Supporting Information

1. Synthetic procedures and characteristic data

1.1. General experimental

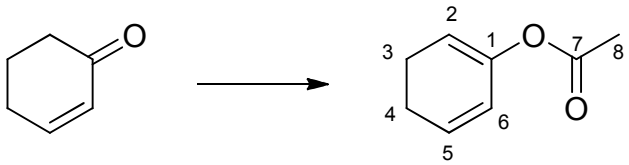
Unless otherwise stated all ^{1}H and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ on Bruker instruments (Avance DPX 300, Avance DRX 500 or Avance II 600). Chemical shifts (d) are reported in parts per million (ppm) from tetramethylsilane using the residual solvent resonance as the internal standard ($CDCl_3$: 7.24 ppm for ^{1}H NMR, 77.0 ppm for ^{13}C NMR). Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad). UV/Vis spectra were recorded in phosphate buffer 0.1 M (pH = 7.4) on a *Beckmann Coultar* DU 800 (cell length 1 cm). IR spectra were recorded on a *Perkin-Elmer* Paragon 1000 FT-IR spectrometer in the ATR mode at room temperature. Relative intensities of the signals are given as strong (s), medium (m), weak (w) and broad (br). Mass spectra were recorded at the Central Analytics Department - Mass Spectroscopy, University of Regensburg and the Analytical Service Unit, University of Cologne on *Finnigan* instruments (MAT Inocs 50 galaxy system (for EI LR-MS) and a MAT 900 (for HR-MS). An Agilent Technologies Model GC 6890N gas chromatograph coupled with an HP 5973N series mass selective detector and an HP 7683 GC autosampler was employed for all GCMS analyses. Samples were separated on a 30 m x 0.25 mm HP-5 MS column. The column temperature was initially held at 50 °C for 2 min, then the temperature was raised to 300 °C at a rate of 25 °C per min and held for 5 min. The total run-time was 17 min. Injector temperature was maintained at 300 °C, and the injection volume was 1.0 μL in the split mode. Mass spectra were scanned from m/z 35-500. Electron impact ionization energy was 70 eV. Enantiomeric analyses through GC were performed on an Agilent (HP 6890) instrument with FID detection using either a BGB-176SE column (A) or a 6TBDMS-2,3-Me-β-CD column (B). Enantiomeric analyses through High Performance Liquid Chromatography (HPLC) were conducted with HPLC units from Merck-Hitachi and Knauer (UV-detection at 220 nm and 254 nm) using one of the following columns: Diacel Chiracel OD-H (1), Diacel Chiracel OJ (2), Diacel Chiralpak AD-H (3), Macherey Nagel Nucleocell (4) and *n*-Hex/*i*-PrOH (99:1, 98:2 or 95:5) as a solvent. Gas chromatograms for the CO-detection were recorded using a Varian CP-3800 gas chromatograph with helium as the carrier gas and a 3 m x 2 mm packed molecular sieve 13X 80-100 column. The gases were detected using a thermal conductivity detector (Varian) operated at 150 C. CHN analyses were measured on an Elementar Vario EL machine. Melting points (uncorrected) were determined on a *Büchi* B-545 instrument. Analytical TLC was carried out using pre-coated silica gel plates (*Merck* TLC plates silica gel $60F_{254}$). Flash column chromatography was performed using silica gel (particle size 40- 63 mM, Acros). All sensitive reactions were carried out in flame dried glassware under an argon atmosphere. Chemicals were purchased from *Merck*, *Sigma-Aldrich*, *Fluka*, *Acros*, *Lancaster* or *Strem* and used without further purification. Solvents were dried as follows: THF and Et_2O were distilled from sodium/benzophenone under argon atmosphere. Cyclohexenone was distilled and stored under argon. Acetic anhydride was shaken with P_2O_5 and K_2CO_3 prior to distillation under argon. Diisopropylamine was refluxed over KOH and stored on KOH. Lipase from *Candida rugosa*

(> 2 units/mg; 90860) and esterase from porcine liver (PLE, > 130 units/mg; 46058) or PLE for the GC-measurements (>15 units/mg) were purchased from *Sigma-Aldrich*. Ethanol was refluxed with sodium and diethyl phthalate prior to distillation.

1.2 General procedure 1 for dienylester formation

To a solution of diisopropylamine in THF was added *n*-butyllithium at -78 °C. After stirring the mixture for 10 min, a solution of the particular enone in THF was added dropwise (ca. 1 h). Stirring was continued for 1 h at -78 °C. Then, the particular acid chloride or acid anhydride in THF was added dropwise (ca. 1 h). After 30 min at -78 °C the reaction mixture was allowed to warm to 25 °C before it was quenched by addition of saturated aqueous NH_4Cl. After 10 min the mixture was extracted with M*t*BE (50 mL) and the organic layer was washed with water (3x 50 mL) and brine (50 mL) and dried over anhydrous $MgSO_4$. Finally, the solvent was evaporated and the crude product purified.

1.2.1 Cyclohexa-1,5-dien-1-yl acetate (S1)



19 **S1**

According to general procedure 1 for dienylester formation, diisopropylamine (2.6 mL, 18.4 mmol, 1.5 eq) and *n*-butyllithium (11.6 mL, 16.7 mmol, 1.3 eq, 1.44 M in hexane) in THF (20 mL) were reacted with a solution of enone **19** (1.2 mL, 12.6 mmol, 1.0 eq) in THF (10 mL) and acetic anhydride (3.0 mL, 31.8 mmol, 2.5 eq) in THF (20 mL). The raw product was purified by column chromatography (silica gel, EtOAc/CyHex = 1:20) to yield 990 mg (7.2 mmol, 57%) of the dienolacetate **S1** as a colourless oil.

TLC: R_f (CyHex/EtOAc = 10:1) = 0.54.

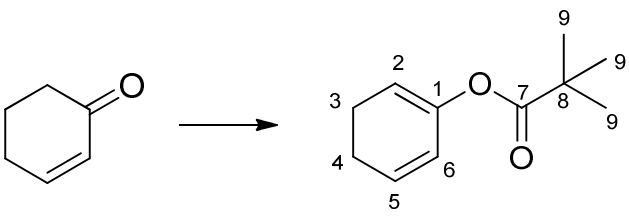
^{1}H NMR (500 MHz, $CDCl_3$) δ = 5.85-5.82 (m, 1H, H5), 5.64-5.62 (m, 1H, H6), 5.30 (Ψbs, 1H, H2), 2.26-2.21 (m, 2H, H3), 2.16-2.14 (m, 2H, H4), 2.07 (s, 3H, H8).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 169.1 (C7), 145.6 (C1), 128.7 (C5), 122.9 (C6), 110.7 (C2), 21.7 (C4), 21.1 (C3), 20.7 (C8).

FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3080 (w, ν(C_{sp2}-H)), 2935 (w, ν(C_{sp3}-H)), 2875 (w, ν(C_{sp3}-H)), 2830 (w, ν(C_{sp3}-H)), 1751 (s, ν(C=O)), 1659 (m), 1426 (m), 1400 (m), 1367 (m), 1206 (s), 1137 (s), 1075 (m), 1009 (m), 951 (m), 908 (s), 864 (m), 825 (m), 725 (m), 692 (m).

LR-MS (GC-MS) m/z (%) = 138 (18, $[M]^+$), 96 (100, $[M\text{-}CH_2CO]^+$), 67 (24), 43 (52).

1.2.2 Cyclohexa-1,5-dien-1-yl pivalate (S2)

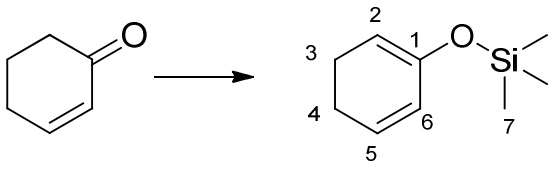


19 **S2**

According to general procedure 1 for dienylester formation, diisopropylamine (1.2 mL, 8.7 mmol, 1.7 eq) and *n*-butyllithium (6.0 mL, 8.6 mmol, 1.7 eq, 1.44 M in hexane) in THF (20 mL) were reacted with a

solution of enone **19** (0.51 mL, 502 mg, 5.2 mmol, 1.0 eq) in THF (10 mL) and pivaloyl chloride (1.6 mL, 13.1 mmol, 2.5 eq) in THF (20 mL). The raw product was purified by column chromatography (silica gel, EtOAc/CyHex = 1:20) to yield 448 mg (2.5 mmol, 48%) of dienyl pivalate **S2** as a colourless oil.
TLC: R_f (CyHex/EtOAc = 10:1) = 0.43.
^{1}H NMR (300 MHz, $CDCl_3$) δ = 5.86-5.80 (m, 1H, H5), 5.58 (Ψddd, *J* = 1.8, 3.6, 10.0 Hz, 1H, H6), 5.27 (Ψbs, 1H, H2), 2.28-2.20 (m, 2H, H3), 2.17-2.10 (m, 2H, H4), 1.18 (s, 9H, H9).
^{13}C NMR (75 MHz, $CDCl_3$) δ = 177.0 (C7), 145.9 (C1), 128.8 (C5), 123.1 (C6), 110.5 (C2), 38.7 (C8), 27.0 (C9), 21.9 (C4), 21.3 (C3).
FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3037 (w, ν(C_{sp2}-H)), 2970 (s, ν(C_{sp3}-H)), 2827 (m, ν(C_{sp3}-H)), 1747 (s, ν(C=O)), 1659 (m), 1479 (m), 1456 (m), 1425 (w), 1401 (m), 1364 (m), 1276 (s), 1232 (m), 1119 (bs), 1075 (m), 977 (w), 948 (m), 897 (m), 868 (w), 831 (w), 797 (w), 780 (m), 761 (m), 729 (m), 688 (w).
LR-MS (GC-MS) m/z (%) = 180 (24, $[M]^+$), 96 (100), 77 (14), 57 (73, $[C(CH_3)_3]^+$), 41 (31).

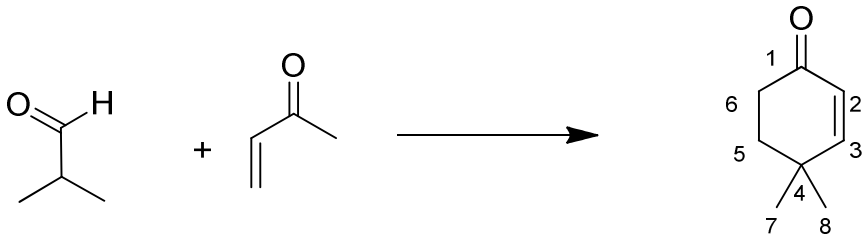
1.2.3 (Cyclohexa-1,5-dien-1-yloxy)trimethylsilane (32)



19 **32**

To a solution of diisopropylamine (3.2 mL, 22.9 mmol, 1.5 eq) in THF (24 mL) was added *n*-butyllithium (15.0 mL, 20.3 mmol, 1.3 eq, 1.34 M in hexane) at -78 °C. After stirring the mixture for 10 min, a solution of cyclohexenone **19** (1.5 mL, 15.7 mmol, 1.0 eq) in THF (10 mL) was added dropwise (ca. 1 h). Stirring was continued for 10 min at -78 °C. Then, TMSCl (2.0 mL, 15.7 mmol, 1.0 eq) in THF was added dropwise (ca. 1 h). After 30 min at -78 °C the reaction mixture was allowed to warm to 25 °C before it was washed with ice cold 10% aqueous $NaHCO_3$. The aqueous phase was extracted with petrol ether and M*t*BE and the combined organic phases were dried over $MgSO_4$. The solvents were evaporated and the raw product was purified by bulb to bulb distillation to yield 2.38 g (14.13 mmol, 90%) of the desired product **32** as a colourless oil.
^{1}H NMR (300 MHz, $CDCl_3$) δ = 5.87-5.81 (m, 1H, H5), 5.69-5.65 (m, 1H, H6), 4.87-4.85 (m, 1H, H2), 2.20-2.02 (m, 4H, H4, H3), 0.17 (s, 9H,H7).
^{13}C NMR (75 MHz, $CDCl_3$) δ = 148.0 (C1), 128.9 (C5), 126.4 (C6), 102.4 (C2), 22.4 (C4/C3), 21.7 (C4/C3), 0.1 (C7).
FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3044 (w, ν(C_{sp2}-H)), 2954 (w, ν(C_{sp3}-H)), 2929 (w, ν(C_{sp3}-H)), 2887 (w, ν(C_{sp3}-H)), 2819 (w, ν(C_{sp3}-H)), 1649 (m), 1588 (w), 1537 (w), 1400 (m), 1248 (s), 1196 (s), 956 (m), 908 (s), 840 (s), 752 (m), 616 (m).
LR-MS (GC-MS) m/z (%) = 168 (73, $[M]^+$), 151 (41), 91 (4), 73 (100), 59 (7), 45 (19), 27 (4).

1.2.4 4,4-Dimethylcyclohex-2-enone (21)



S3 **S4** **21**

To a solution of isobutyric aldehyde (30 mL, 0.33 mol, 1.5 eq) and methyl vinyl ketone (17.0 mL, 0.22 mol, 1.0 eq) was CAUTIOUSLY added conc. H_2SO_4 (0.1 mL, 0.5 mmol) in a way, that the temperature did not exceed 45 °C. The mixture was stirred at 20 °C (1 h) and subsequently refluxed under removal of water at a dean stark apparatus for 3 h. The solvent was evaporated and the raw product was purified by distillation (50 mbar, 70-100 °C) to yield 19.67 g (0.156 mol, 72%) of the enone **21** as a colourless oil.

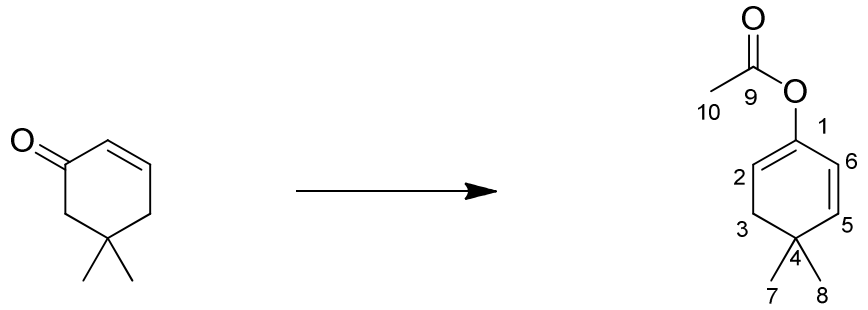
^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.63 (d, *J* = 10.1 Hz, 1H, H3), 5.81 (d, *J* = 10.1 Hz, 1H, H2), 2.43 (t, *J* = 6.6 Hz, 2H, H6), 1.84 (t, *J* = 6.6 Hz, 2H, H5), 1.14 (s, 6H, H7, H8).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 199.7 (C1), 159.8 (C3), 126.8 (C2), 36.1 (C6), 34.4 (C5), 27.7 (C7, C8).

LR-MS (GC-MS) m/z (%) = 124 (47, $[M]^+$), 109 (12, $[M\text{-}CH_3]^+$), 96 (97), 81 (100), 67 (68), 53 (36), 39 (35).

FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2959 (s, ν(C_{sp3}-H)), 2927 (s, ν(C_{sp3}-H)), 2860 (m, ν(C_{sp3}-H)), 1751 (w, ν(C=O)), 1681 (s), 1459 (m), 1378 (m), 1232 (m), 1202 (m), 1119 (m), 1031 (w), 1014 (w), 953 (w), 912 (w), 888 (w), 802 (s).

1.2.5 4,4-Dimethylcyclohexa-1,5-dien-1-yl acetate (22)



21 **22**

According to general procedure 1 for dienylester formation, diisopropylamine (2.6 mL, 18.4 mmol, 1.5 eq) and *n*-butyllithium (12.4 mL, 17.4 mmol, 1.4 eq, 1.40 M in hexane) in THF (20 mL) were reacted with a solution of enone **21** (1.56 g, 12.6 mmol, 1.0 eq) in THF (10 mL) and acetic anhydride (3.0 mL, 31.8 mmol, 2.5 eq) in THF (20 mL). The raw product was purified by column chromatography (silica gel, EtOAc/CyHex = 1:20) to yield 1.49 g (8.8 mmol, 70%) of the dienyl acetate **22** as a colourless oil.

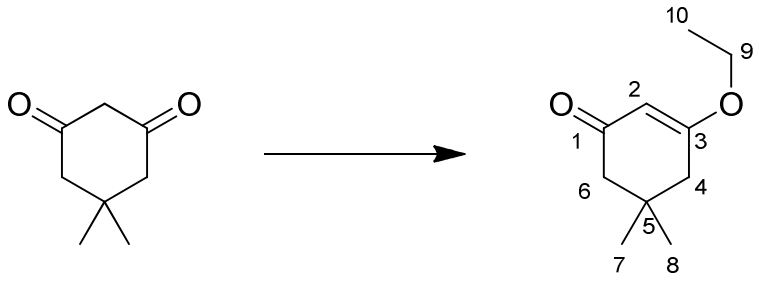
TLC: R_f (CyHex/EtOAc = 20:1) = 0.43.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 5.55 (m, 2H, H6, H5), 5.24 (m, 1H, H2), 2.19 (d, *J* = 1.0 Hz, 2H, H3), 2.09 (s, 3H, H9), 1.01 (s, 6H, H7).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 169.2 (C8), 145.0 (C1), 140.0 (C5), 120.4 (C6), 109.8 (C2), 36.5 (C3), 31.2 (C4), 27.6 (C7), 20.9 (C9).

FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3017 (w, $\nu(C_{sp2}$-H)), 2957 (s, $\nu(C_{sp3}$-H)), 2866 (m, $\nu(C_{sp3}$-H)), 2819 (w, $\nu(C_{sp3}$-H)), 1759 (s, ν(C=O)), 1662 (s), 1466 (m), 1405 (m), 1367 (s), 1316 (w), 1211 (br s), 1174 (s), 1139 (s), 1038 (s), 1008 (s), 932 (s), 909 (s), 865 (w), 824 (m), 794 (m), 738 (s), 707 (w), 641 (m).
LR-MS (GC-MS) m/z (%) = 166 (20, $[M]^+$), 124 (46), 109 (100), 91 (15), 81 (15), 67 (8), 55 (10), 43 (14).

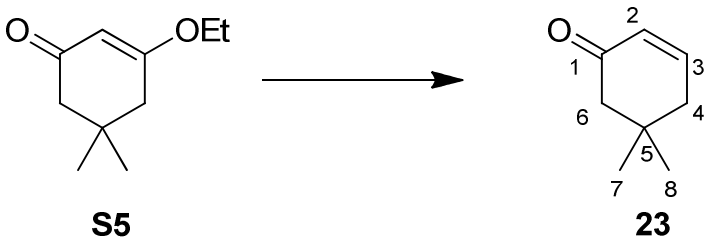
1.2.6 3-Ethoxy-5,5-dimethylcyclohex-2-en-1-one (S5)



27 **S5**

A solution of dimedone (**27**) (19.62 g, 0.14 mol, 1.0 eq), dry ethanol (27 mL, 0.46 mmol, 3.3 eq) and *p*TsOH (700 mg, 3.68 mmol, 0.03 eq) in toluene (200 mL) was refluxed in a Dean-Stark apparatus for water removal. After 1 h additional 1.0 g (5.26 mmol, 0.04 eq) of *p*TsOH were added and refluxing was continued until the conversion was complete (TLC, 6 h). The solvent was evaporated and the raw product was purified by column chromatography (CyHex: EtOAc = 5:1) to yield 22.85 g (0.136 mol, 97%) of the enolether **S5** as a white solid.
TLC: R_f(CyHex: EtOAc = 1:1) = 0.44.
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.34 (s, 1H, H2), 3.91 (q, *J* = 7.0 Hz, 2H, H9), 2.28 (s, 2H, H4), 2.21 (s, 2H, H6), 1.37 (t, *J* = 7.0 Hz, 3H, H10), 1.07 (s, 6H, H7, H8).
^{13}C NMR (75 MHz, $CDCl_3$) δ 199.5 (C1), 176.1 (C3), 101.4 (C2), 64.2 (C9), 50.7 (C6), 42.9 (C4), 32.4 (C5), 28.2 (C7, C8), 14.1 (C10).
FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2959 (w, $\upsilon(C_{sp3}$-H)), 2886 (w, $\upsilon(C_{sp3}$-H)), 1652 (s, υ(C=O), 1606 (s, υ(C=C)), 1375 (m), 1356 (m), 1319 (w), 1218 (s), 1143 (m), 1033 (m), 812 (w).
GC-MS: m/z (%) = 168 (92, $[M]^+$), 153, (20, $[M\text{-}CH_3]^+$), 137 (27, $[M\text{-}2CH_3]^+$), 125 (10), 112 (100), 97 (8), 84 (100), 68 (100), 55 (36), 43 (39).
T_m (DCM) = 57.2 °C.

1.2.7 5,5-Dimethylcyclohex-2-enone (23)



S5 **23**

A solution of enolether **S5** (10.1 g, 0.060 mol, 1.00 eq) in Et_2O (50 mL) was added dropwise to an ice cold suspension of $LiAlH_4$ (0.82 g, 0.022 mol, 0.37 eq) in Et_2O (200 mL) and the reaction mixture was stirred at 20 °C (24 h). Afterwards, water (50 mL) and 10% aqueous H_2SO_4 (50 mL) were added. The organic phase was separated and washed with aqueous Na_2SO_4 (50 mL) and brine (50 mL). The aqueous phases were re-extracted with M*t*BE. The combined organic phases were dried over $MgSO_4$ and the

solvent was evaporated. The raw product was purified by column chromatography (CyHex: EtOAc = 5:1) to yield 4.70 g (0.038 mol, 63%) of the desired enone **23** and 2.27 g (0.013 mol, 23%) of the starting material **S5**.

TLC: R_f(CyHex: EtOAc = 1:1) = 0.6.

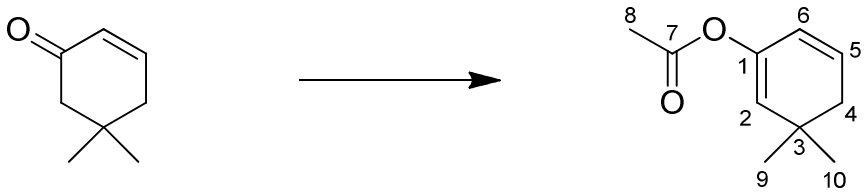
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.87 (dt, *J* = 9.9, 4.1 Hz, 1H, H3), 6.03 (d, *J* = 9.9 Hz, 1H, H2), 2.34 – 2.21 (m, 4H, H4/H6), 1.06 (s, 6H, H7, H8).

^{13}C NMR (75 MHz, $CDCl_3$) δ 199.9 (C1), 148.4(C3), 128.9 (C2), 51.7 (C6), 39.9 (C4), 33.9 (C5), 28.3 (C7, C8).

FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2993 (w, υ(C_{sp3}-H)), 2956 (w, υ(C_{sp3}-H)), 1675 (w, υ(C=O), 1596 (m, υ(C=C)), 1354 (s), 1176 (s), 1094 (w), 1004 (m), 918 (m), 817(m), 778 (w), 662 (w).

GC-MS: m/z (%) = 124 (14, $[M]^+$), 109 (4, $[M\text{-}CH_3]^+$), 95 (10, $[M\text{-}2CH_3]^+$), 83 (23), 68 (100), 55 (21).

1.2.8 3,3-Dimethylcyclohexa-1,5-dien-1-yl acetate (24)



23 **24**

According to general procedure 1 for dienylester formation, diisopropylamine (2.6 mL, 18.4 mmol, 1.5 eq) and *n*-butyllithium (11.6 mL, 16.7 mmol, 1.3 eq, 1.44 M in hexane) in THF (12 mL) were reacted with a solution of enone **23** (1.561 g, 12.6 mmol, 1.0 eq) in THF (10 mL) and acetic anhydride (3.0 mL, 31.8 mmol, 2.5 eq) in THF (50 mL). The raw product was purified by column chromatography (silica gel, EtOAc/CyHex = 1:10) to yield 1.36 g (8.1 mmol, 65%) of dienyl acetate **24** as a colourless oil.

TLC: R_f (CyHex/EtOAc = 5:1) = 0.61.

