Supporting Information

for

1,1'-Diacetyloctamethylferrocene: An overlooked and overdue synthon leading to the facile synthesis of an octamethylferrocenophane.

Max Roemer*, Brian W. Skelton, Matthew J. Piggott, and George A. Koutsantonis*

Chemistry, M310, School of Chemistry and Biochemistry, The University of Western Australia, 35 Stirling Hwy, Crawley, WA 6009, Australia

Corresponding authors: * max.roemer@uwa.edu.au; *george.koutsantonis@uwa.edu.au

This supporting information contains the following supplementary material:

1. General

Reactions were performed under Ar atmospheres using standard Schlenk techniques unless otherwise stated. Dichloromethane (DCM) and hexane were purified by an Innovative Technology SPS-400 solvent purification system. N,N'-Dimethylformamide (DMF) was distilled from CaH_2. Other solvents were purified by distillation. Flash chromatography was performed on basic aluminum oxide (Sigma-Aldrich). Octamethylferrocene was purchased from Sigma-Aldrich and prepared according to the procedure described below. Tetramethylcyclopentadiene was purchased from Acros Organics. Other compounds were purchased from Sigma-Aldrich. X-ray single crystal diffraction was performed on an Oxford Diffraction Gemini diffractometer. Cyclic voltammetry was performed on a Princeton Applied Research VersaSTAT 3 potentiostat using a three electrode setup with Pt working electrode, and Pt coated titanium rods as counter and pseudo reference electrode. NMR spectra were recorded on Bruker AV500 and AV600 spectrometers. Mass spectra were recorded on a Waters LCT Premier mass spectrometer in ESI+ and APCI modes. Elemental analyses were obtained from Elemental Analysis Service of the London metropolitan university. Infrared spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrometer equipped with an ATR Sampling Accessory. Melting points were determined using a Reichert melting point microscope.

2. Syntheses

1: A Schlenk flask was charged with 4.72 g (38.6 mmol) tetramethylcyclopentadiene (isomeric mixture) and 100 ml THF, and cooled to 0 °C. n-BuLi (1.6 M in hexanes, 26.6 ml, 42.5 mmol) was added slowly over 0.5 h. A thick white precipitate formed immediately during addition. After stirring for another 0.5 h, 5.00 g (23.2 mmol) of anhydrous $FeBr_2$ were added and the mixture was allowed to warm up to room temperature. Stirring was continued for 1 h, followed by the addition of 100 ml water. The mixture was extracted with 3 x 100 ml hexane. The organic layers were combined and dried over sodium sulfate. Solvent evaporation and drying in high vacuum

afforded 5.65 g (19.0 mmol, 98 %) of an orange crystalline solid, which was analytically pure. Spectroscopic data was in agreement with a commercial sample.

2: A Schlenk tube was charged with 300 mg (1.0 mmol) octamethylferrocene and 12 ml dichloromethane. The solution was cooled to 0 °C. A second Schlenk tube was charged with 12 ml dichloromethane and 0.6 ml (8.0 mmol / 8 eq.) of acetyl chloride and 1073 mg (8.0 mmol) aluminum(III) chloride. The mixture was stirred for 10 min and added dropwise to the solution of octamethylferrocene. The solution was allowed to warm up to room temperature and stirring was continued overnight. Additional 0.2 ml of acetylchloride and 40 mg of aluminum chloride were added and stirring was continued for another hour. The reaction was quenched with 30 ml water, extracted with 30 ml dichloromethane and the deep red organic phase was collected and dried over Na_2SO_4. The solvent was evaporated affording a deep red oil, which crystallized within several minutes. The crude product was subject to flash chromatography on aluminum oxide using hexane/EtOAc (10:1) as eluent. Solvent evaporation and drying under high vacuum afforded 281 mg (0.74 mmol, 73%) of **2** as intense red crystalline material.

^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 2.28 (s, 6H; CH_3), 1.96 (s, 12H; Cp-CH_3), 1.71 (s, 12H; Cp-CH_3). ^{13}C NMR ($CDCl_3$): δ = 204.90 (*C*O), 85.44 (Cp), 83.12 (Cp), 76.49 (*ipso*-C), 32.53 (CO*C*H_3), 11.48 (Cp-*C*H_3), 9.24 (Cp-*C*H_3). Elemental analysis (%): calcd: C 69.11, H 7.91; found: C 69.15, H 7.85. MS (ESI+): 383 (M^++1, 100%). HRMS (ESI+): calcd for $C_{22}H_{31}O_2Fe$: 383.1673; found: 383.1667. IR (ATR): 3267 (w), 2985 (w), 2959 (w), 2901 (w), 1638 (s), 1465 (w), 1442 (w), 1405 (m), 1395 (m), 1380 (s), 1341 (m), 1226 (m), 1216 (m), 1148 (w), 1111 (w), 1089 (w), 1034 (m), 1017 (m) 958 (w), 940 (m), 831 (w), 760 (w), 665 (w), 617 (m), 586 (w), 576 (w), 557 (m), 538 (w), 520 (w). M.p.: subliming > 230 °C.

We purified **2** on a 1.0 g scale alternatively by taking up the crude product with hexane, filtered the solution and concentrated it dryness. The crude solids were washed twice with small amounts of hexane, which afforded the title compound in a yield of ~ 50 % analytically pure. The remaining

deep green solid (after taking up the product in hexane) was re-dissolved in dichloromethane, filtered through a syringe filter and slow evaporation of the solvent afforded a deep green solid, which contained crystals suitable for X-ray diffraction. The mass spectrum shows signals at 299, 313, and 327, 341, corresponding to a mixture of **1**, and monoacylated octamethylferrocene (**1b**). MS (APCI): 299 (M^+(**1**)+1), 341 (M^+(**1b**)+1), 327 (M^+(**1b**)+1-CH_3), 313 (M^+(**1b**)+1-OCH_3).

