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Application of Propargylic 1,3-Substitution and Cyclopropylidene-Allenyl Transformations to the Synthesis of η^4-Fe(CO)3-Complexed γ-Dienylallenes

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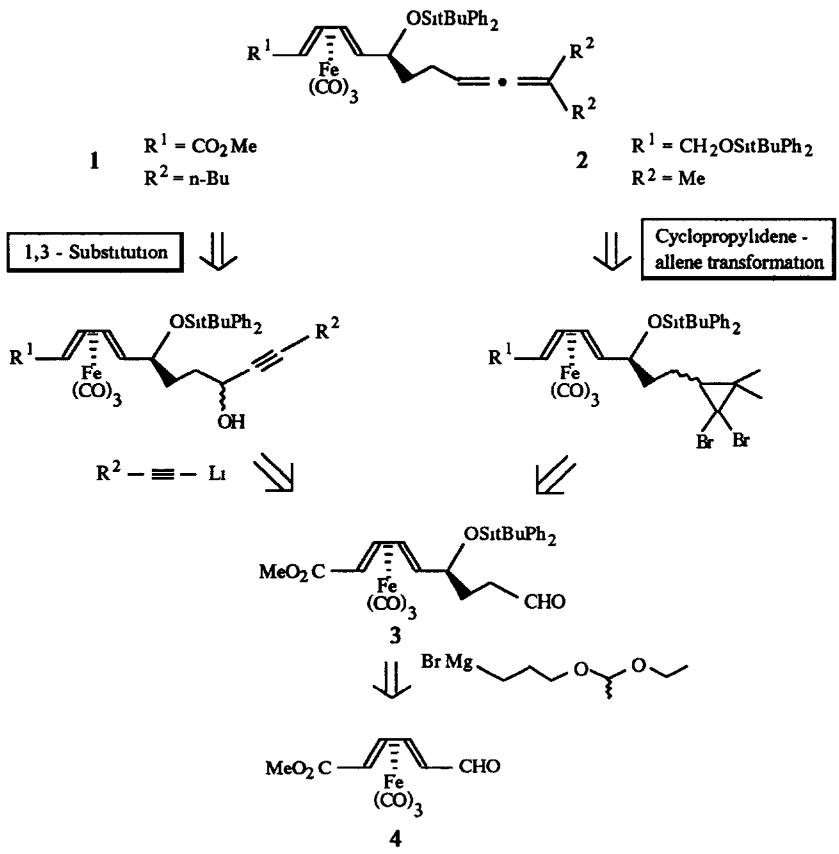
Abstract . *An allene functionality was successfully introduced in the presence of an organometallic butadienyl-Fe(CO)3 moiety by the use of two classical methods Both 1,3-substitution of propargylic mesylates by organocopper(I) reagents and cyclopropylidene-allene transformation were found applicable thus allowing the synthesis of* η^4*-dienyl Fe(CO)3-complexed γ-dienylallenes in good overall yields*

INTRODUCTION

During the last two decades, the evaluation of the synthetic potential of (η^4-diene)Fe(CO)3 complexes has resulted in numerous examples of their utilisations in organic synthesis [1,2] Due to their ease of preparation, their chiral properties and the facile removal of the Fe(CO)3 group, the (η^4-diene)Fe(CO)3 complexes are frequently applied in stereocontrolled syntheses leading to enantiomerically pure, acyclic polyenic compounds [2] In this context, we investigated how allenes could be prepared in the presence of the butadiene-tricarbonyliron moiety In a first part of this programme, the synthesis of various allenes *vicinal* to such (η^4-diene)Fe(CO)3 complexes was achieved using two independent routes the first involved 1,3-substitution of suitable propargylic derivatives by organocopper(I) reagents,[3] another subsequent method relied on the chemistry of cyclopentadienyl-tricarbonyliron cations [4] The purpose of our present study was to determine how an allenic group could be introduced *in a more remote position* with regard to such an organometallic moiety Therefore, the application of classical methods for allene preparation was investigated for the synthesis of model (η^4-diene)Fe(CO)3 complexed γ-dienylallenes Among these methods, the propargyl-allene transformation is the most widely applicable since the introduction of various substituents is not only allowed but this transformation is also stereoselective leading to *anti*-configurated products [5] Another method that we envisaged was the cyclopropylidene-allene transformation Addition of dibromocarbene to an olefin gives an intermediate geminal dibromocyclopropane[6] which gives an allene upon metal-halogen exchange using methyllithium [7,8]

In our retrosynthetic approach (Scheme 1),[9] to the desired (η^4-diene)Fe(CO)3 complexed γ-dienylallenes 1 and 2, the aldehyde 3 arises as a common key intermediate via the two proposed routes In order to avoid any additional chiral unit, two equal groups R^2 were selected on the terminal carbon (C_{11}) of the allene moiety The key aldehyde 3 should be available from reaction of the known complex 4[10] with a ω-functionalized 1-propylmagnesium reagent

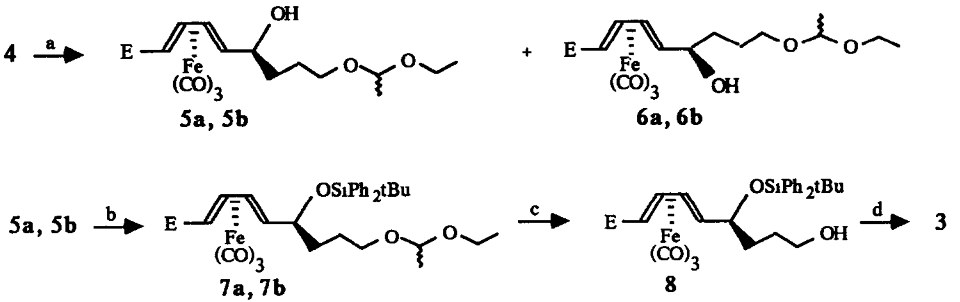


Scheme 1

RESULTS

Synthesis of 1 via a propargyl 1,3-substitution

The carbon lateral chain was introduced by reacting the aldehyde 4 with 3-(1-ethoxy)ethoxypropylmagnesium bromide [11] It afforded ψ-exo and ψ-endo alcohols[12] in respectively 72 and 15% yield after easy separation by chromatography on silica gel (Scheme 2) Each of these diastereoisomers was isolated as a mixture of both (1-ethoxy)ethoxy epimers **5a**,**5b** for the ψ-exo alcohols and **6a**,**6b** for the ψ-endo alcohols Further elaboration to the key intermediate 3 was accomplished using standard reactions Protection of the secondary alcohol group of the ψ-exo epimers **5a**,**5b** by *tert*-butyldiphenylsilyl chloride in the presence of imidazole afforded silyl ethers **7a**,**7b** Selective cleavage of the acetal moiety by trichloroacetic acid in aqueous THF afforded the monoprotected diol **8** Oxidation of the free alcohol group was accomplished using a reagent combination (*n*-PrMgBr/ ADD) which had previously proved suitable for such organometallic substrates,[13] providing the desired aldehyde 3



