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Directed semi-hydrogenation of triple bonds in diene tricarbonyliron complexes

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Abstract

Catalytic hydrogenation of a triple bond in β-position to the diene tricarbonyliron moiety, using palladium on carbon as catalyst, surprisingly stopped at the olefinic stage and the corresponding olefins were obtained. This protective effect seemed independent of many factors: the stereochemistry (*E,E* or *E,Z*) of the organometallic unit, the configuration and the nature of the vicinal functionality as well as of the substitution of the triple bond, particularly its electrophilicity.

Keywords: Semi-hydrogenation; Palladium; Diene tricarbonyliron complexes; Alkenols

1. Introduction

Acyclic diene tricarbonyliron complexes proved to be valuable intermediates particularly for the asymmetric synthesis of polyenic natural products and structural analogs [1]. The planar chirality of these organometallic complexes usually enables a good stereocontrol and thus the preparation of optically active compounds. Furthermore, the diene system is temporarily protected and this allows reactions to occur at remote centers without interference with it. Another point is that chemical reactivity can be altered or completely modified compared to the uncomplexed compounds. A classical example is the formation and use of pentadienyl cations complexed to an $Fe(CO)_3$ unit [1]. Herein, we wish to report on the modification of reactivity of propargylic derivatives which are close to a diene–$Fe(CO)_3$ complex towards catalytic hydrogenation (the poisoning effect of $Fe(CO)_3$ on catalytic hydrogenation was previously observed with the tricarbonyliron complex of tropone [2]).

Two sets of propargylic substrates were prepared from aldehydes **1** and **11** whose complexed diene systems respectively have *E,E* and *E,Z* stereochemistries. Reaction of aldehyde **1** with metallated alkynes such as the di-Grignard derivative of but-3-yn-1-ol or the dilithium derivative of pent-4-ynoic acid (followed by esterification in situ in the latter case) afforded a mixture of easily separable diastereoisomeric propargylic alcohols: ψ-*exo* **2** or **4** and ψ-*endo* **3** or **5** (Scheme 1) (for the ψ-*exo* and ψ-*endo* terminologies, see [3]; as the ψ-*endo* alcohol is always noticeably less polar than the ψ-*exo* isomer, separation can be easily performed by chromatography on silica gel). Complete hydrogenation of the triple bond would introduce a saturated functionalized chain in order to get a convenient route to fatty acid metabolites and structural analogs, eventually in a labeled form (with deuterium or tritium). However, catalytic hydrogenation of such substrates under standard conditions using palladium on carbon as catalyst surprisingly stopped at the olefinic stage and the corresponding allylic alcohols were obtained in good yields: **2** and **3** gave respectively **6** and **7** while **8** and **9** were isolated from **4** and **5**. The *Z* configuration of the created double bond was established by ^1H NMR. A marked decrease in reactivity was thus observed for these substrates and this result seemed independent of the relative configuration as well as of the nature of the functional group (although we worked with racemic compounds, only one enantiomer is shown for clarity, it should be noted that the starting complex **1** can be easily resolved, see Ref. [4]).

This directed semi-hydrogenation of triple bonds was

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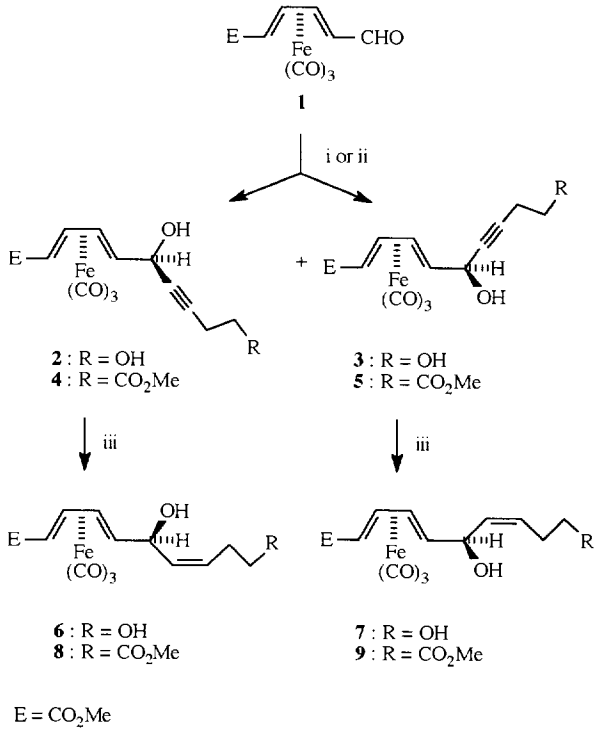
also studied with another set of substrates: *E,Z*-diene tricarbonyliron complexes with an electrophilic triple bond. These compounds were planned to be intermediates for a synthesis of pyrenolides [5]. Aldehyde **11** was obtained from known ester **10** [6] by sequential protection of the alcohol group as a *tert*-butyldimethylsilyl ether [7], reduction of the ester group, and oxidation of the resulting alcohol into an aldehyde using the method described by Saigo and coworkers [8] (Scheme 2). Addition of ethyl propiolate as its organocerium derivative to aldehyde **11** afforded a mixture of easily separable diastereoisomeric propargylic alcohols: ψ-*exo* **12** and ψ-*endo* **13** (the lithiated derivative of ethyl propiolate only afforded low yields of alcohols and mainly degradation of complex **11** resulted). In agreement with previous results [9], the *E,Z* configuration of the complexed diene unit was retained during this sequence.

Catalytic hydrogenation of **12** and **13** using palladium on carbon as catalyst also afforded the corresponding allylic alcohols **14** and **15**. The *Z* configuration of the created double bond was confirmed by ^{1}H NMR spectroscopy (J = 11.7 Hz in $CDCl_3$). Even in the case of a highly electrophilic triple bond such as that of ketone **16**, it is worth noting that this selective reduction is again observed, giving enone **17** without any saturated compound being detected. Only a minor isomerization of the *Z* double bond was observed since **15** and **17** were separated by chromatography from small amounts (respectively 14 and 20%) of the *E* isomers.



Scheme 1. Reagents, conditions and yields: (i) 2 equiv. $BrMgC{\equiv}CCH_2CH_2OMgBr$ (from but-3-yn-1-ol and EtMgBr in THF, 66°C, 1.5 h), THF/HMPA (4:1), 0°C, 1 h then dilute HCl, 60% of **2** and 26% of **3**; (ii) 1.65 equiv. $LiC{\equiv}CCH_2CH_2CO_2Li$ (from pent-4-ynoic acid and MeLi in HMPA, 0°C, 1 h), HMPA, 0°C, 0.5 h then MeI (6.5 equiv.), 0°C, 1 h and finally dilute HCl, 26% of **4** and 16% of **5**; (iii) 10% Pd on C (100 mg/g alkynol), H_2 (1 atm), MeOH (10 ml/g alkynol), r.t., 4 h for **3**, **4**, and **5**, 30 h for **2**, 72% of **6**, quant. **7**, 88% of **8**, 83% of **9**.

In conclusion, the presence of diene tricarbonyliron organometallic complexes stopped catalytic hydrogenation of triple bonds in β-position at the olefinic stage. With such complexes, less active catalysts [10] such as for instance the Lindlar catalyst [11] or P_2–Ni [12] which are classically used for this purpose, are not necessary (furthermore, as another confirmation of the decreased reactivity of these acetylenic organometallic complexes, P_2–Ni did not catalyze the hydrogenation of **4** for instance). This protective effect seemed independent of many factors: the stereochemistry (*E,E* or *E,Z*) of the organometallic unit, the configuration and nature of the vicinal functionality as well as of the substitution of the triple bond, particularly its electrophilicity. The determination of the origin of this unusual effect would require more detailed studies even if the steric hindrance of the organometallic complex is probably strongly involved. It is also possible to speculate that such an effect could also occur with other transition metal complexes, thus making it attractive for synthetic planning (this directed semi-hydrogenation was already used by one of us for an epoxide synthesis in the butadiene–iron tricarbonyl series, see Ref. [13]).