3b: Compound **2** (400 mg (1.05 mmol)) was dissolved in 10 ml DMF in a round bottom flask. $POCl_3$ (0.2 ml, 2.14 mmol) was added dropwise under rapid stirring. After 1-2 minutes, the deep red mixture turned pale yellow and then greenish. The reaction was worked-up after 15 min by dilution with 20 ml water, extraction with dichloromethane (3 x 20 ml), and drying of the organic phase over Na_2SO_4. Solvent evaporation afforded a greenish crystalline solid. The solid was taken up in 20 ml pentane, separating a bright orange solution from a green residue. The solution was filtered through a syringe filter (PTFE, 0.45 μm) and concentrated under a stream of Ar, affording orange crystals. Drying under vacuum afforded 435 mg (1.04 mmol, 99 %) of the title compound. ^{1}H NMR ($CDCl_3$): 5.66 (d, ^2J=1Hz, 1H; CCl=CH_2), 5.55 (d, ^2J=1Hz, 1H; CCl=CH_2), 1.84 (s, 12H; CH_3), 1.73 (s, 12H; CH_3). ^{13}C NMR ($CDCl_3$): 138.19 (CCl=CH_2), 117.27 (CCl=CH_2), 84.45 (Cp), 81.35 (Cp), 79.80 (Cp), 10.64 (CH$_3$), 9.48 (CH$_3$). Elemental analysis (%): calcd: C 63.03, H 6.73; found: C 62.85, H 6.83. MS (ESI+): 418 (M^++1), HRMS (ESI+): calcd for $C_{22}H_{29}Cl_2Fe$: 419.0996; found: 419.0999. IR (ATR): 3305 (w), 3116 (w), 2973 (m), 2950 (m), 2908 (m), 2859 (m), 2098 (w), 1747 (w), 1668 (w), 1655 (w), 1616 (m), 1602 (s), 1472 (m), 1428 (m), 1401 (m), 1378 (s), 1359 (m), 1338 (m), 1259 (w), 1222 (w), 1180 (m), 1146 (w), 1100 (m), 1026 (s), 1004 (m), 882 (m), 870 (s), 834 (w), 804 (m), 707 (m), 690 (s), 682 (s), 648 (m), 639 (m), 615 (w), 599 (m), 566 (m), 544 (w), 530 (m), 522 (m). M.p.: subliming > 135 °C.

3c: Compound **2** (75 mg, 0.20 mmol) was dissolved in 2 ml DMF in a Schlenk tube, followed by drop-wise addition of 0.2 ml (2.14 mmol) $POCl_3$ under stirring. The reaction mixture turned deep

green within a few minutes. We stopped the reaction after one hour by addition of 20 ml water. The deep green solution was transferred into a separatory funnel and extracted with 3 x 50 ml dichloromethane. The combined organic extracts were dried over sodium sulfate. Solvent evaporation afforded the crude product as intense green oil, which was subject to column chromatography on Al_2O_3 using hexane/EtOAc (4:1) as eluent. Compound **3c** (0.040 g, 0.08 mmol; 42 %) was obtained from the purple main fraction after solvent evaporation and drying in high vacuum as purple crystalline solid.

^{1}H NMR ($CDCl_3$): 10.12 (d, ^3J=7 Hz, 1H, CO*H*), 6.29 (d, ^3J =7 Hz, 1H, C*H*COH), 5.65 (d, ^2J=1 Hz, 1H, CCl=CH_2), 5.40 (d, ^2J=7 Hz, 1H, CCl=CH_2), 1.91 (s, 6H, CH_3), 1.83 (s, 6H, CH_3), 1.77 (s, 6H, CH_3), 1.69 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): 191.42 (*C*OH), 155.79 (CCl=CHCOH), 137.63 (CCl=CH_2), 127.64 (CCl=CHCOH), 117.40 (CCl=CH_2), 84.95 (Cp), 84.31 (Cp), 81.91(Cp) , 81.47 (Cp), 81.24 (Cp), 80.59 (Cp), 11.39 (*C*H_3), 10.53 (*C*H_3), 9.63 (*C*H_3), 9.40 (*C*H_3). Elemental analysis (%): calcd: C 61.77, H 6.31; found: C 61.89, H 6.46. MS (ESI+): 446 (M^+), HRMS (ESI+): calcd for $C_{23}H_{29}OCl_2Fe$: 447.0945; found: 447.0952. IR (ATR): 3299 (w), 2974 (w), 2950 (w), 2902 (m), 2858 (w), 2266 (w), 1655 (s, CO), 1619 (m), 1583 (s, C=C), 1573 (s, C=C), 1479 (m), 1448 (m), 1434 (m), 1398 (m), 1380 (m), 1228 (m), 1193 (w), 1182 (w), 1134 (s), 1094 (m), 1027 (s), 1004 (m), 959 (w), 874 (s), 841 (m), 826 (m), 804 (w), 793 (w), 709 (m), 688 (m), 673 (w), 652 (w), 643 (w), 615 (w), 600 (w), 586 (w), 568 (w), 559 (w), 536 (w), 528 (m). M.p.: 72-74 °C.