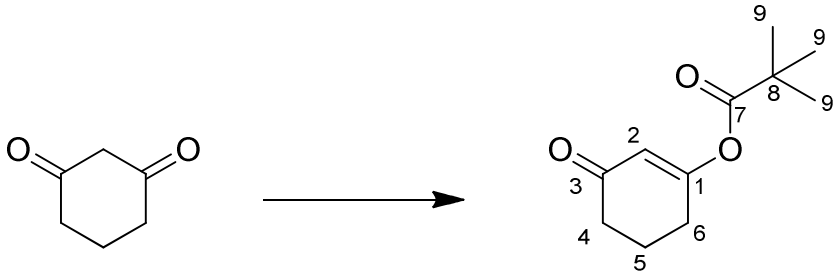
^{1}H NMR (300 MHz, $CDCl_3$) δ = 5.83 – 5.74 (m, 1H, H6), 5.66 (ddd, *J* = 9.9, 3.7, 1.9 Hz, 1H, H5), 5.10 (Ψd, *J* = 1.7 Hz, 1H, H2), 2.12 (Ψdd, *J* = 4.3, 1.9 Hz, 2H, H4), 2.10 (s, 3H, H8), 1.02 (s, 6H, H9, H10).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 169.2 (C7), 144.4 (C1), 127.7 (C6), 122.0 (C5), 121.9 (C2), 37.5 (C4), 31.7 (C3), 28.1 (C9, C10), 21.0 (C8).

FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2955 (m, ν(C_{sp3}-H)), 2923 (m, ν(C_{sp3}-H)), 2865 (w, ν(C_{sp3}-H)), 1759 (s, ν(C=O)), 1659 (m), 1464 (m), 1400 (m), 1368 (s), 1212 (s), 1196 (s), 1112 (s), 1044 (w), 1009 (m), 1001 (m), 948 (w), 910 (m), 899 (m), 874 (w), 835 (m), 729 (w), 703 (w).

LR-MS (GC-MS) m/z (%) = 166 (9, $[M]^+$), 124 (10, $[M\text{-}CH_2CO]^+$), 109 (100), 91 (9), 79 (10), 68 (8), 43 (20).

1.2.9 3-Oxocyclohex-1-en-1-yl pivalate (28)



26 **28**

A solution of cyclohexa-1,3-dione **26** (4.00 g, 35.6 mmol, 1.0 eq) and pyridine (5.8 ml, 71.4 mmol, 2.0 eq) in DCM (80 mL) was cooled to 0 °C. Pivaloylchloride (6.6 mL, 53.6 mmol, 1.5 eq) was added dropwise and the reaction mixture was stirred for 1 h. Afterwards water was added, the phases were separated and the aqueous phase was extracted with DCM. The combined organic phases were dried over anhydrous $MgSO_4$, the solvent was evaporated and the raw product was purified by column chromatography (silica gel, EtOAc/CyHex = 1:3) to yield 5.80 g (29.2 mmol, 82%) of the enone **28** as a colourless oil.

TLC: R_f (CyHex/EtOAc = 1:1) = 0.78.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 5.80 (s, 1H, H2), 2.46 (t, *J* = 6.1 Hz, 2H, H4), 2.35 (t, *J* = 6.7 Hz, 2H, H6), 2.08 – 1.93 (Ψq, , *J* = 6.4 Hz, 2H, H5), 1.22 (s, 9H, H9).

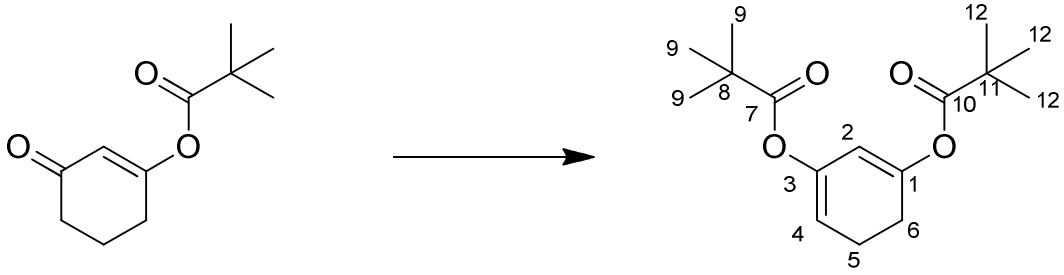
^{13}C NMR (75 MHz, $CDCl_3$) δ = 199.4 (C3), 175.1 (C7), 170.3 (C1), 117.4 (C2), 39.2 (C8), 36.6 (C4), 28.1 (C6), 26.8 (C9), 21.2 (C5).

FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2971 (m, ν(C_{sp3}-H)), 2874 (m, ν(C_{sp3}-H)), 1748 (s, ν(C=O)), 1681 (s), 1642 (s), 1479 (s), 1456 (m), 1427 (m), 1396 (m), 1363 (s), 1344 (m), 1325 (9), 1303 (m), 1271 (s), 1229 (m), 1140 (s), 1116 (bs), 1075 (s), 1025 (s), 965 (s), 941 (m), 906 (m), 878 (w), 831 (w), 789 (w), 754 (m), 662 (m).

LR-MS (GC-MS) m/z (%) = 196 (1, $[M]^+$), 153 (3), 125 (4), 113 (35), 96 (4), 85 (71), 83 (43), 69 (21), 57 (100).

HR-MS (DIP-MS, 70 eV) m/z 196.109±0.0005 (calcd ($[M]^+$) m/z 196.1099).

1.2.10 Cyclohexa-1,3-diene-1,3-diyl di(2,2-dimethylpropanoate) (30)



28 **30**

According to general procedure 1 for dienylester formation, diisopropylamine (1.2 mL, 8.7 mmol, 1.7 eq) and *n*-butyllithium (6.0 mL, 8.6 mmol, 1.7 eq, 1.44 M in hexane) in THF (8 mL) were reacted with a solution of enone **28** (1.02 g, 5.2 mmol, 1.0 eq) in THF (10 mL) and pivaloyl chloride (1.6 mL, 13.1 mmol, 2.5 eq) in THF (30 mL). The raw product was purified by column chromatography (silica gel, EtOAc/CyHex = 1:5) to yield an impure product containing ca. 583 mg (2.08 mmol, 39%) of diene **30** as a yellow oil, that could not be further purified and was used for further transformations without additional purification.

TLC:R_f(CyHex: EtOAc = 10:1) = 0.45.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.50 (s, 1H, H2), 5.26 (s, 1H, H4), 2.59 – 2.23 (m, 4H, H5, H6), 1.25 (s, 18H, H9, H12).

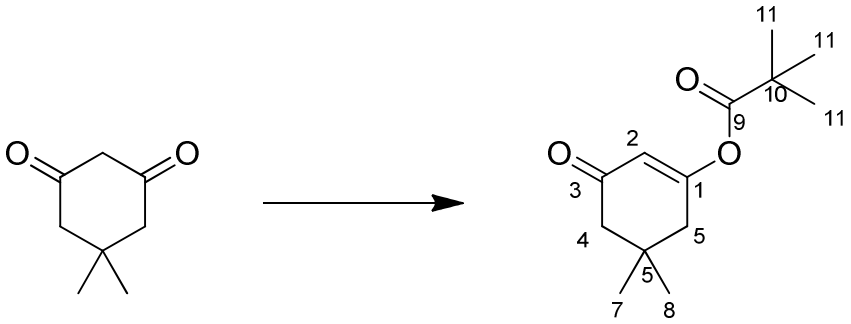
^{13}C NMR (75 MHz, $CDCl_3$) δ 176.9 (C7/C10), 176.3 (C7/C10) 151.0 (C1/C3), 144.9 (C1/C3), 110.0 (C2), 107.7 (C4), 39.0 (C8/C11), 38.8 (C8/C11), 27.0 (C9, C12), 25.3 (C6), 21.6 (C5).

FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2971 (m, υ(C_{sp3}-H)), 2880 (w, υ(C_{sp3}-H)), 1747 (s, υ(C=O), 1478 (m), 1395 (m), 1365 (m), 1275(w), 1106 (bs), 1025 (m), 892 (m), 759 (w), 681 (w).

LR-MS (GC-MS) m/z (%) = 280 (4, $[M]^+$), 196 (10), 112 (39), 85 (10), 68 (22), 57 (100), 41 (64).

HR-MS (DIP-MS, 70 eV) m/z 280.167 (calcd ($[M]^+$) m/z 280.1674).

1.2.11 5,5-Dimethyl-3-oxocyclohex-1-en-1-yl pivalate (29)



27 **29**

A solution of dimedone (**27**) (9.98 g, 71.2 mmol, 1.0 eq) and pyridine (11.6 ml, 142.8 mmol, 2.0 eq) in DCM (160 mL) was cooled to 0 °C. Pivaloylchloride (13.2 mL, 107.2 mmol, 1.5 eq) was added dropwise and the reaction mixture was stirred (1 h). Afterwards water was added, the phases were separated and the aqueous phase was extracted with DCM. The combined organic phases were dried over anhydrous $MgSO_4$, the solvent was evaporated and the raw product was purified by column chromatography (silica gel, EtOAc/CyHex = 1:4) to yield 14.37 g (68.04 mmol, 90%) of the enone **29** as a colourless oil.

TLC: R_f(CyHex: EtOAc = 1:1)= 0.76.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.86 (s, 1H, H2), 2.40 (s, 2H, H4), 2.27 (s, 2H, H6), 1.28 (s, 9H, H11), 1.12 (s, 6H, H7, H8).

^{13}C NMR (75 MHz, $CDCl_3$) δ 199.3 (C3), 175.4 (C9), 168.7 (C1), 116.6 (C2), 50.8 (C4), 42.0 (C6), 39.3 (C10), 33.1 (C5), 28.2 (C11), 26.9 (C7, C8).

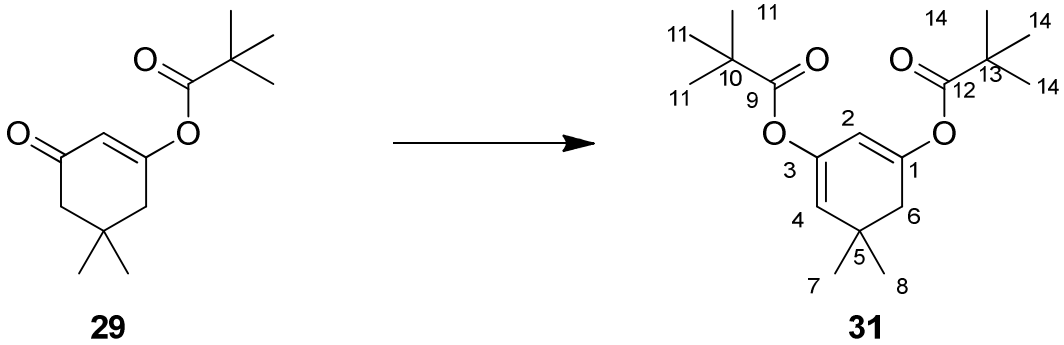
FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2966 (w, υ(C_{sp3}-H)), 2866 (w, υ(C_{sp3}-H)), 1754 (m, υ(C=O)), 1673 (s, υ(C=C)), 1643 (w, υ(C=C)), 1359 (m), 1273 (w), 1183 (w), 1116 (s), 1027(w).

GC-MS: m/z (%) = 224 (<1, $[M]^+$), 181 (4), 141 (66, $[M\text{-}C_5H_7O]^+$), 112 (10), 85 (100), 57 (100), 41 (50).

T_m (DCM) < 30 °C.

HR-MS (DIP-MS, 70 eV) m/z 224.140±0.0005 (calcd ($[M]^+$) m/z 224.1410).

1.2.12 5,5-Dimethylcyclohexa-1,3-diene-1,3-diyl di(2,2-dimethylpropanoate) (31)



29 **31**

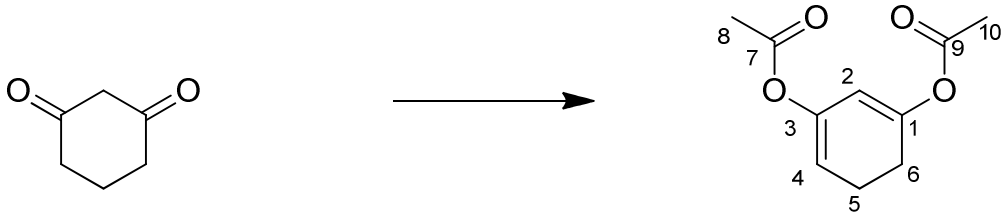
According to general procedure 1 for dienylester formation, diisopropylamine (2.6 mL, 18.4 mmol, 1.5 eq) and *n*-butyllithium (8.4 mL, 16.7 mmol, 1.3 eq, 2.00 M in hexane) in THF (20 mL) were reacted with a solution of enone **29** (2.28 g, 12.6 mmol, 1.0 eq) in THF (10 mL) and acetic anhydride (3.5 mL, 28.6 mmol, 2.27 eq) in THF (20 mL). The raw product was purified by column chromatography (silica gel, EtOAc/CyHex = 1:20) to yield 1.77 g (5.8 mmol, 46%) of dienolpivalate **31** as a colourless oil.

TLC: R_f(CyHex: EtOAc = 10:1) = 0.58.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.49 (s, 1H, H2), 5.06 (Ψd, *J* = 1.2 Hz, 1H, H6), 2.28 (s, 2H, H4), 1.25 (s, 18H, H11, H14), 1.14 (s, 6H, H7, H8).

^{13}C NMR (75 MHz, $CDCl_3$) δ 176.9 (C9/C12), 176.6 (C9/C12), 150.4 (C1/C3), 143.2 (C1/C3), 119.1 (C2), 109.1 (C6), 40.3 (C4), 39.0 (C10/C13), 38.8 (C10/C13), 33.2 (C5), 28.3 (C7, C8), 27.0 (C11, C14).
FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2965 (m, υ(C_{sp3}-H)), 2866 (w, υ(C_{sp3}-H)), 1747 (s, υ(C=O), 1673 (w,υ(C=C)), 1479 (m), 1395 (w), 1362(m), 1276 (m), 1110 (bs), 1029(w), 900 (w), 760 (w).
GC-MS: m/z = 308 (8, $[M]^+$), 224 (11, $[M\text{-}C_5H_8O]^+$), 209 (25), 140 (7), 125 (41), 109 (4), 85 (8), 57 (100), 41 (36).
T_m (DCM) < 30 °C.
HR-MS (DIP-MS, 70 eV) m/z 280.198 (calcd ($[M]^+$) m/z 280.1987).

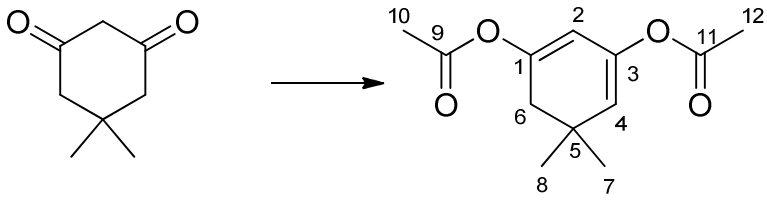
1.2.13 Cyclohexa-1,3-diene-1,3-diyl diacetate (S6)



26 **S6**

A mixture of the dione **26** (3.00 g, 26.76 mmol, 1 eq), *p*TsOH (1.50 g, 7.89 mmol, 0.3 eq) and isopropenyl acetate (150 mL) was heated to 90 °C (72 h). The produced acetone is distilled of during the reaction. The reaction mixture was washed with water and the solvent was evaporated. The raw product was purified by column chromatography (EtOAc:CyHex = 1:4) to yield 1.90 g (5.74 mmol, 37%) of the dienyl diacetate **S6** as a colourless oil.
TLC:R_f(CyHex: EtOAc = 10:1) = 0.62.
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.53 (s, 1H, H2), 5.24 (Ψd, *J* = 4.4 Hz, 1H, H4), 2.41 (Ψdt, *J* = 9.5, 4.6 Hz, 4H, H5, H6), 2.11 (s, 3H, H9/ H10), 2.10 (s, 3H, H9/ H10).
^{13}C NMR (75 MHz, $CDCl_3$) δ 169.2(C7/C8), 168.5 (C7/C8), 150.7 (C1/ C3), 144.5 (C1/ C3), 110.2 (C2), 108.2 (C4), 25.3 (C5/C6), 21.6 (C5/C6), 21.1 (C8/C10), 20.9 (C8/C10).
FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2938 (w), 2826 (w), 1754 (s), 1672 (m), 1621 (w), 1484 (w), 1426 (w), 1364 (s), 1191 (s), 1128 (s), 1095 (s), 1067 (s), 1043 (m), 1003 (s), 918 (m), 888 (m).
GC-MS: m/z = 196 (5, $[M]^+$), 154 (15), 112 (100), 111 (39), 84 (7), 69 (11), 43 (66).

1.2.14 5,5-Dimethylcyclohexa-1,3-diene-1,3-diyl diacetate (S7)

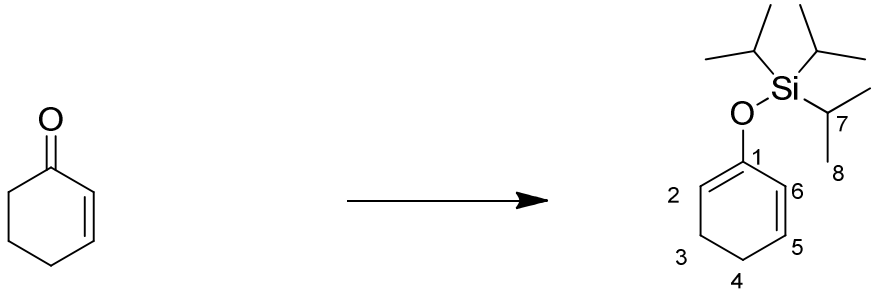


27 **S7**

A mixture of dimedone (**27**) (1.15 g, 8.2 mmol, 1 eq), *p*TsOH (300 mg , 1.6 mmol, 0.2 eq) and isopropenyl acetate (75 mL) was heated to 90 °C (72 h). The produced acetone is distilled of during the reaction. The reaction mixture was washed with water and the solvent was evaporated. The raw product was purified by column chromatography (EtOAc:CyHex = 1:4) to yield 1.30 g (5.74 mmol, 70%) of the diene as a colourless oil.
TLC: R_f (CyHex/EtOAc = 1:1) = 0.57.

^{1}H-NMR (300 MHz, $CDCl_3$) δ = 5.55 (Ψdd, *J* = 2.80, 1.34 Hz, 1H, H2), 5.06 (Ψd, *J* = 1.62 Hz, 1H, H4), 2.28 (Ψd, *J* = 1.36 Hz, 2H, H6), 2.11 (s, 3H, H10/H12), 2.09 (s, 3H, H10/H12), 1.09 (s, 6H, H7, H8).
^{13}C-NMR (75 MHz, $CDCl_3$) δ = 169.0 (C8), 168.6 (C8), 150.0 (C1), 142.9 (C3), 119.4 (C4), 109.1 (C2), 40.4 (C6), 33.1 (C5), 28.2 (C7, C8), 21.1 (C10/C12), 20.9 (C10/C12).
FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2955 (m, ν(C_{sp3}-H)), 2860 (w, ν(C_{sp3}-H)), 1759 (s, ν(C=O)), 1673 (s), 1619 (m), 1466 (m), 1425 (m), 1361 (s), 1189 (br s), 1138 (s), 1085 (s), 925 (s), 895 (s), 820 (m), 718 (w), 671 (m).
LR-MS (GC-MS) m/z (%) = 224 (10, $[M]^+$), 182 (40, $[M\text{-}CH_2CO]^+$), 140 (88, $[M\text{-}2CH_2CO)]^+$), 125 (88, $[M\text{-}2CH_2CO\text{-}CH_3]^+$), 107 (7), 84 (10), 69 (23), 43 (84).

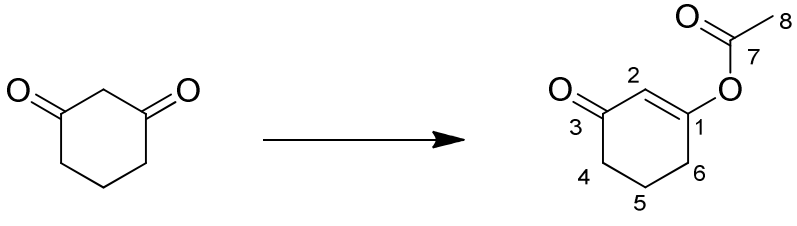
1.2.15 (Cyclohexa-1,5-dien-1-yloxy)triisopropylsilane (37)



19 **37**

According to general procedure 1 for dienylester formation, diisopropylamine (3.2 mL, 22.9 mmol, 1.5 eq) and *n*-butyllithium (12.5 mL, 20.1 mmol, 1.1 eq, 1.60 M in hexane) in THF (30 mL) were reacted with a solution of enone **19** (1.45 g, 15.7 mmol, 1.0 eq) in THF (10 mL) and TIPSOTf (4.6 mL, 16.6 mmol, 1.1 eq) in THF (20 mL). The raw product was purified by column chromatography (silica gel, EtOAc/CyHex = 1:40, 1% NEt_3) to yield 3.77 g (15.5 mmol, 99%) of dienolsilylether **37** as a colourless oil.
TLC: R_f (CyHex/EtOAc = 10:1) = 0.84.
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.87-5.83 (m, 1H, H5), 5.76-5.72 (d, *J* = 6.0 Hz, 1H, H6), 4.89 (Ψ s, 1H, H2), 2.14-2.07 (m, 4H, H3, H4), 1.17-1.10 (d, *J* = 1.1 Hz, 18H, H8), 1.07-1.05 (m, 3H, H7).
^{13}C NMR (75 MHz, $CDCl_3$) δ 148.6 (C1), 128.7 (C5), 126.7 (C6), 101.9 (C2), 22.6-21.8 (C3/C4), 17.9 (C8), 12.5 (C7).
FT-IR (ATR) $\tilde{\nu}$ [cm^-] = 3020 (w, ν (C_{sp2}-H)), 2940 (s, ν (C_{sp3}-H)), 2860 (s, ν (C_{sp3}-H)), 1700 (m), 1646 (s), 1593 (w), 1490 (w), 1460 (m), 1423 (w), 1380 (m), 1250 (s), 1200 (s), 1143 (m), 1066 (m), 996 (m).
LR-MS (GC-MS) m/z (%) = 252 (100, $[M]^+$), 237 (1), 209 (30), 179 (50), 151 (83), 121 (16), 103 (11), 75 (36), 59 (35), 41 (28).
HR-MS (DIP-MS, 70 eV) m/z 252.191 (calcd ($[M]^+$) m/z 252.1909).

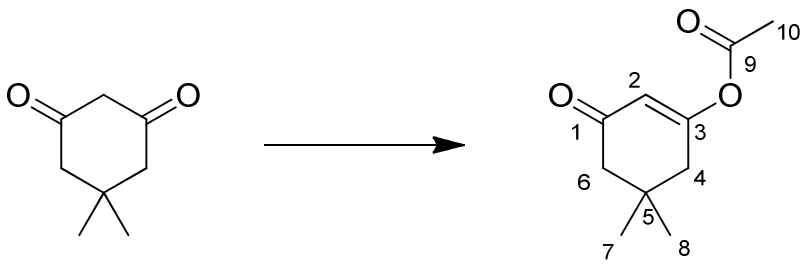
1.2.16 3-Oxocyclohex-1-en-1-yl acetate (39)



26 **39**

A solution of cyclohexadione **26** (4.00 g, 35.6 mmol, 1.0 eq) and pyridine (5.8 ml, 71.4 mmol, 2.0 eq) in DCM (80 mL) was cooled to 0 °C. Acetyl chloride (3.8 mL, 4.21 g, 53.6 mmol) was added dropwise and the reaction mixture was stirred (1 h). Afterwards water was added, the phases were separated and the aqueous phase was extracted with DCM. The combined organic phases were dried over anhydrous $MgSO_4$, the solvent was evaporated and the raw product was purified by column chromatography (silica gel, EtOAc/CyHex = 1:3) to yield 4.12 g (26.7 mmol, 75%) of the enone **39** as a colourless oil.
TLC: R_f (CyHex/EtOAc = 2:1) = 0.40.
^{1}H NMR (300 MHz, $CDCl_3$) 5.77 (s, 1H, H2), 2.47 – 2.35 (m, 2H, H6), 2.35 – 2.21 (m, 2H, H4), 2.10 (s, 3H, H8), 1.93 (q, *J* = 1.1 Hz, 2H, H5).
^{13}C NMR (75 MHz, $CDCl_3$) δ = 199.2 (C1), 169.5 (C3), 167.1 (C7), 117.2 (C2) , 36.4 (C4), 28.0 (C6), 21.0 (C5), 21.0 (C8).
FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2952 (w, ν(C_{sp3}-H)), 2872 (w, ν(C_{sp3}-H)), 1765 (s, ν(C=O)), 1666 (s), 1639 (s), 1516 (w), 1454 (m), 1426 (m), 1361 (s), 1345 (m), 1327 (m), 1304 (m), 1182 (s), 1142 (s), 1113 (s), 1048 (s), 1006 (s), 969 (s), 918 (s), 877 (s) 823 (m), 758 (m), 705 (m), 694 (m).
LR-MS (GC-MS) m/z (%) = 154 (5, $[M]^+$), 127 (5), 112 (17), 84 (58), 69 (19), 43 (100).

