SUPPORTING INFORMATION

Synthesis of (μ_2,η^3-allyl-η^5-oxapentadienyl)diiron pentacarbonyl complexes, an unusual reaction product from η^4-(vinylketene)Fe(CO)$_3$ complexes. Structure and Electron density distribution analysis

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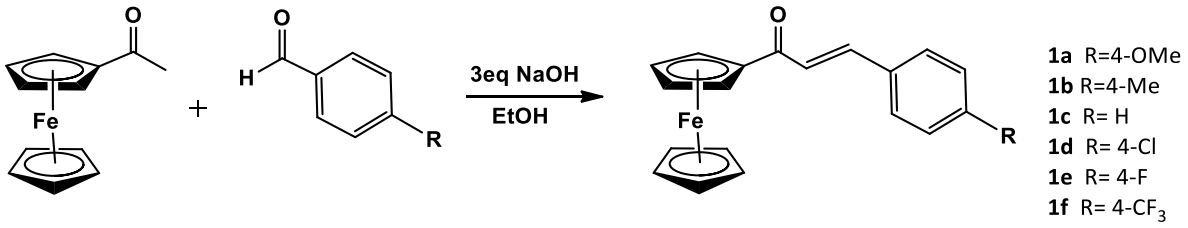
1. Materials and methods

All the reactions were performed under argon or carbon monoxide atmosphere. Anhydrous ether and anhydrous CH_2CL_2 were purchased from the Aldrich Chemical Company. Enneacarbonyldiiron(0) was prepared by a published procedure.[1] The compounds **1a-f**, **2a-f** and **3a-f** were prepared following the methodologies previously reported by our group.[2] All reagents and solvents were obtained from commercial suppliers and used without further purification. Column chromatography was performed using 70-230 mesh silica gel and preparative Thin-Layer plates were performed using MN-Silica Gel/UV_{254}, and compounds were visualized by ultraviolet light (254 nm). The relative proportion in mixed chromatography solvents refers to volume/volume ratio. The yields are based on the pure products isolated. Melting points, which are uncorrected, were obtained on a Stuart Melting Point Apparatus SMP10. Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR, using ATR technique for solid samples and a NaCl pathlength sealed cell for samples acquired in solution of cyclohexane, and all data are expressed in wavenumbers (cm^{-1}). NMR spectra were measured at room temperature on Bruker Avance 300 (300.52 MHz ^1H, 75.56 MHz, ^{13}C) spectrometer, using $CDCl_3$ as solvent. Chemical shifts are reported in parts per million (δ), relative to TMS. Coupling constants (*J* values) are reported in hertz (Hz), and spin multiplicities are indicated by the following symbols: s(singlet), d (doublet), t (triplet), q (quartet), m (multiplet), broad (br). Mass spectra were recorded on a JEOL JMS-AX505 instrument by using EI and FAB (matrix–*m*-nitrobenzylalcohol) techniques. Elemental analyses for carbon, hydrogen and nitrogen atoms were performed on a Thermo Scientific elemental analyzer, Flash 2000 using sulfanilamide as standard.

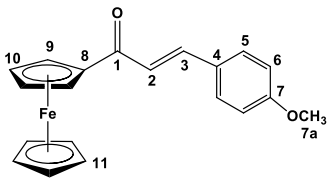
2. Synthesis of 1a-f and NMR spectra

To an absolute ethanol solution (25mL) of NaOH (3eq) was added the substituted *p*-benzaldehyde (1.2eq). The reaction mixture was cooled in ice, and a solution of acetylferrocene (1eq) in 5 mL of ethanol was added dropwise, and it was stirred for 24h. Subsequently, the ethanol was evaporated *in vacuo*. The reaction mixture was extracted with CH_2Cl_2 (2x50mL). The organic layer was dried with anhydrous Na_2SO_4, and concentrated *in vacuo*. Purification by column chromatography, using 9/1 hexane/ethyl acetate as the mobile phase gave the expected deep purple crystalline solid products.



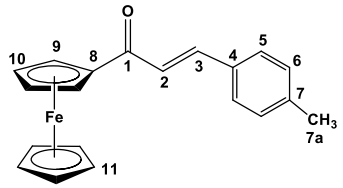
Scheme S1. Reaction for the generation of ferrocenylchalcone **1a-f.**

(**1a**) 3-(4'-Methoxyphenyl)-1-ferrocenylprop-2*E*-en-1-one



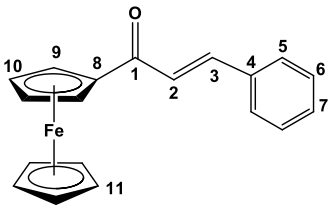
Purple crystal, 85% yield, $C_{20}H_{18}FeO_2$: 346 g/mol, mp 149-150 °C (lit[3b,c] 51% yield, mp 122-123°C). **IR** (ATR, cm^{-1}): 3008, 3083 (C_{sp2}-H); 1645 (C=O); 1579(C=C). **^{1}H NMR** ($CDCl_3$, ppm): 3.8 (s, 3H, H-7a); 4.2 (s,5H, H-11); 4.56 (s, 2H, H-10); 4.90 (s, 2H, H-9); 6.94 (d, 2H, H-6); 7.02 (d, 1H, *J*=15.6Hz, H-2); 7.60 (d, 2H, H-5) and 7.76 (d, 1H, *J*=15,6 Hz, H-3). **^{13}C{1H} NMR** ($CDCl_3$, ppm): 55.5 (C-7a); 69.7 (C-10); 70.1 (C-11); 72.6 (C-9); 80.6 (C-8); 114.4 (C-6); 120.8 (C-2); 127.9 (C-4); 130.0 (C-5); 140.7 (C-3); 161.4 (C-7) and 193.1 (C-1). **MS-IE** [*m/z*, (%)]: 346 [M^+] (100%); 331 [M^+–CH_3] (4%); 281 [M^+–Cp] (17%); 121 [Cp^+–Fe] (11%).

(**1b**) 3-(4'-Methylphenyl)-1-ferrocenylprop-2*E*-en-1-one



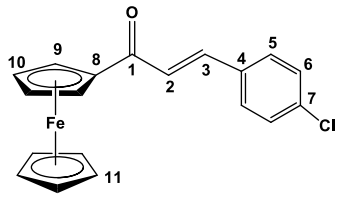
Purple crystal in 97% yield, $C_{20}H_{18}FeO$: 330 g/mol, mp 163-165 °C (lit[3b,c] 57% yield, mp 169-170°C). **IR** (ATR, cm^{-1}): 3110,3081 (C_{sp2}-H); 1645 (C=O); 1585(C=C). **^{1}H NMR** ($CDCl_3$, ppm): 2.40 (s, 3H, H-7a); 4.21 (s,5H, H-11); 4.58 (s, 2H, H-10); 4.91 (s, 2H, H-9); 7.09 (d, 1H, *J*=15.6Hz, H-2); 7.23 (d, 2H, *J*=7.8Hz, H-6); 7.55 (d, 2H, J=7.5Hz, H-5) and 7.78 (d, 1H, *J*=15,6 Hz, H-3). **^{13}C{1H} NMR** ($CDCl_3$, ppm) : 21.6 (C-7a); 69.7 (C-10); 70.1 (C-11); 72.7 (C-9); 80.7 (C-8); 122.0 (C-2); 128.3 (C-5); 129.7 (C-6); 132.5 (C-4); 140.6 (C-7); 140.9 (C-3) and 193.1 (C-1). **MS-IE** [*m/z*, (%)]: 330 [M^+] (100%); 265 [M^+–Cp] (22%); 237 [M^+–(Cp-CO)] (5%); 157 [M^+–(C_4H_4FeCp)] (10%); 121 [Fe–Cp]$^+$ (12%).

(**1c**) 3-Phenyl-1-ferrocenylprop-2*E*-en-1-one



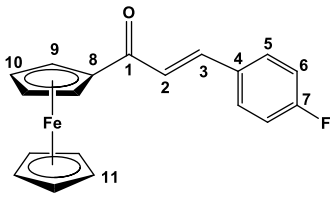
Purple crystal in 93% yield $C_{19}H_{16}FeO$: 316 g/mol, mp 134-135 °C (lit[3b,c] 68% yield, mp 130-131°C). **IR** (ATR, cm^{-1}): 3101,3086 (C_{sp2}-H); 1648 (C=O); 1594(C=C). **^{1}H NMR** ($CDCl_3$, ppm): 4.21 (s, 5H, H-11); 4.59 (s, 2H, H-10); 4.92 (s, 2H, H-9); 7.11 (d, 1H, *J*=15.6Hz, H-2); 7.42 (s, 3H, H-6 y H-7); 7.66 (m, 2H, H-5) and 7.80 (d, 1H, *J*=15,6 Hz, H-3). **^{13}C{1H} NMR** ($CDCl_3$, ppm): 69.8 (C-10); 70.2 (C-11); 72.8 (C-9); 80.5 (C-8); 123.1 (C-2); 128.3 (C-5); 129.0 (C-6); 130.2 (C-7); 135.3 (C-4); 140.8 (C-3) and 193.0 (C-1). **MS-IE** [*m/z*, (%)]: 316 [M^+] (100%); 251 [M^+–Cp] (16%); 121 [Cp-Fe]$^+$ (9%).

(**1d**) 3-(4'-Chlorophenyl)-1-ferrocenylprop-2*E*-en-1-one



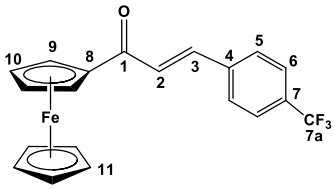
Purple crystal in 93% yield $C_{19}H_{15}ClFeO$: 350.5 g/mol, mp 152-153 °C (lit[3] 51% yield, mp 155-156°C) **IR** (ATR, cm^{-1}): 3094 (C_{sp2}-H); 1650 (C=O); 1593(C=C). **^{1}H NMR** ($CDCl_3$, ppm): 4.22 (s,5H, H-11); 4.60 (s, 2H, H-10); 4.91 (s, 2H, H-9); 7.08 (d, 1H, *J*=15.6Hz, H-2); 7.40 (d, 2H, H-6); 7.58 (d, 2H, H-5) and 7.74 (d, 1H, *J*=15,6 Hz, H-3). **^{13}C{1H} NMR** ($CDCl_3$, ppm): 69.8 (C-10); 70.2 (C-11); 73.0 (C-9); 80.5 (C-8); 124.0 (C-2); 129.2 (C-6); 129.4 (C-5); 133.7 (C-4); 136.0 (C-7) 139.4 (C-3) and 192.7 (C-1). **MS-IE** [*m/z*, (%)]: 350 [M^+] (100%); 352 [M^++ 2] (34%); 316 [M^+–Cl] (5%); 285 [(M^+–Cp)] (10%); 165 [M^+–(CpFeCp)] (14%); 121 [Fe–Cp]$^+$ (9%).

(**1e**) 3-(4'-Fluorophenyl)-1-ferrocenylprop-2*E*-en-1-one



Purple crystal in 89% yield $C_{19}H_{15}FFeO$: 334 g/mol, mp 151-152 °C (lit[3] 50% yield, mp 148-149°C). **IR** (ATR, cm^{-1}): 3107, 3088 (C_{sp2}-H); 1651 (C=O); 1595 (C=C); 1226 (C_{sp2}-F). **^{1}H NMR** ($CDCl_3$, ppm): 4.21 (s, 5H, H-11); 4.59 (s, 2H, H-10); 4.91 (s, 2H, H-9); 7.05 (d, 1H, *J*=15.6Hz, H-2); 7.10 (m, 2H, H-6); 7.63 (m, 2H, H-5) and 7.75 (d, 1H, *J*=15,6 Hz, H-3). **^{13}C{1H} NMR** ($CDCl_3$, ppm): 69.8 (C-10); 70.2 (C-11); 72.9 (C-9); 80.5 (C-8); 116.1 (d, C-6, J_{C-F}=21.75 Hz); 122.7 (C-2); 130.1 (d, C-5, J_{C-F}=8.25Hz); 131.4 (d, C-4, J_{C-F}= 3Hz); 139.6 (C3); 163.8 (d,C-7, J_{C-F}=249Hz) and 192.8 (C-1). **MS-IE** [*m/z*, (%)]: 334 [M^+] (100%); 277 [M^+–(C_3H_2F)] (34%); 269 [M^+–Cp] (18%); 155 [Cp–CO-C=C-C_3H_2]$^+$ (34%); 121 [Cp–Fe]$^+$ (18%).

(**1f**) 3-(4'-Trifluoromethylphenyl)-1-ferrocenylprop-2*E*-en-1-one



Purple crystal in 71% yield, $C_{20}H_{15}F_3FeO$: 384 g/mol, mp 168-170 °C (lit[3] 40% yield, mp 171-172°C). **IR** (ATR, cm^{-1}): 3085 (C_{sp2}-H); 1651 (C=O); 1596(C=C). **^{1}H NMR** ($CDCl_3$, ppm): 4.22 (s, 5H, H-11); 4.63 (s, 2H, H-10); 4.92 (s, 2H, H-9); 7.16 (d, 1H, *J*=15.6Hz, H-2); 7.71 (m, 4H, H-5 and H-6) and 7.79 (d, 1H, *J*=15.6 Hz, H-3). **^{13}C{1H} NMR** ($CDCl_3$, ppm): 69.8 (C-10); 70.21 (C-11); 73.1 (C-9); 80.3 (C-8); 125.2 (C-2); 123.9 (q, C-7a, J_{C-F}=270Hz); 125.2 (C-3); 125.9 (q, C-6, J_{C-F}=3.75Hz); 128.4 (C-5); 131.5 (q, C-7, J_{C-F}=32.25Hz), 138.7 (C-4); 138.9 (C-2) and 192.5 (C-1). **MS-IE** [*m/z*, (%)]: 384 [M^+] (100%); 365 [M^+–F] (3%); 244 [M^+–FeCp–F] (3%); 195 [M^+–FeCp-CF_3] (5%); 157 [(CH-Ph-CF_3)]$^+$ (16%); 121 [Fe-Cp]$^+$ (4%).

Compound 1a

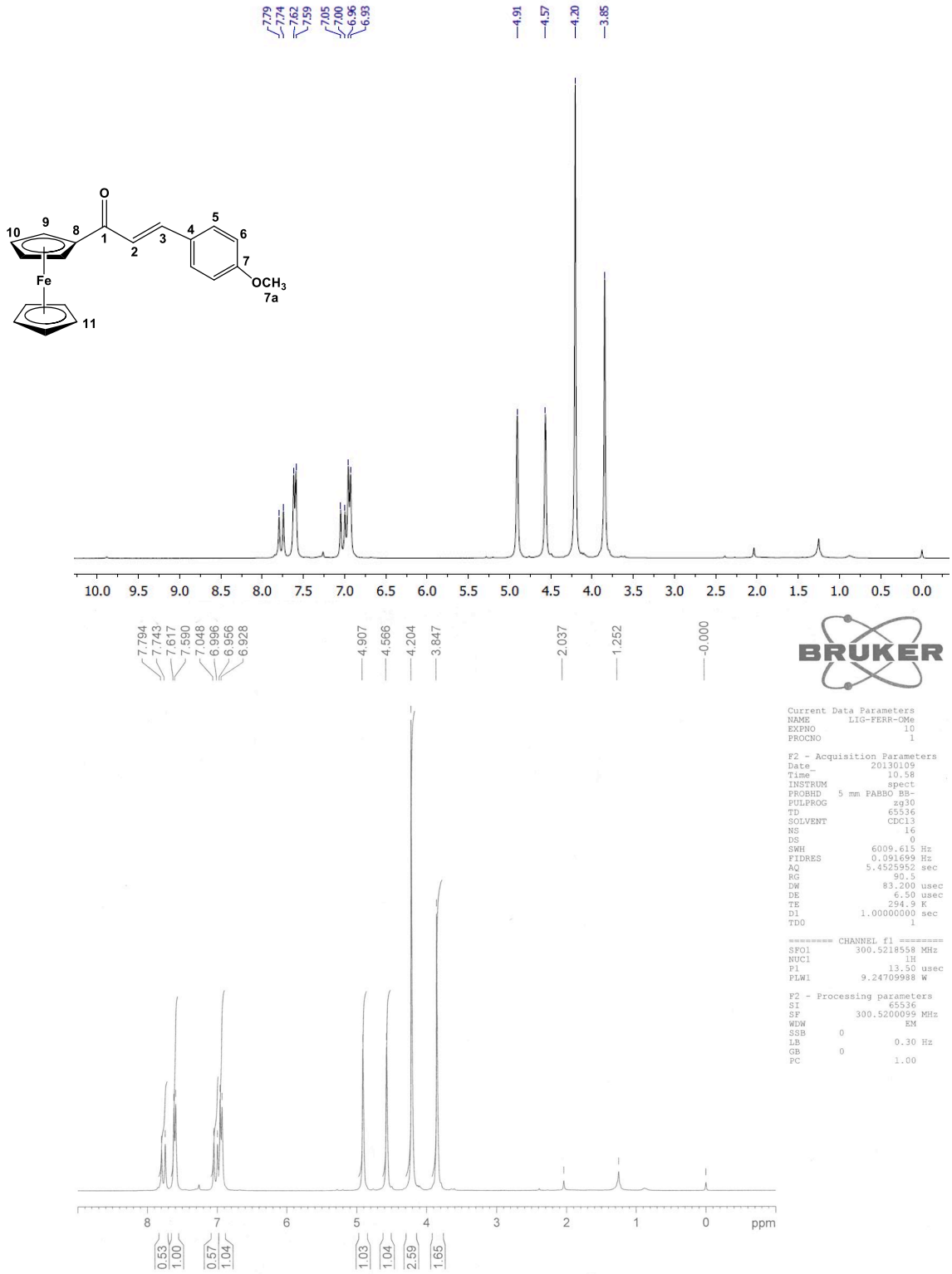


Figure S1. ^{1}H NMR spectrum 300 MHz ($CDCl_3$) of compound **1a**

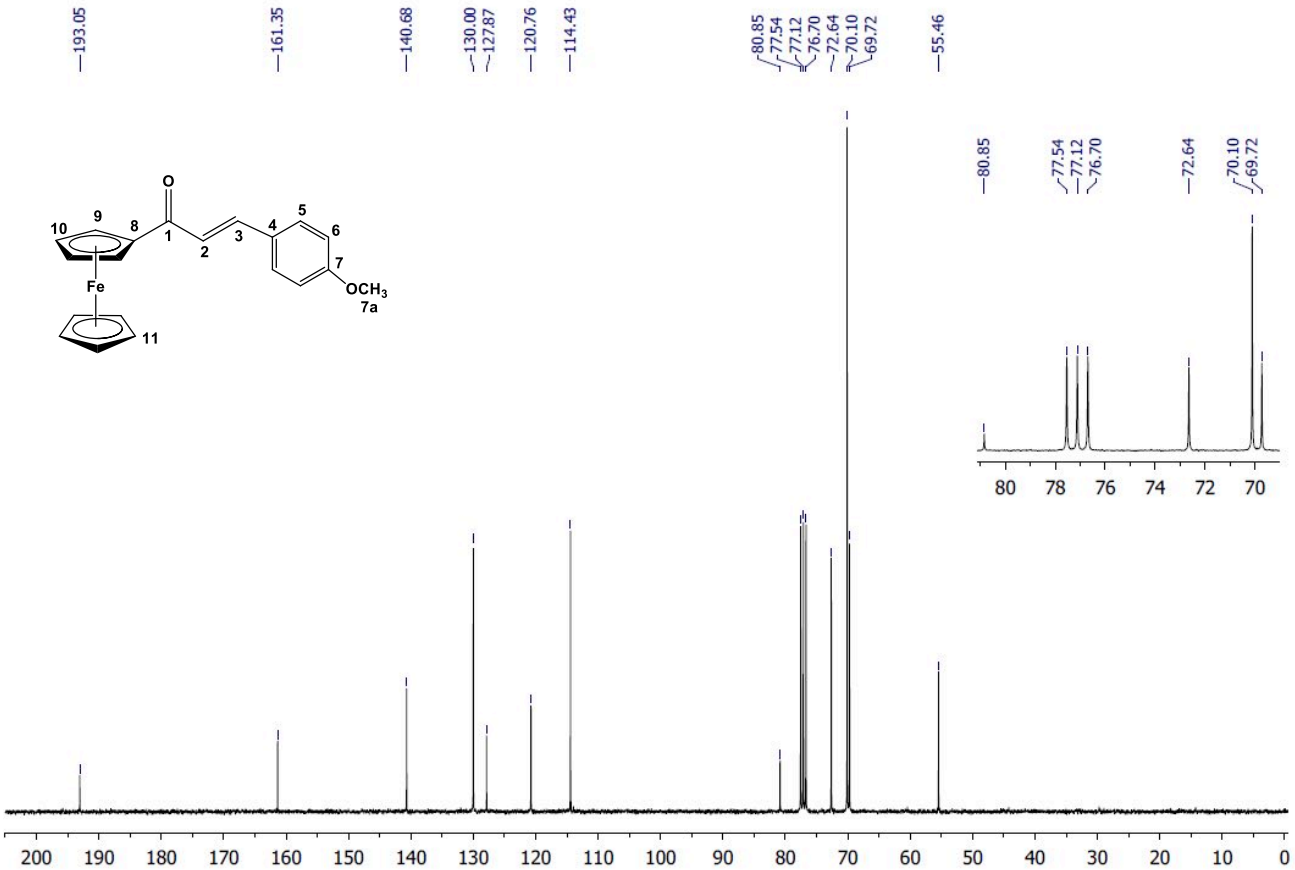
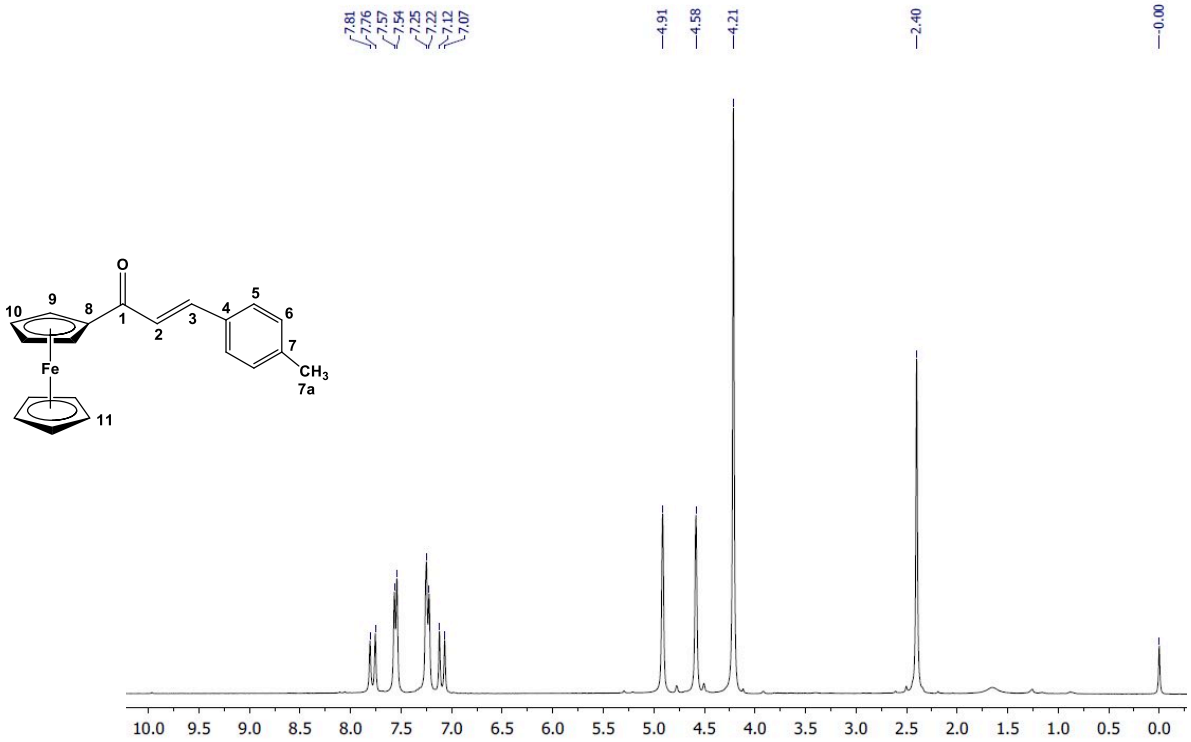