3d: The reaction was carried out in analogy to the above described preparation of **3c**, but the reaction time was 16 h instead of 1 h. After column chromatography, we isolated a minor amount of **3c** (3 mg) from the first fraction. The second fraction contained 21 mg (0.04 mmol) of the title compound. We transferred the deep green aqueous phase from the aqueous work-up into a conical flask and allowed it to rest for one hour. Compound **3d** crystallised quantitatively in form of small black needles, resulting a colourless aqueous phase. These needles were filtered off using a Büchner

funnel, washed with water and dissolved in dichloromethane. Drying over sodium sulfate, filtration and solvent evaporation afforded the additional 65 mg (0.13 mmol) of the title compound. The combined yield was 86 mg (0.18 mmol, 91 %).

^{1}H NMR ($CDCl_3$): 10.10 (d, ^{3}J = 7 Hz, 2H, CO*H*), 6.22 (d, ^{3}J = 7 Hz, 2H, C*H*COH), 1.90 (s, 12H, CH_3), 1.73 (s, 12H, CH_3). ^{13}C NMR ($CDCl_3$): 191.15 (*C*O), 154.40 (CCl=CH), 128.18 (CCl=CH), 84.56 (Cp), 81.98 (Cp, 2 signals overlapping), 11.20 (*C*H_3), 9.56 (*C*H_3). IR (ATR): 1664 (CO), 1596 (C=C). Elemental analysis (%): calcd: C 60.66; H, 5.94; found: C 60.44, H 5.70. MS (APCI): 475 (M^+), HRMS (APCI): calcd for $C_{24}H_{29}O_2Cl_2Fe$: 475.0894; found: 475.0894. IR (ATR): 3303 (w), 2980 (w), 2958 (w), 2909 (m), 2850 (w), 2734 (w), 2252 (w), 1664 (s, CO), 1596 (s, C=C), 1478 (m), 1451 (m), 1433 (m), 1397 (m), 1370 (m), 1226 (m), 1194 (w), 1152 (w), 1131 (s), 1082 (w), 1023 (m), 988 (w), 963 (w), 863 (m), 844 (m), 828 (m), 736 (w), 711 (m), 680 (w), 672 (w), 652 (w), 626 (w), 612 (w), 607 (w), 585 (m), 566 (w), 549 (w), 535 (w), 527 (w). M.p.:155-156 °C.

4: A Schlenk flask was charged with 100 mg (0.24 mmol) of **3b** and 60 ml DMF. Degassed aqueous NaOH (20 ml, 0.75 M) was added and the solution was stirred at 60 °C for 45 min. The reaction mixture was cooled down to room temperature and diluted with 100 ml degassed hexane and 100 ml degassed water. The organic layer was collected and the aqueous layer was extracted twice with 100 ml hexane. Combination of the organic phases, drying over Na_2SO_4 and solvent evaporation afforded a crude solid, which was taken up in 10 ml pentane and filtered through a syringe filter. Evaporation of the pentane under a stream of argon, followed by drying under vacuum afforded 87 mg (0.22 mmol, 93 %) of an orange crystalline material.

^{1}H NMR (C_6D_6): 6.00 (dd, ^{3}J = 8.4 Hz, ^{3}J = 12.8 Hz, 1H, CH=C*H*-CH), 5.93 (d, ^{3}J = 12.8 Hz, 1H), 4.74 (d, ^{3}J = 8.4 Hz, 1H), 2.27 (s, 6H, N(CH_3)$_2$), 2.06 (s, 6H, Cp-CH_3), 2.02 (s, 6H, Cp-CH_3), 1.72 (s, 6H, Cp-CH_3), 1.65 (s, 6H, Cp-CH_3). ^{13}C NMR (C_6D_6): 151.07, 130.05, 118.97, 100.98, 81.25 (Cp), 80.75 (Cp), 79.65 (Cp), 77.27 (Cp), 77.25 (Cp), 75.94, 39.96 (N(*C*H_3)$_2$), 10.0.72 (Cp-*C*H_3), 10.62 (Cp-*C*H_3), 10.04 (Cp-*C*H_3), 9.93 (Cp-*C*H_3). Elemental analysis[i] (%): calcd: C 73.65, H 8.50,

N 3.58; found: C 72.58, H 8.66, N 3.30. MS (ESI+): 392 (M^+), HRMS (ESI+): calcd for $C_{24}H_{34}NFe$: 392.2041; found: 392.2016. IR (ATR): 2962 (m), 2940 (m), 2903 (s), 2857 (m), 2827 (m), 2782 (m), 1751 (w), 1653 (w), 1579 (s, C=C), 1477 (m), 1445 (s), 1428 (s), 1370 (s), 1325 (s), 1280 (w), 1260 (w), 1234 (w), 1178 (w), 1163 (w), 1134 (m), 1099 (s), 1060 (m), 1026 (s), 1011 (s), 981 (m), 961 (w), 942 (w), 907 (s), 841 (w), 828 (w), 804 (m), 774 (w), 742 (w), 718 (s), 693 (s), 640 (w), 625 (m), 613 (w), 599 (w), 588 (w), 581 (w), 552 (w), 535 (w), 524 (w). M.p.: 118-120 °C.

[i] The measured value for C is deviating 1.07 % from from the calculated value, which likely due to the detected trace impurities. Attempted purification by sublimation (~$1*10^{-2}$ mbar) at a temperature as low as 35 °C and re-crystallisation from pentane at -50 °C did not improve the purity as detected by ^{1}H NMR spectroscopy.

3. Details of the of X-ray crystal structure determination.

Table S1. Crystal data and structure refinement for compounds $\mathbf{1}^{+}\bullet Cl^{-}\bullet H_2O$, **2**, **3b**, **3d** and **4**.