1.2.17 5,5-Dimethyl-3-oxocyclohex-1-en-1-yl acetate (40)



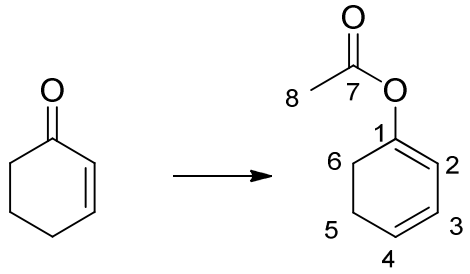
27 **40**

A solution of dimedone (**27)** (5.00 g, 35.6 mmol, 1.0 eq) and pyridine (5.8 ml, 71.4 mmol, 2.0 eq) in DCM (80 mL) was cooled to 0 °C. Acetyl chloride (3.8 mL, 4.21 g, 53.6 mmol) was added dropwise and the reaction mixture was stirred (1 h). Afterwards water was added, the phases were separated and the aqueous phase was extracted with DCM. The combined organic phases were dried over anhydrous $MgSO_4$, the solvent was evaporated and the raw product was purified by column chromatography (silica gel, EtOAc/CyHex = 1:3) to yield 4.740 g (26.01 mmol, 73%) of the enone **40** as a colourless oil.
TLC: R_f (CyHex/EtOAc = 2:1) = 0.44.
^{1}H NMR (300 MHz, $CDCl_3$) 5.81 (s, 1H, H2), 2.32 (d, *J* = 0.9 Hz, 2H, H6), 2.17 (s, 2H, H4), 2.12 (s, 3H, H10), 1.01 (s, 6H, H7, H8).
^{13}C NMR (75 MHz, $CDCl_3$) δ = 199.3 (C1), 167.9 (C3), 167.3 (C7), 116.3 (C2), 50.6 (C4), 42.0 (C6), 33.0 (C5), 28.0 (C7, C8), 21.1 (C10).
FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2958 (m, ν(C_{sp3}-H)), 2870 (m, ν(C_{sp3}-H)), 1768 (s, ν(C=O)), 1668 (s), 1642 (s), 1468 (m), 1424 (m), 1412 (m), 1388 (m), 1358 (s), 1312 (m), 1297 (m), 1280 (m), 1258 (w), 1176 (s), 1143 (m), 1113 (s), 1044 (m), 1009 (s), 994 (m), 953 (m), 928 (m), 917 (m), 896 (m), 879 (m), 856 (m), 824 (m), 800 (w), 685 (m).
LR-MS (GC-MS) m/z (%) = 154 (7, $[M]^+$), 167 (2), 140 (24), 125 (10), 84 (92), 69 (30), 43 (100).

1.3 General procedure 2 for dienyl- ester and silylenolether formation

To a solution of hexamethyldisilazane in THF was added *n*-butyllithium at -78 °C. After 10 min TPPA was added and stirring was continued for 20 min at -78 °C. Then the particular enone in THF was added dropwise (1 h). Afterwards the particular acid chloride, acid anhydride, or TIPSOTf in THF was added dropwise (1 h). The mixture was stirred for additional 30 min at -78 °C and then allowed to warm to 25 °C before it was quenched with saturated aqueous NH_4Cl. After extraction with M*t*BE (50 mL), the organic solution was washed with water (3x50 mL) and brine (50 mL) and dried over anhydrous $MgSO_4$. Finally, the solvent was evaporated and the crude product purified by column chromatography.

1.3.1 Cyclohexa-1,3-dienyl acetate (S8)



19 **S8**

According to general procedure 2 for dienylester formation, hexamethyldisilazane (2.6 mL, 12.1 mmol, 1.5 eq), *n*-butyllithium (7.3 mL, 10.5 mmol, 1.3 eq, 1.44 M in hexane) and TPPA (5.0 mL, 18 mmol, 2.5 eq) in THF (100 mL) were reacted with a solution of enone **19** (0.8 mL, 8.1 mmol, 1.0 eq) in THF (10 mL) and acetic anhydride (1.8 mL, 18.4 mmol, 2.27 eq) in THF (20 mL). The raw product was purified by column chromatography (silica gel, EtOAc/CyHex = 1:20) and gave 731mg (5.3 mmol, 65%) of dienylacetate **S8** as a colourless oil.

TLC: R_f (CyHex/EtOAc = 10:1) = 0.54.

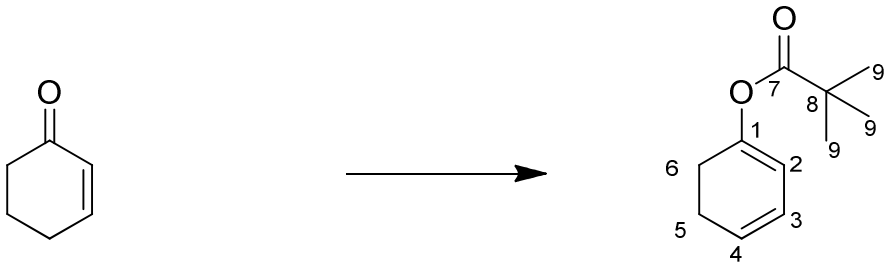
^{1}H NMR (500 MHz, $CDCl_3$) δ = 5.84-5.81 (m, 1H, H3), 5.63-5.59 (m, 2H, H2, H4), 2.33 (Ψbs, 4H, H5, H6), 2.11 (s, 3H, H8).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 169.0 (C7), 149.1 (C1), 123.5 (C4), 122.7 (C3), 110.9 (C2), 25.4 (C6), 23.6 (C5), 21.0 (C8).

FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3045 (w, ν(C_{sp2}-H)), 2932 (m, ν(C_{sp3}-H)), 2871 (m, ν(C_{sp3}-H)), 1755 (s, ν(C=O)), 1665 (w), 1593 (w), 1495 (w), 1365 (m), 1205 (s), 1137 (m), 1010 (m), 912 (s), 747 (s), 692 (m).

LR-MS (GC-MS) m/z (%) = 138 (17, $[M]^+$), 96 (100, $[M-CH_2CO]^+$), 79 (60), 67 (44), 54 (29), 43 (50).

1.3.2 Cyclohexa-1,3-dienyl pivalate (20)



19 **20**

According to general procedure 2 for dienylester formation, hexamethyldisilazane (2.6 mL, 12.1 mmol, 1.5 eq), *n*-butyllithium (7.3 mL, 10.5 mmol, 1.3 eq, 1.44 M in hexane) and TPPA (5.0 mL, 18 mmol, 2.5 eq) in THF (100 mL) were reacted with a solution of enone **19** (0.8 mL, 8.1 mmol, 1.0 eq) in THF (10 mL) and pivaloylchloride (2.2 mL, 2.22 g, 18.4 mmol, 2.27 eq) in THF (20 mL). The raw product was purified by column chromatography (silica gel, EtOAc/CyHex = 1:20) and gave 900 mg (5.0 mmol, 62%) of dienylpivalate **20** as a colourless oil.

TLC: R_f (CyHex/EtOAc = 10:1) = 0.45.

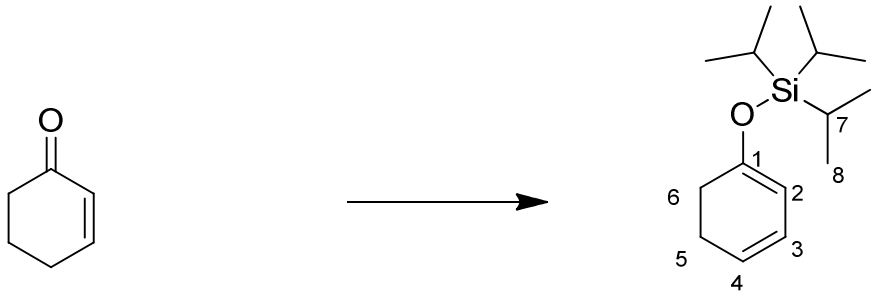
^{1}H NMR (500 MHz, $CDCl_3$) δ = 5.94 – 5.77 (m, 1H, H3), 5.70 – 5.51 (m, 2H, H2, H4), 2.43 – 2.21 (m, 4H, H5, H6), 1.23 (s, 9H, H9).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 176.7 (C7), 149.4 (C1), 123.3 (C3/C4), 122.9 (C3/C4), 110.6 (C2), 38.9 (C8), 27.0 (C9), 25.3 (C5/C6), 23.6 (C5/C6).

FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] 2968 (m, ν(C_{sp3}-H)), 2933 (w, ν(C_{sp3}-H)), 2871 (w, ν(C_{sp3}-H)), 1742 (s, ν(C=O)), 1684 (m), 1529 (w), 1479 (m), 1458 (m), 11395 (m), 1364 (m), 1277 (s), 1239 (s), 1027 (m), 938 (m), 897 (w), 799 (w), 761 (w), 689 (w).

LR-MS (GC-MS) m/z (%) = 180 (10, $[M]^+$), 96 (98), 79 (12), 67 (15), 57 (100, $[C(CH_3)_3]^+$), 41 (47).

1.3.3 (Cyclohexa-1,3-dien-1-yloxy)triisopropylsilane (37)



19 **37**

According to general procedure 2 for dienylester formation, hexamethyldisilazane (2.6 mL, 12.1 mmol, 1.5 eq), *n*-butyllithium (8.8 mL, 12.1 mmol, 1.5 eq, 1.39 M in hexane) and TPPA (5.0 mL, 18.0 mmol, 2.5 eq) in THF (100 mL) were reacted with a solution of enone **19** (0.8 mL, 8.1 mmol, 1.0 eq) in THF (10 mL) and triisopropylsilyl triflate (2.6 mL, 9.72 mmol, 1.2 eq) in THF (20 mL). The raw product was purified by column chromatography (silica gel, EtOAc/CyHex = 1:40) and gave 1.90 g (7.5 mmol, 85%) of the silylenolether **37** as a colourless oil.

TLC: R_f (CyHex/EtOAc = 10:1) = 0.89.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.94 – 5.69 (m, 1H, H3), 5.39 (Ψdd, *J* = 9.2, 3.8 Hz, 1H, H4), 5.12 (d, *J* = 5.8 Hz, 1H, H2), 2.25 (Ψd, *J* = 12.0 Hz, 4H, H5, H6), 1.24 – 1.15 (m, 3H, H7), 1.10 (s, 12H, H8), 1.08 (s, 6H, H8).

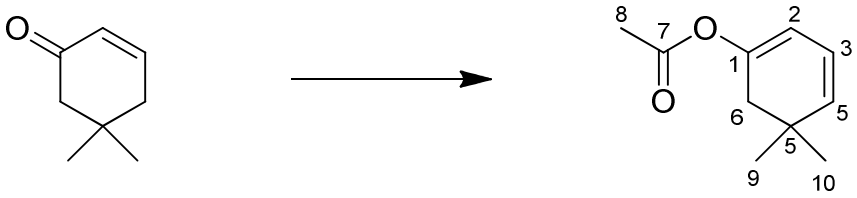
^{13}C NMR (75 MHz, $CDCl_3$) δ 154.1 (C1), 124.7 (C3), 117.8 (C4), 101.7 (C2), 28.7 (C5/C6), 24.0 (C5/C6), 17.9 (C7), 12.6 (C8).

FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3039 (w, ν(C_{sp2}-H)), 2941 (s, ν(C_{sp3}-H)), 2889 (m, ν(C_{sp3}-H)), 2864 (s, ν(C_{sp3}-H)), 1644 (s), 1583 (s), 1462 (s), 1435 (w), 1421 (w), 1382 (m), 1365 (s), 1252 (s), 1210 (s), 1159 (s), 1070 (w), 1013 (w), 995 (m), 972 (m), 900 (s), 881 (s), 847 (s), 824 (m), 751 (m), 714 (m), 676 (s).

LR-MS (GC-MS) m/z (%) = 252 (90, $[M]^+$), 207 (59), 179 (59), 151 (100), 137 (71), 121 (23), 77 (37), 59 (26), 41 (23).

HR-MS (DIP-MS, 70 eV) m/z 252.191 (calcd ($[M]^+$) m/z 252.1909).

1.3.4 5,5-Dimethylcyclohexa-1,3-dien-1-yl acetate (25)



23 **25**

According to general procedure 2 for dienylester formation, hexamethyldisilazane (2.6 mL, 12.1 mmol, 1.5 eq), *n*-butyllithium (7.3 mL, 10.5 mmol, 1.3 eq, 1.44 M in hexane) and TPPA (5.0 mL, 18 mmol, 2.5 eq) in THF (100 mL) were reacted with a solution of enone **23** (1.00 g, 8.1 mmol, 1.0 eq) in THF (10 mL) and acetic anhydride (1.8 mL, 18.4 mmol, 2.27 eq) in THF (20 mL). The raw product was purified by column chromatography (silica gel, EtOAc/CyHex = 1:20) and gave 881 mg (5.3 mmol, 65%) of dienylacetate **25** as a colourless oil.

TLC: R_f (CyHex/EtOAc = 5:1) = 0.58.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 5.70 (dd, *J* = 9.4, 5.8 Hz, 1H, H3), 5.57 (d, *J* = 5.8 Hz, 1H, H4), 5.37 (d, *J* = 9.4 Hz, 1H, H2), 2.22 (Ψd, *J* = 1.1 Hz, 2H, H6), 2.11 (s, 3H, H8), 1.04 (s, 6H, H9, H10).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 169.0 (C7), 148.7 (C1), 135.2 (C2), 119.8 (C3), 109.6 (C4), 40.3 (C6), 33.8 (C5), 27.9 (C9, C10), 21.0 (C8).

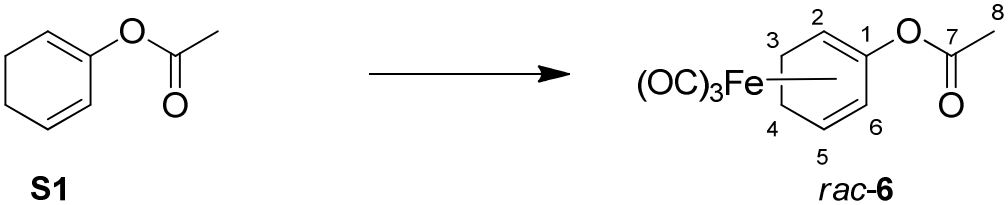
FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2946 (m, ν(C_{sp3}-H)), 2920 (s, ν(C_{sp3}-H)), 2851 (m, ν(C_{sp3}-H)), 1756 (s, ν(C=O)), 1673 (w), 1593 (w), 1464 (w), 1366 (m), 1209 (s), 1117 (s), 1066 (w), 1011 (m), 802 (w), 727 (w).

LR-MS (GC-MS) m/z (%) = 166 (17, $[M]^+$), 124 (26, $[M-CH_2CO]^+$), 109 (100), 91 (9), 79 (10), 43 (25).

1.4 General complexation procedure (preparation of diene-$Fe(CO)_3$ complexes)

A Schlenk tube was charged with the diene and $Fe_2(CO)_9$ and set under argon by three evacuation/argon flush cycles. Then, degassed diethylether was added and the reaction mixture was heated to reflux for 20 h under argon. Finally, the solvent was evaporated and the crude mixture purified by column chromatography (silica gel, EtOAc/CyHex = 1:40, if not otherwise stated) to yield the desired complex.

1.4.1 (*RS*)-Tricarbonyl-η^4-(1-acetoxy-1,5-cyclohexadiene)iron(0) (*rac*-6)

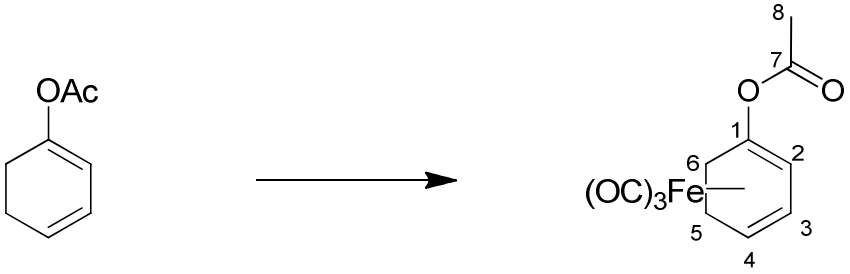


S1 ***rac*-6**

According to the general complexation protocol, diene **S1** (500 mg, 3.6 mmol, 1.0 eq) and $Fe_2(CO)_9$ (3.90 g, 10.7 mmol, 3.0 eq) were heated in Et_2O (30 mL) for 16 h. After purification, 687 mg (2.5 mmol, 69%) of complex *rac*-**6** were isolated as a yellow oil.

TLC: R_f (CyHex/EtOAc = 10:1) = 0.51.
^{1}H NMR (500 MHz, $CDCl_3$) δ = 5.49 (Ψdd, *J* = 1.9, 6.6, 1H, H6), 3.34 (Ψtd, *J* = 2.3, 4.5 Hz, 1H, H2), 2.83 (dt, *J* = 3.0, 6.30 Hz, 1H, H5), 2.17 (s, 3H, H8), 1.86-1.67 (m, 2H, H3), 1.6-1.50 (m, 2H, H4).
^{13}C NMR (125 MHz, $CDCl_3$) δ = 210.8 (Fe(*C*O)$_3$), 170.1 (C7), 128.2 (C1), 79.8 (C6), 59.0 (C2), 52.0 (C5), 24.5 (C3), 23.4 (C4), 21.0 (C8).
FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2921 (w, ν(C$_{sp3}$-H)), 2839 (w, ν(C$_{sp3}$-H)), 2047 (s, ν(Fe(*C*O)$_3$)), 1967 (bs, ν(Fe(*C*O)$_3$)), 1764 (s, ν(C=O)), 1452 (m), 1428 (m), 1367 (m), 1206 (s), 1170 (s), 1123 (w), 1085 (w), 1011 (w), 899 (w).
LR-MS (DIP-MS, 70 eV) m/z (%) = 250 (10, [M-CO]$^+$), 222 (28, [M-2CO]$^+$), 194 (32, [M-3CO]$^+$), 192 (100), 164 (21), 150 (31), 134 (30), 121 (17), 95 (12), 84 (20), 71 (10), 57 (14), 56 (69, [Fe]$^+$).
HR-MS (DIP-MS, 70 eV) m/z 249.992±0.0010 (calcd ([M-CO]$^+$) m/z 249.9928).
EA: Calcd for $C_{11}H_{10}FeO_5$: C 47.52; H 3.63. Found: C 47.23; H 3.63.

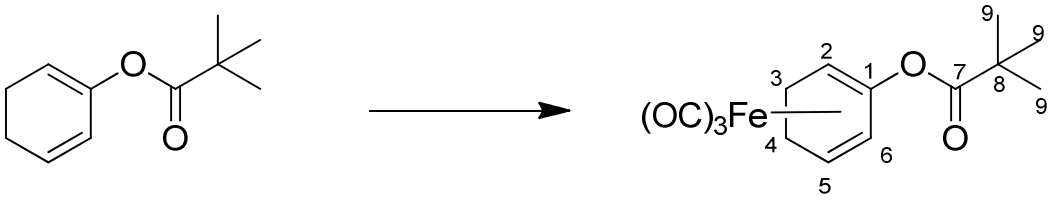
1.4.2 (*RS*)-Tricarbonyl-η^4-(1-acetoxy-1,3-cyclohexadiene)iron(0) (*rac*-8)



S8 *rac*-**8**

According to the general complexation protocol, diene **S8** (800 mg, 5.8 mmol, 1.0 eq) and $Fe_2(CO)_9$ (6.30 g, 17.1 mmol, 3.0 eq) were heated in Et_2O (50 mL) for 16 h. After purification, 1.26 g (4.6 mmol, 79%) of complex *rac*-**8** were isolated as a yellow crystalline solid. The sample used for the X-ray crystallographic analysis was re-crystallized from $CDCl_3$.
TLC: R_f (CyHex/EtOAc = 10:1) = 0.51.
^{1}H NMR (500 MHz, $CDCl_3$) δ = 5.36 (d, *J* = 4.2 Hz, 1H, H2), 3.34 (t, *J* = 5.0 Hz, 1H, H3), 3.08-3.06 (m, 1H, H4), 2.17-1.62 (m, 4H, H5, H6), 2.17 (s, 3H, H8).
^{13}C NMR (125 MHz, $CDCl_3$) δ = 169.2 (C7), 103.3 (C1), 80.6 (C2), 80.3 (C3), 60.3 (C4), 24.5 (C5/C6), 23.4 (C5/C6), 21.2 (C8).
FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2929 (m, ν(C$_{sp3}$-H)), 2852 (m, ν(C$_{sp3}$-H)), 2047 (s, ν(Fe(*C*O)$_3$)), 1967 (bs, ν(Fe(*C*O)$_3$)), 1751 (s, ν(C=O)), 1470 (m), 1427 (m), 1366 (s), 1328 (m), 1266 (m), 1209 (s), 1180 (m), 1014 (m), 909 (m), 890 (m), 865 (w), 759 (m).
LR-MS (DIP-MS, 70 eV) m/z (%) = 278 (1, [M]$^+$), 250 (15, [M-CO]$^+$), 222 (34, [M-2CO]$^+$], 194 (35, [M-3CO]$^+$), 192 (100), 164 (11), 150 (19), 134 (20), 121 (10), 56 (26, [Fe]$^+$).
HR-MS (DIP-MS, 70 eV) m/z 277.9883±0.0005 (calcd ([M]$^+$) m/z 277.9878).
EA: Calcd for $C_{11}H_{10}FeO_5$: C 47.52; H 3.63. Found: C 48.09; H 3.80.
T_m (DCM) = 43.1 °C.

1.4.3 (*RS*)-Tricarbonyl-η⁴-(1-(2,2-dimethylpropanoyloxy)-1,5-cyclohexadiene)iron(0) (*rac*-7)



S2 *rac*-**7**

According to the general complexation protocol, diene **S2** (500 mg, 2.8 mmol, 1.0 eq) and $Fe_2(CO)_9$ (2.0 g, 5.5 mmol, 2.0 eq) were heated in Et_2O (30 mL) for 16 h. After purification, 699 mg (2.2 mmol, 78%) of complex *rac*-**7** were isolated as a yellow oil.

TLC: R_f (CyHex/EtOAc = 10:1) = 0.78.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 5.47 (Ψdd, *J* = 1.5, 6.6 Hz, 1H, H6), 3.31 (Ψtd, *J* = 2.2, 4.08 Hz, 1H, H2), 2.82 (td, *J* = 3.0, 6.2 Hz, 1H, H5), 1.85-1.79 (m, 1H, H3), 1.77-1.71 (m, 1H, H3), 1.58-1.50 (m, 2H, H4), 1.242 (s, 9H, H9).

^{13}C NMR (150 MHz, $CDCl_3$) δ = 210.8 (Fe(*C*O)$_3$), 177.9 (C7), 128.8 (C1), 79.3 (C6), 59.4 (C2), 51.8 (C5), 39.1 (C8), 26.9 (C9), 24.6 (C3), 23.5 (C4).

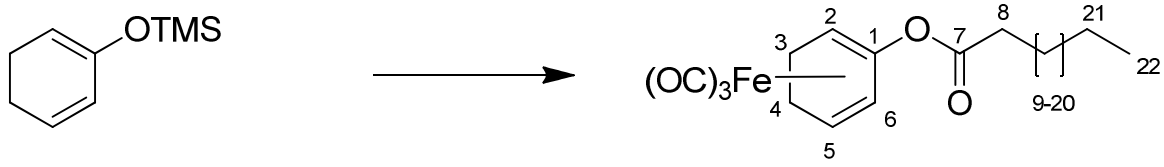
FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2970 (m, ν(C_{sp3}-H)), 2950 (m, ν(C_{sp3}-H)), 2900 (m, ν(C_{sp3}-H)), 2042 (s, ν(Fe(*CO*)$_3$)), 1965 (bs, ν(Fe(*CO*)$_3$)), 1750 (s, ν(C=O)), 1457 (m), 1428 (m), 1396 (m), 1275 (m), 1171 (s), 1108 (s), 1022 (m), 885 (m), 759 (w), 672 (m).

LR-MS (DIP-MS, 70 eV) m/z (%) = 292 (1, $[M\text{-}CO]^+$), 264 (21, $[M\text{-}2CO]^+$], 236 (17, $[M\text{-}3CO]^+$), 234 (100), 149 (32), 134 (60), 121 (10), 95 (15), 84 (14), 71 (7), 57 (40, $[C(CH_3)_3]^+$), 56 (30, $[Fe]^+$).

HR-MS (DIP-MS, 70 eV) m/z 292.040±0.0012 (calcd ($[M\text{-}CO]^+$) m/z 292.0398).

EA: Calcd for $C_{14}H_{16}FeO_5$: C 52.53; H 5.04. Found: C 53.08; H 5.19.