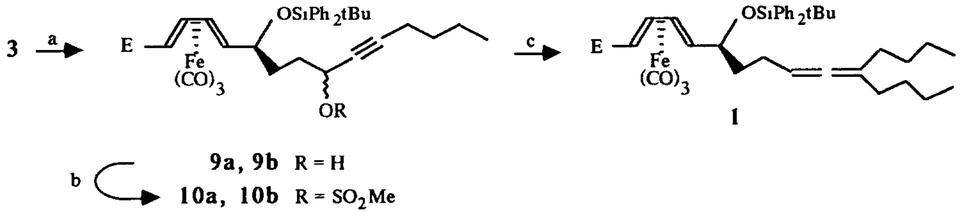
E = CO_2Me

(a) BrMg $(CH_2)_3OCH(OEt)CH_3$, THF, -40°, 2h (72 % of **5a**, 15 % of **5b**) (b) $tBuPh_2SiCl$, imidazole, DMF, 6°, 18 h, 79 % (c) Cl_3CCO_2H, THF/H_2O 2:1, rt, 66 h, 92 % (d) *n*-PrMgBr, ADD, THF, 0°, 30 mn, 77 %

Scheme 2

The propargyl-allene transformation via a 1,3-substitution process was investigated by the study of the selected synthesis of allene **1**. Reaction of aldehyde **3** with 1.2 equivalents of 1-lithiohex-1-yne in the presence of 1.2 equivalents of lithium bromide in THF afforded a non-separable mixture of C_9 epimeric propargylic alcohols **9a** and **9b** (Scheme 3). Mesylation by methanesulfonyl chloride and triethylamine in dichloromethane afforded the rather unstable C_9 epimeric mesylates **10a** and **10b** which were purified by chromatography on silica gel in the presence of triethylamine. Mesylates **10a,b** could be stored in the presence of Et_3N at -30°C for some days with the risk of minor decomposition. In order to avoid any decomposition, these mesylates were usually employed in the 1,3-substitution reaction immediately after isolation. Reaction of **10a,b** with (*n*-BuCuBr)MgBr LiBr at -60 to -50°C gave the expected stable allene **1** as a single isomer. Its structure was confirmed spectroscopically. In particular, ^{13}C NMR spectrum (in $CDCl_3$) showed characteristic resonances of the allene unit, namely that of the central carbon C_{10} at 200.68 ppm and those of the external carbons C_9 and C_{11} respectively at 91.07 and 105.13 ppm. Interestingly, mass spectrum under electronic impact showed two intense characteristic peaks at m/z = 614 (M^+ - 3 CO) and m/z = 358 (M^+ - 3 CO - $^tBuPh_2SiOH$). A weak signal (2%) was also observed at m/z = 667 (M^+ - OCH_3).

The synthesis of allene **1** demonstrates that the allene functionality can be chemoselectively introduced, via a propargyl 1,3-substitution, in a remote position with regard to a butadiene-tricarbonyliron complex.



E = CO_2Me

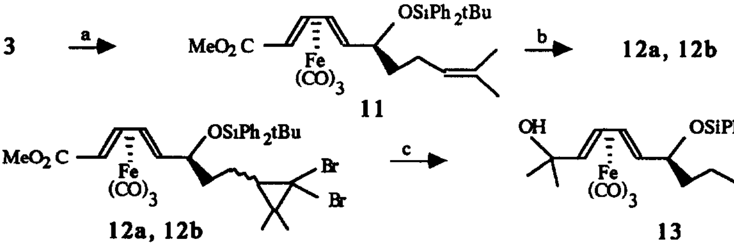
(a) Li $C{\equiv}C(CH_2)_3CH_3$, LiBr, THF, -78°, 90 mn, 80 % (b) $MeSO_2Cl$, Et_3N, CH_2Cl_2, -50°, 1 h then warming to rt in 30 mn, 96 % (c) (*n*-BuCuBr) MgBr·LiBr, THF, -60 to -50°, 1 h then warming to rt in 30 mn, 75 %

Scheme 3

Synthesis of 2 via a cyclopropylidene-allene transformation

For the investigation of the cyclopropylidene-allene transformation, we introduced the required additional non-complexed double bond by reaction of aldehyde 3 and isopropylidenetriphenylphosphorane (Scheme 4) Addition of dibromocarbene, generated under phase-transfer conditions ($HCBr_3$, NaOH, Et_3BzNCl)[14], to the free double bond of 11 gave rather unstable dibromocyclopropanes as a mixture of C_1 cyclopropyl epimers **12a** and **12b**

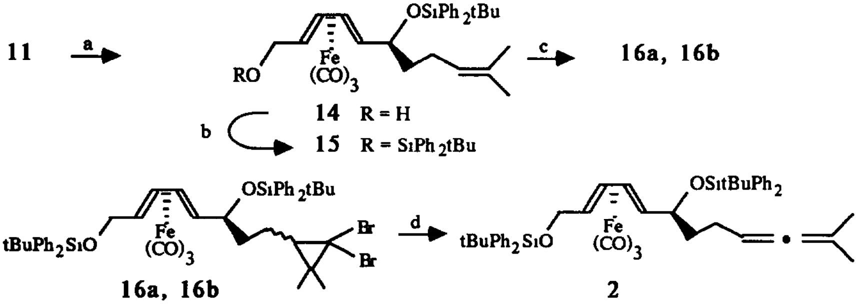
Conversion of dibromocyclopropanes to allenes was shown to be achieved more effectively by using methyllithium than by other reagents (Mg or Na,[7] *n*-butyllithium[8]) However, it appeared that the metal-halogen exchange by MeLi and the addition of MeLi to the ester function of **12a,b** at -70°C have similar rates In this attempt, the reduced allene 13 was isolated in 29% yield after purification on silica gel



(a) $Ph_3P{=}C(CH_3)_2$, THF, 0° to rt, 45 min, 70 % (b) $CHBr_3$, 50 % aq NaOH, $PhCH_2NEt_3Cl$, rt, 70 min, 77% (c) Me Li, Et_2O, -70°, 1 h, 29 %

Scheme 4

In order to avoid selectivity problems, the ester group was converted to a protected hydroxyl function by reduction (Dibal, ether, 96%) to primary alcohol 14 and subsequent silylation (t-$BuPh_2SiCl$, imidazole, 84%) thus affording silyl ether 15 (Scheme 5). Addition of dibromocarbene, generated under phase-transfer conditions, afforded a mixture of epimeric gem-dibromocyclopropanes **16a** and **16b** (62%) and recovered starting olefin 15 (34%). These rather unstable dibromo-compounds readily underwent the MeLi-induced cyclopropylidene-allene transformation at -70°C to provide η^4-dienyl($Fe(CO)_3$)-complexed γ-dienylallene 2 in 73% yield Its structure was confirmed by examination of NMR and MS data although allene 2 was shown to be contaminated by small amounts of non-polar by-products which could not be separated chromatographically



(a) DIBAL-H, Et_2O, -45°, 20 min, 96 % (b) $tBuPh_2SiCl$, imidazole, DMF, 6°, 18 h, 84 % (c) $CHBr_3$, 50 % aq NaOH, $PhCH_2NEt_3Cl$, rt, 85 min, 62 % (d) MeLi, Et_2O, -70°, 1 h then warming to rt in 2 h, 73 %

Scheme 5

These results demonstrate that the allene function can also be introduced in a remote position with regard to a diene-tricarbonyliron complex in good yield providing that no other functionalities interfere with MeLi. In the case of allene 13 such interference is demonstrated by observation of a reduced yield.