Compound	$\mathbf{1}^{+}\bullet Cl^{-}\bullet H_2O$	**2**	**3b**	**3d**	**4**
CCDC number	1498867	1498868	1498869	1498870	1498871
Empirical formula	$C_{18}H_{28}ClFeO$	$C_{22}H_{30}FeO_2$	$C_{22}H_{28}Cl_2Fe$	$C_{24}H_{28}Cl_2FeO_2$	$C_{24}H_{33}FeN$
Formula weight	351.7	382.33	419.22	475.21	391.36
Temperature/K	100(2)	100.15	100.15	100(2)	100(2)
Crystal system	triclinic	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	P-1	C2/c	$P2_1$	$Pna2_1$	P2/c
a/Å	8.6240(5)	13.8130(2)	10.27788(19)	27.0594(8)	28.4563(5)
b/Å	9.5939(8)	9.90152(15)	11.63128(18)	7.3493(2)	8.6547(2)
c/Å	11.1935(8)	13.7349(3)	17.0381(3)	10.7309(4)	16.6461(4)
α/°	91.012(6)	90	90	90	90
β/°	102.395(6)	95.2622(14)	105.7771(19)	90	91.822(2)
γ/°	107.446(7)	90	90	90	90
Volume/Å^3	859.58(11)	1870.59(5)	1960.08(6)	2134.03(12)	4097.54(15)
Z	2	4	4	4	8
ρ_{calc}g/cm^3	1.359	1.3575	1.4205	1.479	1.269
μ/mm^{-1}	1.03	0.818	1.044	8.109	5.926
F(000)	374.0	817.7	882.8	992.0	1680.0
Crystal size/mm^3	0.648 × 0.574 × 0.197	0.426 × 0.194 × 0.128	0.382 × 0.272 × 0.04	0.215 × 0.046 × 0.014	0.323 × 0.143 × 0.028
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	3.74 to 69.138	5.06 to 64.1	4.12 to 65.5	6.532 to 134.61	6.216 to 134.828
Index ranges	$-13 \le h \le 13$, $-15 \le k \le 15$, $-16 \le l \le 17$	$-10 \le h \le 20$, $-14 \le k \le 14$, $-19 \le l \le 20$	$-14 \le h \le 15$, $-17 \le k \le 16$, $-18 \le l \le 25$	$-32 \le h \le 22$, $-8 \le k \le 8$, $-12 \le l \le 12$	$-29 \le h \le 33$, $-10 \le k \le 10$, $-19 \le l \le 19$
Reflections collected	12302	9835	26962	18254	35857
Independent reflections	6826 [R_{int} = 0.0221, R_{sigma} = 0.0404]	3090 [R_{int} = 0.0223, R_{sigma} = 0.0237]	12931 [R_{int} = 0.0419, R_{sigma} = 0.0584]	3551 [R_{int} = 0.0714, R_{sigma} = 0.105]	7342 [R_{int} = 0.072, R_{sigma} = 0.1018]
Data/restraints/parameters	6826/2/209	3090/0/118	12931/0/467	3551/1/271	7342/217/731
Goodness-of-fit on F^2	1.038	1.086	1.059	1.045	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0345, wR_2 = 0.0840	R_1 = 0.0280, wR_2 = 0.0717	R_1 = 0.0447, wR_2 = 0.1020	R_1 = 0.0445, wR_2 = 0.1051	R_1 = 0.0578, wR_2 = 0.1378
Final R indexes [all data]	R_1 = 0.0422, wR_2 = 0.0888	R_1 = 0.0307, wR_2 = 0.0742	R_1 = 0.0534, wR_2 = 0.1073	R_1 = 0.0531, wR_2 = 0.1101	R_1 = 0.0889, wR_2 = 0.1580
Largest diff. peak/hole / e Å^{-3}	0.69/-0.37	0.50/-0.31	1.07/-0.54	1.05/-0.27	0.83/-0.58

4. Kinetic profiling of the formylation of compound 2 by ^{1}H NMR spectroscopy in DMF-d^7

We dissolved compound **2** (2 mg, 5.2 μmol) in 0.5 ml DMF-d^7 in an NMR-tube and recorded an ^{1}H NMR spectrum of the unreacted compound. This was followed by the addition of two drops $POCl_3$ (~ 11 mg, 72 μmol). To achieve a homogeneous distribution, the NMR tube was shaken vigorously for a few seconds, after that it was immediately placed into the NMR spectrometer, followed by recording of spectra with one scans in intervals of 1 min for 1 h. Figure S1 shows selected spectra (recorded in two second intervals) of the vinylic range. The first spectrum recorded was recorded before the addition and consequently shows no resonances in the selected range. The second spectrum recorded immediately after the addition shows signals of **3a** and **3b**, whereas the concentration of **3a** increases in the following spectra and that of **3a** decreases, respectively. Both 1-chlorovinyl groups of **3b** are chemically equivalent, giving rise to two dublets with small geminal coupling constants of 1 Hz. Compound **3a** bears one 1-chlorovinyl group, hence giving rise to one dublet too. Before the addition of $POCl_3$, the aliphatic range (Figure S2) shows two resonances for the pairwise equivalent methyl groups of the Cp rings and one resonance for both formyl groups. Immediately after the addition of $POCl_3$, one can see ten resonances in this range. Compound **3b** bears only Cp-methyl protons, which are pairwise equivalent and hence give rise to two singlets. Compound **3a** instead bears two chemically inequivalent Cp rings, giving rise to four signals for those, and one for the unreacted formyl group. Unreacted **2** shows three signals, two for the Cp-methyl protons, and one for the formyl group, explaining the total number of ten resonances observed.

Figures S3 and S4 show spectra of the same reaction, but in five second intervals. Compound **3a** is consumed after 30 s to form **3b** (Figure S3). A further vinylic signal appears in the range of 4.48 ppm, which we assign to **3c**.