1.4.4 (*RS*)-Tricarbonyl-η⁴-(1-hexadecanoyloxy)-1,5-cyclohexadiene)iron(0) (*rac*-17)



32 *rac*-**17**

According to the general complexation protocol, diene **32** (565 mg, 3.35 mmol, 1.0 eq) and $Fe_2(CO)_9$ (2.43 g, 6.7 mmol, 2.0 eq) were heated in Et_2O (30 mL) for 16 h. The solvent was evaporated, the residue was dissolved in DMF (20 mL) and the solution was added to NaH (600 mg, 50%, 12.52 mmol, 3.7 eq). The reaction mixture was cooled (0 °C) and TBAF (5 mL, 6 mmol, 1.8 eq) was added dropwise. After 45 min palmitoyl chloride (2.0 mL, 6.6 mmol, 2 eq) was added and the reaction was stirred at 20 °C (3 h, TLC). The reaction mixture was diluted with CyHex/EtOAc = 1:1 and washed with brine. The aqueous phase was extracted with M*t*BE and the combined organic phases were dried over $MgSO_4$. After evaporation of the solvents and purification by column chromatography (DCM:CyHex = 1:3), 986 mg (2.08 mmol, 62%) of complex *rac*-**96** were isolated as a yellow solid.

TLC: R_f (CyHex/EtOAc = 10:1) = 0.78.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.53 (Ψdd, *J* = 6.6, 1.2 Hz, 1H, H6), 3.38 (Ψdt, *J* = 3.8, 2.2 Hz, 1H, H2), 2.88 (dt, *J* = 6.4, 2.9 Hz, 1H, H5), 2.45 (t, *J* = 7.5 Hz, 2H, H8), 1.91 – 1.74 (m, 2H, H3), 1.73 – 1.65 (m, 2H, H21), 1.62-1.54 (m, 2H, H4), 1.41 – 1.25 (m, 24H, H9-H20), 0.90 (t, *J* = 7.0 Hz, 3H, H22).

^{13}C NMR (126 MHz, $CDCl_3$) δ 210.5 (Fe(*C*O)$_3$), 173.0 (C7), 128.1 (C1), 79.4 (C6), 58.9 (C2), 51.7 (C5), 33.9 (C8), 31.7 (C9-C20), 29.4 (C9-C20), 29.4 (C9-C20), 29.4 (C9-C20), 29.3 (C9-C20), 29.2 C9-C20 (C9-C20), 29.1 (C9-C20), 28.9 (C9-C20), 28.7 (C9-C20), 24.7 (C3/C21), 24.5 (C3/C21), 23.2 (C4), 22.4 (C9-C20), 13.9 (C22).
FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2921 (s, ν(C$_{sp3}$-H)), 2851 (m, ν(C$_{sp3}$-H)), 2045 (s, ν(Fe(*C*O)$_3$)), 1967 (bs, ν(Fe(*C*O)$_3$)), 1762 (m, ν(C=O)), 1457 (m), 1170 (m), 1134 (m), 1117 (m), 923 (w).
LR-MS (DIP-MS, 70 eV) m/z (%) = 446 (1, [M-CO]$^+$), 418 (5, [M-2CO]$^+$], 390 (100, [M-3CO]$^+$), 310 (29), 309 (35), 226 (34), 212 (56), 198 (39), 184 (25), 170 (19), 156 (17), 151 (40), 97 (36), 83 (28), 71 (37), 57 (87), 56 (46, [Fe]$^+$).
HR-MS (DIP-MS, 70 eV) m/z 418.217±0.0021 (calcd ([M-2CO]$^+$) m/z 418.2170).
EA: Calcd for $C_{25}H_{38}FeO_5$: C 63.29; H 8.07. Found: C 62.81; H 8.15.
T_m (DCM) = 36.7 °C

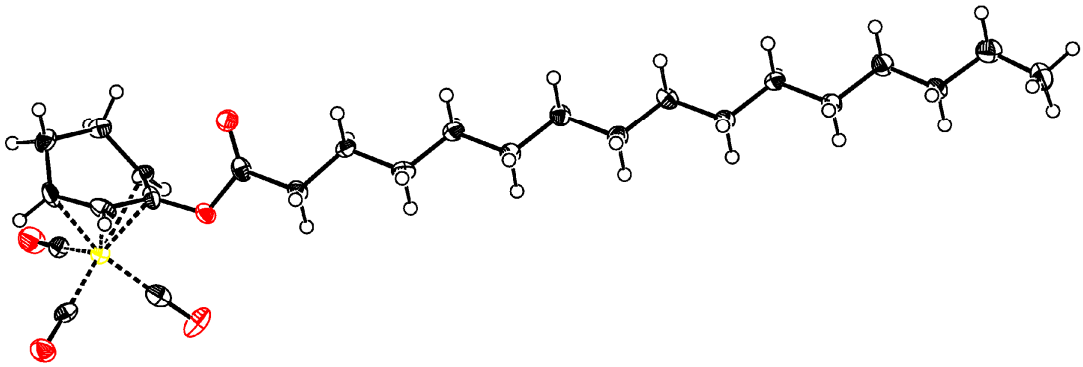


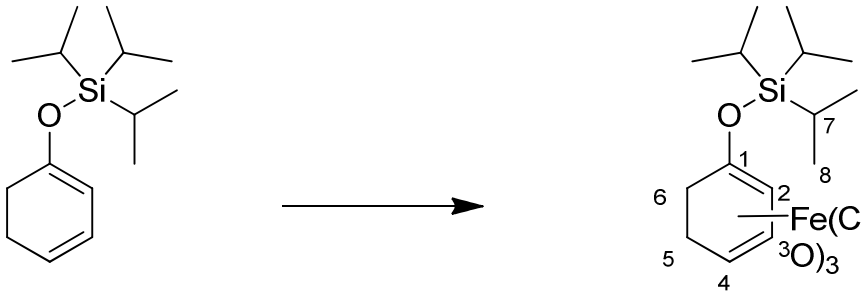
Figure S1: Molecular structure of *rac*-**17**. Ellipsoids are drawn at the 50% probability level.

Table S1. Crystal data and structure refinement for *rac*-**17**.

Identification code	SvBo07n
Empirical formula	$C_{25}H_{38}FeO_5$
Moiety formula	$C_{25}H_{38}FeO_5$
Formula weight	474.40
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P $\bar{1}$
Unit cell dimensions	a = 8.6905(3) Å α = 89.975(2)°.
	b = 10.0025(4) Å β = 87.653(2)°.
	c = 28.6690(12) Å γ = 82.287(2)°.
Volume	2467.45(17) Å^3
Z, Calculated density	4, 1.277 Mg/m^3
Absorption coefficient	0.643 mm^{-1}
F(000)	1016
Crystal size	.15 x .05 x .01 mm
Theta range for data collection	1.42 to 27.00°.
Limiting indices	-11<=h<=11, -12<=k<=12, -36<=l<=33
Reflections collected / unique	16558 / 10724 [R(int) = 0.0389]

Reflection observed [I>2σ (I)]	7271
Completeness to theta = 27.00	99.7%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10724 / 0 / 561
Goodness-of-fit on F^2	1.036
Final R indices [I>2σ (I)]	R1 = 0.0601, wR2 = 0.1438
R indices (all data)	R1 = 0.1006, wR2 = 0.1641
Largest diff. peak and hole	1.036 and -0.681 e Å $^{-3}$

1.4.5 (*RS*)-Tricarbonyl-η^4-(1-triisopropylsiloxy-1,3-cyclohexadiene)iron(0) (*rac*-38)



37 *rac*-**38**

According to the general complexation protocol, diene **37** (1.00 g, 3.96 mmol, 1.0 eq) and $Fe_2(CO)_9$ (4.32 g, 11.88 mmol, 3.0 eq) were heated in Et_2O (60 mL) for 16 h. After purification by column chromatography (CyHex), 1.38 g (3.51 mmol, 89%) of complex *rac*-**38** were isolated as a yellow oil.

TLC: R_f (CyHex/EtOAc = 10:1) = 0.89.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.18 (d, *J* = 4.3 Hz, 1H, H2), 5.94 (Ψt, 1H, *J* = 9.0 Hz), 2.89 – 2.78 (m, 1H, H4), 2.28 – 2.10 (m, 1H, H6), 2.06 – 1.81 (m, 2H, H5, H6), 1.68 – 1.75 (m, 1H, H5), 1.09 (s, 21H, H7, H8).

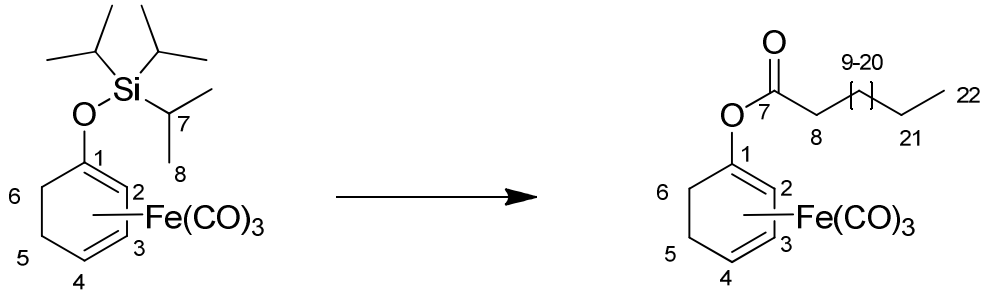
^{13}C NMR (75 MHz, $CDCl_3$) δ 213.3 (Fe(*C*O)$_3$), 113.9 (C1), 78.1 (C2), 76.0 (C3), 56.7 (C4), 31.0 (C6), 24.6 (C5), 18.0 (C8), 13.2 (C7).

FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2942 (s, ν(C_{sp3}-H)), 2889 (m, ν(C_{sp3}-H)), 2865 (s, ν(C_{sp3}-H)), 2031 (s, ν(Fe(*CO*)$_3$)), 1948 (bs, ν(Fe(*CO*)$_3$)), 1456 (m), 1437 (m), 1426 (w), 1382 (s), 1329 (m), 1267 (m), 1239 (m), 1210 (s), 1171 (s), 1128 (w), 1066 (w), 1027 (s), 1006 (s), 915 (m), 879 (s), 855 (s), 674 (s).

LR-MS (DIP-MS, 70 eV) m/z (%) = 392 (1, [M]$^+$), 364 (32, [M-CO]$^+$), 336 (9, [M-2CO]$^+$], 334 (25), 308 (7, [M-3CO]$^+$), 306 (95), 290 (15), 265 (17), 264 (100), 252 (16), 248 (21), 222 (33), 207 (15), 179 (15), 164 (11), 151 (20), 137 (17), 121 (5), 100 (5).

HR-MS (DIP-MS, 70 eV) m/z 364.116±0.0004 (calcd ([M-CO]$^+$) m/z 364.1157).

1.4.6 (*RS*)-Tricarbonyl-η⁴-(1-hexadecanoyloxy)-1,3-cyclohexadiene)iron(0) (*rac*-18)



rac-**38** *rac*-**18**

A solution of TBAF (2.5 mL, 3.00 mmol, 1.2 M in THF, 3.5 eq) was added to a solution of complex *rac*-**38** (333 mg, 0.85 mmol, 1 eq) in DMF (10 mL) and the reaction was stirred (10 min, TLC). Afterwards DIPEA (0.51 mL, 3.00 mmol, 3.5 eq) was added, followed by the addition of palmitoyl chloride (0.91 mL, 3.00 mmol, 3.5 eq). After stirring at 20 °C to completion of the reaction (10 min, TLC), the reaction was quenched by the addition of water and extracted with hexane und M*t*BE. The combined organic solvents were dried over $MgSO_4$ and evaporated. After purification by column chromatography (DCM: CyHex = 1:3), 393 mg (0.83 mmol, 97%) of complex *rac*-**18** were isolated as a yellow solid.

TLC: R_f (CyHex/EtOAc = 10:1) = 0.79.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.39 (d, *J* = 4.3 Hz, 1H, H2), 5.21 – 5.06 (m, 1H, H3), 3.11 (ddd, *J* = 5.5, 3.8, 1.8 Hz, 1H, H4), 2.32 (t, *J* = 7.6 Hz, 2H, H8), 2.17 (ddd, *J* = 12.6, 3.0, 1.6 Hz, 1H, H6), 1.89 (ddt, *J* = 15.0, 11.6, 3.4 Hz, 1H, H5), 1.84 – 1.75 (m, 1H, H6), 1.75 – 1.66 (m, 1H, H6), 1.63 (dd, *J* = 14.2, 7.3 Hz, 2H, H21), 1.36 – 1.23 (m, 24H, H9-H20), 0.90 (t, *J* = 6.9 Hz, 3H, H22).

^{13}C NMR (126 MHz, $CDCl_3$) δ 211.3 (Fe(*C*O)$_3$), 172.0 (C7), 103.2 (C1), 80.5 (C3), 80.3 (C2), 60.2 (C4), 34.5 (C8), 31.9 (C9-C20), 29.7 (C9-C20), 29.7 (C9-C20), 29.6 (C9-C20), 29.6 (C9-C20), 29.4 (C9-C20), 29.4 (C9-C20), 29.2 (C9-C20), 29.0 (C9-C20), 26.7 (C6), 24.8 (C21), 24.0 (C5), 22.7 (C9-C20), 14.1 (C22).

FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2920 (s, ν(C_{sp3}-H)), 2850 (s, ν(C_{sp3}-H)), 2046 (s, ν(Fe(*C*O)$_3$)), 1962 (bs, ν(Fe(*C*O)$_3$)), 1748 (s, ν(C=O)), 1466 (m), 1380 (w), 1327 (m), 1181 (m), 1133 (s), 1114 (s), 1065 (w), 1029 (w), 1004 (m), 907 (w), 865 (w), 753 (w), 720 (w).

LR-MS (DIP-MS, 70 eV) m/z (%) = 446 (2, $[M\text{-}CO]^+$), 418 (6, $[M\text{-}2CO]^+$], 390 (100, $[M\text{-}3CO]^+$), 362 (4), 334 (6), 310 (17), 309 (28), 254 (18), 240 (22), 198 (15), 156 (8), 149 (21), 134 (14), 97 (12), 96 (40), 57 (33), 56 (22, $[Fe]^+$).

HR-MS (DIP-MS, 70 eV) m/z 446.2115±0.0004 (calcd ($[M\text{-}CO]^+$) m/z 446.2119).

EA: Calcd for $C_{25}H_{38}FeO_5$: C 63.29; H 8.07. Found: C 63.45; H 8.08.

T_m (DCM) = 29.5 °C.

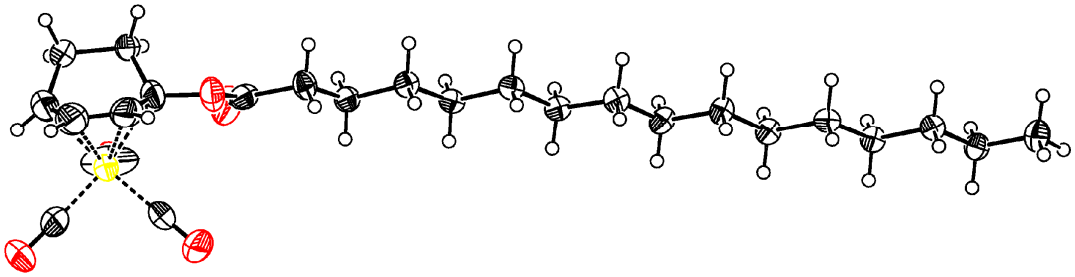
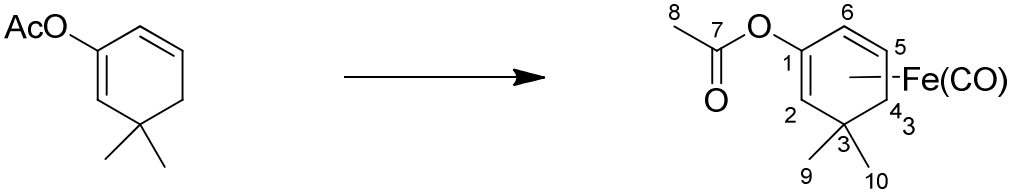


Figure S2: Molecular structure of *rac*-**18**. Ellipsoids are drawn at the 50% probability level.

Table S2. Crystal data and structure refinement for *rac*-**18**.

Identification code	stro491
Empirical formula	$C_{25}H_{38}FeO_5$
Moiety formula	$C_{25}H_{38}FeO_5$
Formula weight	474.40
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	a = 6.6635(14) Å α = 85.849(5)°.
	b = 6.7003(15) Å β = 86.939(6)°.
	c = 28.213(6) Å γ = 82.030(7)°.
Volume	1243.0(5) A^3
Z, Calculated density	2, 1.268 Mg/m^3
Absorption coefficient	0.638 mm^{-1}
F(000)	508
Crystal size	.3 x .1 x .03 mm
Theta range for data collection	1.45 to 27.00°.
Limiting indices	-7<=h<=8, -8<=k<=8, -35<=l<=34
Reflections collected / unique	6049 / 4841 [R(int) = 0.0563]
Reflection observed [I>2σ (I)]	2451
Completeness to theta = 27.00	89.1%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4841 / 0 / 281
Goodness-of-fit on F^2	1.048
Final R indices [I>2σ (I)]	R1 = 0.0775, wR2 = 0.1873
R indices (all data)	R1 = 0.1692, wR2 = 0.2221
Largest diff. peak and hole	1.136 and -0.419 e $Å^{-3}$

1.4.7 (*RS*)-Tricarbonyl-η^4-(1-acetoxy-3,3-dimethyl-1,5-cyclohexadiene)iron(0) (*rac*-12)



24 *rac*-**12**

According to the general complexation protocol, diene **24** (500 mg, 3.01 mmol, 1.0 eq) and $Fe_2(CO)_9$ (2.75 g, 7.53 mmol, 2.4 eq) were heated in Et_2O (30 mL) for 20 h. After purification (silica gel, EtOAc/CyHex = 1:20), 525 mg (1.72 mmol, 57%) of complex *rac*-**12** were isolated as a yellow oil, which solidified after several weeks at -18 °C.

TLC: R_f (CyHex/EtOAc = 5:1) = 0.65.

^{1}H NMR (600 MHz, $CDCl_3$) δ = 5.62 (d, *J* = 6.0 Hz, 1H, H6), 3.07 (Ψd, *J* = 2.0 Hz, 1H, H2), 2.75-2.72 (m, 1H, H5), 2.17 (s, 3H, H8), 1.56-1.41 (m, 2H, H4), 1.08 (s, 3H, H9/H10), 1.03 (s, 3H, H9/H10).
^{13}C NMR (150 MHz, $CDCl_3$) δ = 211.0 (Fe(*C*O)$_3$), 169.7 (C7), 126.6 (C1), 81.1 (C6), 71.1 (C2), 51.4 (C5), 42.1 (C4), 36.1 (C3), 34.6 (C9/C10), 30.8 (C9/C10), 21.2 (C8).
FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2953 (m, ν(C$_{sp3}$-H)), 2866 (w, ν(C$_{sp3}$-H)), 2043 (s, ν(Fe(*C*O)$_3$)), 1961 (bs, ν(Fe(*C*O)$_3$)), 1767 (s, ν(C=O)), 1446 (m), 1367 (m), 1192 (s), 1146 (s), 1120 (m), 1020 (m), 893 (m).
LR-MS (DIP-MS, 70 eV) m/z (%) = 278 (12, [M-CO]$^+$), 250 (26, [M-2CO]$^+$], 222 (24, [M-3CO]$^+$), 206 (100), 178 (12), 164 (19), 146 (9), 134 (10), 109 (17), 97 (24), 91 (14), 71 (8), 68 (12), 56 (57, [Fe]$^+$).
HR-MS (DIP-MS, 70 eV) m/z 278.0145±0.0004 (calcd ([M-CO]$^+$) m/z 278.0241).
EA: Calcd for $C_{13}H_{14}FeO_5$: C 51.01; H 4.61. Found: C 51.00; H 4.65.
T_m (DCM) = 54.1 °C.

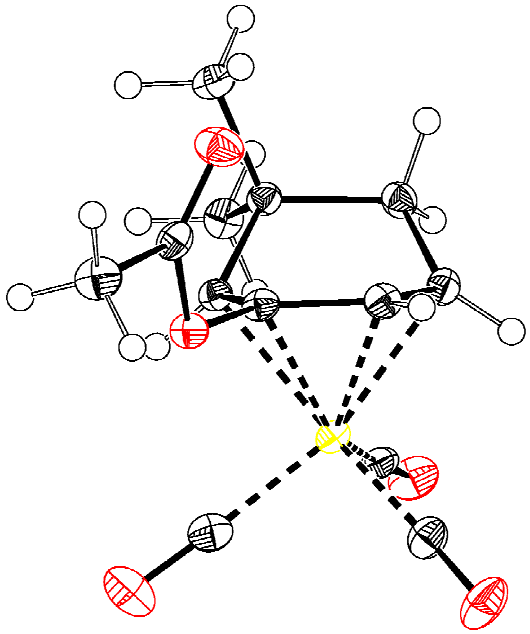


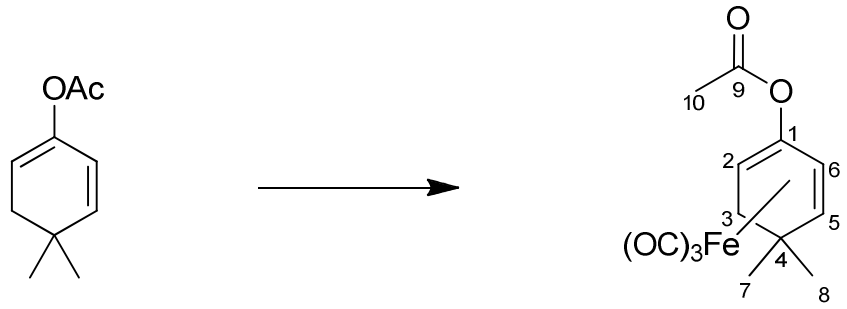
Figure S3: Molecular structure of *rac*-**12**. Ellipsoids are drawn at the 50% probability level.

Table S3. Crystal data and structure refinement for *rac*-**12**.

Identification code	stro242
Empirical formula	$C_{13}H_{14}FeO_5$
Moiety formula	$C_{13}H_{14}FeO_5$
Formula weight	306.09
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	a = 6.1260(4) Å α = 77.693(4)°.
	b = 7.5018(5) Å β = 89.267(3)°.
	c = 15.0179(10) Å γ = 78.463(3)°.
Volume	660.36(8) Å^3

Z, Calculated density	2, 1.539 Mg/m^3
Absorption coefficient	1.154 mm^{-1}
F(000)	316
Crystal size	.2 x .2 x .07 mm
Theta range for data collection	1.39 to 26.99°.
Limiting indices	-7<=h<=7, -9<=k<=9, -19<=l<=13
Reflections collected / unique	4112 / 2877 [R(int) = 0.0166]
Reflection observed [I>2σ (I)]	2615
Completeness to theta = 26.99	99.6%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2877 / 0 / 175
Goodness-of-fit on F^2	1.063
Final R indices [I>2σ (I)]	R1 = 0.0276, wR2 = 0.0730
R indices (all data)	R1 = 0.0320, wR2 = 0.0784
Largest diff. peak and hole	0.728 and -0.662 e $Å^{-3}$

1.4.8 (*RS*)-Tricarbonyl-η⁴-(1-acetoxy-4,4-dimethyl-1,5-cyclohexadiene)iron(0) (*rac*-11)



22 *rac*-**11**

According to the general complexation protocol, diene **22** (500 mg, 3.01 mmol, 1.0 eq) and $Fe_2(CO)_9$ (2.18 g, 6.00 mmol, 2.0 eq) were heated in Et_2O (30 mL) for 20 h. After purification (silica gel, EtOAc/CyHex = 1:40), 659 mg (2.15 mmol, 72%) of complex *rac*-**11** were isolated as a yellow oil, which solidified after several weeks at -18 °C.

TLC: R_f (CyHex/EtOAc = 10:1) = 0.61.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 5.45 (Ψdd, *J* = 1.9, 6.6 Hz, 1H, H6), 3.20 (dd, *J* = 2.7, 4.9 Hz, 1H, H2), 2.50 (d, *J* = 6.3 Hz, 1H, H5), 2.18 (s, 3H, H10), 1.78 (dd, J_1 = 2.8, 14.9 Hz, 1H, H3), 1.60 (dd, J_1 = 3.0, 14.9 Hz, 1H, H3), 1.00 (s, 3H, H7/H8), 0.96 (s, 3H, H7/H8).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 210.9 (Fe(*C*O)$_3$), 170.2 (C9), 128.8 (C1), 76.7 (C6), 65.1 (C5), 58.2 (C2), 43.0 (C3), 34.7 (C4), 34.2 (C7/C8), 30.7 (C7/C8), 21.0 (C9).

FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2995 (m, ν(C_{sp3}-H)), 2859 (w, ν(C_{sp3}-H)), 2043 (s, ν(Fe(*CO*)$_3$)), 1967 (bs, ν(Fe(*CO*)$_3$)), 1762 (s, ν(C=O)), 1456 (m), 1369 (s), 1283 (w), 1207 (s), 1179 (s), 1163 (s), 1119 (w), 1044 (m), 1011 (m), 978 (w), 949 (w), 898 (m), 738 (w), 656 (w).