CONCLUSION

The reaction of propargylic esters with organocopper(I) reagents and the metal-halogen exchange induced cyclopropylidene-allene transformation are readily applicable to the generation of two cumulated double bonds in presence of the organometallic butadienyl-Fe(CO)$_3$ moiety. None of the investigated reaction conditions interfere with the organometallic moiety, thus allowing the straightforward synthesis of η^4-dienyl(Fe(CO)$_3$)-complexed γ-dienylallenes in good overall yields The elaborated synthetic route represents another interesting example of the utilisation of diene-tricarbonyliron complexes for the preparation of polyenic systems which should be prone, for instance, to intramolecular reactions.

EXPERIMENTAL SECTION

General Infrared spectra were recorded on Beckman Acculab 1,3 and 8 spectrometers Nuclear magnetic resonance spectra were obtained on a Jeol FX-90Q, a Bruker AM 300 WB or a Jeol JNM-GX 400 instrument, in CDCl$_3$ solution Chemical shifts were referenced to Me$_4$Si Mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded under electronic impact at 70 eV using respectively a Varian MAT CH-48 and a Varian MAT 311 spectrometer UV spectra were recorded on a Beckman DU-64 instrument. Elemental analyses were performed on a Heraeus CHN elemental analyzer

(2R*,5S*,6S*,9(1RS))-(2E,4E)-Tricarbonyliron [Methyl (η^4-2,5)-9-(1-ethoxy)ethoxy-6-hydroxynona-2,4-dienoate] **(5a,5b)**, *(2R*,5S*,6R*,9(1RS))-(2E,4E)-Tricarbonyliron [Methyl (η^4-2,5)-9-(1-ethoxy)ethoxy-6-hydroxynona-2,4-dienoate]* **(6a,6b)**

To magnesium turnings (870 mg, 35 7 mmol, 8 9 equiv) suspended in THF (8 mL) was added a few drops of 1-bromo-3-(1-ethoxyethoxy)propane. The reaction was initiated with ultrasound Then, the remaining of the bromide (2 8 g overall, 13 2 mmol, 3 3 equiv) was added dropwise and stirring was continued for further 1 hour The resulting Grignard solution was cooled down to -40°C and a solution of aldehyde 4 (1.12 g, 4 0 mmol) in THF (20 mL) was added dropwise After 2 hours stirring at -40°C, the reaction mixture was quenched by adding 25% aqueous ammonium chloride and extracted twice with ether Combined organic phases were washed with 1 M aqueous sodium bicarbonate, dried over MgSO$_4$ and concentrated Chromatography of the residue on silica gel using ether/petroleum ether 1 4 sequentially afforded the ψ-endo (249 mg, 15%, Rf = 0 42 with ether/petroleum ether 7 3) and ψ-exo (1 18 g, 72%, Rf = 0 20 with ether/petroleum ether 7 3) isomers **6a,6b** and **5a,5b** as yellow oils

ψ-endo isomer (mixture of both (1-ethoxy)ethoxy epimers) **(6a,6b)** IR (neat) 3450 (OH), 2060 and 1980 (C=O), 1720 and 1710 (C=O) cm^{-1}, ^{1}H NMR (400 MHz, CDCl$_3$) δ 0 94 (d, 1H, J = 8 2 Hz), 1 20 (m, 3H), [1 30 (d, J = 5 2 Hz), 1 31 (d, J = 5 Hz), 3H], 1 37 (dd, 1H, J = 8.7, 6 0 Hz, 1 44 - 1 87 (m, 4H), 3 02 (broad m, 1H), 3 39 - 3 53 (m, 2H), 3 66 (s, 3H), 3 58 - 3 77 (m, 3H), 4 65 - 4 73 (m, 1H), 5 43 - 5 49 (m, 1H), 5 82 (dd, 1H, J = 8 2, 5 3 Hz), ^{13}C NMR (100 MHz, CDCl$_3$) δ 15 27 and 15 30 ($CH_2\underline{C}H_3$), 19 69 and 19 79 ($CH\underline{C}H_3$), 26 69 and 26 72 (C_8), 38 33 and 38 36 (C_7), 45 51 (C_2), 51.64 ($O\underline{C}H_3$), 60 93 and 60 97 ($\underline{C}H_2CH_3$), 65 03 and 65 17 (C_9), 70 57 (C_5), 72 31 and 72.36 (C_6), 82 80 (C_4), 84 02 (C_3), 99 65 and

99 76 ($\underline{C}HCH_3$), 172.71 (C_1) , MS m/z· 381 (M^+-OCH_3), 367 (M^+-OEt), 356 (M^+-2 CO), 328 (M^+-3 CO), 323 (M^+-$CH_3CH(O)OEt$), 283 (M^+-3 CO-OEt), 238 (M^+-3 CO-$CH_3CH(OH)OEt$, base peak), 73, 45 Anal Calcd. for $C_{17}H_{24}O_8Fe$ C, 49.54; H, 5 83. Found· C, 49 70; H, 5 95

ψ-exo isomer (mixture of both (1-ethoxy)ethoxy epimers) (**5a**,**5b**). IR (neat) 3450 (OH), 2060 and 1980 (C=O), 1715 (C=O) cm^{-1} , ^1H NMR (400 MHz, $CDCl_3$) δ 1 04 (d, 1H, J = 8 2 Hz), 1 21 (t, 3H, J = 7.2 Hz), ≈1.3 (m, 1H), 1.31 (d, 3H, J = 5 5 Hz), 1 59 - 1 91 (m, 4H), 3 27 (m, 1H), 3.55 - 3 72 (m, 3H), 3 66 (s, 3H), 4.67 - 4.73 (m, 1H), 5 52 (dd, 1H, J = 8 6, 5 1 Hz), 5 84 (dd, 1H, J = 8 2, 5 1 Hz) , ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.29 ($CH_2\underline{C}H_3$), 19.73 and 19.76 ($CH\underline{C}H_3$), 25.94 and 25.99 (C_8), 36 52 and 36 61 (C_7), 45 05 (C_2), 51 72 ($O\underline{C}H_3$), 61.02 and 61.08 ($\underline{C}H_2CH_3$), 65 09 and 65 21 (C_9), 67 21 and 67 24 (C_5), 72 71 and 72.75 (C_6), 83.94 (C_3), 85 46 (C_4), 99.74 and 99 77 ($\underline{C}HCH_3$), 172.59 (C_1) ; MS m/z 421 (M^+), 381 (M^+-OCH_3), 367 (M^+-OEt), 356 (M^+-2 CO), 328 (M^+-3 CO), 323 (M^+-$CH_3CH(O)OEt$), 283 (M^+-3 CO-OEt), 238 (M^+-3 CO-$CH_3CH(OH)OEt$, base peak), 73, 45 Anal Calcd for $C_{17}H_{24}O_8Fe$· C, 49.54; H, 5 83. Found C, 49.34, H, 6 09

(2R*,5S*,6S*,9(1RS))-(2E,4E)-Tricarbonyliron [Methyl (η^4-2,5)-9-(1-ethoxy)ethoxy-6-t-butyldiphenylsilyloxy-nona-2,4-dienoate] (**7a**,**7b**)