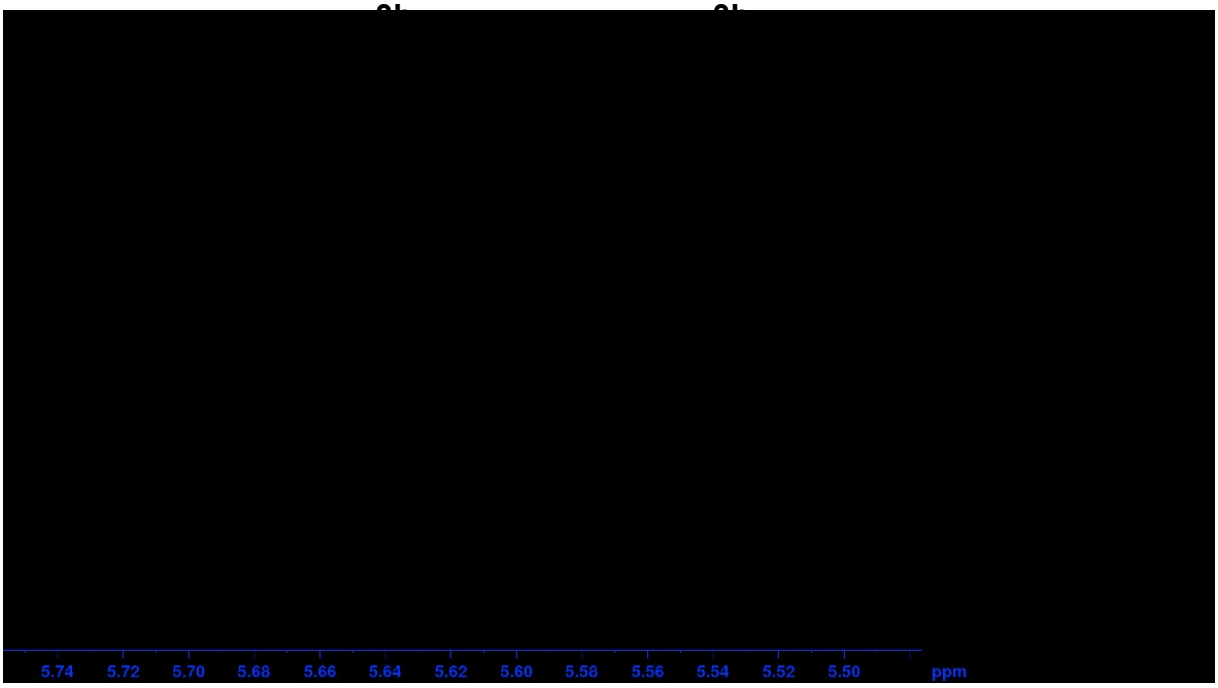


Figure S1. Vinylic range of time dependent ^{1}H NMR spectra of the formylation of **2** in DMF-d^{7}. The first spectrum was recorded before the addition of $POCl_3$, the second spectrum immediately after the addition, and each depicted spectrum 2 min later.

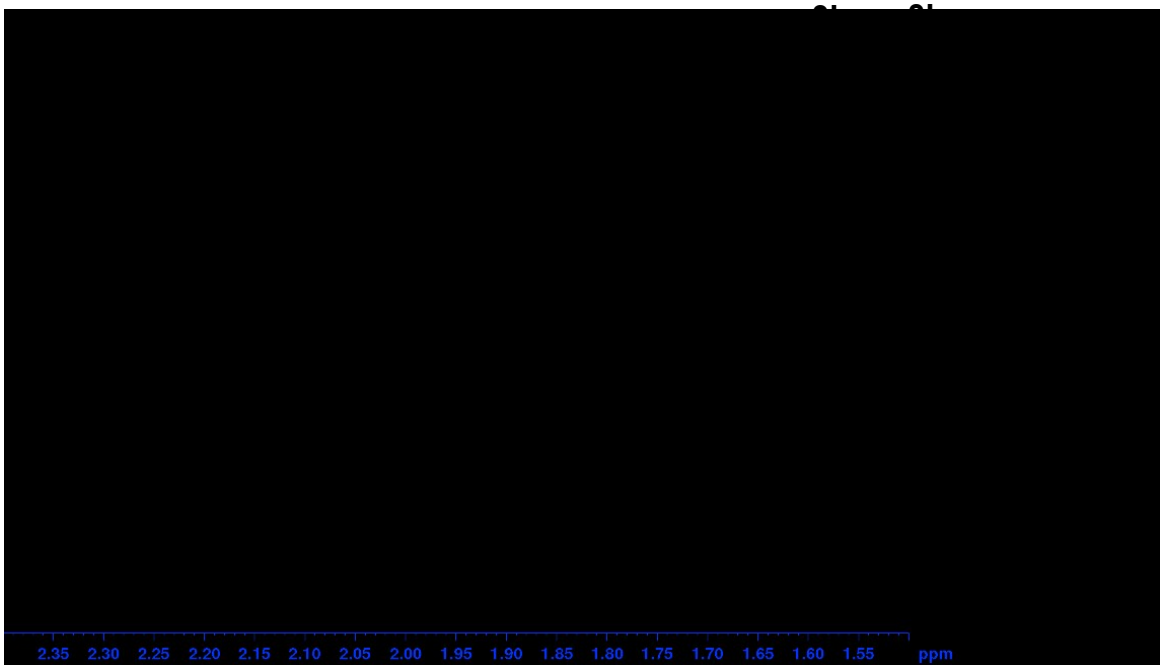


Figure S2. Aliphatic range of time dependent ^{1}H NMR spectra of the formylation of **2** in DMF-d^{7}. The first spectrum was recorded before the addition of $POCl_3$, the second spectrum directly after the addition, and each following spectrum 2 min later.