LR-MS (DIP-MS, 70 eV) m/z (%) = 278 (5, $[M\text{-}CO]^+$), 250 (15, $[M\text{-}2CO]^+$], 222 (3, $[M\text{-}3CO]^+$), 206 (100), 178 (12), 164 (20), 146 (11), 134 (9), 119 (10), 109 (17), 97 (24), 91 (20), 83 (28), 71 (43), 69 (43), 57 (81) 56 (57, $[Fe]^+$).

HR-MS (DIP-MS, 70 eV) m/z 278.024±0.0011 (calc ($[M\text{-}CO]^+$) m/z 278.0241).

EA: Calcd for $C_{13}H_{14}FeO_5$: C 51.01; H 4.61. Found: C 51.27; H 4.69.
T_m (DCM) = 44.7 °C.

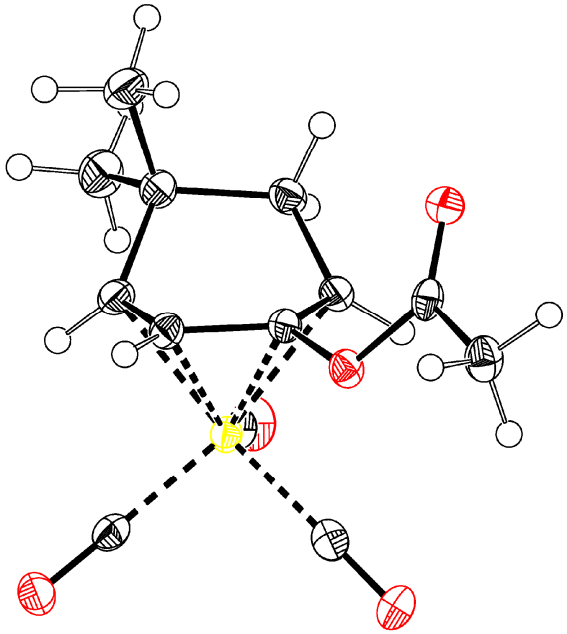


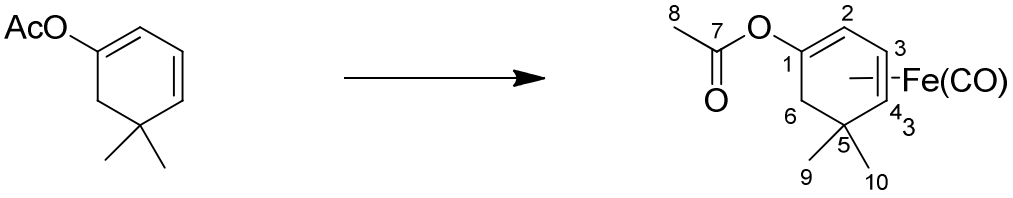
Figure S4: Molecular structure of *rac*-**11**. Ellipsoids are drawn at the 50% probability level.

Table S4. Crystal data and structure refinement for *rac*-**11**.

Identification code	srom87
Empirical formula	$C_{13}H_{14}FeO_5$
Moiety formula	$C_{13}H_{14}FeO_5$
Formula weight	306.09
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	a = 9.6264(7) Å α = 90°. b = 14.1259(7) Å β = 124.757(4)°. c = 11.9873(7) Å γ = 90°.
Volume	1339.21(16) $Å^3$
Z, Calculated density	4, 1.518 Mg/m^3
Absorption coefficient	1.138 mm^{-1}
F(000)	632
Crystal size	.2 x .07 x .02 mm
Theta range for data collection	2.52 to 26.99 deg.
Limiting indices	-10<=h<=12, -18<=k<=16, -15<=l<=10
Reflections collected / unique	6848 / 2918 [R(int) = 0.0380]
Reflection observed [I>2σ (I)]	2169
Completeness to theta = 26.99	99.9%
Absorption correction	None

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2918 / 0 / 175
Goodness-of-fit on F^2	1.038
Final R indices [I>2σ (I)]	R1 = 0.0356, wR2 = 0.0881
R indices (all data)	R1 = 0.0573, wR2 = 0.0961
Largest diff. peak and hole	0.638 and -0.611 e Å $^{-3}$

1.4.9 (*RS*)-Tricarbonyl-η^4-(1-acetoxy-5,5-dimethyl-1,3-cyclohexadiene)iron(0) (*rac*-13)



25 *rac*-**13**

According to the general complexation protocol, diene **25** (500 mg, 3.01 mmol, 1.0 eq) and $Fe_2(CO)_9$ (2.75 g, 7.53 mmol, 2.4 eq) were heated in Et_2O (30 mL) for 20 h. After purification (silica gel, EtOAc/CyHex = 1:20), 525 mg (1.72 mmol, 57%) of complex *rac*-**13** were isolated as a yellow oil.

TLC: R_f (CyHex/EtOAc = 5:1) = 0.65.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 5.40-5.35 (m, 1H, H2), 5.07 (dd, *J* = 4.5, 6.5 Hz, 1H, H3), 2.76 (Ψdd, *J* = 1.0, 6.5 Hz, 1H, H4), 2.20-2.10 (m, 1H, H6), 2.02 (s, 3H, H8), 1.76-1.70 (m, 1H, H6), 1.09 (s, 3H, H9/H10), 0.96 (s, 3H, H9/H10).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 169.7 (C7), 101.9 (C1), 81.3 (C2), 77.4 (C3), 72.6 (C4), 44.9 (C6), 34.9 (C9/C10), 30.9 (C9/C10), 20.9 (C8). C5 could not be detected

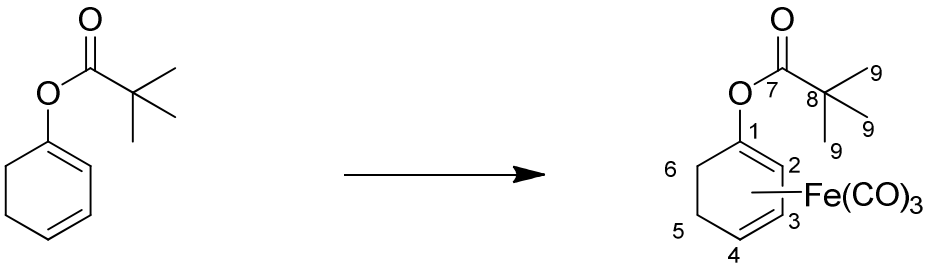
FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2957 (m, ν(C_{sp3}-H)), 2860 (w, ν(C_{sp3}-H)), 2044 (s, ν(Fe(*CO*)$_3$)), 1962 (bs, ν(Fe(*CO*)$_3$)), 1752 (s, ν(C=O)), 1470 (w), 1440 (m), 1366 (s), 1212 (s), 1184 (s), 1095 (s), 1052 (m), 1013 (w), 908 (m).

LR-MS (DIP-MS, 70 eV) m/z (%) = 306 (1, $[M]^+$), 278 (12, $[M\text{-}CO]^+$), 250 (36, $[M\text{-}2CO]^+$], 222 (29, $[M\text{-}3CO]^+$), 206 (100), 178 (12), 164 (15), 146 (11), 134 (9), 119 (10), 91 (11), 83 (28), 71 (9), 56 (26, $[Fe]^+$).

HR-MS (DIP-MS, 70 eV) m/z 278.021±0.0001 (calc ($[M\text{-}CO]^+$) m/z 278.0241).

EA: Calcd for $C_{13}H_{14}FeO_5$: C 51.01; H 4.61. Found: C 50.81; H 4.94.

1.4.10 (*RS*)-Tricarbonyl-η^4-(1-(2,2-dimethylpropanoyloxy)-1,3-cyclohexadiene)iron(0) (*rac*-10)



20 *rac*-**10**

According to the general complexation protocol, diene **20** (700 mg, 3.88 mmol, 1.0 eq) and $Fe_2(CO)_9$ (3.5 g, 9.6 mmol, 2.4 eq) were heated in Et_2O (30 mL) for 16 h. After purification, 895 mg (2.79 mmol, 72%) of complex *rac*-**10** were isolated as a yellow crystalline solid.

TLC: R_f (CyHex/EtOAc = 10:1) = 0.80.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 5.39 (d, *J* = 4.0 Hz, 1H, H2), 5.13 (Ψt, *J* = 5.5 Hz, 1H, H3), 3.13-3.08 (m, 1H, H4), 2.18-2.09 (m, 1H, H5/H6), 1.92-1.85 (m, 1H, H5/H6), 1.81-1.74 (m, 1H, H5/H6), 1.74-1.64 (m, 1H, H5/H6), 1.22 (s, 9H, H9).
^{13}C NMR (125 MHz, $CDCl_3$) δ = 211.4 (Fe(*C*O)$_3$), 176.7 (C7), 103.4 (C1), 80.4 (C2/C3), 80.3 (C2/C3), 60.2 (C4), 38.9 (C8), 27.0 (C9), 26.5 (C5/C6), 24.0 (C5/C6).
FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2931 (s, ν(C$_{sp3}$-H)), 2859 (m, ν(C$_{sp3}$-H)), 2047 (s, ν(Fe(*C*O)$_3$)), 1970 (bs, ν(Fe(*C*O)$_3$)), 1739 (s, ν(C=O)), 1455 (w), 1380 (w), 1327 (w), 1277 (m), 1181 (m), 1129 (s), 1004 (w), 904 (m).
LR-MS (DIP-MS, 70 eV) m/z (%) = 292 (8, [M-CO]$^+$), 264 (49, [M-2CO]$^+$], 236 (44, [M-3CO]$^+$), 234 (100), 180 (1), 150 (1), 134 (12), 96 (2), 57 (3, [C(CH$_3$)$_3$]$^+$).
HR-MS (DIP-MS, 70 eV) m/z 292.040±0.0002 (calcd ([M-CO]$^+$) m/z 292.0398).
EA: Calcd for $C_{14}H_{16}FeO_5$: C 52.53; H 5.04. Found: C 52.36; H 5.05.
T_m (DCM) = 50.5 °C.

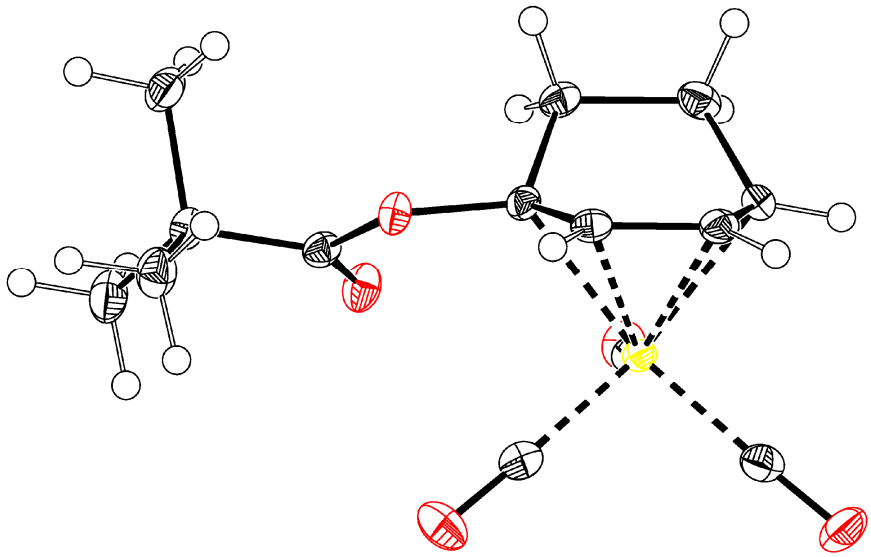


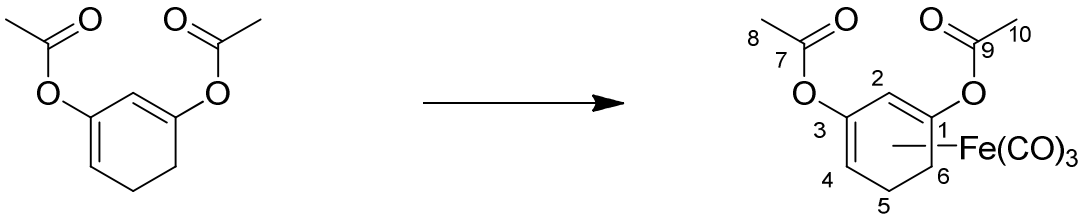
Figure S5: Molecular structure of *rac*-**10**. Ellipsoids are drawn at the 50% probability level.

Table S5. Crystal data and structure refinement for *rac*-**10**.

Identification code	z_absk
Empirical formula	$C_{14}H_{16}FeO_5$
Moiety formula	$C_{14}H_{16}Fe\ O_5$
Formula weight	320.12
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	a = 12.4124(4) Å α = 90°.
	b = 6.4417(2) Å β = 104.644(2)°.
	c = 18.6015(7) Å γ = 90°.
Volume	1439.00(8) Å^3
Z, Calculated density	4, 1.478 Mg/m^3

Absorption coefficient	1.063 mm^{-1}
F(000)	664
Crystal size	.2 x .15 x .07 mm
Theta range for data collection	1.70 to 26.99°.
Limiting indices	-14<=h<=15, -8<=k<=8, -23<=l<=17
Reflections collected / unique	13203 / 3140 [R(int) = 0.0626]
Reflection observed [I>2σ (I)]	2688
Completeness to theta = 26.99	100.0%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0979 and 0.7390
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3140 / 0 / 212
Goodness-of-fit on F^2	1.061
Final R indices [I>2σ (I)]	R1 = 0.0276, wR2 = 0.0698
R indices (all data)	R1 = 0.0348, wR2 = 0.0720
Largest diff. peak and hole	0.419 and -0.305 $eÅ^{-3}$

1.4.11 (*RS*)-Tricarbonyl-η^4-(1,3-diacetoxy-1,3-cyclohexadiene)iron(0) (*rac*-16)



S6 *rac*-**16**

According to the general complexation protocol, diene **S6** (500 mg, 2.55 mmol, 1.0 eq) and $Fe_2(CO)_9$ (1.85 g, 5.10 mmol, 2.0 eq) were heated in Et_2O (30 mL) for 16 h. After purification by column chromatography (CyHex:EtOAc = 20:1), 464 mg (1.38 mmol, 55%) of complex *rac*-**16** were isolated as a yellow oil which solidified after several weeks at -18 °C.

TLC: R_f (CyHex/EtOAc = 10:1) = 0.24.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.67 – 5.60 (m, 1H, H2), 3.28 (dd, *J* = 5.2, 2.9 Hz, 1H, H4), 2.16 (s, 3H, H8/H10), 2.11 – 2.05 (m, 1H, H6), 2.04 (s, 3H, H8/H10), 1.85 – 1.78 (m, 2H, H5), 1.72 – 1.64 (m, 1H, H6).

^{13}C NMR (126 MHz, $CDCl_3$) δ 208.3 (Fe(*C*O)$_3$), 169.8 (C7/C9), 169.2 (C7/C9), 123.6 (C3), 95.0 (C1), 75.2 (C2), 56.9 (C4), 26.3 (C6), 23.7 (C5), 21.2 (C8/C10), 21.0 (C8/C10).

FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2867 (w, ν(C_{sp3}-H)), 2052 (s, ν(Fe(*CO*)$_3$)), 1982 (bs, ν(Fe(*CO*)$_3$)), 1760 (br s, ν(C=O)), 1461 (m), 1429 (w), 1367 (m), 1323 (w), 1194 (s), 1090 (m), 1053 (m), 1027 (m), 896 (w).

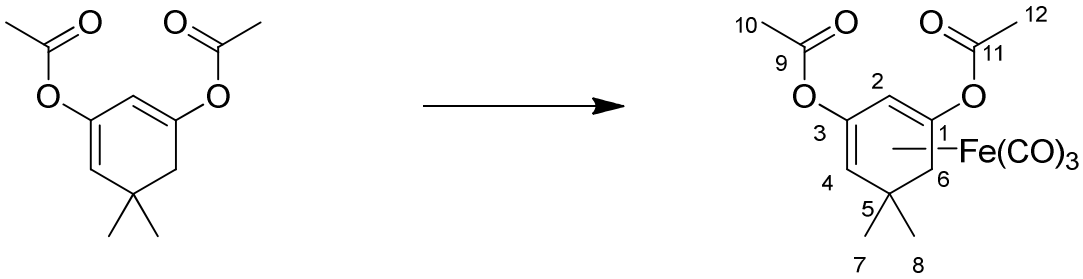
LR-MS (DIP-MS, 70 eV) m/z (%) = 308 (2, $[M\text{-}CO]^+$), 280 (25, $[M\text{-}2CO]^+$], 252 (100, $[M\text{-}3CO]^+$), 224 (12), 210 (15), 209 (35), 196 (18), 180 (55), 165 (37), 150 (23), 134 (24), 121 (18), 115 (38), 84 (25), 71 (25), 56 (82, $[Fe]^+$).

HR-MS (DIP-MS, 70 eV) m/z 307.998±0.002 (calcd ($[M\text{-}CO]^+$) m/z 307.9983).

EA: Calcd for $C_{13}H_{12}FeO_7$: C 46.46; H 3.60. Found: C 46.48; H 3.69.

T_m (DCM) = 31.9 °C.

1.4.12 (*RS*)-Tricarbonyl-η⁴-(1,3-diacetoxy-5,5-dimethyl-1,3-cyclohexadiene)iron(0) (*rac*-9)



S7 *rac*-**9**

Similar to the general complexation protocol, diene **S7** (300 mg, 1.34 mmol, 1.0 eq) and $Fe_2(CO)_9$ (1.50 g, 4.13 mmol, 3.0 eq) were heated in toluene (20 mL) to 41 °C (4.5 h). After purification by column chromatography (CyHex:EtOAc = 15:1), 400 mg (1.10 mmol, 82%) of complex *rac*-**9** were isolated as a yellow oil which solidified after several weeks at -18 °C.

TLC: R_f (CyHex/EtOAc = 5:1) = 0.62.

^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.81 (d, *J* = 2.2 Hz, 1H, H2), 3.06 (d, *J* = 2.2 Hz, 1H, H4), 2.21 (s, 3H, H10/H12), 2.07 (s, 3H, H10/H12), 1.68 (d, *J* = 14.8 Hz, 2H, H6), 1.16 (s, 3H, H7/H8), 1.14 (s, 3H, H7/H8).

^{13}C-NMR (126 MHz, $CDCl_3$) δ 210.0 (Fe(*C*O)$_3$), 169.2 (C9/C11), 169.1 (C9/C11), 122.0 (C3), 93.6 (C1), 76.7 (C2), 68.7 (C4), 44.7 (C6), 35.7 (C5), 34.6 (C7/C8), 30.7 (C7/C8), 21.2 (C9, C12).

FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2960 (w, ν(C_{sp3}-H)), 2914 (w, ν(C_{sp3}-H)), 2853 (w, ν(C_{sp3}-H)), 2049 (s, ν(Fe(*CO*)$_3$)), 1974 (bs, ν(Fe(*CO*)$_3$)), 1770 (br s, ν(C=O)), 1469 (w), 1451 (m), 1415 (w), 1366 (s), 1300 (w), 1191 (br s), 1146 (s), 1119 (m), 1068 (s), 1009 (s), 963 (m), 901 (m), 844 (m), 635 (m).

LR-MS (DIP-MS, 70 eV) m/z (%) = 308 (16, [M-2CO]$^+$], 280 (100, [M-3CO]$^+$), 264 (33), 237 (60), 222 (50), 195 (95), 179 (37), 168 (12), 150 (15), 148 (23), 134 (27), 105 (12), 97 (16), 91 (24), 84 (31), 71 (40), 57 (15), 56 (84, [Fe]$^+$).

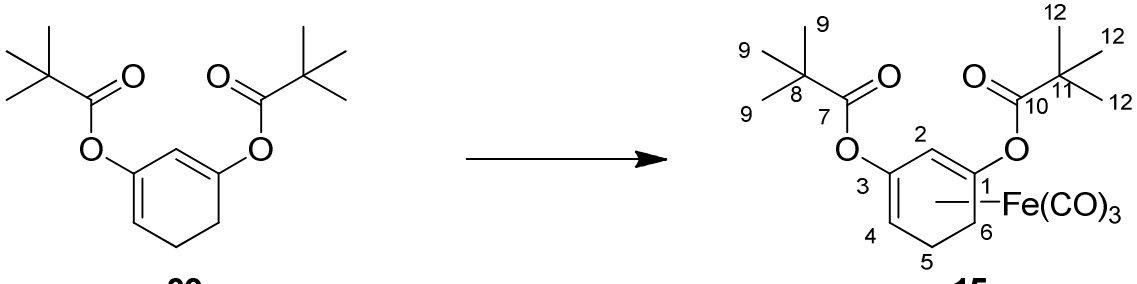
HR-MS (DIP-MS, 70 eV) m/z 308.034±0.0004 (calcd ([M-2CO]$^+$) m/z 308.0347).

EA: Calcd for $C_{15}H_{16}FeO_7$: C 49.48; H 4.43. Found: C 49.56; H 4.44.

T_m (DCM) = 56.9 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.81 (d, *J* = 2.2 Hz, 1H), 3.06 (d, *J* = 2.2 Hz, 1H), 2.21 (s, 3H), 2.07 (s, 3H), 1.68 (d, *J* = 14.8 Hz, 2H), 1.16 (s, 3H), 1.14 (s, 3H).

1.4.13 (*RS*)-Tricarbonyl-η⁴-(1,3-di(2,2-dimethylpropanoyloxy)-1,3-cyclohexadiene)iron(0) (*rac*-15)



30 *rac*-**15**

According to the general complexation protocol, a mixture containing diene **30** (1.00 g, 1.42 mmol, 1.0 eq) and $Fe_2(CO)_9$ (2.60 g, 7.14 mmol, 2.0 eq) were heated in Et_2O (60 mL) for 16 h. After purification, 899 mg (2.14 mmol, 67%) of complex *rac*-**89** were isolated as a yellow oil which solidified after several weeks at -18 °C.

TLC: R_f (CyHex/EtOAc = 10:1) = 0.52.
^{1}H NMR (600 MHz, $CDCl_3$) δ = 5.72 – 5.55 (m, 1H, H2), 3.26 – 3.25 (m, 1H, H4), 2.12 – 1.93 (m, 1H, H6), 1.84 – 1.81 (m, 2H, H5), 1.69 – 1.62 (m, 1H, H6), 1.23 (s, 9H, H9/H12), 1.17 (s, 9H, H9/H12).
^{13}C NMR (150 MHz, $CDCl_3$) δ = 177.7 (C7/C10), 176.7 (C7/C10), 124.1 (C3), 94.9 (C1), 74.9 (C2), 57.1 (C4), 39.1 (C8/C11), 39.0 (C8/C11), 27.0 (C9/C12), 26.9 (C9/C12), 26.2 (C6), 23.6 (C5).
FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2974 (m, ν(C_{sp3}-H)), 2926 (m, ν(C_{sp3}-H)), 2900 (w, ν(C_{sp3}-H)), 2052 (s, ν(Fe(*CO*)$_3$)), 1979 (bs, ν(Fe(*CO*)$_3$)), 1753 (s, ν(C=O)), 1740 (s, ν(C=O)), 1480 (m), 1460 (m), 1396 (w), 1365 (w), 1276 (m), 1175 (m), 1104 (s), 1045 (w), 1028 (m), 886 (m), 671 (m).
LR-MS (DIP-MS, 70 eV) m/z (%) = 364 (6, $[M\text{-}CO]^+$), 336 (40, $[M\text{-}2CO]^+$], 308 (6, $[M\text{-}3CO]^+$), 293 (10), 266 (5), 252 (41), 224 (38), 196 (15), 168 (17), 165 (27), 138 (6), 122 (4), 112 (7), 85 (10), 57 (100), 56 (17, $[Fe]^+$).
HR-MS (DIP-MS, 70 eV) m/z 364.097±0.004 (calcd ($[M\text{-}CO]^+$) m/z 364.0973).
EA: Calcd for $C_{19}H_{24}FeO_7$: C 54.30; H 5.76. Found: C 54.46; H 5.78.
T_m (DCM) = 58.3 °C.