Imidazole (680 mg, 10 0 mmol, 4 0 equiv) followed by t-butylchlorodiphenylsilane (1 29 mL, 5 0 mmol, 2 0 equiv) were added to a cooled solution of alcohols **5a**,**5b** (1 05 g, 2 5 mmol) in anhydrous DMF (8 mL) at 0°C After 18 hours leaving aside at 6°C, the reaction mixture was diluted with 1 M aqueous $NaHCO_3$ and then extracted three times with ether Combined organic phases were washed with brine, dried ($MgSO_4$) and concentrated Chromatography of the residue on silica gel using ether/petroleum ether 1.9 afforded a yellow oil (1 94 g, Rf = 0 42 with ether/petroleum ether 3:7) whose NMR indicated that it was a 5:6 molar ratio of expected silyl ethers **7a**,**7b** and *t*-butyldiphenylsilanol (characteristic odour) That gave a 79% estimated yield of **7a**,**7b** An analytically pure sample of **7a**,**7b** was obtained by chromatography on basic (pH = 9 7) alumina A partial decomposition resulted either using basic or neutral (pH = 7 00) alumina ^1H NMR (400 MHz, $CDCl_3$) δ 0 97 (d, 1H, J = 8 2 Hz), 1.03 (s, 9H), [1 21 (t, J = 7 2 Hz), 1 21 (t, J = 7 0 Hz), 3H], 1 31 (d, 3H, J = 5 5 Hz), 1 32 (m, 1H), 1 62 - 1 91 (m, 4H), 3 39 - 3 69 (m, 5H), 3 62 (s, 3H), 4 42 (dd, 1H, J = 8 6, 5 1 Hz), [4 69 (q, J = 5 5 Hz), 4 69 (q, J = 5 5 Hz), 1H], 5 40 (dd, 1H, J = 8 2, 5.1 Hz), 7 36 - 7 45 (m, 6H), 7 66 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 15 33 ($CH_2\underline{C}H_3$), 19 45 ($\underline{C}(CH_3)_3$), 19 84 ($CH\underline{C}H_3$), 24 99 (C_8), 26 94 ($C(\underline{C}H_3)_3$), 35 76 and 35 87 (C_7), 46 30 (C_2), 51 67 ($O\underline{C}H_3$), 60 60 and 60 64 ($\underline{C}H_2CH_3$), 64 97 and 65 00 (C_9), 65 97 (C_5), 75 15 and 75 20 (C_6), 83 42 (C_3), 86 49 (C_4), 99 48 ($\underline{C}HCH_3$), 127 58 and 127 79 (4C ortho), 129 81 and 129 93 (2C para), 133 64 and 134 05 (2C ipso), 135 96 and 136 16 (4C ortho), 172 37 (C_1), MS m/z 650 (M^+), 619 (M^+-OCH_3), 594 (M^+-2 CO), 566 (M^+-3 CO), 238 (M^+-3 CO-$CH_3CH(OEt)OSi$t-BuPh_2, base peak), 73, 45 Anal Calcd for $C_{33}H_{42}O_8FeSi$ C, 60 92, H, 6 46 Found C, 61 16, H, 6 41

(2R*,5S*,6S*)-(2E,4E)-Tricarbonyliron [Methyl (η^4-2,5)-6-t-butyldiphenylsilyloxy-9-hydroxynona-2,4-dienoate] (**8**)

Trichloroacetic acid (150 mg, 0 92 mmol, 1 4 equiv) was added to a solution of the previously obtained mixture of acetals **7a**,**7b** and silanol (635 mg, ≈ 430 mg contained **7a**,**7b**, 0 66 mmol) in THF (20 mL) and water (10 mL). After 66 hours, 1 M aqueous $NaHCO_3$ was added and the resulting mixture was extracted three times with ether. Combined organic phases were washed with brine, dried ($MgSO_4$) and concentrated. Chromatography on silica gel using ether/petroleum ether 3:7 as eluent afforded alcohol **8** as a yellow oil (352 mg, 92%, Rf = 0.12 with ether/petroleum ether 3:7). IR (neat): 3400 (OH), 2060 and 1980 (C=O), 1710 (C=O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01 (d, 1H, J = 8.2 Hz), 1.35 (dd, 1H, J = 9.4, 8.7 Hz), 1.70 (broad s, 1H), 1.68 - 1.88 (m, 4H), 3.54 (ddd, 1H, J = 9.4, 5.7, 3.6 Hz), 3.62 - 3.67 (m, 2H), 3.63 (s, 3H), 4.44 (dd, 1H, J = 8.7, 5.1 Hz), 5.42 (ddd, 1H, J = 8.2, 5.1, 0.8 Hz), 7.37 - 7.46 (m, 6H), 7.67 - 7.70 (m, 4H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.41 ($\underline{C}(CH_3)_3$), 26.94 ($C(\underline{C}H_3)_3$), 27.73 (C_8), 35.43 (C_7), 46.39 (C_2), 51.70 ($O\underline{C}H_3$), 62.87 (C_9), 65.38 (C_5), 75.14 (C_6), 83.61 (C_3), 86.54 (C_4), 127.64 and 127.87 (4C meta), 129.92 and 130.05 (2C para), 133.45 and 133.83 (2C ipso), 135.96 and 136.19 (4C ortho), 172.37 (C_1)

(2R*,5S*,6S*)-(2E,4E)-Tricarbonyliron [Methyl (η^4-2,5)-6-t-butyldiphenylsilyloxy-9-oxonona-2,4-dienoate] **(3)**

A solution of *n*-propylmagnesium bromide [prepared by reacting magnesium turnings (18 mg, 0.75 mmol, 1.25 equiv) with 1-bromopropane (0.071 mL, 0.78 mmol, 1.3 equiv) in THF (2 mL)] was added dropwise to a stirred solution of alcohol **8** (347 mg, 0.60 mmol) in THF (2.4 mL) cooled at 0°C. After 10 min at 0°C, a solution of 1,1'(Azodicarbonyl)dipiperidine (ADD) (182 mg, 0.72 mmol, 1.2 equiv) in THF (1.6 mL) was added. After 20 min further reaction at 0°C, the resulting mixture was quenched by addition of brine and extracted twice with ether. Combined organic phases were washed with 1 M aqueous $NaHCO_3$ and then with water. Drying ($MgSO_4$), concentration and chromatography on silica gel using ether/petroleum ether 1:9 as eluent afforded aldehyde **3** as a yellow oil (265 mg, 77%, Rf = 0.37 with ether/petroleum ether 3:7). IR (neat): 2740 (C-H of CHO), 2060 and 1980 (C=O), 1720 (C=O) cm^{-1}, ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (d, 1H, J = 8.2 Hz), 1.02 (s, 9H), 1.23 (dd, 1H, J = 9, 8.8 Hz), 1.91 (dtd, 1H, J = 14, 8, ≈6.5 Hz), 2.11 (dtd, 1H, J = 14, 8, 3 Hz), 2.63 - 2.77 (m, 2H), 3.57 (ddd, 1H, J = 9, ≈6.5, 3 Hz), 3.62 (s, 3H), 4.38 (dd, 1H, J = 8.8, 4.9 Hz), 5.39 (dd, 1H, J = 8.2, 4.9 Hz), 7.36 - 7.48 (m, 6H), 9.80 (s, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.34 ($\underline{C}(CH_3)_3$), 26.86 ($C(\underline{C}H_3)_3$), 31.48 (C_8), 39.24 (C_7), 46.45 (C_2), 51.65 ($O\underline{C}H_3$), 64.83 (C_5), 74.44 (C_6), 83.45 (C_3), 86.31 (C_4), 127.62 (2C meta), 127.91 (2C meta), 129.91 (C para), 130.10 (C para), 133.15 (C ipso), 133.62 (C ipso), 135.80 (2C ortho), 136.09 (2C ortho), 172.16 (C_1), 201.62 (C_9), MS m/z 545 (M^+-OCH_3), 520 (M^+-2 CO), 492 (M^+-3 CO), 449, 435 (M^+-3 CO-^{t}Bu), 255, 236 (M^+-3 CO-$^tBuPh_2SiOH$, base peak), 199 (Ph_2SiOH^+), 107, 79. Anal. Calcd for $C_{29}H_{32}O_7FeSi$: C, 60.42, H, 5.60. Found: C, 60.52, H, 5.84.