Figure S2. ^{13}**C{1H} NMR** spectrum 75 MHz ($CDCl_3$) of compound **1a**

Compound 1b



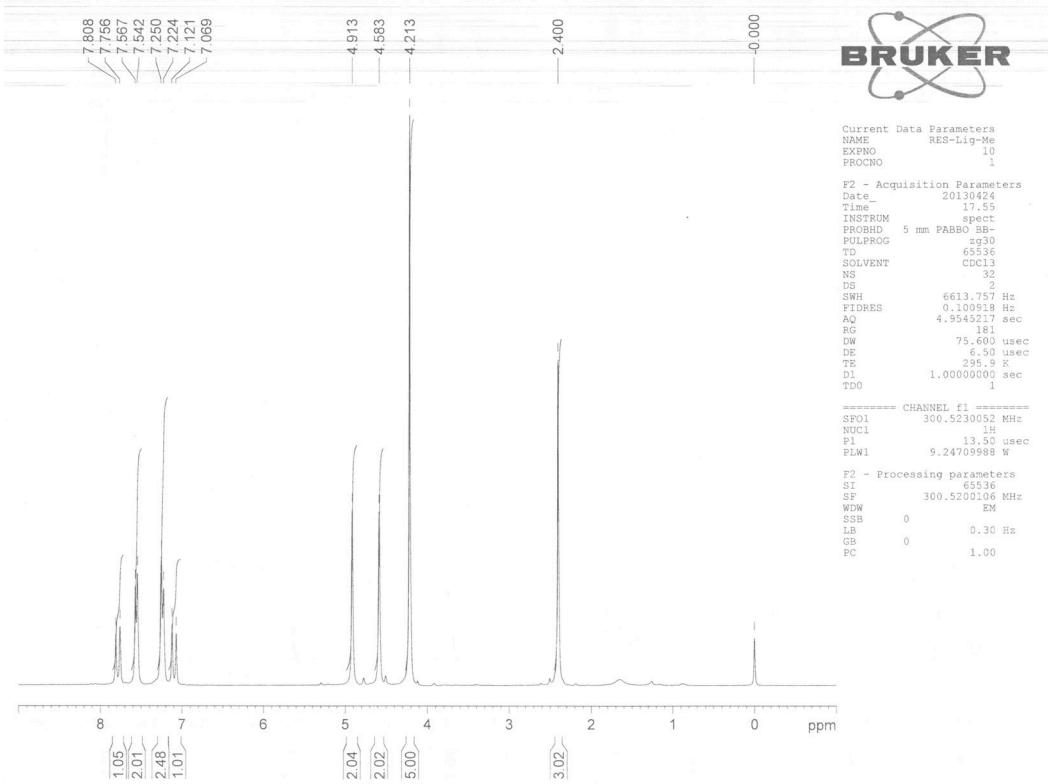


Figure S3. ^{1}H NMR spectrum 300 MHz ($CDCl_3$) of compound **1b**

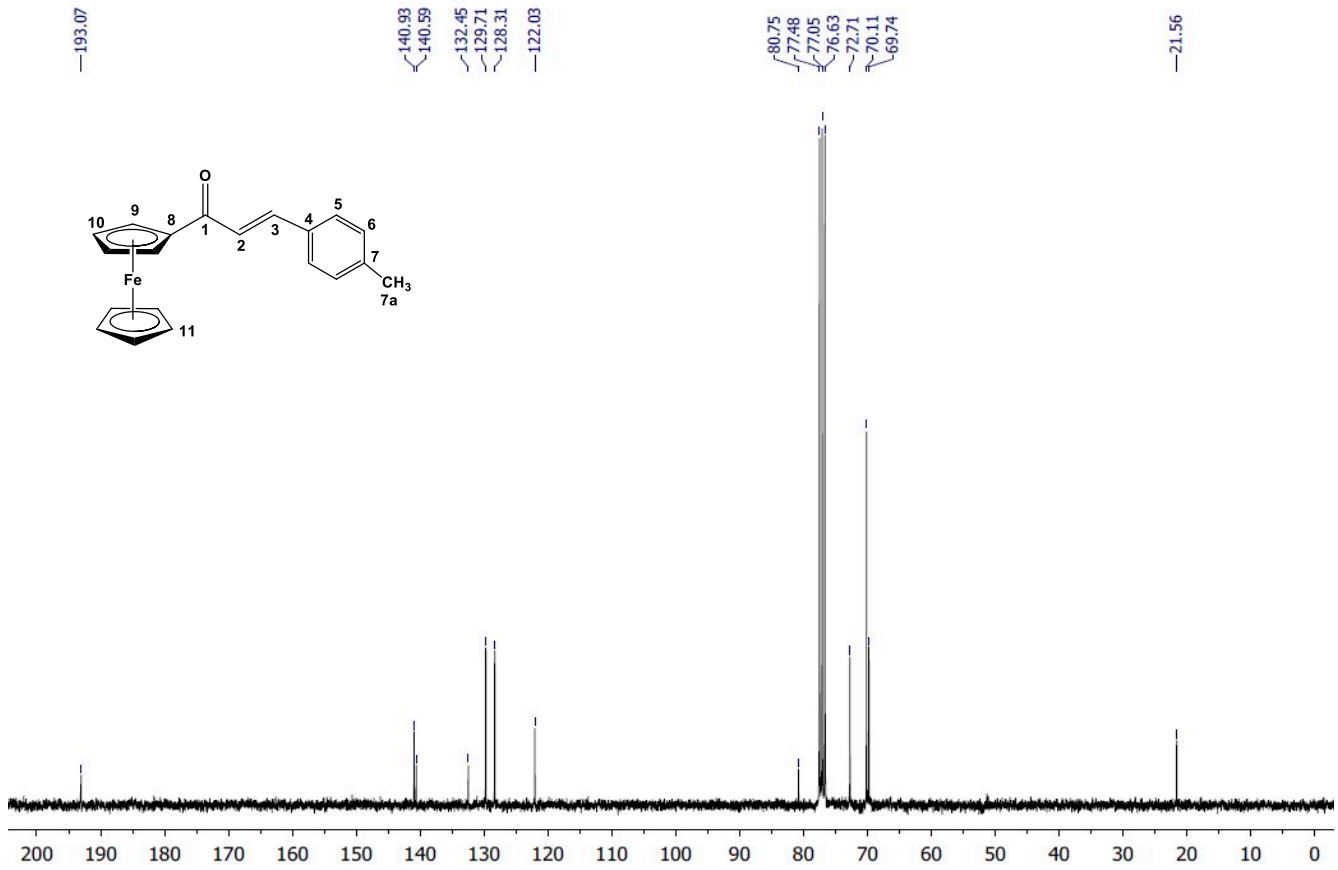


Figure S4. ^{13}**C{1H} NMR** spectrum 75 MHz ($CDCl_3$) of compound **1b**

Compound 1c

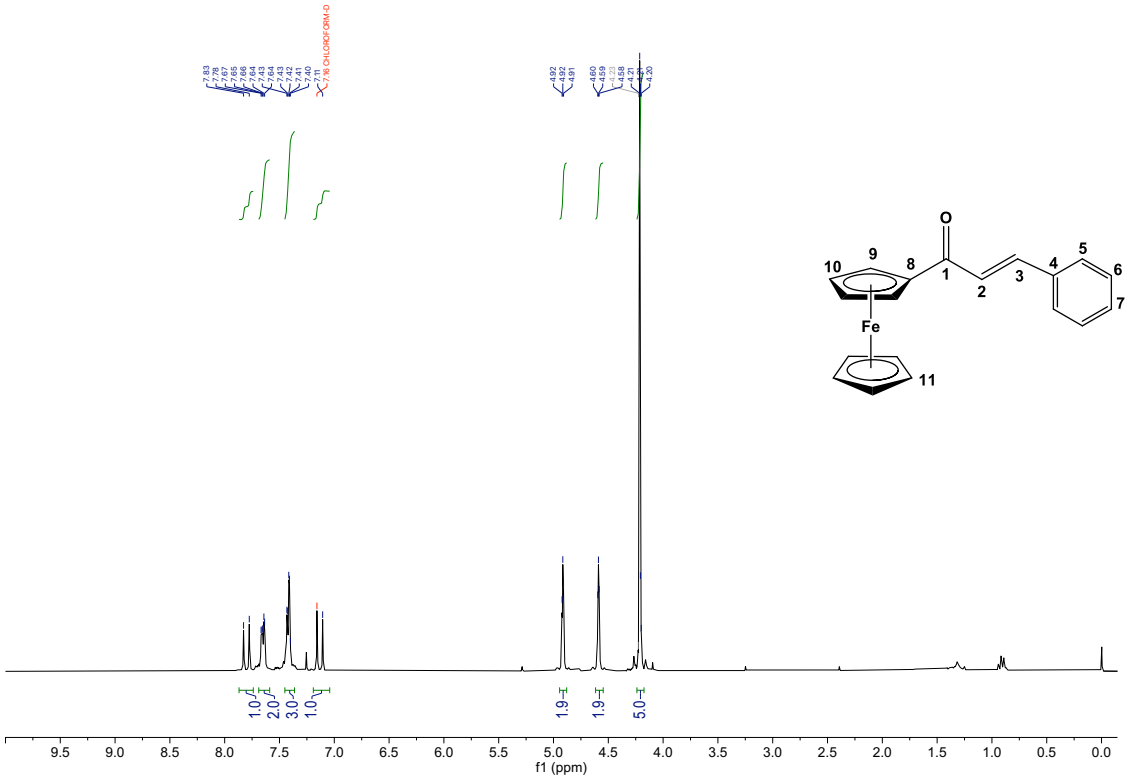


Figure S5. ^{1}H NMR spectrum 300 MHz of ($CDCl_3$) of compound **1c**

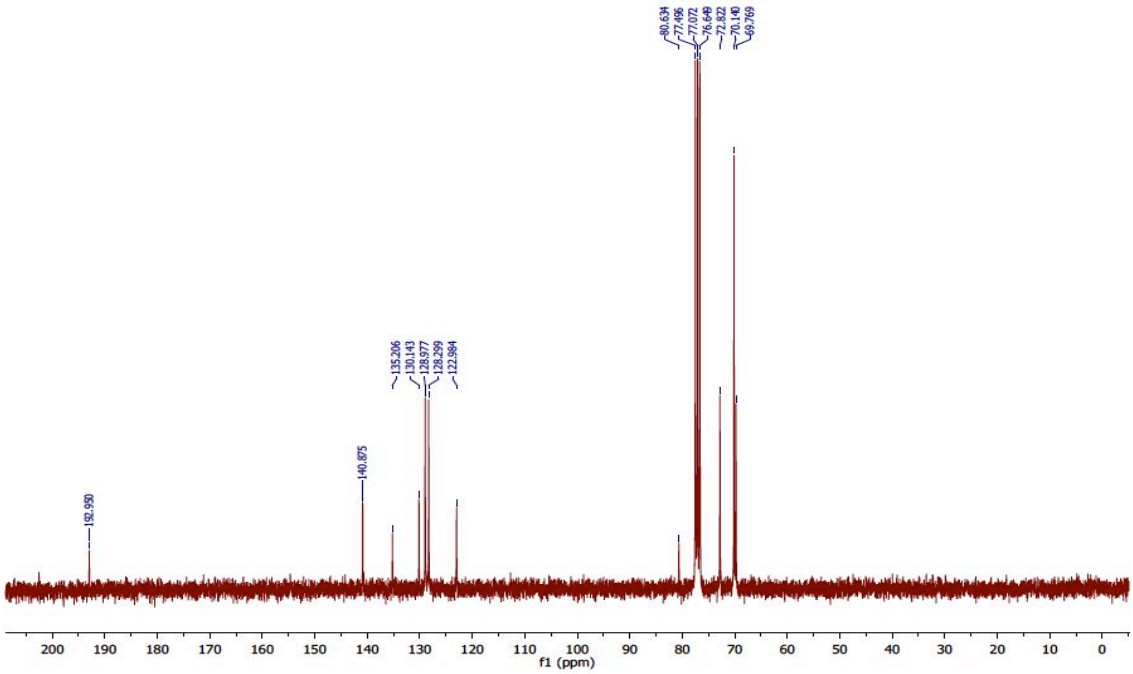


Figure S6. ^{13}C{1H} NMR spectrum 75 MHz ($CDCl_3$) of compound **1c**

Compound 1d

Figure S7. ^{1}H NMR spectrum 300 MHz of ($CDCl_3$) of compound **1d**

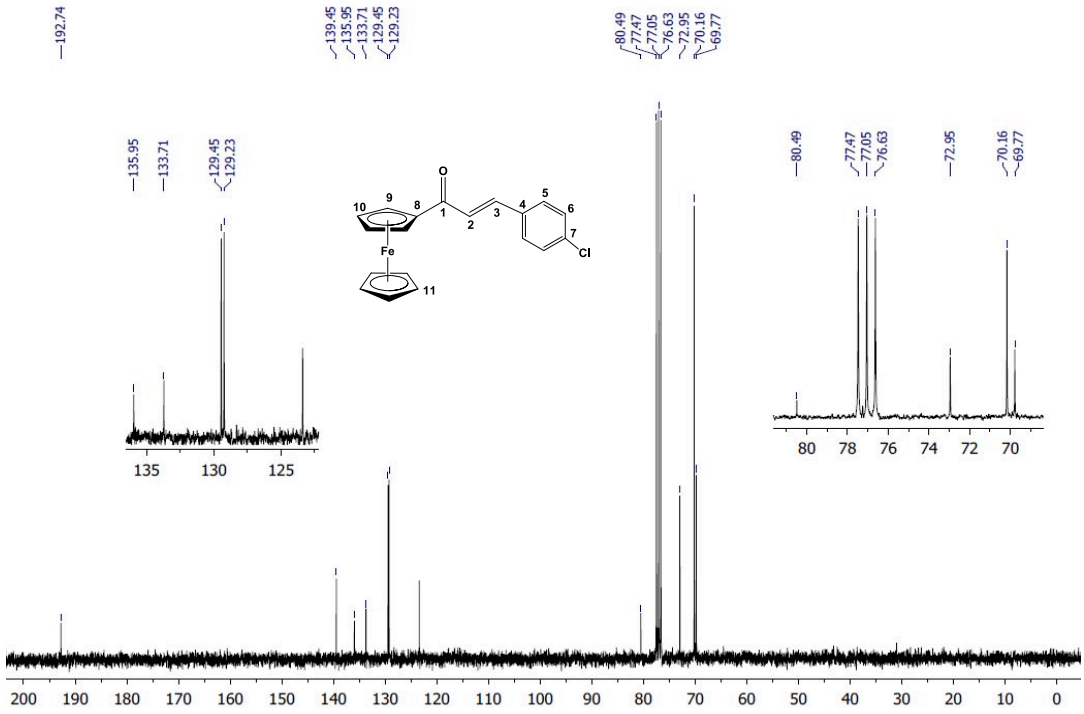
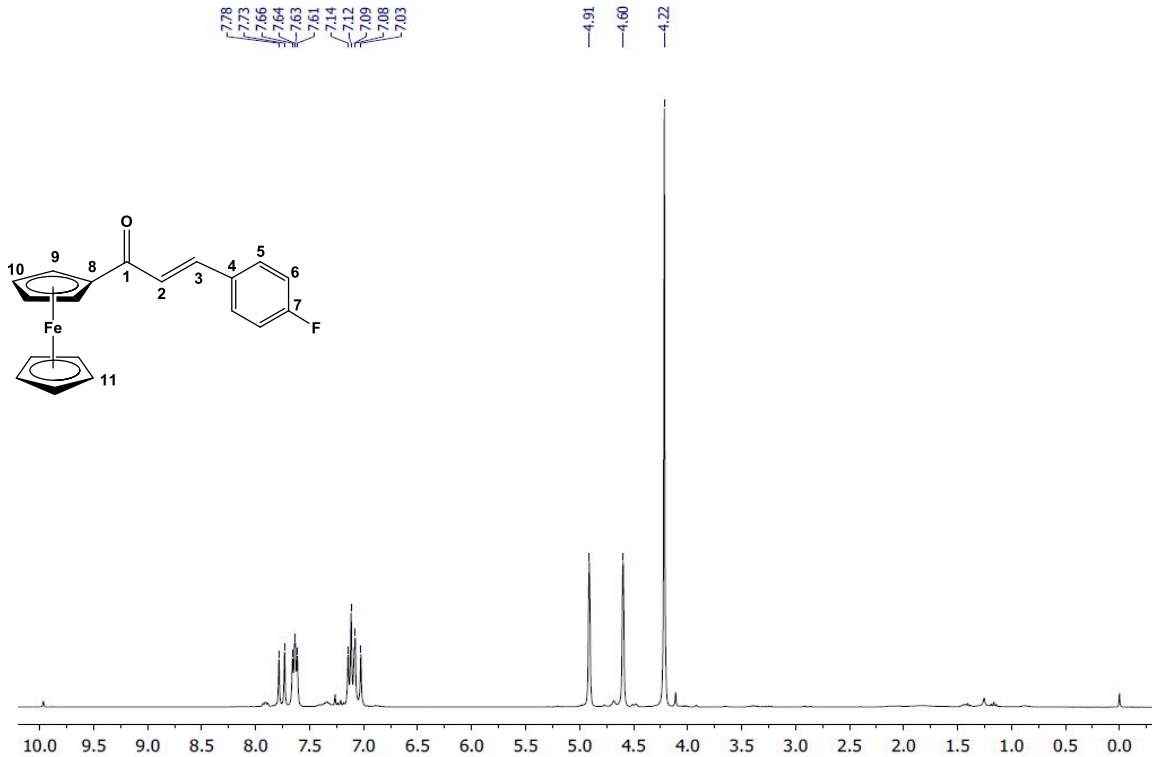


Figure S8. ^{13}C{1H} NMR spectrum 75 MHz ($CDCl_3$) of compound **1d**

Compound 1e



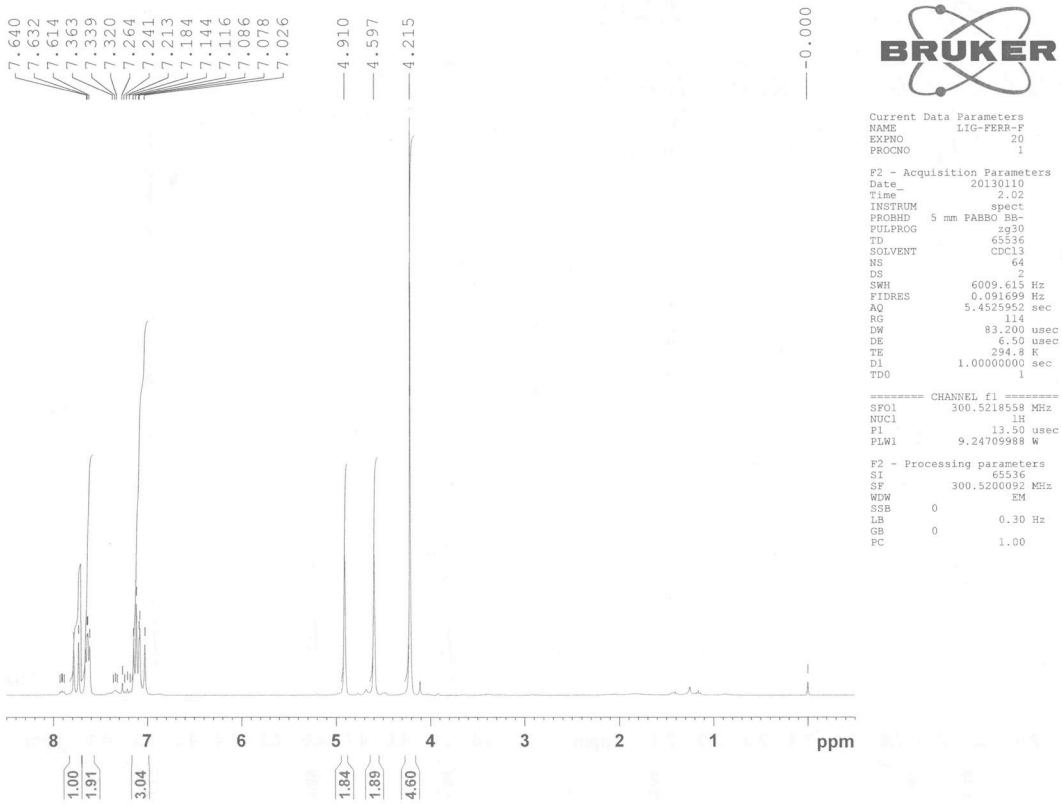


Figure S9. ^{1}H NMR spectrum 300 MHz of ($CDCl_3$) of compound **1e**

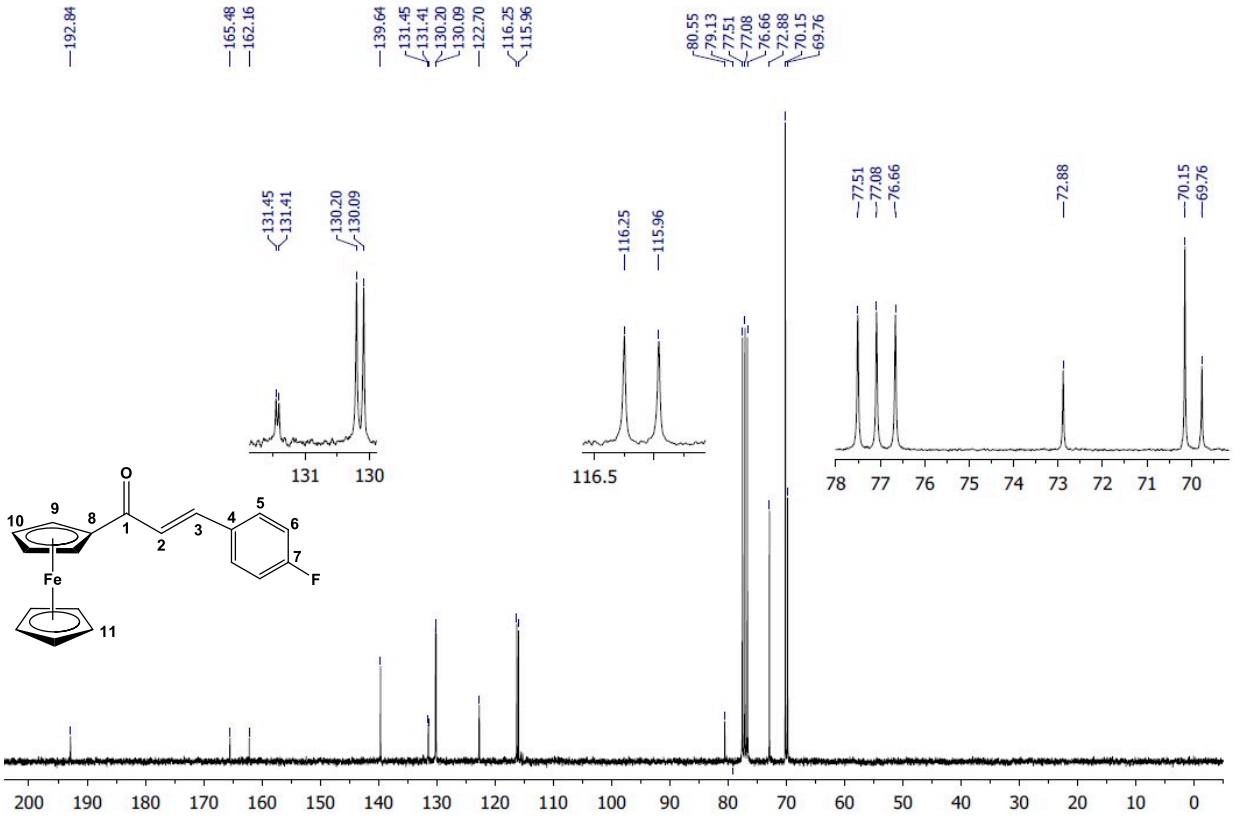


Figure S10. ^{13}C{1H} NMR spectrum 75 MHz ($CDCl_3$) of compound **1e**

Compound 1f

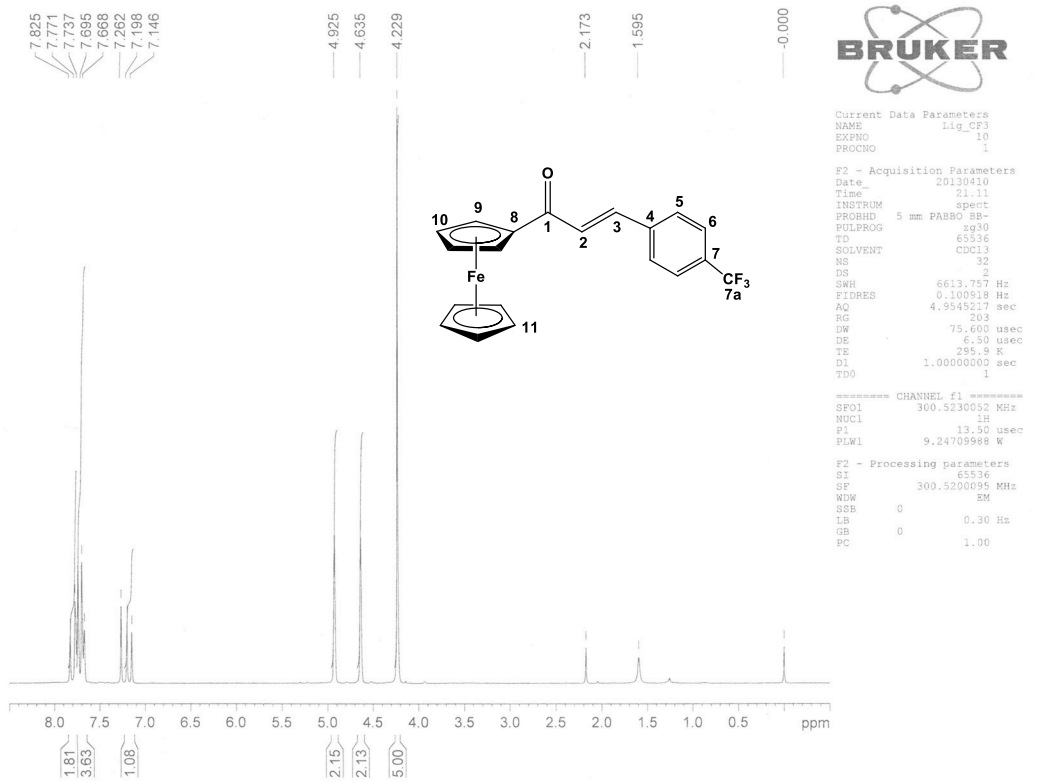


Figure S11. ^{1}H NMR spectrum 300 MHz of ($CDCl_3$) of compound **1f**

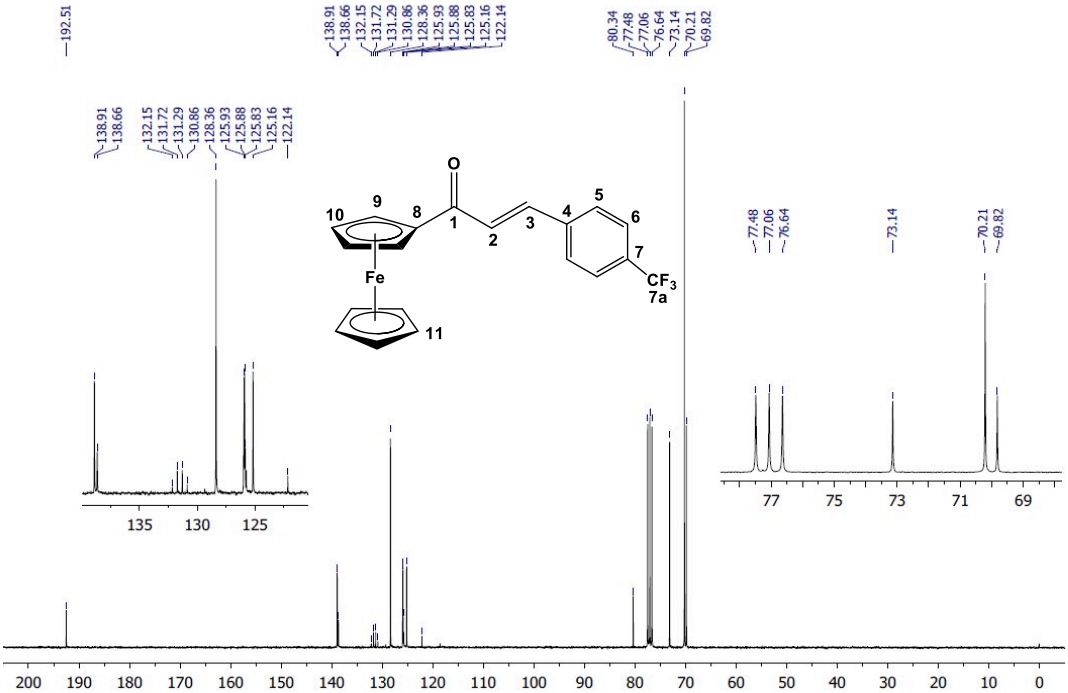
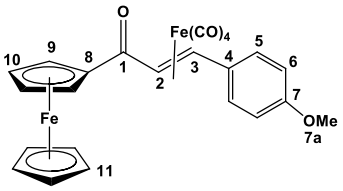


Figure S12. ^{13}C{1H} NMR spectrum 75 MHz ($CDCl_3$) of compound **1e**

3. Synthesis of 2a-f and NMR spectra

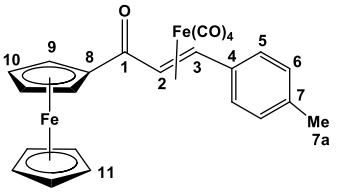
To an anhydrous ethyl ether/CH_2Cl_2 solvent mixture (20mL, ratio 1:2) were added ferrocenylchalcone (**1**) (1 eq) and $Fe_2(CO)_9$ (1.5eq). The reaction mixture was stirred for 5h at room temperature, under Argon atmosphere. After the reaction was completed, the crude product was filtered off through a Celite/Neutral Alumina/Na_2SO_4 column (length 5 cm), and the solvent was evaporated *in vacuo*. Purification by preparative Thin-Layer plate chromatography using 9/1 hexane/ethyl acetate as the mobile phase, recovering through solid/liquid extraction with CH_2CL_2 and evaporation *in vacuo*, gave the expected η^2–[ferrocenylchalcone]$Fe(CO)_4$ **2(a-f)** complexes as red crystals.

(**2a**) Tetracarbonyl[3-(4'-methoxyphenyl)-1-ferrocenyl-(2-3η)-prop-2*e*-en-1-one]iron(0)



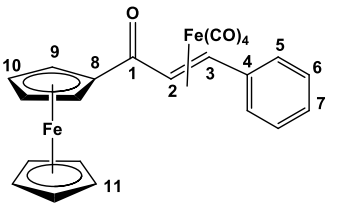
Red crystal in 95% yield, $C_{24}H_{18}Fe_2O_6$: 514 g/mol, mp 149-150 °C. **IR** (ATR, cm^{-1}): 3085, 3006 (C_{sp2}-H); 2089, 2023, 2012, 1987 (M–CO); 1647 (C=O). **^{1}H NMR** ($CDCl_3$, ppm): 3.83 (s, 3H, H-7a); 4.29 (s, 5H, H-11); 4.61 (s, 2H, H-10); 4.83 (d, J = 11.5 Hz, 1H, H-2); 4.98 (s, 2H, H-9); 5.35 (d, J = 11.5 Hz, 1H, H-3); 6.88 (d, J = 8.3 Hz, 2H, H-6) and 7.33 (d, J = 8.4 Hz, 2H, H-5). **^{13}C{1H} NMR** ($CDCl_3$, ppm): 58.0 (C-7a); 50.4 (C-3); 58.0 (C-2); 68.7 (C-10); 70.1 (C-11); 72.3 (C-9 o C-9'); 72.4 (C-9 o C-9'); 79.6 (C-8); 114.4 (C-6); 127.2 (C-5); 130.0 (C-4); 158.4 (C-7) and 207.9 (M–CO). **MS-FAB** [*m/z*, (%)]: 515 [M^++1] (16%); 486 [M^+–CO] (4%); 458 [M–2CO]$^+$ (2%); 430 [M^+–3CO] (72%); 402 [M^+–4CO] (39%); 346 [M^+–$Fe(CO)_4$] (75%); 281 [M^+–$Fe(CO)_4$–Cp] (17%). HRMS-FAB: [M – 3CO]+ Calcd for $C_{21}H_{18}Fe_2O_3$: 429.9955. Found: 429.9955, Error (ppm): -1.1.

(**2b**) Tetracarbonyl[3-(4'-methylphenyl)-1-ferrocenyl-(2-3η)-prop-2*E*-en-1-one]iron(0)



Red crystal in 99% yield, $C_{24}H_{18}Fe_2O_5$: 498 g/mol, mp 127-129 °C. **IR** (ATR, cm^{-1}): 3099 (C_{sp2}-H); 2091, 2026. 2012, 1981 (M–CO); 1646 (C=O). **^{1}H NMR** ($CDCl_3$, ppm): 2.33 (s, 3H, H-7a); 4.27 (s, 5H, H-11); 4.59 (s, 2H, H-10); 4.83 (d, 1H, *J*=12 Hz, H-2); 4.96 (s, 2H, H-9); 5.31 (d, 1H, *J*=12 Hz, H-3); 7.13 (br s, 2H, H-6) and 7.26 (br s, 2H, H-5). **^{13}C{1H} NMR** ($CDCl_3$, ppm): 21.2 (C-7a); 50.1 (C-3); 57.6 (C-2); 68.7 (C-10); 70.1 (C-11); 72.3 (C-9 o C-9'); 72.4 (C-9 o C-9'); 79.5 (C-8); 125.9 (C-5); 129.7 (C-6); 136.6 (C-7), 139.3 (C-4) and 207.7 (M–CO). **MS-FAB** [*m/z*, (%)]: 414 [M^+–3CO] (24%); 386 [M^+–4CO] (41%); 330 [M^+–$Fe(CO)_4$] (28%); 265 [M^+-$Fe(CO)_4$-Cp] (22%). HRMS-FAB [M – 3CO]+ Calcd for $C_{21}H_{18}Fe_2O_2$: 414.0001. Found: 414.0001, Error (ppm): -1.1

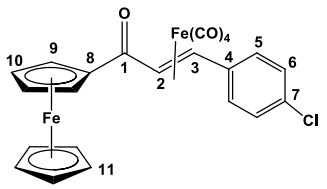
(**2c**) Tetracarbonyl[3-phenyl-1-ferrocenyl-(2-3η)-prop-2*E*-en-1-one]iron(0)



Red crystal in 92% yield, $C_{23}H_{16}Fe_2O_5$: 484 g/mol, mp 134-135 °C. **IR** (ATR, cm^{-1}): 3101 (C_{sp2}-H); 2090 ,2025 ,2010, 1980 (M–CO); 1624 (C=O). **^{1}H NMR** ($CDCl_3$, ppm): 4.28 (s, 5H, H-11); 4.60 (s, 2H, H-10); 4.83 (d, 1H, H-2, *J*=12 Hz); 4.91 (br s, 2H, H-9); 5.31 (d, 1H, H-3, *J*=12 Hz); 7.04-7.55 (m, 1H, H-5, H-6, H-7). **^{13}C{1H} NMR** ($CDCl_3$, ppm): 49.9 (C-3); 57.1 (C-2); 68.7 (C-10); 70.1 (C-11); 72.3 (C-9 o C-9'); 72.5 (C-9 o C-9'); 79.6 (C-8); 126.0 (C-5); 126.7 (C-7); 129.0 (C-6), 142.5 (C-4) and 207.5 (M–CO). **MS-FAB** [*m/z*, (%)]: 485 [M^++1] (15%); 456 [M^+–CO] (6%); 400 [M^+–3CO] (100%); 372 [M^+–4CO] (66%);

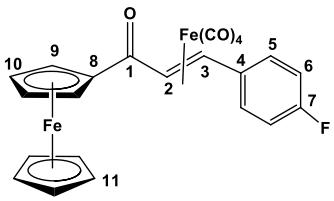
316 [M^+–$Fe(CO)_4$] (72%); 251 [M^+–$Fe(CO)_4$–Cp] (24%). HRMS-FAB [M + H]+ Calcd for $C_{23}H_{17}Fe_2O_5$: 484.9775. Found: 484.9767, Error (ppm): -1.6.

(**2d**) Tetracarbonyl[3-(4'-chlorophenyl)-1-ferrocenyl-(2-3η)-prop-2*E*-en-1-one]iron(0)



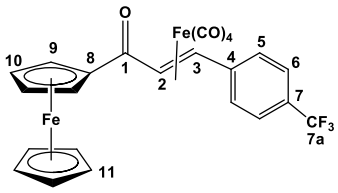
Red crystal in 96% yield, $C_{23}H_{15}ClFe_2O_5$: 517.5 g/mol, mp 152-153 °C. **IR** (ATR, cm^{-1}): 3087 (C_{sp2}-H); 2088, 2028, 2007, 1996 (M–CO); 1650 (C=O). **^{1}H NMR** ($CDCl_3$, ppm): 4.27 (s, 5H, H-11); 4.61 (s, 2H, H-10); 4.74 (d, 1H, *J*=11.4Hz, H-2); 4.96 (d, 2H, H-9); 5.22 (d, 1H, *J*=11.2Hz, H-3) and 7.28 (br s, 4H, H-5 and H-6). **^{13}C{1H} NMR** ($CDCl_3$, ppm): 49.7 (C-3); 55.4 (C-2); 68.7 (C-10); 70.1 (C-11); 72.4 (C-9 o C-9'); 72.5 (C-9 o C-9'); 79.3 (C-8); 127.1 (C-6); 129.2 (C-5); 132.0 (C-7), 141.3 (C-4) and 207.2 (M–CO). **MS-FAB** [*m/z*, (%)]: 434 [M^+–3CO] (3%); 406 [M^+–4CO] (5%); 350 [M^+–$Fe(CO)_4$] (87%); 285 [M^+–$Fe(CO)_4$–Cp] (10%). HRMS-FAB [M – 3CO]$^+$ Calcd for $C_{20}H_{15}ClFe_2O_2$: 433.9459. Found: 433.9471, Error (ppm): +2.7.

(**2e**) Tetracarbonyl[3-(4'-fluorophenyl)-1-ferrocenyl-(2-3η)-prop-2*E*-en-1-one]iron(0)



Red crystal in 97% yield, $C_{23}H_{15}FFe_2O_5$: 502 g/mol, mp 151-152 °C. **IR** (ATR, cm^{-1}): 3090, 3041 (C_{sp2}-H); 2089, 1999, 1979, 1954 (M–CO); 1600 (C=O). **^{1}H NMR** ($CDCl_3$, ppm): 4.27 (s, 5H, H-11); 4.62 (s, 2H, H-10); 4.75 (d, 1H, *J*=10.8Hz, H-2); 4.96 (s, 2H, H-9); 5.23 (d, 1H, *J*=10.8 Hz, H-3); 7.45 (s, 2H, H-6) and 7.56 (s, 2H, H-5). **^{13}C{1H} NMR** ($CDCl_3$, ppm): 50.2 (C-3); 56.0 (C-2); 68.7 (C-10 or C-10'); 69.8 (C-10 or C-10'); 70.1 (C-11); 72.4 (C-9 or C-9'); 72.5 (C-9 or C-9'); 116.0 (d, C-6, $J_{C\text{-}F}$=21.75Hz); 127.4 (d, C-5, $J_{C\text{-}F}$=8.25Hz); 128.3 (C-4), 161.4 (d, C-7, $J_{C\text{-}F}$=244.5Hz) and 207.4 (M–CO). **MS-FAB** [*m/z*, (%)]: 503 [M^++1] (9%); 474 [M^+–CO] (2%); 418 [M^+–3CO] (96%); 390 [M^+–4CO] (97%); 334 [M^+–$Fe(CO)_4$] (100%). HRMS-FAB [M + H]$^+$ Calcd for $C_{23}H_{16}FFe_2O_5$: 502.9681. Found: 502.9685, Error (ppm): +0.9.