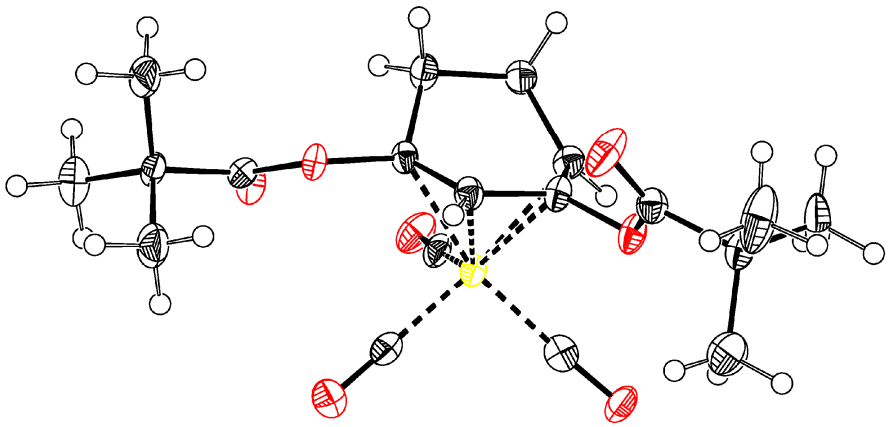


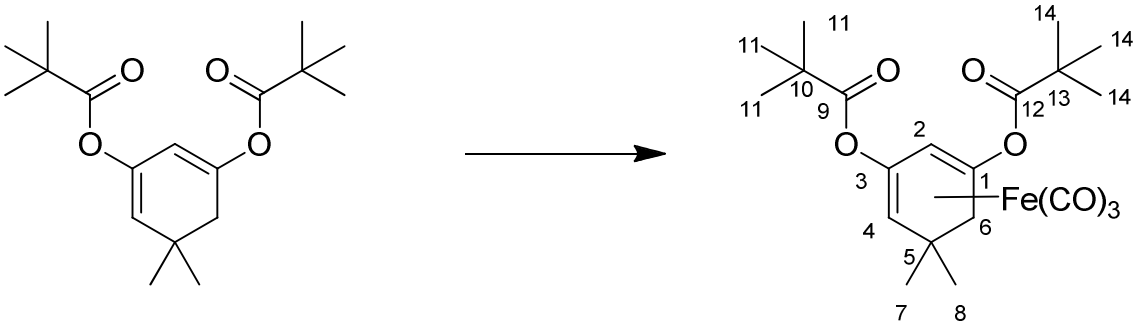
Figure S6: Molecular structure of *rac*-**15**. Ellipsoids are drawn at the 50% probability level.

Table S6. Crystal data and structure refinement for *rac*-**15**.

Identification code	stro472
Empirical formula	$C_{19}H_{24}FeO_7$
Moiety formula	$C_{19}H_{24}FeO_7$
Formula weight	420.23
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	a = 13.5179(16) Å α = 90°.
	b = 12.1754(7) Å β = 100.201(3)°.
	c = 12.5175(15) Å γ = 90°.

Volume	2027.6(4) $Å^3$
Z, Calculated density	4, 1.377 Mg/m^3
Absorption coefficient	0.779 mm^{-1}
F(000)	880
Crystal size	.1 x .07 x .02 mm
Theta range for data collection	1.53 to 26.99°.
Limiting indices	-17<=h<=17, -12<=k<=12, -15<=l<=15
Reflections collected / unique	14333 / 4048 [R(int) = 0.0812]
Reflection observed [I>2σ (I)]	2746
Completeness to theta = 26.99	91.5%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4048 / 0 / 250
Goodness-of-fit on F^2	1.154
Final R indices [I>2σ (I)]	R1 = 0.0648, wR2 = 0.1650
R indices (all data)	R1 = 0.1072, wR2 = 0.1891
Largest diff. peak and hole	1.132 and -0.495 e $Å^{-3}$

1.4.14 (*RS*)-Tricarbonyl-η⁴-(1,3-bis(2,2-dimethylpropanoate)-5,5-dimethyl-1,3-cyclohexadiene)iron(0) (*rac*-14)



31 *rac*-**14**

According to the general complexation protocol, diene **31** (1.100 g, 2.45 mmol, 1.0 eq) and $Fe_2(CO)_9$ (2.6 g, 7.14 mmol, 2.9 eq) were heated in Et_2O (30 mL) for 16 h. After purification (a second column chromatography with CyHex:DCM = 10:1 was necessary), 1.23 g (1.89 mmol, 77%) of complex *rac*-**14** were isolated as a yellow oil which solidified after several hours at 30 °C.

TLC: R_f(CyHex: EtOAc = 10:1) = 0.63.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.79 – 5.77 (m, 1H, H2), 3.04 (Ψd, *J* = 2.2 Hz, 1H, H4), 2.03 (Ψd, *J* = 14.0 Hz, 1H, H6), 1.64 (Ψd, *J* = 14.0 Hz, 1H, H6),1.26 (s, 9H, H11/H14), 1.19 (s, 9H, H11/H14), 1.14 (Ψd, *J* = 2.9 Hz, 6H, H7, H8).

^{13}C NMR (125 MHz, $CDCl_3$) δ 210.2 (Fe(*C*O)$_3$), 177.1 (C9/C12), 176.7 (C9/C12), 122.5 (C3), 93.5 (C1), 76.4 (C2), 69.1 (C4), 44.7 (C6), 39.2 (C10/C13), 39.0 (C10/C13), 35.7 (C5), 34.7 (C7/C8), 30.7 (C7/C8), 27.0(C11/C14), 26.9 (C11/C14).

FT-IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2970 (m, υ(C_{sp3}-H)), 2860 (w, υ(C_{sp3}-H)), 2050 (s, υ(Fe(CO)$_3$)), 1970 (bs, υ(Fe(CO)$_3$)), 1742 (s, υ(C=O)), 1471 (m), 1396 (w), 1366 (m), 1275 (m), 1120 (bs), 1102 (bs), 1028 (w), 853 (w).

LR-MS (DIP-MS, 70 eV) m/z (%) = 420 (1, $[M\text{-}CO]^+$), 392 (3, $[M\text{-}2CO]^+$], 364 (34, $[M\text{-}3CO]^+$), 348 (2), 321 (8), 280 (25), 265 (12), 252 (15), 196 (17), 195 (24), 179 (14), 157 (5), 135 (6), 111 (7), 96 (5), 85 (7), 57 (100), 56 (18, $[Fe]^+$).
HR-MS (DIP-MS, 70 eV) m/z 392.129±0.0004 (calcd ($[M\text{-}2CO]^+$) m/z 392.1286).
EA: Calc für $C_{21}H_{28}FeO_7$ (%) C = 56.26, H = 6.30. Found (%) C = 56.56 H = 6.26.
T_m (DCM) = 38.4 °C.

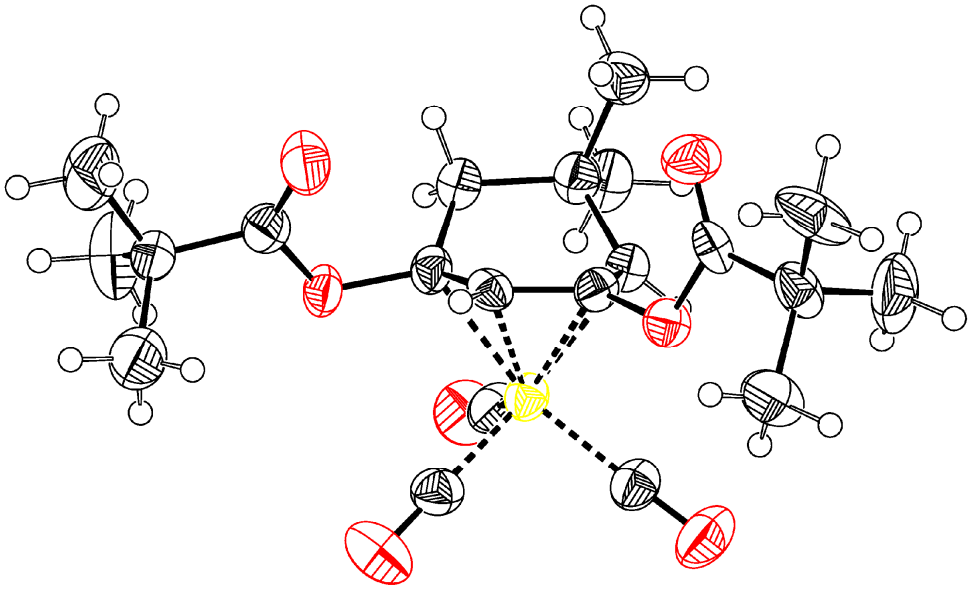


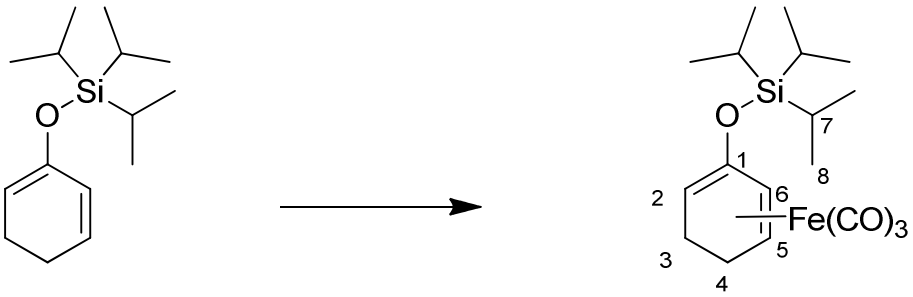
Figure S7: Molecular structure of *rac*-**14**. Ellipsoids are drawn at the 50% probability level.

Table S7. Crystal data and structure refinement for *rac*-**14**.

Identification code	stro-srws14-150k
Empirical formula	$C_{21}H_{28}FeO_7$
Moiety formula	$C_{21}H_{28}FeO_7$
Formula weight	448.28
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	a = 11.0195(8) Å α = 75.189(4)°.
	b = 13.4293(8) Å β = 86.972(3)°.
	c = 16.2464(10) Å γ = 89.571(3)°.
Volume	2321.0(3) $Å^3$
Z, Calculated density	4, 1.283 Mg/m^3
Absorption coefficient	0.685 mm^{-1}
F(000)	944
Crystal size	.2 x .2 x .1 mm
Theta range for data collection	1.30 to 27.00°.
Limiting indices	-14<=h<=14, -17<=k<=17, -19<=l<=20
Reflections collected / unique	15189 / 10119 [R(int) = 0.0534]
Reflection observed [I>2σ (I)]	5007

Completeness to theta = 27.00	99.9%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10119 / 0 / 539
Goodness-of-fit on F^2	0.965
Final R indices [I>2σ (I)]	R1 = 0.0677, wR2 = 0.1537
R indices (all data)	R1 = 0.1572, wR2 = 0.1865
Largest diff. peak and hole	0.566 and -0.421 e $Å^{-3}$

1.4.15 (*RS*)-Tricarbonyl-η^4-(1-triisopropylsiloxy-1,5-cyclohexadiene)iron(0) (*rac*-35)



33 *rac*-**35**

According to the general complexation protocol, diene **33** (2.00 g, 7.92 mmol, 1.0 eq) and $Fe_2(CO)_9$ (8.64 g, 23.80 mmol, 3.0 eq) were heated in Et_2O (70 mL) for 16 h. After purification by column chromatography (CyHex), 2.85 g (7.28 mmol, 92%) of complex *rac*-**35** were isolated as a yellow oil.

TLC: R_f (CyHex/EtOAc = 10:1) = 0.90.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.28 (d, *J* = 6.5 Hz, 1H, H6), 3.39 (Ψs, 1H, H2), 2.70 (d, *J* = 2.7 Hz, 1H, H5), 1.84 – 1.62 (m, 2H, H3), 1.48 (Ψddd, *J* = 19.3, 14.4, 9.0 Hz, 2H, H4), 1.22 (Ψdd, *J* = 14.4, 6.9 Hz, 3H, H7), 1.11 (s, 18H, H8).

^{13}C NMR (75 MHz, $CDCl_3$) δ 211.6 ($Fe(CO)_3$), 136.5 (C1), 76.7 (C6), 58.6 (C2), 50.5 (C5), 25.4 (C3), 23.1 (C4), 17.7 (C8), 12.4 (C7).

FT-IR (ATR) $\tilde{\nu}$ [cm^-] = 2944 (s, ν (C_{sp3}-H)), 2889 (m, ν (C_{sp3}-H)), 2865 (s, ν (C_{sp3}-H)), 2040 (s, ν ($Fe(CO)_3$)), 1960 (bs, ν ($Fe(CO)_3$), 1469 (m), 1442 (m), 1390 (w), 1259 (m), 1215 (s), 1175 (w), 1119 (w), 1071 (w), 994 (m), 941 (m), 921 (m), 901 (m), 881 (s), 845 (s), 678 (m), 620 (s), 609 (s).

LR-MS (DIP-MS, 70 eV) m/z (%) = 392 (2, $[M]^+$), 364 (31, $[M\text{-}CO]^+$), 336 (9, $[M\text{-}2CO]^+$], 334 (30), 308 (14, $[M\text{-}3CO]^+$), 306 (100), 290 (30), 265 (17), 264 (98), 252 (5), 248 (19), 222 (45), 207 (15), 179 (15), 164 (25), 151 (10), 137 (15), 121 (9), 100 (5).

HR-MS (DIP-MS, 70 eV) m/z 364.115±0.0004 (calcd ($[M\text{-}CO]^+$) m/z 364.1157).

2. Kinetic Resolution and CO-Release

2.1 General Procedure 2 for studying the enzymatic ester hydrolysis of the complexes (kinetic resolution)

In an open tube 10 mg (36 µmol) of the complex were dissolved in 0.5 mL of DMSO and 5 mL of phosphate buffer (0.1 M, pH = 7.4) were added. After taking a first sample as starting point, the particular enzyme was added and the reaction monitored by taking samples over a certain time. From time to time samples of 0.5 mL were taken and extracted with 5 mL of a solution of 160 mg of bromobenzene in 100 mL of M*t*BE. The organic phase was separated, dried over $MgSO_4$ and the solvent was evaporated. The residue was dissolved in *n*-hexane and the conversion and the enantiomeric excess were determined by chiral HPLC or GC on a chiral phase. The enantiomeric excess of *rac*-**8** could not be determined exactly, because it was impossible to base-line separate the enantiomers through HPLC or GC. In table S1 and S2 conversion and enantiomeric excess are shown for the enzymatic reactions with LCR and PLE.

Table S8: Kinetic enzymatic resolution with LCR.

Complex	*rac*-**6**	*rac*-**8**	*rac*-**7**	*rac*-**11**	*rac*-**13**	*rac*-**16**
m enzyme (mg)	20	20	15	20	20	20
time (min)	conversion (%) / ee (%)					
0	0/0	0/0	0/0	0/1	0/1	0/1
30	60/62	65**/43	-	50/25	19/6	19/16
60	79/67	77/71	-	57/53	55/64	56/64
120	85/70	*79*/96	47/14	68/72	67/68	68/68
240	97/70	81/100	60/20	96/87	61/95	62/95
24 h			73/58			

** corrected value.

Table S9: Kinetic enzymatic resolution with PLE.

Complex	*rac*-**8**		*rac*-**9**		*rac*-**10**	*rac*-**13**	*rac*-**16**
m enzyme (mg)	2		2		2	2	2
time (min)		time (min)	conversion / ee (%)	time (min)	conversion / ee (%)		
0	0/5	5	0/10	0	0/0	0/4	0/8
120	28/11	15	3/13	30	31/85	66/80	92/32
180	45/17	30	12/18	60	48/89	80/51	99/64
300	52/33	45	54/27	110		84/57	
420	77/69	150	64/37	240		99/54	
540	84/73	210	80/100	24 h			
660	89/74						

2.2. General Procedure for CO-release measurements (Mb-assay)

The CO-release was monitored by the change of the Q-band region of the UV/Vis spectra of a horse skeletal myoglobin (Mb) solution in phosphate buffer (0.1 M, pH = 7.4).[1] For this purpose, a solution of 30 mg Mb in 15 mL buffer was degassed by bubbling argon for 10 min, reduced by the addition of an excess of $Na_2S_2O_4$ and degassed for additional 10 min. The concentration was determined by measuring a 1:10 diluted solution and using the following equation:

$$A = \varepsilon_\lambda \cdot c \cdot l \quad \text{with} \quad \varepsilon_{408\ nm} = 188000\ L\ mol^{-1}\ cm^{-1}$$

To determine the CO-release properties of the complexes, 2.3 mL of the Mb solution were filled into a UV cuvette. Afterwards a solution of the complex in DMSO and a solution of the esterase in phosphate buffer were added under argon before the cell was closed to prevent re-oxidation of the Fe(II) in the Mb solution to Fe(III). The cell was heated to 37 °C in a water bath and the CO-release monitored over time. At 25 °C no CO-release was detected. For all substances the CO-release was measured with and without esterase. Equivalents of the esterase are given relative to the complex.
For *rac*-**12** no CO-release was observed with the enzymes that are suitable for the Mb-assay.

2.2.1 CO-release from *rac*-6

The Mb solution (c = 88 µM) was reduced by the addition of 22 mg (126.4 µmol, 95 eq) of $Na_2S_2O_4$ in 0.1 mL buffer. 3.4 mg (12 µmol) of *rac*-**6** were dissolved in 300 µl DMSO to give a 0.041 M solution. For the measurement 6 µl (2.45^{-7} mol, 1.2 eq) of this solution were added to 2.3 mL of the Mb solution (2.03^{-7} mol, 1 eq) and 70 µl (ca. 0.09 eq) of a solution of 5 mg *Candida rugosa* in 240 µl buffer. The CO-release with esterase is shown in Figure S8 on the left hand side. Without lipase no CO-release was detected (Figure S8, right hand side).

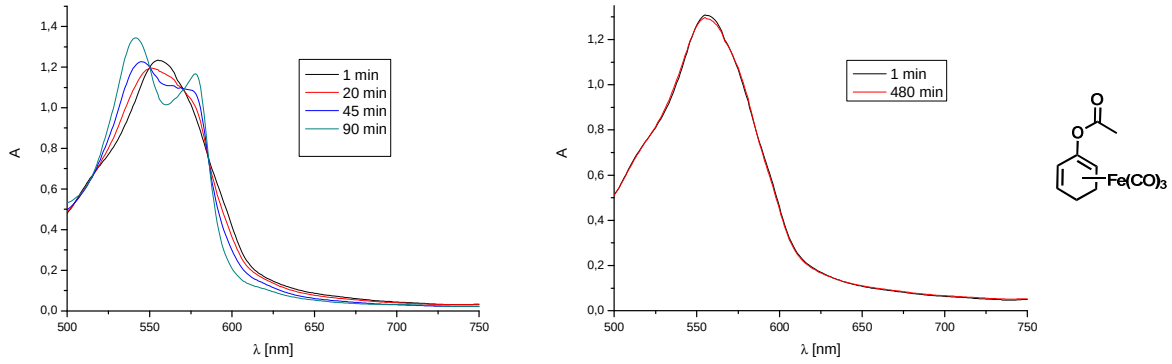


Figure S8: Detection of CO-release from *rac*-**6** with LCR (left) and without lipase (right).

2.2.2 CO-release from *rac*-7

The Mb solution (c = 95 µM) was reduced by the addition of 23 mg (132.1 µmol, 92 eq) of $Na_2S_2O_4$ in 0.1 mL buffer. 1.8 mg (5.6 µmol) of *rac*-**7** were dissolved in 180 µl DMSO to give a 0.031 M solution. For the measurement 12 µl (3.74^{-7} mol, 2.2 eq) of this solution were added to 2.3 mL of the Mb solution (2.19^{-7} mol, 1 eq) and 140 µl (ca. 0.17 eq) of a solution of 15 mg candida rugosa in 500 µl buffer. There

[1] R. Motterlini, J. E. Clark, R. Foresti, P. Sarathchandra, B. E. Mann, C. J. Green, *Circ. Res.* **2002**, *90*, e17–e24.

was no CO-release in the closed cell, so the cells were opened for 2 s after 480 min. The CO-release with esterase is shown in Figure S9 on the left hand side. Without lipase no CO-release was detected (Figure S9, right side).

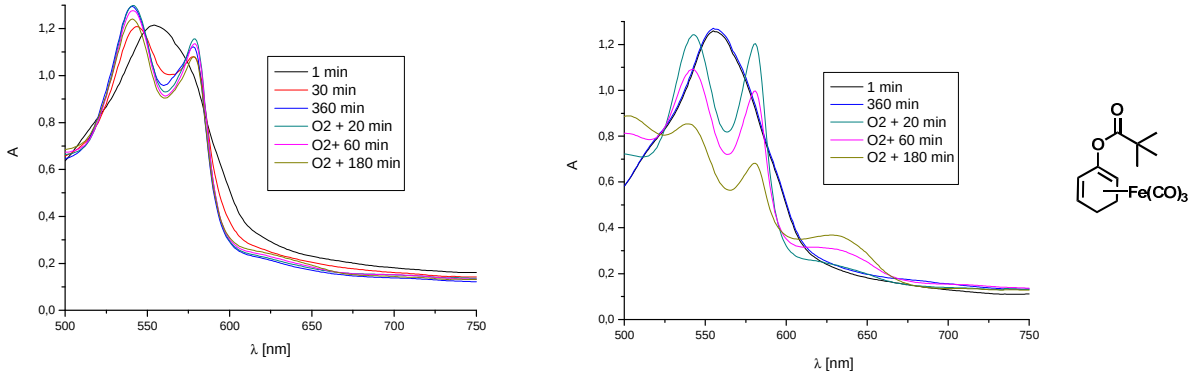


Figure S9: Detection of CO-release from *rac*-**7** with LCR (left) and without lipase (right). After exposure to the air an Mb-O_2 species is detected. With LCR the conversion of Mb-O_2 to Mb-CO was detected. Without lipase no CO-release was detected, but oxidation of the Mb solution occurred.

2.2.3 CO-release from *rac*-17

The Mb solution (c = 89 µM) was reduced by the addition of 23 mg (132.1 µmol, 93 eq) of $Na_2S_2O_4$ in 0.1 mL buffer. 1.1 mg (2.3 µmol) of *rac*-**17** were dissolved in 100 µl DMSO to give a 0.023 M solution. For the measurement 18 µl (4.18^{-7} mol, 2.0 eq) of this solution were added to 2.3 mL of the Mb solution (2.05^{-7} mol, 1 eq) and 100 µl (ca. 0.33 eq) of a solution of 20 mg LCR in 450 µl buffer. The CO-release with esterase is shown in Figure S10 on the left hand side. Without esterase no CO-release was detected (Figure S10, right hand side).

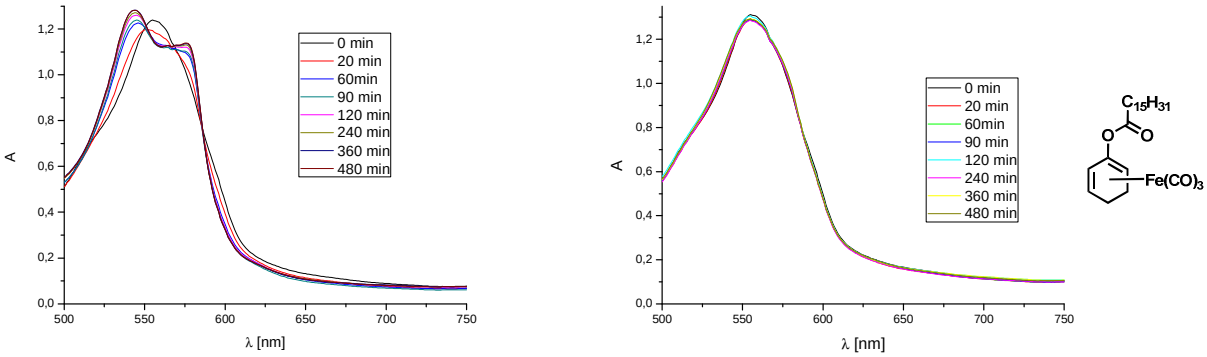


Figure S10: Detection of CO-release from *rac*-**17** with LCR (left) and without lipase (right).

2.2.4 CO-release from *rac*-8

The Mb solution (c = 76 µM) was reduced by the addition of 23 mg (132.1 µmol, 116 eq) of $Na_2S_2O_4$ in 0.1 mL buffer. 1.7 mg (6.2 µmol) of *rac*-**8** were dissolved in 160 µl DMSO to give a 0.038 M solution. For the measurement 6 µl (2.29^{-7} mol, 1.3 eq) of this solution were added to 2.3 mL of the Mb solution (1.75^{-7} mol, 1 eq) and 70 µl (ca. 0.01 eq) of a solution of 0.7 mg PLE in 240 µl buffer. The CO-release with esterase is shown in Figure S11 on the left hand side. Without esterase no CO-release was detected (Figure S11, right hand side).

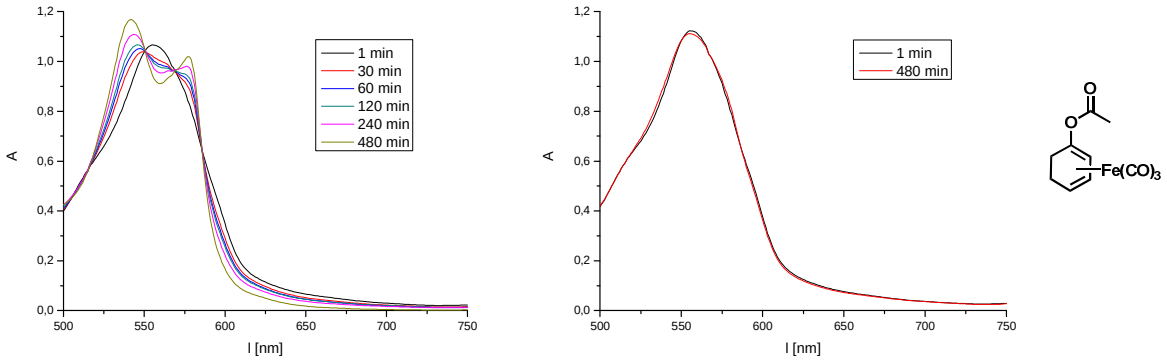


Figure S11: Detection of CO-release from *rac*-**8** with PLE (left) and without esterase (right).