2. Experimental section

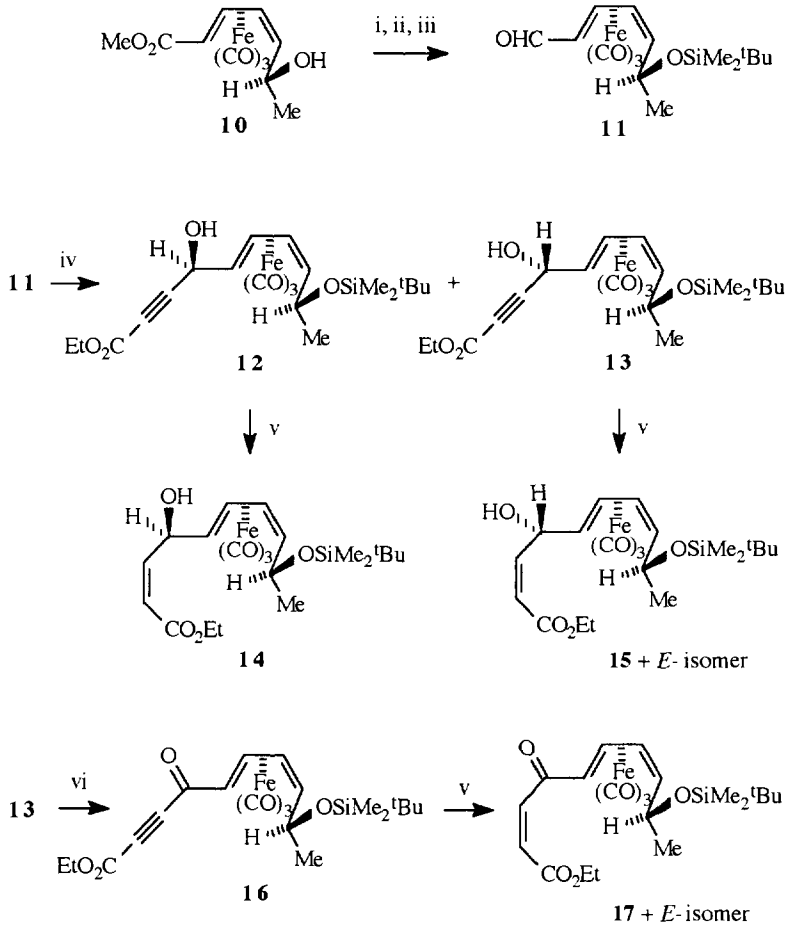
2.1. General information

IR spectra were recorded on a Shimadzu IR 435 and a Nicolet 205 (FT) spectrometer. NMR spectra were measured on a Jeol FX-90Q, a Bruker AM 300 WB or a Bruker ARX 400 spectrometer. Chemical shifts were recorded in ppm downfield from tetramethylsilane on the δ scale. Thin layer chromatography (TLC) was carried out on aluminium sheets precoated with silica gel $60F_{254}$ (Merck). The plates were inspected by UV light followed by development with iodine vapor or an acidic solution of *p*-anisaldehyde in ethanol followed by heating. Purifications were performed by chromatography on silica gel (Merck 60 G, thickness 2 mm for preparative TLC, Merck Kieselgel 60 (40–63 μ) or Amicon (35–70 μ) for columns). High resolution mass spectra (HRMS) were obtained under electronic impact at 70 eV from a Varian MAT 311 spectrometer at the Centre Régional de Mesures Physiques de l'Ouest (Rennes).

2.2. (2R*,5S*,6S*)-(2E,4E)-tricarbonyliron [methyl (η^4-2,3,4,5)-6,10-dihydroxydeca-2,4-dien-7-ynoate] (2) and (2R*,5S*,6R*)-(2E,4E)-tricarbonyliron [methyl (η^4-2,3,4,5)-6,10-dihydroxydeca-2,4-dien-7-ynoate] (3)

A 1 M solution of ethylmagnesium bromide in THF (22 ml) was added dropwise under nitrogen to a solution of 3-butyn-1-ol (0.77 g, 11 mmol) in THF (10 ml) at 0 °C. Then, the resulting mixture was refluxed for 90 min. An abundant white precipitate was formed. After cooling at 0 °C, anhydrous HMPA (5 ml) was added followed by the dropwise addition of a solution of aldehyde **1** (1.5 g, 5.4 mmol) in THF (10 ml). After 1 h at 0 °C, water (80 ml) was added and 1 N hydrochloric acid until the pH was acid. The resulting mixture was extracted twice with ether. Combined organic extracts were washed with water, dried (Na_2SO_4), and concentrated. Purification of the residue by preparative TLC using ether as eluent afforded diols ψ-*exo* **2** (1.14 g, 60%, $R_f = 0.18$ with ether) and ψ-*endo* **3** (0.49 g, 26%, $R_f = 0.25$ with ether) as yellow orange viscous oils. Diol **3** was shown to be easily oxidized into the corresponding ω-hydroxy ketone upon air contact. In this preparation, HMPA can be replaced by DMPU with similar yields and a longer reaction time (3 h at 0 °C).

Data for **2**. IR (neat, KBr): ν 3390 (broad, O–H), 2954, 2231 (weak, C≡C), 2061 and 1995 (C≡O), 1712 (C=O), 1459, 1319, 1198, 1179, 1045, 612, 566 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 5.81 (ddd, 1H, $J = 8.1$, 5.1, 1.2 Hz, H–C_3), 5.48 (ddd, 1H, $J = 8.3$, 5.1, 1.0 Hz, H–C_4), 4.22 (very broad d, 1H, $J = 6.1$ Hz, d after addition of D_2O, $J = 8.1$ Hz, H–C_6), 3.76 (broad t, 2.5H, $J = 5.1$ Hz, t after addition of D_2O, $J = 5.8$ Hz, H–C_{10} e.g. CH_2OH and 1/2OH), 3.68 (s, 3H, CO_2Me), 2.86 (broad s, 0.5H, 1/2OH), 2.79 (broad s, 0.5H, 1/2OH), 2.52 (td, 2H, $J = 6.1$, 1.9 Hz, H–C_9), 1.97 (broad, 0.5H, 1/2OH), 1.51 (td, 1H, $J = 8.3$, 1.1 Hz, H–C_5), 1.13 (dd, 1H, $J = 8.1$, 1.1 Hz, H–C_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.86 (CO axial), 207.70 and 206.46 (CO basal), 172.88 (C_1), 86.15 (dp, $J =$ 169.4, 2.8 Hz, C_4), 84.26 (ddt, $J = 174.5$, 2.7, 2.4 Hz, C_3), 83.31 and 81.66 (C≡C), 65.22 (dm, $J = 162.0$ Hz,



Scheme 2. Reagents, conditions and yields: (i) 1.5 equiv. $CF_3SO_3SiMe_2{}^tBu$, 2 equiv. 2,6-lutidine, THF, −40 °C, 45 min, 31% silyl ether plus 27% recovered **10**; (ii) 2.4 equiv. Dibal–H, Et_2O, −40 °C, 25 min, 87%; (iii) 1.3 equiv. ^nPrMgBr, THF, 5 min then 2 equiv. ADD, 0 °C, 25 min, 86%; (iv) 4.5 equiv. Cl_2Ce–C≡C–CO_2Et (from ethyl propiolate, LDA then $CeCl_3$ in THF, 1 h at −78 °C), THF, −78 °C, 20 min, 68% of **12** and 16% of **13**; (v) 10% Pd on C (250 mg/mmol alkynol), H_2 (1 atm), MeOH (40 ml/mmol alkynol), r.t., 1 h, 89% of **14** (crude and unstable), 64% of **15**, 73% of **17**; (vi) as (iii), 69%.

C_5), 64.15 (dm, $J = 147.5$ Hz, C_6), 60.63 (pseudo ddt, $J = 146.8$, 143.2, 4.6 Hz, C_{10}), 51.87 (q, $J = 147.0$ Hz, CO_2Me), 46.08 (ddd, $J = 164.9$, 7.9, 1.0 Hz, C_2), 22.82 (ddd, $J = 131.7$, 129.9, 1.9 Hz, C_9). MS (70 eV, EI) Calc. mass for $C_{12}H_{14}^{56}FeO_5$ $[M - 2CO]^+$: 294.0191; Found: 294.0196. Main fragment ions m/z (%): 294 (0.4) $[M - 2CO]^+$, 266 (7.6) $[M - 3CO]^+$, 218 (19.7) $[M - 3CO - CH_2O - H_2O]^+$, 28 (100) $[CO]^+$.