(**2f**) Tetracarbonyl[3-(4'-trifluoromethylphenyl)-1-ferrocenyl-(2-3η)-prop-2*E*-en-1-one]iron(0)



Red crystal in 98% yield, $C_{24}H_{15}F_3Fe_2O_5$: 552 g/mol, mp 144-146 °C. **IR** (ATR, cm^{-1}): 3085 (C_{sp2}-H); 2091, 2033, 2012, 1989 (M–CO); 1617 (C=O). **^{1}H NMR** ($CDCl_3$, ppm): 4.27 (s, 5H, H-11); 4.62 (s, 2H, H-10); 4.75 (d, 1H, *J*=11.1Hz, H-2); 4.97 (s, 2H, H-9); 5.22 (d, 1H, J=11.1Hz, H-3); 7.44 (d, 2H, H-6, *J*=7.2Hz) and 7.57 (d, 2H, H-5, J=7.2Hz). **^{13}C{1H} NMR** ($CDCl_3$, ppm): 49.3 (C-3); 54.3 (C-2); 68.8 (C-10 or C-10'); 69.8 (C-10 or C-10'); 70.1 (C-11); 72.5 (C-9 or C-9'); 72.6 (C-9 or C-9'); 79.2 (C-8); 122.3 (C-6, $J_{C\text{-}F}$=3.8Hz); 128.1 (C-7, $J_{C\text{-}F}$=32.3Hz); 127.0 (C-5), 147.0 (C-4) and 206.8 (M–CO). **MS-FAB** [*m/z*, (%)]: 553 [M^++1] (6%); 524 [M^+–CO] (4%); 468 [M^+–3CO] (73%); 440 [M^+–4CO] (100%); 384 [M^+–$Fe(CO)_4$] (72%). **HRMS-FAB** [M + H]$^+$ Calcd for $C_{24}H_{16}F_3Fe_2O_5$: 552.9649 Found: 552.9649, Error (ppm): +0.1.

Table S1. IR Data (cm^{-1}) for [η^2-(ferrocenylchalcone)]$Fe(CO)_4$ complexes acquired in solution of *n*-hexane

Entry	Product	R	ν(CO)			
1	2a	OMe	2092	2029	2015	1989
2	2b	Me	2093	2030	2016	1991
3	2c	H	2094	2032	2018	1992
4	2d	Cl	2095	2034	2019	1995
5	2e	F	2095	2036	2020	1993
6	2f	CF_3	2097	2037	2021	1998

Compound 2a

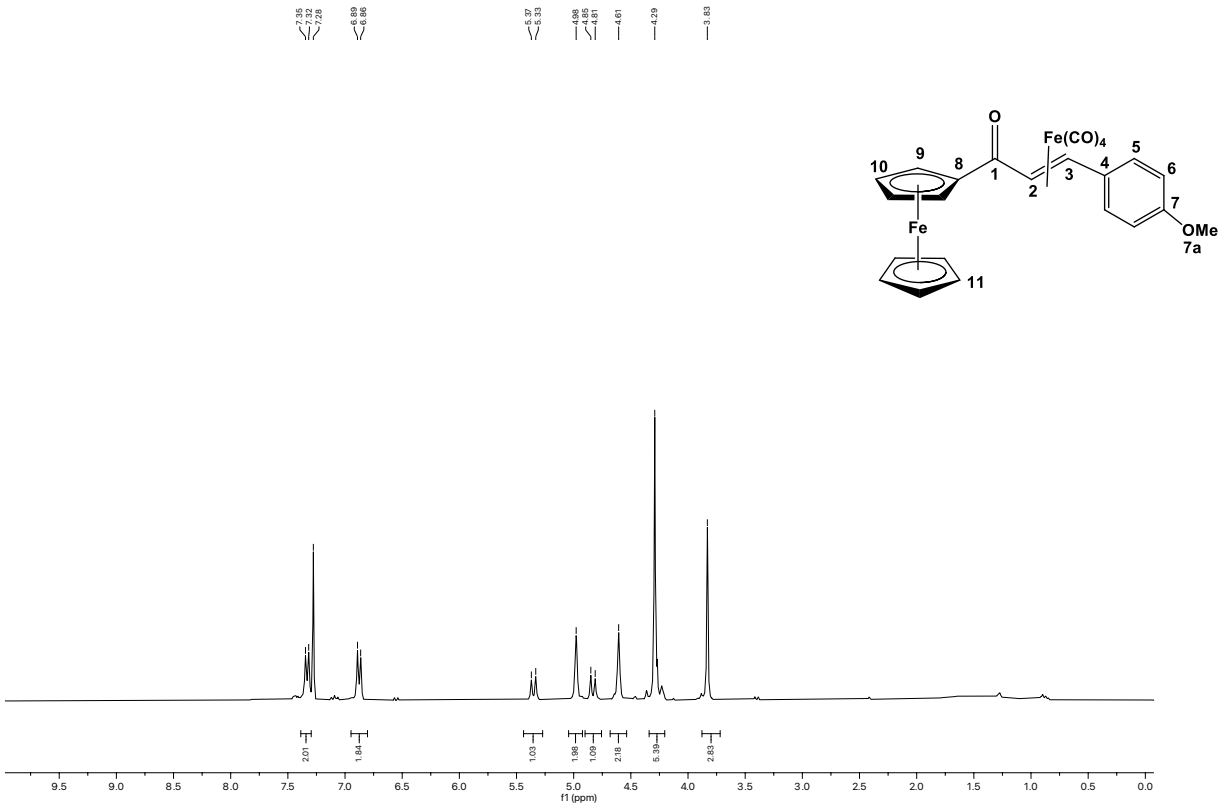


Figure S13. ^{1}H NMR spectrum 300 MHz of ($CDCl_3$) of compound **2a**

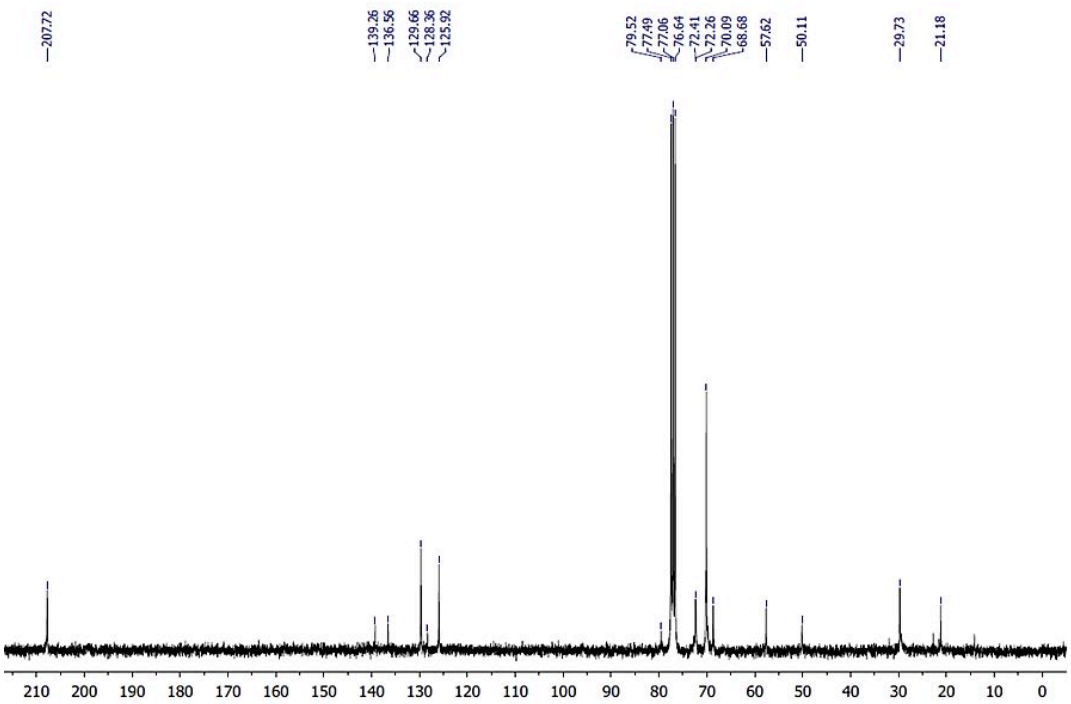


Figure S14. ^{13}C{1H} NMR spectrum 75 MHz of ($CDCl_3$) of compound **2a**

Compound 2b

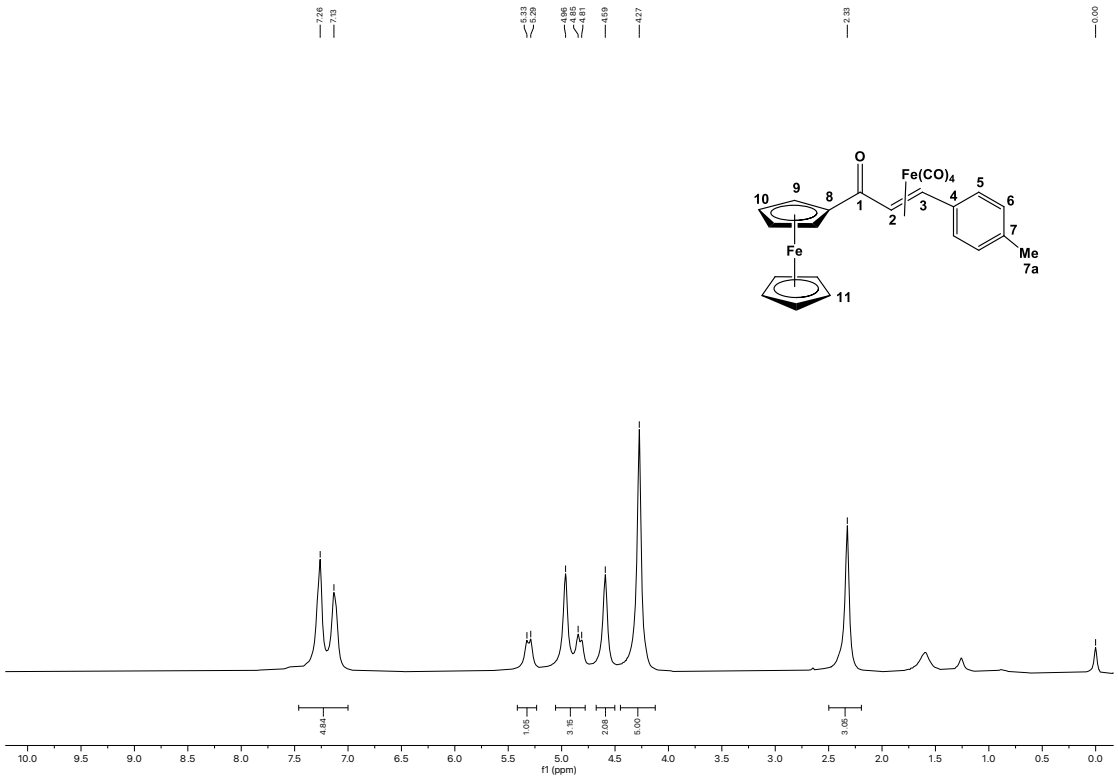


Figure S15. ^{1}H NMR spectrum 300 MHz of ($CDCl_3$) of compound **2b**

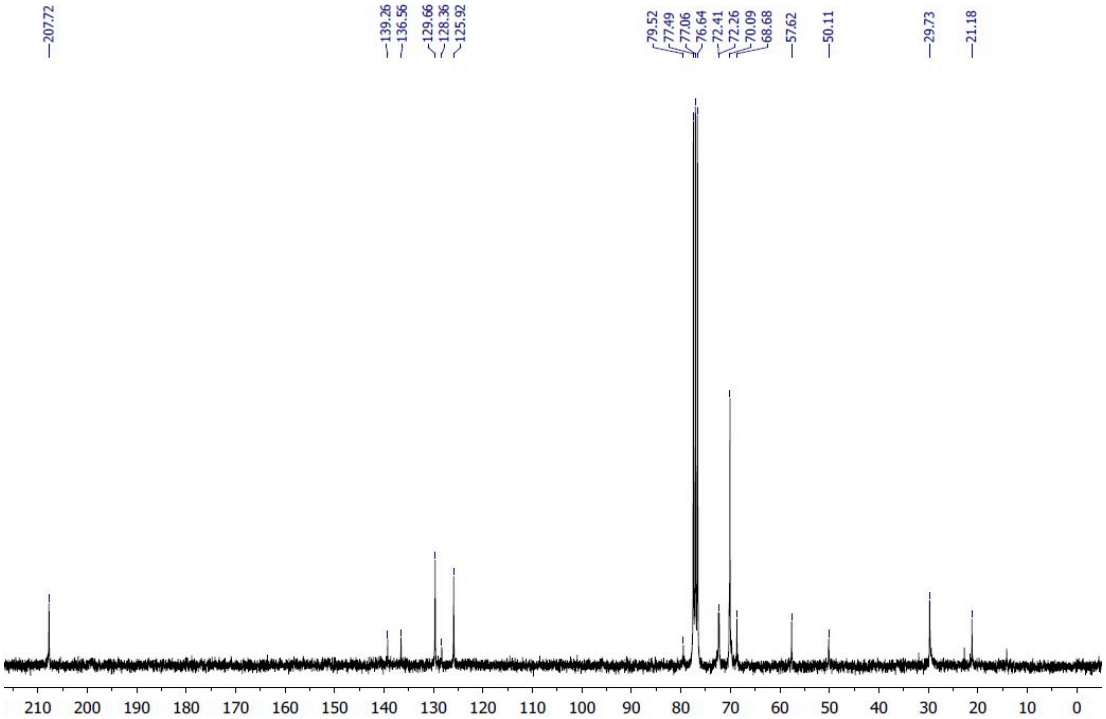


Figure S16. ^{13}C{1H} NMR spectrum 75 MHz ($CDCl_3$) of compound **2b**

Compound 2c

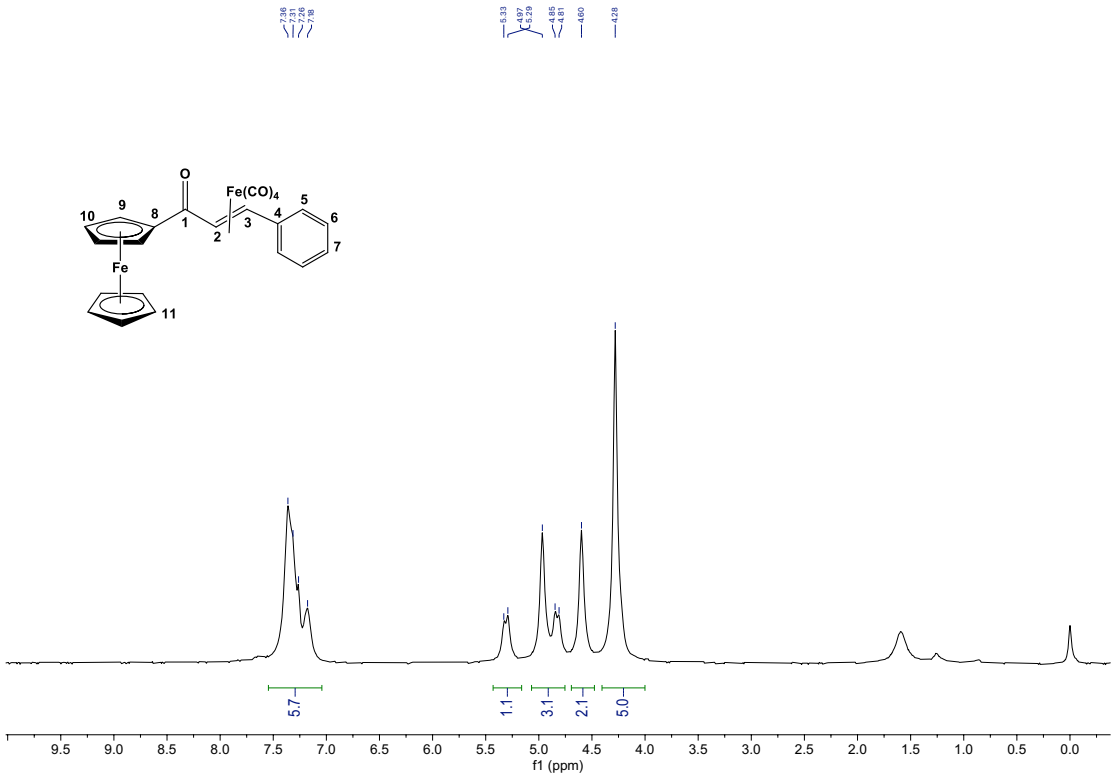


Figure S17. ^{1}H NMR spectrum 300 MHz of ($CDCl_3$) of compound **2c**

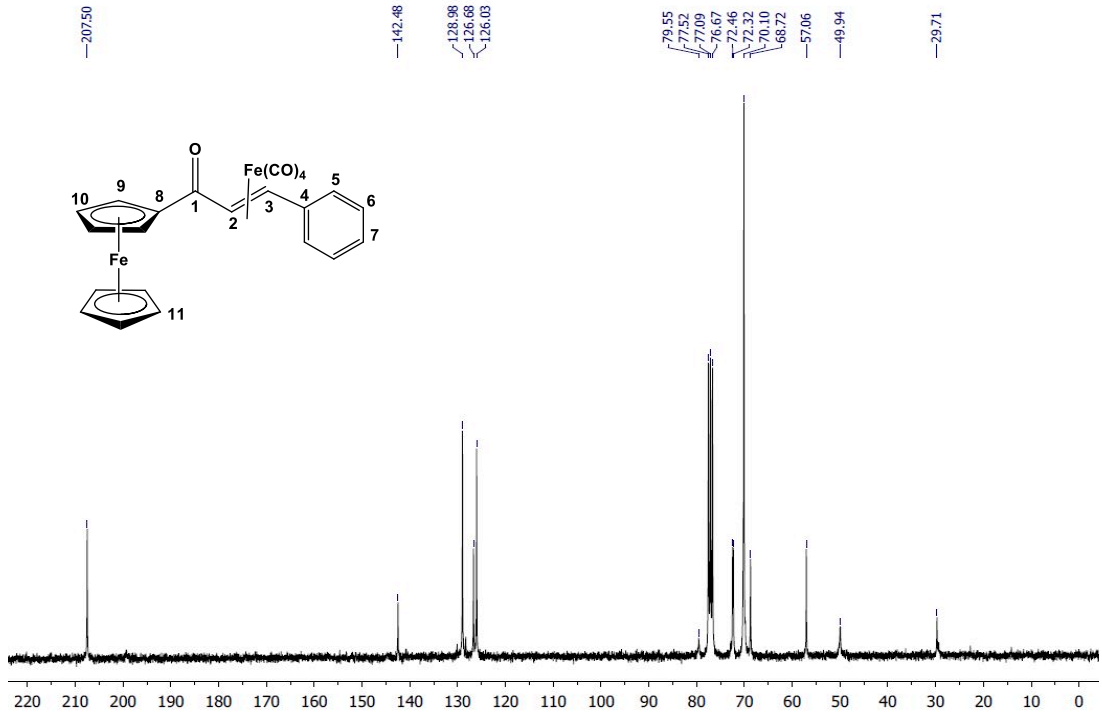


Figure S18. ^{13}C{1H} NMR spectrum 75 MHz ($CDCl_3$) of compound **2c**

Compound 2d

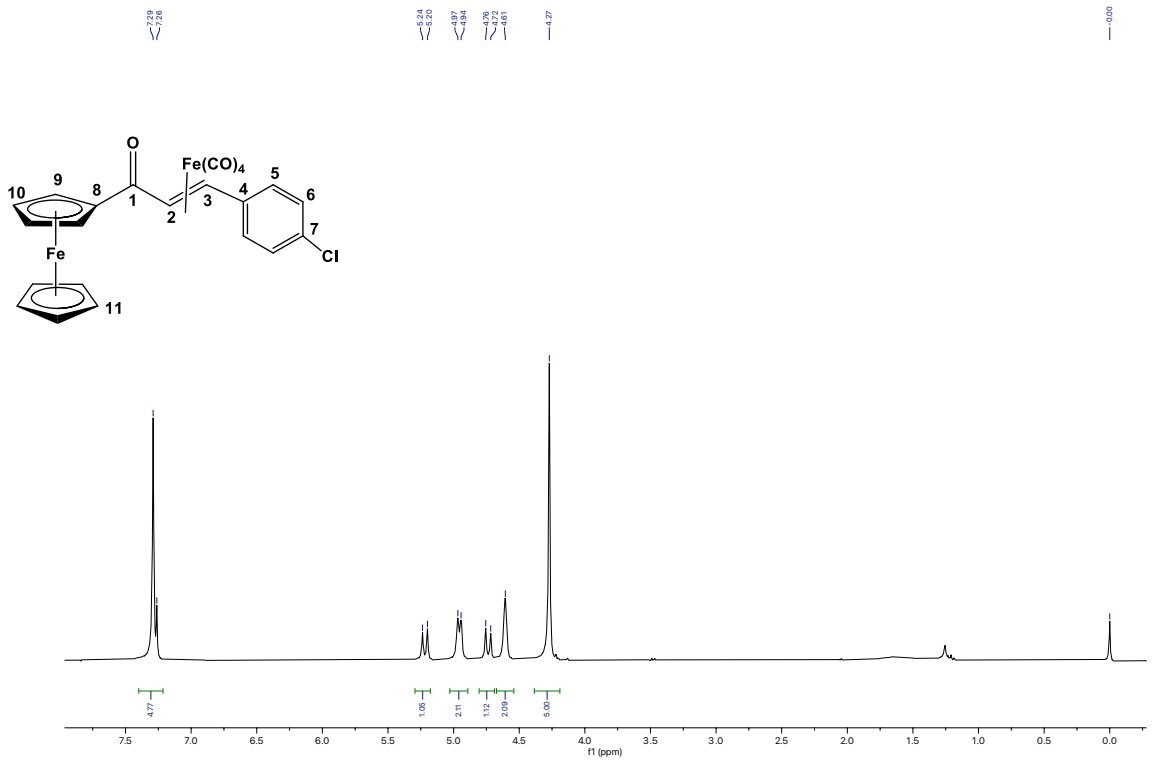


Figure S19. ^{1}H NMR spectrum 300 MHz of ($CDCl_3$) of compound **2d**

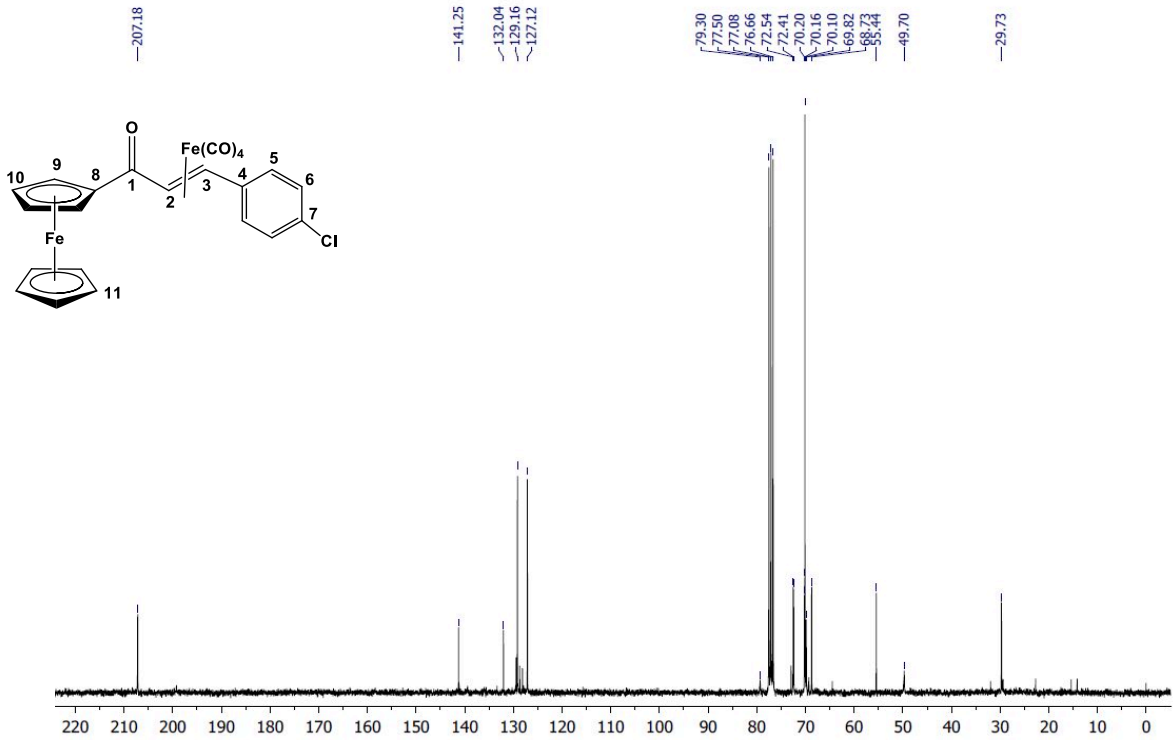


Figure S20. ^{13}C{1H} NMR spectrum 75 MHz of ($CDCl_3$) of compound **2d**

Compound 2e

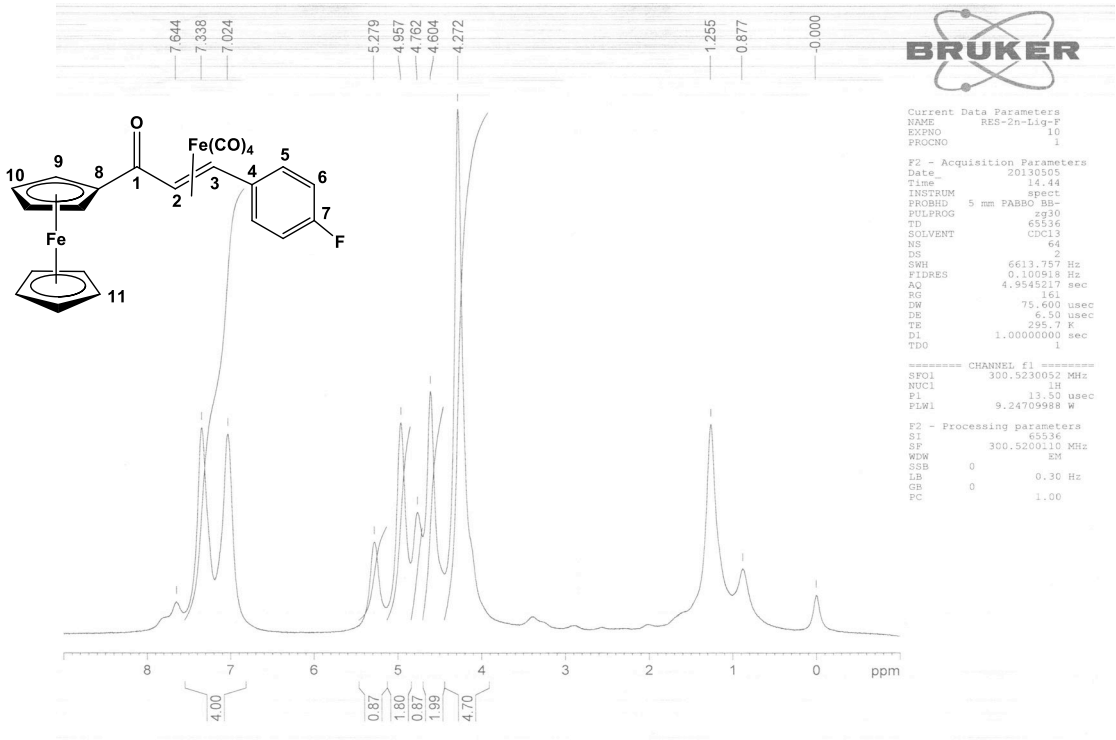


Figure S21. ^{1}H NMR spectrum 300 MHz of ($CDCl_3$) of compound **2e**

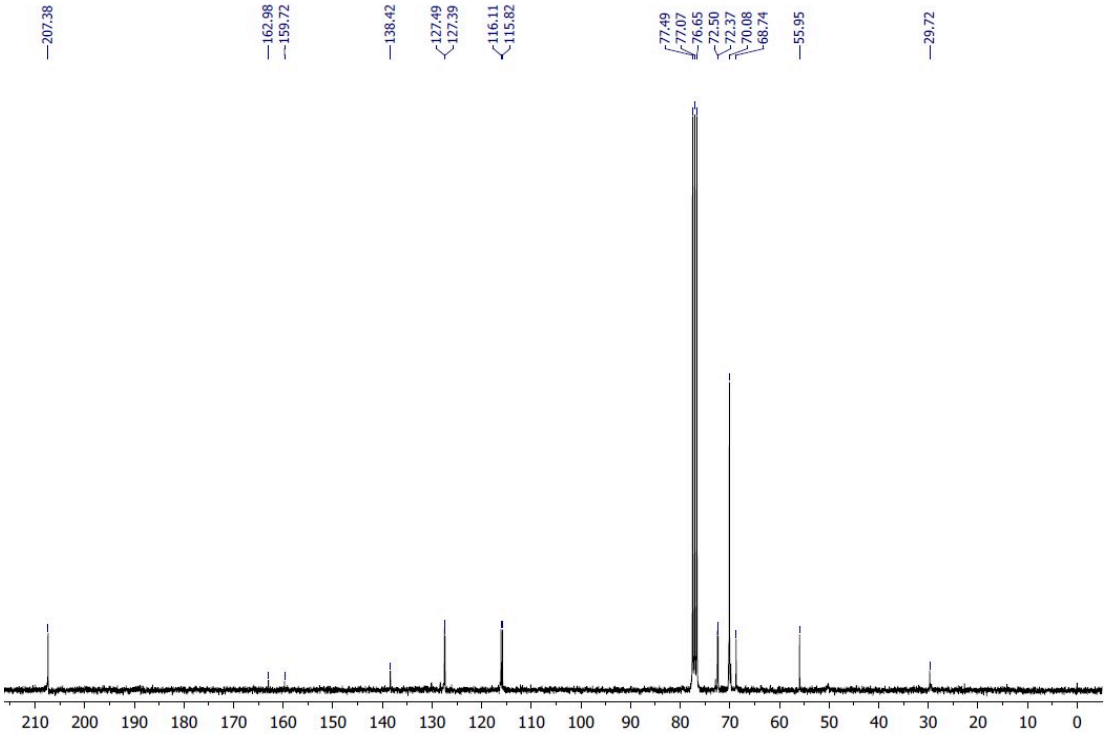


Figure S22. ^{13}C{1H} NMR spectrum 75 MHz of ($CDCl_3$) of compound **2e**

Compound 2f

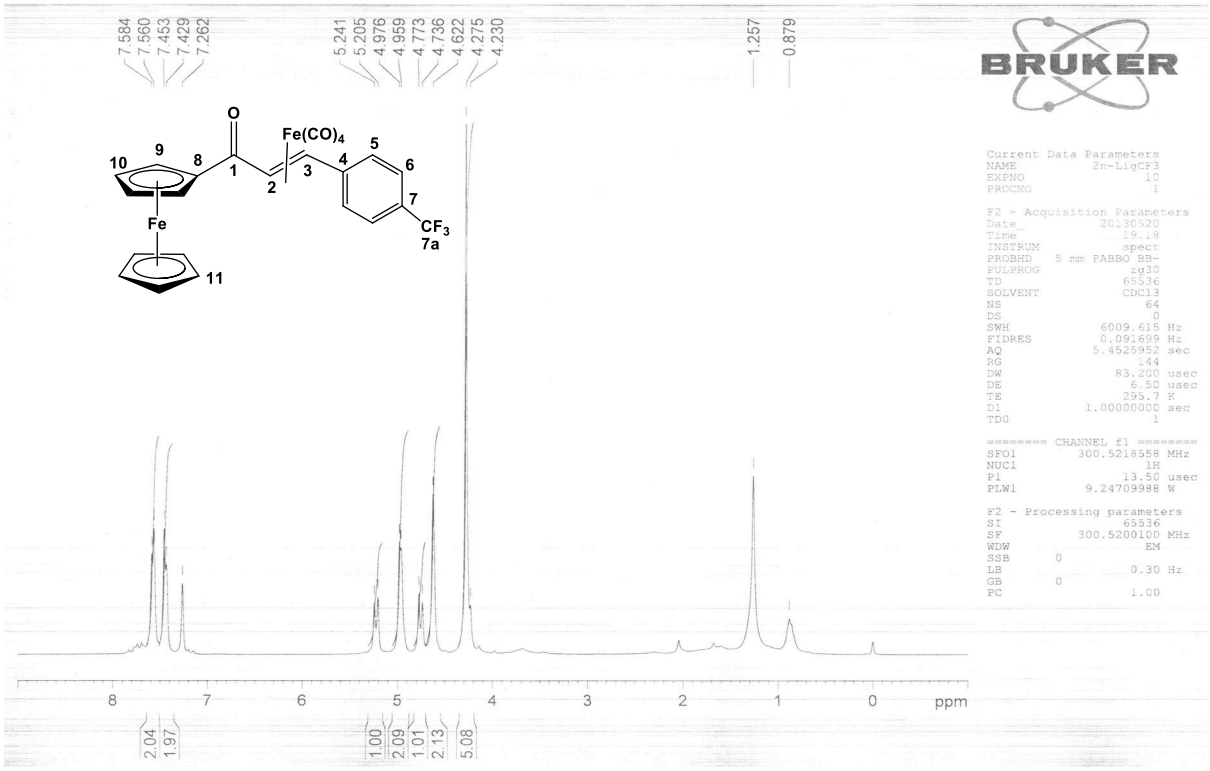


Figure S23. ^{1}H NMR spectrum 300 MHz of ($CDCl_3$) of compound **2f**

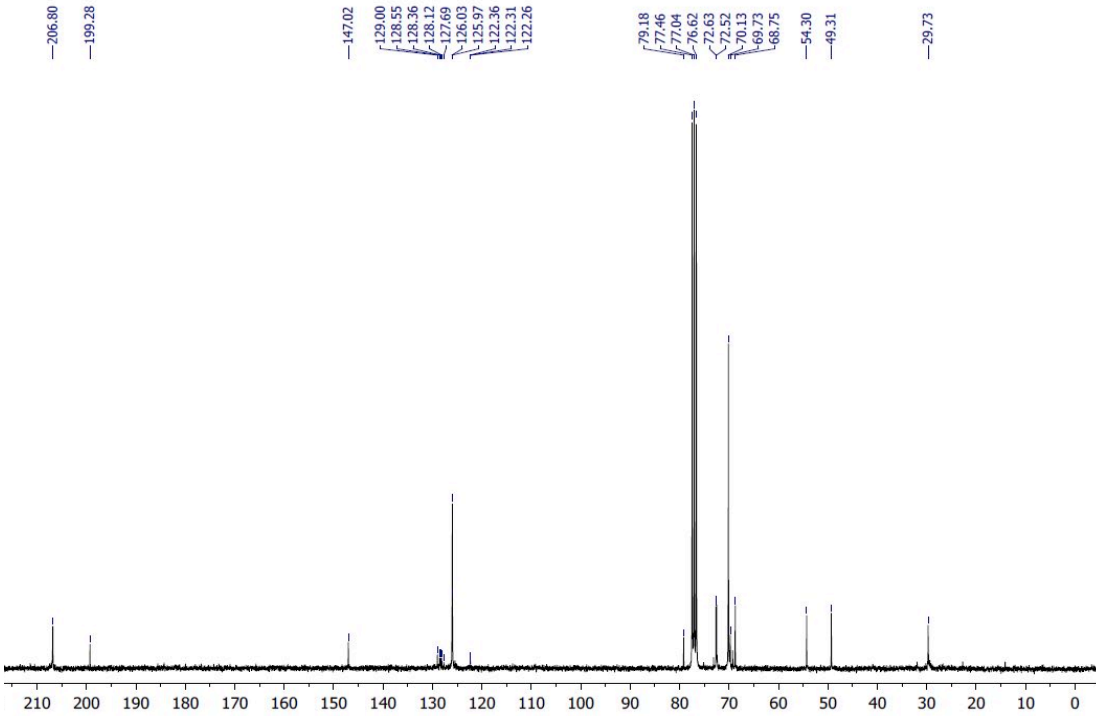
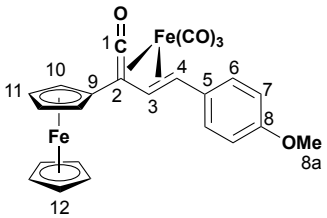


Figure S24. ^{13}C{1H} NMR spectrum 75 MHz of ($CDCl_3$) of compound **2f**

4. Synthesis of 3a-f and NMR spectra

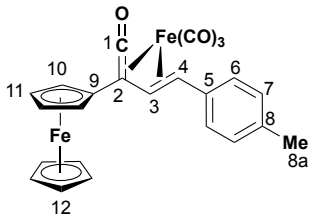
To a solution of **2** (1eq) in anhydrous CH_2Cl_2 at -78°C under Ar atmosphere was added MeLi (1.1eq, 1.6 M). After stirring at -78 °C for one hour, the Argon atmosphere was interchanged with a balloon of CO. The mixture was stirred and warmed slowly to room temperature until 4h had elapsed. The reaction mixture was passed through a Celite/Neutral Alumina/Na_2SO_4 column, and the solvent was evaporated under vacuum. Chromatography by silica gel column (9/1 hexane/CH_2Cl_2) of the resulting crude product led to the isolation of η^4-[ferrocenyl ketene]$Fe(CO)_3$ complexes as red crystals.