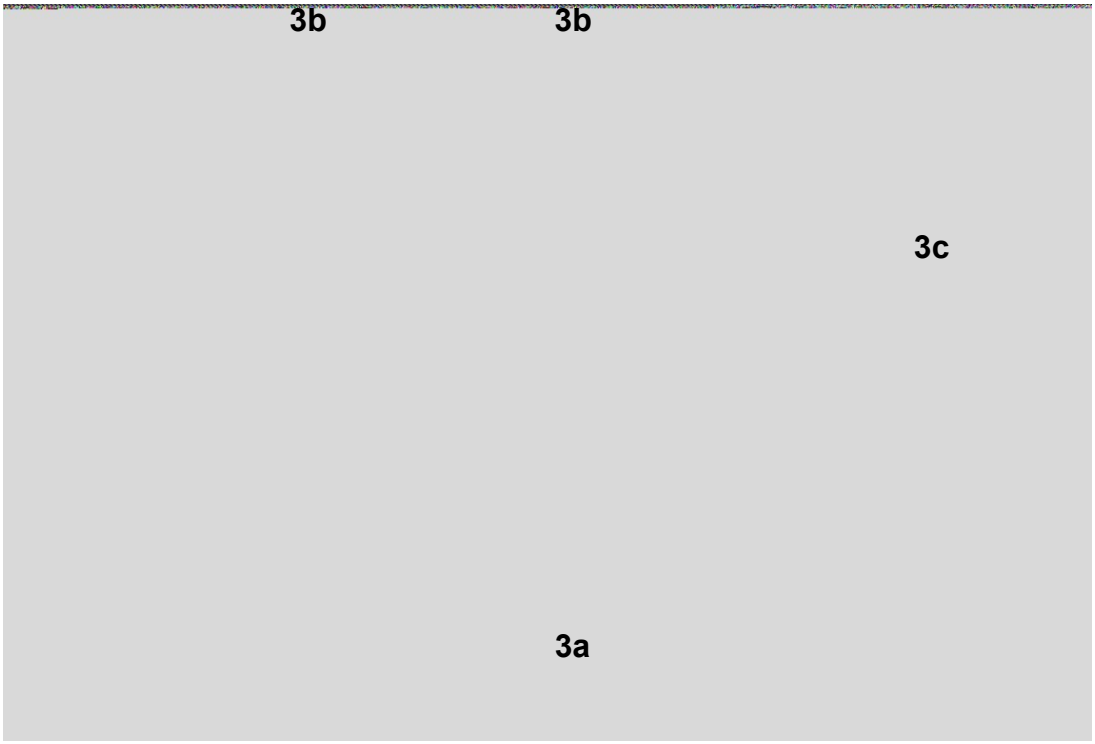


Figure S3. Vinylic range of time dependent ^{1}H NMR spectra of the formylation of **2** in DMF-d^{7}. The first spectrum was recorded before the addition of $POCl_3$, the second spectrum directly after the addition, and each following spectrum 5 min later.

Figure S4. Aliphatic range of time dependent ^{1}H NMR spectra of the formylation of **2** in DMF-d^{7}. The first spectrum was recorded before the addition of $POCl_3$, the second spectrum 5 min after the addition, and each following spectrum 5 min later.

Increasing the amount of $POCl_3$ to 55 mg (0.36 mmol) resulted in a remarkably faster conversion (Figure S5). The first scan after addition of $POCl_3$ shows no traces of compound **2**, whereas compound **3c** is the major product. After ~ 20 min compound **3b** is totally consumed.