Data for **3**. IR (neat, KBr): ν 3400 (broad, O–H), 2955, 2220 (medium, C≡C), 2060 and 1995 (C≡O), 1712 (C=O), 1458, 1199, 1178, 1045, 611, 562 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 5.82 (ddd, 1H, $J = 8.1$, 5.1, 1.1 Hz, H–C_3), 5.57 (broad dd, 1H, $J = 8.6$, 5.1 Hz, H–C_4), 4.55 (broad s, 1H, broad dt after addition of D_2O, $J = 5.2$, 2.0 Hz, H–C_6), 3.76 (broad t, 2H, $J =$ 5.5 Hz, t after addition of D_2O, $J = 6.0$ Hz, H–C_{10}), 3.67 (s, 3H, CO_2Me), 2.57 (broad d, 1H, $J = 3.5$ Hz, OH), 2.52 (td, 2H, $J = 6.2$, 1.9 Hz, H–C_9), 1.46 (ddd, 1H, $J = 8.5$, 5.2, 1.0 Hz, H–C_5), 1.02 (dd, 1H, $J = 8.1$, 1.0 Hz, H–C_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.6 (CO axial), 208.0 and 207.3 (CO basal), 172.84 (C_1), 84.08 (C≡C), 83.98 (dm, $J = 170$ Hz, C_4), 83.19 (dm, $J = 174.5$ Hz, C_3), 81.72 (C≡C), 66.21 (dm, $J =$ 161.7 Hz, C_5), 62.52 (d pseudo dd, $J = 148$, 4, 1.4 Hz, C_6), 60.72 (tt, $J = 145.4$, 5.3 Hz, C_{10}), 51.79 (q, $J =$ 146.8 Hz, CO_2Me), 45.68 (ddd, $J = 164.4$, 8.1, 1.6 Hz, C_2), 22.90 (broad t, $J = 131$ Hz, C_9). HRMS (70 eV, EI) Calc. mass for $C_{11}H_{14}^{56}FeO_4$ $[M - 3CO]^+$: 266.0241; Found: 266.0242. Main fragment ions m/z (%): 294 (1.8) $[M - 2CO]^+$, 266 (22.1) $[M - 3CO]^+$, 218 (42.6) $[M - 3CO - CH_2O - H_2O]^+$, 160 (54.6), 28 (100) $[CO]^+$.

2.3. (2R,5S*,6S*)-(2E,4E)-tricarbonyliron [dimethyl (η^4-2,3,4,5)-6-hydroxyundeca-2,4-dien-7-yndioate] (**4**) and (2R*,5S*,6R*)-(2E,4E)-tricarbonyliron [dimethyl (η^4-2,3,4,5)-6-hydroxyundeca-2,4-dien-7-yndioate] (**5**)*

A 1.6 M solution of methyllithium in ether (1.25 ml, 2 mmol) was added (an *n*-butyllithium solution in hexanes can also be used) dropwise under nitrogen to a solution of 4-pentynoic acid (98 mg, 1 mmol) in anhydrous HMPA (2 ml) at 0 °C. After 1 h at 0 °C, a solution of aldehyde **1** (168 mg, 0.6 mmol) in HMPA (1 ml) was added dropwise. After 30 min further stirring at 0 °C, iodomethane (0.25 ml, 4 mmol) was added and the resulting mixture was allowed to react for 1 h at 0 °C. Water (15 ml) and 2 M hydrochloric acid (2 ml) were added. After four extractions with ether, combined organic extracts were washed with water (5 × 5 ml), dried (Na_2SO_4), and concentrated. Chromatography of the residue on silica gel plates with three elutions using an ether/petroleum ether mixture (2:3) afforded, by increasing polarity, hydroxyesters ψ-*exo* **4** (61 mg, 26%, $R_f = 0.42$ with ether) and ψ-*endo* **5** (37 mg, 16%, $R_f =$ 0.50 with ether) as yellow orange viscous oils, and starting aldehyde **1** (17 mg).

Data for **4**. IR (neat, KBr): ν 3440 (broad, O–H), 2955, 2850, 2232 (C≡C), 2061 and 1993 (C≡O), 1739 and 1716 (C=O), 1458, 1438, 1198, 1177, 1005, 624, 613, 567 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 5.82 (ddd, 1H, $J = 8.1$, 5.1, 1.1 Hz, H–C_3), 5.48 (ddd, 1H, $J = 8.4$, 5.1, 1.0 Hz, H–C_4), 4.28 (ddm, 1H, $J = 7.9$, 5.5 Hz, H–C_6), 3.71 (s, 3H, OMe), 3.67 (s, 3H, OMe), 2.60–2.55 (m, 4H, H–$C_{9,10}$), 2.11 (d, 1H, $J = 5.5$ Hz, OH), 1.45 (ddd, 1H, $J = 8.4$, 7.9, 1.1 Hz, H–C_5), 1.11 (dd, 1H, $J = 8.1$, 1.0 Hz, H–C_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.4 (CO axial), 207.45 and 206.5 (CO basal), 172.56 (C_1), 172.47 (C_{11}), 85.97 (dp, $J = 169.5$, 2.8 Hz, C_4), 84.46 (C_8), 84.24 (ddt, $J = 174.6$, 3.2, 2.4 Hz, C_3), 80.68 (C_7), 64.86 (dm, $J = 163.5$ Hz, C_5), 64.22 (dd, $J = 147.9$, 4.6 Hz, C_6), 51.92 (q, $J =$ 147.0 Hz, OMe), 51.81 (q, $J = 146.8$ Hz, OMe), 46.18 (ddd, $J = 164.6$, 8.0, 1.5 Hz, C_2), 32.92 (tt, $J = 131.8$, 6.7 Hz, C_{10}), 14.58 (dddd, $J = 135.3$, 133.8, 6.0, 5.0 Hz, C_9). HRMS (70 eV, EI) Calc. mass for $C_{14}H_{16}^{56}FeO_6$ $[M - 2CO]^+$: 336.0296; Found: 336.0301. Main fragment ions m/z (%): 364 (0.1) $[M - CO]^+$, 361 (0.4) $[M - OMe]^+$, 336 (2.0) $[M - 2CO]^+$, 308 (10.5) $[M - 3CO]^+$, 290 (29.5) $[M - 3CO - H_2O]^+$, 28 (100) $[CO]^+$.

Data for **5**. IR (neat, KBr): ν 3470 (broad, O–H), 2955, 2851, 2221 (C≡C), 2060 and 1992 (C≡O), 1738 and 1716 (C=O), 1458, 1432, 1197, 1175, 611, 563 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 5.81 (ddd, 1H, $J = 8.1$, 5.1, 1.1 Hz, H–C_3), 5.56 (dddd, 1H, $J =$ 8.5, 5.1, 1.1, 0.4 Hz, H–C_4), 4.54 (broad d, 1H, $J =$ 5.1 Hz, H–C_6), 3.71 (s, 3H, OMe), 3.67 (s, 3H, OMe), 2.60–2.53 (m, 4H, H–$C_{9,10}$), 2.00 (broad, 1H, OH), 1.44 (ddd, 1H, $J = 8.5$, 5.1, 1.1 Hz, H–C_5), 1.01 (dd, 1H, $J = 8.1$, 1.1 Hz, H–C_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.55 (C_1), 172.22 (C_{11}), 85.32 (C_8), 83.79 and 83.23 (C_3 and C_4), 80.62 (C_7), 65.80 (C_5), 62.68 (C_6), 51.88 (OMe), 51.73 (OMe), 45.81 (C_2), 32.91 (C_{10}), 14.60 (C_9). HRMS (70 eV, EI) Calc. mass for $C_{13}H_{16}^{56}FeO_5$ $[M - 3CO]^+$: 308.0347; Found: 308.0340 and for $C_{13}H_{14}^{56}FeO_4$ $[M - 3CO - H_2O]^+$: 290.0241; Found: 290.0242. Main fragment ions m/z (%): 336 (0.8) $[M - 2CO]^+$, 308 (4.5) $[M - 3CO]^+$, 290 (10.2) $[M - 3CO - H_2O]^+$, 28 (100) $[CO]^+$.