(**3a**) Tricarbonyl[4-(4'-methoxyphenyl)-2-ferrocenyl-1-oxo-(1-4η)-but-1,3*E*-dienyl]iron(0)



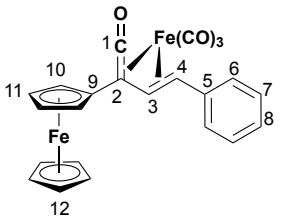
Red crystal in 59% yield, $C_{24}H_{18}Fe_2O_5$: 498 g/mol, mp 113-114 °C. **IR** (ATR, cm^{-1}): 3011, 2971 (C_{sp2}-H); 2047, 1987, 1968 (M-CO); 1735 (C=C=O). **^{1}H NMR** ($CDCl_3$, ppm): 3.50 (d, 1H, *J*=9.3Hz, H-4); 3.83 (s, 3H, H-8a); 4.24 (s, 5H, H-12); 4.33 (m, 2H, H-11); 4.42 (s, 1H, H-10 o H-10'); 4.62 (s, 1H, H-10 o H-10'); 6.53 (d, 1H, *J*=9.3Hz, H-3); 6.91 (d, 2H, *J*=8.4Hz, H-7) and 7.40 (d, 2H, *J*=8.4Hz, H-6). **^{13}C{1H} NMR** ($CDCl_3$, ppm): 53.5 (C-2); 55.4 (C-8a); 61.1 (C-4); 65.4 (C-11 o C-11'); 69.2 (C-11 o C-11'); 69.8 (C-12); 69.9 (C-10 o C-10'); 70.3 (C-11 o C-11'); 76.1 (C-9); 90.2 (C-3); 114.8 (C-7); 128.0 (C-6); 130.2 (C-5); 159.3 (C-8) and 234.5 (C-1). **MS-FAB** [*m/z*, (%)]: 498 [M^+] (3%); 470 [M^+–CO] (3%); 442 [M^+–2CO] (1%); 414 [M^+–3CO] (12%); 386 [M^+–4CO] (8%). HRMS-FAB [M^+] Calcd for $C_{24}H_{18}Fe_2O_5$: 497.9853. Found: 497.9840, Error (ppm): -2.6.

(**3b**) Tricarbonyl[4-(4'-methylphenyl)-2-ferrocenyl-1-oxo-(1-4η)-but-1,3*E*-dienyl]iron(0)



Red crystal in 66% yield, $C_{24}H_{18}Fe_2O_4$: 482 g/mol, mp 97-99 °C. **IR** (ATR, cm^{-1}): 3089, 3027 (C_{sp2}-H); 2050, 1989, 1971 (M–CO); 1737 (C=C=O). **^{1}H NMR** ($CDCl_3$, ppm): 2.34 (s, 3H, H-8a); 3.44 (d, 1H, *J*=9.3Hz, H-4); 4.24 (s, 5H, H-12); 4.34 (d, 2H, H-11); 4.43 (s, 1H, H-10 or H-10'); 4.63 (s, 1H, H-10 or H-10'); 6.58 (d, 1H, *J*=9.3Hz, H-3); 7.17 (d, 2H, *J*=7.8Hz, H-7) and 7.34 (d, 2H, *J*=7.8Hz, H-6). **^{13}C{1H} NMR** ($CDCl_3$, ppm): 21.3 (C-8a); 53.7 (C-2); 60.3 (C-4); 65.5 (C-11 or C-11'); 69.2 (C-11 or C-11'); 69.8 (C-12); 70.0 (C-10 or C-10'); 70.4 (C-10 or C-10'); 76.0 (C-9); 90.7 (C-3); 127.0 (C-7); 130.0 (C-6); 135.2 (C-5); 137.7 (C-8) and 234.3 (C-1). **MS-FAB** [*m/z*, (%)]: 482 (35%) [M^+]; 454 (32%) [M^+–CO]; 426 (6%) [M^+–2CO]; 398 (100%) [M^+–3CO]; 370 (66%) [M^+–4CO]; 314 (11%) [M^+–$Fe(CO)_4$]. HRMS-FAB [M]$^+$ Calcd for $C_{24}H_{18}Fe_2O_4$: 481.9904. Found: 481.9904, Error (ppm): +1.9.

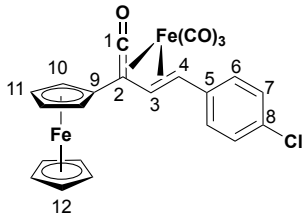
(**3c**) Tricarbonyl[4-phenyl-2-ferrocenyl-1-oxo-(1-4η)-but-1,3*E*-dienyl]iron(0)



Red crystal in 78% yield, $C_{23}H_{16}Fe_2O_4$: 468 g/mol, mp 109-110 °C. **IR** (ATR, cm^{-1}): 3087, 2918 (C_{sp2}-H); 2051, 1992, 1969 (M-CO); 1737(C=C=O). **^{1}H NMR** ($CDCl_3$, ppm): 3.32 (d, 1H, *J*= 9.2 Hz, H-4); 4.25 (s, 5H, H-12); 4.34 (s, 2H, H-11); 4.44 (s, 1H, H-10 or H-10'); 4.64 (s, 1H, H-10 or H-10'); 6.55 (d, 1H, *J*=9.2 Hz, H-3) and 7.29-7.43 (m, 5H, H-6, H-7, H-8). **^{13}C{1H} NMR** ($CDCl_3$, ppm): 54.0 (C-2); 59.5 (C-4); 65.5 (C-11 or C-11'); 69.2 (C-11 o C-11'); 69.8 (C-12); 70.1 (C-10 or C-10'); 70.4 (C-10 or C-10'); 75.8 (C-9); 91.0 (C-3); 126.7

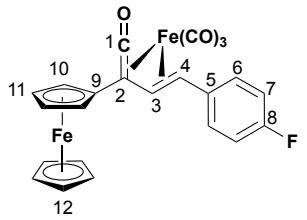
(C-7); 127.6 (C-5); 129.2 (C-6); 138.4 (C-8) and 234.2 (C-1). **MS-FAB** [*m/z*, (%)]: 468 [M$^+$](12%); 440 [M$^+$–CO] (11%); 412 [M$^+$–2CO] (3%); 384 [M$^+$–3CO] (45%); 356 [M$^+$–4CO] (22%); 300 [M$^+$–Fe(CO)$_4$] (4%). HRMS-FAB [M + OH]$^+$ Found for $C_{23}H_{17}Fe_2O_5$: 484.9769, Error (ppm): -1.2.

(**3d**) Tricarbonyl[4-(4'-chlorophenyl)-2-ferrocenyl-1-oxo-(1-4η)-but-1,3*E*-dienyl]iron(0)



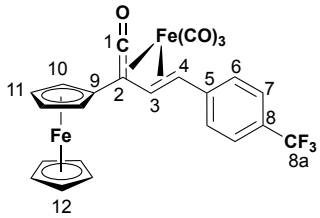
Red crystal in 50% yield, $C_{23}H_{15}ClFe_2O_4$: 502.5 g/mol, mp 116-117 °C. **IR** (ATR, cm^{-1}): 3010, 2932 (C_{sp2}-H); 2061, 2001 (M–CO); 1715 (C=C=O). **^{1}H NMR** ($CDCl_3$, ppm): 3.33 (d, 1H, *J*=9.18Hz, H-4); 4.25 (s, 5H, H-12); 4.34 (m, 2H, H-11); 4.45 (s, 1H, H-10 or H-10'); 4.63 (s, 1H, H-10 or H-10'); 6.56 (d, 1H, *J*=9.18Hz, H-3) and 7.36-7.38 (m, 4H, H-6 and H-7). **^{13}C{1H} NMR** ($CDCl_3$, ppm): 54.4 (C-2); 57.8 (C-4); 65.5 (C-11 or C-11'); 69.3 (C-11 or C-11'); 69.9 (C-12); 70.3 (C-10 or C-10'); 70.6 (C-10 or C-10'); 75.5 (C-9); 90.8 (C-3); 127.8 (C-7); 129.5 (C-6); 133.3 (C-5); 137.3 (C-8) and 233.8 (C-1). **MS-FAB** [*m/z*, (%)]: 502 [M$^+$] (4%); 474 [M$^+$–CO] (3%); 418 [M$^+$–3CO] (31%); 390 [M$^+$–4CO] (35%); 350 [M$^+$–Fe(CO)$_4$] (3%). HRMS-FAB [M – 3CO]$^+$ Calcd for $C_{20}H_{15}ClFe_2O$: 417.9510. Found: 417.9514, Error (ppm): +0.9.

(**3e**) Tricarbonyl[4-(4'-fluorophenyl)-2-ferrocenyl-1-oxo-(1-4η)-but-1,3*E*-dienyl]iron(0)



Red crystal in 62% yield, $C_{24}H_{18}FFe_2O_4$: 486 g/mol, mp 100-101 °C. **IR** (ATR, cm^{-1}): 3086, 2923 (C_{sp2}-H); 2055, 1996, 1972 (M–CO); 1733 (C=C=O). **^{1}H NMR** ($CDCl_3$, ppm): 3.38 (d, 1H, *J*=9.3Hz, H-4); 4.25 (s, 5H, H-12); 4.34 (m, 2H, H-11); 4.44 (s, 1H, H-10 o H-10'); 4.63 (s, 1H, H-10 o H-10'); 6.54 (d, 1H, *J*=9.3Hz, H-3); 7.07 (m, 2H, H-7) and 7.41 (m, 2H, H-6). **^{13}C{1H} NMR** ($CDCl_3$, ppm): 54.0 (C-2); 58.4 (C-4); 65.5 (C-11 or C-11'); 69.2 (C-11 or C-11'); 69.8 (C-12); 70.1 (C-10 or C-10'); 70.5 (C-10 or C-10'); 75.6 (C-9); 90.7 (C-3); 116.3 (d, C-7, $J_{C\text{-}F}$=21.75Hz); 128.1 (d, C-6, $J_{C\text{-}F}$=7.5Hz); 134.4 (d, C-5, $J_{C\text{-}F}$=3.75Hz); 162.1 (d, C-8, $J_{C\text{-}F}$=246.75Hz) and 233.9 (C-1). **MS-FAB** [m/z, (%)]: 486 [M$^+$] (14%); 458 [M$^+$–CO] (19%); 430 [M$^+$–2CO] (7%); 402 [M$^+$–3CO] (100%); 374 [M$^+$–4CO] (92%); 318 [M$^+$–Fe(CO)$_4$] (22%). HRMS-FAB [M]$^+$ Calcd for $C_{23}H_{15}FFe_2O_4$: 485.9653. Found: 485.9657, Error (ppm): +0.8.

(**3f**) Tricarbonyl[4-(4'-trifluoromethylphenyl)-2-ferrocenyl-1-oxo-(1-4η)-but-1,3*E*-dienyl]iron(0)



Red crystal in 61% yield, $C_{24}H_{15}F_3Fe_2O_4$: 536 g/mol, mp 118-120 °C. **IR** (ATR, cm^{-1}): 3087 (C_{sp2}-H); 2063, 2007, 1973 (M–CO); 1736 (C=C=O). **^{1}H NMR** ($CDCl_3$, ppm): 3.29 (d, 1H, *J*=8.7Hz, H-4); 4.26 (s, 5H, H-12); 4.35 (s, 2H, H-11); 4.47 (s, 1H, H-10 or H-10'); 4.65 (s, 1H, H-10 or H-10'); 6.62 (d, 1H, *J*=8.7Hz, H-3); 7.52 (d, 2H, J=7.2Hz, H-7) and 7.61 (d, 2H, *J*=7.2Hz, H-6). **^{13}C{1H} NMR** ($CDCl_3$, ppm): 54.8 (C-2); 56.1 (C-4); 65.5 (C-11 or C-11'); 69.3 (C-11 or C-11'); 69.9 (C-12); 70.3 (C-10 or C-10'); 70.7 (C-10 or C-10'); 75.1 (C-9); 91.1 (C-3); 124.1 (d, C-8a, $J_{C\text{-}F}$=207 Hz); 126.1 (q, C-7, $J_{C\text{-}F}$=3.8 Hz); 126.6 (C-6); 129.1 (d, C-8, $J_{C\text{-}F}$=32.25 Hz), 142.9 (C-5) and 233.3 (C-1). **MS-FAB** [*m/z*, (%)]: 536 [M$^+$] (20%); 508 [M$^+$–CO] (16%); 480 [M$^+$–2CO] (5%); 452 [M$^+$–3CO] (100%); 424 [M$^+$–4CO] (42%); 368 [M$^+$–Fe(CO)$_4$] (7%). HRMS-FAB [M]$^+$ Calcd for $C_{24}H_{15}F_3Fe_2O_4$: 535.9621. Found: 535.9621, Error (ppm): 0.0.

Table S2. IR Data (cm^{-1}) for the [η^4-ferrocenylketene]$Fe(CO)_3$ complexes acquired in solution of n-hexane

Entry	Compound	R	$\nu(CO)_{Met}$			$\nu(C=C=O)$
1	**2a**	OMe	2057	2026	1996	1778
2	**2b**	Me	2058	2026	1997	1779
3	**2c**	H	2059	2026	1999	1782
4	**2d**	Cl	2060	2026	2000	1779
5	**2e**	F	2062	2026	2003	1782
6	**2f**	CF_3	2063	2027	1973	1736