2.2.5 CO-release from *rac*-10

The Mb solution (c = 80 µM) was reduced by the addition of 23 mg (132.1 µmol, 103 eq) of $Na_2S_2O_4$ in 0.1 mL buffer. 1.0 mg (3.1 µmol) of *rac*-**10** were dissolved in 140 µl DMSO to give a 0.022 M solution. For the measurement 6 µl (1.34^{-7} mol, 0.7 eq) of this solution were added to 2.3 mL of the Mb solution (1.83^{-7} mol, 1 eq) and 70 µl (ca. 0.02 eq) of a solution of 2.0 mg PLE in 300 µl buffer. The CO-release with esterase is shown in Figure S12 on the left hand side. Without esterase no CO-release was detected (Figure S12, right hand side).

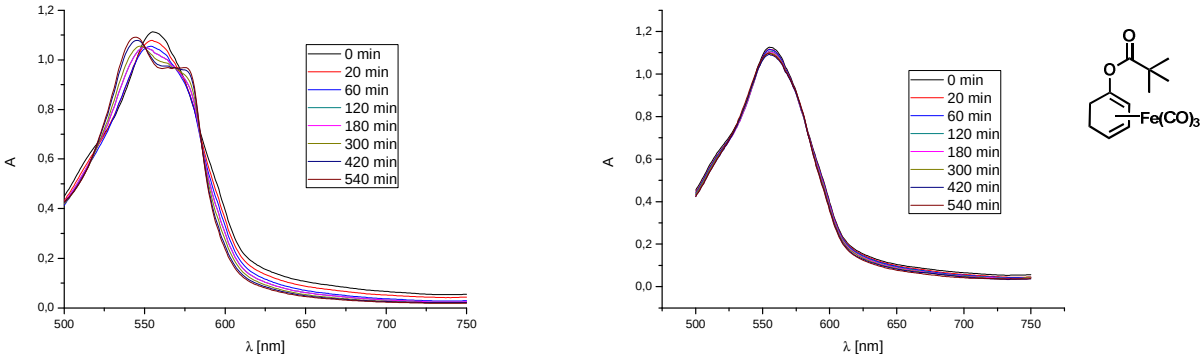


Figure S12: Detection of CO-release from *rac*-**231** with PLE (left) and without esterase (right).

2.2.6. CO-release from *rac*-18

The Mb solution (c = 64 µM) was reduced by the addition of 23 mg (132.1 µmol, 129 eq) of $Na_2S_2O_4$ in 0.1 mL buffer. 1.9 mg (4.0 µmol) of *rac*-**18** were dissolved in 200 µl EtOH to give a 0.020 M solution. For the measurement 9 µl (1.80^{-7} mol, 1.2 eq) of this solution were added to 2.3 mL of the Mb solution (1.47^{-7} mol, 1 eq) and 70 µl (ca. 0.02 eq) of a solution of 2.0 mg PLE in 320 µl buffer. The CO-release with esterase is shown in Figure S13 on the left hand side. Without esterase no CO-release was detected (Figure S13, right hand side).

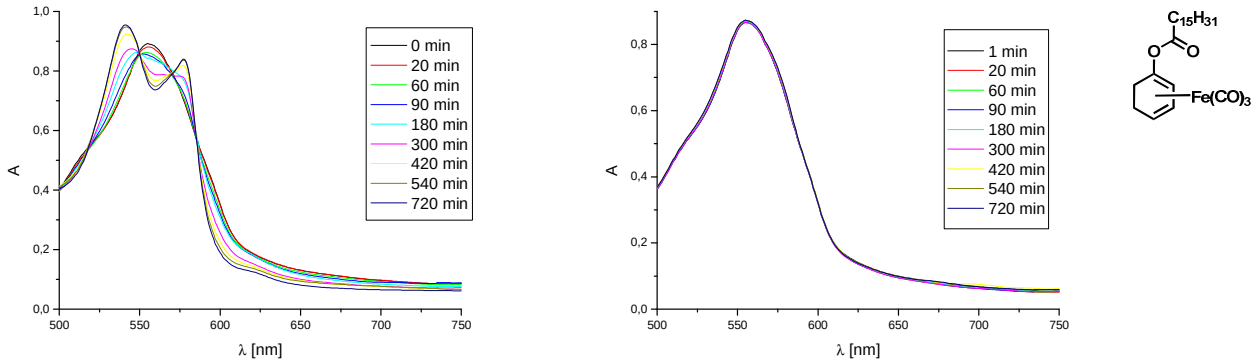


Figure S13: Detection of CO-release from *rac*-**18** with PLE (left) and without esterase (right).

2.2.7 CO-release from *rac*-16

The Mb solution (c = 83 µM) was reduced by the addition of 23 mg (132.1 µmol, 100 eq) of $Na_2S_2O_4$ in 0.1 mL buffer. 1.0 mg (3.0 µmol) of *rac*-**16** were dissolved in 200 µl DMSO to give a 0.020 M solution. For the measurement 3 µl (5.95^{-8} mol, 0.3 eq) of this solution were added to 2.3 mL of the Mb solution (1.90^{-7} mol, 1 eq) and 50 µl (ca. 0.01 eq) of a solution of 1.7 mg PLE in 240 µl buffer. The CO-release with esterase is shown in Figure S14 on the left hand side. Without esterase no CO-release was detected (Figure S14, right hand side).

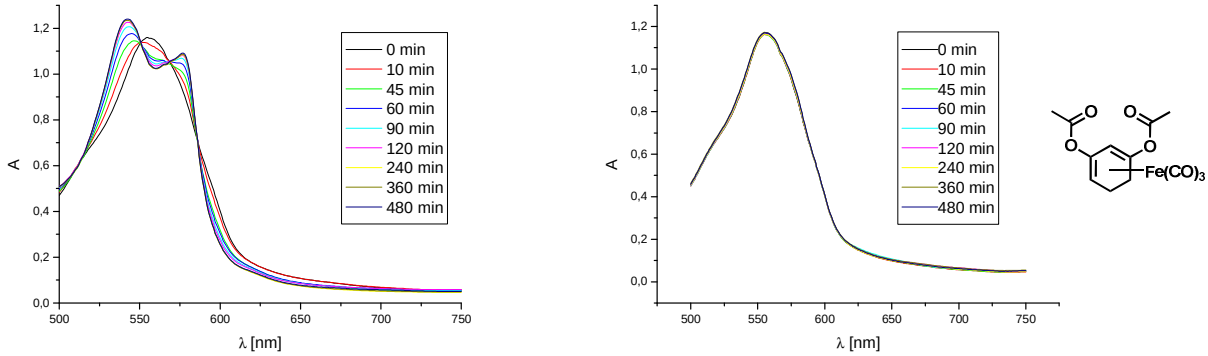


Figure S14: Detection of CO-release from *rac*-**16** with PLE (left) and without esterase (right).

2.2.8 CO-release from *rac*-9

The Mb solution (c = 56 µM) was reduced by the addition of 22 mg (126.4 µmol, 151 eq) of $Na_2S_2O_4$ in 0.1 mL buffer. 1.1 mg (3.0 µmol)of *rac*-**9** were dissolved in 100 µl DMSO to give a 0.030 M solution. For the measurement 3 µl (9.06^{-8} mol, 0.7 eq) of this solution were added to 2.3 mL of the Mb solution (1.28^{-7} mol, 1 eq) and 70 µl (ca. 0.01 eq) of a solution of 0.6 mg PLE in 240 µl buffer. The CO-release with esterase is shown in Figure S15 on the left hand side. Without esterase nearly no CO-release was detected (Figure S15, right hand side).

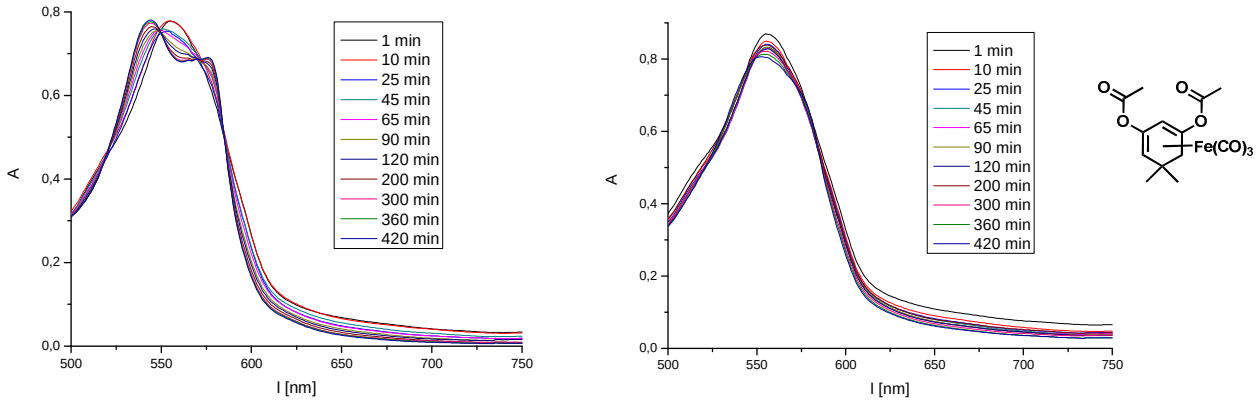


Figure S15: Detection of CO-release from *rac*-**9** with PLE (left) and without esterase (right).

2.2.9 CO-release from *rac*-15

The Mb solution (c = 92 µM) was reduced by the addition of 23 mg (132.1 µmol, 92 eq) of $Na_2S_2O_4$ in 0.1 mL buffer. 2.0 mg (4.8 µmol) of *rac*-**15** were dissolved in 250 µl DMSO to give a 0.019 M solution. For the measurement 9 µl (1.71^{-7} mol, 0.8 eq) of this solution were added to 2.3 mL of the Mb solution (2.11^{-7} mol, 1 eq) and 50 µl (ca. 0.02 eq) of a solution of 2.5 mg PLE in 280 µl buffer. The CO-release with esterase is shown in Figure S16 on the left hand side. Without esterase no CO-release was detected (Figure S16, right hand side).

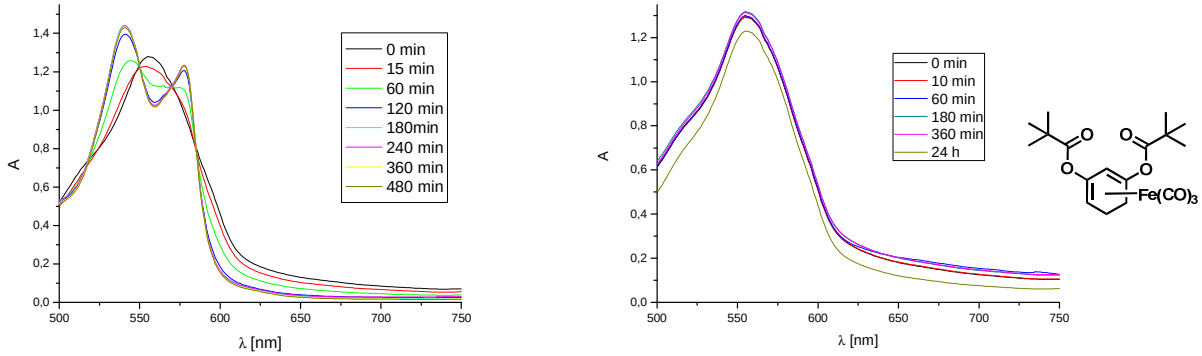


Figure S16: Detection of CO-release from *rac*-**15** with PLE (left) and without esterase (right).

2.2.10 CO-release from *rac*-14

The Mb solution (c = 91 µM) was reduced by the addition of 23 mg (132.1 µmol, 91 eq) of $Na_2S_2O_4$ in 0.1 mL buffer. 1.6 mg (3.6 µmol) of *rac*-**14** were dissolved in 160 µl DMSO to give a 0.022 M solution. For the measurement 3 µl (6.69^{-8} mol, 0.3 eq) of this solution were added to 2.3 mL of the Mb solution (2.10^{-7} mol, 1 eq) and 50 µl (ca. 0.01 eq) of a solution of 2.0 mg PLE in 240 µl buffer. The CO-release with esterase is shown in Figure S17 on the left hand side. Without esterase no CO-release was detected (Figure S17, right hand side).

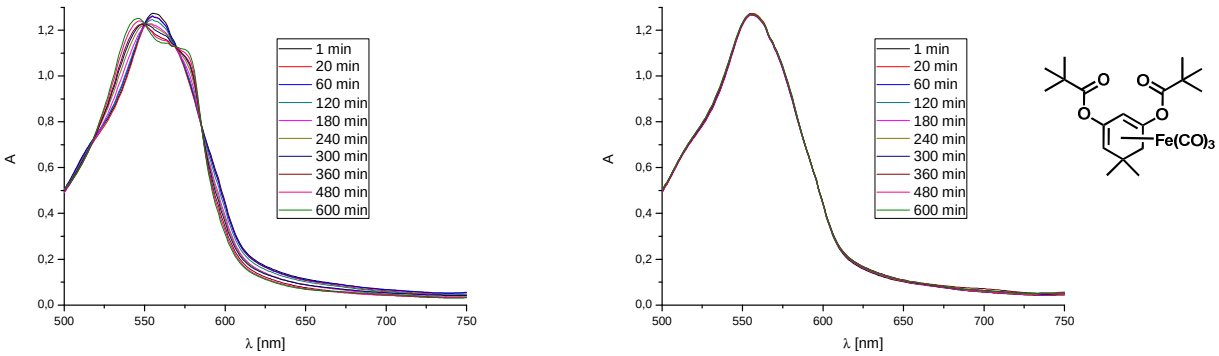


Figure S17: Detection of CO-release from *rac*-**14** with PLE (left) and without esterase (right).

2.2.11 CO-release from *rac*-13

The Mb solution (c = 84 µM) was reduced by the addition of 23 mg (132.1 µmol, 99 eq) of $Na_2S_2O_4$ in 0.1 mL buffer. 1.0 mg (3.3 µmol) of *rac*-**13** were dissolved in 200 µl DMSO to give a 0.016 M solution. For the measurement 4 µl (6.53^{-7} mol, 0.3 eq) of this solution were added to 2.3 mL of the Mb solution (1.92^{-7} mol, 1 eq) and 50 µl (ca. 0.01 eq) of a solution of 2.0 mg PLE in 240 µl buffer. The CO-release with esterase is shown in Figure S18 on the left hand side. Without esterase no CO-release was detected (Figure S18, right hand side).

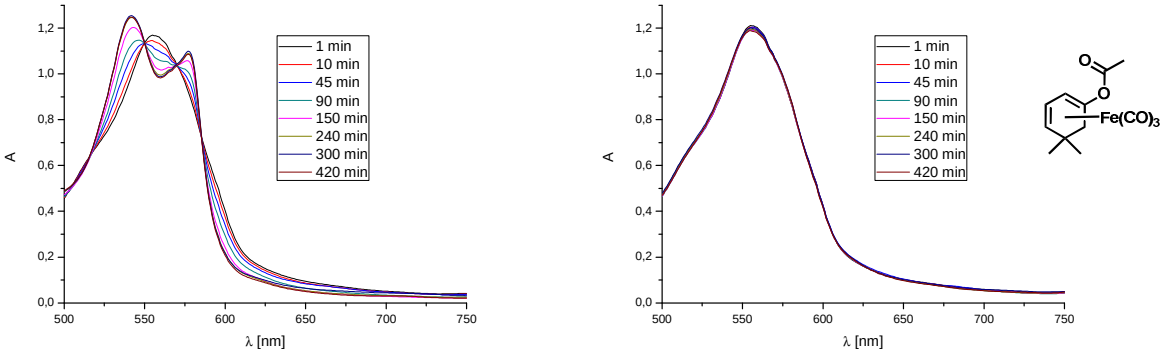


Figure S18: Detection of CO-release from *rac*-**13** with PLE (left) and without esterase (right).

2.2.12 CO-release from *rac*-11

The Mb solution (c = 80 µM) was reduced by the addition of 23 mg (132.1 µmol, 103 eq) of $Na_2S_2O_4$ in 0.1 mL buffer. 1.0 mg (3.3 µmol) of *rac*-**11** were dissolved in 160 µl DMSO to give a 0.020 M solution. For the measurement 9 µl (183^{-7} mol, 1.0 eq) of this solution were added to 2.3 mL of the Mb solution (1.83^{-7} mol, 1 eq) and 160 µl (ca. 0.7 eq) of a solution of 15 mg LCR in 1200 µl buffer. The CO-release with lipase is shown in Figure S19 on the left hand side. Without esterase no CO-release was detected (Figure S19, right hand side).

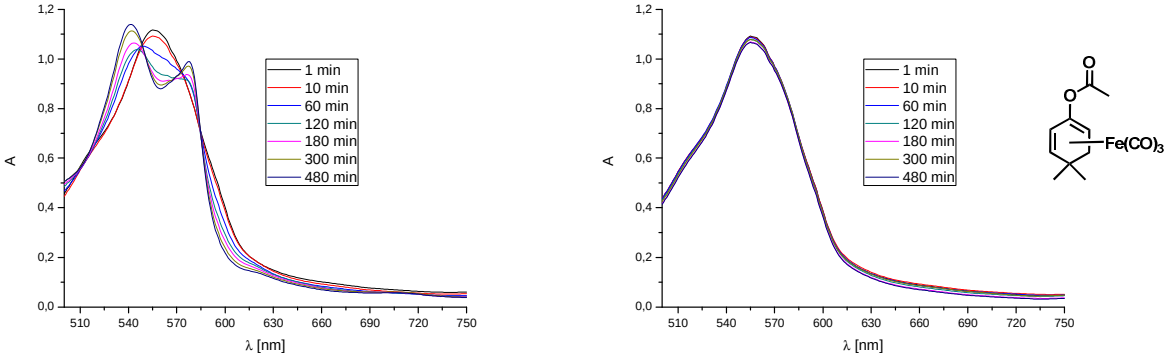


Figure S19: Detection of CO-release from *rac*-**11** with LCR (left) and without lipase (right).

2.3. General Procedures for CO-release measurements (GC)

2.3.1 General Procedure for CO-release measurements in the presence of oxygen (GC)

All reactions were performed in headspace vials-10 mL (*BGB-analytics*, Cat.No. 200410-F).
Prior to the detection of the CO-release a calibration was done. Calibrations were done with the solvent mixture (phosphate buffer (1 mL, (0.1 M, pH = 7.4)) and DMSO (0.2 mL)) that was used for the CO-release experiments. For the CO-calibration, the consumption of oxygen had to be included. For this purpose, the reaction vial was filled with the solvent mixture and completely degassed with nitrogen. Afterwards, 21% of the gas volume was replaced by oxygen to generate the composition of air (2.250 mL). To generate gas mixtures that are formed when a particular amount of O_2 is consumed in the course of the CO-release, the volume of added oxygen was decreased by the amount that is theoretically needed for the release of the added CO. The resulting gas mixture was warmed to 37 °C for 10 min prior to the injection and analysis of 50 µL by GC.
As an example the calibration for 2 eq of released CO per consumed O_2 is shown.

Added O_2 (mL)	Added CO (mL)
2.25	0
2.23	0.05
2.20	0.10
2.13	0.25
2.00	0.50
1.75	1.00
1.25	2.00
0.75	3.00

The determined areas from the GC were plotted against the amount of O_2 or CO (calculated with the ideal gas law) and fitted (linear for 1.0 eq, 1.5 eq and 2.0 eq and exponential for 4.0 eq and no O_2-consumption) . For the CO and O_2 calibration, different equivalents of released CO per consumed O_2 were used (1.0 eq, 1.5 eq, 2.0 eq, 4.0 eq and no O_2-consumption) and the calibration data were compared to the experimental data of the CO release curves. The data for 1.0 eq, 1.5 eq and 2.0 eq matched best and were quite similar. Therefore, an average of the three slopes was taken for the calculation of the released CO.

For the monitoring of the enzyme triggered CO release, the particular complex (36 µmol) was dissolved in DMSO (0.2 ml) and phosphate buffer (1 mL, (0.1 M, pH = 7.4)) was added. The particular enzyme (15 mg of PLE or 20 of mg LCR) was added and the vial was closed with a rubber vial cap. The reaction mixture was stirred at 37 °C. From time to time samples (50 µL) were taken and the CO release was quantified. The half-life times were determined directly from an exponential fit of the CO-release (first or second order).
The same procedure was repeated without enzyme for every complex, but there was no CO release (or a very slow CO-release for *rac*-**9** and *rac*-**16**) without enzyme.

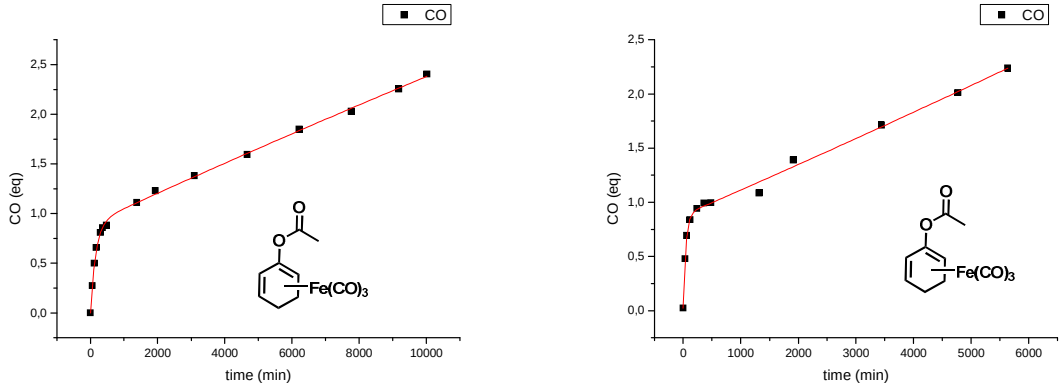


Figure S20: Detection of CO-release from *rac*-**6** with LCR (left) and from *rac*-**6** with PLE (right).

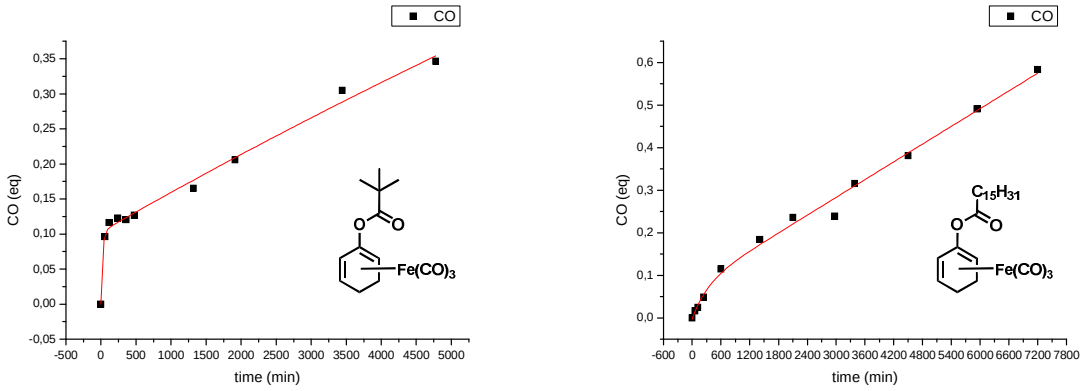


Figure S21: Detection of CO-release from *rac*-**7** with PLE (left) and from *rac*-**17** with LCR (right).

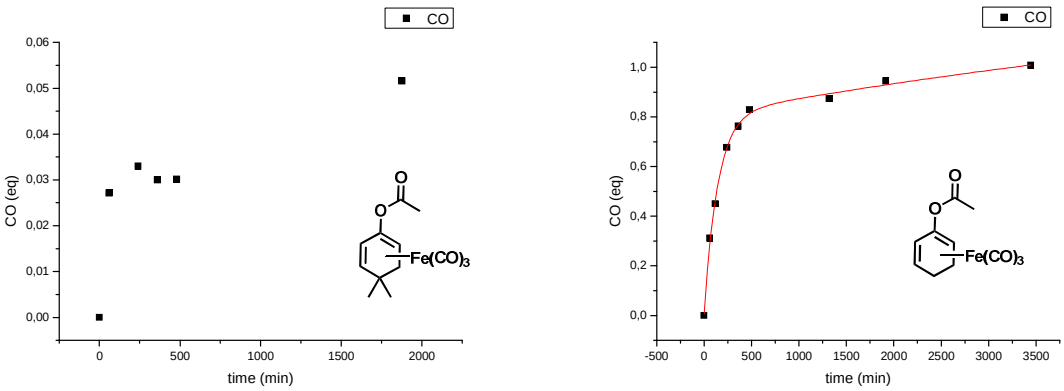


Figure S22: Detection of CO-release from *rac*-**11** with PLE (left) and from *rac*-**12** with PLE (right).