*2.4. General procedure for catalytic hydrogenation of alkynols **2**, **3**, **4**, and **5***

To a solution of alkynol (0.5 g) in methanol (5 ml) was added 10% palladium on activated carbon (50 mg). The resulting mixture was well stirred (magnetically) under an atmospheric pressure of hydrogen respectively for 4 h in the case of **3**, **4**, and **5** and 30 h in the case of **2**. The catalyst was removed by filtration and washed with ether. Concentration and purification either by

preparative TLC or with a silica gel column using ethyl acetate/petroleum ether (1:9 to 2:3) as eluent afforded the corresponding alkenols **6**, **7**, **8**, and **9**.

2.5. (2R*,5S*,6S*)-(2E,4E,7Z)-tricarbonyliron [methyl (η^4-2,3,4,5)-6,10-dihydroxydeca-2,4,7-trienoate] (6)

$R_f = 0.13$ with ether. This compound was obtained as a yellow oil which crystallized very slowly in the refrigerator to afford yellow crystals melting at 99 °C. IR (neat, KBr): ν 3470 (broad, O–H), 2954, 2059 and 1994 (C≡O), 1713 (C=O), 1460, 1318, 1197, 1178, 1126, 755, 613, 561 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 5.85 (ddd, 1H, $J = 8.1$, 5.0, 1.1 Hz, H–C_3), 5.79 (ddt, 1H, $J = 10.8$, 8.7, 1.1 Hz, H–C_7), 5.61 (dddd, 1H, $J = 10.8$, 9.6, 6.5, 1.0 Hz, H–C_8), 5.53 (ddd, 1H, $J =$ 8.4, 5.0, 1.1 Hz, H–C_4), 4.26 (t, 1H, $J = 8.5$ Hz, H–C_6), 3.79 (dt, 1H, $J = 10.1$, 4.4 Hz, H–C_{10}), 3.67 (s, 3H, CO_2Me), 3.58 (ddd, 1H, $J = 10.6$, 10.1, 3.3 Hz, H–C_{10}), 3.22 (broad, 1H, OH), 2.60–2.45 (m, 1H, H–C_9), 2.33 (broad, 1H, OH), 2.25–2.14 (m, 1H, H–C_9), 1.36 (ddd, 1H, $J = 8.4$, 8.1, 1.1 Hz, H–C_5), 1.11 (dd, 1H, $J = 8.1$, 1.1 Hz, H–C_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.4 (CO axial), 207.7 (2CO basal), 172.76 (C_1), 134.07 (dm, $J = 159.5$ Hz, C_7), 129.13 (dm, $J =$ 155.5 Hz, C_8), 85.94 (dtt, $J = 169.1$, 3.2, 2.5 Hz, C_4), 84.46 (ddt, $J = 174.5$, 3.2, 2.4 Hz, C_3), 68.60 (dddd, $J = 143.0$, 10.1, 4.1, 2.3 Hz, C_6), 65.61 (dddt, $J =$ 159.7, 7.7, 3.7, 2.6 Hz, C_5), 60.76 (tm, $J = 143$ Hz, C_{10} e.g. CH_2OH), 51.79 (q, $J = 146.9$ Hz, OMe), 46.14 (ddd, $J = 164.8$, 8.0, 1.5 Hz, C_2), 30.50 (tdm, $J =$ 126.9 Hz, C_9). HRMS (70 eV, EI) Calc. mass for $C_{12}H_{16}^{56}FeO_5$ $[M - 2CO]^+$: 296.0347; Found: 296.0333. Main fragment ions m/z (%): 321 (1.1) $[M - OMe]^+$, 296 (3.1) $[M - 2CO]^+$, 268 (19.4) $[M - 3CO]^+$, 250 (9.7) $[M - 3CO - H_2O]^+$, 220 (85.0) $[M - 3CO - CH_2O - H_2O]^+$, 134 (81.3), 28 (100) $[CO]^+$.

2.6. (2R*,5S*,6R*)-(2E,4E,7Z)-tricarbonyliron [methyl (η^4-2,3,4,5)-6,10-dihydroxydeca-2,4,7-trienoate] (7)

$R_f = 0.26$ with ether. IR (neat, KBr): ν 3420 (broad, O–H), 2953, 2057 and 1989 (C≡O), 1712 (C=O), 1458, 1197, 1177, 611, 560 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 5.82 (ddd, 1H, $J = 8.1$, 5.1, 1.0 Hz, H–C_3), 5.69 (ddt, 1H, $J = 10.8$, 8.2, 1.2 Hz, H–C_7), 5.59 (dddd, 1H, $J = 10.8$, 8.8, 6.9, 1.0 Hz, H–C_8), 5.46 (broad dd, 1H, $J = 8.7$, 5.1 Hz, H–C_4), 4.52 (ddt, 1H, $J = 8.2$, 6.1, 0.8 Hz, H–C_6), 3.78 (dt, 1H, $J = 10.3$, 5.1 Hz, H–C_{10}), 3.70 (broad s, 1H, OH), 3.66 (s, 3H, CO_2Me), 3.69–3.62 (m, 1H of H–C_{10}), 2.49 (pseudo tddd, 1H, $J = 11.5$, 8.8, 4.9, 1.0 Hz, H–C_9), 2.35–2.26 (m, 1H, H–C_9), 1.65 (broad s, OH and H_2O), 1.38 (ddd, 1H, $J = 8.8$, 6.1, 1.1 Hz, H–C_5), 0.97 (dd, 1H, $J = 8.1$, 1.1 Hz, H–C_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.6 (CO axial), 207.8 (2CO basal), 172.94 (C_1), 135.63 (dm, $J = 159$ Hz, C_7), 128.63 (dm, $J = 154.5$ Hz, C_8), 83.91 (dm, $J = 168$ Hz, C_4), 83.09 (dm, $J = 174.2$ Hz, C_3), 68.80 (ddm, $J = 159.5$, 7 Hz, C_5), 67.40 (ddm, $J = 141.5$, 9.8 Hz, C_6), 60.93 (tm, $J = 143$ Hz, C_{10} e.g. CH_2OH), 51.71 (q, $J = 146.7$ Hz, OMe), 45.46 (ddd, $J = 163.6$, 7.6, 1.0 Hz, C_2), 30.83 (tm, $J = 126$ Hz, C_9). HRMS (70 eV, EI) Calc. mass for $C_{12}H_{16}^{56}FeO_5$ $[M - 2CO]^+$: 296.0347; Found: 296.0333. Main fragment ions m/z (%): 324 (0.4) $[M - CO]^+$, 296 (3.2) $[M - 2CO]^+$, 268 (5.5) $[M - 3CO]^+$, 250 (11.0) $[M - 3CO - H_2O]^+$, 220 (36.7) $[M - 3CO - CH_2O - H_2O]^+$, 28 (100) $[CO]^+$.