Compound 3a

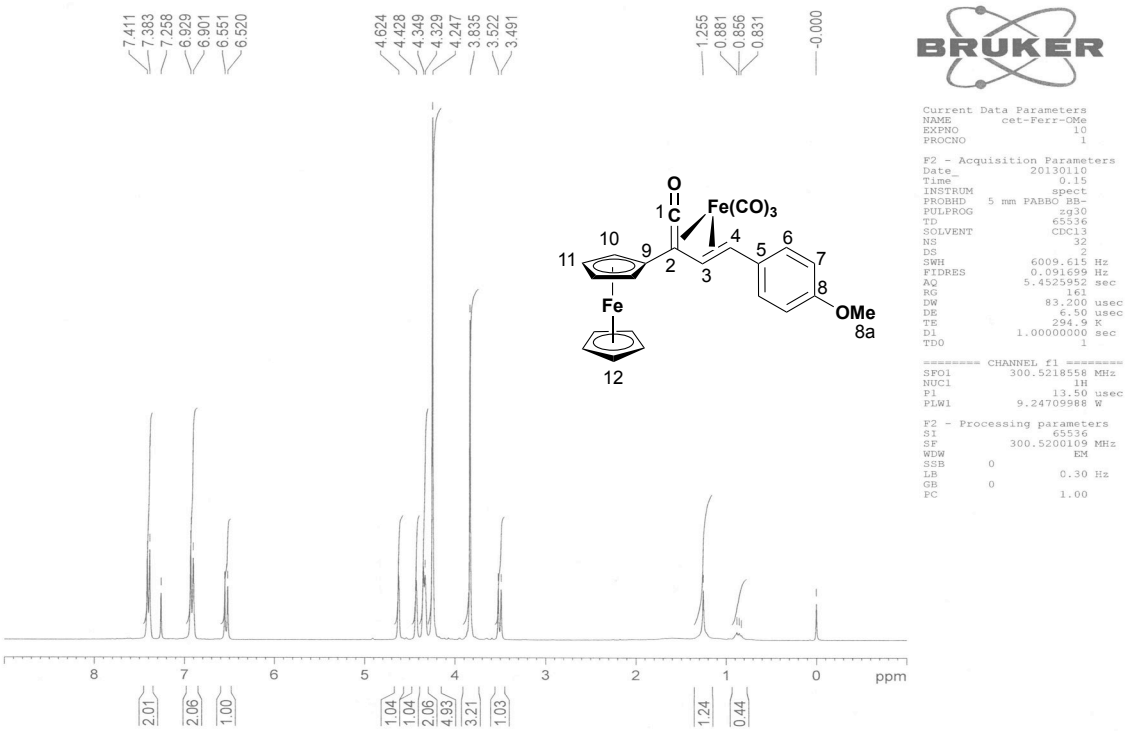


Figure S25. ^{1}H NMR spectrum 300 MHz of ($CDCl_3$) of compound **3a**

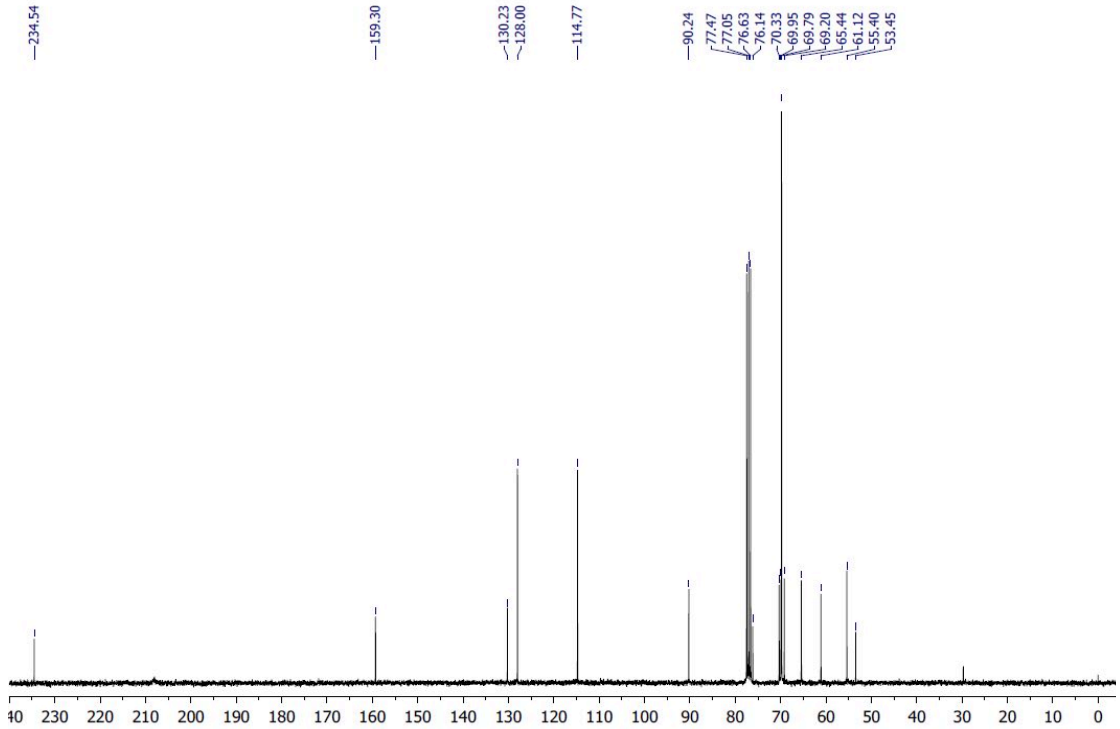


Figure S26. ^{13}C{1H} NMR spectrum 75 MHz of ($CDCl_3$) of compound **3a**

Compound 3b

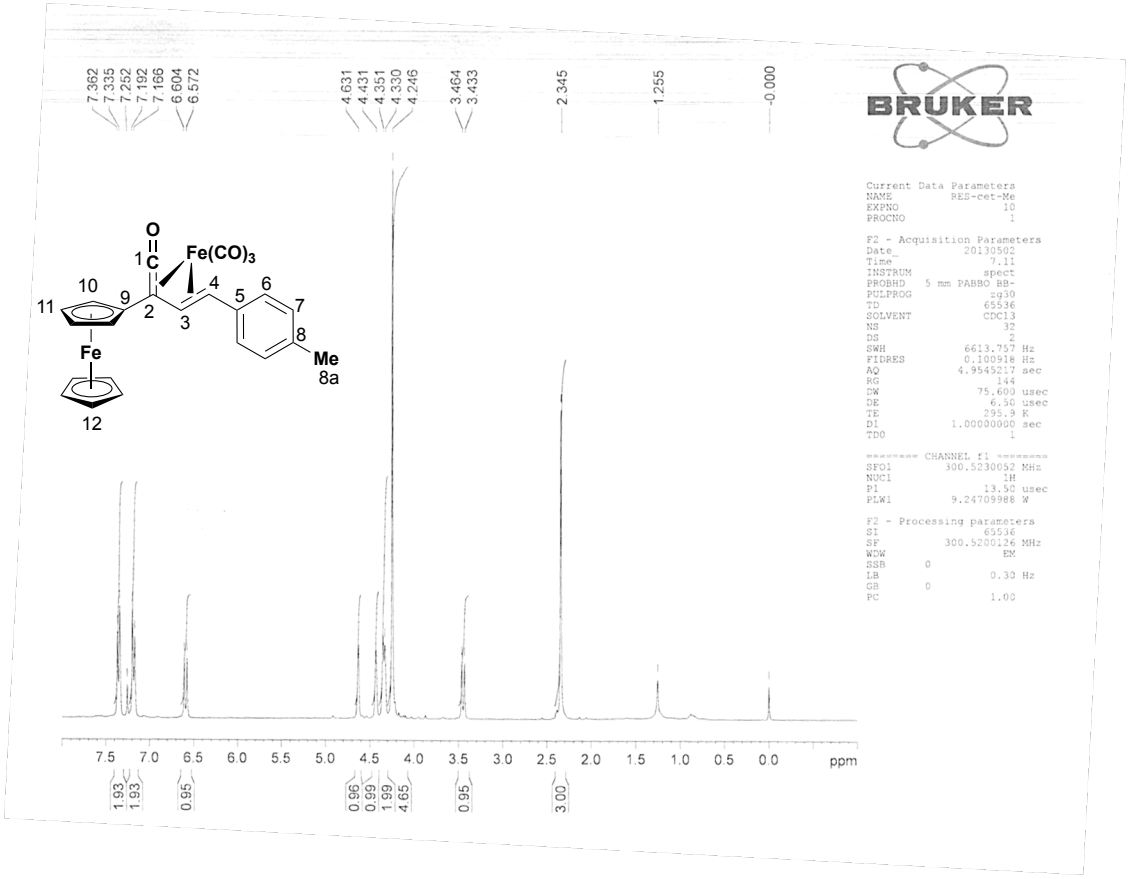


Figure S27. ^{1}H NMR spectrum 300 MHz of ($CDCl_3$) of compound **3b**

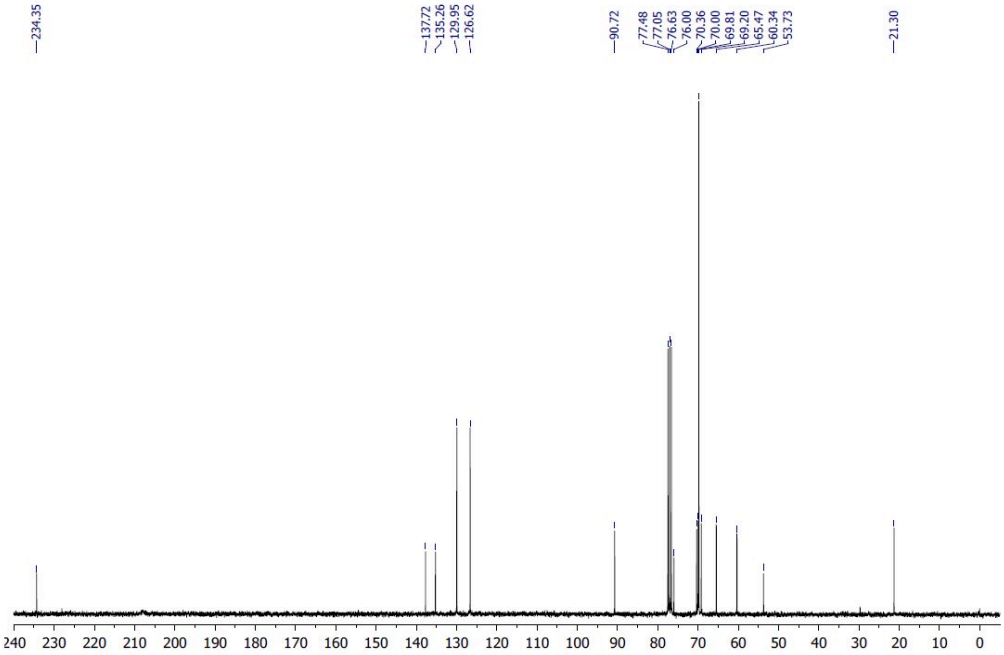


Figure S28. ^{13}C{1H} NMR spectrum 75 MHz of ($CDCl_3$) of compound **3b**

Compound 3c

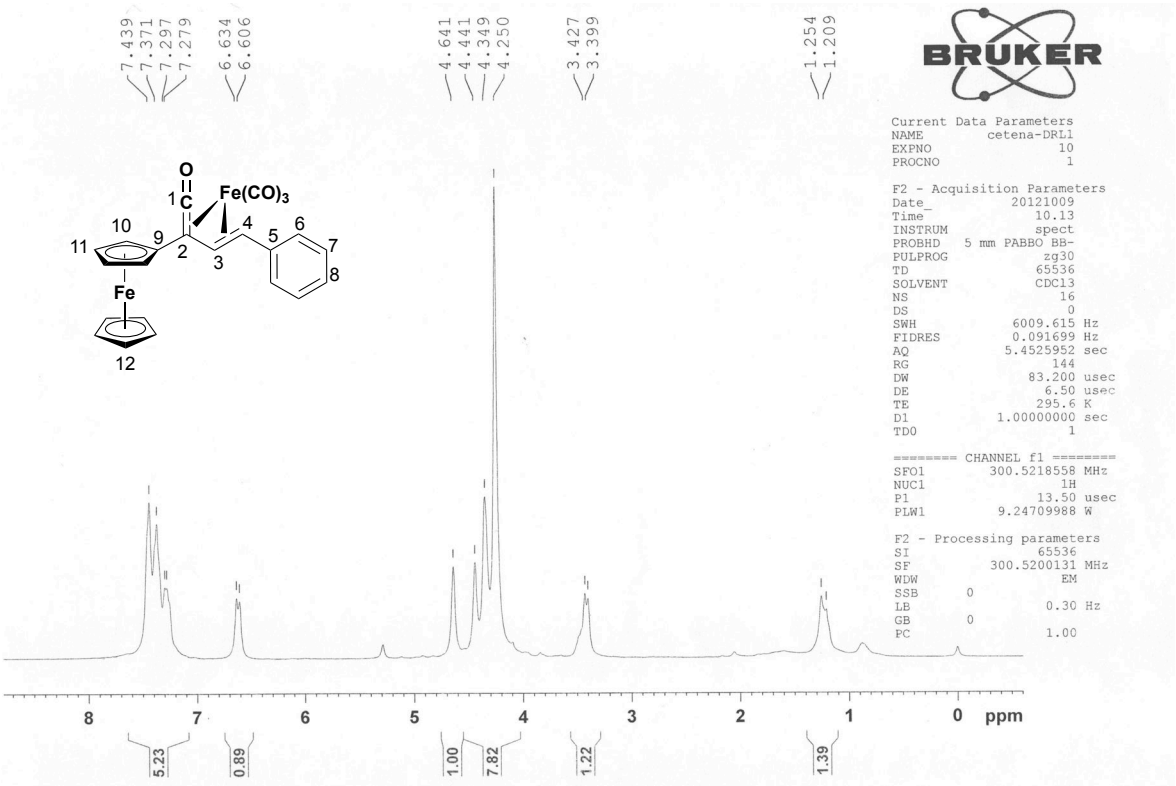


Figure S29. ^{1}H NMR spectrum 300 MHz of ($CDCl_3$) of compound **3c**

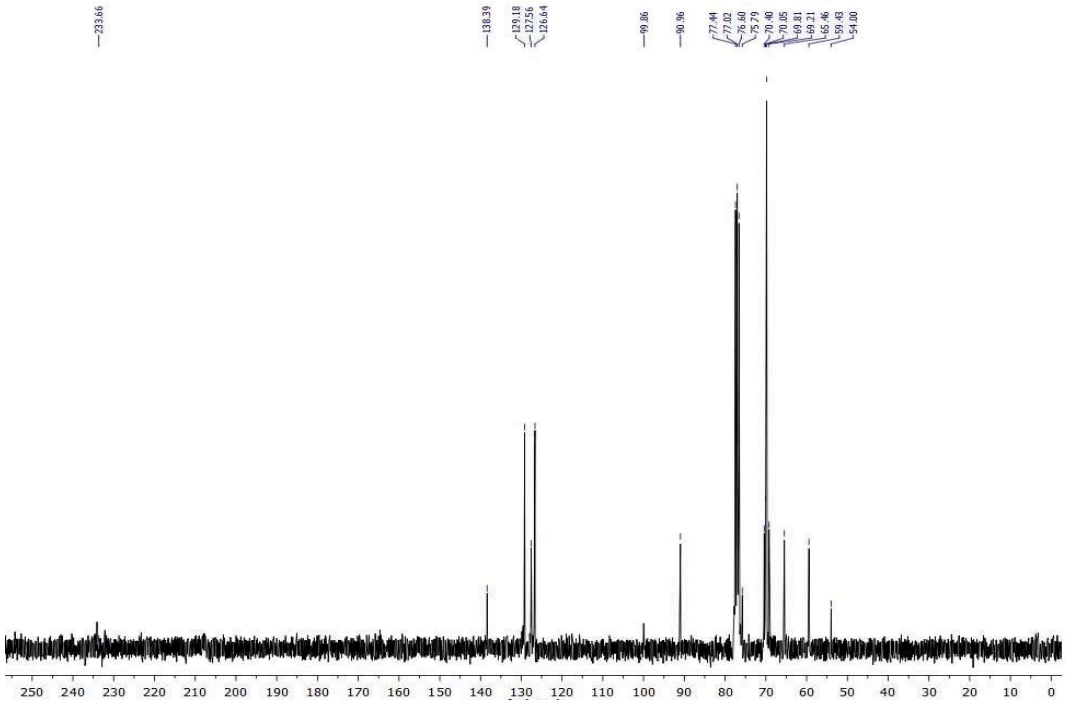


Figure S30. ^{13}**C{1H} NMR** spectrum 75 MHz of ($CDCl_3$) of compound **3c**

Compound 3d

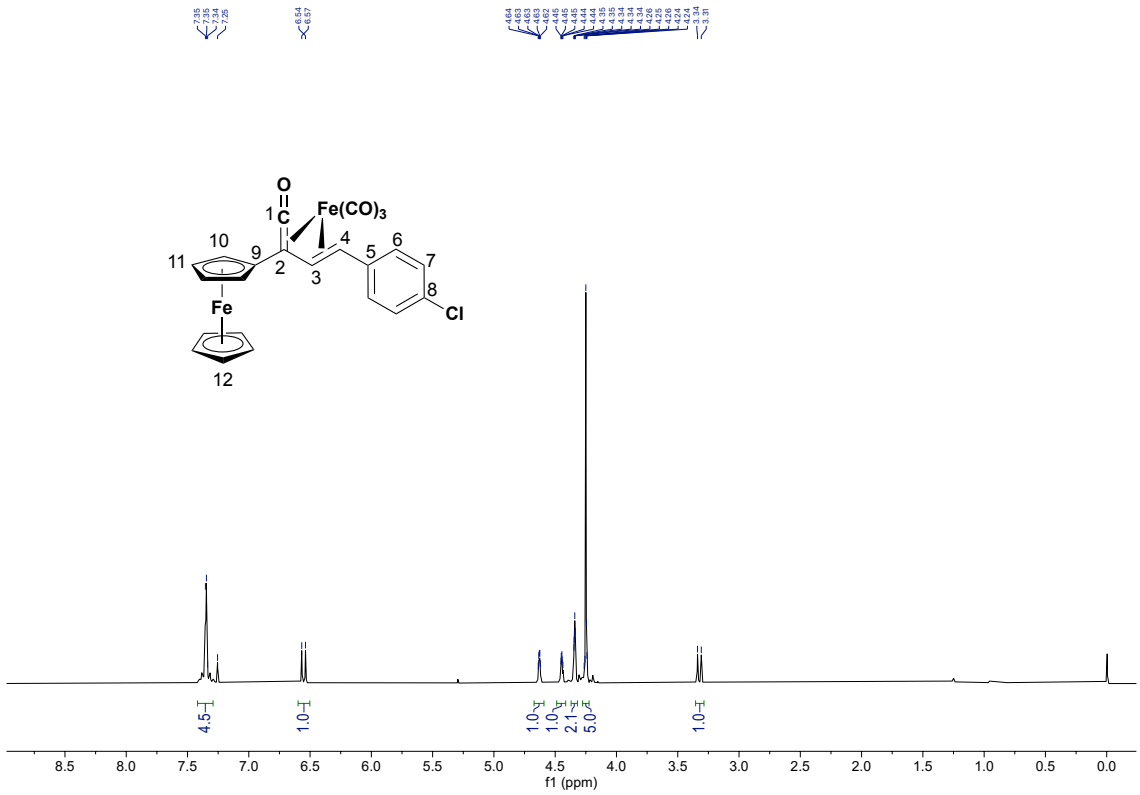


Figure S31. ^{1}H NMR spectrum 75 MHz of ($CDCl_3$) of compound **3d**

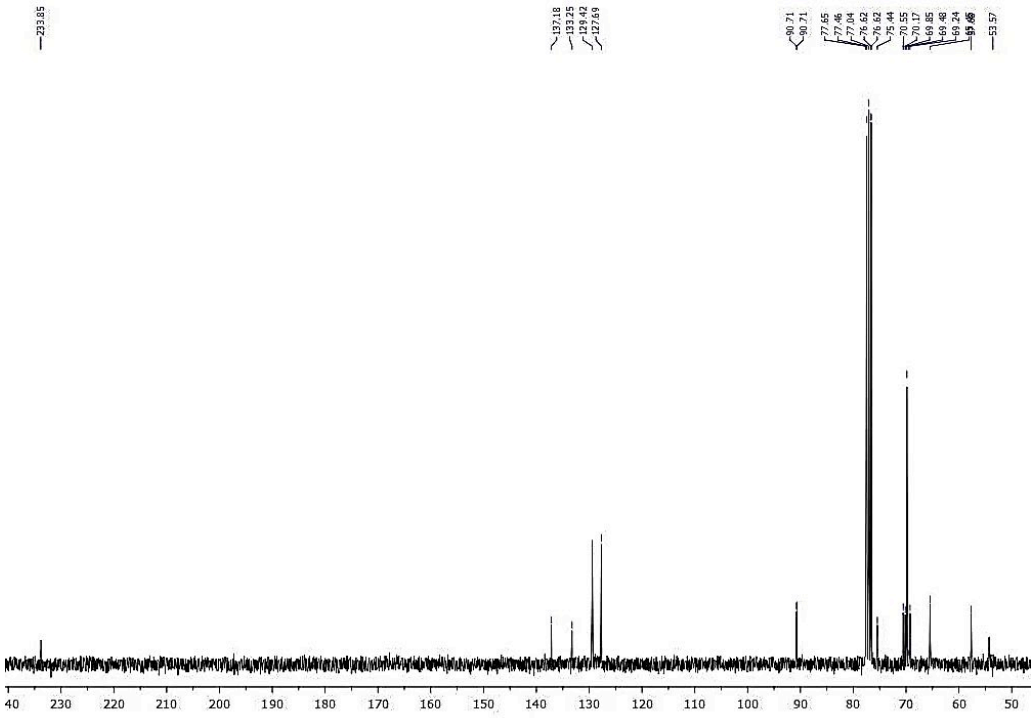


Figure S32. ^{13}**C{1H} NMR** spectrum 75 MHz of ($CDCl_3$) of compound **3d**

Compound 3e

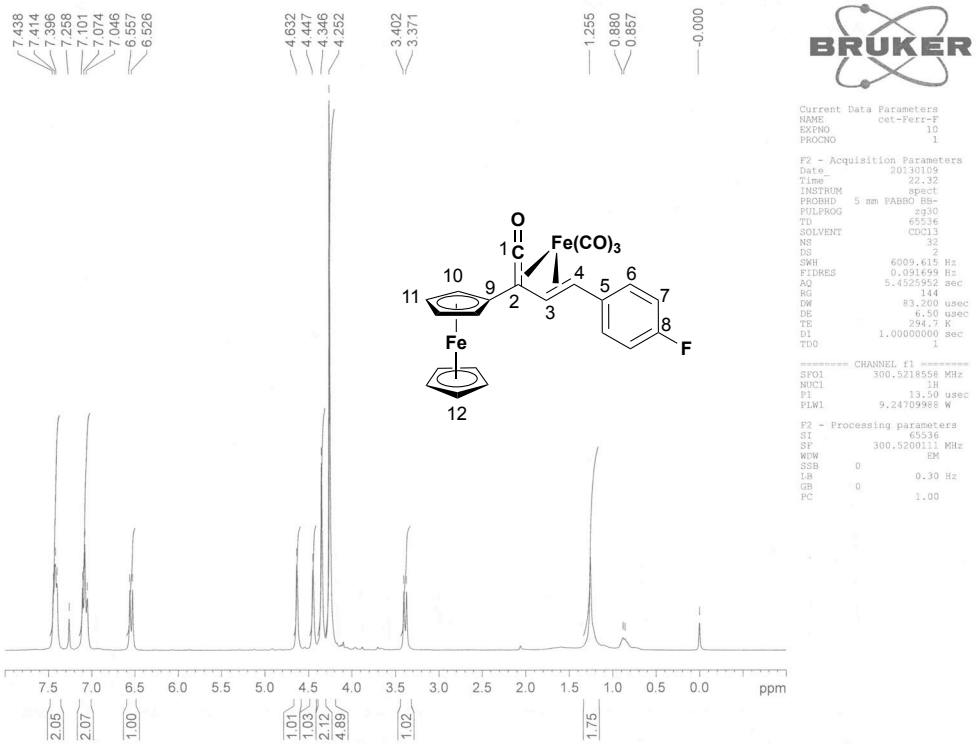


Figure S33. ^{1}H NMR spectrum 75 MHz of ($CDCl_3$) of compound **3e**

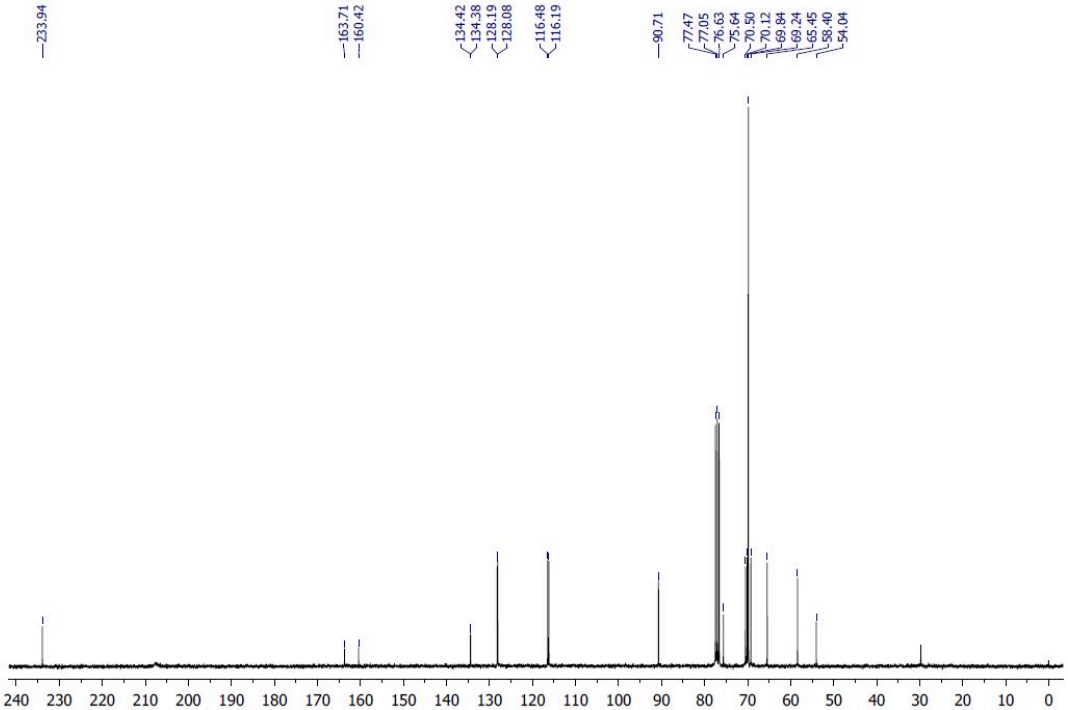
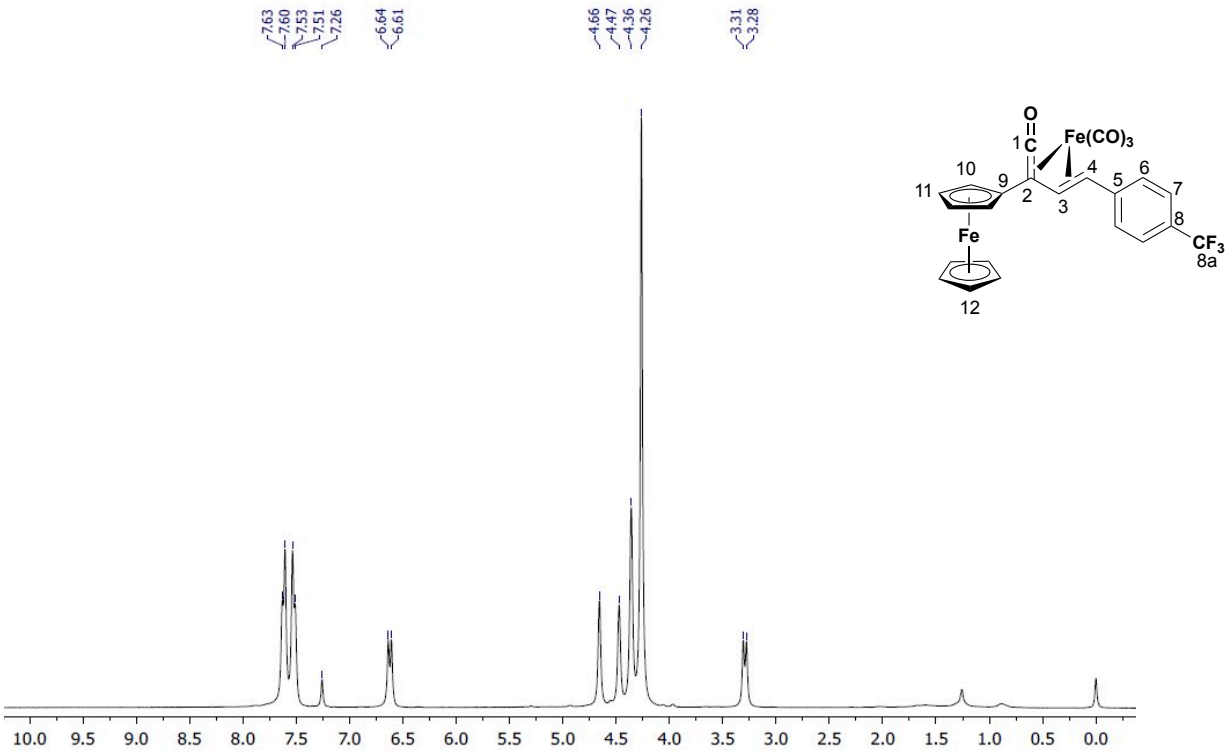


Figure S34. ^{13}**C{1H} NMR** spectrum 75 MHz of ($CDCl_3$) of compound **3e**

Compound 3f



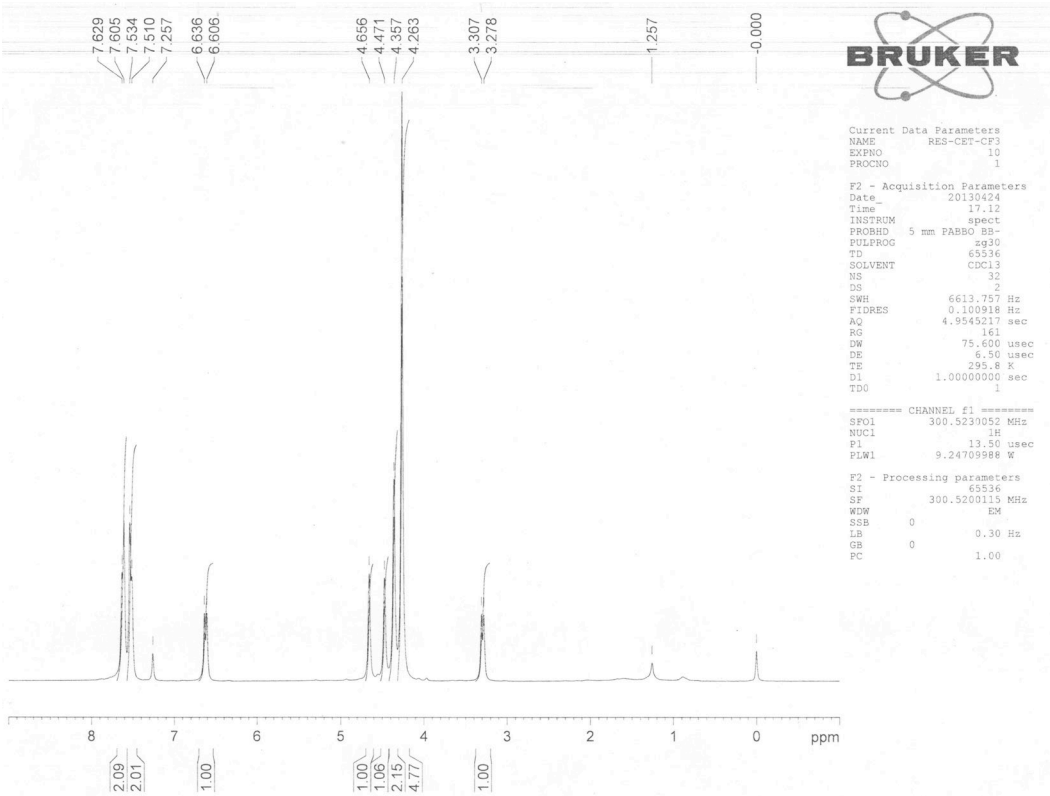


Figure S35. ^{1}H NMR spectrum 75 MHz of ($CDCl_3$) of compound **3e**

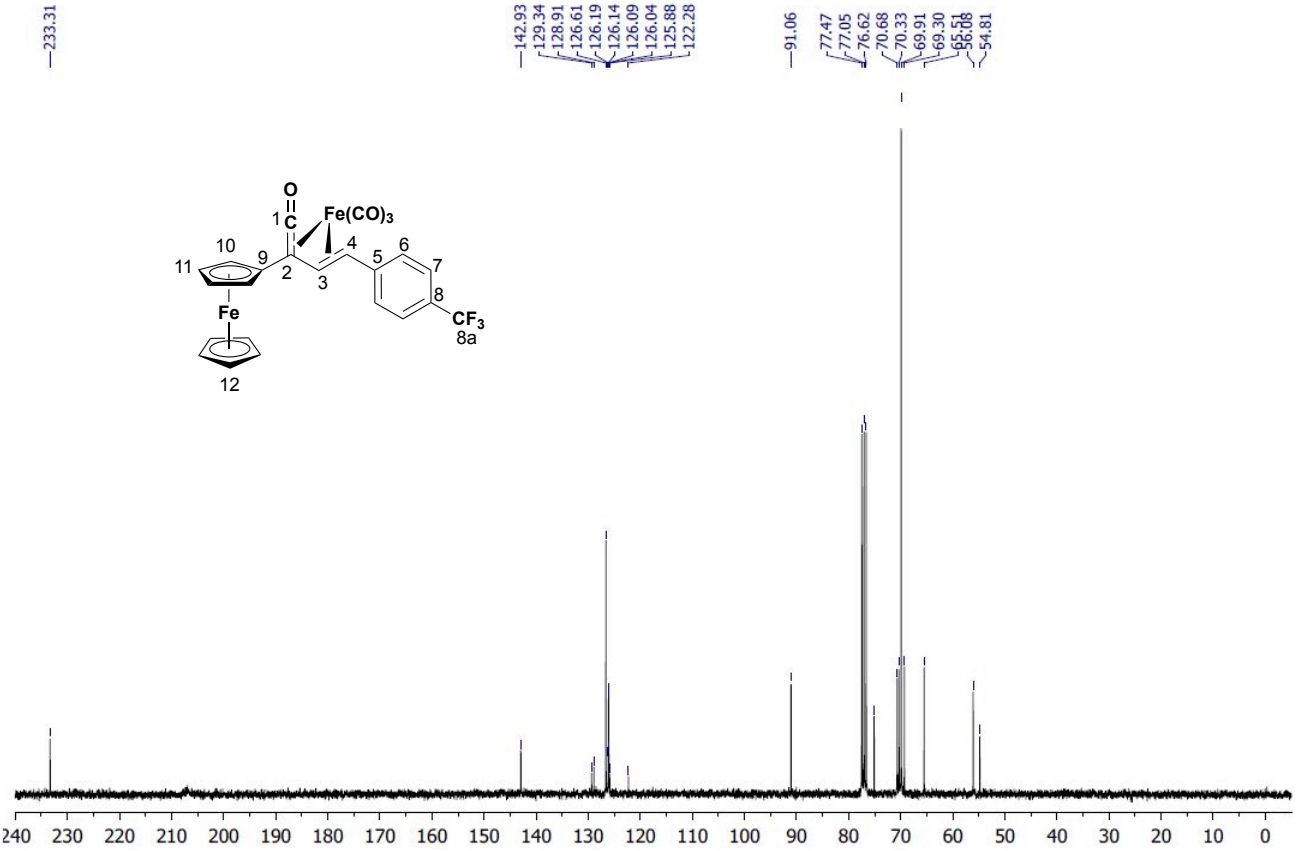
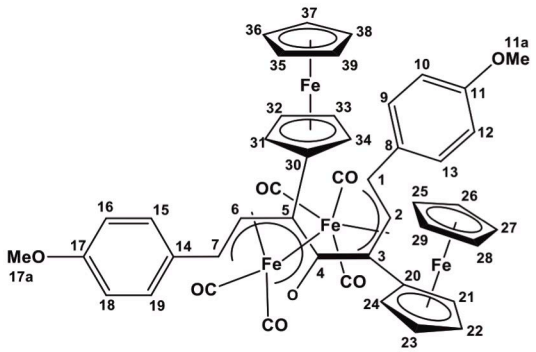


Figure S36. ^{13}C{1H} NMR spectrum 75 MHz of ($CDCl_3$) of compound **3e**

5. Synthesis of 5a-f and NMR spectra

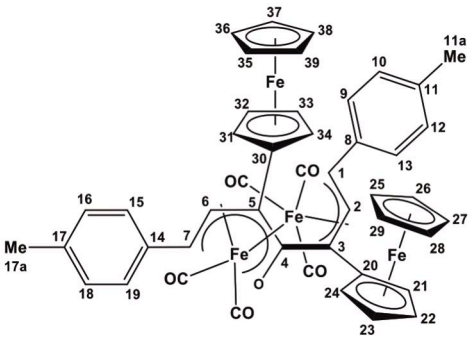
A solution of the corresponding η^4-[ferrocenylvinylketene]Fe(CO)$_3$ (**3**) in 5mL of benzene was refluxed under Argon atmosphere for 5h. After the reaction was completed, the reaction mixture was filtered off through a Celite/Na_2SO_4 (length 5cm), and the solvent was evaporated under vacuum. Purification by preparative Thin-Layer plate chromatography using 9/1 hexane/ethyl acetate as the mobile phase, recovering through solid/liquid extraction with CH_2CL_2 and evaporation *in vacuo*, allow the isolation of dinuclear iron(I) complexes **5(a-f)** as deep purple crystals.

(**5a**) [1,7-di(4'-Methoxyphenyl)-3,5-diferrocenyl-4-oxo-κO-μ-{1κO-(4,7η):2(1-3η)}-hepta-1,4,6-trien-1-yl](pentacarbonyl-1κ^2C,2κ^3C)diiron(*Fe–Fe*)



Deep purple crystals, 44% yield, $C_{46}H_{36}Fe_4O_8$: 940.16 g/mol, mp 121-123 °C. **IR** (ATR, cm^{-1}): 3088, 2918 (C_{sp2}-H); 2032, 1970, 1936 (M–CO); 1732(C=C=O). **^{1}H NMR** ($CDCl_3$, ppm): 3.73 (s, 3H, H-17a,); 3.88 (s, 3H, H-11a); 3.91 (s, 1H, H-7); 4.22 (s, 5H, H35-39); 4.33 (s, 2H, H-32,33); 4.44 (s, 6H, H25-29, H-31,34); 4.53 (s, 1H, H-22,23); 4.60 (d, 1H, H-2, *J*=12.3Hz); 4.69 (s, 1H, H-22,23); 4.75 (s, 1H, H-21,24); 5.17 (s, 1H, H-21,24); 5.87 (d, 1H, H-6, *J*=12Hz); 6.20 (d, 1H, H-1, *J*=12Hz); 6.70 (d, 2H, H-16,18, *J*=8.1Hz); 6.87 (d, 2H, H15-19, *J*=8.1Hz); 6.99 (d, 2H, H-6, *J*=8.1Hz) and 7.42 (d, 2H, H-9,13, *J*=8.1Hz). **^{13}C{1H} NMR** ($CDCl_3$, ppm): 55.2 (C-17a); 55.4 (C-11a); 65.2 (C-7); 66.7 (C-32,33); 67.8 (C-22,23); 68.2 (C-32,33); 69.2 (C-22,23); 69.4 (C-35-39); 69.6 (C-31,34); 70.1 (C-21,24); 70.3 (C-31,34); 70.4 (C-25-29); 71.7 (C-21,24); 79.7 (C-30); 82.8 (C-20); 89.5 (C-3); 90.3 (C-6); 92.6 (C-2); 101.7 (C-5); 104.4 (C-1); 114.3 (C-16,18); 114.8 (C-10,12); 121.1 (C-4); 126.6 (C-15,19); 128.2 (C-9,13); 131.3 (C-14); 132.1 (C-8); 158.6 (C-17); 159.6 (C-11); 213.7 and 220.0 (M–CO). **MS-FAB** [*m/z*, (%)]: 941 [M$^+$+1] (3%); 912 [M$^+$–CO] (7%); 884 [M$^+$–2CO] (4%); 856 [M$^+$–3CO] (13%); 828 [M$^+$–4CO] (38%); 800 [M$^+$–5CO] (69%), 772 [M$^+$–6CO] (9%); 688 [M$^+$–$Fe_2(CO)_5$] (18%). Elemental Analysis (%): calcd for $C_{46}H_{36}Fe_4O_8$, %C 58.77, %H 3.86; found: %C 59.67, %H 3.98.

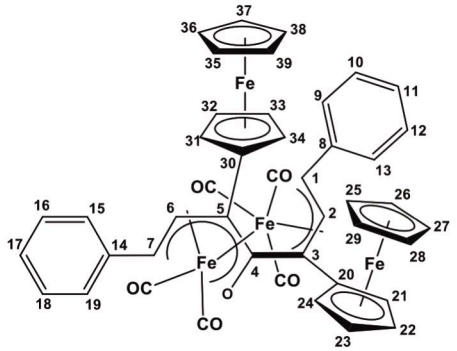
(**5b**) [1,7-di(4'-Methylphenyl)-3,5-diferrocenyl-4-oxo-κO-μ-{1κO-(4,7η):2(1-3η)}-hepta-1,4,6-trien-1-yl](pentacarbonyl-1κ^2C,2κ^3C)diiron(*Fe–Fe*)



Deep purple crystals, 30% yield, $C_{46}H_{36}Fe_4O_6$: 908.16 g/mol, mp 158-160 °C. **IR** (ATR, cm^{-1}): 3087 (C_{sp2}-H); 2034, 1978, 1958, 1937 (M-CO); 1730 (C=C=O). **^{1}H NMR** ($CDCl_3$, ppm): 2.23 (s, 3H, H-17a,); 2.40 (s, 3H, H-11a); 3.84 (d, 1H, *J*=12Hz, H-7); 4.22 (s, 5H, H35-39); 4.33 (s, 2H, H-32,33); 4.37 (s, 1H, H-31,34); 4.44 (s, 5H, H25-29); 4.52-4.56 (m, 2H, H-22,23, H2); 4.69 (s, 1H, H-22,23); 4.75 (s, 1H, H-21,24); 5.17 (s, 1H, H-21, 24); 5.94 (d, 1H, *J*=12.3Hz, H-6); 6.27 (d, 1H, *J*=12.3Hz, H-1); 6.83 (d, 2H, *J*=7.8Hz, H-16,18); 6.96 (d, 2H, *J*=7.8Hz, H15-19); 7.26 (d, 2H, *J*=7.8Hz, H-10,12) and 7.37 (d, 2H, *J*=7.8Hz, H-9,13). **^{13}C{1H} NMR**

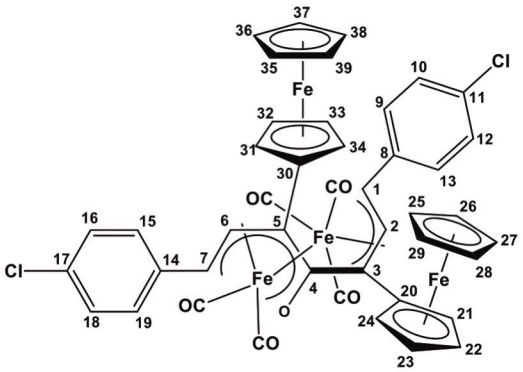
($CDCl_3$, ppm): 21.2 (C-17a); 21.4 (C-11a); 64.8 (C-7); 66.7 (C-32,33); 67.9 (C-22,23); 68.3 (C-32,33); 69.3 (C-22,23); 69.5 (C-35-39); 69.7 (C-31,34); 70.1 (C-21,24); 70.2 (C-31,34); 70.4 (C-25-29); 71.6 (C-21,24); 80.2 (C-30); 82.7 (C-20); 89.4 (C-3); 90.8 (C-6); 91.9 (C-2); 102.1 (C-5); 105.2 (C-1); 121.3 (C-4); 125.3 (C-15,19); 126.8 (C-9,13); 129.5 (C-16,18); 130.1 (C-10,12); 136.2 (C-14); 136.6 (C-8); 137.0 (C-17); 138.0 (C-11); 213.4 and 219.9 (M–CO). **MS-FAB** [*m/z*, (%)]: 880 [M^+–CO] (4%); 852 [M^+–2CO] (1%); 824 [M^+–3CO] (5%); 796 [M^+–4CO] (17%); 768 [M^+–5CO] (42%); 740 [M^+–6CO] (8%). Elemental Analysis (%): calcd for $C_{46}H_{36}Fe_4O_6$, %C 60.84, %H 3.99; found: %C 61.21, %H 4.12.

(**5c**) [1,7-Diphenyl-3,5-diferrocenyl-4-oxo-κo-μ-{1κo-(4,7η):2(1-3η)}-hepta-1,4,6-trien-1-yl](pentacarbonyl-1κ^2c,2κ^3c)diiron(*Fe–Fe*)



Deep purple crystal in 37% yield, $C_{44}H_{32}Fe_4O_6$: 880.10 g/mol, mp 88-90 °C. **IR** (ATR, cm^{-1}): 3084, 2919 (C_{sp2}-H); 2035, 1972, 1936 (M–CO); 1732(C=C=O). **^{1}H NMR** ($CDCl_3$, ppm): 3.82 (d, 1H, *J*=12Hz, H-7); 4.23 (s, 5H, H35-39); 4.34 (s, 2H, H-32,33); 4.39 (s, 1H, H-31,34); 4.45 (s, 6H, H25-29, H31-34); 4.50-4.55 (m, 2H, H-22,23, H2); 4.70 (s, 1H, H-22,23); 4.76 (s, 1H, H-21,24); 5.18 (s, 1H, H-21, 24); 5.99 (d, 1H, *J*=12Hz, H-6); 6.92-6.94 (m, 2H, H-16,18, H17a); 7.09-7.18 (m, 3H, H16-18, H-15,19); 7.36-7.38 (m, 1H, H-11a) and 7.42-7.47 (m, 4H, H-10,12, H-9,13). **^{13}C{1H} NMR** ($CDCl_3$, ppm): 64.3 (C-7); 66.7 (C-32,33); 68.0 (C-22,23); 68.3 (C-32,33); 69.4 (C-22,23); 69.5 (C35-39); 69.8 (C-31,34); 70.2 (C-21,24); 70.2 (C-31,34); 70.4 (C25-29); 71.6 (C-21,24); 80.6 (C-30); 82.6 (C-20); 89.2 (C-3); 91.1 (C-6); 91.2 (C-2); 102.3 (C-5); 105.8 (C-1); 121.4 (C-4); 125.4 (C-16,18); 126.8 (C-14); 126.9 (C-10,12); 128.0 (C-8); 128.8 (C-15,19); 129.3 (C-9,13); 139.2 (C-17); 139.9 (C-11); 211.0, 213.3 and 219.8 (M–CO). **MS-FAB** [*m/z*, (%)]: 852 [M^+–CO] (6%); 824 [M^+–2CO] (2%); 796 [M^+–3CO] (5%); 768 [M^+–4CO] (17%); 740 [M^+–5CO] (19%), 712 [M^+–6CO] (7%); 628 [M^+–$Fe_2(CO)_5$] (5%). HRMS-FAB [M]$^+$ Calcd for $C_{43}H_{32}Fe_4O_5$: 851.9647. Found: 851.9644, Error (ppm): -0.4.