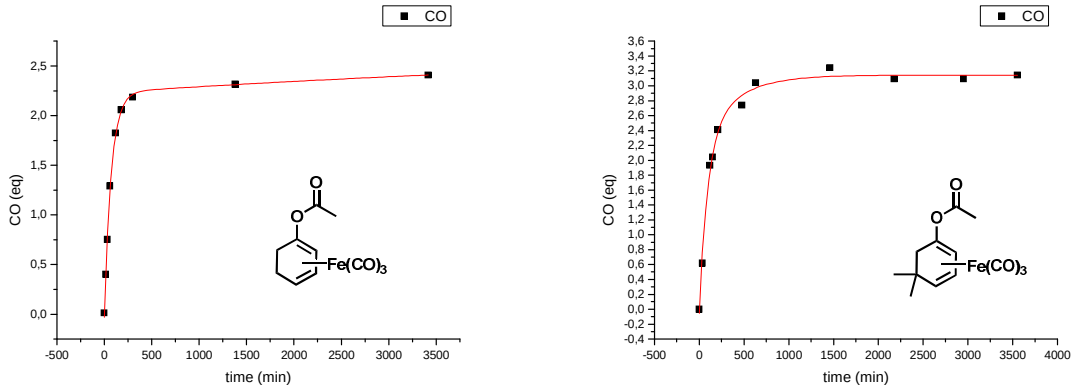


Figure S23: Detection of CO-release from *rac*-**8** with PLE (left) and from *rac*-**13** with PLE (right).

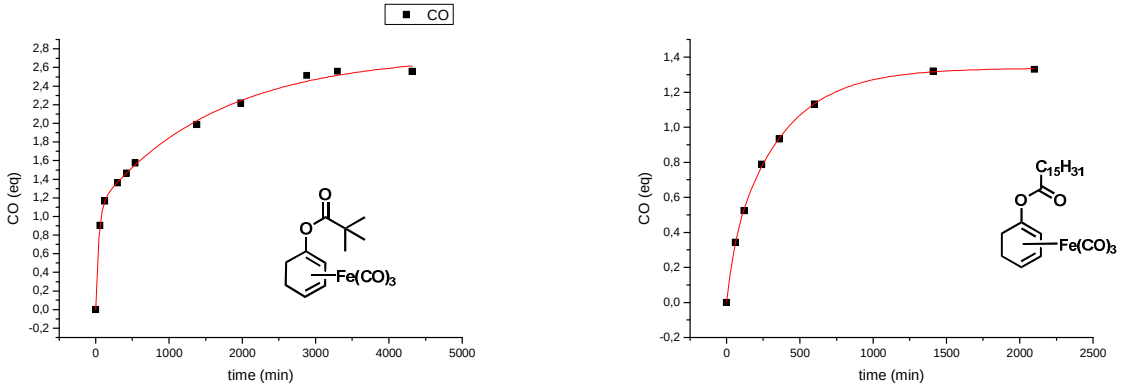


Figure S24: Detection of CO-release from *rac*-**10** with PLE (left) and from *rac*-**18** with PLE (right).

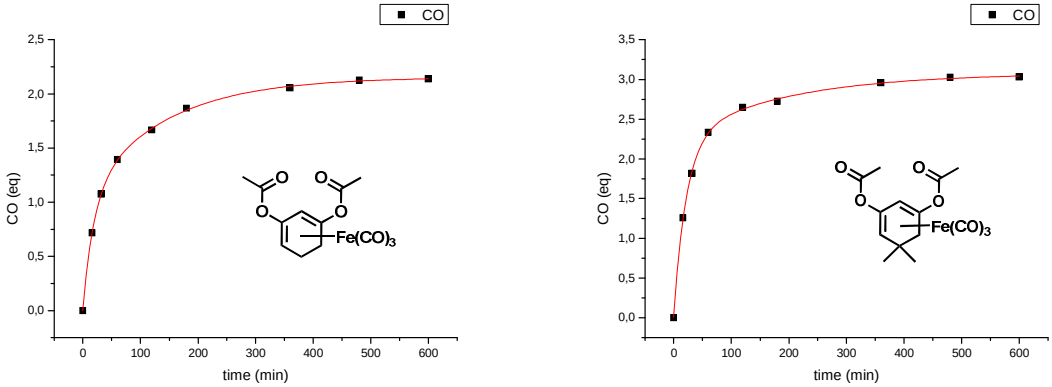


Figure S25: Detection of CO-release from *rac*-**16** with PLE (left) from *rac*-**9** with PLE (right).

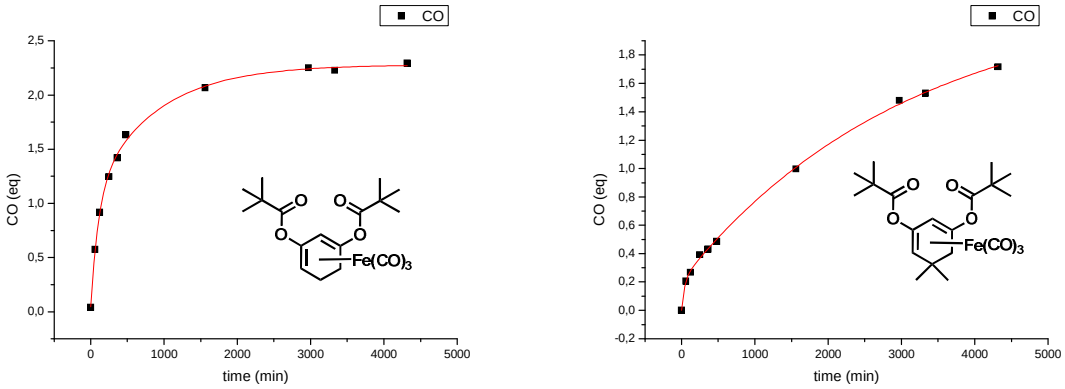


Figure S26: Detection of CO-release from *rac*-**15** with PLE (left) from *rac*-**14** with PLE (right).

3. Cytotoxicity and iNOS inhibitions assays

3.1 Cells and cell culture

The murine macrophage cell line RAW264.7[2] was kept under standard cell culture conditions using RPMI 1640 with 10% heat-inactivated fetal calf serum (FCS) and 2 mM glutamine (Invitrogen, Karlsruhe, Germany).

3.2 Determination of cell viability by MTT assay

Cell viability was evaluated by MTT assays as described.[3] This assay is based upon the conversion of the yellow MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazoliumbromid) by mitochondrial dehydrogenases to a violet formazan dye, which can be photometrically quantified.

In brief, cells were seeded in 96-well plates at a density of 5×10^3 per well and cultured for 24 h. Then, cells were incubated for another 24 h with medium supplemented with compounds (ET-CORMs) and 10 ng/ml LPS (*Escherichia coli* serotype 111:B4, Sigma). Controls received only culture medium with LPS, or solvent and LPS, respectively.Afterwards, supernatants were removed and 100 µl MTT solution (0.4 mg/ml in culture medium) was added to each well, and cells were incubated for another 3 h at 37 °C. Subsequently, 100 µl of a SDS-solution (10% in phosphate buffered saline) were added, and the formazan crystals were allowed to dissolve overnight. The absorbance was determined with a multi-well plate photometer (TiterTek) at 560 nm.

3.3 Determination of cell proliferation by crystal violet staining

Crystal violet is used to stain the nuclei of cells. The photometrically measured intensity of the dye directly correlates with the number of cells.[4]

According to the MTT assays, cells were seeded in 96-well plates at a density of 5×10^3 per well and cultured for 24 h. Then, the cells were incubated for another 24 h with medium supplemented with compounds and 10 ng/ml LPS (*Escherichia coli* serotype 111:B4, Sigma). Controls received only culture medium with LPS, or solvent and LPS, respectively.

Afterwards, supernatants were removed and cells were stained with 30 µl crystal violet solution (0.5% crystal violet in 20% methanol) per well for 10 min. The crystal violet solution was removed, then the cells were washed twice with 200 µl water and air-dried over night. Following, crystal violet was solubilized by addition of 100 µl EtOH/Na-Citrate-solution (EtOH + 0.1 M Na-citrate, (v/v) 1:1) per well and the absorbance was determined at 560 nm.

3.4 Measurement of nitrite production by Griess assay

The generation of NO was determined by measuring the accumulation of nitrite in the cell culture medium by a microplate assay method based on the Griess reaction and performed as described previously[5]. Briefly, cells were seeded in 96-well plates at a density of 8×10^4 per well and cultured for

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[2] W. C. Raschke, S. Baird, et al. "Functional macrophage cell lines transformed by Abelson leukemia virus." *Cell* **1978**, *15*(1) 261-267.

[3] T. Mosmann, "Rapid colorimetric assay for cellular growth and survival: application to proliferation and cytotoxicity assays." *J Immunol Methods* **1983**, *65*(1-2), 55-63.

[4] R. Gillies, N. Didier, M. Denton, "Determination of cell number in monolayer cultures", *Anal Biochem* **1986**, *159*, 109-113.

[5] E. Park, M. R. Quinn, "Taurine chloramine inhibits the synthesis of nitric oxide and the release of tumor necrosis factor in activated RAW 264.7 cells." *J Leukoc Biol* **1993**, *54*(2), 119-124.

24 h. Subsequently, cells were incubated for another 24 h with medium supplemented with compounds (ET-CORMs) and 10 ng/ml LPS (*Escherichia coli* serotype 111:B4). Controls received only culture medium with LPS, or solvent and LPS, respectively. Following, a volume of 100 µl culture supernatant was mixed with 100 µl Griess reagent (1% sulfanilamide, 0.1% naphthylethylene-diamine dihydrochloride in 2% phosphoric acid). After 15 min incubation at room temperature, the absorbance was determined at 560 nm. The nitrite content was determined by using sodium nitrite as a standard.

Supporting information

Table S10 Biological activities of ET-CORMs: cytotoxicity data determined by MTT or crystal violet assay, and inhibition of NO-production in LPS stimulated RAW264.7 murine macrophages. Significant minimum and maximum NO-inhibition values are given at concentrations that had no toxic effects.

	MTT or crystal violet*		**inhibition of NO-production [%]**		
Compound	**IC_{50} [µM]**	**IC_{20} [µM]**	**minimum (conc [µM])**	**maximum (conc [µM])**	**at 10 µM**
rac-**6**	67.1 ± 3.6[a]	28.1 ± 0.6[a]	16.5 ± 10.2 (25)[a]	16.5 ± 10.2 (25)[a]	[a,b]
rac-**7**	> 100* [a]	> 100* [a]	- [a]	- [a]	- [a]
rac-**8**	39.6 ± 0.9 [a]	11.2 ± 2.2 [a]	4.6 ± 0.94 (0.5) [a]	49.3 ± 19.8 (10) [a]	49.3 ± 19.8 [a]
rac-**9**	54.3 ± 1.0 [a]	21.8 ± 0.6 [a]	32.7 ± 5.5 (5) [a]	65.8 ± 8.0 (20) [a]	57.3 ± 13.2 [a]
rac-**10**	> 100	57.2 ± 7.4	11.3 ± 5.2 (10)	23.2 ± 7.7 (50)	11.3 ± 5.2
rac-**11**	40.6 ± 2.3	11.2 ± 3.5	11.2 ± 8.3 (10)	11.2 ± 8.3 (10)	11.2 ± 8.3
rac-**12**	48.7 ± 3.3	18.0 ± 1.7	9.1 ± 3.9 (5)	17.3 ± 7.3 (10)	17.3 ± 7.3
rac-**13**	> 100	> 100	18.9 ± 9.4 (5)	79.1 ± 1.5 (100)	32.5 ± 5.1
rac-**14**	52.4 ± 7.2	17.4 ± 4.5	-	-	[b]
rac-**15**	68.8 ± 4.0*	25.3 ± 2.3*	15.8 ± 8.0 (15)	41.8 ± 12.4 (25)	[b]
rac-**16**	35.3 ± 5.8	5.2 ± 8.2	7.7 ± 4.2 (1)	33.5 ± 6.2 (5)	[c]
rac-**17**	> 100	48.9 ± 7.6	-	-	[b]
rac-**18**	90.2 ± 13.9	30.5 ± 12.8	-	-	[b]
19	61.9 ± 3.5	20.1 ± 1.3	12.4 ± 4.3 (1)	60.4 ± 10.3 (20)	54.7 ± 2.4
23	> 100	> 100	17.9 ± 7.2 (5)	82.7 ± 2.8 (100)	36.6 ± 13.3
39	> 100	> 100	11.7 ± 0.8 (50)	15.0 ± 1.7 (100)	[b]
40	> 100	> 100	5.6 ± 4.0 (10)	9.4 ± 3.2 (100)	5.6 ± 4.0

* An unusual color was observed with *rac*-**7** and *rac*-**15** in the MTT assay prohibiting a correct assessment of the cell viability, therefore a cell count was done via the crystal violet assay.

[a] Values taken from ref. [14]; [b] no significant inhibition was observed at this concentration; [c] no inhibition could be assigned due to toxicity at this concentration.

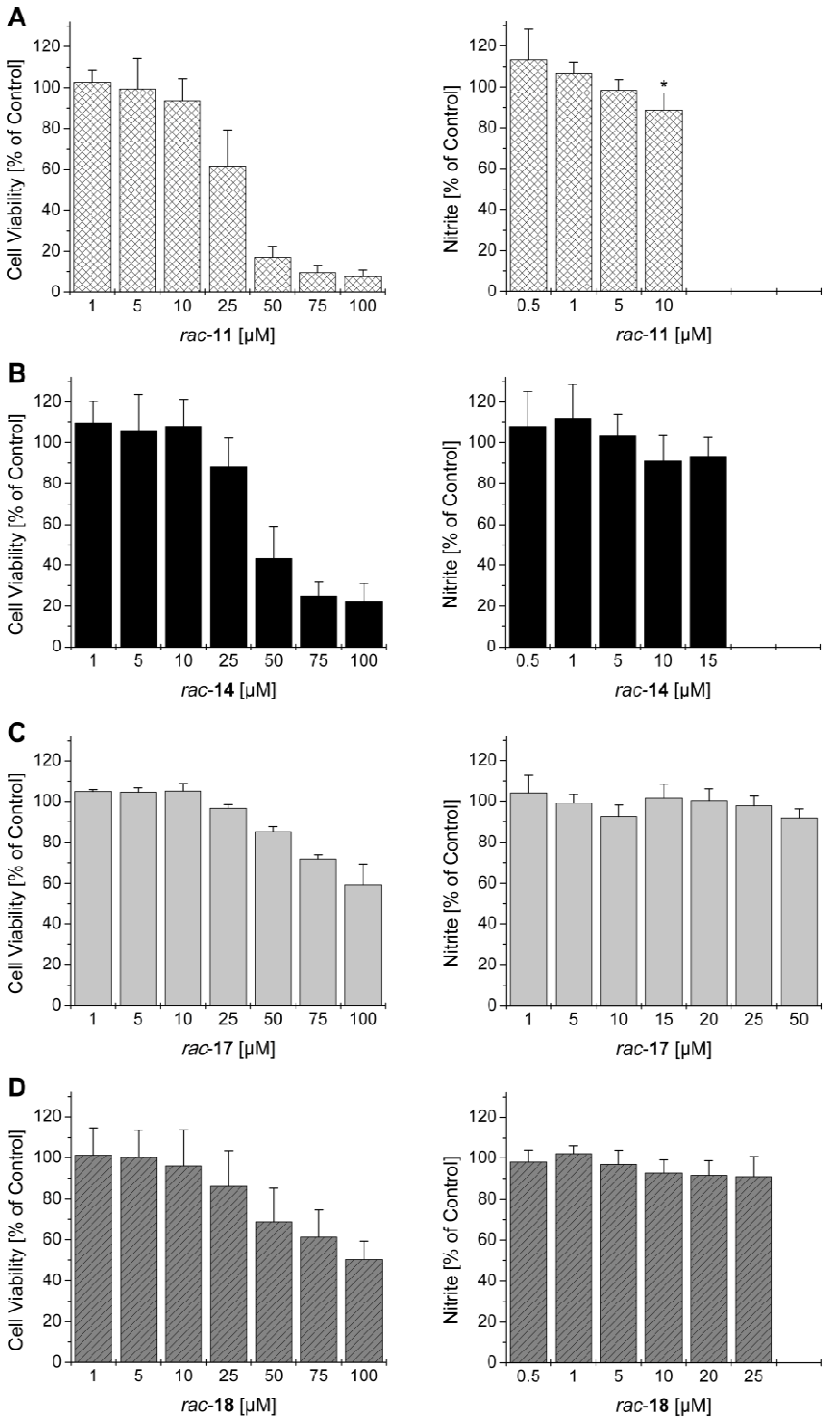

Figure S27 Results of the in vitro assays performed with RAW264.7 cells stimulated with 10 ng/mL LPS. Charts on the left side refer to MTT tests after an incubation time of 24 h at different concentrations. Charts on the right display the influence of ET-CORMs on NO-production (Griess assay). Data represent at least three independent experiments performed in quadruplicates. Level of significance: * $p \leq 0.05$.

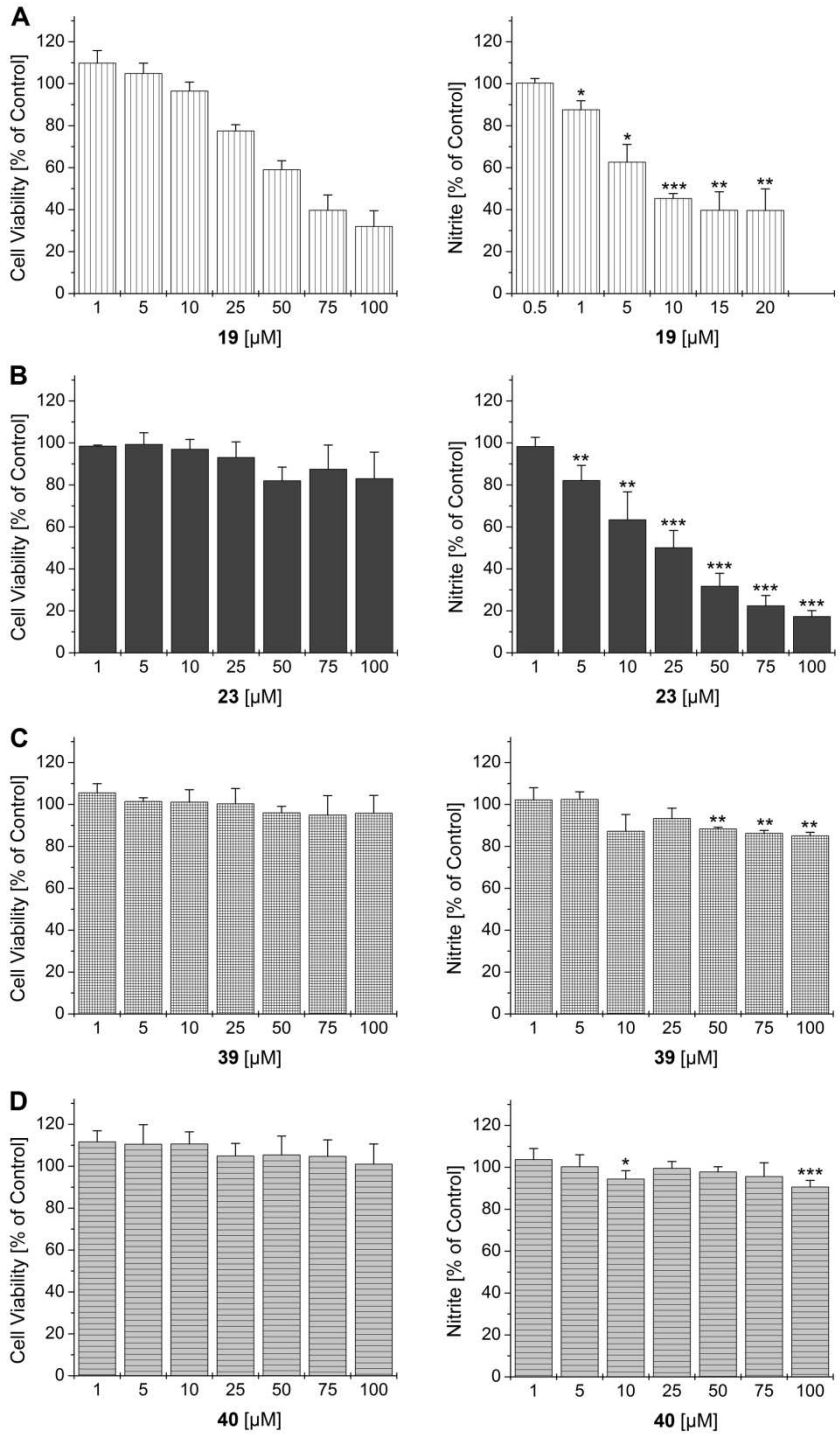

Figure S28 Results of the in vitro assays performed with RAW264.7 cells stimulated with 10 ng/mL LPS. Charts on the left side refer to MTT tests after an incubation time of 24 h at different concentrations. Charts on the right display the influence of ET-CORM-derived enones **19**, **23**, **39**, and **40** on NO-production (Griess assay). Data represent at least three independent experiments performed in quadruplicates. Levels of significance: * $p \leq 0.05$, ** $p \leq 0.01$, *** $p \leq 0.001$.

Table S11 Biological activities of $FeCl_2$ and $FeCl_3$ (both used as anhydrous salts) cytotoxicity data determined by MTT in LPS stimulated RAW264.7 murine macrophages.

	$FeCl_2$	**$FeCl_3$**
IC_{50}	> 100 µM	> 100 µM
IC_{20}	33.7 (± 17.2) µM	39.7 (± 15.3) µM

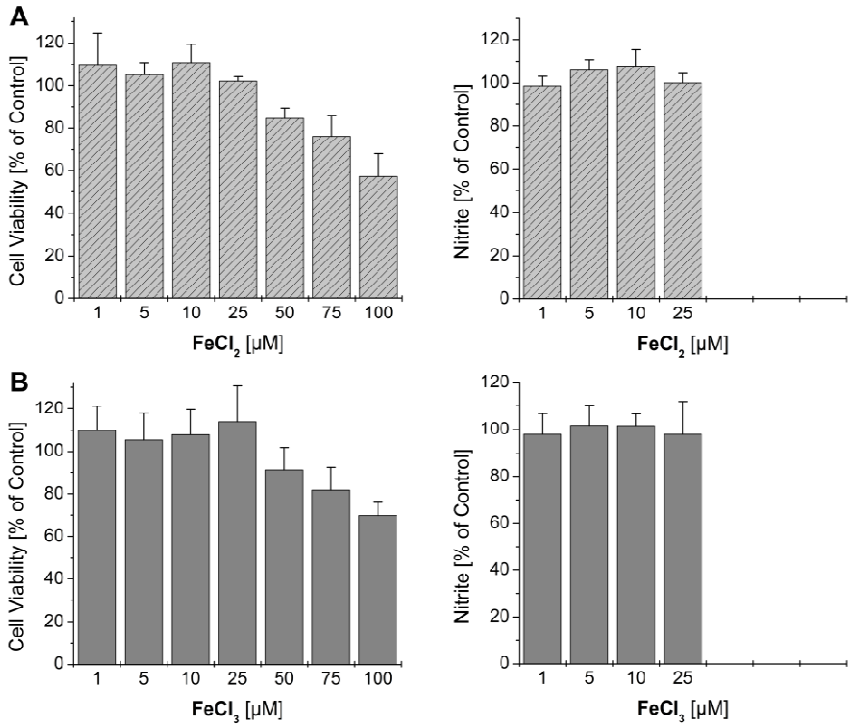

Figure S29 Results of the in vitro assays performed with RAW264.7 cells stimulated with 10 ng/mL LPS. Charts on the left side refer to MTT tests after an incubation time of 24 h at different concentrations. Charts on the right display the influence of $FeCl_2$ and $FeCl_3$ (both used as anhydrous salts) on NO-production (Griess assay). Data represent at least three independent experiments performed in quadruplicates.

3.5 Statistical analysis

Experiments were carried out with four parallels and repeated independently at least three times. Results are expressed as mean ± SD and are depicted as a percentage of untreated controls. A sigmoidal logistic function was used to fit dose-response curves and to determine IC_{50} and IC_{20} values, using an excel calculation sheet (Ed50plus, MH Vargas). Statistical analysis was performed using the software Prism (GraphPad Software). Quantitative data were tested with a two-tailed Student´s *t*-test referring to the untreated control. Levels of significance: $p<0.05$ (*), $p<0.01$ (**), $p<0.001$ (***).