2.7. (2R*,5S*,6S*)-(2E,4E,7Z)-tricarbonyliron [dimethyl (η^4-2,3,4,5)-6-hydroxyundeca-2,4,7-triendioate] (8)

$R_f = 0.42$ with ether. IR (CCl_4, KBr): ν 3480 (broad, O–H), 2954, 2060 (C≡O), 1997 and 1987 (C≡O), 1736 (C=O), 1717 (C=O), 1459, 1438, 1196, 1175, 614, 560 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 5.85 (ddd, 1H, $J = 8.1$, 5.1, 1.0 Hz, H–C_3), 5.62 (broad ddd, 1H, $J = 10.8$, 9.2, 1.0 Hz, H–C_7), 5.55 (ddd, 1H, $J =$ 8.5, 5.1, 0.9 Hz, H–C_4), 5.44 (ddd, 1H, $J = 10.8$, 10.1, 5.4 Hz, H–C_8), 4.40 (broad dd, 1H, $J = 9.2$, 7.8 Hz, H–C_6), 3.67 (2s, 6H, 2 CO_2Me), 3.05 (broad d, 1H, $J = 1.6$ Hz, OH), 2.66 (broad dtdd, 1H, $J = 14.2$, 10.1, 4.9, 0.9 Hz, H–C_9), 2.51 (ddd, 1H, $J = 17.1$, 5.8, 5.1 Hz, H–C_{10}), 2.41 (ddd, 1H, $J = 17.1$, 10.3, 4.8 Hz, H–C_{10}), 2.23–2.13 (m, 1H, H–C_9), 1.34 (ddd, 1H, $J = 8.5$, 8.1, 0.7 Hz, H–C_5), 1.10 (dd, 1H, $J = 8.1$, 1.0 Hz, H–C_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 213.17 (CO axial), 208.8 and 207.9 (CO basal), 174.08 (C_{11}), 172.61 (C_1), 132.99 (dm, $J = 160.3$ Hz, C_7), 129.90 (dm, $J =$ 155 Hz, C_8), 85.73 (dm, $J = 168.8$ Hz, C_4), 84.39 (ddt, $J = 174.3$, 3.4, 2.4 Hz, C_3), 68.78 (ddm, $J = 143.0$, 10.1 Hz, C_6), 65.61 (dm, $J = 159.5$ Hz, C_5), 51.84 (q, $J = 147.0$ Hz, OMe), 51.72 (q, $J = 146.6$ Hz, OMe), 46.15 (ddd, $J = 164.6$, 7.8, 1.3 Hz, C_2), 33.07 (tm, $J = 128$ Hz, C_{10}), 22.67 (tm, $J = 128$ Hz, C_9). HRMS (70 eV, EI) Calc. mass for $C_{14}H_{18}^{56}FeO_6$ $[M - 2CO]^+$: 338.0453; Found: 338.0438. Main fragment ions m/z (%): 363 (0.2) $[M - OMe]^+$, 338 (4.4) $[M - 2CO]^+$, 310 (22.9) $[M - 3CO]^+$, 292 (9.1) $[M - 3CO - H_2O]^+$, 278 (14.7) $[M - 3CO - MeOH]^+$, 28 (100) $[CO]^+$.

2.8. (2R*,5S*,6R*)-(2E,4E,7Z)-tricarbonyliron [dimethyl (η^4-2,3,4,5)-6-hydroxyundeca-2,4,7-triendioate] (9)

$R_f = 0.61$ with ether. IR (neat, KBr): ν 3490 (broad, O–H), 2954, 2058 and 1990 (C≡O), 1737 and 1716 (C=O), 1453, 1439, 1197, 1177, 1175, 1118, 611, 560 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 5.82 (ddd, 1H, $J = 8.1$, 5.2, 1.0 Hz, H–C_3), 5.56–5.39 (m, 3H, H–$C_{4,7,8}$), 4.62 (dddd, 1H, $J = 8.3$, 5.6, 1.0, 0.9 Hz,

H–C_6), 3.68 (s, 3H, CO_2Me), 3.66 (s, 3H, CO_2Me), 2.63–2.25 (m, 5H, H–$C_{9,10}$ and OH), 1.36 (ddd, 1H, $J = 8.6$, 5.6, 1.0 Hz, H–C_5), 0.97 (dd, 1H, $J = 8.1$, 0.9 Hz, H–C_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.74 (C_{11}), 172.72 (C_1), 134.19 (C_7), 129.95 (C_8), 83.85 and 83.15 (C_3 and C_4), 68.31 and 67.73 (C_5 and C_6), 51.83 (OMe), 51.67 (OMe), 45.60 (C_2), 33.21 (C_{10}), 22.96 (C_9). HRMS (EI) Calc. mass for $C_{14}H_{18}^{56}FeO_6$ $[M - 2CO]^+$: 338.0453; Found: 338.0438. Main fragment ions m/z (%): 338 (2.4) $[M - 2CO]^+$, 310 (26.6) $[M - 3CO]^+$, 292 (9.1) $[M - 3CO - H_2O]^+$, 278 (13.2) $[M - 3CO - MeOH]^+$, 28 (100) $[CO]^+$.

2.9. (2R*,5S*,6S*)-(2E,4Z)-tricarbonyliron [methyl (η^4-2,3,4,5)-6-tert-butyldimethylsilyloxyhepta-2,4-dienoate]

To a stirred solution (N_2, −40 °C) of alcohol **10** (287 mg, 0.97 mmol) in anhydrous THF (16 ml) was added 2,6-lutidine (0.23 ml, 1.94 mmol). After 10 min, *tert*-butyldimethylsilyl triflate (0.334 ml, 1.45 mmol, 1.5 equiv.) was added dropwise. The reaction mixture was then maintained at −40 °C for 45 min, hydrolyzed by 8% aqueous $NaHCO_3$ (20 ml), and extracted twice with ether. Drying ($MgSO_4$) of combined organic extracts, concentration and flash-chromatography on silica gel using ether/petroleum ether (1:19) as eluent afforded the title silyl ether as yellow crystals (m.p. 52 °C, 123 mg, 31%, $R_f = 0.74$ with ether/petroleum ether (1:4) and starting alcohol **10** (77 mg, 27%)).

M.p. 52 °C. IR (Nujol, NaCl): ν 2055 and 1983 (C≡O), 1720 (C=O), 1284, 1256, 1162, 1081, 1040, 978, 957, 828, 772 cm^{-1}. ^{1}H NMR (90 MHz, $CDCl_3$): δ 6.08 (ddd, 1H, $J = 8.7$, 5.4, 1.2 Hz, H–C_3), 5.23 (ddd, 1H, $J = 7.8$, 5.4, 0.9 Hz, H–C_4), 3.69 (s, 3H, CO_2Me), 3.28 (dq, 1H, $J = 8.0$, 5.9 Hz, H–C_6), 2.74 (ddd, 1H, $J = 9.4$, 8.0, 1.2 Hz, H–C_5), 2.17 (dd, 1H, $J = 8.7$, 1.1 Hz, H–C_2), 1.32 (d, 3H, $J = 5.9$ Hz, H–C_7 e.g. Me), 0.84 (s, 9H, ^{t}Bu), −0.01 (s, 3H, Si–CH_3), −0.03 (s, 3H, Si–CH_3). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 208.85 (C≡O), 172.80 (C_1), 94.38 (C_3), 83.98 (C_4), 68.10 (C_6), 67.19 (C_5), 51.59 (OMe), 45.10 (C_2), 25.70 (C_7 and C(CH_3)$_3$), 17.92 (C(CH$_3$)$_3$), −4.36 (Si(CH_3)$_2$).

2.10. (2R*,5S*,6S*)-(2E,4Z)-tricarbonyliron [(η^4-2,3,4,5)-6-tert-butyldimethylsilyloxyhepta-2,4-dien-1-ol]