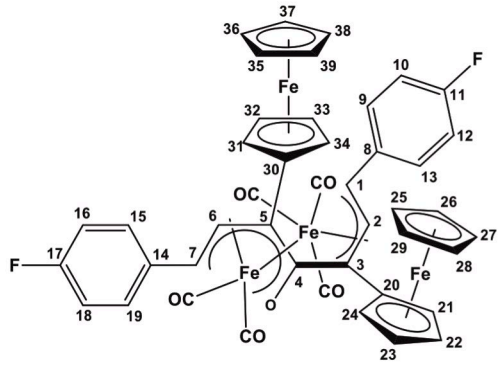
(**5d**) [1,7-Di(4'-chlorophenyl)-3,5-diferrocenyl-4-oxo-κo-μ-{1κo-(4,7η):2(1-3η)}-hepta-1,4,6-trien-1-yl](pentacarbonyl-1κ^2c,2κ^3c)diiron(*Fe–Fe*)



Deep purple crystal in 39% yield, $C_{44}H_{30}Cl_2Fe_4O_6$: 948.99 g/mol, mp 148-150 °C. **IR** (ATR, cm^{-1}): 3090, 2922 (C_{sp2}-H); 2037, 1975, 1937 (M–CO); 1730(C=C=O). **^{1}H NMR** ($CDCl_3$, ppm): 3.73 (d, 1H, *J*=12Hz, H-7); 4.23 (s, 5H, H-35,39); 4.31 (s, 1H, H-32,33); 4.35 (s, 2H, H-31,34, H-32,33); 4.40-4.41 (m, 1H, H-31,34); 4.44 (s, 6H, H2, H-31,34); 4.51 (s, 1H, H-22,23); 4.68 (s, 1H, H-22,23); 4.75 (s, 1H, H-21,24); 5.16 (s, 1H, H-21,24); 5.92 (d, 1H, *J*=12Hz, H-6); 6.24 (d, 2H, *J*=12Hz, H-1); 6.84 (d, 2H, *J*=8.4Hz, H-16,18); 7.12 (d, 2H, *J*=8.4Hz, H-15,19) and 7.39-7.42 (m, 4H, H-9,13, H-10,12). **^{13}C{1H} NMR** ($CDCl_3$, ppm): 62.6 (C-7); 66.6 (C-32,33); 68.1 (C-22,23); 68.2 (C-32,33); 69.4 (C-22,23); 69.5 (C35-39); 69.9 (C-31,34); 70.2 (C-21,24); 70.3 (C-31,34); 70.5 (C25-29); 71.6 (C-

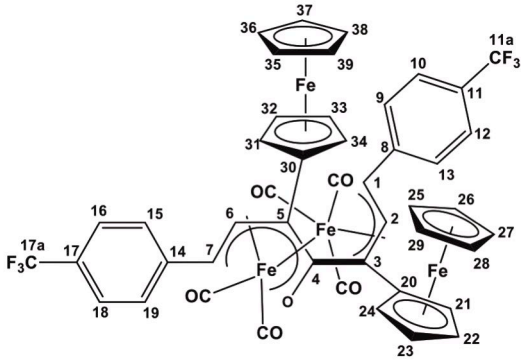
21,24); 81.0 (C-30); 82.3 (C-20); 88.7 (C-3); 89.6 (C-6); 90.9 (C-2); 102.4 (C-5); 105.8 (C-1); 121.5 (C-4); 126.4 (C-16,18); 128.0 (C-10,12); 129.1 (C-15,19); 129.6 (C-9,13); 132.4 (C-14); 133.8 (C-8); 137.8 (C-17); 138.5 (C-11); 213.2, 219.5 (M–CO). **MS-FAB** [*m/z*, (%)]: 950 [M^++1] (4%); 921 [M^+–CO] (9%); 893 [M^+–2CO] (5%); 865 [M^+–3CO] (12%); 837 [M^+–4CO] (48%); 807 [M^+–5CO] (78%), 779 [M^+–6CO] (6%); 697 [M^+–$Fe_2(CO)_5$] (10%). Elemental Analysis (%): calcd for $C_{44}H_{30}Cl_2Fe_4O_6$, %C 55.69, %H 3.19; found: %C 56.74, %H 3.45.

(**5e**) [1,7-Di(4'-fluorophenyl)-3,5-diferrocenyl-4-oxo-κo-μ-{1κo-(4,7η):2(1-3η)}-hepta-1,4,6-trien-1-yl](pentacarbonyl-1κ^2c,2κ^3c)diiron(*Fe–Fe*)



Deep purple crystal in 39% yield, $C_{44}H_{30}F_2Fe_4O_6$: 916.08 g/mol, mp 78-79°C. **IR** (ATR, cm^{-1}): 3086, 2919 (C_{sp2}-H); 2035, 1974, 1937 (M–CO); 1731(C=C=O). **^{1}H NMR** ($CDCl_3$, ppm): 3.82 (d, 1H, *J*=11.7Hz, H-7); 4.27 (s, 5H, H35-39); 4.38 (s, 3H, H-31,34, H-32,33); 4.43 (s, 1H, H-32,33); 4.48 (s, 6H, H2, H-25-29); 4.55 (s, 1H, H-22,23); 4.72 (s, 1H, H-22,23); 4.79 (s, 1H, H-21,24); 5.20 (s, 1H, H-21,24); 5.92 (d, 1H, *J*=12.3Hz, H-6); 6.24 (d, 2H, *J*=12.3Hz, H-1); 6.89-6.92 (m, 4H, H-5,19, H-16,18); 7.19 (t, 2H, H-15,19); 7.46 (q, 2H, H-9,13). **^{13}C{1H} NMR** ($CDCl_3$, ppm): 63.3 (C-7); 66.7 (C-32,33); 68.0 (C-22,23); 68.2 (C-32,33); 69.4 (C-22,23); 69.5 (C35-39); 69.9 (C-31,34); 70.2 (C-21,24, C-31,34); 70.5 (C25-29); 71.6 (C-21,24); 80.6 (C-30); 82.4 (C-20); 88.9 (C-3); 90.3 (C-6); 90.9 (C-2); 102.1 (C-5); 105.6 (C-1); 115.9 (d, C-16,18, J_{C-F}=21.75Hz); 116.4 (d, C-10,12, J_{C-F}=21.75Hz); 121.4 (C-4); 126.78 (d, C-15,19, J_{C-F}=8.75Hz); 128.4 (d, C-9,13, J_{C-F}=8.75Hz); 135.1 (d, C-14, J_{C-F}=3.75Hz); 135.9 (d, C-8, J_{C-F}=3.75Hz); 161.6 (d, C-17, J_{C-F}=245.25Hz); 162.5 (d, C-11, J_{C-F}=245.25Hz); 207.0, 213.4 (M–CO). **MS-FAB** [*m/z*, (%)]: 917 [M^++1] (4%); 888 [M^+–CO] (9%); 860 [M^+–2CO] (4%); 832 [M^+–3CO] (8%); 804 [M^+–4CO] (41%); 776 [M^+–5CO] (32%), 748 [M^+–6CO] (5%); 664 [M^+–$Fe_2(CO)_5$] (7%). Elemental Analysis (%): calcd for $C_{44}H_{30}F_2Fe_4O_6$, %C 57.69, %H 3.30; found: %C 58.87, %H 3.85.

(**5f**) [1,7-Di(4'-trifluoromethylphenyl)-3,5-diferrocenyl-4-oxo-κo-μ-{1κo-(4,7η):2(1-3η)}-hepta-1,4,6-trien-1-yl](pentacarbonyl-1κ^2c,2κ^3c)diiron(*Fe–Fe*)



Deep purple crystal in 28% yield, $C_{46}H_{30}F_6Fe_4O_6$: 1016.10 g/mol, mp 156-158 °C. **IR** (ATR, cm^{-1}): 3088 (C_{sp2}-H); 2041, 1985, 1969, 1956 (M–CO); 1728(C=C=O). **^{1}H NMR** ($CDCl_3$, ppm): 3.71 (d, 1H, *J*=12Hz, H-7); 4.25 (s, 5H, H35-39); 4.37 (s, 3H, H-31,34, H-32,33); 4.46 (s, 7H, H-2, H25-29, H-32,33); 4.55 (s, 1H, H-22,23); 4.70 (s, 1H, H-22,23); 4.78 (s, 1H, H-21,24); 5.18 (s, 1H, H-21,24); 6.02 (d, 1H, *J*=11.7Hz, H-6); 6.34 (d, 2H, *J*=12Hz, H-1); 7.00 (d, 2H, *J*=7.5Hz, H-16,18); 7.41 (d, 2H, *J*=7.8Hz, H-15,19); 7.55 (d, 2H, *J*=7.5Hz, H-10,12); 7.71 (d, 2H, *J*=7.8Hz, H-9,13). **^{13}C{1H} NMR** ($CDCl_3$, ppm): 60.4 (C-32,33); 61.5 (C-7); 66.6 (C-22,23); 68.2 (C-32,33); 68.3 (C-22,23); 69.6 (C-35-39); 70.1 (C-31,34); 70.2 (C-21,24); 70.4 (C31,34); 70.5 (C25-29); 71.6 (C-21,24); 82.0 (C-30);

82.1 (C-20); 88.0 (C-6); 88.2 (C-3); 91.4 (C-2); 102.9 (C-5); 106.7 (C-1); 121.8 (C-4); 124.1 (q, C-17a, J_{CF}=270Hz); 124.2 (q, C-11a, J_{CF}=270Hz); 125.3 (C-15,19); 125.8 (q, C-16,18, J_{CF}=3.75Hz); 126.3 (d, C-10,12, J_{CF}=3.75Hz); 127.0 (C-9,13); 128.9 (q, C-17, J_{CF}=32.25Hz); 129.6 (q, C-11, J_{CF}=32.25Hz); 212.9, 219.1 (M–CO). **MS-FAB** [*m/z*, (%)]: 960 [M^+–2CO] (2%); 932 [M^+–3CO] (3%); 904 [M^+–4CO] (13%); 876 [M^+–5CO] (28%), 764 [M^+–$Fe_2(CO)_5$] (5%). Elemental Analysis (%): calcd for $C_{46}H_{30}F_6Fe_4O_6$, %C 54.37, %H 2.98; found: %C 55.73, %H 3.12.

Table S3. IR Data (cm^{-1}) for the complexes **5a-d** acquired in solution of *n*-hexane

Complex	R	$\nu(C_{sp2}\text{-}H)$	$\nu(M\text{-}C\equiv O)$			$\nu(C=O)$
5a	OMe	3087	2043	1989	1935	1732
5b	Me	3086	2045	1985	1937	1730
5c	H	3088	2044	1982	1936	1731
5d	Cl	3091	2046	1978	1936	1732
5e	F	3088	2044	1985	1938	1731
5f	CF_3	3088	2048	1985	1945	1728