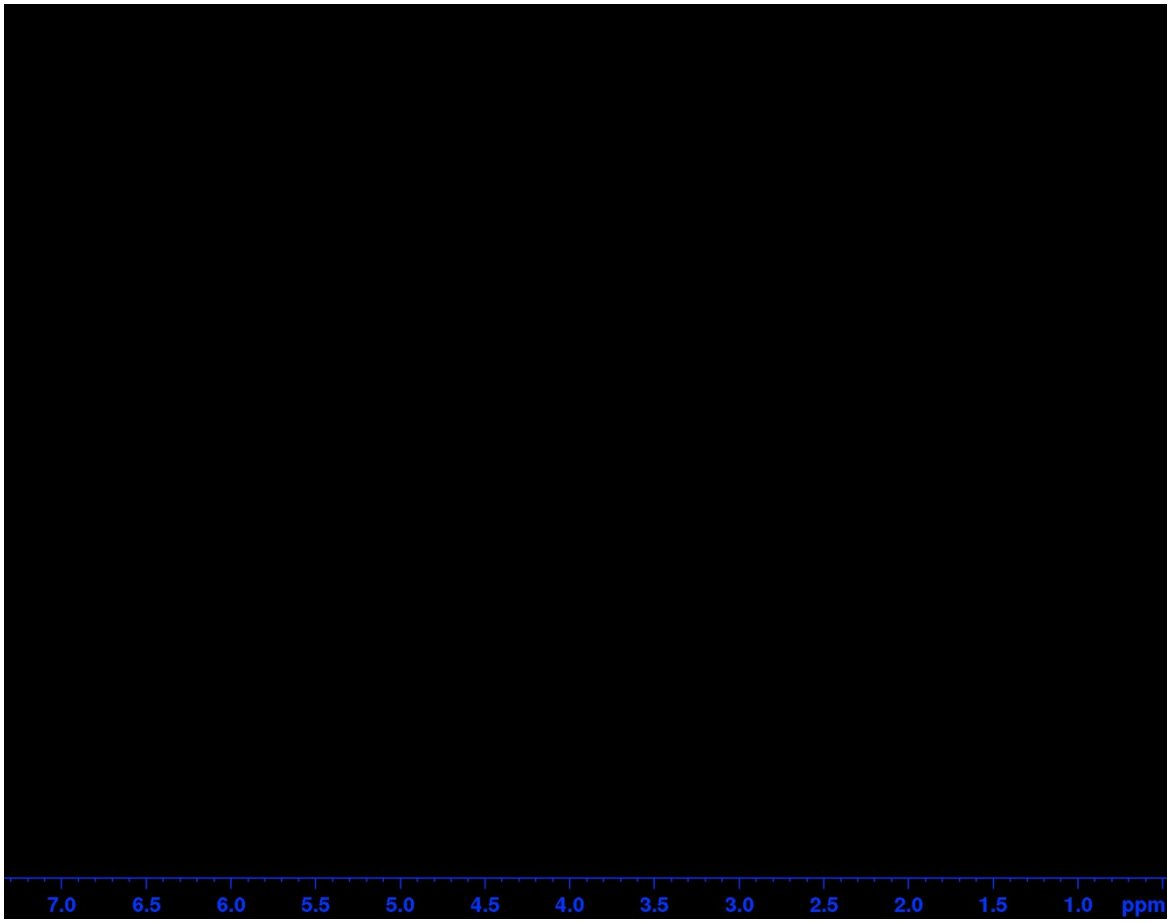
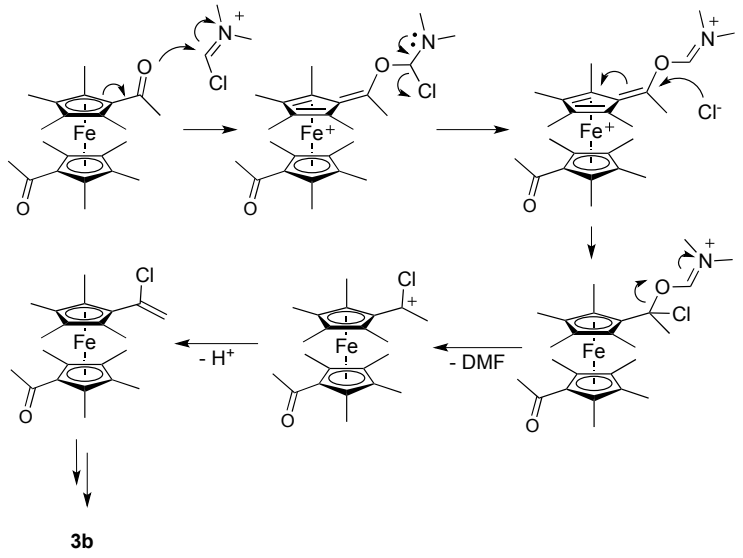


Figure S5. Selected range of time dependent ^{1}H NMR spectra of the formylation of **2** in DMF-d^7. The first spectrum was recorded after the addition of $POCl_3$, the following spectra were recorded every 30s. The figure shows selected spectra every 20 scans.

5. Proposed mechanism



Scheme S1: Proposed mechanism for formation of compound **3b**.

6. Cyclic voltammetry

All measurements were performed in 0.1 M solutions of Bu_4NPF_6 in dichloromethane with an analyte concentration of ~ 3 mM or 1 mM. The graphs shown represent scans at 100 mV/s. Decamethylferrocene (DmFc) and ferrocene were used as internal standards and determined potentials are reported versus the Fc/Fc^+ couple ($E_{Fc} = E_{DmFc} + 480$ mV[1]). The half-width potentials ($E_{1/2}$) were determined by using middle between anodic (E_{pa}) and cathodic peak potentials (E_{pc}). All redox processes show a good reversibility ($i_{pa}/i_{pc} \approx 1$) within the chosen scanrate and bias range.