To a stirred solution (N_2, −40 °C) of the foregoing silyl ether (267 mg, 0.65 mmol) in anhydrous ether (12 ml) was added dropwise a 1 M solution of diisobutylaluminium hydride in toluene (1.6 ml, 2.4 equiv.). After 25 min at −40 °C, the reaction mixture was hydrolyzed by aqueous potassium sodium tartrate and extracted four times with ether. Drying ($MgSO_4$) of combined organic extracts, concentration and flash-chromatography on silica gel using ether/petroleum ether (1:9) as eluent afforded the title primary alcohol as an orange oil (217 mg, 87%, $R_f = 0.63$ with ether/petroleum ether (4:1)). IR (neat, NaCl): ν 3385 (broad, O–H), 2050 and 1967 (C≡O), 1253, 1081, 1042, 976, 826, 771 cm^{-1}. ^{1}H NMR (90 MHz, $CDCl_3$): δ 5.45 (ddd, 1H, $J = 9.0$, 5.3, 1.3 Hz, H–C_3), 5.11 (ddd, 1H, $J = 7.6$, 5.3, 1.1 Hz, H–C_4), 3.82 (dd, 1H, $J = 12.2$, 5.8 Hz, H–C_1 e.g. CH_2OH), 3.65 (dd, 1H, $J = 12.2$, 6.8 Hz, H–C_1), 3.31 (dq, 1H, $J = 8.4$, 5.9 Hz, H–C_6), 2.62 (ddd, 1H, $J = 9.6$, 7.9, 1.2 Hz, H–C_5), 2.49–2.21 (m, 1H, H–C_2), 1.28 (d, 3H, $J = 5.9$ Hz, H–C_7 e.g. Me), 0.85 (s, 9H, ^{t}Bu), 0.01 (s, 3H, Si–CH_3), −0.02 (s, 3H, Si–CH_3). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 210.69 (C≡O), 93.83 and 81.79 (C_3 and C_4), 68.14 (C_6), 66.83, 65.43, and 60.55 (C_1, C_2, and C_5), 25.80 (C(CH_3)$_3$), 25.59 (C_7), 18.03 (C(CH$_3$)$_3$), −4.20 (Si–CH_3), −4.26 (Si–CH_3). HRMS (70 eV, EI) Calc. mass for $C_{14}H_{26}^{56}FeO_3Si$ $[M - 2CO]^+$: 326.1000; Found: 326.1008. Main fragment ions m/z (%): 326 (1.6) $[M - 2CO]^+$, 298 (2.4) $[M - 3CO]^+$, 241 (3.8) $[M - 3CO - C(CH_3)_3]^+$, 75 (100).

2.11. (2R*,5S*,6S*)-(2E,4Z)-tricarbonyliron [(η^4-2,3,4,5)-6-tert-butyldimethylsilyloxyhepta-2,4-dienal] (11)

To a stirred solution (N_2, 0 °C) of the foregoing alcohol (295 mg, 0.77 mmol) in anhydrous THF (3 ml) was added a freshly prepared 0.4 M solution of *n*-propylmagnesium bromide in THF (2.5 ml, 1.0 mmol, 1.3 equiv.). After 5 min, a solution of ADD (390 mg, 1.54 mmol, 2 equiv.) in anhydrous THF (3 ml) was added. After 25 min further stirring at 0 °C, brine was added and the resulting mixture was extracted three times with ether. Combined organic extracts were washed with water, dried ($MgSO_4$) and concentrated. Flash-chromatography on silica gel using ether/petroleum ether (1:4) as eluent afforded aldehyde **11** as an orange oil (251 mg, 86%, $R_f = 0.57$ with ether/petroleum ether (3:7)). IR (neat, NaCl): ν 2950, 2930, 2855, 2070 and 1980 (C≡O), 1692 and 1680 (C=O), 1253, 1084, 1043, 976, 825, 772 cm^{-1}. ^{1}H NMR (90 MHz, $CDCl_3$): δ 9.34 (d, 1H, $J = 4.1$ Hz, H–C_1 e.g. CHO), 6.06 (ddd, 1H, $J = 8.6$, 5.3, 1.2 Hz, H–C_3), 5.30 (broad dd, 1H, $J = 7.6$, 5.3 Hz, H–C_4), 3.37 (dq, 1H, $J = 8.2$, 5.9 Hz, H–C_6), 2.90 (ddd, 1H, $J = 9.3$, 7.8, 1.1 Hz, H–C_5), 2.47 (ddd, 1H, $J = 8.6$, 4.1, 1.0 Hz, H–C_2), 1.36 (d, 3H, $J = 5.9$ Hz, H–C_7 e.g. Me), 0.85 (s, 9H, ^{t}Bu), 0.00 (s, 3H, Si–CH_3), −0.01 (s, 3H, Si–CH_3). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 208.45 (C≡O), 196.44 (C_1), 92.78 (C_3), 85.16 (C_4), 68.20 (C_5 and C_6), 53.81 (C_2), 25.74 (C(CH_3)$_3$), 25.62 (C_7), 18.00 (C(CH$_3$)$_3$), −4.32 (Si(CH_3)$_2$). HRMS (70 eV, EI) Calc. mass for $C_{14}H_{24}^{56}FeO_3Si$ $[M - 2CO]^+$: 324.0844; Found: 324.0861. Main fragment ions m/z (%): 324 (1.3) $[M - 2CO]^+$, 296 (35.8) $[M - 3CO]^+$, 281 (2.3) [M –

3CO − CH_3]$^+$, 266 (1.7) [M − 3CO − 2CH_3]$^+$, 239 (19.5) [M − 3CO − C(CH_3)$_3$]$^+$, 147 (49), 75 (100).

2.12. (4S,5R*,8S*,9S*)-(5E,7Z)-tricarbonyliron [ethyl (η^4-5,6,7,8)-9-tert-butyldimethylsilyloxy-4-hydroxydeca-5,7-dien-2-ynoate] (12) and (4R*,5R*,8S*,9S*)-(5E,7Z)-tricarbonyliron [ethyl (η^4-5,6,7,8)-9-tert-butyldimethylsilyloxy-4-hydroxydeca-5,7-dien-2-ynoate] (13)*

To a solution of anhydrous diisopropylamine (0.61 ml, 4.32 mmol) in THF (5 ml) was added at 0 °C a 1.6 M solution of *n*-butyllithium in hexane. After 20 min, the resulting solution of LDA was cooled at −78 °C and ethyl propiolate (0.44 ml, 4.32 mmol) was added. After one additional hour at −78 °C, a suspension of anhydrous cerium chloride (obtained by dehydration of cerium chloride heptahydrate at 150 °C under vacuum (1 mmHg) for 2 h) (1.92 g, 7.8 mmol) in THF (8 ml) was introduced. After 1 h reaction at −78 °C with $CeCl_3$, a solution of aldehyde **7** (365 mg, 0.96 mmol) in THF (3 ml) was added. After 20 min further reaction, the reaction was hydrolyzed by an aqueous saturated solution of ammonium chloride and extracted three times with ether. Combined organic extracts were washed with water, dried ($MgSO_4$) and concentrated. Flash-chromatography on silica gel using ether/petroleum ether (1:19) as eluent afforded the diasteroisomeric alcohols ψ-*endo* **13** (78 mg, 16%, R_f = 0.39 with ether/petroleum ether (3:7)) and then ψ-*exo* **12** (321 mg, 68%, R_f = 0.31 with ether/petroleum ether (3:7)) as orange oils.

Data for 12. IR (neat, NaCl): ν 3390 (broad, O–H), 2240 (C≡C), 2050 and 1970 (C≡O), 1711 (C=O), 1250, 1084, 972, 828, 773 cm^{-1}. ^{1}H NMR (90 MHz, $CDCl_3$): δ 5.58 (ddd, 1H, *J* = 8.2, 5.2, 0.9 Hz, H–C_6), 5.11 (ddd, 1H, *J* = 7.7, 5.2, 0.8 Hz, H–C_7), 4.56–4.35 (m, 1H, H–C_4), 4.25 (q, 2H, *J* = 7.1 Hz, CH_2CH$_3$), 3.33 (dq, 1H, *J* = 8.3, 5.9 Hz, H–C_9), 2.89 (broad d, 1H, *J* = 4.8 Hz, OH), 2.63 (broad dd, 1H, *J* = 9.5, 7.7 Hz, H–C_8), 2.31 (broad dd, 1H, *J* = 8.2, 7.0 Hz, H–C_5), 1.31 (t, 3H, *J* = 7.1 Hz, CH_2CH_3), 1.28 (d, 3H, *J* = 5.9 Hz, H–C_{10} e.g. Me), 0.84 (s, 9H, ^{t}Bu), 0.01 (s, 3H, Si–CH_3), −0.01 (s, 3H, Si–CH_3). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 209.97 (C≡O), 153.48 (C_1), 93.32 (C_6), 86.17 (C_3), 82.26 (C_7), 76.99 (C_2), 67.99, 66.80, 65.01, 62.30, and 60.01 (C_4, C_5, C_8, C_9, and OCH_2CH$_3$), 25.83 (C(CH_3)$_3$), 25.65 (C_{10}), 18.06 (*C*(CH$_3$)$_3$), 13.97 (OCH_2CH_3), −4.17 (Si–CH_3), −4.23 (Si–CH_3). HRMS (70 eV, EI) Calc. mass for $C_{18}H_{30}^{56}FeO_4Si$ [M − 3CO]$^+$: 394.1262; Found: 394.1235. Main fragment ions *m*/*z* (%): 394 (1.2) [M − 3CO]$^+$, 337 (3.4) [M − 3CO − ^{t}C(CH_3)$_3$]$^+$, 296 (10), 75 (100).