Compound 5a

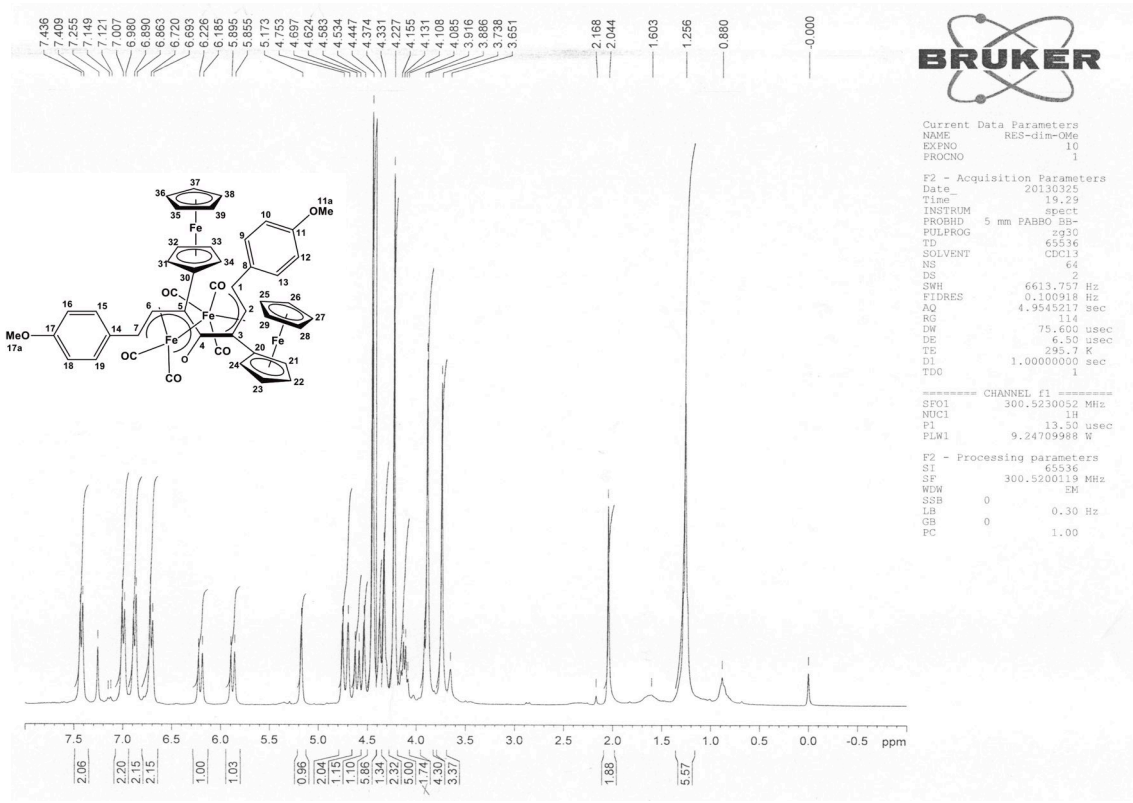


Figure S37. ^{1}H NMR spectrum 300 MHz of ($CDCl_3$) of compound **5a**

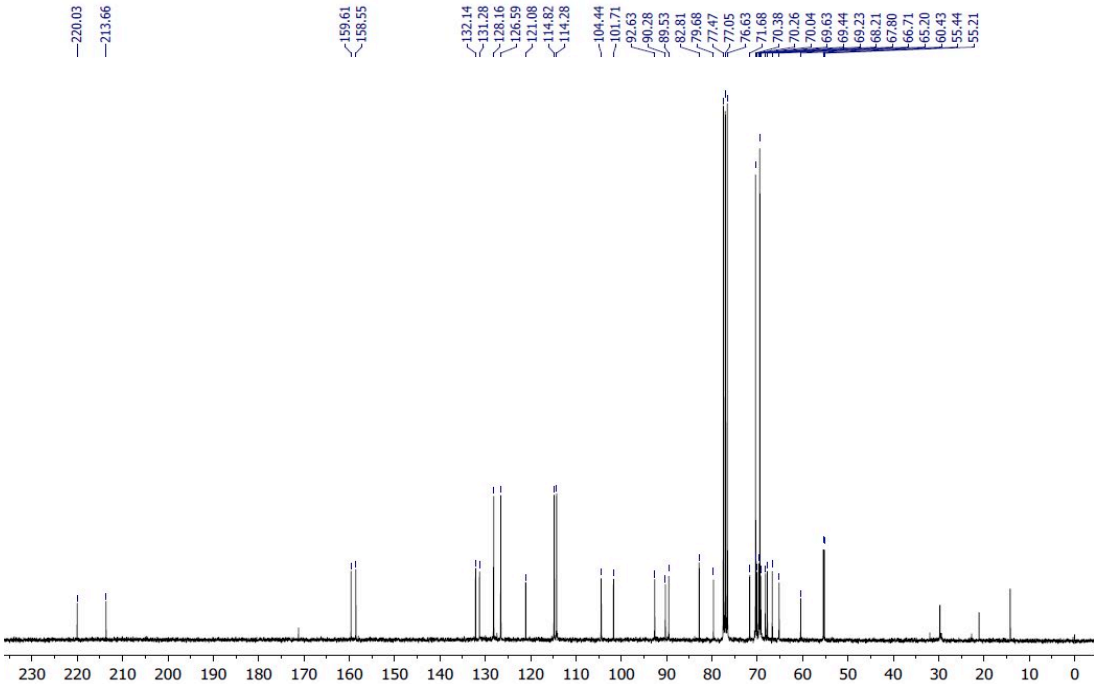


Figure S38. ^{13}C{1H} NMR spectrum 75 MHz of ($CDCl_3$) of compound **5a**

Compound 5b

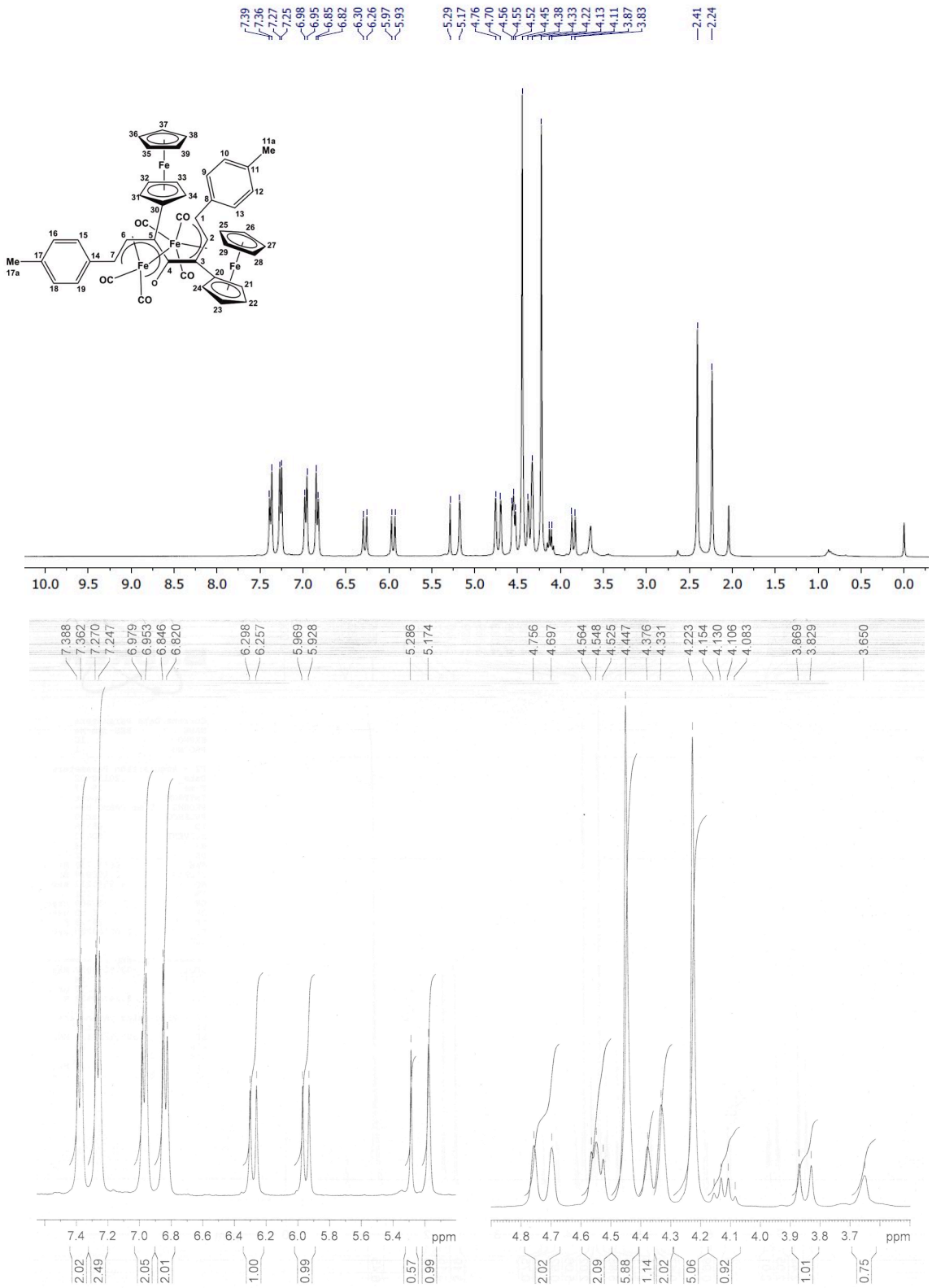


Figure S39. ^{1}H NMR spectrum 300 MHz of ($CDCl_3$) of compound **5b**

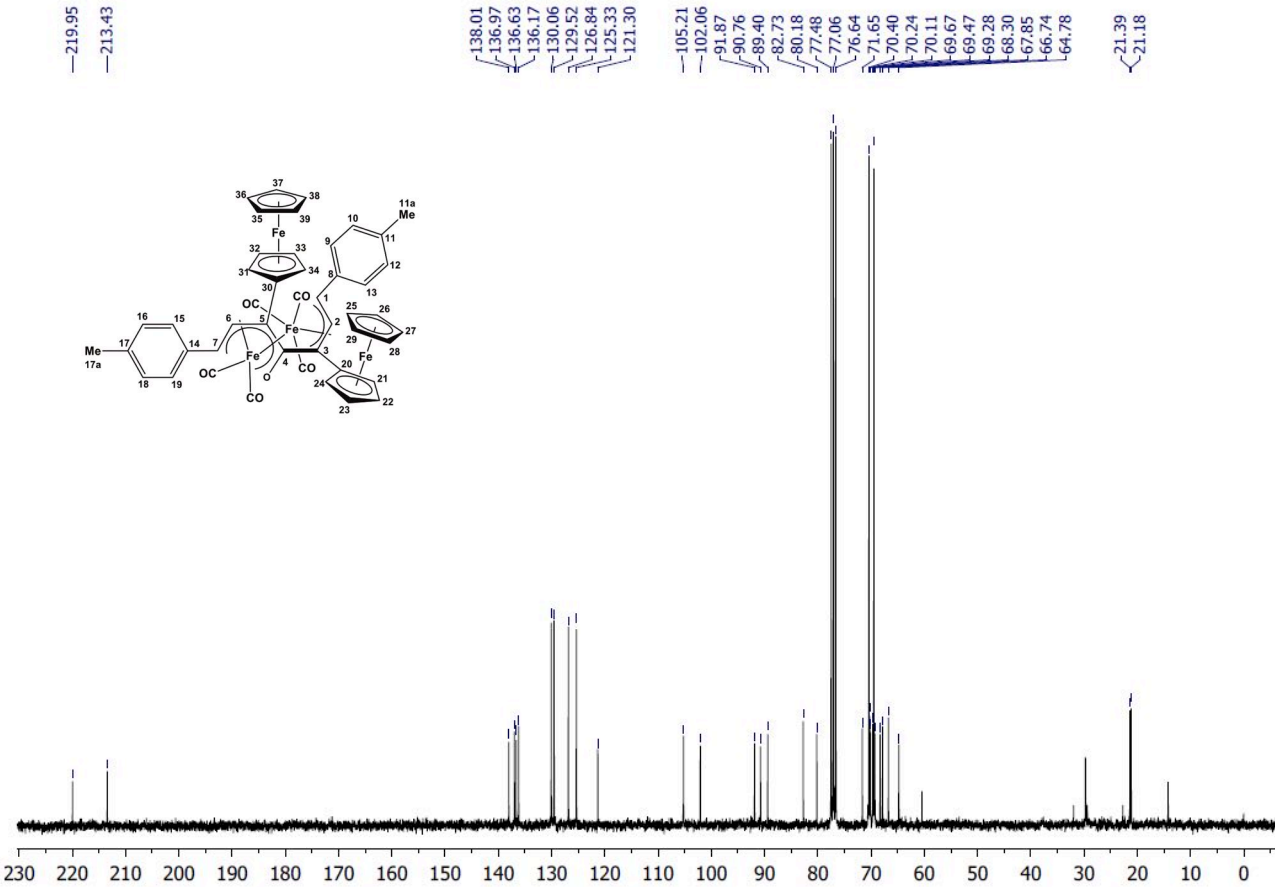


Figure S40. ^{13}C{1H} NMR spectrum 75 MHz of ($CDCl_3$) of compound **5b**

Compound 5c

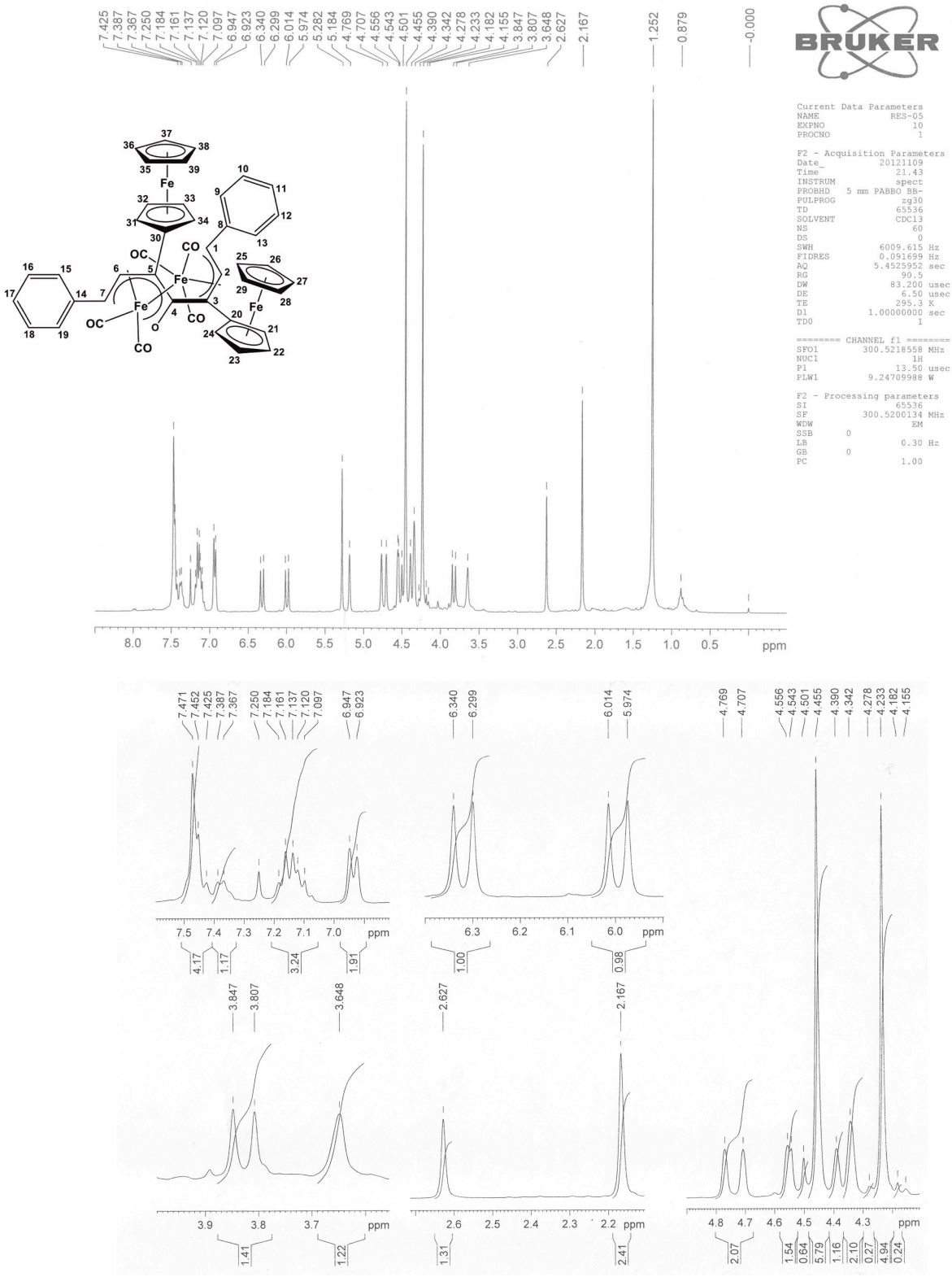


Figure S41. ^{1}H NMR spectrum 300 MHz of ($CDCl_3$) of compound **5c**

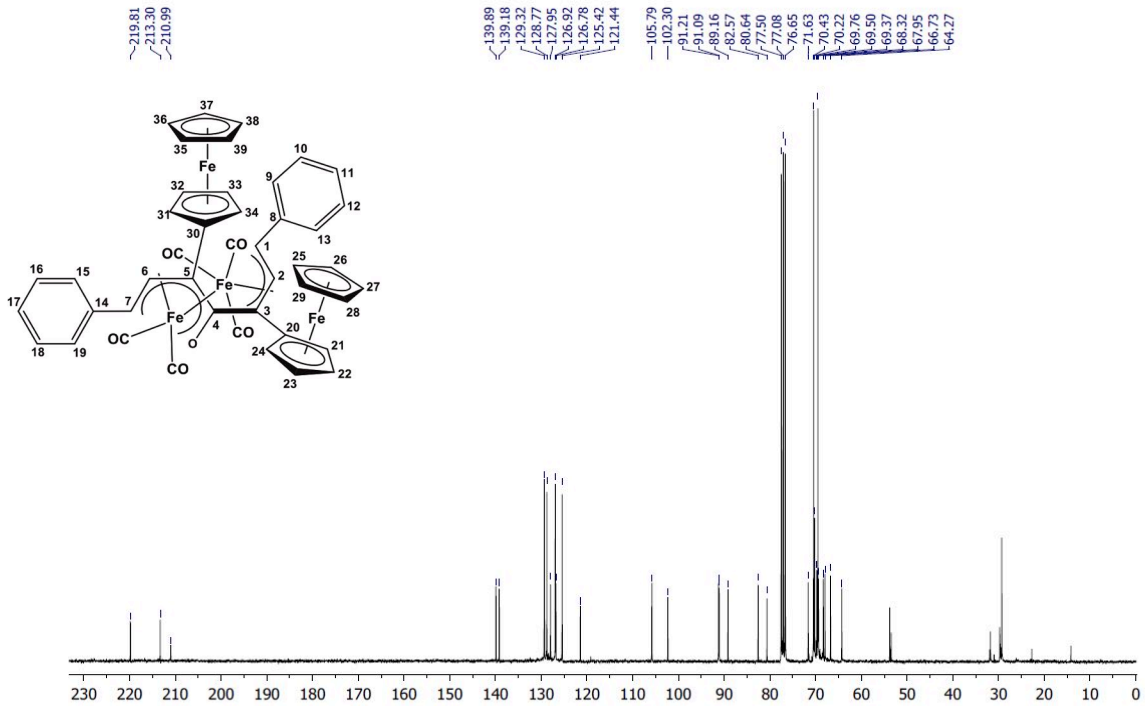


Figure S42. ^{13}C{1H} NMR spectrum 75 MHz of ($CDCl_3$) of compound **5c**

Compound 5d

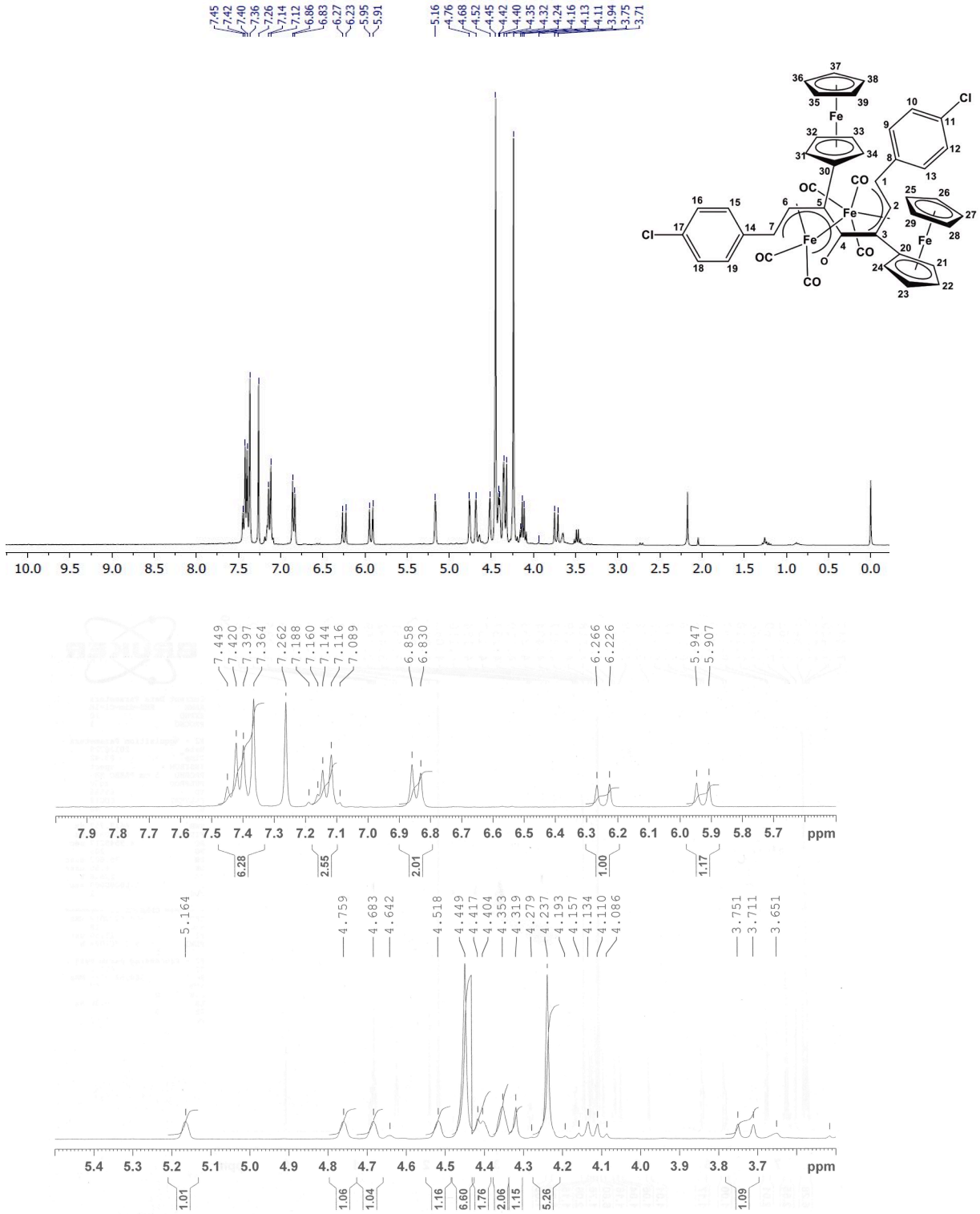


Figure S43. ^{1}H NMR spectrum 300 MHz of ($CDCl_3$) of compound **5d**

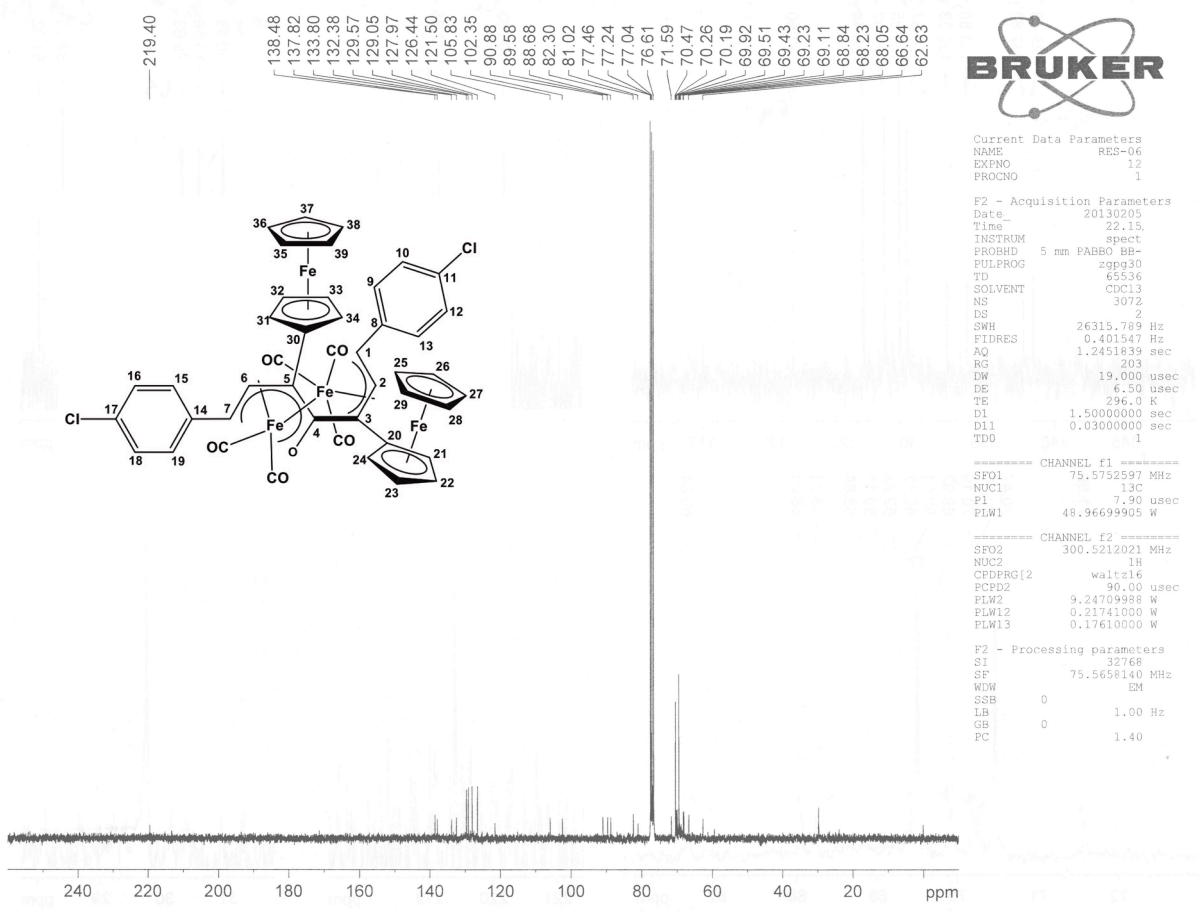


Figure S44. ^{13}**C{1H} NMR** spectrum 75 MHz of ($CDCl_3$) of compound **5d**

Compound 5e

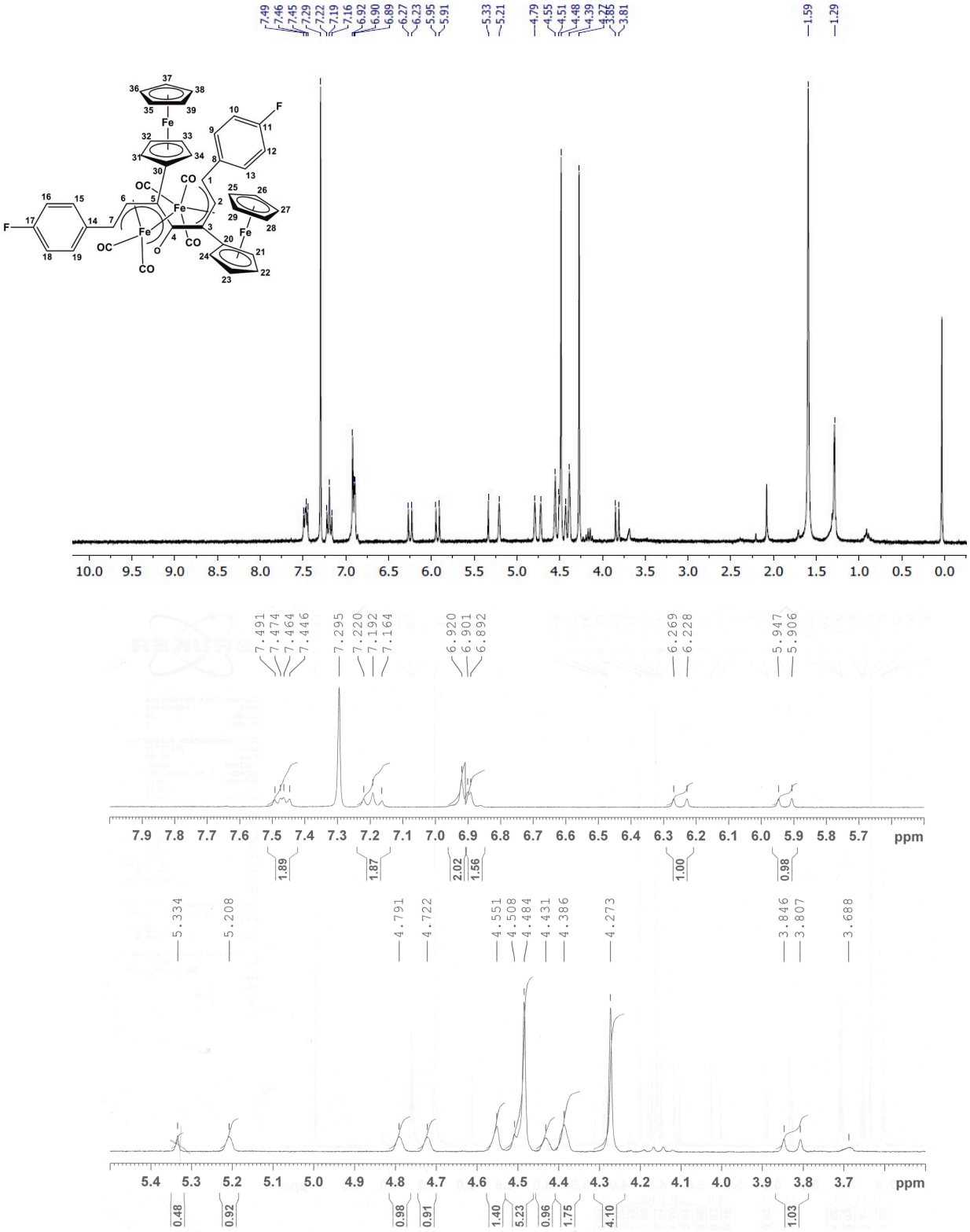


Figure S45. ^{1}H NMR spectrum 300 MHz of ($CDCl_3$) of compound **5e**

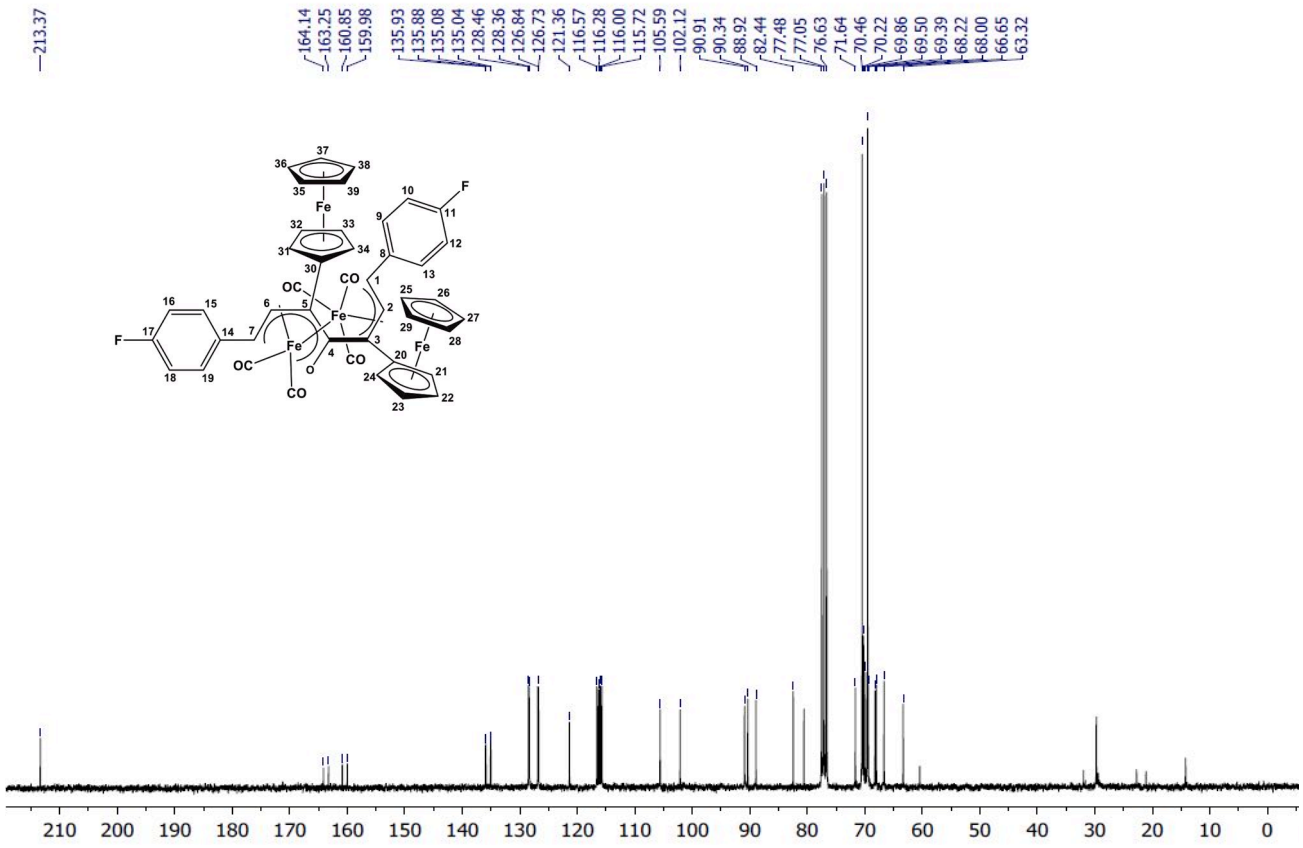


Figure S46. ^{13}C{1H} NMR spectrum 75 MHz of ($CDCl_3$) of compound **5e**

Compound 5f

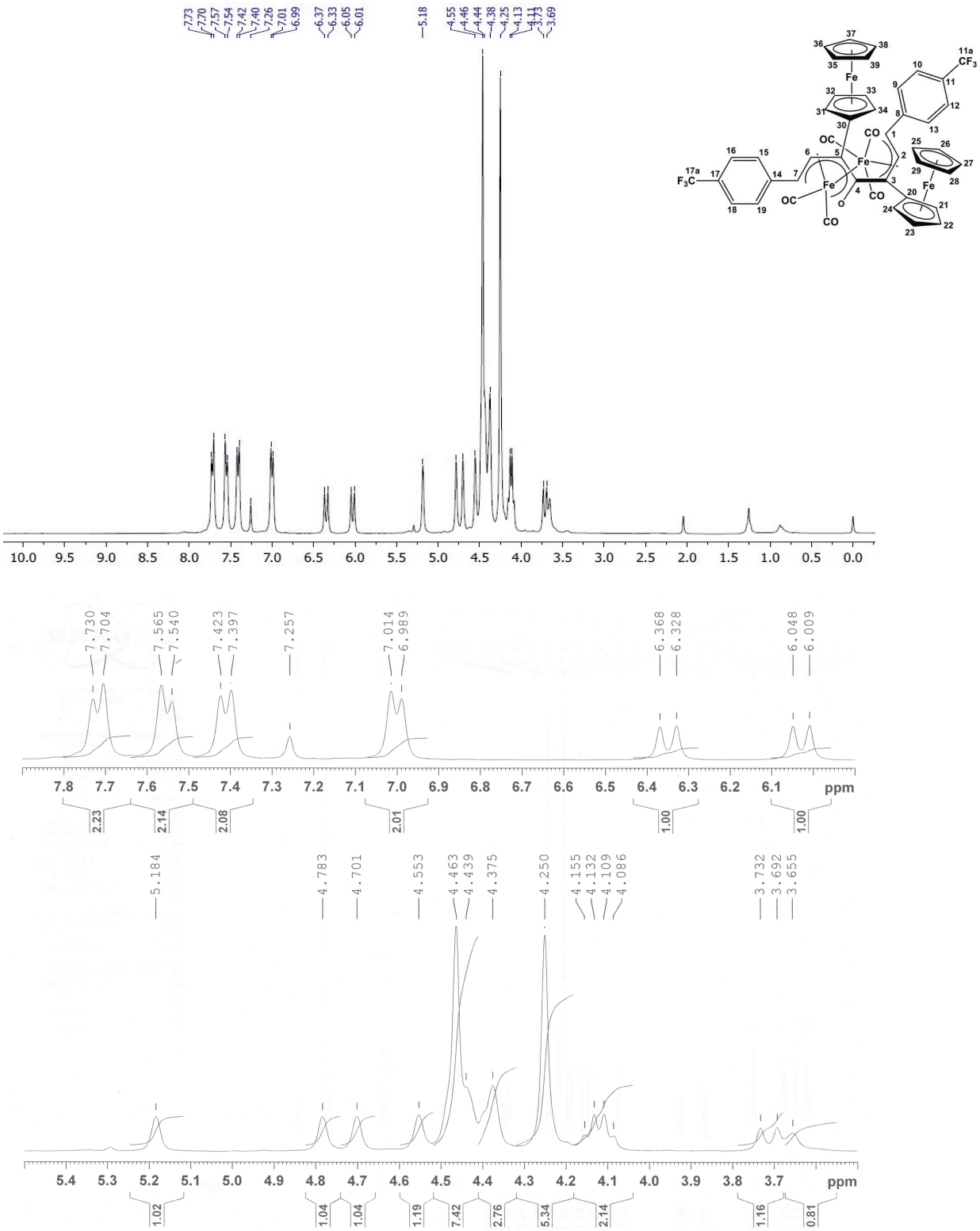


Figure S47. ^{1}H NMR spectrum 300 MHz of ($CDCl_3$) of compound **5f**

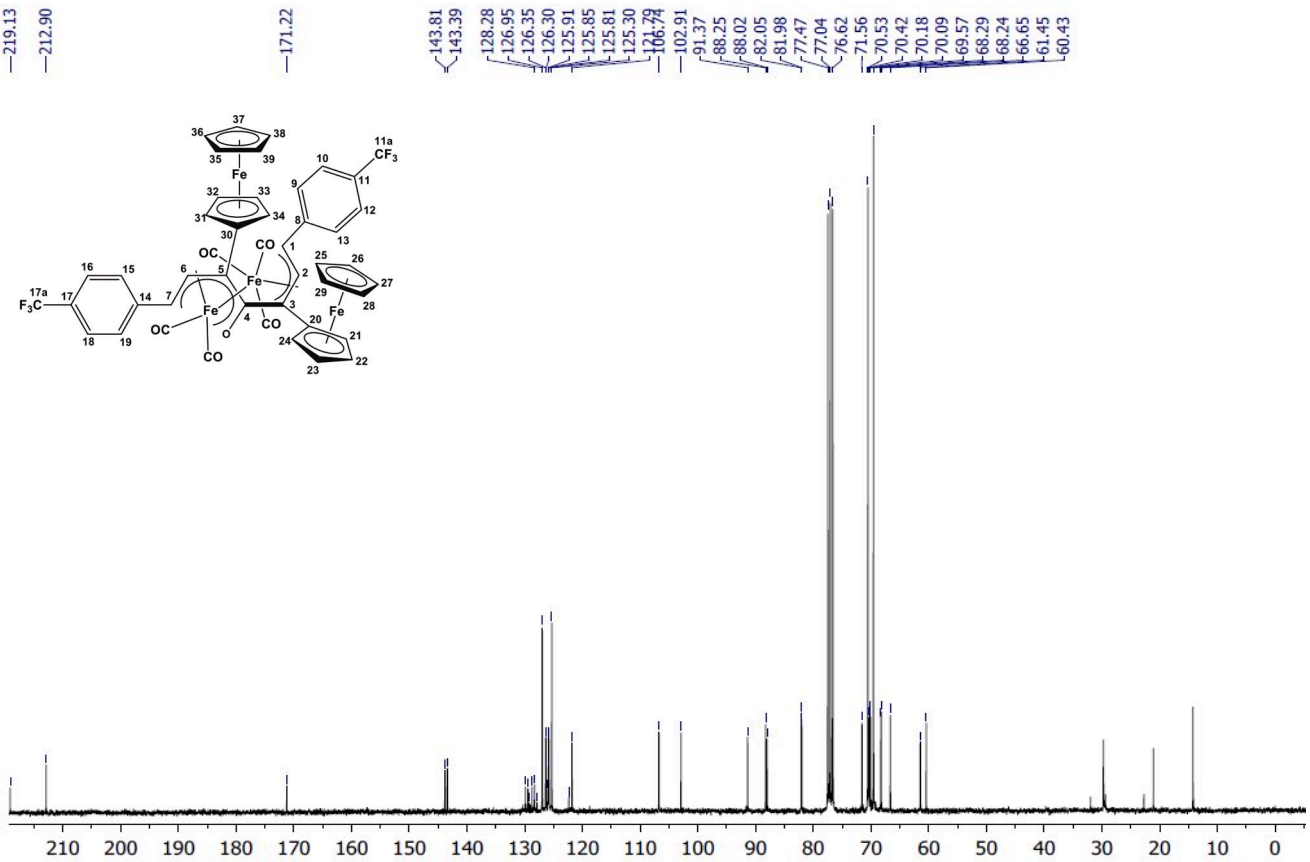


Figure S48. ^{13}C{1H} NMR spectrum 75 MHz of ($CDCl_3$) of compound **5f**

6. **Structure Determination by X-ray Crystallography.**

Table S4. Crystal data and structure refinement for **3b** and **3d**

	3b	**3d**
CCDC	2067662	2067663
Empirical Formula	$C_{24}H_{18}Fe_2O_4$	$C_{23}H_{15}ClFe_2O_4$
Formula Weight (g mol^{-1})	482.08	502.50
Temperature (°C)	25	25
Crystal size (mm)	0.34 x 0.14 x 0.07	0.38 x 0.18 x 0.08
Color	Orange	Red
Crystal system	Monoclinic	Monoclinic
Space Group	$P2_1/c$	$P2_1/n$
a (Å)	16.2932(8)	15.0452(8)
b (Å)	11.1212(6)	6.5941(3)
c (Å)	13.2838(7)	21.3121(11
α (°)	90	90
β (°)	108.853(1)	105.572(1)
γ (°)	90	90
V (Å^3)	2277.9(2)	2036.75(18)
Z	4	4
D_{calc} (g cm^3)	1.406	1.639
Number of collected reflections	18422	16431
Number of independent reflections (R_{int})	4143, R_{int}= 0.0801	3709, R_{int} = 0.0579
Absorption correction method	Multi-scan	Multi-scan
Maximum and minimum transmission	0.553 and 0.745	0.7452 and 0.6312
Data/restraints/parameters	4143/188/317	3712/206/317
Final *R* indices[$I>2\sigma(I)$]	*R* = 0.0488, *wR*2 = 0.1335	*R* = 0.0420, *wR2* = 0.0953
R indices (all data)	*R* = 0.0829, *wR*2 = 0.1156	*R* = 0.0656, *wR2* = 0.0831
Remarks	--	Main residue disorder 17%
Goodness-of-fit on F^2	1.014	1.019

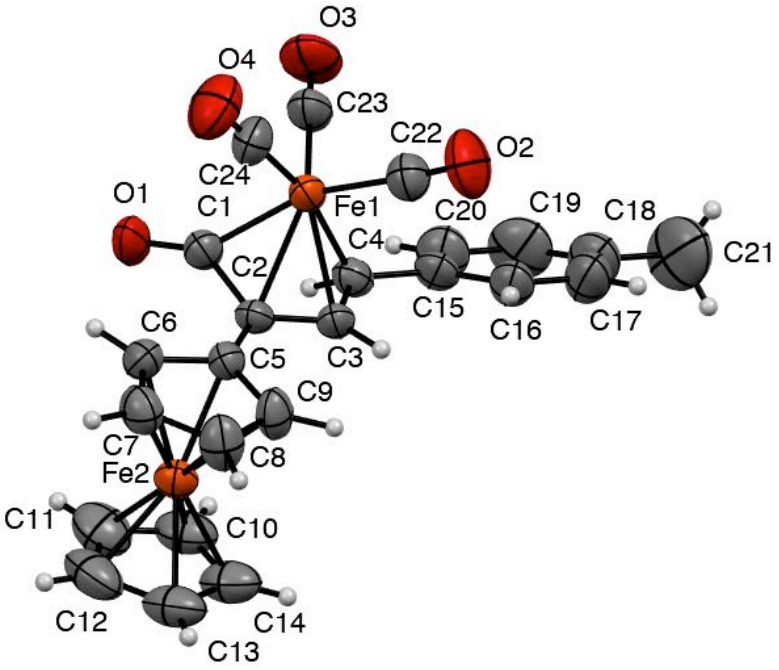


Figure S49. ORTEP projection of compound **3b.** Ellipsoids are showed at 50% of probability. Selected bond distances (Å) and angles (deg): Fe1-C24 1.777(6), Fe1-C23 1.790(5), Fe1-C22 1.842(5), Fe1-C1 1.929(3), Fe1-C3 2.113(4), Fe1-C2 2.131(3), Fe1 C4 2.197(4), O1-C1 1.197(5), O2-C22 1.136(6), O3-C23 1.143(6), O4-C24 1.141(7), C1-C2 1.467(6), C2-C3 1.395(5), C2-C5 1.473(5), C3-C4 1.417(5). C24-Fe1-C4 167.7 (2), O1-C1-C2 136.8(4), C3-C2-C1 112.9(3), C2-C3-C4 118.7(3), C1-Fe1-C4 80.2(2), C24-Fe1-C23 99.3(2), C24-Fe1-C22 91.1(2), C23-Fe1-C22 101.1(2), C24-Fe1-C1 88.2(2), C23-Fe1-C1 101.8(2), C22-Fe1-C1 156.9(2).

7. Crystallographic data collection, structure determination and electron density distribution analysis for 5e.

A dark red plate shaped single crystal of **5e**, 0.109 x 0.068 x 0.026 mm, was selected for measurements. The diffraction data were collected using a RIGAKU AFC-8 diffractometer equipped with a Saturn70 CCD detector with MoKα radiation by an oscillation method about the ω-axis at 90 K. X-rays were monochromated and focused by a confocal mirror. Sixteen data sets were measured with different crystal orientations and detector positions. Bragg spots were integrated, scaled, and averaged up to $\sin\vartheta/\lambda$ = 1.064 Å^{-1} by the program HKL2000.[4] Lorentz, polarization, and absorption corrections were applied during the scaling processes.

The number of measured and independent reflections, completeness, and R_{int} was 296793, 45245, 0.995 and 0.0550, respectively, up to $\sin\vartheta/\lambda$ = 1.064 Å^{-1}.

The initial structure of **5e** was solved by a direct method using the programs SHELXT-2018[5] and refined by a full matrix least-squares method using the program SHELXL-2016.[6] All hydrogen atoms were located on difference Fourier maps, and refined as riding models. The structure was refined as a 2-component inversion twin with a twinning fraction of 0.004(6).

High order refinements were carried out for determining the position of non-hydrogen atoms using 36962 independent reflections with $\sin\vartheta/\lambda \geq 0.60$ Å^{-1}. On the refinements, the positions of the hydrogen atoms bonding to carbon atoms were constrained to be C–H distances of 1.083, 1.080 and 1.073 Å for the aromatic, the oxopentadienyl and the unsaturated cyclopentadienyl groups, respectively.

Refinements of a multipole expansion method using the Hansen-Coppens multipole formalism[7] and topological analyses based on the resulted parameters were performed with the XD2016 package.[8] The refinements were carried out against 36962 independent reflections of $\sin\vartheta/\lambda \leq 1.064$ Å^{-1} with $I > 1.5\sigma(I)$ based on F^2. At the first stage of the refinements, the atomic coordinates and temperature factors of the atoms were fixed on those of the high order refinement. The population parameters, P_v, $P_{lm\pm}$ of the non-hydrogen atoms and scale were refined. The levels of the multipoles were raised up stepwise to hexadecapole for Fe and octupole for F, O and C atoms, and dipole along the C−H bonds for H atoms. Chemical equivalent constraints were applied for multipole parameters of all atoms. The radial screening parameters, κ and κ' were refined after refinements of multipole parameters at hexadecapole level for non-hydrogen atoms. The refinement cycles were repeated until parameters converged. At the second stage, the temperature factors were refined by applying harmonic anisotropic models for the non-H atoms, and isotropic models for H atoms, following the refinements of the radial screening parameters, κ and κ'. The chemical equivalent constraints on the multipole parameters were relaxed in stepwise, and finally only the hydrogen atoms were constrained. The stage was repeated to make the shifts of the parameters converged. At the final stage, the coordinates, temperature factors, and multipoles were refined. The C−H distances were constrained to be 1.083, 1.080 and 1.073 Å for the aromatic, the oxopentadienyl and the unsaturated cyclopentadienyl groups, respectively. The number of parameters at the final cycle of the refinements was 1651. The charge of the molecule was constrained to be neutral. Due to the disorder of a benzene molecule, these parts were kept fixed, and the positional parameters of the solvent molecule were not refined during refinement.

5e: $C_{40}H_{30}F_2Fe_4O_6$, 1.5 C_6H_6, *FW* = 1033.24, monoclinic, space group *Cc*, *a* = 18.2892(3) Å, *b* = 24.9311(5) Å, *c* = 10.3706(2) Å, β = 106.4467(7)°, *V* = 4535.20(15) Å^3, *Z* = 4, crystal size 0.109 × 0.068 × 0.026 mm^3, 296793 reflections collected ($(\sin\theta/\lambda)_{max}$ = 1.064 Å^{-1}, 45245 independent, R_{int} = 0.0550), 669 parameters, GoF on F^2 = 1.007, $R1$ [$I > 2\sigma(I)$] = 0.0348, $wR(F^2)$ [$I > 2\sigma(I)$] = 0.0788, $\Delta\rho_{min}$ and $\Delta\rho_{max}$: -0.762 and 0.742 eÅ^{-3}.

Table S5. Crystal data of **5e** from multipole model.

CCDC	2088388
Empirical formula	$C_{40}H_{30}F_2Fe_4O_6$, 1.5 C_6H_6
Formula weight	1033.24
Temperature [K]	90
Wavelength [Å]	0.71073
Crystal system	Monoclinic
Space group	*Cc*
Unit cell dimensions [Å, °]	a = 18.2892(3)
	b = 24.9311(5)
	c = 10.3706(2)
	β = 106.4467(7)
Volume [Å3]	4535.20(15)
Z	4
Density (calculated) [mg/m^3]	1.513
Absorption coefficient [mm^{-1}]	1.313
F(000)	2108
Crystal size [mm]	0.109 × 0.068 × 0.026
Theta range for data collection [°]	1.634 to 49.132
Index ranges	-38<=h<=38,
	-52<=k<=52
	-22<=l<=22
Reflections collected	296863
Independent reflections	45250 [R_{int} = 0.0550]
Completeness to θ = 49.132°	99.4 %
Absorption correction	Analytical
Max. and min. transmission	0.96636 and 0.90680
Refinement method	Full-matrix least-squares on F^2
Data / parameters	19702 / 1651
GoF on F^2	1.6353
Final R indices [I > 1.5σ(I)]	R_1 = 0.0278, wR_2 = 0.0491
Final R indices based on all data	R_1 = 0.0397, wR_2 = 0.0491
Largest diff. peak and hole [e/Å^3]	0.475 and -0.366

The final parameters of the multipole model (populations, contraction/expansion parameters) can be found in the CIF file.

Table S6. Bond lengths [Å] for **5e** from multipole model (only ordered parts).

FE(1)-FE(2)	2.7906(4)	C(3)-C(20)	1.4847(15)
FE(1)-C(1)	2.1664(13)	C(4)-C(5)	1.4452(15)
FE(1)-C(2)	2.0769(12)	C(5)-C(6)	1.4475(16)
FE(1)-C(3)	2.1603(12)	C(5)-C(30)	1.4711(15)
FE(1)-C(42)	1.7907(15)	C(6)-C(7)	1.4054(17)
FE(1)-C(43)	1.8014(14)	C(7)-C(8)	1.4723(17)
FE(1)-C(44)	1.7994(16)	C(8)-C(9)	1.394(2)
FE(2)-O(1)	2.0275(15)	C(8)-C(13)	1.402(2)
FE(2)-C(4)	2.0483(11)	C(9)-C(10)	1.392(2)
FE(2)-C(5)	2.1435(12)	C(10)-C(11)	1.380(4)
FE(2)-C(6)	2.1200(12)	C(11)-C(12)	1.388(4)
FE(2)-C(40)	1.7547(16)	C(12)-C(13)	1.394(2)
FE(2)-C(41)	1.8028(16)	C(14)-C(15)	1.4034(19)
FE(3)-C(30)	2.0478(12)	C(14)-C(19)	1.4059(19)
FE(3)-C(31)	2.0426(12)	C(15)-C(16)	1.391(2)
FE(3)-C(32)	2.0528(13)	C(16)-C(17)	1.386(3)
FE(3)-C(33)	2.0461(14)	C(17)-C(18)	1.386(3)
FE(3)-C(34)	2.0403(14)	C(18)-C(19)	1.396(2)
FE(3)-C(35)	2.0570(17)	C(20)-C(21)	1.4359(15)
FE(3)-C(36)	2.0640(19)	C(20)-C(24)	1.4369(15)
FE(3)-C(37)	2.0507(17)	C(21)-C(22)	1.4266(16)
FE(3)-C(38)	2.0411(16)	C(22)-C(23)	1.4282(18)
FE(3)-C(39)	2.0473(17)	C(23)-C(24)	1.4302(16)
FE(4)-C(20)	2.0585(12)	C(25)-C(26)	1.430(2)
FE(4)-C(21)	2.0542(13)	C(25)-C(29)	1.426(2)
FE(4)-C(22)	2.0658(13)	C(26)-C(27)	1.429(2)
FE(4)-C(23)	2.0622(13)	C(27)-C(28)	1.428(2)
FE(4)-C(24)	2.0506(13)	C(28)-C(29)	1.430(2)
FE(4)-C(25)	2.0531(14)	C(30)-C(31)	1.4382(16)
FE(4)-C(26)	2.0634(15)	C(30)-C(34)	1.4407(16)
FE(4)-C(27)	2.0701(15)	C(31)-C(32)	1.4286(15)
FE(4)-C(28)	2.0614(15)	C(32)-C(33)	1.4318(18)
FE(4)-C(29)	2.0492(15)	C(33)-C(34)	1.4254(18)
F(1)-C(11)	1.361(3)	C(35)-C(36)	1.426(3)
F(2)-C(17)	1.367(3)	C(35)-C(39)	1.434(3)
O(1)-C(4)	1.3069(17)	C(36)-C(37)	1.430(3)
O(2)-C(40)	1.151(3)	C(37)-C(38)	1.426(3)
O(3)-C(41)	1.149(3)	C(38)-C(39)	1.424(3)
O(4)-C(44)	1.156(2)	C(45)-C(46)	1.388(4)
O(5)-C(42)	1.155(3)	C(45)-C(50)	1.377(3)
O(6)-C(43)	1.144(2)	C(46)-C(47)	1.396(4)
C(1)-C(2)	1.4155(16)	C(47)-C(48)	1.382(5)

C(1)-C(14)	1.4744(17)	C(48)-C(49)	1.390(5)
C(2)-C(3)	1.4217(15)	C(49)-C(50)	1.391(4)
C(3)-C(4)	1.4820(15)		

Table S7. Angles [°] for **5e** from multipole model (only ordered parts).