(2R*,5S*,6S*,9RS)-(2E,4E)-Tricarbonyliron [Methyl (η^4-2,5)-6-t-butyldiphenylsilyloxy-9-hydroxypentadeca-2,4-dien-10-ynoate] **(9a,9b)**

A 1.6 M solution of *n*-butyllithium in hexanes (1.56 mL, 2.50 mmol, 1.25 equiv) was added dropwise to a cooled solution at -78°C of 1-hexyne (0.28 mL, 2.4 mmol, 1.2 equiv) in THF (2 mL). After 45 min at -78°C, anhydrous lithium bromide (0.21 g, 2.4 mmol, 1.2 equiv) was added. After a further 10 min reaction at -78°C, the resulting lithium reagent was transfered and added dropwise to a cooled solution at -78°C of aldehyde **3** (1.16 g, 2.0 mmol) in THF (2 mL). After 90 min additional reaction at -78°C, the reaction mixture was poured into 25% aqueous NH_4Cl (30 mL) and extracted twice with ether. Combined organic phases were washed with brine, dried ($MgSO_4$) and concentrated. Chromatography of the oily residue on silica gel using ether/petroleum ether 1:9 and then 1:4 afforded alcohols **9a**,**9b** (mixture of two unseparable C_9 epimers) as a yellow oil (1 05 g, 80%, Rf = 0.22 with ether/petroleum ether 3.7). IR (neat). 3500 (OH), 2240 (C=C), 2060 and 1980 (C=O), 1715 and 1705 (C=O) cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0 92 (t, 3H, J = 7 2 Hz), 1.00 (d, 1H, J = 8.2 Hz), 1 04 (s, 9H), [1.32 (dd, J = 9, 9 Hz), 1 33 (dd, J = 9, 9 Hz), 1H], 1 38 - 1.54 (m, 4H), 1.73 - 2.01 (m, 4H), [2.04 (d, J = 5.2 Hz), 2.13 (d, J = 6.1 Hz), 1H], 2.23 (tt, 2H, J = 7.0, 1.8 Hz), 3.52 - 3.58 (m, 1H), [3.62 (s), 3.63 (s), 3H], 4.36 - 4 42 (m, 2H), 5.37 - 5.42 (m, 1H), 7.36 - 7.47 (m, 6H), 7 67 - 7 72 (m, 4H) , ^{13}C NMR (100 MHz, $CDCl_3$) δ 13 63 (C_{15}), 18 40 (C_{12}), 19 43 ($\underline{C}(CH_3)_3$), 21 98 (C_{14}), 26 95 ($C(\underline{C}H_3)_3$), 30 74 (C_{13}), 33.08 and 33 20 (C_8), 34.49 and 34.74 (C_7), 46.33 (C_2), 51 70 ($O\underline{C}H_3$), 62 49 and 62.74 (C_9), 65 39 (C_5), 75.08 (C_6), 80.83 and 80 97 (C_{10} or C_{11}), 83.55 and 83 58 (C_3), 85 85 and 85.90 (C_{10} or C_{11}), 86.46 and 86.51 (C_4), 127.64 and 127 85 (C meta), 129 84 and 130 02 (C para), 133 44 and 133.90 (C ipso), 135.99 and 136 19 (C ortho), 172 38 (C_1) , MS m/z 627 (M^+-OCH_3), 602 (M^+-2 CO), 574 (M^+-3 CO), 492 (M^+-3 CO-C_6H_{10}), 435 (M^+-3 CO-C_6H_{11}-^{t}Bu), 318 (M^+-3 CO-$^{t}BuPh_2SiOH$, base peak), 255, 236, 199 (Ph_2SiOH^+), 107, 79. Anal. Calcd. for $C_{35}H_{42}O_7FeSi$ C, 63 83, H, 6 43 Found C, 64.34, H, 6 37

(2R,5S*,6S*)-(2E,4E)-Tricarbonyliron [Methyl (η⁴-2,5)-11-n-butyl-6-t-butyldiphenylsilyloxypentadeca-2,4,9,10-tetraenoate]* (**1**)

Methanesulfonyl chloride (0 11 mL, 1 42 mmol, 1 7 equiv) was added to a cooled solution at -50°C of alcohols **9a**,**9b** (562 mg, 0 85 mmol) and triethylamine (0.22 mL, 1.58 mmol, 1 9 equiv) in anhydrous dichloromethane (6 mL). After 1 hour at -50°C, the reaction mixture was allowed to warm up to room temperature in 30 min. Water was added and the resulting mixture was extracted three times with ether Combined organic phases were successively washed with brine and water, dried ($MgSO_4$) and concentrated Chromatography on silica gel using ether/petroleum ether 1.4 + 3% Et_3N afforded purified mesylates **10a**,**b** as a yellow oil (602 mg, 96%, Rf = 0 30 with ether/petroleum ether 3.7). They were immediately used for the subsequent step since a small decomposition was observed when these mesylates were stored for some days at -30°C with some triethylamine. IR (neat). 2260 (C=C), 2070 and 1980 (C=O), 1720 (C=O) cm^{-1} , ^{1}H NMR (60 MHz, $CDCl_3$) δ 0 8 - 2.5 (m, 15H), 1 0 (s, 9H), 3 1 (s, 3H), 3.55 (m, 1H), 3 6 (s, 3H), 4 4 (m, 1H), 5.1 - 5 6 (m, 2H), 7.3 - 7.8 (m, 10H)