Data for 13. IR (neat, NaCl): ν 3410 (broad, O–H), 2225 (C≡C), 2055 and 1970 (C≡O), 1710 (C=O), 1248, 1081, 826, 773 cm^{-1}. ^{1}H NMR (90 MHz, $CDCl_3$): δ 5.58 (broad dd, 1H, *J* = 8.6, 5.6 Hz, H–C_6), 5.10 (broad dd, 1H, *J* = 7.7, 5.6 Hz, H–C_7), 4.46 (broad dd, 1H, *J* = 6.5, 4.7 Hz, H–C_4), 4.25 (q, 2H, *J* = 7.1 Hz, CH_2CH$_3$), 3.29 (dq, 1H, *J* = 8.4, 5.9 Hz, H–C_9), 2.63 (broad dd, 1H, *J* = 9.4, 8.2 Hz, H–C_8), 2.42–2.16 (m, 2H, H–C_5 and OH), 1.31 (t, 3H, *J* = 7.1 Hz, CH_2CH_3), 1.28 (d, 3H, *J* = 5.9 Hz, H–C_{10} e.g. Me), 0.84 (s, 9H, ^{t}Bu), 0.00 (s, 3H, Si–CH_3), −0.02 (s, 3H, Si–CH_3). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 210.09 (C≡O), 153.17 (C_1), 91.44 (C_6), 85.72 (C_3), 81.83 (C_7), 77.80 (C_2), 67.89 (C_9), 66.70, 63.95, 62.25, and 61.35 (C_4, C_5, C_8, and OCH_2CH$_3$), 25.80 (C(*C*H$_3$)$_3$), 25.66 (C_{10}), 18.06 (*C*(CH$_3$)$_3$), 13.99 (OCH_2CH_3), −4.22 (Si–*C*H$_3$), −4.25 (Si–*C*H$_3$). HRMS (EI) Calc. mass for $C_{19}H_{30}^{56}FeO_5Si$ [M − 2CO]$^+$: 422.1212; Found: 422.1231. Main fragment ions *m*/*z* (%): 422 (0.1) [M − 2CO]$^+$, 394 (1.2) [M − 3CO]$^+$, 337 (2.8) [M − 3CO − ^{t}C(CH_3)$_3$]$^+$, 291 (0.8) [M − 3CO − ^{t}SiMe$_2$^{t}Bu − ^{t}OCH_2CH_3]$^+$, 75 (100).

2.13. (4S,5R*,8S*,9S*)-(2Z,5E,7Z)-tricarbonyliron [ethyl (η^4-5,6,7,8)-9-tert-butyldimethylsilyloxy-4-hydroxydeca-2,5,7-trienoate] (14)*

Alkynol **12** (68 mg, 0.142 mmol) was catalytically hydrogenated as described below for the ψ-*endo* isomer **13**. Crude ψ-*exo* alkenol **14** was isolated (61 mg, 89%, R_f = 0.38 with ether/petroleum ether (1:4)) as an unstable orange oil. IR (neat, NaCl): ν 3410 (broad, O–H), 2970, 2935, 2860, 2050 and 1963 (C≡O), 1712 (C=O), 1641 (weak, C=C), 1256, 1184, 1082, 1025, 972, 826, 774 cm^{-1}. ^{1}H NMR (90 MHz, $CDCl_3$): δ 6.39 (dd, 1H, *J* = 11.8, 7.2 Hz, H–C_3), 5.87 (dd, 1H, *J* = 11.8, 0.8 Hz, H–C_2), 5.60 (ddd, 1H, *J* = 9.3, 5.5, 1.0 Hz, H–C_6), 5.13 (broad dd, 1H, *J* = 7.7, 5.6 Hz, H–C_7), 4.79–4.45 (m, 1H, H–C_4), 4.20 (q, 2H, *J* = 7.1 Hz, CH_2CH$_3$), 3.30 (dq, 1H, *J* = 8.0, 6.1 Hz, H–C_9), 2.61 (ddd, 1H, *J* = 9.3, 7.7, 1.1 Hz, H–C_8), 2.28 (ddd, 1H, *J* = 8.8, 7.6, 1.0 Hz, H–C_5), 2.1–1.5 (broad, 1H, OH), 1.29 (t, 3H, *J* = 7.1 Hz, CH_2CH_3), 1.26 (d, 3H, *J* = 6.1 Hz, H–C_{10} e.g. Me), 0.85 (s, 9H, ^{t}Bu), 0.01 (s, 3H, Si–CH_3), −0.02 (s, 3H, Si–CH_3).

2.14. (4R,5R*,8S*,9S*)-(2Z,5E,7Z)-tricarbonyliron [ethyl (η^4-5,6,7,8)-9-tert-butyldimethylsilyloxy-4-hydroxydeca-2,5,7-trienoate] (15)*

To a solution of ψ-*endo* alkynol **13** (42 mg, 0.088 mmol) in anhydrous methanol (3.5 ml) was added 10% palladium on carbon (20 mg). This mixture was well stirred magnetically under hydrogen. The reaction was monitored by TLC and was finished after about 1 h. After removal of the catalyst by filtration and of solvents, flash-chromatography on silica gel using ether/petroleum ether (1:19) as eluent afforded *Z*-al-

kenol **15** as an orange oil (27 mg, 64%, $R_f = 0.38$ with ether/petroleum ether (3:7)) and its *E* isomer (6 mg, 14%). **15**: IR (neat, NaCl): ν 3390 (broad, O–H), 2052 and 1967 (C≡O), 1711 (C=O), 1642 (weak, C=C), 1183, 1082, 1027, 825 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ 6.27 (dd, 1H, $J = 11.7$, 7.0 Hz, H–C_3), 5.84 (dd, 1H, $J = 11.7$, 1.2 Hz, H–C_2), 5.70 (ddm, 1H, $J = 8.5$, 5.3 Hz, H–C_6), 5.16–4.94 (m, 1H, H–C_4), 5.09 (ddd, 1H, $J = 7.8$, 5.3, 0.8 Hz, H–C_7), 4.21 (q, 2H, $J = 7.1$ Hz, CH_2CH_3), 3.29 (dq, 1H, $J = 8.2$, 6.0 Hz, H–C_9), 3.12 (broad d, 1H, $J = 3.7$ Hz, OH), 2.58 (ddd, 1H, $J = 9.6$, 8.0, 1.2 Hz, H–C_8), 2.30 (ddd, 1H, $J = 8.9$, 6.9, 0.9 Hz, H–C_5), 2.0–1.55 (broad, 1H, OH), 1.31 (t, 3H, $J = 7.1$ Hz, CH_2CH_3), 1.26 (d, 3H, $J = 6.0$ Hz, H–C_{10} e.g. Me), 0.83 (s, 9H, ^{t}Bu), 0.03 (s, 3H, Si–CH_3), −0.05 (s, 3H, Si–CH_3). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 210.7 (C≡O), 166.50 (C_1), 150.65 (C_3), 119.45 (C_2), 91.86 (C_6), 81.40 (C_7), 69.81, 68.02, 66.42, 64.99, and 60.78 (C_4, C_5, C_8, C_9, and OCH_2CH_3), 25.80 ($C(CH_3)_3$), 25.68 (C_{10}), 18.06 ($C(CH_3)_3$), 14.18 (OCH_2CH_3), −4.23 (Si–CH_3), −4.26 (Si–CH_3). HRMS (70 eV, EI) Calc. mass for $C_{18}H_{32}^{56}FeO_4Si$ $[M - 3CO]^+$: 396.1419; Found: 396.1415. Main fragment ions m/z (%): 396 (2.5) $[M - 3CO]^+$, 378 (2.5) $[M - 3CO - H_2O]^+$, 350 (3.7) $[M - 3CO - EtOH]^+$, 339 (3.0) $[M - 3CO - C(CH_3)_3]^+$, 293 (21.6) $[M - 3CO - C(CH_3)_3 - EtOH]^+$, 75 (98), 28 (100).