FE(2)-FE(1)-C(1)	90.21(3)	C(22)-FE(4)-C(27)	106.00(6)
FE(2)-FE(1)-C(2)	98.41(3)	C(22)-FE(4)-C(28)	121.72(6)
FE(2)-FE(1)-C(3)	76.17(3)	C(22)-FE(4)-C(29)	158.62(6)
FE(2)-FE(1)-C(42)	87.24(5)	C(23)-FE(4)-C(24)	40.70(5)
FE(2)-FE(1)-C(43)	167.26(5)	C(23)-FE(4)-C(25)	160.37(6)
FE(2)-FE(1)-C(44)	75.28(4)	C(23)-FE(4)-C(26)	157.25(6)
C(1)-FE(1)-C(2)	38.90(4)	C(23)-FE(4)-C(27)	121.55(6)
C(1)-FE(1)-C(3)	71.26(4)	C(23)-FE(4)-C(28)	107.15(6)
C(1)-FE(1)-C(42)	93.23(7)	C(23)-FE(4)-C(29)	123.57(6)
C(1)-FE(1)-C(43)	101.94(6)	C(24)-FE(4)-C(25)	124.62(6)
C(1)-FE(1)-C(44)	160.83(6)	C(24)-FE(4)-C(26)	160.32(6)
C(2)-FE(1)-C(3)	39.15(4)	C(24)-FE(4)-C(27)	158.42(6)
C(2)-FE(1)-C(42)	131.33(7)	C(24)-FE(4)-C(28)	123.50(6)
C(2)-FE(1)-C(43)	88.91(5)	C(24)-FE(4)-C(29)	109.05(6)
C(2)-FE(1)-C(44)	129.90(6)	C(25)-FE(4)-C(26)	40.65(6)
C(3)-FE(1)-C(42)	156.93(6)	C(25)-FE(4)-C(27)	68.29(6)
C(3)-FE(1)-C(43)	103.95(5)	C(25)-FE(4)-C(28)	68.38(6)
C(3)-FE(1)-C(44)	92.80(5)	C(25)-FE(4)-C(29)	40.68(6)
C(42)-FE(1)-C(43)	95.76(7)	C(26)-FE(4)-C(27)	40.46(6)
C(42)-FE(1)-C(44)	98.41(7)	C(26)-FE(4)-C(28)	68.12(7)
C(43)-FE(1)-C(44)	92.02(7)	C(26)-FE(4)-C(29)	68.31(6)
FE(1)-FE(2)-O(1)	81.56(4)	C(27)-FE(4)-C(28)	40.45(6)
FE(1)-FE(2)-C(4)	66.70(3)	C(27)-FE(4)-C(29)	68.28(6)
FE(1)-FE(2)-C(5)	93.21(3)	C(28)-FE(4)-C(29)	40.71(6)
FE(1)-FE(2)-C(6)	132.70(4)	FE(2)-O(1)-C(4)	72.17(8)
FE(1)-FE(2)-C(7)	156.67(4)	FE(1)-C(1)-C(2)	67.13(7)
FE(1)-FE(2)-C(40)	89.32(5)	FE(1)-C(1)-C(14)	125.84(9)
FE(1)-FE(2)-C(41)	101.97(5)	C(2)-C(1)-C(14)	121.84(11)
O(1)-FE(2)-C(4)	37.40(5)	FE(1)-C(2)-C(1)	73.97(7)
O(1)-FE(2)-C(5)	67.75(5)	FE(1)-C(2)-C(3)	73.59(7)
O(1)-FE(2)-C(6)	82.40(6)	FE(1)-C(2)-C(4)	71.01(4)
O(1)-FE(2)-C(7)	76.09(6)	FE(1)-C(2)-C(14)	89.53(5)
O(1)-FE(2)-C(40)	164.65(7)	FE(1)-C(2)-C(20)	88.14(5)
O(1)-FE(2)-C(41)	101.33(7)	FE(1)-C(2)-C(43)	41.40(4)
C(4)-FE(2)-C(5)	40.25(4)	C(1)-C(2)-C(3)	125.35(11)
C(4)-FE(2)-C(6)	73.69(5)	FE(1)-C(3)-C(2)	67.26(6)
C(4)-FE(2)-C(7)	91.12(5)	FE(1)-C(3)-C(4)	95.36(7)
C(4)-FE(2)-C(40)	127.37(6)	FE(1)-C(3)-C(20)	121.02(8)
C(4)-FE(2)-C(41)	136.50(7)	C(2)-C(3)-C(4)	124.87(10)

C(5)-FE(2)-C(6)	39.69(4)	C(2)-C(3)-C(20)	117.88(10)
C(5)-FE(2)-C(7)	72.27(5)	C(4)-C(3)-C(20)	115.76(10)
C(5)-FE(2)-C(40)	100.70(6)	FE(2)-C(4)-O(1)	70.43(8)
C(5)-FE(2)-C(41)	159.94(7)	FE(2)-C(4)-C(3)	121.58(8)
C(6)-FE(2)-C(7)	37.73(4)	FE(2)-C(4)-C(5)	73.42(7)
C(6)-FE(2)-C(40)	95.01(6)	O(1)-C(4)-C(3)	117.83(11)
C(6)-FE(2)-C(41)	124.75(6)	O(1)-C(4)-C(5)	115.35(11)
C(7)-FE(2)-C(40)	110.91(6)	C(3)-C(4)-C(5)	126.68(10)
C(7)-FE(2)-C(41)	89.02(6)	FE(2)-C(5)-C(4)	66.33(6)
C(40)-FE(2)-C(41)	92.60(8)	FE(2)-C(5)-C(6)	69.28(7)
C(30)-FE(3)-C(31)	41.17(5)	FE(2)-C(5)-C(30)	133.31(8)
C(30)-FE(3)-C(32)	69.04(5)	C(4)-C(5)-C(6)	119.61(10)
C(30)-FE(3)-C(33)	69.03(5)	C(4)-C(5)-C(30)	122.43(10)
C(30)-FE(3)-C(34)	41.27(5)	C(6)-C(5)-C(30)	117.66(10)
C(30)-FE(3)-C(35)	107.08(6)	FE(2)-C(6)-C(5)	71.03(7)
C(30)-FE(3)-C(36)	125.07(7)	FE(2)-C(6)-C(7)	74.89(7)
C(30)-FE(3)-C(37)	162.71(8)	C(5)-C(6)-C(7)	128.74(11)
C(30)-FE(3)-C(38)	154.70(8)	FE(2)-C(7)-C(6)	67.38(7)
C(30)-FE(3)-C(39)	119.52(7)	FE(2)-C(7)-C(8)	123.20(9)
C(31)-FE(3)-C(32)	40.83(4)	C(6)-C(7)-C(8)	122.38(12)
C(31)-FE(3)-C(33)	68.87(5)	C(7)-C(8)-C(9)	118.72(15)
C(31)-FE(3)-C(34)	69.25(5)	C(7)-C(8)-C(13)	122.88(14)
C(31)-FE(3)-C(35)	119.18(7)	C(9)-C(8)-C(13)	118.36(15)
C(31)-FE(3)-C(36)	106.62(7)	C(8)-C(9)-C(10)	121.5(2)
C(31)-FE(3)-C(37)	125.30(8)	C(9)-C(10)-C(11)	118.3(2)
C(31)-FE(3)-C(38)	163.12(8)	F(1)-C(11)-C(10)	120.4(4)
C(31)-FE(3)-C(39)	154.32(8)	F(1)-C(11)-C(12)	117.2(4)
C(32)-FE(3)-C(33)	40.89(5)	C(10)-C(11)-C(12)	122.39(17)
C(32)-FE(3)-C(34)	68.96(5)	C(11)-C(12)-C(13)	118.3(2)
C(32)-FE(3)-C(35)	153.85(9)	C(8)-C(13)-C(12)	121.1(2)
C(32)-FE(3)-C(36)	119.28(8)	C(1)-C(14)-C(15)	123.39(12)
C(32)-FE(3)-C(37)	107.49(7)	C(1)-C(14)-C(19)	118.14(13)
C(32)-FE(3)-C(38)	126.07(7)	C(15)-C(14)-C(19)	118.40(13)
C(32)-FE(3)-C(39)	163.73(8)	C(14)-C(15)-C(16)	121.15(15)
C(33)-FE(3)-C(34)	40.83(5)	C(15)-C(16)-C(17)	118.49(17)
C(33)-FE(3)-C(35)	163.89(9)	F(2)-C(17)-C(16)	118.9(3)
C(33)-FE(3)-C(36)	154.45(8)	F(2)-C(17)-C(18)	118.5(3)
C(33)-FE(3)-C(37)	120.17(7)	C(16)-C(17)-C(18)	122.55(16)
C(33)-FE(3)-C(38)	107.93(7)	C(17)-C(18)-C(19)	118.22(17)
C(33)-FE(3)-C(39)	126.27(8)	C(14)-C(19)-C(18)	121.14(16)
C(34)-FE(3)-C(35)	126.13(8)	C(3)-C(20)-C(21)	127.47(10)
C(34)-FE(3)-C(36)	163.16(8)	C(3)-C(20)-C(24)	125.31(10)
C(34)-FE(3)-C(37)	154.85(8)	C(21)-C(20)-C(24)	107.22(10)
C(34)-FE(3)-C(38)	119.91(8)	C(20)-C(21)-C(22)	108.30(11)

C(34)-FE(3)-C(39)	107.53(8)	C(21)-C(22)-C(23)	108.29(10)
C(35)-FE(3)-C(36)	40.48(9)	C(22)-C(23)-C(24)	107.78(10)
C(35)-FE(3)-C(37)	68.14(8)	C(20)-C(24)-C(23)	108.42(10)
C(35)-FE(3)-C(38)	68.52(8)	C(26)-C(25)-C(29)	107.90(13)
C(35)-FE(3)-C(39)	40.91(9)	C(25)-C(26)-C(27)	108.09(13)
C(36)-FE(3)-C(37)	40.66(8)	C(26)-C(27)-C(28)	107.89(13)
C(36)-FE(3)-C(38)	68.71(9)	C(27)-C(28)-C(29)	107.99(13)
C(36)-FE(3)-C(39)	68.71(10)	C(25)-C(29)-C(28)	108.12(13)
C(37)-FE(3)-C(38)	40.80(9)	C(5)-C(30)-C(31)	126.37(10)
C(37)-FE(3)-C(39)	68.53(9)	C(5)-C(30)-C(34)	126.25(11)
C(38)-FE(3)-C(39)	40.77(8)	C(31)-C(30)-C(34)	107.37(10)
C(20)-FE(4)-C(21)	40.87(4)	C(30)-C(31)-C(32)	108.30(10)
C(20)-FE(4)-C(22)	68.47(5)	C(31)-C(32)-C(33)	107.87(11)
C(20)-FE(4)-C(23)	68.72(5)	C(32)-C(33)-C(34)	108.39(10)
C(20)-FE(4)-C(24)	40.94(4)	C(30)-C(34)-C(33)	108.06(11)
C(20)-FE(4)-C(25)	108.66(5)	C(36)-C(35)-C(39)	108.45(17)
C(20)-FE(4)-C(26)	123.21(6)	C(35)-C(36)-C(37)	107.41(19)
C(20)-FE(4)-C(27)	158.31(6)	C(36)-C(37)-C(38)	108.42(18)
C(20)-FE(4)-C(28)	160.30(6)	C(37)-C(38)-C(39)	108.08(18)
C(20)-FE(4)-C(29)	124.36(6)	C(35)-C(39)-C(38)	107.63(19)
C(21)-FE(4)-C(22)	40.52(5)	FE(2)-C(40)-O(2)	177.4(2)
C(21)-FE(4)-C(23)	68.40(5)	FE(2)-C(41)-O(3)	176.1(2)
C(21)-FE(4)-C(24)	68.58(5)	FE(1)-C(42)-O(5)	177.05(19)
C(21)-FE(4)-C(25)	123.21(6)	FE(1)-C(43)-O(6)	177.04(19)
C(21)-FE(4)-C(26)	106.89(6)	FE(1)-C(44)-O(4)	174.84(16)
C(21)-FE(4)-C(27)	121.44(6)	C(46)-C(45)-C(50)	120.0(2)
C(21)-FE(4)-C(28)	157.29(6)	C(45)-C(46)-C(47)	120.5(2)
C(21)-FE(4)-C(29)	160.10(6)	C(46)-C(47)-C(48)	119.5(3)
C(22)-FE(4)-C(23)	40.48(5)	C(47)-C(48)-C(49)	119.6(2)
C(22)-FE(4)-C(24)	68.25(5)	C(48)-C(49)-C(50)	120.7(2)
C(22)-FE(4)-C(25)	158.31(6)	C(45)-C(50)-C(49)	119.6(2)
C(22)-FE(4)-C(26)	121.57(6)		

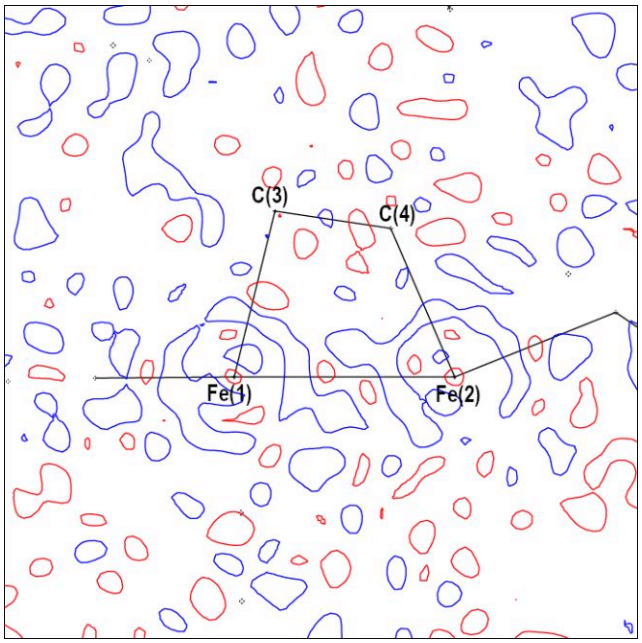


Figure S50. Final residual map for **5e** ($F_{obs} - F_{multi}$) through the plane Fe(1)-Fe(2)-C(3). Contours at ±0.1 eÅ^{-3}.

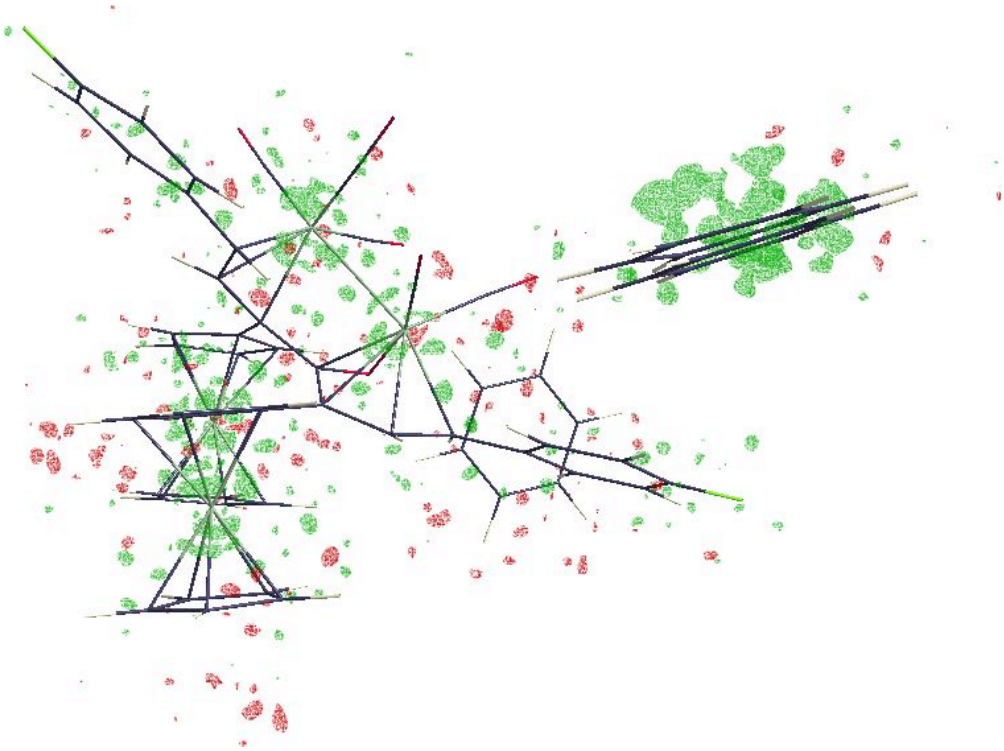


Figure S51. Residual density map of **5e** after final refinement cycle. Contours at ±0.20 eÅ^{-3}.

Table S8. XDFTT output

no	peak		x	y	z	height
	PK(1)	is 0.79 A from Fe(3)	0.6441	0.8525	0.427	0.47
	PK(2)	is 0.82 A from Fe(4)	0.595	0.9292	0.9151	0.46
123	PK(3)	.....	0.3771	0.4798	0.2375	0.43
	PK(4)	is 0.74 A from C(59)	0.3754	0.5224	0.2972	0.42
	PK(5)	is 0.71 A from C(23)	0.499	0.9654	0.7962	0.42
124	PK(6)	.....	0.5216	0.2883	0.0738	0.41
	PK(7)	is 0.81 A from Fe(1)	0.3237	0.8401	0.5433	0.4
	PK(8)	is 0.76 A from Fe(1)	0.3767	0.8411	0.4585	0.37
125	PK(9)	.....	0.5081	0.1025	0.302	0.37
126	PK(10)	.....	0.8854	0.0063	0.5585	0.36
	HL(1)	is 0.57 A from Fe(4)	0.5716	0.9326	0.8891	-0.37
127	HL(2)	.....	0.8443	0.2164	0.8686	-0.33
128	HL(3)	.....	0.6659	0.2469	0.6839	-0.32
129	HL(4)	.....	0.4558	0.1931	0.6685	-0.31
	HL(5)	is 0.49 A from C(49)	0.633	0.6785	1.0919	-0.31
130	HL(6)	.....	0.3652	0.1859	0.4806	-0.3
131	HL(7)	.....	0.5749	0.0698	0.5353	-0.3
132	HL(8)	.....	0.9191	0.221	0.0606	-0.3
133	HL(9)	.....	0.2934	0.3382	0.6666	-0.3
	HL(10)	is 1.15 A from Fe(1)	0.4119	0.8452	0.5533	-0.3

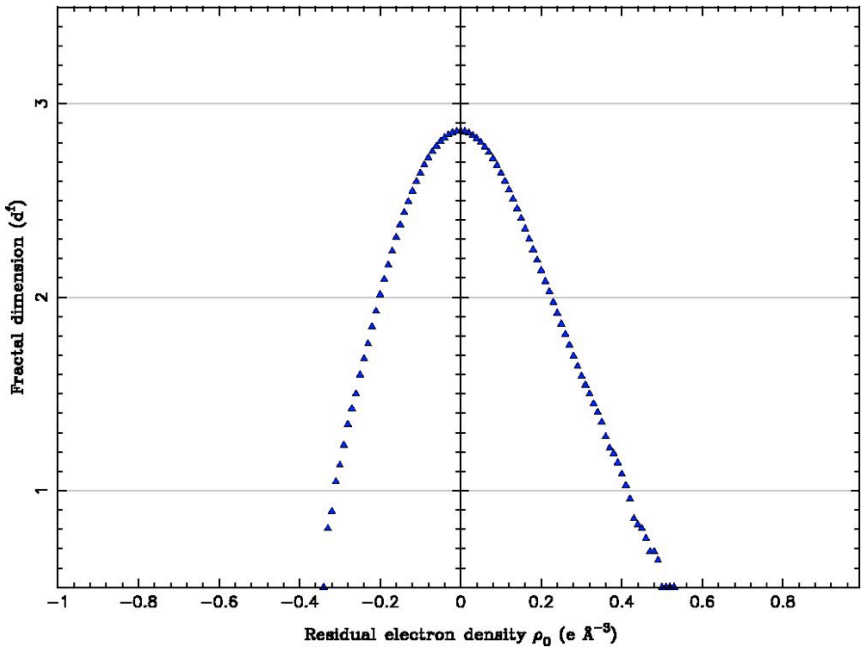


Figure S52. Distribution of the Fractal dimension (d^f) *vs* Residual density ρ_0 (eÅ^{-3}) (S6). The small deviation from the ideal Gaussian shape mainly originates from the non-ideal description of the disordered solvent molecules.

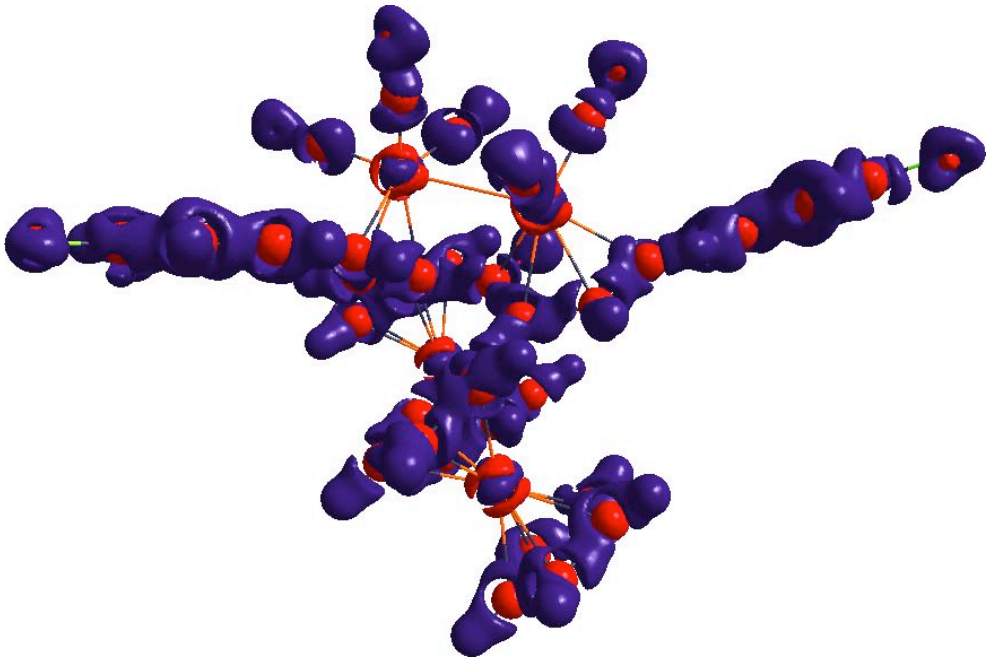


Figure S53. Isosurface Laplacian map of **5e** from the multipole model (red contour drawn at -150 eÅ^{-5}; blue contour drawn at 5 eÅ^{-5}).

8. DFT Studies for 5e

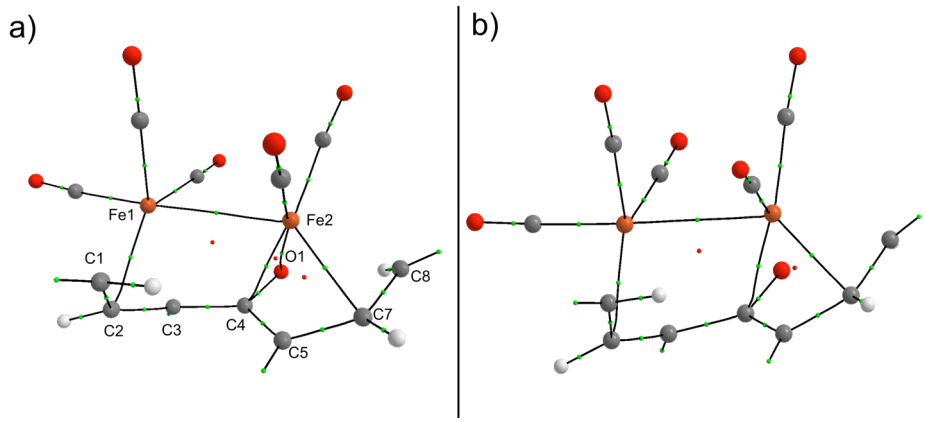


Figure S54. DFT calculated molecular graphs of complex **5e** a) H atoms optimized and b) fully optimized.

Table S9. DFT calculated topological properties at the vicinity of the dinuclear core in complex **5e i**n which only the H atoms were optimized.

bond	BP_{length}	$\rho(r)$	$\nabla^2\rho(r)$	ε	G(r)	V(r)	H(r)	G(r)/$\rho(r)$	H(r)/$\rho(r)$	|V(r)|/G(r)
Fe1-Fe2	2.8049	0.228	0.414	0.14	0.0759	-0.1227	-0.0469	0.3322	-0.2052	1.6177
Fe1-C2	2.0870	0.553	5.324	1.33	0.5511	-0.7295	-0.1784	0.9973	-0.3228	1.3237
Fe2-C4	2.0533	0.563	6.011	1.07	0.6056	-0.7904	-0.1848	1.0748	-0.3279	1.3051
Fe2-C6	2.1271	0.507	5.256	1.73	0.5130	-0.6581	-0.1451	1.0118	-0.2861	1.2828
Fe2-O1	2.0543	0.546	9.622	2.15	0.7922	-0.9109	-0.1187	1.4523	-0.2175	1.1498
C1-C2	1.4131	2.013	-19.049	0.22	0.7062	-2.7460	-2.0398	0.3507	-1.0131	3.8883
C2-C3	1.4240	1.973	-18.248	0.24	0.6779	-2.6334	-1.9554	0.3437	-0.9913	3.8843
C3-C4	1.4853	1.834	-17.746	0.11	0.4579	-2.1582	-1.7003	0.2497	-0.9272	4.7129
C4-C5	1.4478	1.925	-17.790	0.27	0.6141	-2.4736	-1.8595	0.3190	-0.9658	4.0280
C5-C6	1.4505	1.877	-16.836	0.19	0.6037	-2.3860	-1.7823	0.3216	-0.9494	3.9524
C6-C7	1.4016	2.057	-19.779	0.23	0.7347	-2.8540	-2.1194	0.3571	-1.0301	3.8847
C4-O1	1.3094	2.293	-17.658	0.09	2.4679	-6.1719	-3.7040	1.0764	-1.6155	2.5009

Table S10. DFT calculated topological properties at the vicinity of the dinuclear core in complex **5e** without any geometry optimization.

bond	BP_{length}	$\rho(r)$	$\nabla^2\rho(r)$	ε	G(*r*)	V(*r*)	H(*r*)	G(*r*)/ρ(*r*)	H(*r*)/ρ(*r*)	|V(*r*)|/G(*r*)
Fe1-Fe2	2.8053	0.228	0.415	0.15	0.0756	-0.1221	-0.0465	0.3315	-0.2041	1.6159
Fe1-C2	2.0887	0.552	5.226	1.33	0.5447	-0.7236	-0.1789	0.9864	-0.3239	1.3283
Fe2-C4	2.0528	0.563	6.026	1.12	0.6061	-0.7903	-0.1842	1.0768	-0.3273	1.3040
Fe2-C6	2.1298	0.509	5.071	1.89	0.5016	-0.6483	-0.1467	0.9864	-0.2884	1.2924
Fe2-O1	2.0557	0.546	9.535	2.23	0.7869	-0.9062	-0.1193	1.4408	-0.2185	1.1517
C1-C2	1.4131	2.015	-19.049	0.19	0.7095	-2.7526	-2.0431	0.3520	-1.0137	3.8795
C2-C3	1.4241	1.967	-18.070	0.24	0.6808	-2.6266	-1.9458	0.3461	-0.9891	3.8582
C3-C4	1.4852	1.835	-17.781	0.10	0.4575	-2.1598	-1.7023	0.2493	-0.9277	4.7208
C4-C5	1.4481	1.927	-17.867	0.26	0.6112	-2.4732	-1.8620	0.3172	-0.9664	4.0463
C5-C6	1.4507	1.870	-16.632	0.20	0.6067	-2.3777	-1.7710	0.3245	-0.9473	3.9192
C6-C7	1.4019	2.060	-19.825	0.20	0.7349	-2.8577	-2.1228	0.3567	-1.0304	3.8884
C4-O1	1.3094	2.297	-17.899	0.09	2.4551	-6.1633	-3.7082	1.0689	-1.6144	2.5104

Table S11. DFT calculated topological properties at the vicinity of the dinuclear core in complex **5e** fully optimized.

bond	BP_{length}	$\rho(r)$	$\nabla^2\rho(r)$	ε	G(*r*)	V(*r*)	H(*r*)	G(*r*)/ρ(*r*)	H(*r*)/ρ(*r*)	|V(*r*)|/G(*r*)
Fe1-Fe2	2.7884	0.233	0.397	0.25	0.0765	-0.1253	-0.0487	0.3291	-0.2095	1.6366
Fe1-C2	2.0783	0.564	5.501	1.51	0.5696	-0.7541	-0.1845	1.0108	-0.3274	1.3239
Fe2-C4	2.0545	0.568	6.072	1.11	0.6117	-0.7984	-0.1866	1.0771	-0.3286	1.3051
Fe2-C6	2.1085	0.527	5.559	2.05	0.5452	-0.7012	-0.1560	1.0354	-0.2963	1.2862
C1-C2	1.4051	2.045	-19.652	0.22	0.7249	-2.8255	-2.1006	0.3544	-1.0271	3.8979
C2-C3	1.4155	2.003	-18.752	0.24	0.7005	-2.7138	-2.0133	0.3497	-1.0051	3.8739
C3-C4	1.4770	1.866	-18.340	0.11	0.4698	-2.2234	-1.7537	0.2518	-0.9399	4.7330
C4-C5	1.4421	1.952	-18.344	0.26	0.6219	-2.5279	-1.9060	0.3186	-0.9765	4.0650
C5-C6	1.4321	1.943	-17.908	0.20	0.6476	-2.5488	-1.9012	0.3332	-0.9784	3.9360
C6-C7	1.3949	2.082	-20.200	0.24	0.7546	-2.9233	-2.1687	0.3625	-1.0419	3.8740
C4-O1	1.2871	2.395	-15.655	0.08	2.9140	-6.9240	-4.0099	1.2166	-1.6741	2.3761

Table S12. Selected DFT calculated delocalization indices (DI) of complex **5e**.

bond	DI (H opt)	DI (no opt)	DI (fully opt)
Fe1-Fe2	0.4434	0.4409	0.4404
Fe1-C1	0.4806	0.4928	0.4966
Fe1-C2	0.3628	0.3653	0.3633
Fe1-C3	0.4659	0.4615	0.4675
Fe2-O1	0.4865	0.4931	0.4802
Fe2-C4	0.3137	0.3131	0.3060
Fe2-C5	0.3748	0.3751	0.3864
Fe2-C6	0.3450	0.3490	0.3448
Fe2-C7	0.4189	0.4365	0.4432

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