A solution of *n* -butylmagnesium bromide [prepared by reacting magnesium (30 mg, 1 2 mmol, 1 5 equiv) with 1-bromobutane (0 11 mL, 1 02 mmol, 1 2 equiv) in THF (3 mL)] was added to a solution cooled at -55°C of copper(I) bromide (140 mg, 0 98 mmol, 1 2 equiv) and lithium bromide (85 mg, 0 98 mmol, 1 2 equiv) in THF (3 mL) The resulting orange brown solution was stirred for 30 min at -55°C The mesylates **10a**,**b** were dissolved in THF (6 mL) and then added to the solution of ($\underline{n}$-BuCuBr)MgBr LiBr. After 1 hour at -60 to -50°C, the reaction mixture was allowed to warm up to room temperature in 30 min and then poured into 25% aqueous NH_4Cl (20 mL) containing sodium cyanide (2 g). After three extractions with ether, combined organic phases were washed with water, dried ($MgSO_4$), and concentrated Chromatography on silica gel successively using ether/petroleum ether 1 19, 1.9 and 1 4 as eluents afforded allene **1** as a yellow oil (429 mg, 75%, Rf = 0 27 with ether/petroleum ether 1 9) IR (neat) 2060 and 1980 (C=O), 1720 (C=O) cm^{-1} , ^{1}H NMR (400 MHz, $CDCl_3$) δ 0 91 (t, 3H, J = 7 2 Hz), 0 91 (t, 3H, J = 7 2 Hz), 0 96 (d, 1H, J = 8 2 Hz), 1 03 (s, 9H), 1 29 - 1 45 (m, 9H), 1 72 - 1 80 (m, 2H), 1 93 (td, 4H, J = ≈7 5, 3 Hz), 2 16 (m, 1H), 2 26 (m, 1H), 3 52 (m, 1H), 3 62 (s, 3H), 4 42 (dd, 1H, J = 8 7, 5 0 Hz), 5 13 (pent t, 1H, J = 3, 3 Hz), 5 39 (ddd, 1H, J = 8 2, 5 0, 0.8 Hz), 7.35 - 7.45 (m, 6H), 7.66 - 7 70 (m, 4H) ; ^{13}C NMR (100 MHz, CDCl$_3$) δ 14.04 (C_{15}), 19.47 ($\underline{C}(CH_3)_3$), 22.53 (C_{14}), 24 71 (C_8), 26 96 ($C(\underline{C}H_3)_3$), 29.98 (C_{12}), 32.50 (C_{13}), 39 03 (C_7), 46 21 (C_2), 51 65 ($O\underline{C}H_3$), 66.24 (C_5), 75 41 (C_6), 83 32 (C_3), 86.54 (C_4), 91.07 (C_9), 105 13 (C_{11}), 127.56 and 127.78 (C meta), 129.78 and 129.92 (C para), 133 70 and 134 15 (C ipso), 135 97 and 136 15 (C ortho), 172 40 (C_1), 200 68 (C_{10}) ; MS m/z: 667 (M^+-OCH_3), 614 (M^+-3 CO), 492 (M^+-3 CO-C_6H_{10}), 435 (M^+-3 CO-C_6H_{11}-^{t}Bu), 358 (M^+-3 CO-^{t}BuPh$_2$SiOH, base peak), 255, 193 Anal Calcd for $C_{39}H_{50}O_6FeSi$ C, 67 04, H, 7.21 Found: C, 66.62, H, 7 38

(2R*,5S*,6S*)-(2E,4E)-Tricarbonyliron [Methyl (η^4-2,5)-6-t-butyldiphenylsilyloxy-10-methylundeca-2,4,9-trienoate] (**11**)

A solution of *n*-butyllithium (0 75 mL, 1 0 equiv, 1 6 M in hexanes) was added to a cooled at 0°C suspension of dried (for 2 hours at 100°C under 0 1 mbar) isopropyltriphenylphosphonium bromide (565 mg, 1 32 mmol, 1 1 equiv) in THF (8 5 mL) After 30 min stirring at 0°C of the resulting red solution, it was added in 1 min to a cooled at 0°C solution of aldehyde 3 (695 mg, 1 2 mmol) in THF (5 6 mL) The reaction mixture was then allowed to warm up to room temperature in 30 min and then left for further 15 min After filtration and concentration, chromatography of the residue on silica gel using ether/petroleum ether 1 19 as eluent afforded olefin **11** as a yellow oil (507 mg, 70%, Rf = 0 48 with ether/petroleum ether 1 4) IR (neat) 2060 and 1980 (C=O), 1705 (C=O) cm^{-1} , ^{1}H NMR (400 MHz, CDCl$_3$) δ 0 95 (dd, 1H, J = 8 2, 1 Hz), 1 04 (s, 9H), 1 35 (dd, 1H, J = 9, 9 Hz), 1 61 (s, 3H), 1.69 (s, 3H), 1 58 - 1 76 (m, 2H), 2 14 - 2 32 (m, 2H), 3 50 (dm, 1H, J = 9 Hz), 3 62 (s, 3H), 4 44 (dd, 1H, J = 9, 5 2 Hz), 5 09 (tm, 1H, J = 7 0 Hz), 5 39 (ddd, 1H, J = 8 2, 5 2, 0 9 Hz), 7.35 - 7 46 (m, 6H), 7 67 - 7 71 (m, 4H) , ^{13}C NMR (100 MHz, CDCl$_3$) δ 17 67 ($\underline{C}H_3$), 19 41 ($\underline{C}(CH_3)_3$), 23 37 (C_8), 25 66 (C_{11}), 26 91 ($C(\underline{C}H_3)_3$), 39 28 (C_7), 46 16 (C_{12}), 51 61 ($O\underline{C}H_3$), 66 28 (C_5), 75 30 (C_6), 83 30 (C_3), 86 53 (C_4), 123 92 (C_9), 127 52 and 127 71 (C meta), 129 73 (C para), 131 95 (C_{10}), 133 66 and 134 09 (C ipso), 135 94 and 136 15 (C ortho), 172 37 (C_1) , MS m/z 571 (M^+-OCH_3), 546 (M^+-2 CO), 518 (M^+-3 CO), 461 (M^+-3 CO-^{t}Bu), 262 (M^+-3 CO-^{t}BuPh$_2$SiOH, base peak), 193, 107 Anal Calcd for $C_{32}H_{38}O_6FeSi$ C, 63 78, H, 6 36 Found C, 64 07, H, 6 55

(2R*,5S*,6S*,8(1RS))-(2E,4E)-Tricarbonyliron [Methyl (η^4-2,5)-6-t-butyldiphenylsilyloxy-8-(2,2-dibromo-3,3-dimethylcycloprop-1-yl)octa-2,4-dienoate] (**12a,b**)

A 50% aqueous sodium hydroxide solution (0 050 mL) and triethylbenzylammonium chloride (20 mg, 0 088 mmol, 0 35 equiv) were successively added to a solution of olefin **11** (149 mg, 0 25 mmol) in bromoform (1 mL) After 70 min vigorous stirring, the resulting brown mixture was diluted with water and extracted three times with chloroform Combined organic phases were washed with water, dried (MgSO$_4$) and concentrated Chromatography of the residue on silica gel using ether/petroleum ether 1 9 as eluent afforded cyclopropanes **12a,b** (mixture of both 1-cyclopropyl epimers) as a yellow oil (147 mg, 77%, Rf = 0 35 with ether/petroleum ether 1 9) IR (neat) 2060 and 1980 (C=O), 1700 (C=O) cm^{-1} , ^{1}H NMR (400 MHz, CDCl$_3$) δ [0 98 (dd, 1H, J = 8, 1 Hz), 0 99 (dd, 1H, J = 8, 1 Hz), 1H], [1 03 (s), 1 03 (s), 9H], [1 18 (s), 1 22 (s), 3H], 1 20 - 1 35 (m, 3H), [1 38 (s), 1 38 (s), 3H], 1 43 - 1 88 (m, 3H), 3 48 - 3 54 (m, 1H), [3 63 (s), 3 63 (s), 3H], 4 40 - 4 45 (m, 1H), 5 36 - 5 41 (m, 1H), 7 32 - 7 48 (m, 6H), 7 60 - 7 73 (m, 4H) ; ^{13}C NMR (100 MHz, CDCl$_3$) δ 19 27, 19 32 and 19 43 (CH_3 and $\underline{C}(CH_3)_3$), 23 90 and 24 04 (C_8), 26 92 and 26 96 ($C(\underline{C}H_3)_3$), 27 41 and 27 47 ($\underline{C}H_3$), 28 03 and 28 11 (cyclopropyl-C_3), 37 67 and 37 76 (C_7), 39 49 and