2.15. *(5R*,8S*,9S*)-(5E,7Z)-tricarbonyliron [ethyl (η^4-5,6,7,8)-9-tert-butyldimethylsilyloxy-4-oxodeca-5,7-dien-2-ynoate] (16)*

The same procedure as that described for the preparation of aldehyde **11** was used with ψ-*exo* alkynol **12** (or ψ-*endo* **13**). Starting from **12** (104 mg, 0.22 mmol), ketone **16** (71 mg, 69%, $R_f = 0.61$ with ether/petroleum ether (3:7)) was isolated as an orange oil after purification by flash-chromatography on silica gel. IR (neat, NaCl): ν 2060 and 1984 (C≡O), 1719 and 1642 (C=O), 1470, 1238, 1086, 826, 773 cm^{-1}. ^1H NMR (90 MHz, $CDCl_3$): δ 6.19 (ddd, 1H, $J = 8.8$, 5.3, 1.2 Hz, H–C_6), 5.28 (ddd, 1H, $J = 7.8$, 5.3, 1.0 Hz, H–C_7), 4.31 (q, 2H, $J = 7.1$ Hz, CH_2CH_3), 3.36 (dq, 1H, $J = 8.0$, 5.9 Hz, H–C_9), 2.91 (ddd, 1H, $J = 9.3$, 7.8, 1.2 Hz, H–C_8), 2.56 (dd, 1H, $J = 8.8$, 0.9 Hz, H–C_5), 1.37 (d, 3H, $J = 5.9$ Hz, H–C_{10}), 1.35 (t, 3H, $J = 7.1$ Hz, CH_2CH_3), 0.85 (s, 9H, ^{t}Bu), 0.01 (s, 3H, Si–CH_3), 0.00 (s, 3H, Si–CH_3). ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 211.72 (CO axial), 207.90 (2CO basal), 181.03 (d, $J = 4.0$ Hz, C_4), 152.36 (t, $J = 3.3$ Hz, C_1), 101.38 (C_2 or C_3), 92.12 (ddm, $J = 165.0$, 12.0 Hz, C_6), 85.11 (ddm, $J = 161.0$, 10.0 Hz, C_7), 80.97 (s, C_2 or C_3), 68.46 (dq, $J = 143.0$, 4.0 Hz, C_9), 68.16 (dm, $J = 154.0$ Hz, C_8), 63.01 (tq, $J = 149.0$, 4.0 Hz, OCH_2CH_3), 54.69 (dd, $J = 163.0$, 10.0 Hz, C_5), 25.88 (qd, $J = 124.0$, 5.0 Hz, C_{10}), 25.79 (q septet, $J = 125.0$, 6.0 Hz, $C(CH_3)_3$), 18.04 (q, $J = 3.0$ Hz, $C(CH_3)_3$), 14.00 (qt, $J = 127.0$, 3.0 Hz, OCH_2CH_3), −4.12 ($^1J_{CH} = 118.5$ Hz, Si–CH_3), −4.24 (Si–CH_3). HRMS (70 eV, EI) Calc. mass for $C_{18}H_{28}^{56}FeO_4Si$ $[M - 3CO]^+$: 392.1106; Found: 392.1095. Main fragment ions m/z (%): 420 (0.2) $[M - 2CO]^+$, 392 (4.9) $[M - 3CO]^+$, 377 (0.7) $[M - 3CO - CH_3]^+$, 335 (12.4) $[M - 3CO - C(CH_3)_3]^+$, 320 (0.8) $[M - 3CO - CH_3 - C(CH_3)_3]^+$, 75 (100).

2.16. *(5R*,8S*,9S*)-(2Z,5E,7Z)-tricarbonyliron [ethyl (η^4-5,6,7,8)-9-tert-butyldimethylsilyloxy-4-oxodeca-2,5,7-trienoate] (17)*

The same procedure as that described for the preparation of alkene **15** was used. Starting from **16** (30 mg, 0.06 mmol), flash-chromatography on silica gel afforded *Z*-enone **17** (22 mg, 73%, $R_f = 0.30$ with ether/petroleum ether (1:4)) and its *E* isomer (6 mg, 20%, $R_f = 0.35$ with ether/petroleum ether (1:4)) as orange oils. **17**: IR (neat, NaCl): ν 2965, 2935, 2865, 2070 and 1975 (C≡O), 1732 and 1679 (C=O), 1634 (weak, C=C), 1472, 1252, 1106, 1084, 1035, 968, 828, 772 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 6.42 (d, $J = 12.0$ Hz, H–C_2 or H–C_3), 6.19 (ddd, 1H, $J = 8.6$, 5.4, 1.2 Hz, H–C_6), 6.13 (d, $J = 12.0$ Hz, H–C_2 or H–C_3), 5.29 (ddd, 1H, $J = 7.8$, 5.4, 0.9 Hz, H–C_7), 4.22 (q, 2H, $J = 7.1$ Hz, CH_2CH_3), 3.32 (dq, 1H, $J = 8.0$, 6.0 Hz, H–C_9), 2.83 (ddd, 1H, $J = 9.3$, 8.0, 1.2 Hz, H–C_8), 2.55 (dd, 1H, $J = 8.6$, 0.9 Hz, H–C_5), 1.34 (d, 3H, $J = 6.0$ Hz, H–C_{10}), 1.29 (t, 3H, $J = 7.1$ Hz, CH_2CH_3), 0.84 (s, 9H, ^{t}Bu), 0.00 (s, 3H, Si–CH_3), −0.03 (s, 3H, Si–CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 209.51 (broad s, C≡O), 196.83 (d, $J = 9.9$ Hz, C_4), 165.53 (tm, $J = 13.0$ Hz, C_1), 138.73 (d, $J = 157.1$ Hz, C_2 or C_3), 127.06 (d, $J = 163.1$ Hz, C_2 or C_3), 92.57 (dd, $J = 170.9$, 9.7 Hz, C_6), 84.81 (d, $J = 167.9$ Hz, C_7), 68.38 (d, $J = 142.8$ Hz, C_9), 67.63 (dm, $J = 147.9$ Hz, C_8), 61.17 (tq, $J = 148.2$, 4.3 Hz, OCH_2CH_3), 52.74 (dd, $J = 162.2$, 9.0 Hz, C_5), 25.78 (q septet, $J = 130.5$, 5.1 Hz, $C(CH_3)_3$), 25.72 (q, $J = 130.0$ Hz, C_{10}), 18.04 (m, $C(CH_3)_3$), 14.03 (q, $J = 127.0$ Hz, OCH_2CH_3), −4.09 (Si–CH_3), −4.16 (Si–CH_3). Data for the 2*E* isomer of **17**: ^1H NMR (300 MHz, $CDCl_3$): δ 7.08 (dd, 1H, $J = 15.8$, 0.8 Hz, H–C_2 or H–C_3), 6.74 (d, 1H, $J = 15.8$ Hz, H–C_2 or H–C_3), 6.23 (broad dd, 1H, $J = 8.7$, 5.5 Hz, H–C_6), 5.33 (broad dd, 1H, $J = 7.5$, 5.5 Hz, H–C_7), 4.29 (q, 2H, $J = 7.1$ Hz, CH_2CH_3), 3.38 (dq, 1H, $J = 8.1$, 5.9 Hz, H–C_9), 2.90 (ddd, 1H, $J = 8.1$, 7.5, 0.8 Hz, H–C_8), 2.57 (d, 1H, $J = 8.7$ Hz, H–C_5), 1.39 (d, 3H, $J = 5.9$ Hz, H–C_{10}), 1.35 (t, 3H, $J = 7.1$ Hz, CH_2CH_3), 0.85 (s, 9H, ^{t}Bu), 0.08 (s, 3H, Si–CH_3), −0.01 (s, 3H, Si–CH_3).

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