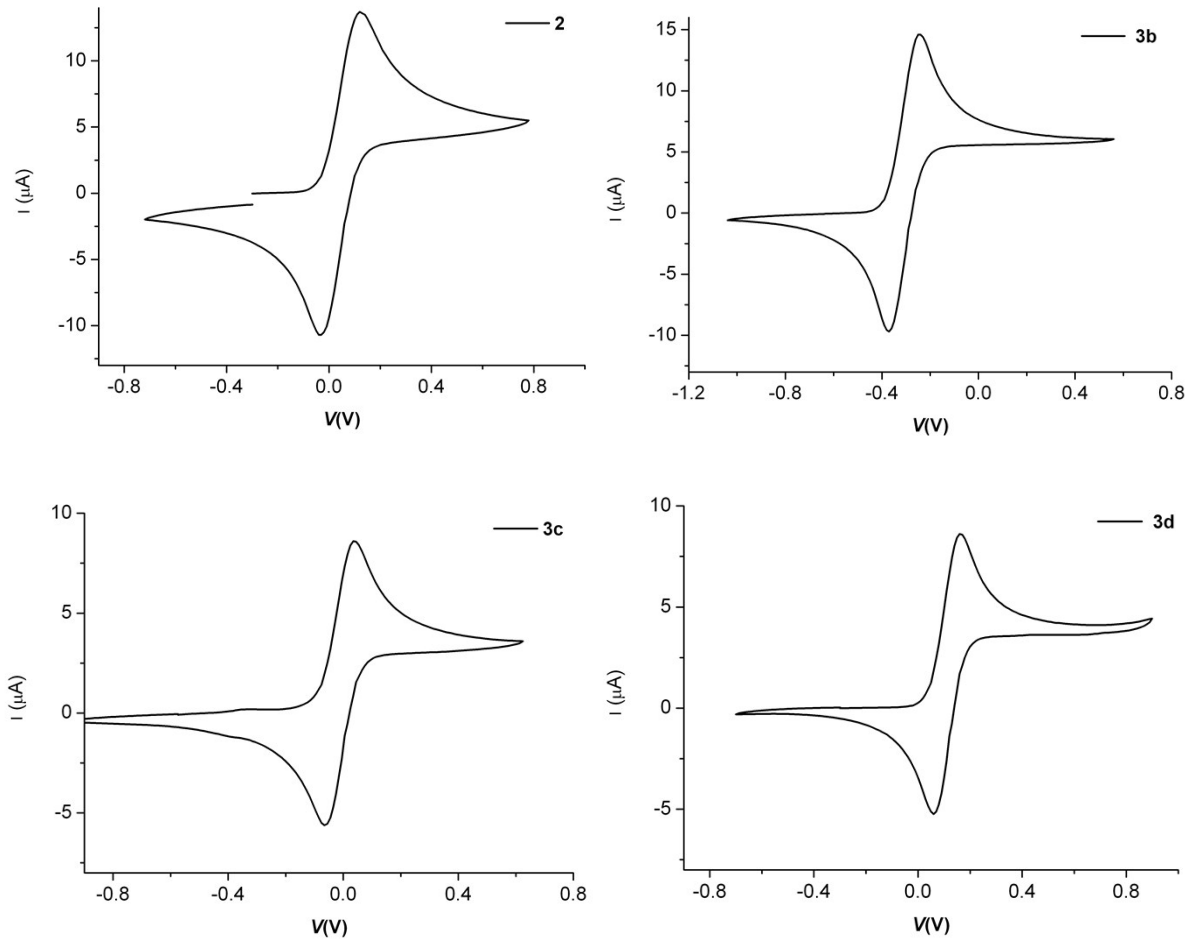


Figure S6. Cyclic voltammograms of compounds **2**, **3b**, **3c**, **3d** with a scanrate of 100 mV/s. All potentials are reported vs Fc/Fc^+.

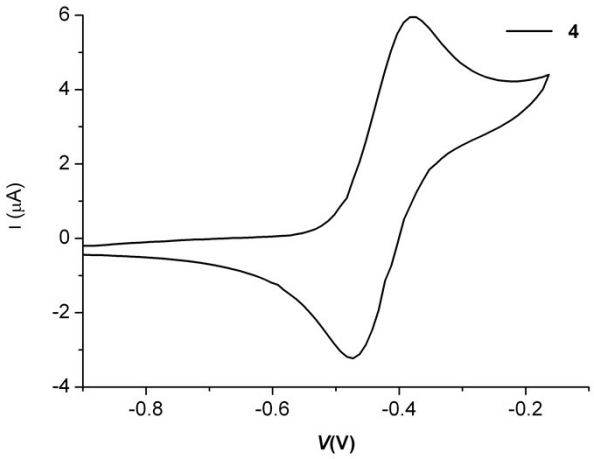


Figure S7. Cyclic voltammogram of compound **4**. The potential is reported vs Fc/Fc^{+}.

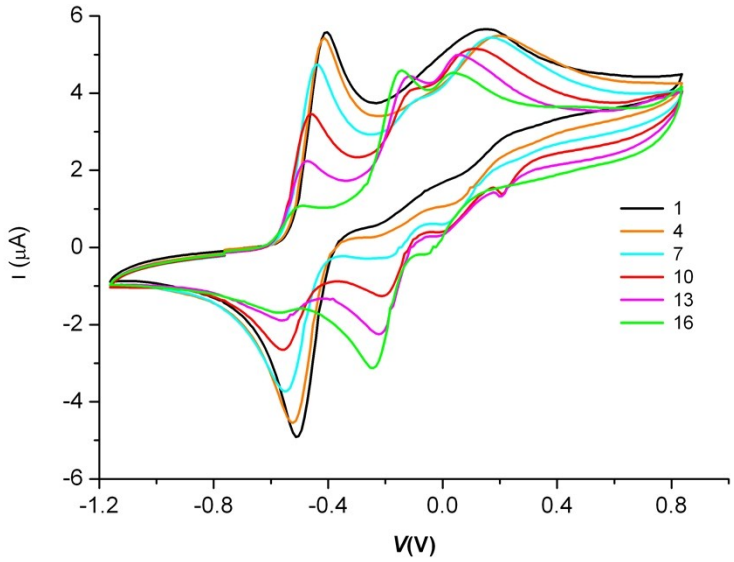


Figure S8. Selected repeated cyclic voltammograms of compound **4**. After an initial scan at 100 mV/s, the same scan was repeated for 16 times. The graph shows every third recorded curve. The potential is reported vs Fc/Fc^{+}. The distinct redox process at - 425 mV for the first scan vanishes with increasing number of scans, giving rise to a minimum of two further processes in the vicinities of - 193 mV and 8 mV, respectively.

7. Appendix: ^{1}H- and ^{13}C NMR spectra

Figure S9. ^{1}H NMR spectrum of compound **2**.

Figure S10. ^{13}C NMR spectrum of compound **2**.

Figure S11. ^{1}H NMR spectrum of compound **3b**.

Figure S12. ^{13}C NMR spectrum of compound **3b**.

Figure S13. ^{1}H NMR spectrum of compound **3c**.

Figure S14. ^{13}C NMR spectrum of compound **3c**.

Figure S15. ^{1}H NMR spectrum of compound **3d**.

Figure S16. ^{13}C NMR spectrum of compound **3d**.

Figure S17. ^{1}H NMR spectrum of compound **4**.

Figure S18. ^{13}C NMR spectrum of compound **4**.

References

1. N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877-910.