39.52 (cyclopropyl-C_1), 46.37 and 46.40 (C_2), 47 67 and 47 89 (cyclopropyl-C_2), 51 67 (O<u>C</u>H_3), 65 92 (C_5), 75 16 and 75.33 (C_6), 83.30 and 83 36 (C_3), 86 43 (C_4), 127.56 and 127.84 (C meta), 128 84, 129 99 and 130 02 (C para), 133.31, 133.47 and 133 89 (C ipso), 135.94, 135.99 and 136.20 (C ortho), 172.28 (C_1), MS m/z 690 (M^+-3 CO), 610 (M^+-3 CO-HBr), 497, 379, 263, 199 (Ph_2SiOH^+, base peak), 79. Anal Calcd. for $C_{33}H_{38}Br_2O_6FeSi$ C, 51 15; H, 4 95 Found· C, 50 95; H, 4 64

(3R,6S*,7S*)-(3E,5E)-Tricarbonyliron [(η^4-3,6)-7-t-Butyldiphenylsilyloxy-2,12-dimethyltrideca-3,5,10,11-tetraen-2-ol]* (13)

A solution of methyllithium (0.075 mL, 0.92 equiv, 1 6 M in ether) was added to a cooled at -70°C solution of cyclopropanes **12a,b** (100 mg, 0 13 mmol) in anhydrous ether (1 mL). After 1 hour at -70°C, 1 M aqueous $NaHCO_3$ was added to the resulting red brown solution and the mixture was extracted three times with ether Combined ethereal layers were washed with water, dried ($MgSO_4$) and concentrated Chromatography on silica gel using ether/petroleum ether 1 19 as eluent afforded allenic alcohol **13** as a yellow oil (23 mg, 29%, Rf = 0 31 with ether/petroleum ether 1.4). MS indicated the presence of a trace of a reduced dibromo compound which was not detected by ^{1}H NMR IR (neat) 3450 (OH), 2040 and 1960 (C=O) cm^{-1}, ^{1}H NMR (400 MHz, $CDCl_3$) δ 0 85 - 0 90 (m, 2H), 1 03 (s, 9H), 1 30 (s, 3H), 1 31 (s, 3H), 1 69 (d, 3H, J = 2 4 Hz), 1.66 - 1 76 (m, 2H), 2.11 - 2.27 (m, 2H), 3.58 (ddd, 1H, J = 9 5, 6 4, 4 0 Hz), 4 34 (dd, 1H, J = 9 3, 5 2 Hz), 4.93 (ddd, 1H, J = 8.5, 5 2, 1 Hz), 5 00 (t septuplet, 1H, J = 3, 2 4 Hz), 7 33 - 7 47 (m, 6H), 7 68 - 7.71 (m, 4H) , MS m/z 614 (M^+), 558 (M^+-2 CO), 530 (M^+-3 CO), 512 (M^+-3 CO-H_2O), 401, 199 (Ph_2SiOH^+, base peak), 133, 107, 95

(2R,5S*,6S*)-(2E,4E)-Tricarbonyliron [(η^4-2,5)-6-t-Butyldiphenylsilyloxy-10-methylundeca-2,4,9-trien-1-ol]* (14)

A solution of diisobutylaluminium hydride (1 94 mL, 2 3 equiv, 1 M in hexanes) was added to a cooled solution of methyl ester **11** (507 mg, 0 84 mmol) at -45°C in anhydrous ether After 20 min at -45°C, water (1.7 mL) was added and the resulting mixture was warmed to room temperature Then, saturated aqueous potassium sodium tartrate (10 mL) and ether (8 mL) were added When a clear mixture resulted, the organic phase was separated and the aqueous phase was extracted twice with ether Combined organic extracts were successively washed with brine and water, dried ($MgSO_4$) and concentrated Chromatography of the oily residue on silica gel using ether/petroleum ether 1 4 afforded alcohol **14** as a yellow oil (464 mg, 96%, Rf = 0 10 with ether/petroleum ether 1 4) IR (neat) 3400 (OH), 2050 and 1980 (C=O) cm^{-1}, ^{1}H NMR (400 MHz, $CDCl_3$) δ 1 04 (s, 9H), 1 10 (m, 1H), 1 17 (dd, 1H, J = 9, 8 5 Hz), 1 60 (s, 3H), 1 68 (s, 3H), 1 58 - 1 75 (m, 3H), 2 12 - 2.27 (m, 2H), 3 46 - 3 62 (m, 3H), 4 35 (dd, 1H, J = 8 5, 4 9 Hz), 4 80 (dd, 1H, J = 8 5, 4 9 Hz), 5 09 (tm, 1H, J = 7 0 Hz), 7 35 - 7 45 (m, 6H), 7 68 - 7 70 (m, 4H) , ^{13}C NMR (100 MHz, $CDCl_3$) δ 17 68 (<u>C</u>H_3), 19.45 (<u>C</u>$(CH_3)_3$), 23 41 (C_8), 25 71 (C_{11}), 26 99 (C(<u>C</u>$H_3)_3$), 39 24 (C_7), 61 25 (C_2), 64 54 (C_1), 65 65 (C_5), 75 58 (C_6), 82.85 (C_3 or C_4), 84 61 (C_3 or C_4), 124 17 (C_9), 127 49 and 127 69 (C meta), 129 63 and 129 77 (C para), 131 77 (C_{10}), 133 94 and 134 37 (C ipso), 135 99 and 136 24 (C ortho) , MS m/z 574 (M^+), 518 (M^+-2 CO), 490 (M^+-3 CO), 473, 433 (M^+-3 CO-^{t}Bu), 199 (Ph_2SiOH^+, base peak), 93, 69 Anal Calcd for $C_{31}H_{38}O_5FeSi$ C, 64 80, H, 6 67 Found C, 64 86, H, 6 37

(2R*,5S*,6S*)-(2E,4E)-Tricarbonyliron [(η^4-2,5)-1,6-Di(t-butyldiphenylsilyloxy)-10-methylundeca-2,4,9-triene] (**15**)

Alcohol **14** (330 mg, 0.57 mmol) was silylated as described for the preparation of **7a,b** Purification by chromatography on silica gel using 2% ether-petroleum ether as eluent afforded the silyl ether **15** as a yellow oil (393 mg, 84%, Rf = 0.74 with ether/petroleum ether 1 9) IR (neat)· 2050 and 1980 (C=O) cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1 04 (s, 9H), 1 06 (s, 9H), 1 03 - 1 10 (m, 2H), 1 61 (s, 3H), 1.67 (s, 3H), 1.58 - 1 72 (m, 2H), 2 11 - 2.28 (m, 2H), 3 46 (m, 1H), 3 58 (dd, 1H, J = 11 9, 6 7 Hz), 3 66 (dd, 1H, J = 11 9, 5 5 Hz), 4 28 (dd, 1H, J = 8 7, 4 9 Hz), 4 58 (dd, 1H, J = 8 6, 4 9 Hz), 5 10 (tm, 1H, J = 7 0 Hz), 7 34 - 7.45 (m, 12H), 7 63 - 7 71 (m, 8H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 17 68 ($\underline{C}H_3$), 19 14 and 19.47 ($\underline{C}(CH_3)_3$), 23 47 (C_8), 25 71 (C_{11}), 26 79 and 27 00 ($C(\underline{C}H_3)_3$), 39 28 (C_7), 61 90 (C_2), 65 18 (C_5), 65 42 (C_1), 75 73 (C_6), 82 63 (C_3 or C_4), 84 04 (C_3 or C_4), 124 25 (C_9), 127 40, 127 67 and 127 70 (C meta), 129 58 and 129 73 (C para), 131 69 (C_{10}), 133.48, 133 53, 133 92 and 134 41 (C ipso), 135.59, 136 00 and 136 26 (C ortho) , MS m/z 728 (M^+-3 CO), 551, 509, 472 (M^+-3 CO-$^tBuPh_2SiOH$), 312, 199 (Ph_2SiOH^+, base peak), 93, 69, 41 Anal Calcd for $C_{47}H_{56}O_5FeSi_2$ C, 69 44, H, 6 94 Found C, 69 49, H, 6 91

