDCl_3$):** 0.07 (3H, s, Si(CH_3)), 0.09 (3H, s, Si(CH_3)), 0.89 (9H, s, SiC(CH_3)$_3$), 0.89 (3H, t, *J* 7.1, 14-H x 3), 1.19-1.61 (18H, m, 4-H x 2, 5-H x 2, 6-H x 2, 7-H x 2, 8-H x 2, 10-H x 2, 11-H x 2, 12-H x 2, 13-H x 2), 2.05 (1H, s, 9-OH), 2.51 (2H, m, 2-H x 2), 3.58 (1H, m, 9-H), 4.17 (1H, quint., *J* 5.5, 3-H), 9.81 (1H, t, *J* 2.2, 1-H); δ_C **(100 MHz, $CDCl_3$):** 202.3 (C=O), 71.9, 68.2, 50.8, 37.7, 37.4, 37.3, 34.2, 31.8, 30.3, 29.6, 25.7 (SiC(CH_3)$_3$), 25.5, 25.3, 25.1, 22.6, 18.0 (SiC(CH_3)$_3$), 14.0, -4.5 (Si(CH_3)), -4.7 (Si(CH_3)); ***m/z*** **(+ES)** Found: $[MNa]^+$ 381.2803. $C_{20}H_{42}O_3SiNa$ requires *M*Na, 381.2801; $[\alpha]_D^{25}$ -2.6 (*c* 0.75 in $CHCl_3$).

1.6.15 Preparation of (3*R*,9*R*)-3-(*tert*-butyl-dimethyl-silanyloxy)-tetradecanal-9-yl pent-4'-enoate (**303**)

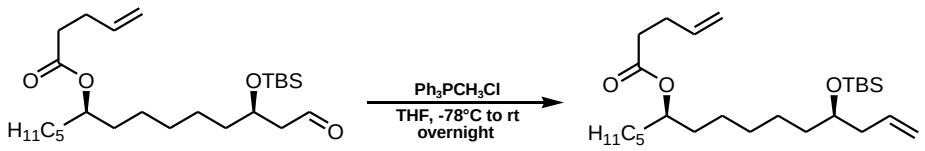


302 **303**

4-Pentenoyl chloride (2 eq., 14.5 mg, 13.5 μl, MW=118.56, d=1.074) was added to aldehyde **302** (22 mg, 0.061 mmol, MW=358.63) and DMAP (3 eq., 0.18 mmol, 22.3 mg, MW=122.17) in DCM (2 ml) at 0°C. The reaction mixture was stirred and allowed to warm to rt over 3 h, then filtered through a pad of Florisil®. The residue was washed with Et_2O (3 x 10 ml). Concentration of the filtrate *in vacuo* followed by flash column chromatography (PE:Et_2O 9:1 to 2:1) afforded ester **303** (5.3 mg, 0.012 mmol, 30% conversion, 65% yield) as an oil*; **δ_H (400 MHz, $CDCl_3$):** 0.07 (3H, s, $Si(CH_3)$), 0.09 (3H, s, $Si(CH_3)$), 0.89-0.94 (12H, s, $SiC(CH_3)_3$, 14-H x 3), 1.23-1.69 (18H, m, 4-H x 2, 5-H x 2, 6-H x 2, 7-H x 2, 8-H x 2, 10-H x 2, 11-H x 2, 12-H x 2, 13-H x 2), 2.30 (4H, m, 2'-H x 2, 3'-H x 2), 2.43 (2H, m, 2-H x 2), 4.08 (1H, app. t, *J* 5.5, 9-H), 4.79 (1H, quint., *J* 5.2, 3-H), 4.95 (2H, app. q, 5'-H x 2), 5.75 (1H, m, 4'-H), 9.78 (1H, t, *J* 2.2, 1-H.

* Due to the instability of the aldehyde it was used immediately in the following reaction. IR, ^{13}C NMR data, MS and OR data were not obtained on this unstable aldehyde.

1.6.16 Preparation of (4*R*,10*R*)-4-(*tert*-butyl-dimethyl-silanyloxy)-pentadec-1-en-10-yl pent-4'-enoate (**262**)



303 **262**

Methyltriphenylphosphonium chloride* (0.2 mmol, 63 mg, MW=312.78) was deprotonated by stirring with ^{n}BuLi (1M in THF, 0.19 mmol, 190 μl) in THF (2 ml) at rt for 30 min. The pre-cooled (-78°C) ylid (3.0 eq., 37.4 μmol, 11.7 mg) was then added to aldehyde **303** (5.3 mg, 12 μmol, MW=440.74) in THF (1 ml) at -78°C. The reaction mixture was stirred and allowed to warm to rt overnight, then filtered through a pad of Florisil®. The residue was washed with Et_2O (3 x 5 ml). Concentration of the filtrate *in vacuo* followed by flash column chromatography (PE:Et_2O 40:2 to 40:3) afforded diene **262** (4.2 mg, 9.6 μmol, 77%) as an oil; ν_{max} **(neat)/cm^{-1}**: 2928, 2858, 1735 (C=O), 1255, 1093, 835, 822; δ_H **(400 MHz, $CDCl_3$):** 0.07 (3H, s, Si(CH_3)), 0.09 (3H, s, Si(CH_3)), 0.79-0.89 (12H, s, SiC(CH_3)$_3$, 15-H x 3), 1.21-1.50 (18H, m, 5-H x 2, 6-H x 2, 7-H x 2, 8-H x 2, 9-H x 2, 11-H x 2, 12-H x 2, 13-H x 2, 14-H x 2), 2.15 (2H, t, *J* 6.8, 3-H x 2), 2.29-2.35 (4H, m, 2'-H x 2, 3'-H x 2), 3.61 (1H, quint., *J* 5.5, 4-H), 4.80 (1H, quint., *J* 6.1, 10-H), 4.98-5.11 (4H, m, 1-H x 2, 5'-H x 2), 5.65-5.80 (2H, m, 2-H, 4'-H); δ_C **(100 MHz, $CDCl_3$):** 172.9 (C=O), 136.8 (C=C), 135.4 (C=C), 116.6 (C=C), 115.4 (C=C), 74.3, 71.9, 41.9, 36.7, 34.0, 33.8, 31.7, 29.7, 29.6, 29.0, 25.9

* Methyltriphenylphosphonium chloride was dried *prior* to use by dissolving it in little toluene and concentration *in vacuo* (2 x) and leaving it on a high vacuum pump overnight.

(SiC(CH$_3$)$_3$), 25.3, 25.2, 24.9, 22.5, 18.1 (SiC(CH$_3$)$_3$), 14.0, 13.9, 1.0, -4.4 (Si(CH$_3$)), -4.5 (Si(CH$_3$)); ***m/z* (+ES)** Found: [MNa]$^+$ 461.3431. $C_{26}H_{50}O_3SiNa$ requires *M*Na, 461.3427; $[\alpha]_D^{25}$ +10.5 (*c* 0.1 in $CHCl_3$). Data was consistent with those reported in the literature.[127]