(2R*,5S*,6S*)-(2E,4E)-Tricarbonyliron [(η^4-2,5)-1,6-Di(t-butyldiphenylsilyloxy)-8-(2,2-dibromo-3,3-dimethylcyclopropyl)octa-2,4-diene] (**16a,16b**)

A mixture of olefin **15** (295 mg, 0 36 mmol), bromoform (2 0 mL), triethylbenzylammonium chloride (44 mg, 0 19 mmol, 0.5 equiv) and 50% aqueous sodium hydroxide (0 1 mL) was vigorously stirred for 85 min Work-up as described for the preparation of **12a,b** and purification by chromatography on silica gel using 2% ether-petroleum ether as eluent afforded starting olefin **15** (99 mg, 34%) and dibromo cyclopropanes **16a,b** (mixture of both 1-cyclopropyl epimers) as a rather unstable yellow oil (220 mg, 62%, Rf = 0.37 with 2% ether-petroleum ether) IR (neat) 2040 and 1980 (C=O) cm^{-1} , ^{1}H NMR (400 MHz, $CDCl_3$) δ [1 03 (s), 1 04 (s) 9H], [1 06 (s), 1 06 (s), 9H], 1 01 - 1 15 (m, 2H), [1 17 (s), 1.22 (s), 3H], [1 37 (s), 1 38 (s), 3H], 1 61 - 1 90 (m, 5H), 3 42 - 3 48 (m, 1H), [3 58 (dd, 1H, J = 12 1, ~6 5 Hz), 3 59 (dd, 1H, J = 12 1, ~6 5 Hz), 1H], 3 67 (dd, 1H, J = 12 1, 5 6 Hz), 4 27 (dd, 1H, J = 8 5, 4 9 Hz), 4 55 - 4 60 (m, 1H), 7 34 - 7 45 (m, 12H), 7 62 - 7 74 (m, 8H) , ^{13}C NMR (100 MHz, $CDCl_3$) δ 19 15 ($\underline{C}(CH_3)_3$), 19 29 and 19 34 ($\underline{C}H_3$), 19 47 ($\underline{C}(CH_3)_3$), 23 98 and 24 18 (C_8), 26 79, 27 00 and 27 03 ($C(\underline{C}H_3)_3$), 27 47 and 27 53 ($\underline{C}H_3$), 28 00 and 28 06 (cyclopropyl-C_3), 37 72 (C_7), 39 54 and 39 66 (cyclopropyl-C_1), 47 93 and 48 11 (cyclopropyl-C_2), 62 14 and 62 20 (C_2), 64 81 (C_5), 65 37 (C1), 75 53 and 75 58 (C_6), 82 60 and 82 65 (C_3 or C_4), 83.92 (C_3 or C_4), 127 41, 127 65, 127 71 and 127 84 (C meta), 129 64, 129 75, 129 87 and 129 91 (C para), 133 41, 133 47, 133 50, 133 66 and 134 16 (C ipso), 135 56, 135 60, 135 99, 136 03 and 136 31 (C ortho) , MS m/z 820 (M^+-3 CO-HBr), 764 (M^+-3 CO-HBr-C_4H_8), 707 (M^+-3 CO-HBr-C_4H_8-^tBu), 564 (M^+-3 CO-HBr-$^tBuPh_2SiOH$), 555, 472, 377, 257, 199 (Ph_2SiOH^+, base peak), 78

(2R*,5S*,6S*)-(2E,4E)-Tricarbonyliron [(η^4-2,5)-1,6-Di(t-butyldiphenylsilyloxy)-11-methyldodeca-2,4,9,10-tetraene] (**2**)

A solution of methyllithium (0 050 mL, 0 9 equiv, 1 6 M in ether) was added to a cooled at -70°C solution of cyclopropanes **16a,b** (85 mg, 0 9 mmol) in anhydrous ether (1 mL) After 1 hour stirring at -70°C, the reaction solution was allowed to warm up to room temperature in 2 hours Work-up as described for the preparation of **13** and purification of the crude product by chromatography on silica gel using ether/petroleum ether 1:19 as eluent afforded allene 2 as a yellow oil (52 mg, 73%, Rf = 0 69 with ether/petroleum ether 1·9). Nevertheless, ^{1}H and ^{13}C NMR as well as elemental analysis indicated the presence of unpolar contaminants which could have not been separated IR (neat)· 2050 and 1980 (C=O) cm^{-1} ; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.03 (s, 9H), 1.05 (s, 9H), 1 00 - 1 10 (m, 2H), 1 69 (d, 3H, J = 3 Hz), 1 69 (d, 3H, J = 3 Hz), 1 65 - 1 77 (m, 2H), 2.09 - 2.26 (m, 2H), 3.50 (m, 1H), 3 57 (dd, 1H, J = 12 2, 6 7 Hz), 3 66 (dd, 1H, J = 12 2, 5 0 Hz), 4 26 (dd, 1H, J = 8.9, 4 9 Hz), 4 57 (dd, 1H, J = 8 5, 4 9 Hz), 4 99 (t sept, 1H, J = 3, 3 Hz), 7 36 - 7 46 (m, 12H), 7.62 - 7.71 (m, 8H) ; ^{13}C NMR (100 MHz, CDCl$_3$) δ 19 14 and 19 49 ($\underline{C}(CH_3)_3$), 20 70 and 20.75 ($=\cdot=C(\underline{C}H_3)_2$), 24 47 (C$_8$), 26.77 and 26 97 ($C(\underline{C}H_3)_3$), 38 87 (C$_7$), 61.85 (C$_2$), 65.19 (C$_5$), 65 42 (C$_1$), 75 51 (C$_6$), 82.59 (C$_3$ or C$_4$), 83 94 (C$_3$ or C$_4$), 88 52 (C$_9$), 95 47 (C$_{11}$), 127 41 and 127 68 (C meta), 129.58 and 129.73 (C para), 133 47, 133.51, 133 94, 134.41 (C ipso), 135 56, 135 59, 135.99, 136 20 (C ortho), 201 68 (C$_{10}$), 211 (Fe-$\underline{C}$O) , MS m/z: 768 (M$^+$-2 CO), 740 (M$^+$-3 CO), 509, 199 (Ph$_2$SiOH$^+$, base peak). Anal. Calcd. for $C_{48}H_{56}O_5FeSi_2$· C, 69 88; H, 6.84. Found. C, 70 78, H, 7 76

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